Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cu-catalyzed tertiary alkylation of α-(trifluoromethyl)styrenes with tertiary alkylmagnesium reagents

Wenpeng Dai, Yingyin Lin, Yan Wan and Song Cao*

Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (*ECUST*), Shanghai 200237, China

*Corresponding author. E-mail address: scao@ecust.edu.cn

Table of contents

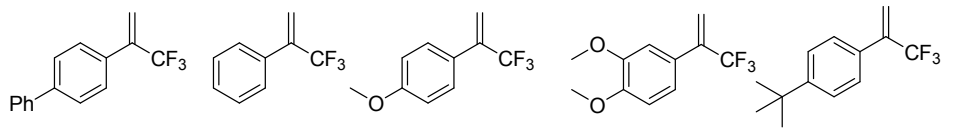
1. General information

All reagents were of analytical grade, and obtained from Adamas-beta and other suppliers and used without further purification. THF and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR, respectively) using TMS as internal standard. $CDCl_3$ was used as the NMR solvent in all cases. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. Silica gel (300−400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. General procedures for the synthesis of target compounds 3

To a solution of α-(trifluoromethyl)styrenes (1.0 mmol) and 25 mol% (22.5 mg) CuCN in THF (3 mL) was added dropwise a solution of the Grignard reagents (1.5 mmol) in THF at room temperature under argon atmosphere. The mixture was stirred for about 3 h at room temperature (monitored by TLC and GC-MS). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using *n*-hexane as eluent to afford the pure target compounds **3**.

The α-(trifluoromethyl)styrenes (**1a–n**) used in this reaction:



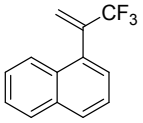
1a

1b

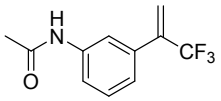
1c

1d

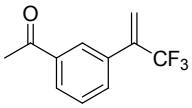
1e



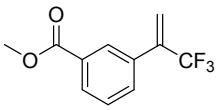
1f



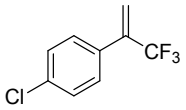
1g



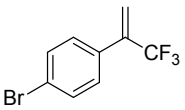
1h



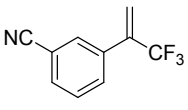
1i



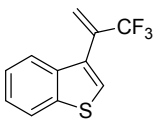
1j



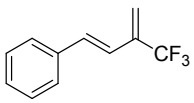
1k



1l



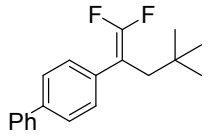
1m



1n

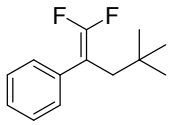
The α-(trifluoromethyl)styrenes (**1a–n**) were prepared according to the reported procedure(S. Barroso, G. Blay, L. Cardona, I. Fernández, B. García and J. R. Pedro, *J. Org. Chem.* 2004, **69**, 6821−6829).

3. Analytical data of the target compounds 3



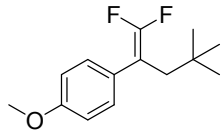
3aa

4-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl (**3aa**). yield 93% (266.0 mg), yellow solid, Mp: 72−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.54 (m, 4H), 7.42–7.36 (m, 4H), 7.33–7.29 (m, 1H), 2.36 (t, J = 2.0 Hz, 2H), 0.83 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (dd, $^1J_{CF}$ = 288.7, 286.0 Hz), 140.6, 139.8, 134.6 (dd, $^3J_{CF}$ = 4.7, 2.9 Hz), 128.9, 128.8, 127.4, 127.0, 126.9, 90.9 (dd, $^2J_{CF}$ = 21.6, 12.6 Hz), 41.1, 32.8 (t, $^3J_{CF}$ = 2.5 Hz), 29.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –89.2 (d, J = 40.6 Hz, 1F), –91.8 (d, J = 40.2 Hz, 1F); HRMS (EI) calcd for $C_{19}H_{20}F_2$ $[M]^+$ 286.1533, found 286.1534.



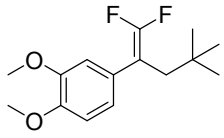
3ba

(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)benzene (**3ba**). yield 80% (168.0 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.22 (m, 5H), 2.34 (t, J = 2.4 Hz, 2H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4 (dd, $^1J_{CF}$ = 288.2, 285.5 Hz), 135.6 (dd, $^3J_{CF}$ = 4.7, 2.8 Hz), 128.5 (t, $^4J_{CF}$ = 2.8 Hz), 128.3, 127.0, 91.1 (dd, $^2J_{CF}$ = 21.3, 12.9 Hz), 41.2, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) : δ −89.9 (d, J = 41.0 Hz, 1F), −92.5 (d, J = 41.0 Hz, 1F); HRMS (EI) calcd for $C_{13}H_{16}F_2$ $[M]^+$ 210.1220, found 210.1219.



3ca

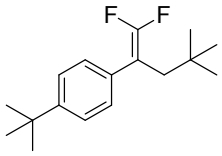
1-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)-4-methoxybenzene (**3ca**). yield 92% (220.8 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.21 (m, 2H), 6.88−6.85 (m, 2H), 3.80 (s, 3H), 2.29 (t, J = 2.6 Hz, 2H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 154.3 (dd, $^1J_{CF}$ = 287.1, 285.1 Hz), 129.5 (t, $^4J_{CF}$ = 2.8 Hz), 127.7 (dd, $^3J_{CF}$ = 4.6, 2.6 Hz), 113.7, 90.5 (dd, $^2J_{CF}$ = 21.4, 13.2 Hz), 55.2, 41.2, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 29.8; ^{19}F NMR (376 MHz, $CDCl_3$) : δ −90.8 (d, J = 43.6 Hz, 1F), −93.3 (d, J = 43.6 Hz, 1F); HRMS (EI) calcd for $C_{14}H_{18}F_2O$ $[M]^+$ 240.1326, found 240.1327.



3da

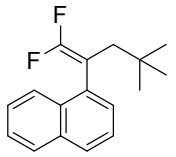
4-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)-1,2-dimethoxybenzene (**3da**). yield 89% (240.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88–6.84 (m, 2H), 6.82 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.30 (t, J = 2.4 Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3 (dd, $^1J_{CF}$ = 287.3, 285.3 Hz), 148.6, 148.0, 128.0 (dd, $^3J_{CF}$ = 4.6, 2.7 Hz), 120.9 (t, $^4J_{CF}$ = 2.8 Hz), 111.8 (t, $^4J_{CF}$ = 3.0 Hz), 110.9, 90.8 (dd, $^2J_{CF}$ = 21.5, 12.9 Hz), 55.9, 55.8, 41.3, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 29.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –90.5 (d, J = 43.2 Hz, 1F), –92.6 (d, J = 42.9

Hz, 1F); HRMS (EI) calcd for $C_{15}H_{20}F_2O_2$ $[M]^+$ 270.1431, found 270.1430.



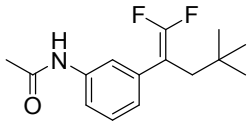
3ea

1-(Tert-butyl)-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (**3ea**). yield 91% (242.1 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.4 Hz, 2H), 7.24–7.22 (m, 2H), 2.32 (t, J = 2.4 Hz, 2H), 1.31 (s, 9H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4 (dd, $^1J_{CF}$ = 288.1, 285.2 Hz), 149.9, 132.4 (dd, $^3J_{CF}$ = 4.6, 2.8 Hz), 128.0 (t, $^4J_{CF}$ = 2.8 Hz), 125.1, 90.8 (dd, $^2J_{CF}$ = 21.2, 12.8 Hz), 41.1, 34.5, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 31.3, 29.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ –90.0 (d, J = 42.1 Hz, 1F), –92.6 (d, J = 42.1 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{24}F_2$ $[M]^+$ 266.1846, found 266.1847.



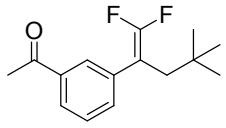
3fa

1-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)naphthalene (**3fa**). yield 74% (192.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 1H), 7.86–7.84 (m, 1H), 7.78 (dd, J = 7.2, 2.4 Hz, 1H), 7.54–7.41 (m, 4H), 2.53–2.44 (m, 2H), 0.82 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0 (dd, $^1J_{CF}$ = 287.6, 286.9 Hz), 133.9, 133.3 (dd, $^3J_{CF}$ = 4.6, 1.6 Hz), 131.2 (t, $^4J_{CF}$ = 1.7 Hz), 128.7, 128.1, 127.5 (dd, $^4J_{CF}$ = 3.4, 1.2 Hz), 126.2, 125.8, 125.4 (d, $^4J_{CF}$ = 1.5 Hz), 125.2, 88.9 (dd, $^2J_{CF}$ = 21.6, 15.8 Hz), 43.5, 32.9 (t, $^3J_{CF}$ = 2.4 Hz), 29.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –86.5 (d, J = 38.0 Hz, 1F), –89.9 (d, J = 38.0 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{18}F_2$ $[M]^+$ 260.1377, found 260.1378.



3ga

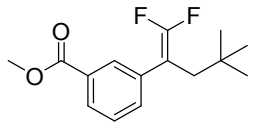
N-(3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)acetamide (**3ga**). yield 55% (147.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.47–7.43 (m, 2H), 7.26 (t, J =7.8 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 2.31 (t, J = 2.4 Hz, 2H), 2.16 (s, 3H), 0.79 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 154.4 (dd, $^1J_{CF}$ = 288.7, 285.8 Hz), 138.0, 136.5 (dd, $^3J_{CF}$ = 4.6, 2.6 Hz), 128.9, 124.4 (t, $^4J_{CF}$ = 2.4 Hz), 119.8 (t, $^4J_{CF}$ = 2.8 Hz), 118.5, 90.9 (dd, $^2J_{CF}$ = 21.8, 12.7 Hz), 41.1, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 29.7, 24.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –89.3 (d, J = 40.2 Hz, 1F), –91.7 (d, J = 39.9 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{19}F_2NO$ $[M]^+$ 267.1435, found 267.1434.



3ha

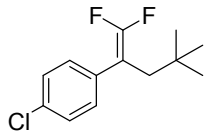
1-(3-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)ethanone (**3ha**). yield 72% (181.5 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.92 (m, 1H), 7.85–7.82 (m, 1H), 7.54–7.51(m, 1H), 7.44 (t, J = 7.6 Hz, 1H), 2.62 (s, 3H), 2.38 (t, J = 2.8 Hz, 2H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 154.6 (dd, $^1J_{CF}$ = 289.0,

286.6 Hz), 137.2, 136.3 (dd, $^3J_{CF}$ = 4.9, 2.8 Hz), 133.1 (t, $^4J_{CF}$ = 2.8 Hz), 128.6, 128.1 (t, $^4J_{CF}$ = 2.8 Hz), 127.1, 90.6 (dd, $^2J_{CF}$ = 22.2, 12.6 Hz), 41.2, 32.8 (t, $^3J_{CF}$ = 2.4 Hz), 29.7, 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –88.7 (d, J = 38.7 Hz, 1F), –91.5 (d, J = 38.7 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{18}F_2O$ $[M]^+$ 252.1326, found 252.1324.



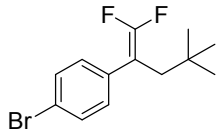
3ia

Methyl 3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzoate (**3ia**). yield 71% (190.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–8.00 (m, 2H), 7.41–7.38 (m, 2H), 3.91 (s, 3H), 2.36 (t, J = 2.8 Hz, 2H), 0.79 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 154.5 (dd, $^1J_{CF}$ = 290.4, 287.1 Hz), 140.6, (dd, $^3J_{CF}$ = 4.9, 3.1 Hz), 129.6, 128.7, 128.4 (t, $^4J_{CF}$ = 3.0 Hz), 90.9 (dd, $^2J_{CF}$ = 22.2, 12.2 Hz), 52.0, 40.9, 32.8 (t, $^3J_{CF}$ = 2.4 Hz), 29.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –87.8 (d, J = 36.5 Hz, 1F), –90.5 (d, J = 36.1 Hz, 1F). HRMS (EI) calcd for $C_{15}H_{18}F_2O_2$ $[M]^+$ 268.1275, found 268.1273.



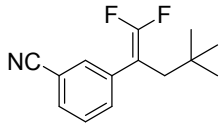
3ja

1-Chloro-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (**3ja**). yield 82% (200.1 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.26–7.23 (m, 2H), 2.31 (t, J = 2.6 Hz, 2H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4 (dd, $^1J_{CF}$ = 288.8, 286.2 Hz), 134.1 (dd, $^3J_{CF}$ = 4.8, 2.8 Hz), 132.8, 129.7 (t, $^4J_{CF}$ = 2.9 Hz), 128.5, 90.3 (dd, $^2J_{CF}$ = 22.2, 12.7 Hz), 41.1, 32.8 (t, $^3J_{CF}$ = 2.5 Hz), 29.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –89.0 (d, J = 39.5 Hz, 1F), –91.7 (d, J = 39.5 Hz, 1F). HRMS (EI) calcd for $C_{13}H_{15}ClF_2$ $[M]^+$ 244.0830, found 244.0828.



3ka

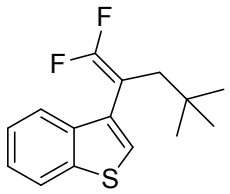
1-Bromo-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (**3ka**). yield 86% (249.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.54 (m, 2H), 7.42–7.36 (m, 2H), 2.36 (t, J = 2.0 Hz, 2H), 0.83 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (dd, $^1J_{CF}$ = 288.7, 286.0 Hz), 134.6 (dd, $^3J_{CF}$ = 4.7, 2.9 Hz), 128.9, 127.4 127.0, 90.9 (dd, $^2J_{CF}$ = 21.6, 12.7 Hz), 41.1, 32.8 (t, $^3J_{CF}$ = 2.5 Hz), 29.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –89.2 (d, J = 40.2 Hz, 1F), –91.8 (d, J = 40.2 Hz, 1F); HRMS (EI) calcd for $C_{13}H_{15}BrF_2$ $[M]^+$ 290.0305, found 290.0308.



3la

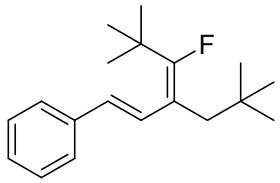
3-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)benzonitrile (**3la**). yield 90% (211.6 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.50–7.44 (m, 2H), 7.39–7.35 (m, 1H), 2.26 (t, J = 2.6 Hz, 2H), 0.72 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7 (dd, $^1J_{CF}$ = 290.2, 287.6 Hz), 136.1 (dd, $^3J_{CF}$ = 5.2, 2.9 Hz), 131.8 (t, $^4J_{CF}$ =

2.8 Hz), 130.9 (t, $^4J_{CF}$ = 3.0 Hz), 129.6, 128.2, 117.5, 111.7, 89.0 (dd, $^2J_{CF}$ = 23.0, 12.4 Hz), 39.9, 31.8 (t, $^3J_{CF}$ = 2.4 Hz), 28.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –87.4 (d, J = 35.7 Hz, 1F), –90.5 (d, J = 35.7 Hz, 1F); HRMS (EI) calcd for $C_{14}H_{15}F_2N$ $[M]^+$ 235.1173, found 235.1174.



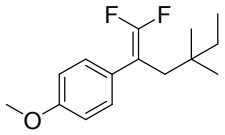
3ma

3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzo[b]thiophene (**3ma**). yield 84% (223.4 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.83 (m, 1H), 7.72−7.70 (m, 1H), 7.43−7.33 (m, 2H), 7.28−7.22 (m, 1H), 2.41−2.40 (m, 2H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2 (t, $^1J_{CF}$ = 288.2 Hz), 140.0, 137.5, 131.1 (dd, $^3J_{CF}$ = 4.8, 1.8 Hz), 124.7 (dd, $^3J_{CF}$ = 4.5, 1.2 Hz), 124.4, 124.3, 123.0, 122.9, 85.4 (dd, $^2J_{CF}$ = 24.0, 15.1 Hz), 42.8, 32.7 (t, $^3J_{CF}$ = 2.5 Hz), 29.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ −85.2 (d, J = 36.5Hz, 1F), −89.2 (d, J = 36.5 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{16}F_2S$ $[M]^+$ 266.0941, found 266.0942.



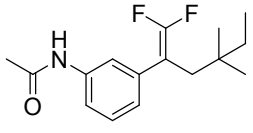
3na

((1E,3E)-4-fluoro-5,5-dimethyl-3-neopentylhexa-1,3-dien-1-yl)benzene (**3na**). yield 88% (241.1 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.18 (m, 6H), 6.49 (d, J = 16.4 Hz, 1H), 2.33 (d, J = 5.2 Hz, 2H), 1.34 (d, J = 2.0 Hz, 9H), 0.92 (d, J = 1.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 (t, $^1J_{CF}$ = 259.4 Hz), 138.2, 128.7, 128.3 (d, $^3J_{CF}$ = 10.0 Hz), 127.0, 126.3 (d, $^3J_{CF}$ = 8.9 Hz), 126.0, 114.3 (d, $^2J_{CF}$ = 24.4 Hz), 39.1 (t, $^3J_{CF}$ = 7.3 Hz), 36.8 (d, $^2J_{CF}$ = 26.9 Hz), 32.6 (d, $^4J_{CF}$ = 1.3 Hz), 30.5 (d, $^4J_{CF}$ = 1.7 Hz), 29.9 (d, $^4J_{CF}$ = 5.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −91.8 (s, 1F); HRMS (EI) calcd for $C_{19}H_{27}F$ $[M]^+$ 274.2097, found 274.2096.



3cb

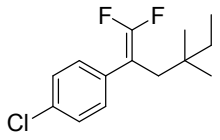
1-(1,1-Difluoro-4,4-dimethylhex-1-en-2-yl)-4-methoxybenzene (**3cb**). yield 88% (223.6 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.28 (t, J = 2.4 Hz, 2H), 1.16 (q, J = 7.6 Hz, 2H), 0.74 (t, J = 7.6 Hz, 3H), 0.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 154.3 (dd, $^1J_{CF}$ = 286.6, 285.2 Hz), 129.6 (t, $^3J_{CF}$ = 2.8 Hz), 127.8 (dd, J_{CF} = 4.6, 2.6 Hz), 113.7, 90.4 (dd, $^2J_{CF}$ = 21.4, 13.4 Hz), 55.2, 39.3, 35.2 (t, $^3J_{CF}$ = 2.4 Hz), 34.7, 26.6, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –90.7 (d, J = 44.0 Hz, 1F), –93.1 (d, J = 43.6 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{20}F_2O$ $[M]^+$ 254.1482, found 254.1483.



3gb

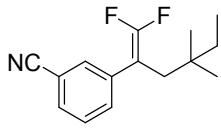
N-(3-(1,1-difluoro-4,4-dimethylhex-1-en-2-yl)phenyl)acetamide (**3gb**). yield 45% (126.5 mg), yellow oil; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.46–7.44 (m, 2H), 7.28–7.24 (m, 1H), 7.05 (d, J = 7.6 Hz, 1H), 2.30 (t, J = 2.2 Hz, 2H), 2.16 (s, 3H), 1.15 (q, J = 7.5 Hz, 2H), 0.73 (t, J = 7.6 Hz, 3H), 0.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 154.3 (dd, $^1J_{CF}$ = 288.3, 285.9 Hz), 138.0, 136.6 (dd, $^3J_{CF}$ = 4.7, 2.6 Hz), 128.8, 124.5 (t, $^4J_{CF}$ = 2.3 Hz), 119.9 (t, $^4J_{CF}$ = 2.6 Hz), 118.5, 90.7 (dd, $^2J_{CF}$ = 12.8, 21.6 Hz), 39.2, 35.2 (t, $^3J_{CF}$ = 2.4 Hz), 34.7, 26.5, 24.6, 8.3; ^{19}F NMR(376 MHz, $CDCl_3$): δ –89.3 (d, J = 40.2 Hz, 1F), –91.5 (d, J = 39.9 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{21}F_2NO$ $[M]^+$ 281.1591, found 281.1592.



3jb

1-Chloro-4-(1,1-difluoro-4,4-dimethylhex-1-en-2-yl)benzene (**3jb**). yield 75% (193.6 mg), light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.25–7.22 (m, 2H), 2.30 (t, J = 2.4 Hz, 2H), 1.15 (q, J = 7.5 Hz, 2H), 0.74 (t, J = 7.6 Hz, 3H), 0.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3 (dd, $^1J_{CF}$ = 288.4, 286.2 Hz), 134.2 (dd, $^3J_{CF}$ = 5.0, 2.7 Hz), 132.8, 129.8 (t, $^4J_{CF}$ = 2.8 Hz), 128.5, 90.2 (dd, $^2J_{CF}$ = 22.1, 12.9 Hz), 39.2, 35.3 (t, $^3J_{CF}$ = 2.4 Hz), 34.7, 26.6, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –89.0 (d, J = 39.5 Hz, 1F), –91.5 (d, J = 39.9 Hz, 1F); HRMS (EI) calcd for $C_{14}H_{17}ClF_2$ $[M]^+$ 258.0987, found 258.0989.

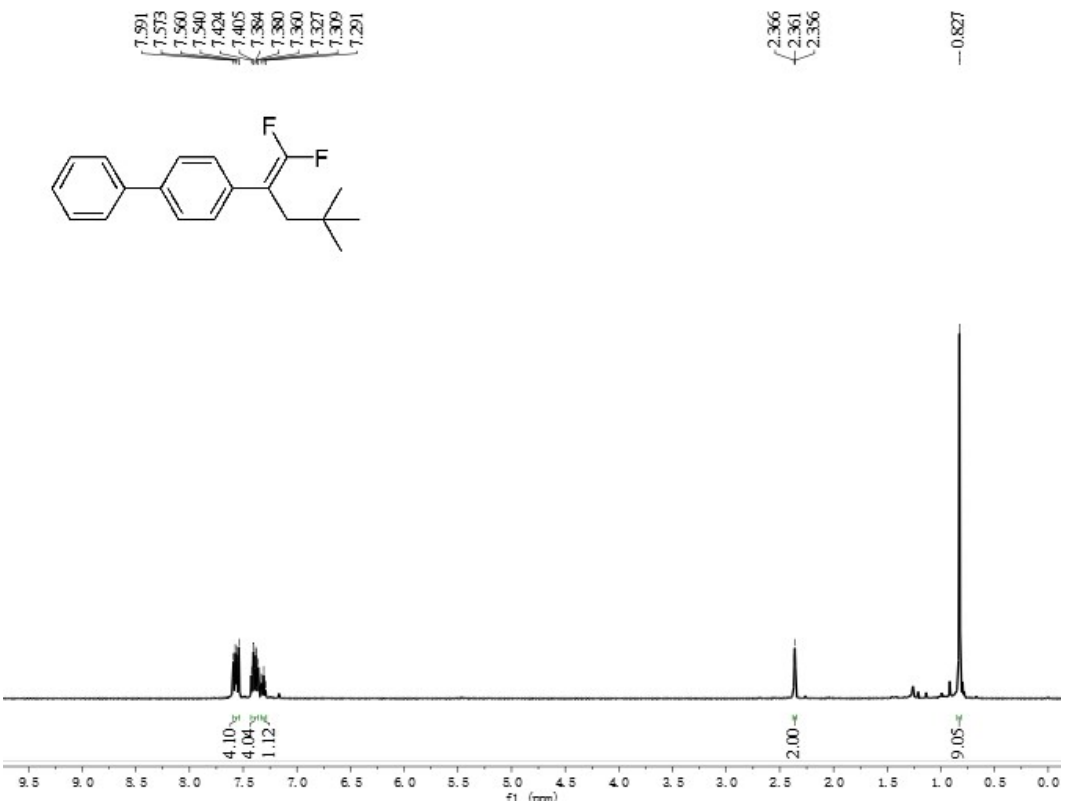


3lb

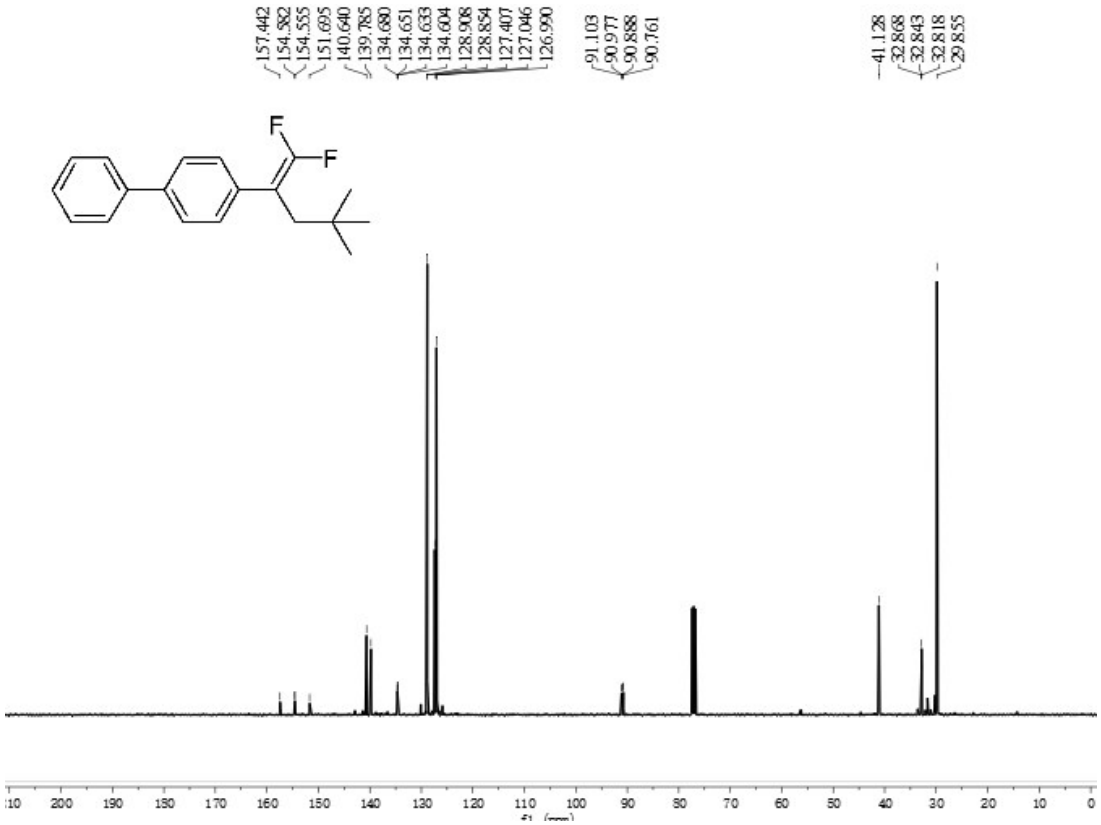
3-(1,1-Difluoro-4,4-dimethylhex-1-en-2-yl)benzonitrile (**3lb**). yield 84% (209.3 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.60 (m, 1H), 7.57–7.53 (m, 2H), 7.47–7.43 (m, 1H), 2.33 (t, J = 2.6 Hz, 2H), 1.16 (q, J = 7.6 Hz, 2H), 0.75 (t, J = 7.4 Hz, 3H), 0.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (dd, $^1J_{CF}$= 289.8, 287.6 Hz), 137.3 (dd, $^3J_{CF}$ = 5.2, 2.8 Hz), 132.9 (t, $^4J_{CF}$ = 2.8 Hz), 132.0 (t, $^4J_{CF}$ = 3.0 Hz), 130.6, 129.2, 118.6, 112.7, 89.8 (dd, $^2J_{CF}$ = 23.0, 12.4 Hz), 39.1, 35.4, 34.7, 26.5, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –87.4 (d, J = 36.5 Hz, 1F), –90.3 (d, J = 36.1 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{17}F_2N$ $[M]^+$ 249.1329, found 249.1331.

