Supporting Information

Efficient synthesis of functionalized trifluoromethyl cyclopropanes via cyclopropanation of α-trifluoromethyl styrenes with chloroacetonitrile and ethyl chloroacetate

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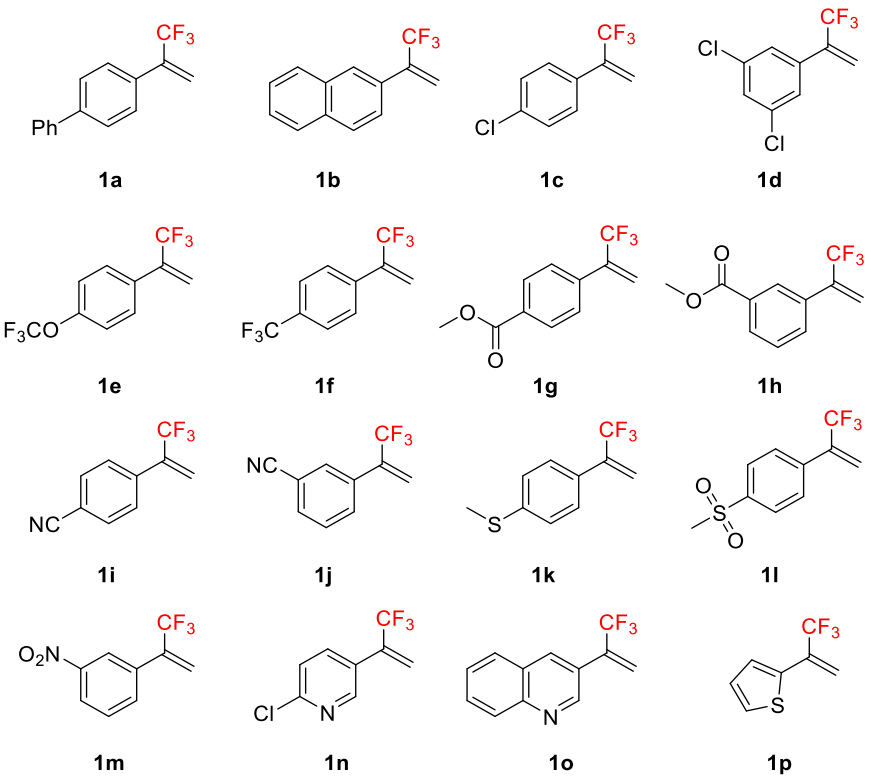
Table of contents

1. General information

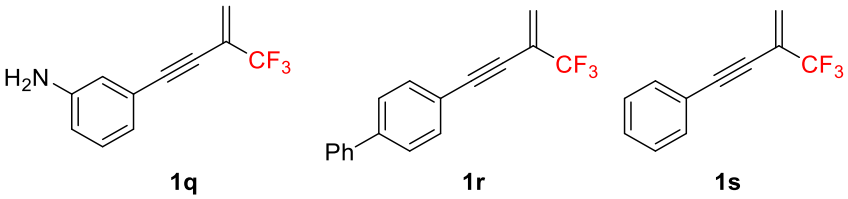
All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. Melting points were measured in an open capillary using EZ-Melt automated melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively) using TMS as an internal standard. The ^{19}F NMR spectra were obtained on a 400 spectrometer (376 MHz) or 600 spectrometer (564 MHz) with CF_3COOH as an internal standard. $CDCl_3$ was used as the NMR solvents. High resolution mass spectra (HRMS) were acquired in the EI or ESI mode using a TOF mass analyzer. The GC and GC-MS were recorded on HP 5973 MSD with 6890 GC. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. α-(Trifluoromethyl)styrenes (1a–p)



The α-(trifluoromethyl)styrenes (**1a–p**) were prepared according to the reported procedure.[1–5]

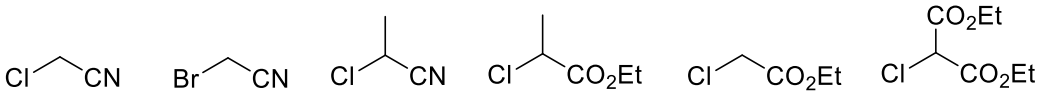
3. 2-Trifluoromethyl-1,3-conjugated enynes (1q–s) used in this reaction



The enynes **1q–s** were prepared according to the reported procedure.[6]

4. Substrates 2a–f used in this reaction

The starting materials **2a–f** were obtained from commercial suppliers.



2a **2b** **2c** **2d** **2e** **2f**

5. General procedure for the synthesis of the target compounds 3aa–sa, 3ac, 3hc, 3nc

To a glass tube charged with a stirring bar were added NaO*t*Bu (134.4 mg, 1.4 mmol, 2.0 equiv), $ClCH_2CN$ (**2a**) or 2-chloropropanenitrile (**2c**) (0.84 mmol, 1.2 equiv), α-(trifluoromethyl)styrenes or 2-trifluoromethyl-1,3-conjugated enynes **1a**–**s** (0.7 mmol, 1.0 equiv), and DMF (3 mL) under argon atmosphere. The tube was flushed with argon three times and sealed with a septum. And then the reaction mixture was stirred at 60 ℃ for 12 h or 18 h (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (30 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated in vacuo. The resultant residue was purified by column chromatography on silica gel using *n*-hexane/ ethyl acetate (20/1~2/1) as eluent to afford the pure target compounds **3aa–sa**, **3ac, 3hc, 3nc**.

6. General procedure for the synthesis of the target compounds 3ad–af′, 3qc–sc

To a glass tube charged with a stirring bar were added LiHMDS (1.4 mL, 1.4 mmol, 2.0 equiv, 1 M in THF), **2d**–**f** (0.84 mmol, 1.2 equiv), α-(trifluoromethyl)styrenes **1a, 1b, 1n** or 2-trifluoromethyl-1,3-conjugated enynes **1q**–**s** (0.7 mmol, 1.0 equiv), and DMF (3 mL) under argon atmosphere. The tube was flushed with argon three times and sealed with a rubber septum. And then the reaction mixture was stirred at 80 ℃ under argon atmosphere for 12 h or 18 h (monitored by TLC and GC/MS). After completion of the reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (30 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated in vacuo. The resultant residue was purified by column chromatography on silica gel using *n*-hexane/ ethyl acetate (20/1~2/1) as eluent to afford the pure target compounds **3ad–af′**, **3qc–sc**.

7. ^{1}H-^{19}F HOESY experiments

The cyclopropanes ***tran*-3da** and ***cis*-3da** were analyzed to find their relative stereochemistry via ^{1}H-^{19}F HOESY experiments. HOSEY spectra were recorded by a Bruker AMX-400 spectrometer with a {^{19}F, ^{1}H} probe. The spectra were recorded in $CDCl_3$ at 295.8 K. A spectral width of 90909.1 Hz in f_2 dimension (^{19}F) and 5197.5 Hz in f_1 dimension (^{1}H) were used. 8 scans were collected for each of the 8 increments, with a relaxation of 1.0 s. The analysis of ^{1}H-^{19}F HOESY spectrum of ***trans*-3da** revealed that there are strong correlations between the CF_3 group

at −70.8 ppm and two cyclopropane protons at 2.32 (Hc) and 1.97 (Ha) ppm, indicating that the CF_3 group and two protons (Hc and Ha) lie on the same face of the cyclopropyl ring. Weak NOE was observed for the cyclopropane proton at 1.75 (Hb) ppm, suggesting that Hb proton lies on the face opposite to CF_3 group.[7]

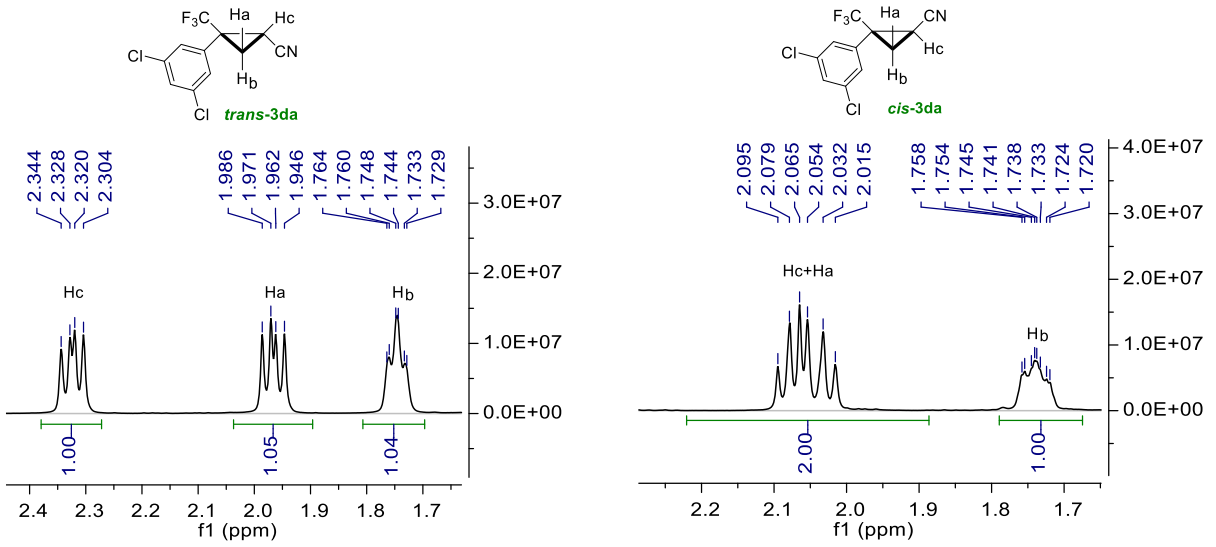


Figure S1. Part of ^{1}H NMR spectra for *trans*-3da and *cis*-3da

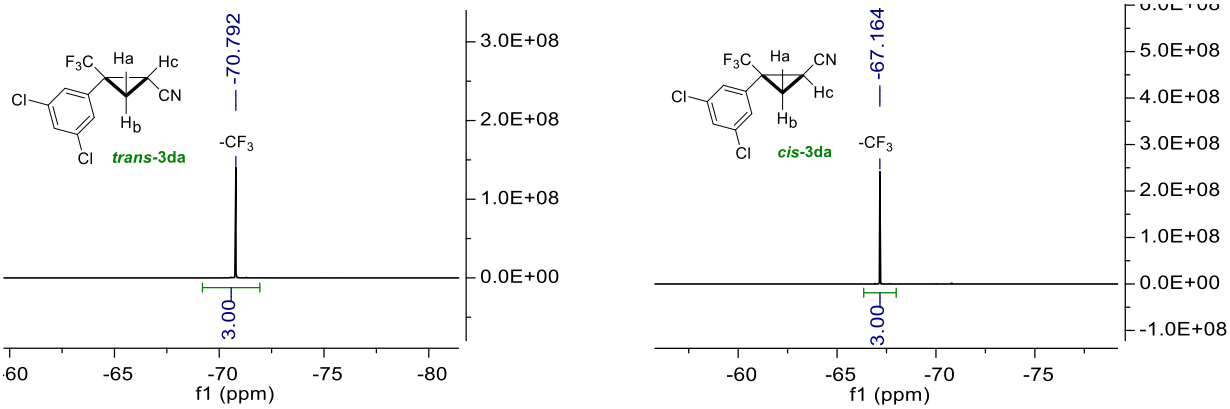


Figure S2. ^{19}F NMR spectra for *trans*-3da and *cis*-3da

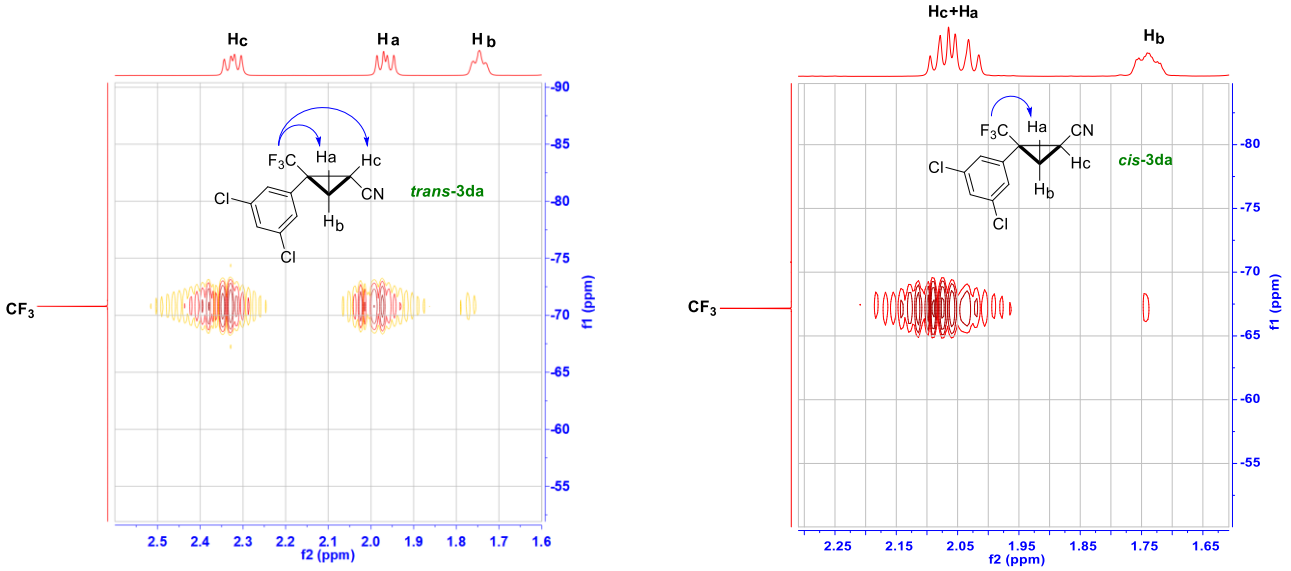
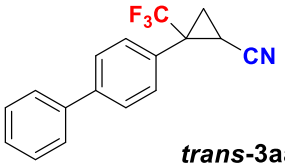


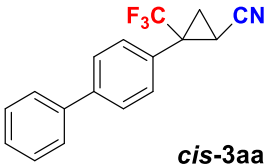
Figure S3. ^{1}H-^{19}F HOESY spectra for *trans*-3da and *cis*-3da

8. Analytical data of the target compounds



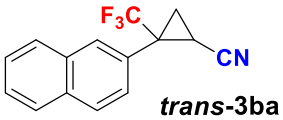
***trans*-3aa**

***trans*-2-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3aa).** Yield 68% (136.6 mg), yellow solid, m.p.: 111.3–113.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.64 (m, 2H), 7.60–7.55 (m, 4H), 7.46–7.42 (m, 2H), 7.38–7.35 (m, 1H), 2.31 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.95 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.76 (td, J = 6.0 Hz, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.1, 130.7, 127.9, 127.5, 127.4, 127.1, 126.8, 126.7, 126.2, 123.2 (q, $^{1}J_{CF}$ = 273.6 Hz), 116.0, 33.5 (q, $^{2}J_{CF}$ = 34.2 Hz), 15.2 (q, $^{3}J_{CF}$ = 1.8 Hz), 7.3 (q, $^{3}J_{CF}$ = 3.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.0 (s, 3F); HRMS (EI): calcd for $C_{17}H_{12}F_3N$ $[M]^+$: 287.0922, found: 287.0919.



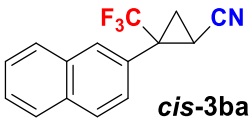
***cis*-3aa**

***cis*-2-([1,1'-Biphenyl]-4-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3aa).** Yield 15% (30.1 mg), yellow solid, m.p.: 133.3–137.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.56 (m, 4H), 7.51–7.44 (m, 4H), 7.40–7.37 (m, 1H), 2.10–2.03 (m, 2H), 1.80–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.0, 131.7, 131.0, 129.0, 128.0, 127.9, 127.7, 127.2, 124.1 (q, $^{1}J_{CF}$ = 274.0 Hz), 116.6, 35.5 (q, $^{2}J_{CF}$ = 35.9 Hz), 16.6 (q, $^{3}J_{CF}$ = 2.1 Hz), 9.0 (q, $^{3}J_{CF}$ = 1.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.3 (s, 3F).



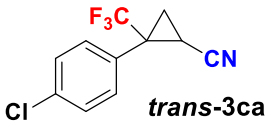
***trans*-3ba**

***trans*-2-(Naphthalen-2-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ba).** Yield 73% (133.4 mg), white solid, m.p.: 96.8–99.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91–7.84 (m, 3H), 7.58–7.50 (m, 3H), 2.32 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 1.96 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.83 (td, J = 5.9 Hz, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 133.1, 131.7, 129.0, 128.3, 127.9, 127.8, 127.4, 127.2, 126.8, 124.4 (q, $^{1}J_{CF}$ = 273.7 Hz), 117.1, 35.0 (q, $^{2}J_{CF}$ = 34.0 Hz), 16.4 (q, $^{3}J_{CF}$ = 1.8 Hz), 8.5 (q, $^{3}J_{CF}$ = 3.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.8 (s, 3F); HRMS (EI): calcd for $C_{15}H_{10}F_3N$ $[M]^+$: 261.0765, found: 261.0768.



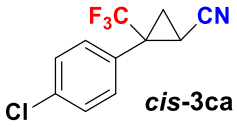
cis-3ba

***cis*-2-(Naphthalen-2-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3ba).** Yield 13% (23.8 mg), white solid, m.p.: 104.8–106.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.85 (m, 4H), 7.56–7.50 (m, 3H), 2.14–2.09 (m, 2H), 1.86–1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 132.9, 130.6, 130.1, 129.0. 128.1, 127.8, 127.4, 127.2, 127.1, 124.2 (q, $^{1}J_{CF}$ = 274.1 Hz), 116.7, 35.9 (q, $^{2}J_{CF}$ = 34.3 Hz), 16.7 (q, $^{3}J_{CF}$ = 2.2 Hz), 9.1 (d, $^{3}J_{CF}$ = 0.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.1 (s, 3F).



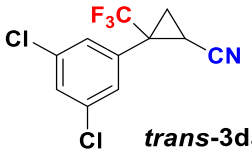
trans-3ca

***trans*-2-(4-Chlorophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ca).** Yield 68% (116.6 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 4H), 2.30 (dd, *J* = 8.8 Hz, 6.4 Hz, 1H), 1.94 (dd, *J* = 8.8 Hz, 6.4 Hz, 1H), 1.70 (t, *J* = 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 131.7, 128.3, 127.3, 127.2, 122.9 (q, $^{1}J_{CF}$ = 273.6 Hz), 115.7, 33.2 (q, $^{2}J_{CF}$ = 34.3 Hz), 15.3 (q, $^{3}J_{CF}$ = 1.9 Hz), 7.4 (q, $^{3}J_{CF}$ = 3.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.2 (s, 3F); HRMS (EI): calcd for $C_{11}H_7ClF_3N$ $[M]^+$: 245.0219, found: 245.0218.



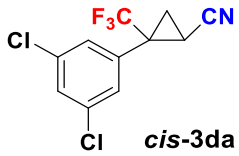
cis-3ca

***cis*-2-(4-Chlorophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3ca).** Yield 18% (30.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H), 2.08–1.98 (m, 2H), 1.72–1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 130.9, 130.2, 128.9, 128.6, 128.3, 122.8 (q, $^{1}J_{CF}$ = 274.0 Hz), 115.2, 34.1 (q, $^{2}J_{CF}$ = 34.1 Hz), 15.5 (q, $^{3}J_{CF}$ = 2.2 Hz), 8.0 (d, $^{3}J_{CF}$ = 1.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.5 (s, 3F).



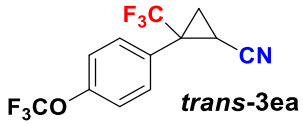
trans-3da

***trans*-2-(3,4-Dichlorophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3da).** Yield 60% (117.2 mg), yellow solid, m.p.: 83.8–84.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.40 (s, 2H), 2.32 (dd, *J* = 9.6 Hz, 6.4 Hz, 1H), 1.97 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 1.75 (td, *J* = 6.2 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.8, 130.6, 130.0, 124.1 (q, $^{1}J_{CF}$ = 273.9 Hz), 116.3, 34.2 (q, $^{2}J_{CF}$ = 34.6 Hz), 16.2 (q, $^{3}J_{CF}$ = 1.8 Hz), 8.6 (q, $^{3}J_{CF}$ = 3.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.8 (s, 3F); HRMS (EI): calcd for $C_{11}H_6Cl_2F_3N$ $[M]^+$: 278.9829, found: 278.9826.



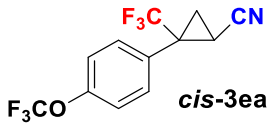
cis-3da

***cis*-2-(3,4-Dichlorophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3da).** Yield 20% (39.1 mg), yellow solid, m.p.: 125.2–126.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34 (s, 2H), 2.10–2.02 (m, 2H), 1.76–1.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 129.2, 128.9, 128.4, 128.1, 127.4, 122.5 (q, $^{1}J_{CF}$ = 274.4 Hz), 114.7, 34.0 (q, $^{2}J_{CF}$ = 34.5 Hz), 15.4 (q, $^{3}J_{CF}$ = 2.0 Hz), 8.1 (q, $^{3}J_{CF}$ = 1.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.2 (s, 3F).



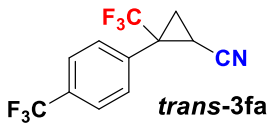
trans-3ea

***trans*-2-(4-(Trifluoromethoxy)phenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ea).** Yield 78% (161.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 2.36 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 2.02 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.77 (t, J = 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 134.9, 132.3, 131.3, 126.6 (q, $^{1}J_{CF}$ = 274.1 Hz), 121.6, 121.4, 120.4 (q, $^{1}J_{CF}$ = 273.5 Hz), 116.2, 35.1 (q, $^{2}J_{CF}$ = 34.5 Hz), 16.6 (q, $^{3}J_{CF}$ = 2.2 Hz), 9.1 (d, $^{3}J_{CF}$ = 1.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –57.8 (s, 3F), -71.2 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_6NO$ $[M]^+$: 295.0432, found: 295.0429.



cis-3ea

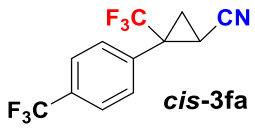
***cis*-2-(4-(Trifluoromethoxy)phenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3ea).** Yield 13% (26.8 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 9.2 Hz, 2H), 2.10–2.00 (m, 2H), 1.75–1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 131.3, 130.3, 122.8 (q, $^{1}J_{CF}$ = 273.8 Hz), 120.6, 120.3, 119.7 (q, $^{1}J_{CF}$ = 274.2 Hz), 118.0, 115.2, 34.0 (q, $^{2}J_{CF}$ = 33.0 Hz), 15.5 (q, $^{3}J_{CF}$ = 2.4 Hz), 8.0 (q, $^{3}J_{CF}$ = 1.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –57.9 (s, 3F), –67.5 (s, 3F).



trans-3fa

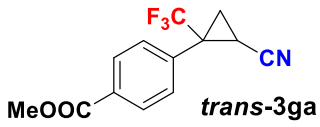
***trans*-2-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (*trans*-3fa).** Yield 73% (142.6 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 2.34 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 1.98 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.75 (td, J = 6.2 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 131.4 (q, $^{2}J_{CF}$ = 32.6 Hz), 130.4, 125.2 (q, $^{3}J_{CF}$ = 3.5 Hz), 123.1 (q, $^{1}J_{CF}$ = 273.6 Hz), 122.9 (q, $^{1}J_{CF}$

= 270.7 Hz), 115.8, 33.7 (q, $^{2}J_{CF}$ = 34.4 Hz), 15.4 (q, $^{3}J_{CF}$ = 1.5 Hz), 7.5 (q, $^{3}J_{CF}$ = 3.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1 (s, 3F), –71.1 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_6N$ $[M]^+$: 279.0483, found: 279.0480.



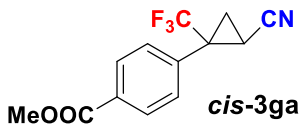
cis-3fa

***cis*-2-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (*cis*-3fa).** Yield 16% (31.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 2.11–2.05 (m, 2H), 1.78–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 131.0 (q, $^{2}J_{CF}$ = 32.7 Hz), 130.2, 125.0 (q, $^{3}J_{CF}$ = 3.8 Hz), 122.7 (q, $^{1}J_{CF}$ = 274.1 Hz), 122.5 (q, $^{1}J_{CF}$ = 270.7 Hz), 115.1, 34.4 (q, $^{2}J_{CF}$ = 34.2 Hz), 15.4 (q, $^{3}J_{CF}$ = 2.1 Hz), 7.9 (q, $^{3}J_{CF}$ = 1.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0 (s, 3F), –67.3 (s, 3F).



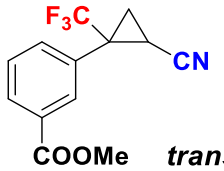
trans-3ga

***trans*-Methyl 4-(2-cyano-1-(trifluoromethyl)cyclopropyl)benzoate (*trans*-3ga).** Yield 67% (126.1 mg), yellow solid, m.p.: 109.5–112.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 2.34 (dd, *J* = 9.6 Hz, 6.4 Hz, 1H), 1.99 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 1.77 (td, *J* = 6.1 Hz, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 133.3, 130.7, 130.5, 129.2, 127.2, 122.9 (q, $^{1}J_{CF}$ = 273.6 Hz), 115.6, 51.3, 33.6 (q, $^{2}J_{CF}$ = 34.3 Hz), 15.2 (q, $^{3}J_{CF}$ = 1.8 Hz), 7.4 (q, $^{3}J_{CF}$ = 3.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.9 (s, 3F); HRMS (EI): calcd for $C_{13}H_{10}F_3NO_2$ $[M]^+$: 269.0664, found: 269.0667.



cis-3ga

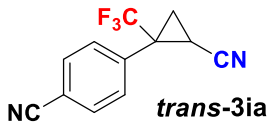
***cis*-Methyl 4-(2-cyano-1-(trifluoromethyl)cyclopropyl)benzoate (*cis*-3ga).** Yield 15% (28.2 mg), yellow solid, m.p.: 129.7–132.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 2.11–2.02 (m, 2H), 1.78–1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 136.3, 130.5, 129.7, 129.1, 122.7 (q, $^{1}J_{CF}$ = 274.0 Hz), 115.1, 51.4, 34.5 (q, $^{2}J_{CF}$ = 33.9 Hz), 15.4 (q, $^{3}J_{CF}$ = 2.1 Hz), 8.0 (q, $^{3}J_{CF}$ = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.2 (s, 3F).



trans-3ha

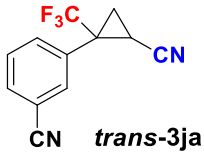
***trans*-Methyl 3-(2-cyano-1-(trifluoromethyl)cyclopropyl)benzoate (*trans*-3ha).** Yield 64% (120.5 mg), yellow

solid, m.p.: 72.6–73.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 3.95 (s, 3H), 2.35 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 2.00 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.80 (td, J = 6.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 135.9, 132.6, 131.3, 130.3, 129.3, 128.7, 124.1 (q, $^1J_{CF}$ = 273.6 Hz), 116.8, 52.5, 34.6 (q, $^2J_{CF}$ = 34.4 Hz), 16.4 (q, $^3J_{CF}$ = 1.4 Hz), 8.5 (q, $^3J_{CF}$ = 3.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.0 (s, 3F); HRMS (ESI): calcd for $C_{13}H_{10}F_3NO_2Na$ $[M+Na]^+$: 292.0562, found: 292.0563.



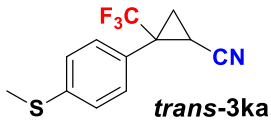
***trans*-3ia**

***trans*-4-(2-Cyano-1-(trifluoromethyl)cyclopropyl)benzonitrile (*trans*-3ia).** Yield 72% (118.9 mg), white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 2.38 (dd, J = 9.6Hz, 6.0 Hz, 1H), 2.02 (dd, J = 9.2 Hz, 6.0 Hz, 1H), 1.77 (t, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 131.8, 131.4, 122.7 (q, $^1J_{CF}$ = 273.8 Hz), 116.9, 115.4, 113.2, 33.6 (q, $^2J_{CF}$ = 34.5 Hz), 15.2 (q, $^3J_{CF}$ = 1.9 Hz), 7.5 (q, $^3J_{CF}$ = 3.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.7 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_3N_2$ $[M]^+$: 236.0561, found: 236.0559.



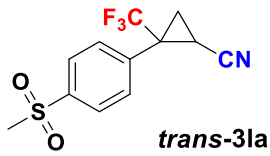
***trans*-3ja**

***trans*-3-(2-Cyano-1-(trifluoromethyl)cyclopropyl)benzonitrile (*trans*-3ja).** Yield 75% (123.9 mg), white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.76 (m, 3H), 7.61 (t, J = 7.8 Hz, 1H), 2.38 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 2.03 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 1.77 (td, J = 6.1 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.1, 133.7, 131.5, 130.1, 123.7 (q, $^1J_{CF}$ = 273.8 Hz), 117.8, 116.4, 133.7, 34.3 (q, $^2J_{CF}$ = 34.6 Hz), 16.2 (d, $^3J_{CF}$ = 1.7 Hz), 8.5 (d, $^3J_{CF}$ = 3.1 Hz) ; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.9 (s, 3F); HRMS (EI): calcd for $C_{12}H_7F_3N_2$ $[M]^+$: 236.0561, found: 236.0558.



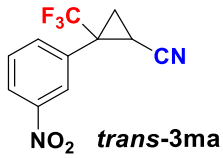
***trans*-3ka**

***trans*-2-(4-(Methylthio)phenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ka).** Yield 75% (134.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 6.8 Hz, 2H), 2.47 (s, 3H), 2.27– 2.20 (m, 1H), 1.90–1.83 (m, 1H), 1.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 130.6, 127.2, 126.6, 125.1, 124.9, 123.1 (q, $^1J_{CF}$ = 273.6 Hz), 116.0, 33.2 (q, $^2J_{CF}$ = 34.2 Hz), 15.2 (q, $^3J_{CF}$ = 1.8 Hz), 14.1, 7.3 (q, $^3J_{CF}$ = 3.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.2 (s, 3F); HRMS (EI): calcd for $C_{12}H_{10}F_3NS$ $[M]^+$: 257.0486, found: 257.0483.



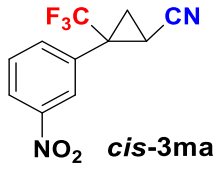
***trans*-3la**

***trans*-2-(4-(Methylsulfonyl)phenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3la).** Yield 76% (153.7 mg), yellow solid, m.p.: 132.8–133.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 3.09 (s, 3H), 2.40 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 2.05 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.79 (td, J = 6.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 135.6, 132.7, 128.2, 126.6, 125.1, 123.7 (q, $^{1}J_{CF}$ = 274.0 Hz), 116.5, 44.4, 34.6 (q, $^{2}J_{CF}$ = 34.3 Hz), 16.4 (q, $^{3}J_{CF}$ = 1.8 Hz), 8.5 (q, $^{3}J_{CF}$ = 3.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.7 (s, 3F); HRMS (EI): calcd for $C_{12}H_{10}F_3NO_2S$ $[M]^+$: 289.0384, found: 289.0381.



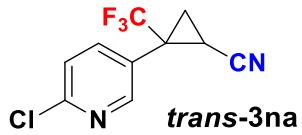
***trans*-3ma**

***trans*-2-(3-Nitrophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ma).** Yield 67% (120.1 mg), white solid, m.p.: 68.3–70.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40–8.33 (m, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 2.43 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 2.07 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 1.85 (td, J = 6.2 Hz, 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 136.5, 130.8, 129.3, 125.5, 124.1, 122.7 (q, $^{1}J_{CF}$ = 273.9 Hz), 115.4, 33.3 (q, $^{2}J_{CF}$ = 34.8 Hz), 15.3, 7.6 (q, $^{3}J_{CF}$ = 3.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.8 (s, 3F); HRMS (EI): calcd for $C_{11}H_7F_3N_2O_2$ $[M]^+$: 256.0460, found: 256.0458.



***cis*-3ma**

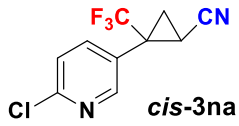
***cis*-2-(3-Nitrophenyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3ma).** Yield 24% (43.0 mg), white solid, m.p.: 108.3–110.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.21 (m, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 2.12–2.03 (m, 2H), 1.78–1.74 (m, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 135.7, 133.6, 129.3, 124.7, 123.8, 122.6 (q, $^{1}J_{CF}$ = 274.4 Hz), 114.7, 34.1 (q, $^{2}J_{CF}$ = 34.2 Hz), 15.5, 8.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.2 (s, 3F).



***trans*-3na**

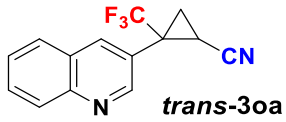
***trans*-2-(6-Chloropyridin-3-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3na).** Yield 68% (117.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 2.4 Hz, 1H), 7.83 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.46 (d,

J = 8.4 Hz, 1H), 2.39 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 2.03 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.78 (td, J = 6.2 Hz, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 152.3, 141.7, 125.1, 124.8, 123.6 (q, $^1J_{CF}$ = 273.7 Hz), 116.3, 32.1 (q, $^2J_{CF}$ = 35.0 Hz), 16.0 (q, $^3J_{CF}$ = 1.8 Hz), 8.2 (q, $^3J_{CF}$ = 3.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.0 (s, 3F); HRMS (EI): calcd for $C_{10}H_6ClF_3N_2$ $[M]^+$: 246.0172, found: 246.0170.



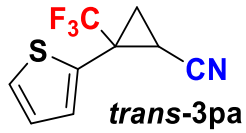
***cis*-3na**

***cis*-2-(6-Chloropyridin-3-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3na).** Yield 17% (29.3 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 2.0 Hz, 1H), 7.76 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 2.16–2.04 (m, 2H), 1.79–1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 151.6, 141.0, 127.9, 124.8, 123.6 (q, $^1J_{CF}$ = 274.2 Hz), 115.8, 33.0 (q, $^2J_{CF}$ = 34.8 Hz), 16.2 (q, $^3J_{CF}$ = 1.8 Hz), 9.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.4 (s, 3F).



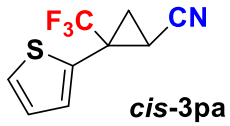
***trans*-3oa**

***trans*-2-(Quinolin-3-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3oa).** Yield 65% (119.2 mg), yellow solid, m.p.: 84.4–85.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.36 (s, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 2.44 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 2.09 (dd, J = 9.2 Hz, 6.0 Hz, 1H), 1.88 (td, J = 6.2 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.4, 138.7, 130.0, 128.4, 127.1, 126.6, 126.2, 122.9 (q, $^1J_{CF}$ = 273.8 Hz), 121.9, 115.5, 31.7 (q, $^2J_{CF}$ = 34.8 Hz), 15.0 (q, $^3J_{CF}$ = 1.6 Hz), 7.2 (q, $^3J_{CF}$ = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.8 (s, 3F); HRMS (ESI): calcd for $C_{14}H_{10}F_3N_2$ $[M+H]^+$: 263.0796, found: 263.0794.



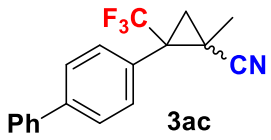
***trans*-3pa**

***trans*-2-(Thiophen-2-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3pa).** Yield 58% (88.5 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 4.4 Hz, 1H), 7.28 (s, 1H), 7.06 (t, J = 4.0 Hz, 1H), 2.33 (dd, J = 8.8 Hz, 6.4 Hz, 1H), 1.97 (dd, J = 8.8 Hz, 6.8 Hz, 1H), 1.88 (t, J = 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.5, 130.3, 127.2, 126.4, 122.6 (q, $^1J_{CF}$ = 273.6 Hz), 115.5, 28.9 (q, $^2J_{CF}$ = 35.8 Hz), 16.6 (q, $^3J_{CF}$ = 1.9 Hz), 9.4 (q, $^3J_{CF}$ = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.2 (s, 3F); HRMS (ESI): calcd for $C_9H_7F_3NS$ $[M+H]^+$: 218.0251, found: 218.0247.



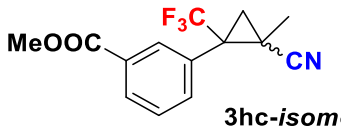
cis-3pa

***cis*-2-(Thiophen-2-yl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3pa).** Yield 19% (29.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 4.8 Hz, 1H), 7.18 (d, J = 3.2 Hz, 1H), 7.00 (t, J = 4.4 Hz, 1H), 2.14–2.08 (m, 2H), 1.88–1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 130.2, 127.6, 127.2, 123.5 (q, $^{1}J_{CF}$ = 274.1 Hz), 115.9, 30.7 (q, $^{2}J_{CF}$ = 35.6 Hz), 18.1 (q, $^{3}J_{CF}$ = 2.2 Hz), 11.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.5 (s, 3F).



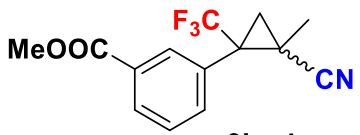
3ac

2-([1,1'-Biphenyl]-4-yl)-1-methyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile (3ac, *trans*/*cis*=1/1). Yield 79% (166.5 mg), yellow solid, m.p.: 97.3–100.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.58 (m, 4.21H), 7.48–7.44 (m, 3.14H), 7.40–7.36 (m, 2.10H), 2.20 (d, J = 6.0 Hz, 1H), 2.04 (s, 0.05H), 1.84 (d, J = 1.6 Hz, 0.07H), 1.54–1.51 (m, 1H), 1.24 (s, 0.16H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.9, 130.3, 130.0, 128.0, 127.9, 127.8, 127.1, 126.7, 126.6, 126.2, 126.1, 123.3 (q, $^{1}J_{CF}$ = 274.3 Hz), 118.8, 38.0 (q, $^{2}J_{CF}$ = 32.9 Hz), 21.5 (q, $^{3}J_{CF}$ = 2.6 Hz), 19.0, 12.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.0 (s, 0.15F), –65.9 (s, 3F); HRMS (ESI): calcd for $C_{18}H_{14}F_3NNa$ $[M+Na]^+$: 324.0976, found: 324.0977.



3hc-*isomer 1*

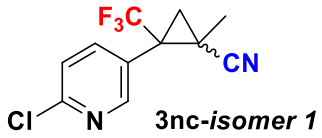
Methyl 3-(2-cyano-2-methyl-1-(trifluoromethyl)cyclopropyl)benzoate (3hc-*isomer 1*). Yield 40% (79.2mg), yellow solid, m.p.: 117.4–121.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.69 (s, 1H), 7.53 (t, J = 7.8 Hz, 1H), 3.94 (s, 3H), 2.02 (dd, J = 6.4 Hz, 1.6 Hz, 1H), 1.86 (d, J = 6.4 Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 134.1, 131.8, 130.8, 130.0, 129.8, 128.1, 123.5 (q, $^{1}J_{CF}$ = 274.3 Hz), 119.0, 51.3, 37.1 (q, $^{2}J_{CF}$ = 33.4 Hz), 22.0 (q, $^{3}J_{CF}$ = 2.0 Hz), 16.6, 15.5 (q, $^{3}J_{CF}$ = 2.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.0 (s, 3F); HRMS (ESI): calcd for $C_{14}H_{12}F_3NO_2Na$ $[M+Na]^+$: 306.0718, found: 306.0721.



3hc-*isomer 2*

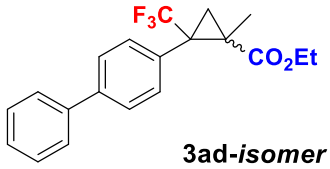
Methyl 3-(2-cyano-2-methyl-1-(trifluoromethyl)cyclopropyl)benzoate (3hc-*isomer 2*). Yield 40% (79.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 3.95 (s, 3H), 2.23 (d, J = 6.0 Hz, 1H), 1.56 (s, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 134.3, 130.9, 130.1, 129.7, 129.5,

128.2, 123.1 (q, $^{1}J_{CF}$ = 274.3 Hz), 118.5, 51.4, 37.9 (q, $^{2}J_{CF}$ = 33.1 Hz), 21.5 (q, $^{3}J_{CF}$ = 2.2 Hz), 19.0, 12.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –65.9 (s, 3F).



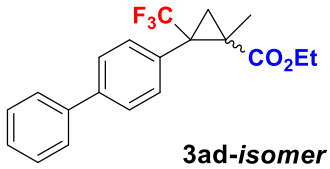
3nc-*isomer 1*

2-(6-Chloropyridin-3-yl)-1-methyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile (3nc-*isomer 1*). Yield 40% (72.8 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.69 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 2.27 (d, *J* = 6.4 Hz, 1H), 1.52 (s, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 150.7, 140.0, 124.3, 123.7, 122.7 (q, $^{1}J_{CF}$ = 274.4 Hz), 117.8, 35.5 (q, $^{2}J_{CF}$ = 34.7 Hz), 21.2 (q, $^{3}J_{CF}$ = 1.6 Hz), 19.1, 12.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.0 (s, 3F); HRMS (ESI): calcd for $C_{11}H_9ClF_3N_2$ $[M+H]^+$: 261.0406, found: 261.0404.



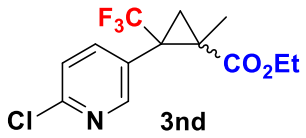
3ad-*isomer 1*

Ethyl 2-([1,1'-biphenyl]-4-yl)-1-methyl-2-(trifluoromethyl)cyclopropane-1-carboxylate (3ad-*isomer 1*). Yield 37% (90.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.51 (m, 4H), 7.44–7.40 (m, 4H), 7.36–7.32 (m, 1H), 3.80–3.64 (m, 2H), 2.24 (dd, *J* = 5.6 Hz, 2.0 Hz, 1H), 1.69 (s, 3H), 1.60 (d, *J* = 6.0 Hz, 1H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 140.3, 139.4, 131.7, 129.8, 127.8, 126.5, 126.1, 125.9, 124.6 (q, $^{1}J_{CF}$ = 274.4 Hz), 60.1, 37.1 (q, $^{2}J_{CF}$ = 32.3 Hz), 29.7, 19.4 (q, $^{3}J_{CF}$ = 2.2 Hz), 14.1 (q, $^{3}J_{CF}$ = 2.2 Hz), 12.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.5 (s, 3F); HRMS (ESI): calcd for $C_{20}H_{19}F_3O_2Na$ $[M+Na]^+$: 371.1225, found: 371.1227.



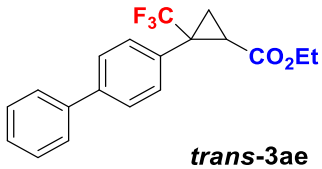
3ad-*isomer 2*

Ethyl 2-([1,1'-biphenyl]-4-yl)-1-methyl-2-(trifluoromethyl)cyclopropane-1-carboxylate (3ad-*isomer 2*). Yield 40% (97.4 mg), yellow solid, m.p.: 92.4–92.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 4H), 7.46–7.43 (m, 4H), 7.38–7.34 (m, 1H), 4.33–4.17 (m, 2H), 2.12 (d, *J* = 6.0 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.29–1.26 (m, 1H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 140.5, 139.3, 130.7, 130.3, 127.8, 126.6, 126.2, 126.1, 124.5 (q, $^{1}J_{CF}$ = 273.6 Hz), 60.5, 36.6 (q, $^{2}J_{CF}$ = 32.4 Hz), 29.9, 19.0, 18.7 (q, $^{3}J_{CF}$ = 2.0 Hz), 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –65.5 (s, 3F).



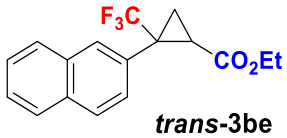
3nd

Ethyl 2-(6-chloropyridin-3-yl)-1-methyl-2-(trifluoromethyl)cyclopropane-1-carboxylate (3nd-*isomer 1*/*isomer 2*=5.7/1). Yield 83% (178.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 2.0 Hz, 1H), 7.62 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1.14H), 4.30–4.12 (m, 0.36H), 3.90–3.80 (m, 2.05H), 2.32 (d, J = 6.4 Hz, 0.16H), 2.19 (s, 1H), 1.68 (d, J = 1.2 Hz, 3H), 1.67 (s, 0.53H), 1.65 (s, 0.51H), 1.58 (s, 0.19H), 1.28–1.25 (m, 1H), 0.97 (t, J = 7.0 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 169.1, 150.6, 150.4, 139.7, 127.9, 124.0 (q, $^{1}J_{CF}$ = 274.4 Hz), 122.9, 61.5, 61.3, 60.6, 60.5, 34.7 (q, $^{2}J_{CF}$ = 31.8 Hz), 32.9, 29.7, 26.9, 19.3 (q, $^{3}J_{CF}$ = 2.1 Hz), 16.7, 13.8 (q, $^{3}J_{CF}$ = 2.5 Hz), 13.0, 12.9, 12.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.6 (s, 3F), –69.6 (s, 0.04F); HRMS (ESI): calcd for $C_{13}H_{14}ClF_3NO_2$ $[M+H]^+$: 308.0665, found: 308.0662.



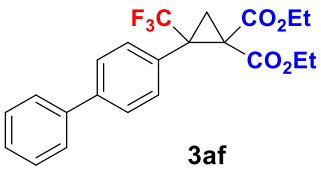
***trans*-3ae**

***trans*-Ethyl 2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (*trans*-3ae).** Yield 80% (187.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 4H), 7.45–7.41 (m, 4H), 7.37–7.33 (m, 1H), 4.01–3.90 (m, 2H), 2.51 (dd, J = 8.8 Hz, 6.4 Hz, 1H), 1.90 (td, J = 5.8 Hz, 1.5 Hz, 1H), 1.74 (dd, J = 8.8 Hz, 5.6 Hz, 1H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 140.7, 139.4, 130.5, 129.4, 127.7, 126.5, 126.2, 126.1,126.0, 124.0 (q, $^{1}J_{CF}$ = 273.2 Hz), 60.1, 34.4 (q, $^{2}J_{CF}$ = 33.4 Hz), 22.7 (q, $^{3}J_{CF}$ = 2.1 Hz), 13.3 (q, $^{3}J_{CF}$ = 1.5 Hz), 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.4 (s, 3F); HRMS (EI): calcd for $C_{19}H_{17}F_3O_2$ $[M]^+$: 334.1181, found: 334.1180.



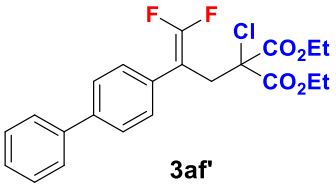
***trans*-3be**

***trans*-Ethyl 2-(naphthalen-2-yl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (*trans*-3be).** Yield 74% (159.5 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.82–7.78 (m, 3H), 7.50–7.42 (m, 3H), 3.97–3.83 (m, 2H), 2.56 (dd, J = 8.4 Hz, 6.0 Hz, 1H), 1.98 (td, J = 5.8 Hz, 1.3 Hz, 1H), 1.79 (dd, J = 8.8 Hz, 5.2 Hz, 1H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 133.4, 133.1, 131.1, 128.9, 128.1 (t, $^{3}J_{CF}$ = 5.3 Hz), 127.8, 126.7, 126.4, 125.2 (q, $^{1}J_{CF}$ = 273.1 Hz), 61.2, 35.9 (q, $^{2}J_{CF}$ = 33.3 Hz), 23.9 (q, $^{3}J_{CF}$ = 1.6 Hz), 14.6 (q, $^{3}J_{CF}$ = 1.8 Hz), 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.2 (s, 3F); HRMS (EI): calcd for $C_{17}H_{15}F_3O_2$ $[M]^+$: 308.1024, found: 308.1022.



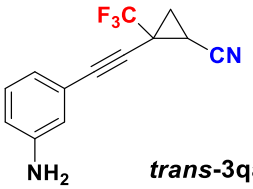
3af

Diethyl 2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)cyclopropane-1,1-dicarboxylate (3af). Yield 44% (125.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 4H), 7.48–7.42 (m, 4H), 7.37–7.33 (m, 1H), 4.36–4.31 (m, 2H), 3.97–3.84 (m, 2H), 2.27 (d, J = 6.0 Hz, 1H), 2.14 (d, J = 5.2 Hz, 1H), 1.36 (t, J = 7.0 Hz, 3H), 0.95 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 140.9, 139.3, 130.1, 129.3, 127.8, 126.6, 126.1, 126.0, 123.4 (q, $^{1}J_{CF}$ = 274.4 Hz), 61.2, 39.2 (q, $^{2}J_{CF}$ = 33.2 Hz), 38.6, 17.8 (q, $^{3}J_{CF}$ = 1.7 Hz), 12.8, 12.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.9 (s, 3F); HRMS (ESI): calcd for $C_{22}H_{21}F_3O_4$ Na $[M+Na]^+$: 429.1290, found: 429.1292.



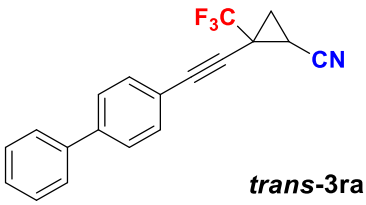
3af'

Diethyl 2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2-chloromalonate (3af'). Yield 36% (106.3 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 4H), 7.46–7.42 (m, 2H), 7.37–7.32 (m, 3H), 4.00–3.92 (m, 2H), 3.88–3.80 (m, 2H), 3.47 (t, J = 1.8 Hz, 2H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 155.4 (t, $^{1}J_{CF}$ = 289.7 Hz), 140.7, 140.4, 131.0 (t, $^{3}J_{CF}$ = 2.9 Hz), 129.7 (t, $^{3}J_{CF}$ = 2.5 Hz), 128.9, 127.6, 127.0, 126.8, 87.0 (t, $^{2}J_{CF}$ = 19.5 Hz), 69.2 (t, $^{3}J_{CF}$ = 2.8 Hz), 63.1, 36.1 (d, $^{3}J_{CF}$ = 2.4 Hz), 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –87.0 (d, J = 8.2 Hz, 1F), –87.5 (d, J = 8.3 Hz, 1F); HRMS (ESI): calcd for $C_{22}H_{21}ClF_2O_4$ Na $[M+Na]^+$: 445.0994, found: 445.0992.



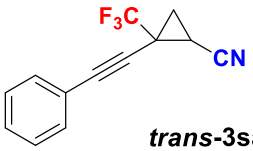
***trans*-3qa**

***trans*-2-((3-Aminophenyl)ethynyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3qa).** Yield 73% (127.8 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.83 (s, 1H), 6.69 (d, J =7.6 Hz, 1H), 3.68 (s, 2H), 2.26 (t, J = 8.2 Hz, 1H), 1.88–1.84 (m, 1H), 1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 128.3, 121.5, 120.5, 121.8 (q, $^{1}J_{CF}$ = 273.4 Hz), 117.3, 115.4, 115.2, 84.5, 77.1, 23.2 (q, $^{2}J_{CF}$ = 38.7 Hz), 17.9 (q, $^{3}J_{CF}$ = 2.3 Hz), 10.2 (q, $^{3}J_{CF}$ = 4.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.0 (s, 3F); HRMS (EI): calcd for $C_{13}H_9F_3N_2$ $[M]^+$: 250.0718, found: 250.0721.



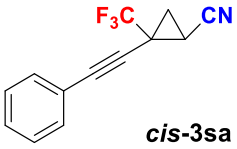
***trans*-3ra**

***trans*-2-([1,1'-Biphenyl]-4-ylethynyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3ra).** Yield 87% (189.4 mg), yellow solid, m.p.: 85.7–86.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 6H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 1H), 2.27 (dd, J = 9.6 Hz, 6.8 Hz, 1H), 1.87 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.81–1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.1, 132.8, 129.0, 127.9, 127.1, 122.9 (q, $^{1}J_{CF}$ = 273.5 Hz), 119.8, 116.3, 85.2, 79.5 (q, $^{3}J_{CF}$ = 1.3 Hz), 24.3 (q, $^{2}J_{CF}$ = 38.8 Hz), 19.0, 11.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.9 (d, J = 1.1 Hz, 3F); HRMS (EI): calcd for $C_{19}H_{12}F_3N$ $[M]^+$: 311.0922, found: 311.0920.



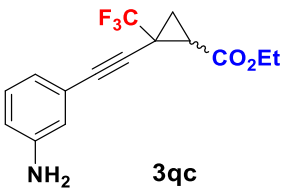
***trans*-3sa**

***trans*-2-(Phenylethynyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*trans*-3sa).** Yield 70% (115.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.38–7.30 (m, 3H), 2.26 (dd, J = 9.6 Hz, 6.8 Hz, 1H), 1.86 (dd, J = 9.6 Hz, 6.0 Hz, 1H), 1.79–1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 129.5, 128.4, 122.9 (q, $^{1}J_{CF}$ = 273.4 Hz), 121.0, 116.2, 85.3, 78.9, 24.3 (q, $^{2}J_{CF}$ = 38.7 Hz), 19.0, 11.4 (q, $^{3}J_{CF}$ = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.0 (s, 3F); HRMS (EI): calcd for $C_{13}H_8F_3N$ $[M]^+$: 235.0609, found: 235.0607.



***cis*-3sa**

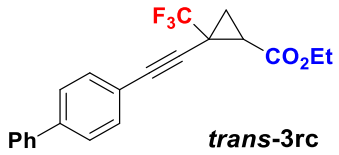
***cis*-2-(Phenylethynyl)-2-(trifluoromethyl)cyclopropane-1-carbonitrile (*cis*-3sa).** Yield 11% (18.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.38–7.31 (m, 3H), 2.24 (t, J = 8.4 Hz, 1H), 2.01–1.98 (m, 1H), 1.85–1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 129.5, 128.5, 122.8 (q, $^{1}J_{CF}$ = 274.2 Hz), 120.9, 115.0, 83.0, 80.9, 19.1 (q, $^{3}J_{CF}$ = 1.2 Hz), 11.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.6 (s, 3F).



3qc

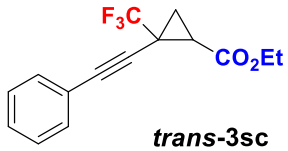
Ethyl 2-((3-aminophenyl)ethynyl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (3qc, *trans/cis*=3/1). Yield 52% (108.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.75 (s, 1H), 6.64 (d, J = 7.2 Hz, 1H), 4.29–4.14 (m, 2H), 3.54 (s, 2H), 2.48–2.41 (m, 1H), 2.02 (dd, J = 8.0 Hz, 6.0 Hz,

0.25H), 1.87–1.84 (m, 0.75H), 1.67 (dd, J = 8.8 Hz, 5.6 Hz, 0.75H), 1.64–1.60 (m, 0.26H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.5, 145.2, 145.1, 128.3, 128.2, 121.6, 121.3, 121.3, 120.0 (q, $^1J_{CF}$ = 272.9 Hz), 117.1, 114.9, 114.7, 82.7, 80.2, 78.6, 60.8, 60.6, 28.7, 28.4, 24.6, 23.2 (q, $^2J_{CF}$ = 37.8 Hz), 16.6 (q, $^3J_{CF}$ = 1.2 Hz), 16.3, 13.2, 13.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –65.5 (s, 1F), –70.7 (s, 3F); HRMS (ESI): calcd for $C_{15}H_{15}F_3NO_2$ $[M+H]^+$: 298.1055, found: 298.1053.



***trans*-3rc**

***trans*-Ethyl 2-([1,1'-biphenyl]-4-ylethynyl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (*trans*-3rc).** Yield 86% (215.5 mg), yellow solid, m.p.: 54.9–56.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.48 (m, 6H), 7.45–7.41 (m, 2H), 7.36–7.33 (m, 1H), 4.24 (q, J = 7.2 Hz, 2H), 2.46 (dd, J = 8.8 Hz, 7.2 Hz, 1H), 1.91–1.87 (m, 1H), 1.69 (dd, J = 8.8 Hz, 5.6 Hz, 1H), 1.29 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 141.5, 140.3, 132.5, 128.9, 127.8, 127.1, 127.0, 123.9 (q, $^1J_{CF}$ = 272.9 Hz), 120.9, 83.4, 81.0, 61.7, 25.7, 24.4 (q, $^2J_{CF}$ = 37.9 Hz), 17.4, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.6 (s, 3F); HRMS (EI): calcd for $C_{21}H_{17}F_3O_2$ $[M]^+$: 358.1181, found: 358.1185.



***trans*-3sc**

***trans*-Ethyl 2-(phenylethynyl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (*trans*-3sc).** Yield 51% (100.7 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 6.8 Hz, 2H), 7.33–7.25 (m, 3H), 4.23 (q, 7.2 Hz, 2H), 2.44 (t, J = 8.0 Hz, 1H), 1.89–1.86 (m, 1H), 1.70–1.66 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 130.9, 128.1, 127.8, 127.7, 127.2, 122.7 (q, $^1J_{CF}$ = 272.8 Hz), 121.0, 82.4, 79.3, 60.6, 24.6, 23.2 (q, $^2J_{CF}$ = 37.9 Hz), 16.3, 13.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.7 (s, 3F); HRMS (ESI): calcd for $C_{15}H_{14}F_3O_2$ $[M+H]^+$: 283.0946, found: 283.0943.

9. References

(1) Y. Q. Guo, Y. P. Cao, H. J. Song, Y. X. Liu and Q. M. Wang, Photoredox relay-catalyzed *gem*-difluoroallylation of alkyl iodides, *Chem. Commun.*, 2021, **57**, 9768.

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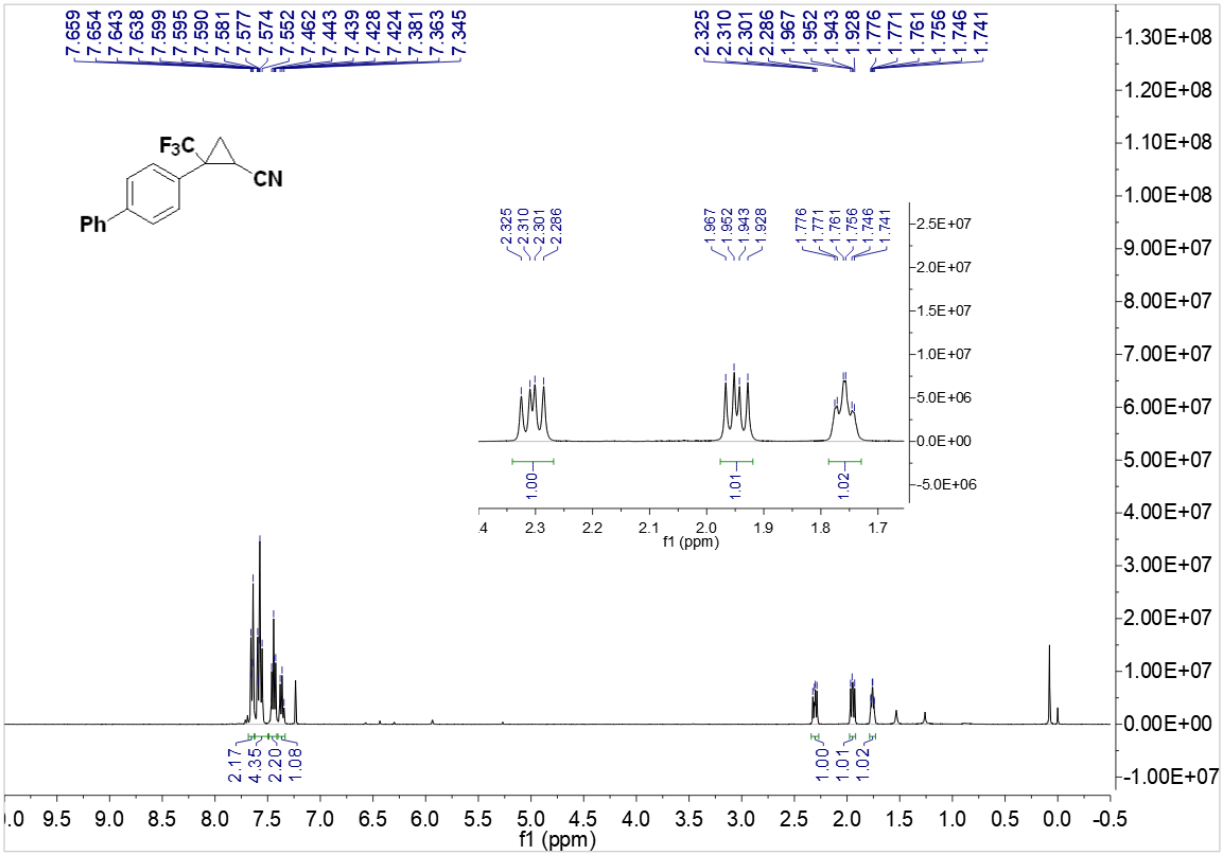
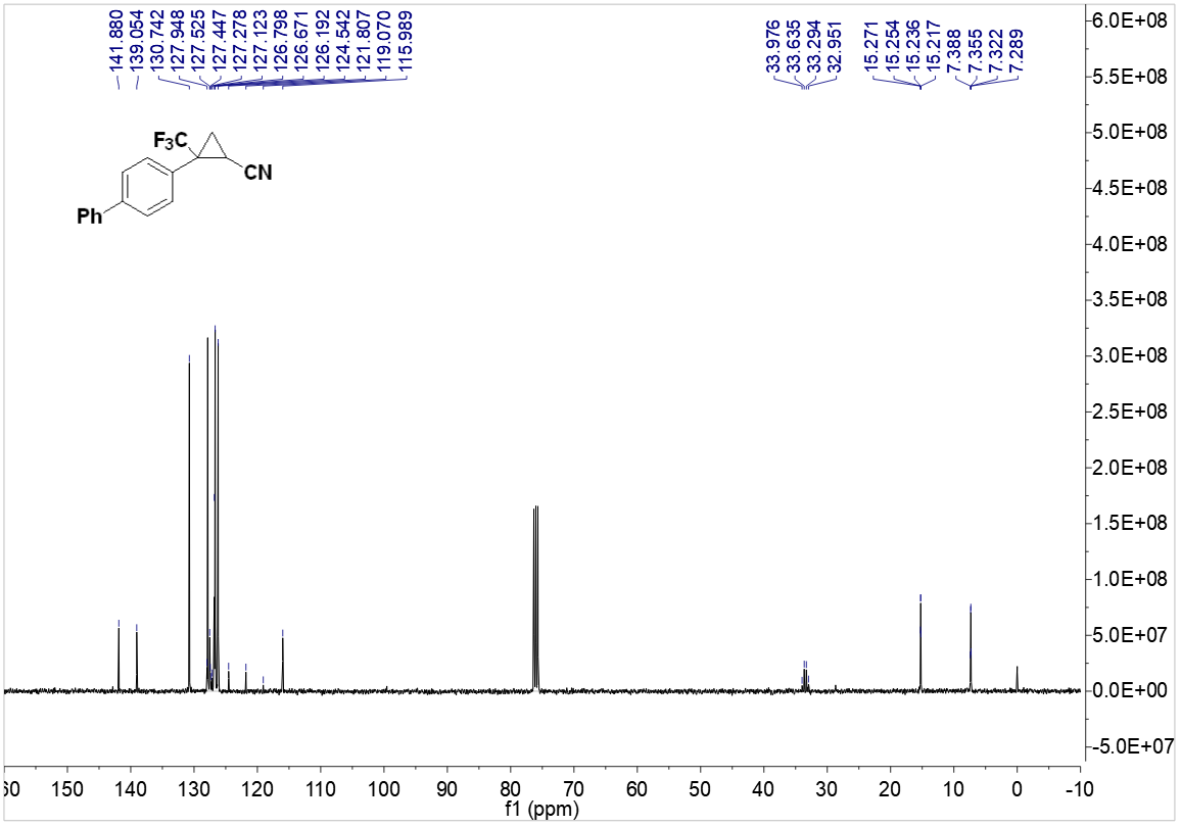
10. ^{1}H, ^{13}C, ^{19}F NMR and HRMS spectra of target compounds

