

## Supporting Information

### For

# ***cis*-Specific cyanofluorination of vinyl azides enabled by electron-donor-acceptor complexes: synthesis of $\alpha$ -azido- $\beta$ -fluoronitriles**

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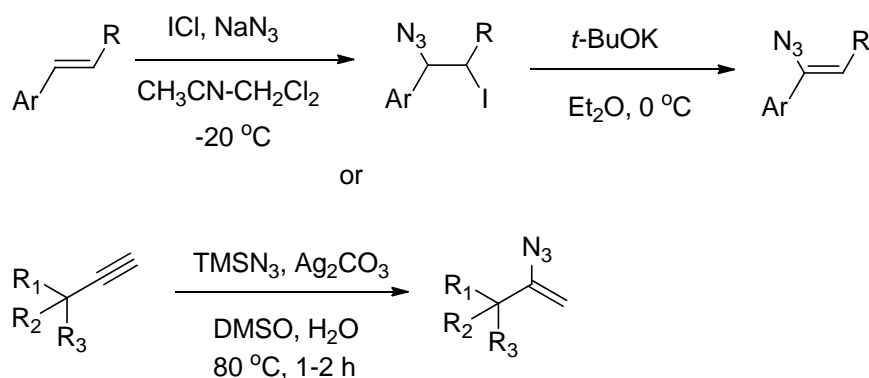
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## General remarks

$^1\text{H}$  NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for  $^{13}\text{C}$  NMR, 376 or 564 MHz for  $^{19}\text{F}$  NMR) agilent NMR spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm,  $\delta$  scale) downfield from TMS at 0.00 ppm and referenced to the  $\text{CDCl}_3$  at 7.26 ppm (for  $^1\text{H}$  NMR) or 77.16 ppm (for  $^{13}\text{C}$  NMR). Mass spectroscopy data of the products were collected on a GCT Premier<sup>TM</sup> (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ . Melting points were measured using SGW, X-4B and values are uncorrected. Dichloromethane and acetonitrile were dried over  $\text{CaH}_2$  and distilled. The substrates were readily prepared from phenylethylenes or alkynes (*Angew. Chem., Int. Ed.* **2014**, *53*, 4390; *Org. Lett.* **2014**, *16*, 3668; *Org. Lett.*, **2016**, *18*, 3642.).

## Synthesis of vinyl azides

Synthetic Scheme:



Typical synthetic procedures:

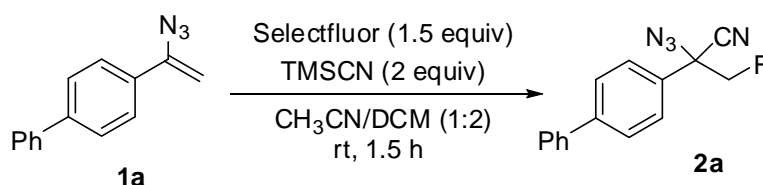
1: To a suspension of  $\text{NaN}_3$  (3.9 g, 60 mmol) in acetonitrile (18 mL) was added dropwise a solution of iodine monochloride (5.8 g, 36 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) at  $-20\text{ }^\circ\text{C}$ , and the mixture was stirred at the same temperature. After 30 min, a solution of 4-vinylbiphenyl (4.3 g, 24 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ , and the organic materials were extracted two times with  $\text{Et}_2\text{O}$ . The

combined extracts were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.

To a solution of the obtained compounds above in Et<sub>2</sub>O (60 mL) was added *t*-BuOK (3.2 g, 28.8 mmol) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction mixture was filtered through celite and the solvent was removed *in vacuo*. The resulting crude materials were purified by flash column chromatography (silica gel; hexane) to give 4-(1-azidovinyl)biphenyl (**1a**) (4.5 g, 84% yield) as a white solid. (*Angew. Chem., Int. Ed.* **2014**, *53*, 4390)

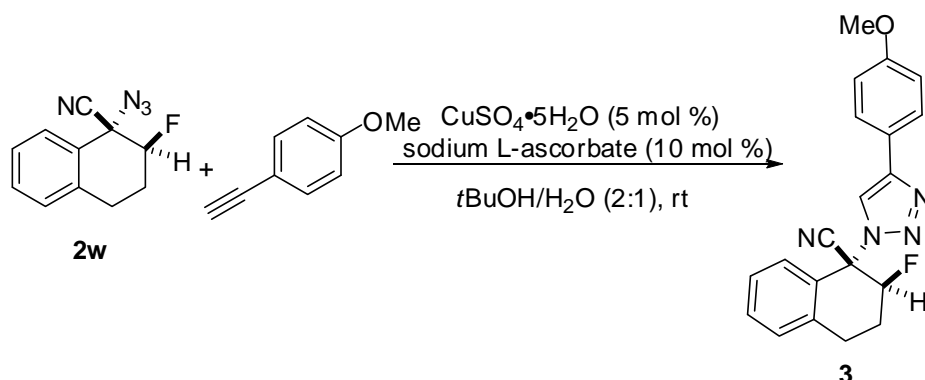
2: To a solution of (prop-2-ynyloxy) benzene (660 mg, 5 mmol), TMSN<sub>3</sub> (1.15 g, 10 mmol) and H<sub>2</sub>O (0.18 mL, 10 mmol) in DMSO (8 mL) at 80 °C, Ag<sub>2</sub>CO<sub>3</sub> (138 mg, 0.5 mmol) was added. The mixture was then stirred for 1-2 h until substrate (prop-2-ynyloxy) benzene consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 × 30 mL). The organic layer was washed with brine (3 × 40 mL), dried over MgSO<sub>4</sub> and concentrated. The resulting crude materials were purified by flash column chromatography (silica gel; hexane) to give (2-azidoallyloxy)benzene (**1y**) (717 mg, 82% yield) as a yellow oil. (*Org. Lett.* **2014**, *16*, 3668)

## Typical experimental procedures

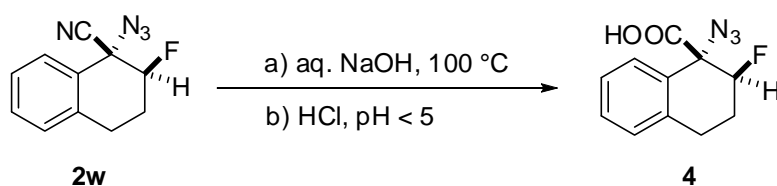


To a solution of vinyl azide **1a** (44.2 mg, 0.2 mmol) in 2 mL of CH<sub>3</sub>CN/DCM (1:2) in a glass vial was added TMSCN (39.6 mg, 0.4 mmol) at rt. After being stirred for 10 min, to the reaction mixture was added Selectfluor (106 mg, 0.3 mmol). After TLC indicated the complete consumption of the substrate, the resulting reaction mixture was concentrated and purified directly by flash column chromatography on silica gel

to give **2a** as a white solid (41.5 mg, 78% yield).

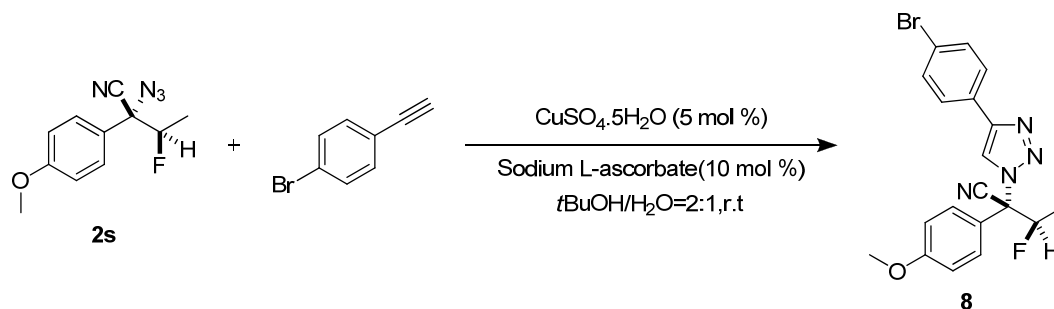


**cis-2-Fluoro-1-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (3):** To a suspension of terminal alkyne (79 mg, 0.6 mmol),  $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  (6 mg, 0.025 mmol), and Sodium L-ascorbate (10 mg, 0.05 mmol) in 5 mL of *t*-BuOH/ $\text{H}_2\text{O}$  (2:1) was added **2w** (108 mg, 0.5 mmol) at rt. The resulting mixture was stirred at room temperature for 4 h. The resulting mixture was extracted with ethyl acetate (15 mL  $\times$  3). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE:EA = 10:1) to give the corresponding product (**3**) as a white solid (141 mg, 81% yield). (*Tetrahedron*, **2012**, 53, 1606.)



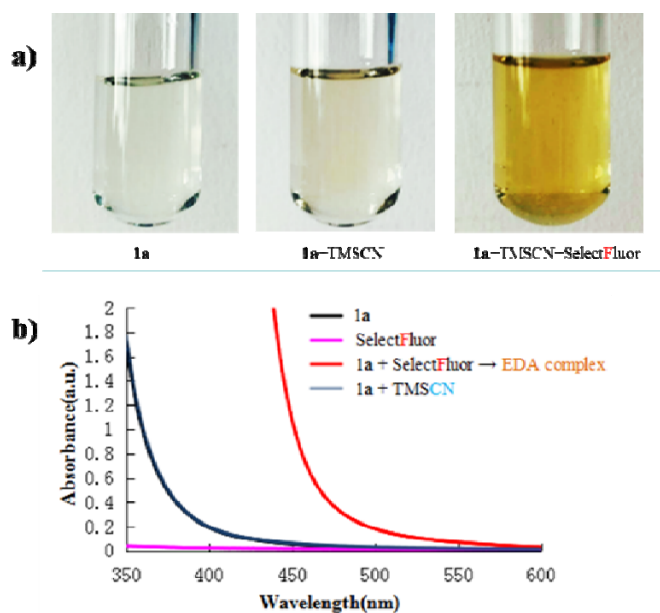
**cis-1-Azido-2-fluoro-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (4):** To a solution of NaOH (160 mg, 4 mmol) in water (10 mL) was added to **2w** (432 mg, 2 mmol). The mixture was heated at reflux for 12 h and then cooled to rt. The mixture was further cooled to 0 °C and acidified with concentrated HCl (*ca* 2 mL) to pH < 5. Then, the mixture was extracted with dichloromethane (15 mL  $\times$  3). The combined dichloromethane layer was brined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (PE:EA = 4:1) to give **4** as a white solid (423 mg, 90% yield).

(Patent: WO2012/110773A1, 2012.)



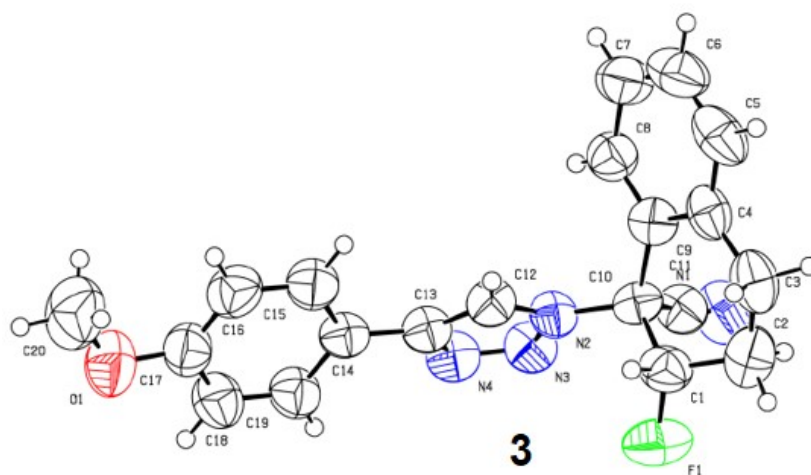
**2-(4-(4-Bromophenyl)-1H-1,2,3-triazol-1-yl)-3-fluoro-2-(4-methoxyphenyl)butane nitrile (8):** To a suspension of 1-bromo-4-ethynylbenzene (107 mg, 0.6 mmol), Cu<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O (6 mg, 0.025 mmol), and Sodium L-ascorbate (10 mg, 0.05 mmol) in 5 mL of *t*-BuOH/H<sub>2</sub>O (2:1) was added **2s** (117 mg, 0.5 mmol) at rt. The resulting mixture was stirred at room temperature for 6h. The resulting mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE:EA = 10:1) to give the corresponding product (**8**) as a white solid (166 mg, 80% yield).

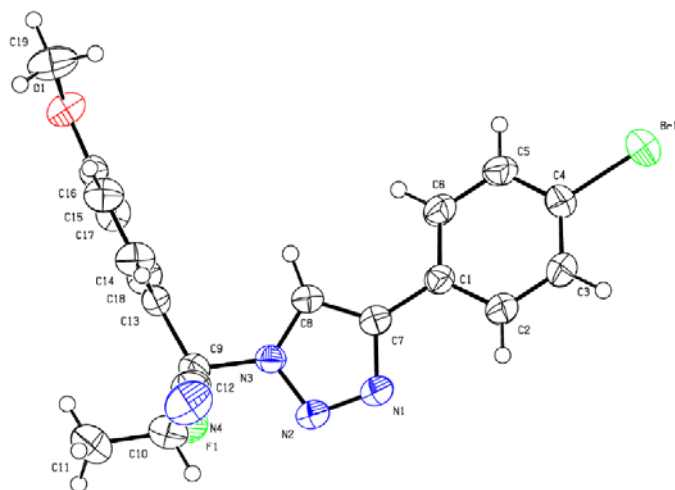
## Evidences of EDA complex formation



**Figure 1** a) Images demonstrating the formation of an EDA complex (yellow). b) Optical absorption spectra recorded in acetonitrile in a 1 cm path quartz cuvettes using a Shimadzu UV-2600 UV-visible spectrophotometer;  $[1a] = 0.1$  M,  $[Selectfluor] = 0.15$  M,  $[TMSCN] = 0.2$  M. The combination of **1a** with Selectfluor determines strong bathochromic shift (red line).

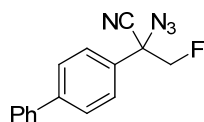
## The crystal structures of compound **3** and **8**



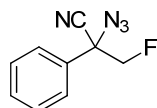


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## Characterization of the products

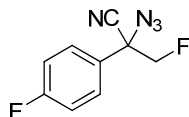


**2-Azido-2-(biphenyl-4-yl)-3-fluoropropanenitrile (2a):** White solid; m.p. 61-63 °C; 78% (41.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.2$  Hz, 2H), 7.65 (d,  $J = 8.2$  Hz, 2H), 7.61 (d,  $J = 7.5$  Hz, 2H), 7.49 (t,  $J = 7.4$  Hz, 2H), 7.42 (t,  $J = 7.2$  Hz, 1H), 4.75 – 4.50 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 139.6, 129.6 (d,  $J_{\text{C-F}} = 3.0$  Hz), 129.1, 128.30, 128.26, 127.3, 126.7, 115.3 (d,  $J_{\text{C-F}} = 2.0$  Hz), 86.3 (d,  $J_{\text{C-F}} = 193.0$  Hz), 65.6 (d,  $J_{\text{C-F}} = 18.8$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -213.95 (t,  $J = 46.5$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2957, 2102, 1486, 1239, 810; HRMS (CI) calcd for  $\text{C}_{15}\text{H}_{12}\text{FN}_4$   $[\text{M} + \text{H}]^+$ : 267.1046, found: 267.1041.

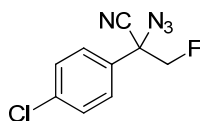


**2-Azido-3-fluoro-2-phenylpropanenitrile (2b):** Orange oil; 75% (28.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.54 (m, 2H), 7.54 – 7.41 (m, 3H), 4.75 – 4.39 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  130.9 (d,  $J_{\text{C-F}} = 3.0$  Hz), 130.8, 129.7, 126.3, 115.3 (d,  $J_{\text{C-F}} = 2.1$  Hz), 86.3 (d,  $J_{\text{C-F}} = 192.9$  Hz), 65.7 (d,  $J_{\text{C-F}} = 18.7$  Hz);  $^{19}\text{F}$  NMR

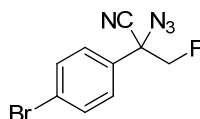
(376 MHz, CDCl<sub>3</sub>)  $\delta$  -213.84 (t,  $J$  = 46.5 Hz, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2945, 2106, 1492, 1234, 666.



**2-Azido-3-fluoro-2-(4-fluorophenyl)propanenitrile (2c):** Yellowish oil; 78% (32.5 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd,  $J$  = 8.2, 5.0 Hz, 2H), 7.19 (t,  $J$  = 8.4 Hz, 2H), 4.73 – 4.40 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.9 (d,  $J_{C-F}$  = 251.6 Hz), 128.4 (d,  $J_{C-F}$  = 8.8 Hz), 126.85 (t,  $J_{C-F}$  = 3.2 Hz), 116.8 (d,  $J_{C-F}$  = 22.3 Hz), 115.1 (d,  $J_{C-F}$  = 2.1 Hz), 86.2 (d,  $J_{C-F}$  = 192.1 Hz), 65.1 (d,  $J_{C-F}$  = 19.1 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -106.66 – -111.89 (m, 1F), -213.96 (t,  $J$  = 46.4 Hz, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2960, 2109, 1509, 1231, 835; HRMS (CI) calcd for C<sub>9</sub>H<sub>7</sub>F<sub>2</sub>N<sub>4</sub> [M + H]<sup>+</sup>: 209.0639, found: 209.0642.



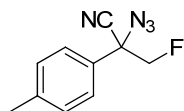
**2-Azido-2-(4-chlorophenyl)-3-fluoropropanenitrile (2d):** Yellow oil; 86% (38.5 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d,  $J$  = 8.5 Hz, 2H), 7.47 (d,  $J$  = 8.6 Hz, 2H), 4.74 – 4.34 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.0, 129.9, 129.5 (d,  $J_{C-F}$  = 2.6 Hz), 127.7, 114.9, 86.1 (d,  $J_{C-F}$  = 193.0 Hz), 65.1 (d,  $J_{C-F}$  = 19.2 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -214.16 (t,  $J$  = 46.4 Hz, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2960, 2109, 1493, 1096, 825; HRMS (CI) calcd for C<sub>9</sub>H<sub>7</sub><sup>35</sup>ClFN<sub>4</sub> [M + H]<sup>+</sup>: 225.0343, found: 225.0337.



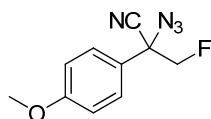
**2-Azido-2-(4-bromophenyl)-3-fluoropropanenitrile (2e):** Yellow oil; 80% (42.9 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d,  $J$  = 8.4 Hz, 2H), 7.45 (d,  $J$  = 8.4 Hz, 2H), 4.71 – 4.33 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  132.8, 130.0 (d,  $J_{C-F}$  = 2.9 Hz), 127.9, 125.2, 114.8 (d,  $J_{C-F}$  = 2.1 Hz), 86.0 (d,  $J_{C-F}$  = 193.1 Hz), 65.1 (d,  $J_{C-F}$  = 19.2



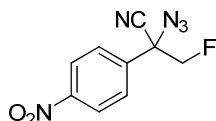
Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -214.16 (t,  $J = 46.4$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2943, 2109, 1489, 1074, 820; HRMS (CI) calcd for  $\text{C}_9\text{H}_7^{79}\text{BrFN}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 268.9838, found: 268.9836.



**2-Azido-3-fluoro-2-p-tolylpropanenitrile (2f):** Yellowish oil; 73% (29.8 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 7.9$  Hz, 2H), 4.75 – 4.34 (m, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 130.3, 127.8 (d,  $J_{\text{C-F}} = 3.0$  Hz), 126.1, 115.4 (d,  $J_{\text{C-F}} = 2.0$  Hz), 86.2 (d,  $J_{\text{C-F}} = 192.7$  Hz), 65.6 (d,  $J_{\text{C-F}} = 18.6$  Hz), 21.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -213.68 (t,  $J = 46.6$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2959, 2106, 1453, 1234, 813; HRMS (CI) calcd for  $\text{C}_{10}\text{H}_{10}\text{FN}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 205.0889, found: 205.0880.

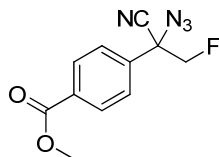


**2-Azido-3-fluoro-2-(4-methoxyphenyl)propanenitrile (2g):** Yellow oil; 55% (24.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.7$  Hz, 2H), 6.99 (d,  $J = 8.7$  Hz, 2H), 4.72 – 4.34 (m, 2H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 127.7, 122.6 (d,  $J_{\text{C-F}} = 2.8$  Hz), 115.5, 115.0, 86.2 (d,  $J_{\text{C-F}} = 192.8$  Hz), 65.4 (d,  $J_{\text{C-F}} = 18.7$  Hz), 55.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -213.48 (t,  $J = 46.5$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2962, 2107, 1511, 1256, 830; HRMS (CI) calcd for  $\text{C}_{10}\text{H}_{10}\text{FN}_4\text{O}$  [ $\text{M} + \text{H}$ ] $^+$ : 221.0839, found: 221.0844.

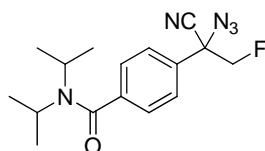


**2-Azido-3-fluoro-2-(4-nitrophenyl)propanenitrile (2h):** Yellow solid; m.p. 48-50  $^{\circ}\text{C}$ ; 70% (32.9 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (d,  $J = 8.7$  Hz, 2H), 7.80 (d,  $J = 8.7$  Hz, 2H), 4.79 – 4.41 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.3, 137.6 (d,  $J_{\text{C-F}} = 2.6$  Hz), 127.8, 124.7, 114.4 (d,  $J_{\text{C-F}} = 2.2$  Hz), 86.0 (d,  $J_{\text{C-F}} = 193.6$

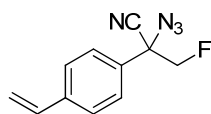
Hz), 64.8 (d,  $J_{C-F} = 19.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -215.16 (t,  $J = 46.0$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2920, 2112, 1624, 1349, 850; HRMS (CI) calcd for  $\text{C}_9\text{H}_7\text{FN}_5\text{O}_2$   $[\text{M} + \text{H}]^+$ : 236.0584, found: 236.0574.



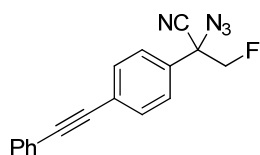
**Methyl-4-(1-azido-1-cyano-2-fluoroethyl)benzoate (2i):** Yellowish solid; m.p. 67-69 °C; 63% (31.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 8.2$  Hz, 2H), 7.65 (d,  $J = 8.3$  Hz, 2H), 4.78 – 4.41 (m, 2H), 3.93 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 135.34 (d,  $J_{C-F} = 2.6$  Hz), 132.5, 130.7, 126.4, 114.8 (d,  $J_{C-F} = 1.6$  Hz), 86.1 (d,  $J_{C-F} = 193.1$  Hz), 65.3 (d,  $J_{C-F} = 19.2$  Hz), 52.6;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -214.69 (t,  $J = 46.3$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2954, 2102, 1716, 1334, 753; HRMS (CI) calcd for  $\text{C}_{11}\text{H}_{10}\text{FN}_4\text{O}_2$   $[\text{M} + \text{H}]^+$ : 249.0788, found: 249.0778.



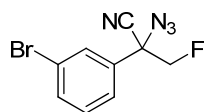
**4-(1-Azido-1-cyano-2-fluoroethyl)-N,N-diisopropylbenzamide (2j):** White solid; m.p. 78-80 °C; 69% (43.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 8.0$  Hz, 2H), 7.42 (d,  $J = 8.0$  Hz, 2H), 4.73 – 4.42 (m, 2H), 3.93 – 3.35 (m, 2H), 1.65 – 0.99 (m, 12H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 141.3, 131.3 (d,  $J_{C-F} = 2.8$  Hz), 126.9, 126.6, 115.0, 86.3 (d,  $J_{C-F} = 193.3$  Hz), 65.4 (d,  $J_{C-F} = 19.0$  Hz), 51.2, 46.2, 20.8;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -213.93 (t,  $J = 46.3$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2974, 2103, 1373, 1157, 828.



**2-Azido-3-fluoro-2-(4-vinylphenyl)propanenitrile (2k):** Yellow oil; 79% (34.1 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.45 (m, 4H), 6.73 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.84 (d,  $J = 17.6$  Hz, 1H), 5.38 (d,  $J = 10.9$  Hz, 1H), 4.65 – 4.46 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 135.5, 129.8 (t,  $J_{\text{C-F}} = 21.5$  Hz), 127.3, 126.5, 116.5, 115.2 (d,  $J_{\text{C-F}} = 1.5$  Hz), 86.2 (d,  $J_{\text{C-F}} = 193.0$  Hz), 65.6 (d,  $J_{\text{C-F}} = 18.9$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -214.08 (t,  $J = 46.4$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2959, 2107, 1632, 1234, 840; HRMS (CI) calcd for  $\text{C}_{11}\text{H}_{10}\text{FN}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 217.0889, found: 217.0888.

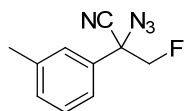


**2-Azido-3-fluoro-2-(4-(phenylethynyl)phenyl)propanenitrile (2l):** White solid; m.p. 94-96 °C; 65% (37.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.2$  Hz, 2H), 7.60 – 7.51 (m, 4H), 7.42 – 7.34 (m, 3H), 4.82 – 4.19 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.6, 131.8, 130.4 (d,  $J_{\text{C-F}} = 2.9$  Hz), 128.9, 128.6, 126.3, 126.1, 122.6, 115.0 (d,  $J_{\text{C-F}} = 2.0$  Hz), 91.8, 87.9, 86.1 (d,  $J_{\text{C-F}} = 193.2$  Hz), 65.4 (d,  $J_{\text{C-F}} = 19.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -214.06 (t,  $J = 46.4$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2922, 2105, 1597, 1244, 844; HRMS (CI) calcd for  $\text{C}_{17}\text{H}_{12}\text{FN}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 291.1046, found: 291.1042.

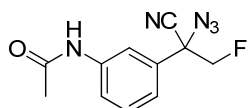


**2-Azido-2-(3-bromophenyl)-3-fluoropropanenitrile (2m):** Yellow oil; 71% (38.0 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (s, 1H), 7.63 (d,  $J = 7.9$  Hz, 1H), 7.52 (d,  $J = 7.8$  Hz, 1H), 7.37 (t,  $J = 7.9$  Hz, 1H), 4.77 – 4.37 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 133.1 (d,  $J_{\text{C-F}} = 2.9$  Hz), 131.1, 129.4 (d,  $J_{\text{C-F}} = 0.5$  Hz), 125.0, 123.7, 114.7 (d,  $J_{\text{C-F}} = 2.1$  Hz), 86.2 (d,  $J_{\text{C-F}} = 193.2$  Hz), 64.9 (d,  $J_{\text{C-F}} = 19.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -214.18 (t,  $J = 46.3$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ )

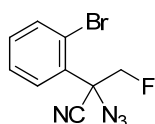
2966, 2109, 1474, 1234, 688; HRMS (CI) calcd for C<sub>9</sub>H<sub>7</sub><sup>79</sup>BrFN<sub>4</sub> [M + H]<sup>+</sup>: 268.9838, found: 268.9846.



**2-Azido-3-fluoro-2-m-tolylpropanenitrile (2n):** Yellow oil; 77% (31.7 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.34 (m, 3H), 7.33 – 7.27 (m, 1H), 4.83 – 4.31 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 139.7, 131.5, 130.7 (d, *J*<sub>C-F</sub> = 2.6 Hz), 129.5, 126.8, 123.2, 115.3, 86.3 (d, *J*<sub>C-F</sub> = 192.6 Hz), 65.8 (d, *J*<sub>C-F</sub> = 18.5 Hz), 21.5; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -213.74 (t, *J* = 46.5 Hz, 1F); FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2959, 2110, 1488, 1234, 696; HRMS (CI) calcd for C<sub>10</sub>H<sub>10</sub>FN<sub>4</sub> [M + H]<sup>+</sup>: 205.0889, found: 205.0885.

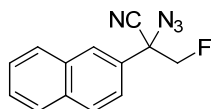


**N-(3-(1-Azido-1-cyano-2-fluoroethyl)phenyl)acetamide (2o):** White solid; m.p. 78-80 °C; 43% (21.2 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.62 (s, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.72 – 4.42 (m, 2H), 2.21 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 168.8, 139.3, 131.8, 130.4, 121.9, 121.8, 117.4, 115.2, 86.3 (d, *J*<sub>C-F</sub> = 192.8 Hz), 65.5 (d, *J*<sub>C-F</sub> = 18.8 Hz), 24.7; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -214.17 (t, *J* = 46.4 Hz, 1F); FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 3300, 2923, 2109, 1667, 1241; HRMS (CI) calcd for C<sub>11</sub>H<sub>11</sub>FN<sub>4</sub>O [M + H]<sup>+</sup>: 248.0948, found: 248.0955.

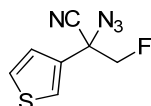


**2-Azido-2-(2-bromophenyl)-3-fluoropropanenitrile (2p):** Yellow oil; 26% (13.9 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.17 (dd, *J* = 46.0, 9.5 Hz, 1H), 4.64

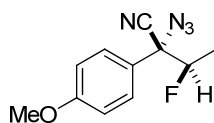
(dd,  $J = 46.3, 9.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.3, 131.5, 129.0 (d,  $J_{\text{C-F}} = 1.3$  Hz), 128.4 (d,  $J = 2.9$  Hz), 127.9, 120.6, 113.0, 83.7 (d,  $J_{\text{C-F}} = 191.2$  Hz), 65.0 (d,  $J_{\text{C-F}} = 19.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -217.26 (t,  $J = 46.1$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2926, 2107, 1466, 1242, 1025; HRMS (CI) calcd for  $\text{C}_9\text{H}_6^{79}\text{BrFN}_4$  [M]: 267.9760, found: 267.9751.



**2-Azido-3-fluoro-2-(naphthalen-2-yl)propanenitrile (2q):** Yellow oil; 89% (42.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (s, 1H), 8.07 – 7.83 (m, 3H), 7.75 – 7.47 (m, 3H), 4.86 – 4.42 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , overlapping peaks)  $\delta$  133.9, 132.9, 129.9, 128.6, 128.0, 127.9, 127.5, 126.8 (d,  $J_{\text{C-F}} = 0.8$  Hz), 122.3, 115.4 (d,  $J_{\text{C-F}} = 2.0$  Hz), 86.2 (d,  $J_{\text{C-F}} = 192.7$  Hz), 66.0 (d,  $J_{\text{C-F}} = 18.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -213.98 (t,  $J = 46.4$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3061, 2109, 1508, 1043, 814; HRMS (CI) calcd for  $\text{C}_{13}\text{H}_{10}\text{FN}_4$  [M + H] $^+$ : 241.0889, found: 241.0885.

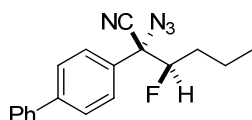


**2-Azido-3-fluoro-2-(thiophen-3-yl)propanenitrile (2r):** Yellow oil; 67% (26.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (s, 1H), 7.56 – 7.38 (m, 1H), 7.17 (d,  $J = 4.9$  Hz, 1H), 4.75 – 4.39 (m, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6 (d,  $J_{\text{C-F}} = 2.8$  Hz), 128.8, 125.7, 124.7, 115.3 (d,  $J_{\text{C-F}} = 2.1$  Hz), 85.4 (d,  $J_{\text{C-F}} = 192.1$  Hz), 62.3 (d,  $J_{\text{C-F}} = 19.9$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -215.55 (t,  $J = 46.3$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3110, 2112, 1415, 1233, 850.

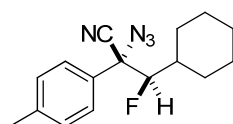


**2-Azido-3-fluoro-2-(4-methoxyphenyl)butanenitrile (2s):** Yellow oil; 72% (33.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.7$  Hz, 2H), 6.99 (d,  $J = 8.7$  Hz, 2H),

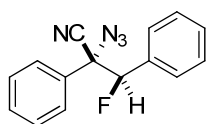
4.78 (dq,  $J = 45.8, 6.1$  Hz, 1H), 3.84 (s, 3H), 1.44 (dd,  $J = 23.8, 6.2$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 127.9, 124.0, 115.7, 114.7, 92.3 (d,  $J_{\text{C-F}} = 186.2$  Hz), 69.0 (d,  $J_{\text{C-F}} = 23.2$  Hz), 55.5, 15.6 (d,  $J_{\text{C-F}} = 21.9$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -175.97 – -176.26 (m, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2944, 2111, 1511, 1253, 828; HRMS (CI) calcd for  $\text{C}_{11}\text{H}_{12}\text{FN}_4\text{O}$   $[\text{M} + \text{H}]^+$ : 235.0995, found: 235.0990.



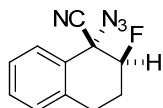
**2-Azido-2-(biphenyl-4-yl)-3-fluorohexanenitrile (2t):** Yellow oil; 89% (54.8 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (t,  $J = 8.1$  Hz, 2H), 7.70 – 7.59 (m, 4H), 7.49 (t,  $J = 7.4$  Hz, 2H), 7.42 (t,  $J = 7.2$  Hz, 1H), 4.68 (dd,  $J = 46.7, 9.9$  Hz, 1H), 1.98 – 1.55 (m, 3H), 1.53 – 1.35 (m, 1H), 0.98 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 139.7, 131.2 (d,  $J_{\text{C-F}} = 1.5$  Hz), 129.1, 128.2, 128.0, 127.3, 127.1 (d,  $J_{\text{C-F}} = 0.8$  Hz), 115.7 (d,  $J_{\text{C-F}} = 2.0$  Hz), 95.5 (d,  $J_{\text{C-F}} = 188.7$  Hz), 68.9 (d,  $J_{\text{C-F}} = 23.7$  Hz), 31.7 (d,  $J_{\text{C-F}} = 20.5$  Hz), 18.4 (d,  $J_{\text{C-F}} = 3.0$  Hz), 13.7;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -184.09 – -184.72 (m, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2964, 2113, 1488, 1246, 696; HRMS (CI) calcd for  $\text{C}_{18}\text{H}_{18}\text{FN}_4$   $[\text{M} + \text{H}]^+$ : 309.1516, found: 309.1508.



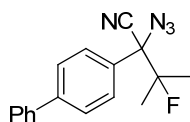
**2-Azido-3-cyclohexyl-3-fluoro-2-p-tolylpropanenitrile (2u):** Yellow oil; 52% (29.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 7.9$  Hz, 2H), 4.38 (dd,  $J = 45.1, 4.7$  Hz, 1H), 2.40 (s, 3H), 2.08 – 1.91 (m, 1H), 1.91 – 1.47 (m, 5H), 1.36 – 1.05 (m, 5H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 130.2, 130.0, 126.4, 116.2 (d,  $J_{\text{C-F}} = 2.1$  Hz), 98.6 (d,  $J_{\text{C-F}} = 190.5$  Hz), 68.0 (d,  $J_{\text{C-F}} = 25.3$  Hz), 38.9 (d,  $J_{\text{C-F}} = 19.3$  Hz), 30.6 (d,  $J_{\text{C-F}} = 3.7$  Hz), 26.8 (d,  $J_{\text{C-F}} = 7.4$  Hz), 26.0, 25.9, 25.7, 21.3;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -189.28 (dd,  $J = 45.1, 20.1$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2929, 2110, 1450, 1235, 814; HRMS (CI) calcd for  $\text{C}_{16}\text{H}_{20}\text{FN}_4$   $[\text{M} + \text{H}]^+$ : 287.1672, found: 287.1685.



**2-Azido-3-fluoro-2,3-diphenylpropanenitrile (2v):** Yellow oil; 32% (17 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.38 (m, 6H), 7.35 (t,  $J = 7.5$  Hz, 2H), 7.23 (d,  $J = 7.5$  Hz, 2H), 5.54 (d,  $J = 43.8$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  132.2 (d,  $J_{\text{C-F}} = 20.7$  Hz), 132.1, 130.4, 130.2, 129.2, 128.2, 127.6 (d,  $J_{\text{C-F}} = 7.0$  Hz), 127.0, 115.3, 95.8 (d,  $J_{\text{C-F}} = 192.1$  Hz), 69.8 (d,  $J_{\text{C-F}} = 27.0$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -178.90 (d,  $J = 43.8$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3066, 2112, 1495, 1025, 653.

