Supporting information

Palladium-Catalyzed *Z*-Selective Alkynylation of *gem*-Difluoro alkenes via Carbon–Fluorine Bond Activation: Mechanistic Insights into Oxygen-Directed Regiocontrol

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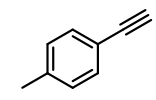
1. Reagents

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. Instruments

NMR spectra were recorded on Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, t = triplet, m = multiplet. HRMS analysis were carried out using a Bruker microTOF–Q instrument or a TOF–MS instrument. Single-crystal X-ray diffraction data were collected on Agilent Xcalibur E detectors with a radiation source of Mo (Kα).



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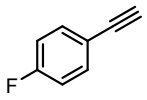

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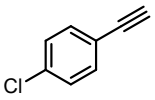

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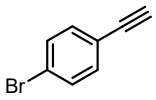

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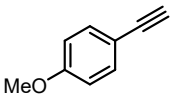

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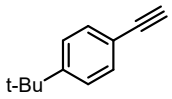

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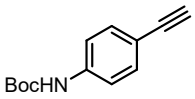

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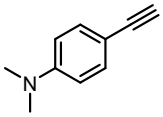

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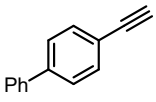

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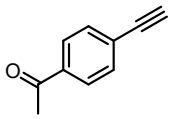

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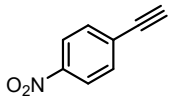

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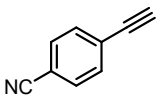

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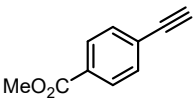

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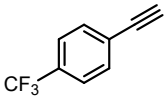

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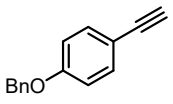

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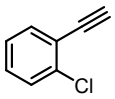

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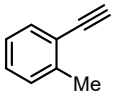

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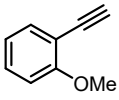

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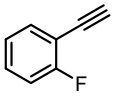

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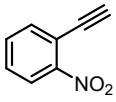

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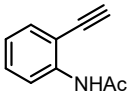

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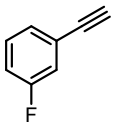

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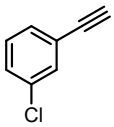

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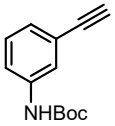

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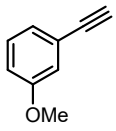

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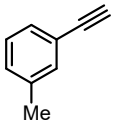

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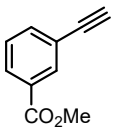

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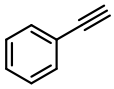

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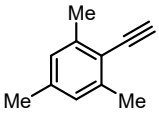

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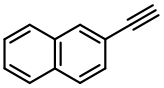

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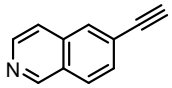

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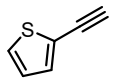

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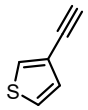

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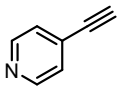

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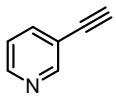

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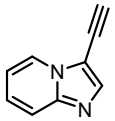

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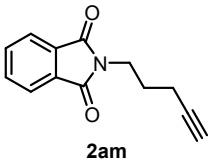

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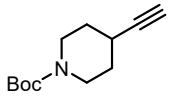

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2ao

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2aq

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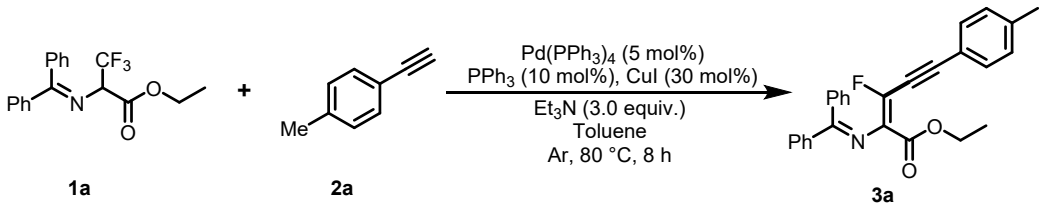
2as

3. Optimization of reaction conditions

Table S1. Control experiment [a]

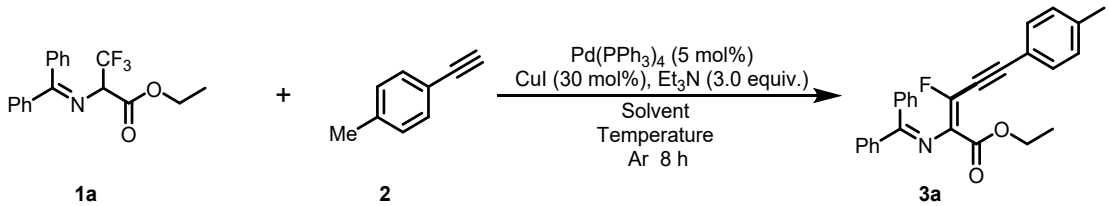


1a **2a** **3a**

Entry	Variation from standard conditions	Yield (%)[b]
1	No $Pd(PPh_3)_4$	0
2	No PPh_3	13
3	No CuI	trace
4	No Et_3N	0
5	Air	0

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), PPh_3 (10 mol%), CuI (30 mol%), Et_3N (3.0 equiv.), Toluene (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [b] Isolation yield

Table S2. Solvent and Temperature Screening [a]



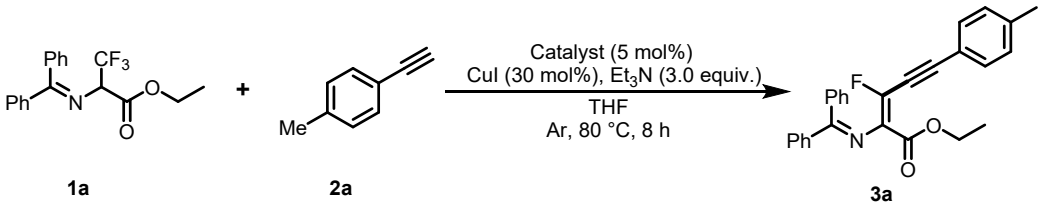
1a **2** **3a**

Entry	Catalyst	Solvent	Temperature	Yield (%)[c]
1[a]	$Pd(PPh_3)_4$	Toluene	80 °C	13
2[a]	$Pd(PPh_3)_4$	1,4–Dioxane	80 °C	18
3[a]	$Pd(PPh_3)_4$	DMF	80 °C	<5
4[a]	$Pd(PPh_3)_4$	DCE	80 °C	trace
5[a]	$Pd(PPh_3)_4$	THF	80 °C	26
6[b]	$Pd(PPh_3)_4$	THF	70 °C	19
7[b]	$Pd(PPh_3)_4$	THF	60 °C	<5
8[b]	$Pd(PPh_3)_4$	THF	90 °C	26

9[b]	$Pd(PPh_3)_4$	THF	100 °C	27

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (30 mol%), Et_3N (3.0 equiv.), Solvent (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [b] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (30 mol%), Et_3N (3.0 equiv.), THF(1.0 mL) at different Temperature for 8 h under argon atmosphere in a sealed tube. [c] Isolation yield

Table S3. Catalyst Screening [a]

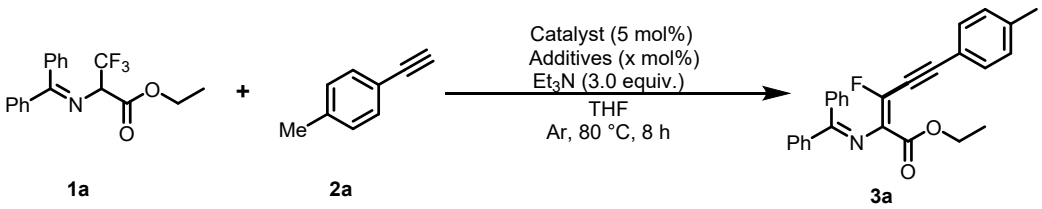


1a **2a** **3a**

Entry	Catalyst	Additives	Base	Yield (%)[b]
1	$Pd(PPh_3)_4$	CuI	Et_3N	26%
2	$Pd(PPh_3)_2Cl_2$	CuI	Et_3N	36%
3	$Pd(dba)_2$	CuI	Et_3N	11%
4	$PdCl_2$	CuI	Et_3N	<10%
5	$Pd(OAc)_2$	CuI	Et_3N	22%
6	$Pd(TFA)_2$	CuI	Et_3N	24%

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), Catalyst (5 mol%), CuI (30 mol%), Et_3N (3.0 equiv.), THF (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [b] Isolation yield

Table S4. Additives Screening [a]



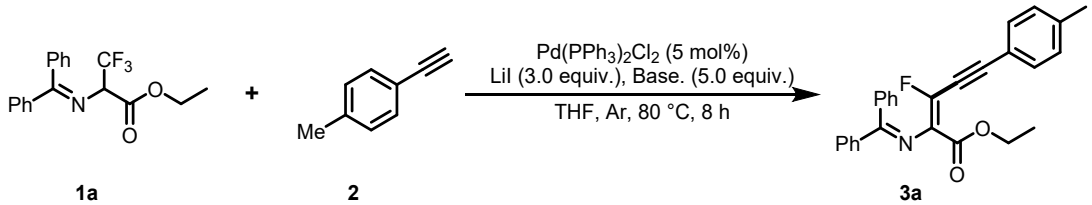
1a **2a** **3a**

Entry	Catalyst	Additives	Base	Yield (%)[c]
1	$Pd(PPh_3)_2Cl_2$	CuI	Et_3N	36%
2	$Pd(PPh_3)_2Cl_2$	CuBr	Et_3N	31%
3	$Pd(PPh_3)_2Cl_2$	CuCl	Et_3N	trace
4	$Pd(PPh_3)_2Cl_2$	CuOAc	Et_3N	trace

5	$Pd(PPh_3)_2Cl_2$	CuOTf	Et_3N	<5%
6	$Pd(PPh_3)_2Cl_2$	KI	Et_3N	24%
7	$Pd(PPh_3)_2Cl_2$	NaI	Et_3N	43%
8	$Pd(PPh_3)_2Cl_2$	LiI	Et_3N	52%
9	$Pd(PPh_3)_2Cl_2$	TBAI	Et_3N	trace
10	$Pd(PPh_3)_2Cl_2$	LiBr	Et_3N	41%
11	$Pd(PPh_3)_2Cl_2$	LiCl	Et_3N	12%
12[b]	$Pd(PPh_3)_2Cl_2$	LiI (2.0 equiv.)	Et_3N	62%
13[b]	$Pd(PPh_3)_2Cl_2$	LiI(3.0 equiv.)	Et_3N	69%
14[b]	$Pd(PPh_3)_2Cl_2$	LiI(4.0 equiv.)	Et_3N	70%

[a] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), Additives (30 mol%), Et_3N (3.0 equiv.), THF (1.0 mL), at 80 °C for 8 h under a nitrogen atmosphere in a sealed tube. [b] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), LiI (x equiv.), Et_3N (3.0 equiv.), THF (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [c] Isolation yield

Table S5. Base Screening [a]



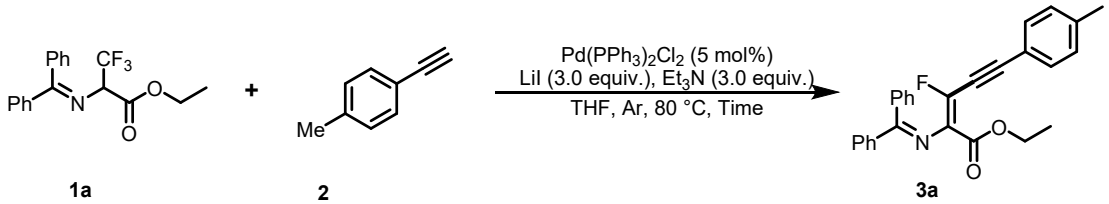
1a **2** **3a**

Entry	Catalyst	Additives	Base	Yield (%)[c]
1	$Pd(PPh_3)_2Cl_2$	LiI	Et_3N	69%
2	$Pd(PPh_3)_2Cl_2$	LiI	DIPEA	51%
3	$Pd(PPh_3)_2Cl_2$	LiI	DMAP	trace
4	$Pd(PPh_3)_2Cl_2$	LiI	DBU	trace
5	$Pd(PPh_3)_2Cl_2$	LiI	K_2CO_3	<10%
6	$Pd(PPh_3)_2Cl_2$	LiI	Cs_2CO_3	29%
7	$Pd(PPh_3)_2Cl_2$	LiI	NaOH	Mess
8	$Pd(PPh_3)_2Cl_2$	LiI	NaO^tBu	Mess
9[b]	$Pd(PPh_3)_2Cl_2$	LiI	Et_3N (4.0 equiv)	72%
10[b]	$Pd(PPh_3)_2Cl_2$	LiI	Et_3N (5.0 equiv)	76%

11[b]	$Pd(PPh_3)_2Cl_2$	LiI	Et_3N (6.0 equiv)	76%

[a] Reaction conditions: **1** (0.2 mmol), **2** (3.0 equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), LiI (3.0 equiv.), Base (3.0 equiv.), THF (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [b] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), LiI (3.0 equiv.), Et_3N (x equiv.), THF (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [c] Isolation yield

Table S6. Substrate equivalents and Time Screening [a]

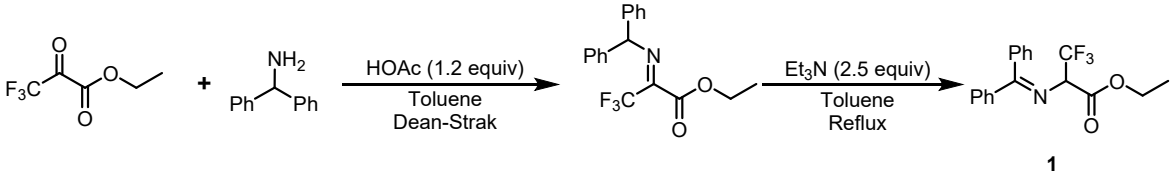


1a **2** **3a**

Entry	2 (x equiv.)	Time	Yield (%)[c]
1[a]	3.0	8 h	76%
2[a]	0.5	8 h	64%
3[a]	1.0	8 h	51%
4[a]	2.0	8 h	63%
5[a]	4.0	8 h	77%
6[b]	3.0	4 h	64%
7[b]	3.0	6 h	71%
8[b]	3.0	12 h	73%
9[b]	3.0	24 h	83%
10[b]	3.0	36 h	81%

[a] Reaction conditions: **1** (0.2 mmol), **2** (x equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), LiI (3.0 equiv.), Et_3N (3.0 equiv.), THF (1.0 mL), at 80 °C for 8 h under argon atmosphere in a sealed tube. [b] Reaction conditions: **1** (0.2 mmol), **2a** (3.0 equiv.), $Pd(PPh_3)Cl_2$ (5 mol%), LiI (3.0 equiv.), Et_3N (3.0 equiv.), THF (1.0 mL), at 80 °C for t h under argon atmosphere in a sealed tube. [c] Isolation yield

4. Preparation of substrates

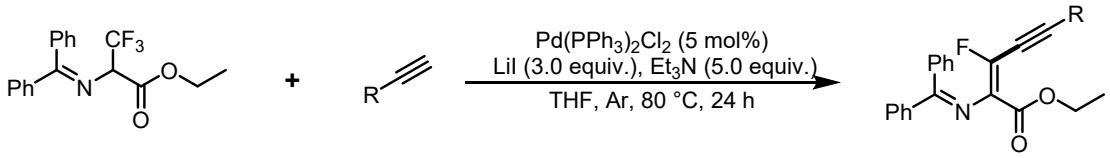


1

General procedure (I) for the synthesis of ethyl 2-((diphenylmethylene)amino)-3,3,3-trifluoropropanoate 1:

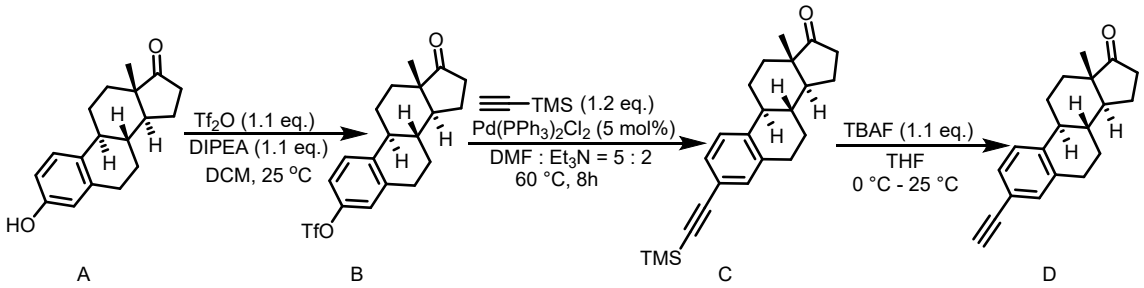
Dissolve 4.4 g of diphenylmethylamine (24 mmol, 1.2 equiv.) in 50 mL of toluene. At room temperature, add 1.45 g of acetic acid (1.2 equiv.), causing the formation of a solid in the mixture. Then, add 3.4 g of ethyl trifluoroacetate (20 mmol) to the system, which will turn into a clear liquid. Heat the mixture at 105 °C and use a Dean-Stark apparatus to remove water via azeotropic distillation for 6 hours. After water separation is complete, add 5 g of triethylamine (50 mmol, 2.5 equiv.) to the system and continue refluxing for an additional 4 hours. After the reaction is finished, concentrate the mixture, then extract with ethyl acetate. Wash the organic phase with saturated sodium chloride solution, concentrate under reduced pressure, and purify the product via flash column chromatography to obtain a colorless to light yellow viscous oily product.

5. General procedure for palladium-catalyzed Sonogashira cross-coupling:



To an oven-dried 10 mL flask equipped with a stir bar was added $Pd(PPh_3)_2Cl_2$ (5 mol%), LiI (3.0 equiv.) and of alkyne (3.0 equiv.) (use a micro-syringe for liquid reagents) into a Schlenk tube under an inert atmosphere. Replace the argon three times using a double manifold. Dissolve the compound in 1 mL of THF, and introduce it into the reaction mixture using a syringe. Then, add 5.0 equiv. of triethylamine with a micro-syringe. Heat the reaction mixture in an 80 °C oil bath for 24 hours. After the reaction is complete, cool the mixture to room temperature, filter, concentrate, extract with ethyl acetate, and wash with saturated brine. The organic phase is purified by flash column chromatography to obtain the target product as an oily substance.

6. General Procedure for the Synthesis of Drug Molecule Derivatives[1]



Step 1:

Substrate A is dissolved in DCM. 1.1 equivalents of trifluoromethanesulfonic anhydride Tf_2O and 1.1 equivalents of DIPEA were added, followed by stirring at room temperature for 1 hour. After completion, water is added for extraction. The DCM phase is purified by column chromatography to obtain compound B.

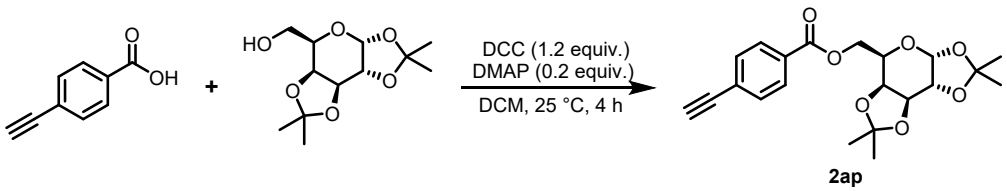
Step 2:

Compound B is dissolved in a 5:2 mixture of DMF and TEA. 5 mol% of $Pd(PPh_3)_2Cl_2$ is added as a catalyst, followed by 1.2 equivalents of TMSA. The reaction mixture is degassed via three nitrogen/vacuum cycles and heated at 60°C overnight. After cooling to room temperature, the mixture is filtered, concentrated, extracted with ethyl acetate, washed with saturated brine, and purified by flash column chromatography to yield compound C.

Step 3:

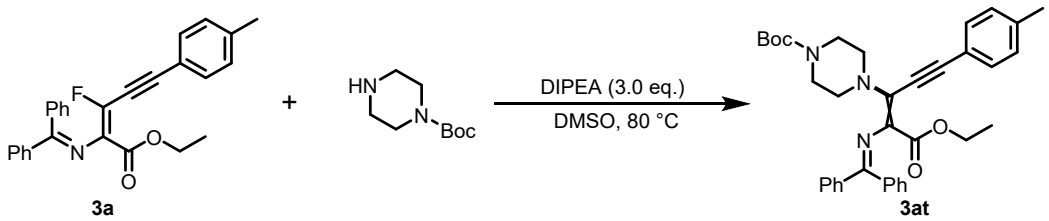
Compound C is dissolved in THF, and 1.1 equivalents of TBAF are added. The reaction is allowed to proceed at room temperature for 1 hour. After completion, the mixture is concentrated, extracted with ethyl acetate, washed with saturated brine, and purified by flash column chromatography to obtain compound D as a white solid.

7. General Steps for the Synthesis of Fructose Derivatives[2]



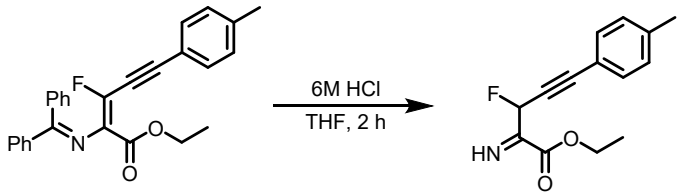
A mixture of 4-ethynylbenzoic acid and diacetone-β-D-fructose 1:1molarratio was dissolved in dichloromethane DCM.1.2 equivalents of DCC and 20 mol% DMAP were added. The reaction mixture was stirred at room temperature for 4 hours. After completion, the solvent was concentrated under reduced pressure. The residue was extracted with ethyl acetate, washed with brine, and the organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography to afford the target compound as a pale yellow oil.The synthetic methods for starting materials **2aq**, **2ar**, and **2as** were consistent with the aforementioned procedures.

8. Experimental Procedure for the Transformation Reaction



General Procedure for Nucleophilic Substitution Experiments: product **3a** was dissolved in DMSO, followed by the addition of 3 equivalents of N–Boc-piperazine and 3 equivalents of DIPEA. The reaction mixture was stirred at 80 °C for 2 hours. After completion, the mixture was cooled to room temperature, extracted with ethyl acetate, and washed with saturated brine. The organic phase was purified by flash column chromatography to afford the target compound **3at**.

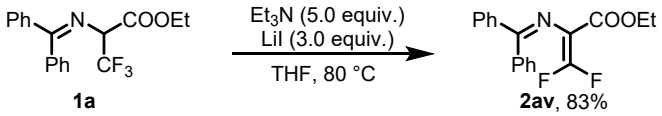
9. Benzophenone Removal Experiment



General procedure for Benzophenone Removal Experiment: A solution of compound **2a** in tetrahydrofuran THF was treated with 2.0 equivalents of 6 M HCl dropwise at room temperature. The reaction mixture was stirred vigorously for 2 h, after which the pH was adjusted to neutral with saturated aqueous Na_2CO_3 solution. The mixture was extracted with dichloromethane DCM, and the organic phase was washed with saturated brine. NaCl aq. The combined organic layers were concentrated under

reduced pressure. The crude product was purified by flash column to afford the target compound **2au**.

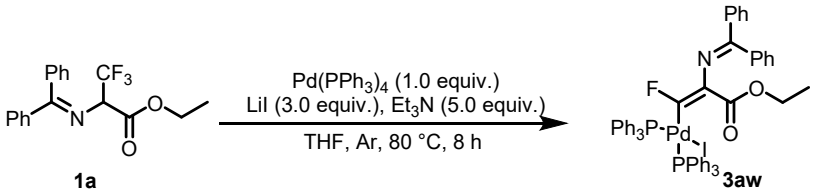
10. Synthesis of gem-Difluoroalkenes



1a **2av**, 83%

General procedure : A mixture of substrate II 1 0.5mmol in THF 2 mL was treated with triethylamine 5.0 equiv. and lithium iodide 3.0 equiv. in a sealed reaction tube. The reaction was stirred at 80 °C for 12 h under an argon atmosphere. After cooling to room temperature, the mixture was filtered through Celite®, concentrated under reduced pressure, and extracted with ethyl acetate 3×10 mL. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and purified by flash column chromatography Hexanes/EtOAc=10:1 to afford the desired product **2av**.

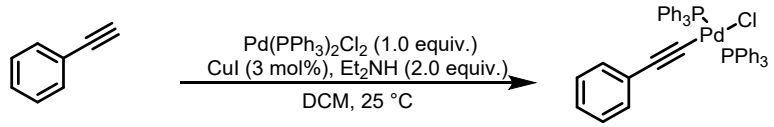
11. Synthesis of a Difluoroolefin-Palladium Intermediate



1a **3aw**

General procedure : A mixture of $Pd(PPh_3)_4$ 116 mg,0.1 mmol and NaI 45 mg,0.3 mmol was added to an oven-dried 10 mL reaction tube equipped with a magnetic stir bar. The tube was sealed with a rubber septum, evacuated, and refilled with argon three times. A solution of ethyl 3,3,3-trifluoroalaninate Schiff base 0.1 mmol and TEA 0.5 mmol in 1.5 mL of THF was injected into the tube via a syringe. The resulting mixture was heated to 80 °C and stirred for 6 h, during which the solution color changed from pale yellow to deep red. After cooling to room temperature, the mixture was filtered through cotton to remove solid residues, followed by washing with 1 mL of THF to afford a clear red filtrate. To this filtrate, 25 mL of dry hexane was added, and an orange precipitate formed upon sonication. The solid was collected by filtration as the crude product Approximately 90 mg. The crude product was sonicated in 4 mL of dry hexane, yielding a mixture of yellow and red solids. Dichloromethane was added dropwise to the mixture until most of the yellow solid dissolved red solids remained. The red solids were filtered off, and the clear yellow filtrate was concentrated under reduced pressure to give the final pale yellow solid product.

12. Synthesis of Palladium-Alkyne Intermediate



2ax

General procedure : A mixture of $Pd(PPh_3)_2Cl_2$ 701 mg,1mmol and Phenylacetylene 102 mg,1mmol in DCM 50 mL was treated with CuI 5.7 mg,3 mol and diethylamine 146 mg,2 mmol. The reaction mixture was stirred at room temperature for 4 h, during which the solution color changed from yellow to pale reddish-brown. The insoluble impurities were removed by filtration. The organic layer was extracted with dichloromethane and water, washed with saturated brine, and dried over anhydrous $MgSO_4$. After filtration to remove the drying agent, the DCM phase was partially concentrated under reduced pressure. The resulting residue was cooled to –30 °C to afford a pale yellow crystalline solid. The structure of the product was confirmed by ^1H NMR spectroscopy, showing data consistent with literature reports.

13. X-ray Crystallographic data of 3aa

The crystal of **3aa** for X-ray diffraction study has been obtained through the dissolving of compound in DCM and n-hexane, followed by slow evaporation of the solvent at room temperature. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with Bruker D8 Quest CCD instrument equipped with graphite-monochromated Mo-Kα radiation (λ =0.71073 Å, multilayer optics). The crystal was kept at 297 K during data collection. The structure was solved by direct methods and refined on F2 with SHELXL Least Squares using Olex2 software. CCDC 2362196 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

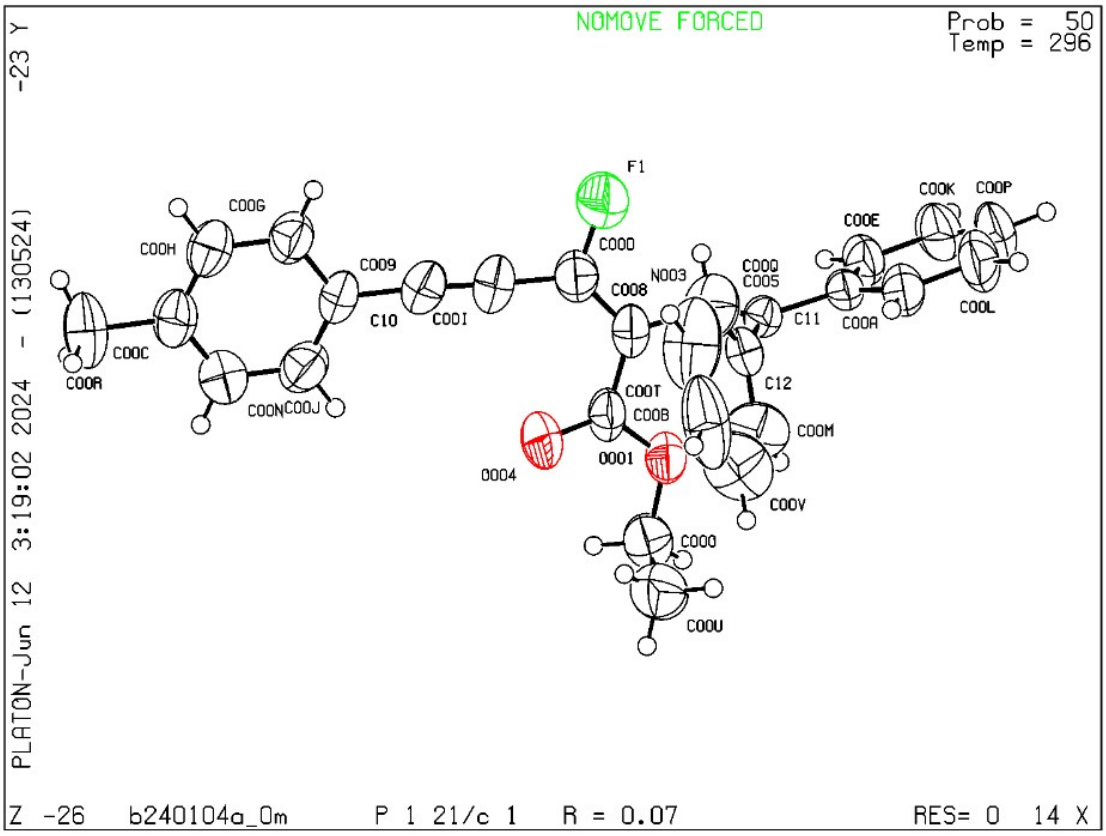


Table S7. Crystal data and structure refinement for 3aa.	
Identification code	mo_mo2342429xe_0ma_a
Empirical formula	$C_{27}H_{22}FNO_2$
Formula weight	411.45
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3024(7)
b/Å	9.1843(8)
c/Å	24.3532(19)
α/°	90
β/°	110.347(2)
γ/°	90
Volume/Å^3	2259.3(3)
Z	4
ρ_{calc}g/cm^3	1.210
μ/mm^{-1}	0.082
F(000)	864.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.032 to 55.094

Index ranges	$-11 \leq h \leq 12$, $-11 \leq k \leq 11$, $-25 \leq l \leq 31$
Reflections collected	24151
Independent reflections	5069 [R_{int} = 0.0899, R_{sigma} = 0.1007]
Data/restraints/parameters	5069/0/282
Goodness-of-fit on F^2	0.988
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1549
Final R indexes [all data]	R_1 = 0.2092, wR_2 = 0.2058
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.16

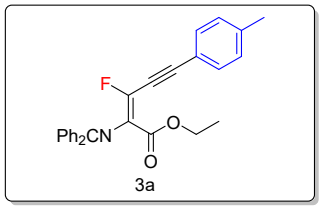
14. References

[1] (a) Izawa, Y.; Shimizu, I.; Yamamoto, A. Palladium-Catalyzed Oxidative Carbonylation of 1-Alkynes into 2-Alkynoates with Molecular Oxygen as Oxidant. *Bull. Chem. Soc. Jpn.*, **2004**, *77*, 2033–2045. (b) Chen, M.; Sun, N.; Chen, H.; Liu, Y. Dioxazoles, a new mild nitrene transfer reagent in gold catalysis: highly efficient synthesis of functionalized oxazoles. *Chem. Commun.*, **2016**, *52*, 6324–6327.

[2] Ye, M.; Hou, M.; Wang, Y.; Ma, X.; Yang, K.; Song, Q. Arylation of terminal alkynes: transition-metal-free sonogashira-type coupling for the construction of C(sp)-C(sp^2) bonds. *Org. Lett.*, **2023**, *25*, 1787–1792.

15. Characterization data

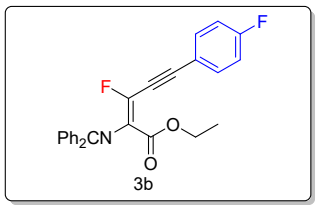
Ethyl (*Z*)-2-((diphenylmethylene)amino)-3-fluoro-5-(p-tolyl)pent-2-en-4-ynoate (3a)



3a

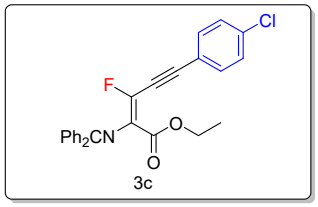
Yellow Solid, Isolated yield: 69 mg, 84%. (**Eluent**: PE : EA = 40 : 1). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.77 – 7.69 (m, 2H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.33 (m, 7H), 7.25 (dd, *J* = 7.0, 3.6 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.0 (d, *J* = 2.3 Hz), 162.7 (d, *J* = 10.9 Hz), 139.9, 138.5, 136.9, 136.6 (d, $J_{C\text{-}F}$ = 242.0 Hz), 131.8, 131.8, 131.5, 131.3 (d, *J* = 23.3 Hz), 129.9, 129.6, 129.3, 128.3, 128.0, 118.5 (d, *J* = 2.6 Hz), 99.0 (d, *J* = 5.2 Hz), 80.2 (d, *J* = 34.0 Hz), 61.4, 21.7, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -102.84. **HRMS** Calcd for $C_{27}H_{23}FNO_2$ $[M+H]^+$: 412.1708; Found: 412.1711

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(4-fluorophenyl)pent-2-en-4-ynoate (3b)



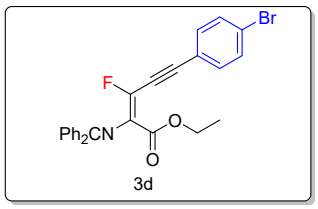
Yellow Solid, Isolated yield: 61.4 mg, 74%. (**Eluent**: PE : EA = 40 : 1). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.47 (td, *J* = 5.4, 2.2 Hz, 3H), 7.43 – 7.34 (m, 5H), 7.30 – 7.23 (m, 2H), 7.01 (t, *J* = 8.8 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.1, 163.3 (d, *J* = 252.2 Hz), 162.6 (d, *J* = 10.7 Hz), 138.4, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 241.2 Hz), 134.2 – 133.7 (m), 131.9, 131.6, 129.9, 129.7, 128.3, 128.0, 117.8, 116.0 (d, *J* = 22.1 Hz), 97.5, 80.5 (d, *J* = 34.3 Hz), 61.4, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -103.95, -108.54. **HRMS** Calcd for $C_{26}H_{20}F_2NO_2$ $[M+H]^+$: 416.1457; Found: 416.1461

Ethyl (Z)-5-(4-chlorophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3c)



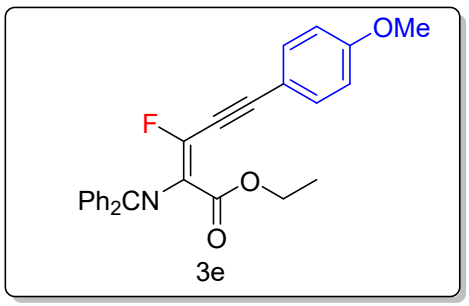
Yellow Solid, Isolated yield: 54.3 mg, 63%. (**Eluent**: PE : EA = 40 : 1). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.41 (dt, *J* = 7.4, 2.2 Hz, 7H), 7.32 – 7.23 (m, 4H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.1 (d, *J* = 2.5 Hz), 162.5 (d, *J* = 10.4 Hz), 138.3, 136.8, 136.1 (d, $J_{C\text{-}F}$ = 241.5 Hz), 135.7, 133.0, 133.0, 132.0 (d, *J* = 22.9 Hz), 131.6, 130.0, 129.7, 128.9, 128.3, 128.0, 120.1 (d, *J* = 2.9 Hz), 97.4 (d, *J* = 5.8 Hz), 81.6 (d, *J* = 33.8 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.45. **HRMS** Calcd for $C_{26}H_{20}ClFNO_2$ $[M+H]^+$: 432.1162; Found: 432.1155

Ethyl (Z)-5-(4-bromophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3d)



Yellow Solid, Isolated yield: 34.2 mg, 36%. (**Eluent**: PE : EA = 40 : 1). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.43 – 7.37 (m, 5H), 7.36 – 7.32 (m, 2H), 7.25 (dd, *J* = 5.6, 2.8 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.1, 162.5 (d, *J* = 10.4 Hz), 138.3, 136.8, 136.1 (d, $J_{C\text{-}F}$ = 241.4 Hz), 133.2, 133.2, 131.9, 131.7, 130.18, 130.0, 129.7, 128.4, 128.0, 124.0, 120.6, 97.5 (d, *J* = 5.4 Hz), 81.8 (d, *J* = 34.3 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.55. **HRMS** Calcd for $C_{26}H_{20}BrFNO_2$ $[M+H]^+$: 476.0656; Found: 476.0654

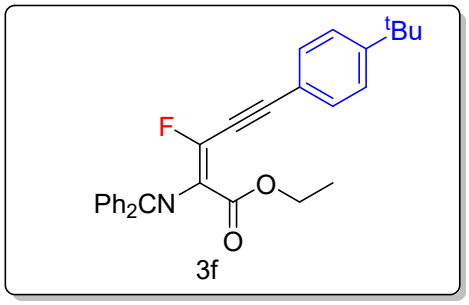
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(4-methoxyphenyl)pent-2-en-4-ynoate (3e)



Yellow Solid, Isolated yield: 70.9 mg, 83%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.35 (m, 8H), 7.26 (dd, *J* = 6.6, 2.6

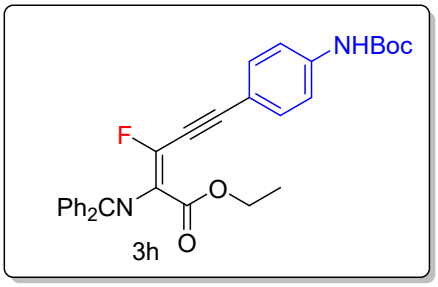
Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0 (d, J = 2.9 Hz), 162.7 (d, J = 11.0 Hz), 160.7, 138.5, 136.9, 136.8 (d, $J_{C\text{-}F}$ = 241.5 Hz), 133.5, 133.5, 131.5, 131.0 (d, J = 23.4 Hz), 129.9, 129.6, 128.29, 128.0, 114.2, 113.6 (d, J = 2.9 Hz), 99.1 (d, J = 5.5 Hz), 79.7 (d, J = 33.8 Hz), 61.3, 55.4, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.41. **HRMS** Calcd for $C_{27}H_{23}FNO_3$ $[M+H]^+$: 428.1657; Found: 428.1655

Ethyl (Z)-5-(4-(tert-butyl)phenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3f)



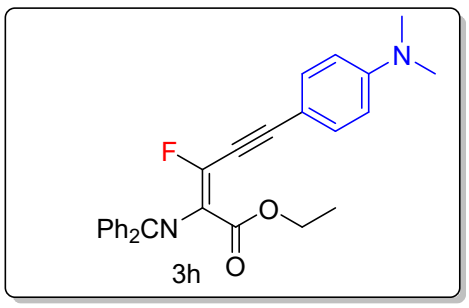
Yellow Solid, Isolated yield: 71.6 mg, 79%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.4 Hz, 1H), 7.44 – 7.31 (m, 9H), 7.26 (dt, J = 7.6, 2.8 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 1.29 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 162.7 (d, J = 10.9 Hz), 153.0, 138.5, 136.9, 136.6 (d, $J_{C\text{-}F}$ = 242.0 Hz), 131.7, 131.6, 131.5, 131.2, 129.9, 129.6, 128.3, 128.0, 125.5, 118.6 (d, J = 2.9 Hz), 99.0 (d, J = 5.3 Hz), 80.2 (d, J = 33.8 Hz), 61.3, 35.0, 31.2, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -102.85. **HRMS** Calcd for $C_{30}H_{29}FNO_2$ $[M+H]^+$: 454.2177; Found: 454.2172

Ethyl (Z)-5-(4-((tert-butoxycarbonyl)amino)phenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3g)



Yellow Gummy, Isolated yield: 65.1 mg, 74%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.42 – 7.35 (m, 7H), 7.33 (d, J = 8.6 Hz, 2H), 7.28 – 7.22 (m, 2H), 6.78 (br, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.50 (s, 9H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1 (d, J = 2.7 Hz), 162.7 (d, J = 10.9 Hz), 152.4, 139.8, 138.4, 136.8, 136.7 (d, $J_{C\text{-}F}$ = 242.0 Hz), 133.4, 132.7 (d, J = 2.8 Hz), 131.5, 131.1 (d, J = 22.7 Hz), 129.8, 129.6, 128.3, 127.9, 118.0, 115.5 (d, J = 2.7 Hz), 98.9 (d, J = 5.7 Hz), 81.0, 80.0 (d, J = 34.1 Hz), 61.3, 28.3, 14.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -102.58. HRMS Calcd for $C_{31}H_{30}FN_2O_4$ $[M+H]+$: 512.2185; Found: 512.287

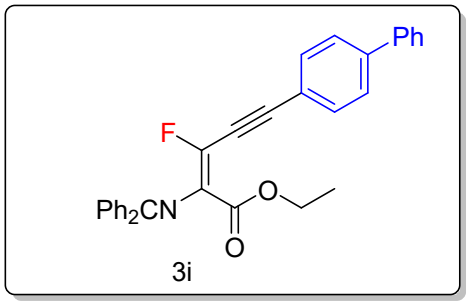
Ethyl (Z)-5-(4-(dimethylamino)phenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3h)



Yellow Solid, Isolated yield: 65.1 mg, 74%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J =

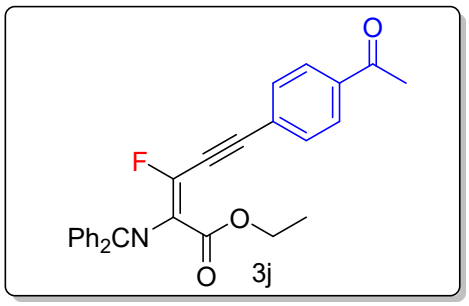
7.2 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.39 (dd, J = 6.8, 2.2 Hz, 5H), 7.35 (d, J = 8.8 Hz, 2H), 7.29 – 7.23 (m, 2H), 6.58 (d, J = 9.0 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 2.97 (s, 6H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8 (d, J = 2.3 Hz), 162.9 (d, J = 11.0 Hz), 150.8, 137.5 (d, $J_{C\text{-}F}$ = 239.6 Hz), 137.0, 133.2, 133.2, 131.4, 129.9 (d, J = 23.5 Hz), 129.9, 129.5, 128.3, 128.1, 111.6, 107.8 (d, J = 2.9 Hz), 101.0 (d, J = 5.5 Hz), 79.4 (d, J = 33.1 Hz), 61.2, 40.1, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -100.69. **HRMS** Calcd for $C_{28}H_{26}FN_2O_2$ $[M+H]^+$: 441.1973; Found: 441.1978

Ethyl (Z)-5-([1,1'-biphenyl]-4-yl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3i)



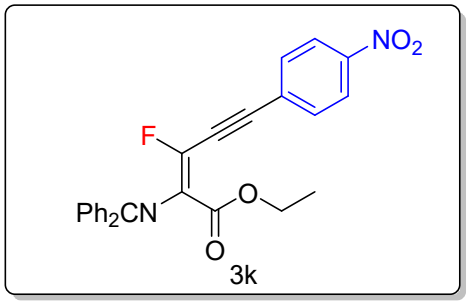
Yellow Solid, Isolated yield: 68.1 mg, 72%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 2H), 7.60 – 7.54 (m, 6H), 7.47 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 7.4 Hz, 2H), 7.41 (d, J = 7.8 Hz, 5H), 7.34 (d, J = 7.4 Hz, 1H), 7.27 (d, J = 6.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1 (d, J = 2.6 Hz), 162.6 (d, J = 10.9 Hz), 142.2, 140.1, 138.4, 136.9, 136.5 (d, $J_{C\text{-}F}$ = 242.0 Hz), 132.3, 132.3, 131.8, 131.6, 129.9, 129.7, 129.0, 128.3, 128.0, 127.2, 120.4 (d, J = 2.9 Hz), 98.7 (d, J = 5.3 Hz), 81.4 (d, J = 34.0 Hz), 61.4, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.46. **HRMS** Calcd for $C_{32}H_{25}FNO_2$ $[M+H]^+$: 474.1864; Found: 474.1862

Ethyl (Z)-5-(4-acetylphenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3j)



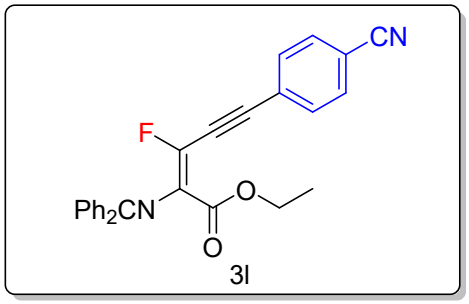
Yellow Solid, Isolated yield: 51.8 mg, 59%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 7.2 Hz, 5H), 7.30 – 7.20 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.59 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3, 173.2 (d, J = 2.7 Hz), 162.4 (d, J = 10.3 Hz), 138.3, 137.1, 136.7, 135.8 (d, $J_{C\text{-}F}$ = 241.5 Hz), 132.6 (d, J = 22.4 Hz), 131., 131.9, 131.7, 130.0, 129.8, 128.4, 128.3, 128.0, 126.3 (d, J = 2.9 Hz), 97.6 (d, J = 5.7 Hz), 83.6 (d, J = 34.3 Hz), 61.6, 26.8, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.38. **HRMS** Calcd for $C_{28}H_{23}FNO_3$ $[M+H]^+$: 440.1657; Found: 440.1663

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(4-nitrophenyl)pent-2-en-4-ynoate (3k)



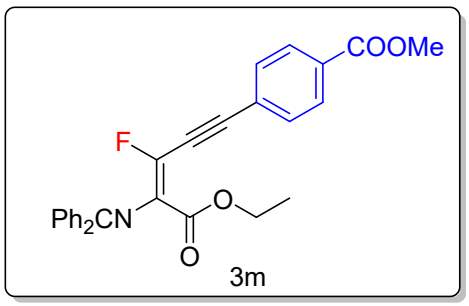
Yellow Solid, Isolated yield: 38 mg, 43%. (**Eluent**: PE : EA = 15 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.24 – 8.14 (m, 2H), 7.84 – 7.69 (m, 2H), 7.67 – 7.58 (m, 2H), 7.55 – 7.36 (m, 6H), 7.33 – 7.16 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.3 (d, *J* = 2.7 Hz), 162.2 (d, *J* = 10.6 Hz), 147.7, 138.1, 136.7, 135.3 (d, $J_{C\text{-}F}$ = 241.8 Hz), 133.4 (d, *J* = 22.1 Hz), 132.5, 132.5, 131.8, 130.0, 129.9, 128.4, 127.9, 123.8, 96.3 (d, *J* = 5.4 Hz), 85.4 (d, *J* = 34.4 Hz), 61.7, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -107.00. **HRMS** Calcd for $C_{26}H_{20}FN_2O_4$ $[M+H]^+$: 443.1402; Found: 443.1406

Ethyl (Z)-5-(4-cyanophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3l)



Yellow Solid, Isolated yield: 39.7 mg, 47%. (**Eluent**: PE : EA = 15 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.82 – 7.68 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 11.4, 4.4 Hz, 5H), 7.31 – 7.18 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2 (d, *J* = 2.8 Hz), 162.2 (d, *J* = 10.6 Hz), 138.1, 135.4 (d, $J_{C\text{-}F}$ = 241.4 Hz), 133.1 (d, *J* = 22.2 Hz), 132.2, 132.2, 132.2, 131.8, 130.0, 129.8, 128.4, 127.9, 126.5 (d, *J* = 2.8 Hz), 118.3, 112.6, 96.5 (d, *J* = 5.2 Hz), 84.6 (d, *J* = 34.1 Hz), 61.6, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -106.62. **HRMS** Calcd for $C_{27}H_{20}FN_2O_2$ $[M+H]^+$: 423.1504; Found: 423.1498

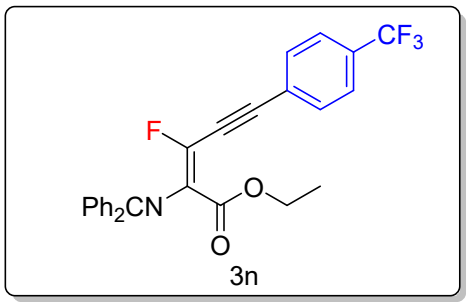
Methyl (Z)-4-(4-((diphenylmethylene)amino)-5-ethoxy-3-fluoro-5-oxopent-3-en-1-yn-1-yl)benzoate (3m)



Yellow Solid, Isolated yield: 61.9 mg, 68%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.30 – 7.19 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2, 166.4, 162.4 (d, *J* = 10.3 Hz), 138.3, 136.8, 135.8 (d, $J_{C\text{-}F}$ = 241.5 Hz), 132.5 (d, *J* = 22.7 Hz), 131.7,

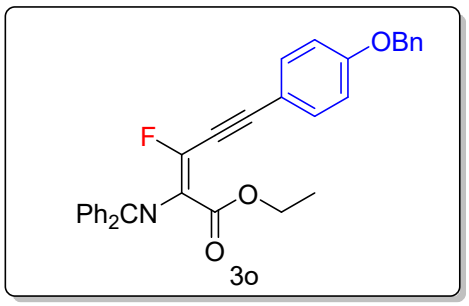
131.7, 130.6, 130.0, 129.7, 129.6, 128.4, 128.0, 126.2 (d, J = 2.9 Hz), 97.6, 83.3 (d, J = 34.4 Hz), 61.6, 52.4, 14.3. **^{19}F NMR** (376 MHz, *$CDCl_3$*) δ -105.22. **HRMS** Calcd for $C_{28}H_{23}FNO_4$ $[M+H]^+$: 456.1606; Found: 456.1611

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(4-(trifluoromethyl)phenyl)pent-2-en-4-ynoate (3n)



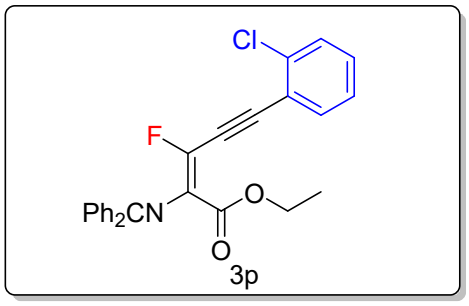
Yellow Solid, Isolated yield: 53.9 mg, 58%. (**Eluent**: PE : EA = 50 : 1) **^{1}H NMR** (400 MHz, *$CDCl_3$*) δ 7.75 (d, J = 7.6 Hz, 2H), 7.58 (s, 4H), 7.53 – 7.46 (m, 1H), 7.46 – 7.35 (m, 5H), 7.27 (q, J = 5.0 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *$CDCl_3$*) δ 173.2 (d, J = 2.7 Hz), 162.4 (d, J = 10.4 Hz), 138.3, 136.8, 135.7 (d, $J_{C\text{-}F}$ = 241.8 Hz), 132.7 (d, J = 22.3 Hz), 132.1, 132.0, 131.7, 131.0 (q, J = 32.9 Hz), 130.0, 129.8, 128.4, 128.2 (d, J = 11.9 Hz), 128.0, 125.5 (q, J = 3.7 Hz), 127.9, 125.2, 122.5, 119.8 (q, J = 273.2 Hz), 96.9 (d, J = 5.5 Hz), 82.8 (d, J = 34.1 Hz), 61.6, 14.3. **^{19}F NMR** (376 MHz, *$CDCl_3$*) δ -62.93, -105.63. **HRMS** Calcd for $C_{27}H_{20}F_4NO_2$ $[M+H]^+$: 466.1425; Found: 466.1428

Ethyl (Z)-5-(4-(benzyloxy)phenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3o)



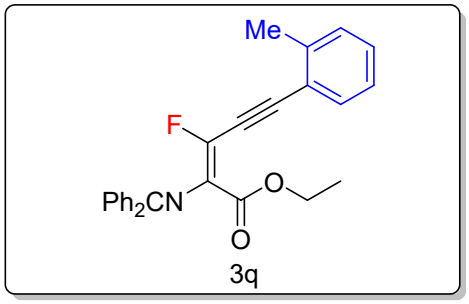
Yellow Solid, Isolated yield: 76.5 mg, 76%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *$CDCl_3$*) δ 7.73 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.44 – 7.30 (m, 12H), 7.25 (dt, J = 10.4, 4.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.04 (s, 2H), 4.14 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *$CDCl_3$*) δ 173.0 (d, J = 2.8 Hz), 162.7 (d, J = 10.9 Hz), 159.8, 138.5, 136.9, 136.8 (d, $J_{C\text{-}F}$ = 241.6 Hz), 136.4, 133.5, 133.5, 131.5, 131.0 (d, J = 23.4 Hz), 129.9, 129.6, 128.7, 128.3, 128.3, 128.0, 127.6, 115.1, 113.9 (d, J = 2.9 Hz), 99.0 (d, J = 5.2 Hz), 79.8 (d, J = 33.8 Hz), 70.1, 61.3, 14.3. **^{19}F NMR** (376 MHz, *$CDCl_3$*) δ -102.45. **HRMS** Calcd for $C_{33}H_{27}FNO_3$ $[M+H]^+$: 504.1970; Found: 504.1965

Ethyl (Z)-5-(2-chlorophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3p)



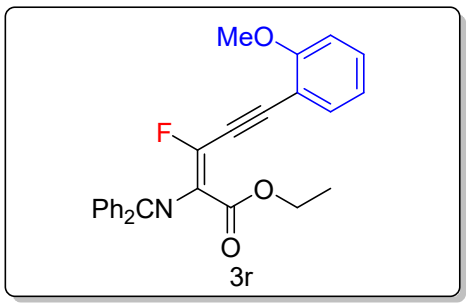
Yellow Solid, Isolated yield: 43.1 mg, 50%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.35 (m, 6H), 7.32 – 7.23 (m, 3H), 7.20 (td, *J* = 7.6, 1.4 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.1 (d, *J* = 2.5 Hz), 162.4 (d, *J* = 10.3 Hz), 138.3, 136.8, 136.0 (d, *J* = 2.9 Hz), 136.0 (d, $J_{C\text{-}F}$ = 242.3 Hz), 133.7 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 22.6 Hz), 131.6, 130.5, 130.0, 129.7, 129.5, 128.3, 128.0, 126.6, 121.8 (d, *J* = 2.9 Hz), 95.2 (d, *J* = 5.3 Hz), 85.3 (d, *J* = 33.9 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.94. **HRMS** Calcd for $C_{26}H_{20}ClFNO_2$ $[M+H]^+$: 432.1162; Found: 432.1160

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(o-tolyl)pent-2-en-4-ynoate (3q)



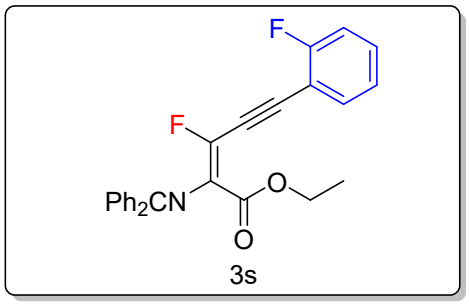
Yellow Solid, Isolated yield: 58.4 mg, 71%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.36 (m, 7H), 7.31 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.12 (td, *J* = 7.4, 1.5 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.0 (d, *J* = 2.8 Hz), 162.6 (d, *J* = 10.9 Hz), 141.0 (d, *J* = 2.3 Hz), 138.5, 136.9, 136.6 (d, $J_{C\text{-}F}$ = 241.9 Hz), 132.3, 132.3, 131.5, 131.3 (d, *J* = 22.8 Hz), 129.9, 129.7, 129.6, 129.6, 128.3, 128.0, 125.7, 121.4 (d, *J* = 2.9 Hz), 97.9 (d, *J* = 5.7 Hz), 84.3 (d, *J* = 33.7 Hz), 61.3, 20.6, 14.3. **^{19}F NMR** (377 MHz, *CDCl$_3$*) δ -102.57. **HRMS** Calcd for $C_{27}H_{23}FNO_2$ $[M+H]^+$: 412.1708; Found: 412.1711

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(2-methoxyphenyl)pent-2-en-4-ynoate (3r)



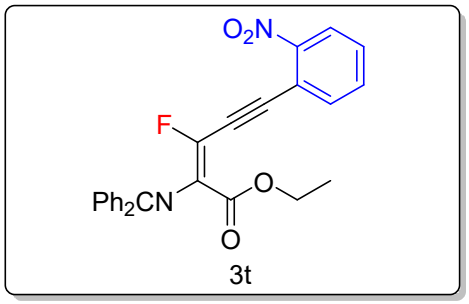
Yellow Solid, Isolated yield: 64 mg, 75%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.42 – 7.34 (m, 5H), 7.34 – 7.22 (m, 3H), 6.89 (td, *J* = 7.6, 1.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 172.9 (d, *J* = 2.8 Hz), 162.6 (d, *J* = 10.4 Hz), 160.4, 138.5, 136.84, 136.6 (d, $J_{C\text{-}F}$ = 242.0 Hz), 133.9, 133.9, 131.5, 131.4, 131.1, 129.9, 129.5, 128.3, 128.0, 120.6, 110.9 (d, *J* = 2.9 Hz), 110.8, 95.6 (d, *J* = 5.3 Hz), 84.5 (d, *J* = 33.8 Hz), 61.3, 55.9, 14.2. **^{19}F NMR** (377 MHz, *CDCl$_3$*) δ -102.73. **HRMS** Calcd for $C_{27}H_{23}FNO_3$ $[M+H]^+$: 428.1657; Found: 428.1659

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(2-fluorophenyl)pent-2-en-4-ynoate (3s)



