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Pd-catalyzed cross-coupling of polyfluoroarenes with cyclic vinyl triflates

YU YanBo[1], WANG Zhen[2] & ZHANG XinGang[1*]

[1]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*
[2]*College of Agriculture, Inner Mongolia Agricultural University, Hohhot 010019, China*

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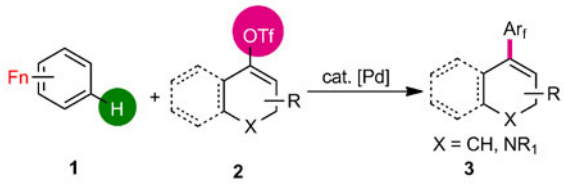
An effective method for Pd-catalyzed cross-coupling between polyfluoroarenes and cyclic vinyl triflates has been developed. This protocol provides a useful and facile access to polyfluoroarylated cyclic alkenes that are difficult to prepare otherwise. The advantages of this method are its high efficiency and operational simplicity.

C–H bond functionalization, cyclic vinyl triflates, palladium, polyfluoroarenes

1 Introduction

It is of great synthetic interest to develop efficient methods to introduce various polyfluoroaryl groups into organic molecules owing to their importance in many functional molecules, such as pharmaceuticals, agrochemicals, liquid crystals, and electronic devices [1]. Traditionally, such valuable structural motif can be prepared from prefunctionalized polyfluoroarenes, such as polyfluoroaryl metals [2]. However, this "prefunctionalization" process suffers from tedious procedures in preparing the organometallic reagents and the incompatibility of important functional groups. From the point of view of synthetic simplicity, the use of readily and commercially available polyfluoroarenes as starting materials would facilitate the accessibility of this fluorinated structure through direct C–H bond functionalization [3]. Recently, impressive progresses have been achieved in this area [4, 5]. However, examples for the preparation of polyfluoroarylated alkenes remain few. In particular, the transition-metal-catalyzed direct olefination of polyfluoroarenes with cyclic vinyl triflates has not been reported so far. Continuing our study in palladium-catalyzed polyfluoroarene chemistry [5], herein, we report an effective method for the preparation of polyfluoroarylated cyclic alkenes catalyzed by palladium. The reaction is made possible by using cyclic vinyl triflates, which can be easily accessed through the reactions of widely available enolates with trifluoromethansesulfonyl reagents [6], thus providing a useful access to polyfluoroarylated derivatives of interest in both life and material sciences (Scheme 1).



Scheme 1 Pd-catalyzed cross-coupling of polyfluoroarenes with cyclic vinyl triflates.

2 Experimental

2.1 Materials and methods

All reagents were used as received from commercial

*Corresponding author (email: xgzhang@mail.sioc.ac.cn)

sources, unless otherwise specified, or prepared as described in the literature. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature. DMF, DMSO were distilled under reduced pressure from CaH_2. Toluene, and 1,4-dioxane were distilled from sodium and benzophenone immediately before use.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300 and AM400 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 and AM400 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

2.2 Synthesis of cyclic vinyl triflates

Vinyl triflates **2a**, **2b**, and **2c** were prepared from the corresponding ketones and trifluoromethanesulphonic anhydride according to the literature procedure [7].

*Typical procedure for the synthesis of cyclic triflates **2a***

Under argon, a solution of 3,4-dihydronaphthalen-1(2*H*)-one (1.46 g, 10.0 mmol) in 200 mL of dry dichloromethane was cooled to 0 °C, sodium carbonate (2.12 g, 20.0 mmol) and trifluoromethanesulphonic anhydride 4.51 g, 16.0 mmol) were then added subsequently to the stirred solution. After the addition, the resulting reaction mixture was warmed up to 25 °C and stirred for 5 h until the ketone was fully consumed (monitored by TLC). The reaction mixture was quenched by ice water, diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether) to provide pure product **2a** (2.5 g, 90%) as a colorless oil. This compound is known [7]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.10 (m, 4H), 5.99 (t, J = 4.7 Hz, 1H), 2.84 (t, J = 8.1 Hz, 2H), 2.50–2.45 (m, 2H) (Supporting Information online).