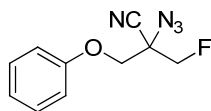


**1-Azido-2-fluoro-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (2w):** Yellow oil; 52% (22.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.2$  Hz, 1H), 7.42 – 7.24 (m, 2H), 7.15 (d,  $J = 7.1$  Hz, 1H), 5.08 – 4.53 (m, 1H), 3.16 – 2.93 (m, 1H), 2.93 – 2.67 (m, 1H), 2.45 – 2.01 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.1, 130.6, 129.8, 128.8, 127.8, 127.7, 116.1 (d,  $J_{\text{C-F}} = 2.2$  Hz), 90.7 (d,  $J_{\text{C-F}} = 186.8$  Hz), 63.0 (d,  $J_{\text{C-F}} = 22.8$  Hz), 24.4 (d,  $J_{\text{C-F}} = 7.6$  Hz), 24.0 (d,  $J_{\text{C-F}} = 19.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -184.99 – -187.00 (m, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2938, 2109, 1491, 1233, 762.

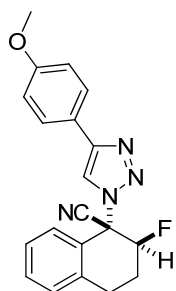


**2-Azido-2-(biphenyl-4-yl)-3-fluoro-3-methylbutanenitrile (2x):** White solid; m.p. 61-63  $^{\circ}\text{C}$ ; 37% (21.8 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.63 (m, 4H), 7.61 (d,  $J = 7.5$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.40 (t,  $J = 7.2$  Hz, 1H), 1.53 (d,  $J = 21.9$  Hz, 3H), 1.47 (d,  $J = 22.0$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 139.8, 131.1, 129.1, 128.2, 128.0, 127.5, 127.3, 116.3 (d,  $J_{\text{C-F}} = 3.0$  Hz), 97.5 (d,  $J_{\text{C-F}} = 186.2$  Hz), 72.6 (d,  $J_{\text{C-F}} = 23.8$  Hz), 23.0 (d,  $J_{\text{C-F}} = 23.1$  Hz), 22.7 (d,  $J_{\text{C-F}} = 23.2$  Hz);  $^{19}\text{F}$

NMR(564 MHz, CDCl<sub>3</sub>)  $\delta$  -139.47– -151.37(m, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 3000, 2114, 1484, 1233, 838; HRMS (CI) calcd for C<sub>17</sub>H<sub>16</sub>FN<sub>4</sub> [M + H]<sup>+</sup>: 295.1359, found: 295.1361.

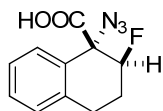


**2-Azido-3-fluoro-2-(phenoxymethyl)propanenitrile (2y):** Yellow oil; 24% (10.6 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 4.84 – 4.58 (m, 2H), 4.26 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.3, 130.0, 122.8, 114.9, 114.2 (d, *J*<sub>C-F</sub> = 4.0 Hz), 82.5 (d, *J*<sub>C-F</sub> = 185.8 Hz), 68.4 (d, *J*<sub>C-F</sub> = 3.9 Hz), 61.3 (d, *J*<sub>C-F</sub> = 20.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -226.13 (t, *J* = 46.1 Hz, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 2931, 2111, 1495, 1043, 753; HRMS (CI) calcd for C<sub>10</sub>H<sub>10</sub>FN<sub>4</sub>O [M + H]<sup>+</sup>: 221.0839, found: 221.0833.

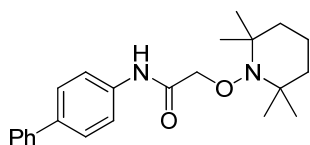


**2-Fluoro-1-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (3):** Yellowish solid; m.p. 141-143 °C; 81% (141 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 – 7.62 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.27 (m, 3H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.69 (dd, *J* = 47.6, 6.8 Hz, 1H), 3.84 (s, 3H), 3.32 – 2.91 (m, 2H), 2.61 – 2.30 (m, 1H), 2.26 – 2.06 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 147.7, 135.8, 131.1, 129.9, 129.1, 128.3, 128.0, 127.4, 122.3, 119.5, 115.6, 114.5, 90.9 (d, *J*<sub>C-F</sub> = 191.3 Hz), 64.7 (d, *J*<sub>C-F</sub> = 22.2 Hz), 55.5, 25.2 (d, *J*<sub>C-F</sub> = 8.5 Hz), 24.6 (d, *J*<sub>C-F</sub> = 19.0 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -176.21 – -193.69 (m, 1F); FT-IR (thin film, KBr):  $\nu$  (cm<sup>-1</sup>) 3106, 2938, 1619, 1251, 1080.

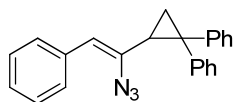




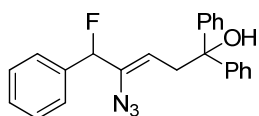
**1-Azido-2-fluoro-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (4):** 90% (423 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.35 (s, 1H), 7.41 (d,  $J = 7.3$  Hz, 1H), 7.37 – 7.26 (m, 2H), 7.20 (d,  $J = 7.1$  Hz, 1H), 5.28 – 5.00 (m, 1H), 3.23 – 2.83 (m, 2H), 2.80 – 2.52 (m, 1H), 2.49 – 2.18 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 135.9, 130.9 (d,  $J_{\text{C-F}} = 3.8$  Hz), 129.4, 129.2, 128.4, 127.2, 94.4 (d,  $J_{\text{C-F}} = 184.0$  Hz), 70.8 (d,  $J_{\text{C-F}} = 21.1$  Hz), 26.2 (d,  $J_{\text{C-F}} = 10.5$  Hz), 25.4 (d,  $J_{\text{C-F}} = 19.1$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -183.92 (dd,  $J = 48.3, 17.4$  Hz, 1F).



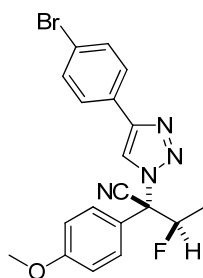
**N-(Biphenyl-4-yl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetamide (5):** 12% (8.8 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (s, 1H), 7.66 (d,  $J = 8.4$  Hz, 2H), 7.63 – 7.54 (m, 4H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.34 (t,  $J = 7.2$  Hz, 1H), 4.48 (s, 2H), 1.58 – 1.47 (m, 4H), 1.44 – 1.24 (m, 2H), 1.22 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 140.6, 137.6, 136.5, 128.9, 127.9, 127.3, 127.0, 120.2, 77.0, 60.4, 39.8, 33.0, 20.5, 17.0; FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3375, 2932, 1679, 1508, 1059; HRMS (CI) calcd for  $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_2$   $[\text{M} + \text{H}]^+$ : 367.2386, found: 367.2395.



**(Z)-(2-(1-Azido-2-phenylvinyl)cyclopropane-1,1-diyl)dibenzene (6):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 6.99 (m, 15H), 5.53 (s, 1H), 2.75 – 2.63 (m, 1H), 2.06 (t,  $J = 5.7$  Hz, 1H), 1.57 (dd,  $J = 8.6, 5.6$  Hz, 1H).



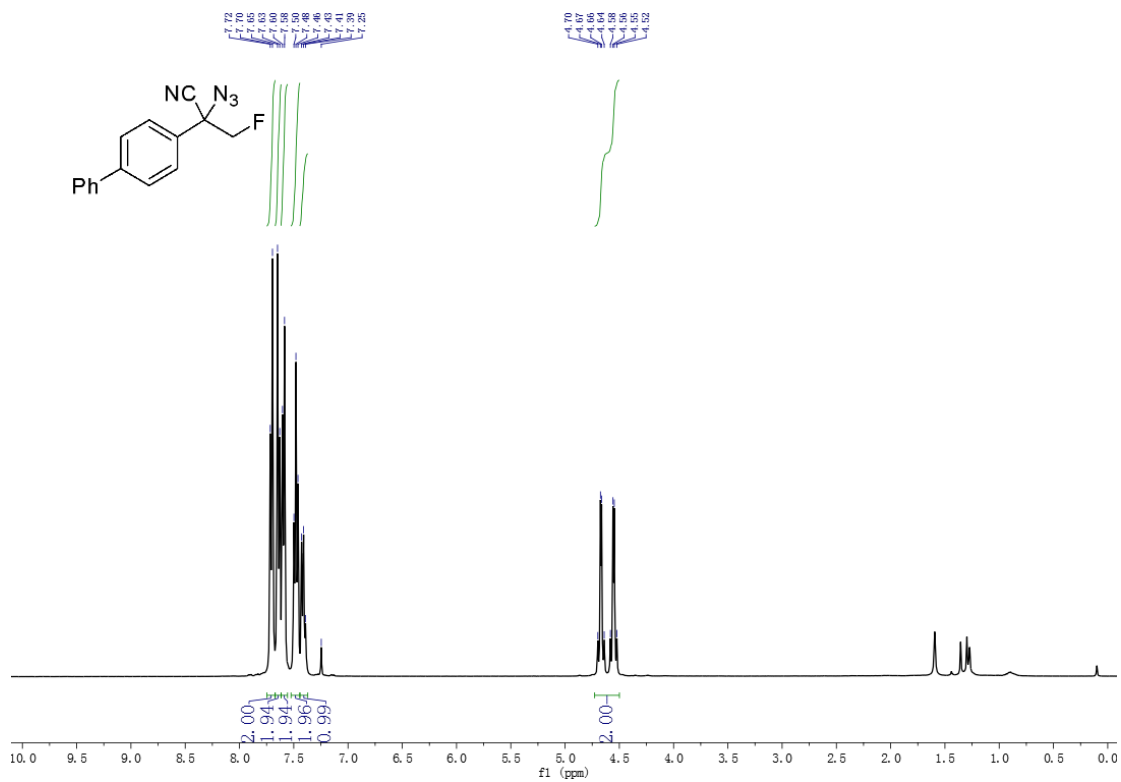
**(Z)-4-Azido-5-fluoro-1,1,5-triphenylpent-3-en-1-ol (7):** 70% (52.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.02 (m, 15H), 6.29 (d,  $J = 46.2$  Hz, 1H), 5.44 (t,  $J = 7.7$  Hz, 1H), 3.30 (d,  $J = 7.5$  Hz, 2H), 2.36 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1 (d,  $J_{\text{C-F}} = 7.4$  Hz), 138.0, 137.9, 136.5 (d,  $J_{\text{C-F}} = 23.0$  Hz), 128.8, 128.7, 128.59, 128.57, 127.53, 127.49, 126.1, 125.7 (d,  $J_{\text{C-F}} = 6.8$  Hz), 115.4 (d,  $J_{\text{C-F}} = 6.0$  Hz), 88.4 (d,  $J_{\text{C-F}} = 174.0$  Hz), 78.0, 39.8;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -179.24 (d,  $J = 46.2$  Hz, 1F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3061, 2115, 1447, 1264, 752.



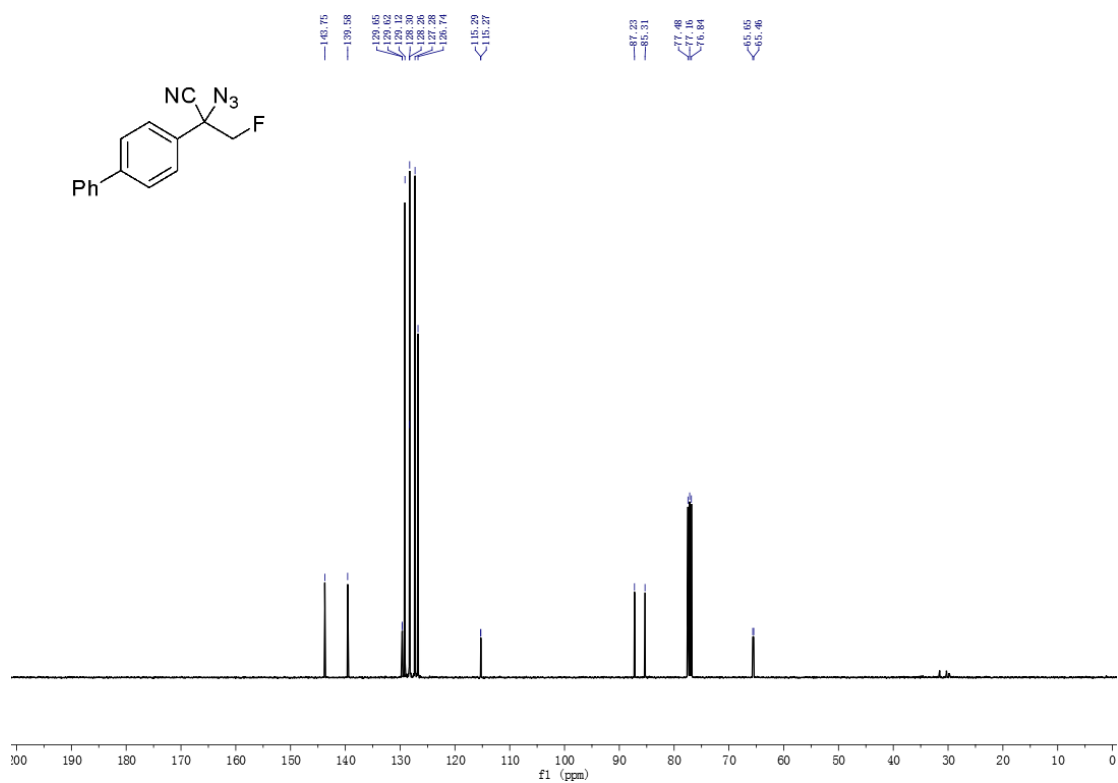
**2-(4-(4-Bromophenyl)-1H-1,2,3-triazol-1-yl)-3-fluoro-2-(4-methoxyphenyl)butane nitrile (8):** White solid; m.p. 106 - 108 °C; 80% (166.0 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 1H), 7.66 (t,  $J = 13.8$  Hz, 2H), 7.62 – 7.44 (m, 4H), 6.97 (d,  $J = 8.4$  Hz, 2H), 5.96 (dq,  $J = 45.4, 5.8$  Hz, 1H), 3.83 (s, 3H), 1.64 (dd,  $J = 23.7, 5.9$  Hz, 3H).

# NMR Spectra for the products

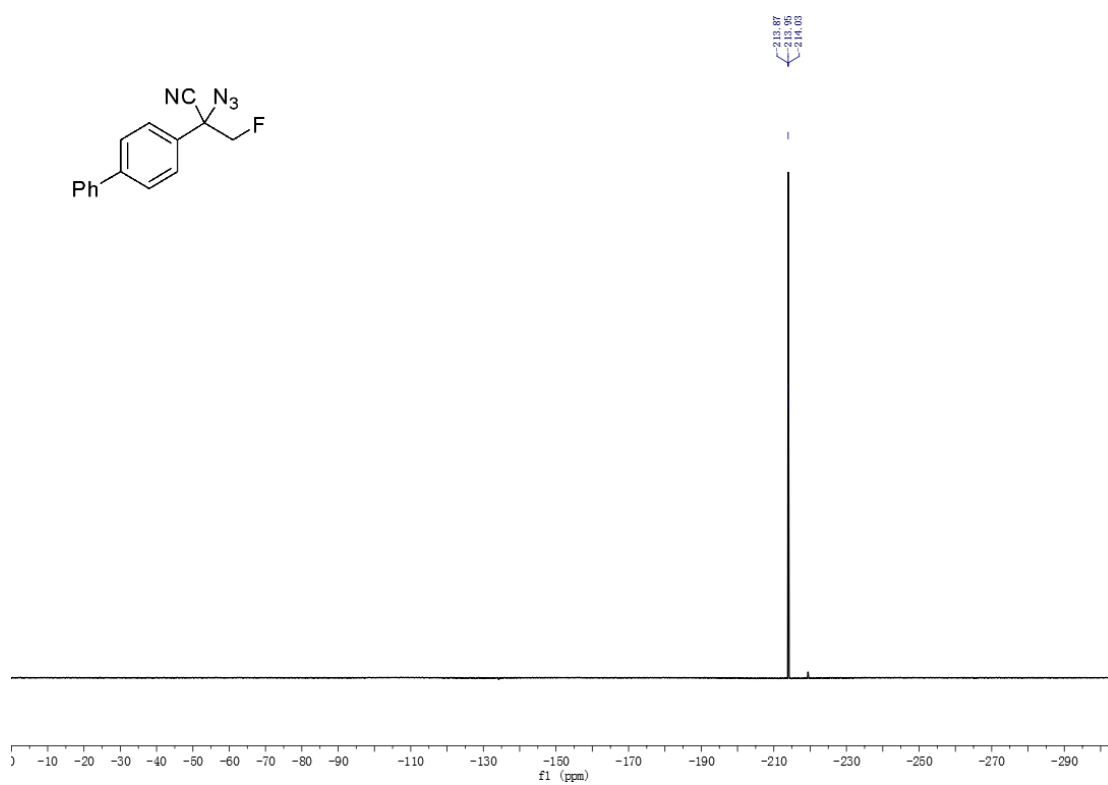
## $^1\text{H}$ NMR of **2a**



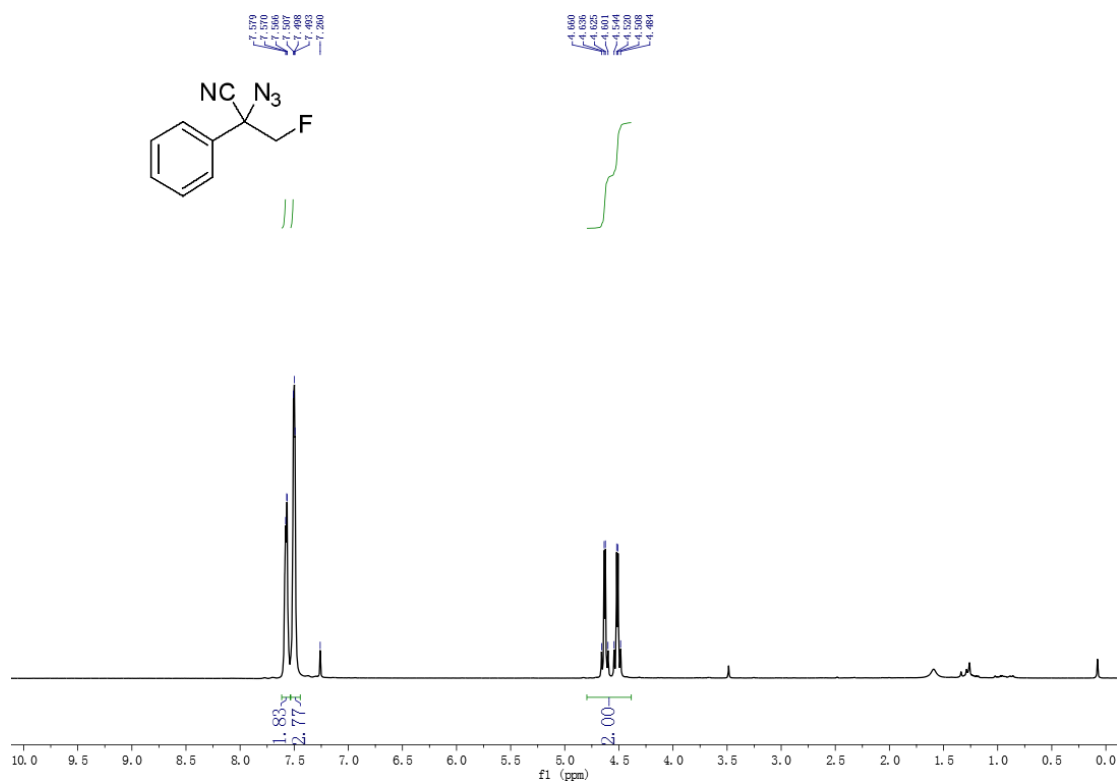
## $^{13}\text{C}$ NMR of **2a**



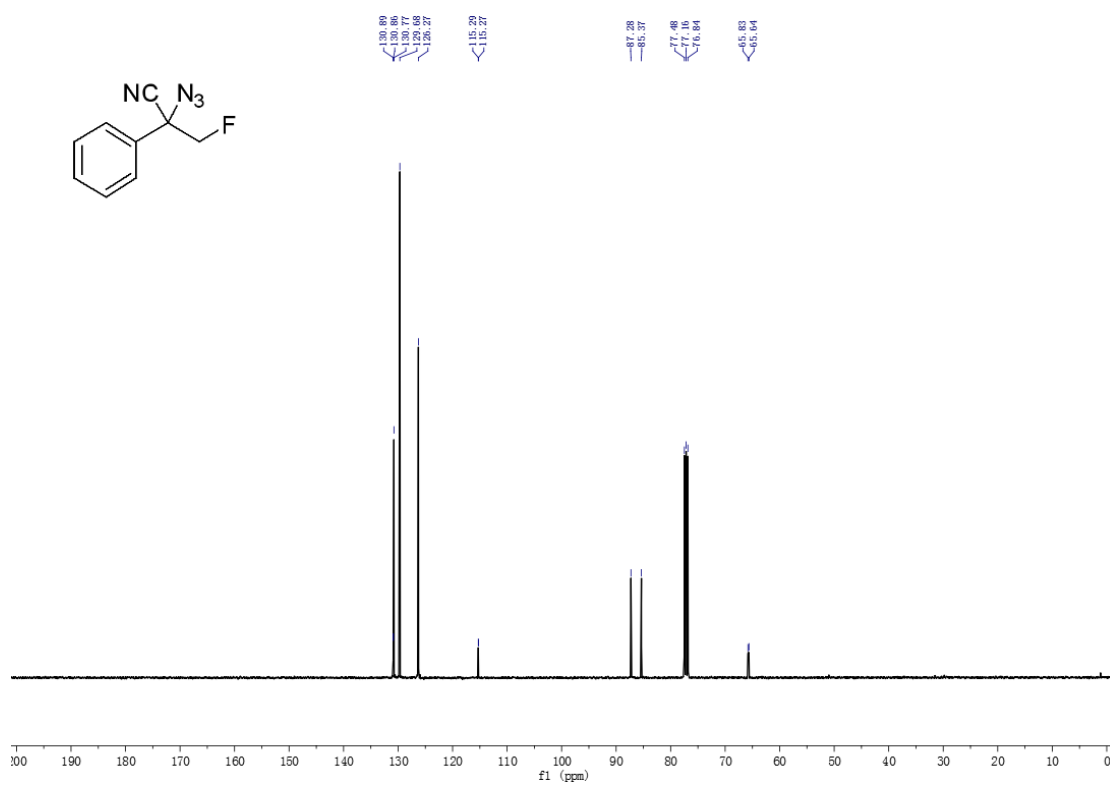
### $^{19}\text{F}$ NMR of **2a**



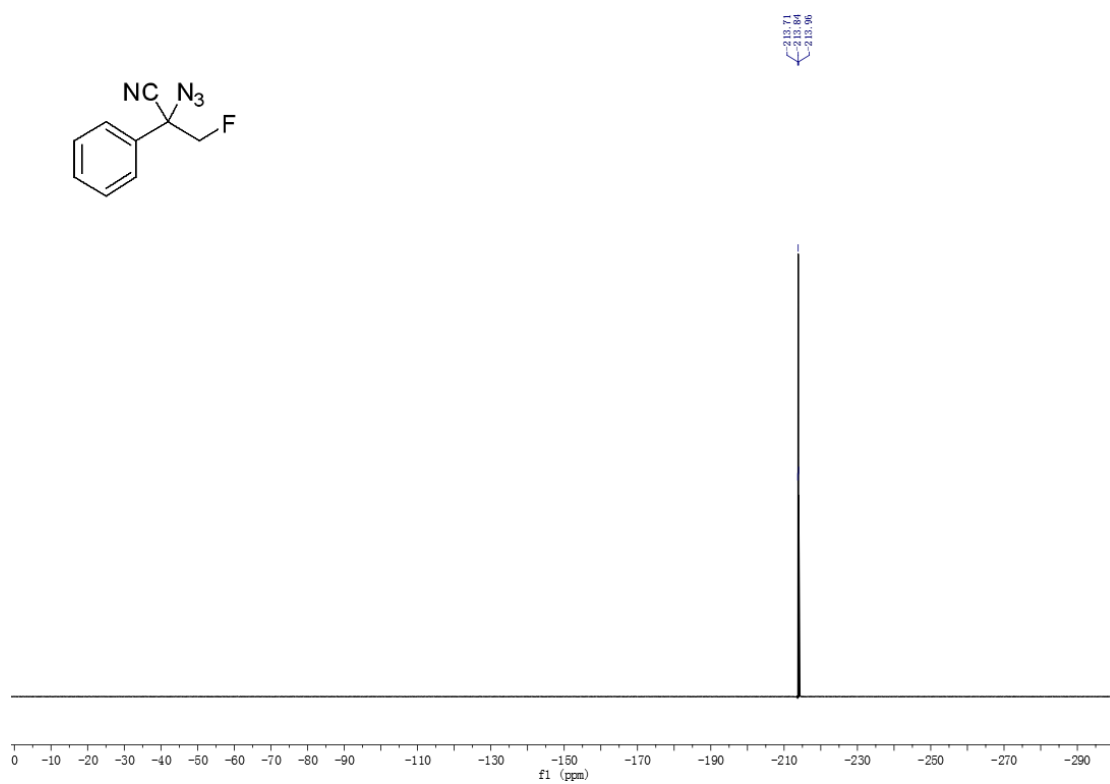
### $^1\text{H}$ NMR of **2b**



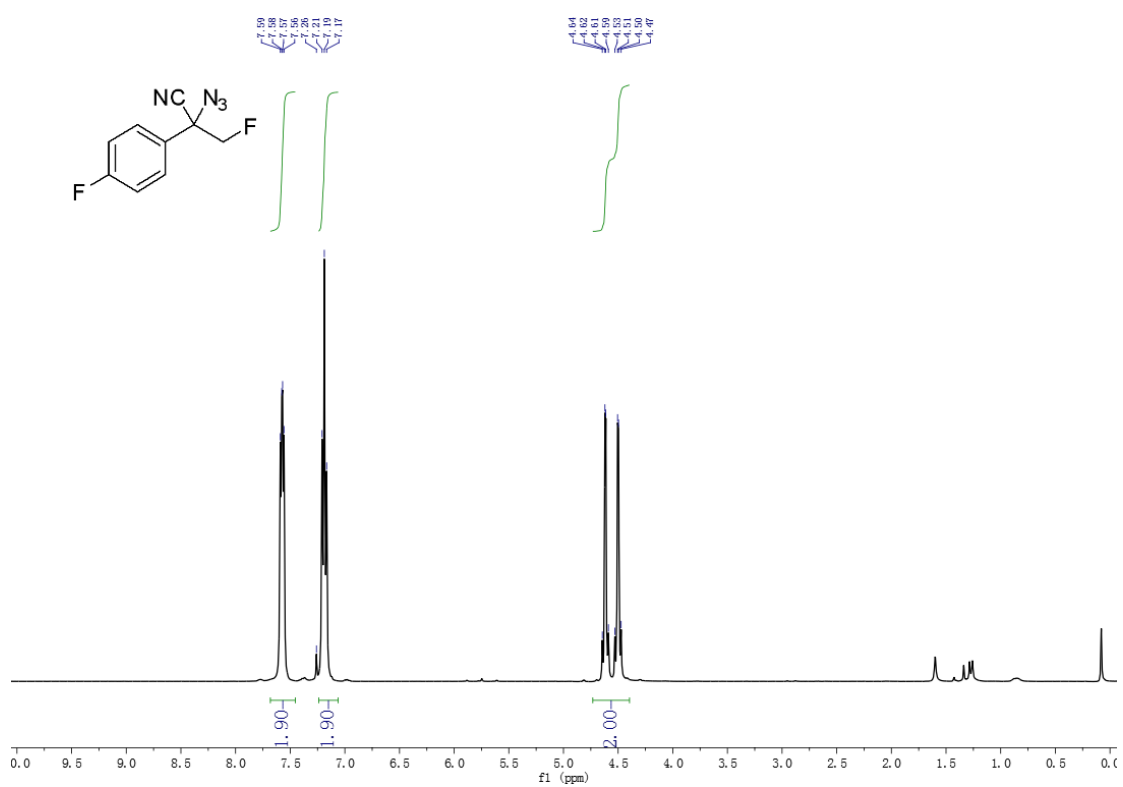
### $^{13}\text{C}$ NMR of **2b**



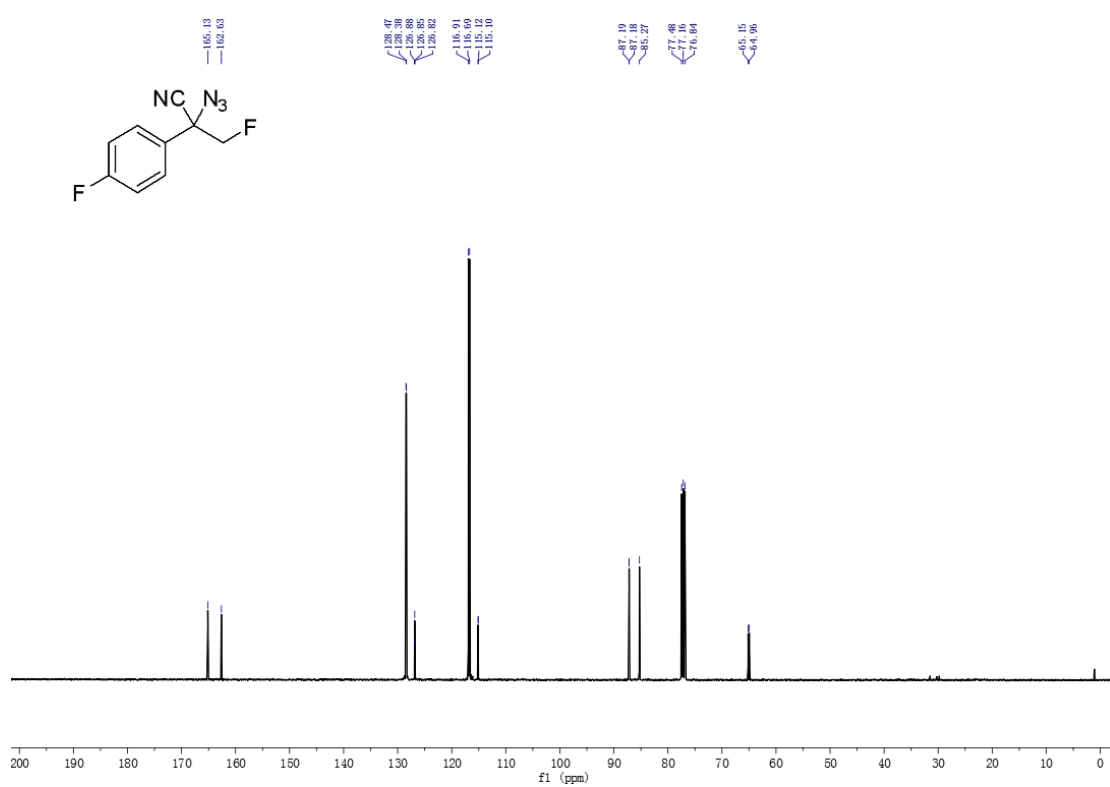
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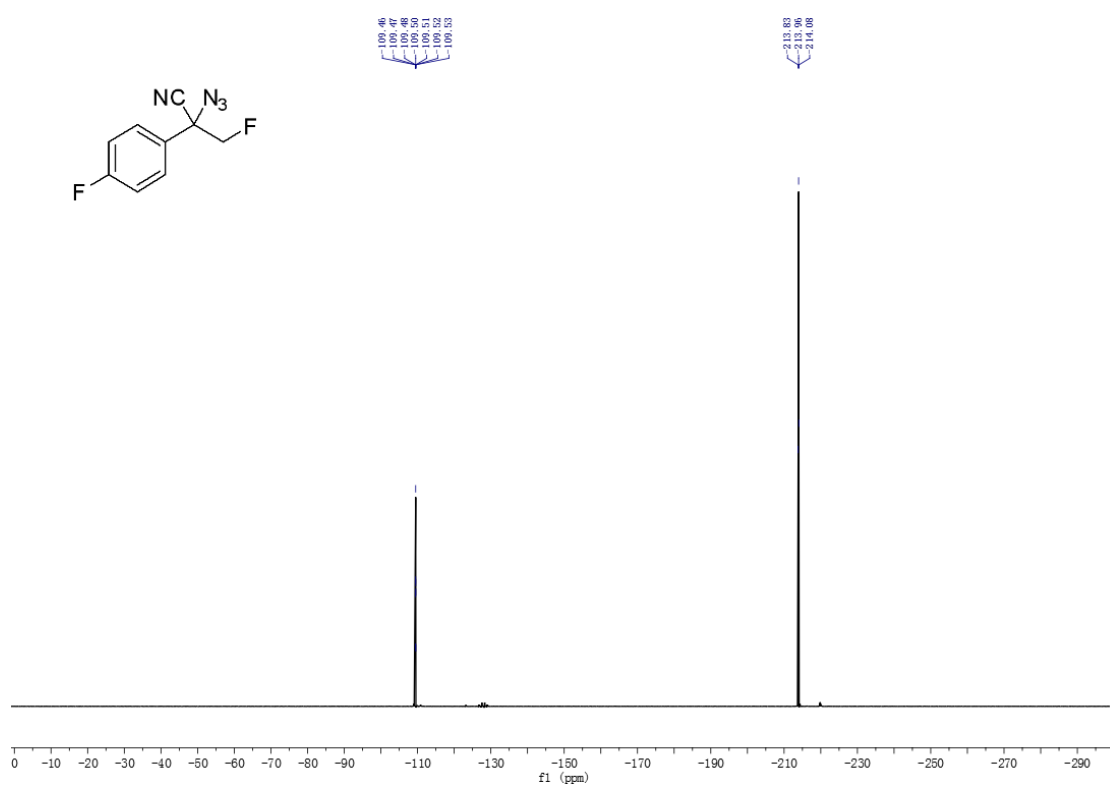
### $^1\text{H}$ NMR of **2c**