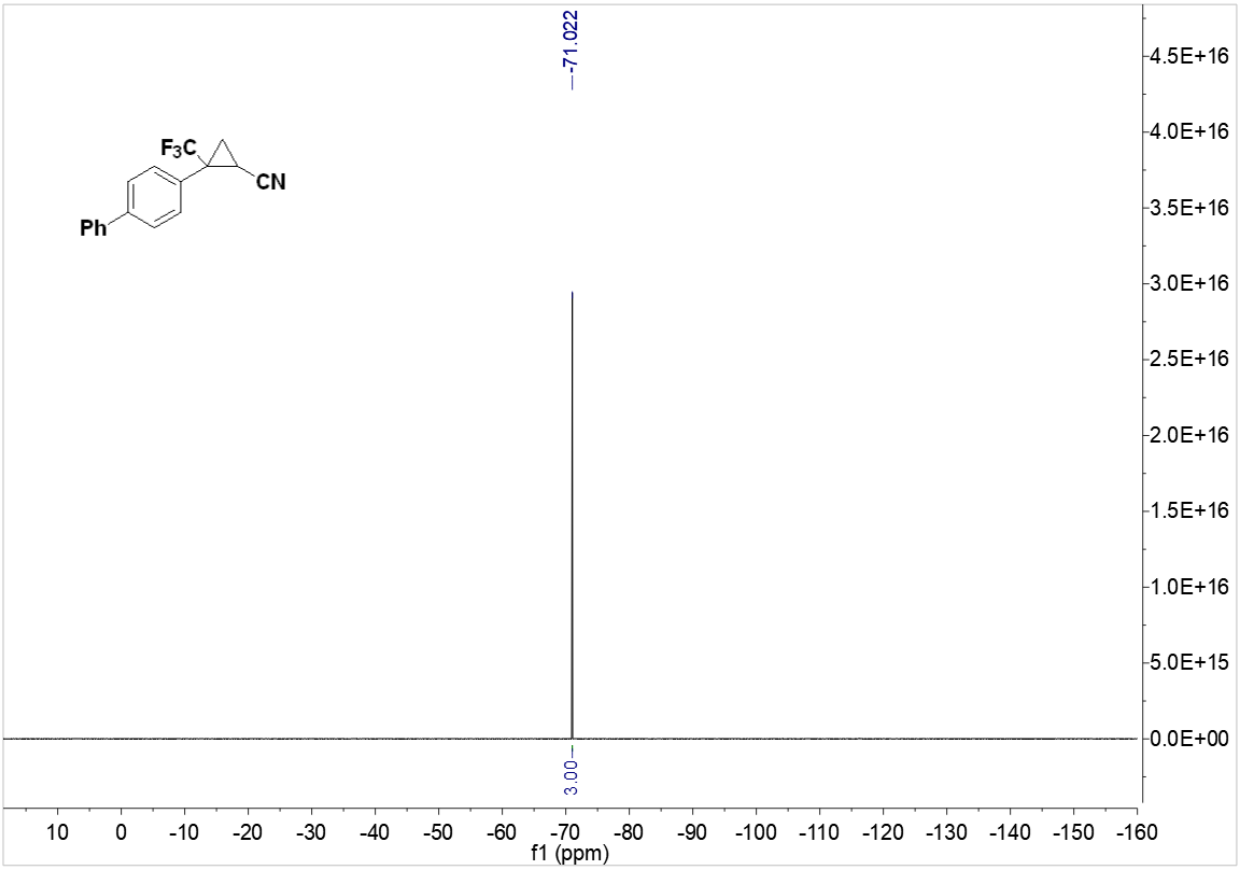
^{1}H NMR spectrum of ***trans*-3aa**



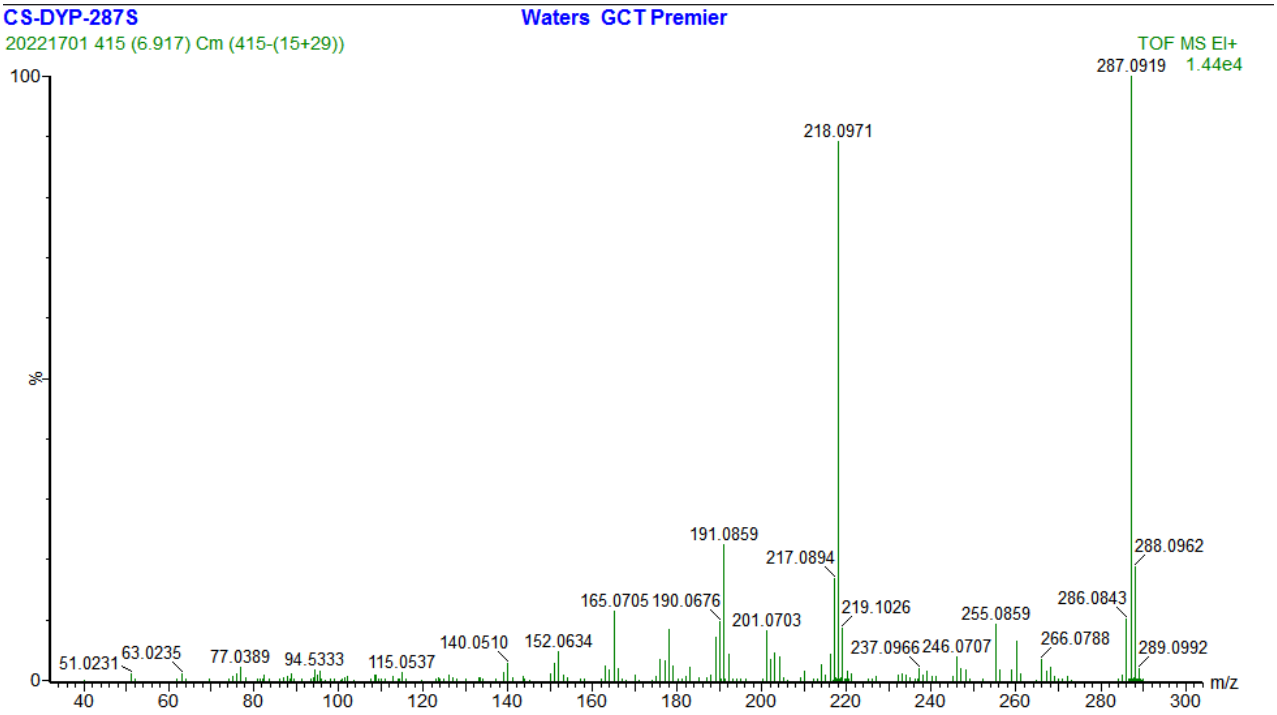
^{13}C NMR spectrum of ***trans*-3aa**



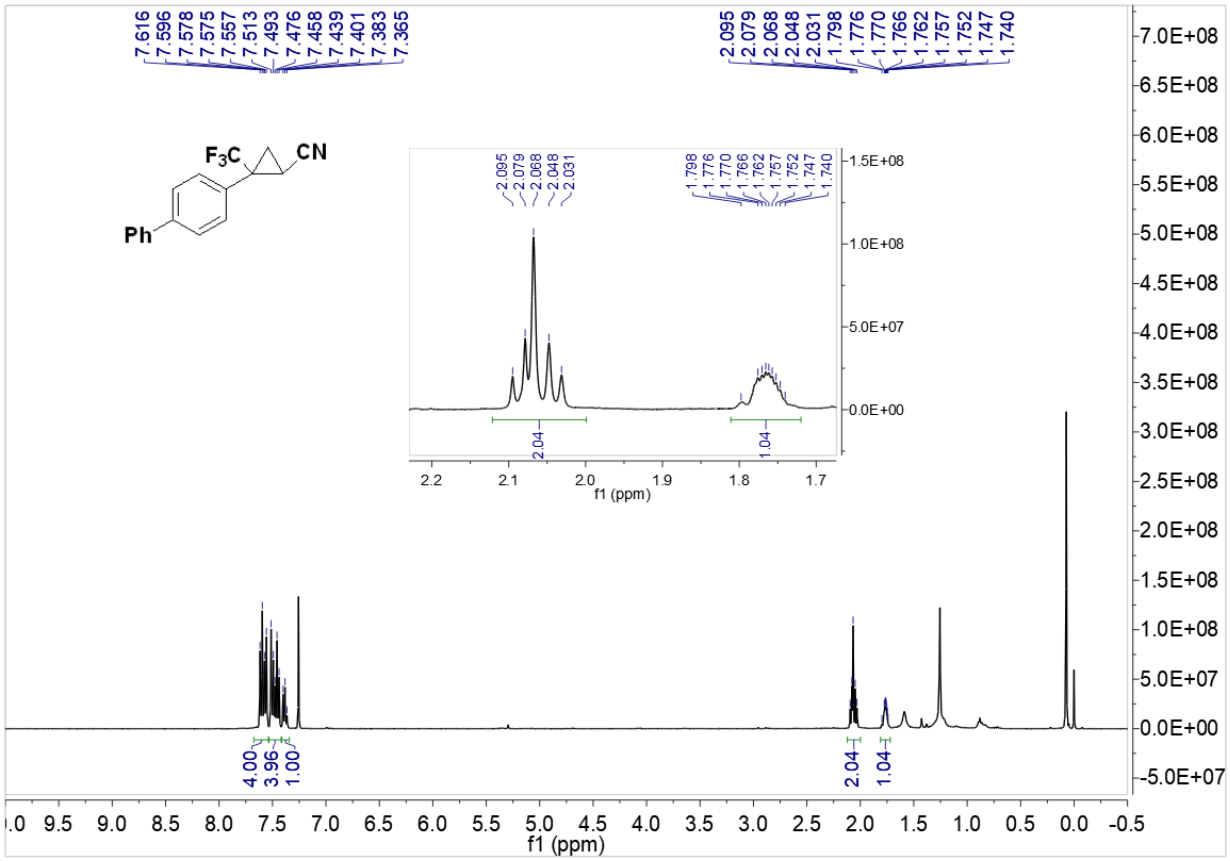
^{19}F NMR spectrum of ***trans*-3aa**



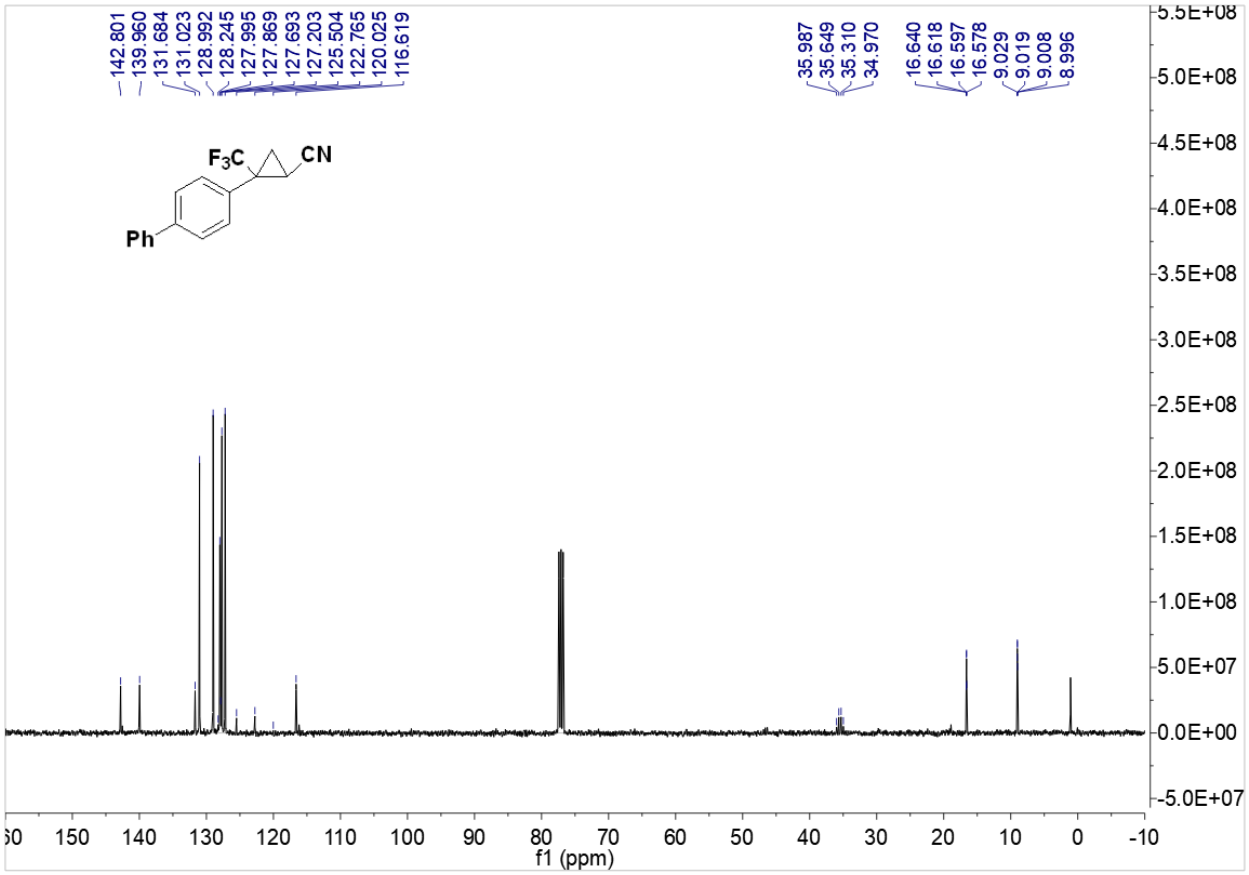
HRMS (EI) spectrum of ***trans*-3aa**



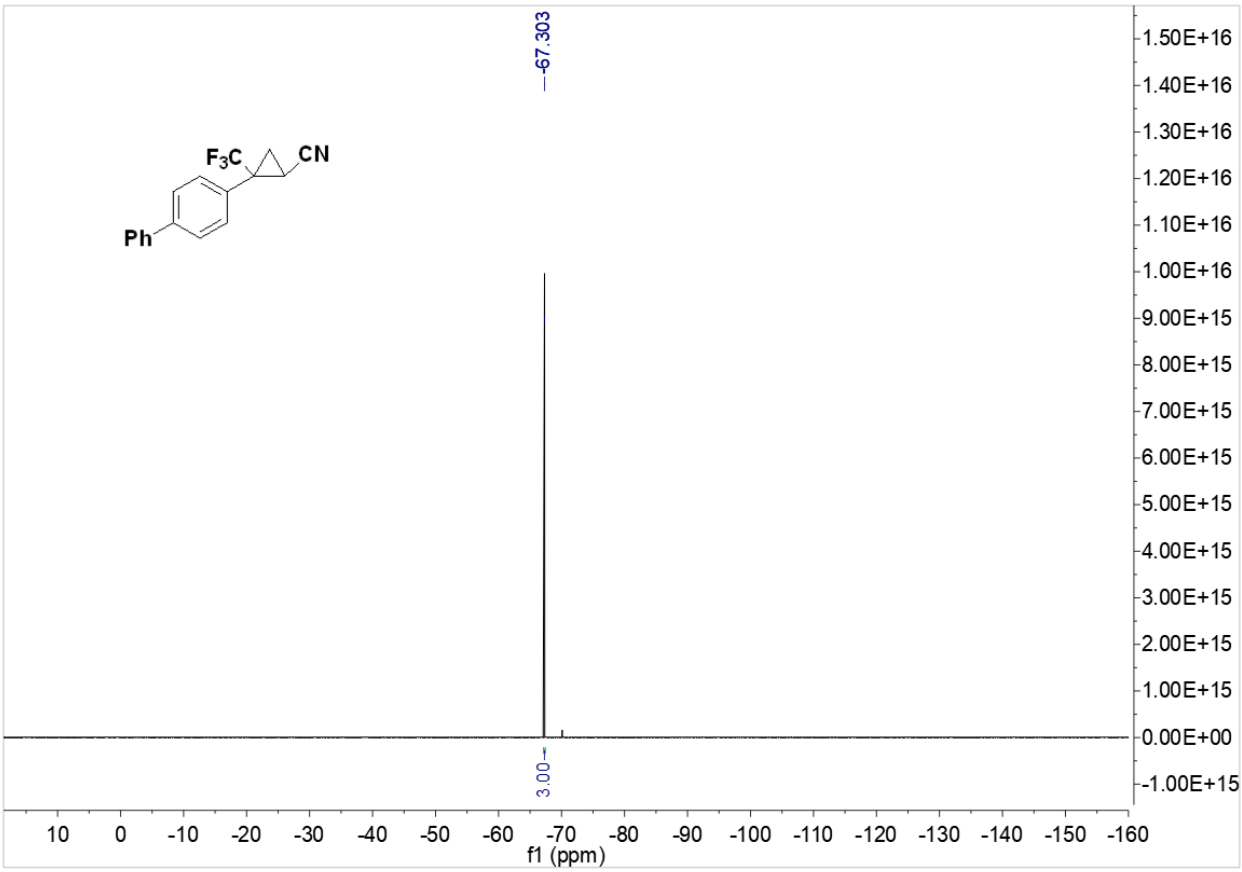
^{1}H NMR spectrum of ***cis*-3aa**



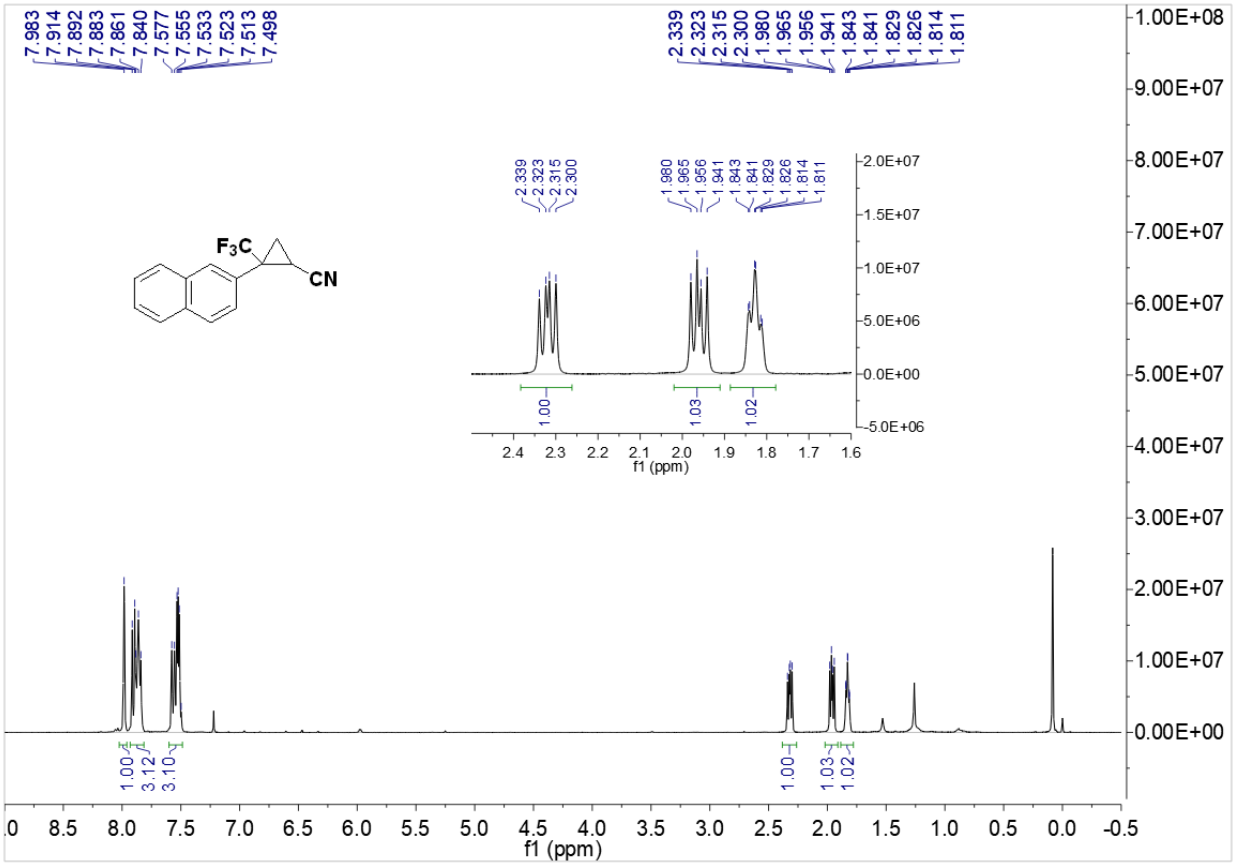
^{13}C NMR spectrum of ***cis*-3aa**



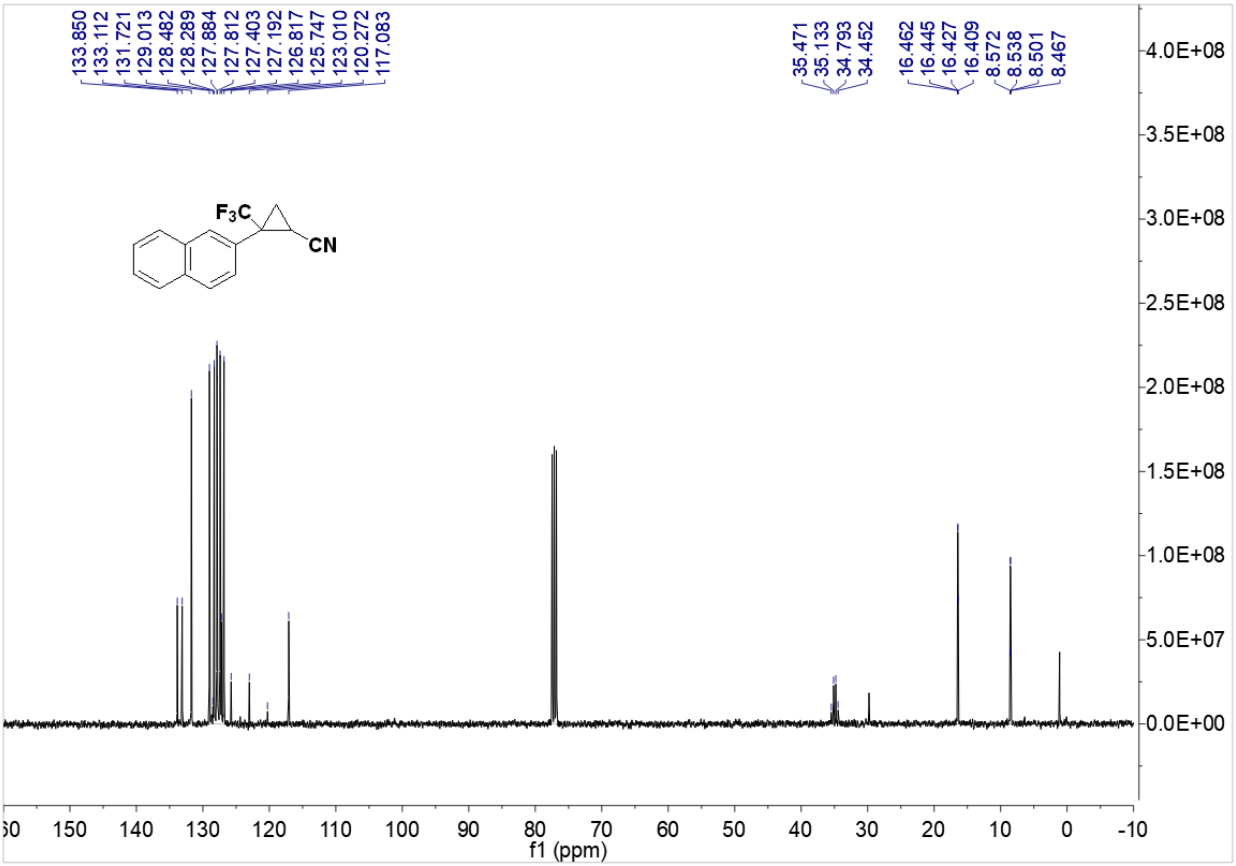
^{19}F NMR spectrum of ***cis*-3aa**



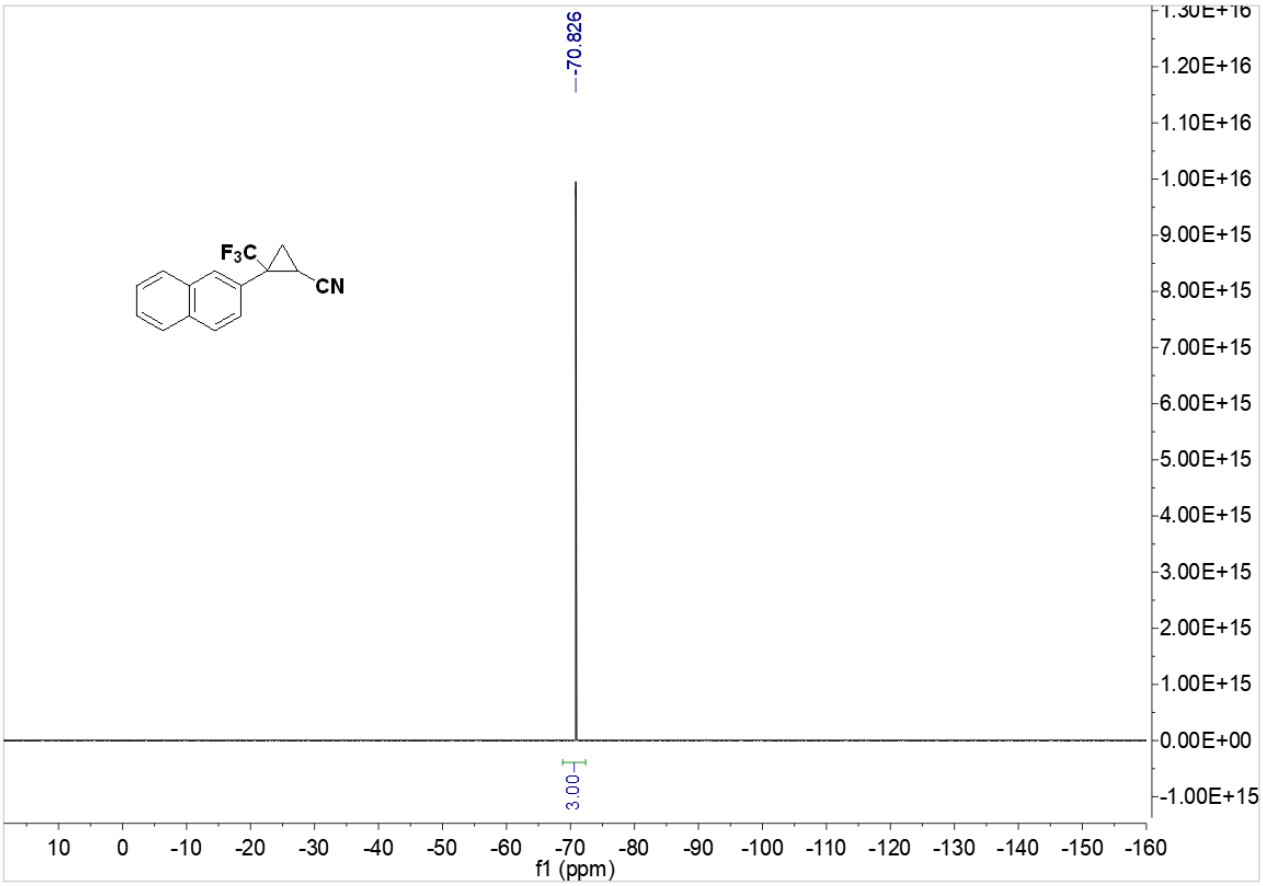
^{1}H NMR spectrum of ***trans*-3ba**



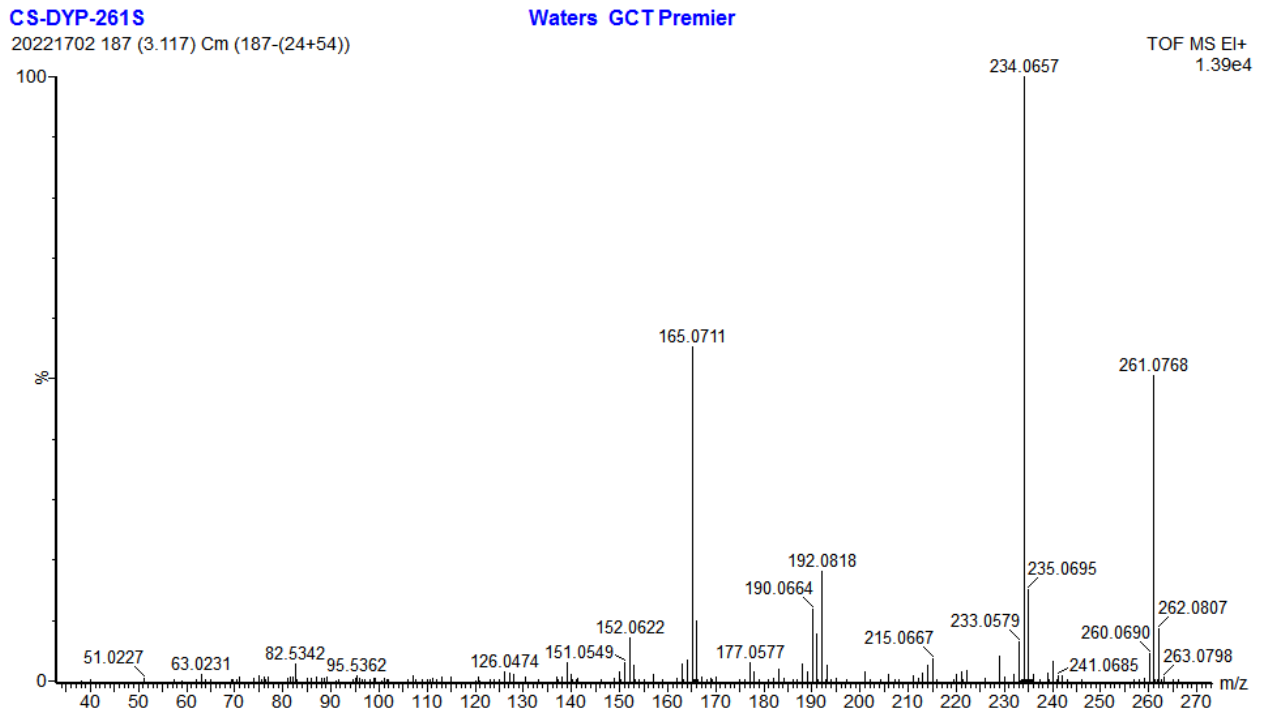
^{13}C NMR spectrum of ***trans*-3ba**



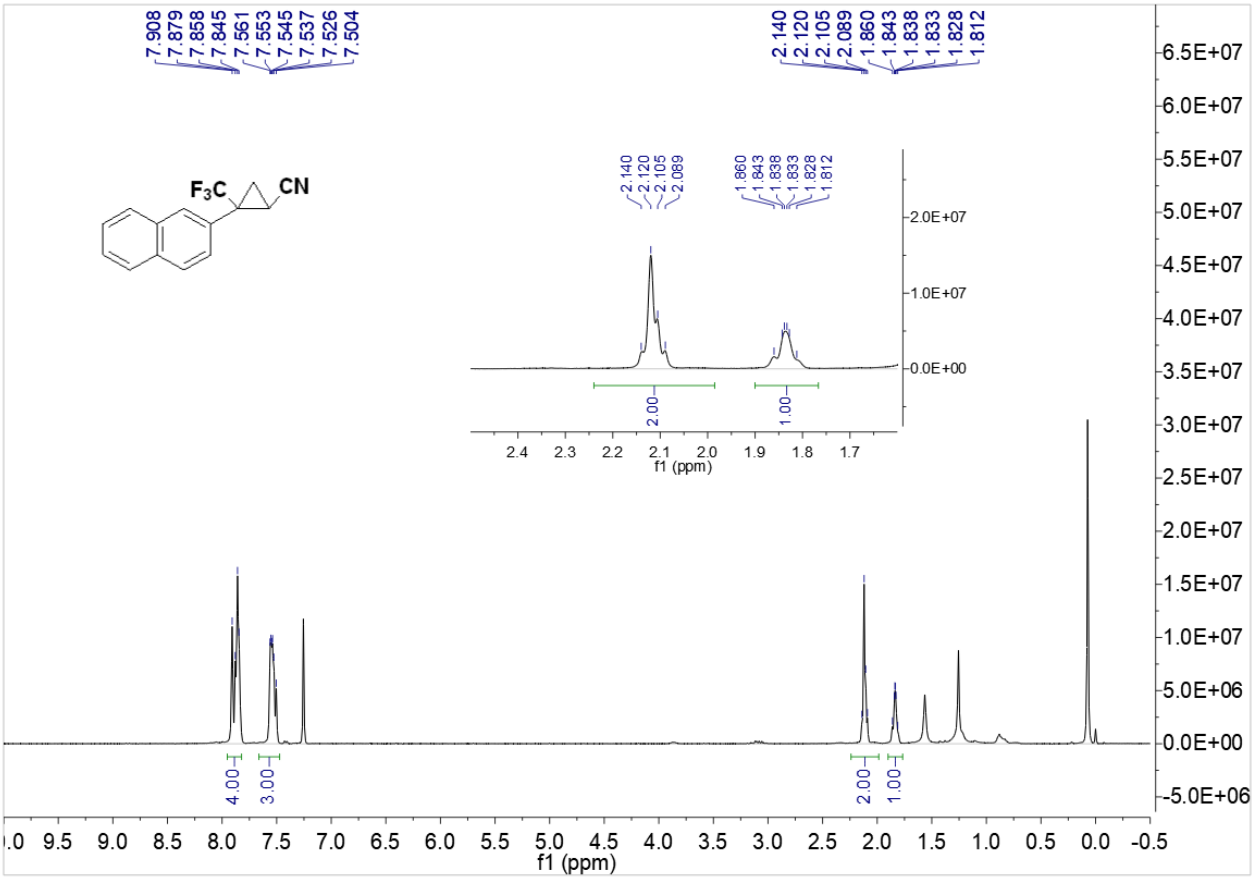
^{19}F NMR spectrum of ***trans*-3ba**



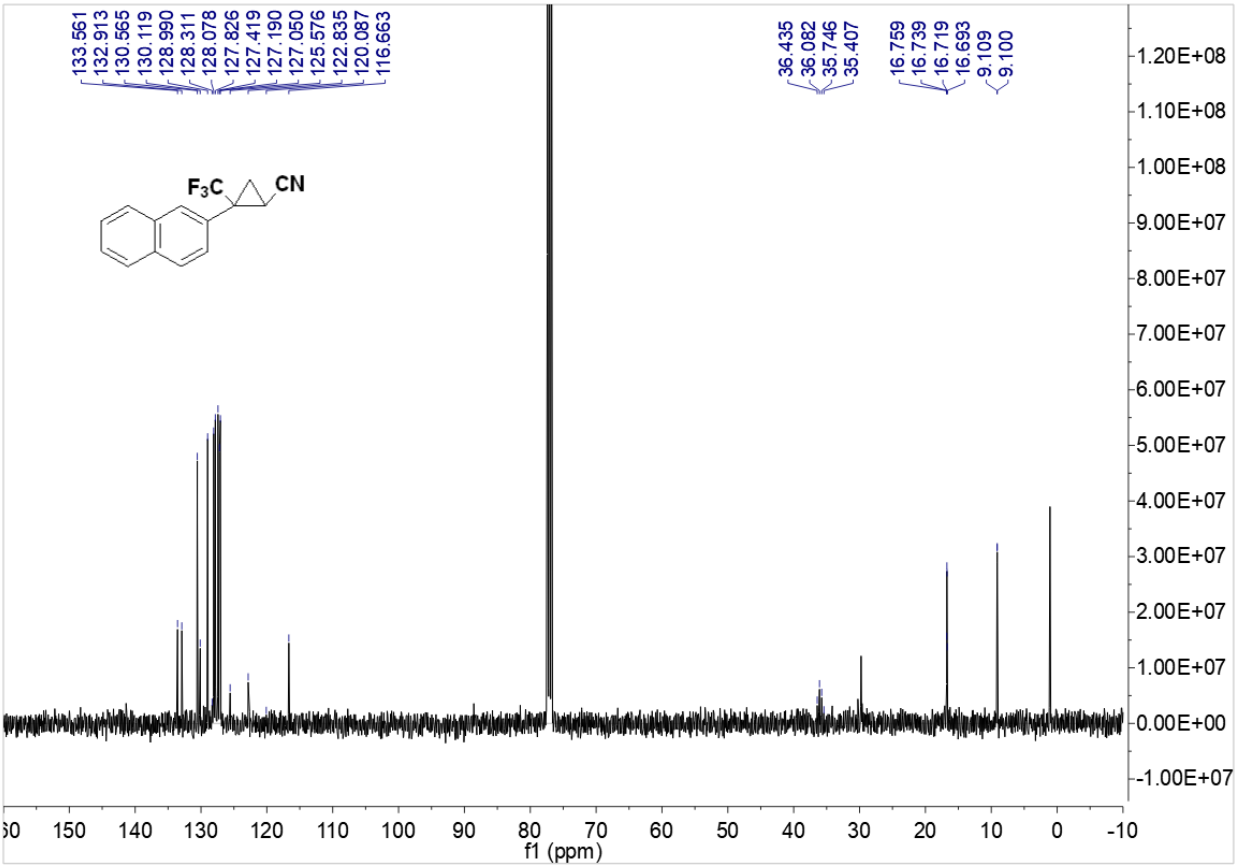
HRMS (EI) spectrum of ***trans*-3ba**



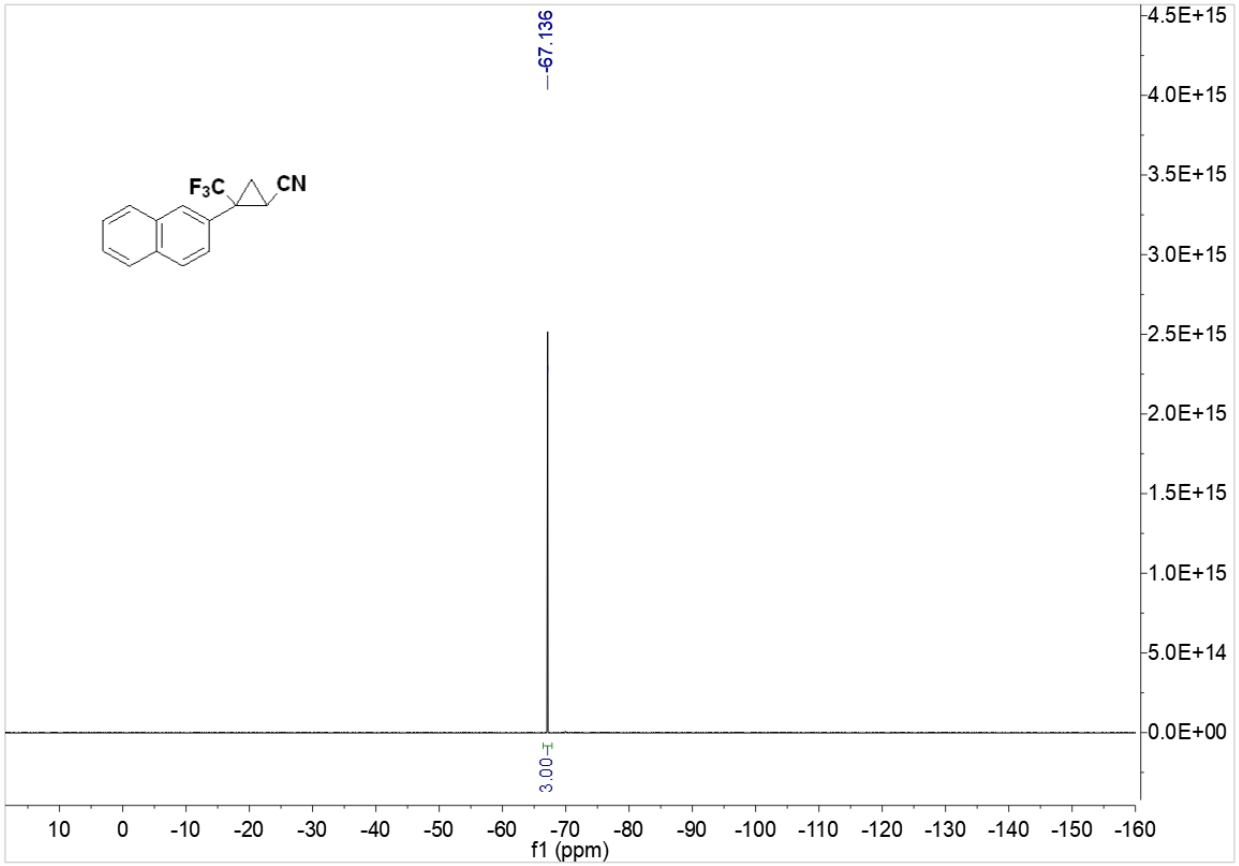
^{1}H NMR spectrum of ***cis*-3ba**



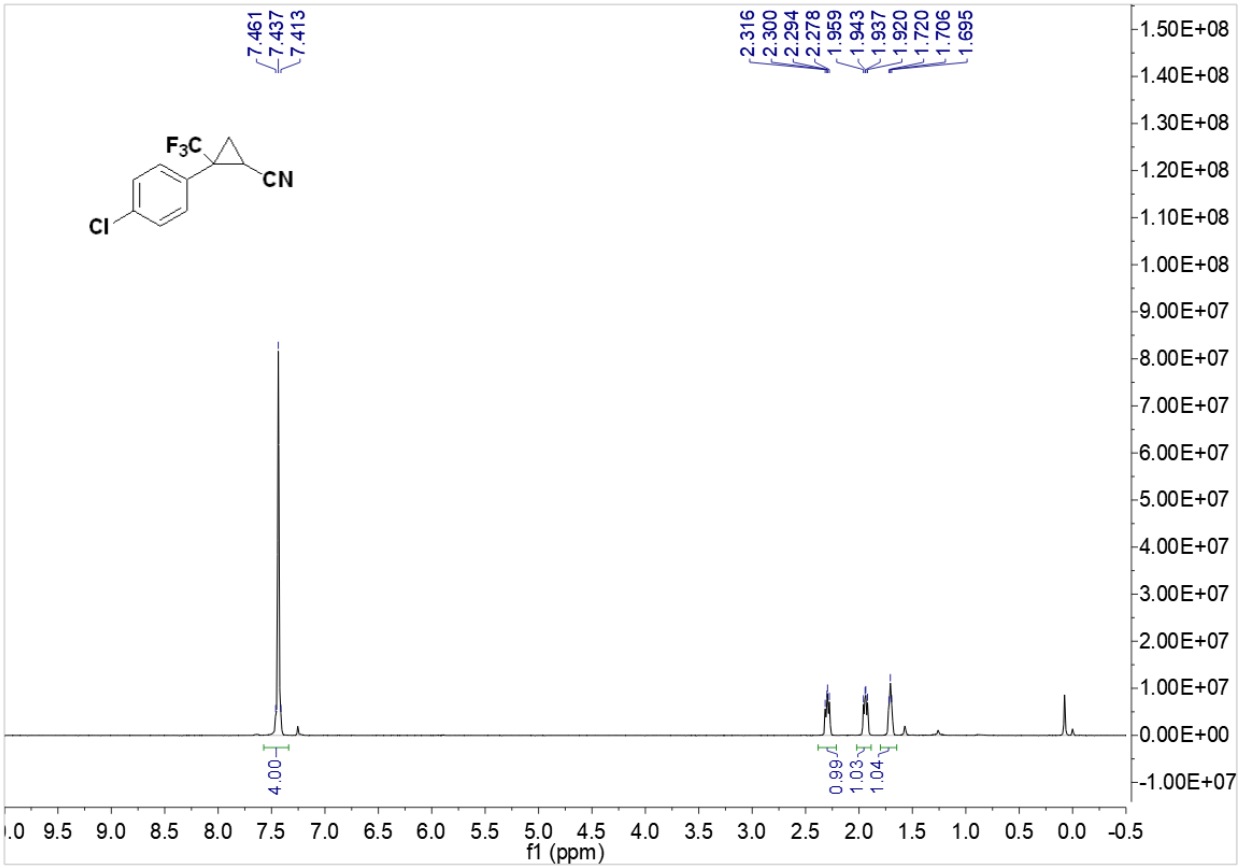
^{13}C NMR spectrum of ***cis*-3ba**



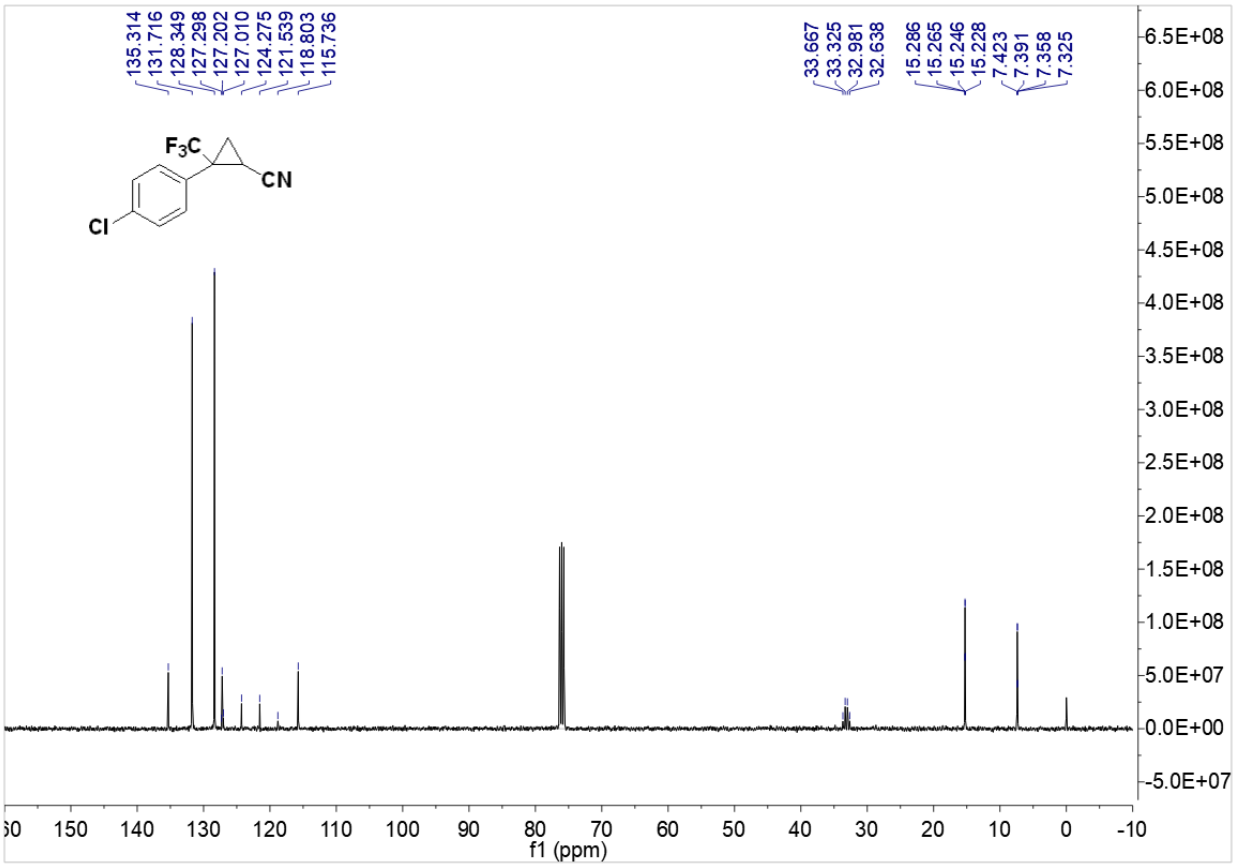
^{19}F NMR spectrum of ***cis*-3ba**



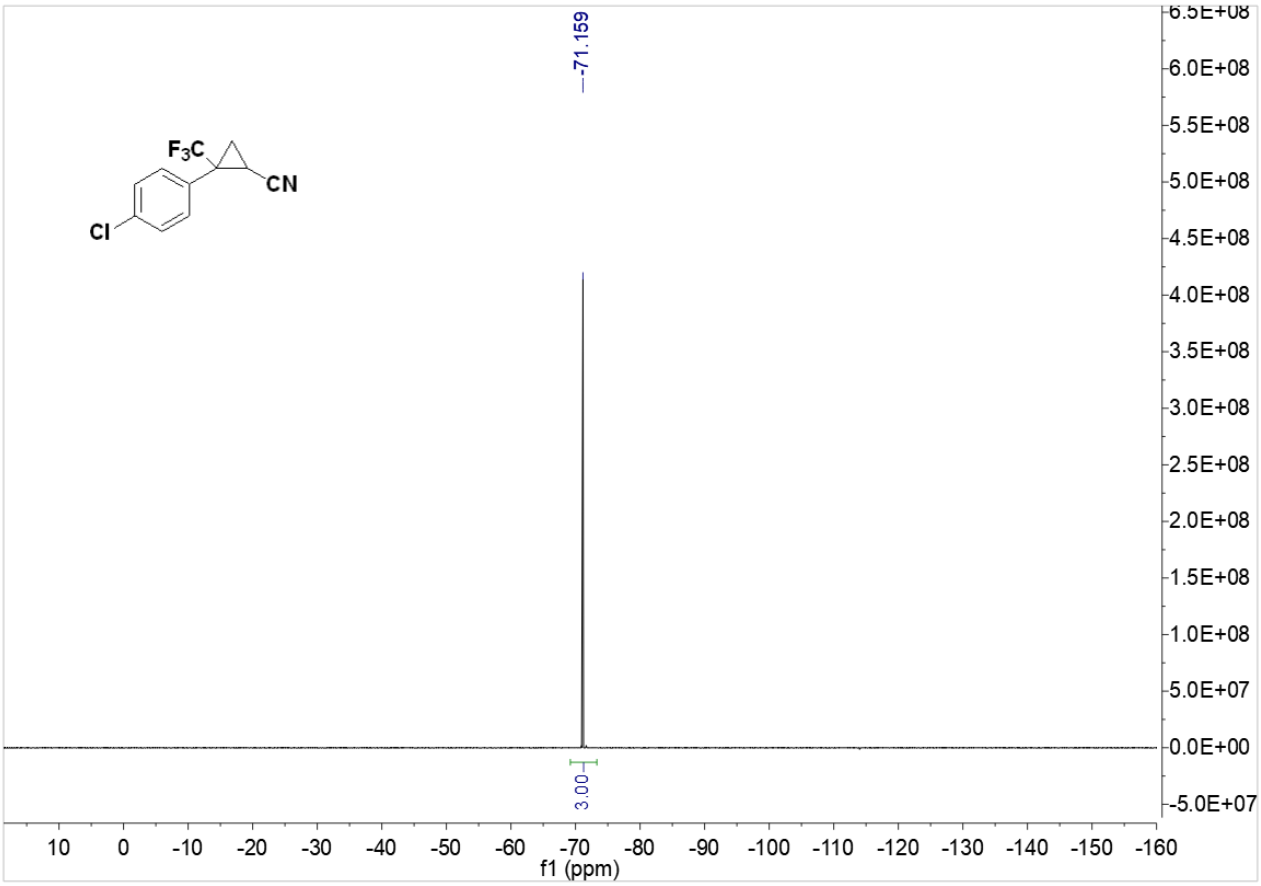
^{1}H NMR spectrum of ***trans*-3ca**



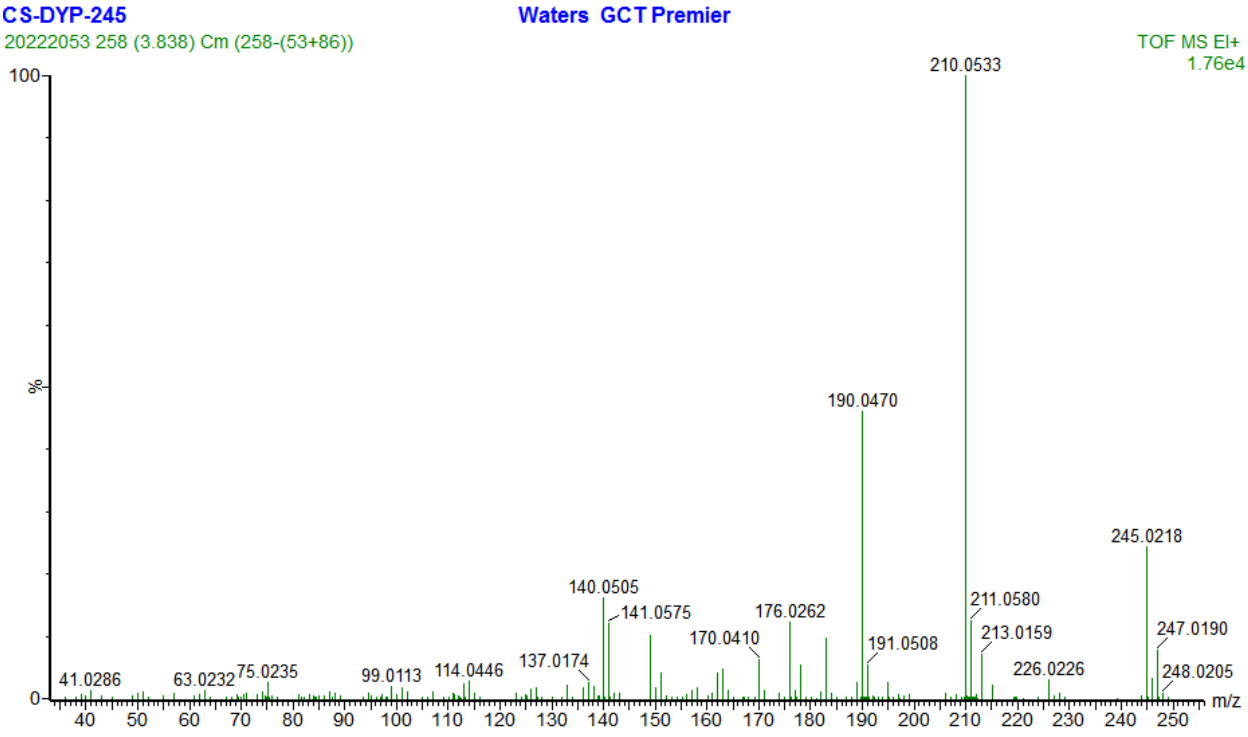
^{13}C NMR spectrum of ***trans*-3ca**



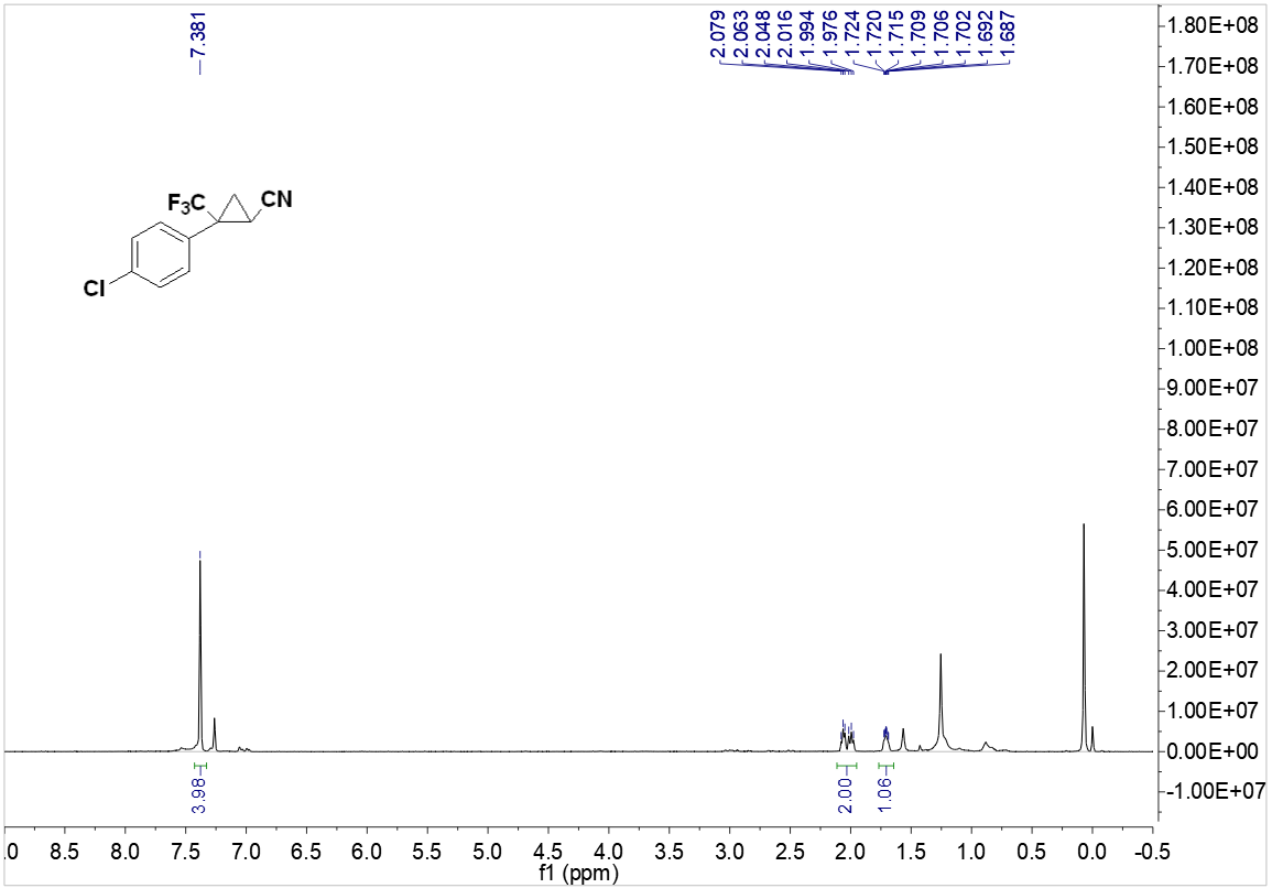
^{19}F NMR spectrum of ***trans*-3ca**



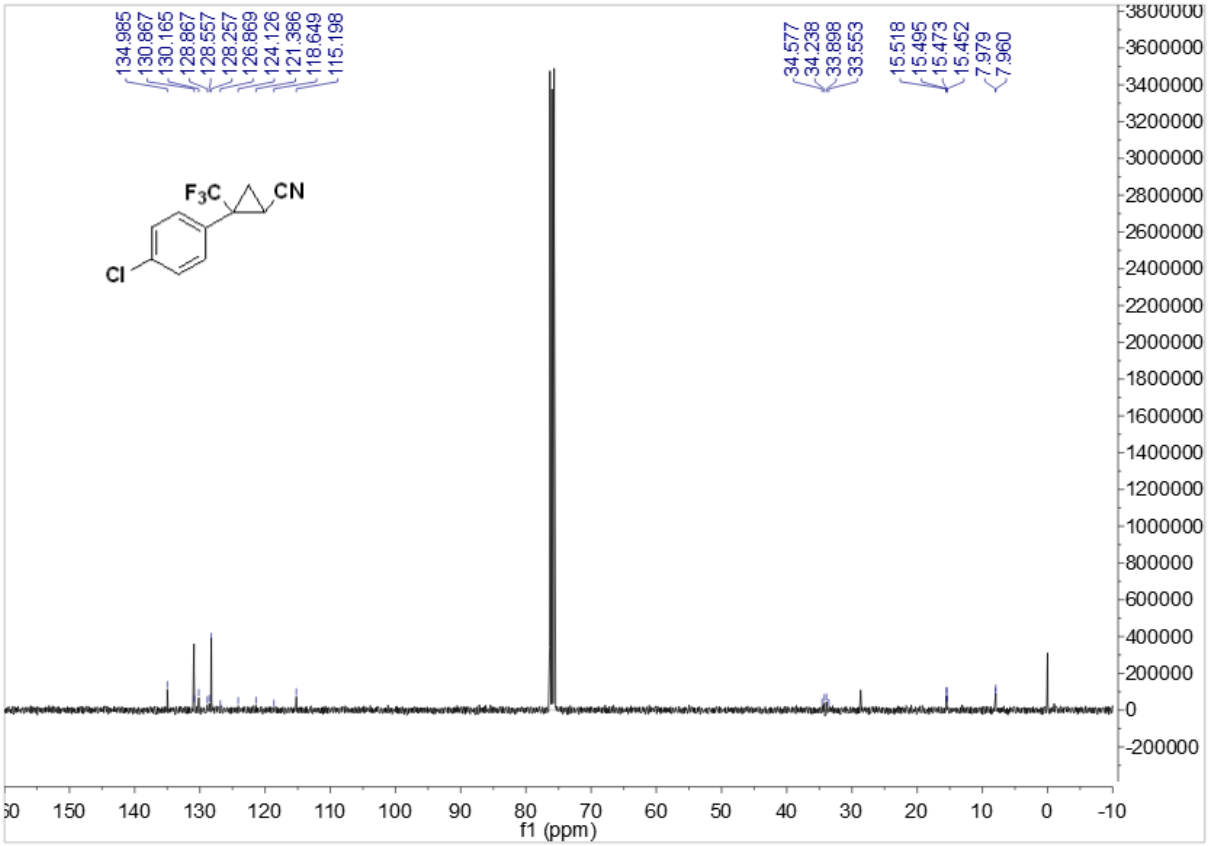
HRMS (EI) spectrum of ***trans*-3ca**



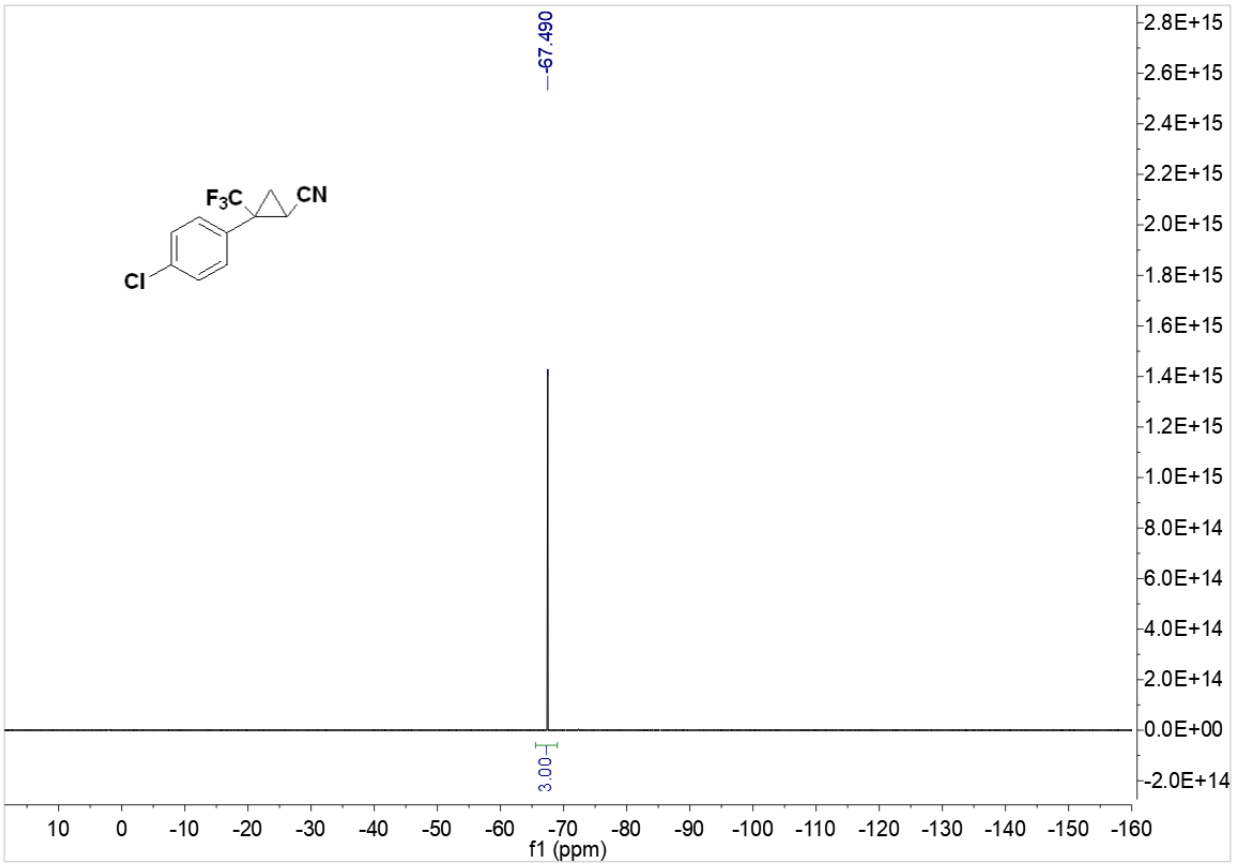
^{1}H NMR spectrum of ***cis*-3ca**



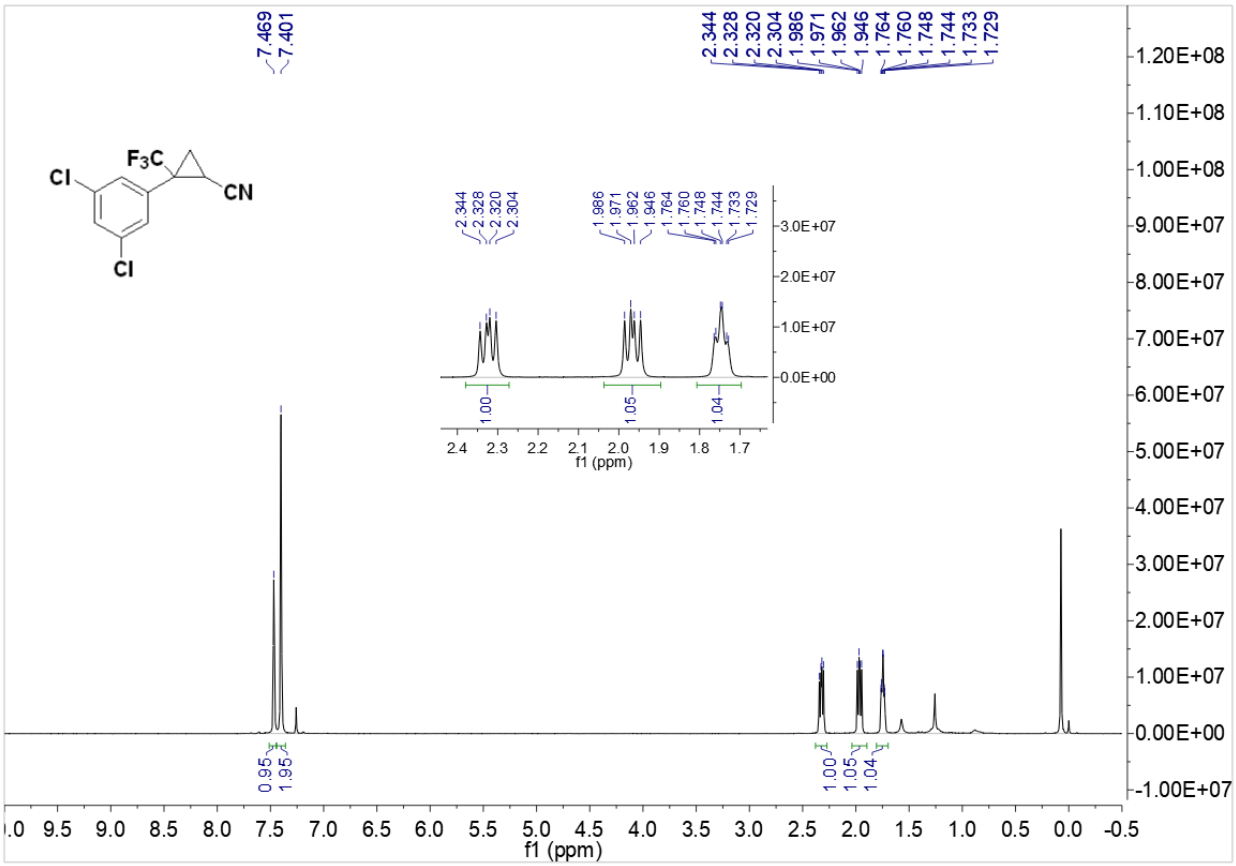
^{13}C NMR spectrum of ***cis*-3ca**



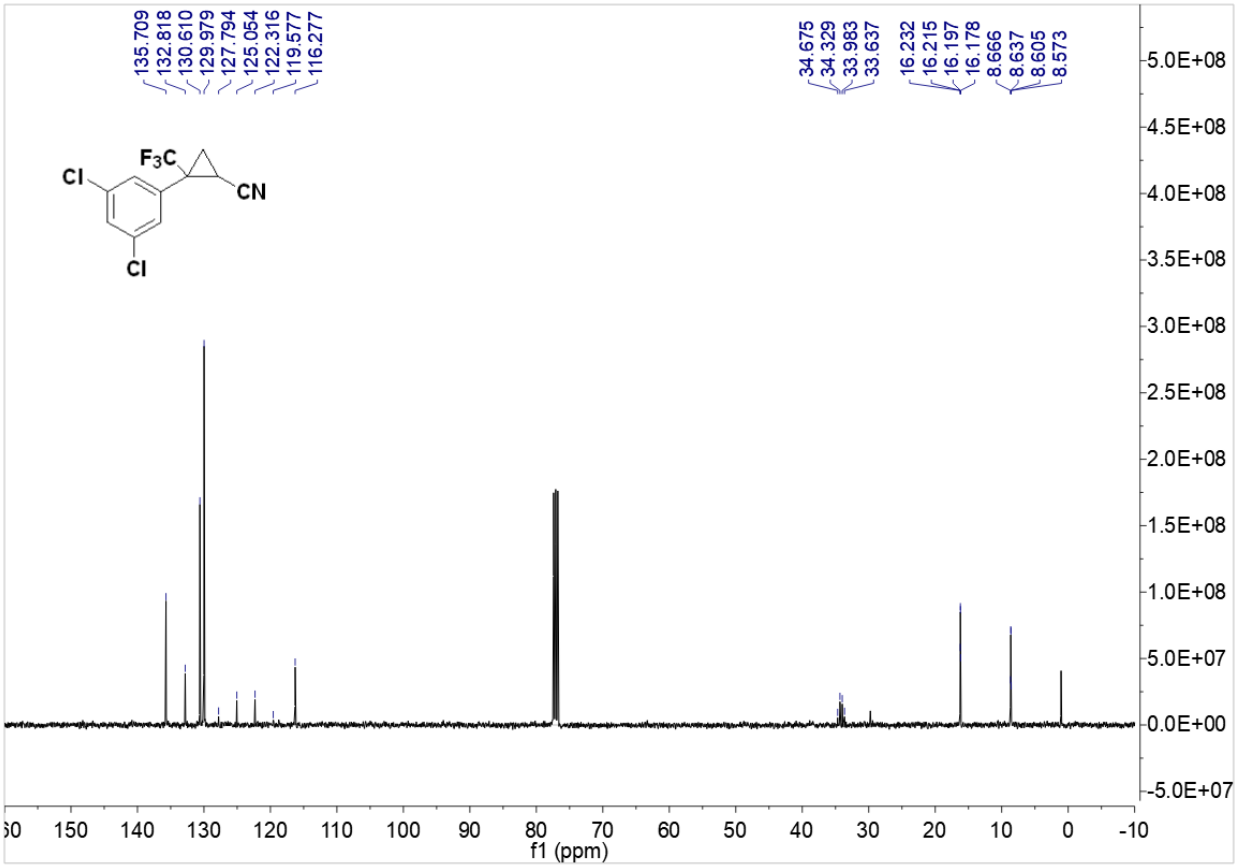
^{19}F NMR spectrum of ***cis*-3ca**



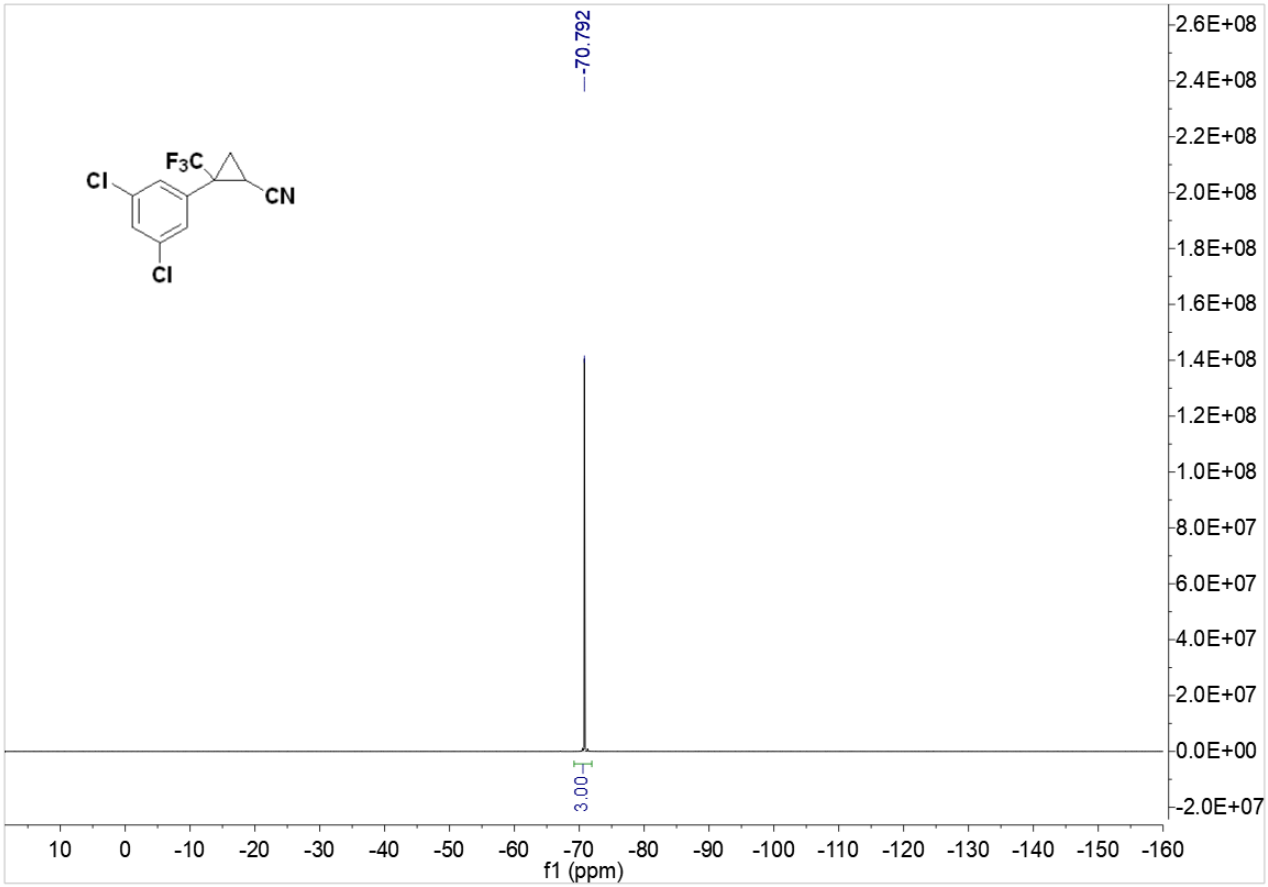
^{1}H NMR spectrum of ***trans*-3da**



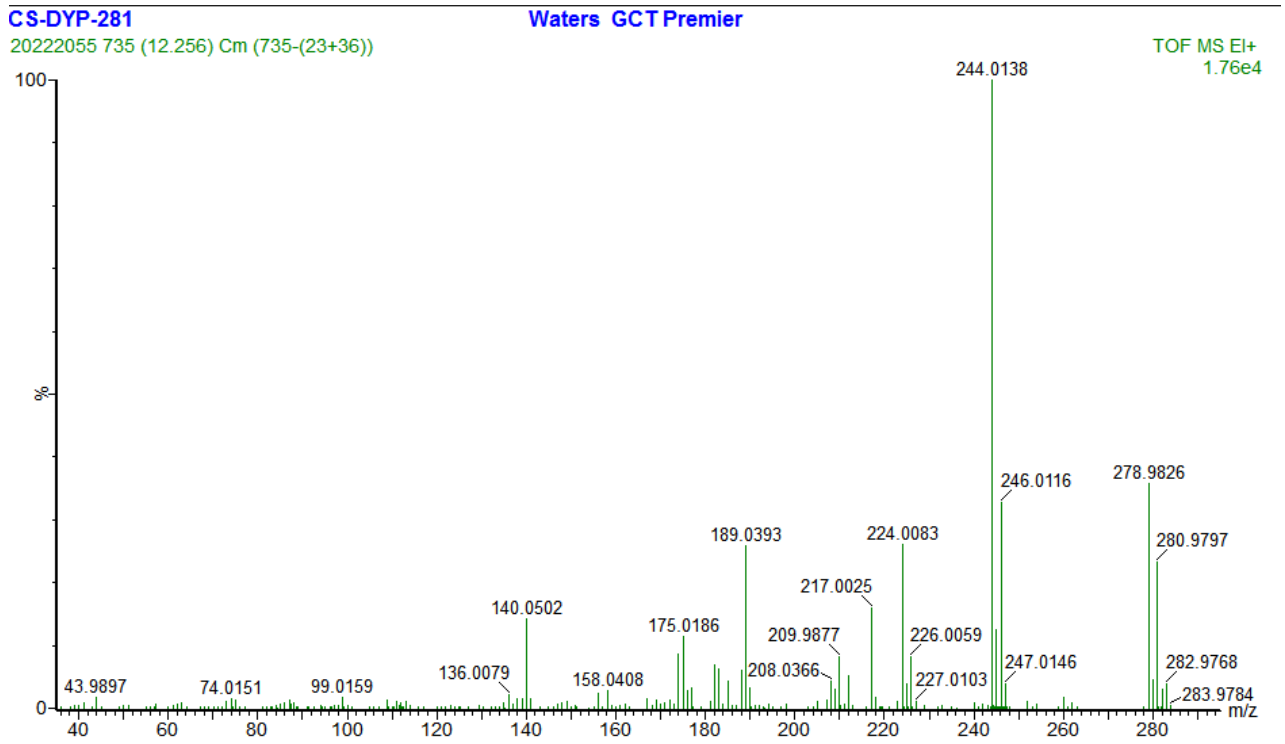
^{13}C NMR spectrum of ***trans*-3da**



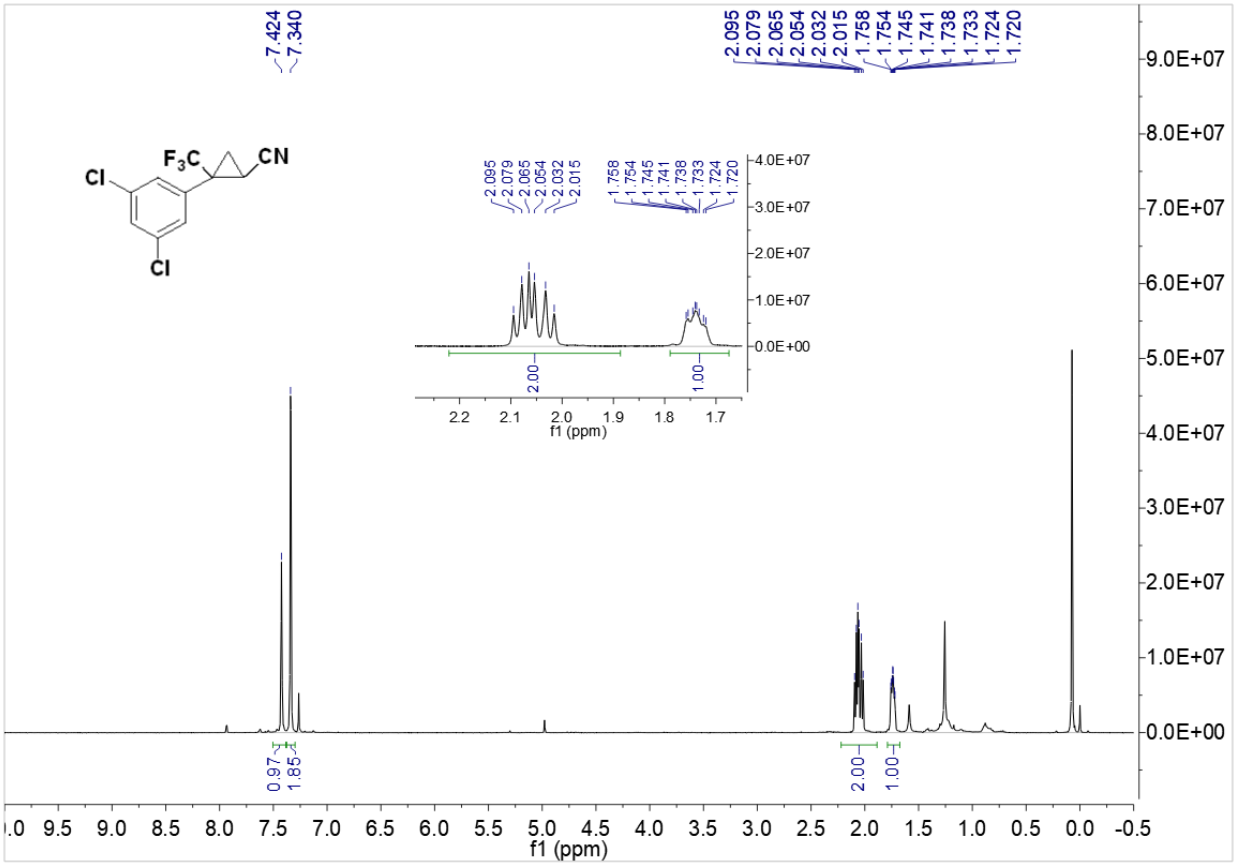
^{19}F NMR spectrum of ***trans*-3da**



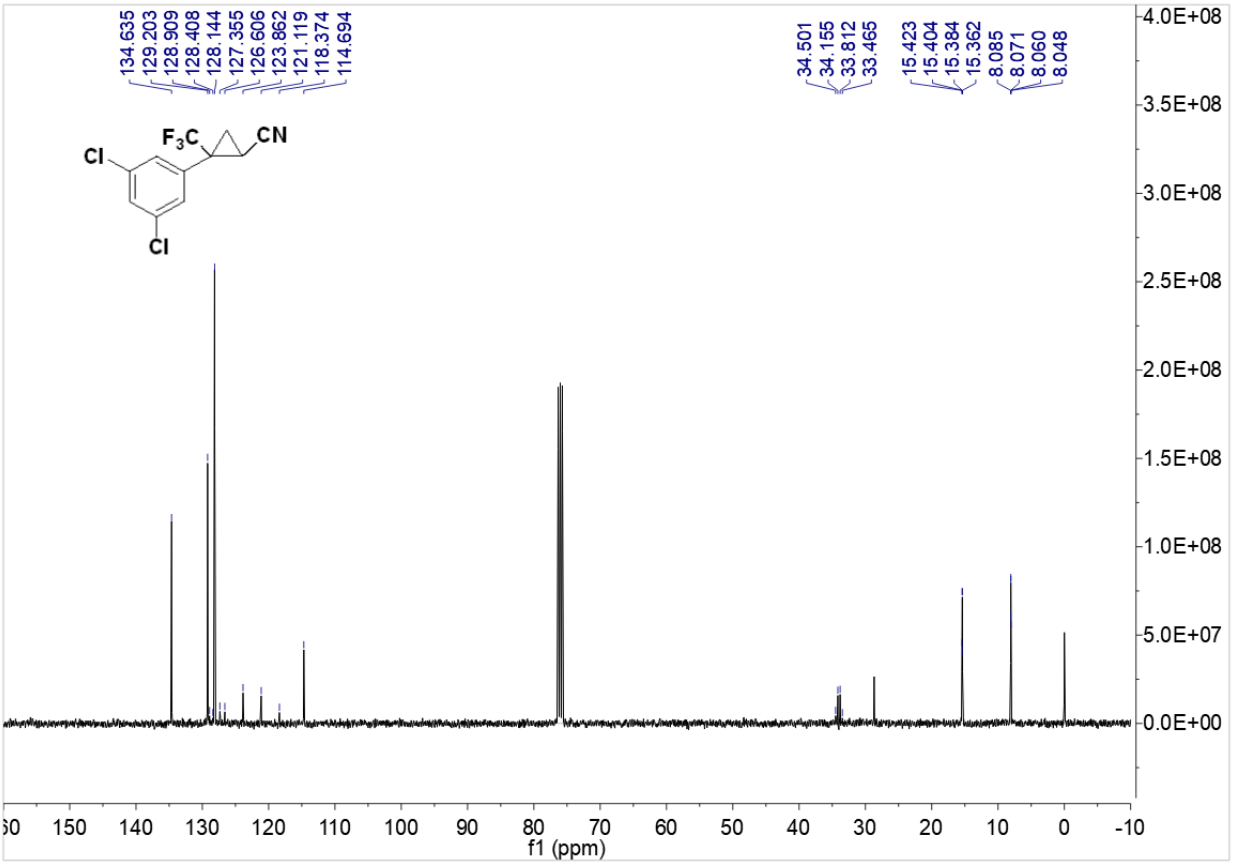
HRMS (EI) spectrum of ***trans*-3da**



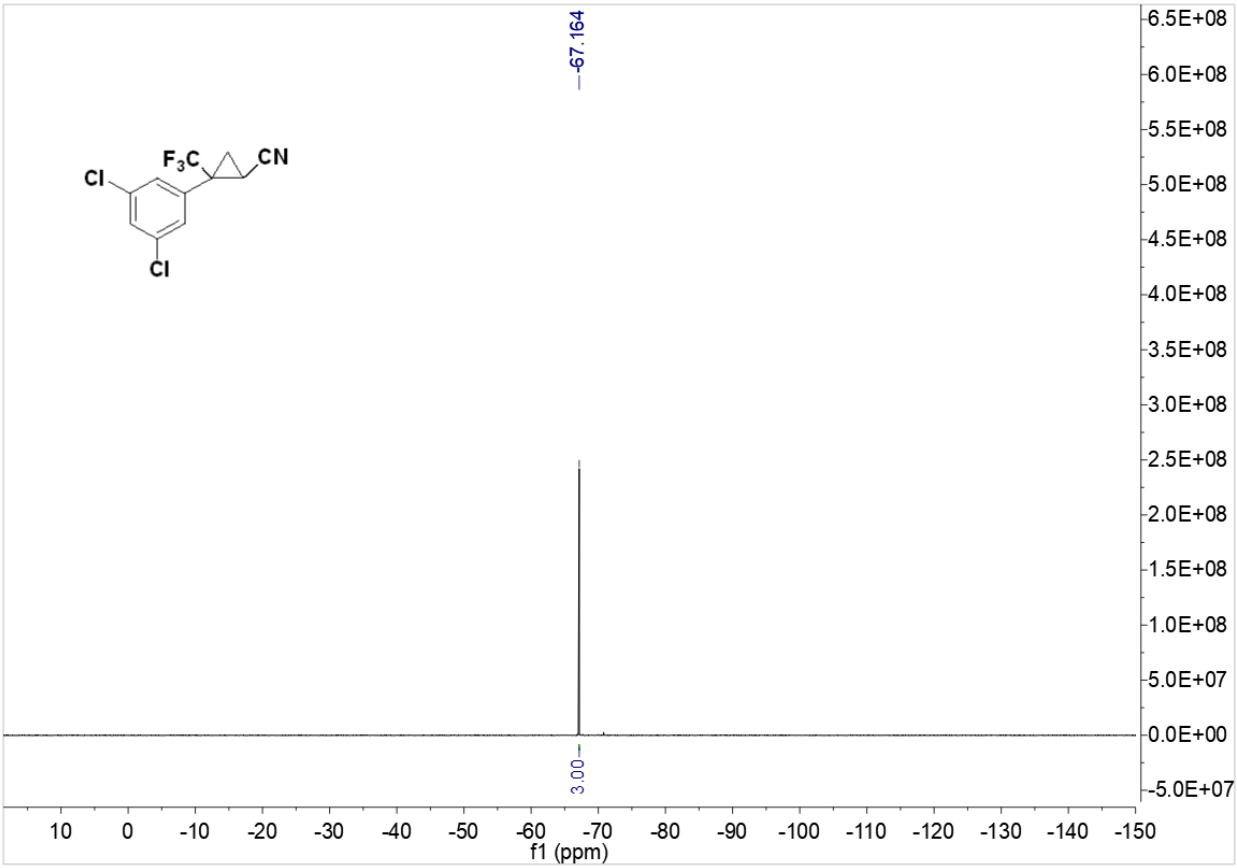
^{1}H NMR spectrum of ***cis*-3da**



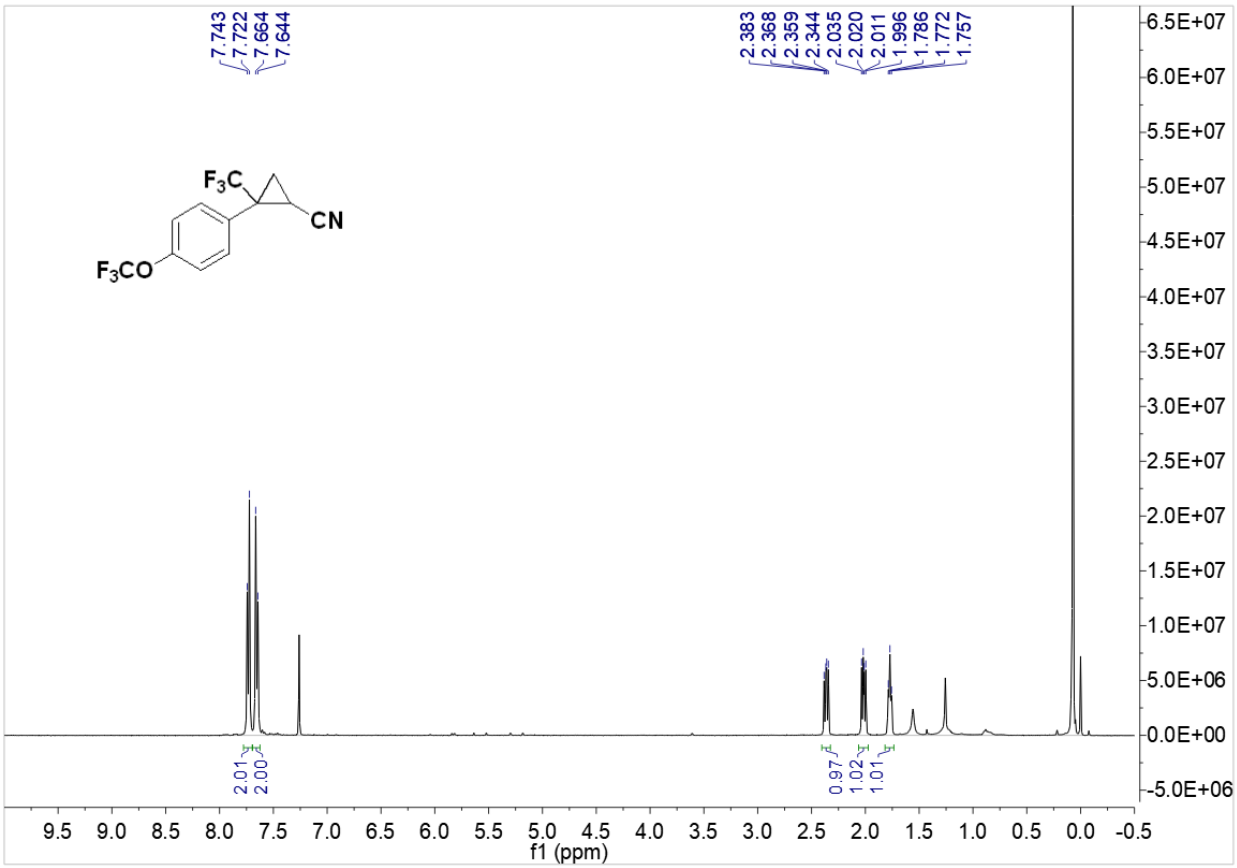
