Regioselective Alkyl Transfer from Phosphonium Ylide to Functionalized Polyfluoroarenes

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General Information
All the reactions were performed using standard schlenk techniques under an atmosphere of dry nitrogen or argon. All the commercial reagents unless otherwise annotated were purchased from Sigma Aldrich, Alfa Aesar and were used without further purification. Dimethoxyethane was distilled from Na/benzophenone under the protection of Argon. THF and 1,4-dioxane were dried by refluxing with Na/benzophenone and oxygen was removed by bubbling with dry nitrogen. NMR spectra were recorded on Bruker Avance 300, Bruker AvanceIII 500 and Bruker Avance 600 spectrometers. Chemical shifts are reported in ppm, and coupling constants \( (J) \) are in Hertz (Hz). The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, br = broad, ddd = doublet of doublet of doublets. Mass spectroscopy was obtained using a GCT-MS (Micromass, UK). HRMS experiments were carried on Waters GCT Premier (EI source, TOF), Bruker Apex IV FTMS (positive-ion mode ESI) or Thermo Scientific LTQ Orbitrap Discovery (negative-ion mode ESI) mass spectrometer. IR analysis was performed on a Bruker Tensor27 spectrometer and a Thermo Scientific Nicolet iZ10 spectrometer. X-ray diffraction study was carried on an Oxford Diffraction Gemini E diffractometer using graphite monochromatic Mo K\( \alpha \) (\( \lambda = 0.7107 \) Å) radiation at 293 K. Column chromatography was performed on 300–400 mesh silica gel (innochem). Purification by preparative HPLC was conducted on a SHIMAZDU LC-6AD chromatography equipped with a LC-6AD UV-Vis detector and a shim-pack PRC-ODS column. The \(^{19}\)F NMR yield of the product was determined by integration of the peaks in the \(^{19}\)F NMR spectra using \( \alpha,\alpha,\alpha \)-trifluorotoluene as an internal standard.

**HPLC condition:**

Flow: 4.0 mL/min
Temperature: ambient temperature
Run time: 100 min
Supplementary Information

Detection wavelength: 254 nm

Gradient eluent:

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Preparation of Starting Materials

1-Pentafluorophenyl-3-phenylpropan-2-one (1a):

1a was prepared according to the literature procedure\(^1\) using phenylacetyl chloride (A) and 1-bromomethyl-2,3,4,5,6-pentafluoro-benzene (B) and obtained as a light yellow solid. The NMR spectral data were in line with the literature values\(^2\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.41 – 7.22 (m, 5H), 3.84 (s, 2H), 3.81 (t, \(J = 1.3\) Hz, 2H). \(^19\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -142.25 – -142.45 (m, 2F), -155.39 (t, \(J = 20.8\) Hz, 1F), -162.32 – -162.61 (m, 2F). LRMS (+EI): \(m/z\) calculated for [M]\(^+\): 300.05, found 300.00.

N-(2,3,4,5,6-pentafluoro-phenyl)acetamide (1g):

1g was prepared according to the literature procedure\(^3\) by reacting 2,3,4,5,6-pentafluorobenzamide (1.744 g, 9.53 mmol) with acetic anhydride (9.729 g, 95.3 mmol) at 90 °C for 17 h. The crude product was poured into cooled water and extracted with dichloromethane. The organic phase was dried over anhydrous sodium.
sulfate, concentrated and recrystallized from petro ether to afford the title compound as a white solid (1.633 g, 76%). The NMR spectral data were in line with the literature values. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.18 (s, 1H), 2.23 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -144.91 (d, $J = 16.4$ Hz, 2F), -156.32 (t, $J = 21.2$ Hz, 1F), -162.31 (t, $J = 19.6$ Hz, 2F).

General procedure: 1-(2-Benzylallyl)-2,3,5,6-tetrafluoro-4-methylbenzene (2a):

In a 25 mL two-neck round bottom flask equipped with a magnetic stir bar, methyltriphenylphosphonium bromide (Y1, 0.625 g, 1.66 mmol) and NaH (0.067 g, 1.66 mmol) (60% dispersion in mineral oil) were added. The flask was evacuated and filled with nitrogen for three times. 5 mL THF was subsequently added by syringe. The mixture was heated to reflux for 48 h, and then cooled down to ambient temperature. To the mixture was added a THF solution of 1-pentafluorophenyl-3-phenylpropan-2-one (1a, 0.1 g, 0.333 mmol) dropwise at room temperature. The mixture was then heated to reflux for another 48 h and cooled down to ambient temperature. The reaction mixture was then dissolved in ethyl acetate (20 mL) and deionized water (20 mL). The organic phase was washed with brine (20 mL), and dried over anhydrous sodium sulfate. The organic phase was concentrated and purified by Silica gel chromatography (eluent: petrol ether) and subsequent HPLC (collected between 83-84.5 min) purification afforded the title compound as a colorless oil (42.1 mg, 43%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 4.85 (d, $J = 1.1$ Hz, 1H), 4.73 (s, 1H), 3.40 (s, 2H), 3.33 (s, 2H), 2.24 (t, $J = 2.1$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -144.86 – -144.87 (m, 2F), -144.68 – -145.30 (m, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.09 – 145.45 (m), 144.63 (s), 144.02 – 143.59 (m), 138.78 (s), 128.91 (s), 128.35 (s), 126.31 (s), 115.13 (t, $J = 18.6$ Hz), 114.05 (t, $J = 20.16$ Hz), 113.39 (s), 42.92 (s), 28.59 (s), 7.41 (s). IR: 3083.1,
3061.0, 3026.2, 2954.3, 2926.9, 2867.1, 1729.7, 1651.1, 1600.7, 1486.6, 1454.2, 1379.6, 1274.5, 1121.3, 1064.6, 1030.2, 956.2, 926.6, 866.6, 758.0, 748.2, 735.2, 699.0, 592.0. HRMS (EI) Exact mass calcd for C_{17}H_{14}F_{4}: 294.1023, found 294.1035.

3-(2,3,5,6-Tetrafluoro-4-methylphenyl)acrylic acid (2b): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (1b, 0.2 g, 0.84 mmol), phosphonium salt Y1 (1.5 g, 4.2 mmol) and NaH (0.168 g, 4.2 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid (192.6 mg, 98%). {\textsuperscript{1}}H NMR (600 MHz, MeOD-d{\textsubscript{4}}) δ 7.61 (d, J = 16.4 Hz, 1H), 6.64 (d, J = 16.4 Hz, 1H), 2.29 (s, 3H). {\textsuperscript{19}}F NMR (282 MHz, MeOD-d{\textsubscript{4}}) δ -142.81 (dd, J = 22.0, 12.4 Hz, 2F), -143.72 – -143.95 (m, 2F). {\textsuperscript{13}}C NMR (151 MHz, MeOD-d{\textsubscript{4}}) δ 167.75 (s), 146.63 – 145.14 (m), 145.06 – 143.40 (m), 128.89 (s), 125.73 (s), 118.08 (s), 111.54 (s), 6.32 (s). IR: 1696.6, 1635.1, 1487.5, 1475.9, 1424.3, 1397.5, 1325.4, 1314.9, 1272.2, 1222.1, 1068.2, 1110.5, 993.6, 946.6, 903.6, 882.7, 520.7. HRMS (ESI) Exact mass calcd for C_{10}H_{7}F_{4}O_{2} [M+H]{\textsuperscript{+}}: 235.0377, found 235.0374.