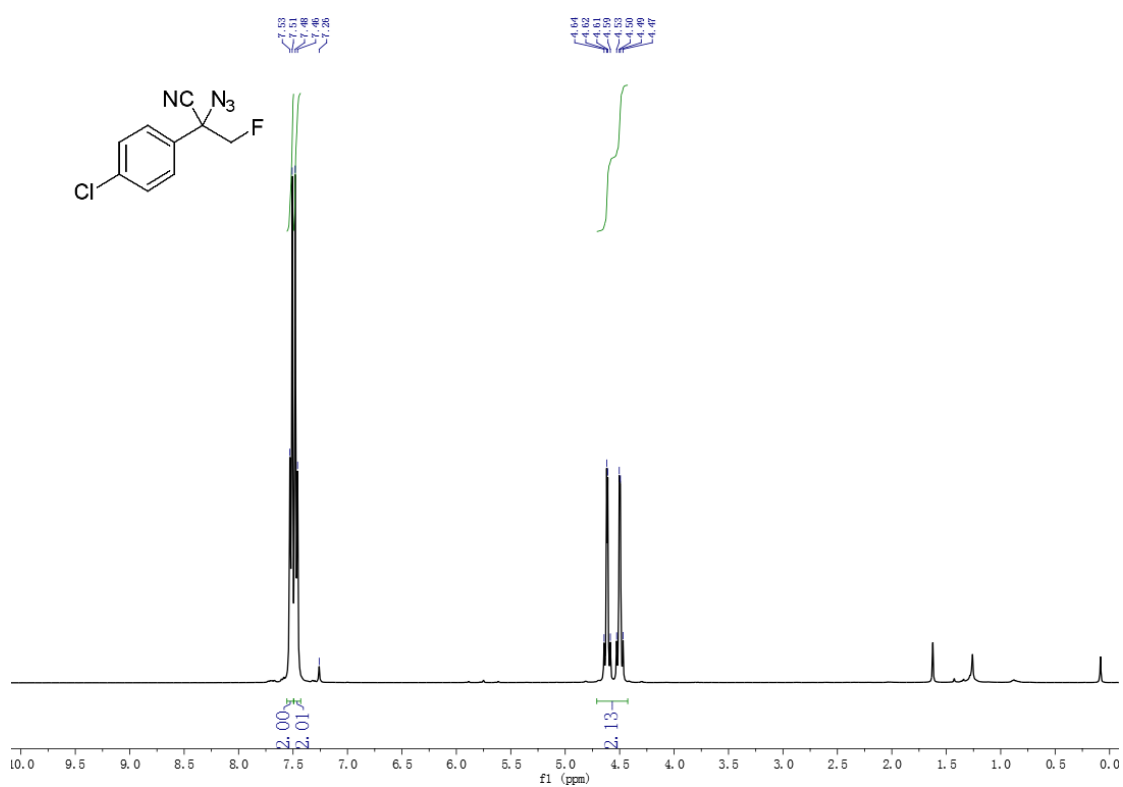
### $^{13}\text{C}$ NMR of **2c**



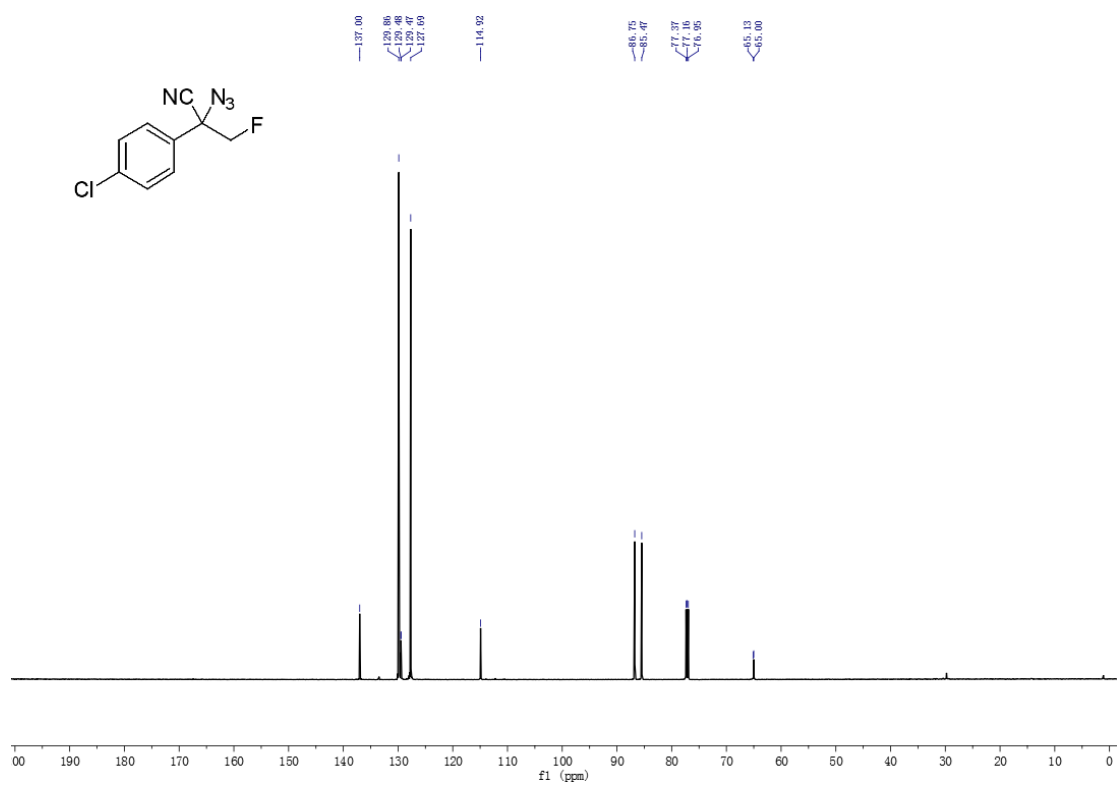
$^{19}\text{F}$  NMR of **2c**



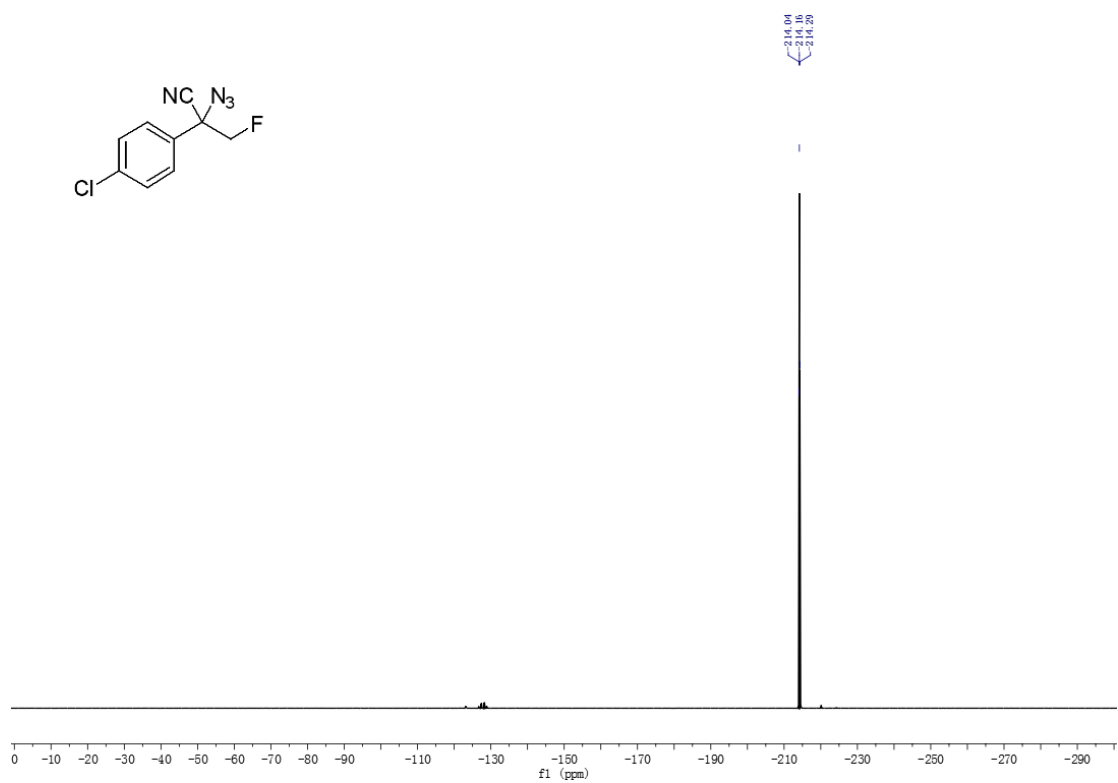
$^1\text{H}$  NMR of **2d**



### $^{13}\text{C}$ NMR of **2d**

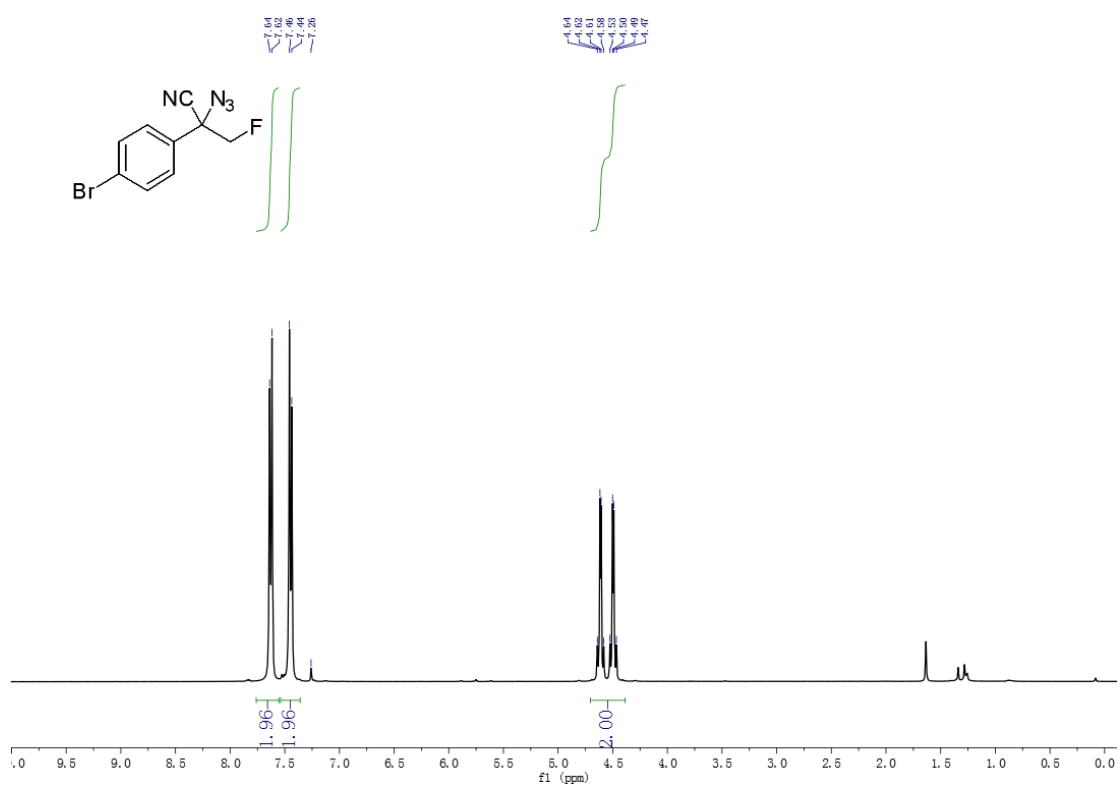


### $^{19}\text{F}$ NMR of **2d**

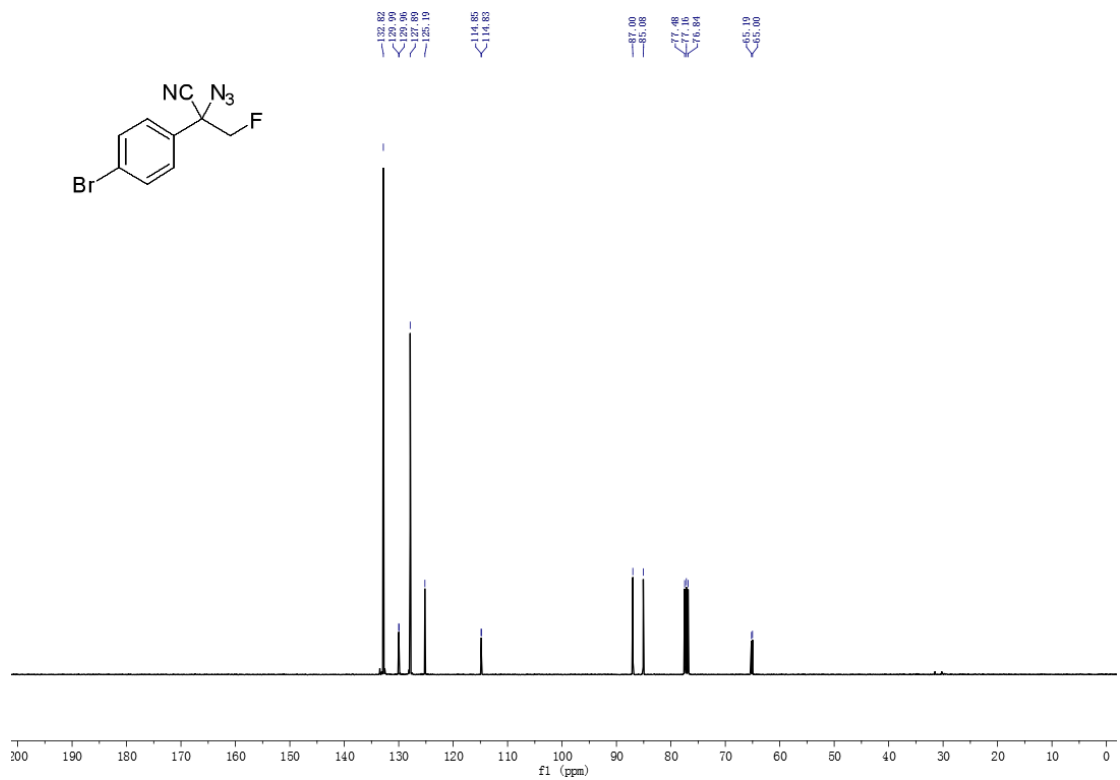




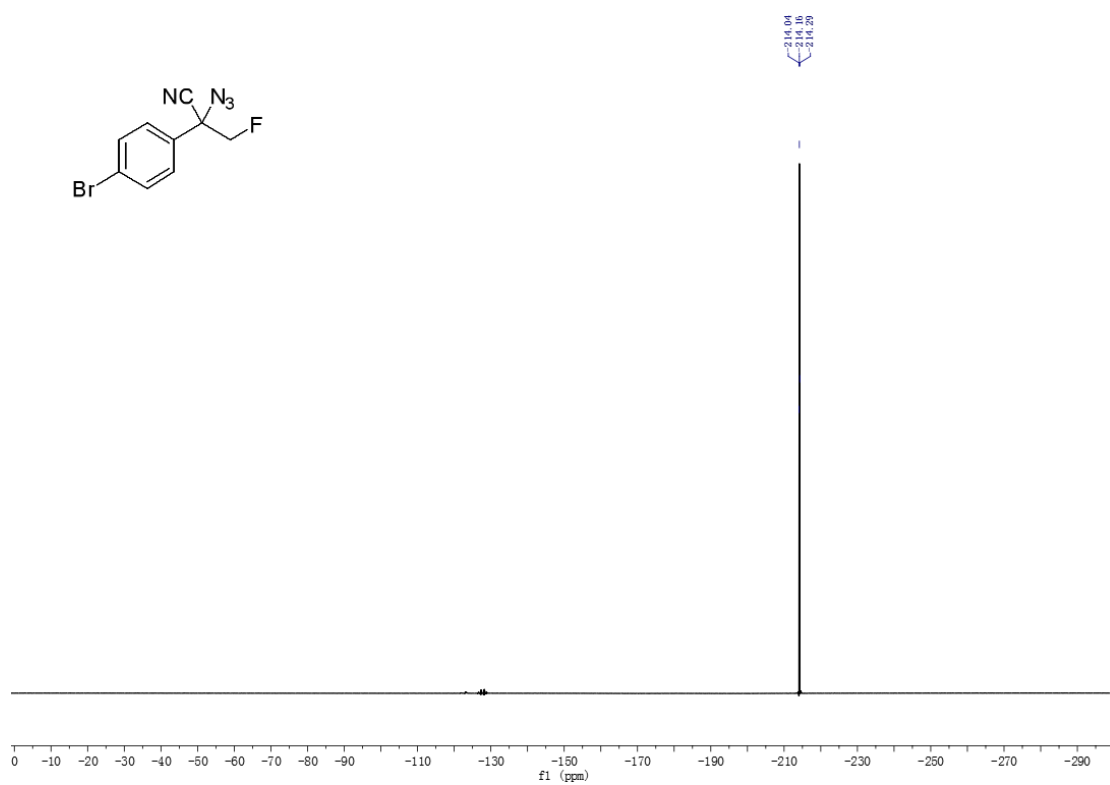
### $^1\text{H}$ NMR of **2e**



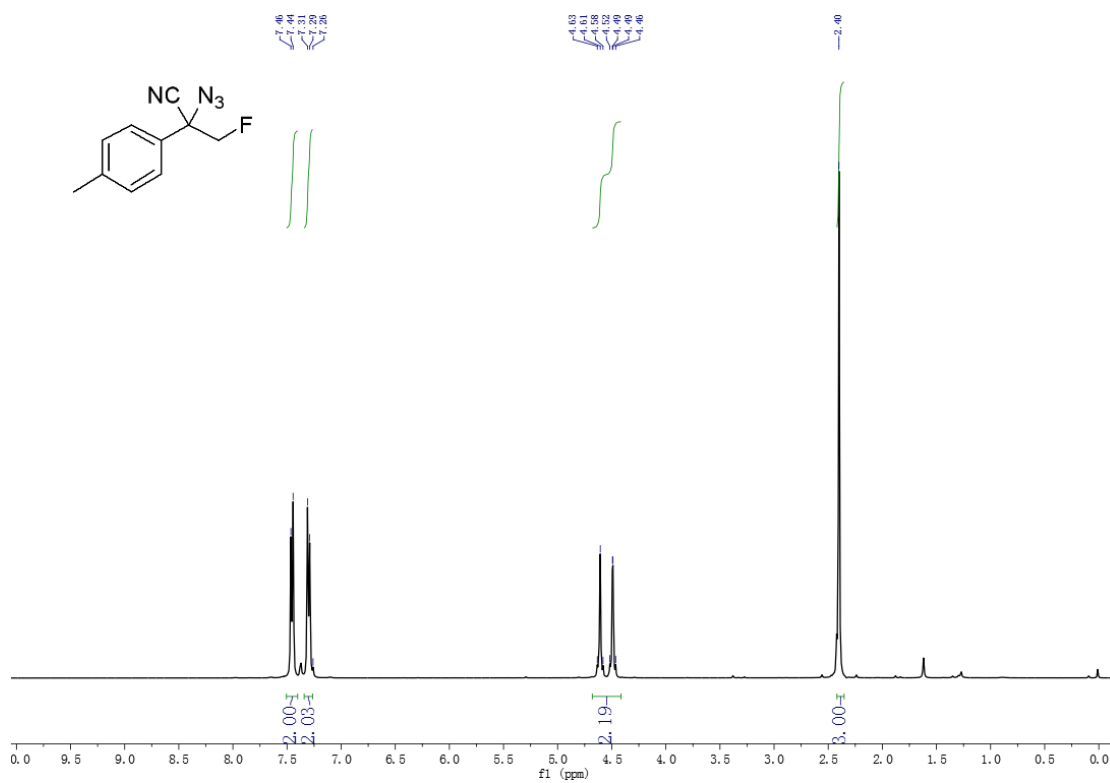
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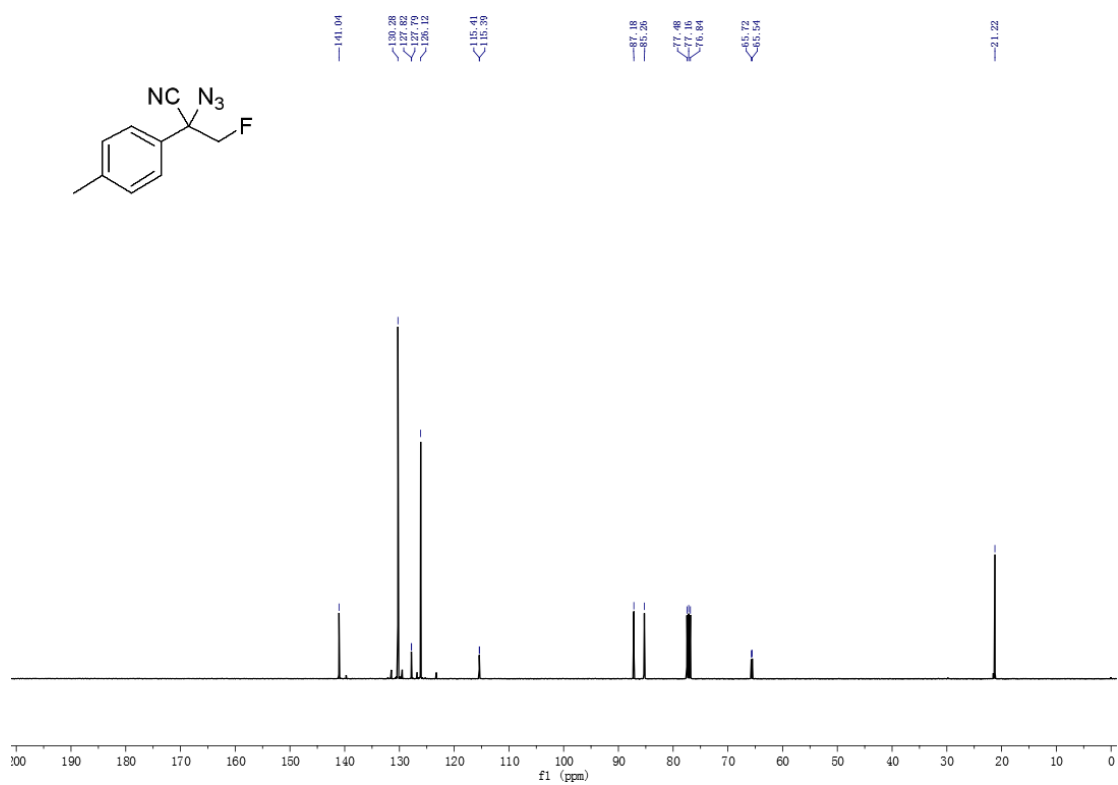
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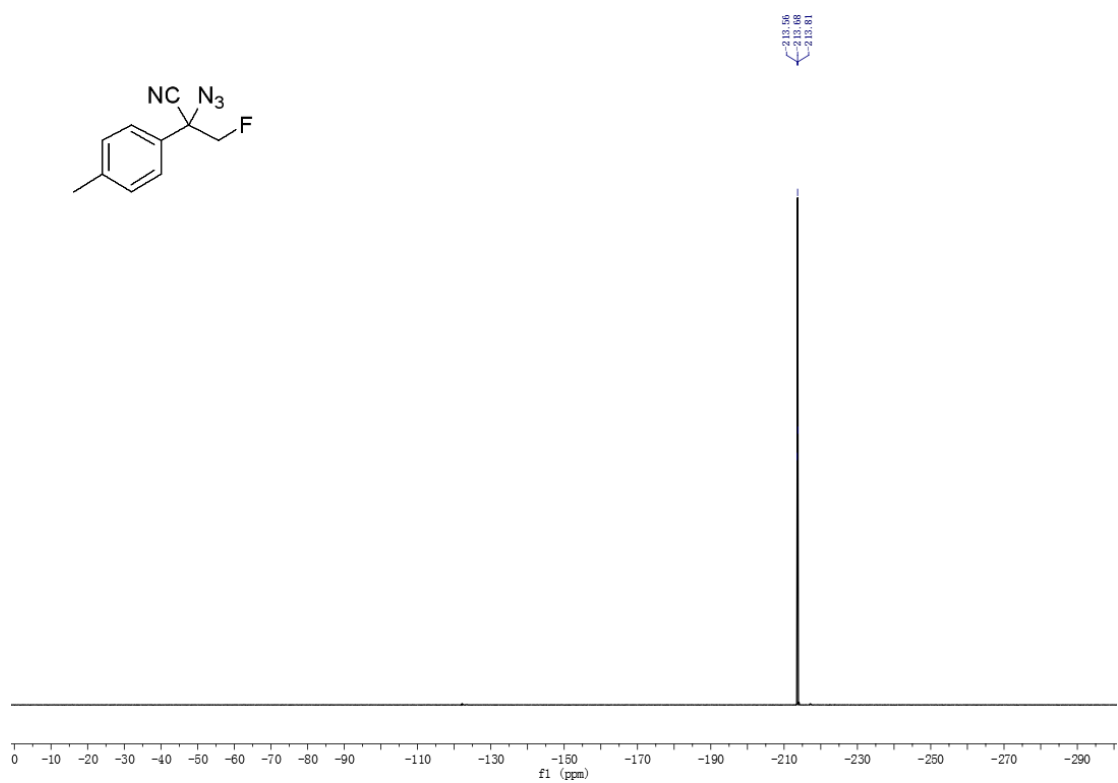
### $^1\text{H}$ NMR of **2f**



