Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Hypervalent Iodide(III)-Mediated Thiofluorination of Alkenes and Alkynes from Thioureas/Thiocarbamoyl Fluorides with Water and Nucleophilic Fluoride Source

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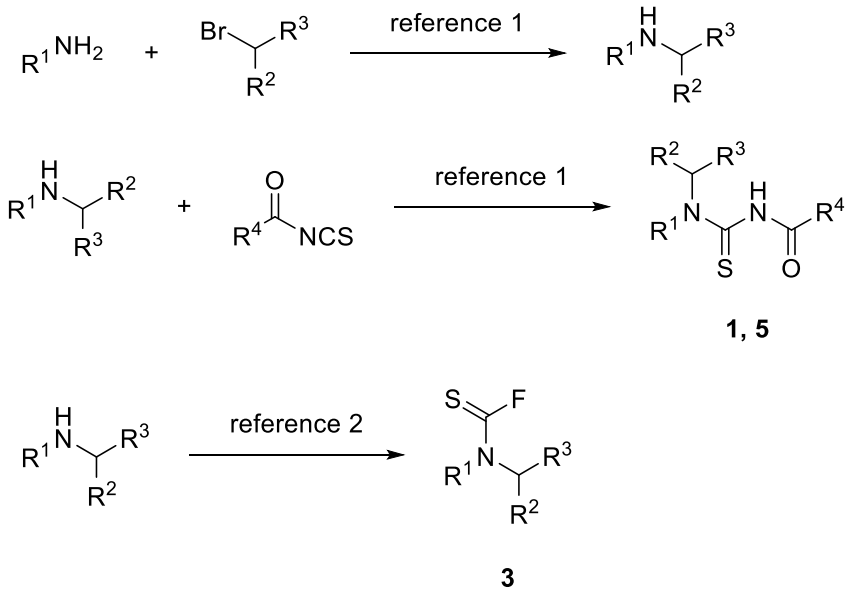
1. General information & materials. .....

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at Bruker 500 MHz or 600 MHz, using $CDCl_3$ as a reference standard (δ = 7.26 ppm) for ^{1}H NMR and (δ = 77.0 ppm) for ^{13}C NMR. Thin-layer chromatography (TLC) was carried out using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. The dilute solvents usually used ethyl acetate/petroleum ether, which was abbreviated as petroleum ether / ethyl acetate. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer equipped with EI or ESI ionization source and a time-of-flight (TOF) mass spectrometer.

2. General experimental procedures for synthesis of (homo)allyl/propargyl amines, alkenyl/alkynyl thioureas, thiocarbamoyl fluorides and $PhI(OPiv)_2$.



2.1 General procedure for preparation of (homo)allyl/propargyl secondary amines[1].

A solution of primary amine (2.0 eq), potassium carbonate (2.0 eq) and (homo)allyl/propargyl bromide (1.0 eq, containing an alkene or alkyne group) in DMF (0.5 M) was stirred at room temperature overnight. The reaction was then quenched with water, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced

pressure and the residue was purified by column chromatography on silica gel using petroleum ether or petroleum ether / ethyl acetate afforded the desired secondary amine.

2.2 General procedure for preparation of alkenyl/alkynyl thioureas 1, 5[1].

Method A

A solution of KSCN (2 eq) and acyl chloride (1 eq) in acetone (1 M) was stirred at room temperature for 1~2 h, then secondary amine was added and the reaction was stirred at room temperature for 2~12 h. The reaction mixture was filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel using petroleum ether / ethyl acetate to give alkenyl/alkynyl thioureas **1a-1o**, **1q-1af**, **1ah**, **lai**, **5a**-**5c**, **5h**, **5k**, **5l**.

Method B

A solution of acyl isothiocyanate (1 eq) and secondary amine (1 eq) in THF (0.1 M) was stirred at room temperature for 1~12 h until one of the reactants was consumed. The reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel using petroleum ether / ethyl acetate to give alkenyl/alkynyl thioureas **1p**, **1ag**, **1aj**,**1ak**, **5d**-**5g**, **5i**, **5j**.

2.3 General procedure for preparation of thiocarbamoyl fluorides 3[2].

Method A

A solution of sulfur (4 eq) and KF (3 eq) in THF (0.1 M) was added $TMSCF_3$ (5 eq) under N_2, followed by the solution of secondary amines (1 eq, it could be dissolved in a small amount of THF if the amine is a solid). The mixture was stirred under N_2 at room temperature for 1-12 h until the secondary amine was consumed. Then the reaction mixture was filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel using petroleum ether / ethyl acetate to give thiocarbamoyl fluorides **3a-3c**, **3e**-**3i**, **3k-3l**, **3n**, **3p**-**3t**.

Method B

A solution of secondary amines (1 eq), $AgSCF_3$ (1.5 eq), KBr (2.5 eq) in acetonitrile (0.05 M) was stirred at atmosphere at room temperature for 2 h until the amine was consumed. Then the reaction mixture was

filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel using petroleum ether / ethyl acetate to give the **3d**, **3j**, **3m**, **3o**.

2.4 General procedure for preparation of $PhI(OPiv)_2$[3].

A known compound, see references[3] for details

Reference:

[1] Liu, S.; Jiang, L. Copper-Catalyzed Multicomponent Reactions of Intramolecular and Intermolecular Thiotrifluoromethylation of Alkenes: Access to CF3–Containing 2-Iminothiazolidines and Isothioureas. *Org. Lett.* **2022**, 39, 7157-7162.