^{13}C NMR spectrum of ***cis*-3da**



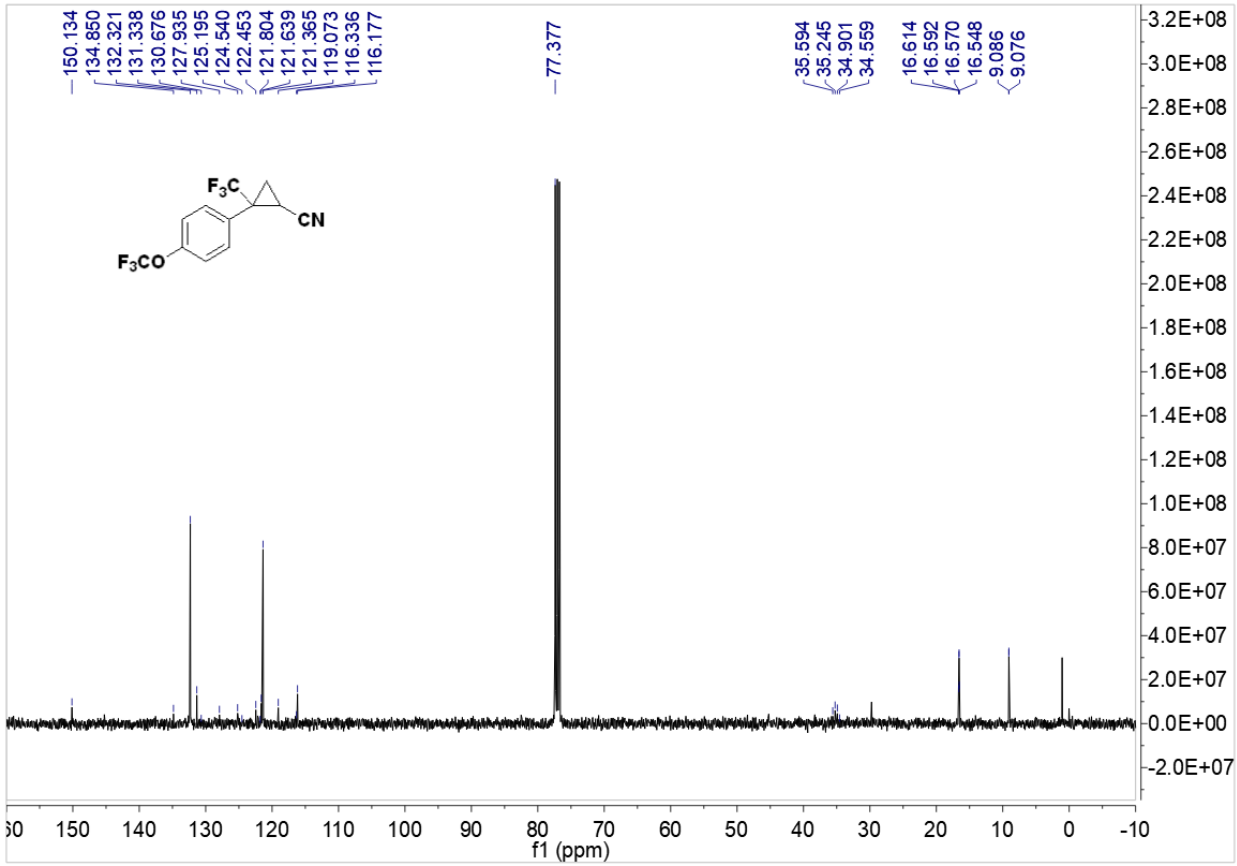
^{19}F NMR spectrum of ***cis*-3da**



^{1}H NMR spectrum of ***trans*-3ea**



^{13}C NMR spectrum of ***trans*-3ea**



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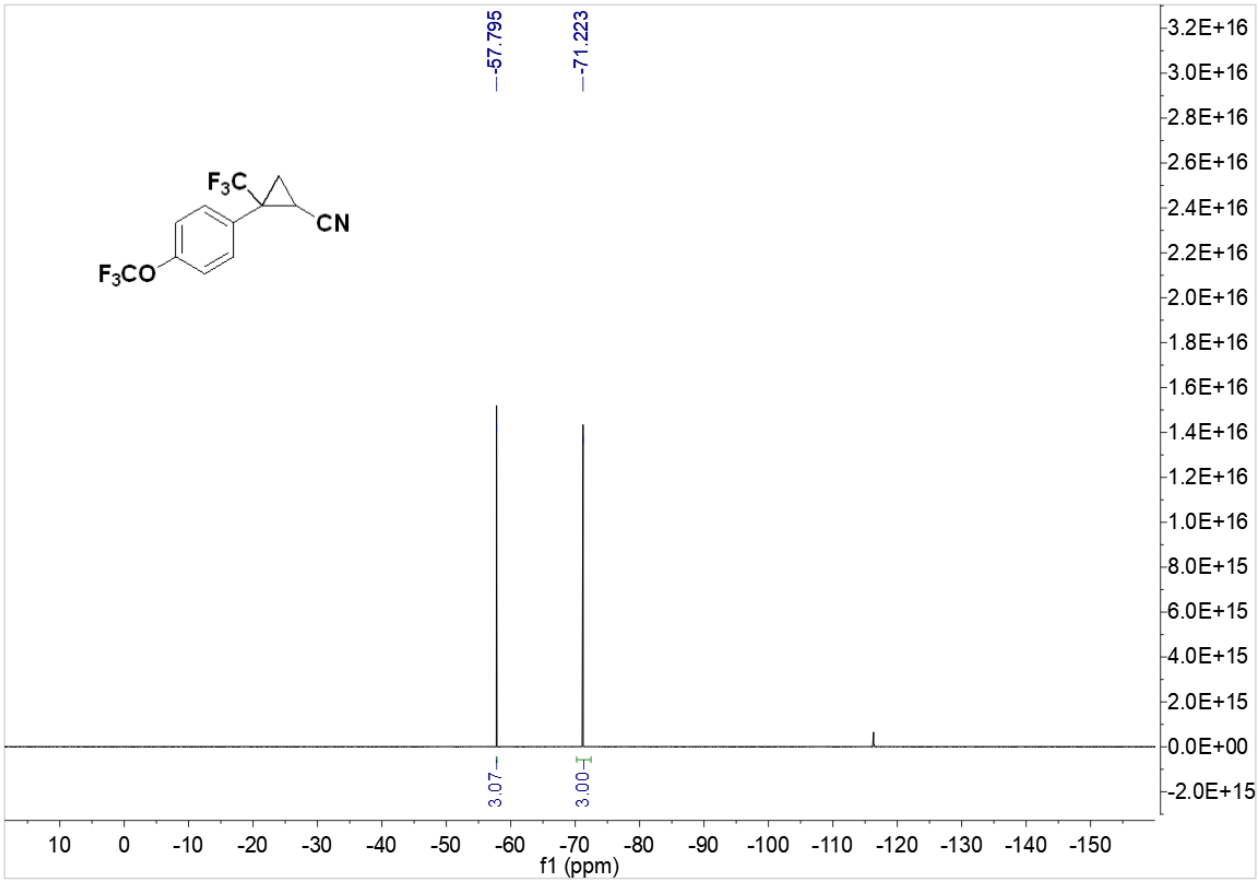
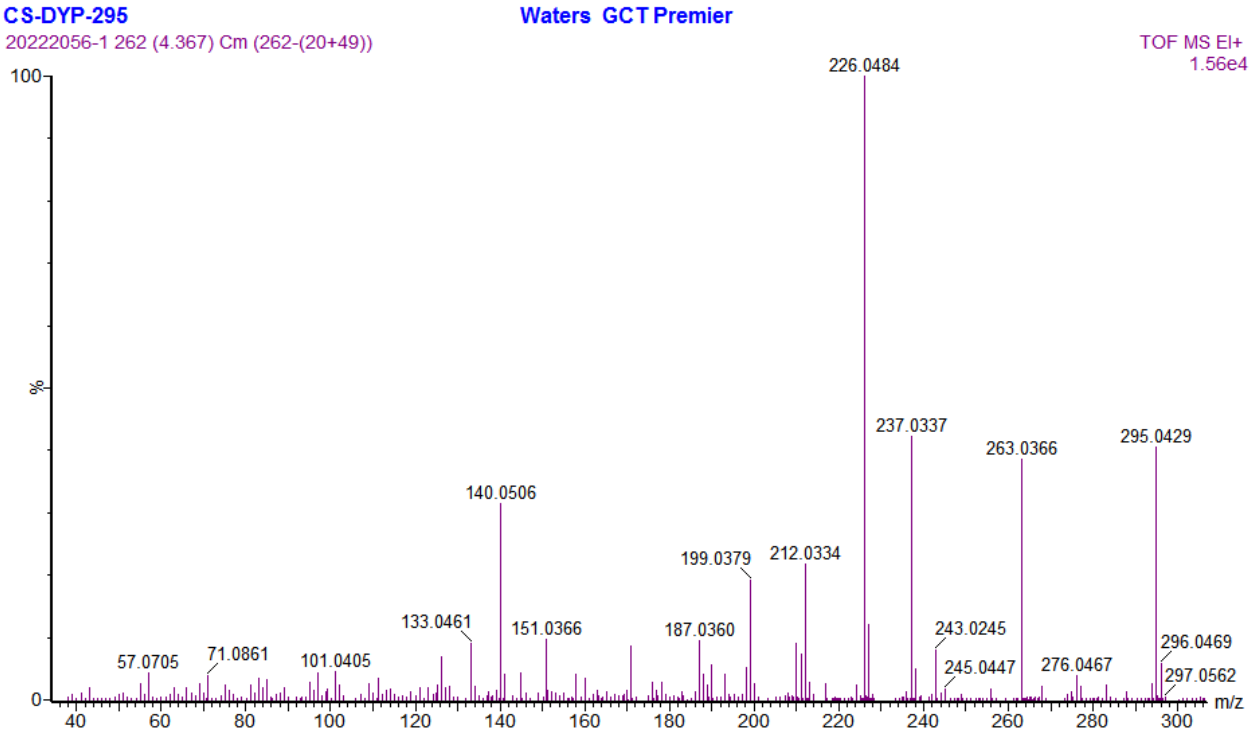
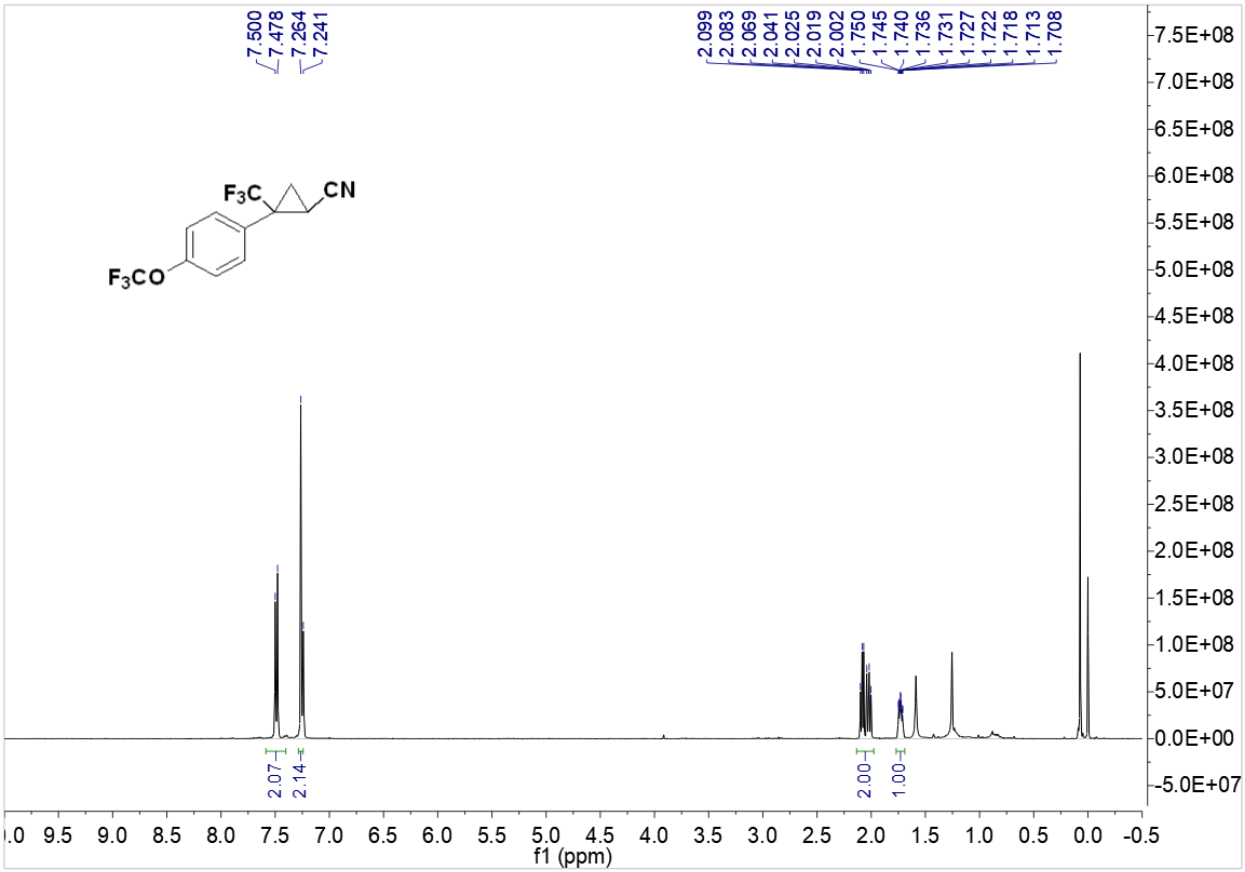


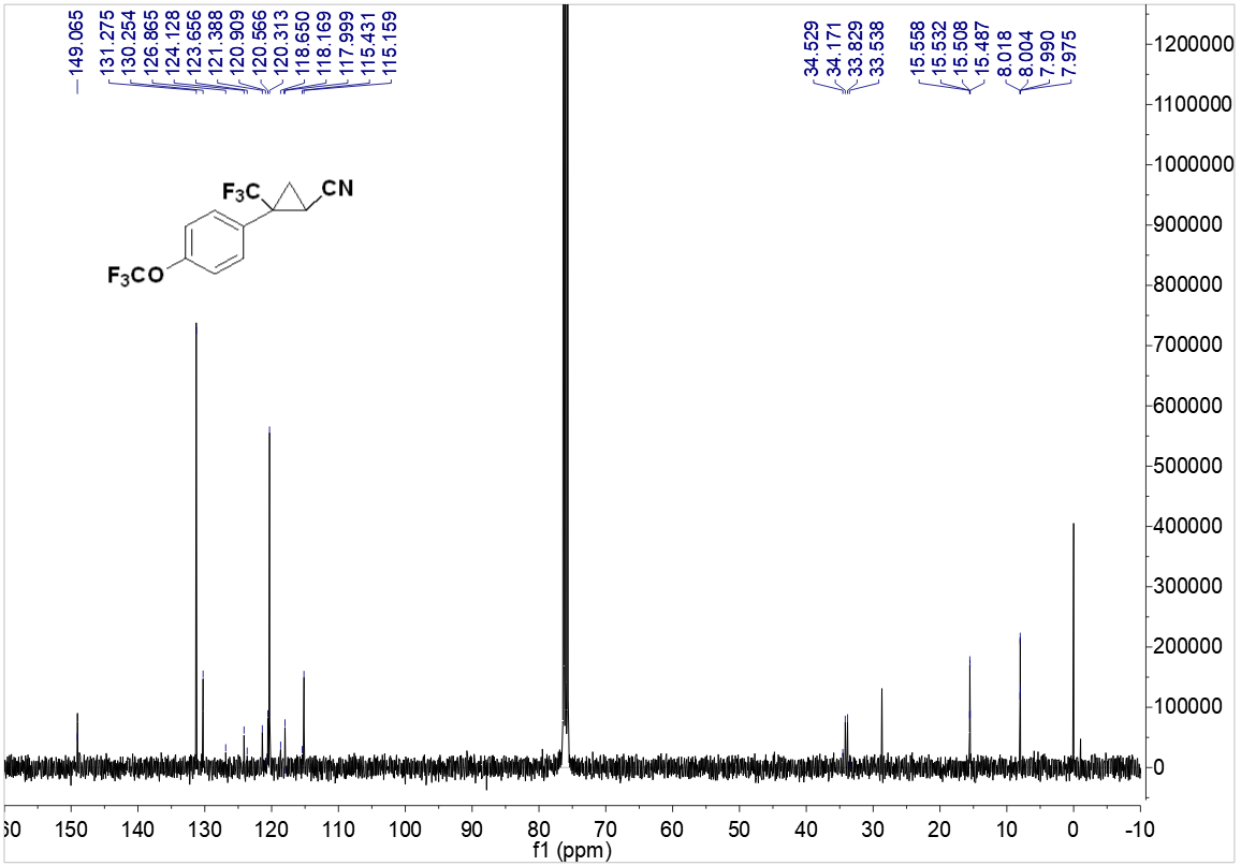
HRMS (EI) spectrum of ***trans*-3ea**



^{1}H NMR spectrum of ***cis*-3ea**



^{13}C NMR spectrum of ***cis*-3ea**



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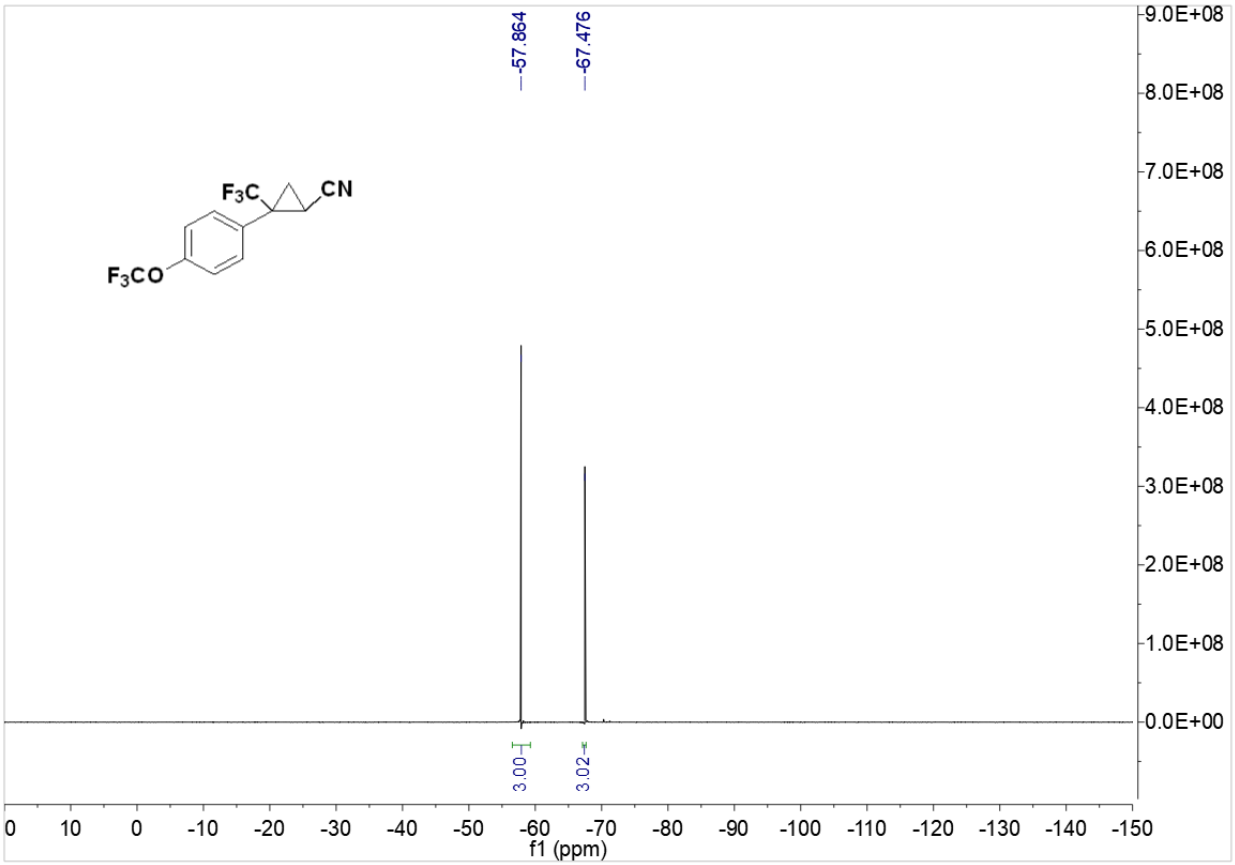
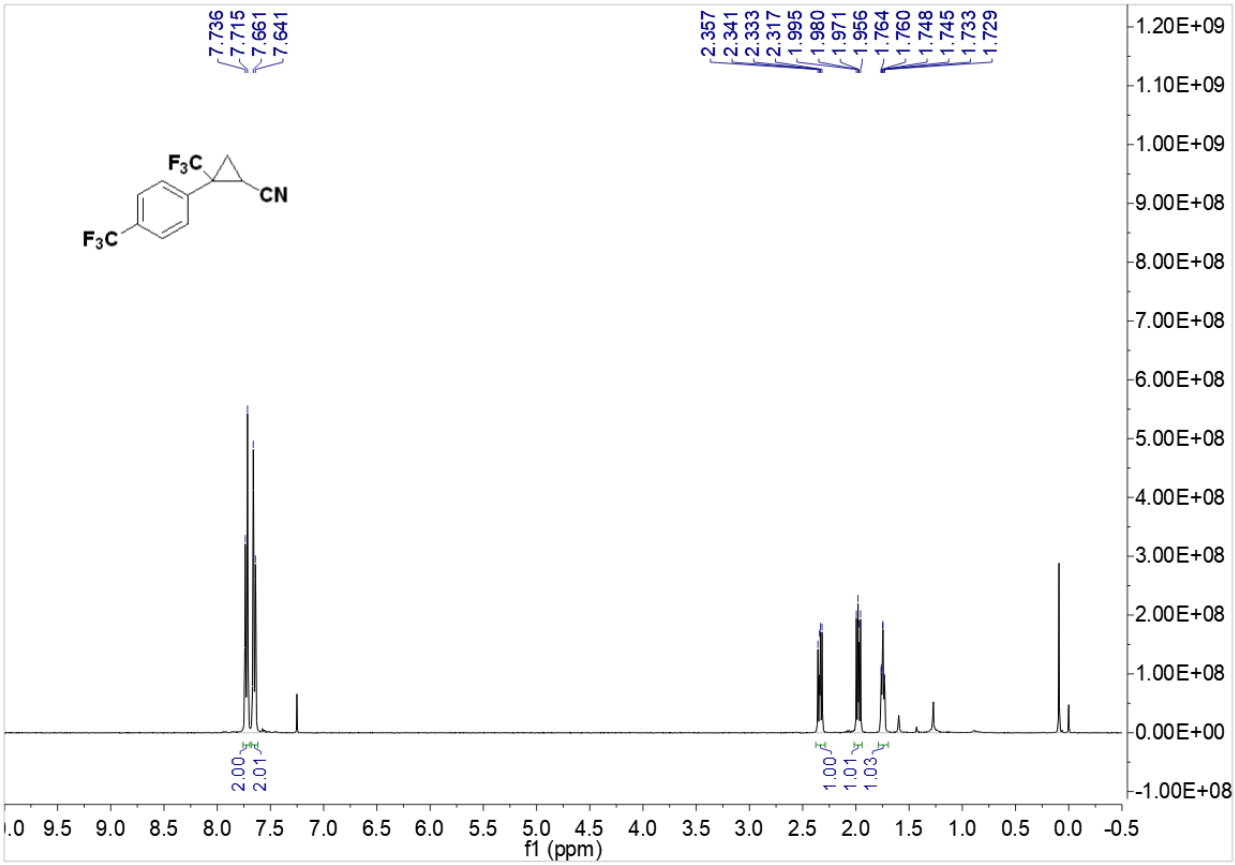
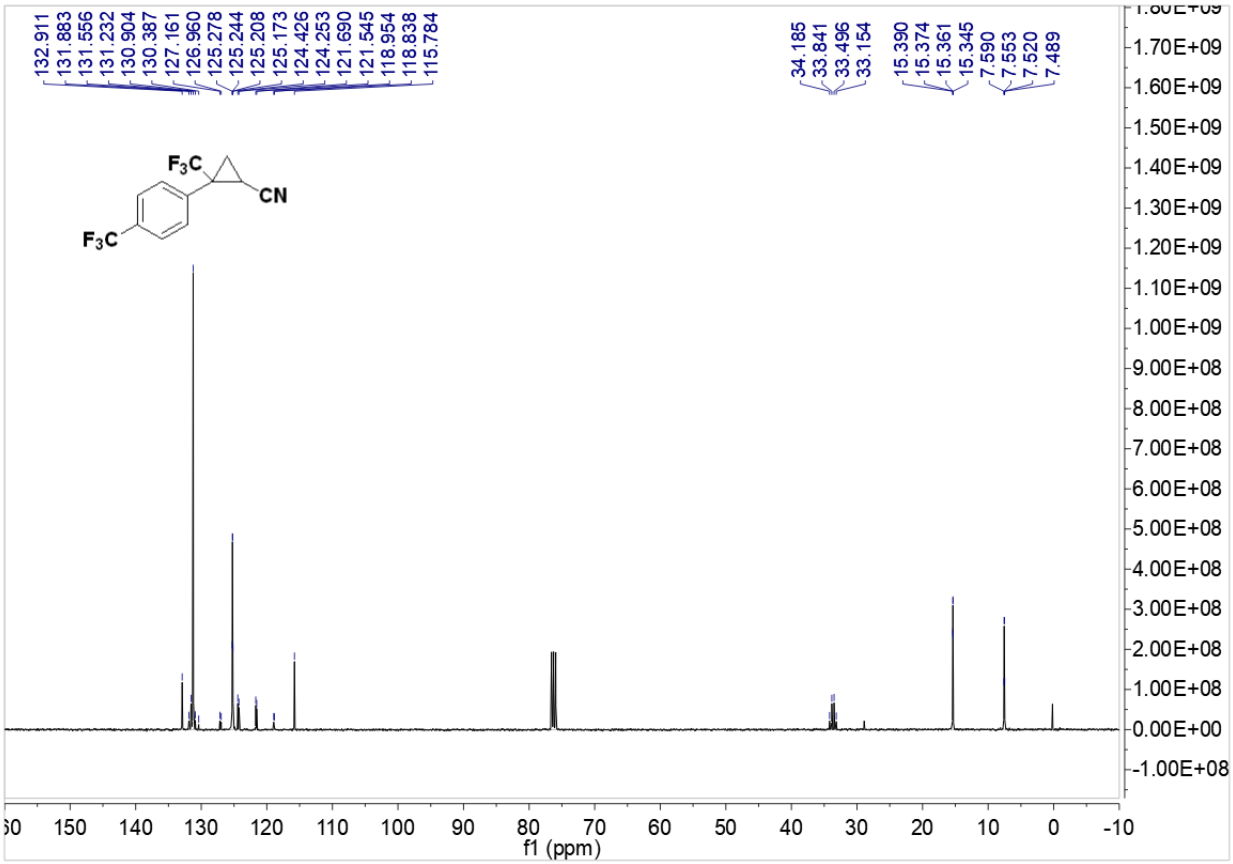


^{1}H NMR spectrum of ***trans*-3fa**



^{13}C NMR spectrum of ***trans*-3fa**



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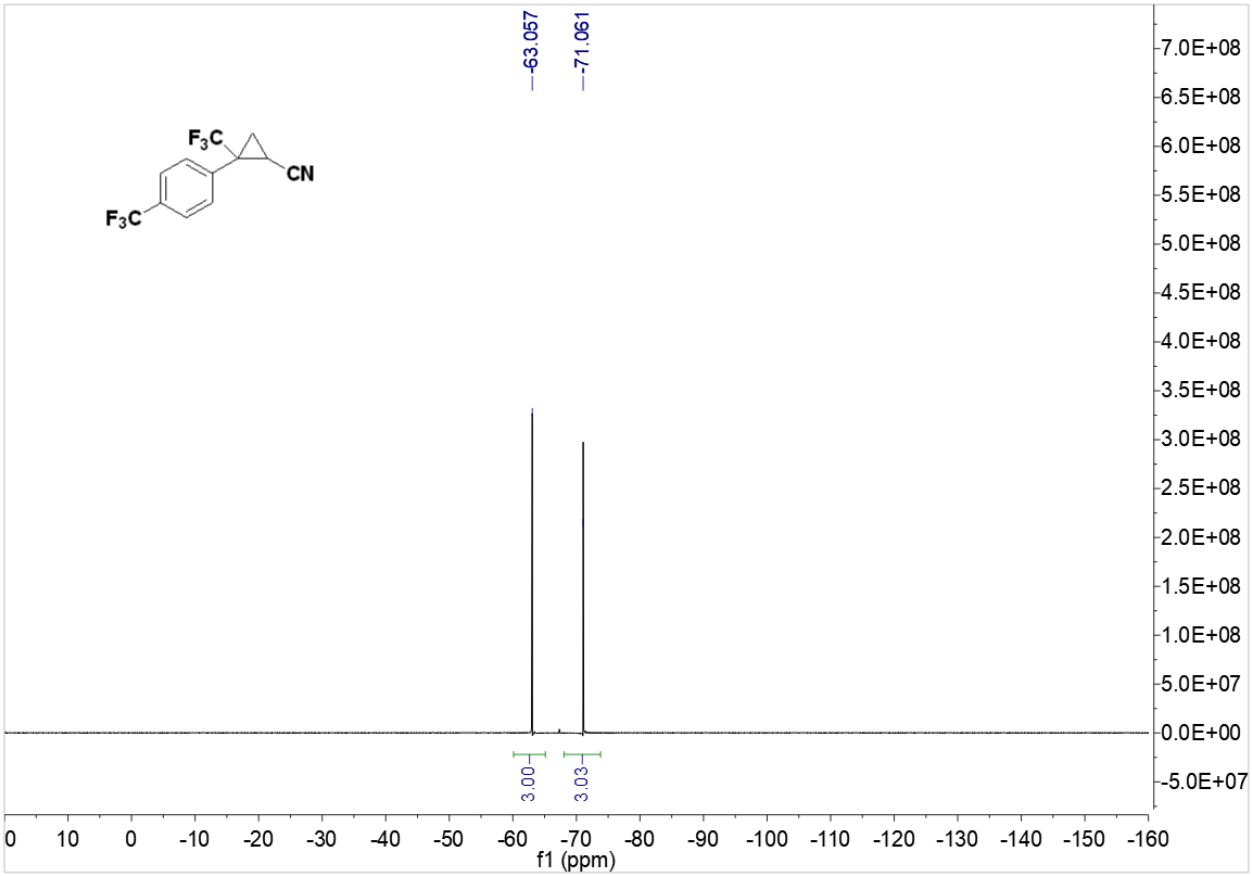
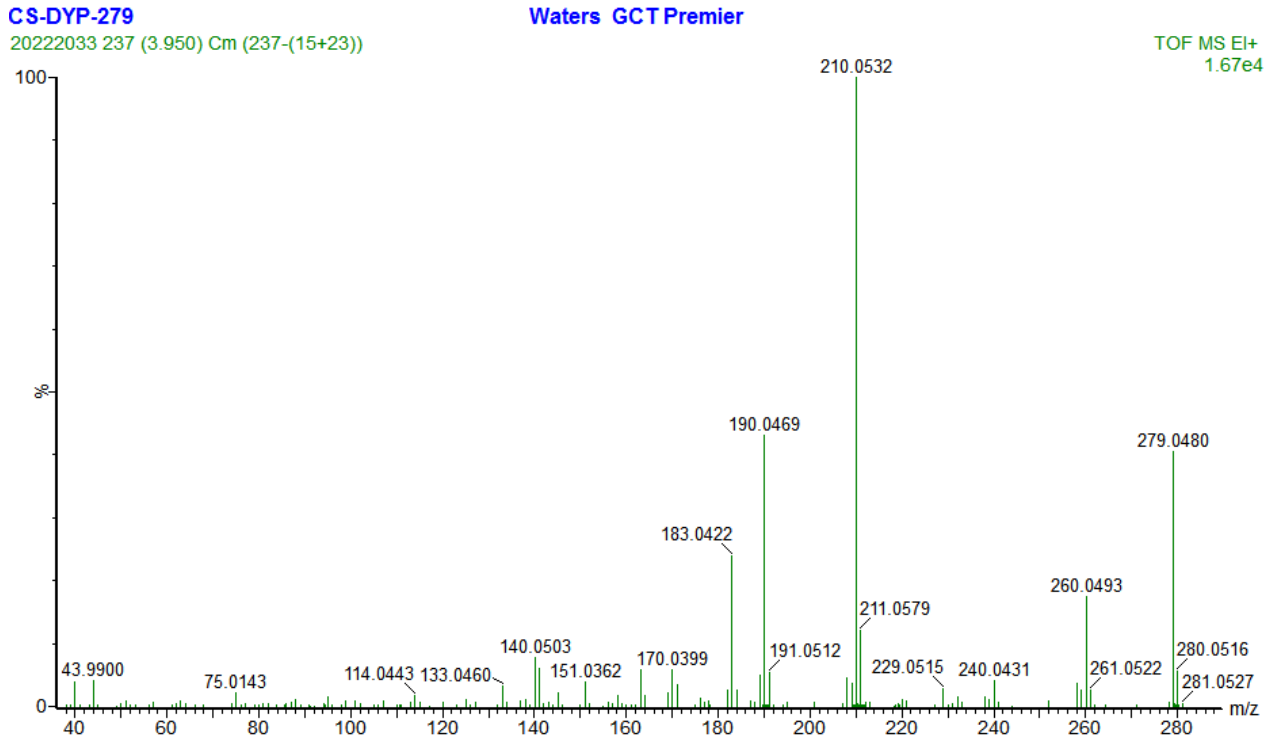
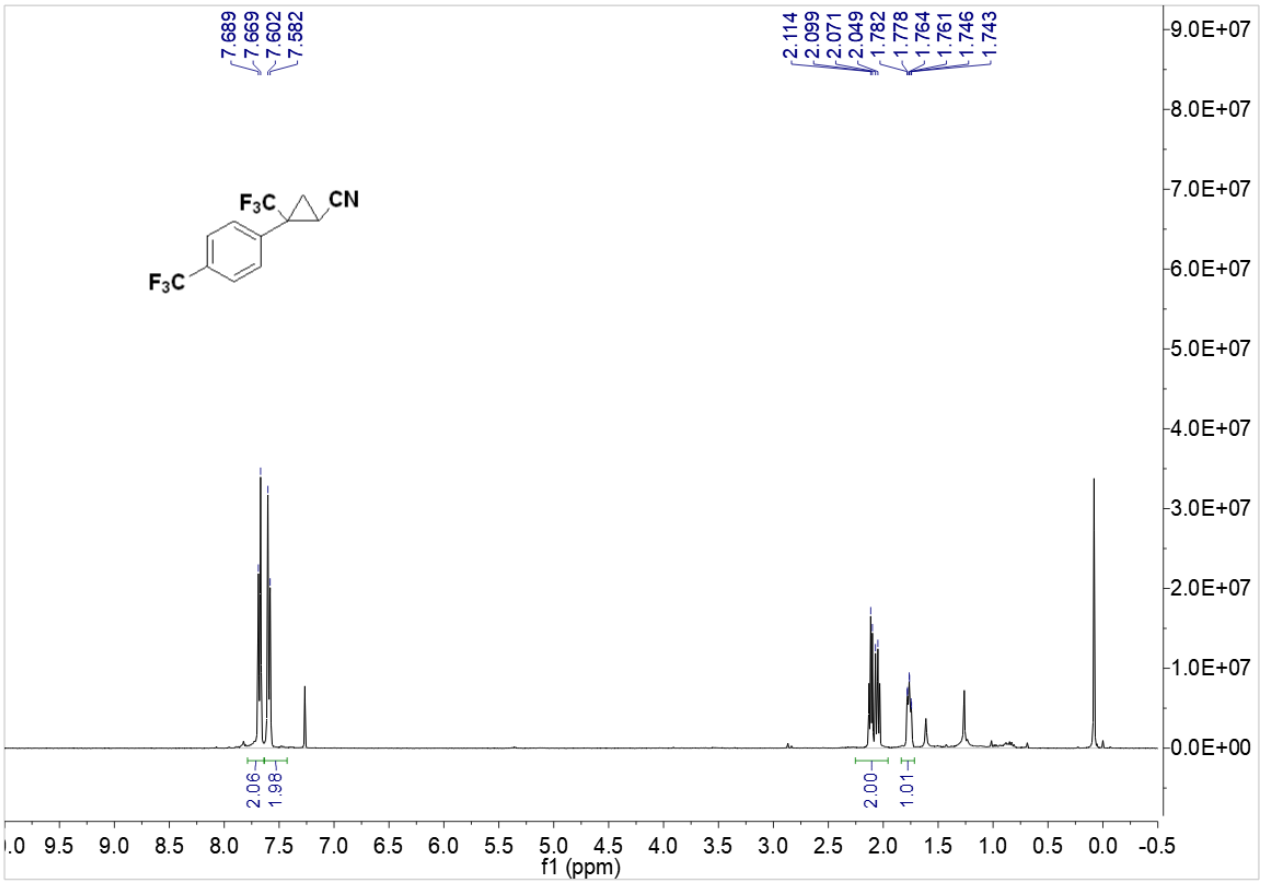


HRMS (EI) spectrum of ***trans*-3fa**



^{1}H NMR spectrum of ***cis*-3fa**



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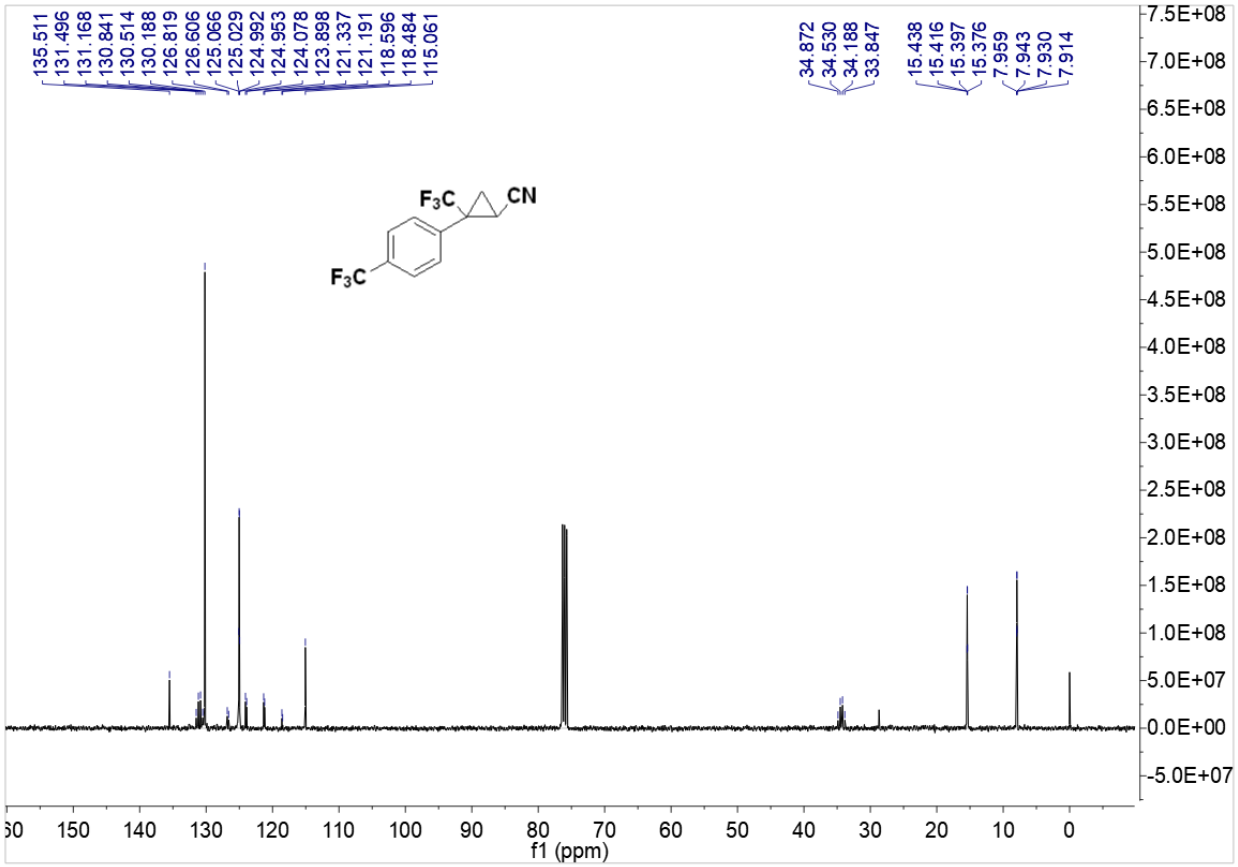
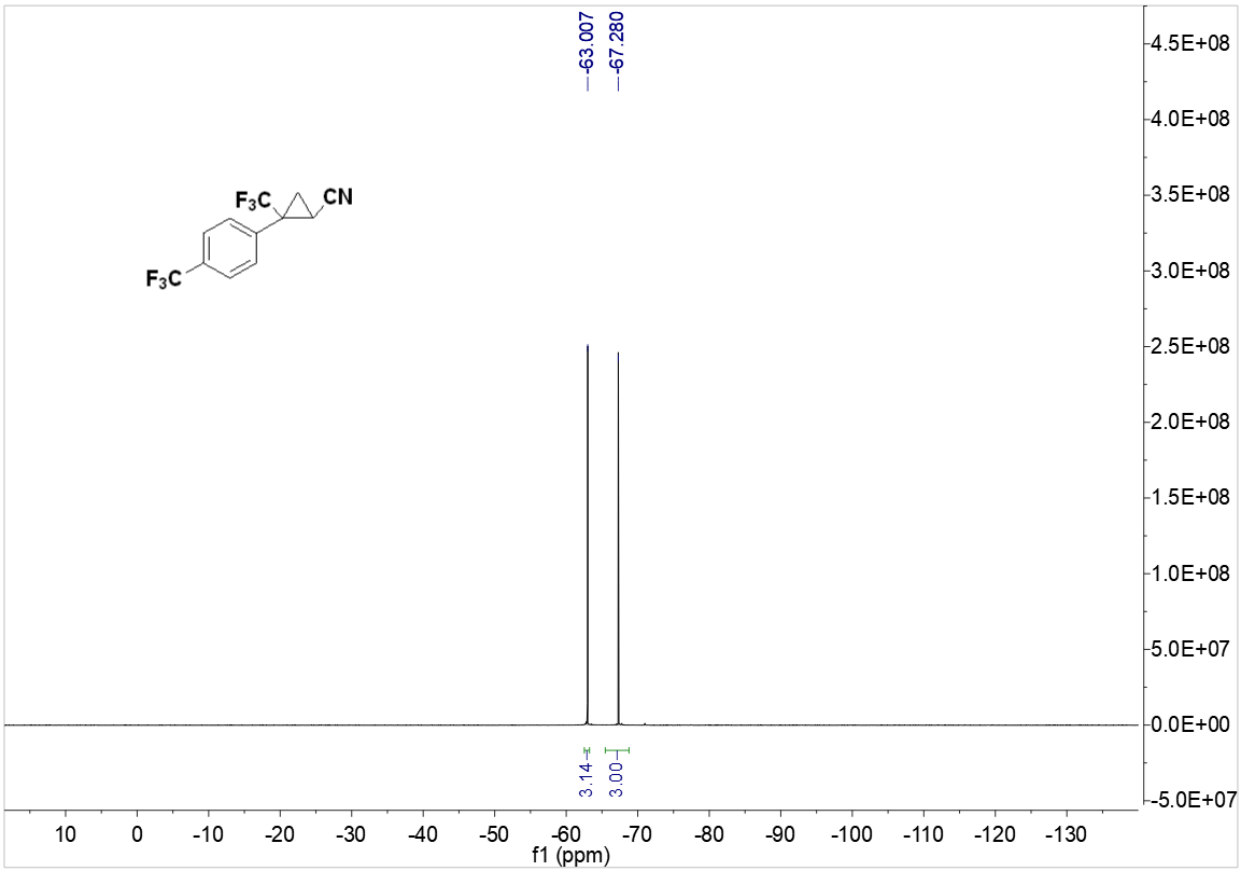
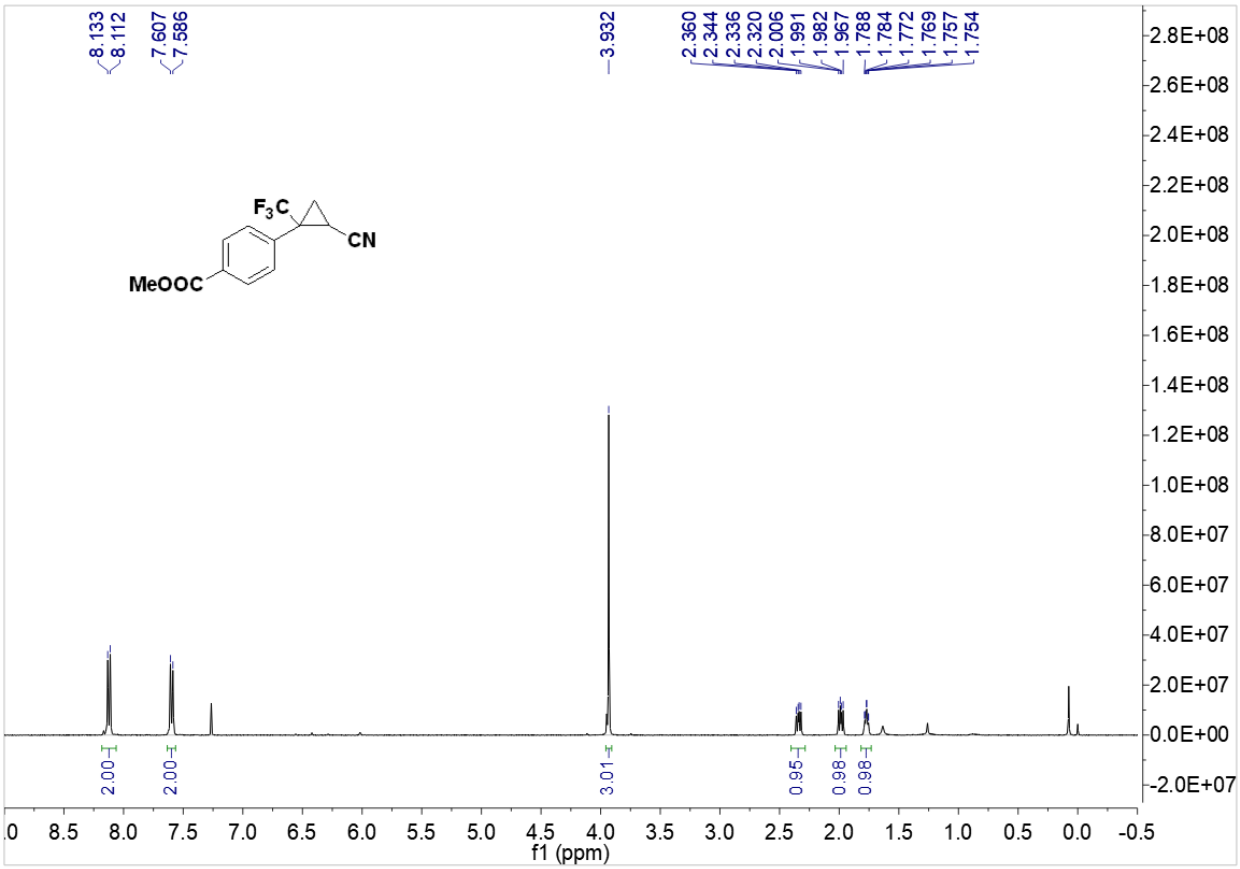


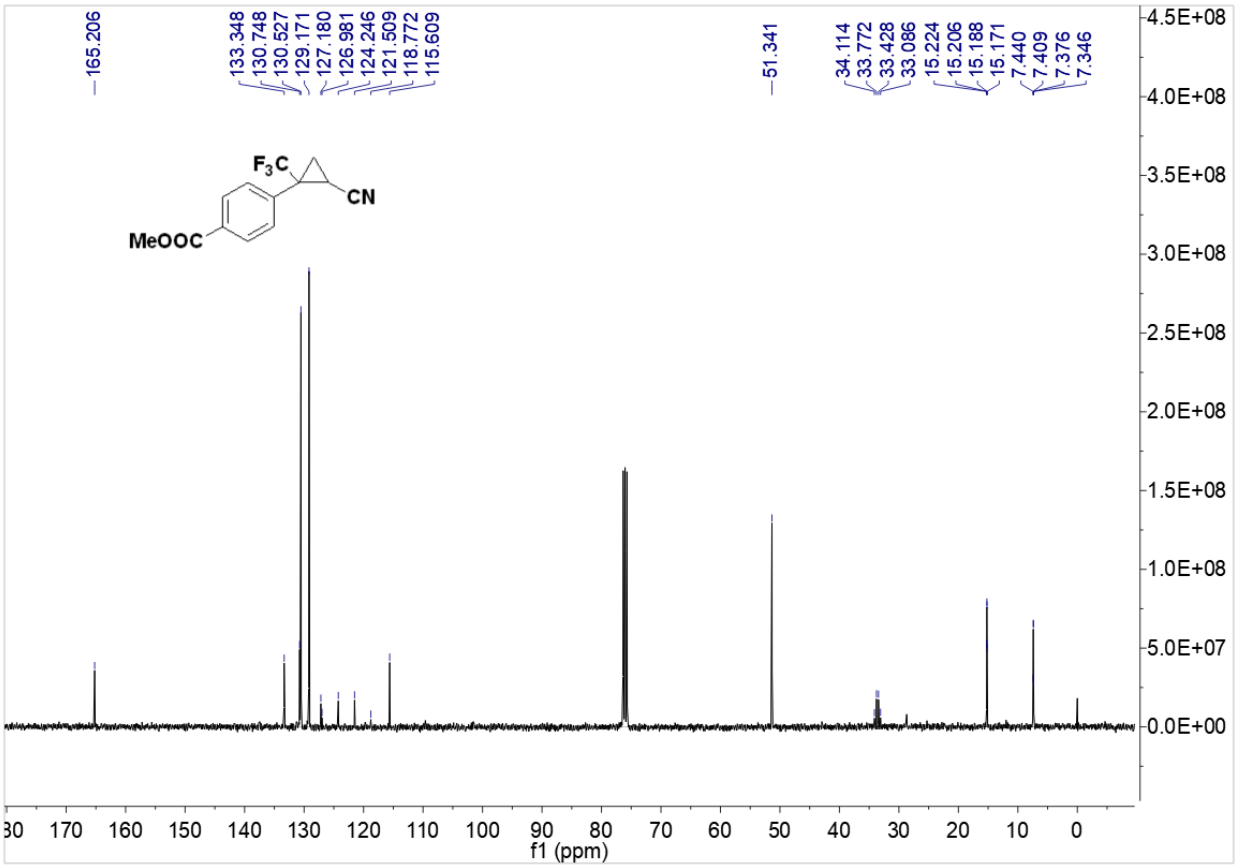
^{19}F NMR spectrum of ***cis*-3fa**



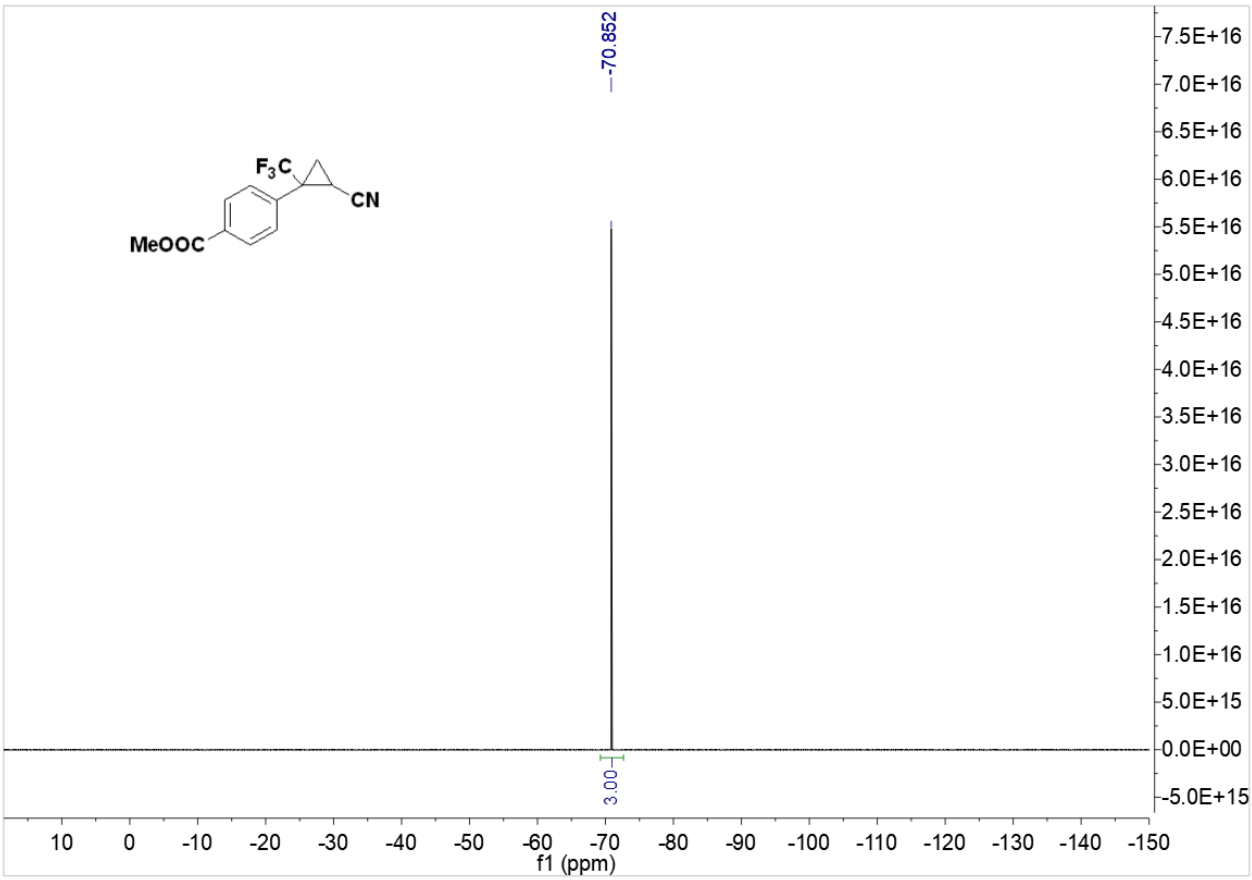
^{1}H NMR spectrum of ***trans*-3ga**



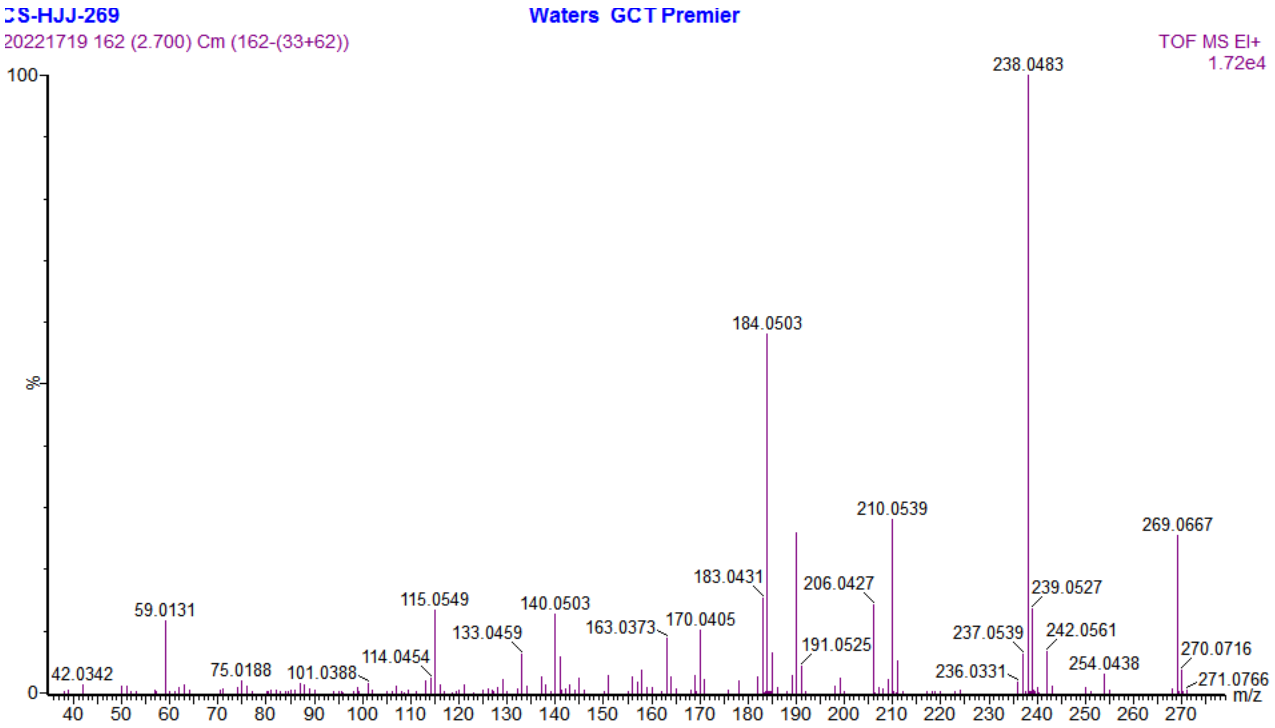
^{13}C NMR spectrum of ***trans*-3ga**



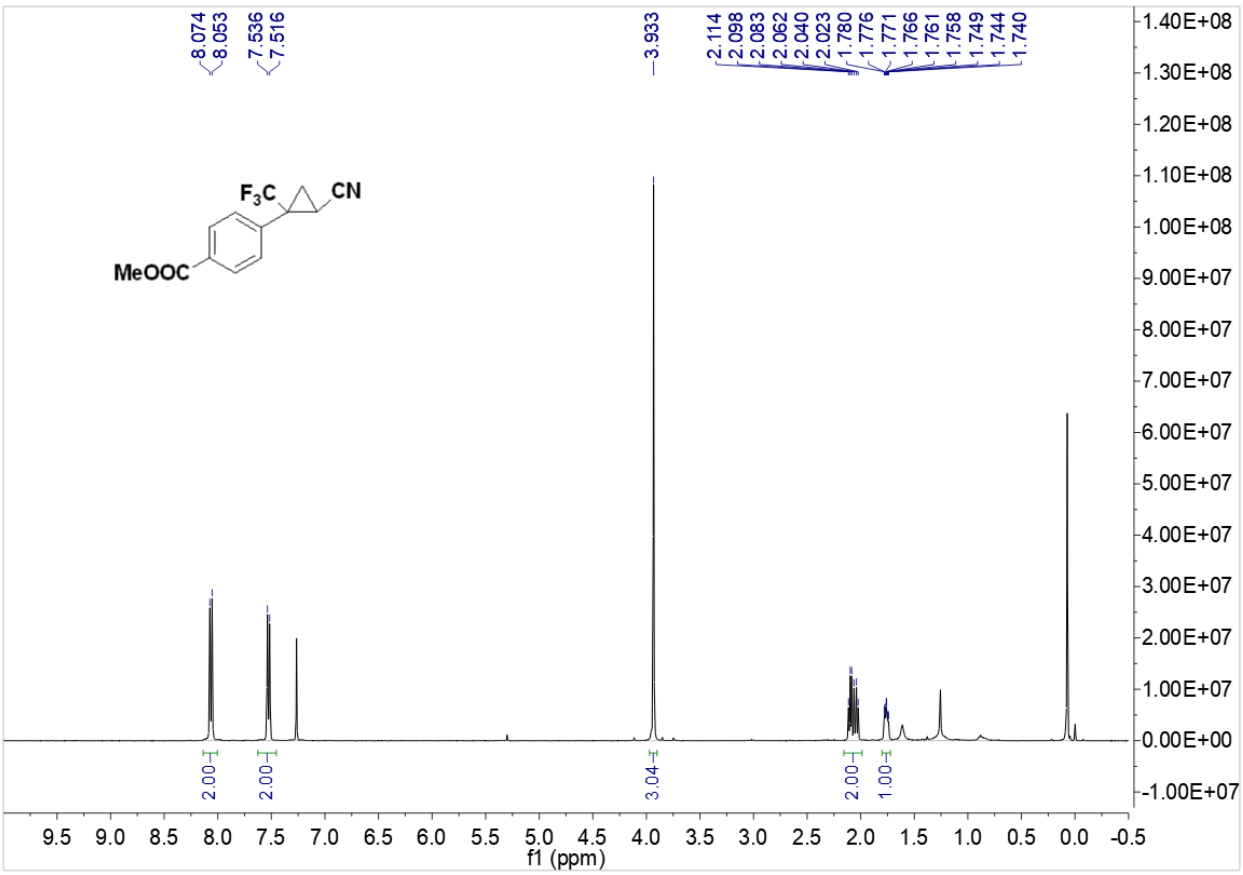
^{19}F NMR spectrum of ***trans*-3ga**



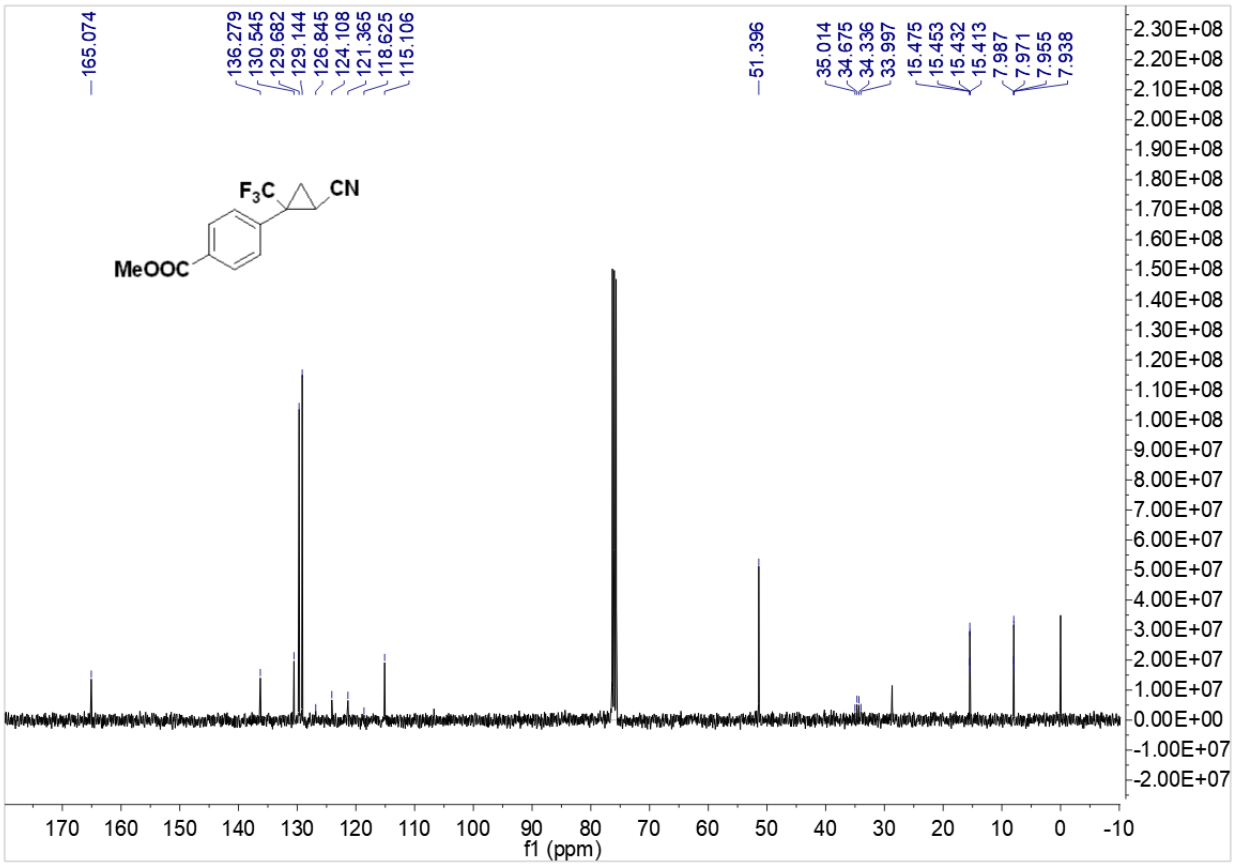
HRMS (EI) spectrum of *trans*-3ga



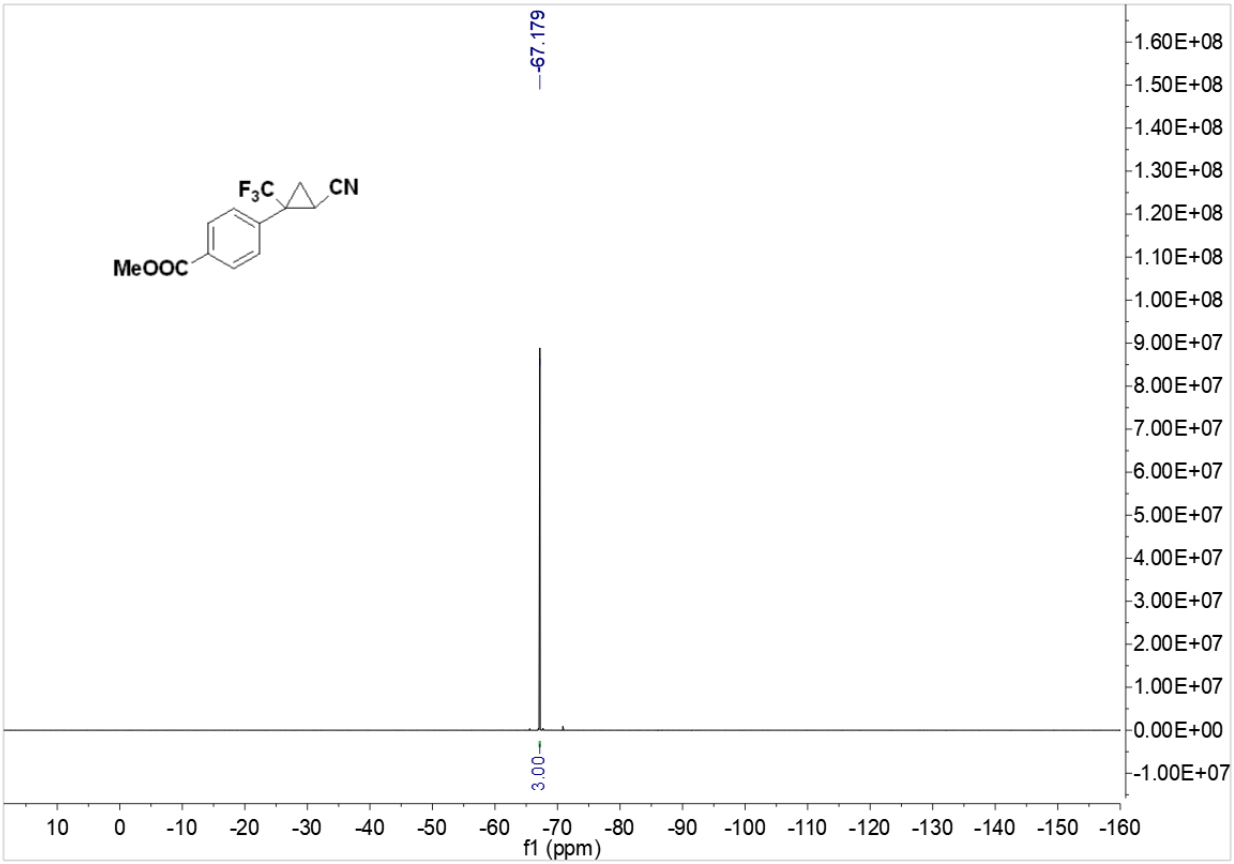
^{1}H NMR spectrum of ***cis*-3ga**



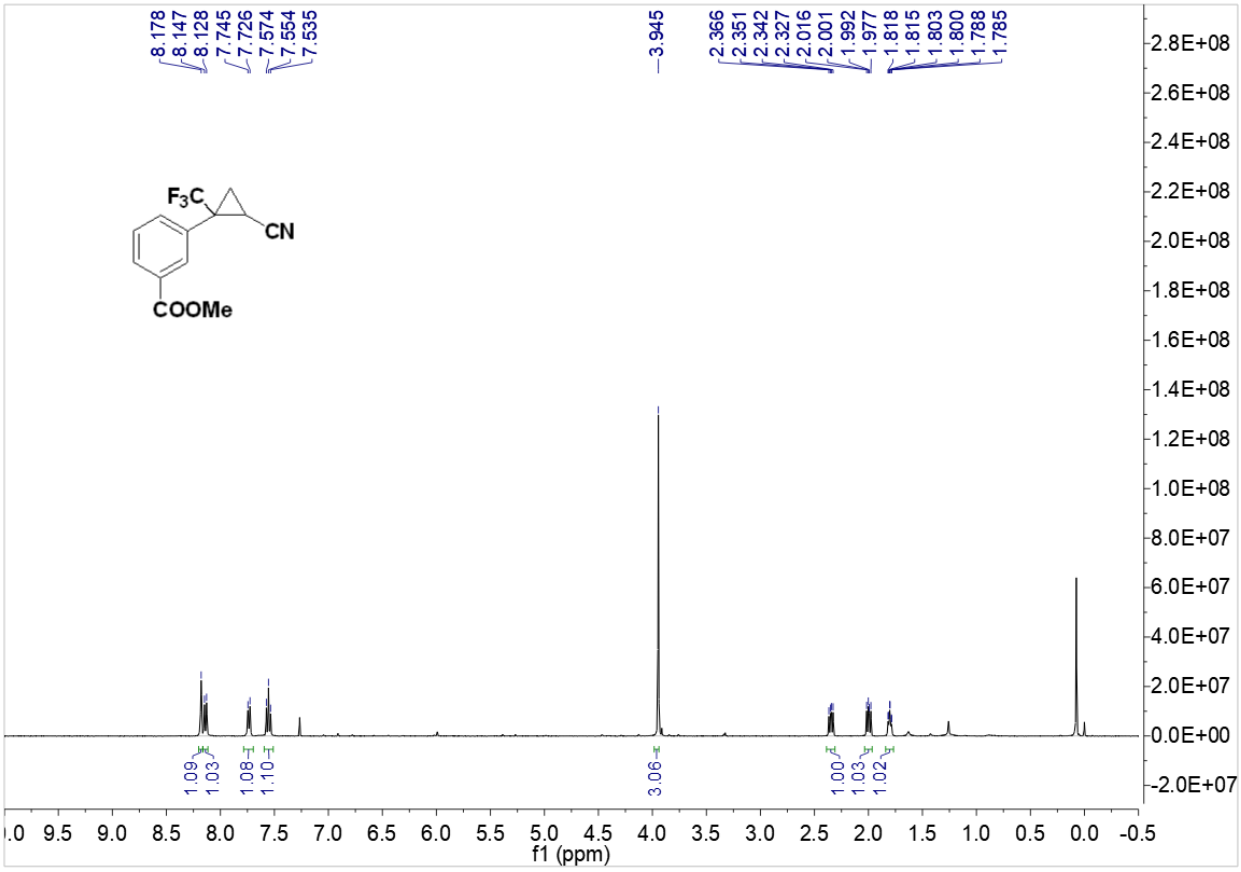
^{13}C NMR spectrum of ***cis*-3ga**



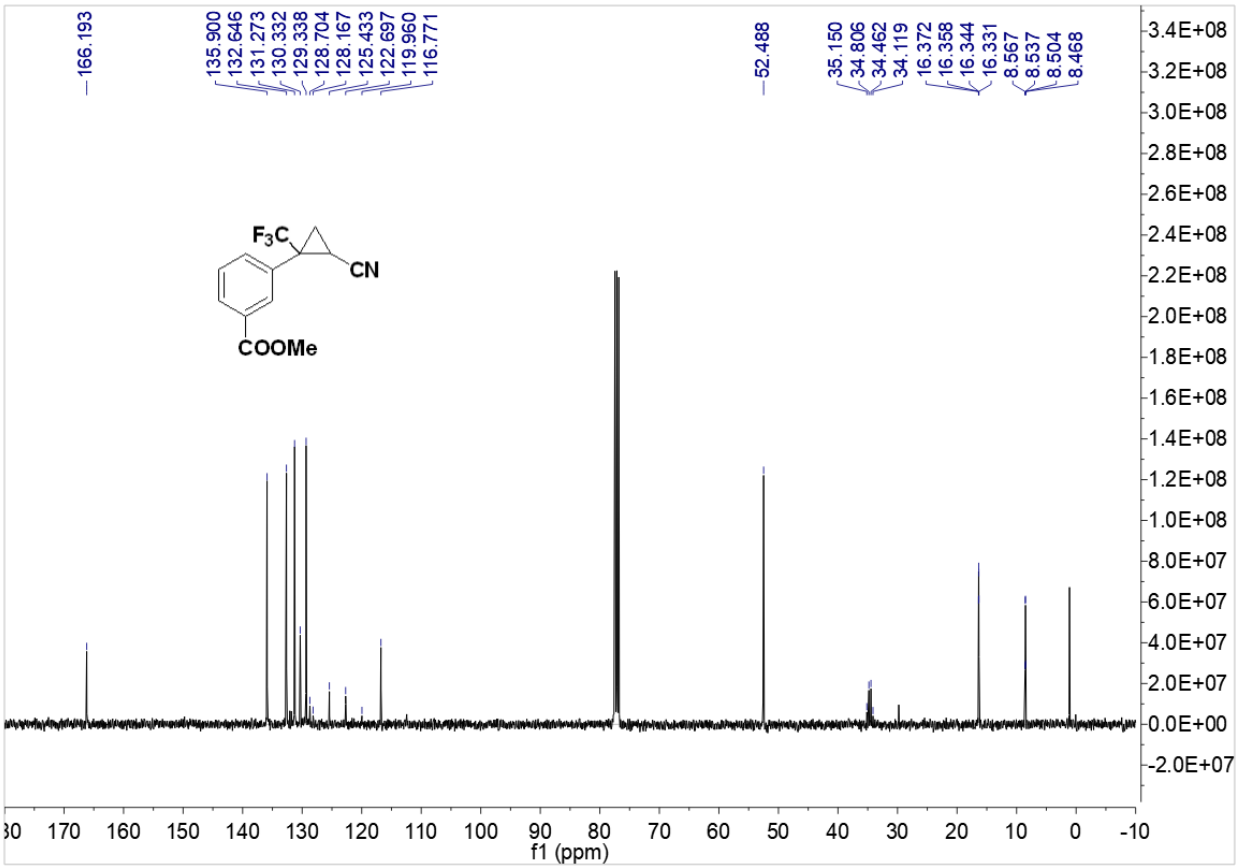
^{19}F NMR spectrum of ***cis*-3ga**



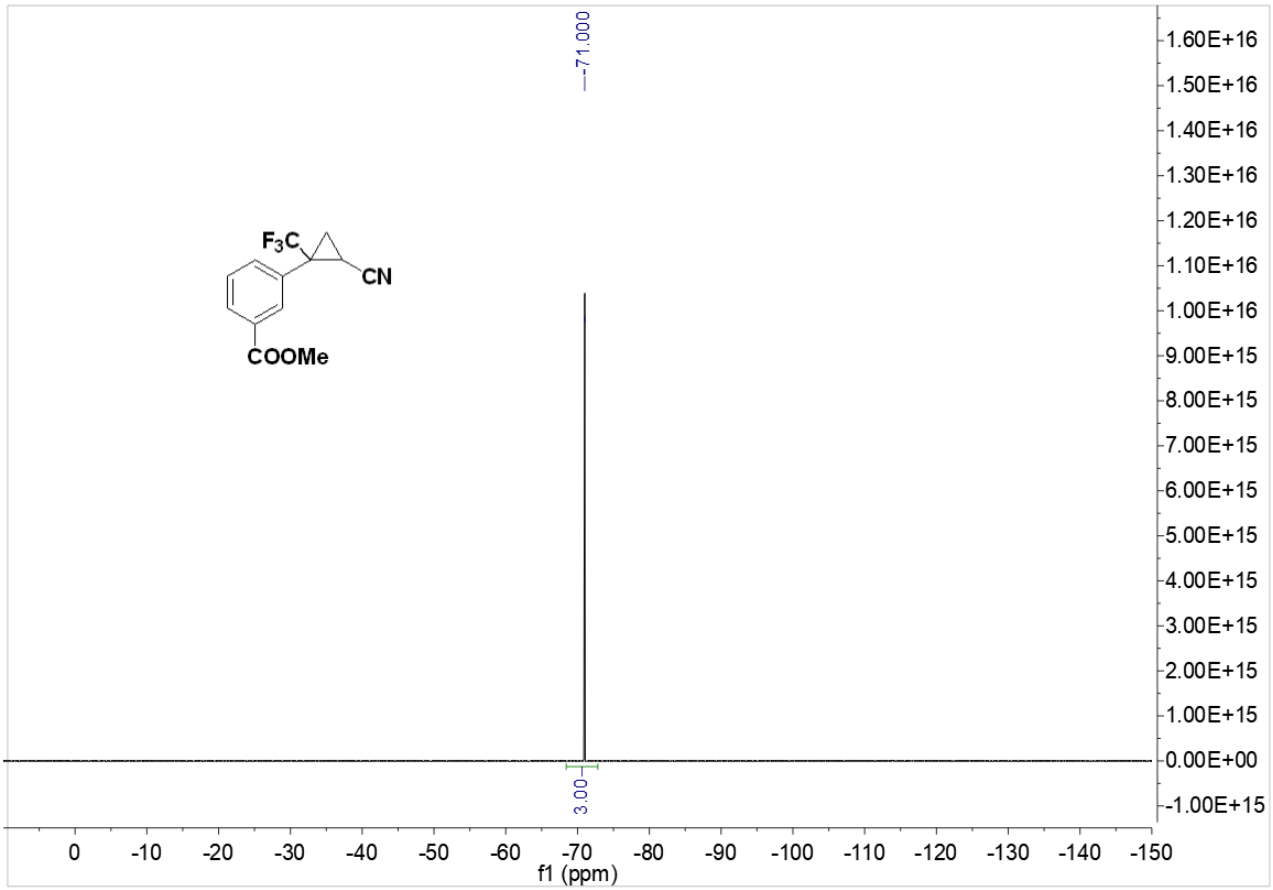
^{1}H NMR spectrum of ***trans*-3ha**



^{13}C NMR spectrum of ***trans*-3ha**



^{19}F NMR spectrum of ***trans*-3ha**



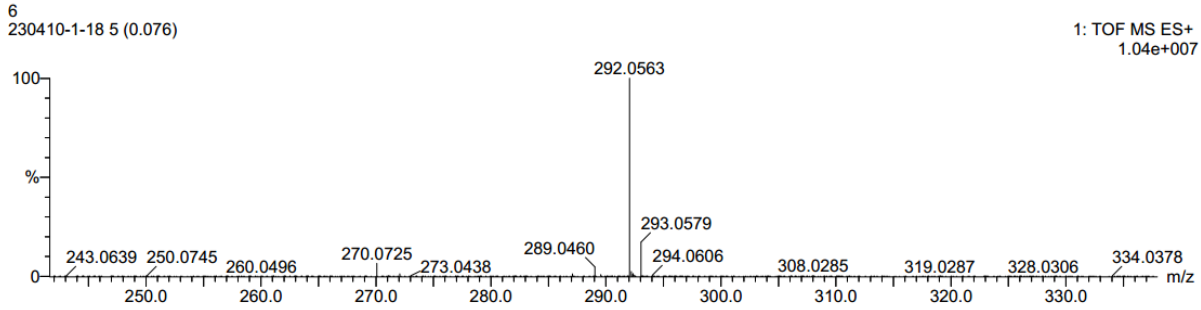
HRMS (ESI) spectrum of ***trans*-3ha**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