4. ^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of the target compounds 3

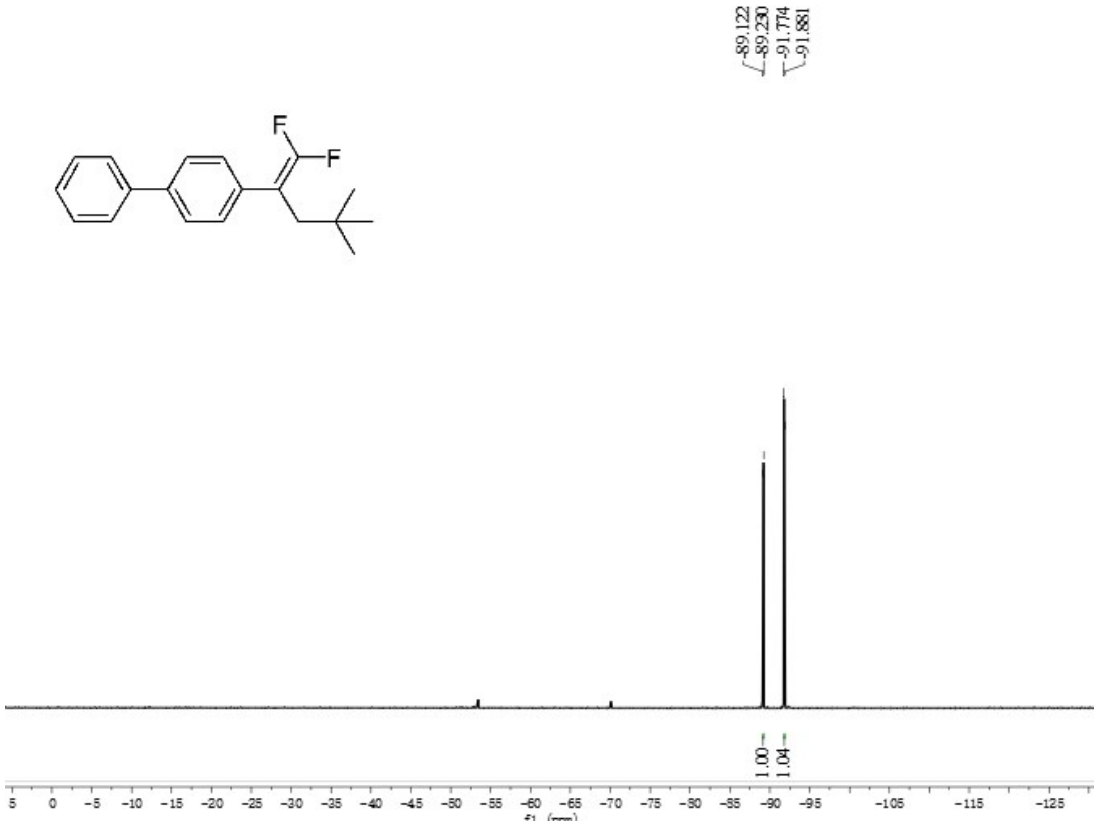
^{1}H NMR spectrum of 3aa



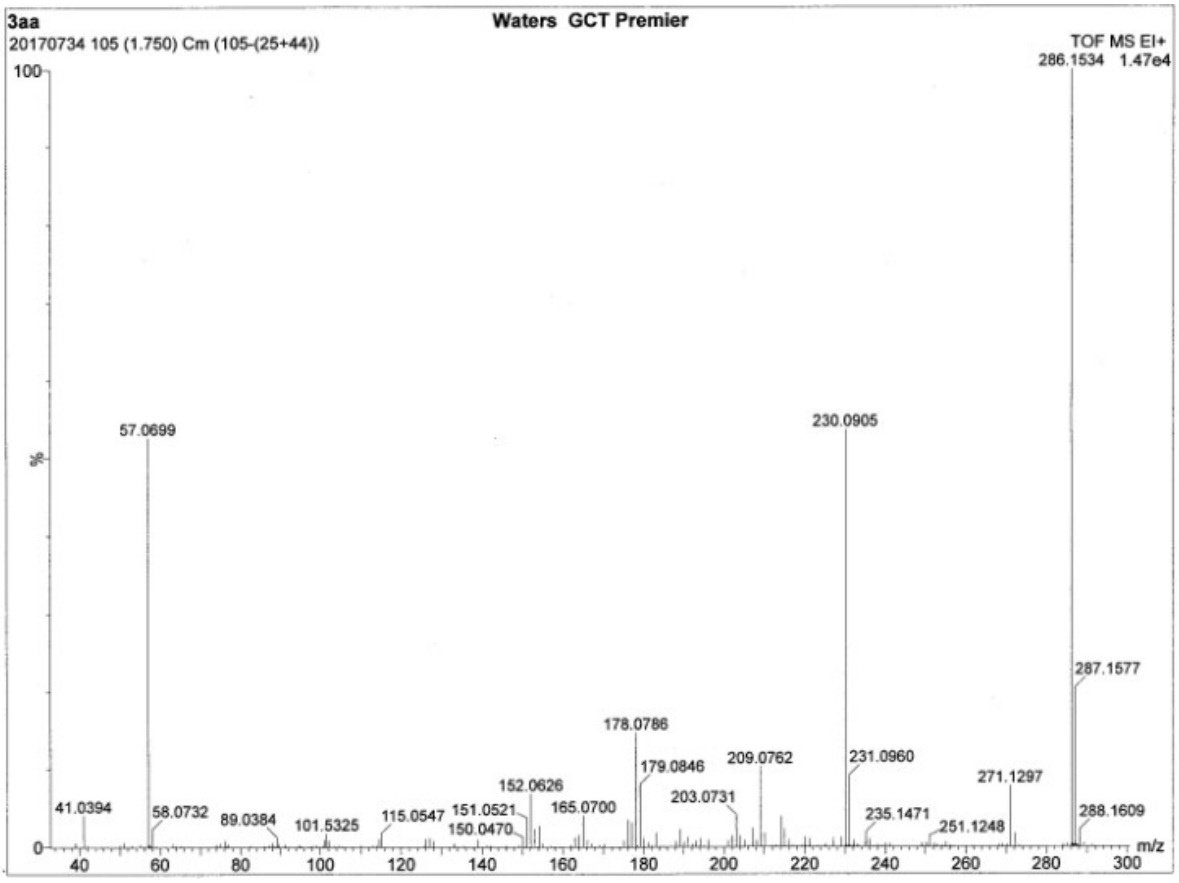
^{13}C NMR spectrum of 3aa



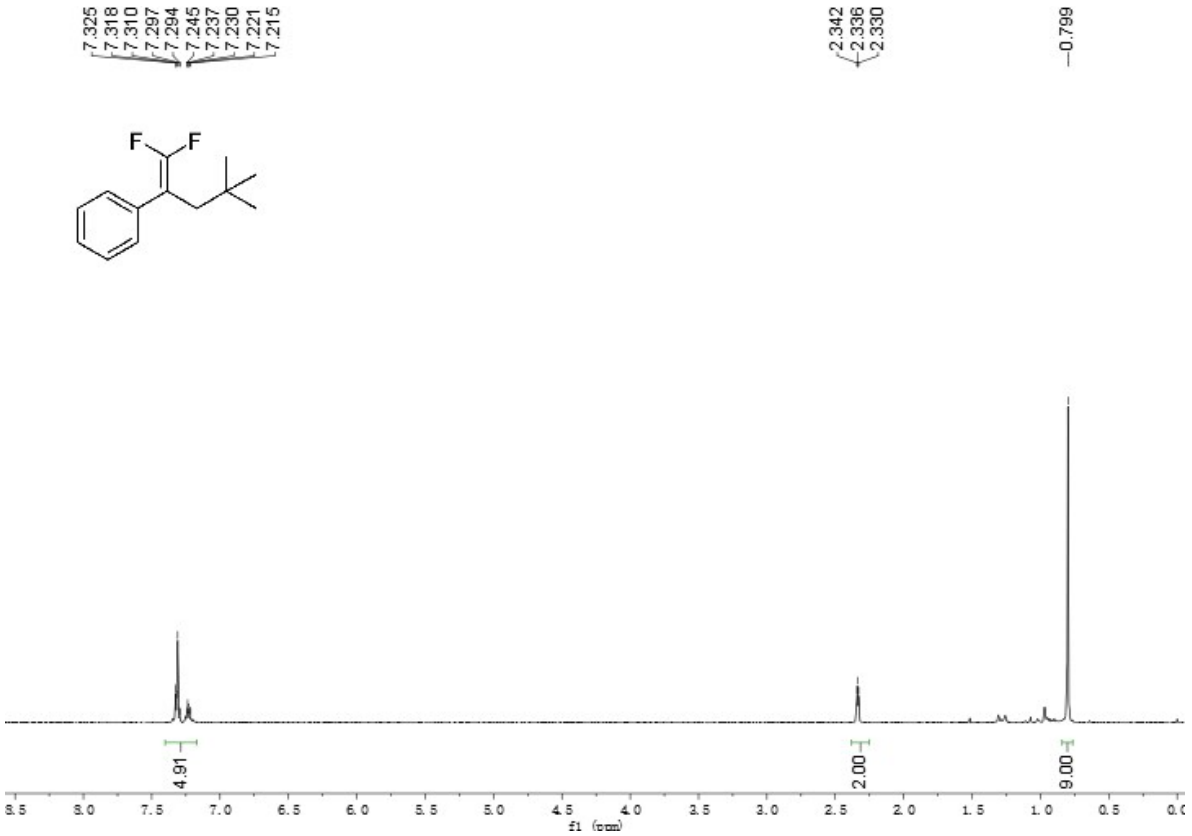
^{19}F NMR spectrum of 3aa



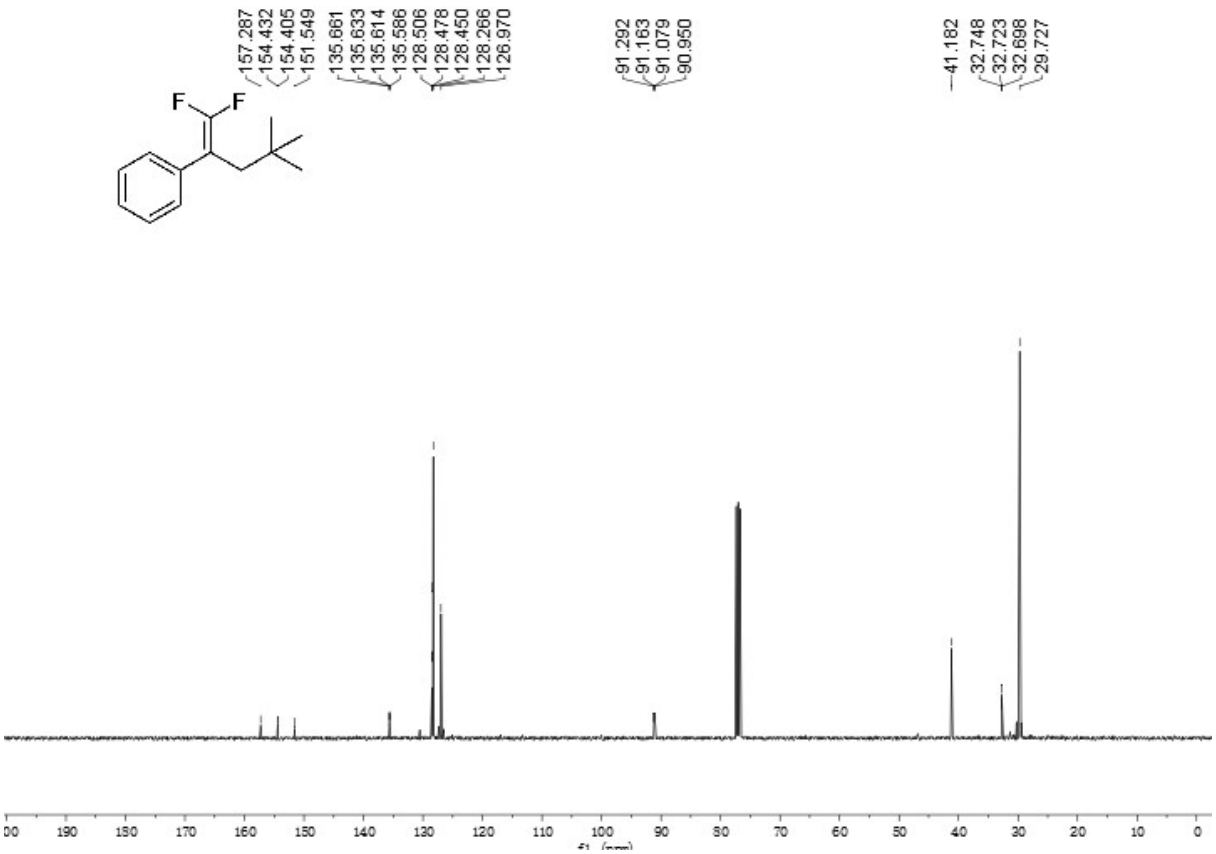
HRMS (EI) spectrum of 3aa



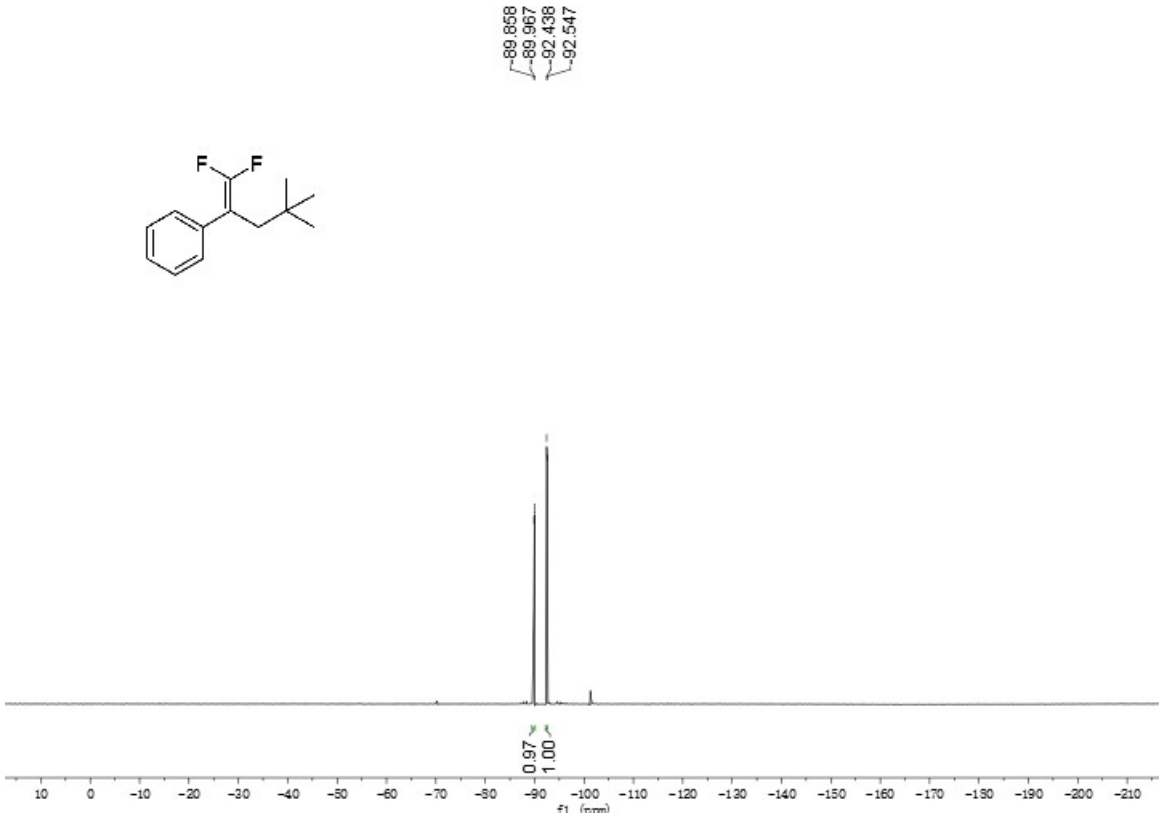
^{1}H NMR spectrum of 3ba



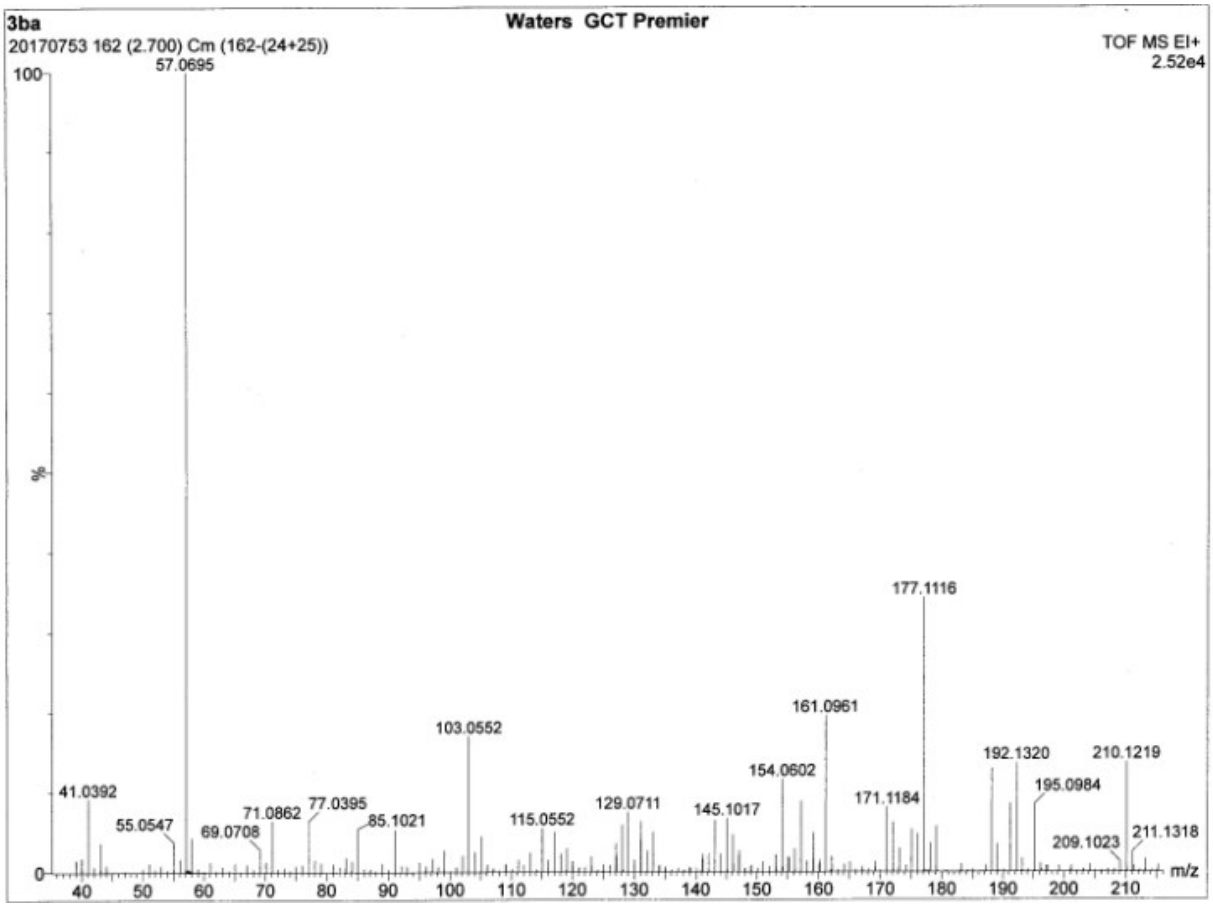
^{13}C NMR spectrum of 3ba



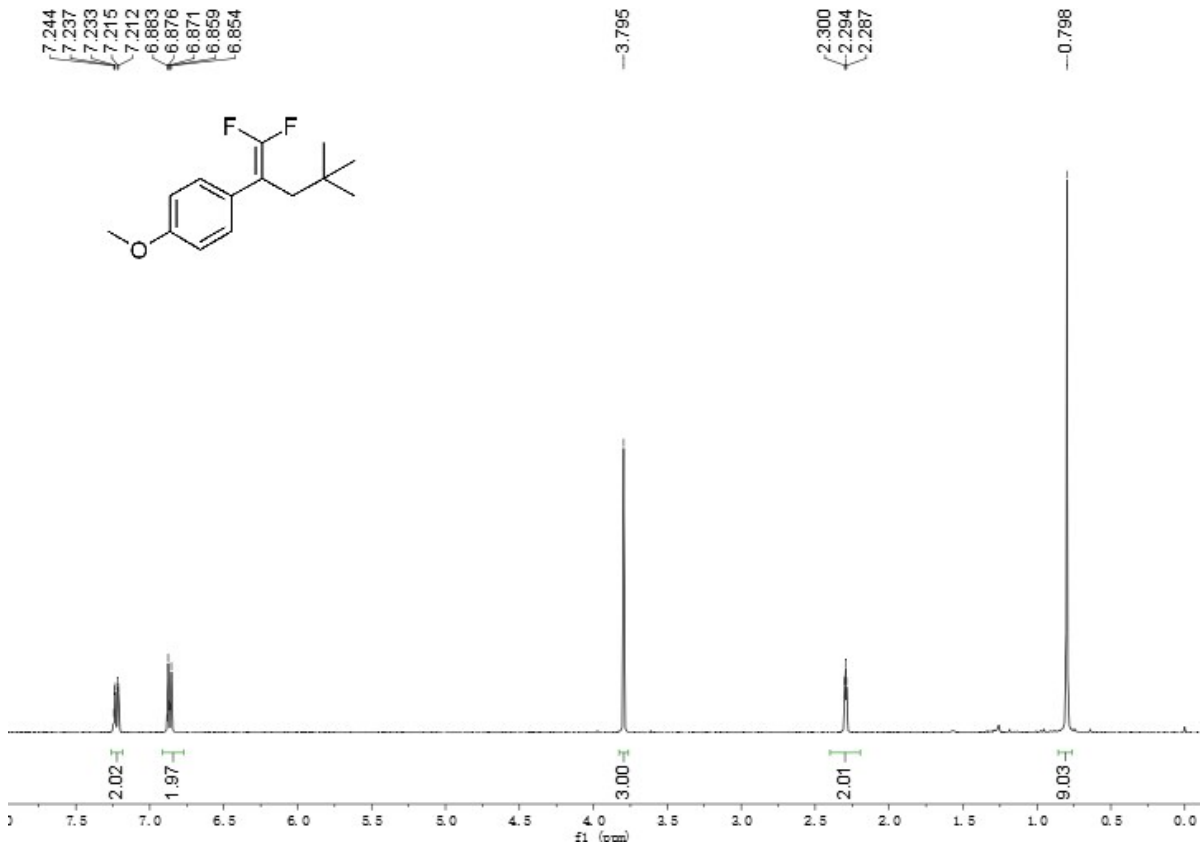
^{19}F NMR spectrum of 3ba



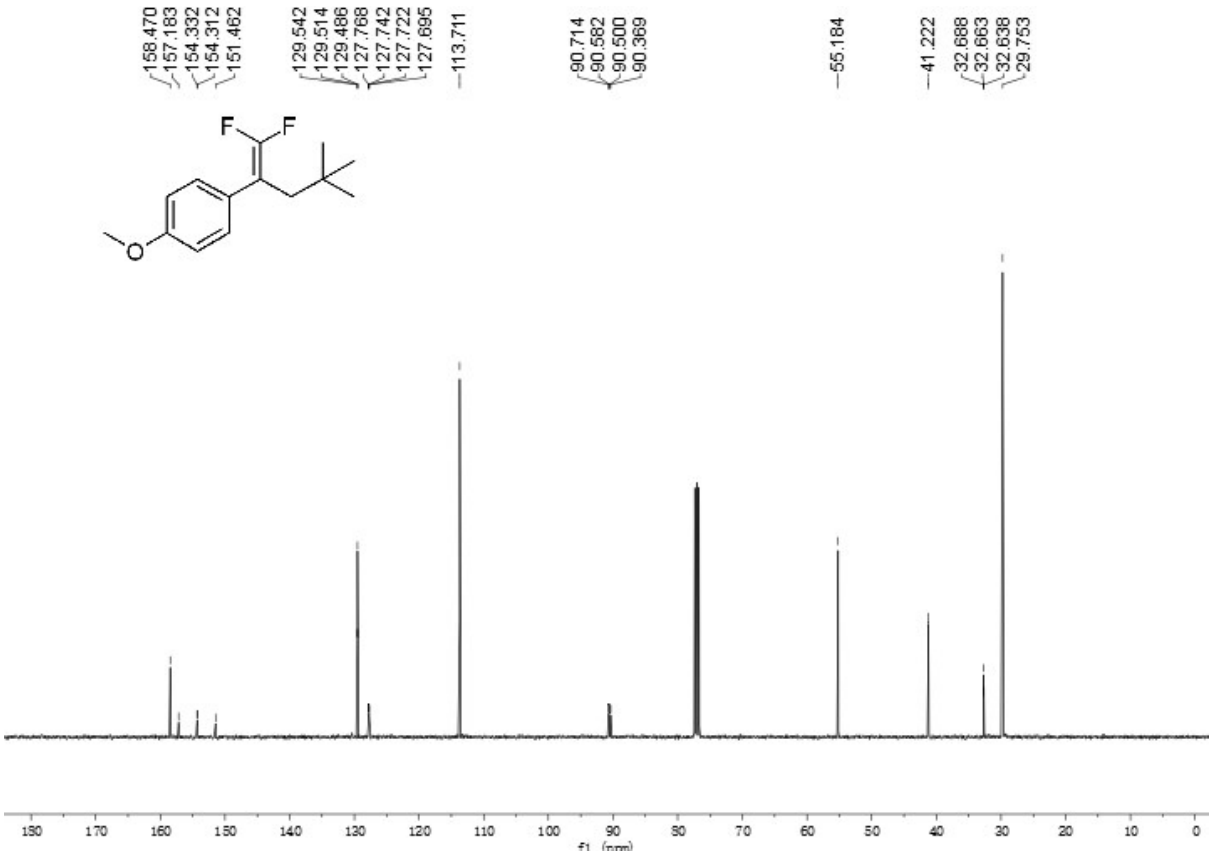
HRMS (EI) spectrum of 3ba



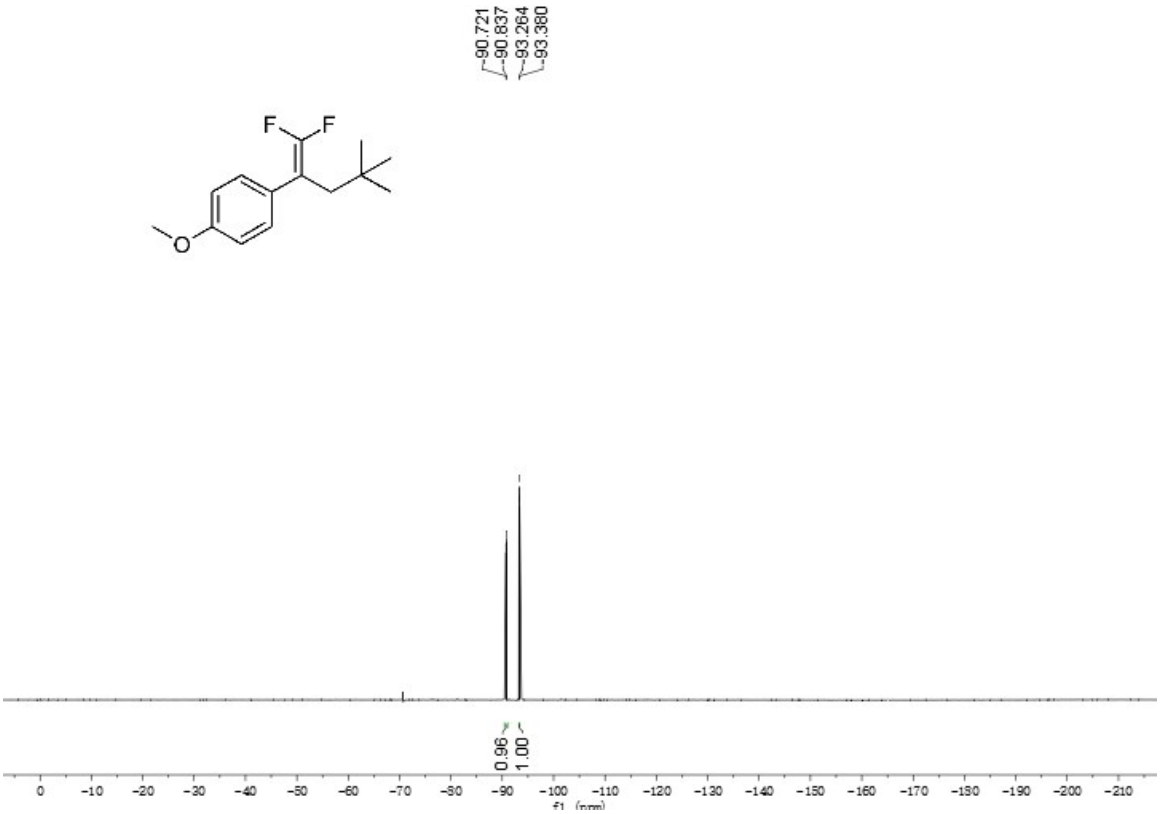
^{1}H NMR spectrum of 3ca