[2] Zhen, L.; Fan, H. Wang, X.; Jiang, L. Synthesis of Thiocarbamoyl Fluorides and Isothiocyanates Using CF_3SiMe_3 and Elemental Sulfur or $AgSCF_3$ and KBr with Amines. *Org. Lett.* **2019**, *21*, 2106−2110.

[3] Atmuri, N.; Reilley, D.; Lubell, W. *Org. Lett.* **2017**, 19, 5066−5069.

2.5 The procedure for reactions of Ph_2S_2/PhSH/*n*-butylthioalcohol, $Et_3N{\cdot}3HF$, and cyclohexane

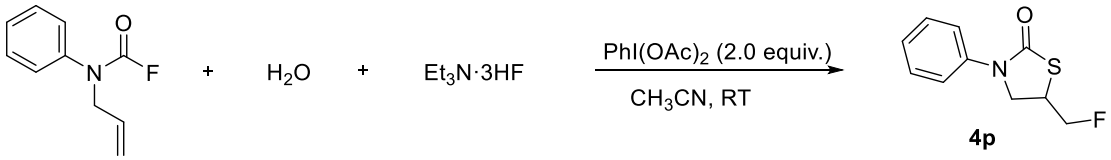
A solution of $PhI(OPiv)_2$ (0.4 mmol) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in CH_2Cl_2 (3 mL) was stirred at room temperature for 5 minutes, then 1,2-diphenyldisulfane (0.16 mmol) or PhSH (0.16 mmol) or *n*-butylthioalcohol (0.16 mmol) was added. The mixture was stirred at the room temperature in N_2 atmosphere for 30 min. Subsequently, a CH_2Cl_2 solution (3 mL) of cyclohexane (0.30 mmol) was added slowly. The mixture was stirred for 1 hour, and the reaction was subjected to detected by TLC and HRMS. The desired alkene 1,2-thiofluorination products were not detected. The PhSF or *n*-butyl-SF species was not been detected.

3. Optimization of reaction conditions for (Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide 2a.

A solution of oxidant and alkenyl thioureas **1a** (0.2 mmol) in solvent (3 mL) was stirred, then fluorinating reagent was added. The mixture was stirred at the room temperature for 2-12 h until **2a** was consumed. Then

the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether: ethyl acetate = 10:1~5:1 to give product **2a**.

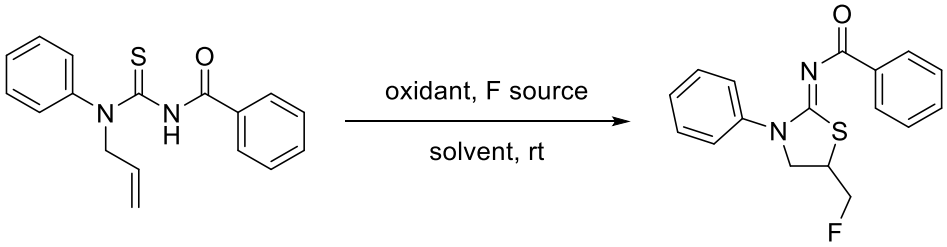
Initial discovery:



4p

29% yield

Table S1. Optimization of the reaction conditions for **2a**[a].



1a **2a**

entry	oxidant	fluorinating reagent	solvent	yield(%)[b]
1	$PhI(OAc)_2$	$Et_3N{\cdot}3HF$	MeCN	54
2	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	MeCN	64
3	$PhI(OAd)_2$	$Et_3N{\cdot}3HF$	MeCN	56
4	PhI, m-CPBA[c]	$Et_3N{\cdot}3HF$	MeCN	45
5	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	CH_2Cl_2	34
6	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	Et_2O	56
7	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhMe	68
8	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	xylene	56
9	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhCl	27
10	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	$PhCF_3$	32
11	Selectfluor	--	PhMe	0
12	Selectfluor	$Et_3N{\cdot}3HF$	PhMe	0
13[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhMe	84
14[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhCl	72
15[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	$PhCF_3$	81
16[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	xylene	79
17[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	MeCN	65

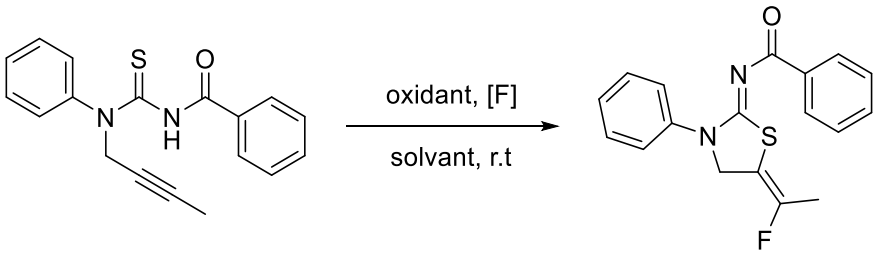
18[d]	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhMe/ Et_2O (2:1)	80
19[d]	$PhI(OPiv)_2$	Py·HF[e]	PhMe	trace
20[d]	$PhI(OPiv)_2$	$BF_3{\cdot}OEt_2$[e]	PhMe	0
21[d]	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$	PhMe	86(86[g])
22[d]	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$[h]	PhMe	77
23[d]	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$[i]	PhMe	75

[a]Reaction conditions: **1a** (0.2 mmol), oxidant (0.4 mmol), fluorinating reagent (0.6 mmol) in 3 ml solvent for 2 h. [b]^1H NMR yield with CH_2Br_2 as internal standard. [c]PhI (20 mol%), m-CPBA (0.4 mmol) at -20 °C for 4 h. [d] Oxidant (0.4 mmol) and fluorinating reagent (0.6 mmol) stirred 5 minutes before **1a** (0.2 mmol) was added and then the mixture stirred for 2 h. [e]Py·HF (0.6 mmol). [f]oxidant (0.23 mmol). [g]Isolated yield. [h]$Et_3N{\cdot}3HF$ (0.5 mmol). [i] $Et_3N{\cdot}3HF$ (0.4 mmol).

