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One-pot synthesis of polyfluoroterphenyls via palladium-catalyzed Suzuki–Miyaura coupling of chlorobromobenzene and C–H bond functionalization of perfluoroarenes

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An efficient tandem route for the synthesis of polyfluoroterphenyl derivatives has been developed. The target compounds were obtained in moderate to good yields by a $Pd(OAc)_2$-catalyzed three-component coupling reaction involving palladium-catalyzed direct C–H activation of perfluoroarenes. This in turn will set the stage for a wide application of this useful reaction for the synthesis of fluorinated liquid crystal compounds containing the privileged polyfluoroterphenyl structure. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: one pot; polyfluoroterphenyls; palladium catalysis; Suzuki–Miyaura; perfluoroarenes

Introduction

Terphenyl compounds are important polyaromatic hydrocarbon derivatives present in nature[1] and many products of biological significance,[2] and are often exploited in the design of organic electroluminescent devices[3] and liquid-crystalline materials[4] because of their unique photophysical properties. Especially, polyfluoroterphenyls like Ar–Ar–Ar_F find diverse applications in liquid crystals, material science, molecular electronics, nonlinear optics, etc. Due to the strong π-stacking interaction between the polyfluoroaryl unit and non-fluorinated aromatic fragment,[5] such compounds tend to form molecular complexes in solutions[6] and well-controlled nanostructures in solids.[7] So the development of convenient and efficient synthesis methods has attracted considerable attention.

To date, general methodologies described for the synthesis of non-symmetric terphenyl derivatives include the coupling reactions of bromobenzenesulfonates with arylboronic acids and aryl magnesium bromides, through separate Pd- and Ni-catalyzed reactions,[8] sequential Negishi coupling reactions of diorganozinc reagents with iodoaryl nonaflates and zinc phenoxides with aryl triflates.[9] Purification of biaryl intermediates by column chromatography is required and the reactivity of these organometallic reagents can also be incompatible with certain electrophilic functional groups, such as carbonyls, enones, and so on. Among the known synthetic routes to obtain the terphenyl skeleton, double Suzuki–Miyaura reactions using various arylboronic acids and aryl dihalides are the most popular methods (Scheme 1), because aryl precursors are widely available and easy to handle and most functional groups can be accommodated by the system.[10] However, some reported sequential coupling reactions suffer disadvantages such as the requirement for two different catalysts, the intermediate products having to be separated prior to the second coupling or requiring not easily available substrates.[11] From the viewpoint of efficiency, one-pot sequential reactions of commercially available inexpensive aryl dihalides with a single catalyst are highly desirable, and so far only a few successful examples have been reported.[10d]

In recent years, transition-metal-catalyzed direct C–H arylation in which the C–H bond is used as a functional group has attracted considerable attention.[12] As an alternative C–C bond-forming strategy, this direct arylation of perfluoroarenes represents a more efficient method because it is straightforward and attractive, and significant progress has been made in the transition-metal-catalyzed direct formation of C–C bonds between perfluoroarenes and arylhalides or arenes.[13] However, transition-metal-catalyzed C–H bond activation associated with more commonplace cross-coupling methods to synthesize polyfluoroterphenyls by one-pot sequential functionalization of aryl dihalides remains very meaningful work. This is because of the synthetic importance of the polyfluoroterphenyl structure and our continuing interest in Pd-catalyzed C–C coupling.[14] Herein, we describe the facile and efficient one-pot sequential reactions of aryl dihalides using Pd-catalyzed Suzuki–Miyaura coupling/C–H functionalization to afford unsymmetrically substituted polyfluoroterphenyls (Scheme 1).

Experimental

Materials and Instrumentation

All reactions were carried out under nitrogen using magnetic stirring unless otherwise noted. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra

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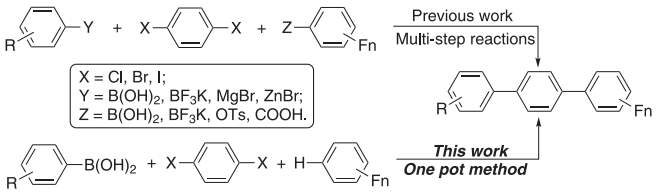


Scheme 1. Strategies towards syntheses of polyfluoroterphenyls.

were recorded at room temperature with a Varian Inova-400 spectrometer in C_6D_6. Electron ionization mass spectra were measured with a high-resolution mass spectrometer (Thermo Finnigan Trace GC/MAT95 XP, USA). Toluene was dried over Na, distilled and stored under nitrogen. 1,4-Dioxane was distilled from calcium hydride and degassed with nitrogen. Column chromatography was performed with silica gel (300–400 mesh) purchased from Qingdao Haiyang Chemical Co. Ltd. Thin-layer chromatography (TLC) was carried out with GF254 plates from the same company. All other reagents were of analytical grade quality purchased commercially and used as received.