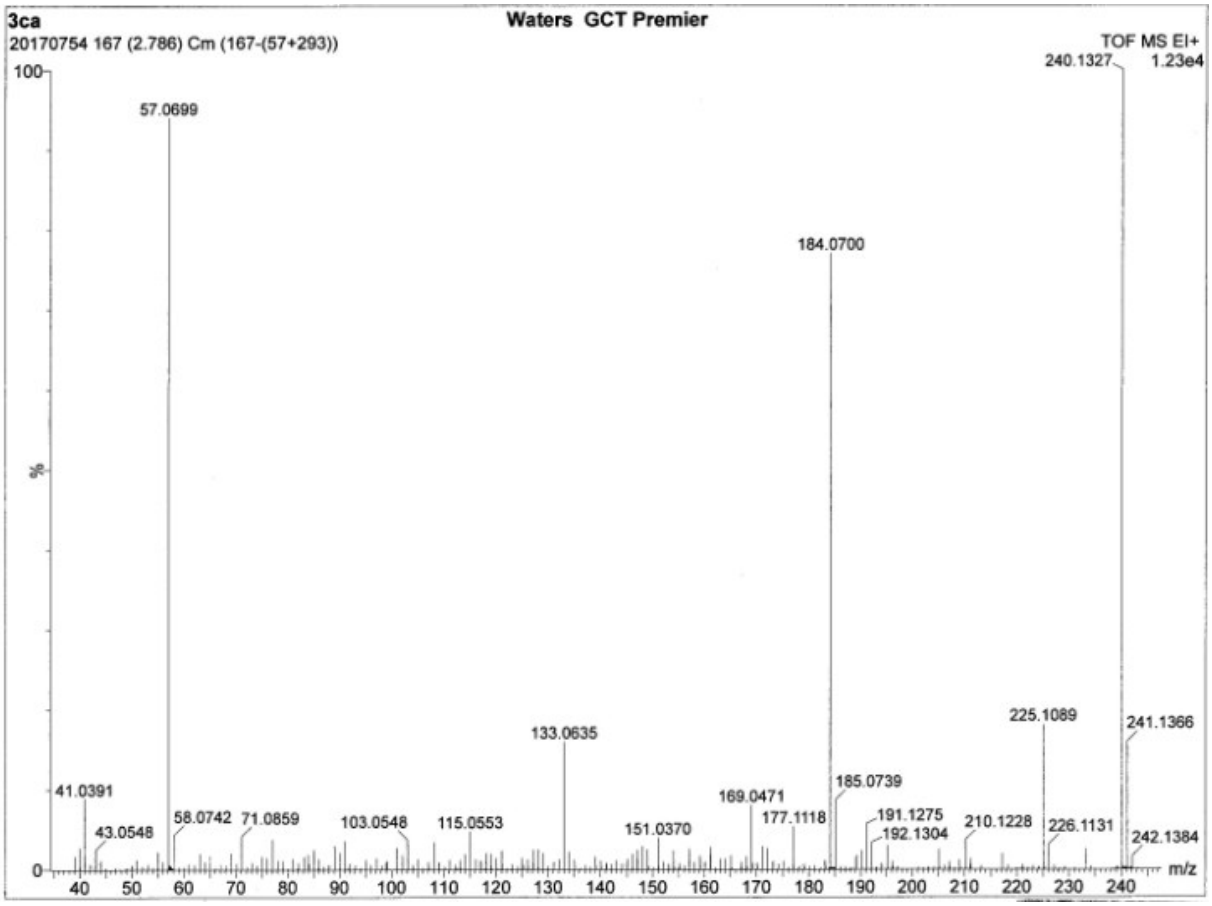
^{13}C NMR spectrum of 3ca



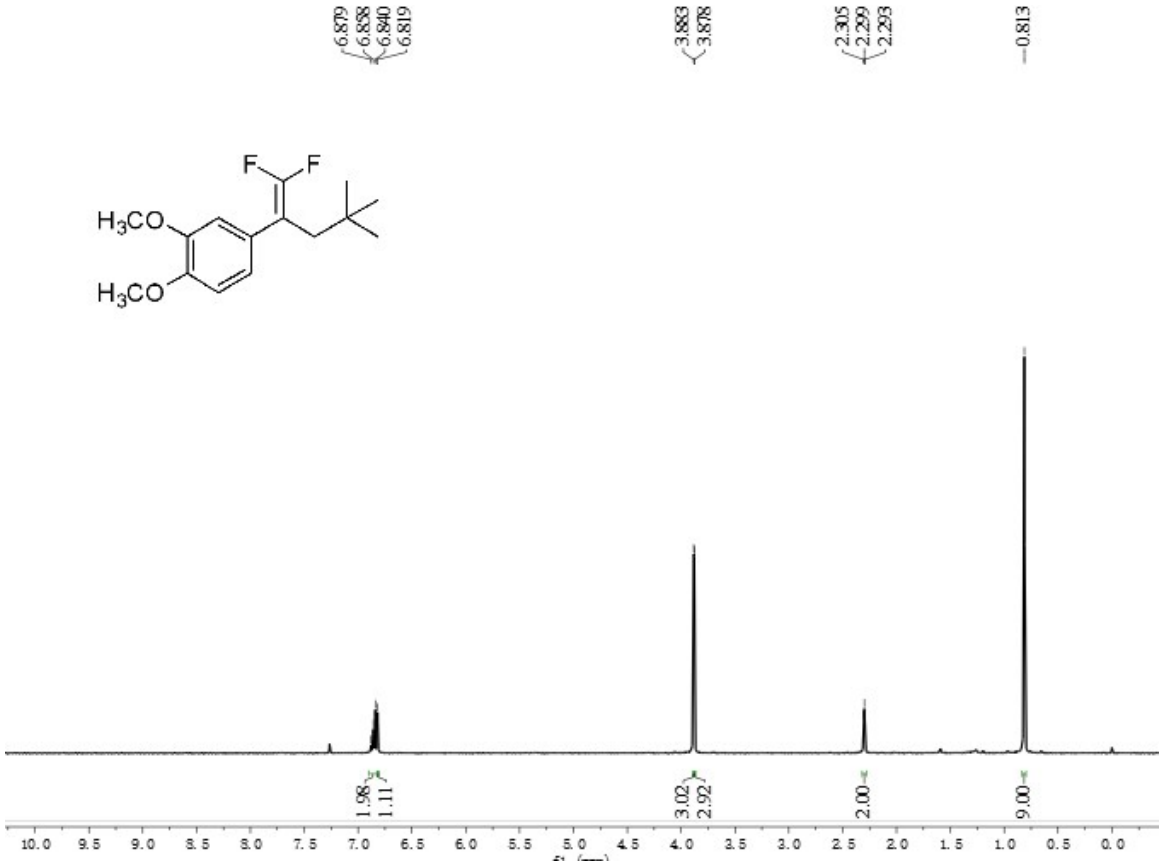
^{19}F NMR spectrum of 3ca



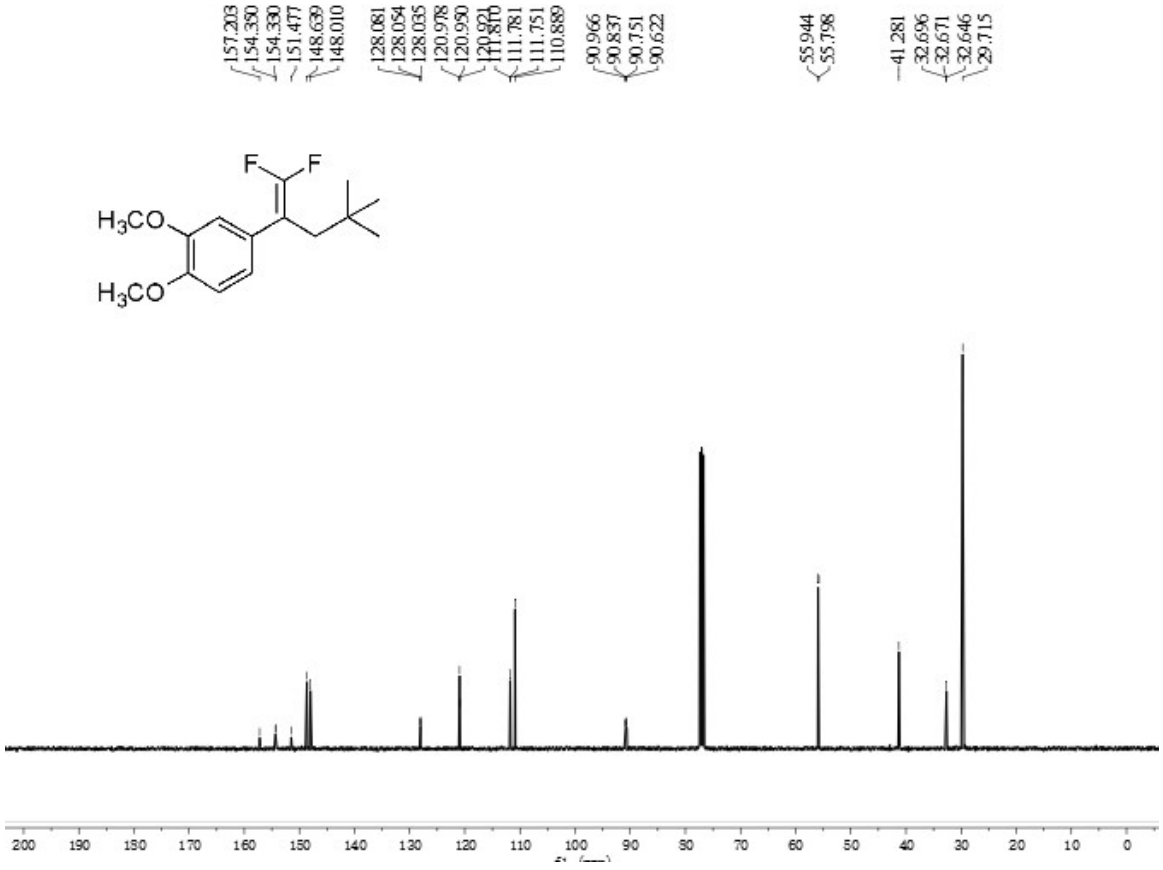
HRMS (EI) spectrum of 3ca



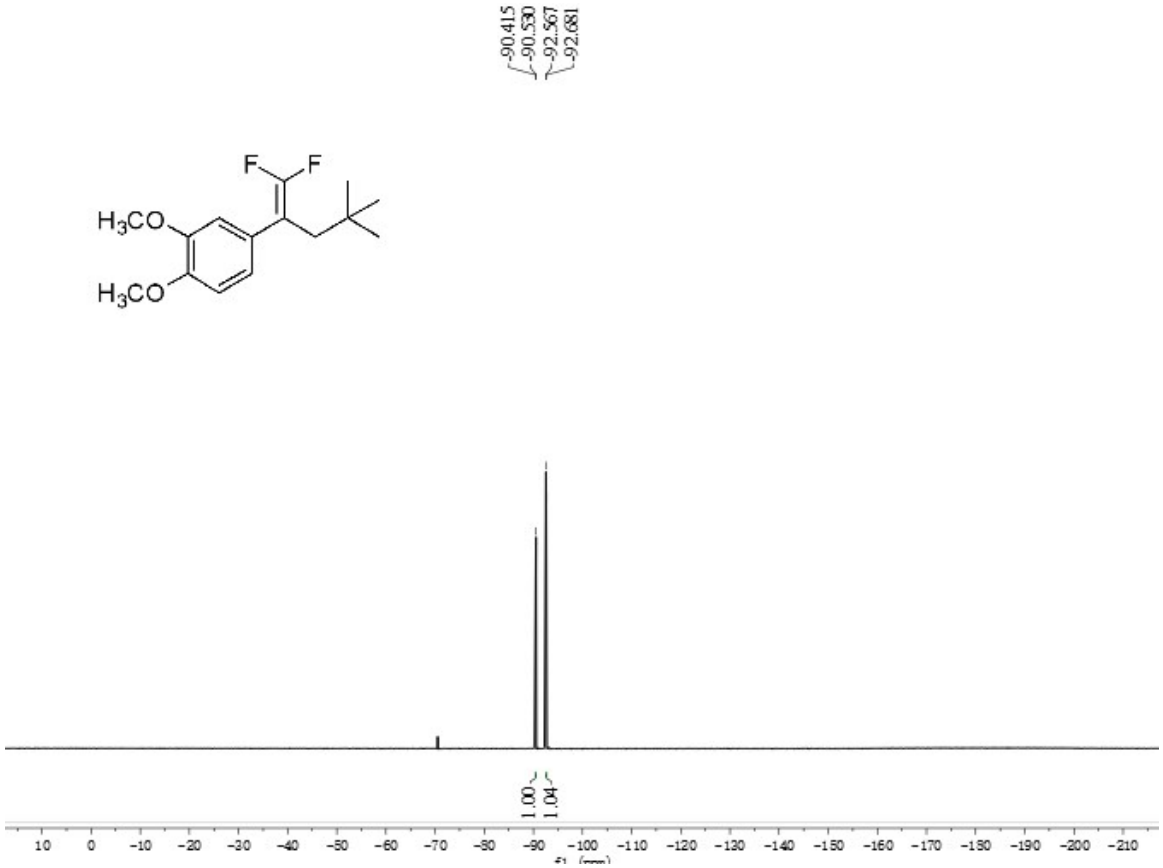
^{1}H NMR spectrum of 3da



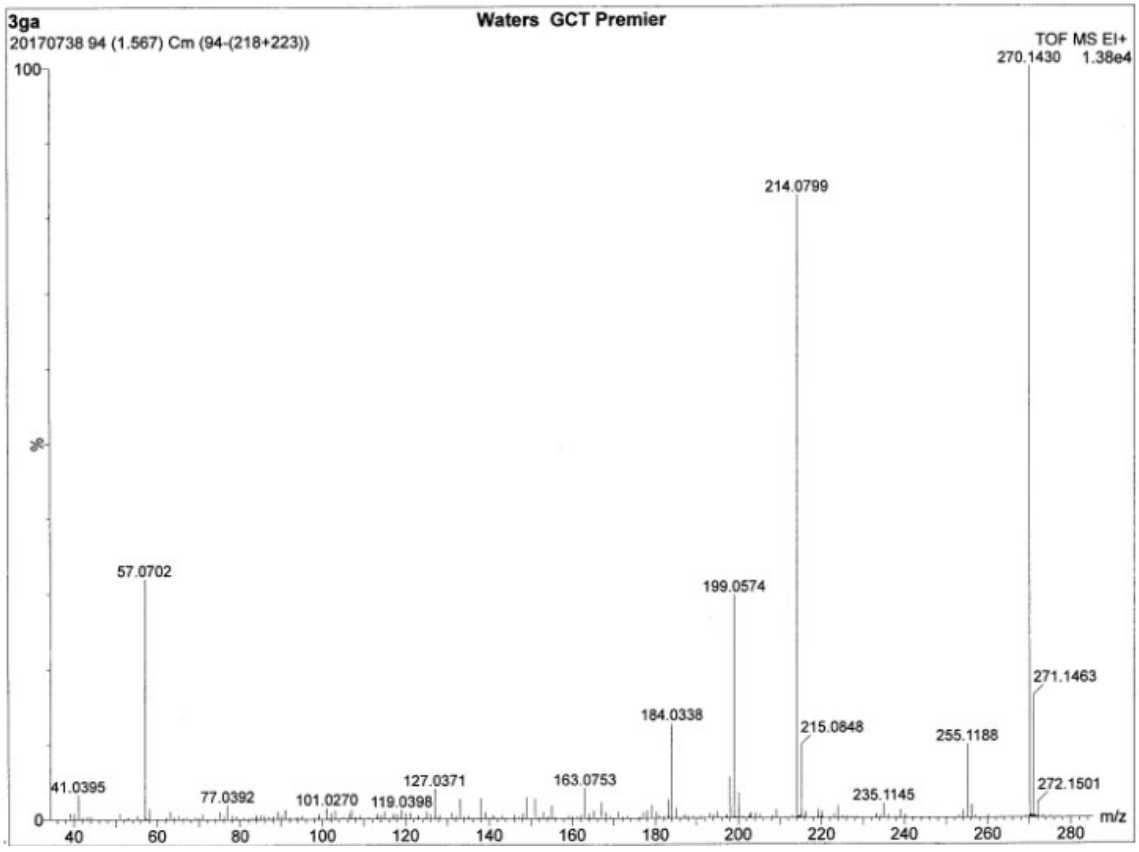
^{13}C NMR spectrum of 3da



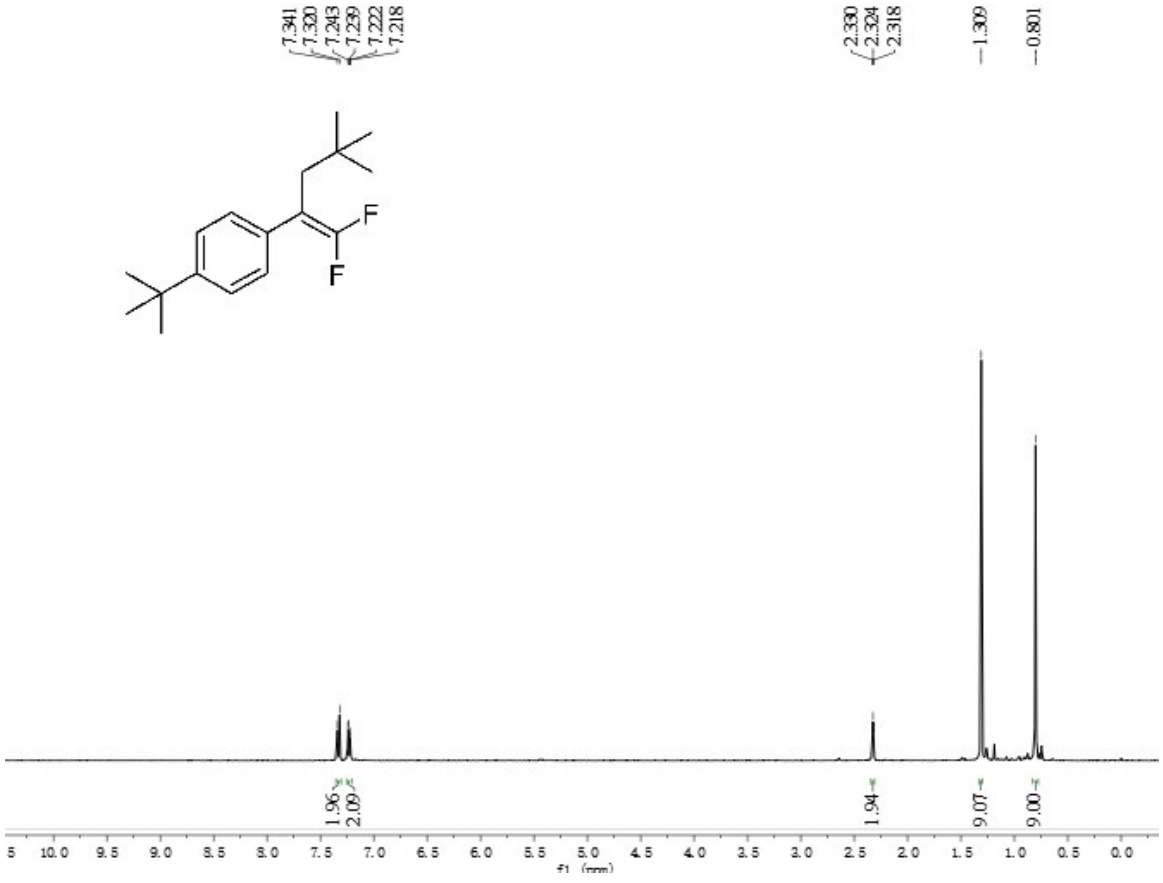
^{19}F NMR spectrum of 3da



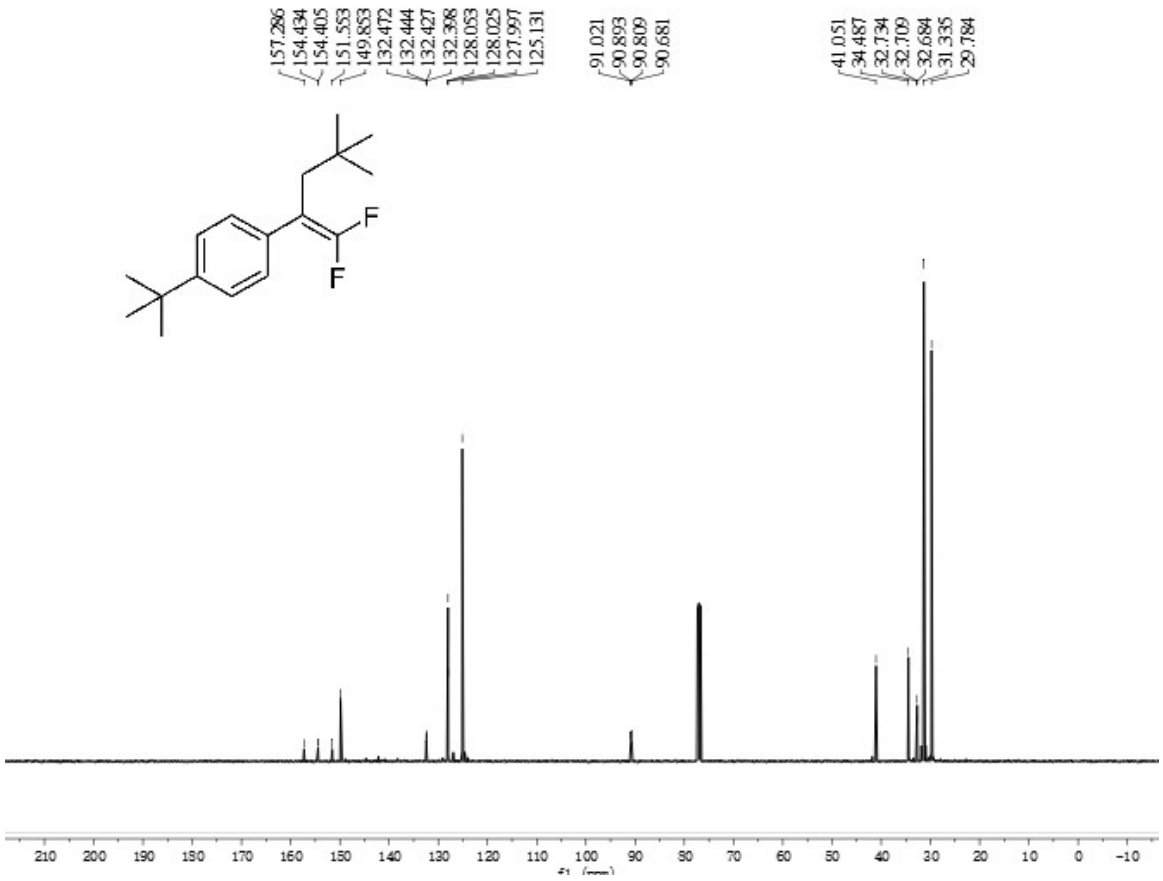
HRMS (EI) spectrum of 3da



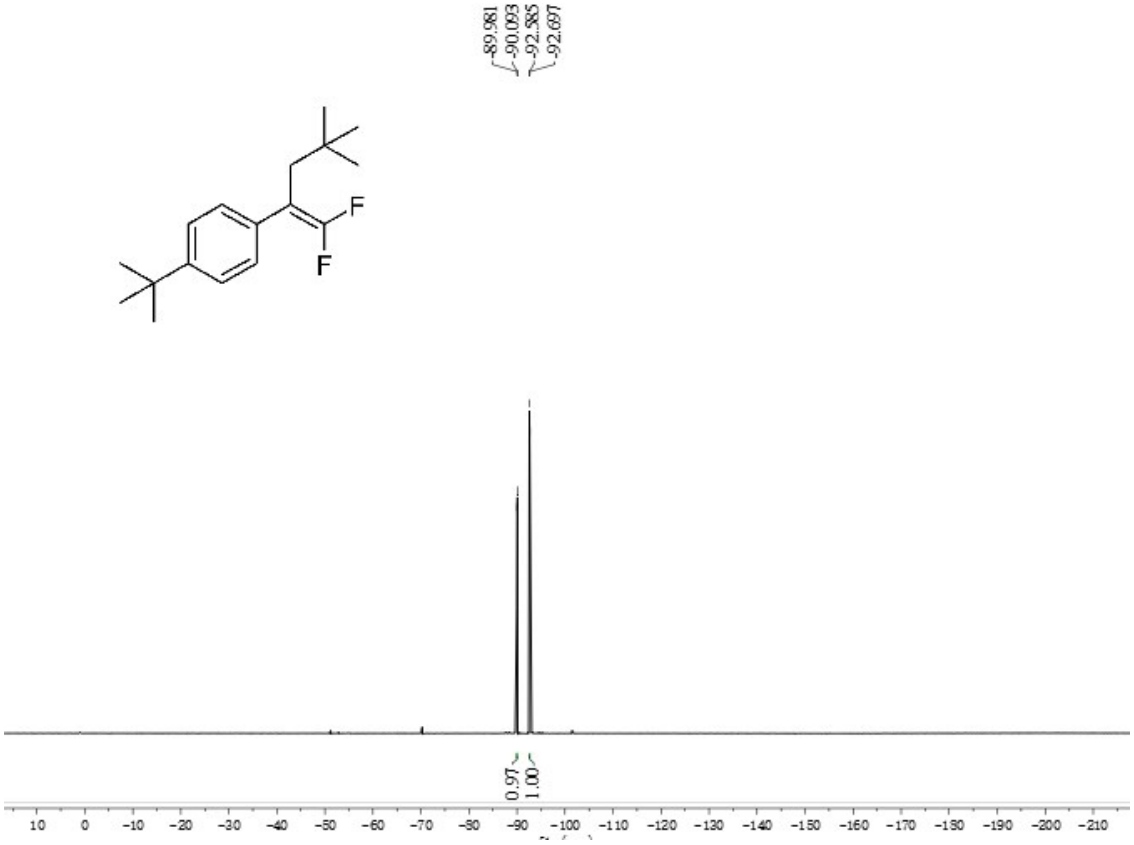
^{1}H NMR spectrum of 3ea



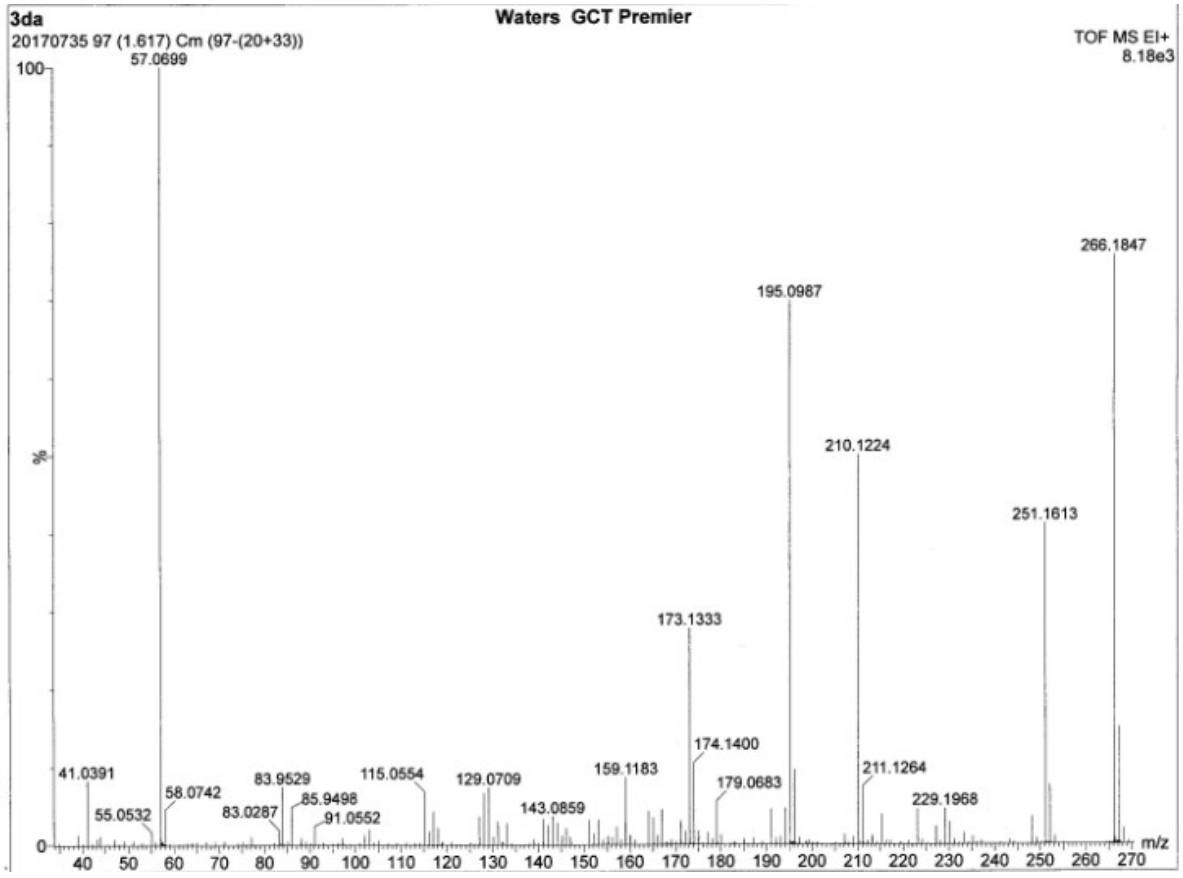
^{13}C NMR spectrum of 3ea



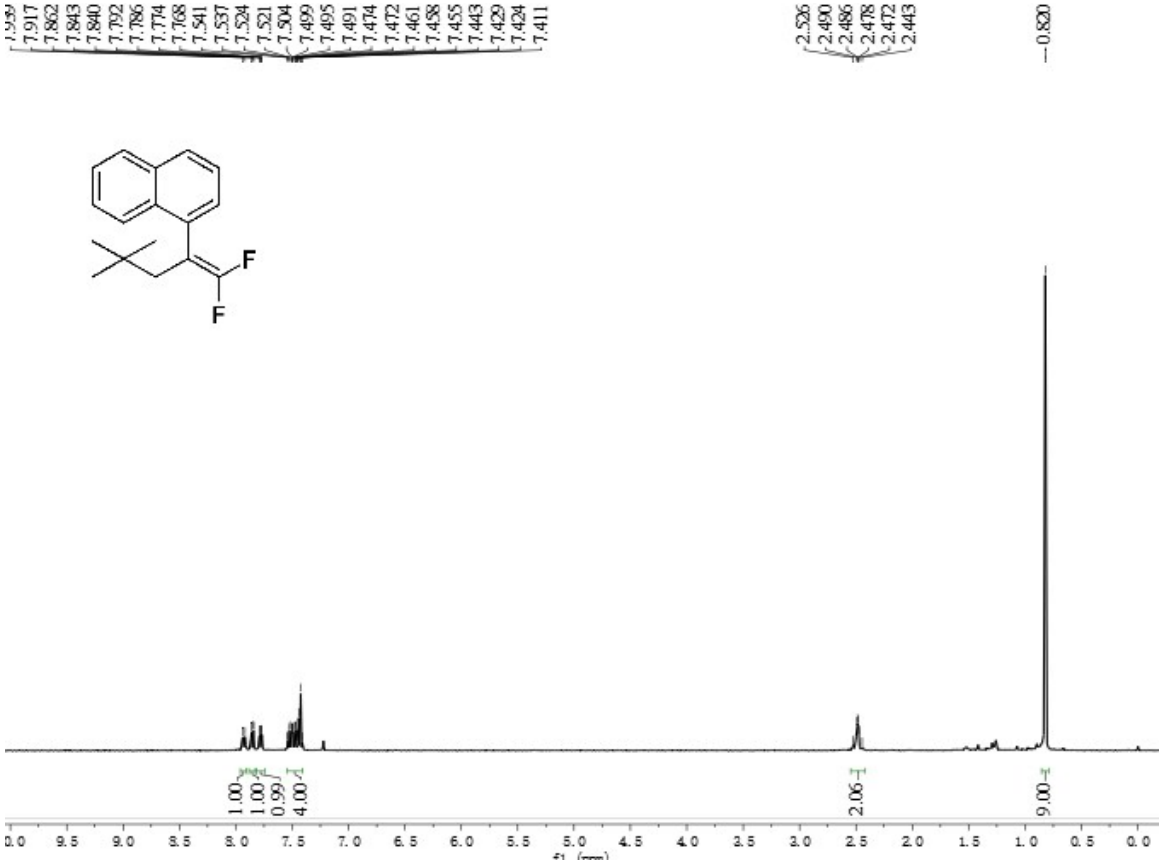
^{19}F NMR spectrum of 3ea