4. Optimization of reaction conditions for *N*-((2Z,5E)-5-(1-fluoroethylidene)-3-phenylthiazolidin-2-ylidene)benzamide 6a.

A solution of oxidant and fluorinating reagent in solvent (3 mL) was stirred at room temperature for 5 minutes, then alkynyl thioureas **5a** (0.2 mmol) was added. The mixture was stirred at the room temperature for 2-12 h until **5a** was consumed. Then the reaction mixture was filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether: ethyl acetate = 10:1 to give product **6a**.

Table S1. Optimization of the reaction conditions for **6a**[a].



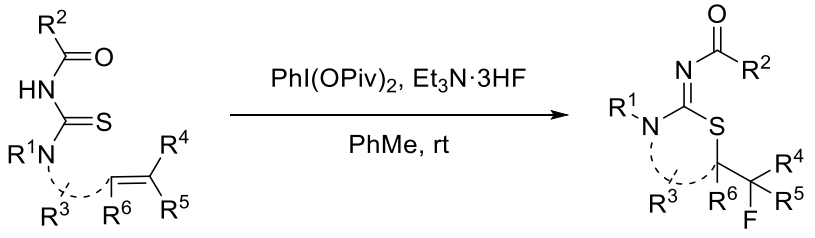
5a **6a**

Entry	oxidant	fluorinating reagent	solvent	yield(%)[b]
1	$PhI(OPiv)_2$[c]	$Et_3N{\cdot}3HF$	PhMe	46
2	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	PhMe	46
3	$PhI(OAc)_2$	$Et_3N{\cdot}3HF$	PhMe	36

4	$PhI(OAd)_2$	$Et_3N{\cdot}3HF$	PhMe	48
5	$PhI(OPiv)_2$[d]	$Et_3N{\cdot}3HF$	PhMe	31
6	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	CH_2Cl_2	30
7	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	Et_2O	56
8	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	DMF	trace
9	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	DMSO	trace
10	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	MeCN	17
11	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	EtOAc	38
12	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	acetone	trace
13	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	THF	53
14	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	1,4-dioxane	77
15	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	DME	67
16	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	MTBE	36
17	$PhI(OPiv)_2$	$Et_3N{\cdot}3HF$	diethylacetal	trace
18	$PhI(OPiv)_2$	py·6HF[e]	1,4-dioxane	50
19	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$	1,4-dioxane	82
20	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$[g]	1,4-dioxane	83
21	$PhI(OPiv)_2$[f]	$Et_3N{\cdot}3HF$[h]	1,4-dioxane	92(82[i])

[a]Reaction conditions: **5a** (0.2 mmol), oxidant (0.22 mmol), fluorinating reagent (0.6 mmol) in 3 ml solvent for 2 h. [b]^{1}H NMR yield with CH_2Br_2 as internal standard. [c]0.23 mmol $PhI(OPiv)_2$. [d] 0.6 mmol $PhI(OPiv)_2$. [e]py·6HF (0.3 mmol). [f]0.21 mmol $PhI(OPiv)_2$. [g]0.5 mmol $Et_3N{\cdot}3HF$. [h]0.7 mmol $Et_3N{\cdot}3HF$. [i]Isolated yield.

5. General procedure for synthesis of acylcarbamimidothioate 2.

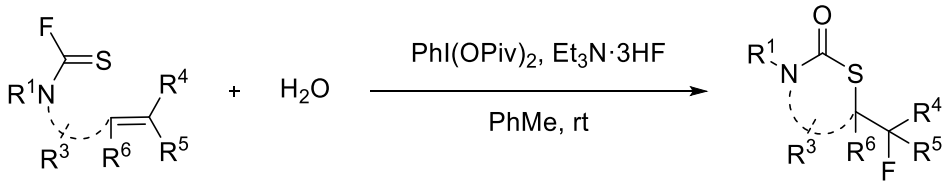


1 **2**

A solution of $PhI(OPiv)_2$ (0.23 mmol, 1.2 eq) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in PhMe (3 mL) was stirred at room temperature for 5 minutes, then alkenyl thioureas **1** (0.2 mmol, 1 eq) was added. The mixture was stirred at the room temperature for 2 h until alkenyl thioureas **1** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were

washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to give product **2**.

