Supplementary Information

Regioselective Alkyl Transfer from Phosphonium Ylide to Functionalized Polyfluoroarenes

Wei Lu,[a,b] *Juan Gao,*[a] *Jingkui Yang,*[b] *Lei Liu,*[a] *Yuliang Zhao,*[a] *Hai-Chen Wu*[a]*

[a]Key Laboratory for Biomedical Effects of Nanomaterials & Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

[b]School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, 100049 Beijing, China

haichenwu@ihep.ac.cn

Contents

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 Kα (λ = 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 α,α,α-trifluorotoluene as an internal standard.

HPLC condition:

Flow: 4.0 mL/min

Temperature: ambient temperature

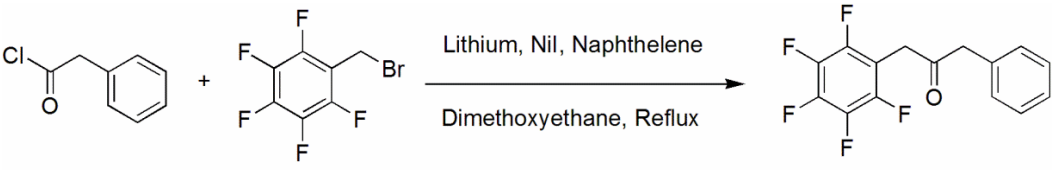
Run time: 100 min

Detection wavelength: 254 nm

Gradient eluent:

Time (min)	Acetonitrile (%)	Water (%)
0	5	95
60	100	0
90	100	0
100	5	95

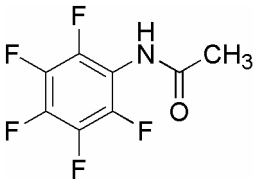
Preparation of Starting Materials



A **B** **1a**

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

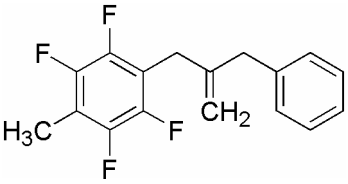
1a was prepared according to the literature procedure[1] using phenylacetyl chloride (**A**) and 1-bromomethyl-2,3,4,5,6-pentafluoro-benzene (**B**) and obtained as a light yellow solid. The NMR spectral data were in line with the literature values[2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 5H), 3.84 (s, 2H), 3.81 (t, *J* = 1.3 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -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):

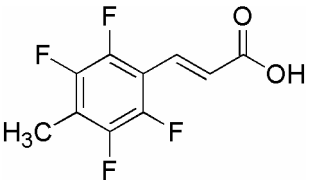
1g was prepared according to the literature procedure[3] by reacting 2,3,4,5,6-pentafluorobenzamide (1.744 g, 9.53 mmol) with acetic anhydride (9.729 g, 95.3 mmol) at 90 °C for 17 h. The crude product was poured into cooled water and extracted with dichloromethane. The organic phase was dried over anhydrous 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[4]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 1H), 2.23 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.91 (d, *J* = 16.4 Hz, 2F), -156.32 (t, *J* = 21.2 Hz, 1F), -162.31 (t, *J* = 19.6 Hz, 2F).

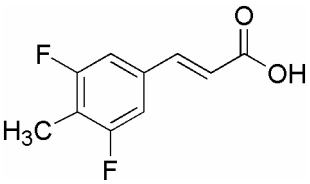


General procedure: 1-(2-Benzylallyl)-2,3,5,6-tetrafluoro-4-methylbenzene (2a): In a 25 mL two-neck round bottom flask equipped with a magnetic stir bar, methyltriphenylphosphonium bromide (**Y1**, 0.625 g, 1.66 mmol) and NaH (0.067 g, 1.66 mmol) (60% dispersion in mineral oil) were added. The flask was 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, $CDCl_3$) δ 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, $CDCl_3$) δ -144.86 – -144.87 (m, 2F), -144.68 – -145.30 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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.

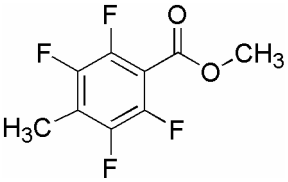


3-(2,3,5,6-Tetrafluoro-4-methylphenyl)acrylic acid (2b): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (**1b**, 0.2 g, 0.84 mmol), phosphonium salt **Y1** (1.5 g, 4.2 mmol) and NaH (0.168 g, 4.2 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl 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%). ^{1}H NMR (600 MHz, MeOD-d_4) δ 7.61 (d, *J* = 16.4 Hz, 1H), 6.64 (d, *J* = 16.4 Hz, 1H), 2.29 (s, 3H). ^{19}F NMR (282 MHz, MeOD-d_4) δ -142.81 (dd, *J* = 22.0, 12.4 Hz, 2F), -143.72 – -143.95 (m, 2F). ^{13}C NMR (151 MHz, MeOD-d_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 $C_{10}H_7F_4O_2$ $[M+H]^+$: 235.0377, found 235.0374.

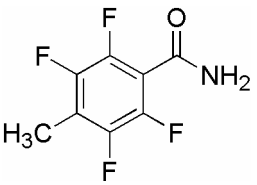


3-(3,5-Difluoro-4-methyl-phenyl)acrylic acid (2c): The general procedure was applied using 3-(3,4,5-trifluorophenyl)acrylic acid (**1c**, 0.202 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol 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) δ 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) δ -116.36 (s, 2F). ^{13}C NMR (151 MHz, DMSO-d_6) δ 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 $C_{10}H_7F_2O_2$ [M-H]$^-$: 197.0408, found 197.0416.

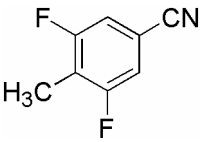


2,3,5,6-Tetrafluoro-4-methylbenzoic acid methyl ester (2d): The general procedure was applied using methyl pentafluorobenzoate (**1d**, 0.226 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (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[5]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (s, 3H), 2.32 (t, *J* = 2.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -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 $C_9H_5F_4O_2$ [M-H]$^-$: 221.0220, found 221.0212.

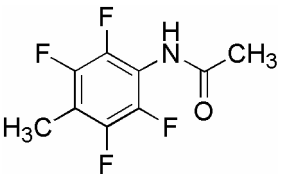


2,3,5,6-Tetrafluoro-4-methylbenzamide (2e): The general procedure was applied to 2,3,4,5,6-pentafluorobenzamide (**1e**, 0.211 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at 80 °C for 48 h.

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 $C_8H_6F_4NO$ $[M+H]^+$: 208.03800, found 208.03760.

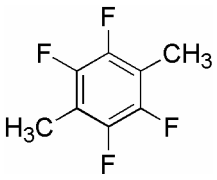


3,5-Difluoro-4-methylbenzonitrile (2f): The general procedure was applied using 3,4,5-trifluorobenzonitrile (**1f**, 0.157 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Basic aluminum oxide column chromatography (eluent: petrol ether) of 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 (dd, *J* = 250.2, 9.6 Hz), 120.24 (t, *J* = 20.9 Hz), 116.83 (t, *J* = 3.4 Hz), 114.94 (dd, *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 $C_8H_5F_2N$: 153.0390, found 153.0392.

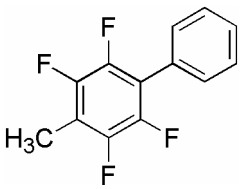


N-(2,3,5,6-Tetrafluoro-4-methylphenyl)acetamide (2g): The general procedure was applied using N-(2,3,4,5,6-pentafluoro-phenyl)acetamide (**1g**, 0.225 g, 1 mmol),

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, $CDCl_3$) δ 7.78 (s, 1H), 2.22 (s, 3H), 2.17 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -144.13 (s, 2F), -147.29 (s, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 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 $C_9H_6F_4NO$ $[M-H]^-$: 220.0380, found 220.0382.

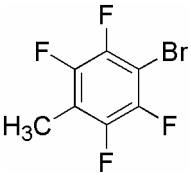


1,2,4,5-Tetrafluoro-3,6-dimethylbenzene (2h): The general procedure was applied using 1,2,3,4,5-pentafluoro-6-methylbenzene (**1h**, 0.910 g, 5 mmol), phosphonium salt **Y1** (8.93 g, 25 mmol) and NaH (1.0 g, 25 mmol) (60% dispersion in mineral oil). Crude product was purified by distillation at reduced 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, $CDCl_3$) δ 2.24 – 2.22 (quintet, J = 0.9 Hz, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -145.57 (s, 4F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 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.

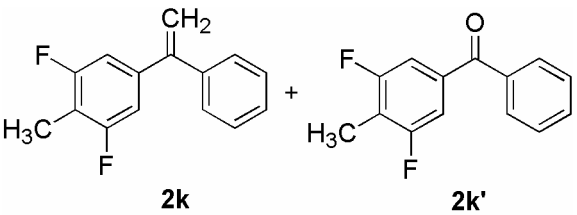


2,3,5,6-Tetrafluoro-4-methylbiphenyl (2i): The general procedure was applied using 2,3,4,5,6-pentafluorobiphenyl (**1i**, 0.244 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5

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, $CDCl_3$) δ 7.51 – 7.38 (m, 5H), 2.31 (t, *J* = 2.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.01 – -144.19 (m, 2F), -145.55 – -145.73 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.28 – 144.57 (d, *J* = 258.2 Hz), 144.49 – 142.86 (dd, *J* = 246.13, 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, $CDCl_3$) δ 2.26 (t, *J* = 2.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -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 $C_7H_3BrF_4$: 241.9354, found 241.9353.

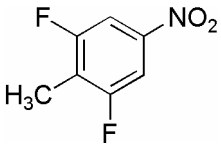


2k **2k'**

1,3-Difluoro-2-methyl-5-(1-phenylvinyl)benzene (2k) and

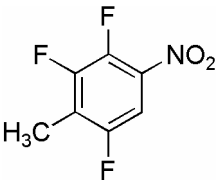
(3,5-Difluoro-4-methylphenyl)phenylmethanone (2k′): The general procedure was applied using 3,4,5-trifluorobenzophenone (**1k**, 0.236 g, 1 mmol), phosphonium salt **Y1** (3.572 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the 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, $CDCl_3$) δ 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, $CDCl_3$) δ -115.28 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ -112.98 (s, 2F).

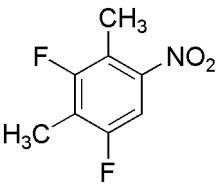


2,6-Difluoro-4-nitrotoluene (2l): The general procedure was applied using 3,4,5-trifluoronitrobenzene (**1l**, 0.177 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (eluent: petrol 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, $CDCl_3$) δ 7.84 – 7.68 (m, 2H), 2.30 (t, *J* = 1.8 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.66 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 1098.8, 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 $C_7H_5F_2NO_2$: 173.0288, found 173.0290.

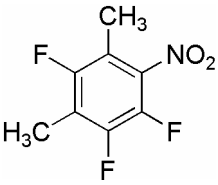


1,3,4-Trifluoro-2-methyl-5-nitrobenzene (2m): The general procedure was applied using 2,3,4,5-tetrafluoronitrobenzene (**1m**, 0.780 g, 4 mmol), phosphonium salt **Y1** (7.145 g, 20 mmol) and NaH (0.8 g, 20 mmol) (60% dispersion in mineral oil) at ambient temperature for 48 h. Silica gel chromatography (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, $CDCl_3$) δ 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, $CDCl_3$) δ -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, $CDCl_3$) δ 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 $C_7H_4F_3NO_2$: 191.0194, found 191.0195.

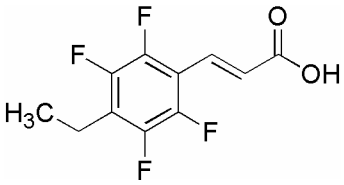


1,3-Difluoro-2,4-dimethyl-5-nitrobenzene (2m′): The general procedure was applied using 2,3,4,5-tetrafluoronitrobenzene (**1m**, 0.195 g, 1 mmol), phosphonium salt **Y1** (3.572 g, 10 mmol) and NaH (0.4 g, 10 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title

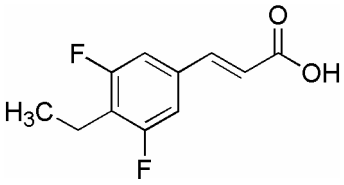
compound as a light yellow oil (71%). The yield of the product was determined by ^{19}F NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.45 (dd, *J* = 2.5, 1.2 Hz, 3H), 2.26 (t, *J* = 2.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.94 (d, *J* = 8.5 Hz, 1F), -115.23 (d, *J* = 8.5 Hz, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 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 $C_8H_7F_2NO_2$: 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 **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 (58%). The yield of the product was determined by ^{19}F NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (t, *J* = 2.2 Hz, 3H), 2.25 (dd, *J* = 2.5, 1.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -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) δ 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, 1127.3, 1065.6, 916.3, 884.2, 812.2, 769.8, 753.4, 580.9. HRMS (EI) Exact mass calcd for $C_8H_6F_3NO_2$: 205.0351, found 205.0354.

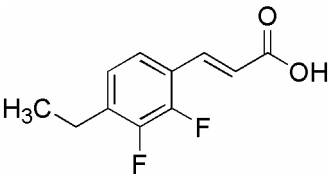


3-(4-Ethyl-2,3,5,6-tetrafluorophenyl)acrylic acid (2o): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (**1b**, 0.238 g, 1 mmol), ethyltriphenylphosphonium bromide (**Y2**, 1.856 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: 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%). ^{1}H NMR (300 MHz, MeOD-d_4) 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). ^{19}F NMR (282 MHz, MeOD-d_4) δ -141.96 – -142.24 (m, 2F), -145.61 – -145.85 (m, 2F). ^{13}C NMR (151 MHz, MeOD-d_4) δ 167.71 (s), 145.82 (d, *J* = 19.4 Hz), 144.11 (s), 128.85 (s), 125.81 (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 $C_{11}H_9F_4O_2$ $[M+H]^+$: 249.0533, found 249.0536.

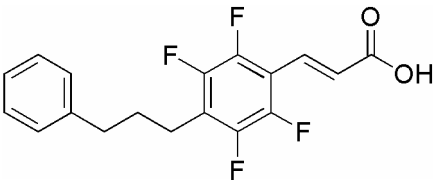


3-(4-Ethyl-3,5-difluorophenyl)acrylic acid (2p): The general procedure was applied using 3-(3,4,5-trifluorophenyl)acrylic acid (**1c**, 0.202 g, 1 mmol), phosphonium salt **Y2** (1.856 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: ethyl acetate/petrol ether = 1/20, and 1% acetic acid) of the crude product afforded the title compound as a white solid (125.1 mg, 59%). ^{1}H NMR (300 MHz, DMSO-d_6) 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). ^{19}F NMR (282 MHz, DMSO-d_6) δ -116.55 (s, 2F). ^{13}C NMR (151 MHz,

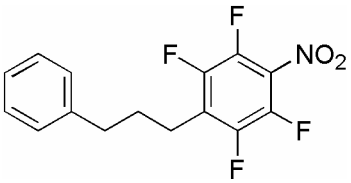
DMSO-d_6) δ 167.77 (s), 161.29 (dd, *J* = 244.6, 10.0 Hz), 142.05 (s), 135.29 (s), 121.91 (s), 120.86 (s), 111.49 (d, *J* = 27.1 Hz), 16.02 (s), 14.37 (s). IR: 3069.9, 2977.1, 2938.9, 2878.6, 1689.2, 1634.4, 1572.5, 1499.7, 1436.5, 1341.8, 1321.5, 1294.9, 1099.4, 983.0, 943.6, 850.0. HRMS (ESI) Exact mass calcd for $C_{11}H_9F_2O_2$ $[M-H]^-$: 211.0565, found 211.0571.



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 **Y2** (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 calcd for $C_{11}H_{11}F_2O_2$ $[M+H]^+$: 213.0722, found 213.0717.

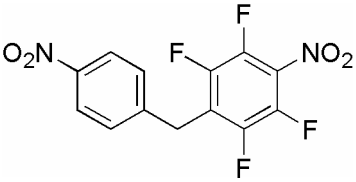


3-[2,3,5,6-Tetrafluoro-4-(3-phenylpropyl)phenyl]acrylic acid (2r): The general procedure was applied using 3-pentafluorophenyl-acrylic acid (**1b**, 0.238 g, 1 mmol), triphenyl-(3-phenylpropyl)phosphonium bromide (**Y3**, 2.306 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica 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) δ 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) δ -142.09 – -142.33 (m, 2F), -144.67 – -144.92 (m, 2F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 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 $C_{18}H_{13}F_4O_2$ $[M-H]^-$: 337.0846, found 337.0847.

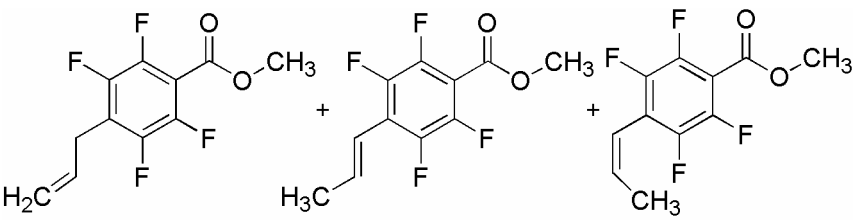


1,2,4,5-Tetrafluoro-3-nitro-6-(3-phenylpropyl)benzene (2s): The general procedure was applied to 2,3,4,5,6-pentafluoronitrobenzene (**1n**, 0.213 g, 1 mmol), phosphonium salt **Y3** (2.306 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil). Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a light yellow oil (162.8 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ -140.30 – -140.58 (m, 2F), -147.16 – -147.41 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 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,

2858.4, 1551.4, 1494.2, 1455.6, 1354.5, 972.5, 763.5, 699.6. HRMS (EI) Exact mass calcd for $C_{15}H_{11}F_4NO_2$: 313.0726, found 313.0729.



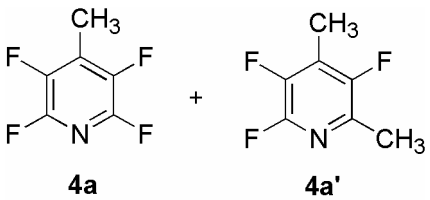
1,2,4,5-Tetrafluoro-3-nitro-6-(4-nitrobenzyl)benzene (2t): Briefly, a mixture of (4-nitrobenzyl)triphenylphosphonium bromide (**Y4**, 1.505 g, 3.15 mmol), NaH (0.12 g, 3.15 mmol) (60% dispersion in mineral oil) and 1,4-dioxane (10 mL) was stirred at ambient temperature for 48 h, followed by a 1,4-dioxane 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, $CDCl_3$) δ 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, $CDCl_3$) δ -139.08 (td, *J* = 16.5, 8.7 Hz), -145.75 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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 $C_{13}H_6F_4N_2O_4$: 330.0264, found 330.0269.



2u **2u'** **2u''**

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, $CDCl_3$) δ 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, $CDCl_3$) δ -140.54 (d, *J* = 376.3 Hz, 2F), -143.40 (d, *J* = 168.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 2928.8, 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 $C_{11}H_9F_4O_2$ $[M+H]^+$: 249.0533, found 249.0540.

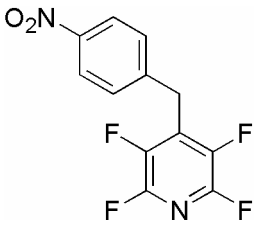
Alkyl Transfer to Heterocyclic and Fused Ring Polyfluoroarenes



4a **4a'**

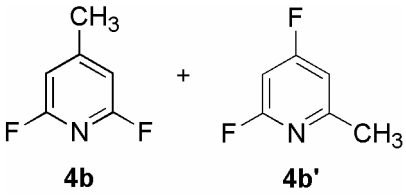
2,3,5,6-Tetrafluoro-4-methyl-pyridine (4a) and 2,3,5-trifluoro-4,6-dimethyl-pyridine (4a′): The general procedure was applied

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.[8] **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).



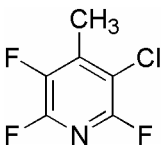
2,3,5,6-Tetrafluoro-4-(4-nitrobenzyl)pyridine (4a″): The general procedure was applied using 2,3,4,5,6-pentafluoropyridine (**3a**, 0.169 g, 1 mmol), phosphonium salt **Y4** (2.389 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) in 1,4-dioxane at 110 °C for 48 h. Silica gel chromatography (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,

989.8, 868.6, 855.2, 811.9, 761.9, 737.6, 698.6. HRMS (EI) Exact mass calcd for $C_{12}H_6F_4N_2O_2$: 286.0365, found 286.0360.

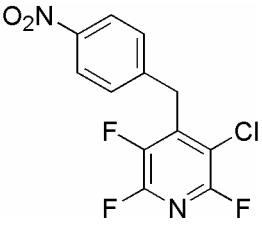


4b **4b'**

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 ^{19}F NMR. **4b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 2H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.23 (d, *J* = 31.9 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) 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, 2923.8, 2852.3, 1737.3, 1589.8, 1459.7, 1435.8, 1377.0, 1260.5, 1184.3, 1119.2, 1027.0, 802.7, 742.8, 721.5, 694.9, 541.5. HRMS (EI) Exact mass calcd for $C_6H_5F_2N$: 129.0390, found 129.0395. **4b′**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.29 (d, *J* = 22.0 Hz, 1F), -98.17 (d, *J* = 22.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_6H_5F_2N$: 129.0390, found 129.0396.

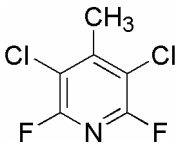


3-Chloro-2,5,6-trifluoro-4-methylpyridine (4c): The general procedure was applied using 3-chloro-2,4,5,6-tetrafluoropyridine (**3c**, 0.185 g, 1 mmol), phosphonium salt **Y1** (1.786 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at ambient temperature for 41 h. Silica gel chromatography (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, $CDCl_3$) δ 2.46 (d, *J* = 2.4 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -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, $CDCl_3$) δ 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 $C_6H_3ClF_3N$: 180.9906, found 180.9910.

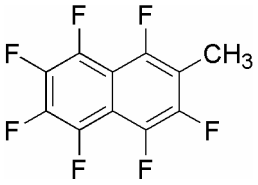


3-Chloro-2,5,6-trifluoro-4-(4-nitrobenzyl)pyridine (4c′): The general procedure was applied using 3-chloro-2,4,5,6-tetrafluoropyridine (**3c**, 0.185 g, 1 mmol), phosphonium salt **Y4** (2.389 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) in 1,4-dioxane at 110 °C for 48 h. Silica 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, $CDCl_3$) δ 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, $CDCl_3$) δ -72.40 (dd, *J* = 28.1, 12.5 Hz, 1F), -88.00 (dd, *J* = 21.4, 12.6 Hz, 1F), -143.66 (dd, *J* = 28.2, 21.5 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.27 (ddd, *J* = 244.7, 12.2, 2.6 Hz), 147.30 (s), 148.42 – 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,

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 ^{19}F NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.07 (s, 2F). ^{13}C 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, 1420.4, 1406.2, 1373.8, 1257.9, 1113.0, 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.

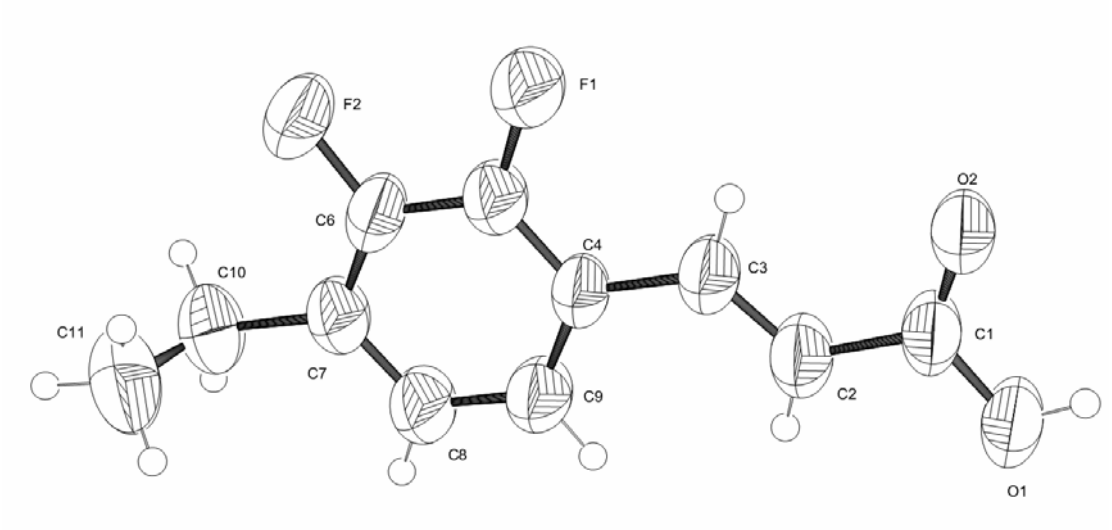


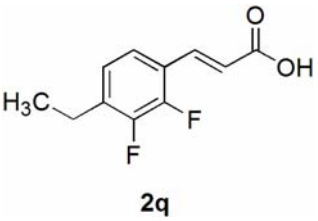
1,2,3,4,5,6,8-Heptafluoro-7-methylnaphthalene (4e): The general procedure was applied using octafluoronaphthalene (**3e**, 0.272 g, 1 mmol), phosphonium salt **Y1** (1.0716 g, 3 mmol) and NaH (0.12 g, 3 mmol) (60% dispersion in mineral oil) at 60 °C for 48 h. Silica gel chromatography (eluent: petrol ether) of the crude product afforded the title compound as a colorless crystal (71%). The yield of the product was determined by ^{19}F NMR. The NMR spectral data were in line with the literature

values.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -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, $CDCl_3$) δ 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 $C_{11}H_3F_7$: 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):





2q

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)

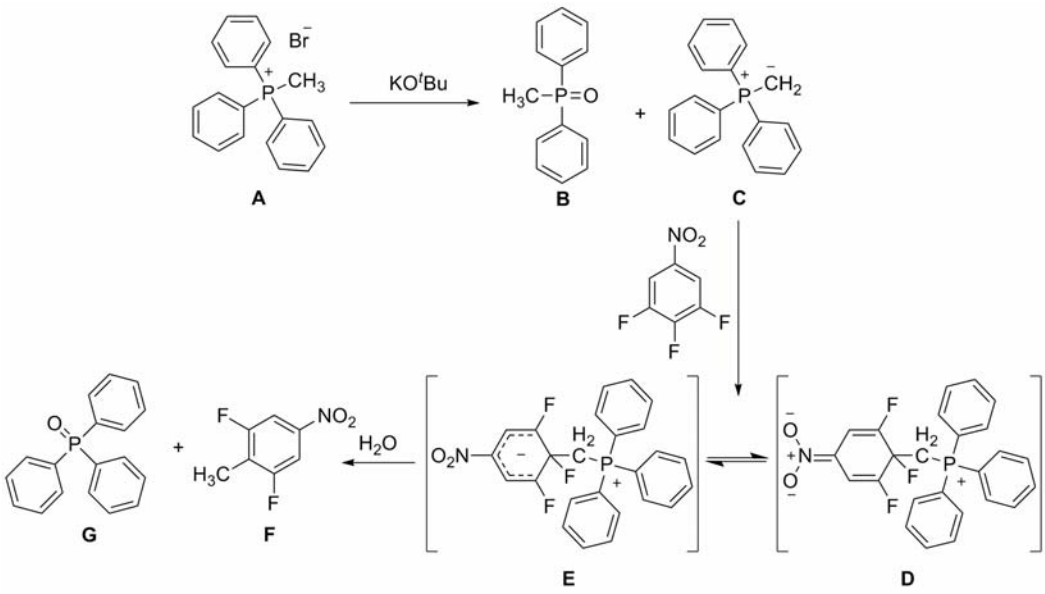
In a three-neck round-bottom flask equipped with a magnetic stirring bar, methyltriphenylphosphonium bromide (1.786 g, 5.0 mmol) and potassium tert-butoxide (0.56 g, 5.0 mmol) were added. The flask was evacuated and re-filled with nitrogen for three times. THF (10 mL) was then added by syringe and the 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_2O 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.

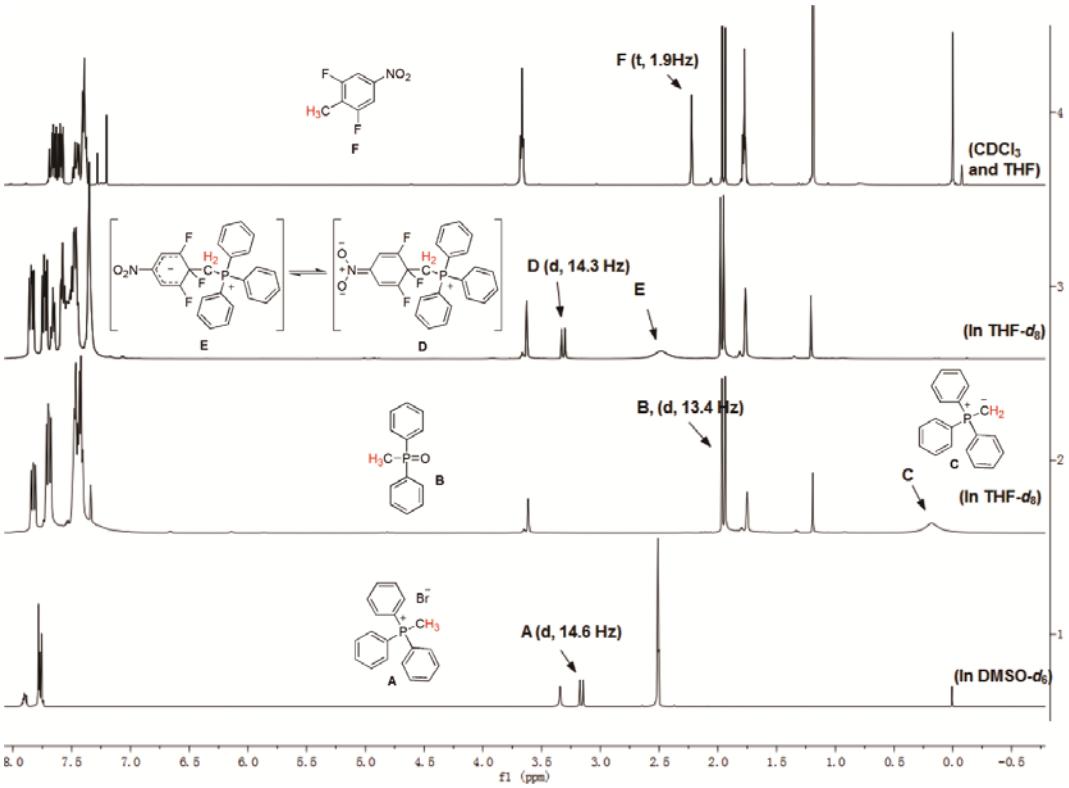


Figure S1. ^{1}H NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.

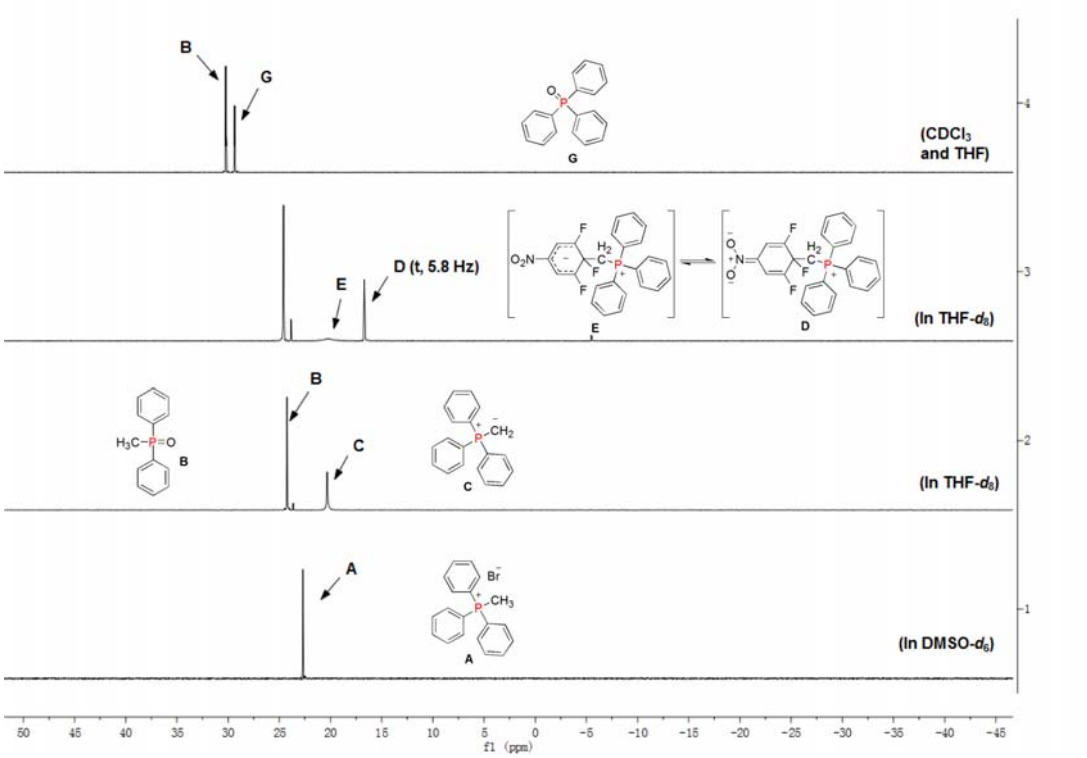


Figure S2. ^{31}P NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.