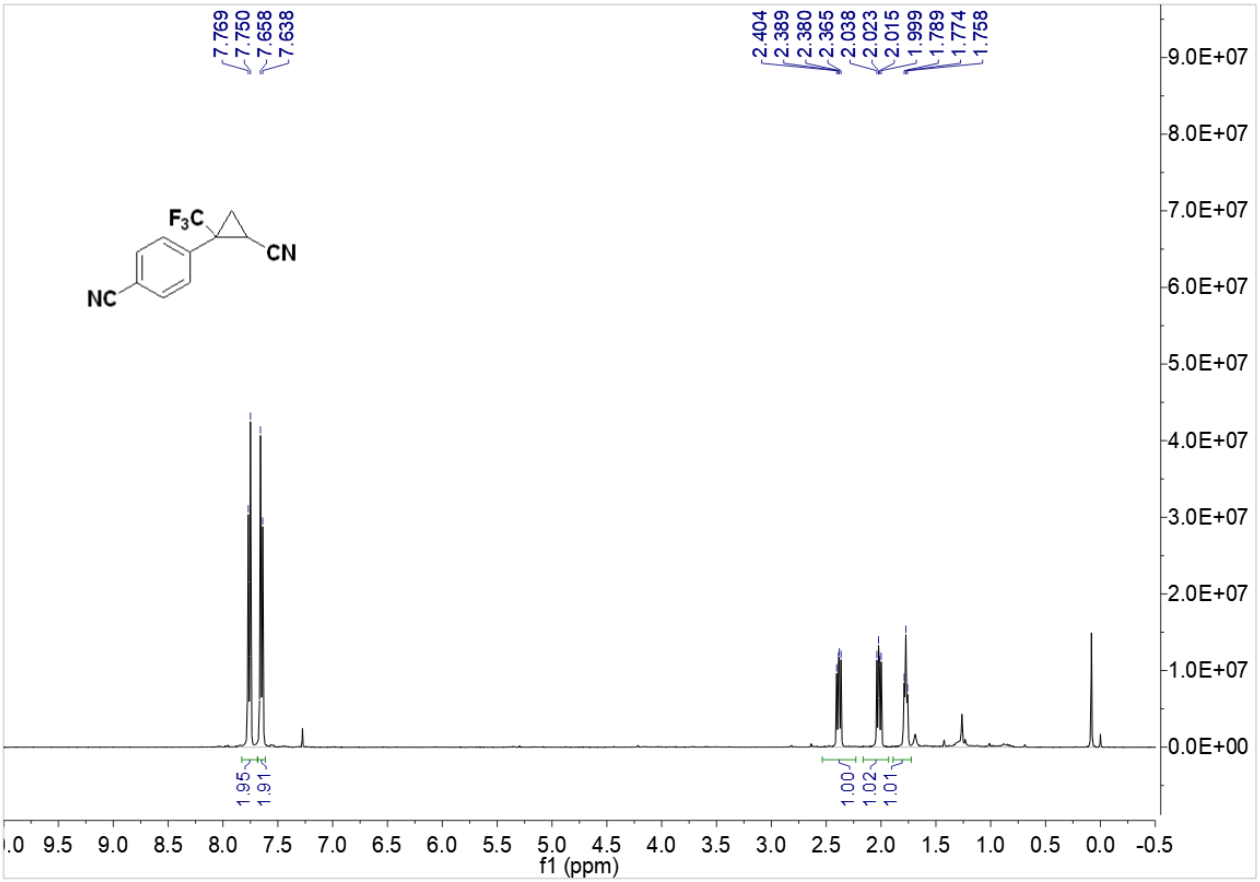
Monoisotopic Mass, Even Electron Ions
385 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 13-13 H: 10-10 N: 0-20 O: 0-20 F: 3-3 Na: 0-3

6
230410-1-18 5 (0.076)

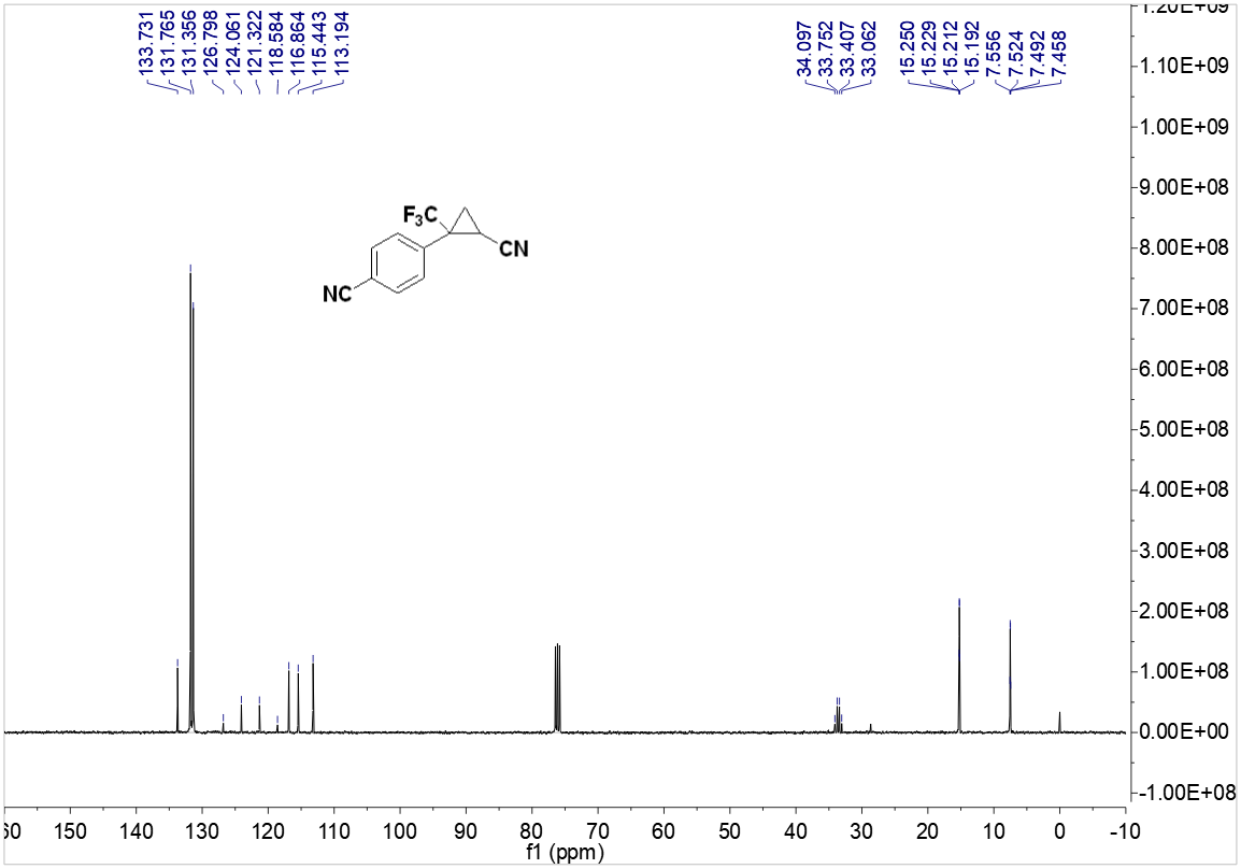


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
292.0563	292.0561	0.2	0.7	7.5	421.9	n/a	n/a	C13 H10 N O2 F3 Na