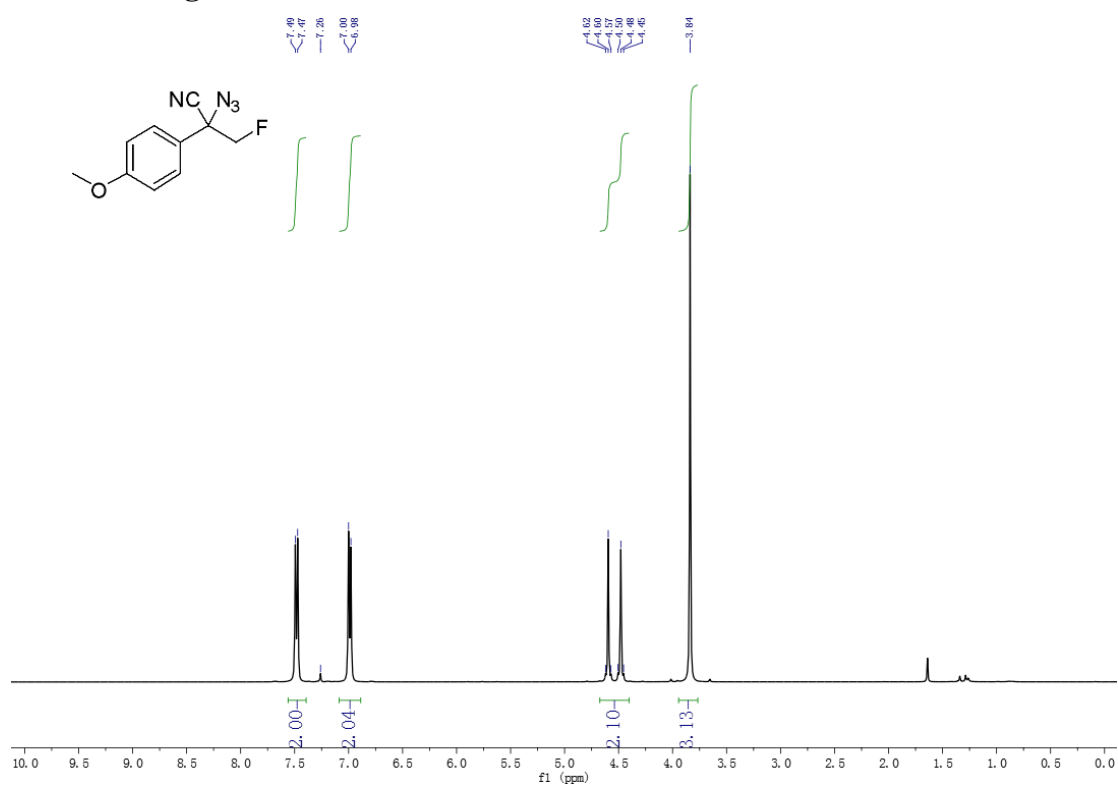
### $^{13}\text{C}$ NMR of **2f**



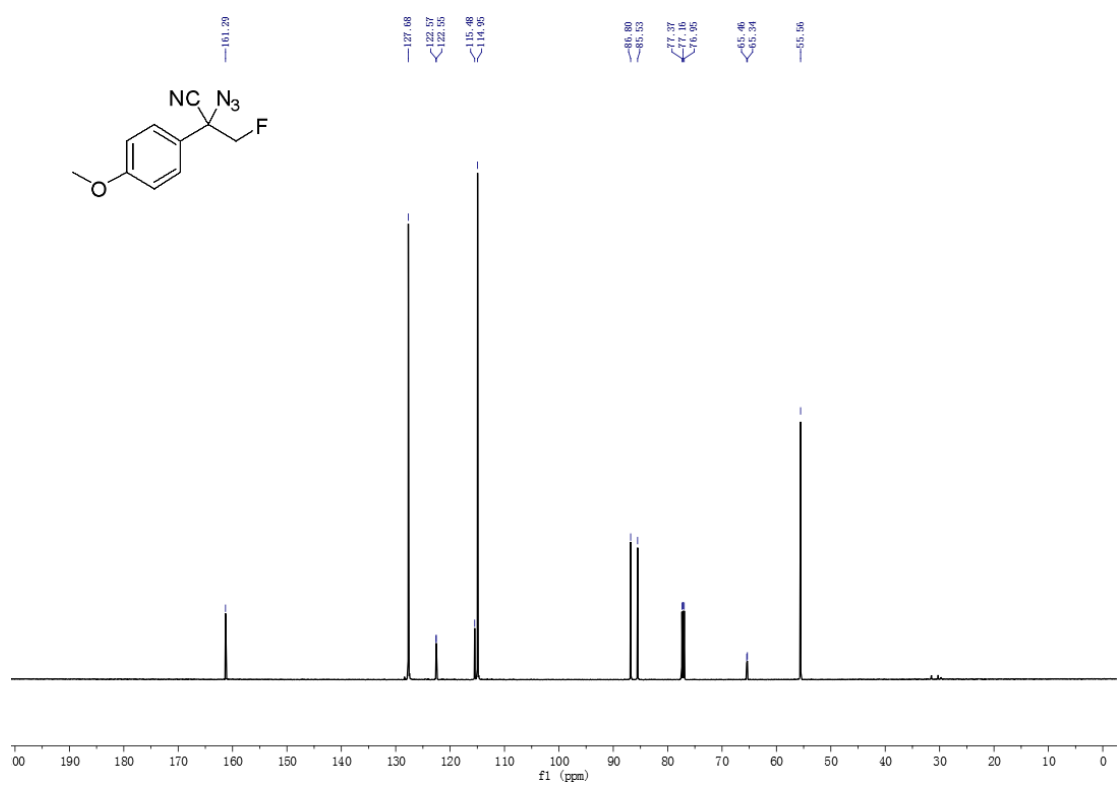
### $^{19}\text{F}$ NMR of **2f**



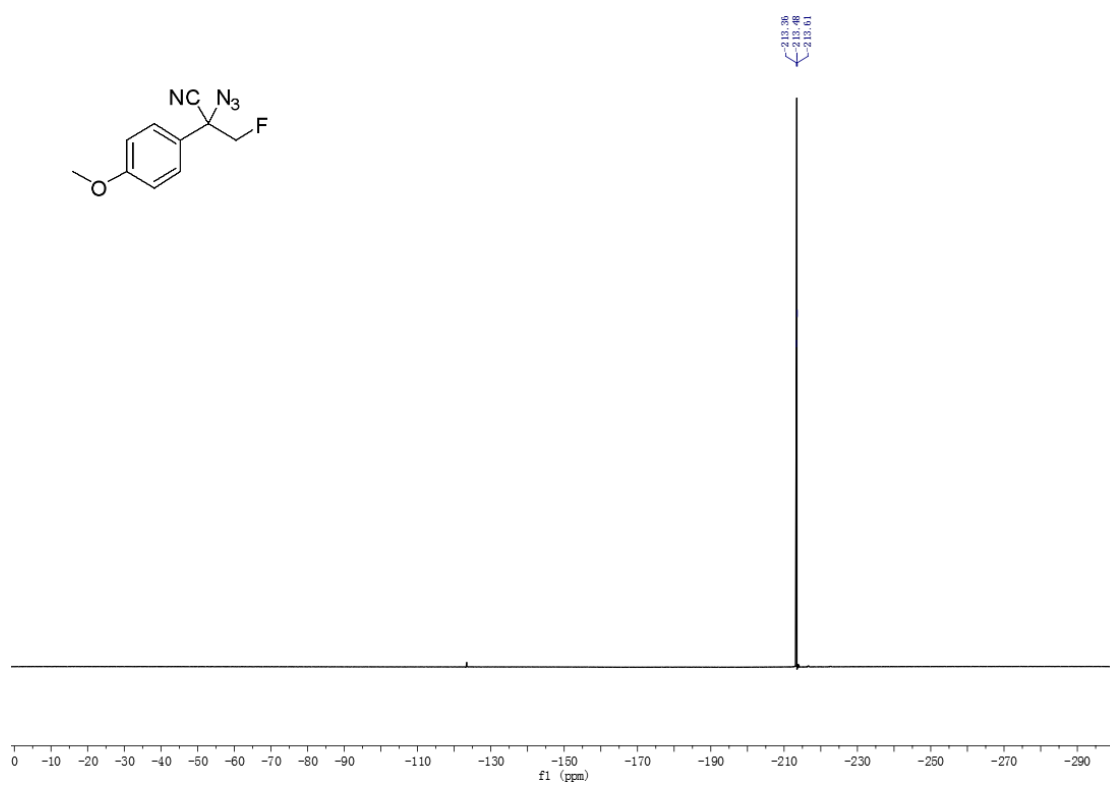
### $^1\text{H}$ NMR of **2g**



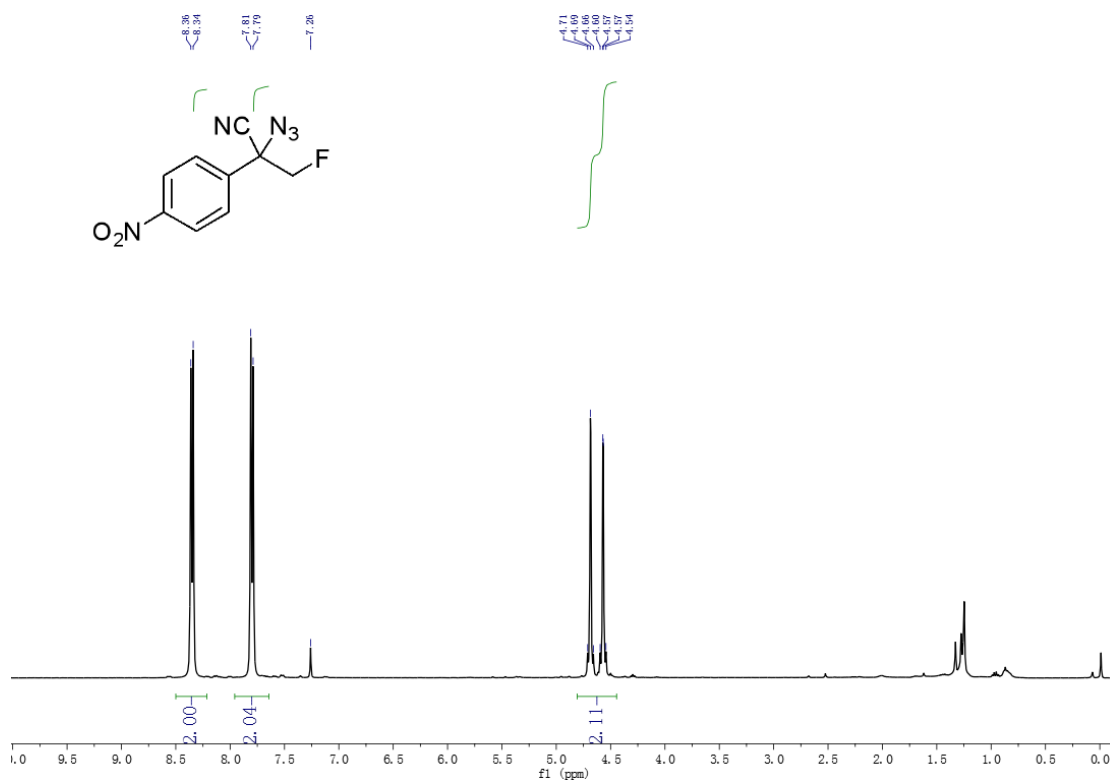
### $^{13}\text{C}$ NMR of **2g**



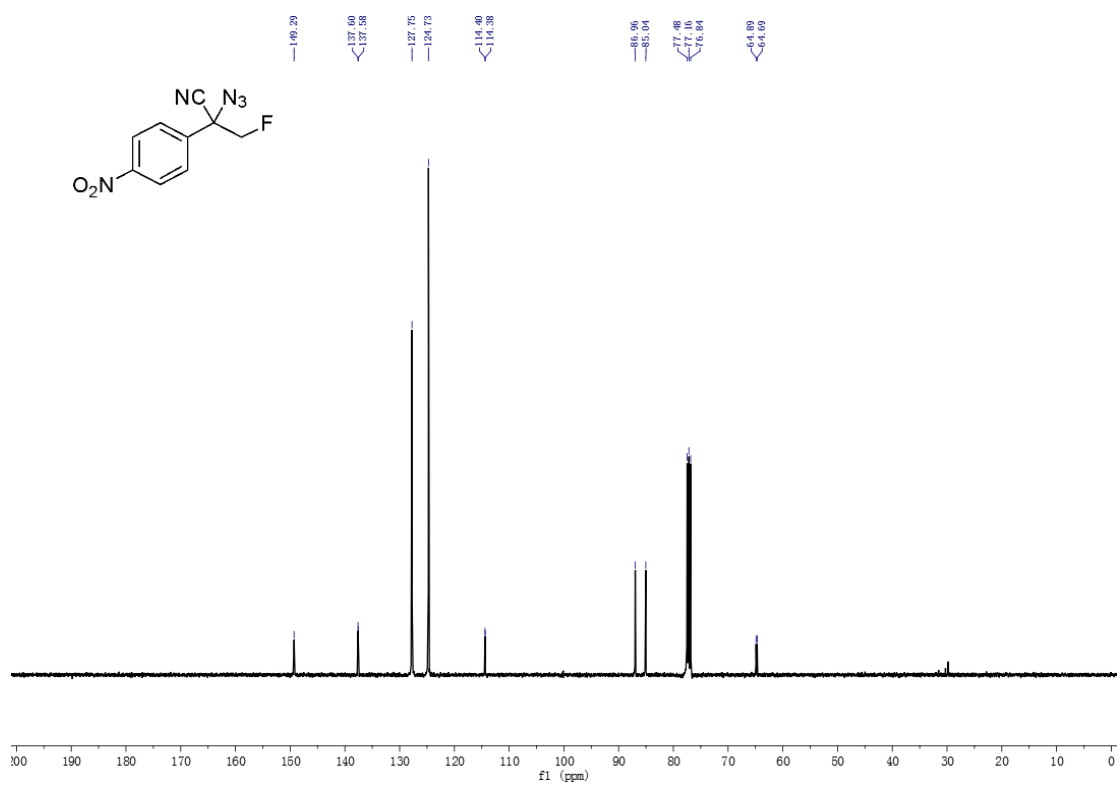
### $^{19}\text{F}$ NMR of **2f**



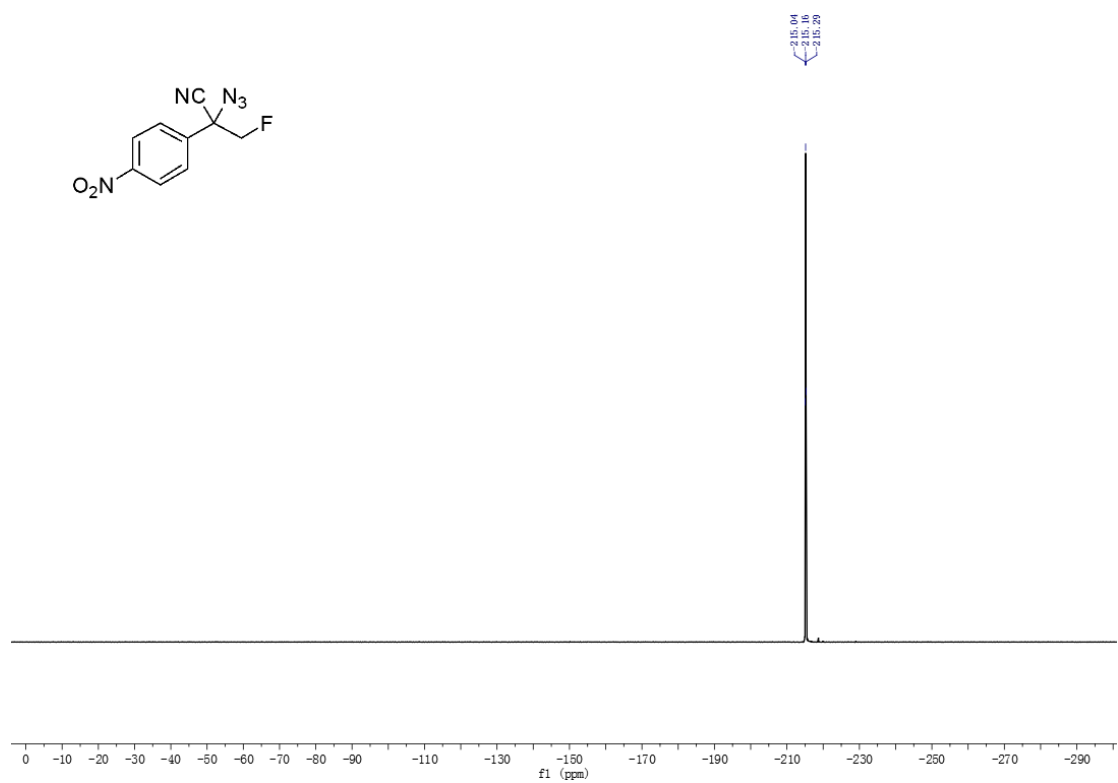
### $^1\text{H}$ NMR of **2h**



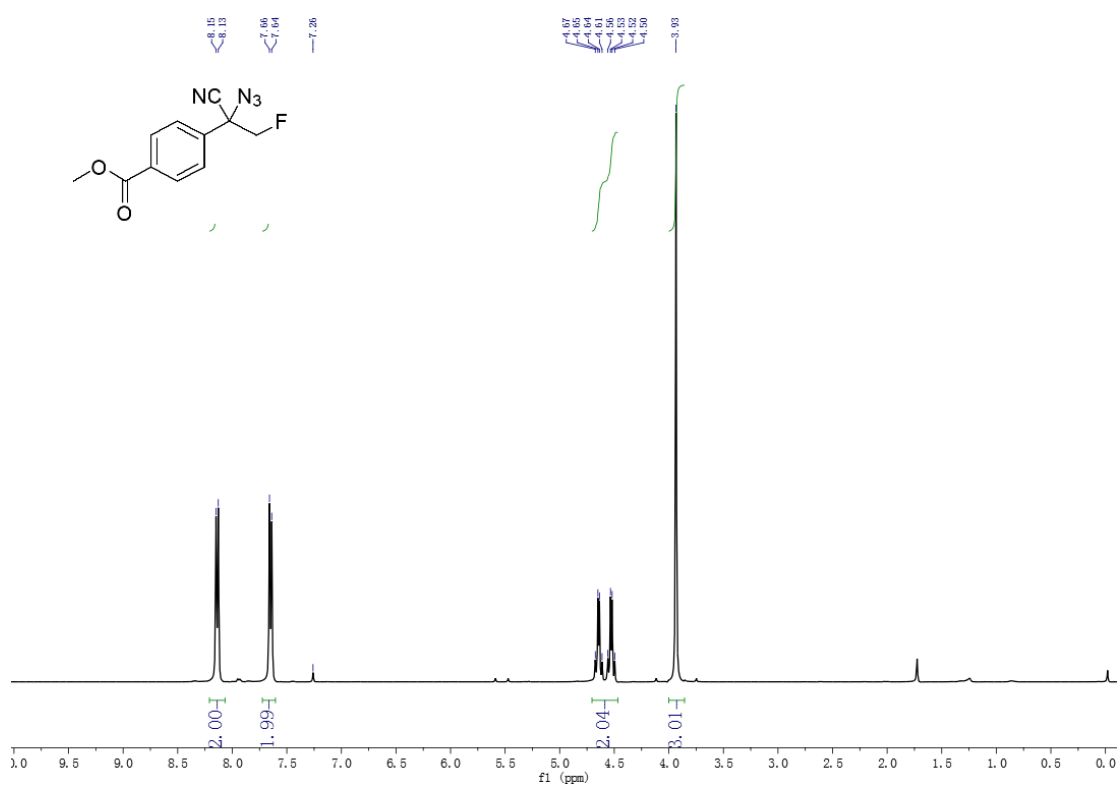
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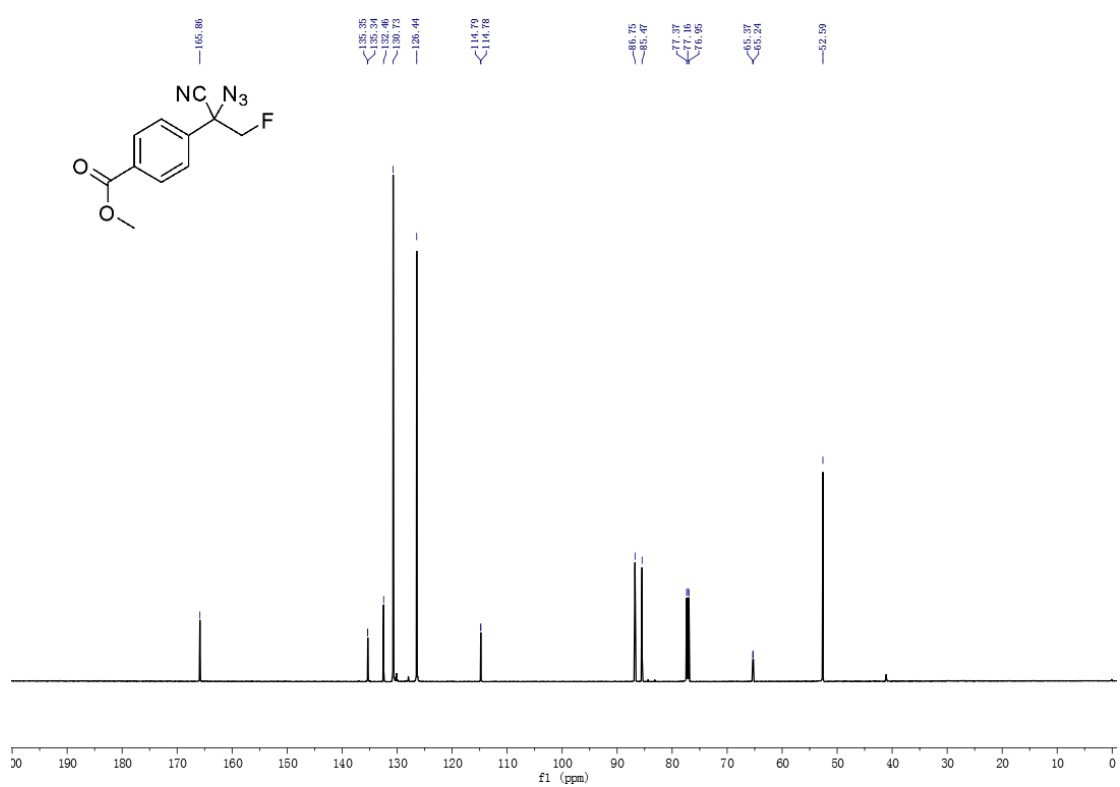
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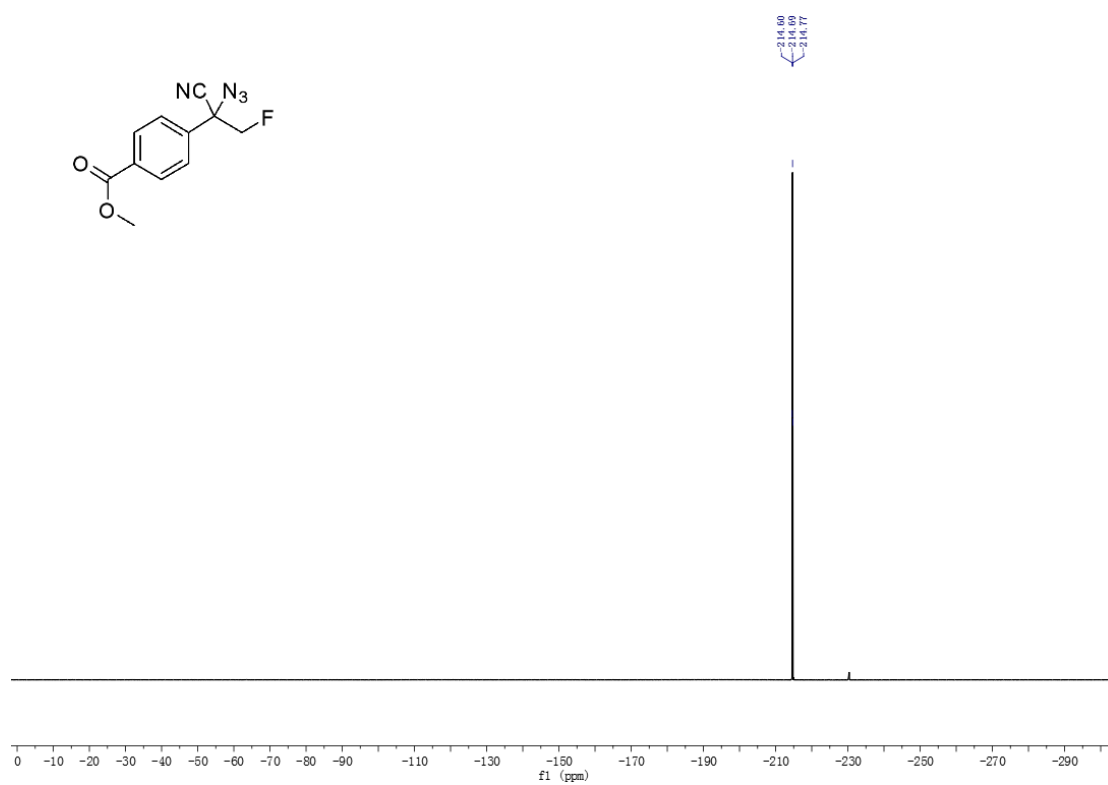
### $^1\text{H}$ NMR of **2i**



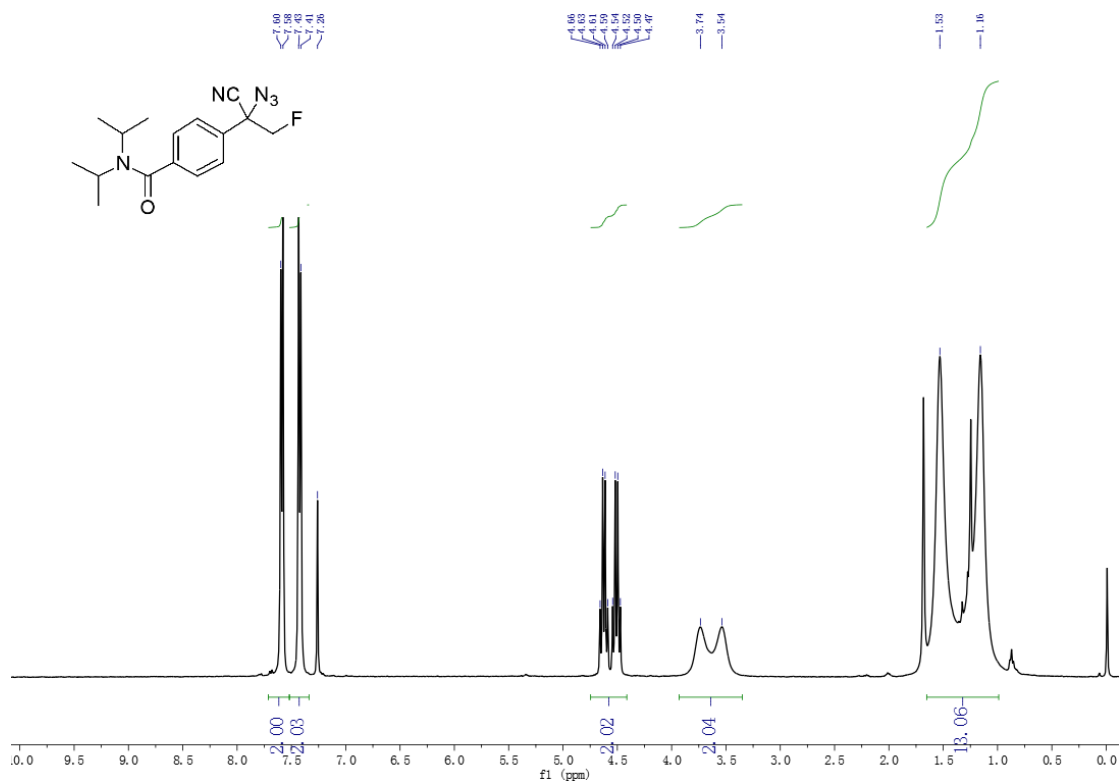
### $^{13}\text{C}$ NMR of **2i**



### $^{19}\text{F}$ NMR of **2i**

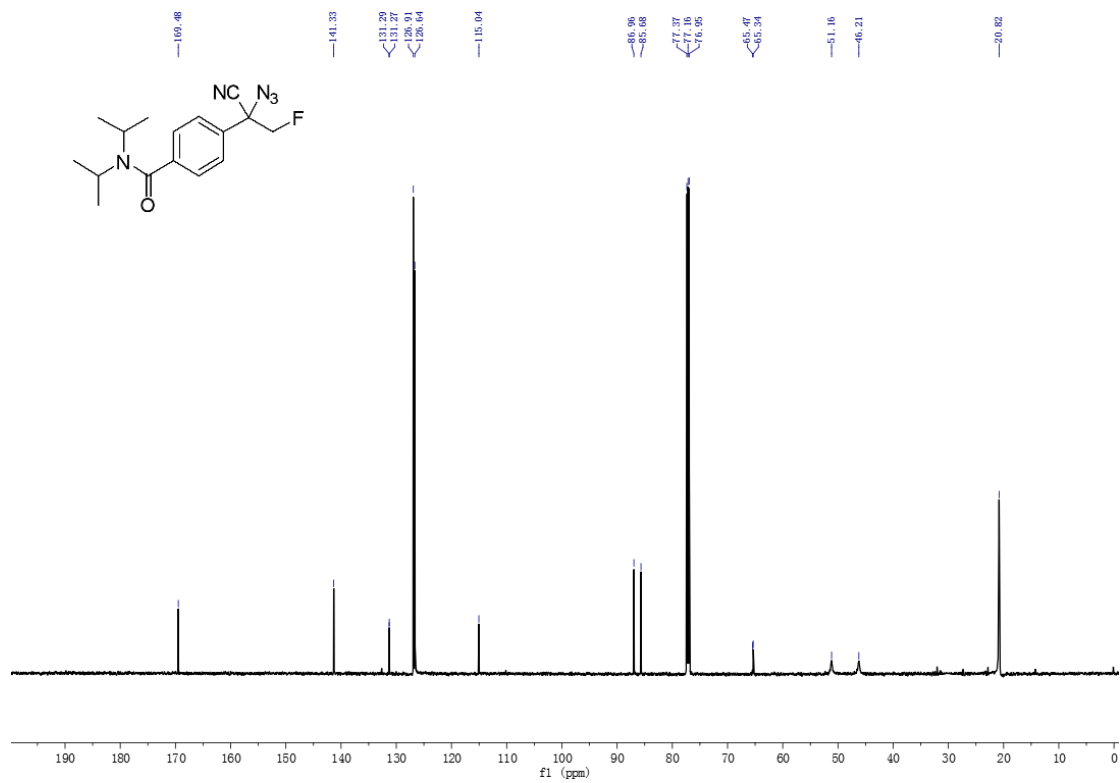


### $^1\text{H}$ NMR of **2j**

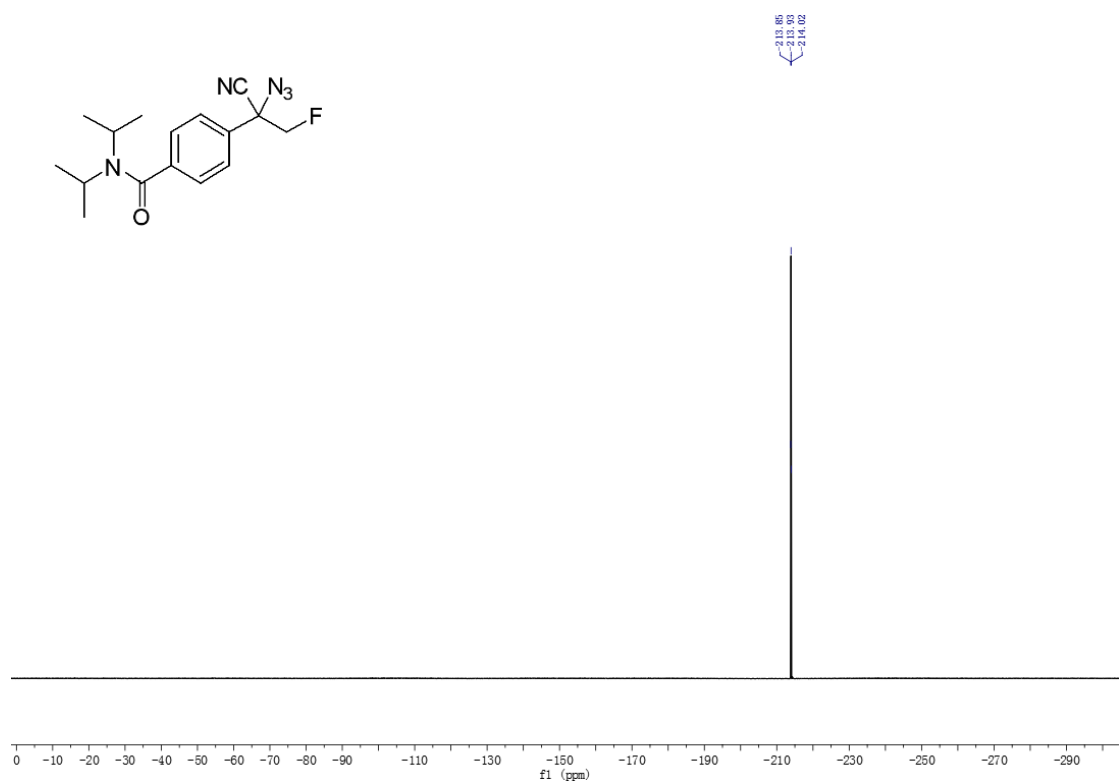




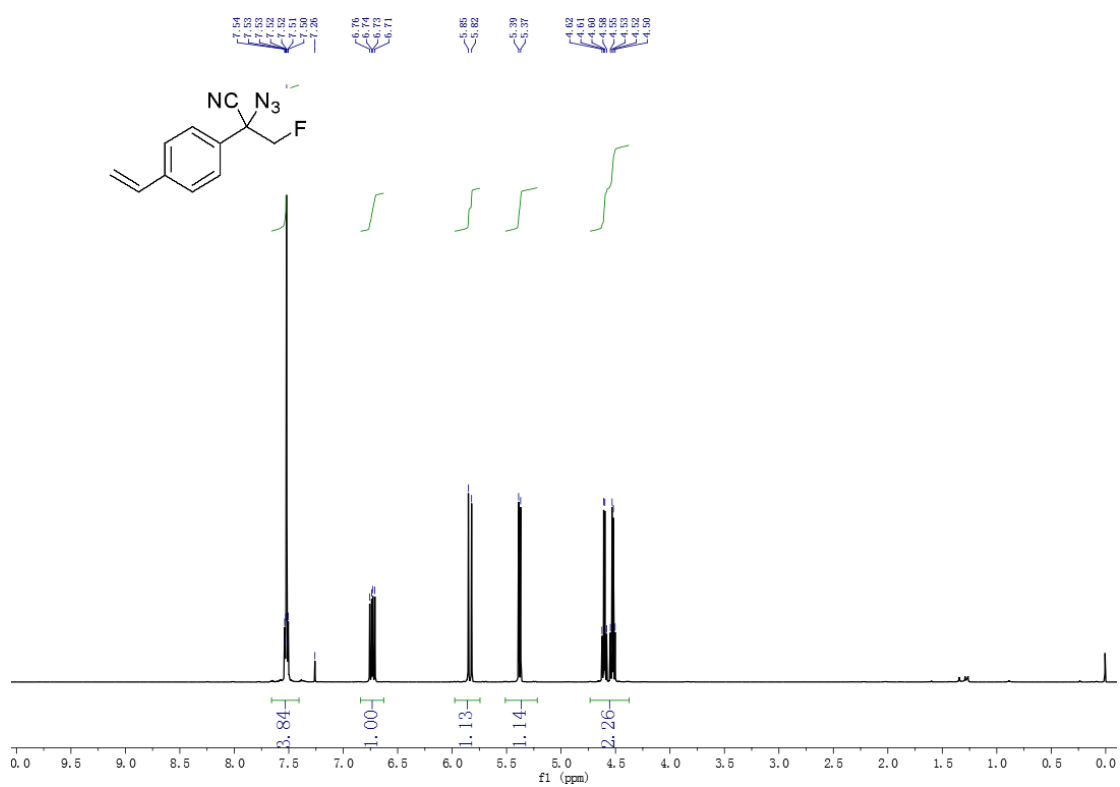
### $^{13}\text{C}$ NMR of **2j**



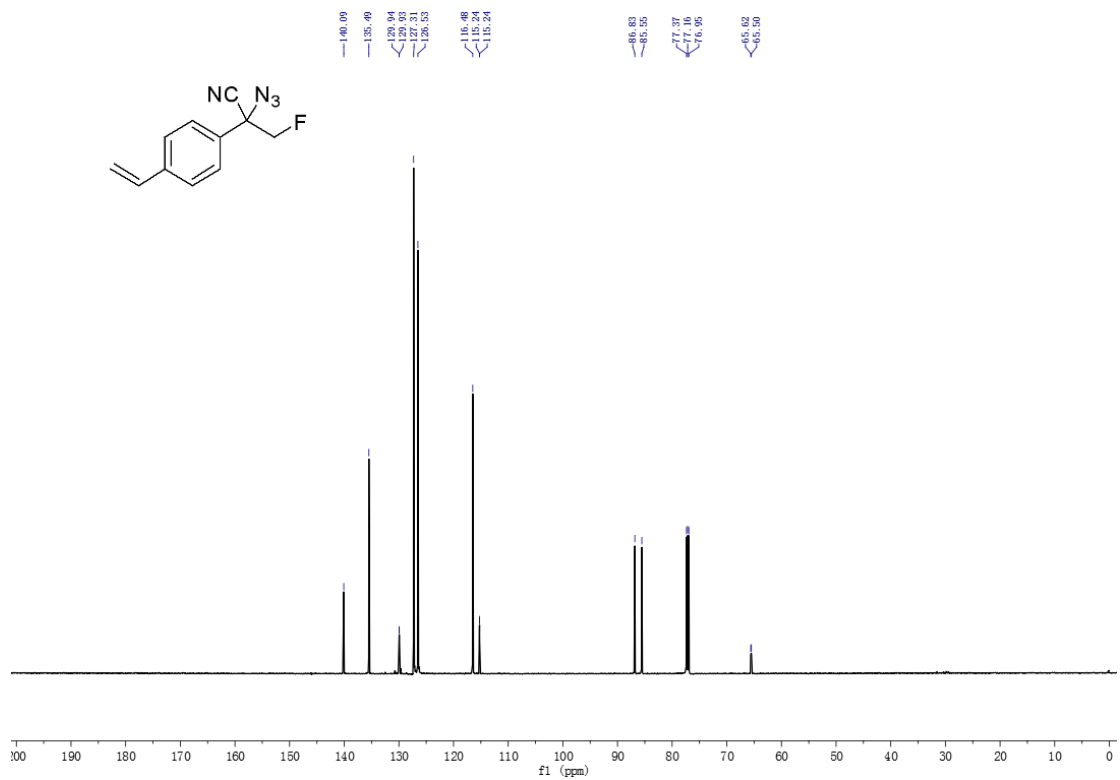
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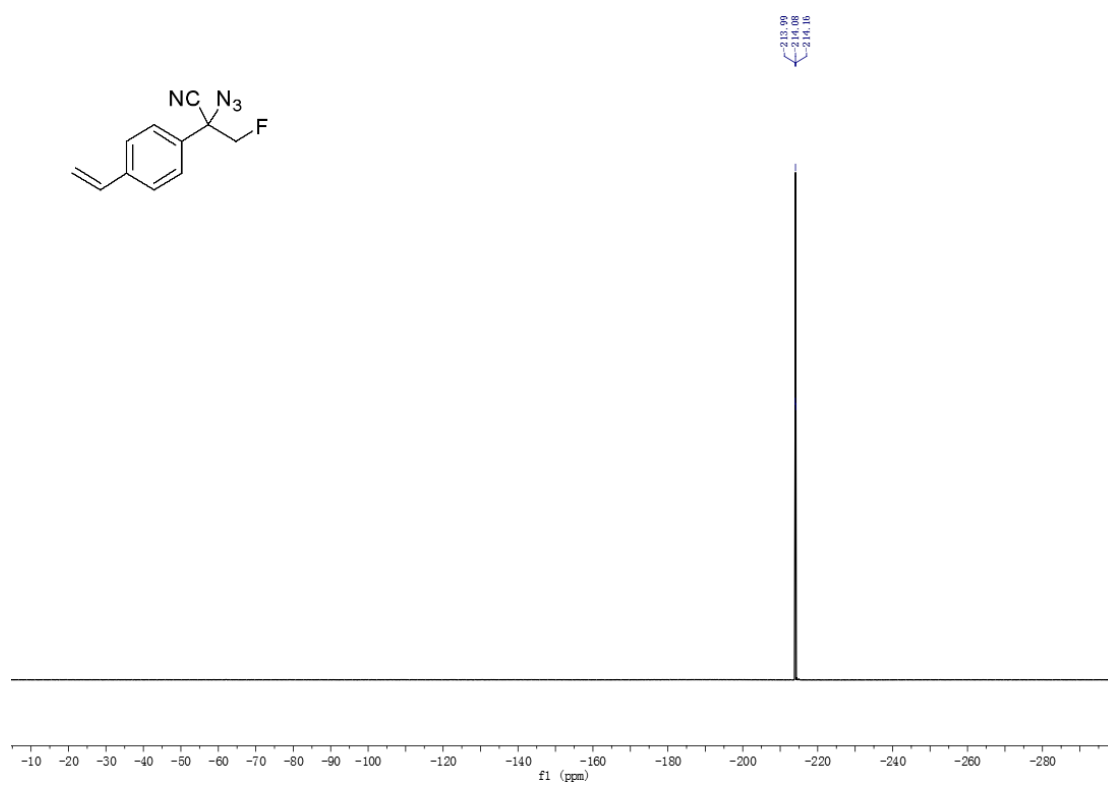
### $^1\text{H}$ NMR of **2k**