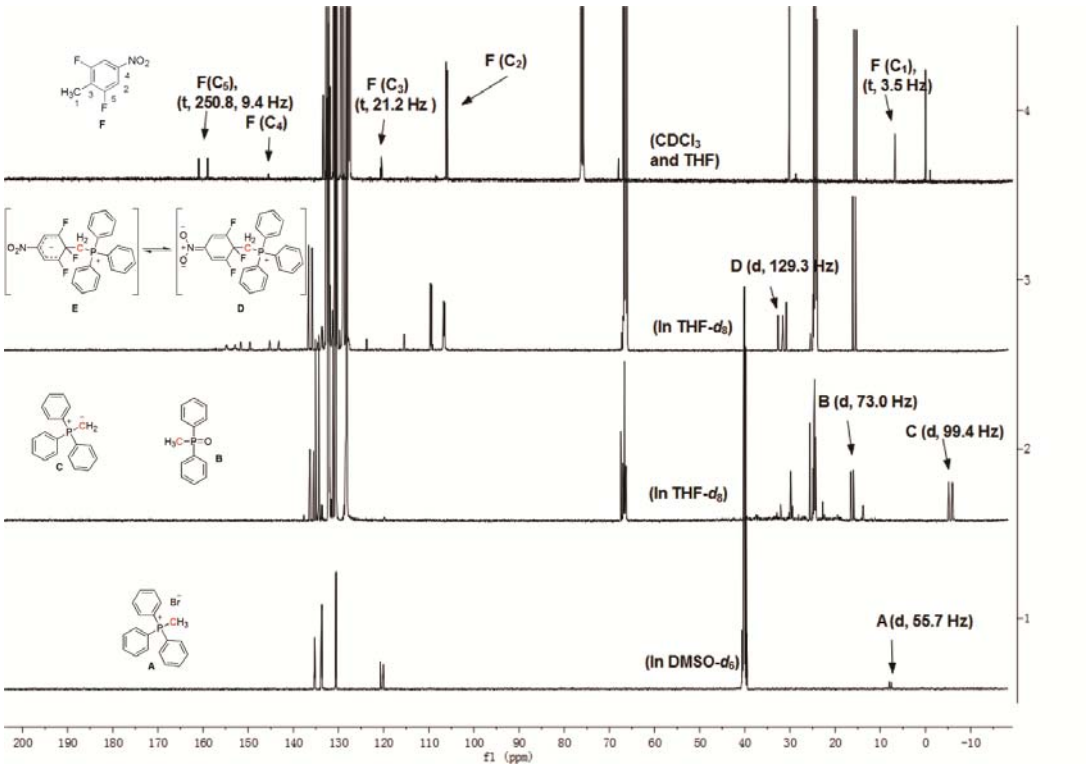
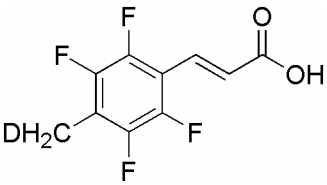


Figure S3. ^{13}C NMR spectra recorded during the reaction of 3,4,5-trifluoronitrobenzene with phosphonium ylide.

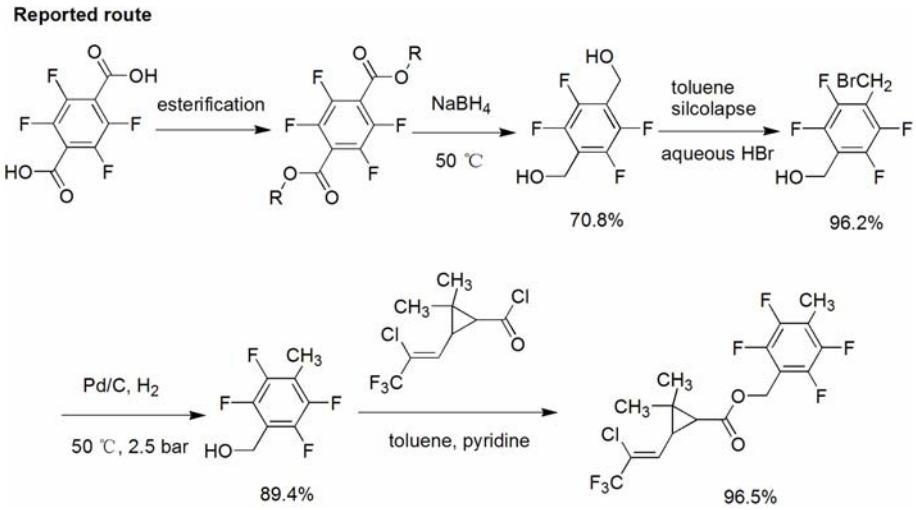
Deuteration Experiment

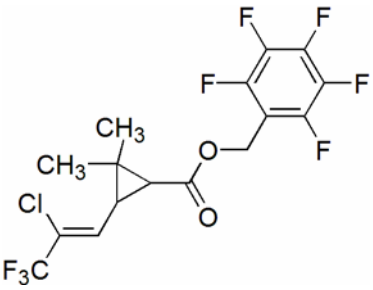


The general procedure was applied using 3-pentafluorophenyl-acrylic acid (**1b**, 0.238 g, 1 mmol), phosphonium salt **Y1** (1.785 g, 5 mmol) and NaH (0.2 g, 5 mmol) (60% dispersion in mineral oil) at 80 °C for 24 h. After the reaction was completed, the workup was conducted using D_2O (0.6 mL) at ambient 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. ^{1}H NMR (500 MHz, MeOD-d_4) δ 7.65 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 16.4 Hz, 1H), 2.33 (s, 2H).

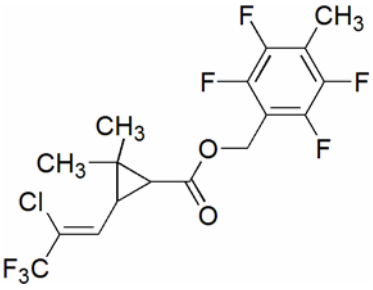
Synthesis of Tefluthrin

Scheme S2. Traditional Synthesis Route of Tefluthrin[10]





3-(2-Chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid pentafluorophenylmethyl ester (10): A THF solution of 4-dimethylamiopyridine (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, $CDCl_3$) δ 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, $CDCl_3$) δ -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, $CDCl_3$) δ 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.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ -68.81 (d, *J* = 4.1 Hz), -143.49 – -143.58 (m), -144.42 – -144.62 (m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 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

1. Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1985,** *50*, 1373.
2. Brooke, G. M.; Wallis, D. I. *J. Chem. Soc., Perkin Trans. 1* **1981,** 1417.
3. Corkill, J. A.; Joppich, M.; Kuttab, S. H.; Giese, R. W. *Anal. Chem.* **1982,** *54*, 481.
4. Inukai, Y.; Oono, Y.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1979,** *52*, 516.
5. Vaidyanathaswamy, R.; Radha, K.; Dharani, M.; Raguraman, T. S.; Anand, R. *J. Fluor. Chem.* **2012,** *144*, 33.
6. Filler, R.; Cantrell, G. L.; Wolanin, D.; Naqvi, S. M. *J. Fluor. Chem.* **1986,** *30*, 399.
7. Li, H.; Liu, J.; Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Org. Lett.* **2010,** *13*, 276.
8. Chambers, R. D.; Iddon, B.; Musgrave, W. K. R.; Chadwick, L. *Tetrahedron* **1968,** *24*, 877.
9. Burdon, J.; Rimmington, T. W. *J. Fluor. Chem.* **1985,** *27*, 257.
10. Wang, D. C; Jiang, Y. F. U.S. Patent 7,312,366, 2007.
11. Punja, N. U.S. Patent 4,405,640, 1983.

NMR Spectra of All the New Compounds

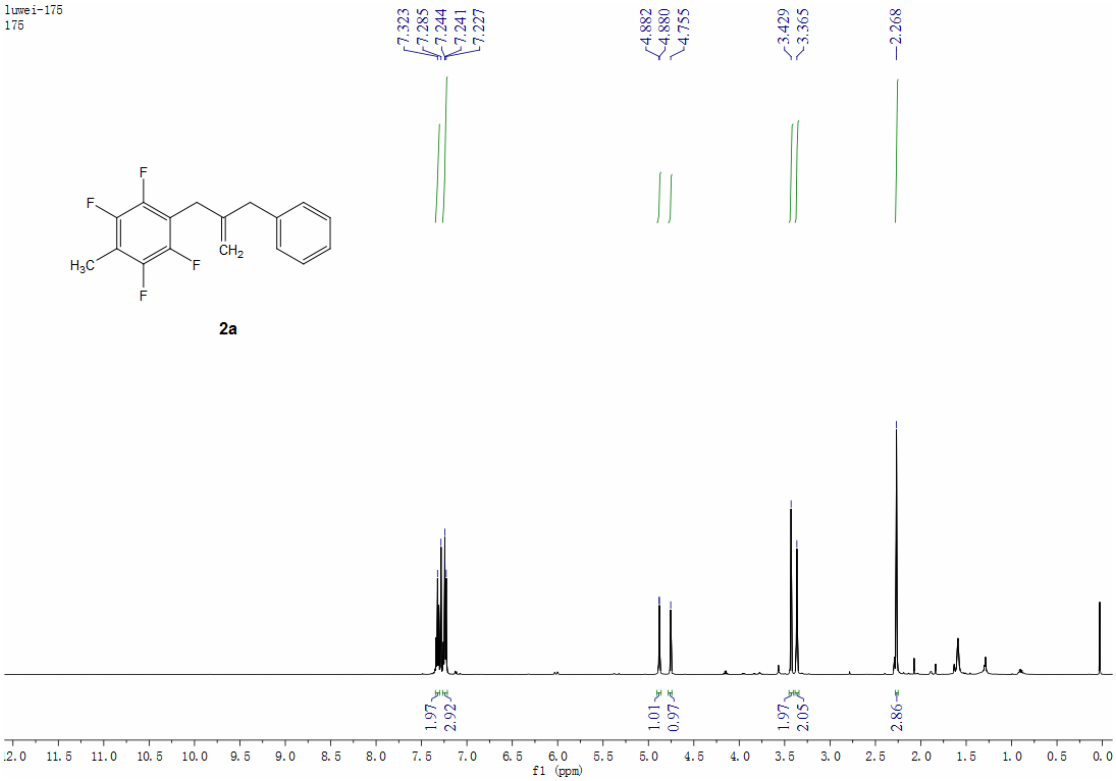


Figure S4. ^{1}H NMR spectrum of **2a**.

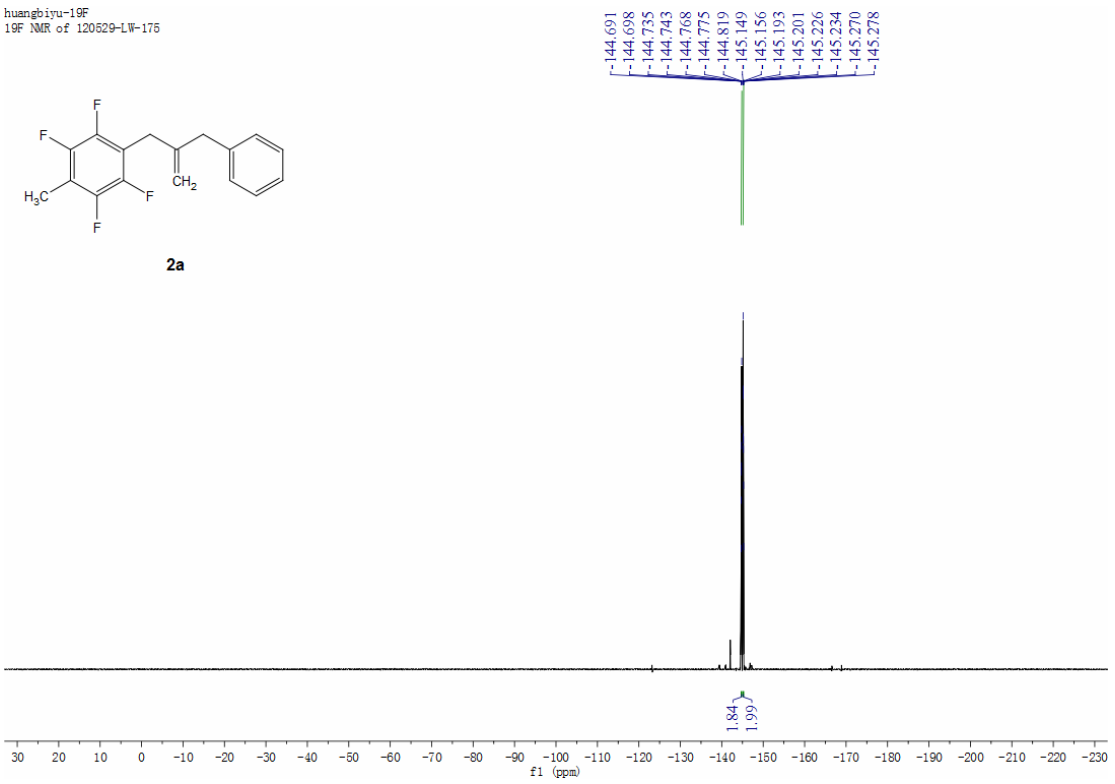


Figure S5. ^{19}F NMR spectrum of **2a**.

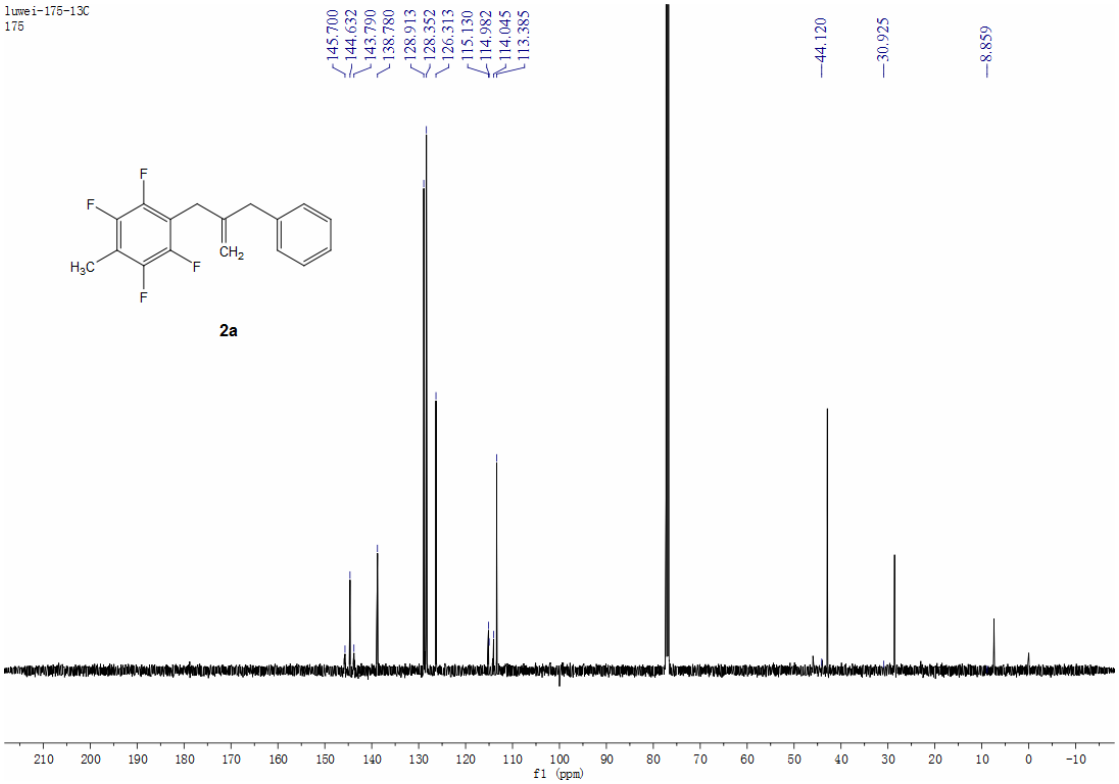


Figure S6. ^{13}C NMR spectrum of **2a**.

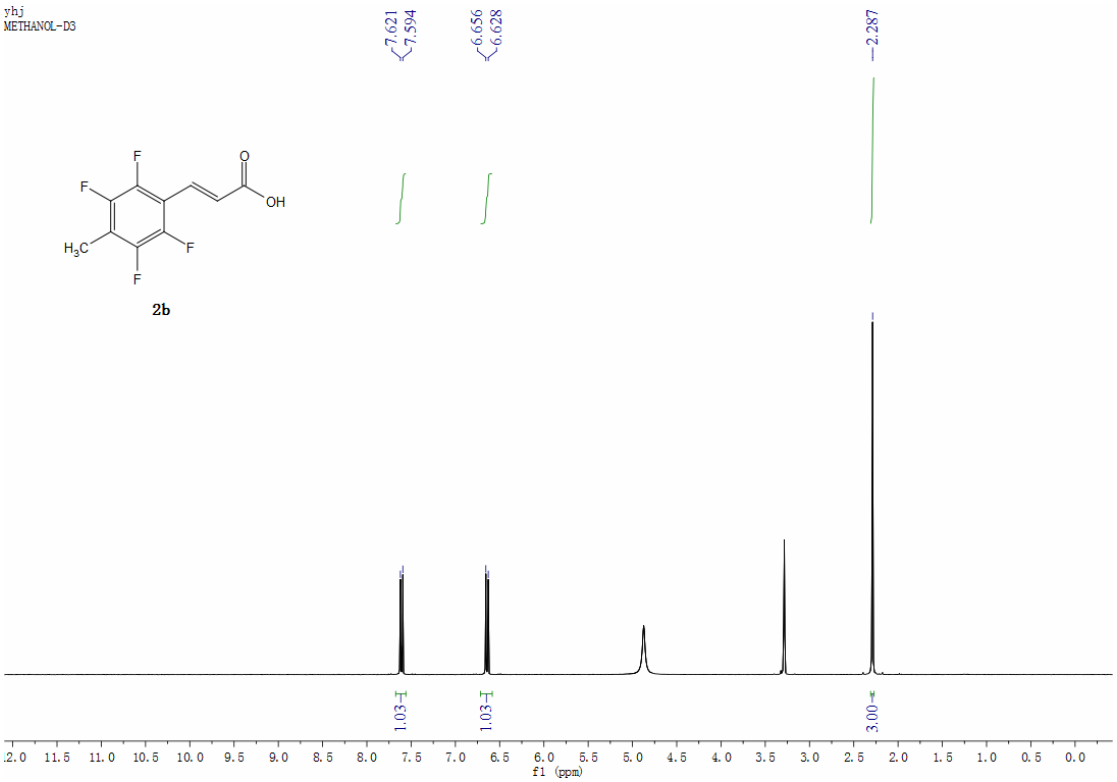


Figure S7. ^{1}H NMR spectrum of **2b**.

Figure S8. ^{19}F NMR spectrum of **2b**.

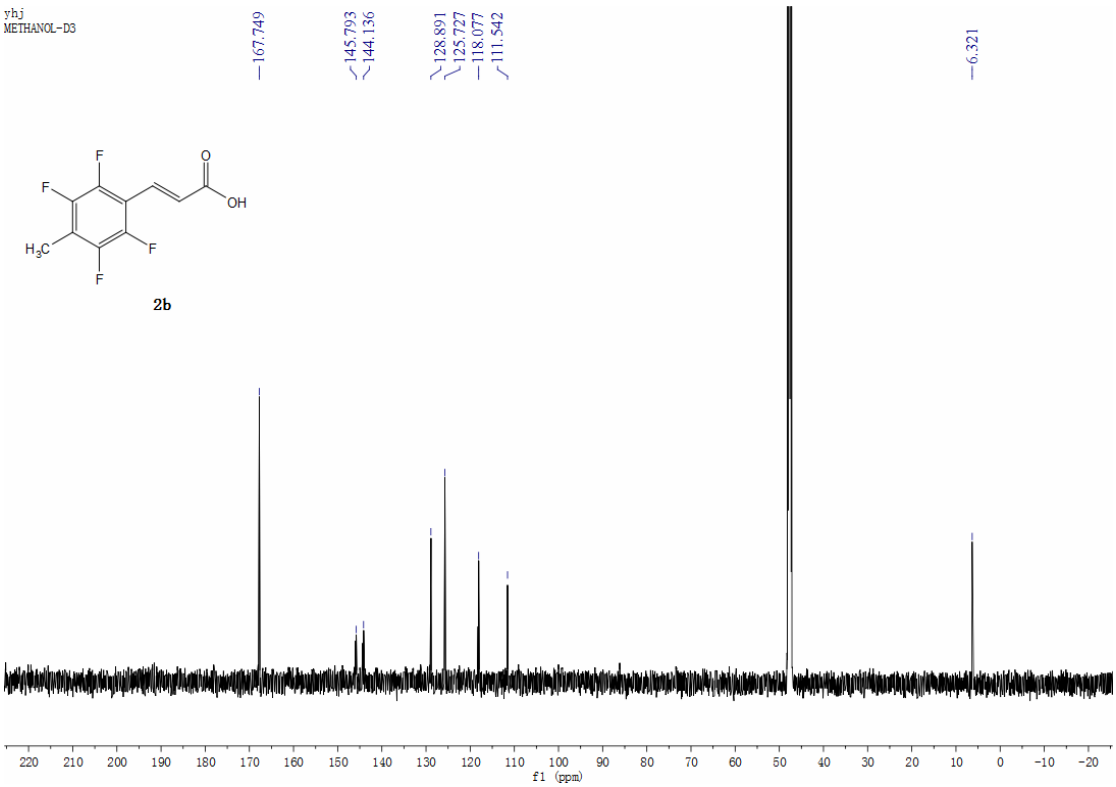


Figure S9. ^{13}C NMR spectrum of **2b**.

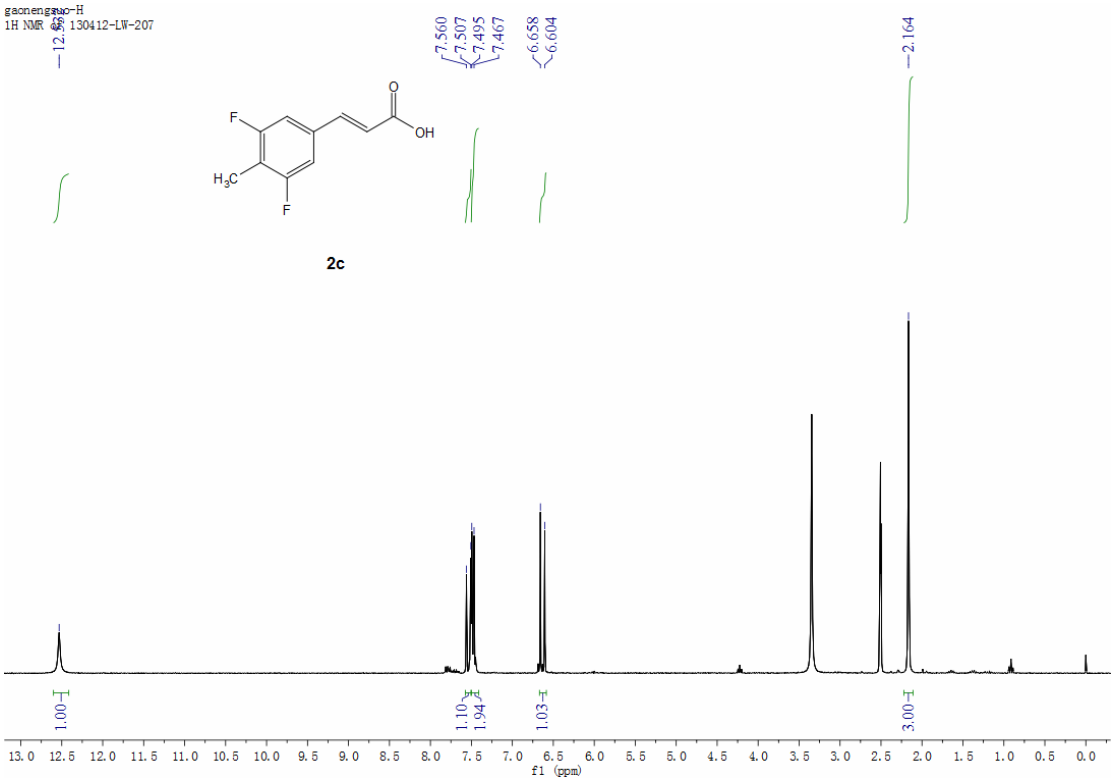


Figure S10. ^{1}H NMR spectrum of **2c**.

Figure S11. ^{19}F NMR spectrum of **2c**.

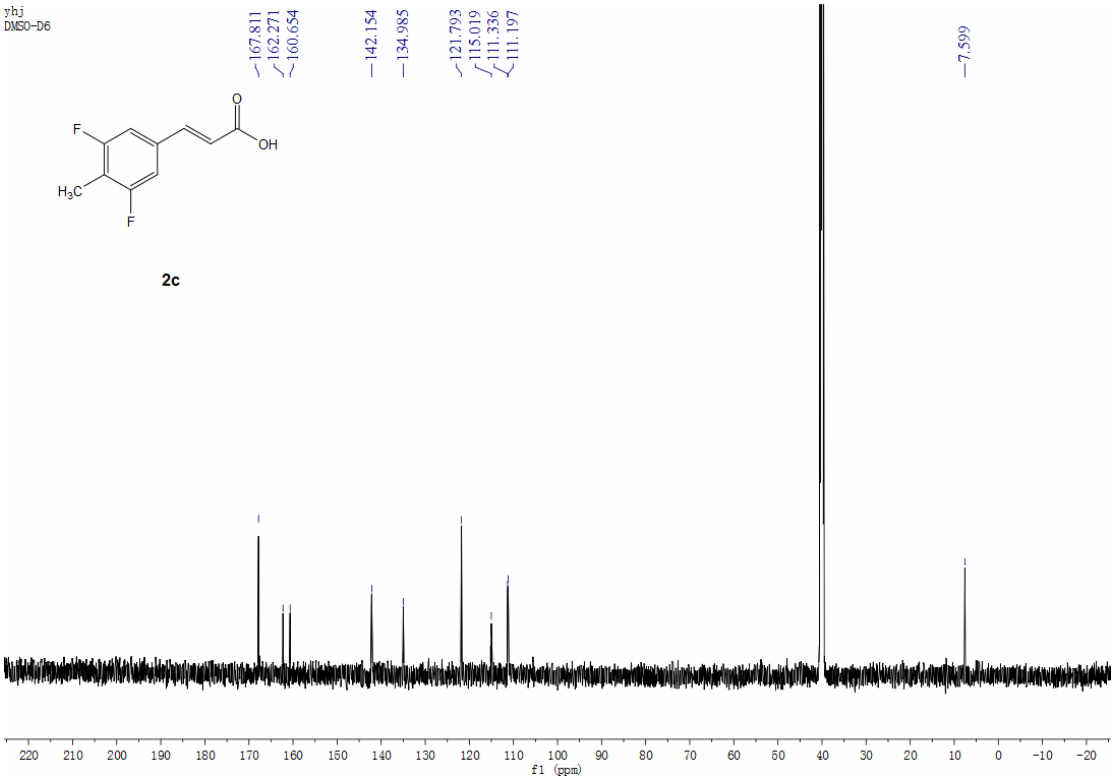


Figure S12. ^{13}C NMR spectrum of **2c**.

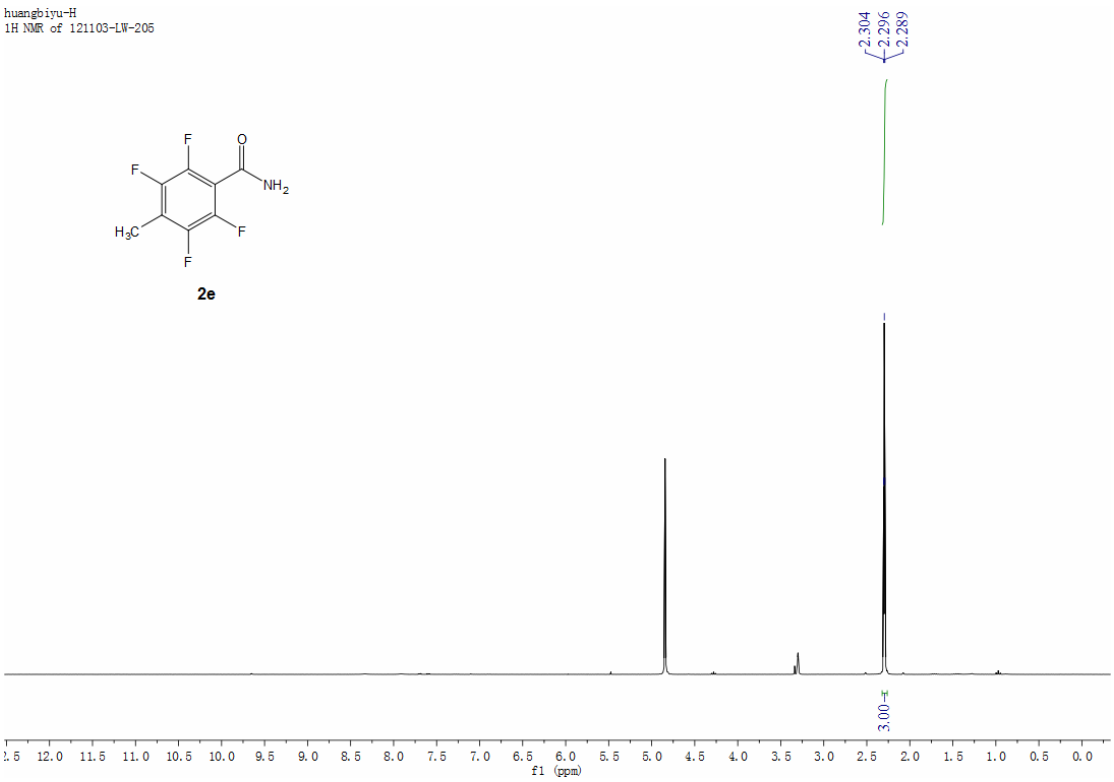


Figure S13. ^{1}H NMR spectrum of **2e**.

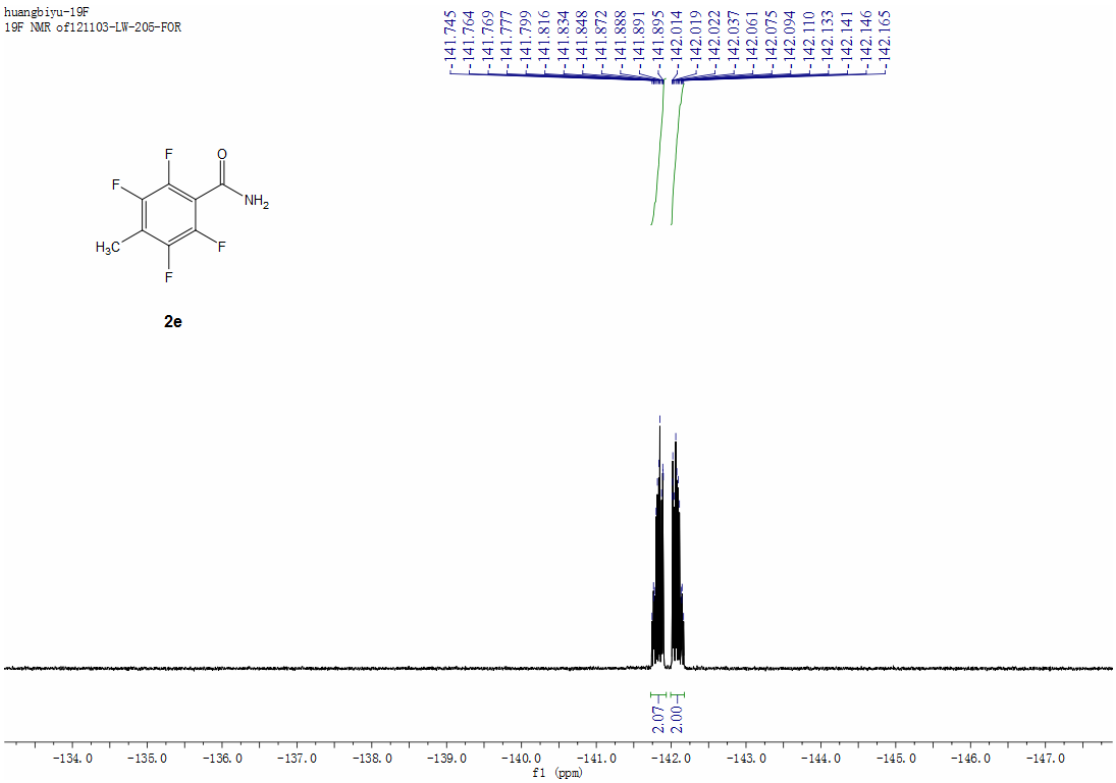


Figure S14. ^{19}F NMR spectrum of **2e**.

