Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Hypervalent iodine(III)-mediated ring-expansive difluorination of alkynylcyclopropanes *en route* to the synthesis of difluorinated alkylidenecyclobutanes

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Table of Contents

1. General information

The solvents used were dried by distillation over the drying agents indicated in parentheses and were transferred under argon: tetrahydrofuran (Na-benzophenone) and toluene (CaH_2), chloroform (CaH_2), dichloromethane (CaH_2). Nitromethane, 1,2-dichloroethane (DCE), tetrachloride (CCl_4), acetonitrile (CH_3CN), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Energy-chemical. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton (^1H), fluorine (^{19}F), and carbon (^{13}C) NMR spectra were recorded at 500 (or 400), 471 (or 376), and 126 (or 101) MHz, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dd = doublet of doublet for proton spectra, p: quintet. Coupling constants (*J*) are reported in hertz (Hz).

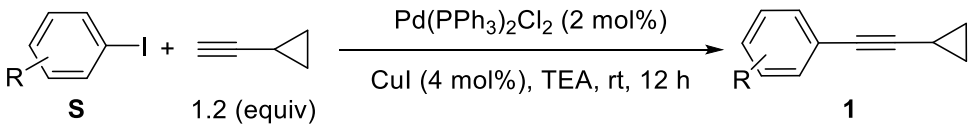
High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. TLCs were visualized with UV light (254 nm) and/or using $KMnO_4$ solution or phosphomolybdic acid in ethanol followed by heating using hot gun. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Preparation of the starting materials

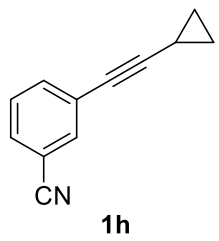
2.1. Synthesis of alkynylcyclopropanes by Sonogashira coupling[1-2]



General procedure A: According to the classical Sonogashira procedure, a dry round bottle was charged with aryl iodide **S** (5.0 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol%), and CuI (4 mol%). The mixture was vacuumed and flushed with N_2 for three times. Et_3N (12 mL) and ethynylcyclopropane (6.0 mmol, 1.2 equiv) was then added. The mixture was stirred at room temperature for 12 h until all the aryl iodide was consumed. The reaction mixture was quenched with saturated NH_4Cl, and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford alkynylcyclopropanes **1**.

According to general procedure A, aryl-substituted alkynylcyclopropanes **1a-1e**, **1g-1r**, **1u-v**, **1y-z**, **1ab**, **and 1ac** were prepared, and compounds **1a-e**, **1g**, **1i-k, 1o, 1y-z, 1ab,** and **1ac** have been reported in literature.[1-7]

3-(cyclopropylethynyl)benzonitrile (1h)

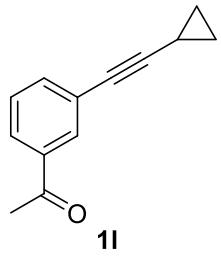


1h

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE:EA = 200:1) to yield a yellow liquid (0.47 g, 56%). R_f = 0.47 (PE:EA = 10:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.63 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 1.45 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.93 – 0.88 (m, 2H), 0.84 – 0.80 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ = 135.72, 134.92,

130.64, 129.11, 125.64, 118.26, 112.63, 96.48, 73.73, 8.81, 0.16. **HRMS** (EI): *m/z* calculated for $C_{12}H_9N^+$ $[M]^+$: 167.0735; found: 167.0729.

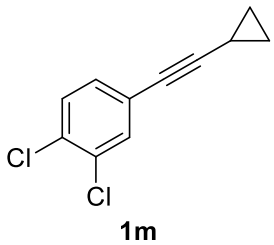
1-(3-(cyclopropylethynyl)phenyl)ethan-1-one (1l)



1l

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE:EA = 50:1) to yield a yellow liquid (0.54 g, 59%). R_f = 0.55 (PE:EA = 15:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.89 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 2.53 (s, 3H), 1.41 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.86 – 0.82 (m, 2H), 0.79 – 0.76 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.43, 137.03, 135.83, 131.56, 128.51, 127.03, 124.56, 93.34, 74.87, 26.59, 8.67, 0.17. **HRMS** (ESI): *m/z* calculated for $C_{13}H_{12}ONa^+$ $[M+Na]^+$: 207.0780; found: 207.0771.

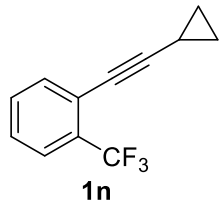
1,2-dichloro-4-(cyclopropylethynyl)benzene (1m)



1m

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE) to yield a yellow liquid (0.65 g, 62%). R_f = 0.71 (PE). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.43 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.42 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.90 – 0.85 (m, 2H), 0.82 – 0.77 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 133.25, 132.33, 131.72, 130.79, 130.17, 124.10, 95.86, 73.76, 8.79, 0.24. **HRMS** (EI): *m/z* calculated for $C_{11}H_8Cl_2^+$ $[M]^+$: 210.0003; found: 209.9998.

1-(cyclopropylethynyl)-2-(trifluoromethyl)benzene (1n)

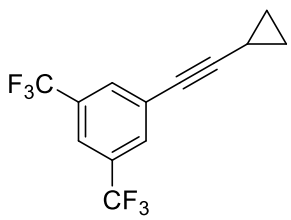


1n

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE) to yield a yellow liquid (0.69 g, 65%). R_f = 0.78 (PE). **^{1}H NMR**

(500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 1.48 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.91 (dtd, *J* = 8.1, 5.4, 2.4 Hz, 2H), 0.86 (dt, *J* = 5.3, 2.9 Hz, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 133.91, 131.64 (q, *J* = 30.1 Hz), 131.36, 127.16, 123.82 (q, *J* = 273.3 Hz), δ 125.80 (q, *J* = 5.1 Hz), 122.53 (q, *J* = 2.4 Hz), 99.98, 71.90, 8.84, 0.50. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.65. **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_3^+$ $[M]^+$: 210.0656; found: 210.0651.

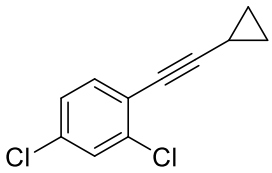
1-(cyclopropylethynyl)-3,5-bis(trifluoromethyl)benzene (1p)



1p

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE) to yield a yellow liquid (0.76 g, 55%). R_f = 0.73 (PE). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.78 (s, 2H), 7.73 (s, 1H), 1.47 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.96 – 0.91 (m, 2H), 0.88 – 0.83 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 131.7 (q, *J* = 33.5 Hz), 131.6 (q, *J* = 3.8 Hz), 126.61, 123.0 (q, *J* = 272.7 Hz), 120.9 (m, *J* = 4.0 Hz), 97.83, 73.43, 8.93, 0.22. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -63.5. **HRMS** (ESI): *m/z* calculated for $C_{13}H_8F_6^+$ $[M]^+$: 278.0530; found: 278.0524.

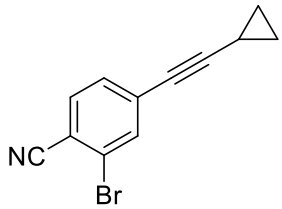
4-dichloro-1-(cyclopropylethynyl)benzene (1q)



1q

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE) to yield a yellow liquid (0.69 g, 66%). R_f = 0.71 (PE). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.36 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 1.52 – 1.47 (m, 1H), 0.91 (ddt, *J* = 8.3, 5.7, 3.0 Hz, 2H), 0.87 – 0.83 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 136.61, 133.87, 133.60, 129.13, 126.85, 122.51, 100.37, 71.83, 9.07, 0.50. **HRMS** (EI): *m/z* calculated for $C_{11}H_8Cl_2^+$ $[M]^+$: 210.0003; found: 209.9997.

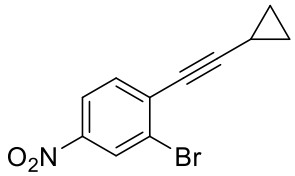
2-bromo-4-(cyclopropylethynyl)benzonitrile (1r)



1r

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE:EA = 100:1) to yield a colorless solid (0.76 g, 62%). R_f = 0.52 (PE:EA = 10:1). m.p.: 66-70 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 1.46 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.93 (dt, *J* = 8.0, 3.3 Hz, 2H), 0.87 – 0.81 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.8, 133.8, 130.6, 130.6, 125.0, 117.2, 114.2, 100.6, 73.7, 9.2, 0.4. **HRMS** (ESI): *m/z* calculated for $C_{12}H_8BrNNa^+$[M+Na]$^+$: 267.9732; found: 267.9743.

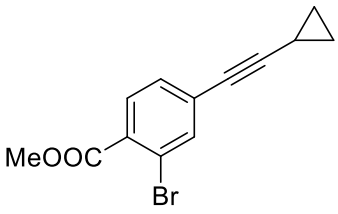
2-bromo-1-(cyclopropylethynyl)-4-nitrobenzene (1u)



1u

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE:EA = 100:1) to yield a pale yellow solid (0.78 g, 59%). R_f = 0.55 (PE:EA = 10:1). m.p.: 68-73 °C. **^{1}H NMR 1H NMR (400 MHz, Chloroform-*d*)** δ 8.39 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 1.53 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.99 (ddt, *J* = 8.3, 5.8, 3.0 Hz, 2H), 0.92 (dt, *J* = 5.3, 3.0 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 146.4, 133.3, 132.9, 127.5, 125.7, 122.0, 105.6, 73.9, 9.5, 0.7. **HRMS** (ESI): *m/z* calculated for $C_{11}H_8BrNO_2^+$ [M]$^+$: 264.9738; found: 264.9735.

methyl 2-bromo-4-(cyclopropylethynyl)benzoate (1v)

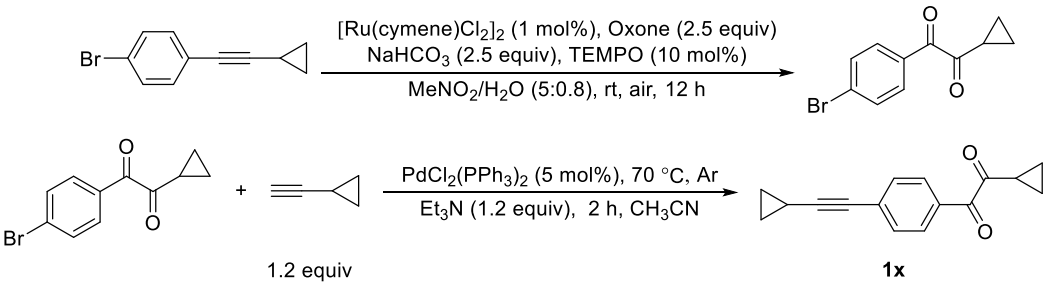


1v

The title compound was prepared following the general procedure A and purified using silica gel chromatography (PE:EA = 100:1) to yield a white solid (0.82 g, 59%). R_f = 0.53 (PE:EA = 10:1). m.p.: 67-69 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, *J* = 1.7

Hz, 1H), 7.86 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 3.90 (s, 3H), 1.57 – 1.46 (m, 1H), 0.98 – 0.92 (m, 2H), 0.92 – 0.87 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.6, 133.4, 133.0, 130.6, 130.0, 128.0, 125.4, 102.6, 74.5, 52.5, 9.3, 0.7. **HRMS** (EI): *m/z* calculated for $C_{13}H_{11}BrO_2^+$ $[M]^+$: 277.9942; found: 277.9938.

2.2. Preparation of 1-cyclopropyl-2-(4-(cyclopropylethynyl)phenyl) ethane-1,2-dione (1x)[8-9]

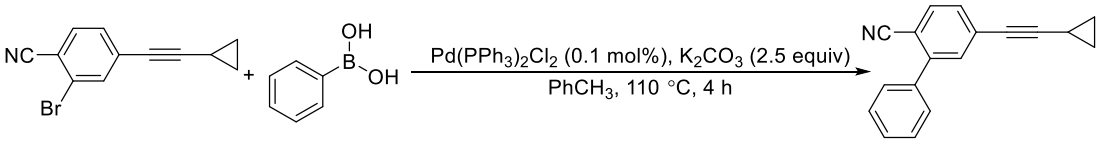


To a vigorously stirred mixture of 1-bromo-4-(cyclopropylethynyl)benzene (6.9 mmol), $NaHCO_3$ (1.45 g, 17.25 mmol), and Oxone (10.6 g, 17.25 mmol) in $MeNO_2$ (31 mL) was added $[Ru(cymene)Cl_2]_2$ (42.1 mg, 0.069 mmol) at room temperature under air. Then, H_2O (6 mL) and TEMPO (0.11 g, 0.69 mmol) were added, and the reaction flask was rinsed with $MeNO_2$ (4 mL). After 12 h, the reaction mixture was quenched by sat. aq. $NaHSO_3$ (75 mL) and extracted with EtOAc (50 mL). The organic layer was washed with brine (75 mL). The combined organic layer was dried over $MgSO_4$, filtered through a glass frit, and concentrated under reduced pressure. The residue was purified by column chromatography (PE:EA = 50:1) to afford 1,2-diketone product (1.2 g, 66%) as a green oil. R_f = 0.40 (PE:EA = 10:1).

According to the reported literature, a dry round bottle was charged with the above 1,2-diketone product (4.5 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), and Et_3N (1.2 equiv). The mixture was vacuumed and flushed with N_2 for three times. CH_3CN (8 mL) and the ethynylcyclopropane (1.2 equiv) was then added. The mixture was stirred at 70 ^oC. After 2 h, the reaction mixture was quenched with saturated NH_4Cl, and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, and

filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography. The product **1x** was obtained in 55% yield (0.59 g) as a yellow liquid after column chromatography (PE:EA = 30:1). R_f = 0.35 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 2.53 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.46 (tt, *J* = 8.2, 5.0 Hz, 1H), 1.32 – 1.25 (m, 2H), 1.15 (dt, *J* = 7.6, 4.0 Hz, 2H), 0.95 – 0.85 (m, 2H), 0.84 (dt, *J* = 5.4, 2.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.5, 191.4, 131.9, 130.7, 130.7, 130.2, 99.0, 75.5, 18.6, 13.4, 9.0, 0.5. **HRMS** (ESI): *m/z* calculated for $C_{16}H_{14}O_2Na^+$ $[M+Na]^+$: 261.0886; found: 261.0899.

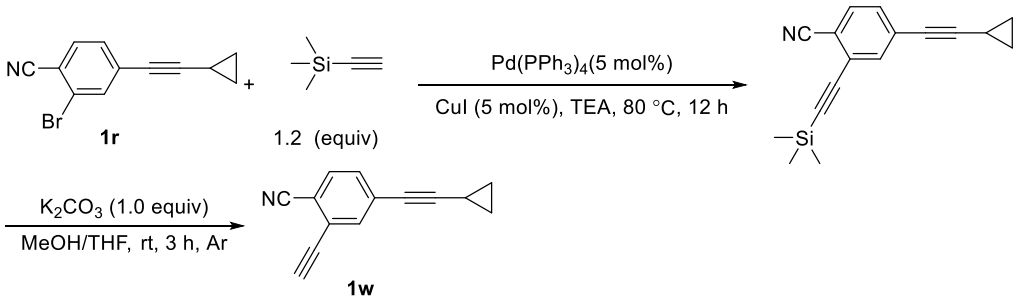
2.3. Preparation of 5-(cyclopropylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1s)



1r **1s**

According to the reported literature, Reaction conditions: **1r** (4.3 mmol, 1.0 equiv), phenylboronic acid (5.2 mmol, 1.2 equiv), K_2CO_3 (10.8 mmol, 2.5 equiv) and the catalyst $PdCl_2(PPh_3)_2$ (0.1 mol%) were stirred in toluene (43 mL) at 110 °C under air atmosphere over 4 h. the product **1s** was obtained in 50% yield (0.52 g) as a white solid after column chromatography (PE:EA = 100:1) , R_f = 0.52 (PE:EA = 10:1). m.p.: 66-68 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.39 (dd, *J* = 8.1, 1.6 Hz, 1H), 1.48 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.96 – 0.90 (m, 2H), 0.87 – 0.82 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.4, 137.7, 133.6, 133.1, 130.4, 129.1, 129.0, 128.8, 128.8, 118.7, 109.7, 98.8, 74.8, 9.1, 0.4. **HRMS** (ESI): *m/z* calculated for $C_{18}H_{13}NNa^+$ $[M+Na]^+$: 266.0940; found: 266.0960.

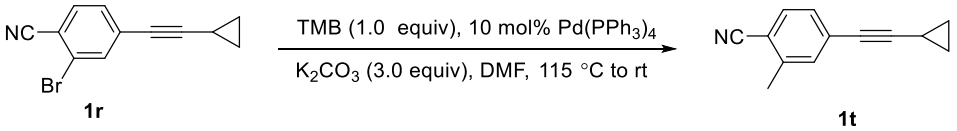
2.4. Preparation of 4-(cyclopropylethynyl)-2-ethynylbenzonitrile (1w)[11-12]



According to the reported literature, in a dry flask under an atmosphere of nitrogen, the **1r** (2.5 mmol) was dissolved in 6 mL Et_3N. 5 mol% of $Pd(PPh_3)_4$, 1.2 equiv of the trimethyl silyl acetylene and 5 mol% of CuI were added. The mixture was stirred at 80 ^oC for 12 hours until complete conversion. The crude reaction mixture was washed by water, dried over Na_2SO_4 and purified by column chromatography on silica gel (PE:EA = 100:1). R_f = 0.56 (PE:EA = 10:1). The product was obtained in 93% yield (0.61 g).

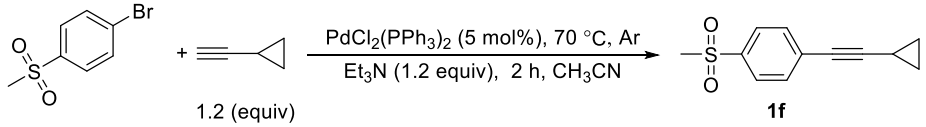
The above product (2.3 mmol), in 1:1 mixture of MeOH/THF (30 mL) was added K_2CO_3 (1.0 equiv). The solution was stirred at room temperature for 3 h under nitrogen. Water was added to quench the reaction and an aqueous work up was performed. The product **1w** was obtained in 90% (0.39 g) yield as a white solid after column chromatography (PE:EA = 100:1), R_f = 0.45 (PE:EA = 10:1). m.p.: 68-71 ^oC. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.53 (s, 1H), 7.52 (d, *J* = 5.2 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.45 (s, 1H), 1.44 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.93 – 0.89 (m, 2H), 0.84 – 0.79 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.7, 132.5, 131.8, 129.1, 125.9, 117.2, 113.9, 99.7, 84.1, 79.1, 74.0, 9.1, 0.3. **HRMS** (ESI): *m/z* calculated for $C_{14}H_9NNa^+$ $[M+Na]^+$: 214.0627; found: 214.0622.

2.5. Preparation of 4-(cyclopropylethynyl)-2-methylbenzonitrile (1t)[13]



1r (1.5 mmol), potassium carbonate (3.0 equiv), $Pd(PPh_3)_4$ (10 mol%), DMF (4 mL) and TMB (1.0 equiv) were charged to a flask and the contents was heated to 115 ^oC (oil bath temperature) under nitrogen for 6 h and then stirred overnight at ambient temperature. The reaction mixture was filtered through a pad of Celite, washed with THF and concentrated in vacuo. The product **1t** was obtained in 50% (0.14 g) yield as a white solid after column chromatography (PE:EA = 120:1), R_f = 0.63 (PE:EA = 10:1). m.p.: 66-69 ^oC. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 2.47 (s, 3H), 1.44 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.92 – 0.87 (m, 2H), 0.83 – 0.79 (m, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 141.8, 133.1, 132.3, 129.3, 128.8, 118.1, 111.3, 98.2, 74.8, 20.3, 9.0, 0.3. **HRMS** (ESI): *m/z* calculated for $C_{13}H_{11}NNa^+$ $[M+Na]^+$: 204.0784; found: 204.0780.

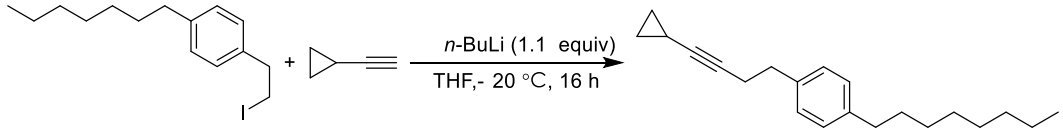
2.6. Preparation of Preparation of 4-(cyclopropylethynyl)-2-methylbenzonitrile (1f)[8]



According to the reported literature, a dry round bottle was charged with aryl bromide (5.0 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%) , Et_3N (1.2 equiv). The mixture was vacuumed and flushed with N_2 for three times. CH_3CN (12 mL) and the ethynylcyclopropane (1.2 equiv) was then added. The mixture was stirred at 70 ^oC 2 h. The reaction mixture was quenched with saturated NH_4Cl, and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic phase washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography. The product **1f** was obtained in 40% yield (0.44 g) as a yellow

solid after column chromatography (PE:EA = 4:1), R_f = 0.52 (PE:EA = 2:1). The product was recrystallized into a white solid. m.p.: 67-70 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 3.03 (s, 3H), 1.47 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.92 (dtd, *J* = 7.4, 5.0, 2.3 Hz, 2H), 0.85 (m, *J* = 5.3, 3.1 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 138.9, 132.4, 130.2, 127.4, 98.6, 74.6, 44.6, 9.0, 0.4. HRMS (EI): *m/z* calculated for $C_{12}H_{12}O_2S^+$ $[M]^+$: 220.0558; found: 220.0553.

2.7. Preparation of Preparation of 4-(cyclopropylethynyl)-2-methylbenzonitrile(1aa)[2]

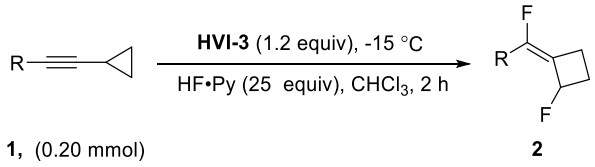


1aa

To a cold (-20 °C), stirred solution of ethynylcyclopropane (0.4 g, 0.5 mL, 6.0 mmol), in anhydrous THF (15 mL) was added dropwise *n*-BuLi (2.2 mL, 2.5 M in hexanes, 5.5 mmol) for the period of 0.5 h. The reaction mixture was stirred for 15 minutes and then the 1-heptyl-4-(2-iodoethyl)benzene (1.72 g, 5 mmol) was added dropwise for the period of 10 minutes. Under stirring, the reaction mixture was allowed to warm up to ambient temperature overnight. The reaction mixture was quenched with water, and the aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography (PE) to yield **1aa** as a colorless oil (0.81 g, 57%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.13 (s, 4H), 2.79 (t, *J* = 7.7, 2H), 2.60 (dd, *J* = 8.7, 6.8, 2H), 2.42 (td, *J* = 7.8, 2.0, 2H), 1.63 (p, *J* = 7.5, 2H), 1.32 (d, *J* = 14.4, 10H), 1.26 – 1.16 (m, 1H), 0.99 – 0.86 (m, 3H), 0.77 – 0.69 (m, 2H), 0.65 – 0.60 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ = 140.75, 138.21, 128.37 , 83.94 , 75.12 , 35.72 , 35.36 , 32.04 , 31.71 , 29.64 , 29.51 , 29.43 ,

22.81 , 21.25 , 14.22 , 8.02 , -0.31 . HRMS (EI): *m/z* calculated for $C_{21}H_{30}^{+}$ $[M]^{+}$: 282.2348; found: 282.2346.

3. Synthesis of difluorinated alkylidenecyclobutanes



General Procedure B : A low density polyethylene tube with a stir bar was charged with **HVI-3** (98.9 mg, 1.2 equiv, stored in glove box), chloroform (1.0 mL), and Py•9HF (adamas, 65% hydrogen fluoride by weight, 140 uL, 25 equiv hydrogen fluoride) carefully at room temperature. After stirring for 2 minutes, the reaction mixture was cooled to -15 ^{o}C. After stirring for another 5 minutes, the mixture was added alkynylcyclopropanes **1** (0.2 mmol). Then, the mixture was stirred at -15 ^{o}C for 2 h. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 ^{o}C, after stirring for another 5 minutes at room temperature followed by filteration. The filter cake was washed with DCM. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography.

Important notes:

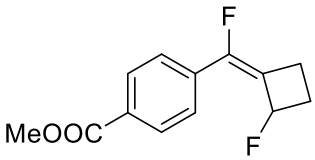
1) Py·9HF should be carefully handled by wearing gloves in a fumehood because of its corrosiveness and toxicity.

2) The equivalent and state of Py·9HF (sensitive to air and humidity) were found to be particularly important to the reaction. The use of Py·9HF storaged for different time may result in different yield and reaction time.

3) Partial products (e.g. **2c**, **2k**, **2n**) should be carefully handled because of its high volatility and instability in air.

4. Characterization data of difluorinated alkylidenecyclobutanes

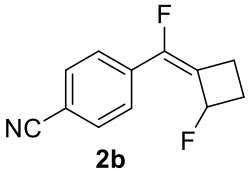
Methyl (*E*)-4-(fluoro (2-fluorocyclobutylidene) methyl)benzoate (2a)



2a

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a white solid (36.2 mg, 76%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.61 (PE:EA = 10:1). m.p.: 84-88 °C. **^{1}H NMR (500 MHz, Chloroform-d)** δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 5.70 (ddq, *J* = 56.1, 7.3, 3.6 Hz, 1H), 3.92 (s, 3H), 3.05 – 2.92 (m, 1H), 2.68 – 2.57 (m, 1H), 2.59 – 2.46 (m, 1H), 2.49 – 2.34 (m, 1H). **^{19}F NMR (470 MHz, Chloroform-*d*, composite pulse decoupling)** δ -118.44 (d, *J* = 3.3 Hz), -162.28 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.61, 153.34 (dd, *J* = 248.0, 6.8 Hz), 134.97 (dd, *J* = 28.3, 3.0 Hz), 130.45, 129.82 (d, *J* = 2.3 Hz), 125.19 (dd, *J* = 7.2, 4.6 Hz), 120.33 (dd, *J* = 27.1, 14.8 Hz), 88.44 (dd, *J* = 208.0, 15.9 Hz), 52.30, 27.54 (d, *J* = 21.8 Hz), 21.10 (dd, *J* = 7.7, 6.1 Hz). **HRMS** (EI): *m/z* calculated for $C_{13}H_{12}F_2O_2^+$ $[M]^+$: 238.0805; found: 238.07990.

(*E*)-4-(fluoro(2-fluorocyclobutylidene)methyl)benzonitrile (2b)

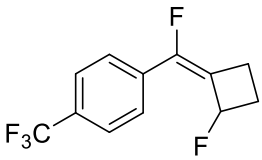


2b

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a white solid (31.2 mg, 76%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.63 (PE:EA = 10:1). m.p.: 85-87 °C. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.67 (d, *J* = 1.1 Hz, 4H), 5.77 (ddq, *J* = 56.0, 7.4, 3.7 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.68 – 2.56 (m, 1H), 2.58 – 2.49 (m, 1H), 2.51 – 2.35 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -119.21 (d, *J* = 2.7 Hz), -162.33 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 152.34 (dd, *J* = 247.7, 6.4 Hz), 135.03 (dd, *J* = 28.8, 2.8 Hz), 132.43 (d, *J* = 2.4 Hz), 125.81 (dd, *J* = 7.3, 5.0 Hz),

121.83 (dd, *J* = 26.9, 14.7 Hz), 118.61, 112.57 (d, *J* = 1.6 Hz), 88.08 (dd, *J* = 209.3, 15.5 Hz), 27.52 (d, *J* = 21.4 Hz), 20.98 (dd, *J* = 8.1, 5.9 Hz). **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_2N^+$ $[M]^+$: 205.0703; found: 205.0698.

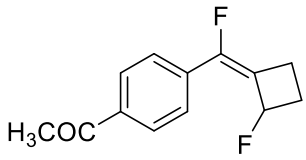
(*E*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-4-(trifluoromethyl)benzene (2c)



2c

The title compound was prepared following a general procedure B and purified using silica gel chromatography (PE) to yield a colourless liquid (24.8 mg, 50%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.65 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (q, *J* = 8.6 Hz, 4H), 5.64 (ddq, *J* =56.17, 7.3, 3.6 Hz, 1H), 3.07 – 2.94 (m, 1H), 2.69 – 2.57 (m, 1H), 2.57 – 2.48 (m, 1H), 2.48 – 2.34 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -62.87, -118.55 (d, *J* = 2.7 Hz), -162.19 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 152.96 (dd, *J* = 248.0, 6.8 Hz), 134.27 (d, *J* = 28.8 Hz), 130.9 (q, *J* =32.81), δ 125.62 (qd, *J* = 6.9, 4.1 Hz), 124.04 (q, *J* = 272.0 Hz), 120.32 (dd, *J* = 26.9, 14.7 Hz). 88.38 (dd, *J* = 208.2, 15.9 Hz), 27.58 (d, *J* = 21.7 Hz), 21.01 (dd, *J* = 7.8, 6.0 Hz). **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_5^+$ $[M]^+$: 248.0624; found: 248.0617.

(*E*)-1-(4-(fluoro(2-fluorocyclobutylidene)methyl)phenyl)ethan-1-one (2d)

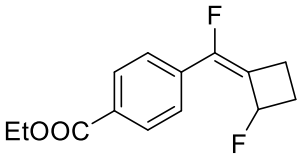


2d

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) using silica gel chromatography (PE:EA = 50:1) to yield a colorless liquid (35.1 mg, 79%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.38 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)**δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 5.72 (ddq, *J* =55.44, 7.3, 3.6 Hz, 1H), 3.09 – 2.91 (m,1H), 2.70 – 2.55 (m, 4H), 2.58 – 2.46 (m, 1H), 2.49 – 2.32 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -118.52 (d, *J* = 2.7 Hz), -162.27 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, CD_3CN)** δ 198.36, 153.46 (dd, *J* = 245.1, 6.4 Hz), 138.25, 135.64 (dd, *J* = 28.5, 2.8

Hz), 129.47 (d, *J* = 2.4 Hz), 126.14 (dd, *J* = 7.2, 4.4 Hz), 122.23 (dd, *J* = 26.8, 14.5 Hz), 89.34 (dd, *J* = 206.6, 15.9 Hz), 28.03 (d, *J* = 21.0 Hz), 27.07, 21.24 (dd, *J* = 8.4, 6.3 Hz). **HRMS** (ESI): *m/z* calculated for $C_{10}H_9F_2NO_2Na^+$ $[M+Na]^+$: 236.0494; found: 236.0503.

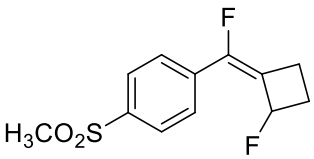
Ethyl(*E*)-4-(fluoro(2-fluorocyclobutylidene)methyl)benzoate (2e)



2e

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a colorless liquid (23.7 mg, 47%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.62 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 5.73 (ddq, *J* = 56.1, 7.1, 3.3 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.10 – 2.94 (m, 1H), 2.72 – 2.57 (m, 1H), 2.60 – 2.47 (m, 1H), 2.51 – 2.34 (m, 1H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -118.36 (d, *J* = 2.7 Hz), -162.25 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 166.21, 153.46 (dd, *J* = 248.2, 7.0 Hz), 134.9 (dd, *J* =28.0, 3.1 Hz), 130.84, 129.83 (d, *J* = 2.3 Hz), 125.21 (dd, *J* = 7.1, 4.7 Hz), 120.24 (dd, *J* = 27.2, 14.7 Hz), 88.53 (dd, *J* = 208.0, 16.1 Hz), 61.28, 27.59 (d, *J* = 21.7 Hz), 21.16(t, *J* =6.8 Hz), 14.45. **HRMS** (ESI): *m/z* calculated for $C_{14}H_{14}F_2O_2Na^+$ $[M+Na]^+$: 275.0854; found: 275.0853.

(*E*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-4-(methylsulfonyl)benzene (2f)

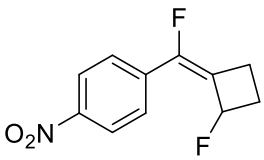


2f

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 4:1) to yield a white solid (30.1 mg, 60%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.52 (PE:EA = 2:1). m.p.: 88-90 °C. **^{1}H NMR (400 MHz, CD_3CN)** δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 5.78 (ddq, *J* = 56.21, 7.3, 3.6 Hz, 1H), 3.07 (s, 3H), 3.02 – 2.86 (m, 1H), 2.69 – 2.47 (m, 2H), 2.43 – 2.26 (m, 1H). **^{19}F NMR (376 MHz, CD_3CN, composite pulse decoupling)** δ -121.19 (d, *J* = 2.7 Hz),

-164.47 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, CD_3CN)** δ 152.59 (dd, *J* = 244.9, 6.3 Hz), 141.96, 136.39 (dd, *J* = 28.9, 2.8 Hz), 128.53 (d, *J* = 2.3 Hz), 126.73 (dd, *J* = 7.2, 4.5 Hz), 123.33 (dd, *J* = 26.5, 14.2 Hz), 89.04 (dd, *J* = 207.2, 15.5 Hz), 44.36, 27.93 (d, *J* = 20.9 Hz), 21.08 (dd, *J* = 8.7, 6.3 Hz). **HRMS** (ESI): *m/z* calculated for $C_{12}H_{12}F_2O_2S\ Na^+$ $[M+Na]^+$: 281.0418; found: 281.0416.

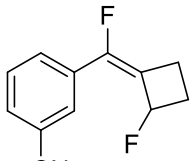
(*E*)-1-(fluoro(2-fluorocyclobutylidene) methyl)-4-nitrobenzene (2g)



2g

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 100:1) to yield a pare yellow solid (34.6 mg, 77%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.60 (PE:EA = 10:1). m.p.: 84-86 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.9 Hz, 2H), 5.85 – 5.63 (ddq, 1H), 3.07 – 2.93 (m, 1H), 2.70 – 2.58 (m, 1H), 2.58 – 2.47 (m, 1H), 2.47 – 2.36 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -118.52 (d, *J* = 2.7 Hz), -162.44 (d, *J* = 2.6 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 152.06 (dd, *J* = 247.7, 6.3 Hz), 147.78, 136.76 (dd, *J* = 28.7, 2.7 Hz), 126.06 (dd, *J* = 7.3, 5.0 Hz), 123.91 (d, *J* = 2.3 Hz), 122.69 (dd, *J* = 26.6, 14.4 Hz), 87.97 (dd, *J* = 209.6, 15.4 Hz), 27.47 (d, *J* = 21.3 Hz), 20.97 (dd, *J* = 8.3, 6.1 Hz). **HRMS** (EI): *m/z* calculated for $C_{11}H_9F_2NO_2^+$ $[M]^+$: 225.0601; found: 225.0595.

(*E*)-3-(fluoro(2-fluorocyclobutylidene)methyl)benzonitrile (2h)

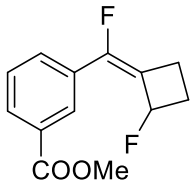


2h

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a colourless liquid (25.0 mg, 61%, *E/Z* = 88:12). The data of major *E*-isomer was shown as below: R_f = 0.62 (PE:EA = 10:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.84 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 10.4 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), δ 5.80 (ddq, *J* = 55.7, 7.2, 3.7 Hz, 1H), 3.03 – 2.94 (m, 1H), 2.67 – 2.55 (m, 1H), 2.58 – 2.48 (m, 1H), 2.51 – 2.35 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -119.09 (d, *J*

= 2.8 Hz), -162.14 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 151.91 (dd, *J* = 247.7, 6.5 Hz), 132.40, 132.14 (d, *J* = 2.9 Hz), 129.54 (d, *J* = 2.4 Hz), 129.48 (dd, *J* = 7.1, 5.2 Hz), 128.82 (dd, *J* = 7.4, 4.7 Hz), 120.49 (dd, *J* = 26.6, 14.7 Hz), 118.49, 113.09 (d, *J* = 2.4 Hz), 88.02 (dd, *J* = 209.0, 15.6 Hz), 27.55 (d, *J* = 21.4 Hz), 20.81 (dd, *J* = 8.2, 5.9 Hz). **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_2N^+$ $[M]^+$: 205.0703; found: 205.0698.

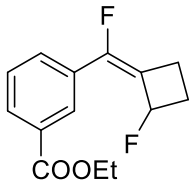
Methyl (*E*)-3-(fluoro(2-fluorocyclobutylidene)methyl)benzoate (2i)



2i

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a white solid (28.1 mg, 59%, *E/Z* = 89:11). The data of major *E*-isomer was shown as below: R_f = 0.62 (PE:EA = 10:1). m.p.: 84-86 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.24 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 5.66 (ddq, *J* = 56.3, 7.2, 3.5 Hz, 1H), 3.93 (s, 3H), 3.06 – 2.92 (m, 1H), 2.71 – 2.56 (m, 1H), 2.56 – 2.45 (m, 1H), 2.45 – 2.35 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -118.08 (d, *J* = 2.7), -162.25 (d, *J* = 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 166.70, 153.30 (dd, *J* = 248.4, 6.8), 131.35 (dd, *J* = 28.8, 3.0), 130.69 (d, *J* = 2.3), 130.16, 129.71 (dd, *J* = 7.0, 4.8), 128.77 (d, *J* = 2.3), 126.43 (dd, *J* = 7.3, 4.5), 118.81 (dd, *J* = 26.8, 15.0), 88.50 (dd, *J* = 207.8, 16.1), 52.41, 27.62 (d, *J* = 21.8), 20.98 (dd, *J* = 7.7, 5.9). **HRMS** (ESI): *m/z* calculated for $C_{13}H_{12}F_2O_2Na^+$ $[M+Na]^+$: 261.0698; found: 261.0691.

Ethyl (*E*)-3-(fluoro(2-fluorocyclobutylidene)methyl)benzoate (2j)

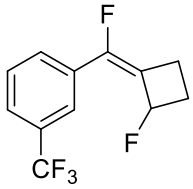


2j

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a colourless liquid (19.6 mg, 39%, *E/Z* = 90:10). The data of major *E*-isomer was shown as below: R_f = 0.60 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 8.25 (s, 1H), 8.02 (d, *J* = 7.8, 1H), 7.74 (d, *J* = 7.9, 1H), 7.46 (t, *J* = 7.8, 1H), 5.71 (ddq, *J* = 57.3, 7.1, 3.5, 1H),

4.38 (q, *J* = 7.1, 2H), 3.04 – 2.91 (m, 1H), 2.62 (dddd, *J* = 15.5, 10.9, 5.7, 3.2, 1H), 2.55 – 2.45 (m, 1H), 2.45 – 2.32 (m, 1H), 1.39 (t, *J* = 7.2, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -118.37 (d, *J* = 2.7), -162.26 (d, *J* = 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 166.19, 153.39 (dd, *J* = 248.0, 6.8), 131.29 (dd, *J* = 28.8, 3.0), 131.03 (d, *J* = 1.8), 130.12, 129.58 (dd, *J* = 7.0, 4.8), 128.71 (d, *J* = 2.3), 126.43 (dd, *J* = 7.3, 4.1), 118.74 (dd, *J* = 27.2, 15.0), 88.52 (dd, *J* = 207.8, 16.1), 61.31, 27.62 (d, *J* = 21.8), 20.99 (dd, *J* = 7.7, 5.9), 14.39. **HRMS** (ESI): *m/z* calculated for $C_{14}H_{14}F_2O_2Na^+$ $[M+Na]^+$: 275.0854; found: 275.0858.

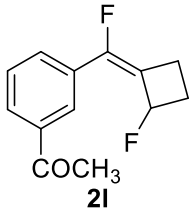
(*E*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-3-(trifluoromethyl)benzene (2k)



2k

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE) to yield a colourless liquid (21.8 mg, 44%, *E/Z* = 83:17). The data of major *E*-isomer was shown as below: R_f = 0.65 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.83 (s, 1H), 7.76 (d, *J* = 7.9, 1H), 7.60 (d, *J* = 7.9, 1H), 7.52 (t, *J* = 7.8, 1H), 5.71 (ddq, *J* = 55.9, 7.3, 3.5, 1H), 3.07 – 2.92 (m, 1H), 2.68 – 2.57 (m, 1H), 2.57 – 2.48 (m, 1H), 2.47 – 2.37 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -62.96, -118.51 (d, *J* = 2.7), -162.18 (d, *J* = 3.4). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 152.88 (dd, *J* = 248.0, 6.8), 131.80 (dd, *J* = 29.1, 3.2), 131.23 (dd, *J* = 32.7, 2.3), 129.18 (d, *J* = 2.3), 128.65 (t, *J* = 5.9), 125.78 (q, *J* = 3.9), δ = 124.01 (q, *J* = 272.4), 122.19 (dp, *J* = 8.2, 4.1), 119.60 (dd, *J* = 27.0, 14.8), 88.35 (dd, *J* = 208.4, 15.9), 27.61 (d, *J* = 21.8), 20.94 (dd, *J* = 7.7, 5.9). **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_5^+$ $[M]^+$: 248.0624; found: 248.0619.

(*E*)-1-(3-(fluoro(2-fluorocyclobutylidene)methyl)phenyl)ethan-1-one (2l)

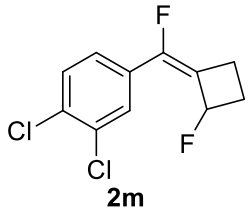


2l

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 50:1) to yield a yellow liquid (27.5 mg, 62%, *E/Z* = 91:9). The data of major *E*-isomer was shown as below: R_f = 0.38 (PE:EA = 10:1). **^{1}H NMR**

(400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 5.72 (ddq, *J* = 56.48, 7.4, 3.6 Hz, 1H), 3.07 – 2.92 (m, 1H), 2.69 – 2.57 (m, 4H), 2.57 – 2.48 (m, 1H), 2.48 – 2.36 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -117.87 (d, *J* = 3.0 Hz), -161.71 (d, *J* = 3.1 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.80, 153.44 (dd, *J* = 248.4, 6.8 Hz), 137.46 (d, *J* = 1.9 Hz), 131.49 (dd, *J* = 28.8, 3.0 Hz), 129.76 (dd, *J* = 6.7, 4.6 Hz), 129.04 (d, *J* = 2.2 Hz), 128.73, 125.52 (dd, *J* = 7.1, 4.7 Hz), 118.92 (dd, *J* = 27.1, 14.9 Hz), 88.58 (dd, *J* = 207.7, 16.1 Hz), 27.63 (d, *J* = 21.5 Hz), 26.78, 20.96 (dd, *J* = 7.8, 6.0 Hz). **HRMS** (ESI): *m/z* calculated for $C_{13}H_{12}F_2ONa^+$ $[M+Na]^+$: 245.0748; found: 245.0746.

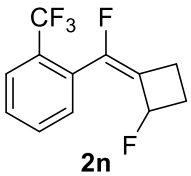
(*E*)-1,2-dichloro-4-(fluoro(2-fluorocyclobutylidene)methyl)benzene (2m)



2m

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE) to yield a colourless liquid (26.3 mg, 53%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.65 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.65 (d, *J* = 2.6, 1H), 7.45 (d, *J* = 8.4, 1H), 7.40 (dd, *J* = 8.6, 2.1, 1H), 5.67 (ddq, *J* = 55.8, 7.2, 3.6, 1H), 3.03 – 2.91 (m, 1H), 2.67 – 2.55 (m, 1H), 2.55 – 2.44 (m, 1H), 2.44 – 2.35 (m, 1H). **^{19}F NMR (470 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -118.27(d, *J* = 2.7), -161.99 (d, *J* = 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 152.14 (dd, *J* = 247.7, 6.6), 133.20 (dd, *J* = 32.5, 2.0), 130.99 (d, *J* = 2.7), 130.76 (d, *J* = 3.2), 130.67 (d, *J* = 2.3), 127.14 (dd, *J* = 7.5, 4.8), 124.69 (dd, *J* = 7.3, 5.0), 119.62 (dd, *J* = 26.8, 15.0), 88.23 (dd, *J* = 208.4, 15.9), 27.54 (d, *J* = 21.8), 20.92 (dd, *J* = 8.2, 5.9). **HRMS** (EI): *m/z* calculated for $C_{11}H_8Cl_2F_2^+$ $[M]^+$: 247.9971; found: 247.9967.

(*E*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-2-(trifluoromethyl)benzene (2n)

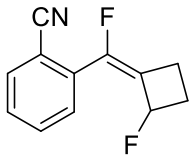


2n

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE) to yield a colourless liquid (19.3 mg, 39%, *E/Z* = 81:19). The data of major

E-isomer was shown as below: R_f = 0.65 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.73 (d, *J* = 7.4, 1H), 7.56 (dd, *J* = 15.5, 6.4, 3H), 5.37 (ddq, *J* = 57.3, 7.0, 4.0, 1H), 3.02 – 2.90 (m, 1H), 2.66 – 2.52 (m, 1H), 2.53 – 2.38 (m, 1H), 2.42 – 2.24 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -60.68 (d, *J* = 14.9), -99.06 (qd, *J* = 15.0, 3.7), -162.99 (d, *J* = 4.1). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 152.68 (dd, *J* = 256.1, 5.4), 132.19 (t, *J* = 3.6), 131.78, 130.10 (d, *J* = 2.3), 129.03 (q, *J* = 32.0), 129.1 (dt, *J* = 28.4, 2.3), 126.74 (qd, *J* = 5.2, 1.4), 123.72 (q, *J* = 273.6), 120.37 (dd, *J* = 25.0, 15.2), 88.01 (dd, *J* = 208.9, 14.5), 27.75 (d, *J* = 20.9), 20.82 (dd, *J* = 7.7, 4.1). **HRMS** (EI): *m/z* calculated for $C_{12}H_9F_5^+$ $[M]^+$: 248.0624; found: 248.0619.

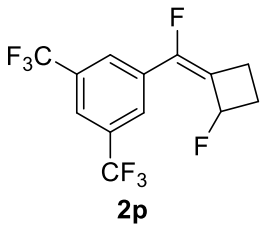
(*E*)-2-(fluoro(2-fluorocyclobutylidene)methyl)benzonitrile (2o)



2o

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 100:1) to yield a colorless liquid (21.7 mg, 53%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.62 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.72 (d, *J* = 7.8, 1H), 7.69 – 7.57 (m, 2H), 7.47 (td, *J* = 7.5, 1.8, 1H), 5.73 (ddq, *J* = 55.8, 7.1, 2.9, 1H), 3.05 – 2.87 (m, 1H), 2.66 – 2.53 (m, 1H), 2.52 – 2.44 (m, 1H), 2.42 – 2.29 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -109.53 (d, *J* = 3.4), -164.62 (d, *J* = 3.4). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 150.18 (dd, *J* = 250.2, 4.5), 134.51 (dd, *J* = 27.8, 1.8), 133.78, 132.52, 129.56, 128.82 (t, *J* = 4.1), 123.06 (dd, *J* = 25.0, 14.5), 117.70, 110.26 (t, *J* = 2.3), 87.37 (dd, *J* = 213.0, 13.6), 27.51 (d, *J* = 19.5), 20.32 (dd, *J* = 9.5, 5.0). **HRMS** (ESI): *m/z* calculated for $C_{12}H_9F_2NNa^+$ $[M+Na]^+$: 228.0595; found: 228.0596.

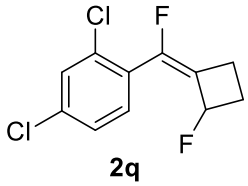
(*E*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-3,5-bis(trifluoromethyl)benzene (2p)



2p

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) and purified using silica gel chromatography (PE) to yield a colorless liquid (38.5 mg, 61%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.64 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 8.01 (s, 2H), 7.85 (s, 1H), 5.75 (ddq, *J* = 56.1, 7.2, 3.7, 1H), 3.07 – 2.95 (m, 1H), 2.68 – 2.58 (m, 1H), 2.58 – 2.50 (m, 1H), 2.50 – 2.38 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -63.14, -119.25 (d, *J* = 2.7), -162.54 (d, *J* = 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 151.27 (dd, *J* = 247.5, 5.9), 133.06 (dd, *J* = 30.0, 3.6), 132.27 (qd, *J* = 33.6, 1.9), 125.40, 123.23 (q, *J* = 272.7), 122.59 (p, *J* = 4.5), 121.95 (dd, *J* = 26.3, 14.5), 87.69 (dd, *J* = 210.7, 15.4), 27.52 (d, *J* = 20.9), 20.63 (dd, *J* = 8.6, 5.9). **HRMS** (EI): *m/z* calculated for $C_{13}H_8F_8^+$ $[M]^+$: 316.0498; found: 316.0492.

(*E*)-2,4-dichloro-1-(fluoro(2-fluorocyclobutylidene)methyl)benzene (2q)

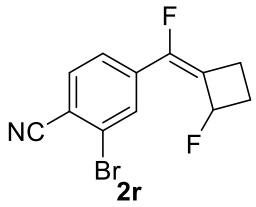


2q

The title compound was prepared following a general procedure B and purified using silica gel chromatography (PE) to yield a colorless liquid (22.8 mg, 46%, *E/Z* = 83:17). The data of major *E*-isomer was shown as below: R_f = 0.64 (PE). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.47 (d, *J* = 2.2, 1H), 7.45 (d, *J* = 8.3, 1H), 7.30 (d, *J* = 8.7, 1H), 5.48 (ddq, *J* = 57.1, 7.2, 4.0, 1H), 3.02 – 2.86 (m, 1H), 2.65 – 2.50 (m, 1H), 2.54 – 2.40 (m, 1H), 2.44 – 2.25 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -105.17 (d, *J* = 3.4), -163.79 (d, *J* = 3.4). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 150.83 (dd, *J* = 253.0, 4.5), 136.29 (d, *J* = 1.8), 133.82 (d, *J* = 2.7), 132.01 (t, *J* = 3.0), 129.96, 128.80 (dd, *J* = 27.2, 2.3), 126.96, 121.50 (dd, *J* = 25.0, 14.5), 87.44 (dd, *J* = 211.6, 14.1), 27.52 (d,

J = 20.4), 20.27 (dd, *J* = 9.1, 4.1). **HRMS** (EI): *m/z* calculated for $C_{11}H_8Cl_2F_2^+$ $[M]^+$: 247.9971; found: 247.9968.

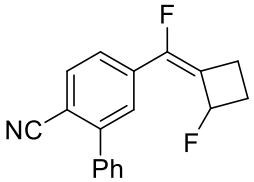
(*E*)-2-bromo-4-(fluoro(2-fluorocyclobutylidene)methyl)benzonitrile (2r)



2r

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 80:1) to yield a white solid (24.9 mg, 44%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.57 (PE:EA = 10:1). m.p.: 101-103 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.86 (s, 1H), 7.66 (d, *J* = 8.2, 1H), 7.60 (d, *J* = 8.3, 1H), 5.71 (ddq, *J* = 55.2, 7.3, 3.8, 1H), 3.09 – 2.92 (m, 1H), 2.61 (ddd, *J* = 15.9, 10.9, 6.4, 1H), 2.57 – 2.50 (m, 1H), 2.50 – 2.38 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -119.47 (d, *J* = 2.7), -162.45 (d, *J* = 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 150.93 (dd, *J* = 248.0, 6.4), 136.29 (dd, *J* = 29.3, 3.0), 134.33 (d, *J* = 2.7), 129.45 (dd, *J* = 7.7, 5.0), 125.66 (d, *J* = 2.3), 124.3 (dd, *J* = 6.1, 1.6), 123.43 (dd, *J* = 26.6, 14.3), 117.03, 115.73 (d, *J* = 1.8), 87.65 (dd, *J* = 210.5, 15.2), 27.45 (d, *J* = 21.3), 20.88 (dd, *J* = 8.6, 5.9). **HRMS** (EI): *m/z* calculated for $C_{12}H_8BrF_2N^+$ $[M]^+$: 282.9808; found: 282.9809.

(*E*)-5-(fluoro(2-fluorocyclobutylidene)methyl)-[1,1'-biphenyl]-2-carbonitrile (2s)

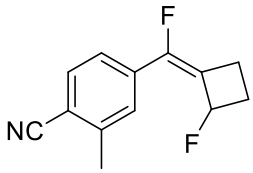


2s

The title compound was prepared following a modified general procedure B (35 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 100:1) to yield a white solid (38.2 mg, 68%, *E/Z* = 84:16). The data of major *E*-isomer was shown as below: R_f = 0.61 (PE:EA = 10:1). m.p.: 97-100 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.78 (d, *J* = 8.2, 1H), 7.72 (d, *J* = 2.0, 1H), 7.63 (dd, *J* = 8.2, 1.8, 1H), 7.58 (dd, *J* = 8.1, 1.5, 2H), 7.53 – 7.45 (m, 3H), 5.74 (ddq, *J* = 55.5, 7.3, 3.7, 1H), 3.07 – 2.92 (m, 1H), 2.63 (dddd, *J* = 16.6, 9.9, 5.1, 2.5, 1H), 2.58 – 2.50 (m, 1H), 2.48 – 2.37 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ = -119.13 (d, *J* = 2.7), -162.37 (d, *J*

= 2.7). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ = 152.24 (dd, *J* = 248.0, 6.4), 145.75 (d, *J* = 2.7), 137.79, 135.05 (dd, *J* = 28.6, 3.2), 134.01 (d, *J* = 3.6), 129.06, 128.93, 128.81, 126.61 (dd, *J* = 7.3, 4.5), 124.16 (dd, *J* = 7.1, 5.6), 122.03 (dd, *J* = 27.2, 14.5), 118.50, 111.33, 87.98 (dd, *J* = 209.8, 15.4), 27.51 (d, *J* = 21.8), 20.91 (dd, *J* = 8.6, 5.9). **HRMS** (ESI): *m/z* calculated for $C_{18}H_{13}F_2NNa^+$ $[M+Na]^+$: 304.0908; found: 304.0912.

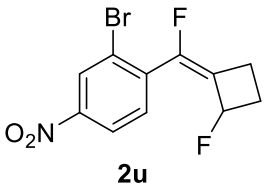
(*E*)-4-(fluoro(2-fluorocyclobutylidene)methyl)-2-methylbenzonitrile (2t)



2t

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 100:1) to yield a colourless liquid (28.9 mg, 66%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.63 (PE:EA = 10:1). **^{1}H NMR (500 MHz, CD$_3$CN)** δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 5.77 (ddq, *J* = 55.6, 8.2, 4.0 Hz, 1H), 2.92 (dddd, *J* = 16.2, 7.9, 5.0, 2.5 Hz, 1H), 2.63 – 2.49 (m, 5H), 2.44 – 2.26 (m, 1H). **^{19}F NMR (470 MHz, CD$_3$CN, composite pulse decoupling)** δ -120.69 (d, *J* = 2.6 Hz), -163.58 (d, *J* = 2.6 Hz). **^{13}C NMR (126 MHz, CD$_3$CN)** δ 152.62 (dd, *J* = 244.8, 6.4 Hz), 143.32 (d, *J* = 2.3 Hz), 135.53 (dd, *J* = 28.6, 2.7 Hz), 133.68 (d, *J* = 2.3 Hz), 127.24 (dd, *J* = 7.3, 4.1 Hz), 123.83 (dd, *J* = 7.3, 4.5 Hz), 123.12 (dd, *J* = 26.6, 14.3 Hz), 118.47, 113.66, 89.00 (dd, *J* = 207.3, 15.7 Hz), 27.91 (d, *J* = 20.9 Hz), 21.09 (dd, *J* = 8.6, 6.4 Hz), 20.65. **HRMS** (EI): *m/z* calculated for $C_{13}H_{11}F_2N^+$ $[M]^+$: 219.0860; found: 219.0854.

