

Supporting Information

Chemo-, Regio- and Stereoselective Synthesis of Monofluoroalkenes *via* a Tandem Fluorination- Desulfonation Sequence

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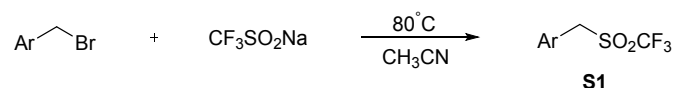
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1. General

^1H NMR (400 MHz, 600 MHz), ^{13}C NMR (100 MHz, 150 MHz) and ^{19}F NMR (376 MHz, 564 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^1H and ^{13}C NMR relative to CHCl_3 , δ 7.26 ppm for ^1H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad). Coupling constants (J) are reported in Hertz (Hz). TLC was developed on silica gel 60 F254 glass plates. The products were purified using a commercial flash chromatography system or a regular glass column. The High-Resolution Mass measurements were conducted using Agilent 7250 GC/Q-TOF equipment.

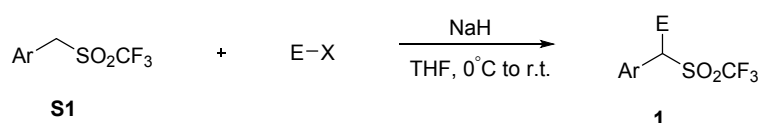
Commercial reagents and solvents were obtained from commercial providers and used without further purification. Work-ups and purifications were performed using commercial reagent-grade solvents. Most benzyl bromides were commercially available from Sigma-Aldrich, TCI, and Bidepharm.

2. General procedure for the synthesis of S1



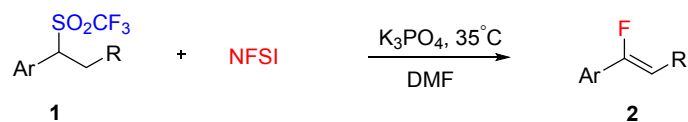
Under nitrogen atmosphere, a mixture of benzyl bromide **1** (1.0 equiv) and NaSO_2CF_3 **2** (2.0 equiv) in acetonitrile (0.2 M) was heated at 80 °C for about 12 to 24 h. The progress of the reaction was monitored by TLC and GC-MS. After completion, the reaction mixture was cooled down to room temperature; the reaction mixture was then concentrated in a vacuum. The residue was washed with dichloromethane and filtered through Celite to give the crude product. The crude product was purified by silica gel chromatography eluted with PE: EtOAc = 20:1 or recrystallization from a mixture of hexane and dichloromethane to give product **S1**.^{1,2}

3. General procedure for the synthesis of 1



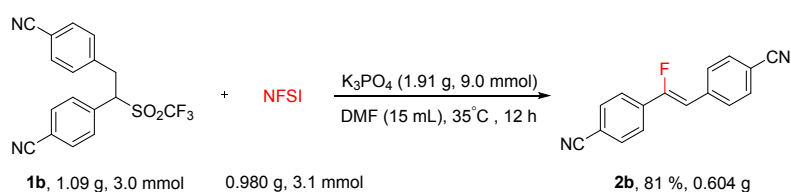
To a solution of **S1** (1.0 equiv.) in THF (0.2 M/L) was added NaH (1.1 equiv) under nitrogen atmosphere at 0 °C. The mixture was stirred at 0 °C for 10 minutes, and then benzyl bromide or alkyl iodide in THF was added via syringe. The mixture was stirred at 0 °C to room temperature for several hours. After completion of the reaction (monitored by TLC), the mixture was diluted with NH_4Cl (aq.), and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , filtered, concentrated under vacuum. The residue was purified by silica gel column chromatography eluting with a mixture of ethyl acetate and petroleum ether to give products **1**.^{1,2}

4. General procedure for the synthesis of monofluoroalkenes (2a-2z)



To a Schlenk tube was added **1** (0.2 mmol, 1.0 equiv), NFSI (0.2 mmol, 1.0 equiv, 65.0 mg) and K_3PO_4 (0.6 mmol, 127 mg) in DMF (1.0 mL). The reaction mixture was stirred at 35 °C for 12-15 h. After completion of the reaction (monitored by TLC), the mixture was diluted with water (10 mL), extracted with ethyl acetate (3 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated under vacuum to give pure products. Compounds **2p-2r** were further purified by column chromatography on silica gel eluting with a mixture of ethyl acetate and petroleum ether (or 100 % petroleum ether) to give the desired product monofluoroalkenes **2**.

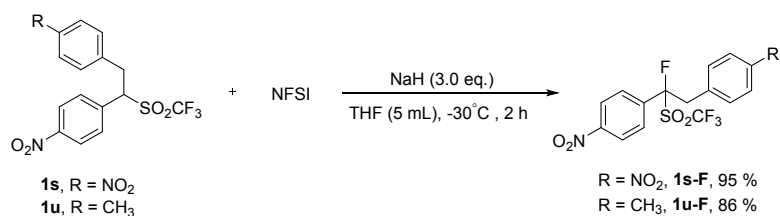
5. Gram scale synthesis of **2b**



To a Schlenk tube was added **1b** (3.0 mmol, 1.09 g, 1.0 equiv), NFSI (3.1 mmol, 0.98 g, 1.0 equiv) and K_3PO_4 (9.0 mmol, 1.91g) in DMF (15 mL). The reaction mixture was stirred at 35 °C for 12 h. After completion of the reaction (monitored by TLC), the mixture was diluted with water (100 mL), and a white solid precipitated. Filtration of the mixture and drying of obtained solids under vacuum gave pure product **2b**.

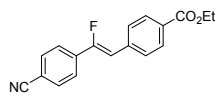
6. Synthesis of intermediate **1s-F** and **1u-F**

Under nitrogen atmosphere, to a solution of **1s** or **1u** (0.5 mmol, 1.0 equiv) and NFSI (0.55 mmol, 170 mg, 1.1 equiv) in THF (5 mL) at -30 °C was added NaH (60% in mineral oil, 60 mg, 1.5 mmol, 3.0 equiv). The reaction mixture was stirred at -30 °C for 1.0 h. After completion of the reaction (monitored by TLC), the mixture was quenched by saturated NH_4Cl (aq.) and extracted with ethyl acetate. Combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated under vacuum. The residue was further purified by silica-gel column chromatography eluting with a mixture of EA and PE to give product **1s-F** and **1u-F**.



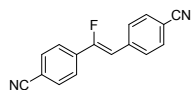
7. The characterization data of compounds

Ethyl (Z)-4-(2-(4-cyanophenyl)-2-fluorovinyl)benzoate (2a)



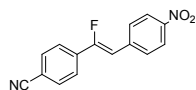
White solid, 48.3 mg, 82%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.08 – 8.05 (m, 2H), 7.77 – 7.70 (m, 6H), 6.49 (d, $J = 38.4$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -96.9 (d, $J = 20.5$ Hz), -112.7 (d, $J = 38.5$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 166.2, 156.5 (d, $J = 261.3$ Hz), 137.0 (d, $J = 3.5$ Hz), 136.5 (d, $J = 28.1$ Hz), 132.5 (d, $J = 2.3$ Hz), 129.9, 129.8 (d, $J = 2.5$ Hz), 129.1 (d, $J = 8.4$ Hz), 124.9 (d, $J = 7.7$ Hz), 118.4, 112.8, 108.3 (d, $J = 9.8$ Hz), 61.1, 14.4. HRMS (EI⁺) calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{NF}$ [M]⁺: 295.1003; found: 295.0999.

(Z)-4,4'-(1-fluoroethene-1,2-diyl)dibenzonitrile (2b)



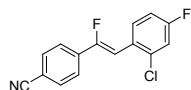
White solid, 45.6 mg, 92%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.79 – 7.73 (m, 6H), 7.68 (d, $J = 8.4$ Hz, 2H), 6.47 (d, $J = 37.8$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -94.0 (d, $J = 19.9$ Hz), δ : -111.0 (d, $J = 37.8$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 157.3 (d, $J = 263.1$ Hz), 137.2 (d, $J = 3.2$ Hz), 136.0 (d, $J = 28.3$ Hz), 132.6 (d, $J = 2.3$ Hz), 132.5, 129.6 (d, $J = 8.6$ Hz), 125.1 (d, $J = 7.7$ Hz), 118.7 (CN), 118.2 (CN), 113.3, 111.4 (d, $J = 3.0$ Hz), 107.5 (d, $J = 9.5$ Hz). HRMS (EI⁺) calcd. for $\text{C}_{16}\text{H}_9\text{N}_2\text{F}$ [M]⁺: 248.0744; found: 248.0748.

(Z)-4-(1-fluoro-2-(4-nitrophenyl)vinyl)benzonitrile (2c)



Yellow solid, 43.4 mg, 81%; ^1H NMR (600 MHz, Chloroform-*d*) δ : 8.26 (d, $J = 8.9$ Hz, 2H), 7.81 – 7.79 (m, 4H), 7.75 (d, $J = 8.5$ Hz, 2H), 6.53 (d, $J = 37.6$ Hz, 1H). ^{19}F NMR (565 MHz, Chloroform-*d*) δ : -92.8 (d, $J = 20.1$ Hz), -110.3 (d, $J = 37.6$ Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 157.6 (d, $J = 264.0$ Hz), 146.9, 139.1 (d, $J = 3.4$ Hz), 135.9 (d, $J = 27.7$ Hz), 132.6 (d, $J = 2.2$ Hz), 129.8 (d, $J = 8.8$ Hz), 125.2 (d, $J = 7.7$ Hz), 124.0, 118.2, 113.4, 107.1 (d, $J = 9.5$ Hz). HRMS (EI⁺) calcd. for $\text{C}_{15}\text{H}_9\text{O}_2\text{N}_2\text{F}$ [M]⁺: 268.0643; found: 268.0646.

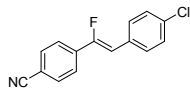
(Z)-4-(2-(2-Chloro-4-fluorophenyl)-1-fluorovinyl)benzonitrile (2d)



White solid, 39.0 mg, 71%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.96 (dd, $J = 8.9, 6.1$ Hz, 1H), 7.76-7.70 (m, 4H), 7.18 (dd, $J = 8.4, 2.7$ Hz, 1H), 7.05 (td, $J = 8.4, 2.7$ Hz, 1H), 6.81 (d, $J = 37.7$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -99.7 (d, $J = 19.9$ Hz), -110.2 (q, $J = 7.9$ Hz), -116.2 (d, $J = 37.9$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 161.7 (d, $J = 250.0$ Hz), 156.0 (d, $J = 259.9$ Hz), 136.5 (d, $J = 28.6$ Hz), 134.3 (dd, $J = 10.0, 1.2$ Hz), 132.5 (d, $J = 2.2$ Hz), 131.8 (dd, $J = 14.1, 8.7$ Hz), 126.9 (t,

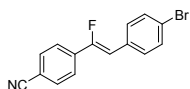
$J = 3.7$ Hz), 124.9 (d, $J = 7.6$ Hz), 118.4 (CN), 117.1 (d, $J = 24.8$ Hz), 114.6 (d, $J = 21.3$ Hz), 112.7, 103.8 (dd, $J = 8.5, 1.4$ Hz). HRMS (EI⁺) calcd. for C₁₅H₈NF₂Cl [M]⁺: 275.0308; found: 275.0305.

(Z)-4-(2-(4-Chlorophenyl)-1-fluorovinyl)benzonitrile (2e)



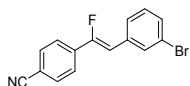
White solid, 43.4 mg, 79%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.73 – 7.68 (m, 4H), 7.59 – 7.56 (m, 2H), 7.38 – 7.34 (m, 2H), 6.40 (d, $J = 38.5$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -115.2 (d, $J = 38.6$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 155.5 (d, $J = 258.9$ Hz), 136.7 (d, $J = 28.4$ Hz), 134.0 (d, $J = 3.8$ Hz), 132.5 (d, $J = 2.4$ Hz), 131.2 (d, $J = 3.2$ Hz), 130.5 (d, $J = 8.4$ Hz), 129.0, 124.6 (d, $J = 7.7$ Hz), 118.4 (CN), 112.5, 108.0 (d, $J = 10.1$ Hz). HRMS (EI⁺) calcd. for C₁₅H₉NFCl [M]⁺: 257.0402; found: 275.0406.

(Z)-4-(2-(4-Bromophenyl)-1-fluorovinyl)benzonitrile (2f)



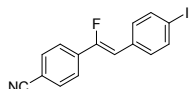
White solid, 43.9 mg, 73%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.73 – 7.68 (m, 4H), 7.51 (brs, 4H), 6.38 (d, $J = 38.4$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -98.8 (d, $J = 20.8$ Hz), -114.8 (d, $J = 38.6$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 155.6 (d, $J = 259.1$ Hz), 136.7 (d, $J = 28.1$ Hz), 132.5 (d, $J = 2.3$ Hz), 131.9, 131.6 (d, $J = 3.2$ Hz), 130.8 (d, $J = 8.3$ Hz), 124.6 (d, $J = 7.7$ Hz), 122.3 (d, $J = 3.7$ Hz), 118.4 (CN), 112.5, 108.1 (d, $J = 10.1$ Hz). HRMS (EI⁺) calcd. for C₁₅H₉NFBr [M]⁺: 300.9897; found: 300.9903.

(Z)-4-(2-(3-Bromophenyl)-1-fluorovinyl)benzonitrile (2g)



White solid, 46.9 mg, 78%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.82 (t, $J = 1.8$ Hz, 1H), 7.74 – 7.69 (m, 4H), 7.55 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.45-7.43 (m, 1H), 7.28 – 7.24 (m, 1H), 6.37 (d, $J = 38.2$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -98.4 (d, $J = 20.6$ Hz), -113.8 (d, $J = 38.2$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 156.0 (d, $J = 260.1$ Hz), 136.5 (d, $J = 28.3$ Hz), 134.7 (d, $J = 3.3$ Hz), 132.5 (d, $J = 2.3$ Hz), 132.0 (d, $J = 9.0$ Hz), 131.2 (d, $J = 2.4$ Hz), 130.2, 127.8 (d, $J = 7.9$ Hz), 124.8 (d, $J = 7.7$ Hz), 122.8, 118.4, 112.7, 107.8 (d, $J = 9.9$ Hz). HRMS (EI⁺) calcd. for C₁₅H₉NFBr [M]⁺: 300.9897; found: 300.9901.

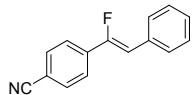
(Z)-4-(1-Fluoro-2-(4-iodophenyl)vinyl)benzonitrile (2h)



White solid, 50.2 mg, 72%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.73 – 7.68 (m, 6H), 7.39 – 7.26 (m, 2H), 6.37 (d, $J = 38.5$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -98.6 (d, $J = 20.7$ Hz), -114.4 (d, $J = 38.4$ Hz). ¹³C NMR (150 MHz, Chloroform-*d*) δ : 155.8 (d, $J = 259.3$ Hz), 137.9, 136.6 (d, $J = 28.2$

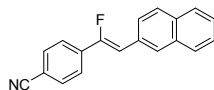
Hz), 132.5 (d, $J = 2.2$ Hz), 132.1 (d, $J = 3.1$ Hz), 130.9 (d, $J = 8.3$ Hz), 124.7 (d, $J = 7.3$ Hz), 118.5 (CN), 112.5, 108.2 (d, $J = 10.0$ Hz), 94.0 (d, $J = 3.8$ Hz). HRMS (EI⁺) calcd. for C₁₅H₉NFI [M]⁺: 348.9758; found: 348.9764.

(Z)-4-(1-fluoro-2-phenylvinyl)benzonitrile (2i)



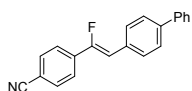
White solid, 31.2 mg, 70%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.75 – 7.65 (m, 6H), 7.43-7.39 (m, 2H), 7.37 – 7.29 (m, 1H), 6.46 (d, $J = 39.0$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -116.0 (d, $J = 38.9$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 155.2 (d, $J = 258.3$ Hz), 137.0 (d, $J = 28.4$ Hz), 132.7 (d, $J = 3.3$ Hz), 132.4 (d, $J = 2.3$ Hz), 129.4 (d, $J = 8.1$ Hz), 128.8, 128.3 (d, $J = 2.6$ Hz), 124.6 (d, $J = 7.6$ Hz), 118.5 (CN), 112.2, 109.2 (d, $J = 10.1$ Hz). HRMS (EI⁺) calcd. for C₁₅H₁₀NF [M]⁺: 223.0792; found: 223.0798.

(Z)-4-(1-fluoro-2-(naphthalen-2-yl)vinyl)benzonitrile (2j)



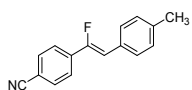
White solid, 43.6 mg, 80%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 8.05 (d, $J = 1.6$ Hz, 1H), 7.83 – 7.77 (m, 4H), 7.68 (d, $J = 8.6$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 7.48 (dt, $J = 6.3, 3.2$ Hz, 2H), 6.54 (d, $J = 39.0$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -115.8 (d, $J = 39.1$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 155.4 (d, $J = 258.3$ Hz), 137.0 (d, $J = 28.3$ Hz), 133.4, 133.0 (d, $J = 2.1$ Hz), 132.4 (d, $J = 2.3$ Hz), 130.3 (d, $J = 3.5$ Hz), 129.0 (d, $J = 8.2$ Hz), 128.4, 128.3, 127.7, 126.7, 126.7 (d, $J = 3.1$ Hz), 126.5, 124.5 (d, $J = 7.7$ Hz), 118.6 (CN), 112.2, 109.3 (d, $J = 9.9$ Hz). HRMS (EI⁺) calcd. for C₁₉H₁₂NF [M]⁺: 273.0948; found: 273.0954.

(Z)-4-(2-([1,1'-Biphenyl]-4-yl)-1-fluorovinyl)benzonitrile (2k)



White solid, 48.4 mg, 81%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.77 – 7.70 (m, 6H), 7.66 – 7.63 (m, 4H), 7.48-7.45 (m, 2H), 7.39 – 7.36 (m, 1H), 6.50 (d, $J = 39.0$ Hz, 1H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : -99.9 (d, $J = 21.3$ Hz), -115.8 (d, $J = 39.0$ Hz). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 155.3 (d, $J = 258.2$ Hz), 140.9 (d, $J = 2.8$ Hz), 140.3, 137.0 (d, $J = 28.4$ Hz), 132.5 (d, $J = 2.3$ Hz), 131.7 (d, $J = 3.4$ Hz), 129.8 (d, $J = 8.1$ Hz), 128.9, 127.7, 127.4, 127.0, 124.5 (d, $J = 7.6$ Hz), 118.6 (CN), 112.2, 108.9 (d, $J = 10.2$ Hz). HRMS (EI⁺) calcd. for C₂₁H₁₄NF [M]⁺: 299.1105; found: 299.1109.

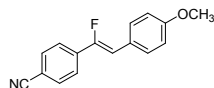
(Z)-4-(1-Fluoro-2-(*p*-tolyl)vinyl)benzonitrile (2l)



White solid, 35.1 mg, 74%; ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.73 – 7.67 (m, 4H), 7.55 (d, $J = 8.2$

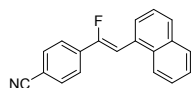
Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.42 (d, $J = 39.2$ Hz, 1H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -117.1 (d, $J = 39.3$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 154.6 (d, $J = 256.5$ Hz), 138.5 (d, $J = 2.7$ Hz), 137.2 (d, $J = 28.3$ Hz), 132.4 (d, $J = 2.5$ Hz), 129.9 (d, $J = 3.2$ Hz), 129.5, 129.3 (d, $J = 8.0$ Hz), 124.4 (d, $J = 7.7$ Hz), 118.6 (CN), 111.9, 109.2 (d, $J = 10.2$ Hz), 21.4. HRMS (EI^+) calcd. for $\text{C}_{16}\text{H}_{12}\text{NF}$ [$\text{M}]^+$: 237.0948; found: 237.0949.

(Z)-4-(1-Fluoro-2-(4-methoxyphenyl)vinyl)benzonitrile (2m)



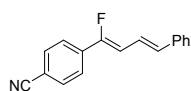
White solid, 38.0 mg, 75%; ^1H NMR (400 MHz, Chloroform- d) δ : 7.72 – 7.66 (m, 4H), 7.62 – 7.60 (m, 2H), 6.95 – 6.92 (m, 2H), 6.41 (d, $J = 39.3$ Hz, 1H), 3.85 (s, 3H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -102.7 (d, $J = 21.6$ Hz), -119.1 (d, $J = 39.4$ Hz). ^{13}C NMR (150 MHz, Chloroform- d) δ : 159.6, 153.9 (d, $J = 255.4$ Hz), 137.3 (d, $J = 28.4$ Hz), 132.4 (d, $J = 2.2$ Hz), 130.8 (d, $J = 8.3$ Hz), 125.4 (d, $J = 3.3$ Hz), 124.2 (d, $J = 7.7$ Hz), 118.7 (CN), 114.2, 111.6, 108.8 (d, $J = 10.5$ Hz), 55.3. HRMS (EI^+) calcd. for $\text{C}_{16}\text{H}_{12}\text{ONF}$ [$\text{M}]^+$: 253.0897; found: 253.0904.

(Z)-4-(1-Fluoro-2-(naphthalen-1-yl)vinyl)benzonitrile (2n)



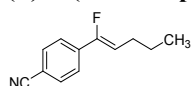
White solid, 42.5 mg, 78%; ^1H NMR (400 MHz, Chloroform- d) δ : 8.07 (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 7.3$ Hz, 1H), 7.91 – 7.83 (m, 4H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.59 – 7.52 (m, 3H), 7.16 (d, $J = 36.3$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -102.4 (d, $J = 20.7$ Hz), -116.6 (d, $J = 36.1$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 155.8 (d, $J = 257.5$ Hz), 137.0 (d, $J = 28.8$ Hz), 133.7, 132.5 (d, $J = 2.4$ Hz), 131.5, 128.9, 128.9, 128.6 (d, $J = 2.2$ Hz), 127.9 (d, $J = 10.0$ Hz), 126.6, 126.0, 125.6, 124.8 (d, $J = 7.4$ Hz), 123.7, 118.6 (CN), 112.4, 105.7 (d, $J = 11.6$ Hz). HRMS (EI^+) calcd. for $\text{C}_{19}\text{H}_{12}\text{NF}$ [$\text{M}]^+$: 273.0948; found: 273.0952.

4-((1Z, 3E)-1-Fluoro-4-phenylbuta-1,3-dien-1-yl)benzonitrile (2o)



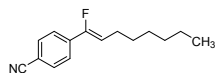
White solid, 37.3 mg, 75%; ^1H NMR (400 MHz, Chloroform- d) δ : 7.69-7.64 (m, 4H), 7.49 (d, $J = 7.3$ Hz, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.19 (m, 1H), 6.76 (d, $J = 15.8$ Hz, 1H), 6.41 (ddd, $J = 34.1, 11.0, 0.8$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -103.2 (d, $J = 19.9$ Hz), -119.4 (d, $J = 34.5$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 154.9 (d, $J = 255.0$ Hz), 136.8 (d, $J = 1.7$ Hz), 136.1 (d, $J = 27.9$ Hz), 134.9 (d, $J = 3.8$ Hz), 132.4 (d, $J = 2.6$ Hz), 128.8, 128.4, 126.8, 124.2 (d, $J = 7.5$ Hz), 120.2 (d, $J = 5.2$ Hz), 118.6 (CN), 111.9, 110.4 (d, $J = 13.8$ Hz). HRMS (EI^+) calcd. for $\text{C}_{17}\text{H}_{12}\text{NF}$ [$\text{M}]^+$: 249.0948; found: 249.0950.

(Z)-4-(1-Fluoropent-1-en-1-yl)benzonitrile (2p)



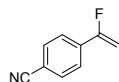
Colorless oil, 25.7 mg, 68%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.64 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 5.59 (dt, J = 36.8, 7.7 Hz, 1H), 2.30 (qd, J = 7.5, 1.9 Hz, 2H), 1.55-1.46 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -105.3 (d, J = 22.6 Hz), -122.3 (d, J = 36.8 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 155.1 (d, J = 245.8 Hz), 136.9 (d, J = 29.6 Hz), 132.3 (d, J = 2.3 Hz), 124.2 (d, J = 7.2 Hz), 118.7 (CN), 111.6, 110.2 (d, J = 17.4 Hz), 26.3 (d, J = 4.4 Hz), 22.4, 13.8. HRMS (EI $^+$) calcd. for $\text{C}_{12}\text{H}_{12}\text{NF}$ [M] $^+$: 189.0948; found: 189.0951.

(*Z*)-4-(1-Fluorooct-1-en-1-yl)benzonitrile (2q)



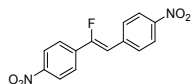
Colorless oil, 33.2 mg, 72%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.64 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 5.59 (dt, J = 36.7, 7.6 Hz, 1H), 2.31 (qd, J = 7.5, 1.9 Hz, 2H), 1.50-1.43 (m, 2H), 1.39 – 1.25 (m, 7H), 0.89 (t, J = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -105.5 (d, J = 22.9 Hz), -122.4 (d, J = 36.8 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 155.0 (d, J = 245.3 Hz), 136.9 (d, J = 29.6 Hz), 132.3 (d, J = 2.3 Hz), 124.2 (d, J = 6.9 Hz), 118.7 (CN), 111.6, 110.5 (d, J = 17.5 Hz), 31.6, 29.1, 29.0, 24.4 (d, J = 4.5 Hz), 22.6, 14.1. HRMS (EI $^+$) calcd. for $\text{C}_{15}\text{H}_{18}\text{NF}$ [M] $^+$: 231.1418; found: 231.1419.

4-(1-Fluorovinyl)benzonitrile (2r)³



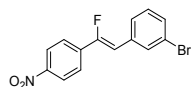
Colorless oil, 15.2 mg, 52%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.70 – 7.64 (m, 4H), 5.27 – 5.03 (m, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -108.9 (dd, J = 48.7, 17.3 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 159.5 (d, J = 263.7 Hz), 138.4, 132.3, 131.9 (d, J = 27.1 Hz), 130.0, 129.3 (d, J = 8.6 Hz), 128.8, 124.7 (d, J = 7.5 Hz), 119.0 (CN), 110.3, 104.4 (d, J = 9.9 Hz).

(*Z*)-4,4'-(1-Fluoroethene-1,2-diyl)bis(nitrobenzene) (2s)



Yellow solid, 47.9 mg, 83%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.32 (d, J = 8.6 Hz, 2H), 8.30 – 8.24 (m, 2H), 7.92 – 7.79 (m, 4H), 6.58 (d, J = 37.4 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -109.7 (d, J = 37.5 Hz). ^{13}C NMR (150 MHz, Chloroform-*d*) δ : 157.4 (d, J = 263.9 Hz), 148.4, 147.0 (d, J = 3.1 Hz), 139.0 (d, J = 3.4 Hz), 137.6 (d, J = 27.6 Hz), 129.9 (d, J = 8.8 Hz), 125.5 (d, J = 7.7 Hz), 124.2 (d, J = 2.1 Hz), 124.1, 107.8 (d, J = 9.4 Hz). HRMS (EI $^+$) calcd. for $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_2\text{F}$ [M] $^+$: 288.0541; found: 288.0545.

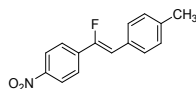
(*Z*)-1-Bromo-3-(2-fluoro-2-(4-nitrophenyl)vinyl)benzene (2t)



Yellow solid, 49.3 mg, 77%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.29 (d, J = 8.8 Hz, 2H), 7.85 (t, J = 1.9 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.58 (dt, J = 7.8, 1.3 Hz, 1H), 7.46 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 6.45 (d, J = 38.1 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -113.2 (d, J

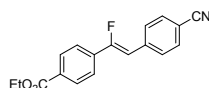
= 38.1 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 155.8 (d, $J = 260.1$ Hz), 147.9, 138.3 (d, $J = 28.1$ Hz), 134.6 (d, $J = 3.3$ Hz), 132.1 (d, $J = 9.1$ Hz), 131.4 (d, $J = 2.4$ Hz), 130.2, 127.9 (d, $J = 8.0$ Hz), 125.0 (d, $J = 7.6$ Hz), 124.1 (d, $J = 2.3$ Hz), 122.9, 108.5 (d, $J = 9.9$ Hz). HRMS (EI⁺) calcd. for $\text{C}_{14}\text{H}_9\text{O}_2\text{NFBBr} [\text{M}]^+$: 320.9795; found: 320.9802.

(Z)-1-(2-Fluoro-2-(4-nitrophenyl)vinyl)-4-methylbenzene (2u)



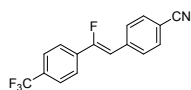
Yellow solid, 38.1 mg, 74%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.26 (d, $J = 8.7$ Hz, 2H), 7.77 (d, $J = 9.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 6.49 (d, $J = 39.1$ Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -101.5 (d, $J = 21.6$ Hz), -116.5 (d, $J = 39.0$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 154.5 (d, $J = 256.7$ Hz), 147.5, 139.0 (d, $J = 28.1$ Hz), 138.7 (d, $J = 2.6$ Hz), 129.8 (d, $J = 3.3$ Hz), 129.5, 129.4 (d, $J = 8.1$ Hz), 124.6 (d, $J = 7.5$ Hz), 124.0 (d, $J = 2.3$ Hz), 110.0 (d, $J = 10.2$ Hz), 21.4. HRMS (EI⁺) calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{NF} [\text{M}]^+$: 257.0847; found: 257.0850.

Ethyl (Z)-4-(2-(4-cyanophenyl)-1-fluorovinyl)benzoate (2v)



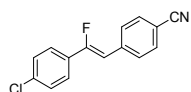
White solid, 41.0 mg, 69%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.11 (d, $J = 8.3$ Hz, 2H), 7.75 – 7.72 (m, 4H), 7.67 (d, $J = 8.5$ Hz, 2H), 6.45 (d, $J = 38.0$ Hz, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -91.8 (d, $J = 20.1$ Hz), -109.9 (d, $J = 38.0$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 165.8, 158.4 (d, $J = 263.5$ Hz), 137.7 (d, $J = 3.2$ Hz), 136.0, 132.4, 131.5, 130.0 (d, $J = 2.1$ Hz), 129.5 (d, $J = 8.6$ Hz), 124.5 (d, $J = 7.7$ Hz), 118.8 (CN), 110.9 (d, $J = 3.1$ Hz), 106.4 (d, $J = 9.7$ Hz), 61.3, 14.3. HRMS (EI⁺) calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{NF} [\text{M}]^+$: 295.1003; found: 295.1006.

(Z)-4-(2-Fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)benzonitrile (2w)



White solid, 44.2 mg, 76%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.79 – 7.66 (m, 8H), 6.43 (d, $J = 38.0$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -62.8, -110.1 (d, $J = 38.2$ Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 157.9 (d, $J = 263.4$ Hz), 137.5 (d, $J = 2.9$ Hz), 135.3 (d, $J = 27.4$ Hz), 132.4, 131.6 (q, $J = 32.9$ Hz), 129.5 (d, $J = 8.6$ Hz), 125.8 (dt, $J = 6.1, 3.7$ Hz), 124.9 (d, $J = 7.6$ Hz), 123.8 (q, $J = 27.2$ Hz), 118.8 (CN), 111.0 (d, $J = 3.2$ Hz), 106.5 (d, $J = 9.6$ Hz). HRMS (EI⁺) calcd. for $\text{C}_{16}\text{H}_9\text{NF}_4 [\text{M}]^+$: 291.0666; found: 291.0670.

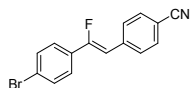
(Z)-4-(2-(4-Chlorophenyl)-2-fluorovinyl)benzonitrile (2x)



White solid, 37.1 mg, 72%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.70 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J =$

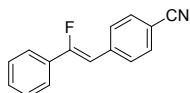
8.5 Hz, 2H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 6.30 (d, $J = 38.2$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -90.5 (d, $J = 20.0$ Hz), -109.4 (d, $J = 38.3$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 158.5 (d, $J = 263.1$ Hz), 138.0 (d, $J = 3.0$ Hz), 136.0, 132.4, 130.4 (d, $J = 28.1$ Hz), 129.3 (d, $J = 8.5$ Hz), 129.1 (d, $J = 2.1$ Hz), 126.0 (d, $J = 7.6$ Hz), 118.9 (CN), 110.6 (d, $J = 3.2$ Hz), 104.9 (d, $J = 9.9$ Hz). HRMS (EI $^+$) calcd. for $\text{C}_{15}\text{H}_9\text{NFCI}$ $[\text{M}]^+$: 257.0402; found: 257.0407.