3-(3,5-Difluoro-4-methyl-phenyl)acrylic acid (2c): The general procedure was applied using 3-(3,4,5-trifluorophenyl)acrylic acid (1c, 0.202 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid.
(140.6 mg, 71%). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.56 (d, $J = 16.0$ Hz, 1H), 7.25 – 7.12 (m, 2H), 6.48 (d, $J = 16.0$ Hz, 1H), 2.19 (t, $J = 1.6$ Hz, 3H). $^{19}$F NMR (282 MHz, DMSO-$d_6$) $\delta$ -116.36 (s, 2F). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 167.81 (s), 161.46 (d, $J = 244.1$ Hz), 142.15 (s), 134.98 (s), 121.79 (s), 116.67 – 112.95 (m), 111.27 (d, $J = 20.9$ Hz), 7.60 (s). IR: 3431.8, 2927.8, 1682.4, 1635.7, 1575.5, 1438.1, 1421.3, 1309.8, 1287.5, 1088.8, 988.6, 930.9, 849.7, 625.6. HRMS (ESI) Exact mass calcd for C$_{10}$H$_7$F$_2$O$_2$ [M-H]$: 197.0408, found 197.0416.

2,3,5,6-Tetrafluoro-4-methylbenzoic acid methyl ester (2d): The general procedure was applied using methyl pentafluorobenzoate (1d, 0.226 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a colorless oil (193.1 mg, 87%). The NMR spectral data were in line with the literature values. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.97 (s, 3H), 2.32 (t, $J = 2.2$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -140.80 (qd, $J = 5.9$, 3.0 Hz, 2F), -142.31 (qd, $J = 6.2$, 3.3 Hz, 2F). IR: 2960.6, 1743.5, 1655.2, 1437.1, 1488.3, 1312.4, 1227.7, 1071.6, 976.1, 933.7, 879.8, 788.5, 756.8, 581.2. HRMS (ESI) Exact mass calcd for C$_9$H$_5$F$_4$O$_2$ [M-H]$: 221.0220, found 221.0212.

2,3,5,6-Tetrafluoro-4-methylbenzamide (2e): The general procedure was applied to 2,3,4,5,6-pentafluorobenzamide (1e, 0.211 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at 80 °C for 48 h.
Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20) of the crude product afforded the title compound as a white solid (186.3 mg, 90%). $^1$H NMR (300 MHz, MeOD-d$_4$) δ 2.30 (t, $J = 2.2$ Hz, 3H). $^{19}$F NMR (282 MHz, MeOD-d$_4$) δ -141.73 – -141.92 (m, 2F), -141.99 – -142.18 (m, 2F). $^{13}$C NMR (151 MHz, MeOD-d$_4$) δ 161.71 (s), 144.90 (d, $J = 244.0$ Hz), 143.19 (d, $J = 253.5$ Hz), 117.87 (t, $J = 19.3$ Hz), 114.23 (t, $J = 20.2$ Hz), 6.17 (s). IR: 3389.8, 3195.5, 2945.0, 2836.1, 1659.2, 1479.7, 1413.5, 1273.6, 1114.1, 1069.5, 1028.9, 933.1, 673.0.

HRMS (ESI) Exact mass calcd for C$_8$H$_6$F$_4$NO $[M+H]^+$: 208.03800, found 208.03760.

3,5-Difluoro-4-methylbenzonitrile (2f): The general procedure was applied using 3,4,5-trifluorobenzonitrile (1f, 0.157 g, 1 mmol), phosphonium salt Y$_1$ (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Basic aluminum oxide column chromatography (eluent: petrol ether) of the crude product afforded the title compound as a white solid (116.3 mg, 76%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.16 (d, $J = 6.3$ Hz, 2H), 2.26 (t, $J = 1.8$ Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -110.61 (d, $J = 3.2$ Hz, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.37 (d, $J = 250.2$, 9.6 Hz), 120.24 (t, $J = 20.9$ Hz), 116.83 (t, $J = 3.4$ Hz), 114.94 (d, $J = 21.5$, 8.7 Hz), 110.74 (t, $J = 12.1$ Hz), 7.46 (t, $J = 3.7$ Hz). IR: 2954.9, 2925.8, 2854.4, 2231.3, 1732.1, 1694.1, 1484.8, 1420.5, 1323.3, 1242.5, 1226.1, 1024.1, 851.3, 747.3, 688.7, 628.9. HRMS (EI) Exact mass calcd for C$_8$H$_5$F$_2$N: 153.0390, found 153.0392.

N-(2,3,5,6-Tetrafluoro-4-methylphenyl)acetamide (2g): The general procedure was applied using N-(2,3,4,5,6-pentafluoro-phenyl)acetamide (1g, 0.225 g, 1 mmol),
phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20) of the crude product afforded the title compound as a white solid (187.9 mg, 85%). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.78 (s, 1H), 2.22 (s, 3H), 2.17 (s, 3H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -144.13 (s, 2F), -147.29 (s, 2F). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.39 (s), 145.06 (d, $J$ = 243.6 Hz), 142.31 (d, $J$ = 246.7 Hz), 114.46 (s), 113.51 (s), 22.80 (s), 7.38 (s). IR: 3207.8, 3042.2, 2997.2, 1684.5, 1654.8, 1527.6, 1503.4, 1476.2, 1367.4, 1285.2, 1256.7, 1131.8, 1072.5, 1013.3, 953.1, 909.5. HRMS (ESI) Exact mass calcd for C$_9$H$_6$F$_4$NO [M-H]$: 220.0380, found 220.0382.

**1,2,4,5-Tetrafluoro-3,6-dimethylbenzene (2h):** The general procedure was applied using 1,2,3,4,5-pentafluoro-6-methylbenzene (1h, 0.910 g, 5 mmol), phosphonium salt Y1 (8.93 g, 25 mmol) and NaH (1.0 g, 25 mmol) (60% dispersion in mineral oil). Crude product was purified by distillation at reduced pressure to afford the title compound as a white solid (84%), the yield of the product was determined by $^{19}$F NMR. The NMR spectral data were in line with the literature values$^6$. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.24 – 2.22 (quintet, $J$ = 0.9 Hz, 6H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -145.57 (s, 4F). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.80 – 143.85 (m), 113.02 (d, $J$ = 4.4 Hz), 7.23 (s). IR: 2954.5, 2924.1, 2853.4, 1654.2, 1592.6, 1484.2, 1466.2, 1437.8, 1377.7, 1120.7.

**2,3,5,6-Tetrafluoro-4-methylbiphenyl (2i):** The general procedure was applied using 2,3,4,5,6-pentafluorobiphenyl (1i, 0.244 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5
mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a white solid (196.8 mg, 82%). NMR spectral data were in line with the literature values\(^7\). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.38 (m, 5H), 2.31 (t, \(J = 2.1\) Hz, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -144.01 – -144.19 (m, 2F), -145.55 – -145.73 (m, 2F). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 146.28 – 144.57 (d, \(J = 258.2\) Hz), 144.49 – 142.86 (dd, \(J = 246.1, 14.6\) Hz), 130.28 (s), 128.97 (s), 128.62 (s), 127.86 (s), 118.05 (t, \(J = 16.8\) Hz), 115.18 (t, \(J = 19.3\) Hz), 7.64 (s).

