Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Copper-catalyzed radical-mediated intermolecular cyanomonofluoroalkylation of alkenes and alkynes

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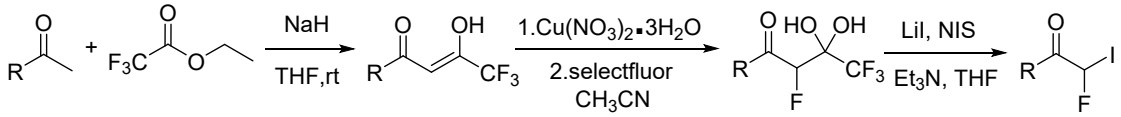
1. General Information

All reagents were commercially available and used without further purification unless indicated otherwise. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatorgraphy (TLC) carried out on GF_{254} plates (0.25mm layer thickness) using UV light as visualizing agent. Flash chromatography was performed with 200-300 mesh silica gels.

All NMR spectra were recorded on a Quantum-I^{plus} NMR Spectrometer (resonance frequencies 400 MHz for ^{1}H , 100 MHz for ^{13}C and 376 MHz for ^{19}F) or Bruker Avance 500 (resonance frequencies 500 MHz for ^{1}H and 125 MHz for ^{13}C) equipped with a 5 mm inverse broadband probe head with z-gradients at 295.8 K with standard Bruker pulse programs. The samples were dissolved in 0.6 mL CDCl3 (99.8%D.TMS). Chemical shifts were given in values of δ H and δ C referenced to residual solvent signals (δ H 7.26 for ^{1}H, δ C 77.0 for ^{13}C in CDCl3). Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. ^{1}H, ^{13}C and ^{19}Fmultiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (td), multiplet (m). High resolution mass spectra (HRMS) were recorded on a Bruker solan X 70 FT-MS (samples was dissolved in CH_3OH and the ion source was ESI).

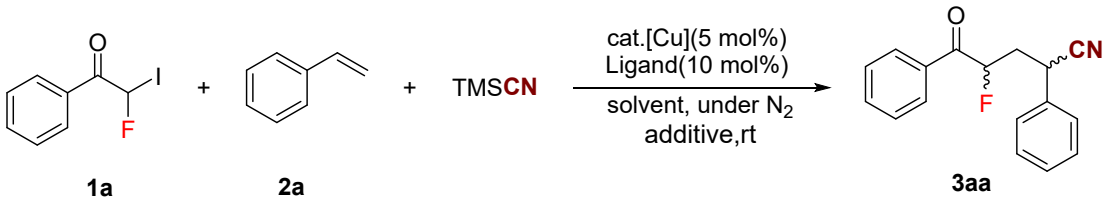
2. Preparation of α-iodine-α-monofluoroketones



The α- iodine-α-monofluoroketones **1a-1o** were prepared according to the reported procedure[1].As shown above, the intermediates enols were obtained from the reaction of ethyl 2,2,2-trifluoroacetate and ketones. The enols reacted with $Cu(NO_3)_2{\cdot}3H_2O$ and Selectfluor to form fluorinated gem-diols, which then reacted with NIS to afford α-iodine-α-monofluoroketones **1a-1o** using the trifluoroacetate release conditions.

3. Optimization of the reaction conditions

Table S1. Screening of reaction conditions[a]

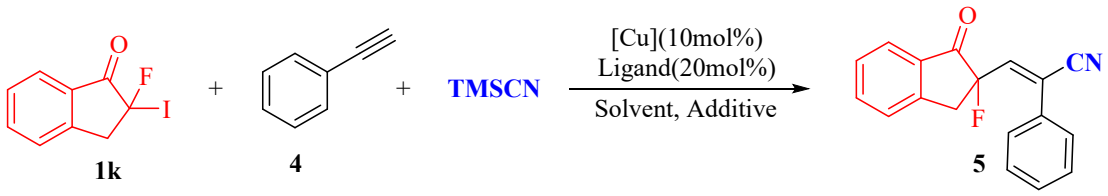


1a **2a** **3aa**

Entry	Cat.	Ligand	Additive	Sol.	Yield[b][%]
1	$Cu(OAc)_2$	L1	LPO	CH_2Cl_2	88
2	CuTc	L1	LPO	CH_2Cl_2	85
3	CuCl	L1	LPO	CH_2Cl_2	60
4	CuBr	L1	LPO	CH_2Cl_2	ND
5	CuI	L1	LPO	CH_2Cl_2	62
6	CuF_2	L1	LPO	CH_2Cl_2	70
7	CuAc	L1	LPO	CH_2Cl_2	79
8	$Cu(CH_3CN)_4PF_6$	L1	LPO	CH_2Cl_2	35
9	$Cu(CF_3SO_{3)2}$	L1	LPO	CH_2Cl_2	30
10	$Cu(CH_3CN)_4BF_4$	L1	LPO	CH_2Cl_2	45
11	$Cu(OAc)_2$	L1	BPO	CH_2Cl_2	39
12	$Cu(OAc)_2$	L1	AIBN	CH_2Cl_2	ND
13	$Cu(OAc)_2$	L1	TBPE	CH_2Cl_2	ND
14	$Cu(OAc)_2$	L1	TBPB	CH_2Cl_2	ND
15	$Cu(OAc)_2$	L1	TBHP	CH_2Cl_2	20
16	$Cu(OAc)_2$	L1	LPO	CH_3CN	64
17	$Cu(OAc)_2$	L1	LPO	THF	50
18	$Cu(OAc)_2$	L1	LPO	DME	48

[a]The reactions were performed by using **1a** (0.2 mmol, 1.0 equiv), **2a** (0.24mmol, 1.2 equiv), TMSCN (0.3 mmol, 1.5 equiv), initiator (0.3 mmol, 1.5 equiv), cat.[Cu] (5 mol%), ligand (10 mol%), solvent (2.0mL), 4 h, under N_2. [b]Isolated yields. ND = not detected

Table S2. Optimization of the reaction conditions for alkynes[a].

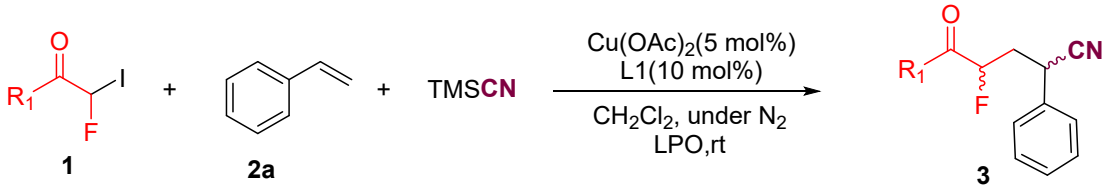


Entry	Cat.	Ligand	Additive	Sol.	Yield[b][%]
1	$Cu(CH_3CN)_4PF_6$	L1	LPO	CH_3OH	61
2	$Cu(CH_3CN)_4PF_6$	L2	LPO	CH_3OH	60
3	$Cu(CH_3CN)_4PF_6$	L3	LPO	CH_3OH	58
4	$Cu(CH_3CN)_4PF_6$	L4	LPO	CH_3OH	55
5	$Cu(CH_3CN)_4PF_6$	L5	LPO	CH_3OH	60
6	$Cu(CH_3CN)_4PF_6$	L6	LPO	CH_3OH	56
7	$Cu(CH_3CN)_4PF_6$	L7	LPO	CH_3OH	65
8	**CuI**	**L7**	**LPO**	**CH_3OH**	**70**
9	CuBr	L7	LPO	CH_3OH	63
10	$Cu(OAc)_2$	L7	LPO	CH_3OH	59
11	$Cu(CH_3CN)_4BF_4$	L7	LPO	CH_3OH	63
12	CuF_2	L7	LPO	CH_3OH	59
13	CuI	L7	BPO	CH_3OH	32
14	CuI	L7	AIBN	CH_3OH	23
15	CuI	L7	TBPE	CH_3OH	20
16	CuI	L7	TBPB	CH_3OH	trace
17	CuI	L7	TBHP	CH_3OH	trace
18[c]	CuI	L7	LPO	DCM	NR
19	CuI	L7	LPO	DMF	45
20	CuI	L7	LPO	CH_3CN	66
21[d]	-	L7	LPO	CH_3OH	trace
22[e]	CuI	-	LPO	CH_3OH	trace
23[f]	CuI	L7	-	CH_3OH	trace

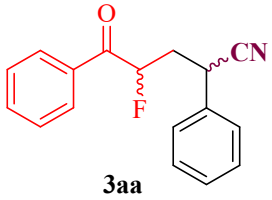
[a]The reactions were performed by using **1k** (0.3 mmol, 1.0 equiv), **4** (0.45 mmol, 1.5 equiv),TMSCN (0.6 mmol, 2.0 equiv), additive (0.75 mmol, 2.5 equiv), [Cu](10 mol%), ligand (20 mol%), solvent (1.5 mL), at 70℃, 5 h, under N_2. [b]Isolated yields. [c]Room temperature. [d]Without CuI catalyst. [e]Without L7. [f]Without LPO. ND = not detected.

4. Preparation and characterization

4.1 General procedure for the synthesis of 3aa-3na



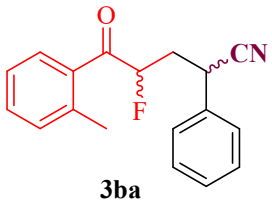
An oven-dried tube was charged with Copper(II) acetate(0.01 mmol, 5 mol %), Ligand **1** (0.02 mmol, 10 mol %), and LPO (0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, α-iodo-α-fluoroacetophenone **1** (0.2 mmol, 1.0 equiv) dissolved in dichloromethane (2.0 mL), styrene **2a** (0.24mmol, 1.2 equiv), and TMSCN (0.3 mmol, 1.5 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at room temperature for 4 h. After the reaction was completed, solvent was removed under reduced pressure by rotary evaporator, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 50:1) to afford the desired product **3aa-3na**.



3aa

4-fluoro-5-oxo-2,5-diphenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 47.1 mg, 88% yield.The compound is known[1c].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 4.0Hz, 2H), 7.79 (d, *J* = 8.0Hz, 2H), 7.65-7.59 (m, 2H), 7.53-7.32 (m, 14H), 6.00-5.87 (m, 1H), 5.42-5.30 (m, 1H), 4.23-4.08 (m, 2H), 2.71-2.38 (m, 4H).



3ba

4-fluoro-5-oxo-2-phenyl-5-(o-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 46.1 mg, 82% yield.

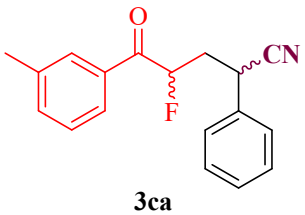
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0Hz, 1H), 7.51-7.23 (m, 17H), 5.94-5.79 (m, 1H), 5.35-5.20 (m, 1H), 4.24-4.08 (m, 2H), 2.66-2.36 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.63 (d, $^2J_{C\text{-}F}$ = 20.0Hz), 198.22 (d, $^2J_{C\text{-}F}$ = 20.0Hz), 139.48, 139.42, 134.45, 133.93, 133.75, 132.62, 132.51, 132.36, 132.33, 129.64,

129.50, 129.03, 128.99, 128.95, 128.81, 128.77, 128.71, 127.94, 127.30, 126.01, 125.75, 120.26, 119.59, 91.24 (d, $^{1}J_{C\text{-}F}$ = 79.0Hz), 89.39 (d, $^{1}J_{C\text{-}F}$ = 79.0Hz), 38.40 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.47 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.72 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 33.16 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz), 21.15, 21.09.

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.39--189.77 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108; found: 304.1114.



3ca

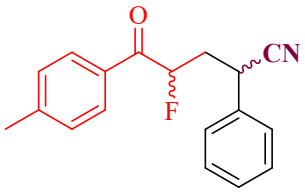
4-fluoro-5-oxo-2-phenyl-5-(m-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 47.7 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0Hz, 2H), δ 7.56 (d, *J* = 8.0Hz, 2H), 7.49-7.30 (m, 14H), 6.00-5.84 (m, 1H), 5.44-5.29 (m, 1H), 4.23-4.06 (m, 2H), 2.70-2.31 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.02 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 189.80 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 134.24, 134.07, 130.42, 130.33, 129.66, 129.17, 129.01, 128.95, 124.85, 124.67, 124.63, 124.60, 124.56, 124.22, 124.13, 124.00, 123.89, 123.15, 122.50, 121.38, 121.34, 121.30, 115.37, 114.89, 85.91 (d, $^{1}J_{C\text{-}F}$ = 65.0Hz), 84.07 (d, $^{1}J_{C\text{-}F}$ = 66.0Hz), 33.80 (d, $^{2'}J_{C\text{-}F}$ = 22.0Hz), 33.00 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 28.85 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 28.37 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 16.59, 16.55.

^{19}F NMR (376 MHz, $CDCl_3$): δ -190.44--190.88 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108, found: 304.1108.



3da

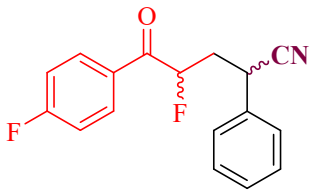
4-fluoro-5-oxo-2-phenyl-5-(p-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 46.7 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0Hz, 2H), δ 7.72 (d, *J* = 8.0Hz, 2H), 7.53-7.27 (m, 14H), 6.04-5.88 (m, 1H), 5.45-5.30 (m, 1H), 4.27-4.10 (m, 2H), 2.75-2.39 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.43 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 189.16 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 140.77, 140.67, 129.73, 129.25, 126.49, 124.97, 124.84, 124.82, 124.67, 124.58, 124.45, 124.32, 124.29, 124.28, 124.18, 124.06, 123.87, 123.11, 122.50, 115.43, 114.94, 85.96 (d, $^{1}J_{C\text{-}F}$ = 60.0Hz), 84.13 (d, $^{1}J_{C\text{-}F}$ = 60.0Hz), 33.84 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 32.98 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 28.3 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 28.35 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz), 17.05, 17.02.

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.97--190.22 (m, 1F), -190.39--190.66 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108; found: 304.1113.



3ea

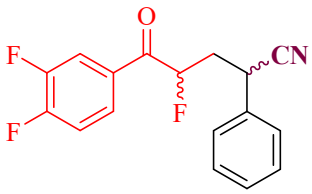
5-(4-fluorophenyl)-4-fluoro-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 53.1 mg, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.01 (m, 2H), 7.91-7.87 (m, 2H), 7.49-7.36 (m, 10H), 7.21-7.11 (m, 4H), 5.97-5.81 (m, 1H), 5.43-5.28 (m, 1H), 4.26-4.10 (m, 2H), 2.70-2.43 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.31 (d, $^2J_{C\text{-}F}$ = 20.0Hz), 192.00 (d, $^2J_{C\text{-}F}$ = 19.0Hz), 167.62 (d, J = 7.0Hz), 165.06 (d, J = 7.0Hz), 134.40, 133.95, 132.02, 131.98, 131.92, 131.88, 130.23, 130.21, 129.65, 129.49, 129.02, 128.73, 127.88, 127.32, 120.22, 119.72, 116.41, 116.29, 116.20, 116.08, 91.05 (d, $^1J_{C\text{-}F}$ = 52.0Hz), 89.22 (d, $^1J_{C\text{-}F}$ = 52.0Hz), 38.30 (d, $^{2'}J_{C\text{-}F}$ = 20.0Hz), 37.50 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.53, 33.08 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.77--102.92 (m, 2F), -189.59--189.74 (m, 1F), -189.85--190.13 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}F_2NONa^+$: 308.0857; found: 308.0861.



3fa

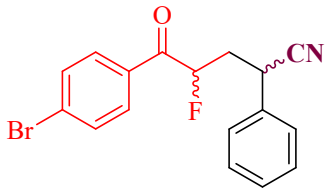
5-(3,4-difluorophenyl)-4-fluoro-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 51.56 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.56 (m, 4H), 7.41-7.12 (m, 12H), 5.78-5.64 (m, 1H), 5.28-5.11 (m, 1H), 4.14-3.98 (m, 2H), 2.62-2.34 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.51 (d, $^2J_{C\text{-}F}$ = 20.0Hz), 192.22 (d, $^2J_{C\text{-}F}$ = 20.0Hz), 155.58, 152.99, 151.77, 149.40, 134.22, 133.79, 130.82, 129.62, 129.48, 129.28, 129.01, 128.74, 127.75, 127.25, 126.44, 126.36, 119.92, 119.46, 118.71, 118.52, 118.06, 117.97, 117.88, 117.79, 91.32 (d, $^1J_{C\text{-}F}$ = 46.0Hz), 89.48 (d, $^1J_{C\text{-}F}$ = 48.0Hz), 38.06 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.38 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.38 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 33.02 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.81--126.98 (m, 2F), -134.85--134.96 (m, 1F), -134.99--135.10 (m, 1F), -188.50--188.96 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{12}F_3NONa^+$: 326.0763; found: 326.0768.



3ga

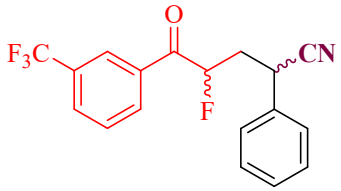
5-(4-bromophenyl)-4-fluoro-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 61.41 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0Hz, 2H), 7.67-7.57 (m, 6H), 7.47-7.33 (m, 10H), 5.92-5.77 (m, 1H), 5.37-5.22 (m, 1H), 4.22-4.06 (m, 2H), 2.70-2.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.04 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 193.71 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 134.29, 133.81, 132.42, 132.30, 130.57, 130.53, 129.86, 129.77, 129.70, 129.54, 129.09, 128.78, 127.90, 127.32, 120.18, 119.69, 91.03 (d, $^{1}J_{C\text{-}F}$ = 53.0Hz), 89.19 (d, $^{1}J_{C\text{-}F}$ = 54.0Hz), 38.30 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.50 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.53 (d, $^{3'}J_{C\text{-}F}$ = 2.0Hz), 33.08 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.43--189.94 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}BrFNONa^+$: 368.0056; found: 368.0059.



3ha

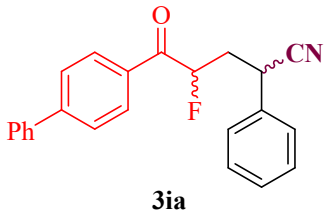
4-fluoro-5-oxo-2-phenyl-5-(3-(trifluoromethyl)phenyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 59.0 mg, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22(s, 1H), 8.15 (d, *J* = 8.0Hz, 1H), 8.06-8.02 (m, 2H), 7.87 (t, *J* = 8.0Hz, 2H), 7.67-7.59 (m, 2H), 7.48-7.34 (m, 10H), 5.93-5.77 (m, 1H), 5.42-5.27 (m, 1H), 4.23-4.08 (m, 2H), 2.74-2.41 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.87 (d, $^{2}J_{C\text{-}F}$ = 16.0Hz), 193.65 (d, $^{2}J_{C\text{-}F}$ = 16.0Hz), 134.27, 134.13, 133.60, 132.23, 130.63, 129.70, 129.63, 129.50, 129.10, 128.78, 127.81, 127.28, 126.04, 124.40, 122.30, 120.00, 119.52, 91.08 (d, $^{1}J_{C\text{-}F}$ = 66.0Hz), 89.61 (d, $^{1}J_{C\text{-}F}$ = 67.0Hz), 38.03 (d, $^{2'}J_{C\text{-}F}$ = 17.0Hz), 37.38 (d, $^{2'}J_{C\text{-}F}$ = 17.0Hz), 33.39, 33.03.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.90 (d, *J* = 7.52Hz, 6F), -189.28--189.53 (m, 1F), -189.80--190.06 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{13}F_4NONa^+$: 358.0825; found: 358.0829.



3ia

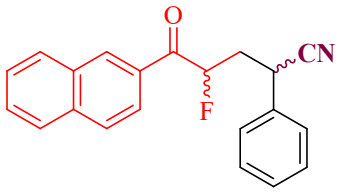
5-([1,1'-biphenyl]-4-yl)-4-fluoro-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 51.51 mg, 75% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 10.0Hz, 2H), 7.87 (d, J = 10.0Hz, 2H), 7.74-7.36 (m, 24H), 6.03-5.91 (m, 1H), 5.46-5.33 (m, 1H), 4.26-4.10 (m, 2H), 2.74-2.41 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.27 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 193.94 (d, $^{2}J_{C\text{-}F}$ = 18.75Hz), 147.05, 146.96, 139.43, 134.40, 133.91, 132.33, 129.63, 129.61, 129.58, 129.47, 129.10, 129.01, 128.66, 127.91, 127.61, 127.48, 127.34, 127.28, 120.21, 119.72, 90.67 (d, $^{1}J_{C\text{-}F}$ = 75.0Hz), 89.22 (d, $^{1}J_{C\text{-}F}$ = 73.75Hz), 38.58 (d, $^{2'}J_{C\text{-}F}$ = 21.25Hz), 37.69 (d, $^{2'}J_{C\text{-}F}$ = 22.50Hz), 33.62, 33.13.

^{19}F NMR (376 MHz, $CDCl_3$): δ -190.02 (s, 1F), -190.35 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{23}H_{18}FNONa^+$: 366.1264; found: 366.1261.



3ja

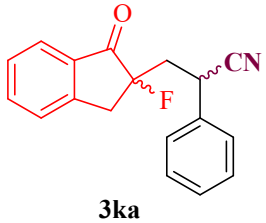
4-fluoro-5-(naphthalen-2-yl)-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 38.1 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 8.0Hz, 2H), 8.04-7.33 (m, 22H), 6.04-5.89 (m, 1H), 5.47-5.32 (m, 1H), 4.21-4.04 (m, 2H), 2.73-2.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.32 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 197.90 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 134.43, 134.09, 134.06, 134.03, 133.98, 133.84, 131.58, 130.57, 129.58, 129.43, 128.94, 128.83, 128.78, 128.72, 128.64, 128.59, 127.87, 127.25, 126.91, 125.23, 124.37, 124.14, 120.14, 119.53, 91.35 (d, $^{1}J_{C\text{-}F}$ = 71.0Hz), 89.49 (d, $^{1}J_{C\text{-}F}$ = 71.0Hz), 38.48 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.63 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.72 (d, $^{3'}J_{C\text{-}F}$ = 2.0Hz), 33.24 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -187.94 (s, 1F), -188.18 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{16}FNONa^+$: 340.1108; found: 340.1112.



3ka

3-(2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2-phenylpropanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 39.1 mg, 70% yield.

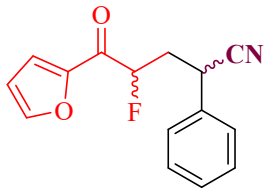
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0Hz, 2H), 7.71-7.63 (m, 2H), 7.50-7.33 (m, 14H), 4.38-4.34 (m, 1H), 4.19 (t, J = 8.0Hz, 1H), 3.76 (t, J = 20.0Hz, 1H), 3.62-3.52 (m, 1H), 3.25-3.05 (m, 2H), 2.90-2.81 (m, 1H), 2.61-2.54 (m, 1H), 2.40-2.26 (m,

2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.36 (d, $^{2}J_{C\text{-}F}$ = 15.0Hz), 199.19 (d, $^{2}J_{C\text{-}F}$ = 16.0Hz), 150.53, 150.01, 136.93, 136.85, 135.60, 133.37, 133.24, 129.43, 128.72, 128.68, 128.63, 128.51, 127.74, 127.28, 126.96, 126.80, 125.44, 120.92, 120.50, 96.50 (d, $^{1}J_{C\text{-}F}$ = 16.0Hz), 94.64 (d, $^{1}J_{C\text{-}F}$ = 15.0Hz), 40.43 (d, $^{2'}J_{C\text{-}F}$ = 8.0Hz), 40.49 (d, $^{2'}J_{C\text{-}F}$ = 10.0Hz), 38.64 (d, $^{2''}J_{C\text{-}F}$ = 9.0Hz), 38.40 (d, $^{2''}J_{C\text{-}F}$ = 10.0Hz), 32.09 (d, $^{3'}J_{C\text{-}F}$ = 6.0Hz), 31.40 (d, $^{3'}J_{C\text{-}F}$ = 5.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -156.32--156.53 (m, 1F), -158.13--158.34 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{14}FNONa^+$: 302.0951; found: 302.0958.



3la

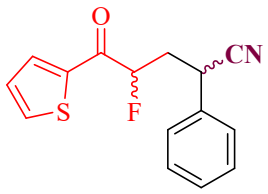
4-fluoro-5-(furan-2-yl)-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 37.1 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67(d, *J* = 16.0Hz, 2H), 7.45-7.32 (m, 12H), 6.61-6.57 (m, 2H), 5.71-5.55 (m, 1H), 5.18-5.02 (m, 1H), 4.19-4.05 (m, 2H), 2.69-2.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.39 (d, $^{2}J_{C\text{-}F}$ = 21.0Hz), 183.14 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 149.54, 148.24, 148.19, 134.33, 133.69, 129.59, 129.47 128.99, 128.73, 127.89, 127.34, 121.61, 121.52, 121.47, 121.38, 120.18, 119.55, 112.93, 112.86, 91.35 (d, $^{1}J_{C\text{-}F}$ = 50.0Hz), 89.50 (d, $^{1}J_{C\text{-}F}$ = 51.0Hz), 38.52 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.77 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.47 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 32.05 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -192.88--193.23 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{12}FNO_2Na^+$: 280.0744; found: 280.0750.



3ma

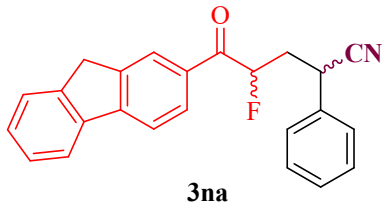
4-fluoro-5-oxo-2-phenyl-5-(thiophen-2-yl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 42.6 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96(d, *J* = 4.0Hz, 1H), 7.82(d, *J* = 4.0Hz, 1H), 7.76 (t, *J* = 4.0Hz, 2H), 7.46-7.33 (m, 10H), 7.20-7.14 (m, 2H), 5.70-5.54 (m, 1H), 5.21-5.05 (m, 1H), 4.20-4.07 (m, 2H), 2.73-2.40 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 188.25 (d, $^{2}J_{C\text{-}F}$ = 22.0Hz), 187.96 (d, $^{2}J_{C\text{-}F}$ = 21.0Hz), 139.96, 139.82, 136.01, 134.72, 134.63, 134.35, 133.82, 129.61, 129.48, 128.98, 128.79, 128.72, 128.69, 127.86, 127.36, 120.16, 119.61, 92.37 (d, $^{1}J_{C\text{-}F}$ = 50.0Hz), 90.51 (d, $^{1}J_{C\text{-}F}$ = 50.0Hz), 38.79 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 38.10 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.48 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 33.13 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -188.30--188.72 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{12}FNOSNa^+$: 296.0515; found: 296.0523.



3na

5-(9H-fluoren-2-yl)-4-fluoro-5-oxo-2-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 35.5 mg, 50% yield.

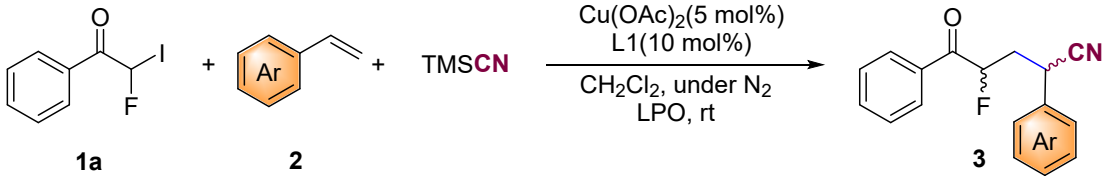
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13(s, 1H), 8.00(d, J = 10.0Hz, 1H), 7.94(s, 1H), 7.87-7.82 (m, 3H), 7.79(s, 2H), 7.60-7.34 (m, 16H), 6.06-5.93 (m, 1H), 5.48-5.36 (m, 1H), 4.26-4.10 (m, 2H), 3.93(d, J = 25.0Hz, 4H), 2.75-2.42 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.27 (d, $^2J_{C\text{-}F}$ = 18.75Hz), 194.01 (d, $^2J_{C\text{-}F}$ = 18.75Hz), 147.77, 147.67, 144.72, 144.67, 143.64, 143.50, 140.12, 134.44, 134.00, 131.88, 129.62, 129.45, 128.99, 128.65, 128.58, 128.36, 128.32, 128.28, 127.94, 127.28, 127.25, 125.61, 125.58, 125.37, 121.21, 121.18, 120.24, 120.11, 119.97, 119.77, 92.57 (d, $^1J_{C\text{-}F}$ = 68.75Hz), 89.11 (d, $^1J_{C\text{-}F}$ = 70.0Hz), 38.67 (d, $^{2'}J_{C\text{-}F}$ = 20.0Hz), 37.85 (d, $^{2'}J_{C\text{-}F}$ = 21.25Hz), 36.93, 36.88, 33.64, 33.17.

^{19}F NMR (376 MHz, $CDCl_3$):δ -189.68 (s, 1F), -189.86 (s, 1F).

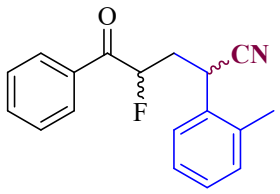
HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{18}FNONa^+$: 378.1264; found: 378.1262.

4.2 General procedure for the synthesis of 3ab-3am



1a **2** **3**

An oven-dried tube was charged with Copper(II) acetate(0.01 mmol, 5 mol %), Ligand **1** (0.02 mmol, 10 mol %), and LPO (0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, α-iodo-α-fluoroacetophenone **1a** (0.2 mmol, 1.0 equiv) dissolved in dichloromethane (2.0 mL), styrene **2** (0.24mmol, 1.2 equiv), and TMSCN (0.3 mmol, 1.5 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at room temperature for 4 h. After the reaction was completed, solvent was removed under reduced pressure by rotary evaporator, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 50:1) to afford the desired product **3ab-3am**.



3ab

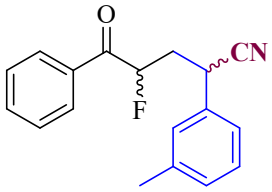
4-fluoro-5-oxo-5-phenyl-2-(o-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 46.1 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01(d, *J* = 8.0Hz, 2H), 7.84(d, *J* = 8.0Hz, 2H), 7.70-7.23 (m, 14H), 6.60-5.95 (m, 1H), 5.50-5.35 (m, 1H), 4.44-4.32 (m, 2H), 2.73-2.26 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.78 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 194.36 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 136.14, 135.11, 134.50, 134.41, 133.73, 133.67, 132.67, 132.30, 131.56, 131.37, 129.13, 129.03, 128.98, 128.94, 128.84, 128.79, 127.89, 127.40, 127.36, 127.21, 120.39, 120.08, 90.91 (d, $^{1}J_{C\text{-}F}$ = 32.0Hz), 89.08 (d, $^{1}J_{C\text{-}F}$ = 33.0Hz), 37.30 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 36.73 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 30.53 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 29.53 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 19.34, 18.99.

^{19}F NMR (376 MHz, $CDCl_3$): δ -187.95--188.21 (m, 1F), -190.85--191.12 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108; found: 304.1106.



3ac

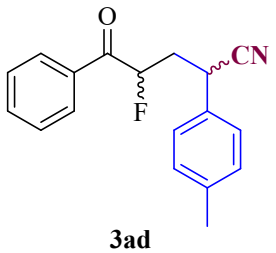
4-fluoro-5-oxo-5-phenyl-2-(m-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 45.6 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00(d, *J* = 8.0Hz, 2H), 7.82(d, *J* = 8.0Hz, 2H), 7.69-7.61 (m, 2H), 7.57-7.18 (m, 12H), 6.05-5.89 (m, 1H), 5.48-5.32 (m, 1H), 4.23-4.06 (m, 2H), 2.74-2.35 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.83 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.49 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 139.62, 139.40, 134.44, 134.35, 134.28, 133.74, 129.79, 129.49, 129.44, 129.35, 129.09, 129.01, 128.97, 128.94, 128.53, 127.95, 125.02, 124.34, 120.36, 119.84, 90.84 (d, $^{1}J_{C\text{-}F}$ = 57.0Hz), 89.01 (d, $^{1}J_{C\text{-}F}$ = 58.0Hz), 38.61 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.65 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.55 (d, $^{3'}J_{C\text{-}F}$ = 2.0Hz), 33.04 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz), 21.50, 21.43.

^{19}F NMR (376 MHz, $CDCl_3$): δ -190.18--190.79 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108; found: 304.1111.



3ad

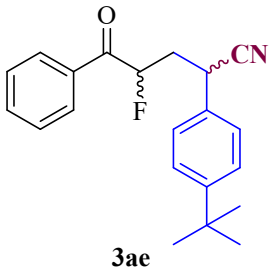
4-fluoro-5-oxo-5-phenyl-2-(p-tolyl)pentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 46.2 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99(d, *J* = 8.0Hz, 2H), 7.82(d, *J* = 8.0Hz, 2H), 7.68-7.61 (m, 2H), 7.56-7.46 (m, 4H), 7.36-7.21 (m, 8H), 6.04-5.88 (m, 1H), 5.47-5.31 (m, 1H), 4.23-4.07 (m, 2H), 2.72-2.35 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.83 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.53 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 138.97, 138.61, 134.44, 134.34, 133.73, 131.37, 130.78, 130.30, 130.11, 129.08, 129.01, 128.97, 128.94, 127.83, 127.19, 120.44, 119.92, 90.83 (d, $^{1}J_{C\text{-}F}$ = 65.0Hz), 89.00 (d, $^{1}J_{C\text{-}F}$ = 65.0Hz), 38.58 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.65 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.25 , 32.73, 21.25, 21.16.

^{19}F NMR (376 MHz, $CDCl_3$): δ -190.34--190.72 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{16}FNONa^+$: 304.1108; found: 304.1105.



3ae

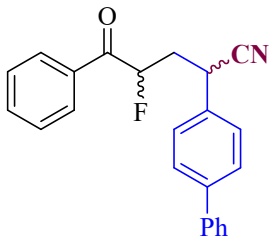
2-(4-(tert-butyl)phenyl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 41.4 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96(d, *J* = 8.0Hz, 2H), 7.78 (d, *J* = 8.0Hz, 2H), 7.65-7.30 (m, 14H), 6.03-5.88 (m, 1H),5.47-5.31 (m, 1H), 4.23-4.06 (m, 2H), 2.70-2.36i (m, 4H), 1.35 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.89 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.53 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 152.15, 151.82, 134.44, 134.34, 133.73, 131.35 130.80, 129.09, 129.05, 129.01, 128.97, 128.93, 127.68, 127.05, 126.59, 126.42, 120.45, 119.91, 90.93 (d, $^{1}J_{C\text{-}F}$ = 53.0Hz), 89.09 (d, $^{1}J_{C\text{-}F}$ = 54.0Hz), 38.62 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.66 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.18 (d, $^{3'}J_{C\text{-}F}$ = 2.0Hz), 32.67 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz), 31.37, 31.33.

^{19}F NMR (376 MHz, $CDCl_3$): δ -190.22--190.48 (m, 1F), -190.74--191.00 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{22}FNONa^+$: 346.1577; found: 346.1579.



3af

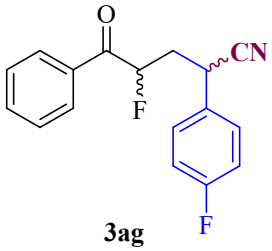
2-([1,1'-biphenyl]-4-yl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 48.1 mg, 70% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98(d, *J* = 8.0Hz, 2H), 7.83 (d, *J* = 4.0Hz, 2H), 7.73-7.36 (m, 24H), 6.06-5.90 (m, 1H), 5.50-5.35 (m, 1H), 4.30-4.12 (m, 2H), 2.77-2.41 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.84 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.48 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 142.01, 141.74, 140.09, 140.03, 134.51, 134.42, 133.72, 133.27, 132.72, 129.13, 129.08, 129.03, 128.99, 128.91, 128.41, 128.32, 128.32, 128.24, 128.17, 127.97, 128.88, 127.79, 127.45, 127.22, 127.20, 127.11, 120.23, 119.74, 90.84 (d, $^{1}J_{C\text{-}F}$ = 57.0Hz), 89.00 (d, $^{1}J_{C\text{-}F}$ = 58.0Hz), 38.58 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.59 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.34 (d, $^{3'}J_{C\text{-}F}$ = 2.0Hz), 33.82 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.95--190.21 (m, 1F), -190.47--190.73 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{23}H_{18}FNONa^+$: 366.1270; found: 366.1265.



3ag

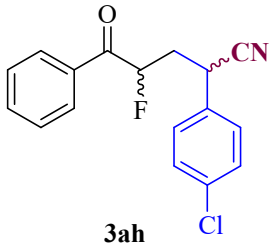
4-fluoro-2-(4-fluorophenyl)-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 51.4 mg, 90% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93(d, *J* = 8.0Hz, 2H), 7.79 (d, *J* = 8.0Hz, 2H), 7.63-7.56 (m, 2H), 7.50-7.32 (m, 8H), 7.15-7.03 (m, 4H), 5.99-5.83 (m, 1H), 5.44-5.28 (m, 1H), 4.22-4.07 (m, 2H), 2.68-2.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.71 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.39 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 163.98 (d, $^{1}J_{C\text{-}F}$ = 18.0Hz), 161.51 (d, $^{1}J_{C\text{-}F}$ = 18.0Hz), 134.51, 134.43, 133.71, 133.67, 130.32, 130.29, 129.83, 129.79, 129.71, 129.23, 129.14, 129.10, 129.02, 128.98, 120.11, 119.64, 116.77, 116.57, 116.35, 90.75 (d, $^{1}J_{C\text{-}F}$ = 57.0Hz), 88.91 (d, $^{1}J_{C\text{-}F}$ = 58.0Hz), 38.41 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.49 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 32.85 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 32.40 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.28--112.35 (m, 1F), -112.79--112.86 (m, 1F), -189.80--190.05 (m, 1F), -190.37--190.63 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}F_2NONa^+$: 308.0857; found: 308.0859.



3ah

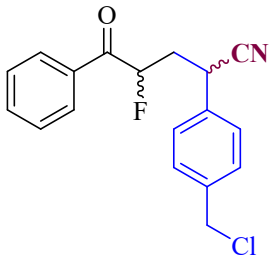
2-(4-chlorophenyl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 53.7 mg, 89% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0Hz, 2H), 7.81 (d, *J* = 8.0Hz, 2H), 7.65-7.59 (m, 2H), 7.52-7.29 (m, 12H), 5.99-5.83 (m, 1H), 5.44-5.28 (m, 1H), 4.21-4.06 (m, 2H), 2.70-2.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.64 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.32 (d, $^{2}J_{C\text{-}F}$ = 18.0Hz), 135.04, 134.74, 134.54, 134.46, 133.71, 133.66, 132.92, 132.46, 129.84, 129.67, 129.29, 129.11, 129.07, 129.03, 129.00, 128.75, 119.81, 119.36, 90.71 (d, $^{1}J_{C\text{-}F}$ = 54.0Hz), 88.88 (d, $^{1}J_{C\text{-}F}$ = 54.0Hz), 38.30 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.35 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.03, 32.56.

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.21--189.46 (m, 1F), -190.10--190.36 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}FNOClNa^+$: 324.0561; found: 324.0564.



3ai

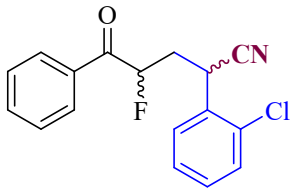
2-(4-(chloromethyl)phenyl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), white solid, mp = 49-52° C, 54.9 mg, 87% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0Hz, 2H), 7.80 (d, *J* = 8.0Hz, 2H), 7.65-7.36 (m, 14H), 7.52-7.29 (m, 12H), 6.00-5.84 (m, 1H), 5.45-5.30 (m, 1H), 4.61 (s, 2H), 4.57 (s, 2H), 4.24-4.08 (m, 2H), 2.71-2.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.61 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 193.29 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 137.36, 137.08, 133.51, 133.35, 133.27, 133.07, 132.70, 132.67, 128.69, 128.56, 127.98, 127.96, 127.92, 127.89, 127.86, 127.20, 126.66, 118.83, 118.37, 89.72 (d, $^{1}J_{C\text{-}F}$ = 52.0Hz), 87.88 (d, $^{1}J_{C\text{-}F}$ = 53.0Hz), 44.34, 37.26 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 36.37 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 32.20 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 31.75 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.60 (s, 1F), -190.41 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{15}ClFNONa^+$: 338.0718; found: 338.0721.



3aj

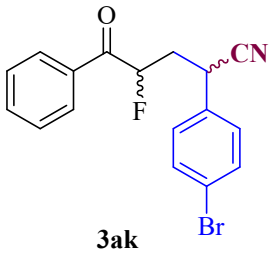
2-(2-chlorophenyl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 48.3 mg, 80% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0Hz, 2H), 7.89 (d, *J* = 8.0Hz, 2H), 7.65-7.29 (m, 14H), 5.99-5.83 (m, 1H), 5.62-5.47 (m, 1H), 4.70-4.58 (m, 2H), 2.74-2.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.70 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 194.36 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 134.40, 134.33, 133.85, 133.77, 133.21, 132.76, 132.14, 130.50, 130.41, 130.34, 130.21, 129.54, 129.14, 129.11, 129.07,129.04, 128.93, 128.07, 127.98, 119.32, 119.10, 91.28 (d, $^{1}J_{C\text{-}F}$ = 9.0Hz), 89.44 (d, $^{1}J_{C\text{-}F}$ = 8.0Hz), 36.38 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 36.05 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 31.28 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 30.93 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -187.16--187.42 (m, 1F), -190.52--190.78 (m, 1F)..

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}ClFNONa^+$: 324.0561; found: 324.0564.



3ak

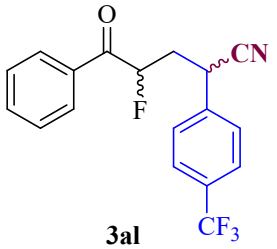
2-(4-bromophenyl)-4-fluoro-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 57.5 mg, 83% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0Hz, 2H), 7.86 (d, *J* = 8.0Hz, 2H), 7.70-7.28 (m, 14H), 6.02-5.87 (m, 1H), 5.47-5.32 (m, 1H), 4.23-4.09 (m, 2H), 2.74-2.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.64 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.30 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 134.55, 134.47, 133.71, 133.65, 133.41, 132.94, 132.82, 132.65, 129.56, 129.11, 129.08, 129.03, 129.00, 123.18, 122.85, 119.70, 119.25, 90.69 (d, $^{1}J_{C\text{-}F}$ = 52.0Hz), 88.86 (d, $^{1}J_{C\text{-}F}$ = 53.0Hz), 38.28 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.30 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.13, 32.65.

^{19}F NMR (376 MHz, $CDCl_3$): δ -189.14--189.39 (m, 1F), -190.10--190.36 (m, 1F)..

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{13}BrFNONa^+$: 368.0056; found: 368.0055.



3al

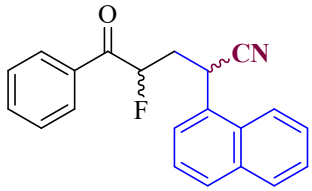
4-fluoro-5-oxo-5-phenyl-2-(4-(trifluoromethyl)phenyl)pentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 52.3 mg, 78% yield**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0Hz, 2H), 7.84 (d, *J* = 8.0Hz, 2H), 7.73-7.45 (m, 14H), 6.01-5.86 (m, 1H), 5.45-5.32 (m, 1H), 4.31-4.17 (m, 2H), 2.76-2.52 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.58 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.20 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 138.38, 138.02, 134.59, 134.52, 133.71, 133.64, 131.26, 129.12, 129.08, 129.04, 129.00, 128.39, 127.89, 126.65, 126.62, 126.53, 126.49, 125.10, 122.39, 119.44, 119.01, 90.69 (d, $^{1}J_{C\text{-}F}$ = 42.0Hz), 88.85 (d, $^{1}J_{C\text{-}F}$ = 43.0Hz), 38.23 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.22 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.42 , 32.98.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.43--63.28 (m, 6F), -188.62--188.87 (m, 1F), -190.15--190.41 (m, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{13}F_4NONa^+$: 358.0825; found: 358.0824.



3am

4-fluoro-2-(naphthalen-1-yl)-5-oxo-5-phenylpentanenitrile, purified by flash column chromatography on silica gel (PE/EA = 50/1), light yellow oily liquid, 38.1 mg, 60% yield**.**

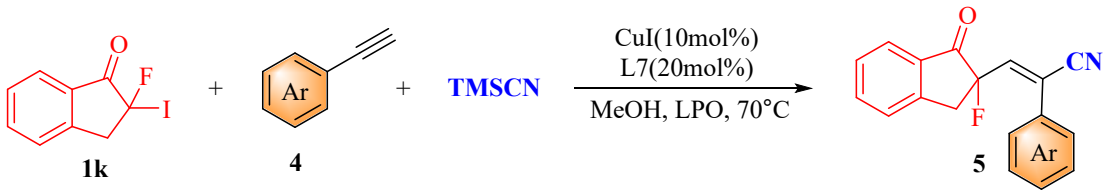
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.80 (m, 12H), 7.68-7.43 (m, 12H), 6.07-5.92 (m, 1H), 5.50-5.35 (m, 1H), 4.44-4.28 (m, 2H), 2.79-2.54 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.77 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 194.49 (d, $^{2}J_{C\text{-}F}$ = 19.0Hz), 134.41, 134.40, 133.78, 133.40, 133.37, 133.23, 133.04, 131.60, 131.08, 129.79, 129.55, 129.05, 129.02, 128.98, 128.90, 128.03, 127.96, 127.93, 127.84, 127.50, 127.14, 127.06, 127.02, 126.89, 126.57, 124.75, 124.54, 120.20, 119.74, 90.86 (d, $^{1}J_{C\text{-}F}$ = 60.0Hz), 89.03 (d, $^{1}J_{C\text{-}F}$ = 60.0Hz), 38.40 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 37.51 (d, $^{2'}J_{C\text{-}F}$ = 21.0Hz), 33.75 (d, $^{3'}J_{C\text{-}F}$ = 3.0Hz), 33.30 (d, $^{3'}J_{C\text{-}F}$ = 4.0Hz).

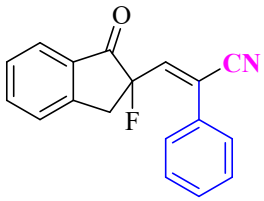
^{19}F NMR (376 MHz, $CDCl_3$): δ -189.91--190.48 (m, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{16}FNONa^+$: 340.1108; found: 340.1112.

4.3 General procedure for the synthesis of 5a-5d



An oven-dried tube was charged with CuI (0.03 mmol, 10 mol %), Ligand **7** (0.06 mmol, 20 mol %), and LPO (0.75 mmol, 2.5 equiv). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, α-iodo-α- fluoroacetophenone **1k** (0.3 mmol, 1.0 equiv) dissolved in methanol (2.0 mL), styrene **4a** (0.45mmol, 1.5 equiv), and TMSCN (0.6 mmol, 2.0 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at 70 °C for 5 h. After the reaction was completed, solvent was removed under reduced pressure by rotary evaporator, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **5a-5d**.



5a

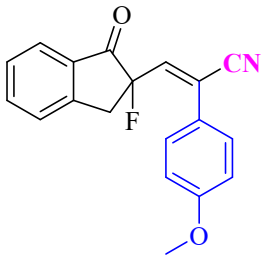
(E)-3-(2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2-phenylacrylonitrile, purifiedby flash column chromatography on silica gel (PE/EA = 30/1), light yellow oily liquid, 58.2 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73(d, *J* = 8.0Hz, 1H), 7.64(t, *J* = 4.0Hz, 1H), 7.43-7.25 (m, 7H), 6.69(d, *J* = 20.0Hz, 1H), 3.38(d, *J* = 16.0Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.82 (d, $^2J_{C\text{-}F}$ = 18.0Hz), 149.49, 149.46, 141.90, 141.64, 136.91, 133.14, 131.39, 129.90, 128.83, 128.80, 128.76, 128.46, 126.65, 125.62, 120.35, 120.27, 118.41, 96.05 (d, $^1J_{C\text{-}F}$ = 187.0Hz), 40.11 (d, $^{2'}J_{C\text{-}F}$ = 25.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -147.50 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{12}FNONa^+$: 300.0795; found: 300.0798.