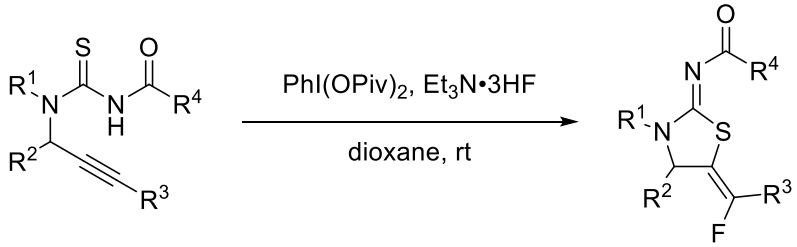
6. General procedure for synthesis of carbamothioate 4.



3 **4**

A solution of $PhI(OPiv)_2$ (0.4 mmol, 2 eq) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in PhMe (3 mL) was stirred at room temperature for 5 minutes, then thiocarbamoyl fluorides **3** (0.2 mmol, 1 eq) was added. The mixture was stirred at the room temperature for 4 h until thiocarbamoyl fluorides **3** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to give product **4**.

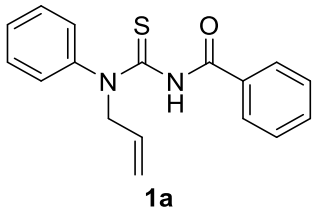
7. General procedure for synthesis of carbamothioate 6.



5 **6**

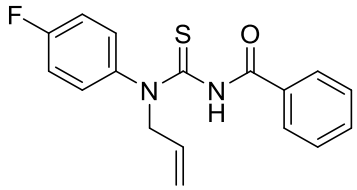
A solution of $PhI(OPiv)_2$ (0.21 mmol, 2 eq) and $Et_3N{\cdot}3HF$ (0.7 mmol, 3 eq) in dioxane (3 mL) was stirred at room temperature for 5 minutes, then alkynyl thioureas **5** (0.2 mmol, 1 eq) was added. The mixture was stirred at the room temperature for 3 h until alkynyl thioureas **5** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to give product **6**.

6. Analytical data.



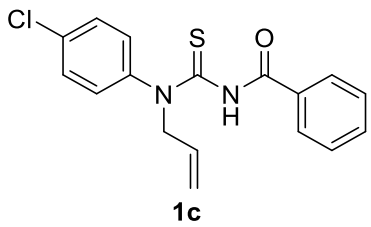
1a

***N*-(allyl(phenyl)carbamothioyl)benzamide (1a):** Known compound[1]. The general procedure from *N*-allylaniline (669.7 mg, 5 mmol), benzoyl chloride (702.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1a** as white solid (963.1 mg, 65% yield).



1b

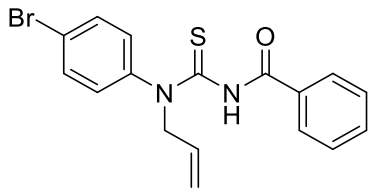
***N*-(allyl(4-fluorophenyl)carbamothioyl)benzamide (1b):** The general procedure from *N*-allyl-4-fluoroaniline (1663 mg, 11 mmol), benzoyl chloride (1546.6 mg, 11 mmol), KSCN (2138 mg, 22 mmol) and acetone (11 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1b** as white solid (2202.8 mg, 64% yield). Mp: 90.3-92.5 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.50 (dd, J = 18.5, 11.4 Hz, 3H), 7.41 – 7.28 (m, 4H), 7.02 (t, J = 8.3 Hz, 2H), 6.02 (m, 1H), 5.27 (dd, J = 25.8, 13.5 Hz, 2H), 5.01 – 4.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 162.6, 161.4 (d, J = 248.4 Hz), 139.7, 132.8, 132.6, 130.5, 128.7, 127.7, 127.5, 119.4, 116.0 (d, J = 22.9 Hz), 60.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}FN_2NaOS$ 337.0781, found 337.0780.



1c

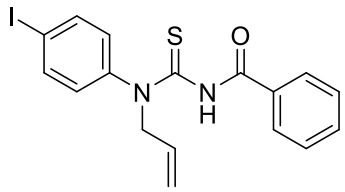
***N*-(allyl(4-chlorophenyl)carbamothioyl)benzamide (1c):** The general procedure from *N*-allyl-4-chloroaniline (2222.9 mg, 13.3 mmol), benzoyl chloride (1870 mg, 13.3 mmol), KSCN (2585 mg, 26.6 mmol) and acetone

(13 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1c** as white solid (2637 mg, 60% yield). Mp: 93.9-95.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.63 – 7.48 (m, 3H), 7.39 (t, J = 7.7 Hz, 2H), 7.32 – 7.24 (m, 4H), 6.02 (m, 1H), 5.38 – 5.22 (m, 2H), 4.86 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 162.5, 142.5, 133.3, 132.8, 132.5, 130.5, 129.2, 128.7, 127.5, 127.1, 119.4, 60.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}ClN_2NaOS$ 353.0486, found 353.0476.



1d

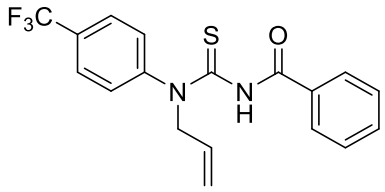
***N*-(allyl(4-bromophenyl)carbamothioyl)benzamide (1d):** The general procedure from *N*-allyl-4-bromoaniline (3245 mg, 15.3 mmol), benzoyl chloride (2151.2 mg, 15.3 mmol), KSCN (2973.7 mg, 30.6 mmol) and acetone (15 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1d** as white solid (3999.1 mg, 70% yield). Mp: 89.9-92.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.64 – 7.48 (m, 3H), 7.48 – 7.34 (m, 4H), 7.23 – 7.16 (m, 2H), 6.01 (m, 1H), 5.38 – 5.21 (m, 2H), 4.86 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 162.5, 143.0, 132.8, 132.4, 132.1, 130.5, 128.7, 127.5, 127.4, 121.3, 119.4, 60.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}BrN_2NaOS$ 396.9981, found 396.9981.