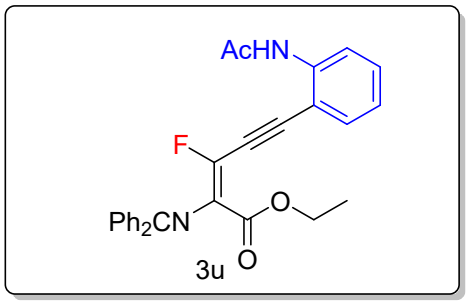
Yellow Solid, Isolated yield: 57.3 mg, 69%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.47 (td, *J* = 7.4, 1.8 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 5H), 7.35 – 7.29 (m, 1H), 7.26 (t, *J* = 5.2 Hz, 2H), 7.13 – 7.03 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2 (d, *J* = 2.8 Hz), 162.7 (d, *J* = 253.1 Hz), 162.5 (d, *J* = 10.8 Hz), 138.3, 136.8, 136.0 (d, $J_{C\text{-}F}$ = 242.0 Hz), 133.7 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 22.3 Hz), 131.6, 131.4 (d, *J* = 8.0 Hz), 130.0, 129.7, 128.3, 128.0, 124.2 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 20.5 Hz), 110.5 (d, *J* = 18.2 Hz), 92.1 (d, *J* = 5.7 Hz), 85.8, 61.5, 14.2. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -105.16, -108.37. **HRMS** Calcd for $C_{26}H_{20}F_2NO_2$ $[M+H]^+$: 416.1457; Found: 416.1459

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(2-nitrophenyl)pent-2-en-4-ynoate (3t)



Yellow Solid, Isolated yield: 26.5 mg, 43%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.11 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.72 (td, *J* = 9.2, 4.2 Hz, 3H), 7.59 (td, *J* = 7.6, 1.4 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.37 (m, 5H), 7.32 – 7.22 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2 (d, *J* = 2.8 Hz), 162.3 (d, *J* = 10.3 Hz), 148.8, 138.2, 135.5 (d, $J_{C\text{-}F}$ = 242.5 Hz), 135.2, 135.2, 133.5 (d, *J* = 22.0 Hz), 133.2, 131.7, 130.0, 129.8, 129.7, 128.4, 128.0, 125.0, 117.6 (d, *J* = 2.9 Hz), 93.9 (d, *J* = 6.0 Hz), 87.8 (d, *J* = 33.8 Hz), 61.7, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -106.74. **HRMS** Calcd for $C_{26}H_{20}FN_2O_4$ $[M+H]^+$: 443.1402; Found: 443.1397

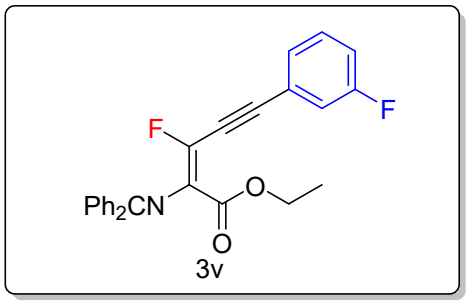
Ethyl (Z)-5-(2-acetamidophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3u)



Yellow Solid, Isolated yield: 48.1 mg, 53%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.91 (s, 1H), 8.54 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.42 (d, J = 6.8 Hz, 5H), 7.39 (s, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 6.6 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.3, 169.9, 163.0 (d, *J* = 11.2 Hz), 141.0,

138.2, 136.72, 136.3 (d, $J_{C\text{-}F}$ = 242.4 Hz), 131.8, 131.6, 131.6, 131.4 (d, J = 23.2 Hz), 131.1, 129.9, 129.8, 128.4, 127.7, 123.0, 119.7, 109.7, 95.4 (d, J = 4.8 Hz), 87.1 (d, J = 34.3 Hz), 61.8, 24.5, 14.2. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -105.27. **HRMS** Calcd for $C_{28}H_{24}FN_2O_3$ $[M+H]^+$: 455.1766; Found: 455.1767

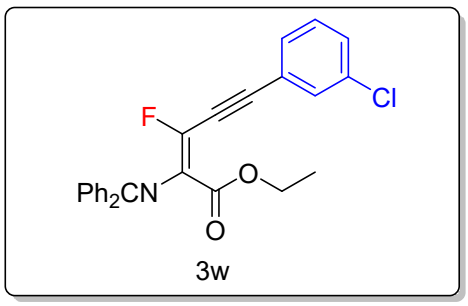
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(3-fluorophenyl)pent-2-en-4-ynoate (3v)



3v

Yellow Solid, Isolated yield: 52.3 mg, 63%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, J = 7.8 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 (d, J = 7.5 Hz, 5H), 7.32 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 7.11 – 6.97 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2 (d, J = 2.7 Hz), 162.4 (d, J = 10.8 Hz), 162.4 (d, J = 247.2 Hz), 138.3, 136.8, 136.0 (d, $J_{C\text{-}F}$ = 241.7 Hz), 132.3 (d, J = 22.4 Hz), 131.7, 130.2 (d, J = 8.7 Hz), 130.0, 129.7, 128.4, 128.0, 127.8 (t, J = 2.9 Hz), 123.4 (d, J = 9.6 Hz), 118.5 (dd, J = 23.4, 2.8 Hz), 116.9 (d, J = 21.3 Hz), 97.1, 81.5 (d, J = 34.4 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.92, -112.36. **HRMS** Calcd for $C_{26}H_{20}F_2NO_2$ $[M+H]^+$: 416.1457 Found: 416.1459

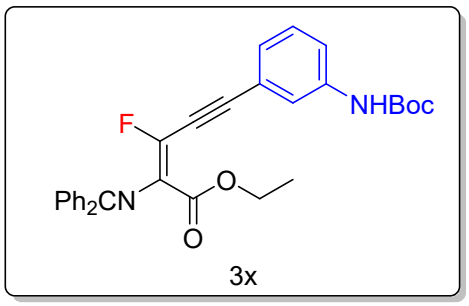
Ethyl (Z)-5-(3-chlorophenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3w)



3w

Yellow Solid, Isolated yield: 54.3 mg, 63%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, J = 7.8 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.44 – 7.30 (m, 7H), 7.25 (td, J = 7.4, 3.8 Hz, 3H), 4.16 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2, 162.4 (d, J = 10.5 Hz), 138.3, 136.8, 135.9 (d, $J_{C\text{-}F}$ = 241.5 Hz), 134.4, 132.3 (d, J = 22.7 Hz), 131.7, 131.6, 131.6, 130.0, 129.9, 129.9, 129.8, 128.4, 128.0, 123.4 (d, J = 2.9 Hz), 97.0, 81.7 (d, J = 33.9 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.95. **HRMS** Calcd for $C_{26}H_{20}ClFNO_2$ $[M+H]^+$: 432.1162 Found: 432.1157

Ethyl (Z)-5-(3-((tert-butoxycarbonyl)amino)phenyl)-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3x)

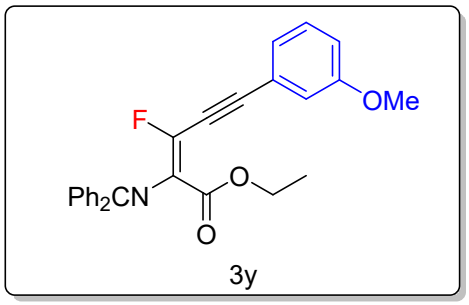


3x

Yellow Solid, Isolated yield: 68 mg, 66%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.73 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 1.8 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.43 – 7.31 (m, 6H), 7.29 – 7.23 (m, 2H), 7.20 (t, J

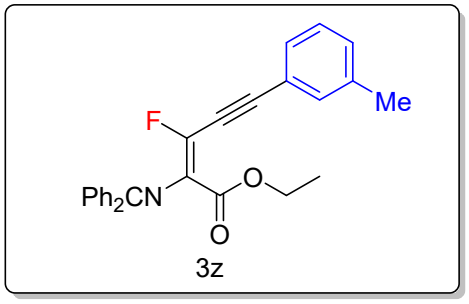
= 7.8 Hz, 1H), 7.12 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.64 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 9H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) *δ* 173.1, 162.6 (d, *J* = 10.7 Hz), 152.6, 138.7, 138.4, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 242.0 Hz), 131.7 (d, *J* = 22.7 Hz), 131.6, 129.9, 129.7, 129.1, 128.3, 128.0, 126.3, 122.2, 122.1, 121.4, 119.7, 98.5 (d, *J* = 5.2 Hz), 80.9, 80.6 (d, *J* = 33.9 Hz), 61.4, 28.4, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) *δ* -103.56. **HRMS** Calcd for $C_{31}H_{30}FN_2O_4$ $[M+H]^+$: 513.2185; Found: 513.2189

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(3-methoxyphenyl)pent-2-en-4-ynoate (3y)



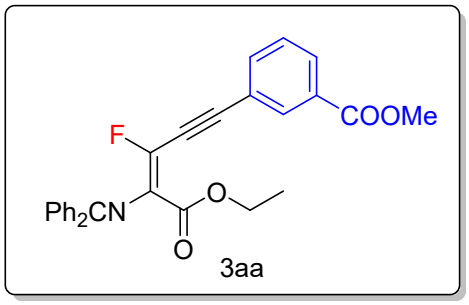
Yellow Solid, Isolated yield: 58.1 mg, 68%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) *δ* 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 9.4, 6.2 Hz, 5H), 7.30 – 7.24 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.08 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.00 (dd, *J* = 2.8, 1.4 Hz, 1H), 6.92 – 6.88 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) *δ* 173.1 (d, *J* = 2.8 Hz), 162.5 (d, *J* = 10.6 Hz), 159.4, 138.4, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 241.5 Hz), 131.7 (d, *J* = 23.2 Hz), 131.6, 129.9, 129.6, 129.6, 128.3, 128.0, 124.5 (d, *J* = 2.8 Hz), 122.5 (d, *J* = 2.8 Hz), 116.4, 116.3 (d, *J* = 3.2 Hz), 98.6 (d, *J* = 5.7 Hz), 80.5 (d, *J* = 33.8 Hz), 61.4, 55.4, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) *δ* -103.65. **HRMS** Calcd for $C_{27}H_{23}FNO_3$ $[M+H]^+$: 428.1657; Found: 428.1662

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(m-tolyl)pent-2-en-4-ynoate (3z)



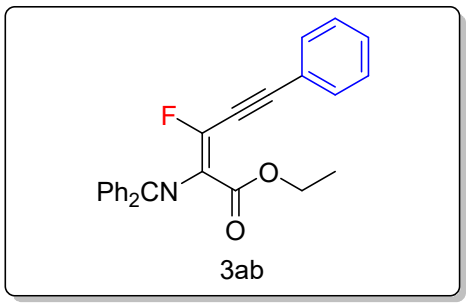
Yellow Solid, Isolated yield: 55.8 mg, 68%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.35 (m, 5H), 7.34 – 7.23 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.13 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0 (d, *J* = 2.8 Hz), 162.6 (d, *J* = 10.8 Hz), 138.4, 138.2, 136.8, 136.5 (d, $J_{C\text{-}F}$ = 242.1 Hz), 132.4, 132.3, 131.5, 131.5 (d, *J* = 22.8 Hz), 130.5, 129.9, 129.6, 129.0 (d, *J* = 2.9 Hz), 128.4, 128.3, 128.0, 121.4 (d, *J* = 2.8 Hz), 98.9 (d, *J* = 5.4 Hz), 80.4 (d, *J* = 33.8 Hz), 61.4, 21.3, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.09. **HRMS** Calcd for $C_{27}H_{23}FNO_2$ $[M+H]^+$: 412.1708; Found: 412.1711

Methyl (Z)-3-(4-((diphenylmethylene)amino)-5-ethoxy-3-fluoro-5-oxopent-3-en-1-yn-1-yl)benzoate (3aa)



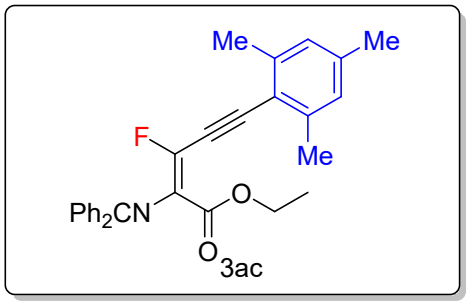
Yellow Solid, Isolated yield: 39.1 mg, 43%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.16 (s, 1H), 8.04 – 7.98 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 (td, *J* = 7.6, 3.0 Hz, 6H), 7.31 – 7.21 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2, 166.2, 162.5 (d, *J* = 10.8 Hz), 138.3, 136.8, 136.0 (d, $J_{C\text{-}F}$ = 242.0 Hz), 135.8 (d, *J* = 2.8 Hz), 132.9 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 22.7 Hz), 131.6, 130.7, 130.4, 130.0, 129.7, 128.7, 128.3, 128.0, 122.1 (d, *J* = 2.8 Hz), 97.4 (d, *J* = 5.8 Hz), 81.5 (d, *J* = 34.3 Hz), 61.5, 52.4, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -104.63. **HRMS** Calcd for $C_{28}H_{23}FNO_4$ $[M+H]^+$: 456.1606; Found: 456.1611

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-phenylpent-2-en-4-ynoate (3ab)



Yellow Solid, Isolated yield: 60.3 mg, 76%. (**Eluent**: PE : EA = 50 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.38 (dt, *J* = 10.8, 4.8 Hz, 5H), 7.33 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.0 (d, *J* = 2.4 Hz), 162.5 (d, *J* = 10.9 Hz), 138.3, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 241.9 Hz), 131.8, 131.8, 131.5, 129.9, 129.6, 129.5, 128.5, 128.3, 127.9, 121.5 (d, *J* = 2.9 Hz), 98.6 (d, *J* = 5.3 Hz), 80.7 (d, *J* = 33.8 Hz), 61.4, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -103.55. **HRMS** Calcd for $C_{26}H_{21}FNO_2$ $[M+H]^+$: 398.1551; Found: 398.1558

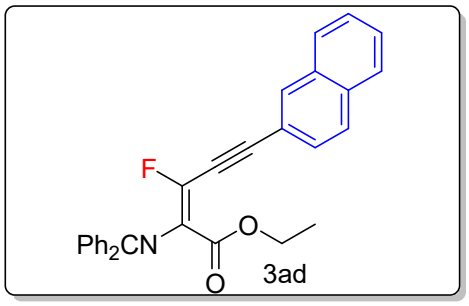
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-mesitylpent-2-en-4-ynoate (3ac)



Yellow Solid, Isolated yield: 66.7 mg, 76%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.40 (m, 5H), 7.32 (dt, *J* = 7.4, 3.8 Hz, 2H), 6.87 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 6H), 2.29 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 172.8 (d, *J* = 2.8 Hz), 162.6 (d, *J* = 10.8 Hz), 141.1, 141.1, 139.3, 138.5, 136.9 (d, $J_{C\text{-}F}$ = 241.8 Hz), 136.9, 131.4, 130.6 (d, *J* = 23.2 Hz), 129.9, 129.6, 128.3, 128.1, 127.8, 118.4 (d, *J* = 2.9 Hz), 97.5 (d, *J* = 5.2 Hz), 87.8 (d, *J* = 33.1

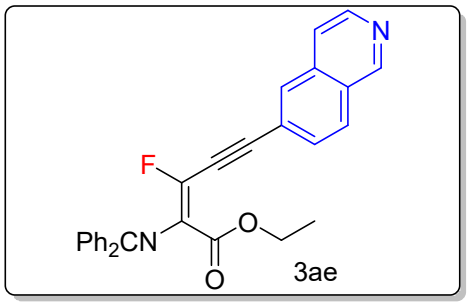
Hz), 61.2, 21.5, 20.8, 14.3. **^{19}F NMR** (377 MHz, *$CDCl_3$*) δ -100.91. **HRMS** Calcd for $C_{29}H_{27}FNO_2$ $[M+H]^+$: 440.2021; Found: 440.2016

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(naphthalen-2-yl)pent-2-en-4-ynoate (3ad)



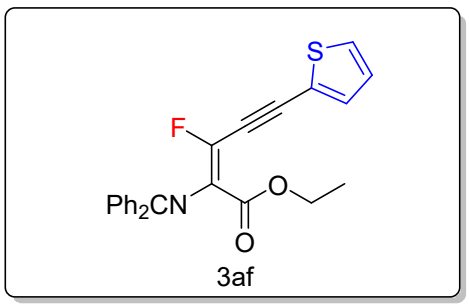
Yellow Solid, Isolated yield: 68.8 mg, 77%. (**Eluent**: PE : EA = 40 : 1) **^{1}H NMR** (400 MHz, *$CDCl_3$*) δ 8.01 (s, 1H), 7.76 (dd, J = 9.0, 4.0 Hz, 5H), 7.52 – 7.47 (m, 4H), 7.44 – 7.35 (m, 5H), 7.28 (dd, J = 6.2, 2.8 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *$CDCl_3$*) δ 173.1, 162.6 (d, J = 10.9 Hz), 138.4, 136.8, 136.5 (d, $J_{C\text{-}F}$ = 241.8 Hz), 133.4, 132.9, 132.4, 132.3, 131.7 (d, J = 23.0 Hz), 131.6, 129.9, 129.7, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.4, 126.9, 118.9 (d, J = 2.9 Hz), 99.2 (d, J = 5.5 Hz), 81.0 (d, J = 33.8 Hz), 61.4, 14.3. **^{19}F NMR** (376 MHz, *$CDCl_3$*) δ -103.42. **HRMS** Calcd for $C_{30}H_{23}FNO_2$ $[M+H]^+$: 448.1708; Found: 448.1711

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(isoquinolin-6-yl)pent-2-en-4-ynoate (3ae)



Yellow Solid, Isolated yield: 61.8 mg, 69%. (**Eluent**: PE : EA = 20 : 1) **^{1}H NMR** (400 MHz, *$CDCl_3$*) δ 9.23 (s, 1H), 8.55 (d, J = 5.8 Hz, 1H), 7.98 (s, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.63 (dt, J = 8.6, 1.0 Hz, 1H), 7.58 (d, J = 5.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.2 Hz, 5H), 7.33 – 7.25 (m, 2H), 4.20 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *$CDCl_3$*) δ 173.2, 162.4 (d, J = 10.9 Hz), 152.4, 144.1, 138.2, 136.8, 135.8 (d, $J_{C\text{-}F}$ = 241.8 Hz), 135.3, 132.7 (d, J = 22.6 Hz), 131.7, 130.5, 130.4, 129.4, 129.4, 128.4, 128.0, 127.9, 127.9, 123.7 (d, J = 2.8 Hz), 120.2, 97.8 (d, J = 5.8 Hz), 82.9 (d, J = 34.3 Hz), 61.6, 14.3. **^{19}F NMR** (376 MHz, *$CDCl_3$*) δ -105.29. **HRMS** Calcd for $C_{29}H_{22}FN_2O_2$ $[M+H]^+$: 449.1660; Found: 449.1655

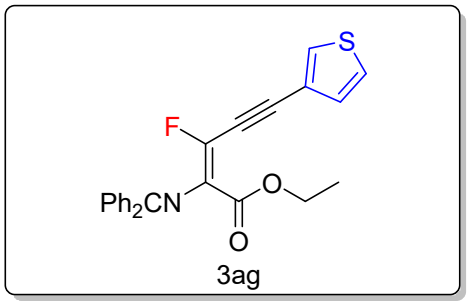
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(thiophen-2-yl)pent-2-en-4-ynoate (3af)



Yellow Solid, Isolated yield: 40.3 mg, 50%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, *$CDCl_3$*) δ 7.73 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.38 (dd, J = 9.8, 6.4 Hz, 5H), 7.32 (dd, J = 5.2, 1.2 Hz, 1H), 7.29 (d, J = 3.6

Hz, 1H), 7.27 – 7.22 (m, 2H), 6.96 (dd, J = 5.2, 3.8 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1 (d, J = 2.7 Hz), 162.4 (d, J = 10.3 Hz), 138.3, 136.7, 136.1 (d, $J_{C\text{-}F}$ = 241.9 Hz), 133.7, 133.7, 131.8, 131.6, 129.9, 129.6, 129.3, 128.3, 127.9, 127.4, 121.4 (d, J = 3.1 Hz), 92.1 (d, J = 5.2 Hz), 84.3 (d, J = 34.1 Hz), 61.4, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.82. **HRMS** Calcd for $C_{24}H_{19}FNO_2S$ $[M+H]^+$: 404.1115; Found: 404.1116

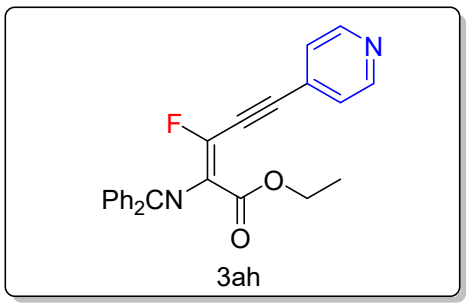
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(thiophen-3-yl)pent-2-en-4-ynoate (3ag)



3ag

Yellow Solid, Isolated yield: 66.1 mg, 82%. (**Eluent**: PE : EA = 20 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 3.2, 1.2 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.38 (dd, J = 9.4, 6.4 Hz, 5H), 7.25 (dt, J = 5.0, 2.8 Hz, 3H), 7.13 (dd, J = 5.0, 1.2 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0 (d, J = 2.4 Hz), 162.5 (d, J = 10.8 Hz), 138.3, 136.8, 136.4 (d, $J_{C\text{-}F}$ = 242.1 Hz), 131.5, 131.5 (d, J = 23.3 Hz), 130.8, 130.7, 129.9, 129.7, 129.6, 129.6, 127.9, 125.8, 120.7 (d, J = 2.9 Hz), 94.0 (d, J = 5.3 Hz), 80.3 (d, J = 33.8 Hz), 61.4, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.45. **HRMS** Calcd for $C_{24}H_{19}FNO_2S$ $[M+H]^+$: 404.1116; Found: 404.1113

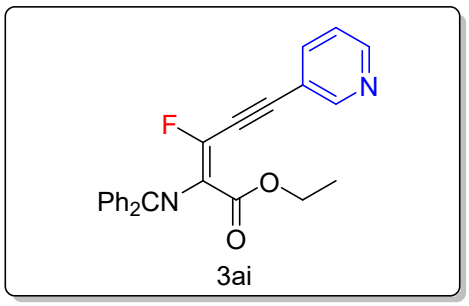
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(pyridin-4-yl)pent-2-en-4-ynoate (3ah)



3ah

Yellow Solid, Isolated yield: 42.2 mg, 53%. (**Eluent**: PE : EA = 15 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, J = 6.2 Hz, 2H), 7.74 (s, 2H), 7.49 (s, 1H), 7.46 – 7.38 (m, 5H), 7.33 (d, J = 6.2 Hz, 2H), 7.26 (s, 2H), 4.17 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3 (d, J = 2.9 Hz), 162.2 (d, J = 10.8 Hz), 150.0, 138.1, 136.7, 135.3(d, $J_{C\text{-}F}$ = 242.0 Hz), 133.4 (d, J = 22.6 Hz), 131.8, 130.0, 129.8, 129.8 (d, J = 2.6 Hz), 128.4, 127.9, 125.3 (d, J = 2.7 Hz), 95.4 (d, J = 5.7 Hz), 84.7 (d, J = 34.5 Hz), 61.7, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -106.99. **HRMS** Calcd for $C_{25}H_{20}FN_2O_2$ $[M+H]^+$: 399.1504; Found: 399.1508

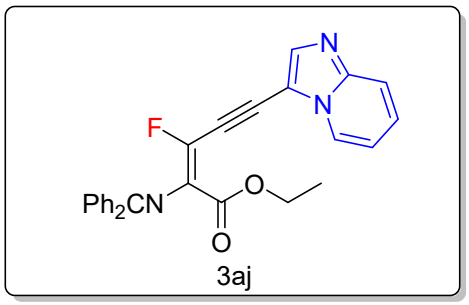
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(pyridin-3-yl)pent-2-en-4-ynoate (3ai)



3ai

Yellow Solid, Isolated yield: 46.2 mg, 58%. (**Eluent**: PE : EA = 15 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.71 (d, *J* = 2.2 Hz, 1H), 8.55 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.75 (dq, *J* = 6.8, 2.4 Hz, 3H), 7.51 – 7.36 (m, 6H), 7.29 – 7.22 (m, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.1 (d, *J* = 2.8 Hz), 162.2 (d, *J* = 10.7 Hz), 152.2 (d, *J* = 2.8 Hz), 149.5, 138.6, 138.5, 138.1, 136.6, 135.6 (d, $J_{C\text{-}F}$ = 241.7 Hz), 132.5 (d, *J* = 22.5 Hz), 131.6, 129.9, 129.7, 128.3, 127.8, 123.1, 118.9 (d, *J* = 2.7 Hz), 95.0 (d, *J* = 5.7 Hz), 83.7 (d, *J* = 34.2 Hz), 61.5, 14.2. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -105.76. **HRMS** Calcd for $C_{25}H_{20}FN_2O_2$ $[M+H]^+$: 399.1504; Found: 399.1499

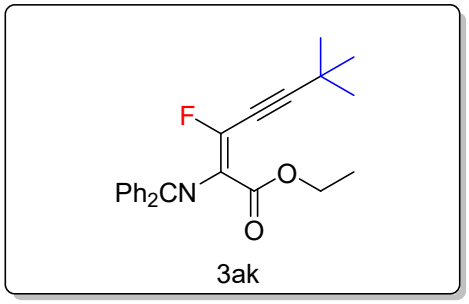
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(imidazo[1,2-a]pyridin-3-yl)pent-2-en-4-ynoate (3aj)



3aj

Yellow Solid, Isolated yield: 40.2 mg, 46%. (**Eluent**: PE : EA = 12 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 8.53 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.93 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.38 (m, 5H), 7.34 – 7.25 (m, 3H), 6.98 (td, *J* = 6.8, 1.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 173.2 (d, *J* = 2.8 Hz), 162.4 (d, *J* = 10.8 Hz), 146.4, 140.0, 138.3, 137.5, 135.97 (d, $J_{C\text{-}F}$ = 170.2 Hz), 131.7, 131.3 (d, *J* = 23.2 Hz), 130.0, 129.8, 128.4, 127.9, 126.8, 126.2, 118.1, 113.9, 107.8, 91.0 (d, *J* = 33.4 Hz), 86.7 (d, *J* = 5.2 Hz), 61.5, 14.3. **^{19}F NMR** (376 MHz, *CDCl$_3$*) δ -106.65. **HRMS** Calcd for $C_{27}H_{21}FN_3O_2$ $[M+H]^+$: 438.1613; Found: 438.1618

Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-6,6-dimethylhept-2-en-4-ynoate (3ak)

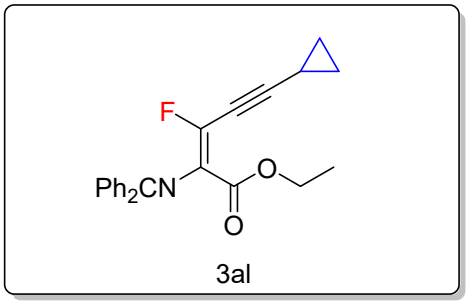


3ak

Yellow Oil, Isolated yield: 33.9 mg, 45%. (**Eluent**: PE : EA = 60 : 1) **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ 7.73 – 7.68 (m, 2H), 7.49 – 7.43 (m, 1H), 7.42 – 7.35 (m, 5H), 7.25 – 7.20 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.27 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, *CDCl$_3$*) δ 172.7 (d, *J* = 2.4 Hz), 162.8 (d, *J* = 11.1 Hz), 138.6, 136.9, 136.8 (d, $J_{C\text{-}F}$ = 242.8 Hz), 131.4, 130.3 (d, *J* = 23.4 Hz), 129.8, 129.4, 128.2, 128.1, 108.4 (d, *J* = 5.2 Hz), 71.0

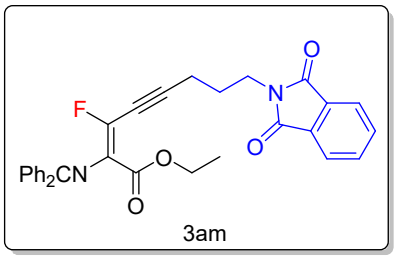
(d, J = 33.9 Hz), 61.1, 30.3, 28.5 (d, J = 2.2 Hz), 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -99.51. **HRMS** Calcd for $C_{24}H_{25}FNO_2$ $[M+H]^+$: 378.1864; Found: 378.1865

Ethyl (Z)-5-cyclopropyl-2-((diphenylmethylene)amino)-3-fluoropent-2-en-4-ynoate (3al)



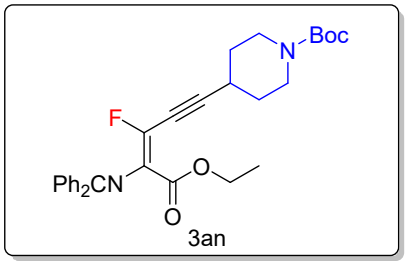
Yellow Oil, Isolated yield: 42.8 mg, 64%. (**Eluent**: PE : EA = 60 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dt, J = 7.2, 1.4 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.42 – 7.35 (m, 5H), 7.24 – 7.19 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 1.50 – 1.42 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H), 0.92 – 0.83 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8 (d, J = 2.4 Hz), 162.9 (d, J = 11.2 Hz), 138.5, 136.8, 136.7 (d, $J_{C\text{-}F}$ = 242.6 Hz), 131.4, 130.6 (d, J = 23.6 Hz), 129.8, 129.5, 128.3, 127.9, 104.3 (d, J = 5.1 Hz), 67.3 (d, J = 33.7 Hz), 61.2, 14.2, 9.2 (d, J = 1.7 Hz), 0.6 (d, J = 3.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.43. **HRMS** Calcd for $C_{23}H_{21}FNO_2$ $[M+H]^+$: 362.1551; Found: 362.1550

Ethyl (Z)-8-(1,3-dioxoisoindolin-2-yl)-2-((diphenylmethylene)amino)-3-fluorooct-2-en-4-ynoate (3am)



Yellow Solid, Isolated yield: 50.8 mg, 50%. (**Eluent**: PE : EA = 8 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dt, J = 7.6, 3.8 Hz, 2H), 7.73 – 7.67 (m, 4H), 7.45 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 7.2 Hz, 5H), 7.22 – 7.14 (m, 2H), 4.09 (q, J = 7.2 Hz, 2H), 3.77 (t, J = 7.0 Hz, 2H), 2.50 (q, J = 6.8 Hz, 2H), 1.97 (p, J = 7.4 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8 (d, J = 2.3 Hz), 168.4, 162.7 (d, J = 11.0 Hz), 138.5, 136.8, 136.4 (d, $J_{C\text{-}F}$ = 242.3 Hz), 134.1, 132.2, 130.9 (d, J = 22.9 Hz), 129.8, 129.5, 128.3, 127.9, 123.4, 99.4 (d, J = 5.2 Hz), 72.7 (d, J = 34.2 Hz), 61.2, 37.3, 27.1 (d, J = 2.1 Hz), 17.9 (d, J = 2.3 Hz), 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.74. **HRMS** Calcd for $C_{31}H_{26}FN_2O_4$ $[M+H]^+$: 509.1872; Found: 509.1868

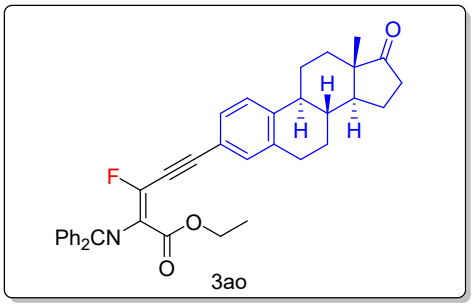
***Tert*-butyl (Z)-4-(4-((diphenylmethylene)amino)-5-ethoxy-3-fluoro-5-oxopent-3-en-1-yn-1-yl)piperidine-1-carboxylate (3an)**



Yellow Solid, Isolated yield: 30.2 mg, 30%. (**Eluent**: PE : EA = 5 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.35 (m, 5H), 7.21 (dd, J = 7.6, 2.0 Hz,

2H), 4.10 (q, J = 7.2 Hz, 2H), 3.71 – 3.63 (m, 2H), 3.25 – 3.71 (m, 2H), 2.85 – 2.76 (m, 1H), 1.84 – 1.76 (m, 2H), 1.69 – 1.59 (m, 2H), 1.45 (s, 9H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9 (d, J = 2.8 Hz), 162.7 (d, J = 11.0 Hz), 154.8, 138.5, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 242.1 Hz), 131.5, 131.0 (d, J = 23.3 Hz), 129.9, 129.6, 128.3, 128.0, 102.2 (d, J = 5.8 Hz), 79.7, 73.6 (d, J = 33.8 Hz), 61.3, 30.8, 28.6, 28.1, 28.1, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -100.86. **HRMS** Calcd for $C_{30}H_{34}FN_2O_4$ $[M+H]^+$: 505.2498; Found: 505.2494

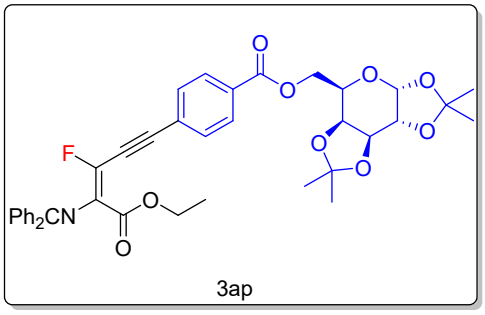
Ethyl (Z)-2-((diphenylmethylene)amino)-3-fluoro-5-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)pent-2-en-4-ynoate (3ao)



3ao

Yellow Solid, Isolated yield: 71.1 mg, 62%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.43 – 7.34 (m, 5H), 7.29 – 7.20 (m, 5H), 4.14 (q, J = 7.2 Hz, 2H), 2.85 (d, J = 4.8 Hz, 2H), 2.48 (dd, J = 18.8, 8.8 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.31 – 2.23 (m, 1H), 2.16 – 1.94 (m, 4H), 1.64 – 1.41 (m, 6H), 1.22 (t, J = 7.2 Hz, 3H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9 (d, J = 2.3 Hz), 162.5 (d, J = 11.0 Hz), 141.7, 138.3, 136.8, 136.7, 136.5 (d, $J_{C\text{-}F}$ = 242.0 Hz), 132.2, 132.2, 131.5, 131.2 (d, J = 22.8 Hz), 129.8, 129.5, 129.1, 129.0, 128.2, 127.9, 125.5, 118.7 (d, J = 2.9 Hz), 99.0 (d, J = 5.2 Hz), 80.1 (d, J = 34.1 Hz), 61.2, 50.5, 47.9, 44.5, 37.8, 35.8, 31.5, 29.0, 26.2, 25.5, 21.6, 14.2, 13.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -102.80. **HRMS** Calcd for $C_{38}H_{37}FNO_3$ $[M+H]^+$: 574.2752; Found: 574.2756

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-((Z)-4-((diphenylmethylene)amino)-5-ethoxy-3-fluoro-5-oxopent-3-en-1-yn-1-yl)benzoate (3ap)

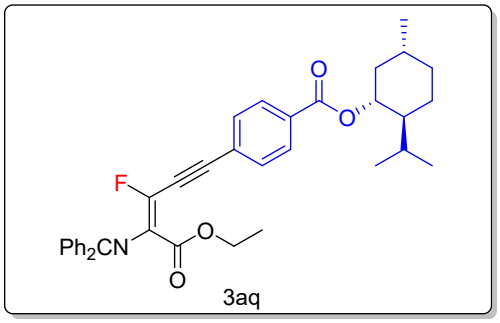


3ap

Yellow Solid, Isolated yield: 86.1 mg, 63%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.2 Hz, 5H), 7.26 (d, J = 6.4 Hz, 2H), 4.70 (d, J = 11.8 Hz, 1H), 4.64 (dd, J = 7.8, 2.6 Hz, 1H), 4.45 (d, J = 2.6 Hz, 1H),

4.33 (d, J = 11.8 Hz, 1H), 4.25 (dd, J = 7.8, 1.8 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.95 (dd, J = 13.2, 1.8 Hz, 1H), 3.80 (d, J = 13.0 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.34 (s, 6H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1 (d, J = 2.8 Hz), 165.2, 162.3 (d, J = 10.8 Hz), 138.2, 136.7, 135.7 (d, $J_{C\text{-}F}$ = 241.9 Hz), 132.6 (d, J = 22.6 Hz), 131.7, 131.7, 130.3, 129.9, 128.3, 127.9, 126.3 (d, J = 2.8 Hz), 109.2, 108.9, 101.7, 97.5 (d, J = 5.3 Hz), 83.4 (d, J = 34.2 Hz), 70.8, 70.7, 70.1, 65.6, 61.5, 61.4, 26.6, 26.0, 25.5, 24.1, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.42. **HRMS** Calcd for $C_{39}H_{39}FNO_9$ $[M+H]^+$: 684.2604; Found: 684.2606

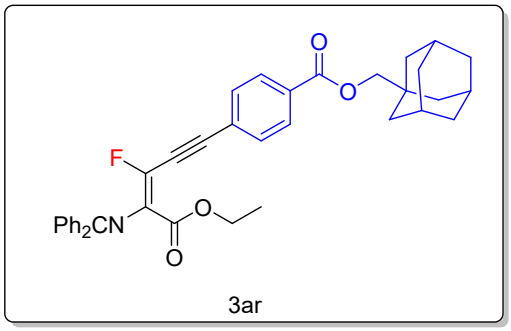
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((Z)-4-((diphenylmethylene)amino)-5-ethoxy-3-fluoro-5-oxopent-3-en-1-yn-1-yl)benzoate (3aq)



3aq

Yellow Solid, Isolated yield: 86.1 mg, 63%. (**Eluent**: PE : EA = 25 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.4 Hz, 1H), 7.40 (d, J = 7.8 Hz, 5H), 7.26 (d, J = 8.4 Hz, 2H), 4.94 (td, J = 10.8, 4.4 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 2.15 – 2.08 (m, 1H), 1.98 – 1.90 (m, 1H), 1.76 – 1.70 (m, 2H), 1.61 – 1.49 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 1.15 – 1.07 (m, 2H), 0.95 – 0.89 (m, 7H), 0.79 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1 (d, J = 2.9 Hz), 165.3, 162.3 (d, J = 10.3 Hz), 138.2, 136.7, 135.8 (d, $J_{C\text{-}F}$ = 241.4 Hz), 132.4 (d, J = 22.5 Hz), 131.6, 131.6, 131.2, 129.9, 129.7, 129.5, 128.3, 127.9, 125.9 (d, J = 2.8 Hz), 97.6 (d, J = 5.7 Hz), 83.2 (d, J = 34.1 Hz), 75.3, 61.4, 47.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.16. **HRMS** Calcd for $C_{37}H_{39}FNO_4$ $[M+H]^+$: 580.2858; Found: 580.2859

((3R,5R,7R)-Adamantan-1-yl)methyl 4-((Z)-4-((diphenylmethylene)amino)-5-ethoxy- 3-Fluoro-5-oxopent-3-en-1-yn-1-yl)benzoate (3ar)

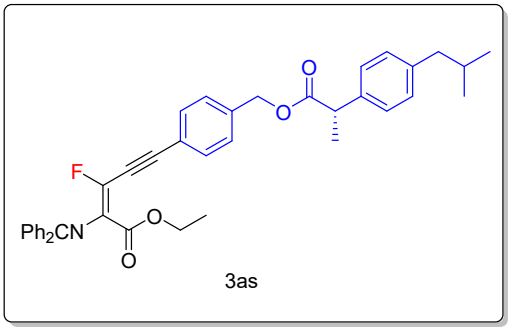


3ar

Yellow Gummy, Isolated yield: 80 mg, 65%. (**Eluent**: PE : EA = 30 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.45 – 7.36 (m, 5H), 7.29 – 7.24 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 3.92 (s, 2H), 2.02 (s, 4H), 1.72 - 1.61 (m, 13H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2 (d, J = 2.7 Hz), 166.0, 162.4 (d, J = 10.4 Hz),

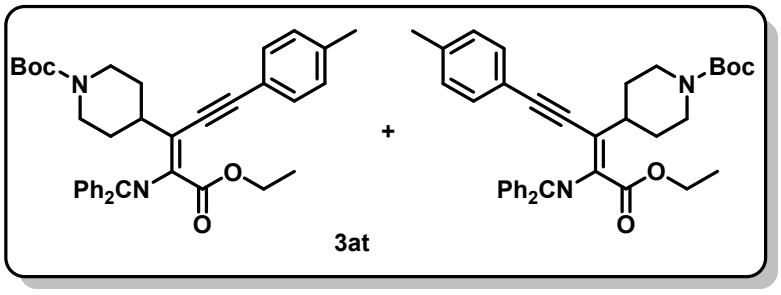
138.3, 136.8, 135.9 (d, $J_{C\text{-}F}$ = 241.4 Hz), 132.5 (d, J = 22.2 Hz), 131.7, 131.7, 131.0, 130.0, 129.7, 129.6, 128.4, 128.0, 126.1 (d, J = 2.6 Hz), 97.7, 83.3 (d, J = 34.3 Hz), 74.8, 61.5, 39.5, 37.1, 33.6, 28.2, 14.3. **^{19}F NMR** (376 MHz, *CDCl3*) δ -105.23. **HRMS** Calcd for $C_{38}H_{37}FNO_4$ $[M+H]^+$: 590.2702; Found: 590.2704

Ethyl (S,Z)-2-((diphenylmethylene)amino)-3-fluoro-5-(4-(((2-(4-isobutylphenyl)propano-yl)oxy)methyl)phenyl)pent-2-en-4-ynoate (3as)



Yellow Solid, Isolated yield: 80 mg, 65%. (**Eluent**: PE : EA = 30 : 1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.42 – 7.34 (m, 7H), 7.26 (dd, J = 6.8, 2.8 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 5.13 – 5.03 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.74 (q, J = 7.2 Hz, 1H), 2.44 (d, J = 7.2 Hz, 2H), 1.90 – 1.78 (m, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 173.0 (d, J = 2.6 Hz), 162.5 (d, J = 10.8 Hz), 140.7, 138.3, 137.6, 137.5, 136.8, 136.3 (d, $J_{C\text{-}F}$ = 241.9 Hz), 131.9, 131.8, 131.6, 131.6, 129.9, 129.6, 129.4, 128.3, 128.0, 127.6, 127.3, 121.2 (d, J = 2.8 Hz), 98.3 (d, J = 5.2 Hz), 81.0 (d, J = 33.8 Hz), 65.7, 61.4, 45.2, 45.1, 30.3, 22.5, 18.4, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.82. **HRMS** Calcd for $C_{40}H_{39}FNO_4$ $[M+H]^+$: 616.2858; Found: 616.2854

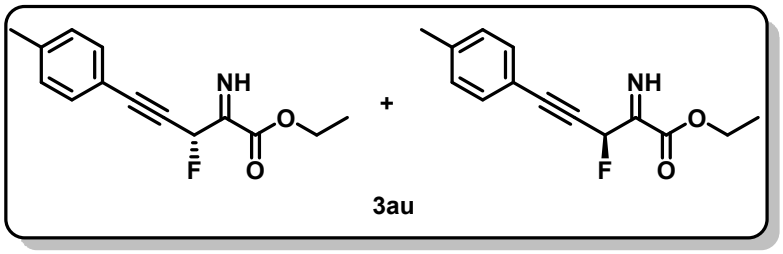
***Tert*-butyl (*E*)-4-(4-((diphenylmethylene)amino)-5-ethoxy-5-oxo-1-(p-tolyl)pent-3-en-1-yn-3-yl)piperidine-1-carboxylate and *Tert*-butyl (*Z*)-4-(4-((diphenylmethylene)a- mino)-5-ethoxy-5-oxo-1-(p-tolyl)pent-3-en-1-yn-3-yl)piperidine-1-carboxylate (3at)**



Yellow Gummy. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.40 – 7.14 (m, 9H), 7.13 – 7.01 (m, 2H), 4.19 – 3.82 (m, 2H), 3.51 – 3.34 (m, 4H), 3.25 – 2.73 (m, 4H), 2.32 (d, J = 9.5 Hz, 3H), 1.45 (s, 9H), 1.29 – 1.08 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 164.7, 154.8, 139.4, 138.9, 137.4, 137.2, 135.6, 131.5, 131.5, 130.9, 130.6, 130.5, 129.6, 129.3, 129.2, 129.1, 129.1, 129.1, 128.7, 128.6, 128.2, 128.1, 127.9, 127.7, 119.7, 98.5, 83.9, 79.8, 79.7, 60.6, 60.3, 51.5, 49.7, 28.4, 21.6, 21.6, 14.5, 14.2.

HRMS Calcd for $C_{37}H_{41}N_2O_4$ $[M+H]^+$: 577.3061; Found: 577.3061

Ethyl (*R*)-3-fluoro-2-imino-5-(p-tolyl)pent-4-ynoate and Ethyl (*S*)-3-fluoro-2-imino-5-(p-tolyl)pent-4-ynoate (3au)

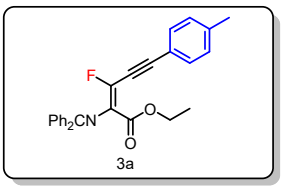


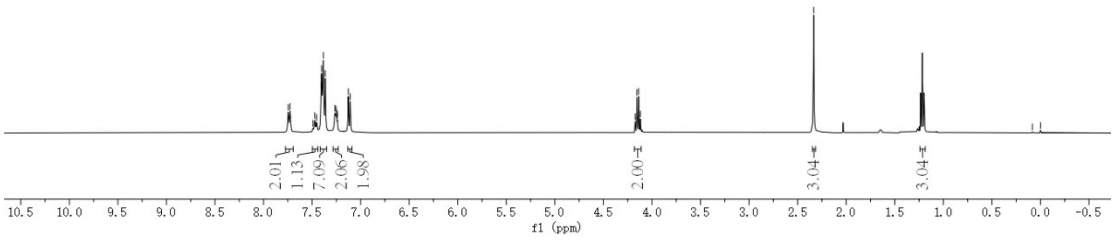
3au

Colorless Oil. **^{1}H NMR** (400 MHz, *CD_3OD*) δ 7.37 – 7.25 (m, 2H), 7.12 – 7.16 (m, 2H), 7.15 – 7.08 (m, 1H), 5.77 – 5.54 (m, 1H), 4.36 – 4.02 (m, 2H), 2.33 (s, 3H), 1.33 – 1.17 (m, 3H). **^{13}C NMR** (100 MHz, *CD_3OD*) δ 170.5, 169.3, 139.7, 139.6, 138.0 (d, J = 6.0 Hz), 137.8 (d, J = 5.9 Hz), 132.5, 132.5, 130.3, 130.1, 129.8 (d, J = 2.0 Hz), 129.7 (d, J = 2.1 Hz), 128.8 (d, J = 10.2 Hz), 128.6 (d, J = 10.7 Hz), 98.6 (d, J = 8.7 Hz), 98.3 (d, J = 13.9 Hz), 90.6 (d, J = 186.0 Hz), 88.7 (d, J = 180.5 Hz), 63.5, 63.2, 21.2, 14.3, 14.2. **^{19}F NMR** (376 MHz, *CD_3OD*) δ -185.95, -190.17. **HRMS** Calcd for $C_{14}H_{15}FNO_2$ $[M+H]^+$: 248.1081; Found: 248.1080

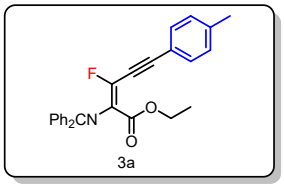
16. NMR spectra

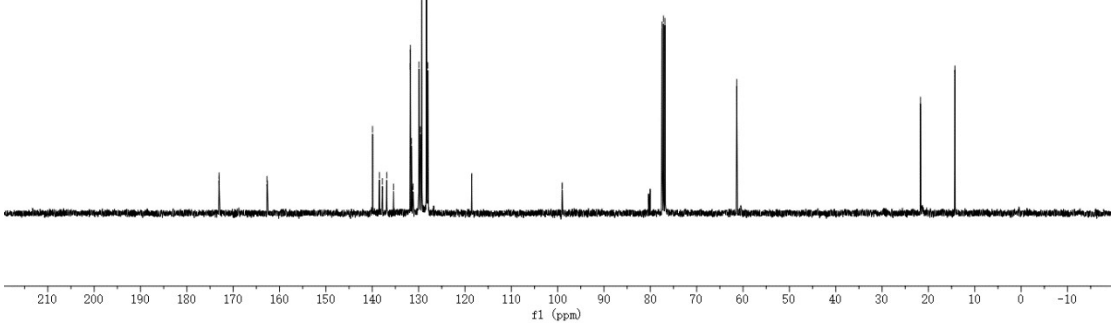
^{1}H NMR of compound 3a (400 MHz, $CDCl_3$)



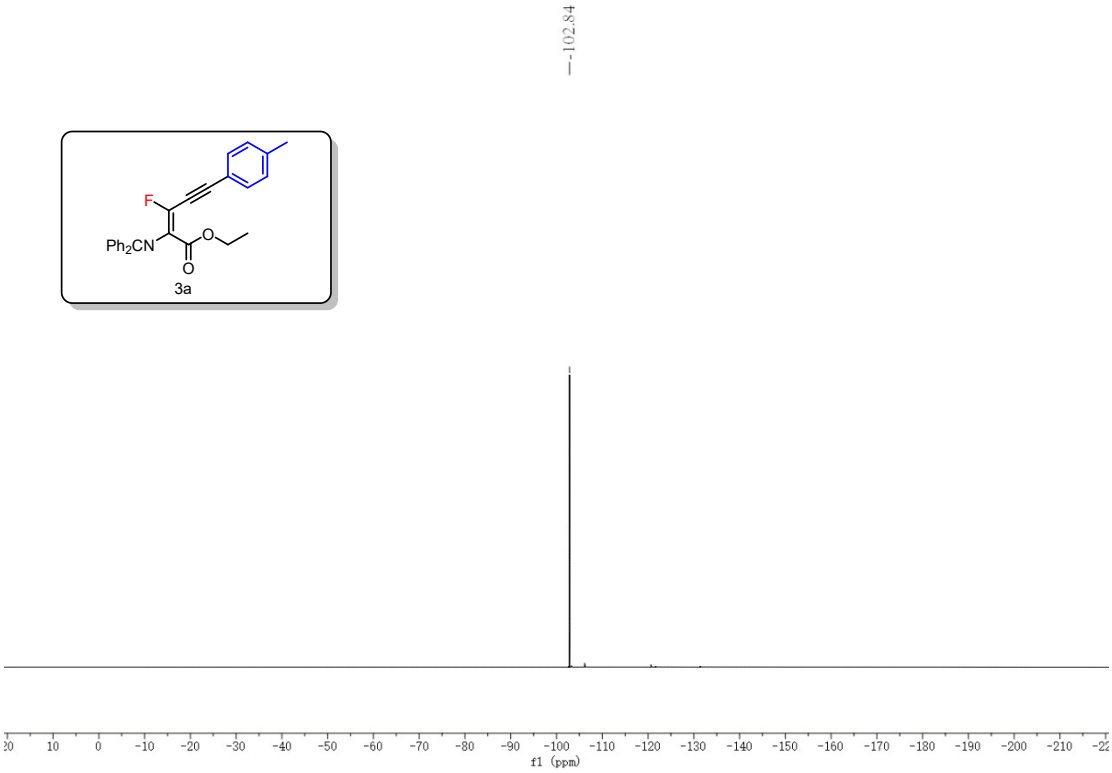


^{13}C NMR of compound 3a (101 MHz, $CDCl_3$)

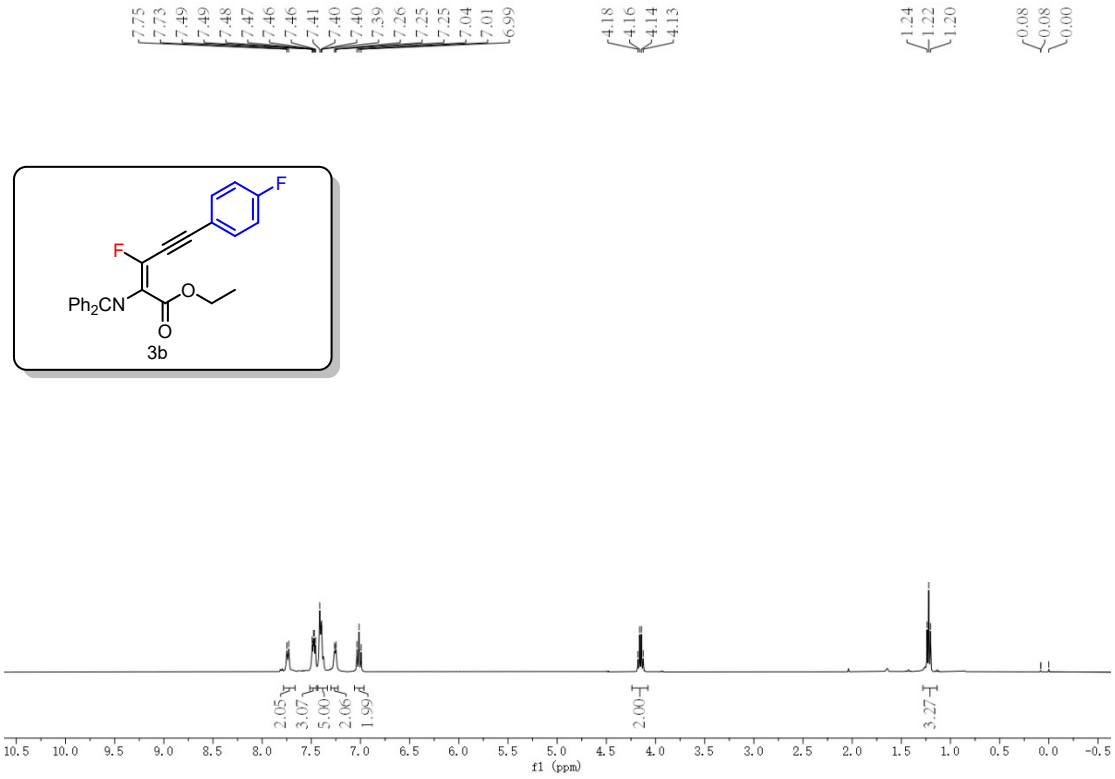




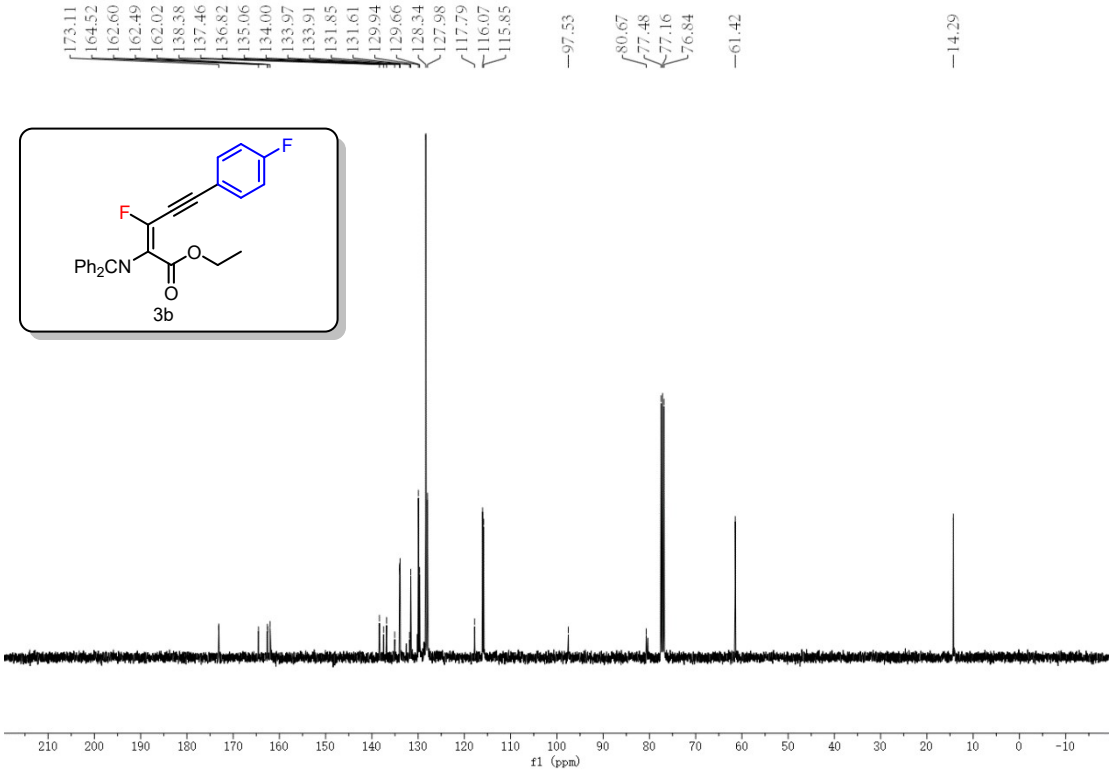
^{19}F NMR of compound 3a (377 MHz, $CDCl_3$)