1-Bromo-2,3,5,6-tetrafluoro-4-methylbenzene (2j): The general procedure was applied using 1-bromo-2,3,4,5,6-pentafluorobenzene (1j, 2.459 g, 10 mmol), phosphonium salt Y1 (17.86 g, 50 mmol) and NaH (2.0 g, 50 mmol) (60% dispersion in mineral oil). The crude product was purified by distillation at reduced pressure to afford the title compound as colorless oil (80%). The yield of the product was determined by \(^{19}\)F NMR. NMR spectral data were in line with the commercially available compound. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.26 (t, \(J = 2.2\) Hz, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -141.74 (dd, \(J = 21.4, 13.1\) Hz, 2F), -145.09 (dd, \(J = 21.4, 13.1\) Hz, 2F). IR: 2956.8, 2922.8, 2851.9, 1659.1, 1632.7, 1507.5, 1468.5, 1260.8, 1098.1, 1047.1, 913.2, 733.6, 646.8, 472.3, 457.1. HRMS (EI) Exact mass calcd for C\(_7\)H\(_3\)BrF\(_4\): 241.9354, found 241.9353.

1,3-Difluoro-2-methyl-5-(1-phenylvinyl)benzene (2k) and...
**Supplementary Information**

**(3,5-Difluoro-4-methylphenyl)phenylmethanone (2k’):** The general procedure was applied using 3,4,5-trifluorobenzophenone (1k, 0.236 g, 1 mmol), phosphonium salt Y1 (3.572 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound 2k (80.5 mg, 35%) and trace amount of 2k’ as colorless oil. (2k) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.37 – 7.26 (m, 5H), 6.83 (d, $J = 8.5$ Hz, 2H), 5.45 (d, $J = 4.1$ Hz, 2H), 2.20 (t, $J = 1.7$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -115.28 (s, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 162.36 (d, $J = 9.8$ Hz), 160.40 (d, $J = 9.8$ Hz), 148.37 (s), 140.96 (t, $J = 9.6$ Hz), 140.52 (s), 128.31 (d, $J = 10.1$ Hz), 128.09 (s), 115.14 (s), 112.63 (t, $J = 21.5$ Hz), 110.54 (dd, $J = 20.0$, 6.9 Hz), 7.02 (t, $J = 3.8$ Hz). IR: 3056.8, 3023.8, 2952.6, 2925.6, 2866.8, 1665.0, 1636.2, 1575.2, 1495.4, 1446.8, 1418.2, 1377.4, 1343.0, 1324.3, 1086.6, 954.6, 937.4, 902.2, 866.0, 777.1, 740.1, 698.7, 613.1. HRMS (EI) Exact mass calcd for C$_{15}$H$_{12}$F$_2$: 230.0907, found 230.0913.

(2k’) $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 – 7.74 (m, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.31 (d, $J = 7.3$ Hz, 2H), 2.28 (t, $J = 1.6$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -112.98 (s, 2F).

![Chemical Structure](image)

**2,6-Difluoro-4-nitrotoluene (2l):** The general procedure was applied using 3,4,5-trifluoronitrobenzene (1l, 0.177 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a light yellow oil (99%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.84 – 7.68 (m, 2H), 7.30 (t, $J = 1.8$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -109.66 (s, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.96 (dd, $J = 250.7$, 9.4 Hz), 146.52 (s), 121.51 (t, $J = 21.3$ Hz), 109.22 – 105.49 (m), 7.66 (t, $J = 3.5$ Hz). IR: 3116.3, 3082.7, 2962.8, 2929.1, 2867.5, 2649.7, 1726.8, 1617.2, 1556.5, 1536.7, 1484.8, 1434.8, 1378.1,
1353.1, 1299.1, 1197.6, 1068.6, 1031.8, 943.7, 876.9, 800.9, 746.3, 731.1, 695.91, 542.2, 518.3. HRMS (EI) Exact mass calcd for C$_7$H$_5$F$_2$NO$_2$: 173.0288, found 173.0290.

1,3,4-Trifluoro-2-methyl-5-nitrobenzene (2m): The general procedure was applied using 2,3,4,5-tetrafluoronitrobenzene (1m, 0.780 g, 4 mmol), phosphonium salt Y1 (7.145 g, 20 mmol) and NaH (0.8 g, 20 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a light yellow oil (69%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 (ddd, $J$ = 8.1, 5.6, 2.3 Hz, 1H), 2.34 (t, $J$ = 2.1 Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -116.12 (dd, $J$ = 14.2, 5.3 Hz, 1F), -132.36 (dd, $J$ = 20.7, 5.2 Hz, 1F), -146.67 (dd, $J$ = 20.9, 14.1 Hz, 1F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.11 (dd, $J$ = 247.9, 7.9 Hz), 150.17 (dd, $J$ = 251.6, 13.2 Hz), 142.22 (dd, $J$ = 265.2, 16.7 Hz), 135.56 – 135.12 (m), 123.06 (dd, $J$ = 23.2, 17.6 Hz), 107.13 (dt, $J$ = 29.4, 3.8 Hz), 8.09 (s). IR: 3086.6, 2930.8, 2869.7, 1540.8, 1490.1, 1467.9, 1351.3, 1302.7, 1257.5, 1176.2, 1104.7, 1060.5, 963.4, 884.5, 867.5, 772.1, 757.6, 719.8, 703.4, 615.7. HRMS (EI) Exact mass calcd for C$_7$H$_4$F$_3$NO$_2$: 191.0194, found 191.0195.

1,3-Difluoro-2,4-dimethyl-5-nitrobenzene (2m'): The general procedure was applied using 2,3,4,5-tetrafluoronitrobenzene (1m, 0.195 g, 1 mmol), phosphonium salt Y1 (3.572 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title...
compound as a light yellow oil (71%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.52 (dd, $J = 8.8$, 2.0 Hz, 1H), 2.45 (dd, $J = 2.5$, 1.2 Hz, 3H), 2.26 (t, $J = 2.0$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -111.94 (d, $J = 8.5$ Hz, 1F), -115.23 (d, $J = 8.5$ Hz, 1F). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.95 (dd, $J = 193.2$, 9.5 Hz), 158.31 (dd, $J = 193.2$, 9.3 Hz), 147.37 (s), 119.49 (dd, $J = 23.1$, 21.0 Hz), 117.58 (dd, $J = 22.1$, 3.8 Hz), 107.52 (dd, $J = 27.6$, 3.8 Hz), 11.00 (d, $J = 5.9$ Hz), 7.81 (s). IR: 3118.8, 3080.8, 2940.1, 2869.7, 1630.1, 1599.7, 1533.5, 1482.5, 1457.8, 1420.1, 1384.4, 1353.1, 1298.3, 1233.3, 1172.2, 1101.8, 1035.9, 931.3, 863.4, 768.1, 755.5, 690.6, 603.8, 474.7. HRMS (EI) Exact mass calcd for C$_8$H$_7$F$_2$NO$_2$: 187.0445, found 187.0452.