5-Methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (**2b**). Colorless oil (85% yield). This compound is known [8]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 1H), 7.10–6.98 (m, 1H), 6.89–6.86 (m, 1H), 6.00 (t, J = 4.6 Hz, 1H), 3.83 (s, 3H), 2.85 (t, J = 8.4 Hz, 2H), 2.51–2.44 (m, 2H).

Cyclohex-1-en-1-yl trifluoromethanesulfonate (**2c**). Colorless oil (75% yield). This compound is known [9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81–5.72 (m, 1H), 2.37–2.26 (m, 2H), 2.23–2.12 (m, 2H), 1.78 (m, 2H), 1.60 (m, 2H).

Vinyl triflates **2d** and **2e** were prepared from the corresponding ketones and $PhNTf_2$ according to the literature procedure [9]. Under argon, a solution of NaHMDS (1.0 M in THF, 11 mL, 1.1 equiv) was added dropwise to a solution of a ketone (10 mmol, 1.0 equiv) and $PhNTf_2$ (1.1 equiv) in THF (0.15 M) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred until the reaction was complete. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The resulting residue was purified by flash column chromatography.

1,2,3,6-Tetrahydro-[1,1′-biphenyl]-4-yl trifluoromethanesulfonate (**2d**). Colorless oil (75% yield). This compound is known [9]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5H), 5.90–5.78 (m, 1H), 2.89–2.82 (m, 1H), 2.59–2.29 (m, 4H), 2.10–1.89 (m, 2H).

1-Pivaloyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (**2e**). Colorless oil (68% yield). This compound is known [9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (s, 1H), 4.23 (d, J = 2.8 Hz, 2H), 3.82 (t, J = 5.6 Hz, 2H), 2.49 (s, 2H), 1.30 (s, 9H).

2.3 General procedure for Pd-catalyzed cross-coupling of polyfluoroarenes with cyclic vinyl triflate

To a Schlenck tube with a magnetic stir bar were added $Pd(OAc)_2$ (5 mol%), SPhos or DavePhos (5 mol%), AdOH (0.1 equiv), K_2CO_3 (1.2 equiv) under N_2, followed by DMF (2.5 mL) with stirring. Polyfluoroarene (1.2 mmol, 2.0 equiv) and vinyl triflate (0.6 mmol, 1 equiv) were added subsequently. The Schlenck tube was sealed and stirred in an oil bath (80 °C) for 8 h. The reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether) to provide pure product.

*4-(Perfluorophenyl)-1,2-dihydronaphthalene (**3a**)*

White solid (155 mg, 87%). m.p. 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.05 (m, 3H), 6.66 (d, J = 7.5 Hz, 1H), 6.16 (t, J = 4.4 Hz, 1H), 2.91 (t, J = 8.1 Hz, 2H), 2.59–2.42 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −140.6 (dd, J = 22.2, 6.7 Hz, 2F), −156.2 (td, J = 20.9, 4.1 Hz, 1F), −156.7 (m, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2 (dm, J = 243.3 Hz), 140.1 (dm, J = 253.3 Hz), 137.2 (dm, J = 252.5 Hz), 135.1, 133.3, 132.4, 127.5, 127.4, 126.2, 124.5, 123.2, 114.0 (m), 27.0, 23.1. IR (thin film) ν_{max} 1493, 1106, 987 cm^{-1}. MS (EI): *m/z* (%) 296 (M^+, 100), 297 (MH^+), 281. HRMS: Calculated for $C_{16}H_9F_5$: 296.0624; found: 296.0625.

*8-Methoxy-4-(perfluorophenyl)-1,2-dihydronaphthalene (**3b**)*

White solid (168 mg, 86%). m.p. 66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.31 (d, J = 7.6 Hz, 1H), 6.15 (t, J = 4.2 Hz, 1H), 3.83 (s, 3H), 2.90 (t, J = 8.3 Hz, 2H), 2.52–2.40 (m, 2H). ^{19}F NMR

(376 MHz, $CDCl_3$) δ −140.2 (dd, J = 23.2, 8.2 Hz, 2F), −156.0 (t, J = 20.8 Hz, 1F), −162.5 (td, J = 23.0, 8.4 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 144.7 (dm, J = 243.2 Hz), 140.5 (dm, J = 253.1 Hz), 137.6 (dm, J = 252.0 Hz), 134.1, 133.8, 126.7, 124.8, 123.5, 116.5, 114.8 (m), 110.4, 55.5, 23.0, 19.2. IR (thin film) ν_{max} 2839, 1496, 989 cm^{-1}. MS (EI): *m/z* (%) 326 (M^+, 100), 327 (MH^+), 311. HRMS: Calculated for $C_{17}H_{11}OF_5$: 326.0730; found: 326.0726.