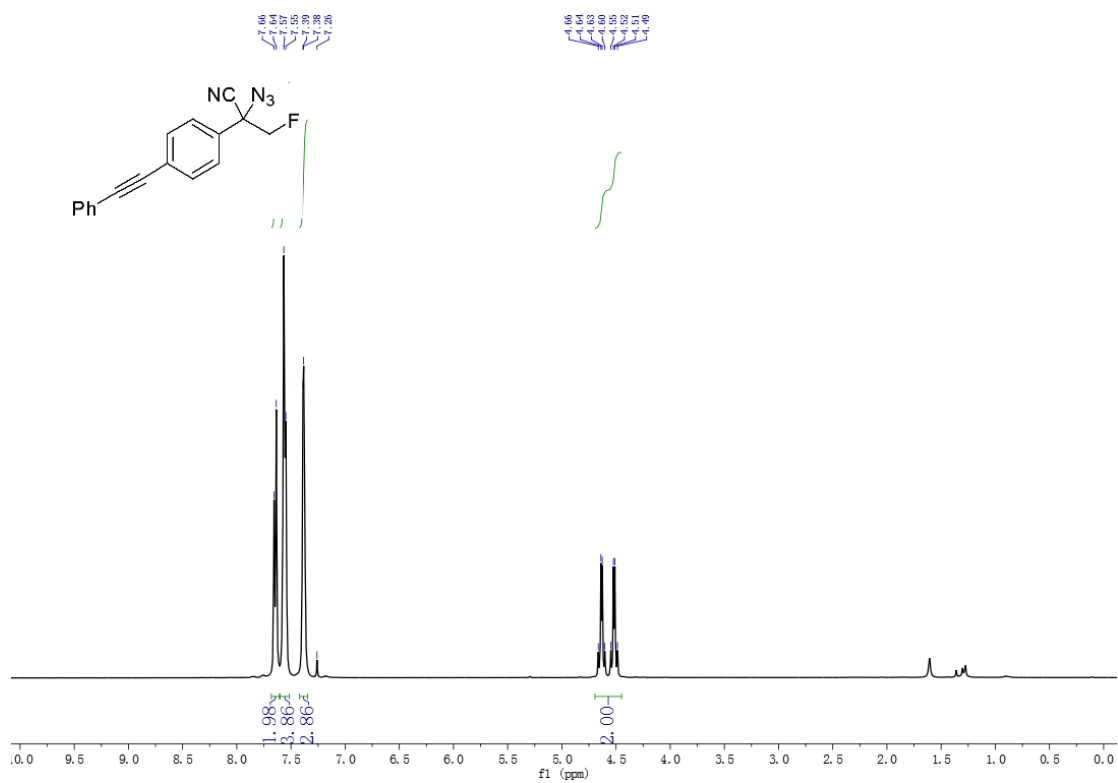
### $^{13}\text{C}$ NMR of **2k**



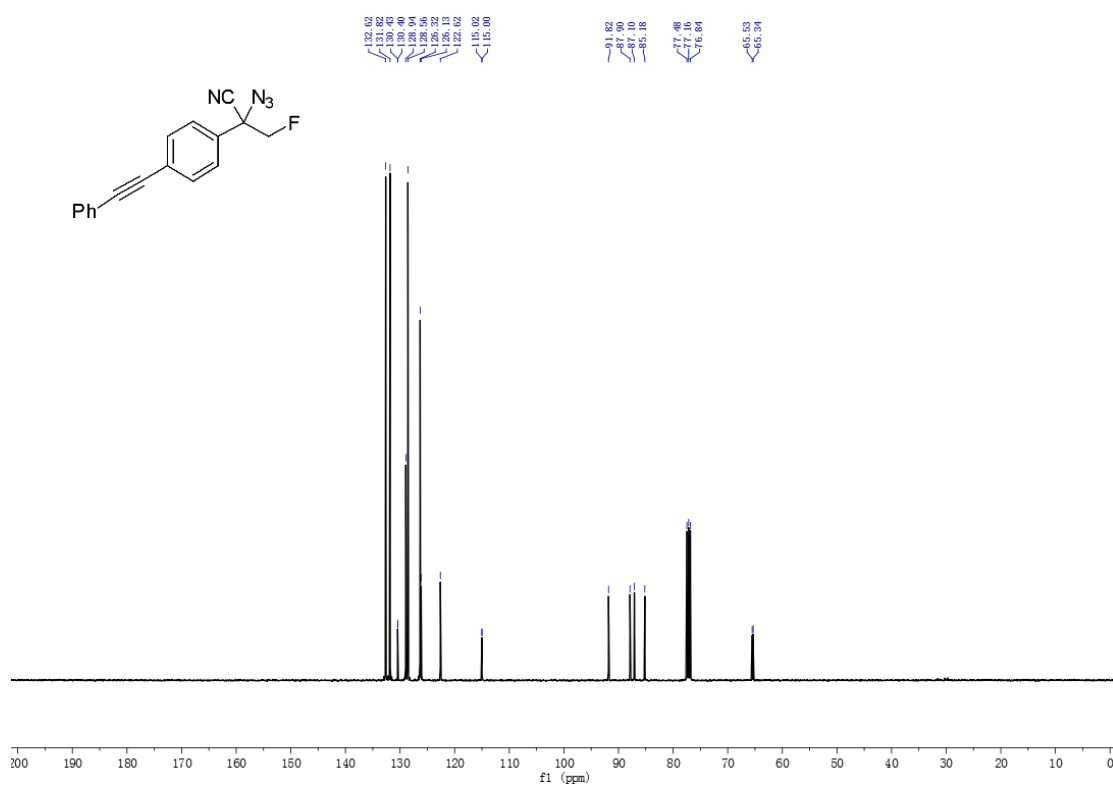
### $^{19}\text{F}$ NMR of **2k**



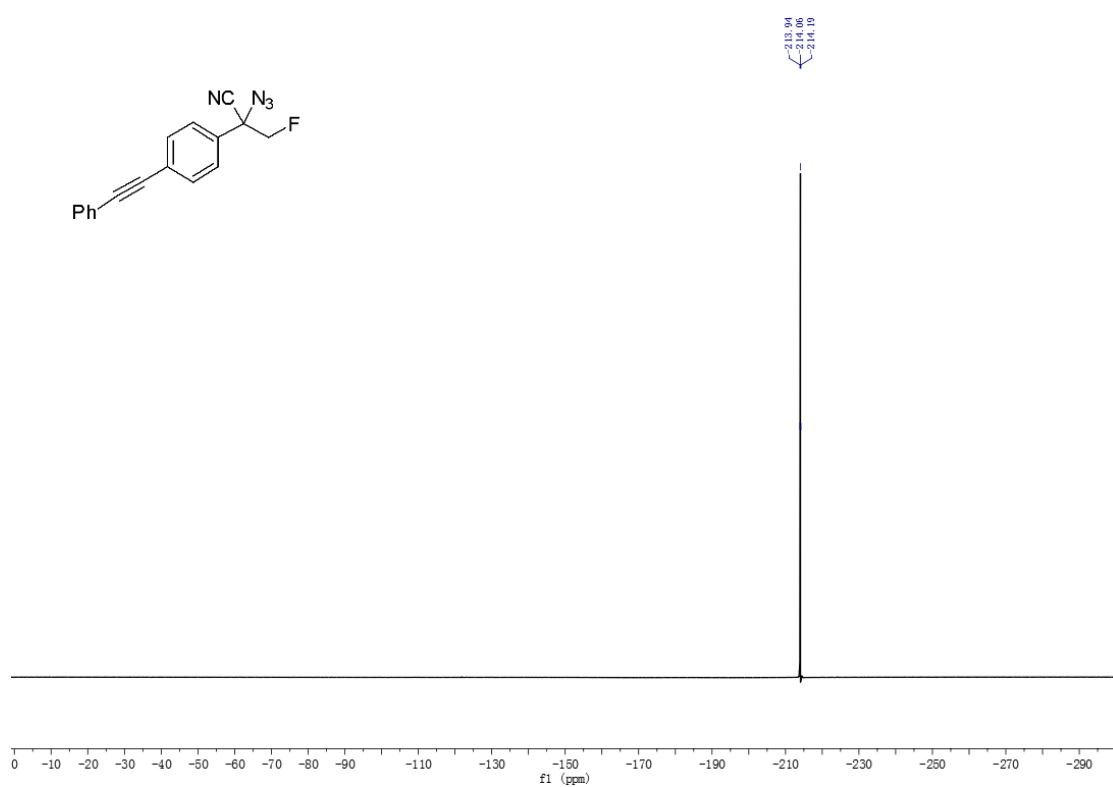
### $^1\text{H}$ NMR of **2l**



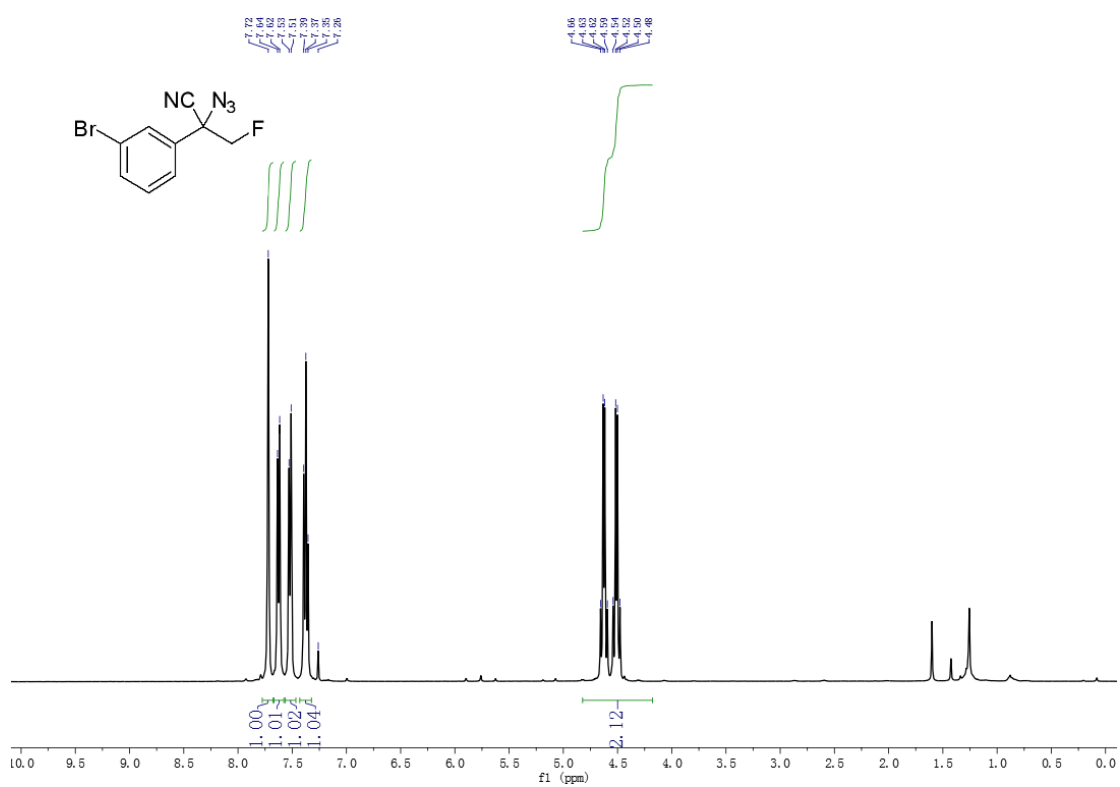
### $^{13}\text{C}$ NMR of **21**



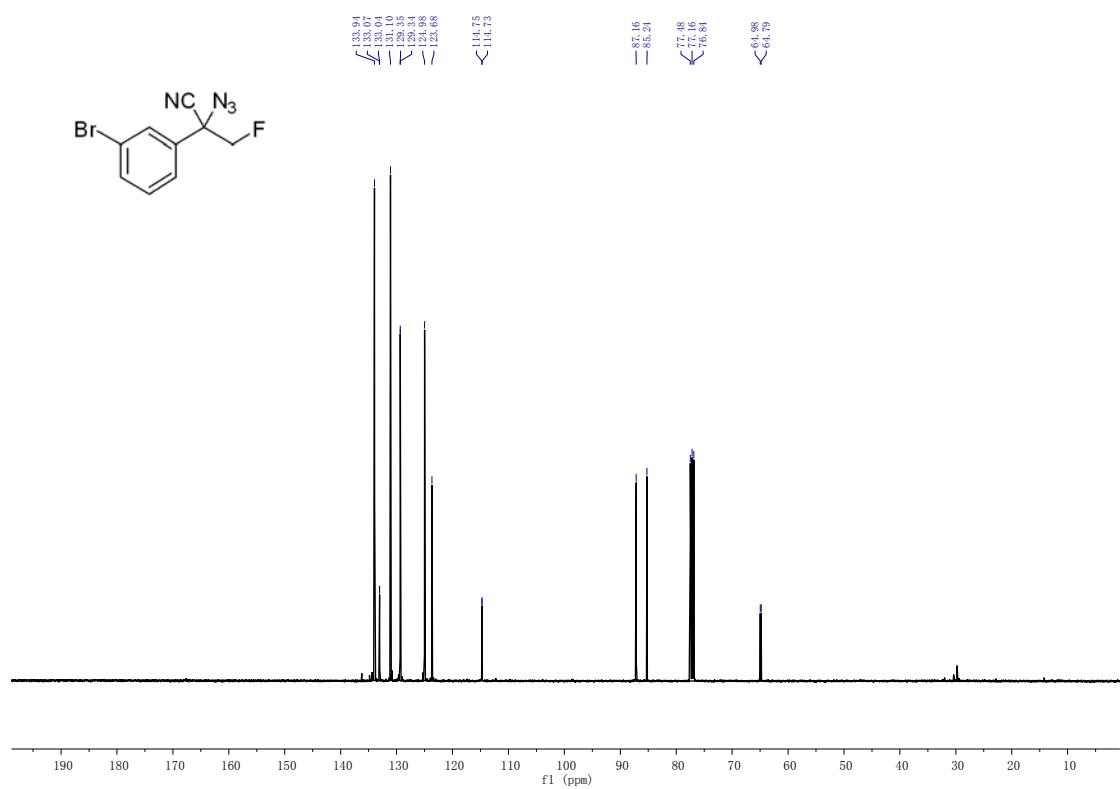
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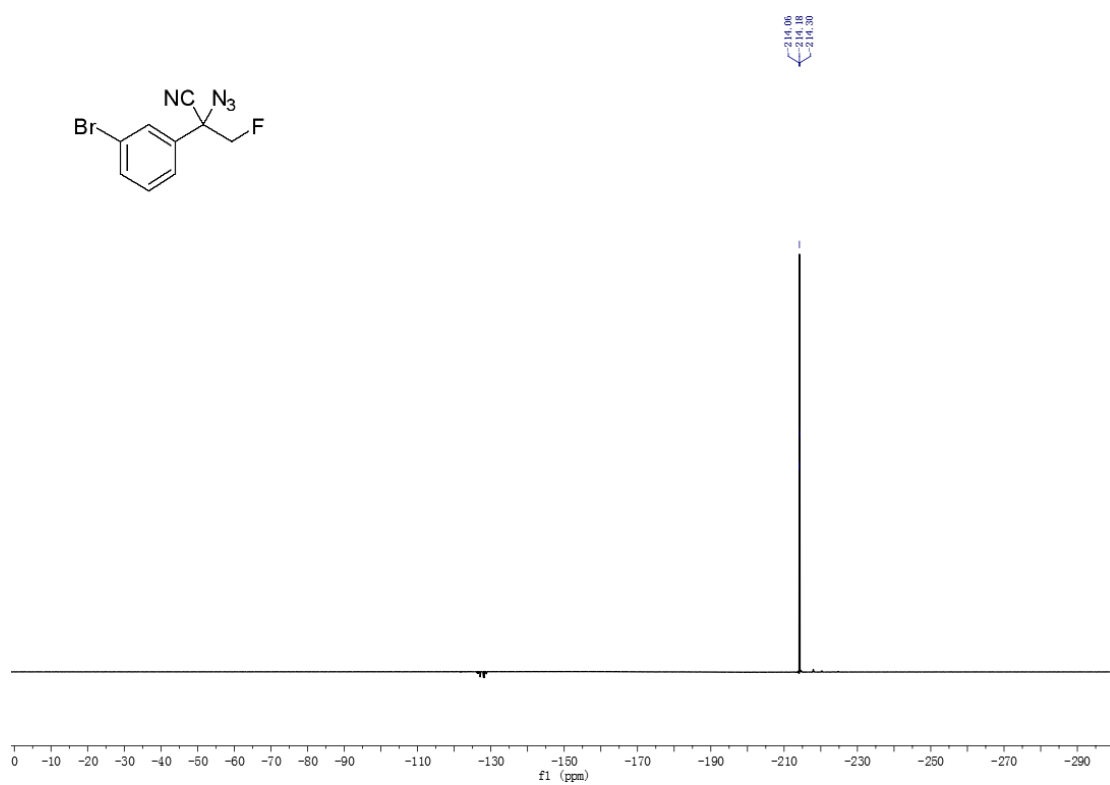
### $^1\text{H}$ NMR of **2m**



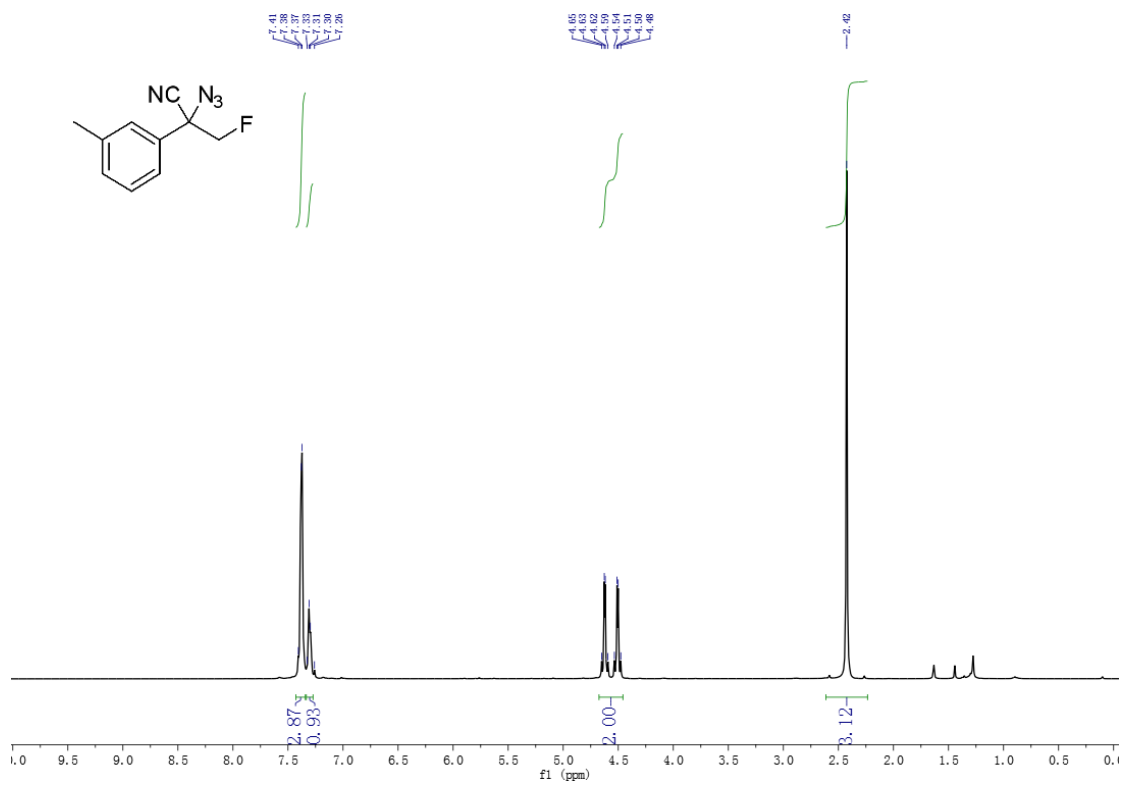
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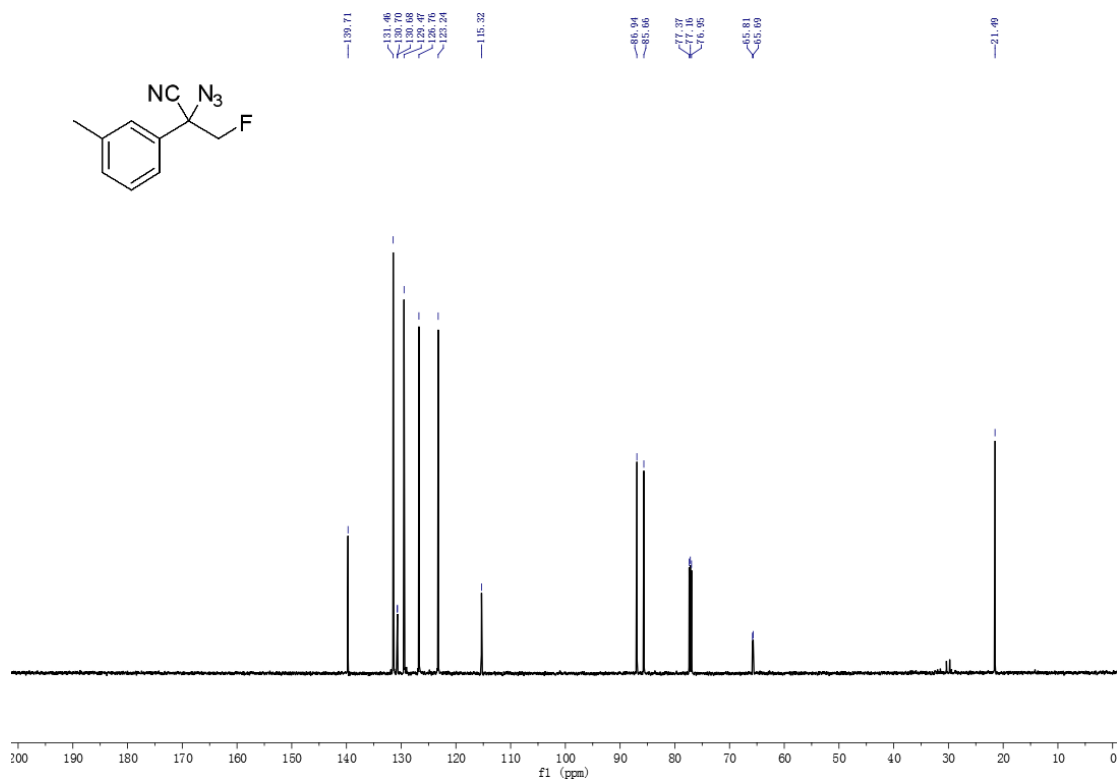
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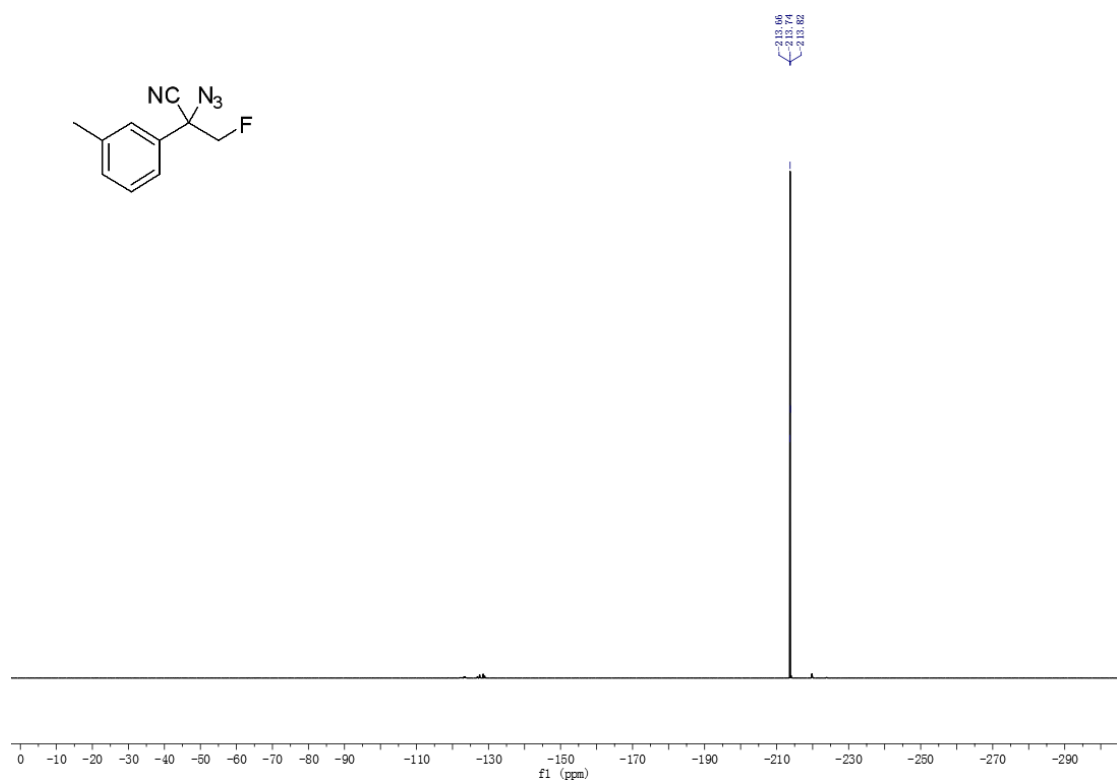
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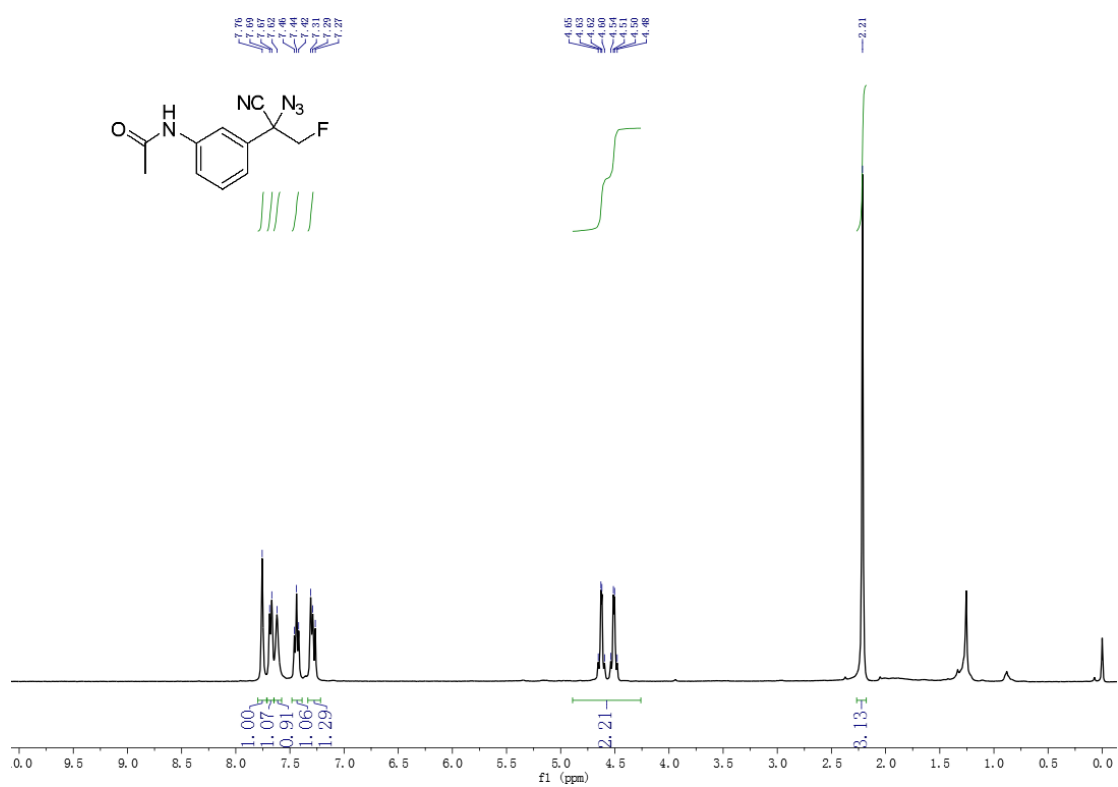
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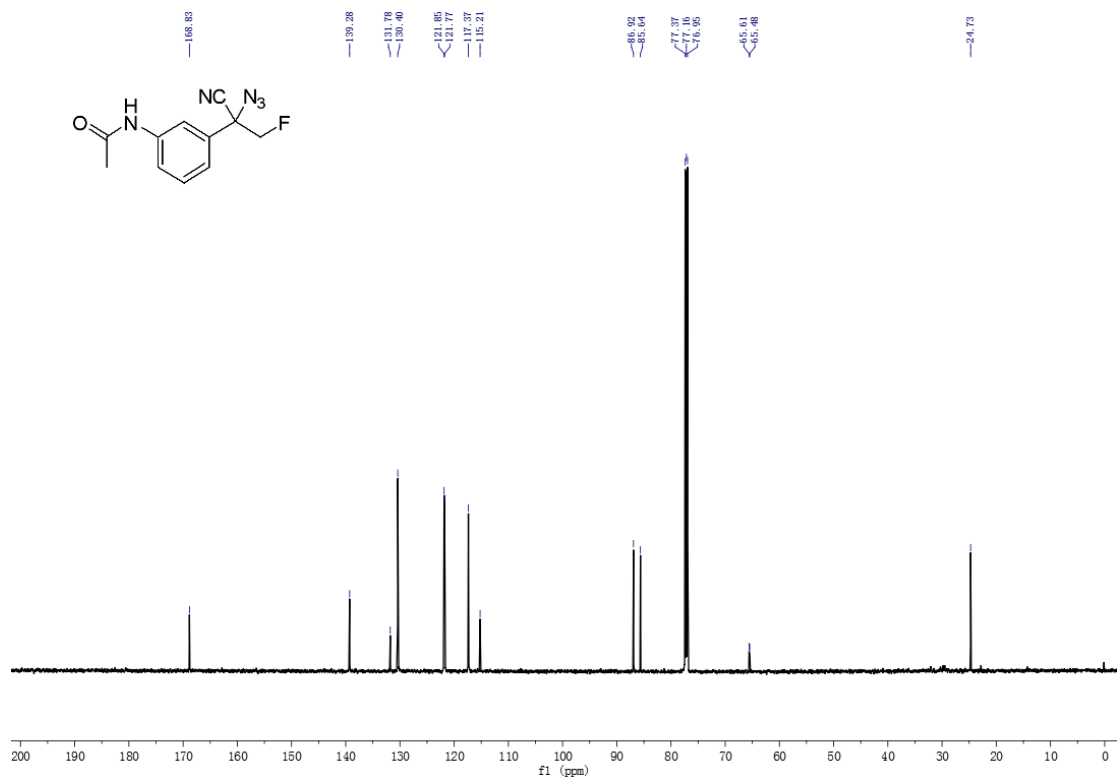
### $^{19}\text{F}$ NMR of **2n**



