A Facile and mild method for the synthesis of terminal bromofluoroolefins via diethylzinc promoted Wittig reaction.

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General Procedure for the obtention of bromofluoroolefins from aldehydes:

To a solution of triphenylphosphine (2.4 mmol, 1.2 eq.), tribromofluoromethane (2.4 mmol, 1.2 eq.), and an appropriate aldehyde (2.0 mmol, 1.0 eq.) in anhydrous THF (30-40 mL), a solution of diethylzinc in hexanes or toluene (2.4 mmol, 1.2 eq.) was added dropwise *via* a syringe pump over 30 min. at room temperature under argon. The mixture was stirred at room temperature for 30 minutes. The resulting solution was then quenched with methanol (10 ml), stirred for 20 min., and concentrated under reduced pressure. The residue was then chromatographed on silica gel (eluent: cyclohexane/ ethyl acetate), affording desired bromofluoroolefins.

General Procedure for the obtention of bromofluoroolefins from ketones:

To a solution of triphenylphosphine (3.0 mmol, 1.5 eq.), tribromofluoromethane (3.0 mmol, 1.5 eq.), and an appropriate ketone (2.0 mmol, 1.0 eq.) in anhydrous THF (30-40 mL), a solution of diethylzinc in hexanes or toluene (3.0 mmol, 1.5 eq.) was added dropwise *via* a syringe pump over 30 min. at room temperature under argon. The mixture was stirred at room temperature for 30 minutes. The resulting solution was then quenched with methanol (10 ml), stirred for 20 min., and concentrated under reduced pressure. The residue was then chromatographed on silica gel (eluent: cyclohexane/ ethyl acetate), affording desired bromofluoroolefins.

Experimental Section:

All commercial solvents were distilled before using. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen atmosphere. TLC was performed on Merck 60F-250 silica gel plates and column chromatography over silica gel SI 60 (230-240 mesh). Flash column chromatography purifications were carried out using silica gel (70-230 mesh). ¹H NMR, ¹³C NMR and ¹⁹F NMR (CFCl₃ as external reference) were recorded at 300.13, 75.47 and 282.40 MHz respectively.

Supplementary materials

^1H NMR (300 MHz, CDCl_3):

7.3-7.1 (m, 5H), 5.6-5.4 (dt, 0.5H, $^3J=7.6\text{Hz}$, $^3J_{\text{H-F}}^{\text{cis}}=12.8\text{Hz}$), 5.1-4.9 (dt, 0.5H, $^3J=7.6\text{Hz}$, $^3J_{\text{H-F}}^{\text{trans}}=31.0\text{Hz}$), 2.7-2.6 (m, 2H), 2.4-2.2 (m, 2H).

^{19}F NMR (282.5 MHz, CDCl_3):

-71.7 (d, $^3J_{\text{H-F}}^{\text{cis}}=13.1\text{Hz}$), 75.4 (dt, $^3J_{\text{H-F}}^{\text{trans}}=31.2\text{Hz}$, $^4J_{\text{H-F}}=2.6\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

139.5 (C5), 136.5-132.4 (d, $^3J_{\text{C-F}}^{\text{cis}}=314.5\text{Hz}$, C1), 132.7-128.5 (d, $^3J_{\text{C-F}}^{\text{trans}}=319.7\text{Hz}$, C1), 127.1-127.2-127.3 (C6, C7), 125 (C8), 110.5 (d, $J_{\text{C-F}}^{\text{cis}}=12.7\text{Hz}$, C2), 107.9 (d, $J_{\text{C-F}}^{\text{trans}}=15.5\text{Hz}$, C2), 33.8 (d, $J_{\text{C-F}}^{\text{trans}}=2.3\text{Hz}$, C4), 33.5 (d, $J_{\text{C-F}}^{\text{trans}}=2.3\text{Hz}$, C4), 28.2 (C3, cis), 28.1 (C3, trans)

MS (EI): 230 (M^+), 149 (M^+-Br), 91

IR (KBr): 3320, 3028, 2927, 1807, 1718, 1667, 1603, 1495, 1454, 1178, 1111, 1088, 1022, 1000, 747, 698

^1H NMR (300 MHz, CDCl_3):

7.7-7.6 (m, 4H, Ar-H), 7.5-7.3 (m, 6H, Ar-H), 5.7-5.5 (dt, 0.5H, $^3J_{\text{H-F}}^{\text{cis}}=13.3\text{Hz}$, $^3J_{\text{H-H}}=7.8\text{Hz}$, H2), 5.2-5.0 (dt, 0.5H, $^3J_{\text{H-F}}^{\text{trans}}=31.2\text{Hz}$, $^3J_{\text{H-H}}=7.8\text{Hz}$, H2), 3.7-3.6 (m, 2H, H4), 2.4-2.2 (m, 2H, H3), 1.1-1.0 (s, 9H, H6)