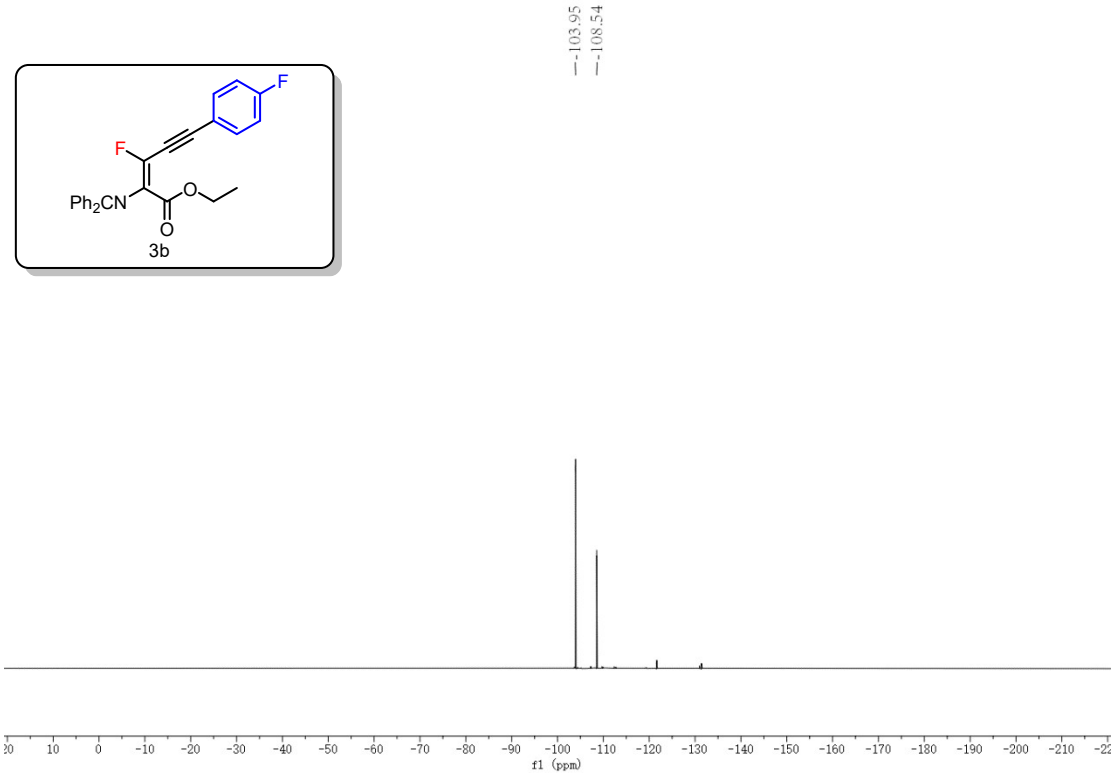
^{1}H NMR of compound 3b (400 MHz, $CDCl_3$)



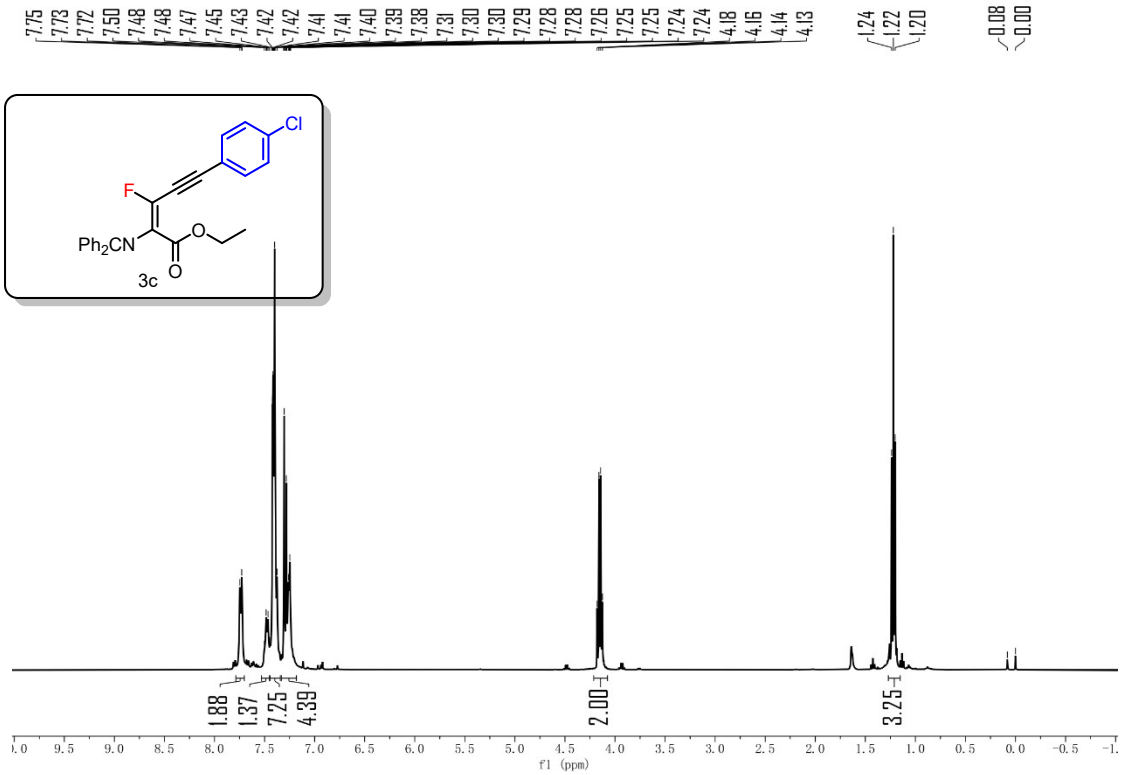
^{13}C NMR of compound 3b (101 MHz, $CDCl_3$)



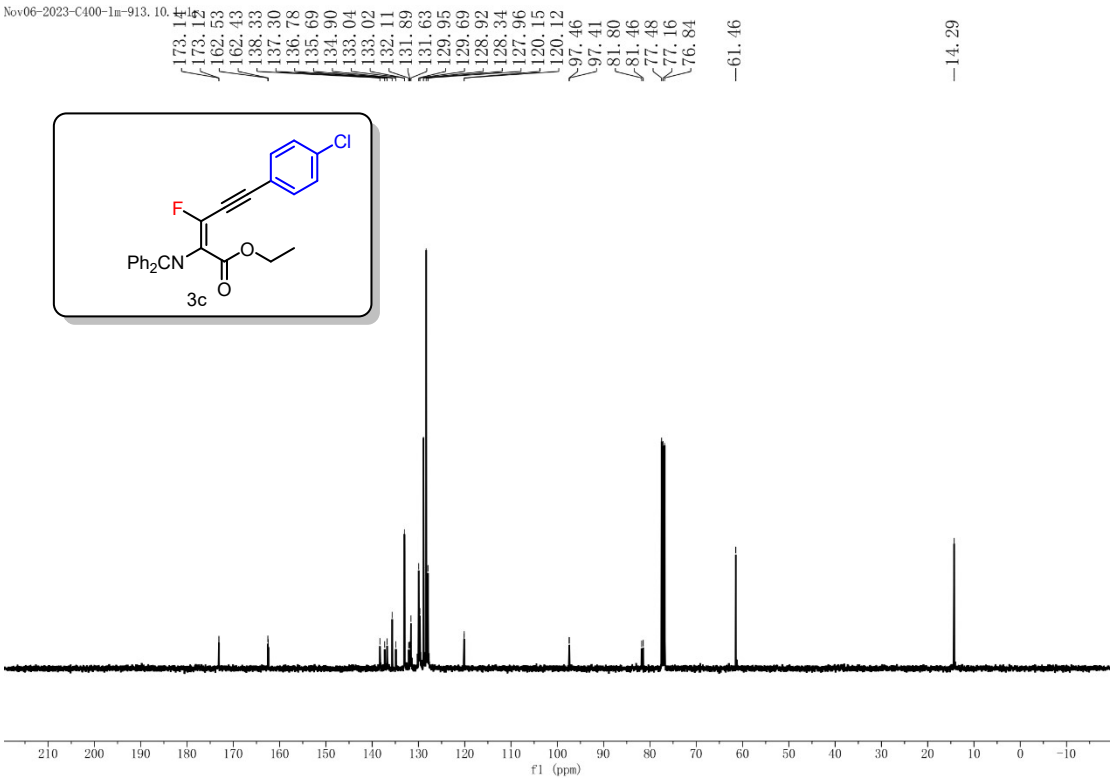
^{19}F NMR of compound 3b (377 MHz, $CDCl_3$)



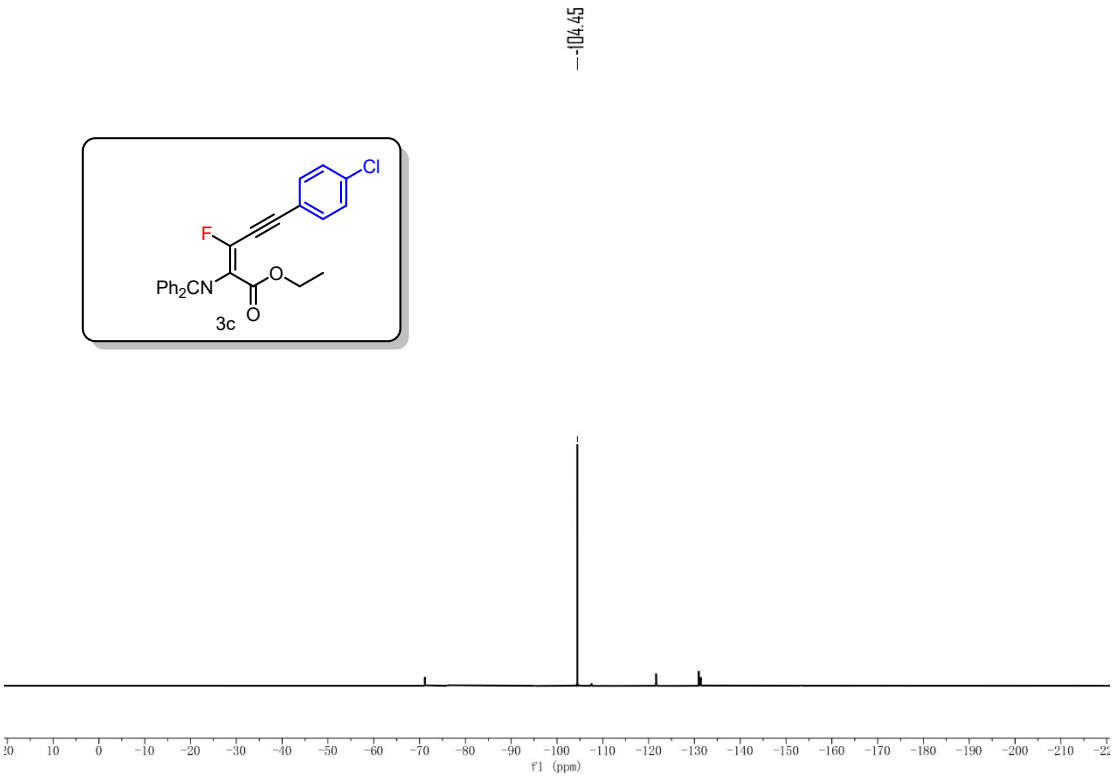
^{1}H NMR of compound 3c (400 MHz, $CDCl_3$)



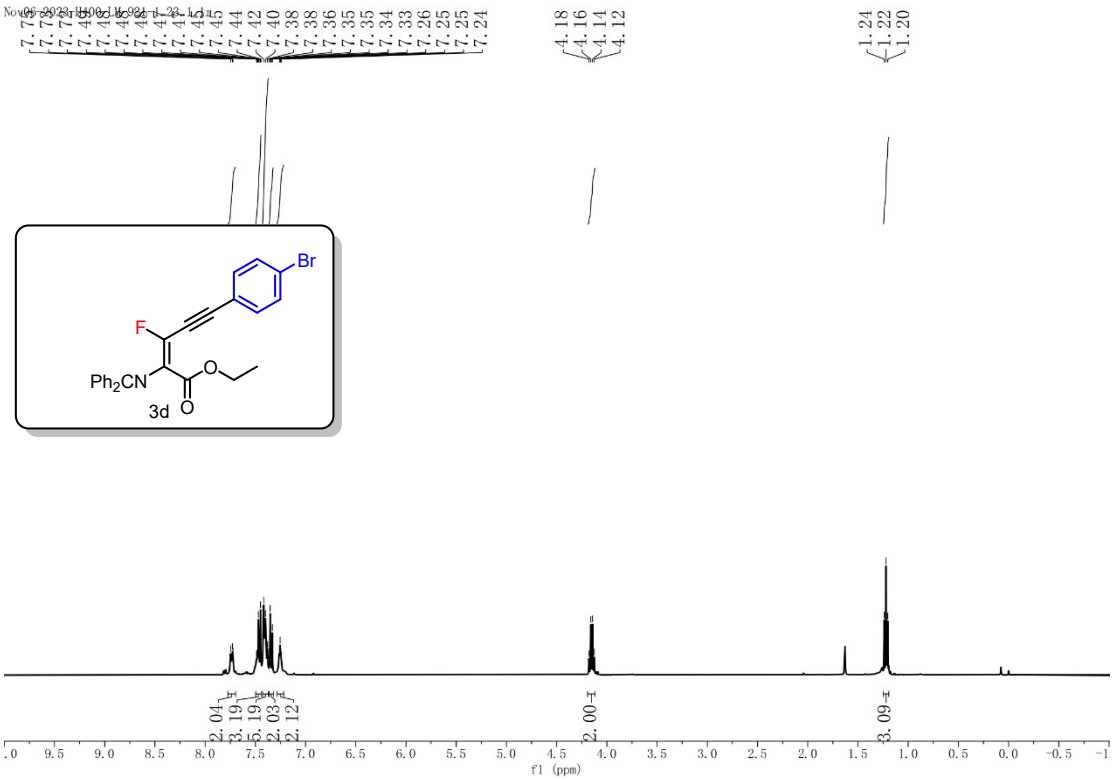
^{13}C NMR of compound 3c (101 MHz, $CDCl_3$)



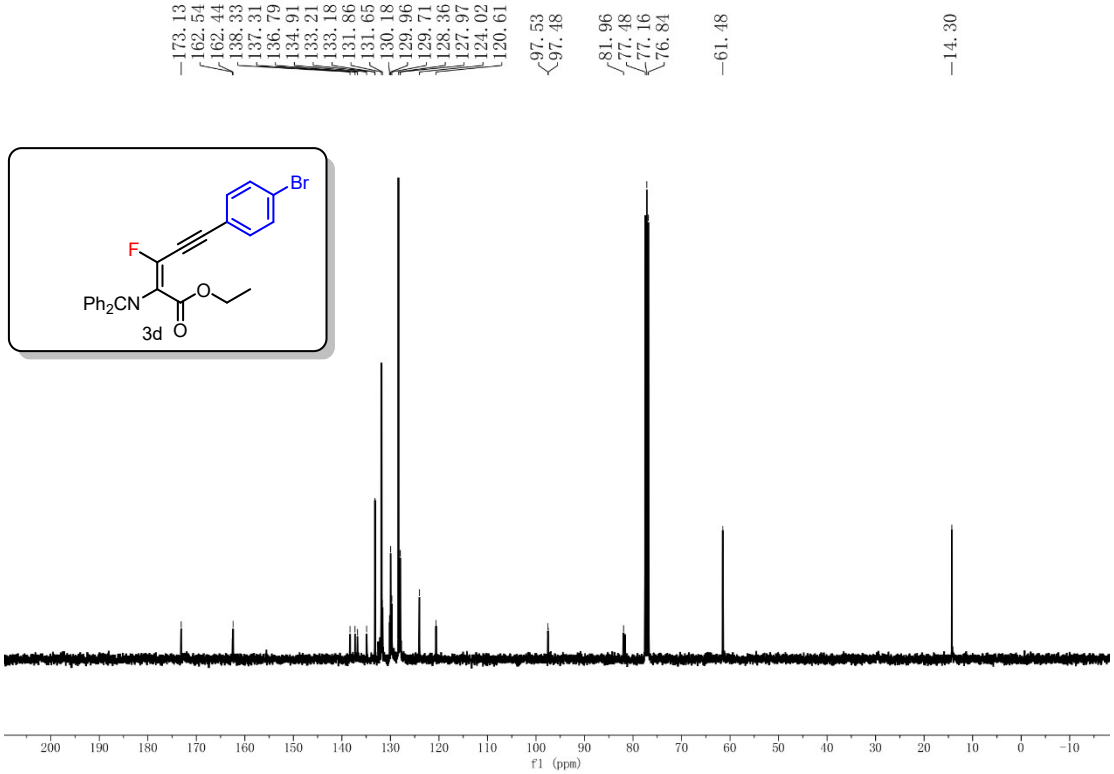
^{19}F NMR of compound 3c (377 MHz, $CDCl_3$)



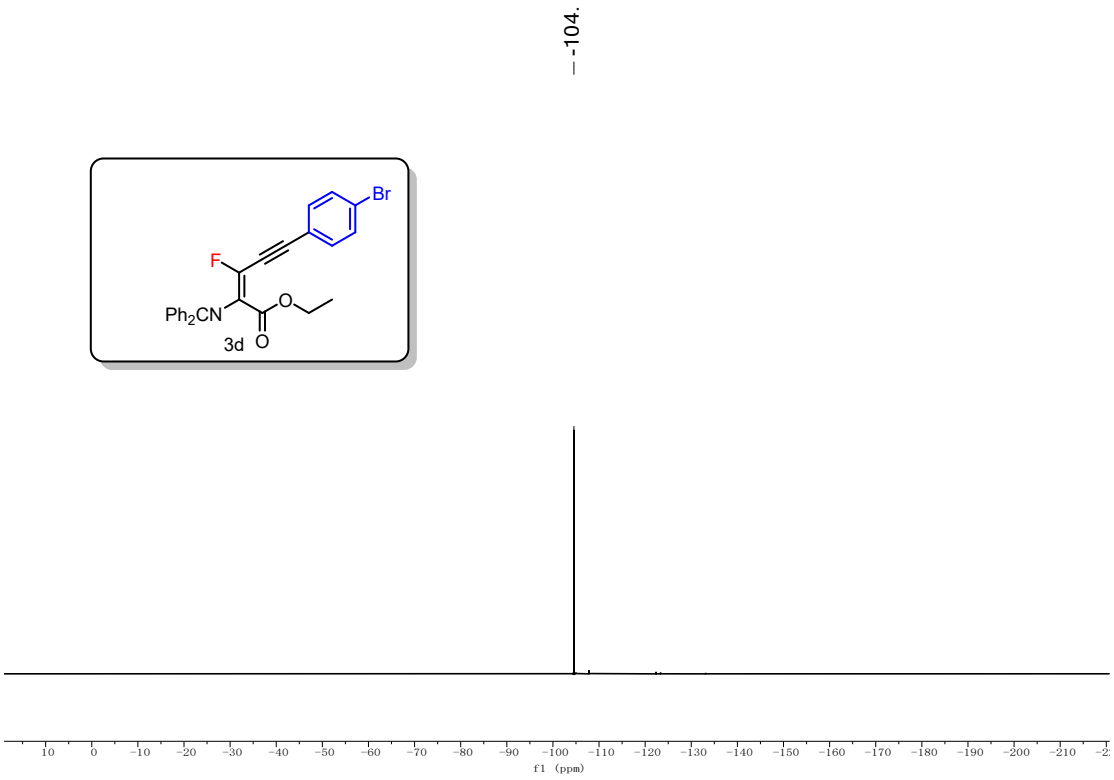
^{1}H NMR of compound 3d (400 MHz, $CDCl_3$)



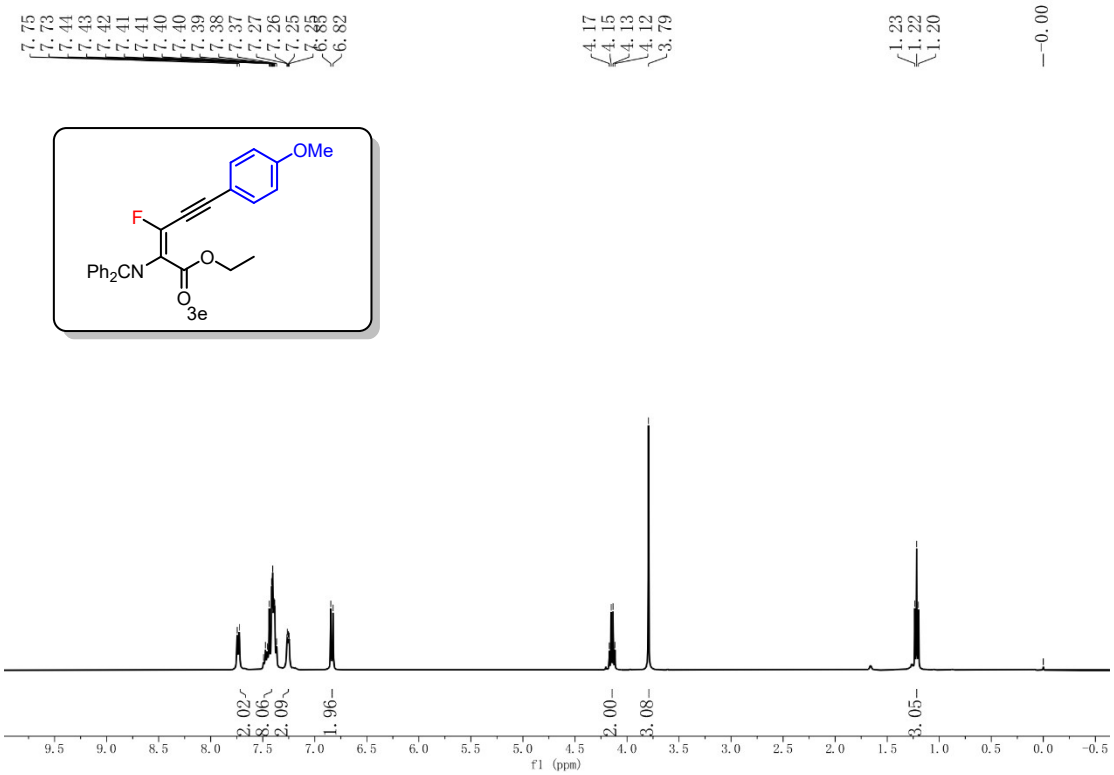
^{13}C NMR of compound 3d (101 MHz, $CDCl_3$)



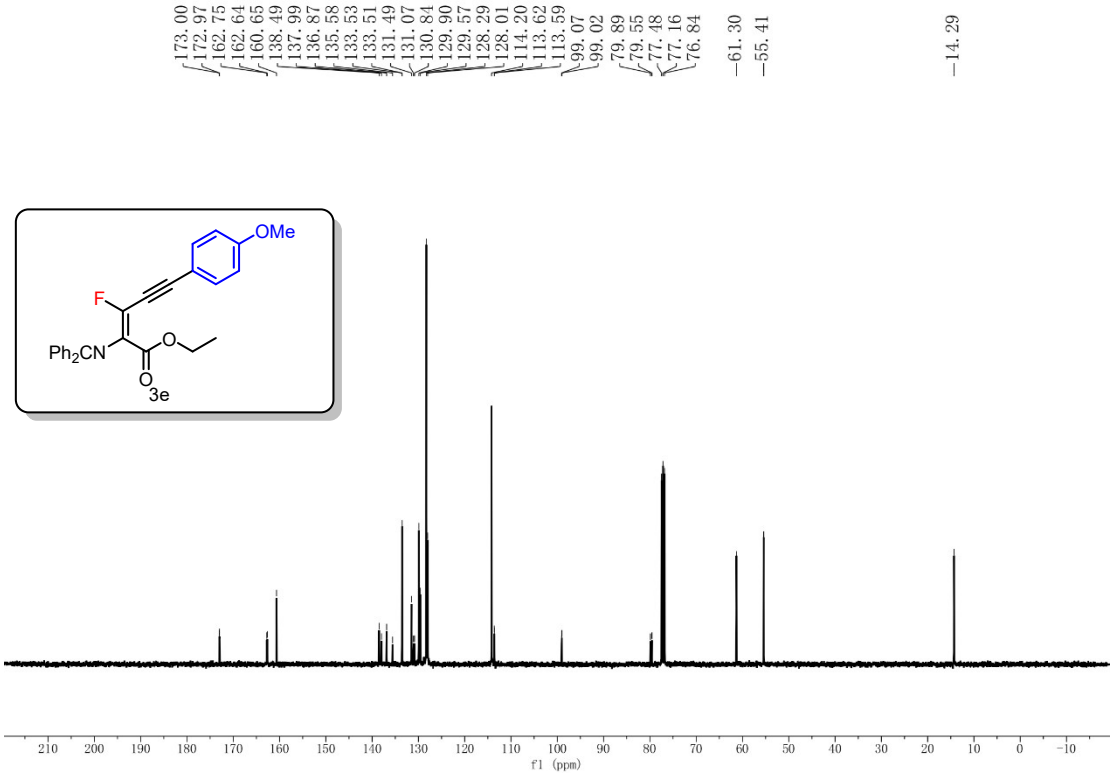
^{19}F NMR of compound 3d (377 MHz, $CDCl_3$)



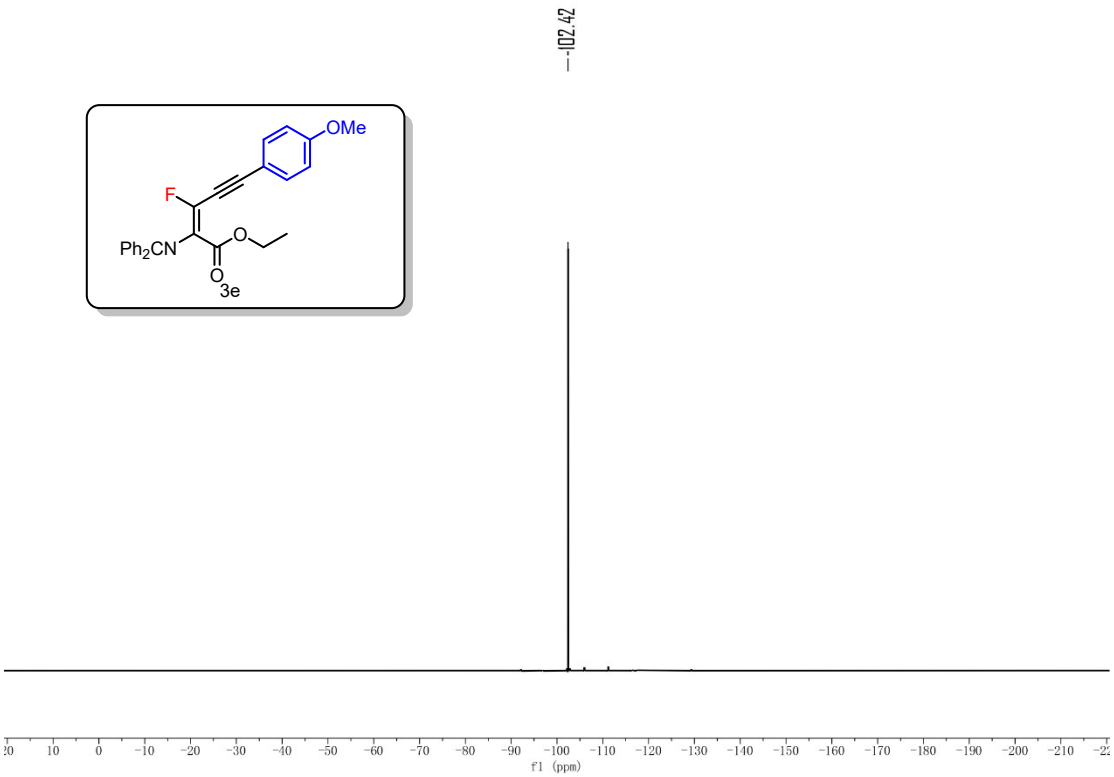
^{1}H NMR of compound 3e (400 MHz, $CDCl_3$)



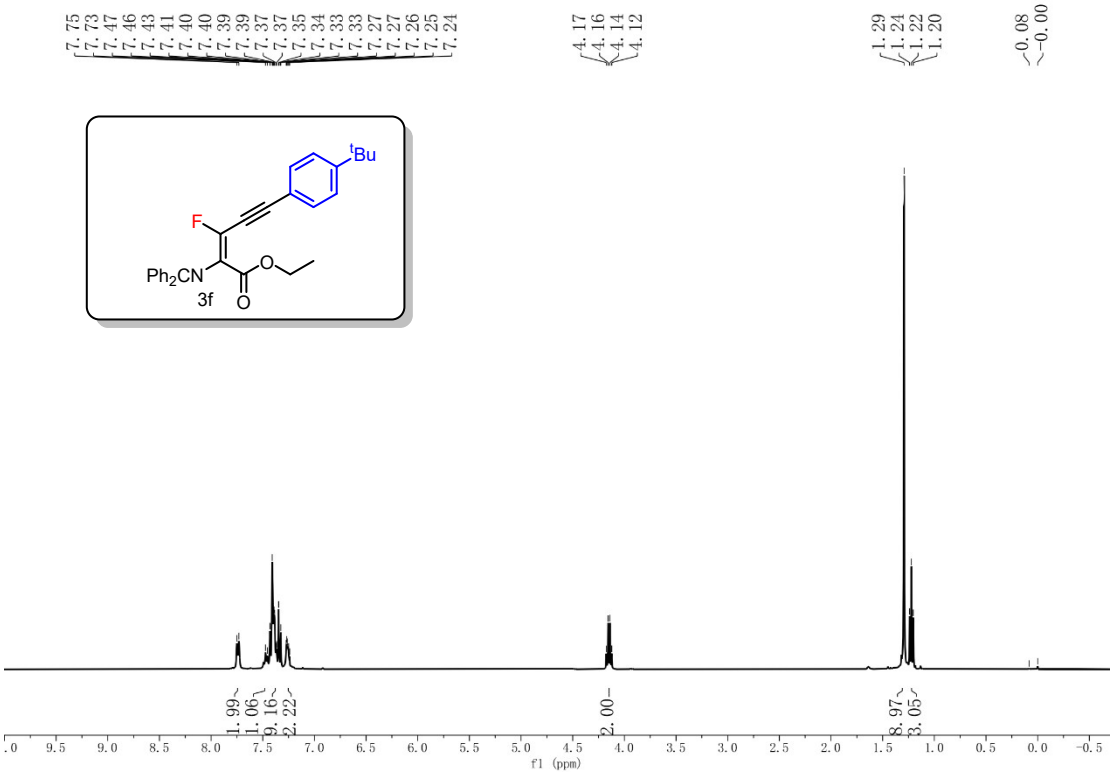
^{13}C NMR of compound 3e (101 MHz, $CDCl_3$)



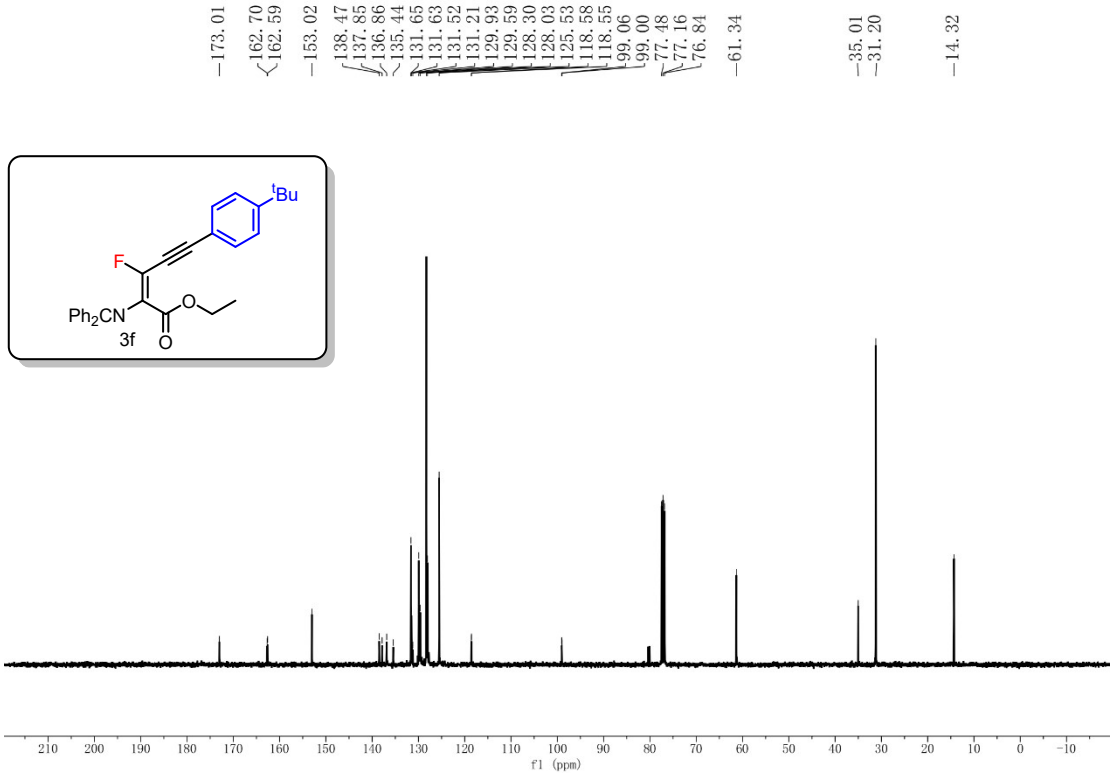
^{19}F NMR of compound 3e (377 MHz, $CDCl_3$)



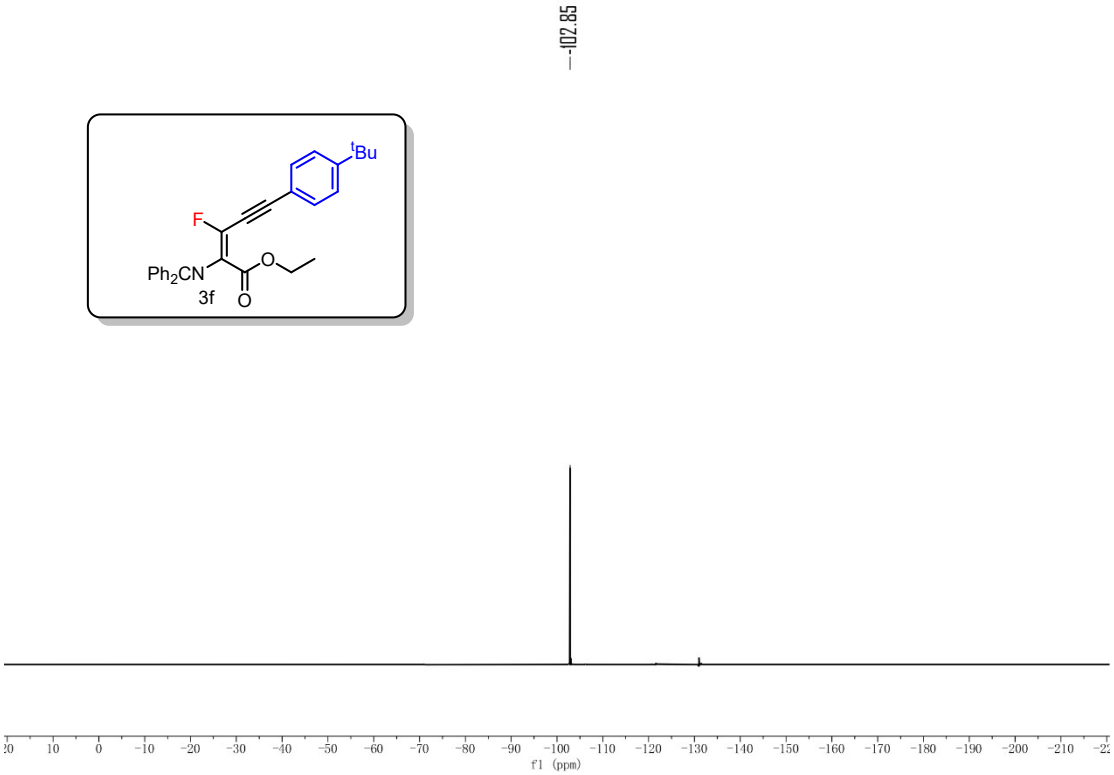
^{1}H NMR of compound 3f (400 MHz, $CDCl_3$)



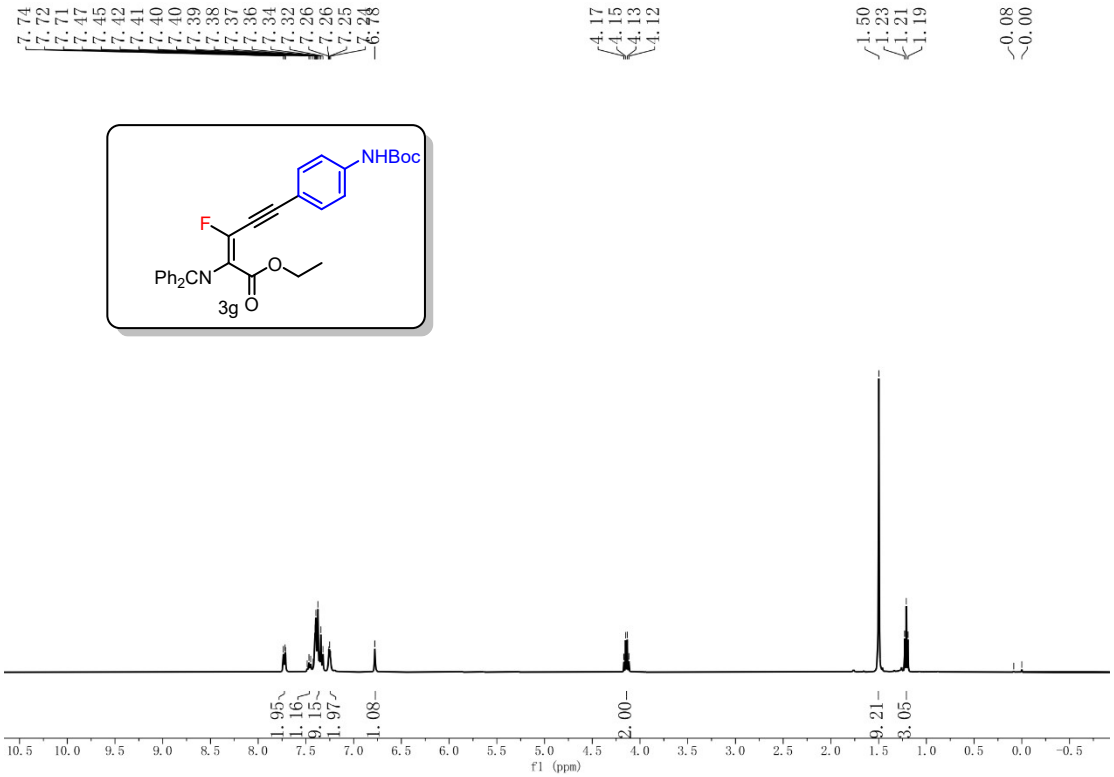
^{13}C NMR of compound 3f (101 MHz, $CDCl_3$)



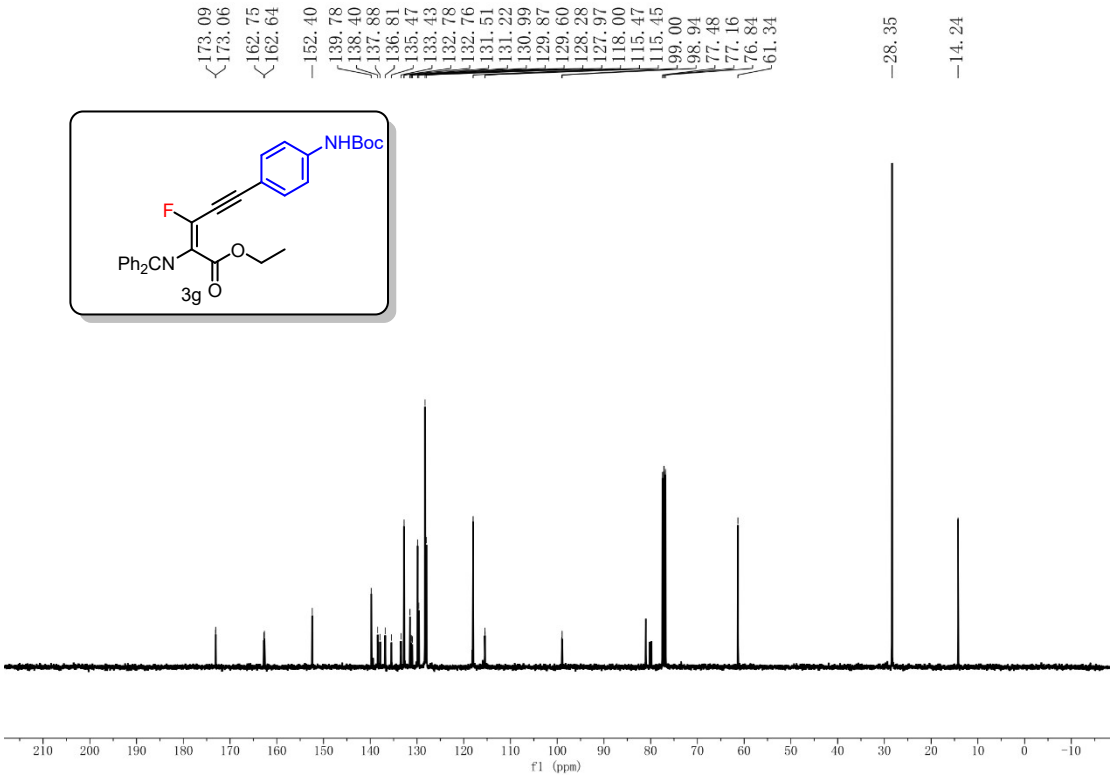
^{19}F NMR of compound 3f (377 MHz, $CDCl_3$)



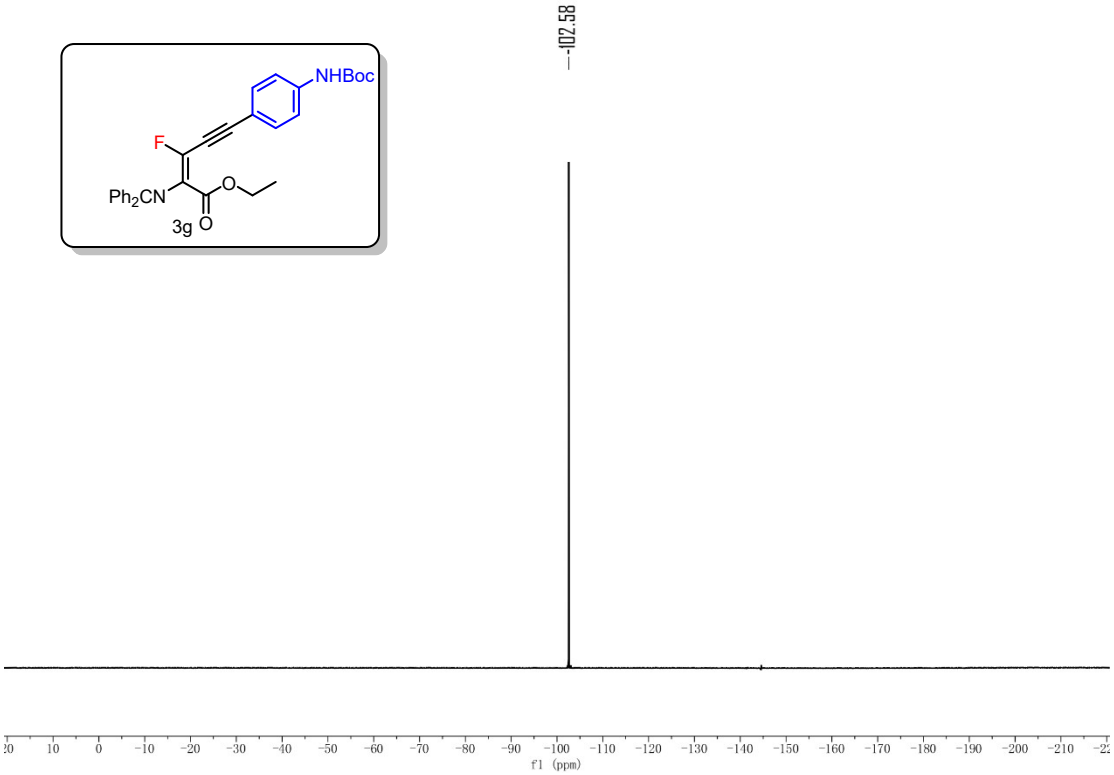
^{1}H NMR of compound 3g (400 MHz, $CDCl_3$)



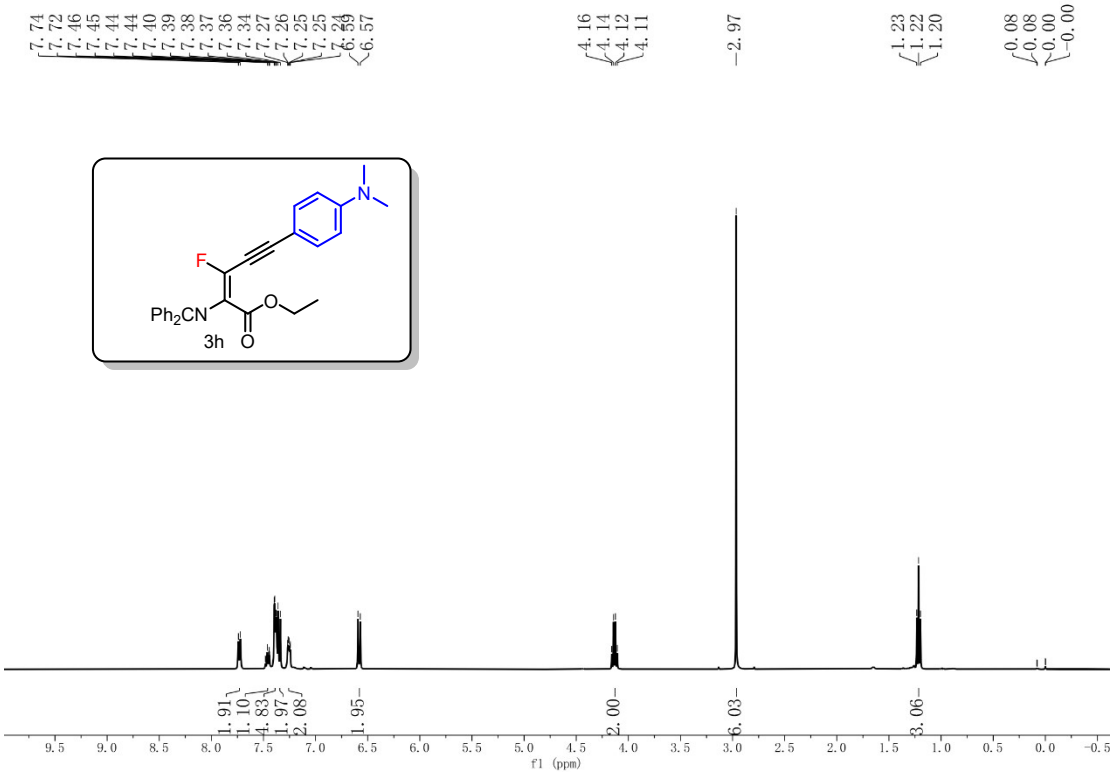
^{13}C NMR of compound 3g (101 MHz, $CDCl_3$)



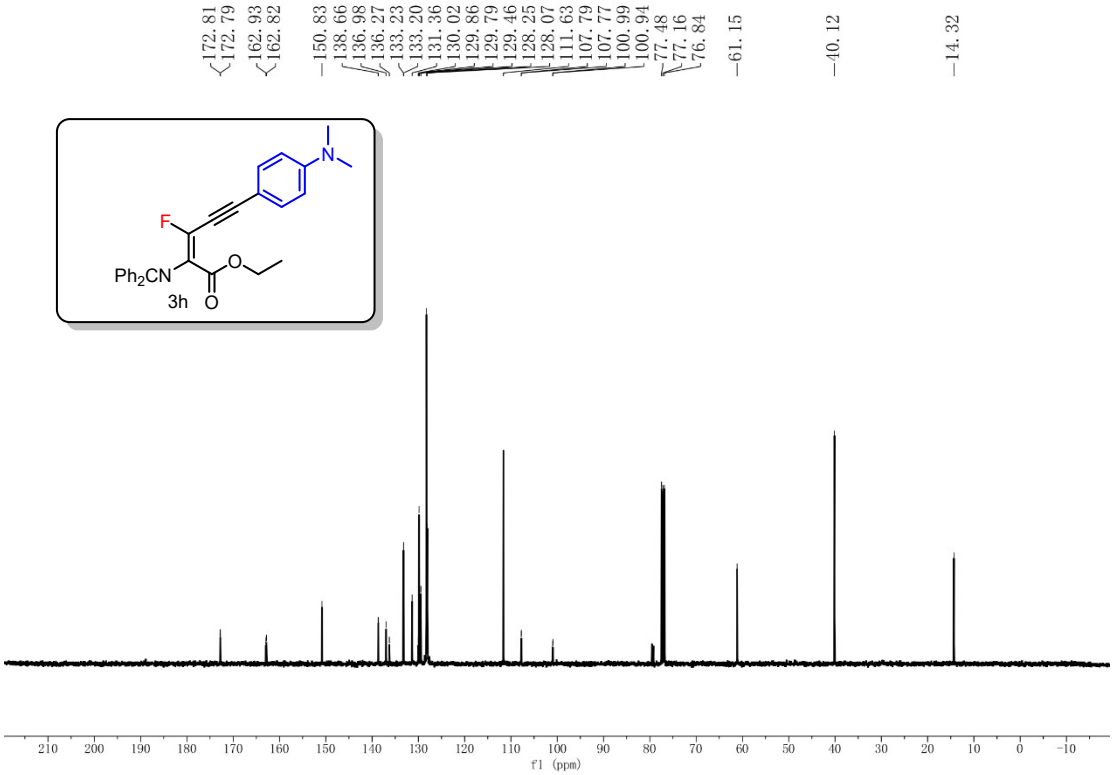
^{19}F NMR of compound 3g (377 MHz, $CDCl_3$)



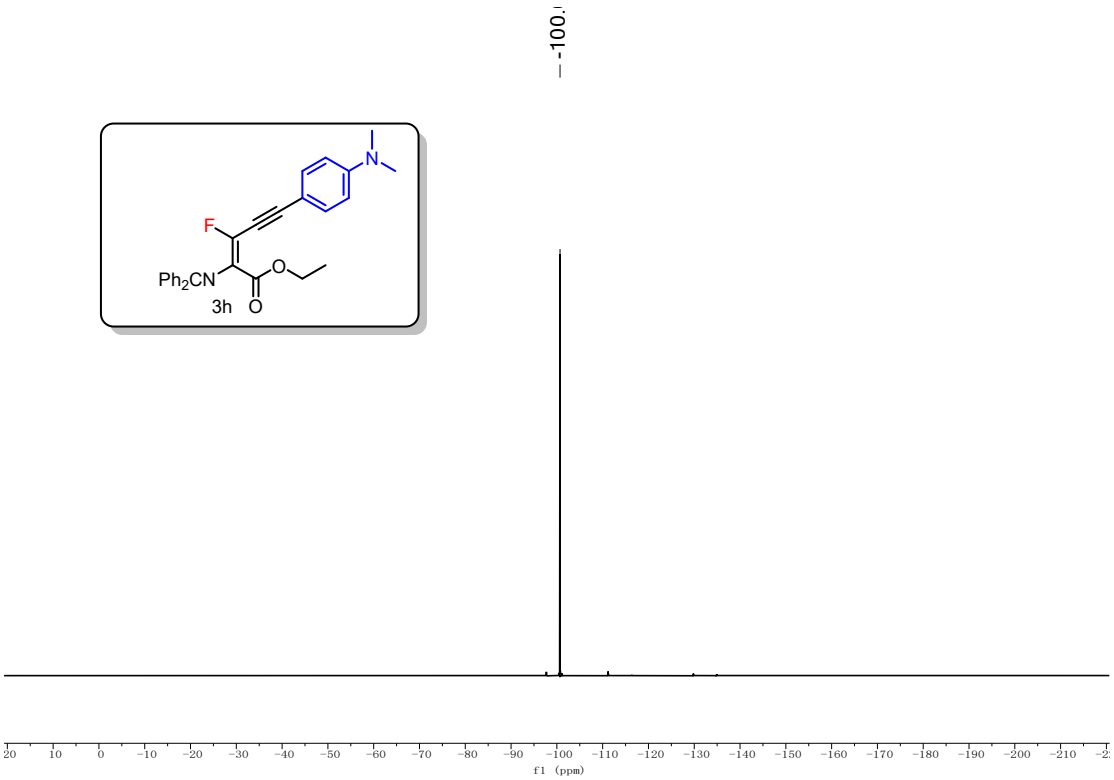
^{1}H NMR of compound 3h (400 MHz, $CDCl_3$)



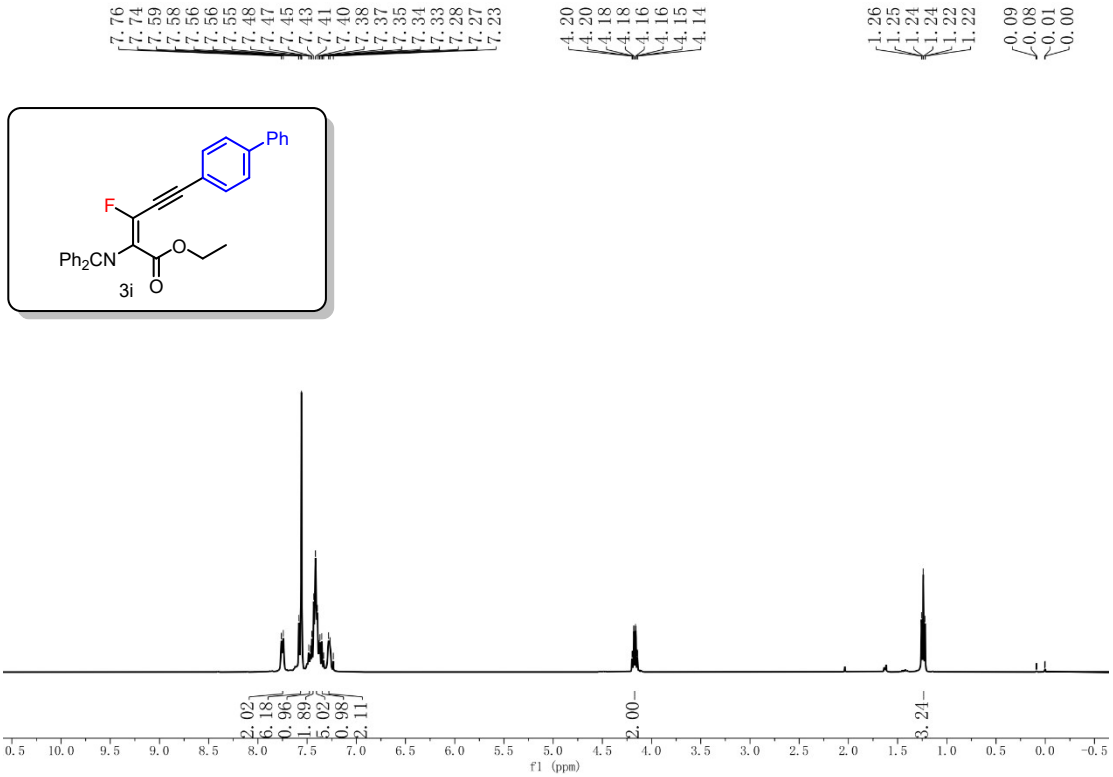
^{13}C NMR of compound 3h (101 MHz, $CDCl_3$)



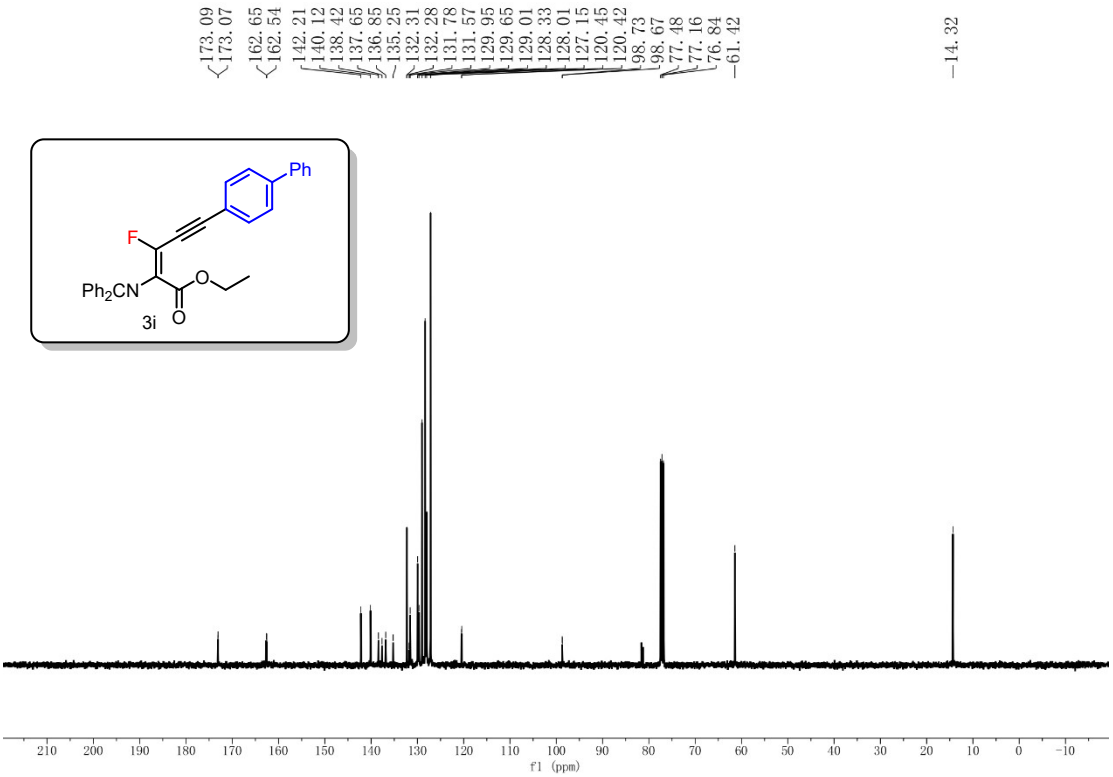
^{19}F NMR of compound 3h (377 MHz, $CDCl_3$)



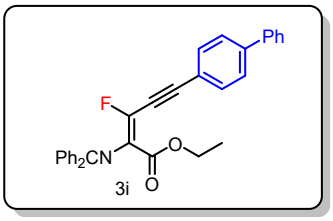
^{1}H NMR of compound 3i (400 MHz, $CDCl_3$)



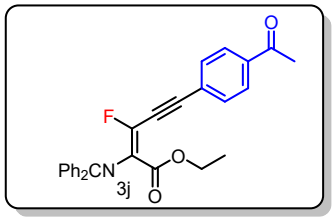
^{13}C NMR of compound 3i (101 MHz, $CDCl_3$)