1e

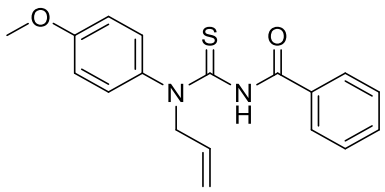
***N*-(allyl(4-iodophenyl)carbamothioyl)benzamide (1e):** The general procedure from *N*-allyl-4-iodoaniline (3808.6 mg, 14.7 mmol), benzoyl chloride (2066.8 mg, 14.7 mmol), KSCN (2857.1 mg, 30.6 mmol) and acetone (15 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1e** as white solid (4611.9 mg, 74% yield). Mp: 105.6-109.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.71 – 7.61 (m, 2H), 7.61 – 7.46 (m, 3H), 7.39 (t, J = 7.7 Hz, 2H), 7.12 – 7.02 (m, 2H), 6.01 (m, 1H), 5.38 – 5.21 (m, 2H), 4.86 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8,

162.5, 143.8, 138.1, 132.8, 132.4, 130.5, 128.7, 127.5, 119.4, 92.9, 60.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}IN_2NaOS$ 444.9842, found 444.9851.



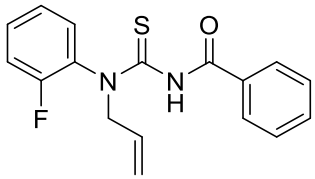
1f

***N*-(allyl(4-(trifluoromethyl)phenyl)carbamothioyl)benzamide (1f):** The general procedure from *N*-allyl-4-(trifluoromethyl)aniline (2454.5 mg, 12.2 mmol), benzoyl chloride (1715.3 mg, 12.2 mmol), KSCN (2371.2 mg, 24.4 mmol) and acetone (12 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1f** as white solid (2708.8 mg, 61% yield). Mp: 92.3-94.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.71 – 7.61 (m, 2H), 7.61 – 7.46 (m, 3H), 7.39 (t, J = 7.7 Hz, 2H), 7.12 – 7.02 (m, 2H), 6.01 (m, 1H), 5.38 – 5.21 (m, 2H), 4.86 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 181.3, 162.6, 147.1, 132.7, 132.1, 130.3, 129.2 (q, J = 32.9 Hz), 128.6, 127.5, 126.1, 126.0 (q, J = 3.6 Hz), 123.4 (q, J = 272.2 Hz), 119.3, 59.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{15}F_3N_2NaOS$ 387.0749, found 387.0748.



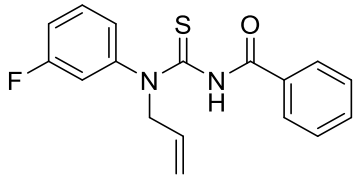
1g

***N*-(allyl(4-methoxyphenyl)carbamothioyl)benzamide (1g):** The general procedure from *N*-allyl-4-methoxyaniline (816.1 mg, 5 mmol), benzoyl chloride (702.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1g** as white solid (1170.8 mg, 68% yield). Mp:93.5-96.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.64 – 7.42 (m, 3H), 7.40 – 7.24 (m, 3H), 6.98 – 6.73 (m, 3H), 6.04 (m, 1H), 5.36 – 5.20 (m, 2H), 4.88 (s, 2H), 3.77 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 163.0, 160.2, 133.2, 132.6, 131.0, 130.1, 128.7, 127.4, 119.2, 118.2, 113.7, 112.0, 59.2, 55.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{18}N_2NaO_2S$ 367.0887, found 349.0972.



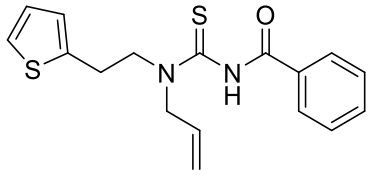
1h

***N*-(allyl(2-fluorophenyl)carbamothioyl)benzamide (1h):** The general procedure from *N*-allyl-2-fluoroaniline (775.9 mg, 5 mmol), benzoyl chloride (702.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1h** as white solid (903.6 mg, 57% yield). Mp: 125.1-127.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.94 – 6.81 (m, 9H), 6.02 (dt, J = 17.0, 8.0 Hz, 1H), 5.43 – 5.14 (m, 2H), 5.08 – 4.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.9, 162.8, 155.9 (d, J = 252 Hz), 132.6 (q, J = 6.3 Hz), 130.3, 129.7 (d, J = 7.8 Hz), 128.7, 128.3, 127.5, 124.4, 119.6, 116.4 (d, J = 20.2 Hz), 59.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}FN_2NaOS$ 337.0781, found 337.0772.