^{19}F NMR (282.5 MHz, CDCl_3):

70.6 (d, $^3J_{\text{H-F}}^{\text{cis}}=13.2\text{Hz}$), 75.0 (dt, $^3J_{\text{H-F}}^{\text{trans}}=31.2\text{Hz}$, $^4J_{\text{H-F}}^{\text{trans}}=2.1\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

138.5-134.9 (d, $^1J_{\text{C-F}}^{\text{E}}=277\text{Hz}$, C1), 134.3-130.6 (d, $^1J_{\text{C-F}}^{\text{Z}}=255\text{Hz}$), 136.0-130.0-128.1 (C_{ArH}), 134.0 (C_{Ar}), 110.0 (d, $^2J_{\text{C-F}}^{\text{E}}=12.7\text{Hz}$, C2), 107.0 (d, $^2J_{\text{C-F}}^{\text{E}}=277\text{Hz}$, C2), 62.0 (dd, $^4J_{\text{C-F}}=2.1\text{Hz}$, $^4J_{\text{C-F}}=2.1\text{Hz}$, C4), 31.5 (d, $^3J_{\text{C-F}}^{\text{Z}}=3.5\text{Hz}$, C3), 30.0 (d, $^3J_{\text{C-F}}^{\text{E}}=2.1\text{Hz}$, C3), 27.0 (C6), 19.6 (C5).

MS (EI): 351, 349 ($\text{M}^+-\text{C}_4\text{H}_9$)

^1H NMR (300 MHz, CDCl_3):

7.8-7.6 (m, 4H, ArH), 7.6-7.4 (m, 6H, ArH), 5.5-5.4 (dd, $^3J_{\text{H-H}}=9.7\text{Hz}$, $^3J_{\text{H-F}}^{\text{cis}}=13.3\text{Hz}$, 0.5H, H2), 5.1-4.9 (dd, $^3J_{\text{H-H}}=9.7\text{Hz}$, $^3J_{\text{H-F}}^{\text{trans}}=31.7\text{Hz}$, 0.5H, H2), 3.7-3.5 (m, 2H, H4), 3.0-2.8 (m, 0.5H, H3trans), 2.7-2.5 (m, 0.5H, H3cis), 1.2 (s, 9H, H6), 1.2-1.1 (m, 3H, H7)

^{19}F NMR (282.5 MHz, CDCl_3):

-71.7 (d, $^3J_{\text{H-F}}^{\text{cis}}=13.3\text{Hz}$), -74.7 (d, $^3J_{\text{H-F}}^{\text{trans}}=31.7\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

137.6-133.5 (d, $^1J_{\text{C-F}}^{\text{cis}}=315\text{Hz}$, C1), 136.1-133.5-128.1 (C_{ArH}), 134.0 (dd, C_{Ar} , cis, trans), 134.3-130.1 ($^1J_{\text{C-F}}^{\text{trans}}=315.7\text{Hz}$, C1), 116.0 (d, $^2J_{\text{C-F}}^{\text{cis}}=12.1\text{Hz}$, C2), 113.3 (d, $^2J_{\text{C-F}}^{\text{trans}}=13.8\text{Hz}$, C2), 68.0 (d, $^4J_{\text{C-F}}^{\text{trans}}=2.3\text{Hz}$, C4), 67.8 (d, $^4J_{\text{C-F}}^{\text{cis}}=2.9\text{Hz}$, C4), 36.7 (d, $^3J_{\text{C-F}}^{\text{cis}}=3.5\text{Hz}$, C3), 34.8 (trans, C3), 27.4 (cis, C6), 27.3 (trans, C6), 19.73 (cis, C5), 19.71 (trans, C5)

MS (EI): 365, 363 ($\text{M}^+ - \text{C}_4\text{H}_9$)

^1H NMR (300 MHz, CDCl_3):

7.5-7.4 (m, 2H, ArH), 7.4-7.2 (2d, $J=8.5\text{Hz}$, $J'=8.7\text{Hz}$, 2H, ArH), 6.5-6.6 (d, 0.5H, $^3J_{\text{H-F}}^{\text{cis}}=17.0\text{Hz}$, H2), 6.0-5.8 (d, 0.5H, $^3J_{\text{H-F}}^{\text{trans}}=32.0\text{Hz}$, H2)

^{19}F NMR (282.5 MHz, CDCl_3):

-64 (d, $^3J_{\text{H-F}}^{\text{cis}}=17.0\text{Hz}$), -67 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.0\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

135.9 (d, $^1J_{\text{C-F}}^{\text{cis}}=317\text{Hz}$, C1), 135.0 (d, $^2J_{\text{C-F}}^{\text{trans}}=331\text{Hz}$, C1), 132.2 (C_5), 131.7 (d, $^6J_{\text{C-F}}^{\text{trans}}=7.47\text{Hz}$, C6), 130.8 (d, $^6J_{\text{C-F}}^{\text{cis}}=8.0\text{Hz}$, C6), 130.1 (d, $^4J_{\text{C-F}}^{\text{cis}}=3.2\text{Hz}$, C4), 122 (m, C3), 112 (d, $^2J_{\text{C-F}}^{\text{trans}}=6.3\text{Hz}$, C2), 111 (d, $^2J_{\text{C-F}}^{\text{cis}}=24.7\text{Hz}$, C2).