General Procedure for Synthesis of Compounds 5

Boronic acid (1.1 equiv.) was added to a solution of aryl dihalide (**1**; 0.20 mmol), $Pd(OAc)_2$ (0.10 equiv.), PCy_3 (0.20 equiv.) and Cs_2CO_3 (5 equiv.) in toluene (1.0 ml). The resulting mixture was heated to 80°C under nitrogen atmosphere for the appropriate time (monitored using GC-MS). Fluoroarene (2.0 equiv.) was then added and the mixture was heated to 110°C (140°C) for the appropriate time (monitored using TLC) in a sealed tube. The resulting mixture was cooled to room temperature and quenched with water and extracted with EtOAc (3 ×10 ml). The combined EtOAc extracts were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with PE or PE–EtOAc as the eluent to obtain the desired products.

*2,3,4,5,6-Pentafluoro-4″-methoxy-1,1′:4′,1″-terphenyl (**5b**)*

Product **5b** (Fig. 1) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 157.9–159.1°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.50–7.45 (m, 2H, H6 and H6′), 7.43–7.38 (m, 2H, H2 and H2′), 7.28–7.23 (m, 2H, H3 and H3′), 6.88–6.83 (m, 2H, H7 and H7′), 3.34 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.3 (s, C1), 144.4 (m, C10 and C10′), 142.4 (s, C5), 133.0 (s, C12), 140.4 (m, C11 and C11′), 136.6 (m, C8), 130.8 (s, C4), 128.6 (s, C3 and C3′), 127.3 (s, C6 and C6′), 124.8 (s, C7 and C7′), 114.8 (s, C9), 115.9 (m, C2 and C2′), 54.9 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −143.99 (m, 2F, F10 and F10′), −156.53 (m, 1F, F12), −162.73 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{11}F_5O$ (M^+): 350.0726; found: 350.0725. Anal. Calcd for $C_{19}H_{11}F_5O$ (%): C, 65.15; H, 3.17. Found (%): C, 65.25; H, 2.97.

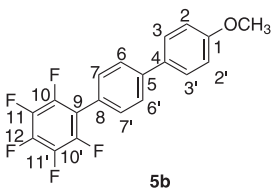


Figure 1. The numbering of carbon atoms in product **5b**.

*2,3,4,4″,5,6-Hexafluoro-1,1′:4′,1″-terphenyl (**5c**)*

Product **5c** (Fig. 2) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 169.7–170.9°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 6.90 (d, J =8.0 Hz, 2H, H2 and H2′), 6.81 (d, J =8.0, 2H, H3 and H3′), 6.78 (d, J =7.8 Hz, 2H, H6 and H6′), 6.46 (d, J =7.8 Hz, 2H, H7 and H7′). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 164.5 (s, C1), 162.0 (s, C5), 144.4 (m, C10 and C10′), 141.5 (s, C12), 140.6 (m, C11 and C11′), 138.1 (m, C4), 136.5 (m, C8), 130.8 (s, C3 and C3′), 129.1 (s, C6 and C6′), 127.5 (s, C9), 125.1 (m, C7 and C7′), 116.0 (m, C2 and C2′). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −114.49 to −114.78 (m, 1F, F1), −144.00 (m, 2F, F10 and F10′), −156.11 (m, 1F, F12), −162.56 (m, 2F, F11 and F11′). HRMS calcd for $C_{18}H_8F_6$ (M^+): 338.0529; found: 338.0525. Anal. Calcd for $C_{18}H_8F_6$ (%): C, 63.92; H, 2.38. Found (%): C, 64.01; H, 2.32.

*2,3,4,5,6-Pentafluoro-4″-methyl-1,1′:4′,1″-terphenyl (**5d**)*

Product **5d** (Fig. 3) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 155.6–156.9°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.53–7.47 (m, 2H, H2 and H2′), 7.43–7.37 (m, 2H, H3 and H3′), 7.28–7.22 (m, 2H, H6 and H6′), 7.10–7.04 (m, 2H, H7 and H7′), 2.17 (s, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.3 (s, C1), 144.4 (m, C10 and C10′), 142.4 (s, C5), 133.0 (s, C12), 140.4 (m, C11 and C11′), 136.6 (m, C8), 130.8 (s, C4), 128.6 (s, C3 and C3′), 127.3 (s, C6 and C6′), 124.8 (s, C7 and C7′), 114.8 (s, C9), 115.9 (m, C2 and C2′), 54.9 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −143.95 (m, 2F, F10 and F10′), −156.46 (m, 1F, F12), −162.72 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{11}F_5$ (M^+): 334.0776; found: 334.0775. Anal. Calcd for $C_{19}H_{11}F_5$ (%): C, 68.27; H, 3.32. Found (%): C, 68.25; H, 3.37.