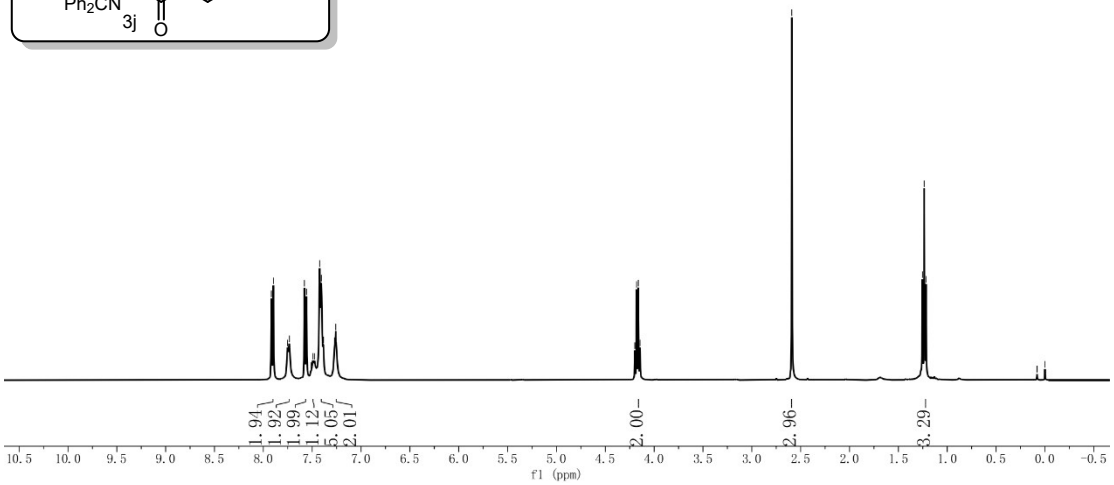


^{19}F NMR of compound 3i (377 MHz, $CDCl_3$)

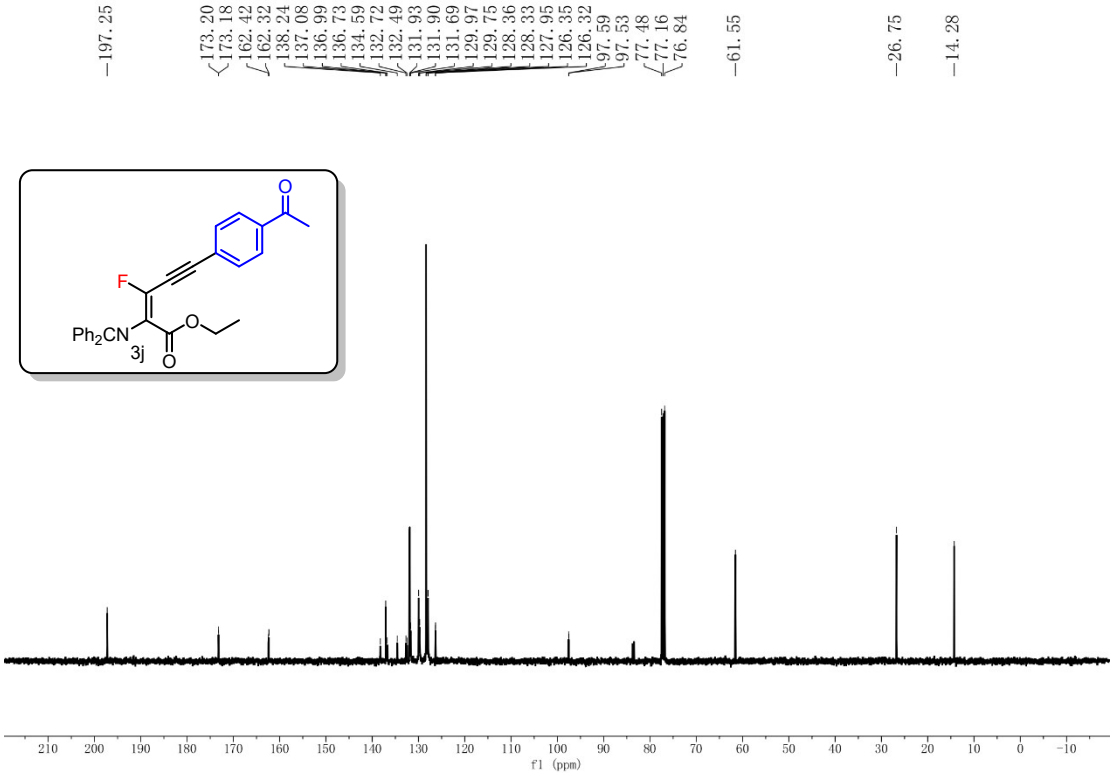


^{1}H NMR of compound 3j (400 MHz, $CDCl_3$)



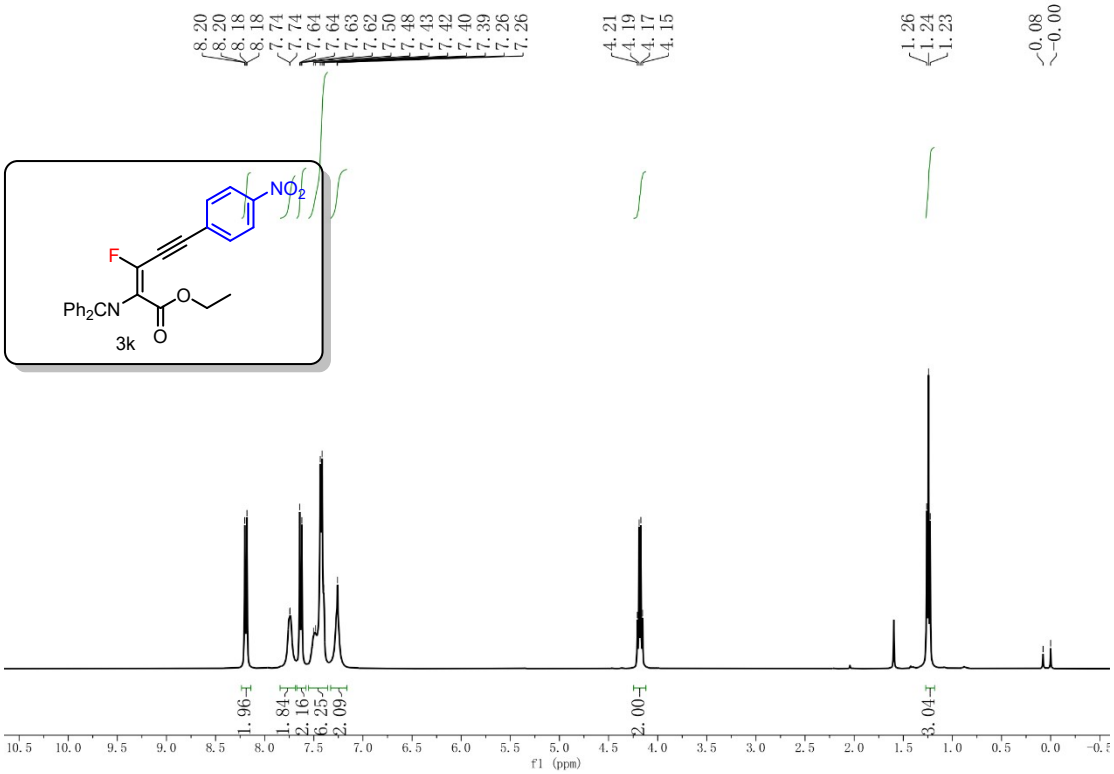


^{13}C NMR of compound 3j (101 MHz, $CDCl_3$)

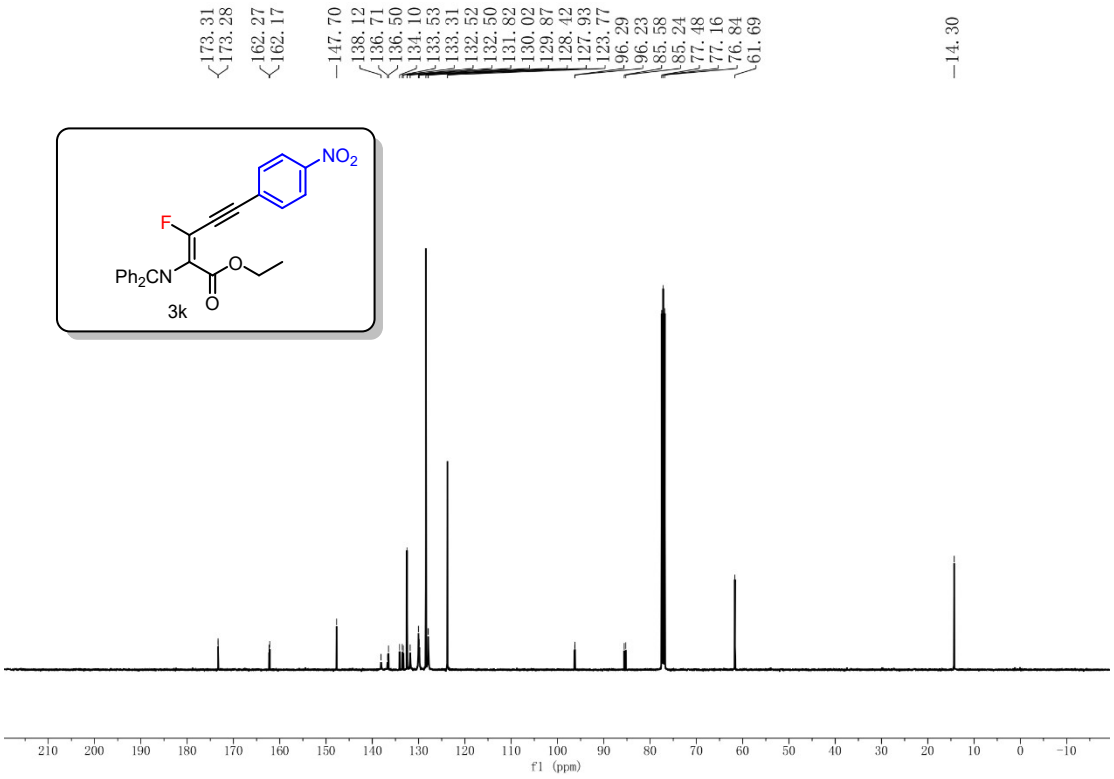


^{19}F NMR of compound 3j (377 MHz, $CDCl_3$)

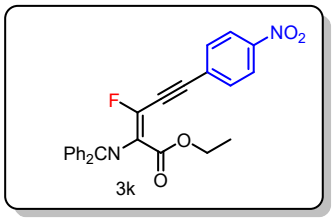
^{1}H NMR of compound 3k (400 MHz, $CDCl_3$)



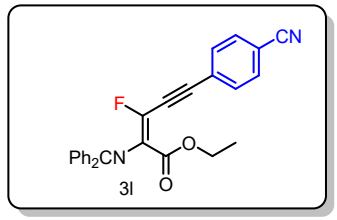
^{13}C NMR of compound 3k (101 MHz, $CDCl_3$)



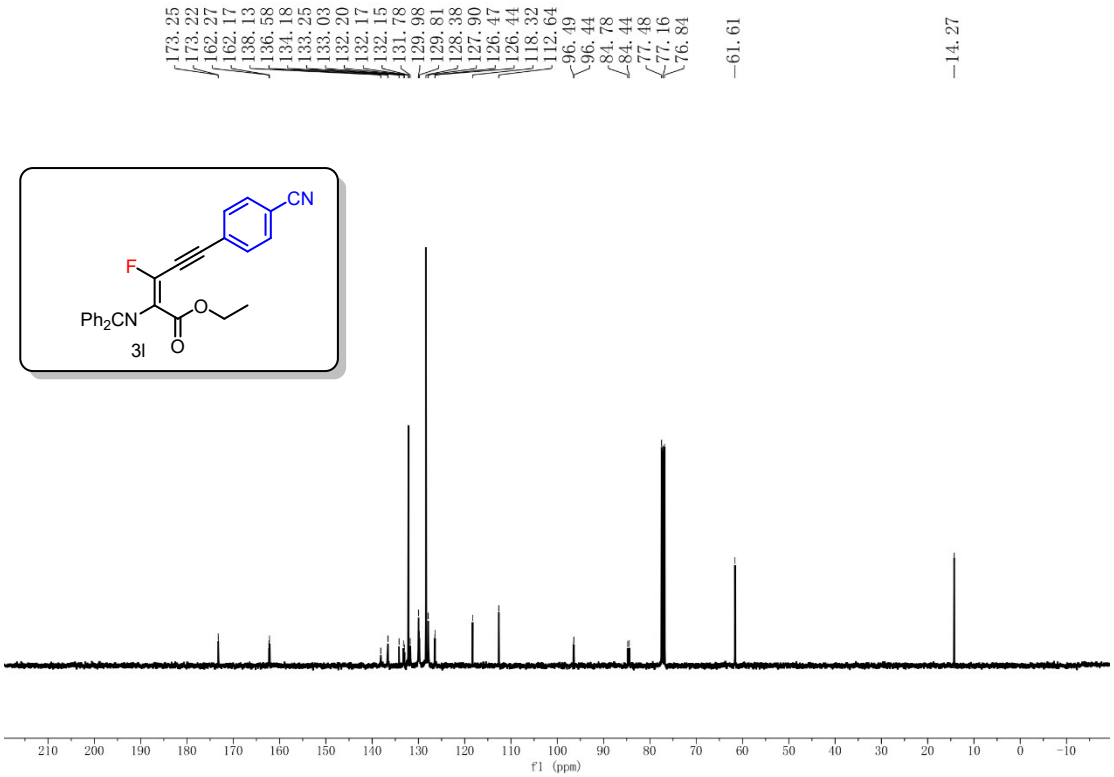
^{19}F NMR of compound 3k (377 MHz, $CDCl_3$)



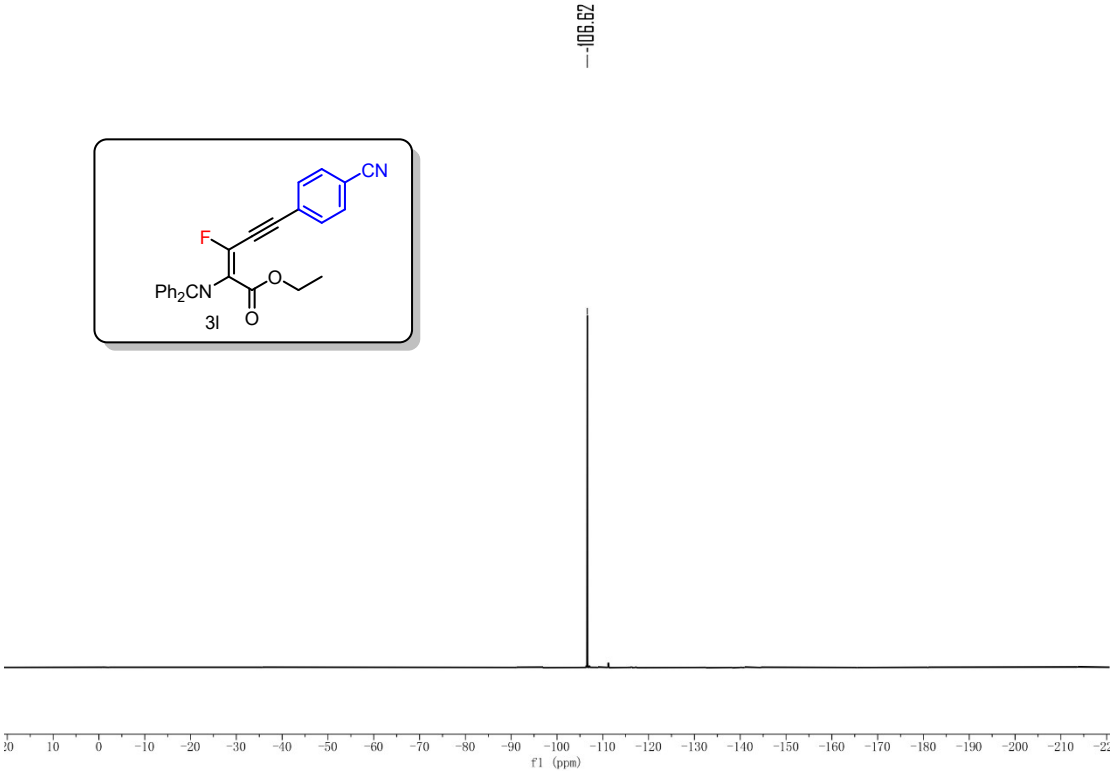
^{1}H NMR of compound 3l (400 MHz, $CDCl_3$)



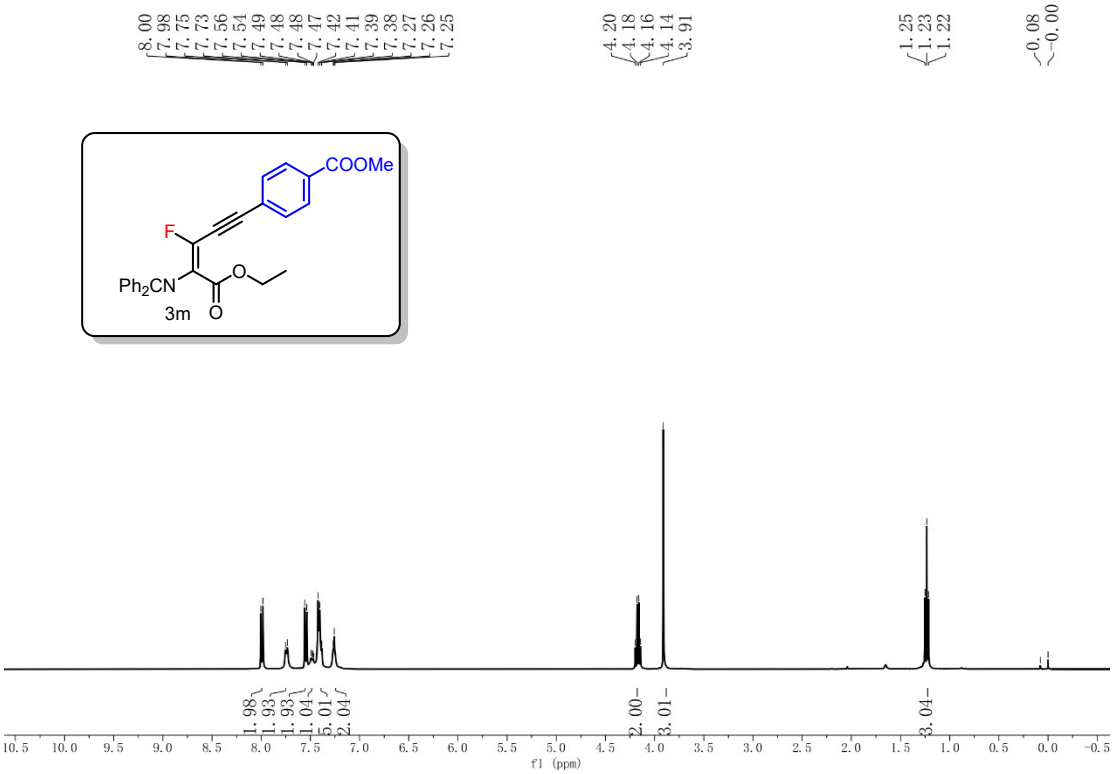
^{13}C NMR of compound 3l (101 MHz, $CDCl_3$)



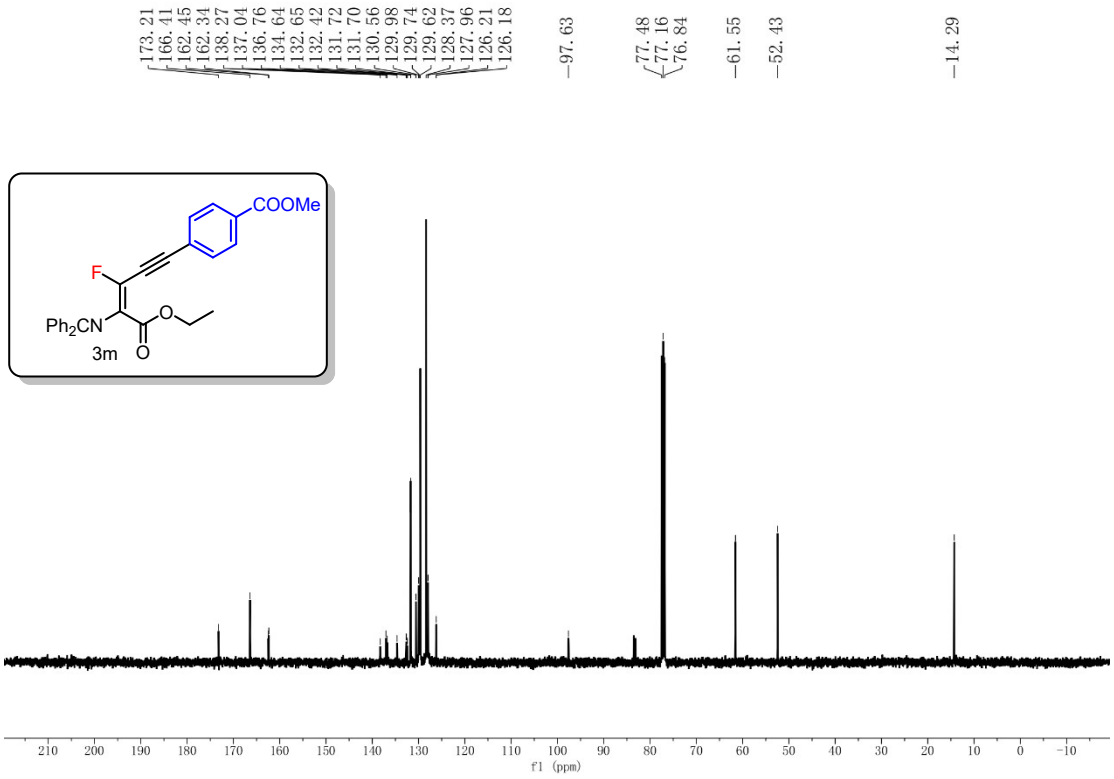
^{19}F NMR of compound 3l (377 MHz, $CDCl_3$)



^{1}H NMR of compound 3m (400 MHz, $CDCl_3$)

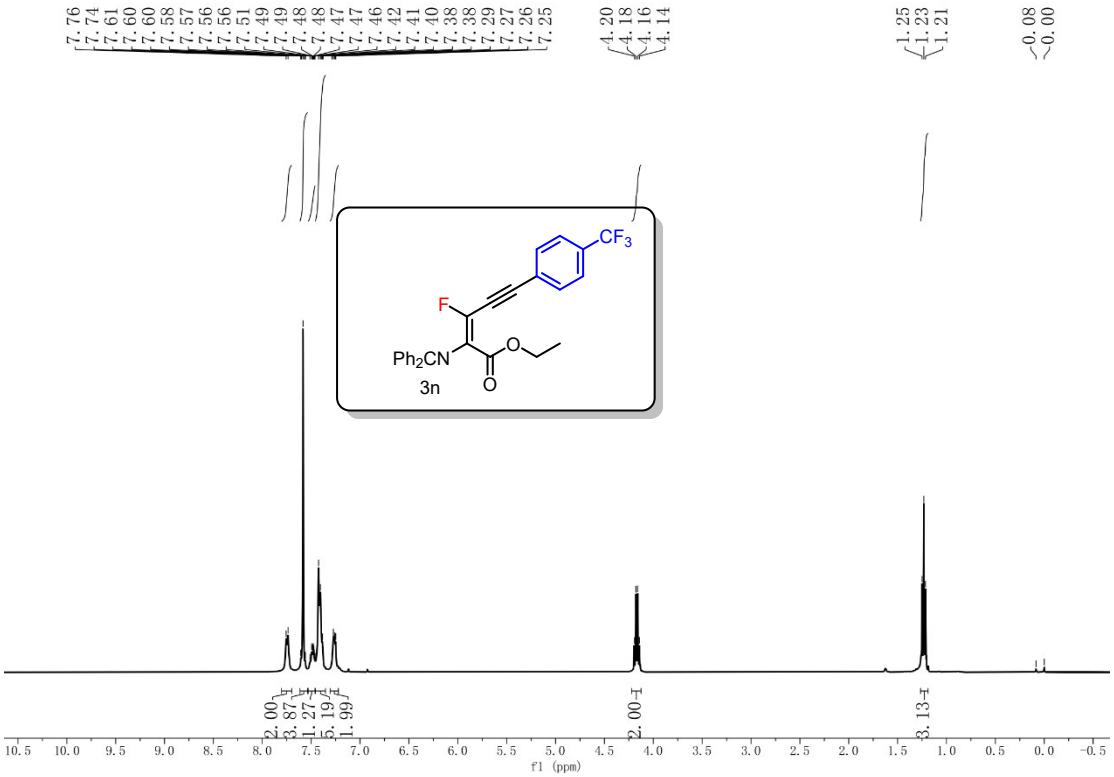


^{13}C NMR of compound 3m (101 MHz, $CDCl_3$)

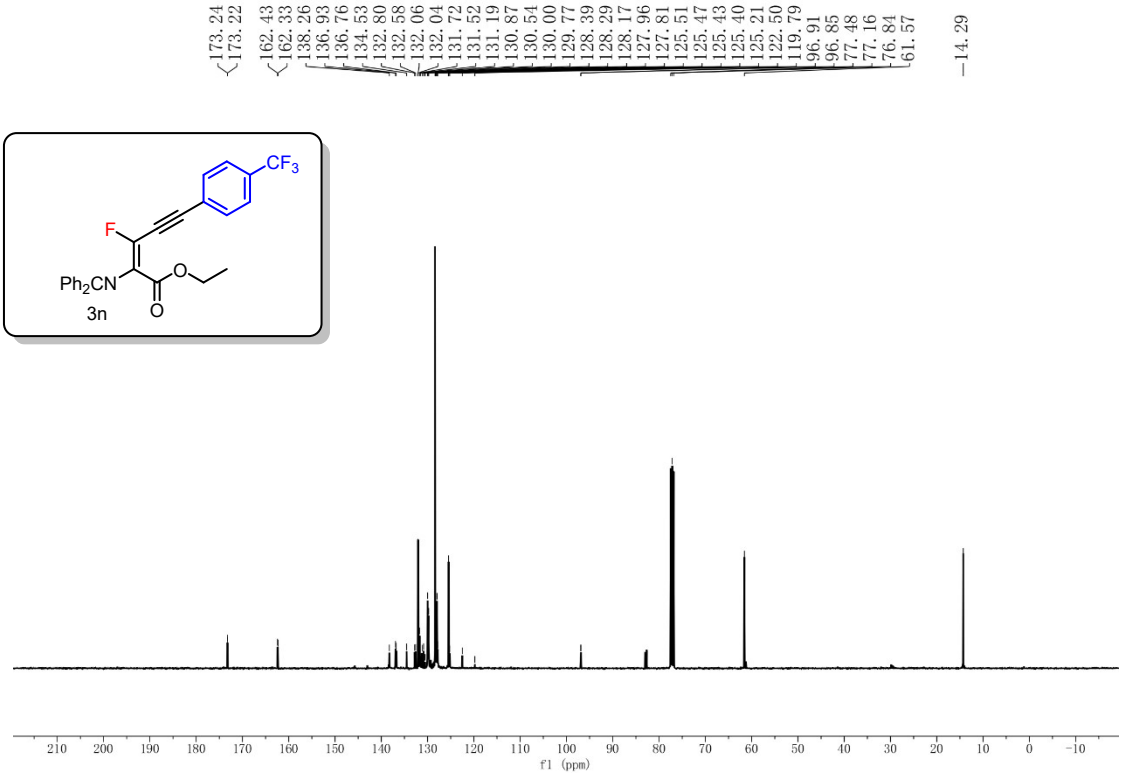


^{19}F NMR of compound 3m (377 MHz, $CDCl_3$)

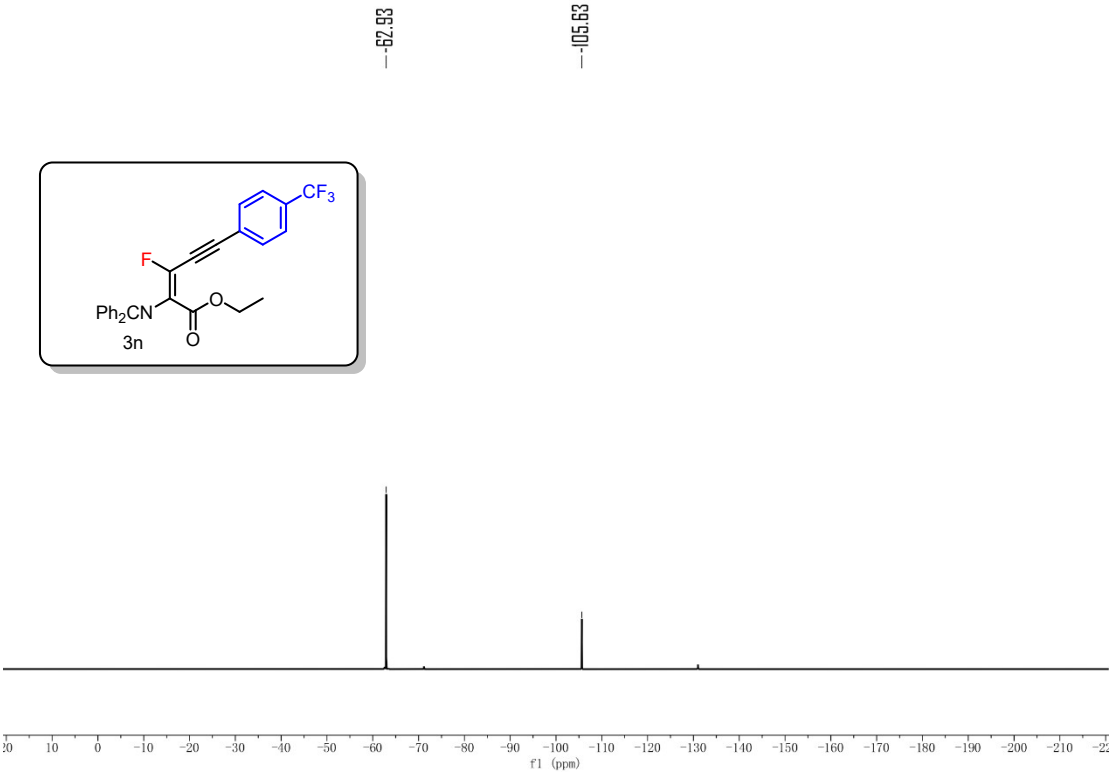
^{1}H NMR of compound 3n (400 MHz, $CDCl_3$)



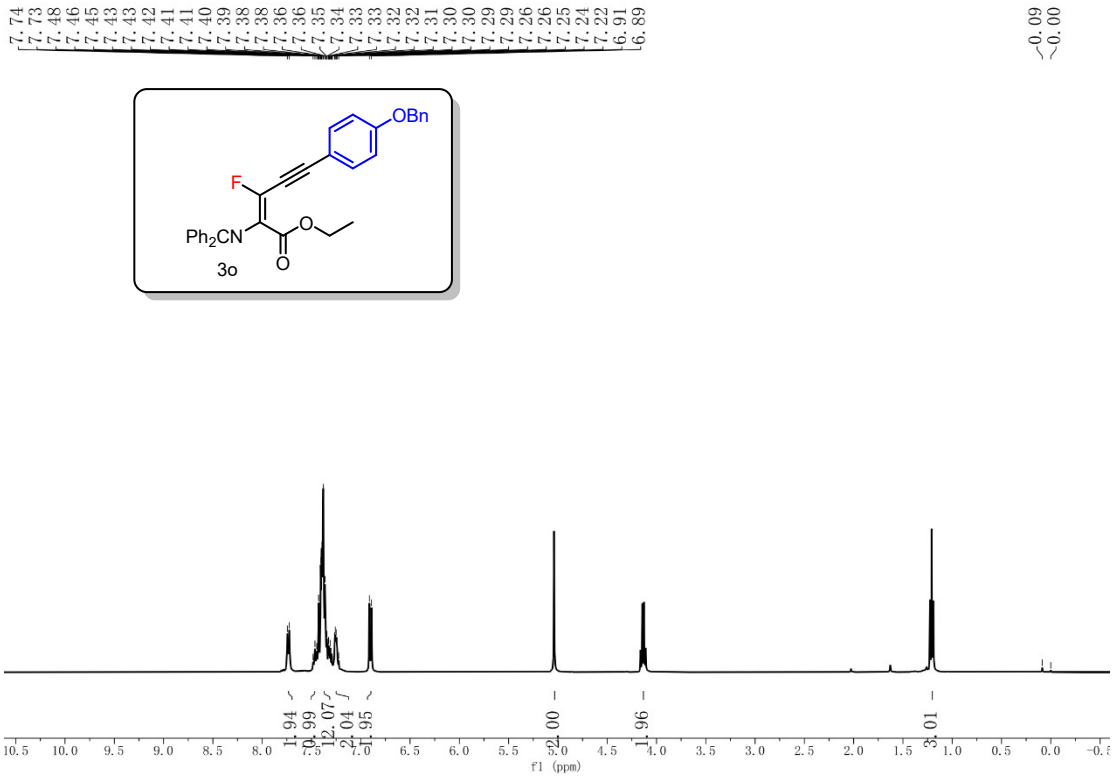
^{13}C NMR of compound 3n (101 MHz, $CDCl_3$)



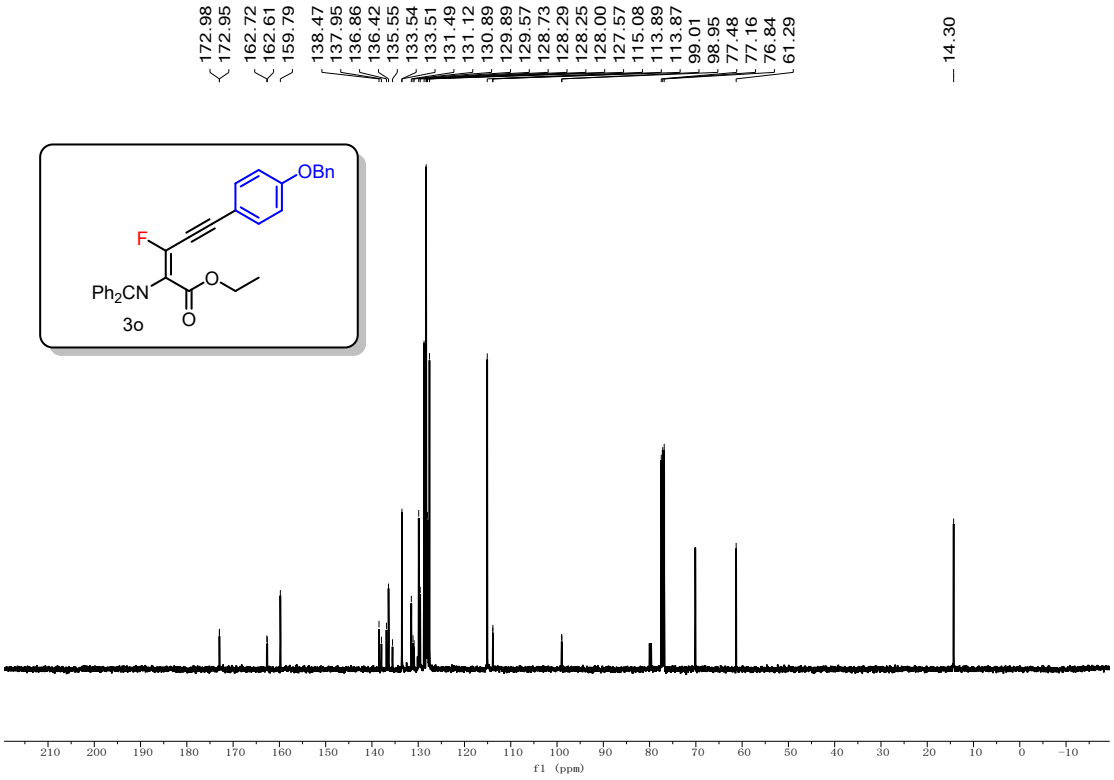
^{19}F NMR of compound 3n (377 MHz, $CDCl_3$)



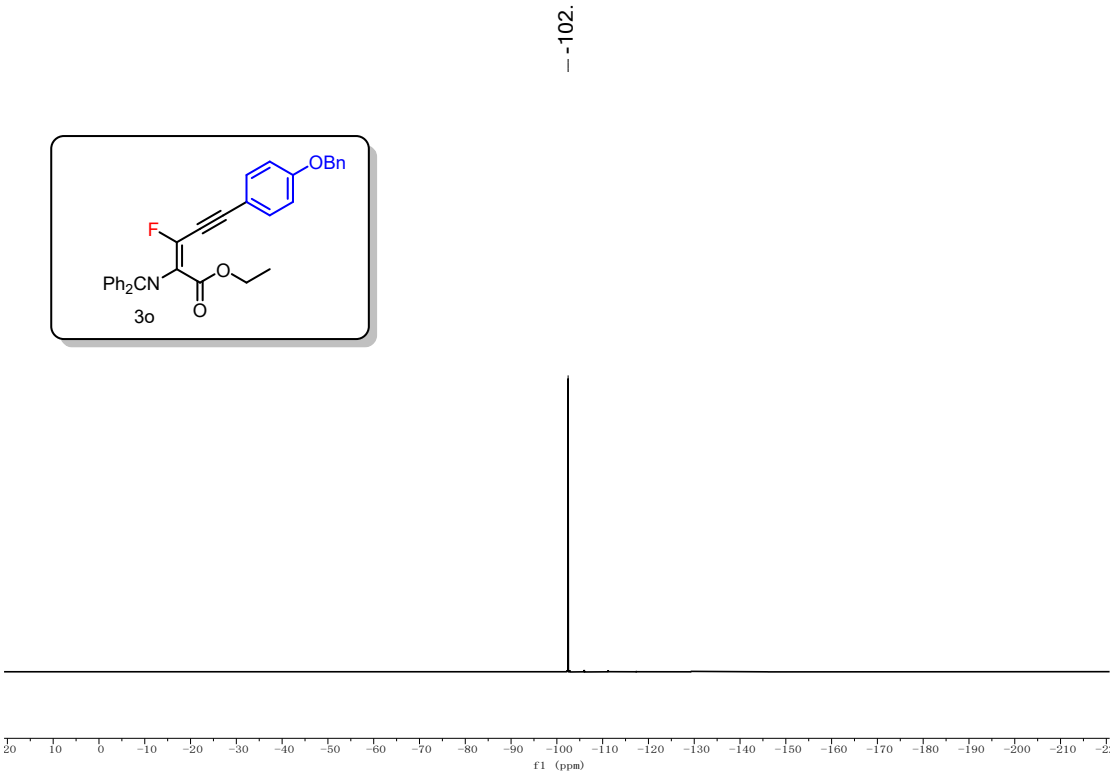
^{1}H NMR of compound 3o (400 MHz, $CDCl_3$)



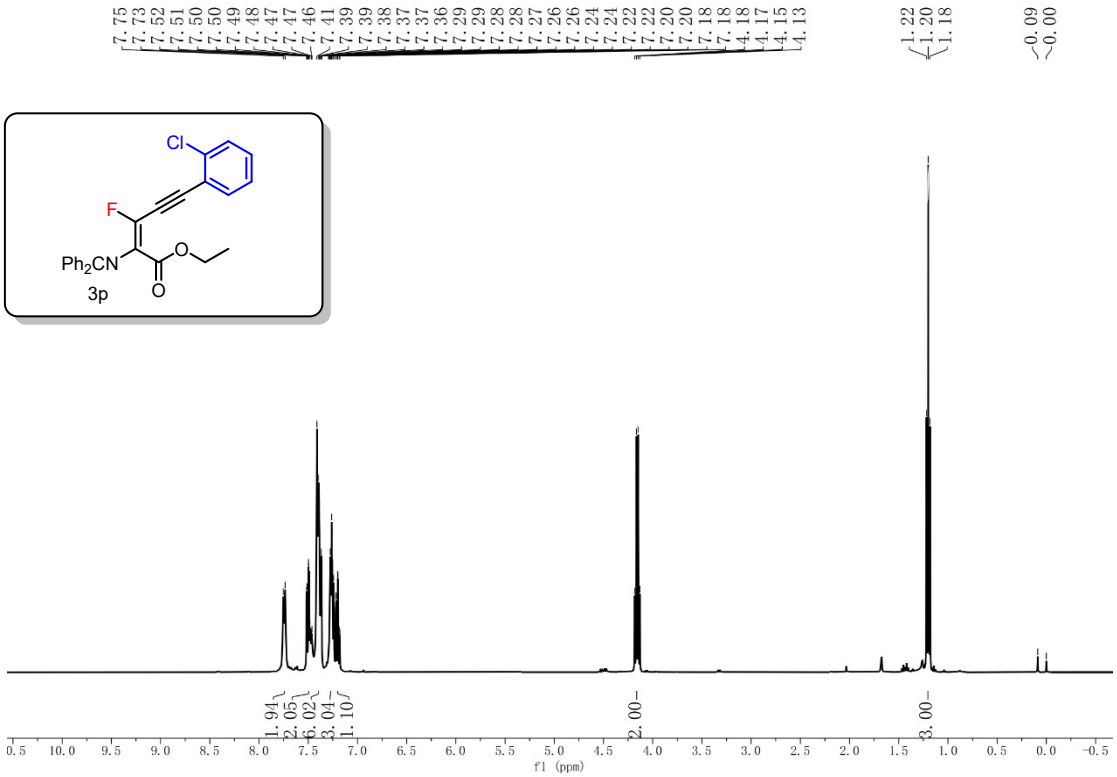
^{13}C NMR of compound 3o (101 MHz, $CDCl_3$)



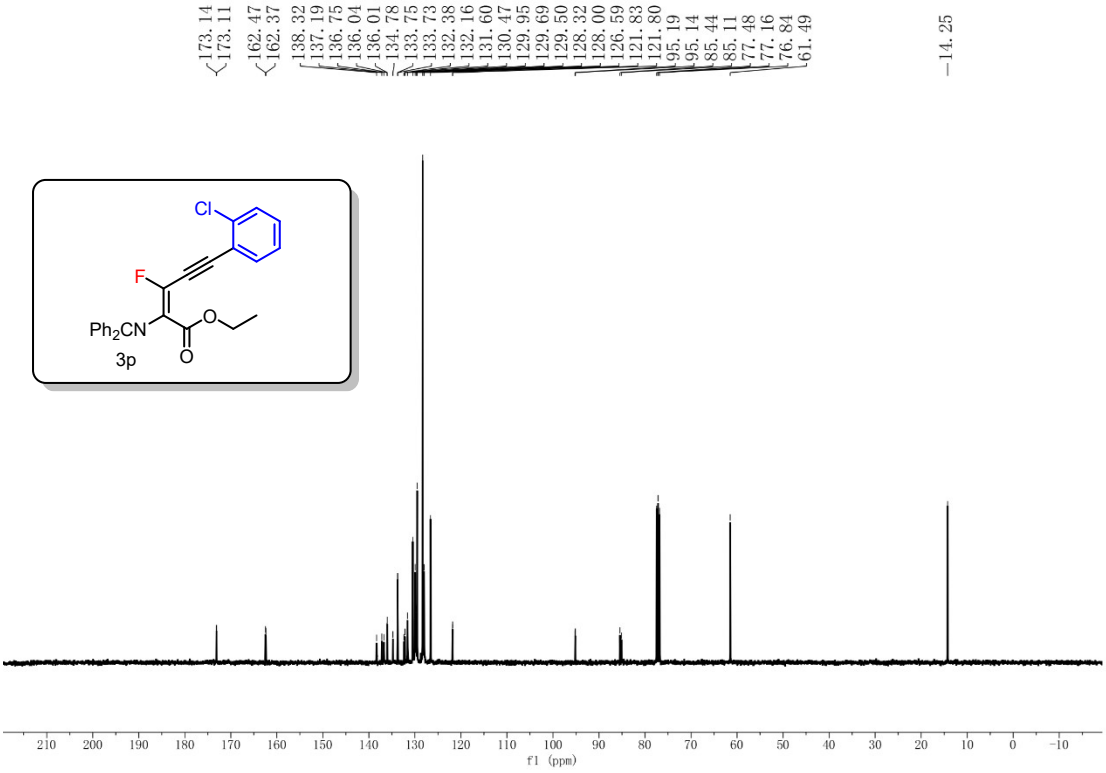
^{19}F NMR of compound 3o (377 MHz, $CDCl_3$)



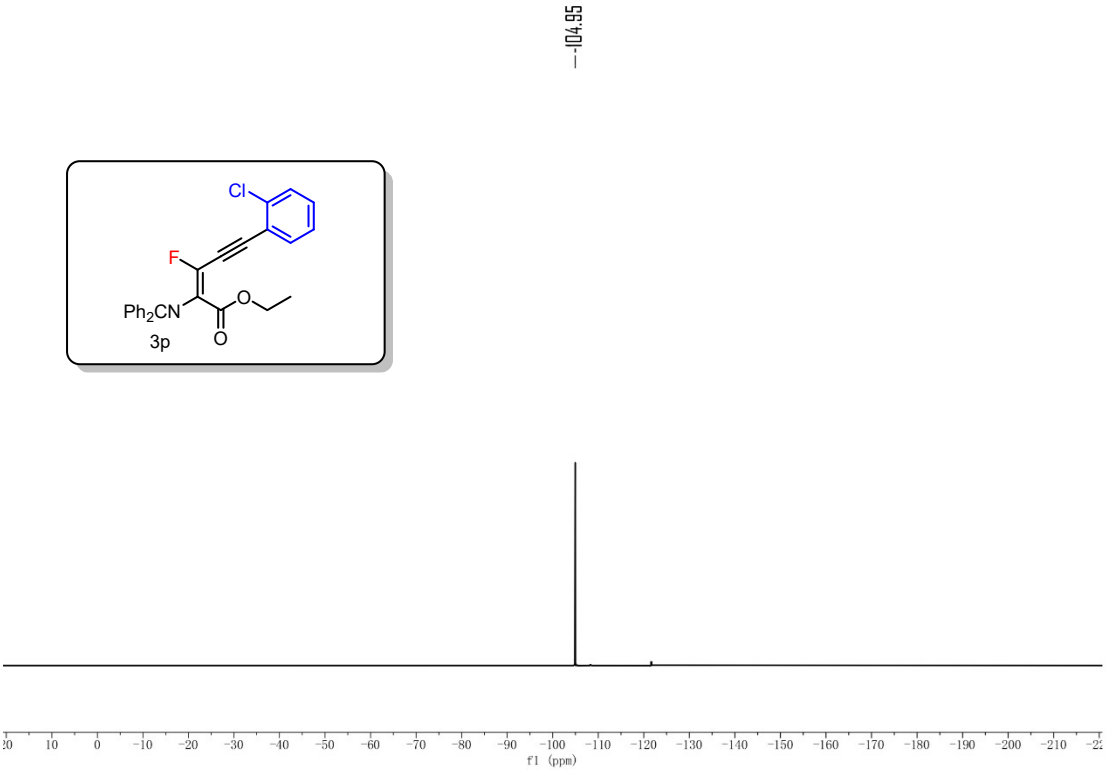
^{1}H NMR of compound 3p (400 MHz, $CDCl_3$)



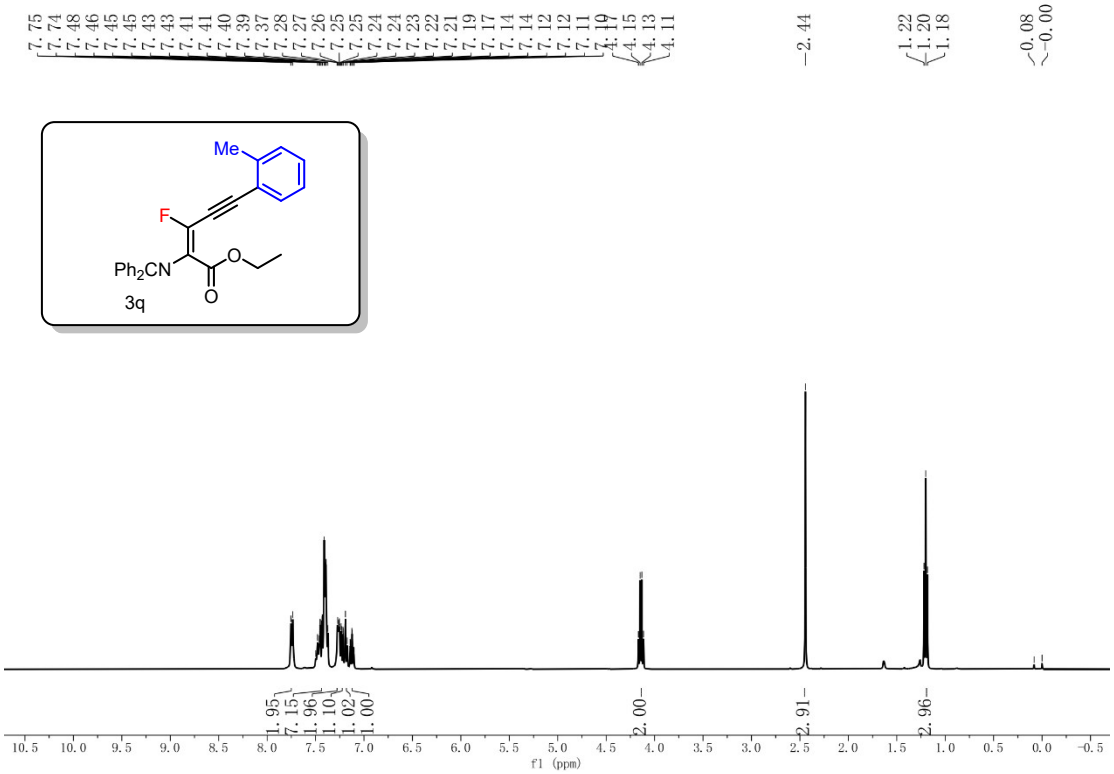
^{13}C NMR of compound 3p (101 MHz, $CDCl_3$)



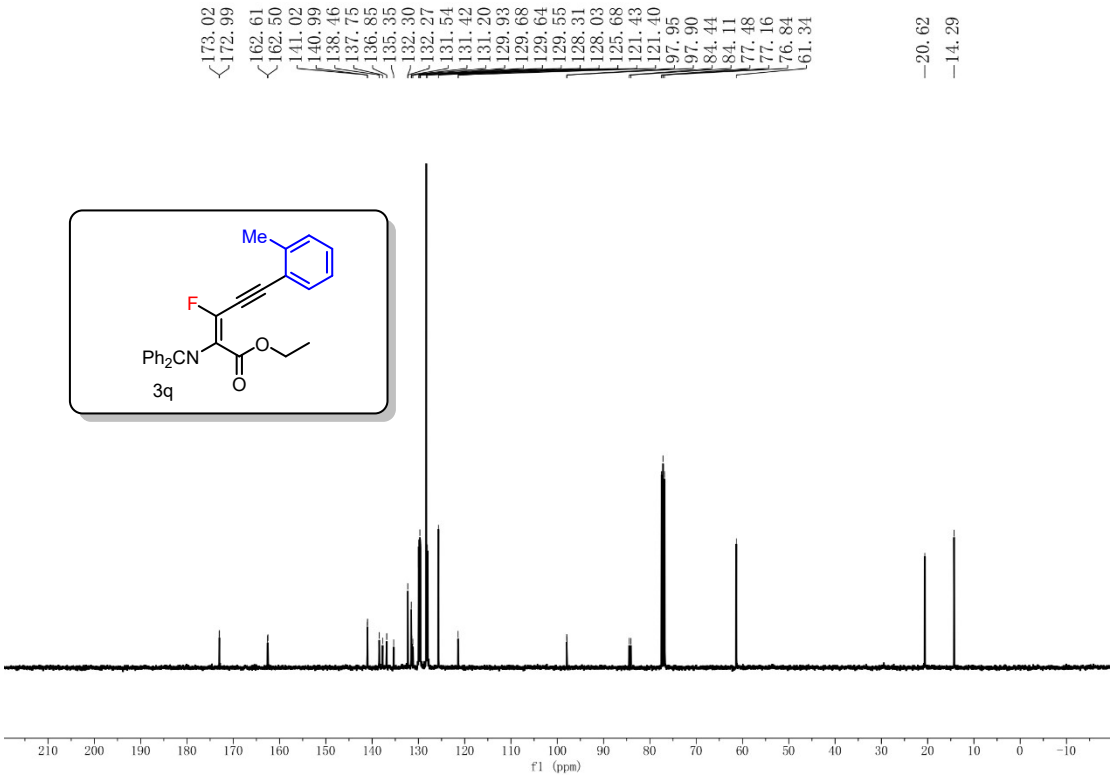
^{19}F NMR of compound 3p (377 MHz, $CDCl_3$)



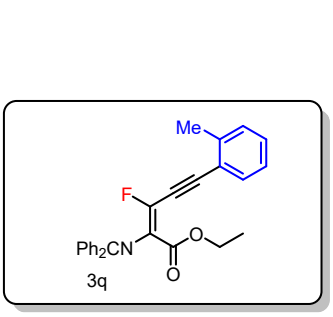
^{1}H NMR of compound 3q (400 MHz, $CDCl_3$)



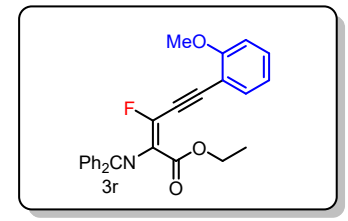
^{13}C NMR of compound 3q (101 MHz, $CDCl_3$)



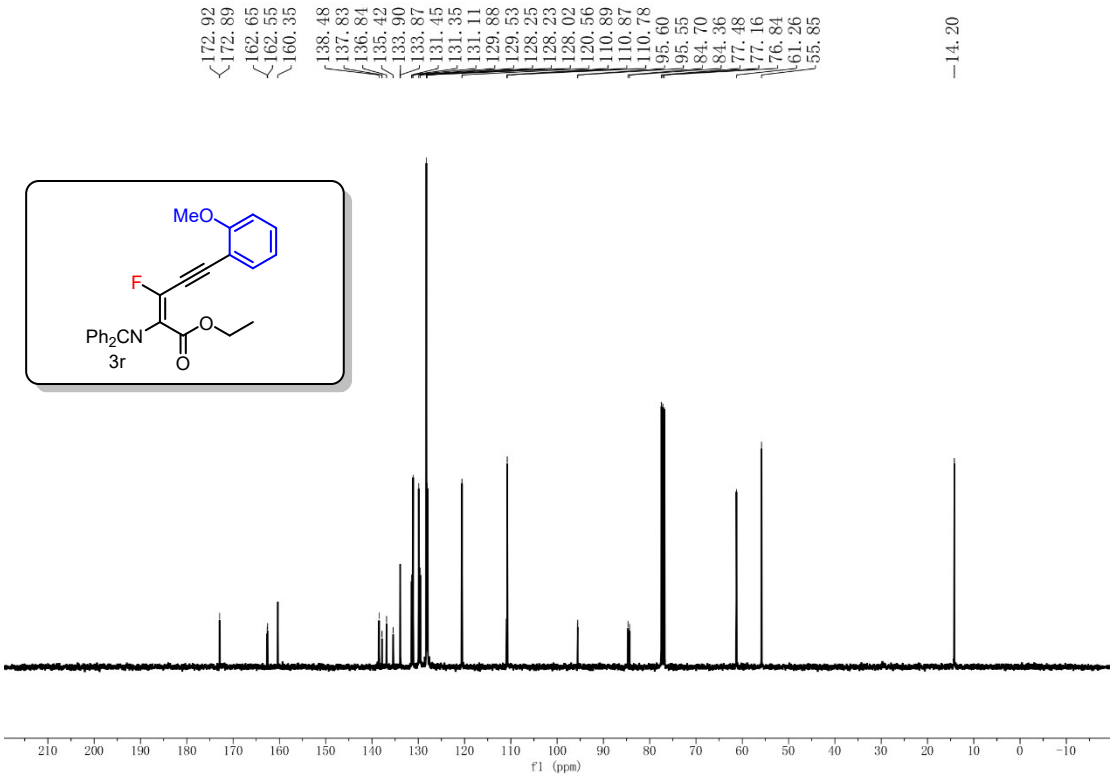
^{19}F NMR of compound 3q (377 MHz, $CDCl_3$)



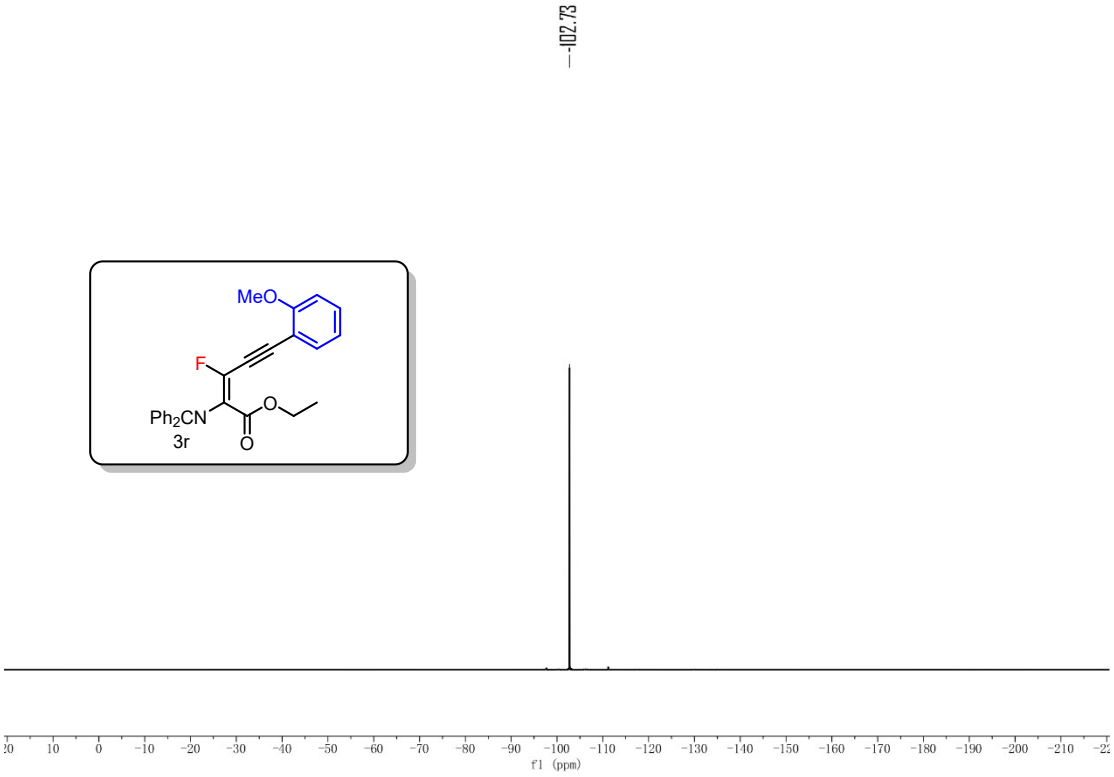
^{1}H NMR of compound 3r (400 MHz, $CDCl_3$)