5b

(E)-3-(2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2-(4-methoxyphenyl)acrylonitrile, purifiedby flash column chromatography on silica gel (PE/EA = 30/1), light yellow oily liquid, 59.9 mg, 65% yield.

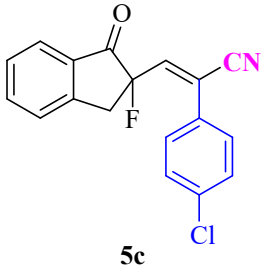
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75(d, *J* = 10.0Hz, 1H), 7.64(t, *J* = 10.0Hz, 1H), 7.43-

7.33 (m, 4H), 6.79(d, *J* = 10.0Hz, 2H), 6.61(d, *J* = 20.0Hz, 1H), 3.78(s, 3H), 3.41-7.36 (m, *2*H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.13 (d, $^{2}J_{C\text{-}F}$ = 20.0Hz), 160.85, 149.63, 140.22, 140.02, 136.91, 133.17, 130.46, 130.43, 128.73, 126.70, 125.62, 123.61, 120.49, 120.44, 118.68, 113.87, 95.86 (d, $^{1}J_{C\text{-}F}$ = 186.25Hz), 55.36, 40.05(d, $^{2'}J_{C\text{-}F}$ = 23.75Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -146.49 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{19}H_{14}FNO_2Na^+$: 330.0900; found: 330.0901.



5c

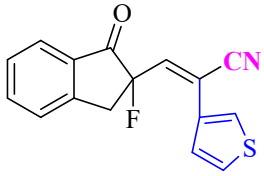
(E)-2-(4-chlorophenyl)-3-(2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)acrylonitrile, purifiedby flash column chromatography on silica gel (PE/EA = 30/1), light yellow oily liquid, 66.4mg, 71% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77(d, *J* = 5.0Hz, 1H), 7.70(t, *J* = 5.0Hz, 1H), 7.48-7.28 (m, 6H), 6.61(d, *J* = 20.0Hz, 1H), 3.47-3.43 (m, *2*H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.54 (d, $^{2}J_{C\text{-}F}$ = 17.5Hz), 149.29, 149.26, 142.00, 141.81, 137.20, 136.11, 133.06, 130.35, 130.32, 129.77, 128.97, 128.64, 126.79, 125.73, 119.00, 118.95, 118.20, 96.18 (d, $^{1}J_{C\text{-}F}$ = 191.25Hz), 40.26(d, $^{2'}J_{C\text{-}F}$ = 23.75Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -151.12 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{11}ClFNONa^+$: 334.0405; found: 334.0407.



5d

(E)-3-(2-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-2-(thiophen-3-yl)acrylonitrile, purifiedby flash column chromatography on silica gel (PE/EA = 30/1), light yellow oily liquid, 63.5 mg, 75% yield.

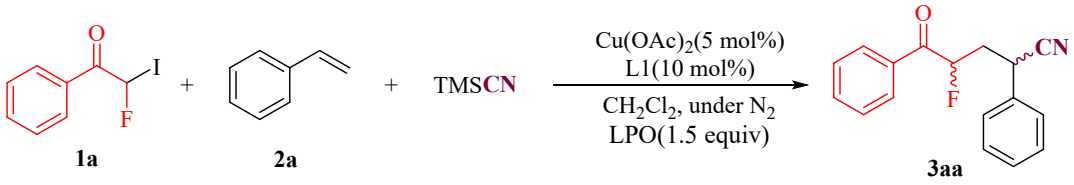
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79(d, *J* = 5.0Hz, 1H), 7.68(t, *J* = 5.0Hz, 1H), 7.61(s, 1H), 7.47-7.28 (m, 4H), 6.53(d, *J* = 20.0Hz, 1H), 3.54-7.41 (m, *2*H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.92 (d, $^{2}J_{C\text{-}F}$ = 18.75Hz), 149.43, 149.40, 140.05, 139.86, 137.10, 133.12, 131.33, 128.93, 128.05, 128.01, 126.81, 126.42, 125.72, 118.30, 115.61, 115.56, 96.15 (d, $^{1}J_{C\text{-}F}$ = 190.0Hz), 40.19(d, $^{2'}J_{C\text{-}F}$ = 25.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -150.18 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{16}H_{10}FNOSNa^+$: 306.0359; found: 306.0366.

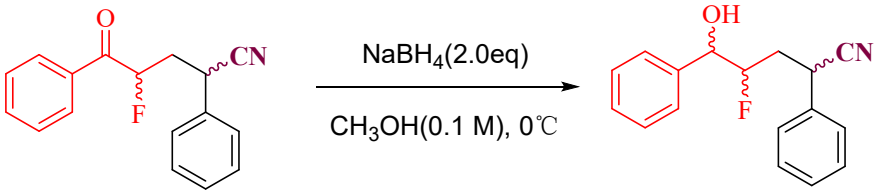
5. Gram scale synthesis and synthetic application



1a **2a** **3aa**

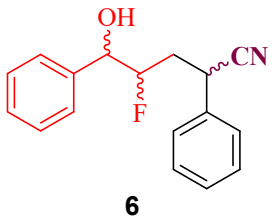
1.58g **0.75g** **0.89g** **1.25g, 78%, 1.1:1 dr**

An oven-dried tube was charged with Copper(II) acetate(0.3 mmol, 5 mol %), Ligand 1 (0.6 mmol, 10 mol %), and LPO (9.0 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, α-iodo-α-fluoroacetophenone **1** (6 mmol, 1.0 equiv) dissolved in dichloromethane (10.0 mL), styrene **2a** (7.2 mmol, 1.2 equiv), and TMSCN (9.0 mmol, 1.5 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at room temperature for 8 h. After the reaction was completed, solvent was removed under reduced pressure by rotary evaporator, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 50:1) to afford the desired product **3aa**, 1.25g, in 78% yield with 1.1:1 dr.



3aa **6**, 60%

To a solution of **3aa** (0.4 mmol, 1.0 equiv) in CH_3OH was added portionwise $NaBH_4$ (0.8 mmol, 2.0 equiv). The reaction was stirred at 0°C for 20 min. After completion of the reaction (as indicated by TLC), the solution poured into a saturated aqueous sodium hydrogencarbonate solution (5 mL), then extracted with ethyl acetate (3*5 mL), the combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 50:1-5:1) to afford desired the product **6**.



6

4-fluoro-5-hydroxy-2,5-diphenylpentanenitrile, purifiedby flash column chromatography on silica gel (PE/EA = 10/1), light white oily liquid, 64.6 mg, 60% yield.

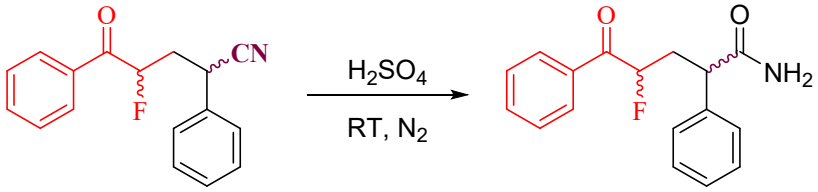
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.24 (m, 20H), 5.03-4.86(m, 2H), 4.76-4.69(m, 1H), 4.47-4.31(m, 1H), 4.08-4.05(m, 1H), 3.90-3.87(m, 1H), 2.48-2.37(m, 1H), 2.77 (br, 2H), 2.52-1.84 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.29, 135.10(d, J = 21.0Hz), 134.13(d, J = 22.0Hz),

129.37, 129.33, 129.28, 128.91, 128.87, 128.79, 128.70, 128.64, 128.57, 128.43, 128.35, 127.76, 127.22, 127.20, 126.97, 126.91, 126.34, 126.30, 120.84(d, J = 17.0Hz), 119.90(d, J = 15.0Hz), 94.40(d, J = 21.0Hz), 93.42, 93.00(d, J = 21.0Hz), 91.84(d, J = 34.0Hz), 75.78, 75.65, 75.62, 75.49, 74.43(d, J = 17.0Hz), 37.69(d, J = 17.0Hz), 36.53(d, J = 17.0Hz), 33.59, 32.99.

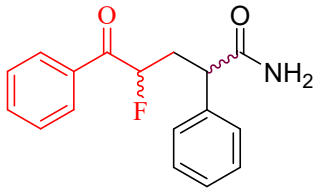
^{19}F NMR (376 MHz, $CDCl_3$): δ -189.37 (s, 1F), -190.72 (s, 1F), -192.15 (d, J = 15.04Hz, 2F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}FNONa^+$: 292.1108; found: 292.1112.



3aa **7**, 80%

In a flame-dried schlenk tube equipped with a magnetic bar, **3aa** (0.4 mmol) was dissolved in H_2SO_4 (1 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3 h. After the reaction was completed, water was added drops wise to reaction mixture in order to quench the reaction. The resulting solution was extracted with EtOAc (3×5 ml), washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate =5:1) to afford product **7**.[2]



7

4-fluoro-5-oxo-2,5-diphenylpentanamide, purifiedby flash column chromatography on silica gel (PE/EA = 5/1), solid white, mp = 60-62°C, 91.3 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (d, J = 8.0Hz, 2H), 7.74-7.21(m, 18H), 6.00-5.88(m, 2H), 5.74-5.60(m, 2H), 5.36-5.23(m, 2H), 3.91-3.79(m, 2H), 2.91-2.40(m, 4H).

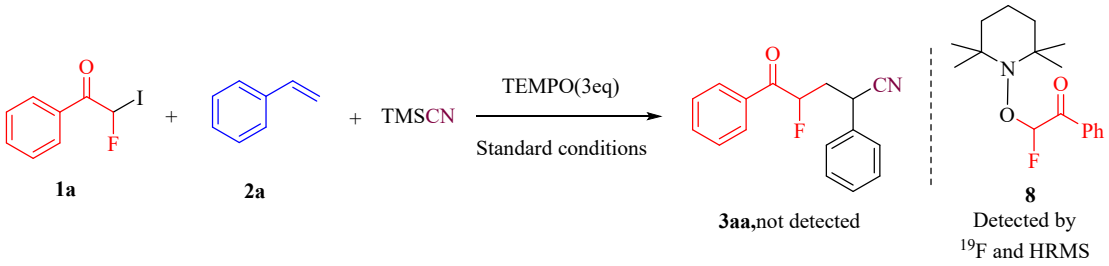
^{13}C NMR (100 MHz, $CDCl_3$): δ 196.14 (d, $^2J_{C\text{-}F}$ = 14.0Hz), 195.64 (d, $^2J_{C\text{-}F}$ = 13.0Hz), 174.80, 171.24, 139.15, 137.87, 134.05, 133.92, 133.86, 133.61, 129.35, 129.12, 128.89, 128.75, 128.72, 128.69, 128.63, 128.43, 128.21, 127.77, 127.66, 126.66, 126.10, 91.85 (d, $^1J_{C\text{-}F}$ = 55.0Hz), 90.40 (d, $^1J_{C\text{-}F}$ = 58.0Hz), 47.77, 47.41, 36.92 (d, $^{2'}J_{C\text{-}F}$ = 16.0Hz), 35.80 (d, $^{2'}J_{C\text{-}F}$ = 16.0Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -192.92 (s, 1F), -195.03 (s, 1F).

HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}FNO_2Na^+$: 308.1057; found: 308.1060.

6. Mechanism investigation

6.1 Trapping experiment with TEMPO free radical

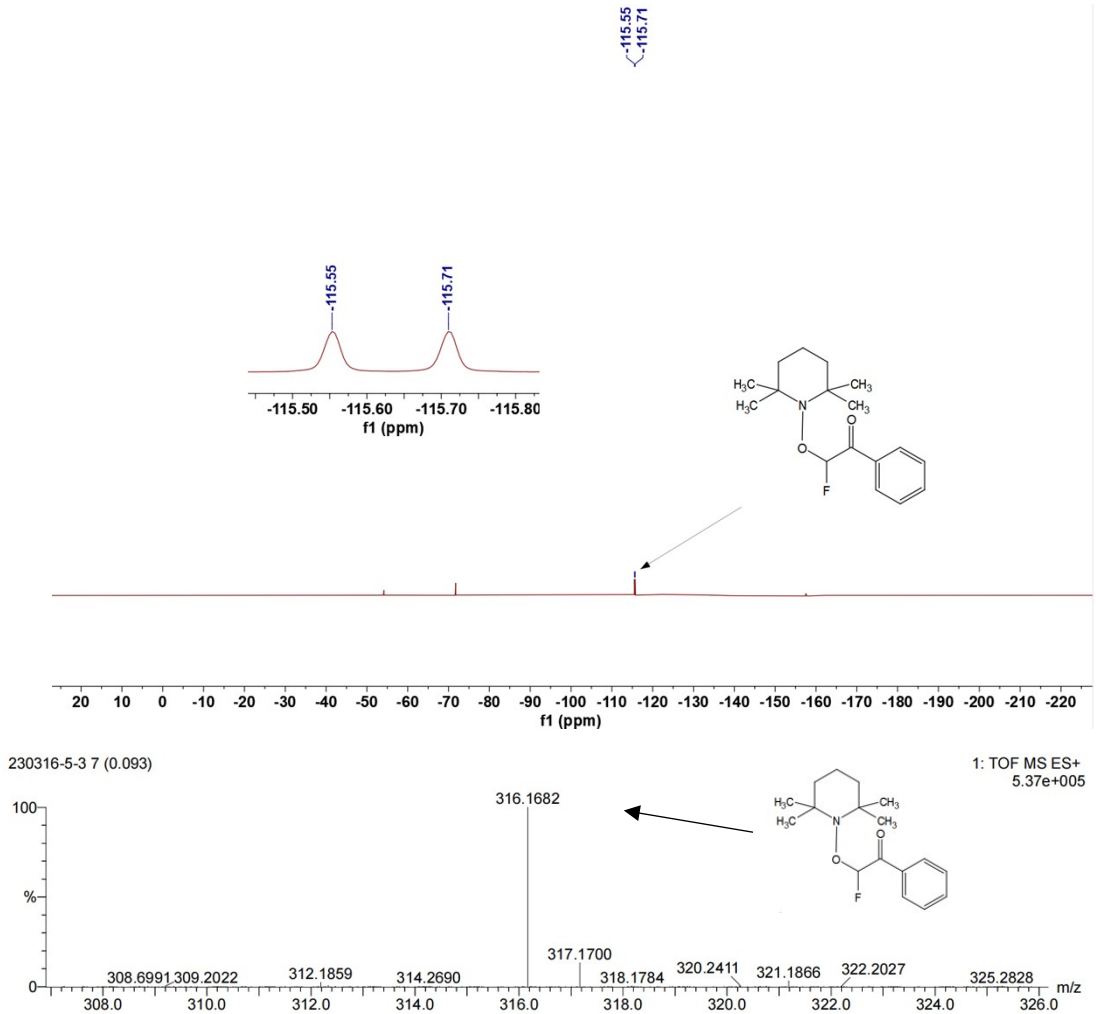


1a **2a** **3aa,**not detected **8** Detected by ^{19}F and HRMS

Three control experiments were designed to rationalized the reaction pathway. First, the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the three-component reaction under standard conditions. No desired product **3aa** was obtained; instead, compound **8** was detected by ^{19}F NMR ((376 MHz, $CDCl_3$):δ -115.63 (d, J = 60.16 Hz), for compound **8**). The result indicates that a monofluoroalkyl radical addition pathway might be involved in this process.[3]

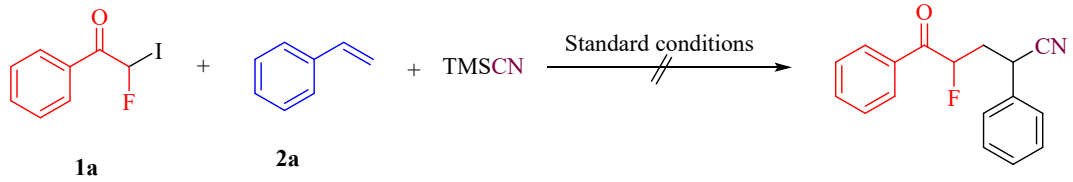
HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{24}FNO_2Na^+$: 316.1689; found: 316.1682.

Scheme 1 Trapping experiment in the standard reaction.(^{19}F NMR and HRMS)



6.2 Control experiment

Another control reaction was carried no desired product 3aa was detected in the absence of LPO.



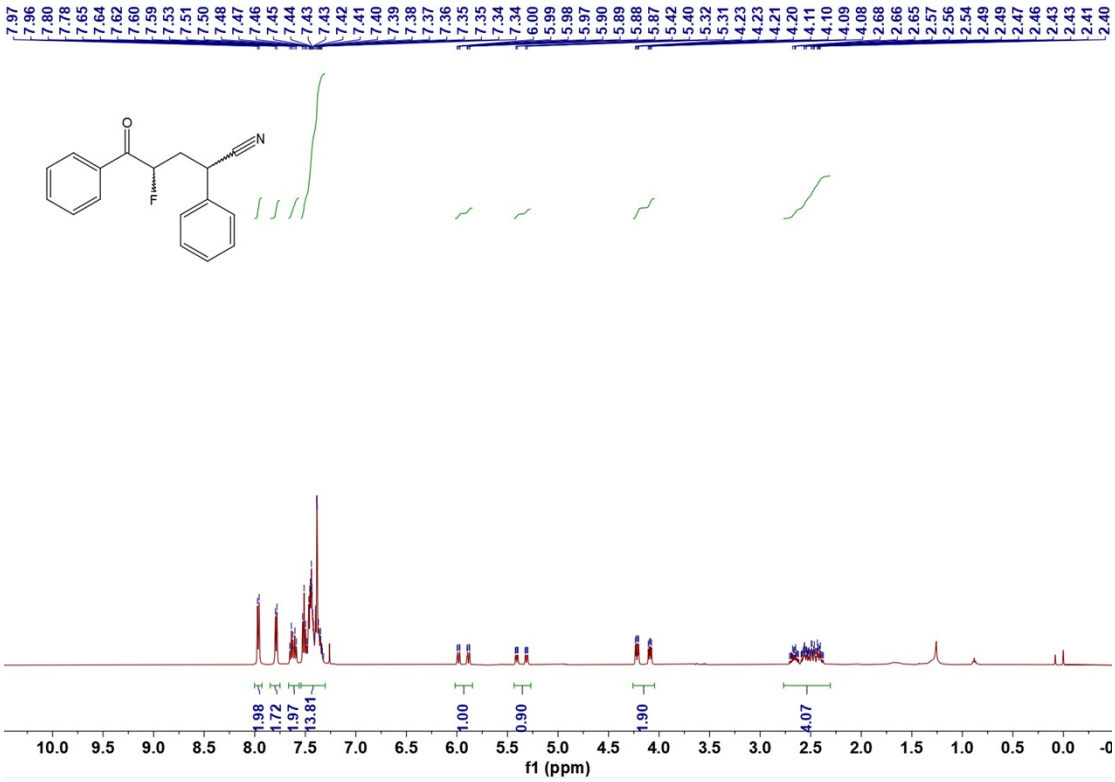
1a **2a** **3aa**,not detected

Scheme 2 The absence of LPO under the standard reaction conditions.

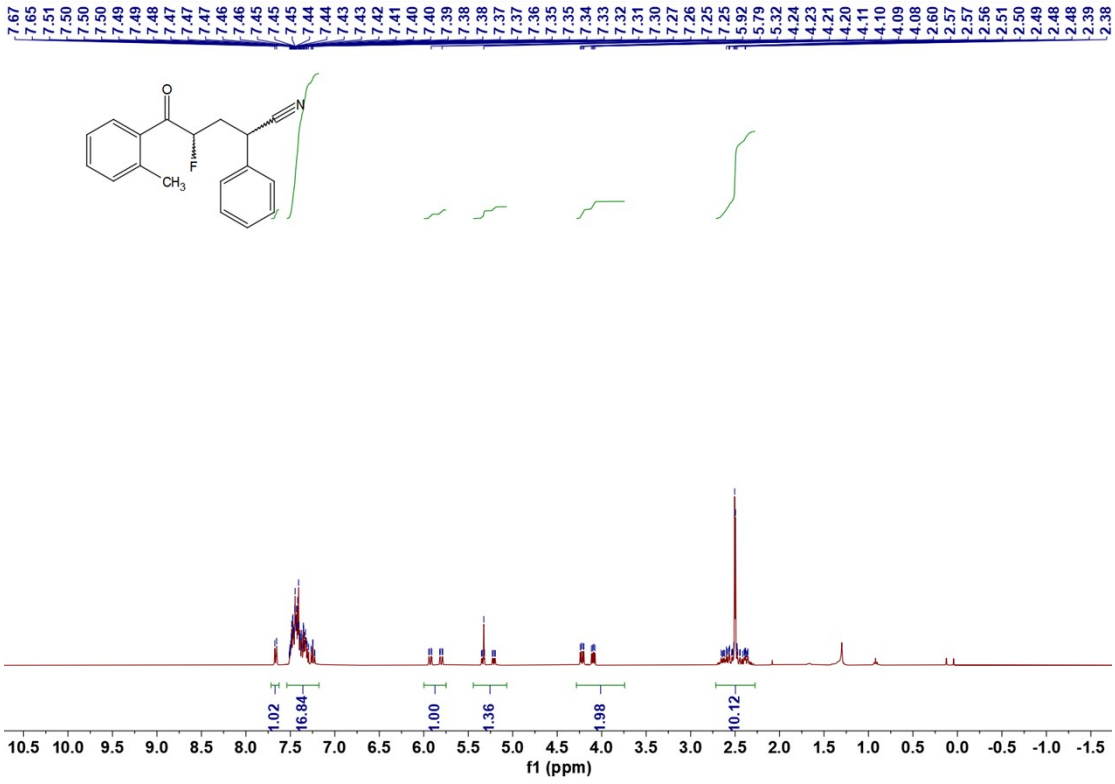
7. References

[1] (a) I. Saidalimu, X. Fang, W.-W. Lv, X.-Y. Yang, X.-P. He, Zhang, Z.-Y, F.-H. Wu. *Adv. Synth. Catal.* **2013**, 355, 857-863. (b) I. Saidalimu, X. Fang, X.-P. He, J. Liang, X.-Y. Yang, F.-H. Wu, *Angew. Chem., Int. Ed*. **2013**, 52, 5566-5570. (c) C. Zheng, X. Cui, J. Wu, P. Wu, Y. Yu, H. Liu, F. Wu, *Eur. J. Org. Chem.* **2022**, e202200952.
[2] X. Zhu, W. Deng, M.-F. Chiou, C. Ye, W. Jian, Y. Zeng, Y. Jiao, L. Ge, Y. Li, X. Zhang, H. Bao, *J. Am. Chem. Soc.* **2019**, 141, 548-559.
[3] J. Ren, X. Fu, Y. Hou, J. Wu and F. Wu, *Tetrahedron. Lett.,* **2020**, 66, 152805.

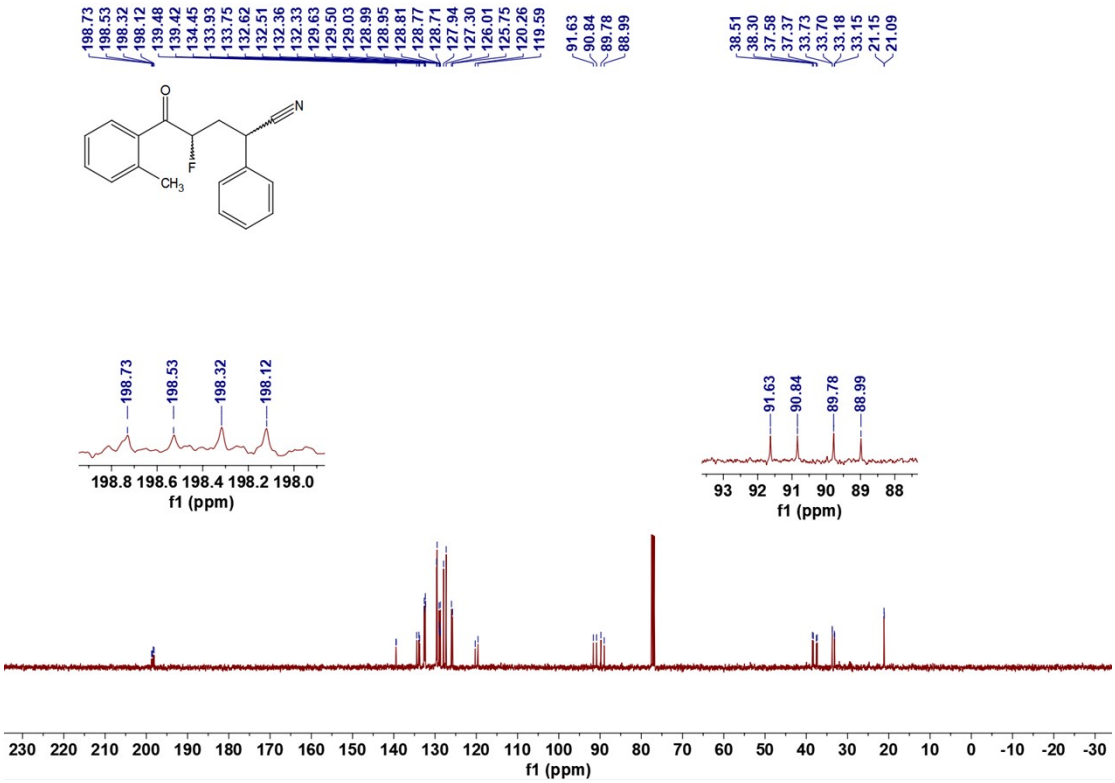
8. H NMR, 13C NMR, 19F NMR Spectra, HRMS and Noesy for 5a