*2,3,4,5,6-Pentafluoro-2″-methyl-1,1′:4′,1″-terphenyl (**5e**)*

Product **5e** (Fig. 4) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 102.8–103.5°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.27–7.17 (m, 5H, H1, H2 and H2′, H3), 7.15–7.07 (m, 4H, H6 and H6′, H7 and H7′), 2.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 144.4 (m, C12 and C12′), 143.6 (s, C14), 141.3 (s, C7), 140.4 (m, C13 and C13′), 136.6 (m, C8 and C8′, C9 and C9′), 135.5 (s, C1), 130.8 (s, C10), 130.2 (s, C6), 130.1 (s, C2), 130.0 (s, C3), 126.3 (s, C4), 125.1 (s, C5), 115.9 (td, J =14.8, 6.5 Hz, C11), 20.4 (s, CH_3). ^{19}F NMR (376 MHz, C_6D_6, δ,

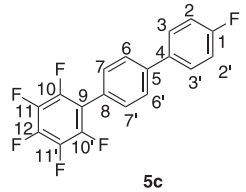


Figure 2. The numbering of carbon atoms in product **5c**.

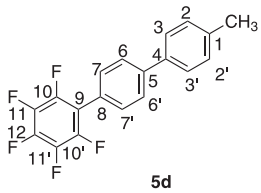


Figure 3. The numbering of carbon atoms in product **5d**.

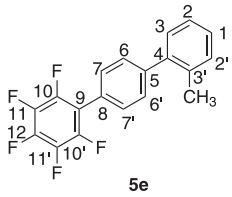


Figure 4. The numbering of carbon atoms in product **5e**.

ppm): −144.01 (m, 2F, F10 and F10′), −156.26 (m, 1F, F12), −162.67 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{11}F_5$ (M^+): 334.0776; found: 334.0775. Anal. Calcd for $C_{19}H_{11}F_5$ (%): C, 68.27; H, 3.32. Found (%): C, 68.15; H, 3.41.

*2,3,4,5,6-Pentafluoro-4″-propyl-1,1′:4′,1″-terphenyl (**5f**)*

Product **5f** (Fig. 5) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 159.9–160.3°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.52 (d, J =8.0 Hz, 2H, H7 and H7′), 7.45 (d, J =8.0 Hz, 2H, H6 and H6′), 7.25 (d, J =7.8 Hz, 2H, H3 and H3′), 7.12 (d, J =7.8 Hz, 2H, H2 and H2′), 2.49 (t, J =7.5 Hz, 2H, $CH_2CH_2CH_3$), 1.63–1.51 (m, 2H, $CH_2CH_2CH_3$), 0.89 (t, J =7.3 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 144.4 (m, C10 and C10′), 142.7 (s, C1), 142.6 (s, C5), 140.4 (m, C11 and C11′), 138.1 (s, C4), 138.0 (m, C12), 130.8 (s, C2 and C2′), 129.4 (s, C8), 127.6 (s, C3 and C3′), 127.4 (s, C6 and C6′), 125.2 (s, C7 and C7′), 115.9 (m, C9), 38.0 (s, $CH_2CH_2CH_3$), 24.8 (s, $CH_2CH_2CH_3$), 13.9 (s, $CH_2CH_2CH_3$). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −143.94 (m, 2F, F10 and F10′), −156.46 (m, 1F, F12), −162.73 (m, 2F, F11 and F11′). HRMS calcd for $C_{21}H_{15}F_5$ (M^+): 362.1088; found: 362.1088. Anal. Calcd for $C_{21}H_{15}F_5$ (%): C, 69.61; H, 4.17. Found (%): C, 69.38; H, 4.23.

*2,3,4,5,6-Pentafluoro-4″-(trifluoromethyl)-1,1′:4′,1″-terphenyl (**5g**)*

Product **5g** (Fig. 6) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 132.4–133.2°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.42 (d, J =8.0 Hz, 2H, H2 and H2′), 7.29 (d, J =8.0 Hz, 2H, H3 and H3′), 7.26–7.18 (m, 4H, H6 and H6′, H7 and H7′). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 144.4 (m, C1), 143.8 (s, C5), 140.9 (s, C12), 140.7 (m, C10 and C10′), 138.1 (m, C11 and C11′), 130.9 (s, C4), 130.1 (m, C3 and C3′), 127.8 (s, C8), 127.7 (s, C9), 126.4 (m, C6 and C6′), 126.1 (m, C7 and C7′), 123.2 (s, C13), 115.4 (m, C2 and C2′). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −62.18 (s, 3F, F13), −143.99 (m, 2F, F10 and F10′), −155.67 (m, 1F, F12), −162.34 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_8F_8$ (M^+): 388.0491; found: 388.0493. Anal. Calcd for $C_{19}H_8F_8$ (%): C, 58.78; H, 2.08. Found (%): C, 58.54; H, 2.14.