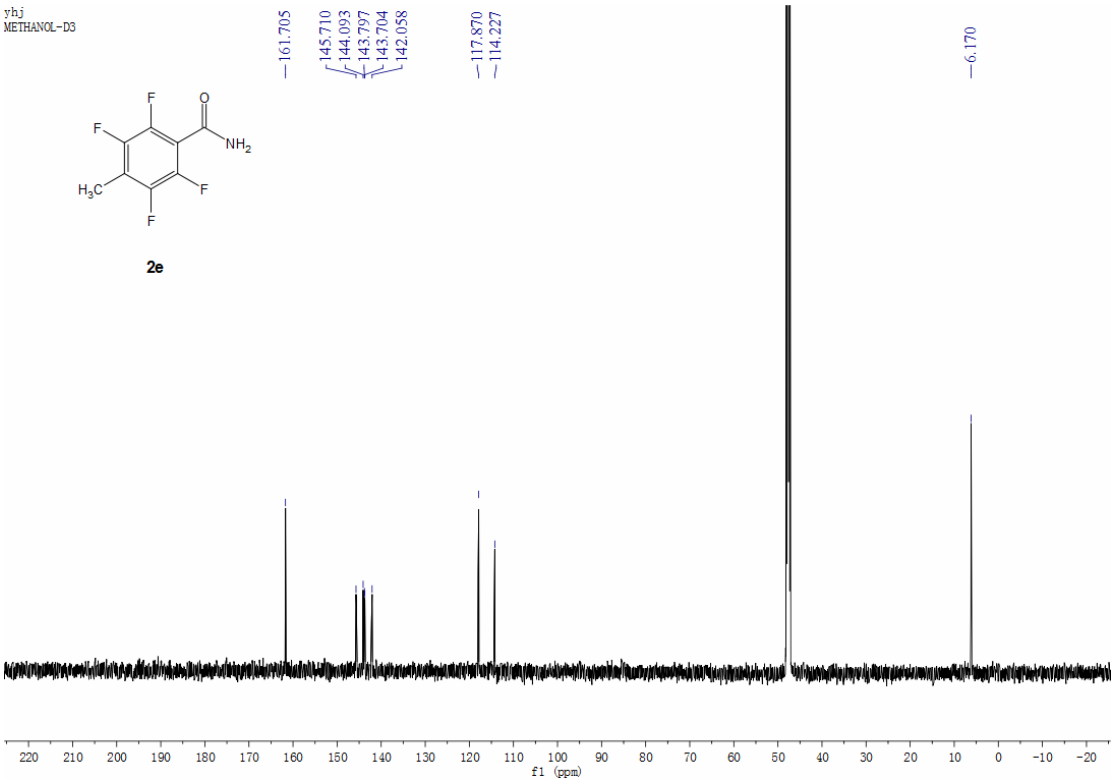


Figure S15. ^{13}C NMR spectrum of **2e**.

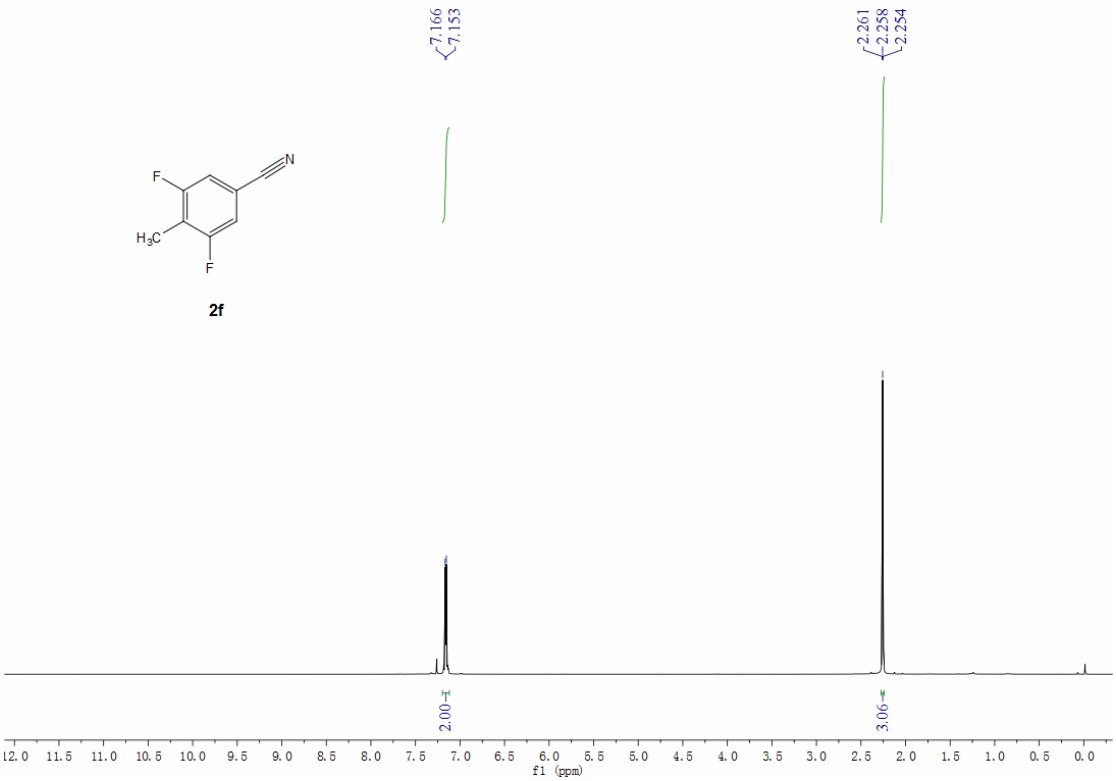


Figure S16. ^{1}H NMR spectrum of **2f**.

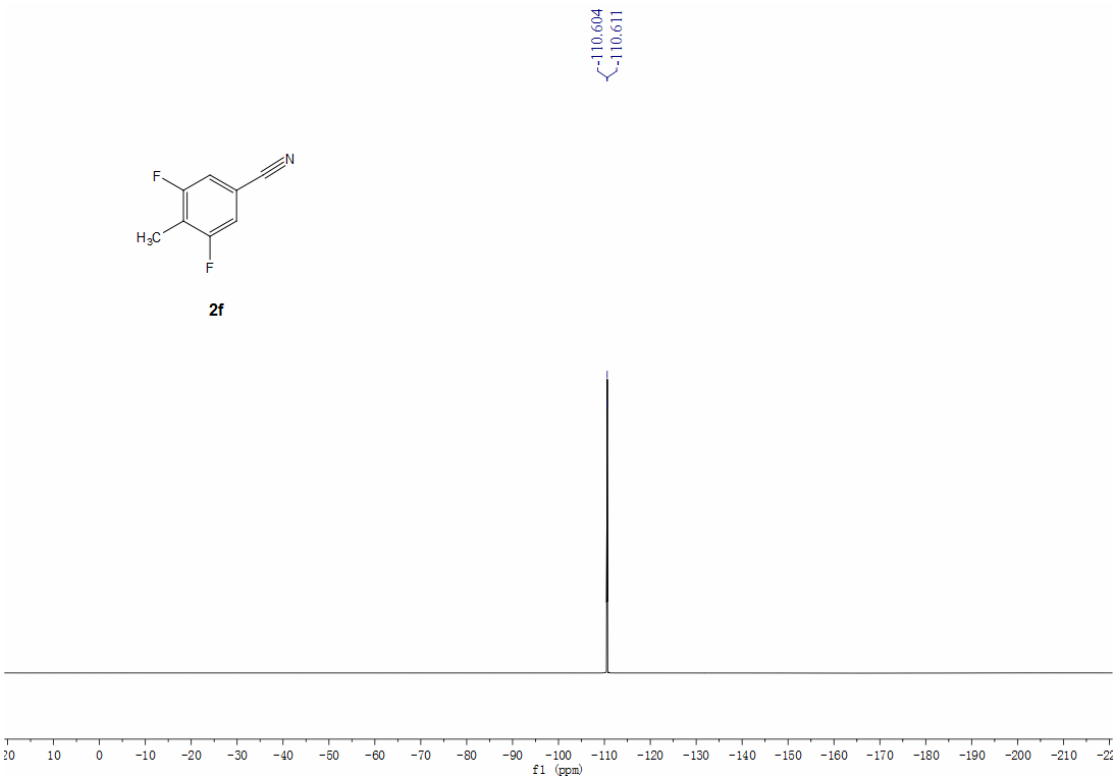


Figure S17. ^{19}F NMR spectrum of **2f**.

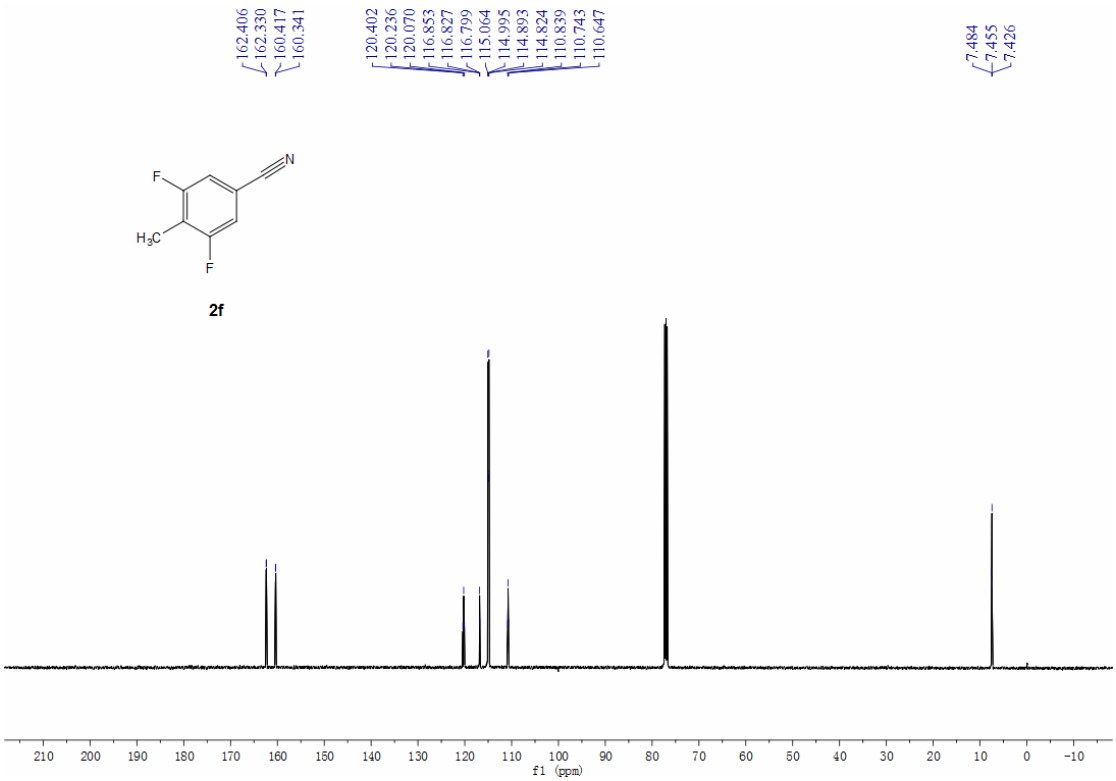


Figure S18. ^{13}C NMR spectrum of **2f**.

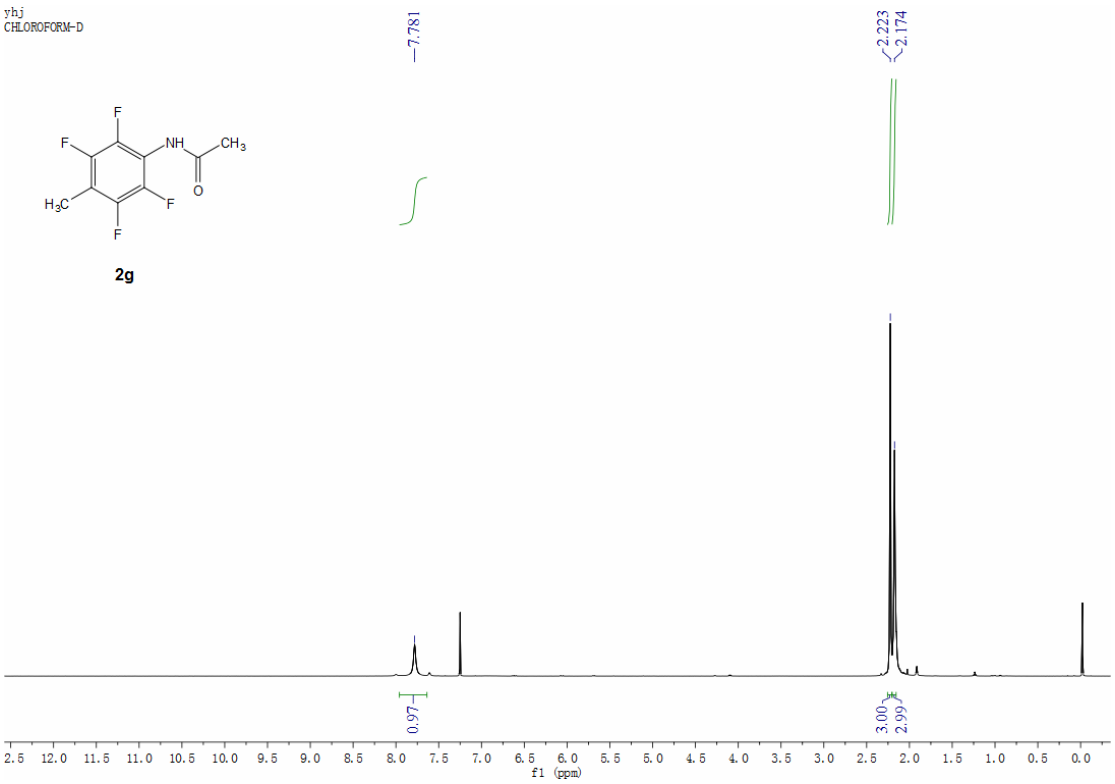


Figure S19. ^{1}H NMR spectrum of **2g**.

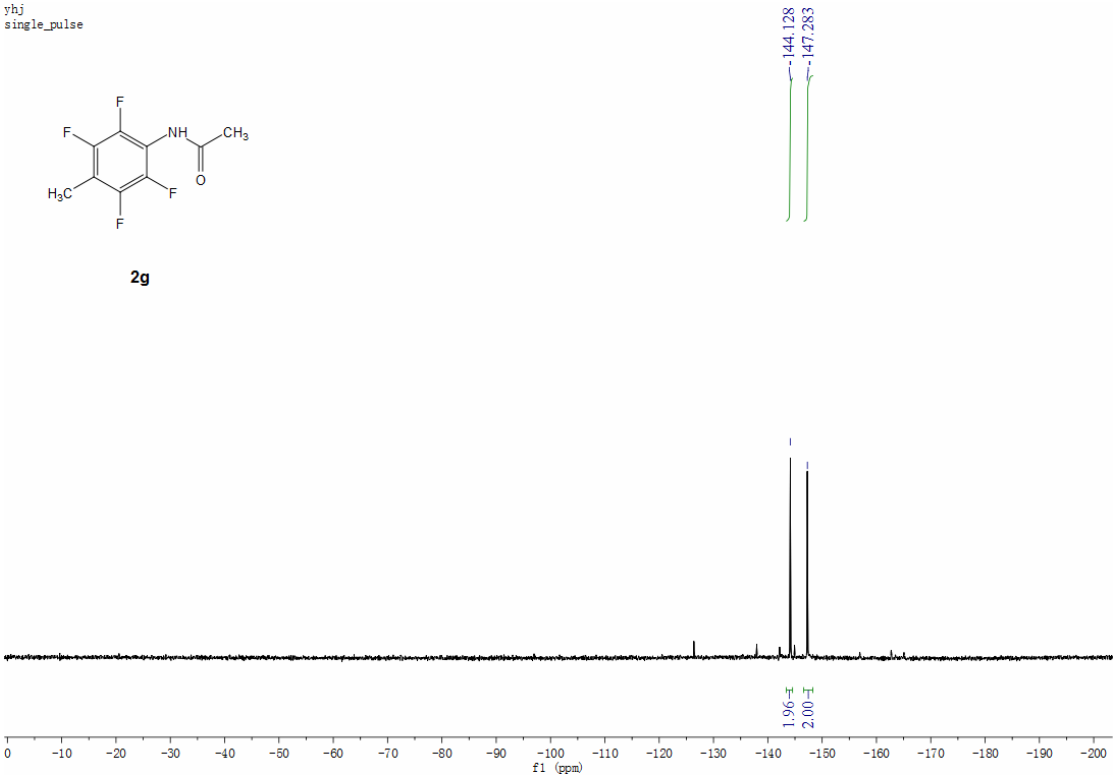


Figure S20. ^{19}F NMR spectrum of **2g**.

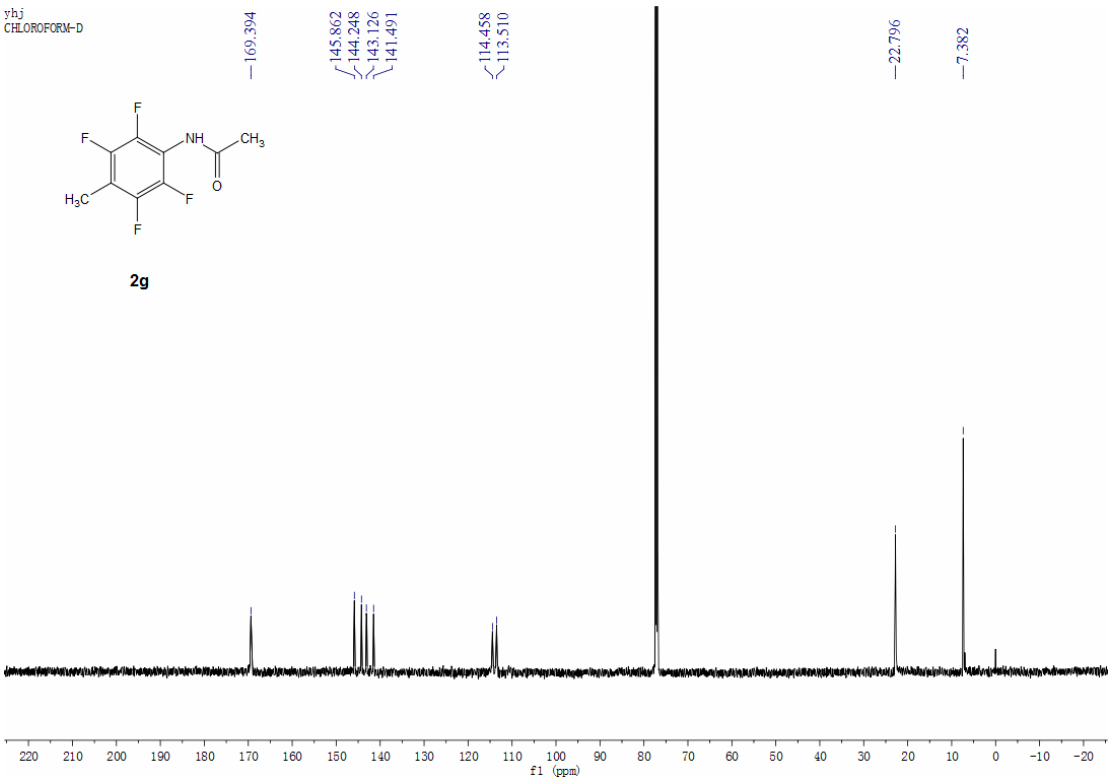
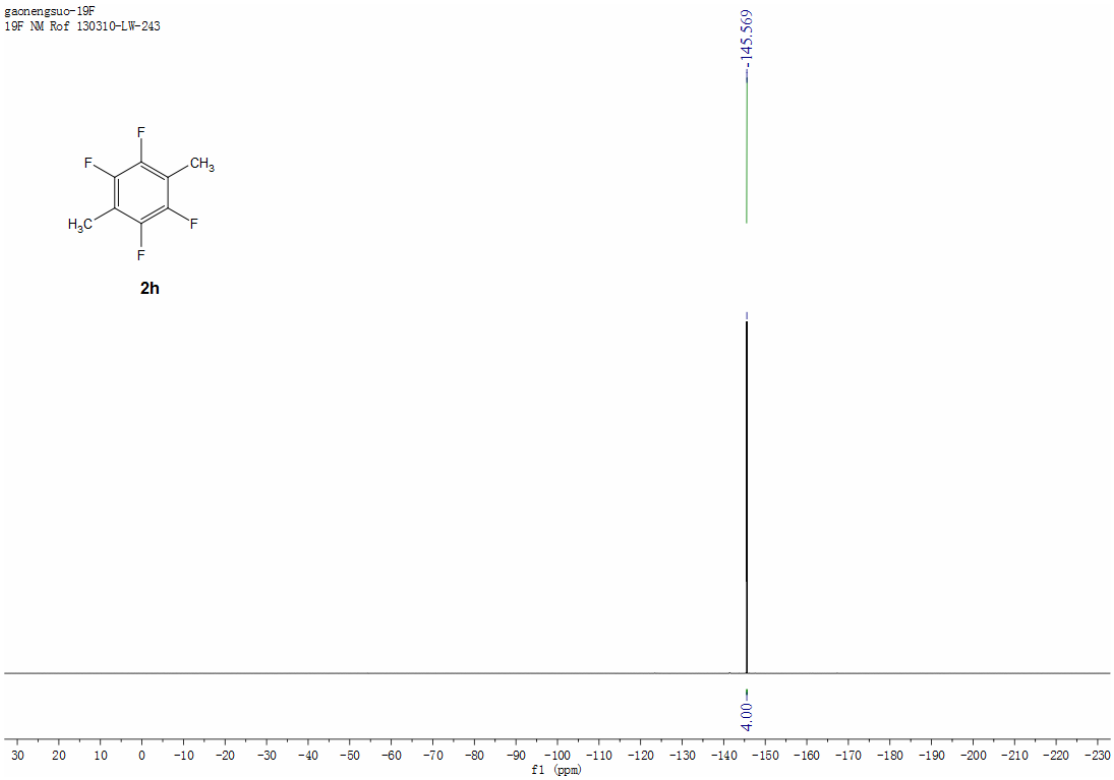
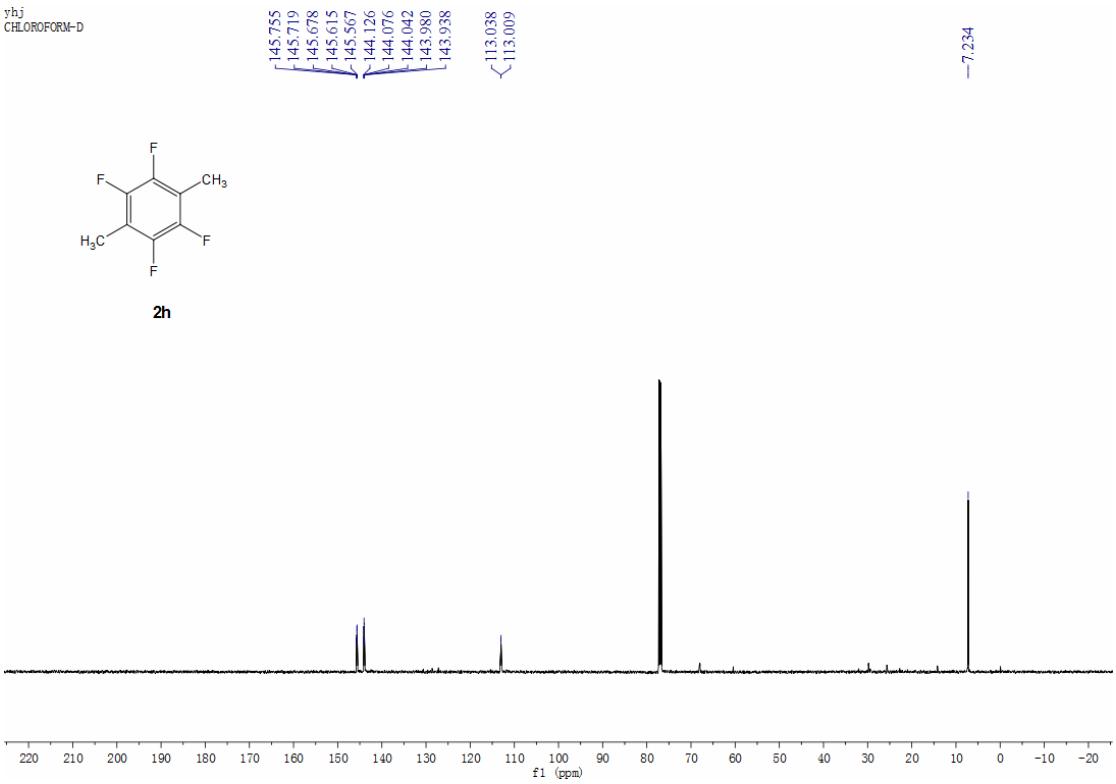


Figure S21. ^{13}C NMR spectrum of **2g**.



2h

Figure S22. ^{19}F NMR spectrum of **2h**.



2h

Figure S23. ^{13}C NMR spectrum of **2h**.

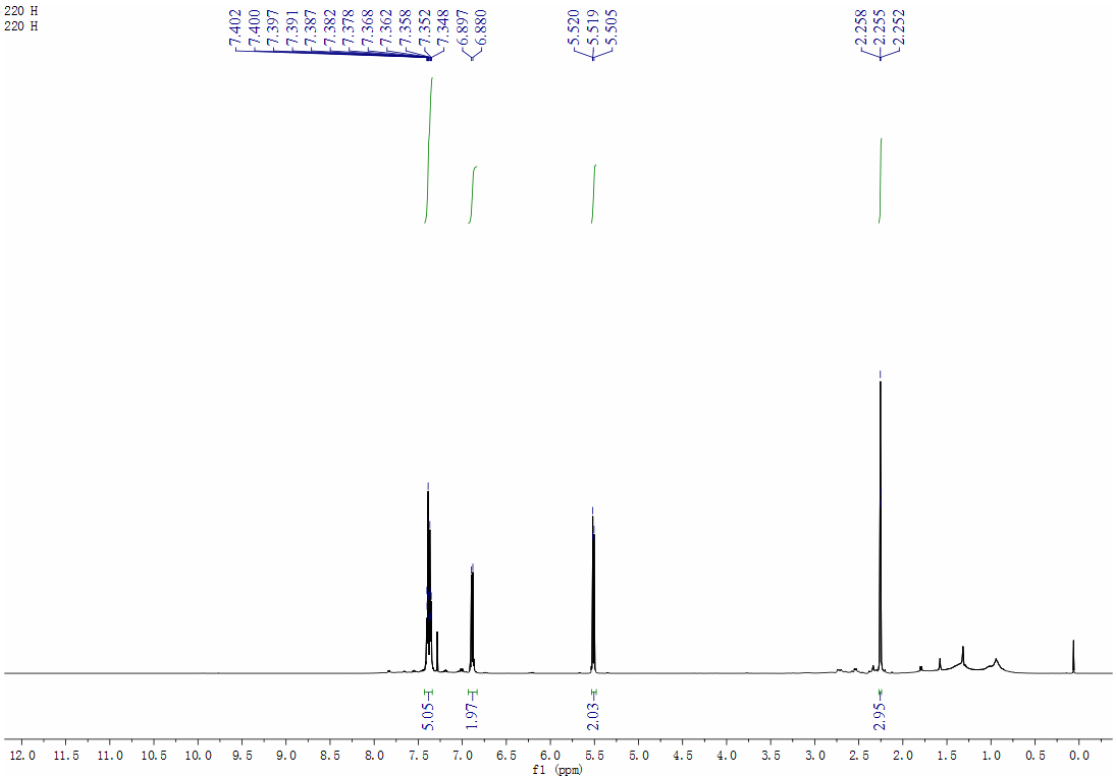


Figure S24. ^{1}H NMR spectrum of **2k**.

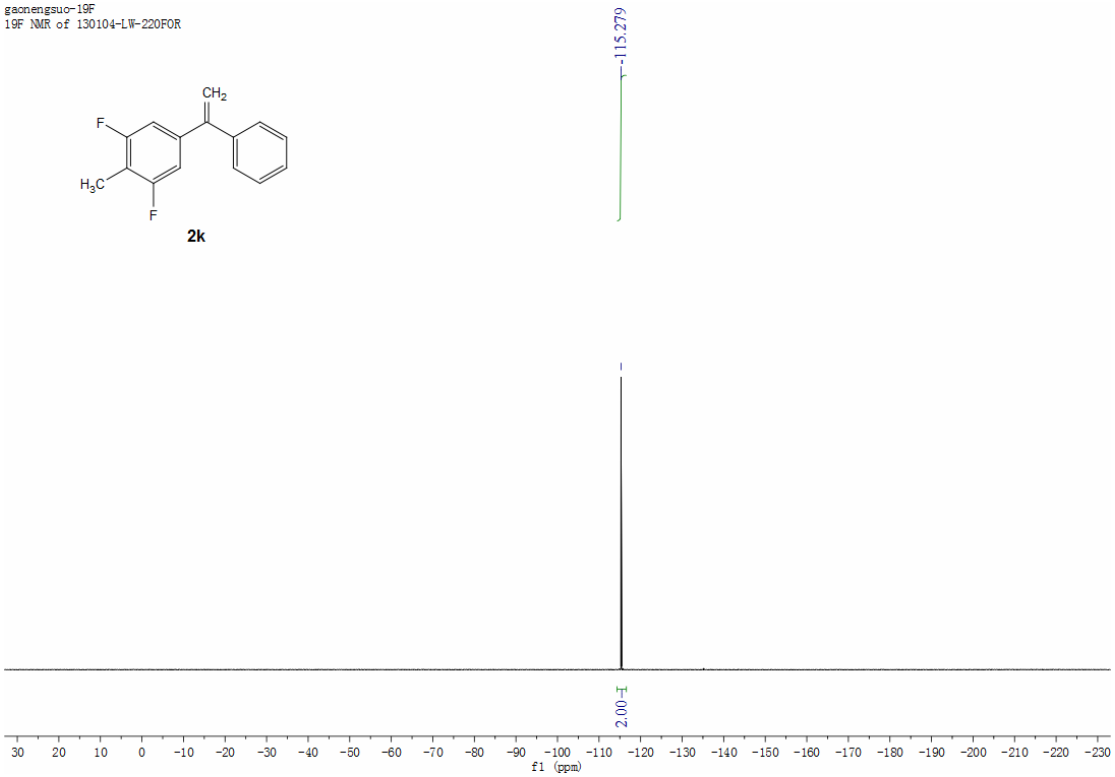


Figure S25. ^{19}F NMR spectrum of **2k**.