1,2,4-Trifluoro-3,5-dimethyl-6-nitrobenzene (2n): The general procedure was applied using 2,3,4,5,6-pentafluoronitrobenzene (1n, 0.213 g, 1 mmol), phosphonium salt Y$_1$ (3.572 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a light yellow oil (58%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.27 (t, $J = 2.2$ Hz, 3H), 2.25 (dd, $J = 2.5$, 1.3 Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -118.43 (dd, $J = 13.9$, 4.7 Hz, 1F), -137.67 (dd, $J = 21.7$, 4.7 Hz, 1F), -151.69 (dd, $J = 21.7$, 13.9 Hz, 1F). $^{13}$C NMR (151 MHz, Acetonitrile-d$_3$) $\delta$ 154.21 (d, $J = 243.5$ Hz), 147.21 (d, $J = 249.3$ Hz), 140.10 (dd, $J = 258.4$, 18.6 Hz), 138.26 (s), 118.76 (dd, $J = 24.3$, 17.4 Hz), 114.92 (d, $J = 24.2$ Hz), 9.96 (s), 7.85 (s). IR: 2956.1, 2927.6, 2868.7, 1635.0, 1544.3, 1488.8, 1464.4, 1365.6, 1291.5, 1267.3, 1172.3, 1065.6, 916.3, 884.2, 812.2, 769.8, 753.4, 580.9. HRMS (EI) Exact mass calcd for C$_8$H$_6$F$_3$NO$_2$: 205.0351, found 205.0354.
3-(4-Ethyl-2,3,5,6-tetrafluorophenyl)acrylic acid (2o): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (1b, 0.238 g, 1 mmol), ethyltriphenylphosphonium bromide (Y2, 1.856 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid (166.2 mg, 67%). ¹H NMR (300 MHz, MeOD-d₄) δ 7.42 (d, J = 16.2 Hz, 1H), 6.54 (d, J = 16.2 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.7 Hz, 3H). ¹⁹F NMR (282 MHz, MeOD-d₄) δ -141.96 – -142.24 (m, 2F), -145.61 – -145.85 (m, 2F). ¹³C NMR (151 MHz, MeOD-d₄) δ 167.71 (s), 145.82 (d, J = 19.4 Hz), 144.11 (s), 128.85 (s), 125.1 (t, J = 8.2 Hz), 123.82 (t, J = 18.8 Hz), 111.75 (t, J = 13.3 Hz), 16.11 (s), 12.66 (s). IR: 3091.9, 2981.8, 2943.3, 1697.28, 1635.2, 1488.2, 1475.3, 1419.0, 1389.3, 1332.2, 1312.0, 1294.3, 1272.8, 1220.2, 1113.7, 1097.3, 995.1, 966.2, 929.1, 900.6, 631.9, 518.4. HRMS (ESI) Exact mass calcd for C₁₁H₉F₄O₂ [M+H]⁺: 249.0533, found 249.0536.

3-(4-Ethyl-3,5-difluorophenyl)acrylic acid (2p): The general procedure was applied using 3-(3,4,5-trifluorophenyl)acrylic acid (1c, 0.202 g, 1 mmol), phosphonium salt Y2 (1.856 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid (125.1 mg, 59%). ¹H NMR (300 MHz, DMSO-d₆) δ 12.54 (br, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 16.0 Hz, 1H), 2.62 (q, J = 7.5 Hz, 2H), 1.12 (t, J = 7.5 Hz, 3H). ¹⁹F NMR (282 MHz, DMSO-d₆) δ -116.55 (s, 2F). ¹³C NMR (151 MHz,
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DMSO-d$_6$ δ 167.77 (s), 161.29 (dd, $J$ = 244.6, 10.0 Hz), 142.05 (s), 135.29 (s), 121.91 (s), 120.86 (s), 111.49 (d, $J$ = 27.1 Hz), 16.02 (s), 14.37 (s). IR: 3069.9, 2977.1, 2938.9, 2878.6, 1689.2, 1634.4, 1572.5, 1499.7, 1436.5, 1341.8, 1321.5, 1294.9, 1099.4, 983.0, 943.6, 850.0. HRMS (ESI) Exact mass calc'd for C$_{11}$H$_9$F$_2$O$_2$ [M-H]: 211.0565, found 211.0571.

![3-(4-Ethyl-2,3-difluorophenyl)acrylic acid (2q)](image)

3-(4-Ethyl-2,3-difluorophenyl)acrylic acid (2q): The general procedure was applied using 3-(2,3,4-trifluorophenyl)acrylic acid (1n, 0.404 g, 2 mmol), phosphonium salt Y$_2$ (3.712 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid (220.5mg, 52%). $^1$H NMR (600 MHz, MeOD-d$_4$) δ 7.68 (d, $J$ = 16.2 Hz, 1H), 7.34 (t, $J$ = 7.3 Hz, 1H), 7.05 (t, $J$ = 7.4 Hz, 1H), 6.50 (d, $J$ = 16.2 Hz, 1H), 2.68 (q, $J$ = 7.6 Hz, 2H), 1.21 (t, $J$ = 7.6 Hz, 3H). $^{19}$F NMR (282 MHz, MeOD-d$_4$) δ -144.10 (dd, $J$ = 18.5, 0.8 Hz, 1F), -146.69 (dd, $J$ = 18.5, 0.7 Hz, 1F). $^{13}$C NMR (151 MHz, MeOD-d$_4$) δ 168.39 (s), 149.85 (dd, $J$ = 28.7, 13.3 Hz), 148.19 (dd, $J$ = 20.9, 13.4 Hz), 135.94 (s), 135.28 (d, $J$ = 13.0 Hz), 124.51 (d, $J$ = 12.3 Hz), 123.03 (d, $J$ = 13.8 Hz), 121.91 (d, $J$ = 8.7 Hz), 121.06 (s), 21.72 (s), 13.15 (s). IR: 2979.6, 2923.1, 2878.6, 2832.8, 1692.5, 1627.7, 1573.0, 1473.3, 1457.5, 1418.0, 1336.8, 1324.7, 1289.5, 1243.1, 1223.2, 1206.2, 1009.6, 981.4, 935.6, 917.3, 872.2, 816.1, 707.8, 610.9, 585.3, 483.0. HRMS (ESI) Exact mass calc'd for C$_{11}$H$_{11}$F$_2$O$_2$ [M+H]: 213.0722, found 213.0717.
3-[2,3,5,6-Tetrafluoro-4-(3-phenylpropyl)phenyl]acrylic acid (2r): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (1b, 0.238 g, 1 mmol), triphenyl-(3-phenylpropyl)phosphonium bromide (Y3, 2.306 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) and subsequent HPLC (collected between 73.5-75.5 min) purification afforded the title compound as white solid (57.5 mg, 17%). $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 7.42 (d, $J = 16.5$ Hz, 1H), 7.29 – 7.09 (m, 5H), 6.54 (d, $J = 16.5$ Hz, 1H), 2.72 (t, $J = 7.5$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 2H), 1.93 – 1.78 (m, 2H). $^{19}$F NMR (282 MHz, DMSO-d$_6$) $\delta$ -142.09 – -142.33 (m, 2F), -144.67 – -144.92 (m, 2F). $^{13}$C NMR (126 MHz, DMSO-d$_6$) $\delta$ 167.02 (s), 145.83 (s), 143.79 (d, $J = 19.2$ Hz), 141.51 (s), 128.79 – 128.58 (m), 128.49 (s), 127.19 (s), 126.33 (s), 122.10 (s), 112.05 (s), 34.99 (s), 30.43 (s), 22.71 (s). IR: 3415.6, 3022.3, 2945.1, 2924.4, 2861.3, 1697.4, 1635.5, 1486.3, 1420.1, 1297.8, 1273.5, 1256.5, 1045.6, 1025.0, 992.6, 979.6, 949.2, 927.3, 750.7, 698.3, 632.1, 506.8. HRMS (ESI) Exact mass calcd for C$_{18}$H$_{13}$F$_4$O$_2$ [M-H]: 337.0846, found 337.0847.