*2,3,3″,4,4″,5,5″,6-Octafluoro-1,1′:4′,1″-terphenyl (**5h**)*

Product **5h** (Fig. 7) was obtained by flash column chromatography on silica gel with PE as the eluent. White solid; m.p. 105.5–106.4°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.15 (d, J =12.0 Hz, 2H, H3 and H3′), 7.00 (d, J =8.1 Hz, 2H, H6 and H6′), 6.69 (t, J =7.2 Hz, 2H, H7 and H7′). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 151.8 (m, C10 and C10′), 144.3 (m, C1), 140.0 (m, C5), 138.1 (m, C4), 139.1 (s, C12), 137.9 (m, C11 and C11′), 130.8 (s, C8), 127.3 (s, C4), 126.5 (s, C5 and C5′), 115.3 (m, C6 and C6′, C7 and C7′), 111.4 (m, C3 and C3′), 110.4 (C9). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −134.00 (m, 2F, F2 and F2′), −144.00 (m, 2F, F10 and F10′), −155.50 (m, 1F, F1), −161.83 (m, 1F, F12), −162.25 (m, 2F, F11 and F11′). HRMS calcd for $C_{18}H_6F_8$ (M^+): 374.0335; found: 374.0336. Anal. Calcd for $C_{18}H_6F_8$ (%): C, 57.77; H, 1.62. Found (%): C, 58.13; H, 1.59.

*2,3,4,5,6-Pentafluoro-1,1′:4′,1″:4″,1‴-quaterphenyl (**5i**)*

Product **5i** (Fig. 8) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 139.9–140.3°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.70–7.68 (m, 2H, H2 and H2′), 7.66–7.63 (m, 4H, H3 and H3′, H6 and H6′), 7.59–7.56 (m, 2H, H7 and H7′), 7.50–7.42 (m, 4H, H10 and H10′, H11 and H11′), 7.40–7.36 (m, 1H, H1). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 140.7 (s, C14), 140.6 (s, C4), 139.3 (m, C5, C8 and C9), 139.0 (s, C16), 133.6 (s, C15 and C15′), 129.1 (s, C12), 129.0 (s, C2 and C2′), 128.4 (s, C3 and C3′), 127.7 (s, C1), 127.6 (m, C6 and C6′, C7 and C7′), 127.5 (s, C10 and C10′, C11 and C11′), 127.2 (C13). ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm): −143.94 (m, 2F, F10 and F10′), −156.26 (m, 1F, F12), −162. 61 (m, 2F, F11 and F11′). HRMS calcd for $C_{24}H_{13}F_5$ (M^+): 396.0936; found: 396.0932. Anal. Calcd for $C_{24}H_{13}F_5$ (%): C, 72.73; H, 3.31. Found (%): C, 72.58; H, 3.43.

*2-(2′,3′,4′,5′,6′-Pentafluoro-[1,1′-biphenyl]-4-yl)naphthalene (**5j**)*

Product **5j** (Fig. 9) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 186.6–187.0°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.91–7.71 (m, 4H,

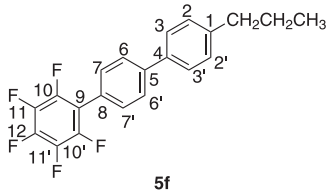


Figure 5. The numbering of carbon atoms in product **5f**.

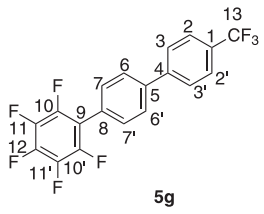


Figure 6. The numbering of carbon atoms in product **5g**.

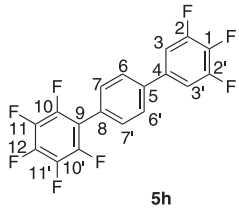


Figure 7. The numbering of carbon atoms in product **5h**.

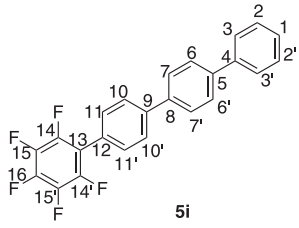


Figure 8. The numbering of carbon atoms in product **5i**.

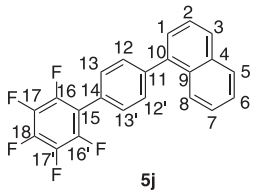


Figure 9. The numbering of carbon atoms in product **5j**.

H12 and H12′, H13 and H13′), 7.60–7.52 (m, 3H, H1, H2, and H3), 7.35–7.25 (m, 4H, H5, H6, H7, and H8). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 144.5 (dm, J =247.8 Hz, C16 and C16′), 142.5 (s, C11), 141.5 (dm, J =245.1 Hz, C17 and C17′), 138.6 (dm, J =248.2 Hz, C18), 137.9 (s, C14), 134.3 (s, C2), 133.5 (s, C10), 130.9 (s, C7), 129.0 (s, C9), 128.6 (s, C3 and C6), 126.8 (s, C8), 126.6 (s, C12, C12′ and C13, C13′), 126.5 (s, C4 and C4′), 125.6 (s, C1). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −143.91 (m, 2F, F10 and F10′), −156.26 (m, 1F, F12), −162.60 (m, 2F, F11 and F11′). HRMS calcd for $C_{22}H_{11}F_5$ (M^+): 370.0776; found: 370.0775. Anal. Calcd for $C_{22}H_{11}F_5$ (%): C, 71.35; H, 2.99. Found (%): C, 71.28; H, 3.04.