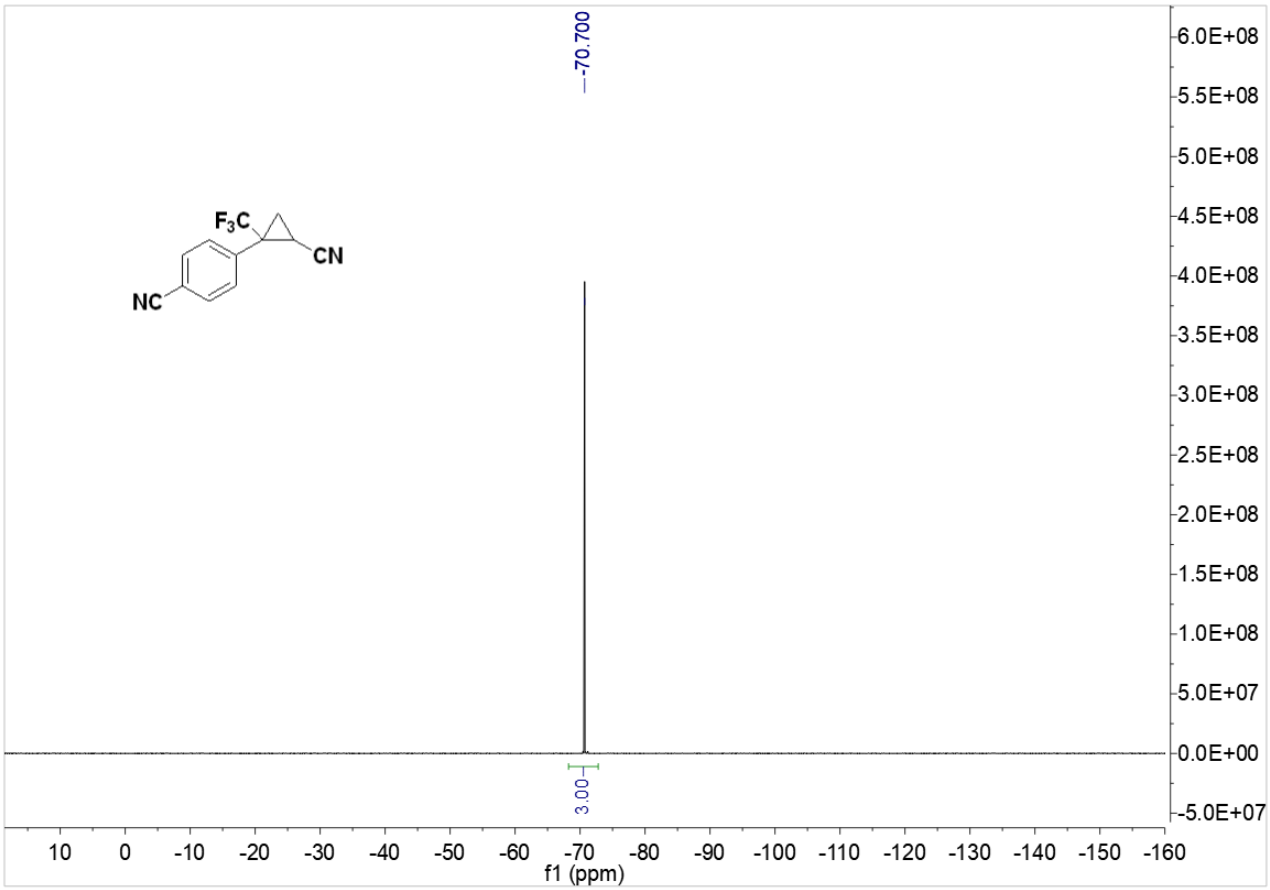
^{1}H NMR spectrum of ***trans*-3ia**



^{13}C NMR spectrum of ***trans*-3ia**

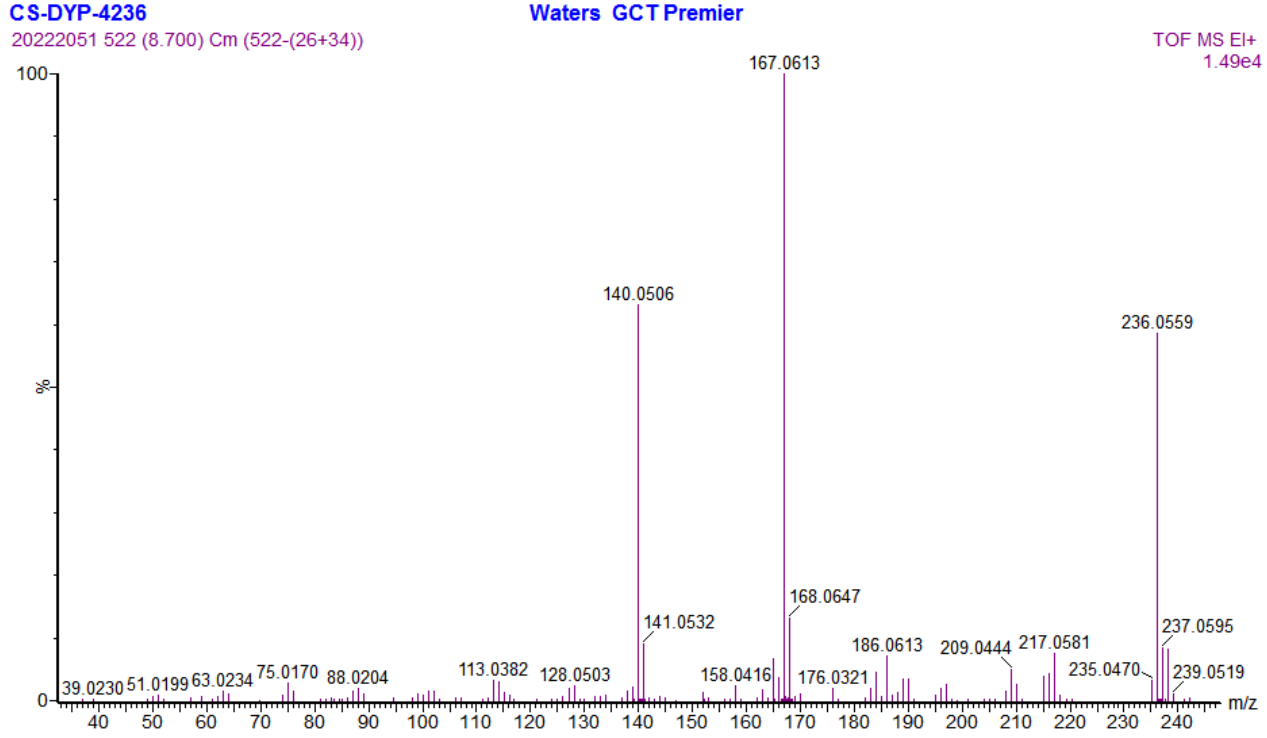


^{19}F NMR spectrum of ***trans*-3ia**

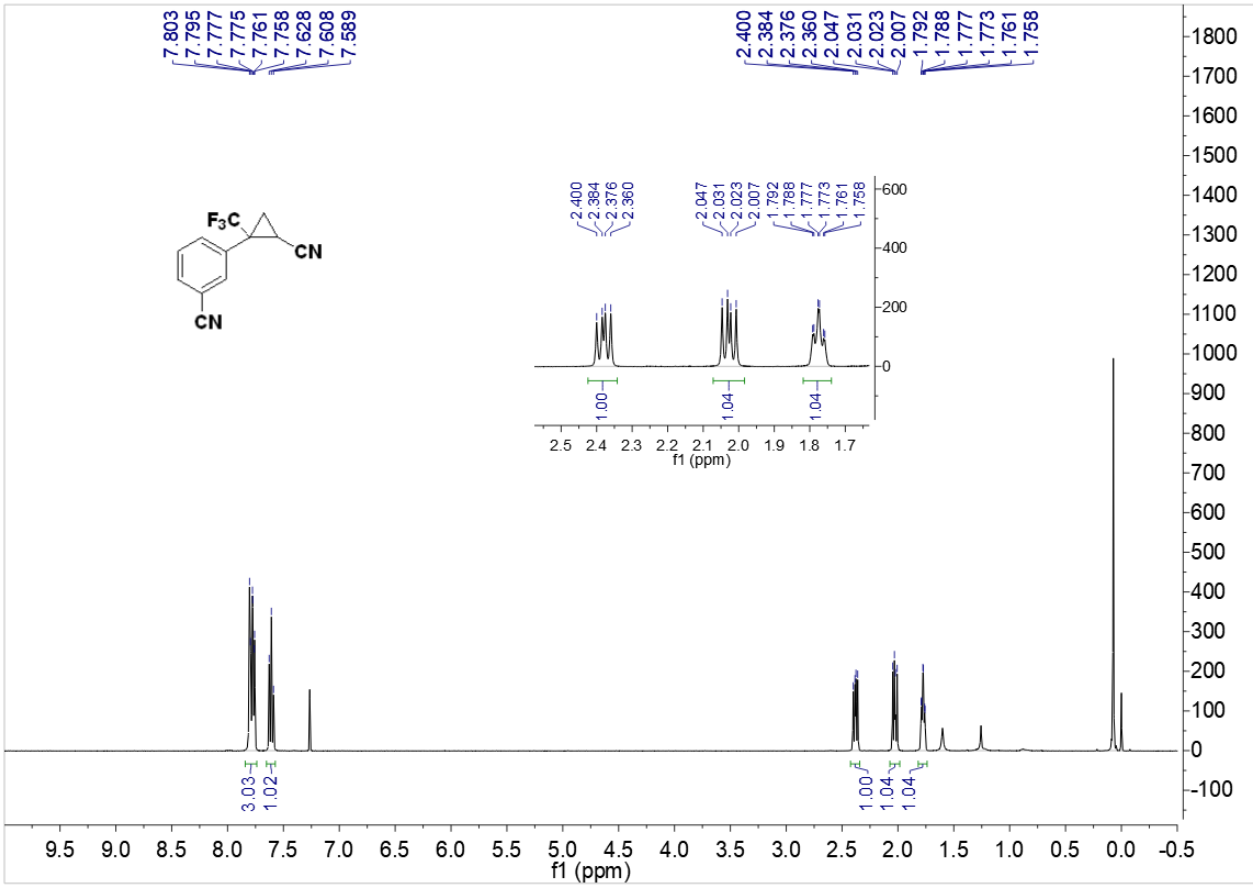


4

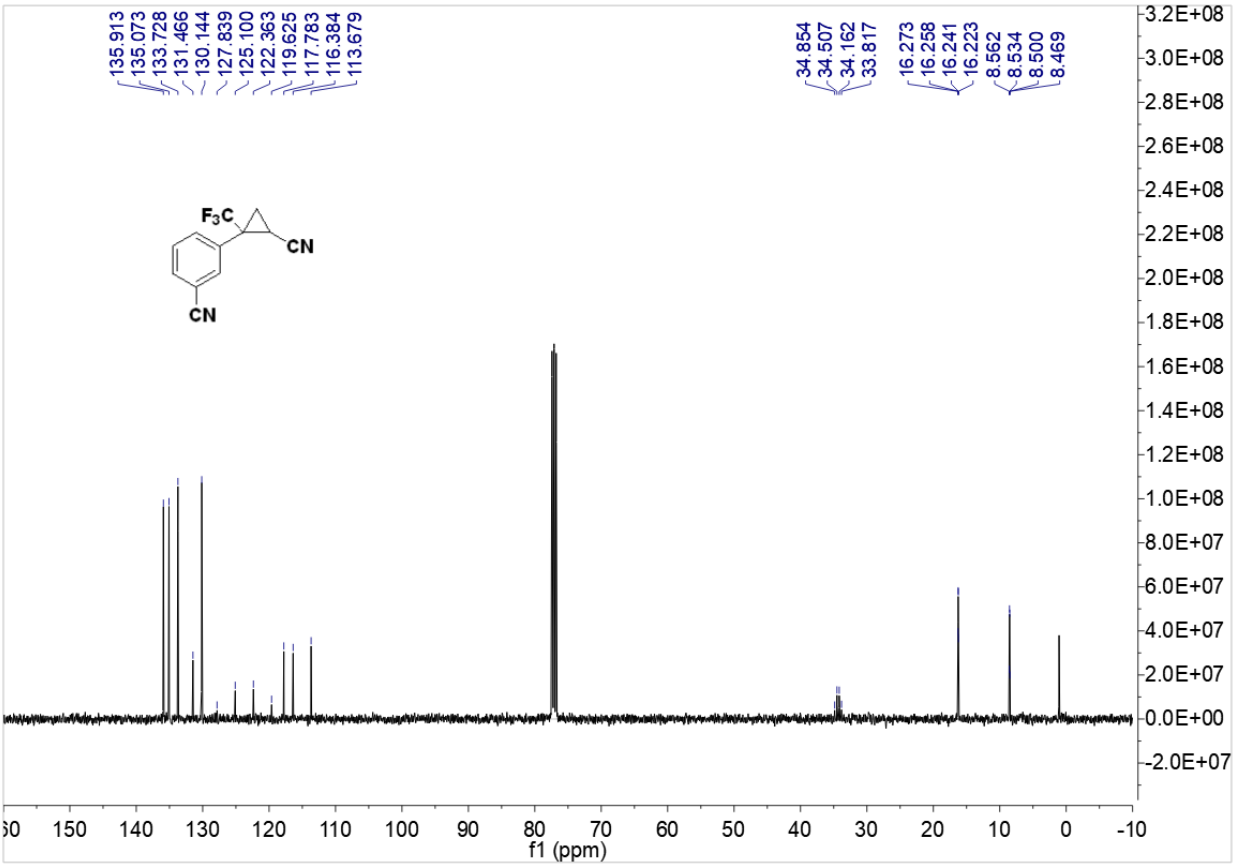
HRMS (EI) spectrum of ***trans*-3ia**



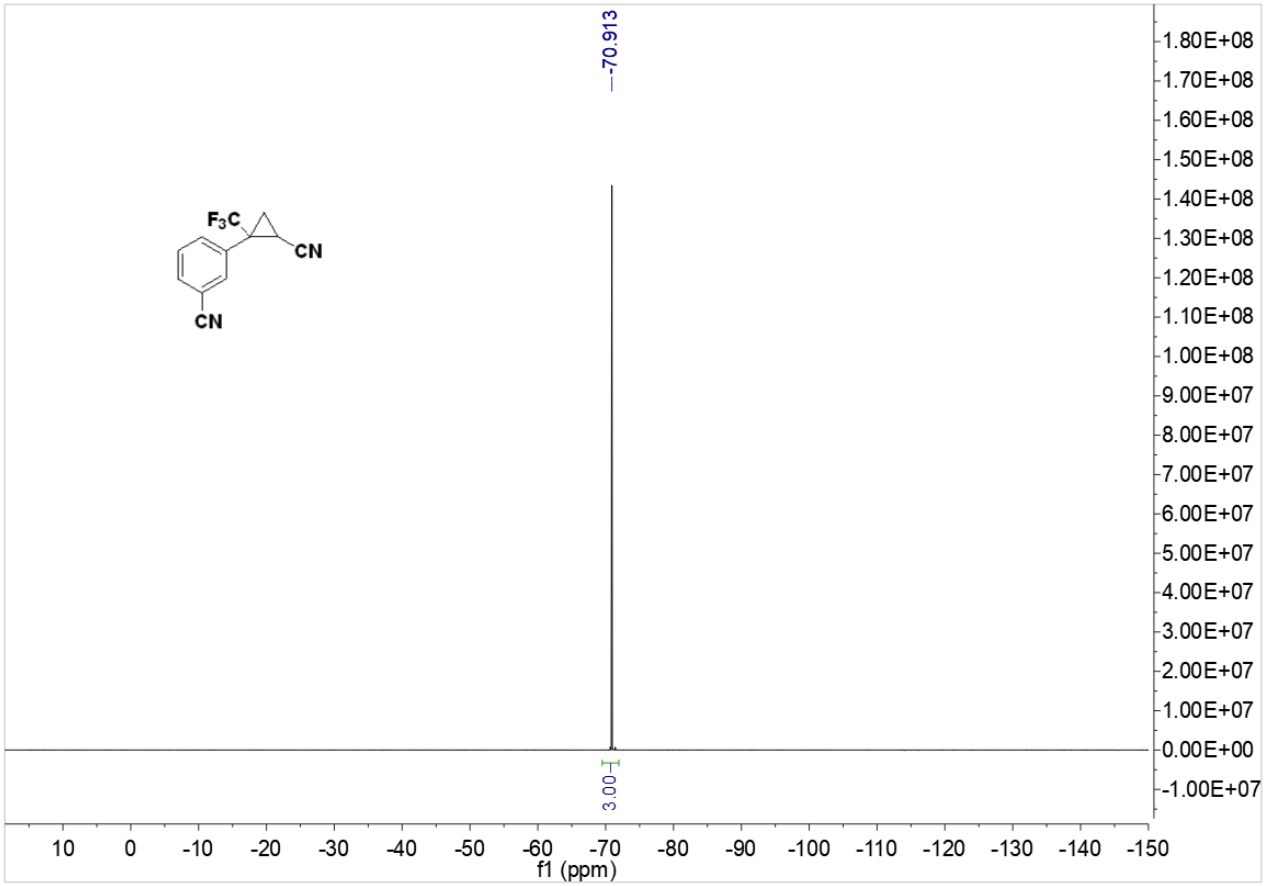
^{1}H NMR spectrum of ***trans*-3ja**



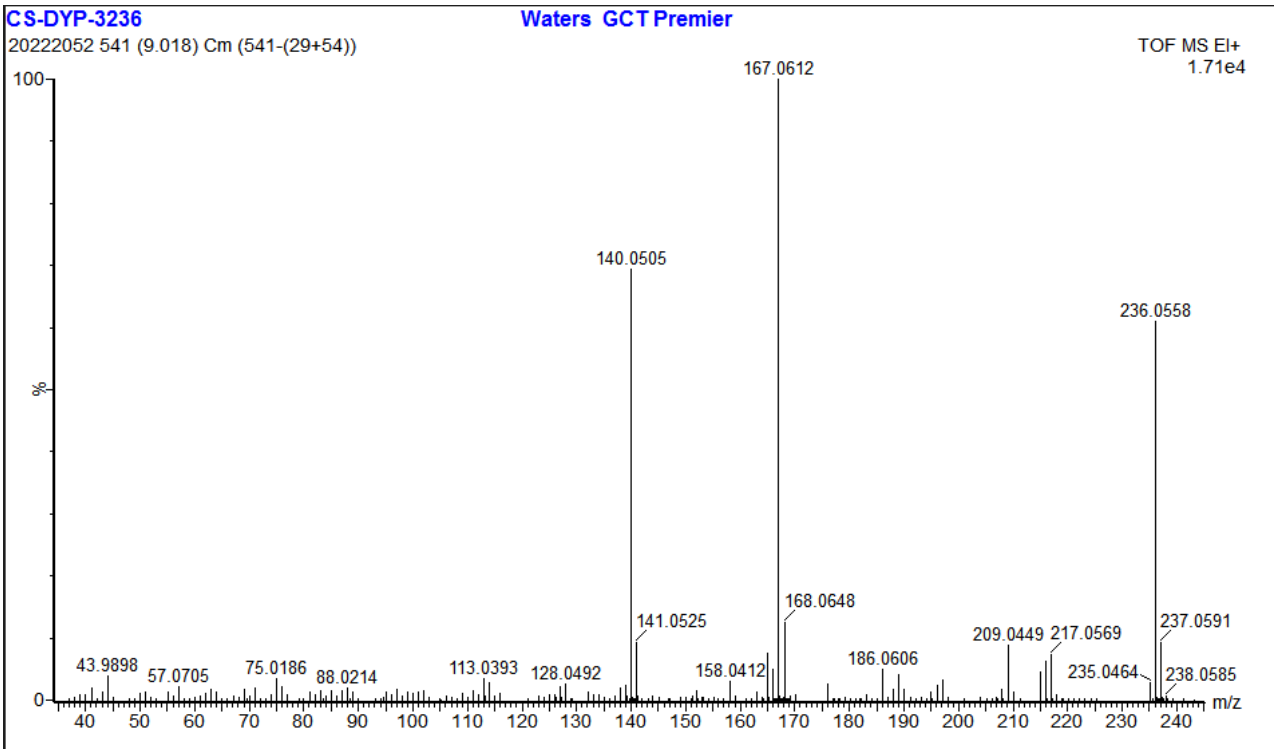
^{13}C NMR spectrum of ***trans*-3ja**



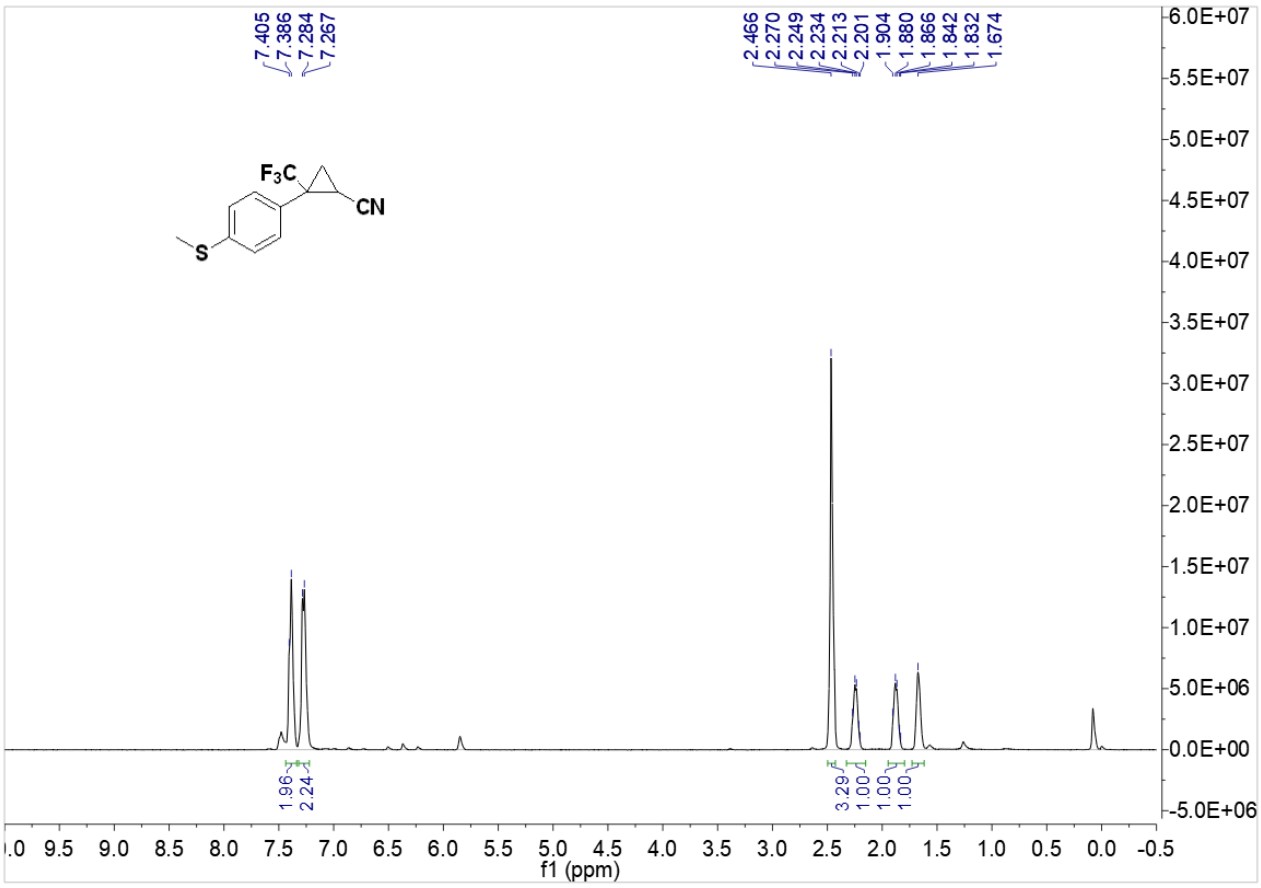
^{19}F NMR spectrum of ***trans*-3ja**



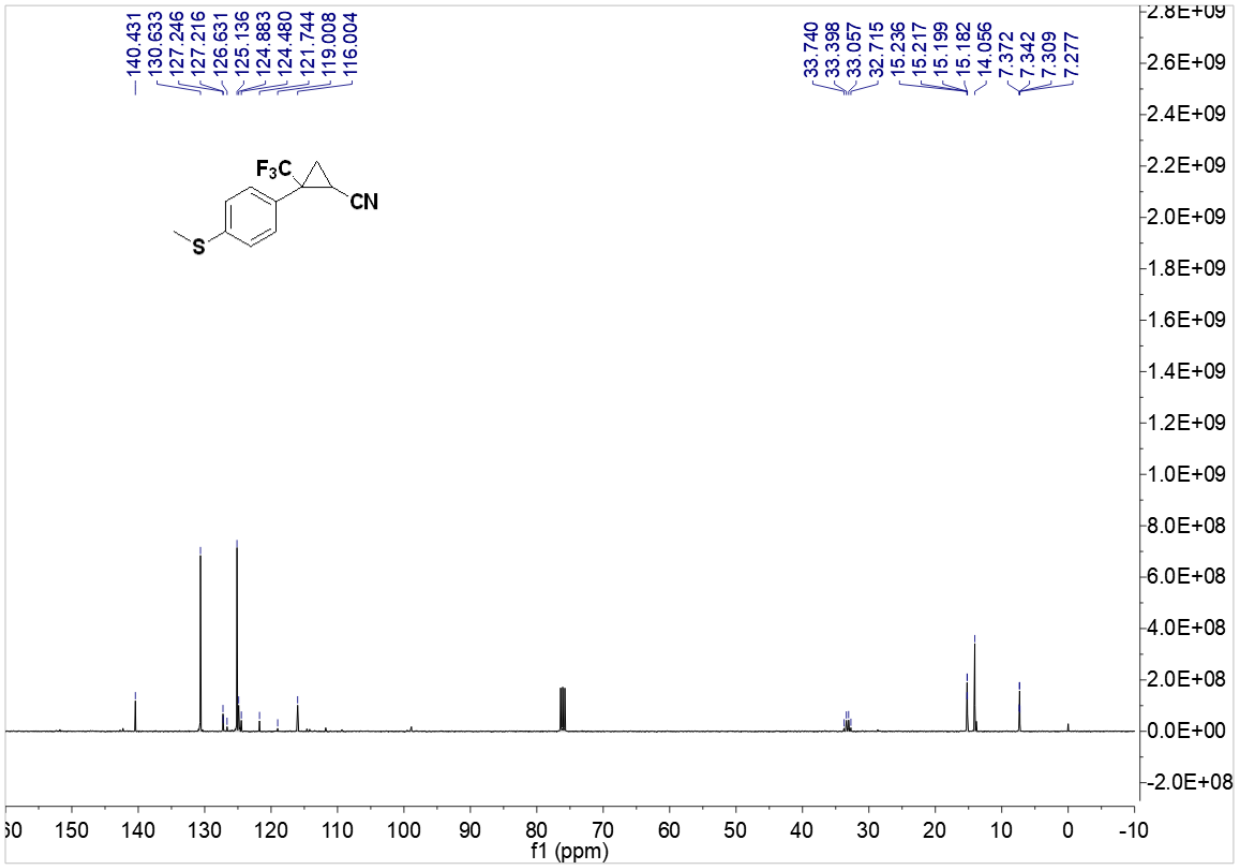
HRMS (EI) spectrum of ***trans*-3ja**



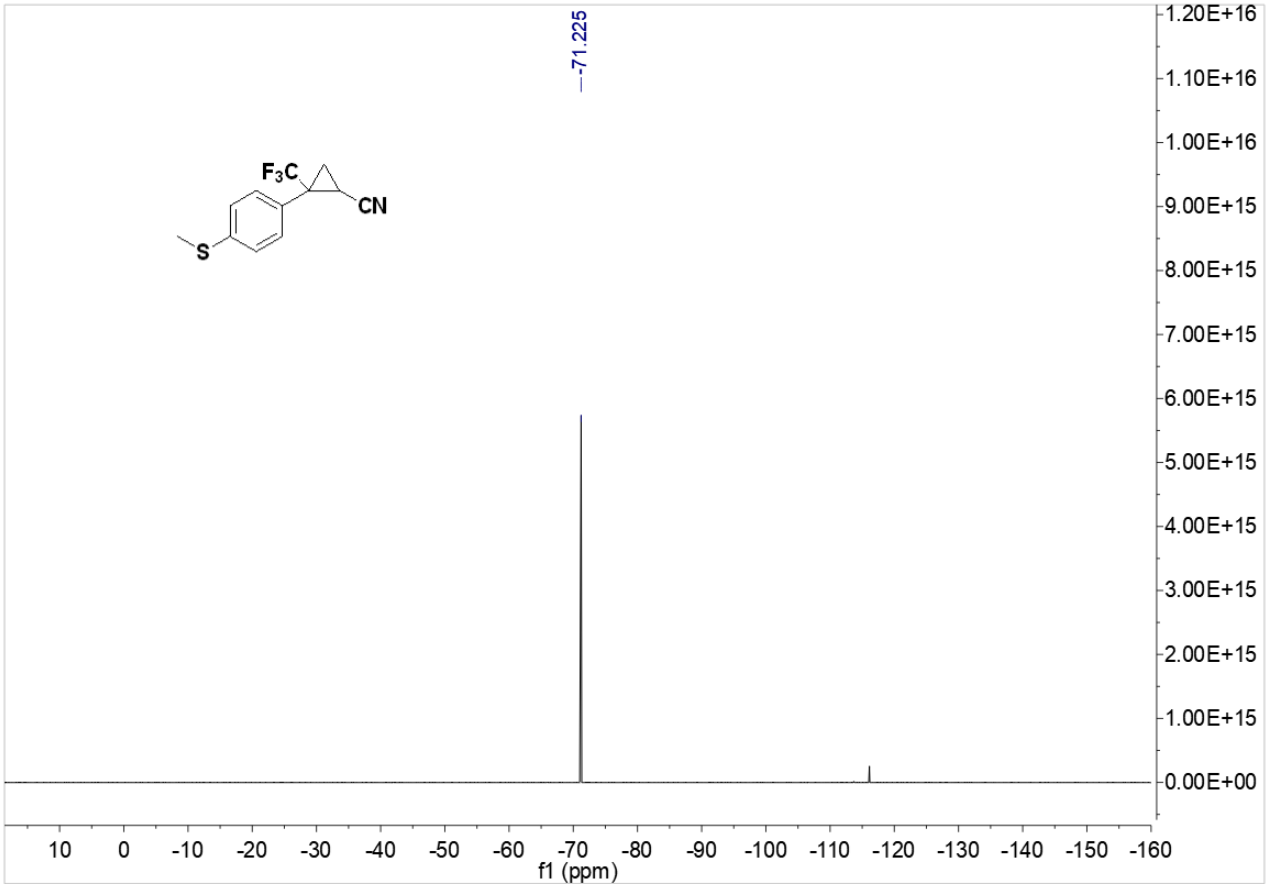
^{1}H NMR spectrum of ***trans*-3ka**



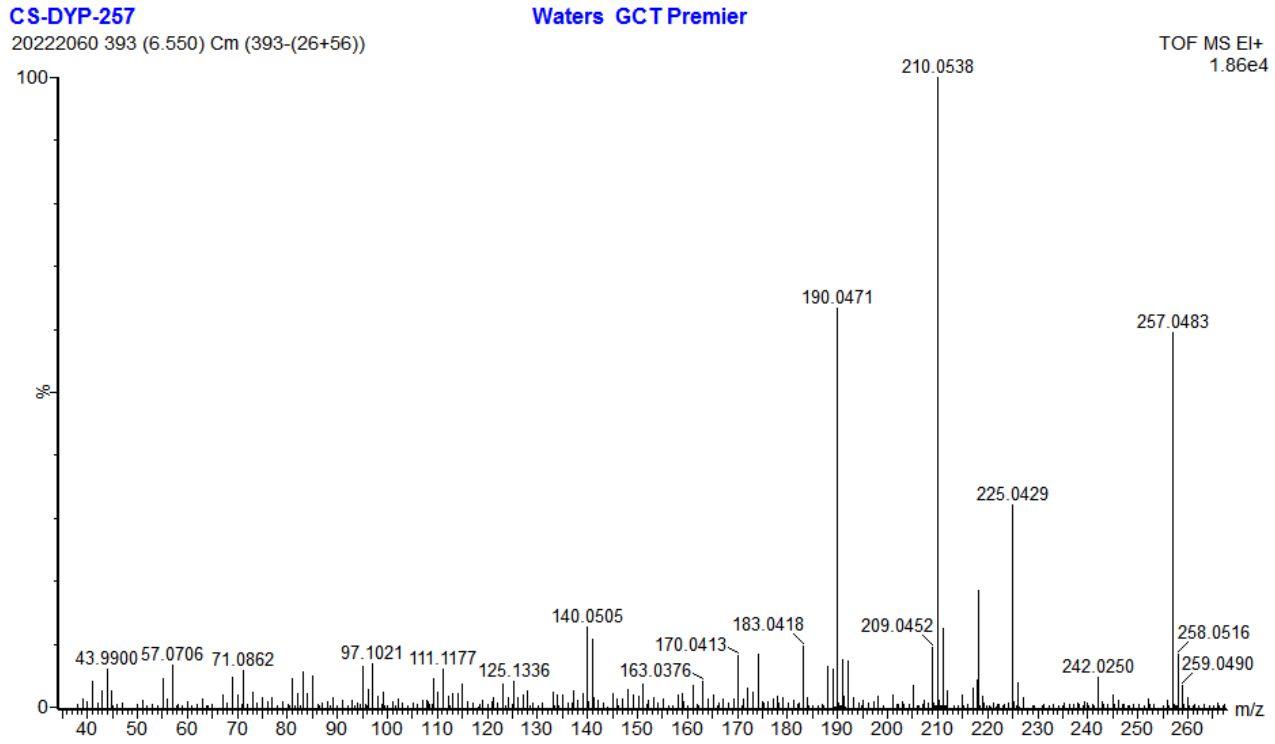
^{13}C NMR spectrum of ***trans*-3ka**



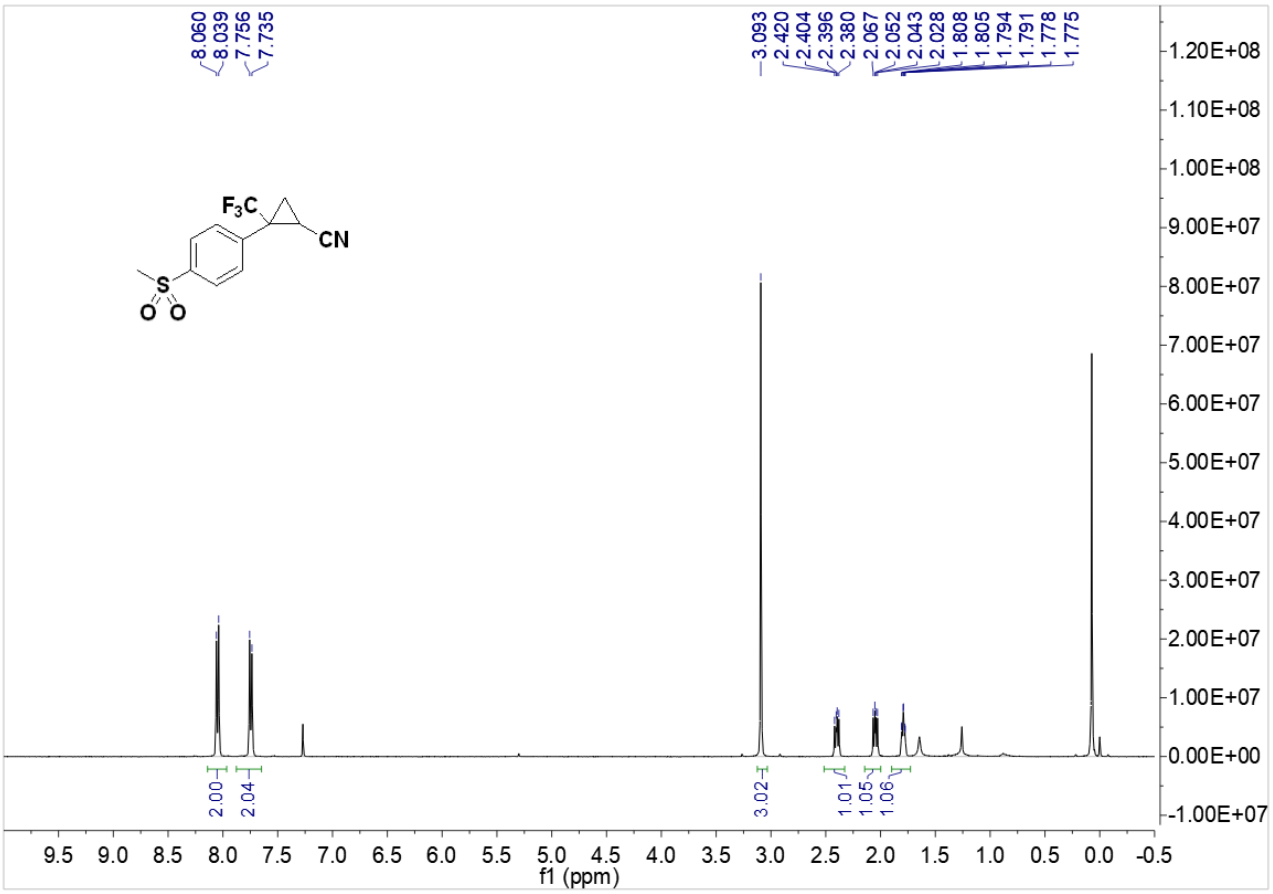
^{19}F NMR spectrum of ***trans*-3ka**



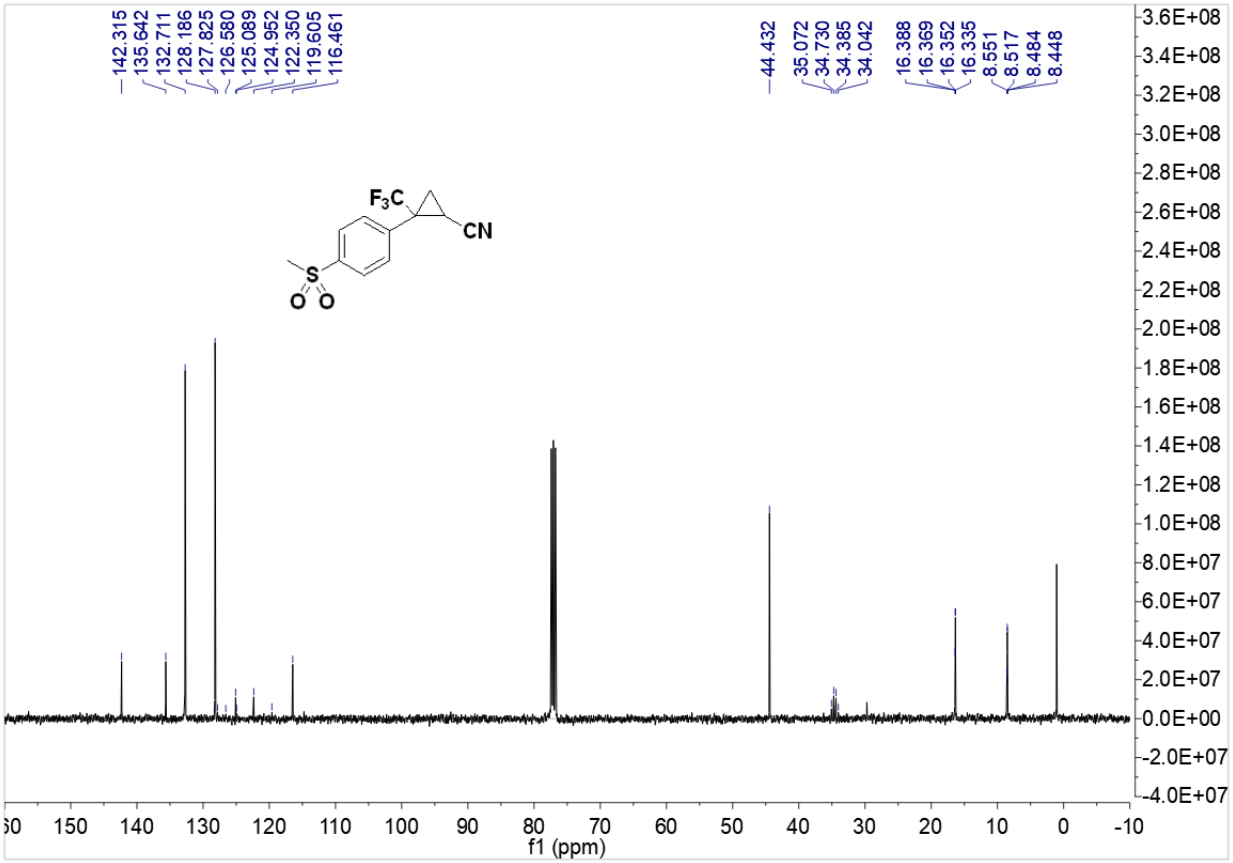
HRMS (EI) spectrum of ***trans*-3ka**



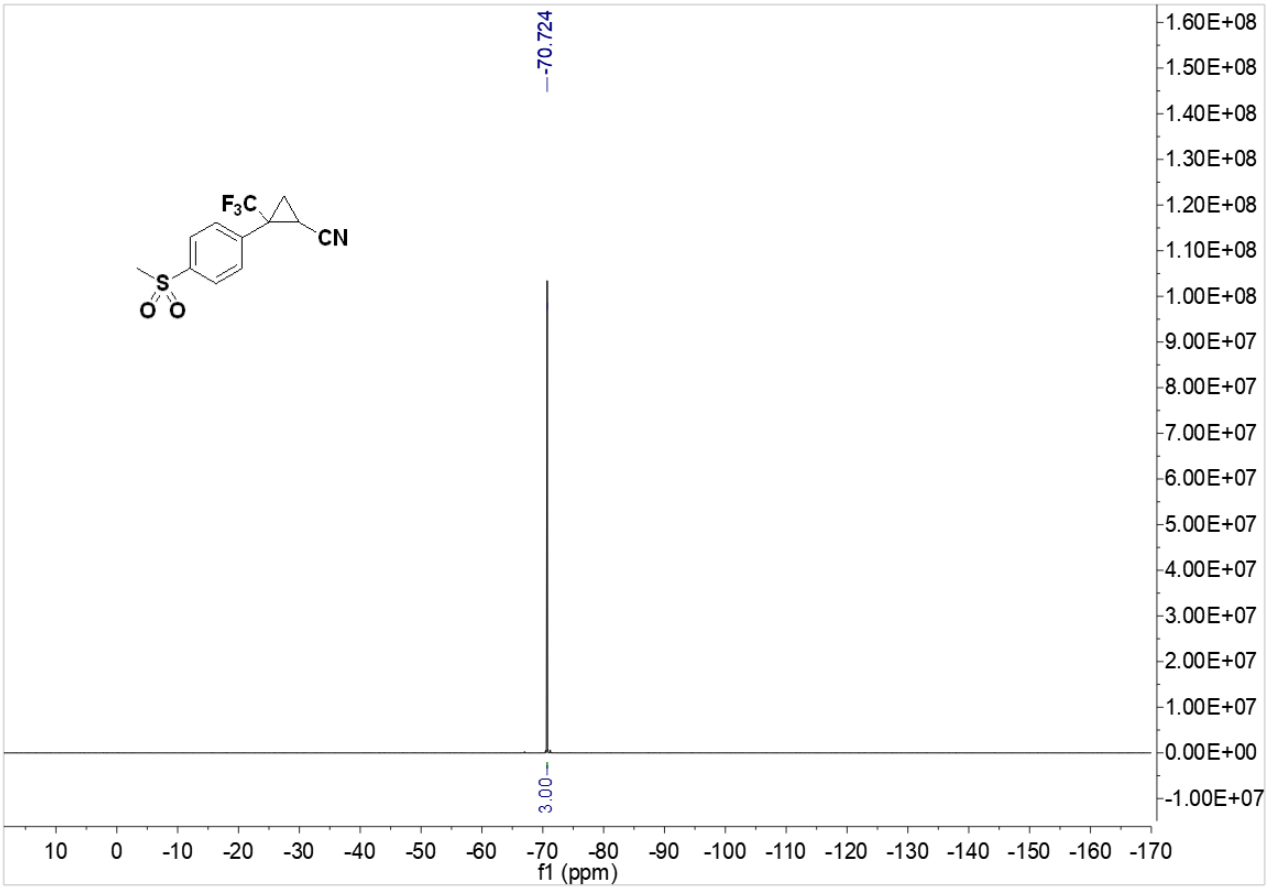
^{1}H NMR spectrum of ***trans*-3la**



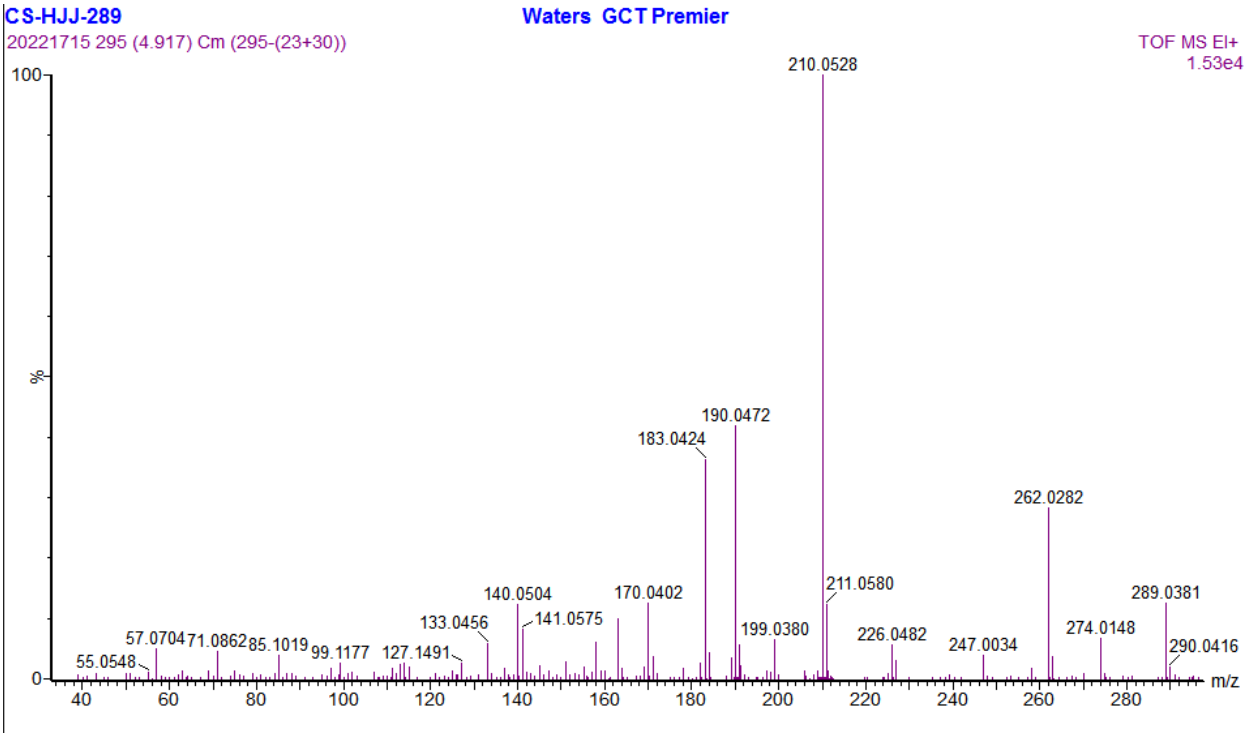
^{13}C NMR spectrum of ***trans*-3la**



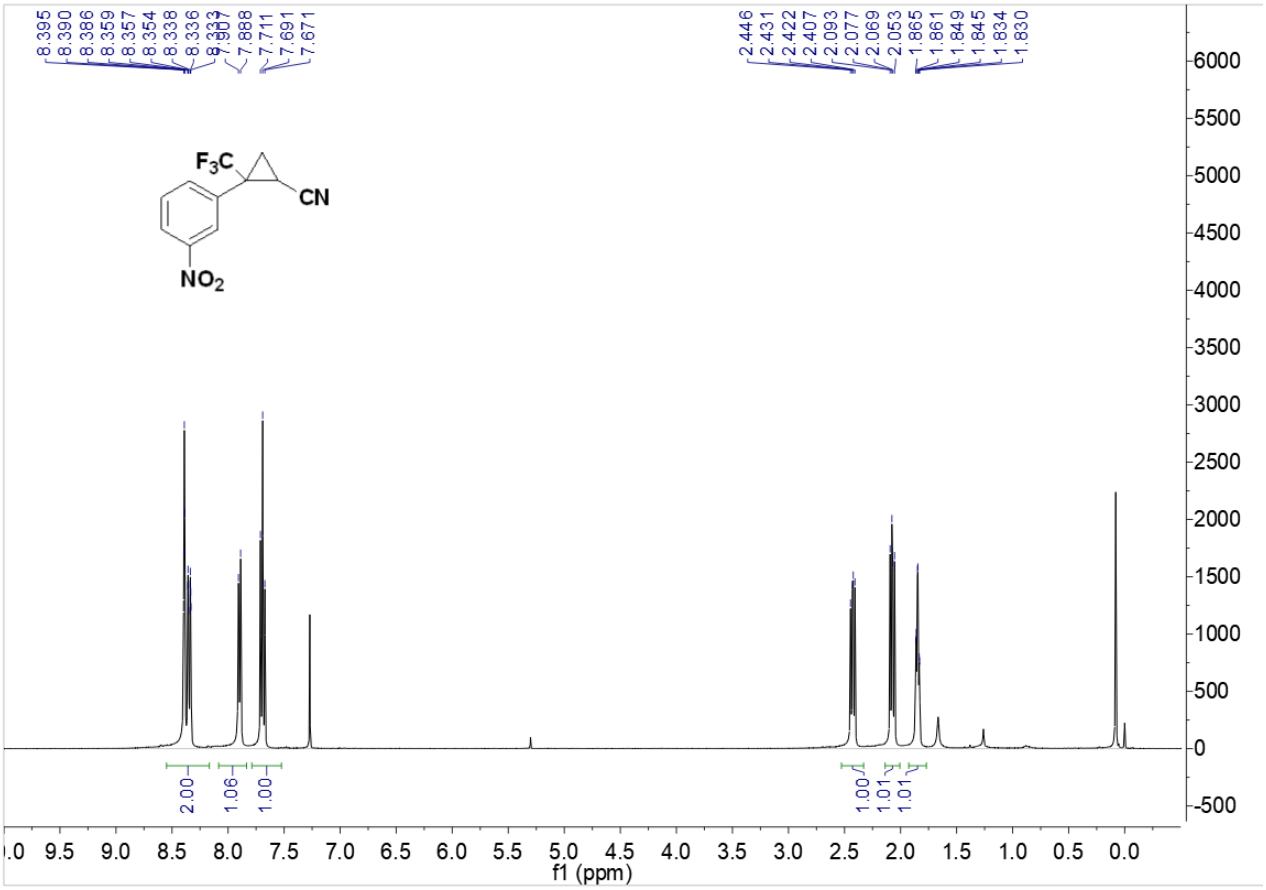
^{19}F NMR spectrum of ***trans*-3la**



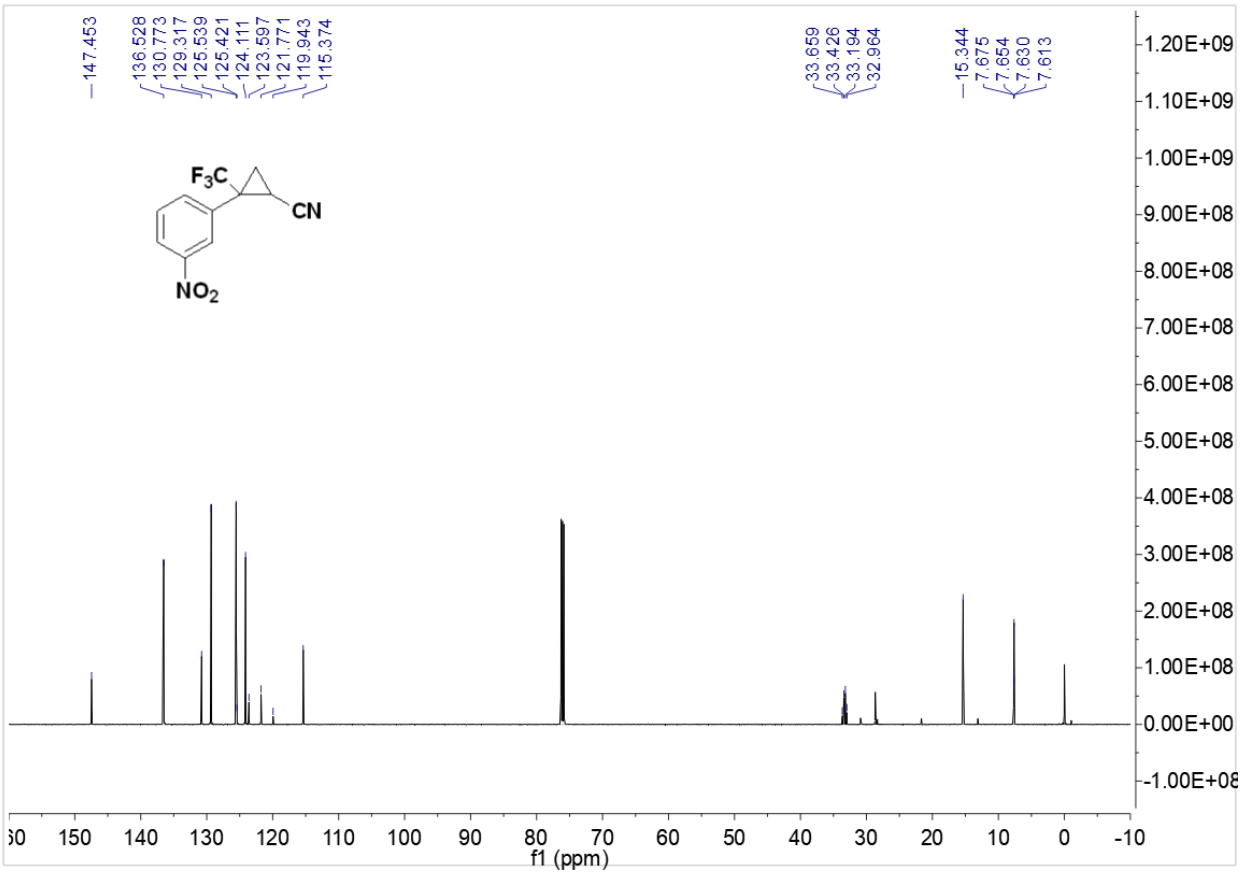
HRMS (EI) spectrum of ***trans*-3la**



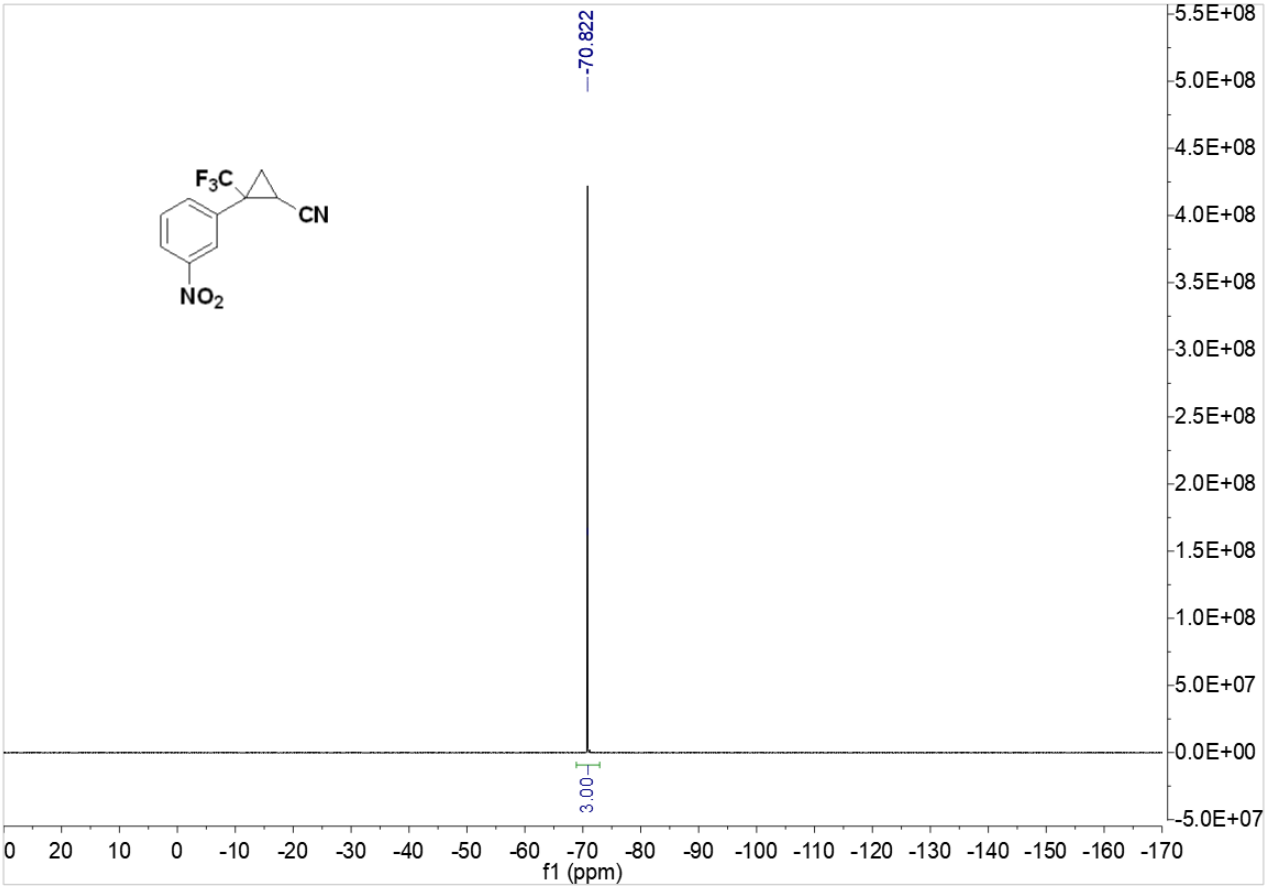
^{1}H NMR spectrum of ***trans*-3ma**



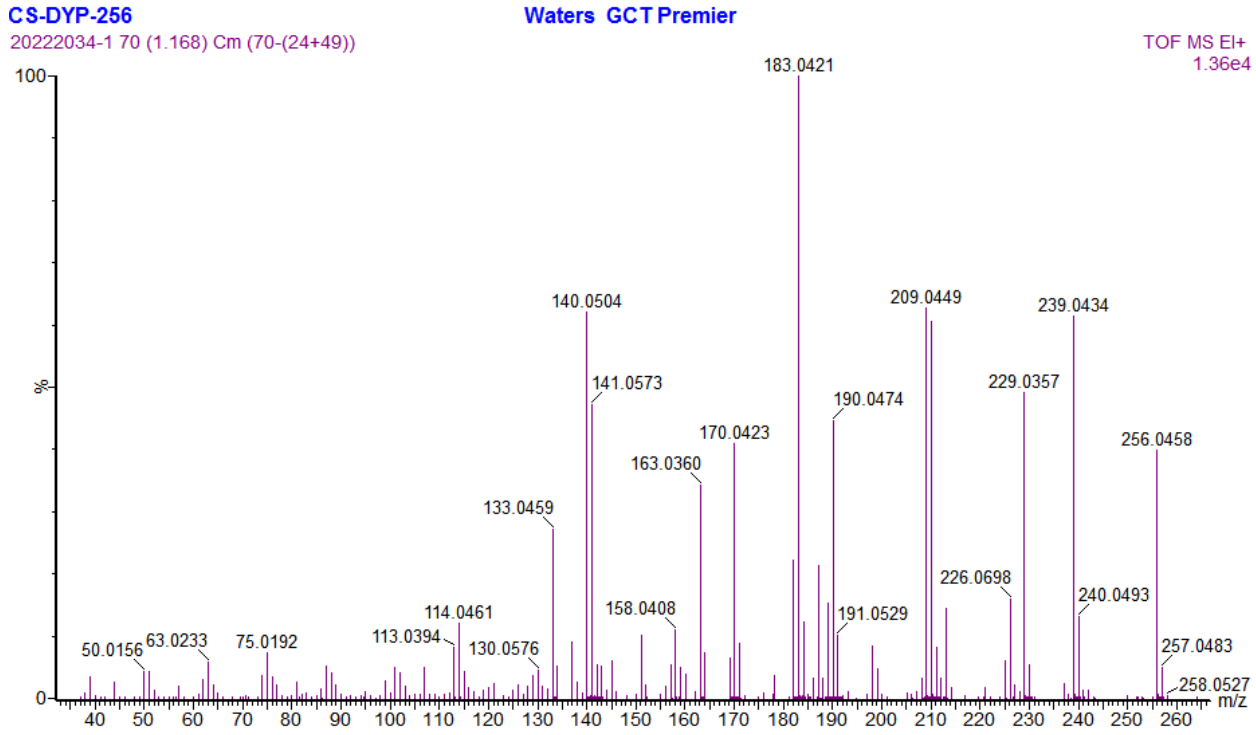
^{13}C NMR spectrum of ***trans*-3ma**



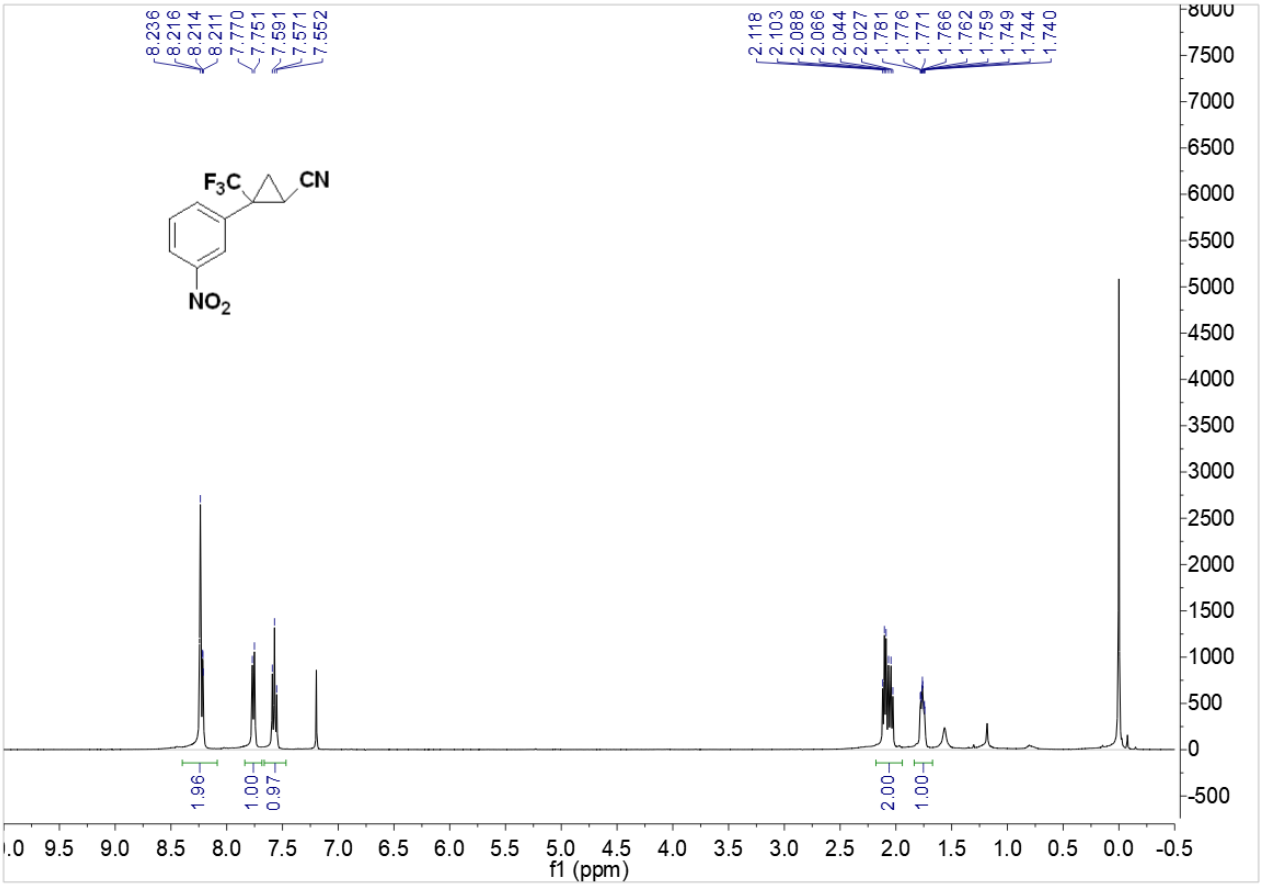
^{19}F NMR spectrum of ***trans*-3ma**



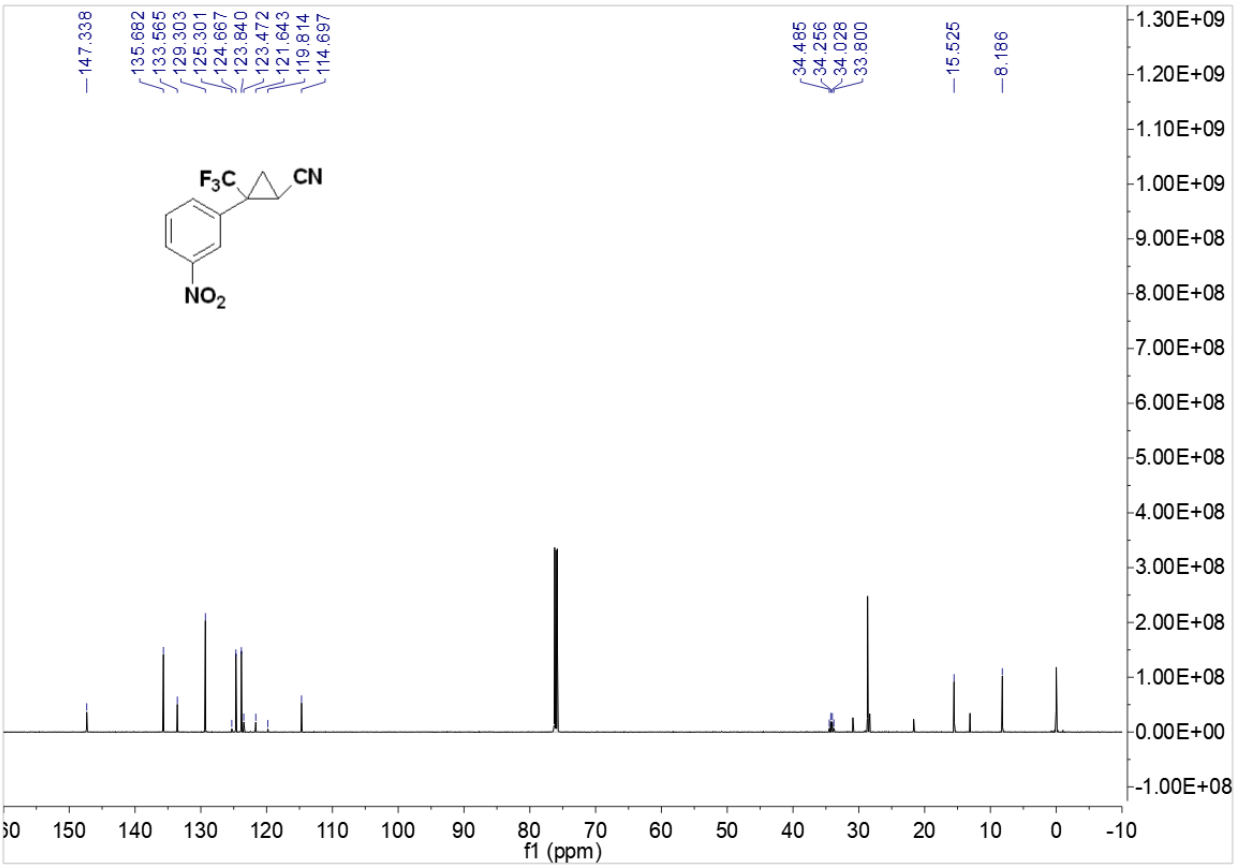
HRMS (EI) spectrum of ***trans*-3ma**



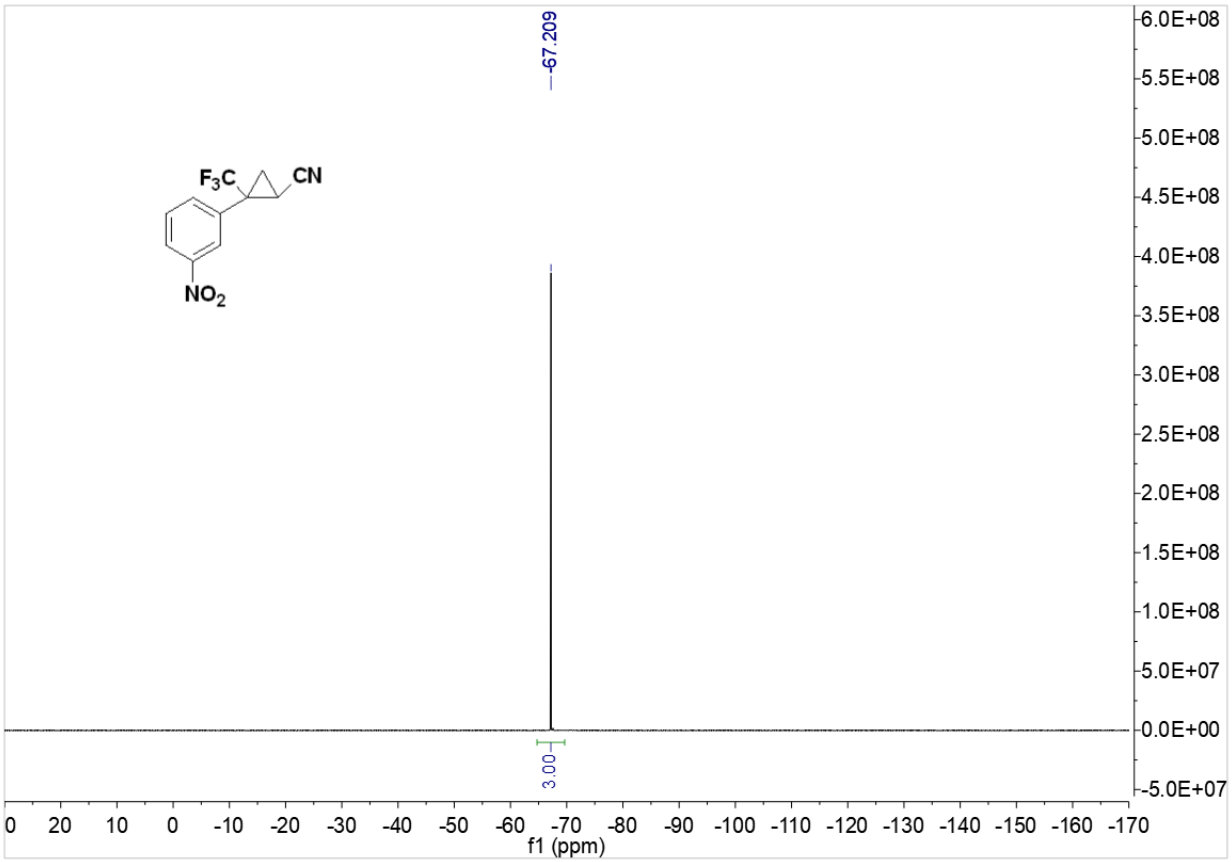
^{1}H NMR spectrum of ***cis*-3ma**



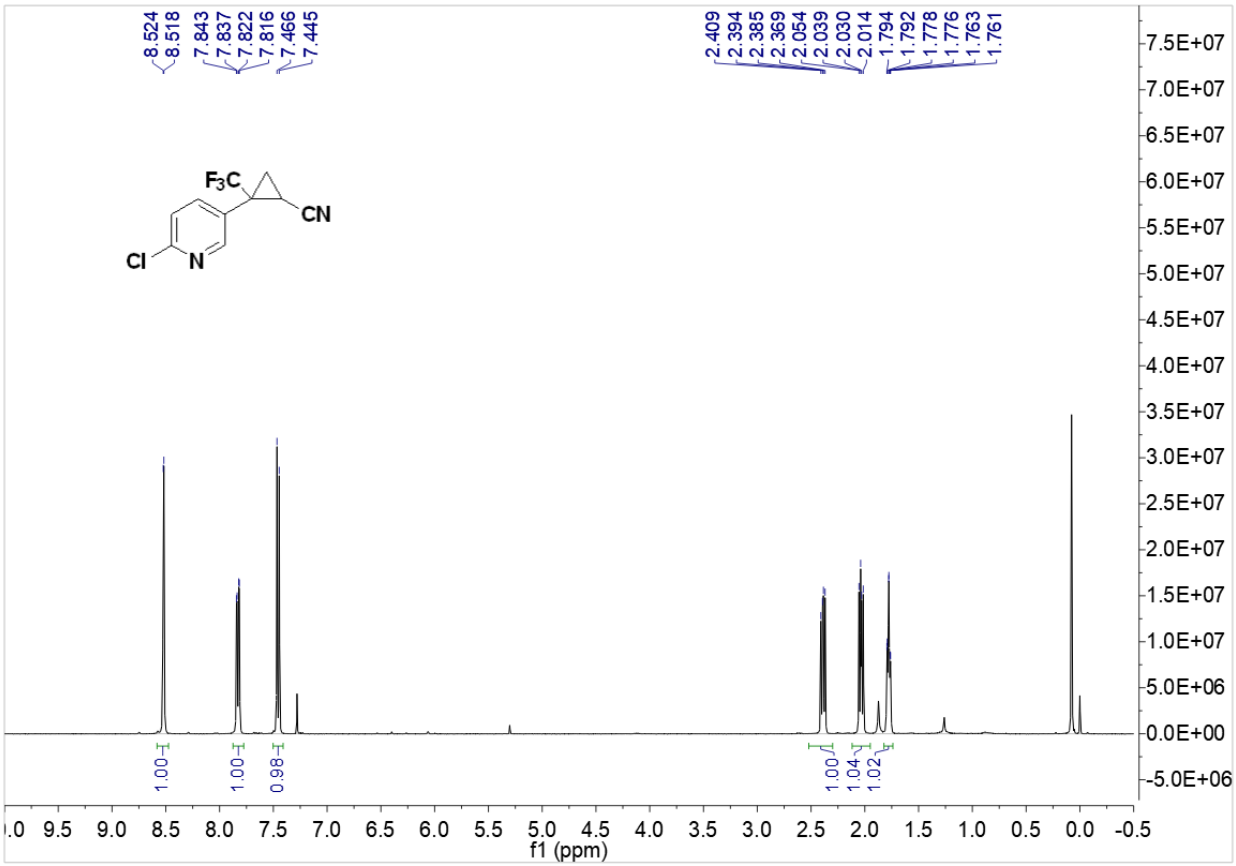
^{13}C NMR spectrum of ***cis*-3ma**



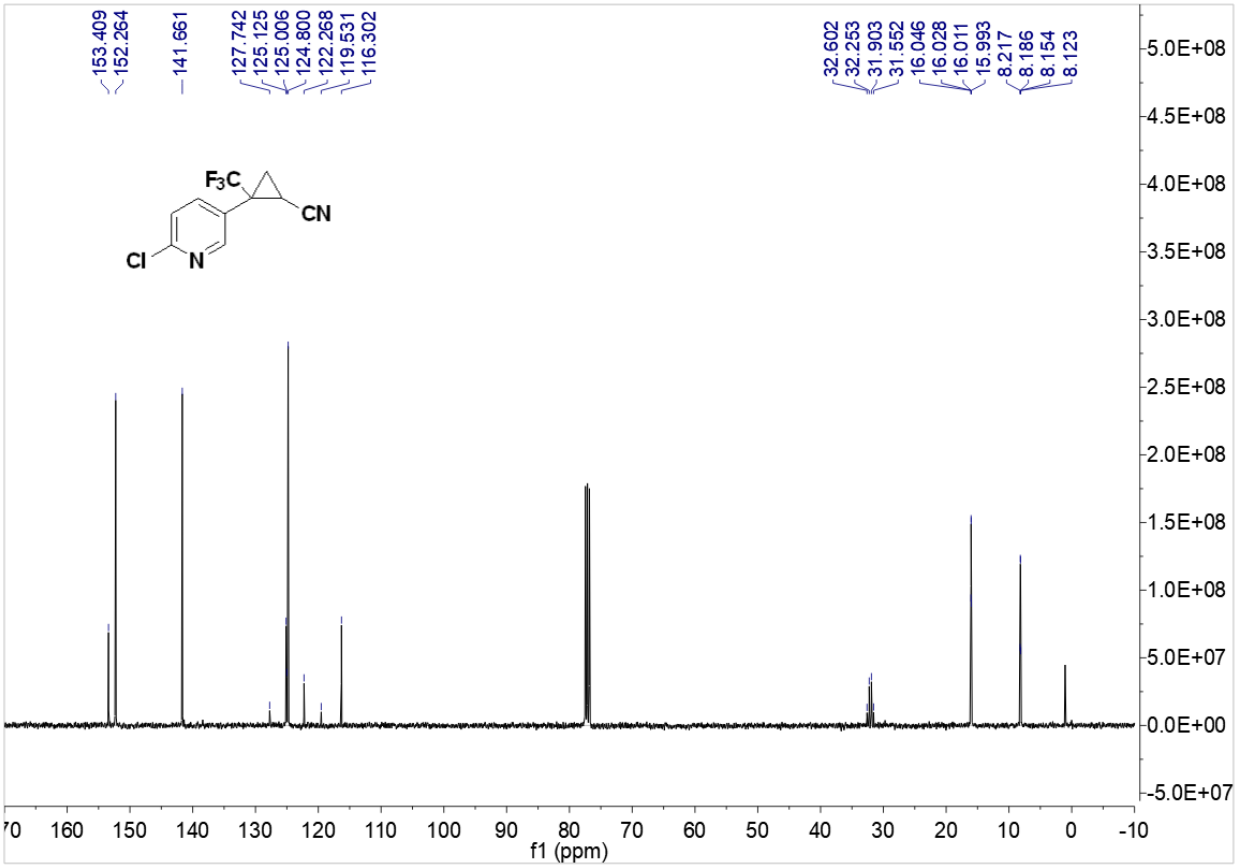
^{19}F NMR spectrum of ***cis*-3ma**



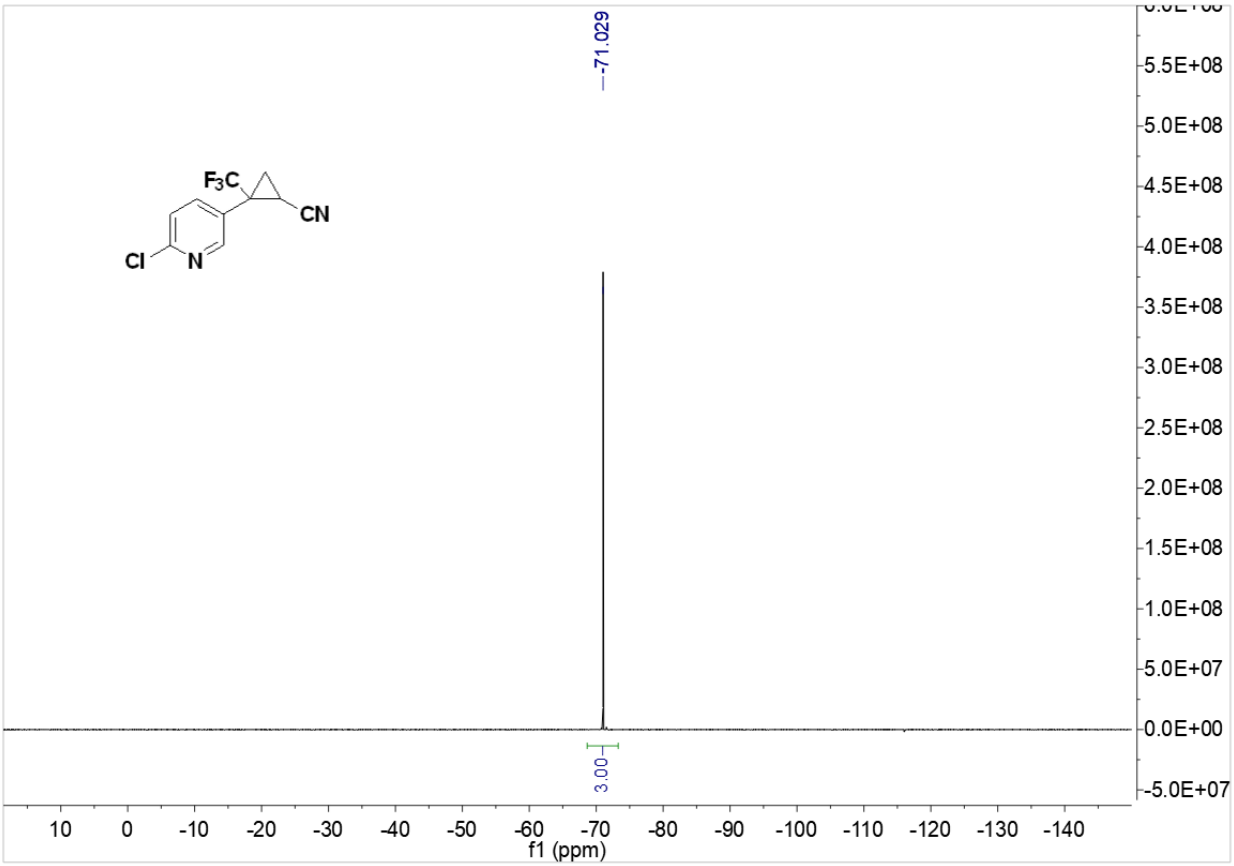
^{1}H NMR spectrum of ***trans*-3na**



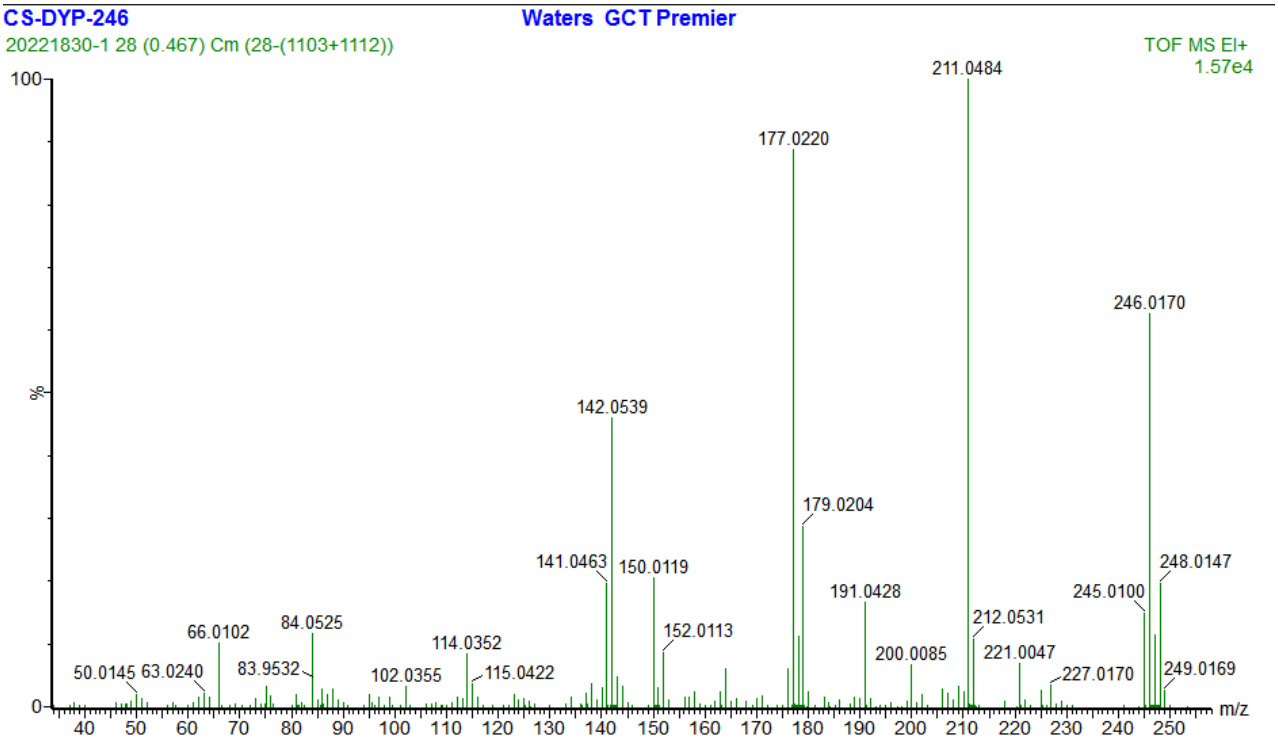
^{13}C NMR spectrum of ***trans*-3na**



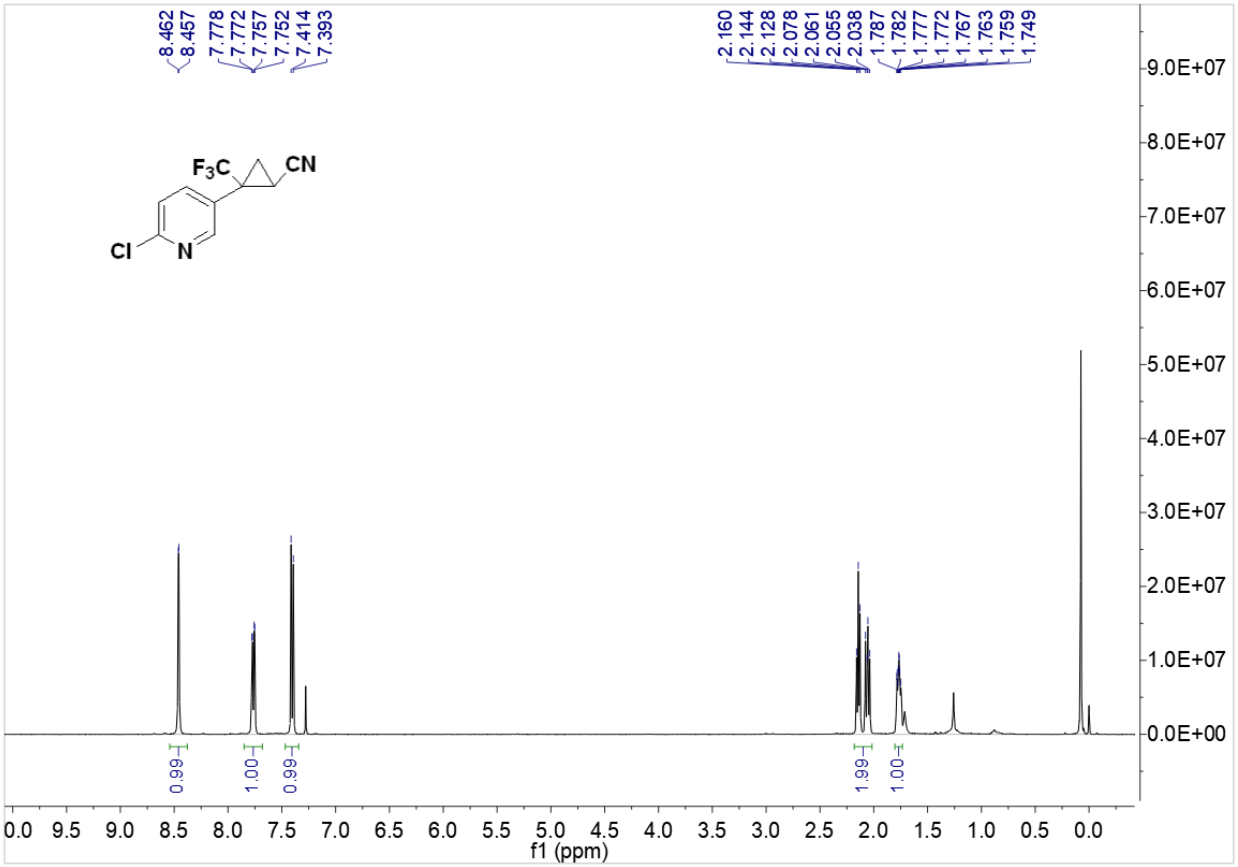
^{19}F NMR spectrum of ***trans*-3na**



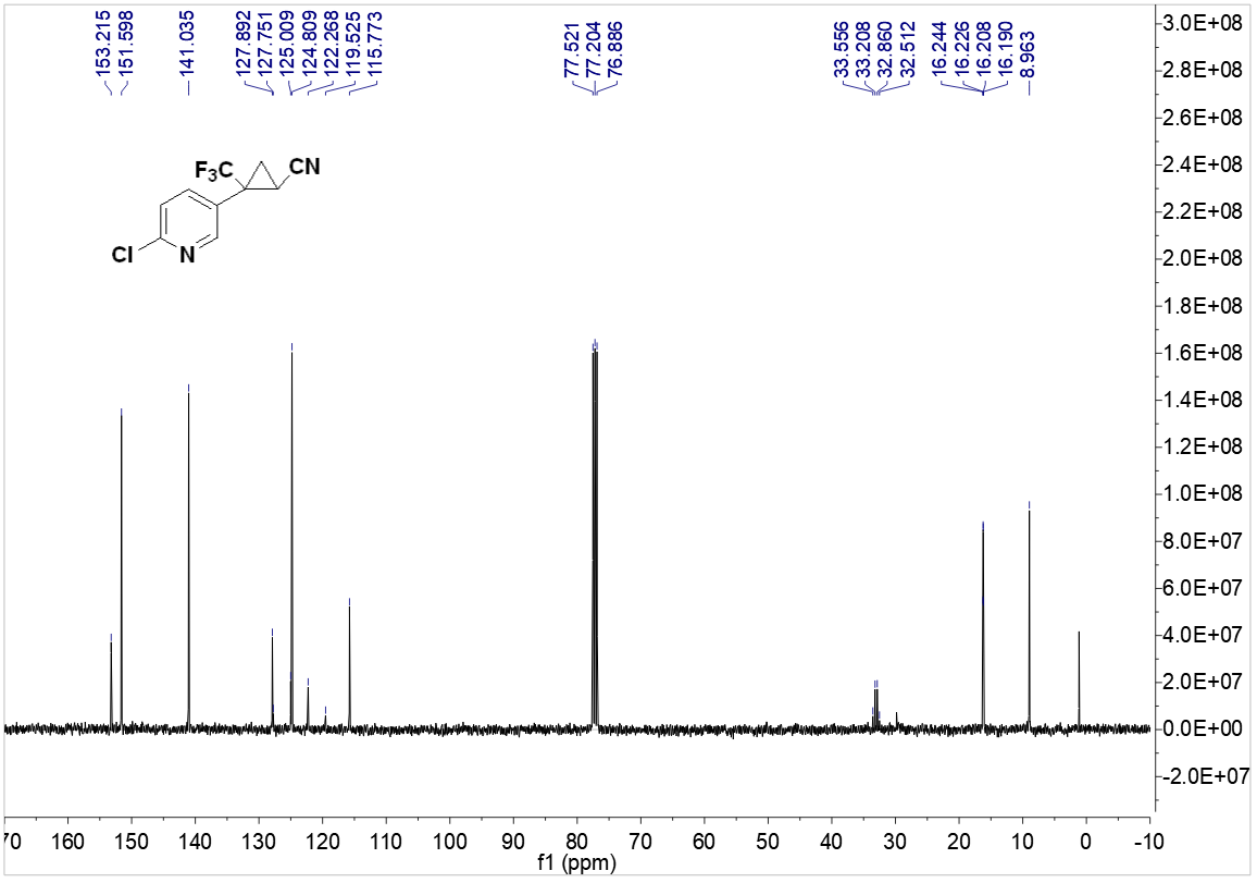
HRMS (EI) spectrum of ***trans*-3na**



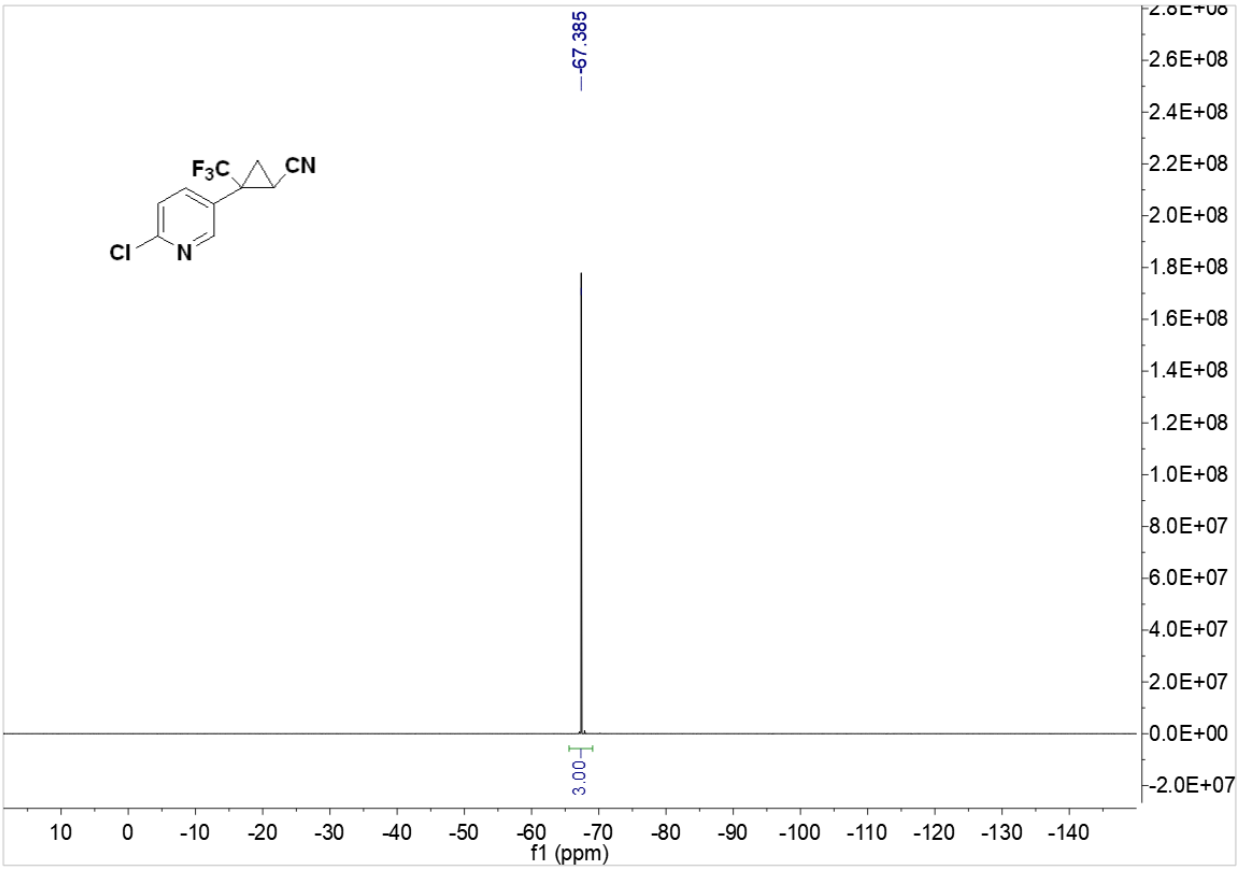
^{1}H NMR spectrum of ***cis*-3na**



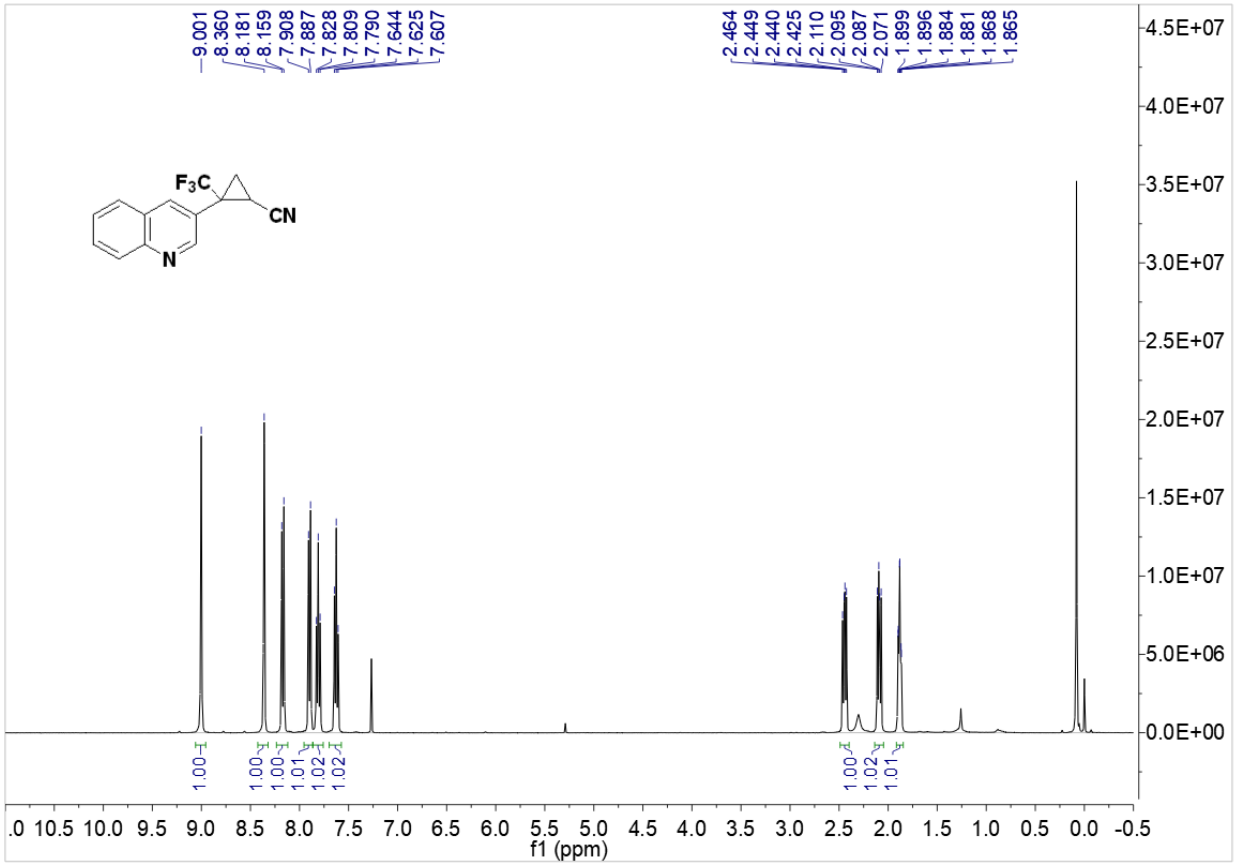
^{13}C NMR spectrum of ***cis*-3na**



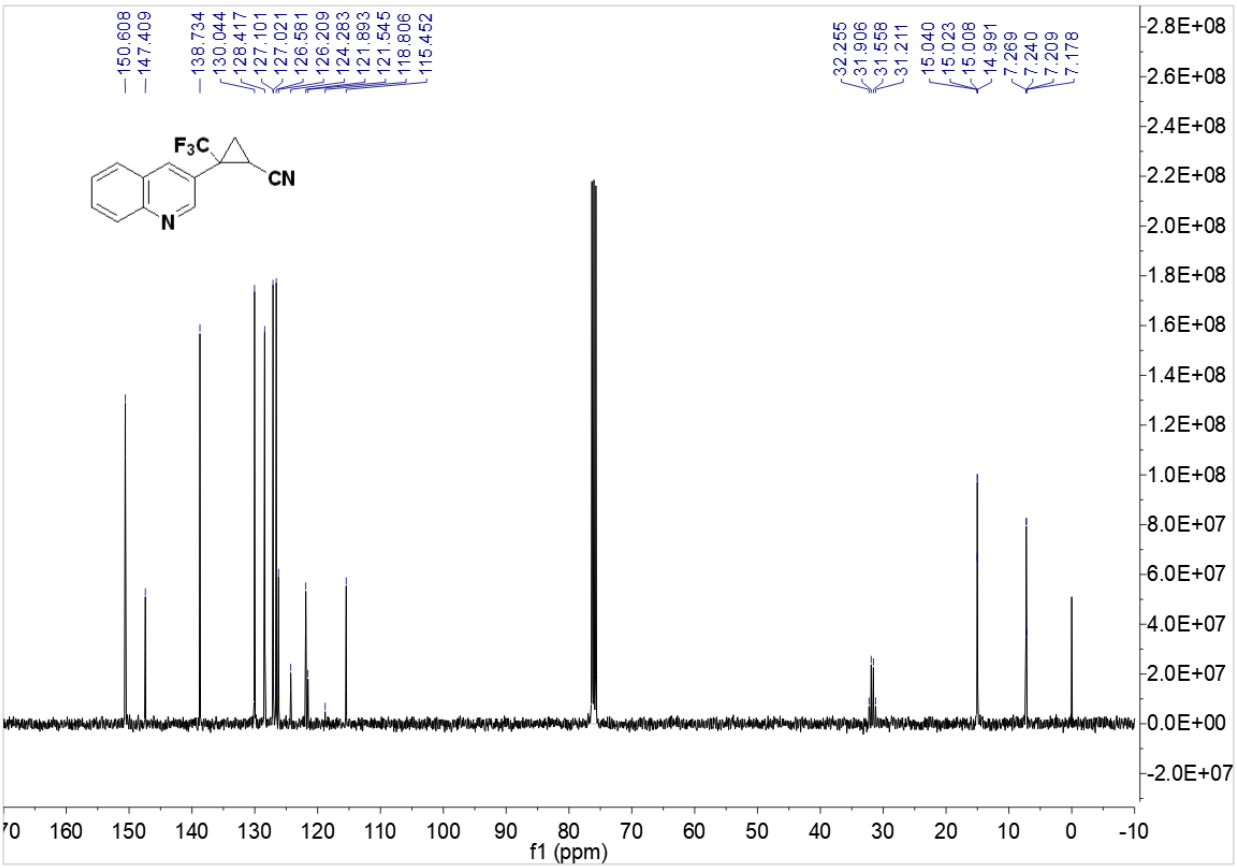
^{19}F NMR spectrum of ***cis*-3na**



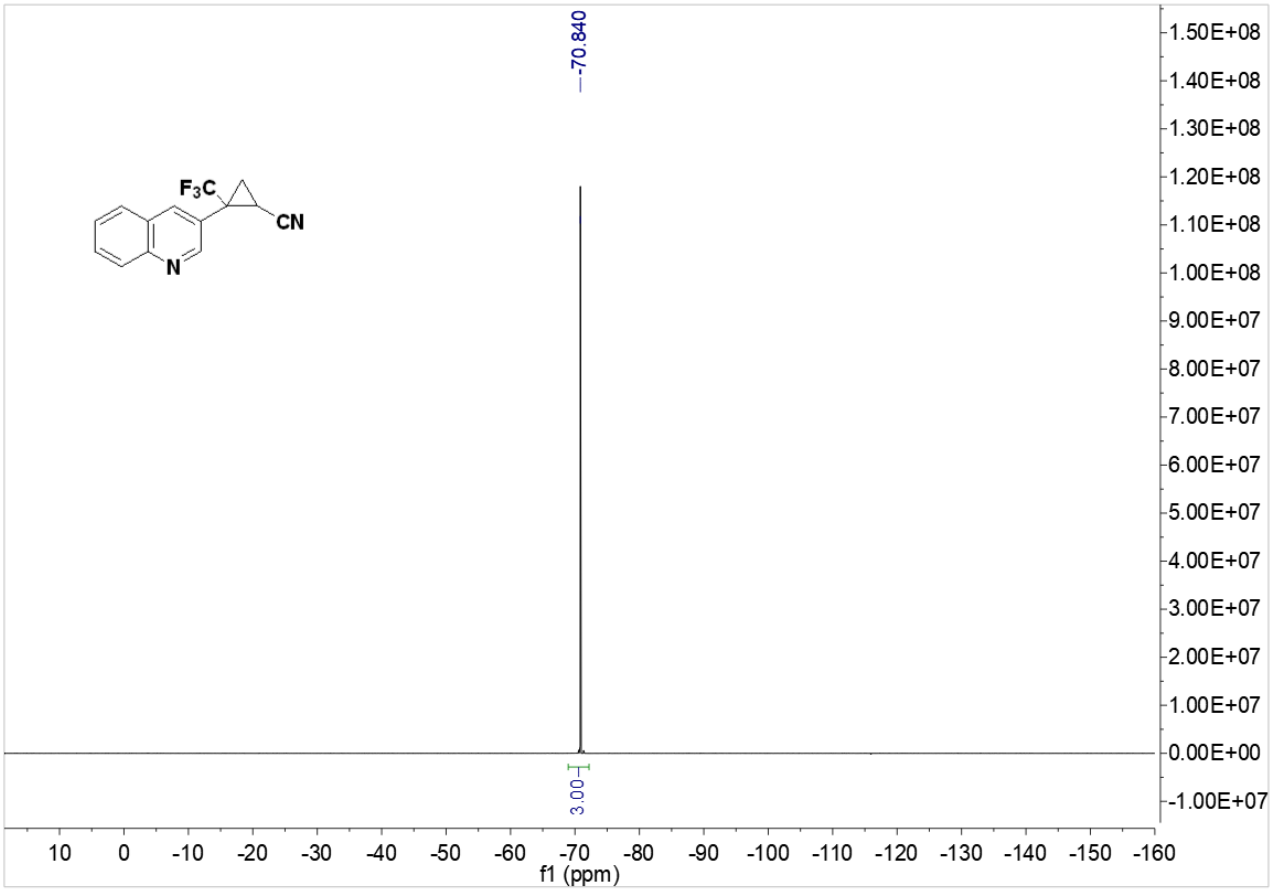
^{1}H NMR spectrum of ***trans*-3oa**



^{13}C NMR spectrum of ***trans*-3oa**



^{19}F NMR spectrum of ***trans*-3oa**

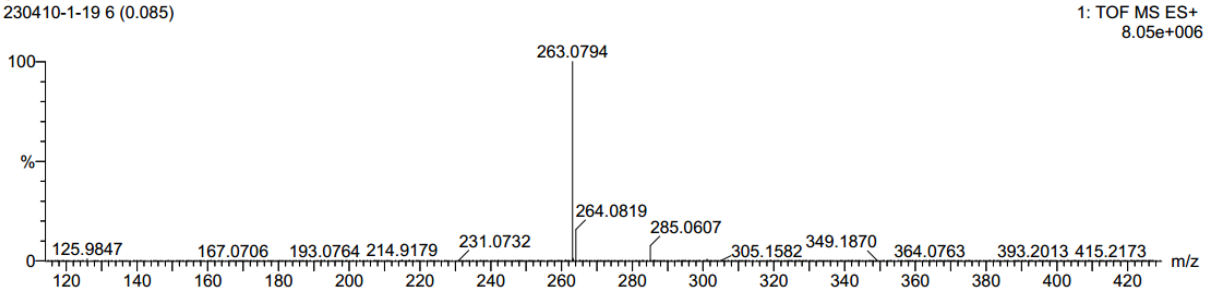


HRMS (ESI) spectrum of ***trans*-3oa**

Elemental Composition Report **Page 1**

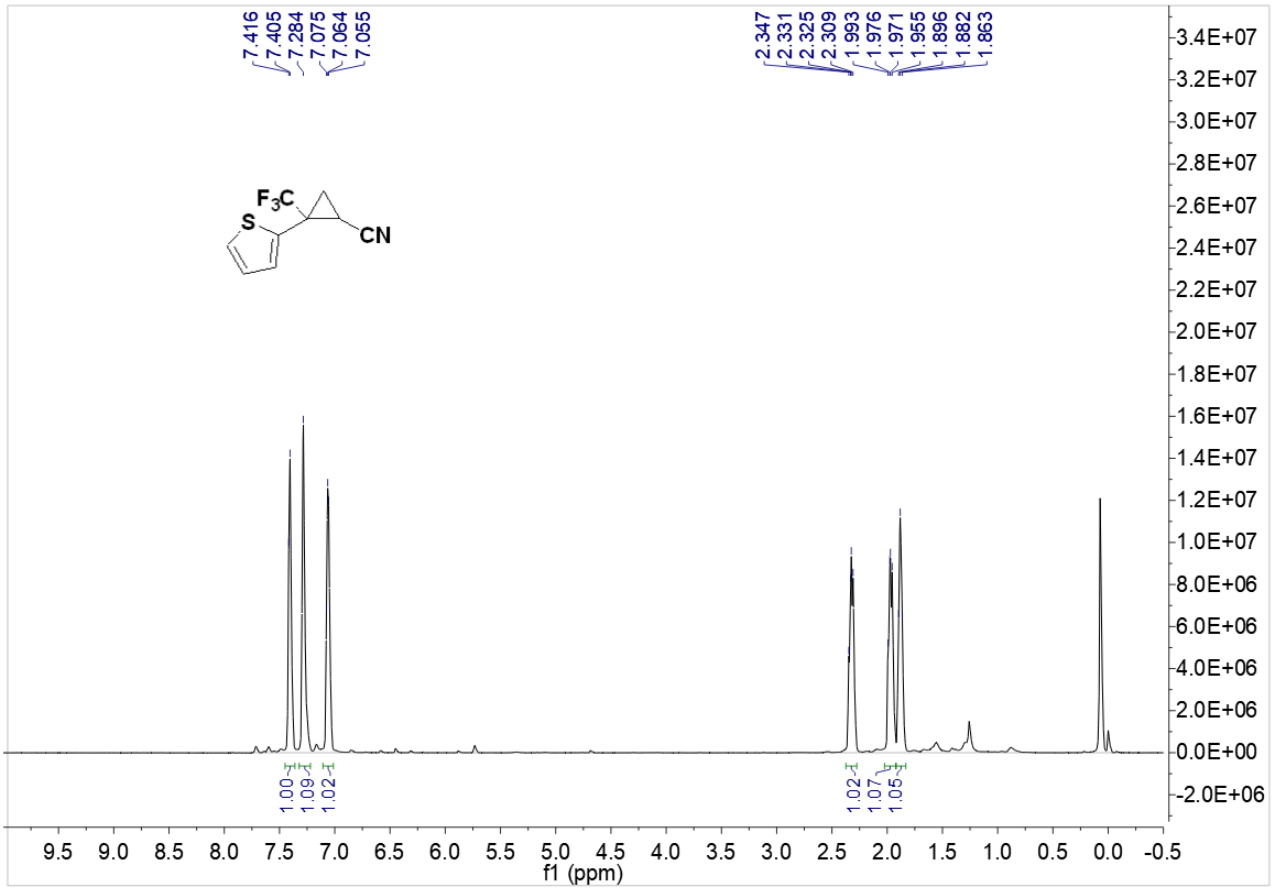
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
308 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 14-14 H: 10-10 N: 0-20 O: 0-20 F: 3-3 Na: 0-3
6
230410-1-19 6 (0.085)

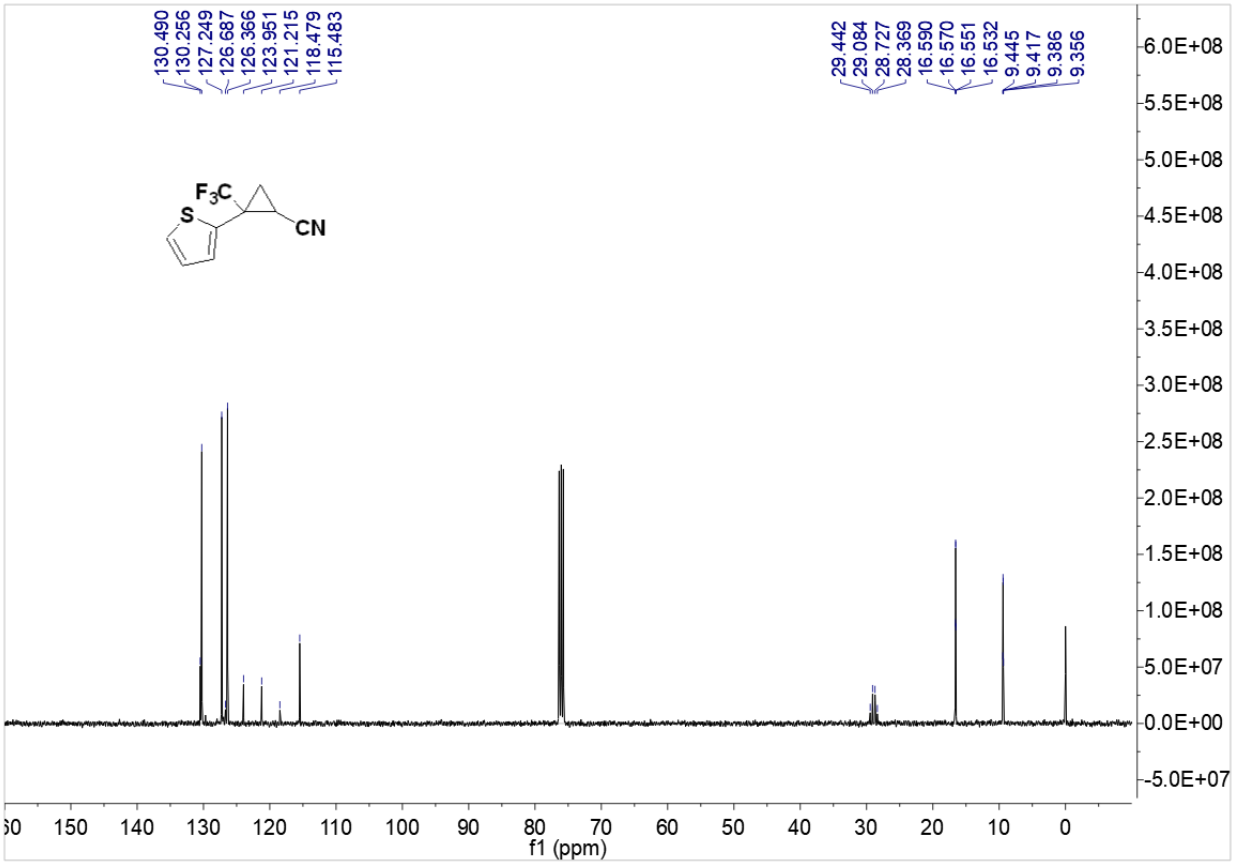


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
263.0794	263.0796	-0.2	-0.8	9.5	253.4	n/a	n/a	C14 H10 N2 F3

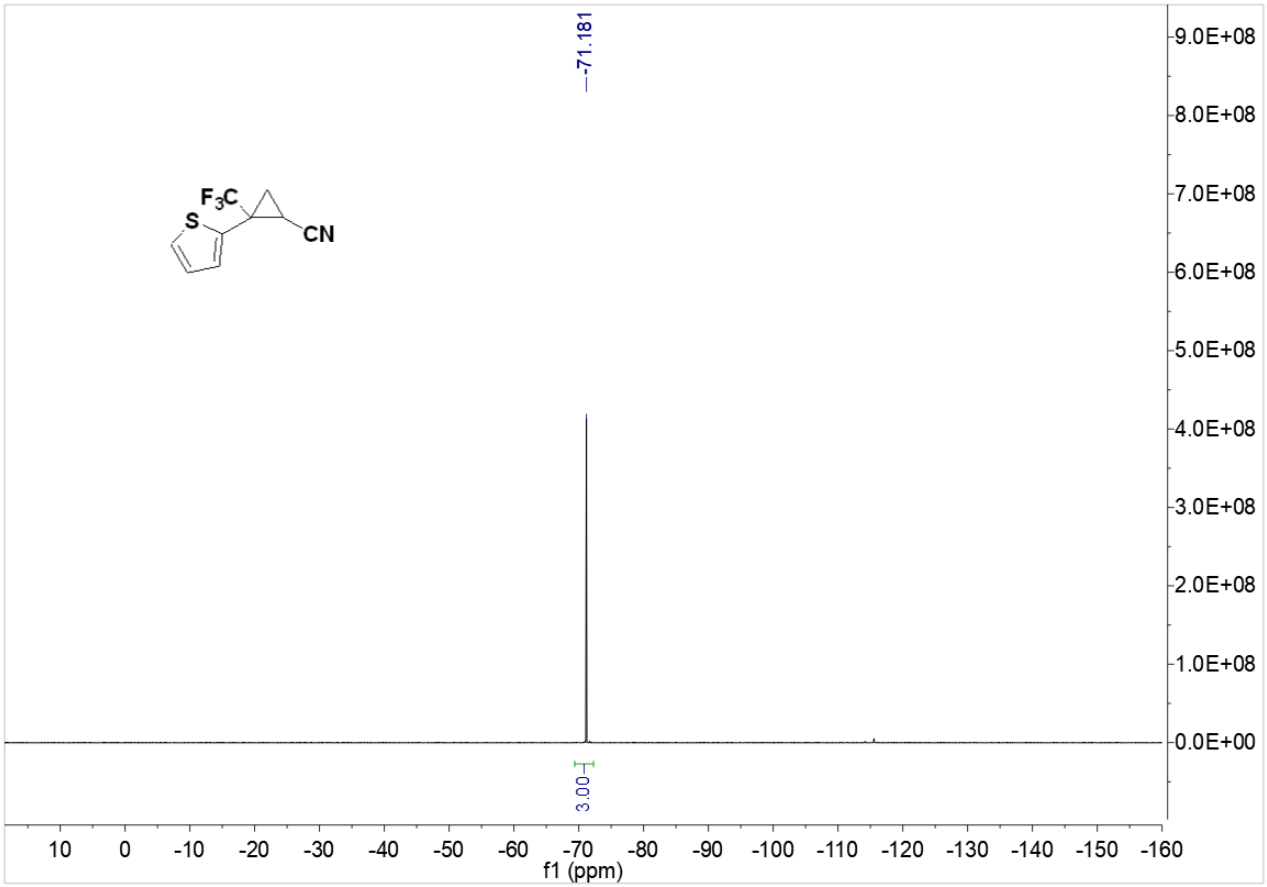
^{1}H NMR spectrum of ***trans*-3pa**



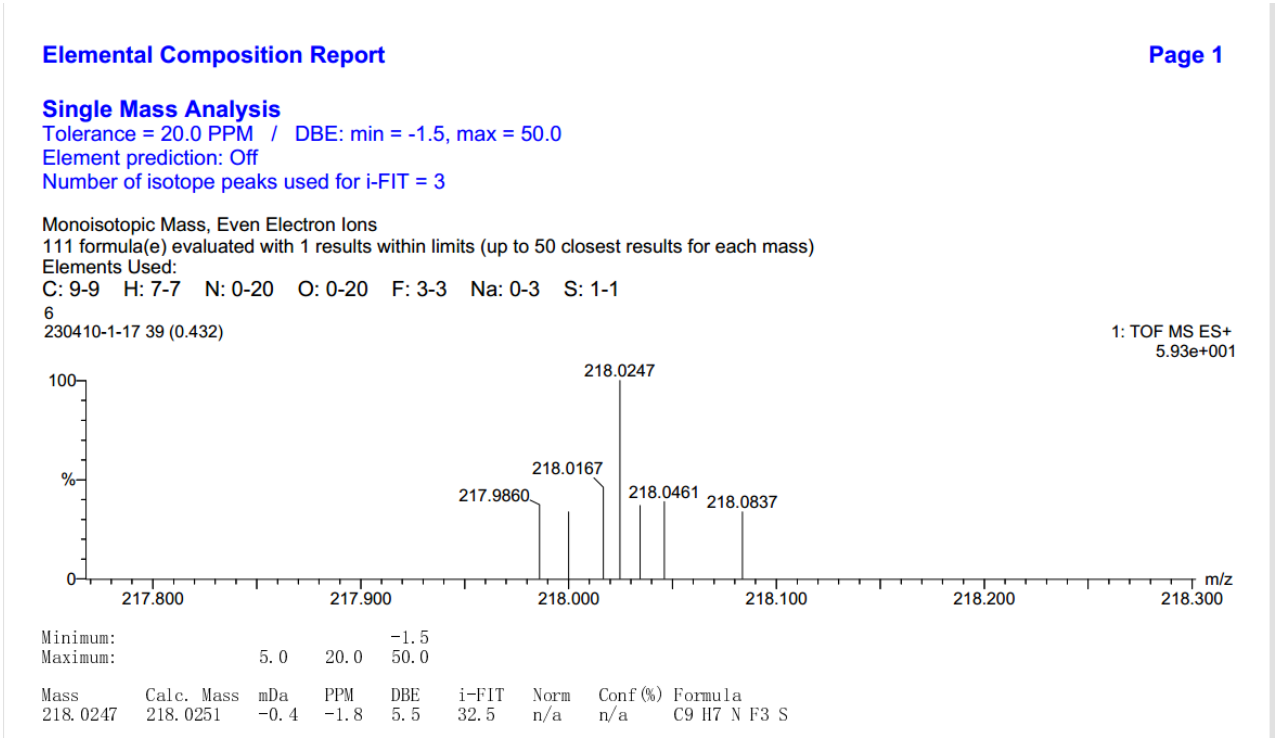
^{13}C NMR spectrum of ***trans*-3pa**



^{19}F NMR spectrum of ***trans*-3pa**



HRMS (ESI) spectrum of ***trans*-3pa**



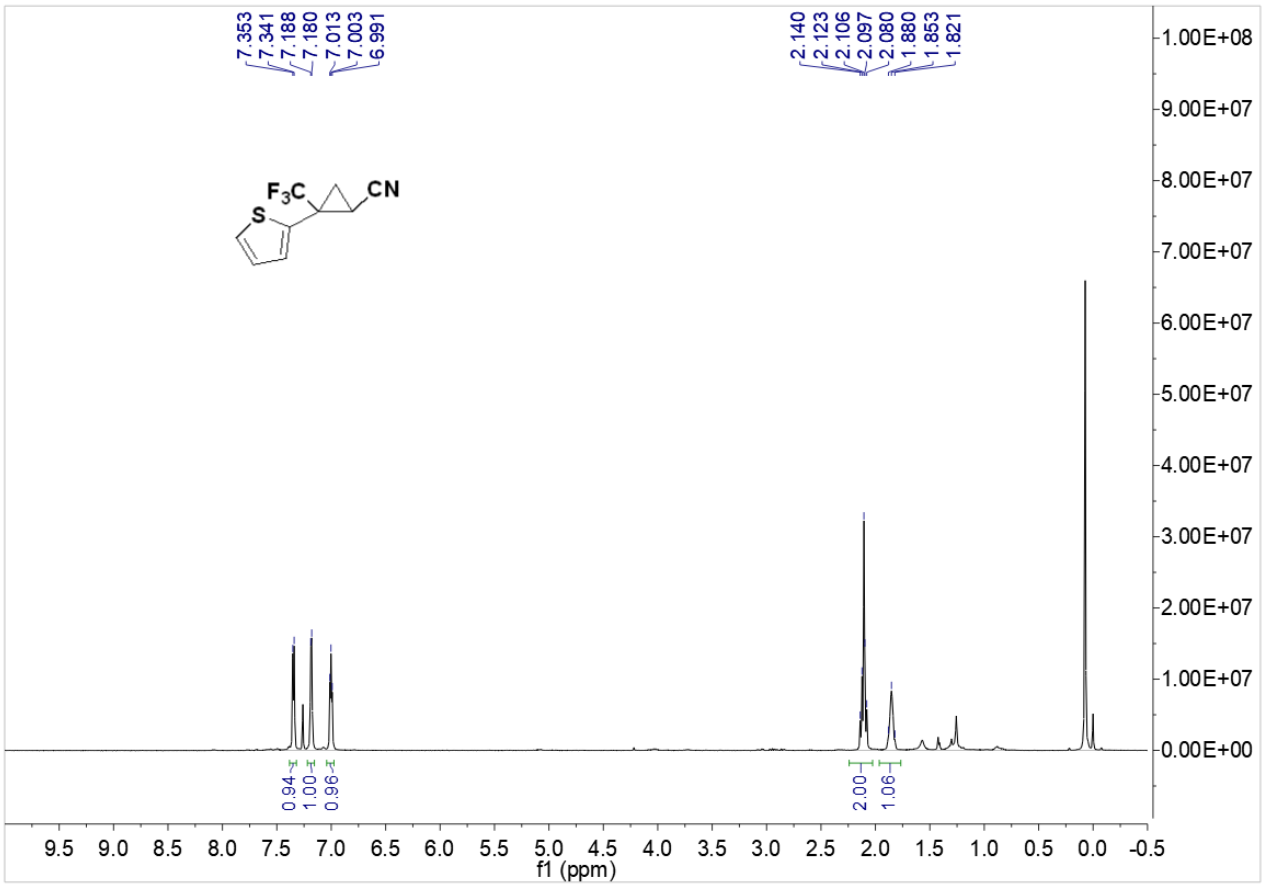
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

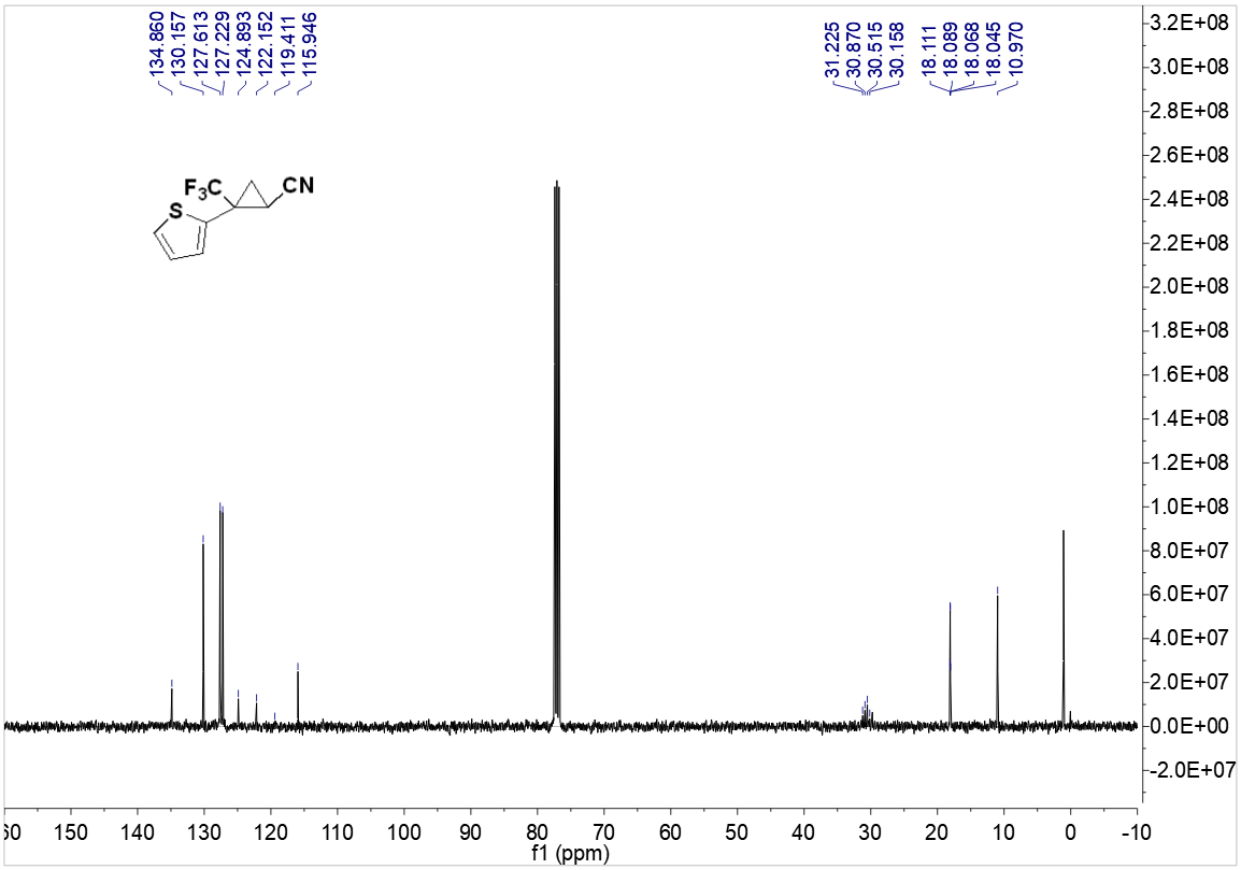
Monoisotopic Mass, Even Electron Ions
111 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-9 H: 7-7 N: 0-20 O: 0-20 F: 3-3 Na: 0-3 S: 1-1
6
230410-1-17 39 (0.432)

Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
218.0247	218.0251	-0.4	-1.8	5.5	32.5	n/a	n/a	C9 H7 N F3 S

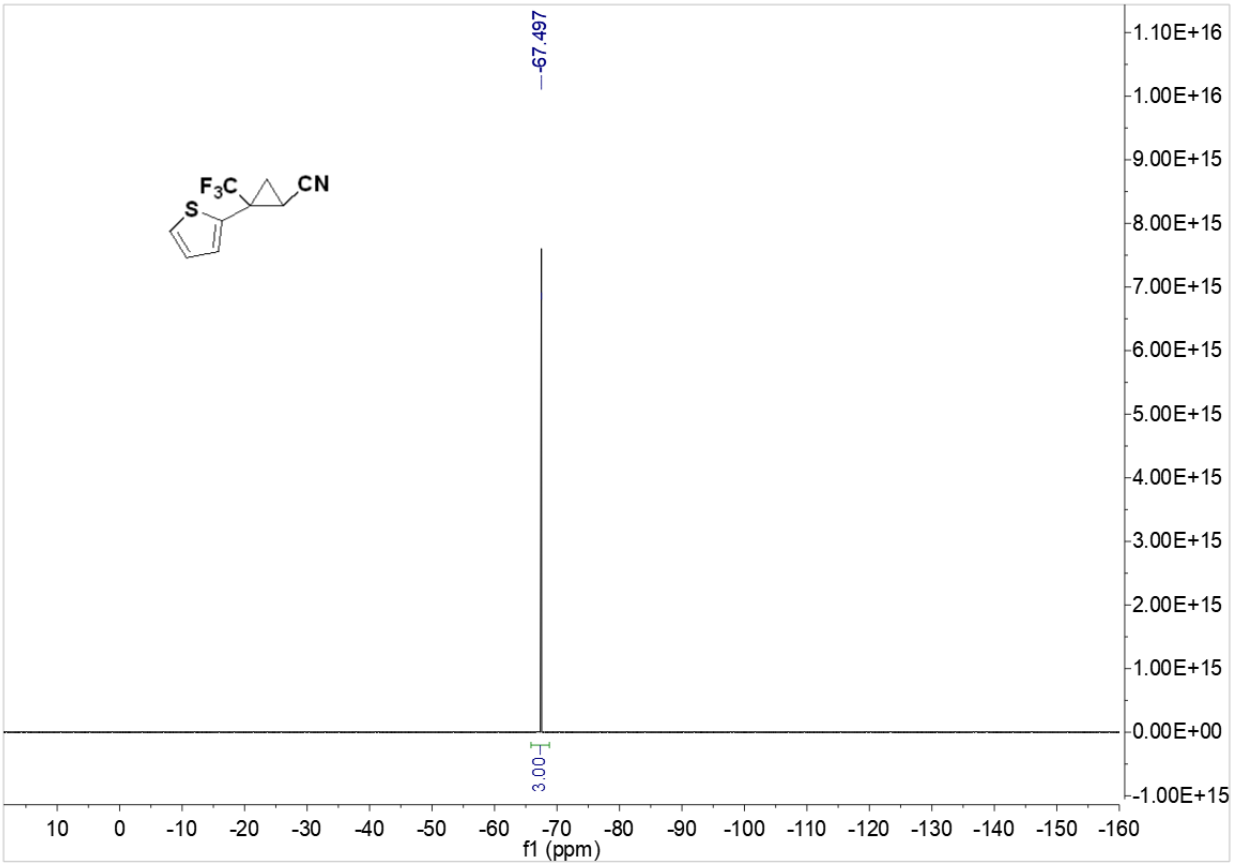
^{1}H NMR spectrum of ***cis*-3pa**



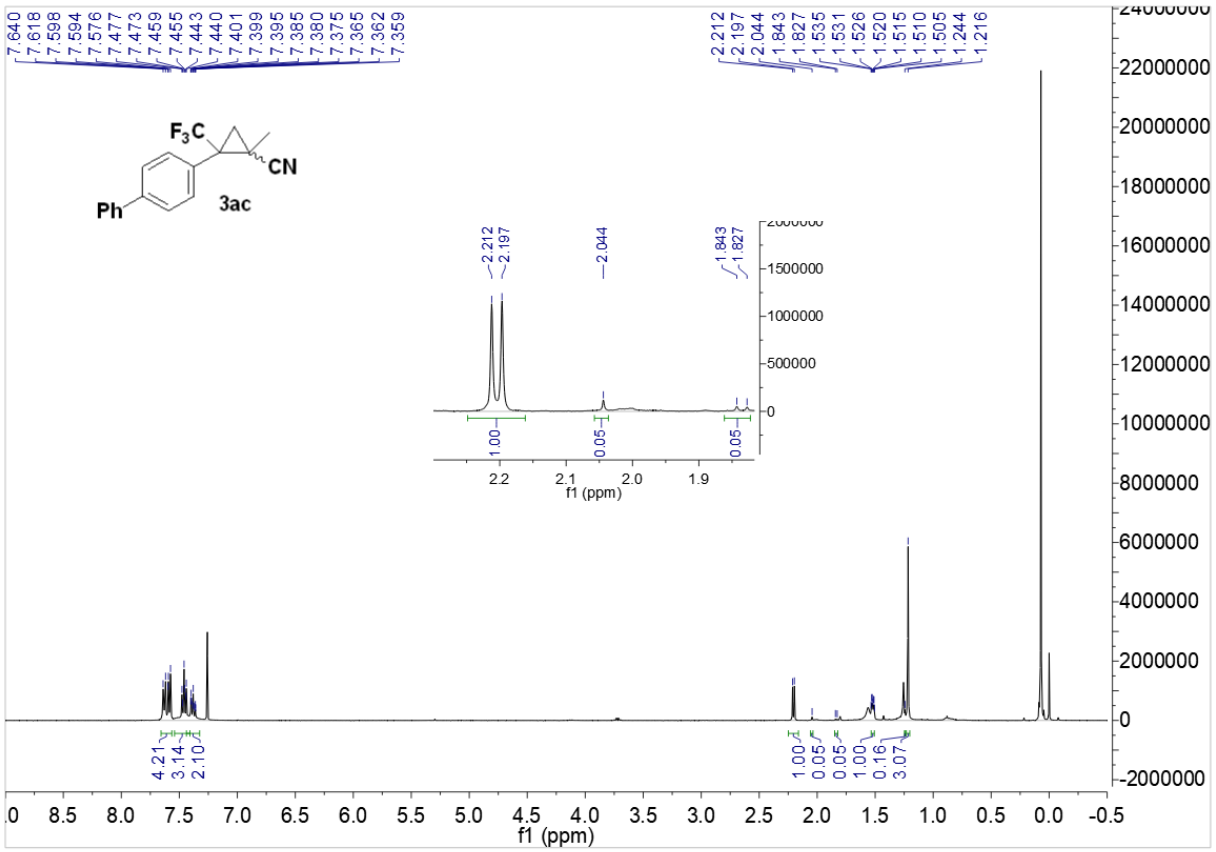
^{13}C NMR spectrum of ***cis*-3pa**



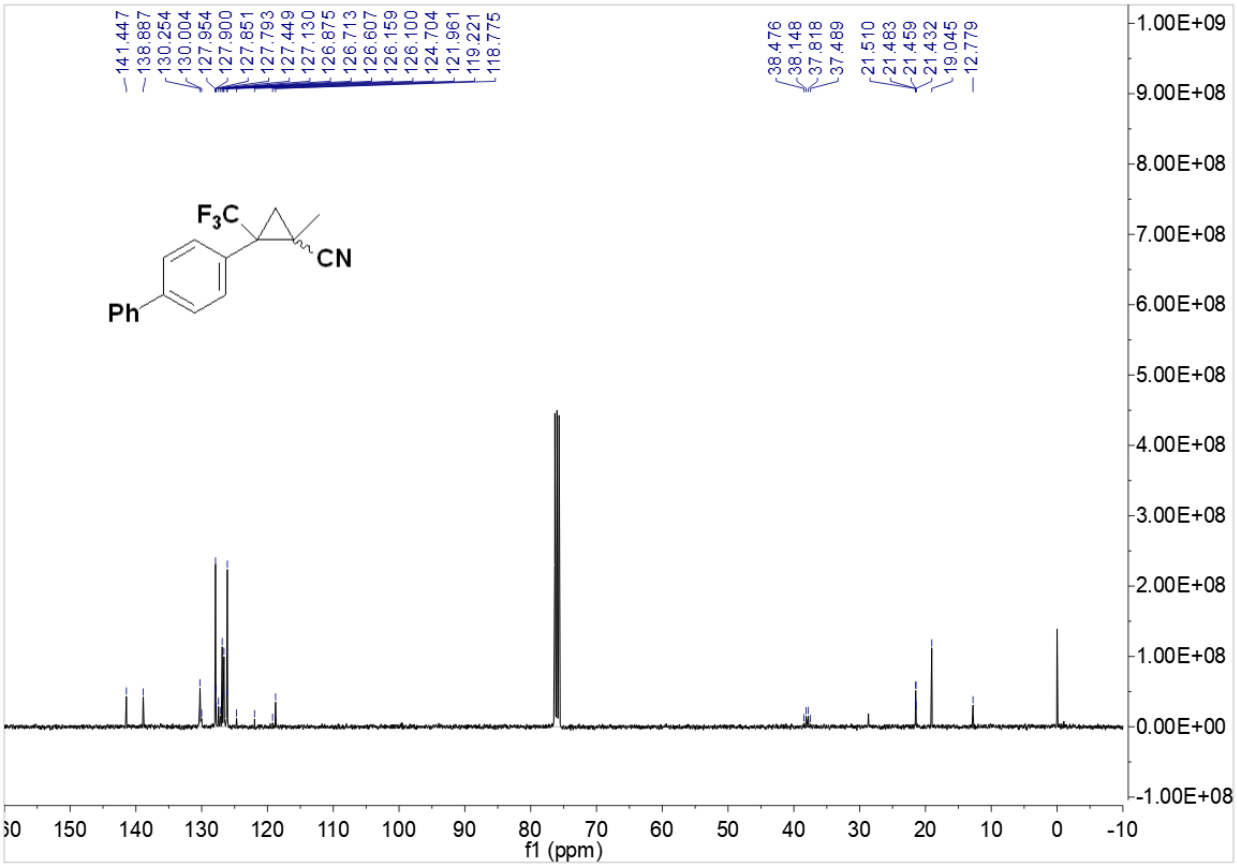
^{19}F NMR spectrum of ***cis*-3pa**



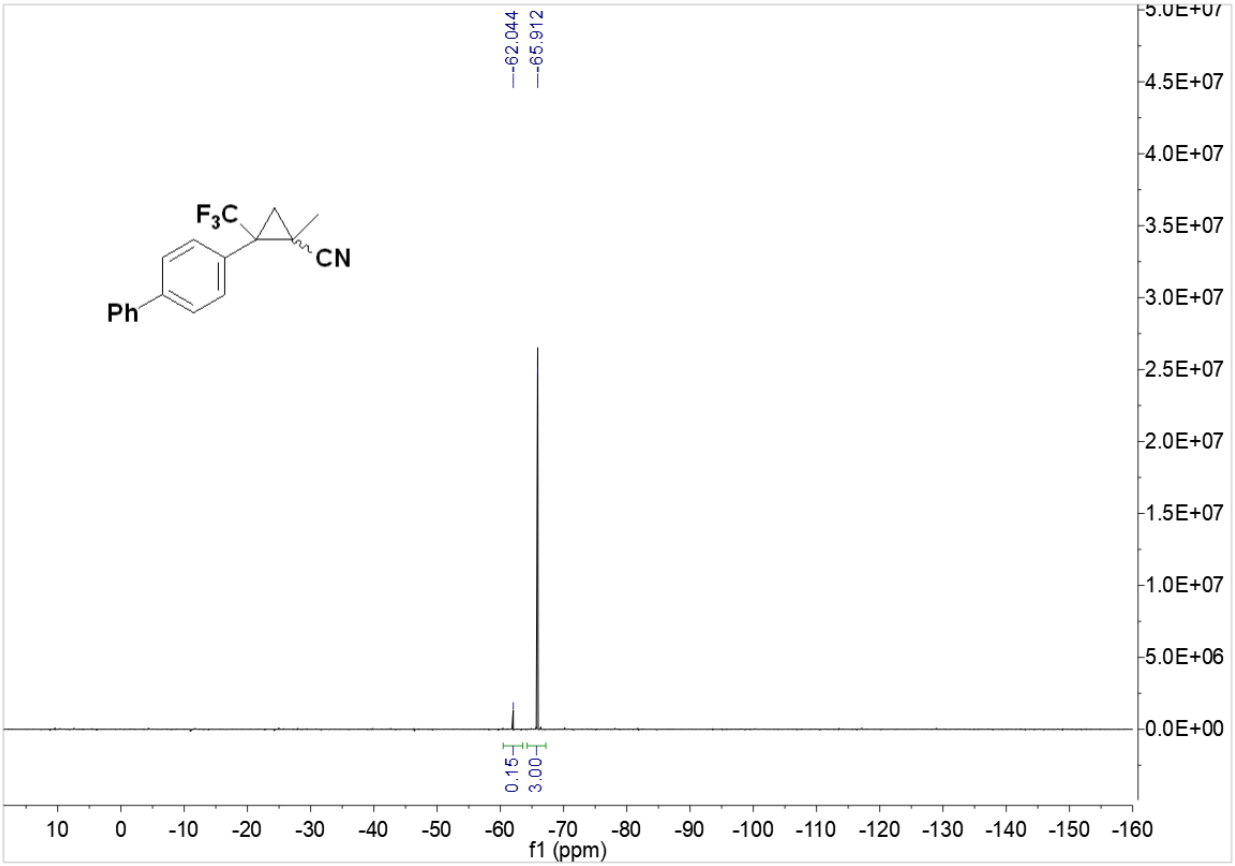
^{1}H NMR spectrum of **3ac**



^{13}C NMR spectrum of **3ac**



^{19}F NMR spectrum of **3ac**



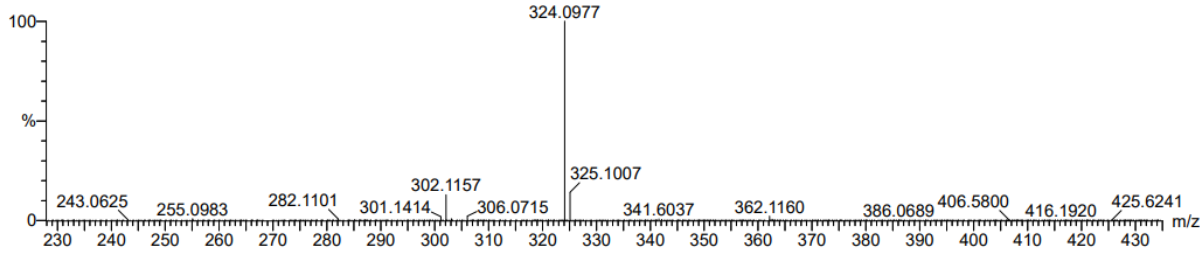
HRMS (ESI) spectrum of **3ac**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