(Z)-4-(2-(4-Bromophenyl)-2-fluorovinyl)benzonitrile (2y)



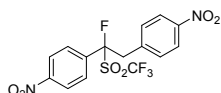
White solid, 47.6 mg, 79%; ^1H NMR (400 MHz, Chloroform- d) δ : 7.71 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.54 – 7.52 (m, 2H), 6.32 (d, $J = 38.2$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -90.9 (d, $J = 20.2$ Hz), -109.6 (d, $J = 38.2$ Hz). ^{13}C NMR (100 MHz, Chloroform- d) δ : 158.5 (d, $J = 263.1$ Hz), 137.9 (d, $J = 3.2$ Hz), 132.4, 132.0 (d, $J = 2.1$ Hz), 130.8 (d, $J = 28.0$ Hz), 129.3 (d, $J = 8.7$ Hz), 126.1 (d, $J = 7.6$ Hz), 124.3, 118.9 (CN), 110.6 (d, $J = 3.2$ Hz), 105.0 (d, $J = 9.7$ Hz). HRMS (EI $^+$) calcd. for $\text{C}_{15}\text{H}_9\text{NFBBr}$ $[\text{M}]^+$: 300.9897; found: 300.9900.

(Z)-4-(2-Fluoro-2-phenylvinyl)benzonitrile (2z)



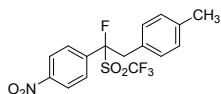
White solid, 36.1 mg, 81%; ^1H NMR (400 MHz, Chloroform- d) δ : 7.72 – 7.62 (m, 6H), 7.45-7.42 (m, 3H), 6.32 (d, $J = 38.4$ Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -109.0 (d, $J = 38.5$ Hz). ^{13}C NMR (150 MHz, Chloroform- d) δ : 159.5 (d, $J = 263.7$ Hz), 138.4, 132.3, 131.9 (d, $J = 27.1$ Hz), 130.0, 129.3 (d, $J = 8.6$ Hz), 128.8, 124.7 (d, $J = 7.5$ Hz), 119.0 (CN), 110.3, 104.4 (d, $J = 9.9$ Hz). HRMS (EI $^+$) calcd. for $\text{C}_{15}\text{H}_{10}\text{NF}$ $[\text{M}]^+$: 223.0792; found: 223.0791.

4,4'-(1-Fluoro-1-((trifluoromethyl)sulfonyl)ethane-1,2-diyl)bis(nitrobenzene) (1s-F)



Pale yellow solid, 200.0 mg, 95%; ^1H NMR (400 MHz, Chloroform- d) δ : 8.29 (d, $J = 8.8$ Hz, 2H), 8.06 (d, $J = 8.6$ Hz, 2H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 4.16-4.09 (m, 1H), 3.97-3.84 (m, 1H). ^{19}F NMR (376 MHz, Chloroform- d) δ : -68.7 (d, $J = 9.6$ Hz), -155.0 (dp, $J = 39.6, 9.9$ Hz). ^{13}C NMR (150 MHz, Chloroform- d) δ : 148.6 (d, $J = 225.0$ Hz), 136.7, 135.0 (d, $J = 20.8$ Hz), 131.6, 129.7 (d, $J = 50.1$ Hz), 127.7 (d, $J = 9.9$ Hz), 124.1 (d, $J = 2.2$ Hz), 123.8, 120.0 (q, $J = 332.3$ Hz), 110.5 (d, $J = 232.8$ Hz), 38.7 (d, $J = 19.4$ Hz). HRMS (ESI $^-$) calcd. for $\text{C}_{15}\text{H}_9\text{O}_6\text{N}_2\text{F}_4\text{S}$ $[\text{M-H}]^-$: 421.0123; found: 421.0111.

1-(2-Fluoro-2-(4-nitrophenyl)-2-((trifluoromethyl)sulfonyl)ethyl)-4-methylbenzene (1u-F)



Pale yellow solid, 168.1 mg, 86%; ^1H NMR (400 MHz, Chloroform-*d*) δ : 8.25 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 7.8 Hz, 2H), 6.85 (d, J = 7.7 Hz, 2H), 4.00-3.93 (m, 1H), 3.80-3.66 (m, 1H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ : -69.0 (d, J = 9.6 Hz), -154.8 (dp, J = 40.5, 9.9 Hz). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 149.1, 138.1, 135.8 (d, J = 20.8 Hz), 130.5, 129.4, 127.9 (d, J = 9.9 Hz), 126.0, 123.7 (d, J = 2.2 Hz), 120.1 (d, J = 332.4 Hz), 111.3 (d, J = 231.2 Hz), 38.5 (d, J = 19.5 Hz), 21.0. HRMS (ESI $^-$) calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_4\text{NF}_4\text{S}$ [M-H] $^-$: 390.0429; found: 390.0423.

8. References

- (1) Y. Maekawa, M. Nambo, D. Yokogawa, C. M. Crudden, *J. Am. Chem. Soc.* **2020**, *142*, 15667-15672.
- (2) R.-Y. Yang, H. Wang, B. Xu, *Chem. Commun.* **2021**, *57*, 4831-4834.
- (3) Y. Su, M. Bai, J.-B. Qiao, X.-J. Li, R. Li, Y.-Q. Tu, P. Gu, *Tetrahedron Lett.* **2015**, *56*, 1805-1807.