*2,3,5,6-Tetrafluoro-4-(4′-methoxy-[1,1′-biphenyl]-4-yl)pyridine (**5k**)*

Product **5k** (Fig. 10) was obtained by flash column chromatography on silica gel with PE–EtOAc =50:1 as the eluent. White solid; m.p. 118.0–119.0°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.43 (d, J =8.2 Hz, 2H, H2 and H2′), 7.38 (d, J =8.6 Hz, 2H, H6 and H6′), 7.21 (d, J =8.2 Hz, 2H, H3 and H3′), 6.85 (d, J =8.6 Hz, 2H, H7 and H7′), 3.35 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.5 (s, C1), 144.3 (m, C10 and C10′), 143.4 (s, C5), 139.5 (m, C11 and C11′), 132.5 (s, C8), 130.5 (m, C9), 128.6 (s, C4), 127.2(s, C3 and C3′), 124.2 (s, C6 and C6′), 114.8 (s, C7 and C7′), 114.7 (m, C2 and C2′), 54.9 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −91.43 (m, 2F, F10 and F10′), −145.63 (m, 2F, F11 and F11′). HRMS calcd for $C_{18}H_{11}F_4NO$ (M^+): 333.0772; found: 333.0772. Anal. Calcd for $C_{18}H_{11}F_4NO$ (%): C, 64.87; H, 3.33; N, 4.20. Found (%): C, 64.74; H, 3.41; N, 4.17.

*2,3,5,6-Tetrafluoro-4″-methoxy-[1,1′:4′,1″-terphenyl]-4-carbonitrile(**5l**)*

Product **5l** (Fig. 11) was obtained by flash column chromatography on silica gel with PE–EtOAc =50:1 as the eluent. White solid; m.p. 105.3–106.4°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.23 (d, J =8.6 Hz, 2H, H2 and H2′), 7.18 (d, J =8.4 Hz, 2H, H6 and H6′), 7.14 (d, J =8.7 Hz, 2H, H3 and H3′), 6.81 (d, J =8.7 Hz, 2H, H7 and H7′), 3.33 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 159.5 (s, C1), 147.5(m, C11 and C11′), 143.4 (m, C10 and C10′), 139.3 (s, C5), 135.4 (s, C8), 132.5 (s, C4), 132.3 (s, C3 and C3′), 128.7 (m, C6 and C6′, C7 and C7′), 127.9 (s, C9), 114.2 (s, C2 and C2′), 112.6 (s, CN), 66.0 (s, C12), 54.5 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −139.54 to −139.66 (m, 2F, F10 and F10′), −144.43 to −144.54 (m, 2F, F11 and F11′). HRMS calcd for $C_{20}H_{11}F_4NO$ (M^+): 357.0777; found: 357.0778. Anal. Calcd for $C_{20}H_{11}F_4NO$ (%): C, 67.23; H, 3.10; N, 3.92. Found (%): C, 67.25; H, 3.07; N, 3.96.

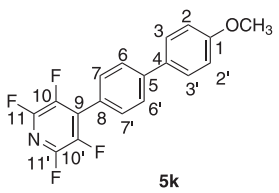


Figure 10. The numbering of carbon atoms in product **5k**.

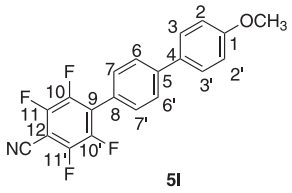


Figure 11. The numbering of carbon atoms in product **5l**.

*2,3,5,6-Tetrafluoro-4″-methoxy-1,1′:4′,1″-terphenyl (**5m**)*

Product **5m** (Fig. 12) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 178.3–179.2°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.45 (d, J =8.0 Hz, 2H, H2 and H2′), 7.39 (d, J =8.4 Hz, 2H, H3 and H3′), 7.30 (d, J =8.0 Hz, 2H, H6 and H6′), 6.85 (d, J =8.5 Hz, 2H, H7 and H7′), 6.32–6.24 (m, 1H, H12), 3.34 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.1 (s, C1), 147.2 (m, C11 and C11′), 142.4 (m, C10 and C10′), 141.8 (s, C5), 132.6 (s, C8), 130.4 (s, C4), 128.1 (s, C3 and C3′), 126.7 (m, C6 and C6′, C7 and C7′), 125.4 (s, C9), 114.3 (s, C2 and C2′), 104.4 (s, C12), 54.5 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −139.35 (m, 2F, F10 and F10′), −144.25 to −143.96 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{12}F_4O$ (M^+): 332.0824; found: 332.0819. Anal. Calcd for $C_{19}H_{12}F_4O$ (%): C, 68.68; H, 3.64. Found: C, 68.74; H, 3.58.