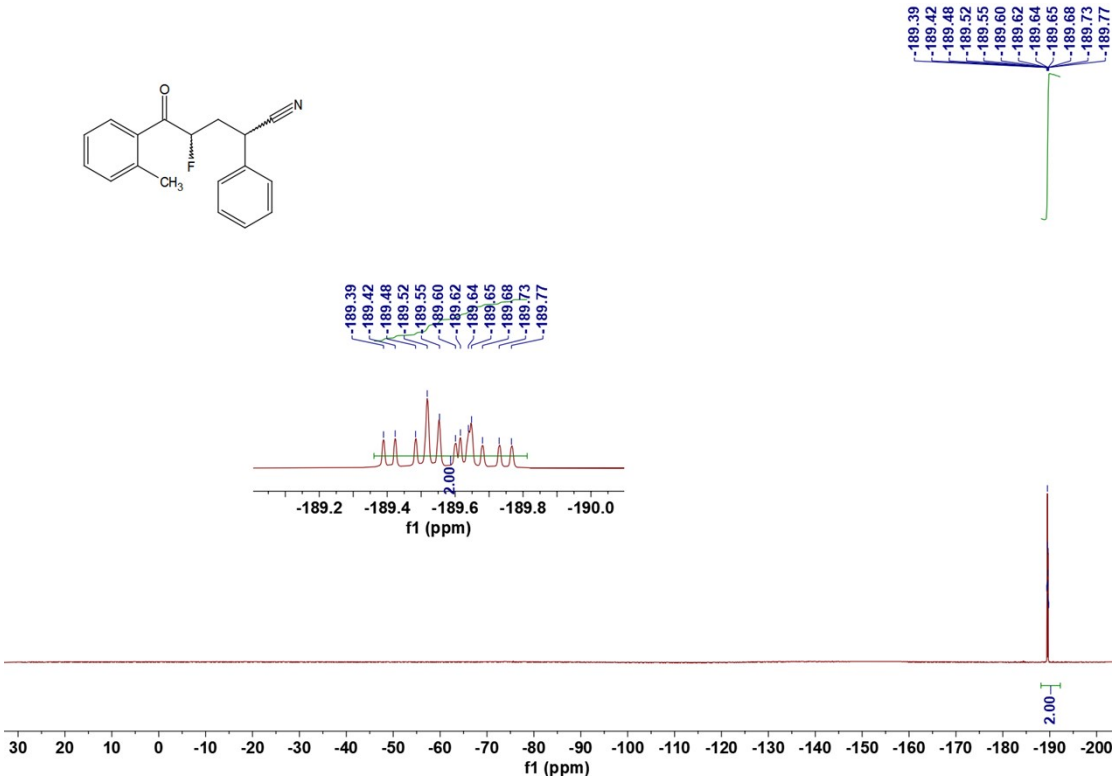
^{1}H NMR of 3aa



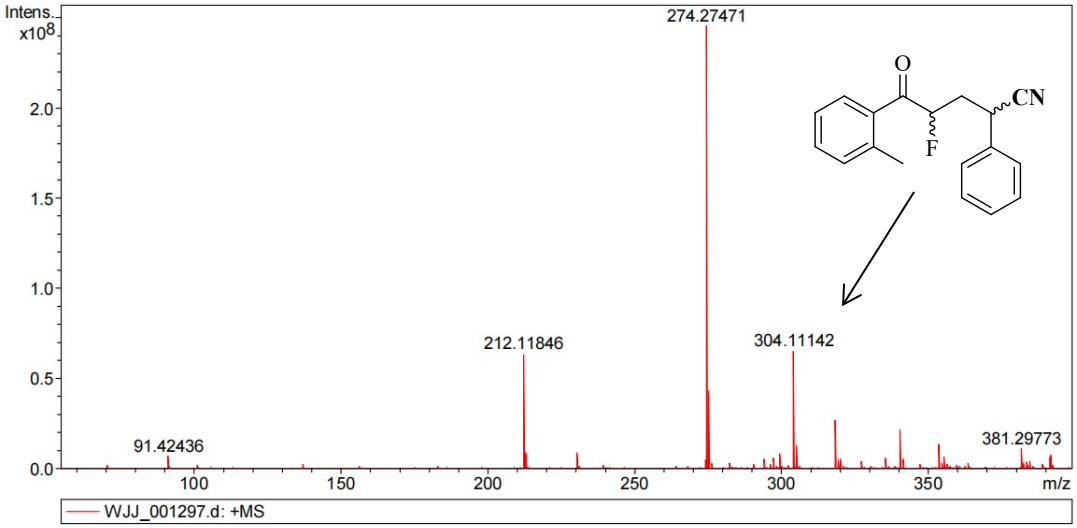
^{1}H NMR of 3ba



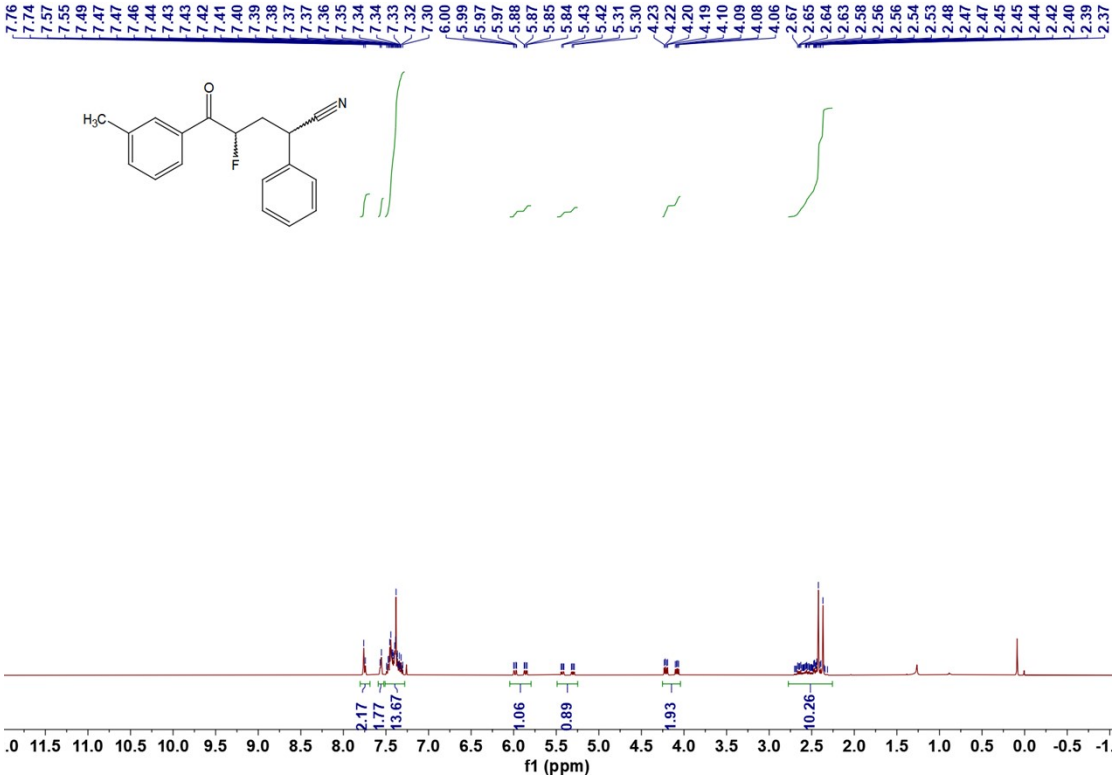
^{13}C NMR of 3ba



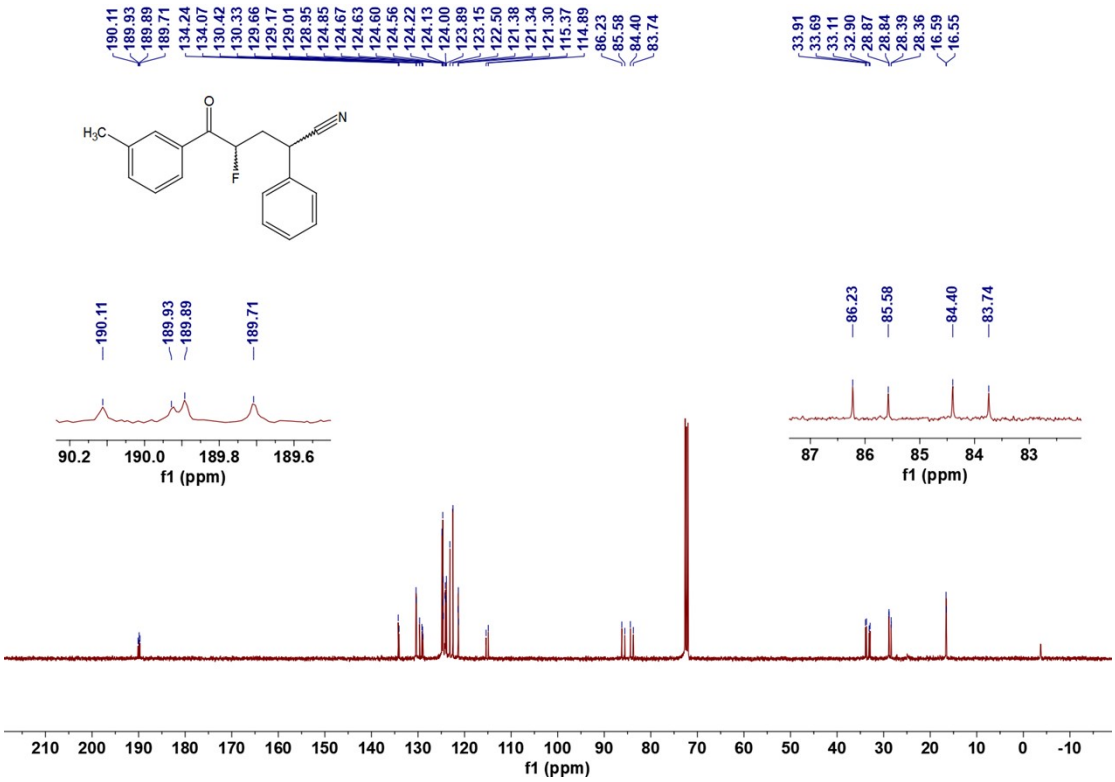
^{19}F NMR of 3ba



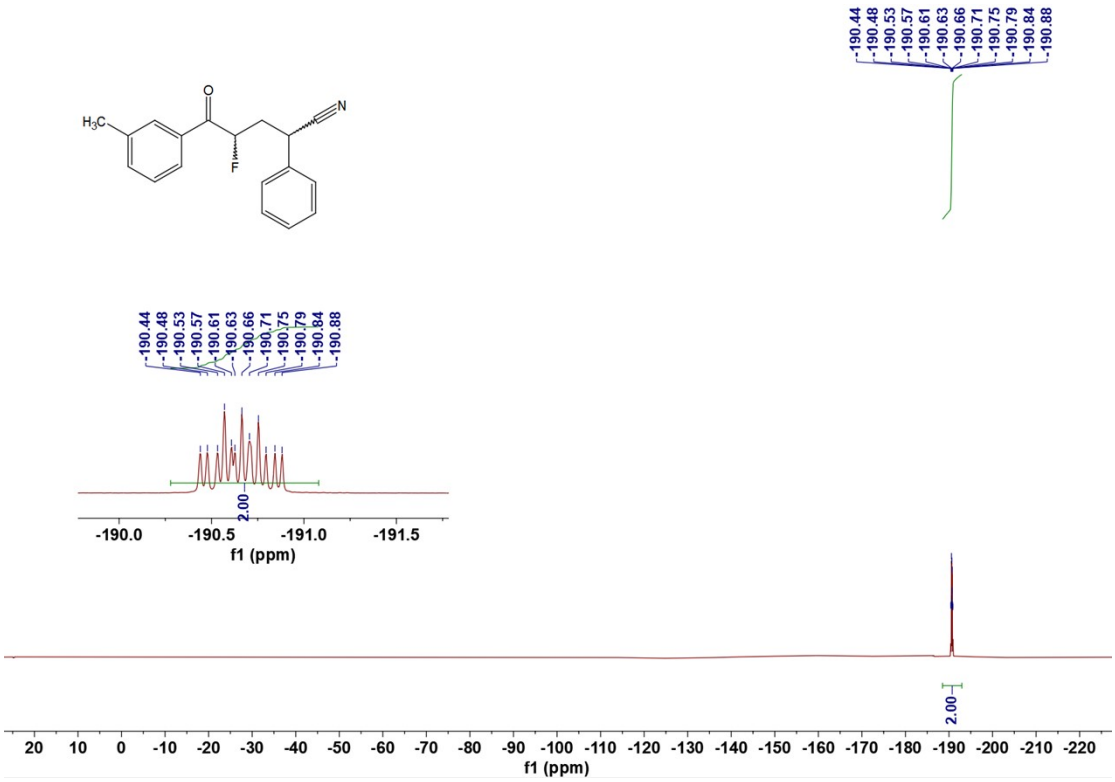
HRMS of 3ba



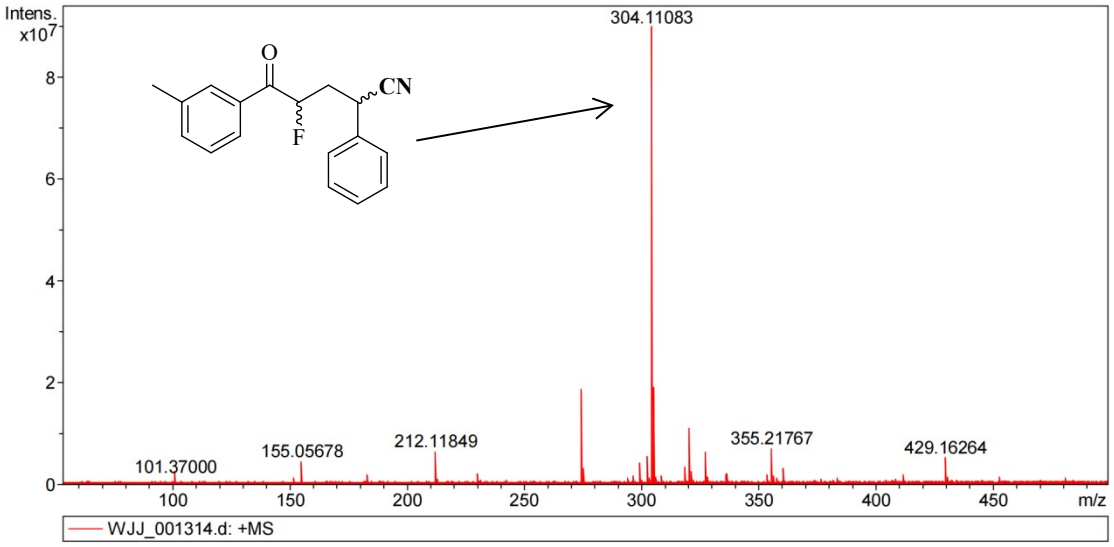
^{1}H NMR of 3ca



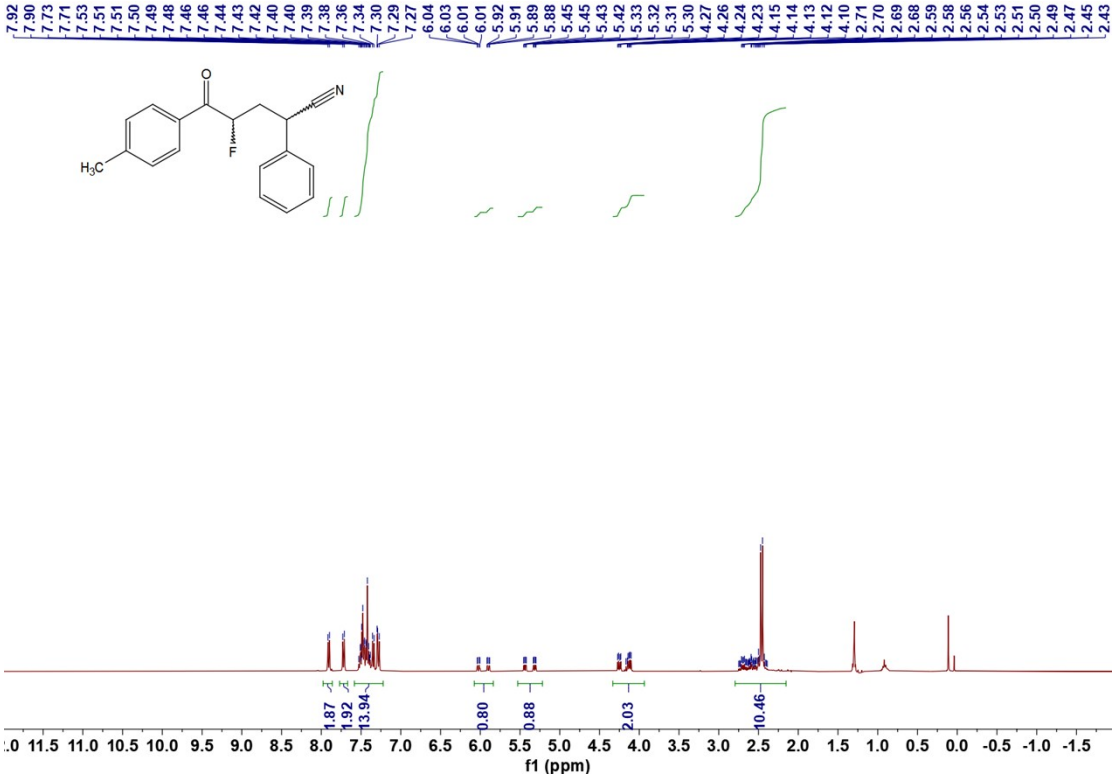
^{13}C NMR of 3ca



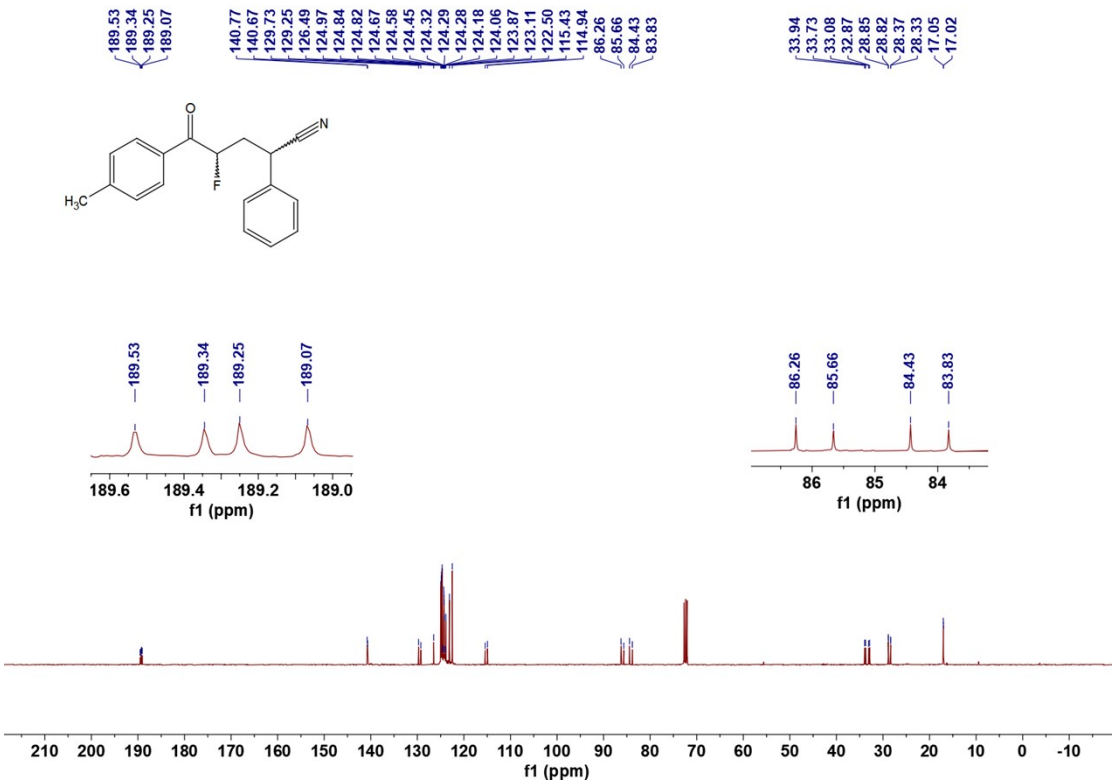
^{19}F NMR of 3ca



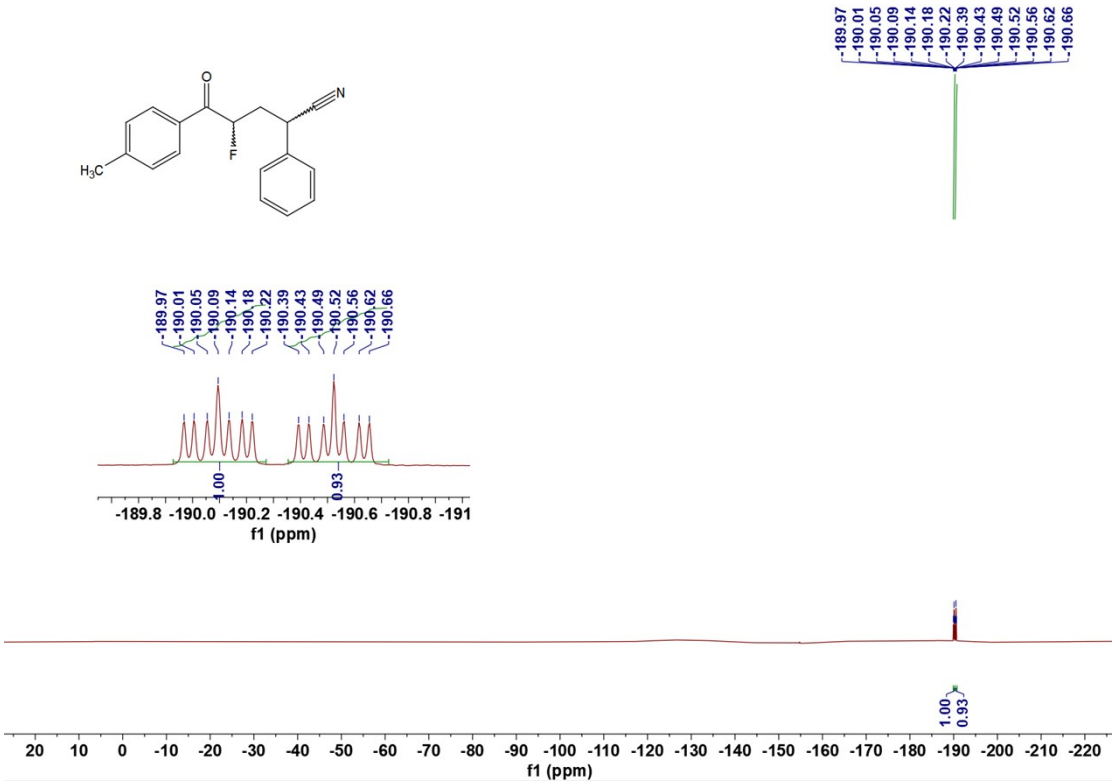
HRMS of 3ca



^{1}H NMR of 3da



^{13}C NMR of 3da



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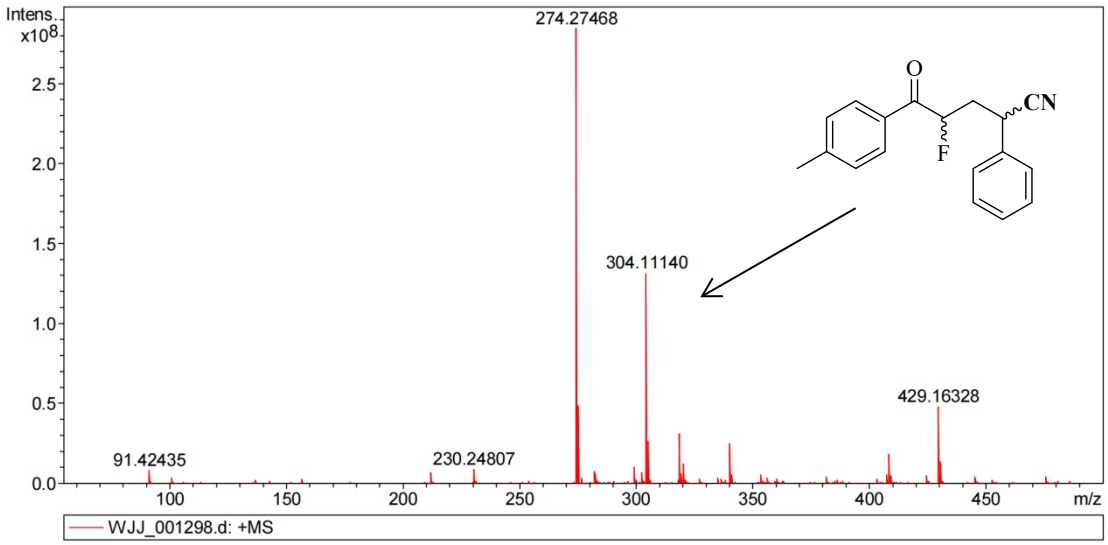
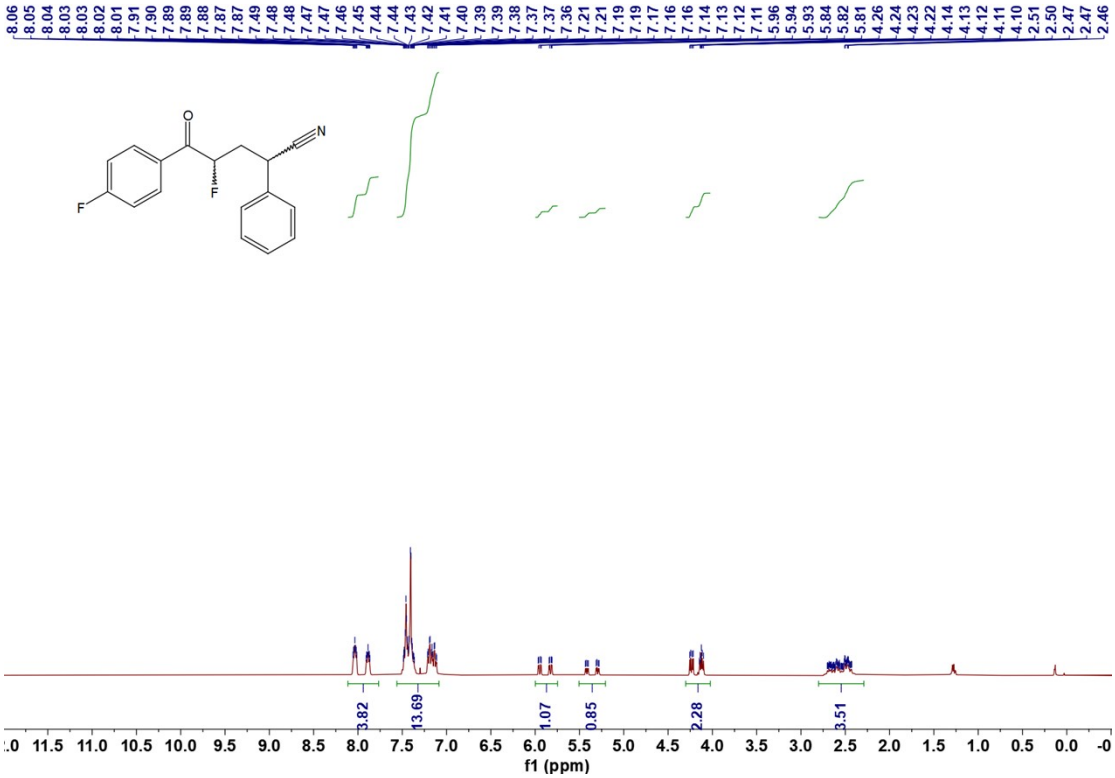
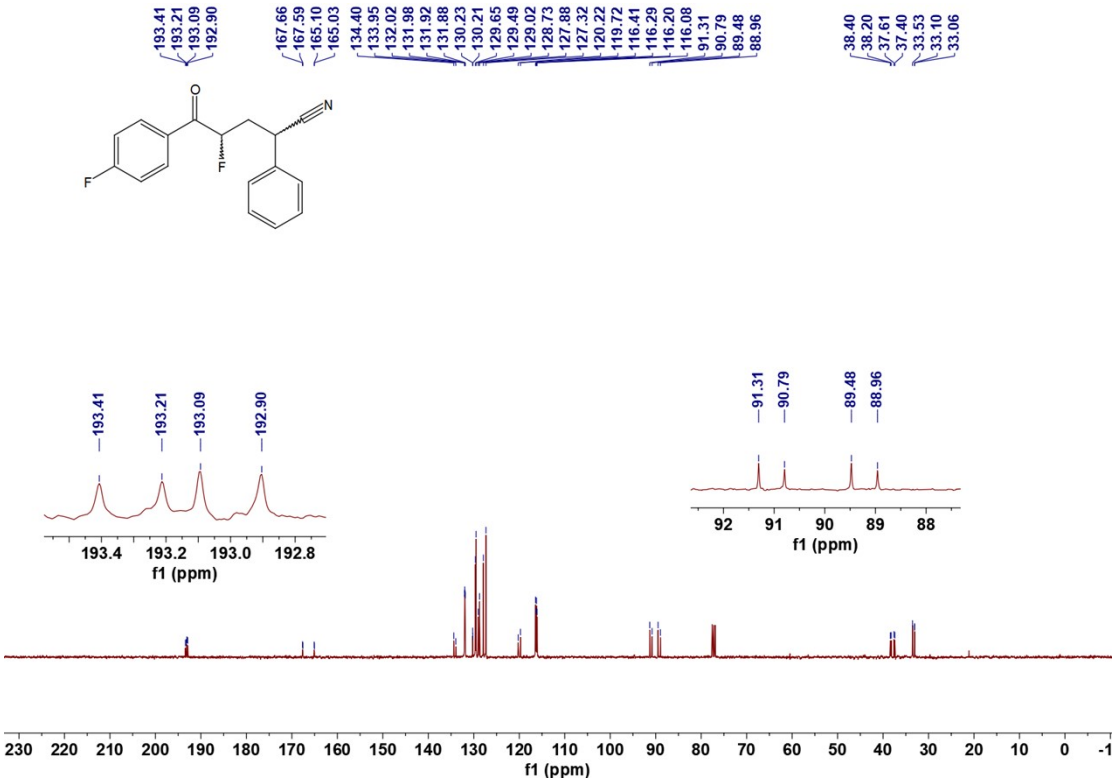


HRMS of 3da



^{1}H NMR of 3ea



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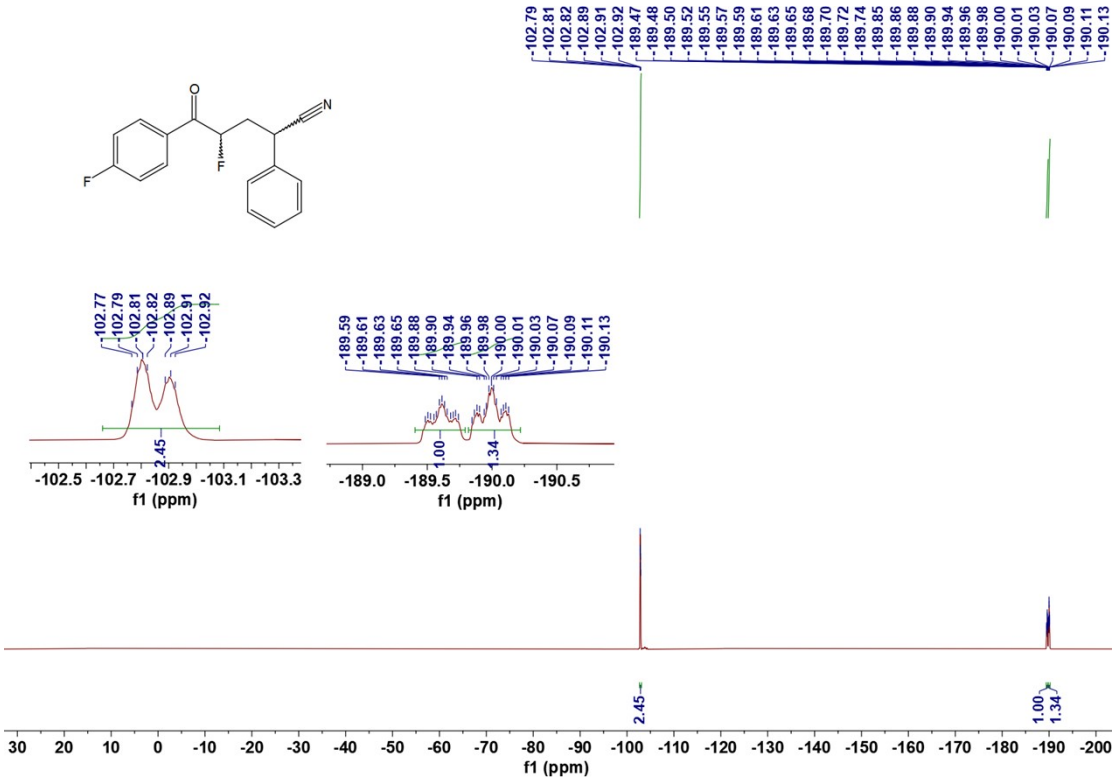
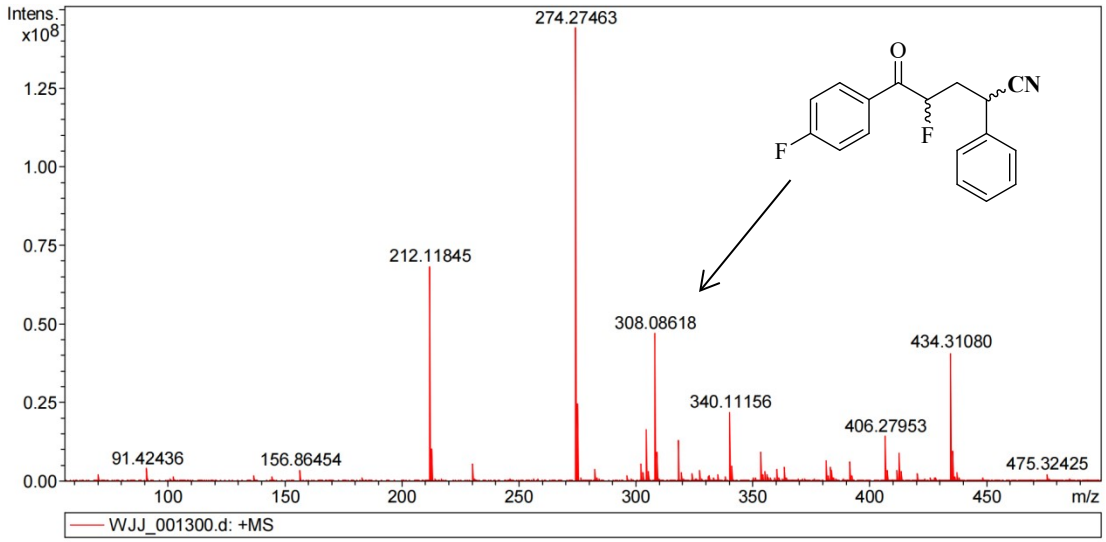
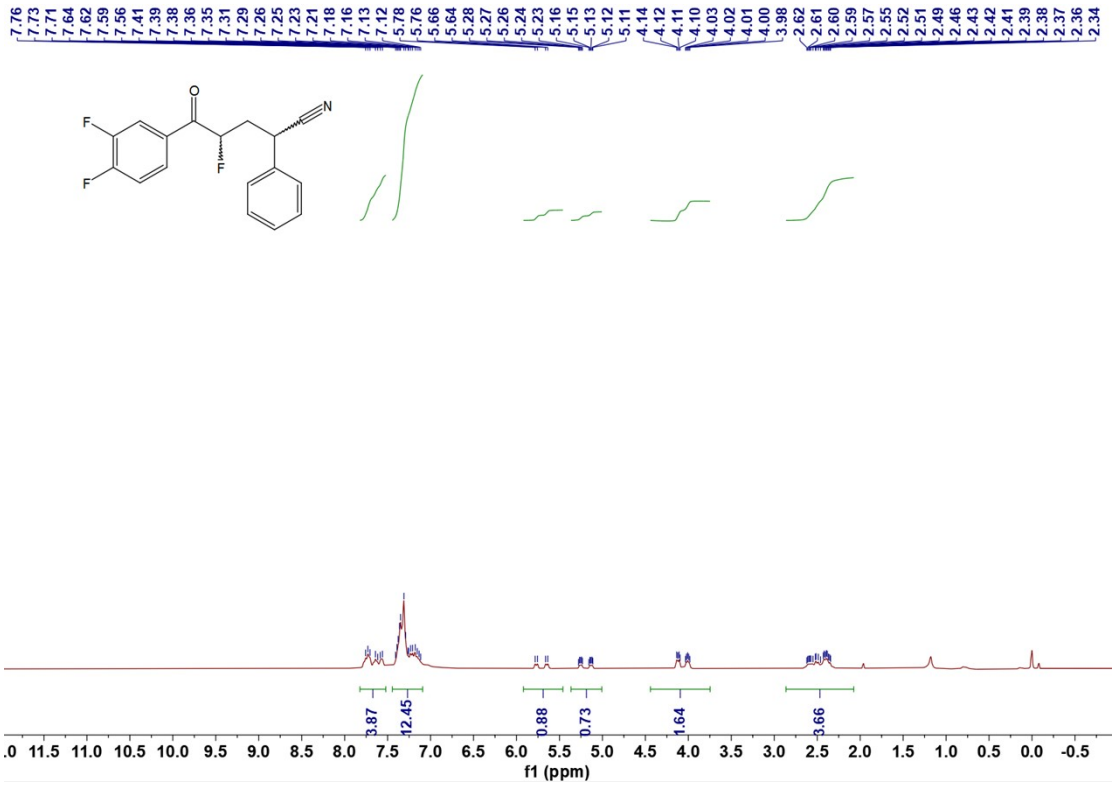


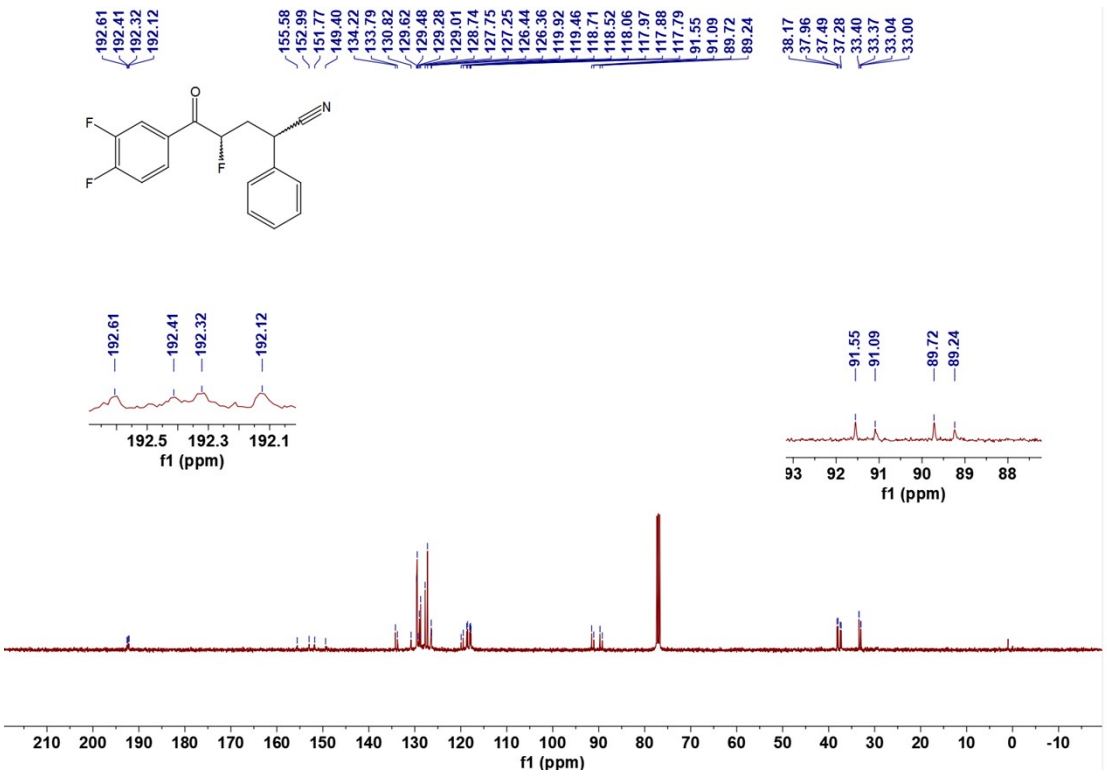
^{19}F NMR of 3ea



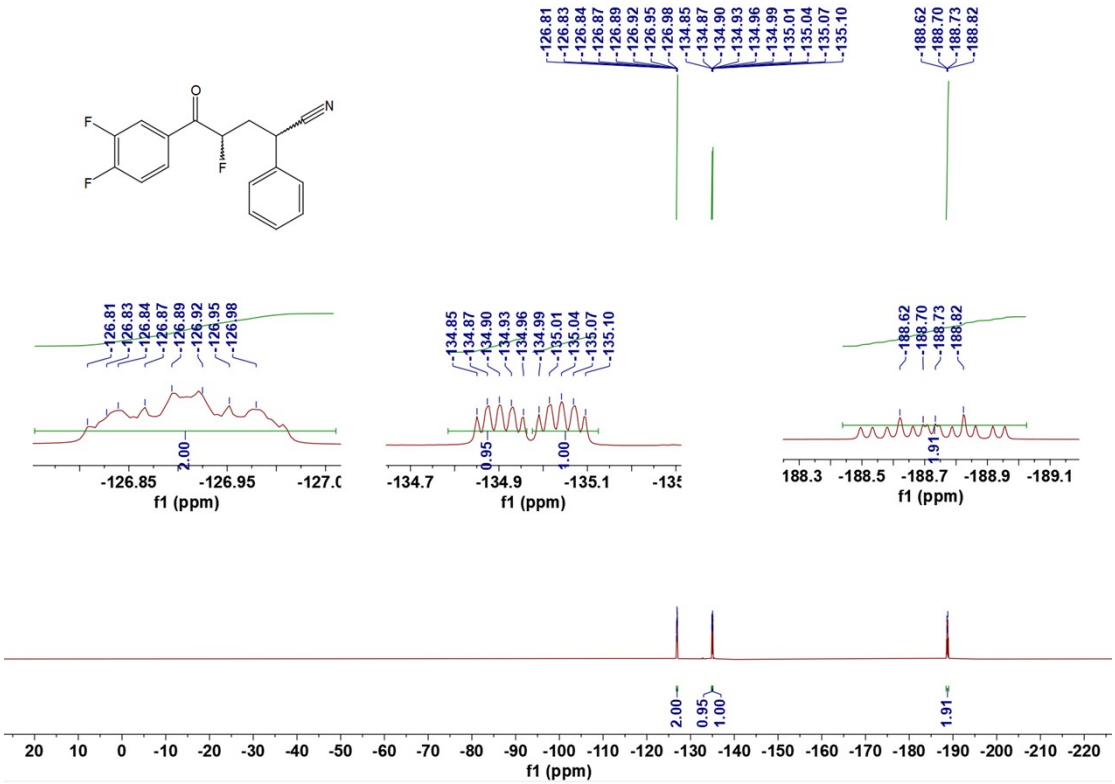
HRMS of 3ea



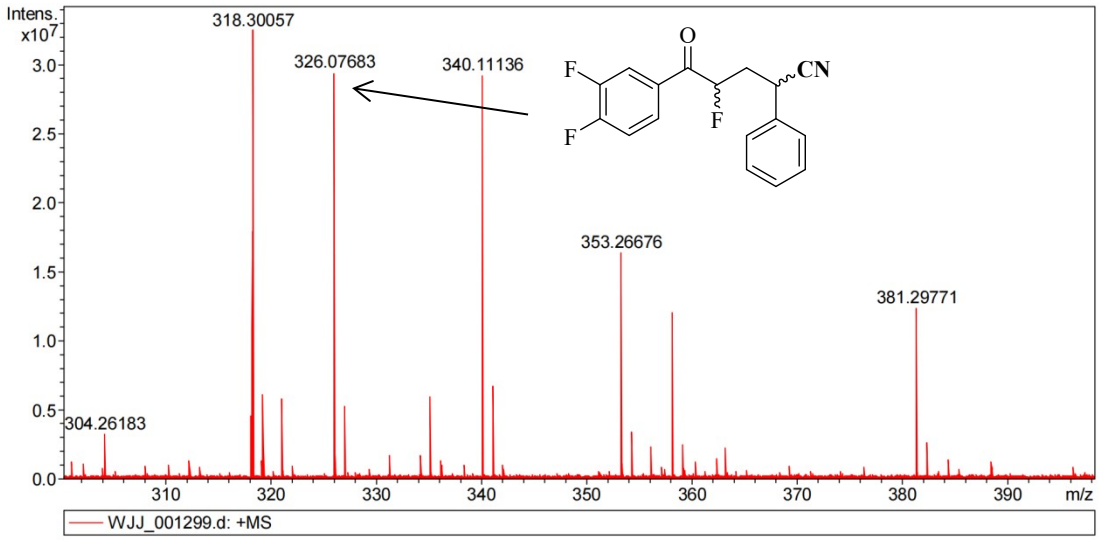
^{1}H NMR of 3fa



^{13}C NMR of 3fa



^{19}F NMR of 3fa



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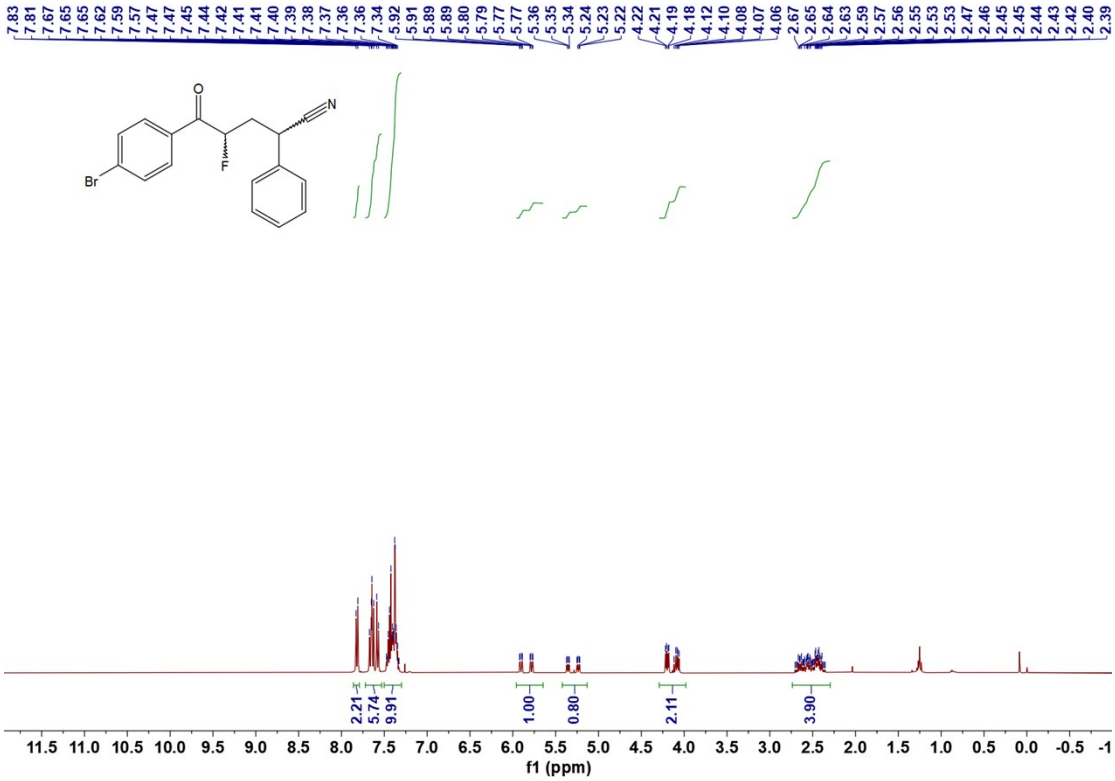
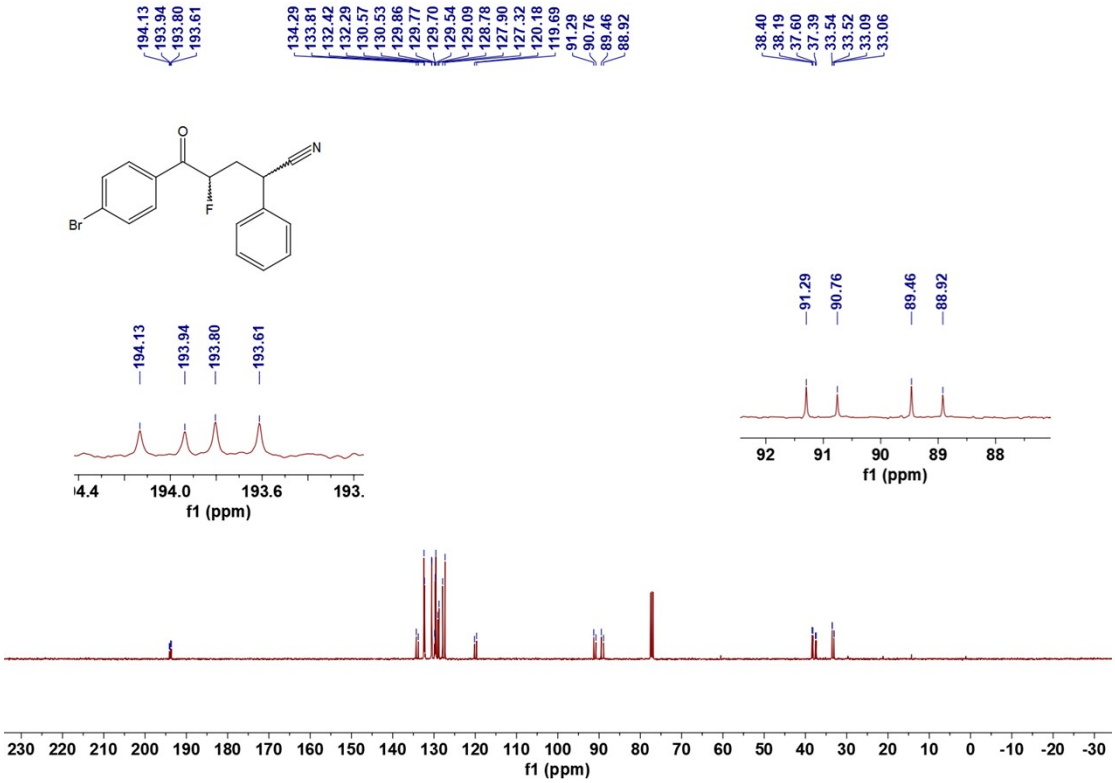


^{1}H NMR of 3ga



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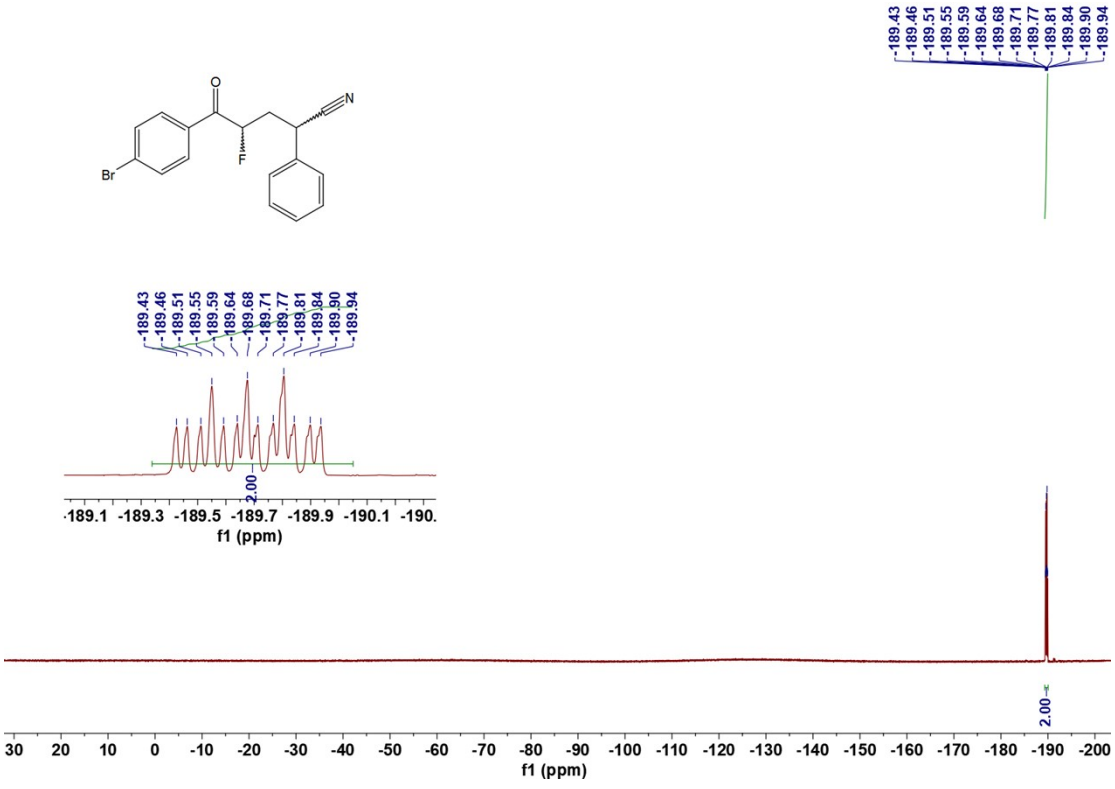

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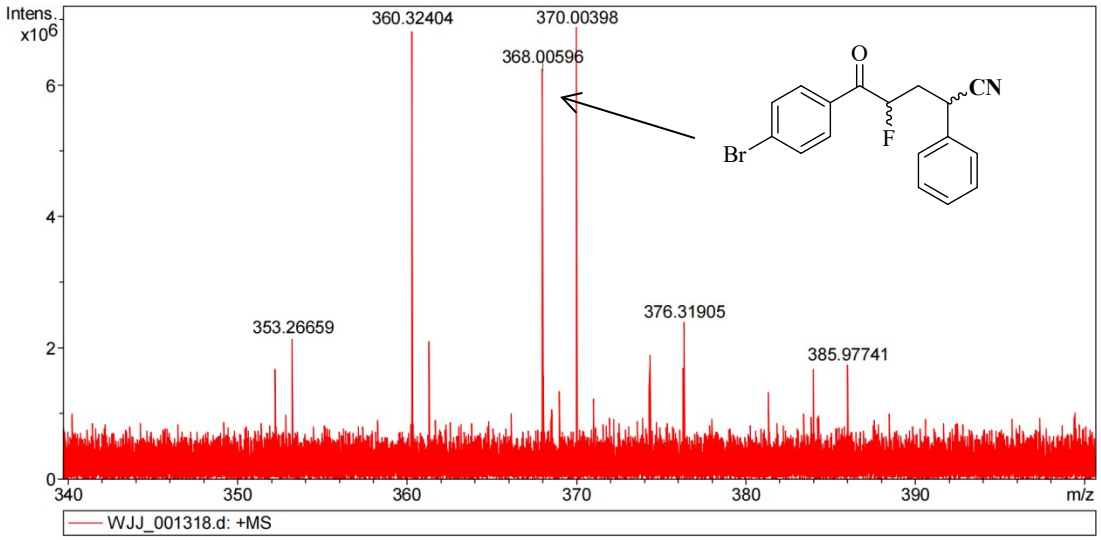
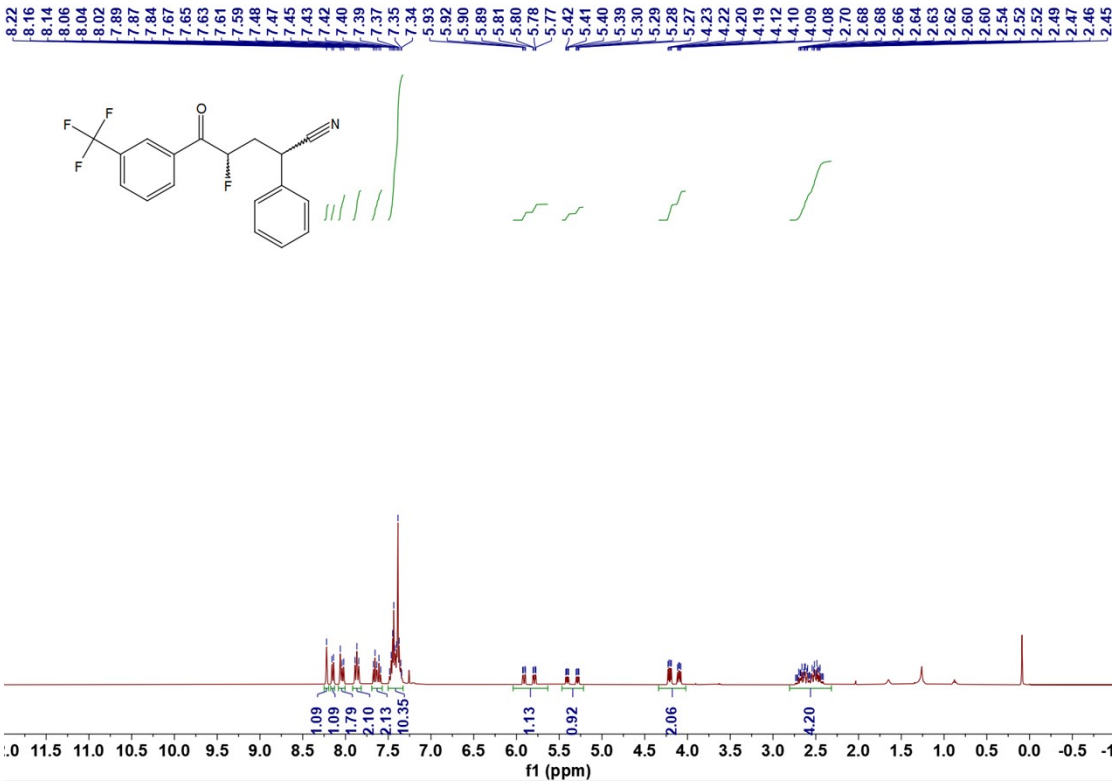
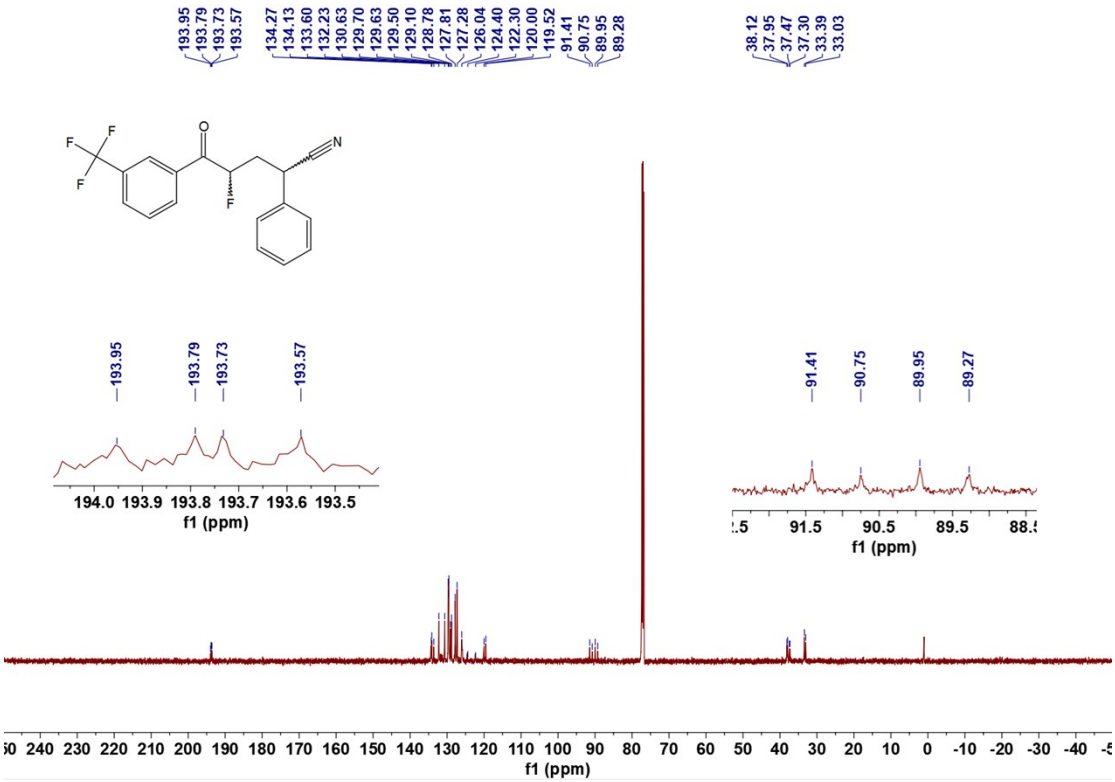


HRMS of 3ga



^{1}H NMR of 3ha



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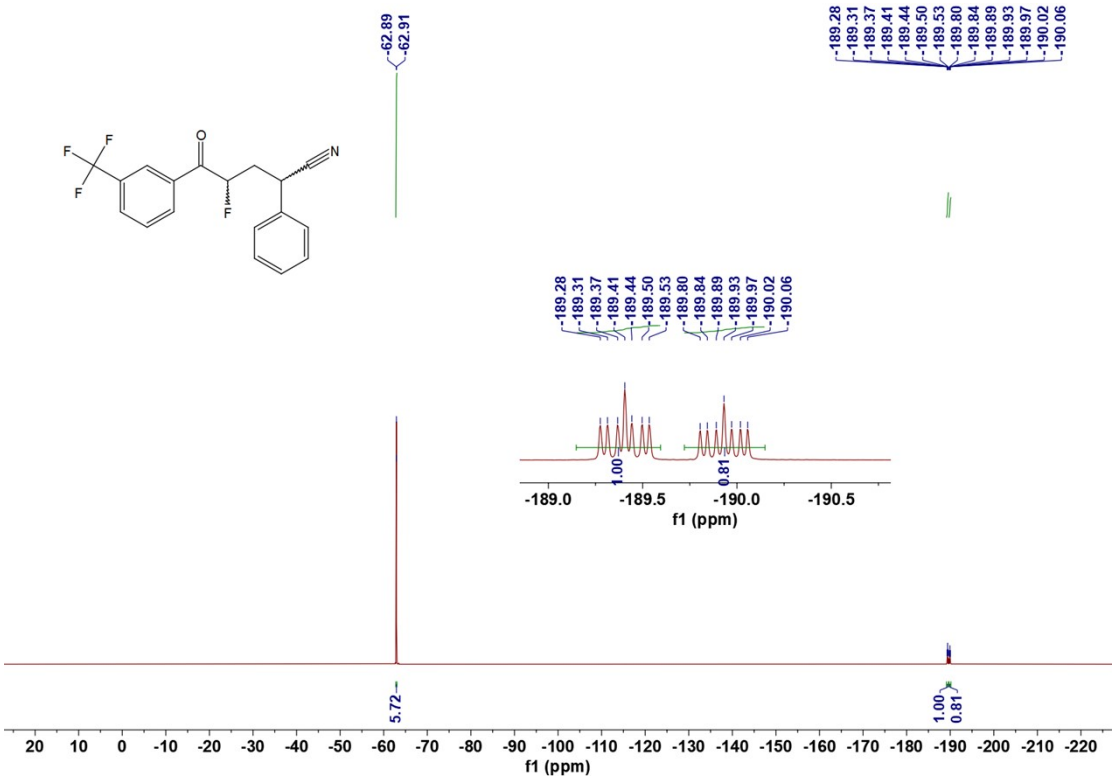
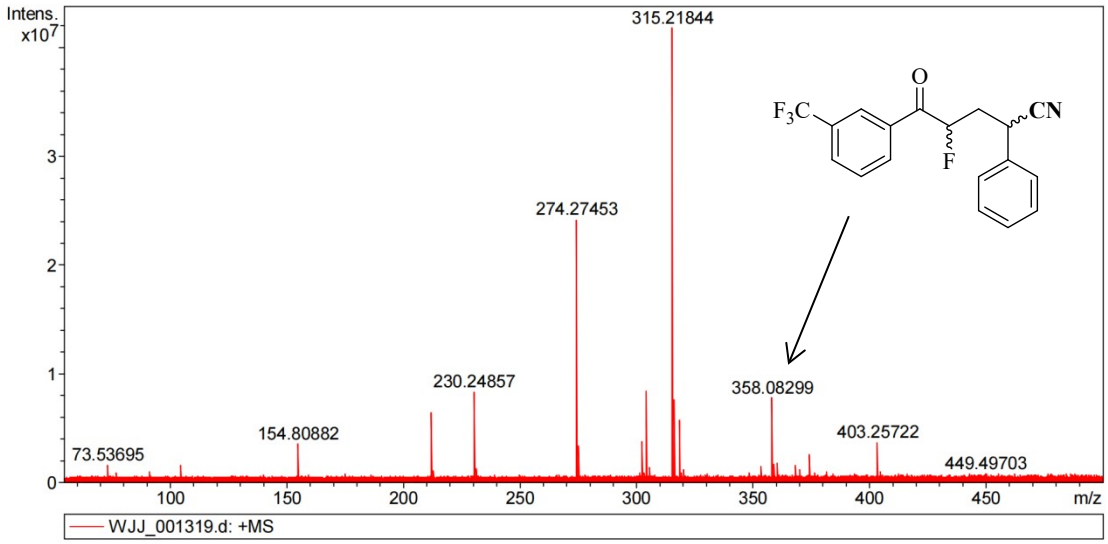


^{19}F NMR of 3ha



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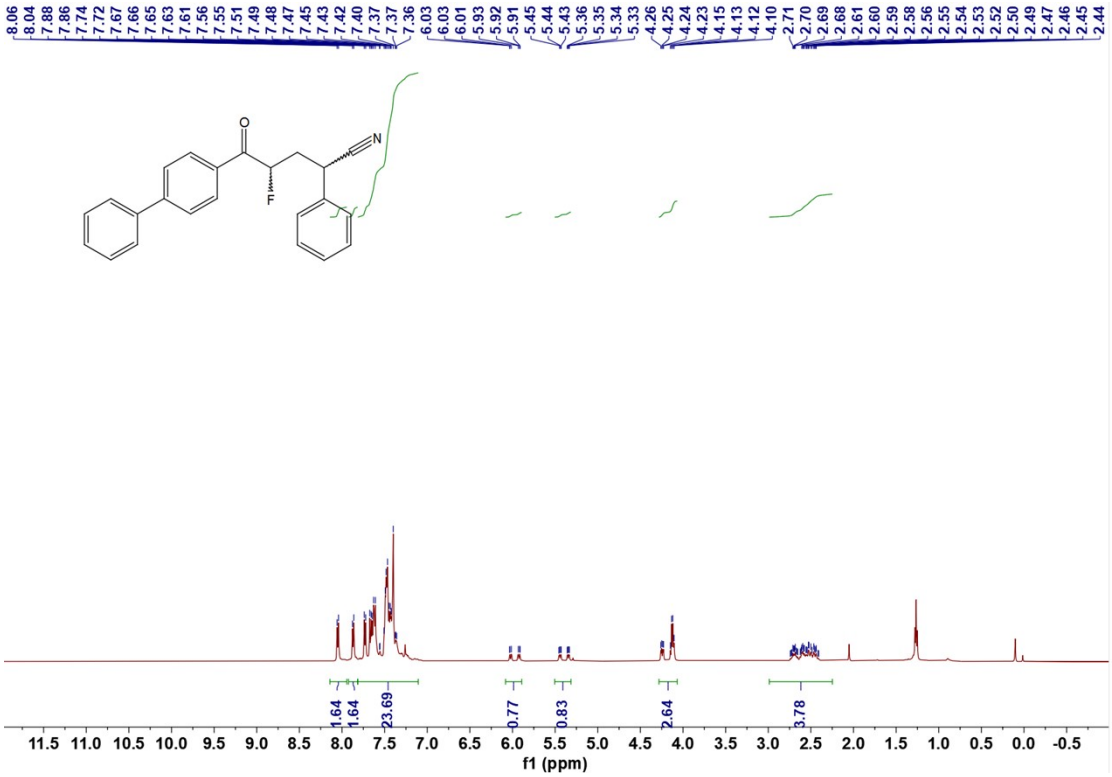
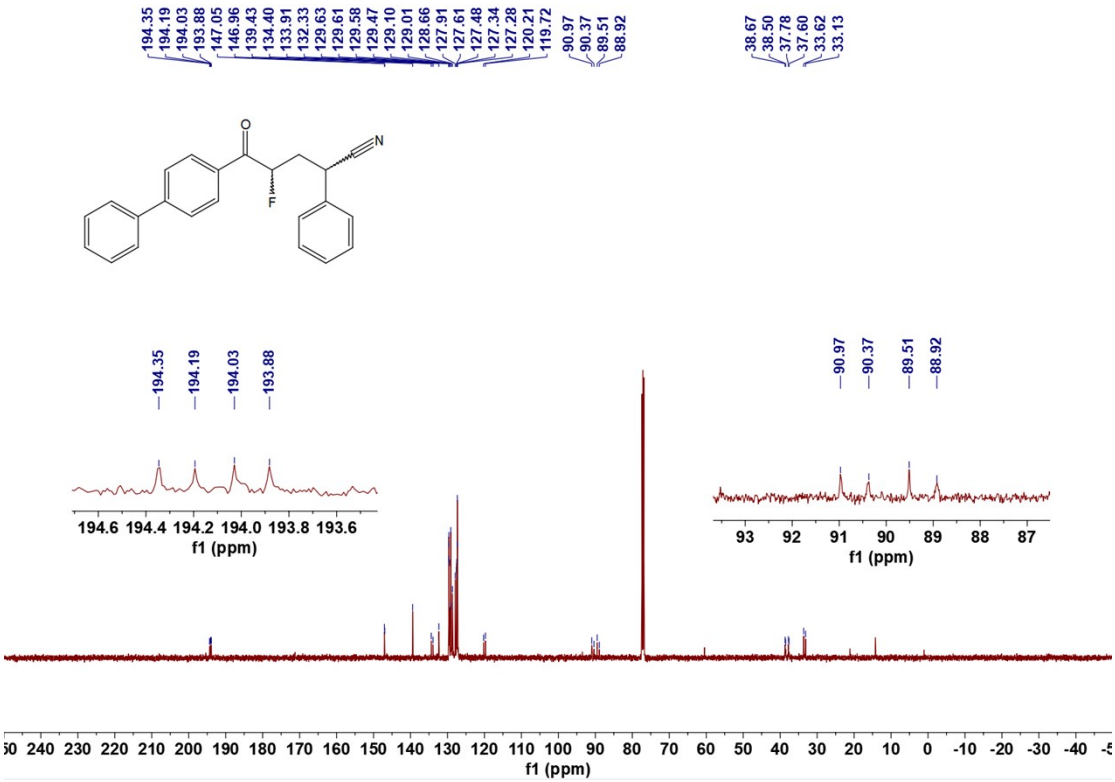