1,2,4,5-Tetrafluoro-3-nitro-6-(3-phenylpropyl)benzene (2s): The general procedure was applied to 2,3,4,5,6-pentafluoronitrobenzene (1n, 0.213 g, 1 mmol), phosphonium salt Y3 (2.306 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a light yellow oil (162.8 mg, 52%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 – 7.14 (m, 5H), 2.87 – 2.78 (m, 2H), 2.71 (t, $J = 6.0$ Hz, 2H), 2.04 – 1.92 (m, 2H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -140.30 – -140.58 (m, 2F), -147.16 – -147.41 (m, 2F). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.74 (s), 144.09 (s), 141.00 (d, $J = 13.5$ Hz), 140.65 (s), 139.26 (d, $J = 13.6$ Hz), 128.58 (s), 128.34 (s), 126.36 (s), 125.54 (t, $J = 18.6$ Hz), 35.43 (s), 30.21 (s), 22.96 (s). IR: 3027.9, 2927.9,
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2858.4, 1551.4, 1494.2, 1455.6, 1354.5, 972.5, 763.5, 699.6. HRMS (EI) Exact mass calcd for C_{15}H_{11}F_{4}NO_{2}: 313.0726, found 313.0729.

1,2,4,5-Tetrafluoro-3-nitro-6-(4-nitrobenzyl)benzene (2t): Briefly, a mixture of (4-nitrobenzyl)triphenylphosphonium bromide (Y4, 1.505 g, 3.15 mmol), NaH (0.12 g, 3.15 mmol) (60% dispersion in mineral oil) and 1,4-dioxane (10 mL) was stirred at ambient temperature for 48 h, followed by a 1,4-dioxane solution of 2,3,4,5,6-pentafluoronitrobenzene (1n, 0.134 g, 0.63 mmol) dropwise at room temperature. Then, the mixture was heated to 110 °C for another 48 h. The mixture was then cooled to ambient temperature, washed with deionized water and extracted with ethyl acetate. Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1:20) of the crude product afforded the title compound as a white crystal (58%). The yield of the product was determined by $^{19}$F NMR. $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J$ = 8.5 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 2H), 4.25 (s, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -139.08 (td, $J$ = 16.5, 8.7 Hz), -145.75 (s). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.41 (s), 145.91 – 145.67 (m), 143.91 – 143.67 (m), 143.04 (s), 141.33 (dd, $J$ = 17.8, 4.7 Hz), 139.23 (dd, $J$ = 17.8, 4.9 Hz), 129.43 (s), 124.33 (s), 122.40 (t, $J$ = 18.1 Hz), 28.67 (s). IR: 3113.1, 3084.1, 1629.1, 1602.8, 1554.5, 1513.1, 1492.2, 1435.7, 1416.1, 1344.4, 1292.7, 1110.8, 1011.4, 916.1, 843.3, 768.2, 724.1. HRMS (EI) Exact mass calcd for C$_{13}$H$_6$F$_4$N$_2$O$_4$: 330.0264, found 330.0269.
4-Allyl-2,3,5,6-tetrafluorobenzoic acid methyl ester (2u), (E)-2,3,5,6-Tetrafluoro-4-propenylbenzoic acid methyl ester (2u′), and (Z)-2,3,5,6-Tetrafluoro-4-propenylbenzoic acid methyl ester (2u″): Preparation procedure of 2t was applied using 2,3,4,5,6-pentafluorobenzoic acid methyl ester (1d, 0.452 g, 2 mmol), allyltriphenylphosphonium bromide (Y5, 3.833 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil) in THF at 80 °C for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compounds as a light yellow oil (218.2 mg, 44%). The ratio of the isomers was determined to be 2.2:1.2:1.0 by $^1$H NMR integrations of characteristic signals at 5.889 – 5.803, 6.374 – 6.345 and 6.345 – 6.316 ppm. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.72 (q, $J = 6.8$ Hz, 0.48H) (2u″), 6.69 (q, $J = 6.8$ Hz, 0.52H) (2u′), 6.36 (q, $J = 1.6$ Hz, 0.54H) (2u′′), 6.33 (q, $J = 1.6$ Hz, 0.46H) (2u″′), 5.91 – 5.79 (m, 1H) (2u), 5.08 (dt, $J = 17.6$, 8.9 Hz, 2H) (2u), 3.94 (s, 3H) (2u′, 2u″), 3.93 (s, 3H) (2u), 3.50 – 3.42 (m, 2H) (2u), 1.95 (d, $J = 6.7$ Hz, 3H) (2u′, 2u″). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -140.54 (d, $J = 376.3$ Hz, 2F), -143.40 (d, $J = 168.2$ Hz, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.35 (s), 146.06 – 145.01 (m), 143.99 – 142.99 (m), 138.56 (t, $J = 7.9$ Hz), 132.22 (s), 121.89 (t, $J = 18.4$ Hz), 120.24 (t, $J = 14.5$ Hz), 117.56 (s), 116.14 (s), 110.64 (t, $J = 15.9$ Hz), 109.31 (t, $J = 15.7$ Hz), 53.12 (s), 53.04 (s), 27.01 (s), 19.98 (s). IR: 3088.1, 2958.6, 2855.3, 1743.0, 1687.0, 1654.3, 1640.0, 1484.9, 1436.9, 1318.9, 1225.3, 1110.7, 1083.3, 1061.4, 989.5, 975.5, 921.8, 872.2, 786.1, 755.7. HRMS (ESI) Exact mass calcd for C$_{11}$H$_9$F$_4$O$_2$ [M+H]$^+$: 249.0533, found 249.0540.

Alkyl Transfer to Heterocyclic and Fused Ring Polyfluoroarenes

2,3,5,6-Tetrafluoro-4-methyl-pyridine (4a) and 2,3,5-trifluoro-4,6-dimethyl-pyridine (4a′): The general procedure was applied
using 2,3,4,5,6-pentafluoropyridine (3a, 0.845 g, 5 mmol), phosphonium salt Y1 (5.36 g, 15 mmol) and NaH (0.6 g, 15 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compounds as colorless oil (4a, 60.2%; 4a’, 5.8%). The yield of the product was determined by $^{19}$F NMR. The NMR spectral data were in line with the literature values.\footnote{4a: $^{19}$F NMR (471 MHz, CDCl$_3$) δ -95.05 (s, 2F), -145.99 – -146.26 (m, 2F). 4a’: $^1$H NMR (500 MHz, CDCl$_3$) δ 2.39 (s, 3H), 2.29 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -91.61 (t, J = 28.2 Hz, 1F), -129.22 (d, J = 30.8 Hz, 1F), -144.60 (d, J = 26.1 Hz, 1F). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 153.39 (dd, J = 251.9, 4.1 Hz), 146.47 (ddd, J = 234.3, 15.9, 8.5 Hz), 141.82 (ddd, J = 258.4, 31.1, 3.9 Hz), 136.85 (ddd, J = 21.2, 13.6, 5.9 Hz), 126.23 (ddd, J = 21.6, 15.3, 3.5 Hz), 17.08 (s), 8.06 (q, J = 2.6 Hz).}

\begin{center}
\includegraphics[width=0.2\textwidth]{2,3,5,6-Tetrafluoro-4-(4-nitrobenzyl)pyridine.png}
\end{center}