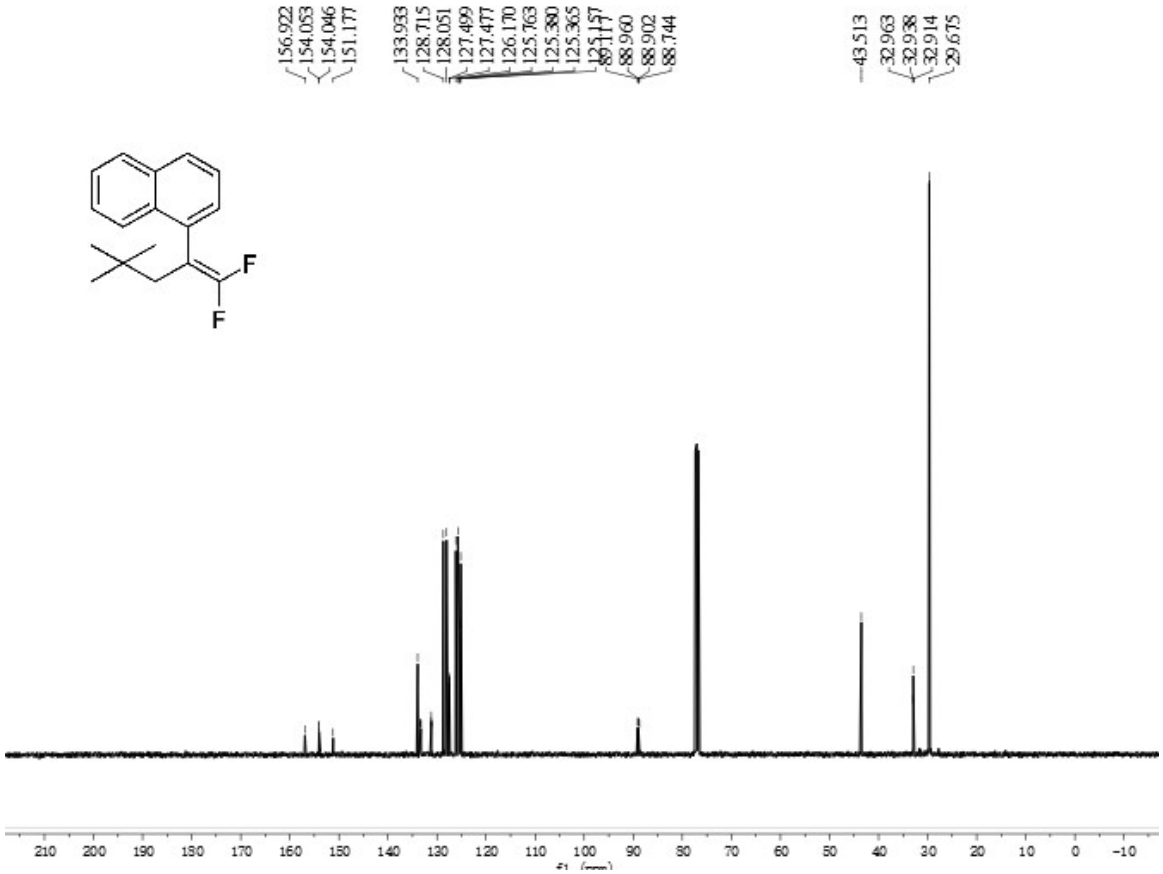
HRMS (EI) spectrum of 3ea



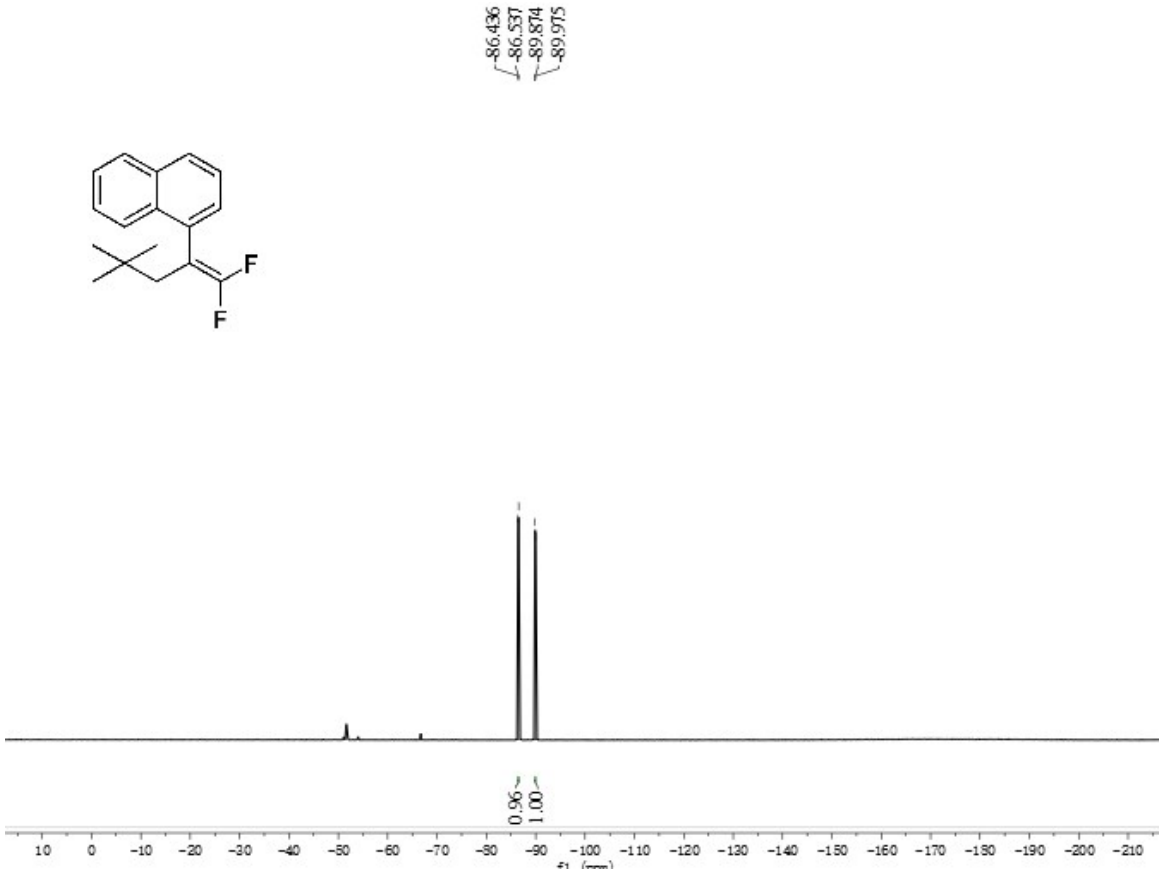
^{1}H NMR spectrum of 3fa



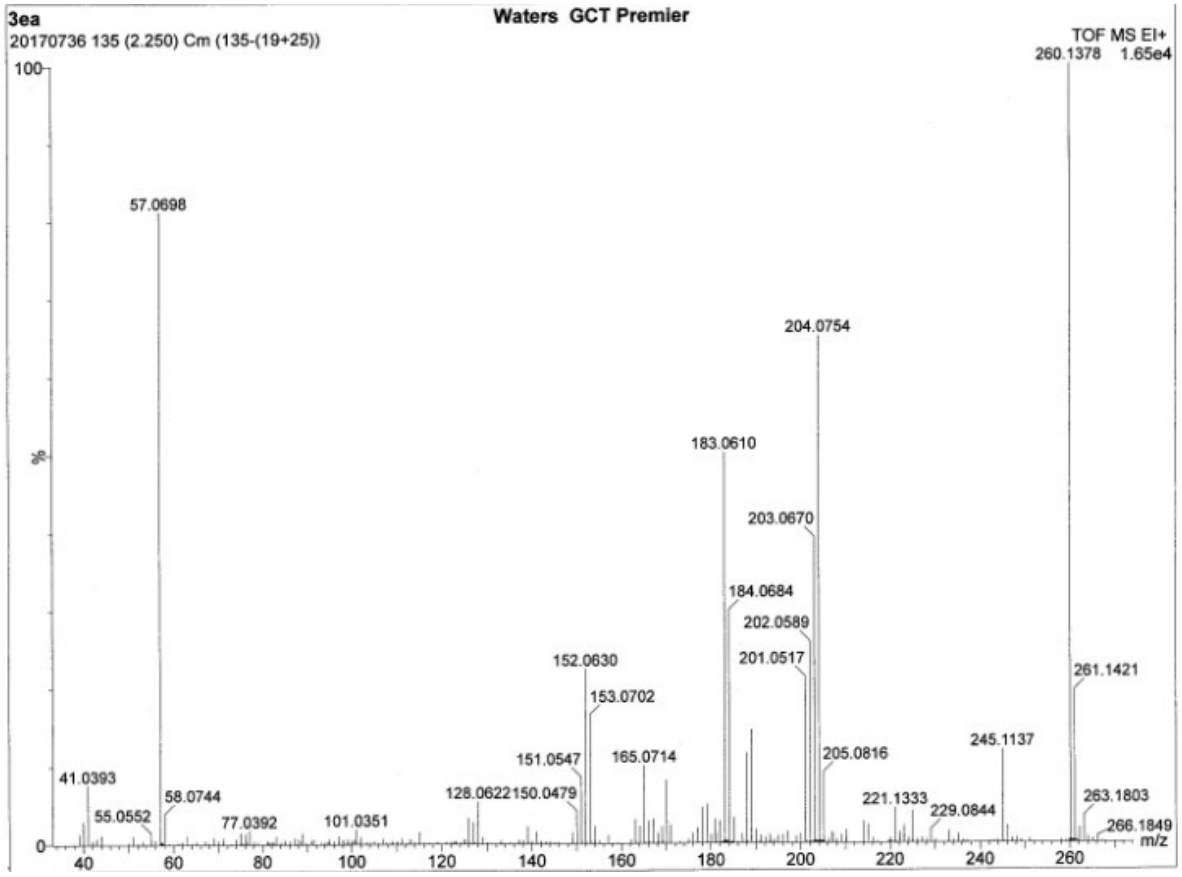
^{13}C NMR spectrum of 3fa



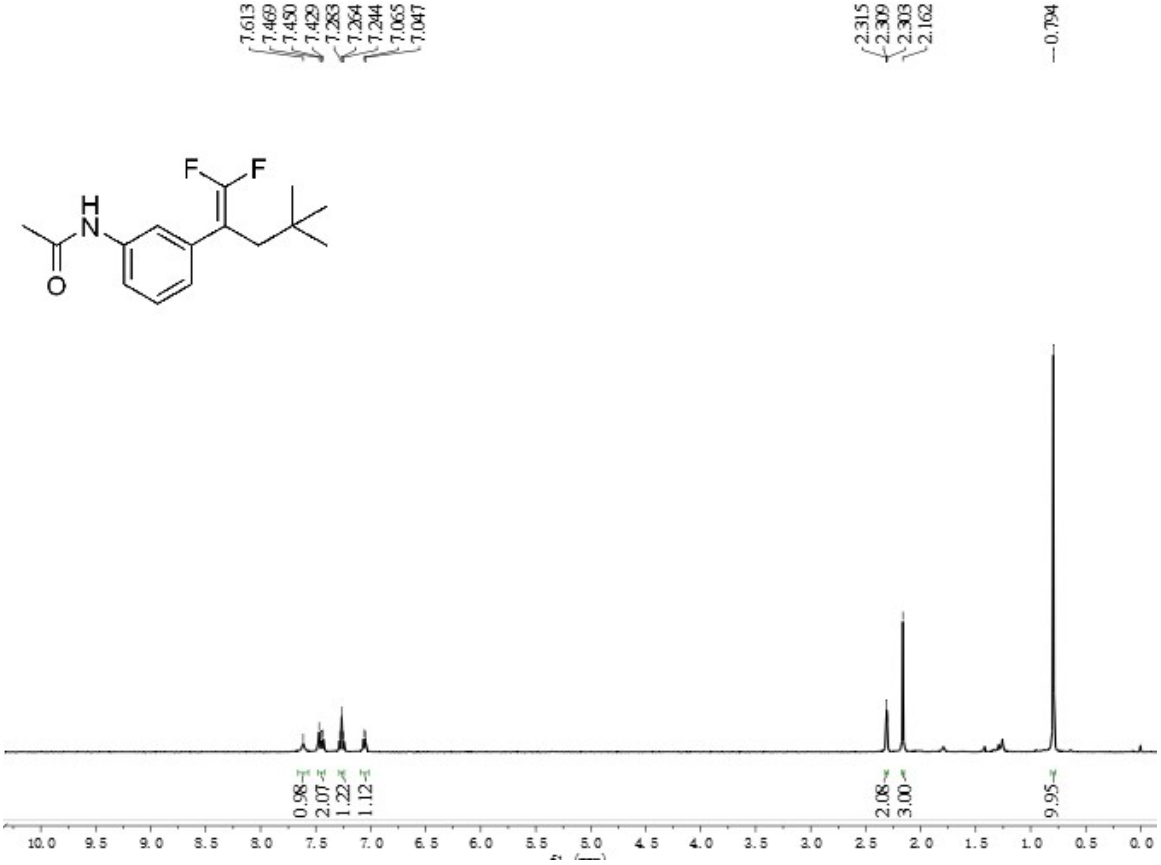
^{19}F NMR spectrum of 3fa



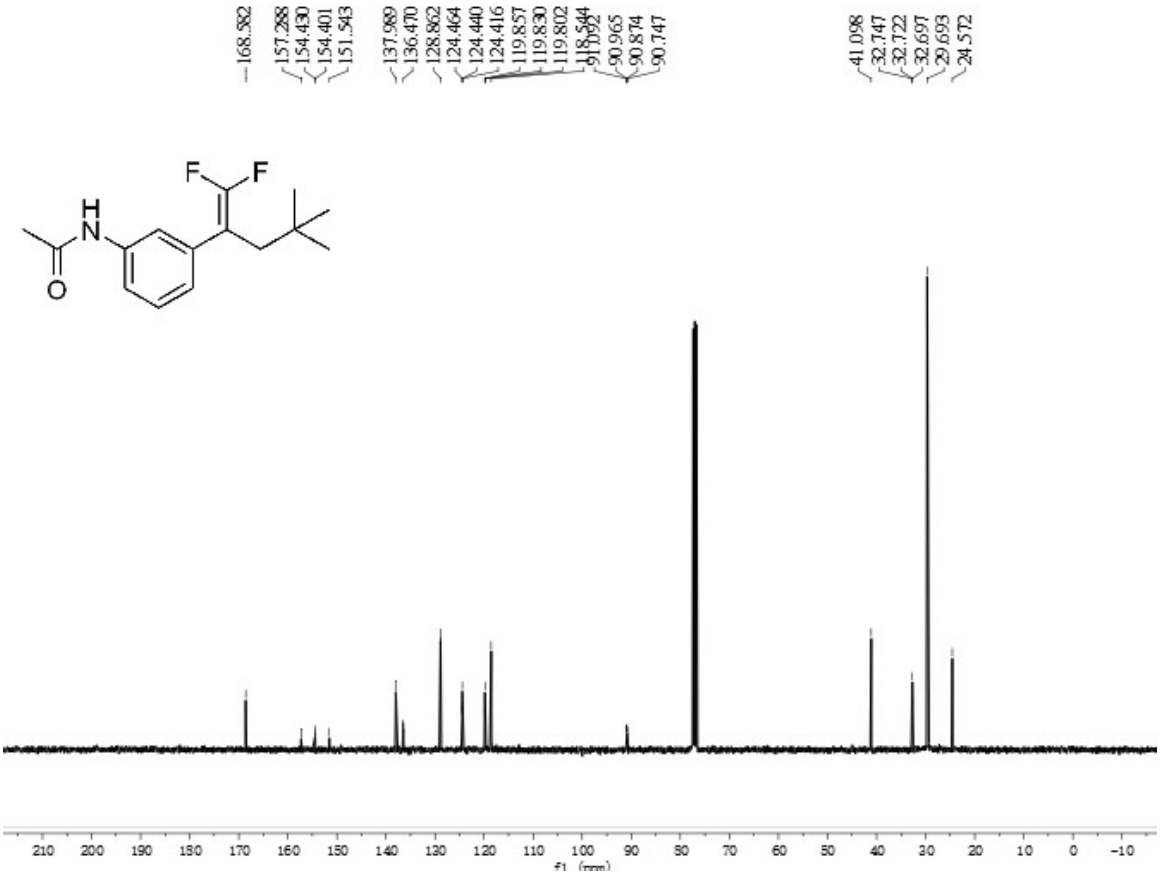
HRMS (EI) spectrum of 3fa



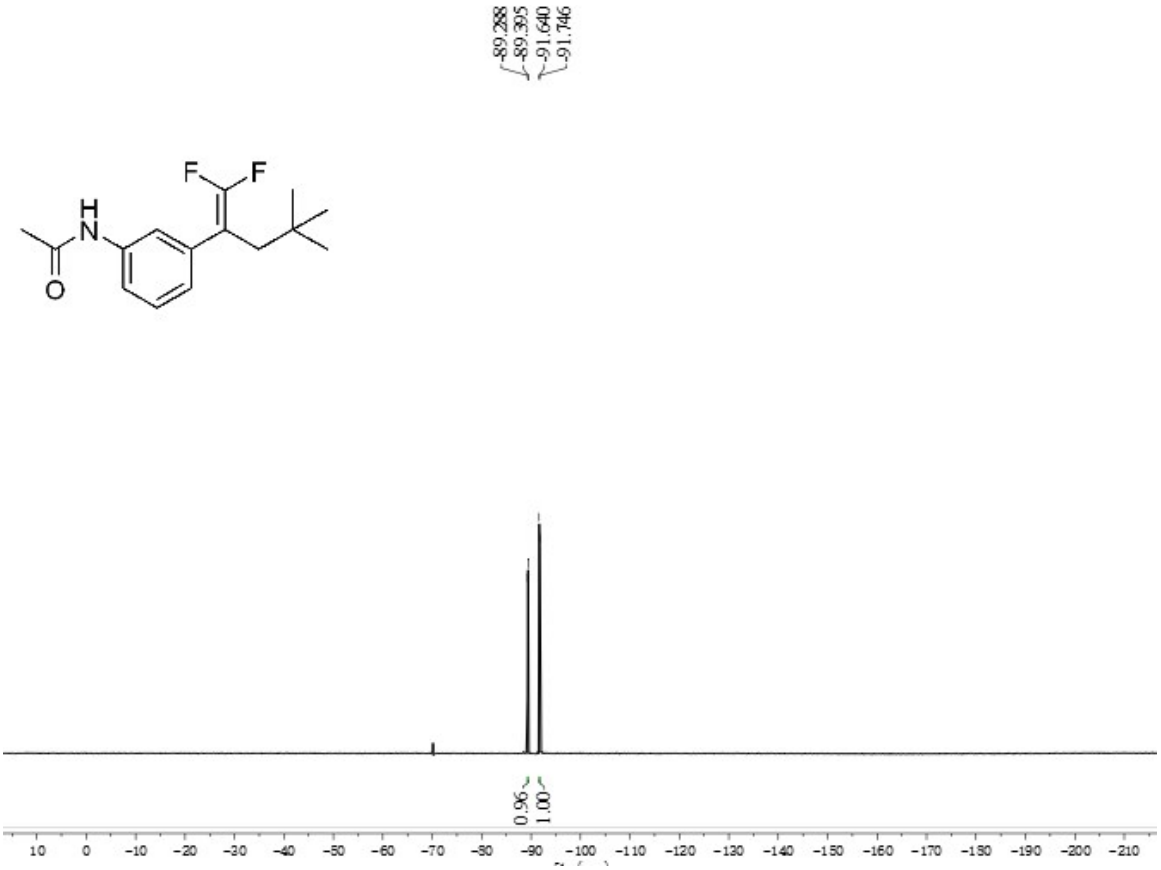
^{1}H NMR spectrum of 3ga



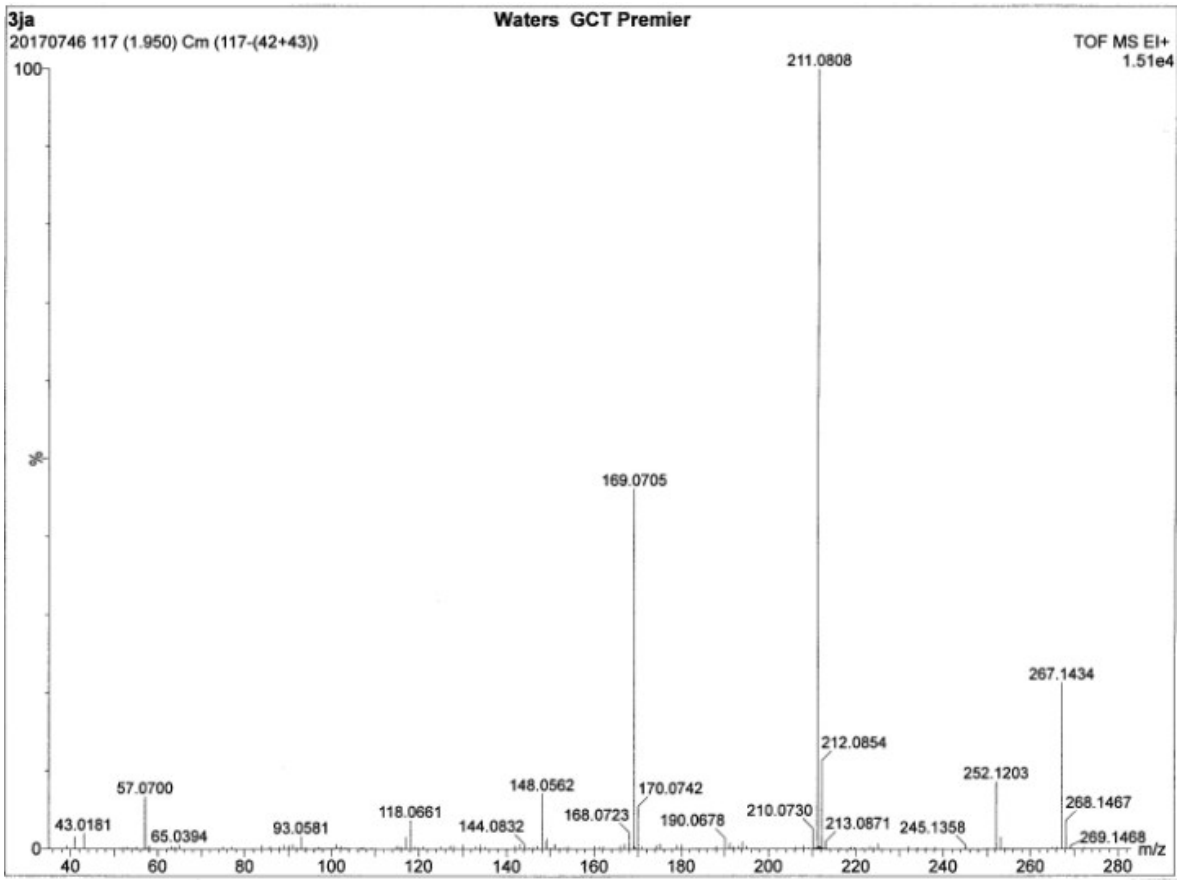
^{13}C NMR spectrum of 3ga



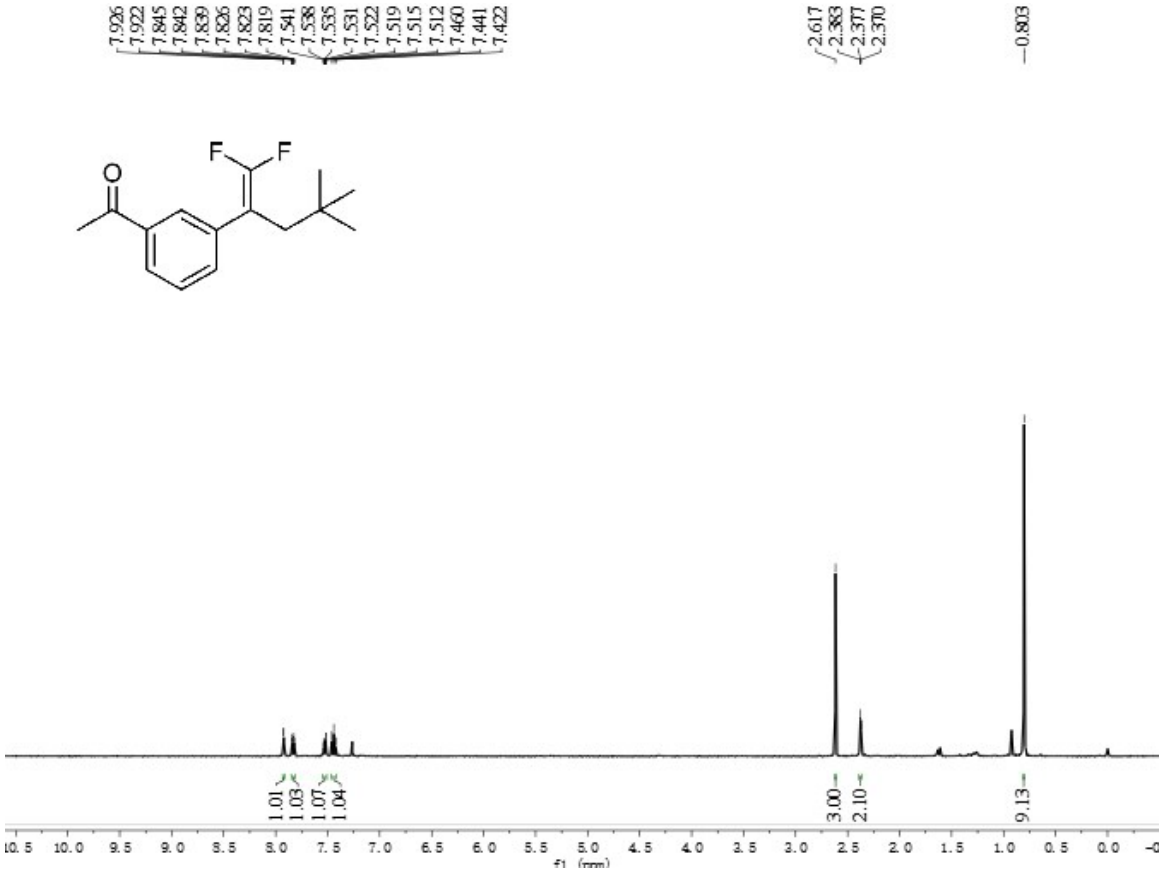
^{19}F NMR spectrum of 3ga



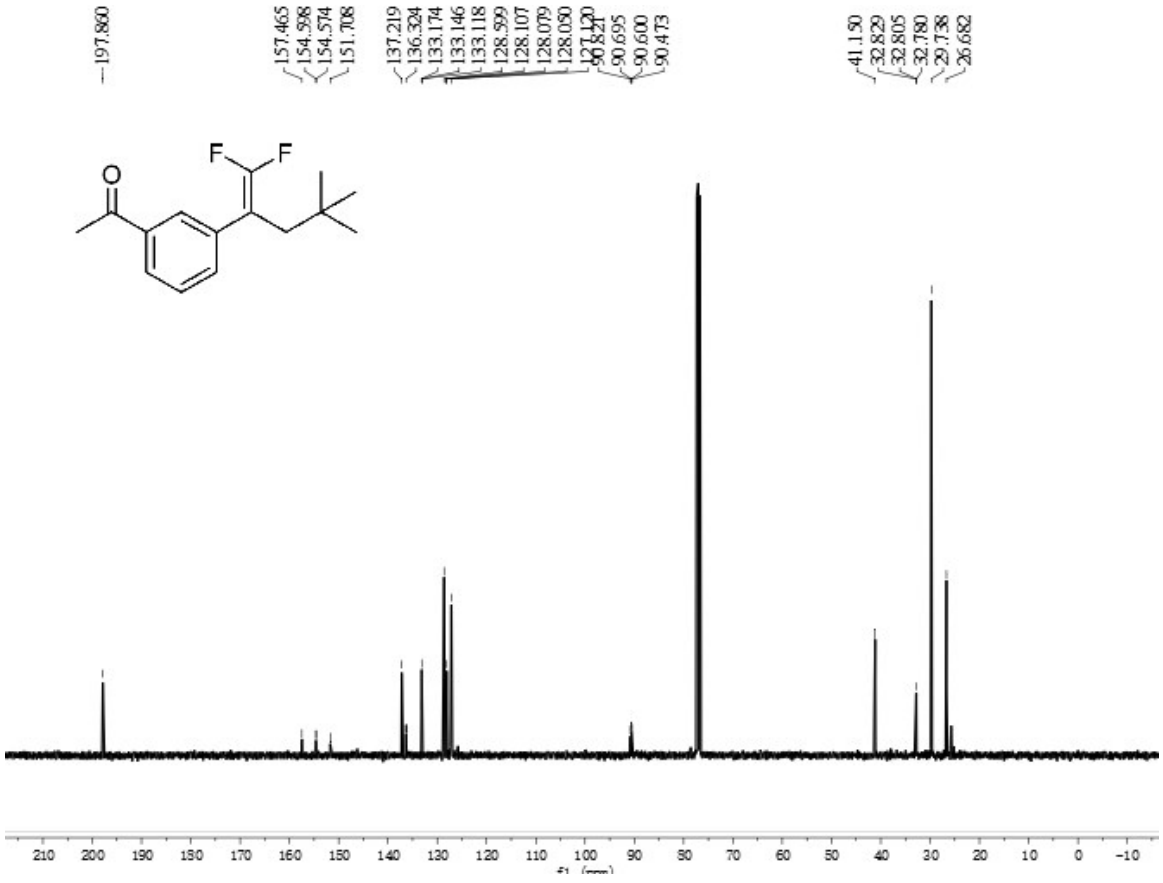
HRMS (EI) spectrum of 3ga



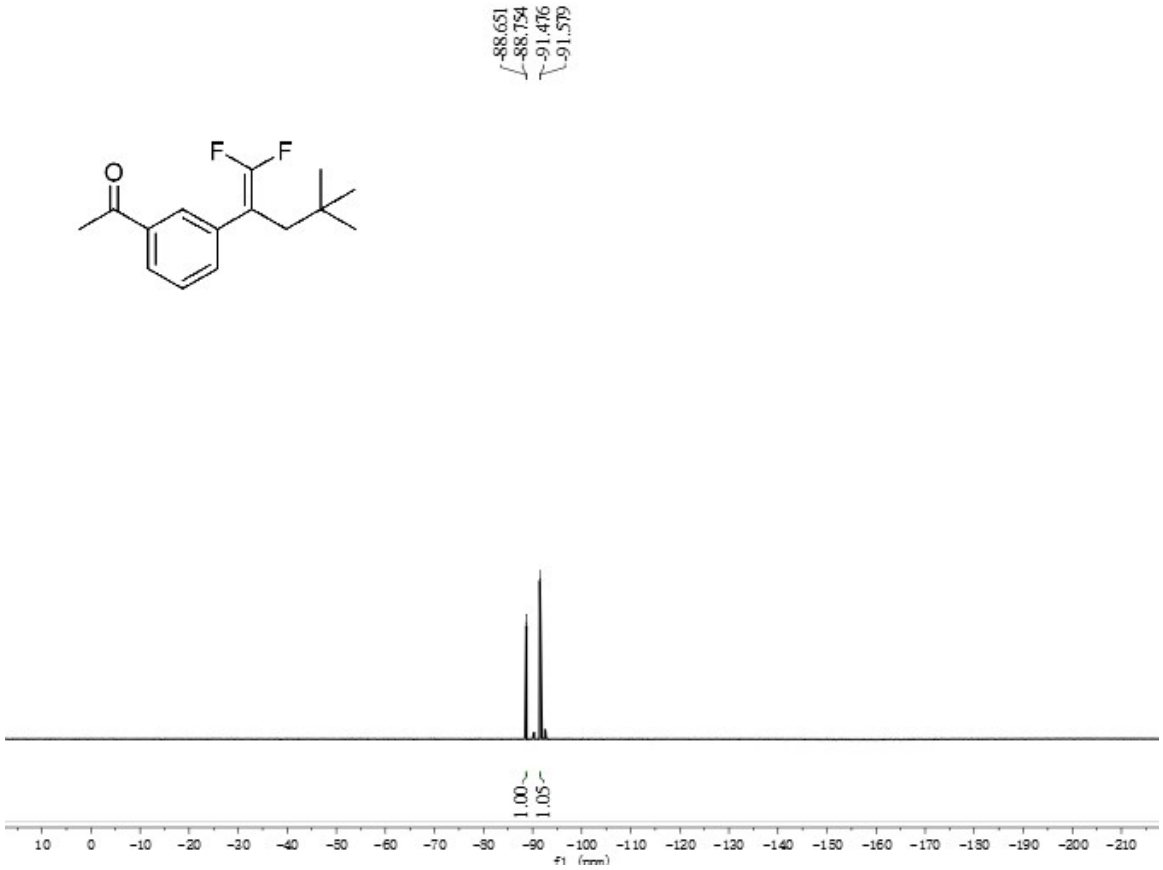
^{1}H NMR spectrum of 3ha



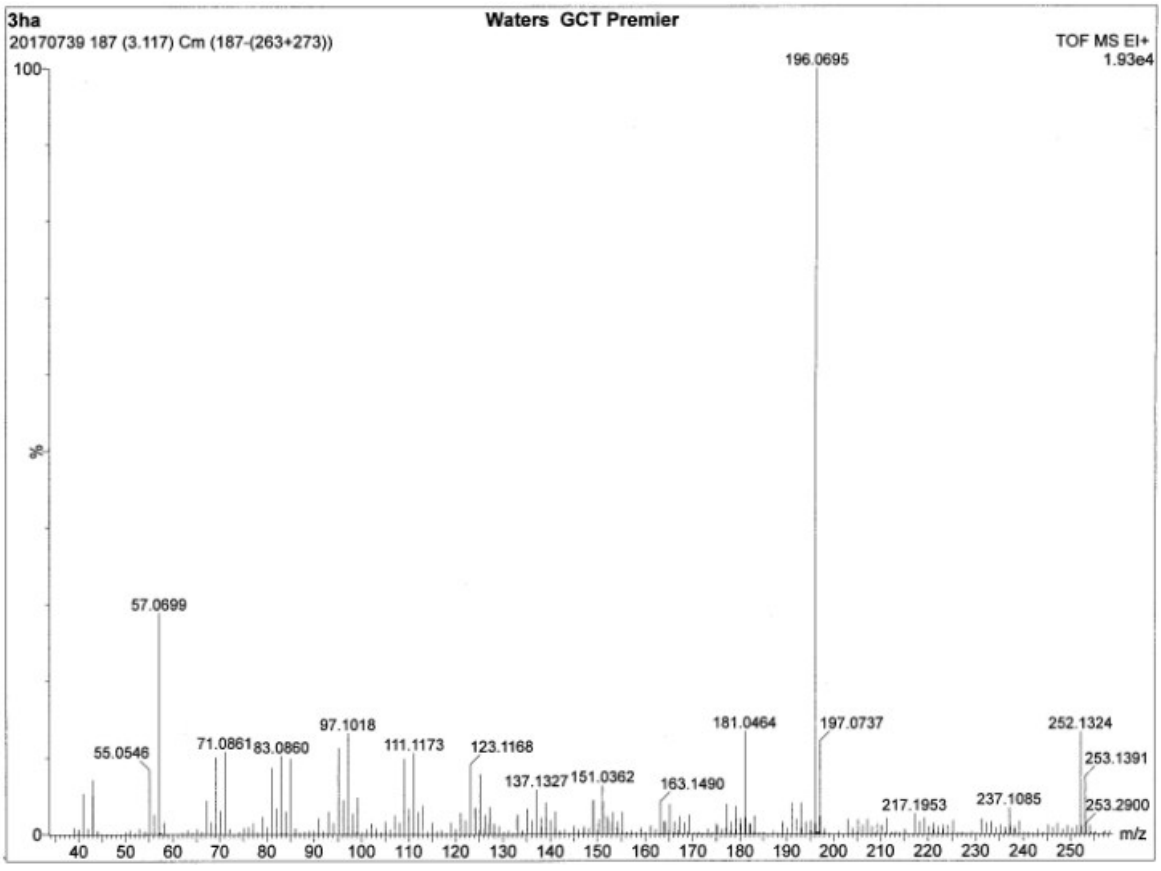