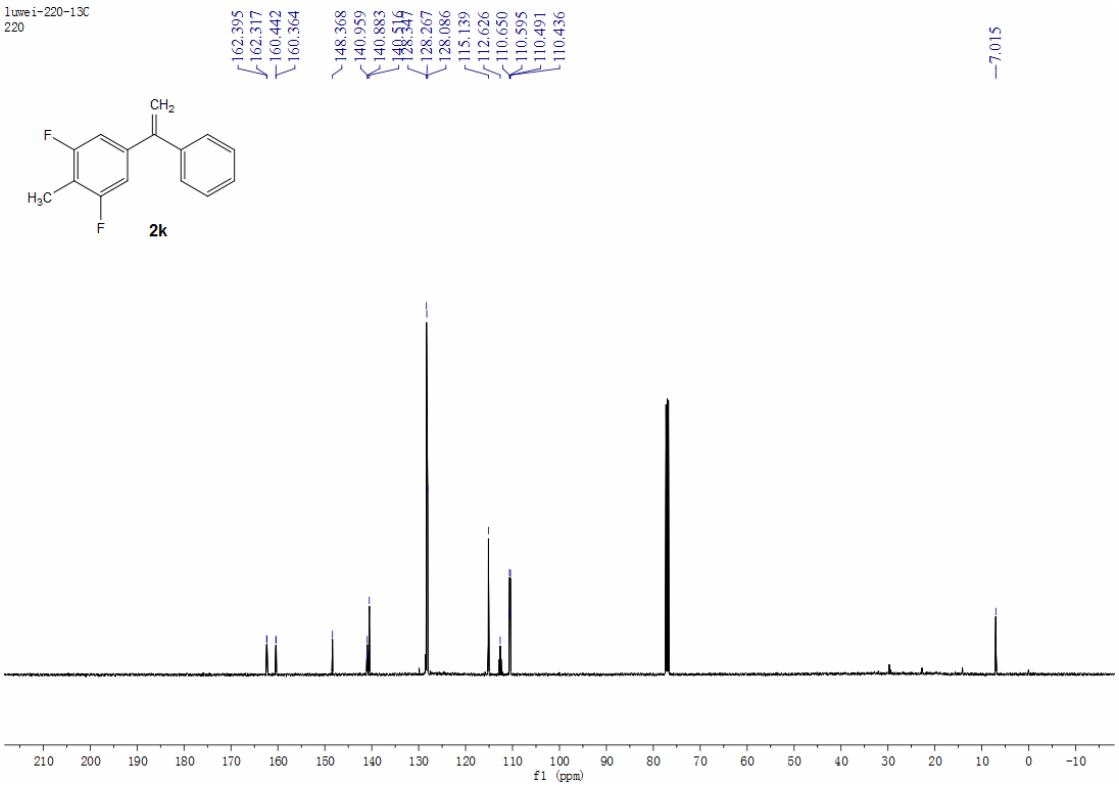


Figure S26. ^{13}C NMR spectrum of **2k**.

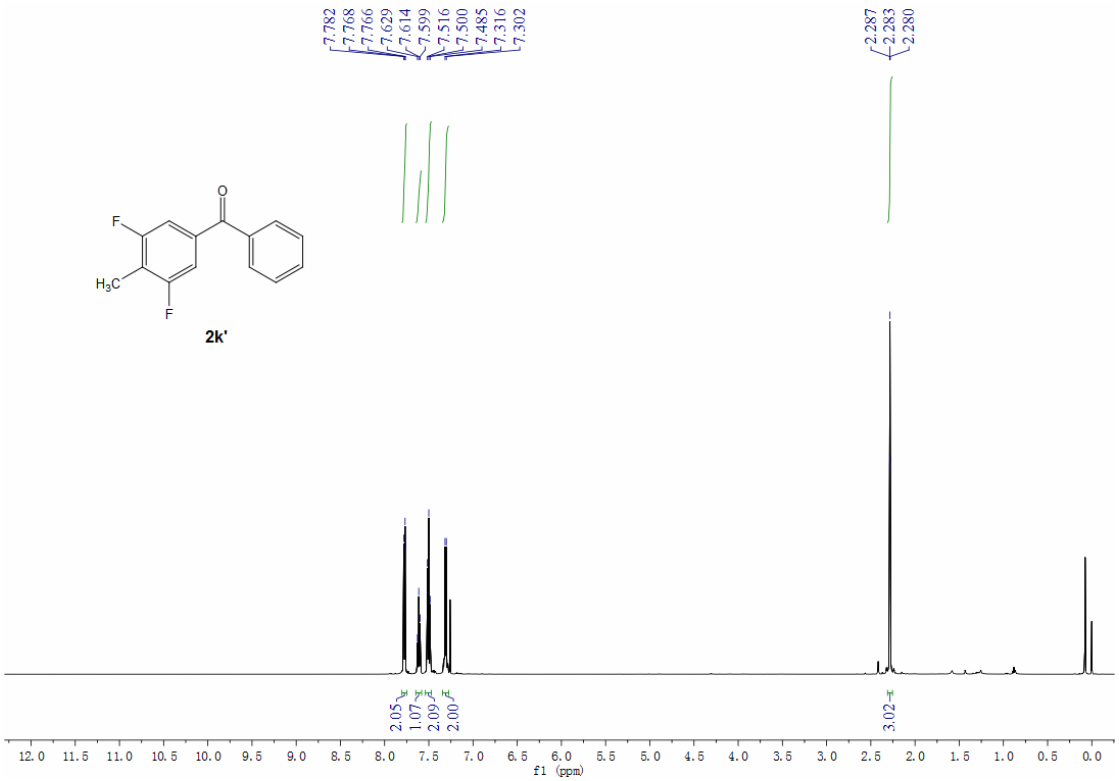


Figure S27. ^{1}H NMR spectrum of **2k′**.

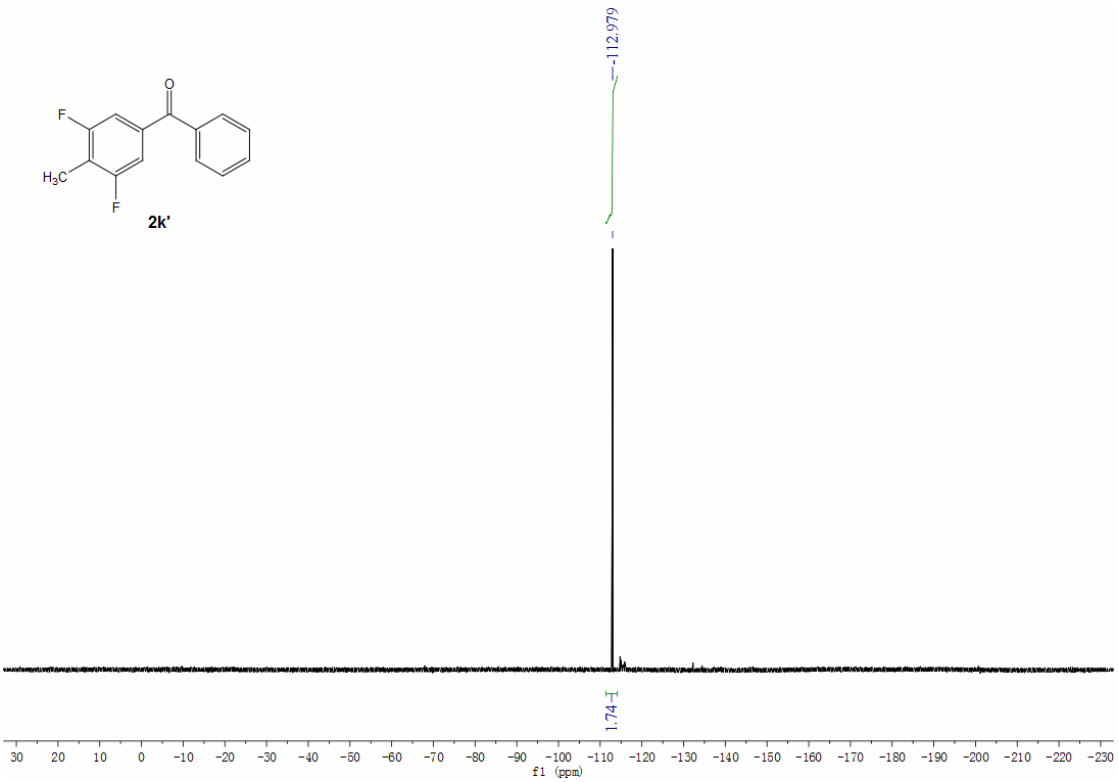


Figure S28. ^{19}F NMR spectrum of **2k′**.

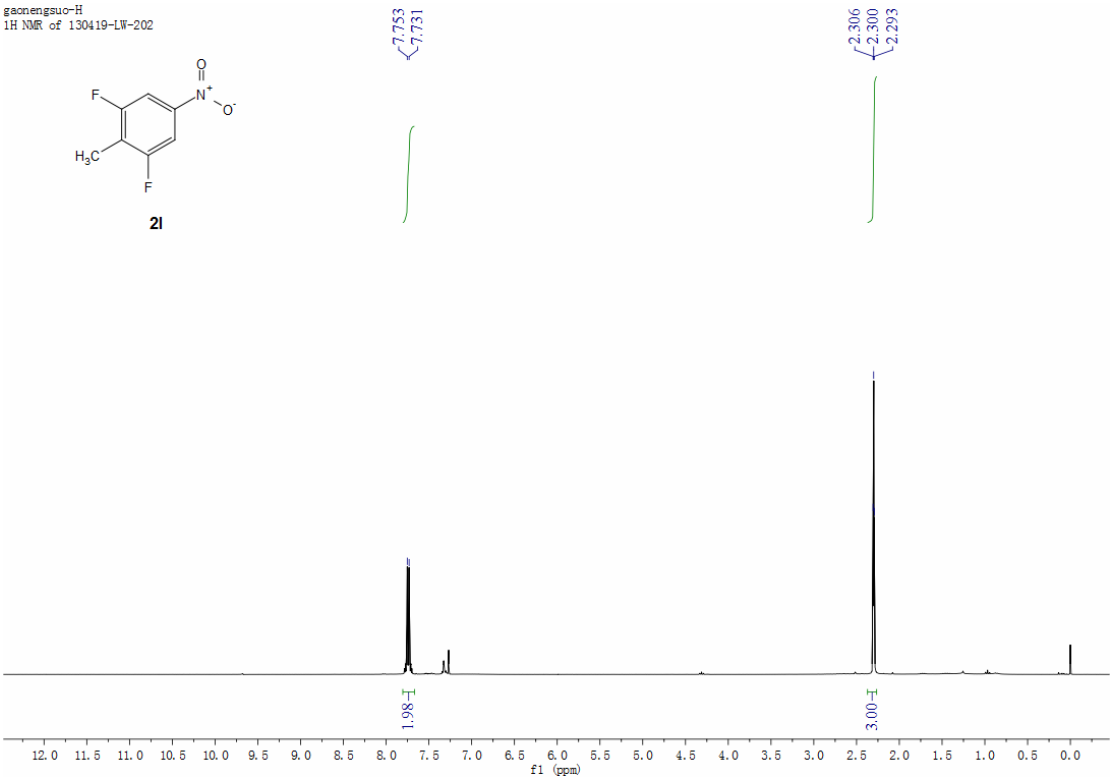
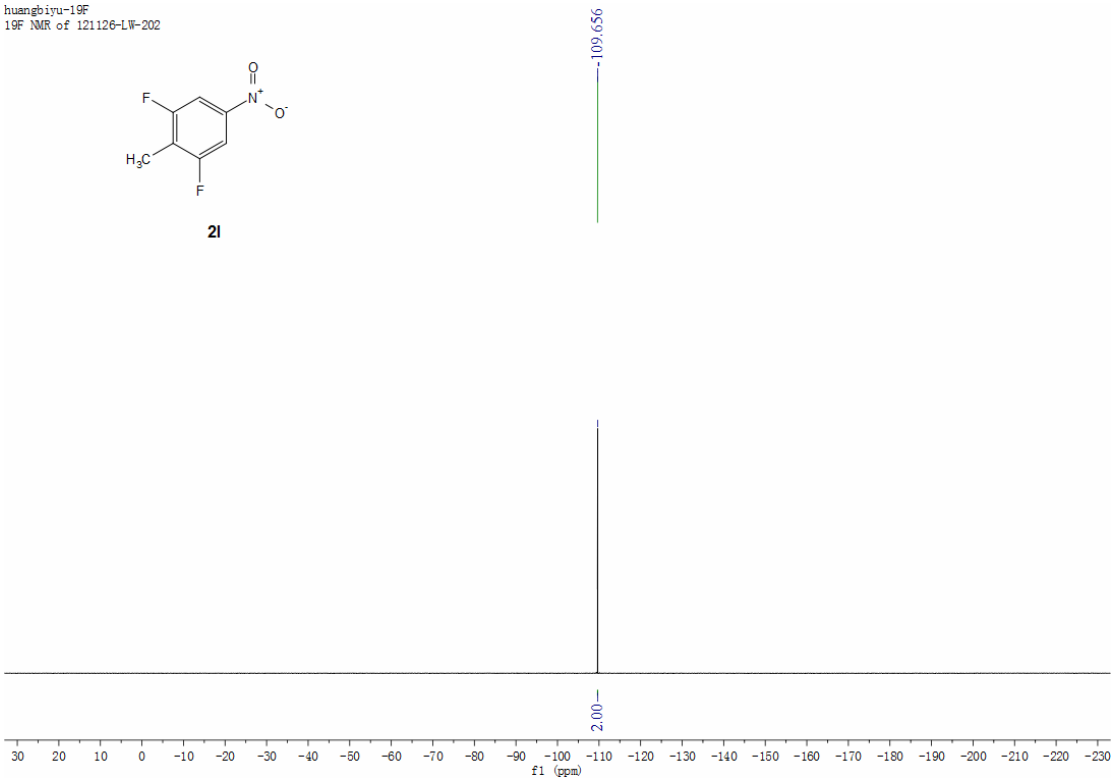
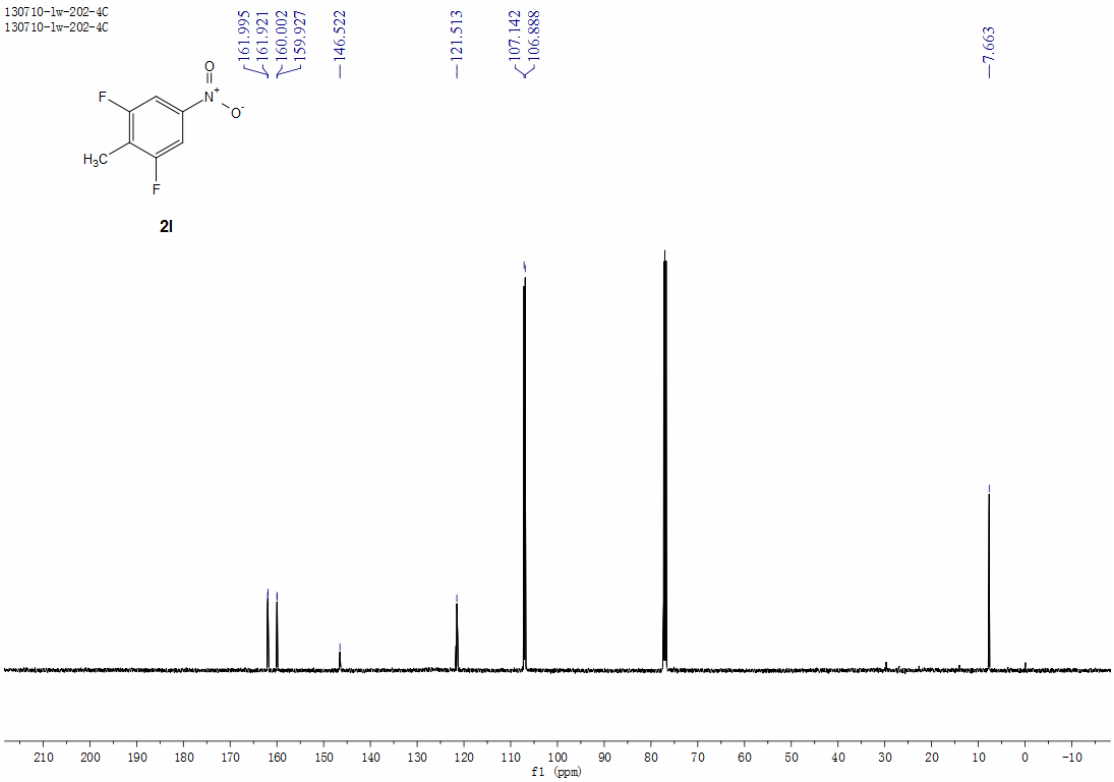


Figure S29. ^{1}H NMR spectrum of **2l**.



2l

Figure S30. ^{19}F NMR spectrum of **2l**.



2l

Figure S31. ^{13}C NMR spectrum of **2l**.

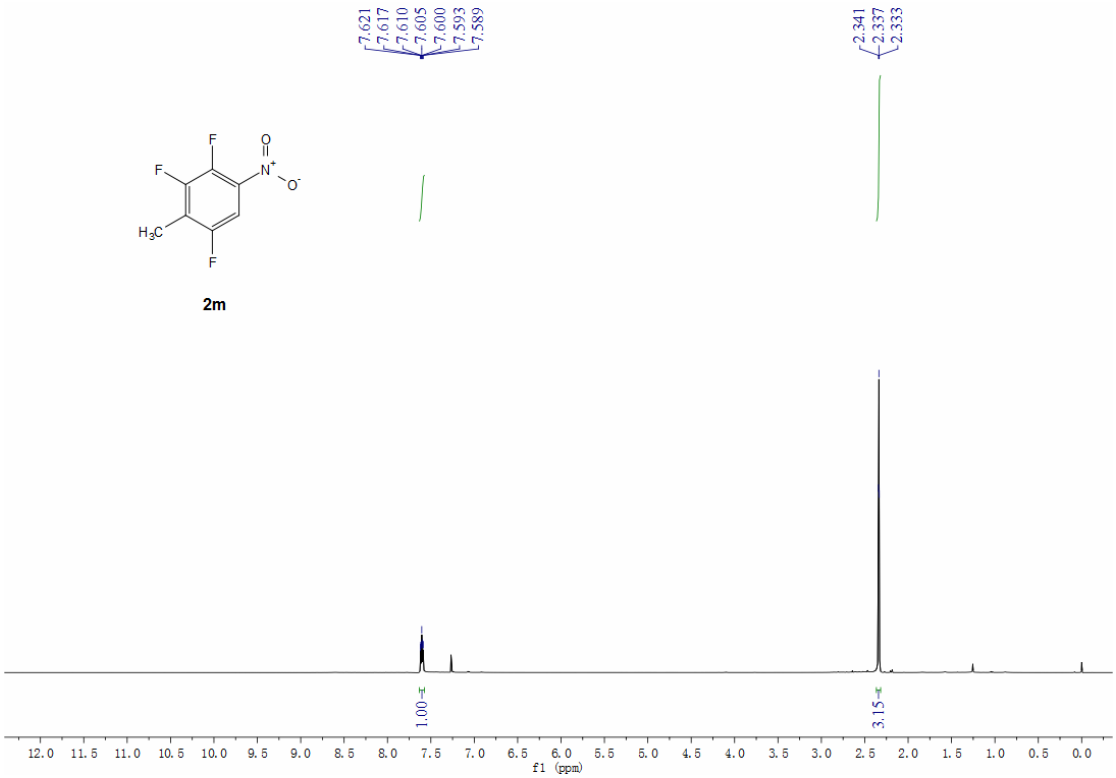


Figure S32. ^{1}H NMR spectrum of **2m**.

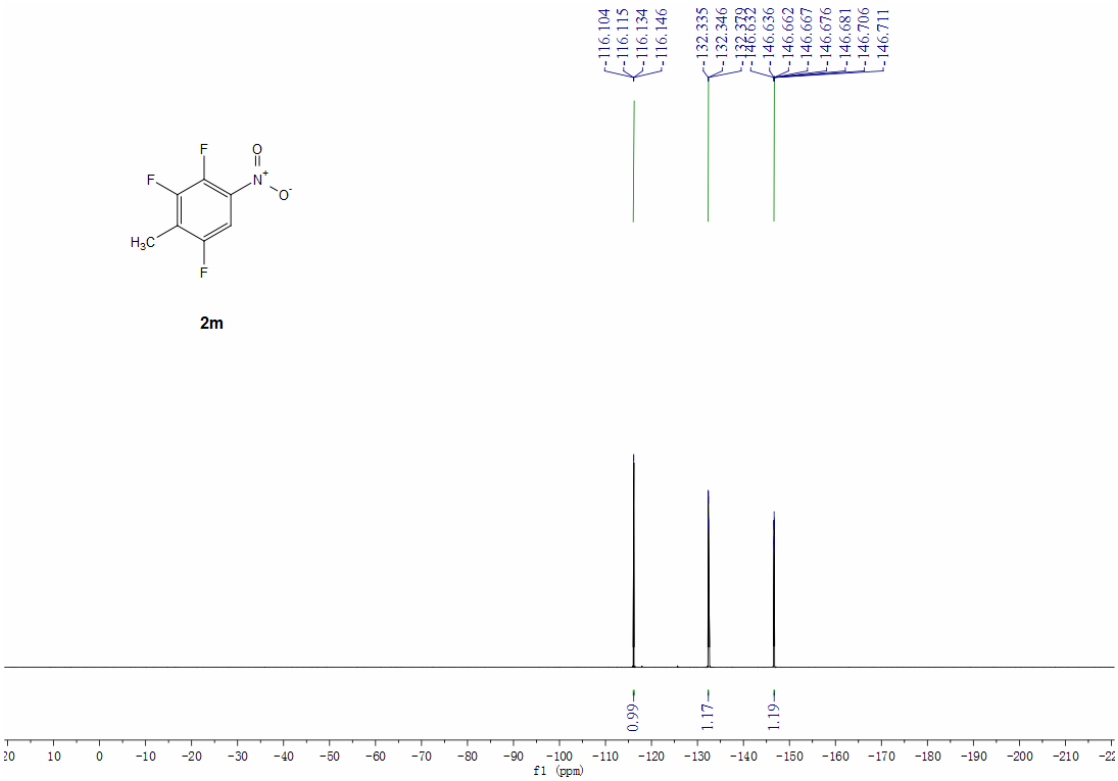


Figure S33. ^{19}F NMR spectrum of **2m**.

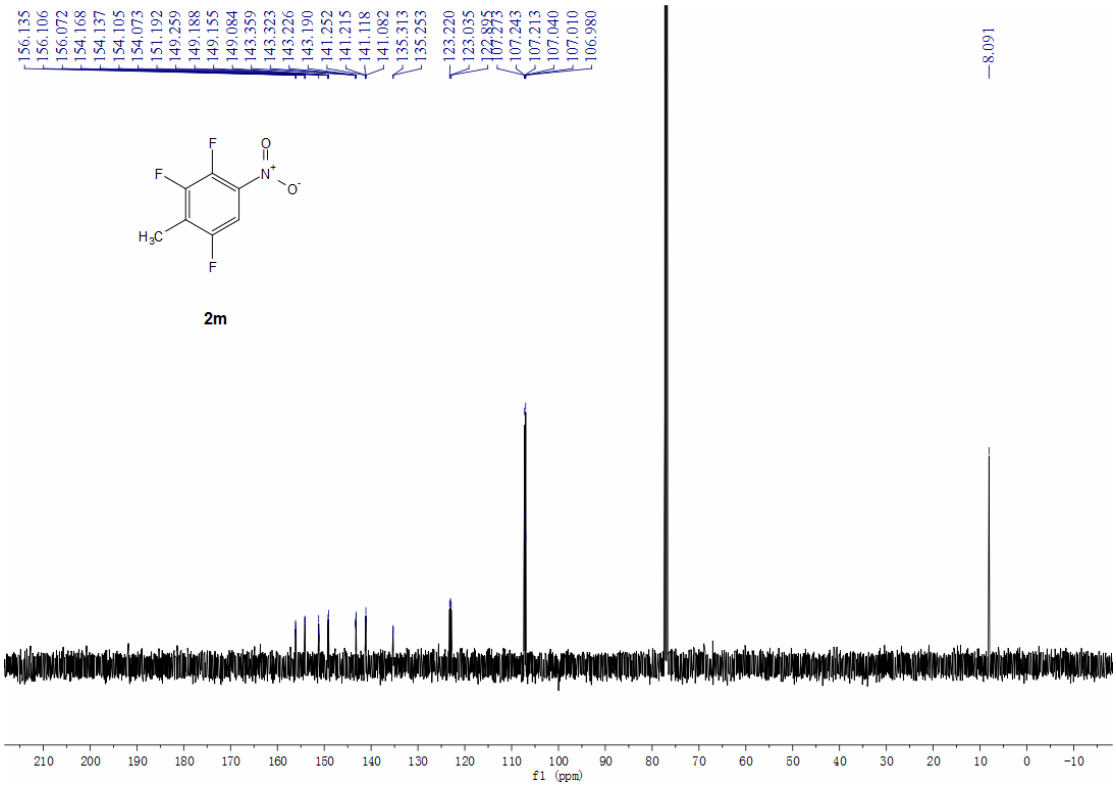


Figure S34. ^{13}C NMR spectrum of **2m**.

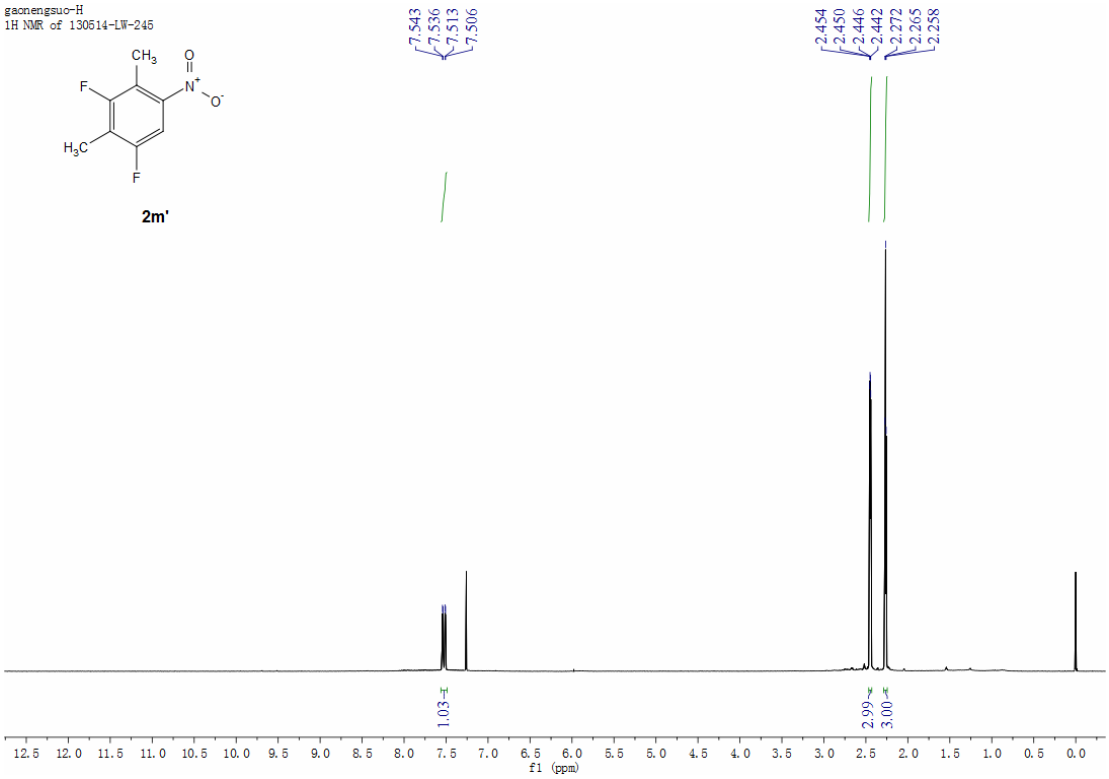


Figure S35. ^{1}H NMR spectrum of **2m′**.

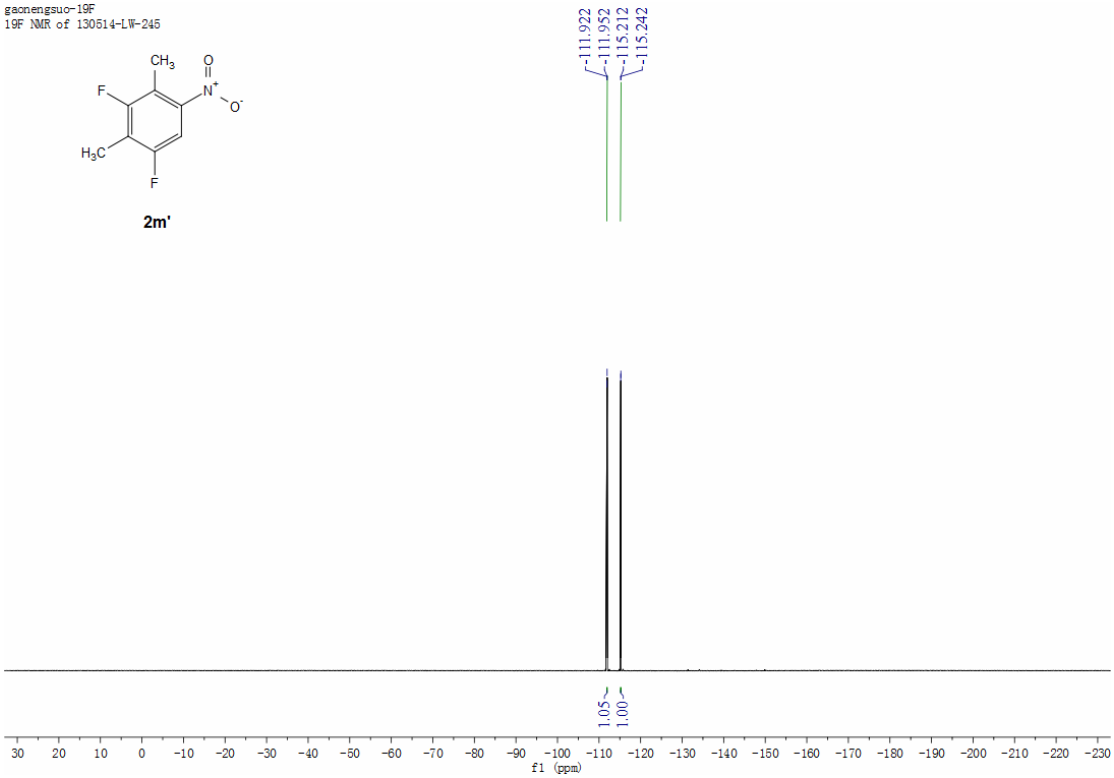


Figure S36. ^{19}F NMR spectrum of **2m′**.

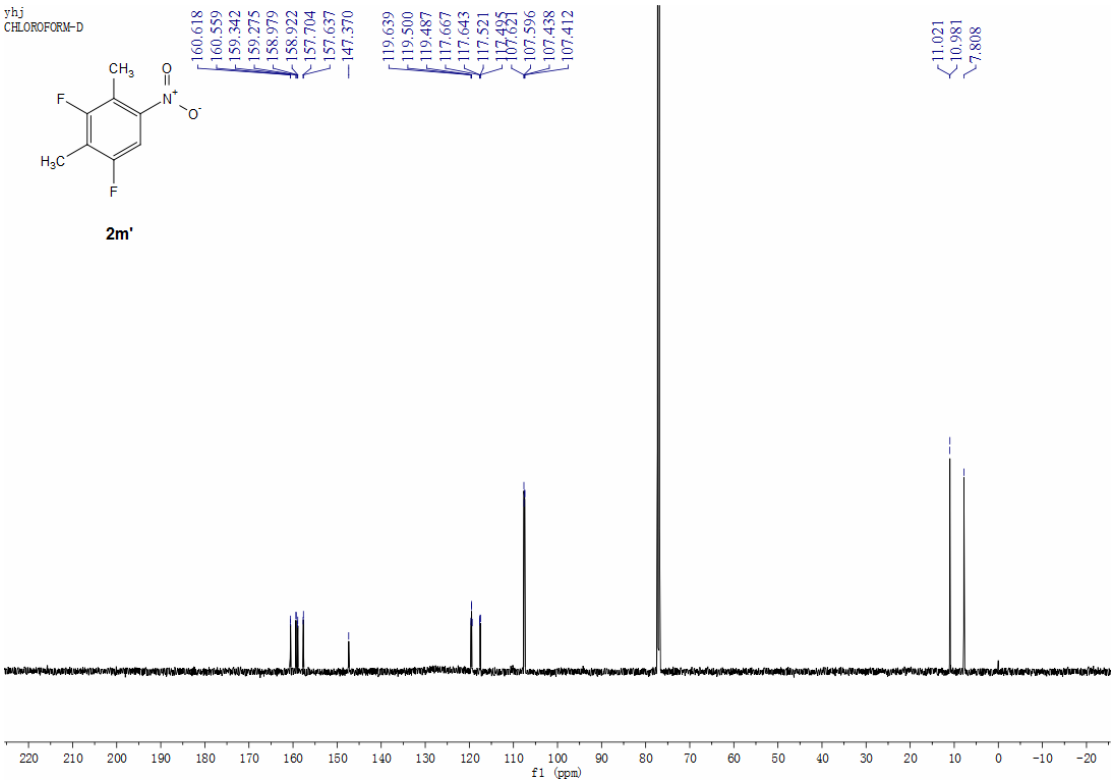


Figure S37. ^{13}C NMR spectrum of **2m′**.