9. Copies of NMR spectra

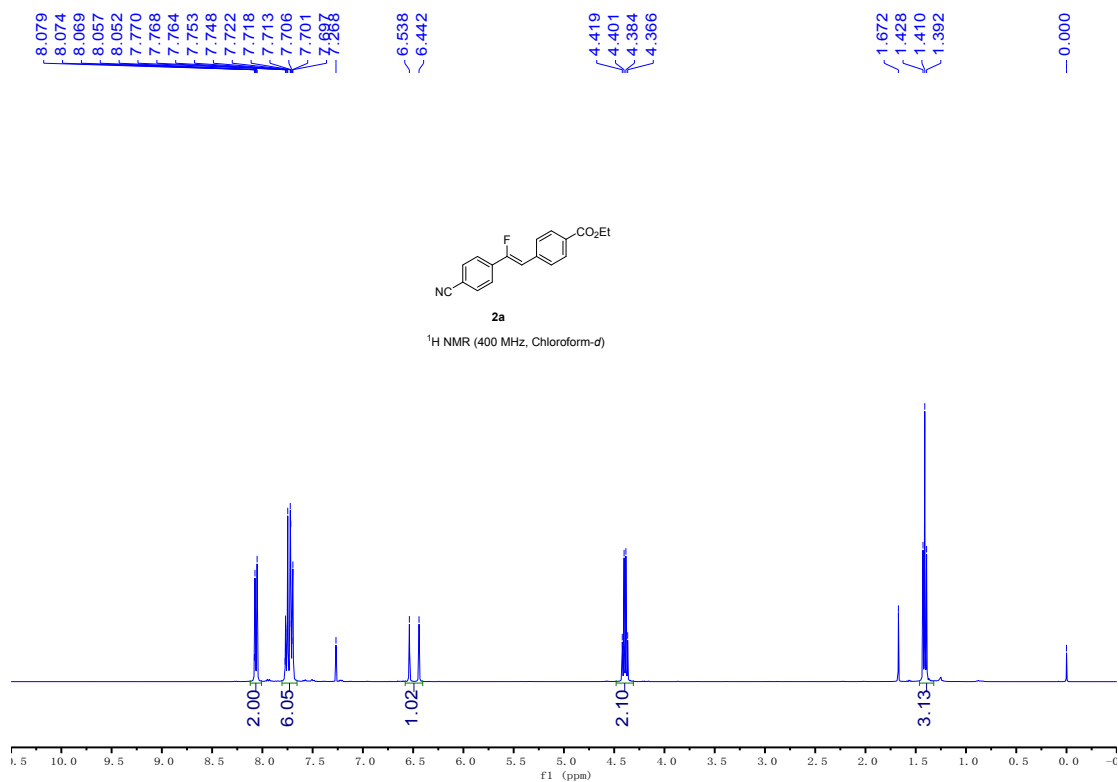


Figure S 1

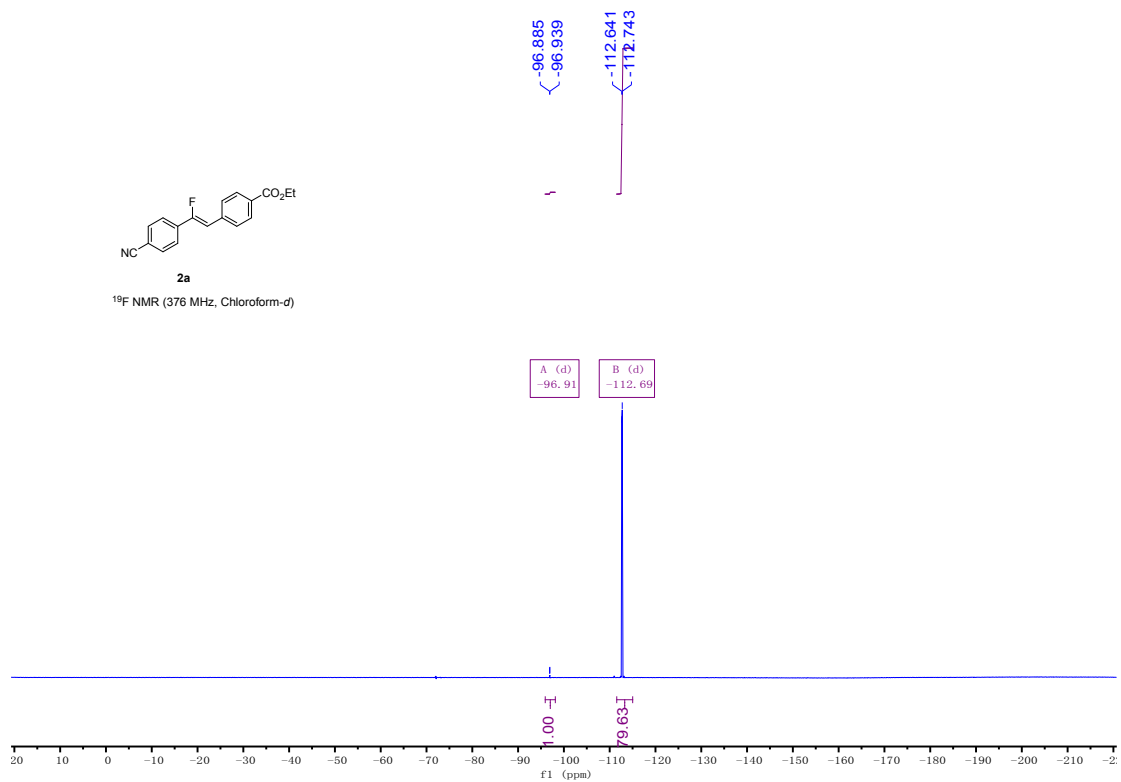


Figure S 2

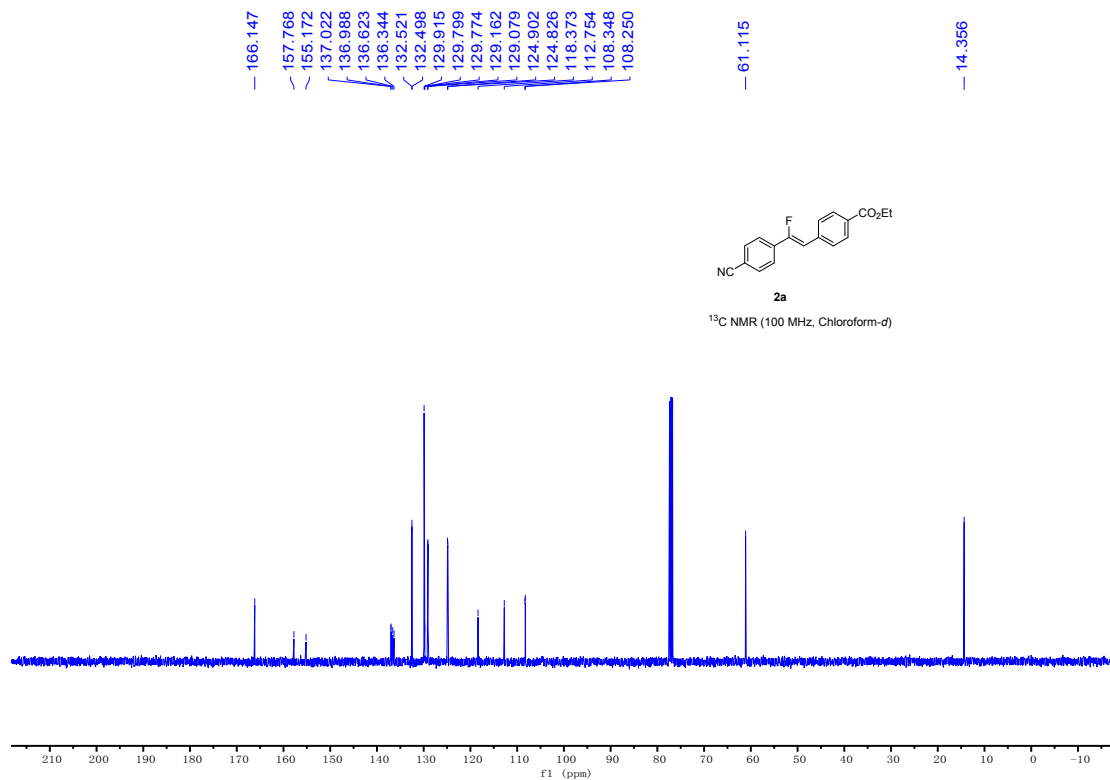


Figure S 3

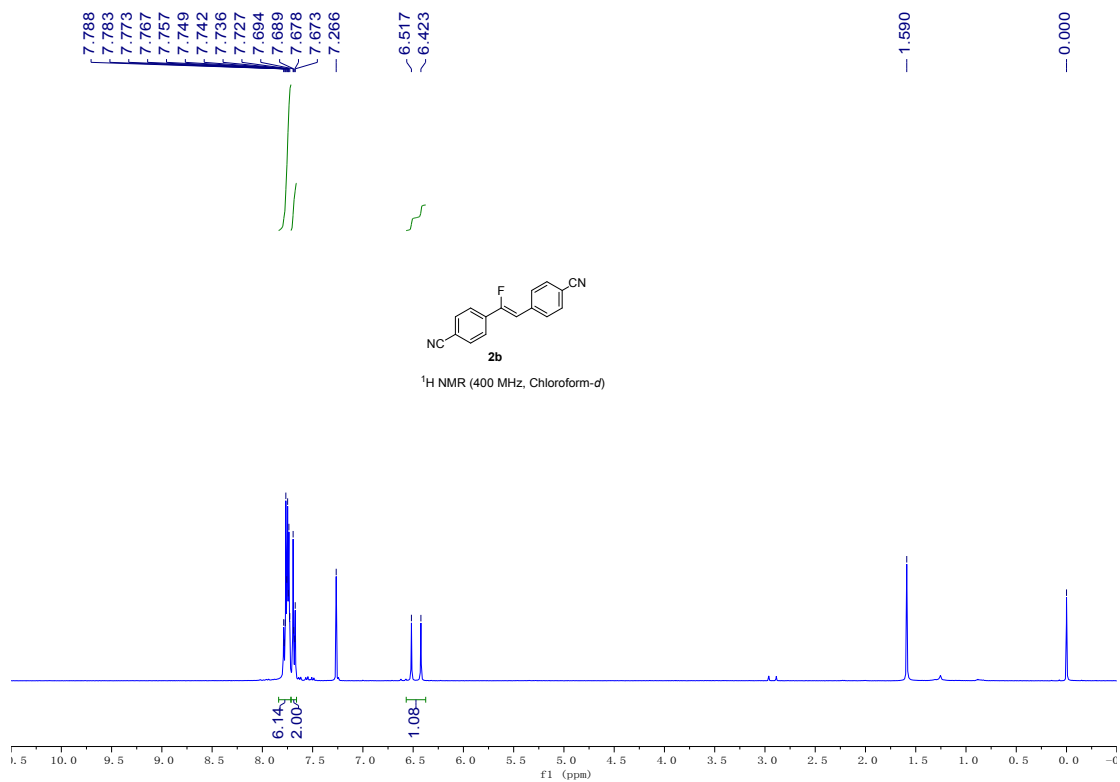


Figure S 4

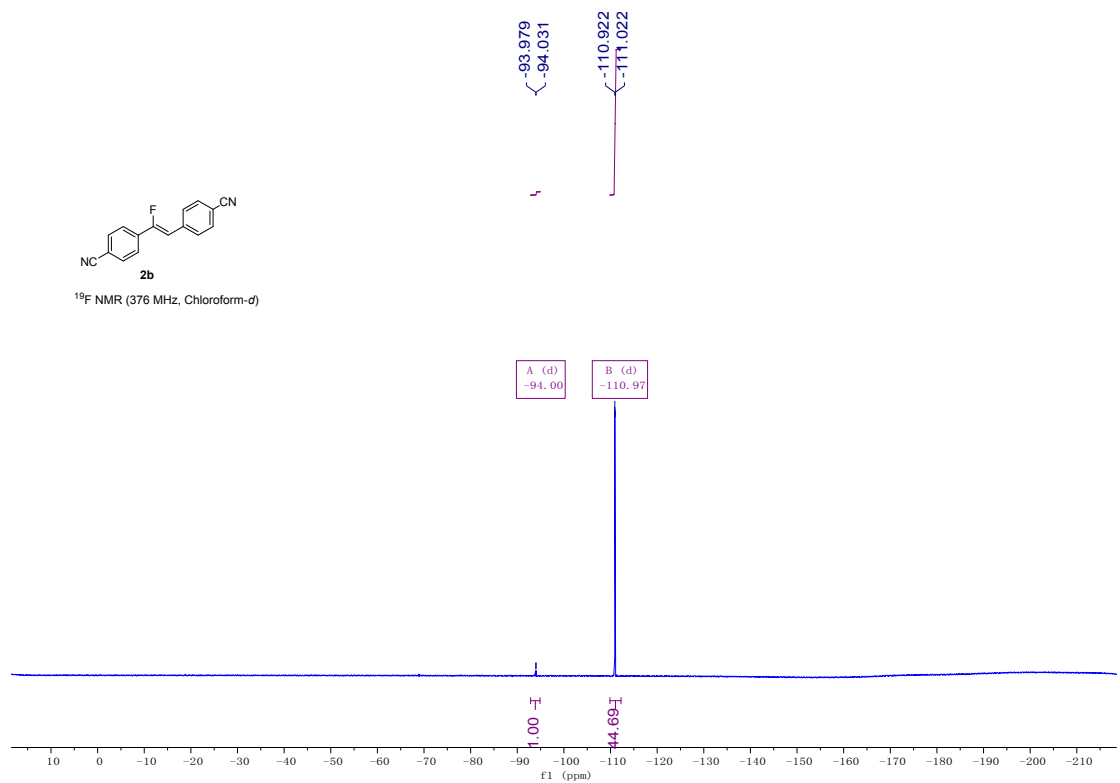


Figure S 5

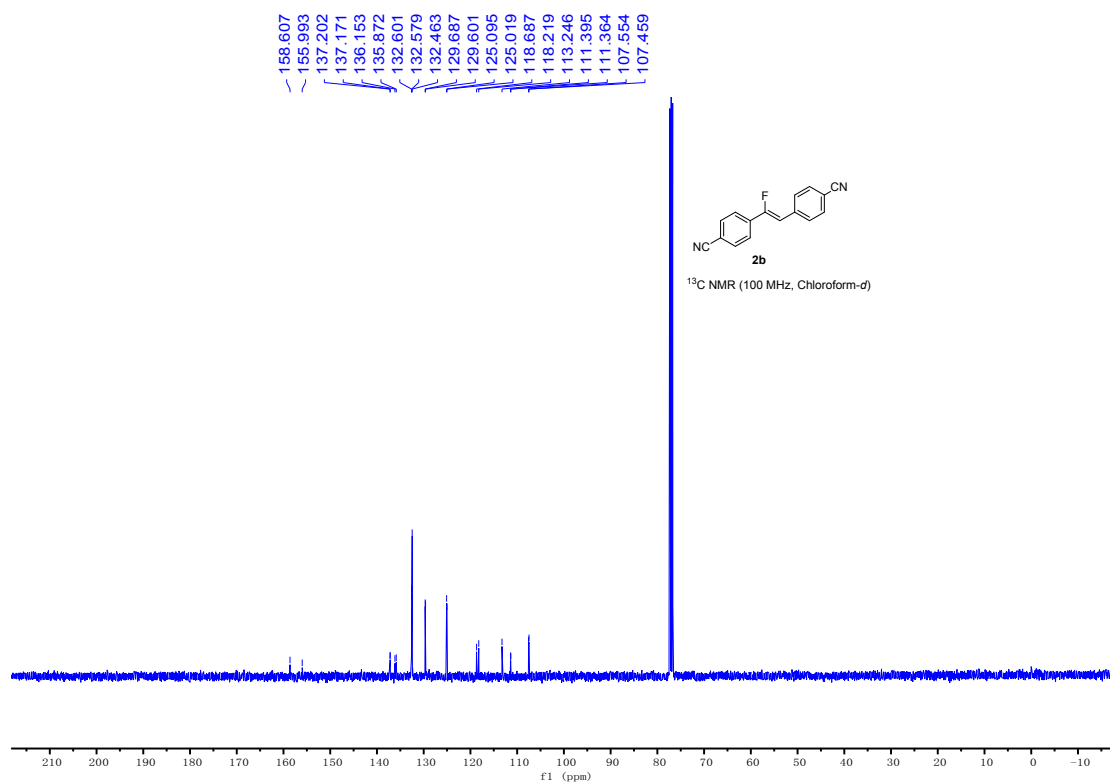


Figure S 6

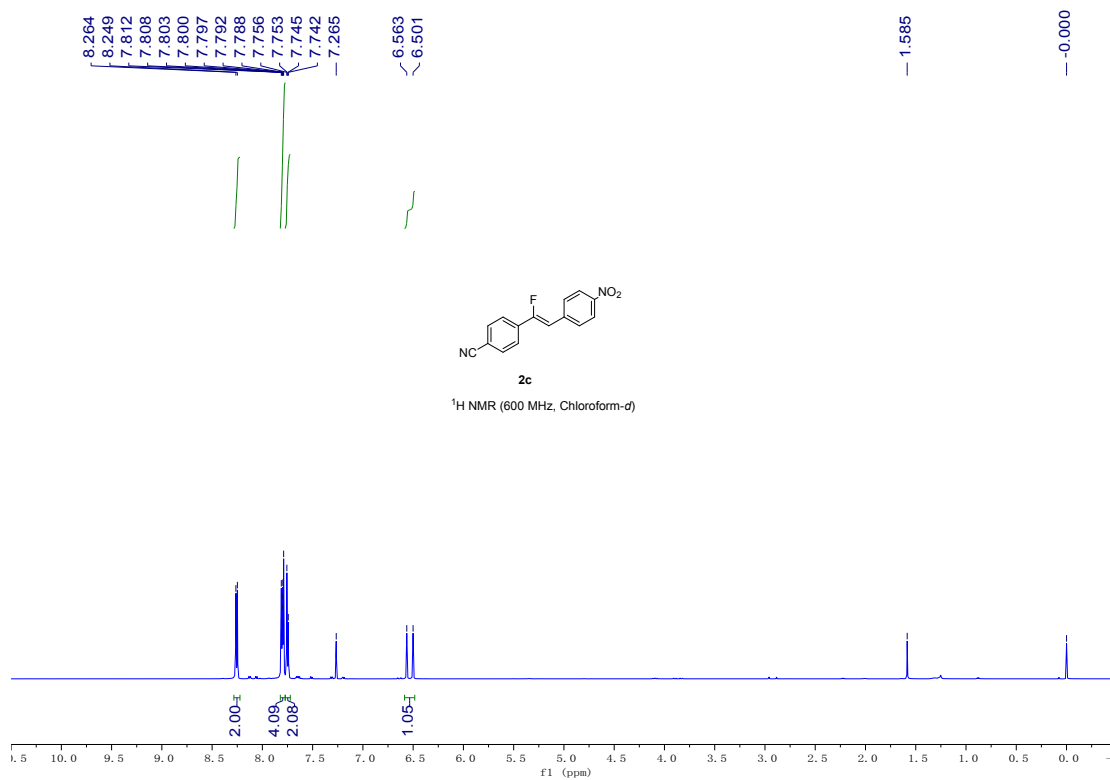


Figure S 7

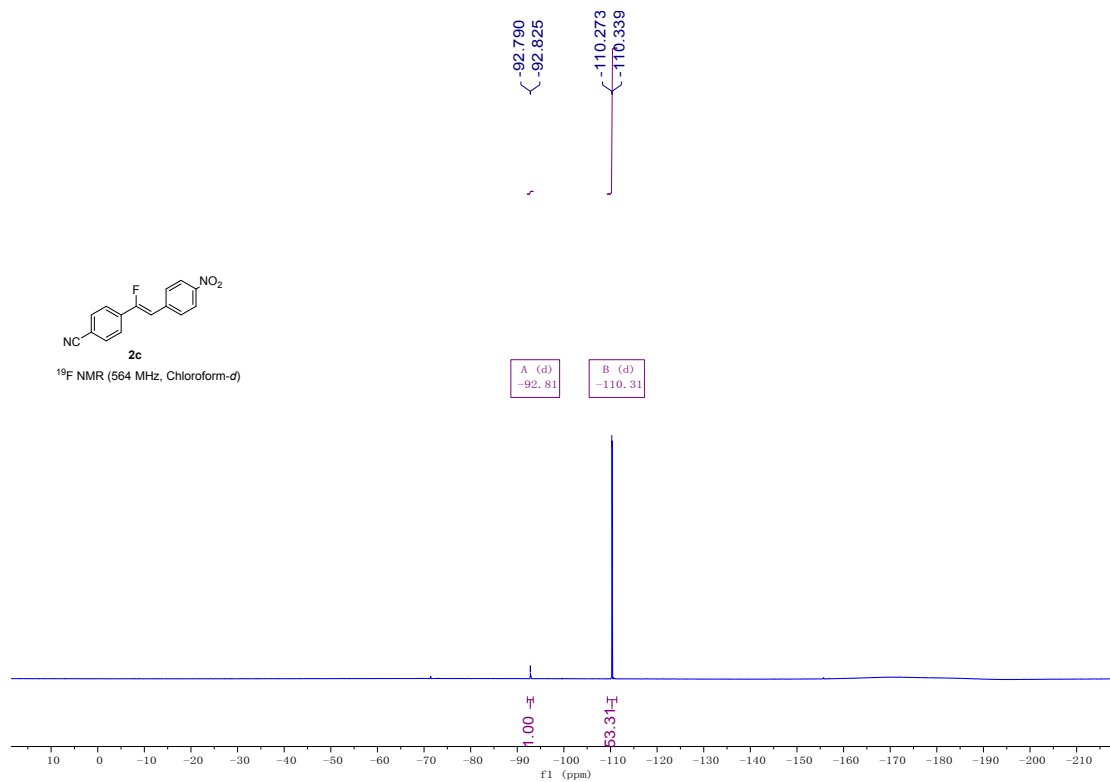


Figure S 8

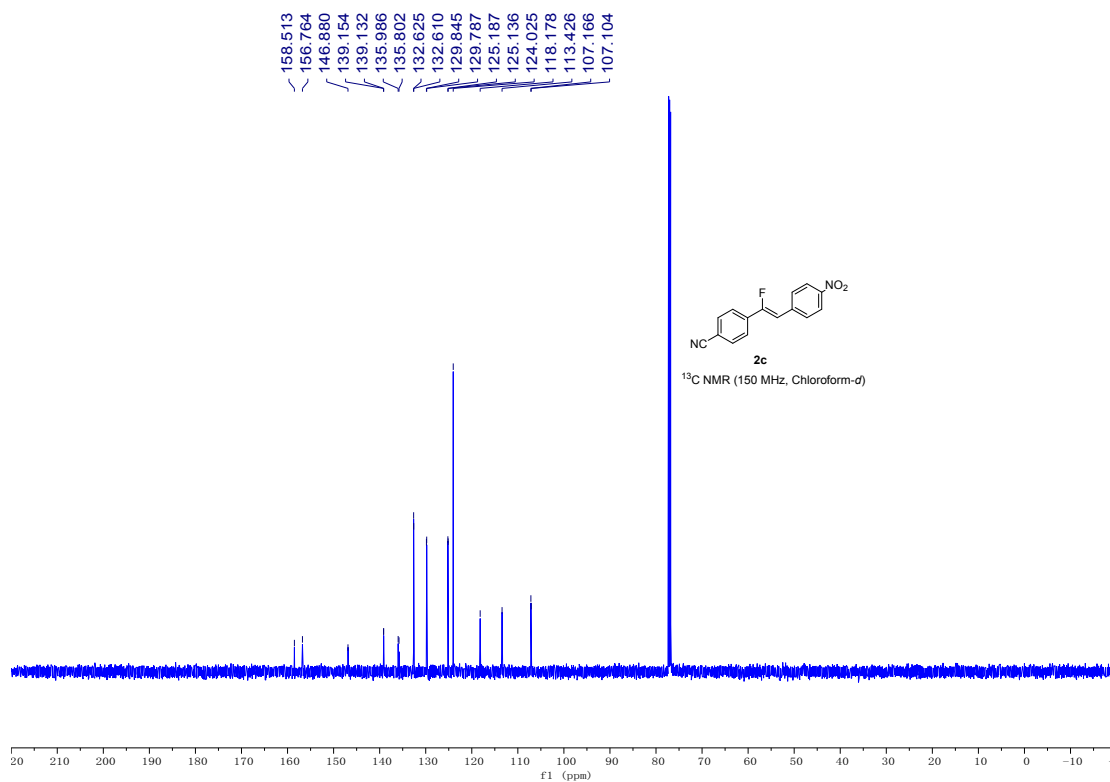


Figure S 9

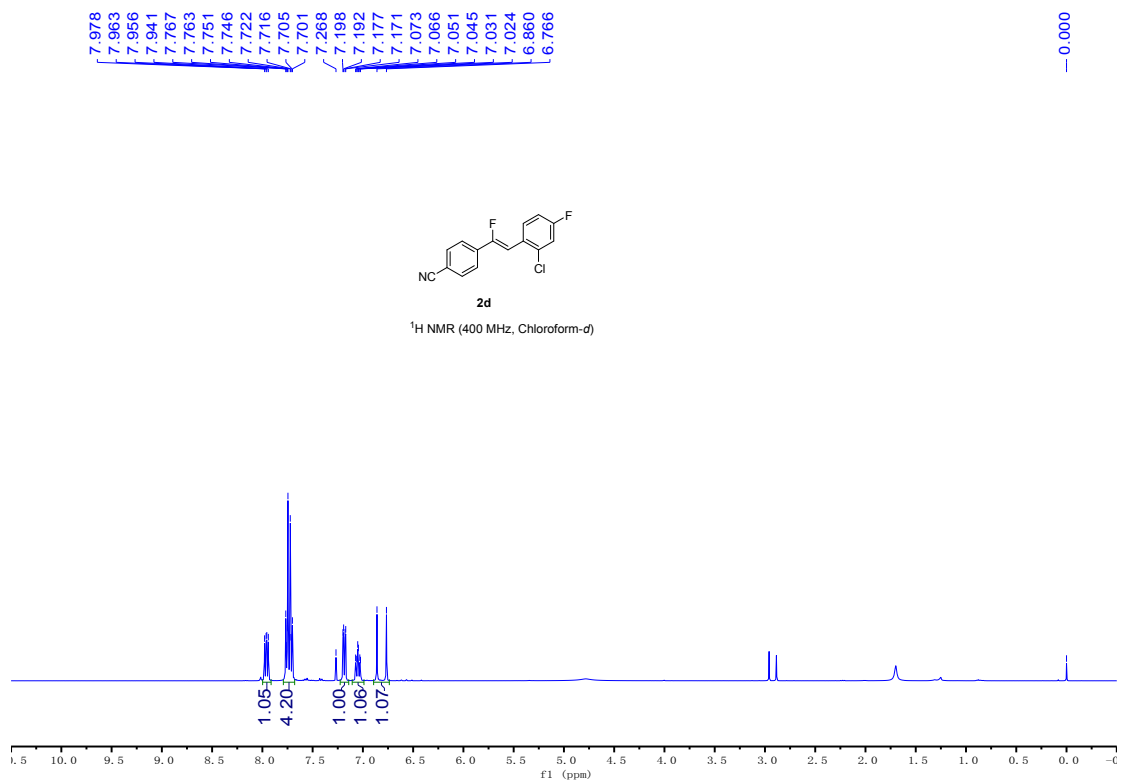


Figure S 10

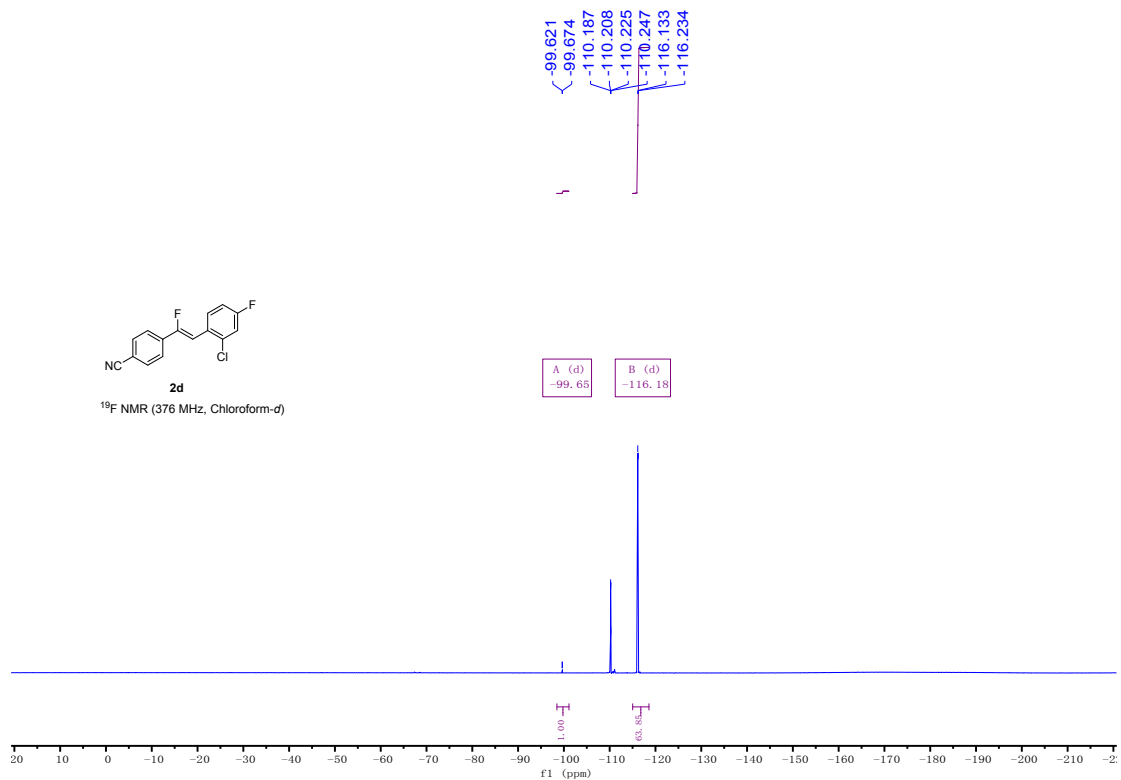


Figure S 11

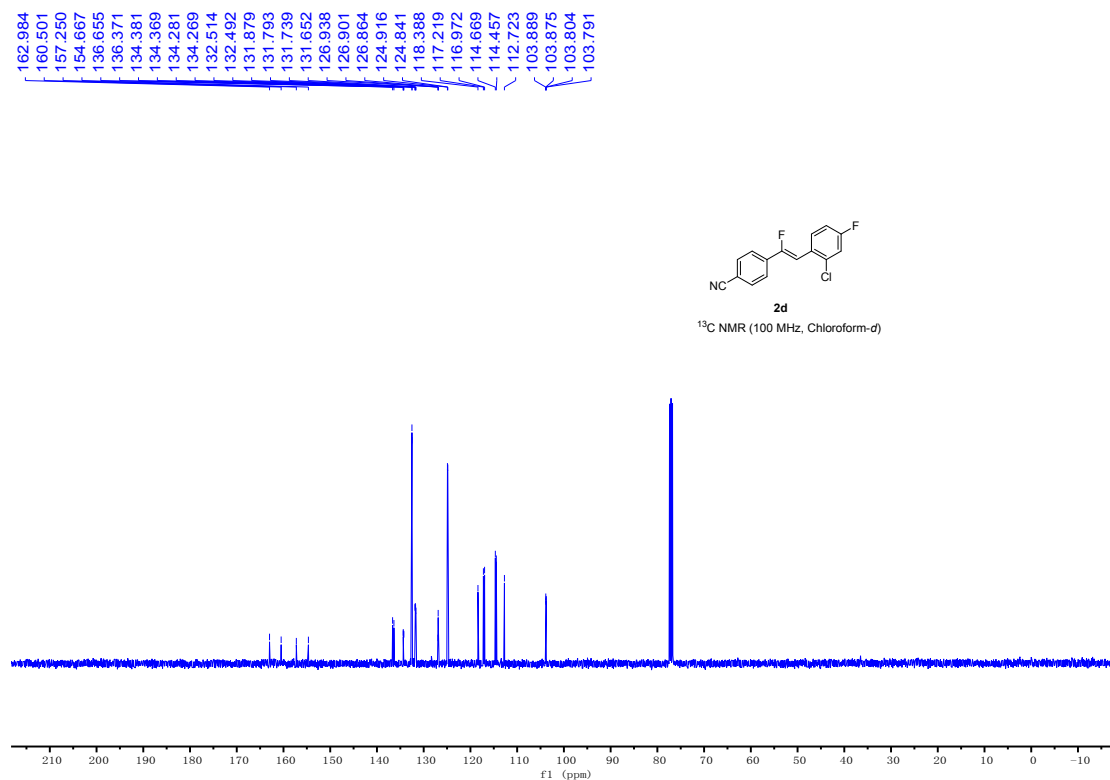


Figure S 12

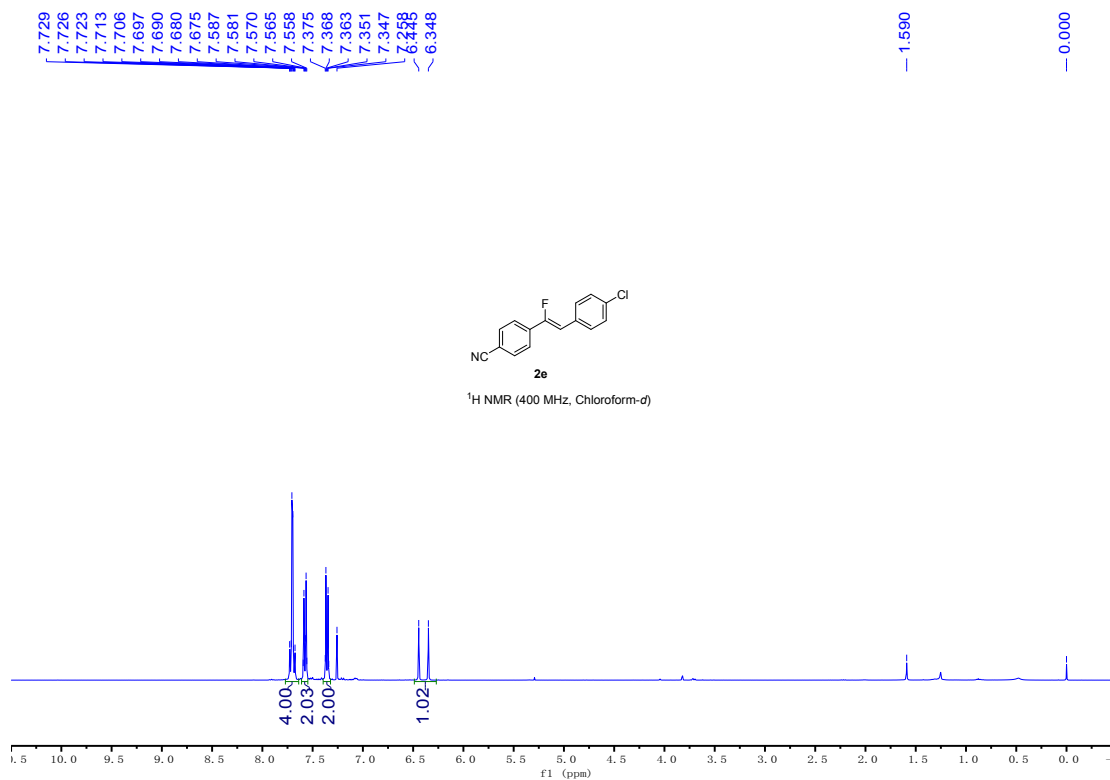


Figure S 13

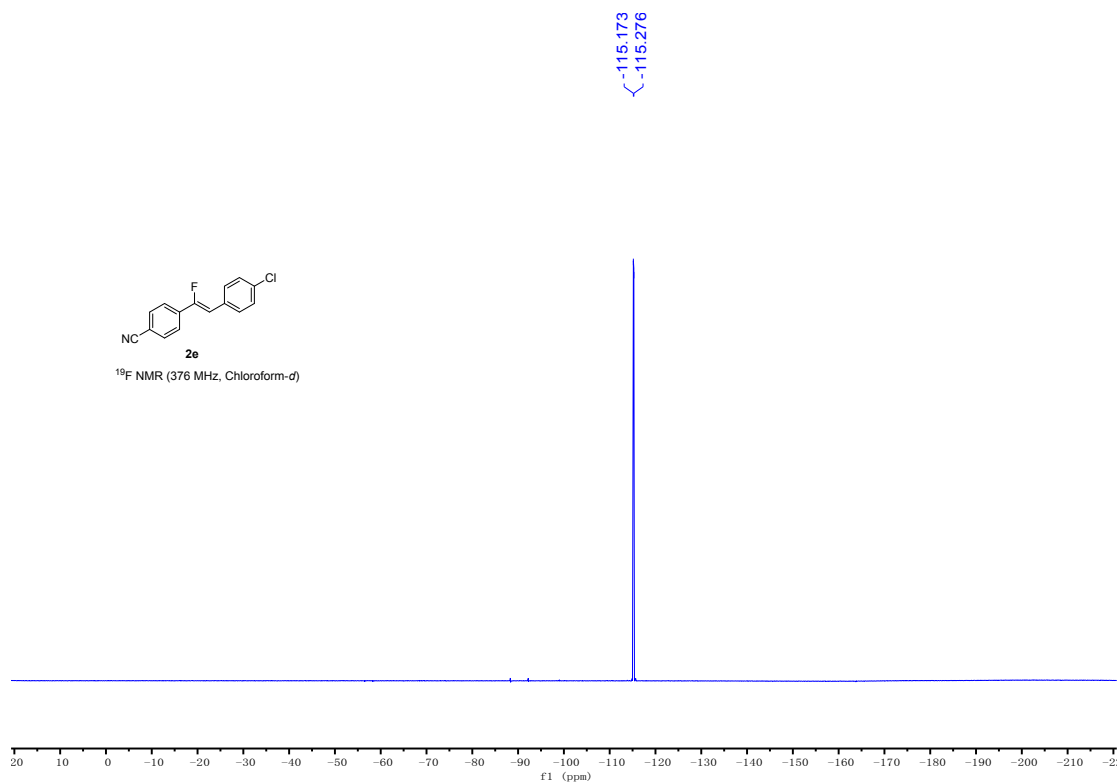


Figure S 14

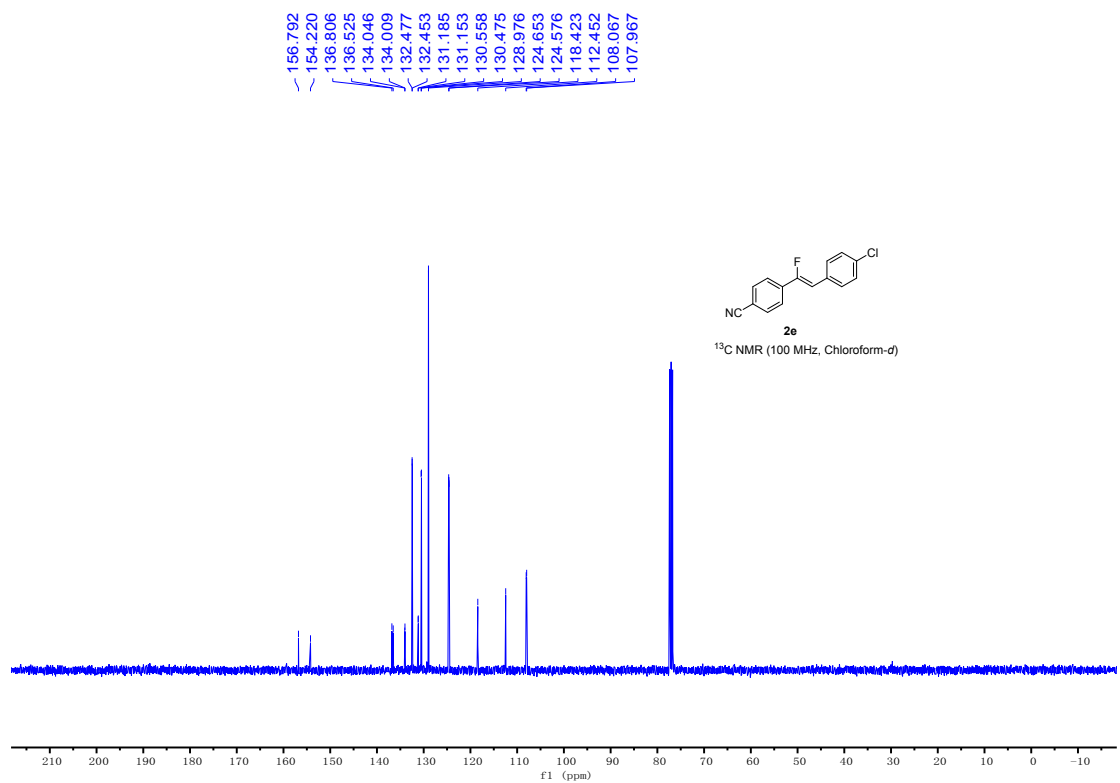


Figure S 15

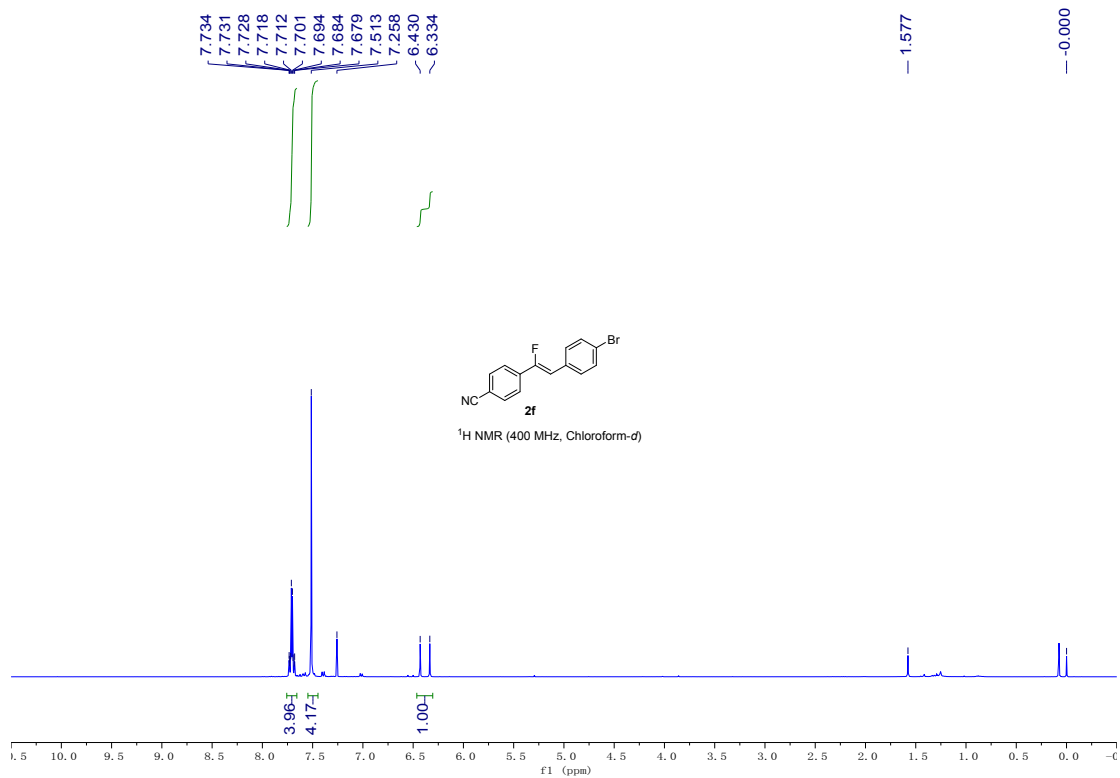


Figure S 16

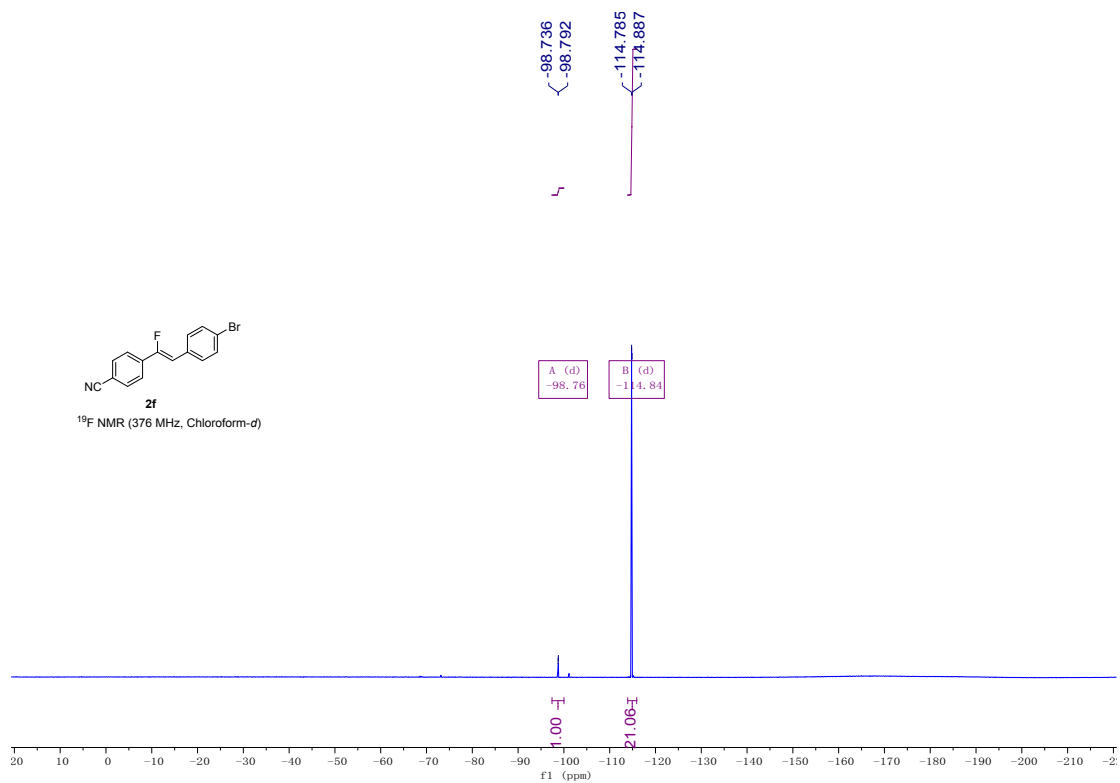


Figure S 17

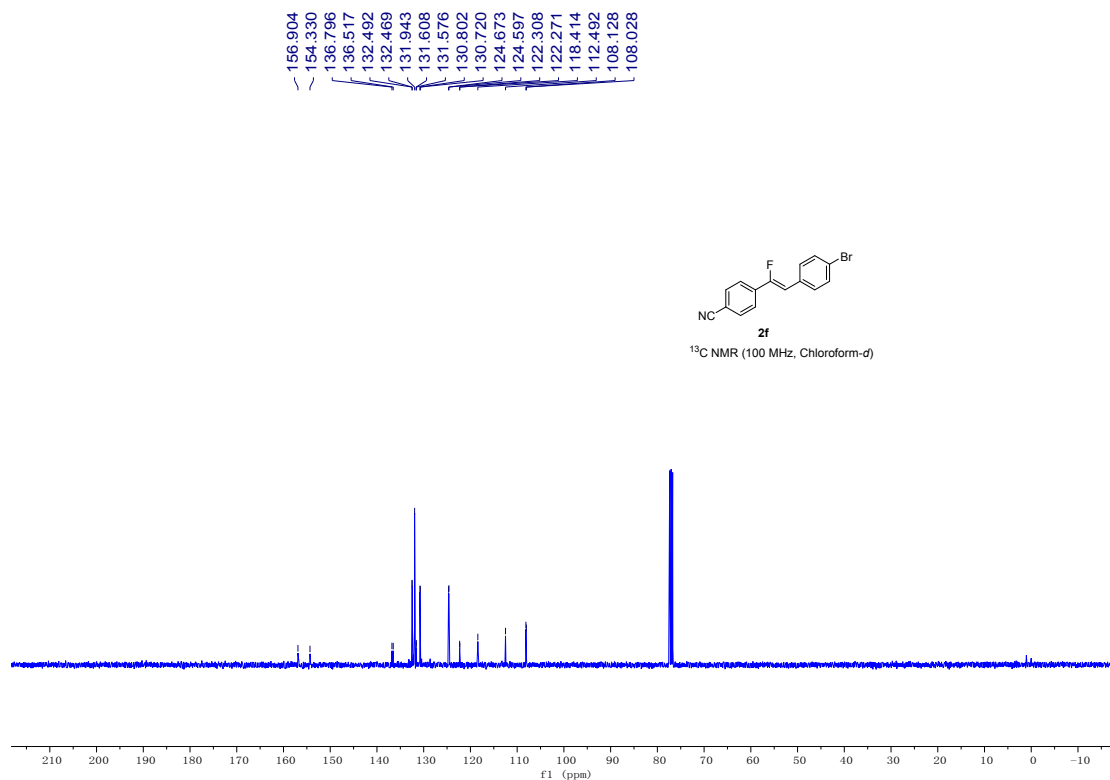


Figure S 18

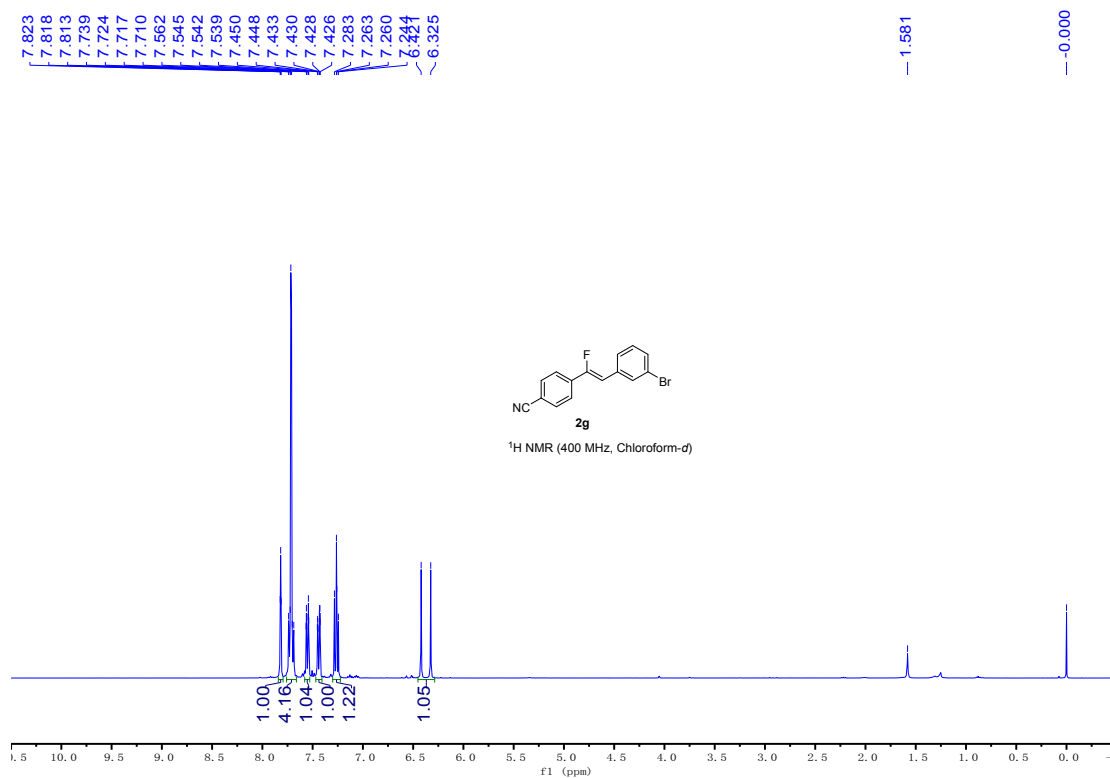


Figure S 19

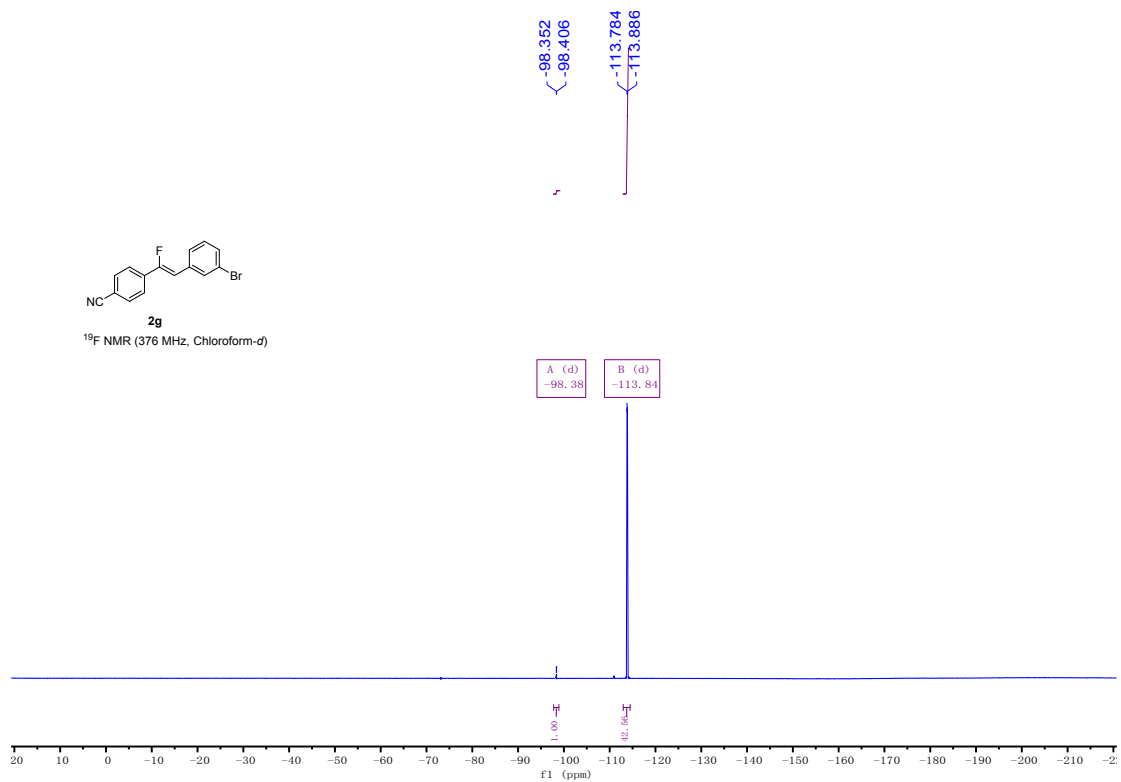


Figure S 20

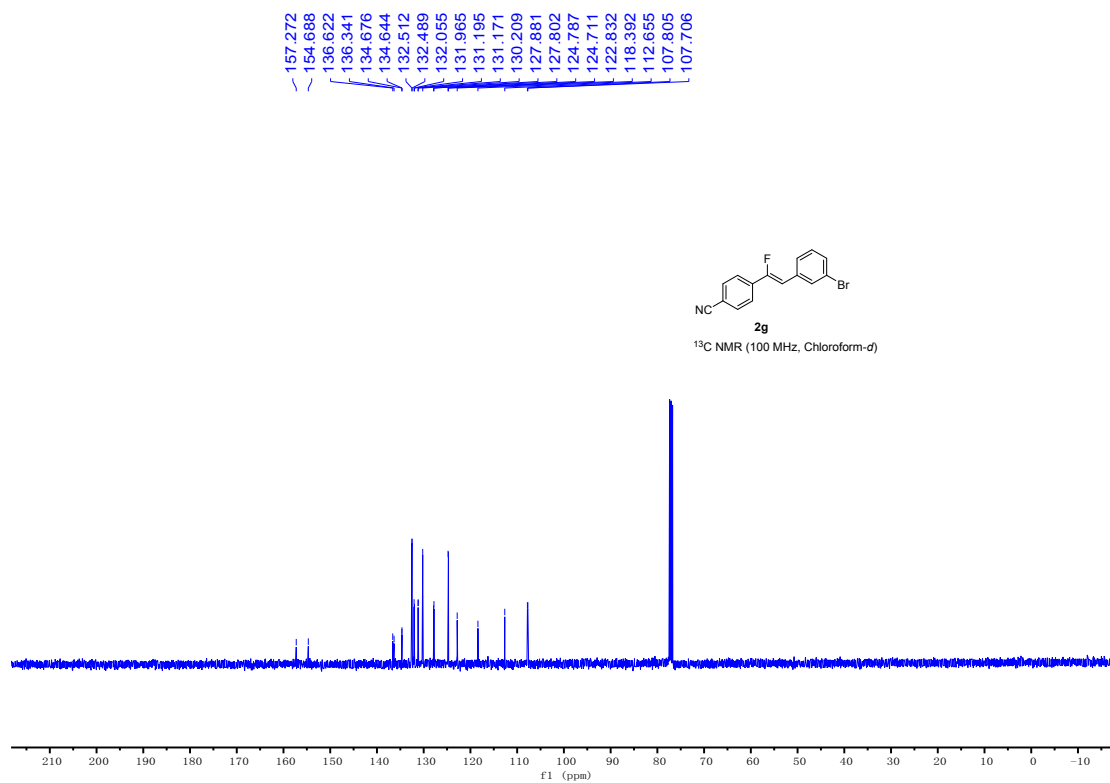


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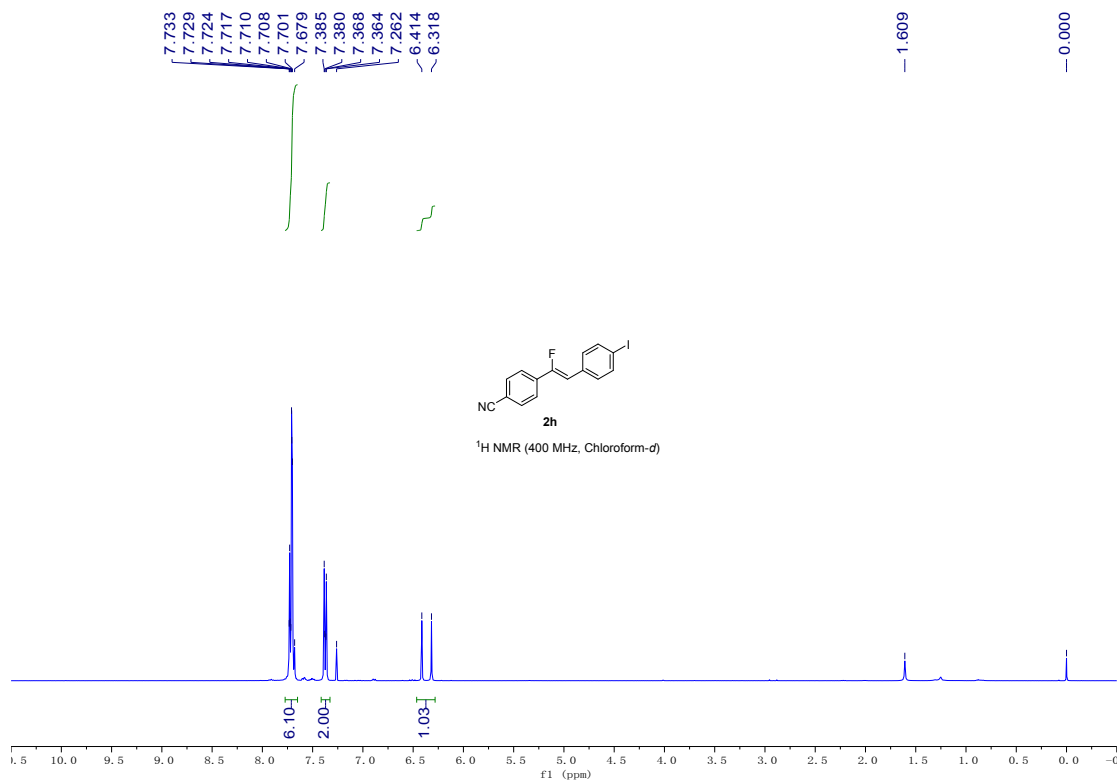