^{13}C NMR spectrum of 3ha



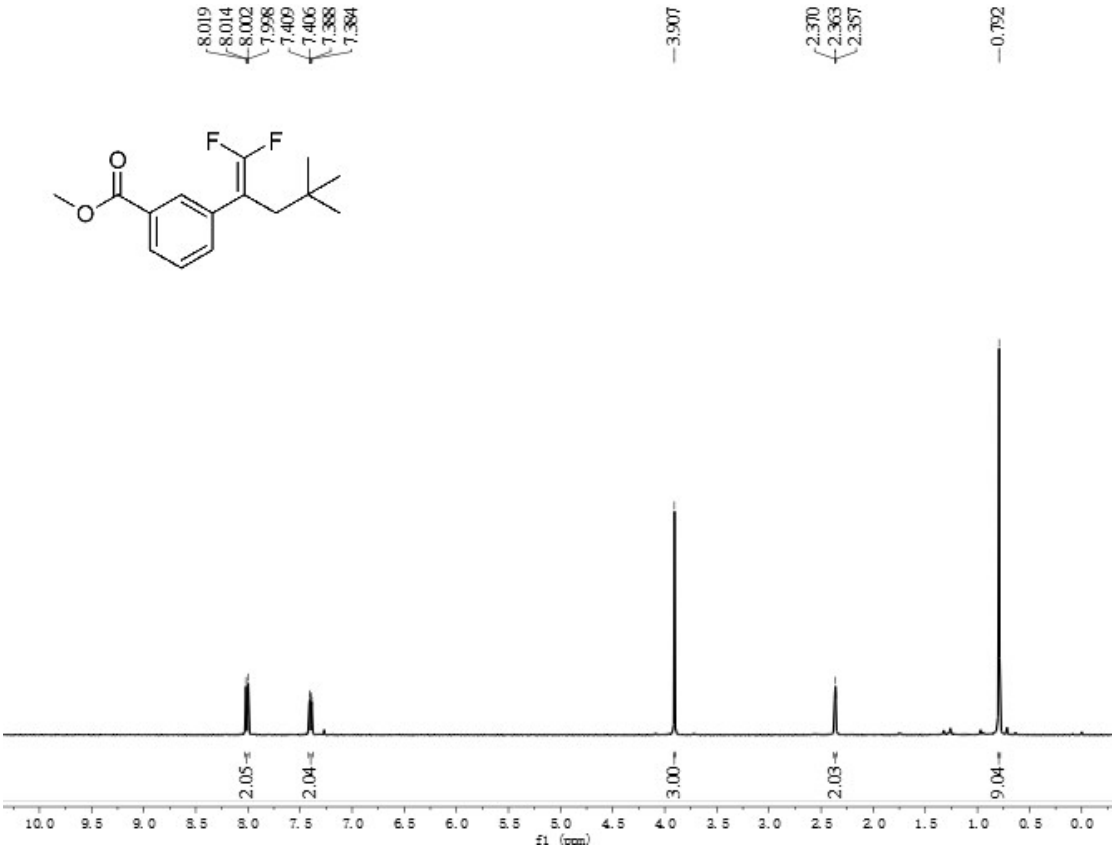
^{19}F NMR spectrum of 3ha



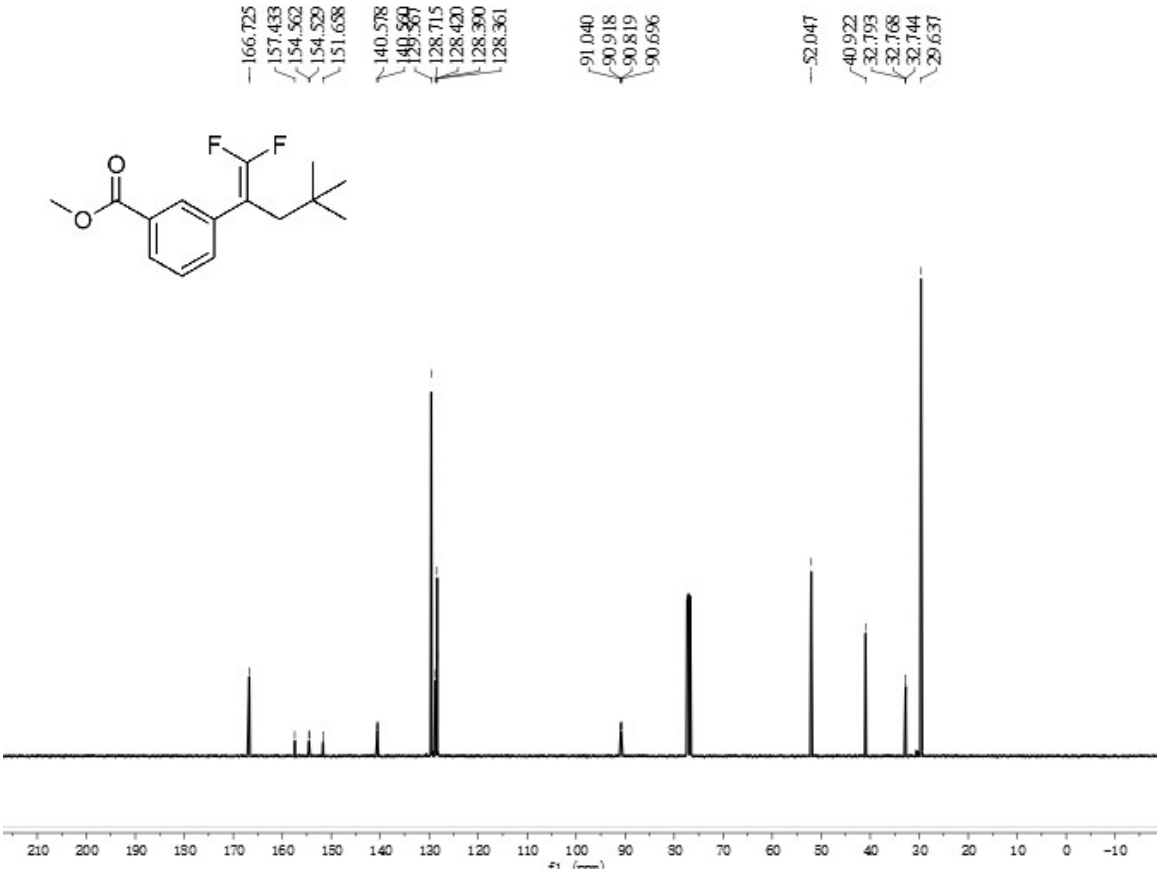
HRMS (EI) spectrum of 3ha



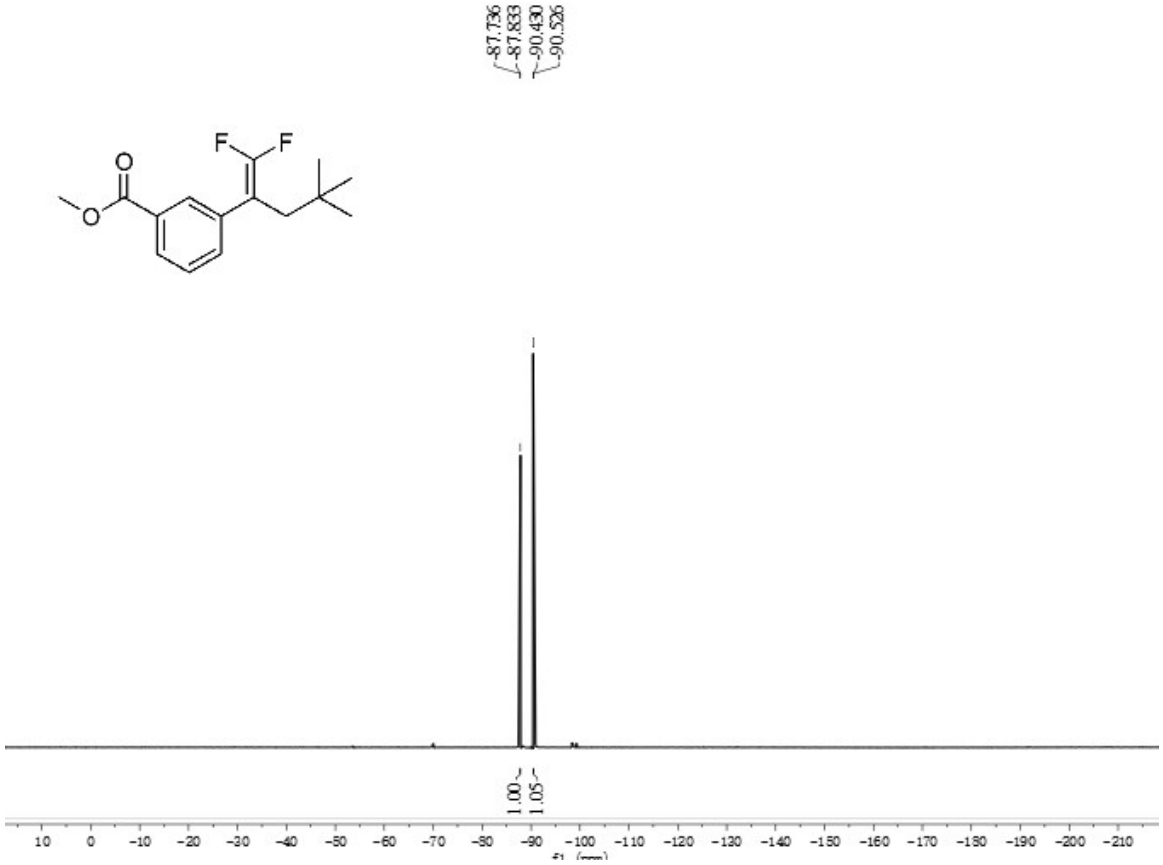
^{1}H NMR spectrum of 3ia



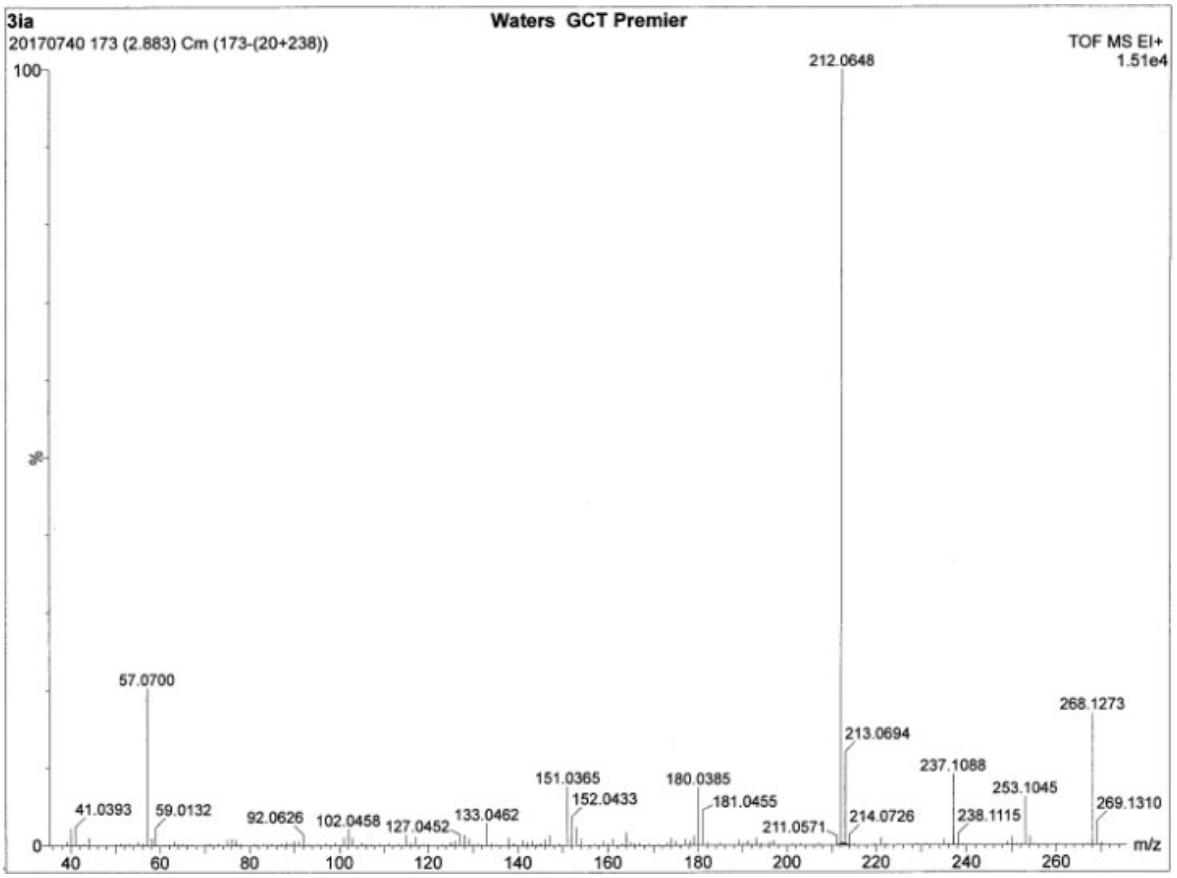
^{13}C NMR spectrum of 3ia



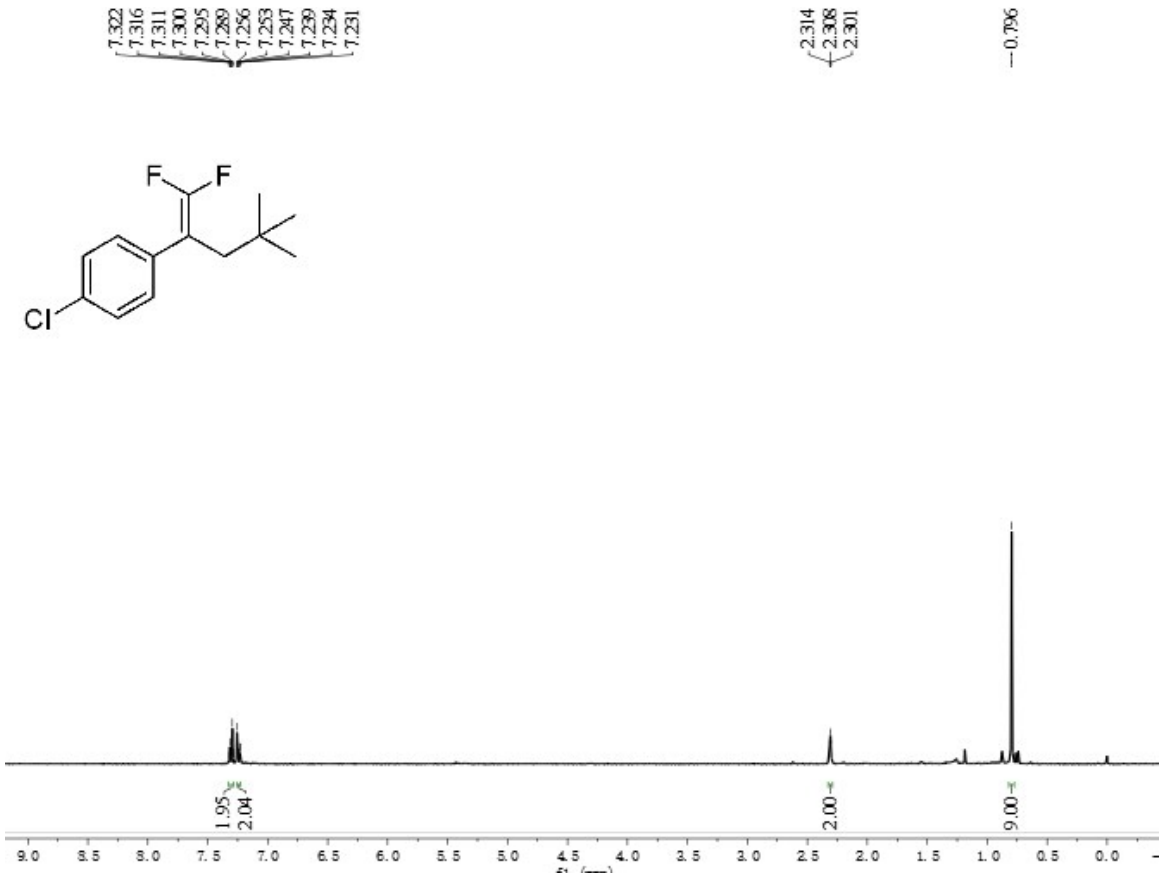
^{19}F NMR spectrum of 3ia



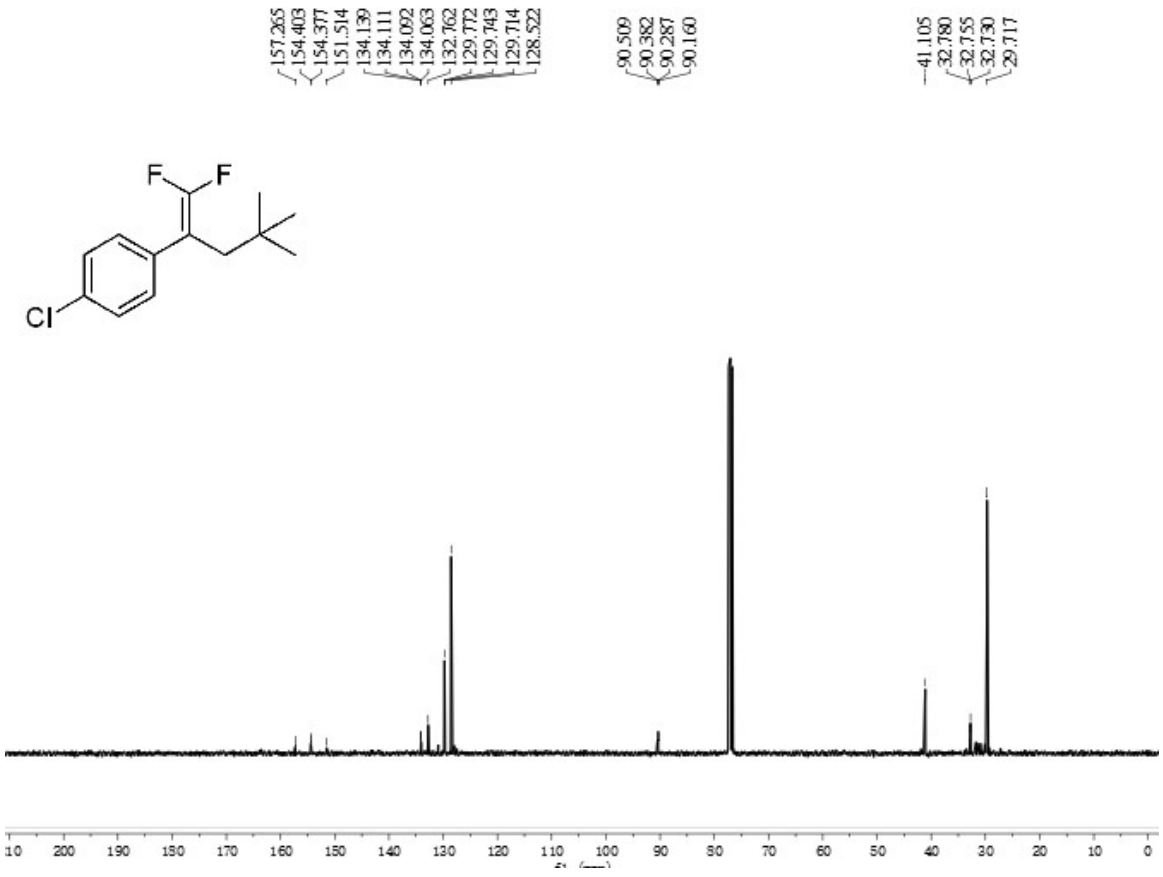
HRMS (EI) spectrum of 3ia



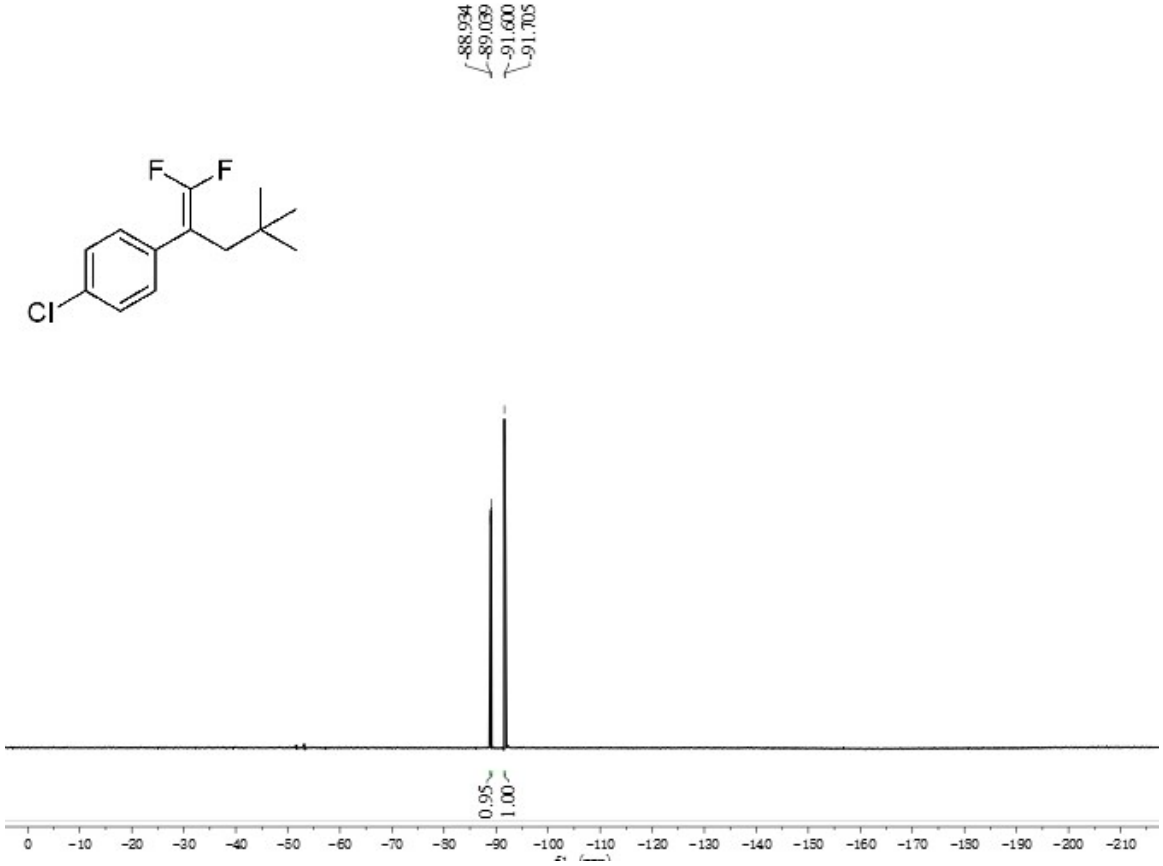
^{1}H NMR spectrum of 3ja



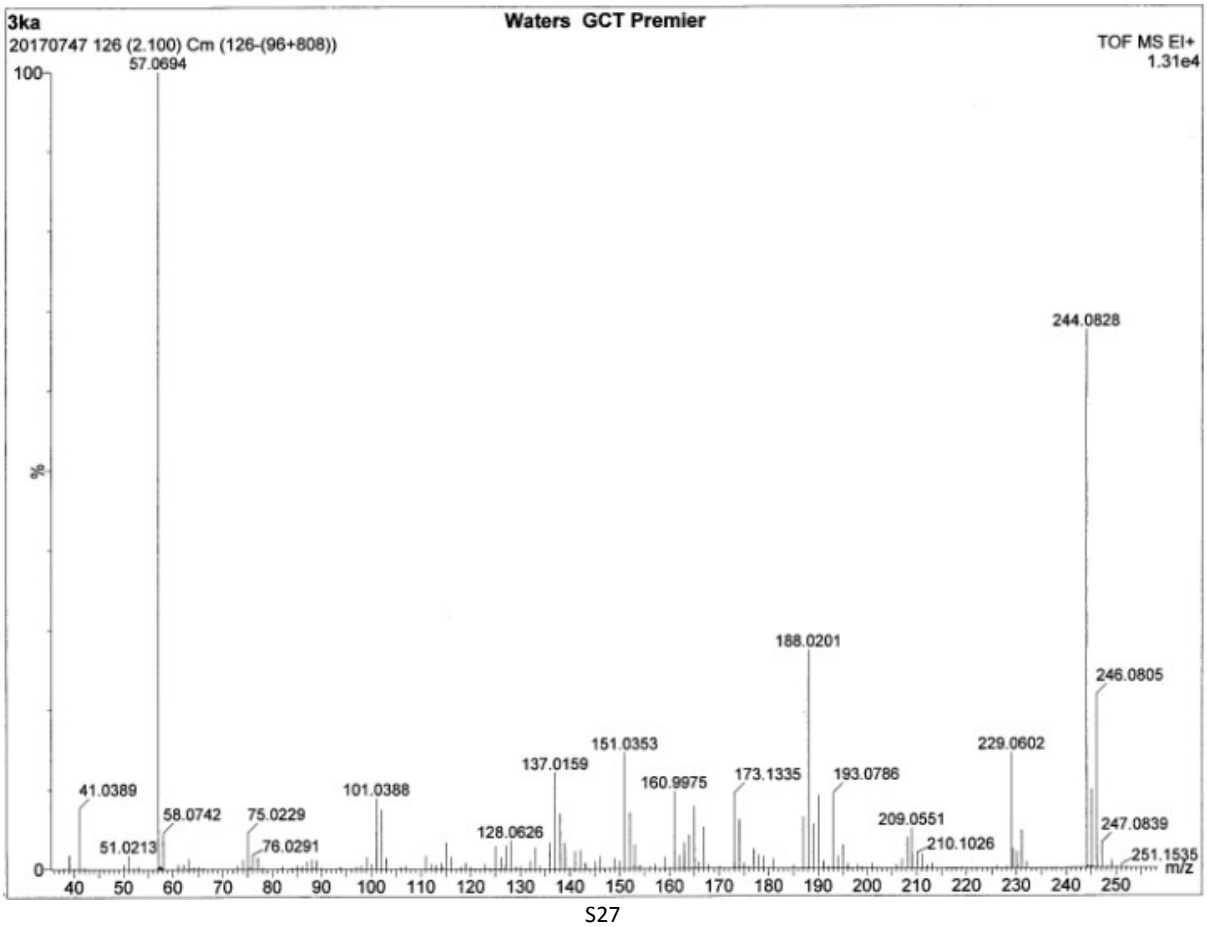
^{13}C NMR spectrum of 3ja



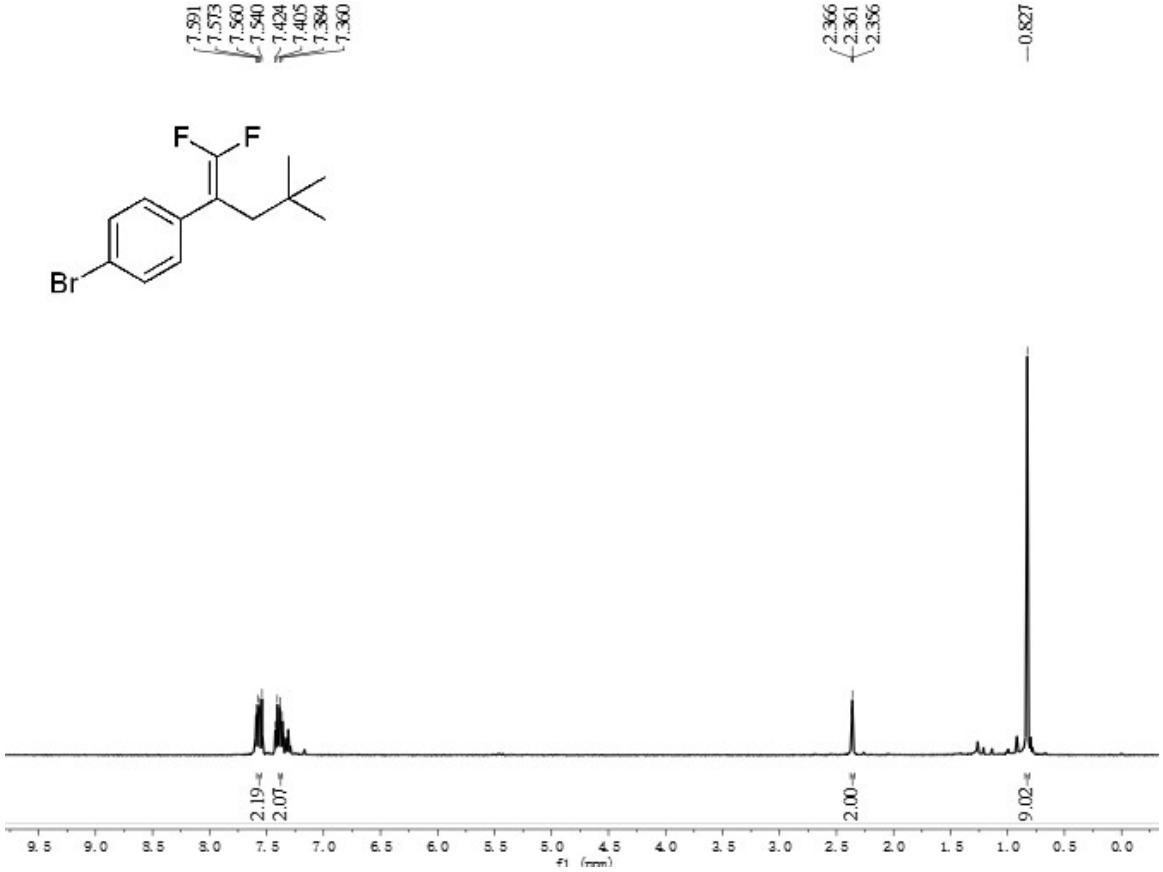
^{19}F NMR spectrum of 3ja



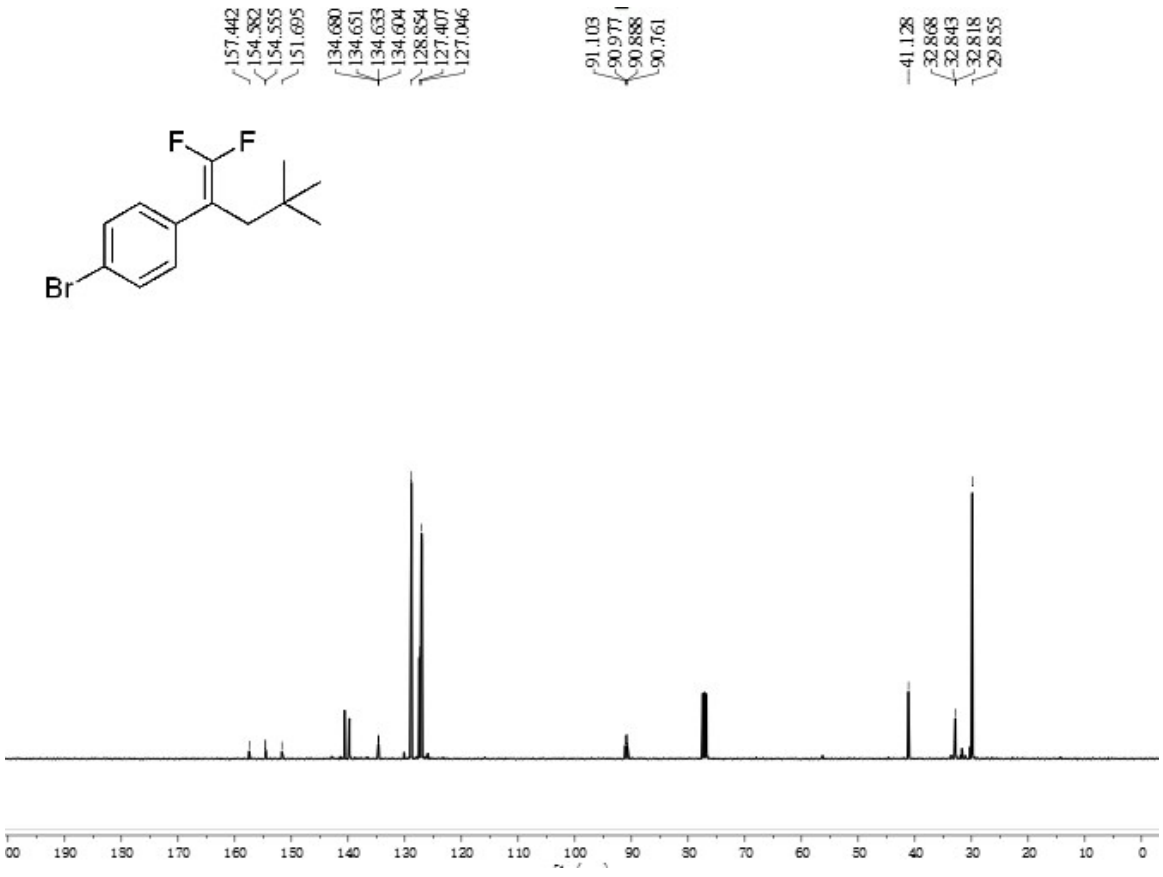