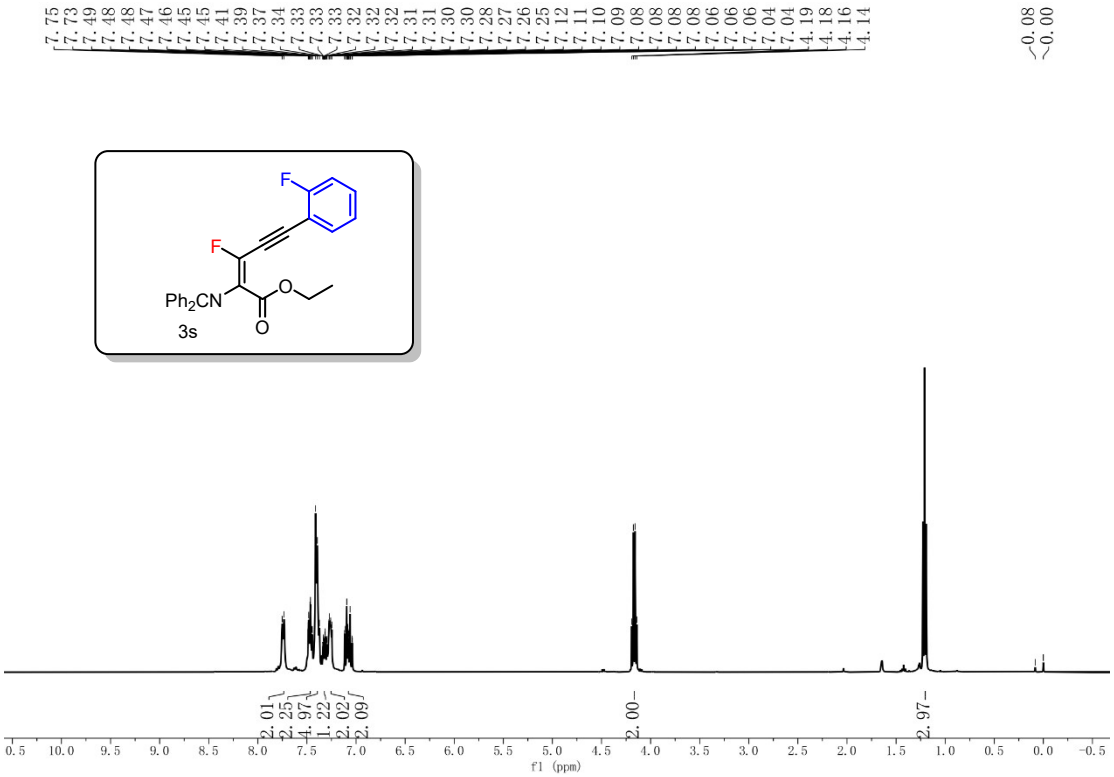
^{13}C NMR of compound 3r (101 MHz, $CDCl_3$)



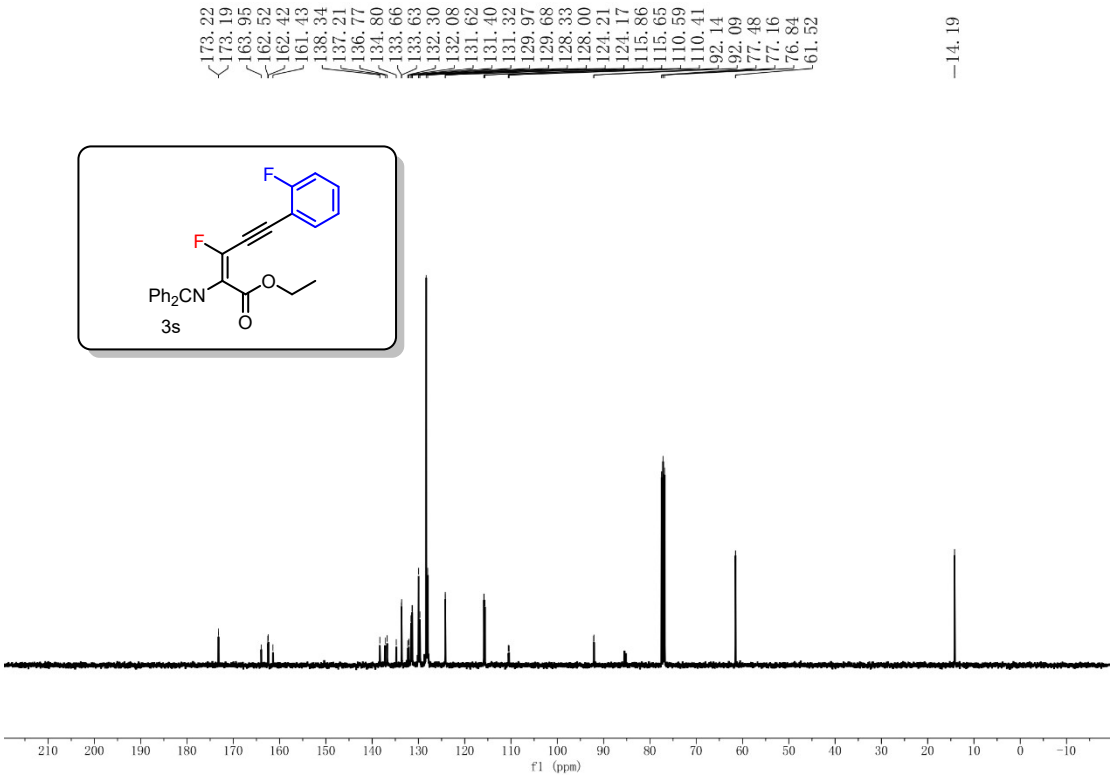
^{19}F NMR of compound 3r (377 MHz, $CDCl_3$)



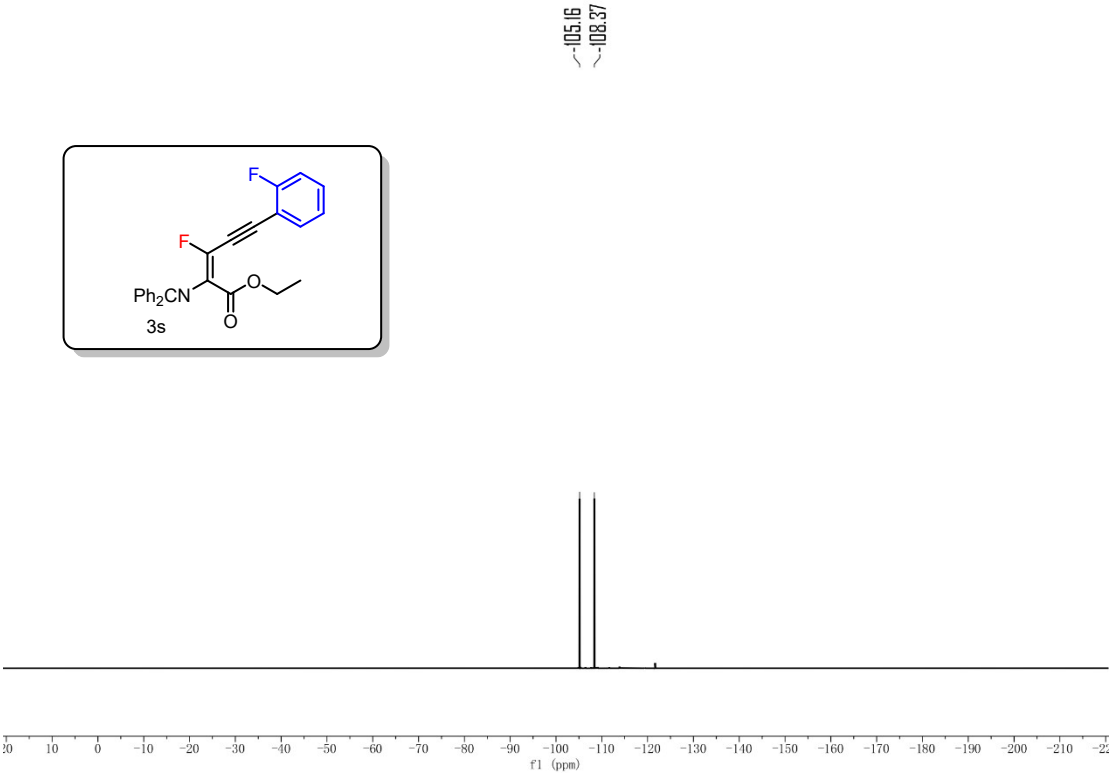
^{1}H NMR of compound 3s (400 MHz, $CDCl_3$)



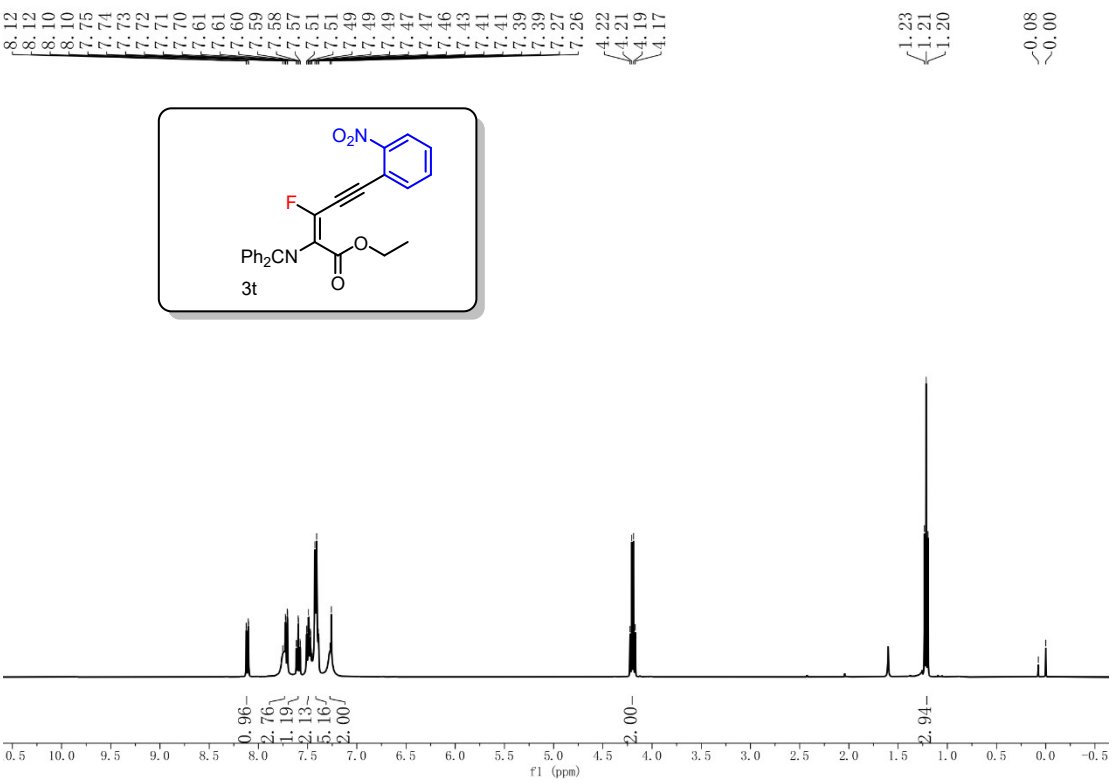
^{13}C NMR of compound 3s (101 MHz, $CDCl_3$)



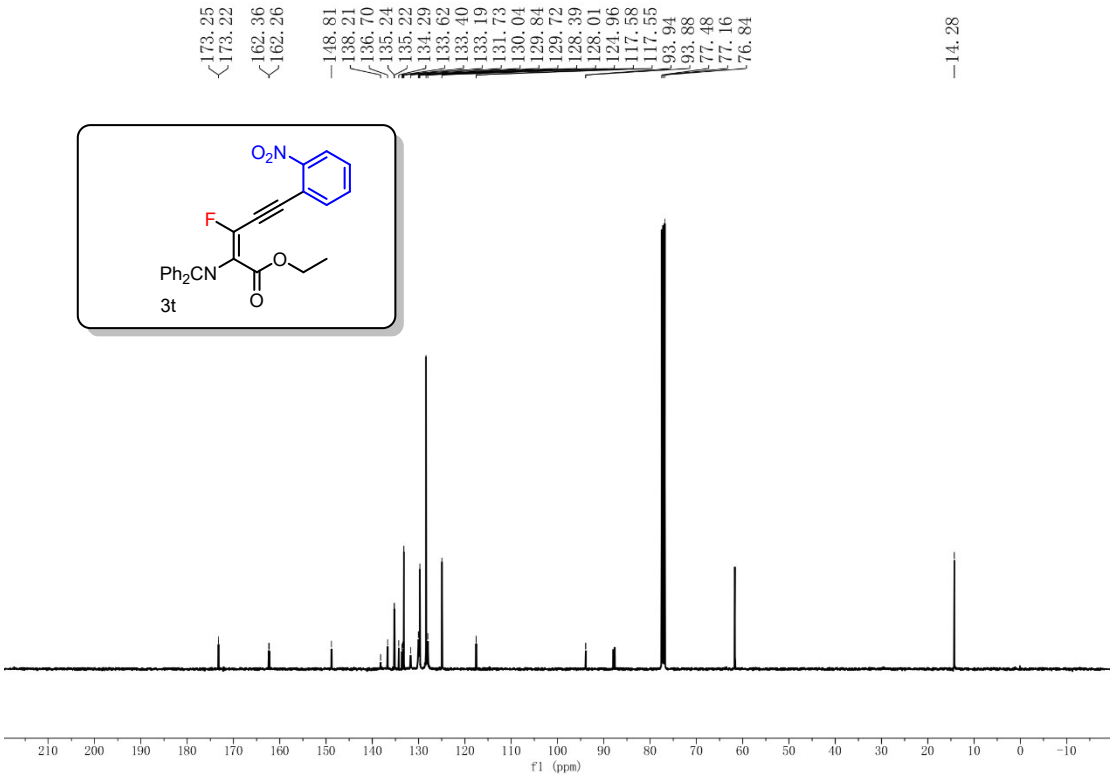
^{19}F NMR of compound 3s (377 MHz, $CDCl_3$)



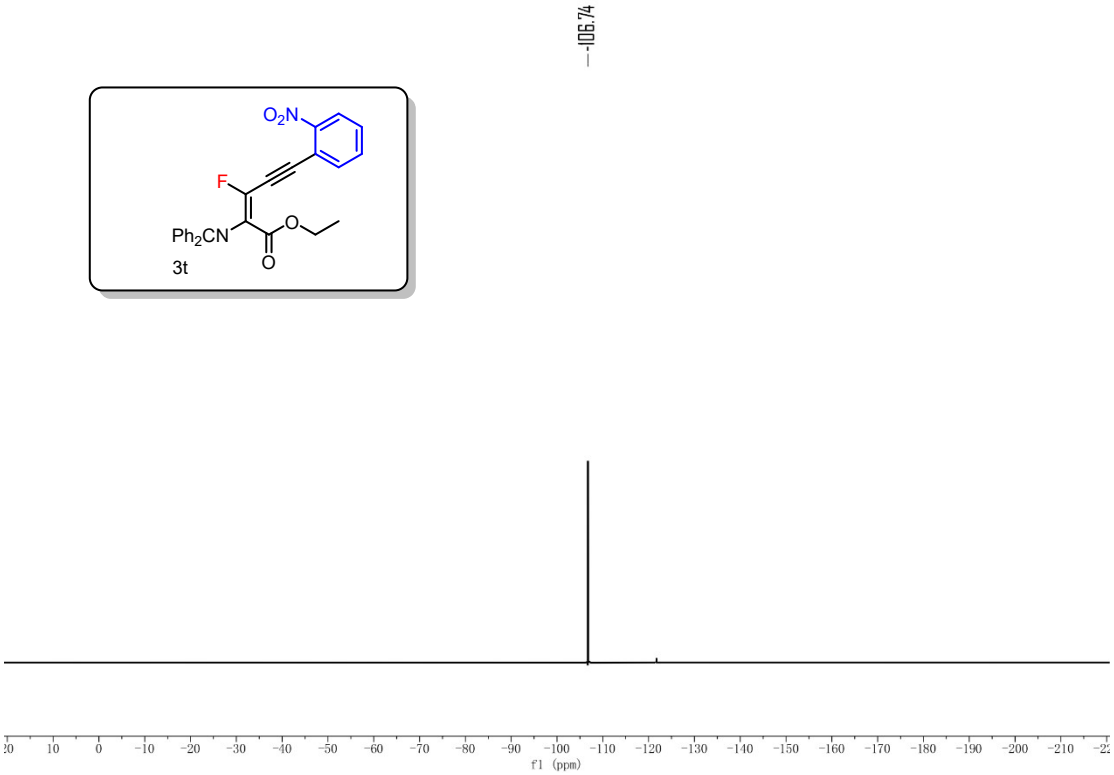
^{1}H NMR of compound 3t (400 MHz, $CDCl_3$)



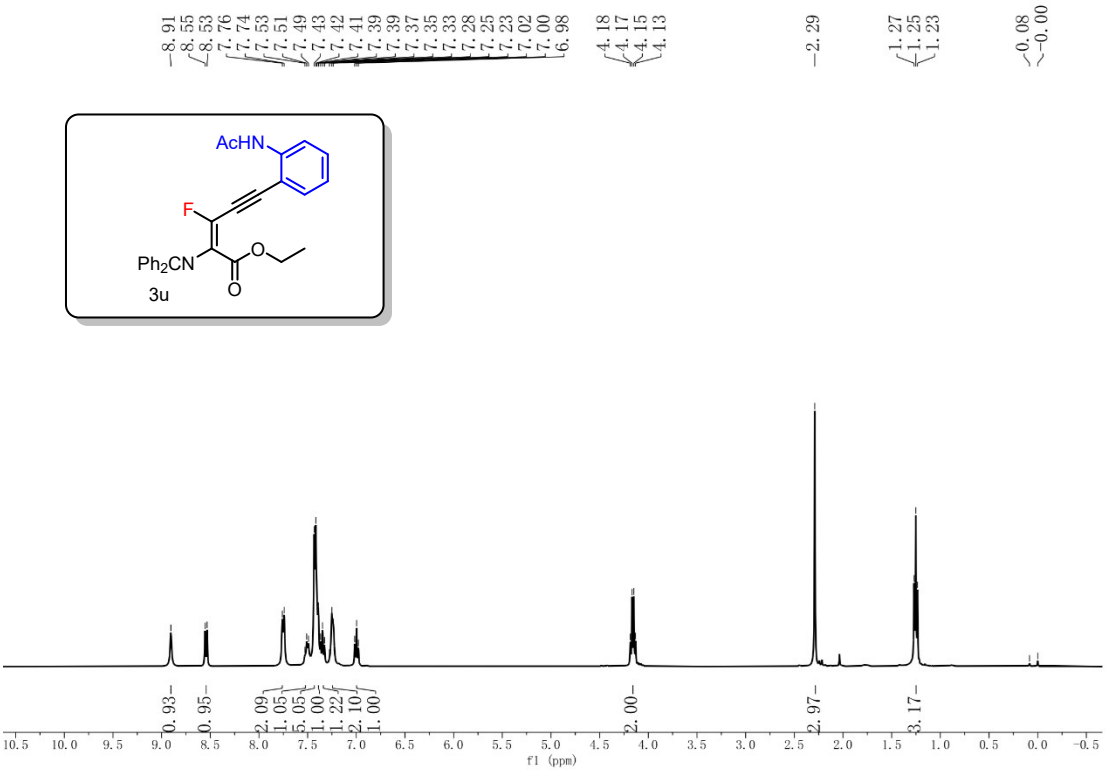
^{13}C NMR of compound 3t (101 MHz, $CDCl_3$)



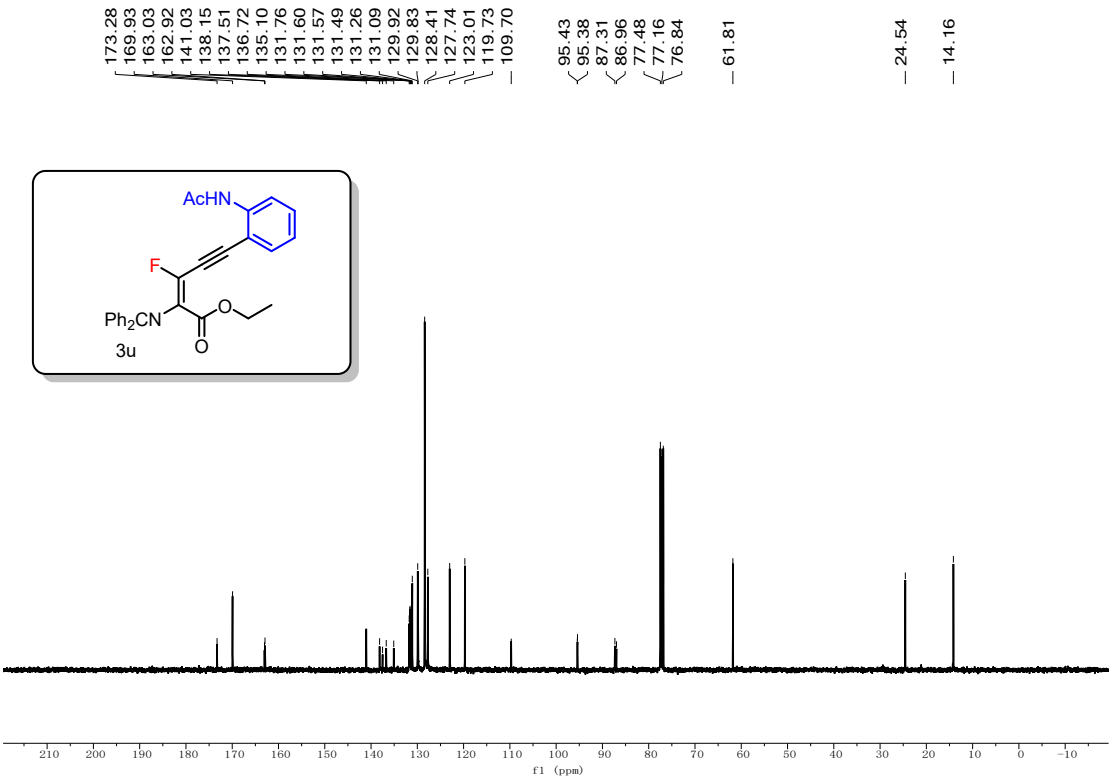
^{19}F NMR of compound 3t (377 MHz, $CDCl_3$)



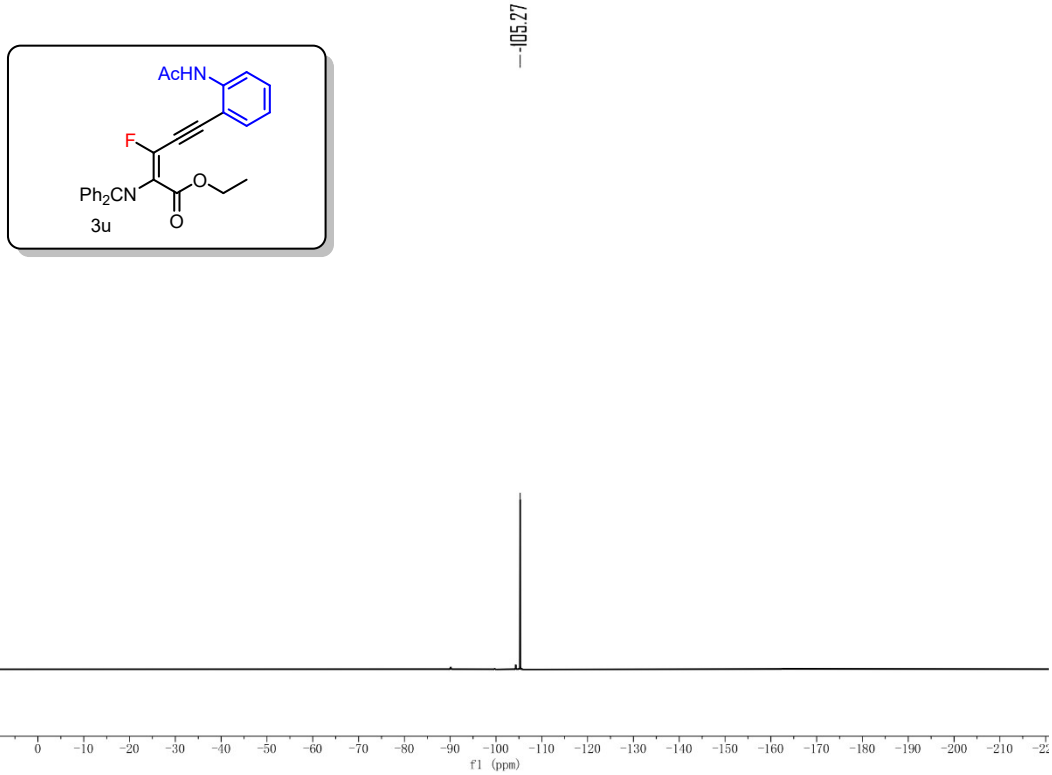
^{1}H NMR of compound 3u (400 MHz, $CDCl_3$)



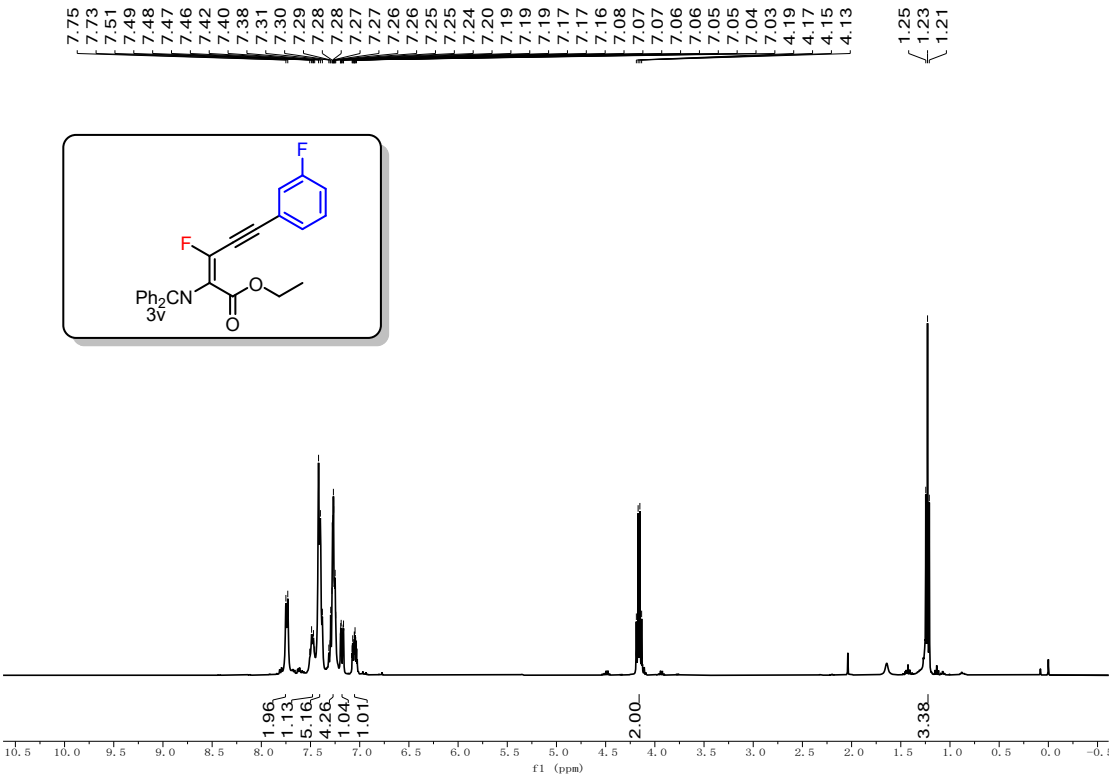
^{13}C NMR of compound 3u (101 MHz, $CDCl_3$)



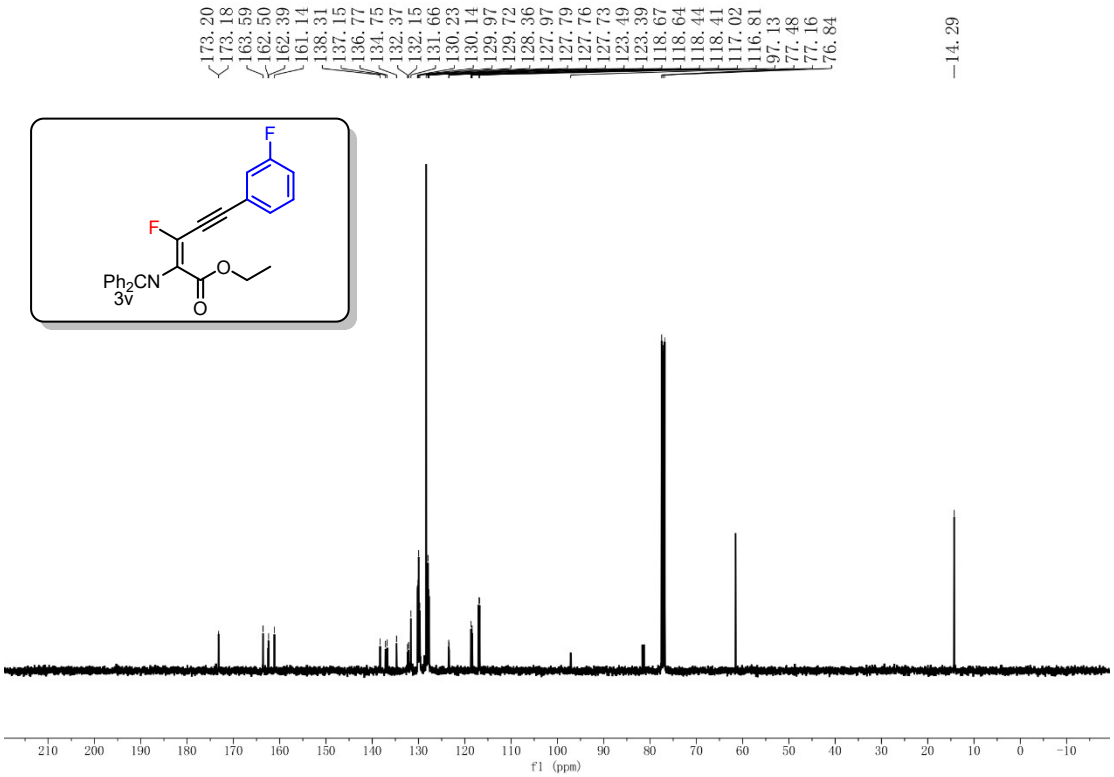
^{19}F NMR of compound 3u (377 MHz, $CDCl_3$)



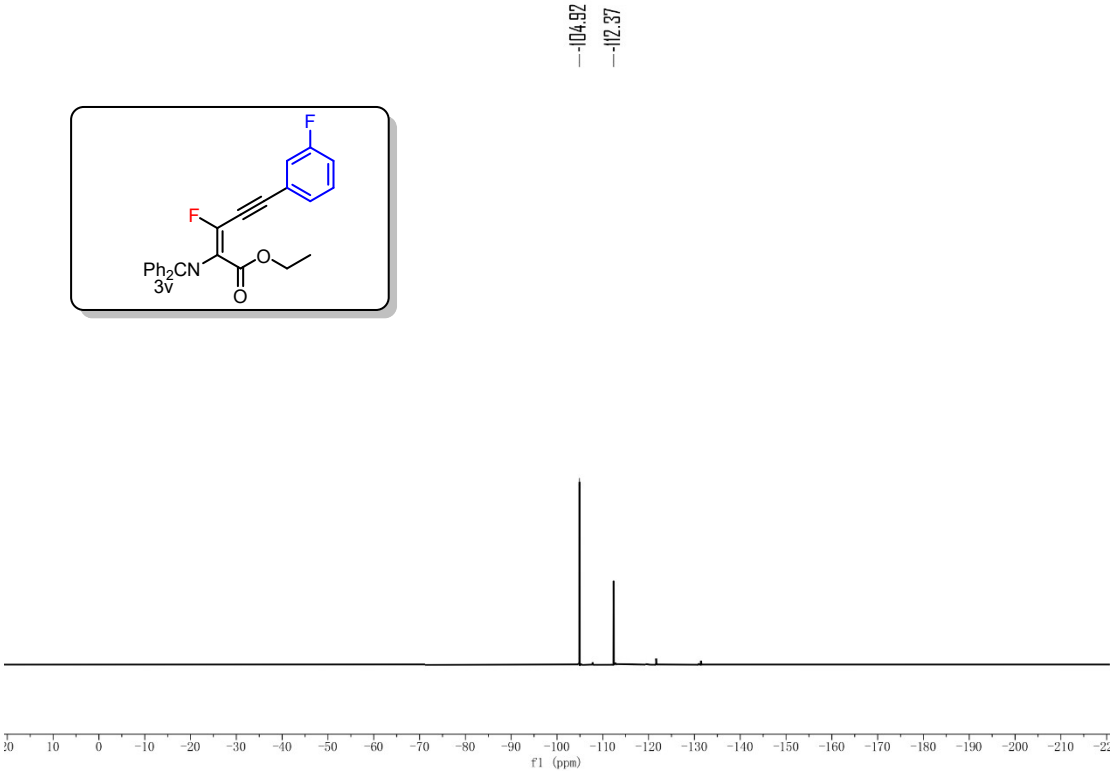
^{1}H NMR of compound 3v (400 MHz, $CDCl_3$)



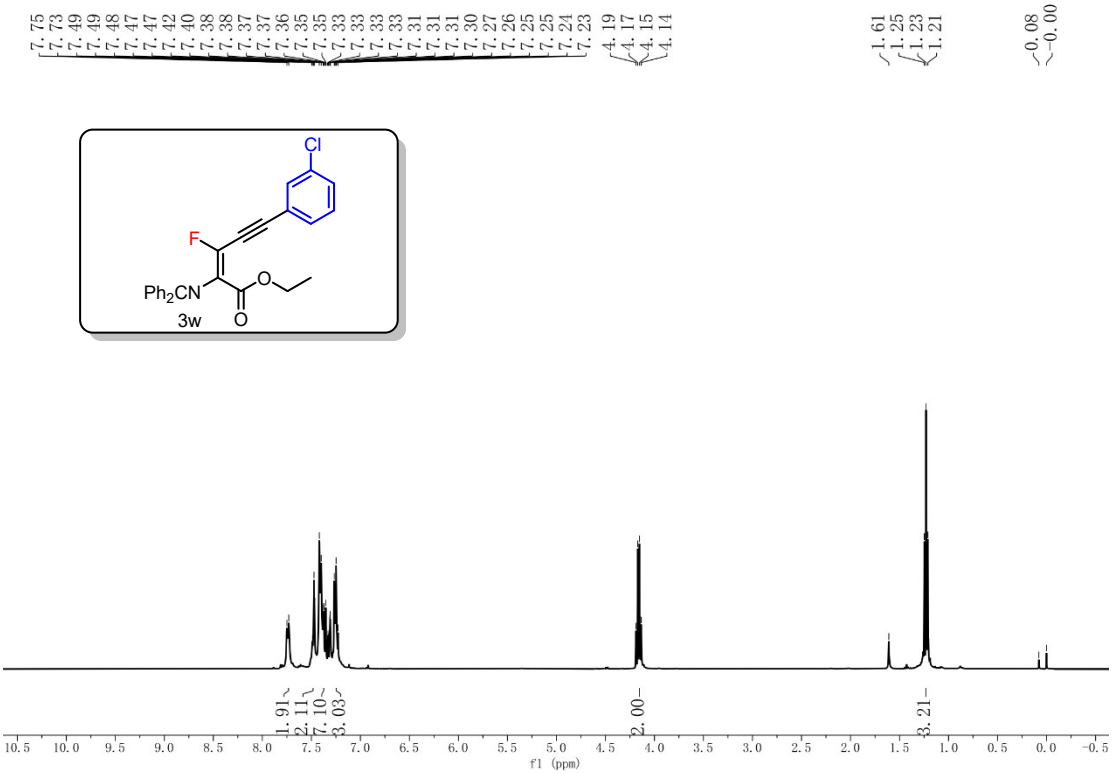
^{13}C NMR of compound 3v (101 MHz, $CDCl_3$)



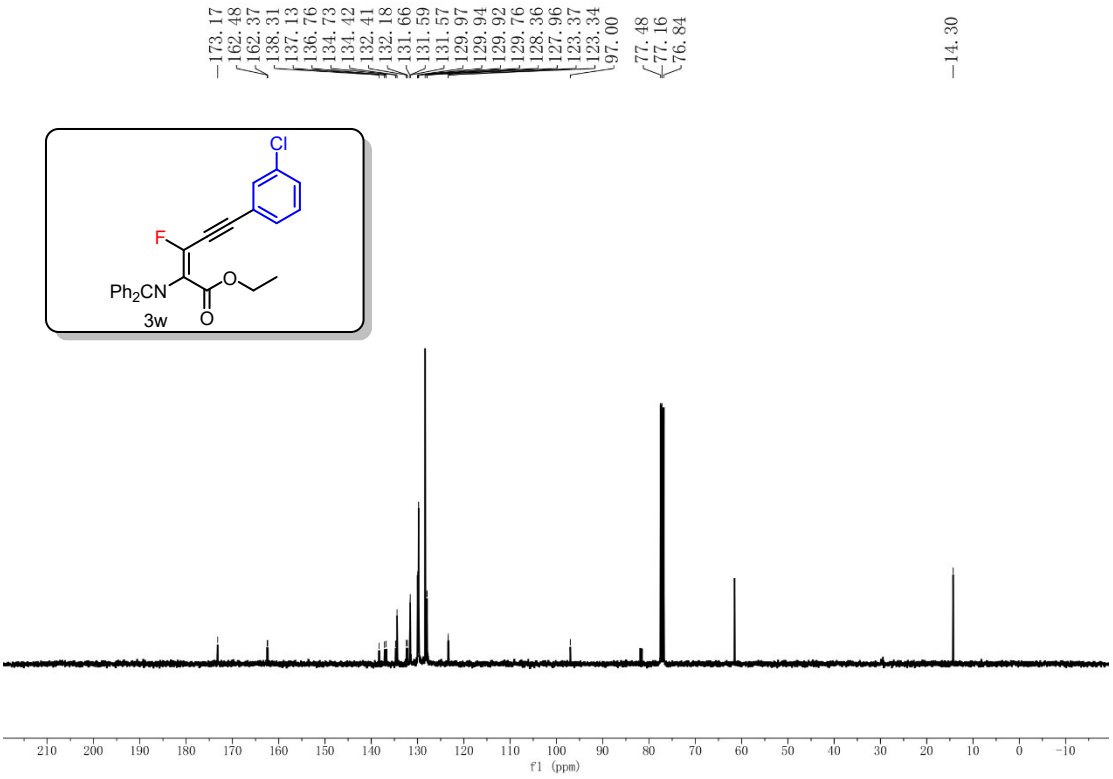
^{19}F NMR of compound 3v (377 MHz, $CDCl_3$)



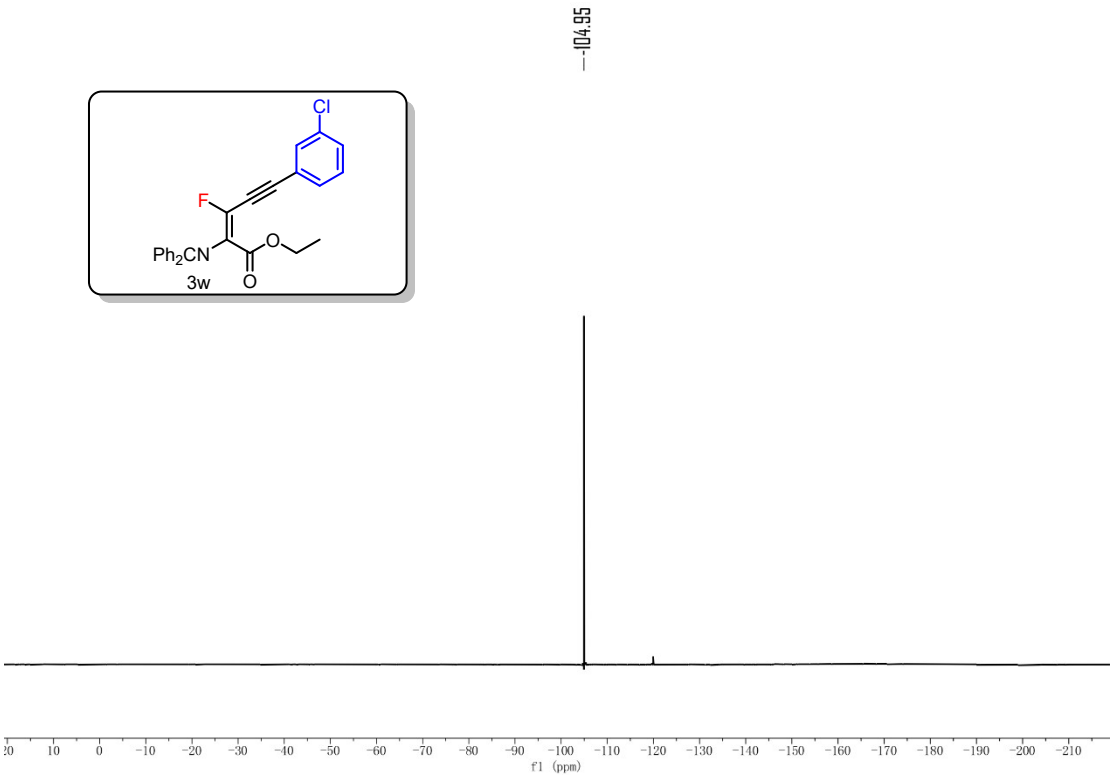
^{1}H NMR of compound 3w (400 MHz, $CDCl_3$)



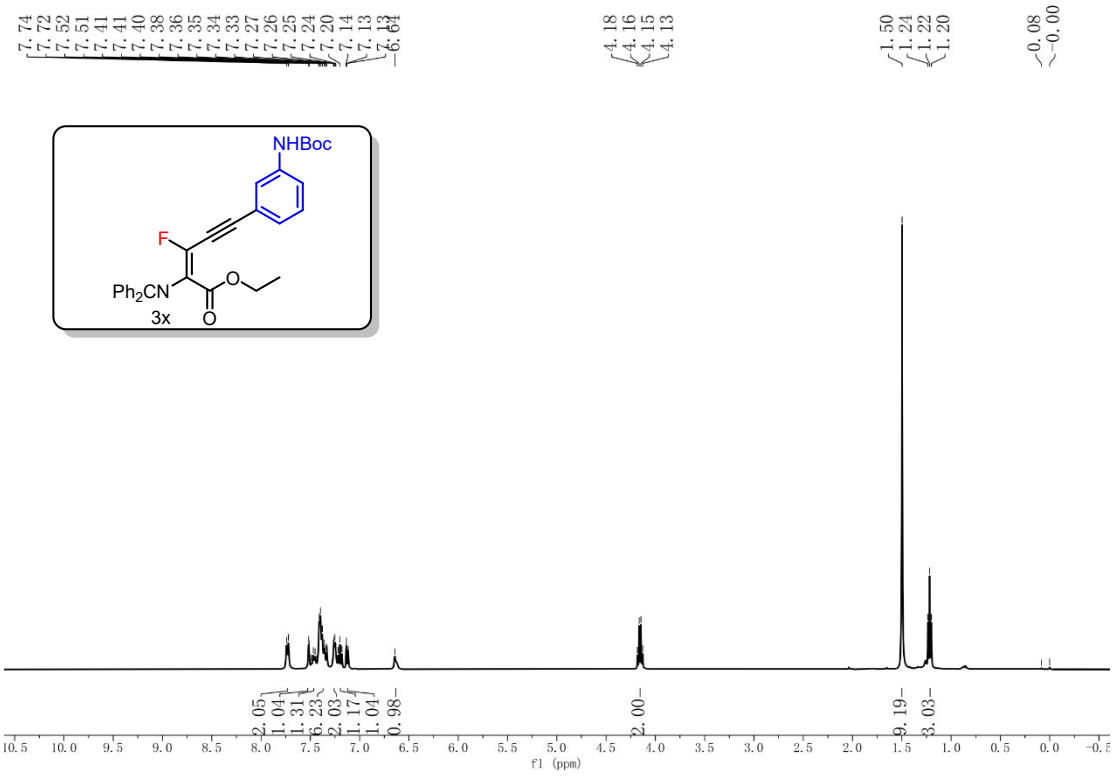
^{13}C NMR of compound 3w (101 MHz, $CDCl_3$)



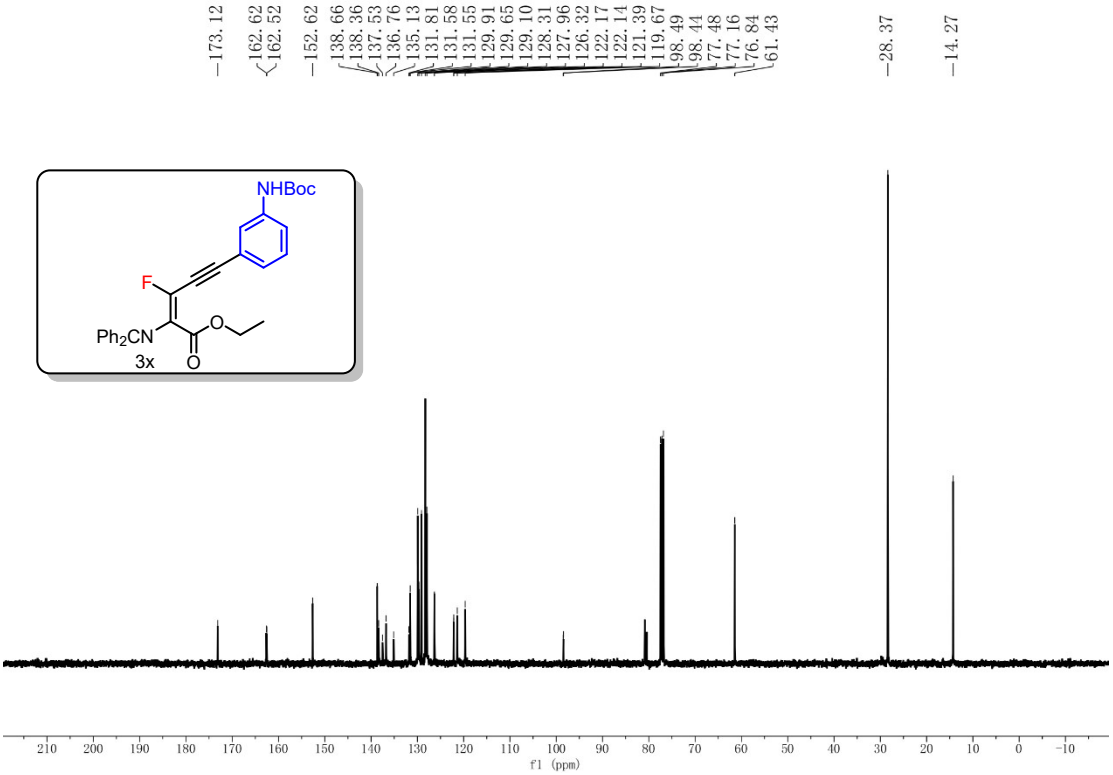
^{19}F NMR of compound 3w (377 MHz, $CDCl_3$)



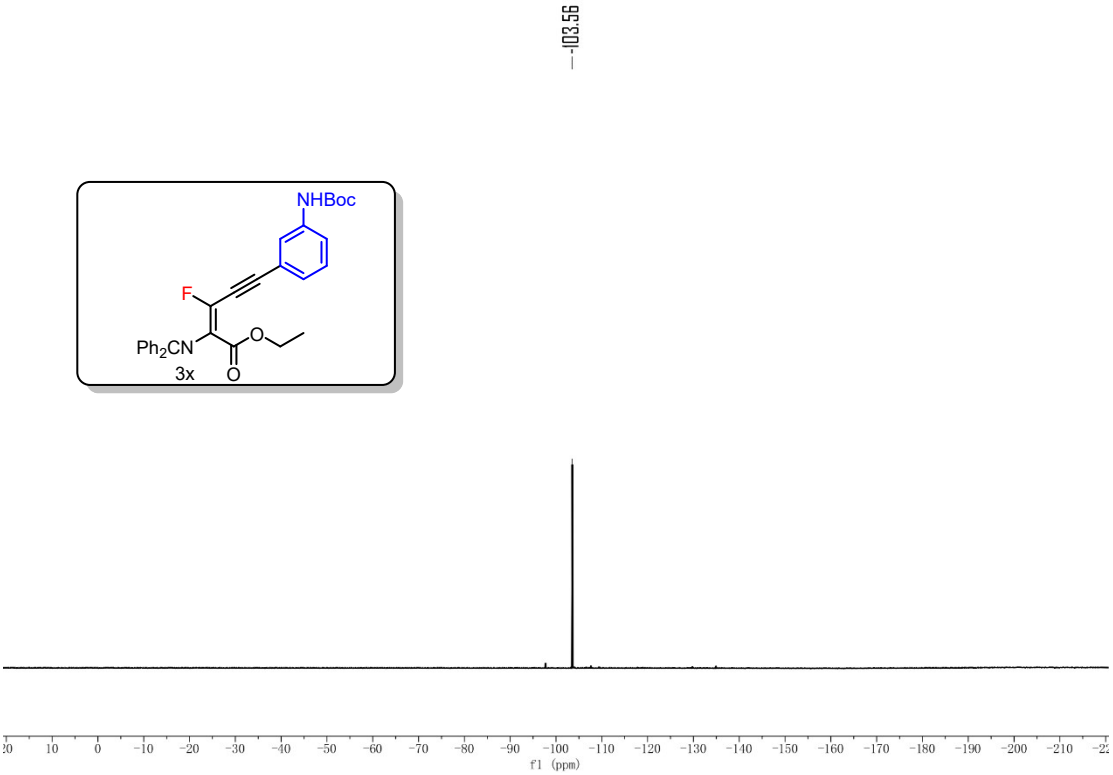
^{1}H NMR of compound 3x (400 MHz, $CDCl_3$)



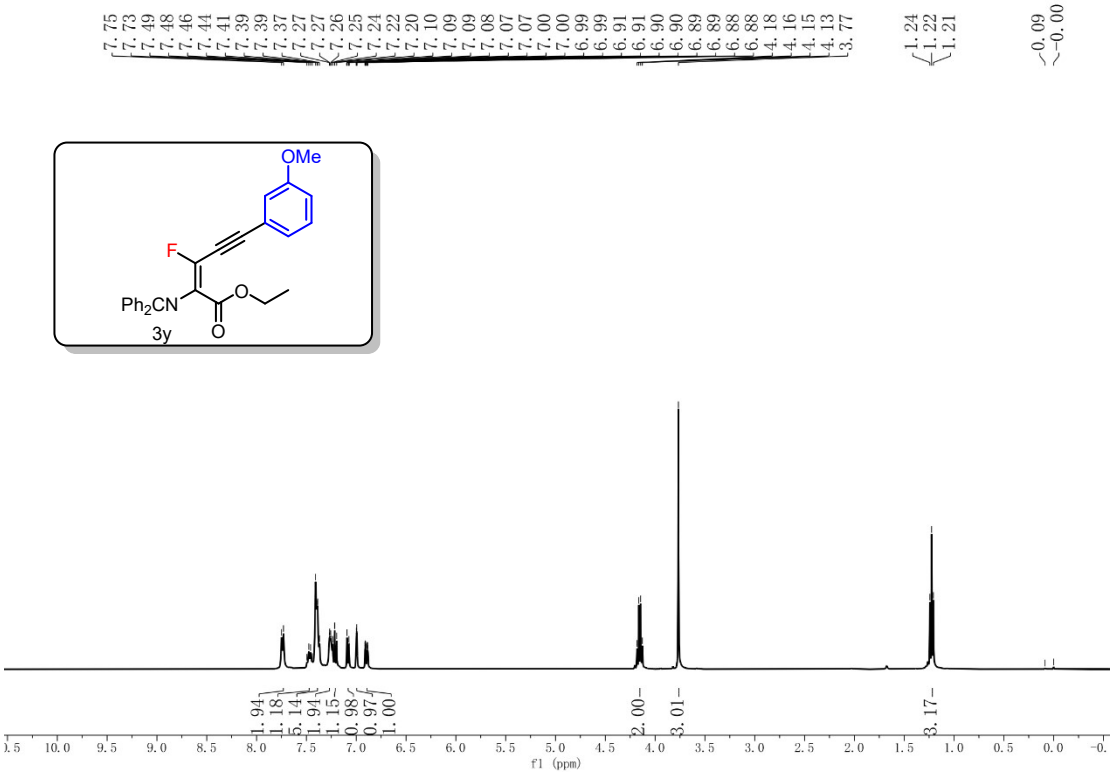
^{13}C NMR of compound 3x (101 MHz, $CDCl_3$)



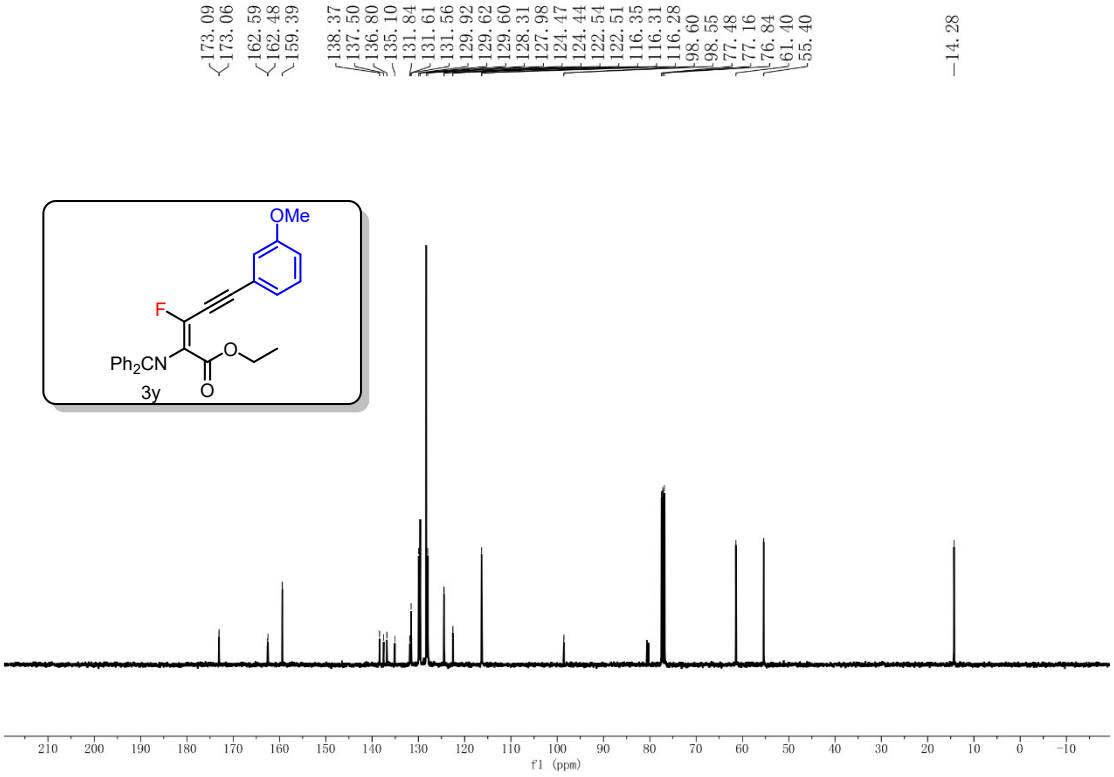
^{19}F NMR of compound 3x (377 MHz, $CDCl_3$)



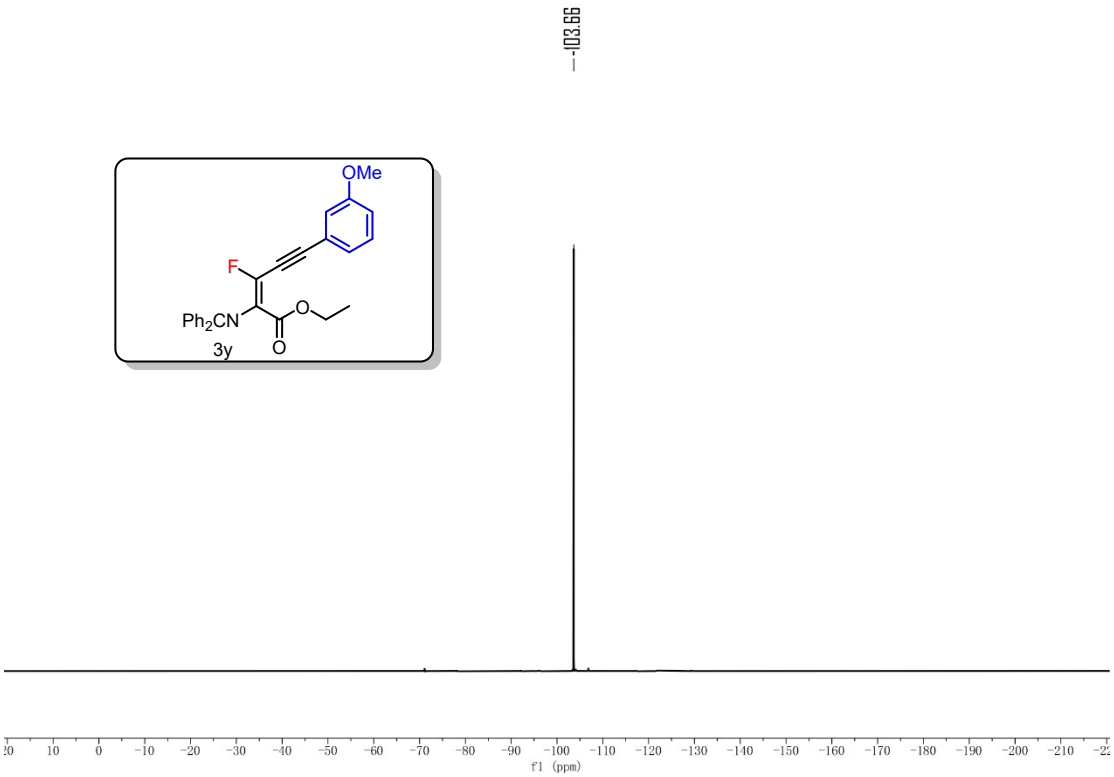
^{1}H NMR of compound 3y (400 MHz, $CDCl_3$)