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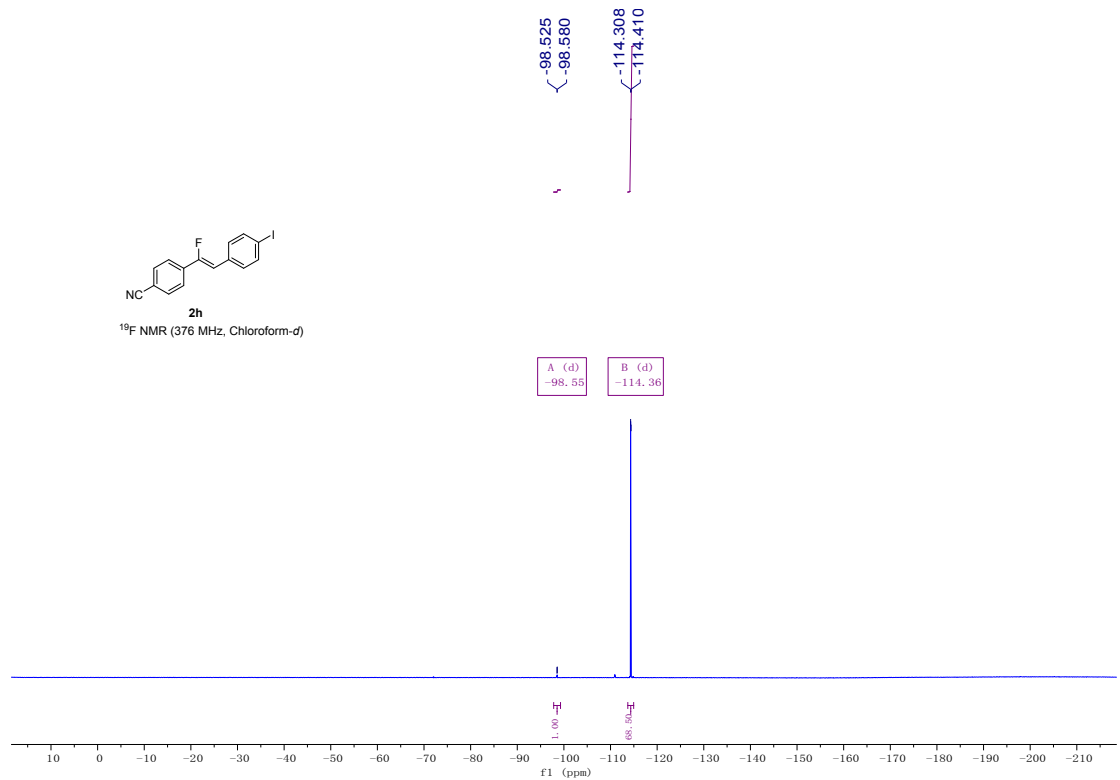


Figure S 23

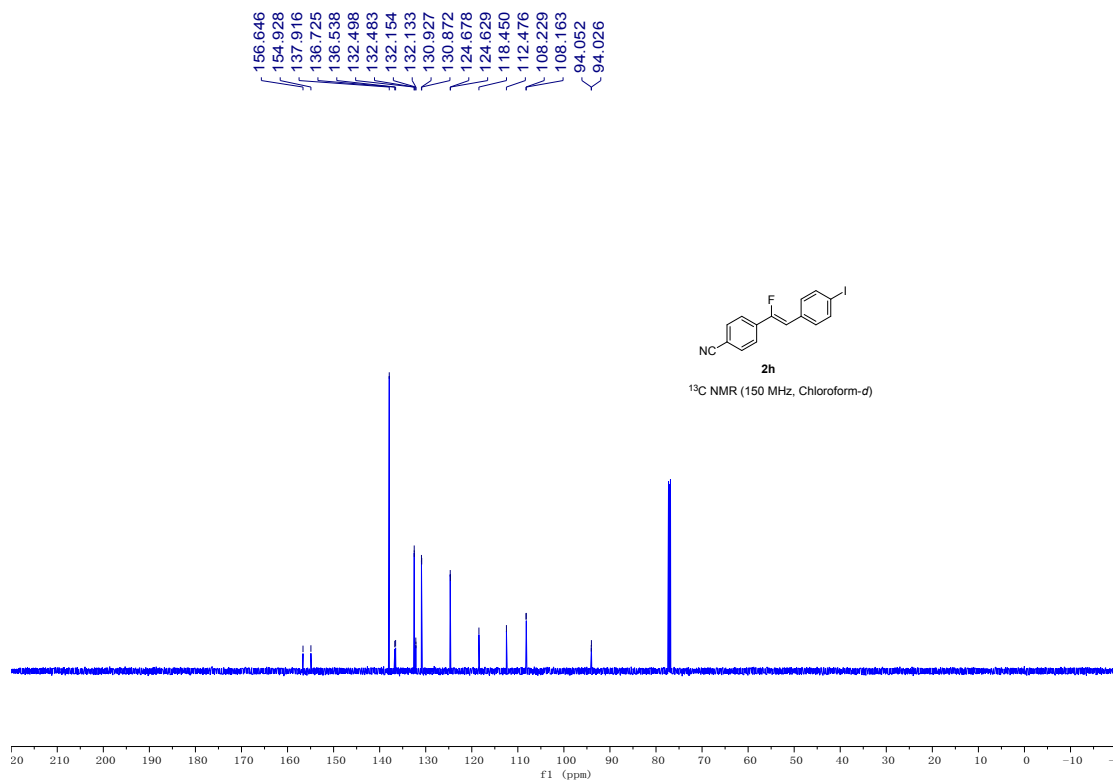


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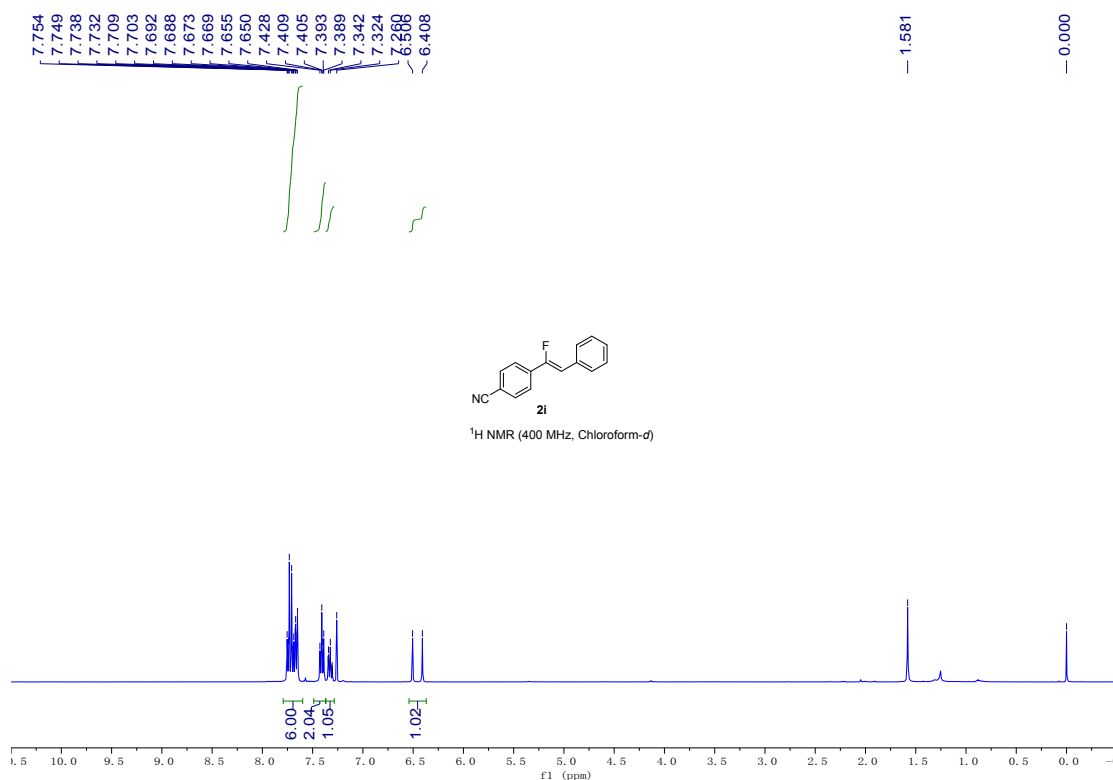