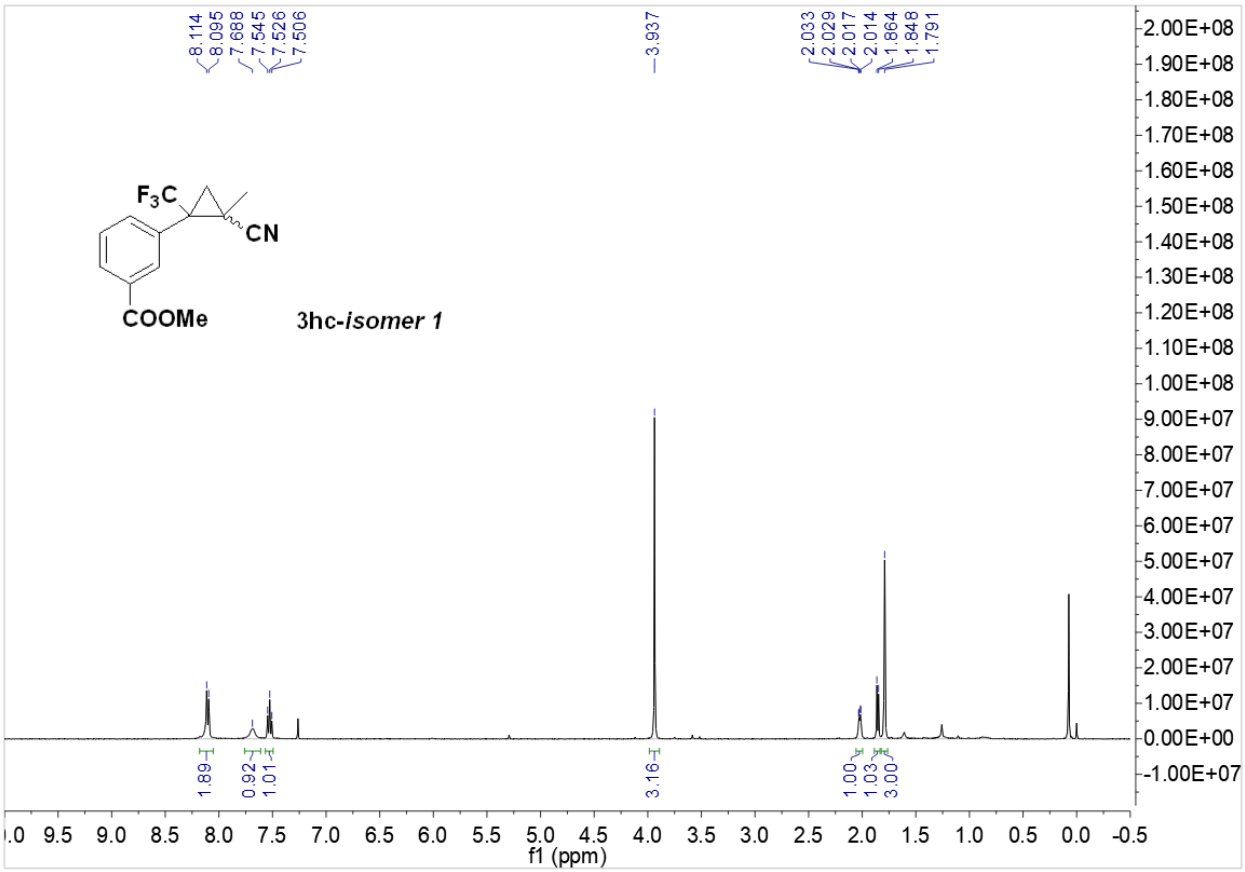
Monoisotopic Mass, Even Electron Ions
312 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 18-18 H: 14-14 N: 0-30 O: 0-100 F: 3-3 Na: 0-1
3
230512-2-3 5 (0.076)

1: TOF MS ES+
1.71e+006

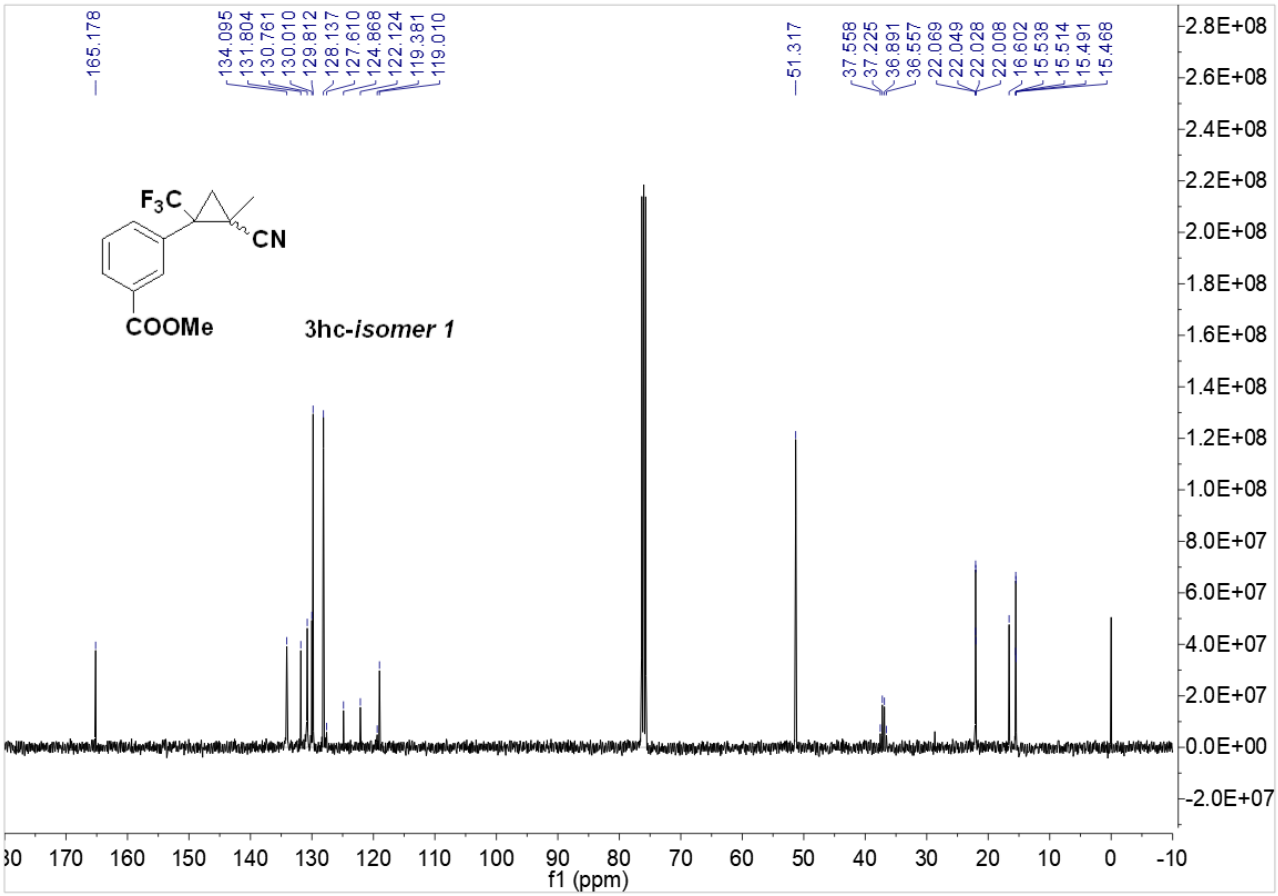


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
324.0977	324.0976	0.1	0.3	10.5	153.3	n/a	n/a	C18 H14 N F3 Na

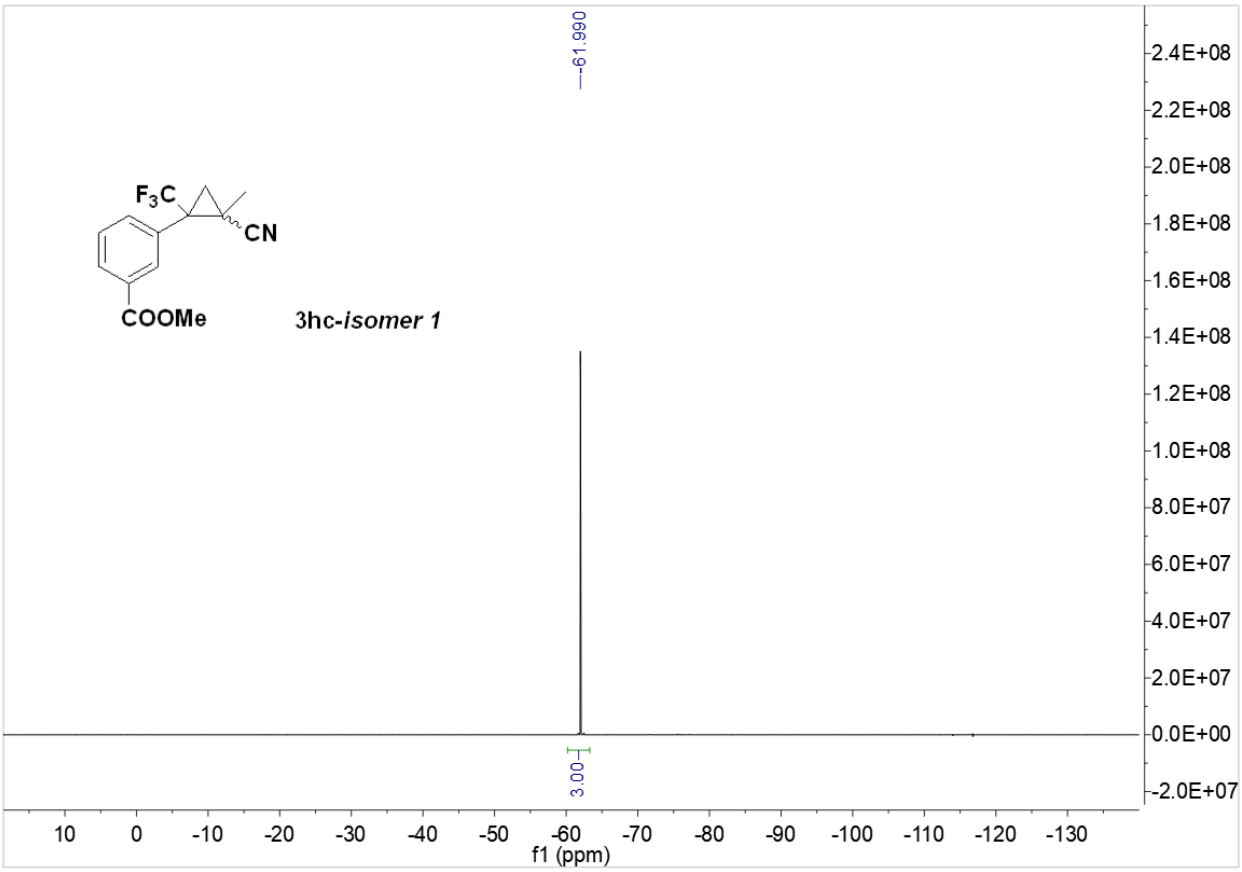
^{1}H NMR spectrum of **3hc-*isomer 1***



^{13}C NMR spectrum of **3hc-*isomer 1***



^{19}F NMR spectrum of **3hc-*isomer 1***



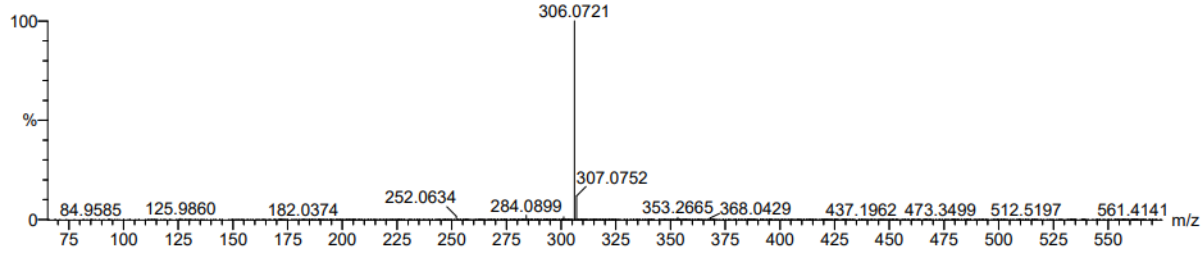
HRMS (ESI) spectrum of **3hc-*isomer 1***

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

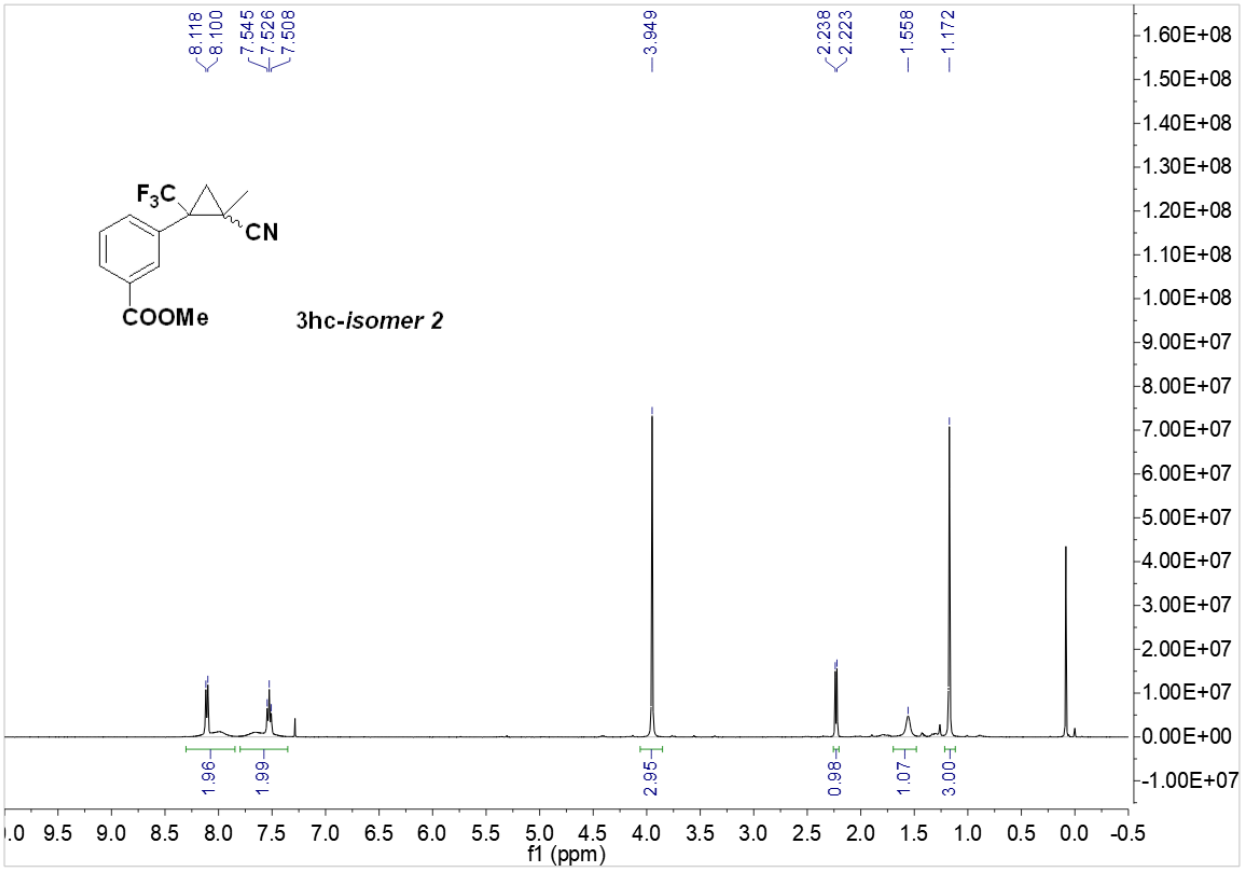
Monoisotopic Mass, Even Electron Ions
256 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 14-14 H: 12-12 N: 0-30 O: 0-100 F: 3-3 Na: 0-1
3
230512-2-2 8 (0.102)

1: TOF MS ES+
3.52e+006

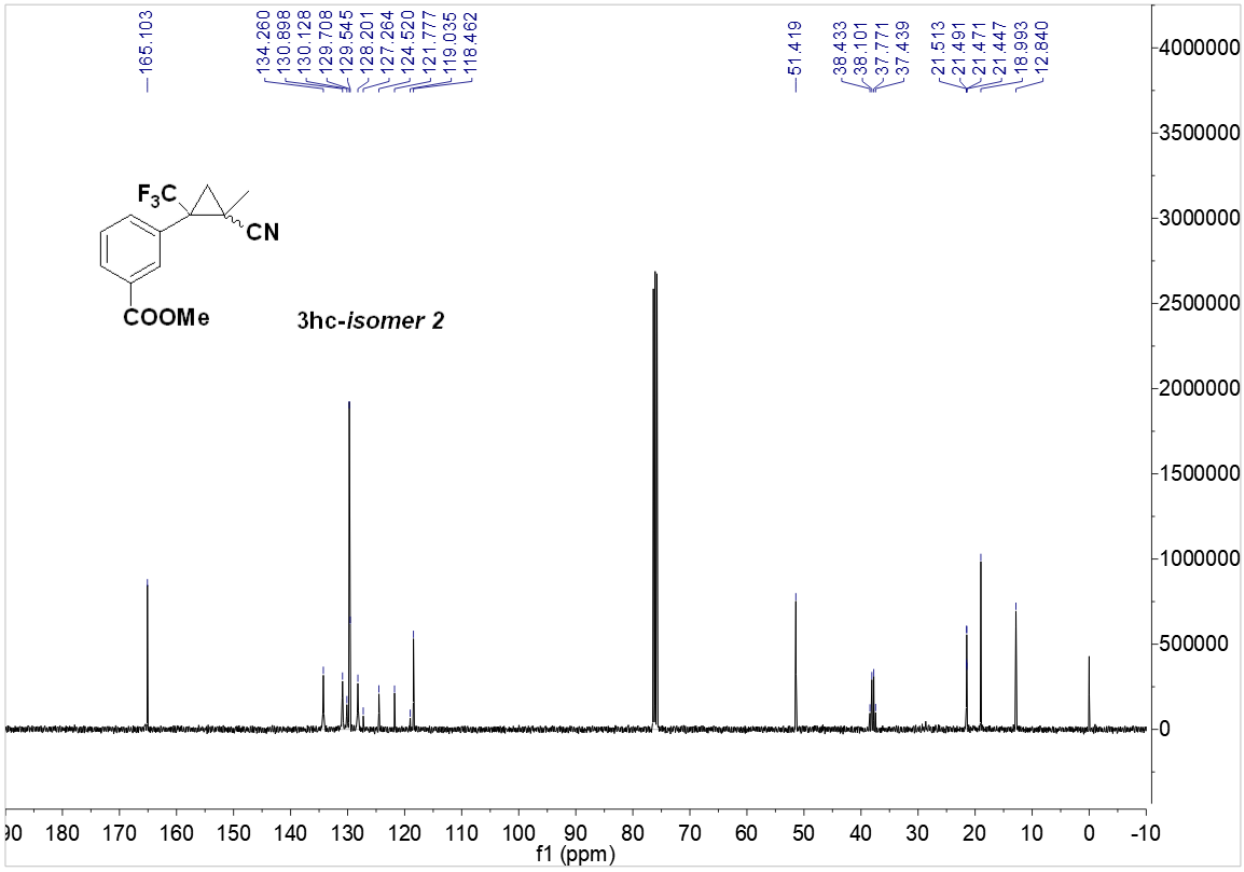


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
306.0721	306.0718	0.3	1.0	7.5	117.0	n/a	n/a	C14 H12 N O2 F3 Na

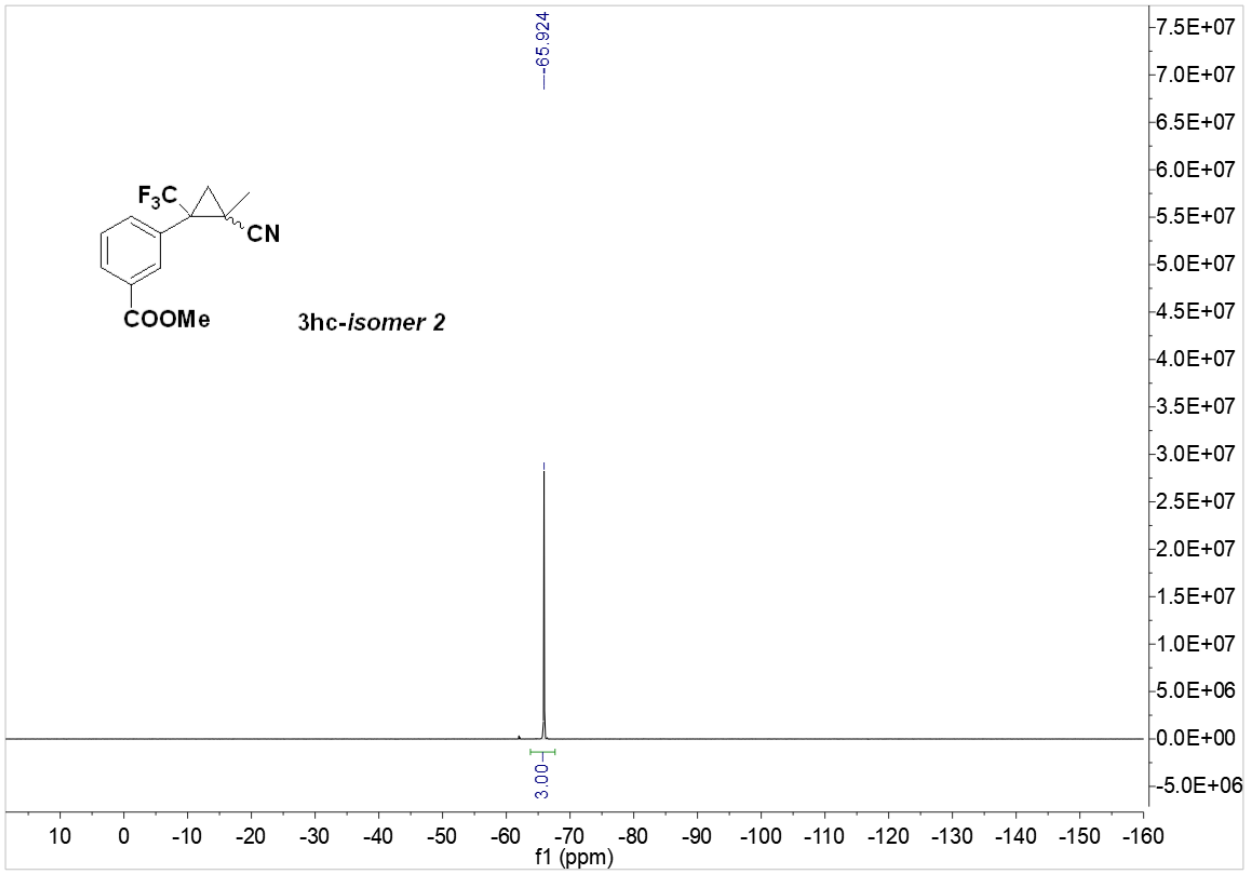
^{1}H NMR spectrum of **3hc-*isomer 2***



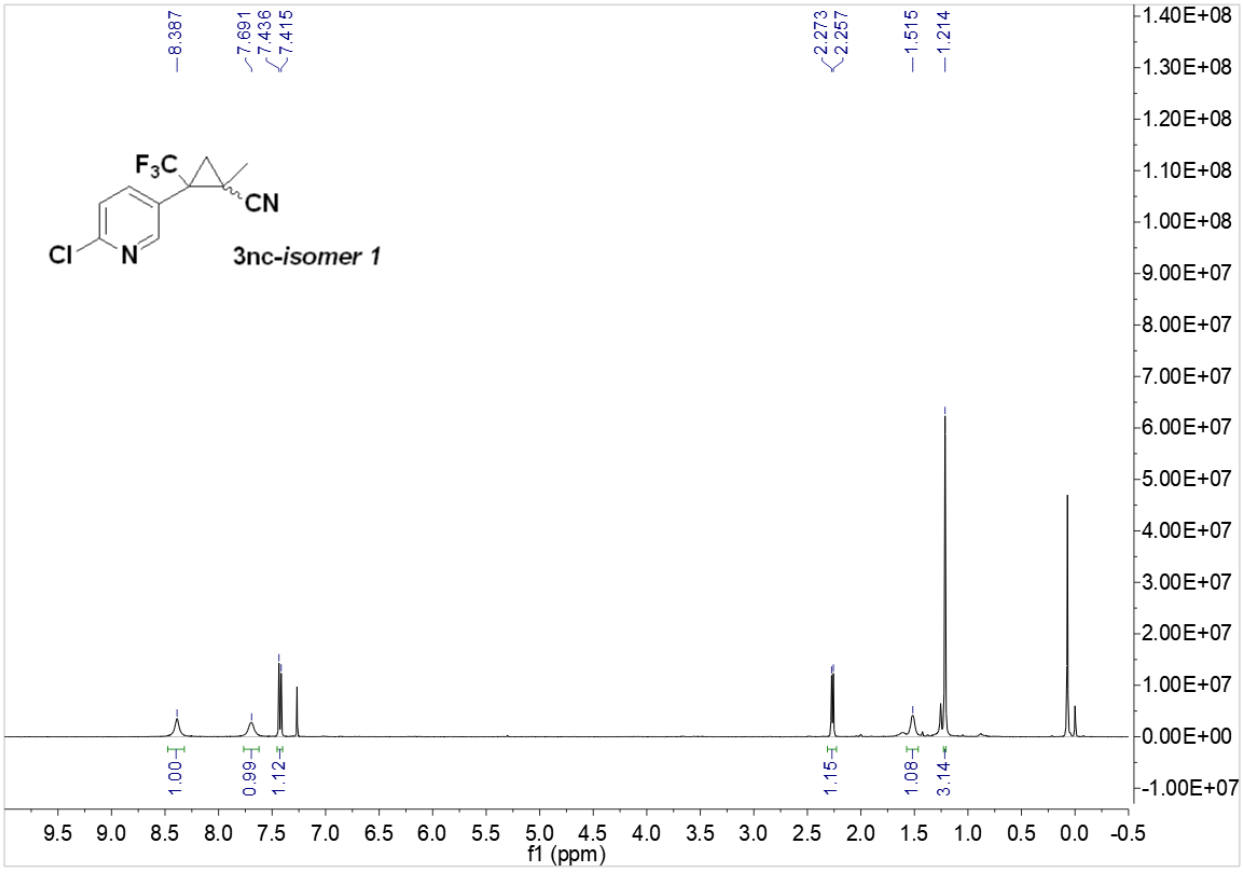
^{13}C NMR spectrum of **3hc-*isomer 2***



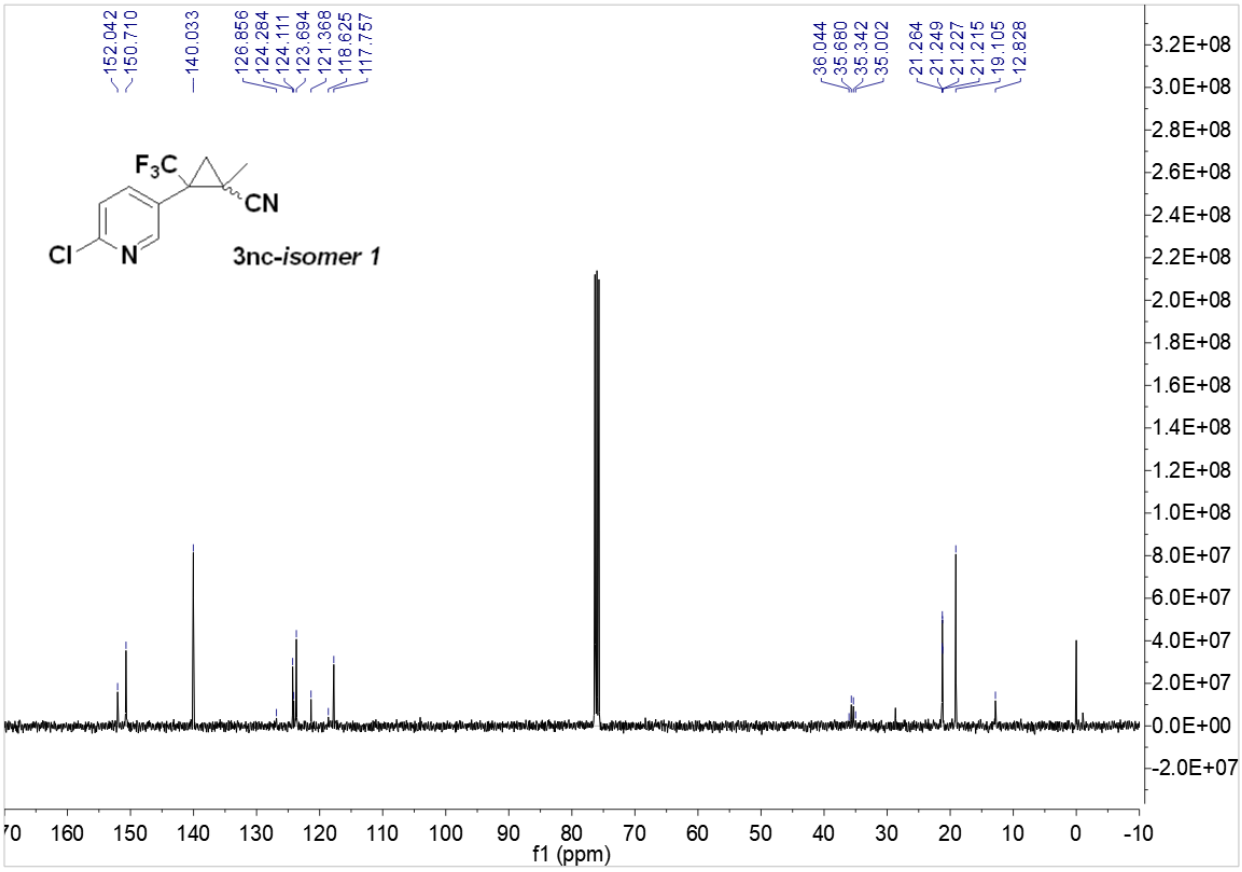
^{19}F NMR spectrum of **3hc-*isomer 2***



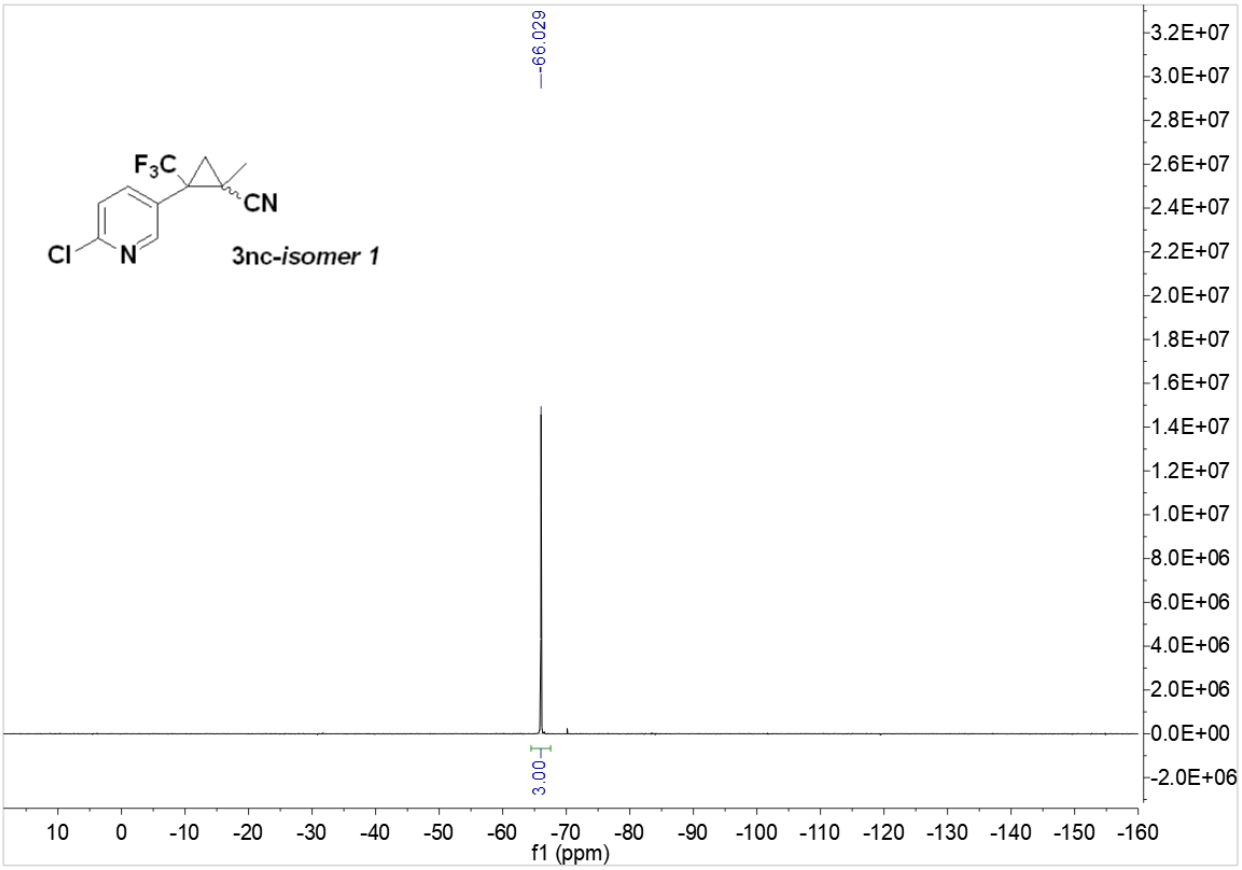
^{1}H NMR spectrum of **3nc-*isomer 1***



^{13}C NMR spectrum of **3nc-*isomer 1***



^{19}F NMR spectrum of **3nc-*isomer 1***



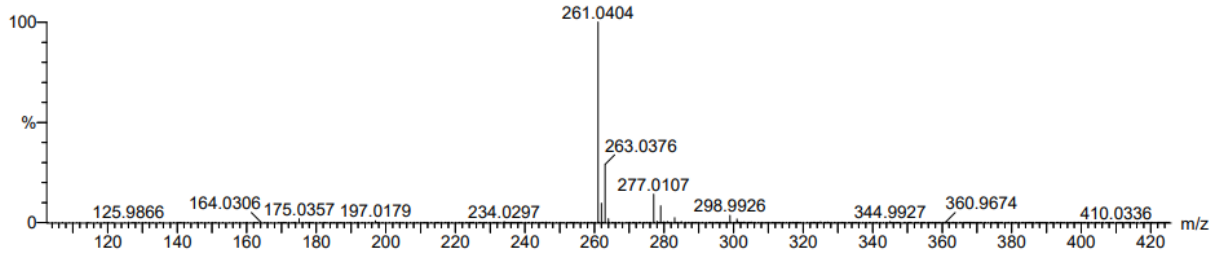
HRMS (ESI) spectrum of **3nc-*isomer 1***

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

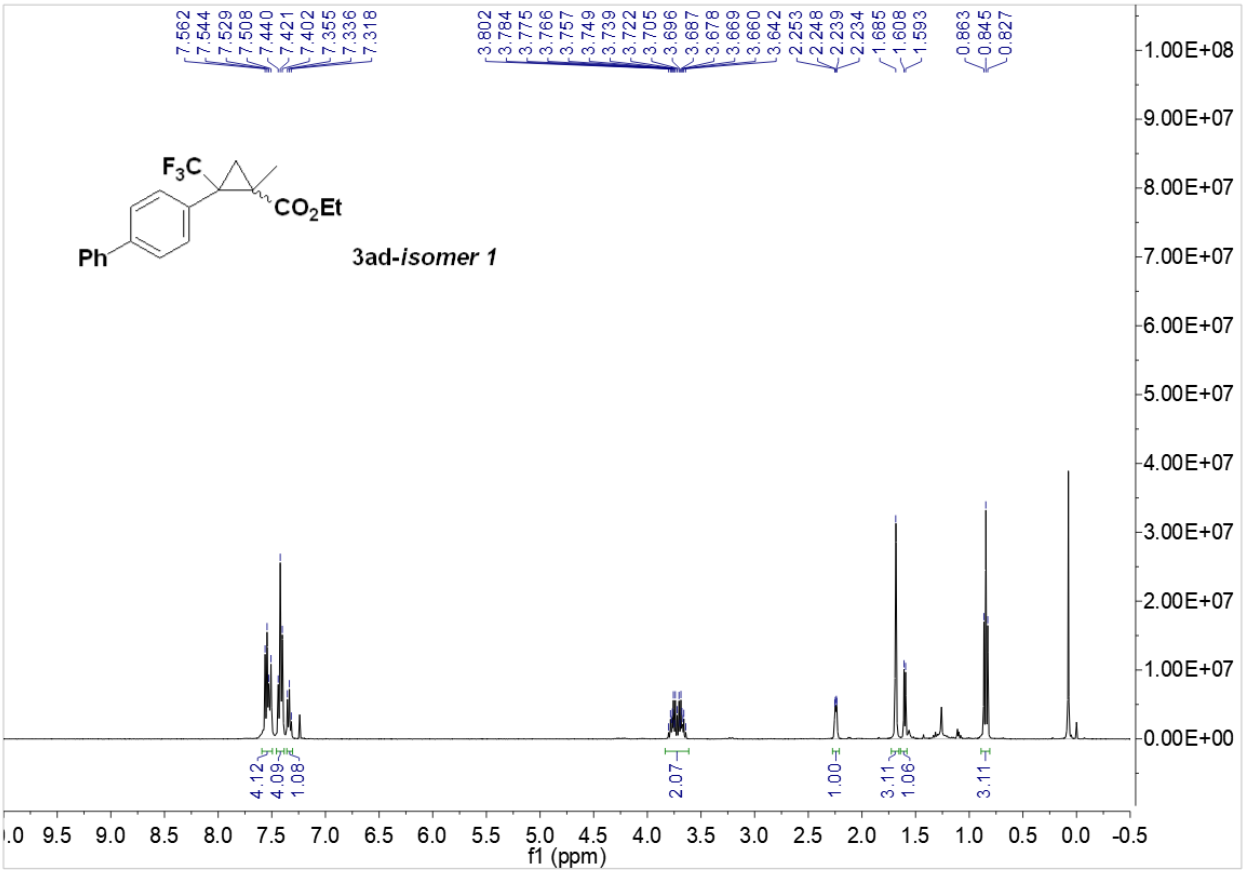
Monoisotopic Mass, Even Electron Ions
209 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 11-11 H: 9-9 N: 0-30 O: 0-100 Na: 0-1 Cl: 1-2 F: 3-3

3
230512-2-1 6 (0.085)

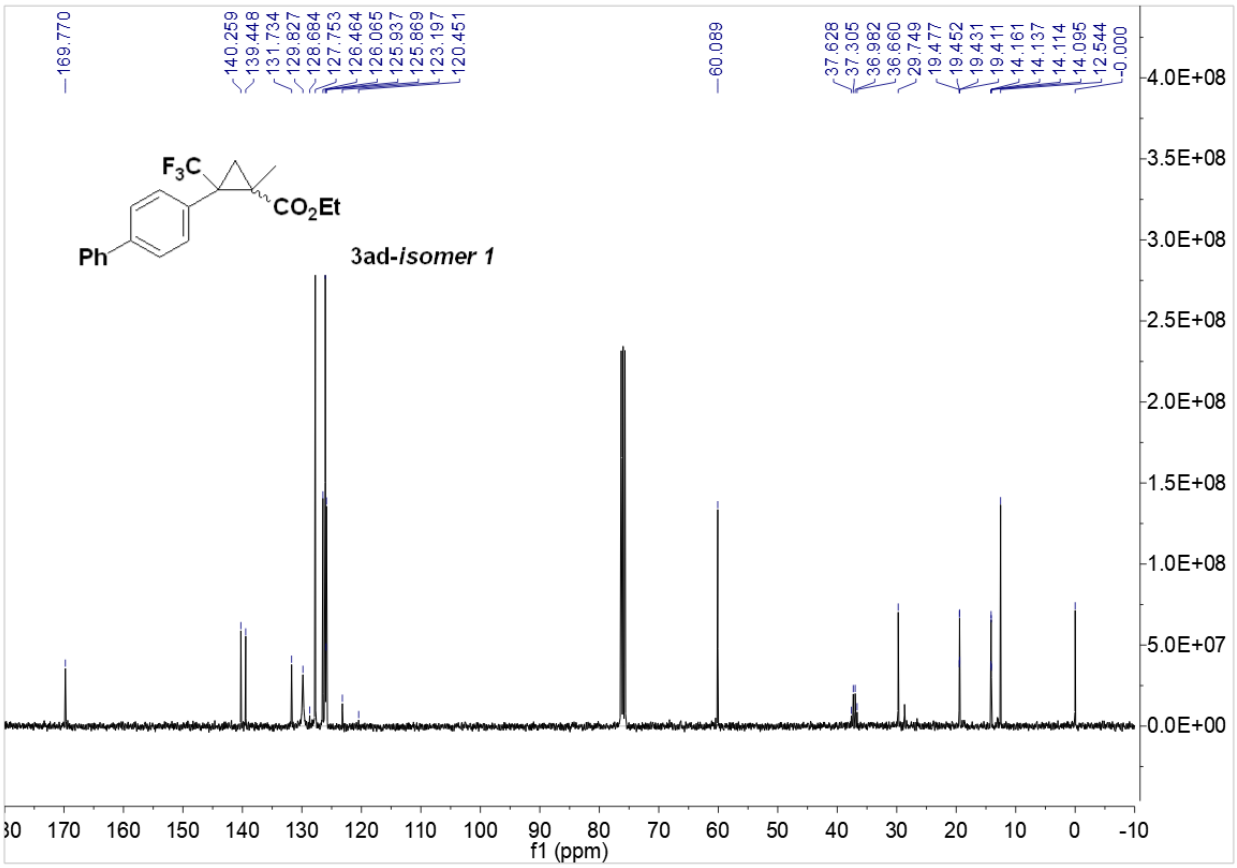


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
261.0404	261.0406	-0.2	-0.8	6.5	164.7	n/a	n/a	C11 H9 N2 Cl F3

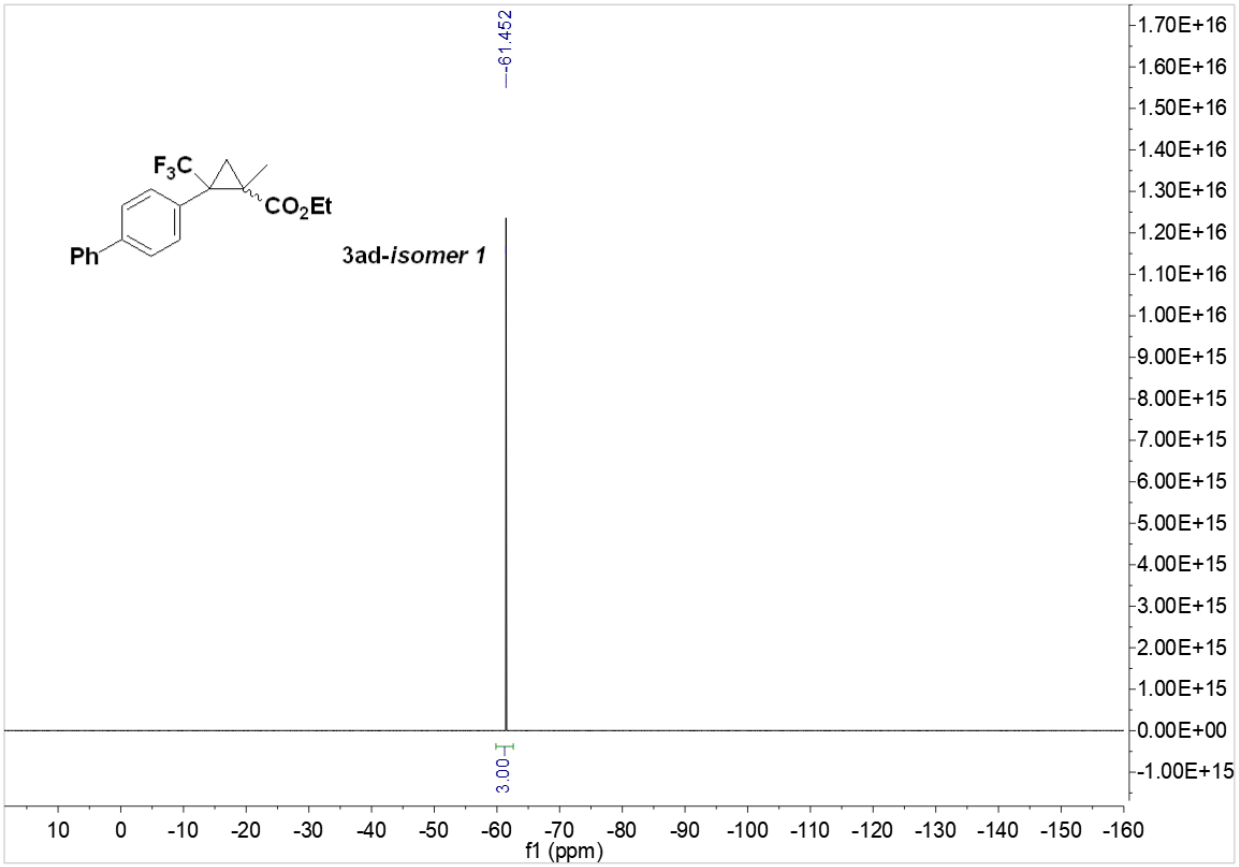
^{1}H NMR spectrum of **3ad-*isomer 1***



^{13}C NMR spectrum of **3ad-*isomer 1***



^{19}F NMR spectrum of **3ad-*isomer 1***

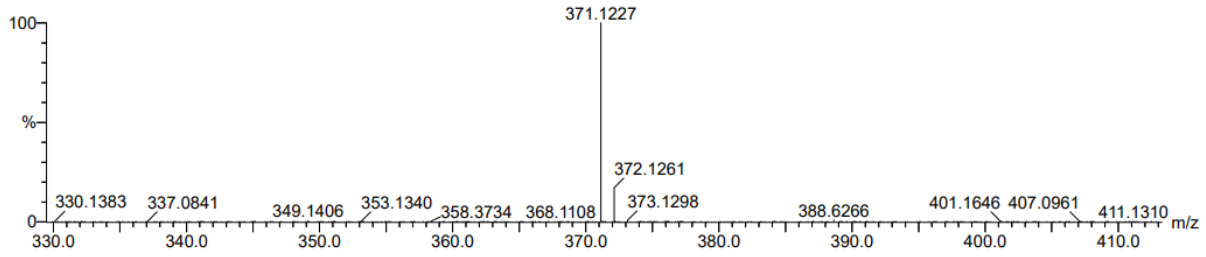


HRMS (ESI) spectrum of **3ad-*isomer 1***

Elemental Composition Report **Page 1**

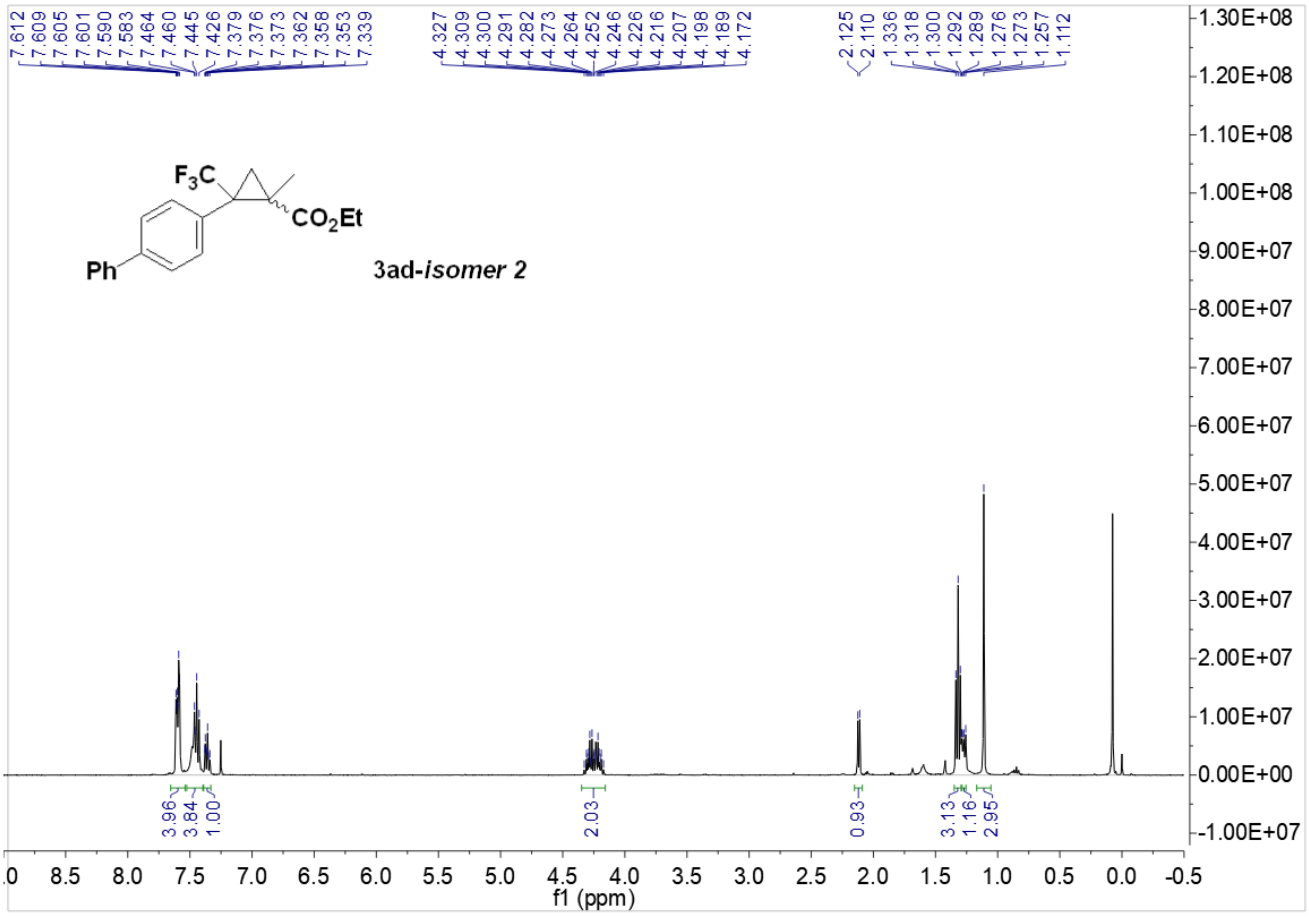
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
422 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 20-20 H: 19-19 N: 0-30 O: 0-100 F: 3-3 Na: 0-1
3
230512-2-5 5 (0.076) 1: TOF MS ES+ 3.41e+006

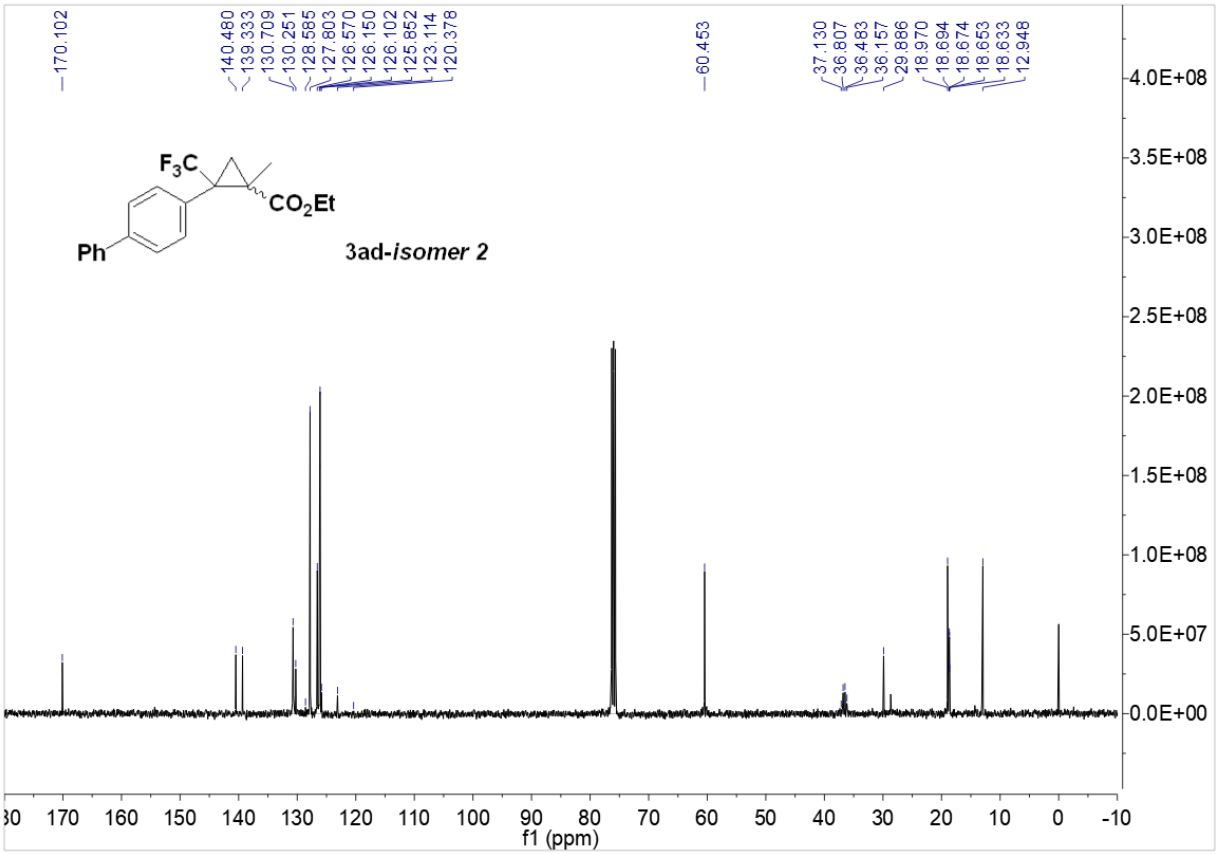


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
371.1227	371.1235	-0.8	-2.2	9.5	131.8	n/a	n/a	C20 H19 O2 F3 Na

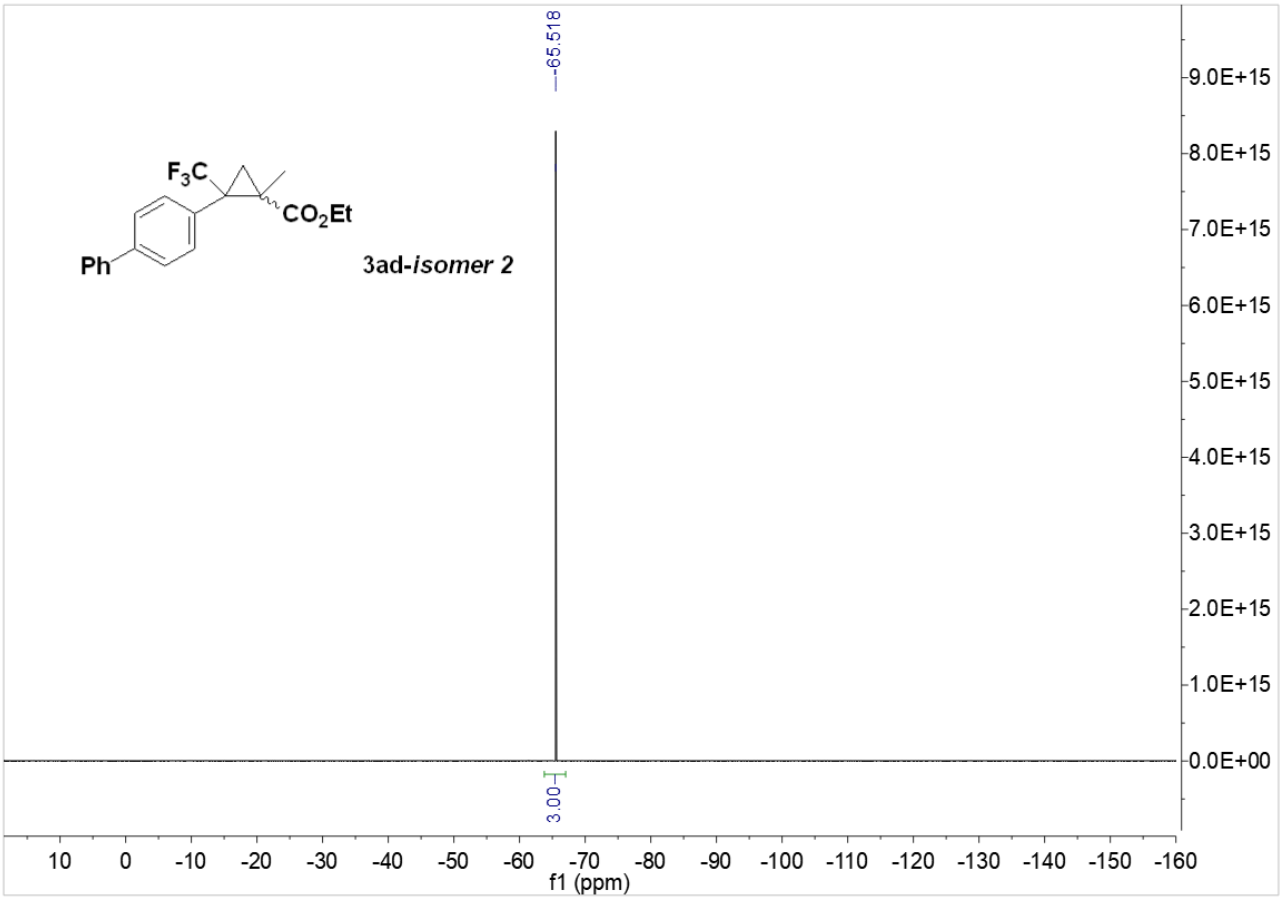
^{1}H NMR spectrum of **3ad-*isomer 2***



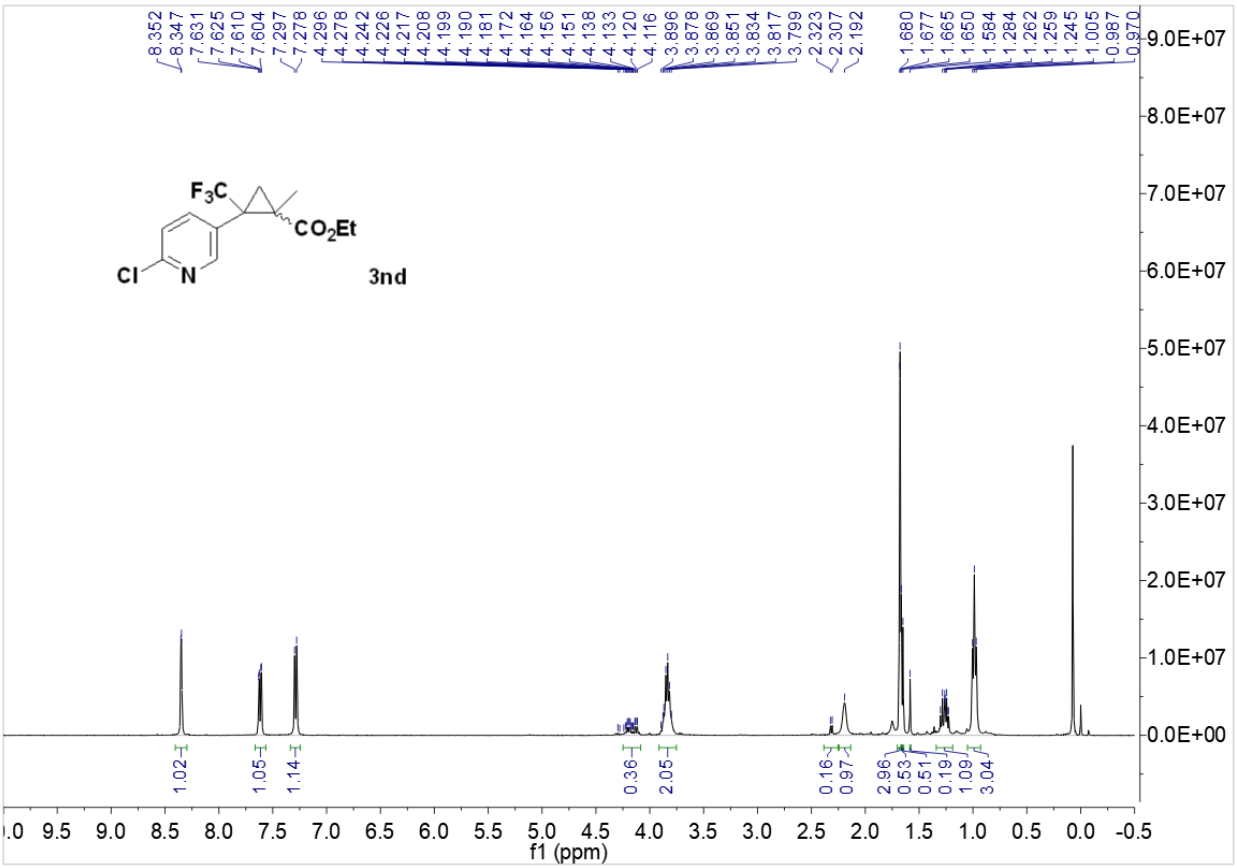
^{13}C NMR spectrum of **3ad-*isomer 2***



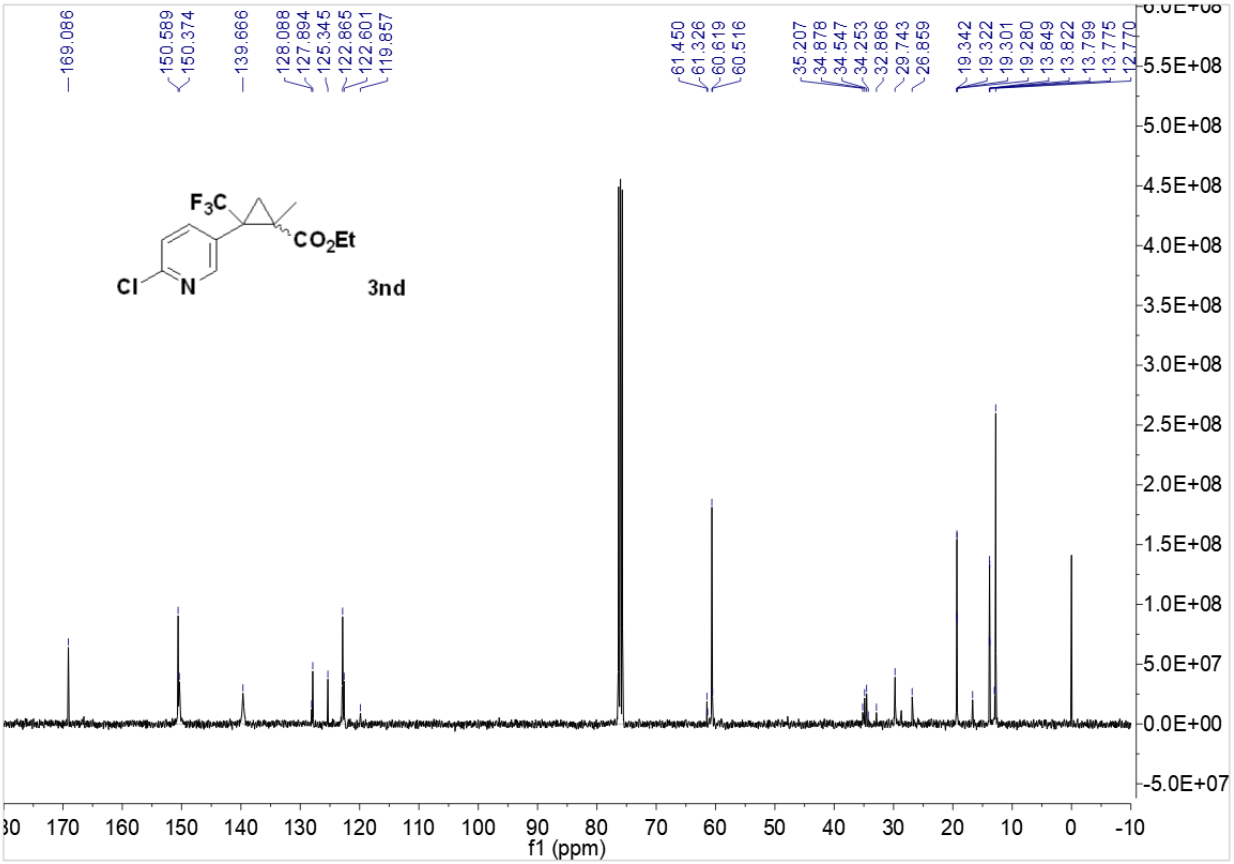
^{19}F NMR spectrum of **3ad-*isomer 2***



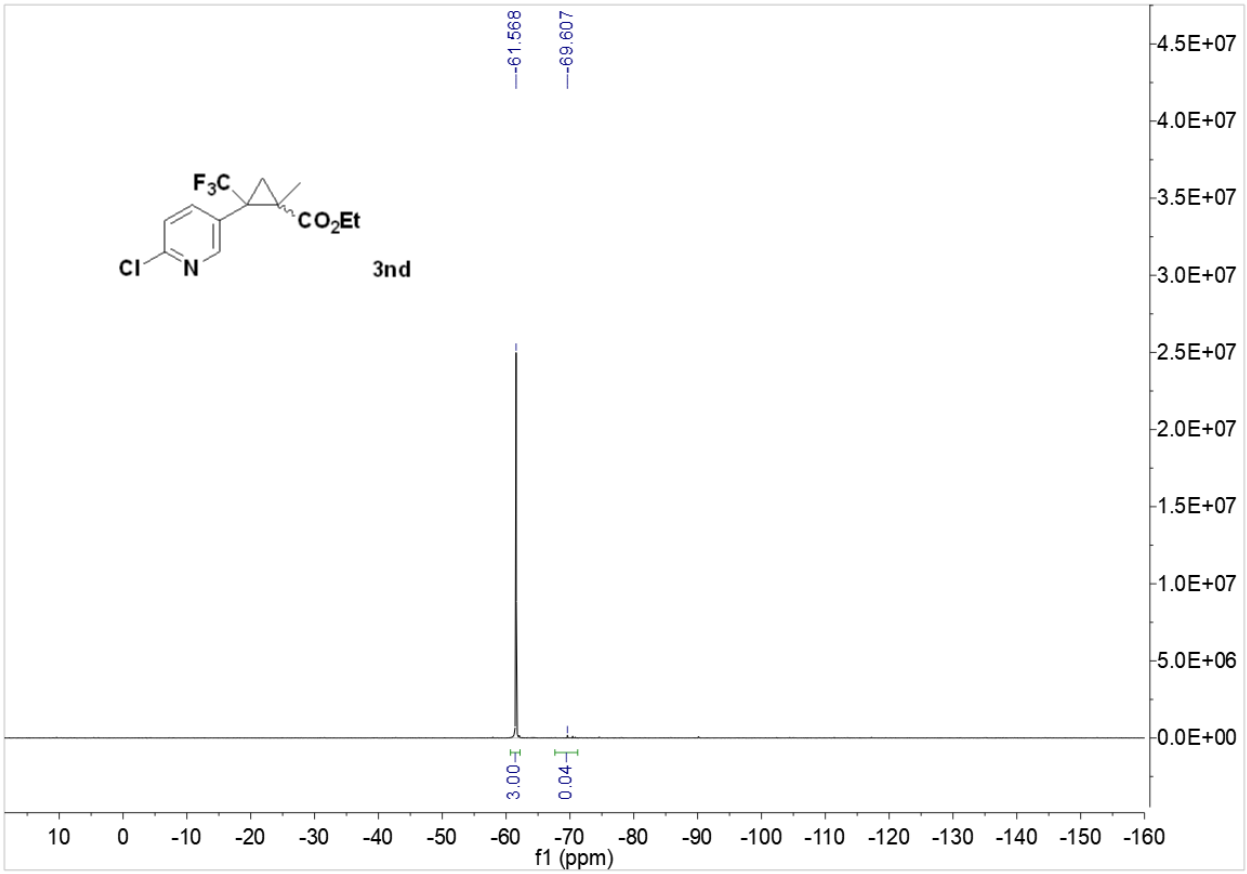
^{1}H NMR spectrum of **3nd**



^{13}C NMR spectrum of **3nd**



^{19}F NMR spectrum of **3nd**



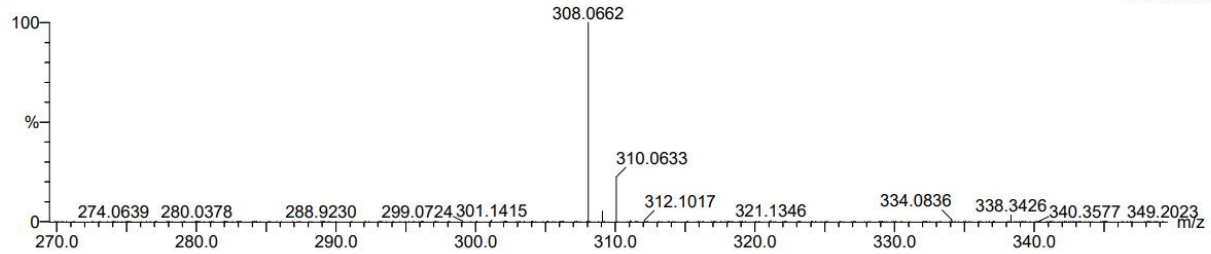
HRMS (ESI) spectrum of **3nd**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

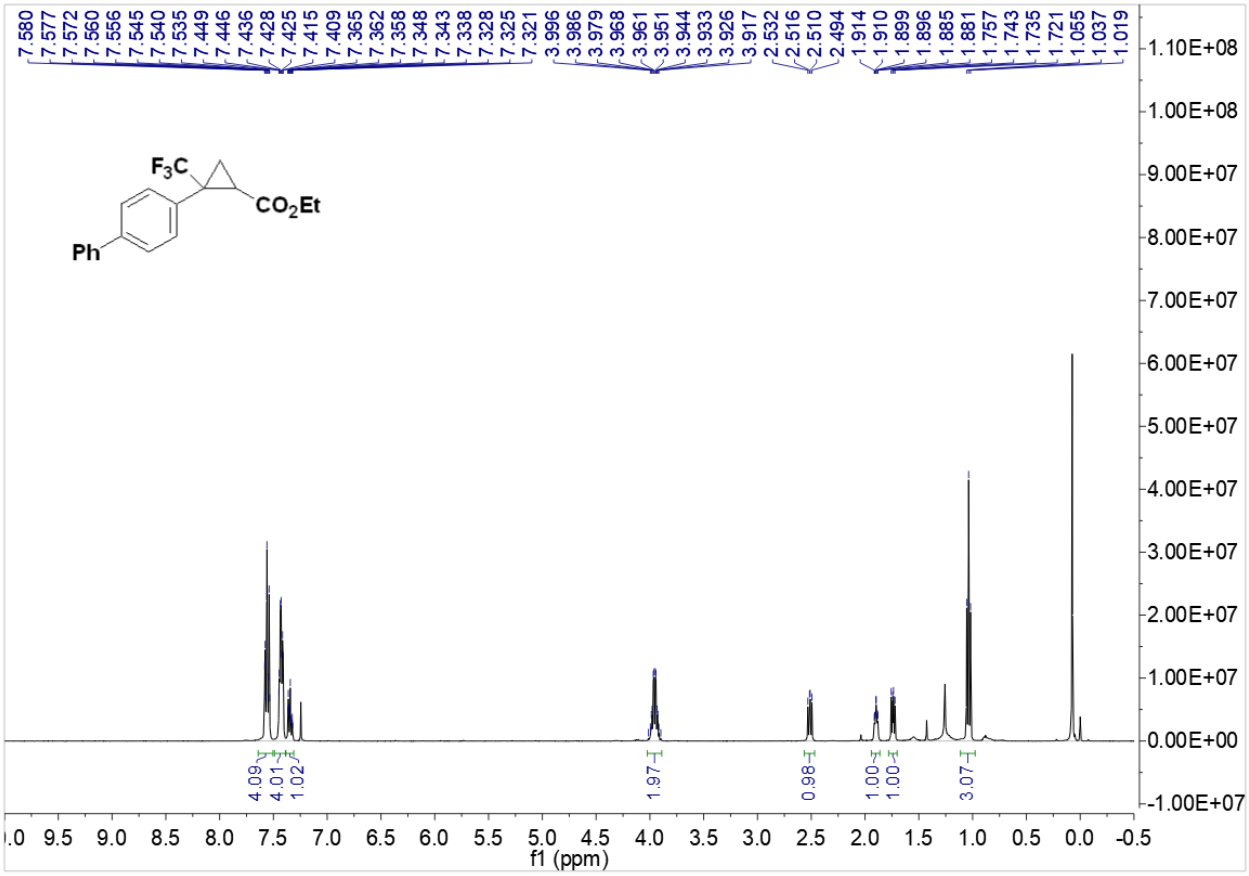
Monoisotopic Mass, Even Electron Ions
344 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 13-13 H: 14-14 N: 0-30 O: 0-100 F: 3-3 Na: 0-1 Cl: 1-2
3
230512-2-4 13 (0.161)

1: TOF MS ES+
5.53e+005

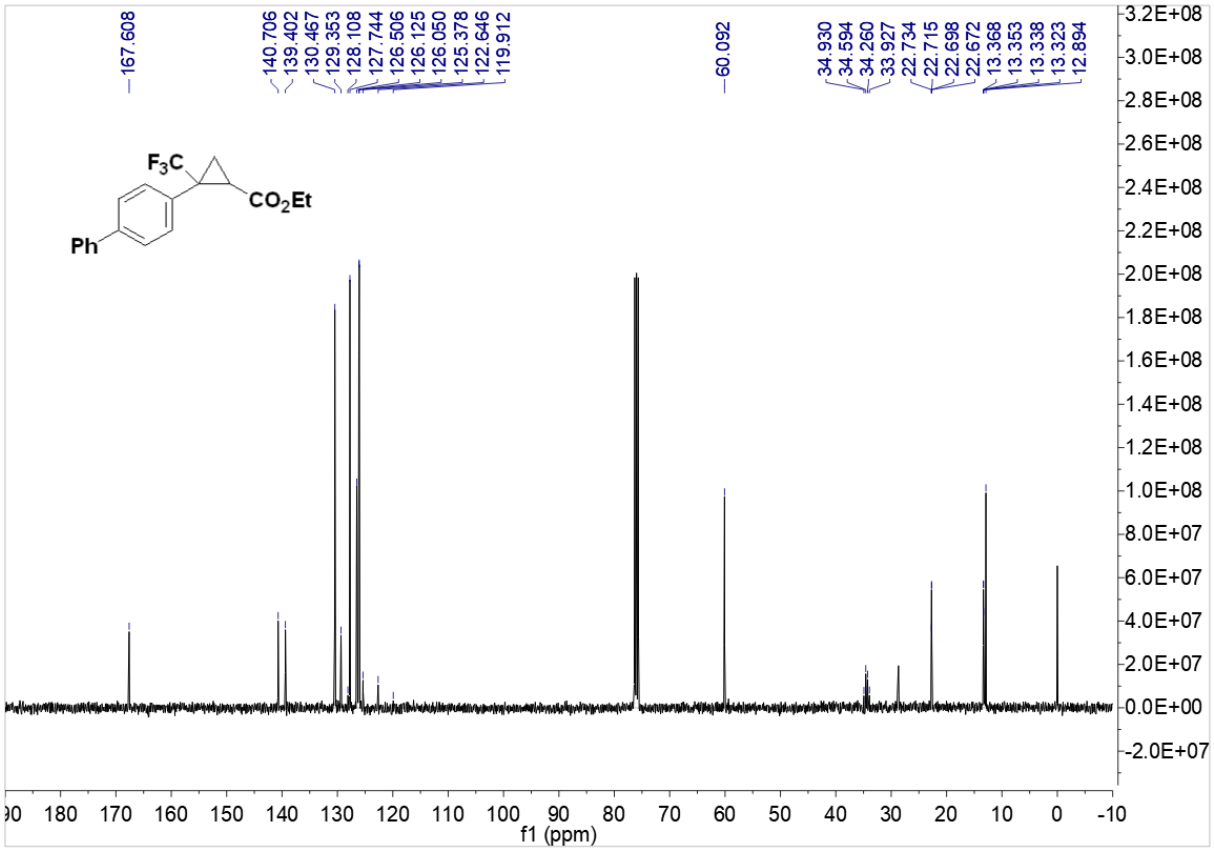


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
308.0662	308.0665	-0.3	-1.0	5.5	75.0	n/a	n/a	C13 H14 N 02 F3 Cl