\textbf{2,3,5,6-Tetrafluoro-4-(4-nitrobenzyl)pyridine (4a’):} The general procedure was applied using 2,3,4,5,6-pentafluoropyridine (3a, 0.169 g, 1 mmol), phosphonium salt Y4 (2.389 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) in 1,4-dioxane at 110 °C for 48 h. Silica gel chromatography (eluent: ethyl acetate/petrol ether=1:20) of the crude product afforded the title compound as a colorless crystal (41%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.21 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 4.27 (s, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -89.95 (td, J = 28.7, 13.4 Hz, 2F), -144.08 (td, J = 28.7, 13.4 Hz, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.39 (s), 144.73 – 142.25 (m), 142.77 (s), 141.67 – 139.03 (m), 131.93 (t, J = 16.6 Hz), 129.55 (s), 124.28 (s), 29.21 (s). IR: 3116.9, 3088.2, 2959.4, 2943.4, 2854.5, 2452.5, 1937.1, 1806.3, 1651.6, 1599.2, 1526.6, 1492.6, 1443.7, 1405.5, 1345.9, 1291.5, 1252.1, 1184.4, 1009.9, 1109.5,
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989.8, 868.6, 855.2, 811.9, 761.9, 737.6, 698.6. HRMS (EI) Exact mass calcd for C_{12}H_{6}F_{4}N_{2}O_{2}: 286.0365, found 286.0360.

2,6-Difluoro-4-methylpyridine (4b) and 2,4-difluoro-6-methylpyridine (4b'): The general procedure was applied using 2,4,6-trifluoropyridine (3b, 0.665 g, 5 mmol), phosphonium salt Y1 (8.93 g, 25 mmol) and NaH (1.0 g, 25 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1:200) of the crude product afforded the title compounds as colorless oil (4b, 53.7%; 4b', 46.3%). The yield of the product was determined by 19F NMR. 4b: 'H NMR (500 MHz, CDCl₃) δ 6.63 (s, 2H), 2.43 (s, 3H). 19F NMR (471 MHz, CDCl₃) δ -70.23 (d, J = 31.9 Hz, 2F). 13C NMR (126 MHz, CDCl₃) δ 161.83 (dd, J = 245.6, 16.3 Hz), 157.54 (t, J = 7.9 Hz), 106.35 (dd, J = 27.6, 11.8 Hz), 21.14 (t, J = 2.9 Hz). IR: 3054.4, 2954.3, 2852.3, 1737.3, 1589.8, 1459.7, 1435.8, 1377.0, 1260.5, 1184.3, 1192.2, 1027.0, 802.7, 742.8, 721.5, 694.9, 541.5. HRMS (EI) Exact mass calcd for C₆H₅F₂N: 129.0390, found 129.0395. 4b': 'H NMR (500 MHz, CDCl₃) δ 6.79 (dd, J = 8.4, 1.6 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 2.50 (s, 3H). 19F NMR (471 MHz, CDCl₃) δ -64.29 (d, J = 22.0 Hz, 1F), -98.17 (d, J = 22.1 Hz, 1F). 13C NMR (126 MHz, CDCl₃) δ 171.32 (dd, J = 262.2, 12.5 Hz), 164.03 (dd, J = 237.1, 13.9 Hz), 159.94 (dd, J = 17.4, 9.5 Hz), 108.96 (dd, J = 18.1, 5.4 Hz), 94.68 (dd, J = 42.0, 22.3 Hz), 24.10 (d, J = 2.7 Hz). IR: 2954.5, 2924.1, 2853.2, 2359.2, 1732.9, 1621.8, 1489.9, 1456.8, 1351.5, 1126.4, 1210.9, 1042.8, 957.4, 850.4, 651.8. HRMS (EI) Exact mass calcd for C₆H₅F₂N: 129.0390, found 129.0396.
3-Chloro-2,5,6-trifluoro-4-methylpyridine (4c): The general procedure was applied using 3-chloro-2,4,5,6-tetrafluoropyridine (3c, 0.185 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 41 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a colorless oil (98%). The yield of the product was determined by $^{19}$F NMR. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.46 (d, $J = 2.4$ Hz, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -74.76 (dd, $J = 27.5, 12.4$ Hz, 1F), -90.21 (dd, $J = 20.4, 13.0$ Hz, 1F), -144.42 – -144.57 (m, 1F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 150.85 (dd, $J = 242.3, 12.7$ Hz), 146.85 (ddd, $J = 245.9, 17.7, 13.9$ Hz), 141.77 – 141.38 (m), 141.32 (ddd, $J = 255.7, 26.3, 6.1$ Hz), 113.55 (dd, $J = 33.9, 6.3$ Hz), 13.05 (d, $J = 2.4$ Hz). IR: 2959.5, 2924.5, 2853.0, 1624.0, 1540.8, 1507.3, 1465.4, 1223.5, 1005.9, 913.1, 846.9, 743.3, 668.8, 418.5. HRMS (EI) Exact mass calcd for C$_6$H$_3$ClF$_3$N: 180.9906, found 180.9910.

3-Chloro-2,5,6-trifluoro-4-(4-nitrobenzyl)pyridine (4c\'): The general procedure was applied using 3-chloro-2,4,5,6-tetrafluoropyridine (3c, 0.185 g, 1 mmol), phosphonium salt Y4 (2.389 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) in 1,4-dioxane at 110 °C for 48 h. Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1:20) of the crude product afforded the title compound as a colorless crystal (292.9 mg, 97%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.19 (dd, $J = 8.8, 2.2$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 4.37 (d, $J = 1.2$ Hz, 2H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -74.76 (dd, $J = 28.1, 12.5$ Hz, 1F), -90.21 (dd, $J = 28.1, 12.5$ Hz, 1F), -144.42 – -144.57 (m, 1F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.27 (ddd, $J = 244.7, 12.2, 2.6$ Hz), 147.30 (s), 146.42 – 146.04 (m), 142.63 (s), 142.01 (d, $J = 15.0$ Hz), 141.21 (ddd, $J = 257.5, 26.6, 6.3$ Hz), 129.55 (s), 124.15 (s), 113.45 (dd, $J = 34.2$, s).
6.6 Hz), 32.60 (s). IR: 3086.9, 2958.7, 2942.1, 2452.5, 2359.9, 2339.9, 1806.2, 1627.0, 1598.1, 1524.3, 1492.7, 1463.0, 1445.4, 1429.5, 1382.4, 1348.8, 1221.5, 1158.5, 1110.5, 1002.2, 702.4, 868.6, 856.0, 842.7, 812.0, 739.4, 761.9. HRMS (EI) Exact mass calcd for C_{12}H_6ClF_3N_2O_2: 302.0070, found 302.0073.