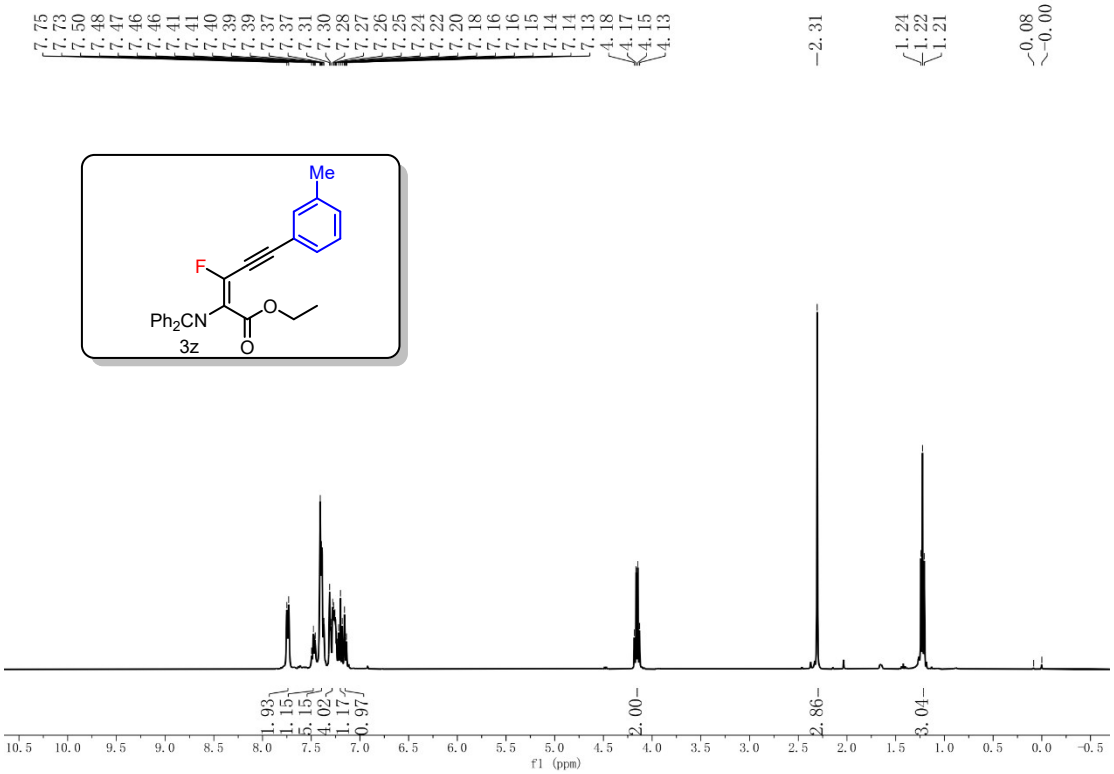
^{13}C NMR of compound 3y (101 MHz, $CDCl_3$)



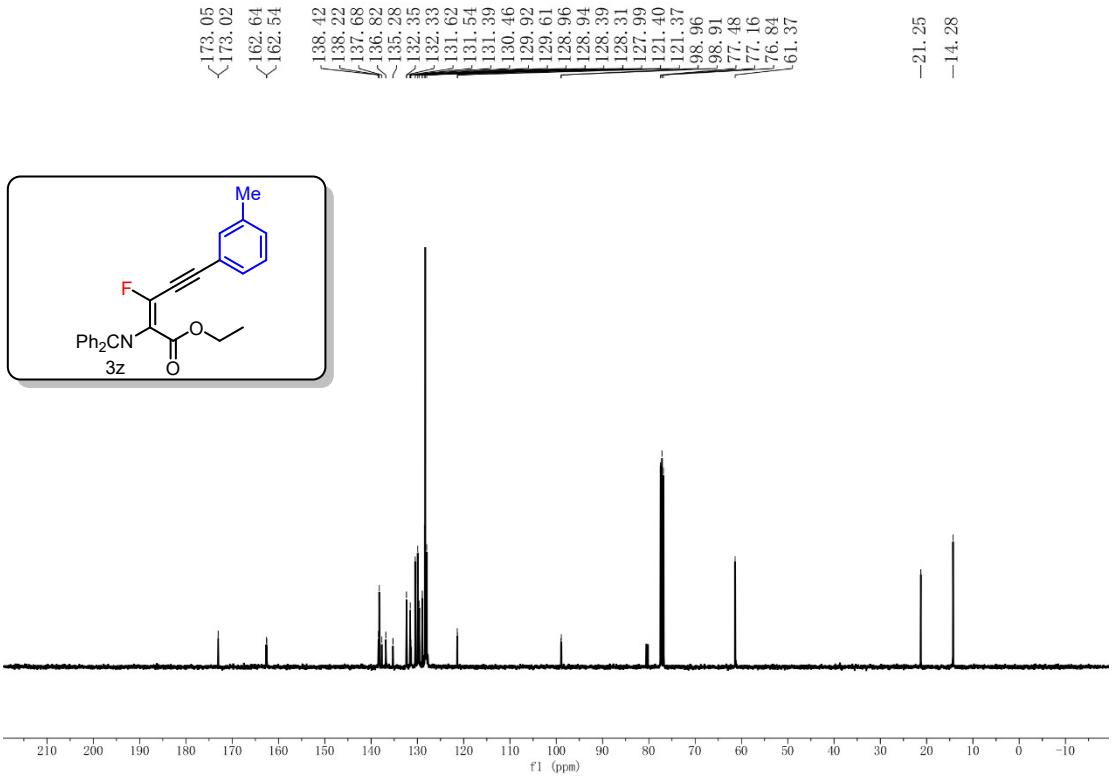
^{19}F NMR of compound 3y (377 MHz, $CDCl_3$)



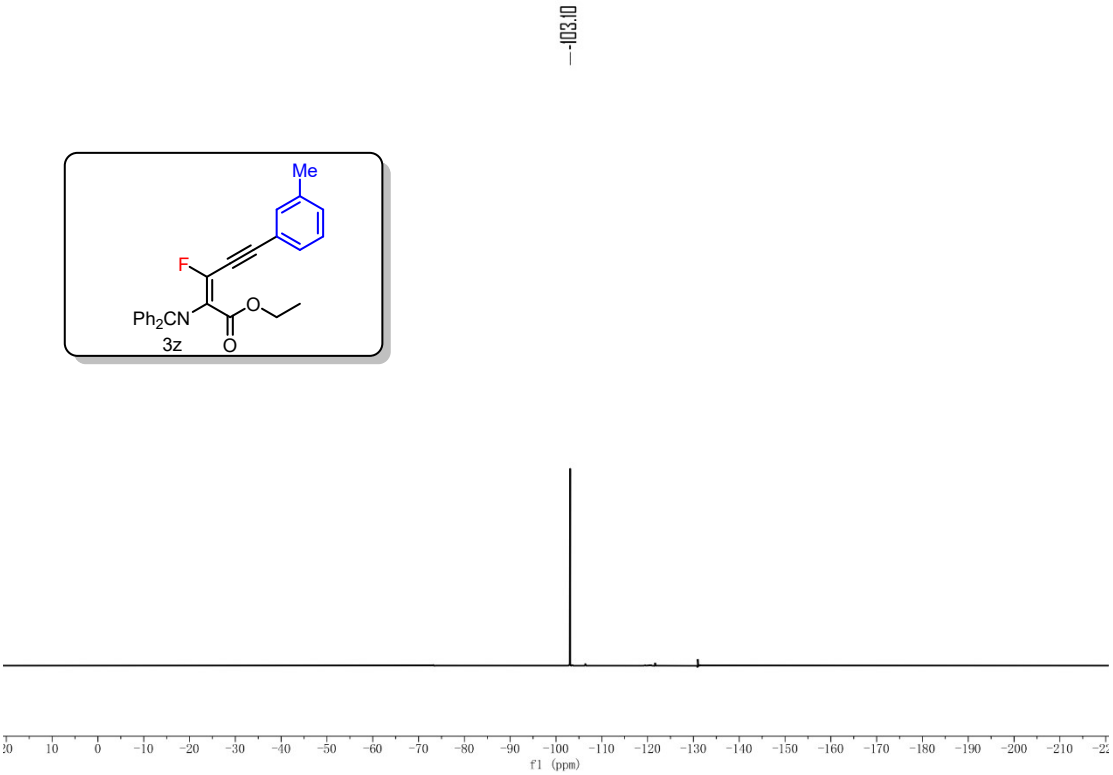
^{1}H NMR of compound 3z (400 MHz, $CDCl_3$)



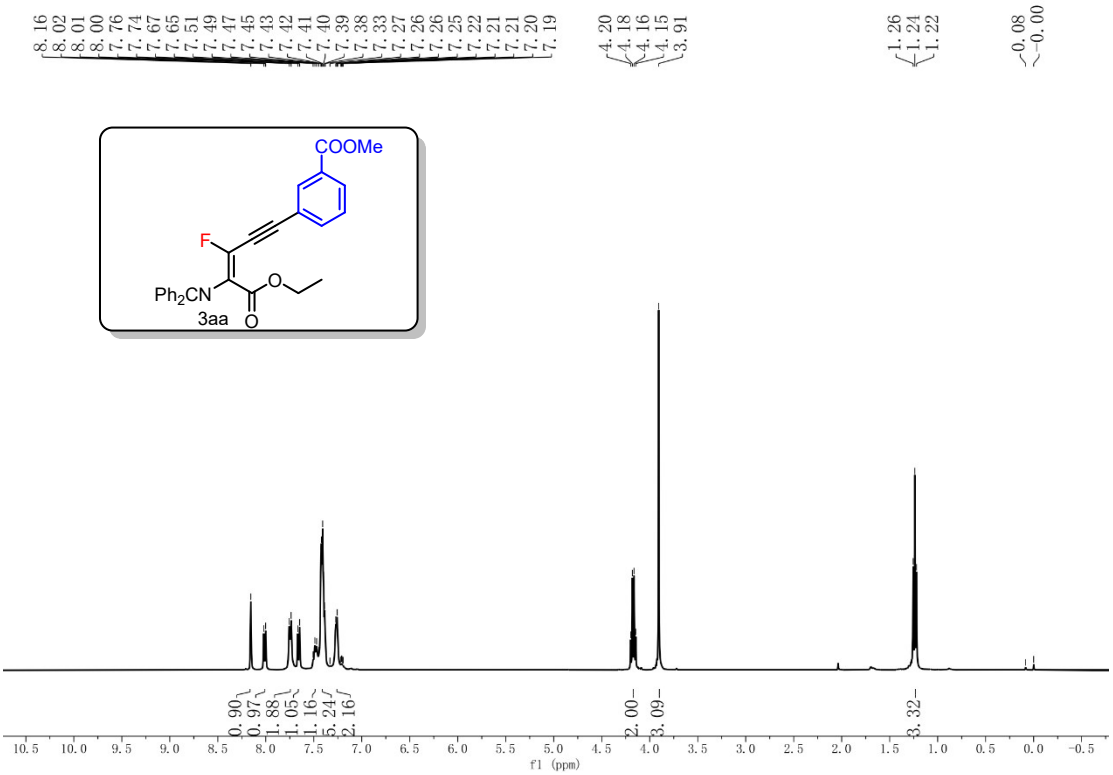
^{13}C NMR of compound 3z (101 MHz, $CDCl_3$)



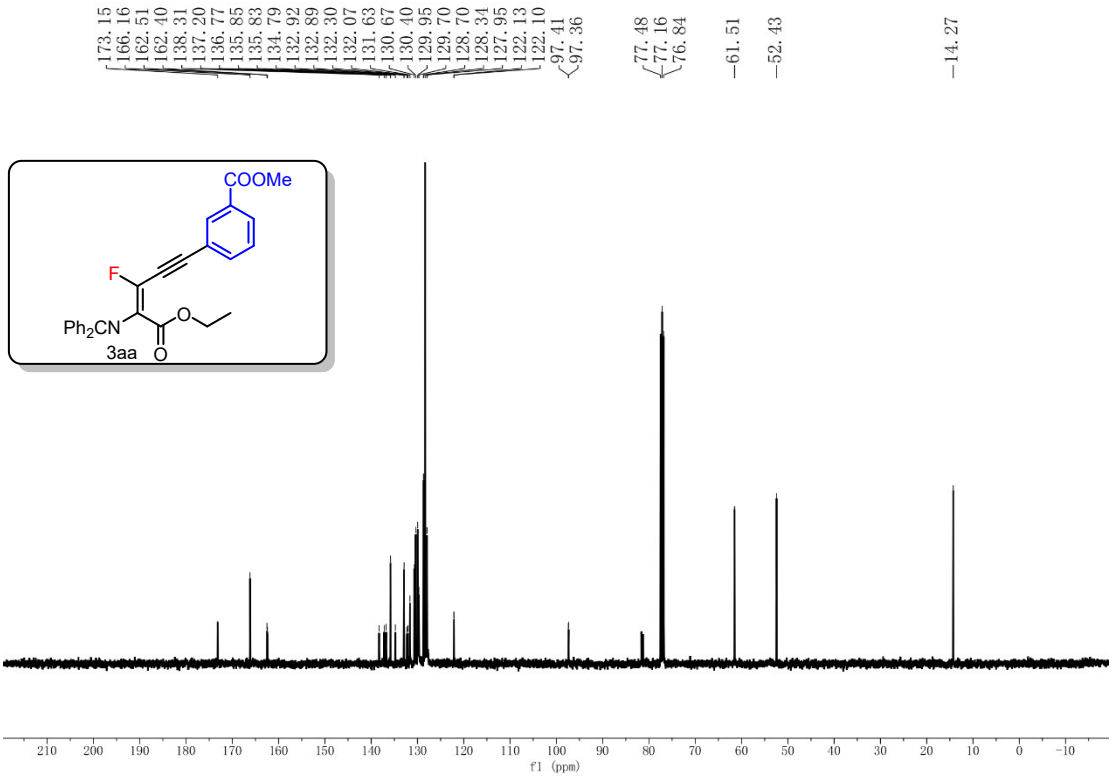
^{19}F NMR of compound 3z (377 MHz, $CDCl_3$)



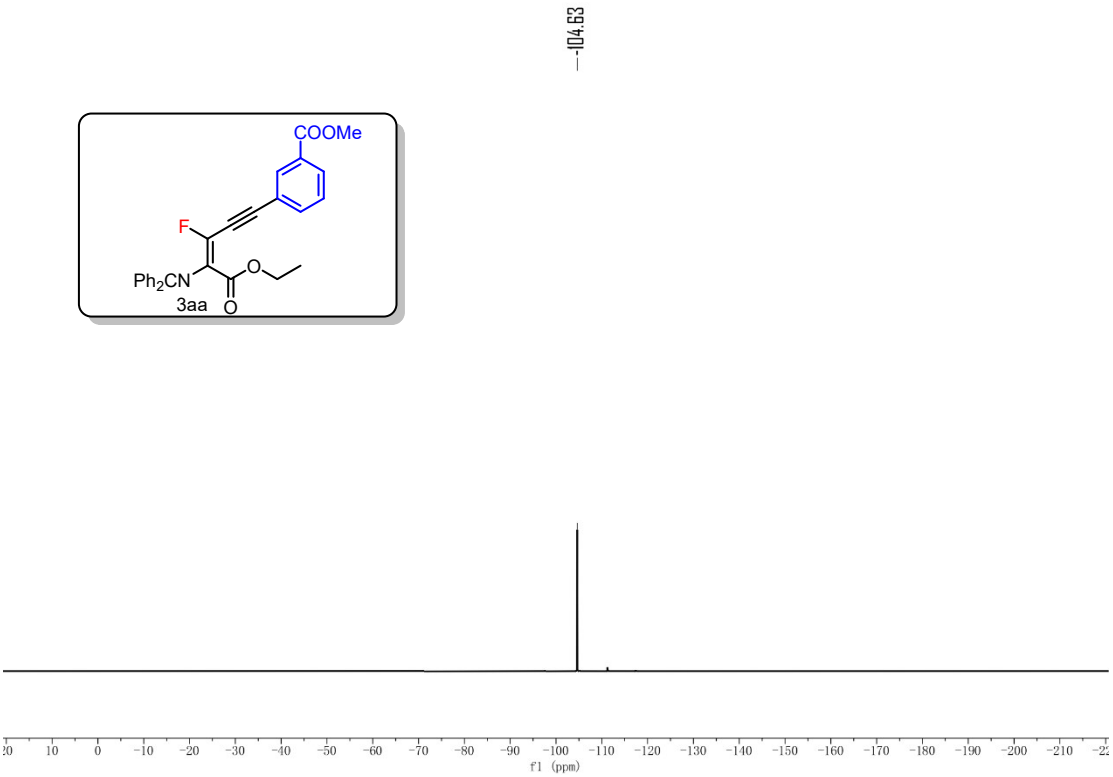
^{1}H NMR of compound 3aa (400 MHz, $CDCl_3$)



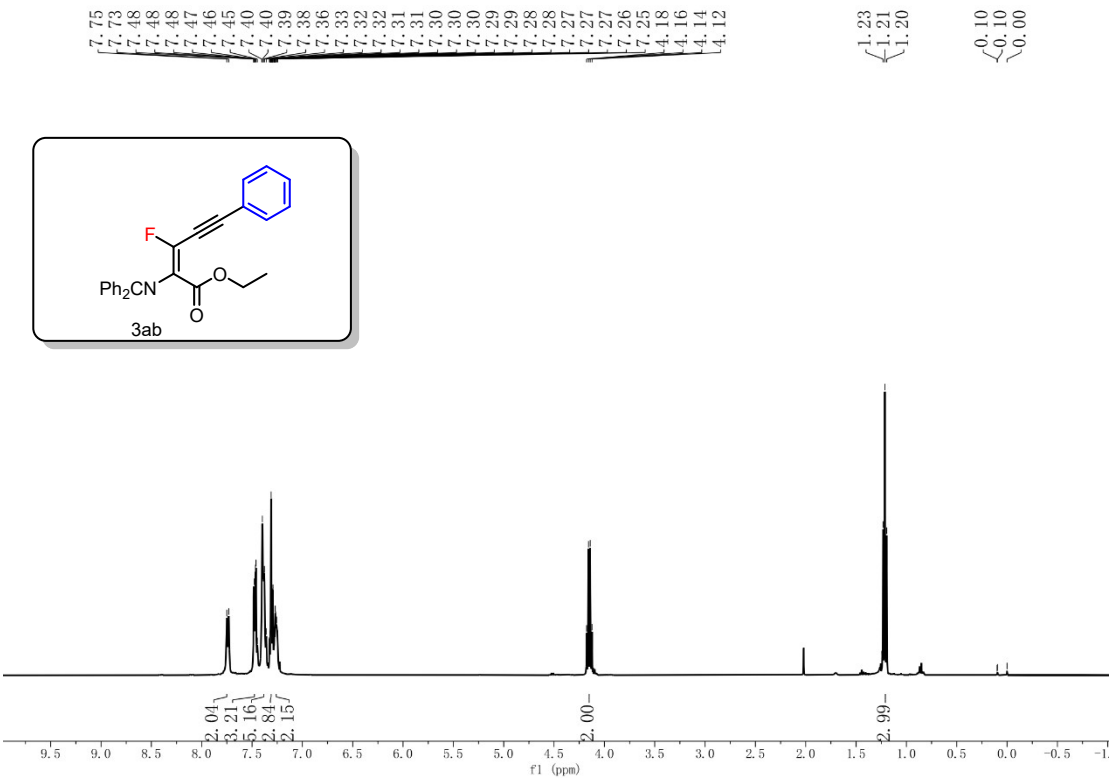
^{13}C NMR of compound 3aa (101 MHz, $CDCl_3$)



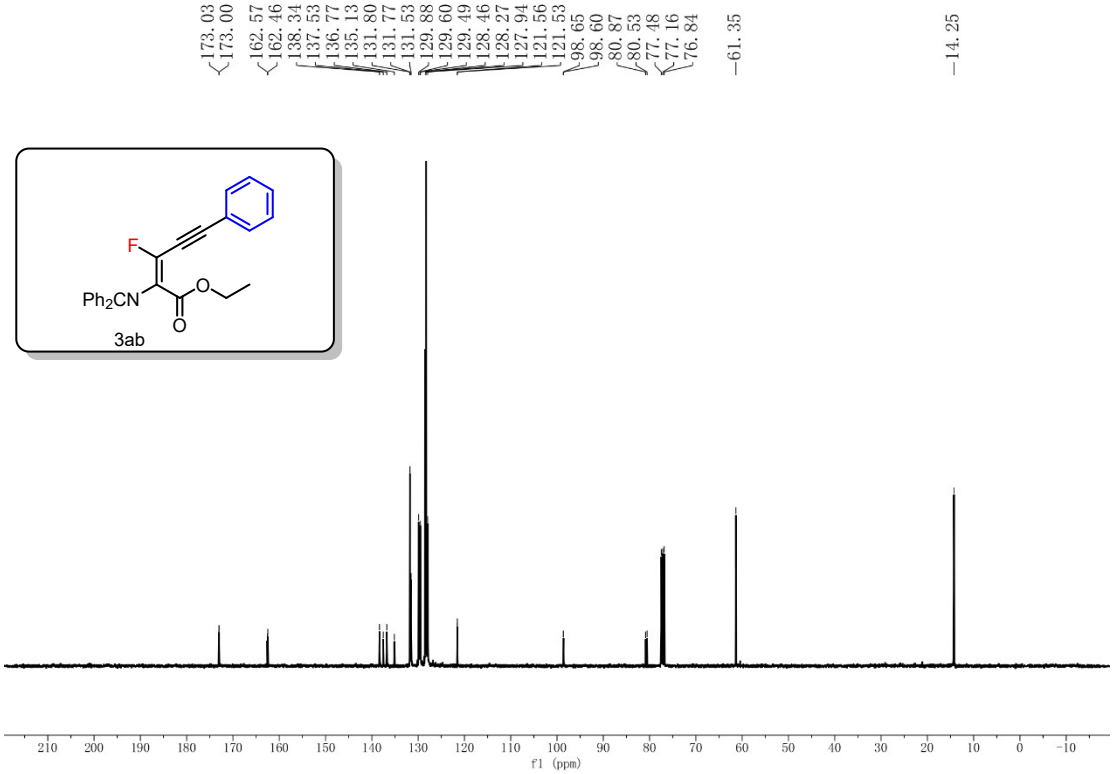
^{19}F NMR of compound 3aa (377 MHz, $CDCl_3$)



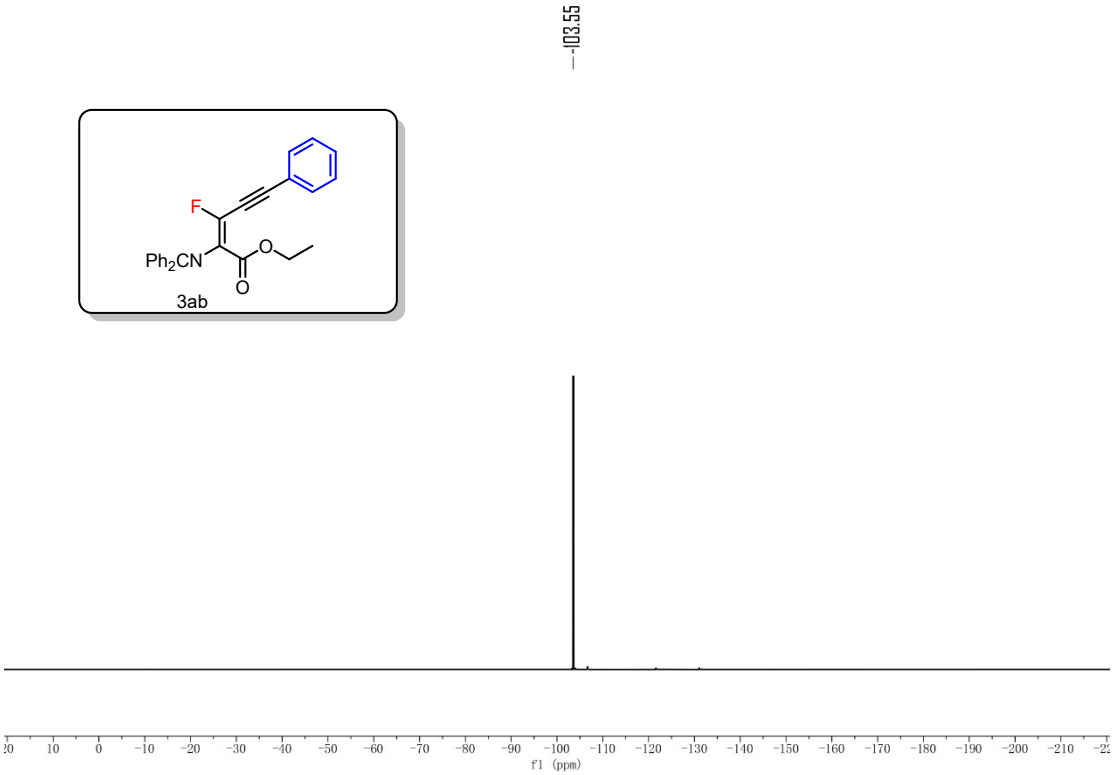
^{1}H NMR of compound 3ab (400 MHz, $CDCl_3$)



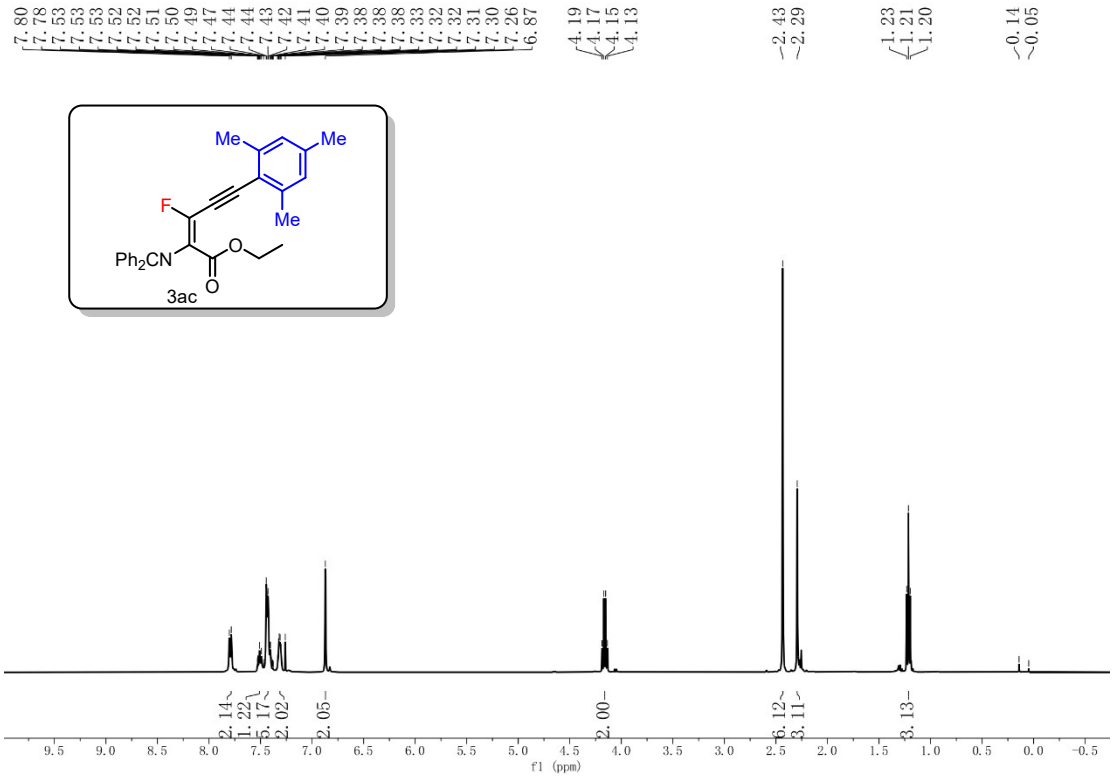
^{13}C NMR of compound 3ab (101 MHz, $CDCl_3$)



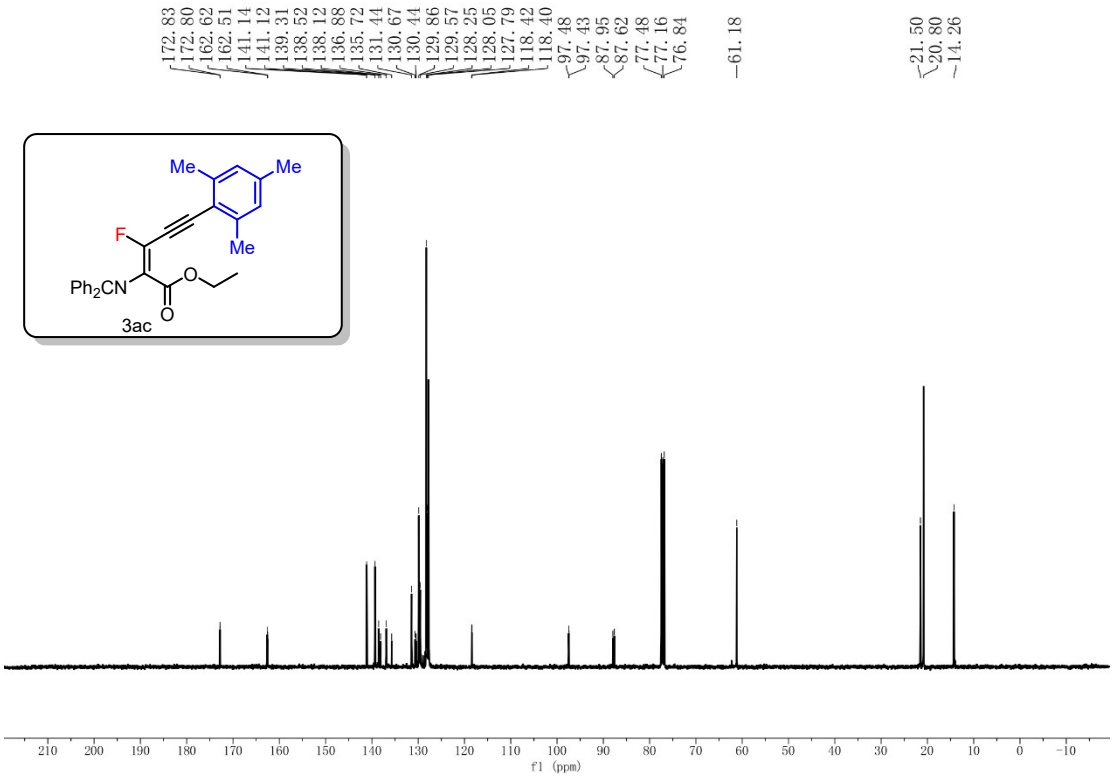
^{19}F NMR of compound 3ab (377 MHz, $CDCl_3$)



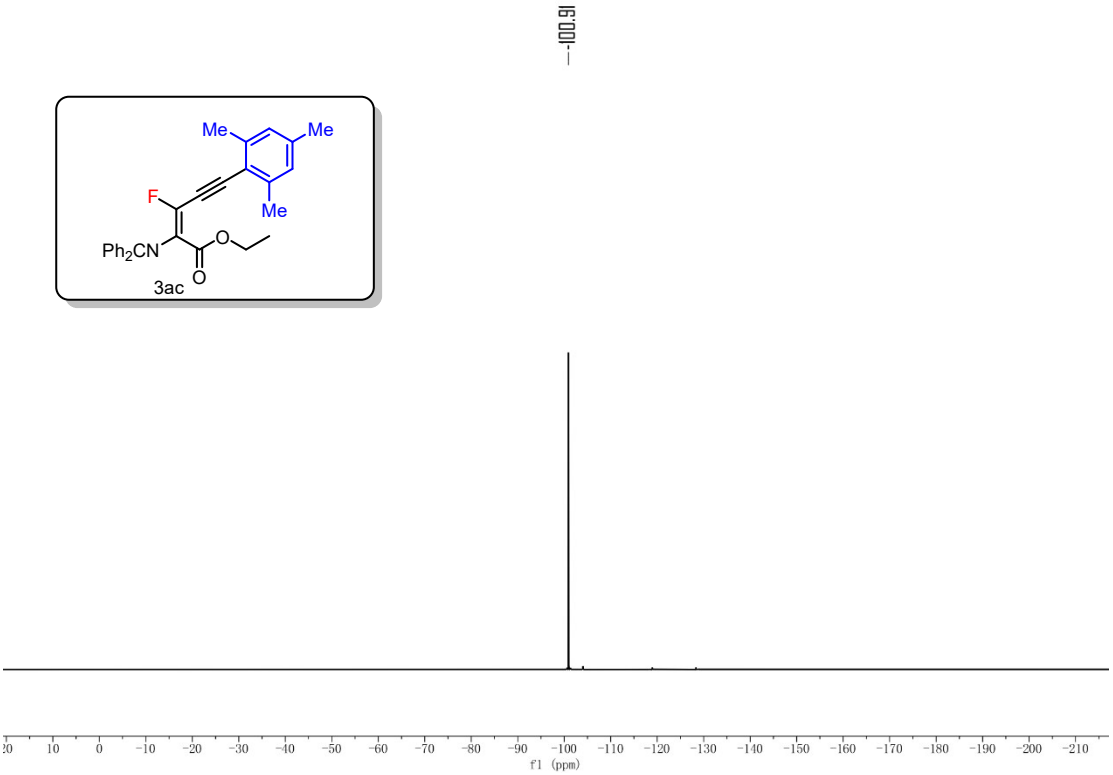
^{1}H NMR of compound 3ac (400 MHz, $CDCl_3$)



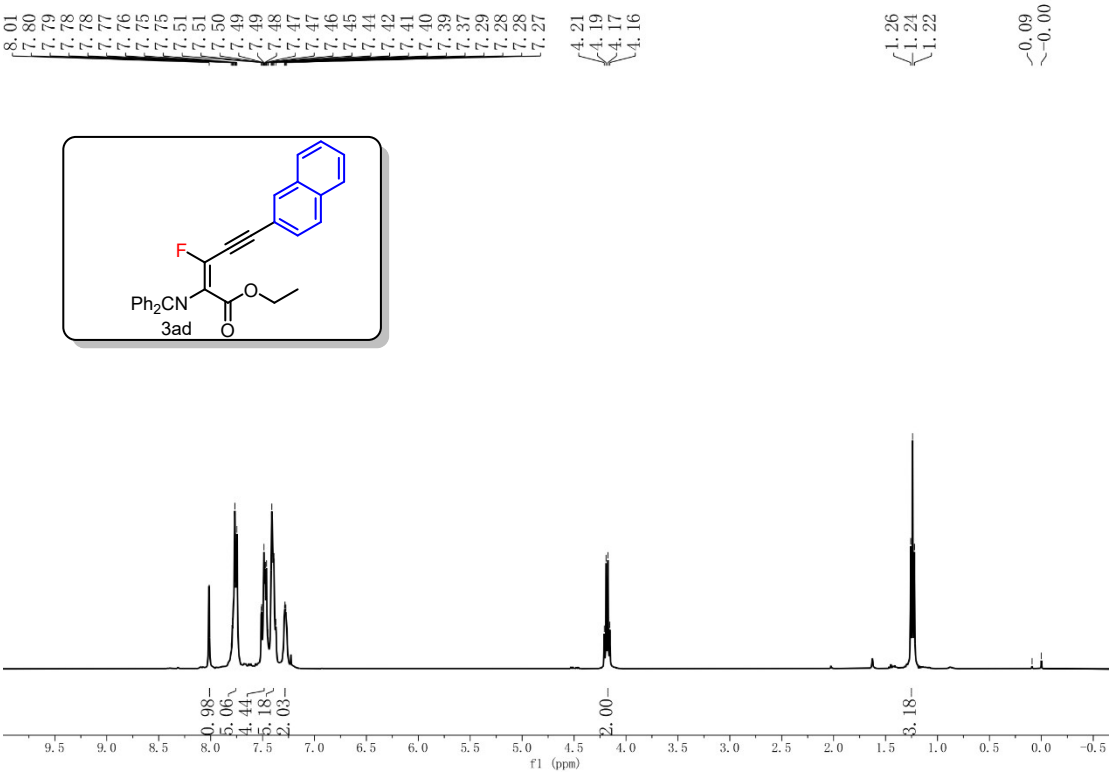
^{13}C NMR of compound 3ac (101 MHz, $CDCl_3$)



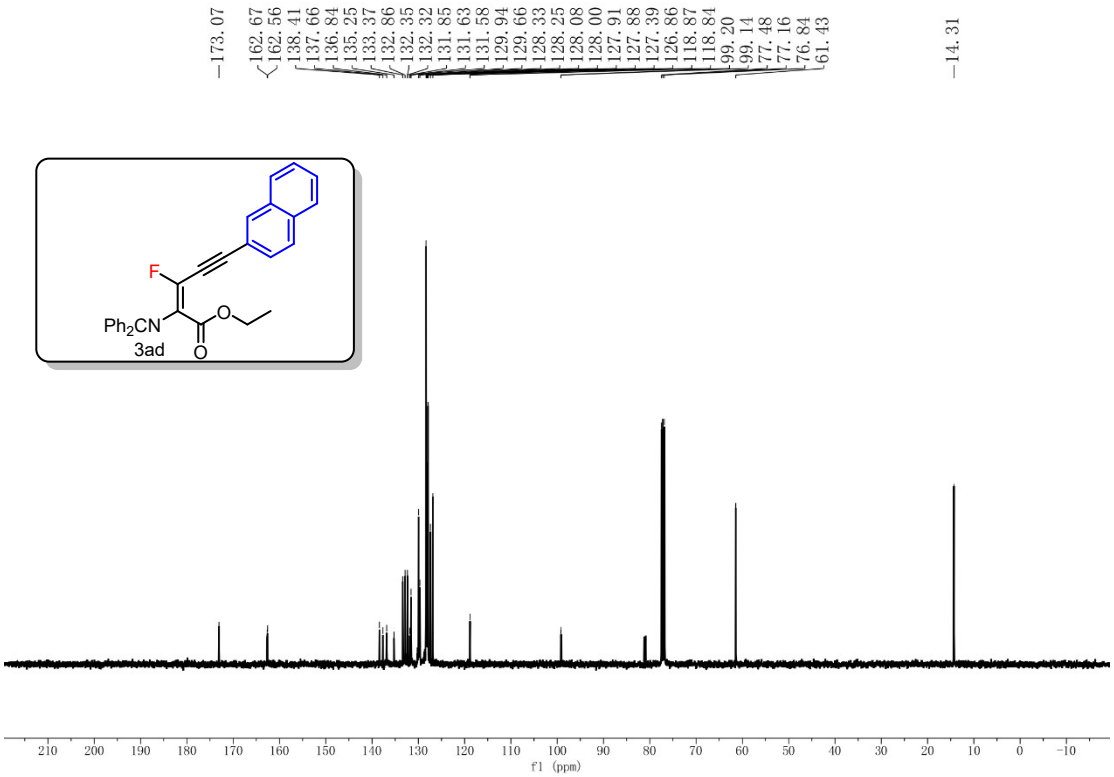
^{19}F NMR of compound 3ac (377 MHz, $CDCl_3$)



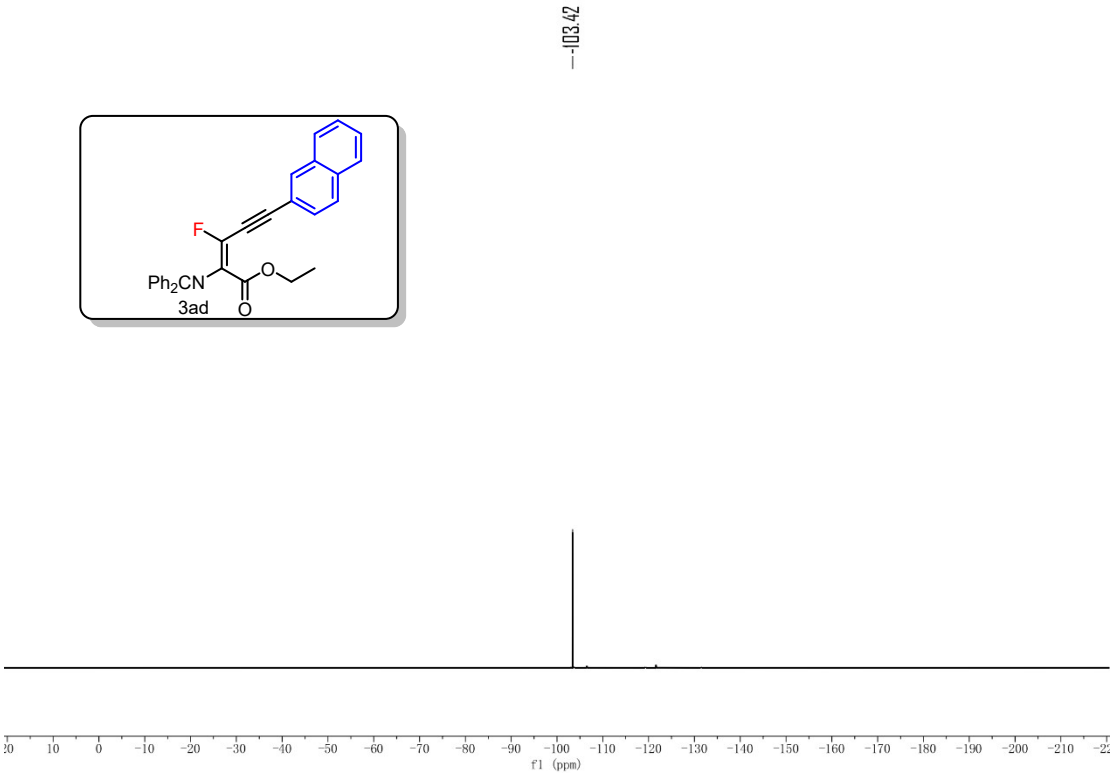
^{1}H NMR of compound 3ad (400 MHz, $CDCl_3$)



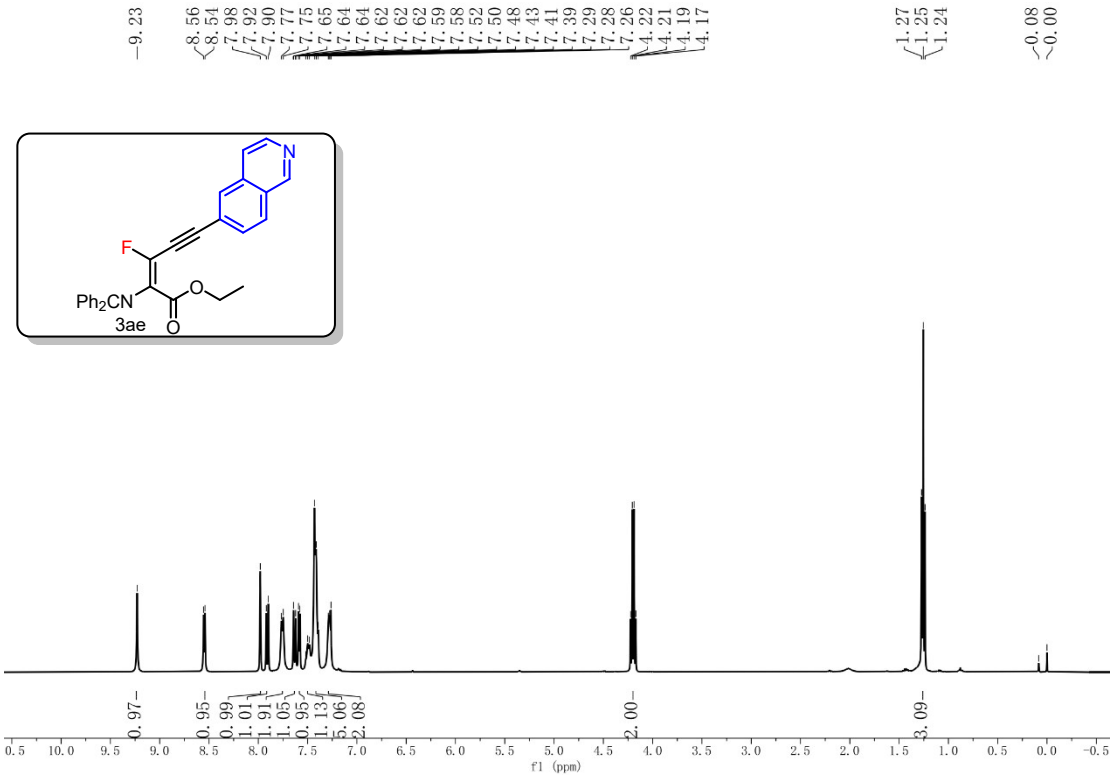
^{13}C NMR of compound 3ad (101 MHz, $CDCl_3$)



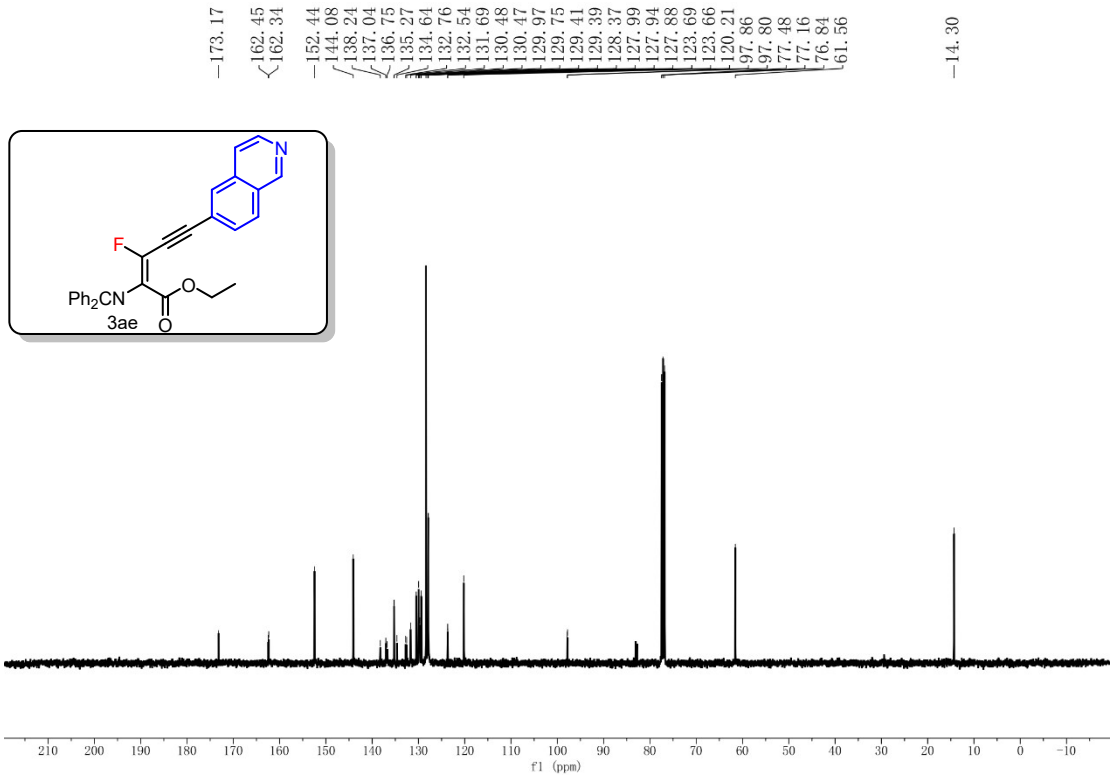
^{19}F NMR of compound 3ad (377 MHz, $CDCl_3$)



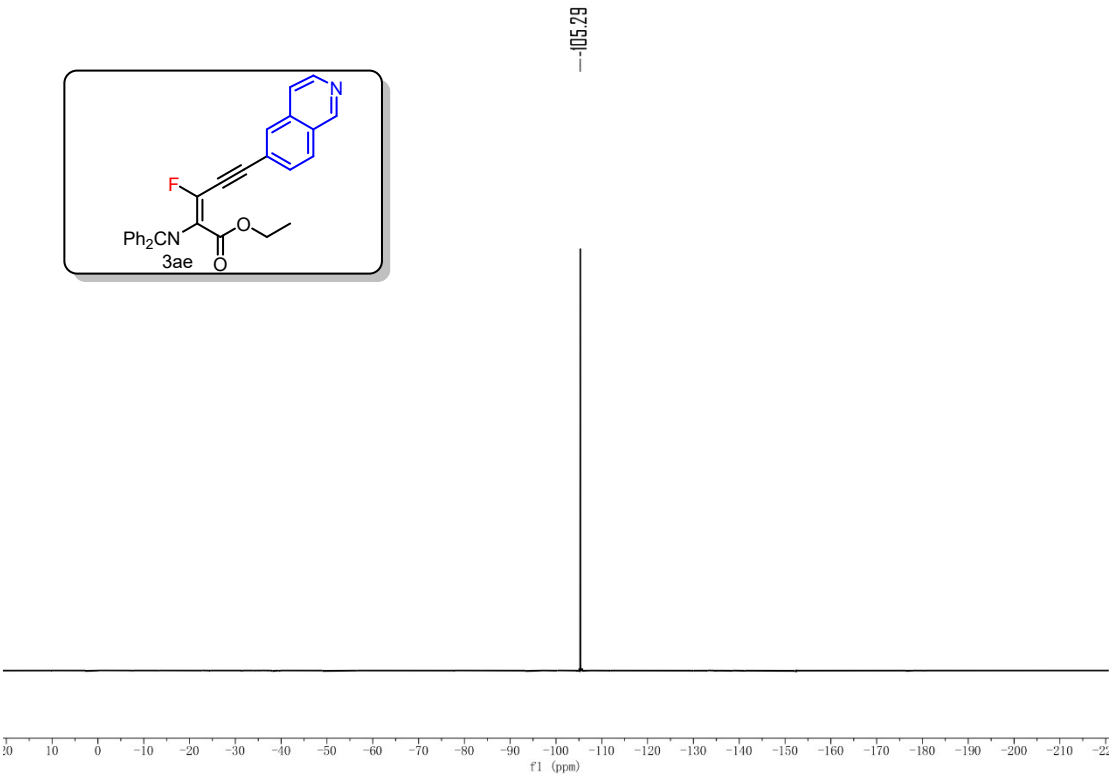
^{1}H NMR of compound 3ae (400 MHz, $CDCl_3$)



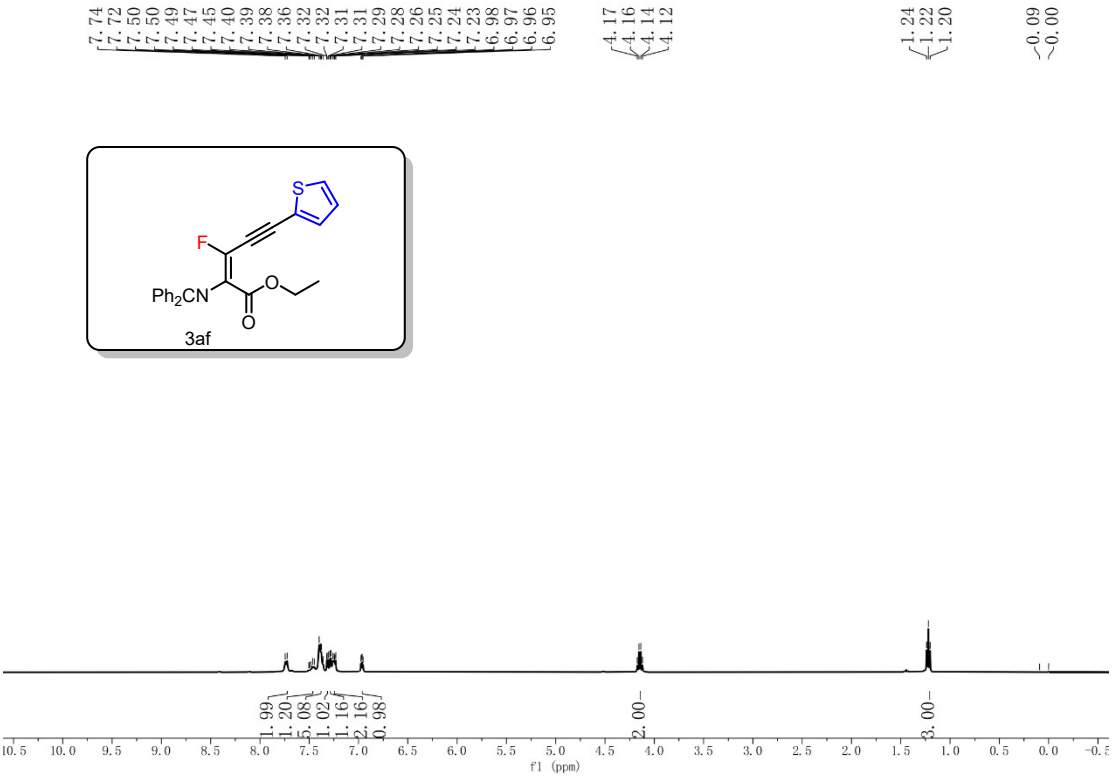
^{13}C NMR of compound 3ae (101 MHz, $CDCl_3$)



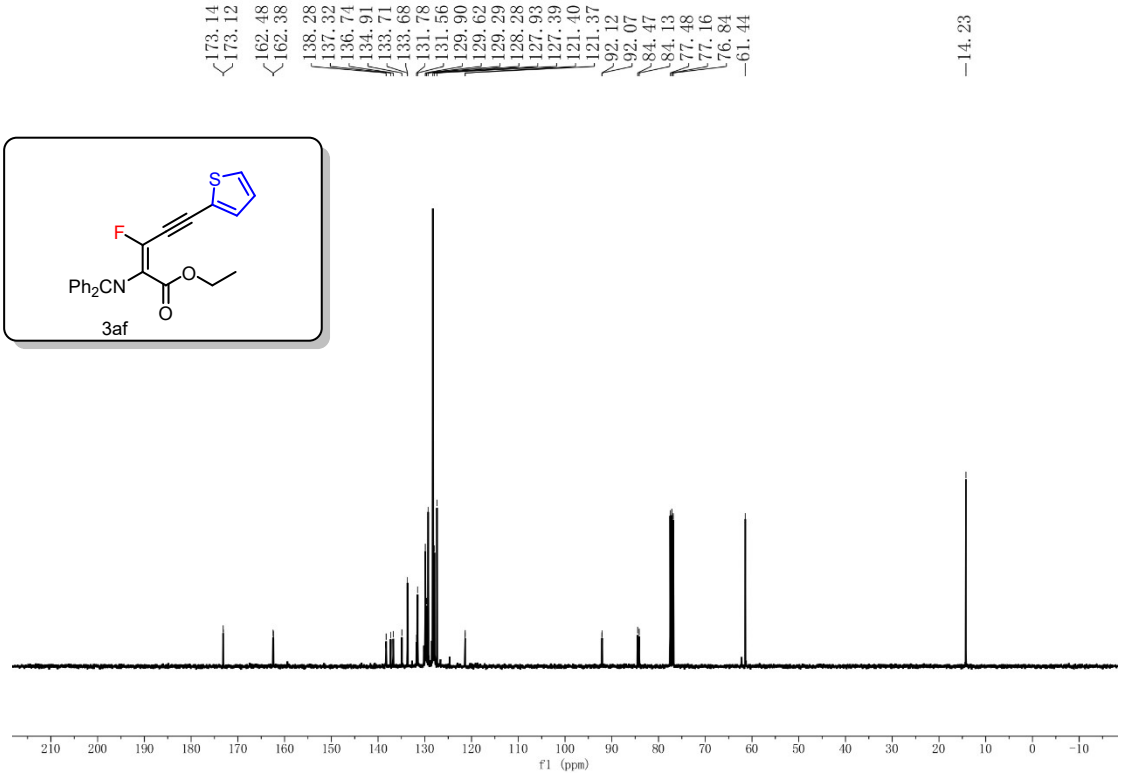
^{19}F NMR of compound 3ae (377 MHz, $CDCl_3$)