^{1}H NMR of 3ia



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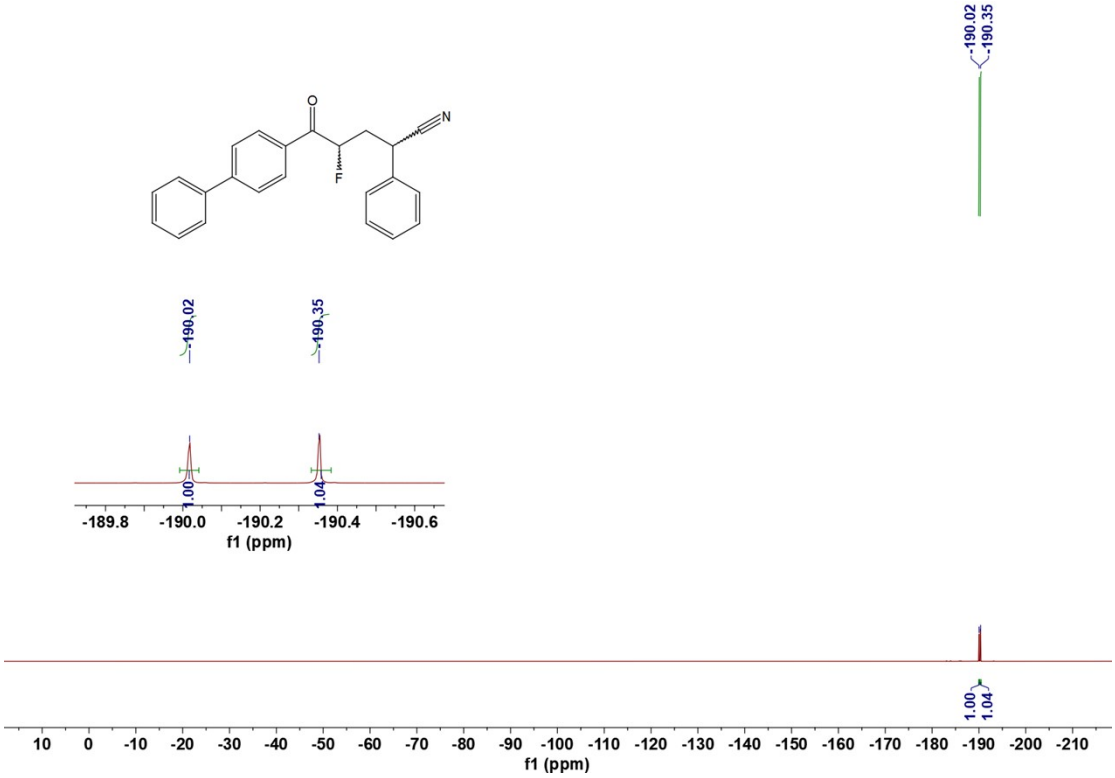

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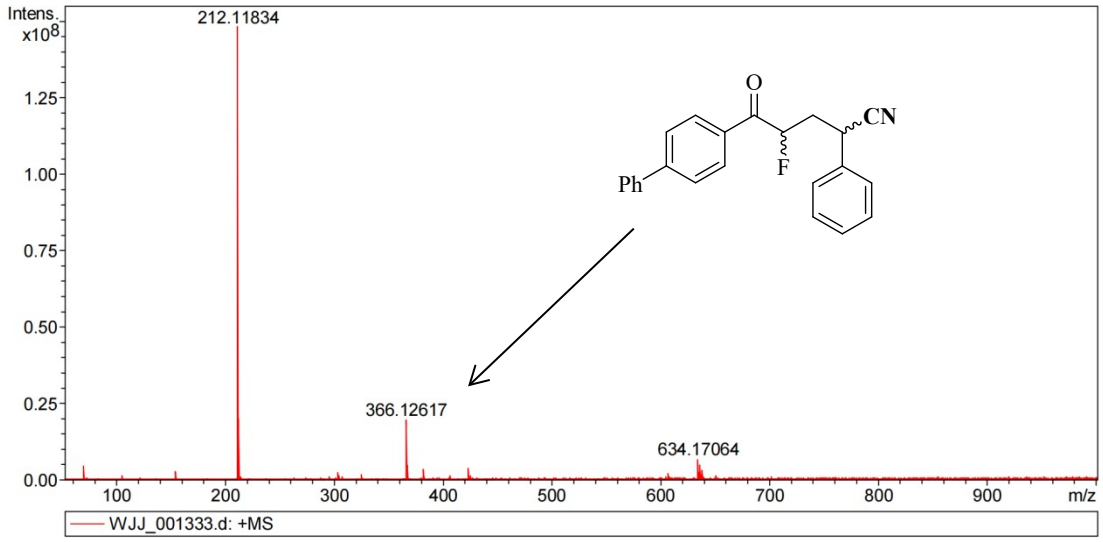

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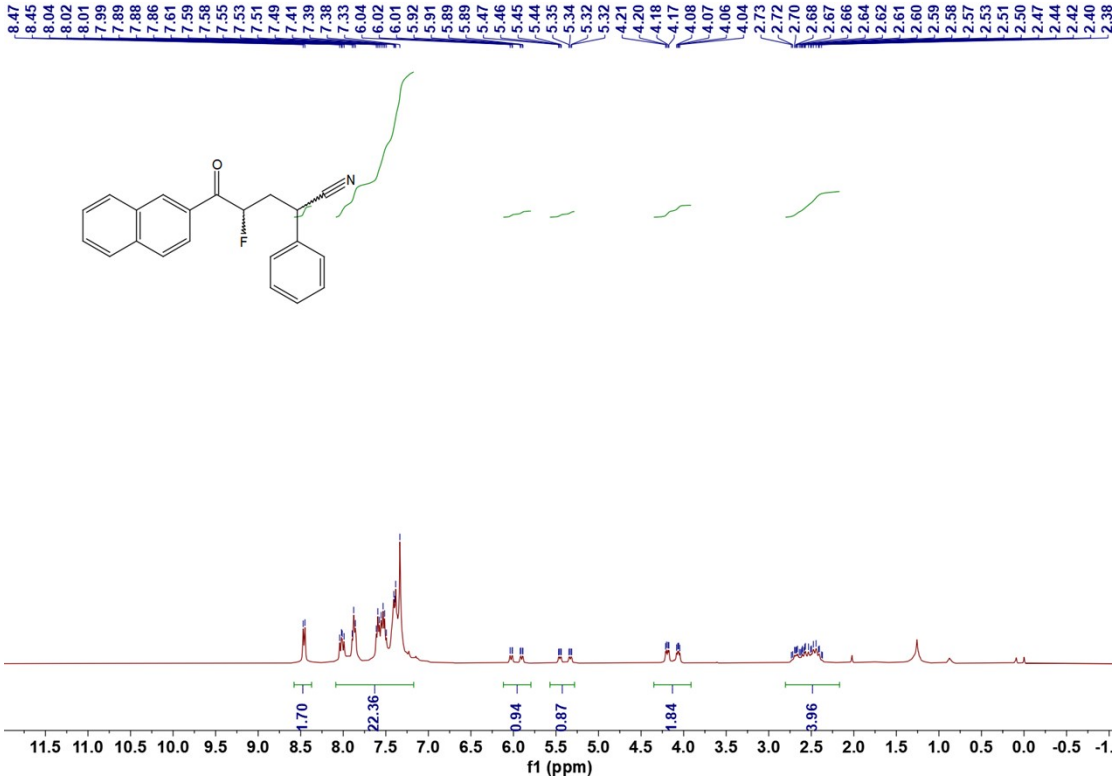

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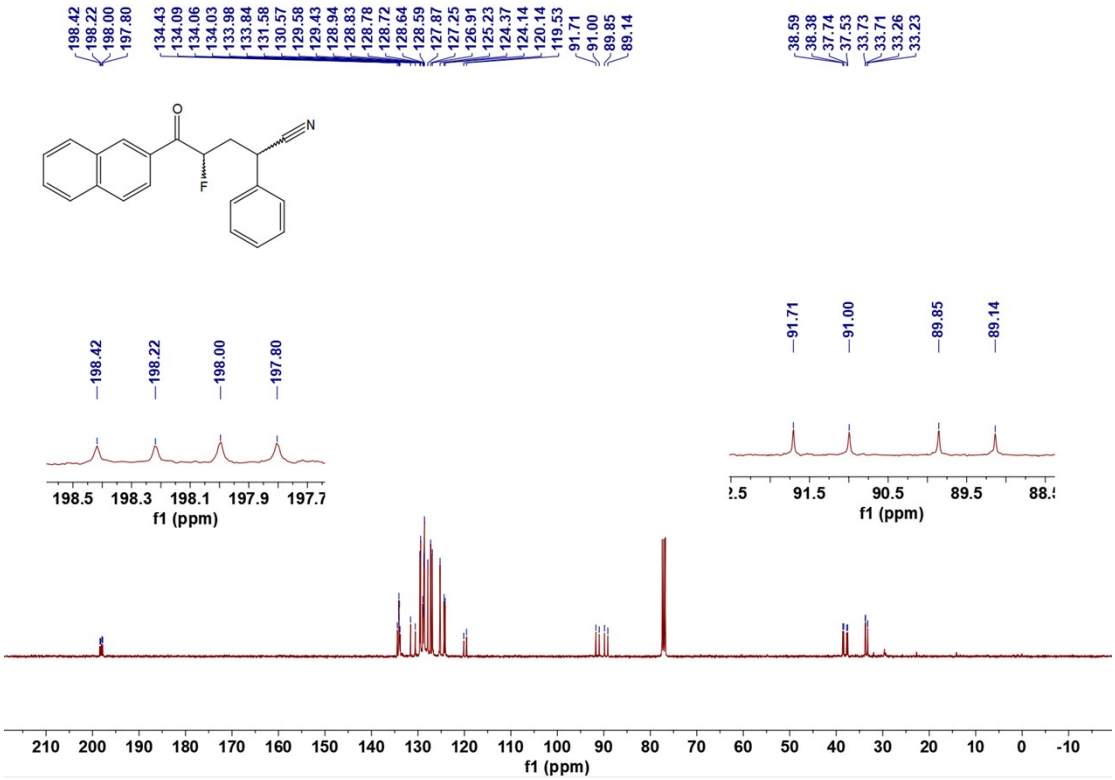

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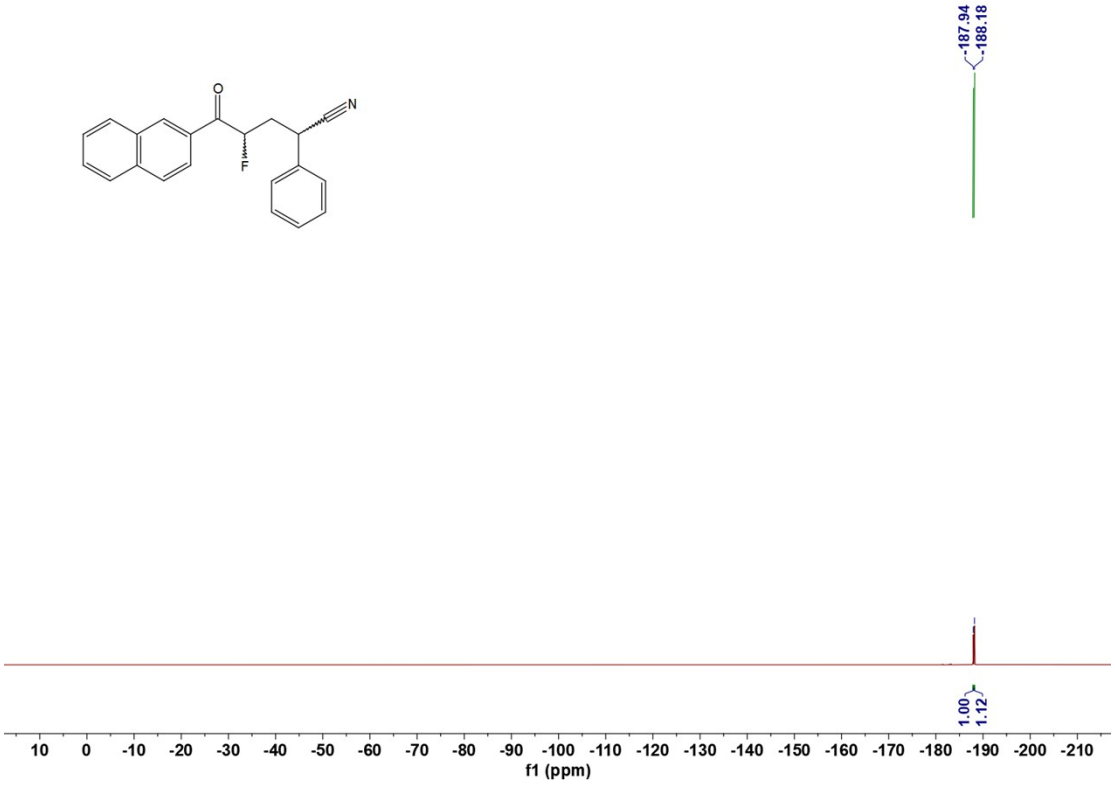

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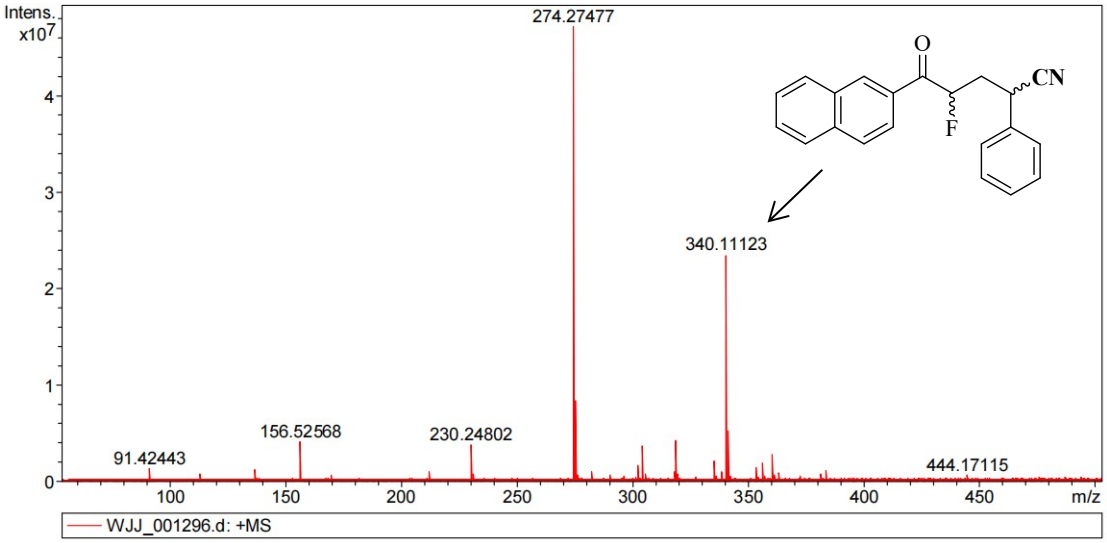
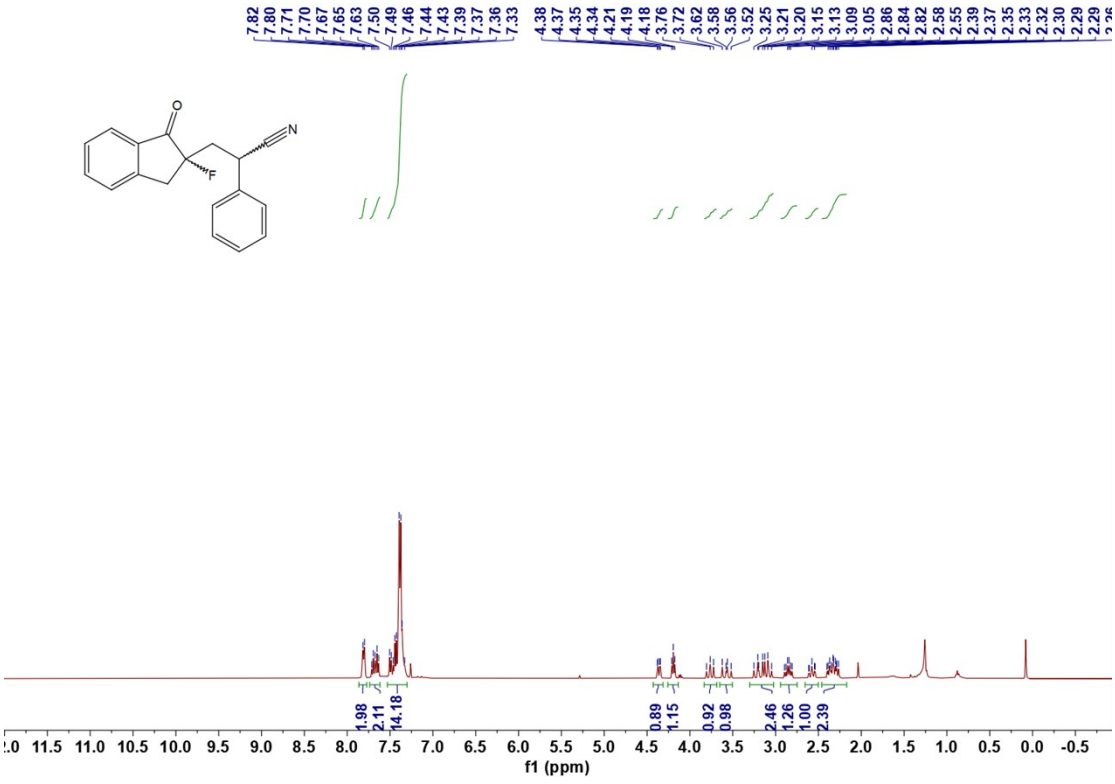
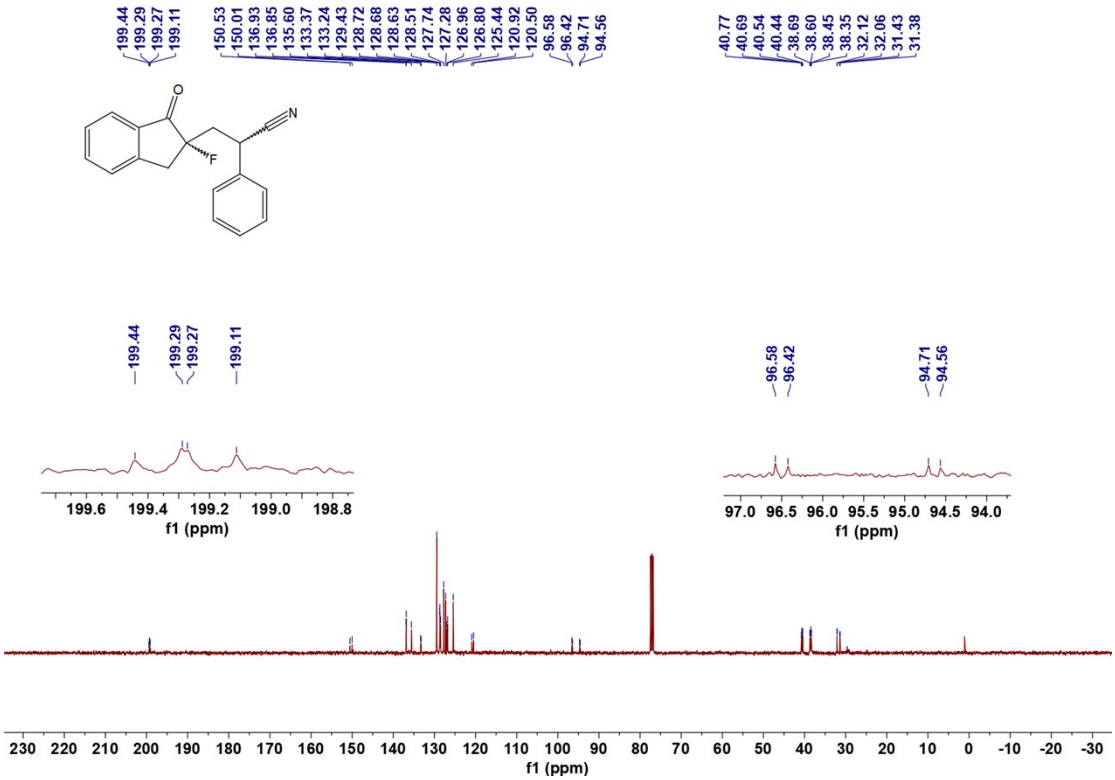


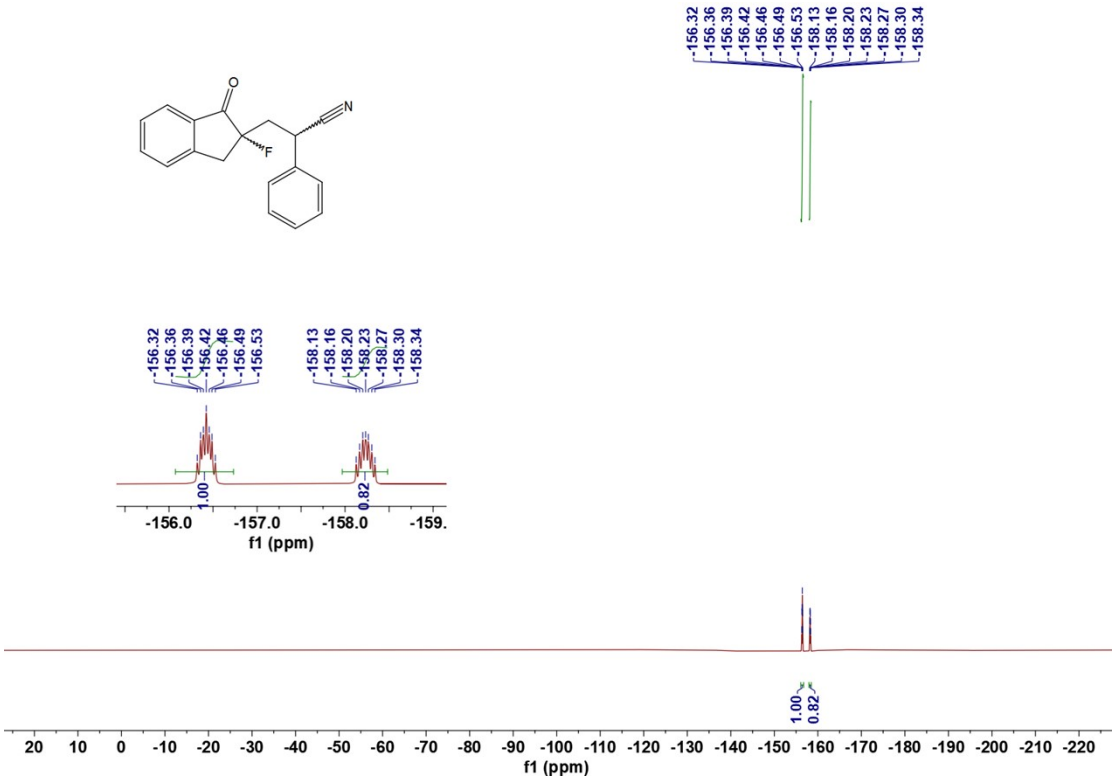
HRMS of 3ja



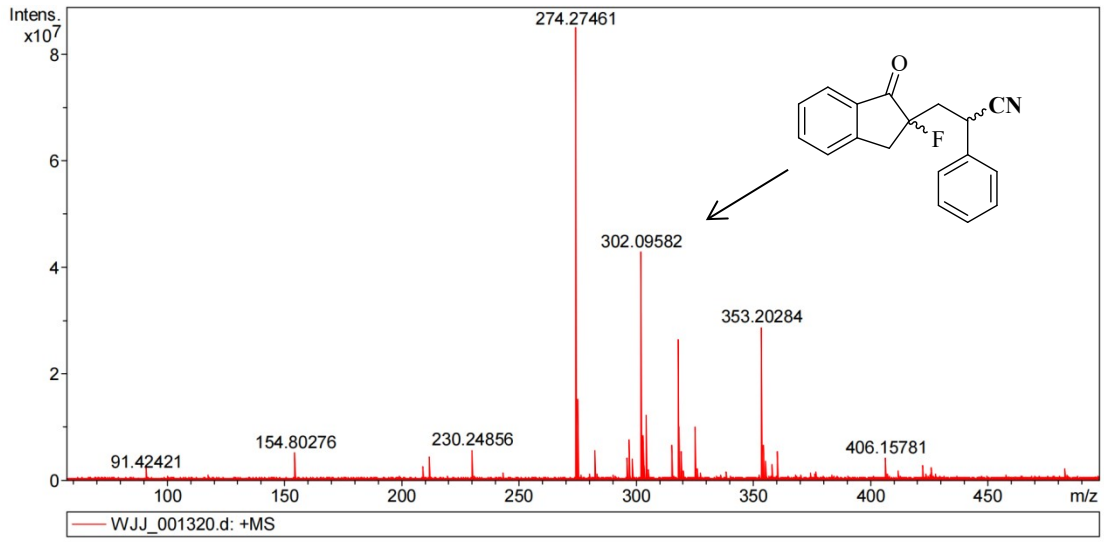
^{1}H NMR of 3ka



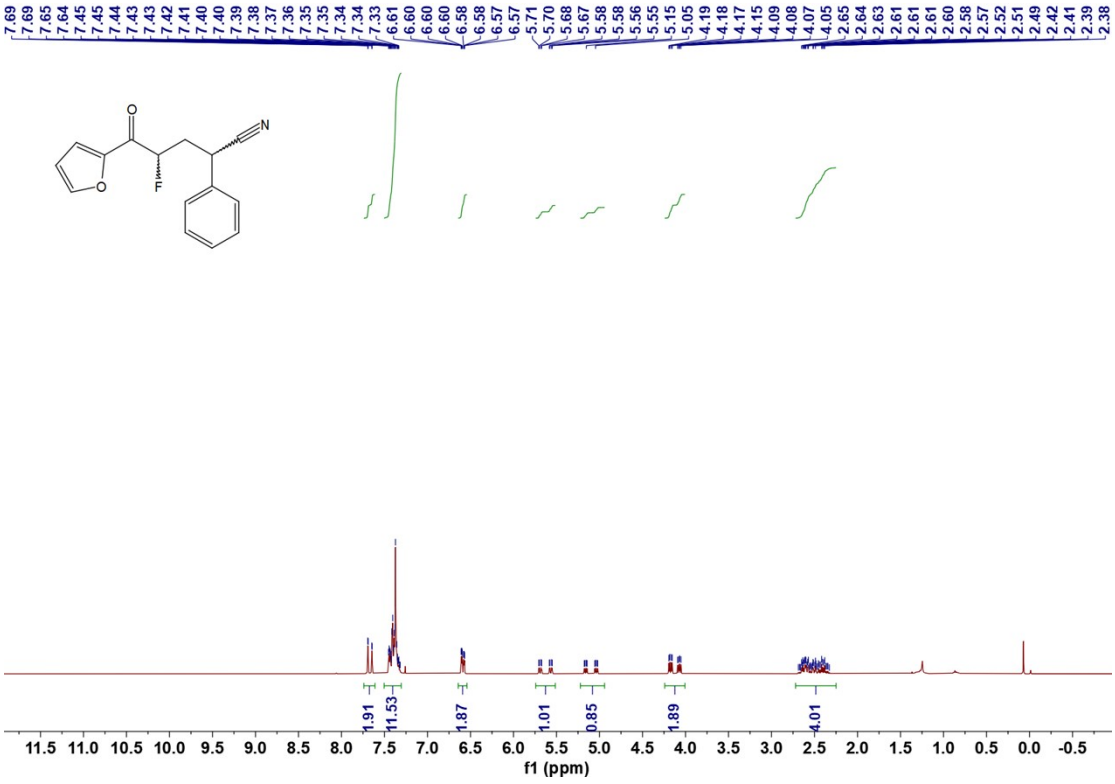
^{13}C NMR of 3ka



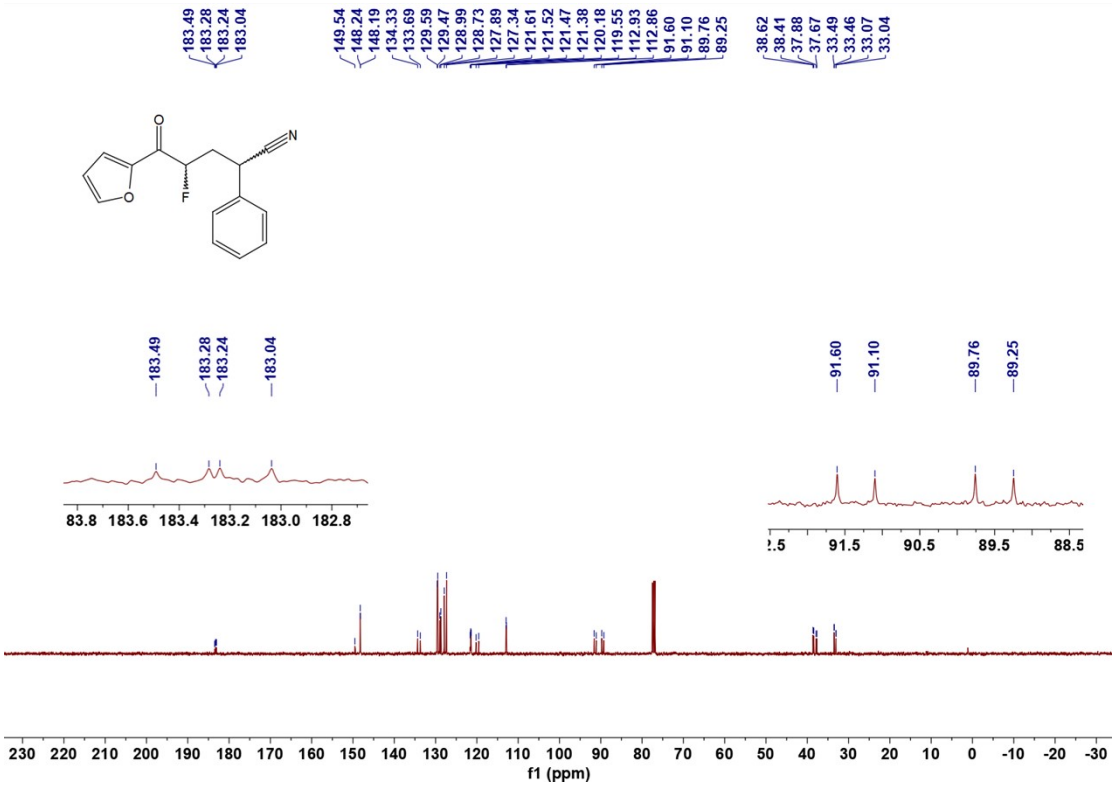
^{19}F NMR of 3ka



HRMS of 3ka



^{1}H NMR of 3la



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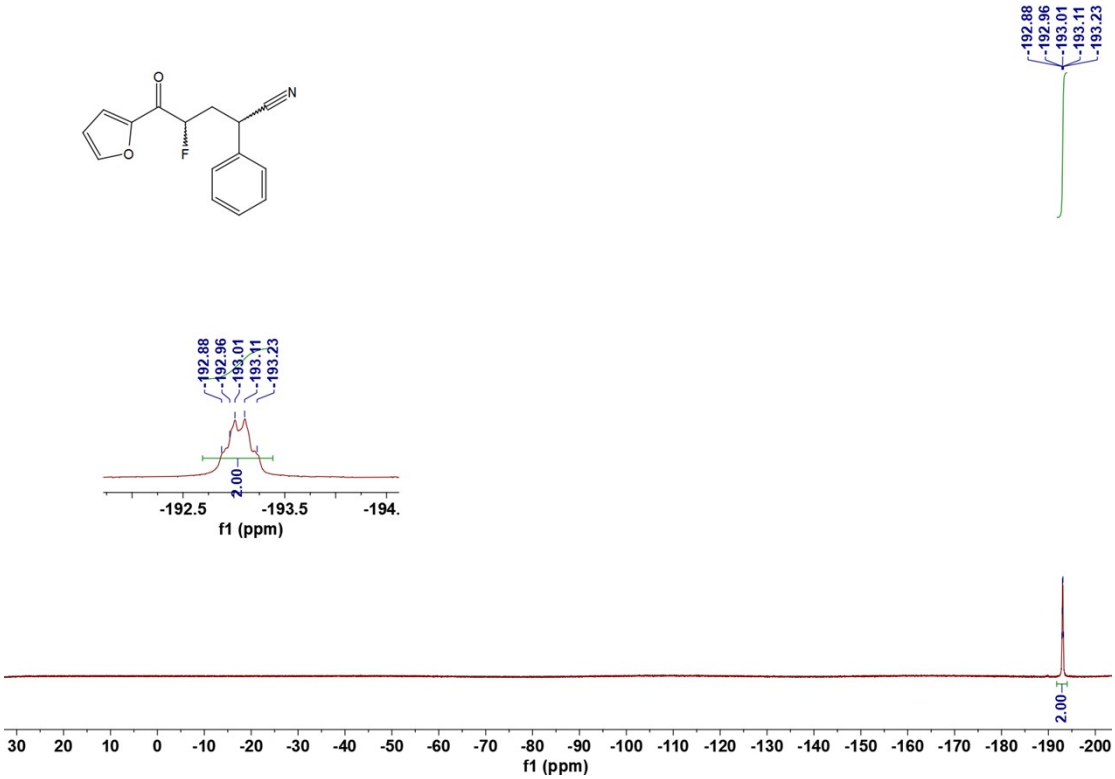
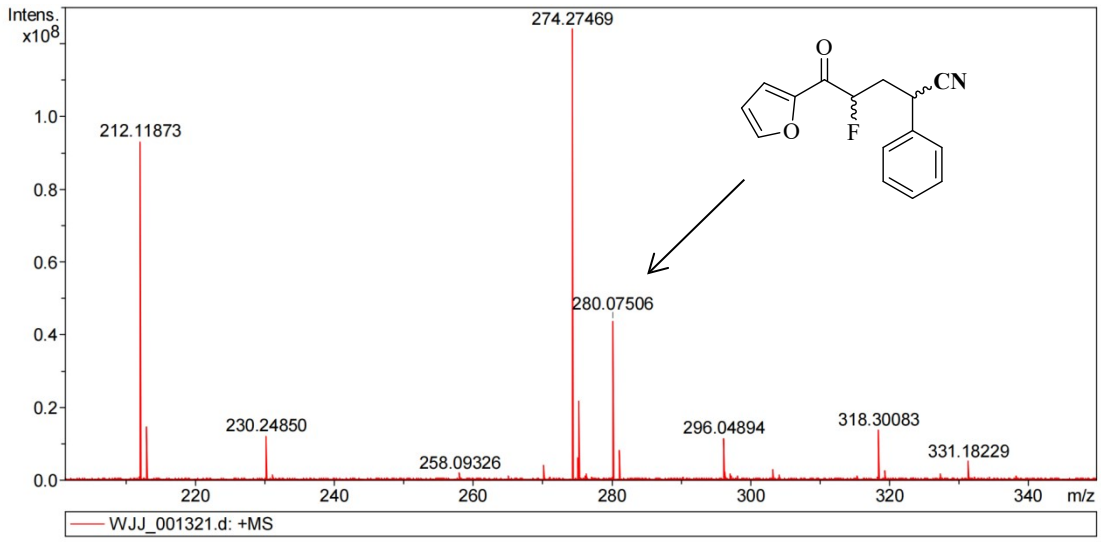
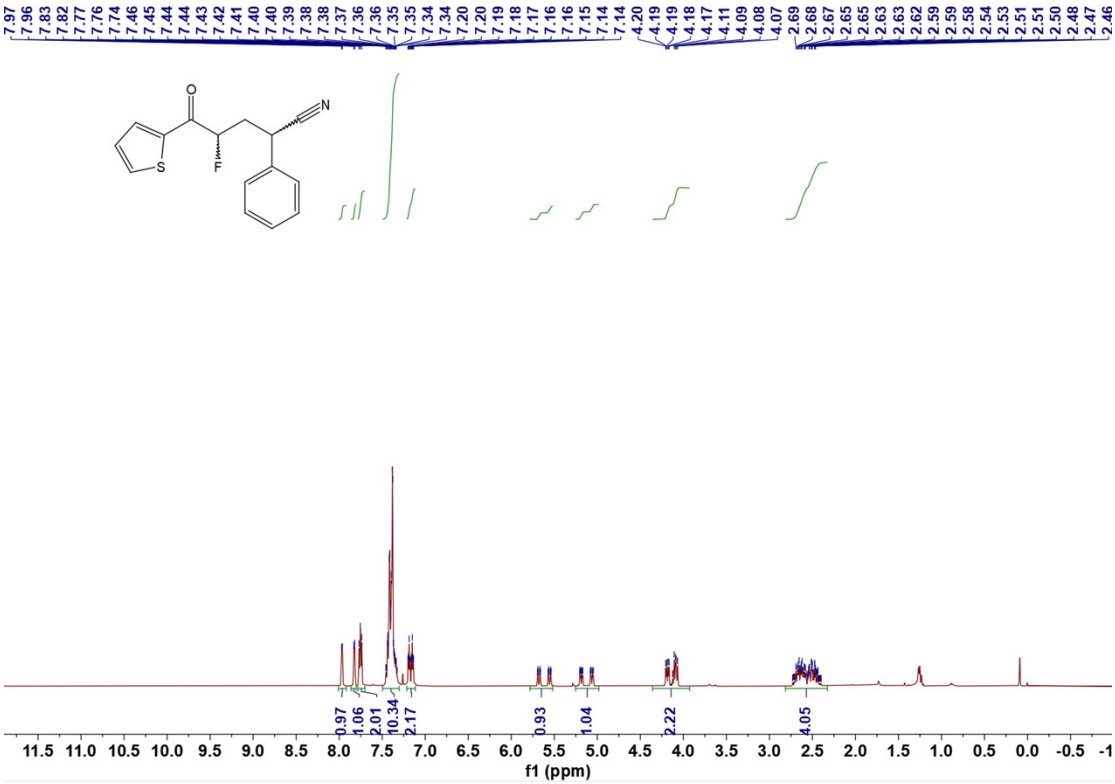