(*E*)-2-bromo-1-(fluoro(2-fluorocyclobutylidene)methyl)-4-nitrobenzene (2u)

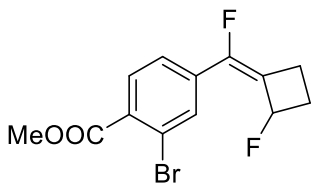


2u

The title compound was prepared following a modified general procedure B (35 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 80:1) to yield a colorless liquid (35.7 mg, 59%, *E/Z* = 83:17). The data of major *E*-isomer was shown as below: R_f = 0.58 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.48 (d, *J* = 2.3 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.65

(d, *J* = 8.6 Hz, 1H), 5.49 (ddq, *J* = 57.3, 7.2, 2.8 Hz, 1H), 3.02 – 2.87 (m, 1H), 2.64 – 2.52 (m, 1H), 2.52 – 2.43 (m, 1H), 2.42 – 2.29 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -106.08 (d, *J* = 3.4 Hz), -163.82 (d, *J* = 3.4 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.50 (dd, *J* = 253.9, 4.5 Hz), 147.48, 137.25 (dd, *J* = 26.3, 2.3 Hz), 131.17 (t, *J* = 3.2 Hz), 127.39, 122.32 (dd, *J* = 23.6, 14.5 Hz), 121.61 (d, *J* = 2.7 Hz), 121.01, 85.94 (dd, *J* = 213.0, 13.6 Hz), 26.53 (d, *J* = 20.0 Hz), 19.16 (dd, *J* = 9.3, 3.9 Hz). **HRMS** (EI): *m/z* calculated for $C_{11}H_8BrF_2NO_2^+$ $[M]^+$: 302.9706; found: 302.9701.

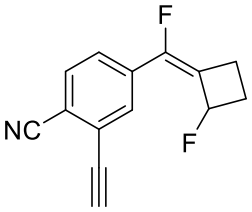
methyl (*E*)-2-bromo-4-(fluoro(2-fluorocyclobutylidene)methyl)benzoate (2v)



2v

The title compound was prepared following a modified general procedure B (35 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 80:1) to yield a white solid (27.9 mg, 60%, *E*/*Z* = 82:18). The data of major *E*-isomer was shown as below: R_f = 0.54 (PE:EA = 10:1). m.p.: 96-99 ºC. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.27 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 5.54 (ddq, *J* = 56.7, 7.2, 4.1 Hz, 1H,), 3.93 (s, 3H), 3.00 – 2.86 (m, 1H), 2.62 – 2.51 (m, 1H), 2.50 – 2.41 (m, 1H), 2.41 – 2.26 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -104.92 (d, *J* = 4.1 Hz), -163.83 (d, *J* = 4.1 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 165.21, 151.90 (dd, *J* = 254.1, 4.8 Hz), 136.29 (dd, *J* = 25.9, 2.3 Hz), 134.30, 132.56 (d, *J* = 1.8 Hz), 131.61 (t, *J* = 3.0 Hz), 128.10, 122.10 (d, *J* = 2.7), 121.83 (dd, *J* = 24.1, 15.0), 87.33 (dd, *J* = 211.6, 14.1 Hz), 52.57, 27.57 (d, *J* = 20.4 Hz), 20.31 (dd, *J* = 8.6, 4.1 Hz). **HRMS** (EI): *m/z* calculated for $C_{13}H_{11}BrF_2O_2^+$ $[M]^+$: 315.9910; found: 315.9901.

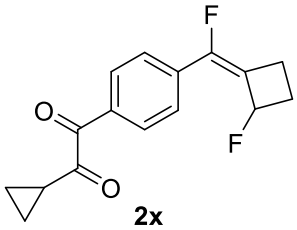
(*E*)-2-ethynyl-4-(fluoro(2-fluorocyclobutylidene)methyl)benzonitrile (2w)



2w

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 80:1) to yield a white solid (32.5 mg, 71%, *E/Z* = 85:15). The data of major *E*-isomer was shown as below: R_f = 0.48 (PE:EA = 10:1). m.p.: 100-103 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ = 7.78 (s, 1H), 7.67 (d, *J* = 8.3, 1H), 7.62 (dd, *J* = 8.4, 2.0, 1H), 5.71 (ddq, *J* = 54.9, 7.2, 3.8, 1H), 3.49 (s, 1H), 2.99 (dddd, *J* = 13.1, 11.0, 5.2, 2.6, 1H), 2.62 (dddd, *J* = 18.8, 10.8, 5.9, 2.4, 1H), 2.56 – 2.47 (m, 1H), 2.47 – 2.38 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -119.57 (d, *J* = 2.7 Hz), -162.43 (d, *J* = 2.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 151.41 (dd, *J* = 248.0, 6.4 Hz), 134.93 (dd, *J* = 29.1, 2.7 Hz), 132.93 (d, *J* = 2.7 Hz), 129.38 (dd, *J* = 7.3, 5.0 Hz), 126.37 (d, *J* = 2.3 Hz), 125.55 (dd, *J* = 7.5, 5.2 Hz), 122.77 (dd, *J* = 26.3, 14.5 Hz), 117.09, 115.67, 87.77 (dd, *J* = 210.0, 15.2 Hz), 84.33, 79.36, 27.46 (d, *J* = 20.9 Hz), 20.89 (dd, *J* = 8.2, 5.9 Hz). **HRMS** (ESI): *m/z* calculated for $C_{14}H_9F_2NNa^+$ $[M+Na]^+$: 252.0595; found: 252.0594.

(*E*)-1-cyclopropyl-2-(4-(fluoro(2-fluorocyclobutylidene)methyl)phenyl)ethane-1, 2-dione (2x)

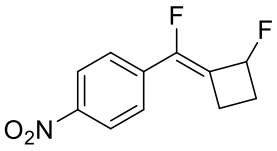


2x

The title compound was prepared following the general procedure B and purified using silica gel chromatography (PE:EA = 30:1) to yield a liquid (33.6 mg, 61%, *E/Z* = 83:17). The data of major *E*-isomer was shown as below: R_f = 0.31 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Acetonitrile-*d*)** δ = 7.98 (d, *J* = 8.4, 2H), 7.70 (d, *J* = 8.5, 2H), 5.83 (ddt, *J* = 54.8, 7.0, 3.6, 1H), 2.94 (dddd, *J* = 18.7, 10.8, 6.3, 3.5, 1H), 2.68 – 2.47 (m, 3H), 2.43 – 2.24 (m, 1H), 1.25 – 1.17 (m, 4H). **^{19}F NMR (376 MHz, Acetonitrile-*d*, composite pulse decoupling)** δ = -121.32 (d, *J* = 2.8), -164.28 (d, *J* = 2.8). **^{13}C NMR (126**

MHz, Chloroform-*d*) δ = 202.21, 191.22, 152.82 (dd, *J* = 248.0, 6.8), 136.15 (dd, *J* = 28.2, 2.7), 132.09, 130.45 (d, *J* = 2.3), 125.38 (dd, *J* = 7.3, 5.0), 121.60 (dd, *J* = 27.2, 14.5), 88.13 (dd, *J* = 208.9, 15.4), 27.40 (d, *J* = 21.3), 21.01 (dd, *J* = 7.9, 6.1), 18.50, 13.41 (d, *J* = 1.5). **HRMS** (EI): *m/z* calculated for $C_{16}H_{14}F_2O_2^+$ $[M]^+$: 276.0962; found: 276.0949.

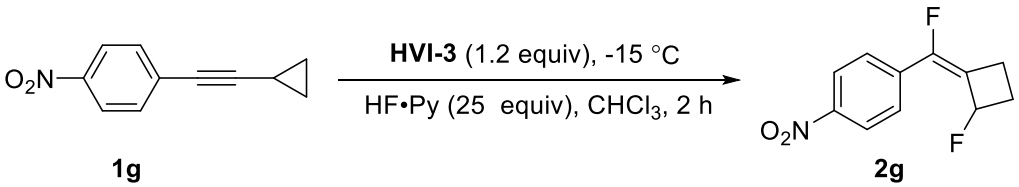
(*Z*)-1-(fluoro(2-fluorocyclobutylidene)methyl)-4-nitrobenzene (Z-2g)



Z-2g

The title compound was prepared following a modified general procedure B (30 equiv Py·9HF was used) and purified using silica gel chromatography (PE:EA = 30:1) to yield a colourless solid (2.4 mg, 12%). R_f = 0.38 (PE:EA = 10:1). The final purification is by recrystallization. m.p.: 123-126 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.26 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 9.0 Hz, 2H), 5.82 (ddq, *J* = 55.7, 7.6, 3.0 Hz, 1H), 3.04 (dddd, *J* = 17.8, 11.6, 5.9, 3.3 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.68 – 2.55 (m, 1H), 2.53 – 2.36 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -119.85 (d, *J* = 6.4 Hz), -166.55 (d, *J* = 6.7 Hz). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 150.33 (dd, *J* = 247.9, 4.6 Hz), 147.66, 137.51 (dd, *J* = 28.6, 2.3 Hz), 125.95 (dd, *J* = 7.0, 1.5 Hz), 123.95 (d, *J* = 2.3 Hz), 122.53 (dd, *J* = 22.4, 13.4 Hz), 87.14 (dd, *J* = 211.6, 8.2 Hz), 28.57 (d, *J* = 20.5 Hz), 22.66 (t, *J* = 8.3 Hz). **HRMS** (EI): *m/z* calculated for $C_{11}H_9F_2NO_2^+$ $[M]^+$: 225.0601; found: 225.0595.

5. Scale-up experiment



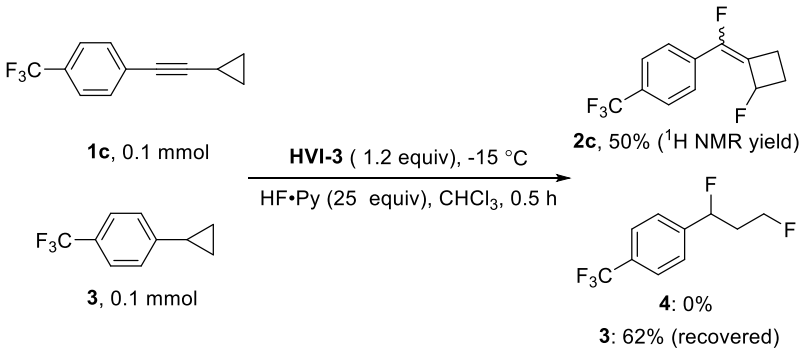
1g **2g**

A 50 ml of polyethylene tube with a stir bar was charged with **HVI-3** (0.99 g, 1.2 equiv, stored in glove box), chloroform (10 ml), and Py•9HF (adamas, 65%

hydrogen fluoride by weight, 1.4 mL, 25 equiv hydrogen fluoride) carefully at room temperature. After stirring for 2 minutes, the reaction mixture was cooled to -15 °C. After stirring for another 5 minutes, the mixture was added alkynylcyclopropanes **1g** (0.37 g, 2 mmol). Then, the mixture was stirred at -15 °C 2 h. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 °C. After stirring for another 5 minutes at room temperature followed by filteration. The filter cake washed with DCM. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography with an eluent (PE:EA = 100:1) to afford product **2g** (0.29 g, 64%, *E:Z*: 83:17) as a pale yellow solid. The *E/Z* ratio was determined by ^{19}F NMR.

6. Mechanistic studies

6.1. Intermolecular competition experiment



A low density polyethylene tube with a stir bar was charged with **HVI-3** (49.4 mg, 1.2 equiv, stored in glove box), chloroform (0.5 mL) and Py•9HF (adamas, 65% hydrogen fluoride by weight, 70 uL, 25 equiv hydrogen fluoride) carefully at room temperature. After stirring for 2 minutes, the reaction mixture was cooled to -15 °C. After stirring for another 5 minutes, the mixture was added alkynylcyclopropanes **1c** (0.1 mmol, 21.0 mg) and cyclopropane **3** (0.1 mmol, 18.6 mg). Then, the mixture was stirred at -15 °C 30 minutes. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 °C. After stirring for another 5 minutes

at room temperature followed by filteration. The filter cake washed with DCM. The filtrate was concentrated under vacuum. The residue was added *p*-iodoanisole (0.05 mmol) as the internal standard. The result of the reaction mixture was determined by ^{1}H and ^{19}F NMR.

Referencing ^{19}F NMR ((no decoupling, 376 MHz, $CDCl_3$) δ -62.68 (s, 3F), -182.56 (ddd, J = 47.3, 30.7, 16.9 Hz, 1F), -222.59 (tdd, J = 46.8, 30.7, 20.9 Hz, 1F)) of 1-(1,3-difluoropropyl)-4-(trifluoromethyl)benzene (**4**).[14] The ^{19}F NMR of the reaction mixture does not show signal of two fluorine atom (δ -182.56, -222.59) (figure 1). And arylcyclopropane was recoveried in 62% yield calculated by ^{1}H NMR. Meanwhile, the target product, alkylidenecyclobutanes, was observed in 50% yield calculated by ^{1}H NMR, and the yield did not decrease compared to reacting alone (figure 2).

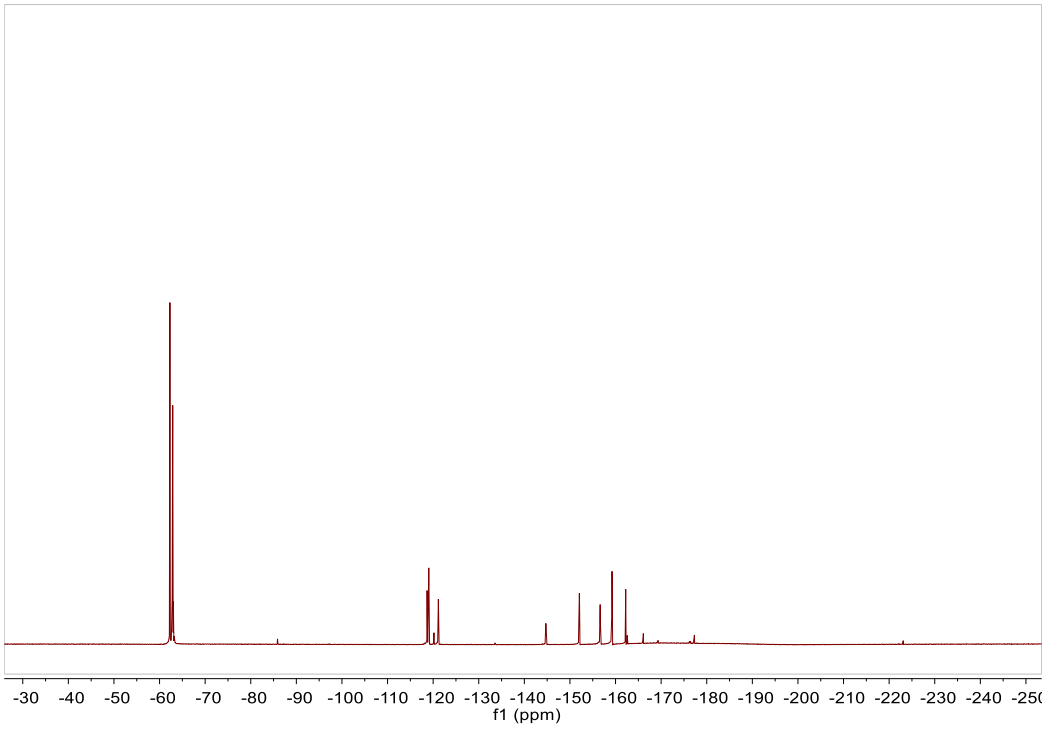


Figure 2. ^{19}F NMR (composite pulse decoupling) of the reaction mixture to intermolecular competition experiment.

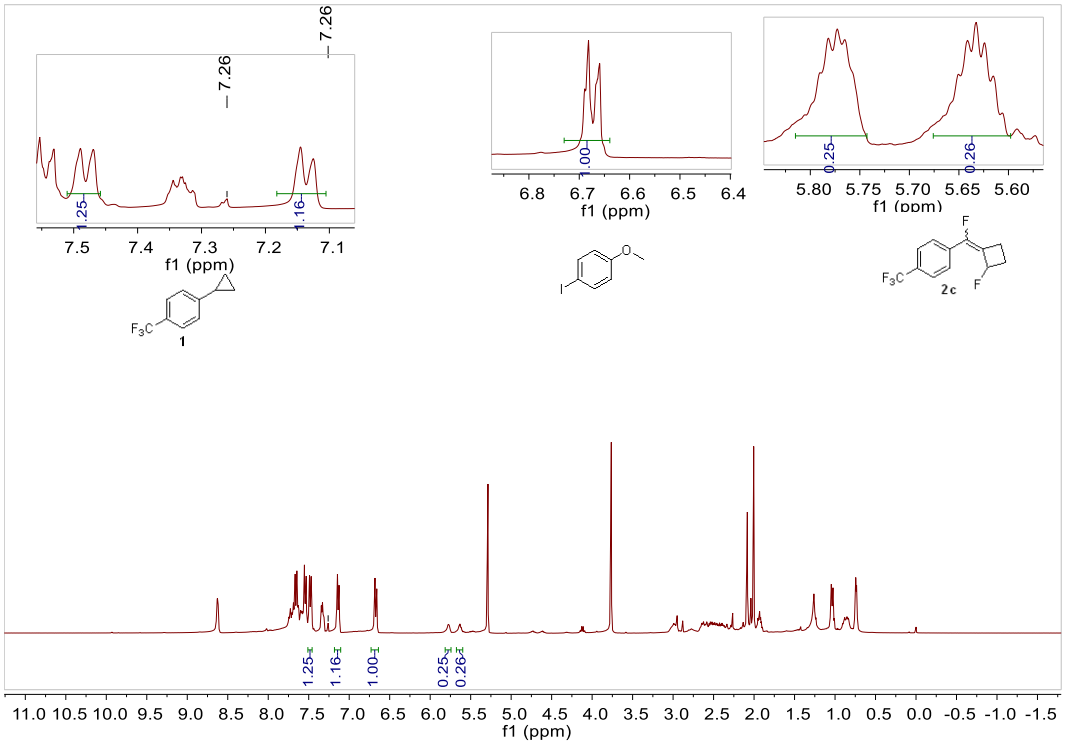
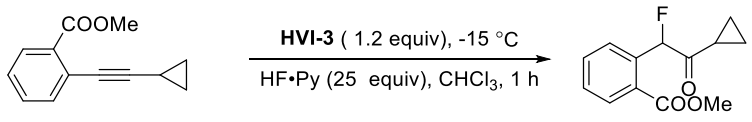


Figure 3. ^{1}H NMR of the reaction mixture to intermolecular competition experiment. (*p*-iodoanisole (0.05 mmol) as the internal standard).

6.2. Direct fluorohydroxylation of compound 1ac by neighbouring group participation

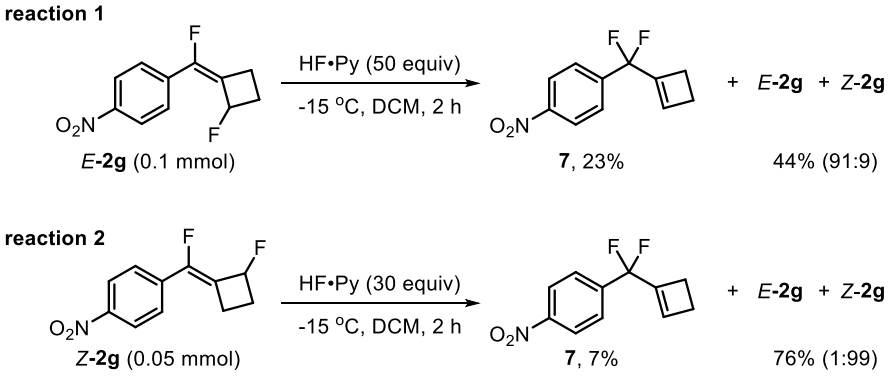


1ac **5**

A low density polyethylene tube with a stir bar was charged with **HVI-3** (49.4 mg, 1.2 equiv, stored in glove box), chloroform (0.50 mL) and Py•9HF (adamas, 65% hydrogen fluoride by weight, 70 uL, 25 equiv hydrogen fluoride) carefully at room temperature. After stirring for 2 minutes, the reaction mixture was cooled to -15 ^{o}C. After stirring for another 5 minutes, the mixture was added alkynylcyclopropanes **1ac** (0.1 mmol, 20.0 mg). Then, the mixture was stirred at -15 ^{o}C 1 h. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 ^{o}C. After stirring for another 5 minutes at room temperature followed by filteration. The filter cake washed with DCM. The filtrate was concentrated under vacuum. The product **5** was obtained in 42% yield (9.9 mg) as a white solid after column

chromatography (PE:EA = 30:1), R_f = 0.37 (PE:EA = 10:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.44 (ddd, *J* = 8.4, 6.0, 2.7 Hz, 1H), 6.92 (d, *J* = 47.7, 1H), 3.90 (s, 3H), δ 2.40 – 2.31 (m, 1H) , 1.13 (dddd, *J* = 9.4, 6.9, 4.6, 2.8 Hz, 1H), 1.07 (dddd, *J* = 9.5, 7.2, 4.7, 2.9 Hz, 1H), 1.00 (tdd, *J* = 8.2, 6.4, 2.7 Hz, 1H), 0.98 – 0.89 (m, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 204.92 (d, *J* = 22.8 Hz), 167.25, 136.11 (d, *J* = 19.5 Hz), 132.66, 130.73, 128.83 (d, *J* = 2.0 Hz), 128.78, 127.33 (d, *J* = 11.0 Hz), 92.42 (d, *J* = 182.1 Hz), 52.36, 17.36, 12.18, 11.96. **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -183.03. **HRMS** (ESI): *m/z* calculated for $C_{13}H_{13}FO_3^+$ $[M]^+$: 236.0849; found: 236.0845.

6.3. Control experiments



A low density polyethylene tube with a stir bar was charged with *E*-**2g** (22.5 mg, 0.1 mmol) in DCM (0.2 ml). The reaction mixture was cooled to -15 °C. After stirring for another 5 minutes, the reaction mixture was added Py•9HF (adamas, 65% hydrogen fluoride by weight, 140 uL, 50 equiv hydrogen fluoride) carefully. The mixture was stirred at -15 °C 2 hours. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 °C. After stirring for another 5 minutes at room temperature followed by filteration. The filter cake washed with DCM. The filtrate was concentrated under vacuum. The substrate *E*-**2g** was recoveried using silica gel chromatography (PE:EA = 100:1) to yield a pare yellow solid (10.1 mg, 44%, *E/Z* = 91:9). The *E/Z* ratio was determined by ^{19}F NMR. The product **7** in

reaction **1** was obtained in 23% yield (5.3 mg) as a white solid after column chromatography (PE:EA = 120:1), R_f = 0.71 (PE:EA = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.29 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 6.05 (td, *J* = 3.3, 1.7, 1H), 2.70 – 2.58 (m, 2H), 2.47 (ddt, *J* = 4.3, 2.1, 1.2 Hz, 2H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 149.0, 142.13 (t, *J* = 33.2 Hz). δ 141.78 (t, *J* = 27.9 Hz), δ 137.07 (t, *J* = 9.2 Hz), δ 126.84 (t, *J* = 5.4 Hz), 123.8,δ 115.44 (t, *J* = 237.4 Hz), δ 28.16 (t, *J* = 2.7 Hz), 27.08 (t, *J* = 2.2 Hz). **^{19}F NMR (376 MHz, Chloroform-*d*, composite pulse decoupling)** δ -97.29. **HRMS** (EI): *m/z* calculated for $C_{11}H_9F_2NO_2^+$ $[M]^+$: 225.0601; found: 225.0596.

A low density polyethylene tube with a stir bar was charged with *Z*-**2g** (11.3 mg, 0.05 mmol) in DCM (0.1 mL). The reaction mixture was cooled to -15 ^{o}C, after stirring for another 5 minutes. The reaction mixture was added Py•9HF (adamas, 65% hydrogen fluoride by weight, 42 uL, 30 equiv hydrogen fluoride) carefully. The mixture was stirred at -15 ^{o}C 2 hours. The reaction mixture was quenched with basic alumina (15 g per 100 mmol Py•9HF) in -15 ^{o}C. After stirring for another 5 minutes at room temperature followed by filteration. The filter cake washed with DCM. The filtrate was concentrated under vacuum. The residue was added *p*-iodoanisole (0.05 mmol) as the internal standard. The yield of product **7** in the reaction **2** was determined by ^{1}H NMR. The substrate *Z*-**2g** was recoveried using silica gel chromatography (PE:EA = 30:1) to yield a colourless solid (8.6 mg, 76%, *E/Z* = 99:1). The *E/Z* ratio was determined by ^{19}F NMR.

7. X-ray data for compound *E*-2a

Single crystals of $C_{13}H_{12}F_2O_2$ were white needle. A suitable crystal was selected and on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

Crystal Data for $C_{13}H_{12}F_2O_2$ (*M* =238.23 g/mol): triclinic, space group P-1 (no. 2), a = 4.0300(3) Å, b = 10.8122(9) Å, c = 12.5820(8) Å, α = 97.471(6)°, β = 91.394(7)°, γ = 94.032(7)°, V = 541.93(7) Å3, Z = 2, T = 99.99(10) K, μ(Cu Kα) = 1.026 mm-1, Dcalc = 1.460 g/cm3, 5032 reflections measured (7.09° ≤ 2Θ ≤ 153.238°), 2080 unique (Rint = 0.0479, Rsigma = 0.0577) which were used in all calculations. The final R1 was 0.0639 (I > 2σ(I)) and wR2 was 0.1936 (all data).

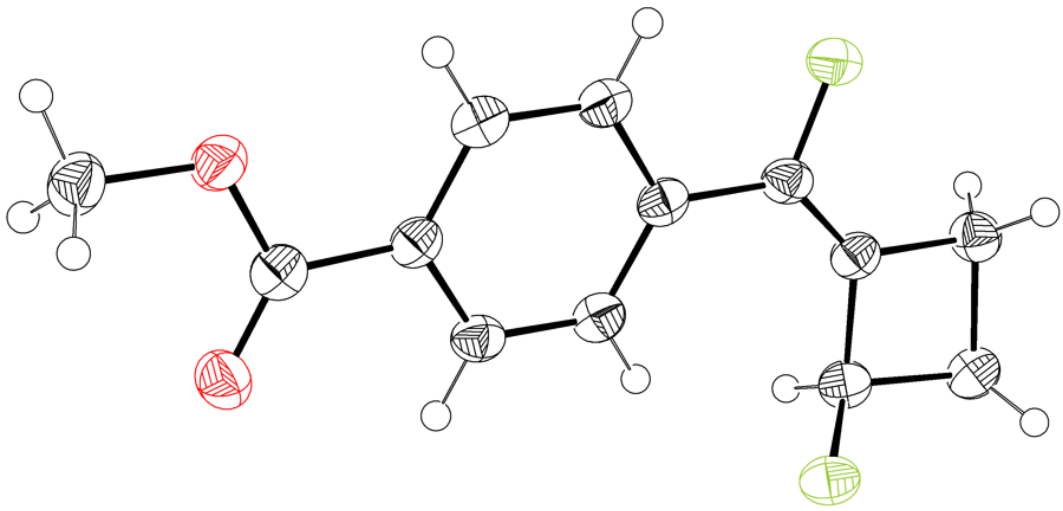


Figure S1. X-Ray Crystallography of *E*-2a.

(ellipsoid contour at 50% probability level**)**

Table 1 Crystal data and structure refinement for *E*-2a

Identification code	***E*-2a**
Empirical formula	$C_{13}H_{12}F_2O_2$
Formula weight	238.23
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	4.0300(3)
b/Å	10.8122(9)
c/Å	12.5820(8)
α/°	97.471(6)
β/°	91.394(7)
γ/°	94.032(7)
Volume/Å^3	541.93(7)
Z	2
ρ_{calc}mg/mm^3	1.460
μ/mm^{-1}	1.026
F(000)	248.0
Crystal size/mm^3	0.25 × 0.25 × 0.05
2Θ range for data collection	7.09 to 153.238°
Index ranges	$-5 \le h \le 2$, $-13 \le k \le 13$, $-15 \le l \le 15$
Reflections collected	5032
Independent reflections	2080[R(int) = 0.0479]
Data/restraints/parameters	2080/0/155
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1817
Final R indexes [all data]	R_1 = 0.0740, wR_2 = 0.1936
Largest diff. peak/hole / e Å^{-3}	0.73/-0.39

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *E*-2a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F8	5906(3)	1715.7(12)	1663.4(11)	34.6(4)
F17	8014(3)	3509.2(13)	5055.5(11)	34.6(4)
O10	1798(4)	7589.2(15)	924.0(14)	33.5(4)
O12	3887(4)	8437.8(15)	2545.3(15)	36.8(4)
C4	4292(5)	6252(2)	1996.0(18)	26.9(5)
C13	8546(5)	2223(2)	3310.8(19)	28.0(5)
C1	6029(5)	3874(2)	2327.3(18)	26.9(5)
C5	6134(5)	6094(2)	2910.4(19)	29.2(5)
C9	3344(5)	7536(2)	1876.3(19)	29.9(5)
C2	4215(5)	4039(2)	1403.7(19)	29.7(5)
C3	3356(5)	5223(2)	1239.9(19)	31.0(5)
C7	6934(5)	2615(2)	2498.0(18)	28.0(5)
C16	10101(5)	2823(2)	4375.5(19)	30.3(5)
C6	7010(5)	4915(2)	3079.8(19)	30.0(5)
C15	10614(5)	1516(2)	4673(2)	32.6(5)
C14	9502(5)	935(2)	3510(2)	32.7(5)
C11	799(6)	8808(2)	756(2)	36.0(6)

Table 3 Anisotropic Displacement Parameters (Å2×103) for *E*-2a. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…]

Atom	U11	U22	U33	U23	U13	U12
F8	42.7(7)	32.5(7)	27.6(8)	-0.4(5)	-0.3(6)	4.0(5)
F17	31.2(7)	42.2(8)	30.2(8)	0.6(6)	5.0(5)	7.8(5)
O10	39.3(8)	34.4(9)	28.3(9)	6.5(6)	0.3(7)	8.1(6)
O12	41.6(9)	30.1(8)	38.5(10)	2.6(7)	-1.9(7)	6.9(6)
C4	23.8(10)	32.2(11)	25.6(12)	5.6(9)	6.4(8)	2.6(7)
C13	26.0(10)	31.9(11)	26.7(12)	3.9(9)	5.4(8)	4.4(7)
C1	22.5(9)	33.5(11)	25.2(11)	4.8(9)	7.2(8)	1.5(7)
C5	28.7(10)	33.1(11)	25.1(12)	1.3(9)	4.3(8)	1.5(8)
C9	23.7(10)	35.1(11)	31.4(12)	5.1(9)	6.0(8)	3.5(8)
C2	30.8(10)	34.0(11)	24.2(11)	4.0(9)	1.7(8)	1.7(8)
C3	29.6(10)	37.2(12)	26.5(12)	4.7(9)	1.0(9)	4.1(8)
C7	26.9(10)	31.4(11)	25.1(12)	0.1(9)	6.4(8)	1.7(7)
C16	26.6(10)	34.8(12)	29.6(12)	2.6(9)	3.6(8)	4.8(8)
C6	29.3(10)	34.5(11)	26.8(12)	5.1(9)	2.0(9)	4.8(8)
C15	28.2(10)	39.4(12)	31.4(13)	7.9(10)	-1.6(9)	5.8(8)
C14	33.2(11)	31.5(11)	33.6(13)	3.0(9)	1.4(9)	6.4(8)
C11	38.6(12)	36.7(12)	35.4(14)	10.2(10)	3.2(10)	9.7(9

Table 4 Bond Lengths for *E*-2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F8	C7	1.370(3)	C13	C16	1.511(3)
F17	C16	1.396(2)	C13	C14	1.520(3)
O10	C9	1.347(3)	C1	C2	1.396(3)
O10	C11	1.445(3)	C1	C7	1.474(3)
O12	C9	1.206(3)	C1	C6	1.401(3)
C4	C5	1.390(3)	C5	C6	1.388(3)
C4	C9	1.491(3)	C2	C3	1.388(3)
C4	C3	1.391(3)	C16	C15	1.534(3)
C13	C7	1.329(3)	C15	C14	1.558(3)

Table 5 Bond Angles for *E*-2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O10	C11	115.29(19)	O12	C9	C4	124.7(2)
C5	C4	C9	117.9(2)	C3	C2	C1	120.3(2)
C5	C4	C3	119.7(2)	C2	C3	C4	120.2(2)
C3	C4	C9	122.4(2)	F8	C7	C1	112.87(19)
C7	C13	C16	135.9(2)	C13	C7	F8	116.07(19)
C7	C13	C14	132.2(2)	C13	C7	C1	131.1(2)
C16	C13	C14	91.94(18)	F17	C16	C13	115.82(17)
C2	C1	C7	120.1(2)	F17	C16	C15	114.04(18)
C2	C1	C6	119.4(2)	C13	C16	C15	89.22(17)
C6	C1	C7	120.6(2)	C5	C6	C1	120.0(2)
C6	C5	C4	120.5(2)	C16	C15	C14	89.65(18)
O10	C9	C4	112.4(2)	C13	C14	C15	88.05(17)
O12	C9	O10	122.9(2)				

Table 6 Torsion Angles for *E*-2a.

A	B	C	D	Angle/°	A	B	C	D
F17	C16	C15	C14	126.10(18)	C7	C13	C14	C15
C4	C5	C6	C1	-0.2(3)	C7	C1	C2	C3
C13	C16	C15	C14	8.01(15)	C7	C1	C6	C5
C1	C2	C3	C4	-0.1(3)	C16	C13	C7	F8
C5	C4	C9	O10	175.12(16)	C16	C13	C7	C1
C5	C4	C9	O12	-4.7(3)	C16	C13	C14	C15
C5	C4	C3	C2	0.9(3)	C16	C15	C14	C13
C9	C4	C5	C6	178.23(17)	C6	C1	C2	C3
C9	C4	C3	C2	-178.03(17)	C6	C1	C7	F8
C2	C1	C7	F8	2.0(3)	C6	C1	C7	C13
C2	C1	C7	C13	-178.0(2)	C14	C13	C7	F8
C2	C1	C6	C5	1.0(3)	C14	C13	C7	C1
C3	C4	C5	C6	-0.8(3)	C14	C13	C16	F17
C3	C4	C9	O10	-5.9(3)	C14	C13	C16	C15
C3	C4	C9	O12	174.31(19)	C11	O10	C9	O12
C7	C13	C16	F17	54.9(3)	C11	O10	C9	C4
C7	C13	C16	C15	171.4(2)				

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *E*-2a.

Atom	*x*	*y*	*z*	U(eq)
H5	6783.32	6783.13	3412.45	35
H2	3578.57	3354.19	896.07	36
H3	2151.27	5327.6	622.32	37
H16	12219.89	3296.4	4289.17	36
H6	8248.32	4816.08	3692.49	36
H15A	9132.21	1266.64	5215.62	39
H15B	12906.79	1393.8	4858.45	39
H14A	11304.45	628.03	3076.66	39
H14B	7634.4	312.44	3472.79	39
H11A	-159.37	8767.72	45.1	54
H11B	2707.54	9400.18	840.01	54
H11C	-816.83	9067.57	1271.34	54

8. X-ray data for compound *Z*-2g

Single crystals of $C_{11}H_9F_2NO_2$ were colourless block. A suitable crystal was selected and on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Crystal Data for $C_{11}H_9F_2NO_2$ (*M* =225.19 g/mol): triclinic, space group P-1 (no. 2), *a* = 6.1659(3) Å, *b* = 7.2541(4) Å, *c* = 10.9186(5) Å, *α* = 78.829(4)°, *β* = 81.971(4)°, *γ* = 82.243(4)°, *V* = 471.48(4) Å^3, *Z* = 2, *T* = 100.01(10) K, μ(Cu Kα) = 1.176 mm^{-1}, *Dcalc* = 1.586 g/cm^3, 4220 reflections measured (8.312° ≤ 2Θ ≤ 150.062°), 1818 unique (R_{int} = 0.0469, R_{sigma} = 0.0453) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1414 (all data).

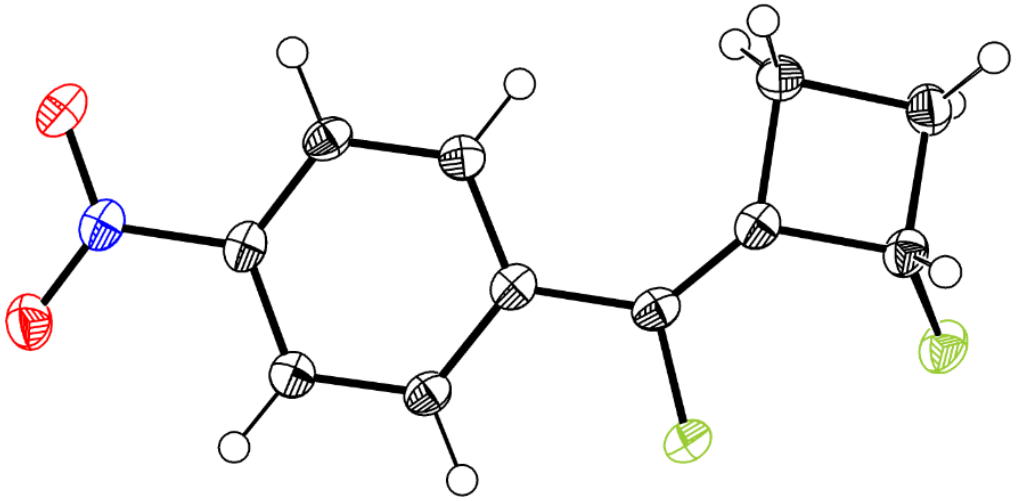


Figure S2. X-Ray Crystallography of *Z*-2g.

(ellipsoid contour at 50% probability level**)**

Table 1' Crystal data and structure refinement for *Z*-2g.

Identification code	*Z*-2g
Empirical formula	$C_{11}H_9F_2NO_2$
Formula weight	225.19
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.1659(3)
b/Å	7.2541(4)
c/Å	10.9186(5)
α/°	78.829(4)
β/°	81.971(4)
γ/°	82.243(4)
Volume/Å^3	471.48(4)
Z	2
ρ_{calc}g/cm^3	1.586
μ/mm^{-1}	1.176
F(000)	232
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.312 to 150.062
Index ranges	$-7 \leq h \leq 7$, $-9 \leq k \leq 8$, $-13 \leq l \leq 13$
Reflections collected	4220
Independent reflections	1818 [R_{int} = 0.0469, R_{sigma} = 0.0453]
Data/restraints/parameters	1818/0/146
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1374
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.1414
Largest diff. peak/hole / e Å^{-3}	0.30/-0.35

Table 2' Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *Z* -2g. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F8	9463.2(13)	6560.4(12)	3984.0(8)	24.6(3)
F16	10036.1(14)	5120.4(12)	1571.0(9)	28.0(3)
O11	-405.2(17)	9189.4(15)	7864.1(11)	28.1(3)
O10	2283.9(18)	8374.6(16)	9017.2(11)	28.4(3)
N9	1518(2)	8569.7(17)	8012.4(13)	22.3(3)
C7	7327(2)	7005(2)	3723.8(15)	20.1(4)
C12	7014(2)	7141.1(19)	2529.4(15)	20.3(4)
C4	2988(2)	8066.7(19)	6920.2(15)	20.4(4)
C1	5798(2)	7301.2(19)	4836.9(14)	19.4(4)
C2	6551(2)	6962.6(19)	6015.3(15)	20.6(4)
C5	2173(2)	8344(2)	5777.0(15)	21.4(4)
C6	3571(2)	7985(2)	4726.0(15)	20.7(4)
C3	5161(2)	7364(2)	7069.4(15)	21.1(4)
C15	8646(2)	6820(2)	1404.2(15)	22.1(4)
C13	5096(2)	7537(2)	1744.2(15)	23.3(4)
C14	6715(3)	6851(2)	650.2(15)	26.6(4

Table 3' Anisotropic Displacement Parameters ($Å^2×10^3$) for *Z*-2g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F8	17.0(5)	29.5(5)	25.7(6)	-5.1(4)	-2.2(4)	2.1(3)
F16	27.2(5)	22.9(5)	30.7(6)	-5.9(4)	1.4(4)	5.3(4)
O11	21.9(6)	25.8(6)	33.6(7)	-5.6(5)	3.0(5)	1.6(4)
O10	32.0(6)	30.7(6)	21.3(7)	-5.0(5)	0.9(5)	-2.6(5)
N9	23.2(6)	16.5(6)	25.1(8)	-2.7(5)	2.3(5)	-2.1(5)
C7	18.1(7)	15.7(7)	25.2(9)	-0.7(6)	-2.4(6)	-1.5(5)
C12	21.2(7)	14.8(7)	23.7(9)	-2.0(6)	-0.4(6)	-1.5(5)
C4	22.7(7)	14.1(7)	23.0(9)	-2.8(6)	2.7(6)	-2.7(5)
C1	20.4(7)	12.7(7)	24.2(9)	-2.0(6)	-1.0(6)	-2.4(5)
C2	19.2(7)	16.6(7)	24.6(8)	-1.7(6)	-2.1(6)	-0.3(5)
C5	18.0(7)	17.6(7)	26.4(9)	-0.4(6)	-1.5(6)	-0.7(5)
C6	22.3(7)	17.1(7)	21.9(8)	-2.0(6)	-3.0(6)	-1.8(5)
C3	23.0(7)	17.8(7)	21.3(8)	-1.1(6)	-2.0(6)	-2.1(5)
C15	23.0(7)	17.9(7)	23.3(8)	-3.9(6)	-0.1(6)	2.0(5)
C13	23.6(7)	22.2(7)	22.6(8)	-2.6(6)	-3.2(6)	0.8(5)
C14	29.0(8)	27.8(8)	21.8(9)	-5.1(6)	-1.2(7)	0.2(6)

Table 4' Bond Lengths for *Z*-2g

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F8	C7	1.3691(16)	C4	C5	1.379(2)
F16	C15	1.4001(17)	C4	C3	1.388(2)
O11	N9	1.2312(16)	C1	C2	1.395(2)
O10	N9	1.2303(18)	C1	C6	1.409(2)
N9	C4	1.468(2)	C2	C3	1.390(2)
C7	C12	1.328(2)	C5	C6	1.381(2)

C7	C1	1.462(2)	C15	C14	1.535(2)
C12	C15	1.509(2)	C13	C14	1.560(2)
C12	C13	1.520(2)			

Table 5' Bond Angles for *Z*-2g

O11	N9	C4	117.99(13)	C2	C1	C7	120.10(13)
O10	N9	O11	123.79(13)	C2	C1	C6	119.37(15)
O10	N9	C4	118.21(12)	C6	C1	C7	120.50(14)
F8	C7	C1	112.46(13)	C3	C2	C1	120.94(13)
C12	C7	F8	115.81(13)	C4	C5	C6	119.44(14)
C12	C7	C1	131.71(13)	C5	C6	C1	119.80(15)
C7	C12	C15	130.05(14)	C4	C3	C2	118.03(15)
C7	C12	C13	138.03(14)	F16	C15	C12	115.06(12)
C15	C12	C13	91.86(12)	F16	C15	C14	115.61(13)
C5	C4	N9	118.82(13)	C12	C15	C14	89.23(11)
C5	C4	C3	122.35(15)	C12	C13	C14	87.90(11)
C3	C4	N9	118.82(14)	C15	C14	C13	89.39(12)

Table 6' Torsion Angles for *Z*-2g

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F8	C7	C12	C15	2.2(2)	C12	C7	C1	C2	176.59(14)
F8	C7	C12	C13	178.53(15)	C12	C7	C1	C6	-5.4(2)
F8	C7	C1	C2	-5.49(18)	C12	C15	C14	C13	9.51(11)
F8	C7	C1	C6	172.54(11)	C12	C13	C14	C15	-9.45(11)
F16	C15	C14	C13	127.12(12)	C4	C5	C6	C1	1.4(2)
O11	N9	C4	C5	1.3(2)	C1	C7	C12	C15	-179.95(13)
O11	N9	C4	C3	-179.93(11)	C1	C7	C12	C13	-3.6(3)
O10	N9	C4	C5	-177.63(12)	C1	C2	C3	C4	1.6(2)
O10	N9	C4	C3	1.12(19)	C2	C1	C6	C5	1.2(2)
N9	C4	C5	C6	176.12(12)	C5	C4	C3	C2	1.1(2)
N9	C4	C3	C2	-177.61(12)	C6	C1	C2	C3	-2.7(2)
C7	C12	C15	F16	49.7(2)	C3	C4	C5	C6	-2.6(2)
C7	C12	C15	C14	167.79(16)	C15	C12	C13	C14	9.61(11)
C7	C12	C13	C14	-167.59(18)	C13	C12	C15	F16	-127.87(13)
C7	C1	C2	C3	175.35(12)	C13	C12	C15	C14	-9.77(11)
C7	C1	C6	C5	-176.85(13)					

Table 7' Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for *Z*-2g

Atom	***x***	***y***	***z***	**U(eq)**
H2	8035.3	6450	6098.6	25
H5	661.73	8779	5713	26
H6	3033.1	8198	3930.7	25
H3	5682.6	7163	7868.5	25
H15	9495	7930	1074.9	26
H13A	4510.6	8889	1560.8	28
H13B	3895.8	6730	2071.1	28
H14A	6488.6	5589	503.89	32
H14B	6766.3	7781	-144.2	32

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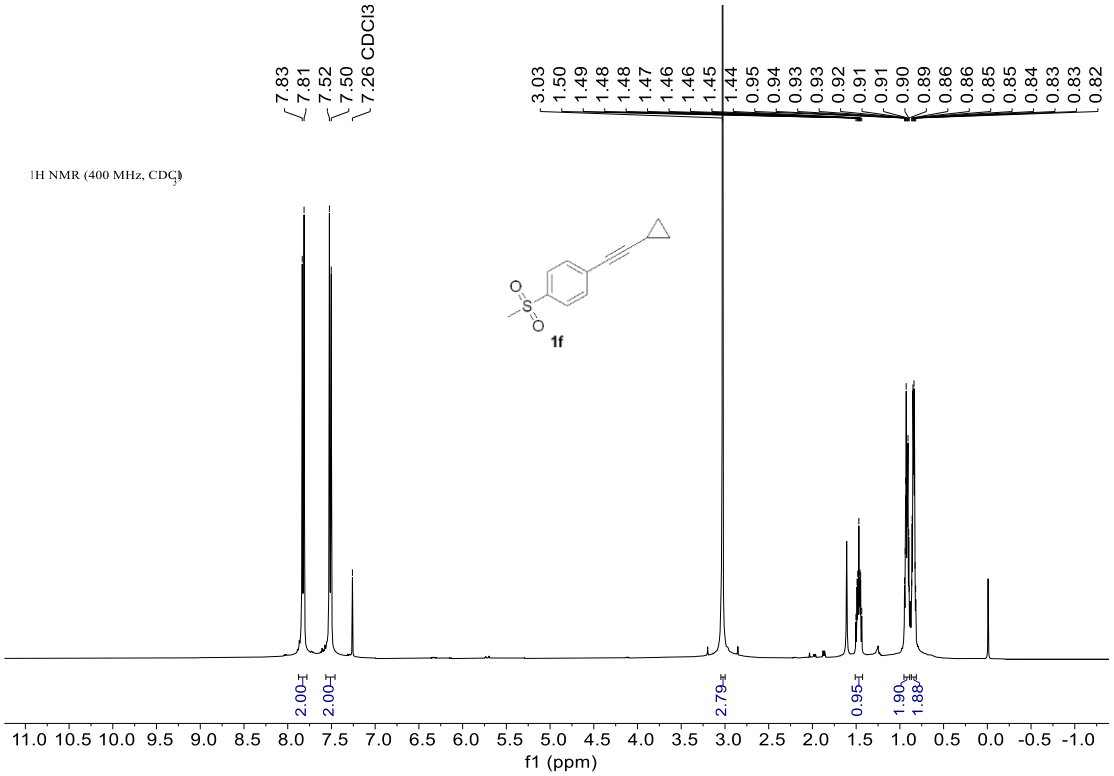
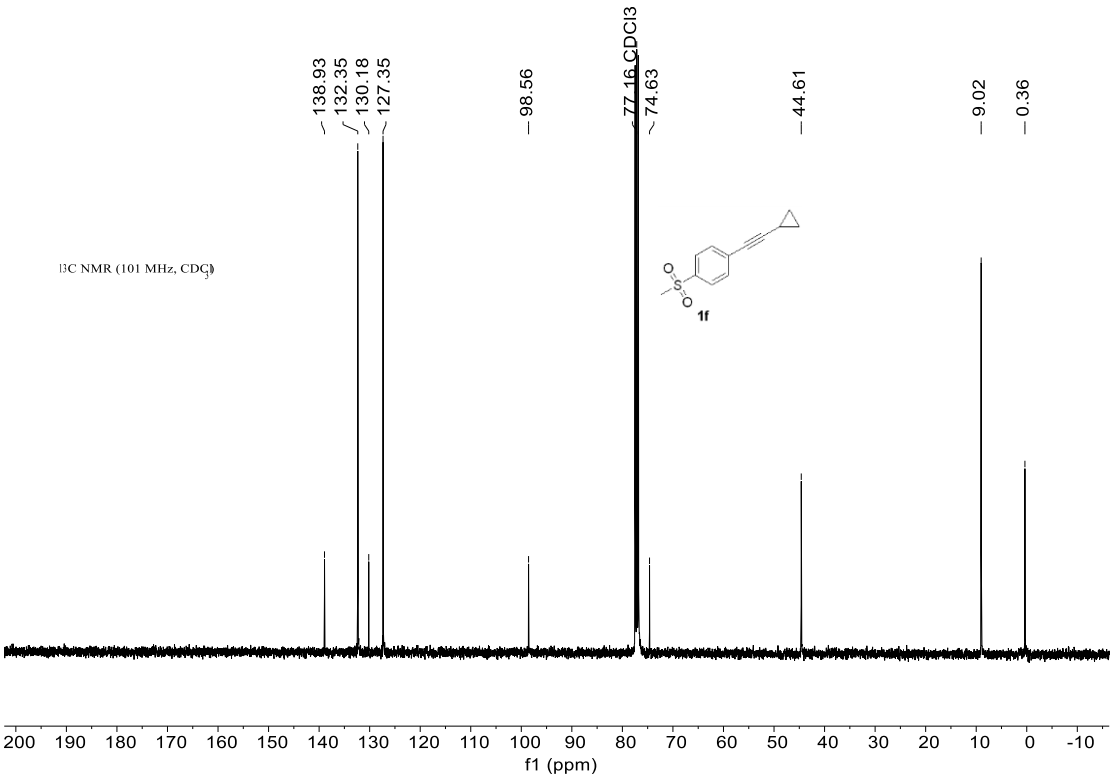
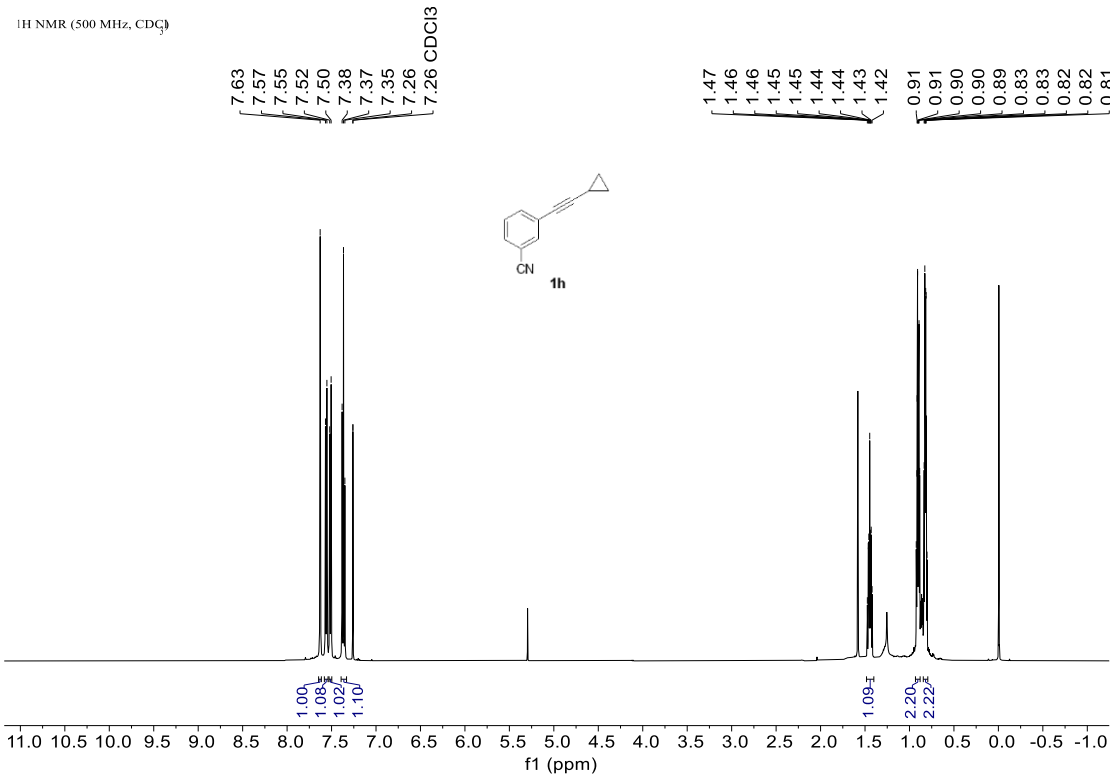
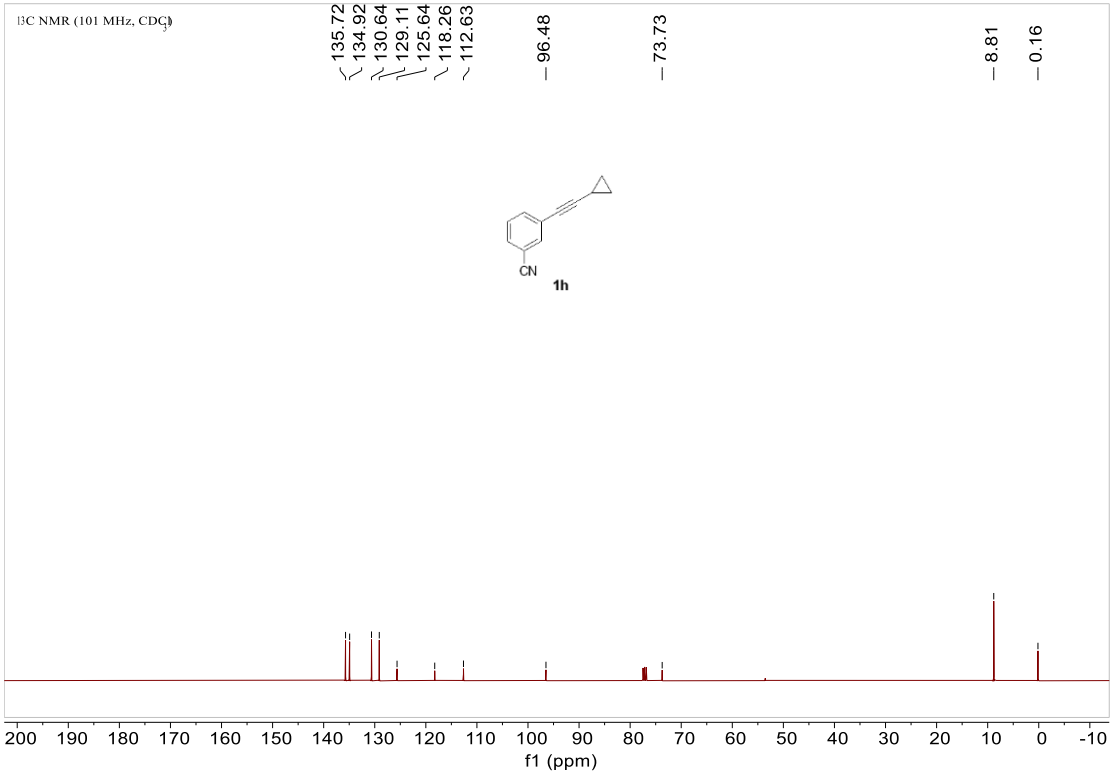
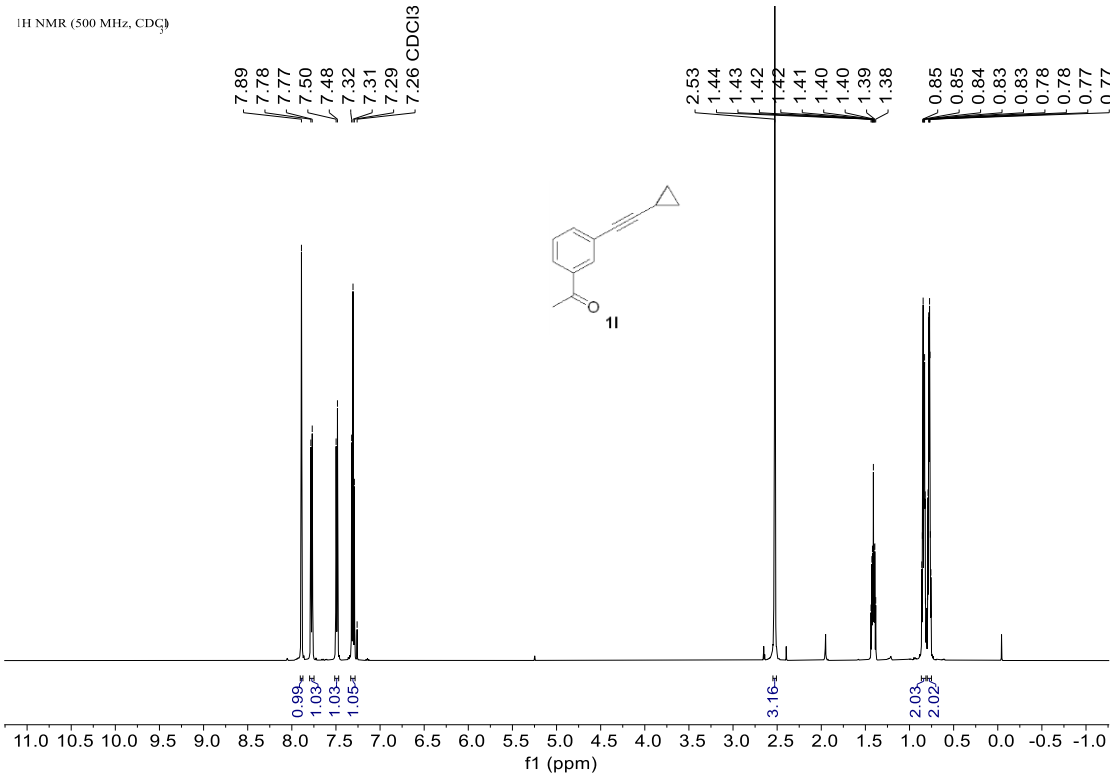
10. NMR spectrum