*4-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)-1,2-dihydronaphthalene (**3c**)*

White solid (153 mg, 83%). m.p. 79 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.05 (m, 3H), 6.71 (d, J = 7.2 Hz, 1H), 6.15 (m, 1H), 4.11 (s, 3H), 2.90 (t, J = 8.0 Hz, 2H), 2.49 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.0 (dd, J = 22.3, 8.7 Hz, 2F), −158.2 (dd, J = 22.4, 8.7 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (dm, J = 245.1 Hz), 141.0 (dm, J = 247.4 Hz), 137.5 (m), 135.6, 133.3, 133.2, 127.8, 127.6, 126.6, 125.5, 123.8, 112.7 (m), 62.2, 27.5, 23.5. IR (thin film) ν_{max} 2834, 1483, 982 cm^{-1}. MS (EI): *m/z* (%) 308 (M^+, 100), 309 (MH^+), 293. HRMS: Calculated for $C_{17}H_{12}OF_4$: 308.0824; found: 308.0829.

*4-[2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl]-1,2-dihydronaphthalene (**3d**)*

Colorless oil (172 mg, 85%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.21–7.20 (m, 2H), 7.17–7.10 (m, 1H), 6.66 (d, J = 7.4 Hz, 1H), 6.21 (t, J = 4.4 Hz, 1H), 2.92 (t, J = 8.1 Hz, 2H), 2.56–2.49 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −56.6 (t, J = 21.6 Hz, 3F), −138.4 (td, J = 15.9, 5.9 Hz, 2F), −141.1 (td, J = 20.9, 10.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (dm, J = 247.9 Hz), 144.1 (dm, J = 260.2 Hz), 135.5, 134.1, 132.2, 128.0, 126.7, 125.1, 123.9 (t, J = 19.0 Hz), 123.6, 119.6 (q, J = 275.3 Hz), 108.7 (m), 27.3, 23.5. IR (thin film) ν_{max} 1479, 1340, 989 cm^{-1}. MS (EI): *m/z* (%) 346 (M^+, 100), 347 (MH^+), 331. HRMS: Calculated for $C_{17}H_9F_7$: 346.0592; found: 346.0596.

*8-Methoxy-4-[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]-1,2-dihydronaphthalene (**3e**)*

White solid (133 mg, 59%). m.p. 83 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 8.0 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.31 (d, J = 7.6 Hz, 1H), 6.20 (t, J = 4.4 Hz, 1H), 3.84 (s, 3H), 2.92 (t, J = 8.3 Hz, 2H), 2.49 (td, J = 8.3, 4.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −56.3 (t, J = 21.7 Hz, 3F), −138.2 (m, 2F), −141.0 (td, J = 21.0, 11.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.4 (dm, J = 249.6 Hz), 143.7 (dm, J = 260.2), 133.9, 132.7, 126.4, 124.5, 123.8 (t, J = 18.8 Hz), 123.0, 120.5 (q, J = 274.4 Hz), 115.9, 110.2, 108.2 (m), 55.1, 22.5, 18.7. IR (thin film) ν_{max} 2957, 1471, 1337 cm^{-1}. MS (EI): *m/z* (%) 376 (M^+, 100), 377 (MH^+), 361. HRMS: Calculated for $C_{18}H_{11}OF_7$: 376.0698; found: 376.0698.

*2,2-Dimethyl-1-[4-(perfluorophenyl)-5,6-dihydropyridin-1(2H)-yl]propan-1-one (**3f**)*

White solid (162 mg, 81%). m.p. 45 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (s, 1H), 4.25 (s, 2H), 3.83 (s, 2H), 2.42 (s, 2H), 1.30 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.2 (d, J = 16.5 Hz, 2F), −156.1 (t, J = 20.6 Hz, 1F), −162.3 (t, J = 18.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 144.0 (dm, J = 246.9 Hz), 140.1 (dm, J = 253.7 Hz), 137.6 (dm, J = 255.8 Hz), 129.8, 123.4, 115.7 (m), 44.7, 42.6, 38.7, 29.1, 28.1. IR (thin film) ν_{max} 2976, 1632, 1492 cm^{-1}. MS (EI): *m/z* (%) 333 (M^+, 100), 334 (MH^+), 84. HRMS: Calculated for $C_{16}H_{16}NOF_5$: 333.1152; found: 333.1154.