### $^1\text{H}$ NMR of **2o**

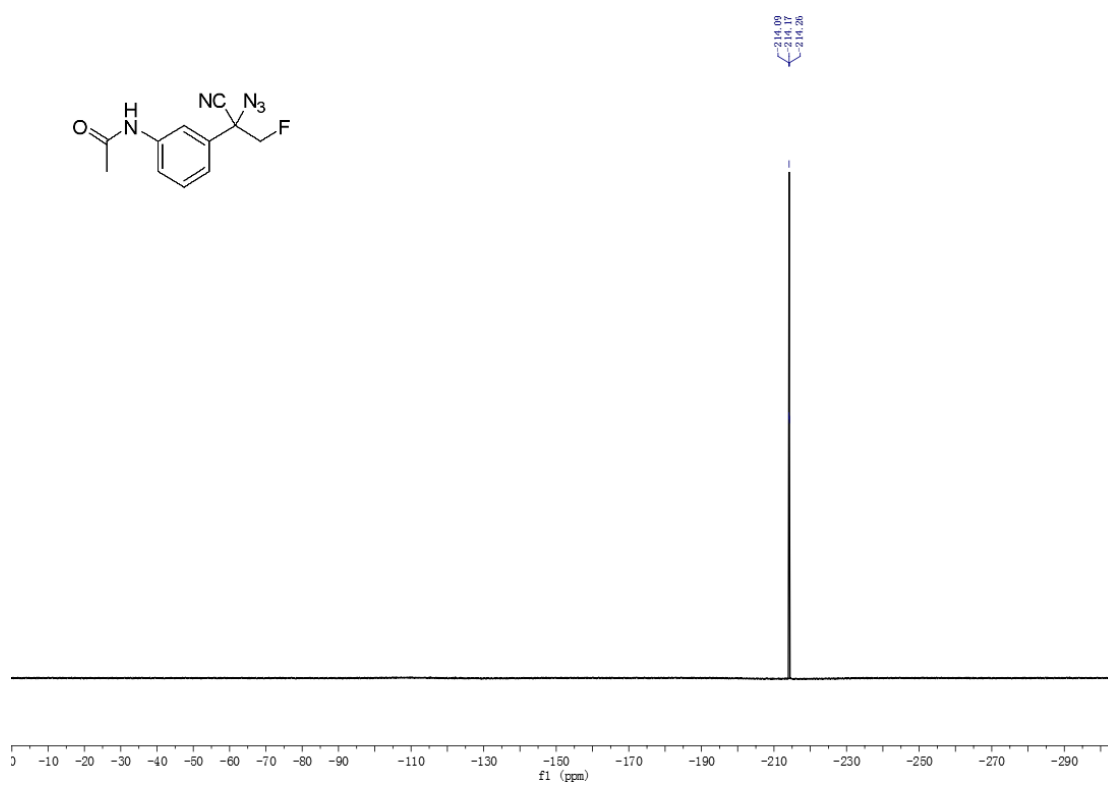


### $^{13}\text{C}$ NMR of **2o**

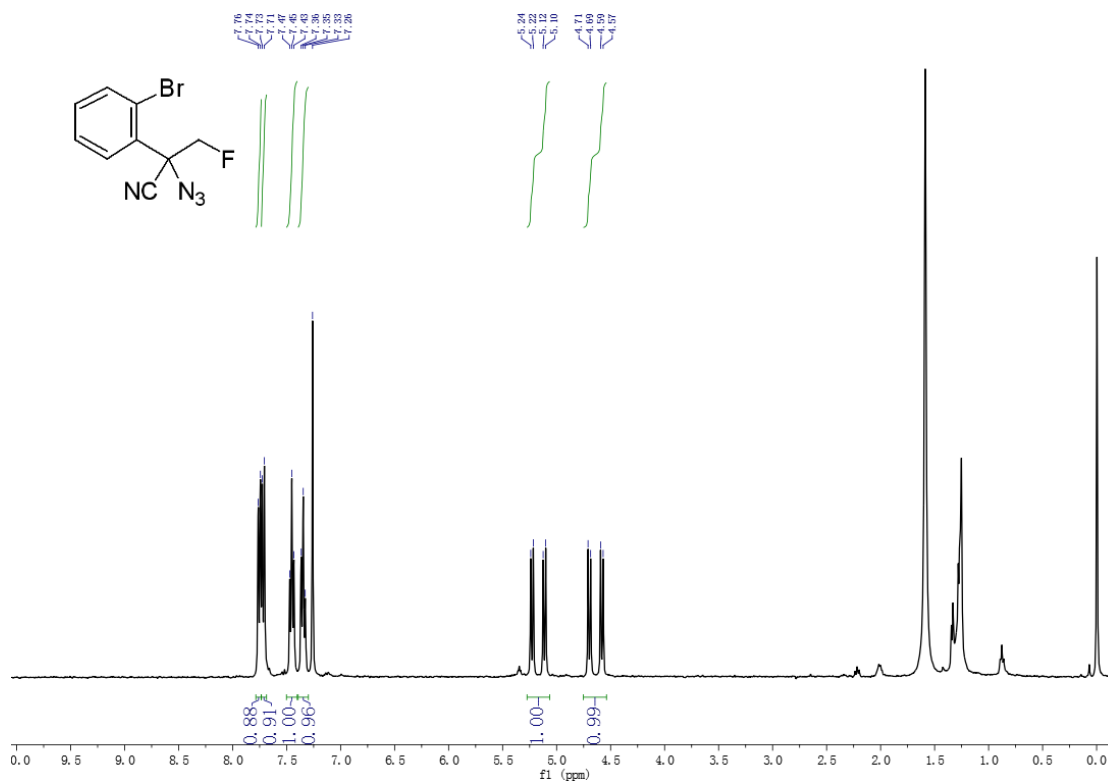




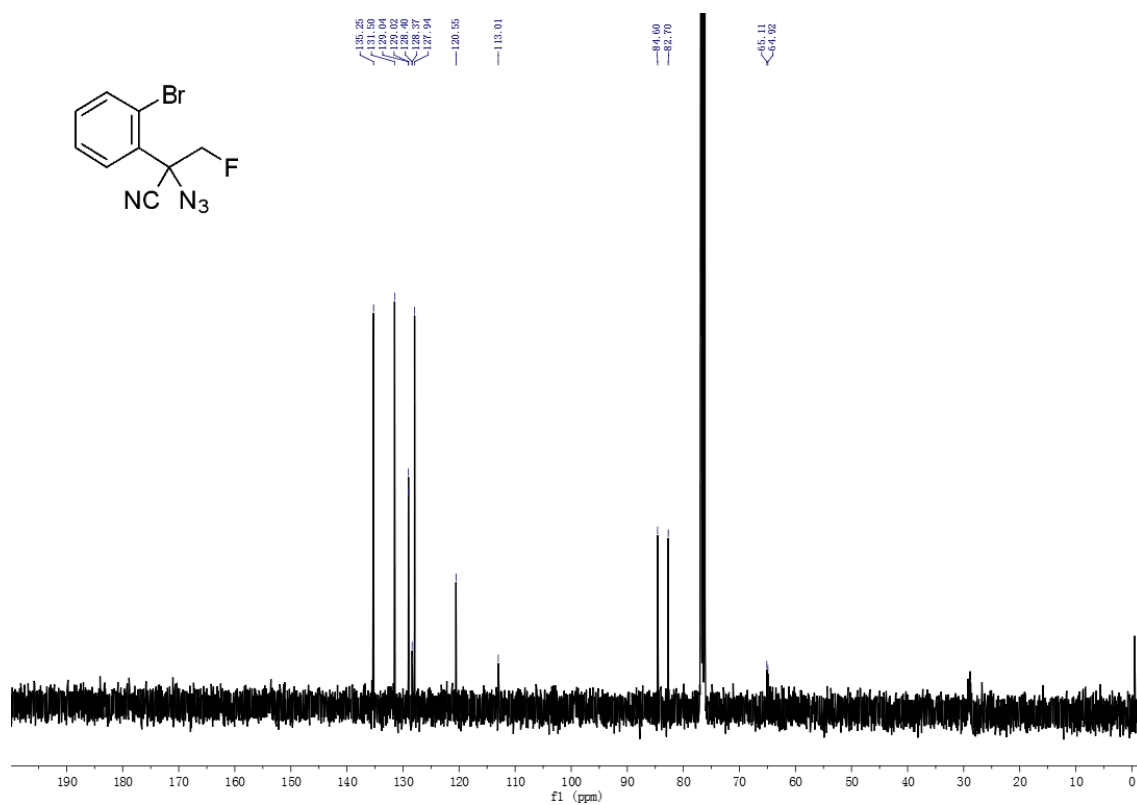
### $^{19}\text{F}$ NMR of **2o**



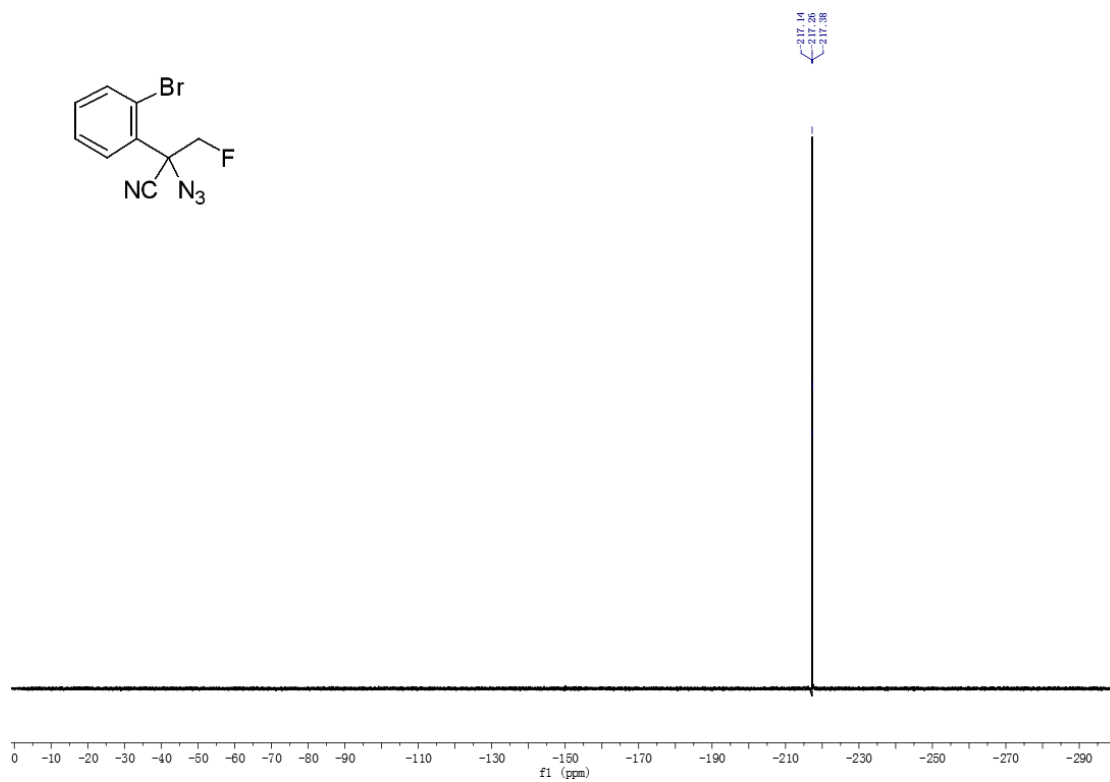
### $^1\text{H}$ NMR of **2p**



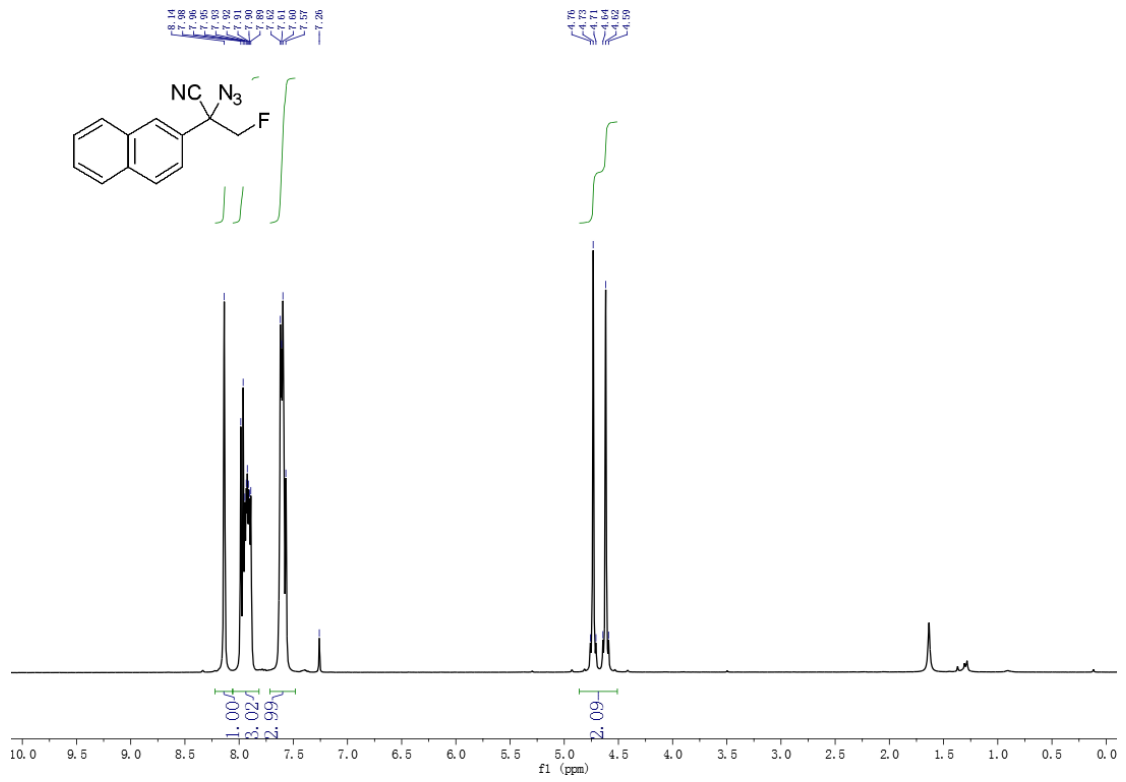
### $^{13}\text{C}$ NMR of **2p**



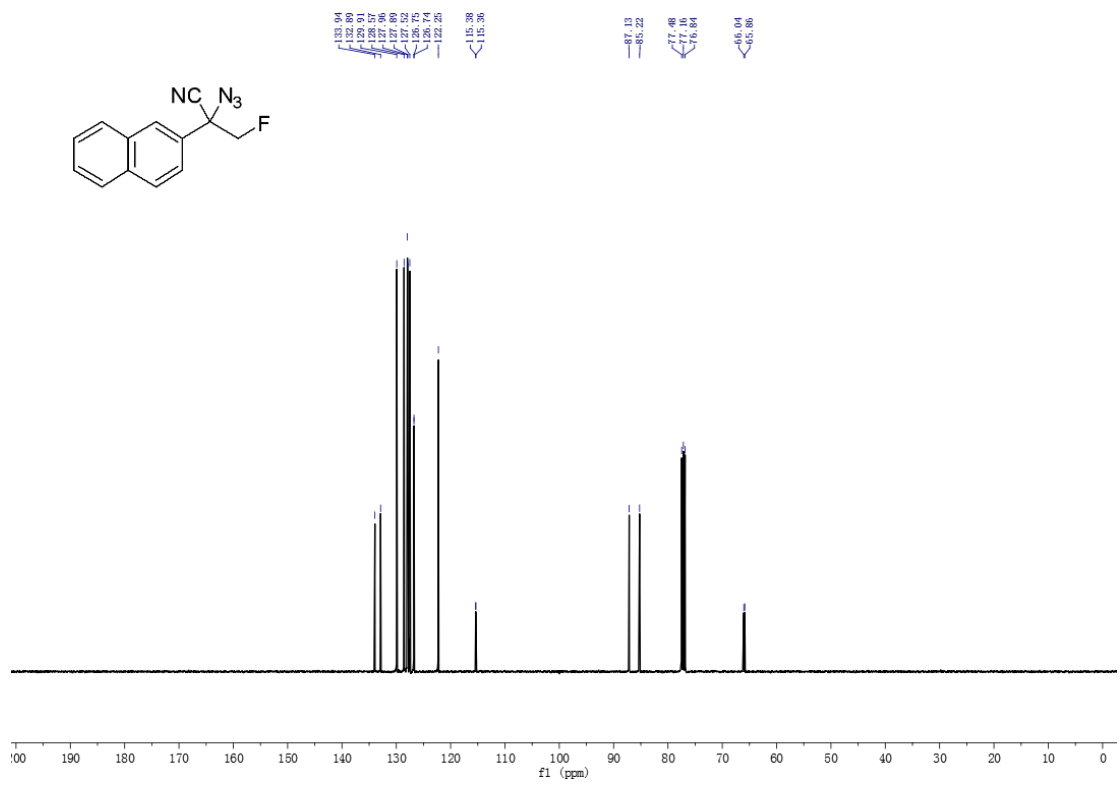
### $^{19}\text{F}$ NMR of **2p**



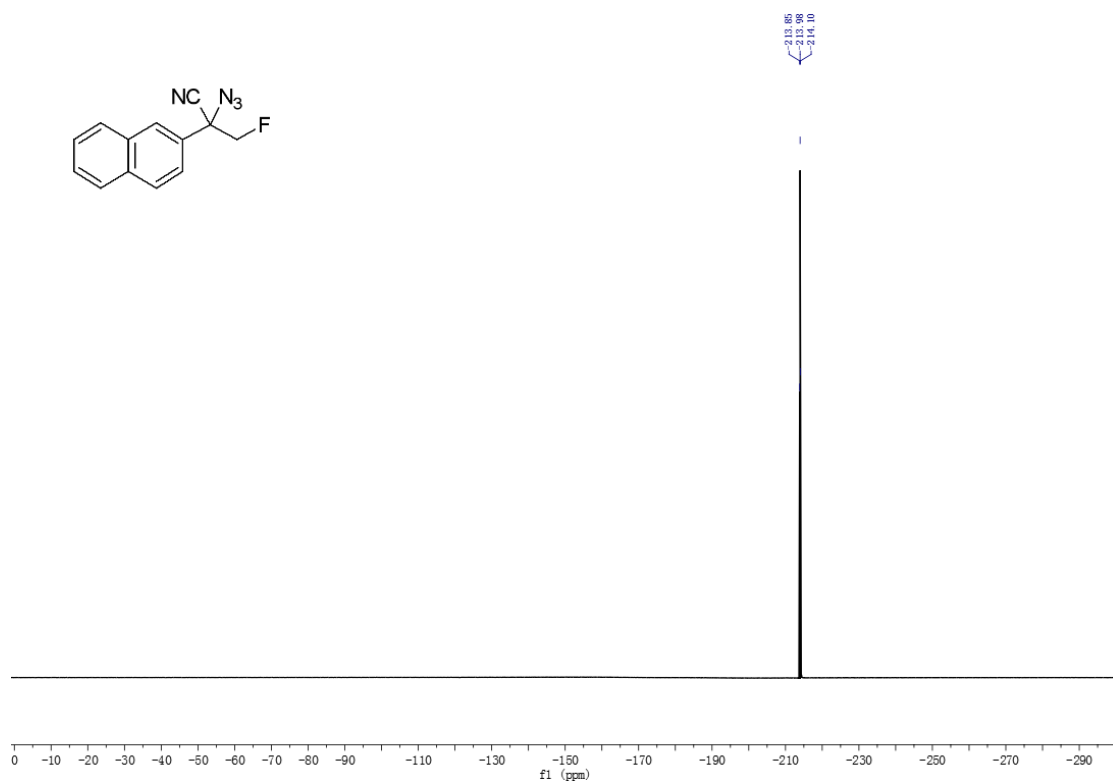
### $^1\text{H}$ NMR of **2q**



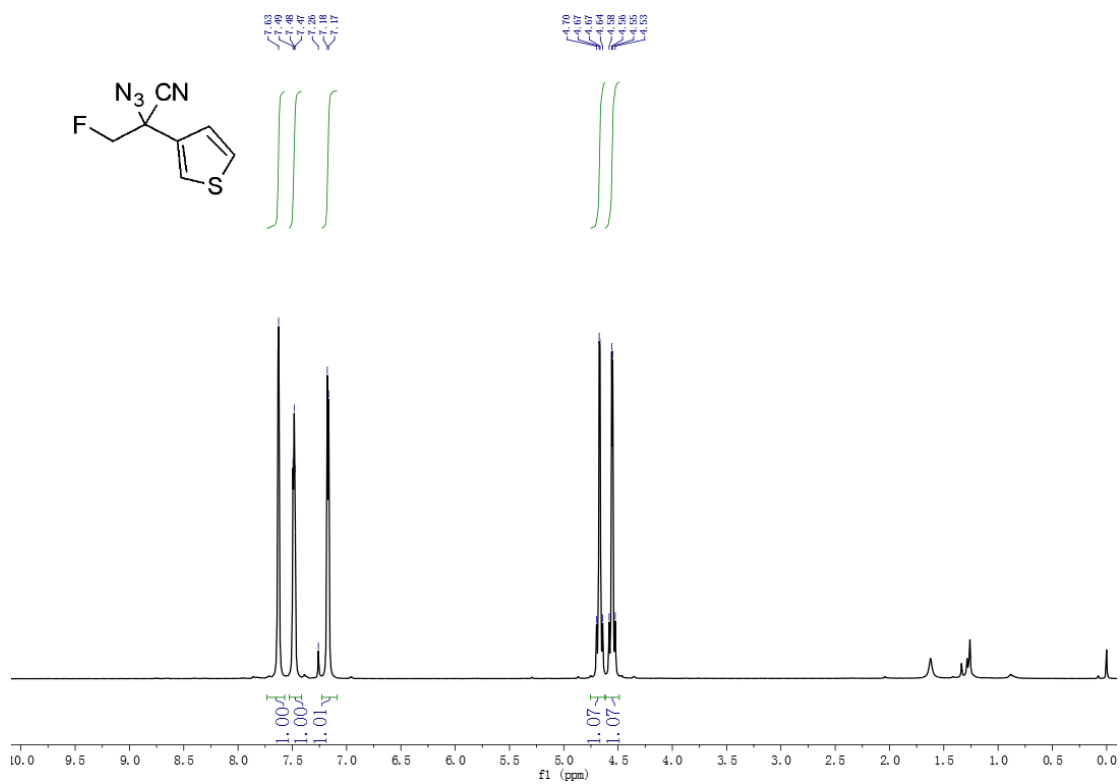
### $^{13}\text{C}$ NMR of **2q**



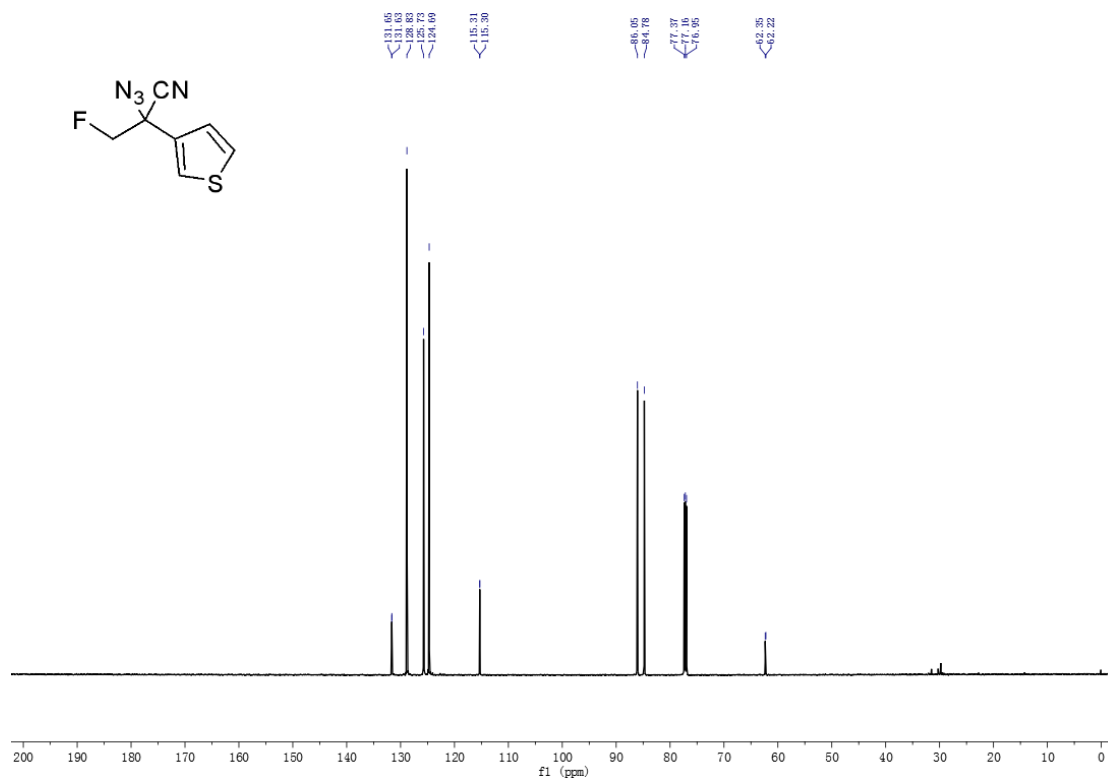
### $^{19}\text{F}$ NMR of **2q**



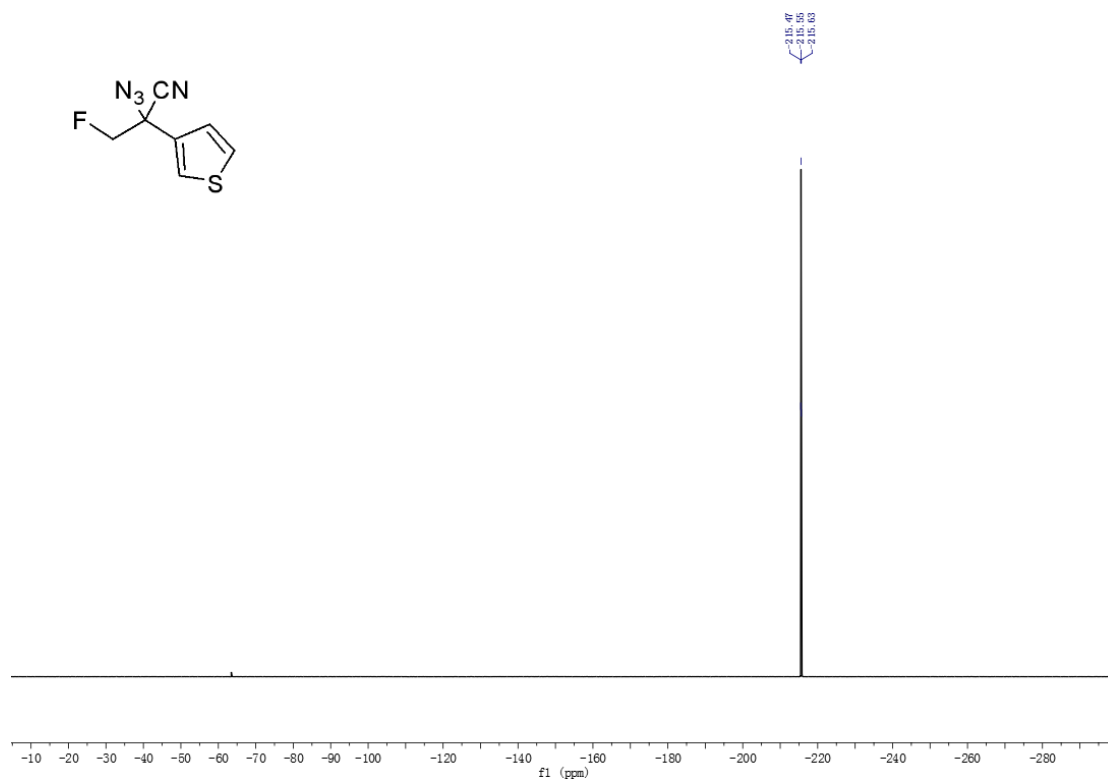
### $^1\text{H}$ NMR of **2r**



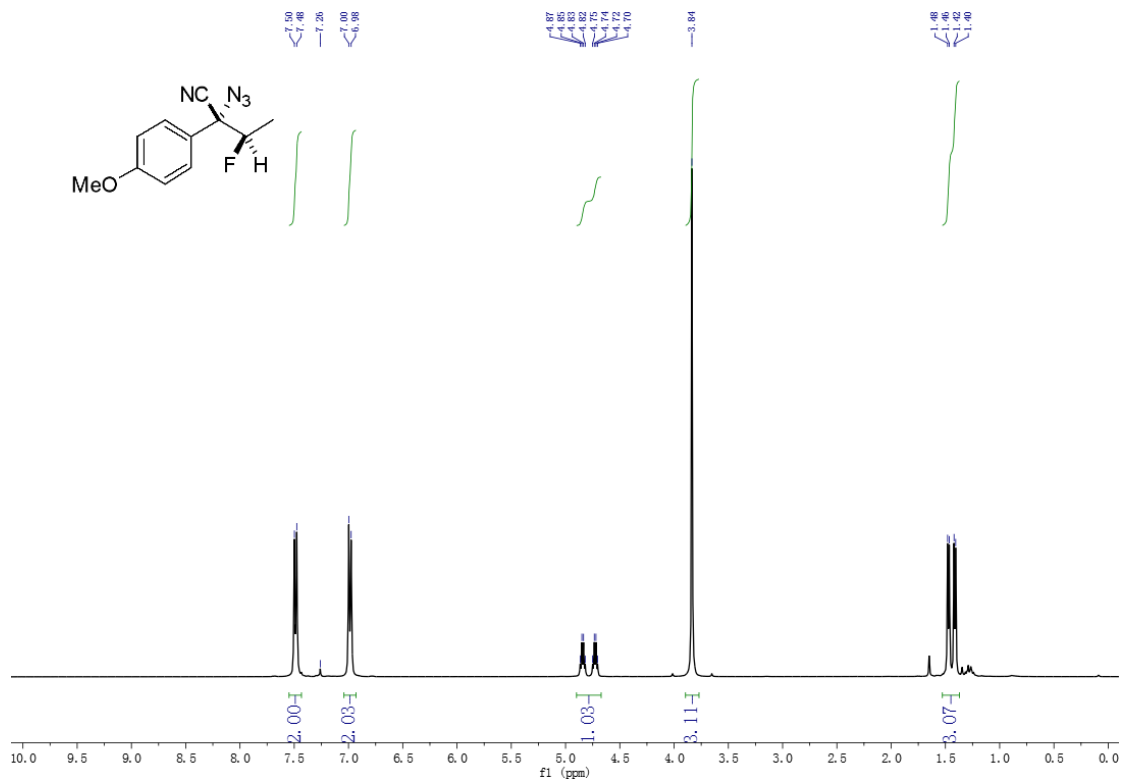
### $^{13}\text{C}$ NMR of **2r**



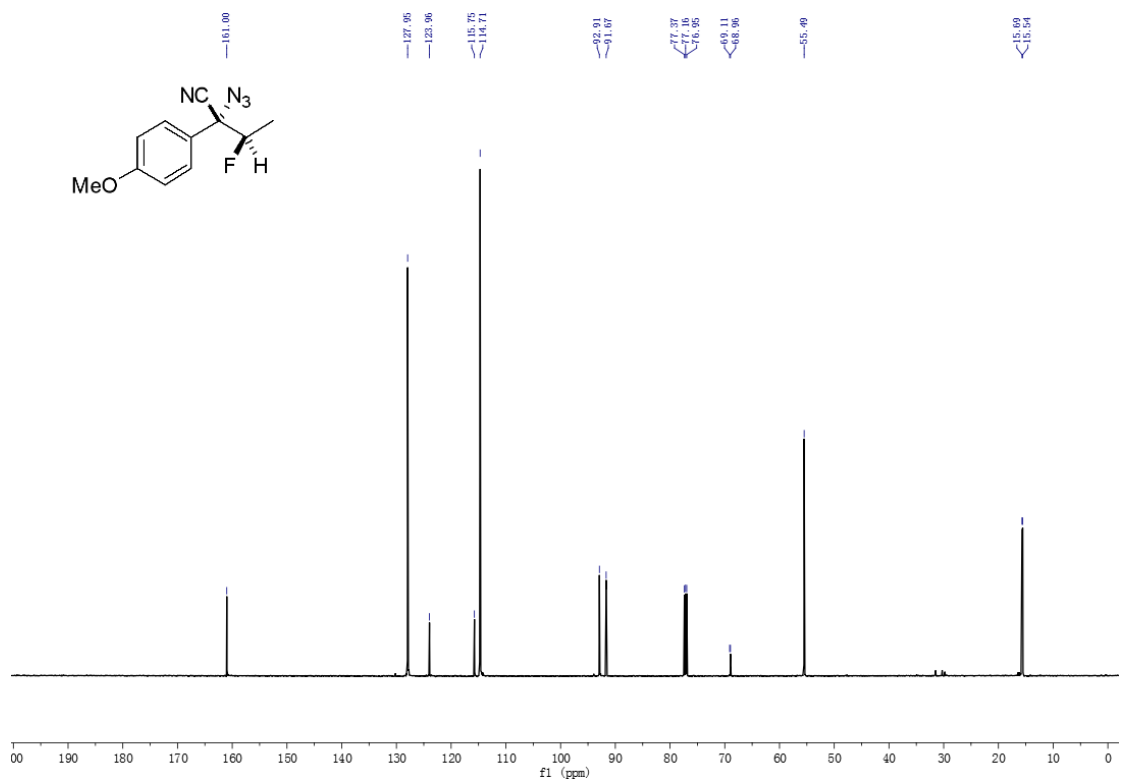
### $^{19}\text{F}$ NMR of **2r**



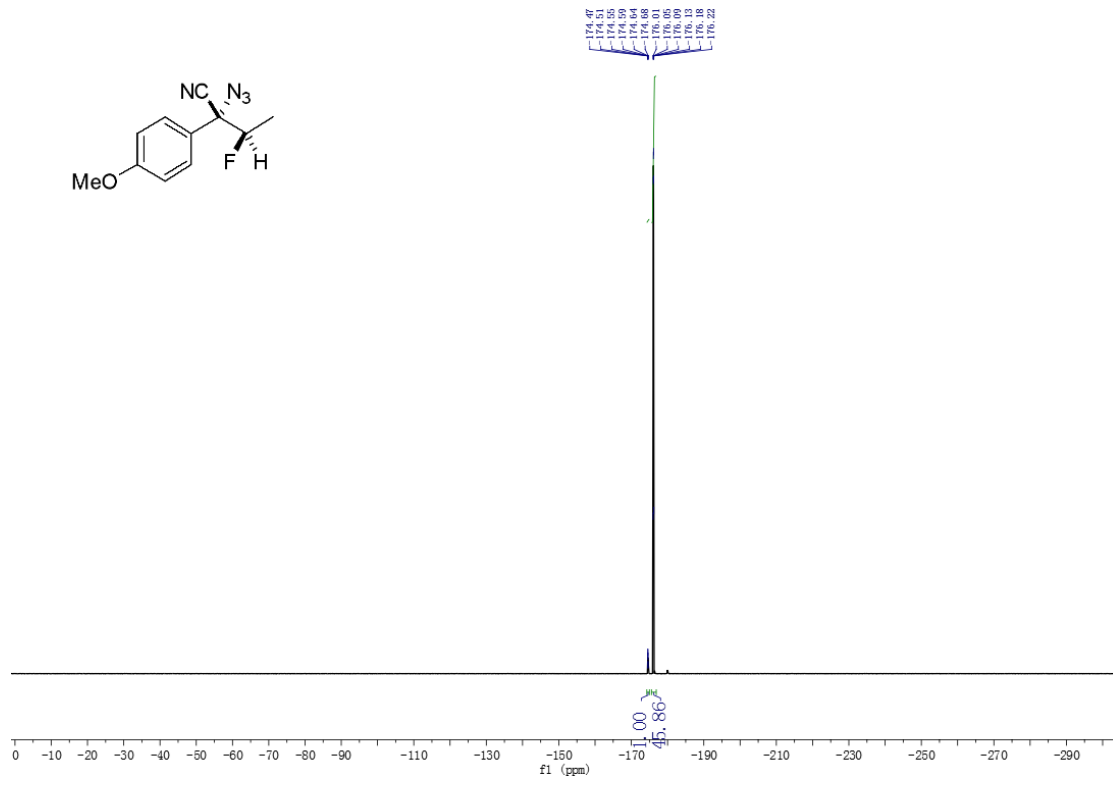
### $^1\text{H}$ NMR of **2s**



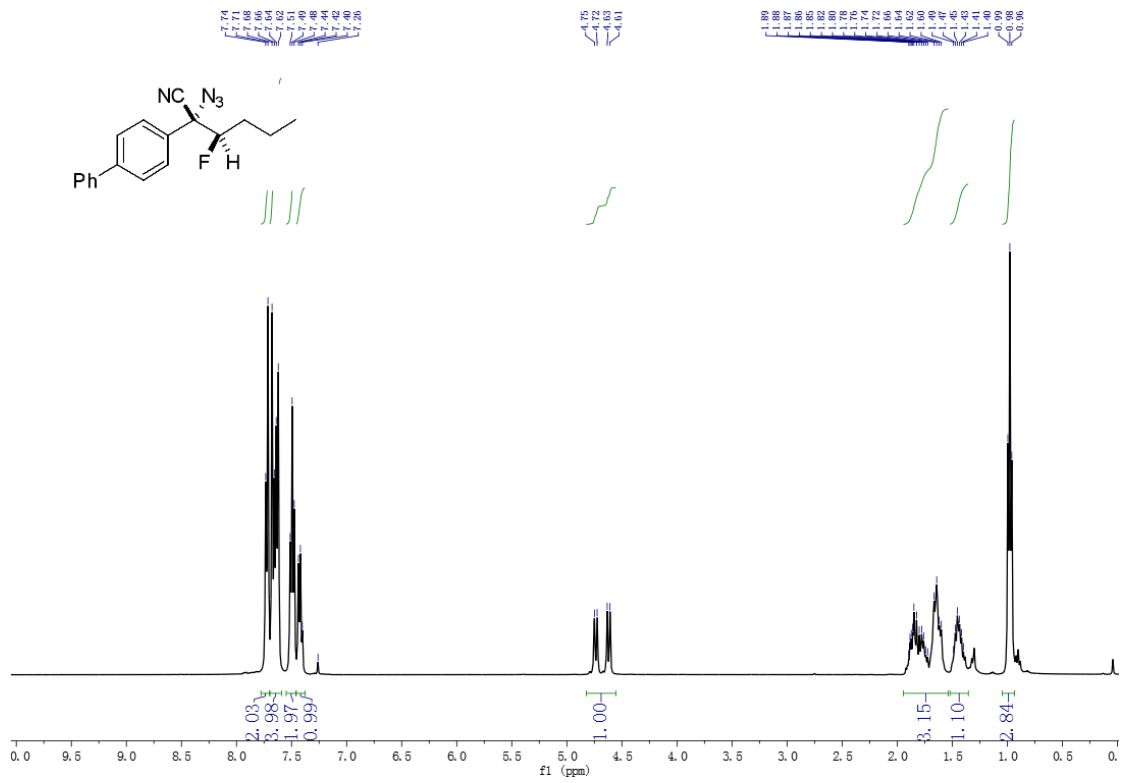
### $^{13}\text{C}$ NMR of **2s**



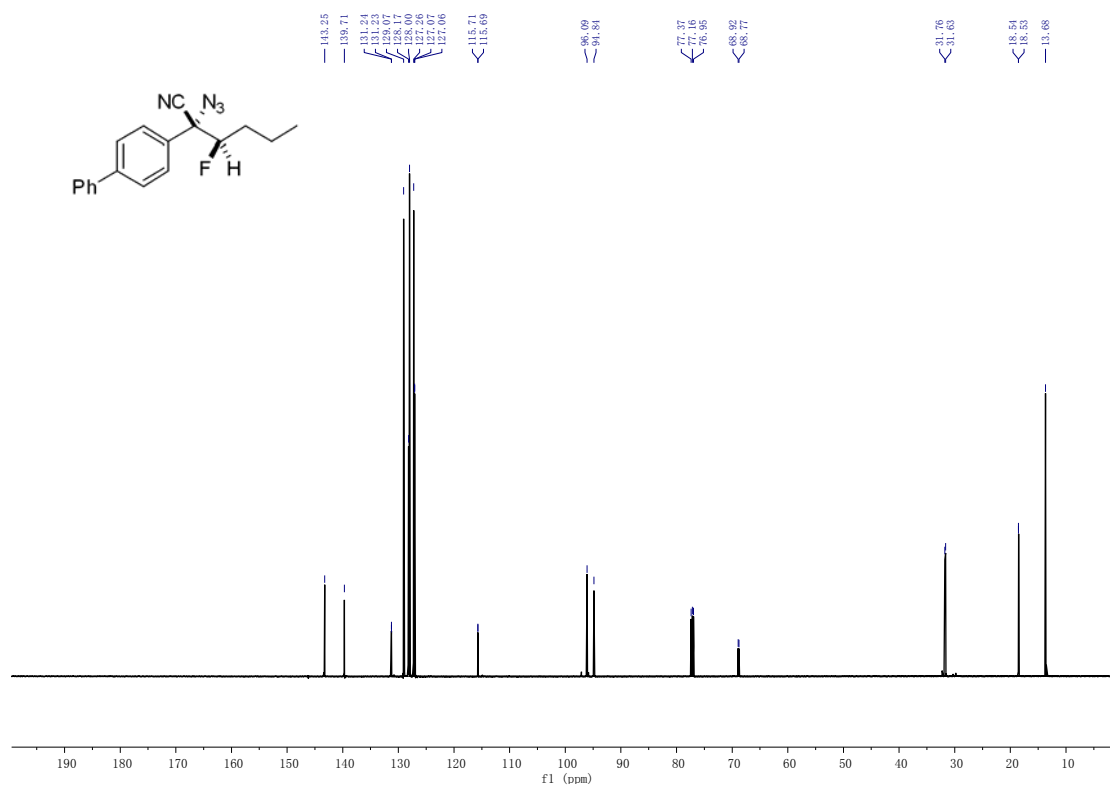