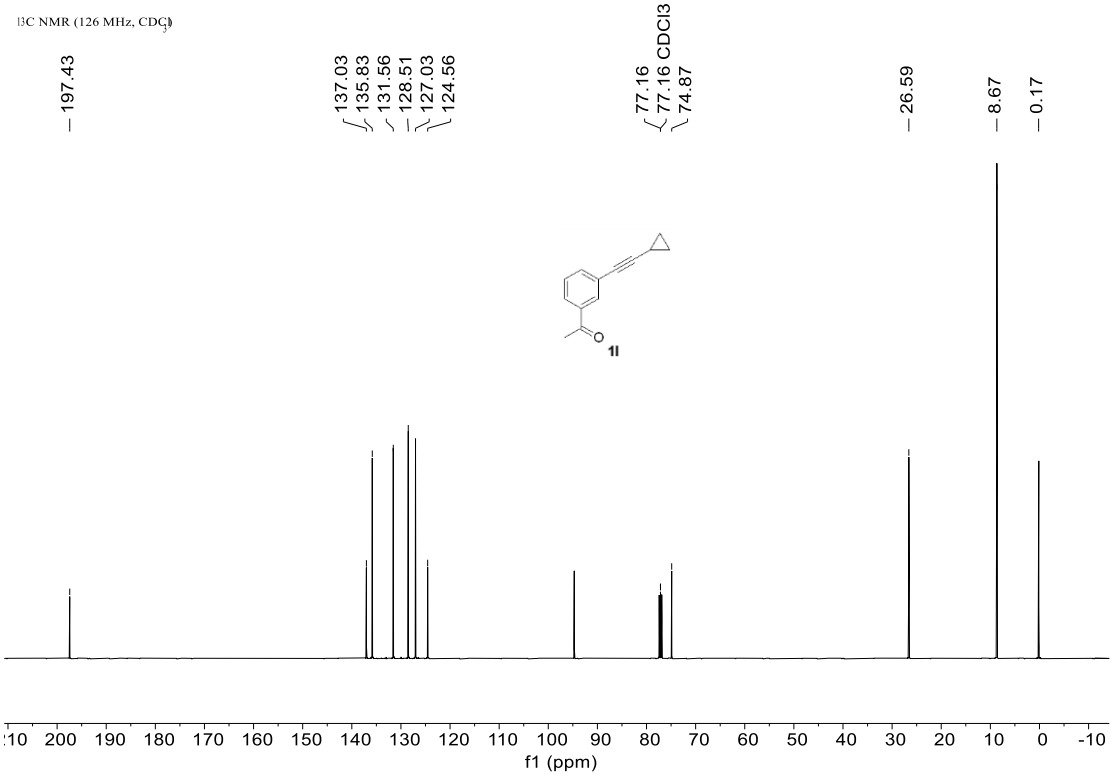


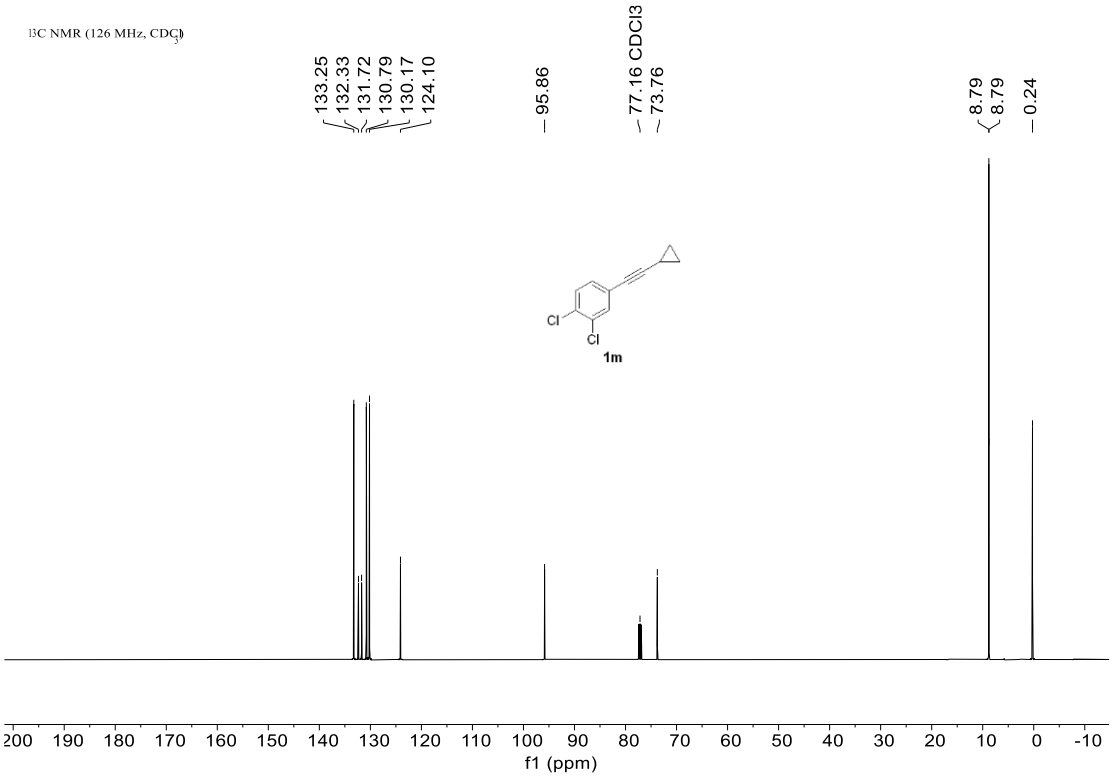


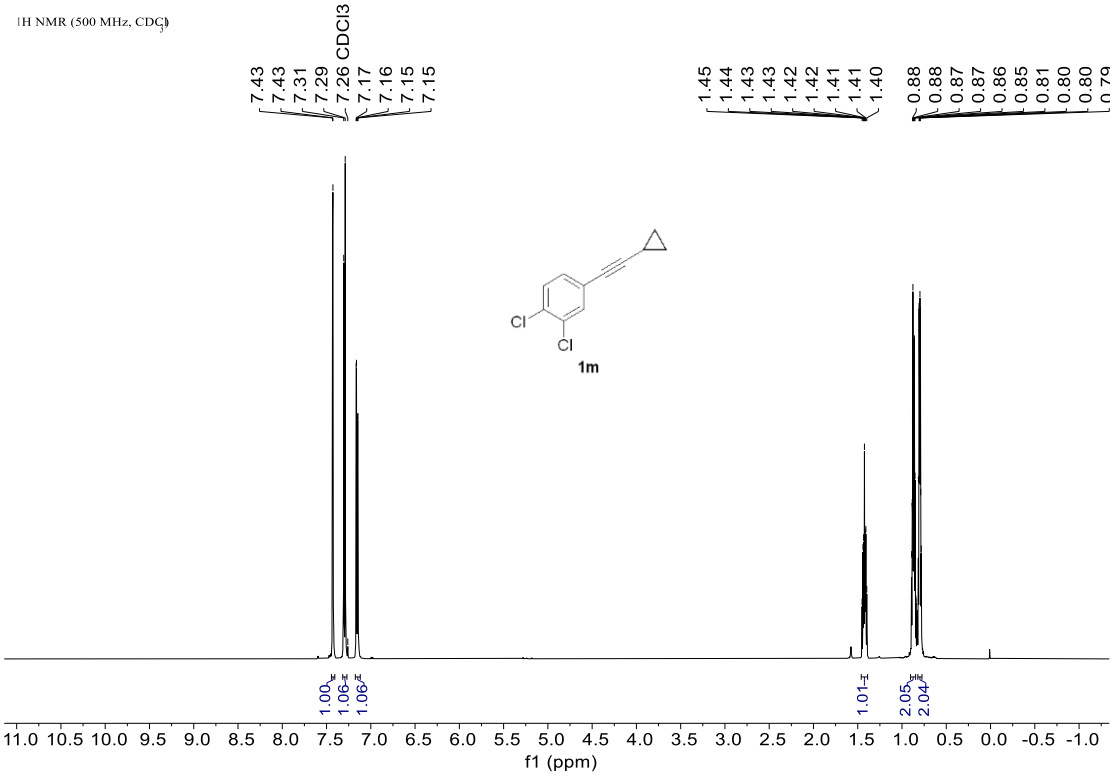

1H NMR (500 MHz, CDCl3)
7.63
7.57
7.55
7.52
7.50
7.38
7.37
7.35
7.26
7.26 CDCl3
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.42
0.91
0.91
0.90
0.90
0.89
0.83
0.83
0.82
0.82
CN
1h
1.00
1.08
1.02
1.10
1.09
2.20
2.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

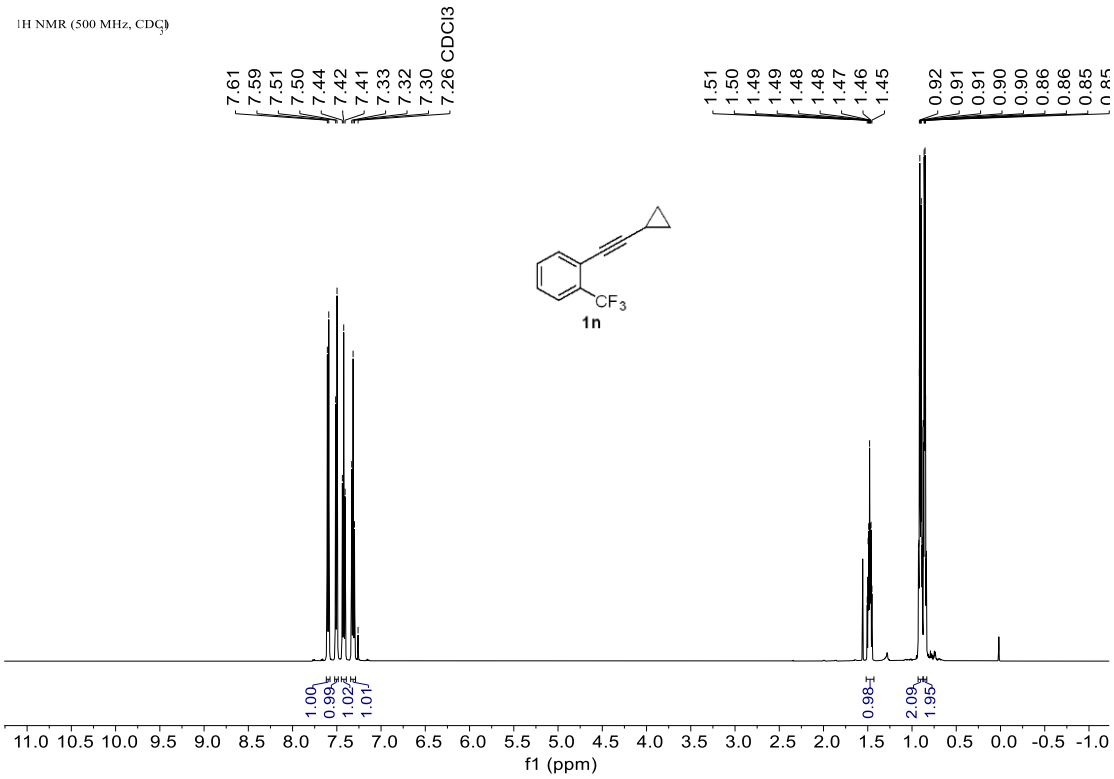

13C NMR (101 MHz, CDCl3)
135.72
134.92
130.64
129.11
125.64
118.26
112.63
96.48
73.73
8.81
0.16
CN
1h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

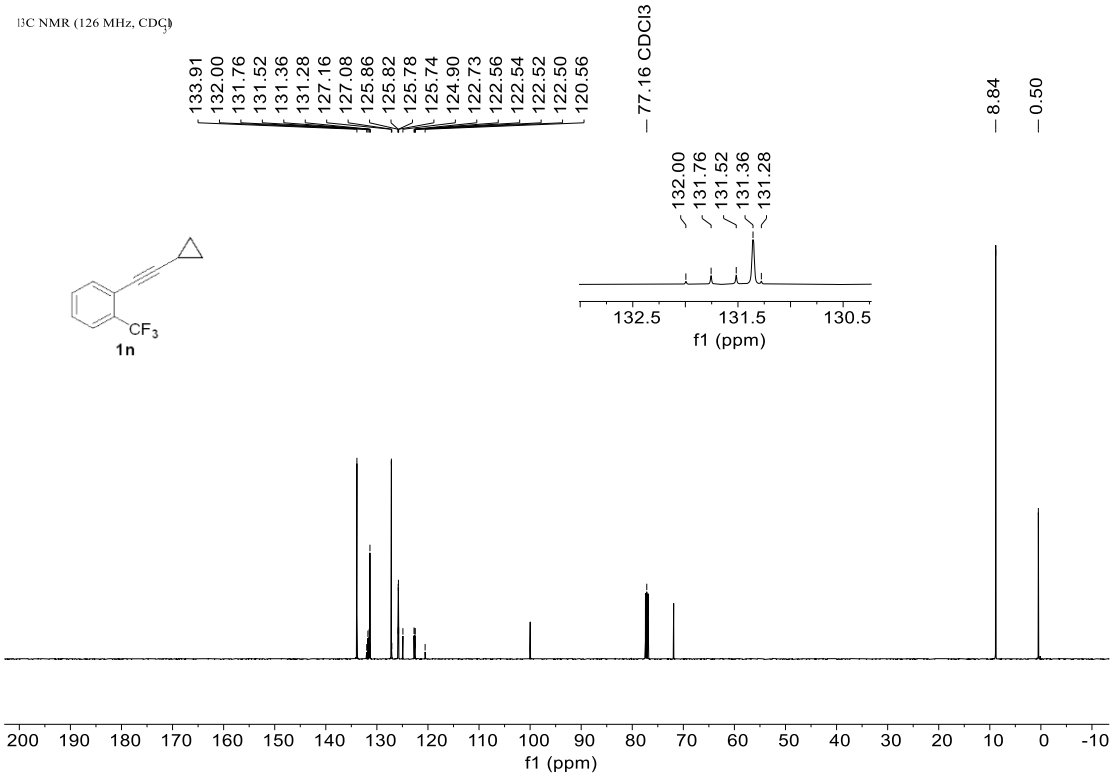

1H NMR (500 MHz, CDCl3)
7.89
7.78
7.77
7.50
7.48
7.32
7.31
7.29
7.26 CDCl3
2.53
1.44
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.38
0.85
0.85
0.84
0.83
0.83
0.78
0.78
0.77
0.77
1l
0.99
1.03
1.03
1.05
3.16
2.03
2.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


13C NMR (126 MHz, CDCl3)
197.43
137.03
135.83
131.56
128.51
127.03
124.56
77.16
77.16 CDCl3
74.87
26.59
8.67
0.17
1l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

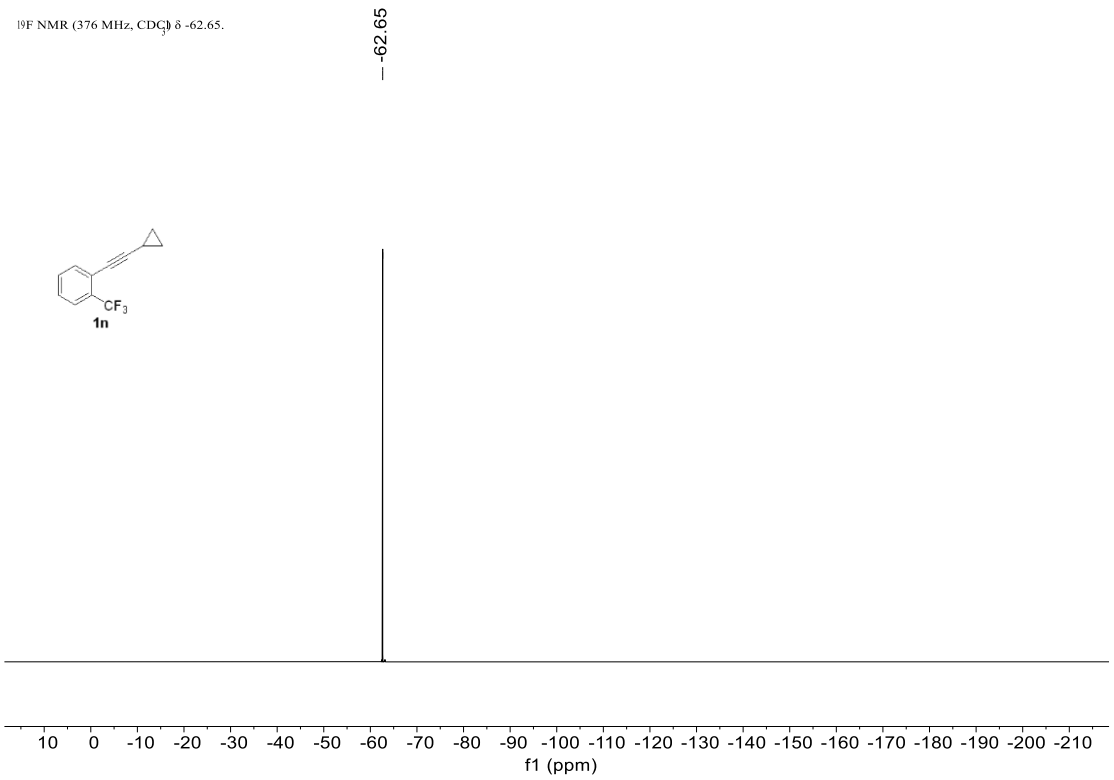

13C NMR (126 MHz, CDCl3)
133.25
132.33
131.72
130.79
130.17
124.10
95.86
77.16 CDCl3
73.76
8.79
8.79
0.24
Cl
Cl
1m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

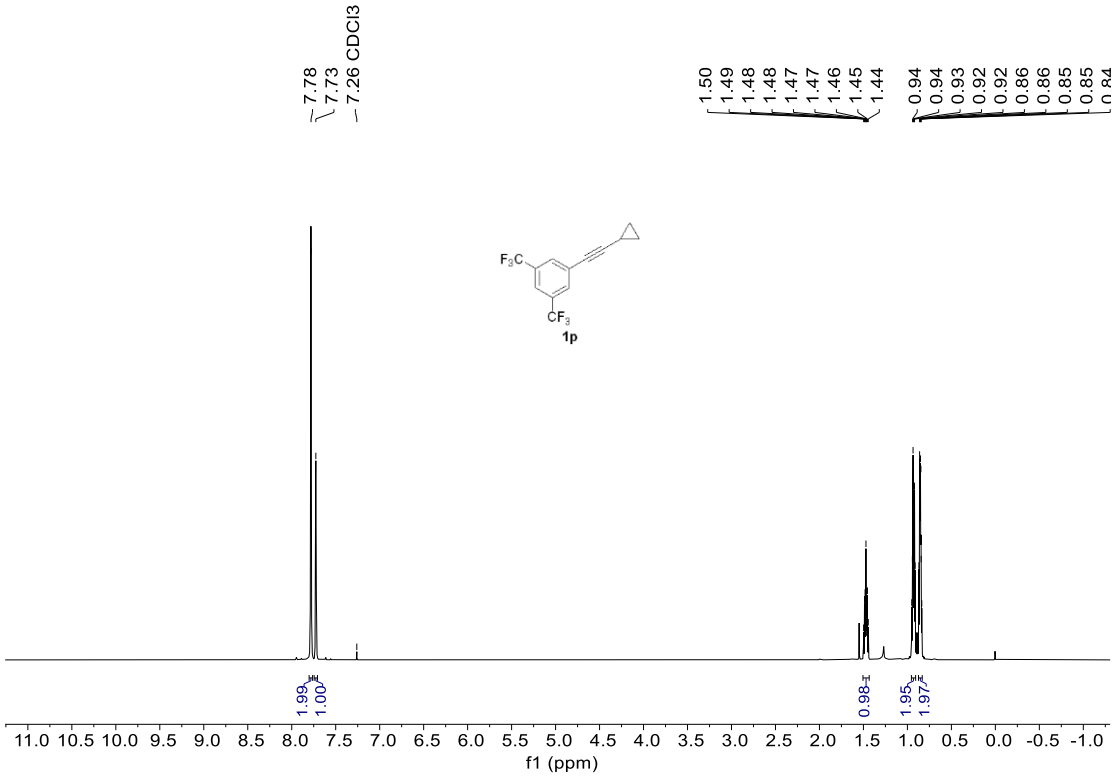

1H NMR (500 MHz, CDCl3)
7.43
7.43
7.31
7.29
7.26 CDCl3
7.17
7.16
7.15
7.15
1.45
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.40
0.88
0.88
0.87
0.87
0.86
0.85
0.81
0.80
0.80
Cl
Cl
1m
1.00
1.06
1.06
1.01
2.05
2.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

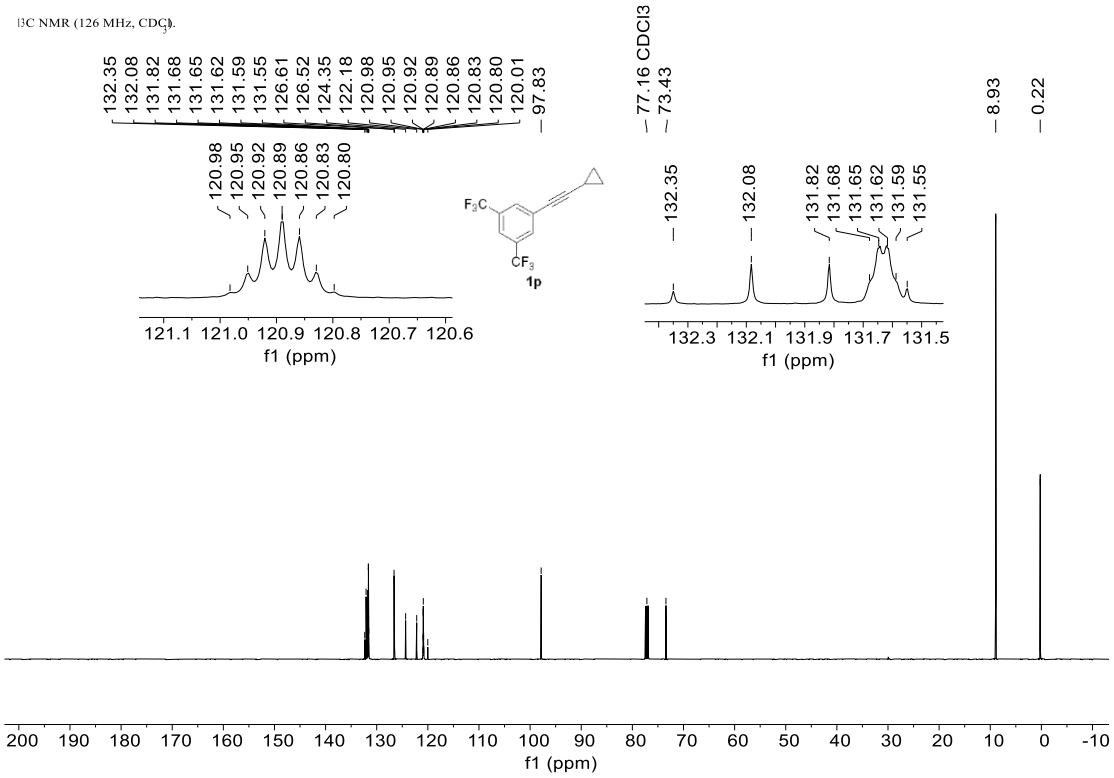

1H NMR (500 MHz, CDCl3)
7.61
7.59
7.51
7.50
7.44
7.42
7.41
7.33
7.32
7.30
7.26 CDCl3
1.51
1.50
1.49
1.49
1.48
1.48
1.47
1.46
1.45
0.92
0.91
0.91
0.90
0.90
0.86
0.86
0.85
CF3
1n
1.00
0.99
1.02
1.01
0.98
2.09
1.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

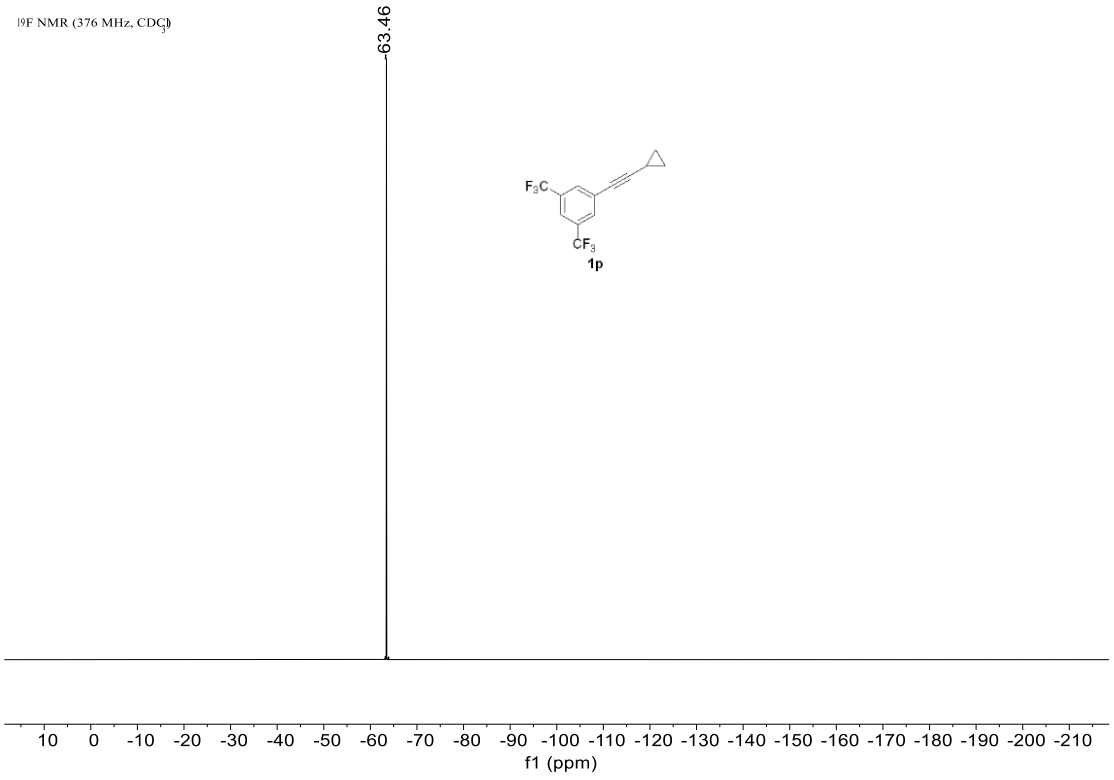

13C NMR (126 MHz, CDCl3)
133.91
132.00
131.76
131.52
131.36
131.28
127.16
127.08
125.86
125.82
125.78
125.74
124.90
122.73
122.56
122.54
122.52
122.50
120.56
77.16 CDCl3
8.84
0.50
132.00
131.76
131.52
131.36
131.28
CF3
1n
132.5
131.5
130.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

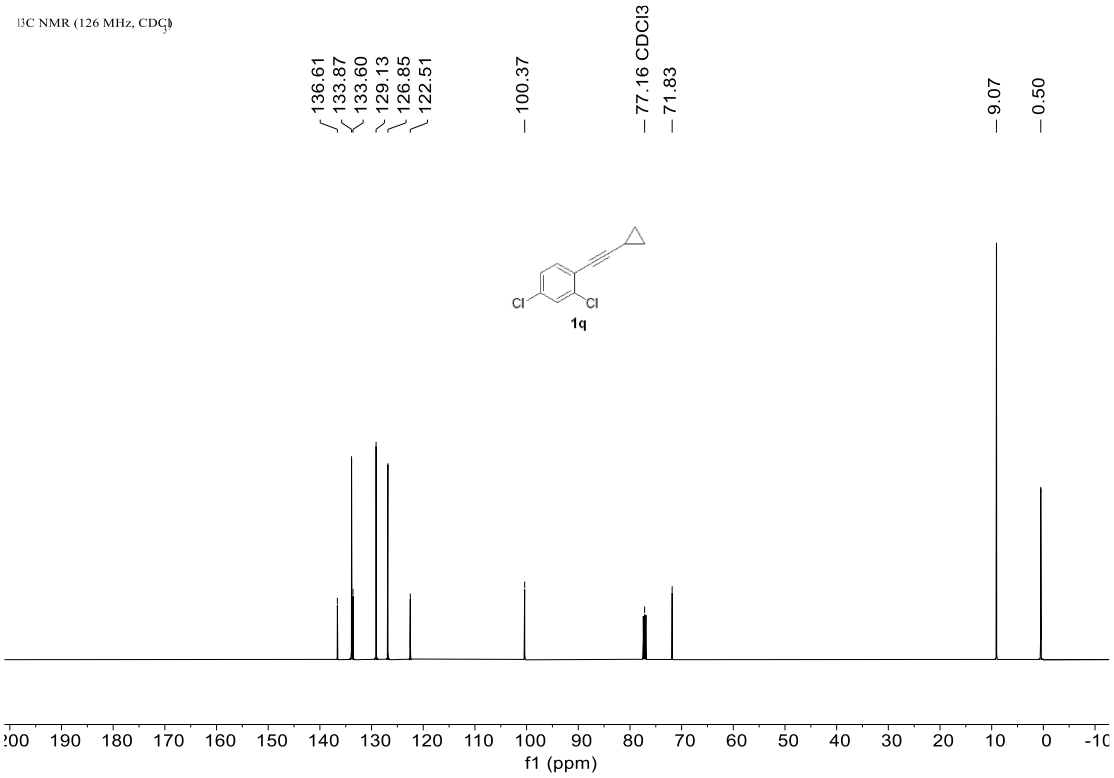
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65.

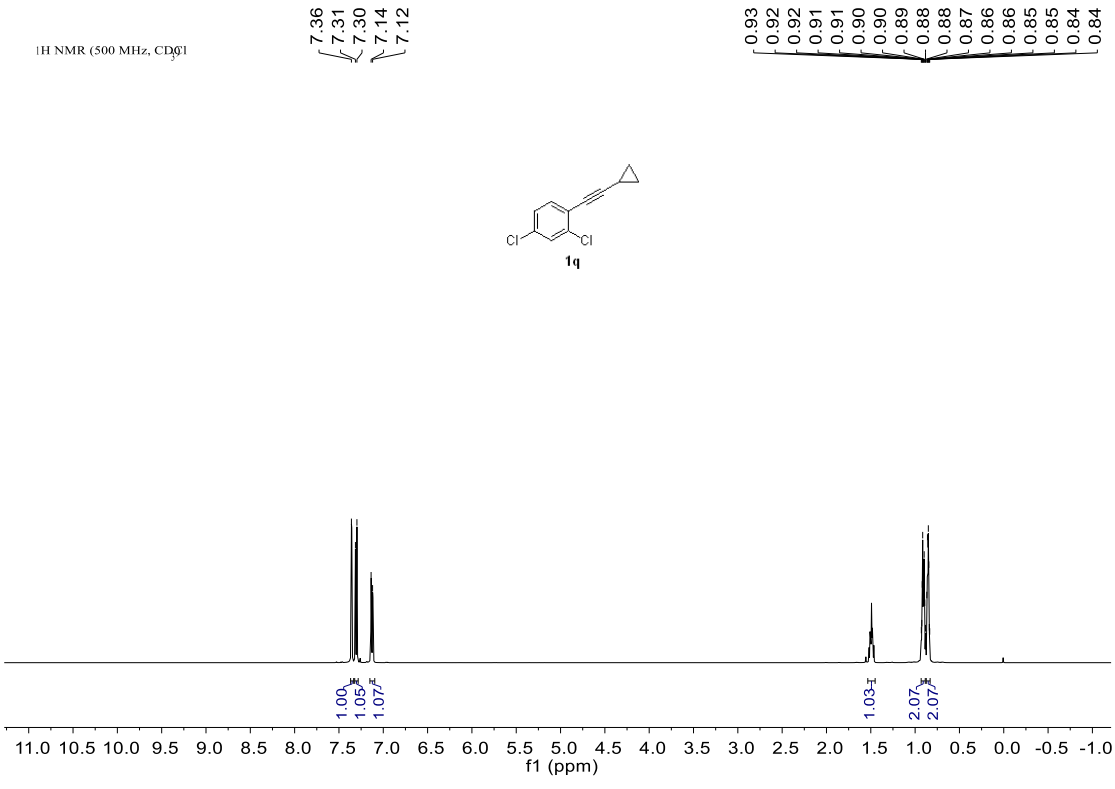


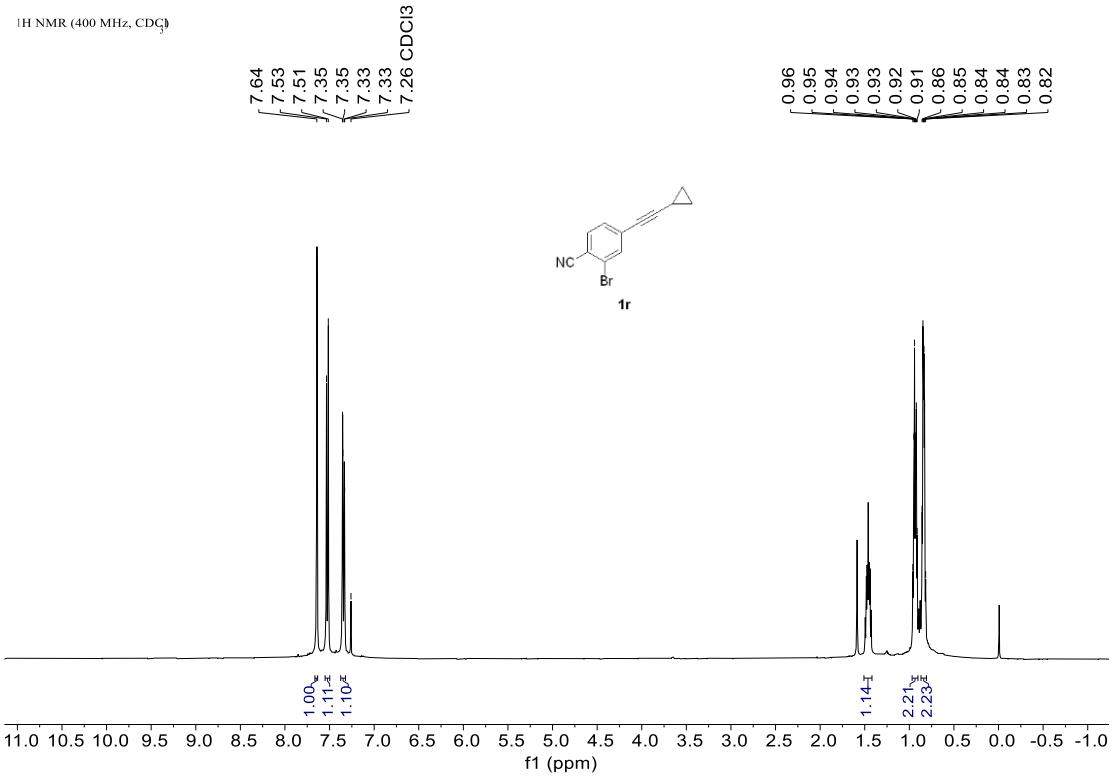


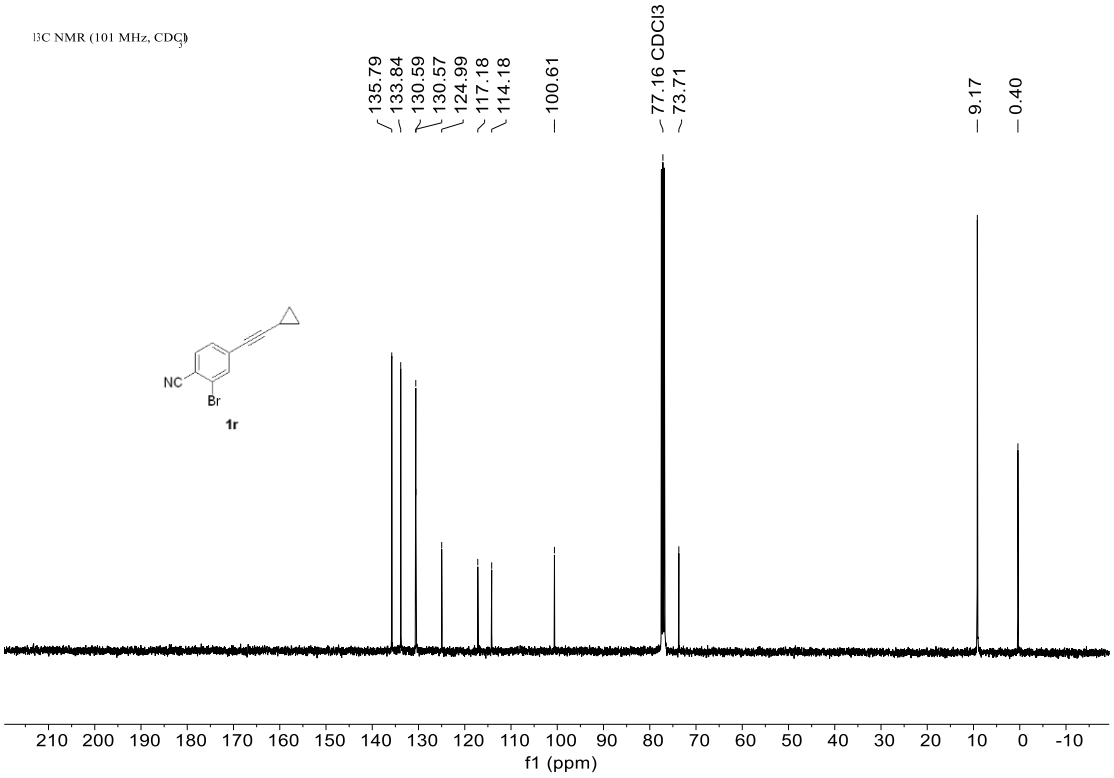

13C NMR (126 MHz, CDCl3)
132.35
132.08
131.82
131.68
131.65
131.62
131.59
131.55
126.61
126.52
124.35
122.18
120.98
120.95
120.92
120.89
120.86
120.83
120.80
120.01
97.83
77.16 CDCl3
73.43
8.93
0.22
F3C
CF3
1p
f1 (ppm)

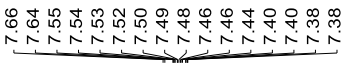

19F NMR (376 MHz, CDCl3)
63.46
F3C
CF3
1p
f1 (ppm)

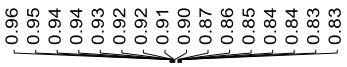

13C NMR (126 MHz, CDCl3)
136.61
133.87
133.60
129.13
126.85
122.51
100.37
77.16 CDCl3
71.83
9.07
0.50
Cl
Cl
1q
f1 (ppm)


1H NMR (500 MHz, CDCl3)
7.36
7.31
7.30
7.14
7.12
0.93
0.92
0.92
0.91
0.91
0.90
0.90
0.89
0.88
0.88
0.87
0.86
0.86
0.85
0.85
0.84
0.84
Cl
Cl
1q
1.00
1.05
1.07
1.03
2.07
2.07
f1 (ppm)

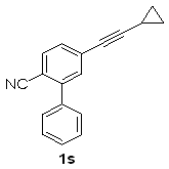

1H NMR (400 MHz, CDCl3)
7.64
7.53
7.51
7.35
7.35
7.33
7.33
7.26 CDCl3
0.96
0.95
0.94
0.93
0.93
0.92
0.91
0.86
0.85
0.84
0.84
0.83
0.82
NC
Br
1r
1.00
1.11
1.10
1.14
2.21
2.23
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


13C NMR (101 MHz, CDCl3)
135.79
133.84
130.59
130.57
124.99
117.18
114.18
100.61
77.16 CDCl3
73.71
9.17
0.40
NC
Br
1r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

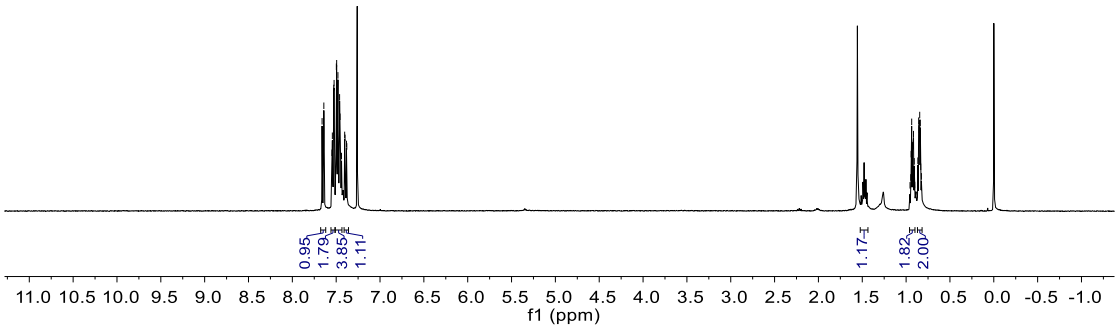




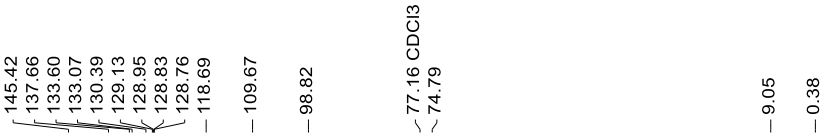
^{1}H NMR (400 MHz, $CDCl_3$)

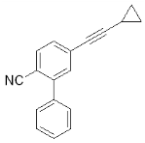


1s

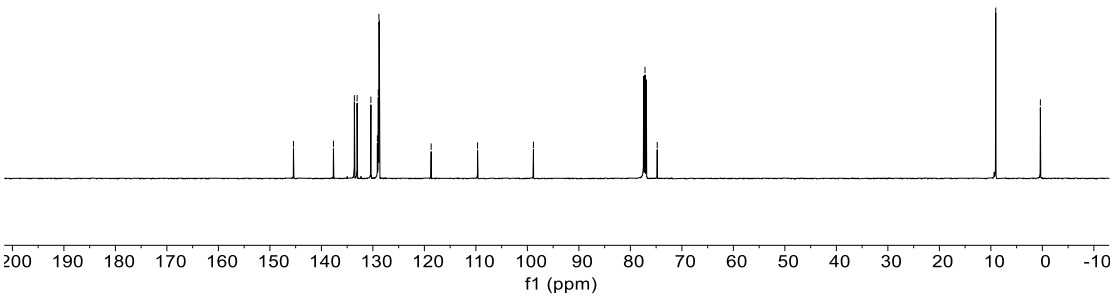


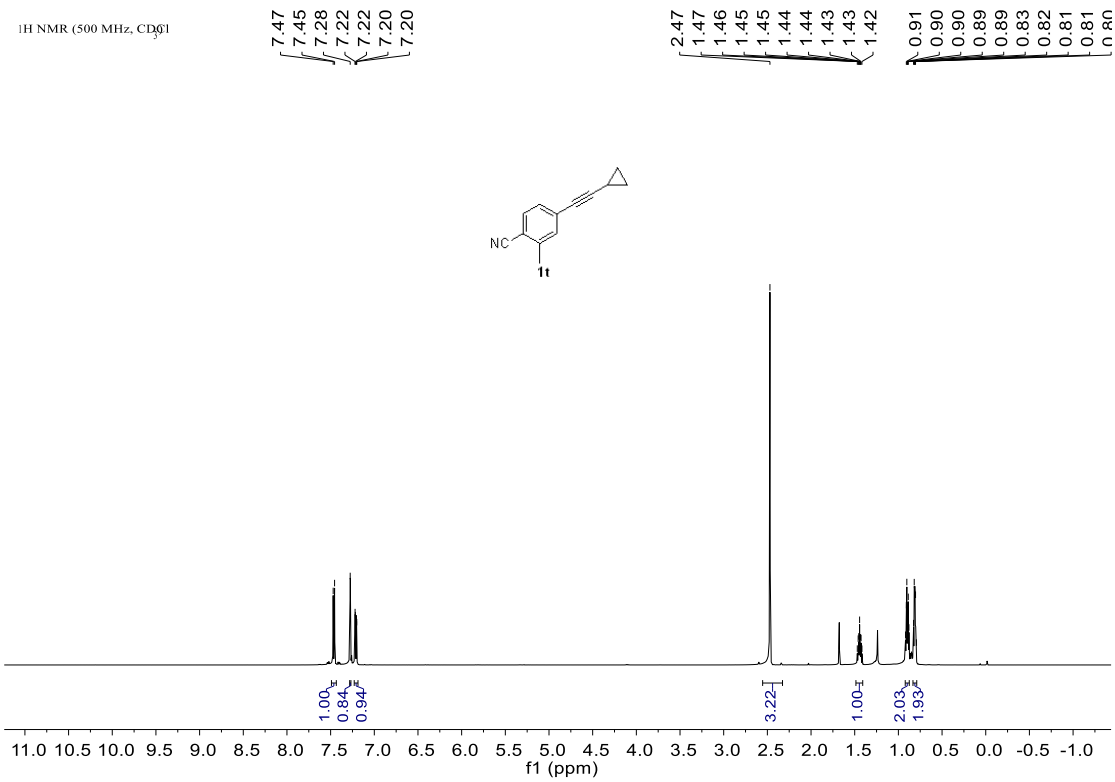
^{13}C NMR (126 MHz, $CDCl_3$)