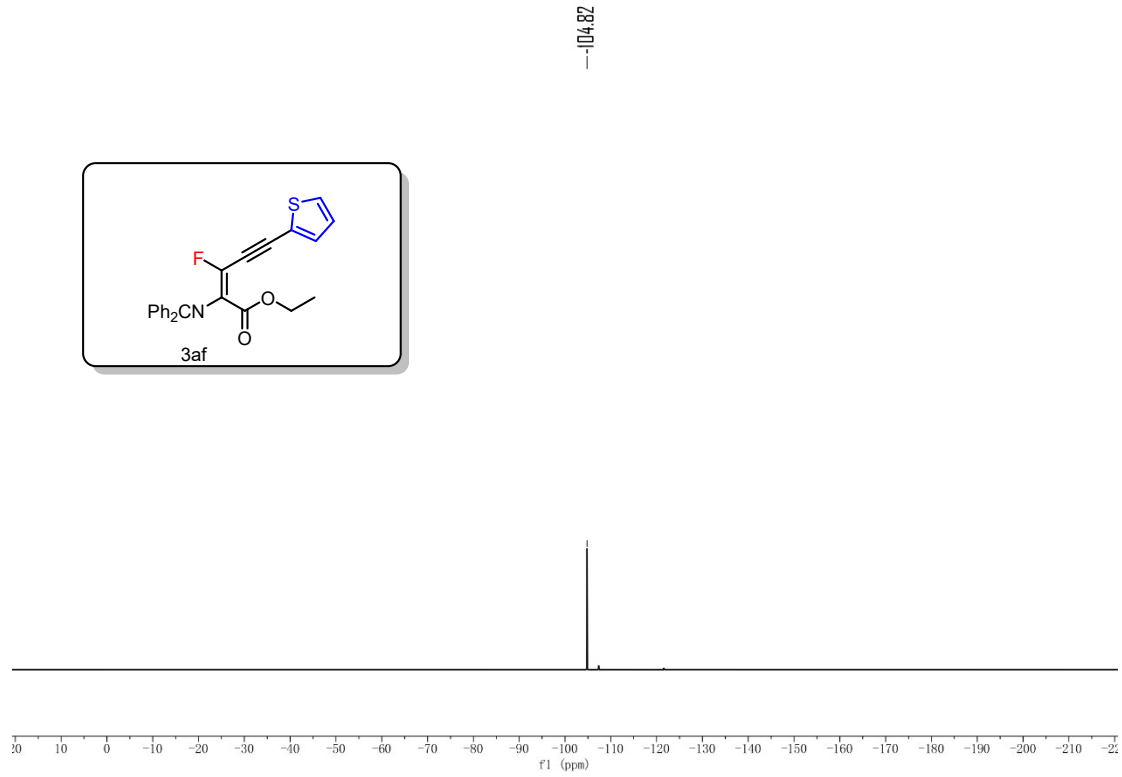
^{1}H NMR of compound 3af (400 MHz, $CDCl_3$)



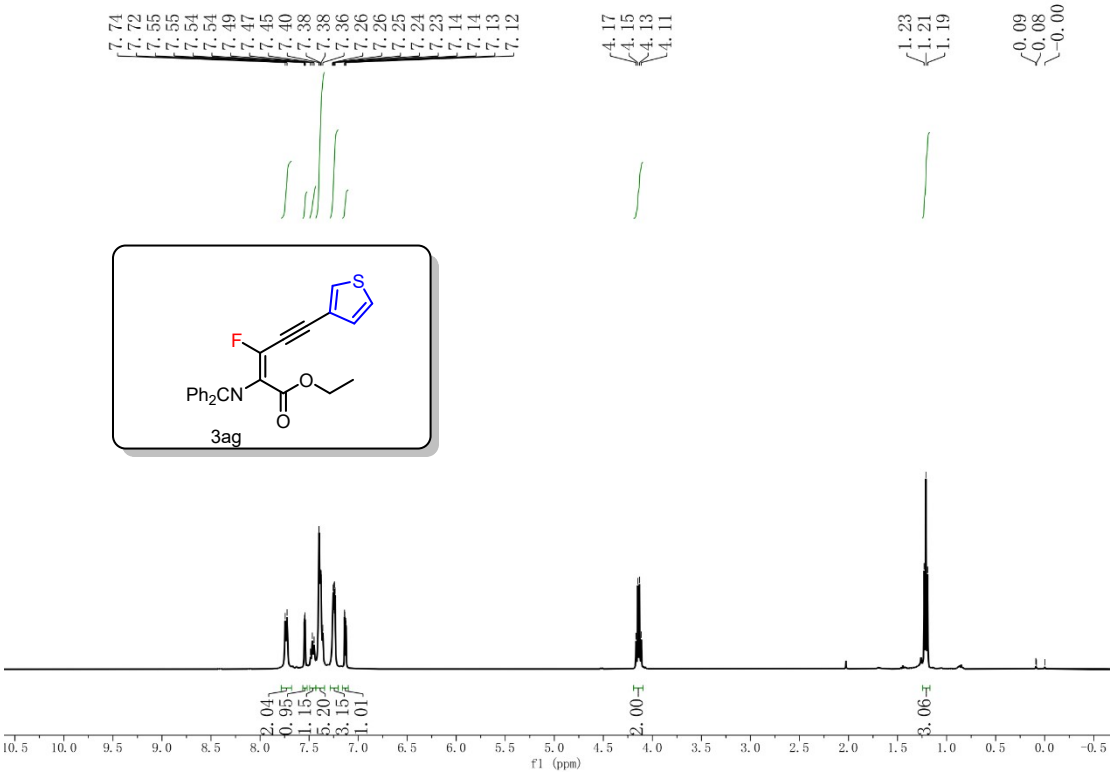
^{13}C NMR of compound 3af (101 MHz, $CDCl_3$)



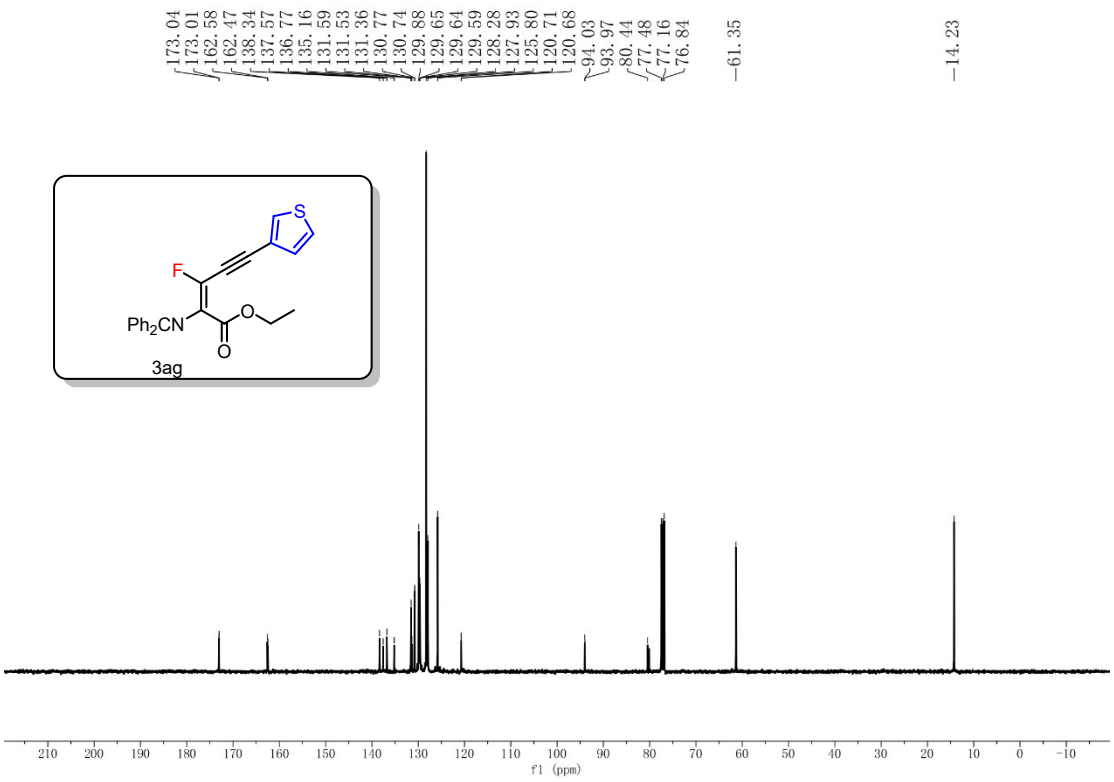
^{19}F NMR of compound 3af (377 MHz, $CDCl_3$)



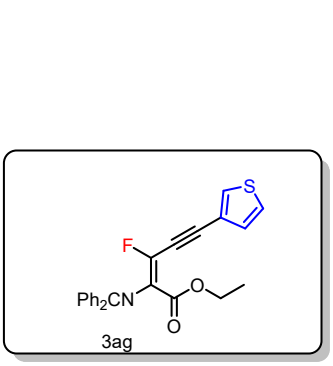
^{1}H NMR of compound 3ag (400 MHz, $CDCl_3$)



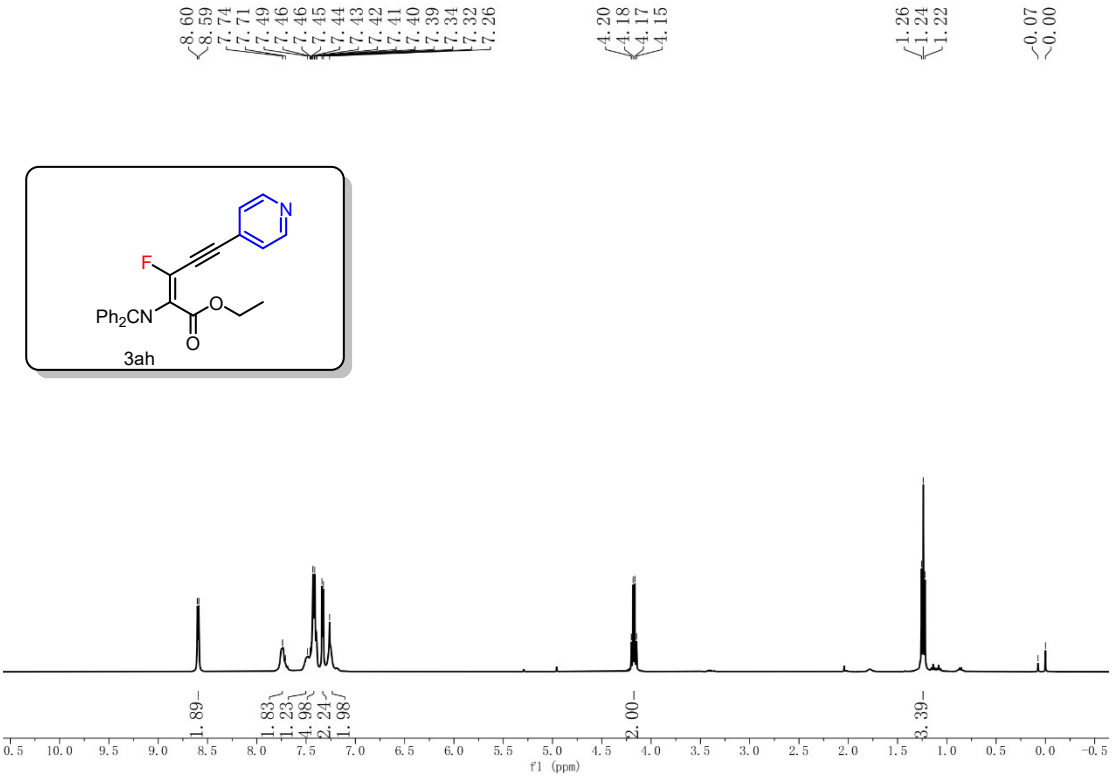
^{13}C NMR of compound 3ag (101 MHz, $CDCl_3$)



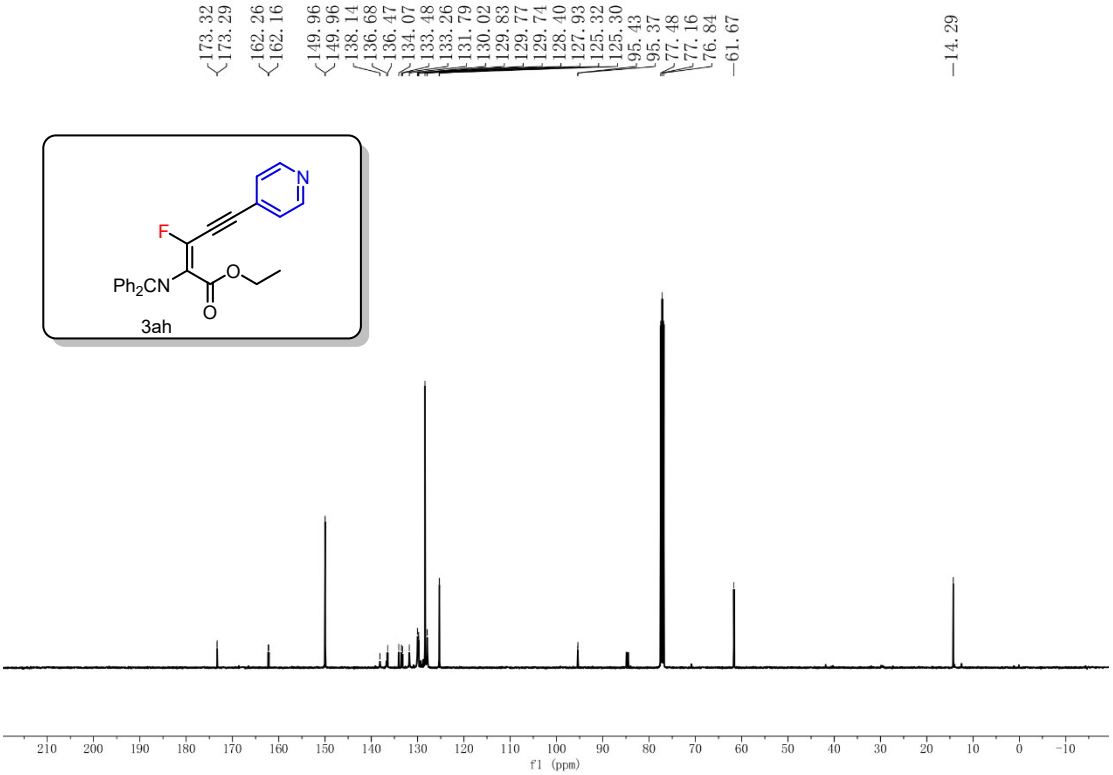
^{19}F NMR of compound 3ag (377 MHz, $CDCl_3$)



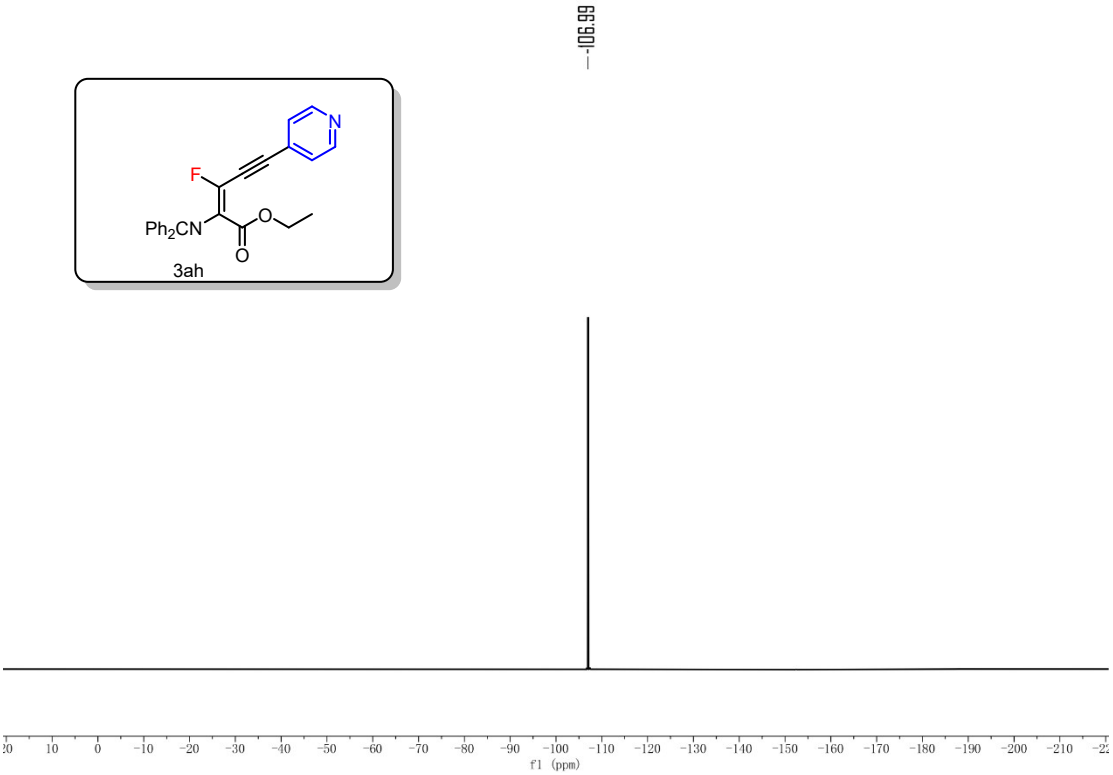
^{1}H NMR of compound 3ah (400 MHz, $CDCl_3$)



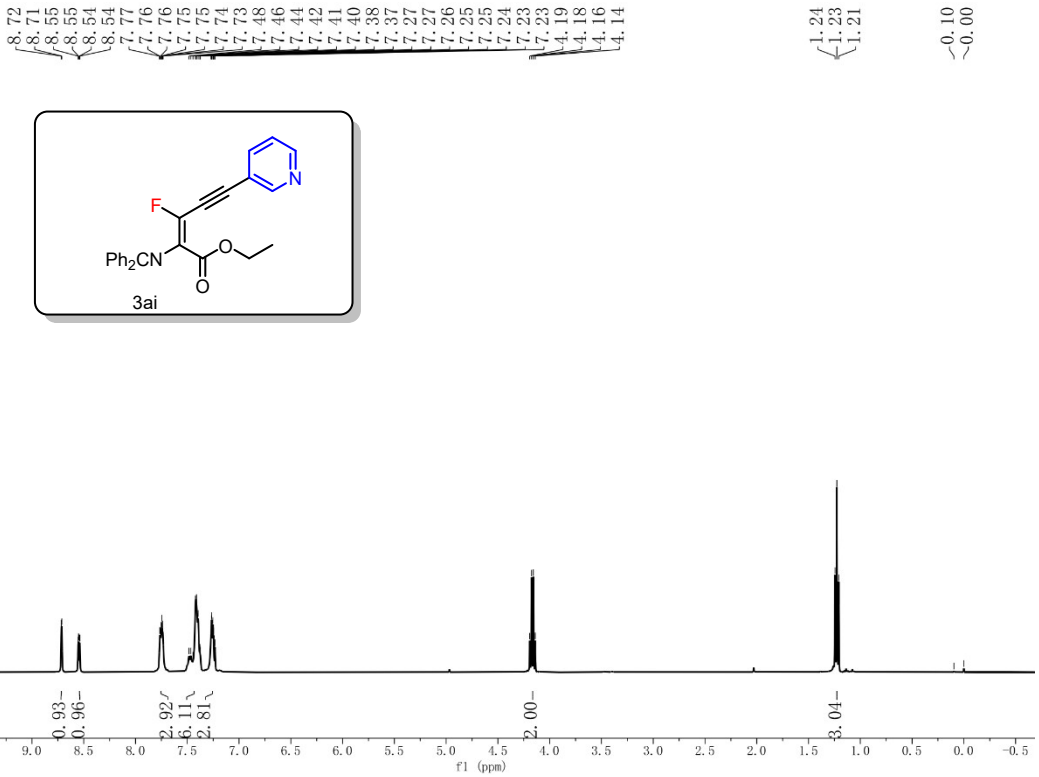
^{13}C NMR of compound 3ah (101 MHz, $CDCl_3$)



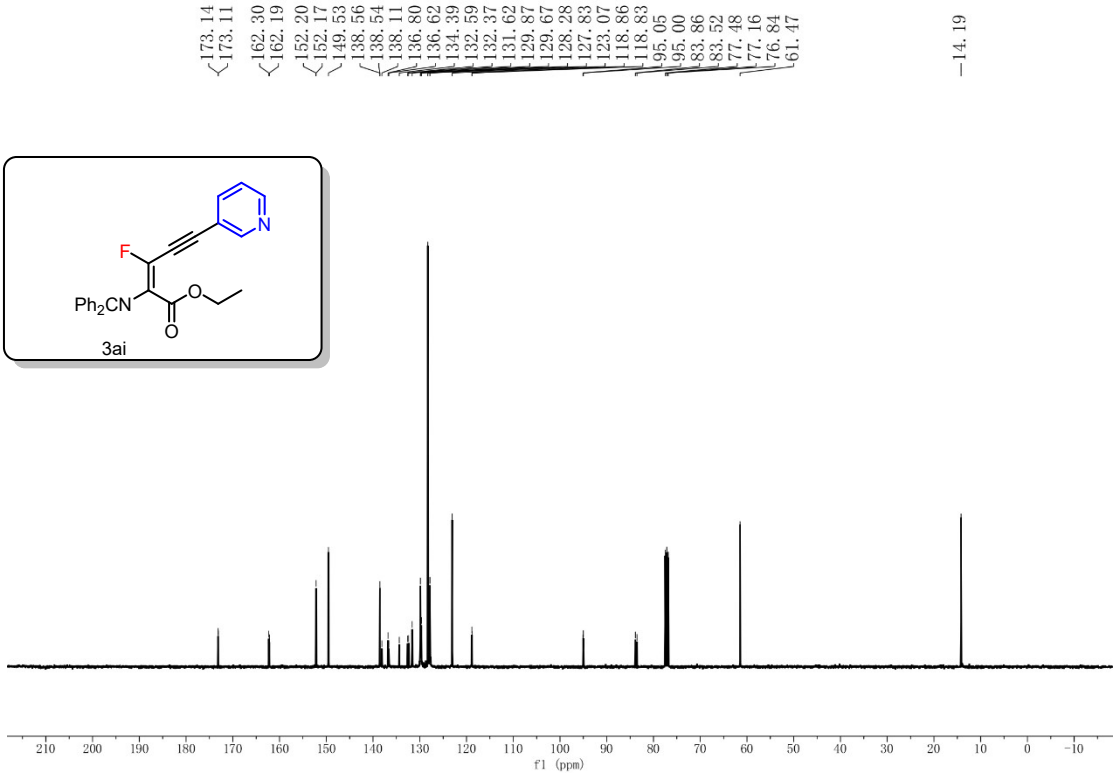
^{19}F NMR of compound 3ah (377 MHz, $CDCl_3$)



^{1}H NMR of compound 3ai (400 MHz, $CDCl_3$)



^{13}C NMR of compound 3ai (101 MHz, $CDCl_3$)



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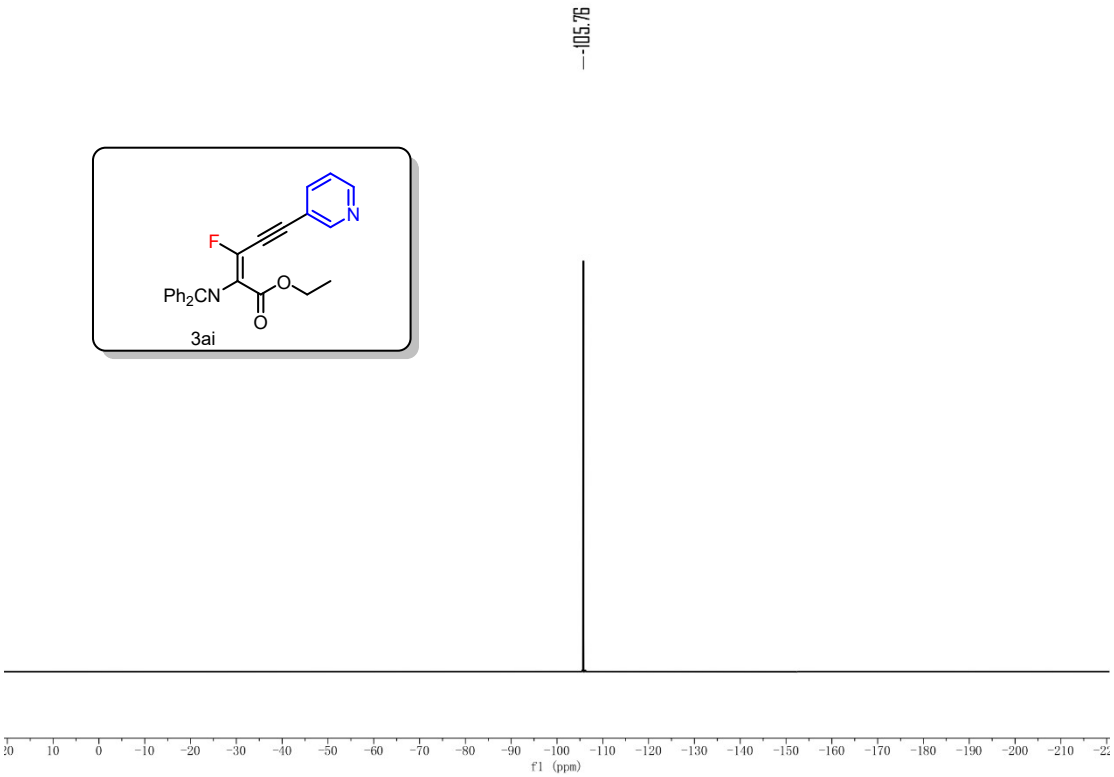

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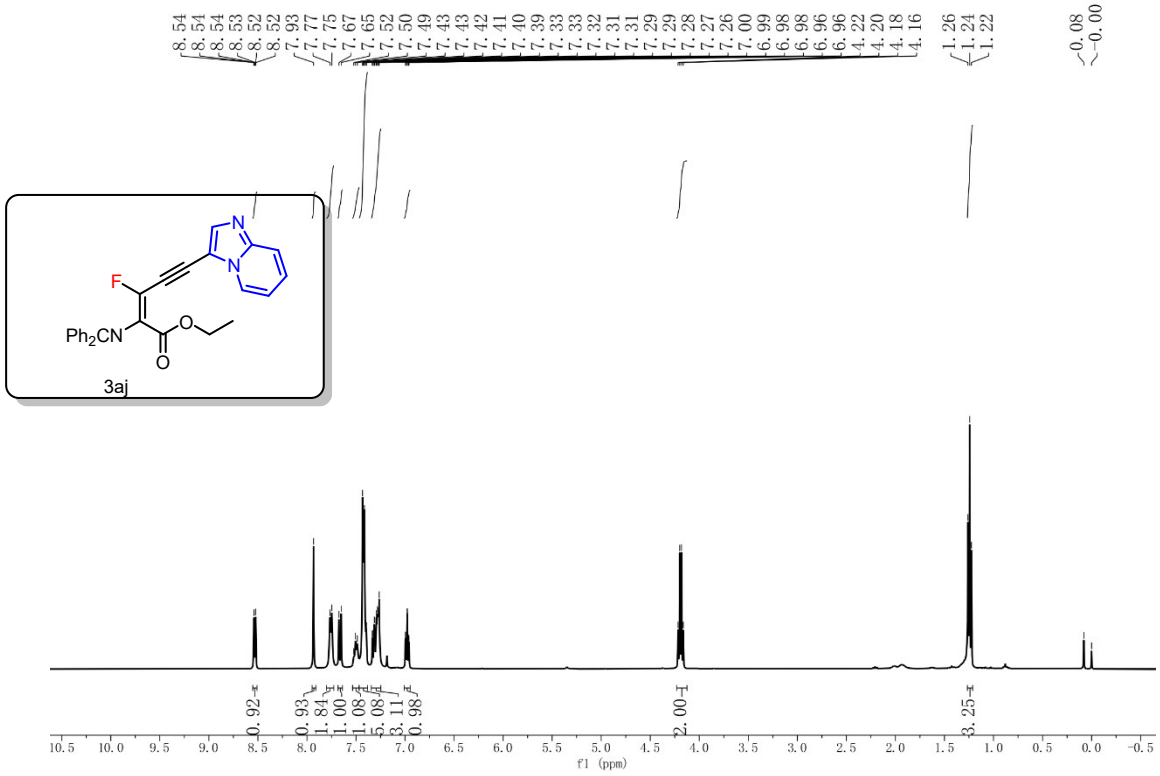
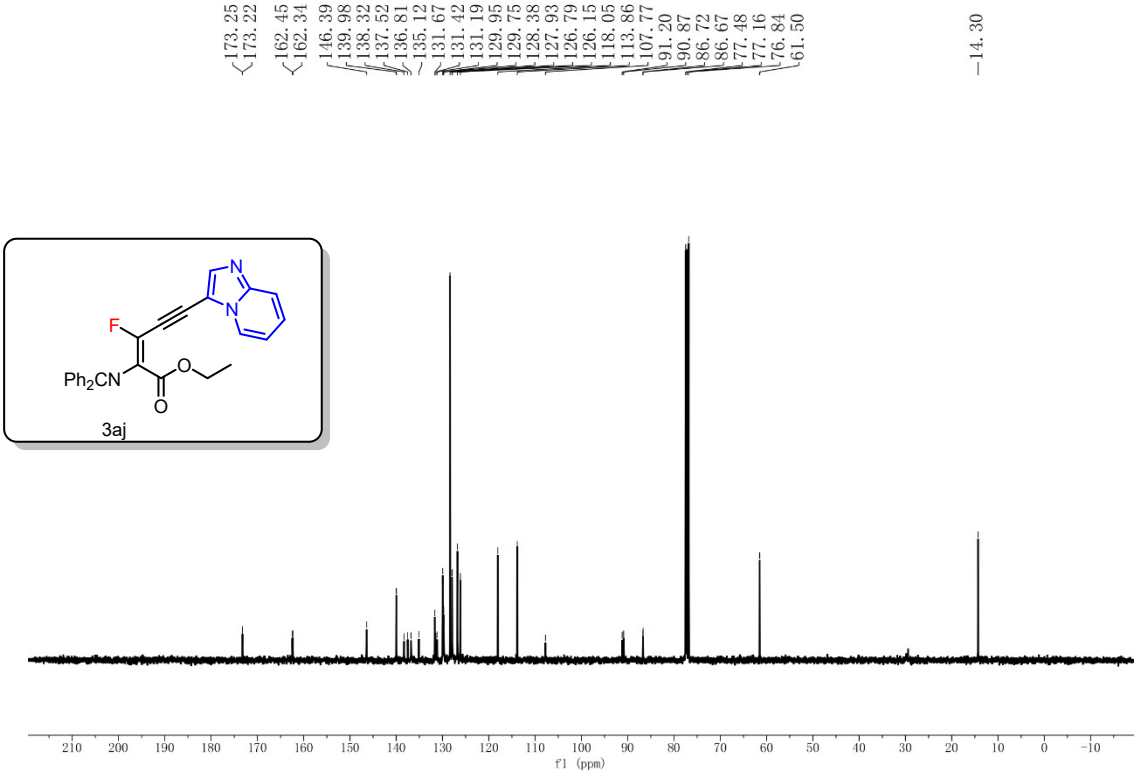
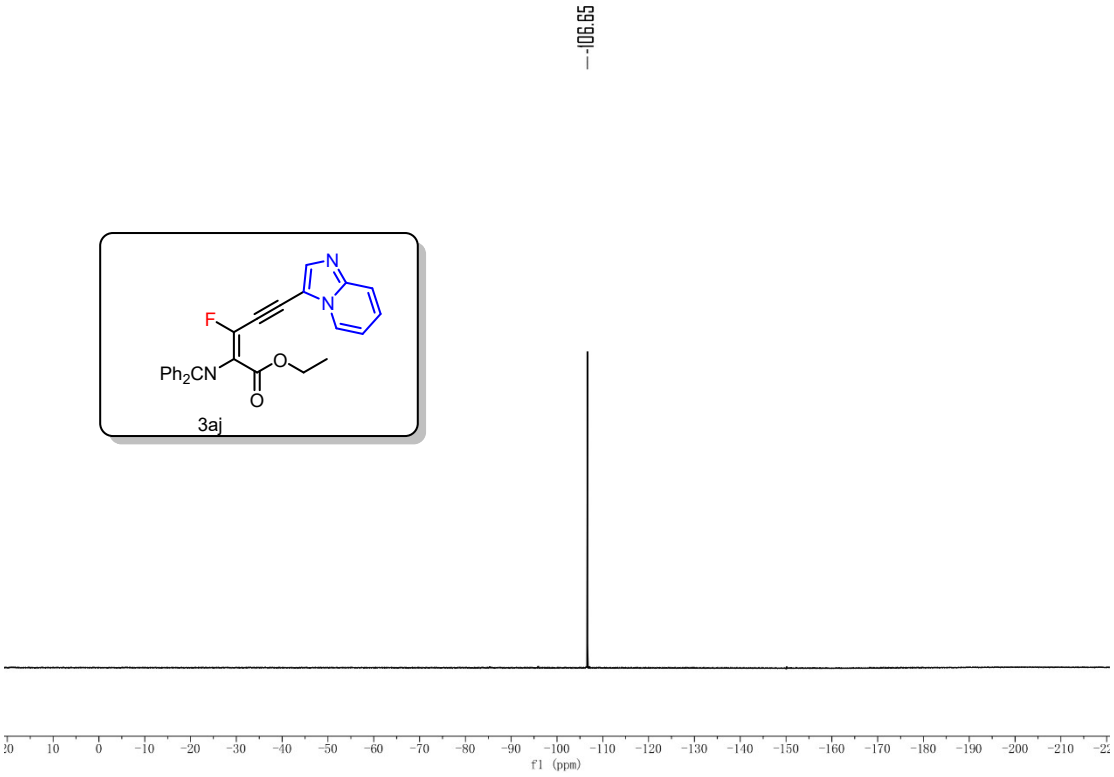


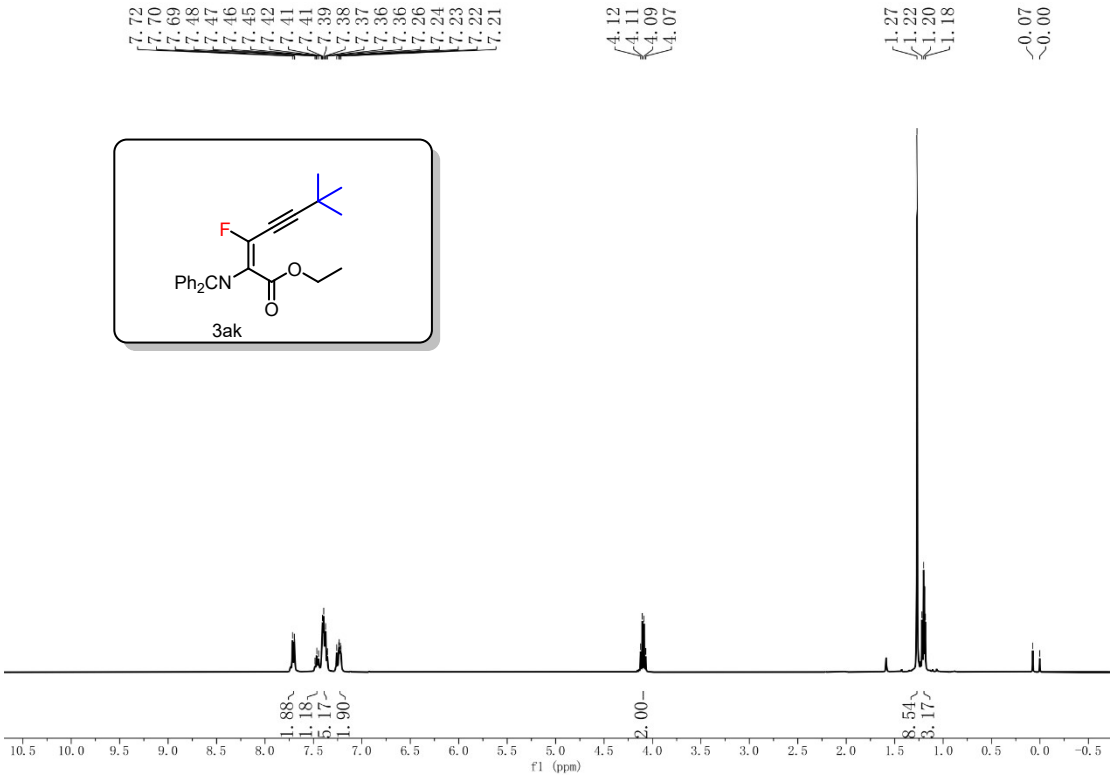
^{13}C NMR of compound 3aj (101 MHz, $CDCl_3$)



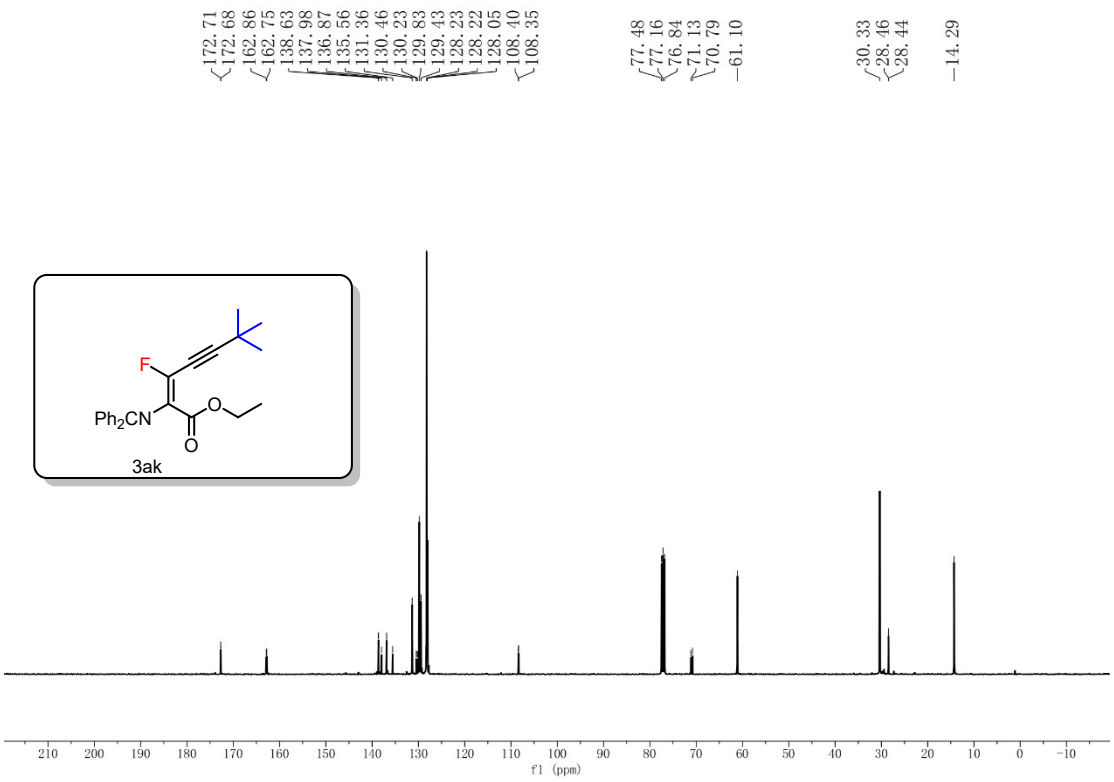
^{19}F NMR of compound 3aj (377 MHz, $CDCl_3$)



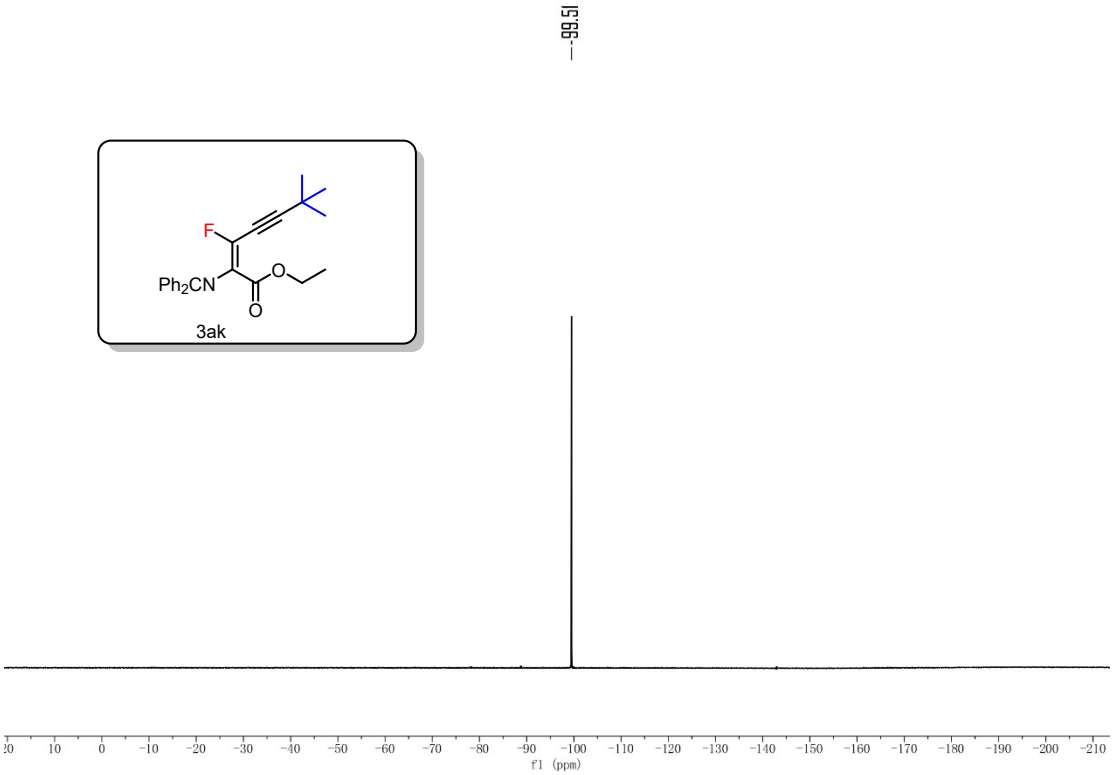
^{1}H NMR of compound 3ak (400 MHz, $CDCl_3$)



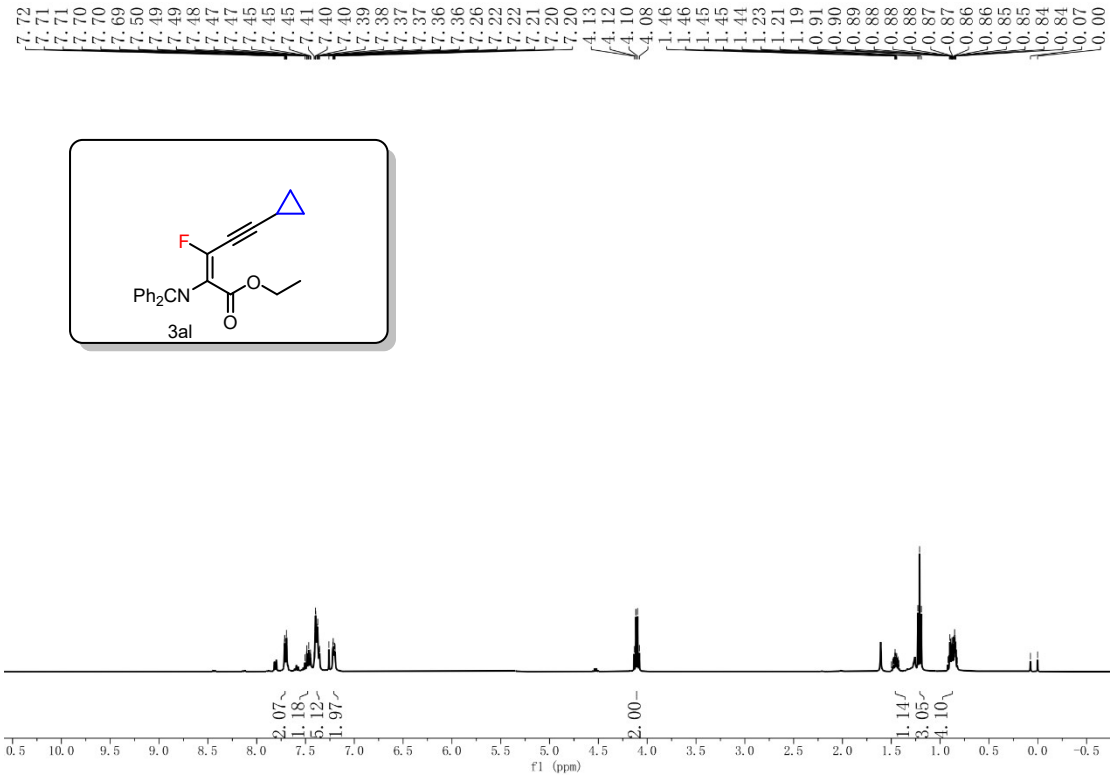
^{13}C NMR of compound 3ak (101 MHz, $CDCl_3$)



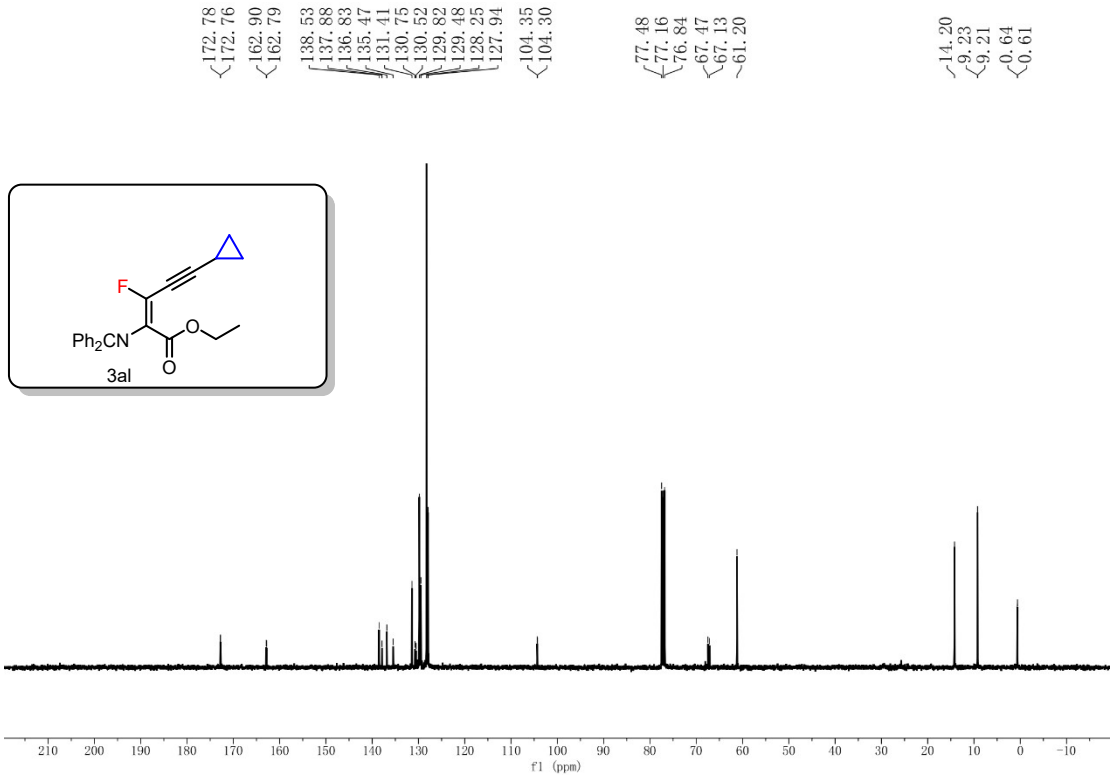
^{19}F NMR of compound 3ak (377 MHz, $CDCl_3$)



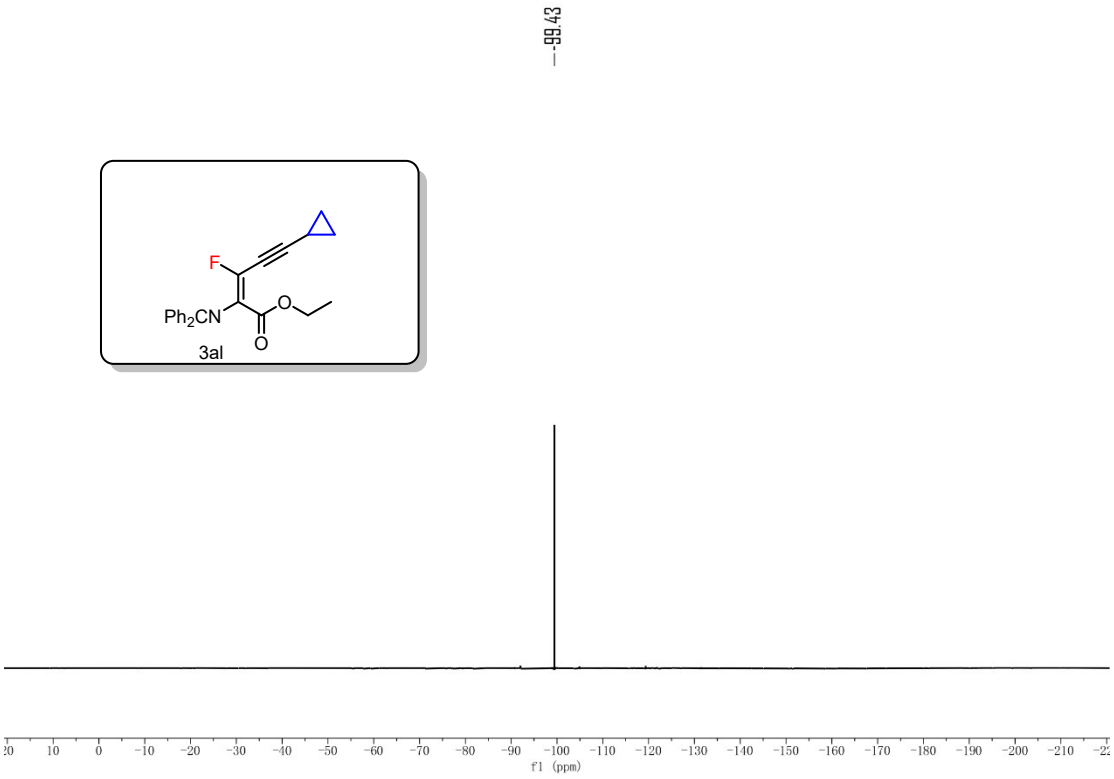
^{1}H NMR of compound 3al (400 MHz, $CDCl_3$)



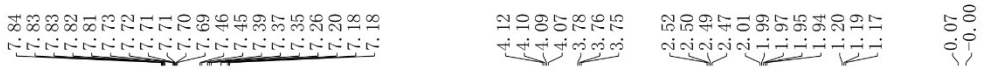
^{13}C NMR of compound 3al (101 MHz, $CDCl_3$)

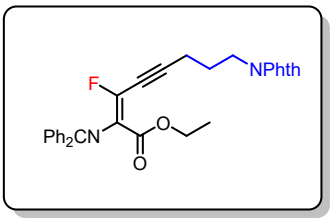


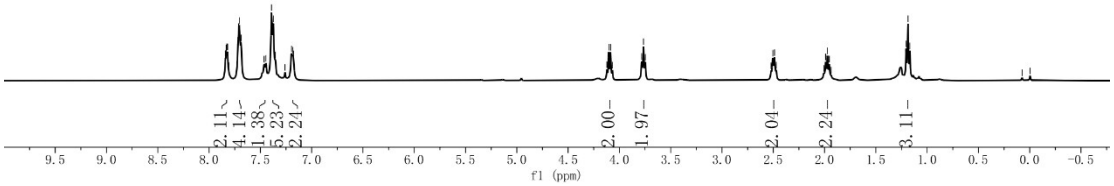
^{19}F NMR of compound 3al (377 MHz, $CDCl_3$)



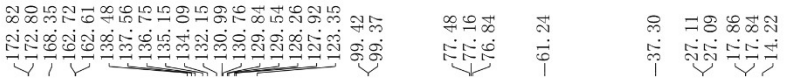
^{1}H NMR of compound 3am (400 MHz, $CDCl_3$)

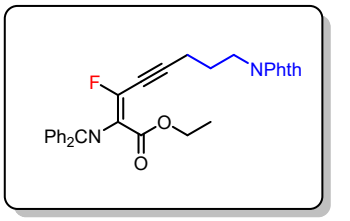


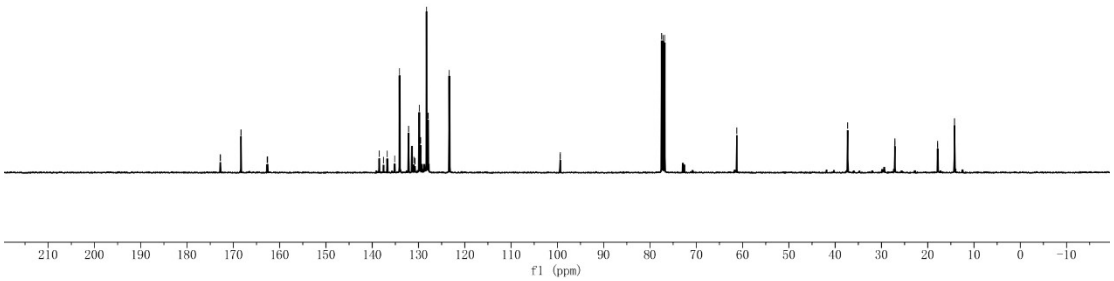




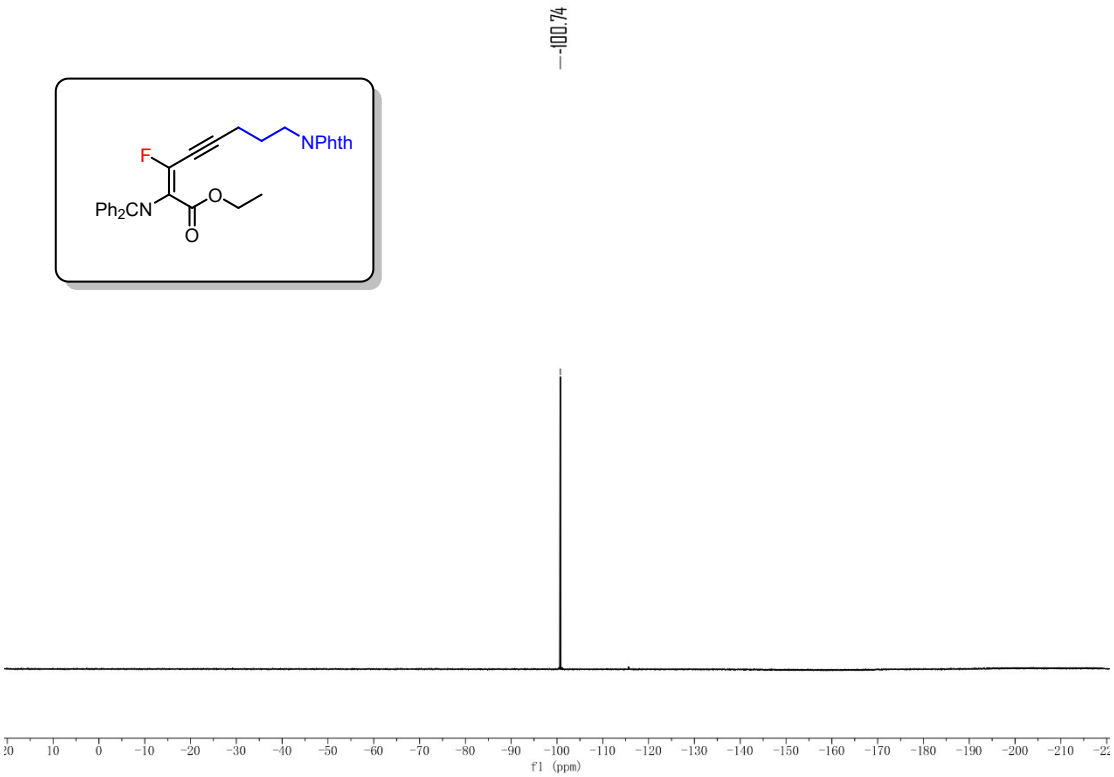
^{13}C NMR of compound 3am (101 MHz, $CDCl_3$)



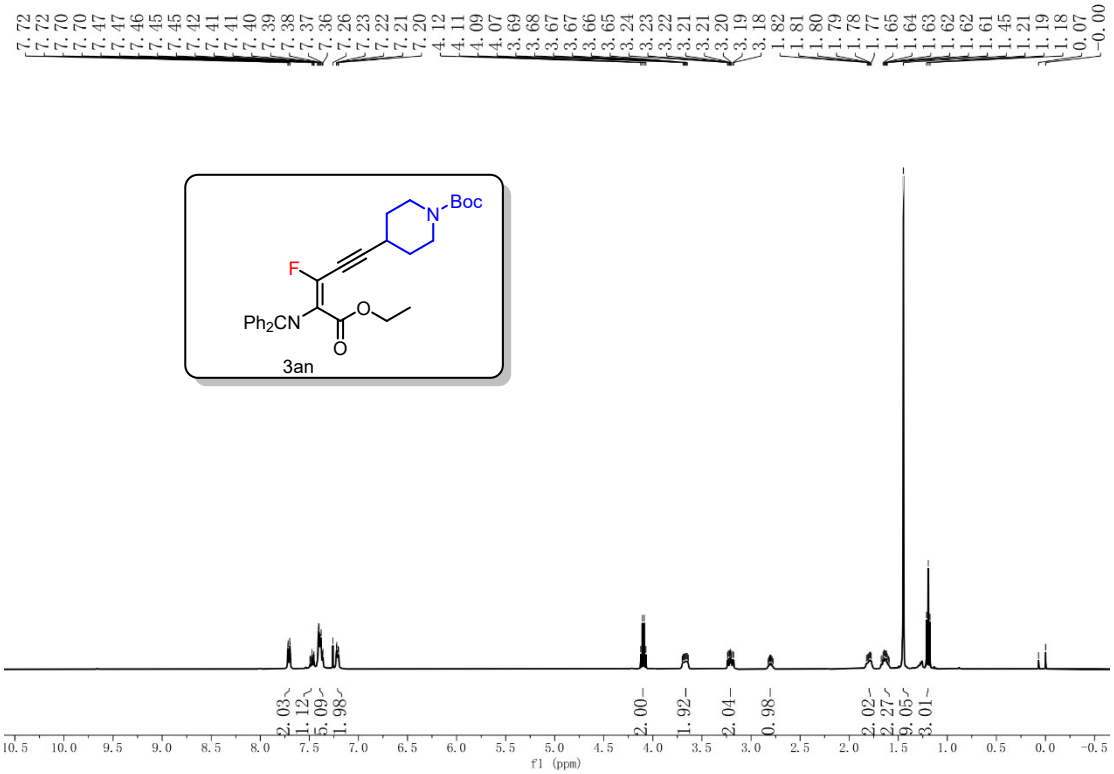




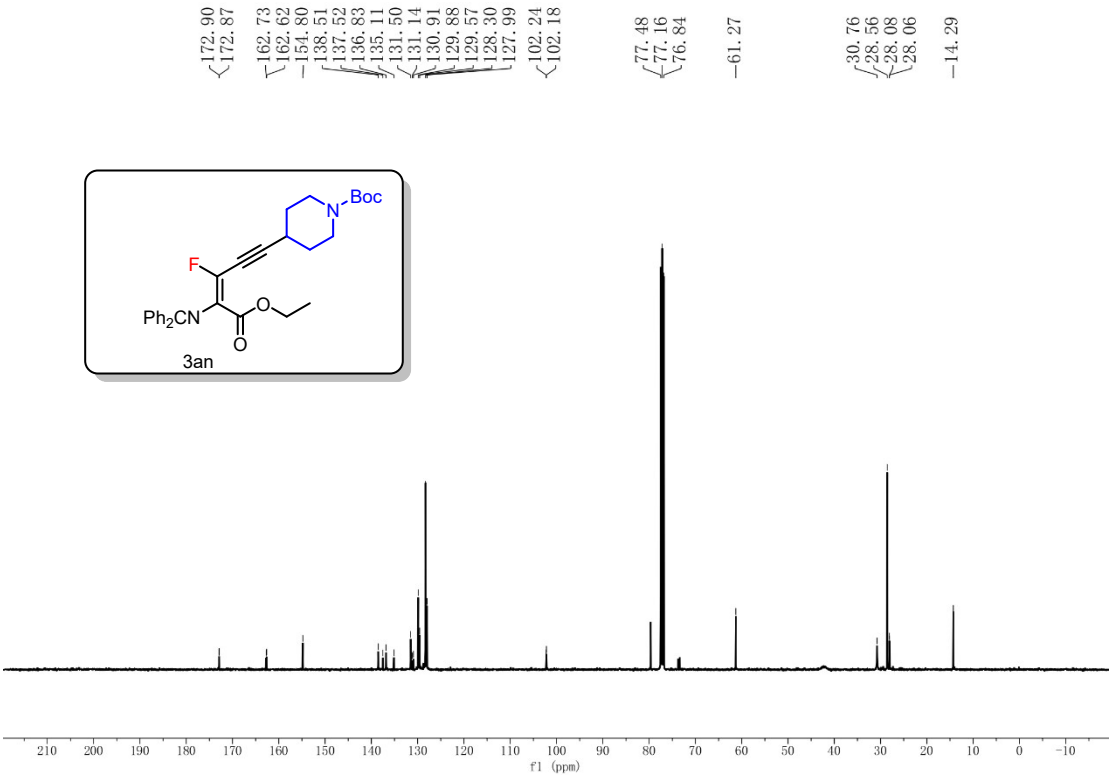
^{19}F NMR of compound 3am (377 MHz, $CDCl_3$)