$^{13}\text{F}$  NMR of **2s**



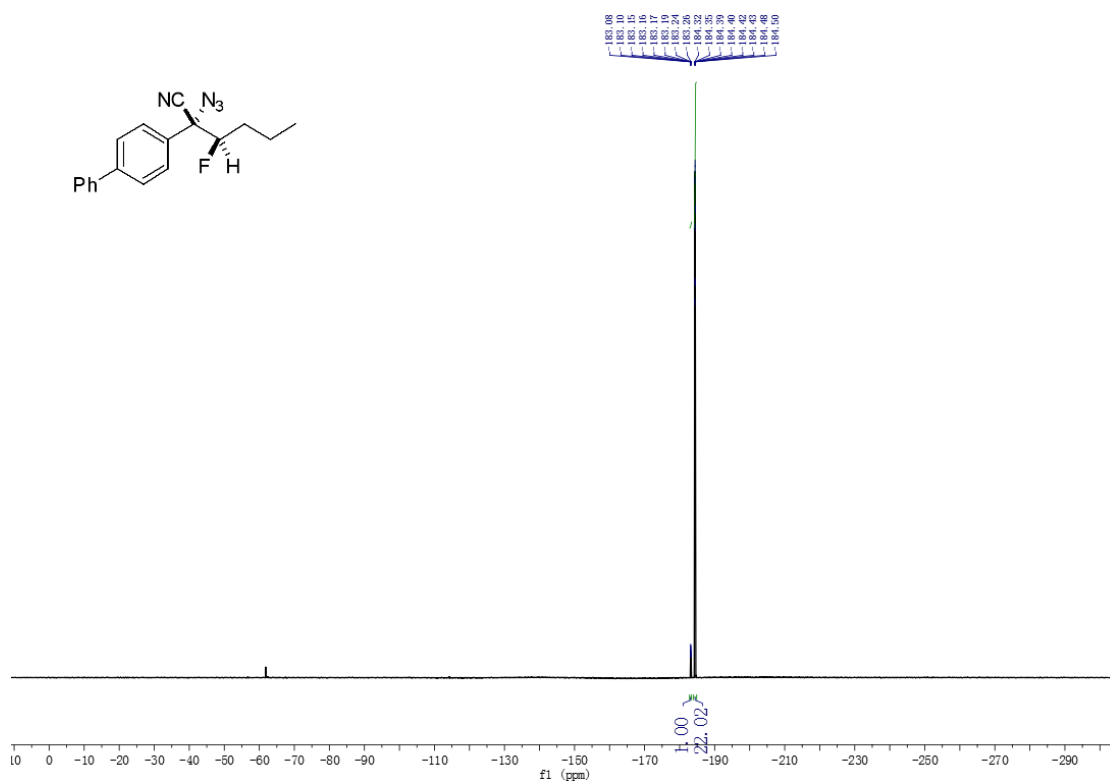
$^1\text{H}$  NMR of **2t**



### <sup>13</sup>C NMR of 2t

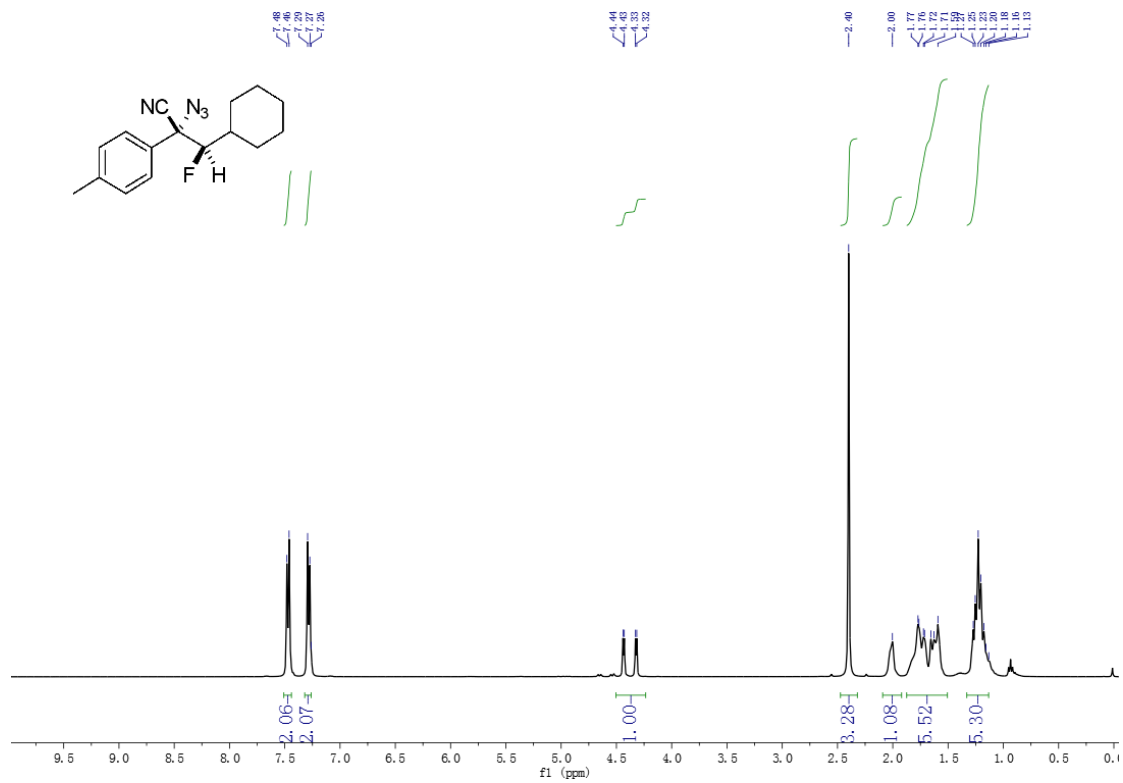


### <sup>19</sup>F NMR of 2t

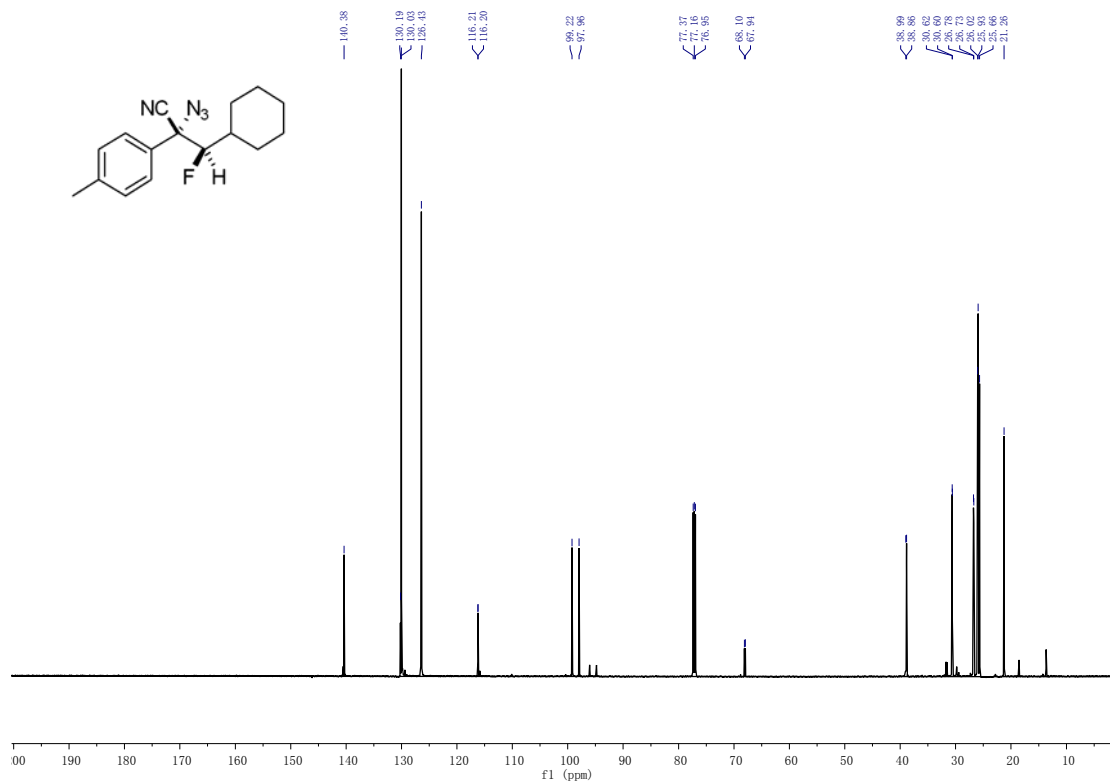




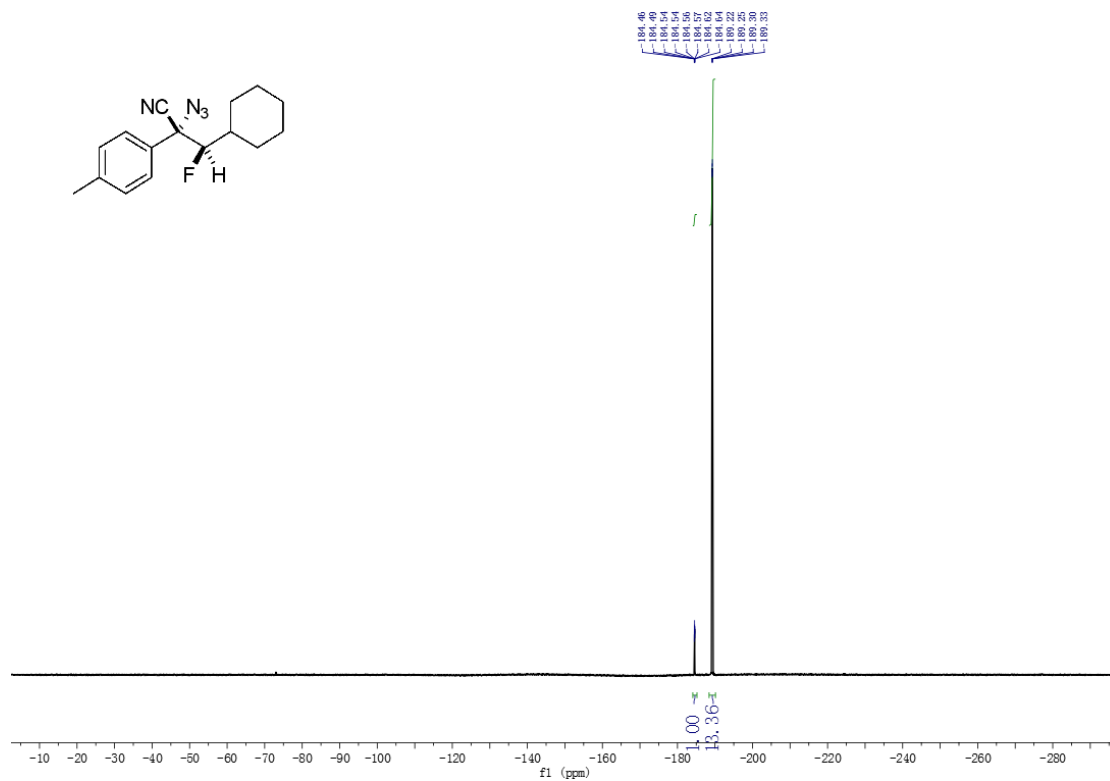
<sup>1</sup>H NMR of **2u**



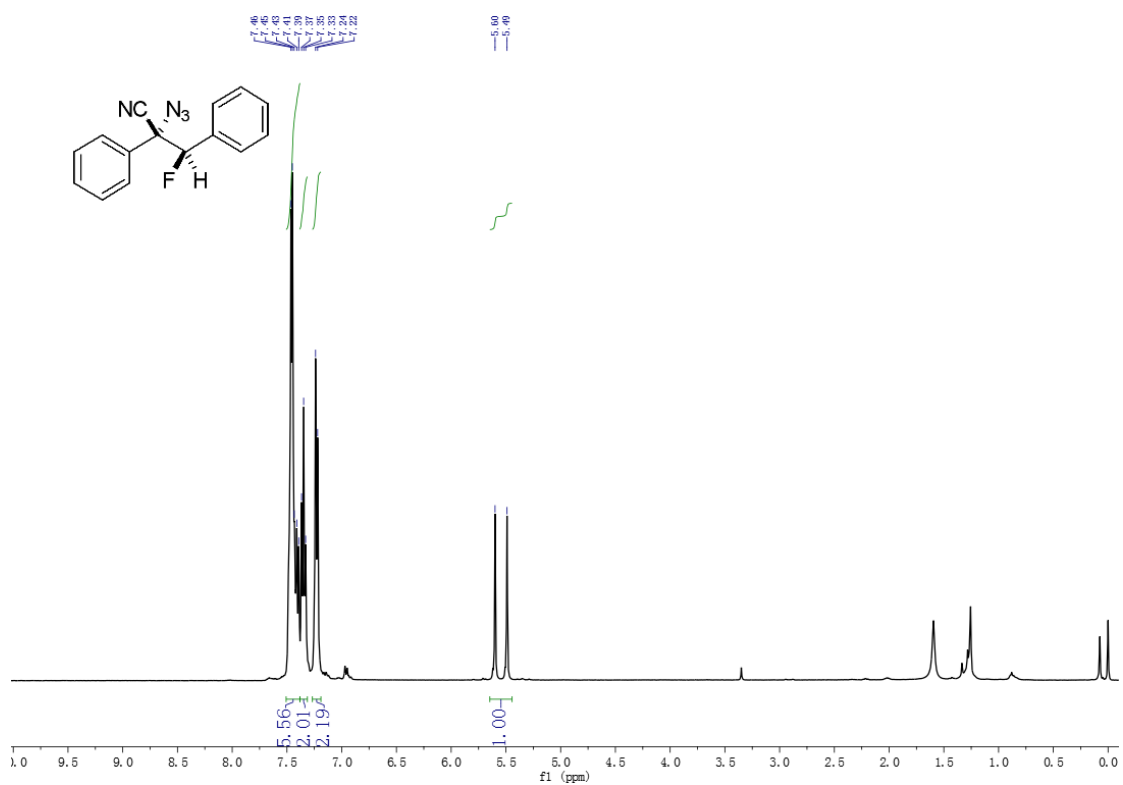
<sup>13</sup>C NMR of **2u**



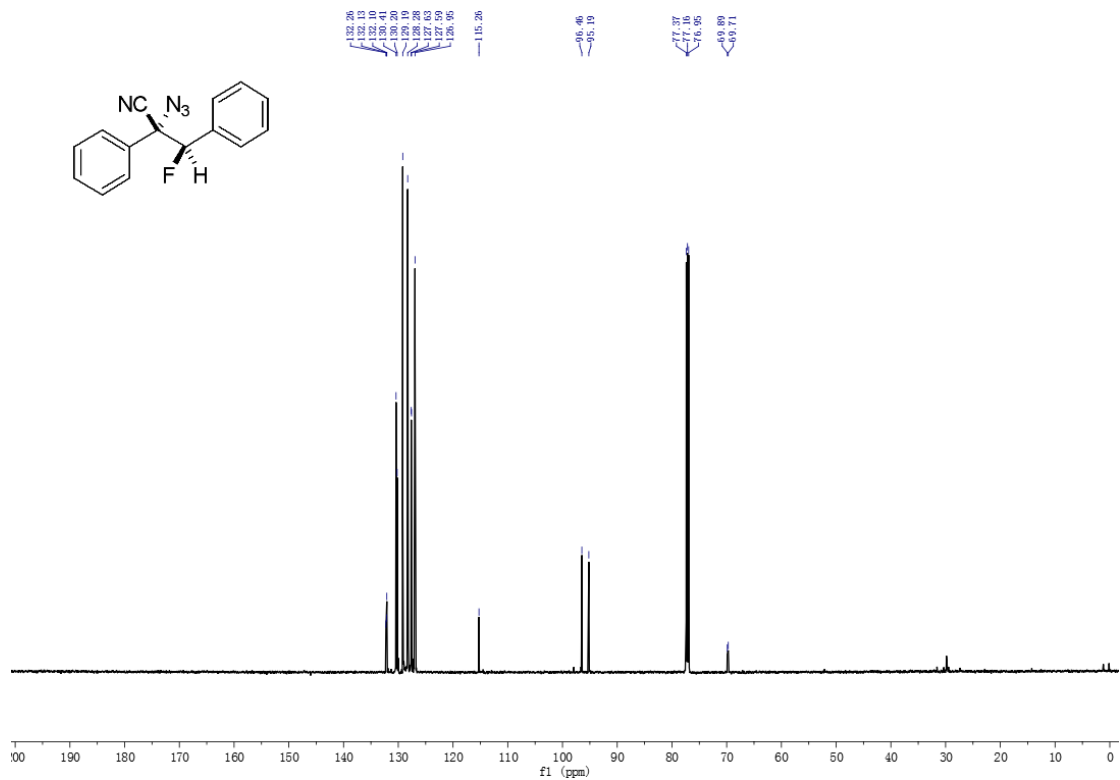
<sup>19</sup>F NMR of **2u**



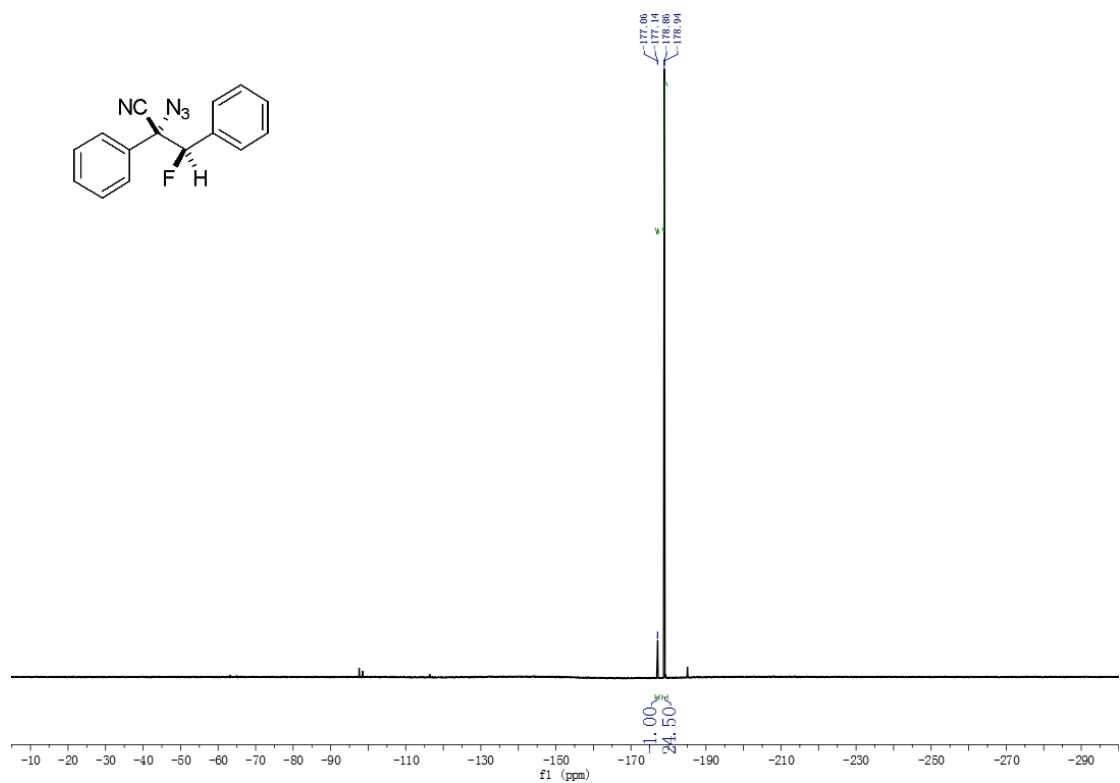
<sup>1</sup>H NMR of **2v**



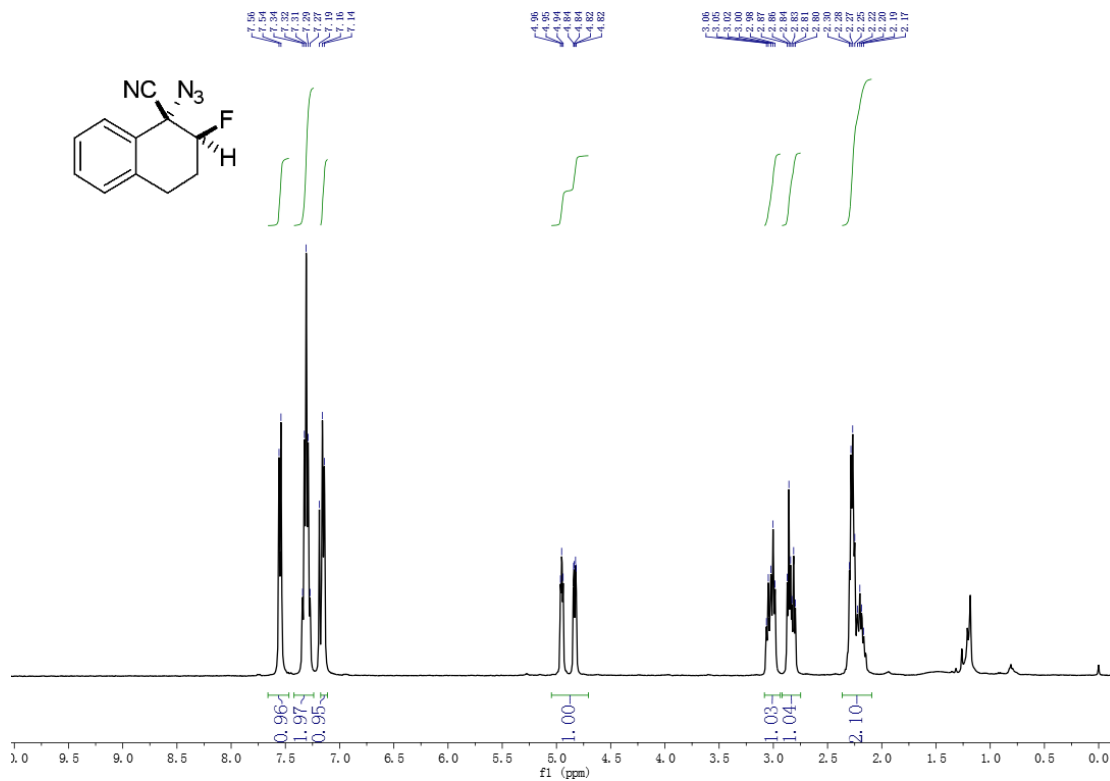
$^{13}\text{C}$  NMR of **2v**



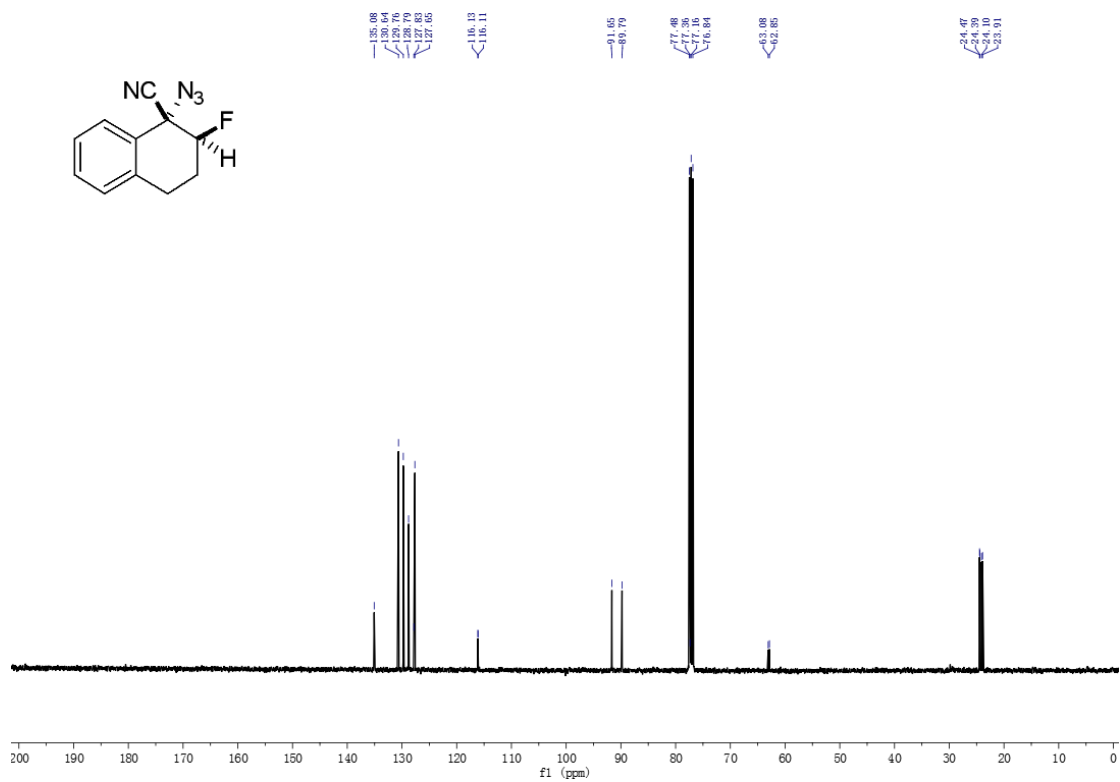
$^{19}\text{F}$  NMR of **2v**



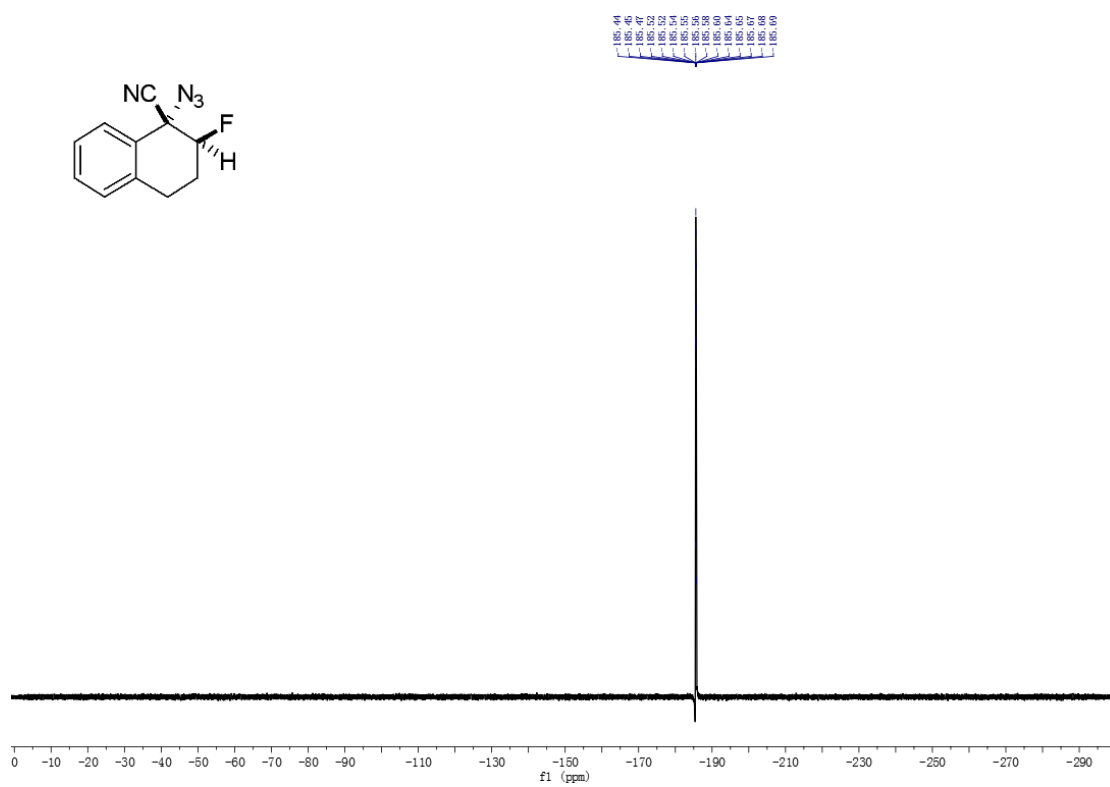
### $^1\text{H}$ NMR of **2w**



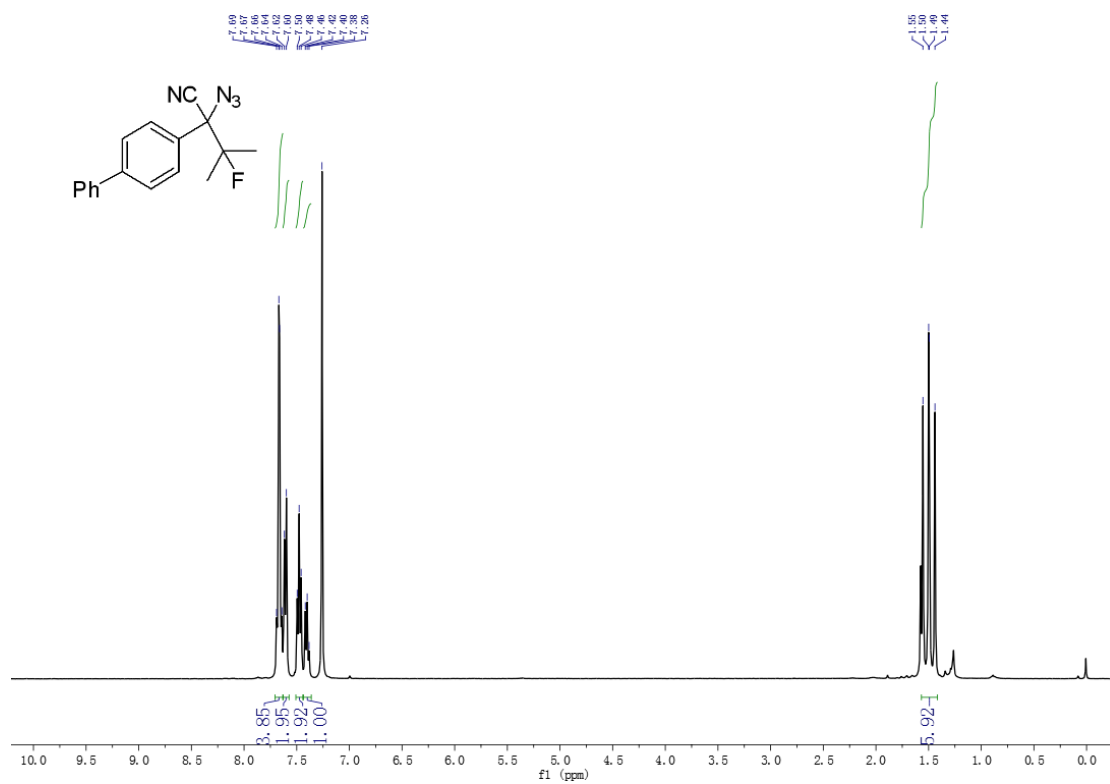
### $^{13}\text{C}$ NMR of **2w**



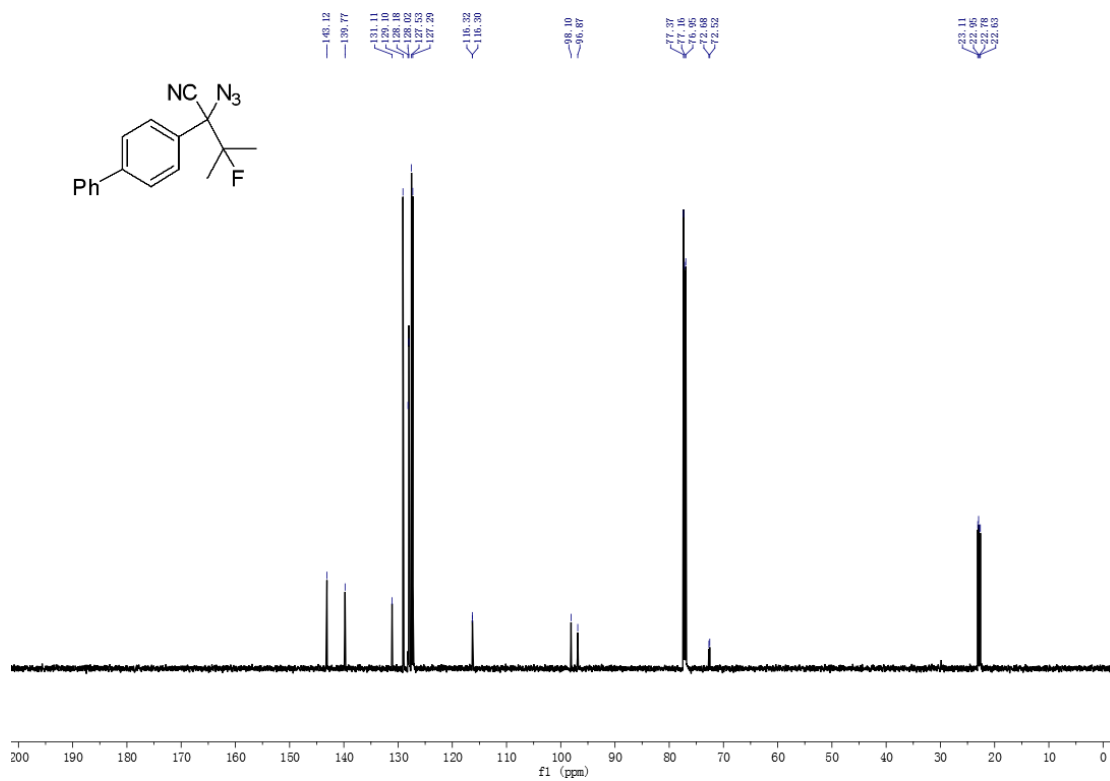
<sup>19</sup>H NMR of **2w**



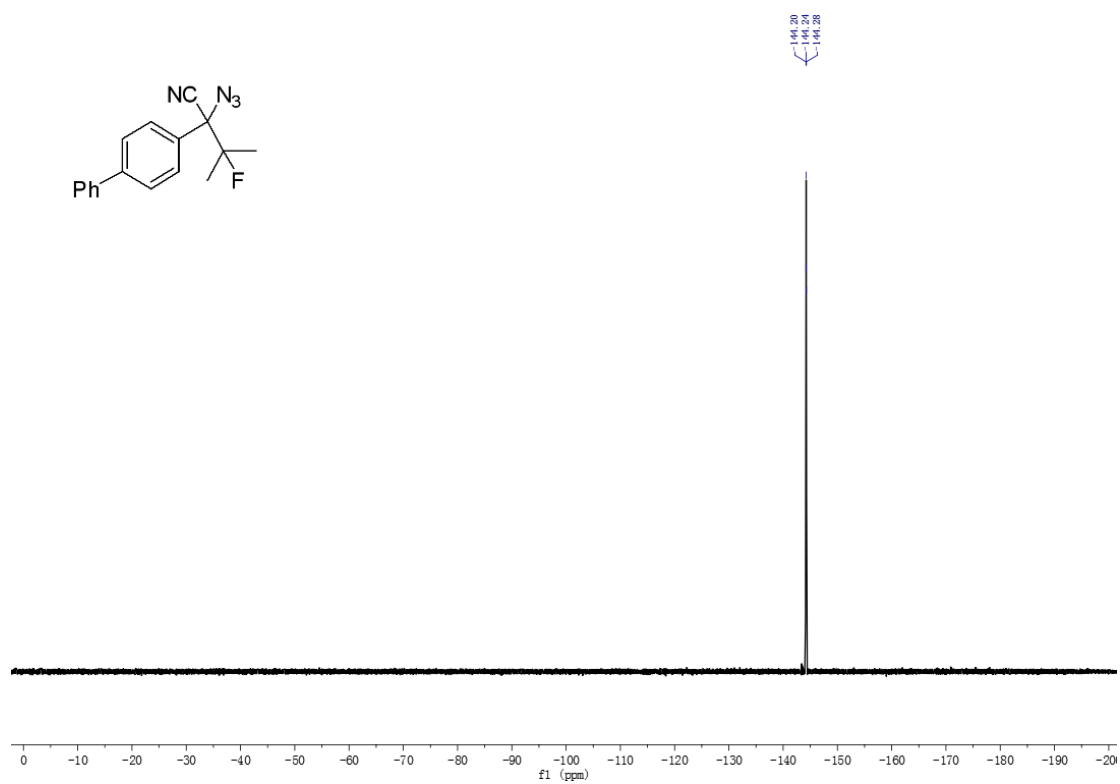
<sup>1</sup>H NMR of **2x**



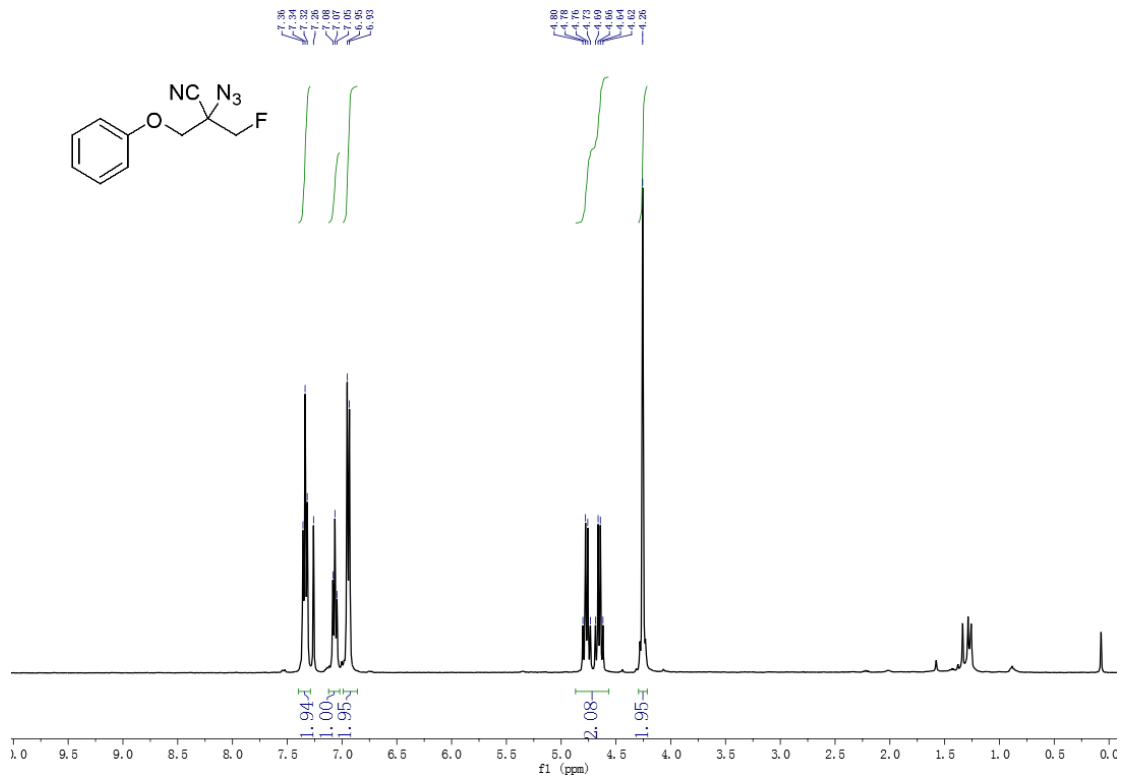
### <sup>13</sup>C NMR of **2x**



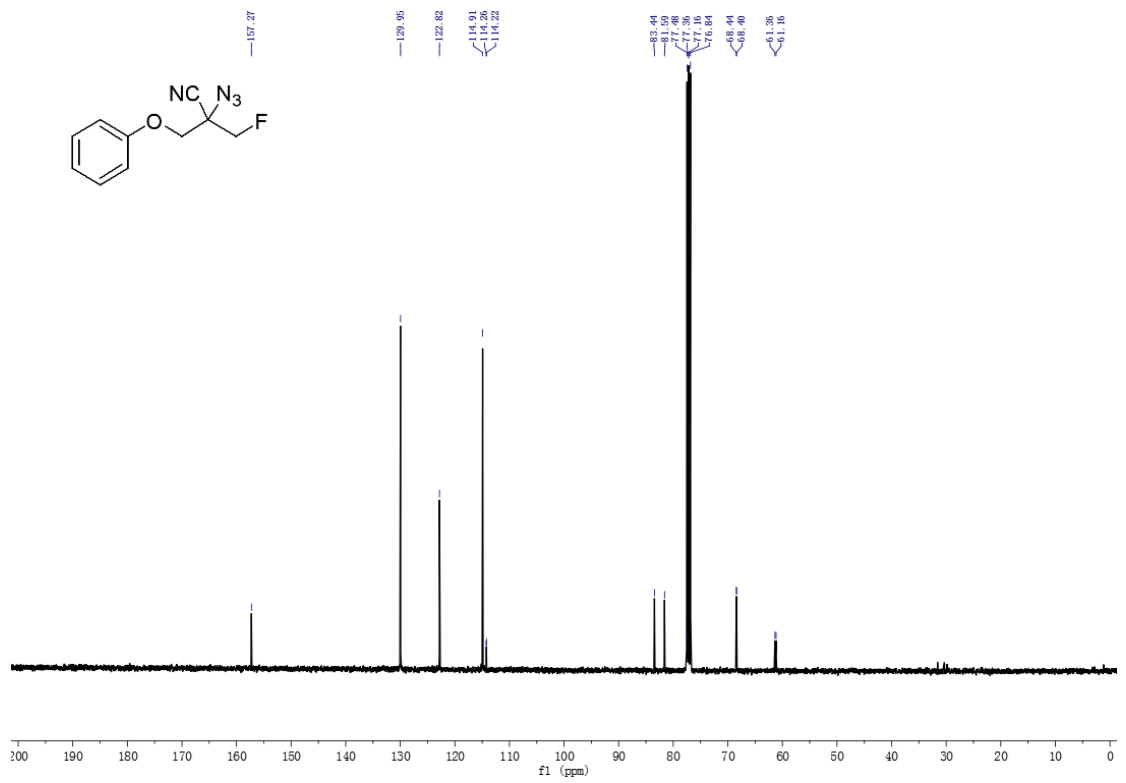