MS (EI): 282 (M^+ , 50%), 280 (M^+ , 100%), 278 (M^+ , 50%), 201 ($\text{M}^+ - \text{Br}$, 20%), 199 ($\text{M}^+ - \text{Br}$, 20%)

^1H NMR (300 MHz, CDCl_3):

7.6-7.3 (m, 2H), 7.2-6.9 (m, 2H), 6.6-6.5 (d, $^2J_{\text{H-F}}^{\text{cis}}=14.6\text{Hz}$, 0.5H, H2), 6.1-5.8 (d, $^2J_{\text{H-F}}^{\text{trans}}=32.5\text{Hz}$, 0.5H, H2)

^{19}F NMR (282.5 MHz, CDCl_3):

-66.2ppm (d, $^2J_{\text{H-F}}^{\text{cis}}=14.6\text{Hz}$, 0.5F), -69.6ppm (d, $^2J_{\text{H-F}}^{\text{trans}}=14.6\text{Hz}$, 0.5F), -113.3ppm (m, 1F).

^{13}C NMR (75.5 MHz, CDCl_3):

162.7 (d, $^1J=248.4\text{Hz}$, C_6^{cis}), 162.4 (d, $^1J=248.4\text{Hz}$, $\text{C}_6^{\text{trans}}$), 135.1 (d, $^1J=317.4\text{Hz}$, C_1^{cis}), 134.0 (d, $^1J=330.0\text{Hz}$, $\text{C}_1^{\text{trans}}$), 130.5 (dd, $J=8.0\text{Hz}$, $J'=2.9\text{Hz}$, C_4^{cis}), 130.2 (dd, $J=7.8\text{Hz}$, $J'=7.8\text{Hz}$, $\text{C}_4^{\text{trans}}$), 129.1 ($\text{C}_3^{\text{trans}}$), 127.9 (C_3^{cis}), 116.1 (d, $J=21.8\text{Hz}$, $\text{C}_5^{\text{trans}}$), 115.9 (d, $J=21.3\text{Hz}$, C_5^{cis}), 112.4 (d, $^2J=6.3\text{Hz}$, $\text{C}_2^{\text{trans}}$), 111.2 (d, $^2J=24.7\text{Hz}$, C_2^{cis})

^1H NMR (300 MHz, CDCl_3):

8.2 (2d, 2H, $J=8.7\text{Hz}$, $J'=8.7\text{Hz}$, H5), 7.6-7.4 (2d, $J=8.7\text{Hz}$, $J'=8.7\text{Hz}$, 2H, H4), 6.7 (d, 0.5H, $^3J_{\text{H-F}}^{\text{cis}}=14.4\text{Hz}$, H2), 6.0 (d, 0.5H, $^3J_{\text{H-F}}^{\text{trans}}=31.9\text{Hz}$, H2)

^{19}F NMR (282.5 MHz, CDCl_3):

-59.3 (d, $^3J_{\text{H-F}}^{\text{cis}}=14.4\text{Hz}$), -62.3 (d, $^3J_{\text{H-F}}^{\text{trans}}=31.9\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

145.9 (cis, C_6), 145.6 (trans, C_6), 136.4 (d, $^2J_{\text{C-F}}^{\text{cis}}=320\text{Hz}$, C_1), 137.6 (d, $^3J_{\text{C-F}}^{\text{trans}}=5.2\text{Hz}$, C_3), 137.2 (d, $^3J_{\text{C-F}}^{\text{cis}}=8.6\text{Hz}$, C_3), 136.2 (d, $^1J_{\text{C-F}}^{\text{trans}}=334\text{Hz}$, C_1), 127.9 (d, $^5J_{\text{C-F}}^{\text{cis}}=2.9\text{Hz}$, C_5), 127.5 (d, $^5J_{\text{C-F}}^{\text{trans}}=8.0\text{Hz}$, C_5), 122.9 (C_4), 122.4 (d, $^4J_{\text{C-F}}^{\text{cis}}=24.1\text{Hz}$, C_4), 110.5 (d, $^2J_{\text{C-F}}^{\text{trans}}=5.7\text{Hz}$, C_2), 109.4 (d, $^2J_{\text{C-F}}^{\text{cis}}=26.4\text{Hz}$, C_2)

MS (EI): 347, 245 (M^+), 217, 215 (M^+-NO), 201, 199 (M^+-NO_2)

^1H NMR (300 MHz, CDCl_3):