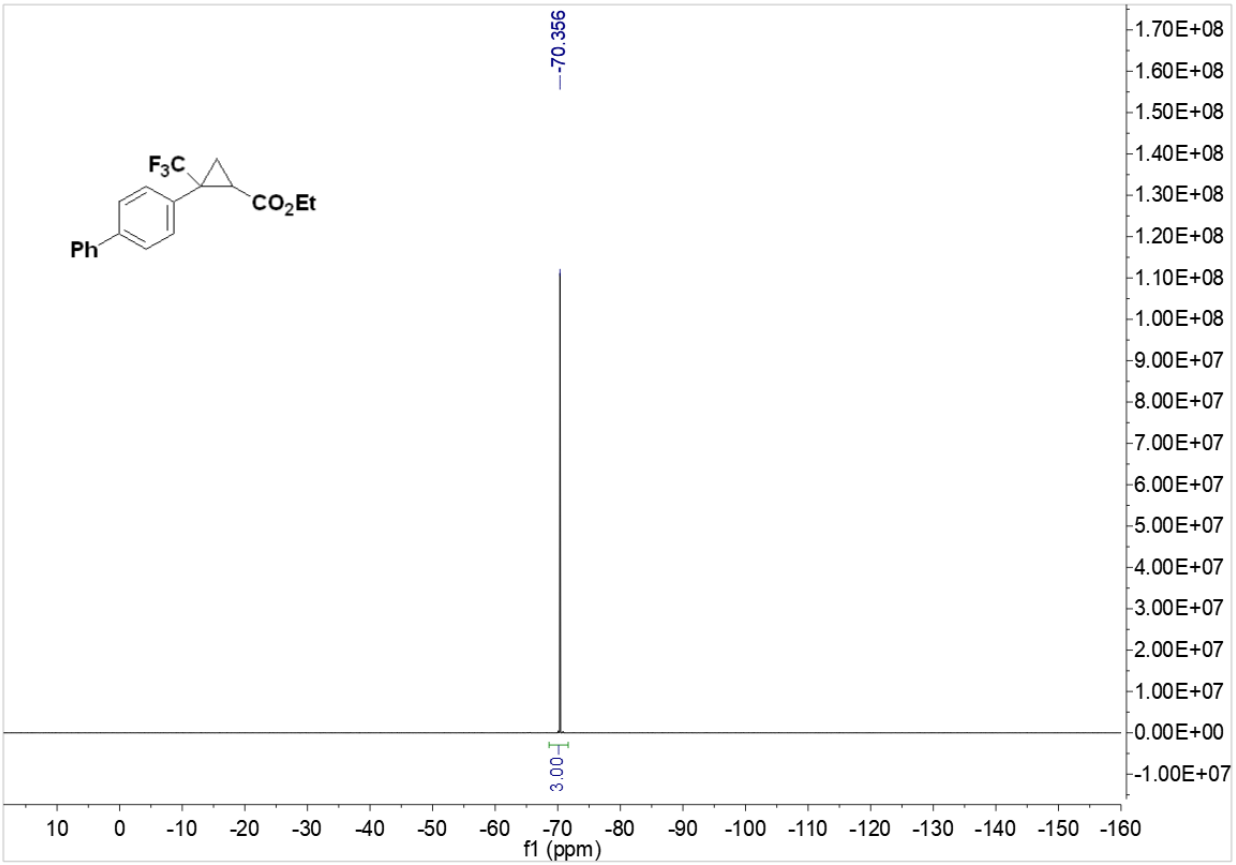
^{1}H NMR spectrum of ***trans*-3ae**



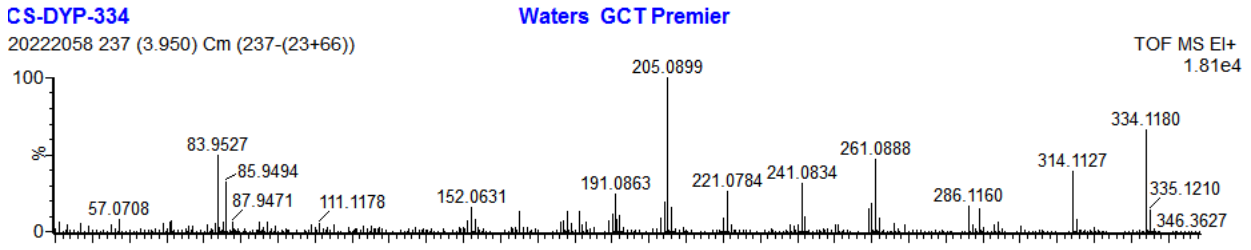
^{13}C NMR spectrum of ***trans*-3ae**



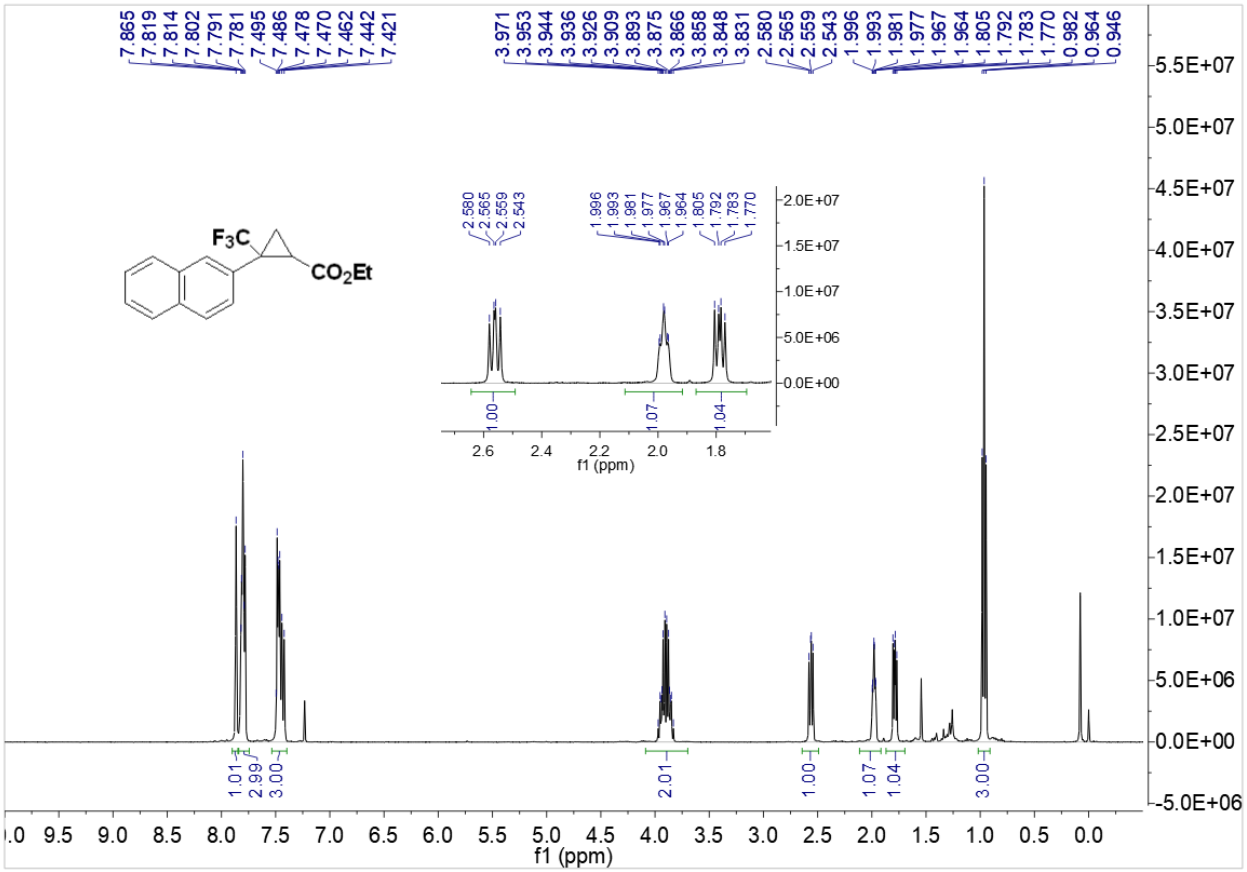
^{19}F NMR spectrum of ***trans*-3ae**



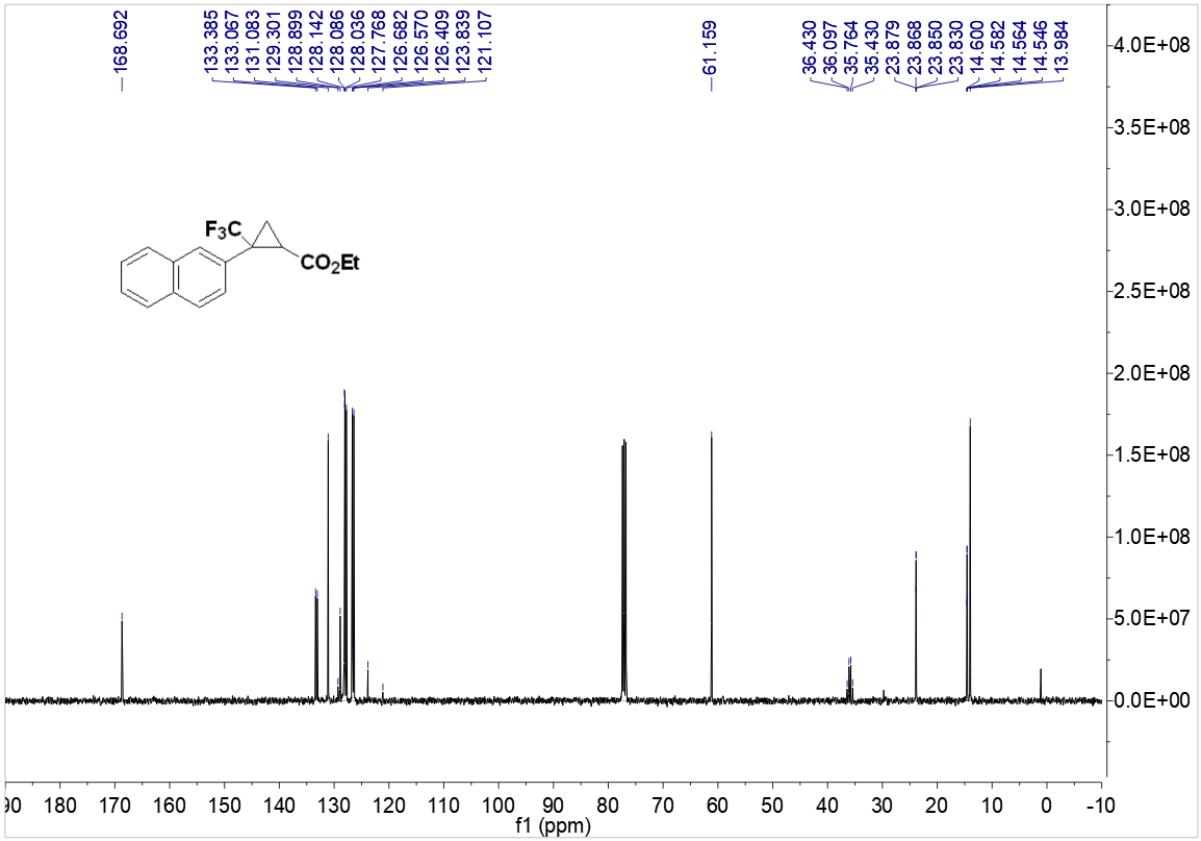
HRMS (EI) spectrum of ***trans*-3ae**



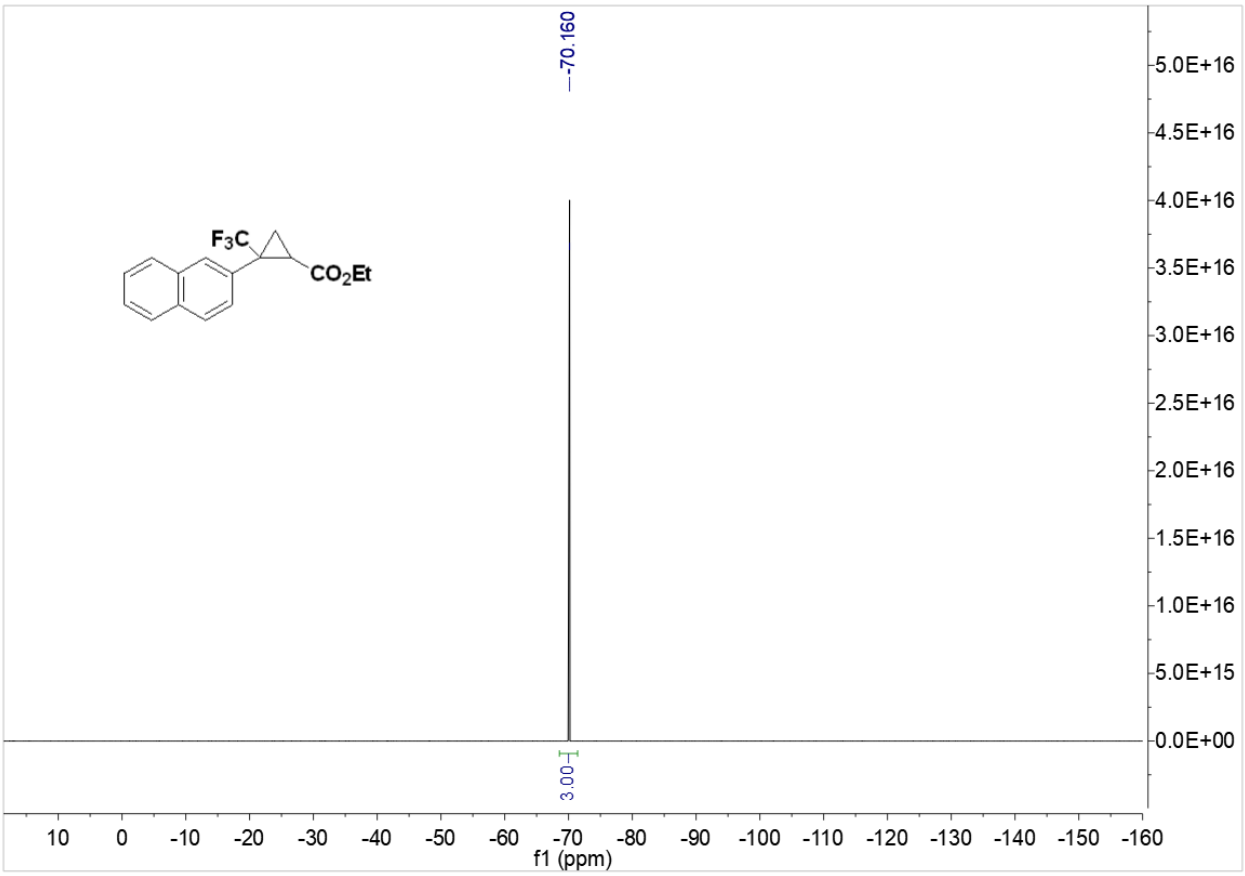
^{1}H NMR spectrum of ***trans*-3be**



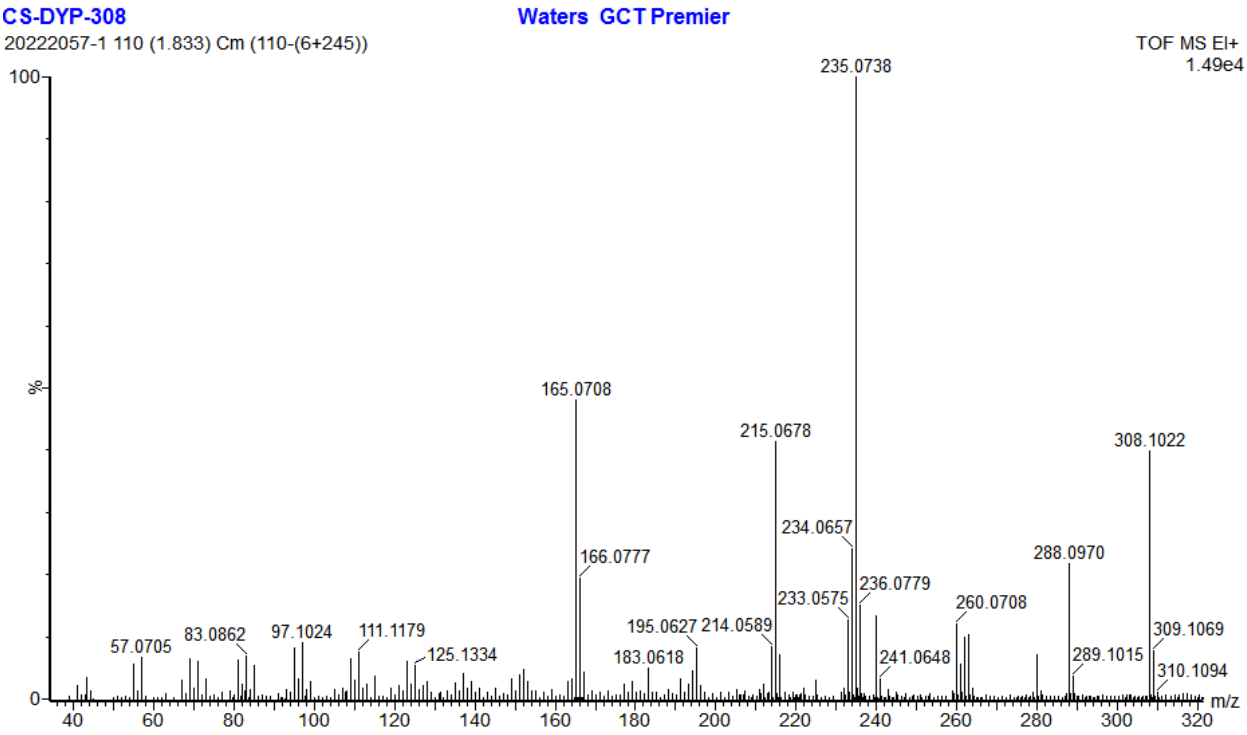
^{13}C NMR spectrum of ***trans*-3be**



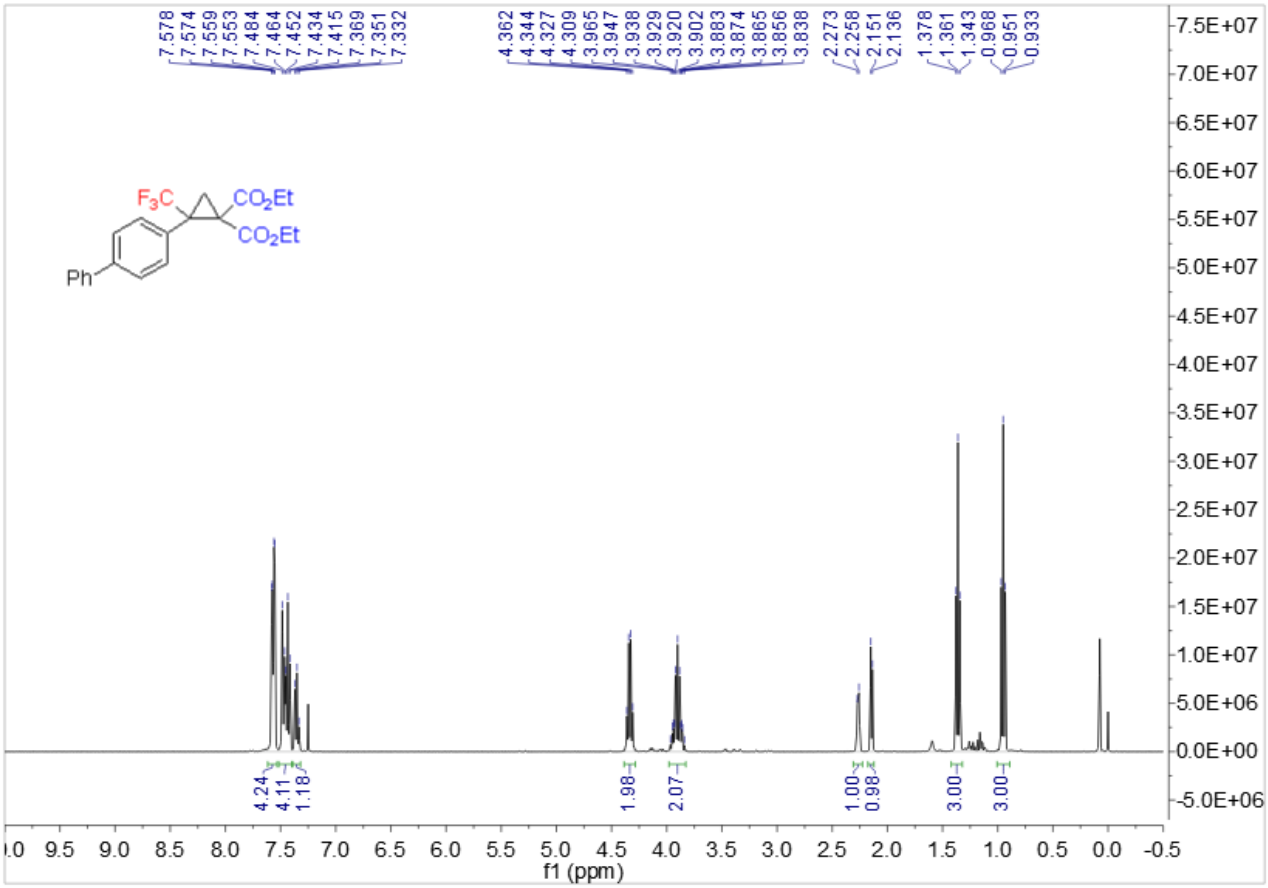
^{19}F NMR spectrum of ***trans*-3be**



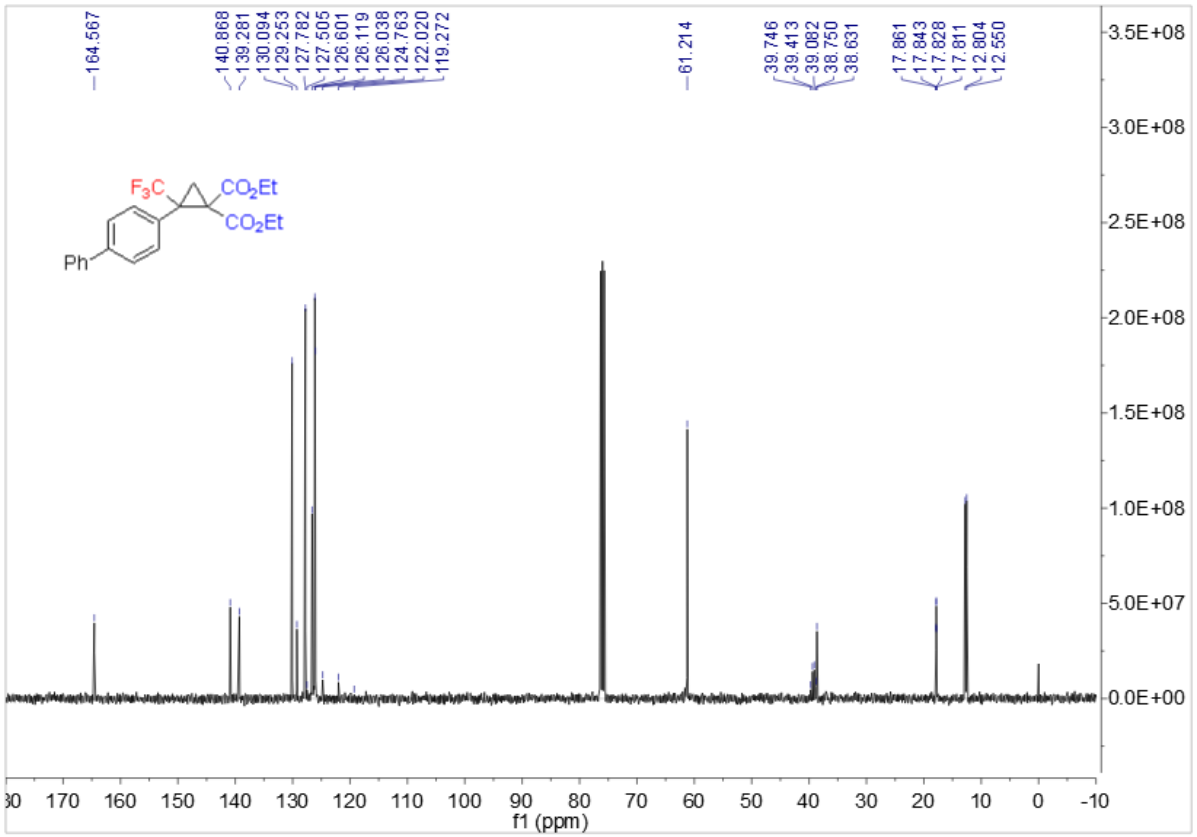
HRMS (EI) spectrum of ***trans*-3be**



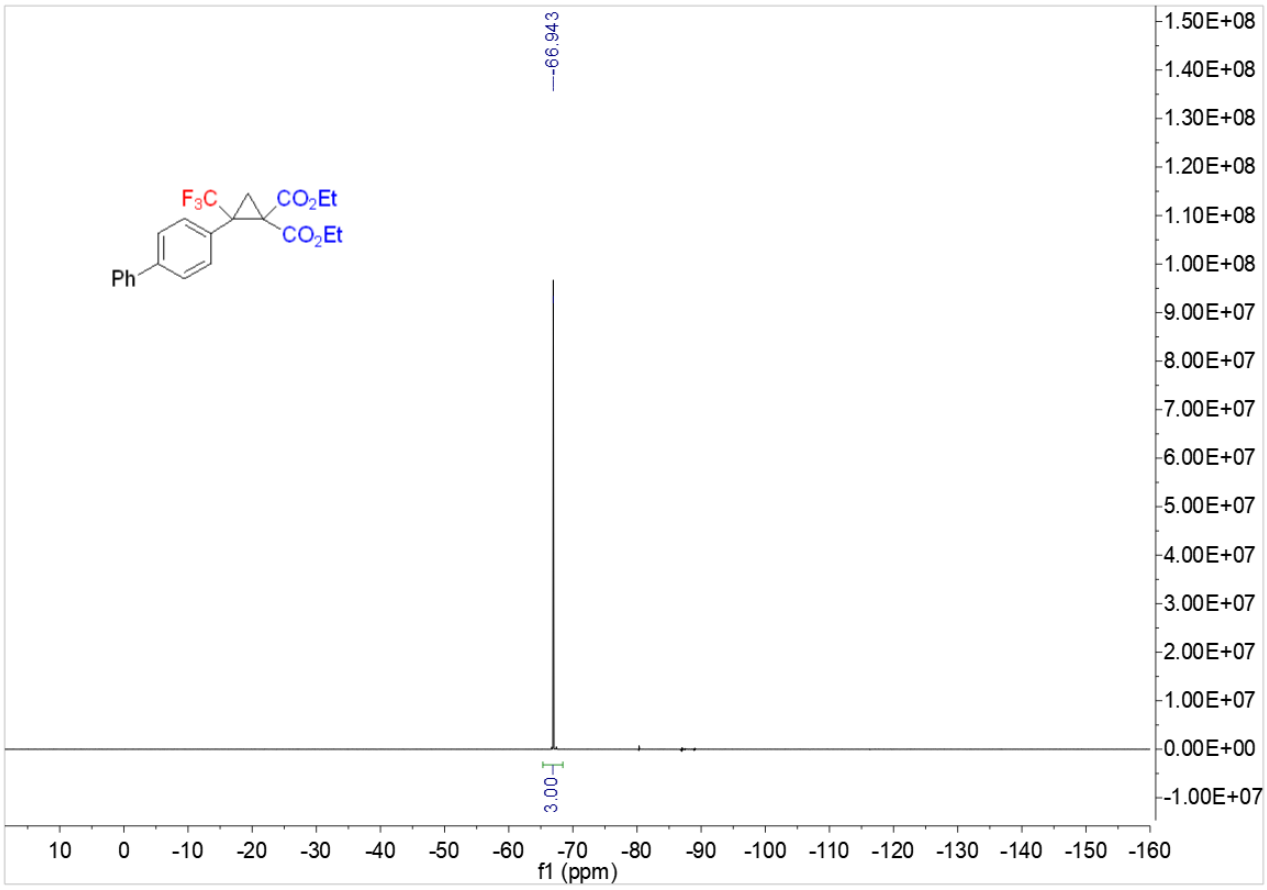
^{1}H NMR spectrum of **3af**



^{13}C NMR spectrum of **3af**



^{19}F NMR spectrum of **3af**



HRMS (ESI) spectrum of **3af**

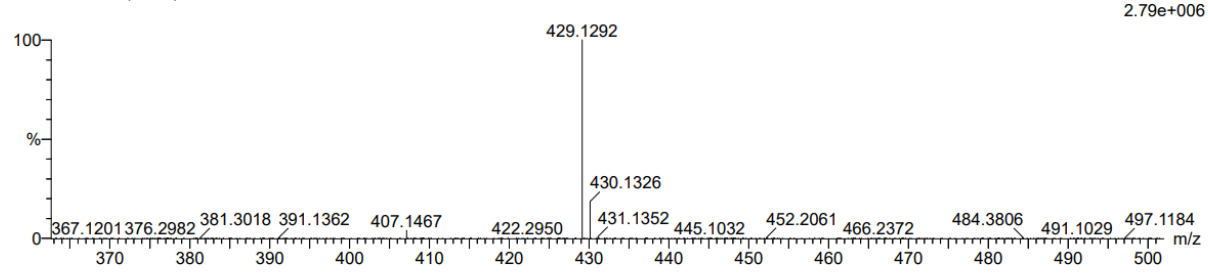
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
576 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 22-22 H: 21-21 N: 0-30 O: 0-100 F: 3-3 Na: 0-1

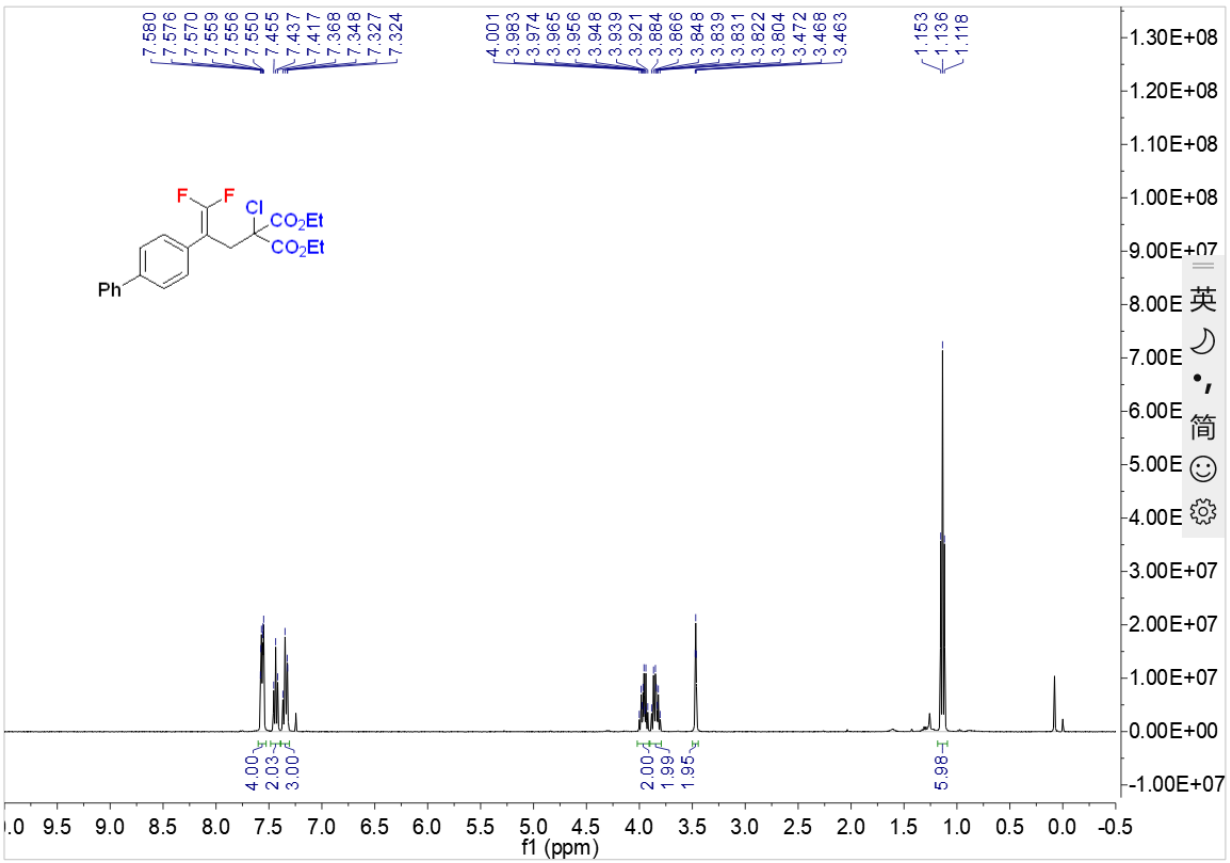
3
230512-2-6 13 (0.161)

1: TOF MS ES+
2.79e+006

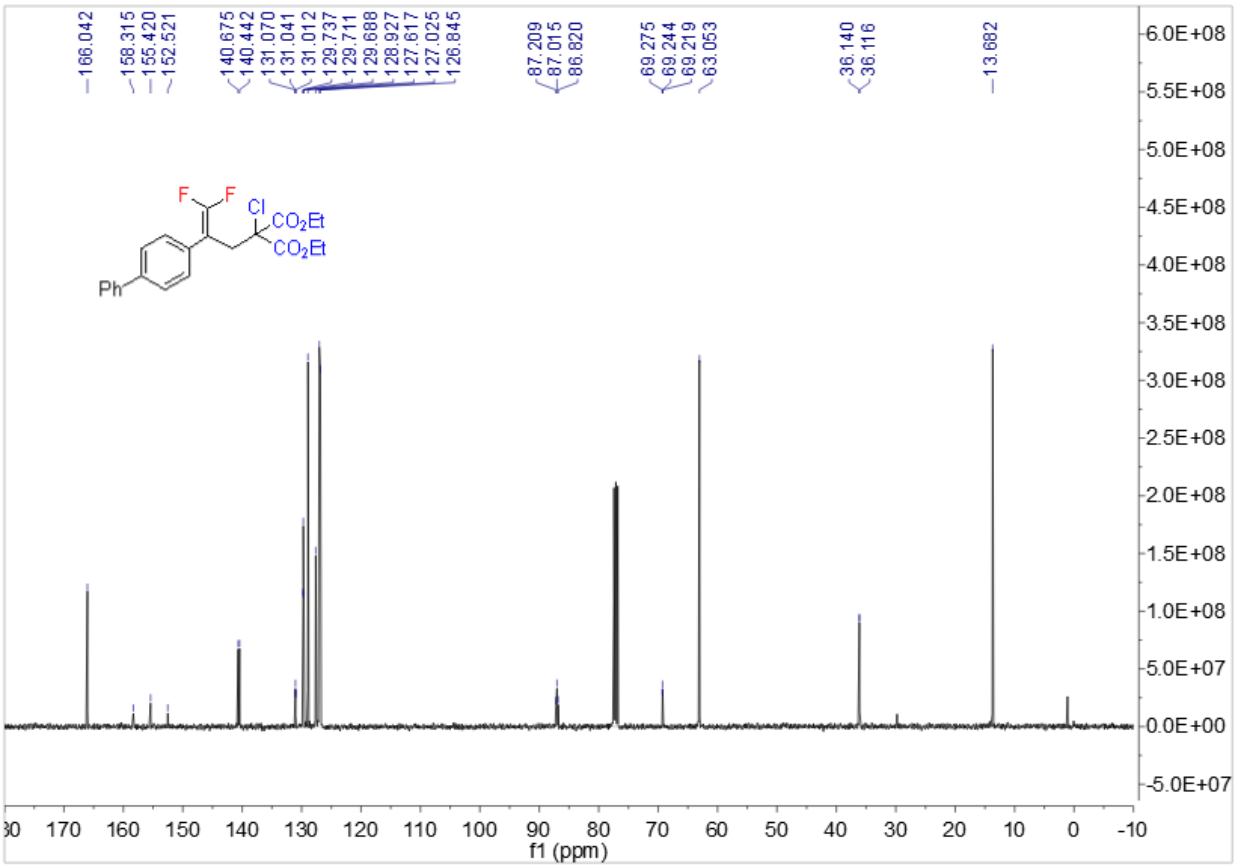


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
429.1292	429.1290	0.2	0.5	10.5	100.6	n/a	n/a	C22 H21 O4 F3 Na

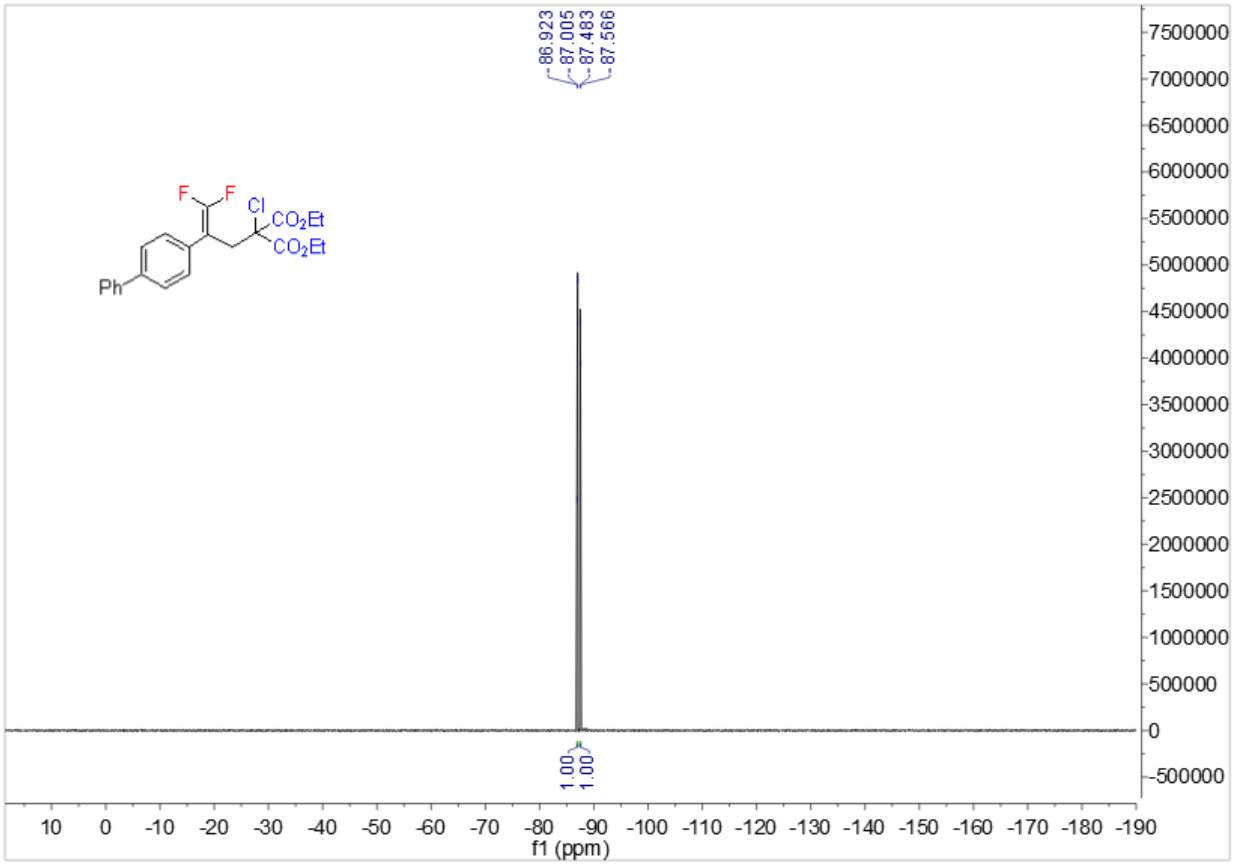
^{1}H NMR spectrum of **3af′**



^{13}C NMR spectrum of **3af′**



^{19}F NMR spectrum of **3af′**



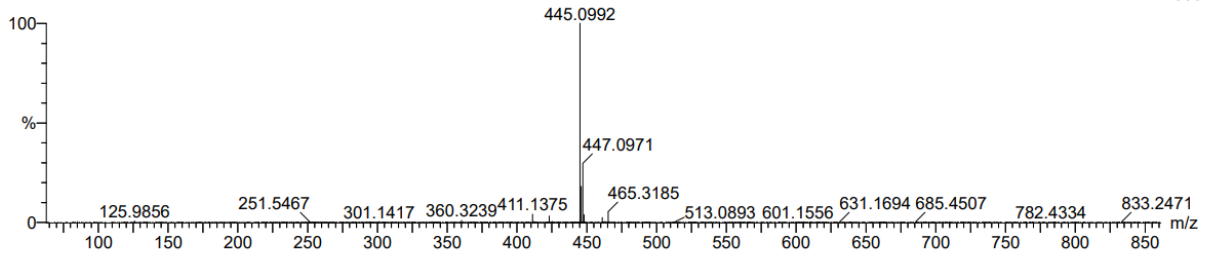
HRMS (ESI) spectrum of **3af′**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

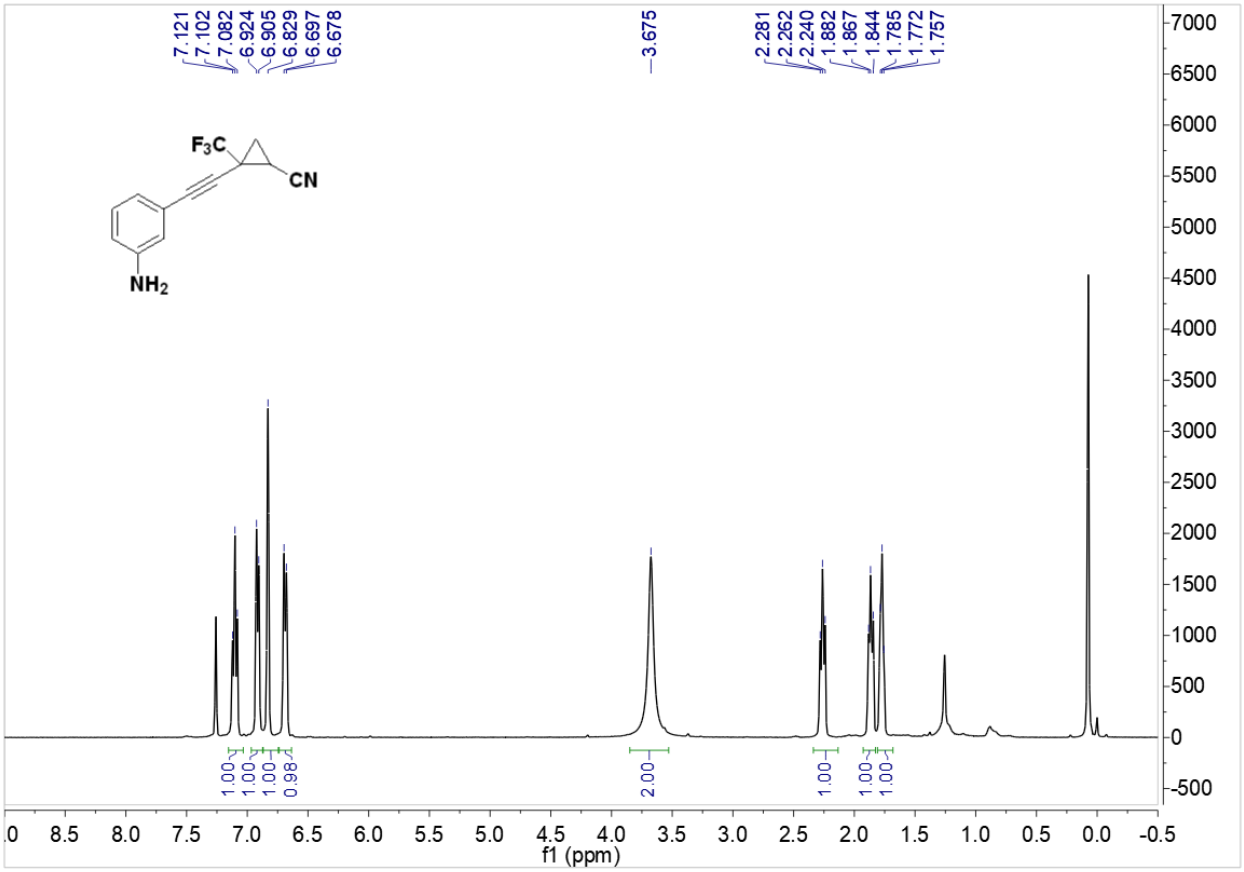
Monoisotopic Mass, Even Electron Ions
2039 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 22-22 H: 21-21 N: 0-30 O: 0-100 F: 2-3 Na: 0-1 Cl: 1-2
3
230512-2-7 17 (0.203)

1: TOF MS ES+
2.44e+006

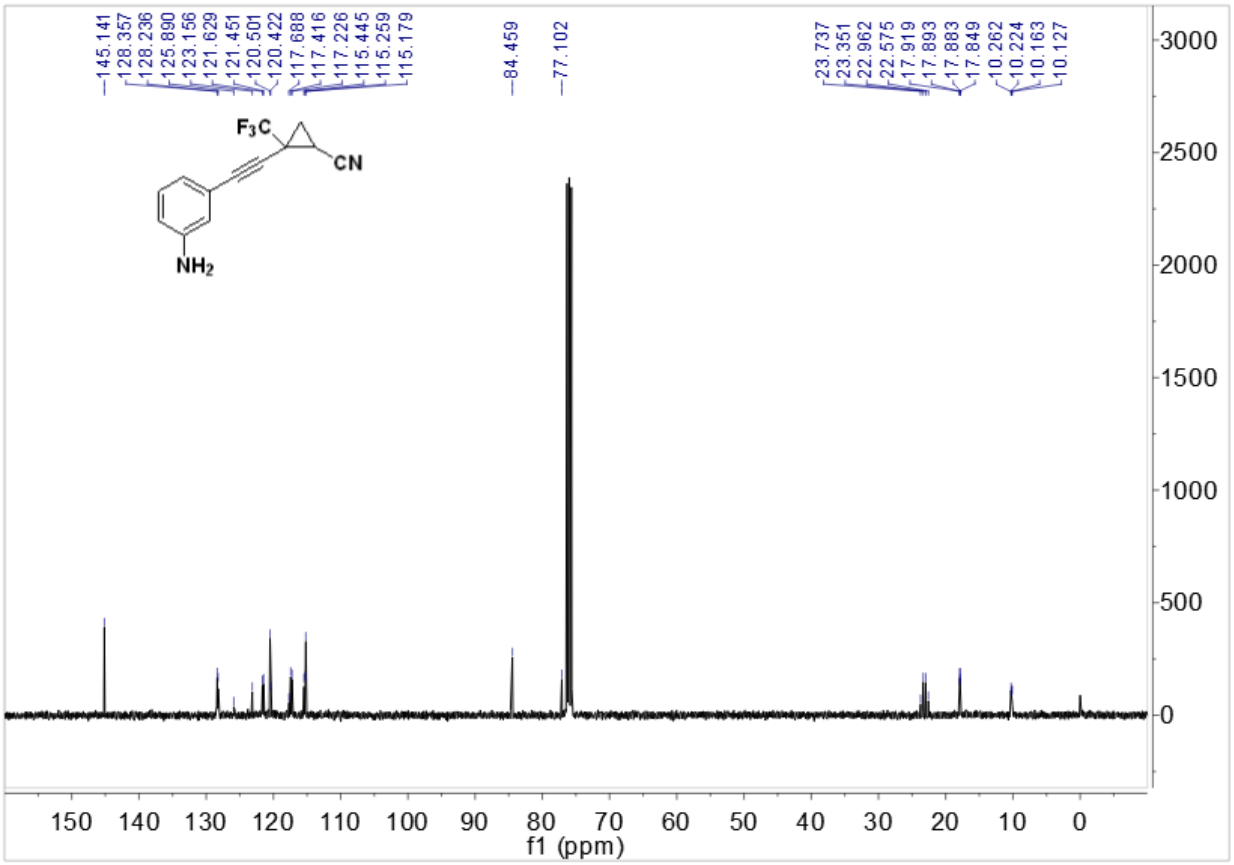


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
445.0992	445.0994	-0.2	-0.4	10.5	167.2	n/a	n/a	C22 H21 O4 F2 Na Cl