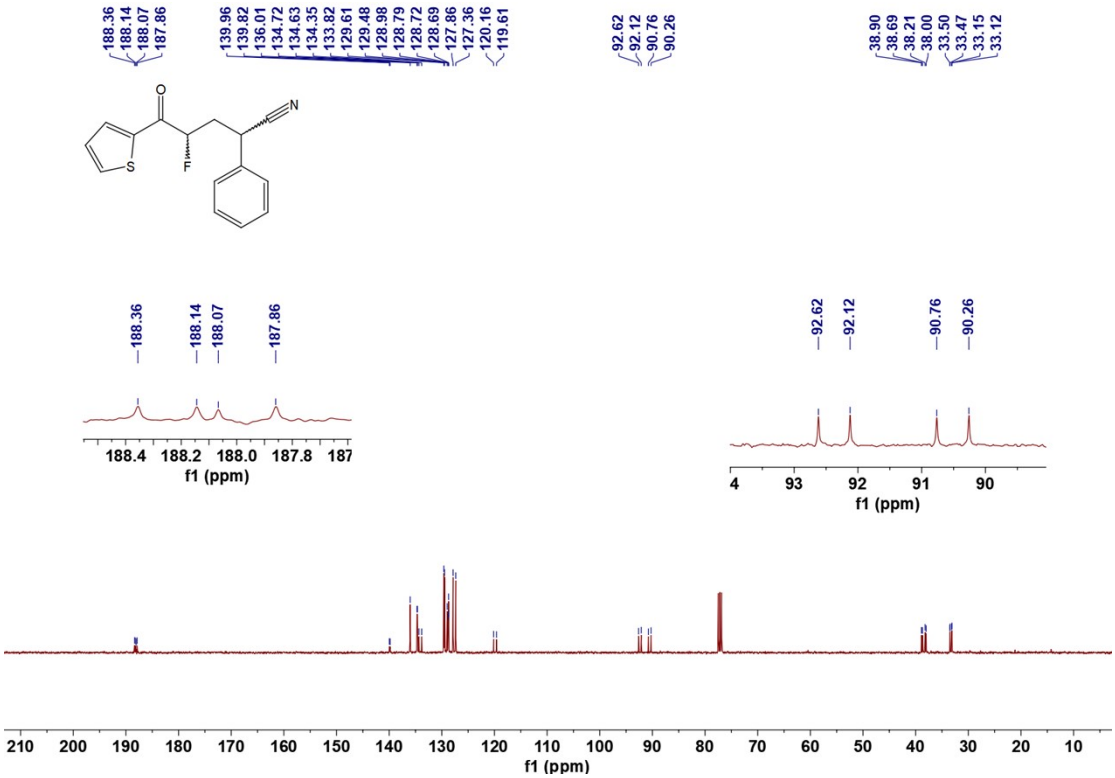
^{19}F NMR of 3la



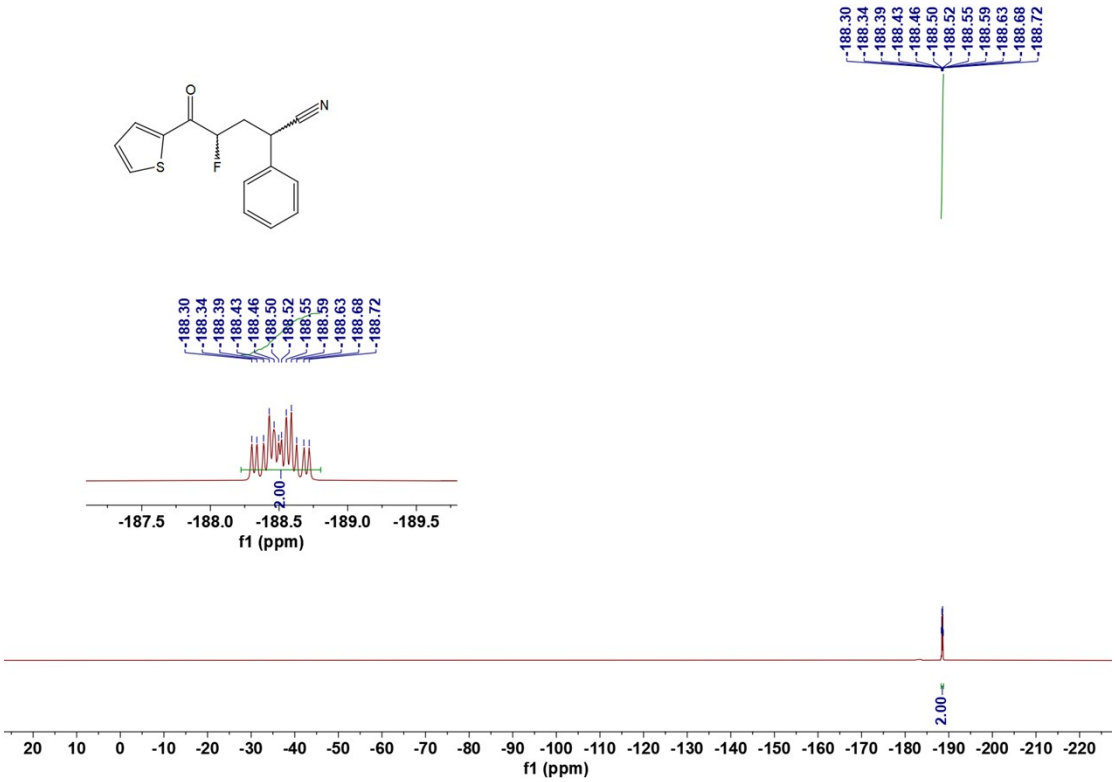
HRMS of 3la



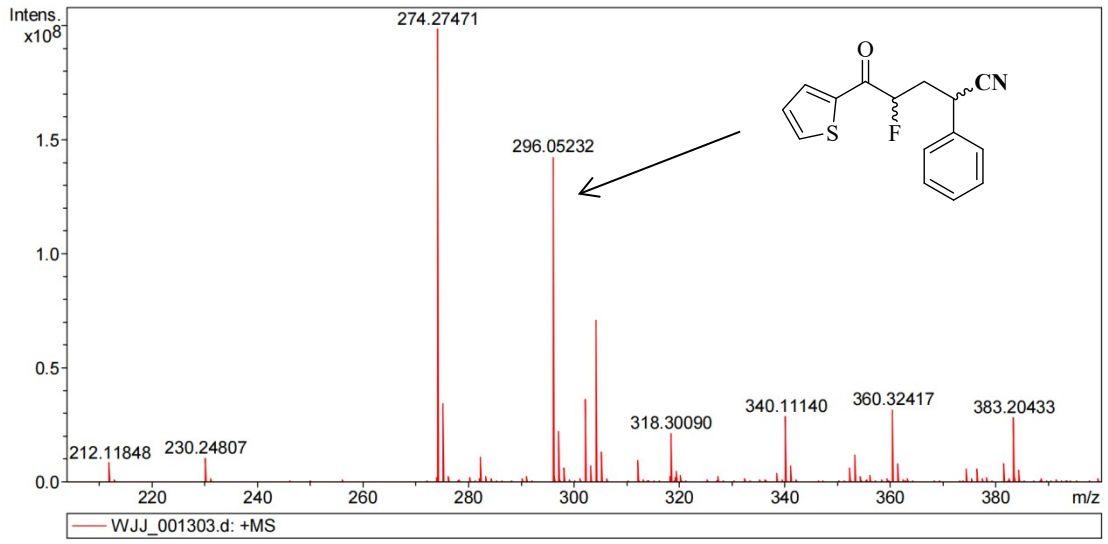
^{1}H NMR of 3ma



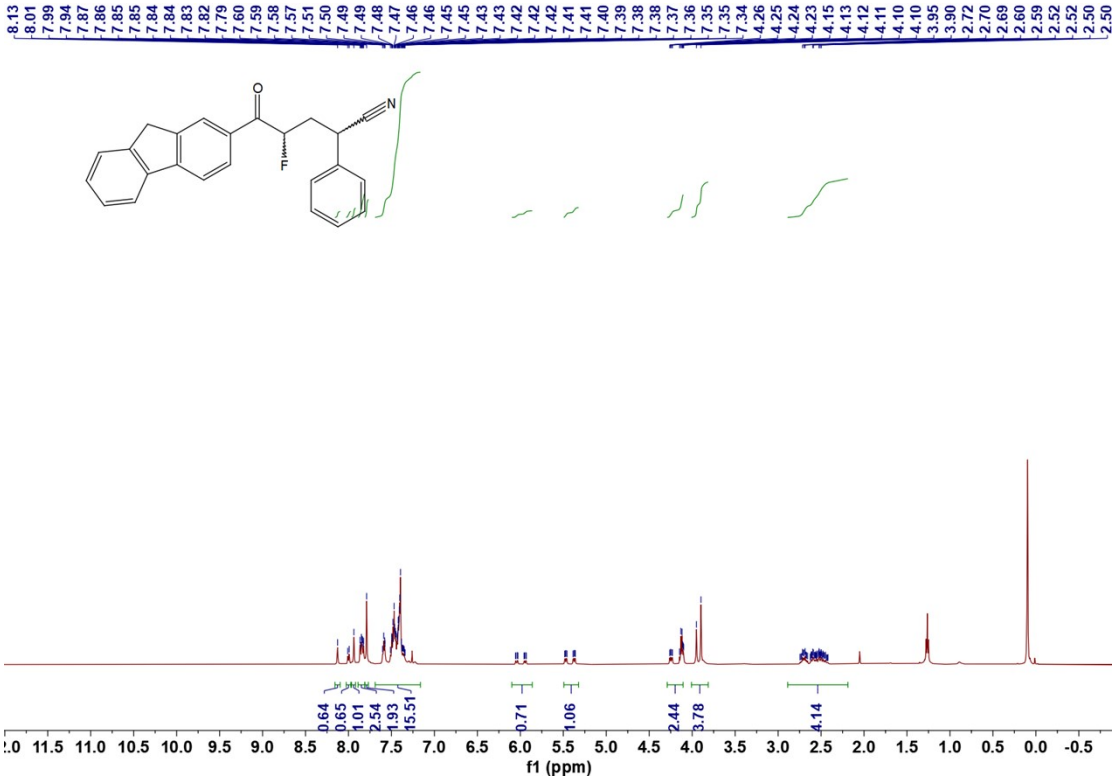
^{13}C NMR of 3ma



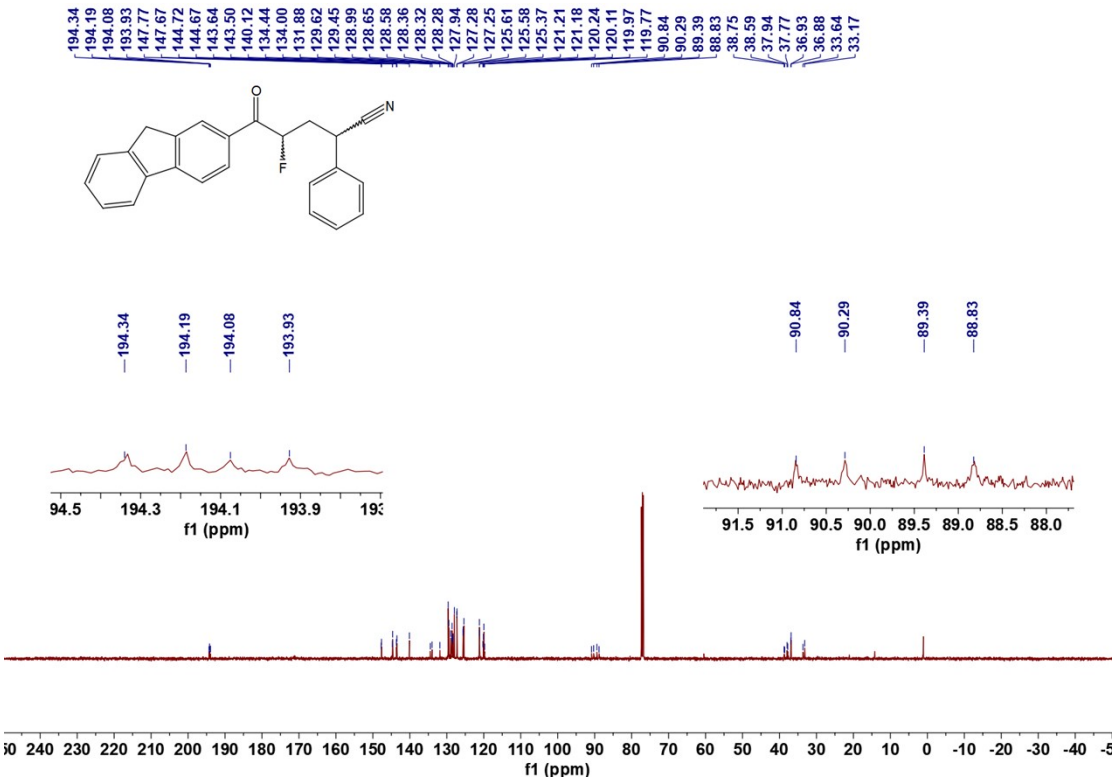
^{19}F NMR of 3ma



HRMS of 3ma



^{1}H NMR of 3na



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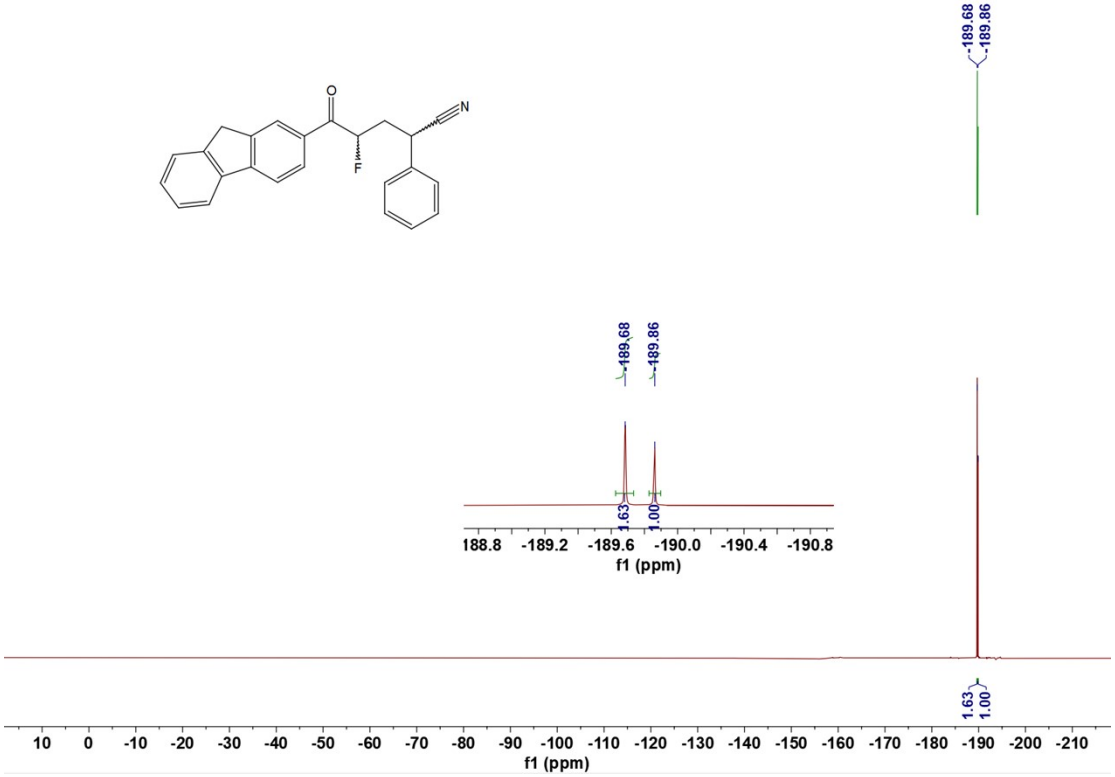
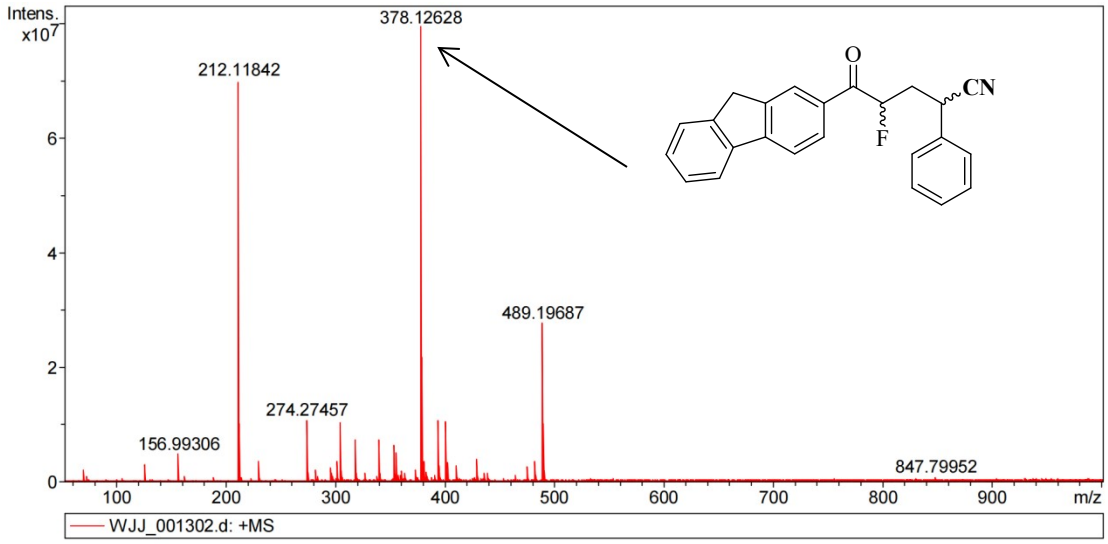
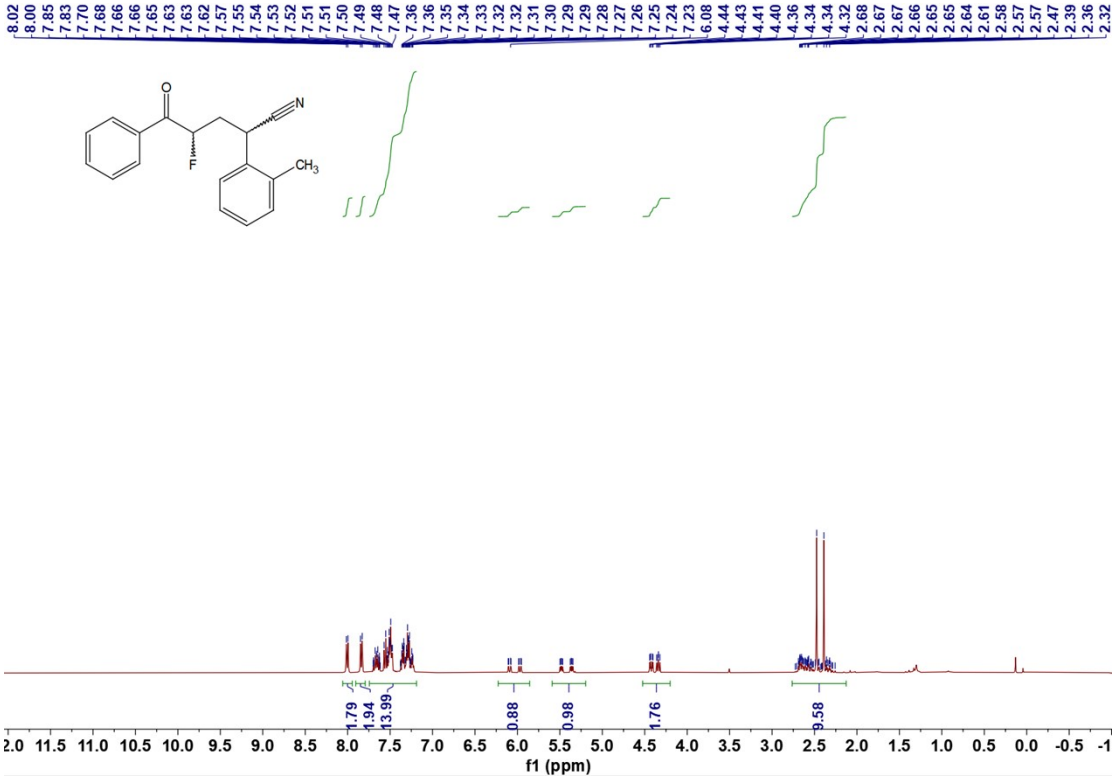


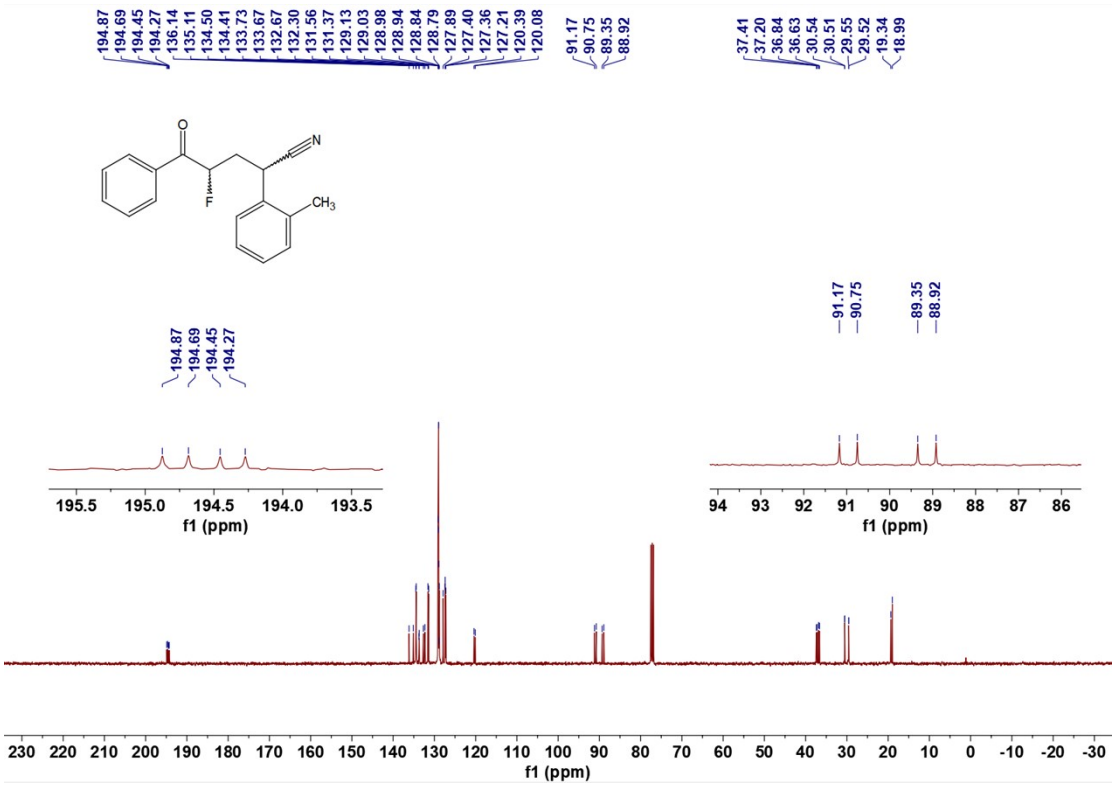
^{19}F NMR of 3na



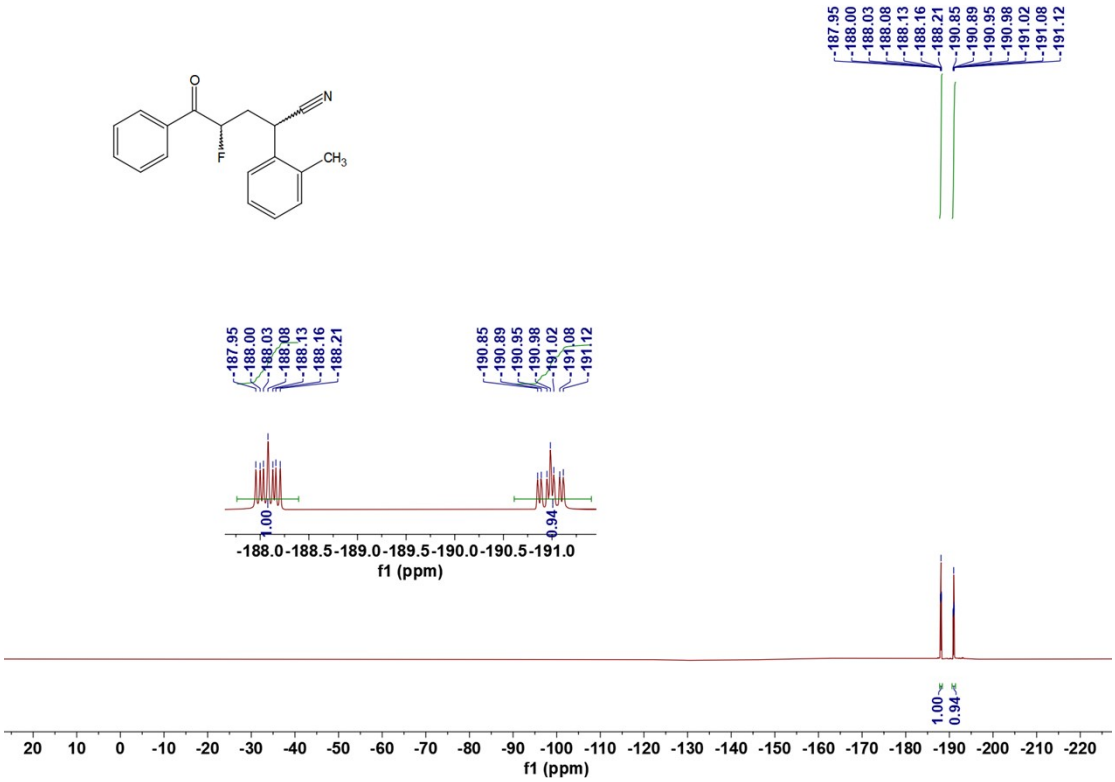
HRMS of 3na



^{1}H NMR of 3ab



^{13}C NMR of 3ab



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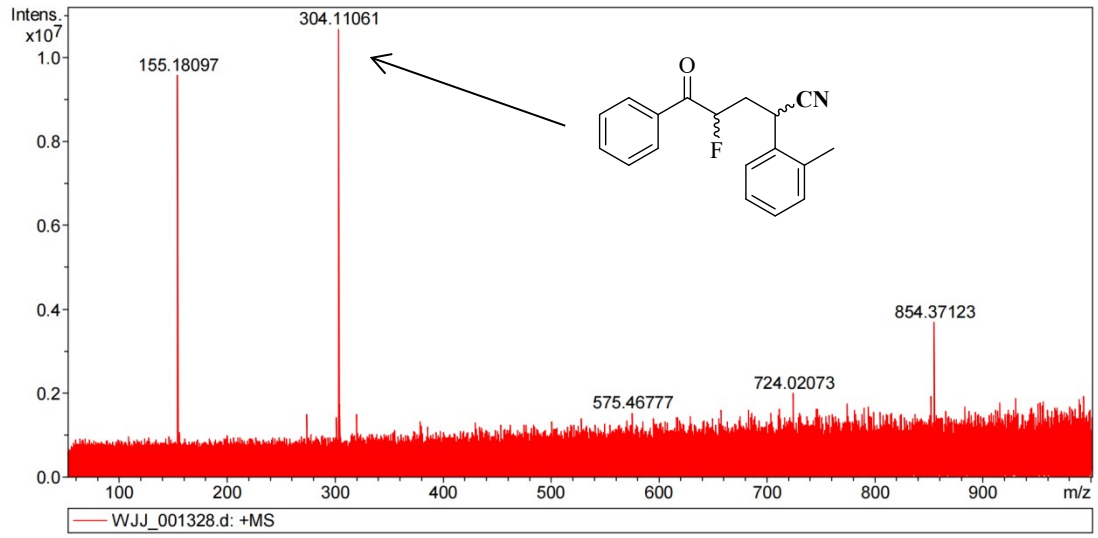
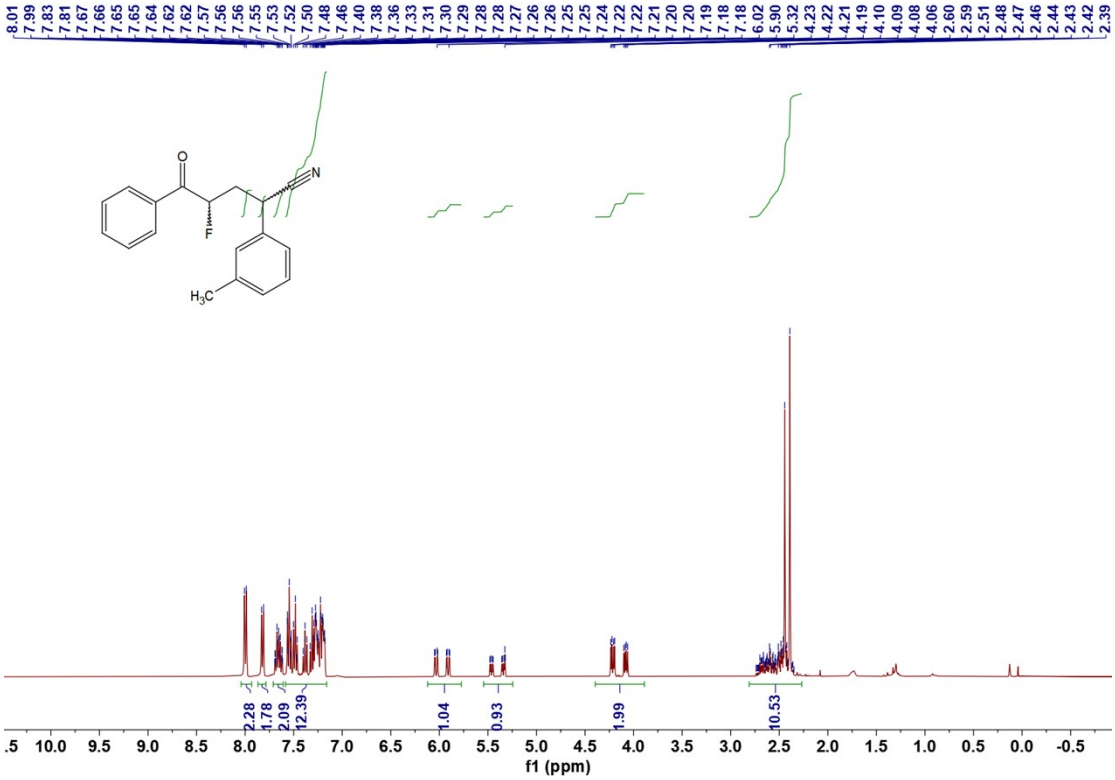
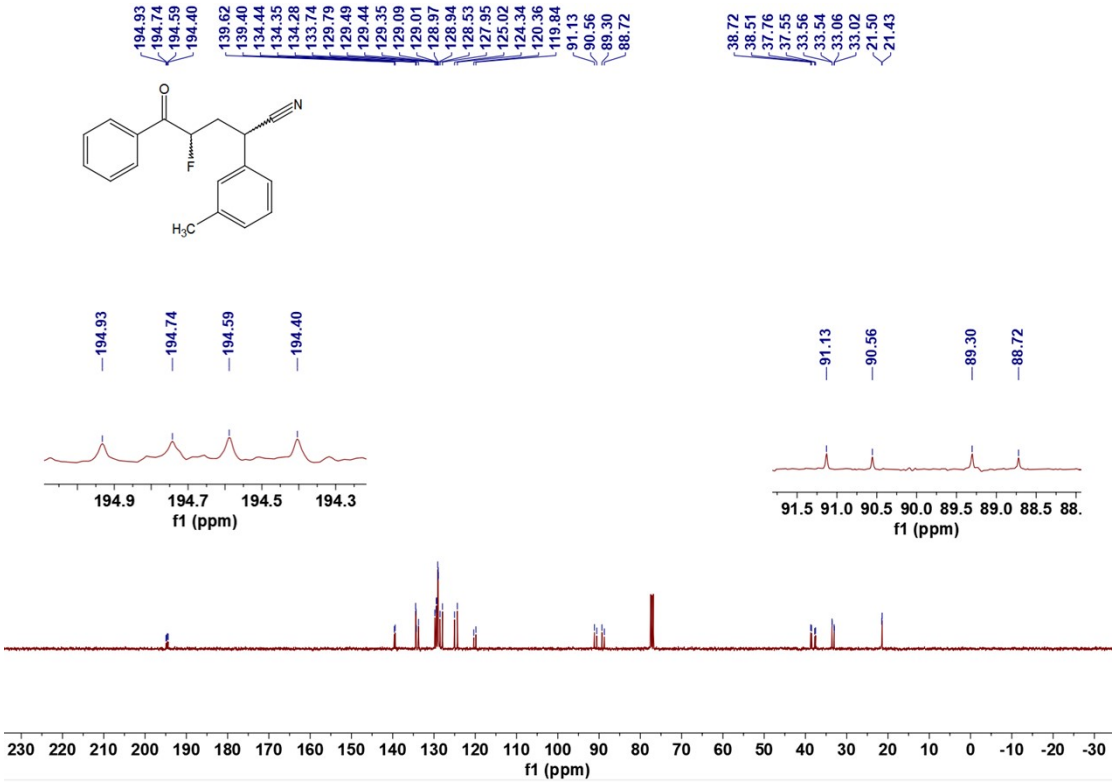


HRMS of 3ab



^{1}H NMR of 3ac



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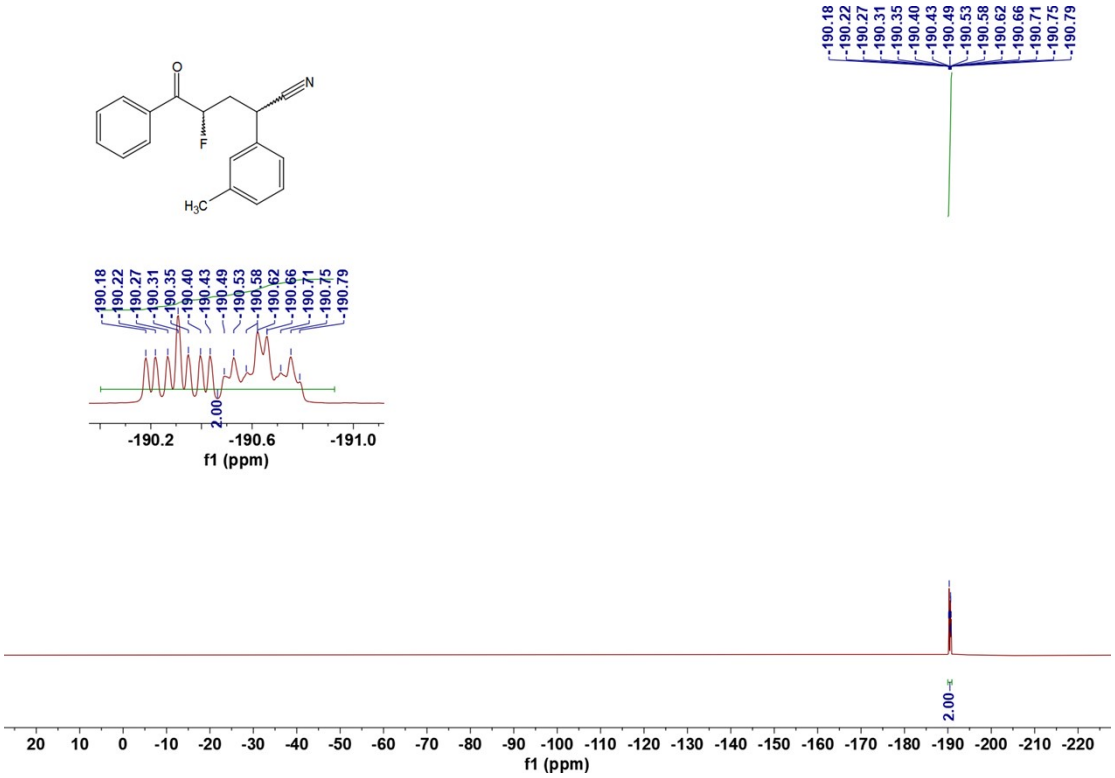

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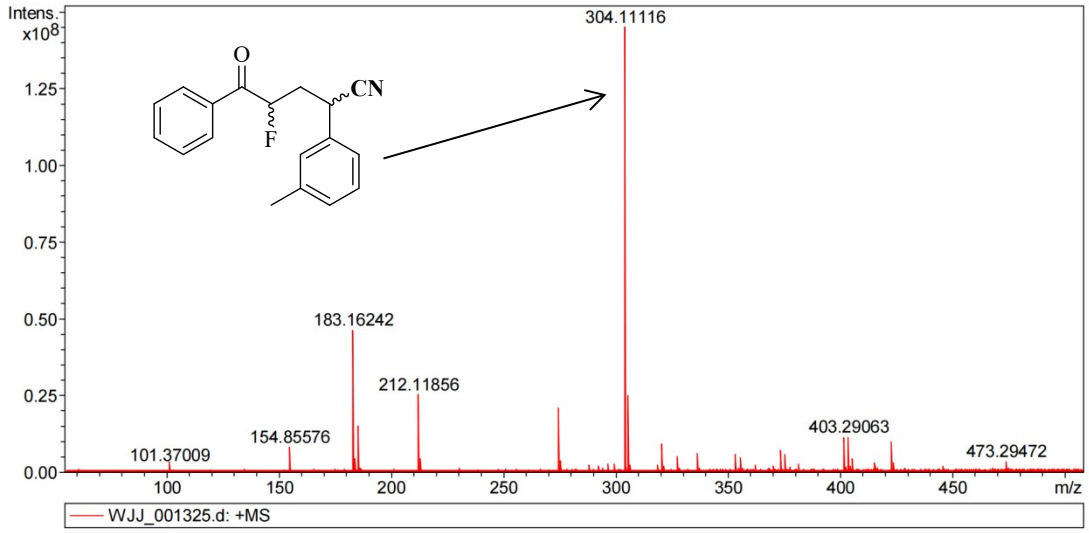

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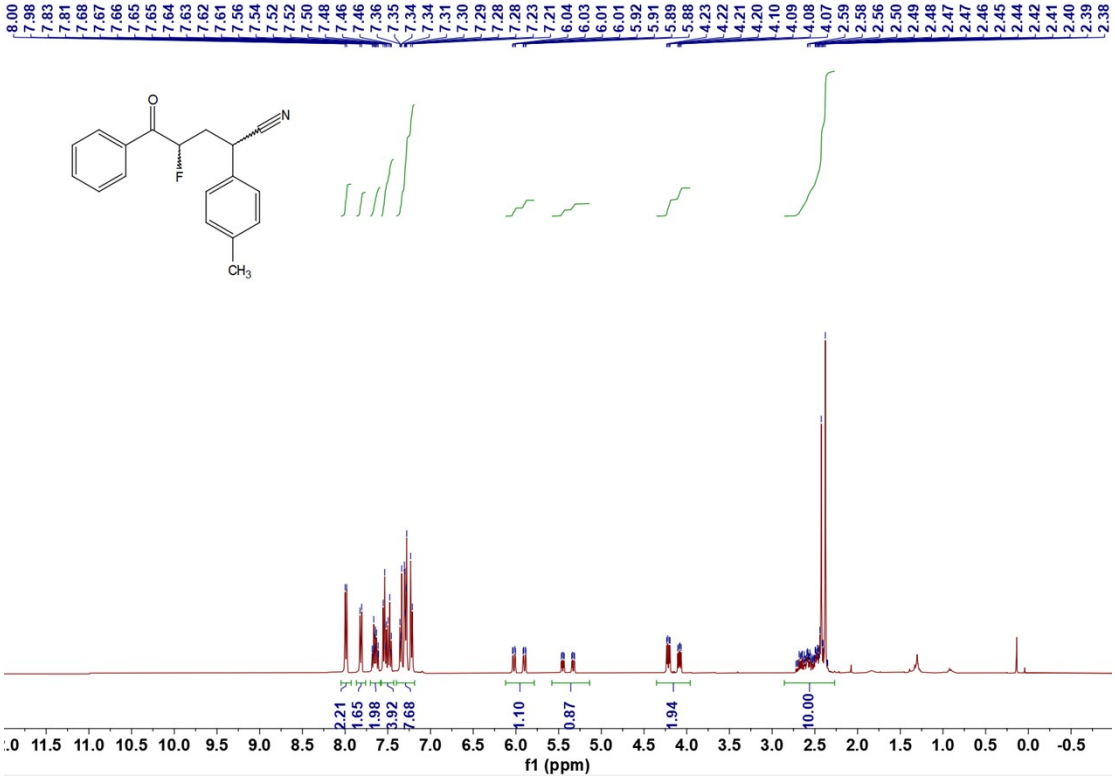

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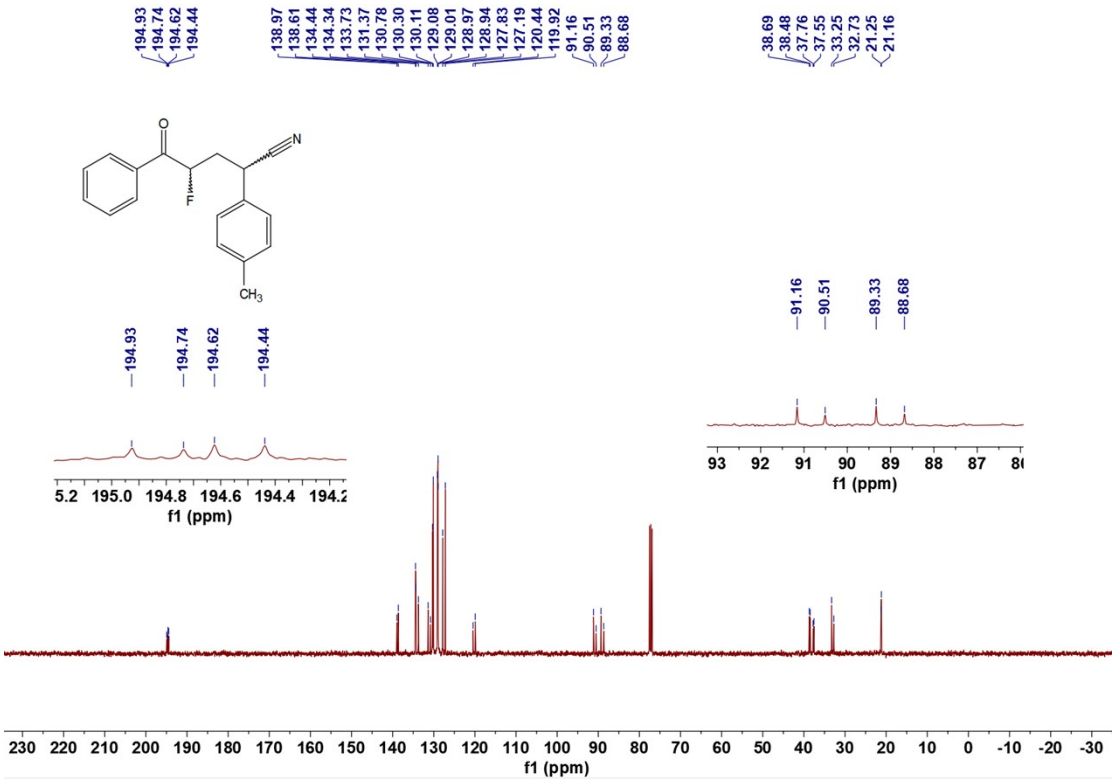
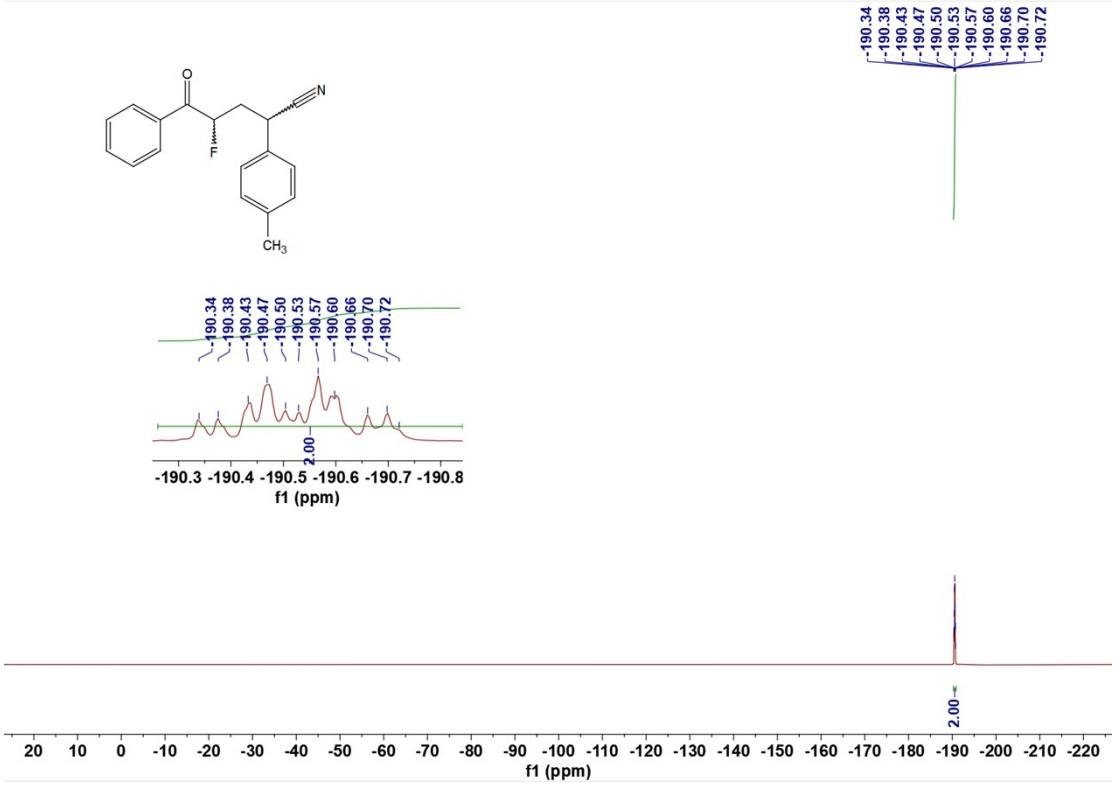


^{13}C NMR of 3ad



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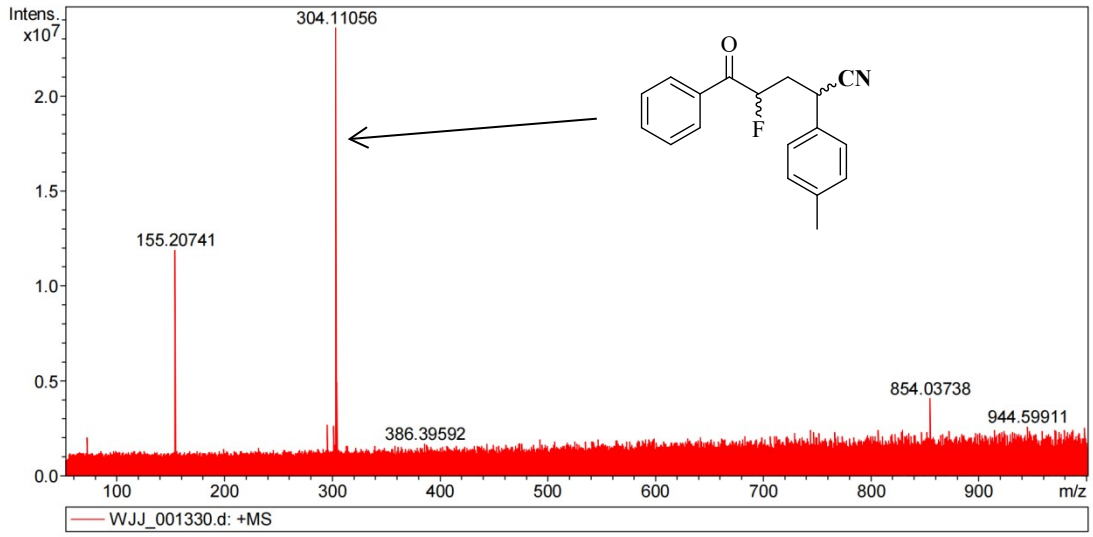

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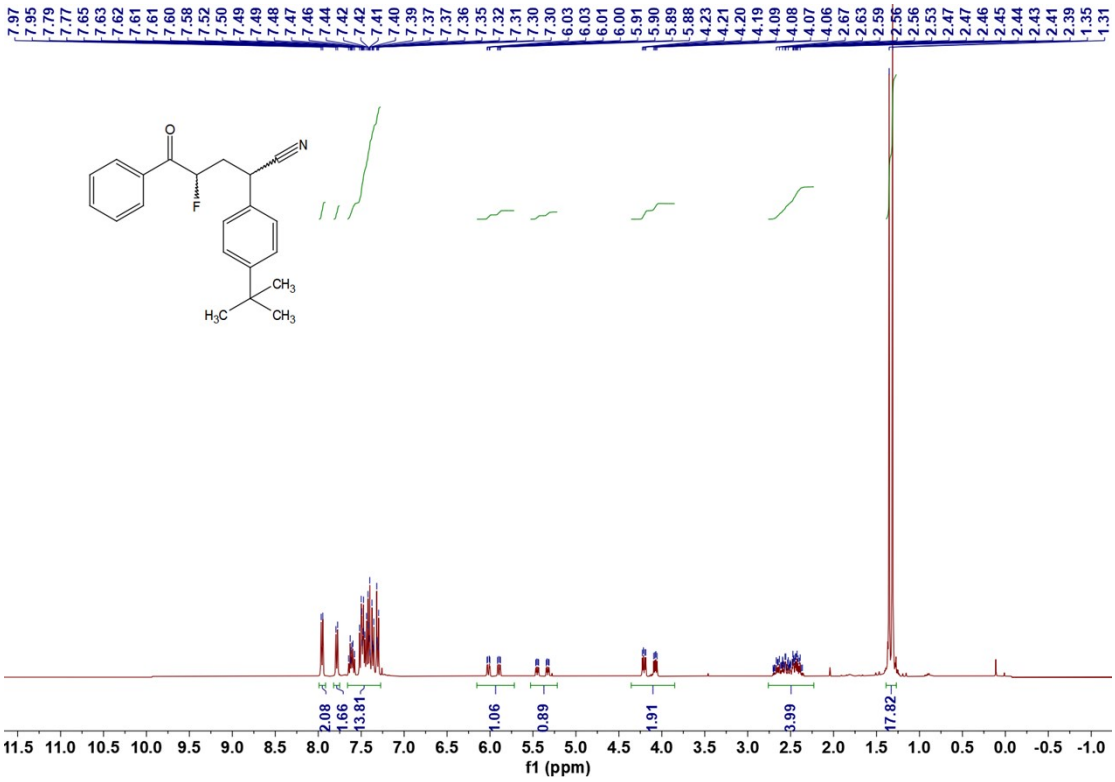

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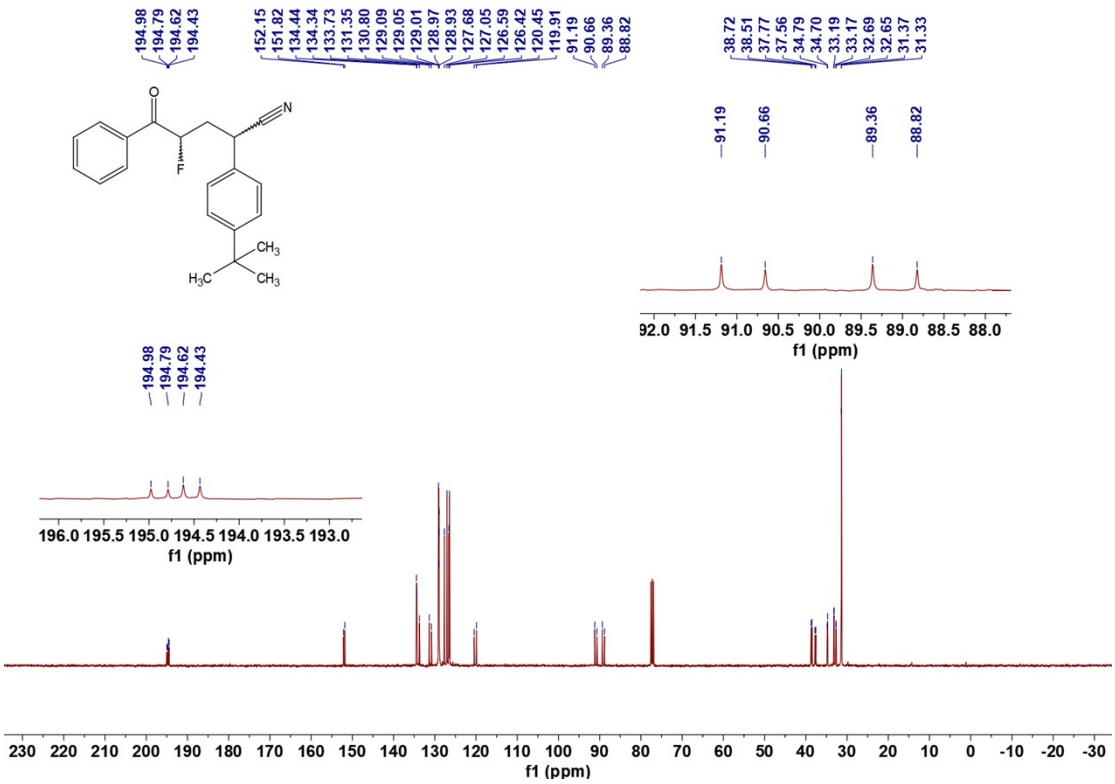
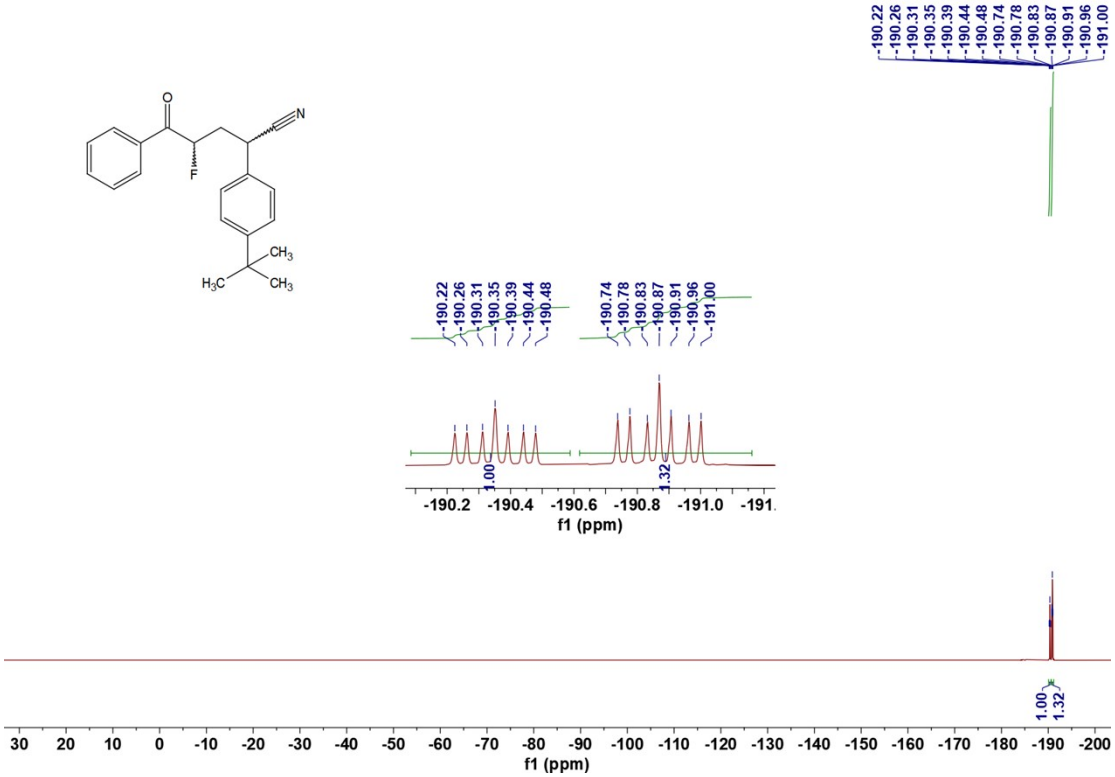