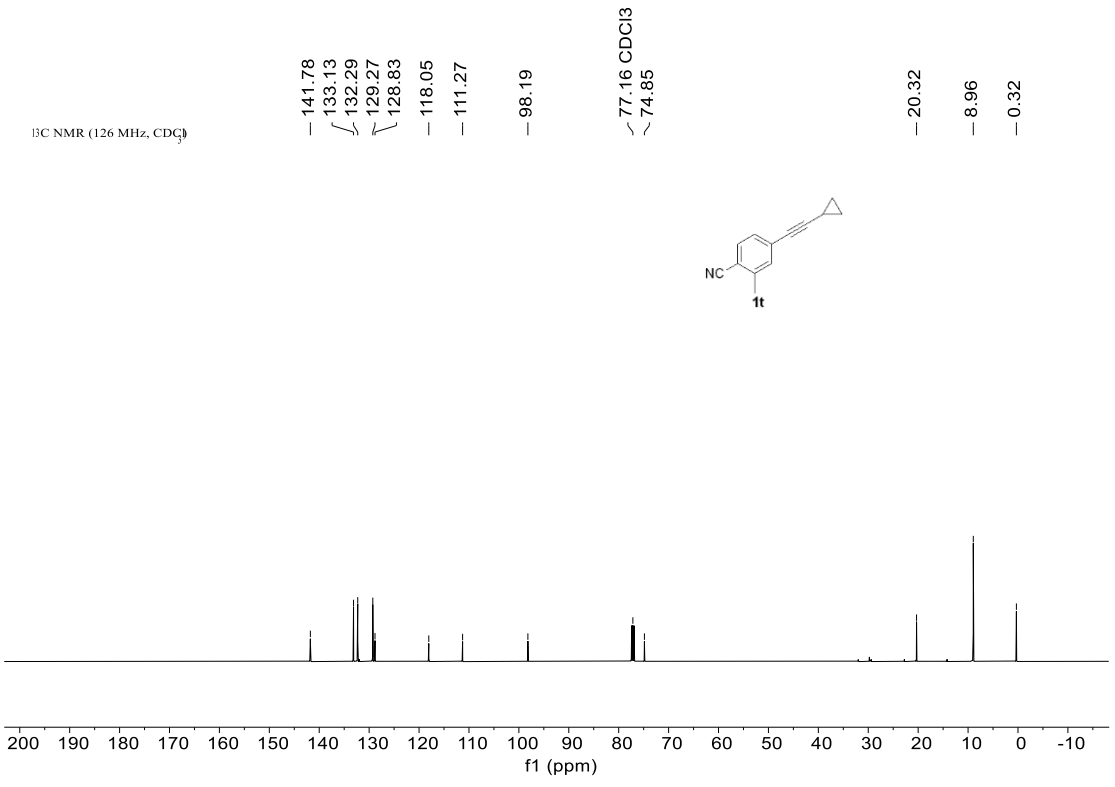


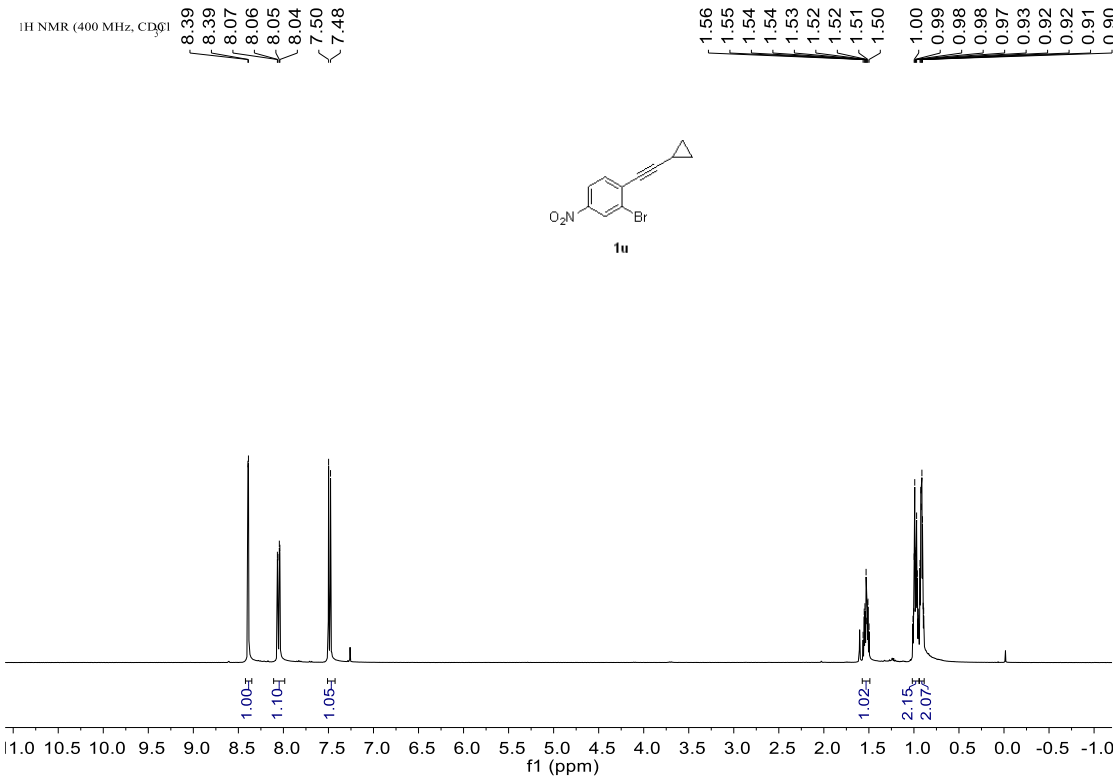


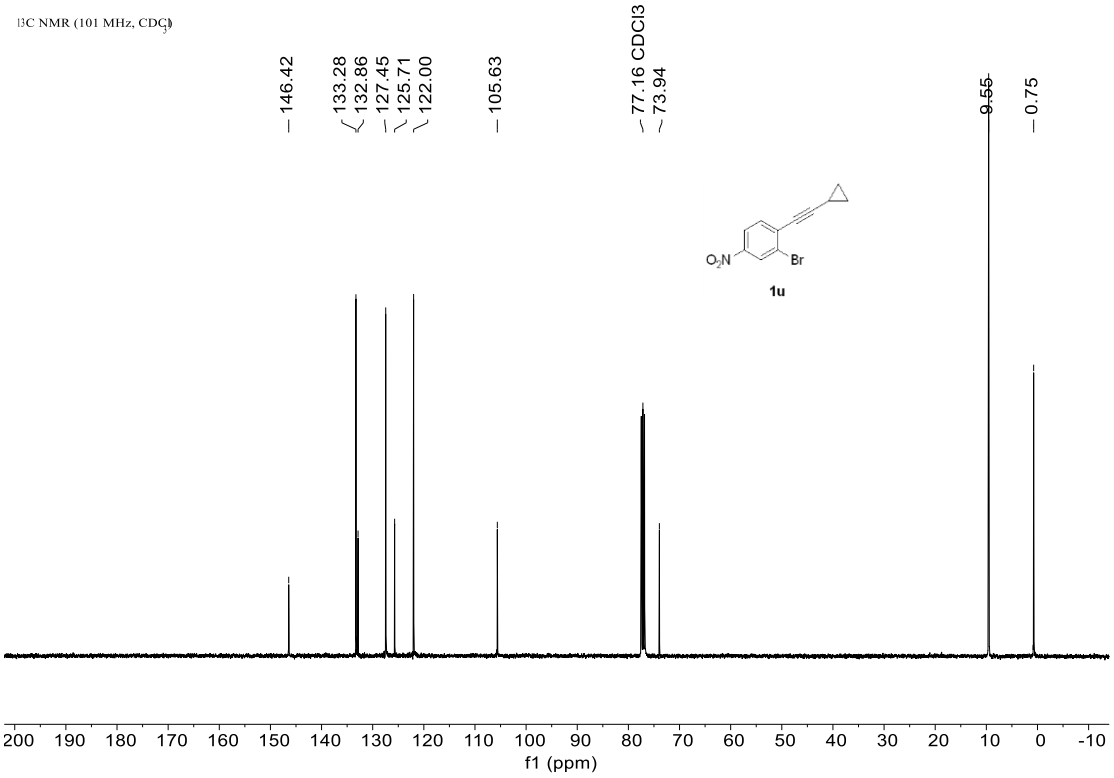
1s

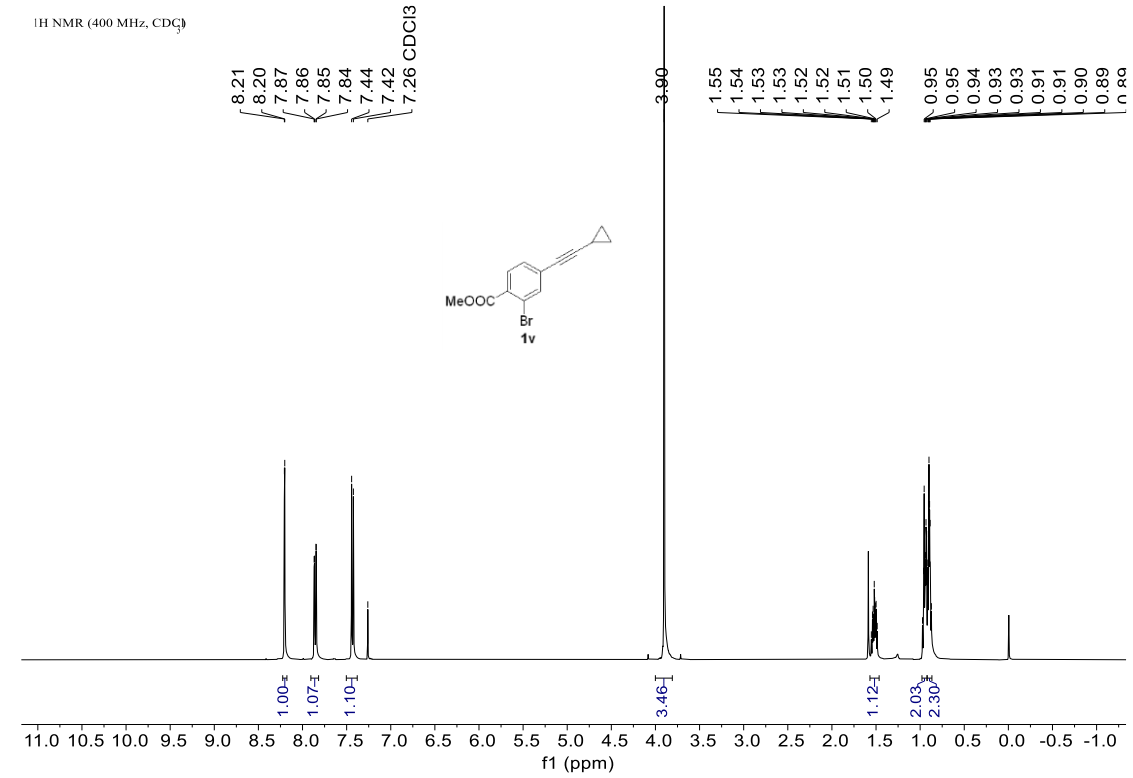


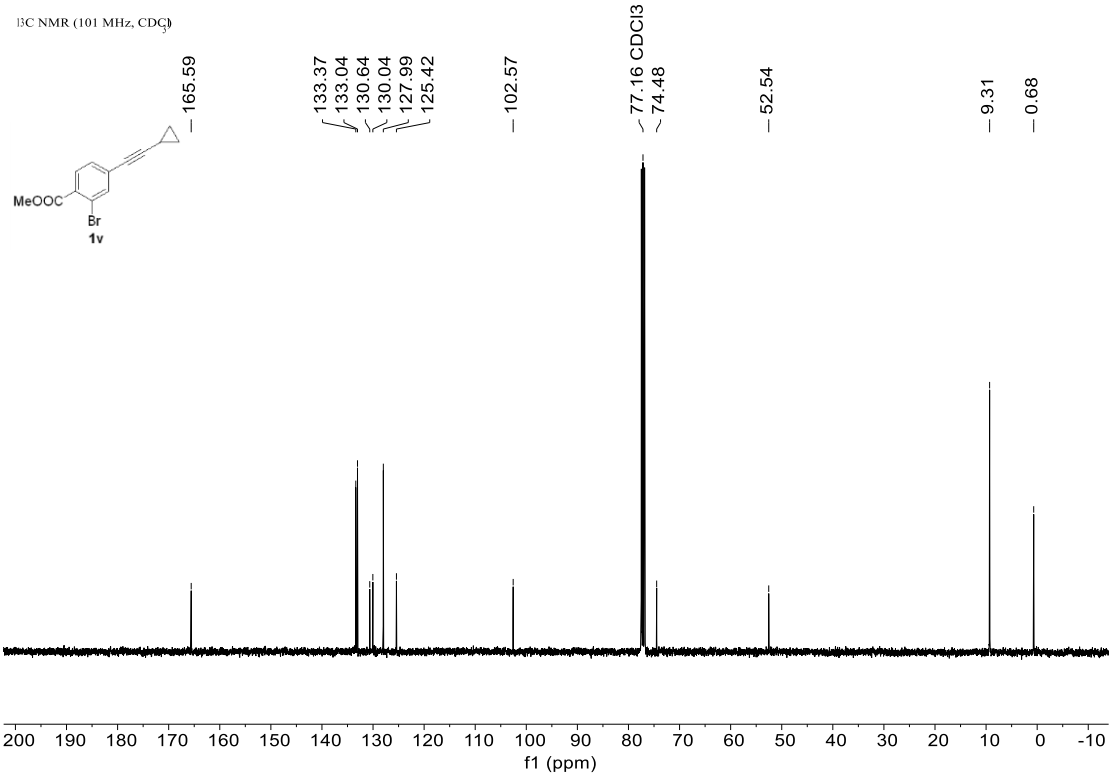

1H NMR (500 MHz, CDCl3)
7.47
7.45
7.28
7.22
7.22
7.20
7.20
2.47
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
0.91
0.90
0.90
0.89
0.89
0.83
0.82
0.81
0.81
NC
1t
1.00
0.84
0.94
3.22
1.00
2.03
1.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

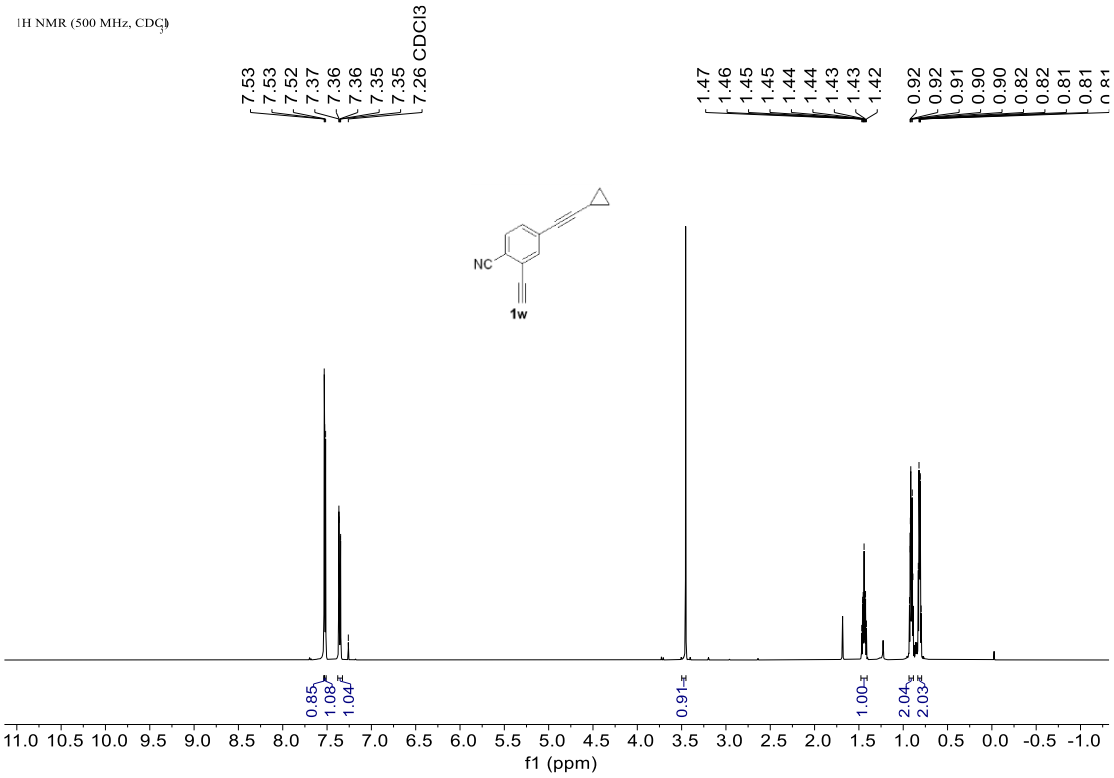

13C NMR (126 MHz, CDCl3)
141.78
133.13
132.29
129.27
128.83
118.05
111.27
98.19
77.16 CDCl3
74.85
20.32
8.96
0.32
NC
1t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

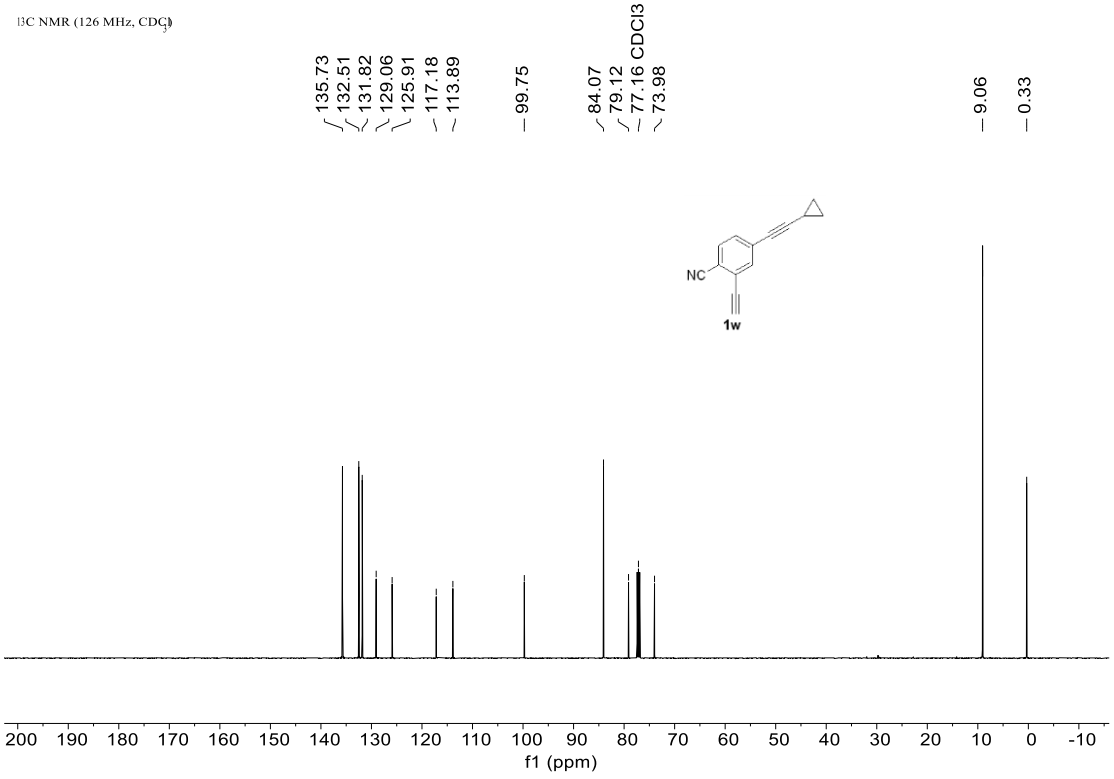

1H NMR (400 MHz, CDCl3)
8.39
8.39
8.07
8.06
8.05
8.04
7.50
7.48
1.56
1.55
1.54
1.54
1.53
1.52
1.52
1.51
1.50
1.00
0.99
0.98
0.98
0.97
0.93
0.92
0.92
0.91
O2N
Br
1u
1.00
1.10
1.05
1.02
2.15
2.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

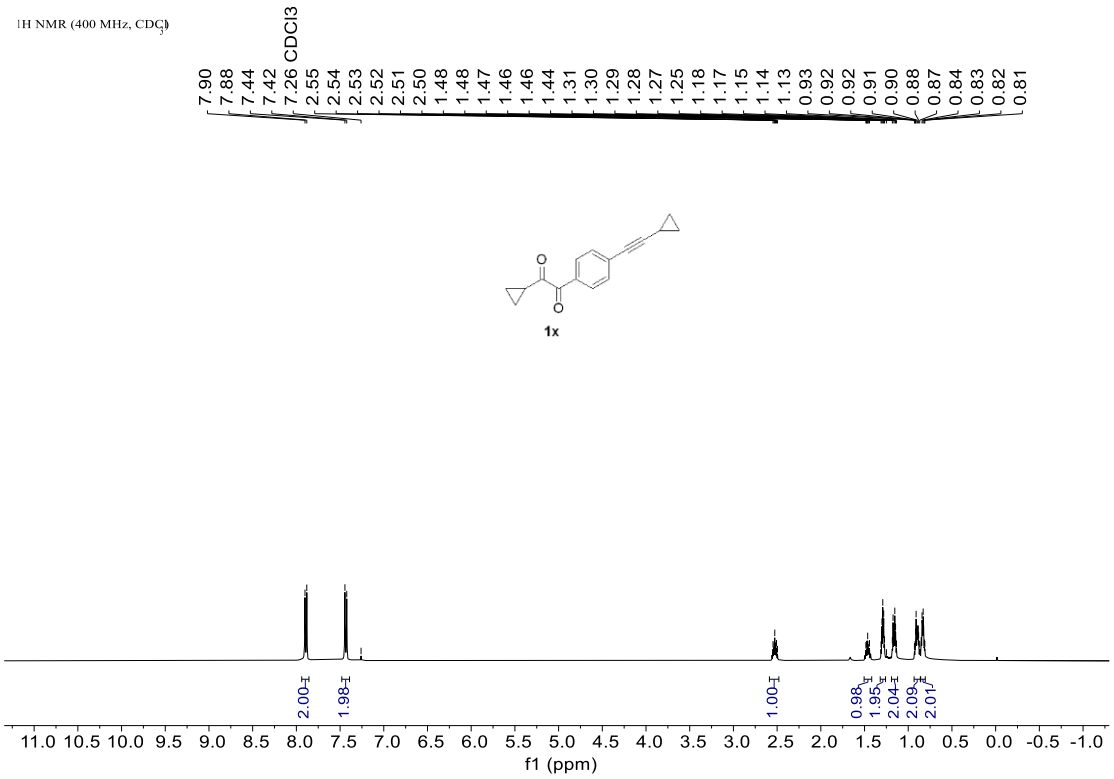

13C NMR (101 MHz, CDCl3)
146.42
133.28
132.86
127.45
125.71
122.00
105.63
77.16 CDCl3
73.94
9.55
0.75
O2N
Br
1u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

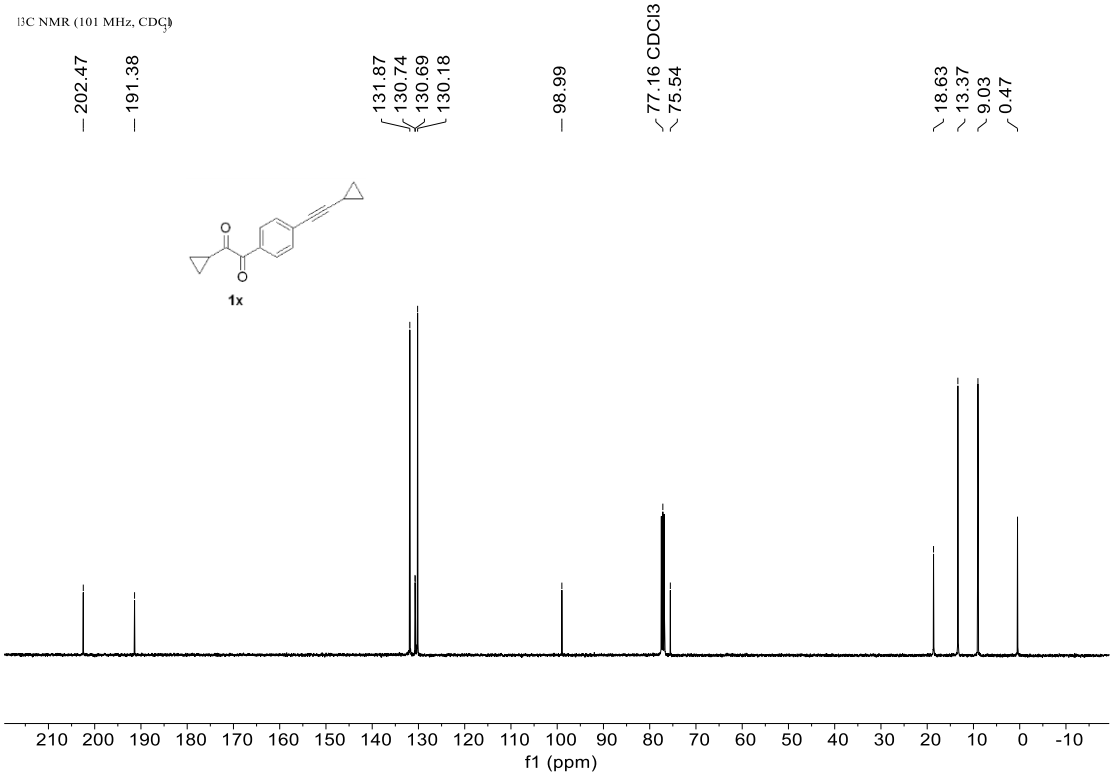

1H NMR (400 MHz, CDCl3)
8.21
8.20
7.87
7.86
7.85
7.84
7.44
7.42
7.26 CDCl3
3.90
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.50
1.49
0.95
0.95
0.94
0.93
0.93
0.91
0.91
0.90
0.89
MeOOC
Br
1v
1.00
1.07
1.10
3.46
1.12
2.03
2.30
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

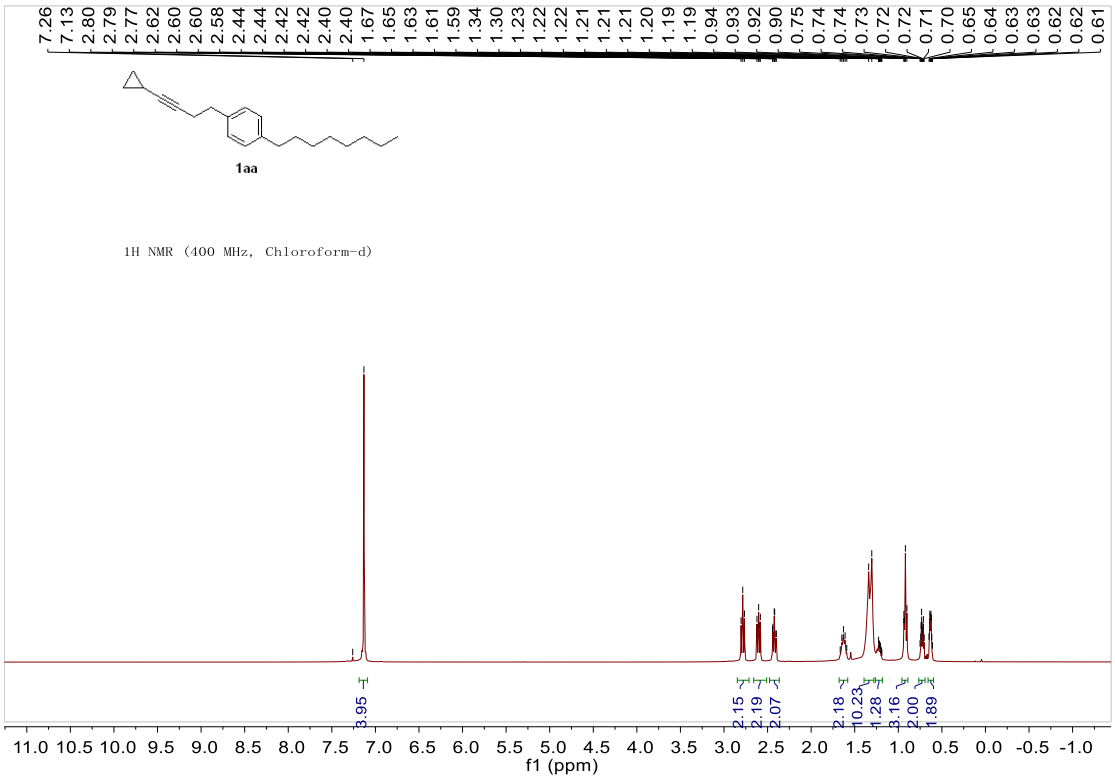

13C NMR (101 MHz, CDCl3)
165.59
133.37
133.04
130.64
130.04
127.99
125.42
102.57
77.16 CDCl3
74.48
52.54
9.31
0.68
MeOOC
Br
1v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

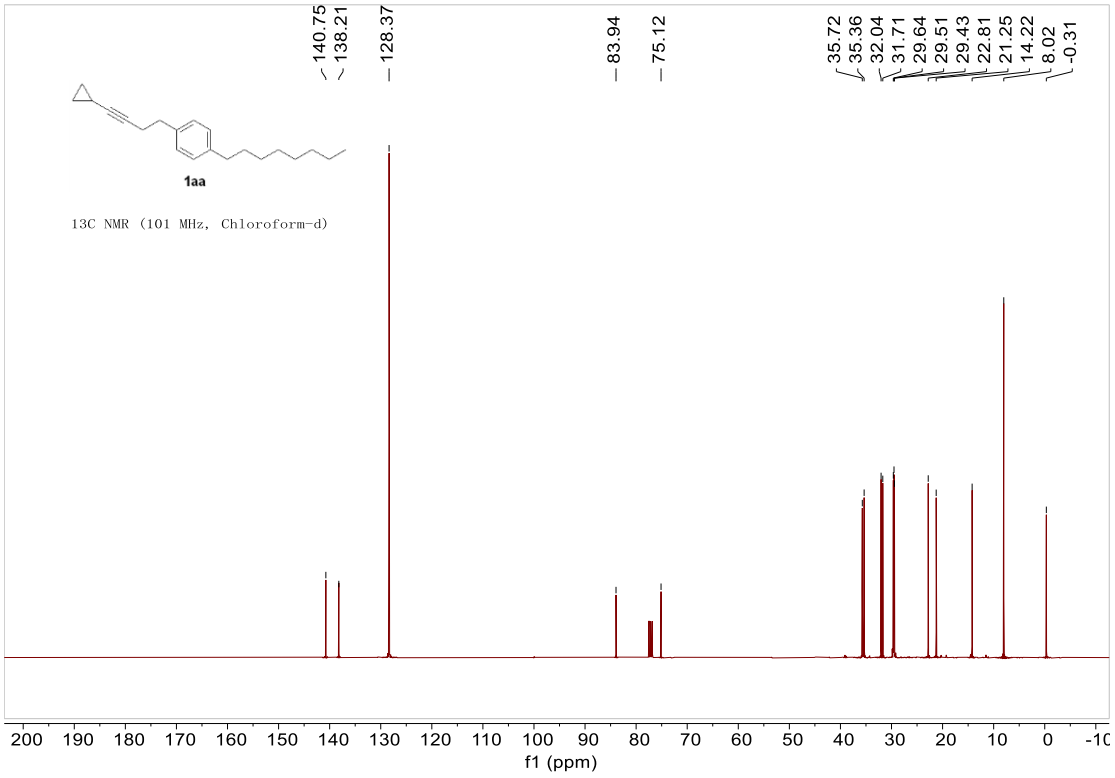

1H NMR (500 MHz, CDCl3)
7.53
7.53
7.52
7.37
7.36
7.36
7.35
7.35
7.26 CDCl3
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
0.92
0.92
0.91
0.90
0.90
0.82
0.81
0.81
NC
1w
0.85
1.08
1.04
0.91
1.00
2.04
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

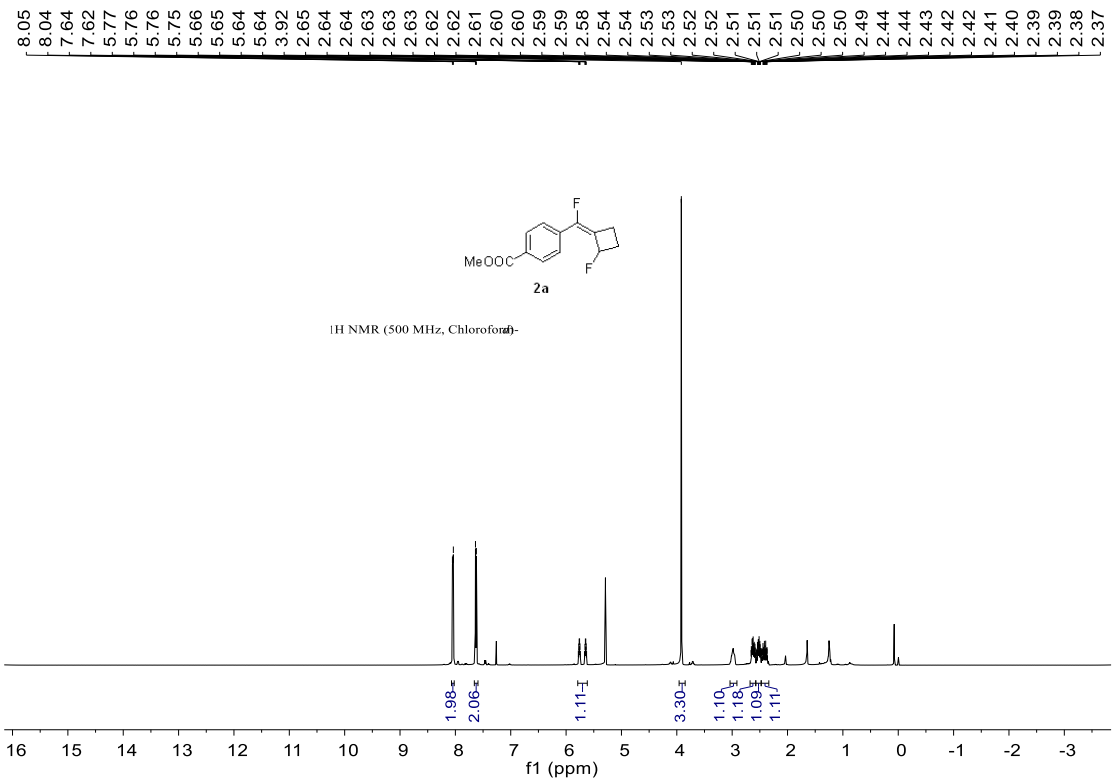

13C NMR (126 MHz, CDCl3)
135.73
132.51
131.82
129.06
125.91
117.18
113.89
99.75
84.07
79.12
77.16 CDCl3
73.98
9.06
0.33
NC
1w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

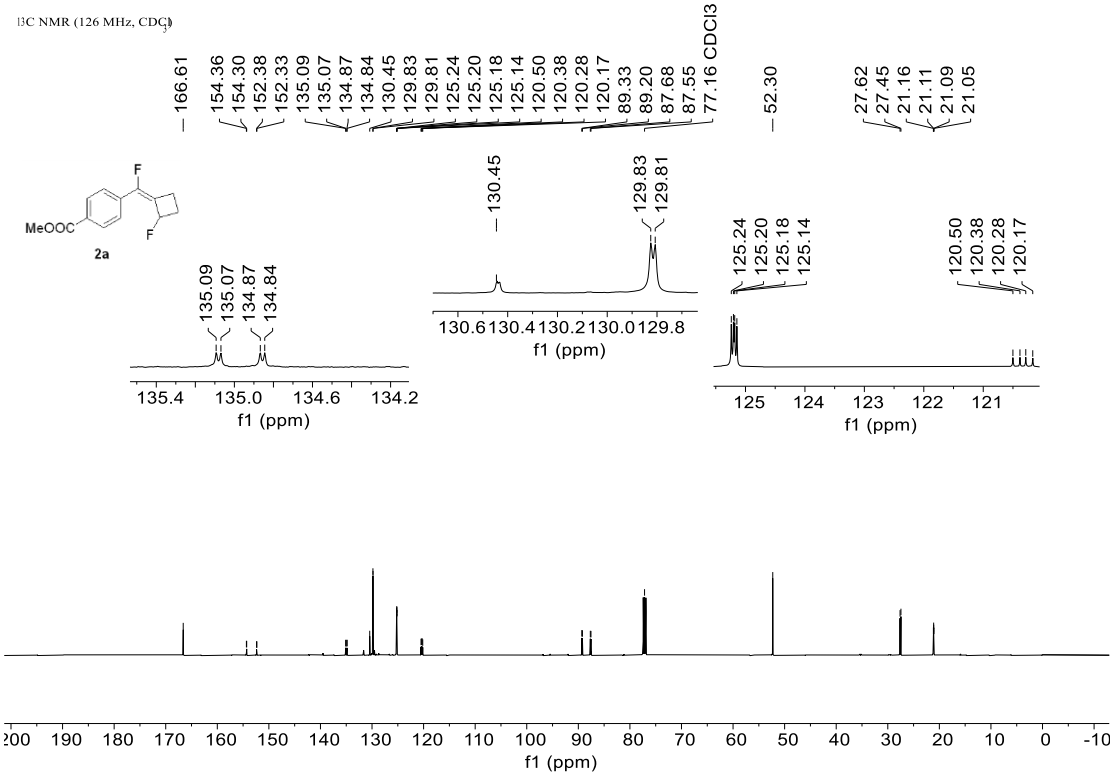

1H NMR (400 MHz, CDCl3)
7.90
7.88
7.44
7.42
7.26 CDCl3
2.55
2.54
2.53
2.52
2.51
2.50
1.48
1.48
1.47
1.46
1.46
1.44
1.31
1.30
1.29
1.28
1.27
1.25
1.18
1.17
1.15
1.14
1.13
0.93
0.92
0.92
0.91
0.90
0.88
0.87
0.84
0.83
0.82
0.81
1x
2.00
1.98
1.00
0.98
1.95
2.04
2.09
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


13C NMR (101 MHz, CDCl3)
202.47
191.38
131.87
130.74
130.69
130.18
98.99
77.16 CDCl3
75.54
18.63
13.37
9.03
0.47
1x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

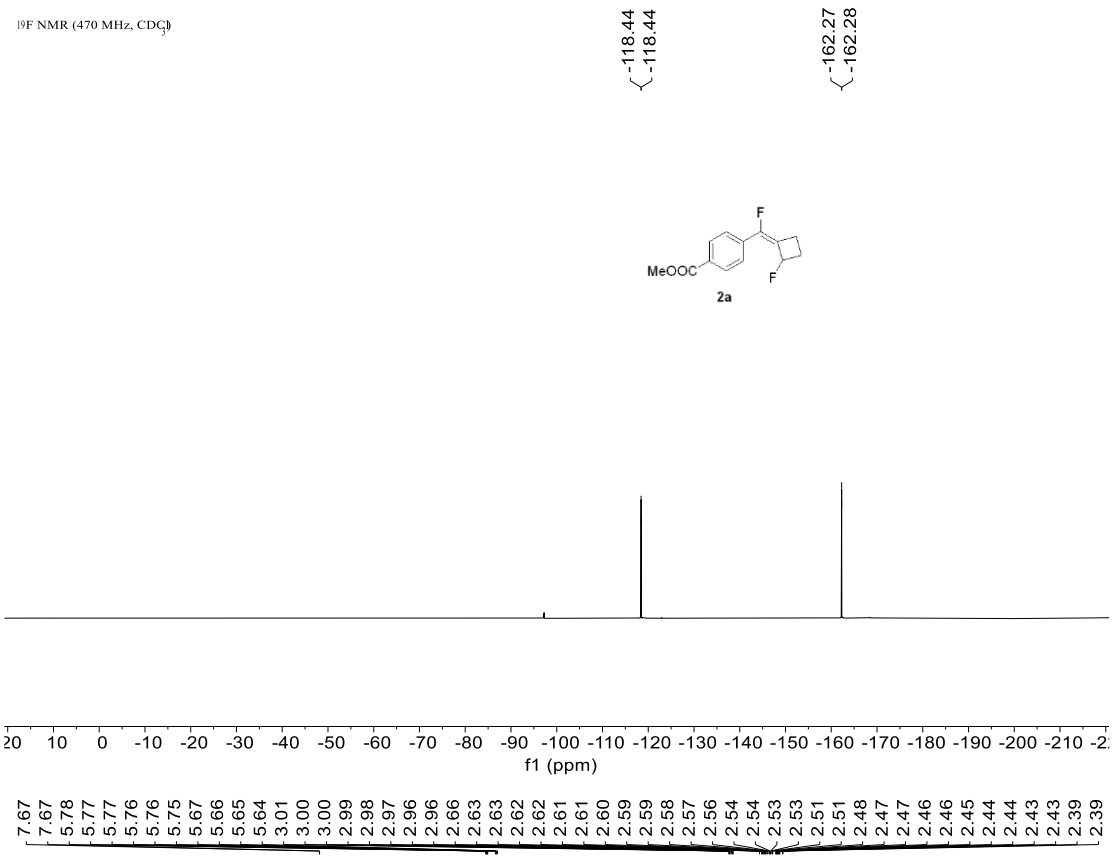

7.26 7.13 2.80 2.79 2.77 2.62 2.60 2.60 2.58 2.44 2.44 2.42 2.42 2.40 2.40 1.67 1.65 1.63 1.61 1.59 1.34 1.30 1.23 1.22 1.22 1.21 1.21 1.21 1.20 1.19 1.19 0.94 0.93 0.92 0.90 0.75 0.74 0.74 0.73 0.72 0.72 0.71 0.70 0.65 0.64 0.63 0.63 0.62 0.62 0.61
1aa
1H NMR (400 MHz, Chloroform-d)
3.95
2.15 2.19 2.07
2.18 10.23 1.28 3.16 2.00 1.89
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


140.75 138.21 128.37 83.94 75.12 35.72 35.36 32.04 31.71 29.64 29.51 29.43 22.81 21.25 14.22 8.02 -0.31
1aa
13C NMR (101 MHz, Chloroform-d)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

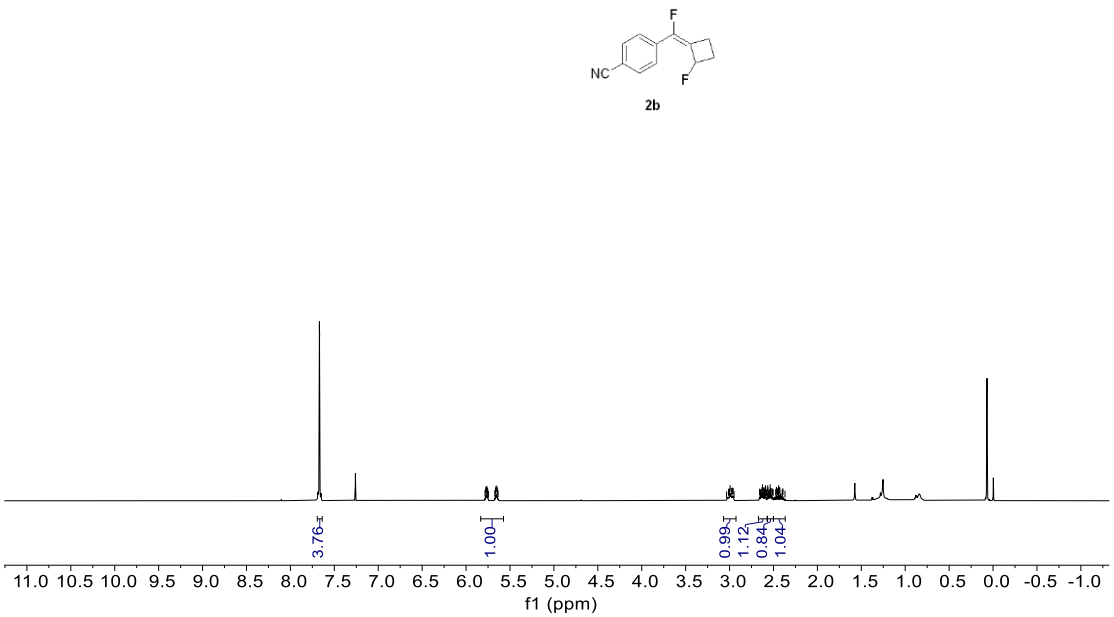

8.05 8.04 7.64 7.62 5.77 5.76 5.76 5.75 5.66 5.65 5.64 5.64 3.92 2.65 2.64 2.64 2.63 2.63 2.62 2.62 2.61 2.60 2.60 2.59 2.59 2.58 2.54 2.54 2.53 2.52 2.52 2.51 2.51 2.51 2.50 2.50 2.50 2.49 2.44 2.44 2.43 2.42 2.42 2.41 2.40 2.39 2.39 2.38 2.37
MeOOC
F
F
2a
1H NMR (500 MHz, Chloroform-d)
1.98 2.06 1.11 3.30 1.10 1.18 1.09 1.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

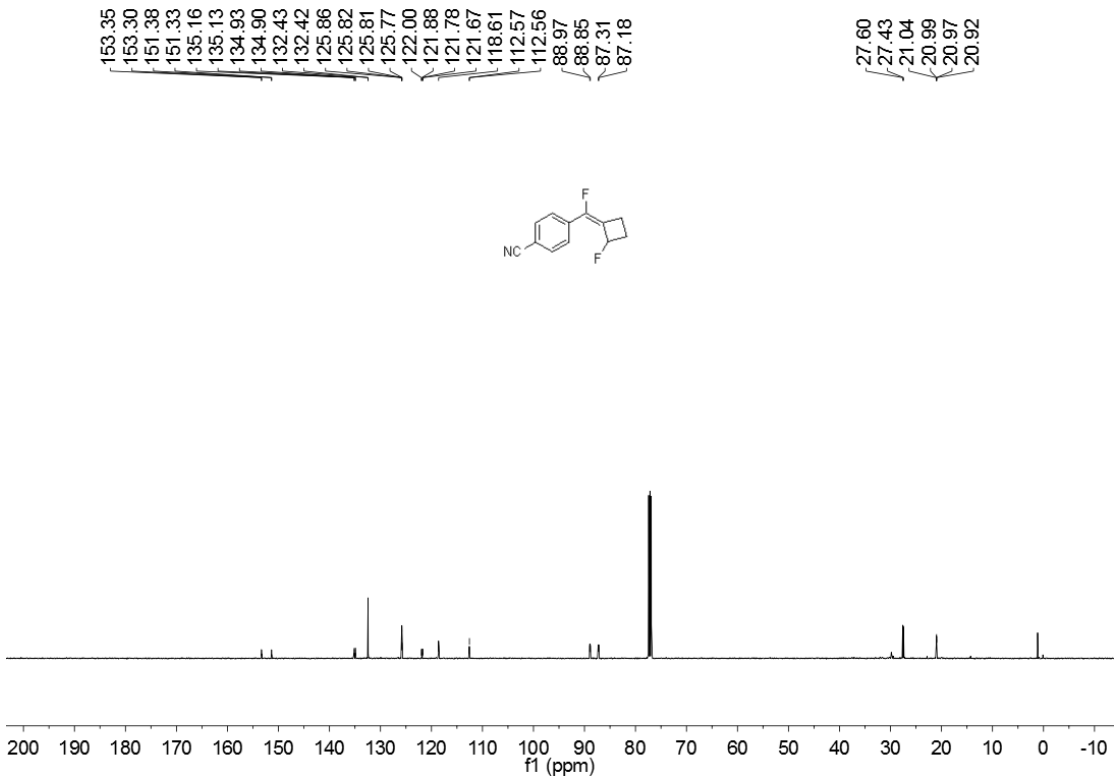

13C NMR (126 MHz, CDCl3)
166.61 154.36 154.30 152.38 152.33 135.09 135.07 134.87 134.84 130.45 129.83 129.81 125.24 125.20 125.18 125.14 120.50 120.38 120.28 120.17 89.33 89.20 87.68 87.55 77.16 CDCl3 52.30 27.62 27.45 21.16 21.11 21.09 21.05
MeOOC
F
F
2a
135.09 135.07 134.87 134.84
135.4 135.0 134.6 134.2
f1 (ppm)
130.45 129.83 129.81
130.6 130.4 130.2 130.0 129.8
f1 (ppm)
125.24 125.20 125.18 125.14 120.50 120.38 120.28 120.17
125 124 123 122 121
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

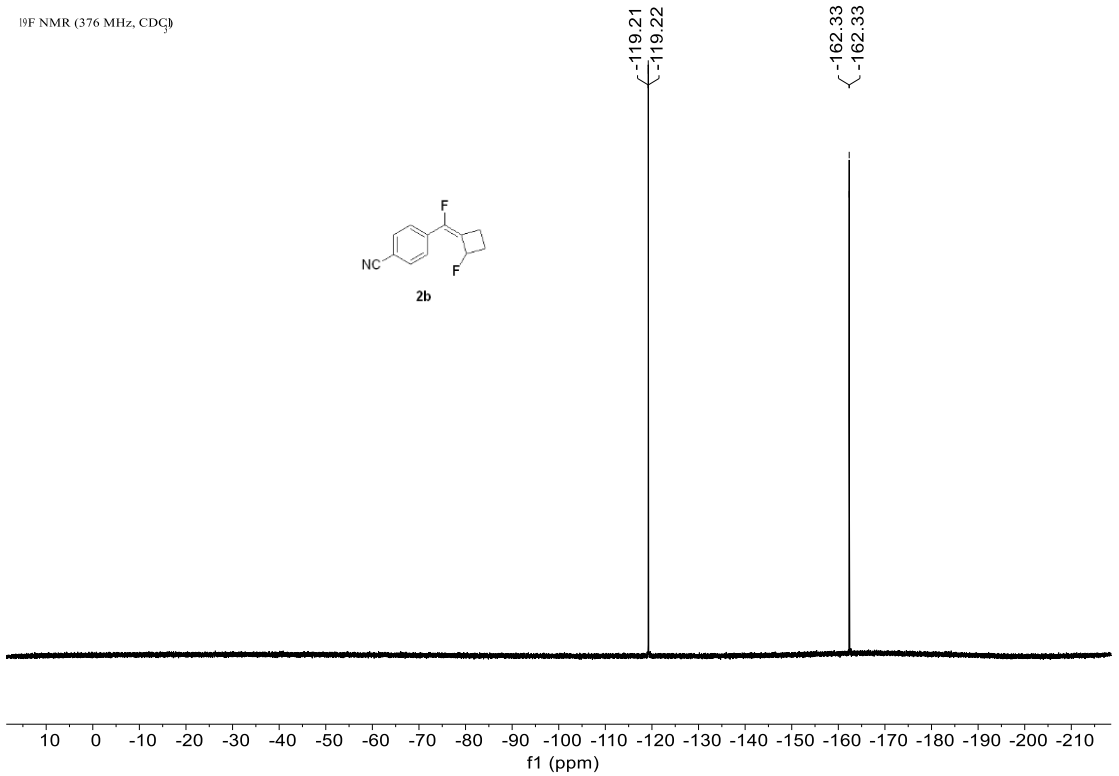
^{19}F NMR (470 MHz, $CDCl_3$)

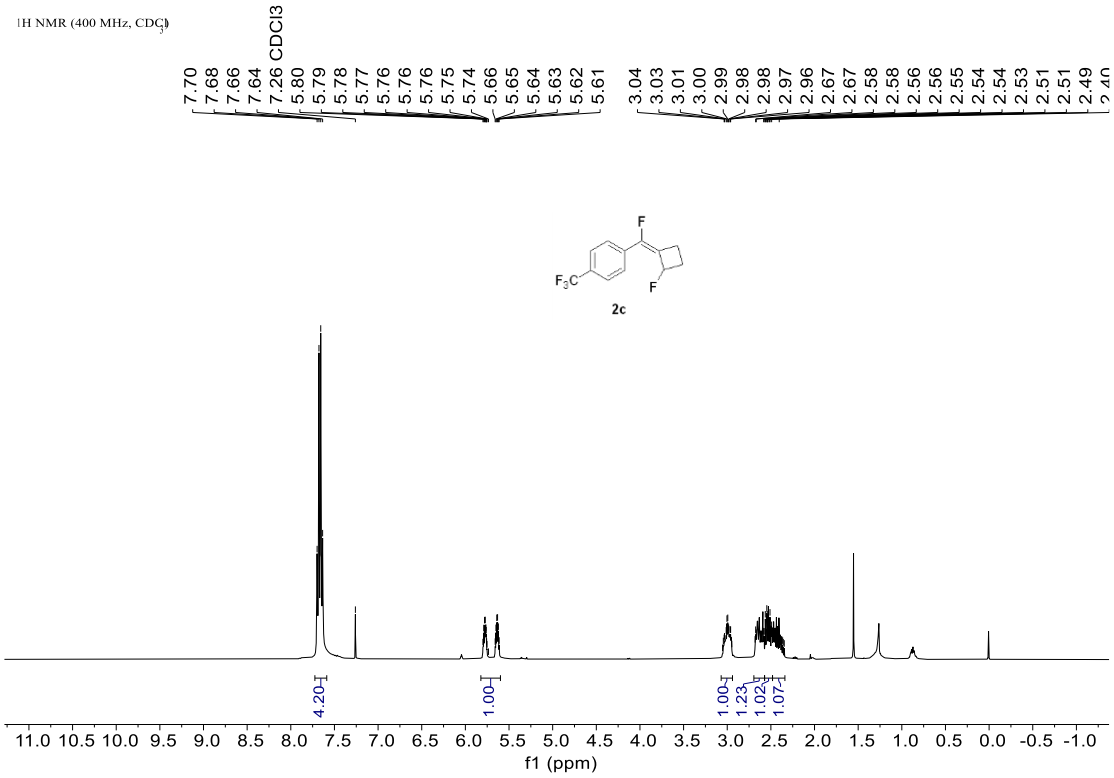


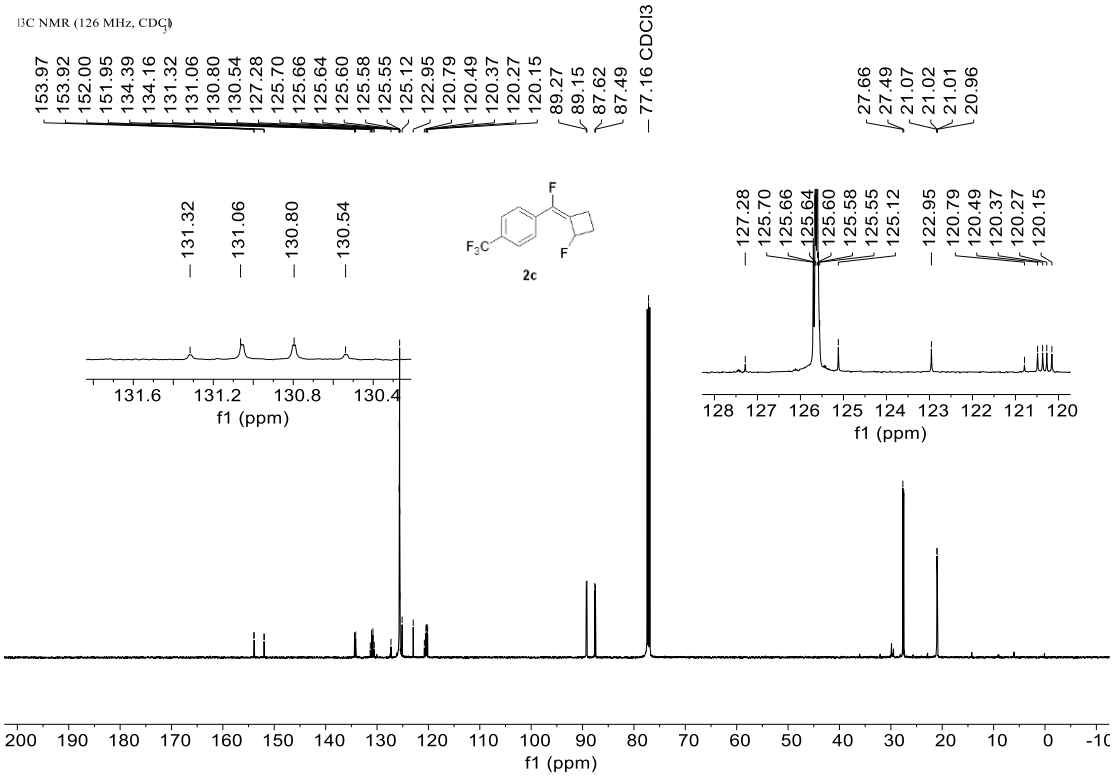
^{1}H NMR (500 MHz, $CDCl_3$)

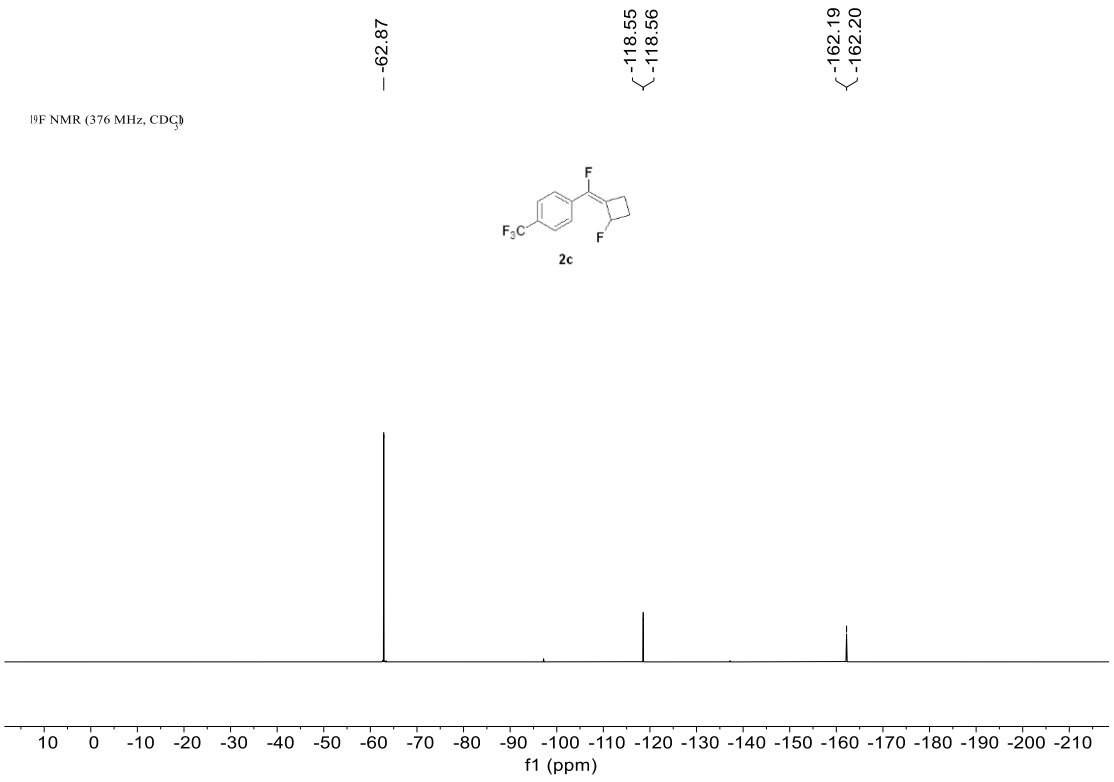


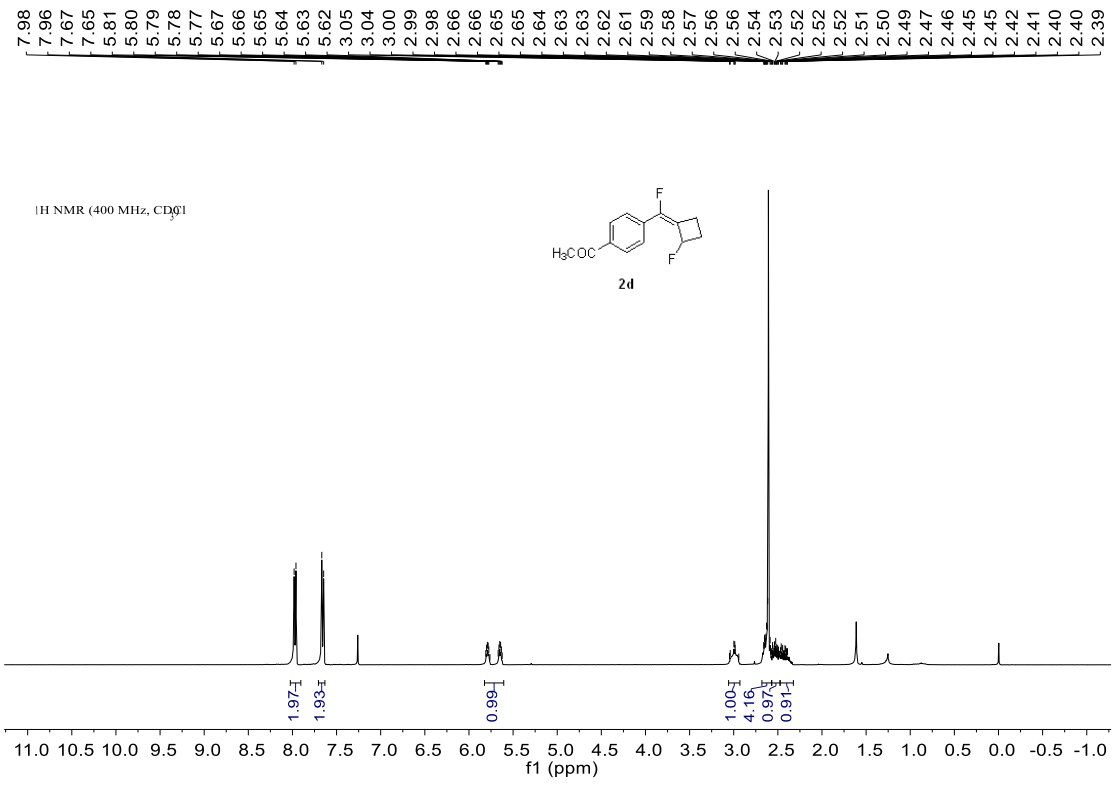

153.35
153.30
151.38
151.33
135.16
135.13
134.93
134.90
132.43
132.42
125.86
125.82
125.81
125.77
122.00
121.88
121.78
121.67
118.61
112.57
112.56
88.97
88.85
87.31
87.18
27.60
27.43
21.04
20.99
20.97
20.92
F
NC
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