*2,3,4,6-Tetrafluoro-4″-methoxy-1,1′:4′,1‴-terphenyl (**5n**)*

Product **5n** (Fig. 13) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 102.4–103.0°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.48 (d, J =8.5 Hz, 2H, H3 and H3′), 7.40 (d, J =8.0 Hz, 2H, H6 and H6′), 7.30 (d, J =8.0 Hz, 2H, H7 and H7′), 6.85 (d, J =8.5 Hz, 2H, H2 and H2′), 6.17 (m, 1H, H11), 3.34 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.3 (s, C1), 146.6 (m, C14), 144.3 (m, C12), 142.3 (s, C10), 133.1 (s, C5), 130.8 (m, C8 and C13), 128.6 (s, C11), 127.2 (s, C4), 125.9 (m, C3 and C3′), 121.7 (m, C6 and C6′, C7 and C7′), 114.8 (s, C9), 104.8 (m, C2 and C2′), 54.9 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −118.25 (m, 1F, F10), −134.07 (m, 1F, F11), −135.87 (m, 1F, F12), −164.99 (m, 1F, F14). HRMS calcd for $C_{19}H_{12}F_4O$ (M^+): 332.0824; found: 332.0821. Anal. Calcd for $C_{19}H_{12}F_4O$ (%): C, 68.68; H, 3.64. Found (%): C, 68.54; H, 3.72.

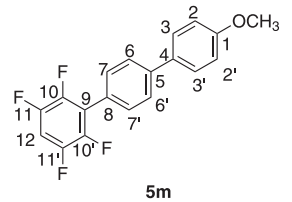


Figure 12. The numbering of carbon atoms in product **5m**.

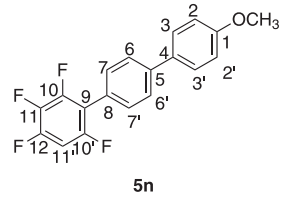


Figure 13. The numbering of carbon atoms in product **5n**.

*2,3,4,5,6-Pentafluoro-4″-methoxy-1,1′:3′,1″-terphenyl (**5o**)*

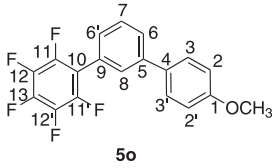
Product **5o** (Fig. 14) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. White solid; m.p. 105.8–106.4°C. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.55 (s, 1H, H8), 7.45–7.39 (m, 3H, H6′, H3 and H3′), 7.23 (m, 1H, H6), 7.13 (m, 1H, H7), 6.89–6.83 (m, 2H, H2 and H2′), 3.34 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6, δ, ppm): 160.0 (s, C1), 144.2 (m, C11 and C11′), 142.0 (s, C5 and C9), 137.8 (m, C12 and C12′), 133.0 (s, C4), 129.2 (s, C3 and C3′), 128.7 (s, C7), 128.5 (s, C6 and C8), 128.3 (s, C10), 127.0 (s, C13), 114.6 (s, C2 and C2′), 54.7 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −143.72 (m, 2F, F10 and F10′), −156.32 (m, 1F, F12), −162.67 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{11}F_5O$ (M^+): 350.0730; found: 350.0732. Anal. Calcd for $C_{19}H_{11}F_5O$ (%): C, 65.15; H, 3.17. Found (%): C, 65.20; H, 3.09.

*2,3,4,5,6-Pentafluoro-4″-methoxy-1,1′:2′,1‴-terphenyl (**5p**)*

Product **5p** (Fig. 15) was obtained by flash column chromatography on silica gel with PE–EtOAc =100:1 as the eluent. Colorless liquid. ^{1}H NMR (400 MHz, C_6D_6, δ, ppm): 7.32–7.28 (m, 1H, H7), 7.20–7.17 (m, 1H, H7′), 7.14–7.09 (m, 2H, H6 and H6′), 7.04–6.98 (m, 2H, H3 and H3′), 6.61–6.55 (m, 2H, H2 and H2′), 3.15 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 159.2 (s, C1), 142.7 (m, C10 and C10′), 140.3 (s, C5 and C8), 132.7 (s, C11 and C11′), 131.9 (s, C7 and C7′), 131.5 (s, C6 and C6′), 130.7 (s, C4), 130.0 (s, C3 and C3′), 128.3 (s, C9), 126.9 (s, C12), 113.6 (s, C2 and C2′), 54.4 (s, OCH_3). ^{19}F NMR (376 MHz, C_6D_6, δ, ppm): −140.70 (m, 2F, F10 and F10′), −155.66 (t, J =21.5 Hz, 1F, F12), −162.75 (m, 2F, F11 and F11′). HRMS calcd for $C_{19}H_{11}F_5O$ (M^+): 350.0730; found: 350.0732. Anal. Calcd for $C_{19}H_{11}F_5O$ (%): C, 65.15; H, 3.17. Found (%): C, 65.23; H, 3.09.

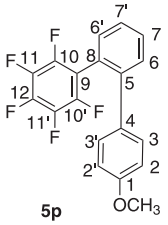
Results and Discussion

The investigation was initiated with 1-bromo-4-chlorobenzene (**1a**), phenylboronic acid (**2a**) and 1,2,3,4,5-pentafluorobenzene (**4a**) as the model substrates to optimize the reaction conditions, including different palladium sources, ligands, bases, temperature and various solvents. The results are summarized in Table 1. The formation of Suzuki–Miyaura coupling product 4-chloro-1,1′-biphenyl (**3a**) was catalyzed by $Pd(OAc)_2$ (10 mol%)/PPh_3 (20 mol%) in the presence of Cs_2CO_3 in toluene at 80°C. The complete conversion of the reaction (monitored using GC-MS) was attained within 2 h.