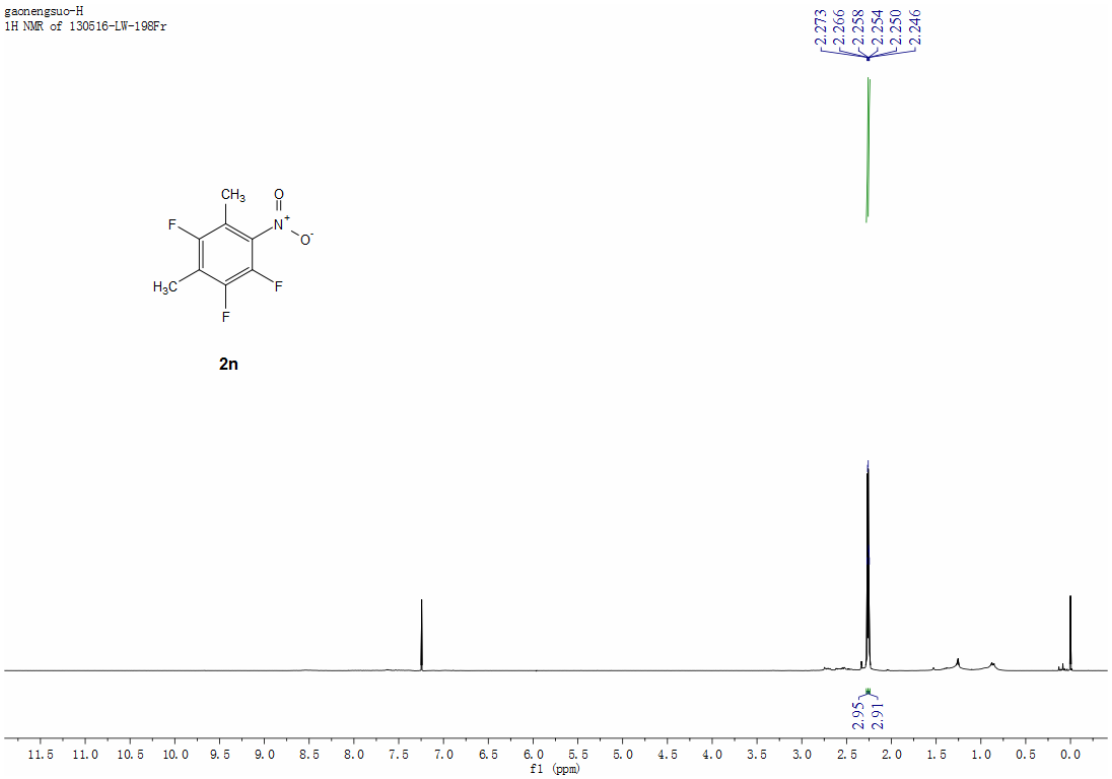


Figure S38. ^{1}H NMR spectrum of **2n**.

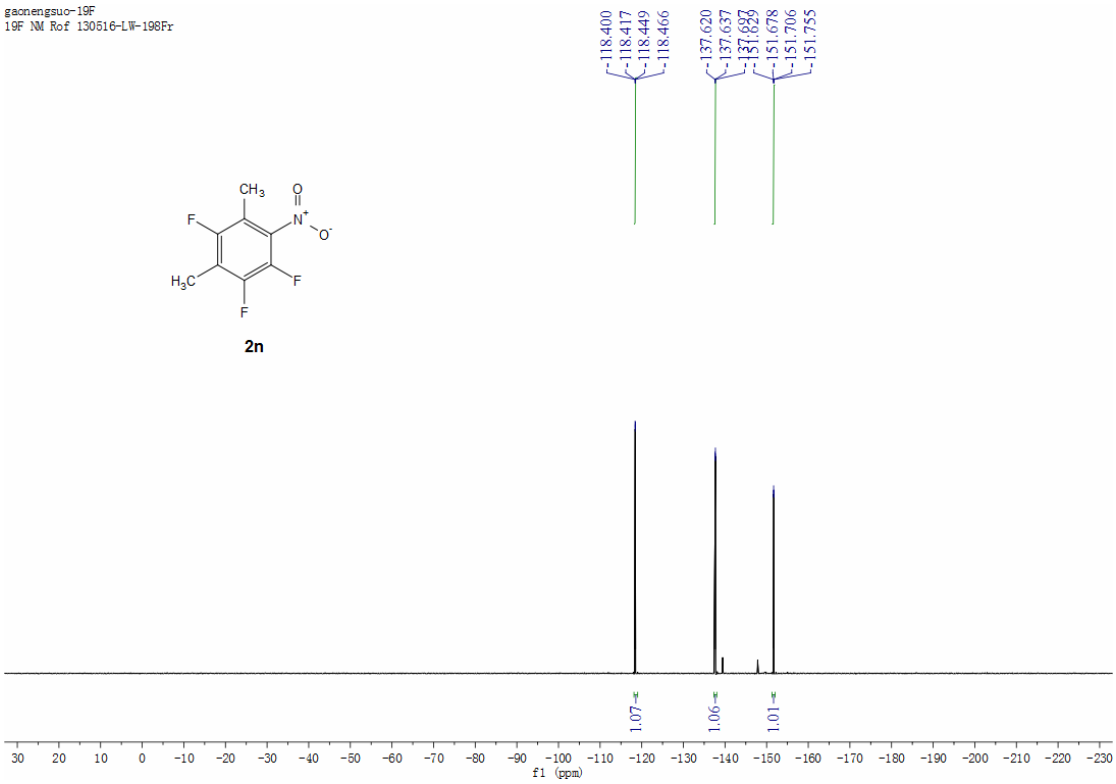


Figure S39. ^{19}F NMR spectrum of **2n**.

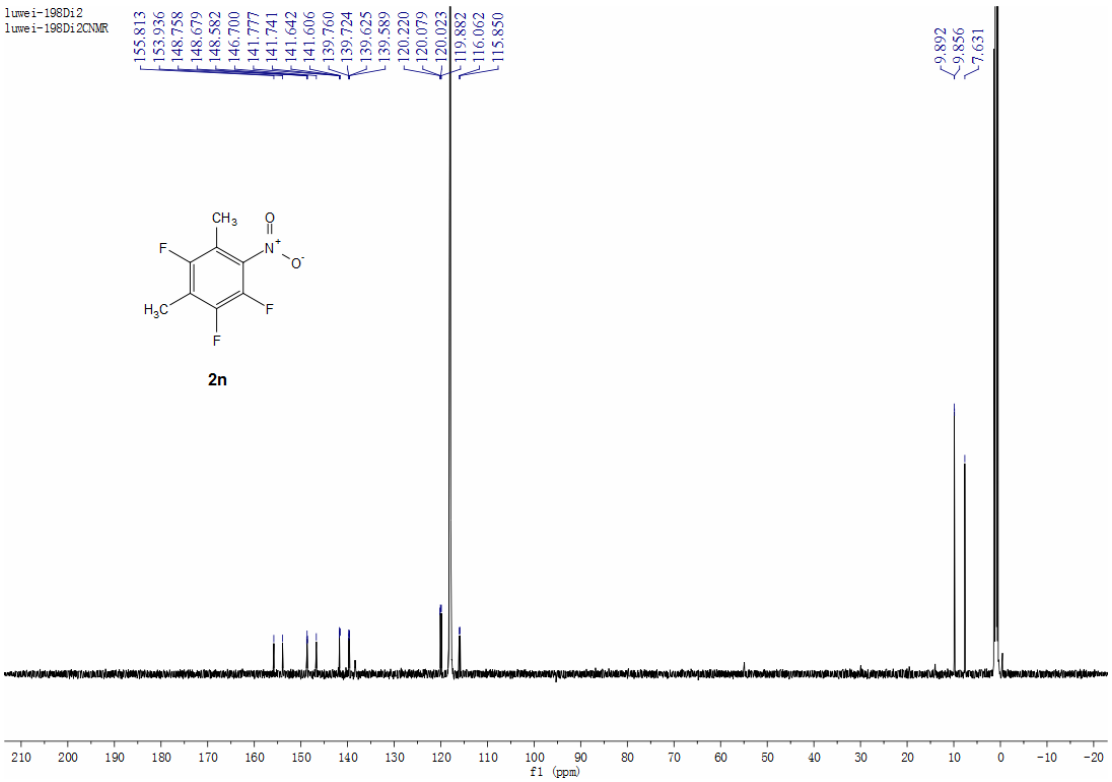


Figure S40. ^{13}C NMR spectrum of **2n**.

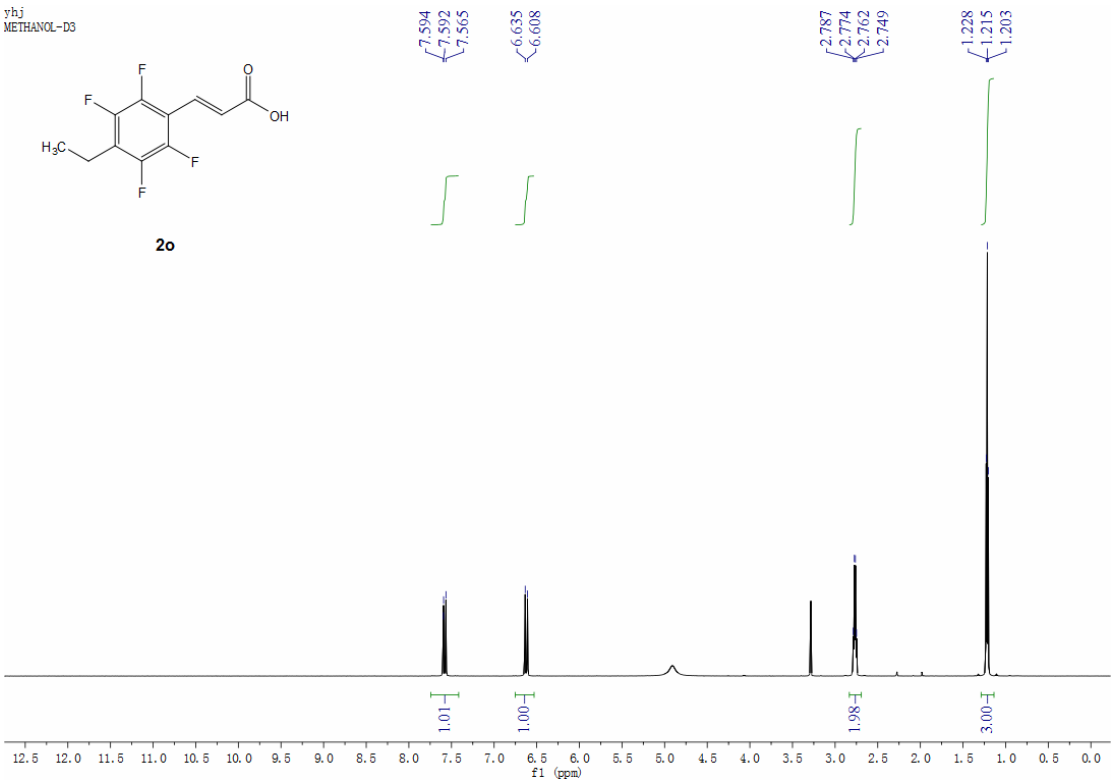


Figure S41. ^{1}H NMR spectrum of **2o**.

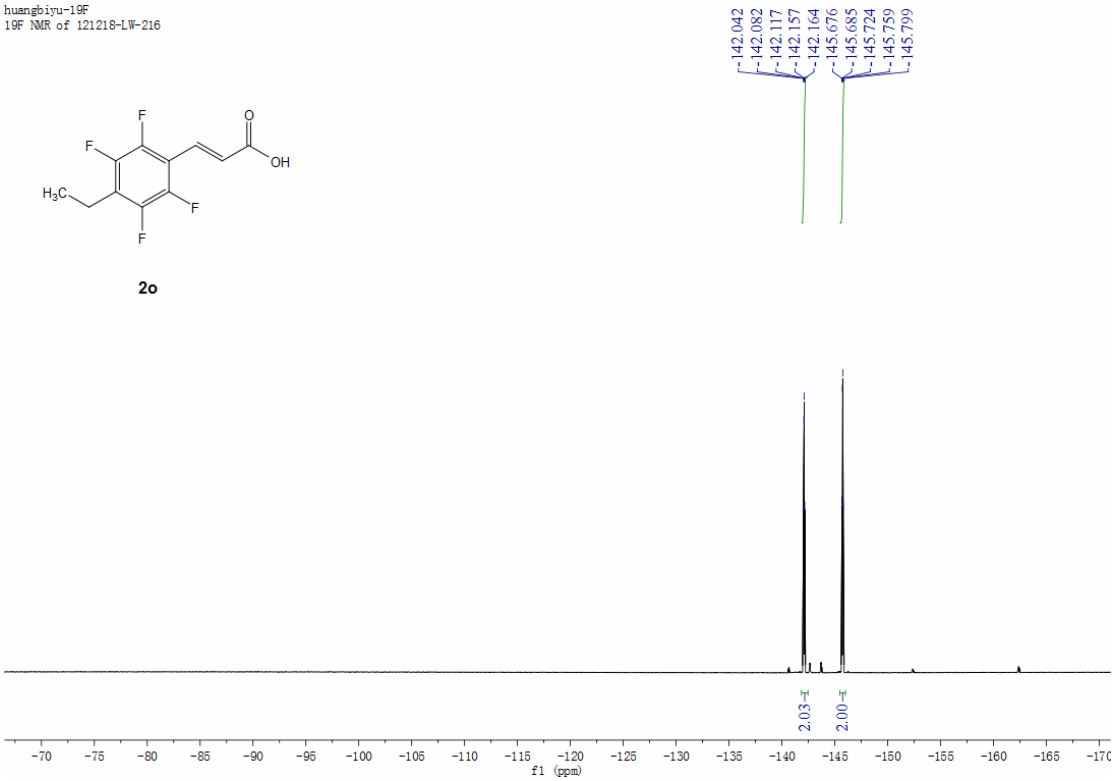


Figure S42. ^{19}F NMR spectrum of **2o**.

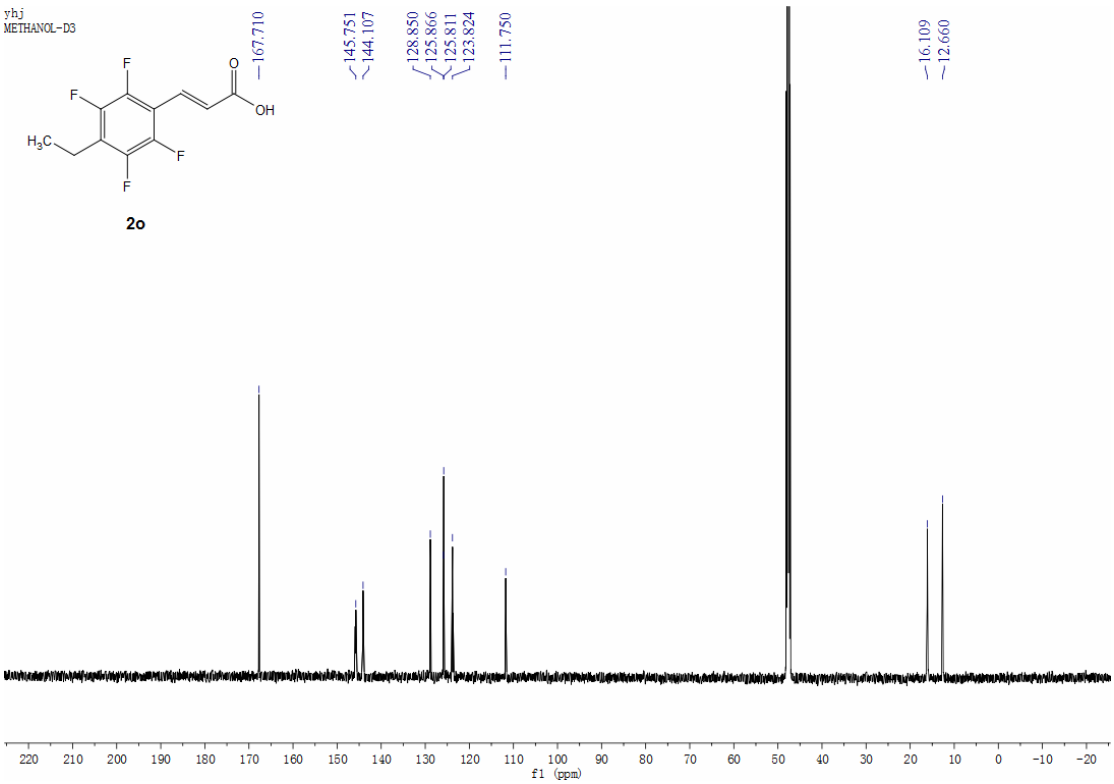


Figure S43. ^{13}C NMR spectrum of **2o**.

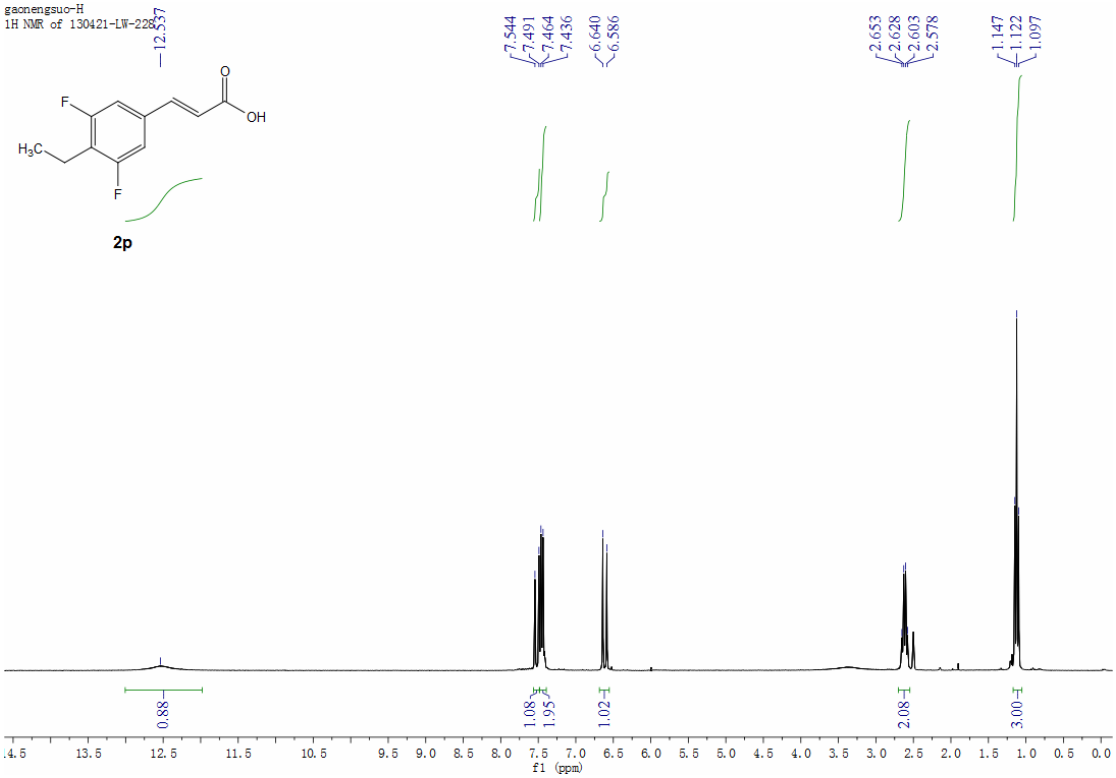


Figure S44. ^{1}H NMR spectrum of **2p**.

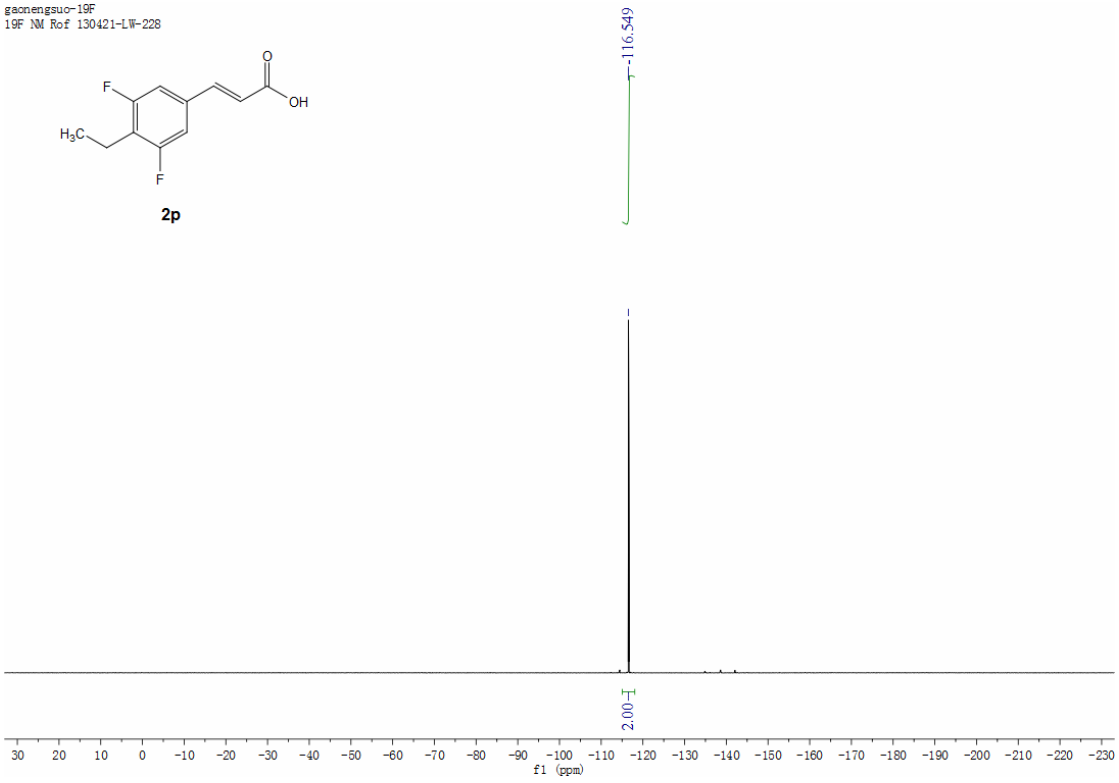


Figure S45. ^{19}F NMR spectrum of **2p**.

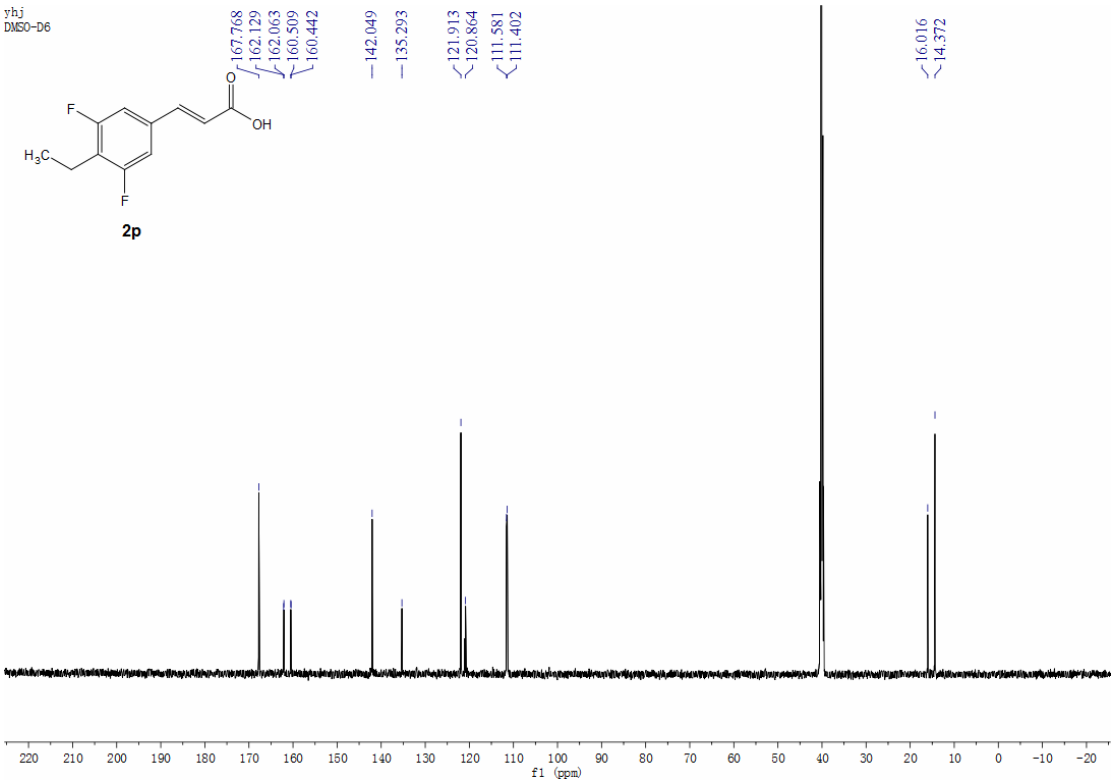


Figure S46. ^{13}C NMR spectrum of **2p**.

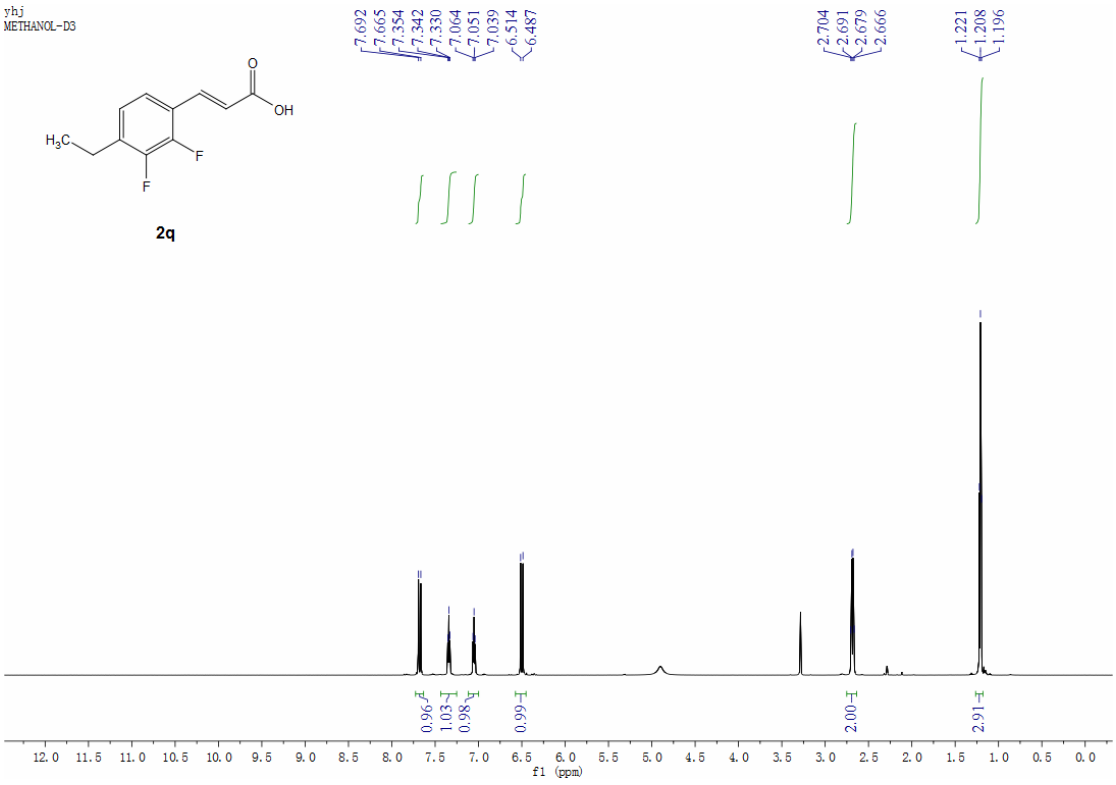


Figure S47. ^{1}H NMR spectrum of **2q**.

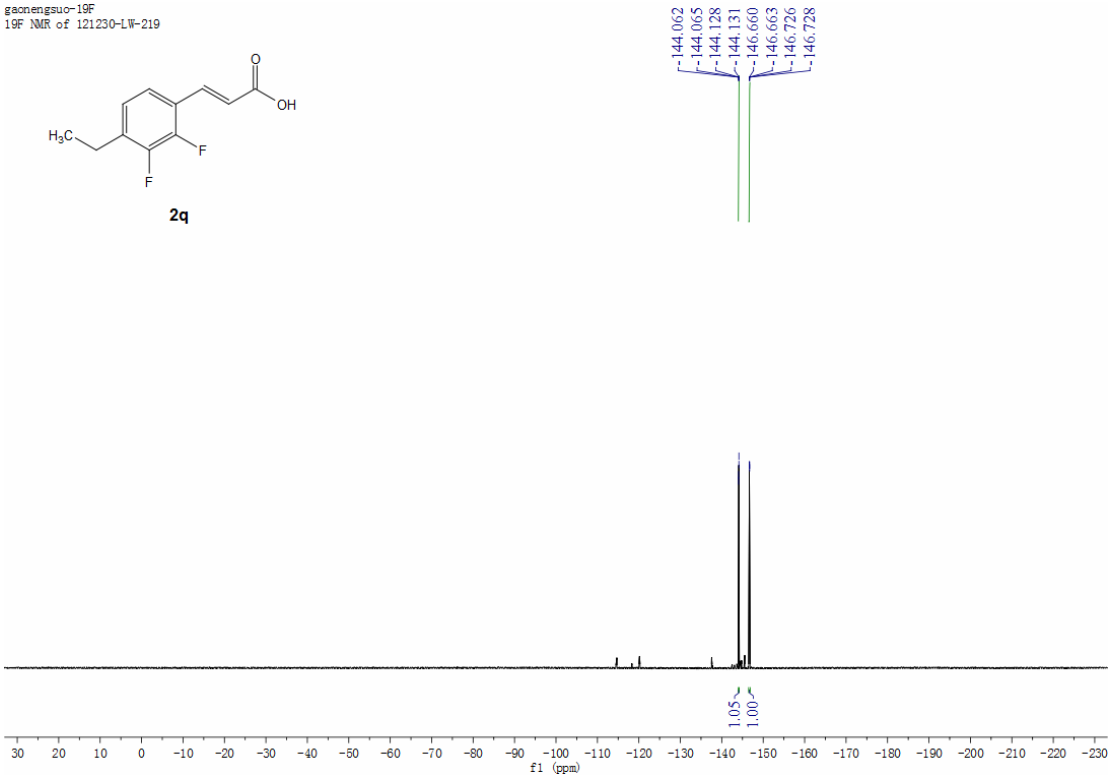


Figure S48. ^{19}F NMR spectrum of **2q**.

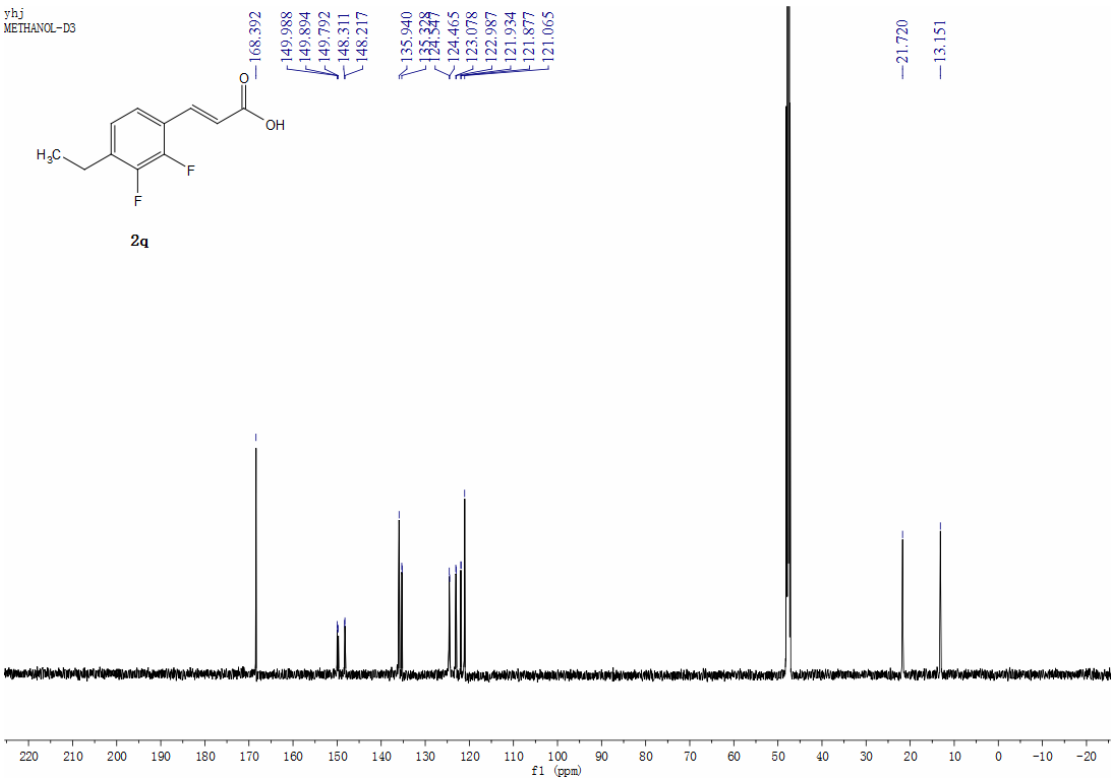


Figure S49. ^{13}C NMR spectrum of **2q**.