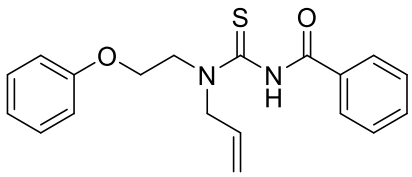
1i

***N*-(allyl(3-fluorophenyl)carbamothioyl)benzamide (1i):** The general procedure from *N*-allyl-3-fluoroaniline (775.9 mg, 5 mmol), benzoyl chloride (702.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1i** as white solid (817.5 mg, 52% yield). Mp: 109.8-112.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.53 (dd, J = 37.0, 7.6 Hz, 3H), 7.44 – 7.23 (m, 3H), 7.10 (dd, J = 30.0, 8.7 Hz, 2H), 6.93 (td, J = 8.3, 2.5 Hz, 1H), 6.02 (m, 1H), 5.30 (dd, J = 32.5, 13.7 Hz, 2H), 4.88 (d, J = 5.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 162.4 (d, J = 249.5 Hz), 162.6, 145.3 (d, J = 9.7 Hz), 132.8, 132.6, 130.6, 130.1 (d, J = 9.1 Hz), 128.8, 127.5, 121.6, 119.4, 114.8 (d, J = 20.8 Hz), 113.4 (d, J = 23.9 Hz), 60.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}FN_2NaOS$ 337.0781, found 337.0770.



1l

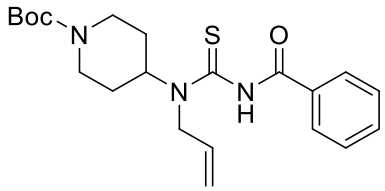
***N*-(allyl(2-(thiophen-2-yl)ethyl)carbamothioyl)benzamide (1l):** The general procedure from *N*-(2-(thiophen-2-yl)ethyl)prop-2-en-1-amine (1421.8 mg, 8.5 mmol), benzoyl chloride (1195.1 mg, 8.5 mmol), KSCN (1652.1 mg, 17 mmol) and acetone (9 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1l** as white solid (2321.5 mg, 71% yield). Mp: 96.4-98.1 °C. The spectra of this compound show more peaks because thioamide compounds are easy to isomerize. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 2H), 8.21 (s, 1H), 7.81 (t, J = 11.5 Hz, 6H), 7.53 (dt, J = 52.7, 7.5 Hz, 9H), 7.17 (d, J = 5.2 Hz, 3H), 6.95 (s, 6H), 5.93 (s, 3H), 5.48 (d, J = 17.2 Hz, 1H), 5.36 – 5.12 (m, 5H), 4.57 (d, J = 109.6 Hz, 3H), 4.26 – 3.99 (m, 8H), 3.83 (s, 2H), 3.30 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.2, 180.4, 163.8, 140.5, 139.8, 132.9, 132.4, 132.1, 130.5, 128.8, 127.8, 127.0, 125.9, 125.6, 124.3, 123.9, 119.8, 118.7, 56.8, 56.1, 54.8, 54.2, 28.3, 26.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}N_2NaOS_2$ 3853.0753, found 353.0746.



1n

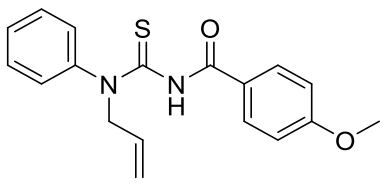
***N*-(allyl(2-phenoxyethyl)carbamothioyl)benzamide (1n):** The general procedure from *N*-(2-phenoxyethyl)prop-2-en-1-amine (1127.3 mg, 6.34 mmol), benzoyl chloride (891.4 mg, 6.34 mmol), KSCN (1232.2 mg, 12.68 mmol) and acetone (6.5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1n** as purple viscous liquid (1044 mg, 48% yield). The spectra of this compound show more peaks because thioamide compounds are easy to isomerize. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (m, 1H), 7.82 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 7.28 (m, 2H), 7.07 – 6.79 (m, 3H), 5.99 (m, 1H), 5.52 – 5.13 (m, 2H), 4.73 (s, 1H), 4.51 – 3.87 (m, 5H).^{13}C NMR (151 MHz, $CDCl_3$) δ 181.3, 180.9, 164.5, 163.8, 158.3, 157.7, 133.0, 132.5, 132.2, 130.7, 129.6, 129.5, 128.8, 127.8, 121.8, 121.1, 119.8, 118.9, 114.7, 114.5, 65.9, 64.9, 57.8, 55.9, 52.4, 51.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$

calculated for $C_{19}H_{20}N_2NaO_2S$ 363.1138, found 363.1130.



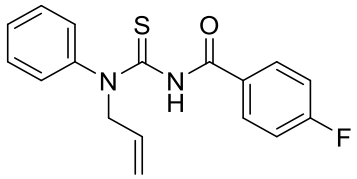
1o

tert-butyl 4-(1-allyl-3-benzoylthioureido)piperidine-1-carboxylate (1o): The general procedure from tert-butyl 4-(allylamino)piperidine-1-carboxylate (2836.1 mg, 11.8 mmol), benzoyl chloride (1659.4 mg, 11.8 mmol), KSCN (2293.4 mg, 23.6 mmol) and acetone (11.8 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1o** as white solid (2203.2 mg, 46% yield). Mp: 133.1-135.2 °C. The spectra of this compound show more peaks because thioamide compounds are easy to isomerize. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.82 (m, 2H), 7.54 (m, 3H), 5.87 (m, 1H), 5.56 – 5.02 (m, 3H), 4.59 (s, 1H), 4.19 (m, 3H), 2.74 (m, 2H), 2.00 (m, 2H), 1.76 – 1.63 (m, 2H), 1.46 (s, 9H).^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 180.4, 164.1, 163.6, 154.3, 133.3, 132.7, 132.6, 132.2, 131.1, 128.5, 127.7, 117.2, 79.6, 62.0, 61.3, 50.8, 50.0, 43.0, 29.6, 28.6, 28.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{29}N_3NaO_3S$ 426.1822, found 426.1830.