^{13}C NMR of 3ae



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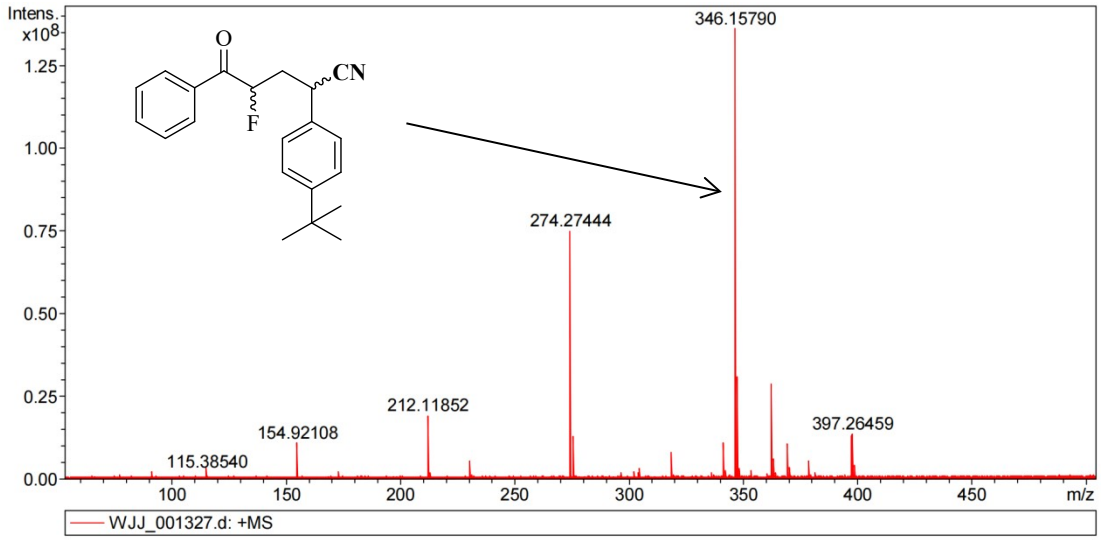
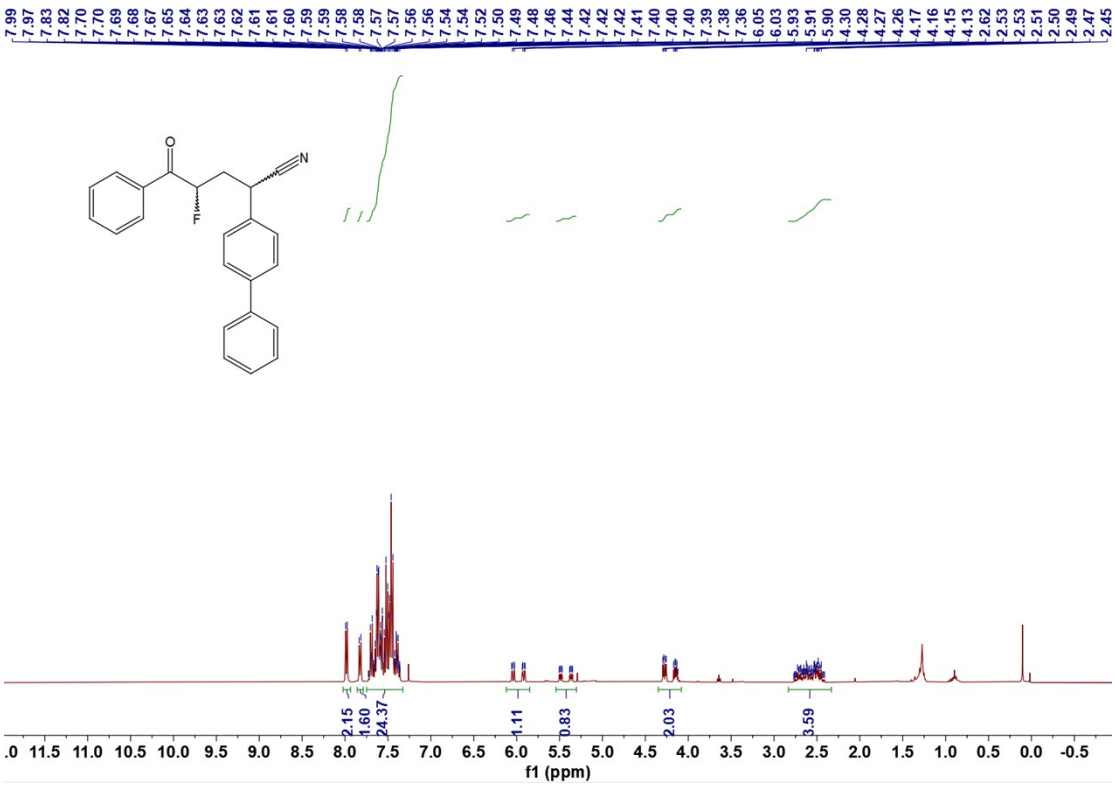


HRMS of 3ae



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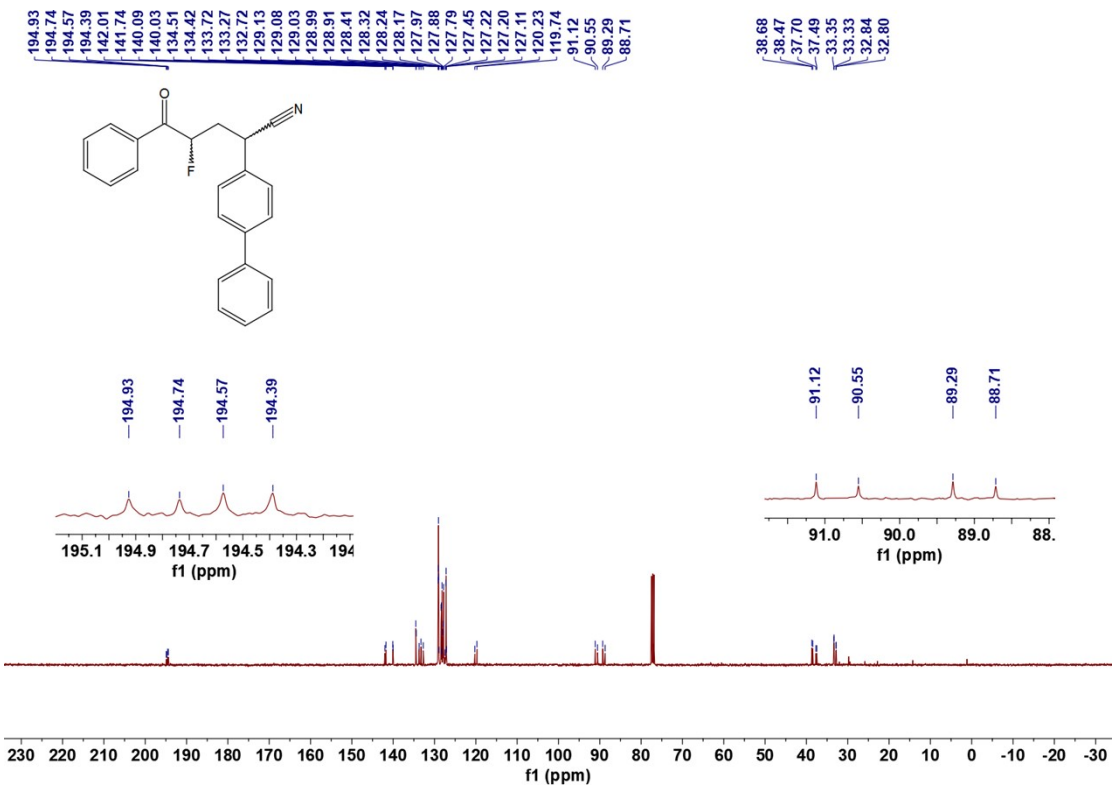

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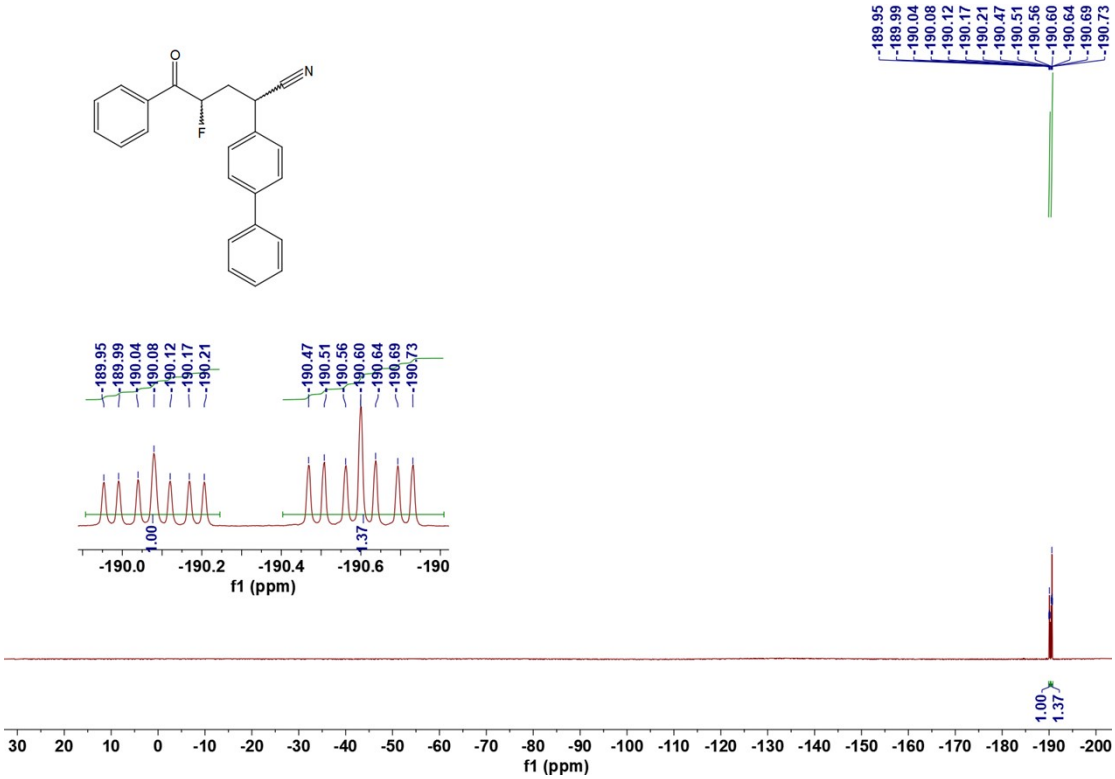

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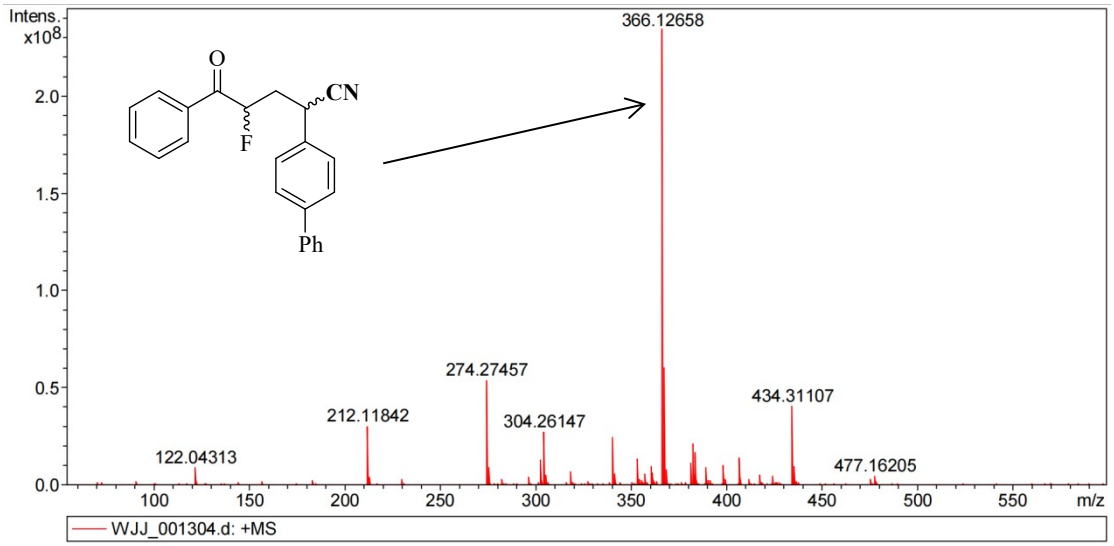

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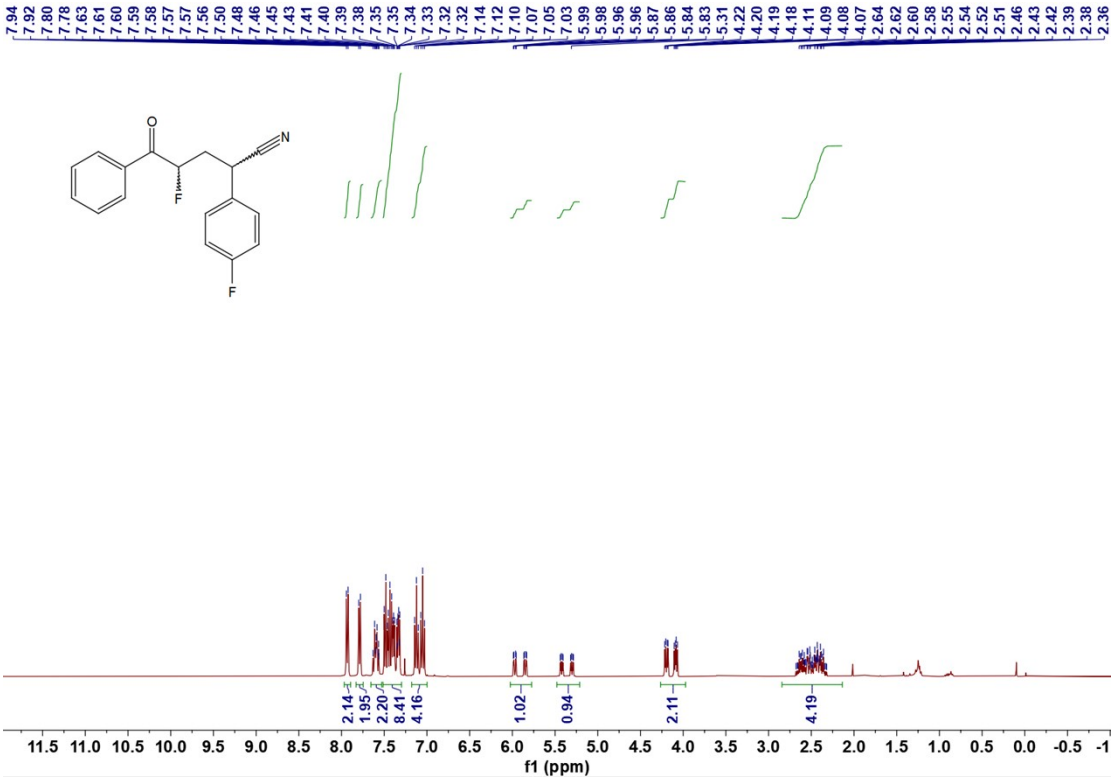

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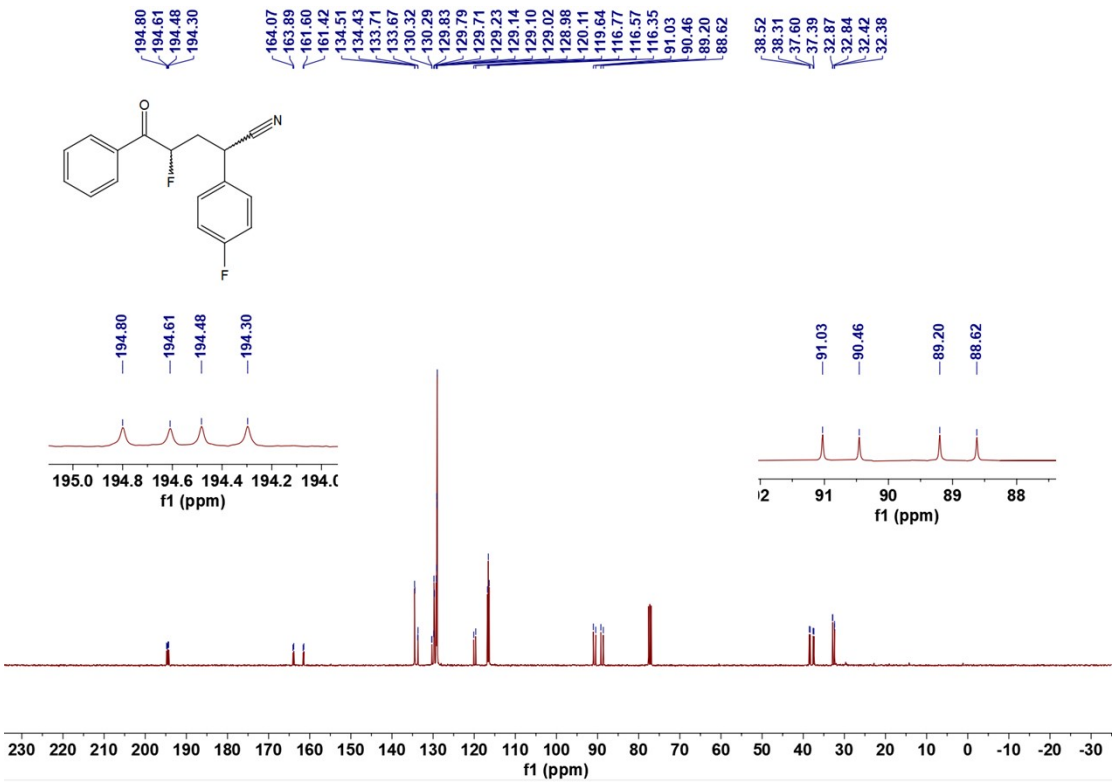

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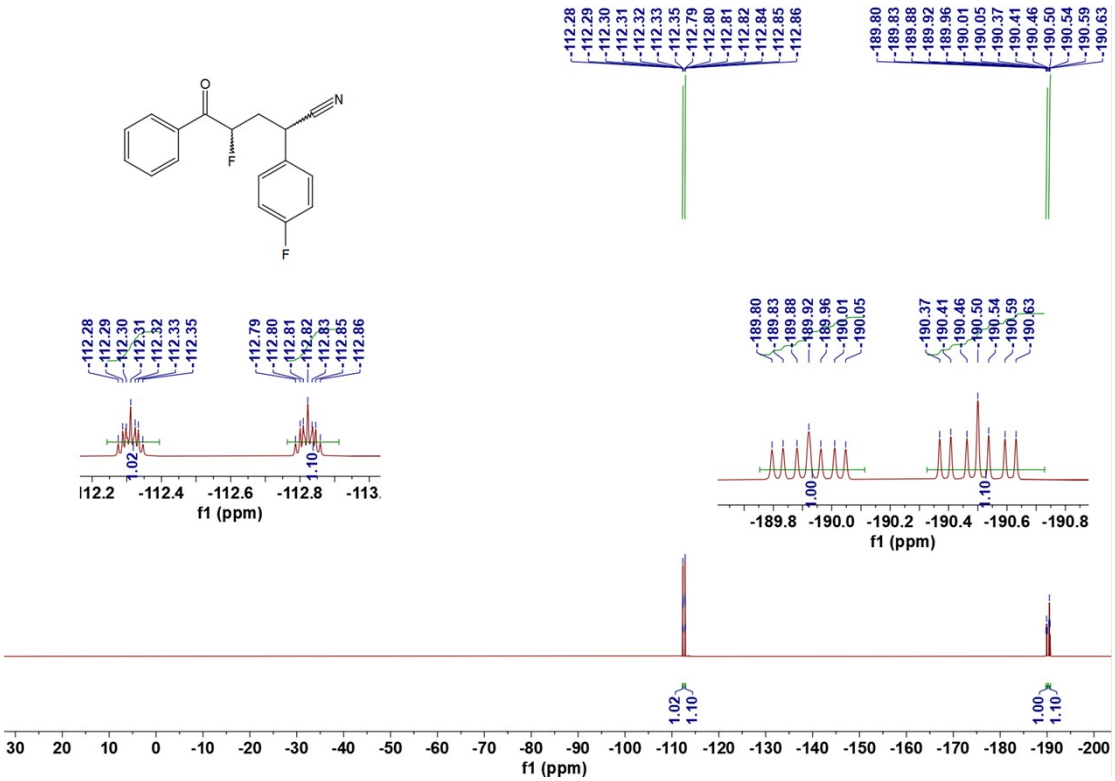

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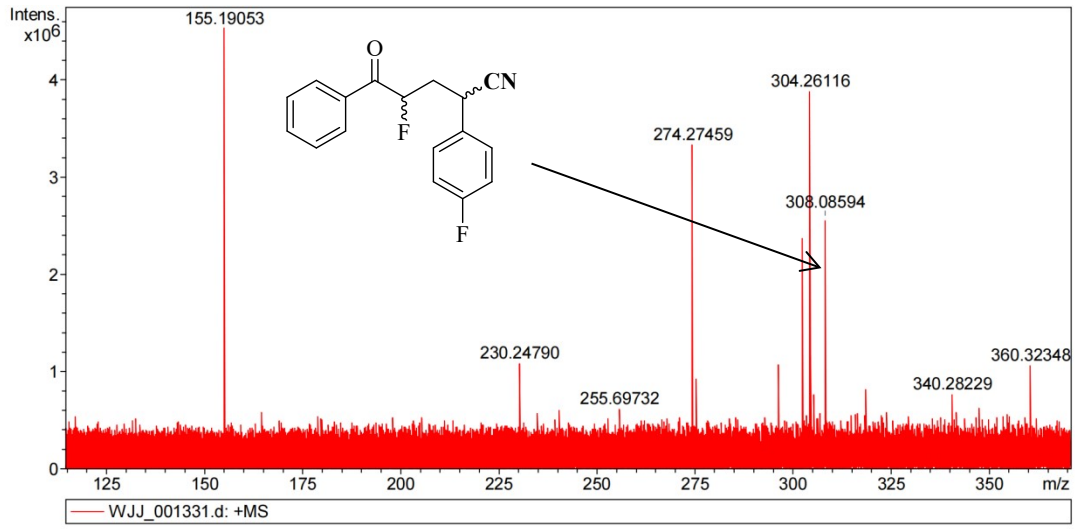
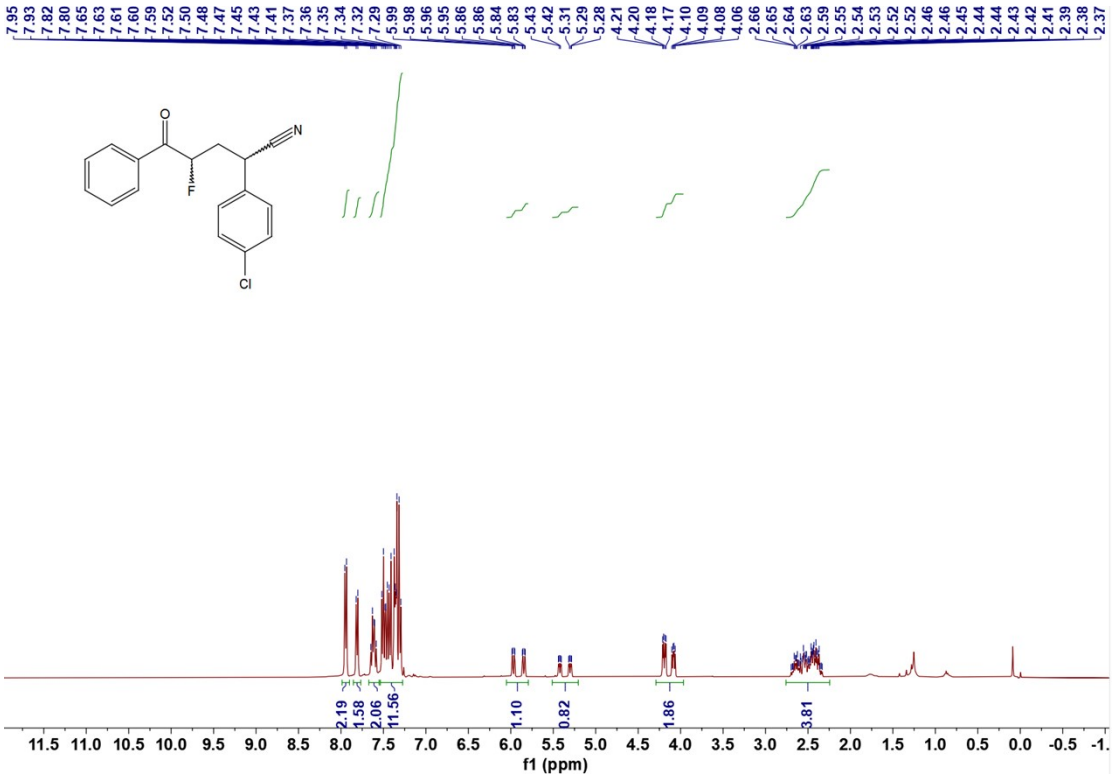
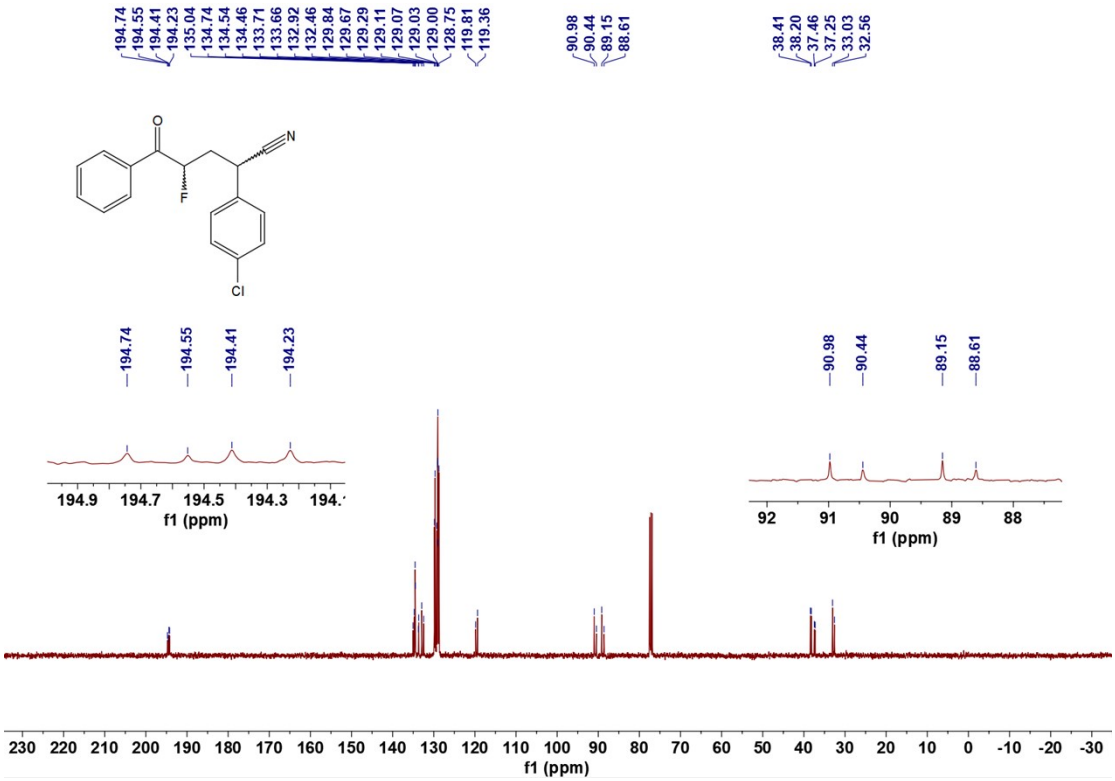


HRMS of 3ag



^{1}H NMR of 3ah



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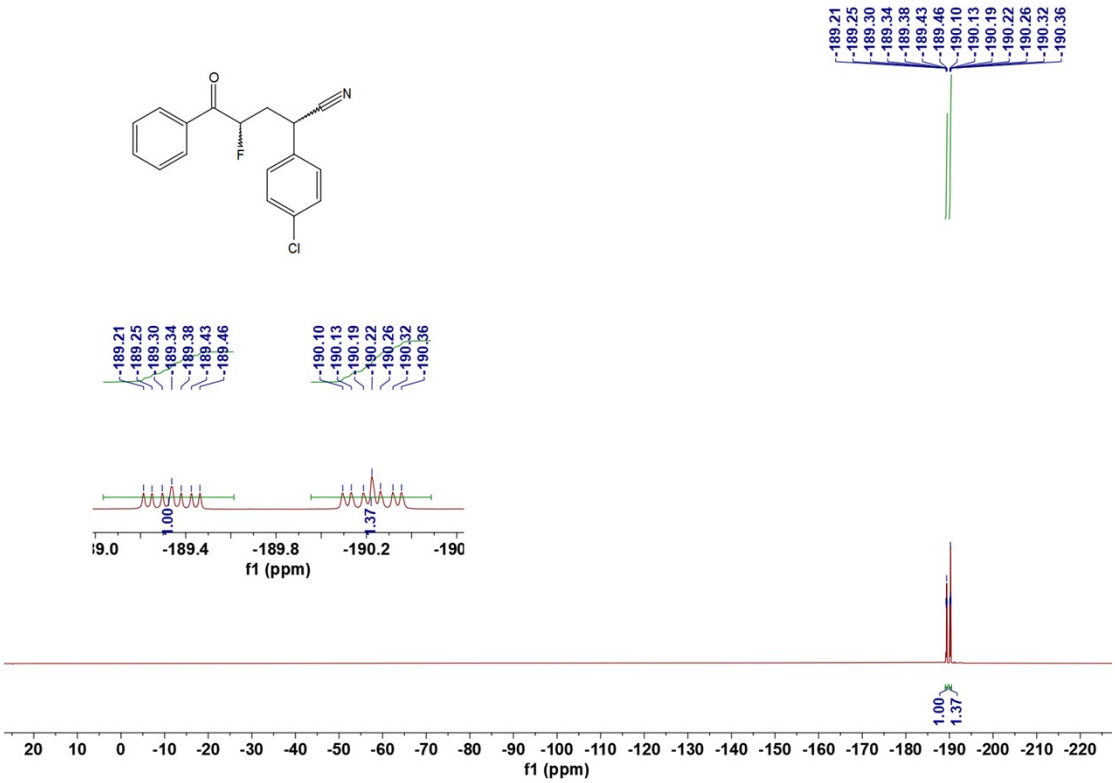
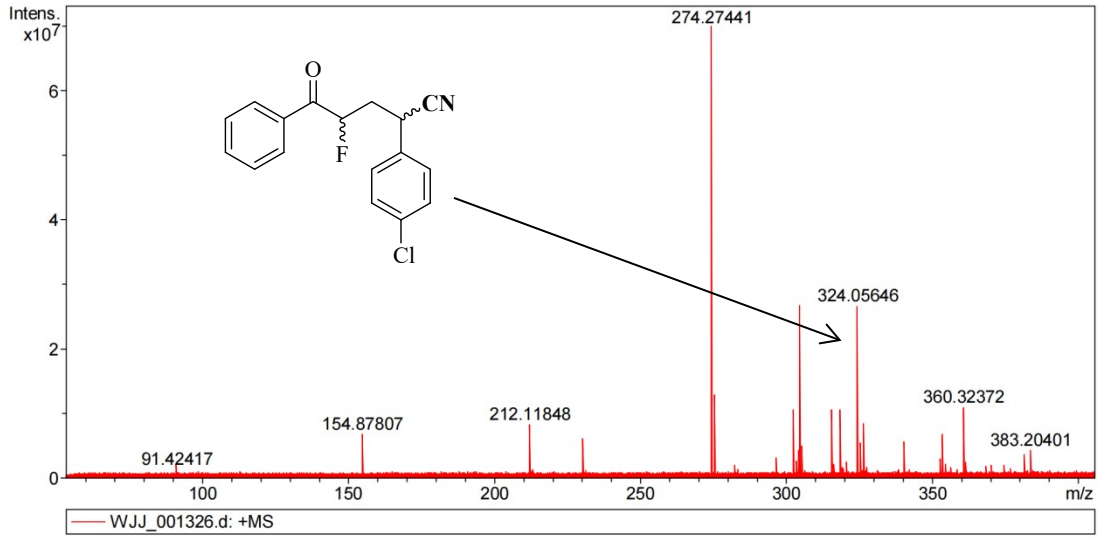
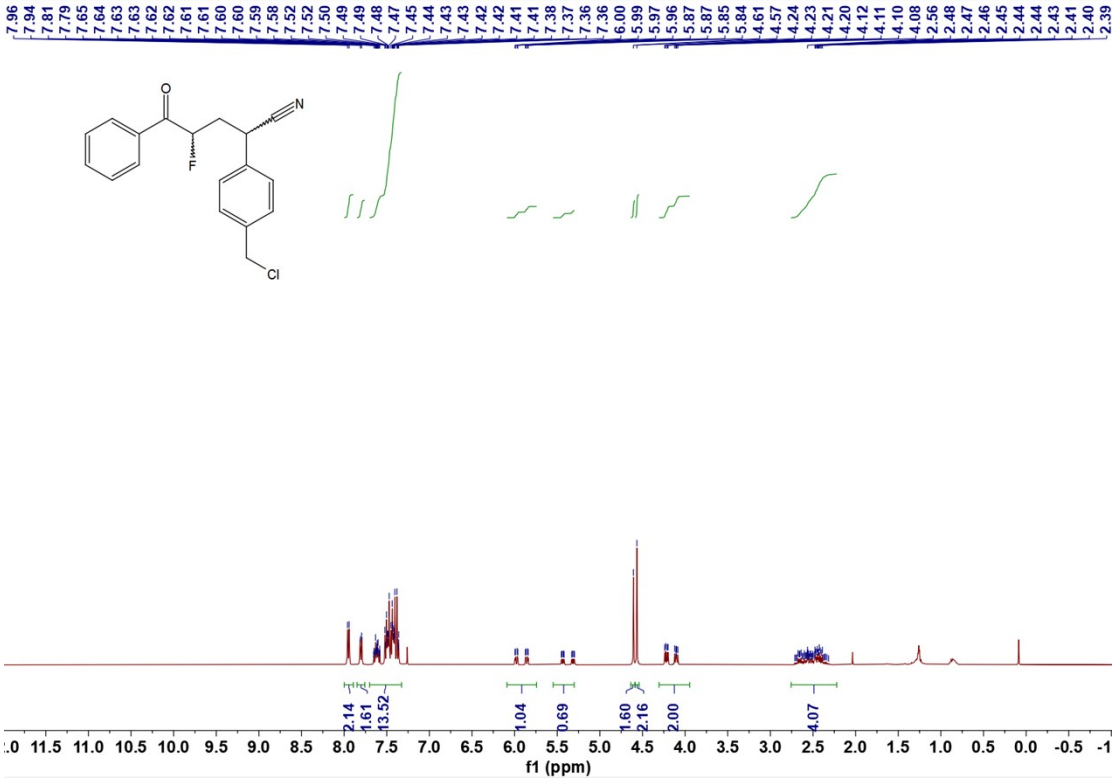


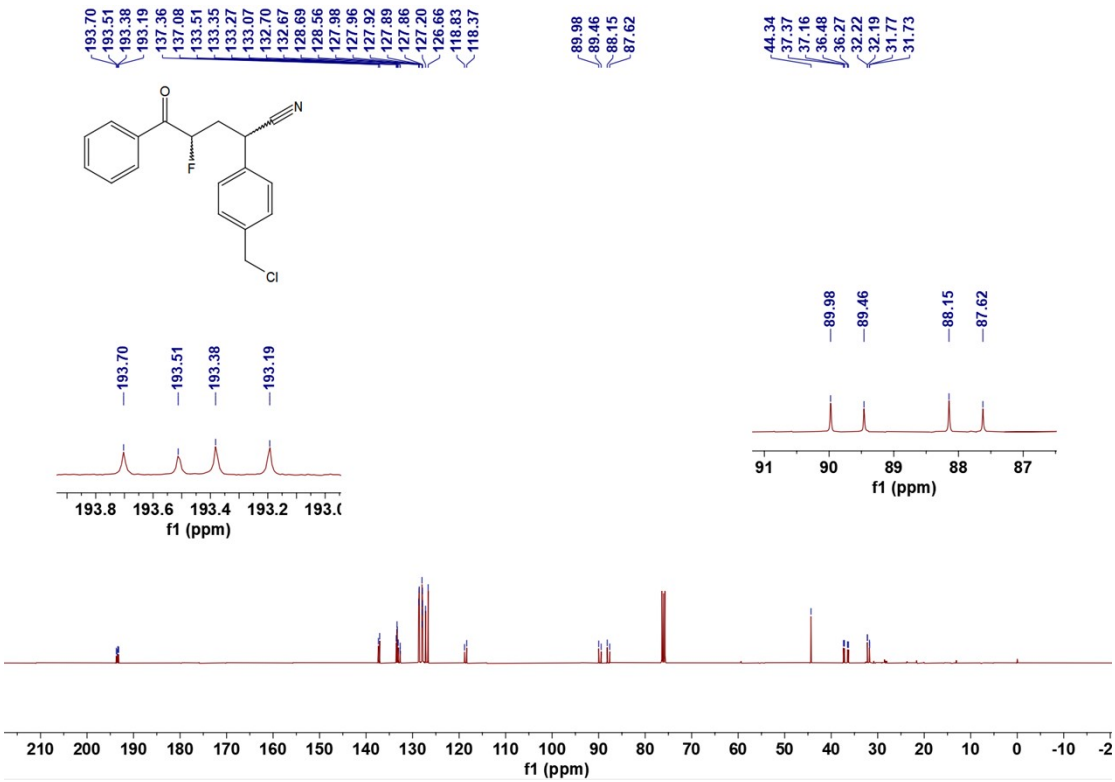
^{19}F NMR of 3ah



HRMS of 3ah



^{1}H NMR of 3ai



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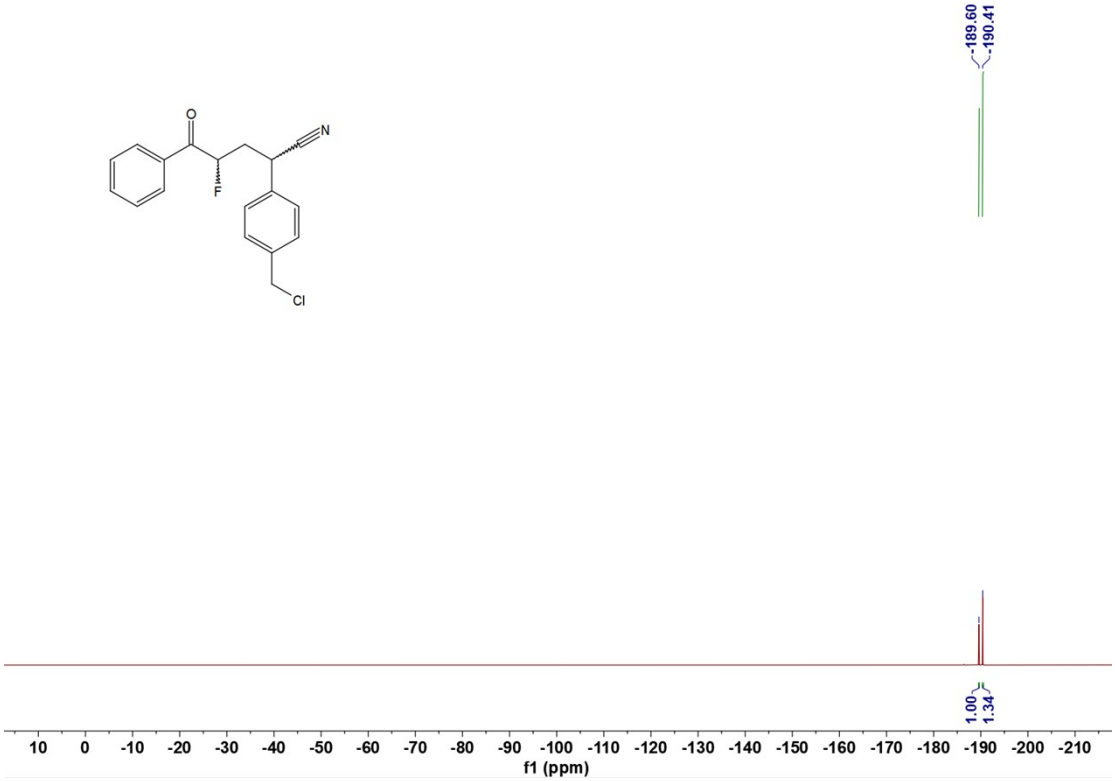

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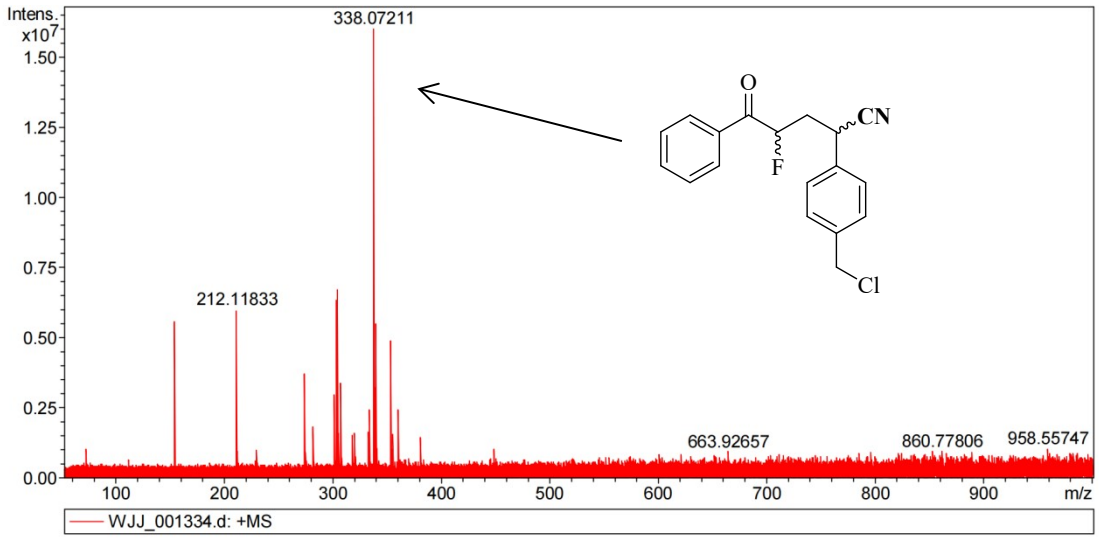
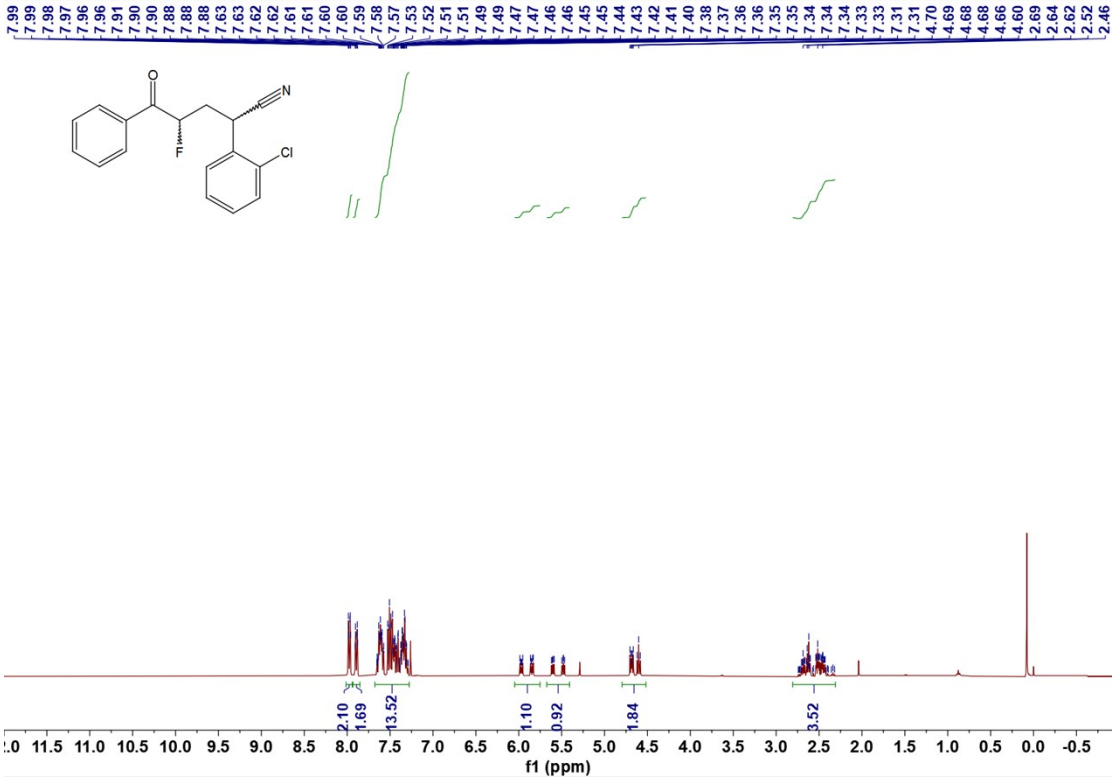


HRMS of 3ai



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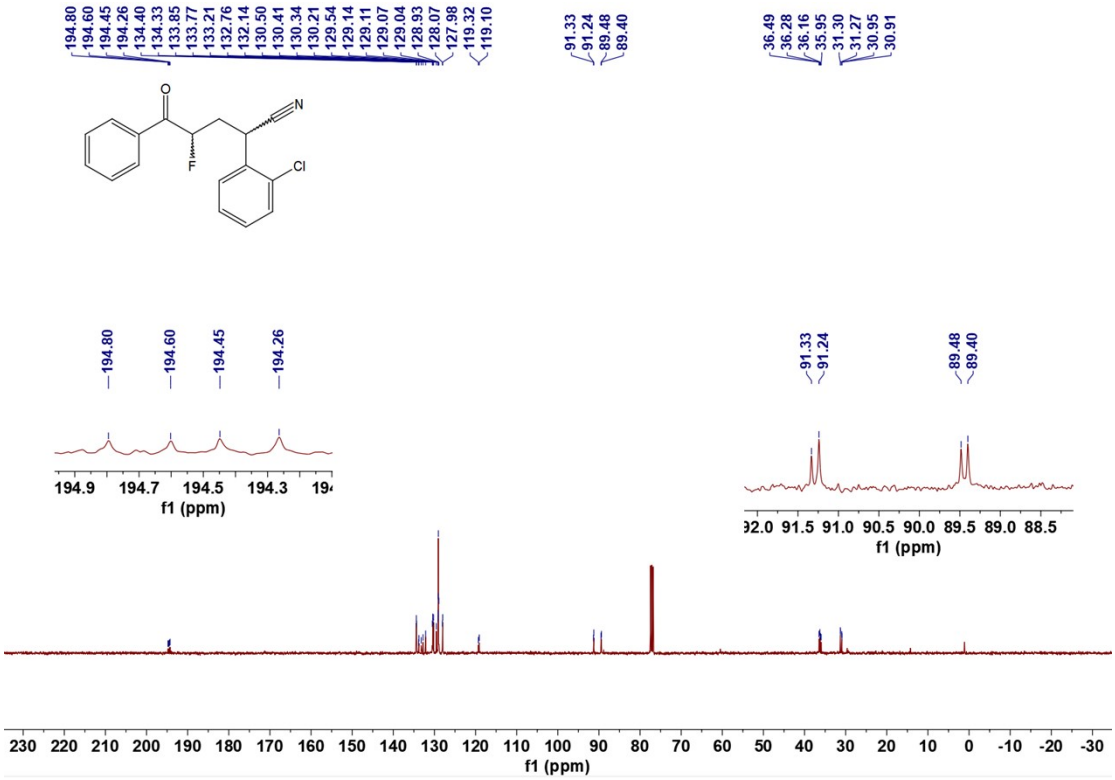

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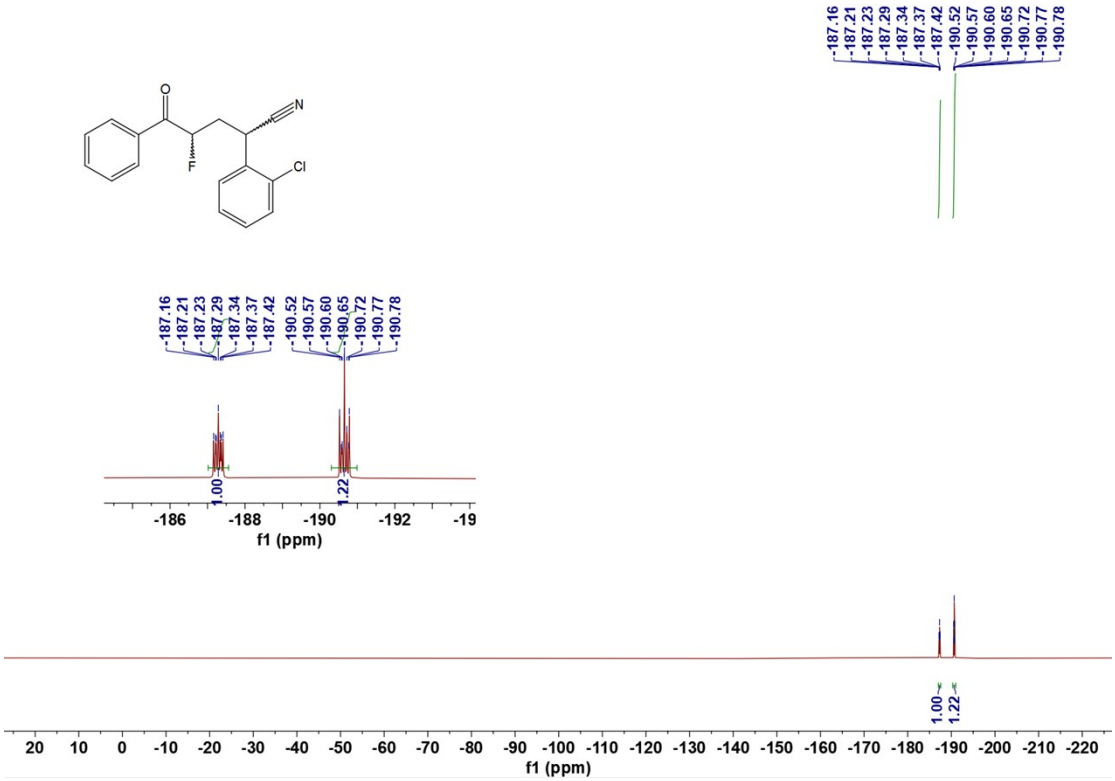