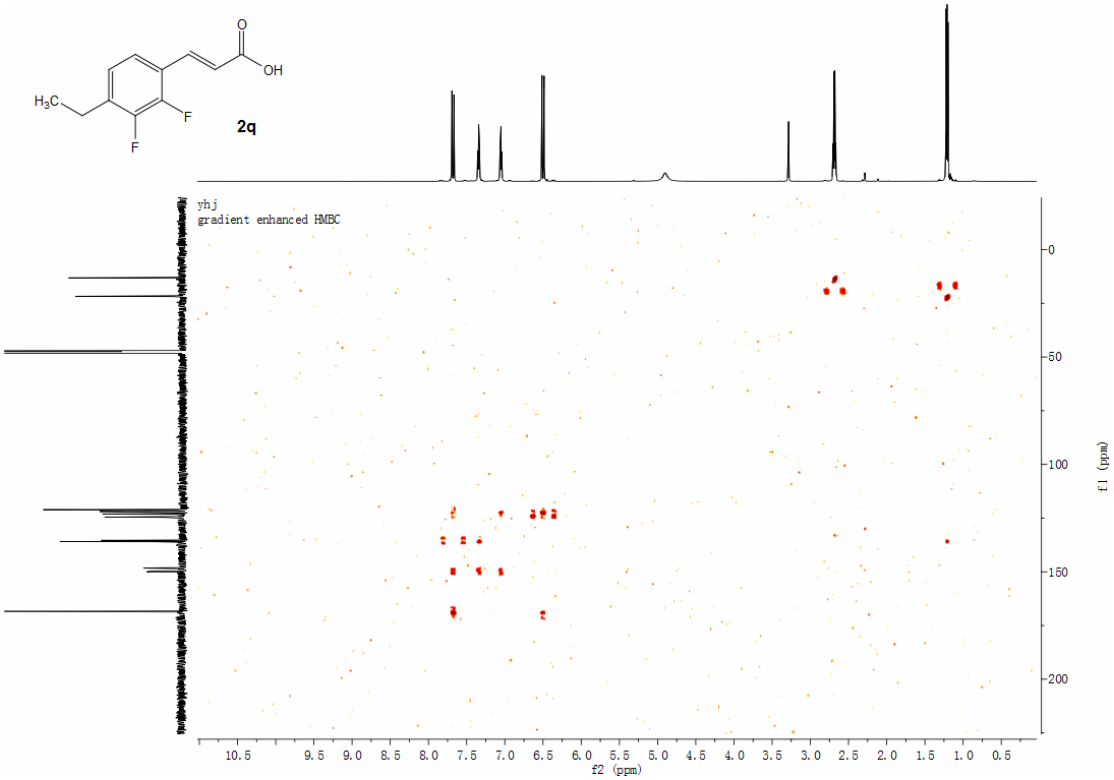


Figure S50. HMBC spectrum of **2q**.

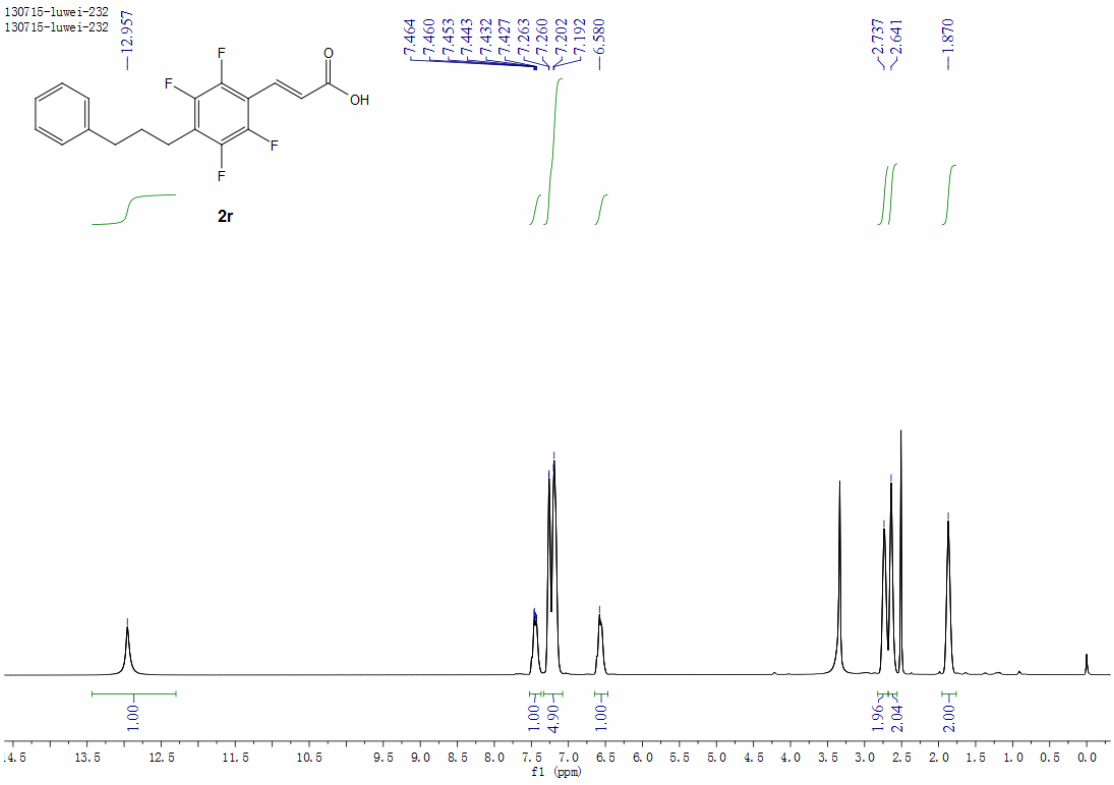


Figure S51. ^{1}H NMR spectrum of **2r**.

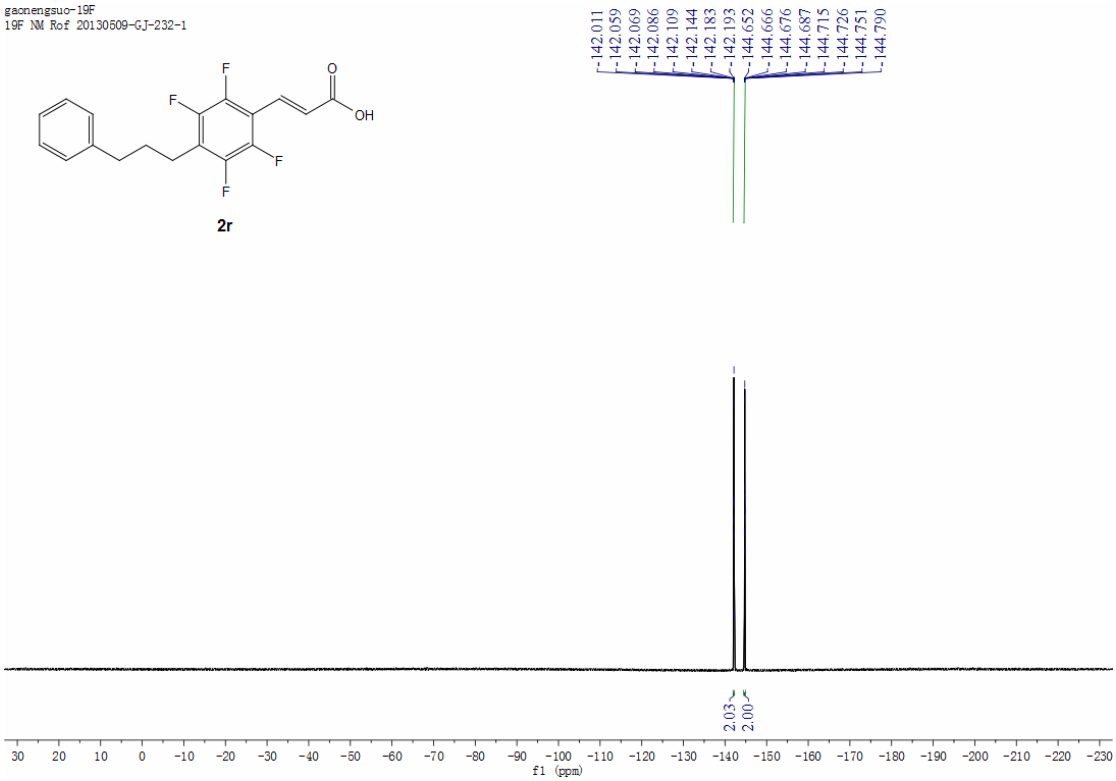


Figure S52. ^{19}F NMR spectrum of **2r**.

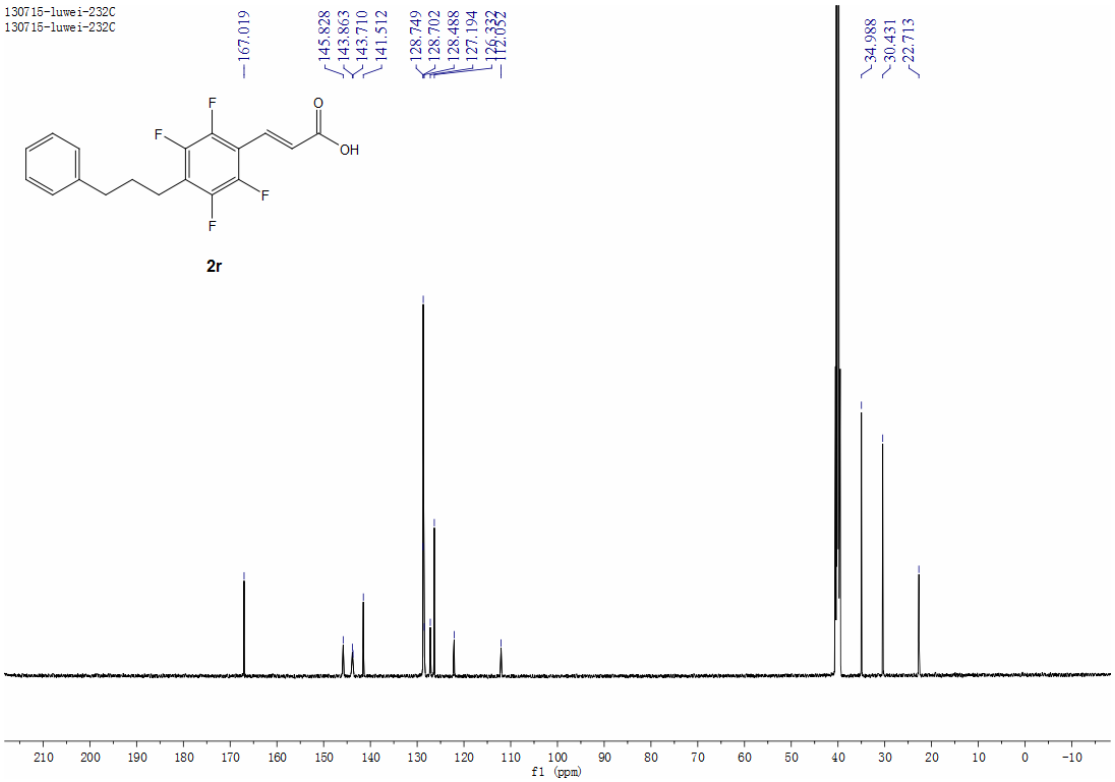


Figure S53. ^{13}C NMR spectrum of **2r**.

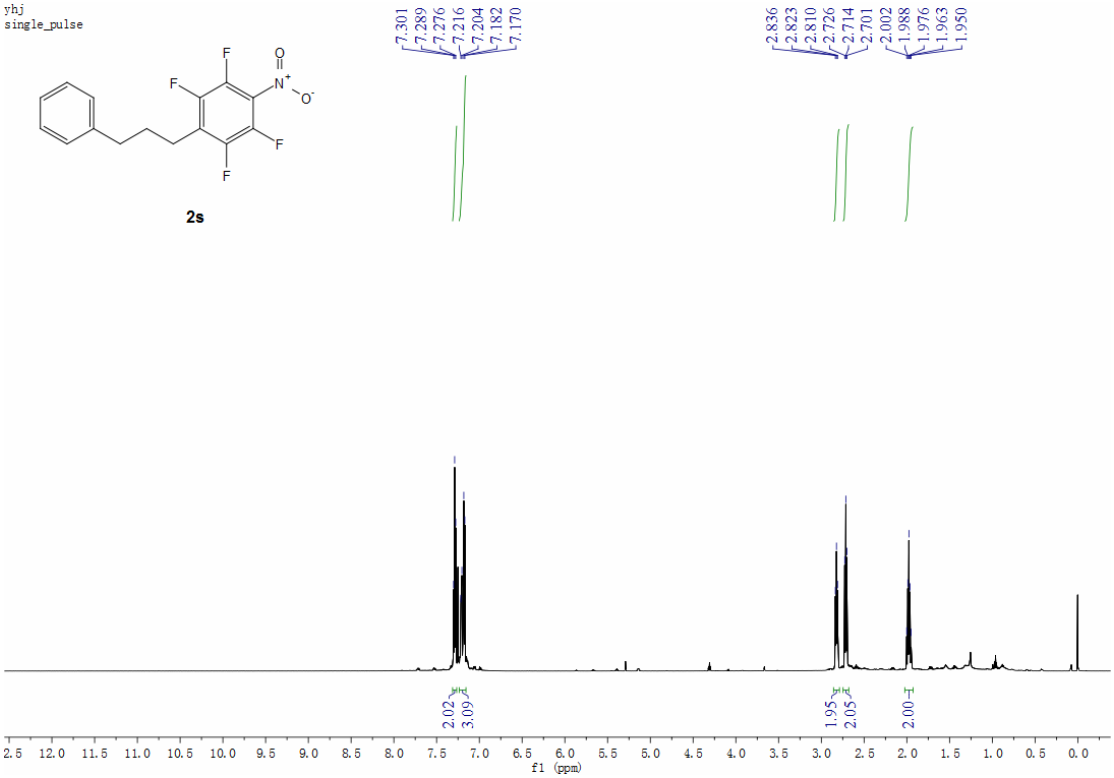


Figure S54. ^{1}H NMR spectrum of **2s**.

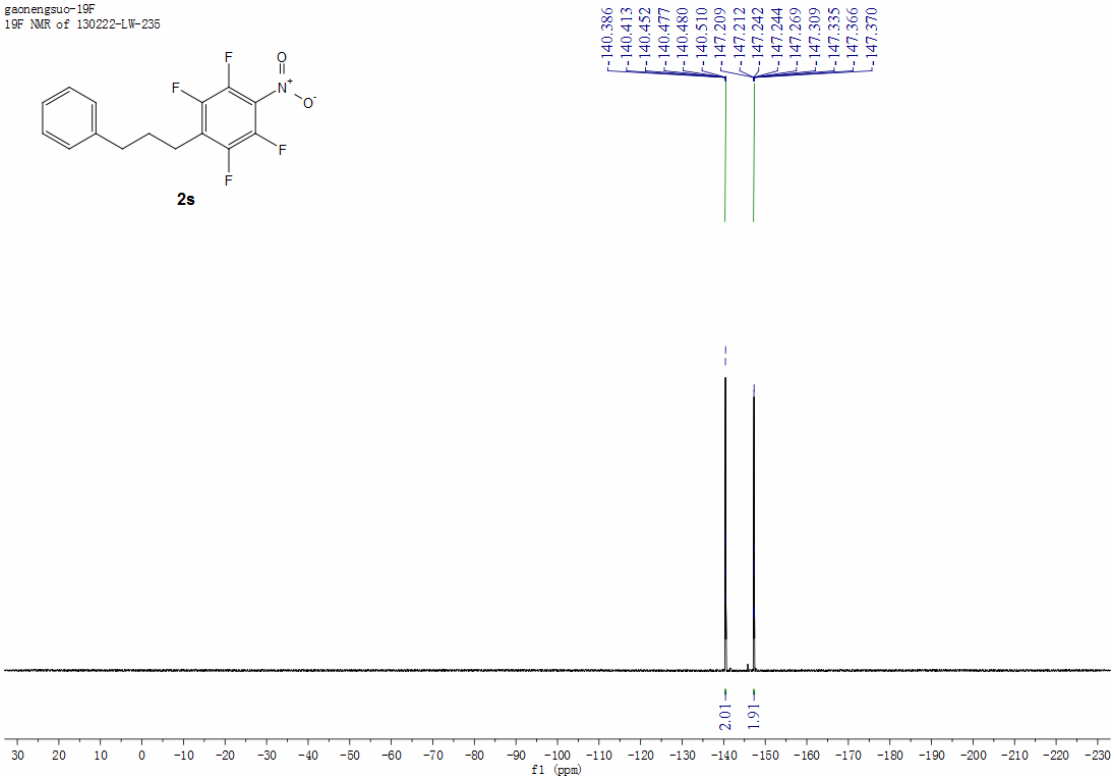


Figure S55. ^{19}F NMR spectrum of **2s**.

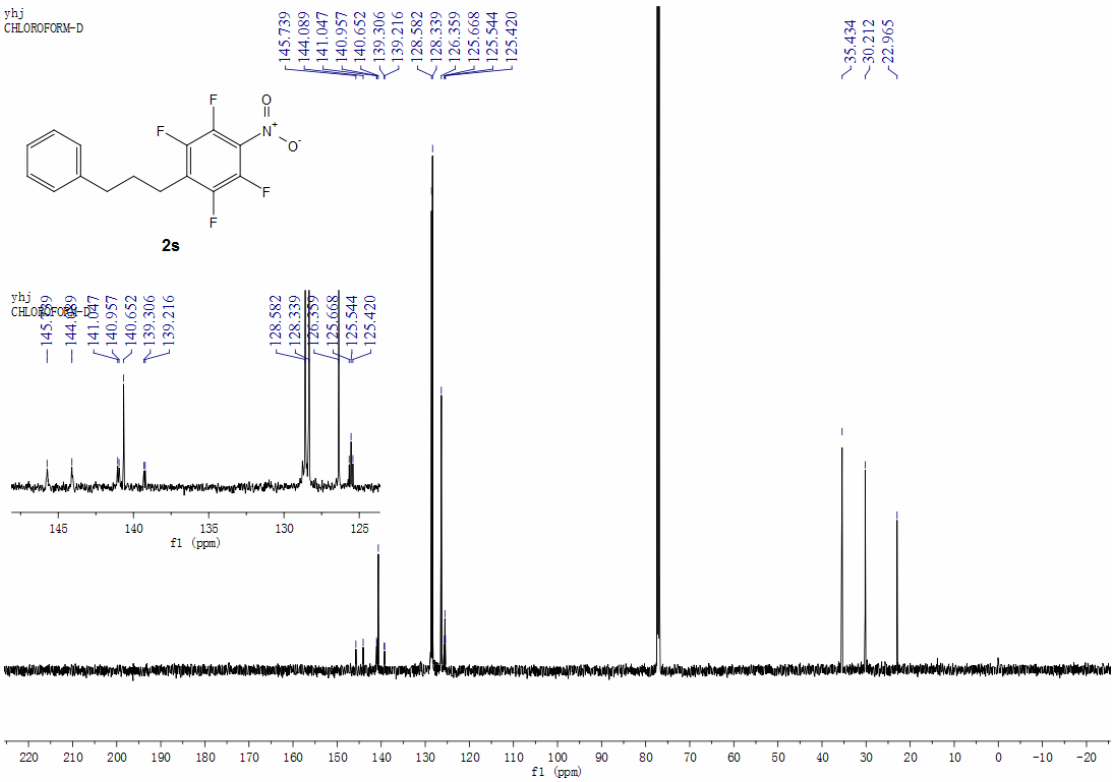


Figure S56. ^{13}C NMR spectrum of **2s**.

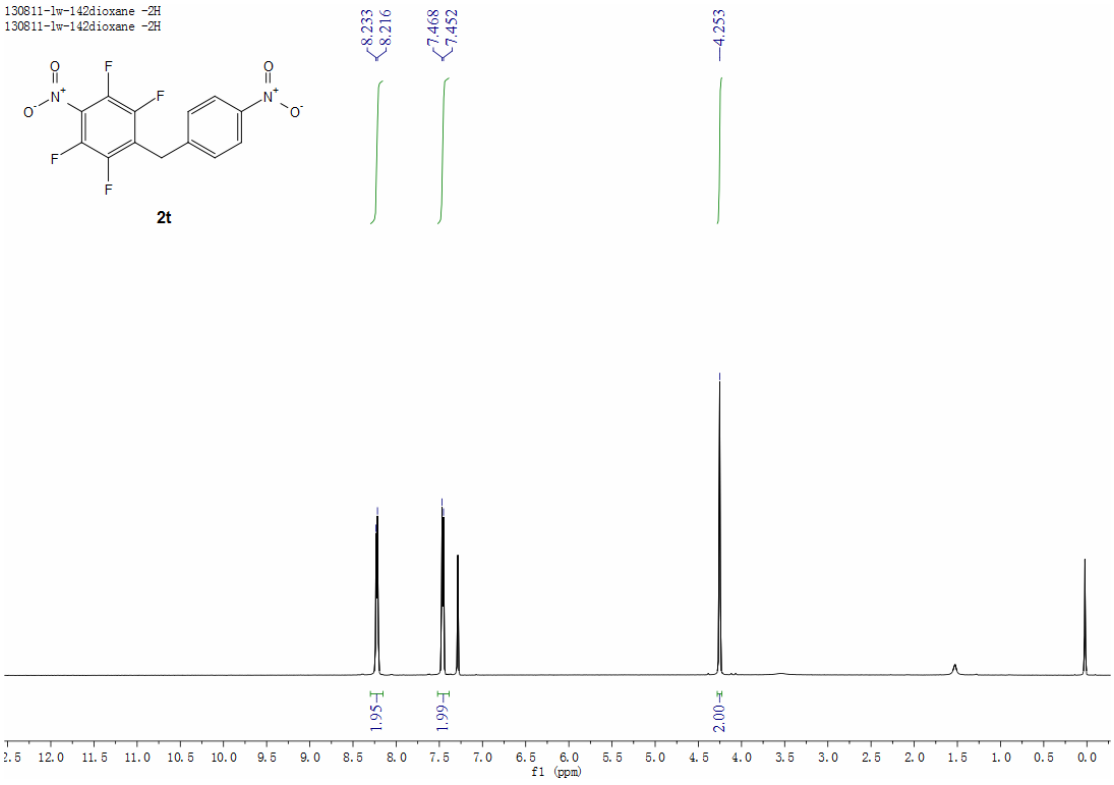


Figure S57. ^{1}H NMR spectrum of **2t**.

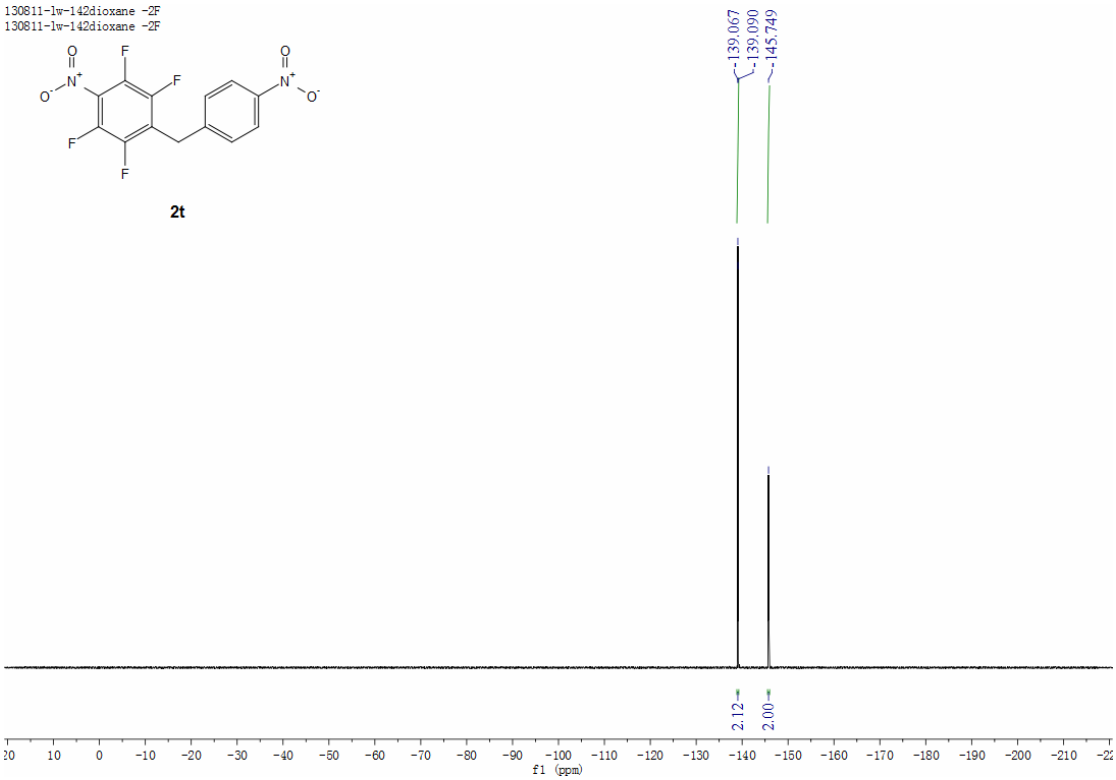


Figure S58. ^{19}F NMR spectrum of **2t**.

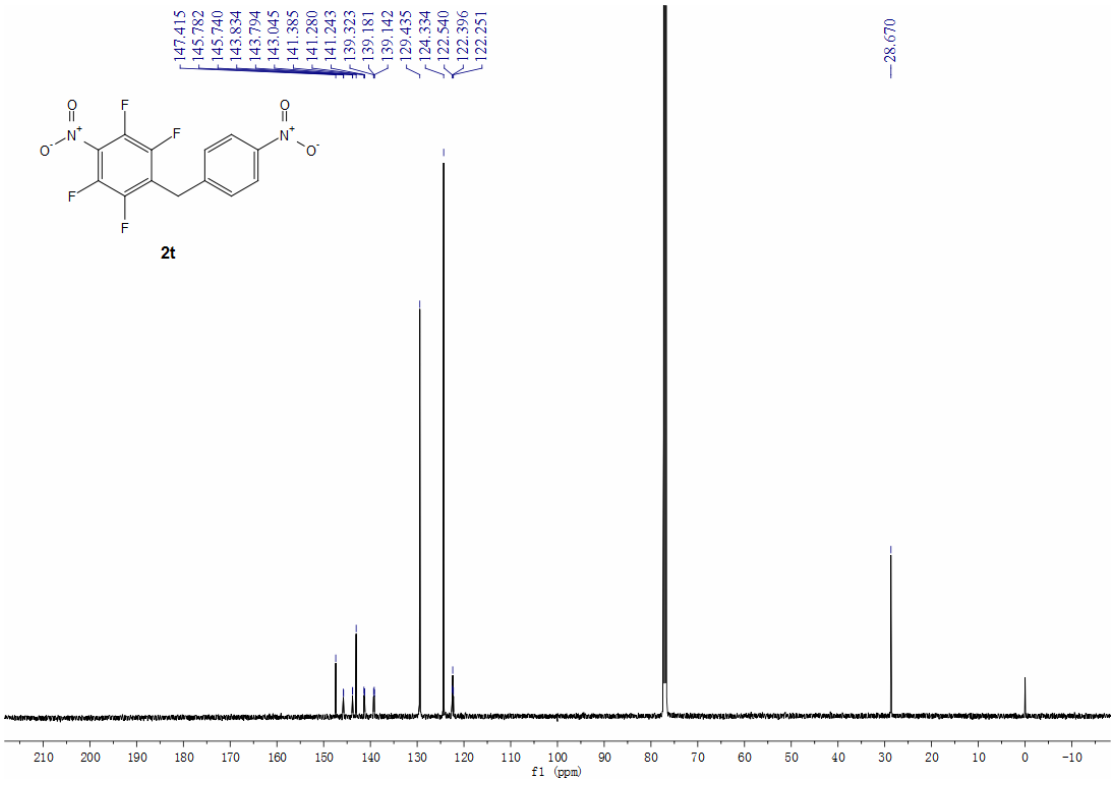


Figure S59. ^{13}C NMR spectrum of **2t**.

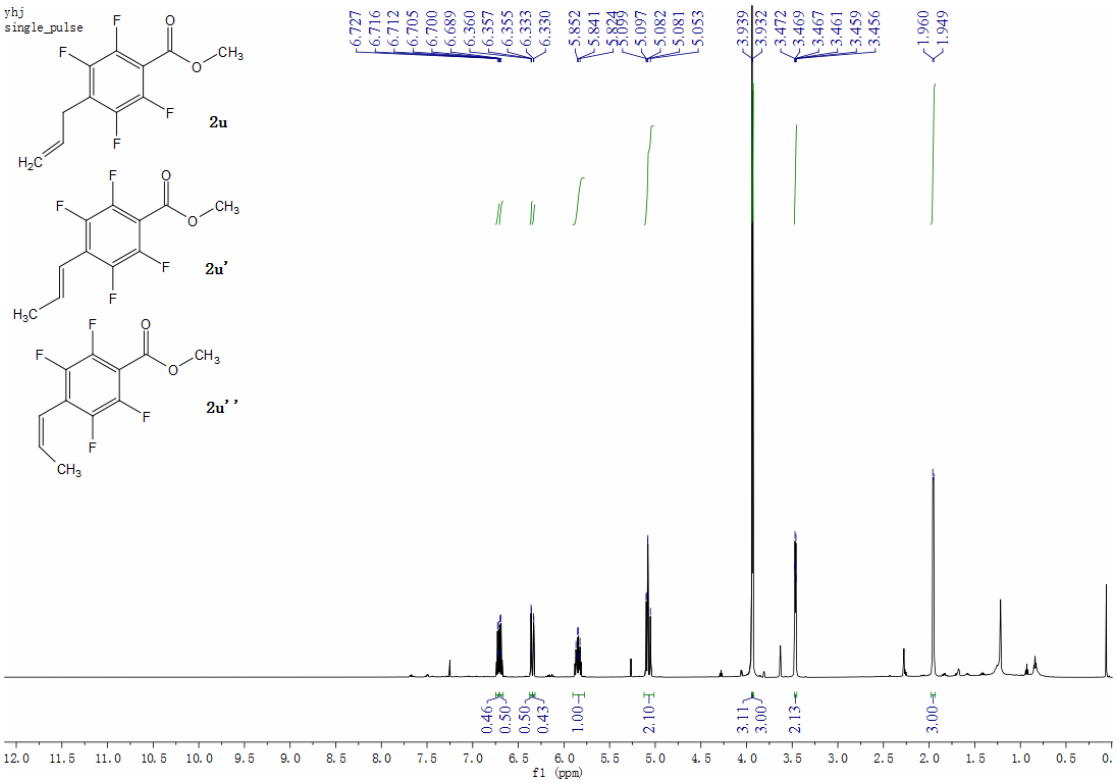


Figure S60. ^{1}H NMR spectrum of **2u, 2u′ and 2u″**.

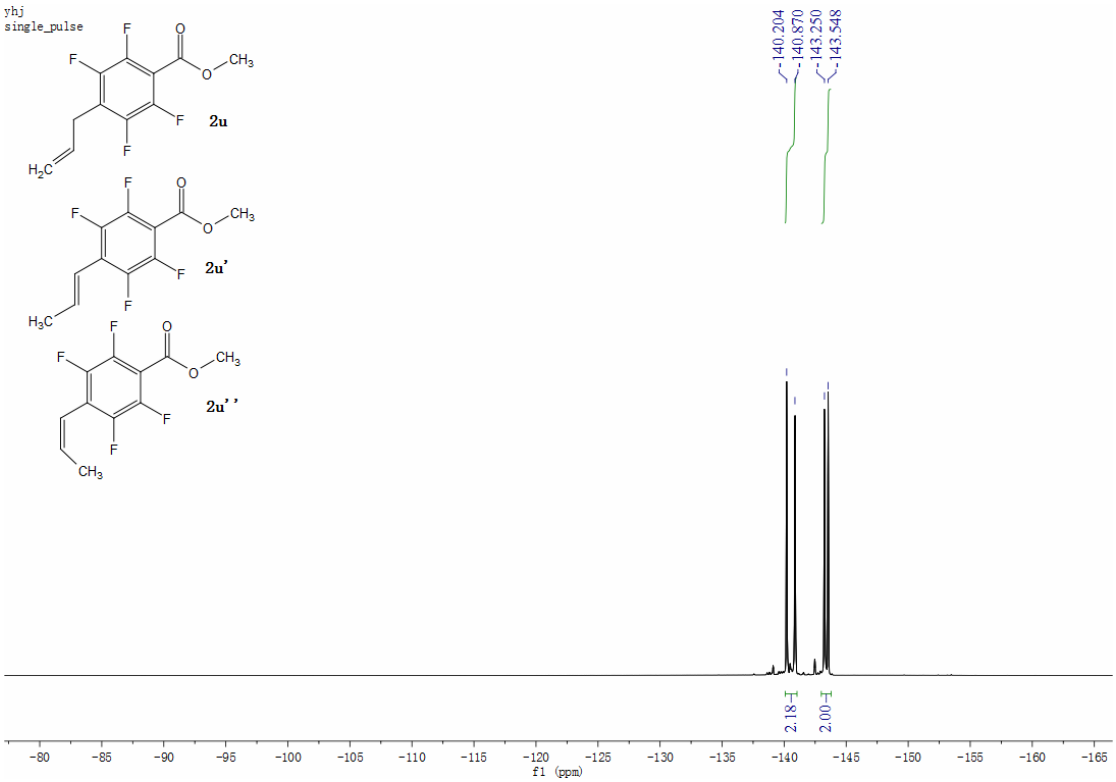


Figure S61. ^{19}F NMR spectrum of **2u, 2u′ and 2u″**.