HRMS (EI) spectrum of 3ja



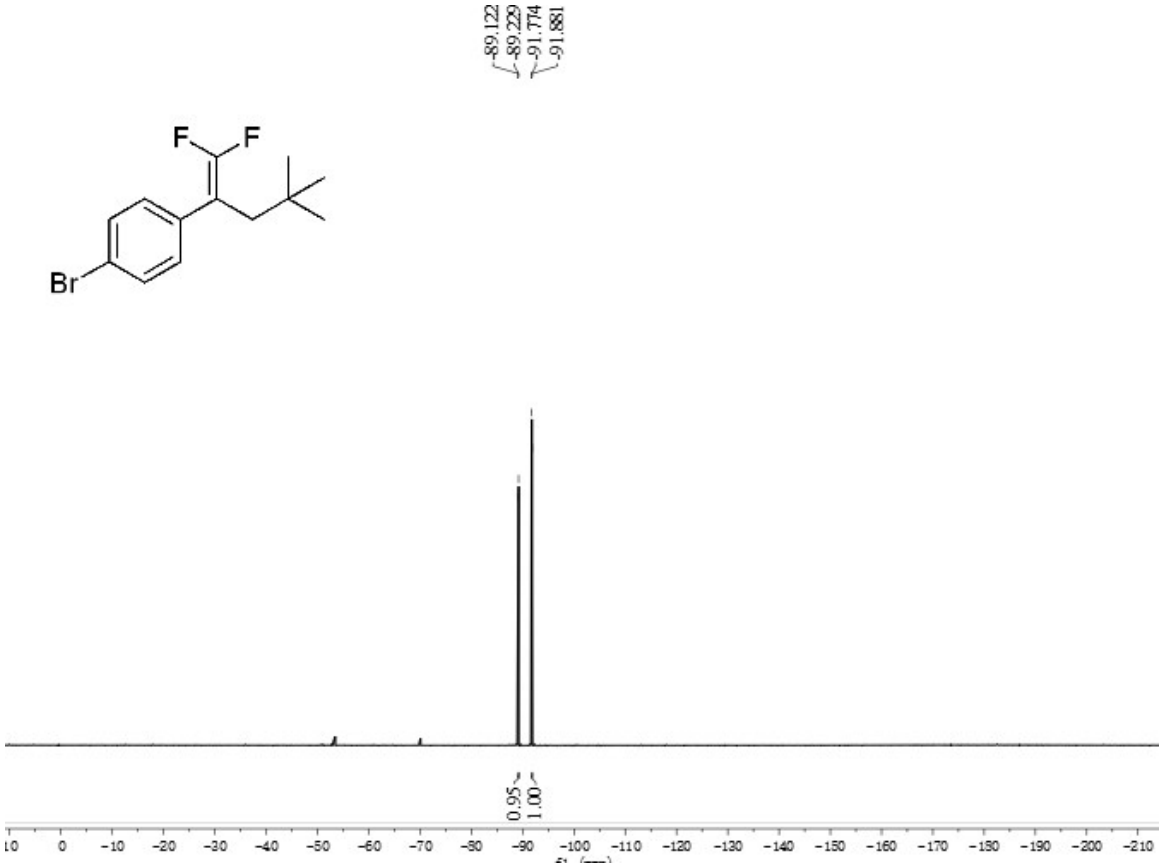
^{1}H NMR spectrum of 3ka



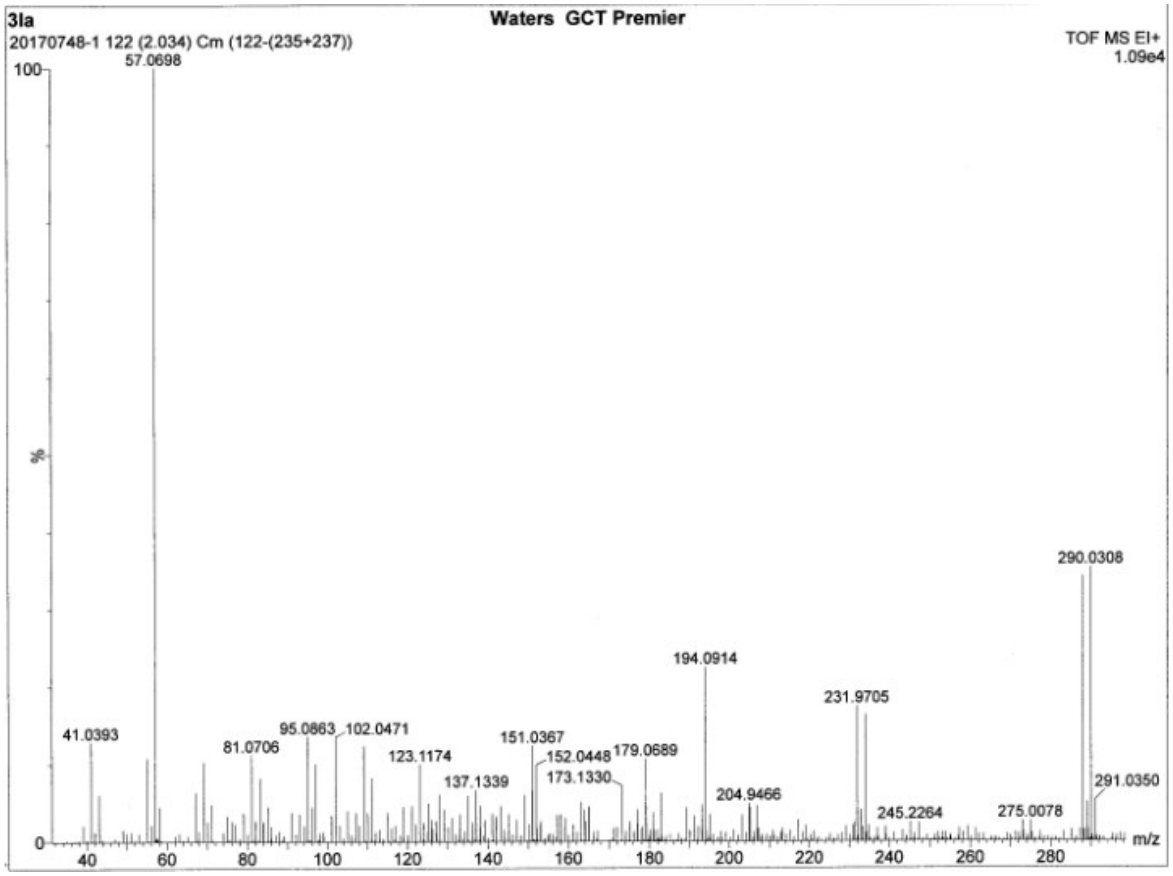
^{13}C NMR spectrum of 3ka



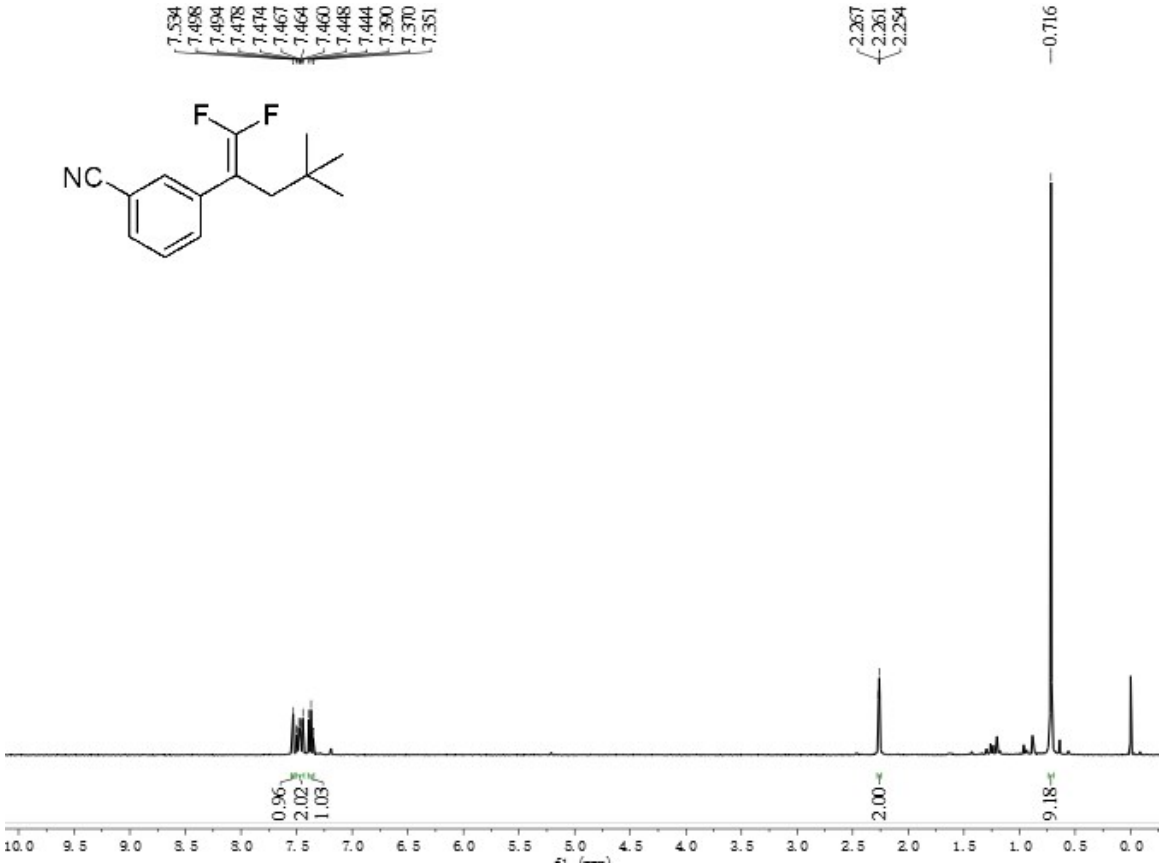
^{19}F NMR spectrum of 3ka



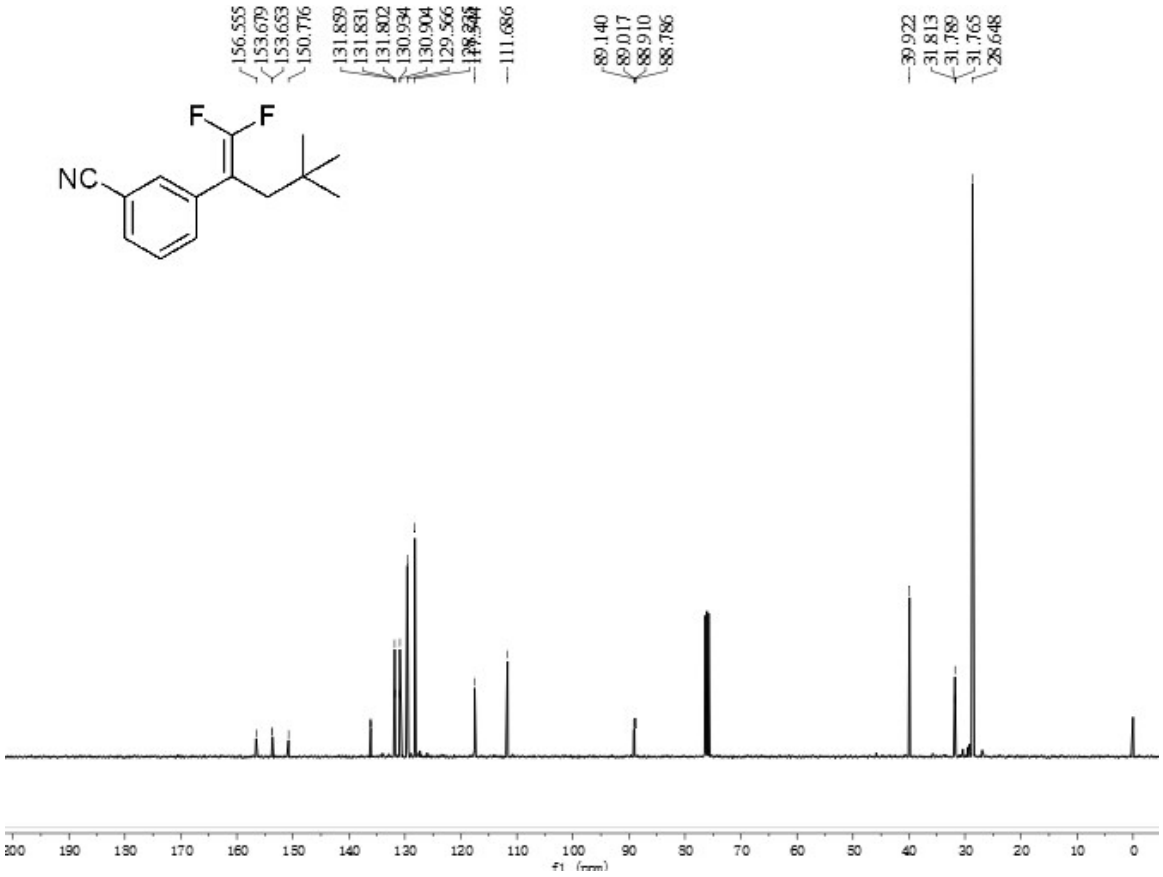
HRMS (EI) spectrum of 3ka



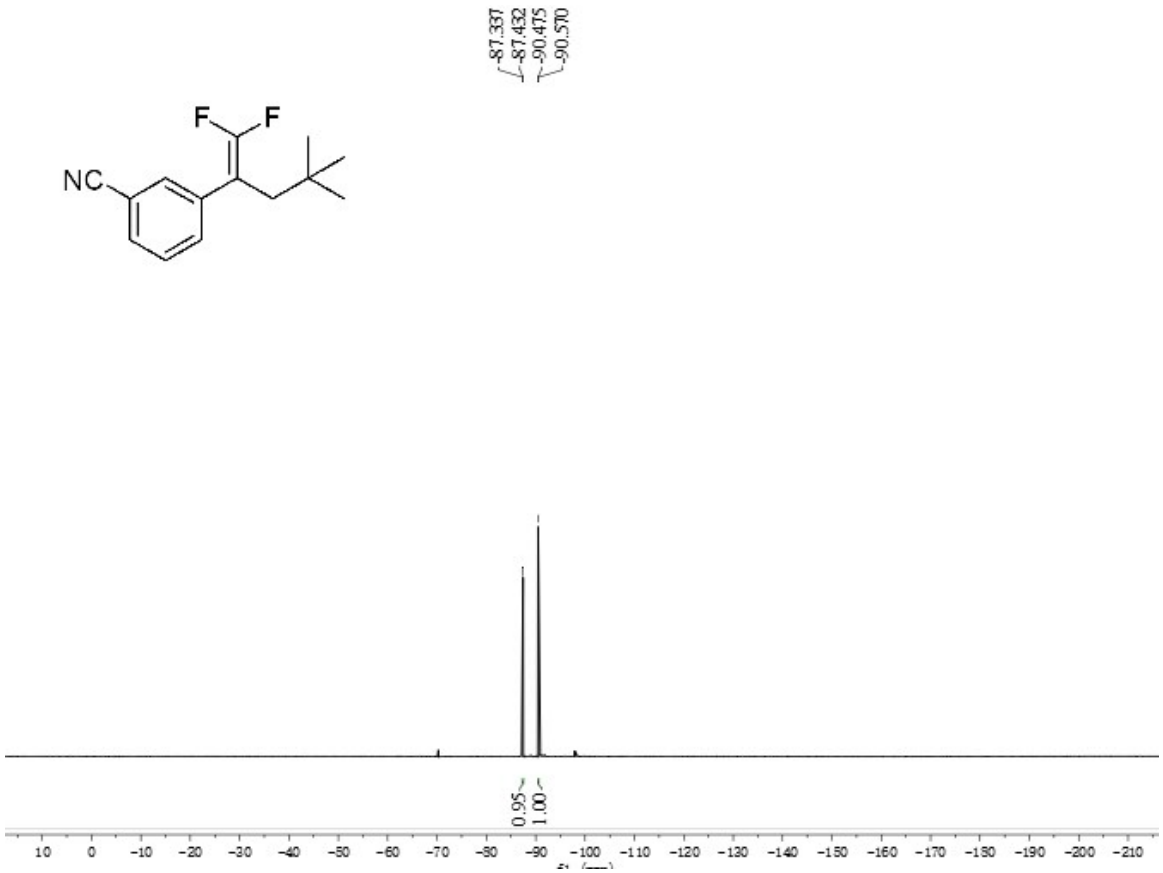
[1]H NMR spectrum of 3la



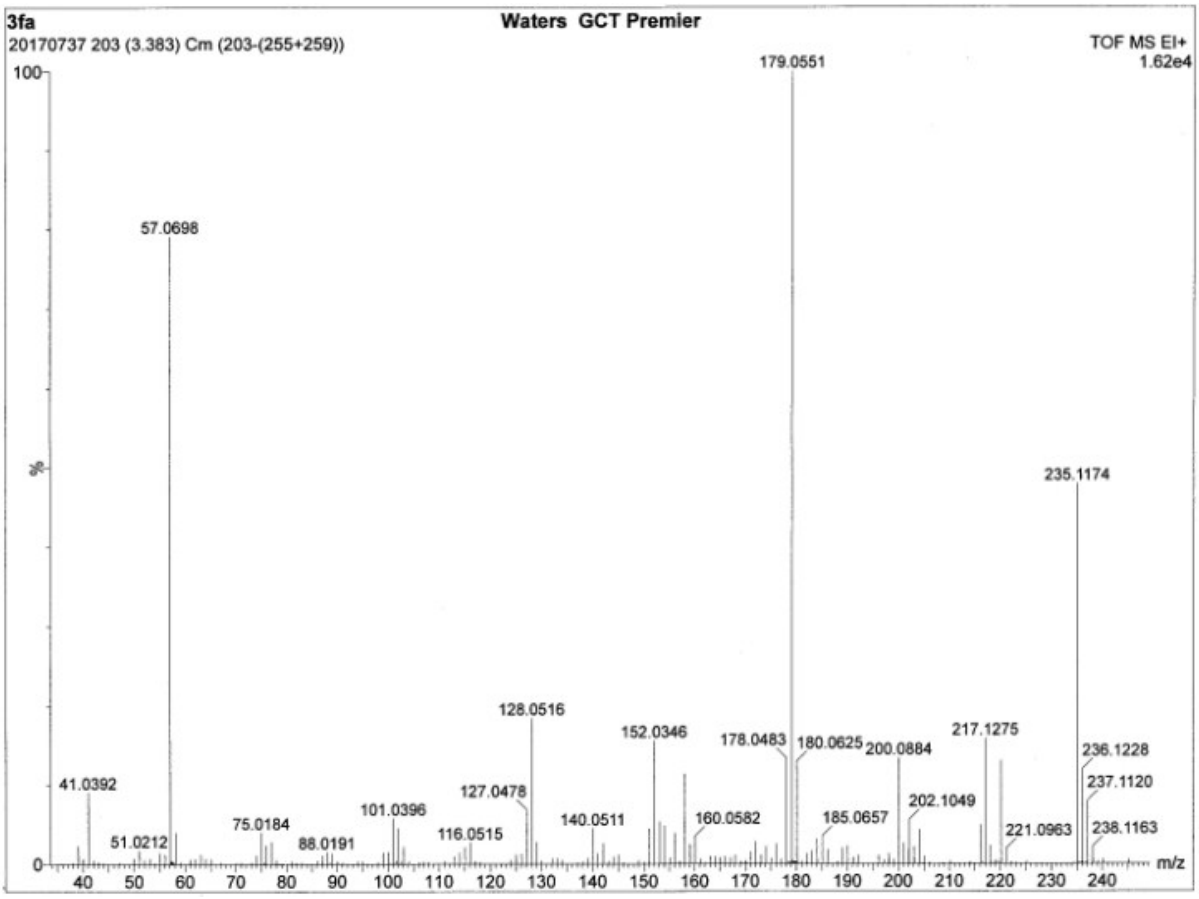
[13]C NMR spectrum of 3la



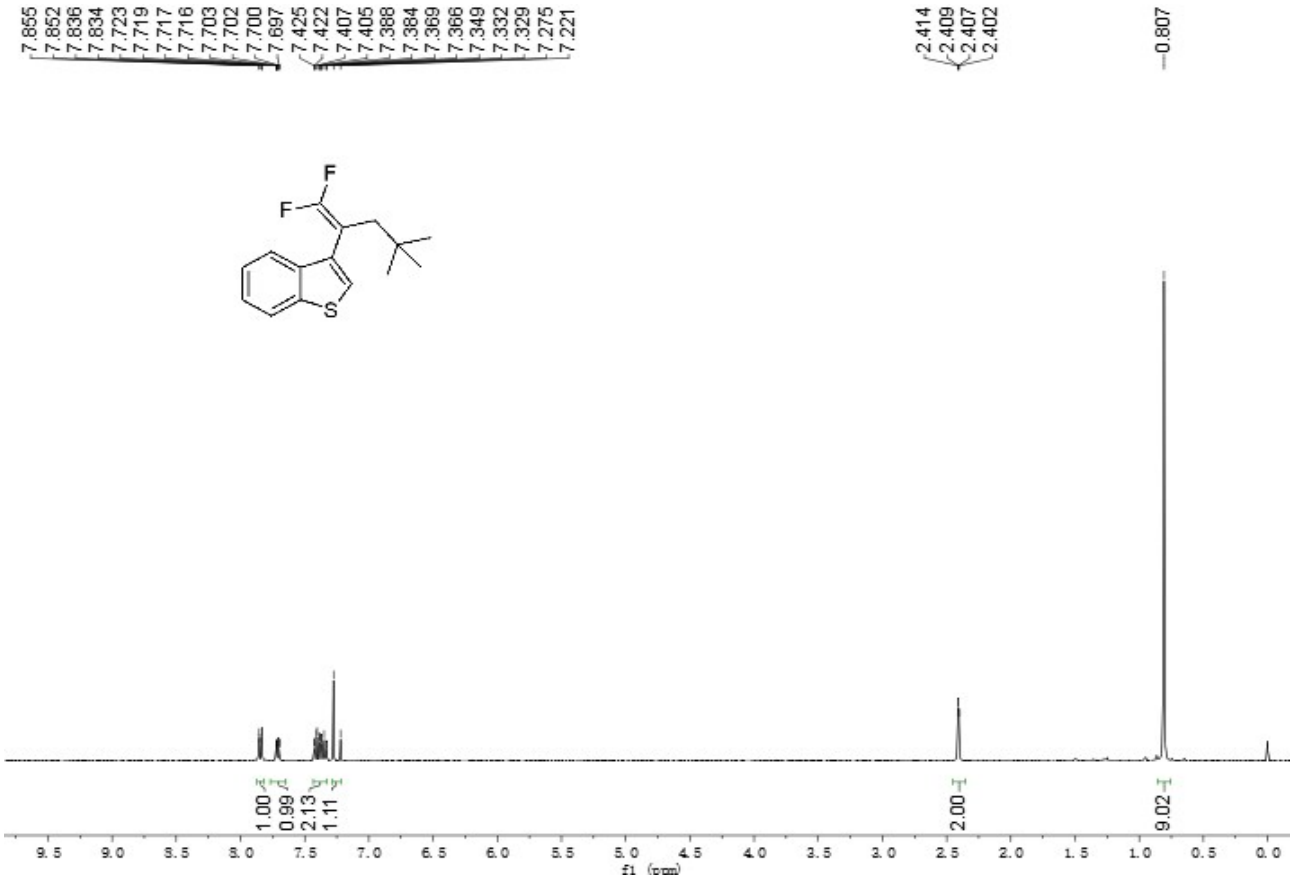
^{19}F NMR spectrum of 3la



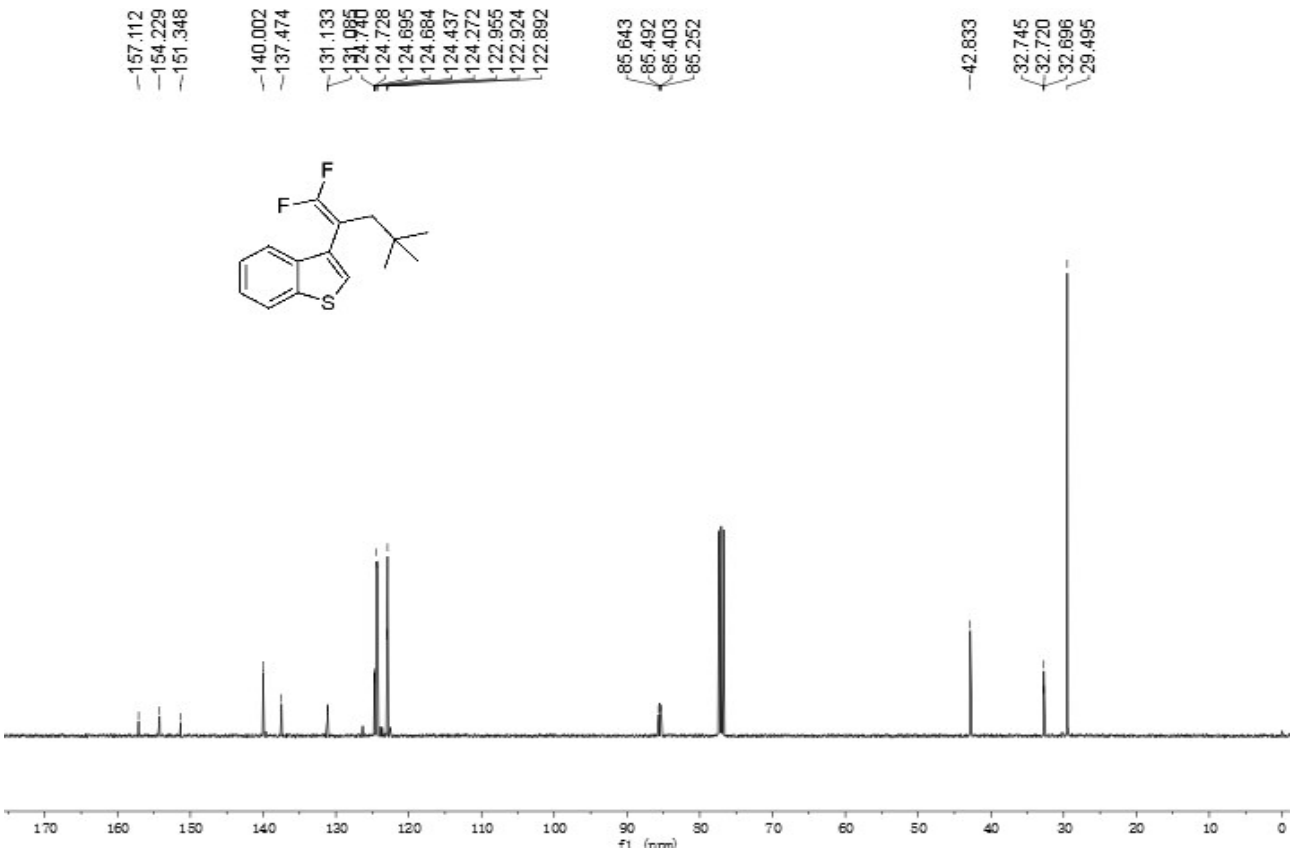
HRMS (EI) spectrum of 3la



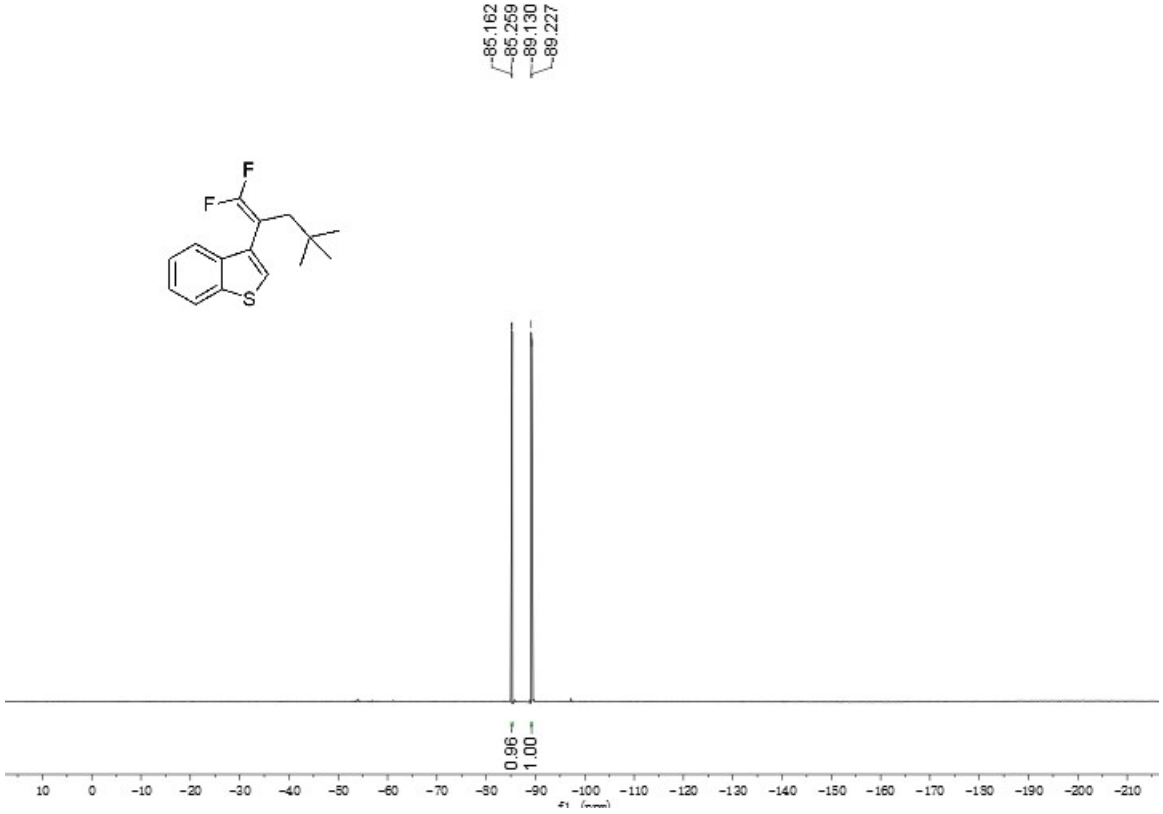
[1]H NMR spectrum of 3ma



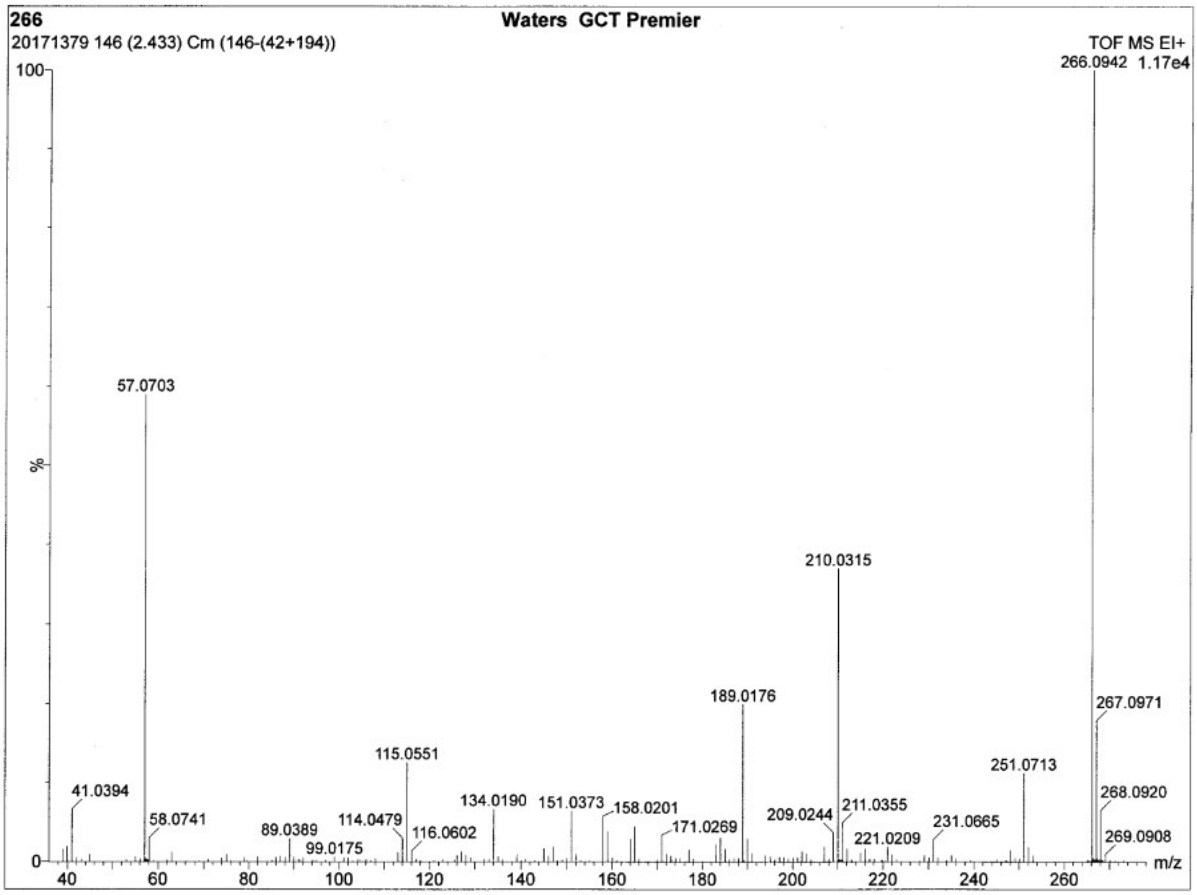
[13]C NMR spectrum of 3ma