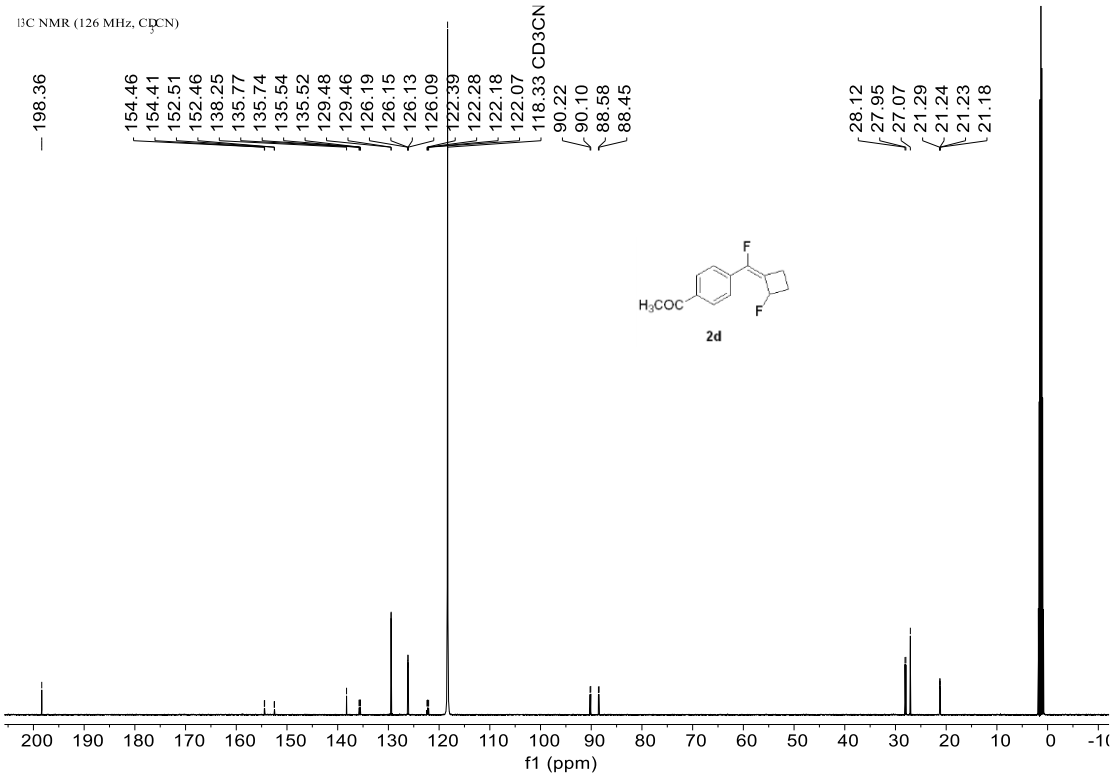

19F NMR (376 MHz, CDCl3)
-119.21
-119.22
-162.33
-162.33
F
NC
F
2b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

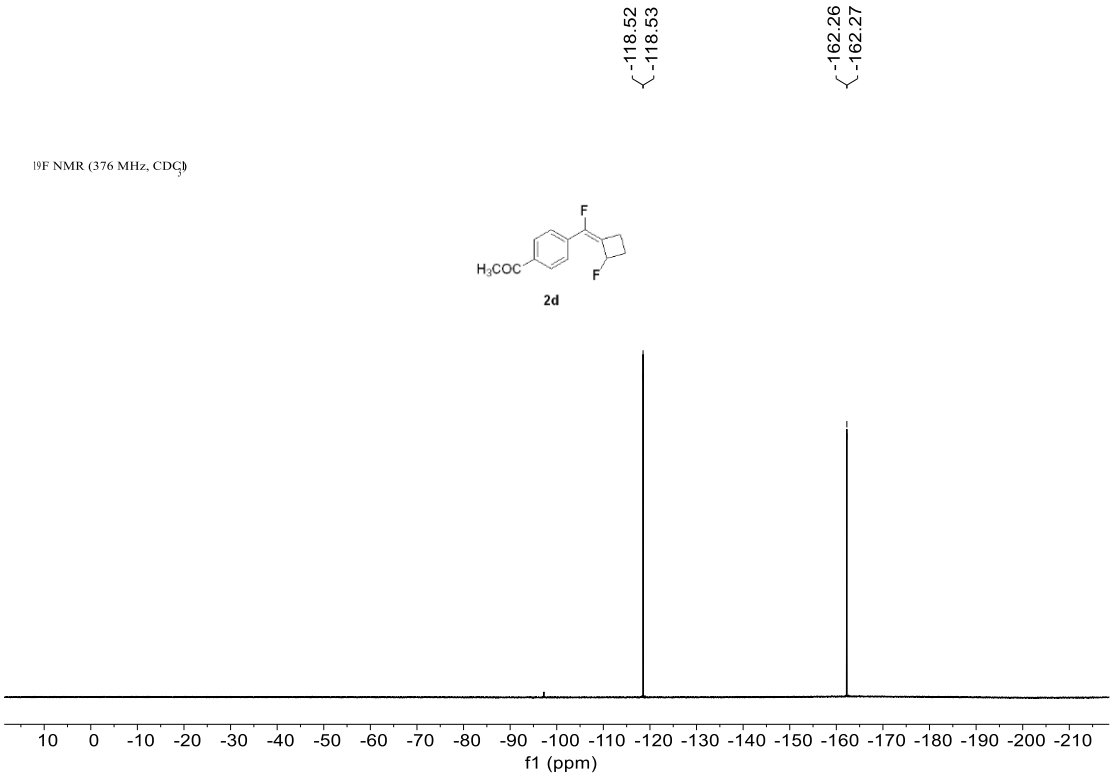

1H NMR (400 MHz, CDCl3)
7.70 7.68 7.66 7.64 7.26 CDCl3 5.80 5.79 5.78 5.77 5.76 5.76 5.76 5.75 5.74 5.66 5.65 5.64 5.63 5.62 5.61
3.04 3.03 3.01 3.00 2.99 2.98 2.98 2.97 2.96 2.67 2.58 2.58 2.56 2.56 2.55 2.54 2.54 2.53 2.51 2.51 2.49
F
F3C
F
2c
4.20 1.00 1.00 1.23 1.02 1.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

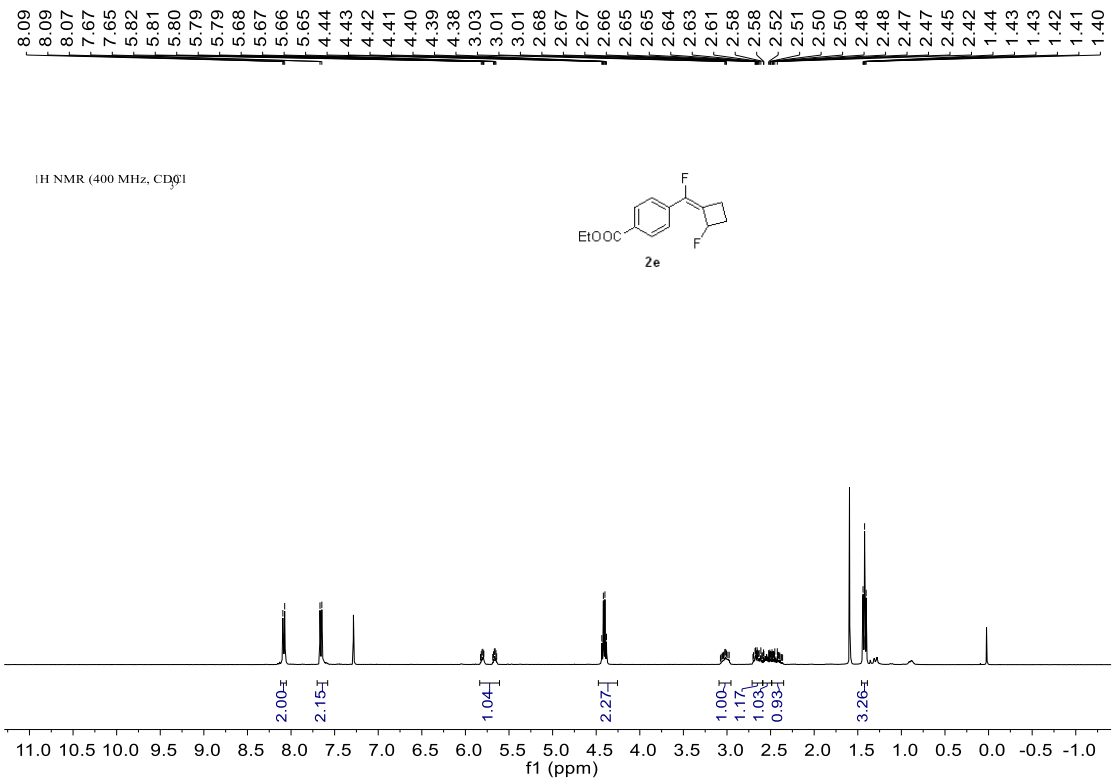

13C NMR (126 MHz, CDCl3)
153.97 153.92 152.00 151.95 134.39 134.16 131.32 131.06 130.80 130.54 127.28 125.70 125.66 125.64 125.60 125.58 125.55 125.12 122.95 120.79 120.49 120.37 120.27 120.15 89.27 89.15 87.62 87.49 77.16 CDCl3
27.66 27.49 21.07 21.02 21.01 20.96
131.32 131.06 130.80 130.54
F
F3C
F
2c
127.28 125.70 125.66 125.64 125.60 125.58 125.55 125.12 122.95 120.79 120.49 120.37 120.27 120.15
131.6 131.2 130.8 130.4
f1 (ppm)
128 127 126 125 124 123 122 121 120
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

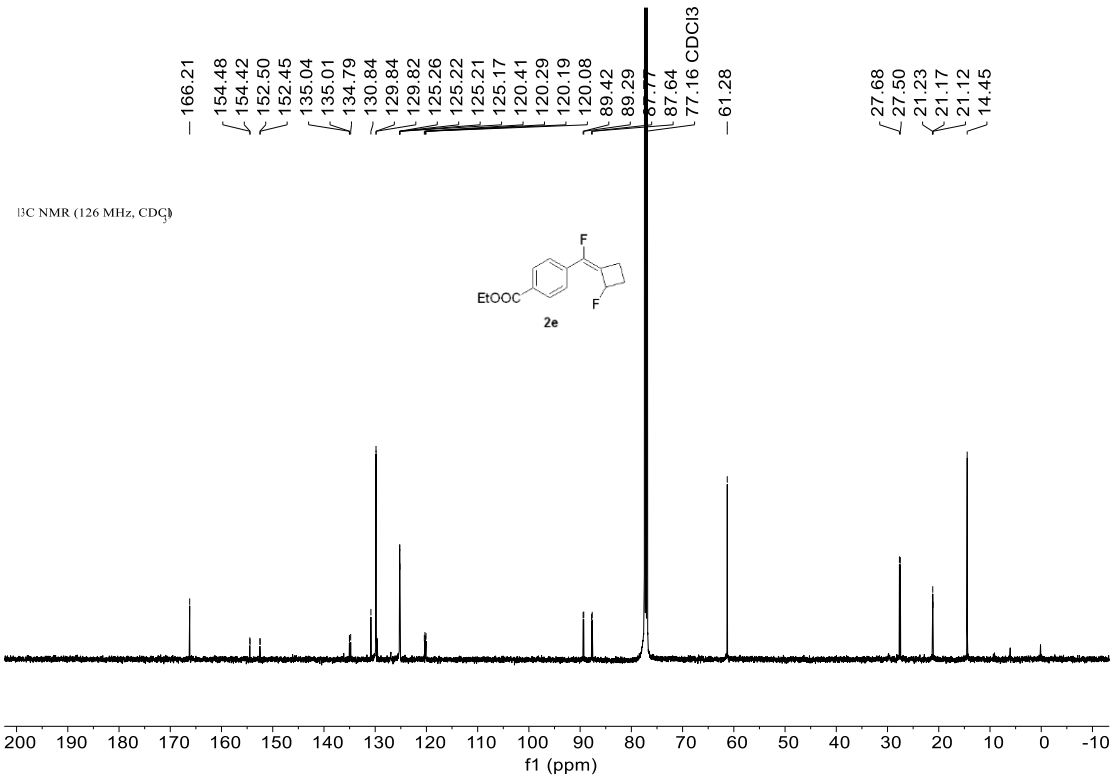

-62.87
-118.55
-118.56
-162.19
-162.20
19F NMR (376 MHz, CDCl3)
F
F3C
F
2c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.98 7.96 7.67 7.65 5.81 5.80 5.79 5.78 5.77 5.67 5.66 5.65 5.64 5.63 5.62 3.05 3.04 3.00 2.99 2.98 2.66 2.66 2.65 2.65 2.64 2.63 2.63 2.62 2.61 2.59 2.58 2.57 2.56 2.56 2.54 2.53 2.52 2.52 2.52 2.51 2.50 2.49 2.47 2.46 2.45 2.45 2.42 2.41 2.40 2.40 2.39
1H NMR (400 MHz, CDCl3)
F
H3COC
F
2d
1.97
1.93
0.99
1.00
4.16
0.97
0.91
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

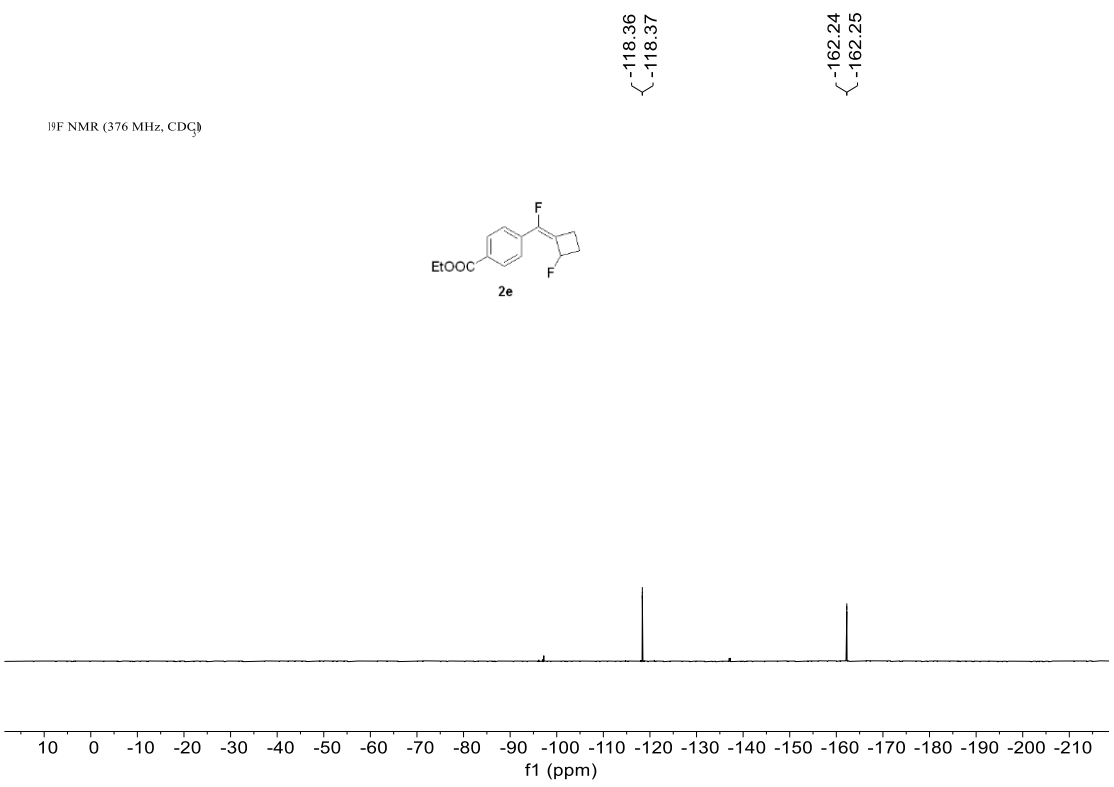

13C NMR (126 MHz, CD3CN)
198.36
154.46
154.41
152.51
152.46
138.25
135.77
135.74
135.54
135.52
129.48
129.46
126.19
126.15
126.13
126.09
122.39
122.28
122.18
122.07
118.33 CD3CN
90.22
90.10
88.58
88.45
28.12
27.95
27.07
21.29
21.24
21.23
21.18
F
H3COC
F
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

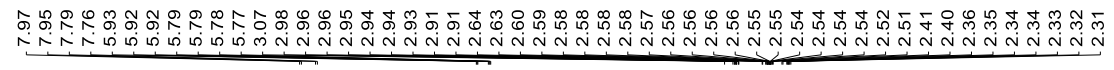

-118.52
-118.53
-162.26
-162.27
19F NMR (376 MHz, CDCl3)
F
H3COC
F
2d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.09 8.09 8.07 7.67 7.65 5.82 5.81 5.80 5.79 5.79 5.68 5.67 5.66 5.65 4.44 4.43 4.42 4.41 4.40 4.39 4.38 3.03 3.01 3.01 2.68 2.67 2.67 2.66 2.65 2.65 2.64 2.63 2.61 2.58 2.58 2.52 2.51 2.50 2.50 2.48 2.48 2.47 2.47 2.45 2.42 1.44 1.43 1.43 1.42 1.41 1.40
1H NMR (400 MHz, CDCl3)
EtOOC
F
F
2e
2.00 2.15 1.04 2.27 1.00 1.17 1.03 0.93 3.26
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

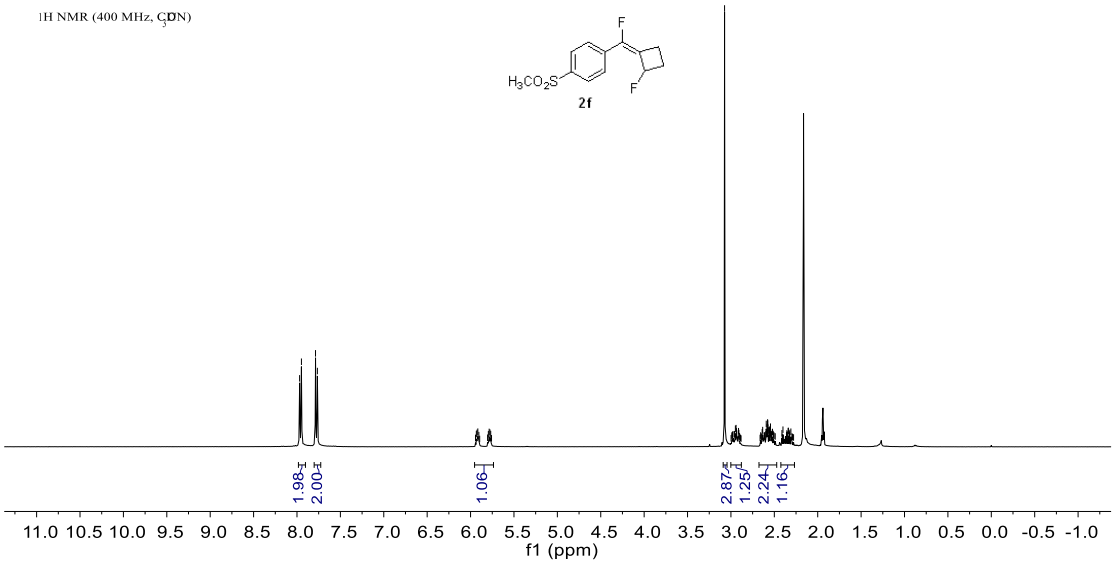

166.21 154.48 154.42 152.50 152.45 135.04 135.01 134.79 130.84 129.84 129.82 125.26 125.22 125.21 125.17 120.41 120.29 120.19 120.08 89.42 89.29 87.77 87.64 77.16 CDCl3 61.28 27.68 27.50 21.23 21.17 21.12 14.45
13C NMR (126 MHz, CDCl3)
EtOOC
F
F
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

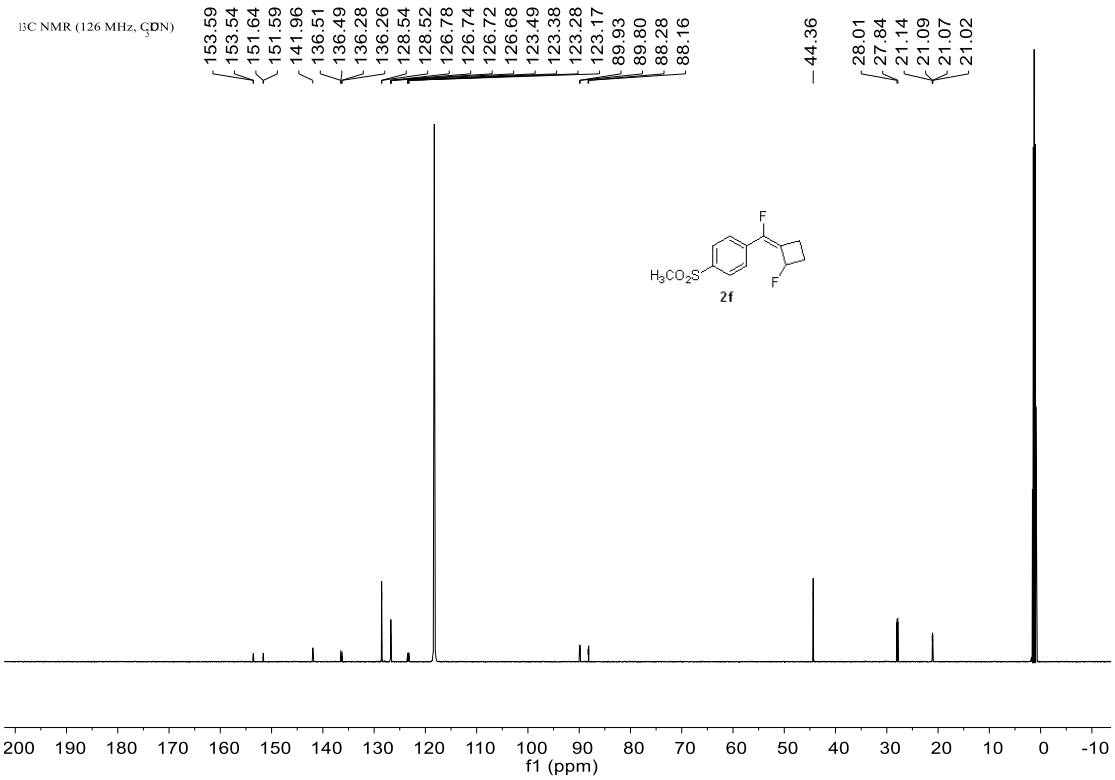
^{19}F NMR (376 MHz, $CDCl_3$)

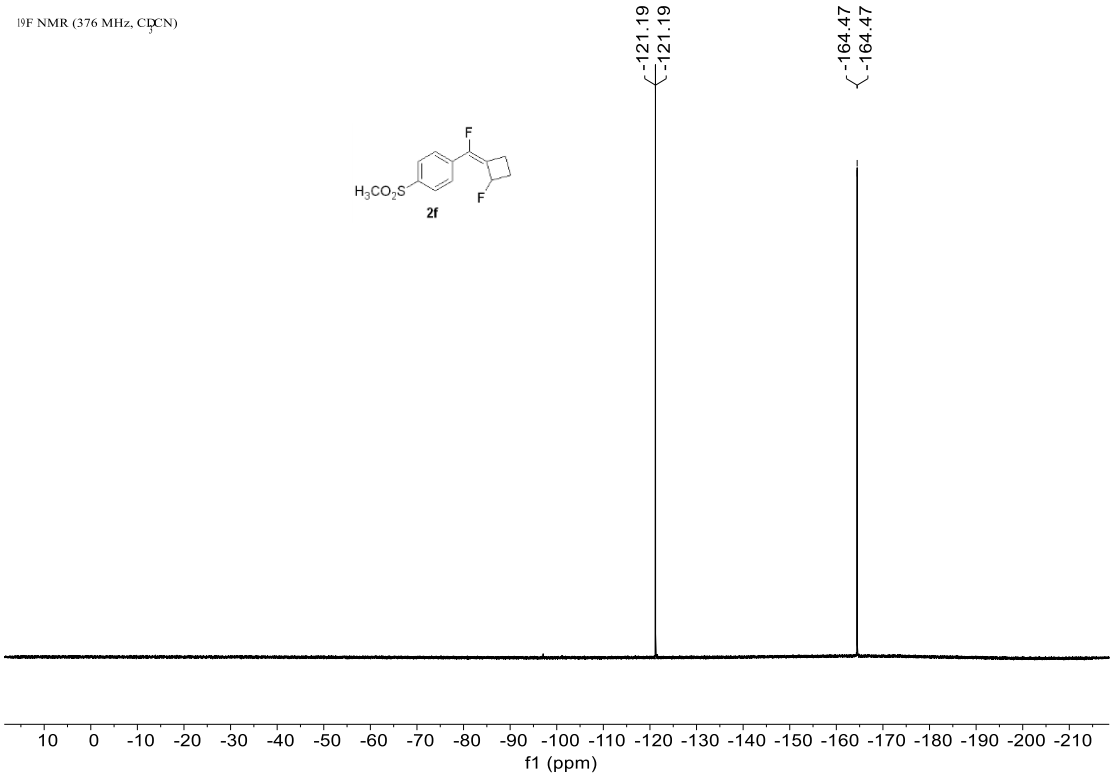


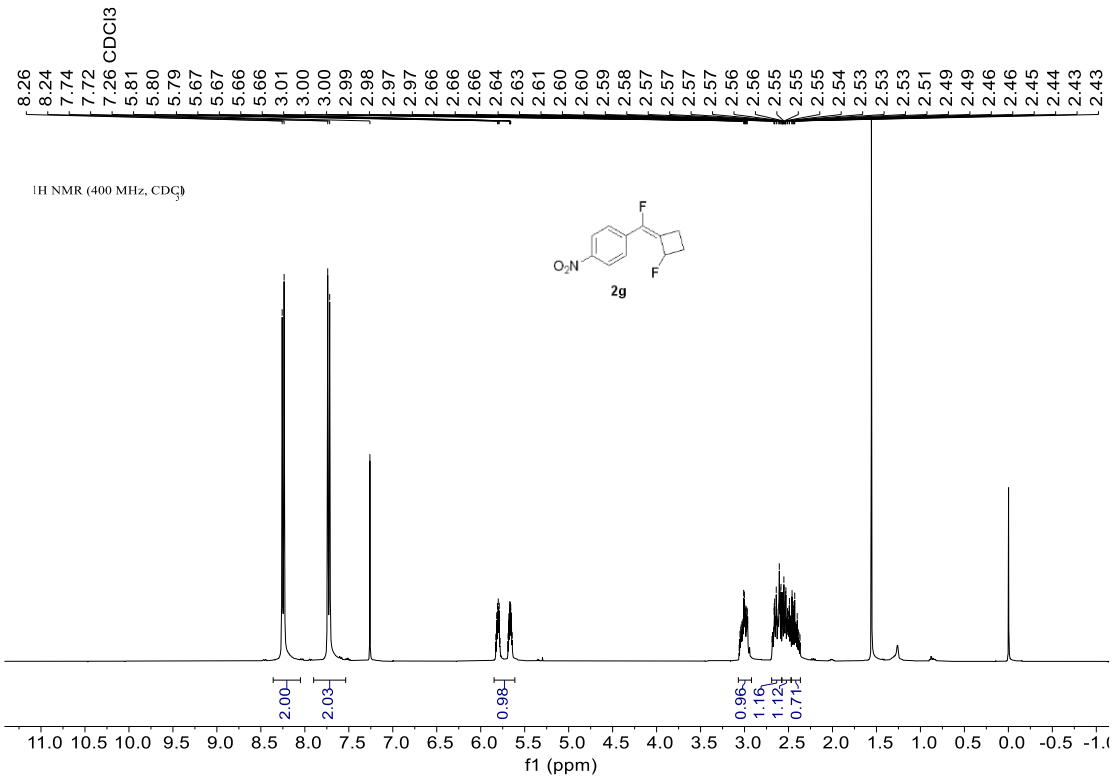


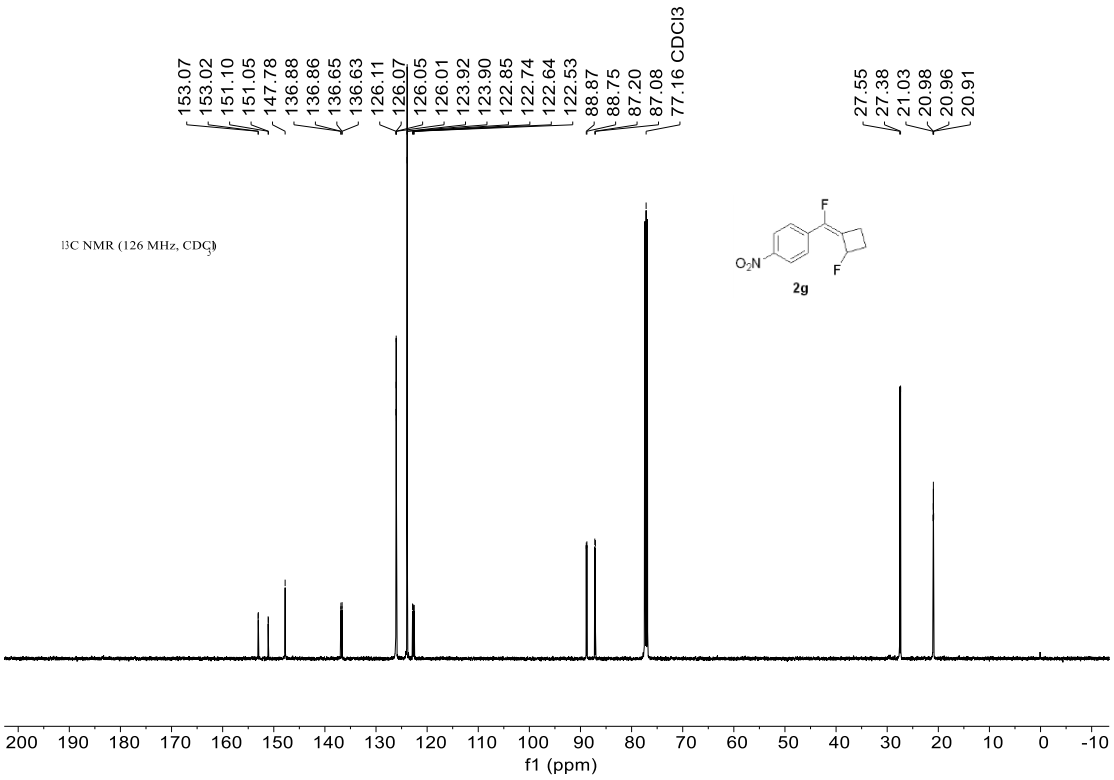
^{1}H NMR (400 MHz, C_3D_6O)



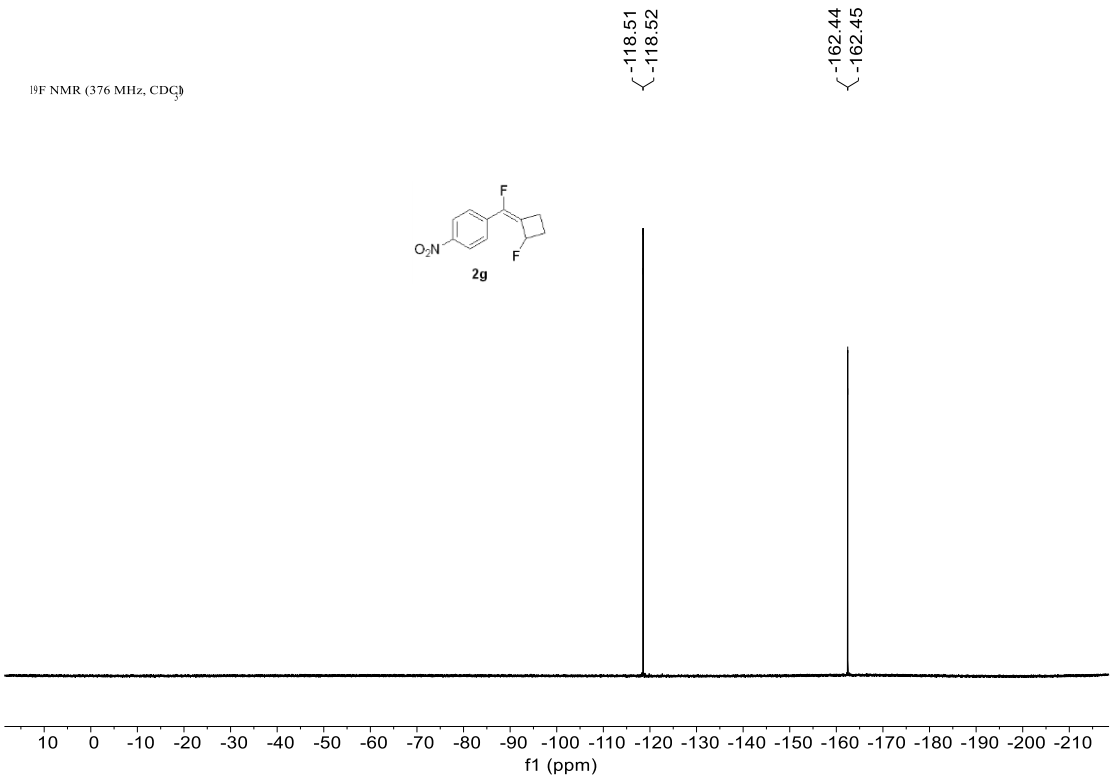

13C NMR (126 MHz, CD3CN)
153.59
153.54
151.64
151.59
141.96
136.51
136.49
136.28
136.26
128.54
128.52
126.78
126.74
126.72
126.68
123.49
123.38
123.28
123.17
89.93
89.80
88.28
88.16
44.36
28.01
27.84
21.14
21.09
21.07
21.02
F
H3CO2S
F
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

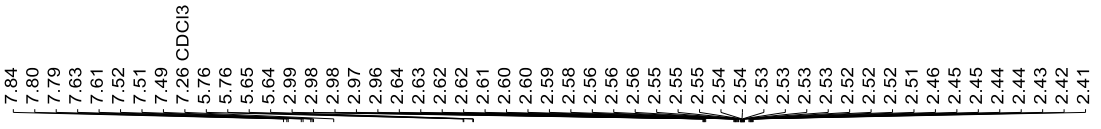

19F NMR (376 MHz, CD3CN)
-121.19
-121.19
-164.47
-164.47
F
H3CO2S
F
2f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.26 8.24 7.74 7.72 7.26 CDCl3 5.81 5.80 5.79 5.67 5.67 5.66 5.66 3.01 3.00 3.00 2.99 2.98 2.97 2.97 2.66 2.66 2.66 2.64 2.63 2.61 2.60 2.60 2.59 2.58 2.57 2.57 2.57 2.57 2.56 2.56 2.55 2.55 2.55 2.54 2.53 2.53 2.53 2.51 2.49 2.49 2.46 2.46 2.45 2.44 2.43 2.43
1H NMR (400 MHz, CDCl3)
F
O2N
F
2g
2.00
2.03
0.98
0.96
1.16
1.12
0.71
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

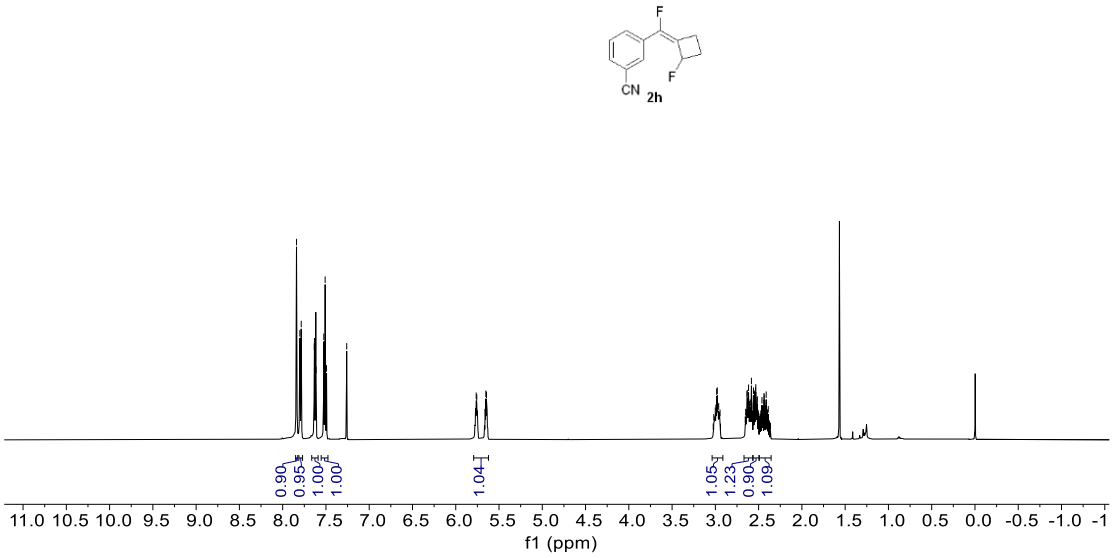

153.07 153.02 151.10 151.05 147.78 136.88 136.86 136.65 136.63 126.11 126.07 126.05 126.01 123.92 123.90 122.85 122.74 122.64 122.53 88.87 88.75 87.20 87.08 77.16 CDCl3
27.55 27.38 21.03 20.98 20.96 20.91
13C NMR (126 MHz, CDCl3)
F
O2N
F
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

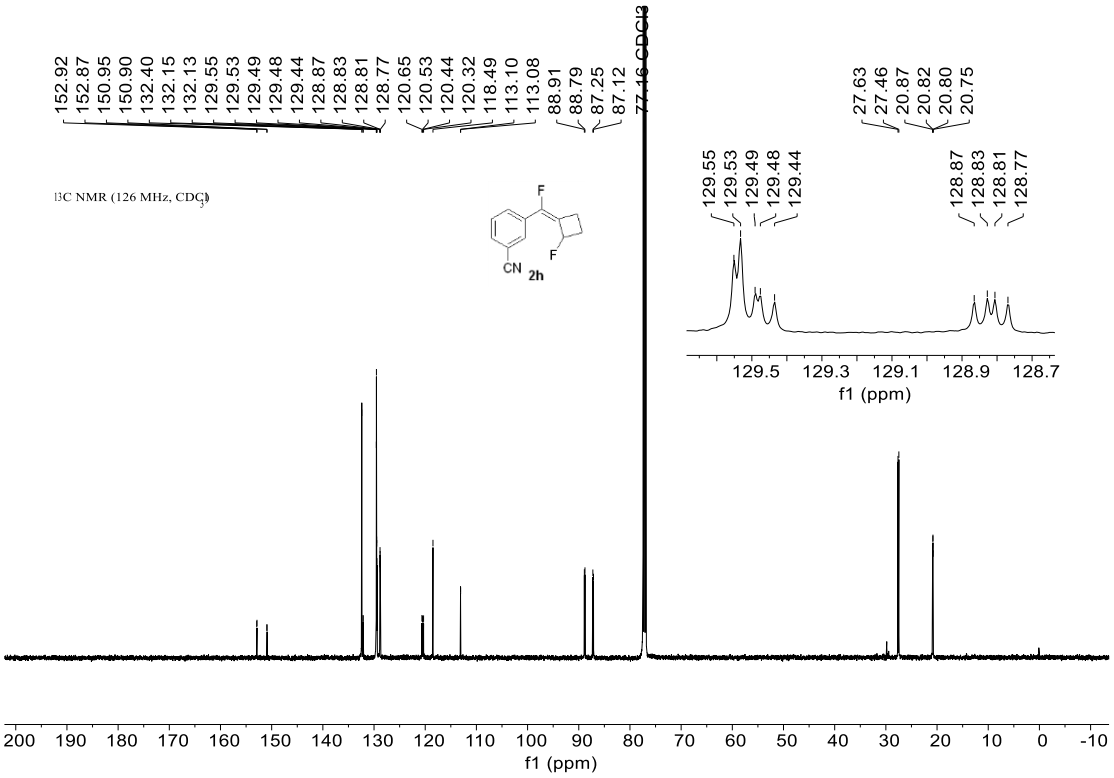
^{19}F NMR (376 MHz, $CDCl_3$)

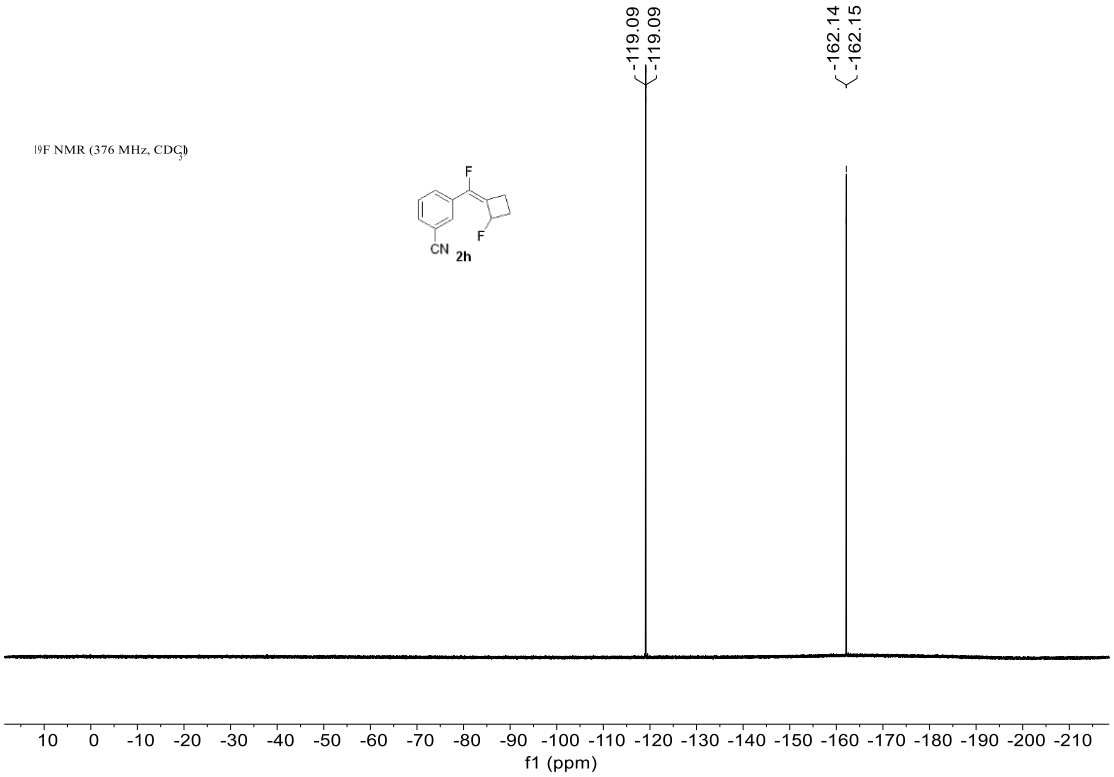


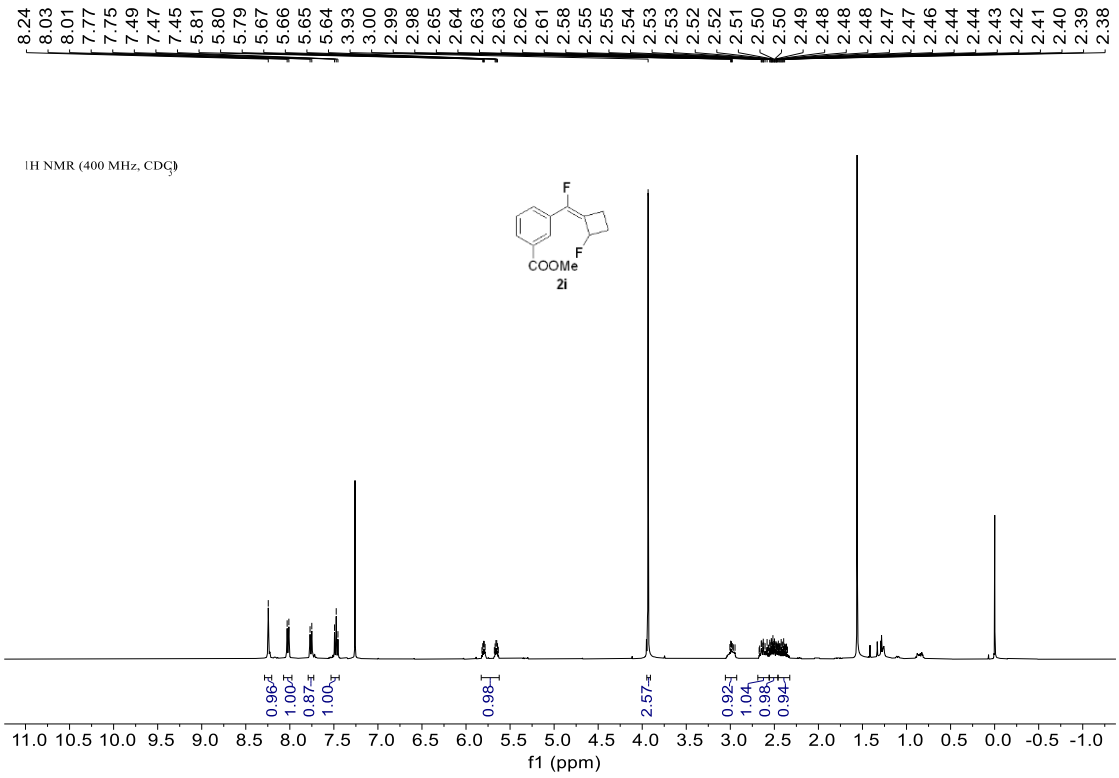


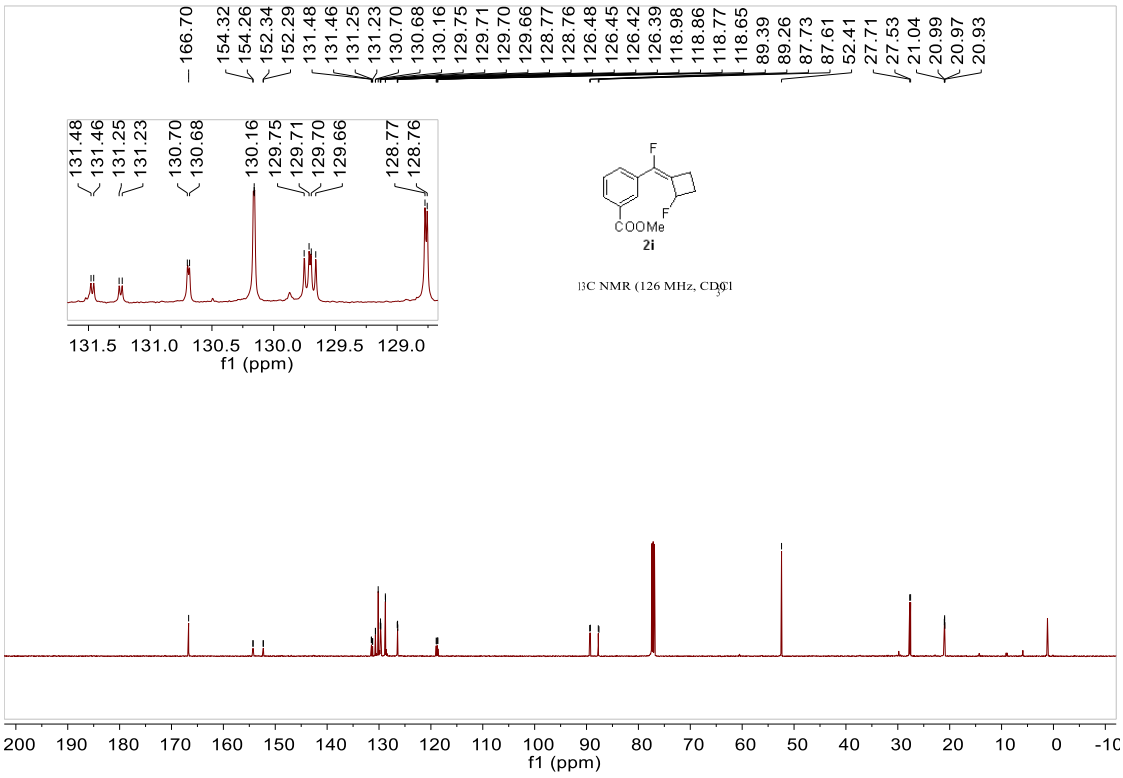
^{1}H NMR (500 MHz, $CDCl_3$)

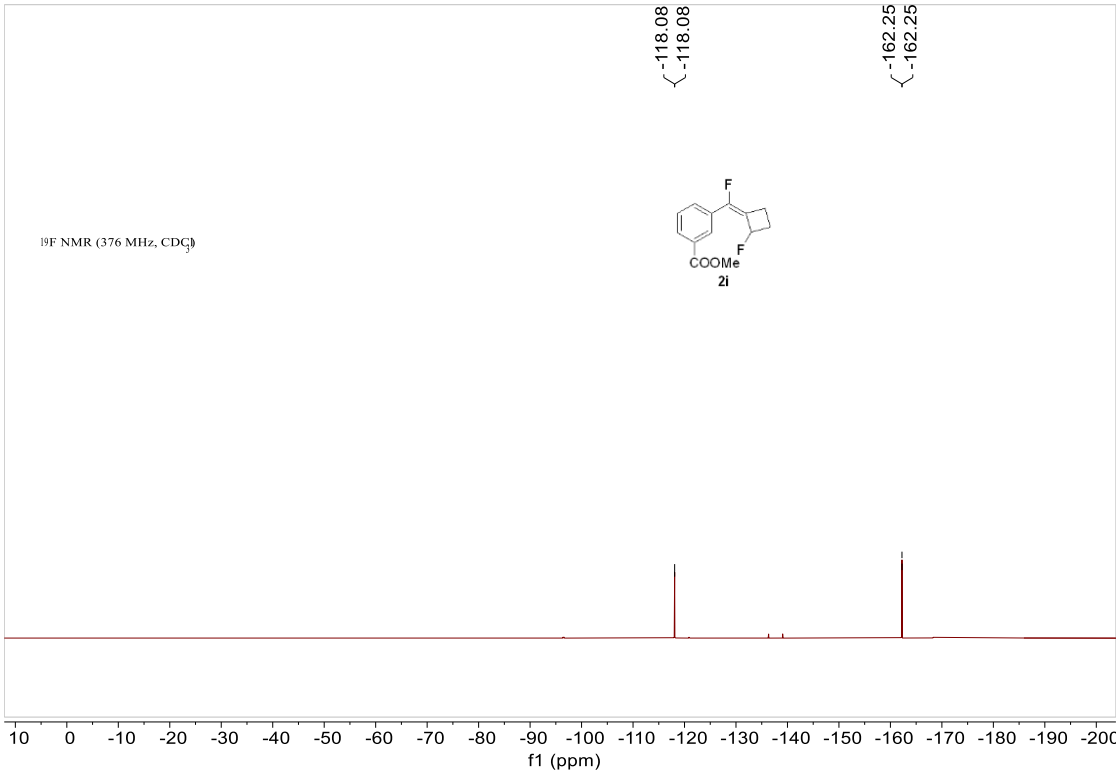


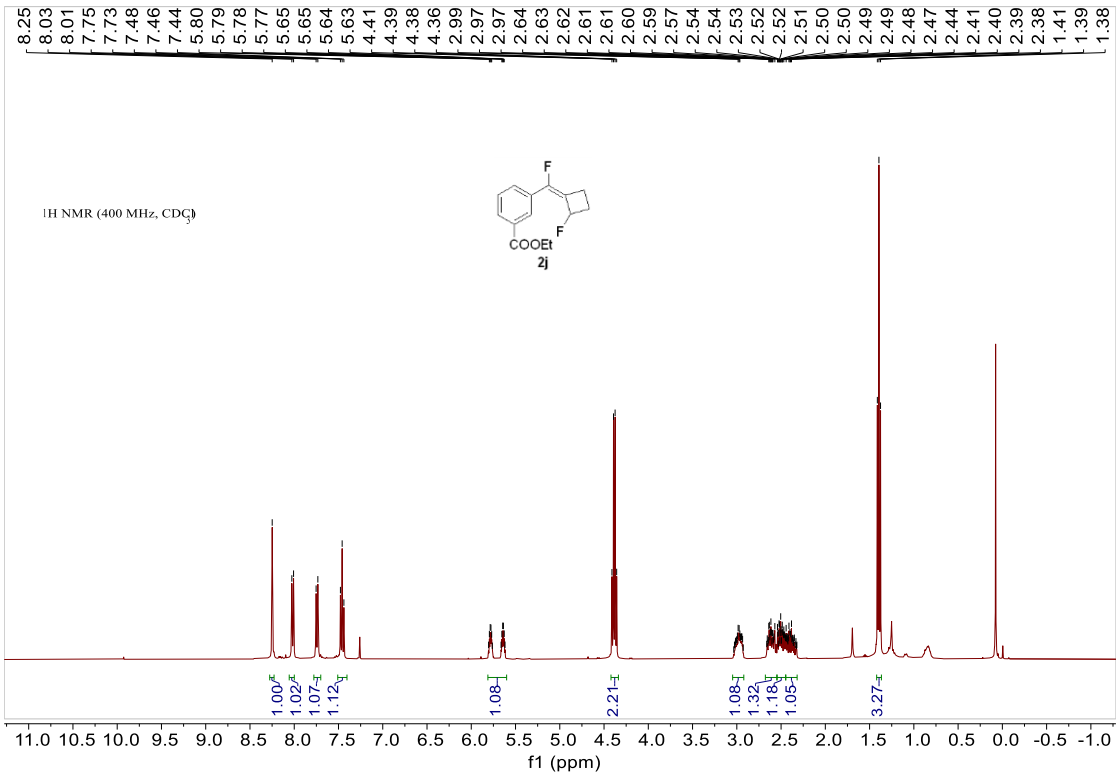

152.92
152.87
150.95
150.90
132.40
132.15
132.13
129.55
129.53
129.49
129.48
129.44
128.87
128.83
128.81
128.77
120.65
120.53
120.44
120.32
118.49
113.10
113.08
88.91
88.79
87.25
87.12
77.16 CDCl3
27.63
27.46
20.87
20.82
20.80
20.75
129.55
129.53
129.49
129.48
129.44
128.87
128.83
128.81
128.77
13C NMR (126 MHz, CDCl3)
F
F
CN
2h
129.5
129.3
129.1
128.9
128.7
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