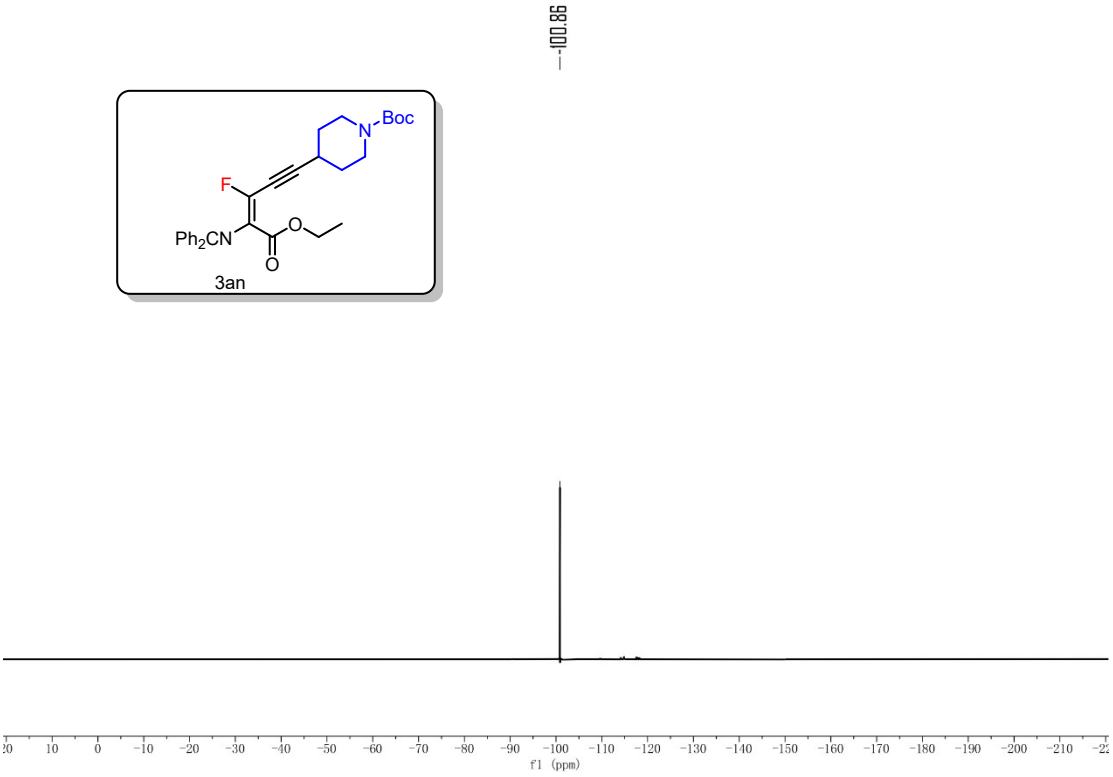
^{1}H NMR of compound 3an (400 MHz, $CDCl_3$)



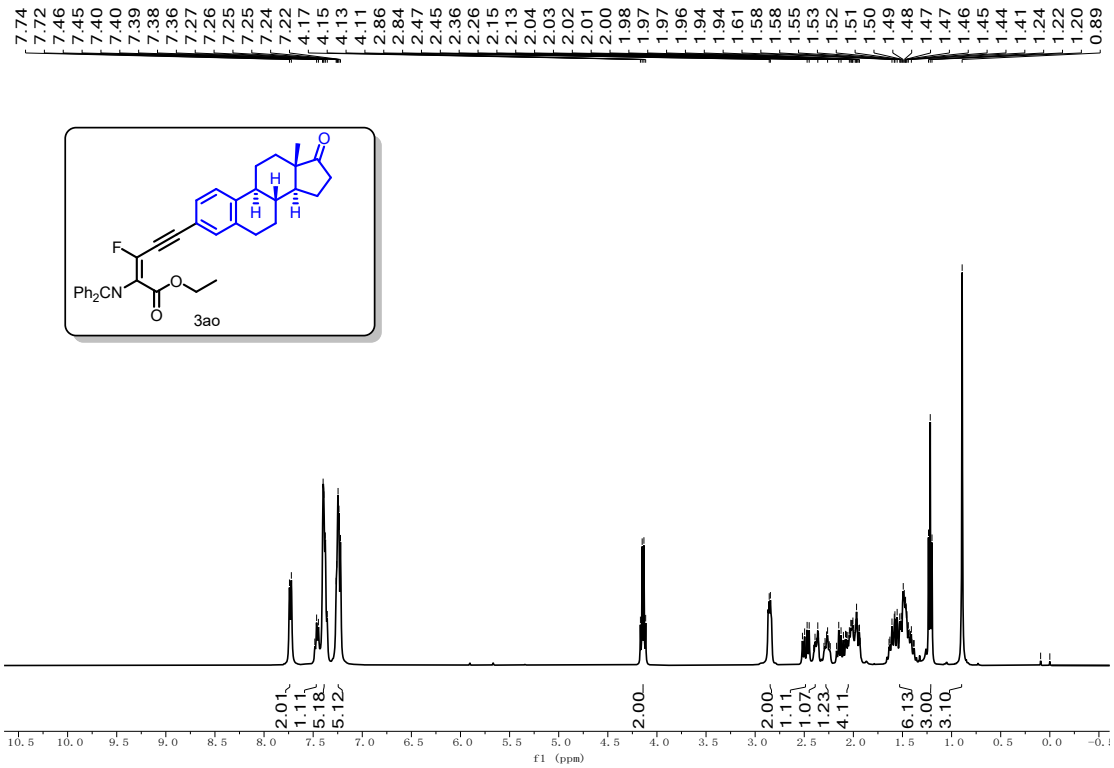
^{13}C NMR of compound 3an (101 MHz, $CDCl_3$)



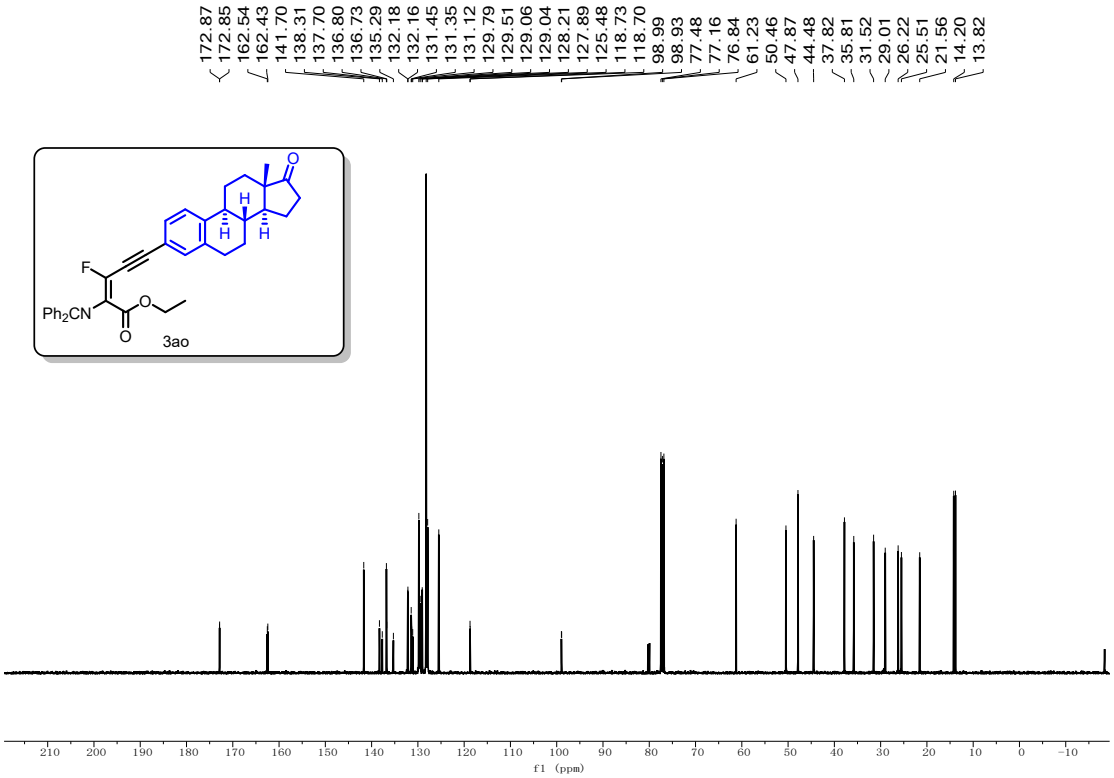
^{19}F NMR of compound 3an (377 MHz, $CDCl_3$)



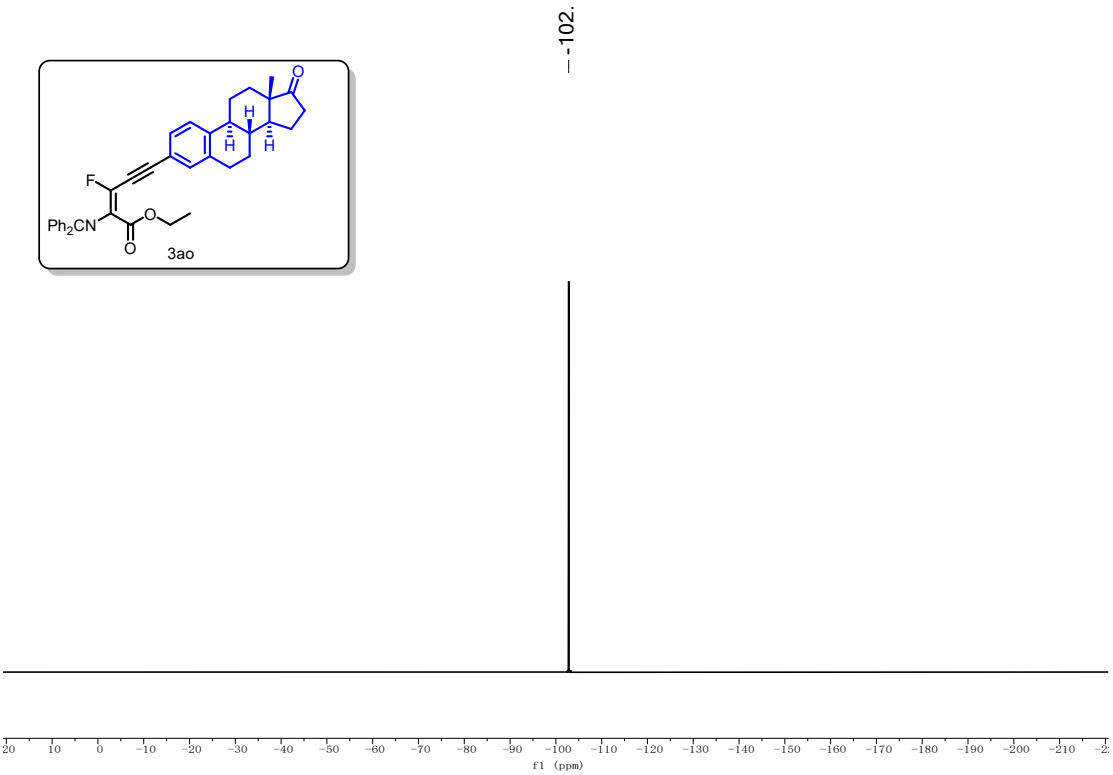
^{1}H NMR of compound 3ao (400 MHz, $CDCl_3$)



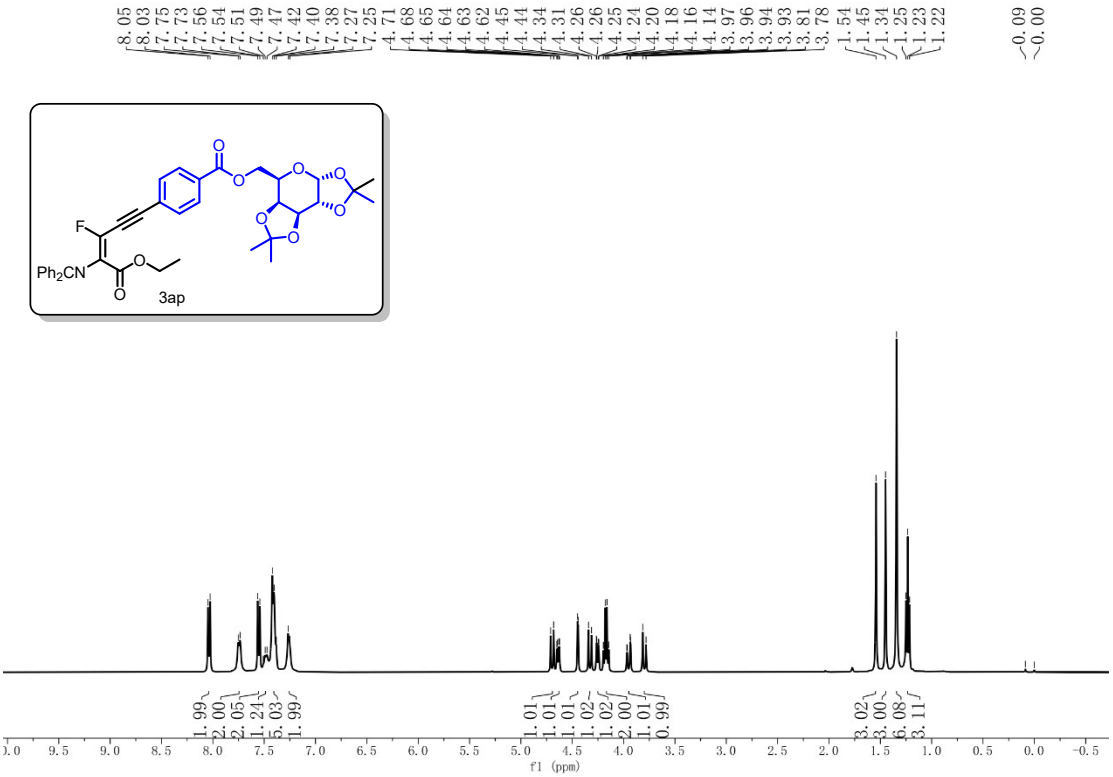
^{13}C NMR of compound 3ao (101 MHz, $CDCl_3$)



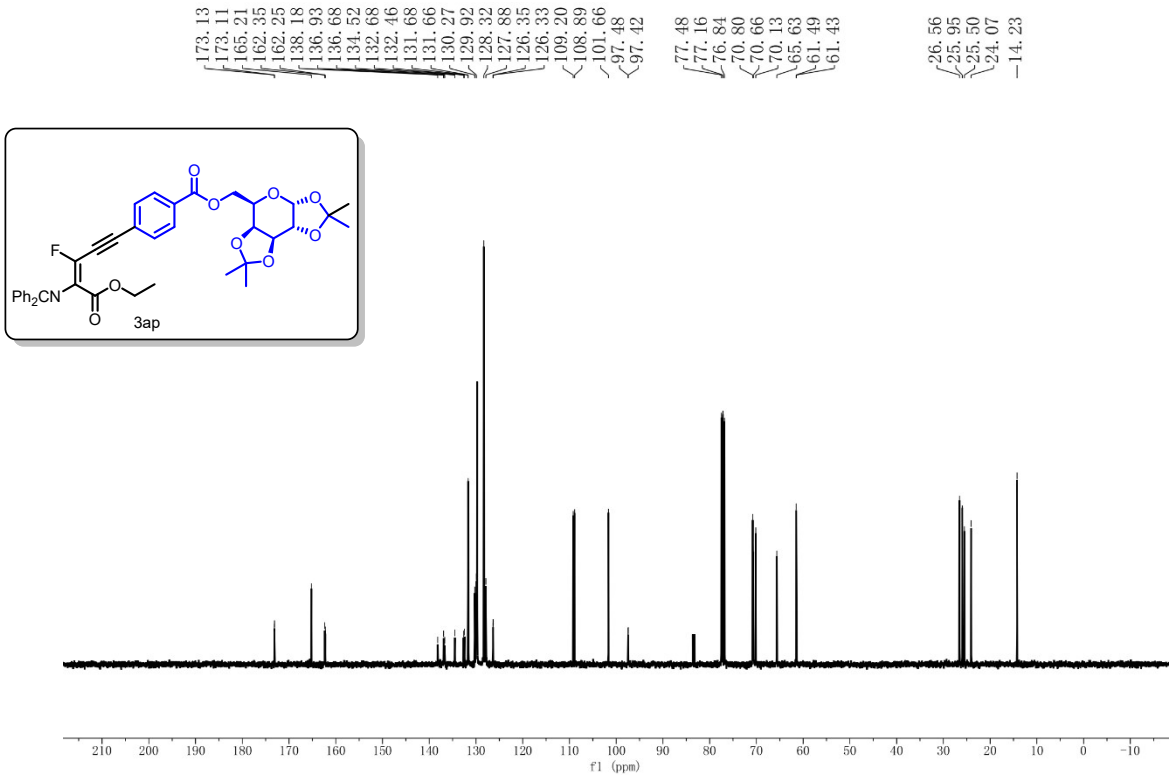
^{19}F NMR of compound 3ao (377 MHz, $CDCl_3$)



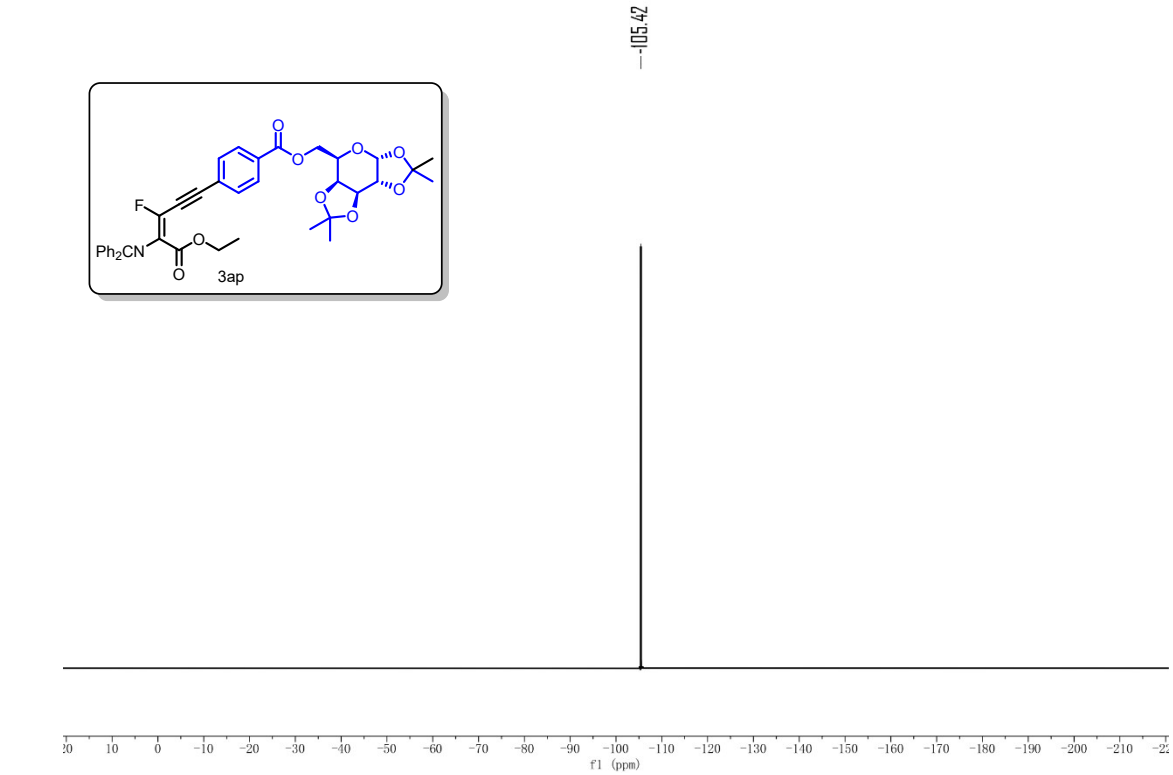
^{1}H NMR of compound 3ap (400 MHz, $CDCl_3$)



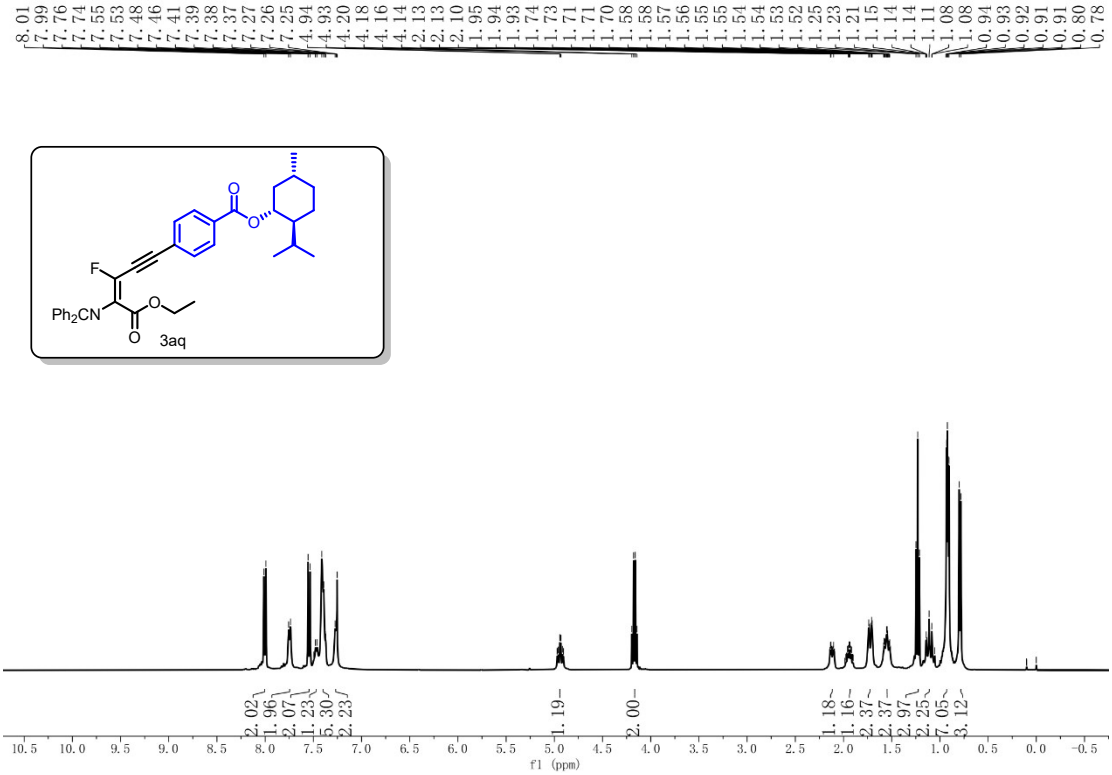
^{13}C NMR of compound 3ap (101 MHz, $CDCl_3$)



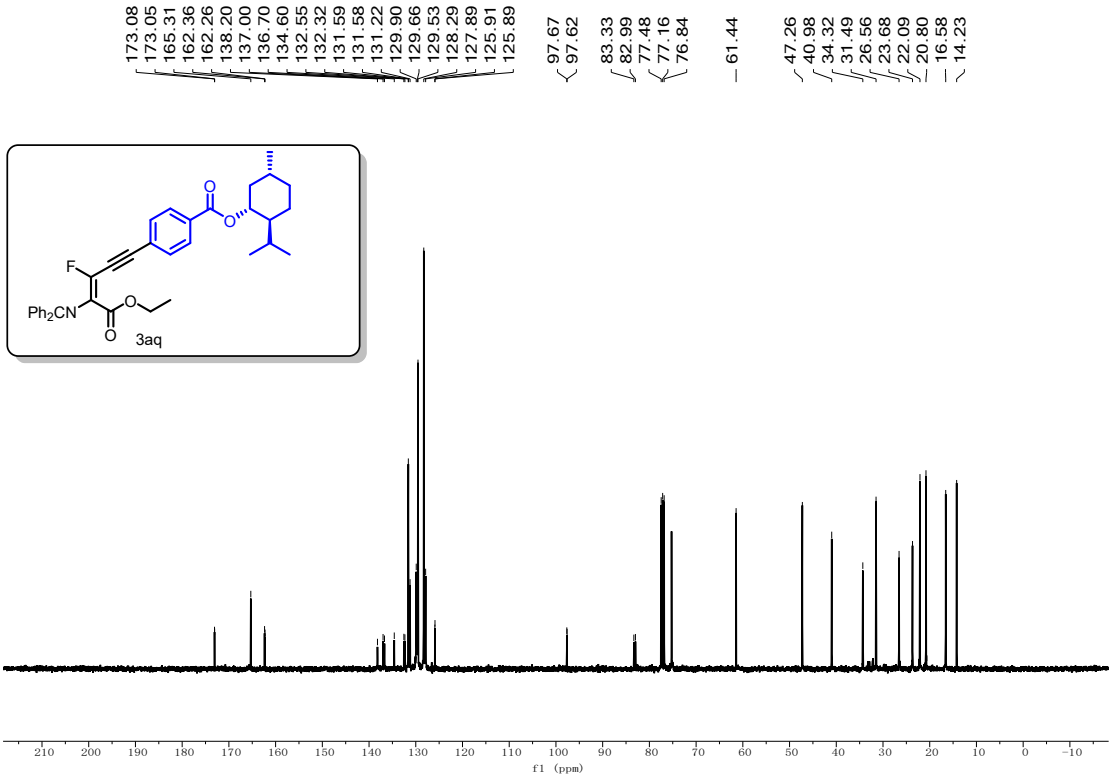
^{19}F NMR of compound 3ap (377 MHz, $CDCl_3$)



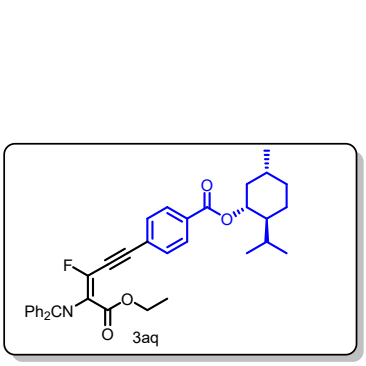
^{1}H NMR of compound 3aq (400 MHz, $CDCl_3$)



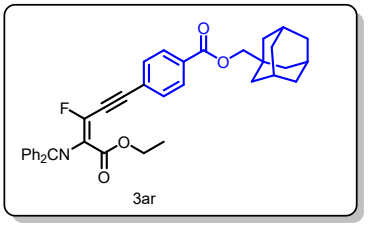
^{13}C NMR of compound 3aq (101 MHz, $CDCl_3$)



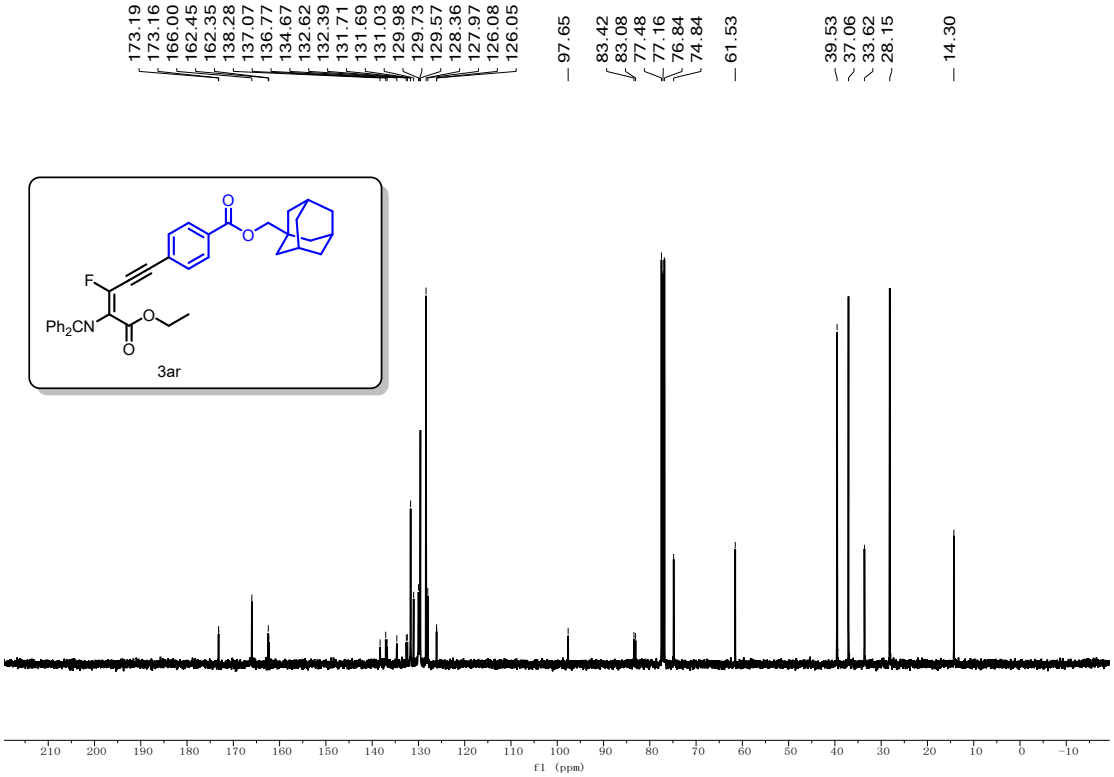
^{19}F NMR of compound 3aq (377 MHz, $CDCl_3$)



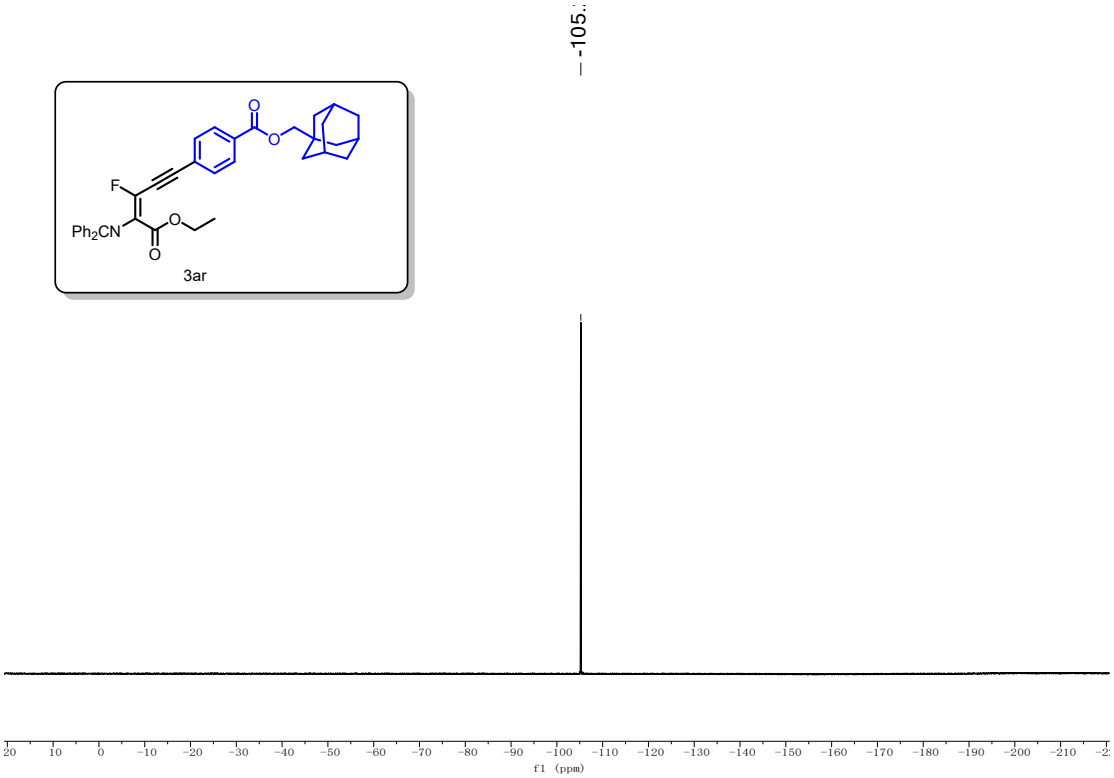
^{1}H NMR of compound 3ar (400 MHz, $CDCl_3$)



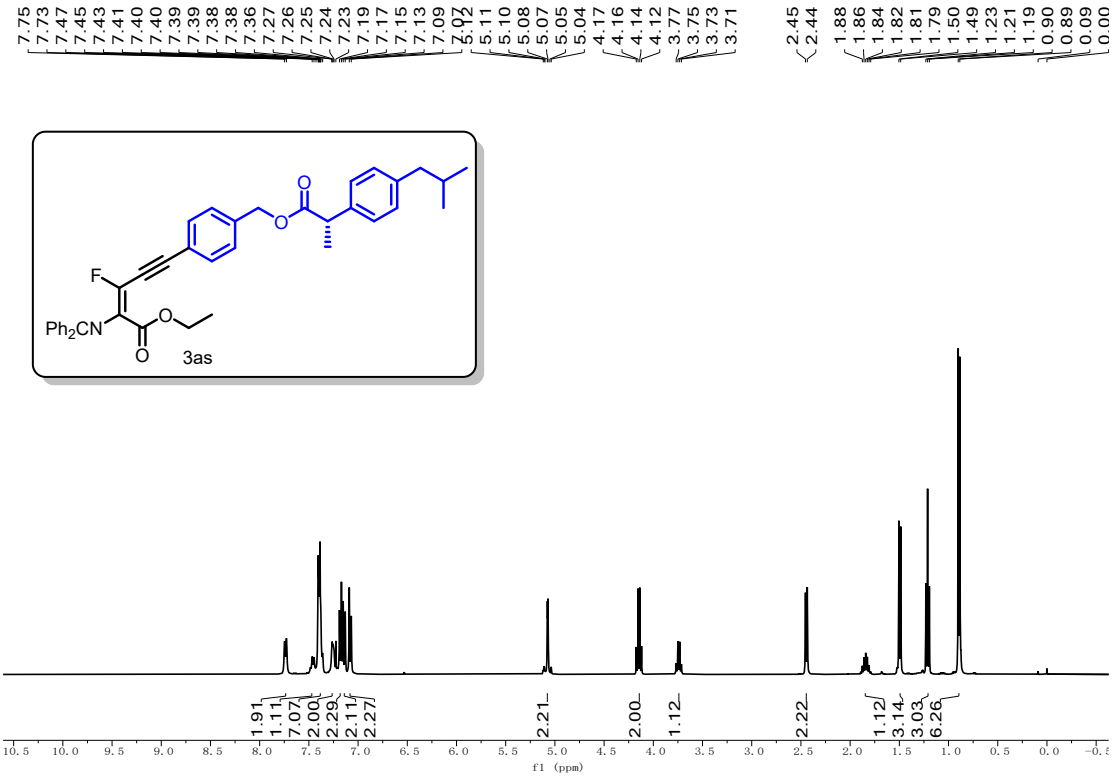
^{13}C NMR of compound 3ar (101 MHz, $CDCl_3$)



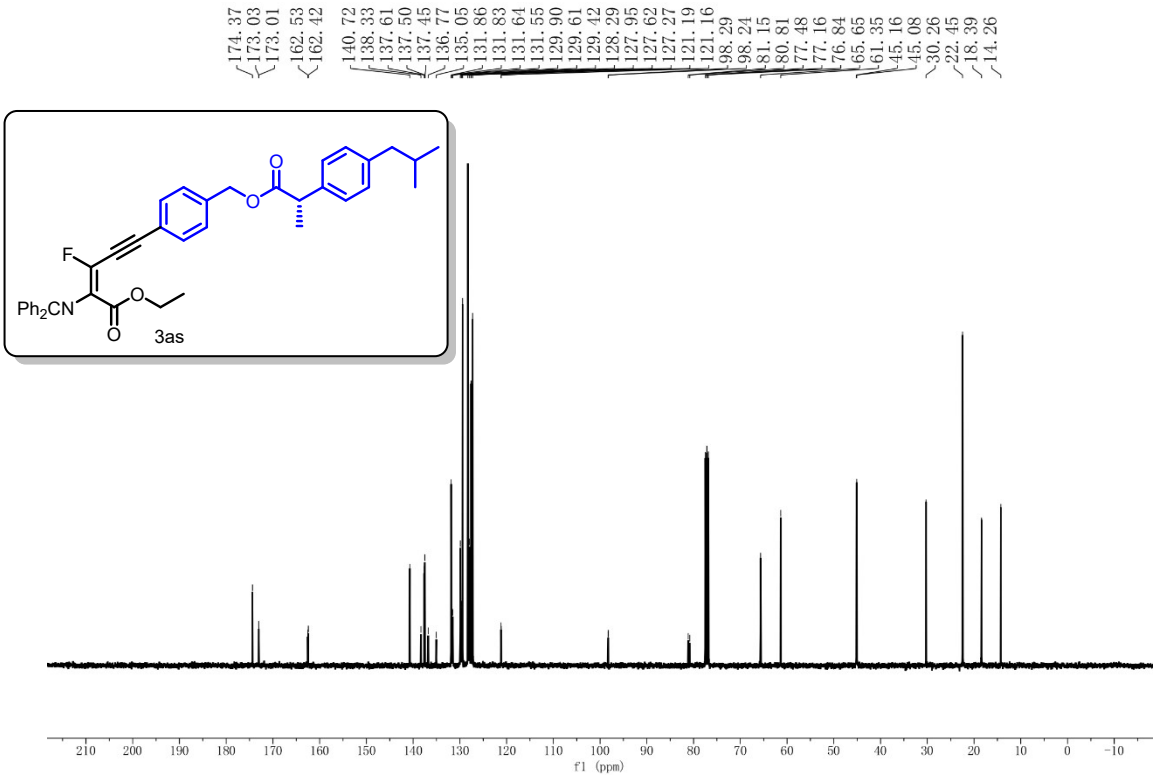
^{19}F NMR of compound 3ar (377 MHz, $CDCl_3$)



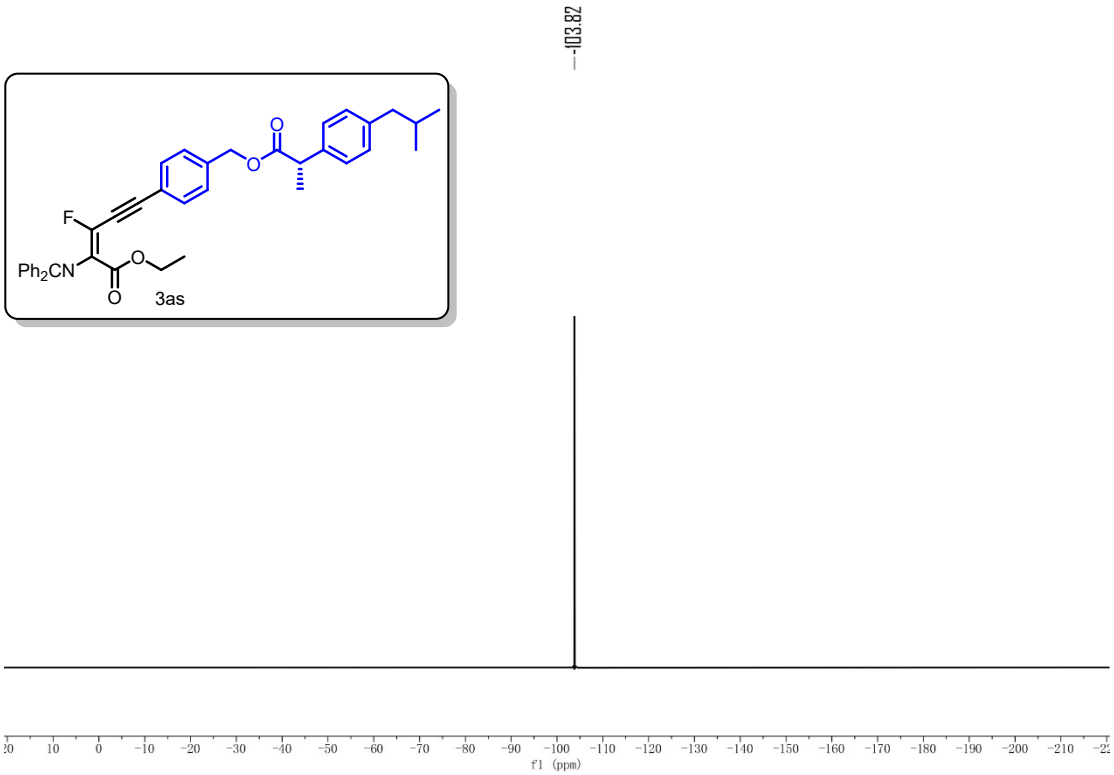
^{1}H NMR of compound 3as (400 MHz, $CDCl_3$)



^{13}C NMR of compound 3as (101 MHz, $CDCl_3$)



^{19}F NMR of compound 3as (377 MHz, $CDCl_3$)



17. Computational Method

All the DFT calculations were carried out in ORCA 5.0.3 package.[1] Molecular geometries were optimized in the gas-phase using M06-L functional,[2] the def2-SVP basis set[3] was used during the geometry optimization. Analytic frequency calculations were performed at the same level of theory to verify optimized structure as either a minimum (no imaginary frequency) or a transition state (only one imaginary frequency). Further single-point energy calculation was calculated using M06-L functional with a larger def2-TZVP basis set,[3] solvation effect was also taken into consideration by SMD solvation model.[4] The calculated 3D structures were visualized with CYLview20 software.[5]

Reference

[1] (a) Neese, F. The ORCA program system. WIREs Comput. Mol. Sci. 2012, 2, 73. (b) Neese, F. Software update: the ORCA program system, version 4.0. WIREs Comput. Mol. Sci. 2018, 8, e1327. (c) Neese, F. Software update: The ORCA program system Version 5.0. WIREs Comput. Mol. Sci. 2022, 12, e1606.

[2] (a) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157−167. (b) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

[3] Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

[4] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

[5] CYLview20; Legault, C. Y. Université de Sherbrooke, 2020 (http://www.cylview.org)

Table S1. Absolute energies table for transition state structures (all energy dates are given in Hartree; E_{el}: absolute electronic energies from high-level solvent phase single-point calculation, G_{coor}: Gibbs energy correction, TS Freq: imaginary frequencies for transition states, unit: cm^{-1}).

species	E_{el}	G_{coor}	TS Freq
Complex	-2511.926694	0.60234	/
TS-Z(major)	-2511.91621	0.602287	-294.20
TS-E(minor)	-2511.911402	0.601536	-282.41

Cartesian coordinates (in Å) of optimized structure

Complex

Pd	2.07215600	1.45061500	0.51633000
P	1.77328000	1.37325500	-1.86503800
C	0.04566400	1.55215500	-2.44472800
C	-0.72959500	0.42072200	-2.73237100
C	-0.56207600	2.81513200	-2.45311000
C	-2.08374700	0.55505800	-3.03356700
H	-0.28229700	-0.57551400	-2.68926600
C	-1.91383000	2.94471900	-2.76133900
H	0.02280500	3.70806900	-2.21369200
C	-2.67791300	1.81515600	-3.05465800
H	-2.67679900	-0.33839600	-3.24462100
H	-2.37420800	3.93560000	-2.76482800
H	-3.73990800	1.91785600	-3.29177200
C	2.64221600	2.81122500	-2.60240500
C	3.28440500	2.78971800	-3.84711600
C	2.66453700	3.99443200	-1.84602500
C	3.91868300	3.93280100	-4.33122600
H	3.30490200	1.87311900	-4.44114500
C	3.28741700	5.13890300	-2.33926400
H	2.19619500	4.00788300	-0.85459700
C	3.91621200	5.10967000	-3.58341900
H	4.42170500	3.90113200	-5.30046900
H	3.29327600	6.05246800	-1.74068400
H	4.41543100	6.00269800	-3.96634100
C	2.39240900	-0.10801000	-2.72355300
C	2.12902200	-0.35865800	-4.07918100
C	3.14314300	-1.03537100	-1.99119100
C	2.63244100	-1.50319500	-4.69245300
H	1.51166700	0.33854700	-4.65370200
C	3.64800500	-2.17887400	-2.60730000
H	3.30770700	-0.87050600	-0.92181900
C	3.39701900	-2.41114600	-3.95831400
H	2.42144000	-1.69101500	-5.74771700
H	4.22792400	-2.89745700	-2.02446700
H	3.78780800	-3.31023900	-4.44039100
C	2.35708800	1.76232000	2.44818500

C	2.45852300	2.03045700	3.64980300
C	2.60579000	2.35632200	5.02423200
C	2.69614500	3.69935200	5.44415100
C	2.61358700	1.35981300	6.02137200
C	2.77858300	4.02334100	6.79247300
H	2.68279000	4.48737100	4.68782100
C	2.69497500	1.69577700	7.36738100
H	2.54093400	0.31246300	5.71881500
C	2.77954300	3.03211700	7.78489500
H	2.84078300	5.07504400	7.08880700
H	2.69198900	0.90112700	8.11987600
C	2.90060200	3.38518900	9.23366200
H	2.40267300	2.64909600	9.87917300
H	3.95461500	3.42144800	9.55331400
H	2.47233400	4.37244400	9.45345300
C	0.18756200	1.82636500	0.80435800
C	-0.88477000	0.98084900	0.66725400
F	-0.06816200	3.10997300	1.05408300
C	-0.62579500	-0.39014100	0.17666600
O	0.48805800	-0.79195900	-0.10827100
O	-1.64259200	-1.25113200	-0.02284500
C	-2.98038400	-1.14985500	0.47814300
H	-2.96839000	-0.80565700	1.52472200
H	-3.54473200	-0.40307100	-0.10002000
C	-3.59268600	-2.51846000	0.36459500
H	-3.03339100	-3.25602900	0.95493500
H	-4.63027000	-2.50485900	0.72265900
H	-3.59696700	-2.85984000	-0.67926200
N	-2.18803200	1.46684100	0.70208600
C	-2.67660600	2.16531100	1.67277300
C	-1.98985300	2.38404500	2.97476900
C	-1.45602700	1.29191700	3.67254600
C	-1.84935800	3.66731500	3.52086400
C	-0.81004100	1.47564200	4.89077900
H	-1.54985800	0.28663200	3.25290100
C	-1.18505900	3.85266300	4.73091300
H	-2.24905400	4.52758100	2.97639100
C	-0.66950800	2.75689900	5.42235900
H	-0.39731600	0.61554600	5.42309300
H	-1.06449800	4.86034700	5.13610300
H	-0.13735400	2.90078100	6.36637400
C	-4.04153400	2.70917800	1.48430000
C	-4.58929300	2.77448000	0.19036100
C	-4.82920800	3.13600200	2.56626400

C	-5.87754700	3.25247600	-0.01322500
H	-3.96916400	2.44318200	-0.64531700
C	-6.12230800	3.61239500	2.35948800
H	-4.43126300	3.07779200	3.58184200
C	-6.65038700	3.67564700	1.07118100
H	-6.28508400	3.30279700	-1.02619000
H	-6.72305400	3.93326300	3.21365000
H	-7.66230300	4.05503100	0.91046700

TS-Z(major)

Pd	2.21121100	1.17229300	0.37504200
P	1.90288700	1.28337100	-1.97549300
C	0.13287200	1.09204800	-2.38703000
C	-0.46362500	-0.16244000	-2.18591400
C	-0.66497600	2.17496900	-2.77706900
C	-1.83137800	-0.32980300	-2.38233000
H	0.14230500	-1.00936500	-1.85216400
C	-2.03365900	1.99895900	-2.98129500
H	-0.21944000	3.16234700	-2.92528400
C	-2.61840800	0.74918900	-2.78612500
H	-2.28317500	-1.30875200	-2.20606600
H	-2.64752000	2.85044200	-3.28576100
H	-3.69307700	0.61757700	-2.93712700
C	2.34508500	2.91427000	-2.67993300
C	2.55207500	3.10394000	-4.05308600
C	2.43693100	4.01162100	-1.81329600
C	2.84075500	4.37283600	-4.54990700
H	2.48897500	2.25344900	-4.73853500
C	2.71899200	5.28161900	-2.31517900
H	2.28430600	3.86030200	-0.73898800
C	2.92200500	5.46316500	-3.68236900
H	3.00415900	4.51180200	-5.62112500
H	2.78638000	6.13123000	-1.63205700
H	3.14961500	6.45713500	-4.07461100
C	2.75791200	0.08994600	-3.06791300
C	2.17563600	-0.45009700	-4.22283100
C	4.06880900	-0.27713700	-2.73242800
C	2.89484600	-1.33489800	-5.02498900
H	1.15156200	-0.17969700	-4.49549500
C	4.78836500	-1.15496800	-3.53921000
H	4.53079300	0.12811000	-1.82625800
C	4.20093800	-1.68714900	-4.68676700
H	2.42971200	-1.75217400	-5.92111200
H	5.80851300	-1.43236200	-3.26498000
H	4.76058200	-2.38302100	-5.31587000

C	2.11694300	1.39501900	2.33412000
C	2.15051700	1.50044500	3.56564300
C	2.23401100	1.58658400	4.97733600
C	2.61026600	2.78590800	5.61652200
C	1.90106600	0.48422400	5.79181300
C	2.64060000	2.87457600	7.00200400
H	2.86044500	3.65358800	5.00209900
C	1.93405600	0.58705800	7.17675000
H	1.60483800	-0.45279400	5.31482900
C	2.30392100	1.78092600	7.81370900
H	2.92989200	3.81921300	7.47279600
H	1.66446500	-0.28126900	7.78546000
C	2.36965100	1.87420200	9.30500100
H	1.64989200	1.20198300	9.79096100
H	3.36636000	1.59342700	9.68180000
H	2.17533400	2.89444800	9.66205000
C	0.46483100	1.78626000	1.05996700
C	-0.67755000	1.01312000	1.09159800
F	0.31500800	3.11097300	1.07081400
C	-0.51902900	-0.45007000	0.91457900
O	0.54734200	-0.98566900	0.68389800
O	-1.60313200	-1.25322200	0.96974700
C	-2.85320900	-0.95410400	1.59707600
H	-2.69104000	-0.32580400	2.48778900
H	-3.48929400	-0.37666600	0.90852300
C	-3.48782400	-2.26601600	1.96958100
H	-2.85949200	-2.82751600	2.67341800
H	-4.46703000	-2.09980100	2.43739800
H	-3.63753300	-2.89441400	1.08151800
N	-1.94511000	1.55494700	0.98687200
C	-2.42950200	2.55070500	1.65309500
C	-1.79033700	3.18061800	2.83837000
C	-1.28755900	2.38277100	3.87547500
C	-1.70076900	4.57540100	2.95698400
C	-0.74034100	2.96520400	5.01574400
H	-1.33741000	1.29280000	3.79316300
C	-1.11957700	5.15662700	4.08016500
H	-2.08091700	5.20597400	2.14843800
C	-0.64617500	4.35252300	5.11733000
H	-0.37418800	2.33197400	5.82700100
H	-1.04160200	6.24429700	4.14964700
H	-0.19916200	4.80432200	6.00634000
C	-3.77484800	3.02347400	1.24540200
C	-4.26411100	2.68974800	-0.03018600

C	-4.60389900	3.76733100	2.10223000
C	-5.53034700	3.09061300	-0.43693200
H	-3.61562800	2.10998600	-0.68929500
C	-5.87565700	4.16480600	1.69366900
H	-4.25881900	4.02083400	3.10710200
C	-6.34315600	3.83338700	0.42300300
H	-5.88841500	2.82768300	-1.43615500
H	-6.50829400	4.73533700	2.37774000
H	-7.33792000	4.15225400	0.10281300

TS-E(minor)

Pd	-0.28745600	0.30973000	-1.25104500
P	1.14908900	2.09503100	-1.93744800
C	0.43688300	3.58320400	-2.72849400
C	-0.15121700	3.44189700	-3.99656600
C	0.39051400	4.83202900	-2.09590200
C	-0.75063400	4.52943100	-4.62428300
H	-0.12951500	2.47013400	-4.50068700
C	-0.22008100	5.91794500	-2.72451600
H	0.83606200	4.96024100	-1.10592800
C	-0.78775900	5.77186900	-3.98819700
H	-1.19575000	4.40615600	-5.61424500
H	-0.24777700	6.88674700	-2.22032000
H	-1.26247600	6.62454200	-4.47877200
C	1.99647900	2.72844200	-0.44493800
C	3.17557400	3.48160800	-0.53880700
C	1.45089600	2.45616500	0.81680100
C	3.79352100	3.96297000	0.61232700
H	3.61582100	3.68830000	-1.51935500
C	2.07262800	2.94192000	1.96742200
H	0.54440300	1.84351800	0.90116100
C	3.24202100	3.69327400	1.86629600
H	4.71391600	4.54595600	0.53126300
H	1.64091300	2.72165100	2.94749000
H	3.73178100	4.06567100	2.76928400
C	2.52175300	1.61661200	-3.04922000
C	3.07342900	2.47739200	-4.00773100
C	3.05749900	0.32990100	-2.89032500
C	4.14532600	2.05586600	-4.79379200
H	2.66472500	3.48298400	-4.14363700
C	4.13345900	-0.08218100	-3.67267300
H	2.62292300	-0.34771100	-2.14736400
C	4.67754200	0.77803300	-4.62673100
H	4.56755200	2.73257800	-5.54045800
H	4.54412300	-1.08556100	-3.54017700

H	5.51668900	0.45037800	-5.24480300
C	0.80857700	-0.86208400	-0.16351500
C	1.61498100	-1.38057300	0.61253300
C	2.48025400	-1.92224100	1.59880600
C	3.00863100	-3.22385500	1.50440300
C	2.77376600	-1.17442600	2.75979300
C	3.78708100	-3.74991200	2.52962300
H	2.78549200	-3.82441700	0.61991600
C	3.55169800	-1.71323400	3.77475300
H	2.36335000	-0.16516500	2.85363800
C	4.07602100	-3.01174000	3.68499100
H	4.17842400	-4.76729200	2.43507200
H	3.75575700	-1.11471700	4.66807300
C	4.93078700	-3.57438900	4.77618800
H	4.99593900	-4.66894400	4.72325400
H	5.96180200	-3.18957200	4.72227500
H	4.55139600	-3.30757400	5.77257200
C	-1.27577700	-1.19221500	-0.33888200
C	-1.82653300	-1.06961400	0.91433700
F	-1.52935100	-2.27170900	-1.06813800
C	-2.80335200	-2.09910800	1.40116100
O	-2.70083200	-3.27500200	1.16948100
O	-3.84999500	-1.66708500	2.14673800
C	-4.27161100	-0.30704100	2.22241000
H	-3.82963300	0.15800500	3.12176900
H	-3.90047400	0.26244300	1.35400900
C	-5.77384000	-0.28784100	2.29151800
H	-6.13315100	-0.86841000	3.15102600
H	-6.14236000	0.74107200	2.39603600
H	-6.21734200	-0.72177500	1.38587500
N	-1.42624900	0.02029700	1.67016800
C	-1.18382000	-0.03730100	2.94047600
C	-1.16015200	-1.28169000	3.75072400
C	-1.75920200	-1.32928600	5.02085000
C	-0.52353000	-2.43187300	3.26086300
C	-1.72925100	-2.49852600	5.77388100
H	-2.26188300	-0.43978800	5.41233300
C	-0.47156600	-3.59233700	4.02661200
H	-0.06444800	-2.41237100	2.26989800
C	-1.07688500	-3.63043600	5.28159100
H	-2.21487700	-2.52755000	6.75201900
H	0.04114100	-4.47227400	3.63216900
H	-1.04503600	-4.54531500	5.87786400
C	-0.87596900	1.24482600	3.61828900

C	-1.36088000	2.45158600	3.08514400
C	-0.08743500	1.29604100	4.78066900
C	-1.07853200	3.66658300	3.69950600
H	-1.96751800	2.40870900	2.17701600
C	0.20092900	2.51536400	5.39079200
H	0.31726600	0.37026100	5.19803900
C	-0.29864400	3.70356600	4.85750400
H	-1.47137400	4.59390000	3.27575700
H	0.82169600	2.53704800	6.28961000
H	-0.08003900	4.65785600	5.34248700