5o

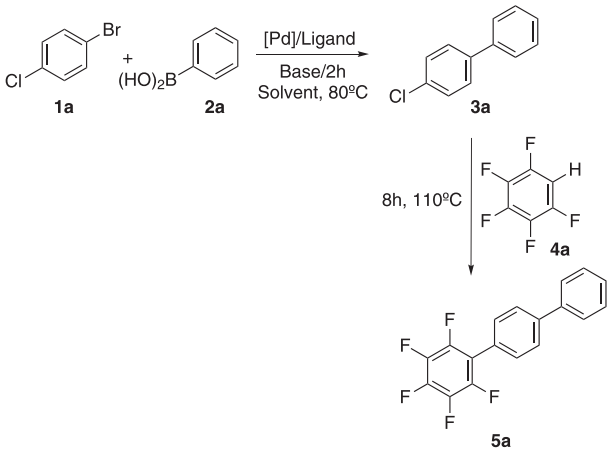
Figure 14. The numbering of carbon atoms in product **5o**.



5p

Figure 15. The numbering of carbon atoms in product **5p**.

Table 1. Optimization of reaction conditions[a]



Entry	Pd source	Ligand	Base	Solvent	Yield of **1a**/**3a**/**5a** (%)[b]
1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	0/99/trace
2	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	Toluene	0/0/84(81)[c]
3	$PdCl_2$	PCy_3	Cs_2CO_3	Toluene	0/97/3
4	$PdCl_2(CH_3CN)_2$	PCy_3	Cs_2CO_3	Toluene	95/5/0
5[d]	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	Toluene	0/43/14
6	$Pd(OAc)_2$	PCy_3	K_2CO_3	Toluene	0/68/31
7	$Pd(OAc)_2$	PCy_3	K_3PO_4	Toluene	0/0/0
8	$Pd(OAc)_2$	PCy_3	*t*-BuONa	Toluene	0/5/0
9	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	1,4-Dioxane	0/0/0
10	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	DME	0/46/27
11	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	DMF	0/0/0
12	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	DMSO	0/3/0

[a]Reaction conditions: a mixture of 10 mol% of Pd source, 20 mol% of ligand, 0.2 mmol of **1a**, 1.1 equiv. of $PhB(OH)_2$ and 5 equiv. of base in 1 ml of solvent heated to 80°C for 2 h, and then 2.0 equiv. of pentafluorobenzene was added and the resulting mixture was heated to 110°C for a further 8 h.

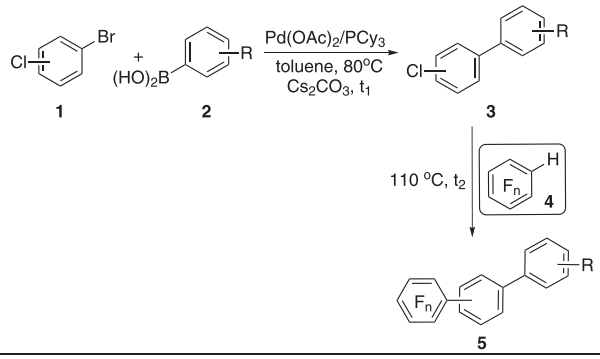
[b]Yields determined by GC-MS.

[c]Isolated yields of **5a**.

[d]5 mol% of $Pd(OAc)_2$ and 10 mol% of PCy_3 were used.

Therefore, the intermediate **3a** was used directly without purification. The sequential C–H activation was then carried out by simply adding **4a** in the wake of the initial Suzuki–Miyaura coupling reaction, the resulting mixture was then stirred for a further 8 h while raising the reaction temperature to 110°C. Unfortunately, the expected polyfluoroterphenyl **5a** is not obtained (entry 1). To our delight, a survey of different palladium sources and ligands reveals that $Pd(OAc)_2$/PCy_3 displays the best performance, providing the expected product **5a** in 81% isolated yield (entry 2). $PdCl_2$ shows lower activity towards this sequential C–H activation of **4a** (entry 3), and $PdCl_2(CH_3CN)_2$ shows no activity at all towards the two reactions (entry 4). A significant drop of the yield (**5a**, 14%) is observed when using a catalyst loading as low as 5 mol% of $Pd(OAc)_2$ and 10 mol% of PCy_3 (entry 5), along with a 43% yield of **3a**. The effect of the base was also studied. When the reaction is performed in the presence of K_2CO_3, polyfluoroterphenyl **5a** is obtained with a lower yield (31%) together with **3a** (68%), pointing to the superiority of Cs_2CO_3 in the C–H bond activation step (entry 6). K_3PO_4 or *t*-BuONa as base and 1,4-dioxane, DME,

Table 2. Synthesis of compounds **5**[a]