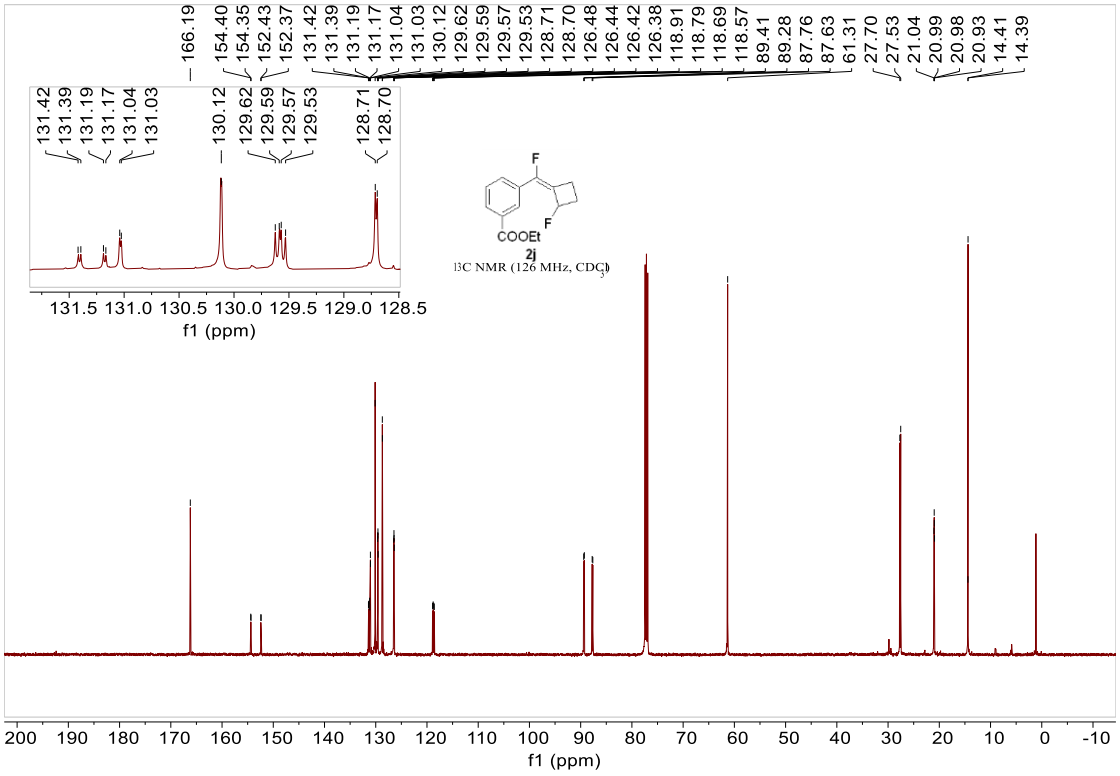

-119.09
-119.09
-162.14
-162.15
19F NMR (376 MHz, CDCl3)
F
F
CN
2h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

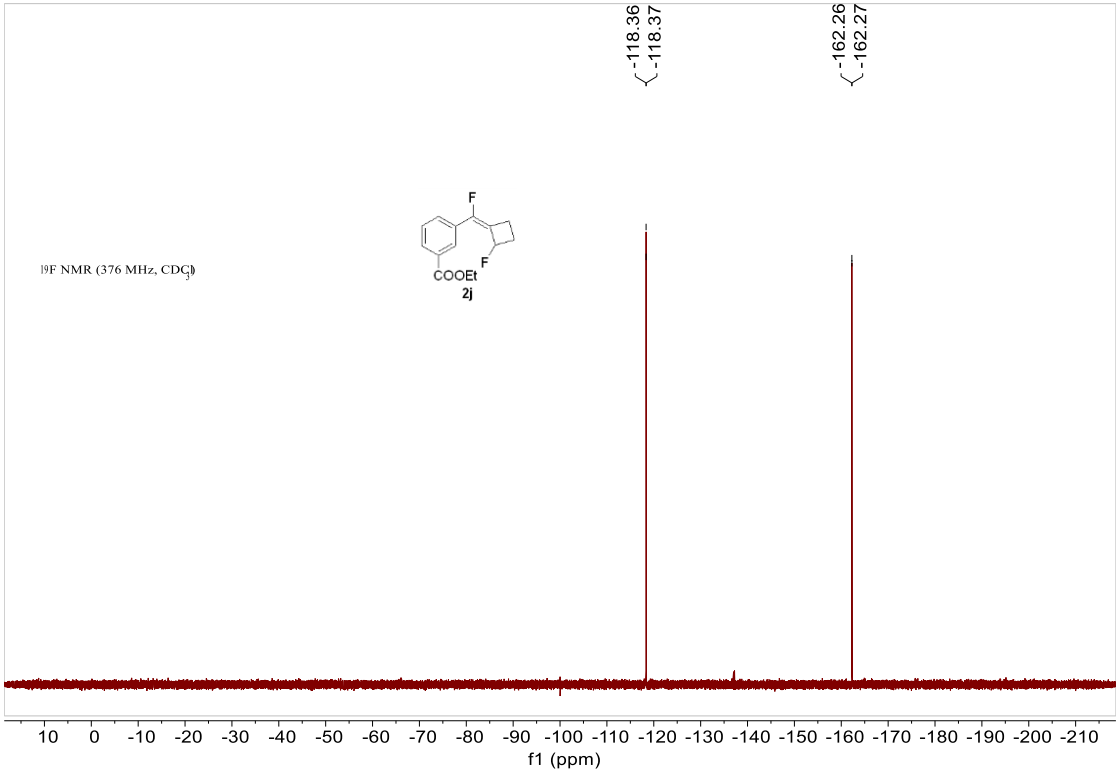

8.24 8.03 8.01 7.77 7.75 7.49 7.47 7.45 5.81 5.80 5.79 5.67 5.66 5.65 5.64 3.93 3.00 2.99 2.98 2.65 2.64 2.63 2.63 2.62 2.61 2.58 2.55 2.55 2.54 2.53 2.53 2.52 2.52 2.51 2.50 2.50 2.49 2.48 2.48 2.48 2.47 2.47 2.46 2.44 2.44 2.43 2.42 2.41 2.40 2.39 2.38
1H NMR (400 MHz, CDCl3)
F
F
COOMe
2i
0.96 1.00 0.87 1.00 0.98 2.57 0.92 1.04 0.98 0.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

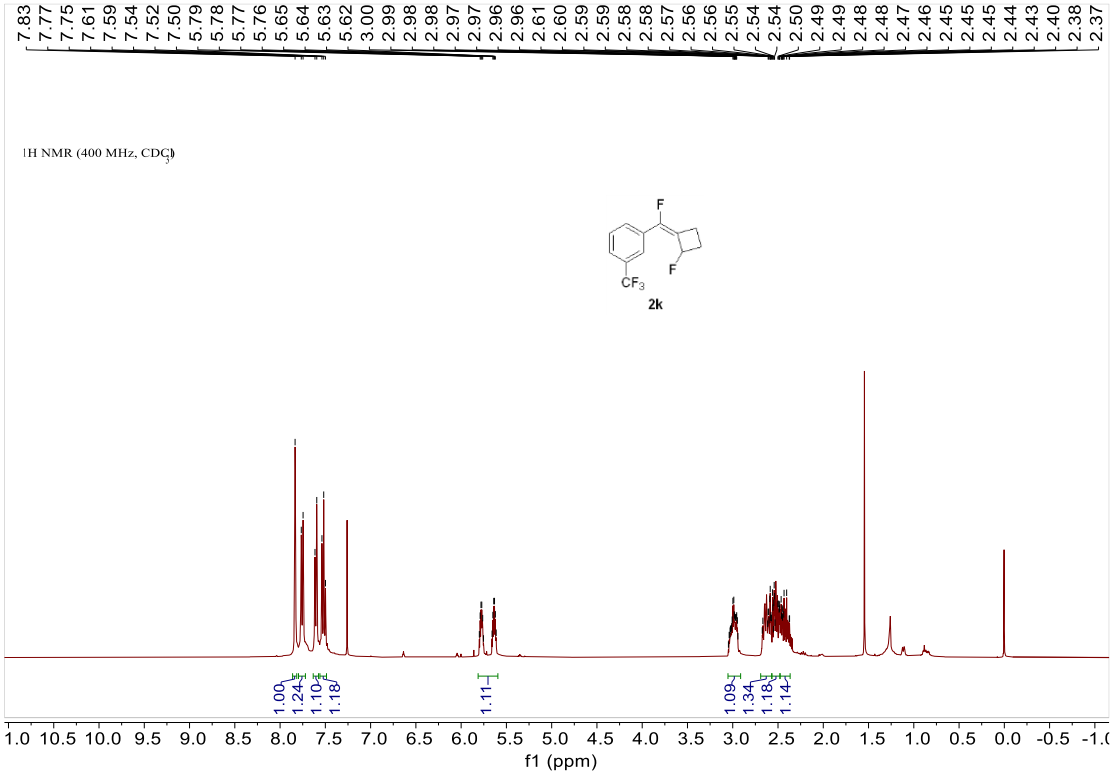

166.70 154.32 154.26 152.34 152.29 131.48 131.46 131.25 131.23 130.70 130.68 130.16 129.75 129.71 129.70 129.66 128.77 128.76 126.48 126.45 126.42 126.39 118.98 118.86 118.77 118.65 89.39 89.26 87.73 87.61 52.41 27.71 27.53 21.04 20.99 20.97 20.93
131.48 131.46 131.25 131.23 130.70 130.68 130.16 129.75 129.71 129.70 129.66 128.77 128.76
131.5 131.0 130.5 130.0 129.5 129.0
f1 (ppm)
F
F
COOMe
2i
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

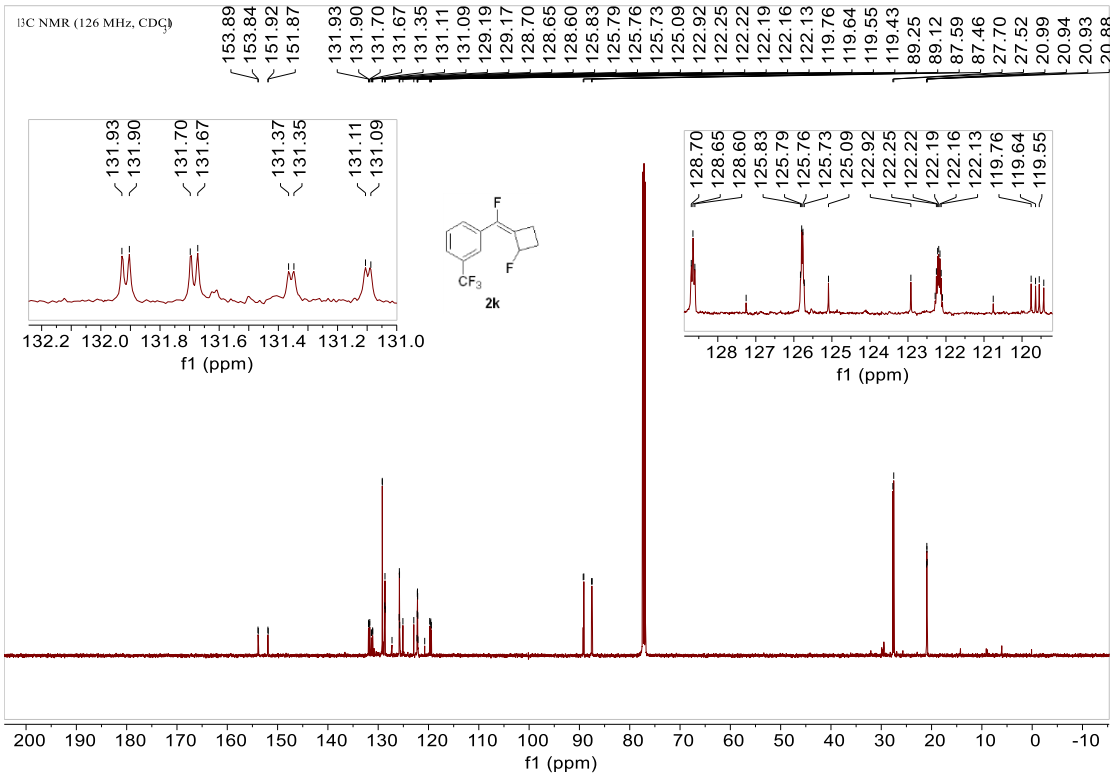

-118.08
-118.08
-162.25
-162.25
19F NMR (376 MHz, CDCl3)
F
F
COOMe
2i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

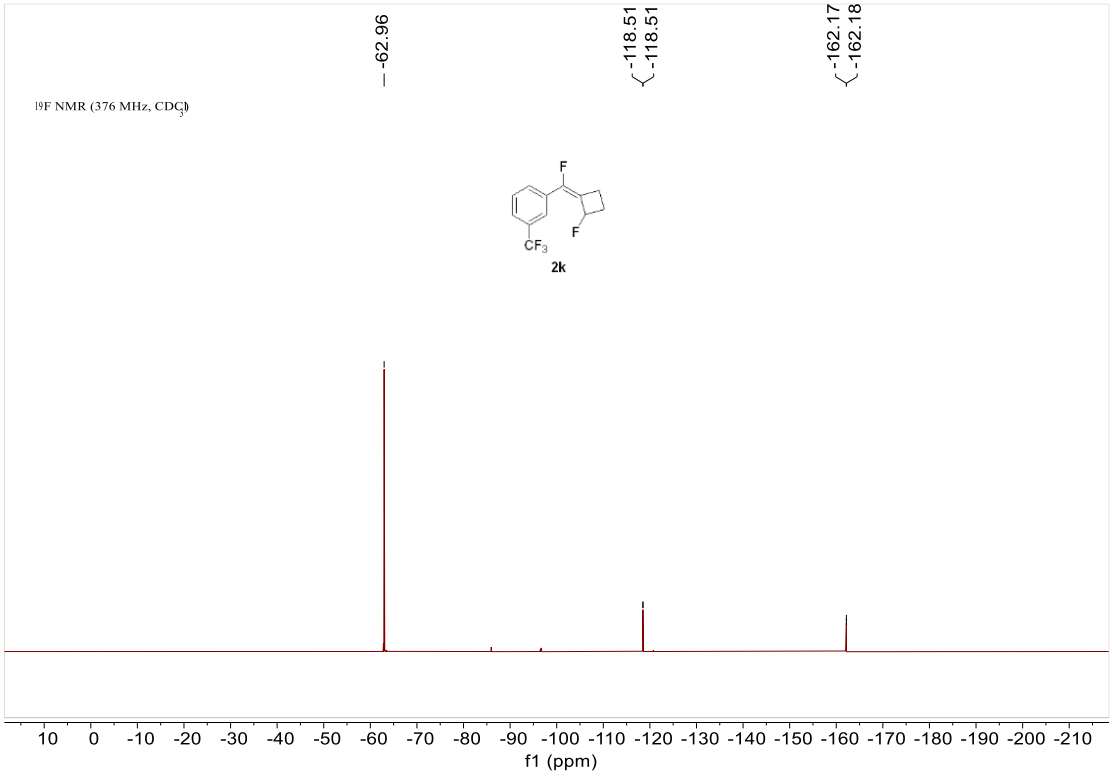

8.25 8.03 8.01 7.75 7.73 7.48 7.46 7.44 5.80 5.79 5.78 5.77 5.65 5.65 5.64 5.63 4.41 4.39 4.38 4.36 2.99 2.97 2.97 2.64 2.63 2.62 2.61 2.61 2.60 2.59 2.57 2.54 2.54 2.53 2.52 2.52 2.51 2.50 2.50 2.49 2.49 2.48 2.47 2.44 2.41 2.40 2.39 2.38 1.41 1.39 1.38
1H NMR (400 MHz, CDCl3)
F
F
COOEt
2j
1.00 1.02 1.07 1.12 1.08 2.21 1.08 1.32 1.18 1.05 3.27
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

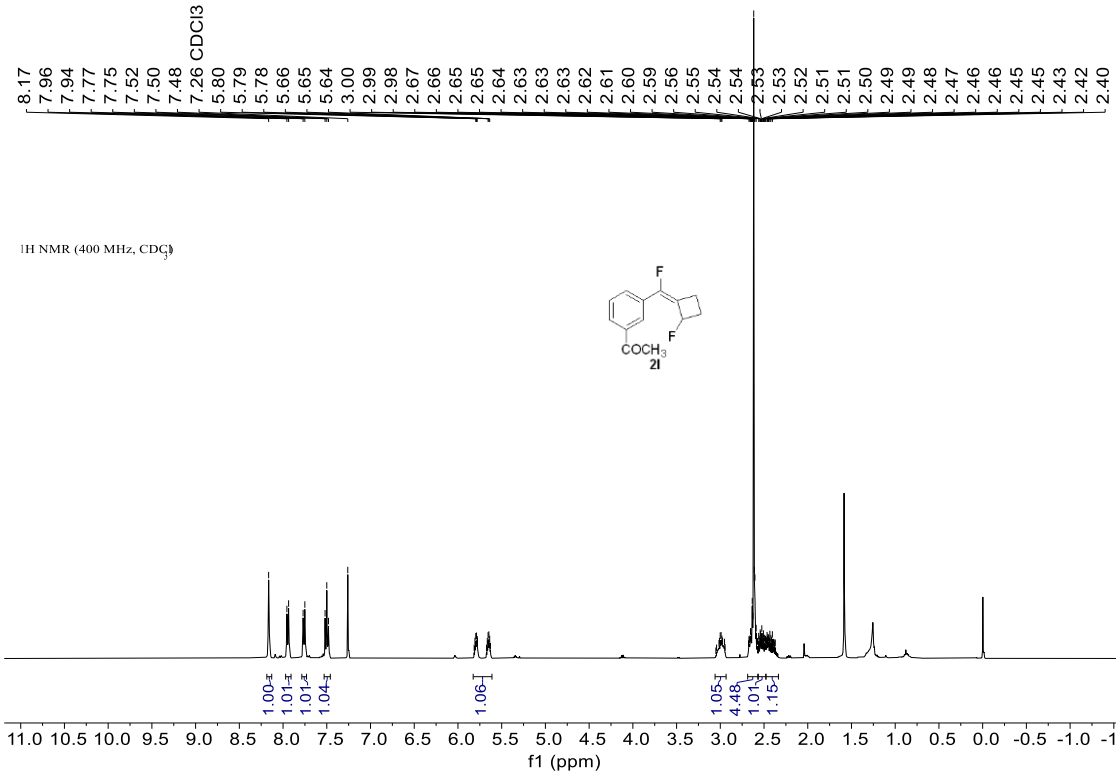

166.19
154.40
154.35
152.43
152.37
131.42
131.39
131.19
131.17
131.04
131.03
130.12
129.62
129.59
129.57
129.53
128.71
128.70
126.48
126.44
126.42
126.38
118.91
118.79
118.69
118.57
89.41
89.28
87.76
87.63
61.31
27.70
27.53
21.04
20.99
20.98
20.93
14.41
14.39
F
F
COOEt
2j
13C NMR (126 MHz, CDCl3)
131.5 131.0 130.5 130.0 129.5 129.0 128.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

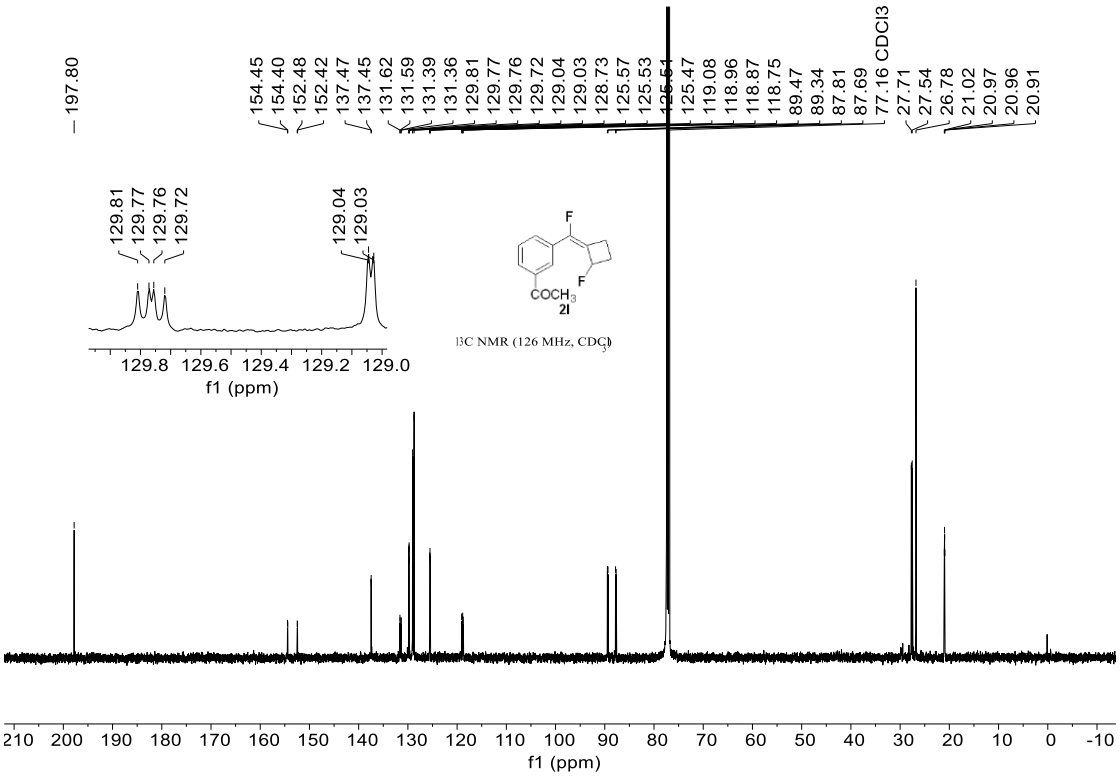

-118.36
-118.37
-162.26
-162.27
19F NMR (376 MHz, CDCl3)
F
F
COOEt
2j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


1H NMR (400 MHz, CDCl3)
F
F
CF3
2k
1.00
1.24
1.10
1.18
1.11
1.09
1.34
1.18
1.14
f1 (ppm)

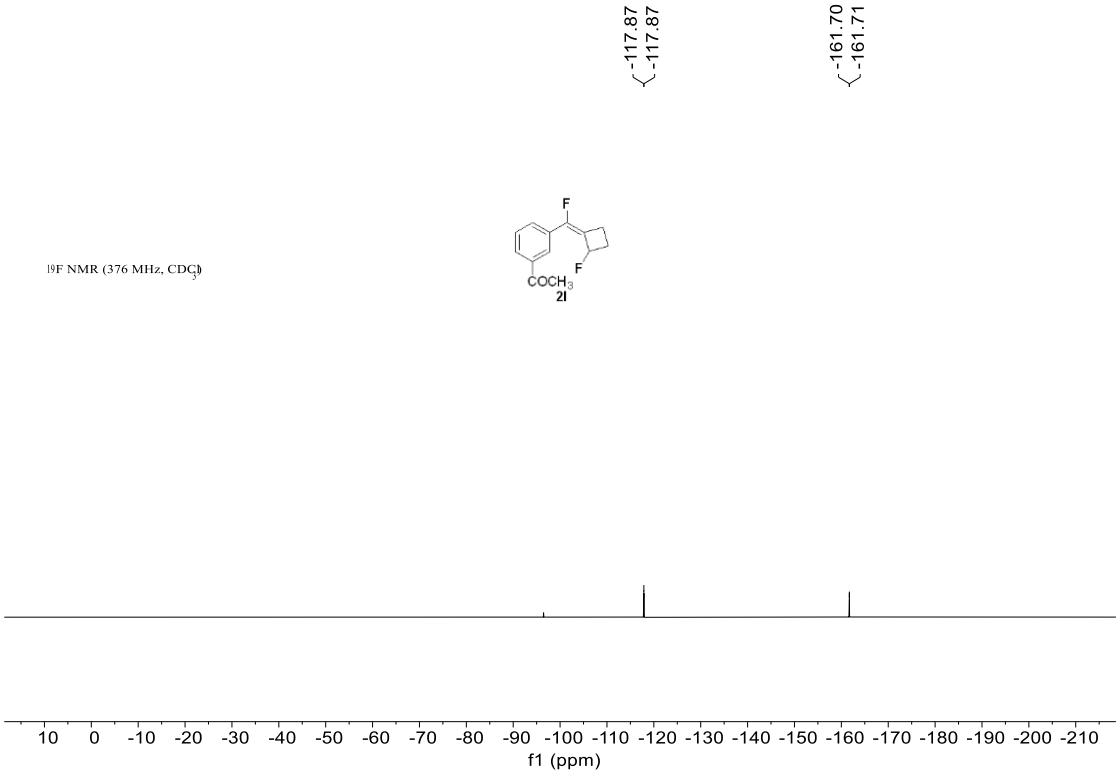

13C NMR (126 MHz, CDCl3)
153.89
153.84
151.92
151.87
131.93
131.90
131.70
131.67
131.35
131.11
131.09
129.19
129.17
128.70
128.65
128.60
125.83
125.79
125.76
125.73
125.09
122.92
122.25
122.22
122.19
122.16
122.13
119.76
119.64
119.55
119.43
89.25
89.12
87.59
87.46
27.70
27.52
20.99
20.94
20.93
F
F
CF3
2k
f1 (ppm)
f1 (ppm)
f1 (ppm)


-62.96
-118.51
-118.51
-162.17
-162.18
19F NMR (376 MHz, CDCl3)
F
F
CF3
2k
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

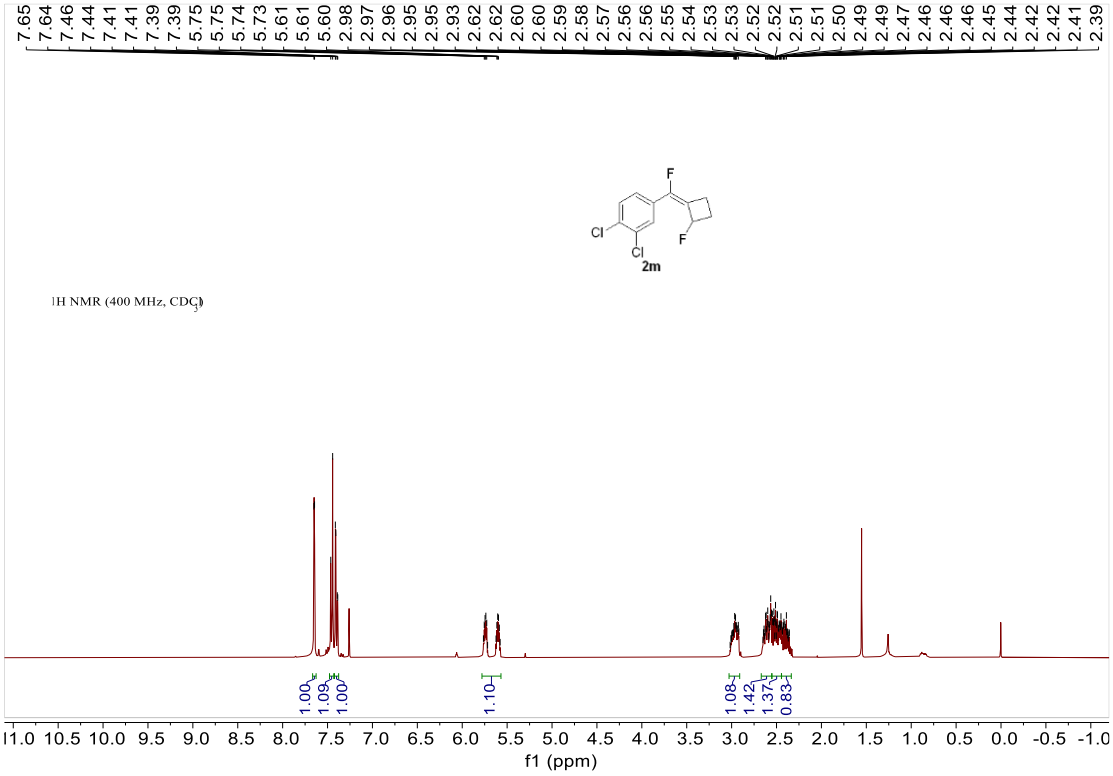

8.17 7.96 7.94 7.77 7.75 7.52 7.50 7.48 7.26 CDCl3 5.80 5.79 5.78 5.66 5.65 5.64 3.00 2.99 2.98 2.67 2.66 2.65 2.65 2.64 2.63 2.63 2.63 2.62 2.61 2.60 2.59 2.56 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.51 2.50 2.49 2.49 2.48 2.47 2.46 2.46 2.45 2.45 2.43 2.42 2.40
1H NMR (400 MHz, CDCl3)
F
F
COCH3
2l
1.00 1.01 1.01 1.04 1.06 1.05 4.48 1.01 1.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

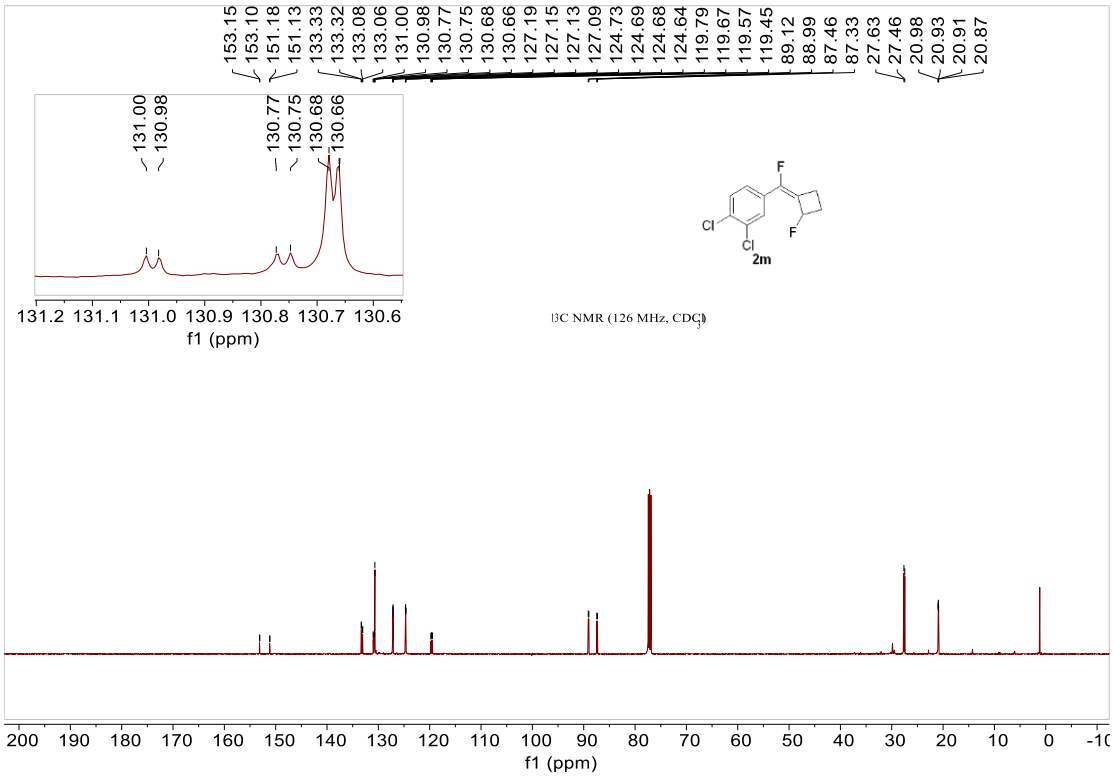


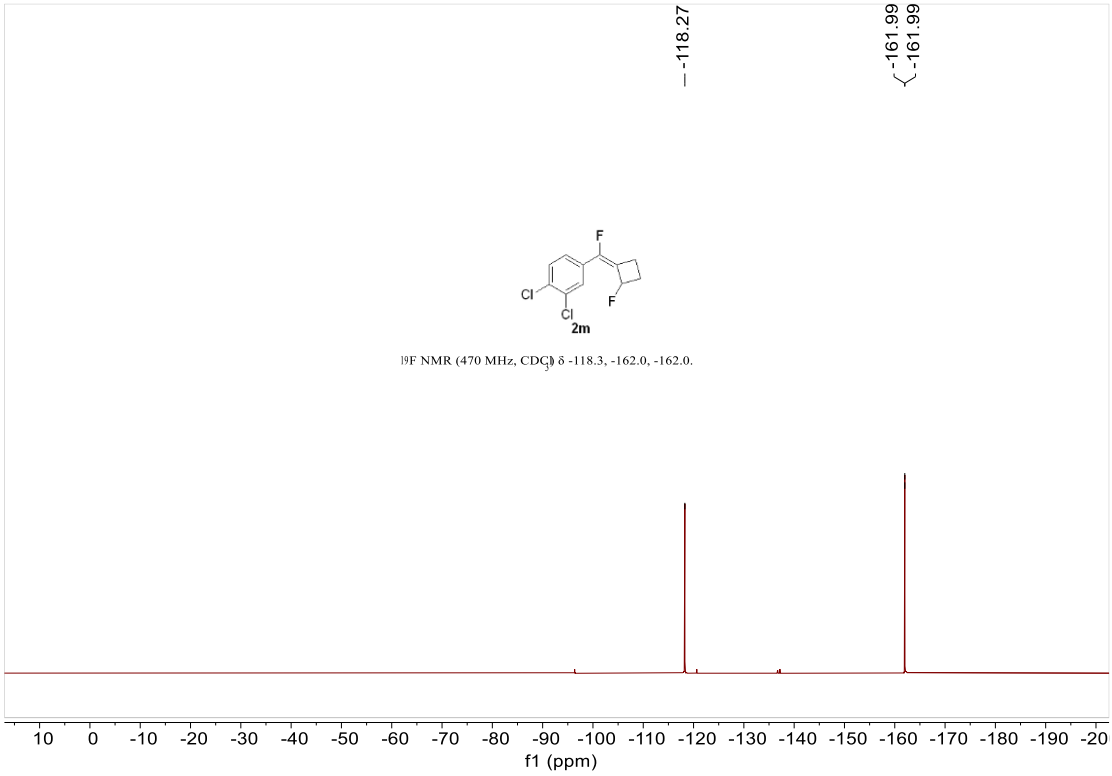
^{13}C NMR (126 MHz, $CDCl_3$)



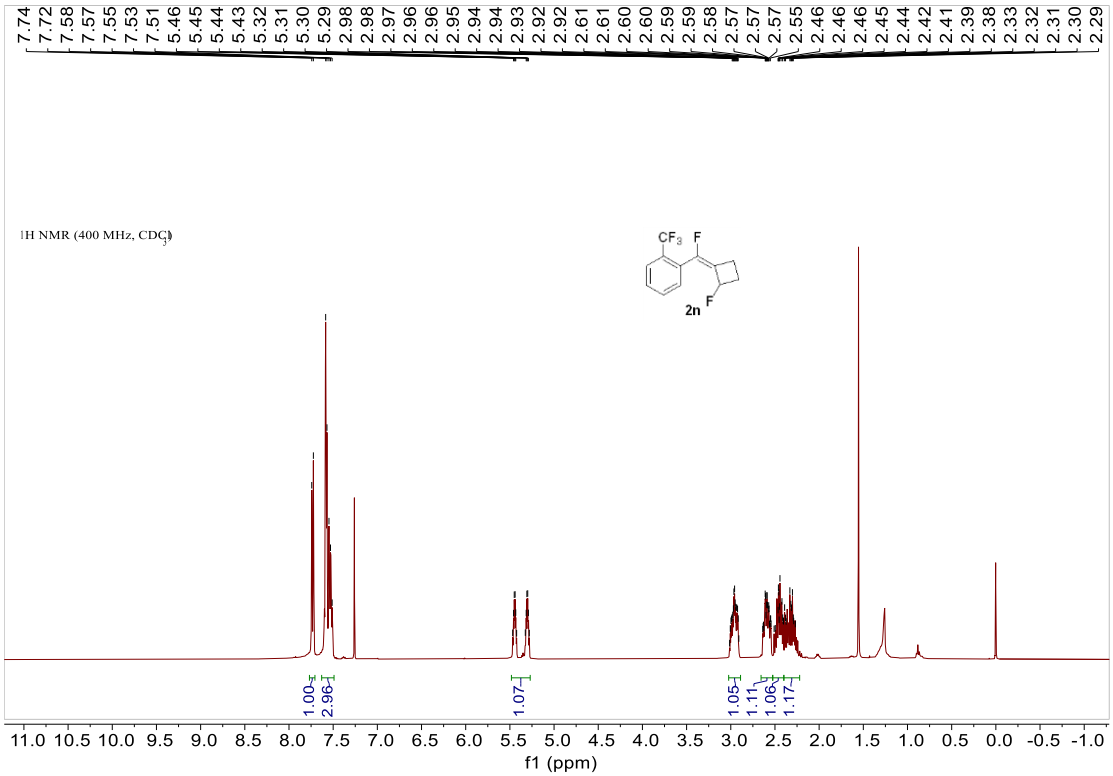
^{19}F NMR (376 MHz, $CDCl_3$)


7.65 7.64 7.46 7.44 7.41 7.41 7.39 7.39 5.75 5.75 5.74 5.73 5.61 5.61 5.60 2.98 2.97 2.96 2.95 2.95 2.93 2.62 2.62 2.60 2.60 2.59 2.58 2.57 2.56 2.56 2.55 2.54 2.53 2.53 2.52 2.52 2.51 2.51 2.50 2.49 2.49 2.47 2.46 2.46 2.46 2.45 2.44 2.42 2.42 2.41 2.39
F
Cl
Cl
F
2m
1H NMR (400 MHz, CDCl3)
1.00 1.09 1.00 1.10 1.08 1.42 1.37 0.83
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

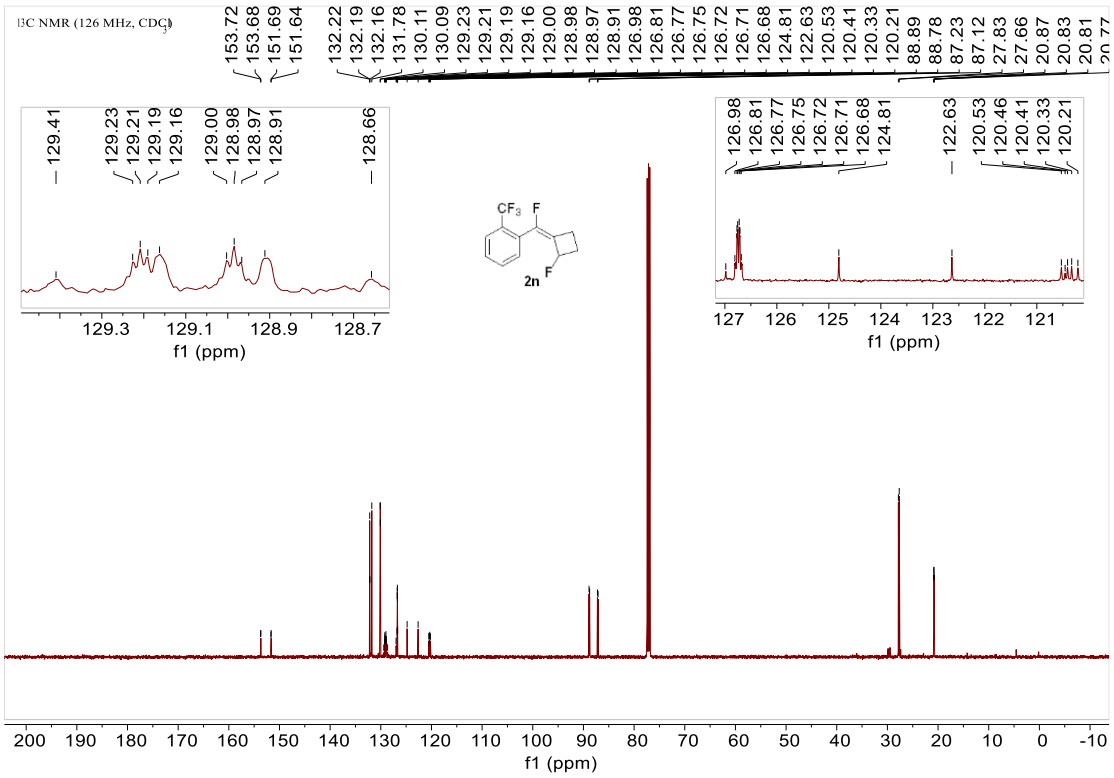

153.15 153.10 151.18 151.13 133.33 133.32 133.08 133.06 131.00 130.98 130.77 130.75 130.68 130.66 127.19 127.15 127.13 127.09 124.73 124.69 124.68 124.64 119.79 119.67 119.57 119.45 89.12 88.99 87.46 87.33 27.63 27.46 20.98 20.93 20.91 20.87
131.00 130.98 130.77 130.75 130.68 130.66
131.2 131.1 131.0 130.9 130.8 130.7 130.6
f1 (ppm)
F
Cl
Cl
F
2m
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

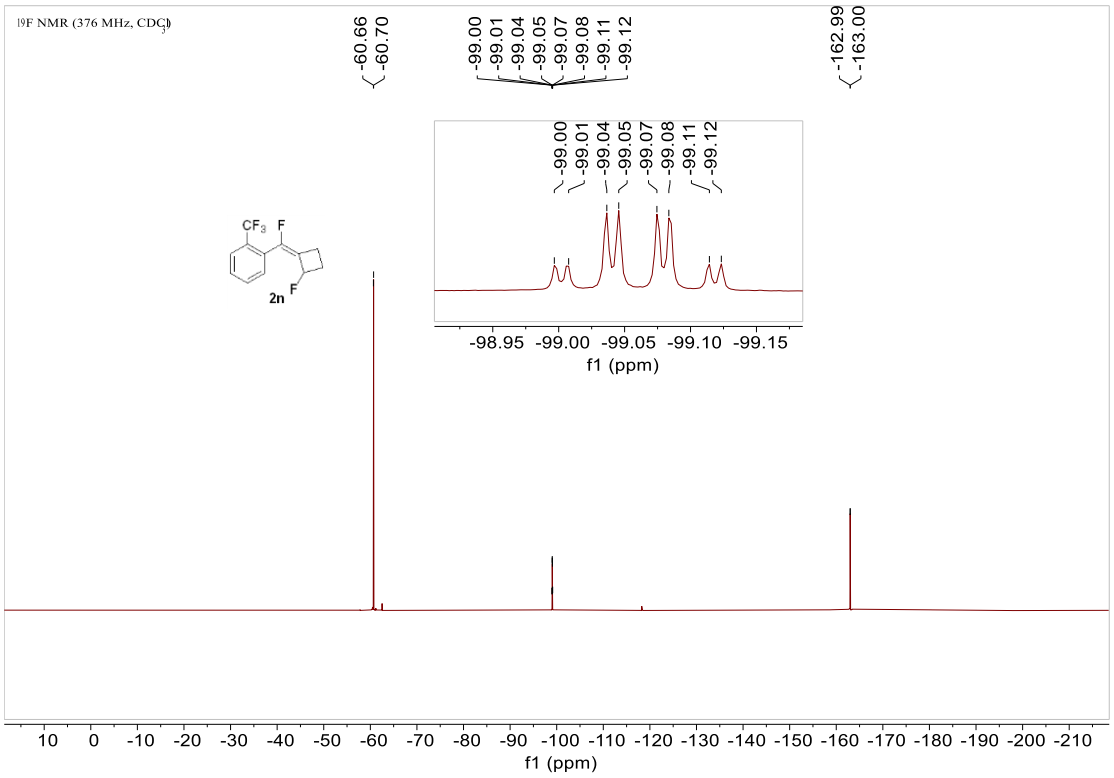


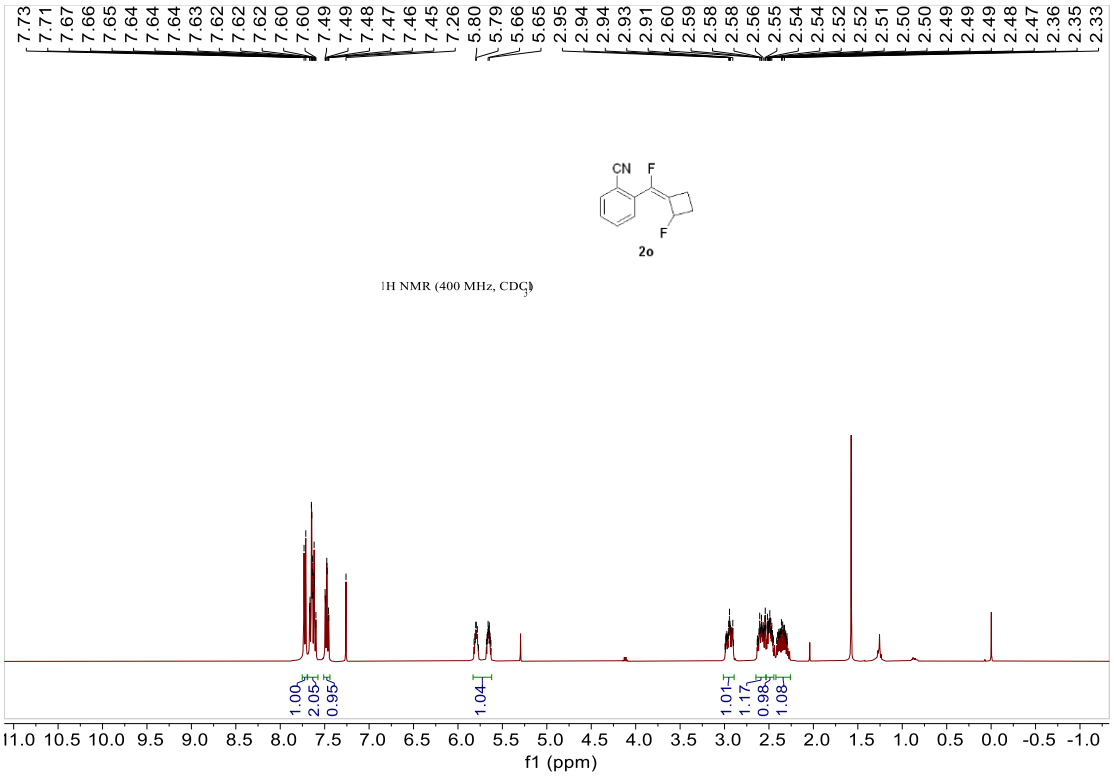
^{19}F NMR (470 MHz, $CDCl_3$) δ -118.3, -162.0, -162.0.