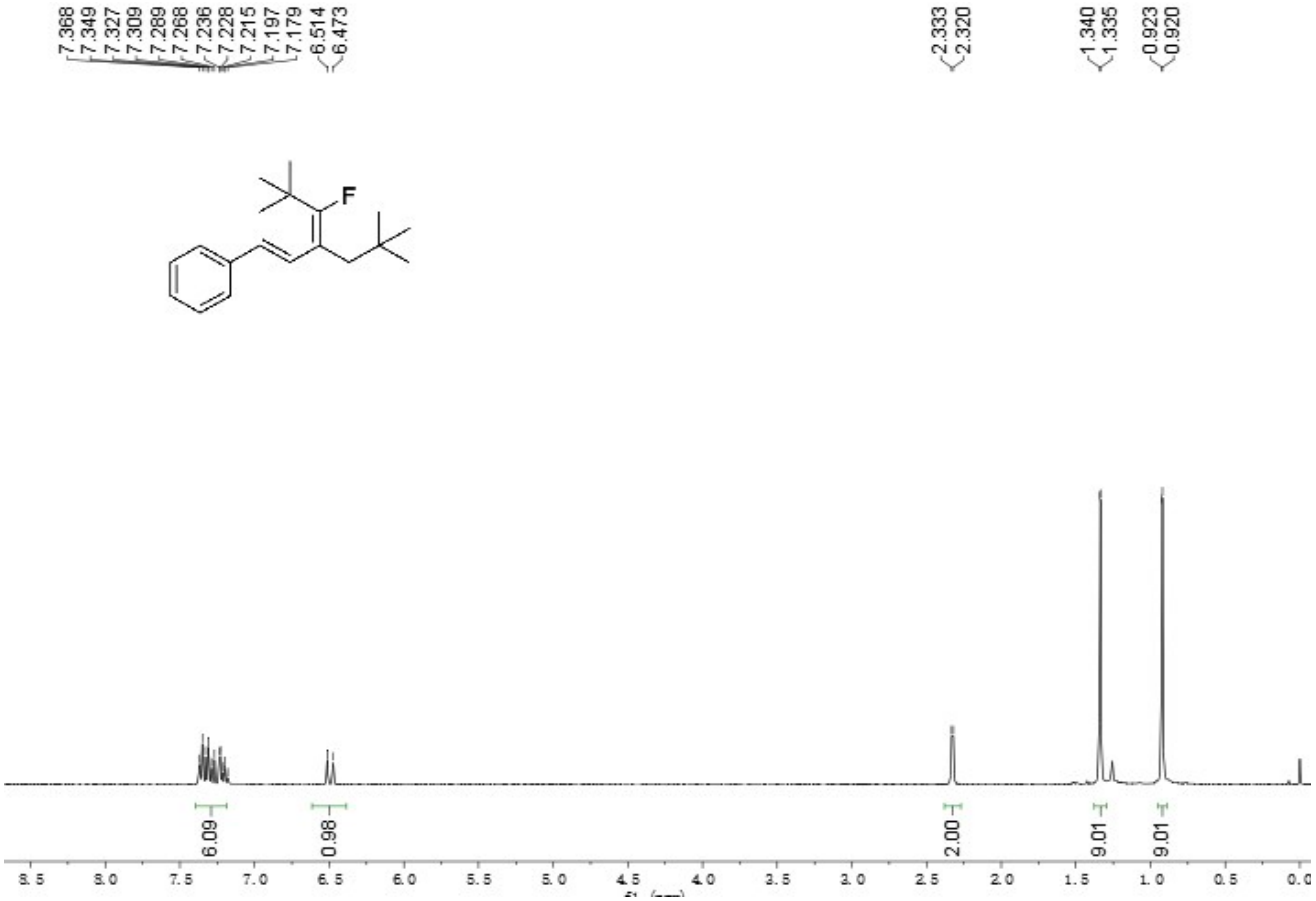
^{19}F NMR spectrum of 3ma



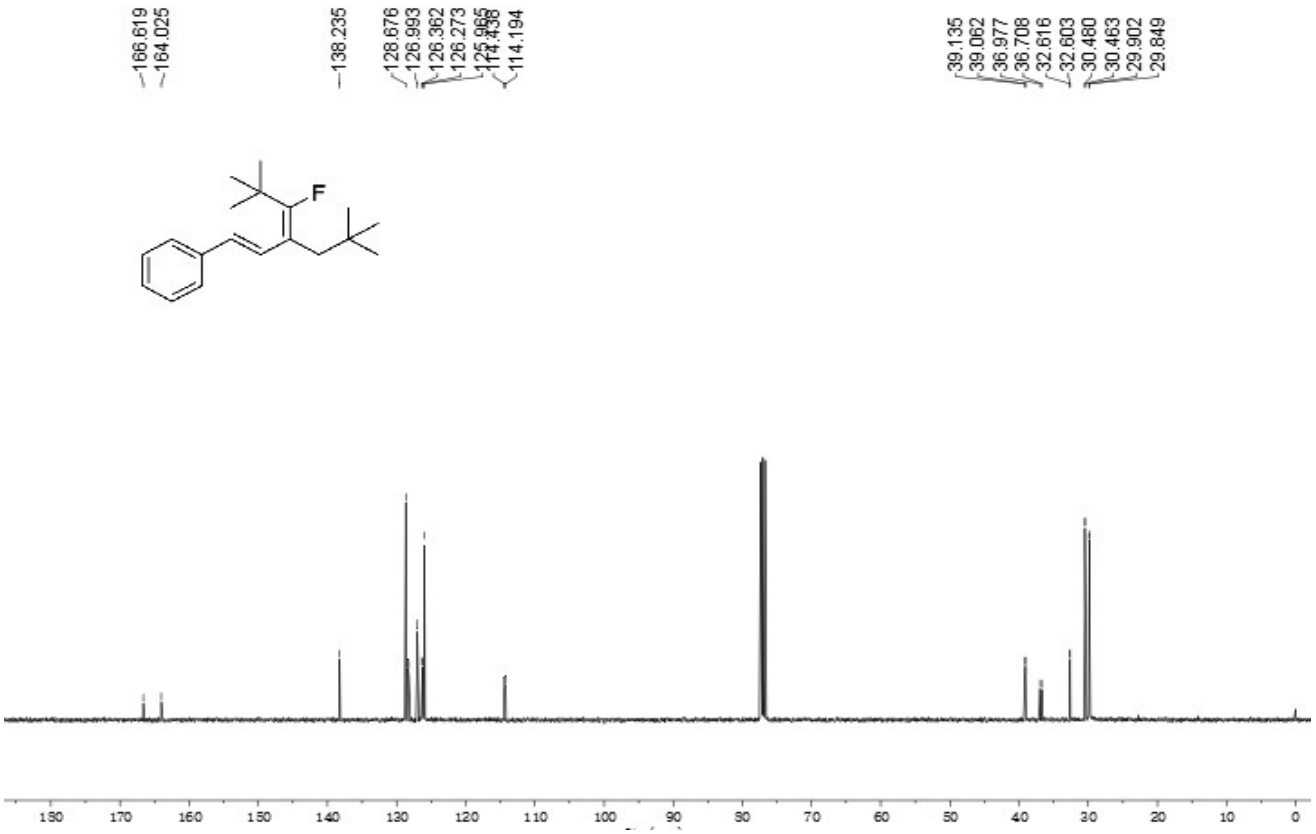
HRMS (EI) spectrum of 3ma



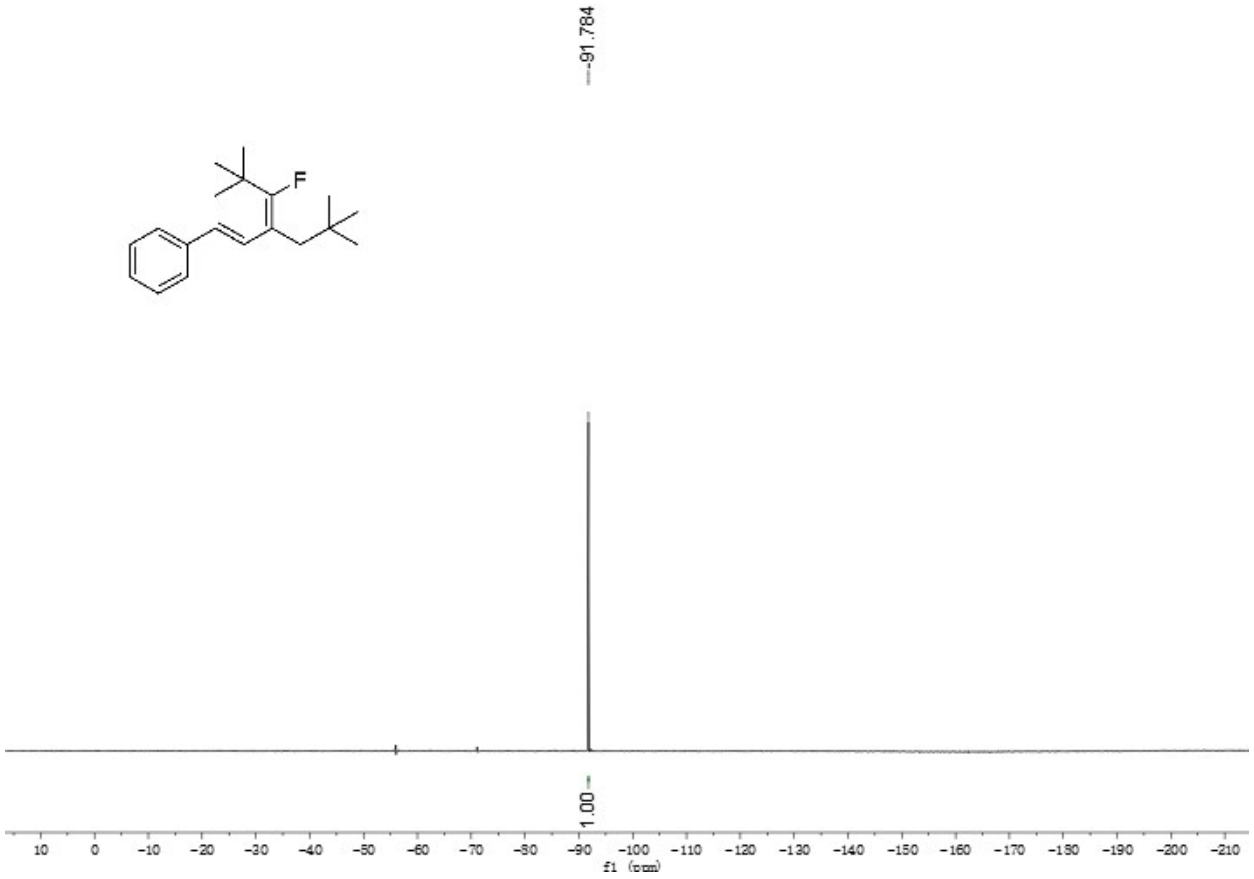
^{1}H NMR spectrum of 3na



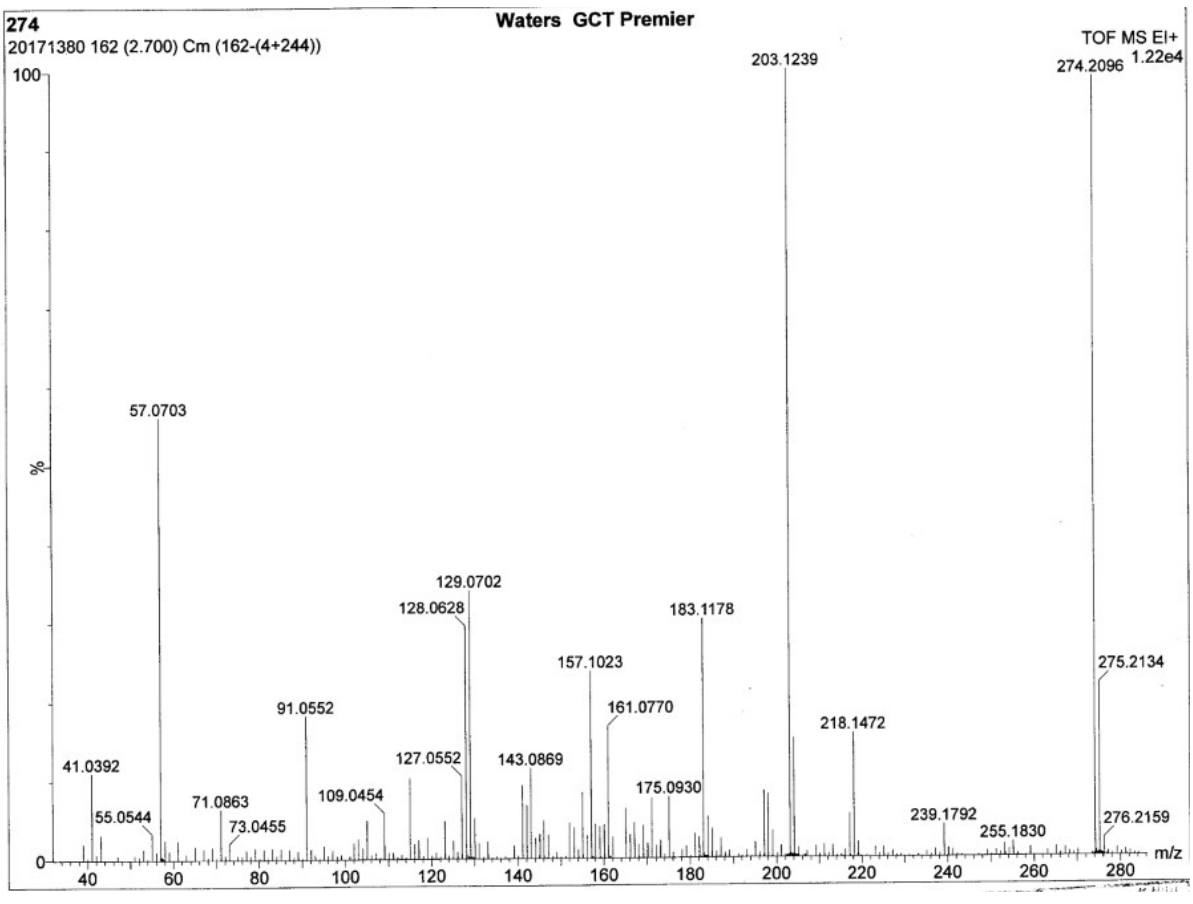
^{13}C NMR spectrum of 3na



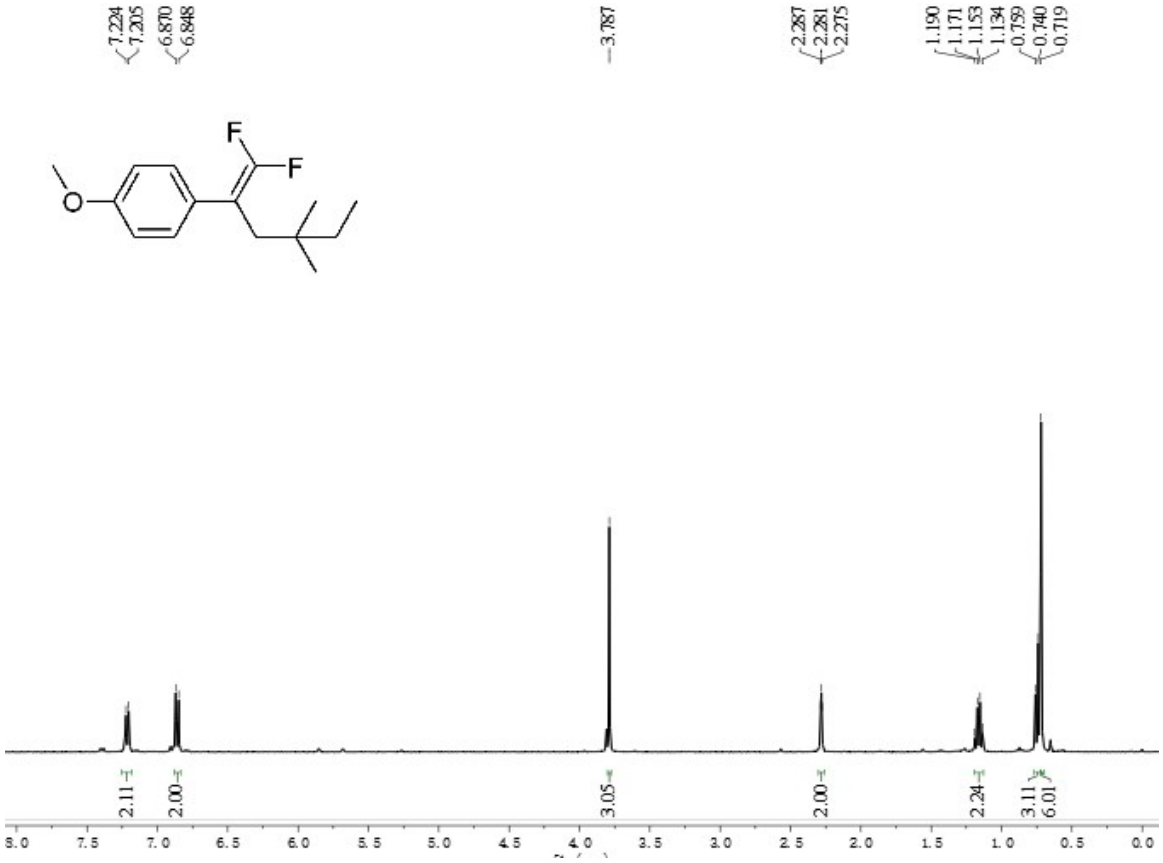
^{19}F NMR spectrum of 3na



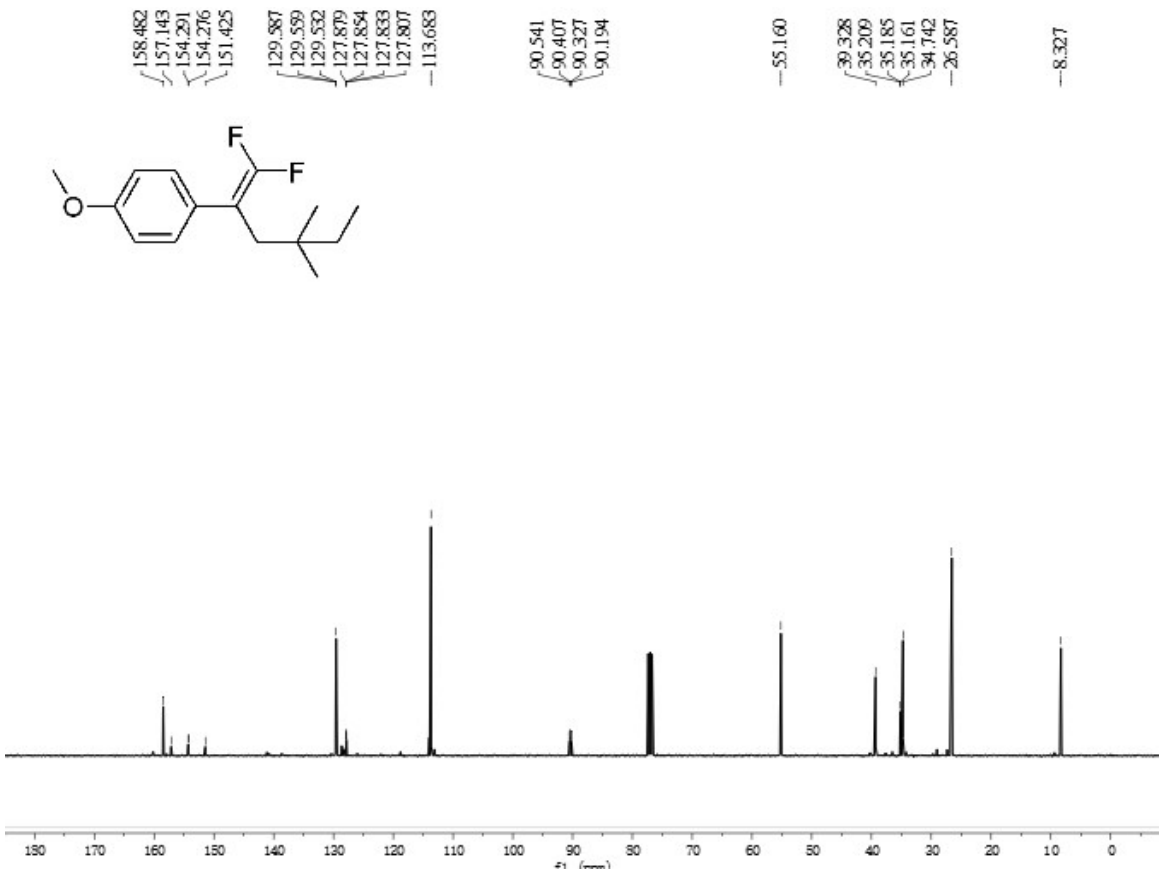
HRMS (EI) spectrum of 3na



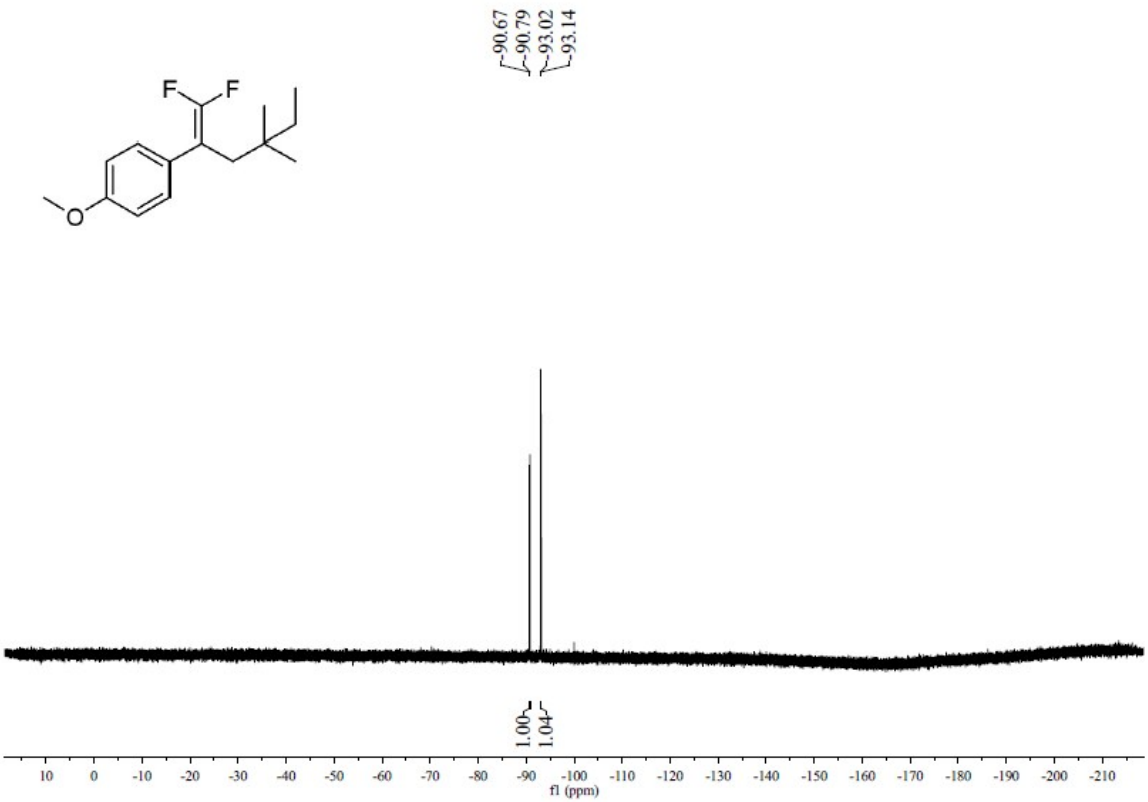
^{1}H NMR spectrum of 3cb



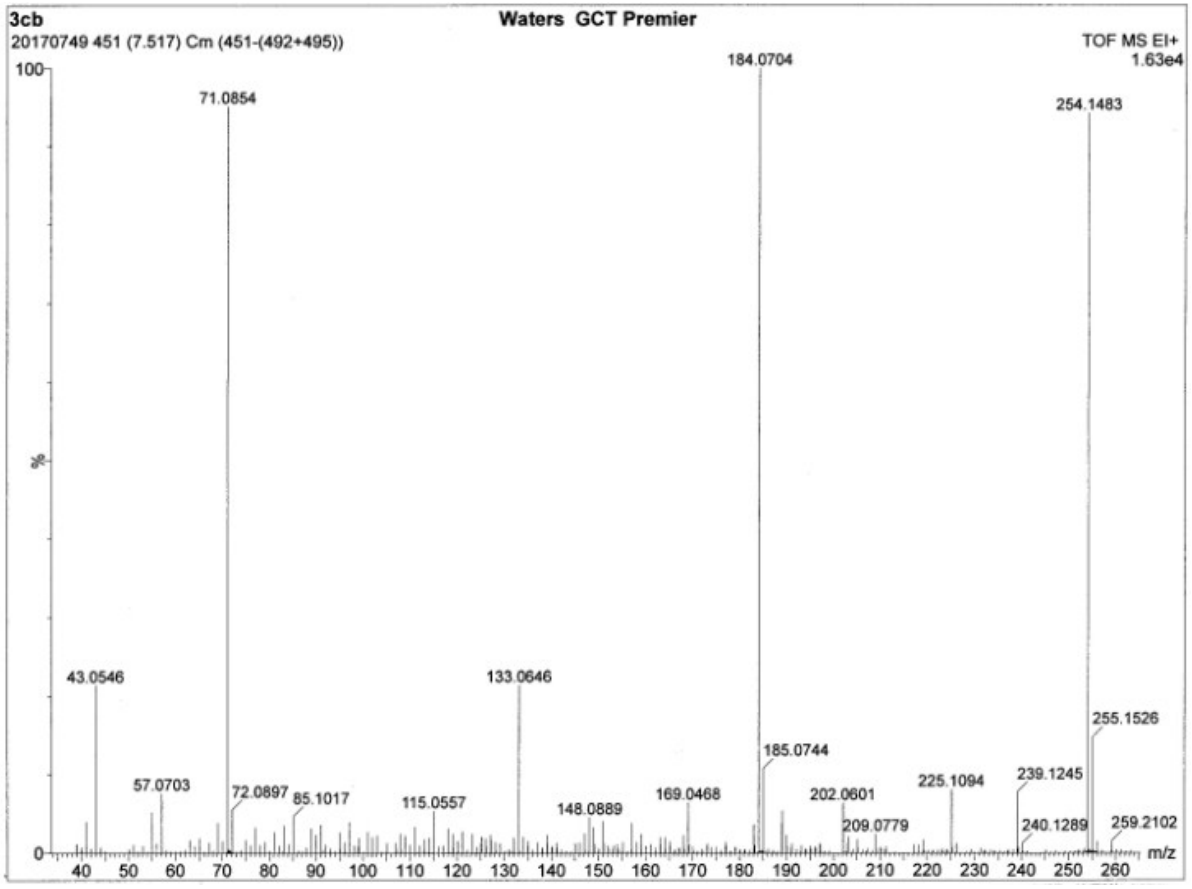
^{13}C NMR spectrum of 3cb



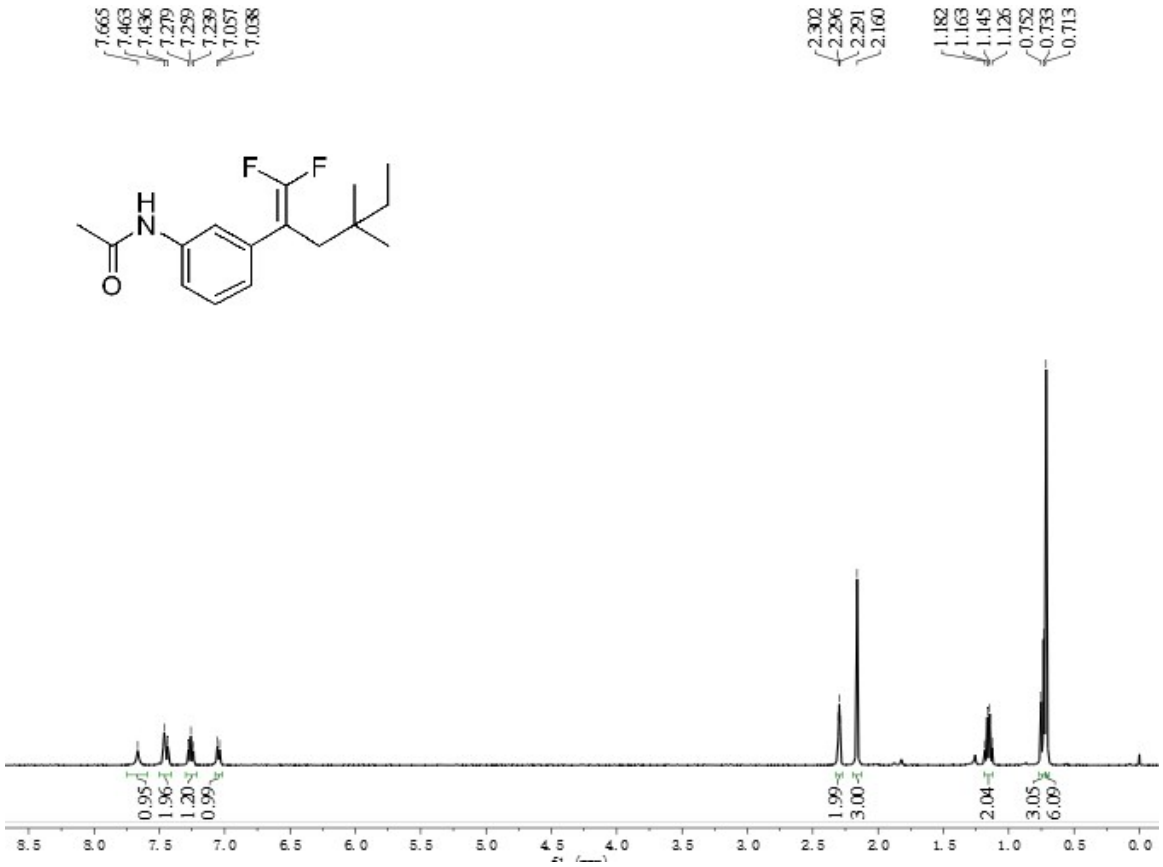
^{19}F NMR spectrum of 3cb



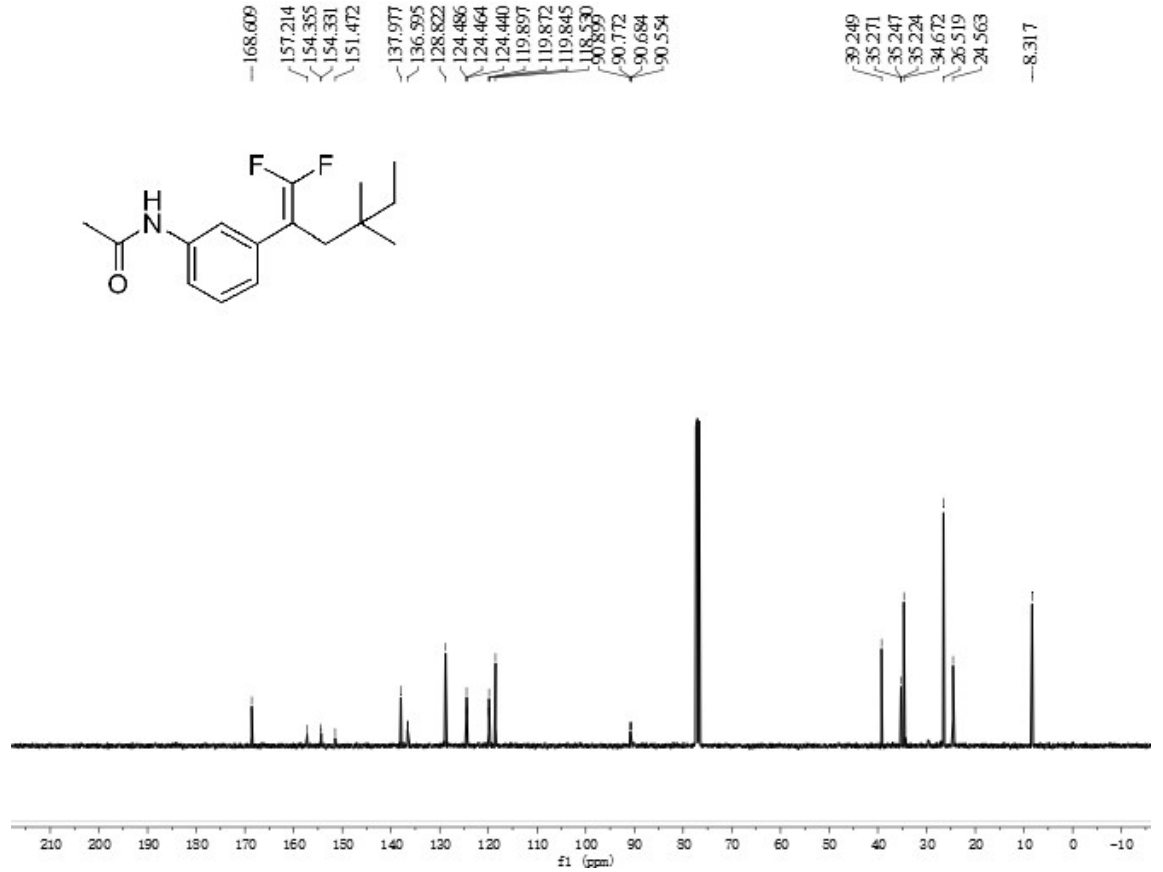
HRMS (EI) spectrum of 3cb