3,5-Dichloro-2,6-difluoro-4-methylpyridine (4d): The general procedure was applied using 3,5-dichloro-2,4,6-trifluoropyridine (3d, 0.201 g, 1 mmol), phosphonium salt Y1 (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 41 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a colorless oil (97%). The yield of the product was determined by 19F NMR. 1H NMR (500 MHz, CDCl_3) δ 2.58 (s, 3H). 19F NMR (471 MHz, CDCl_3) δ -72.07 (s, 2F). 13C NMR (126 MHz, CDCl_3) δ 154.50 (dd, J = 245.0, 14.7 Hz), 152.42 (t, J = 1.7 Hz), 114.23 – 113.88 (m), 18.03 (t, J = 2.8 Hz). IR: 2958.0, 2929.0, 2855.6, 1600.6, 1559.5, 1406.2, 1373.8, 1257.9, 113.0, 1077.8, 998.3, 913.0, 755.6, 735.9, 615.9, 566.2, 405.1. HRMS (EI) Exact mass calcd for C_6H_3Cl_2F_2N: 196.9611, found 196.9611.

1,2,3,4,5,6,8-Heptafluoro-7-methylnaphthalene (4e): The general procedure was applied using octafluoronaphthalene (3e, 0.272 g, 1 mmol), phosphonium salt Y1 (1.0716 g, 3 mmol) and NaH (0.12 g, 3 mmol) (60% dispersion in mineral oil) at 60 °C for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a colorless crystal (71%). The yield of the product was determined by 19F NMR. The NMR spectral data were in line with the literature.
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values.\(^9\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.41 (s, 1H). \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -121.33 – -122.23 (m, 1F), -137.27 (s, 1F), -145.17 (dd, \(J = 67.2, 16.2\) Hz, 1F), -146.31 – -147.10 (m, 1F), -149.78 – -150.76 (m, 1F), -155.12 (d, \(J = 17.9\) Hz, 1F), -156.45 (d, \(J = 14.6\) Hz, 1F). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 150.19 (d, \(J = 257.9\) Hz), 146.91 (d, \(J = 250.4\) Hz), 142.01 (s), 141.28 (s), 140.11 (t, \(J = 14.9\) Hz), 139.66 – 138.97 (m), 137.76 (dt, \(J = 29.1, 14.8\) Hz), 115.19 (t, \(J = 21.2\) Hz), 109.83 (s), 107.62 (s), 7.49 (s). IR: 3014.5, 2934.3, 2870.0, 1655.2, 1614.4, 1496.7, 1439.2, 1409.0, 1381.7, 1265.5, 1176.5, 1150.0, 1117.2, 1091.6, 1021.6, 1003.3, 951.7, 910.3, 774.7, 735.5, 530.9. HRMS (EI) Exact mass calcd for C\(_{11}\)H\(_3\)F\(_7\): 268.0123, found 268.0121.

X-Ray Crystal Structure of 2q

The structure of compound 2q was determined by X-ray crystallography (deposition number CCDC 953222):
**Mechanistic Investigation by NMR Spectroscopy**

To explore the mechanism of the phosphonium ylide-assisted alkyl transfer reaction, we used NMR spectroscopy to monitor the reaction intermediates. It was known that nitro-group might help stabilize the intermediate complexes of nucleophilic substitution, we carried out the alkyl transfer reaction between 3,4,5-trifluoronitrobenzene and methyltriphenylphosphonium bromide. The $^1$H, $^{31}$P and $^{13}$C spectra were obtained and shown in Figures S1, S2 and S3. The reaction pathways were proposed in Scheme S1. It was clear that all the reaction intermediates could be found on the NMR spectra (Figures S1-3).

**Phosphonium Ylide (C)**

In a three-neck round-bottom flask equipped with a magnetic stirring bar, methyltriphenylphosphonium bromide (1.786 g, 5.0 mmol) and potassium tert-butoxide (0.56 g, 5.0 mmol) were added. The flask was evacuated and re-filled with nitrogen for three times. THF (10 mL) was then added by syringe and the mixture was heated to reflux for 3 h. Part of the supernatant (0.5 mL) was taken from the cooled reaction mixture and the solvent was removed under vacuum to afford a yellow solid. The solid was then dissolved in 0.6 mL THF-$d_8$ and transferred into a NMR tube. The $^1$H, $^{31}$P and $^{13}$C spectra were recorded.

**Meisenheimer Complexes (D, E)**

To the mixture of the phosphonium ylide and THF-$d_8$ 0.01 mL 3,4,5-trifluoronitrobenzene was added. A dark red mixture formed immediately. The $^1$H, $^{31}$P and $^{13}$C spectra were rapidly obtained.

**Hydrolysis of the Meisenheimer Complexes**

The mixture of Meisenheimer complexes and THF-$d_8$ was concentrated under vacuum. To the concentrated mixture were added 1.5 mL CDCl$_3$, 2 drops of D$_2$O and a small amount of silica gel. The mixture was stirred for 10 min and filtrated. The $^1$H, $^{31}$P and $^{13}$C spectra were recorded.
Scheme S1. Proposed reaction pathways for alkyl transfer from phosphonium ylide to 3,4,5-trifluoronitrobenzene.

Figure S1-3: spectrum 1, phosphonium salt; spectrum 2, base added; spectrum 3, polyfluoroarene added; spectrum 4, hydrolysis.

Figure S1. $^1$H NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.
Figure S2. $^{31}$P NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.

Figure S3. $^{13}$C NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.
Deuteration Experiment

The general procedure was applied using 3-pentafluorophenyl-acrylic acid (1b, 0.238 g, 1 mmol), phosphonium salt Y1 (1.785 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at 80 °C for 24 h. After the reaction was completed, the workup was conducted using D₂O (0.6 mL) at ambient temperature. The crude product was then purified by silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) to afford the target product 5 as a white solid. ¹H NMR (500 MHz, MeOD-d₄) δ 7.65 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 16.4 Hz, 1H), 2.33 (s, 2H).

Synthesis of Tefluthrin

Scheme S2. Traditional Synthesis Route of Tefluthrin¹⁰
3-(2-Chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid pentafluorophenylmethyl ester (10): A THF solution of 4-dimethylamino pyridine (122.2 mg, 1 mmol), N,N'-dicyclohexylcarbodiimide (4.4 g, 22 mmol), (2,3,4,5,6-pentafluorophenyl)methanol (3.9 g, 20 mmol) and 3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid (9, 7.9 g, 32 mmol) was stirred at ambient temperature for 39 h. The mixture was then concentrated and purified by Silica gel chromatography (eluent: petrol ether) afforded the title compound as a colorless oil (7.78 g, 93%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.88 (d, $J = 9.3$ Hz, 1H), 5.22 (q, $J = 12.2$ Hz, 2H), 2.21 (t, $J = 8.9$ Hz, 1H), 2.09 – 1.87 (m, 1H), 1.31 (s, 3H), 1.30 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -68.87 (s, 3F), -141.98 (dd, $J = 21.9$, 8.2 Hz, 2F), -152.54 (t, $J = 20.6$ Hz, 1F), -161.63 (td, $J = 21.6$, 7.8 Hz, 2F). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.42 (s), 146.79 – 144.57 (m), 143.34 – 139.85 (m), 137.52 (ddd, $J = 34.4$, 29.1, 16.6 Hz), 130.49 – 127.83 (m), 122.10 (q, $J = 37.6$ Hz), 120.36 (q, $J = 271.6$ Hz), 109.43 (t, $J = 17.4$ Hz), 53.15 (s), 32.44 (s), 31.05 (s), 28.88 (s), 28.02 (s), 14.63 (s).