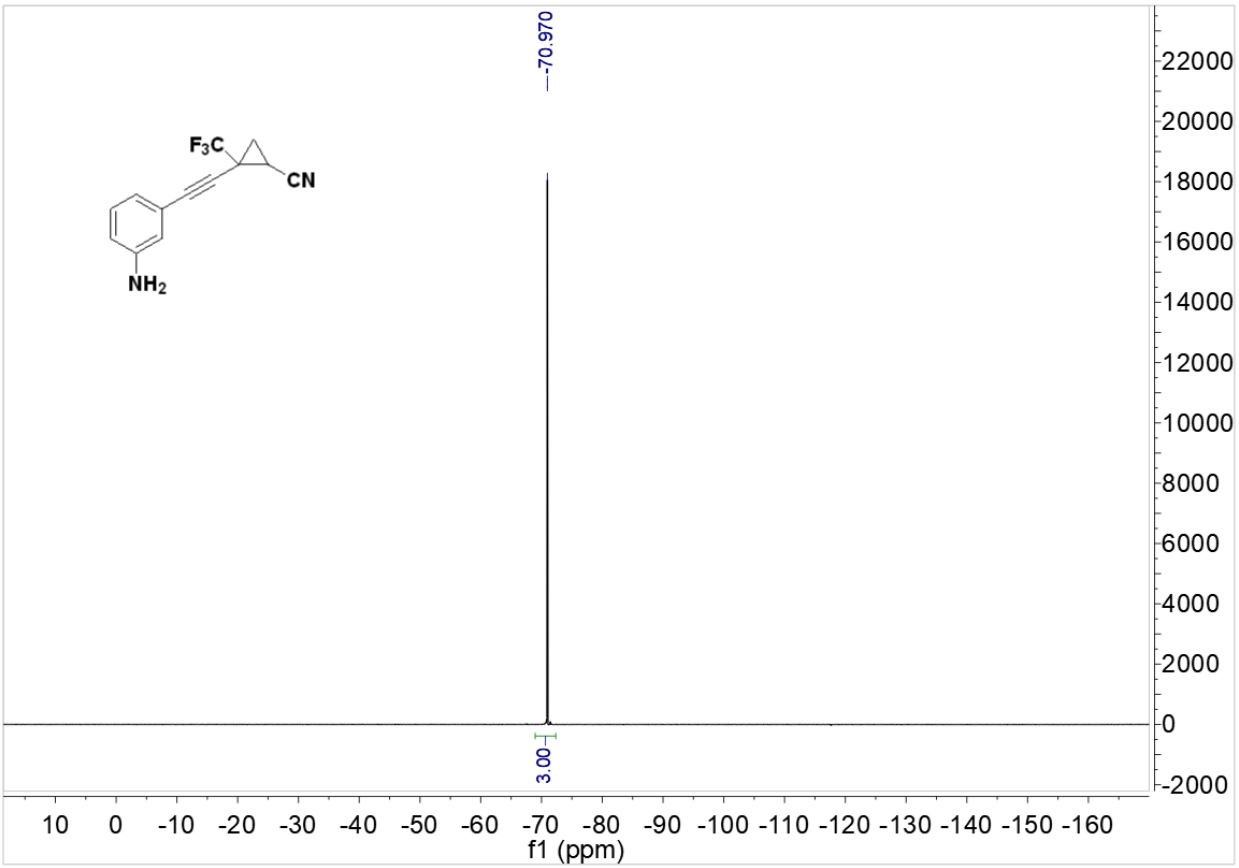
^{1}H NMR spectrum of ***trans*-3qa**



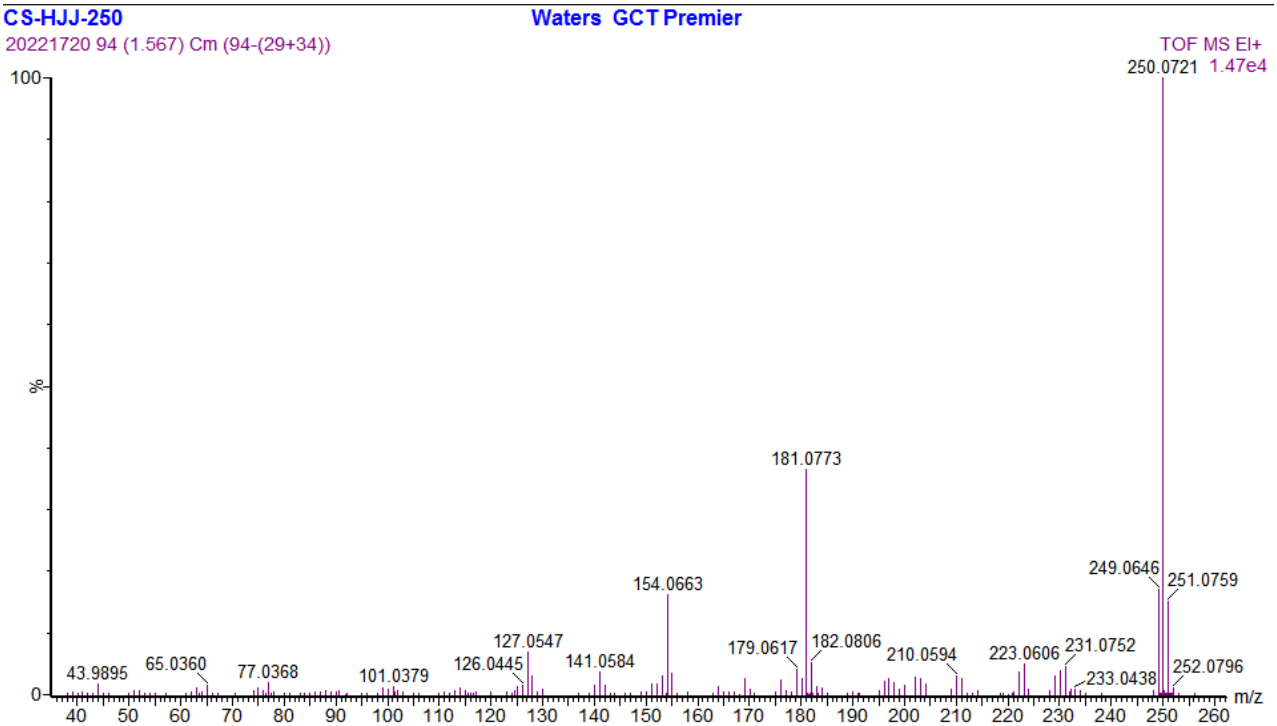
^{13}C NMR spectrum of ***trans*-3qa**



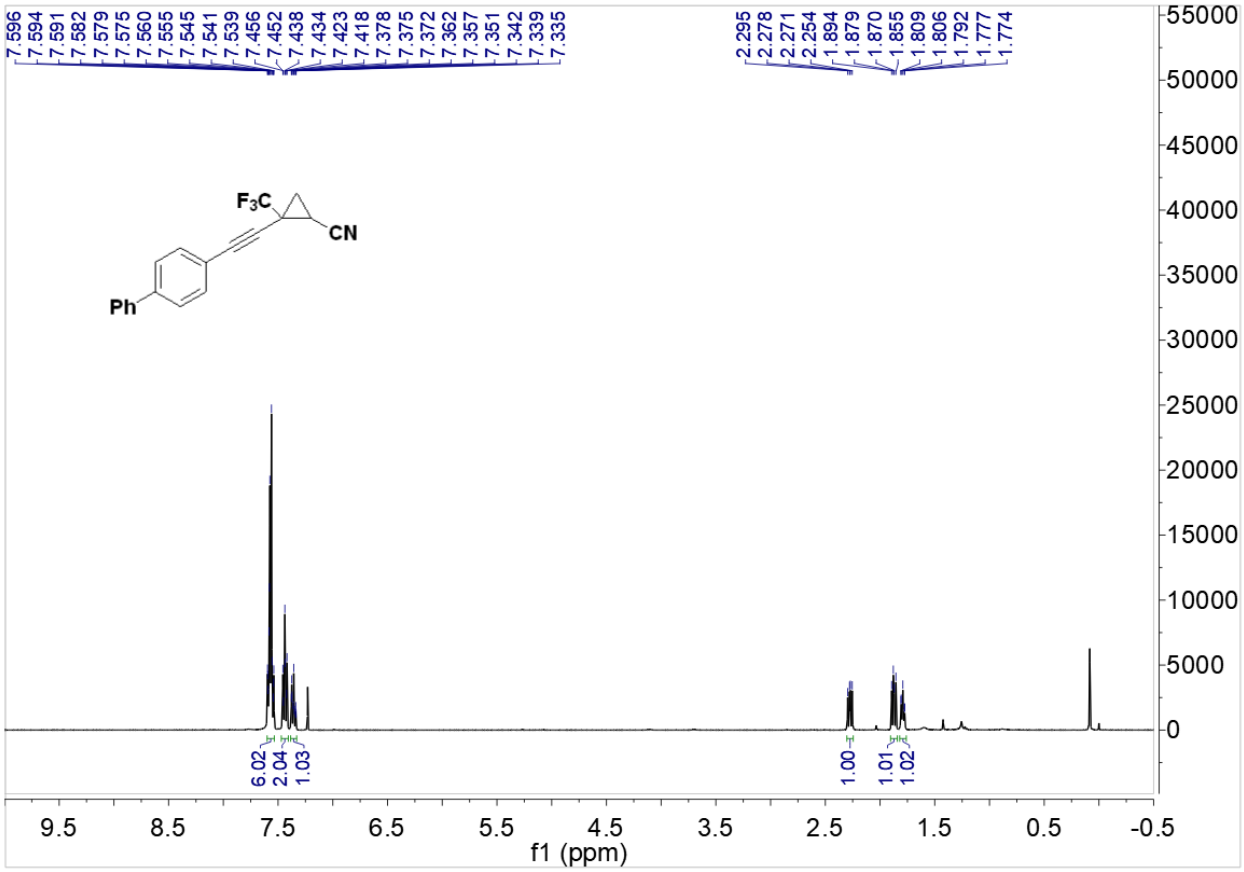
^{19}F NMR spectrum of ***trans*-3qa**



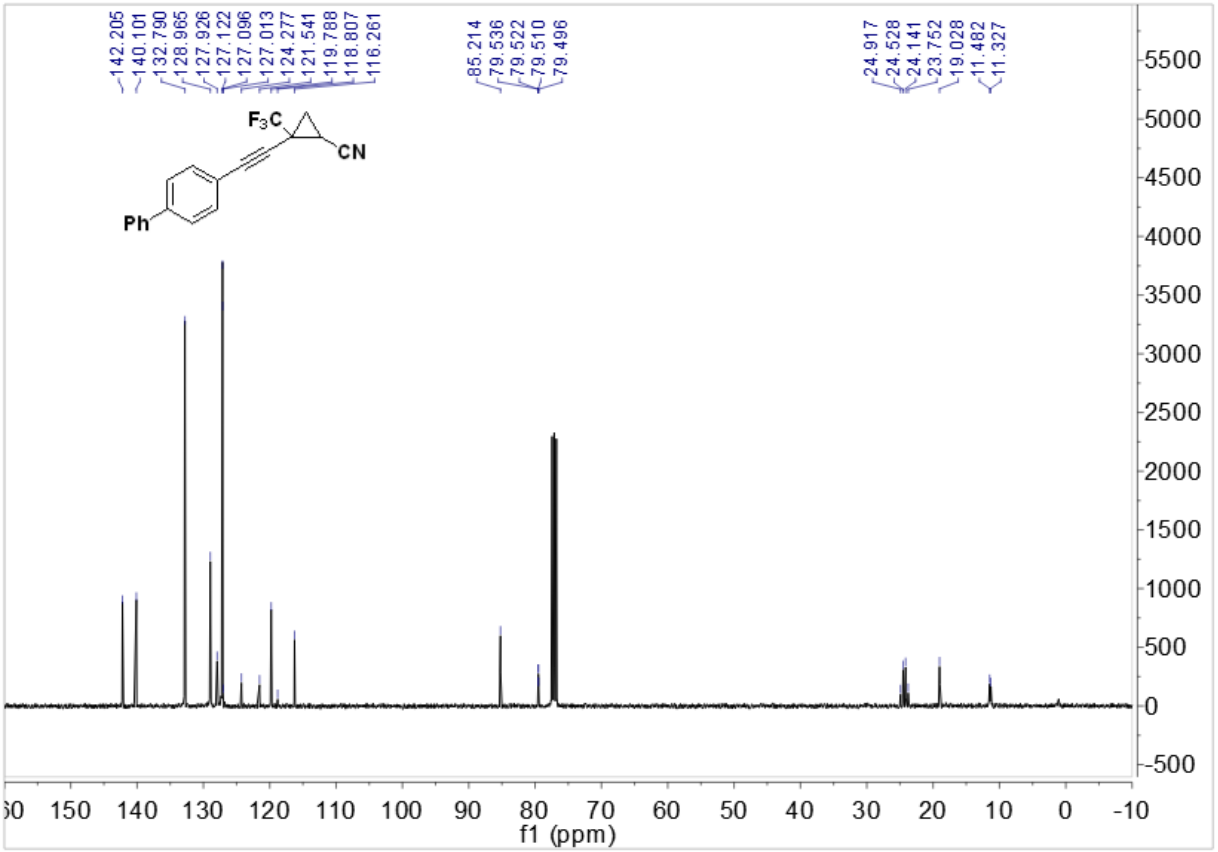
HRMS (EI) spectrum of ***trans*-3qa**



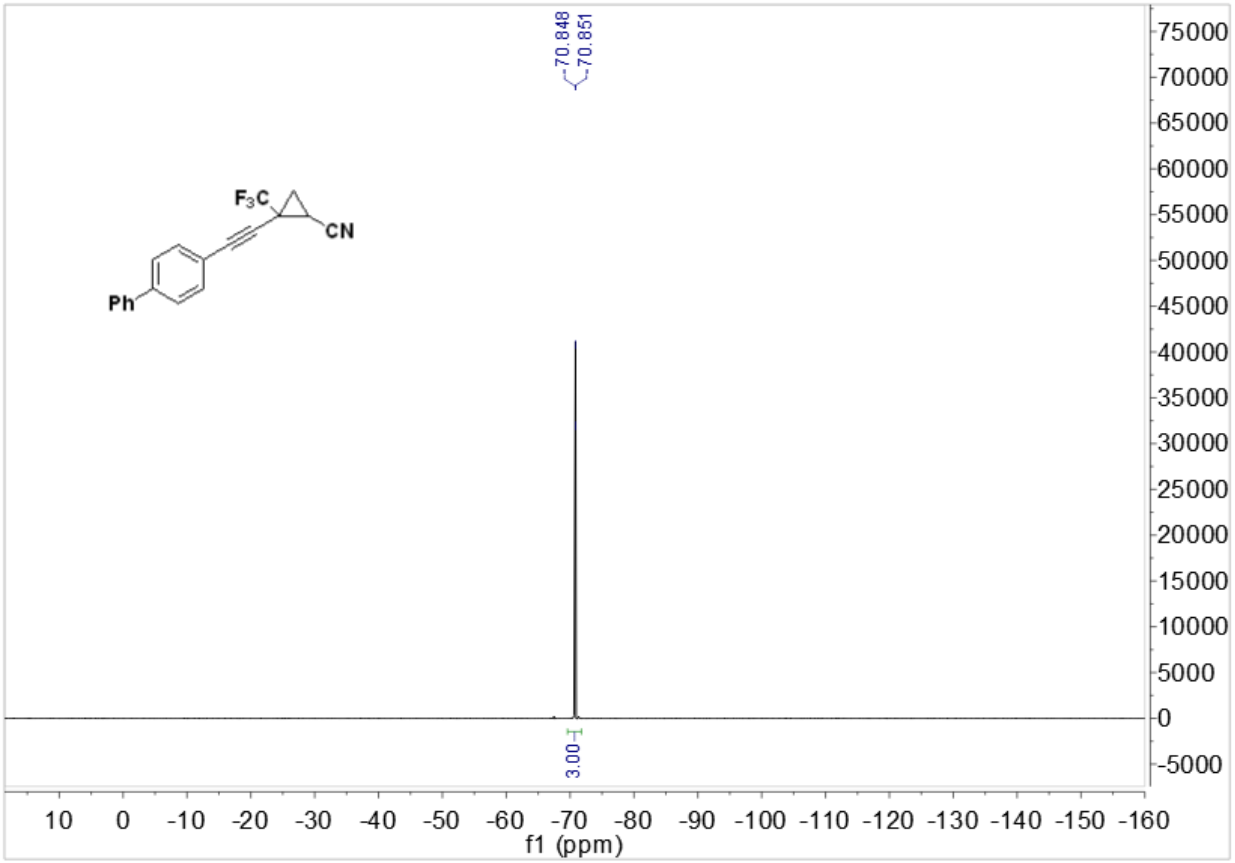
^{1}H NMR spectrum of ***trans*-3ra**



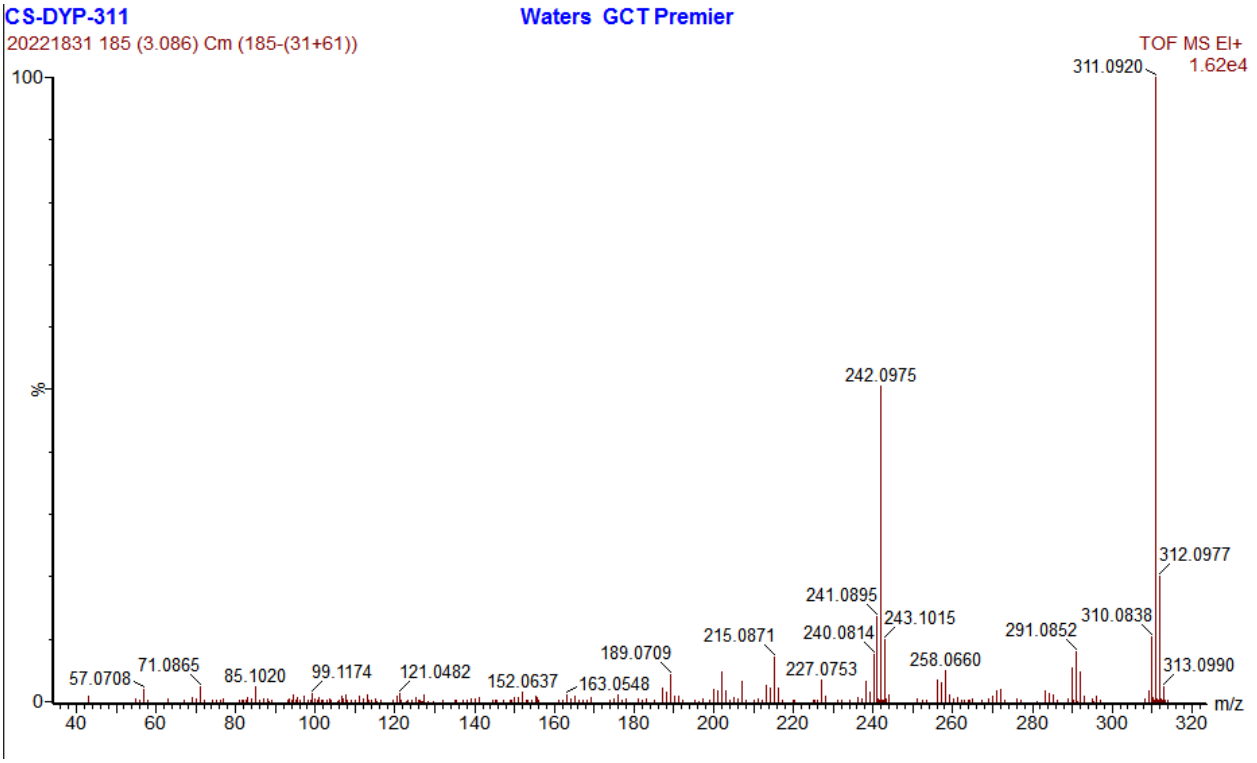
^{13}C NMR spectrum of ***trans*-3ra**



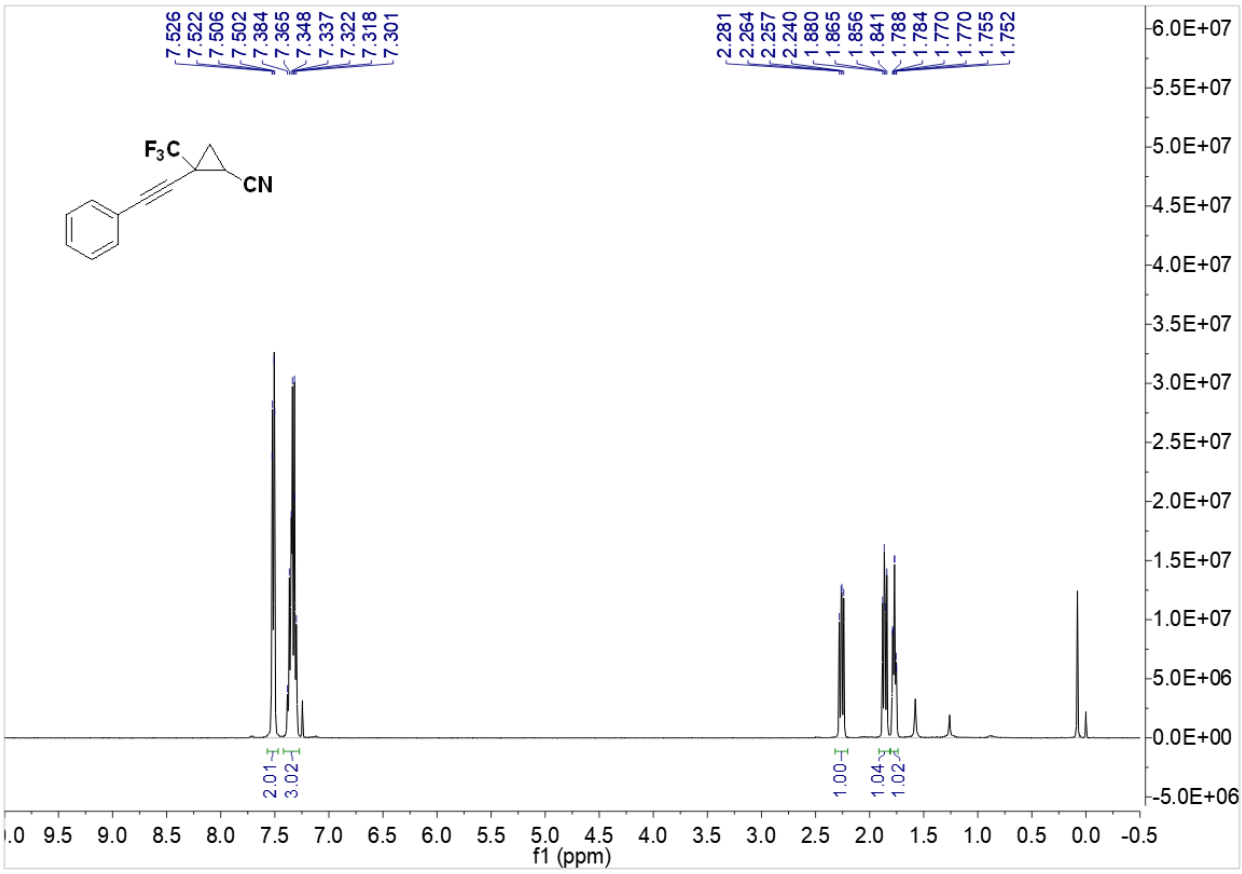
^{19}F NMR spectrum of ***trans*-3ra**



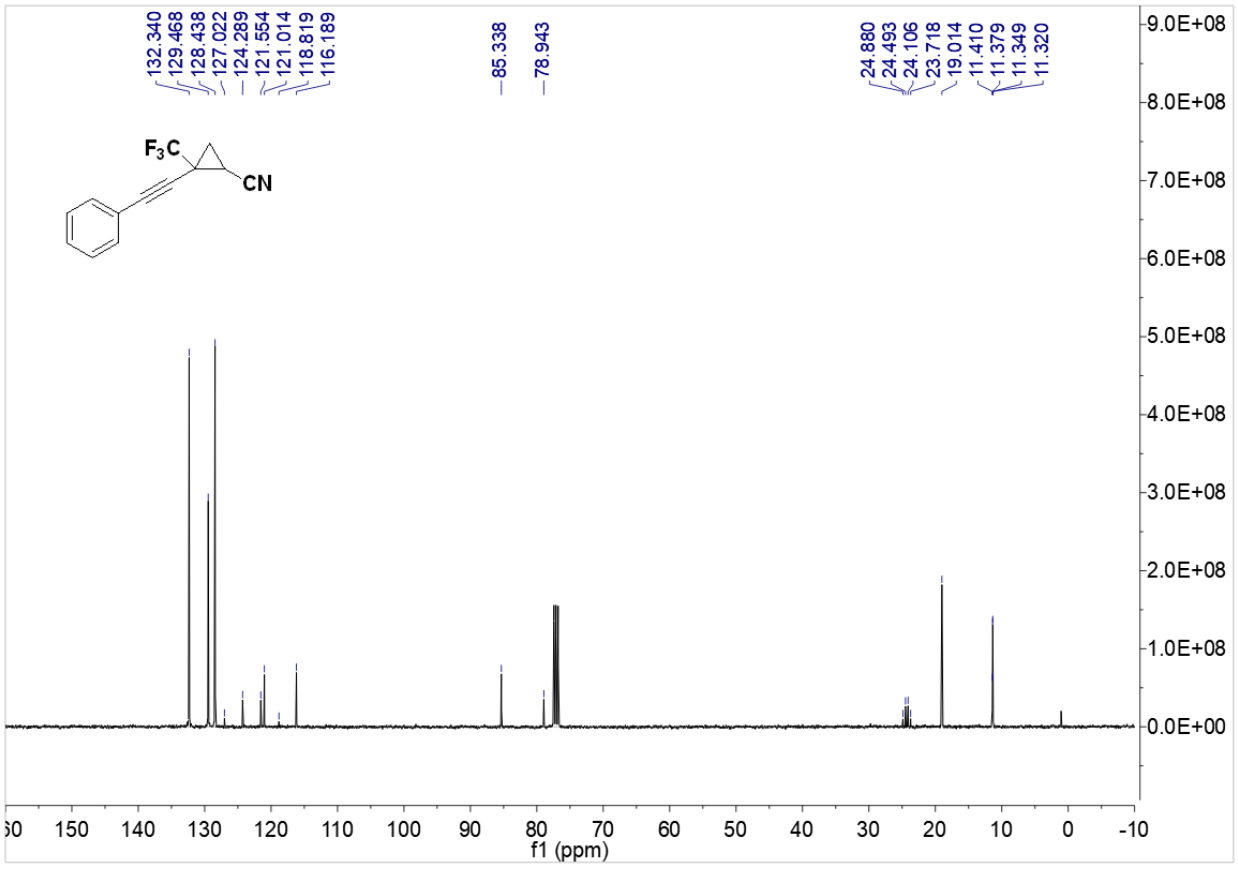
HRMS (EI) spectrum of ***trans*-3ra**



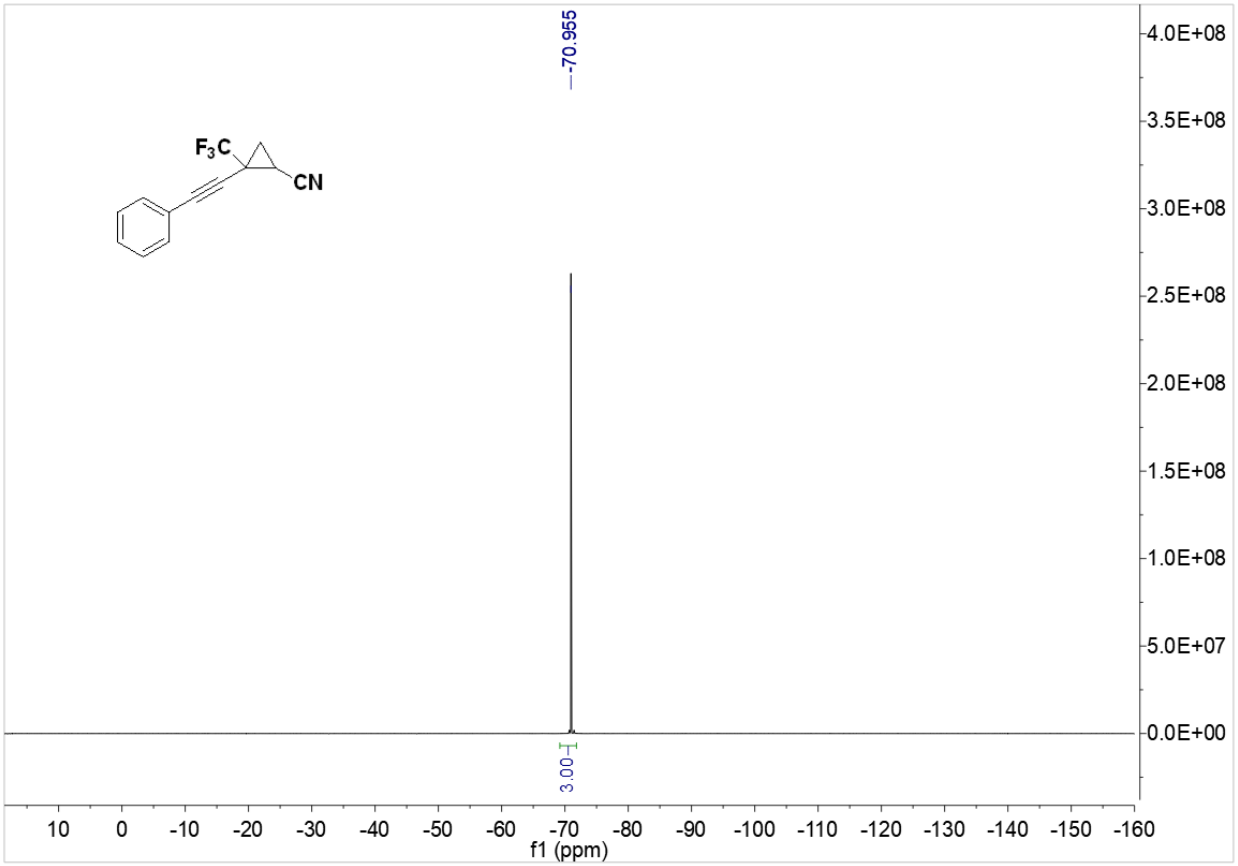
^{1}H NMR spectrum of ***trans*-3sa**



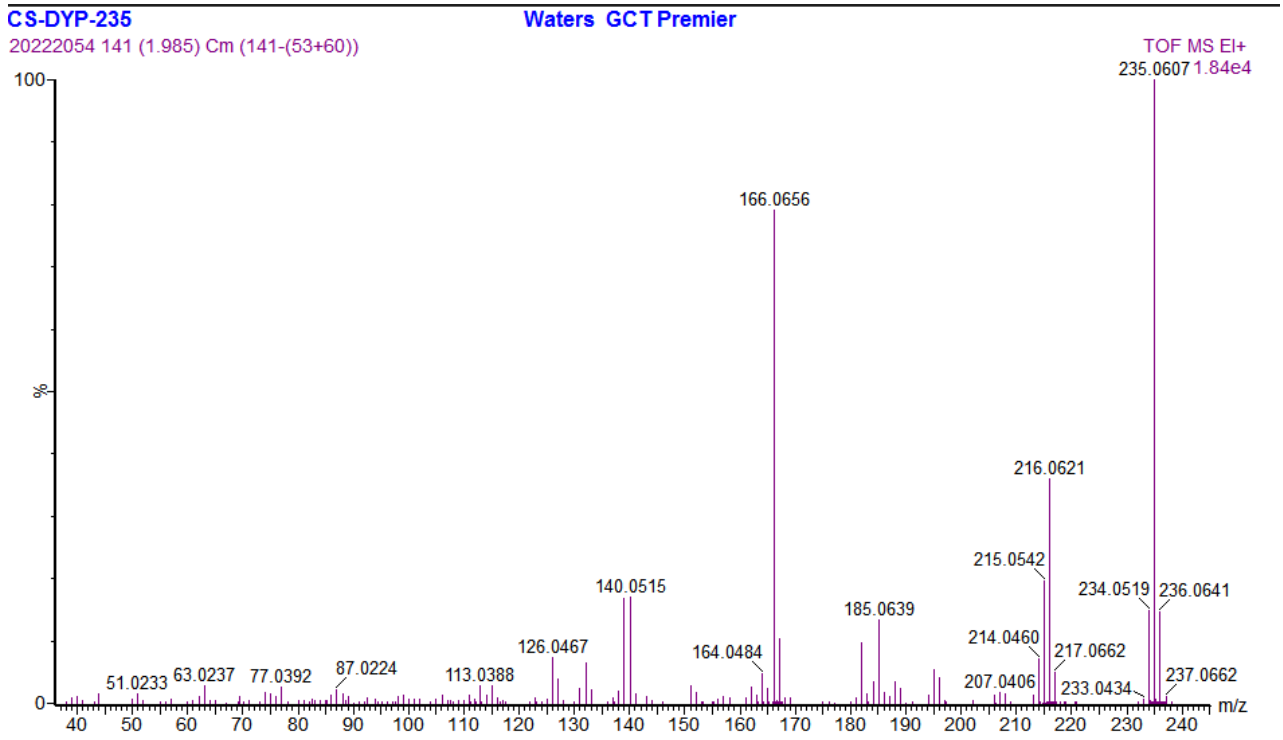
^{13}C NMR spectrum of ***trans*-3sa**



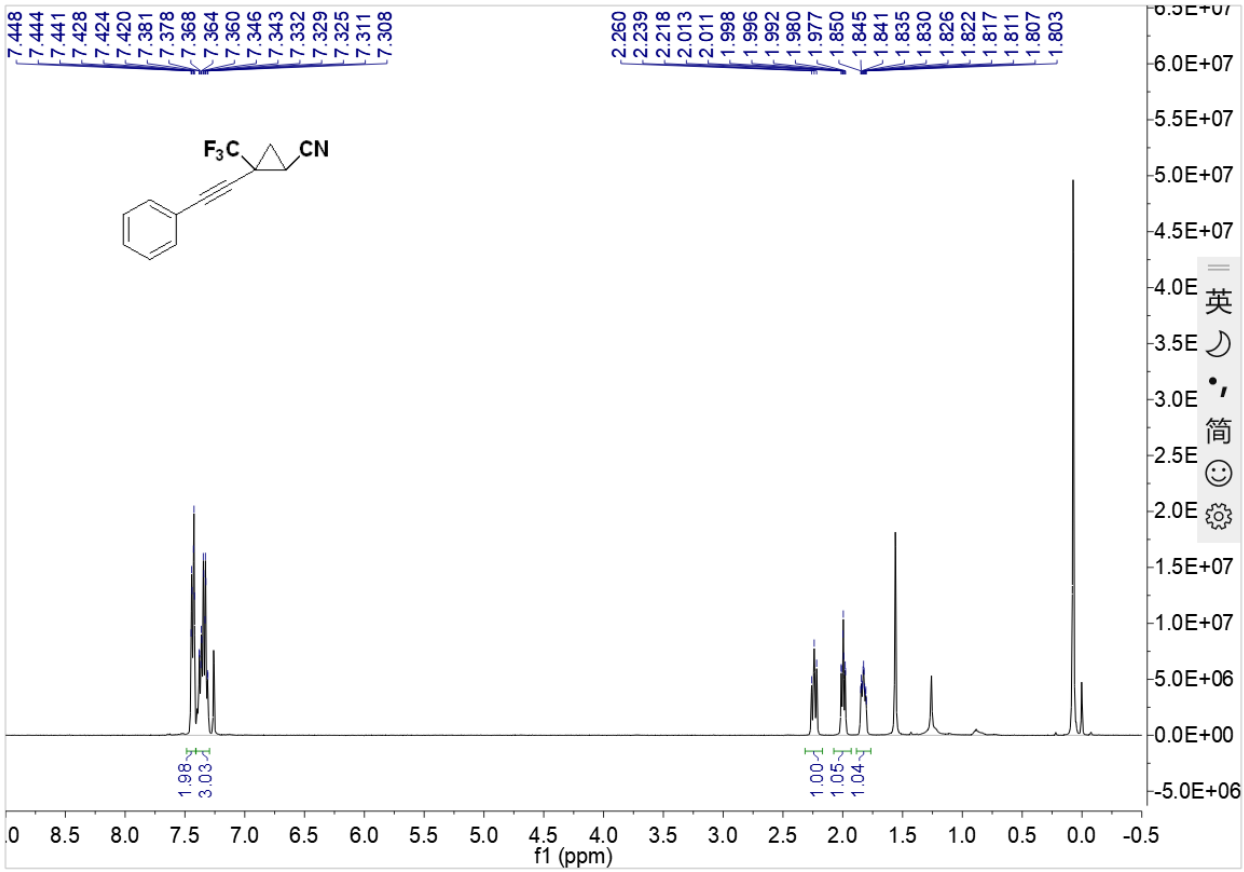
^{19}F NMR spectrum of ***trans*-3sa**



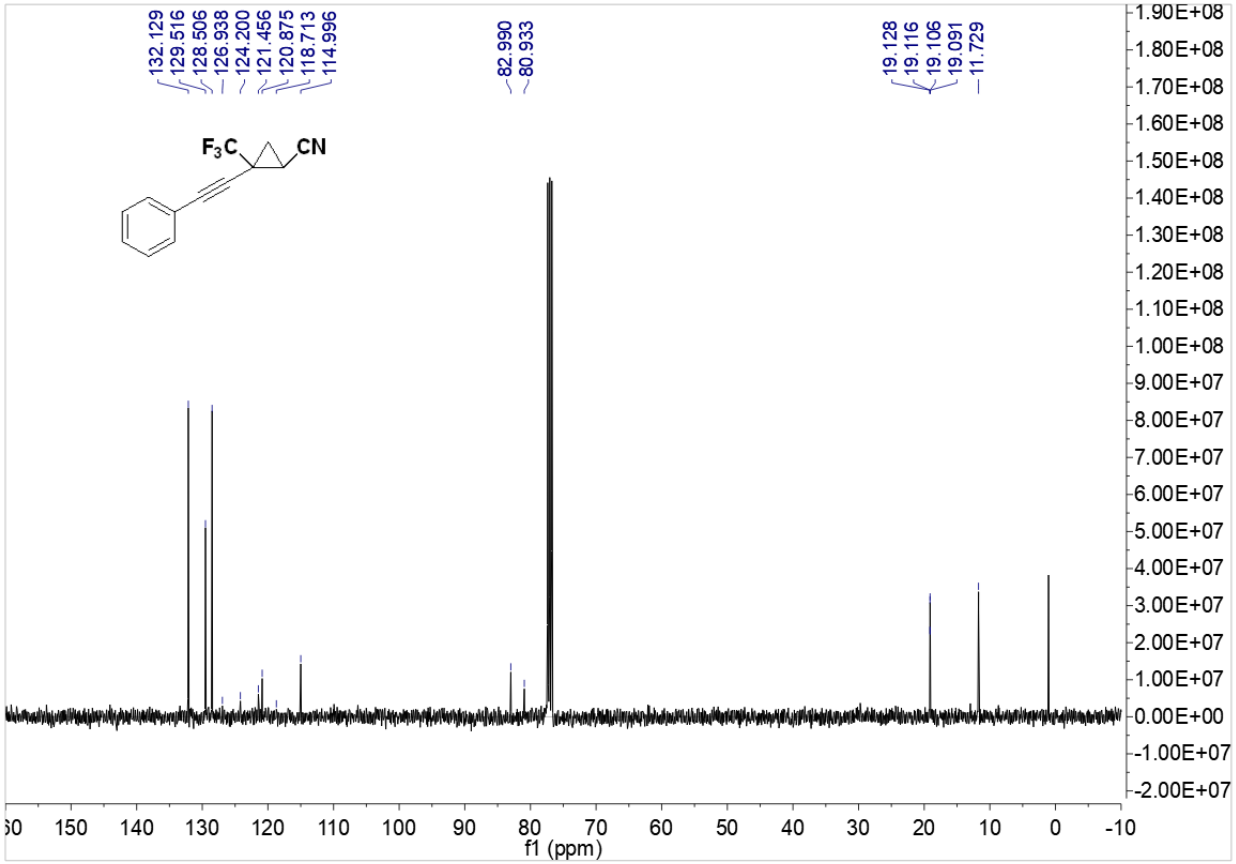
HRMS (EI) spectrum of ***trans*-3sa**



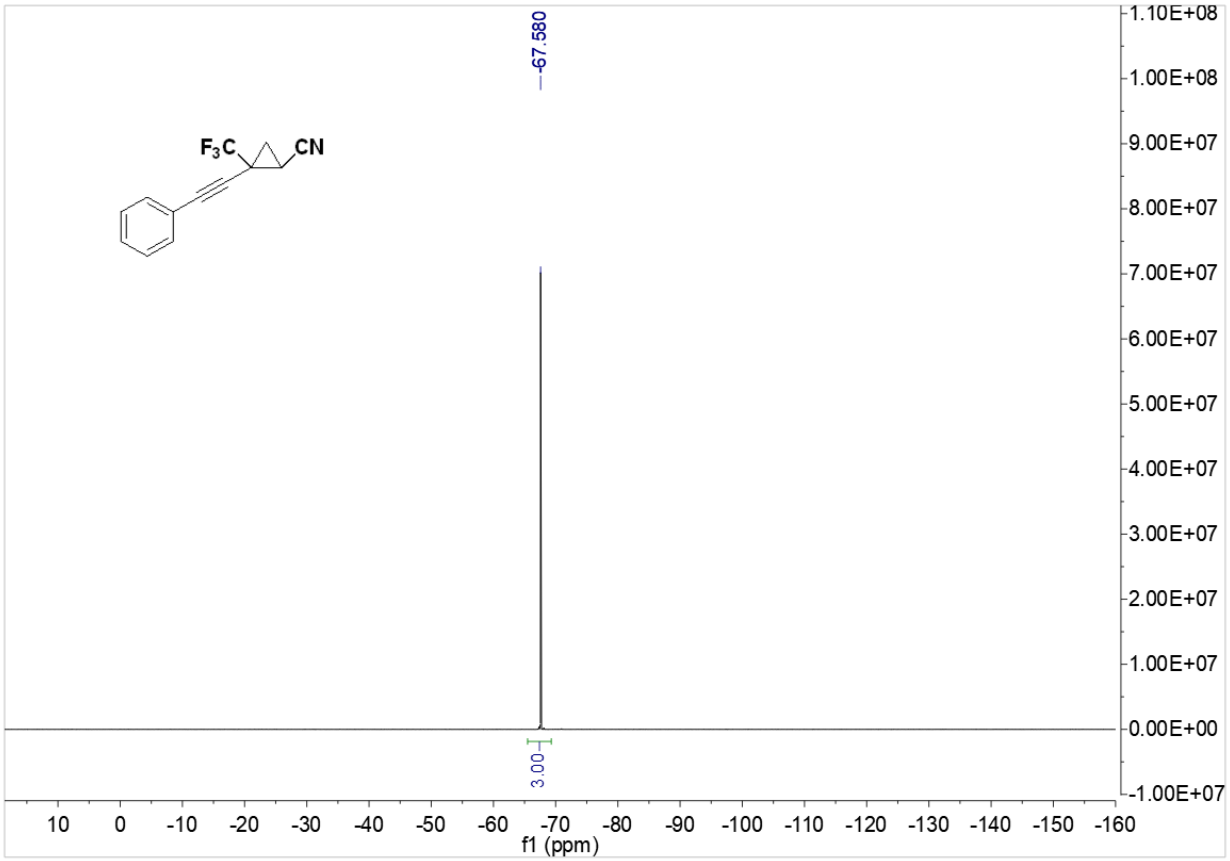
^{1}H NMR spectrum of ***cis*-3sa**



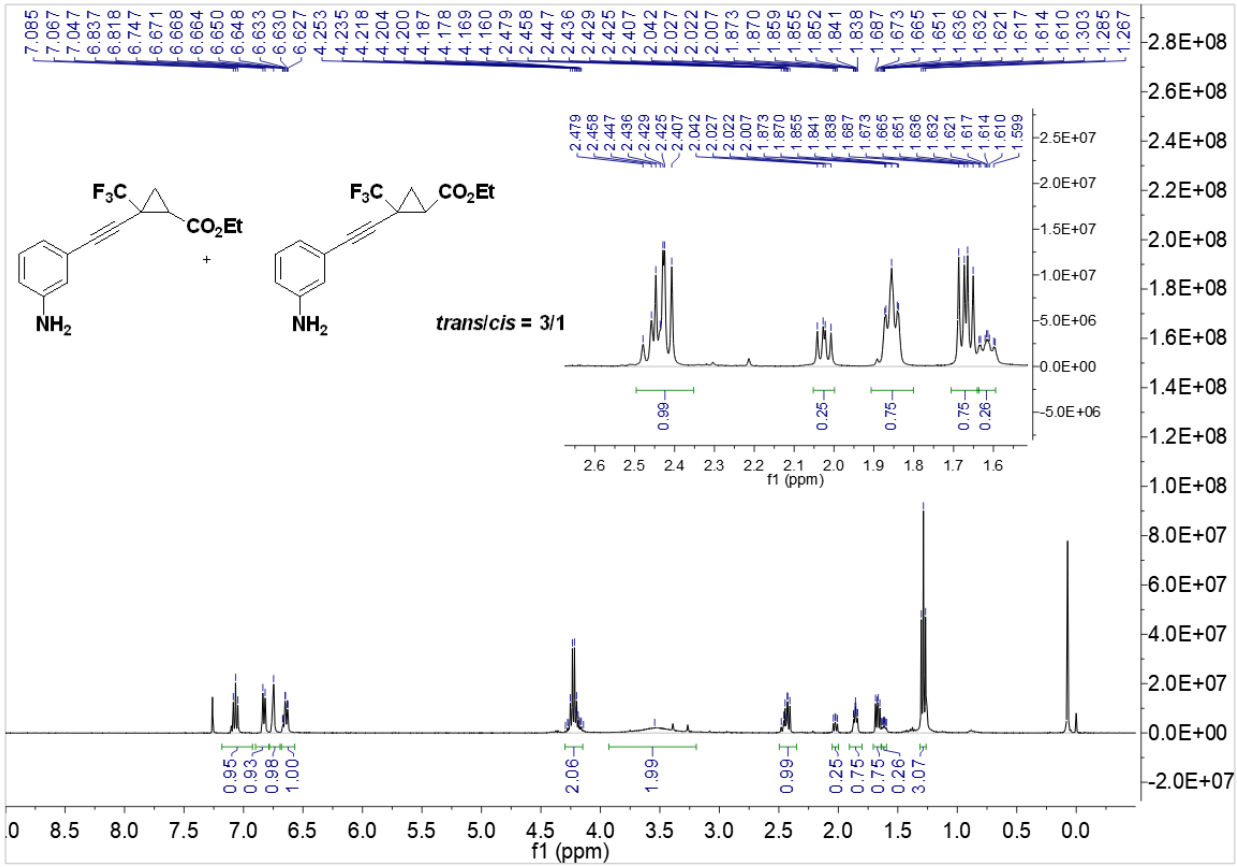
^{13}C NMR spectrum of ***cis*-3sa**



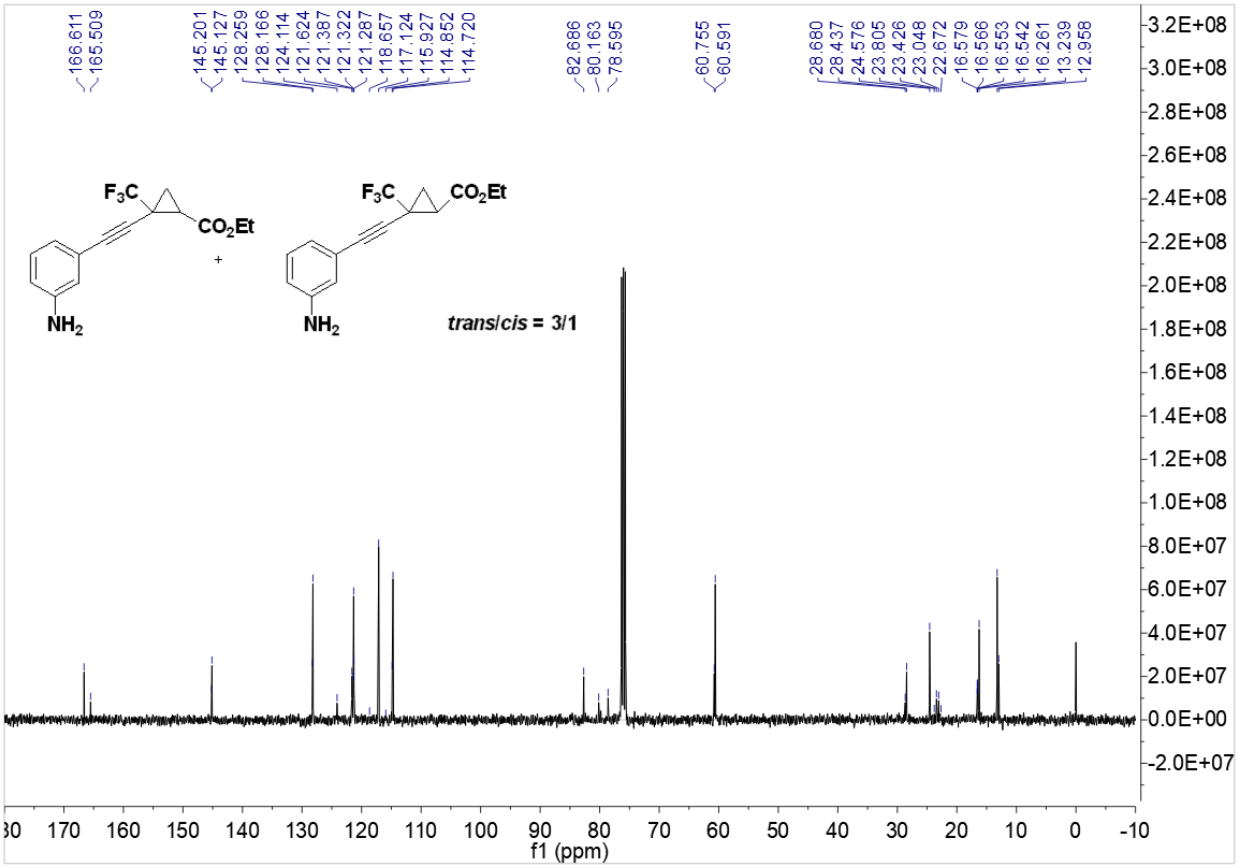
^{19}F NMR spectrum of ***cis*-3sa**



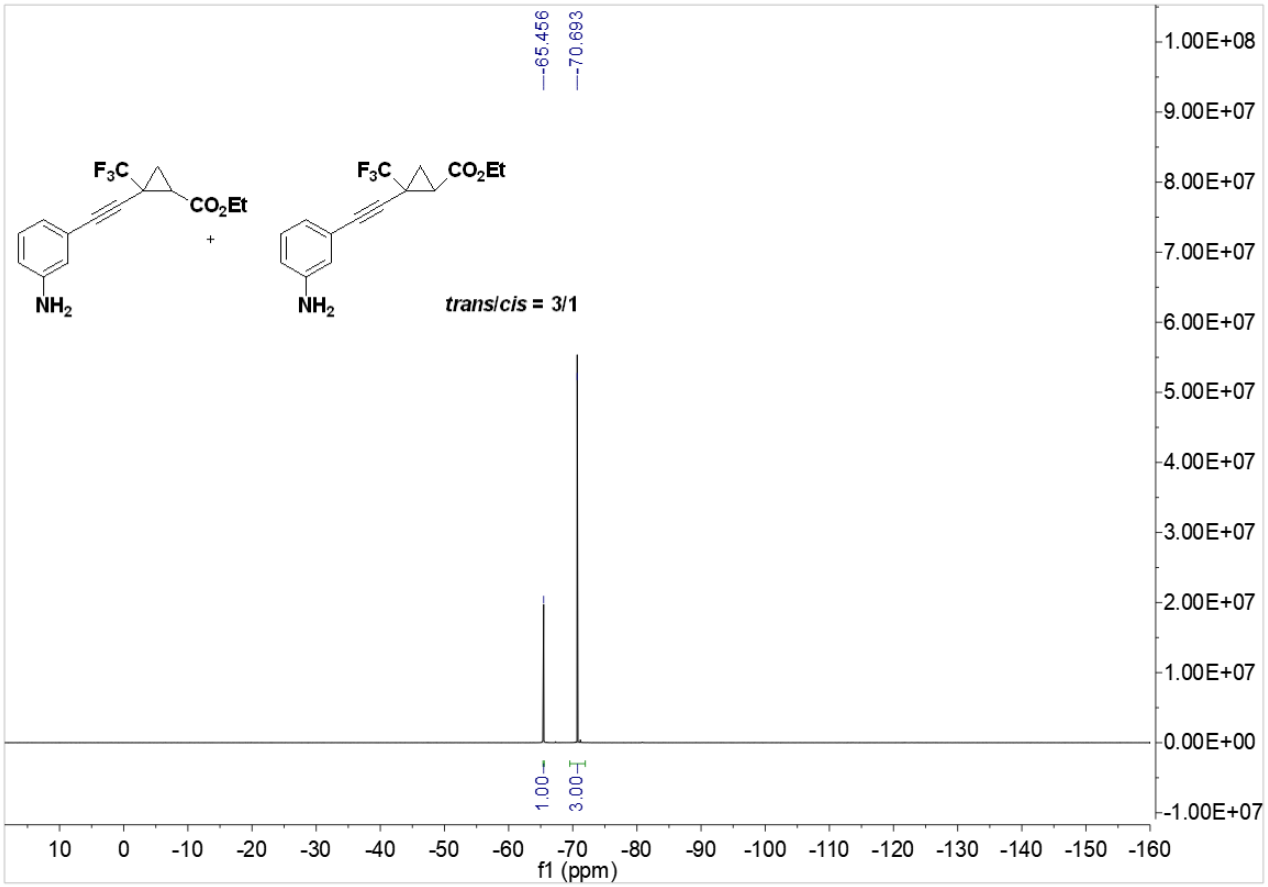
^{1}H NMR spectrum of **3qc**



^{13}C NMR spectrum of **3qc**



^{19}F NMR spectrum of **3qc**



HRMS (ESI) spectrum of **3qc**

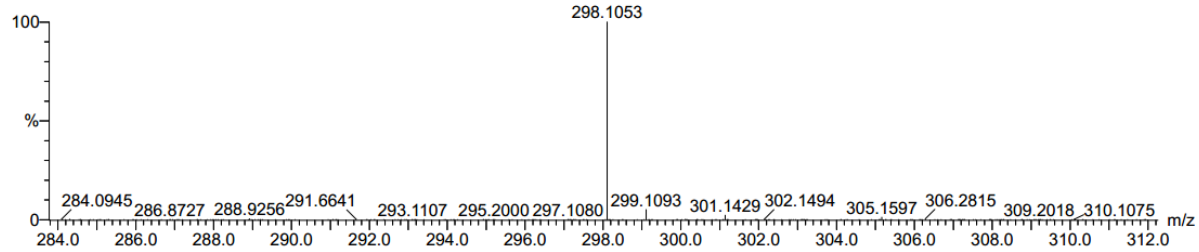
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
423 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 15-15 N: 0-20 O: 0-20 F: 3-3 Na: 0-3

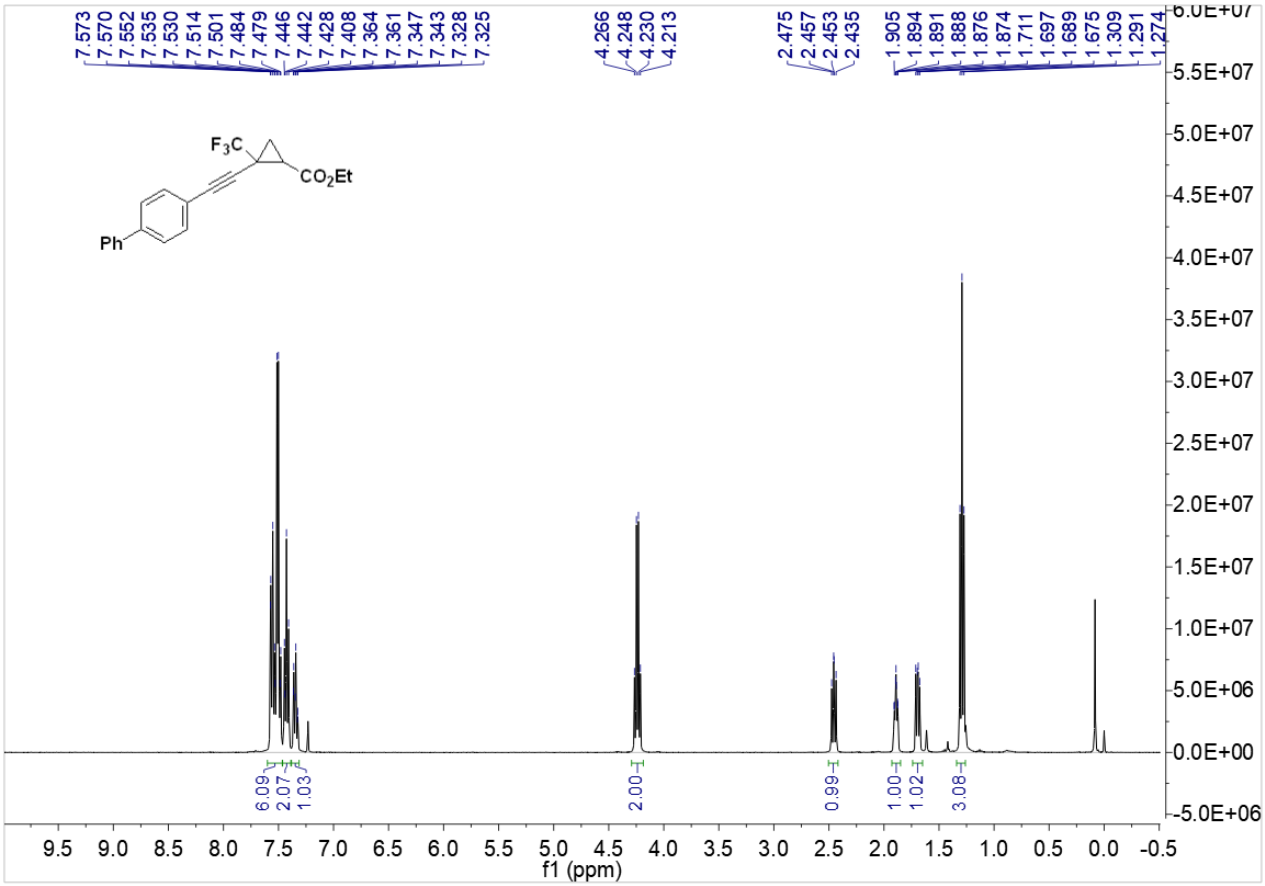
6
230410-1-21 13 (0.161)

1: TOF MS ES+
6.23e+005

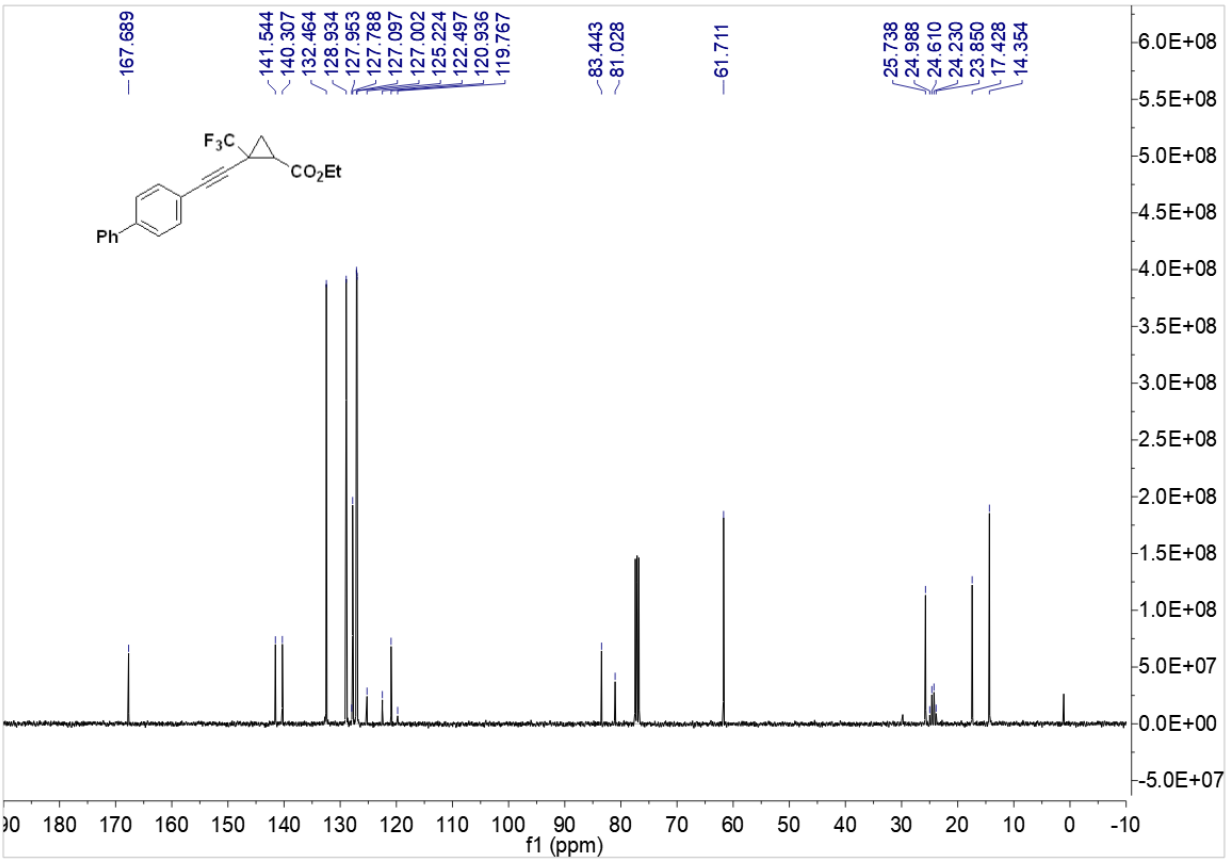


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
298.1053	298.1055	-0.2	-0.7	7.5	195.4	n/a	n/a	C15 H15 N O2 F3

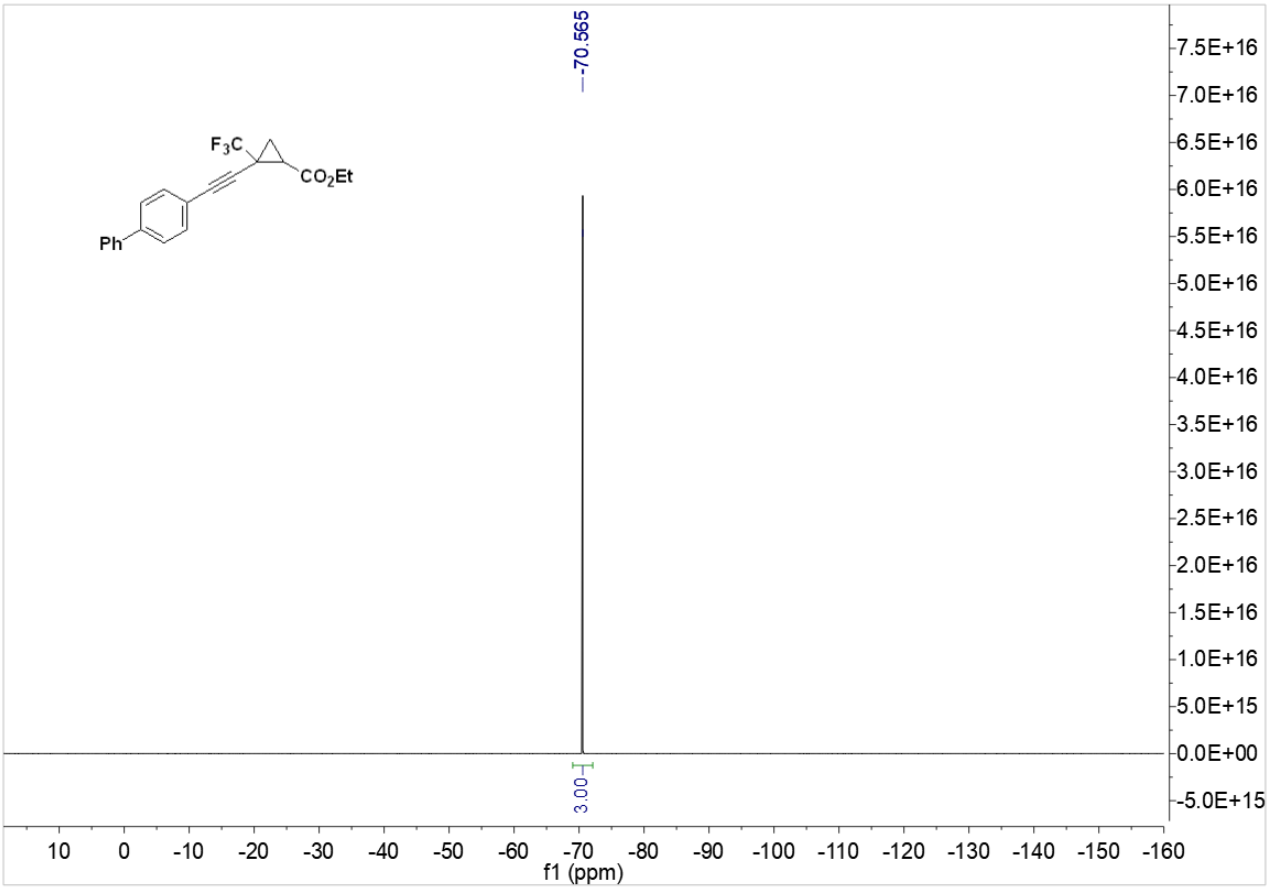
^{1}H NMR spectrum of ***trans*-3rc**



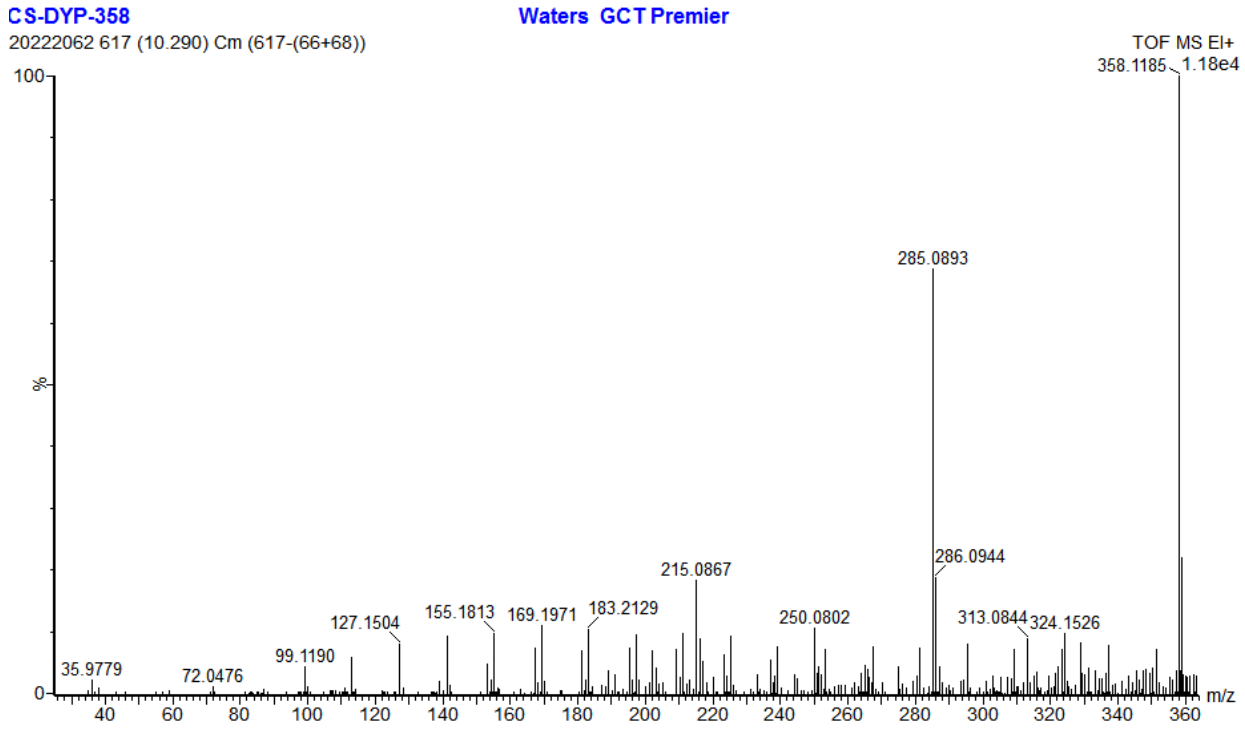
^{13}C NMR spectrum of ***trans*-3rc**



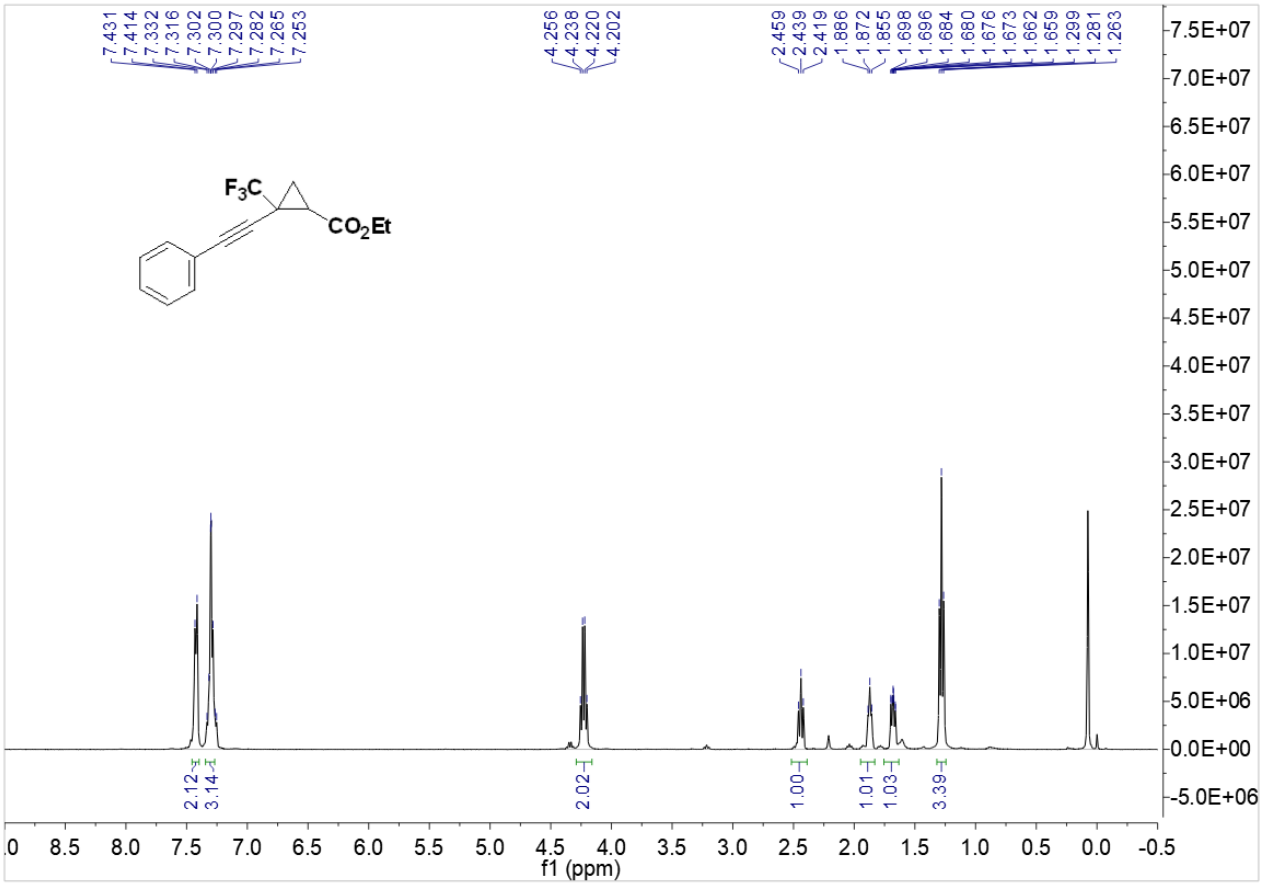
^{19}F NMR spectrum of ***trans*-3rc**



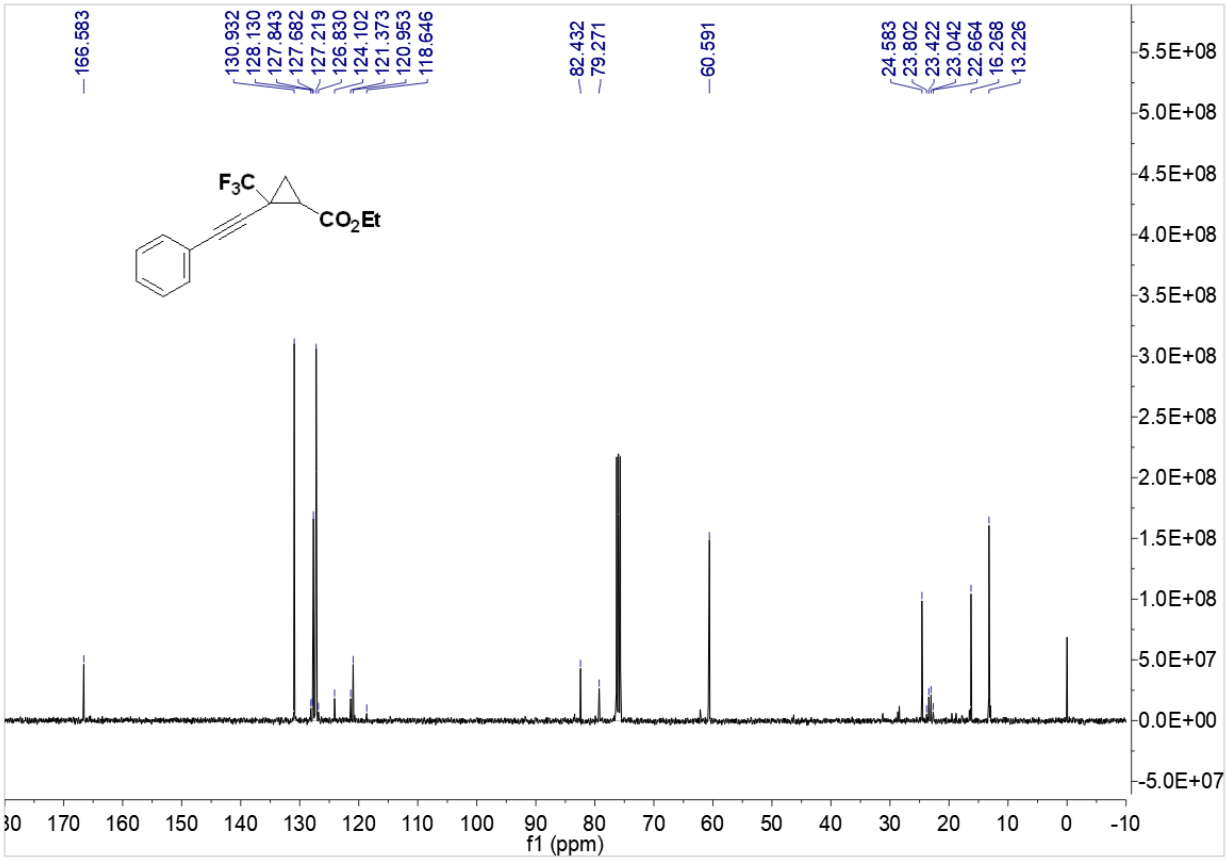
HRMS (EI) spectrum of ***trans*-3rc**



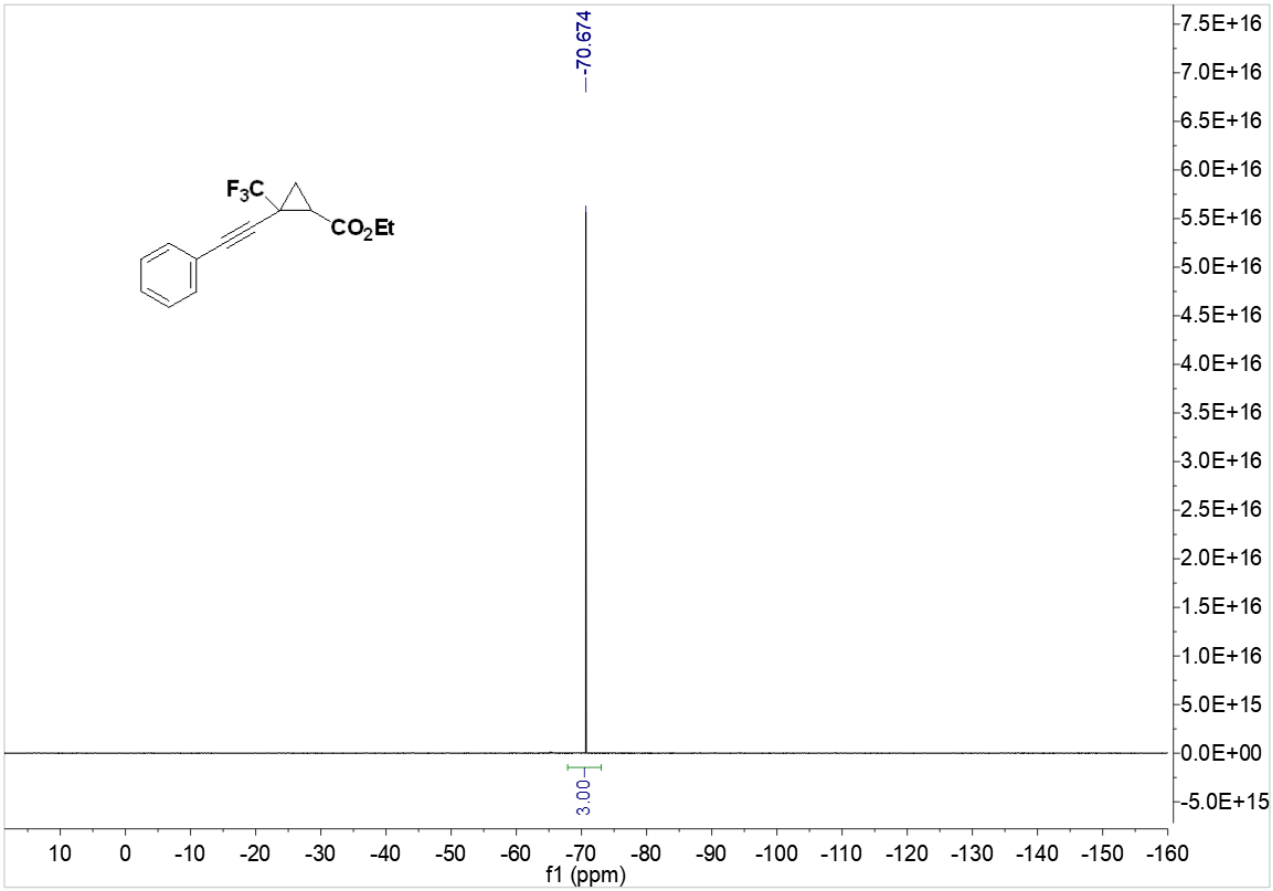
^{1}H NMR spectrum of ***trans*-3sc**



^{13}C NMR spectrum of ***trans*-3sc**



^{19}F NMR spectrum of ***trans*-3sc**



HRMS (ESI) spectrum of ***trans*-3sc**

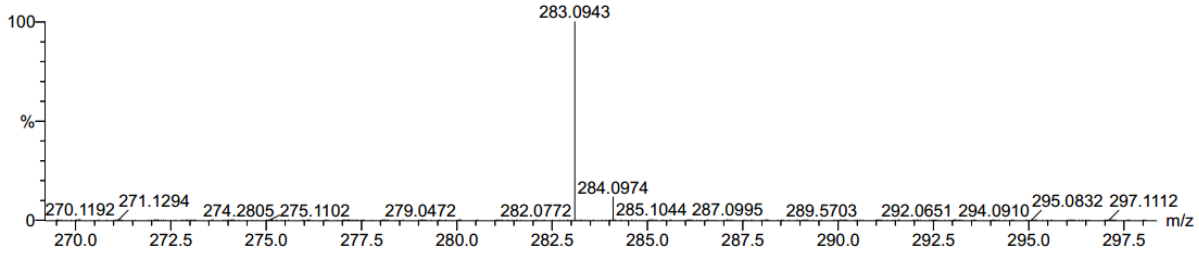
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
374 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 14-14 N: 0-20 O: 0-20 F: 3-3 Na: 0-3

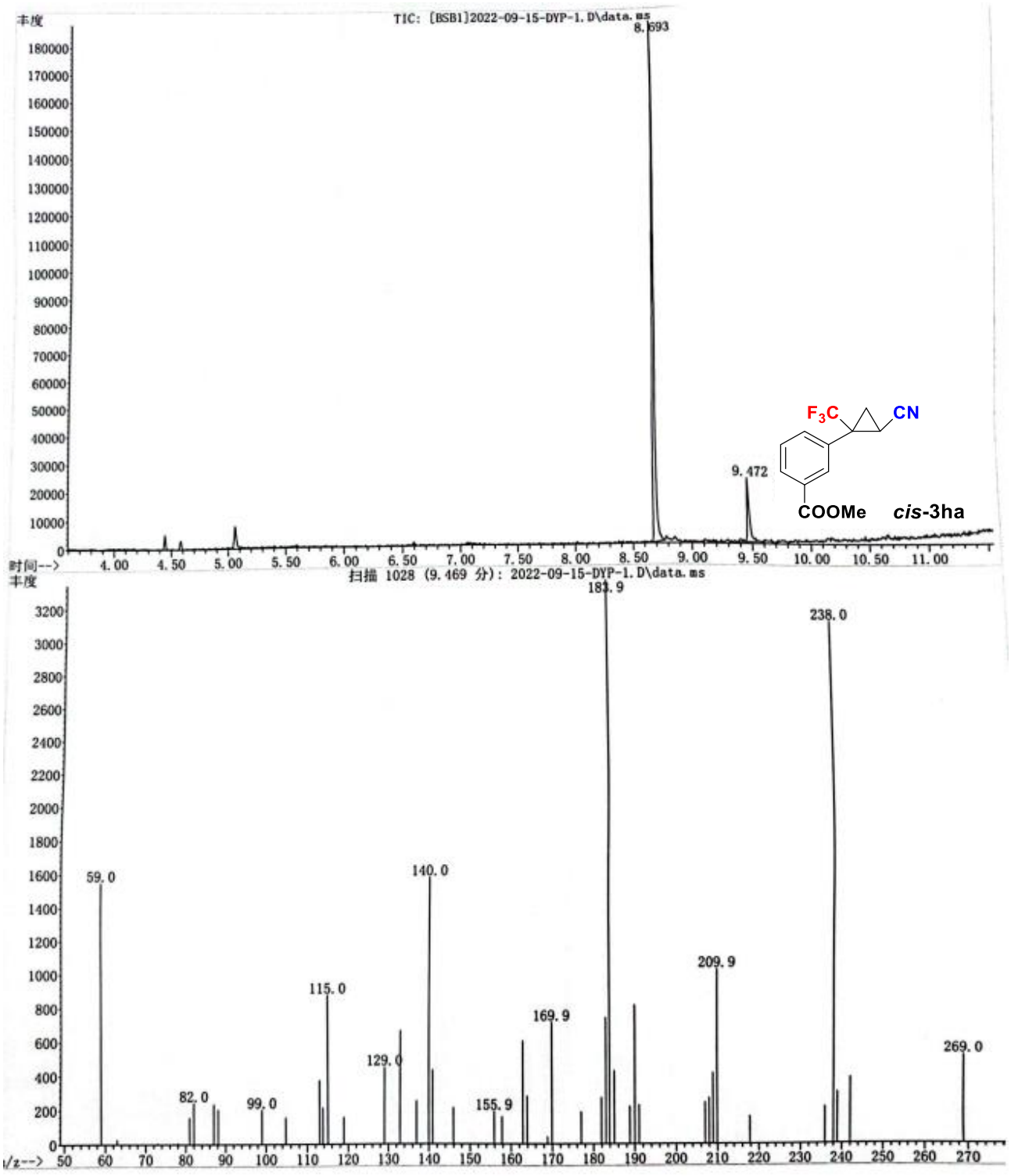
6
230410-1-20 5 (0.076)

1: TOF MS ES+
2.94e+006

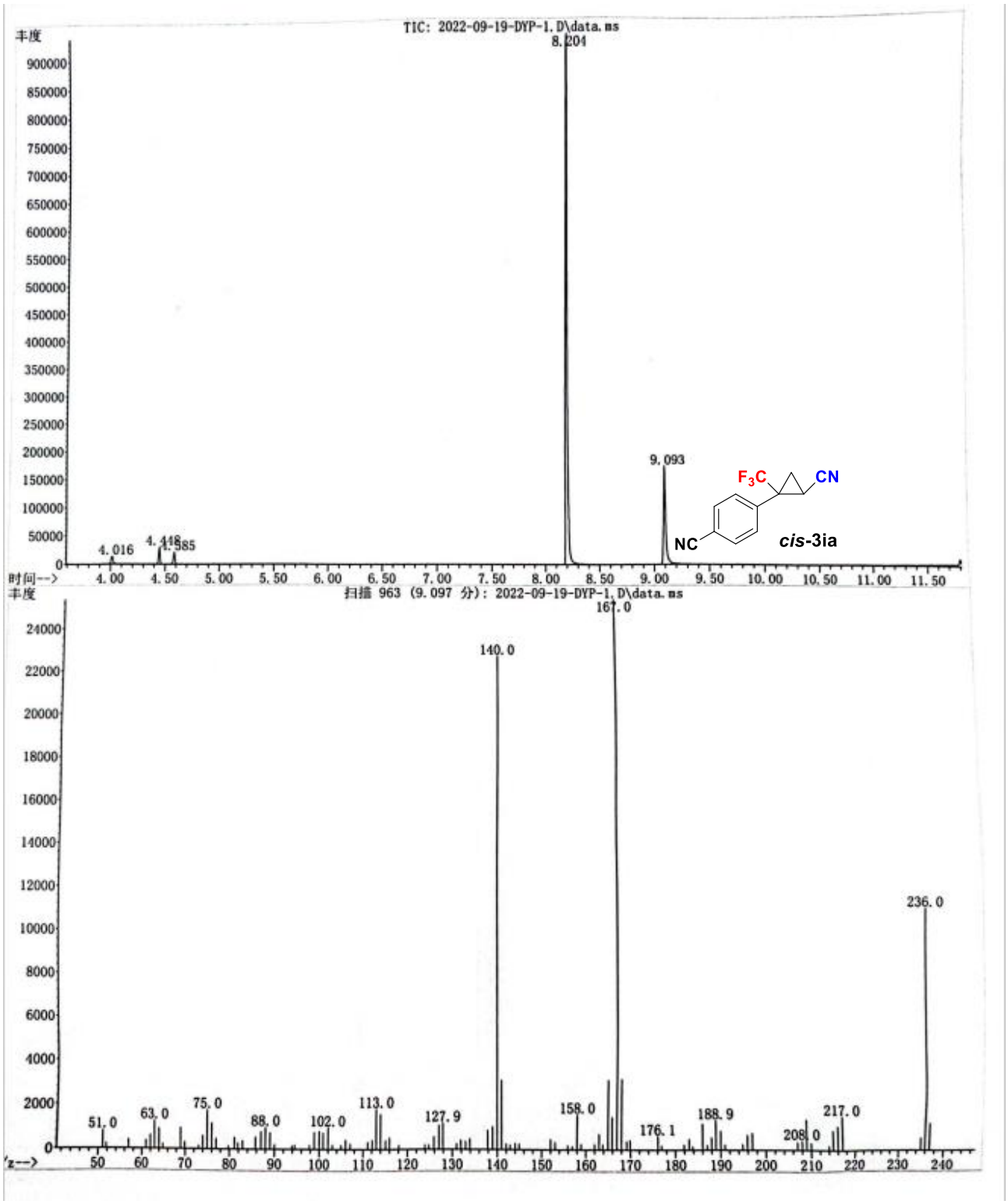


Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
283.0943	283.0946	-0.3	-1.1	7.5	293.7	n/a	n/a	C15 H14 O2 F3

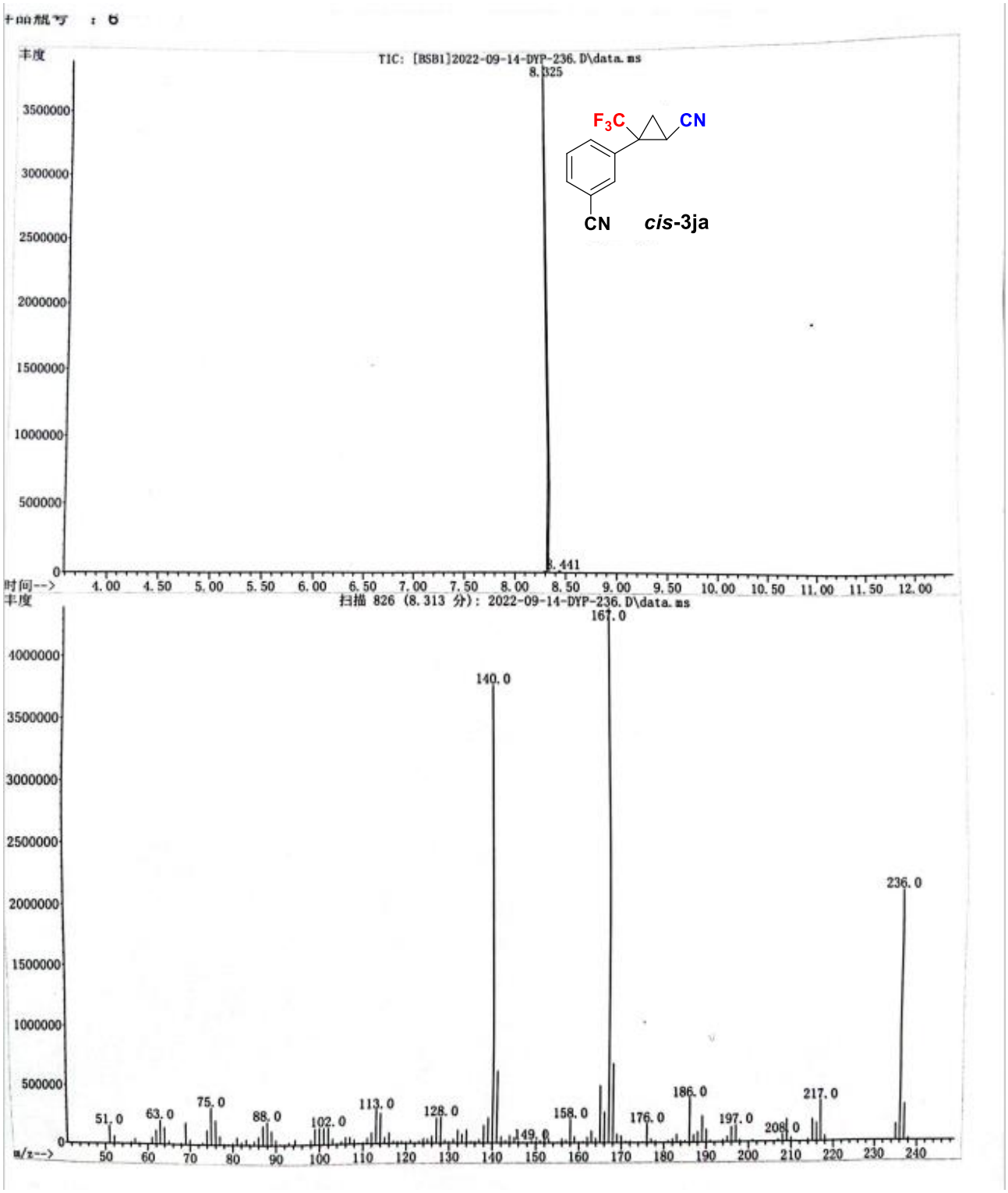
11. GC-MS spectra of compounds *cis*-3ha, *cis*-3ia, *cis*-3ja, *cis*-3ka, *cis*-3la, *cis*-3oa and 3nc-isomer 2



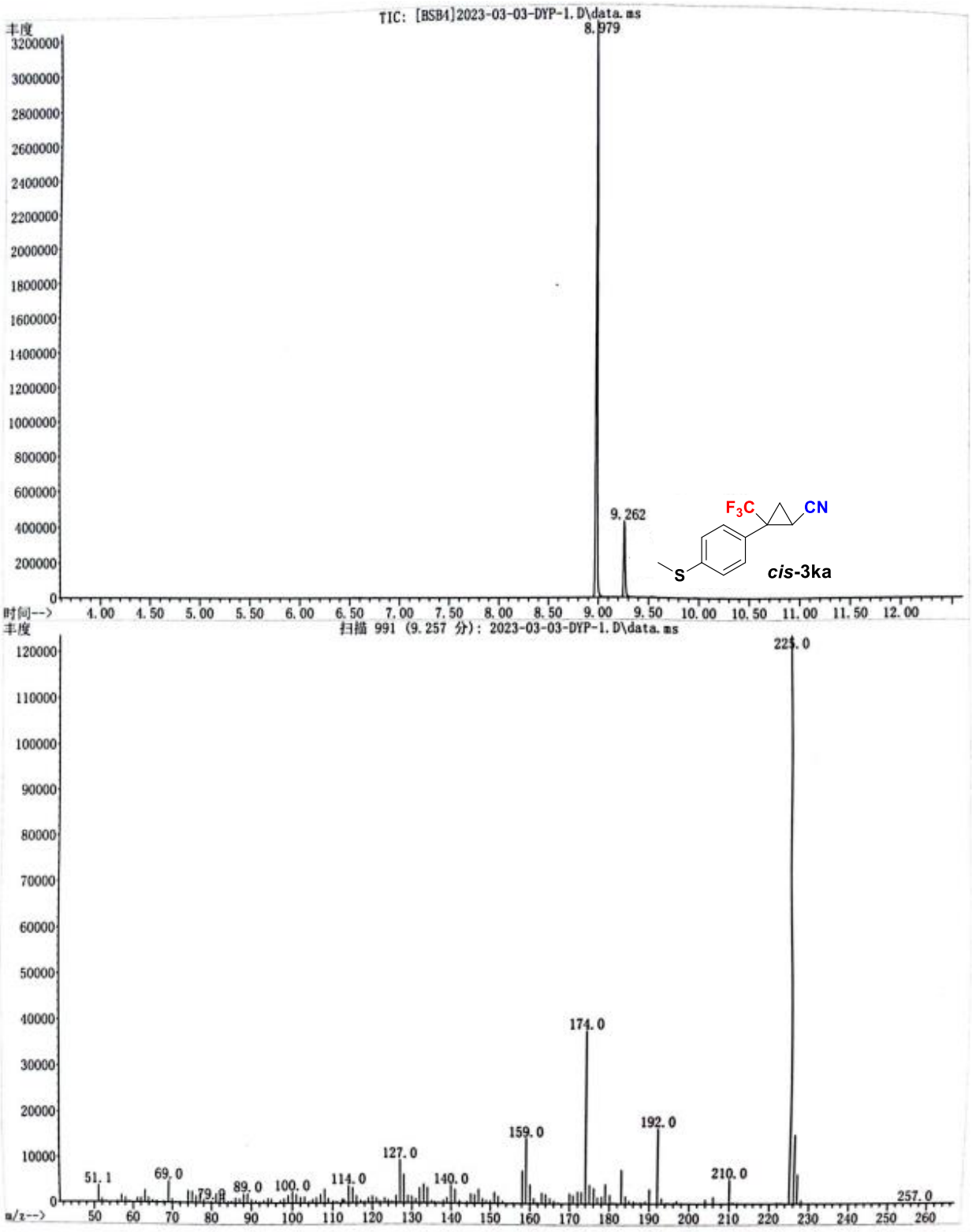
GC-MS spectrum of ***cis*-3ia**



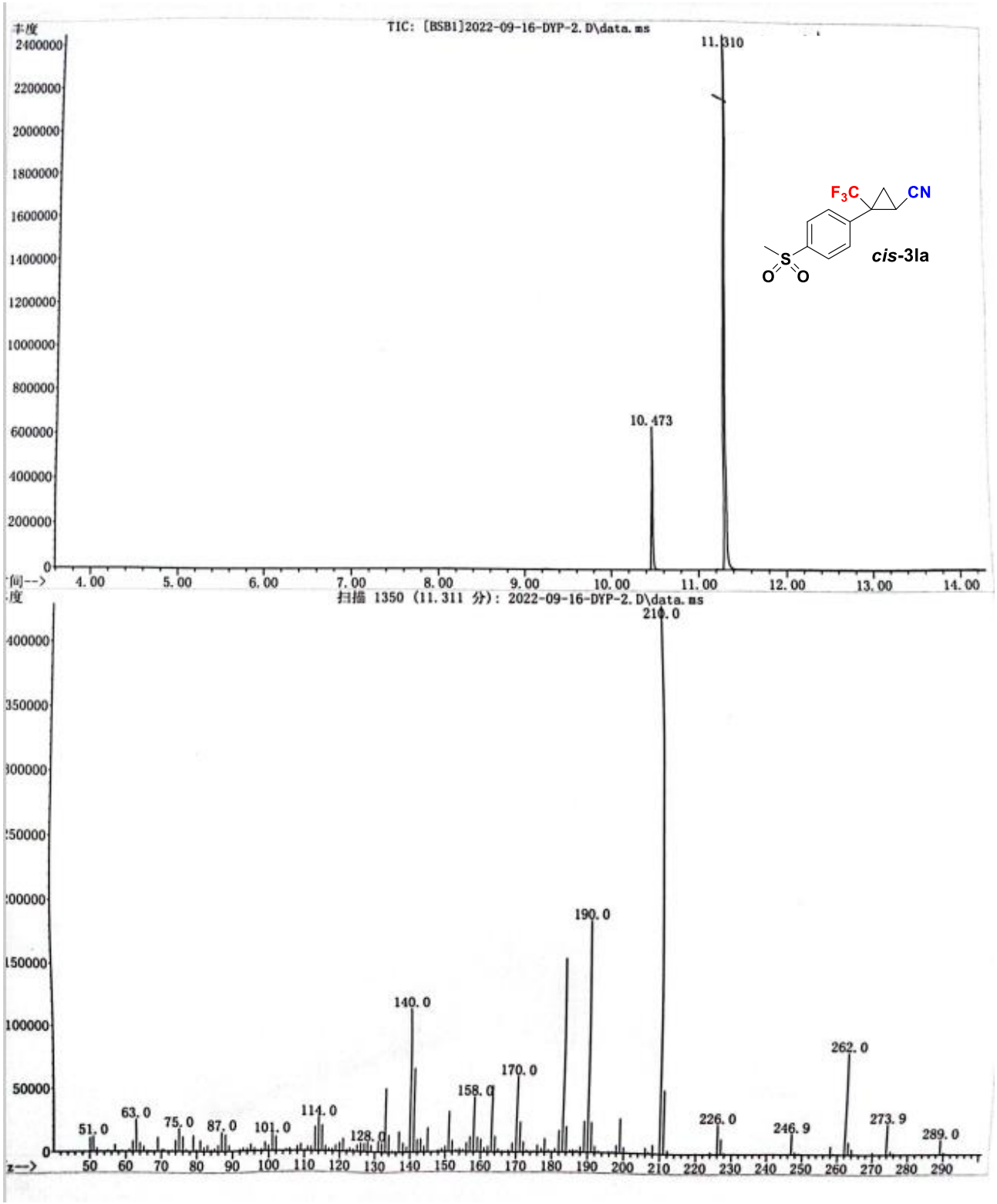
GC-MS spectrum of ***cis*-3ja**



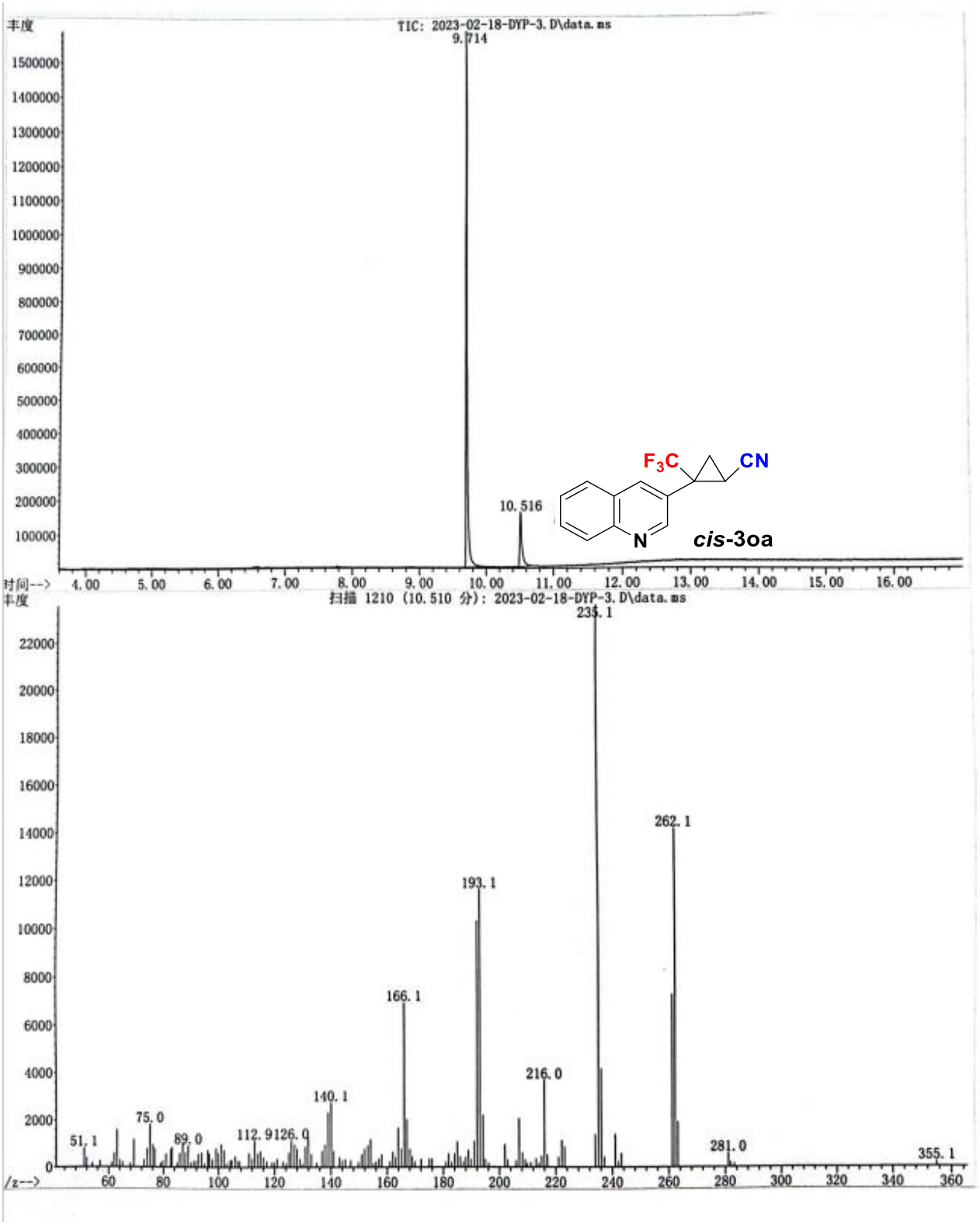
GC-MS spectrum of ***cis*-3ka**



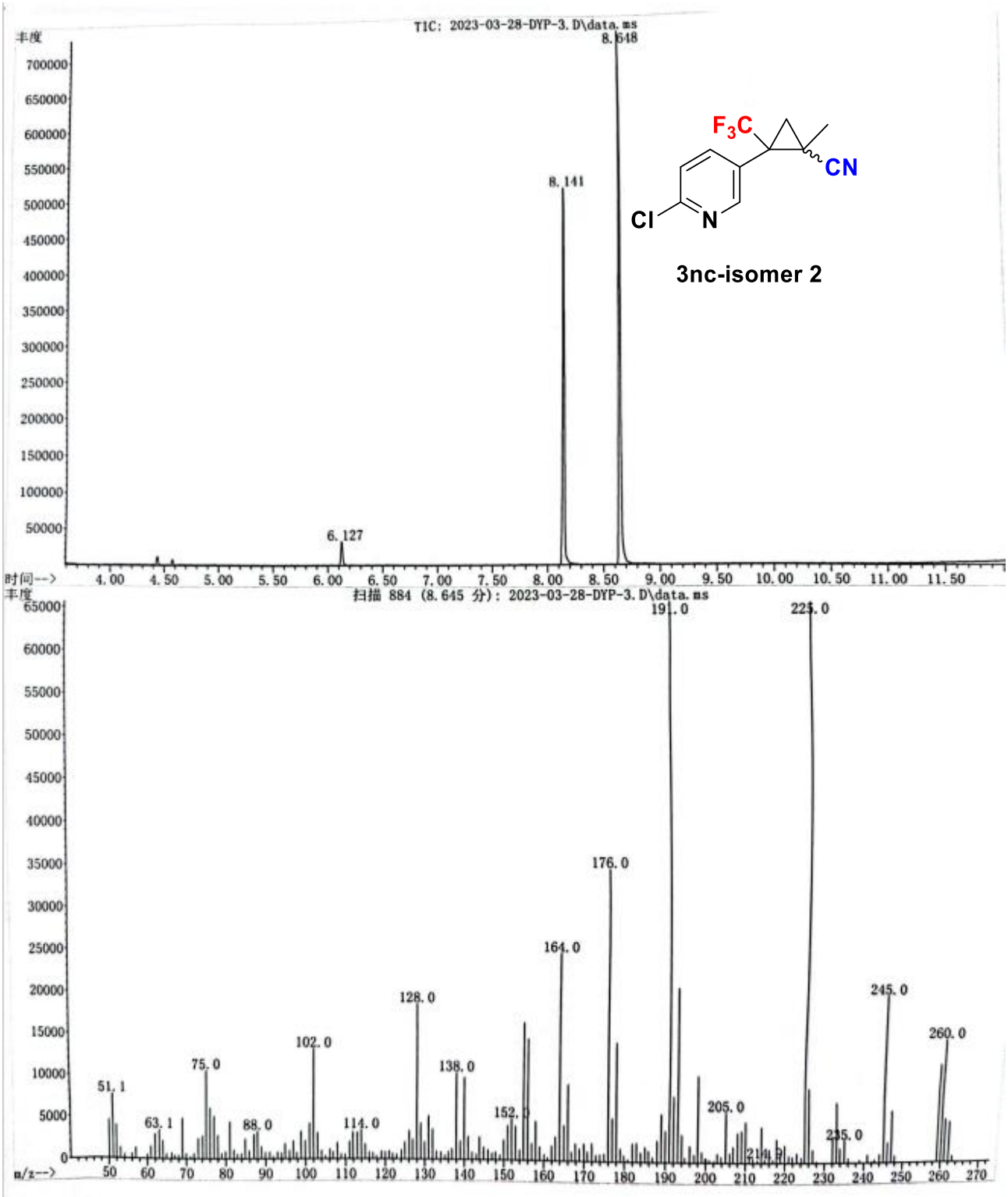
GC-MS spectrum of ***cis*-3la**



GC-MS spectrum of ***cis*-3oa**



GC-MS spectrum of **3nc-isomer 2**



3nc-isomer 2