*2,2-Dimethyl-1-[4-(2,3,5,6-tetrafluoro-4-methoxyphenyl)-5,6-dihydropyridin-1(2H)-yl]propan-1-one (**3g**)*

White solid (145 mg, 70%). m.p. 84 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (s, 1H), 4.27 (s, 2H), 4.08 (s, 3H), 3.84 (t, J = 5.1 Hz, 2H), 2.45 (s, 2H), 1.33 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.9 (dd, J = 21.9, 8.0 Hz, 2F), −158.3 (dd, J = 21.8, 7.0 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 144.2 (dm, J = 245.3 Hz), 140.9 (dm, J = 247.2 Hz), 137.2 (m), 129.0, 124.0, 114.1 (t, J = 17.9 Hz), 62.1, 44.7, 42.7, 38.7, 29.1, 28.1. IR (thin film) ν_{max} 2978, 1621, 1075 cm^{-1}. MS (EI): *m/z* (%) 345 (M+, 100), 346 (MH^+), 330. HRMS: Calculated for $C_{17}H_{19}NO_2F_4$: 345.1352; found: 345.1350.

*2',3',4',5',6'-Pentafluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (**3h**)*

Colorless oil (91mg, 61%). This compound is known [10]. ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (s, 1H), 2.27–2.17 (m, 4H), 1.83–1.75 (m, 2H), 1.71 (dd, J = 7.3, 3.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.8 (dd, J = 23.1, 8.0 Hz, 2F), −157.9 (t, J = 20.9 Hz, 1F), −163.3 (dt, J = 23.1, 8.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (dm, J = 256.2 Hz), 141.4 (dm, J = 250.5 Hz), 139.2 (dm, J = 246.7 Hz), 134.5, 126.3, 119.8 (m), 30.4, 27.2, 24.3, 23.3.

*2',3',5',6'-Tetrafluoro-4'-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (**3i**)*

White solid (132 mg, 74%). m.p. 39 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (s, 1H), 2.26 (s, 4H), 1.76 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −56.4 (t, J = 21.5 Hz, 3F), −140.4 (m, 2F), −141.7 (td, J = 20.5, 10.3 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 (dm, J = 259.5 Hz), 133.8, 127.3 (t, J = 18.1 Hz), 124.8, 120.9 (q, J = 274.2 Hz), 107.1 (m), 28.2, 25.5, 22.4, 21.4. IR (thin film) ν_{max} 2924, 1334, 1148 cm^{-1}. MS (EI): *m/z* (%) 298 (M^+), 299 (MH^+), 283 (M^+, 100). HRMS: Calculated for $C_{13}H_9F_7$: 298.0592; found: 298.0587. Anal. Calcd. for $C_{13}H_9F_7$: C, 53.36, H, 3.04; found: C, 53.18; H, 3.26.

*2'',3'',4'',5'',6''-Pentafluoro-1',2',3',6'-tetrahydro-1,1':4',1''-terphenyl (**3j**)*

White solid (175 mg, 90%). m.p. 162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.18 (m, 5H), 5.96 (s, 1H), 3.02–2.87 (m, 1H), 2.53 (m, 2H), 2.44–2.24 (m, 2H), 2.08 (m, 1H), 1.95 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.5 (dd, J = 23.2, 8.0 Hz, 2F), −157.3 (t, J = 20.9 Hz, 1F), −162.9 (td, J = 22.9, 8.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 146.0 (dm, J = 258.2 Hz), 142.0 (dm, J = 251.4 Hz), 139.3 (dm, J = 259.5 Hz), 134.2, 130.2, 128.6, 128.0, 126.4, 119.4(m), 40.9, 35.4, 31.5, 31.0. IR (thin film) ν_{max} 2920, 1488, 983 cm^{-1}. MS (EI): *m/z* (%) 324 (M^+, 100), 325 (MH^+), 104. HRMS: Calculated for $C_{18}H_{13}F_5$: 324.0937; Found: 324.0935. Anal. Calcd. for $C_{18}H_{13}F_5$: C, 66.67, H, 4.04; Found: C, 66.63; H, 4.05.