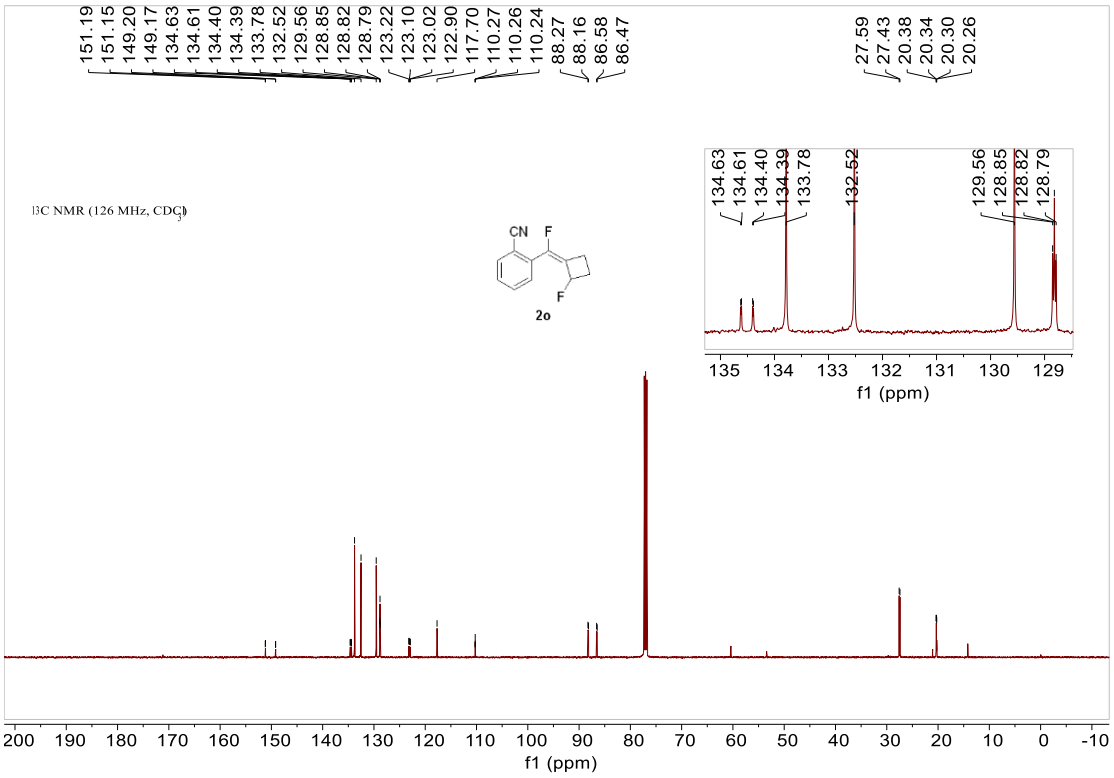


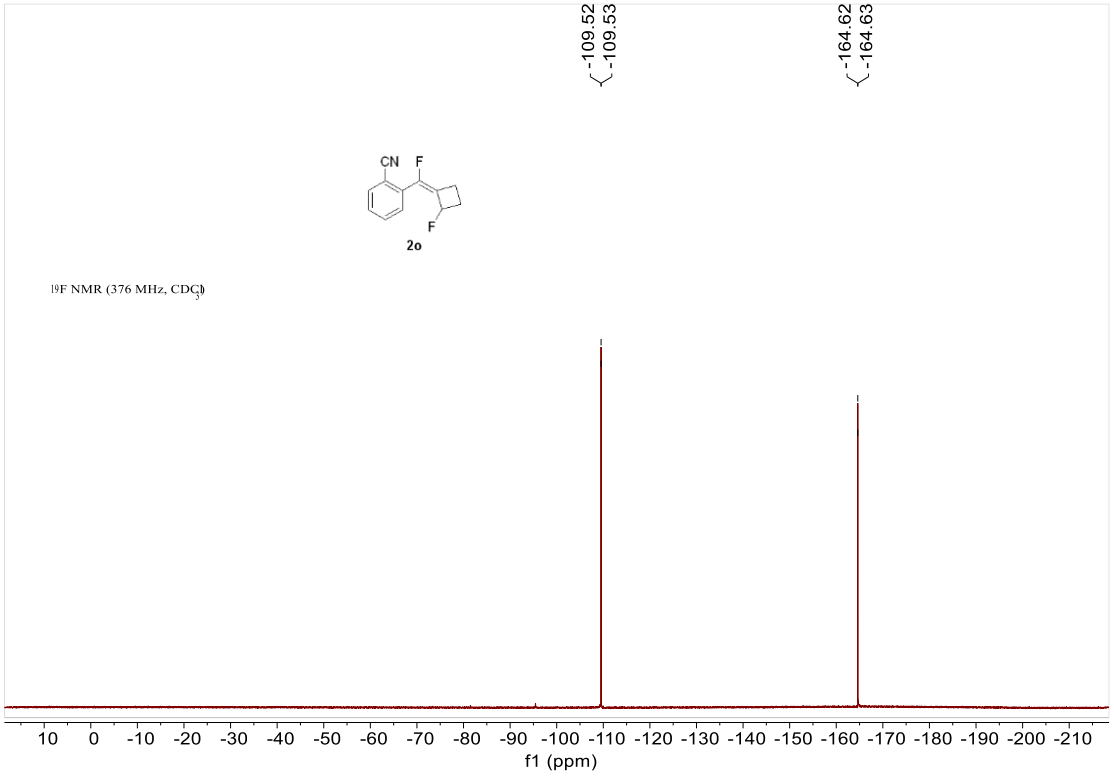
^{1}H NMR (400 MHz, $CDCl_3$)

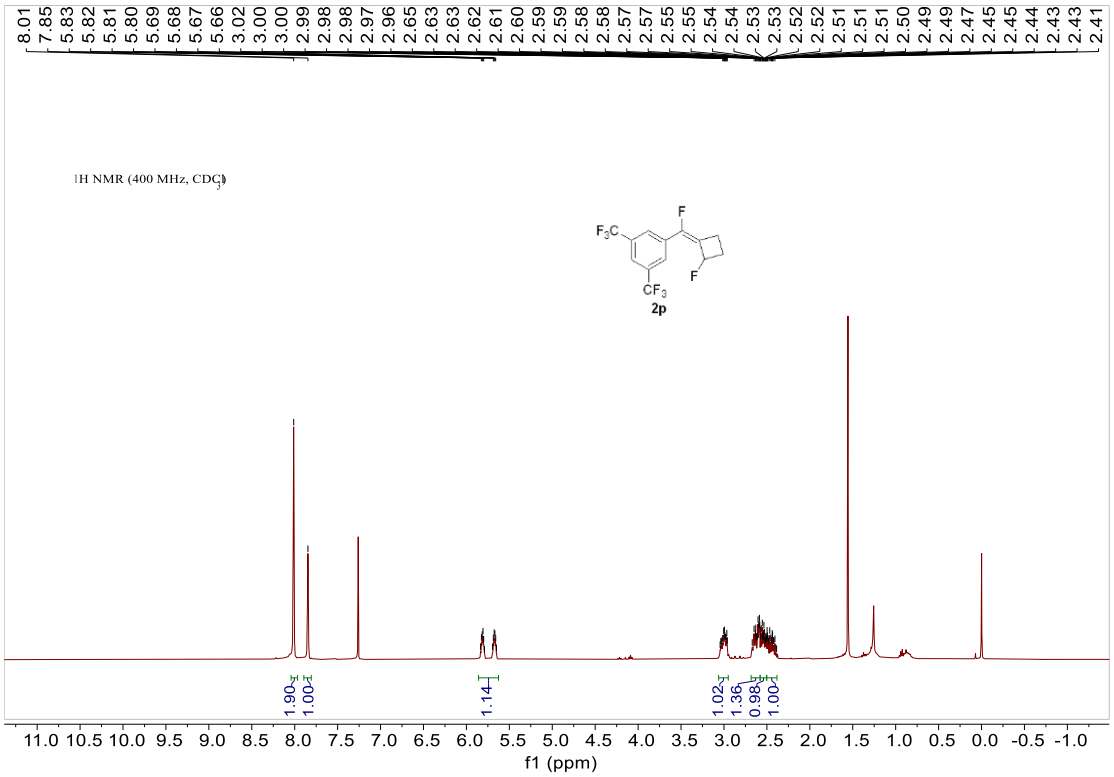

13C NMR (126 MHz, CDCl3)
153.72
153.68
151.69
151.64
132.22
132.19
132.16
131.78
130.11
130.09
129.23
129.21
129.19
129.16
129.00
128.98
128.97
128.91
126.98
126.81
126.77
126.75
126.72
126.71
126.68
124.81
122.63
120.53
120.41
120.33
120.21
88.89
88.78
87.23
87.12
27.83
27.66
20.87
20.83
20.81
129.41
129.23
129.21
129.19
129.16
129.00
128.98
128.97
128.91
128.66
129.3
129.1
128.9
128.7
f1 (ppm)
126.98
126.81
126.77
126.75
126.72
126.71
126.68
124.81
122.63
120.53
120.46
120.41
120.33
120.21
127
126
125
124
123
122
121
f1 (ppm)
CF3
F
F
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

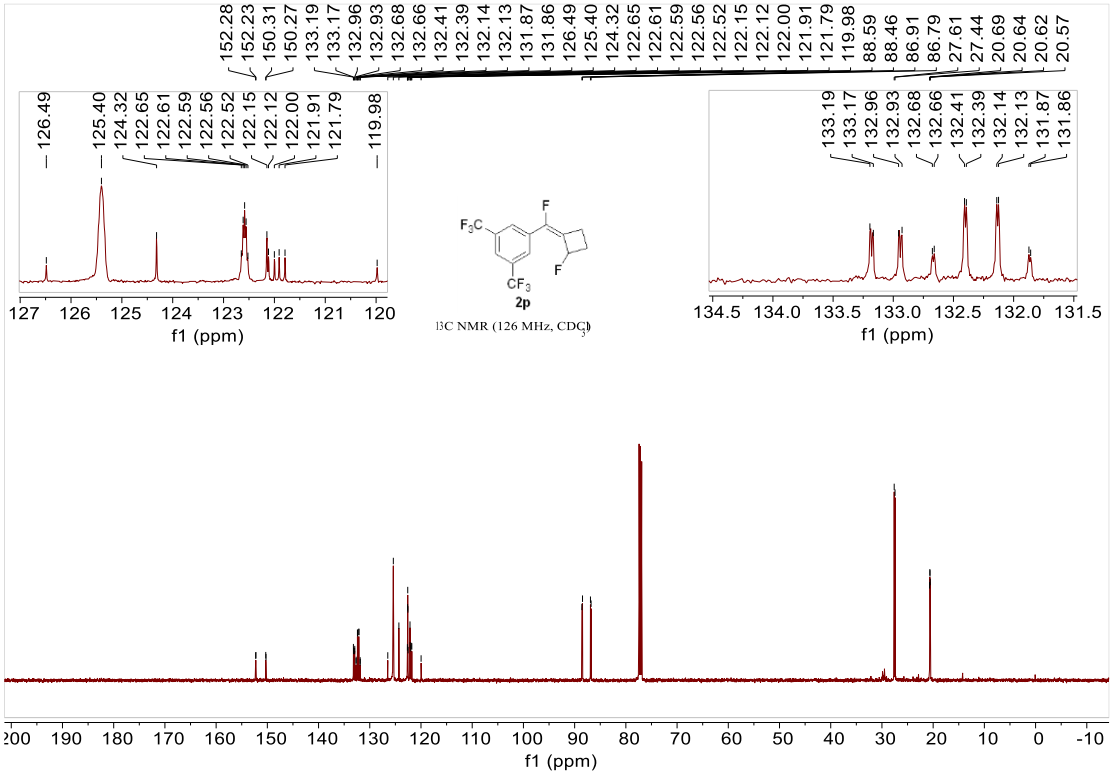

19F NMR (376 MHz, CDCl3)
-60.66
-60.70
-99.00
-99.01
-99.04
-99.05
-99.07
-99.08
-99.11
-99.12
-162.99
-163.00
-98.95
-99.00
-99.05
-99.10
-99.15
f1 (ppm)
CF3
F
F
2n
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

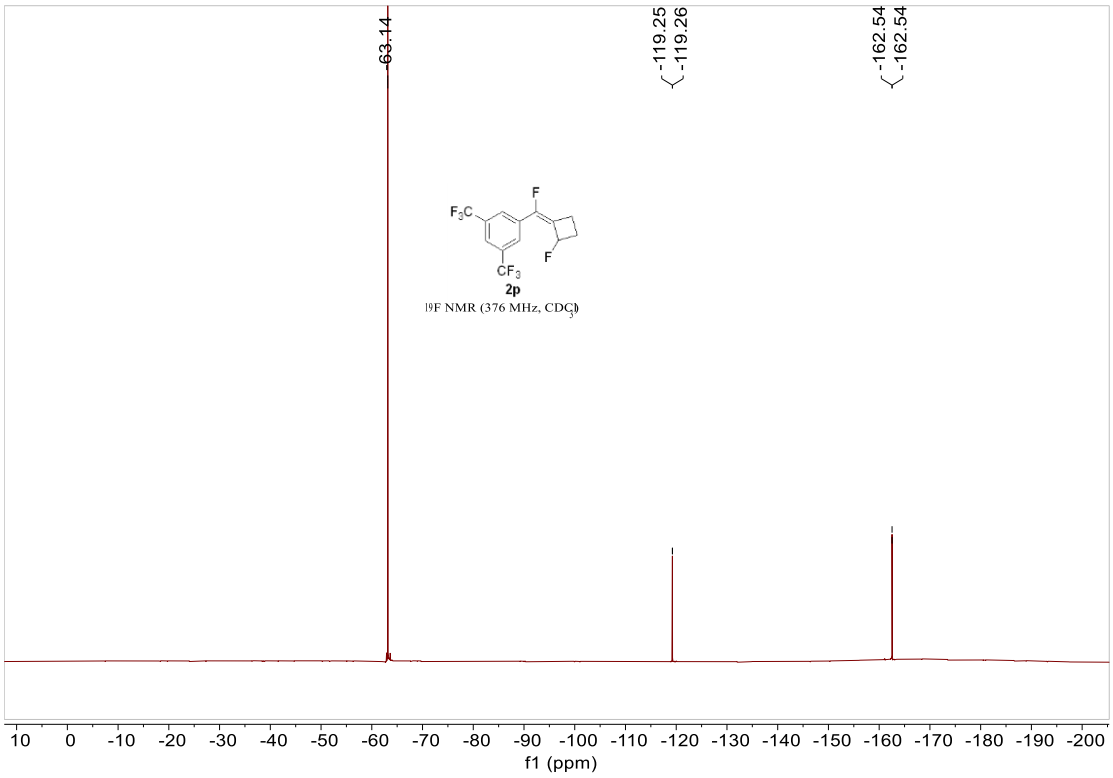

7.73 7.71 7.67 7.66 7.65 7.64 7.64 7.64 7.63 7.62 7.62 7.62 7.60 7.60 7.49 7.49 7.48 7.47 7.46 7.45 7.26 5.80 5.79 5.66 5.65 2.95 2.94 2.94 2.93 2.91 2.60 2.59 2.58 2.58 2.56 2.55 2.54 2.54 2.52 2.52 2.51 2.50 2.50 2.49 2.49 2.49 2.48 2.47 2.36 2.35 2.33
CN F
F
2o
1H NMR (400 MHz, CDCl3)
1.00 2.05 0.95 1.04 1.01 1.17 0.98 1.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

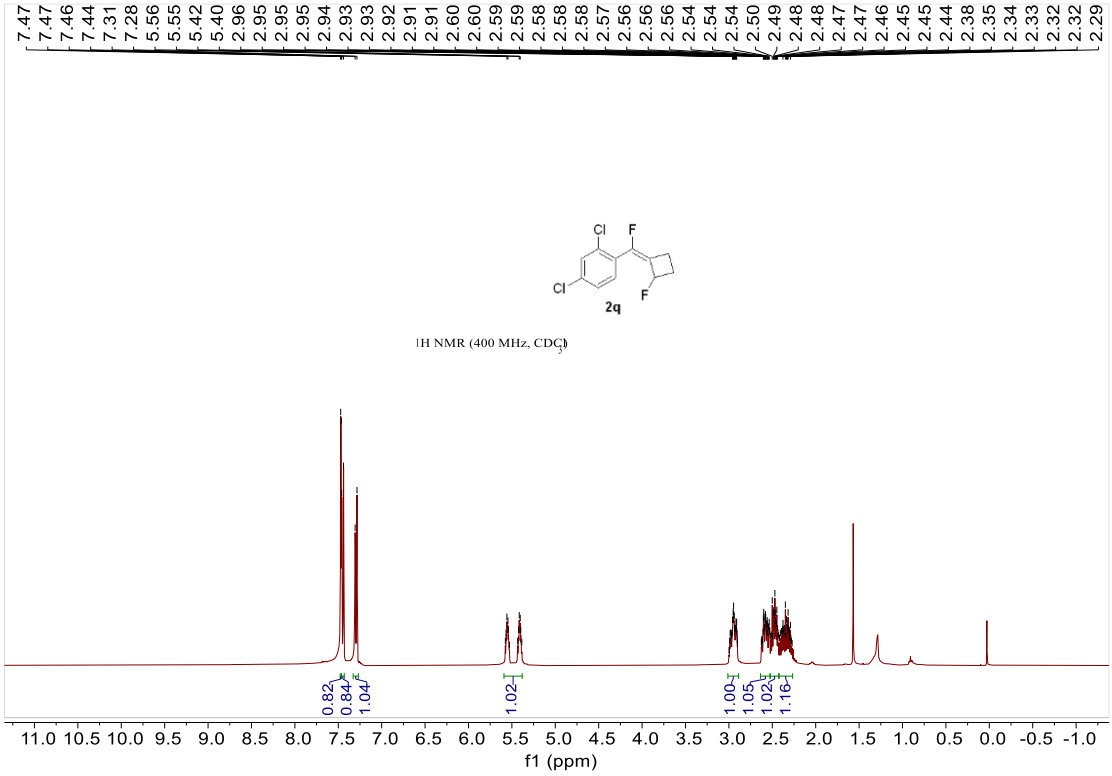

151.19 151.15 149.20 149.17 134.63 134.61 134.40 134.39 133.78 132.52 129.56 128.85 128.82 128.79 123.22 123.10 123.02 122.90 117.70 110.27 110.26 110.24 88.27 88.16 86.58 86.47
27.59 27.43 20.38 20.34 20.30 20.26
13C NMR (126 MHz, CDCl3)
CN F
F
2o
134.63 134.61 134.40 134.39 133.78 132.52 129.56 128.85 128.82 128.79
135 134 133 132 131 130 129
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

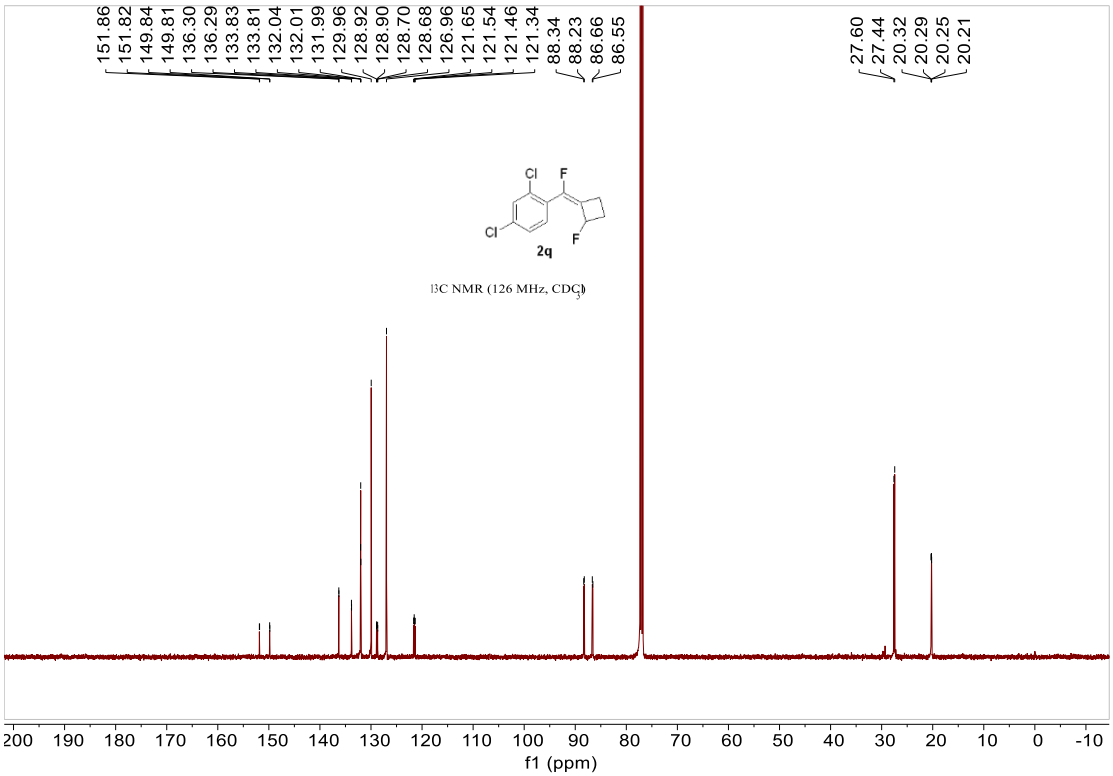

-109.52
-109.53
-164.62
-164.63
CN
F
F
2o
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

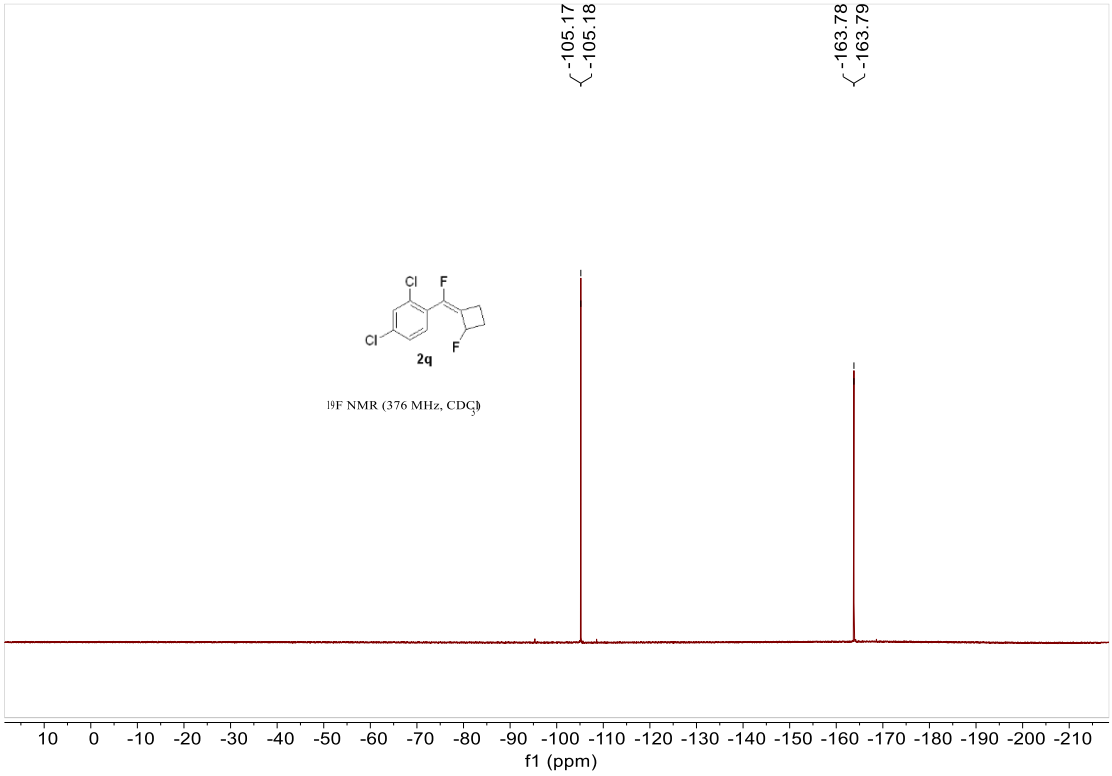

8.01 7.85 5.83 5.82 5.81 5.80 5.69 5.68 5.67 5.66 3.02 3.00 3.00 2.99 2.98 2.98 2.97 2.96 2.65 2.63 2.63 2.62 2.61 2.60 2.59 2.59 2.58 2.58 2.57 2.57 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.52 2.51 2.51 2.51 2.50 2.49 2.49 2.47 2.45 2.45 2.44 2.43 2.43 2.41
1H NMR (400 MHz, CDCl3)
F
F3C
CF3
F
2p
1.90
1.00
1.14
1.02
1.36
0.98
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

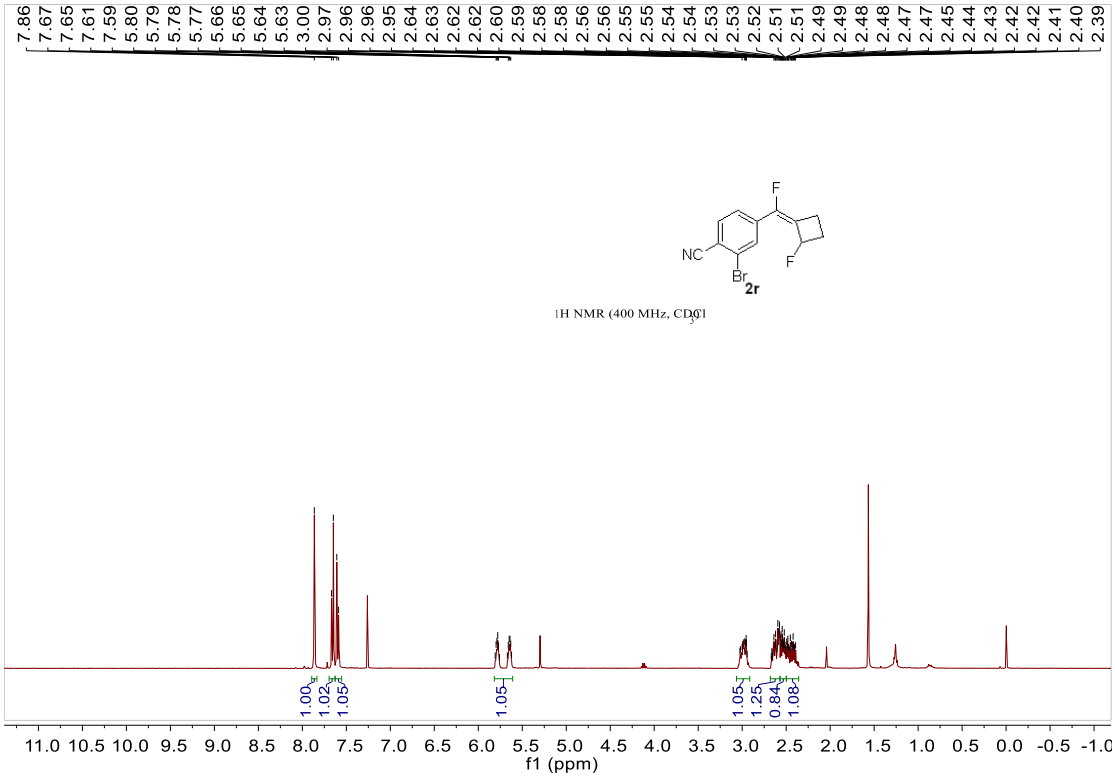

152.28
152.23
150.31
150.27
133.19
133.17
132.96
132.93
132.68
132.66
132.41
132.39
132.14
132.13
131.87
131.86
126.49
125.40
124.32
122.65
122.61
122.59
122.56
122.52
122.15
122.12
122.00
121.91
121.79
119.98
88.59
88.46
86.91
86.79
27.61
27.44
20.69
20.64
20.62
20.57
F3C
CF3
F
F
2p
13C NMR (126 MHz, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)

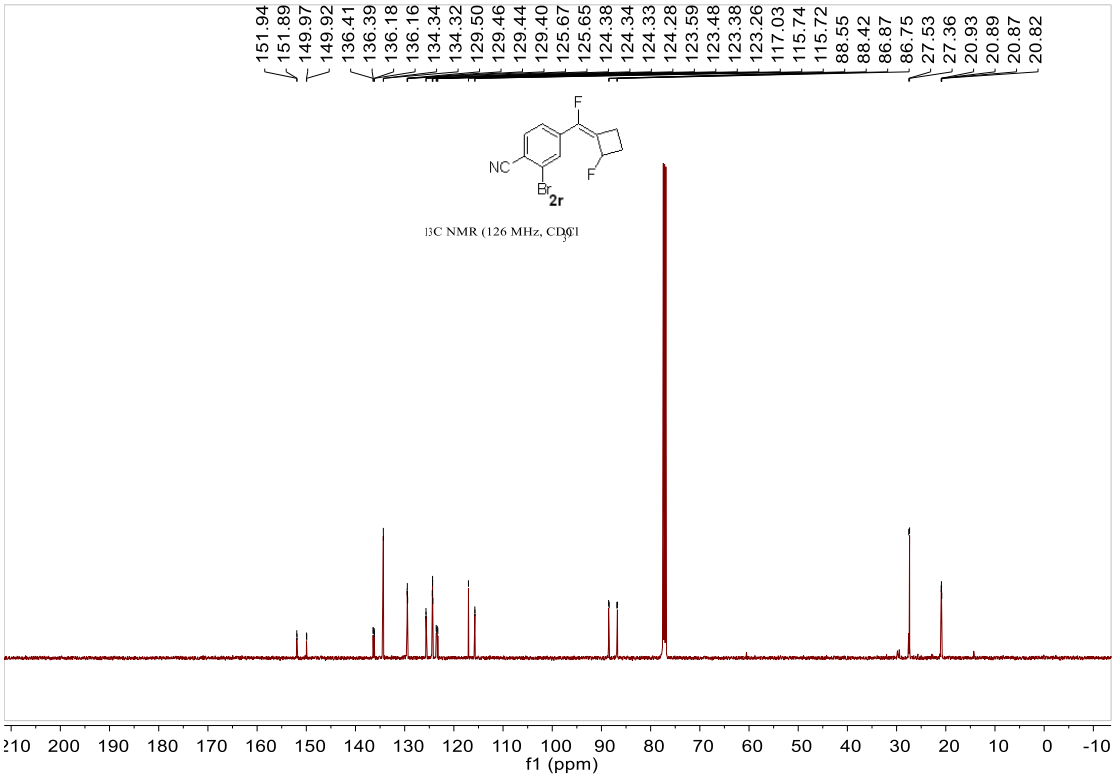

-63.14
-119.25
-119.26
-162.54
-162.54
F3C
CF3
F
F
2p
19F NMR (376 MHz, CDCl3)
f1 (ppm)


7.47 7.47 7.46 7.44 7.31 7.28 5.56 5.55 5.42 5.40 2.96 2.95 2.95 2.95 2.94 2.93 2.93 2.92 2.91 2.91 2.60 2.60 2.59 2.59 2.58 2.58 2.58 2.57 2.56 2.56 2.56 2.54 2.54 2.54 2.50 2.49 2.48 2.48 2.47 2.47 2.46 2.45 2.45 2.44 2.38 2.35 2.34 2.33 2.32 2.32 2.29
Cl F Cl F
2q
1H NMR (400 MHz, CDCl3)
0.82 0.84 1.04 1.02 1.00 1.05 1.02 1.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


151.86 151.82 149.84 149.81 136.30 136.29 133.83 133.81 132.04 132.01 131.99 129.96 128.92 128.90 128.70 128.68 126.96 121.65 121.54 121.46 121.34 88.34 88.23 86.66 86.55
27.60 27.44 20.32 20.29 20.25 20.21
Cl F Cl F
2q
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-105.17
-105.18
-163.78
-163.79
Cl
F
Cl
F
2q
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.86 7.67 7.65 7.61 7.59 5.80 5.79 5.78 5.77 5.66 5.65 5.64 5.63 3.00 2.97 2.96 2.96 2.95 2.64 2.63 2.62 2.62 2.60 2.59 2.58 2.58 2.56 2.56 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.51 2.49 2.49 2.48 2.48 2.47 2.47 2.45 2.44 2.43 2.42 2.42 2.41 2.40 2.39
F
NC
F
Br
2r
1H NMR (400 MHz, CDCl3)
1.00 1.02 1.05 1.05 1.05 1.25 0.84 1.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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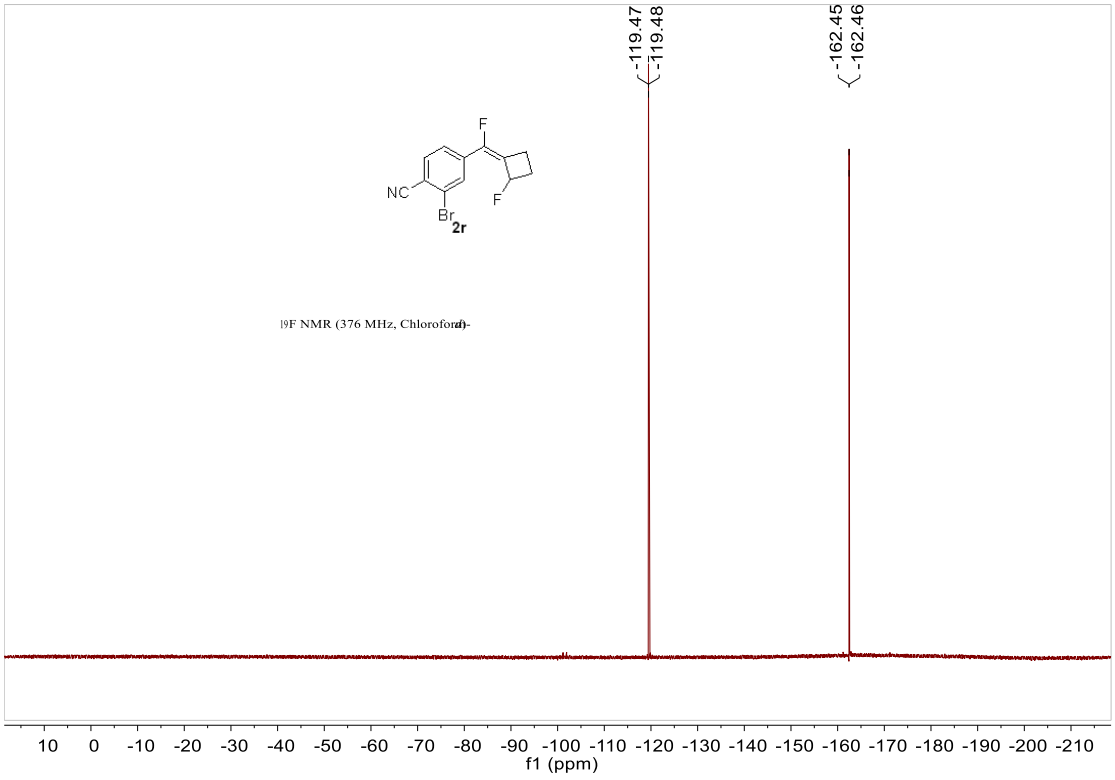
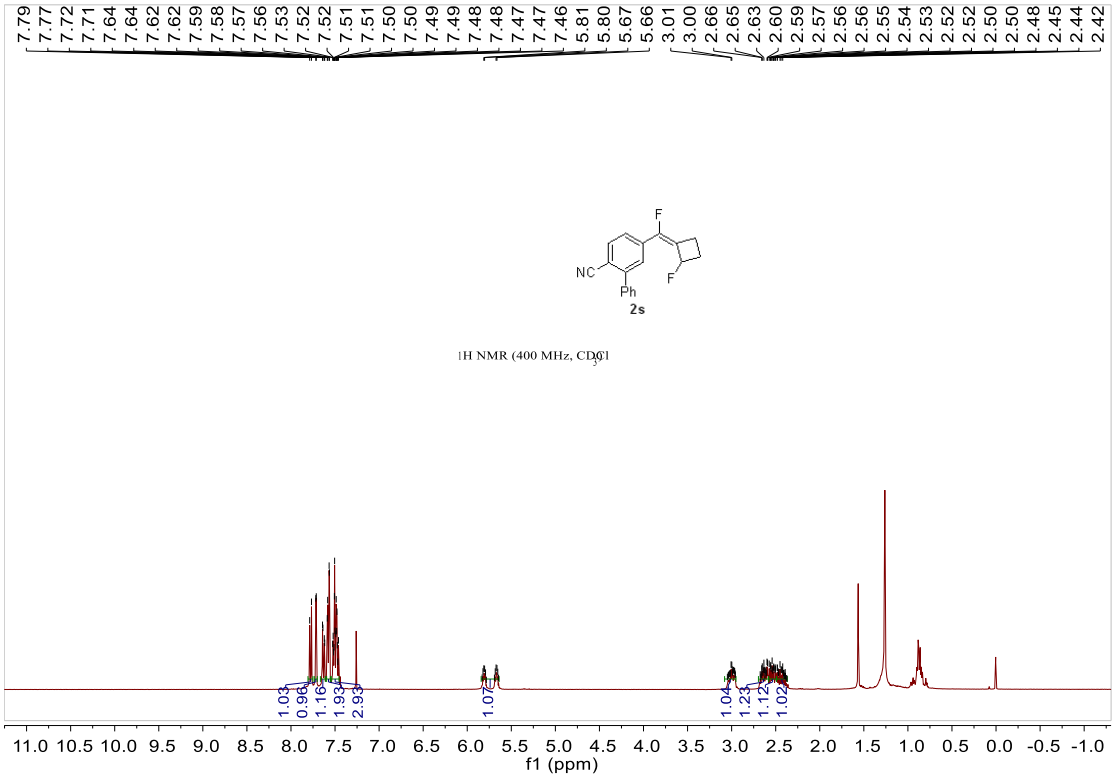
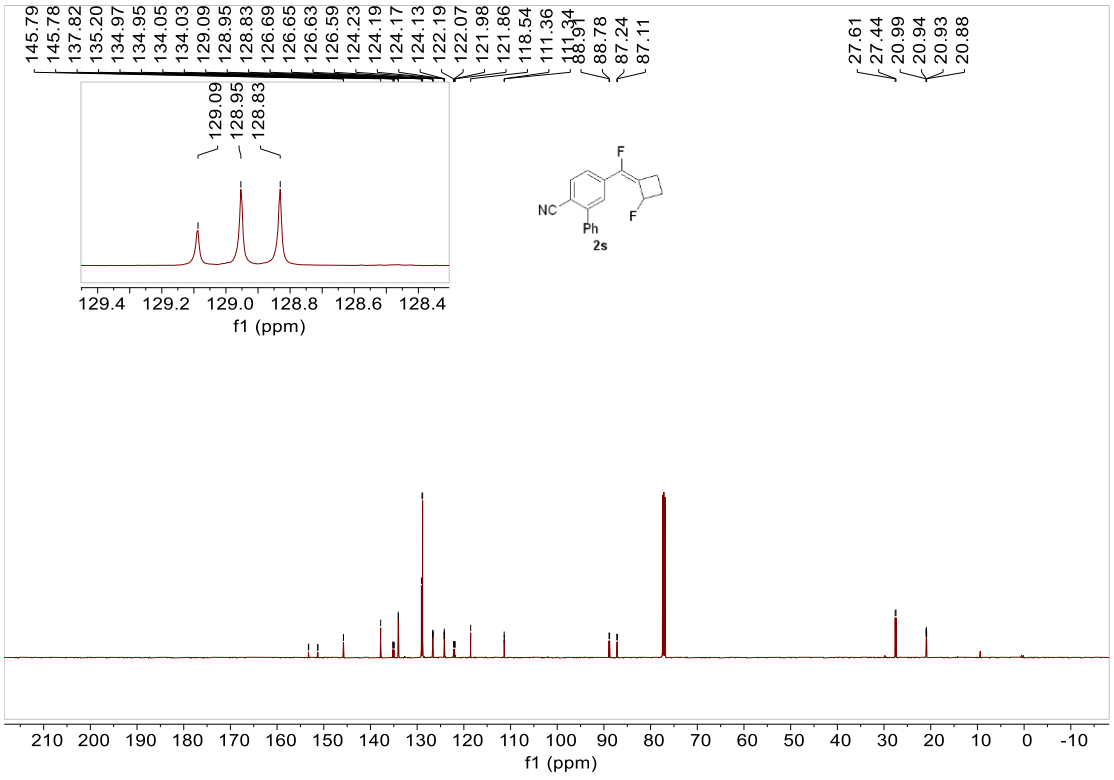
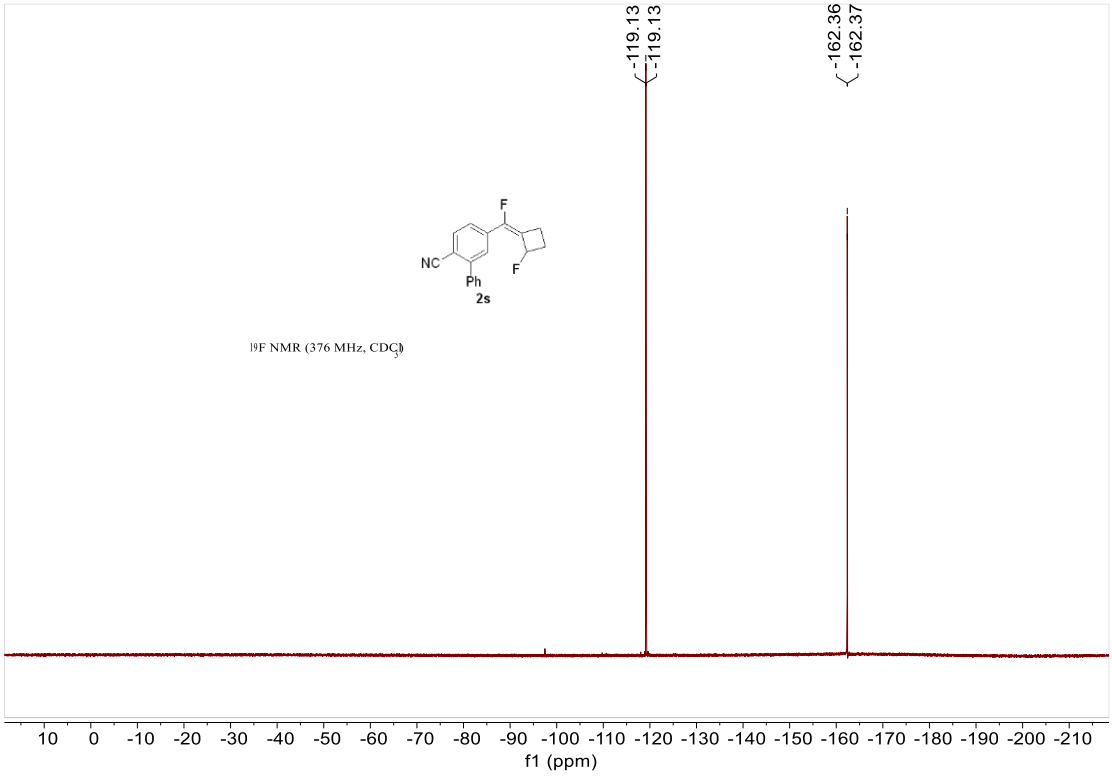
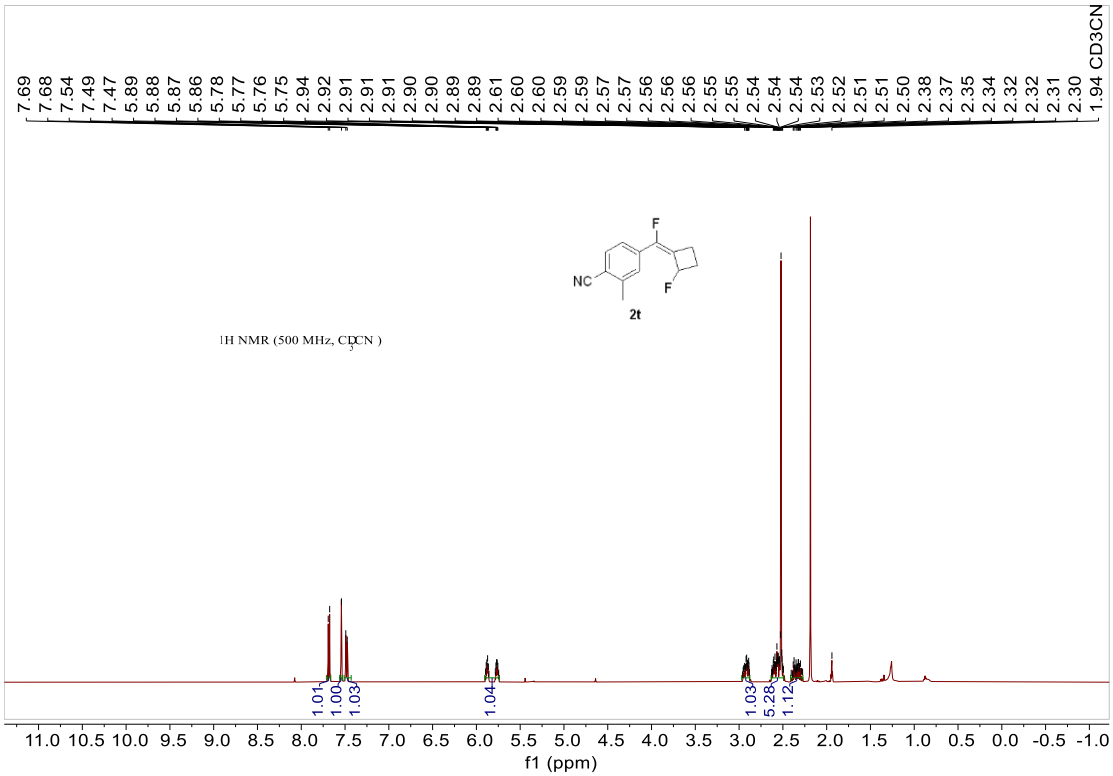
151.89
149.97
149.92
136.41
136.39
136.18
136.16
134.34
134.32
129.50
129.46
129.44
129.40
125.67
125.65
124.38
124.34
124.33
124.28
123.59
123.48
123.38
123.26
117.03
115.74
115.72
88.55
88.42
86.87
86.75
27.53
27.36
20.93
20.89
20.87
20.82
F
NC
Br
F
2r
13C NMR (126 MHz, CDCl3)
f1 (ppm)

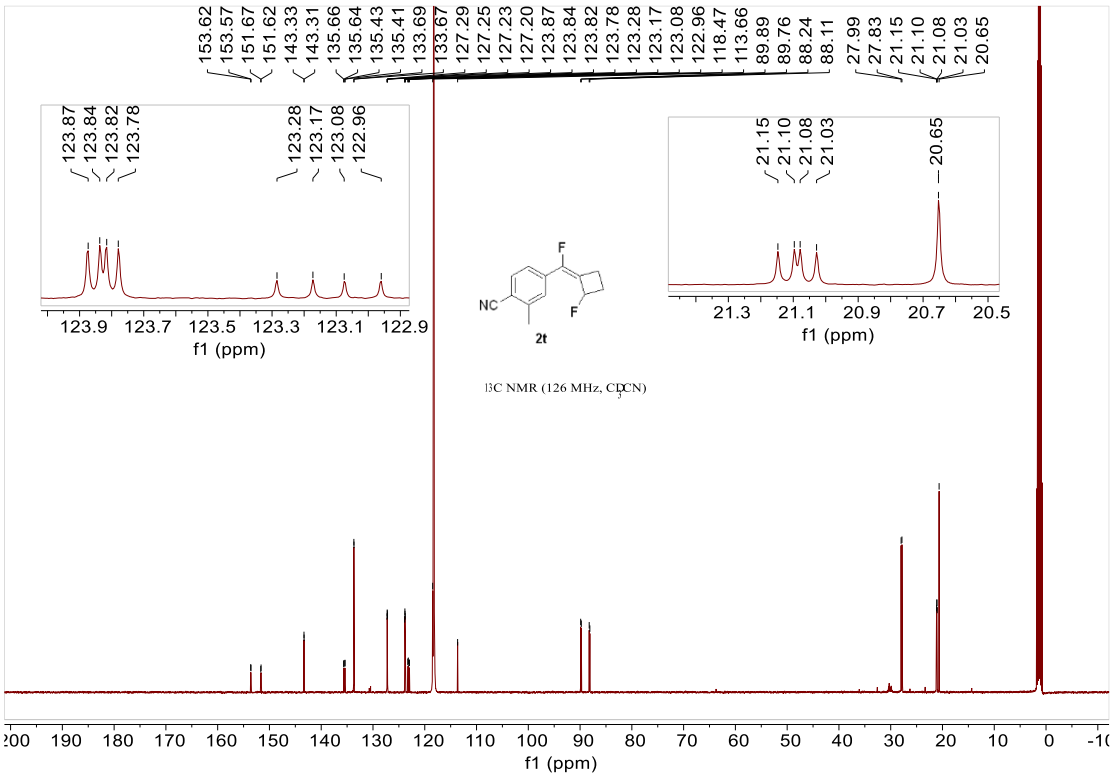

-119.47
-119.48
-162.45
-162.46
F
NC
Br
F
2r
19F NMR (376 MHz, Chloroform-d)
f1 (ppm)


7.79 7.77 7.72 7.71 7.64 7.64 7.62 7.62 7.59 7.58 7.57 7.56 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 5.81 5.80 5.67 5.66 3.01 3.00 2.66 2.65 2.63 2.60 2.59 2.57 2.56 2.56 2.55 2.54 2.53 2.52 2.52 2.50 2.50 2.48 2.45 2.44 2.42
F
NC
Ph
F
2s
1H NMR (400 MHz, CDCl3)
1.03 0.96 1.16 1.93 2.93 1.07 1.04 1.23 1.12 1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


145.79 145.78 137.82 135.20 134.97 134.95 134.05 134.03 129.09 128.95 128.83 126.69 126.65 126.63 126.59 124.23 124.19 124.17 124.13 122.19 122.07 121.98 121.86 118.54 111.36 111.34 88.91 88.78 87.24 87.11
27.61 27.44 20.99 20.94 20.93 20.88
129.09 128.95 128.83
129.4 129.2 129.0 128.8 128.6 128.4
f1 (ppm)
F
NC
Ph
F
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-119.13
-119.13
-162.36
-162.37
F
NC
F
Ph
2s
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.69 7.68 7.54 7.49 7.47 5.89 5.88 5.87 5.86 5.78 5.77 5.76 5.75 2.94 2.92 2.91 2.91 2.91 2.90 2.90 2.89 2.89 2.61 2.60 2.60 2.59 2.59 2.57 2.57 2.56 2.56 2.56 2.55 2.55 2.54 2.54 2.54 2.53 2.52 2.51 2.51 2.50 2.38 2.37 2.35 2.34 2.32 2.32 2.31 2.30 1.94 CD3CN
F
NC
F
2t
1H NMR (500 MHz, CD3CN)
1.01
1.00
1.03
1.04
1.03
5.28
1.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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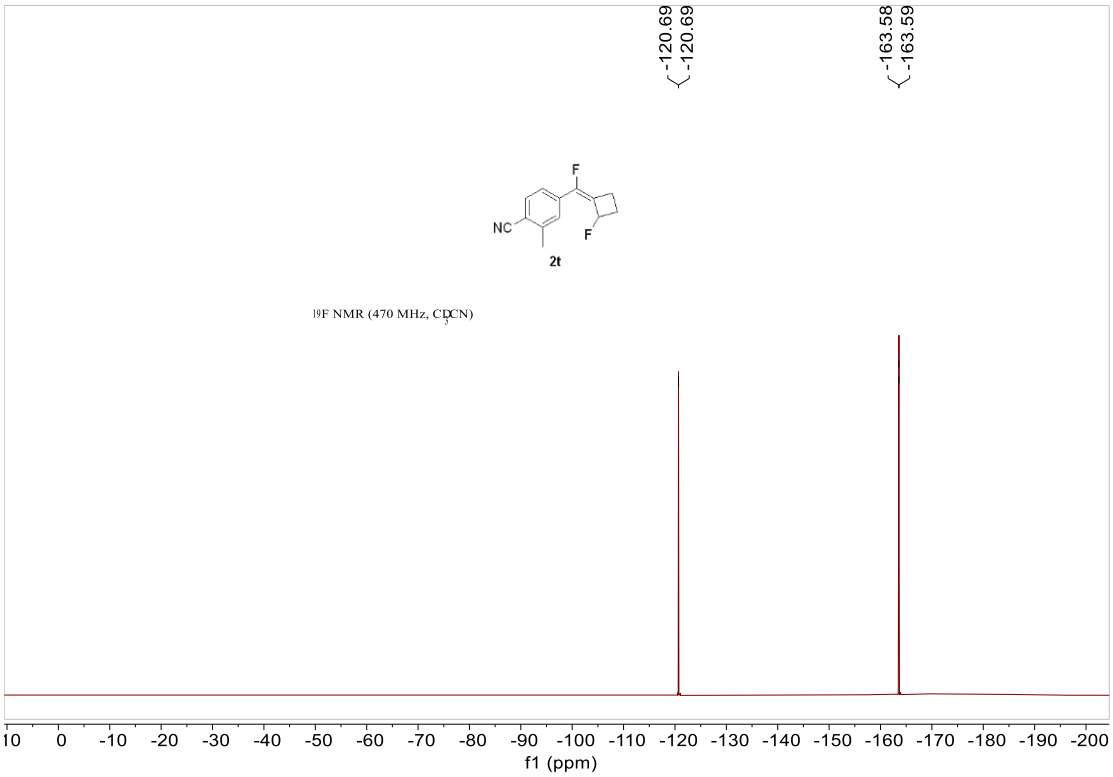
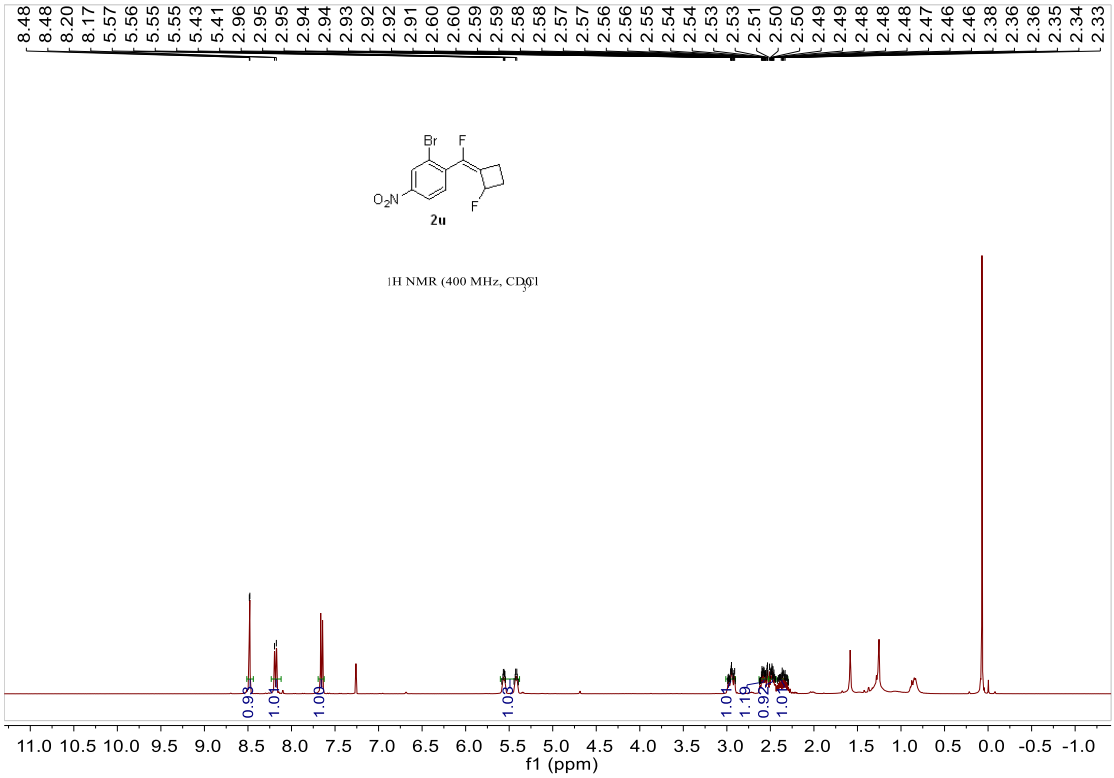
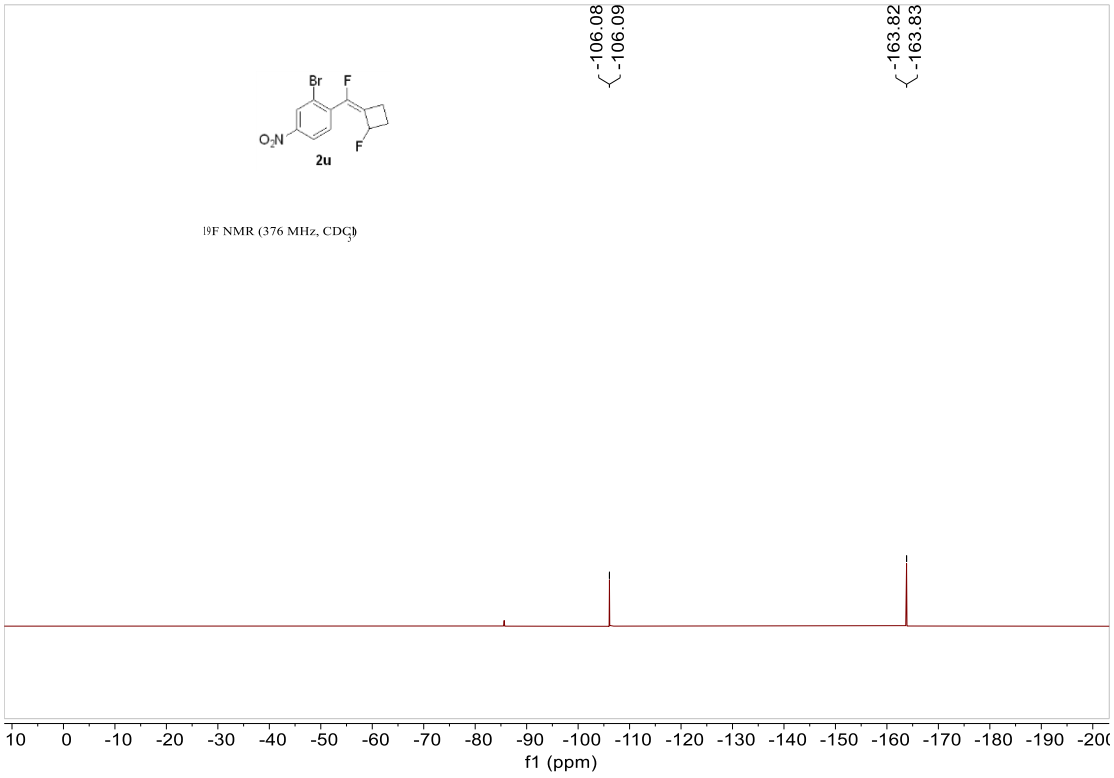
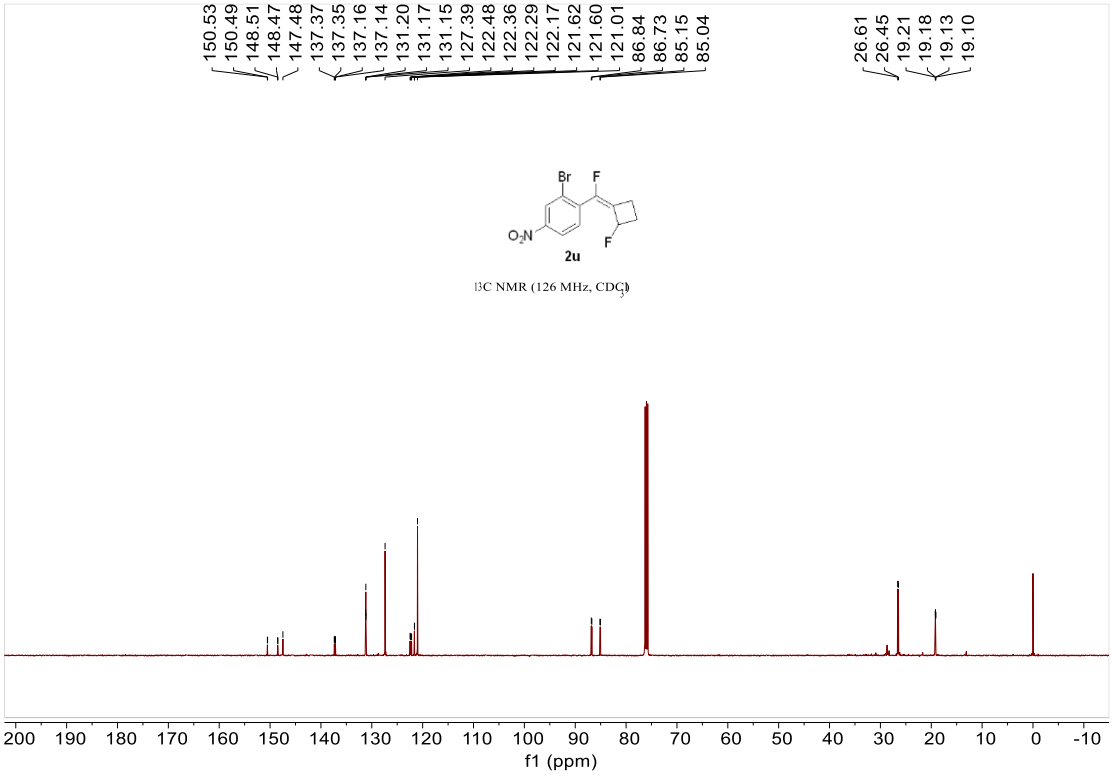
151.67
151.62
143.33
143.31
135.66
135.64
135.43
135.41
133.69
133.67
127.29
127.25
127.23
127.20
123.87
123.84
123.82
123.78
123.28
123.17
123.08
122.96
118.47
113.66
89.89
89.76
88.24
88.11
27.99
27.83
21.15
21.10
21.08
21.03
20.65
123.87
123.84
123.82
123.78
123.28
123.17
123.08
122.96
123.9 123.7 123.5 123.3 123.1 122.9
f1 (ppm)
21.15
21.10
21.08
21.03
20.65
21.3 21.1 20.9 20.7 20.5
f1 (ppm)
F
NC
F
2t
13C NMR (126 MHz, CD3CN)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-120.69
-120.69
-163.58
-163.59
F
NC
F
2t
19F NMR (470 MHz, CD3CN)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