Entry	1	2; R	Intermediate (**3**)	4	Product	t_1 (h)/t_2 (h)	Yield (%)[b]
1	1-Bromo-4-chlorobenzene (**1a**)	4-OMe (**2b**)	**3b**	1,2,3,4,5-Pentafluorobenzene (**4a**)	**5b**	1/4	79
2	**1a**	4-F (**2c**)	**3c**	**4a**	**5c**	5[c]/24	79
3	**1a**	4-Me (**2d**)	**3d**	**4a**	**5d**	1/12	71
4	**1a**	2-Me (**2e**)	**3e**	**4a**	**5e**	2/12	42
5	**1a**	4-C_3H_7 (**2f**)	**3f**	**4a**	**5f**	2/7	71
6	**1a**	4-CF_3 (**2g**)	**3g**	**4a**	**5g**	6/3	62
7	**1a**	3,4,5-F_3 (**2h**)	**3h**	**4a**	**5h**	4/6	70
8	**1a**	4-Ph (**2i**)	**3i**	**4a**	**5i**	1/5	38
9	**1a**	2-Naphthylboronic acid (**2j**)	**3j**	**4a**	**5j**	3/4	57
10	**1a**	**2b**	**3b**	2,3,5,6-Tetrafluoropyridine (**4b**)	**5k**	1/22	77
11	**1a**	**2b**	**3b**	2,3,5,6-Tetrafluorobenzonitrile (**4c**)	**5l**	1/48	60
12	**1a**	**2b**	**3b**	1,2,4,5-Tetrafluorobenzene (**4d**)	**5m**	1/12	40
13	**1a**	**2b**	**3b**	1,2,3,5-Tetrafluorobenzene (**4e**)	**5n**	1/48	65
14	1-Bromo-2-chlorobenzene (**1b**)	**2b**	**3k**	**4a**	**5o**	1/12[d]	80
15	1-Bromo-3-chlorobenzene (**1c**)	**2b**	**3l**	**4a**	**5p**	1/12	83

[a]Reaction conditions: a mixture of 10 mol% of $Pd(OAc)_2$, 20 mol% of PCy_3, 0.2 mmol of **1**, 1.1 equiv. of $ArB(OH)_2$ and 5 equiv. of Cs_2CO_3 in 1 ml of toluene was heated to 80°C under nitrogen until reaction of **1** was completed (GC-MS), and then 2.0 equiv. of **4** was added and the resulting mixture was heated to 110°C for a further appropriate time (determined by TLC).

[b]Isolated yields.

[c]Reaction temperature of 100°C.

[d]The mixture was heated to 140°C after **4** added.

DMF or DMSO as solvent are not efficient for the diarylation reactions (entries 7–12).

The scope and limitation of this Suzuki–Miyaura coupling/C–H bond activation sequence were then investigated using the optimized conditions, namely $Pd(OAc)_2$ (10 mol%), PCy_3 (20 mol%) and Cs_2CO_3 (5.0 equiv.) in toluene using various arylboronic acids, chlorobromobenzene and perfluoroarenes (Table 2). For the first step of the Suzuki–Miyaura coupling reactions, most of the arylboronic acids react smoothly with **1a** to give intermediate products **3** in excellent yields monitored using GC-MS (entries 1–9), although some coupling reactions require high temperature or long reaction time. For example, the coupling reaction of 4-fluorophenylboronic acid (**2c**) and **1a** is carried out at 100°C, and the reactions of 4-(trifluoromethyl) phenylboronic acid (**2g**) and 3,4,5-trifluorophenylboronic acid (**2h**) as substrates take 6 h and 4 h to complete, respectively. More importantly, subsequent to the Suzuki–Miyaura coupling reaction, direct C–H activation of 1,2,3,4,5-pentafluorobenzene could be successfully achieved, and the products **5b–5j** are obtained in 38–79% overall yields. Encouraged by these results, we investigated the arylation of various perfluorobenzenes and the intermediate products **3b**. 2,3,5,6-Tetrafluoropyridine (**4b**) is also a suitable substrate for the coupling reaction and leads to **5k** in 77% yield (entry 10). 2,3,5,6-Tetrafluorobenzonitrile (**4c**) gives rise to product **5l** in 60% yield (entry 11). 1,2,4,5-Tetrafluorobenzene (**4d**) and 1,2,3,5-tetrafluorobenzene (**4e**) also work well, affording the products **5m** and **5n** in moderate yields (entries 12 and 13). In addition, 1-bromo-2-chlorobenzene (**1b**) and 1-bromo-3-chlorobenzene (**1c**) as chlorobromobenzene substrates afford polyfluoroterphenyl compounds **5o** in 80% yield and **5p** in 83% yield, respectively.

Conclusions

In summary, an original two-step single-flask palladium-catalyzed Suzuki–Miyaura cross-coupling/direct C–H functionalization sequence has been developed using readily available chlorobromobenzene and arylboronic acids, allowing the straightforward functionalization with these readily available perfluoroarenes. This sequential cross-coupling approach yields a large range of non-symmetric polyfluoroterphenyl compounds, being potentially relevant fluorinated liquid crystalline products.

Acknowledgements

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