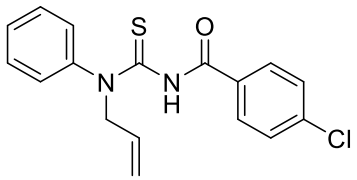
1p

***N*-(allyl(phenyl)carbamothioyl)-4-methoxybenzamide (1p):** The general procedure from *N*-allylaniline (133.2 mg, 1 mmol), 4-methoxybenzoyl isothiocyanate (193.22 mg, 1 mmol) and THF (10 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **1p** as white solid (296.3 mg, 91% yield). Mp: 119.2-121.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.48 (d, J = 8.6 Hz, 2H), 7.41 – 7.19 (m, 5H), 6.82 (d, J = 8.4 Hz, 2H), 6.04 (m, 1H), 5.36 – 5.19 (m, 2H), 4.89 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.4, 163.1, 162.3, 143.7, 131.0, 129.5, 129.3, 127.9, 126.0, 125.1, 119.1, 113.9, 59.6, 55.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}IN_2NaOS$ 444.9842, found 349.0971.



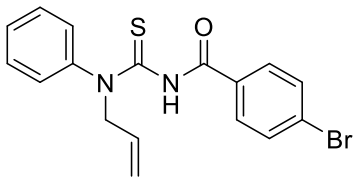
1q

***N*-(allyl(phenyl)carbamothioyl)-4-fluorobenzamide (1q):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 4-fluorobenzoyl chloride (875 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1q** as white solid (786.6 mg, 46% yield). Mp: 79.3-81.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.52 (s, 2H), 7.41 – 7.19 (m, 5H), 7.01 (t, J = 8.2 Hz, 2H), 6.02 (m, 1H), 5.26 (m, 2H), 4.88 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.20, 165.15 (d, J = 254.1 Hz), 161.97, 143.42, 130.59, 130.06 (d, J = 9.3 Hz), 129.12, 128.91 (d, J = 3.1 Hz), 127.89, 125.86, 119.13, 115.64 (d, J = 22.1 Hz), 59.50. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}FN_2NaOS$ 337.0781, found 337.0774



1r

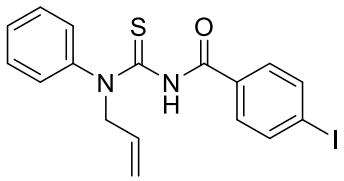
***N*-(allyl(phenyl)carbamothioyl)-4-chlorobenzamide (1r):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 4-chlorobenzoyl chloride (782.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1r** as white solid (757.1 mg, 46% yield). Mp:72.1-74.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.51 – 7.39 (m, 2H), 7.39 – 7.21 (m, 7H), 6.03 (m, 1H), 5.37 – 5.19 (m, 2H), 4.89 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 162.0, 143.4, 138.9, 131.2, 130.6, 129.2, 128.9, 128.9, 128.0, 125.9, 119.2, 59.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}ClN_2NaOS$ 353.0486, found 353.0475.



1s

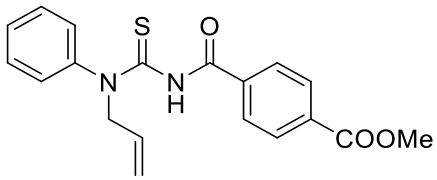
***N*-(allyl(phenyl)carbamothioyl)-4-bromobenzamide (1s):** The general procedure from *N*-allylaniline (666.0

mg, 5 mmol), 4-bromobenzoyl chloride (1097.3 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1s** as white solid (1138.8 mg, 61% yield). Mp: 112.2-113.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.45 – 7.17 (m, 7H), 6.02 (m, 1H), 5.41 – 5.20 (m, 2H), 4.89 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 162.2, 143.3, 131.8, 131.6, 130.5, 129.2, 129.1, 128.0, 127.4, 125.9, 119.2, 59.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}BrN_2NaOS$ 396.9981, found 396.9977.



1t

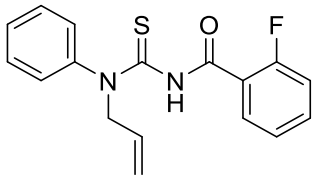
***N*-(allyl(phenyl)carbamothioyl)-4-iodobenzamide (1t):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 4-iodobenzoyl chloride (1332.3 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1t** as white solid (1439.5 mg, 68% yield). Mp: 118.5-121.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.47 – 7.06 (m, 7H), 6.02 (m, 1H), 5.27 (dd, J = 25.2, 13.8 Hz, 2H), 4.88 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 162.4, 143.4, 137.8, 132.2, 130.6, 129.2, 128.9, 128.0, 125.9, 119.3, 100.1, 59.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}IN_2NaOS$ 444.9842, found 444.9846.