3-(2-Chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid 2,3,5,6-tetrafluoro-4-methylbenzyl ester (11): According to the general procedure, a THF solution of phosphonium salt Y1 (1.785 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) was heated to reflux for 48 h, cooled down and
filtrated. To the filtrate was added a THF solution of polyfluoroarene 10 (0.422 g, 1 mmol). Further reaction was carried out at ambient temperature for 48 h, then purified by Silica gel chromatography (eluent: petrol ether) afforded the title compound as a colorless oil (44%). The yield of the product was determined by $^{19}$F NMR. The NMR spectral data were in line with the literature values.\textsuperscript{11} $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.89 (dd, $J = 9.4$, 0.7 Hz, 1H), 5.21 (dd, $J = 28.3$, 12.1 Hz, 2H), 2.29 (t, $J = 2.0$ Hz, 3H), 2.18 (t, $J = 8.8$ Hz, 1H), 1.97 (d, $J = 8.4$ Hz, 1H), 1.30 (s, 3H), 1.29 (s, 3H). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -68.81 (d, $J = 4.1$ Hz), -143.49 – -143.58 (m), -144.42 – -144.62 (m). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.55 (s), 146.22 – 145.65 (m), 144.19 – 143.74 (m), 129.74 (q, $J = 4.4$ Hz), 122.05 (q, $J = 37.9$ Hz), 120.38 (q, $J = 271.9$ Hz), 117.36 (t, $J = 19.1$ Hz), 111.32 (t, $J = 17.1$ Hz), 53.72 (s), 32.59 (s), 31.02 (s), 28.85 (s), 28.25 (s), 14.86 (s), 7.63 (s).

References

NMR Spectra of All the New Compounds

Figure S4. $^{1}H$ NMR spectrum of 2a.

Figure S5. $^{19}F$ NMR spectrum of 2a.
**Figure S6.** $^{13}$C NMR spectrum of 2a.

**Figure S7.** $^1$H NMR spectrum of 2b.
Figure S8. $^{19}$F NMR spectrum of 2b.

Figure S9. $^{13}$C NMR spectrum of 2b.
Figure S10. $^1$H NMR spectrum of 2c.

Figure S11. $^{19}$F NMR spectrum of 2c.
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Figure S12. $^{13}$C NMR spectrum of 2c.

Figure S13. $^1$H NMR spectrum of 2e.
Figure S14. $^{19}$F NMR spectrum of 2e.

Figure S15. $^{13}$C NMR spectrum of 2e.
Figure S16. $^1$H NMR spectrum of 2f.

Figure S17. $^{19}$F NMR spectrum of 2f.
Figure S18. $^{13}$C NMR spectrum of 2f.

Figure S19. $^1$H NMR spectrum of 2g.
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**Figure S20.** $^{19}$F NMR spectrum of 2g.

**Figure S21.** $^{13}$C NMR spectrum of 2g.
Figure S22. $^{19}$F NMR spectrum of 2h.

Figure S23. $^{13}$C NMR spectrum of 2h.
**Figure S24.** $^1$H NMR spectrum of 2k.

**Figure S25.** $^{19}$F NMR spectrum of 2k.
Figure S26. $^{13}$C NMR spectrum of 2k.

Figure S27. $^1$H NMR spectrum of 2k'.
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Figure S28. $^{19}$F NMR spectrum of 2k'.

Figure S29. $^1$H NMR spectrum of 2l.
Figure S30. $^{19}$F NMR spectrum of 2l.

Figure S31. $^{13}$C NMR spectrum of 2l.
Figure S32. $^1$H NMR spectrum of 2m.

Figure S33. $^{19}$F NMR spectrum of 2m.
**Figure S34.** $^{13}$C NMR spectrum of 2m.

**Figure S35.** $^1$H NMR spectrum of 2m'.

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*S44*
**Figure S36.** $^{19}$F NMR spectrum of 2m'.

**Figure S37.** $^{13}$C NMR spectrum of 2m'.
Figure S38. $^1$H NMR spectrum of 2n.

Figure S39. $^{19}$F NMR spectrum of 2n.
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Figure S40. $^{13}$C NMR spectrum of 2n.

Figure S41. $^1$H NMR spectrum of 2o.
Figure S42. $^{19}$F NMR spectrum of 2o.

Figure S43. $^{13}$C NMR spectrum of 2o.
Figure S44. $^1$H NMR spectrum of 2p.

Figure S45. $^{19}$F NMR spectrum of 2p.
**Figure S46.** $^{13}$C NMR spectrum of 2p.

**Figure S47.** $^1$H NMR spectrum of 2q.
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Figure S48. $^{19}$F NMR spectrum of $2q$.

Figure S49. $^{13}$C NMR spectrum of $2q$. 
Figure S50. HMBC spectrum of 2q.

Figure S51. $^1$H NMR spectrum of 2r.
**Figure S52.** $^{19}\text{F}$ NMR spectrum of $2r$.

**Figure S53.** $^{13}\text{C}$ NMR spectrum of $2r$. 
**Figure S54.** $^1$H NMR spectrum of 2s.

**Figure S55.** $^{19}$F NMR spectrum of 2s.
Figure S56. $^{13}$C NMR spectrum of 2s.

Figure S57. $^1$H NMR spectrum of 2t.
Figure S58. $^{19}$F NMR spectrum of 2t.

Figure S59. $^{13}$C NMR spectrum of 2t.
Figure S60. $^1$H NMR spectrum of 2u, 2u'$ and 2u$"$.

Figure S61. $^{19}$F NMR spectrum of 2u, 2u'$ and 2u$"$.
Figure S62. $^{13}$C NMR spectrum of 2u, 2u’ and 2u’’.

Figure S63. $^1$H NMR spectrum of 4a’.
Figure S64. $^{13}$C NMR spectrum of 4a'.

Figure S65. $^1$H NMR spectrum of 4a''.
Figure S66. $^{19}$F NMR spectrum of 4a”.

Figure S67. $^{13}$C NMR spectrum of 4a”.
Figure S68. $^1$H NMR spectrum of 4b.

Figure S69. $^{19}$F NMR spectrum of 4b.
Figure S70. $^{13}$C NMR spectrum of 4b.

Figure S71. $^1$H NMR spectrum of 4b'.
Figure S72. $^{19}$F NMR spectrum of $4b'$.

Figure S73. $^{13}$C NMR spectrum of $4b'$. 
**Figure S74.** $^1$H NMR spectrum of 4c.

**Figure S75.** $^{19}$F NMR spectrum of 4c.
Figure S76. $^{13}$C NMR spectrum of 4c.

Figure S77. $^1$H NMR spectrum of 4c'.
Figure S78. $^{19}$F NMR spectrum of 4c'.

Figure S79. $^{13}$C NMR spectrum of 4c'.
Figure S80. $^1$H NMR spectrum of 4d.

Figure S81. $^{19}$F NMR spectrum of 4d.
Figure S82. $^{13}$C NMR spectrum of 4d.

Figure S83. $^1$H NMR spectrum of 4e.
**Figure S84.** $^{19}$F NMR spectrum of 4e.

**Figure S85.** $^{13}$C NMR spectrum of 4e.
Figure S86. $^1$H NMR spectrum of 5.