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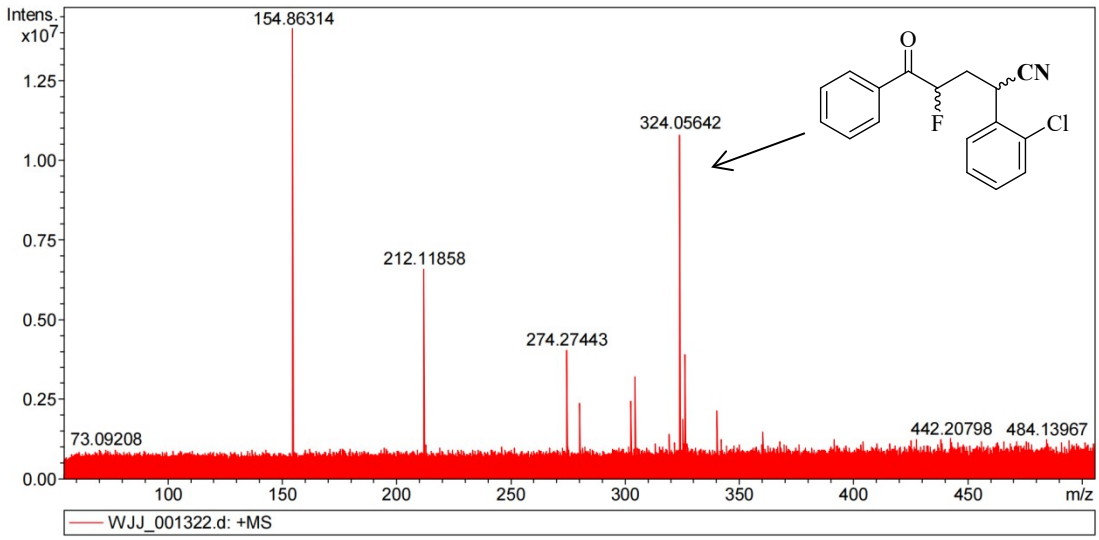
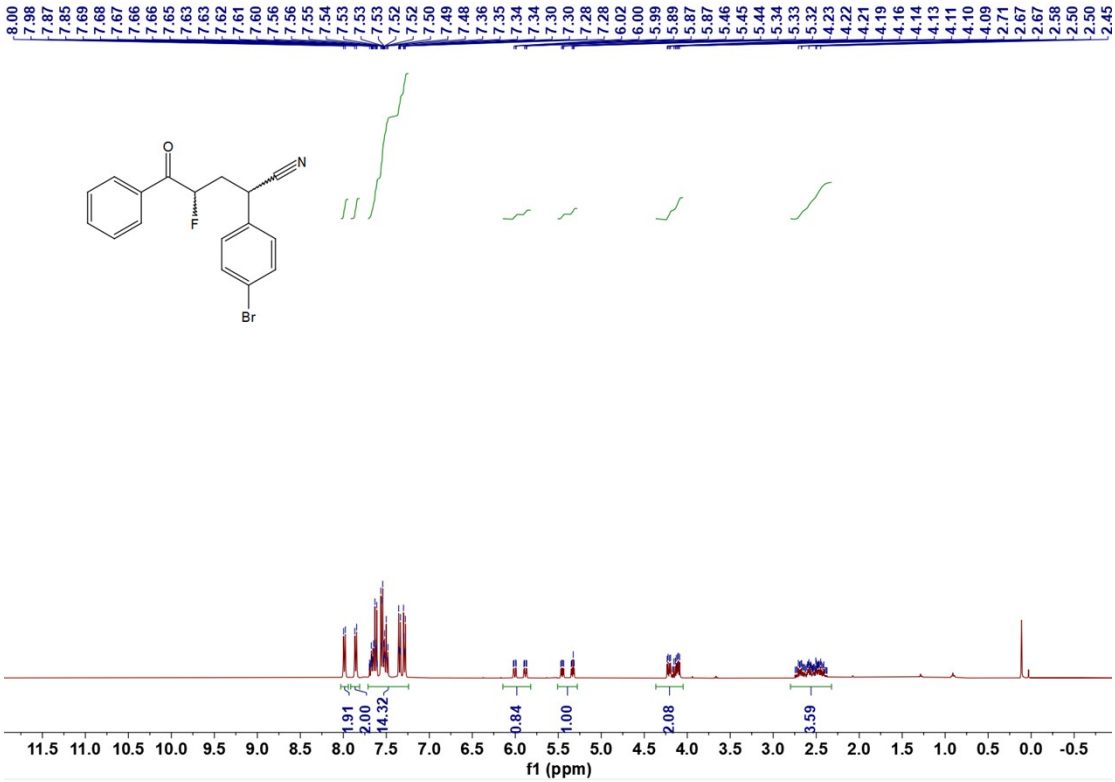
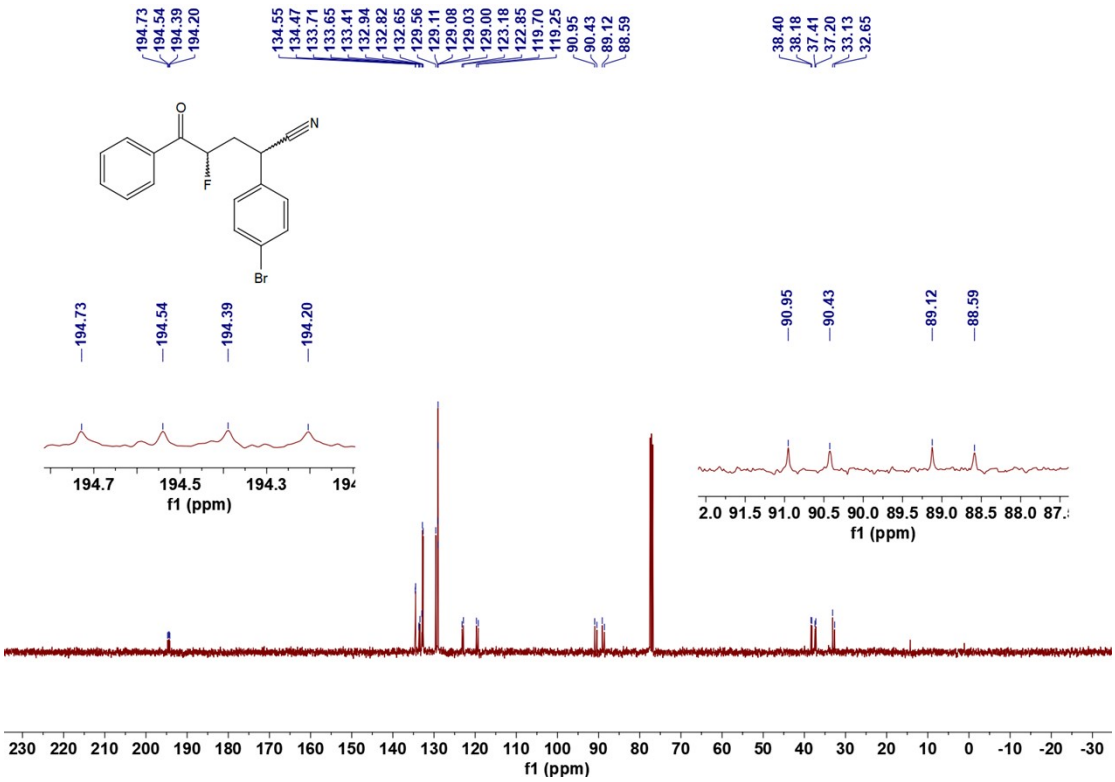


HRMS of 3aj



^{1}H NMR of 3ak



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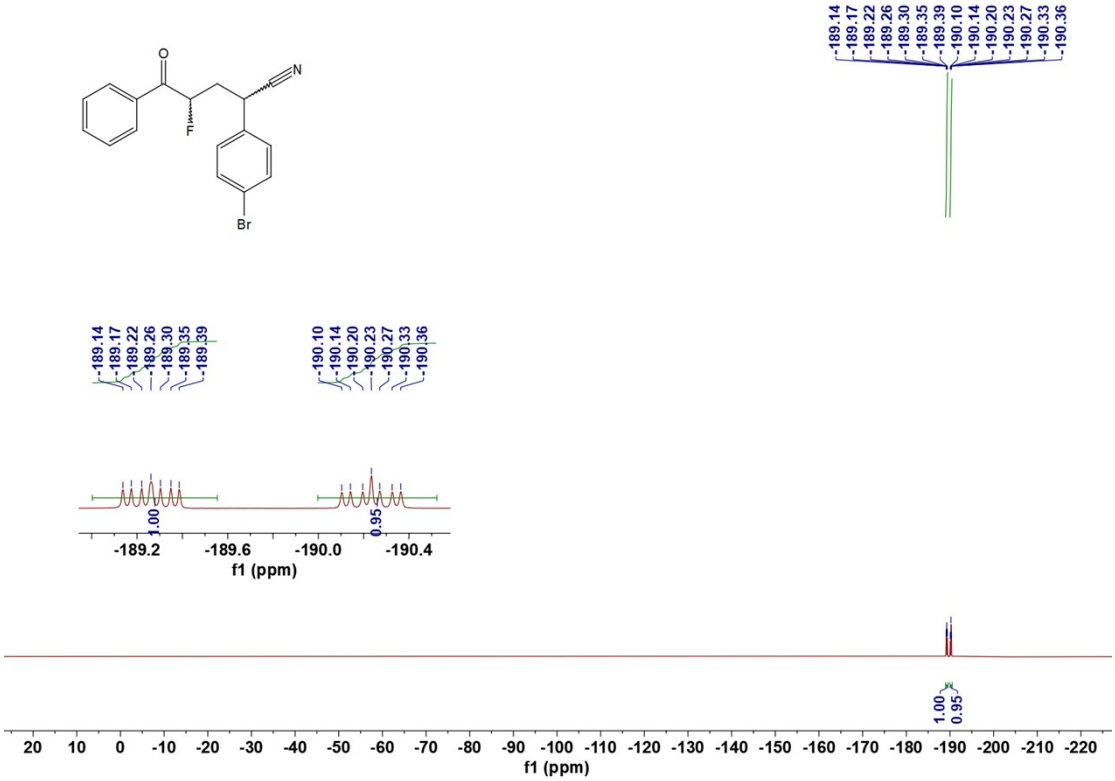

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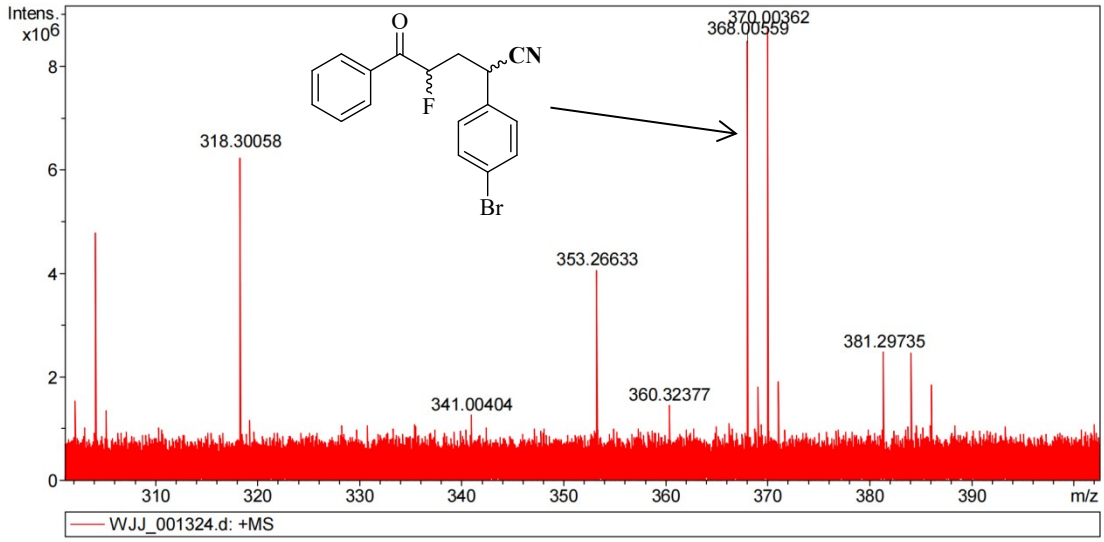
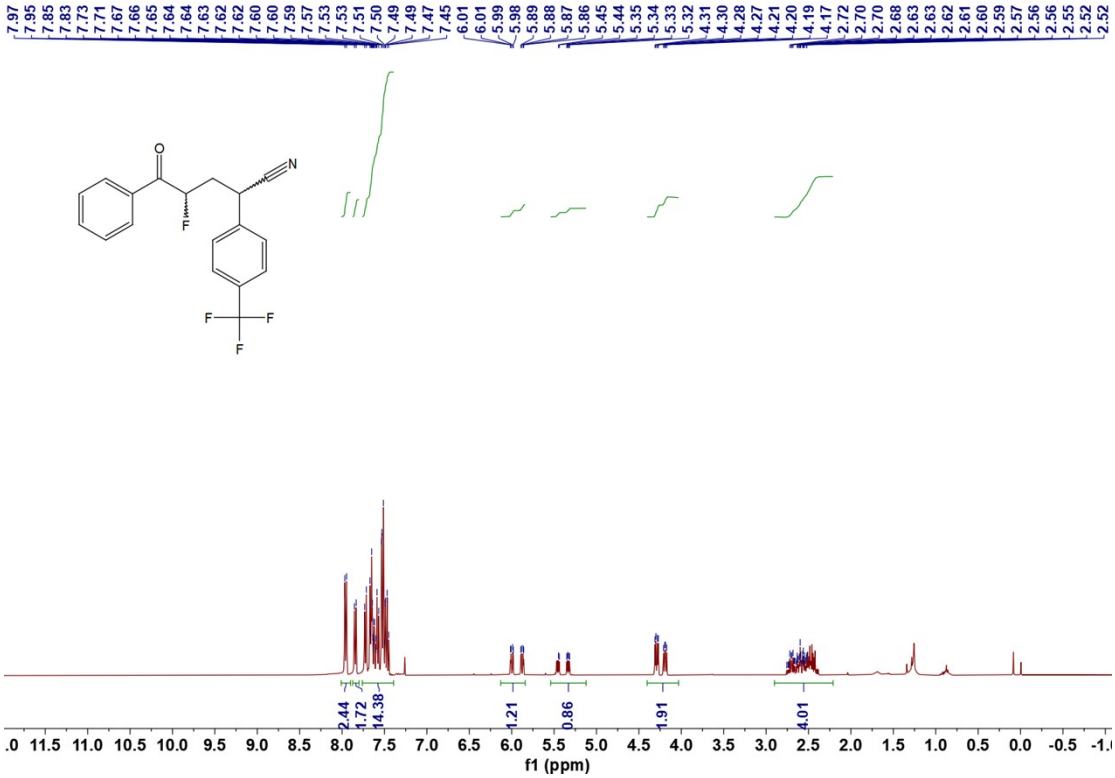


HRMS of 3ak



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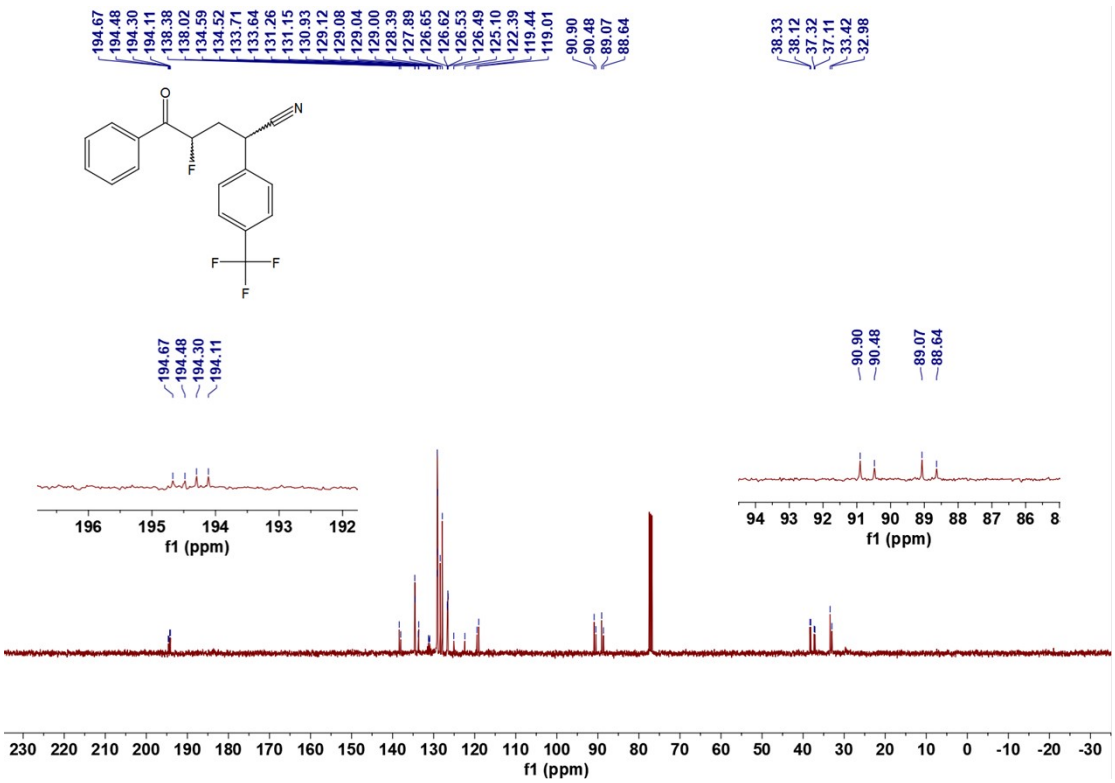

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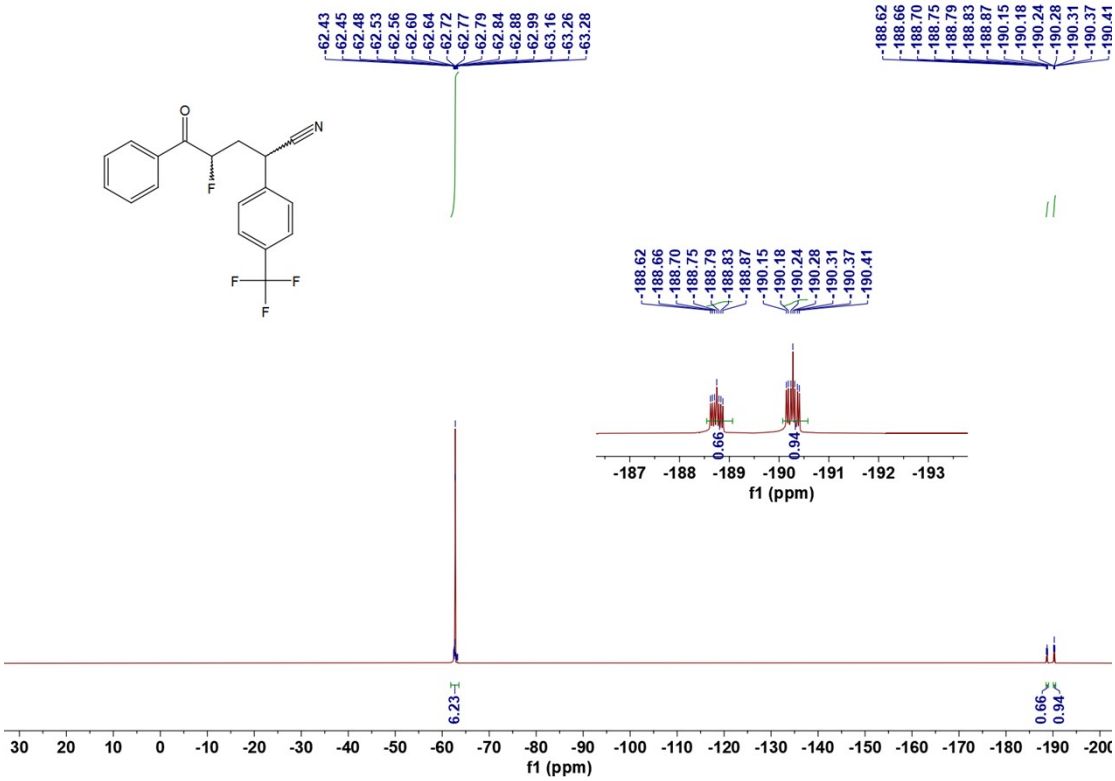

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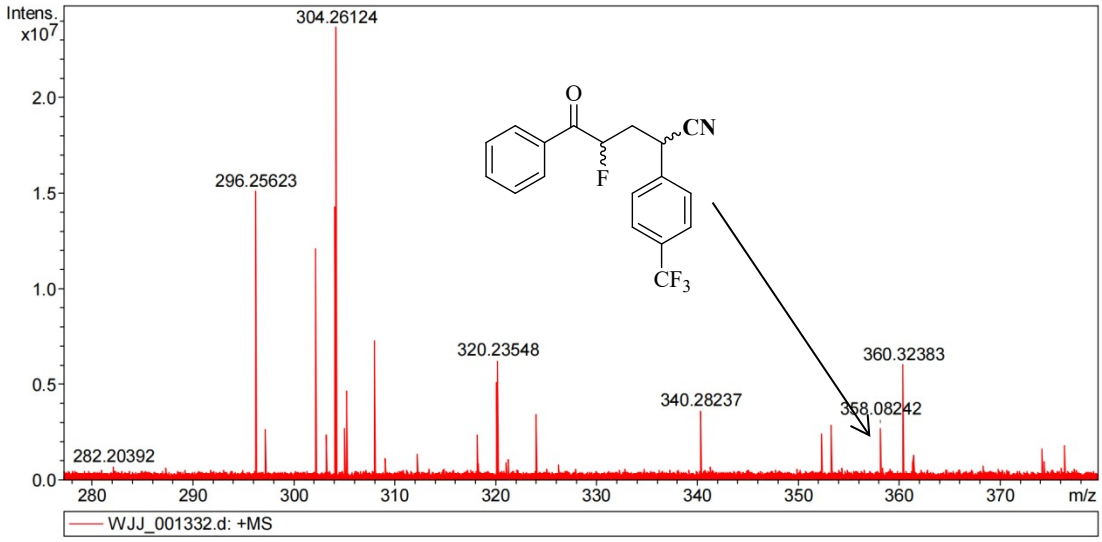
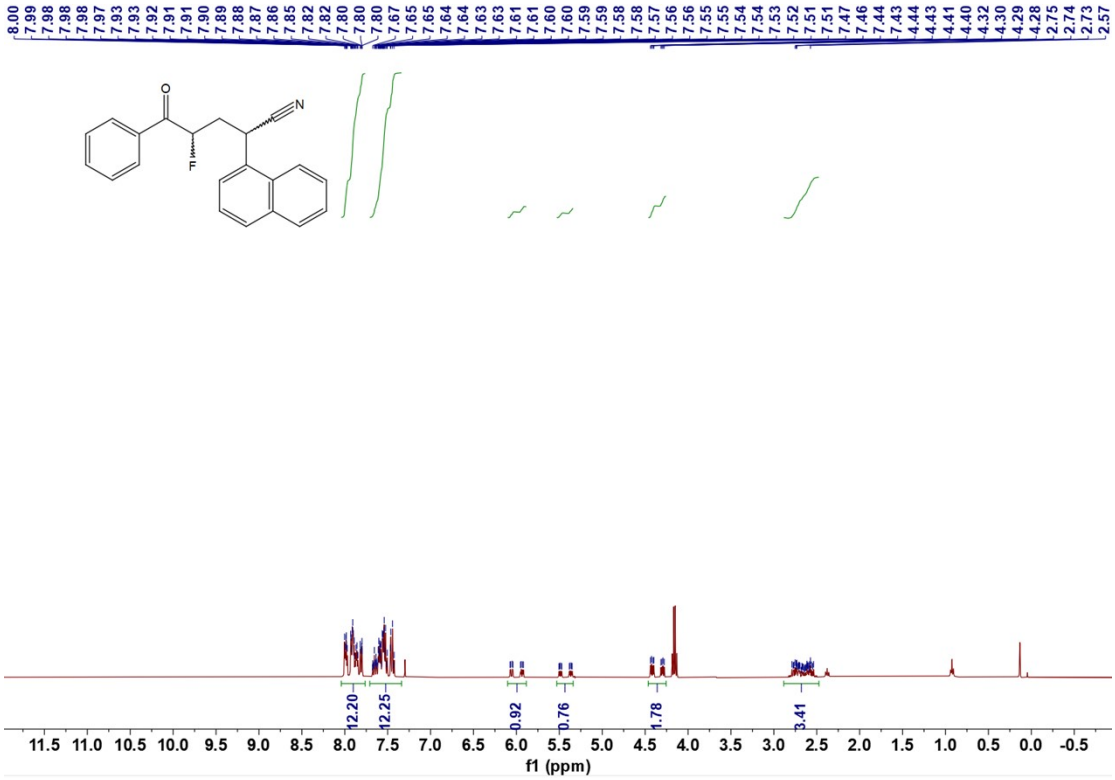
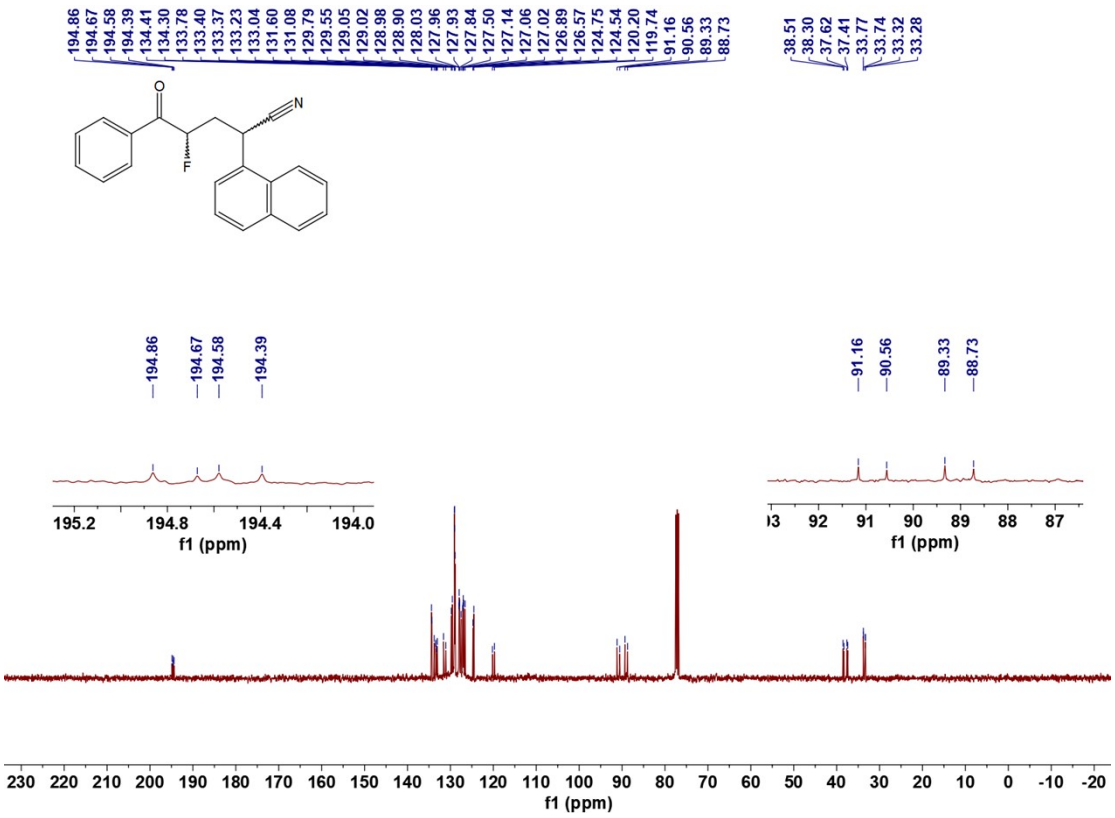


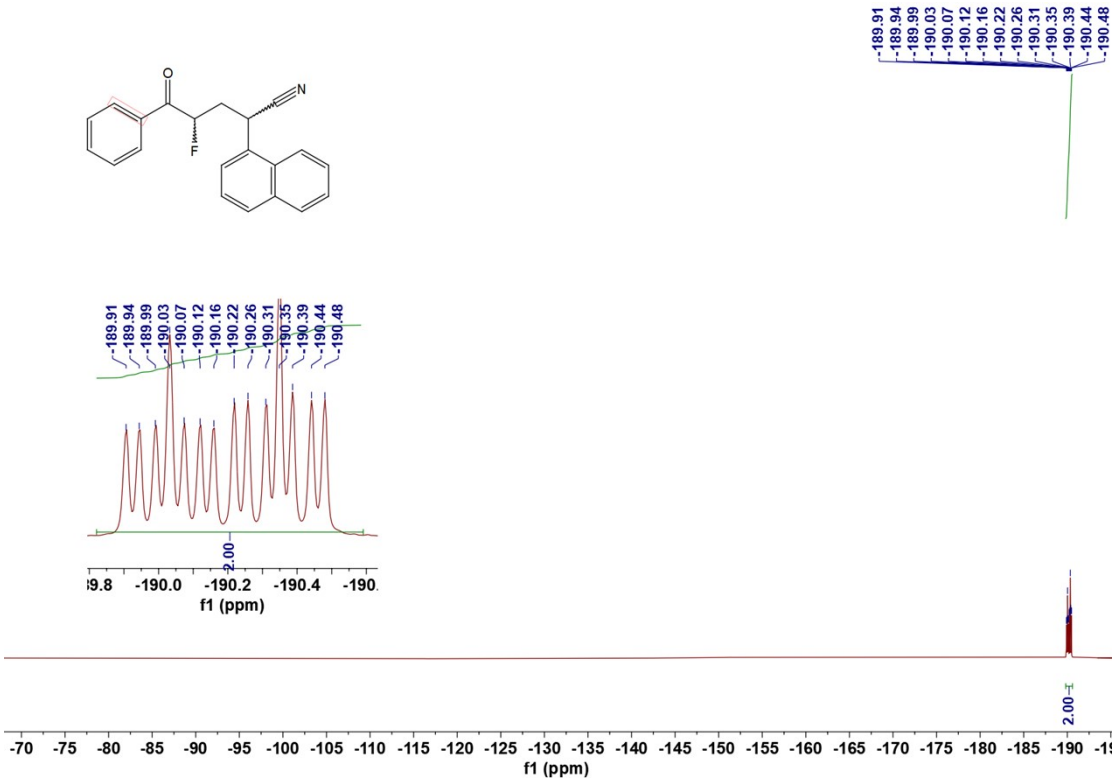
HRMS of 3al



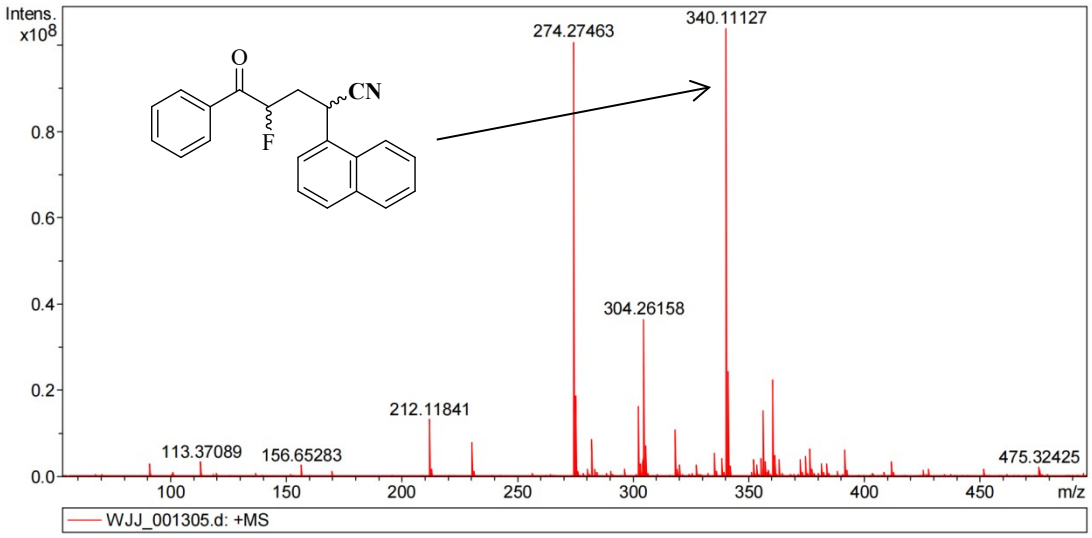
^{1}H NMR of 3am



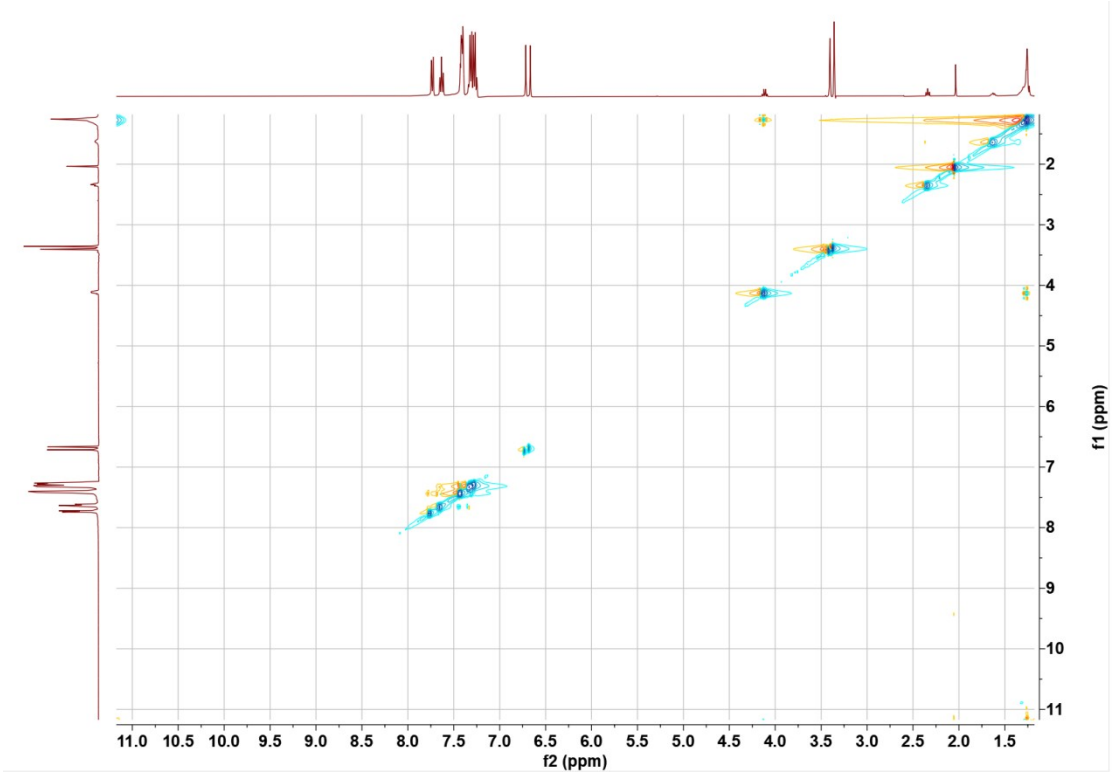
^{13}C NMR of 3am



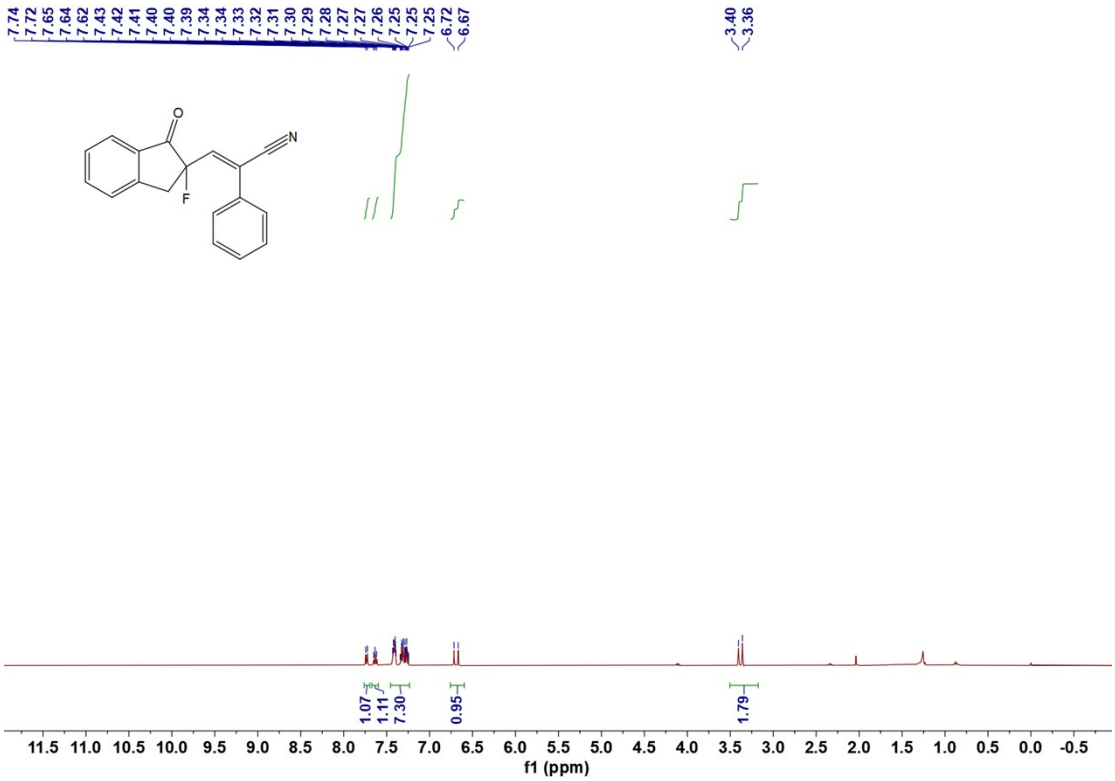
^{19}F NMR of 3am



HRMS of 3am



NOE of 5a



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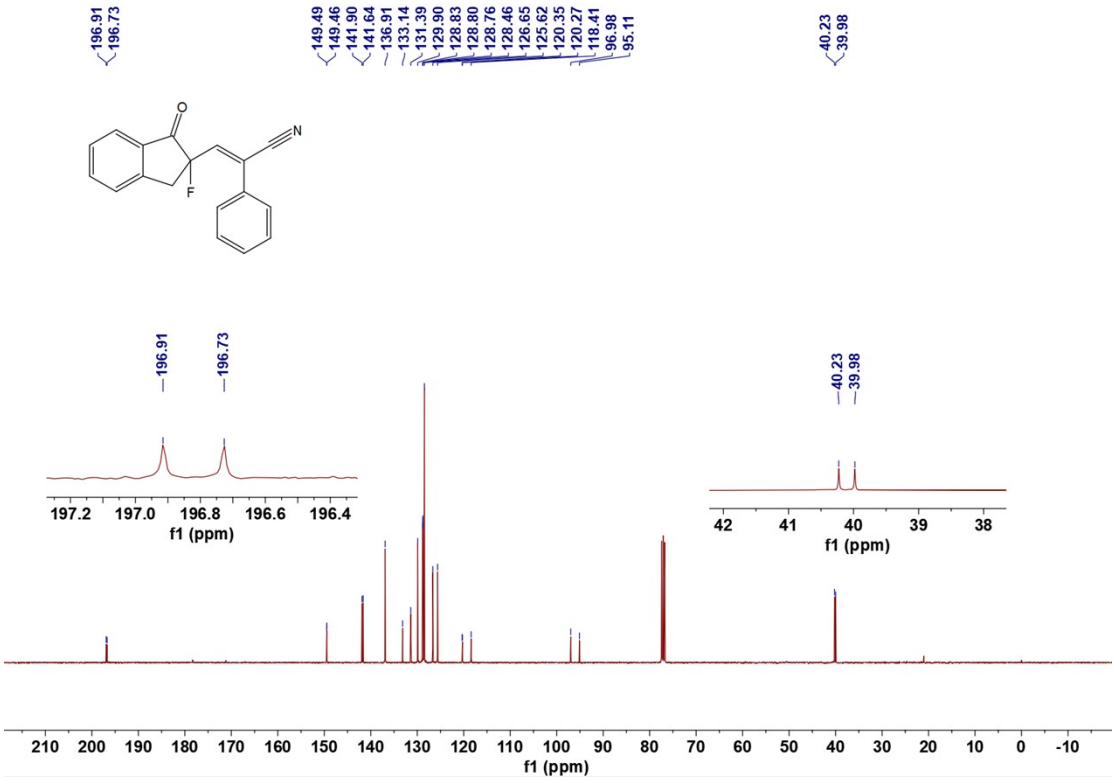

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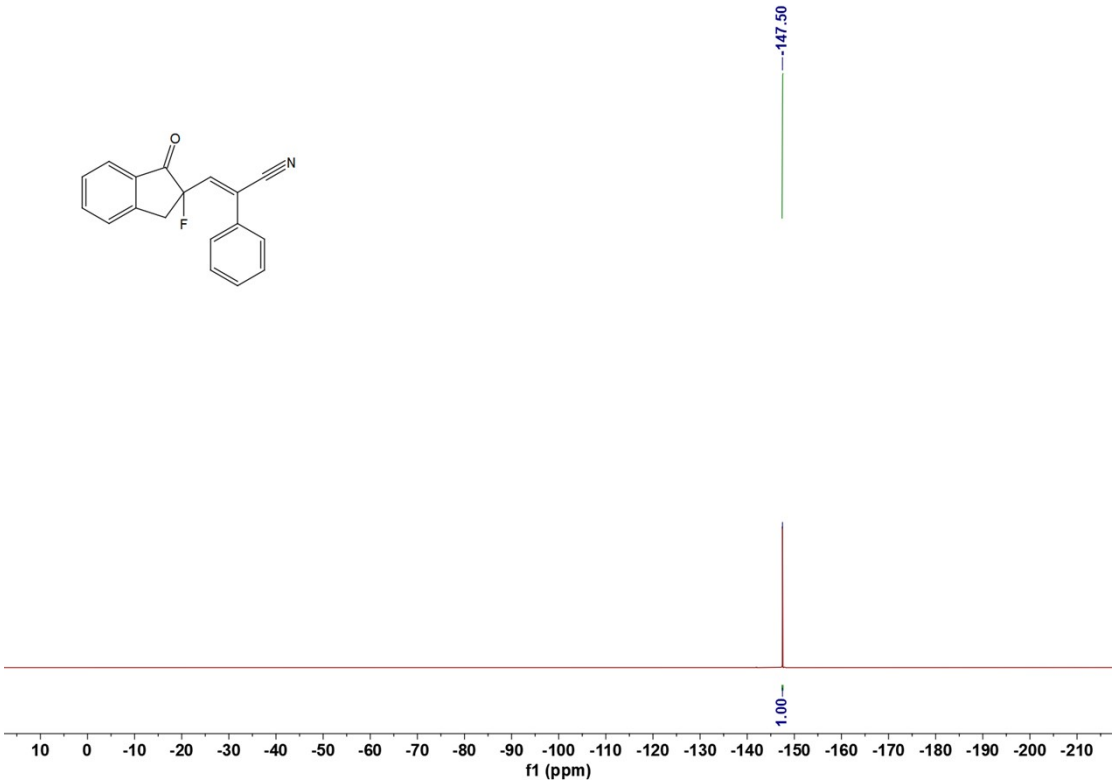
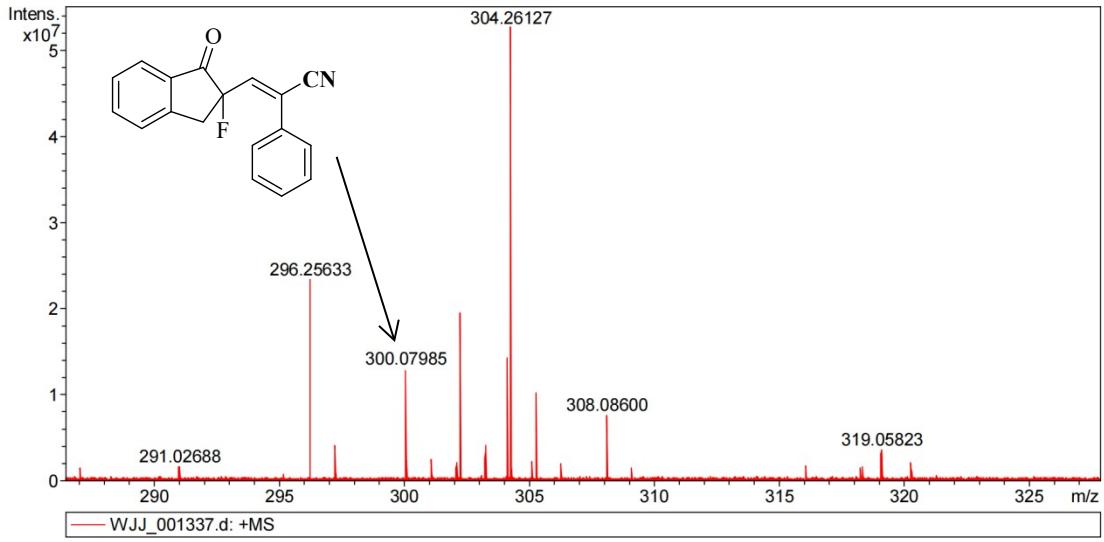
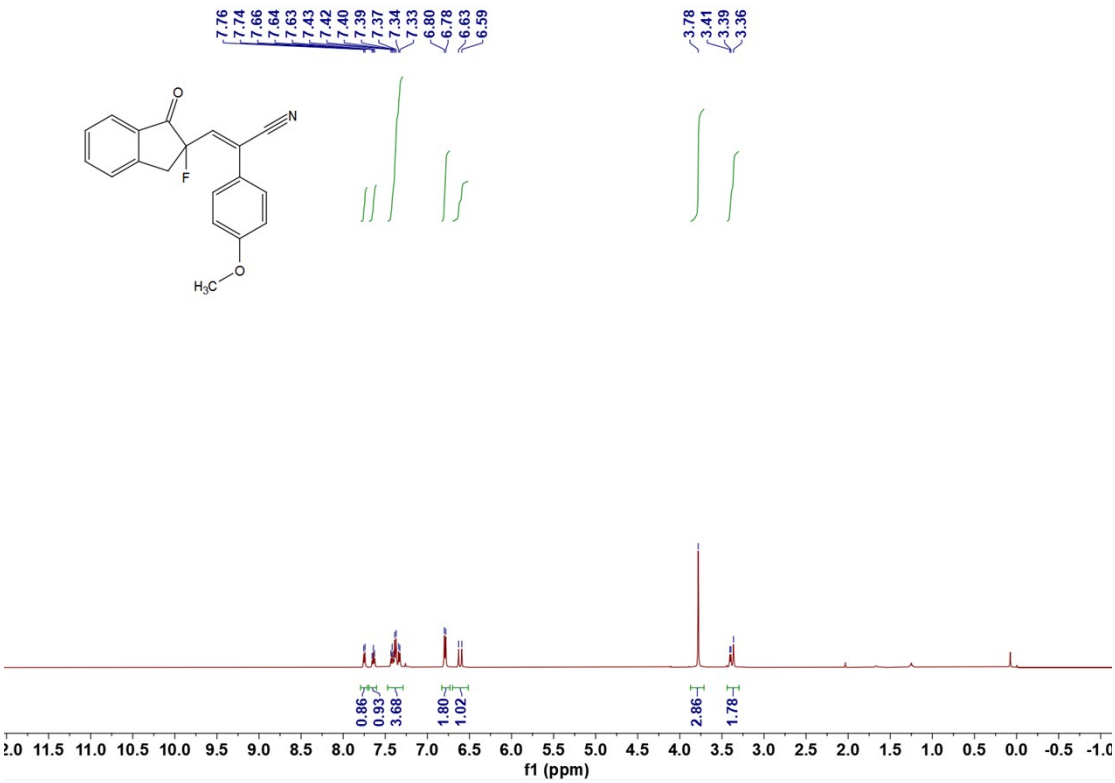