### <sup>19</sup>F NMR of **2x**



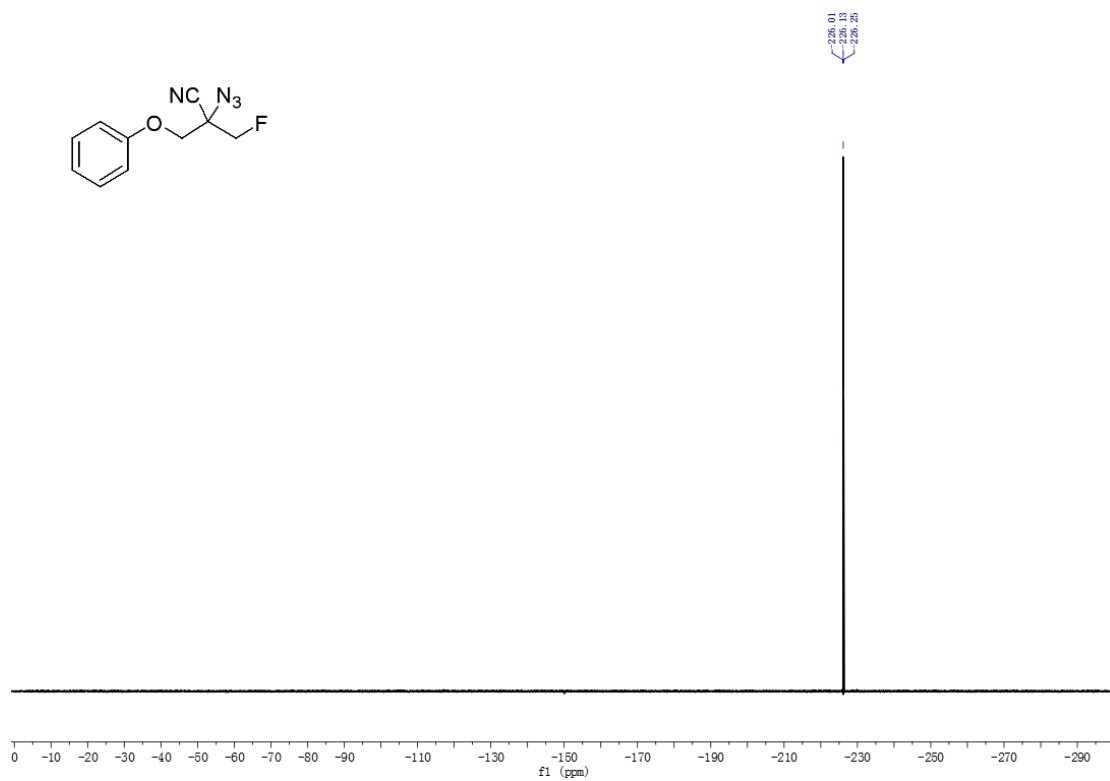
### $^1\text{H}$ NMR of **2y**



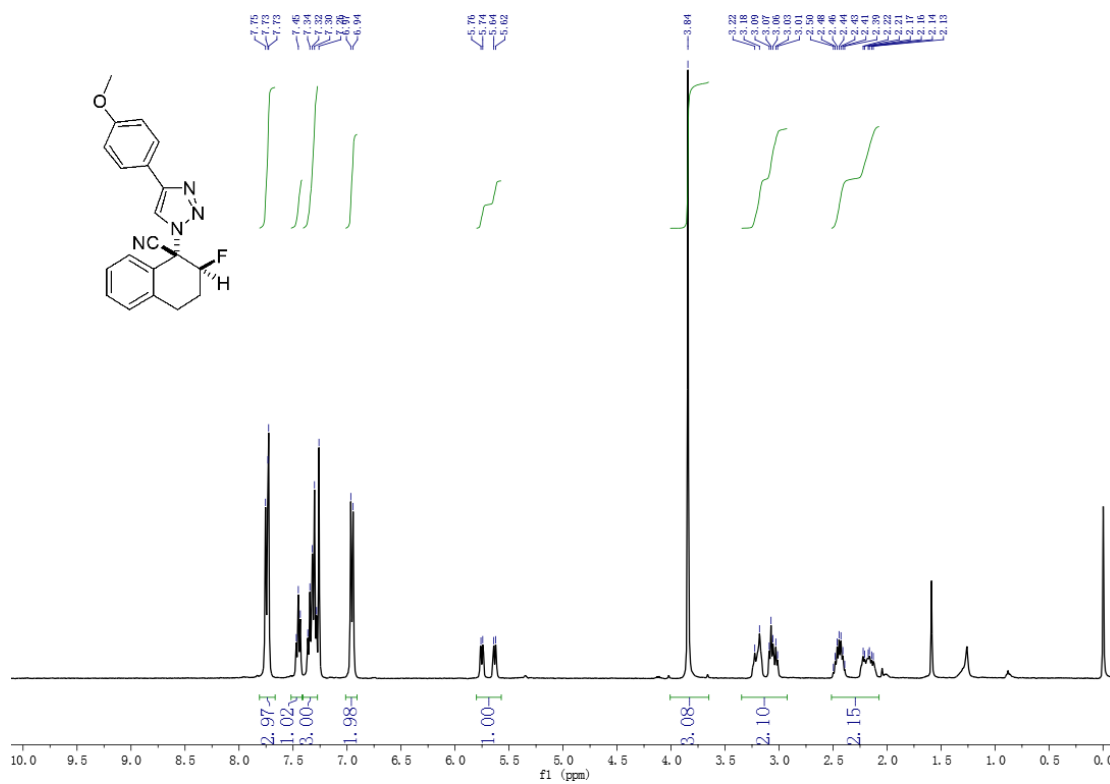
### $^{13}\text{C}$ NMR of **2y**



<sup>19</sup>F NMR of **2y**

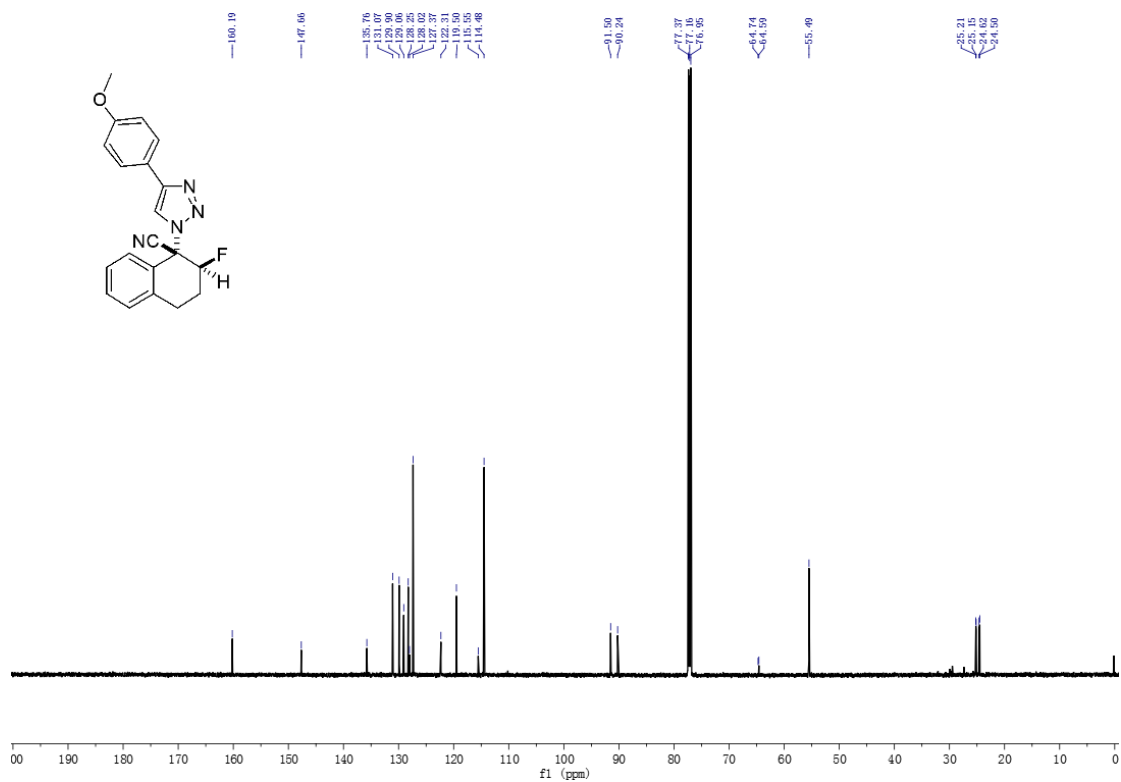


<sup>1</sup>H NMR of **3**

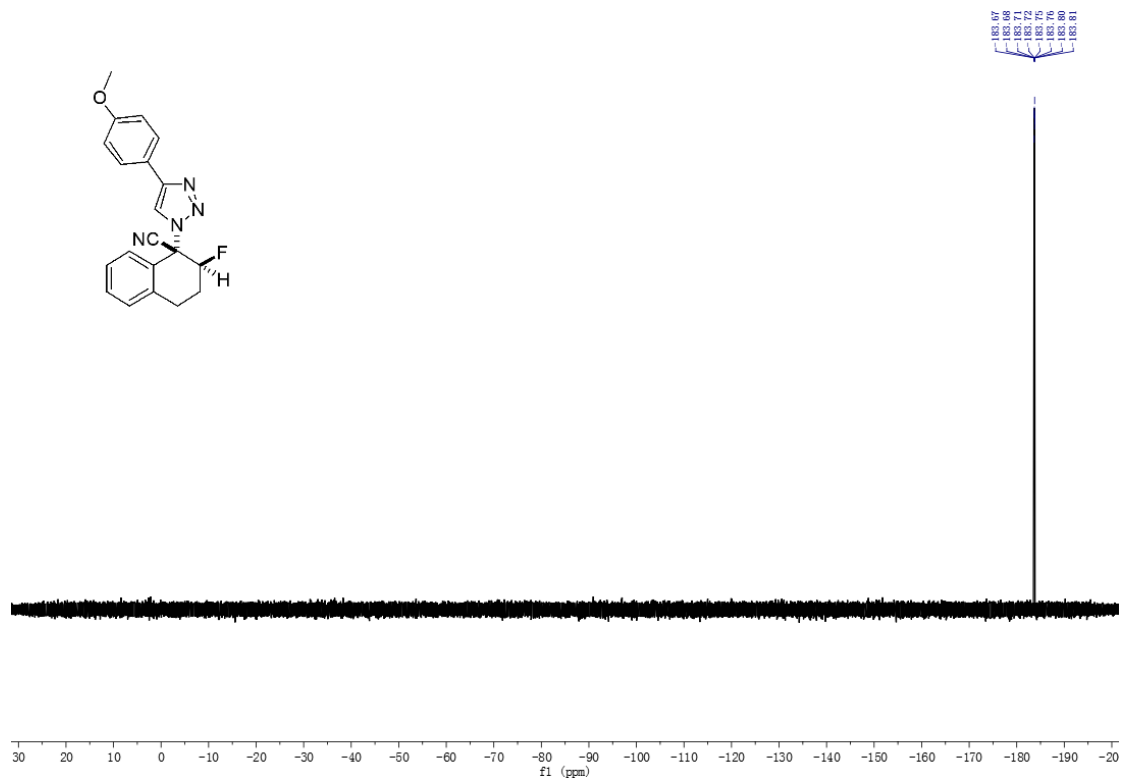




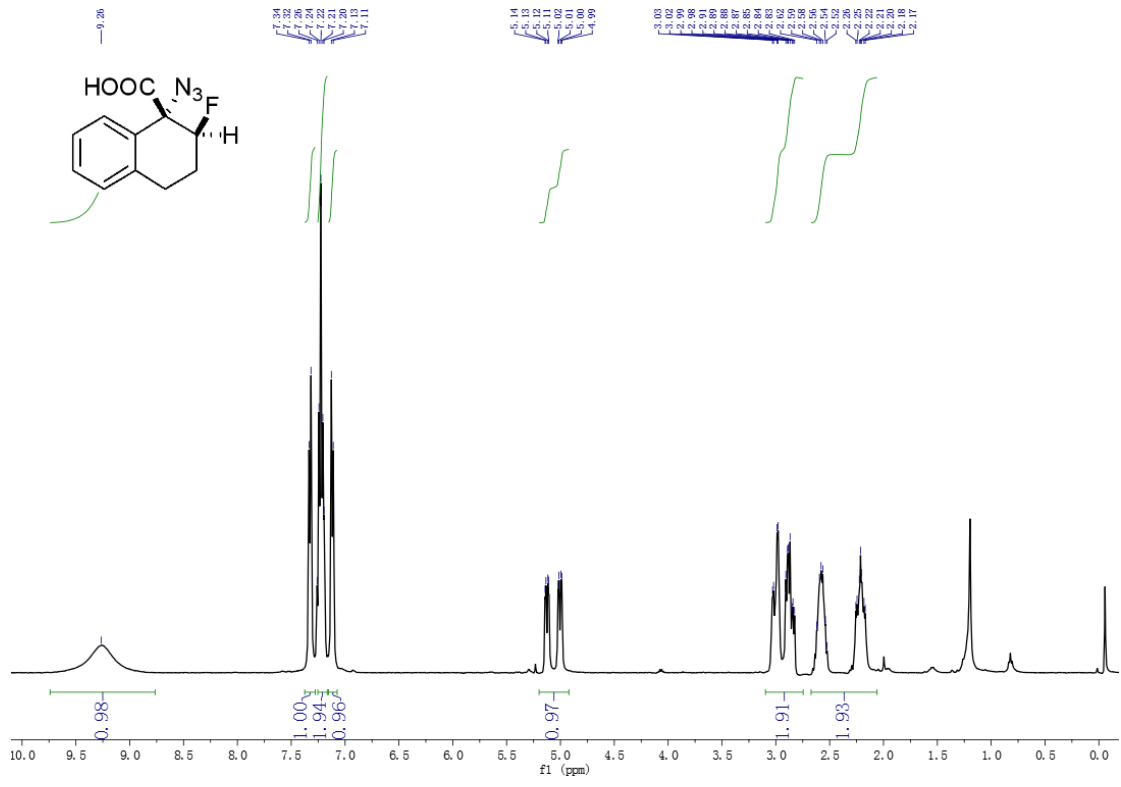
### <sup>13</sup>C NMR of 3



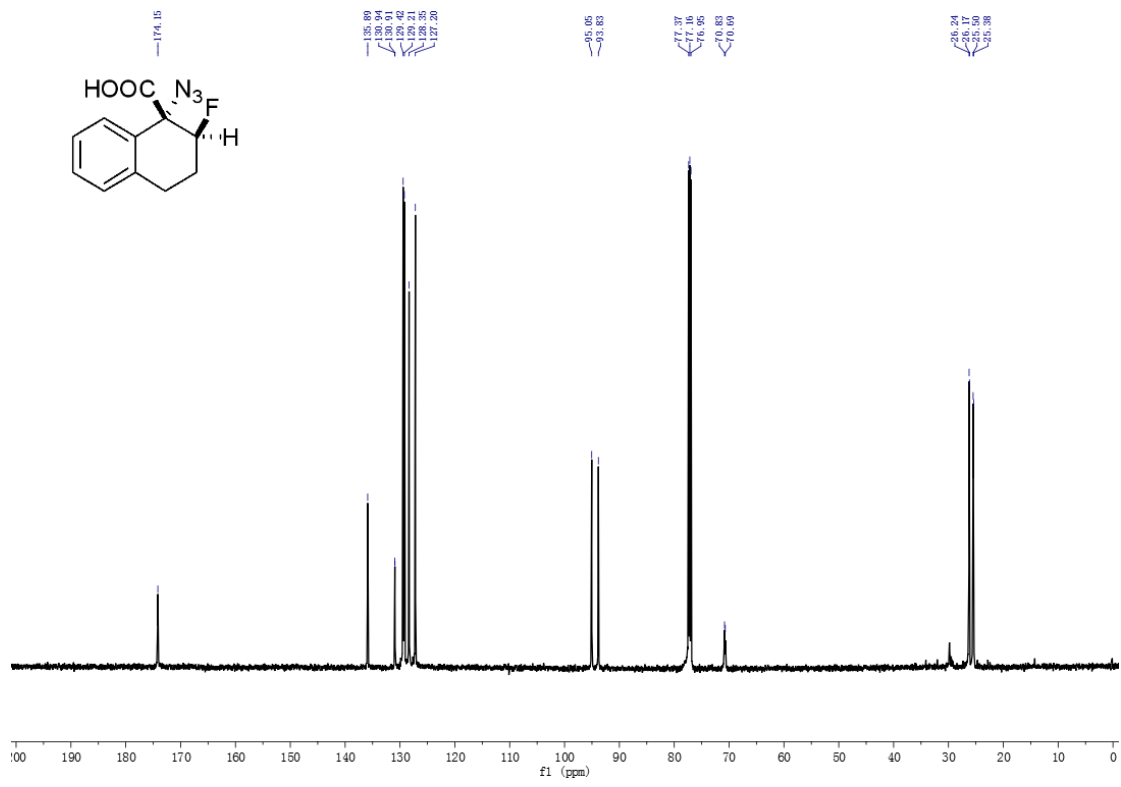
### <sup>19</sup>F NMR of 3



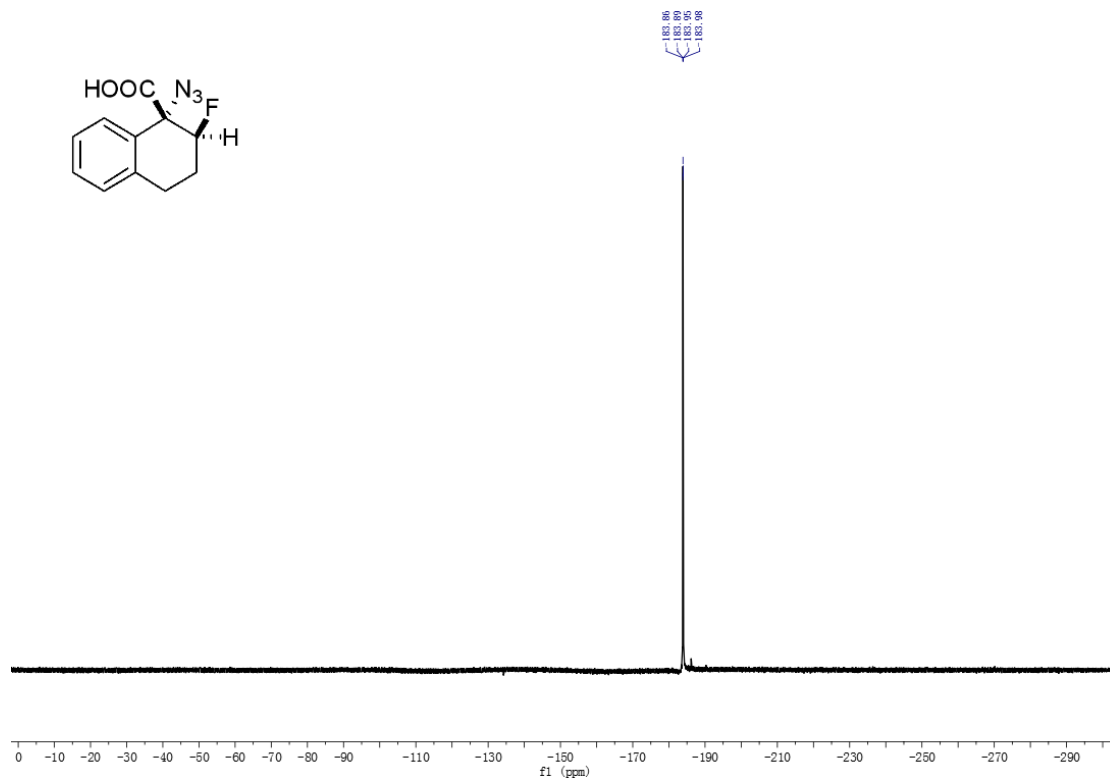
### $^1\text{H}$ NMR of **4**



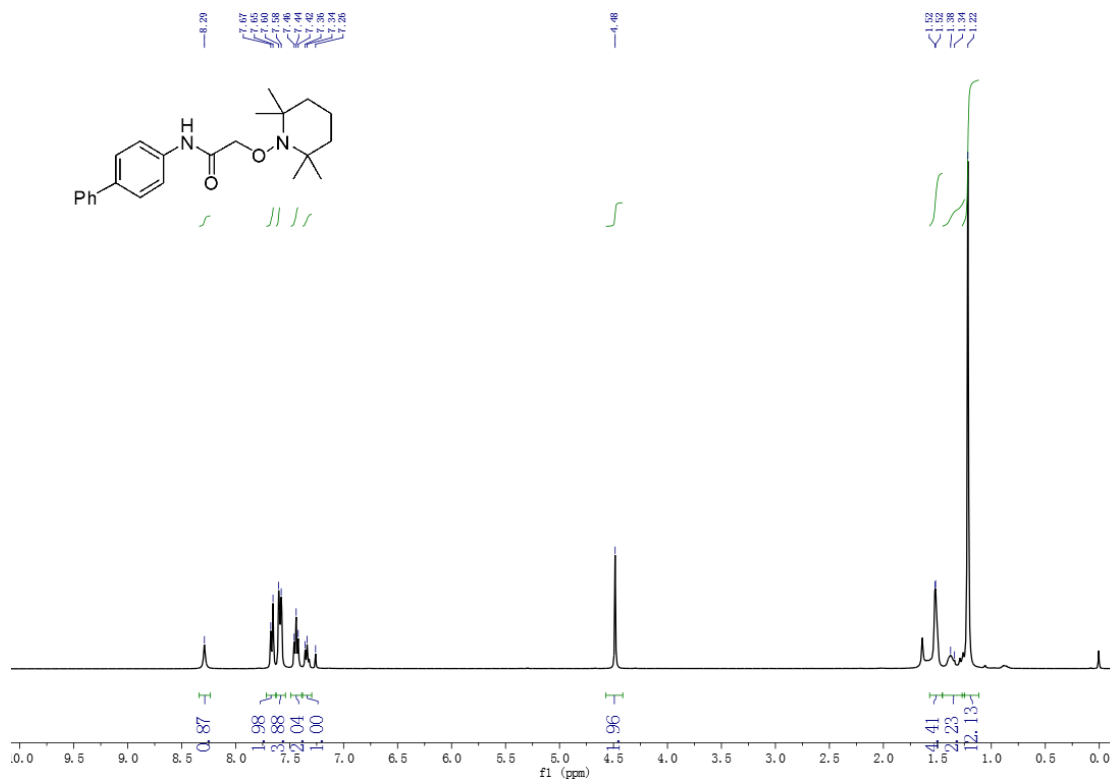
### $^{13}\text{C}$ NMR of **4**



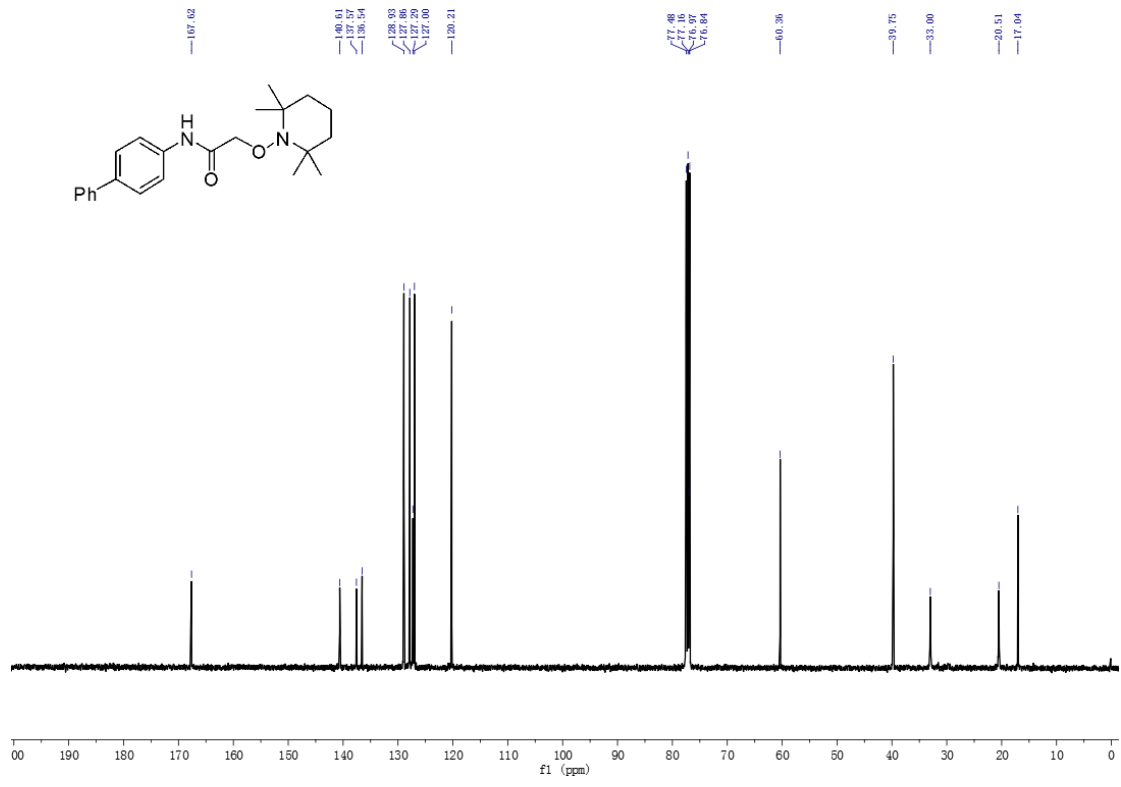
<sup>19</sup>F NMR of 4



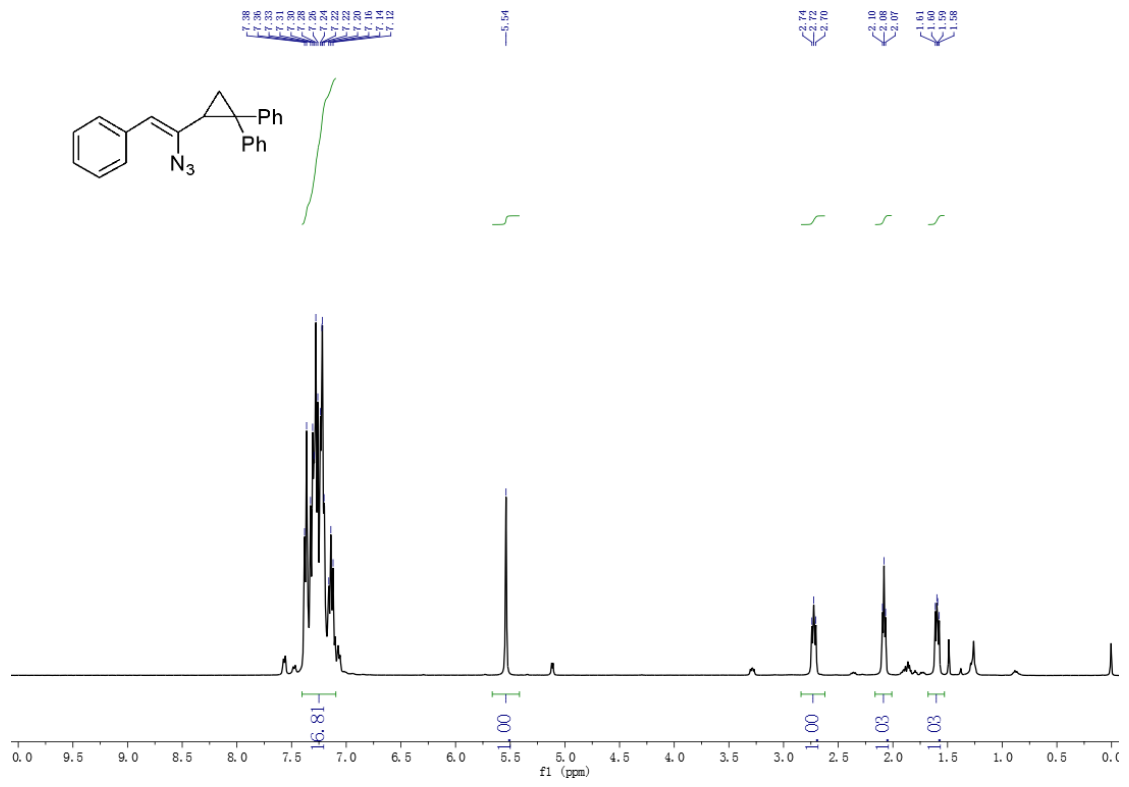
<sup>1</sup>H NMR of 5



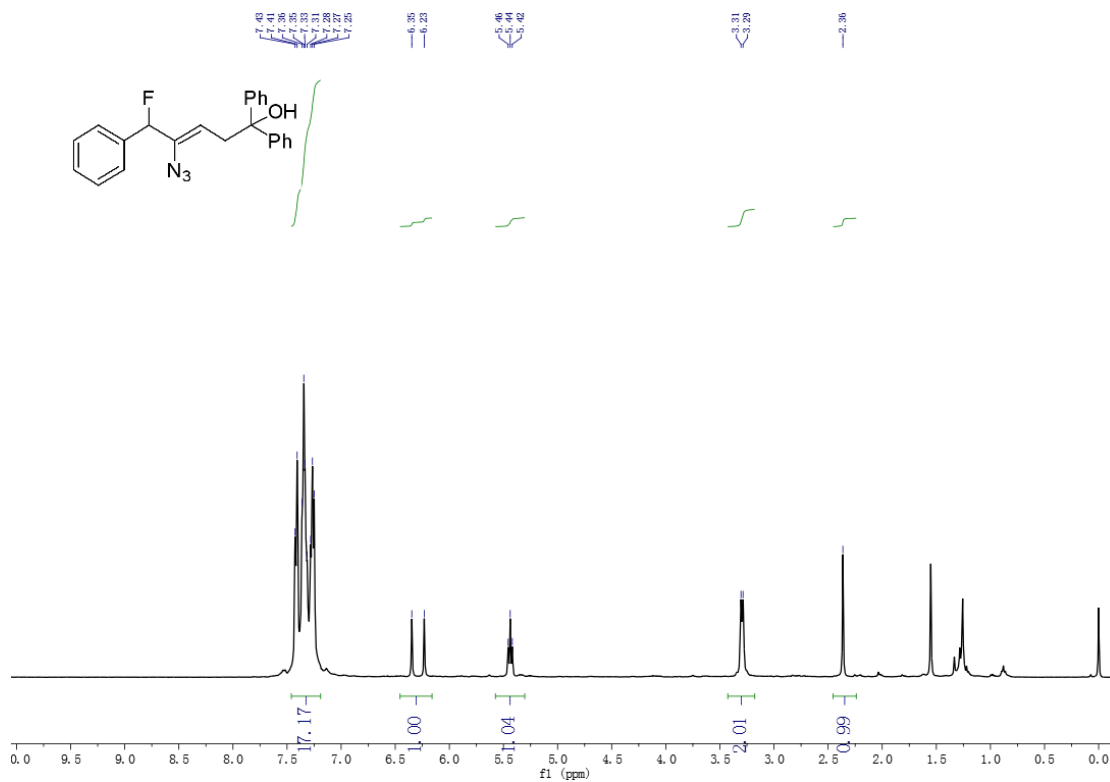
<sup>13</sup>C NMR of 5



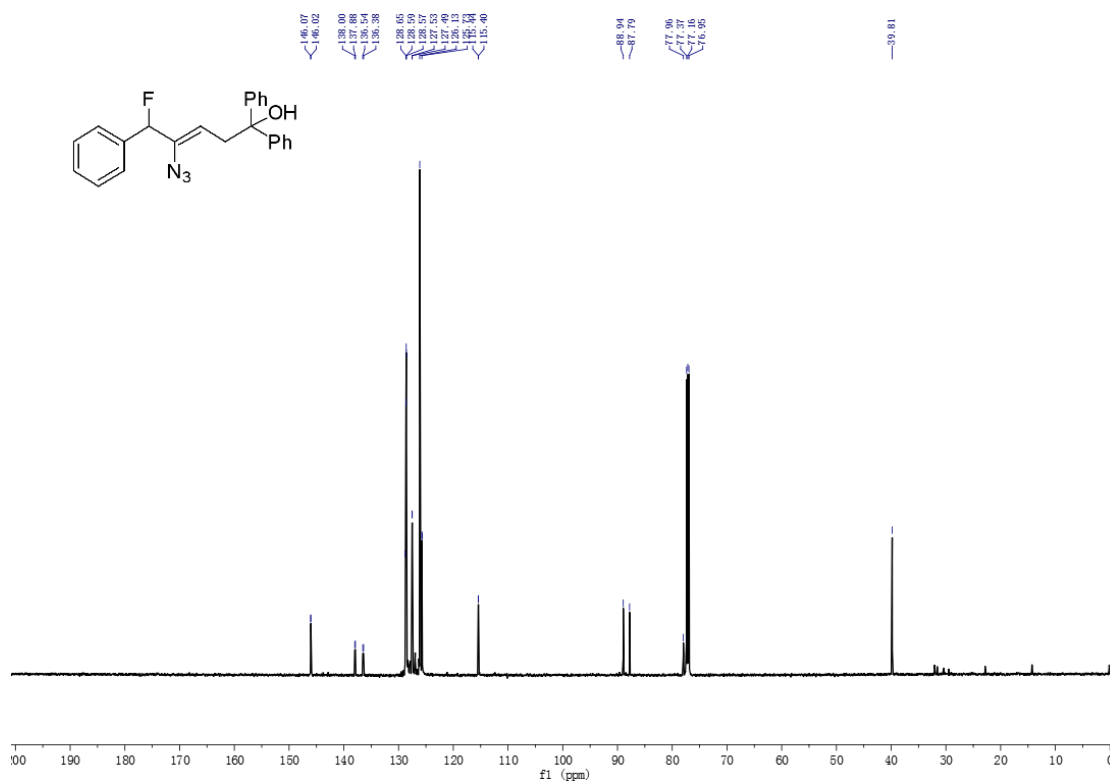
<sup>1</sup>H NMR of 6



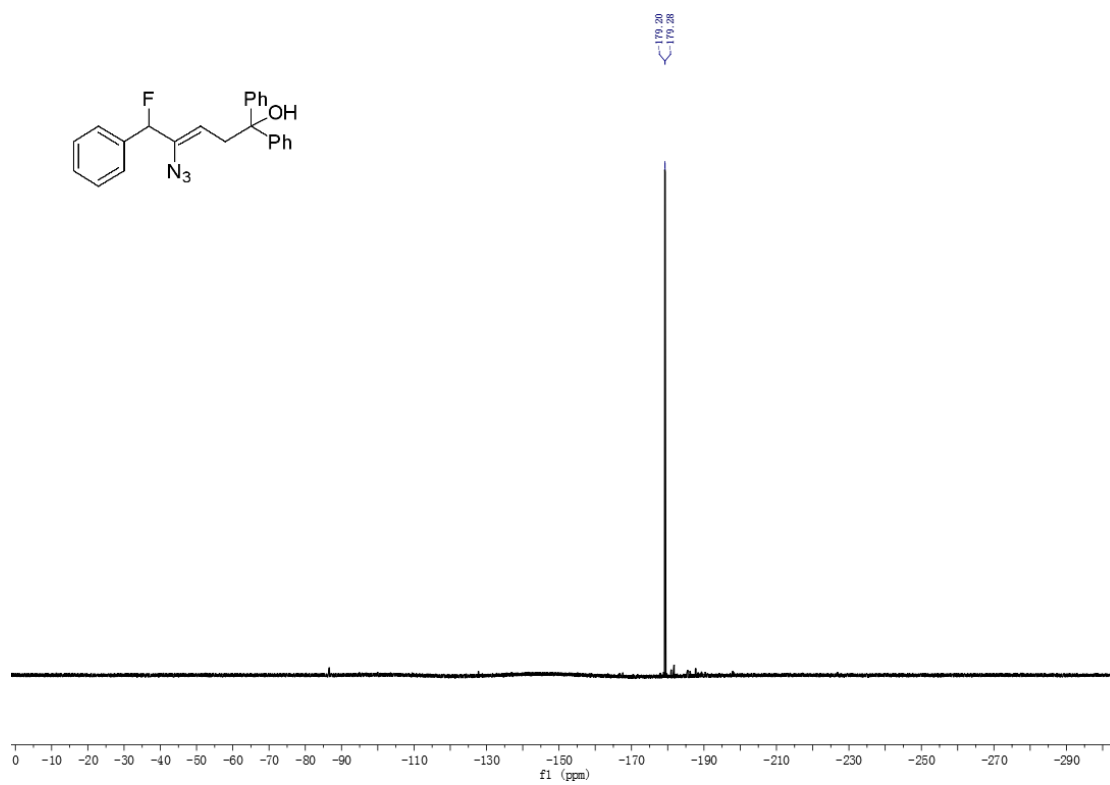
### $^1\text{H}$ NMR of 7



### $^{13}\text{C}$ NMR of 7



### $^{19}\text{F}$ NMR of 7



### $^1\text{H}$ NMR of 8