8.48 8.48 8.20 8.17 5.57 5.56 5.55 5.55 5.43 5.41 2.96 2.95 2.95 2.94 2.94 2.93 2.92 2.92 2.91 2.60 2.60 2.59 2.59 2.58 2.58 2.57 2.57 2.56 2.56 2.55 2.54 2.54 2.53 2.53 2.51 2.50 2.50 2.49 2.49 2.48 2.48 2.48 2.47 2.46 2.46 2.38 2.36 2.36 2.35 2.34 2.33
Br
F
O2N
F
2u
1H NMR (400 MHz, CDCl3
0.93
1.01
1.09
1.08
1.01
1.19
0.92
1.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


-106.08
-106.09
-163.82
-163.83
Br
F
O2N
F
2u
19F NMR (376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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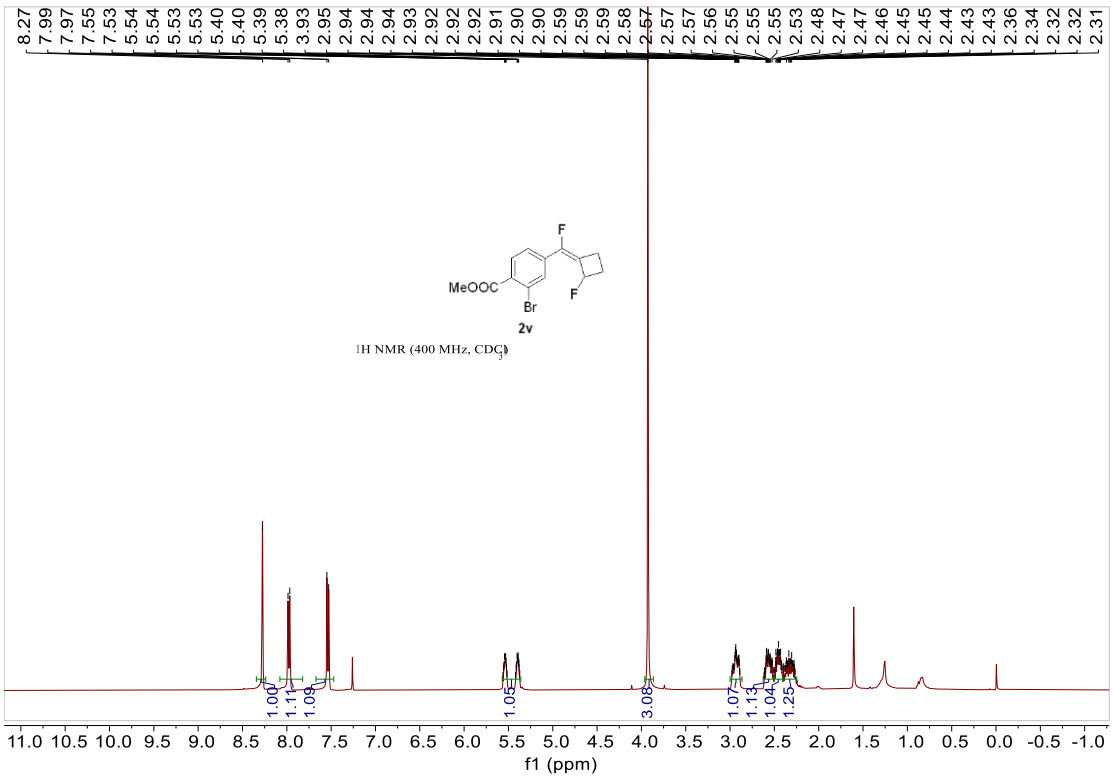
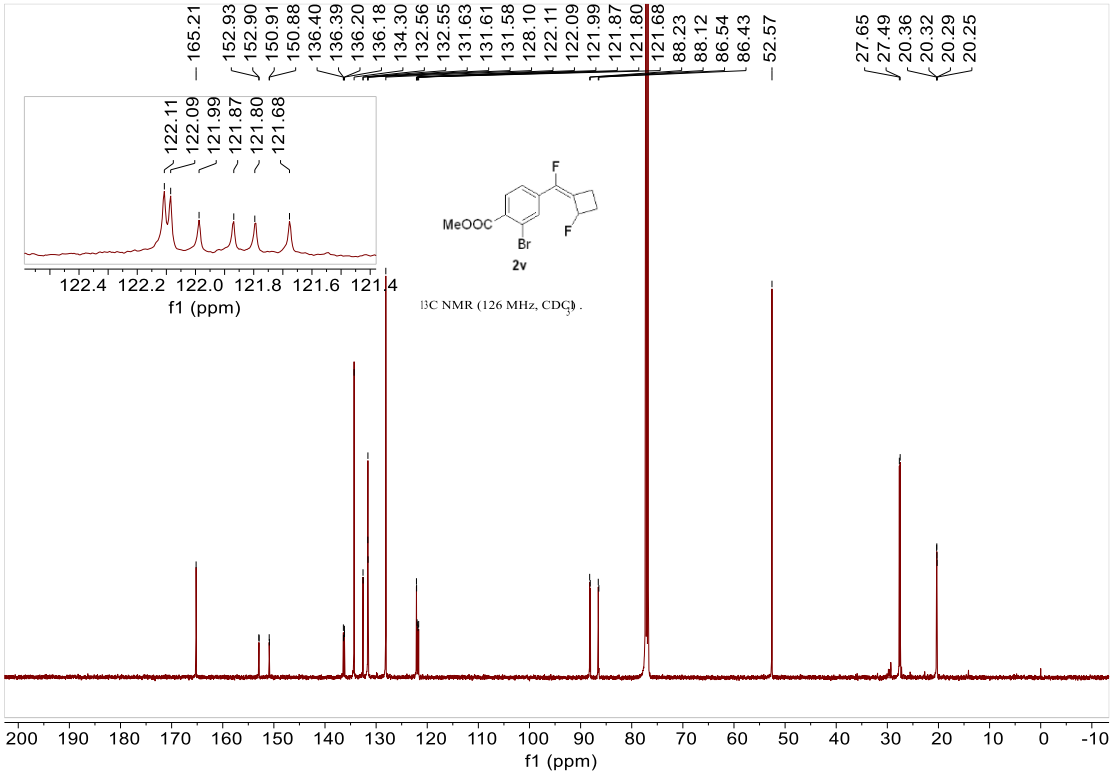
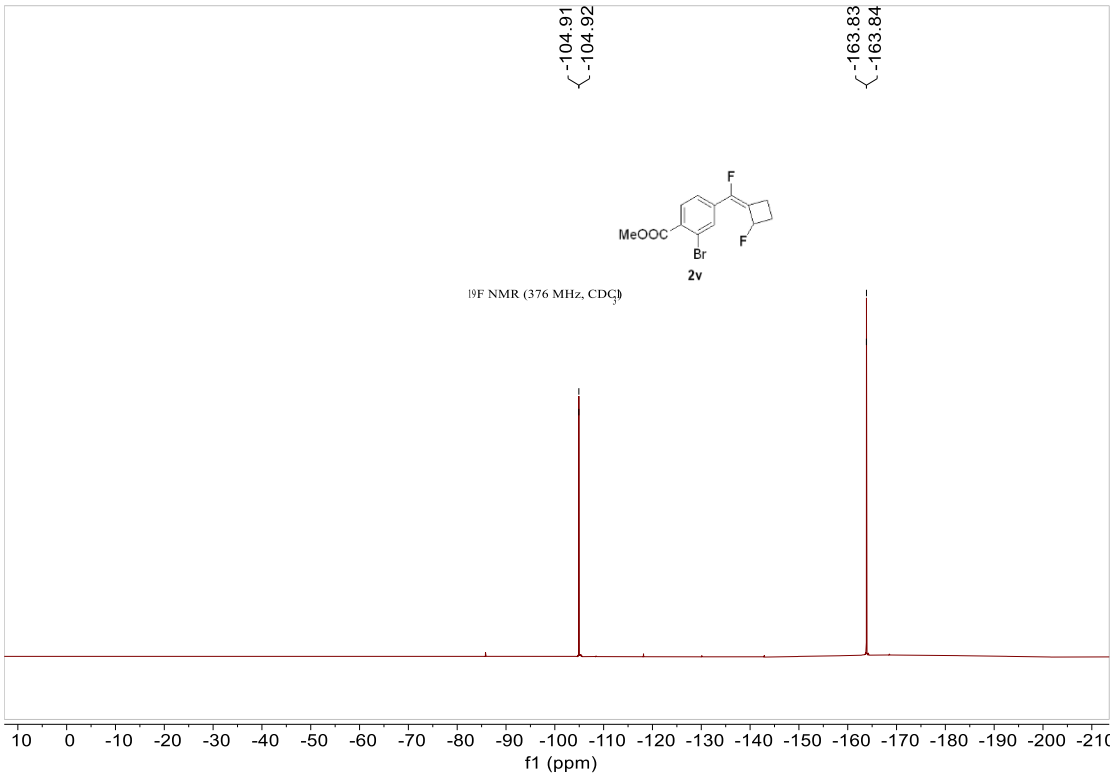
150.49
148.51
148.47
147.48
137.37
137.35
137.16
137.14
131.20
131.17
131.15
127.39
122.48
122.36
122.29
122.17
121.62
121.60
121.01
86.84
86.73
85.15
85.04
26.61
26.45
19.21
19.18
19.13
19.10
Br
F
O2N
F
2u
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

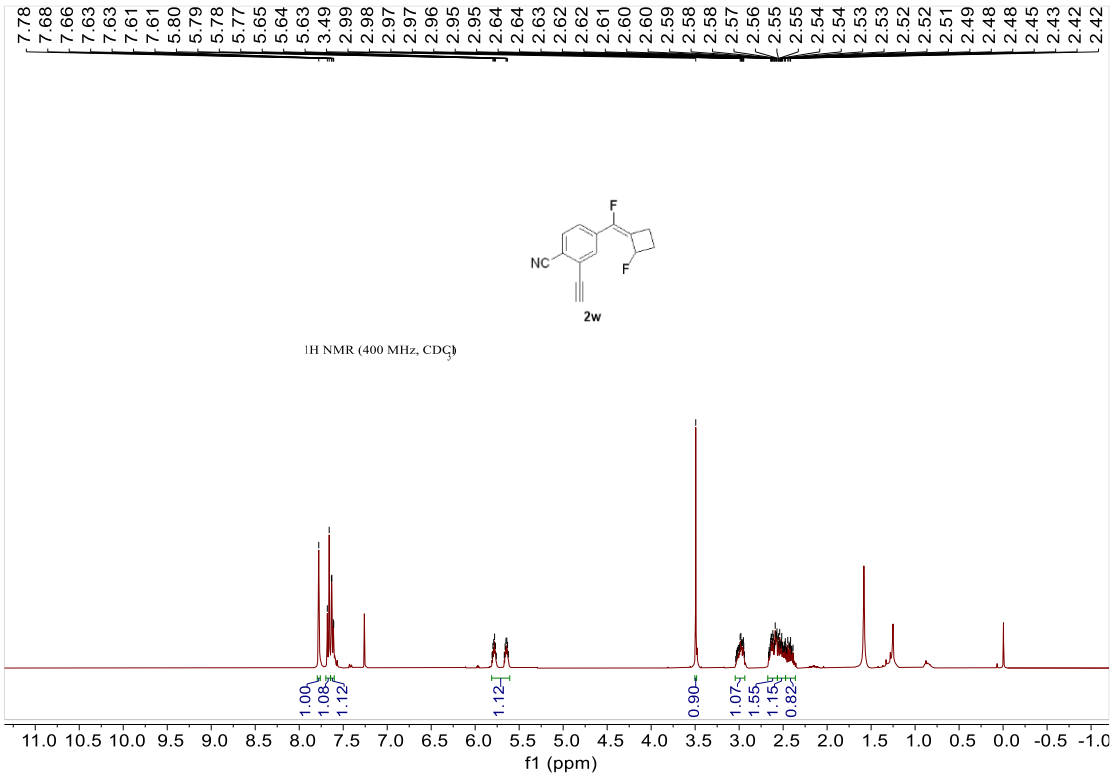

8.27
7.99
7.97
7.55
7.53
5.54
5.54
5.53
5.53
5.40
5.40
5.39
5.38
3.93
2.95
2.94
2.94
2.94
2.93
2.92
2.92
2.92
2.91
2.90
2.90
2.59
2.59
2.59
2.58
2.57
2.57
2.57
2.56
2.55
2.55
2.55
2.53
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.43
2.36
2.34
2.32
2.32
2.31
F
MeOOC
F
Br
2v
1H NMR (400 MHz, CDCl3)
1.00
1.11
1.09
1.05
3.08
1.07
1.13
1.04
1.25
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

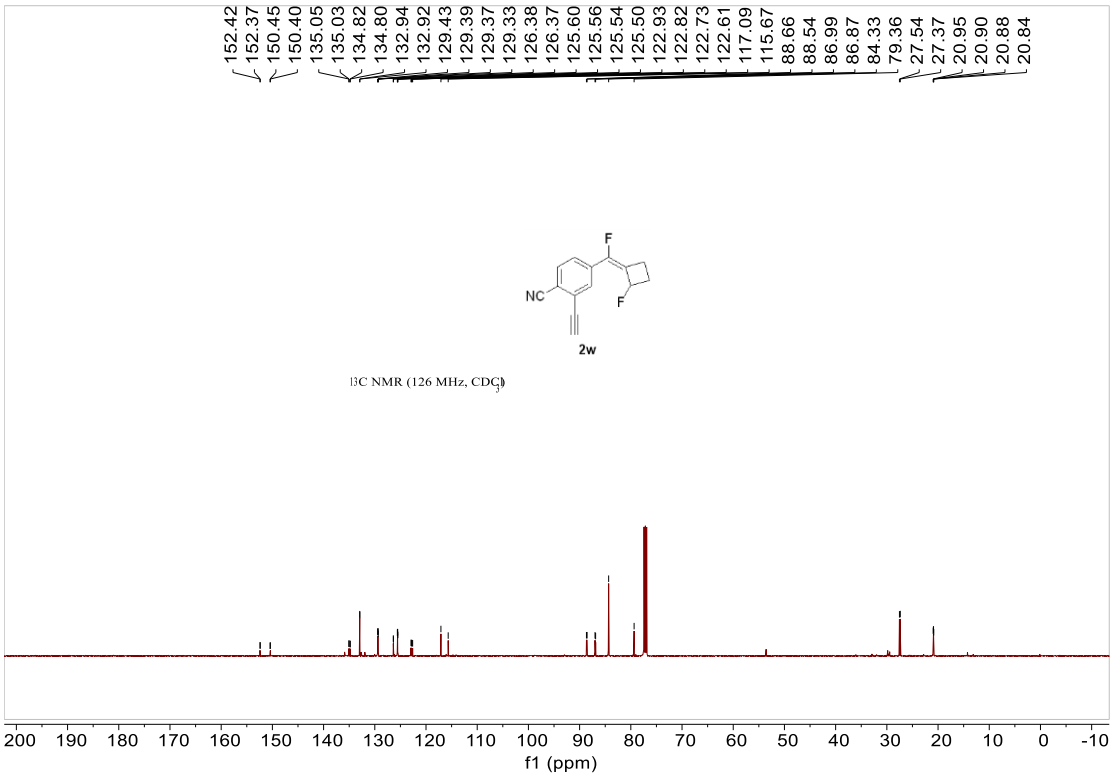


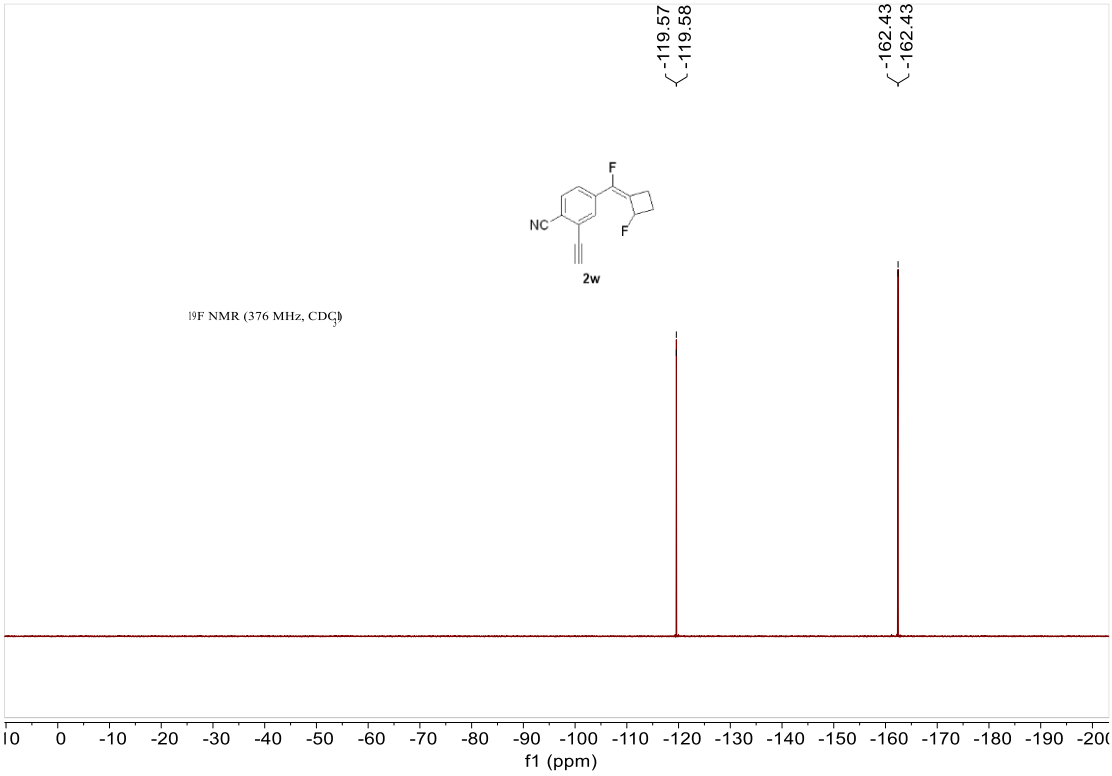
13C NMR (126 MHz, $CDCl_3$) .

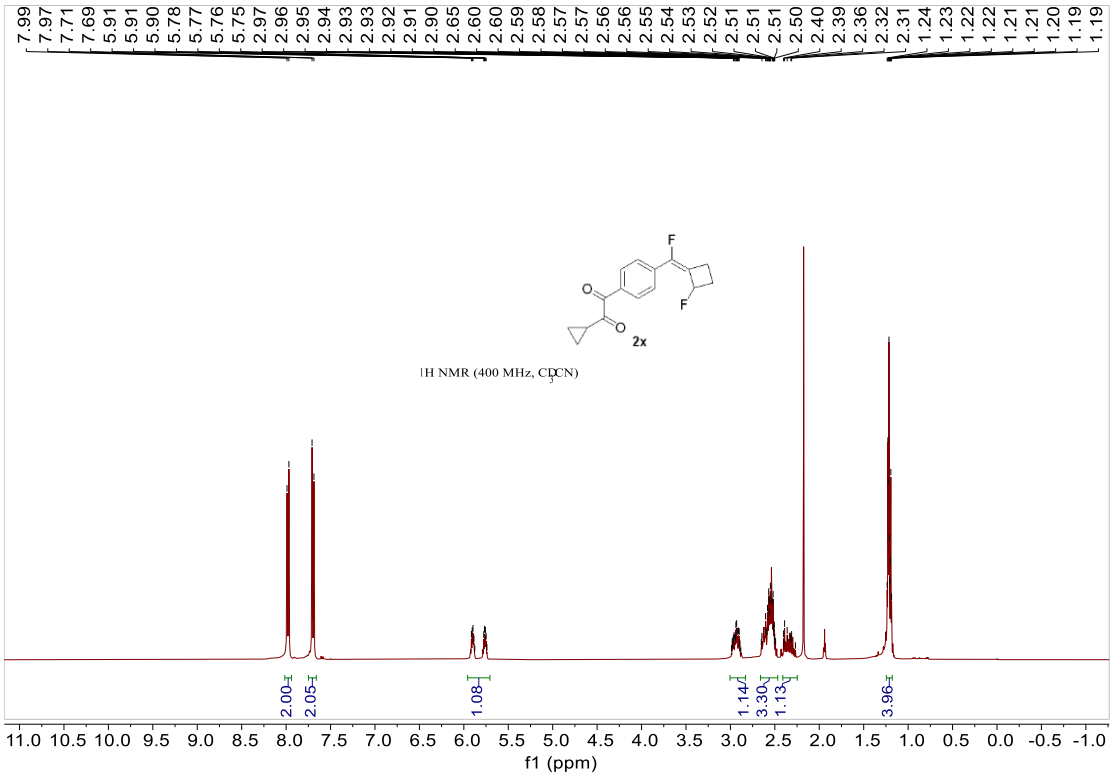


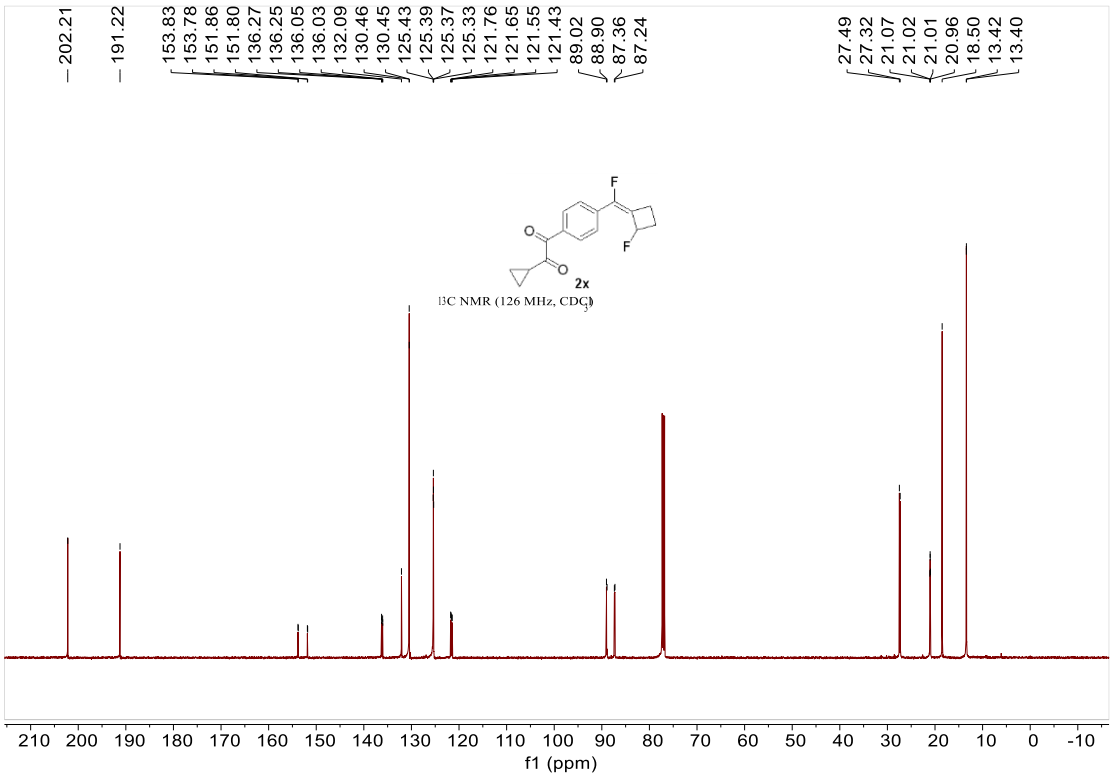
19F NMR (376 MHz, $CDCl_3$)

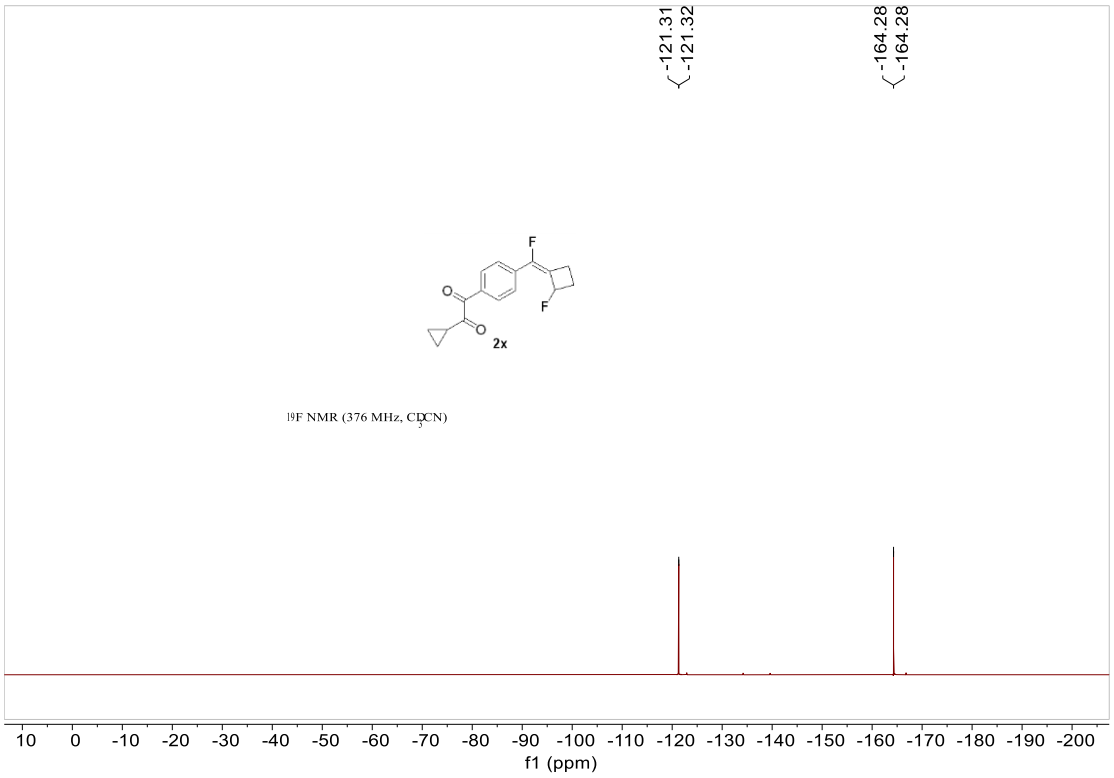

7.78 7.68 7.66 7.63 7.63 7.61 7.61 5.80 5.79 5.78 5.77 5.65 5.64 5.63 3.49 2.99 2.98 2.97 2.97 2.96 2.95 2.95 2.64 2.64 2.63 2.62 2.62 2.61 2.60 2.60 2.59 2.58 2.58 2.57 2.56 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.52 2.51 2.49 2.48 2.48 2.45 2.43 2.42 2.42
F
NC
F
2w
1H NMR (400 MHz, CDCl3)
1.00 1.08 1.12 1.12 0.90 1.07 1.55 1.15 0.82
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

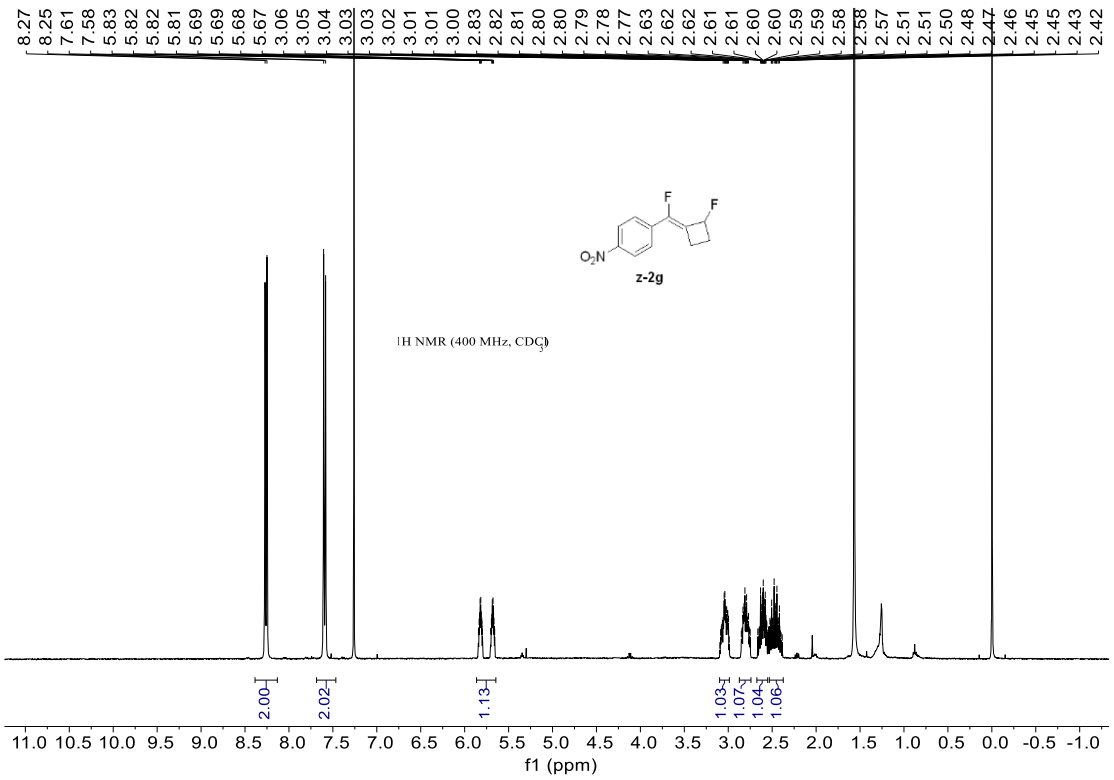

152.42 152.37 150.45 150.40 135.05 135.03 134.82 134.80 132.94 132.92 129.43 129.39 129.37 129.33 126.38 126.37 125.60 125.56 125.54 125.50 122.93 122.82 122.73 122.61 117.09 115.67 88.66 88.54 86.99 86.87 84.33 79.36 27.54 27.37 20.95 20.90 20.88 20.84
F
NC
F
2w
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

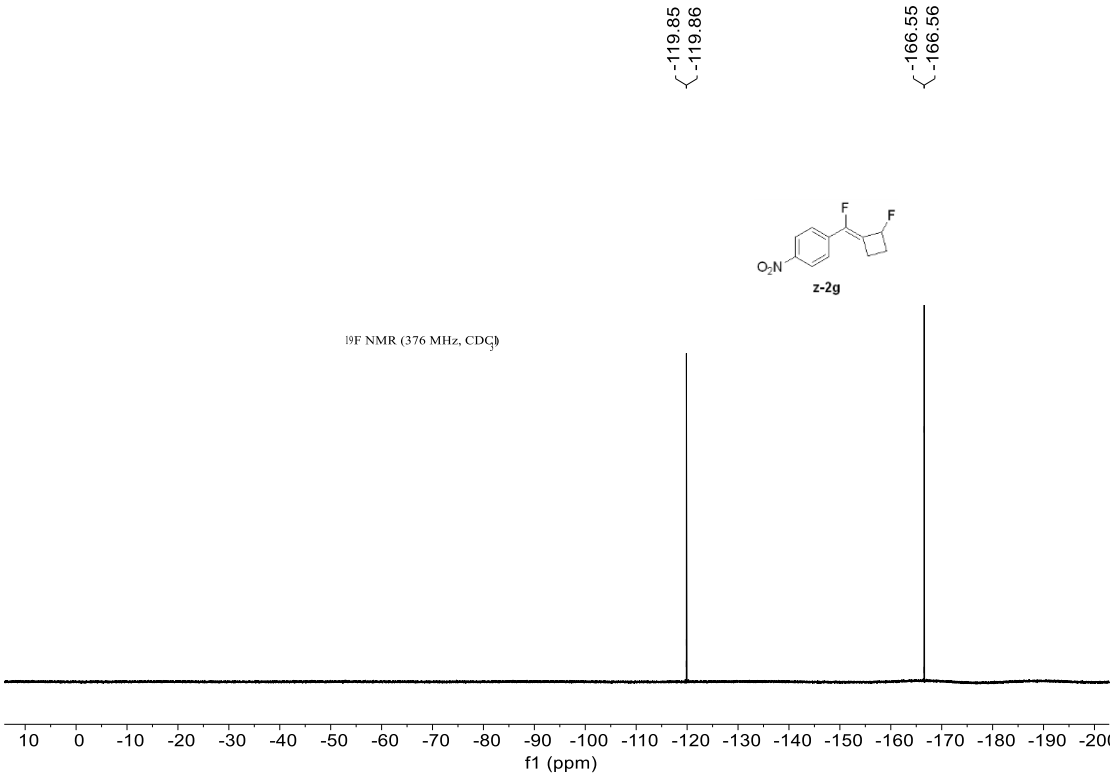

-119.57
-119.58
-162.43
-162.43
F
NC
F
2w
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

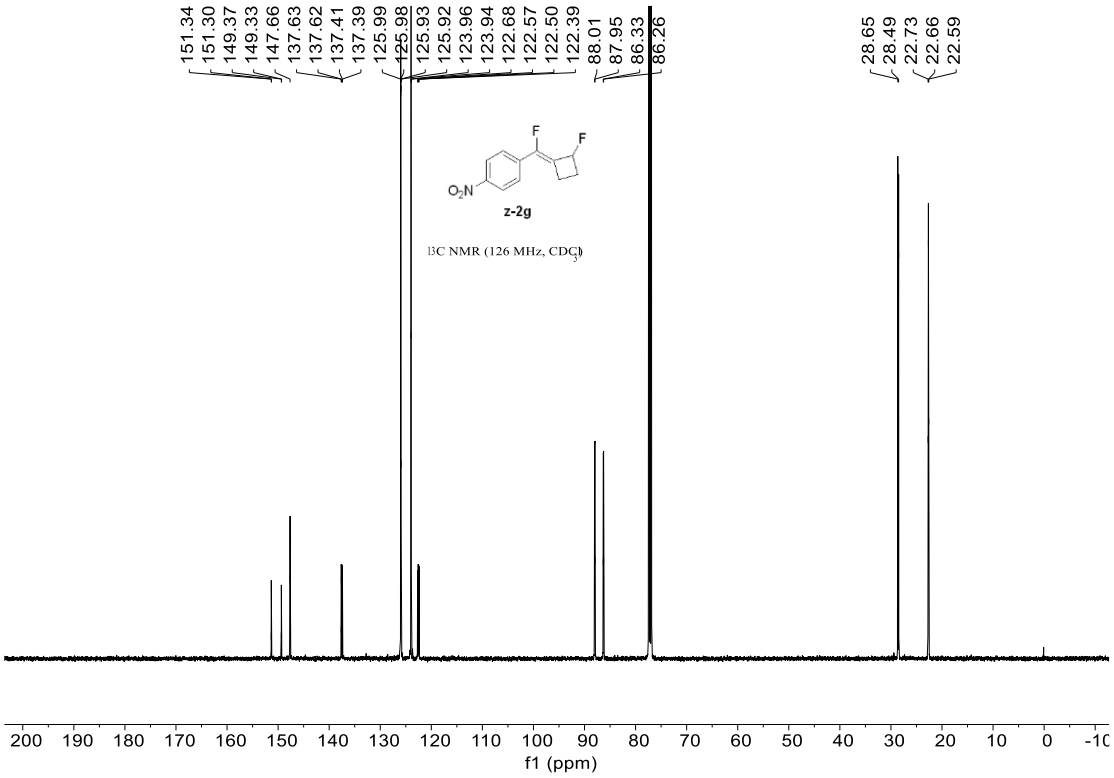

7.99 7.97 7.71 7.69 5.91 5.91 5.90 5.78 5.77 5.76 5.75 2.97 2.96 2.95 2.94 2.93 2.92 2.91 2.90 2.65 2.60 2.60 2.59 2.58 2.57 2.57 2.56 2.56 2.55 2.54 2.53 2.52 2.51 2.51 2.51 2.50 2.40 2.39 2.36 2.32 2.31 1.24 1.23 1.22 1.22 1.21 1.21 1.20 1.19 1.19
F
O
O
F
2x
1H NMR (400 MHz, CD3CN)
2.00
2.05
1.08
1.14
3.30
1.13
3.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

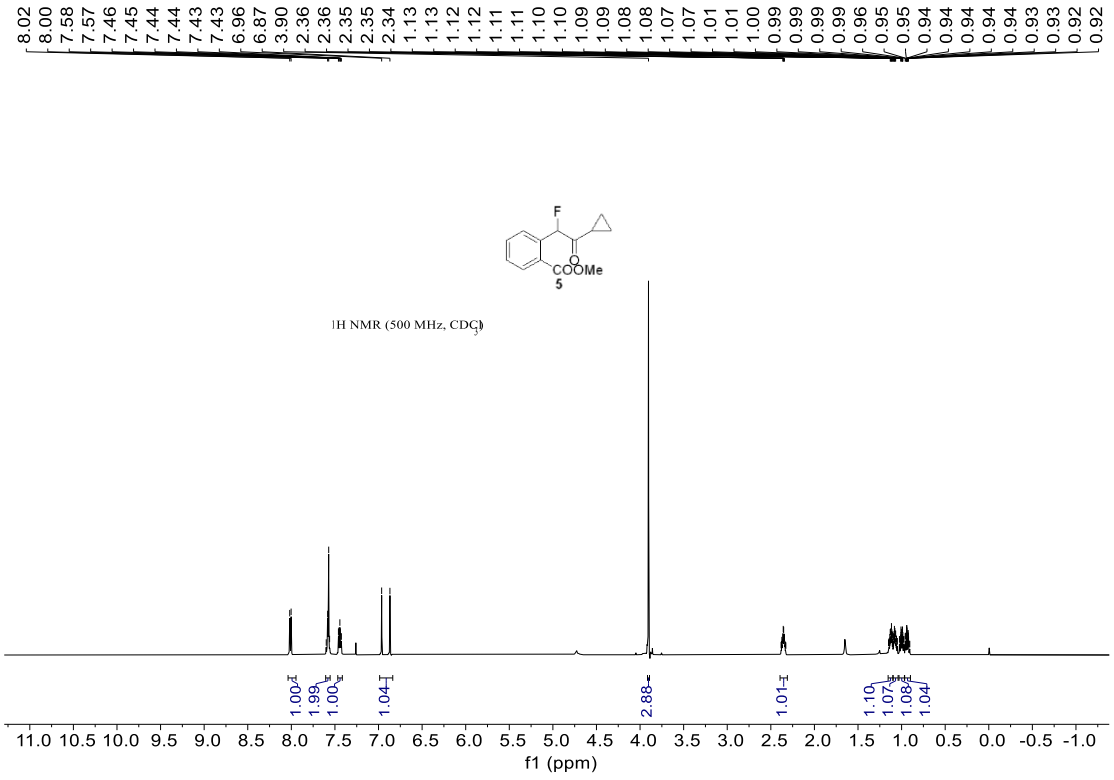

202.21
191.22
153.83
153.78
151.86
151.80
136.27
136.25
136.05
136.03
132.09
130.46
130.45
125.43
125.39
125.37
125.33
121.76
121.65
121.55
121.43
89.02
88.90
87.36
87.24
27.49
27.32
21.07
21.02
21.01
20.96
18.50
13.42
13.40
F
O
O
F
2x
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

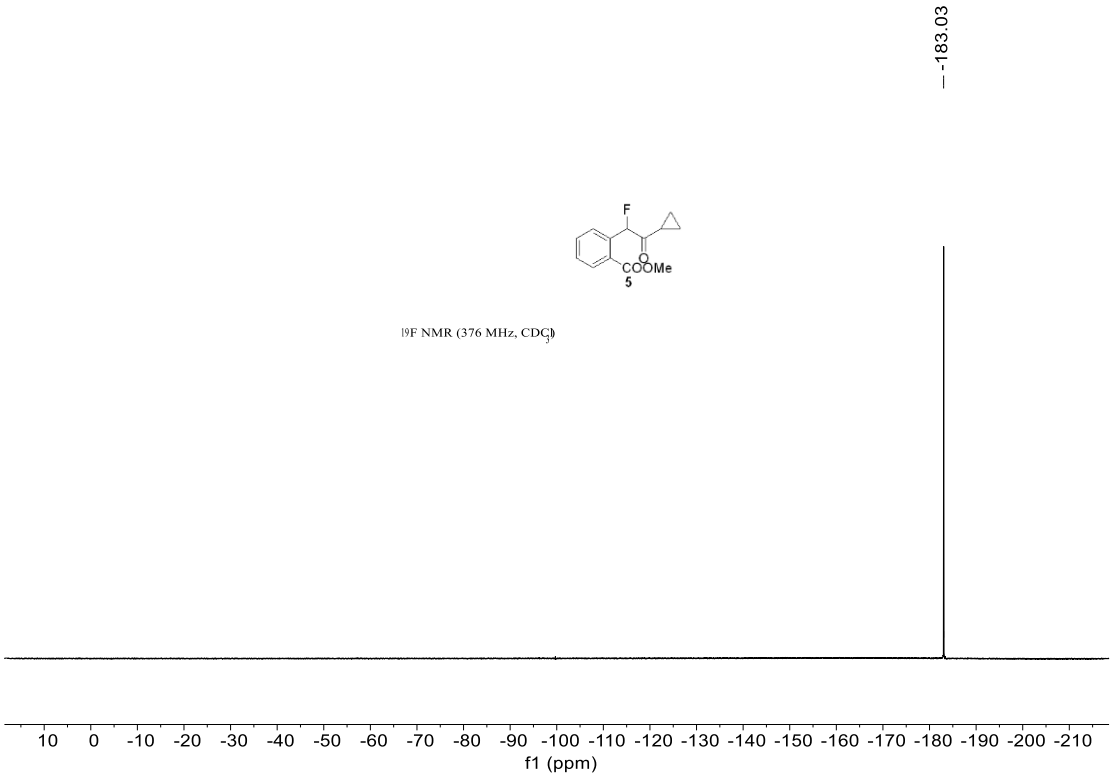

-121.31
-121.32
-164.28
-164.28
F
O
O
F
2x
19F NMR (376 MHz, CD3CN)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

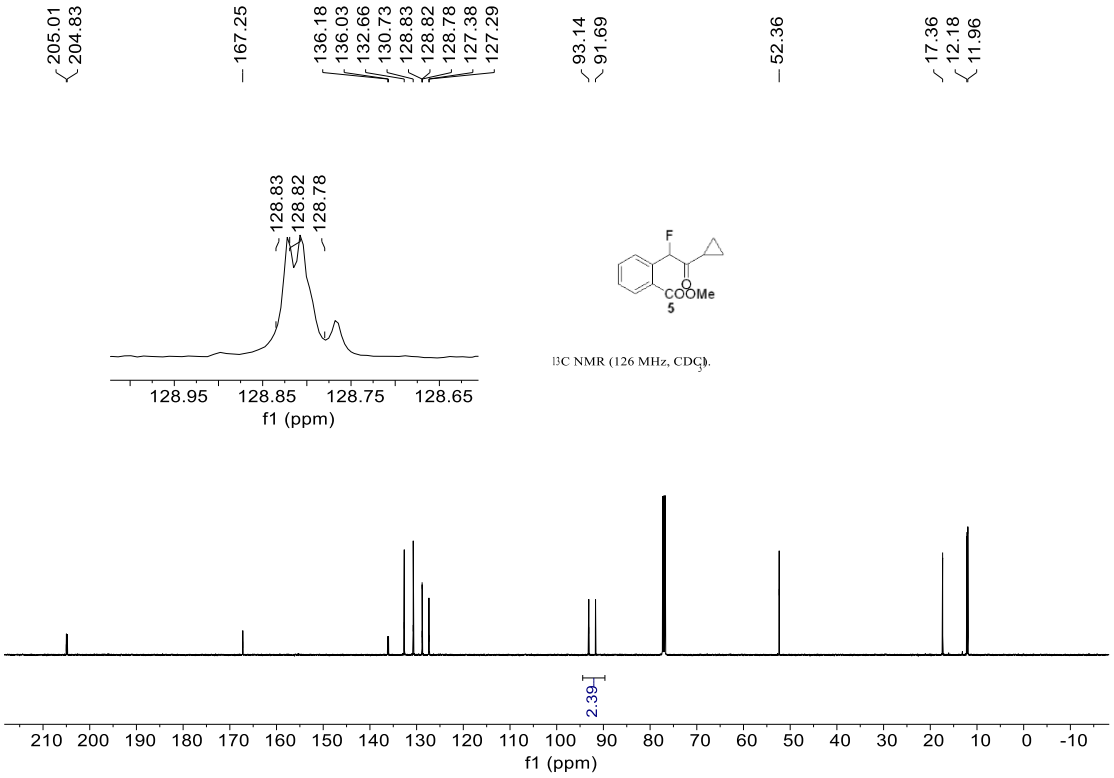

8.27 8.25 7.61 7.58 5.83 5.82 5.82 5.81 5.69 5.69 5.68 5.67 3.06 3.05 3.04 3.03 3.03 3.02 3.01 3.01 3.00 2.83 2.82 2.81 2.80 2.80 2.79 2.78 2.77 2.63 2.62 2.62 2.61 2.61 2.60 2.60 2.59 2.59 2.58 2.58 2.57 2.51 2.51 2.50 2.48 2.47 2.46 2.45 2.45 2.43 2.42
F
F
O2N
z-2g
1H NMR (400 MHz, CDCl3)
2.00
2.02
1.13
1.03
1.07
1.04
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

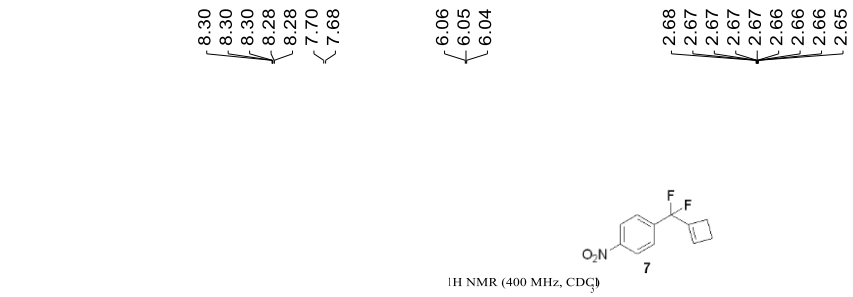

-119.85
-119.86
-166.55
-166.56
F
F
O2N
z-2g
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)


151.34
151.30
149.37
149.33
147.66
137.63
137.62
137.41
137.39
125.99
125.98
125.93
125.92
123.96
123.94
122.68
122.57
122.50
122.39
88.01
87.95
86.33
86.26
28.65
28.49
22.73
22.66
22.59
F
F
O2N
z-2g
13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

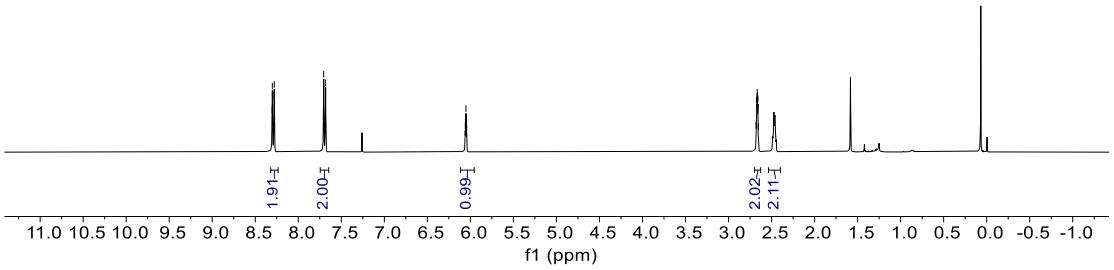

8.02
8.00
7.58
7.57
7.46
7.45
7.44
7.44
7.43
7.43
6.96
6.87
3.90
2.36
2.36
2.35
2.35
2.34
1.13
1.13
1.12
1.12
1.11
1.11
1.10
1.10
1.09
1.09
1.08
1.08
1.07
1.07
1.01
1.01
1.00
0.99
0.99
0.99
0.99
0.96
0.95
0.95
0.94
0.94
0.94
0.94
0.94
0.93
0.93
0.92
0.92
F
O
COOMe
5
1H NMR (500 MHz, CDCl3)
1.00
1.99
1.00
1.04
2.88
1.01
1.10
1.07
1.08
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

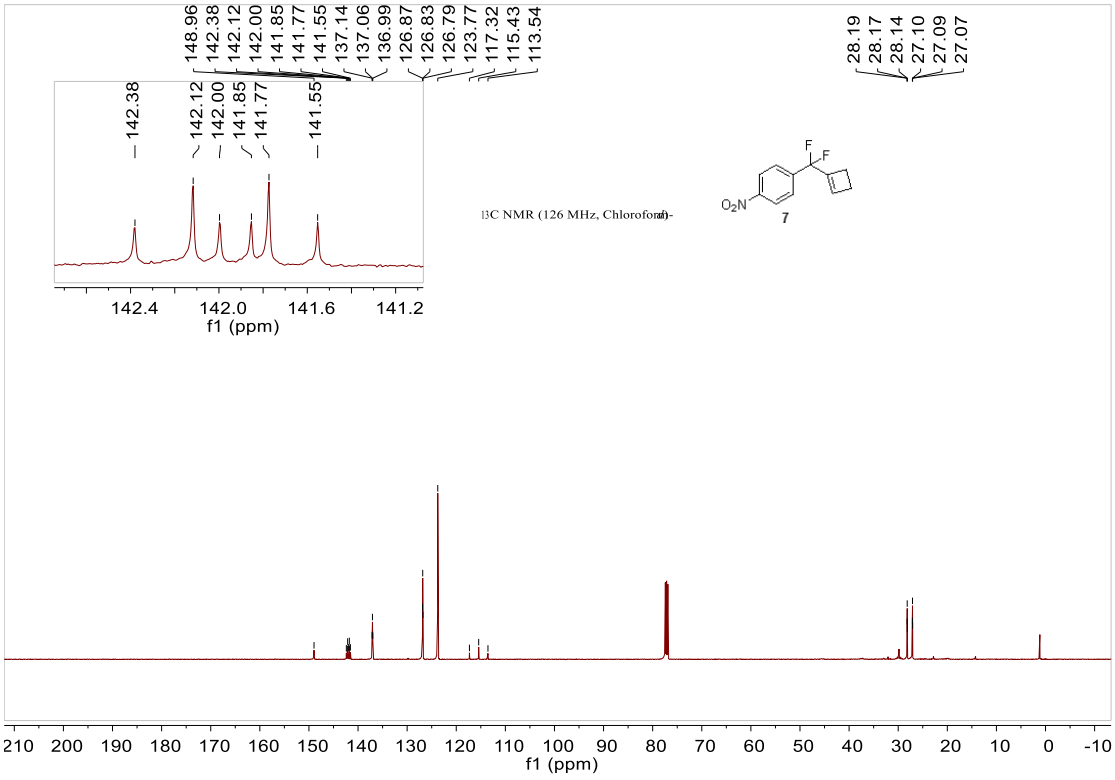

-183.03
F
O
COOMe
5
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


205.01
204.83
167.25
136.18
136.03
132.66
130.73
128.83
128.82
128.78
127.38
127.29
93.14
91.69
52.36
17.36
12.18
11.96
128.83
128.82
128.78
128.95 128.85 128.75 128.65
f1 (ppm)
F
O
COOMe
5
13C NMR (126 MHz, CDCl3)
2.39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

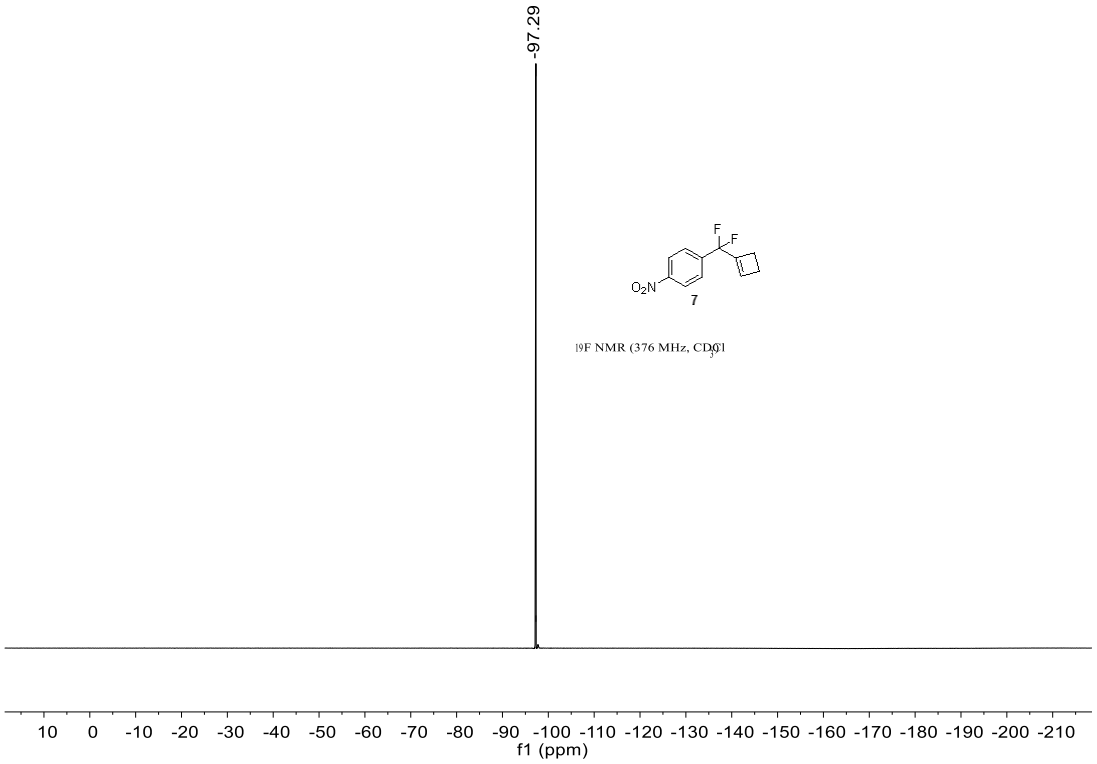


1H NMR (400 MHz, $CDCl_3$)





13C NMR (126 MHz, Chloroform-d)


-97.29
F
F
O2N
7
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)