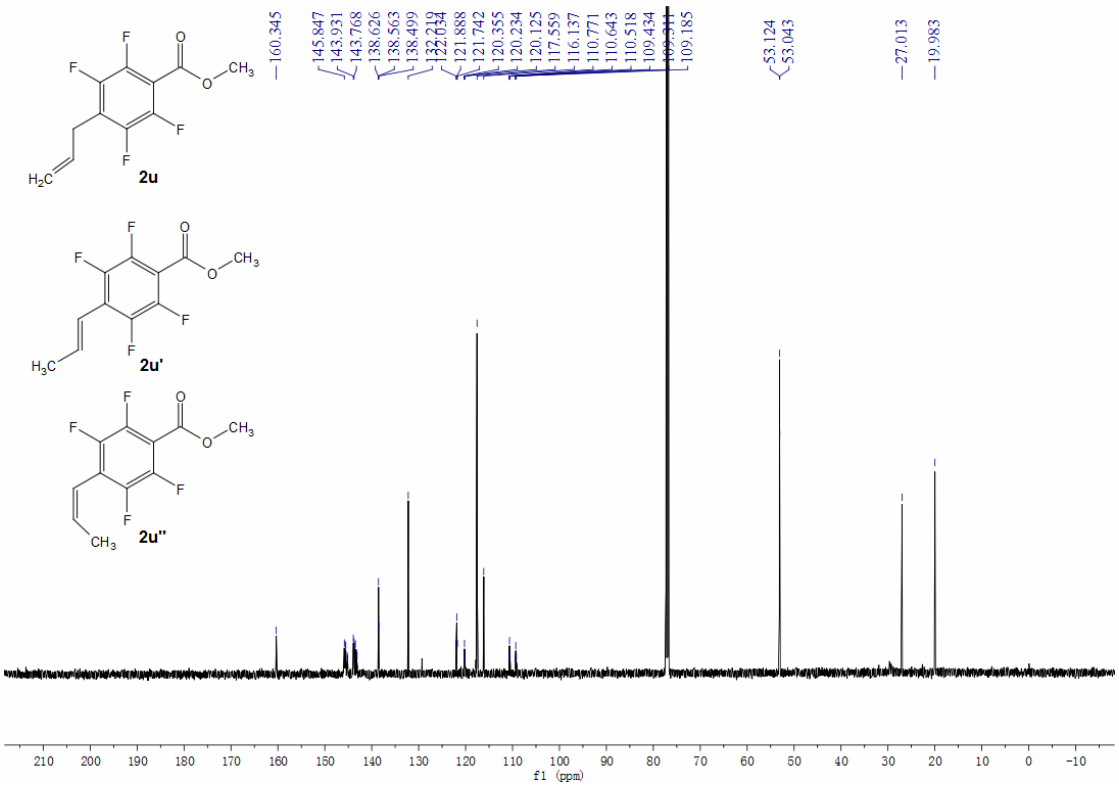


Figure S62. ^{13}C NMR spectrum of **2u, 2u′ and 2u″**.

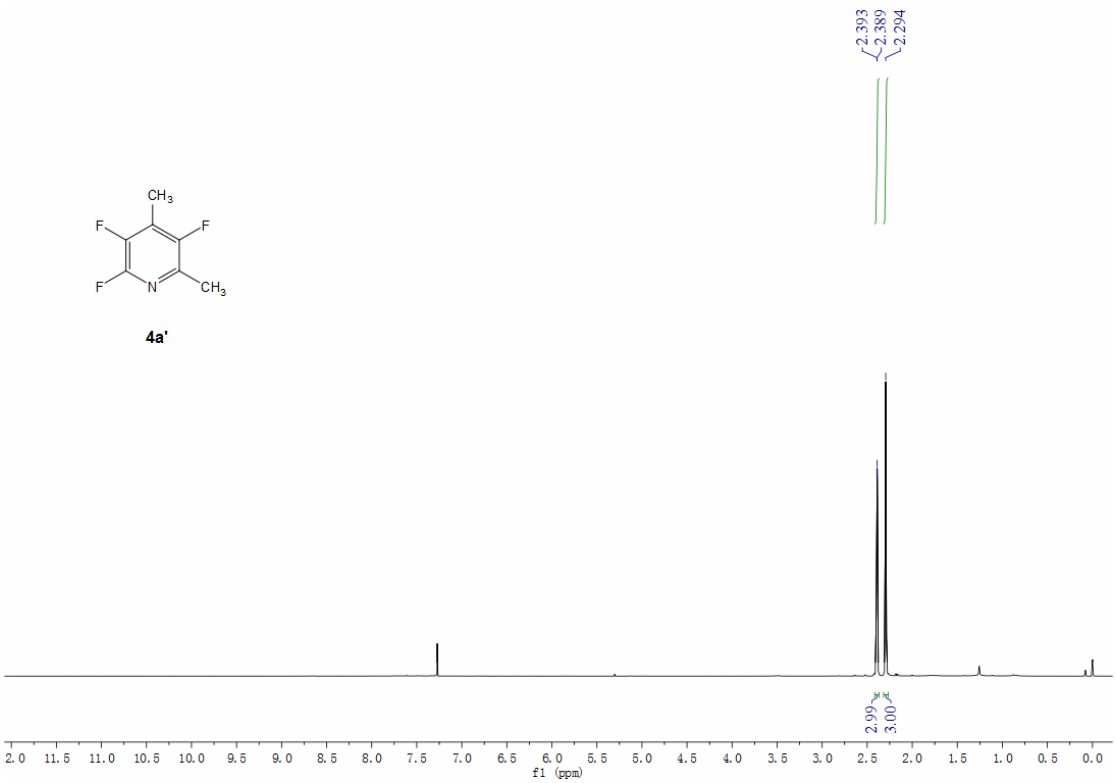


Figure S63. ^{1}H NMR spectrum of **4a′**.

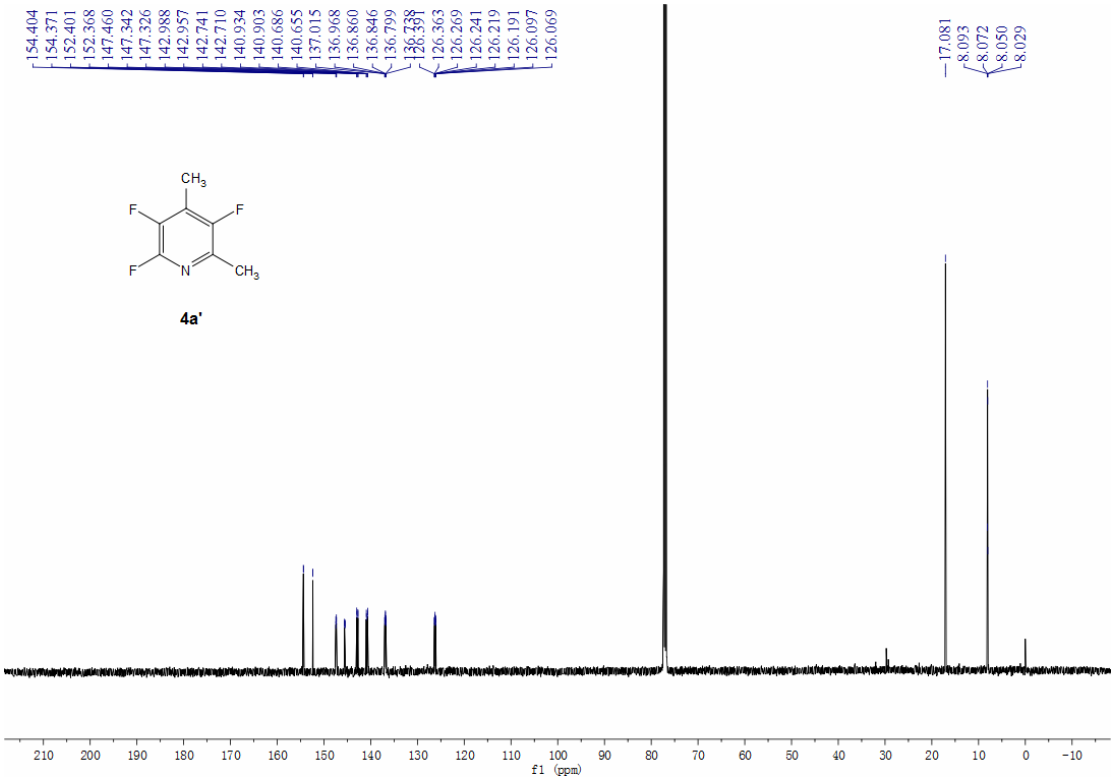


Figure S64. ^{13}C NMR spectrum of **4a′**.

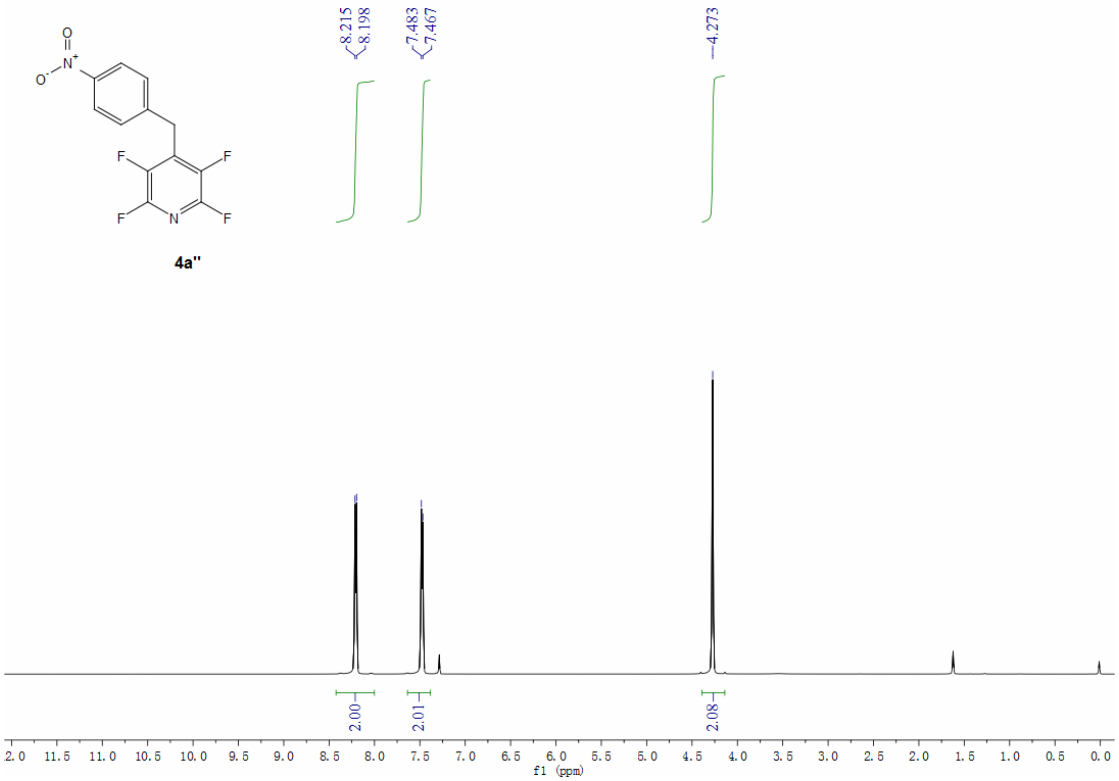


Figure S65. ^{1}H NMR spectrum of **4a″**.

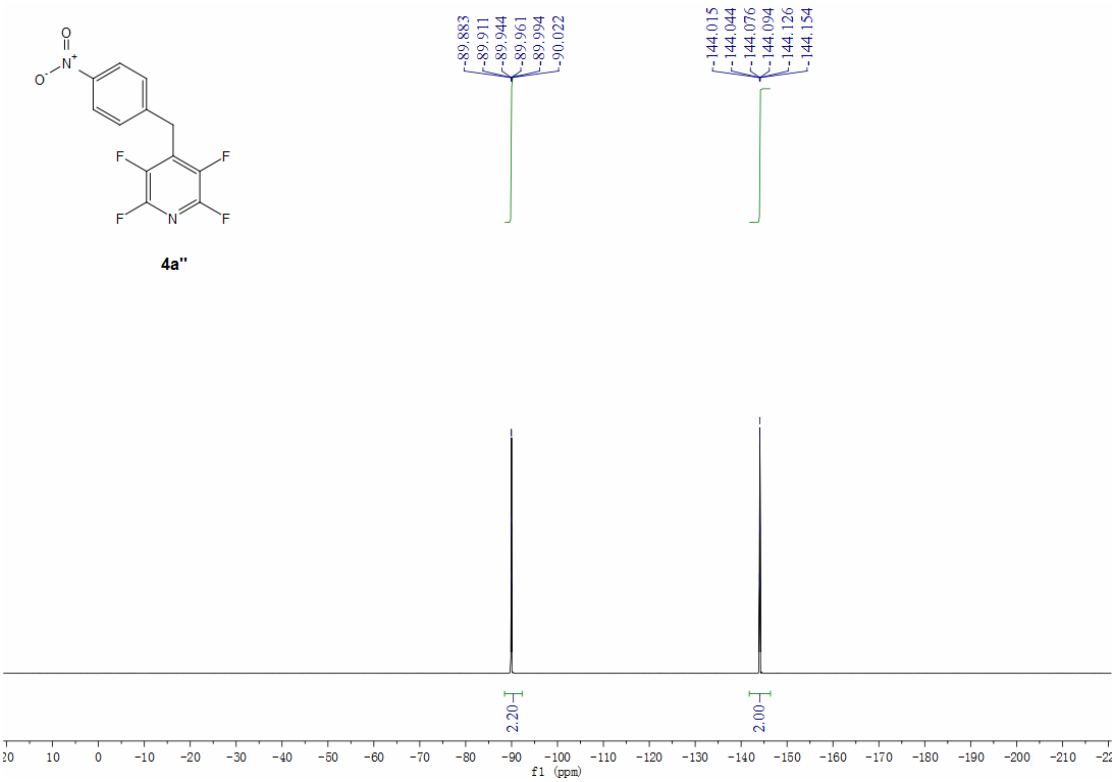


Figure S66. ^{19}F NMR spectrum of **4a″**.

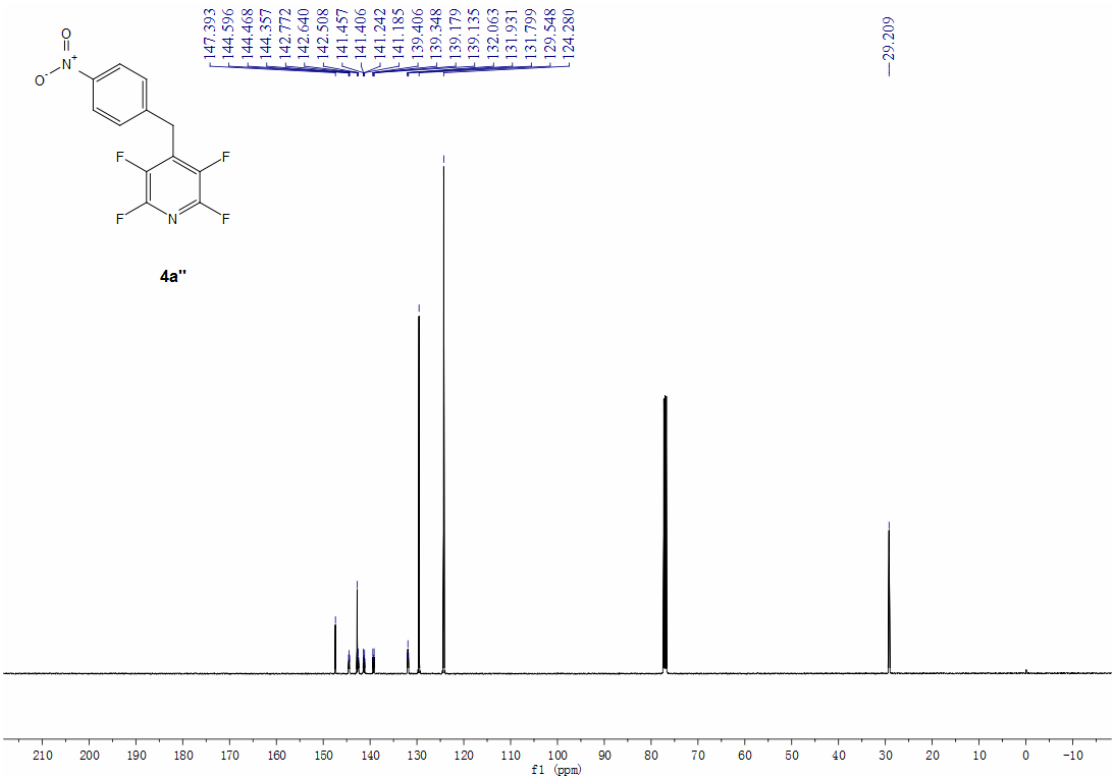


Figure S67. ^{13}C NMR spectrum of **4a″**.

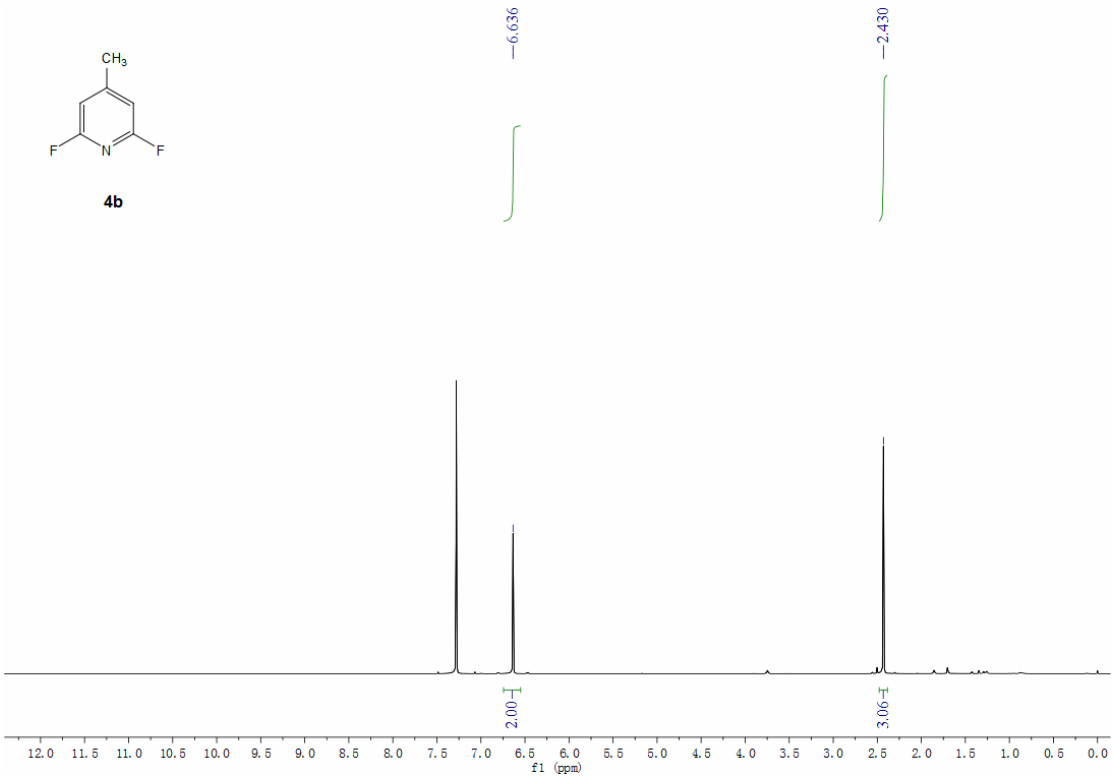


Figure S68. ^{1}H NMR spectrum of **4b**.

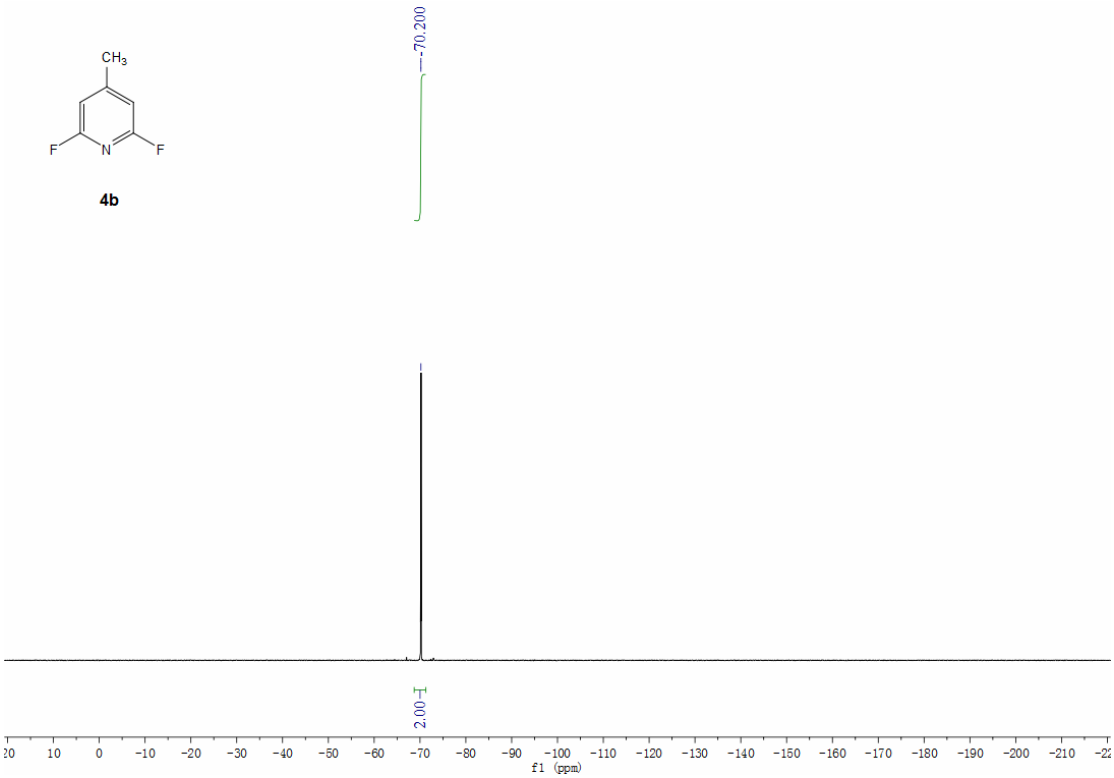


Figure S69. ^{19}F NMR spectrum of **4b**.

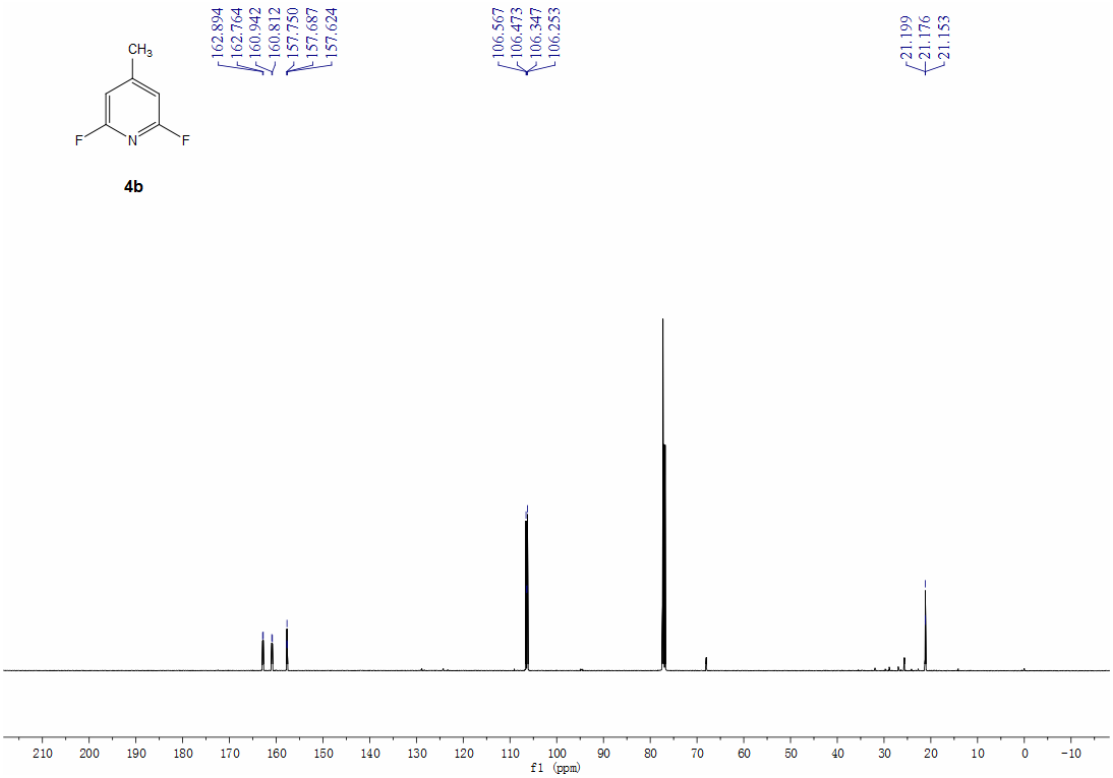


Figure S70. ^{13}C NMR spectrum of **4b**.

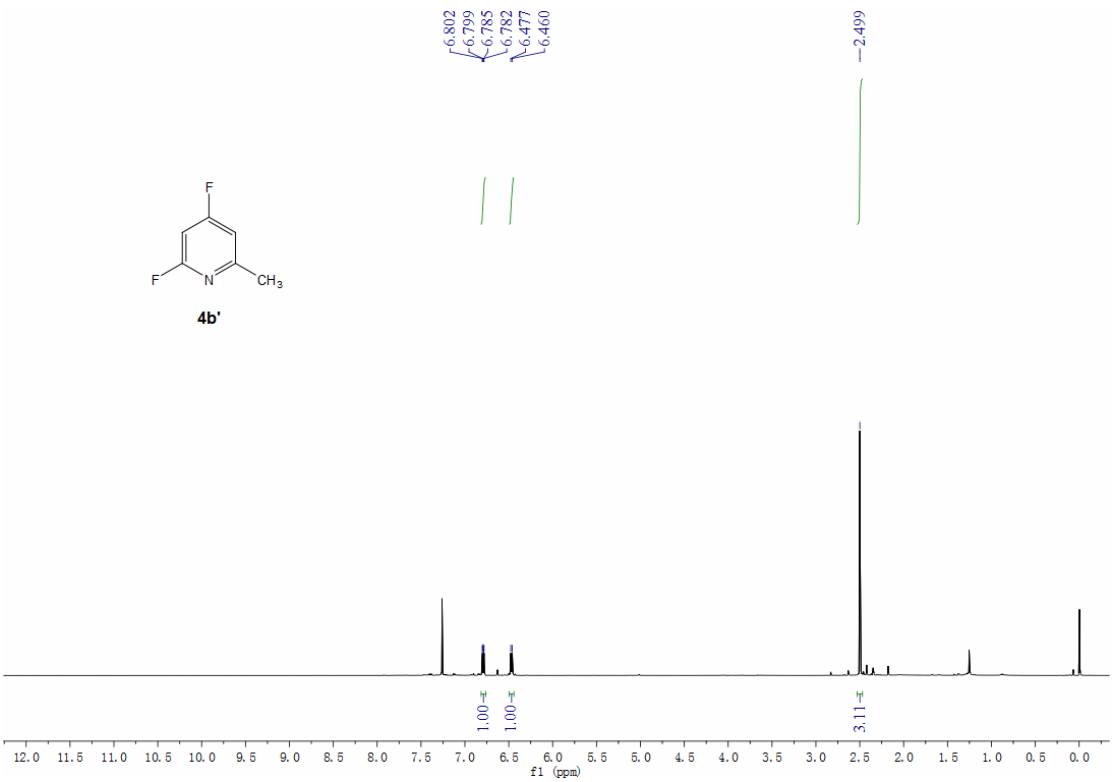


Figure S71. ^{1}H NMR spectrum of **4b′**.

Figure S72. ^{19}F NMR spectrum of **4b′**.

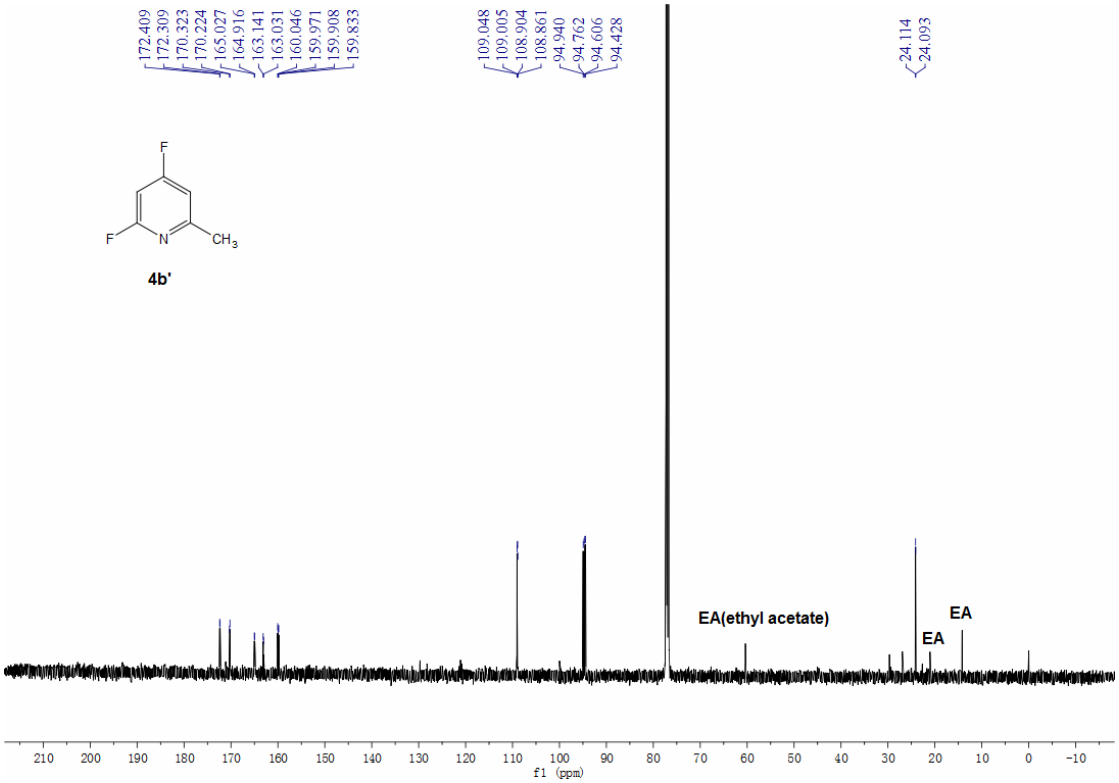


Figure S73. ^{13}C NMR spectrum of **4b′**.