7.4-7.2 (2d, 2H, $J=8.7\text{Hz}$, $J'=8.4\text{Hz}$, H4), 7.0-6.7 (2d, $J=8.7\text{Hz}$, $J'=8.4\text{Hz}$, 2H, H5), 6.5 (d, 0.5H, $^3J_{\text{H-F}}^{\text{cis}}=15.0\text{Hz}$, H2), 5.8 (d, 0.5H, $^3J_{\text{H-F}}^{\text{trans}}=33.3\text{Hz}$, H2), 3.7 (2s, 3H, H7)

^{19}F NMR (282.5 MHz, CDCl_3):

-68.2 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.0\text{Hz}$), -71.4 (d, $^3J_{\text{H-F}}^{\text{trans}}=33.3\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

159.0 (d, $^6J_{\text{C-F}}^{\text{trans}}=2.9\text{Hz}$, C6), 136.0-130.5 (2d, $^1J_{\text{C-F}}^{\text{cis}}=314\text{Hz}$, $^1J_{\text{C-F}}^{\text{trans}}=329\text{Hz}$, C1), 129.0 (d, $^4J_{\text{C-F}}^{\text{trans}}=7.1\text{Hz}$, C4), 125.0-123.0 (2d, $^3J_{\text{C-F}}^{\text{cis}}=8.0\text{Hz}$, $^3J_{\text{C-F}}^{\text{trans}}=4.0\text{Hz}$, C3), 114.3-114.5 (d, $^5J_{\text{C-F}}^{\text{trans}}=4.5\text{Hz}$, C5), 113.1 (d, $^2J_{\text{C-F}}^{\text{trans}}=6.9\text{Hz}$, C2), 111.2 (d, $^2J_{\text{C-F}}^{\text{cis}}=24\text{Hz}$, C2), 56 (C7)

MS (EI): 232, 230 (M^+), 217, 215 (M^+-CH_3)

^1H NMR (300 MHz, CDCl_3):

8.1-7.9 (m, 1H, ArH), 7.7-7.3 (m, 3H, ArH), 7.1-6.9 (d, 0.7H, $^3J_{\text{H-F}}^{\text{cis}}=11.8\text{Hz}$), 6.6-6.4 (d, 0.3H, $^3J_{\text{H-F}}^{\text{trans}}=30.1\text{Hz}$)

^{19}F NMR (282.5 MHz, CDCl_3): -64.3 (d, $^3J_{\text{H-F}}^{\text{cis}}=11.8\text{Hz}$), -67.6 (d, $^3J_{\text{H-F}}^{\text{trans}}=30.1\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

147.3 (cis, C4), 146.6 (trans, C4), 137.0 ($^1J_{\text{C-F}}^{\text{cis}}=319\text{Hz}$, C1), 133.7 (trans, C8), 135.5 (d, $^1J_{\text{C-F}}^{\text{trans}}=332\text{Hz}$, C1), 133.8 (cis, C8), 132.4 (d, $^1J_{\text{C-F}}^{\text{cis}}=1.8\text{Hz}$, C6), 131.5 (d, $^1J_{\text{C-F}}^{\text{trans}}=9.2\text{Hz}$, C6), 128.8 (C7, cis), 128.3 (C7, trans), 127.1 (d, $^3J_{\text{C-F}}^{\text{cis}}=9.2\text{Hz}$, C3), 126.0 (d, $^3J_{\text{C-F}}^{\text{trans}}=4.1\text{Hz}$, C3), 124.0 (C5), 107.7 (d, $^2J_{\text{C-F}}^{\text{trans}}=5.1\text{Hz}$, C2), 109.0 (d, $^2J_{\text{C-F}}^{\text{cis}}=28.2\text{Hz}$, C2),

MS (EI): 247, 245 (M^+), 166 (M^+-Br)

^1H NMR (300 MHz, CDCl_3):

7.6-7.5 (d, $J=8.0\text{Hz}$, 1H, ArH), 7.3-7.1 (m, 1H, ArH), 6.9-6.8 (m, 1H, ArH), 6.8 (d, $J=8.1\text{Hz}$, 1H, ArH), 6.7 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.1\text{ Hz}$, 0.5H, H2), 6.3 (d, 0.5H, $^3J_{\text{H-F}}^{\text{trans}}=34.3\text{Hz}$, H2), 3.7 (s, 3H, H9)

^{19}F NMR (282.5 MHz, CDCl_3):

-65.6 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.1\text{Hz}$), -69.5 (d, $^3J_{\text{H-F}}^{\text{trans}}=34.3\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