Figure S 25

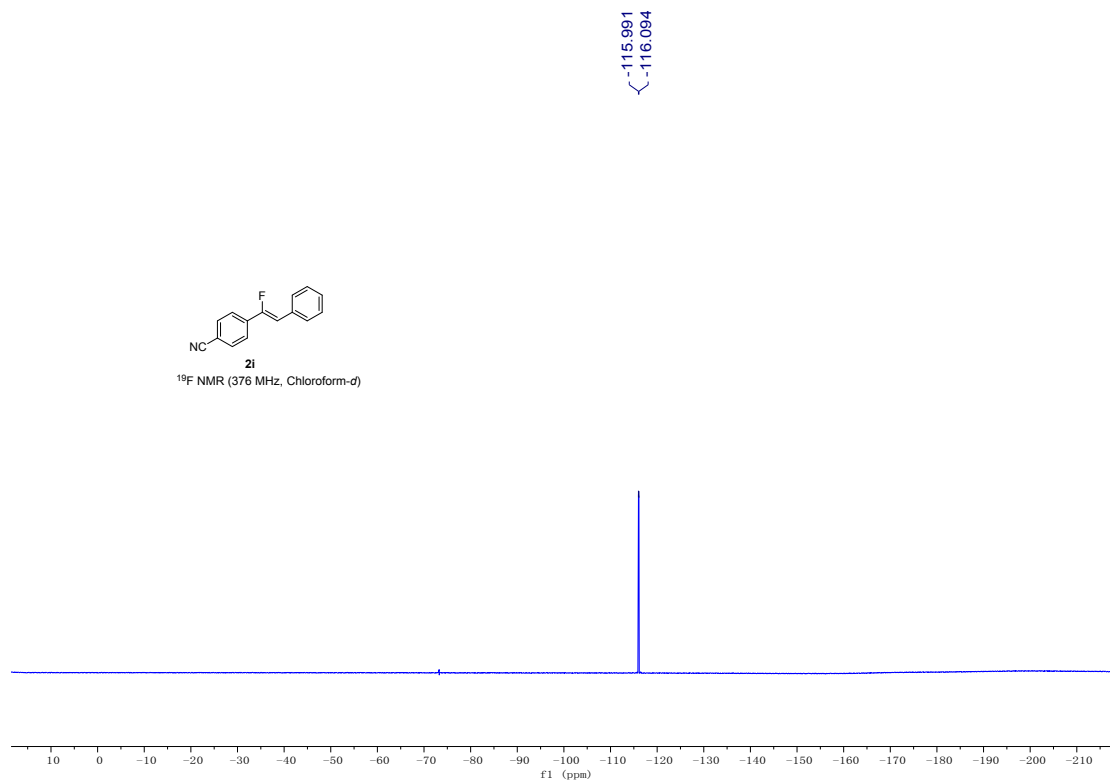


Figure S 26

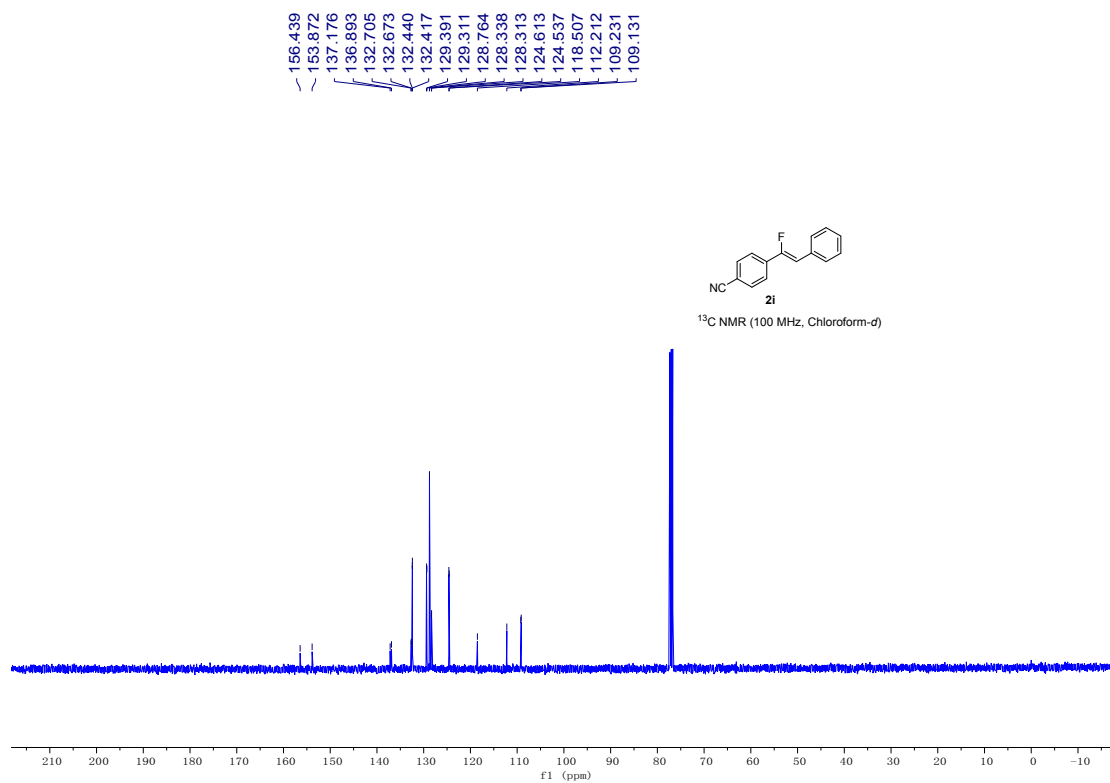


Figure S 27

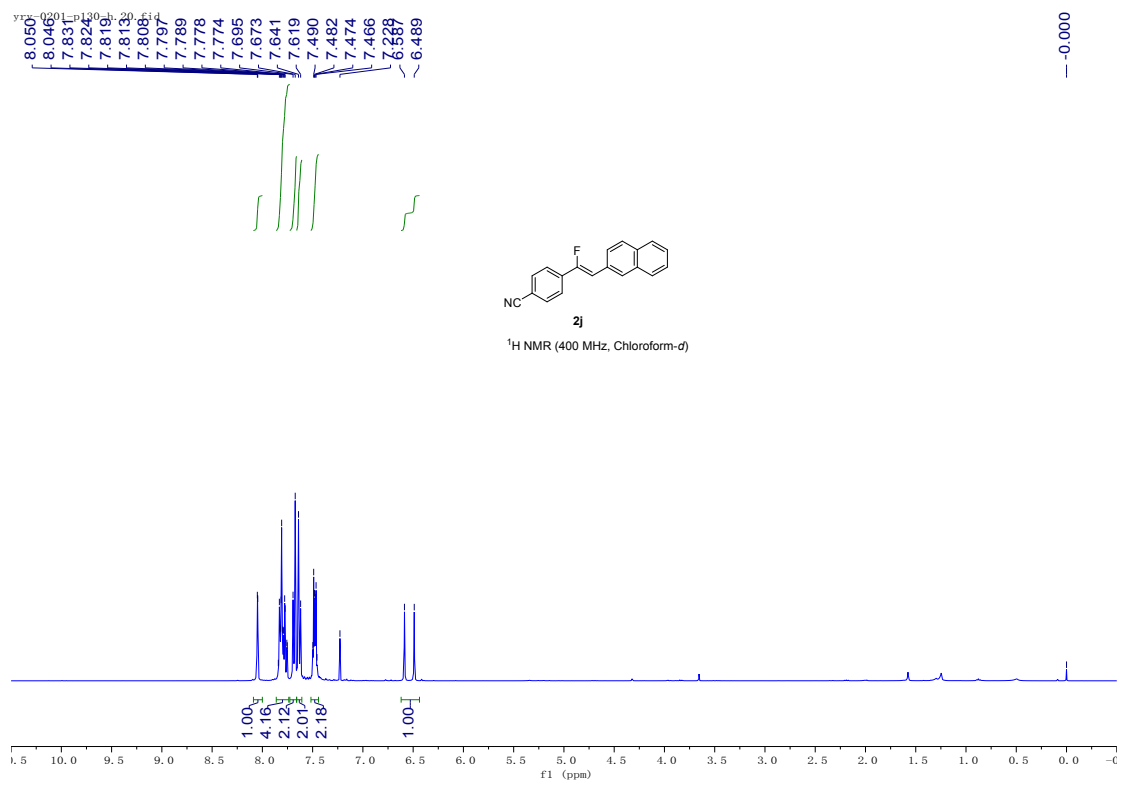


Figure S 28

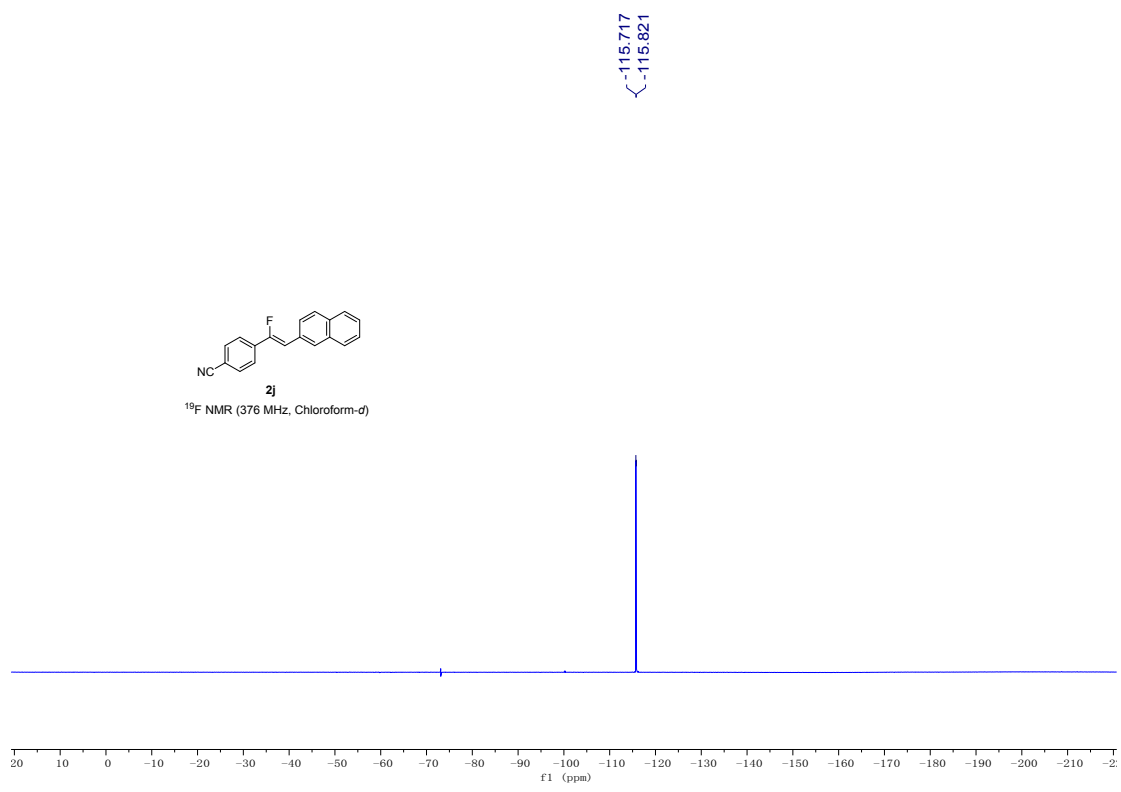


Figure S 29

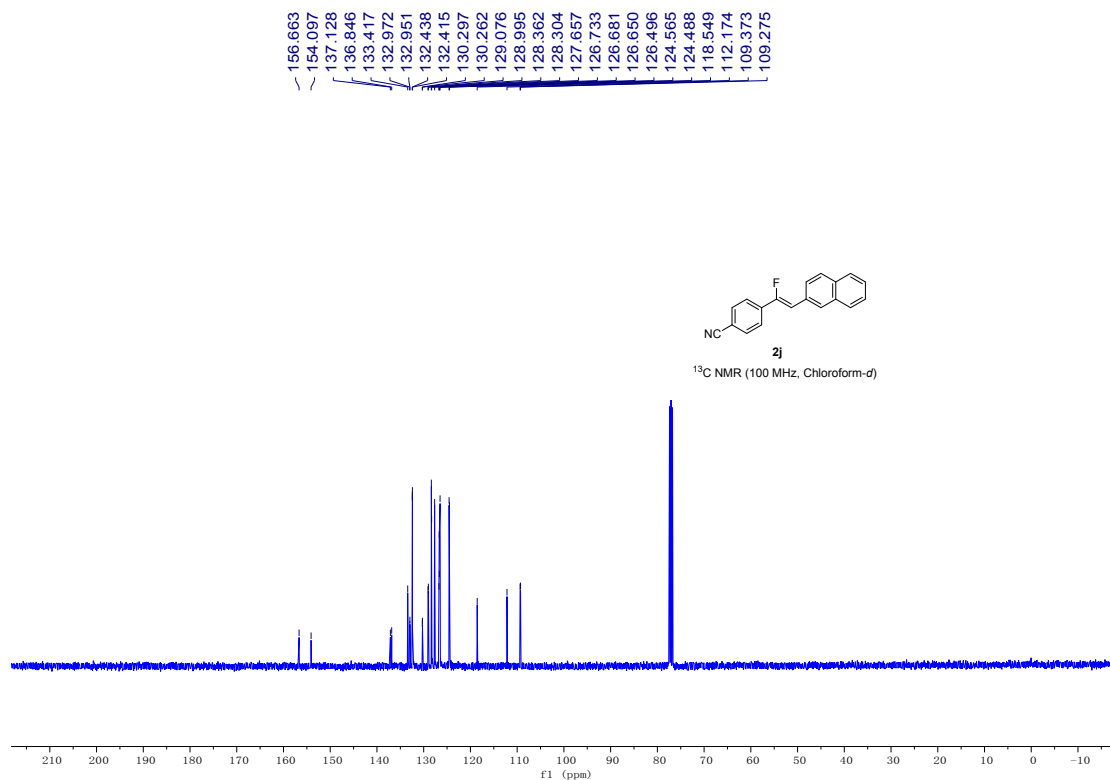


Figure S 30

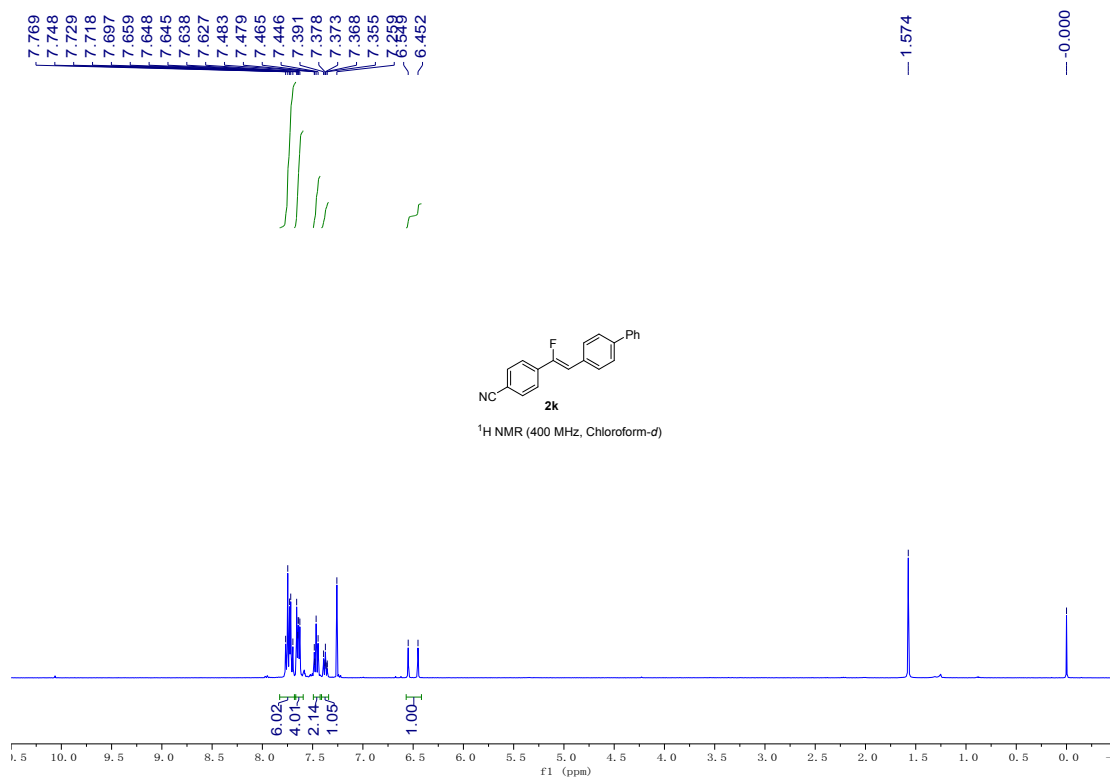


Figure S 31

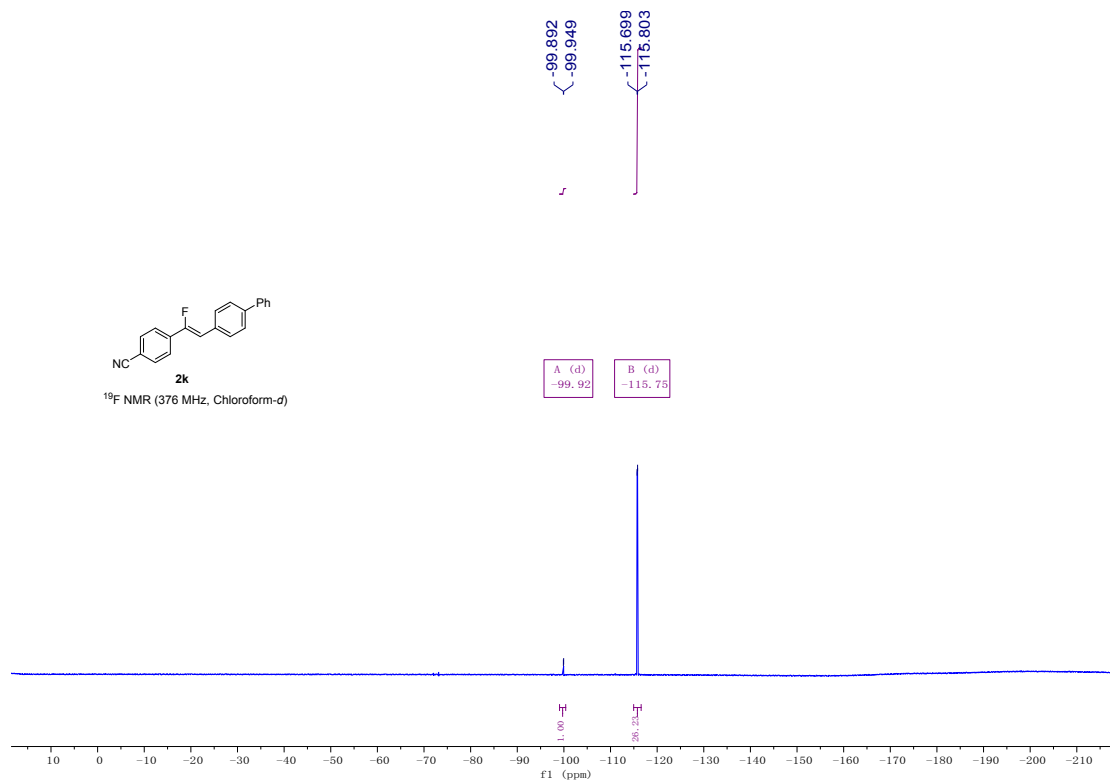


Figure S 32

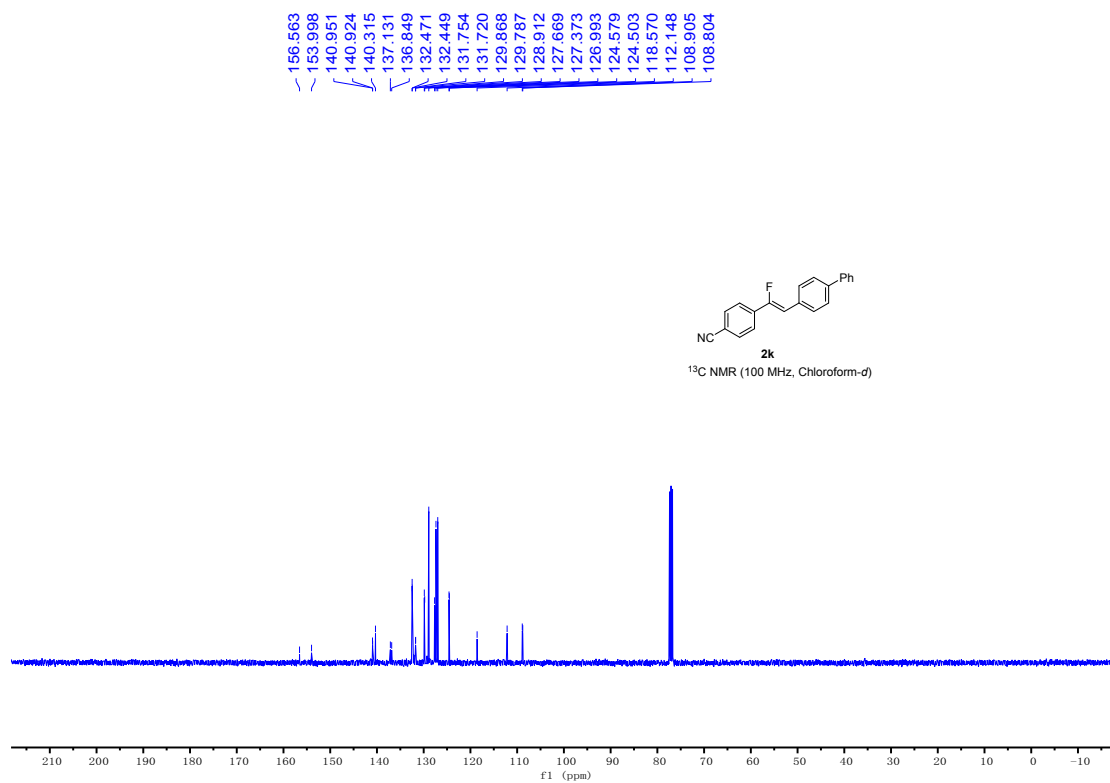


Figure S 33

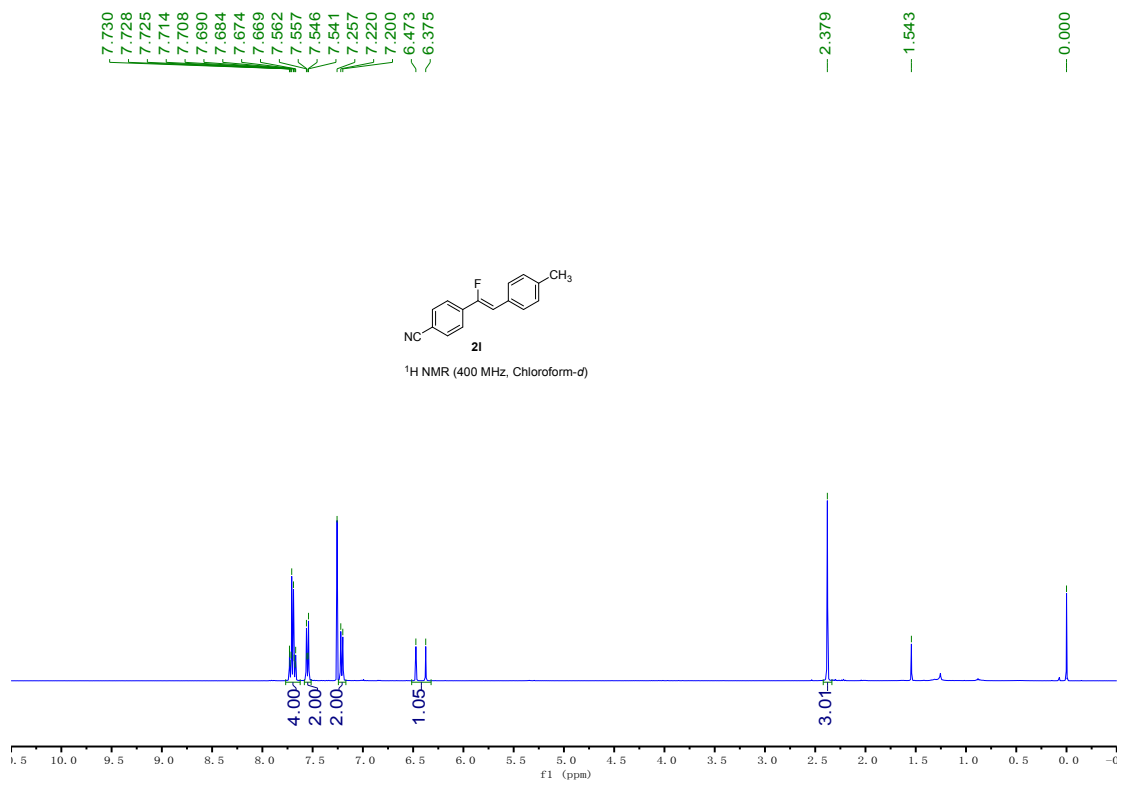


Figure S 34

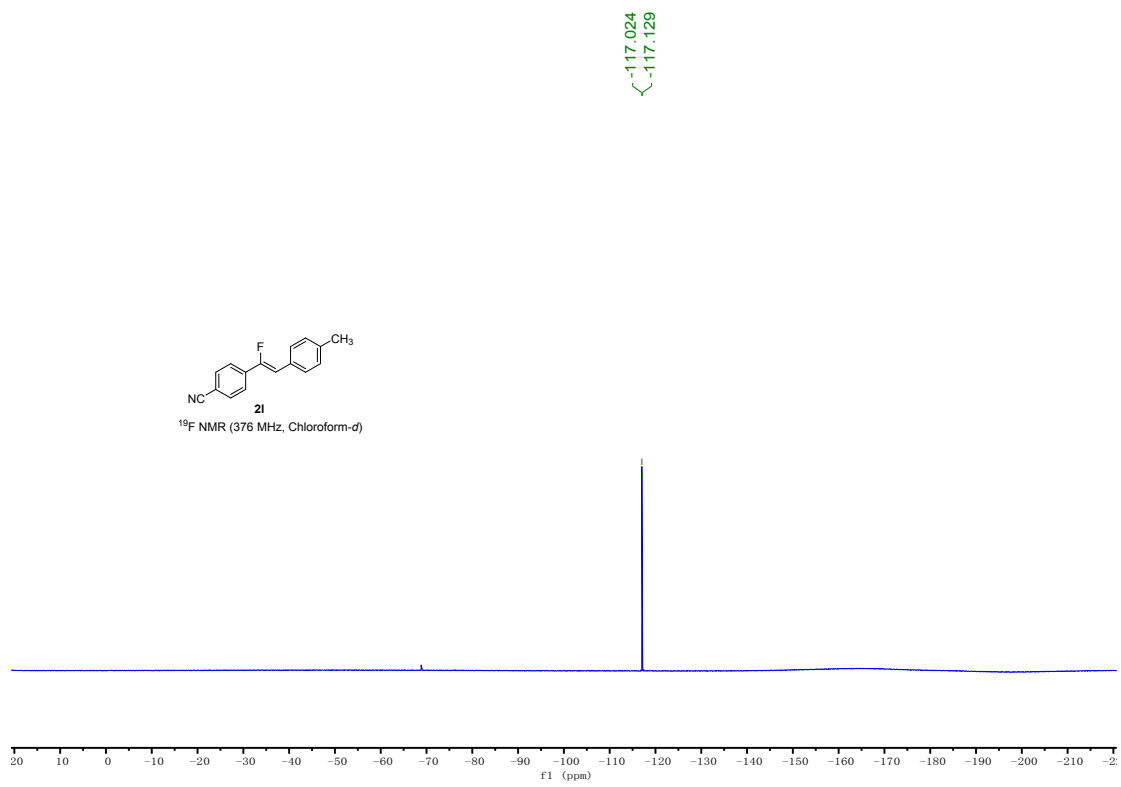


Figure S 35

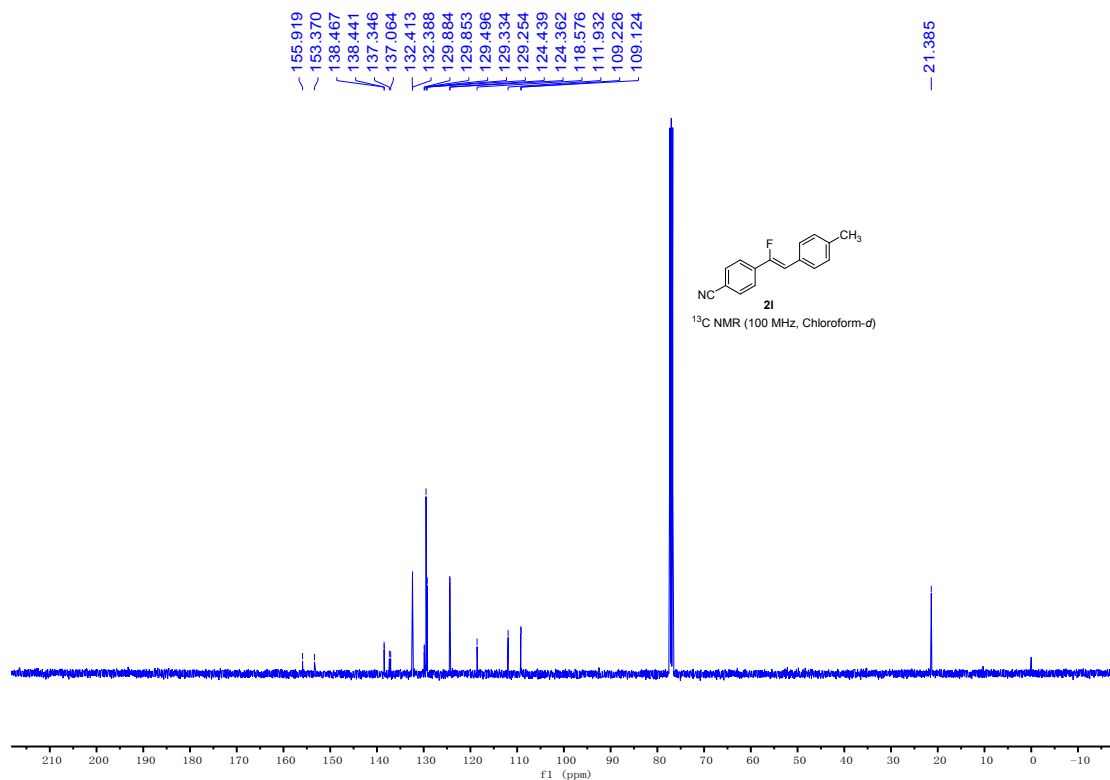


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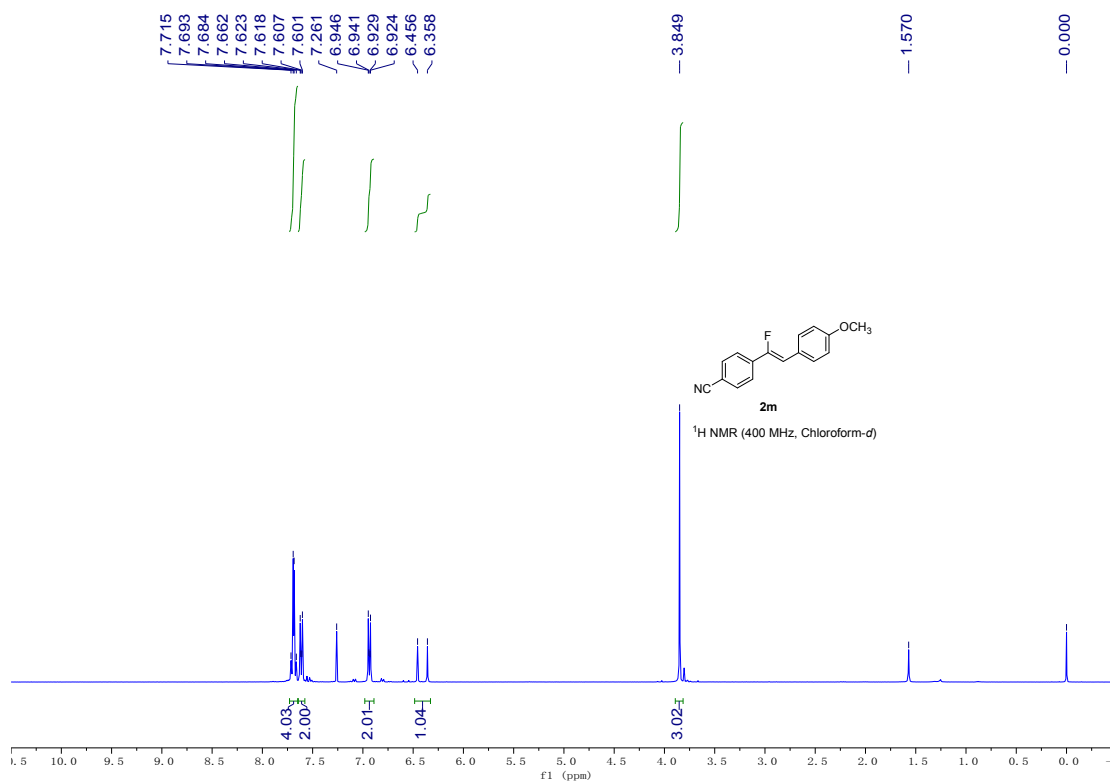


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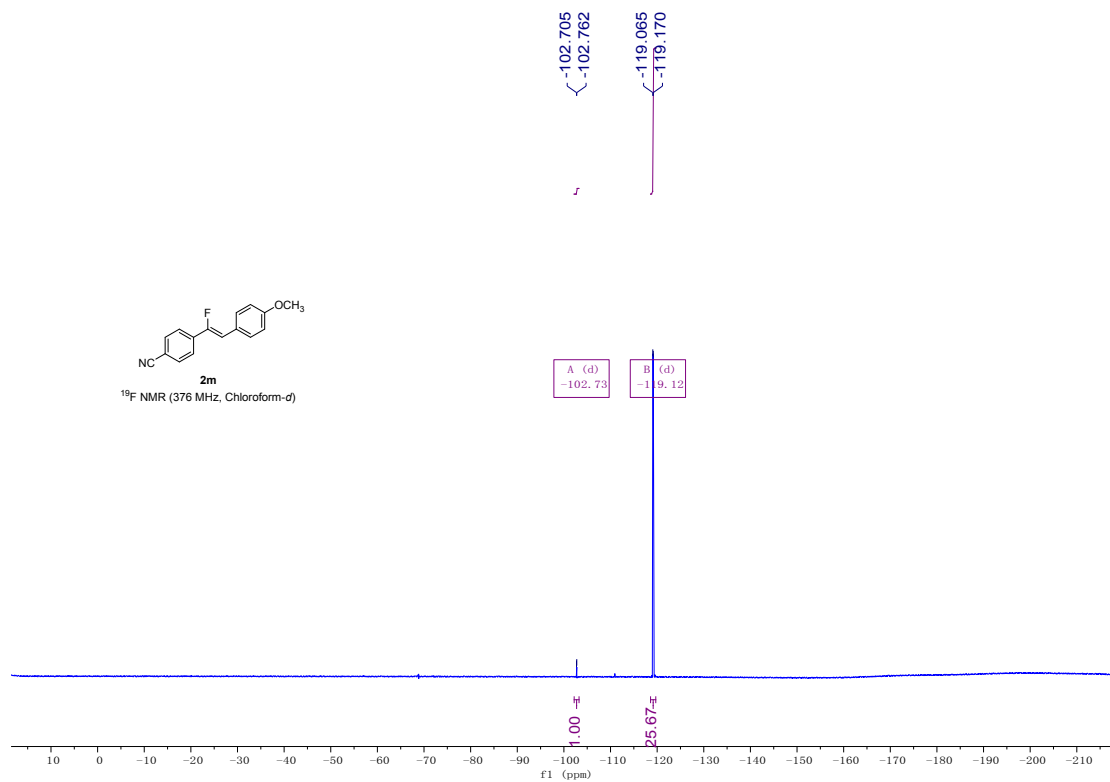


Figure S 38

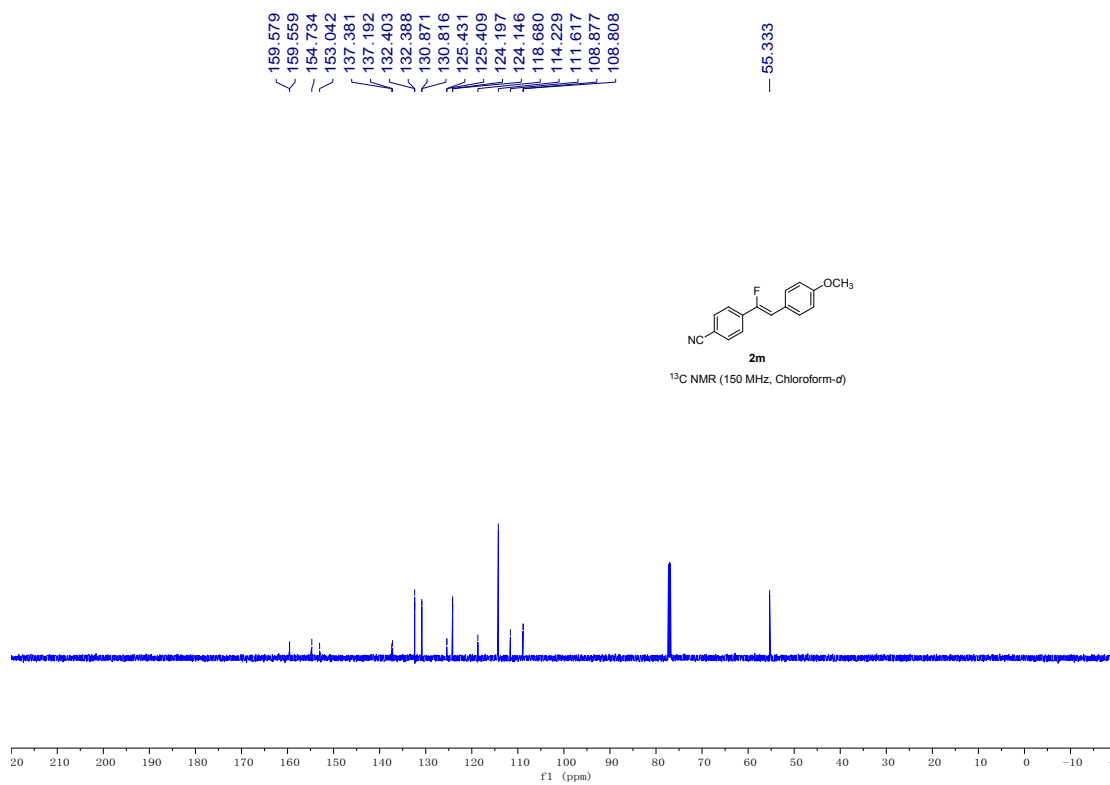


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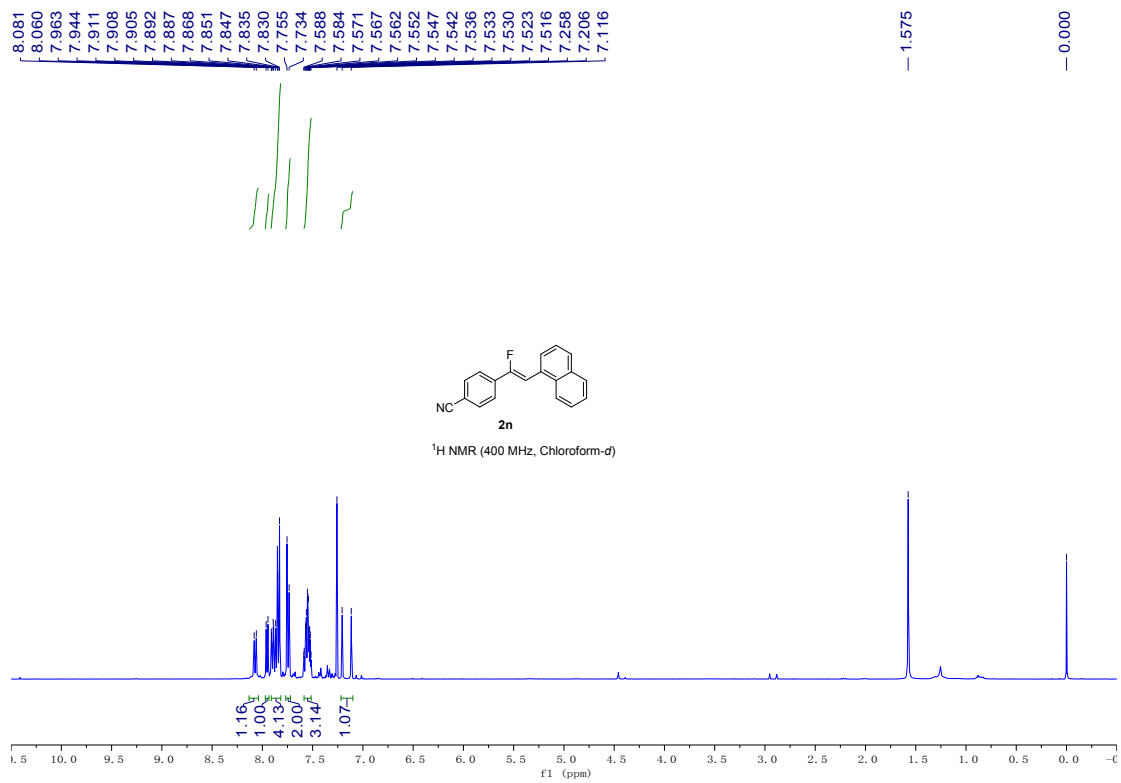


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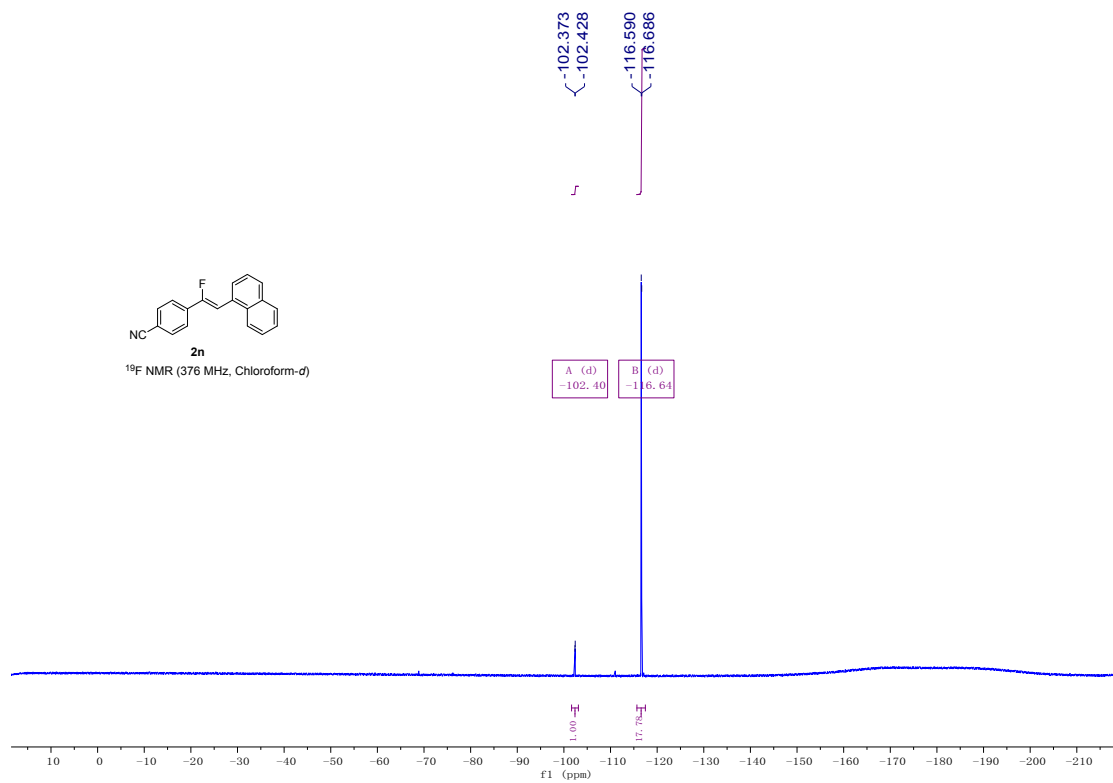


Figure S 41

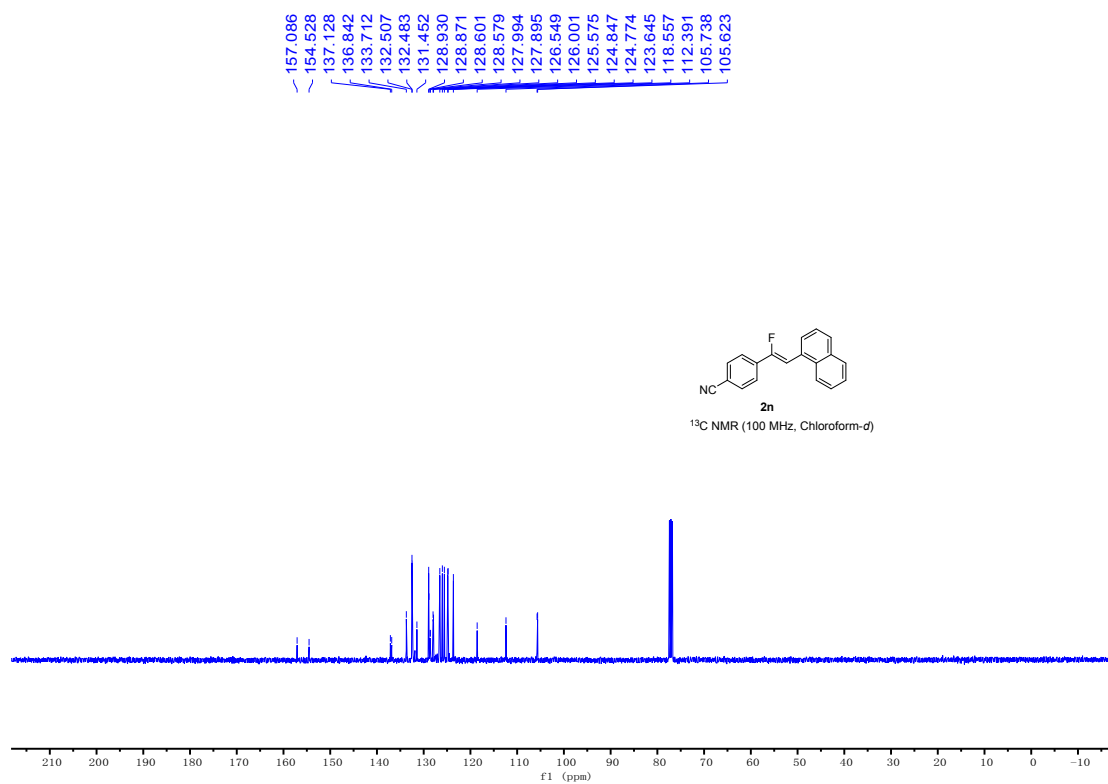


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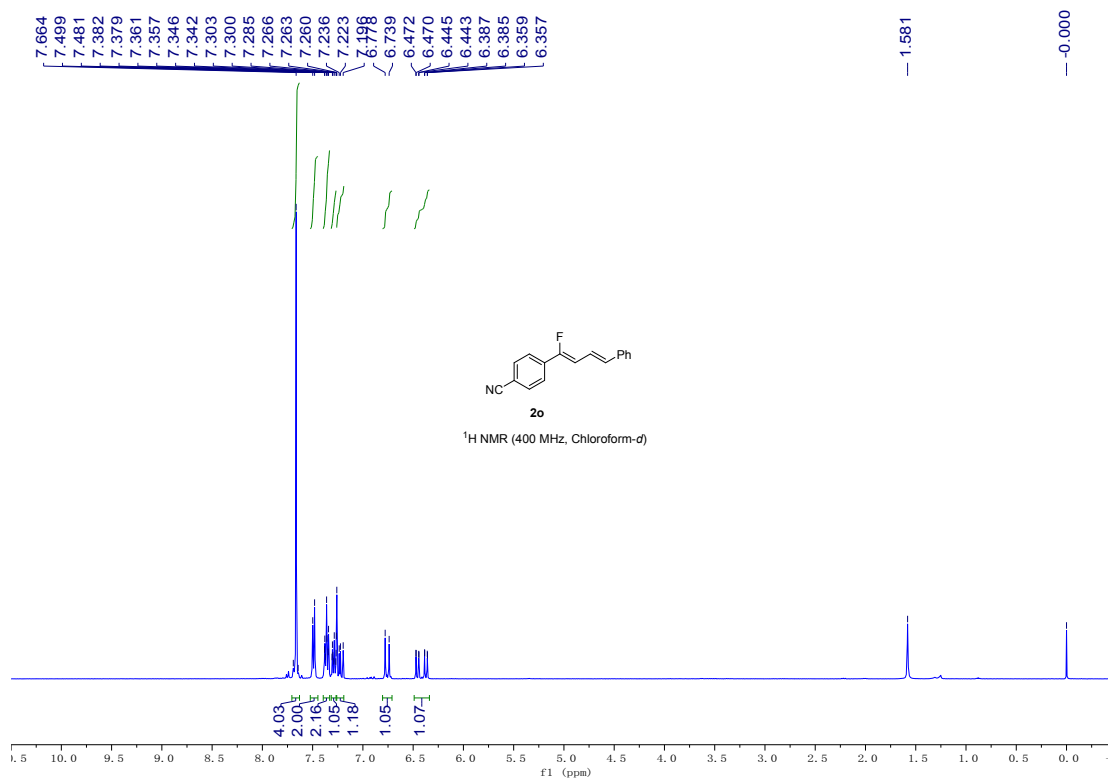


Figure S 43



Figure S 44

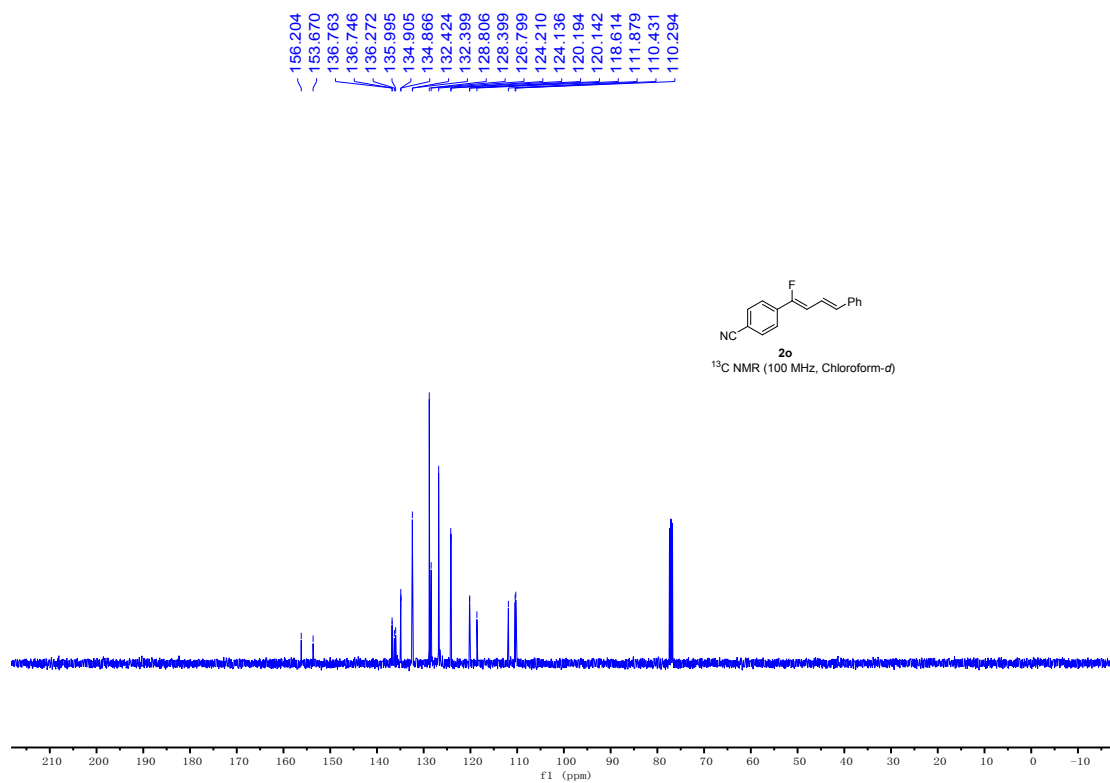


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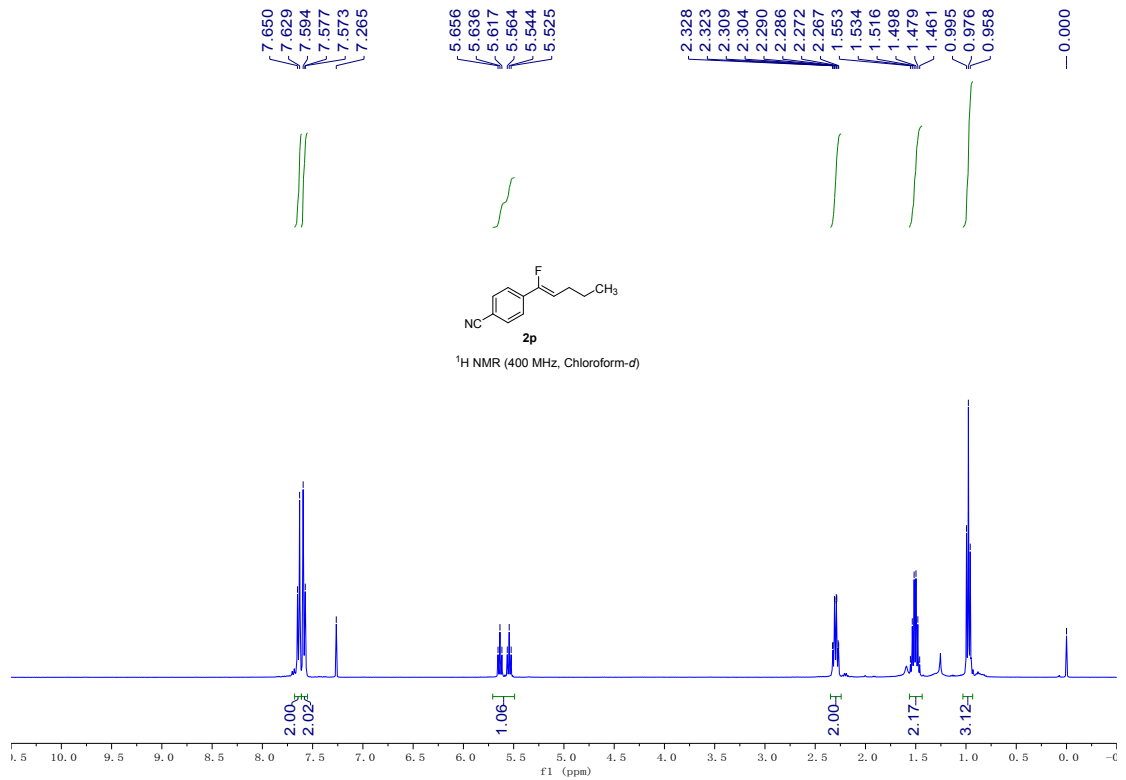