*2'',3'',5'',6''-Tetrafluoro-4''-methoxy-1',2',3',6'-tetrahydro-1,1':4',1''-terphenyl (**3k**)*

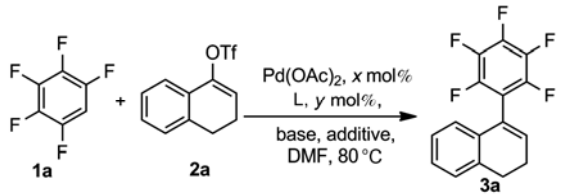
White solid (105 mg, 52%). m.p. 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.04 (m, 5H), 5.93 (s, 1H), 4.04 (s, 2H), 2.92 (s, 1H), 2.48 (s, 2H), 2.33 (m, 2H), 2.19–1.84 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −144.2 (dd, J = 22.3, 8.5 Hz, 2F), −158.7 (dd, J = 22.3, 8.4 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.3 (dm, J = 244.2 Hz), 140.9 (dm, J = 246.7 Hz), 137.2 (m), 131.7, 128.5, 126.9, 126.2, 125.3, 116.2 (m), 62.1, 39.3, 33.7, 29.8, 29.4. IR (thin film) ν_{max} 2935, 1482, 1073 cm^{-1}. MS (EI): *m/z* (%) 336 (M^+, 100), 337 (MH^+), 232 (M^+, 100). HRMS: Calculated for $C_{19}H_{16}OF_4$: 336.1137; found: 336.1133.

3 Results and discussion

We began this study by choosing pentafluorobenzene **1a** and 1-tetralone derived 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate **2a** as model substrates. Initially, a negative result was obtained when the reaction was carried out with $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), and K_2CO_3 (1.2 equiv) in DMF at 80 °C (Table 1, entry 1). After a survey of different phosphane ligands (Table 1, entries 2–6), SPhos was found to be the optimal one, providing **3a** in 66% isolated yield without observation of homocoupling of **1a** (Table 1, entry 4). Other ligands, such as MePhos, Xantphos, and BINAP, showed less or no effectiveness. Encouraged by these results, different bases and solvents were examined to further improve the reaction efficiency (Table 1, entries 7–15). It turned out that K_2CO_3 and DMF remained to be the best choice. Stronger bases did not facilitate the reaction (Table 1, entries 10–12), and 20% yield of defluorinated side product was observed when *t*BuOK was used (Table 1, entry 12). Carboxylic acid was reported to have a beneficial effect on the C–H bond activation of simple arenes [11], thus a series of carboxylic acids were tested (Table 1, entries 16–20). To our delight, when bulky 1-adamantanecarboxylic acid (AdOH) was used as an additive, an improved yield was obtained (Table 1, entries 19–20). It has been demonstrated that phosphine-ligated arylpalladium carboxylates LPd(Ar)(OCOR) typically reacted with arenes to form biarylpalladium complexes through a concerted metallation-deprotonation (CMD) pathway [11b]. We supposed that AdOH may function as a proton shuttle during the pentafluorobenzene C–H cleavage step [11a], as a result, a higher yield was observed. Further optimization of the reaction conditions led to the highest yield (87% isolated yield) by reducing the amount loading of $Pd(OAc)_2$ to 5 mol%, along with utilization of 5 mol% of SPhos, 1.2 equiv of K_2CO_3, and 0.1 equiv of AdOH (Table 1, entry 22).