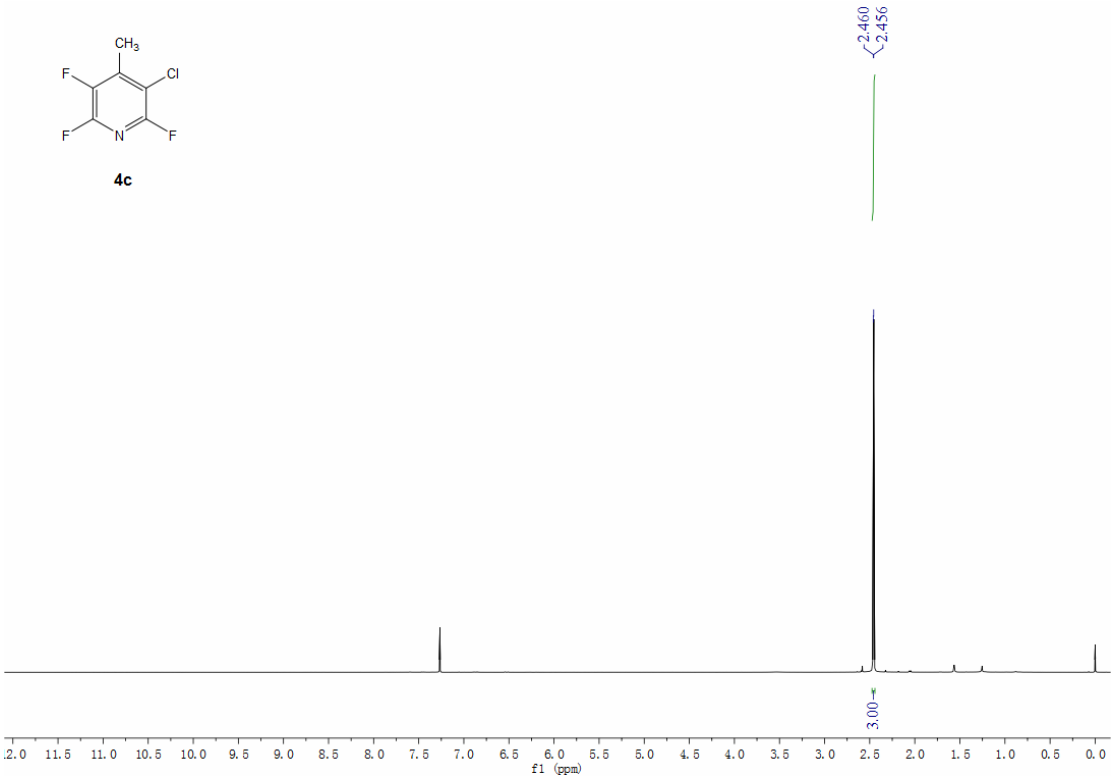


Figure S74. ^{1}H NMR spectrum of **4c**.

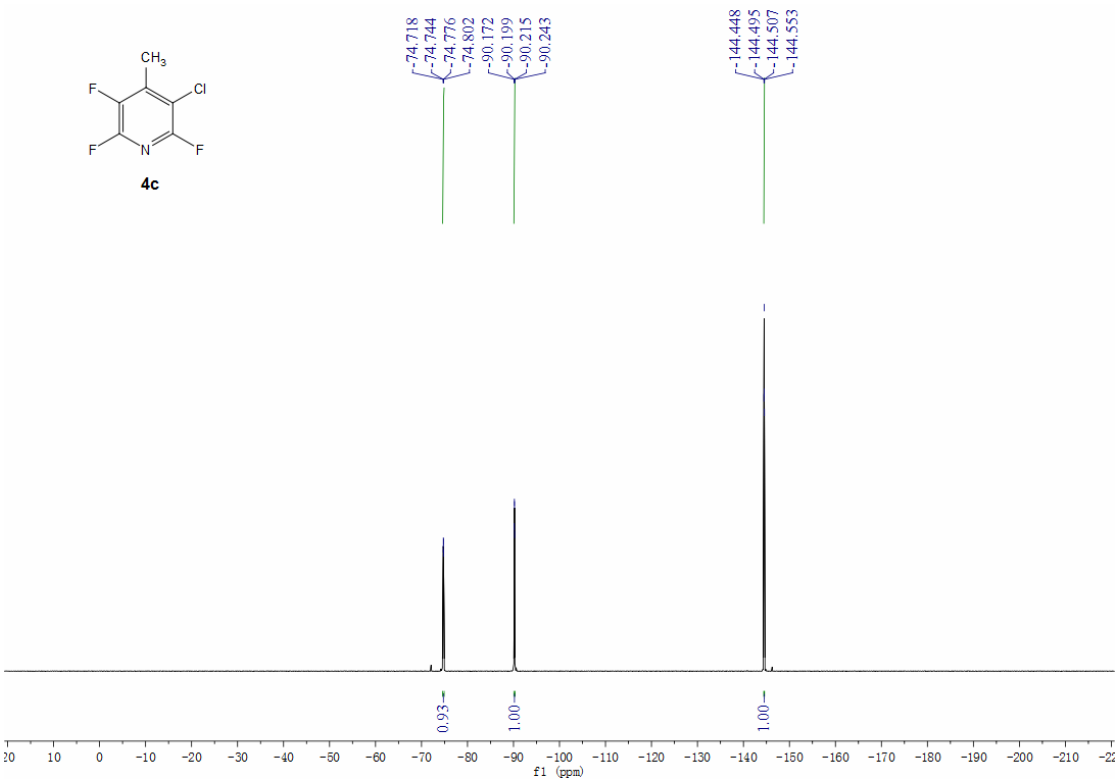


Figure S75. ^{19}F NMR spectrum of **4c**.

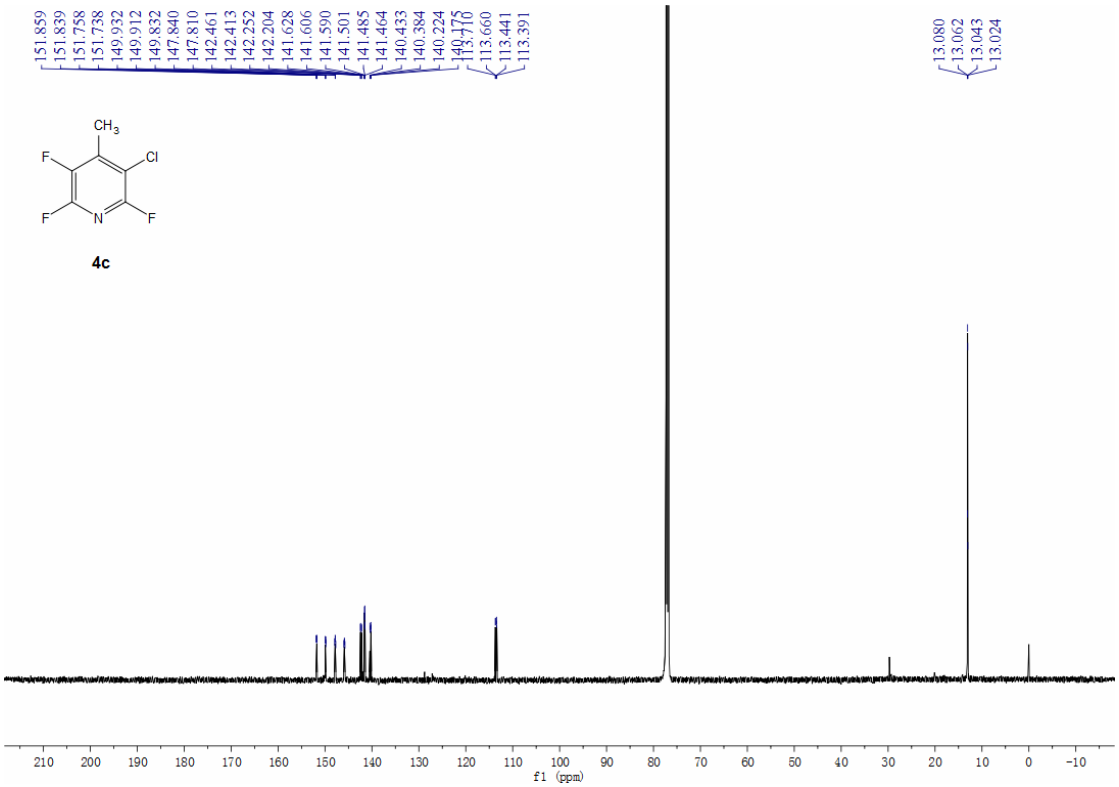


Figure S76. ^{13}C NMR spectrum of **4c**.

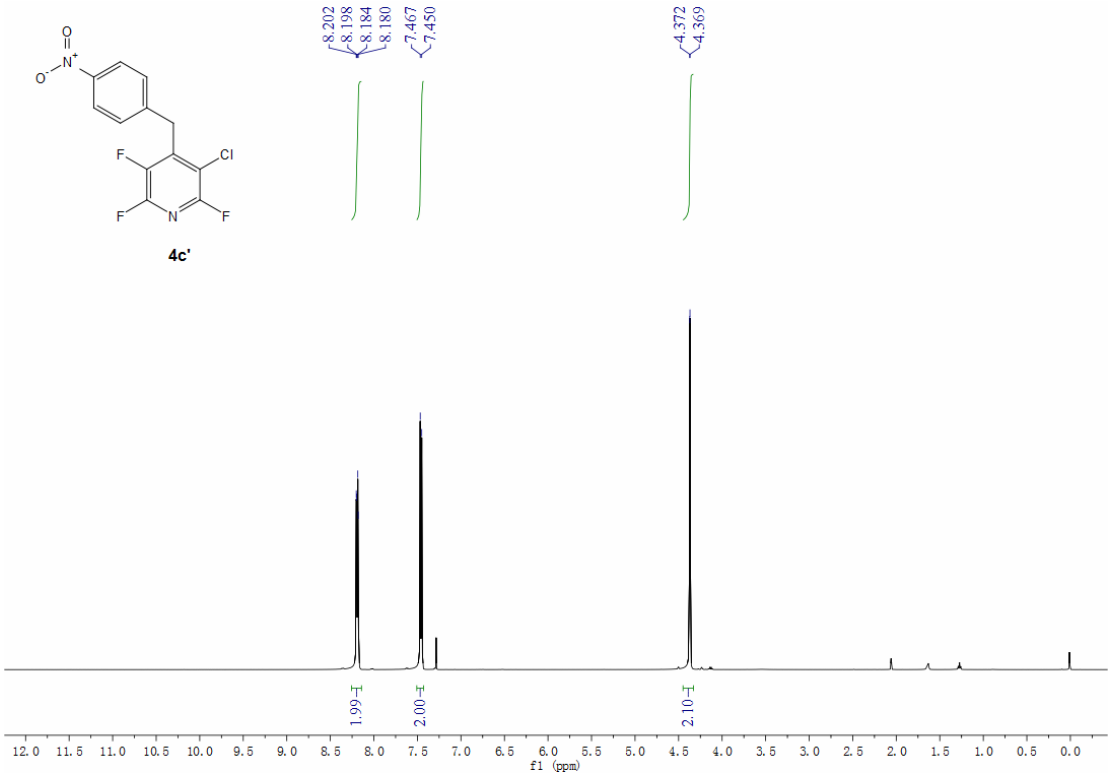


Figure S77. ^{1}H NMR spectrum of **4c′**.

Figure S78. ^{19}F NMR spectrum of **4c′**.

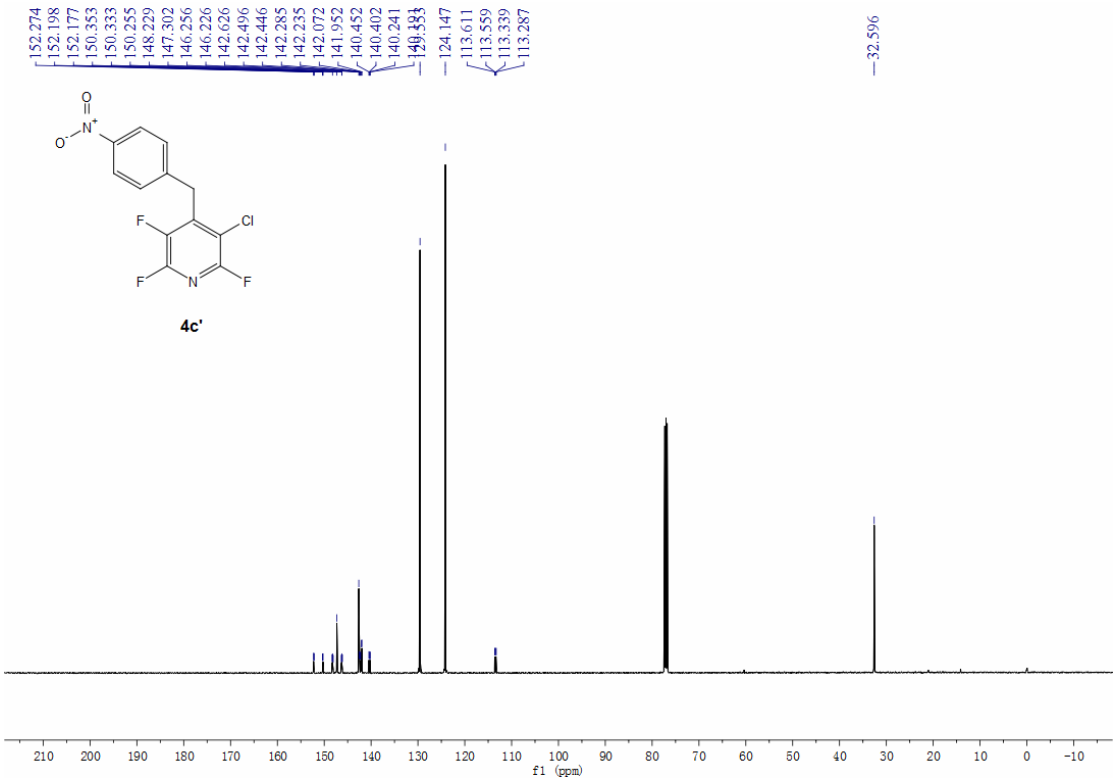


Figure S79. ^{13}C NMR spectrum of **4c′**.

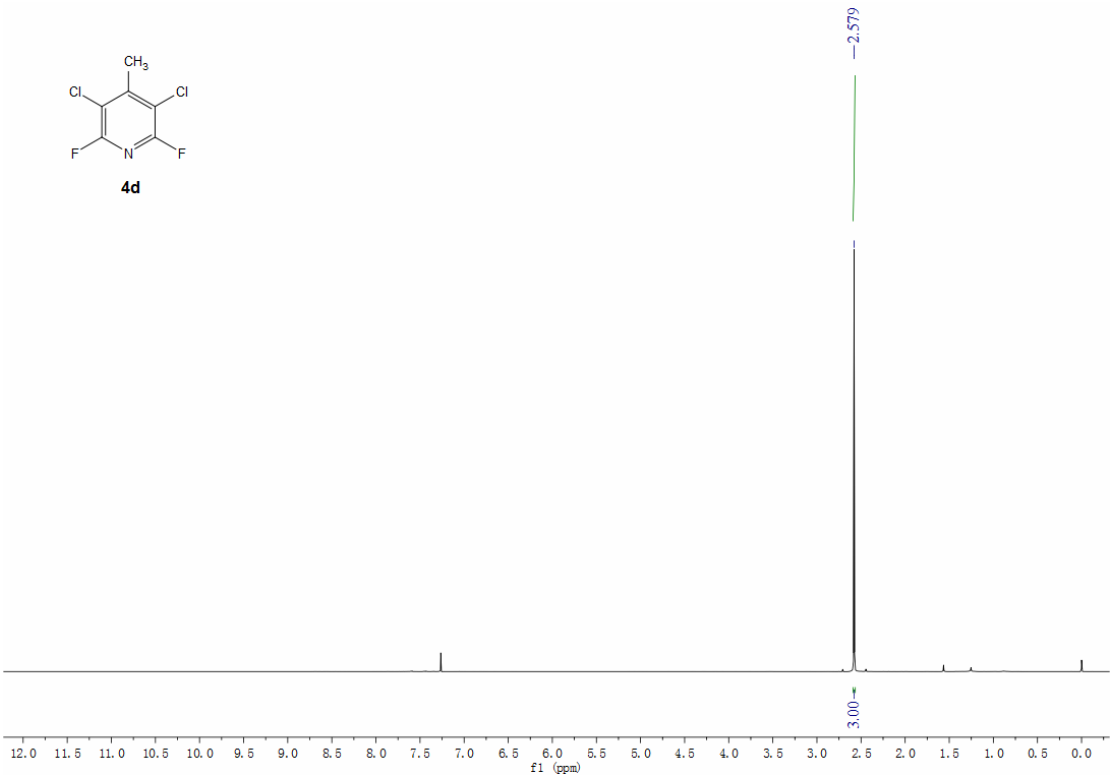


Figure S80. ^{1}H NMR spectrum of **4d**.

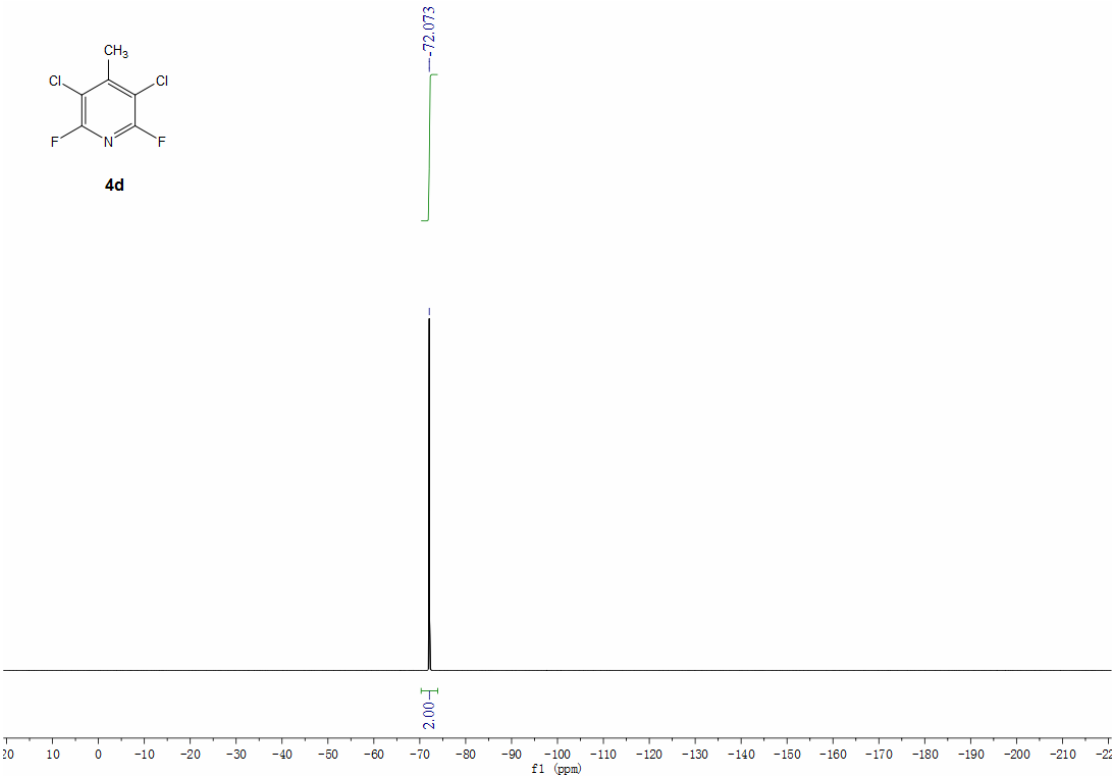


Figure S81. ^{19}F NMR spectrum of **4d**.

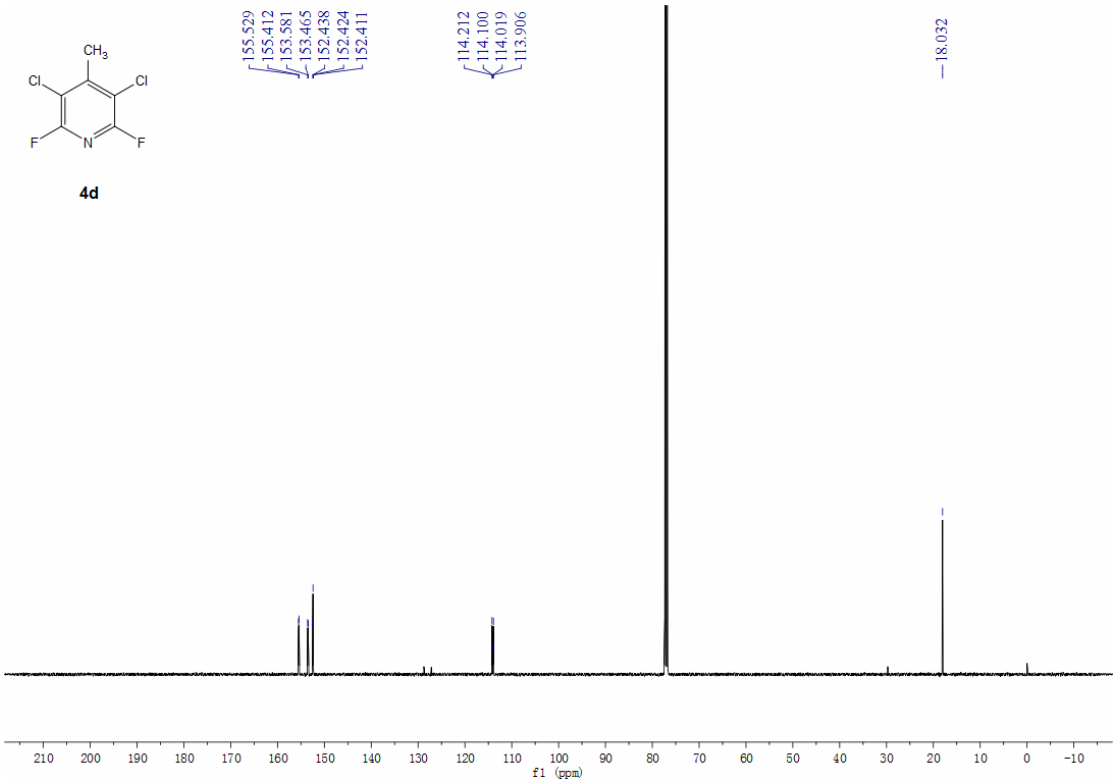


Figure S82. ^{13}C NMR spectrum of **4d**.

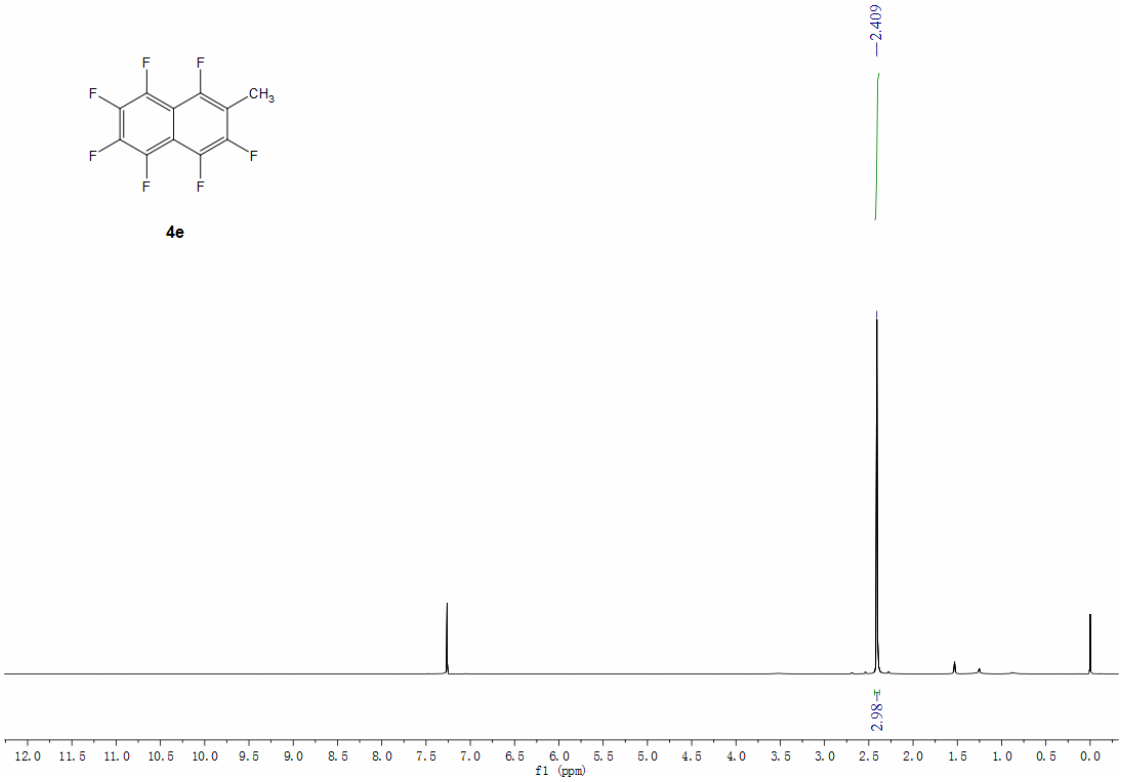


Figure S83. ^{1}H NMR spectrum of **4e**.

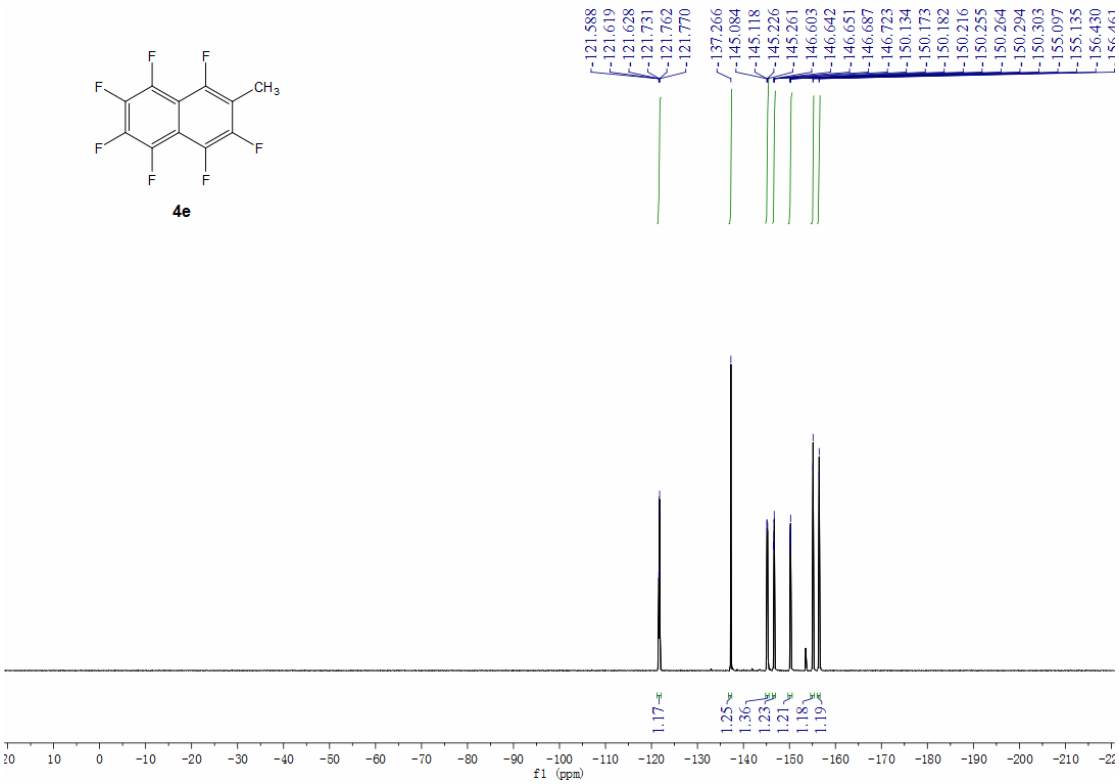


Figure S84. ^{19}F NMR spectrum of **4e**.

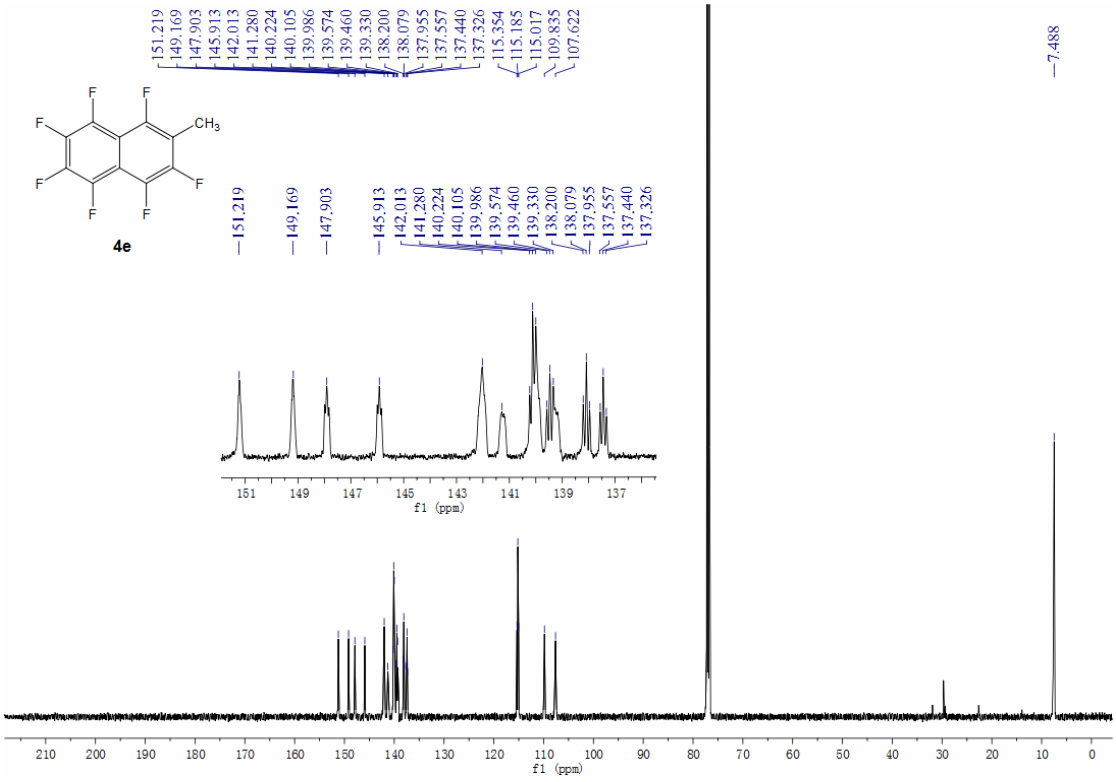


Figure S85. ^{13}C NMR spectrum of **4e**.

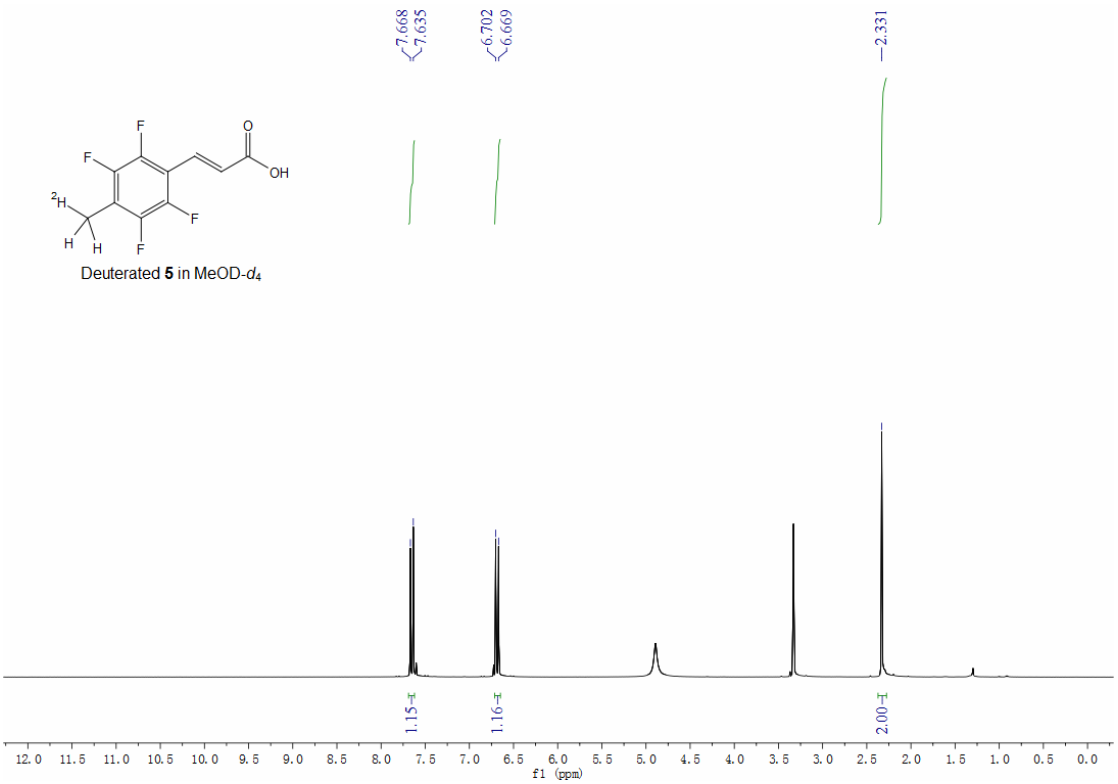


Figure S86. ^{1}H NMR spectrum of **5**.