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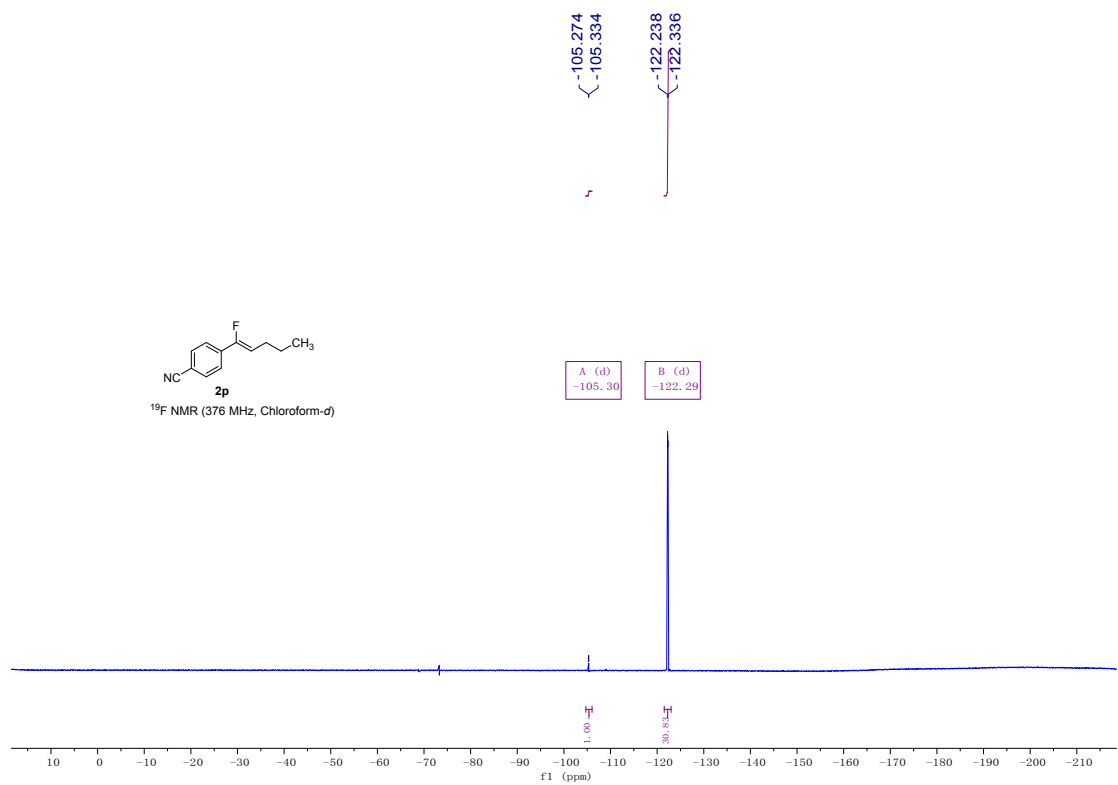


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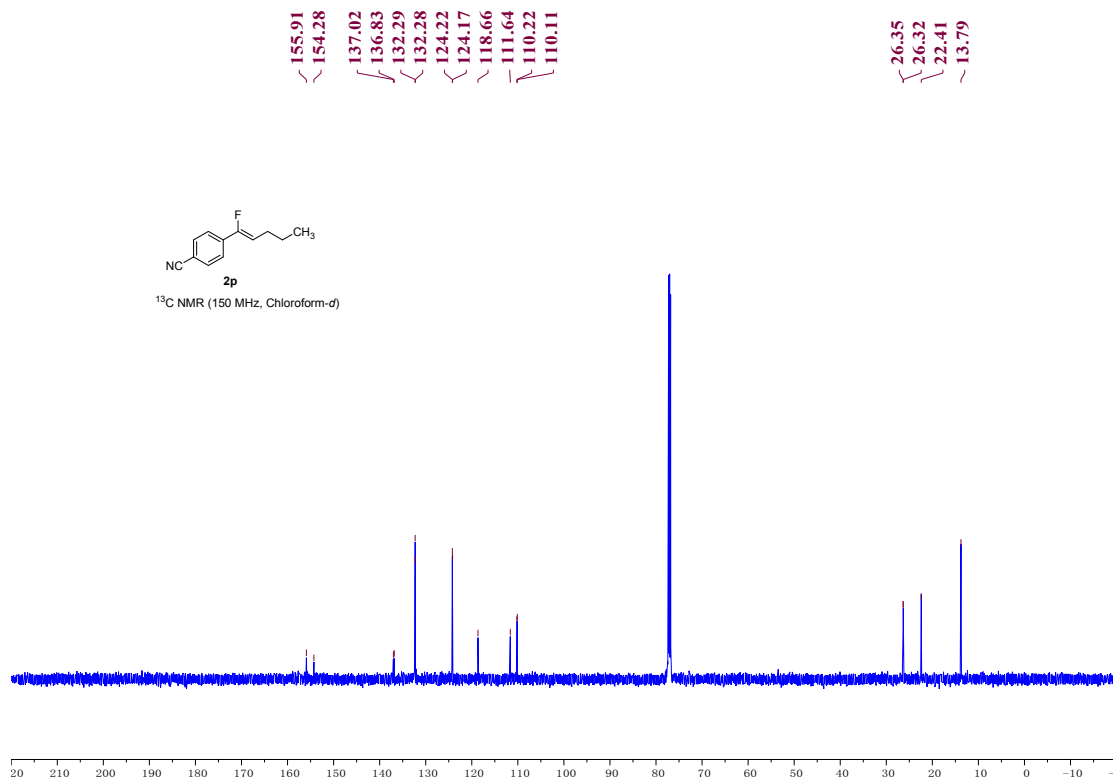


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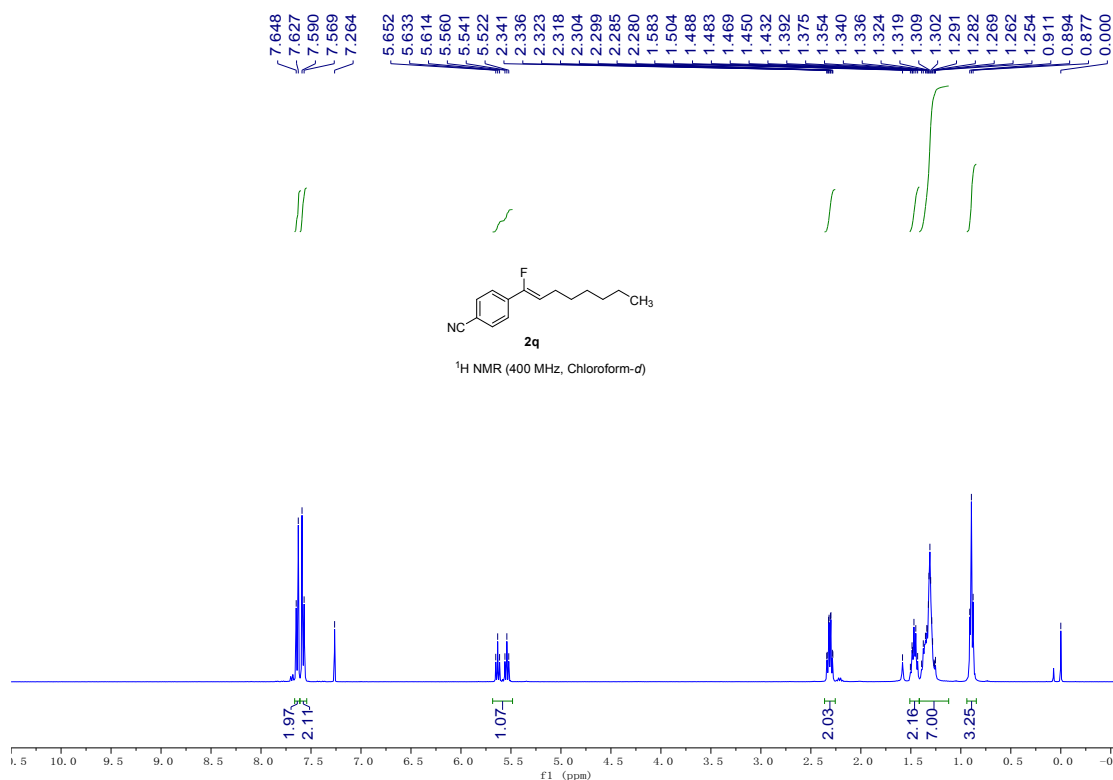


Figure S 49



Figure S 50

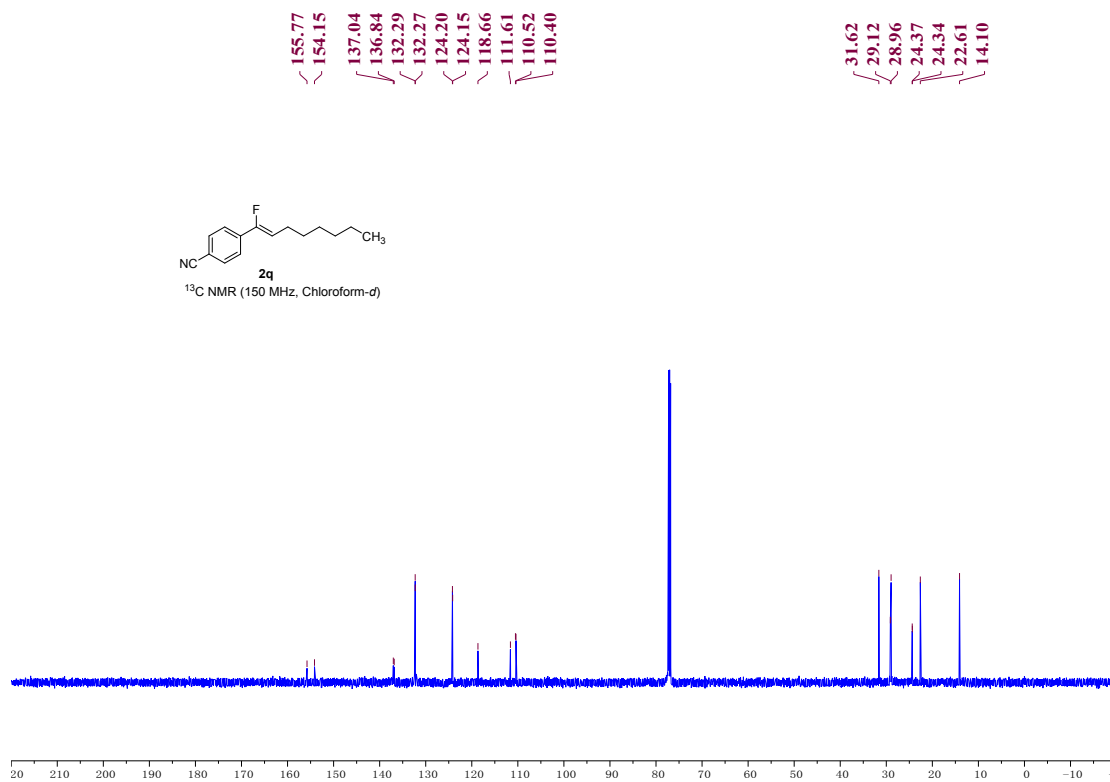


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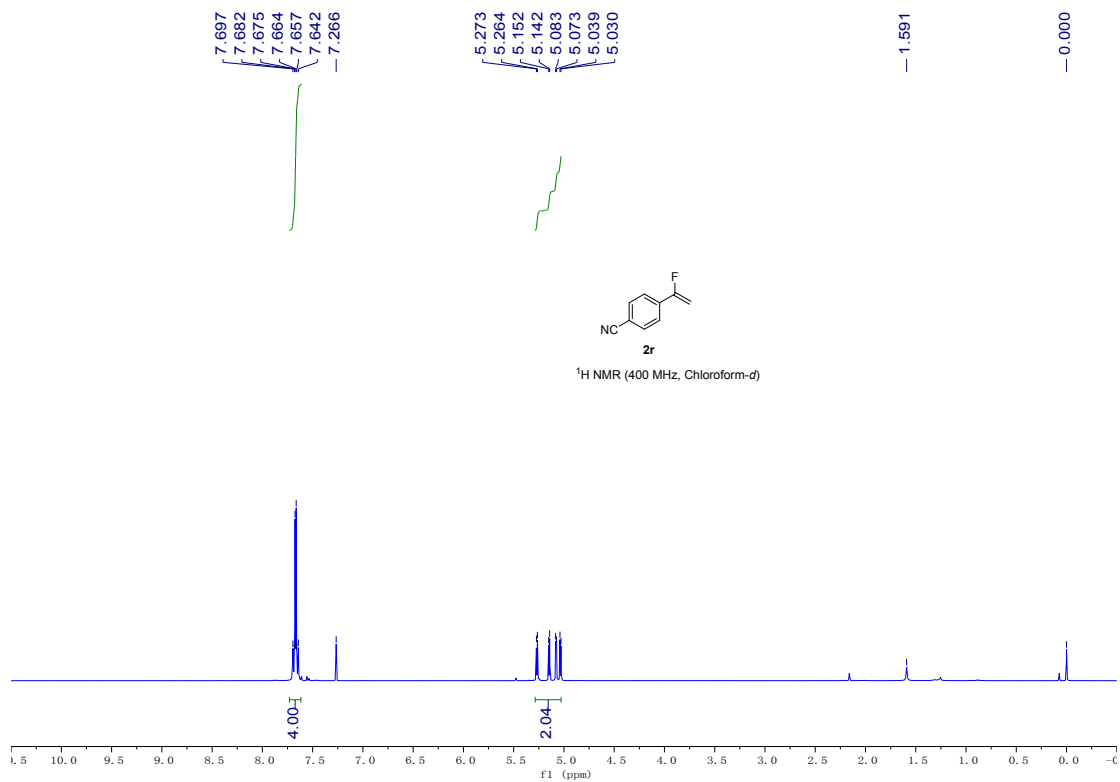