157.2 (d, $J=3.5\text{Hz}$, cis, C4), 156.1 (trans, C4), 135.5 ($^1J_{\text{C-F}}^{\text{cis}}=315\text{Hz}$, C1), 133.7 (d, $^1J_{\text{C-F}}^{\text{trans}}=331\text{Hz}$, C1), 129.8 (cis, ArH), 129.7 (trans, ArH), 129.5 (d, $J=2.2\text{Hz}$, cis, ArH), 129.3 (d, $J=1.8\text{Hz}$, trans, ArH), 121.7 (d, $^3J_{\text{C-F}}^{\text{trans}}=5.2\text{Hz}$, C3), 121.1 (trans, ArH), 120.8 (d, $^3J_{\text{C-F}}^{\text{cis}}=8.0\text{Hz}$, C3), 120.7 (cis, ArH), 111.0 (trans ArH), 110.8 (cis, ArH), 107.7 (d, $^2J_{\text{C-F}}^{\text{cis}}=24.7\text{ Hz}$, C2), 107.3 (d, $^2J_{\text{C-F}}^{\text{trans}}=4.6\text{Hz}$, C2), 55.9-55.8 (C9, cis, trans)

MS (EI): 232, 230 (M^+), 151 (M^+-Br)

^1H NMR (300 MHz, CDCl_3):

7.1 (d, 0.5H, $J=1.5\text{Hz}$, H4 cis), 7.0 (d, 0.5H, $J=1.0\text{Hz}$, H4 trans), 6.9-6.7 (m, 2H, H7, H8), 6.6 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.4\text{Hz}$, 0.5H, H2), 5.97-5.95 (2s, 2H, trans, cis, H9), 5.9 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.5\text{Hz}$, 0.5H, H2)

^{19}F NMR (282.5 MHz, CDCl_3):

-67.6 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.4\text{Hz}$), -70.6 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.5\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

148.3 (C5, trans), 148.1 (C5, cis), 147.8 (C6, cis), 147.6 (d, $J=2.9\text{Hz}$, C6, trans), 136.5-132.3 (d, $^1J_{\text{C-F}}^{\text{cis}}=314\text{Hz}$, C1), 135.1-130.8 (d, $^1J_{\text{C-F}}^{\text{trans}}=329\text{Hz}$, C1), 127.01-127.10 (d, $^3J_{\text{C-F}}^{\text{trans}}=4.6\text{Hz}$, C3), 125.5-125.4 (d, $^3J_{\text{C-F}}^{\text{cis}}=8.6\text{Hz}$, C3), 123.3 (d, $^4J_{\text{C-F}}^{\text{cis}}=3.7\text{Hz}$, C8), 122.8 (d, $^4J_{\text{C-F}}^{\text{trans}}=5.9\text{Hz}$, C8), 108.8 (C7), 113.1 (d, $^2J_{\text{C-F}}^{\text{trans}}=5.8\text{Hz}$, C2), 111.9-111.6 (d, $^2J_{\text{C-F}}^{\text{cis}}=24.1\text{Hz}$, C2), 108.6-108.4 (2d, C4, cis, trans), 101 (C9)

MS (EI): 246, 244 (M^+), 165 (M^+-Br)

^1H NMR (300 MHz, CDCl_3):

8.1-7.9 (b, 2H, H5_{cis}, trans), 7.6 (d, $J=8.4\text{Hz}$, H4_{cis}), 7.5-7.4 (d, $J=8.5\text{Hz}$, H4_{trans}), 6.7 (d, $^3J_{\text{H-F}}^{\text{cis}}=14.9\text{Hz}$, 0.5H, H2), 6.0 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.3\text{Hz}$, 0.5H, H2), 4.0-3.8 (2s, 3H, H8_{cis}, trans)

^{19}F NMR (282.5 MHz, CDCl_3):

-62.2 (d, $^3J_{\text{H-F}}^{\text{cis}}=14.9\text{Hz}$), -64.5 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.3\text{Hz}$)

^{13}C NMR (75.5 MHz, CDCl_3):

167.91 (C_7 , cis), 167.87 (C_7 , trans), 138.1 (d, $^6J_{\text{C-F}}^{\text{trans}}=5.2\text{Hz}$, C_6), 137.6 (d, $^2J_{\text{C-F}}^{\text{cis}}=318\text{Hz}$, C_1), 137.4 (d, $^6J_{\text{C-F}}^{\text{cis}}=8.6\text{Hz}$, C_6), 137.1 (d, $^1J_{\text{C-F}}^{\text{trans}}=333.5\text{Hz}$, C_1), 131.3 (C_5 , trans), 131.0 (C_5 , cis), 130.7 (C_3 , cis), 130.5 (d, $J_{\text{C-F}}^{\text{trans}}=2.9\text{Hz}$, C_3), 129.6 (d, $^4J_{\text{C-F}}^{\text{cis}}=2.9\text{Hz}$, C_4), 129.2 (d, $^4J_{\text{C-F}}^{\text{trans}}=7.5\text{Hz}$, C_4), 113.8 (d, $^2J_{\text{C-F}}^{\text{trans}}=5.6\text{Hz}$, C_2), 112.5 (d, $^2J_{\text{C-F}}^{\text{cis}}=24.7\text{Hz}$, C_2), 53.5 (C_8)