With the optimized reaction conditions in hand, the substrate scope of the cross-coupling of polyfluoroarenes with cyclic vinyl triflates was investigated, and the representative

Table 1 Optimization of Pd-catalyzed cross-coupling of pentafluorobenzene **1a** with vinyl triflate **2a** [a]

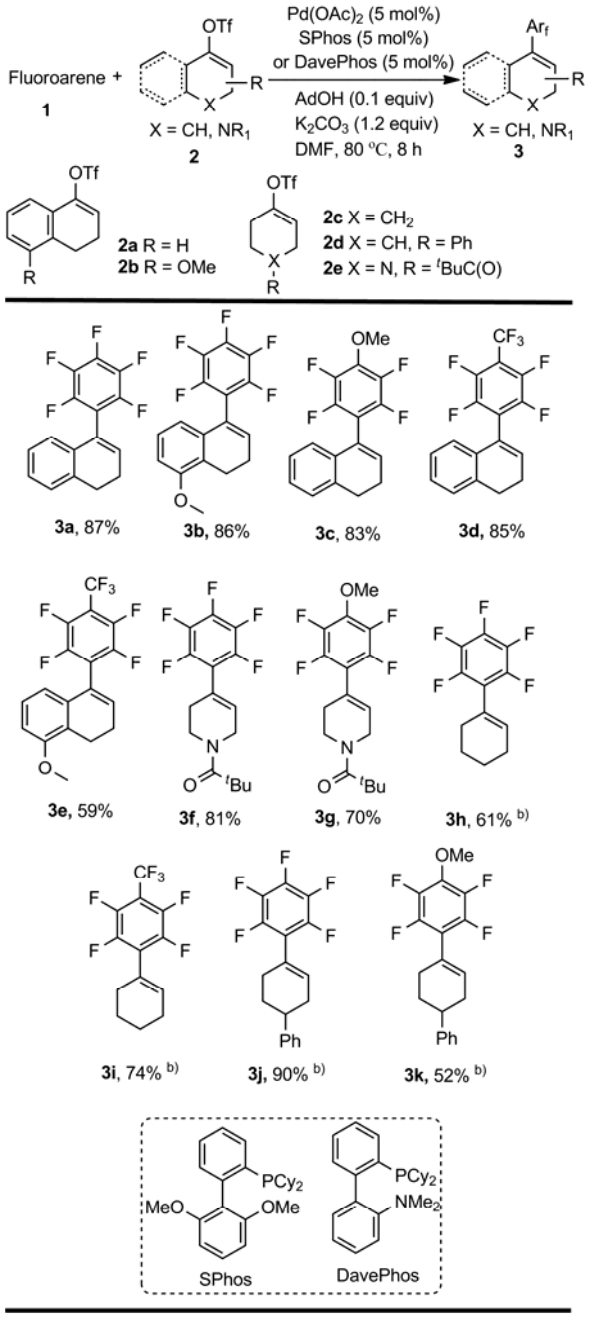


Entry	*x* mol%	L, *y* mol%	Base (equiv)	Additive	Yield [b]
1	10	PPh_3, 20	K_2CO_3, 1.2	/	Trace
2	10	MePhos, 20	K_2CO_3, 1.2	/	52
3	10	RuPhos, 20	K_2CO_3, 1.2	/	70
4	10	SPhos, 20	K_2CO_3, 1.2	/	72 (66)
5	10	XantPhos, 10	K_2CO_3, 1.2	/	trace
6	10	BINAP, 10	K_2CO_3, 1.2	/	18
7	10	SPhos, 20	NaOAc, 1.2	/	64
8	10	SPhos, 20	K_3PO_4, 1.2	/	63
9	10	SPhos, 20	KOAc, 1.2	/	12
10	10	SPhos, 20	*t*BuOLi, 1.2	/	20
11	10	SPhos, 20	*t*BuONa, 1.2	/	18
12	10	SPhos, 20	*t*BuOK, 1.2	/	50 [c]
13 [d]	10	SPhos, 20	K_2CO_3, 1.2	/	trace
14 [e]	10	SPhos, 20	K_2CO_3, 1.2	/	30
15 [f]	10	SPhos, 20	K_2CO_3, 1.2	/	50
16	10	SPhos, 20	K_2CO_3, 2.4	PivOH 1.2	57
17	10	SPhos, 20	K_2CO_3, 2.4	$PhCO_2H$ 1.2	80
18	10	SPhos, 20	K_2CO_3, 2.4	HOAc 1.2	72
19	10	SPhos, 20	K_2CO_3, 2.4	AdOH 1.2	84
20	10	SPhos, 20	K_2CO_3, 1.2	AdOH 0.1	84 (82)
21	5	SPhos, 10	K_2CO_3, 1.2	AdOH 0.1	82 (80)
22	5	SPhos, 5	K_2CO_3, 1.2	AdOH 0.1	90 (87)

a) Conditions (unless otherwise specified): **1a** (0.6 mmol) and **2a** (0.3 mmol) in solvent (2.0 mL), 8 h; b) NMR yield determined by ^{19}F NMR using fluorobenzene as the internal standard and number in parentheses is isolated yield; c) 20% yield of defluorinated side product was observed; d) using DMSO as solvent; e) using toluene as solvent; f) using dioxane as solvent.