Figure S 52



Figure S 53

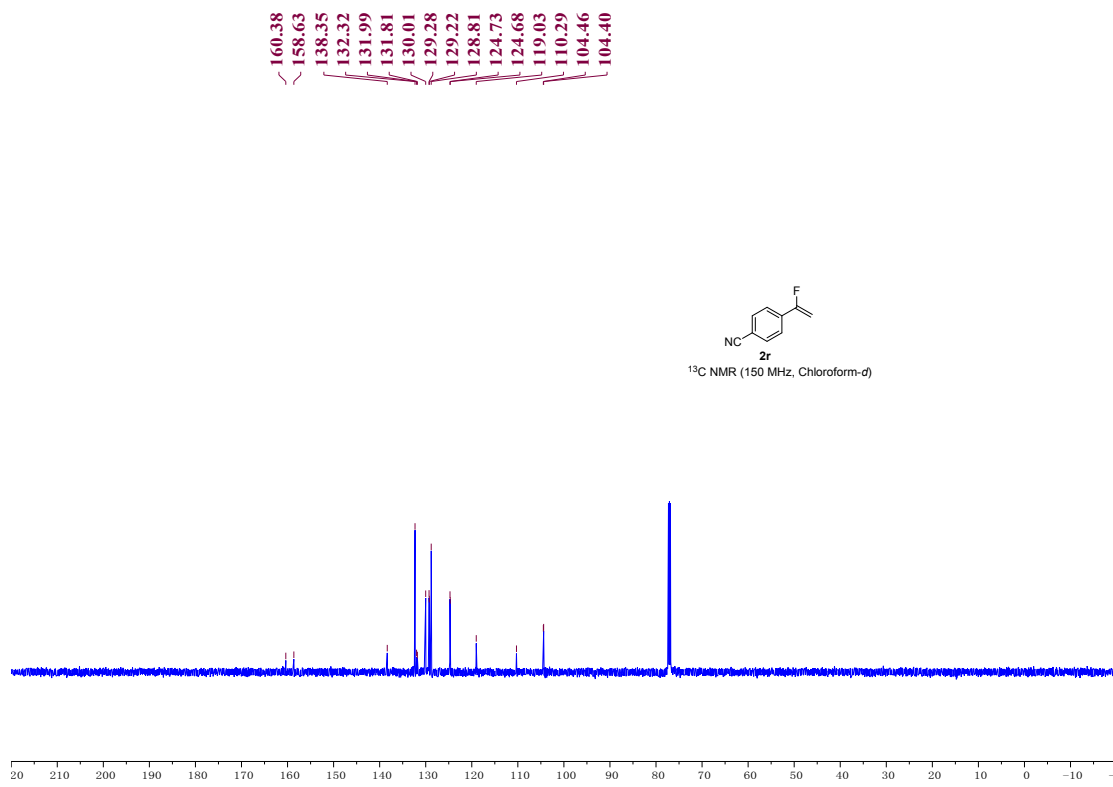


Figure S 54

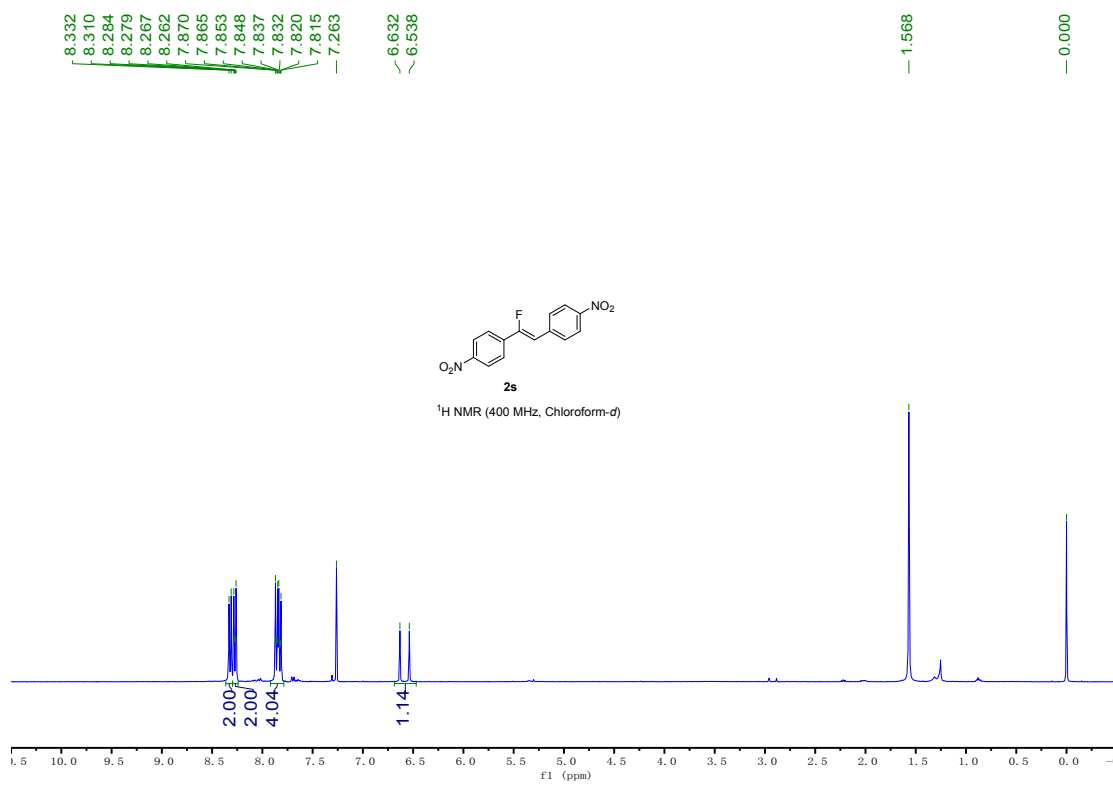


Figure S 55

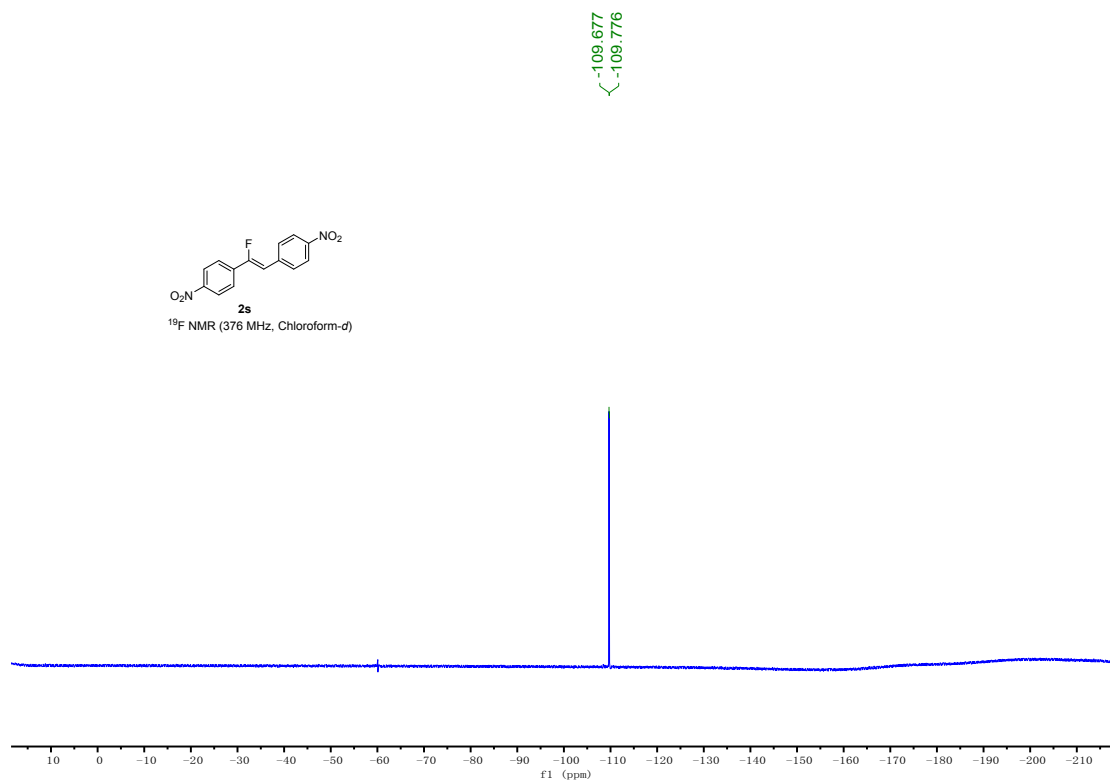


Figure S 56

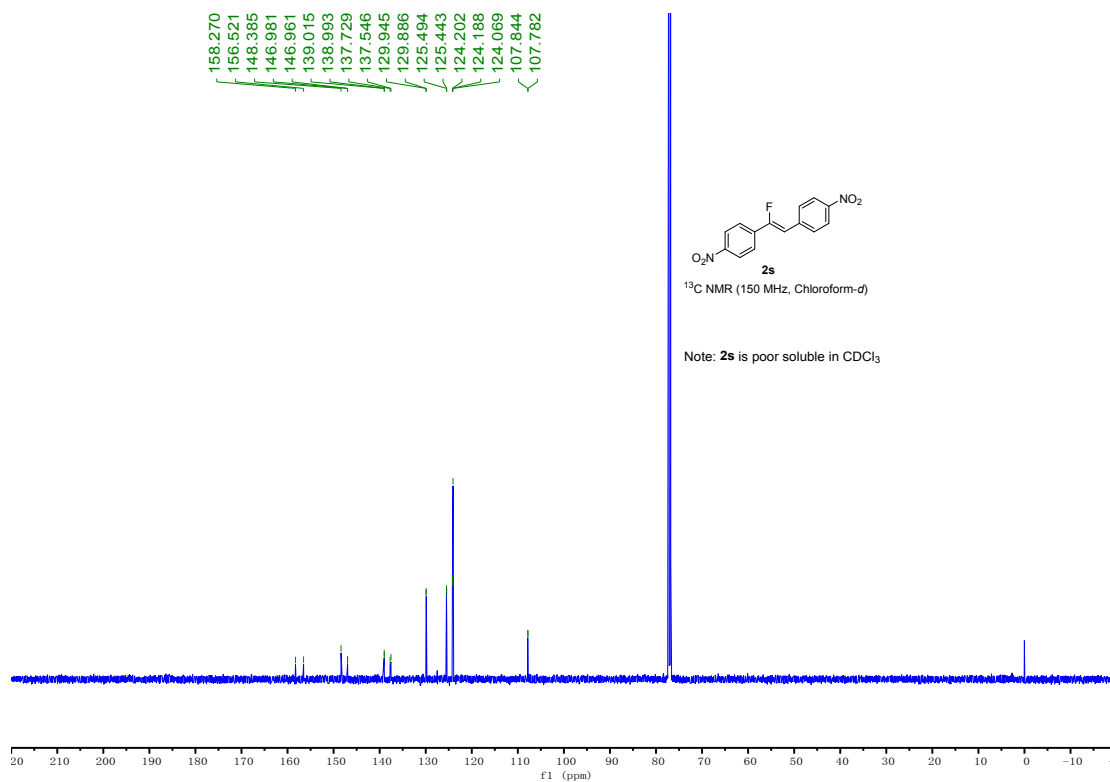


Figure S 57

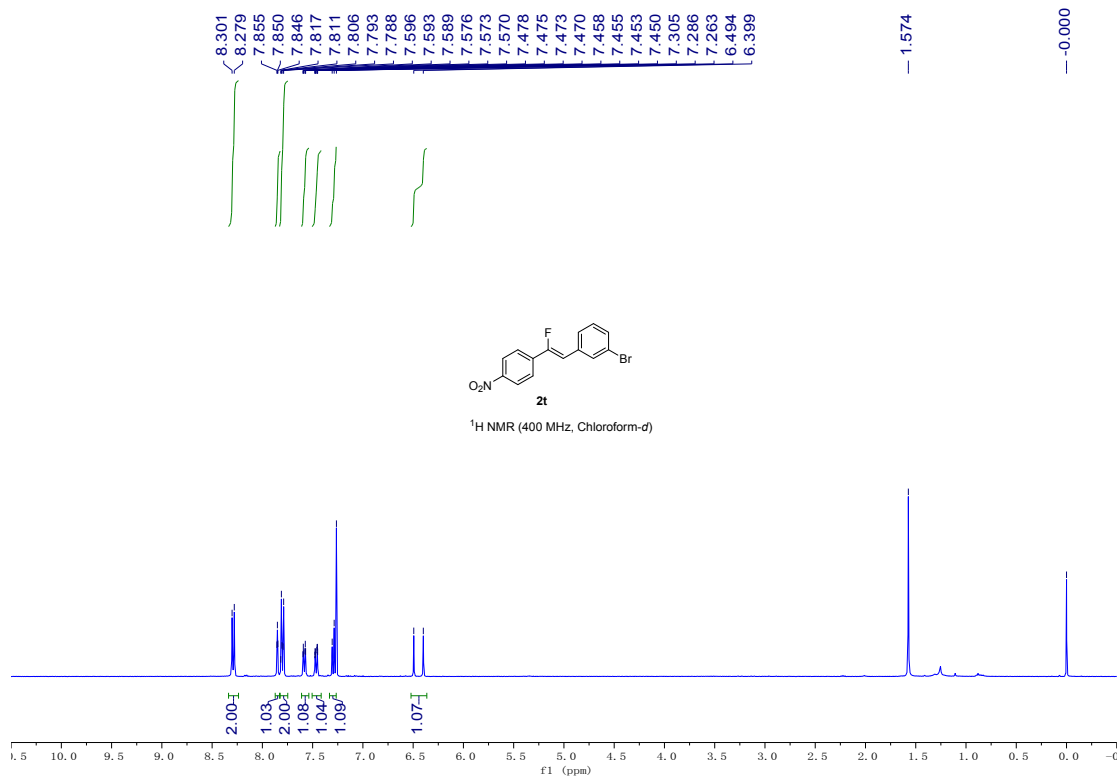


Figure S 58

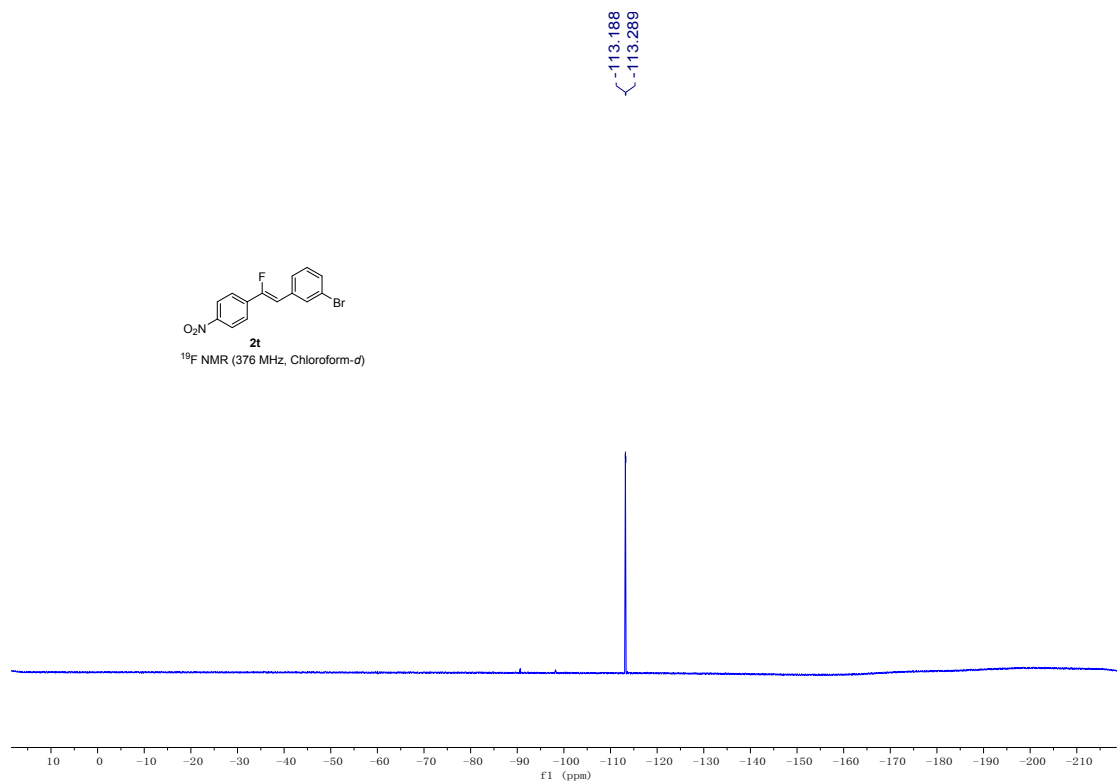


Figure S 59

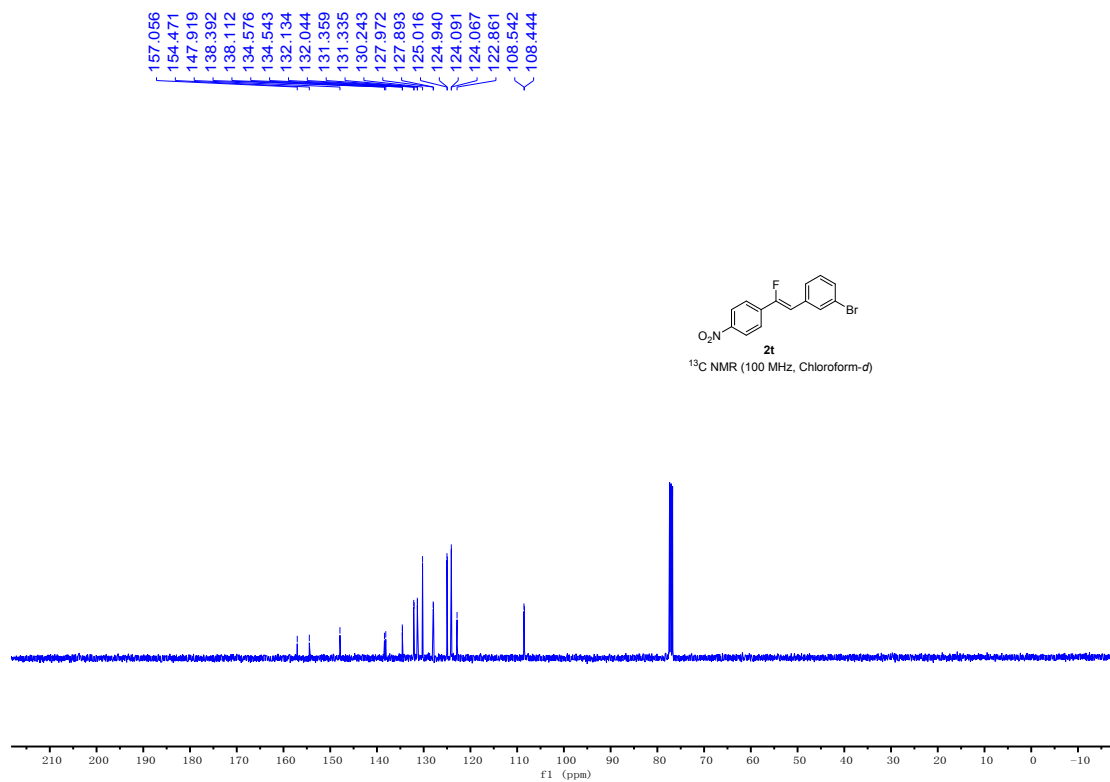


Figure S 60

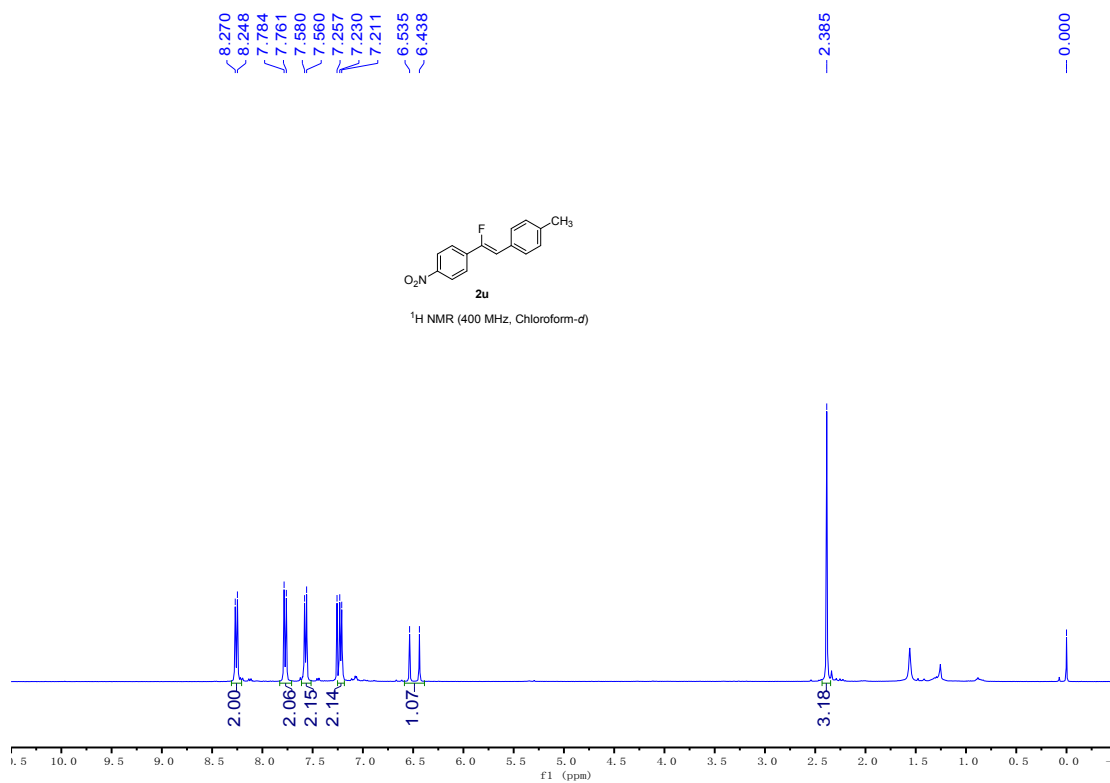


Figure S 61

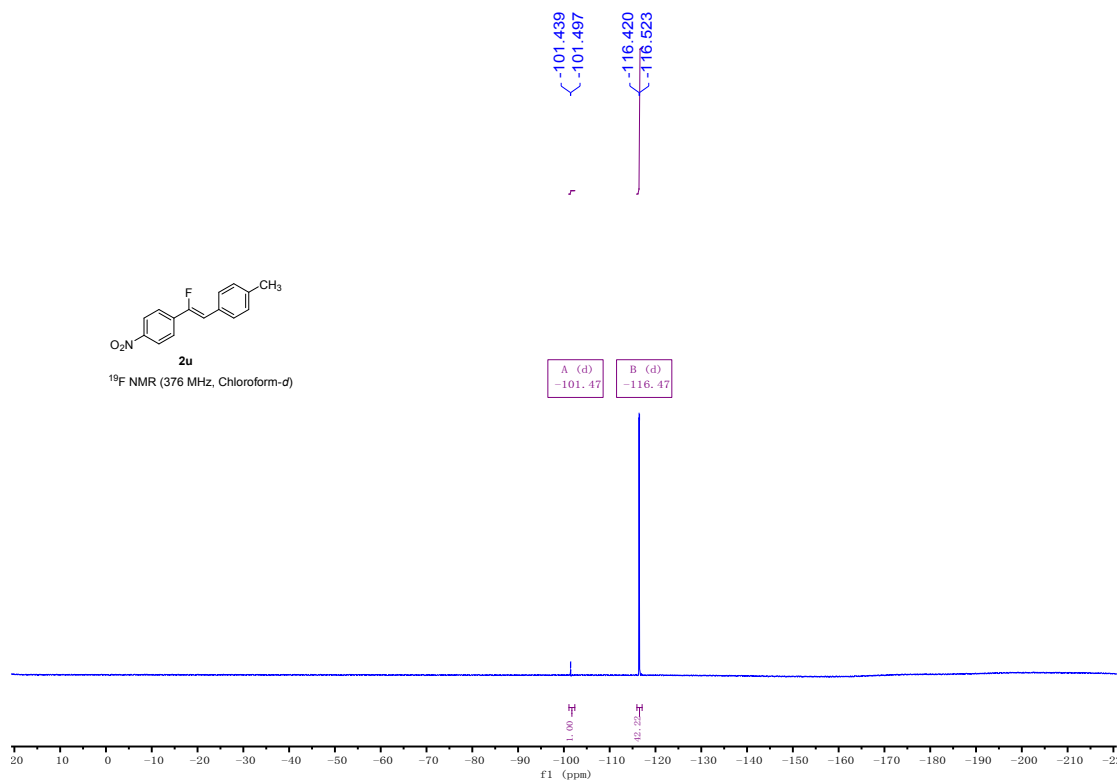


Figure S 62

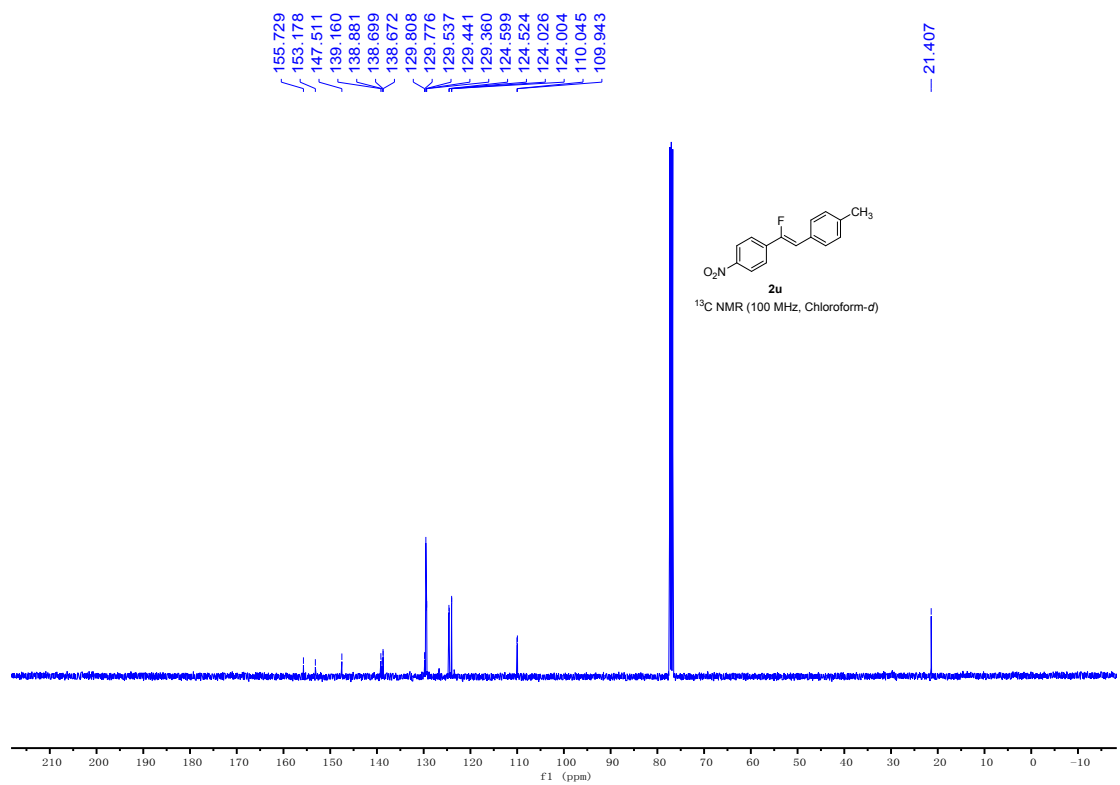


Figure S 63

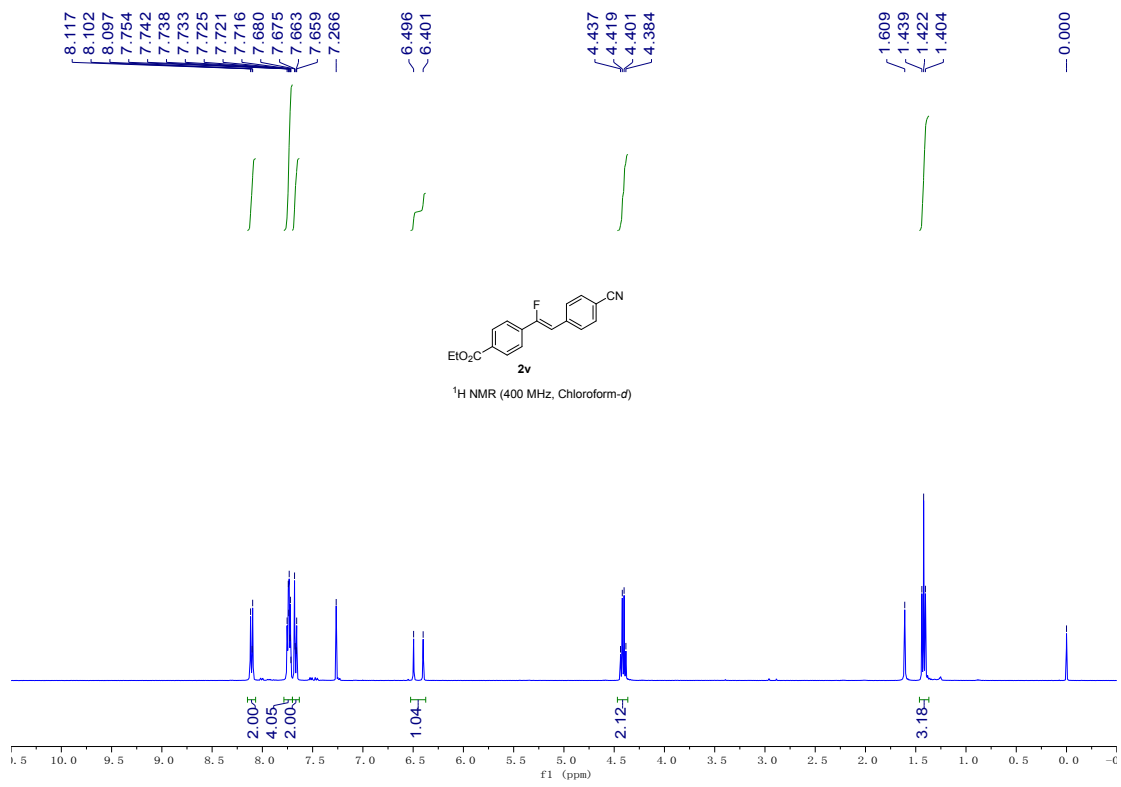


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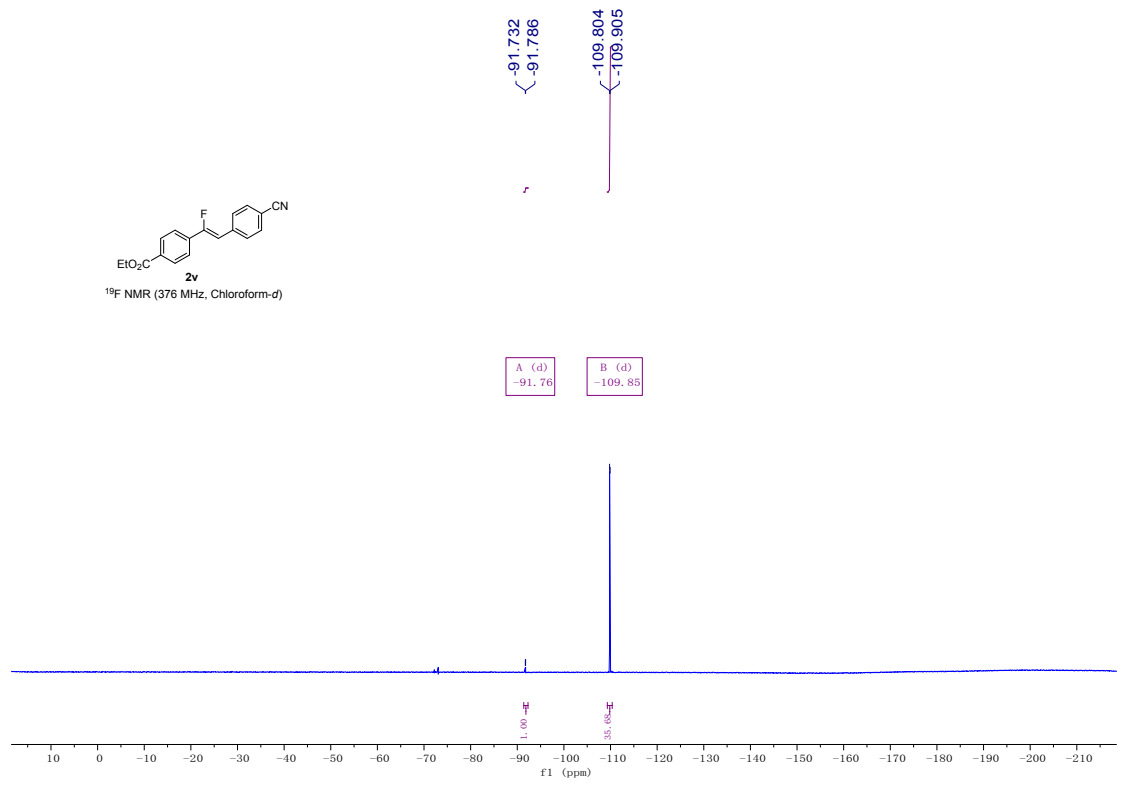