^1H NMR (300 MHz, CDCl_3):

8.0-7.7 (m, 4H), 7.07-7.3 (m, 3H), 6.9-6.7 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.1\text{Hz}$, 0.5H, H2), 6.2-6.0 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.8\text{Hz}$, 0.5H, H2)

^{19}F NMR (282.5 MHz, CDCl_3):

-65.1 (d, $^3J_{\text{H-F}}^{\text{cis}}=15.1\text{Hz}$), -67.9 (d, $^3J_{\text{H-F}}^{\text{trans}}=32.8\text{Hz}$), cis/trans=1/0.93

^{13}C NMR (75.5 MHz, CDCl_3):

135.6 (d, $^1J_{\text{C-F}}^{\text{cis}}=316\text{Hz}$, C_1), 134.5 (d, $^1J_{\text{C-F}}^{\text{trans}}=331.8\text{Hz}$, C_1), 133.7 (C_{11} , trans), 133.6 (C_{11} , cis), 133.2 (C_3 , cis), 133.1 (d, C_3 , $J^{\text{trans}}=1.7\text{Hz}$), 130.4 (d, C_6 , $J^{\text{trans}}=4.6\text{Hz}$), 129.3 (d, C_6 , $J^{\text{cis}}=8.6\text{Hz}$), 128.8 (C_{ArH} , trans), 128.6 (C_{ArH} , trans), 128.5 (C_{ArH} , cis), 128.4 (C_{ArH} , cis), 128.3 (d, C_{12} , $J^{\text{cis}}=4.1\text{Hz}$), 128.1 (C_{ArH} , cis), 128.0 (C_{ArH} , trans), 127.8 (d, C_{12} , $J^{\text{trans}}=6.9\text{Hz}$), 126.9 (C_8 , C_9 , cis, trans), 126.3 (d, C_4 , $J^{\text{cis}}=2.7\text{Hz}$), 126.0 (d, C_4 , $J^{\text{trans}}=7.5\text{Hz}$), 113.7 (d, C_2 , $J^{\text{trans}}=6.0\text{Hz}$), 112.3 (d, C_2 , $J^{\text{cis}}=24.2\text{Hz}$)

^1H NMR (300 MHz, CDCl_3):
7.2-7.5 (m, 10H, Ar-H)

^{19}F NMR (282.5 MHz, CDCl_3):
-71.5 ppm

^{13}C NMR (75.5 MHz, CDCl_3):
138.7 (d, $J=4.0\text{Hz}$, C_{14}), 136.6 (d, $J=2.3\text{Hz}$, C_3), 134.3-132.1 (d, $J=325\text{Hz}$, C_1), 130.5 (d, $J=3.7\text{Hz}$), 129.6 (d, $J=4.6\text{Hz}$), 128.9, 128.7, 128.4, 128.2, 125.2-125.0 (d, $J=10.9\text{Hz}$, C_2)

MS (EI): 278, 276 (M^+), 197 (M-Br), 196 ($\text{M}^+ - \text{HBr}$).

^1H NMR (300 MHz, CDCl_3):
7.9-7.6 (m, 4H), 7.5-7.3 (m, 3H), 2.2-2.0 (m, 3H, H13)

^{19}F NMR (282.5 MHz, CDCl_3):
-74.4 (m, A and B cannot be resolved by ^{19}F NMR)

^{13}C NMR (75.5MHz, CDCl_3):
136.7 ($\text{C}_{\text{Ar}}^{\text{q}}$, C_3 , B), 133.6 ($\text{C}_{\text{Ar}}^{\text{q}}$, C_3 , B), 134.3 ($\text{C}_{\text{Ar}}^{\text{q}}$, A), 133.6 ($\text{C}_{\text{Ar}}^{\text{q}}$, B), 133.1 ($\text{C}_{\text{Ar}}^{\text{q}}$, A), 133.0 ($\text{C}_{\text{Ar}}^{\text{q}}$, A), 133.0 (d, $J=316.8\text{Hz}$, C_1 , A), 131.4 (d, $J=322\text{Hz}$, C_1 , B), 128.6 (C_{ArH} , A, B), 128.5 (C_{ArH} , A), 128.4 (C_{ArH} , B), 128.2 (C_{ArH} , A), 128.1 (C_{ArH} , B), 128.0 (d, $J=3.2\text{Hz}$, C_{ArH} , A), 127.4 (d, $J=4.1\text{Hz}$, C_{ArH} , B), 126.8 (C_{ArH} , C_9 , C_{10} , A, B), 126.6 (d, $J=3.2\text{Hz}$, C_{ArH} , A), 126.2 (d, $J=4.6\text{Hz}$, C_{ArH} , B), 120.0 (C_2 , A), 118.2 (C_2 , B), 21.1 (C_{13} , B), 18.3 (C_{13} , A)