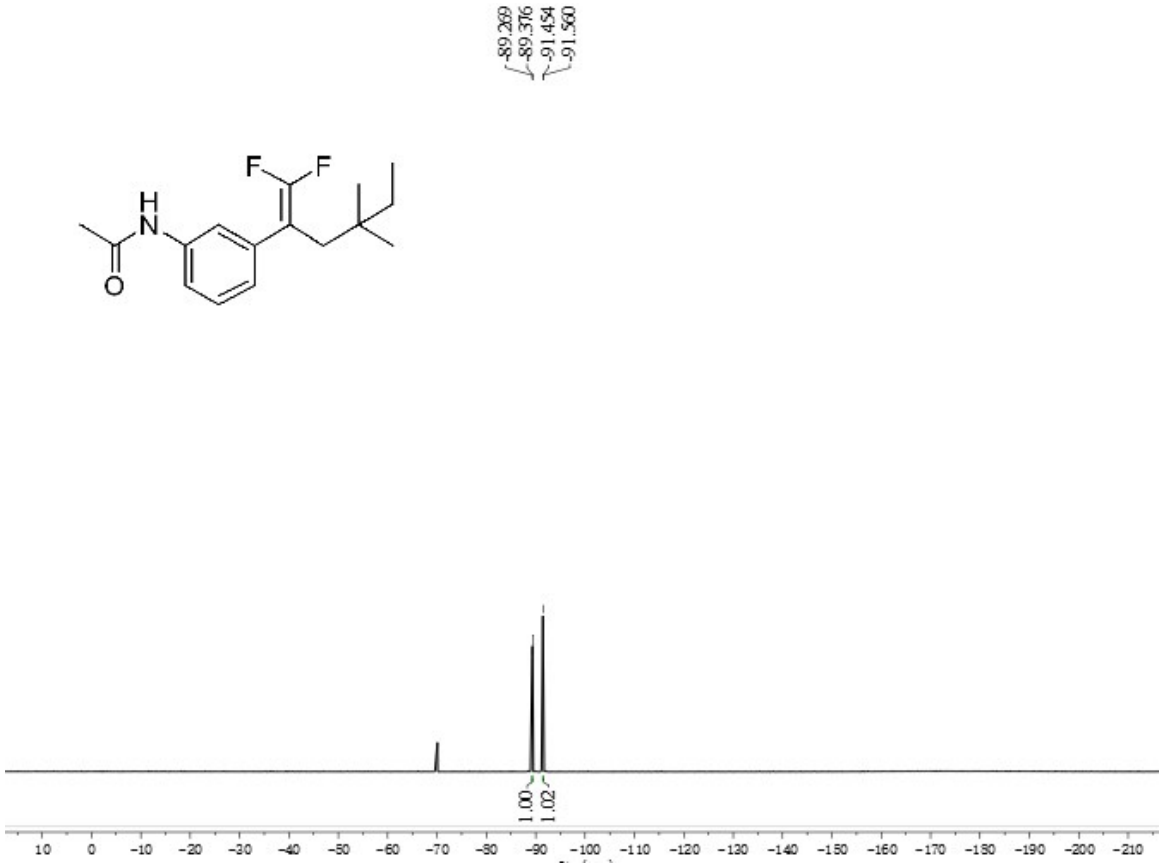
^{1}H NMR spectrum of 3gb



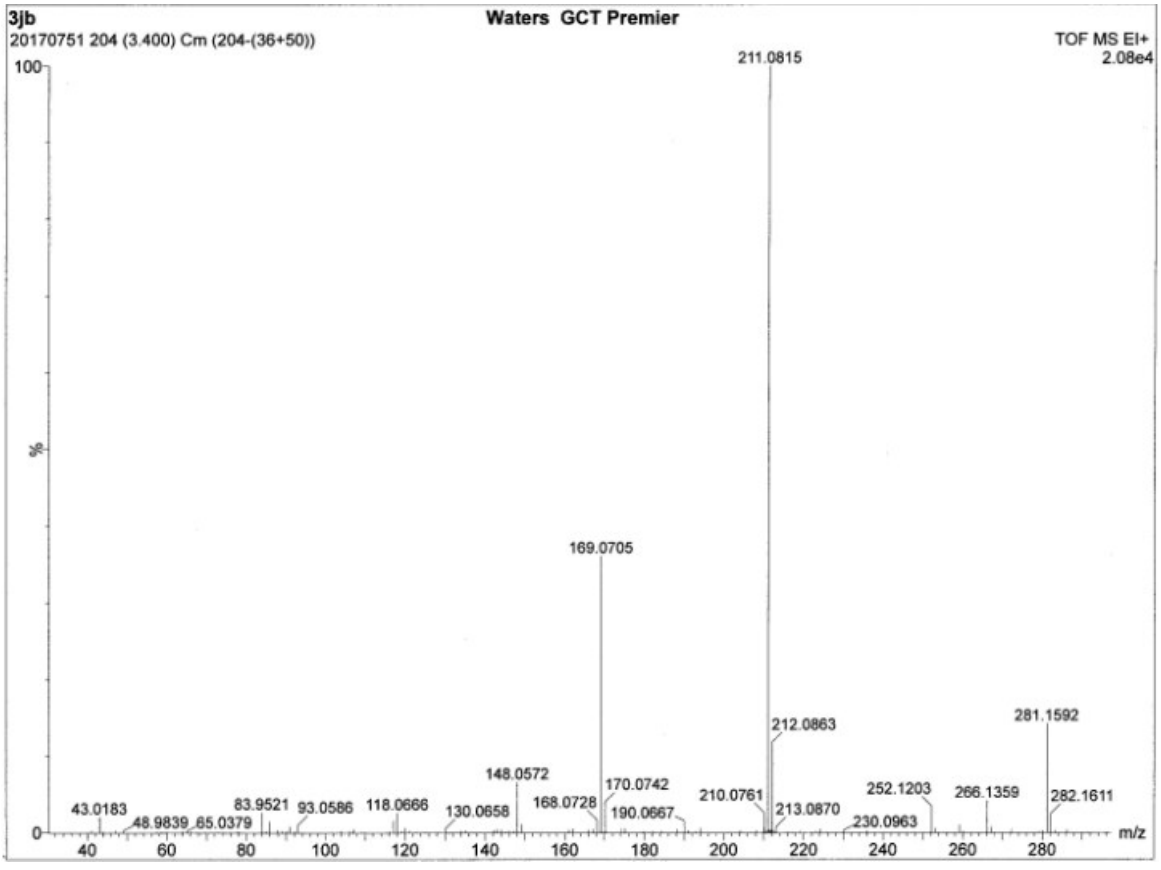
^{13}C NMR spectrum of 3gb



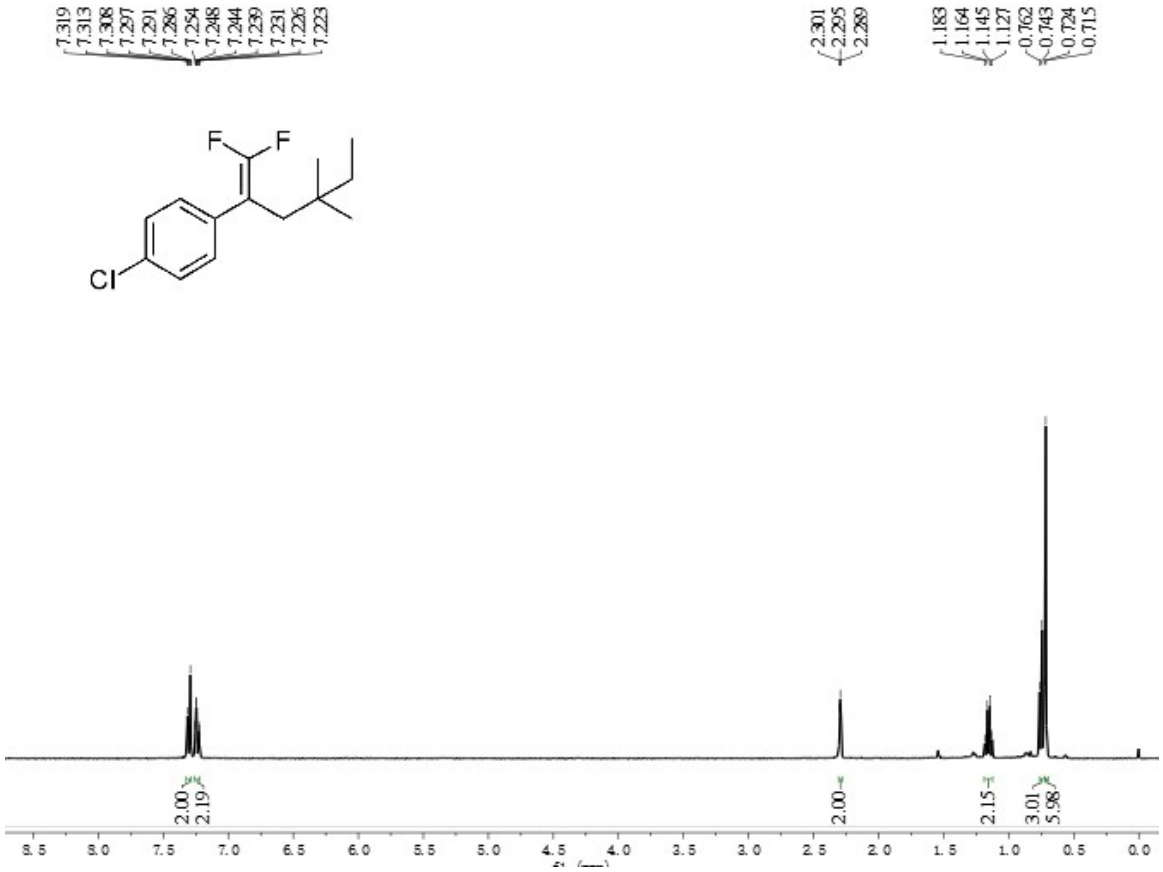
^{19}F NMR spectrum of 3gb



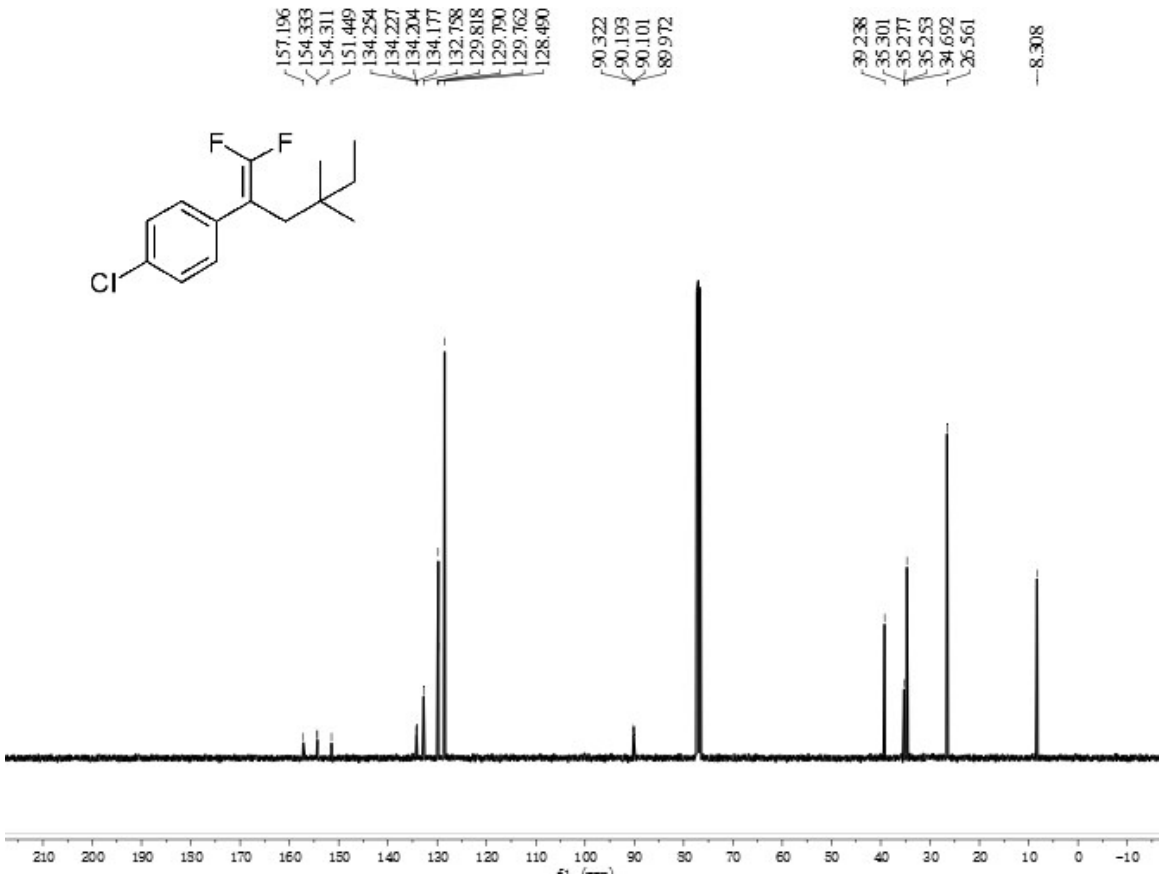
HRMS (EI) spectrum of 3gb



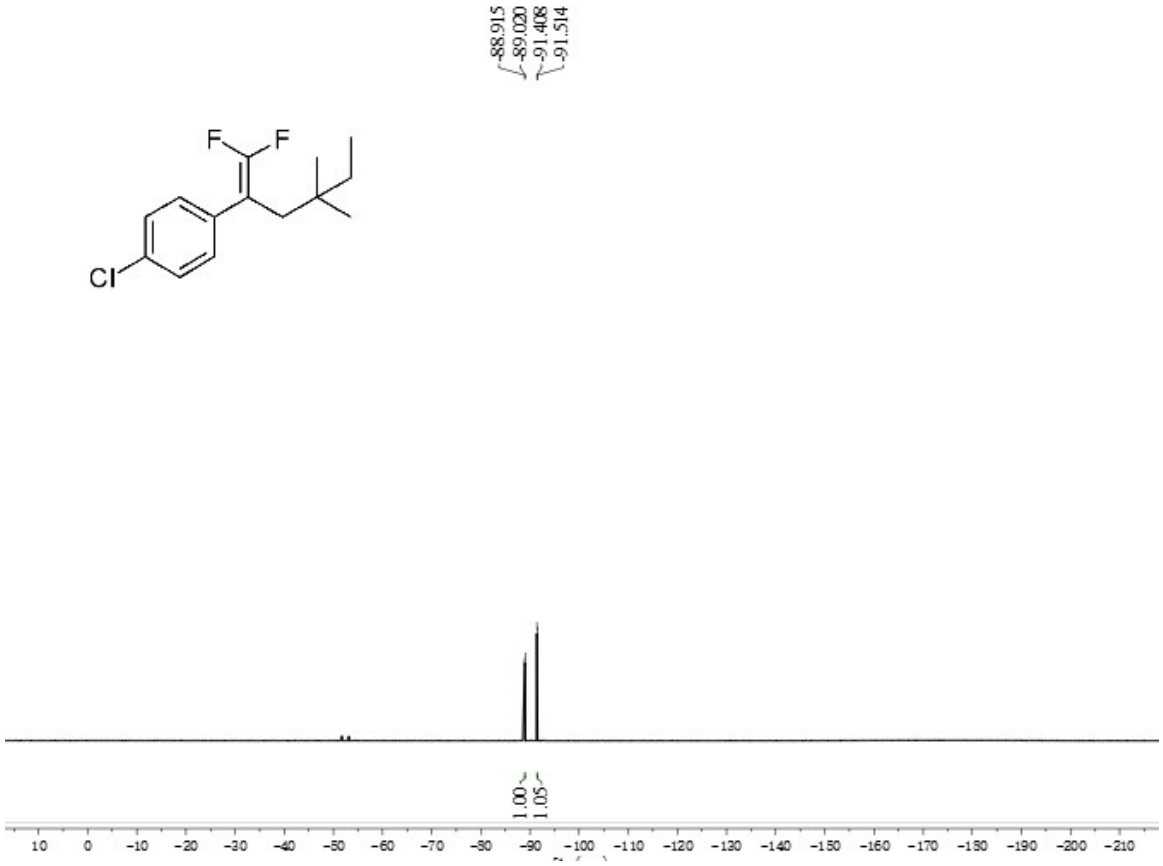
^{1}H NMR spectrum of 3jb



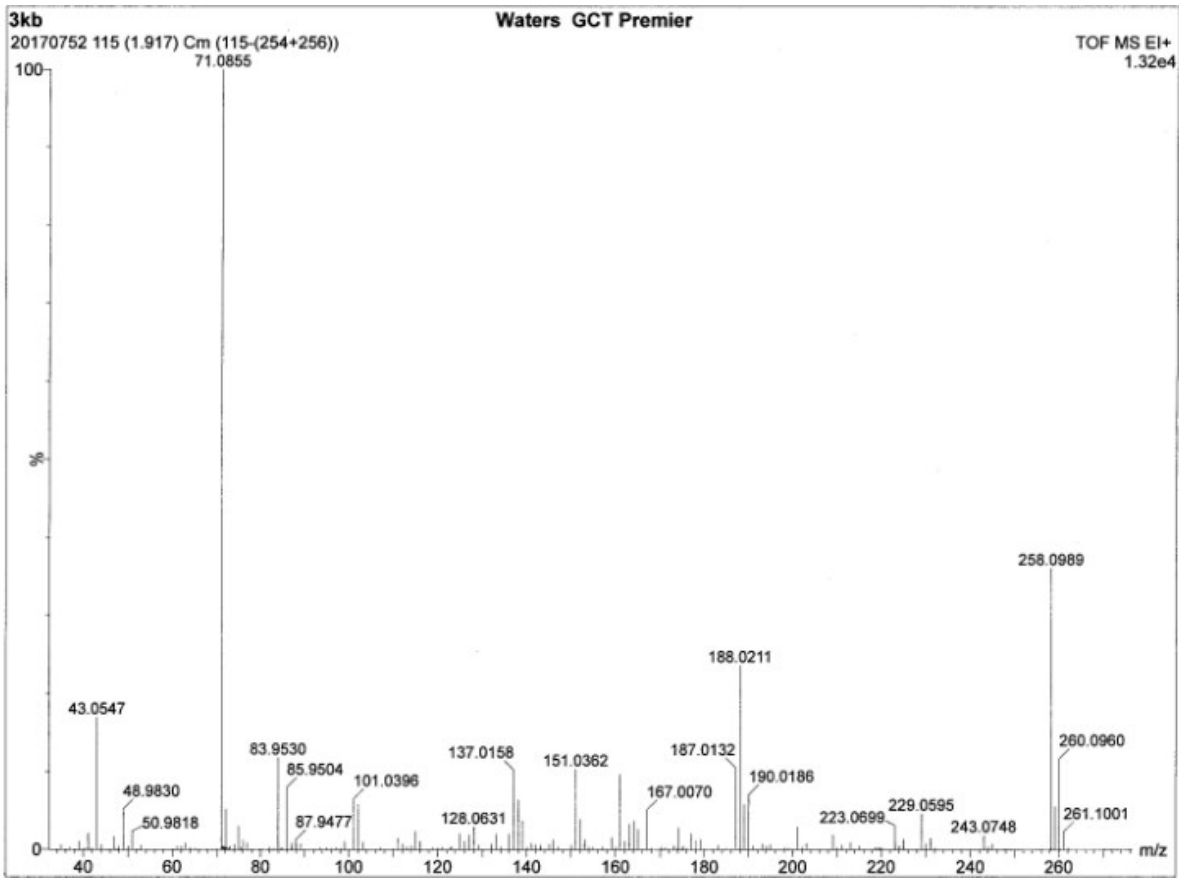
^{13}C NMR spectrum of 3jb



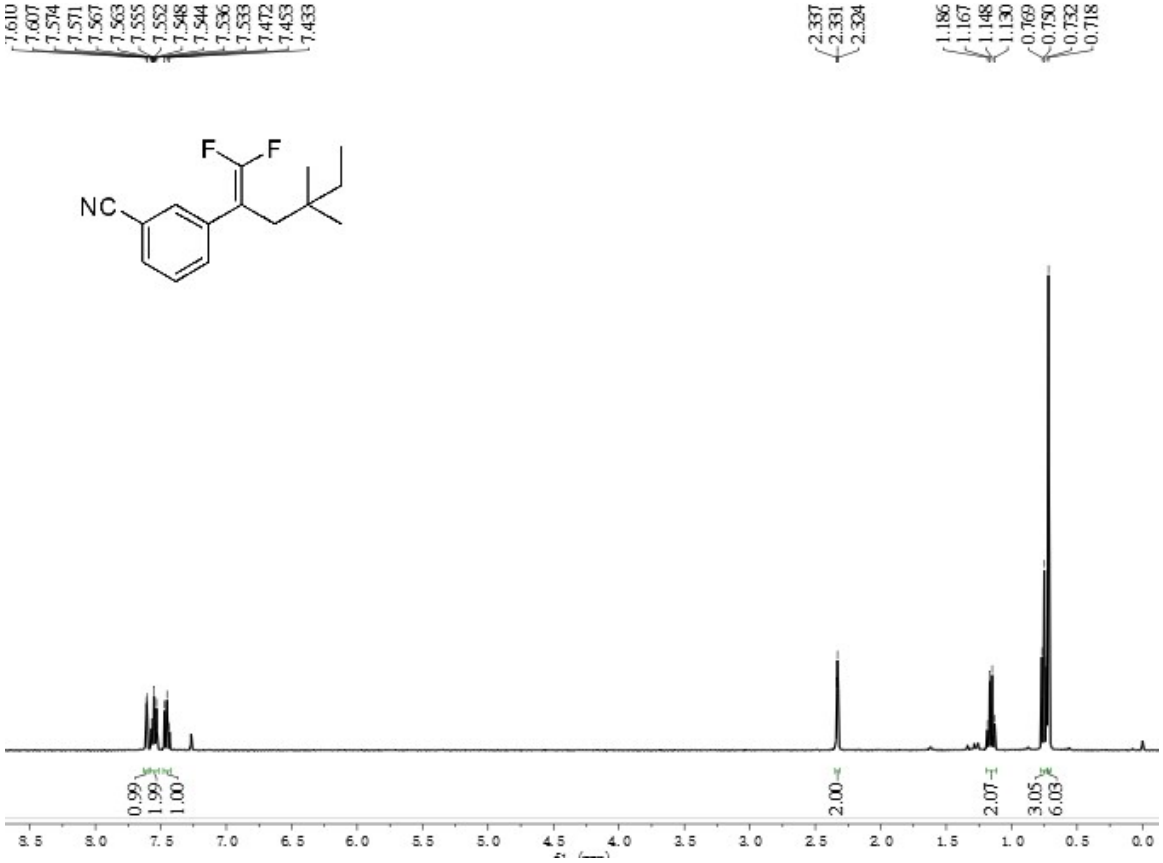
^{19}F NMR spectrum of 3jb



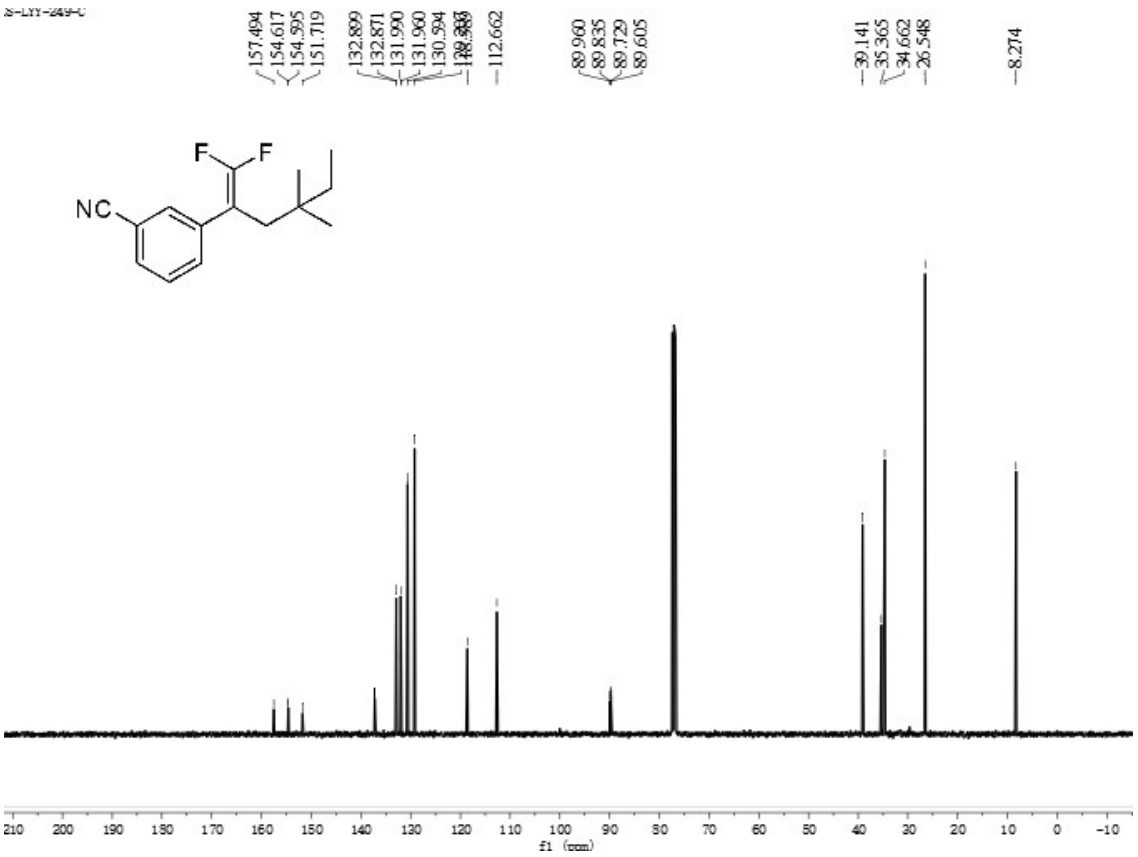
HRMS (EI) spectrum of 3jb



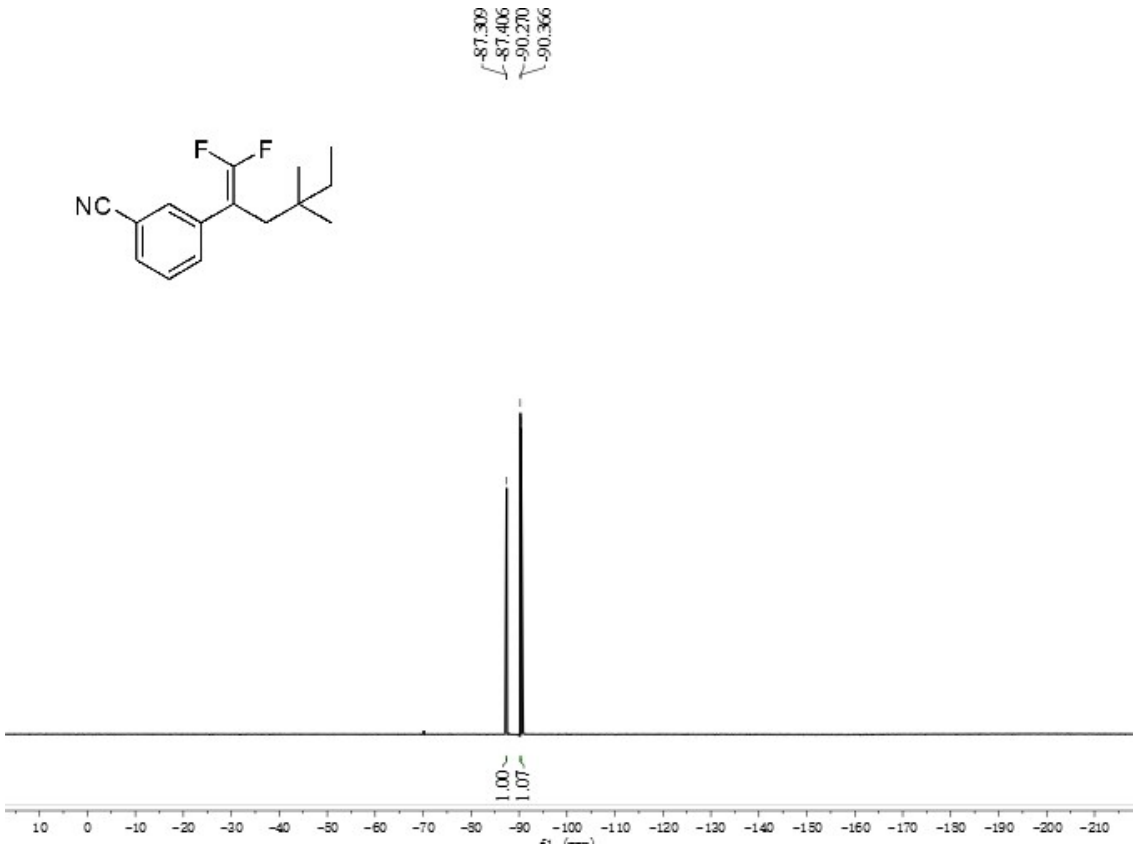
^{1}H NMR spectrum of lb



^{13}C NMR spectrum of 3lb



^{19}F NMR spectrum of 3lb



HRMS (EI) spectrum of 3lb