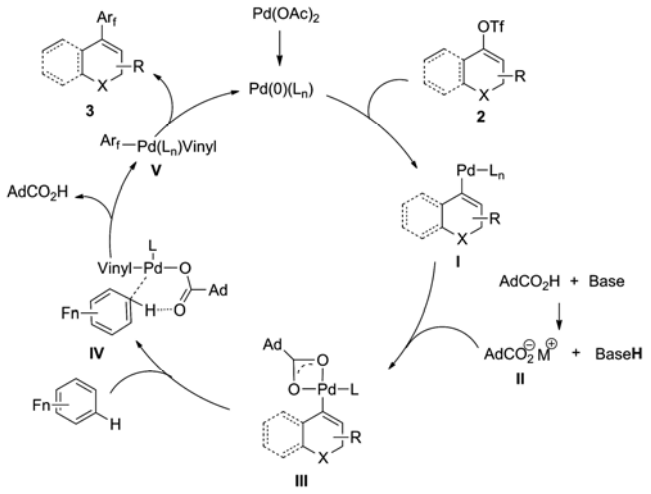
results were illustrated in Table 2. Generally, the standard reaction conditions were quite suitable for 1-tetralone derived substrate (**3b**) and different polyfluoroarenes (**3c**–**e**). Fluoroarenes bearing either electron-donating group or electron-withdrawing group, such as 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene and 1,2,4,5-tetrafluoro-3-methoxybenzene, all furnished their corresponding products smoothly when 1-tetralone derived triflates were used as substrates. Apart from conjugated vinyl triflates, substrate bearing amide group derived from 4-piperidinone also reacted smoothly with polyfluoroarenes in good yields (**3f–g**). However, this standard reaction condition was not applicable to cyclohexenyl triflate. To address this issue, different phosphane ligands were screened. We were pleased to find that a satisfying yield was provided when DavePhos was employed as a ligand (**3h**). Under such modified reaction conditions, other fluoroarenes and cyclohexenyl triflates were all suitable substrates (**3i–k**). It is noteworthy that an excellent yield was obtained when 4-phenyl cyclohexenyl triflate was tested (**3j**). However, five-membered cyclic vinyl substrates failed to provide desired products due to the decomposition of these triflates [9].

Table 2 Pd-catalyzed direct cross-coupling of polyfluoroarenes with cyclic vinyl triflates [a)]



a) Conditions (unless otherwise specified): **1a** (0.6 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), SPhos (5 mol%), AdOH (0.1 equiv) and K_2CO_3 (1.2 equiv) in DMF 2.0 mL, 8 h. All yields are of the isolated products. b) Use DavePhos as ligand.

On the basis of the results reported by others [11] and us [5f], a plausible mechanism is proposed and shown in Scheme 2. An oxidative addition of cyclic vinyl triflates to a zero valent Pd species is envisioned to take place as an initial step, leading to a Pd-vinyl intermediate **I**. **I** subsequently undergoes ligand exchange with 1-adamantanecarboxylate (**II**) to form **III**, which reacts with polyfluoroarenes through the concerted-metallation-deprotonation (CMD) process [11] to generate the key intermediate **V**. As the final step of the catalytic cycle, reductive elimination of **V** produces polyfluoroarylated cyclic alkenes along with the regeneration of Pd(0) species.



Scheme 2 Plausible mechanism of the Pd-catalyzed cross-coupling of polyfluoroarenes with cyclic vinyl triflates.

4 Conclusions

In summary, we have developed an effective and straightforward method for Pd-catalyzed cross-coupling of polyfluoroarenes with cyclic vinyl triflates. This method allows the conversion of easily accessible cyclic vinyl triflates to polyfluoroarylated derivatives of interest in both life and material science.

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