Figure S 65

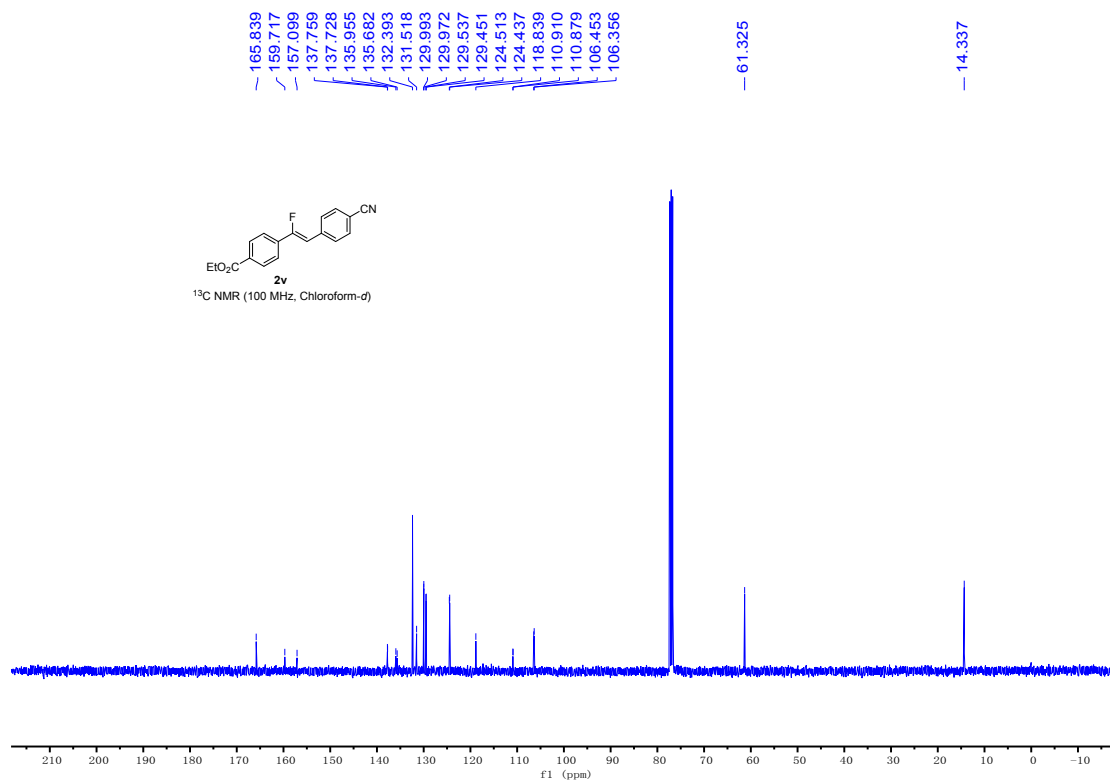


Figure S 66

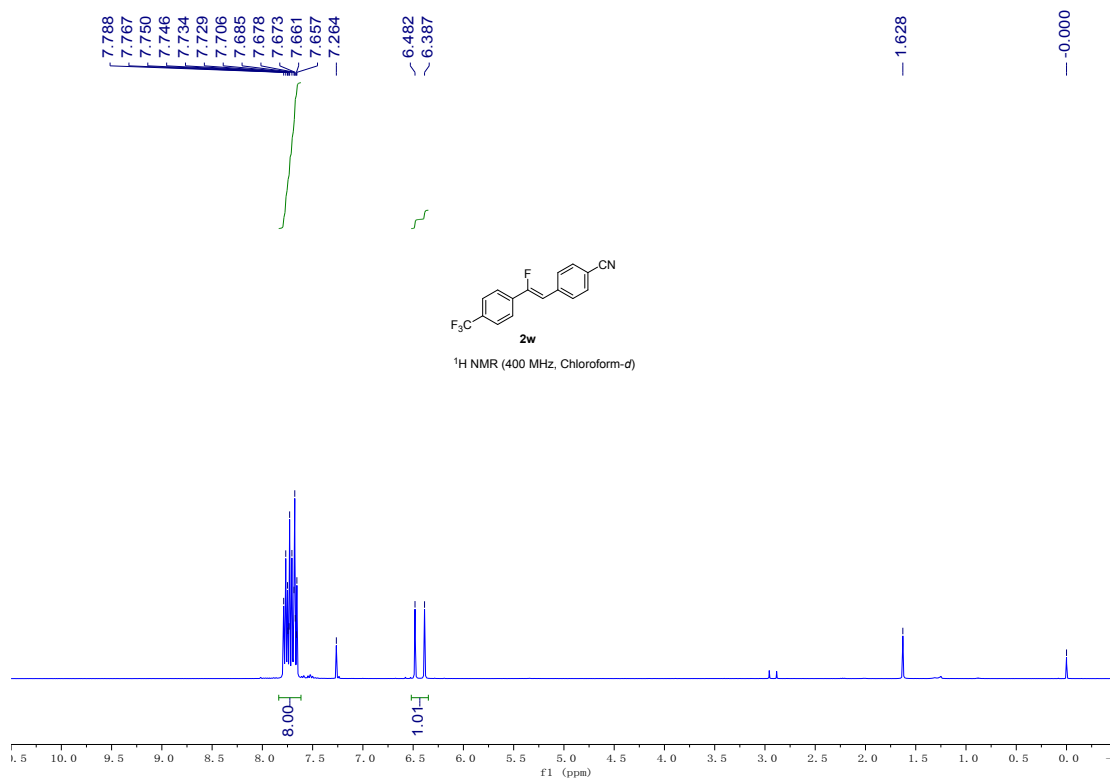


Figure S 67

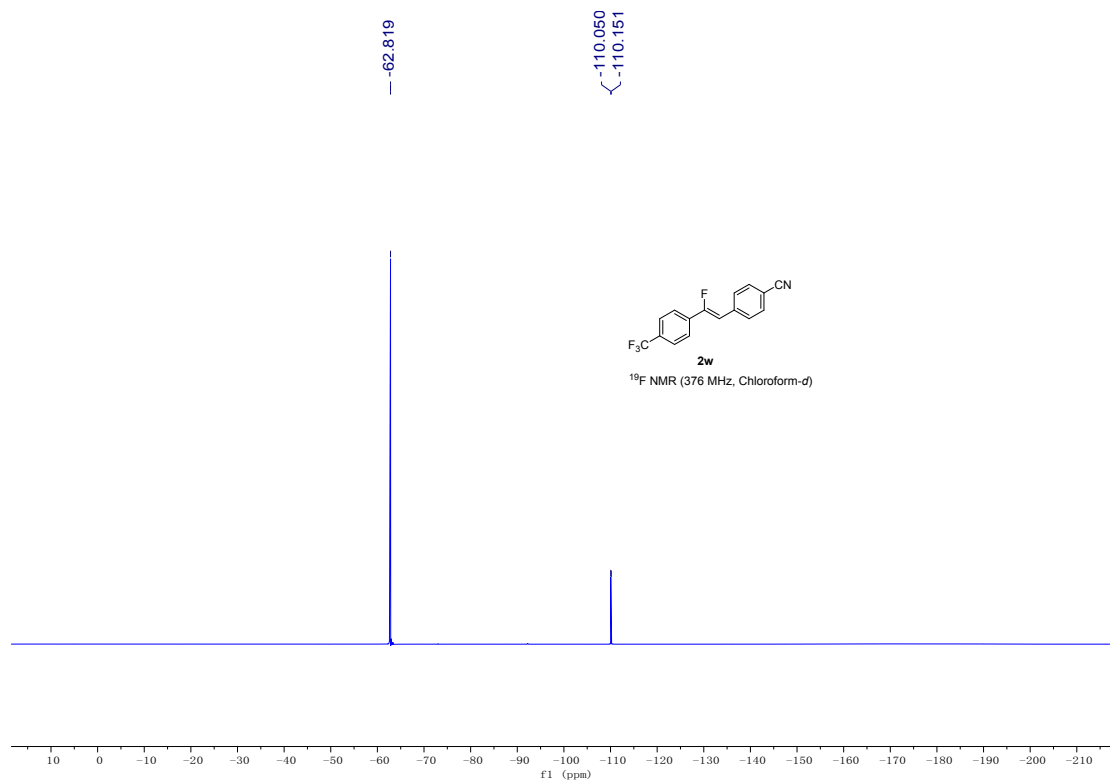


Figure S 68

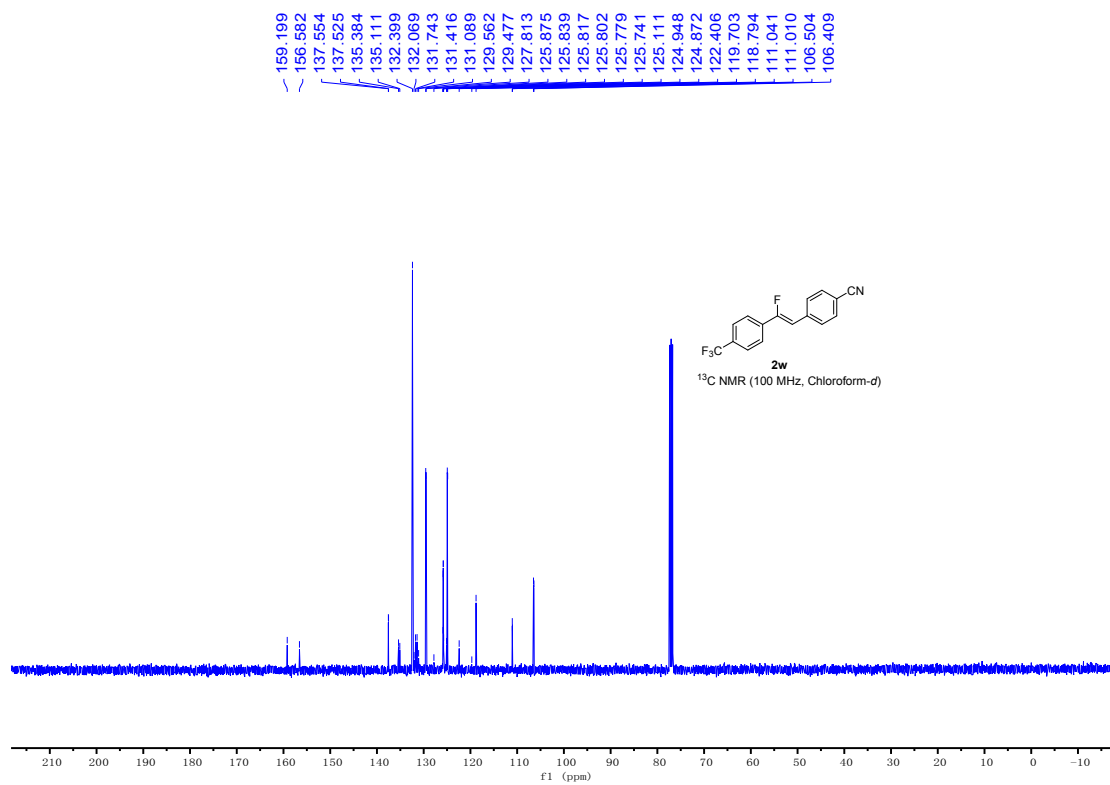


Figure S 69

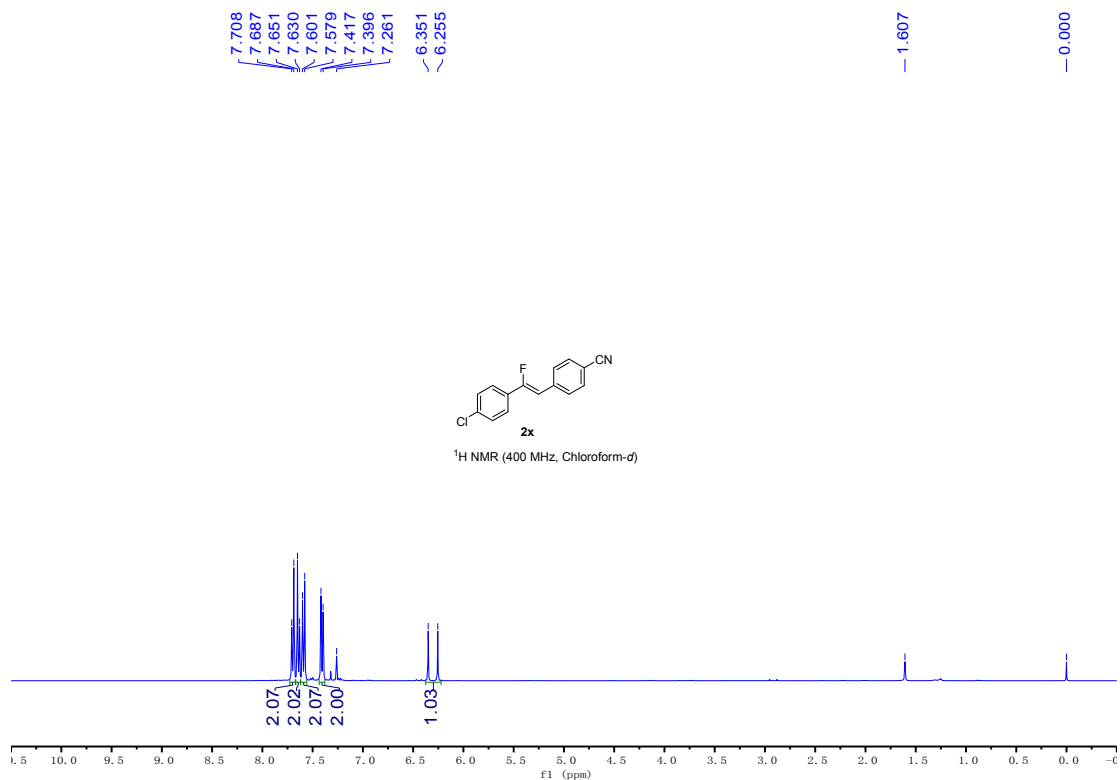


Figure S 70



Figure S 71

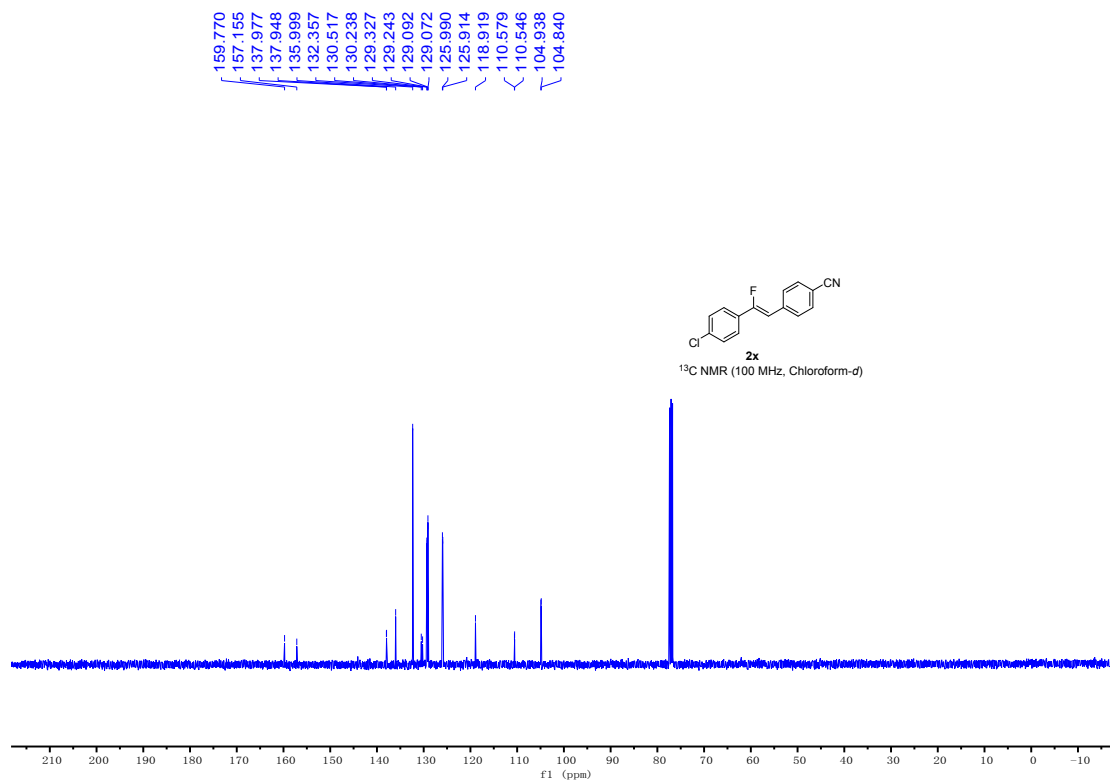


Figure S 72

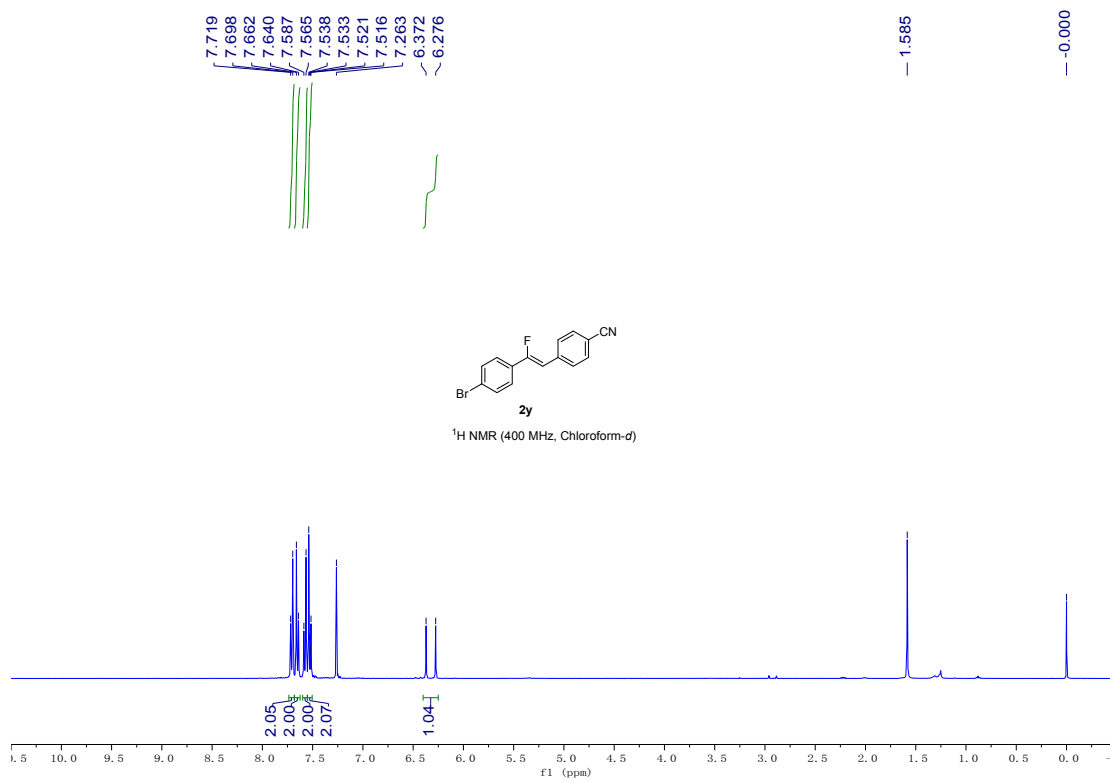


Figure S 73

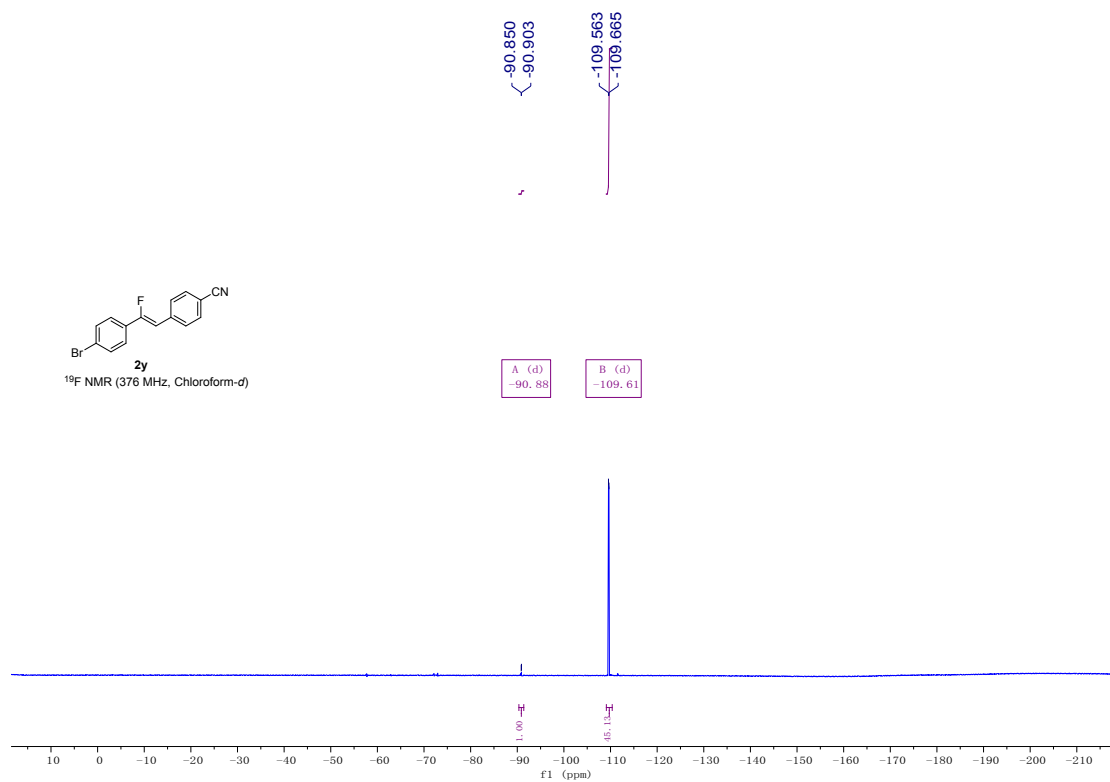


Figure S 74

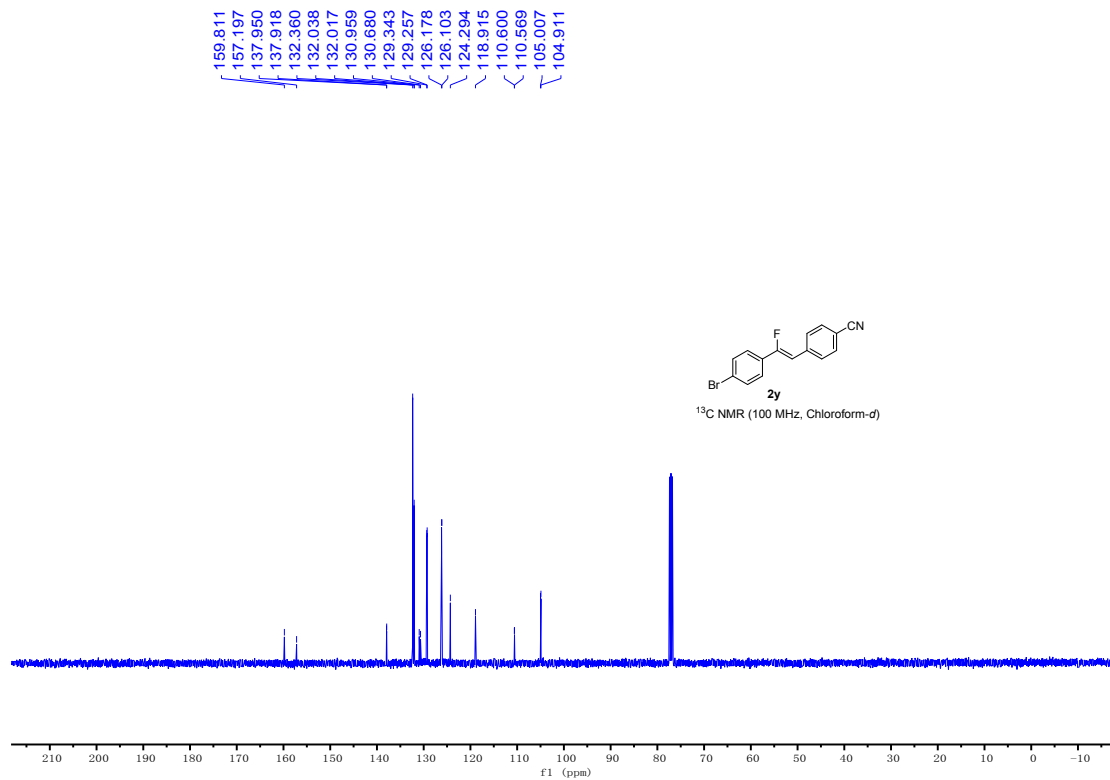


Figure S 75

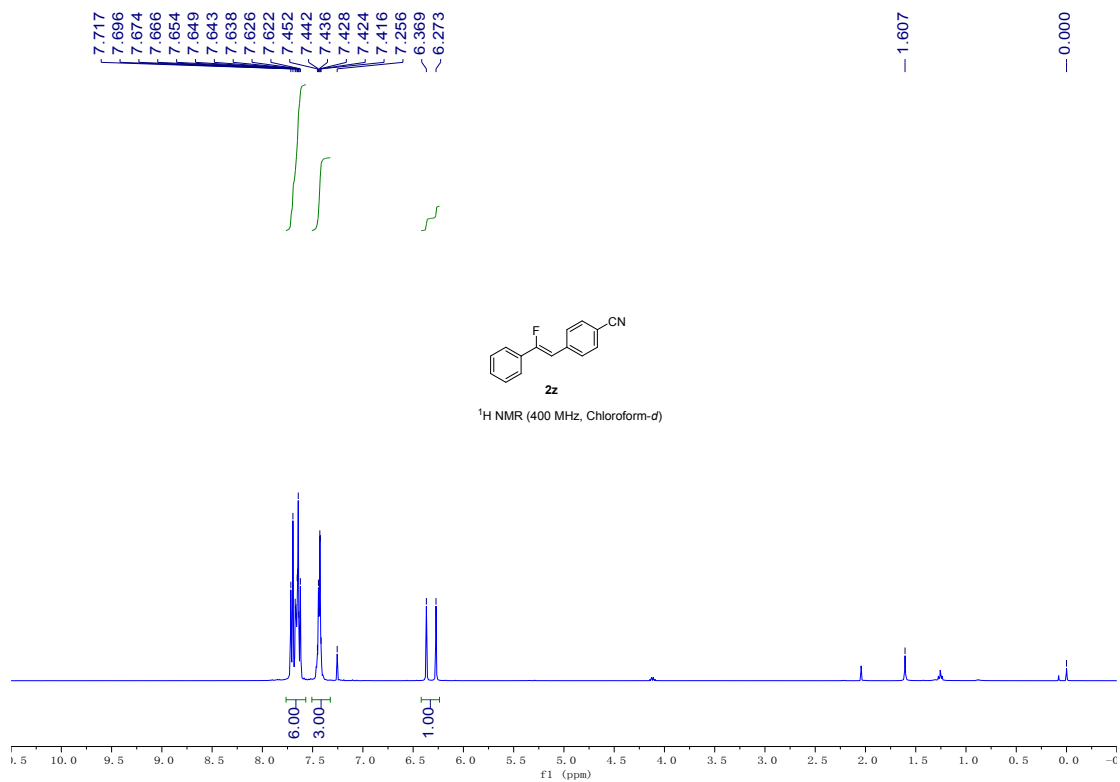


Figure S 76

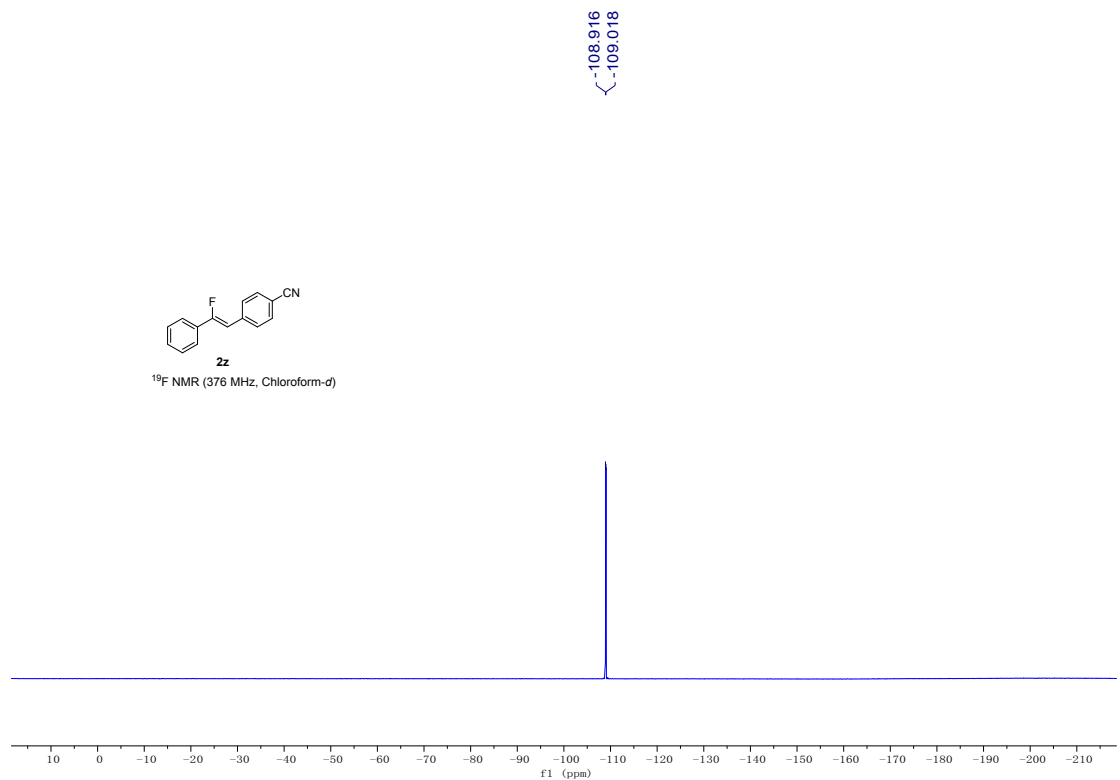


Figure S 77

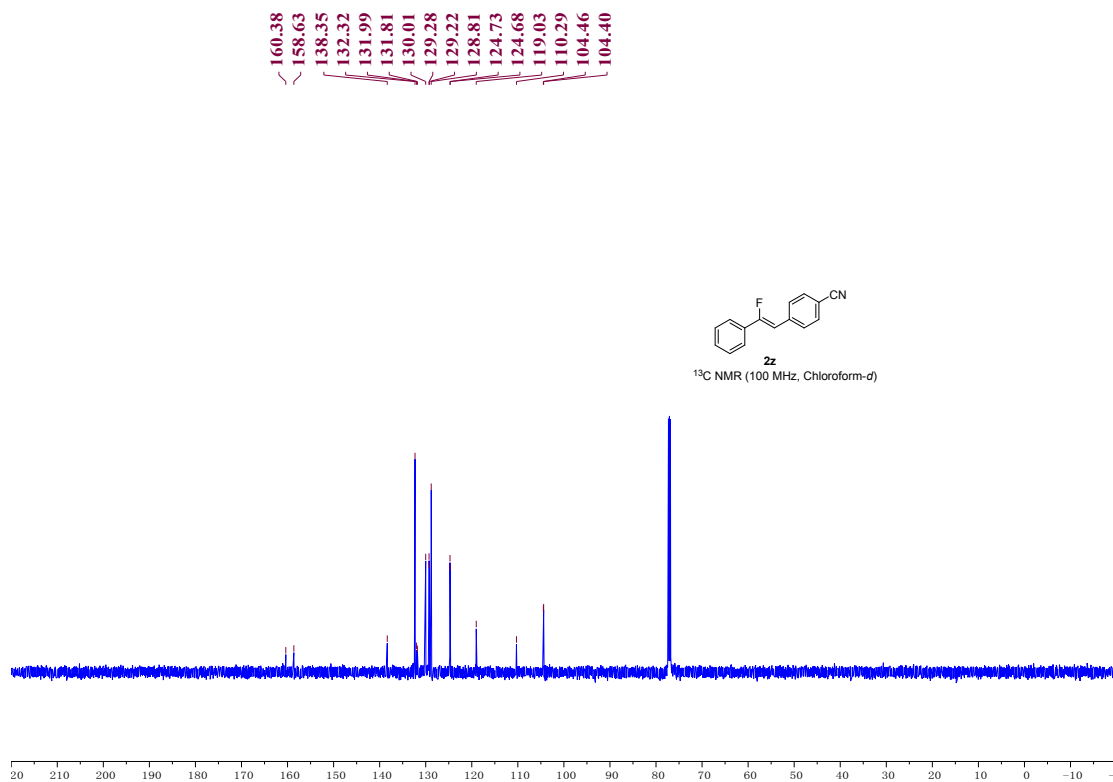


Figure S 78

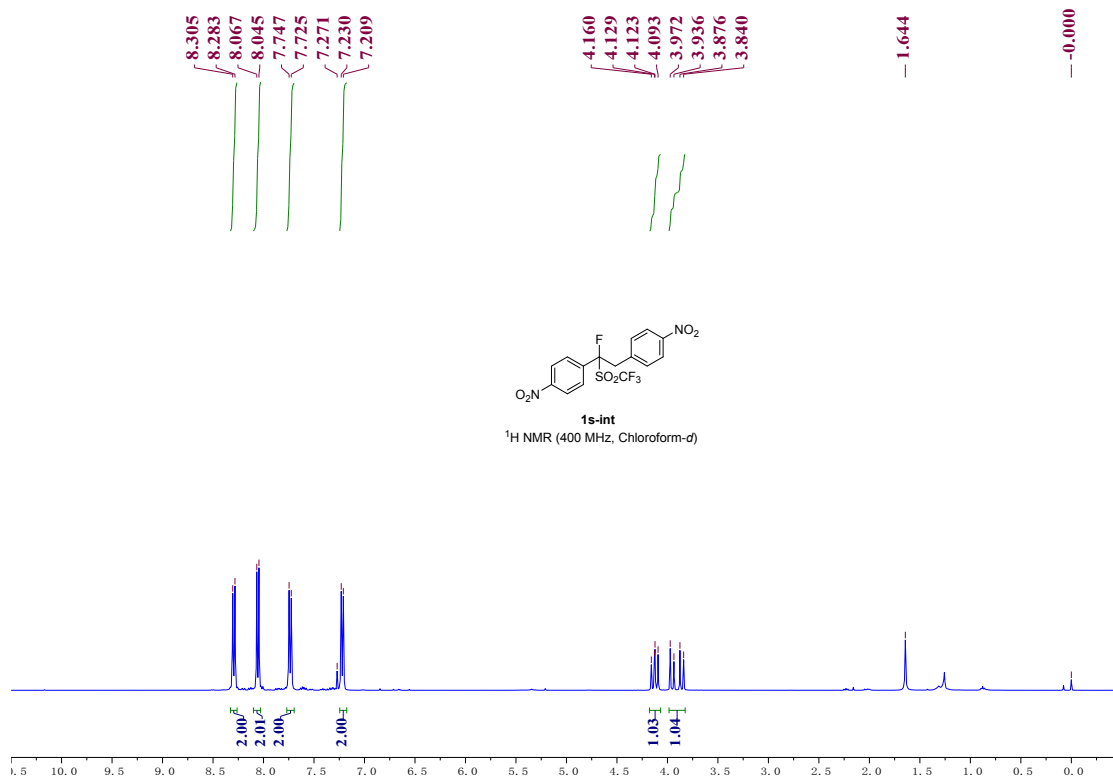


Figure S 79

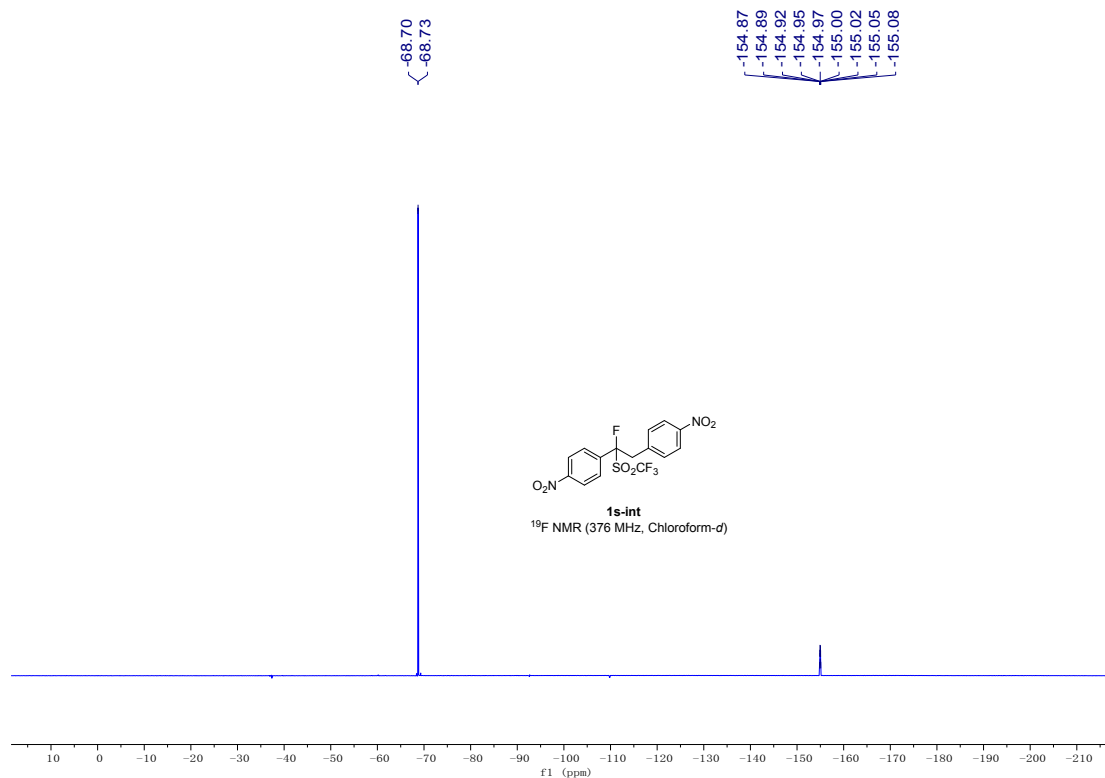


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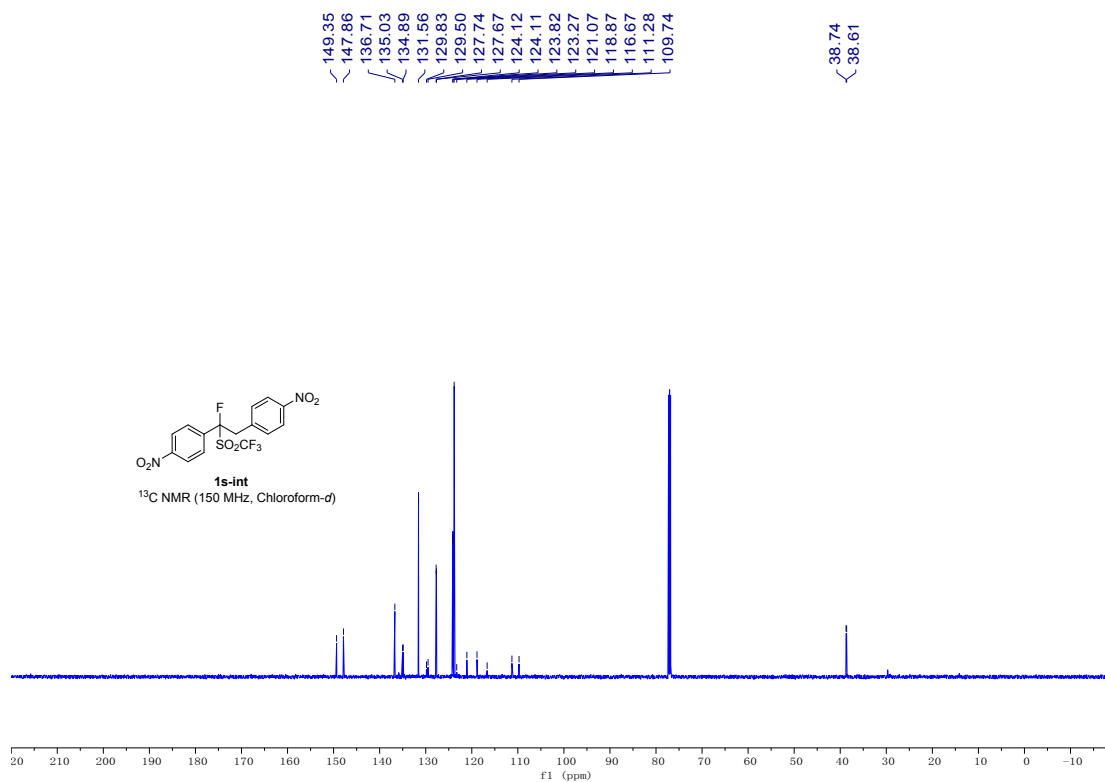


Figure S 81

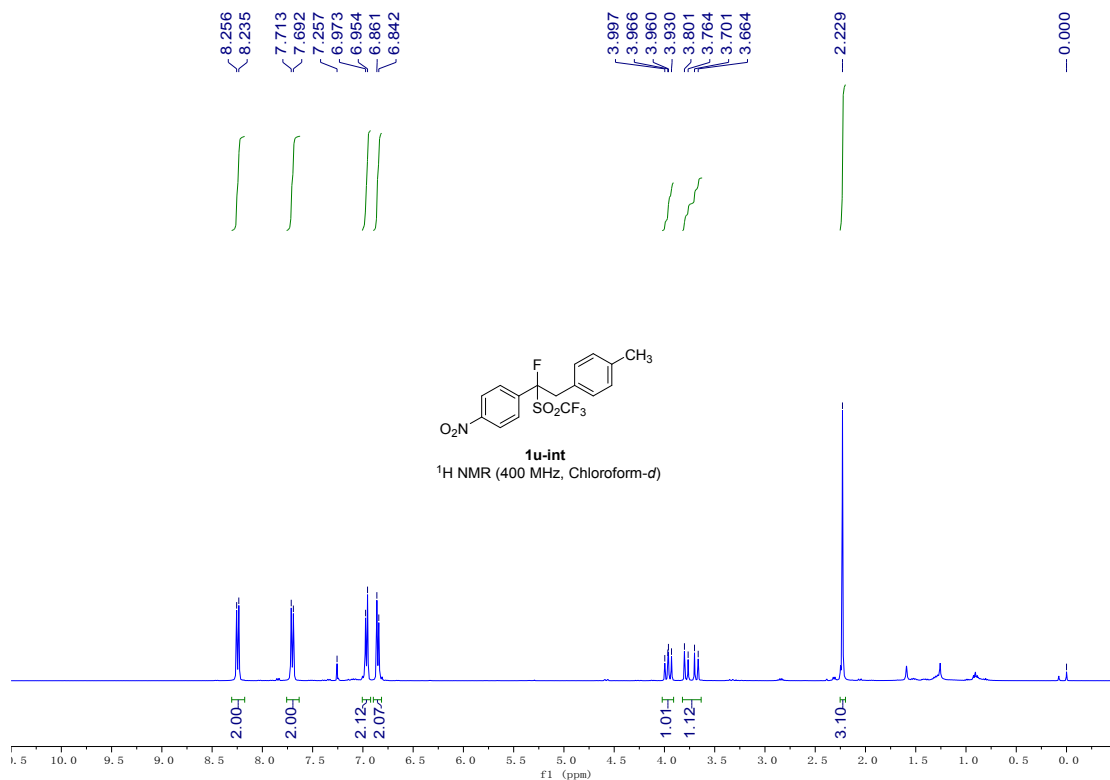


Figure S 82

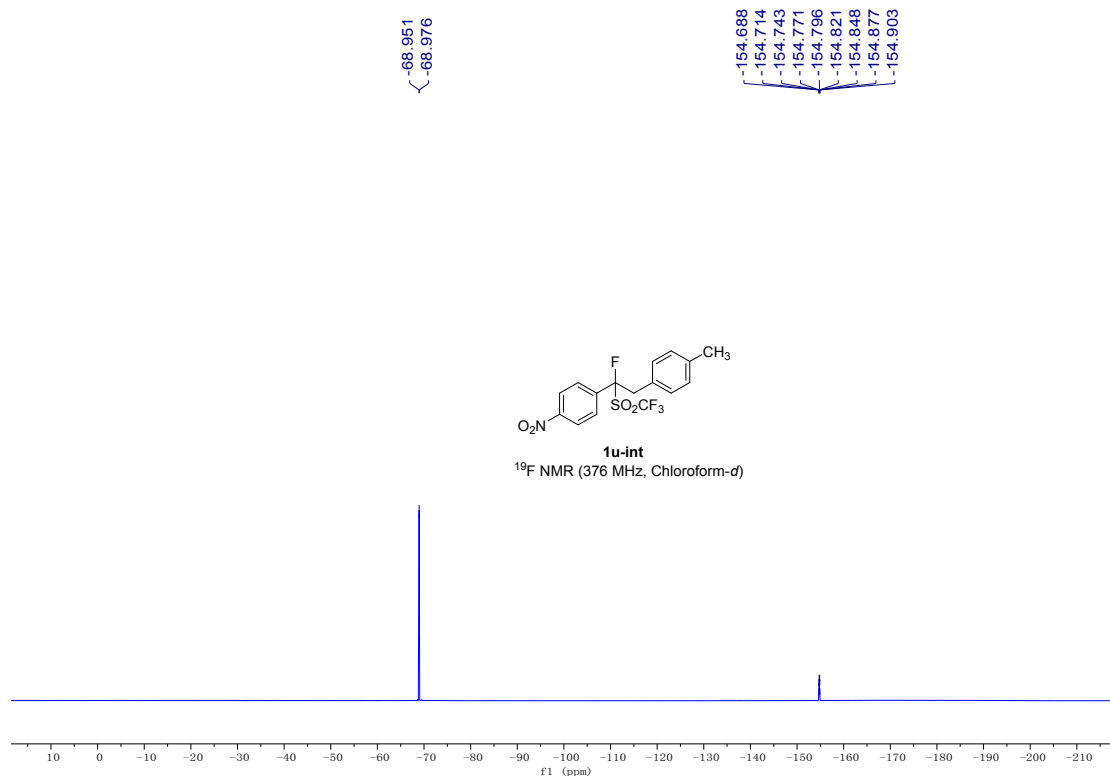


Figure S 83

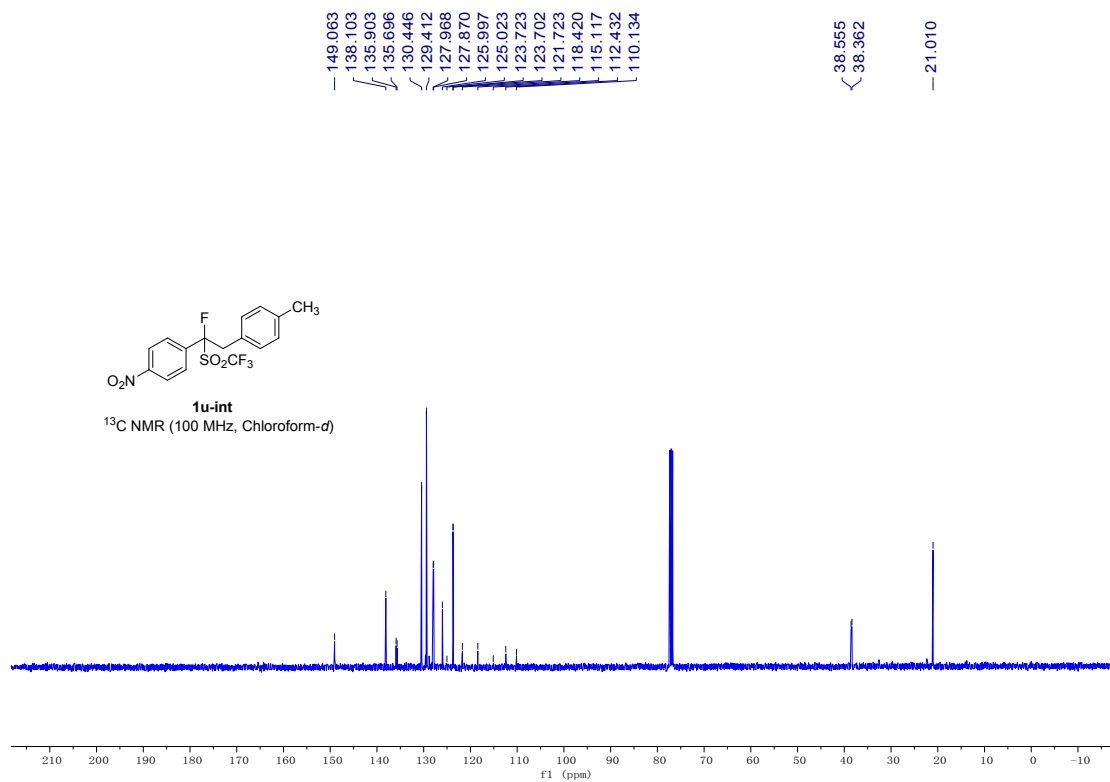


Figure S 84