MS (EI): 266, 264 (M^+), 183 ($\text{M}^+ - \text{Br}$)

IR (KBr): 3056, 2622, 1651, 1589, 1505, 1121, 1013, 857, 817, 747

^1H NMR (300 MHz, CDCl_3):

7.4-7.2 (m, 5H), 7.2-7.0 (m, 2H), 7.0-6.8 (m, 2H), 5.0 (s, 2H, H9), 2.5-2.3 (m, 2H, H2), 1.0-0.8 (q, $J=7.8\text{Hz}$, 3H, H1)

^{19}F NMR (282.5 MHz, CDCl_3):

-76.5 (A), -76.7 (t, $^4J_{\text{H-F}}=3.6\text{Hz}$, B), A/B=1/0.86

^{13}C NMR (75.5MHz, CDCl_3):

158.7 (C₈, A, B), 137.2 (C₁₀, A, B), 131.4 (d, $J=315.7\text{Hz}$, C₄, A), 130.4 (d, $J=2.9\text{Hz}$, C₇, B), 129.8 (d, $J=3.4\text{Hz}$, C₇, A), 129.4 (d, $J=194.9\text{Hz}$, C₄, B), 129.0 (C₁₁, A, B), 128.7 (C₅, A, B), 128.4 (C₁₃, A, B), 128.0 (C₁₂, B), 127.9 (C₁₂, A), 125.6 (C₃, B), 123.5 (d, $J=6.3\text{Hz}$, C₃, A), 115.0-114.9 (C₆, A, B), 70.9 (C₉), 28.2 (C₂, B), 25.5 (d, $J=3.7\text{Hz}$, C₂, A), 12.9 (d, $J=2.3\text{Hz}$, C₁, A), 12.5-12.5 (d, $J=3.7\text{Hz}$, C₁, B)

MS (EI): 336, 334 (M^+), 240 (M^+-Br)

^1H NMR (300 MHz, CDCl_3):

7.9-7.7 (m, 1H), 7.4-7.1 (m, 3H), 2.9-2.7 (m, 3H, 1H3 + 2H5), 2.6-2.5 (m, 1H, 1H3), 2.0-1.8 (m, 2H, H4)

^{19}F NMR (282.5 MHz, CDCl_3):

-69 (t, $4J_{\text{H-F}}=3.6\text{Hz}$), -72.6 (S), A/B=1/1.6

^{13}C NMR (75.5MHz, CDCl_3):

22.7 (d, $^4J_{\text{C-F}}=2.3\text{ Hz}$, A, C₄), 23.2 (d, $^4J_{\text{C-F}}=1.4\text{Hz}$, B, C₄), 26.0 (d, $^5J_{\text{C-F}}=6.4\text{Hz}$, A, C₃), 30.65 (A, C₅), 30.6 (B, C₃), 31.1 (B, C₅), 116 (B, C₂), 119 (d, $^2J=17.0\text{Hz}$, A, C₂), 125.8 (A, C_{Ar-H}), 126.6 (B, C_{Ar-H}), 127.9 (d, $J=1.4\text{Hz}$, B, C_{Ar-H}), 128.1 (A, C_{Ar-H}), 128.5 (B, C_{Ar-H}), 129.0 (A, C_{Ar-H}), 129.1 (B, C_{Ar-H}), 129.2 (A, C_{Ar-H}), 129.7 (d, $J=326.0\text{Hz}$, A, C₁), B, C₁), 131.6 (d, $J=10.3\text{Hz}$, A, C₇), 131.4-131.3 (d, $J=6.9\text{Hz}$, B, C₇), 133.4 (d, $J=335.2\text{Hz}$, 135.9 (C₆, B) 140.3 (d, $J=5.2\text{Hz}$, C₆, A)

MS (EI): 242, 240 (M^+)

^1H NMR (300 MHz, CDCl_3):
7.3-7.0 (m, 3H), 7.0-6.8 (m, 2H), 0.1-0 (s, 3H, two isomers)

^{19}F NMR (300 MHz, CDCl_3):
-39.61 (A), -39.64 (B), A/B=1/2.25

^{13}C NMR (75.5MHz, CDCl_3):
139.8 (d, $J=11.3\text{Hz}$, C3, B), 138.6 (C3, A), 138.2 (d, $J=315$, C1, B), 136.3 (d, $J=331.8\text{Hz}$, C1, A), 129.3 (C4, B), 129.1 (C4, A), 128.9 (d, $J=3.2\text{Hz}$, C5, B), 128.5 (d, $J=1.4\text{Hz}$, C5, A), 127.4 (C6, B), 127.3 (C6, A), 124.8 (d, $J=27.6\text{Hz}$, C2, B), 122.4 (d, $J=9.2\text{Hz}$, C2, A), 0.0 (d, $J=2.5\text{Hz}$, C7, B), -0.1 (d, $J=2.3\text{Hz}$, C7, A)