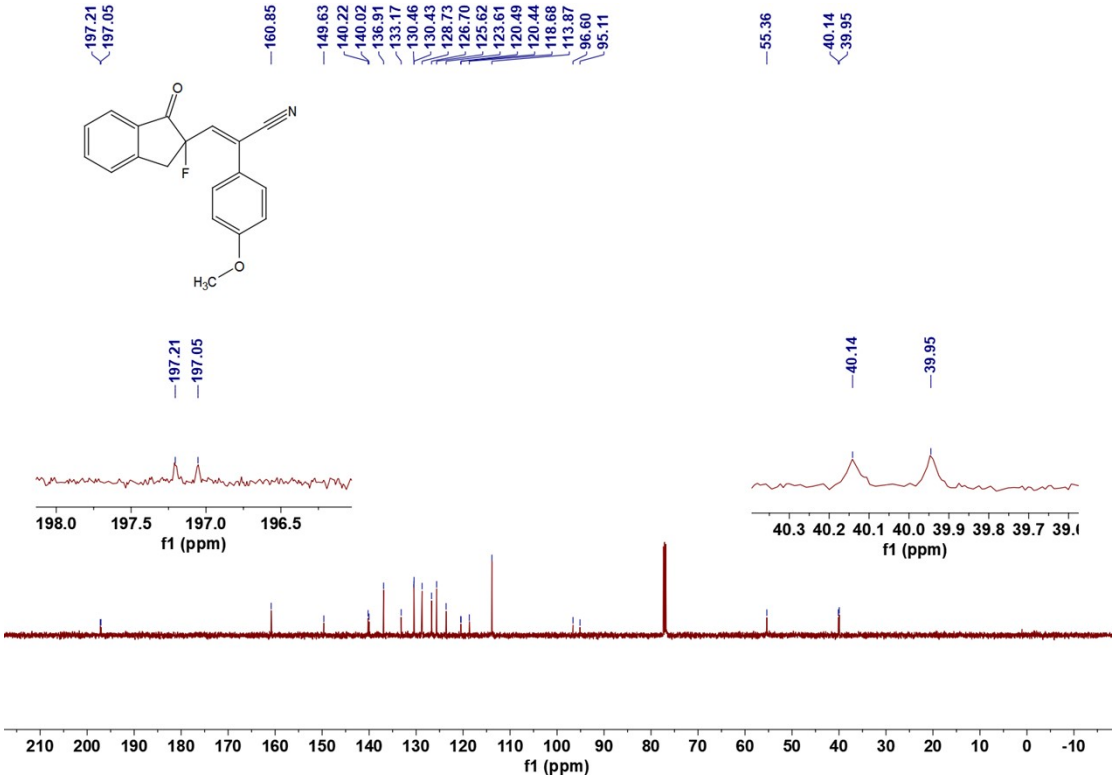
^{19}F NMR of 5a



HRMS of 5a



^{1}H NMR of 5b



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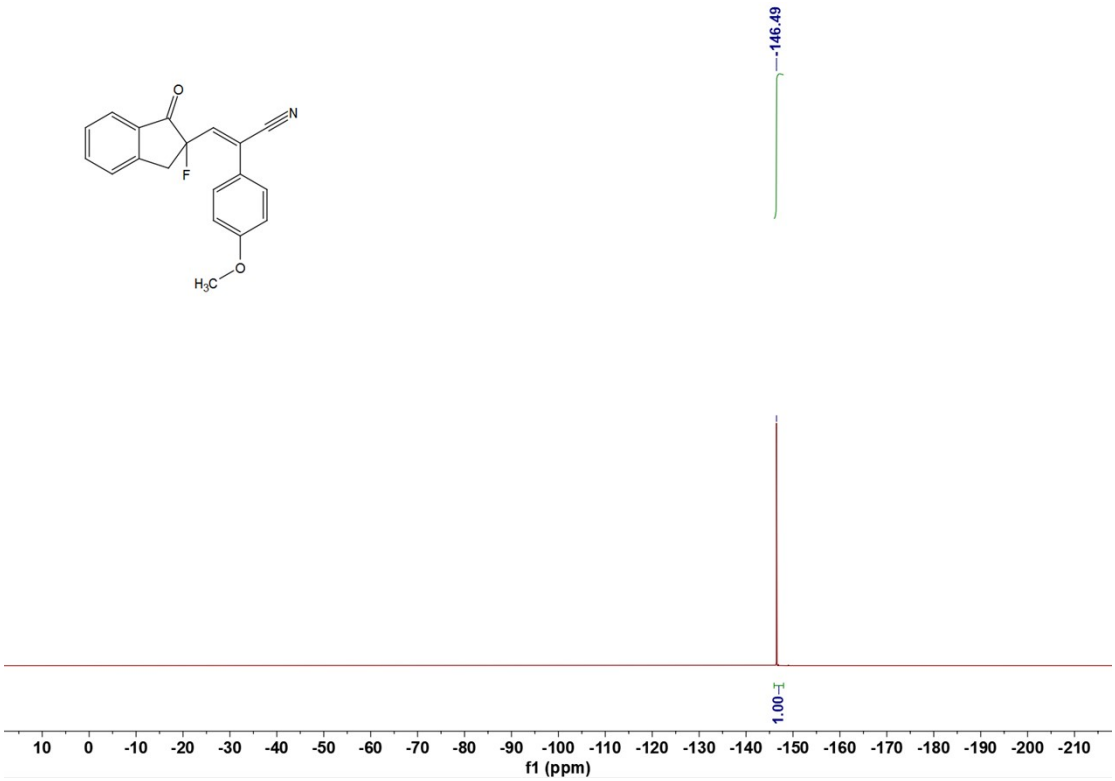

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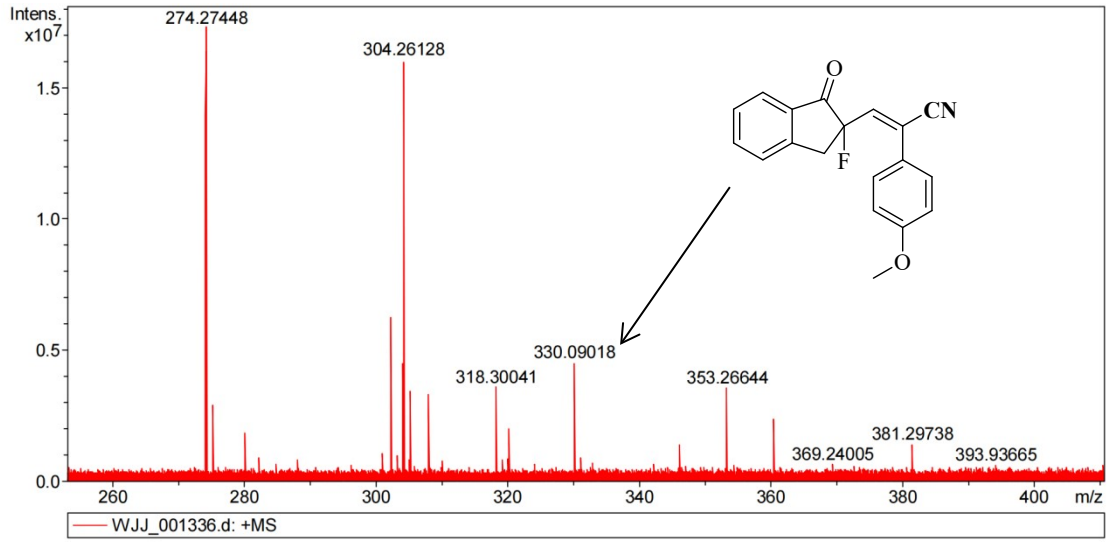

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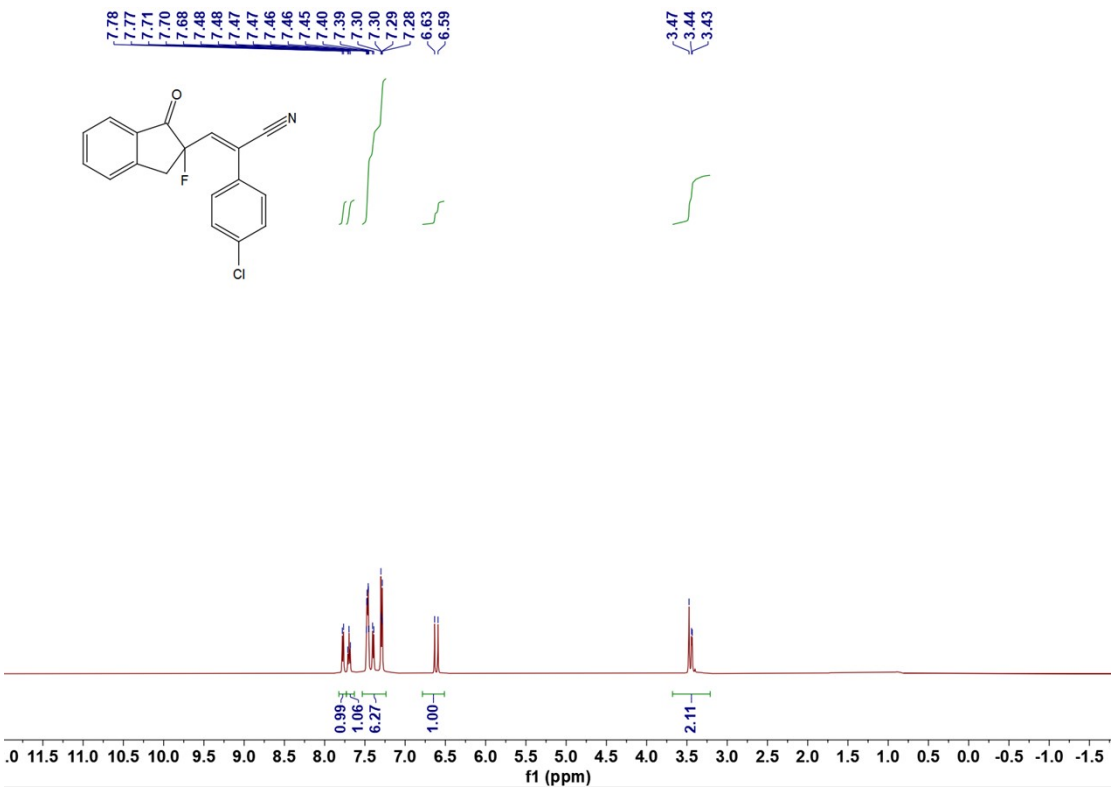

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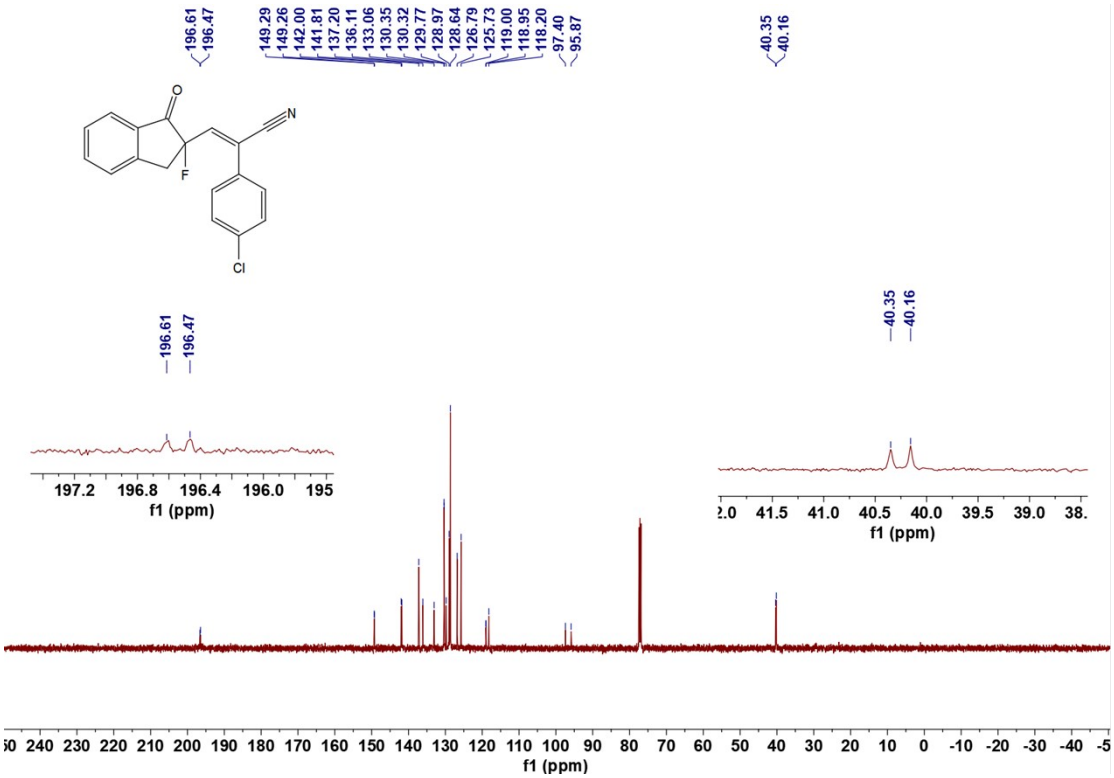

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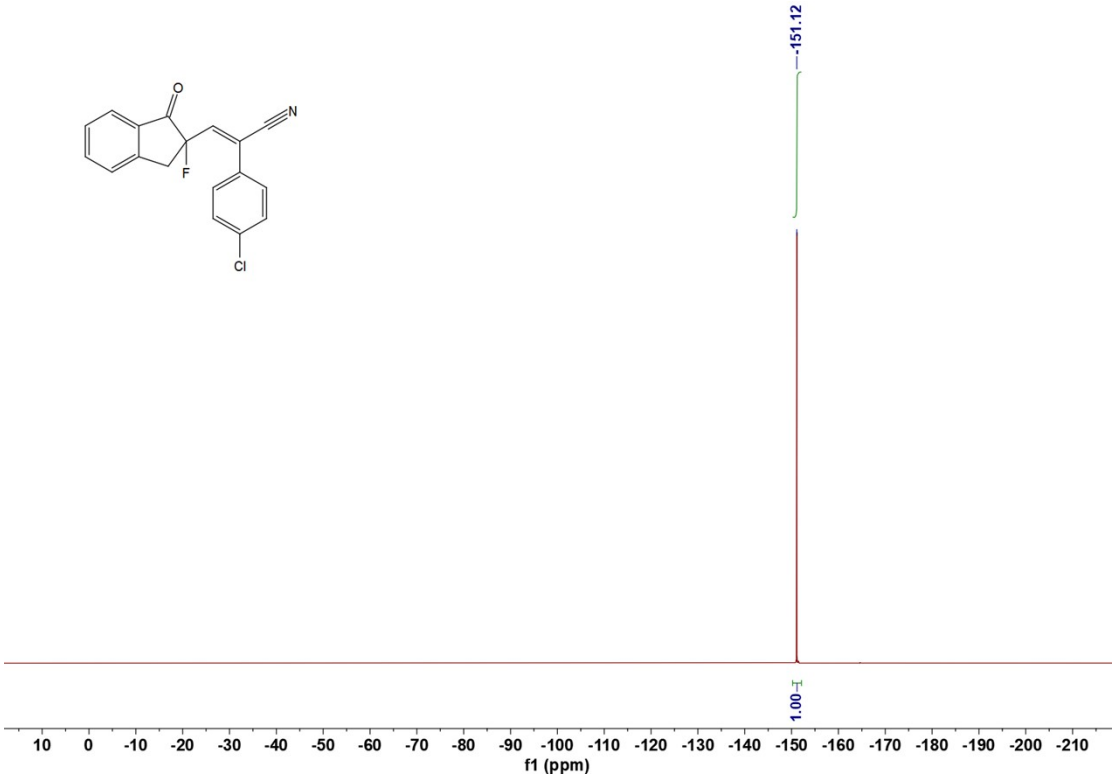

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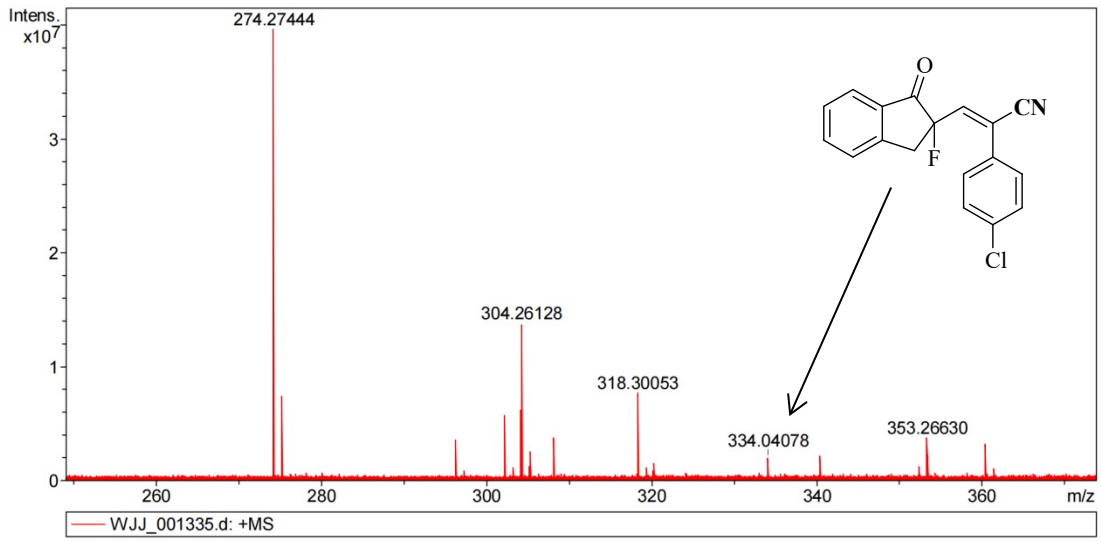

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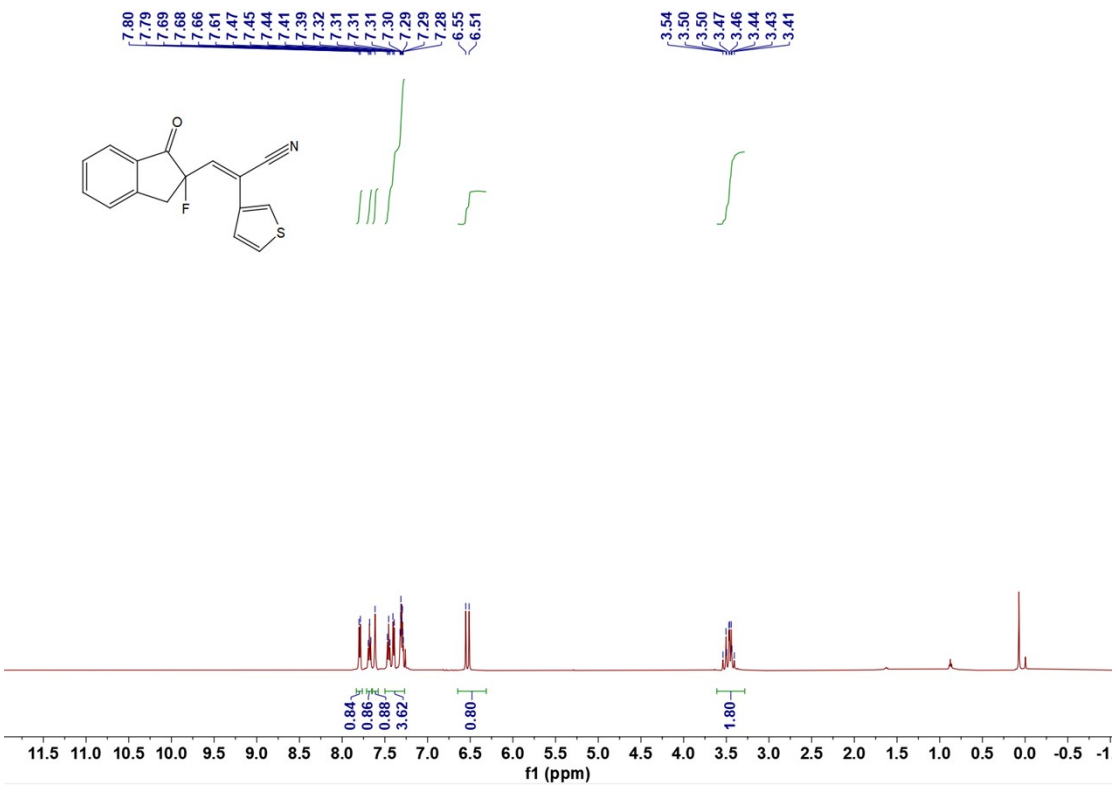
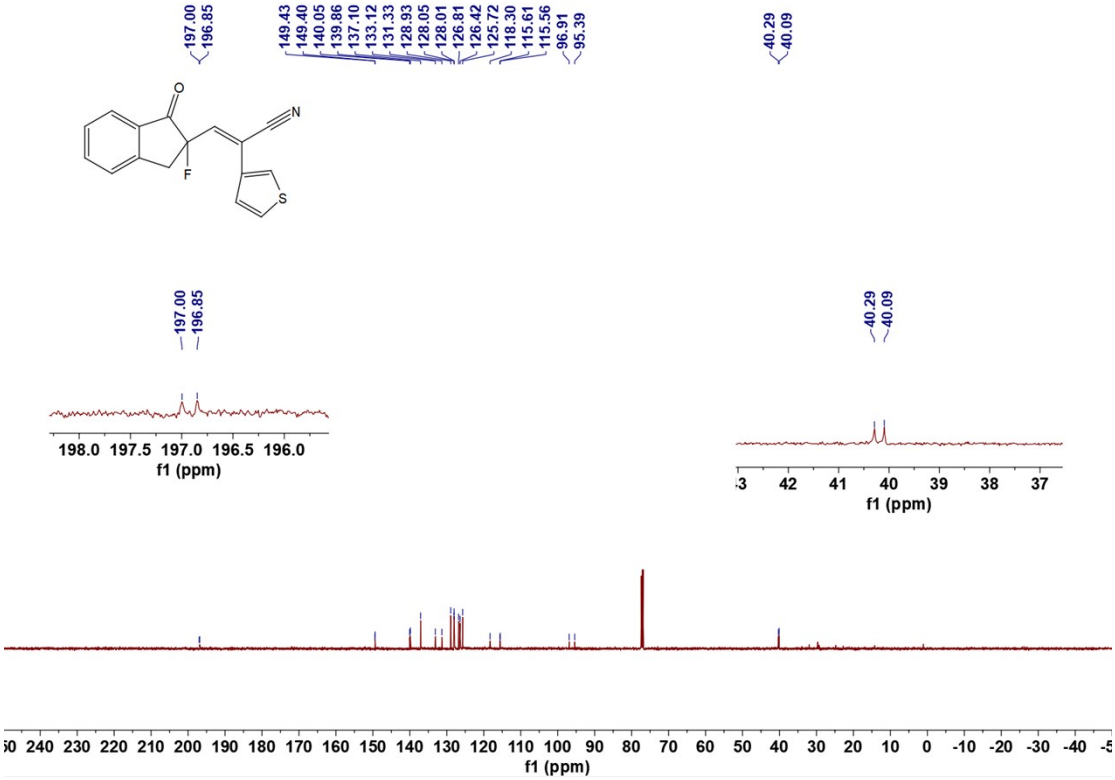


^{1}H NMR of 5d



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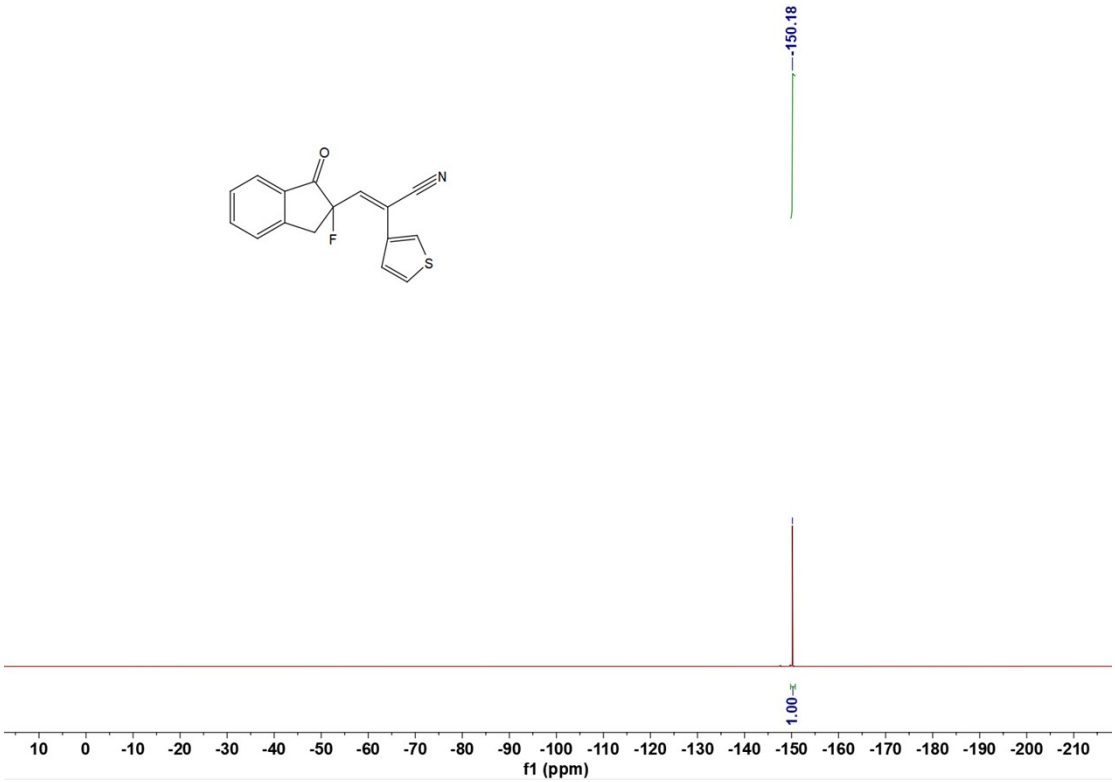

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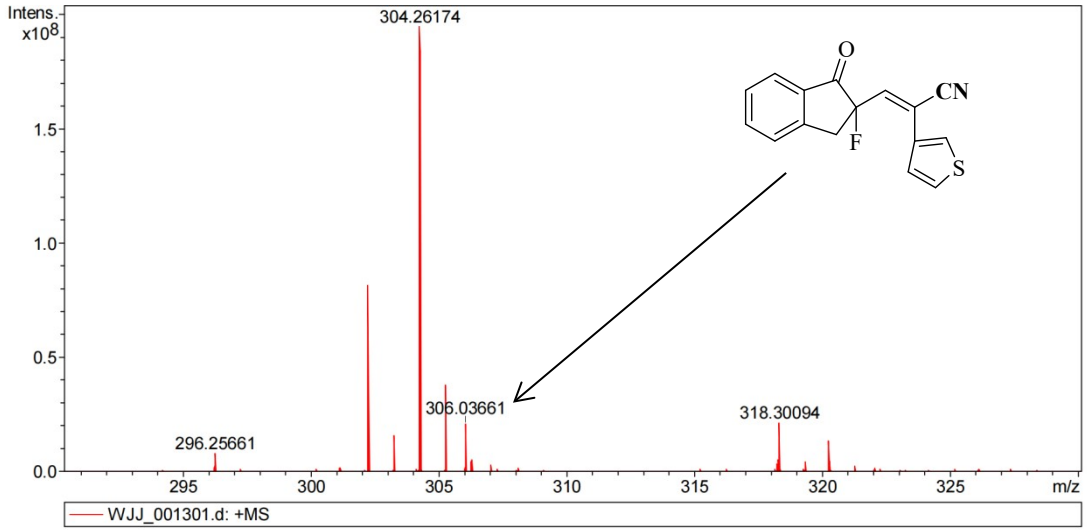
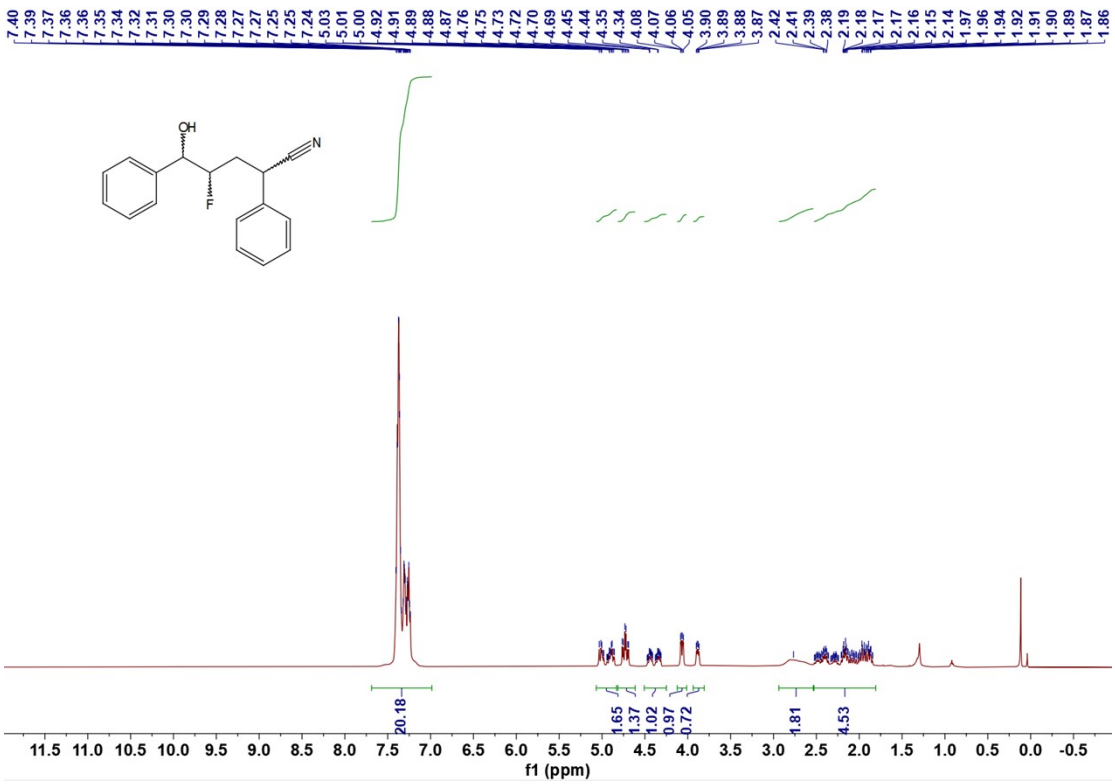


HRMS of 5d



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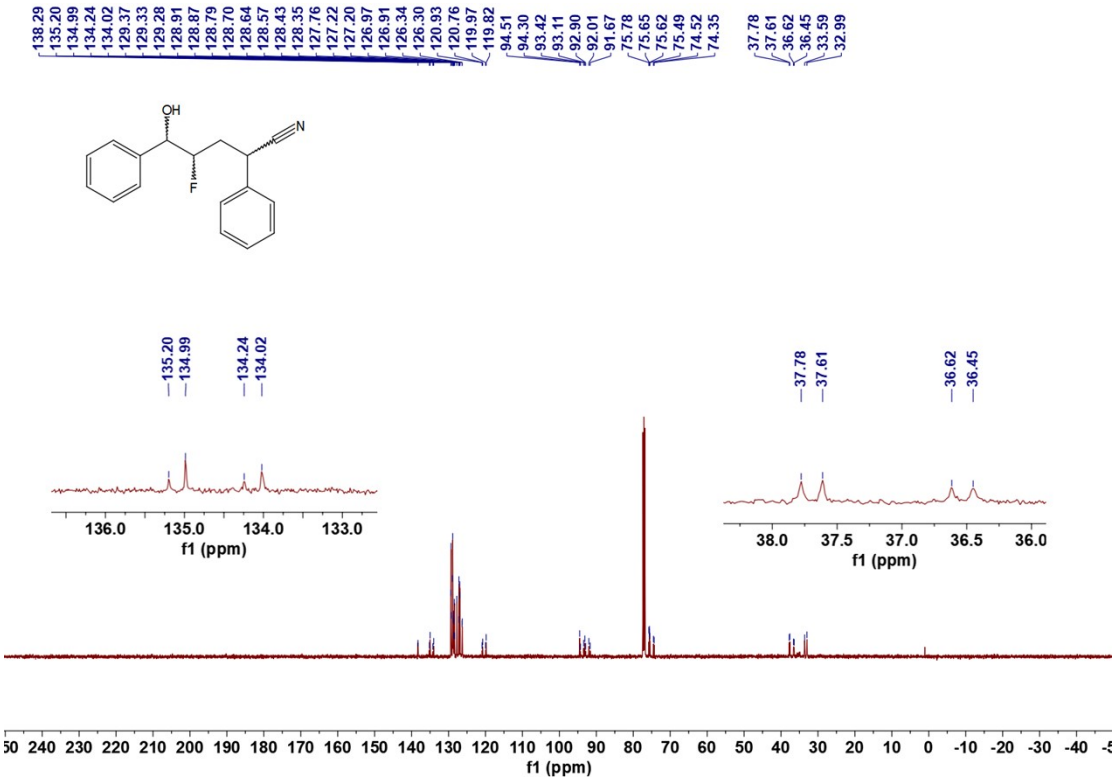

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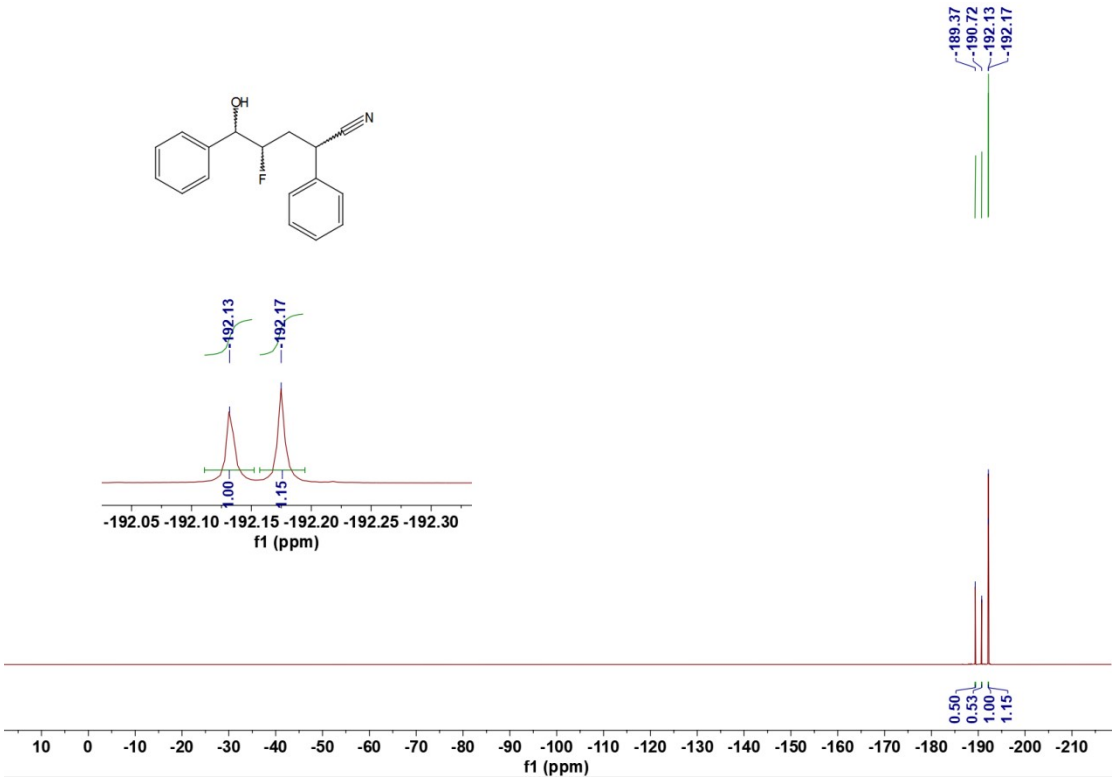

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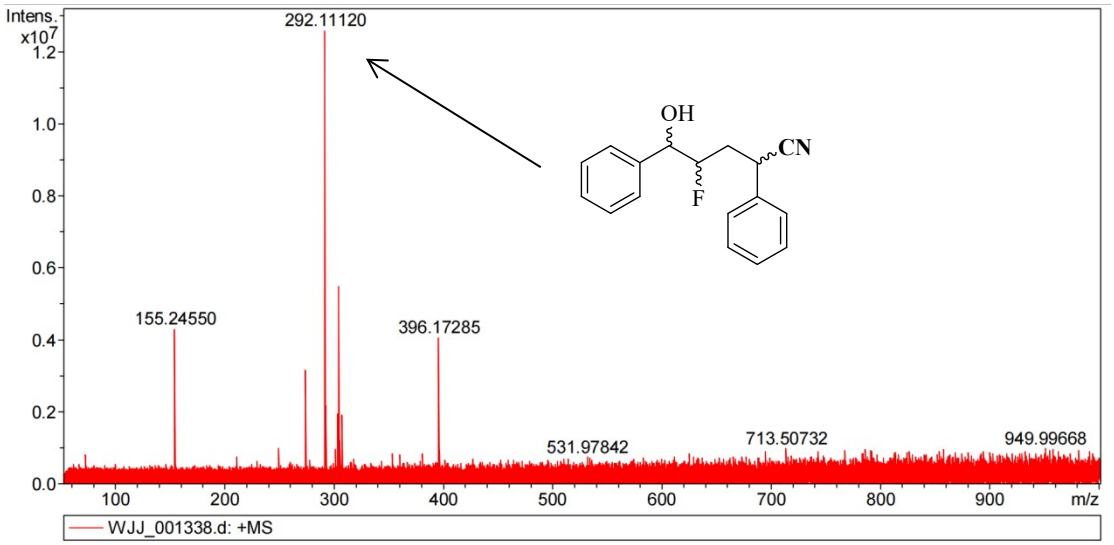
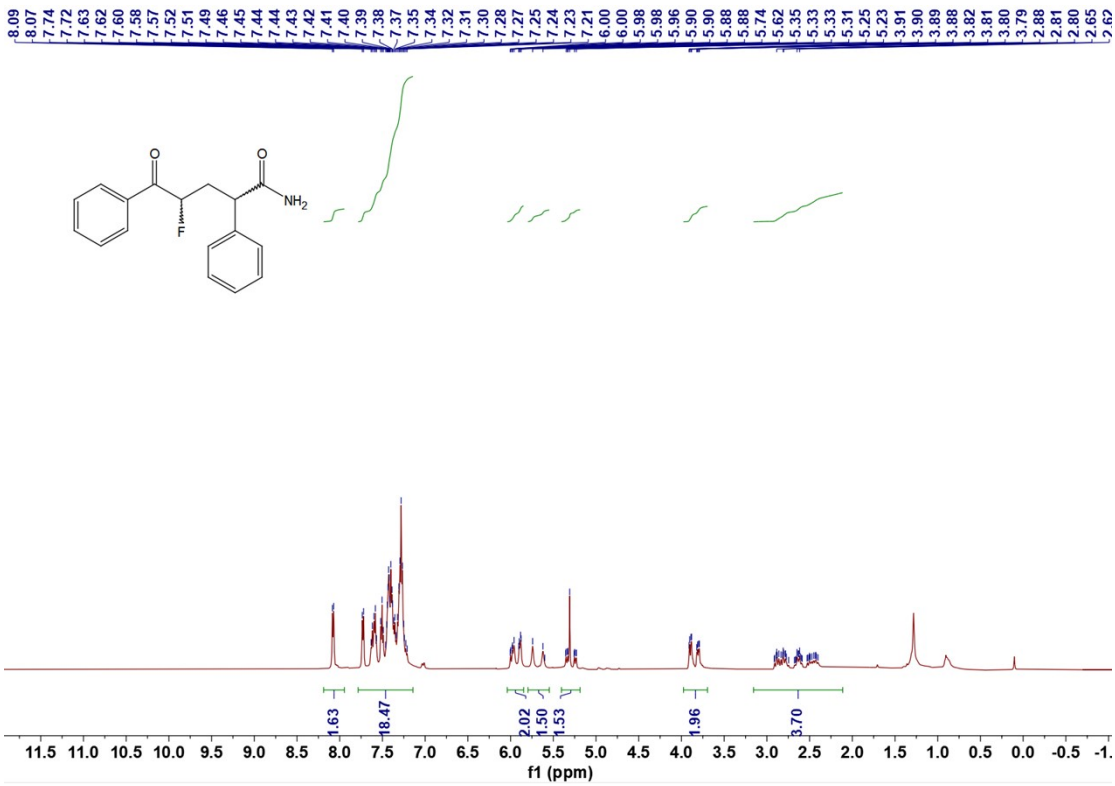


HRMS of 6



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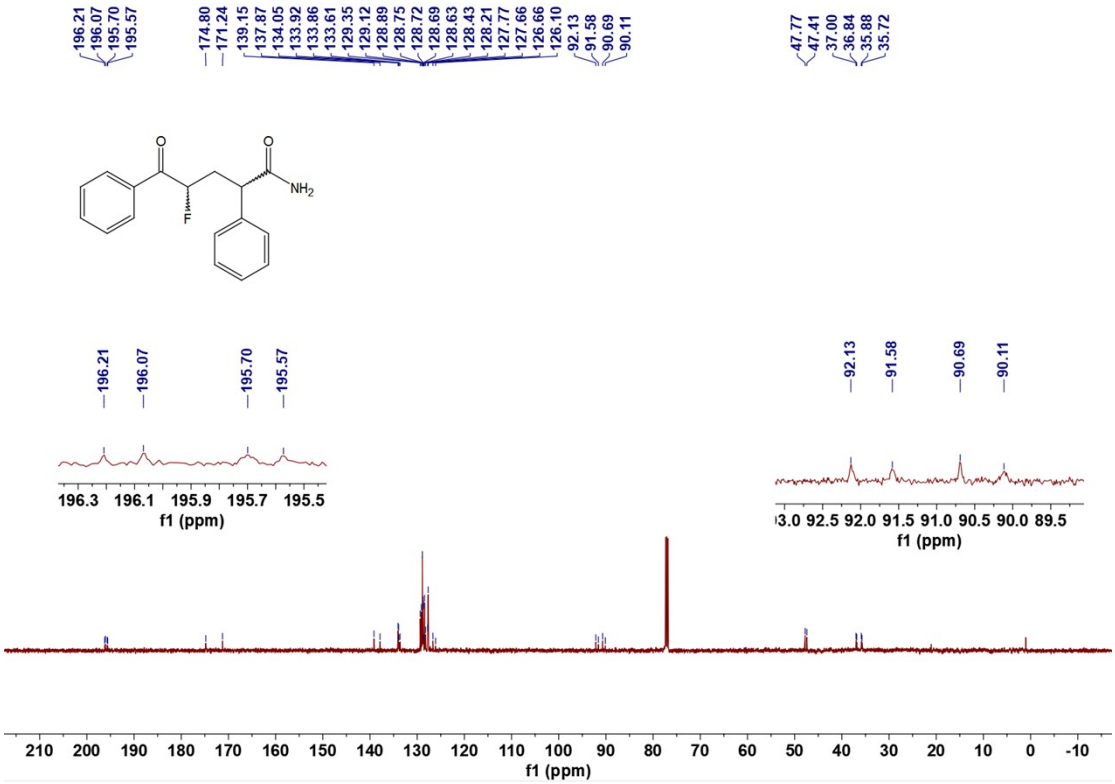

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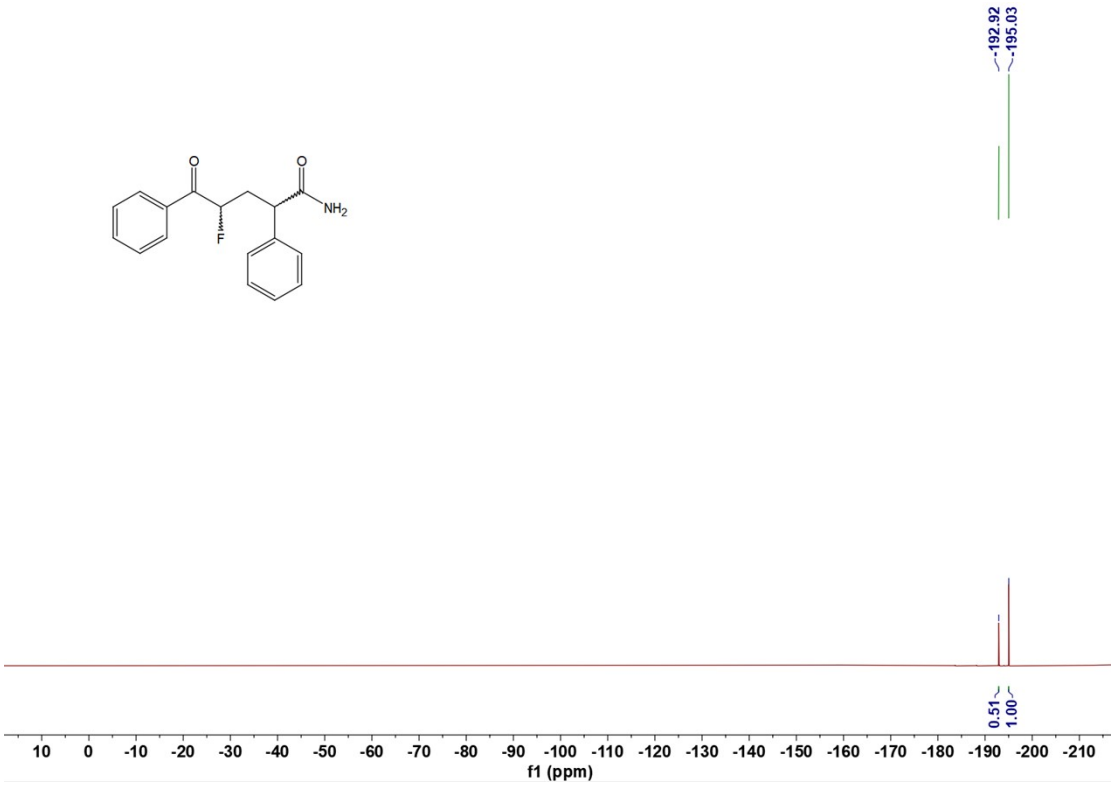

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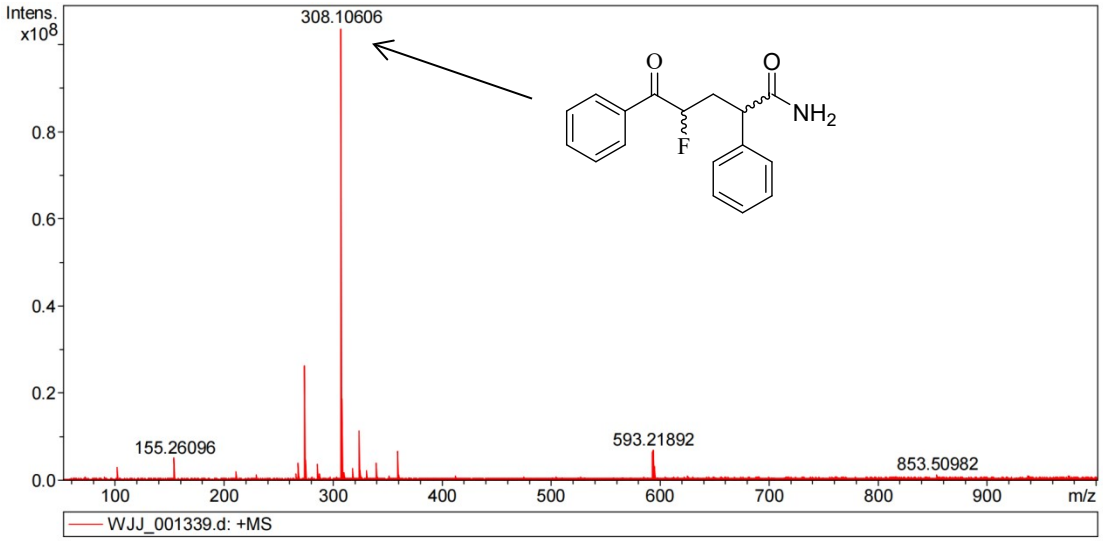

HRMS of 7