MS (EI): 274, 272 (M^+), 259, 257 (M^+-CH_3)

^1H NMR (300 MHz, CDCl_3):
7.4-7.0 (m, 10H), 2.8-2.6 (m, 4H), 2.6-2.4 (m, 2H), 2.4-2.2 (m, 2H)

^{19}F NMR (282.5 MHz, CDCl_3):
-77.6

^{13}C NMR (75.5MHz, CDCl_3):
141.5-141.4 (C5, C11), 131.6 (d, $J=312.8\text{Hz}$, C1), 128.9 (C7, C13), 128.8-128.7 (C6, C12), 126.6 (C8, C14), 120.5 (d, $J=10.4\text{Hz}$, C2), 34.7 (C4), 34.5 (d, $J=6.8\text{Hz}$, C9), 33.9 (d, $J=4.0\text{Hz}$, C10), 31.3 (d, $J=4.6\text{Hz}$, C3)

^1H NMR (300 MHz, CDCl_3):

7.5-7.2 (m, 5H), 7.2-7.1 (d, $J=16\text{Hz}$, 0.5H), 7.0-6.8 (d, $J=16\text{Hz}$, 0.5H), 2.0-1.8 (m, 3H, H9)

^{19}F NMR (282.5 MHz, CDCl_3):

-72.5 (d, $J=3.8\text{Hz}$, A), -74.4 (d, $J=4.3\text{Hz}$, B), A/B=1.00/1.23

^{13}C NMR (75.5MHz, CDCl_3):

137.4 (C_5), 135.1 (d, $J=349.0\text{Hz}$, C_1 , A), 135.0 (d, $J=350.7\text{Hz}$, C_1 , B), 131.4 (d, $J=12.1\text{Hz}$, C_4 , A), 129.8 (d, $J=4.6\text{Hz}$, C_4 , B), 129.1 (C_7), 128.3 (C_8), 127.0 (C_6 , B), 126.9 (d, $J=0.9\text{Hz}$, C_6 , A), 126.1 (d, $J=0.9\text{Hz}$, C_3 , A), 121.8 (d, $J=6.4\text{Hz}$, C_3 , B), 117.4-117.0 (dd, C_2 , A, B), 15.5 (C_9 , B), 12.0 (C_9 , A)

MS (EI):

242, 240 (M^+), 161 (M^+-Br)

IR (KBr):

3048, 3024, 2926, 1802, 1763, 1701, 1633, 1616, 1495, 1447, 1281, 1116, 1030, 958, 749, 691

^1H NMR (300 MHz, CDCl_3):

7.3-7.1 (m, 5H), 3.4 (s, 2H, H7), 2.5-2.3 (m, 6H), 2.3-2.1 (m, 2H)

^{19}F NMR (282.5 MHz, CDCl_3):

-82.1

^{13}C NMR (75.5MHz, CDCl_3):

138.5 (C_8), 129.5-128.7 (C_9 , C_{10}), 127.5 (C_{11}), 127.6-128.7 (d, $J=309.9\text{Hz}$, C_1), 117.8 (d, $J=12.1\text{Hz}$, C_2), 63.2 (C_7), 53.7-53.4 (dd, $J=1.7\text{Hz}$, $J=2.3\text{Hz}$, C_4 , C_5), 30.5 (C_3), 27.2 (d, $J=5.2\text{Hz}$, C_6)

MS (EI): 285, 283 (M^+), 204 (M^+-Br)

^1H NMR (300 MHz, CDCl_3):

7.5-7.2 (m, 5H), 3.8-3.6 (2s, 2H, H6), 3.4-3.3 (m, 1H, H5), 3.2-3.1 (m, 1H, H5), 2.9-2.7 (m, 2H, H4), 2.7-2.5 (m, 1H, H3), 2.5-2.3 (1H, H3)

^{19}F NMR (282.5 MHz, CDCl_3):

-77.2 (A), -79.4 (B), A/B=1/1.26

^{13}C NMR (75.5MHz, CDCl_3):

136.7 (C_7), 127.84, 127.81, 127.4, 126.4 (C_8 , C_9 , C_{10} , A, B), 124.6 (d, $J=312.2\text{Hz}$, C_1 , A), 123.8 (d, $J=312.2\text{Hz}$, C_1 , B), 119.3 (d, $J=5.7\text{Hz}$, C_2 , B), 119.1 (d, $J=3.5\text{Hz}$, C_2 , A), 59.1-58.9 (C_6 , A, B), 56.0 (d, $J=2.3\text{Hz}$, C_5 , B), 54.0 (d, $J=8.9\text{Hz}$, C_5 , A), 53.4 (C_4 , B), 52.3 (C_4 , A), 29.0 (C_3 , A), 27.1 (C_3 , B)

MS (EI): 271, 269 (M^+), 180, 178 ($\text{M}^+ - \text{CH}_2\text{Ph}$)