1u

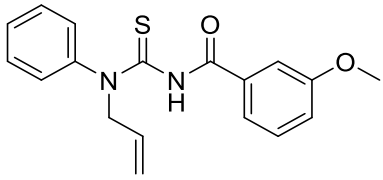
methyl 4-((allyl(phenyl)carbamothioyl)carbamoyl)benzoate (1u): The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), methyl 4-(chlorocarbonyl)benzoate (993 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **1u** as white solid (1034.4 mg, 58% yield). Mp: 112.1-114.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.55 (s, 2H), 7.38 (t, J = 7.7 Hz, 2H),

7.34 – 7.21 (m, 3H), 6.04 (m, 1H), 5.38 – 5.18 (m, 2H), 4.89 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 165.9, 162.2, 143.4, 136.7, 133.6, 130.6, 129.8, 129.3, 128.2, 127.5, 126.0, 119.4, 59.6, 52.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}N_2NaO_3S$ 377.0930, found 377.0921.



1v

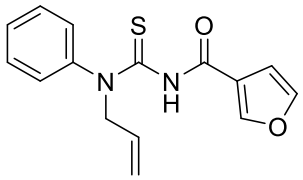
***N*-(allyl(phenyl)carbamothioyl)-2-fluorobenzamide (1v):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 2-fluorobenzoyl chloride (792.8 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1v** as white solid (1114.7 mg, 71% yield). Mp: 103.7-106.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, J = 13.2 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.33 (td, J = 7.2, 1.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 6.99 (dd, J = 12.1, 8.3 Hz, 1H), 6.04 (m, 1H), 5.31 – 5.16 (m, 2H), 4.99 – 4.81 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.50, 159.91 (d, J = 123.5 Hz), 159.30 (d, J = 3.4 Hz), 142.59, 134.26 (d, J = 9.3 Hz), 132.15, 130.76, 129.56, 128.36, 126.31, 124.86 (d, J = 3.2 Hz), 120.25 (d, J = 10.1 Hz), 119.18, 115.98 (d, J = 24.3 Hz), 58.84. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}FN_2NaOS$ 337.0781, found 337.0773.



1w

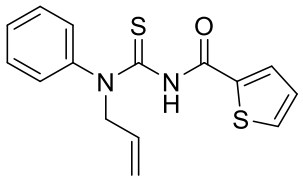
***N*-(allyl(phenyl)carbamothioyl)-3-methoxybenzamide (1w):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 3-methoxybenzoyl chloride (853.0 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **1w** as white solid (1011.5 mg, 62% yield). Mp: 106.3-108.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.44 – 7.15 (m, 6H), 7.11 – 6.89 (m, 3H), 6.04 (m, 1H), 5.27 (m, 2H), 4.89 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.9, 162.6, 159.6, 143.4, 134.1, 130.7, 129.5, 129.2, 127.9, 125.9, 119.2, 119.1, 118.9, 112.3, 59.4, 55.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for

$C_{18}H_{18}FN_2NaO_2S$ 349.0981, found 349.0971.



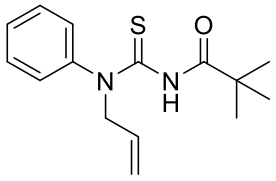
1x

***N*-(allyl(phenyl)carbamothioyl)furan-3-carboxamide (1x):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), furan-3-carbonyl chloride (652.7 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1x** as white solid (901.4 mg, 63% yield). Mp: 97.2-98.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.62 – 7.17 (m, 6H), 7.07 (d, J = 3.7 Hz, 1H), 6.44 (d, J = 3.7 Hz, 1H), 6.02 (m, 1H), 5.24 (m, 2H), 4.88 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 152.6, 146.2, 144.8, 142.9, 130.8, 129.4, 128.1, 126.1, 119.1, 11695, 112.6, 59.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{14}N_2NaO_2S$ 309.0668, found 309.0661.



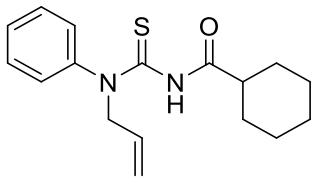
1y

***N*-(allyl(phenyl)carbamothioyl)thiophene-2-carboxamide (1y):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), thiophene-2-carbonyl chloride (733 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1y** as white solid (899.9 mg, 60% yield). Mp: 114.2-117.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.48 (d, J = 4.9 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.28 (dd, J = 13.8, 6.2 Hz, 4H), 6.99 (t, J = 4.3 Hz, 1H), 6.03 (m, 1H), 5.42 – 5.10 (m, 2H), 4.98 – 4.71 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.1, 156.9, 143.0, 137.2, 132.2, 130.7, 129.9, 129.3, 128.0, 127.7, 126.0, 119.1, 59.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{14}N_2NaOS_2$ 325.0440, found 325.0431.



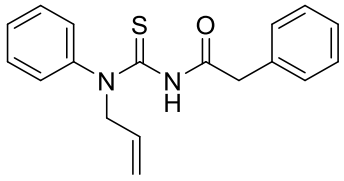
1z

***N*-(allyl(phenyl)carbamothioyl)pivalamide (1z):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), pivaloyl chloride (602.9 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1z** as white solid (931.7 mg, 67% yield). Mp: 102.3-105.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.34 – 7.26 (m, 1H), 7.23 (dd, J = 7.4, 1.7 Hz, 2H), 6.00 (m, 1H), 5.32 – 5.17 (m, 2H), 4.84 (d, J = 6.0 Hz, 2H), 0.90 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.3, 173.2, 143.4, 130.8, 129.1, 127.9, 126.3, 119.1, 59.3, 39.6, 26.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{20}N_2NaOS$ 299.1189, found 299.1184.



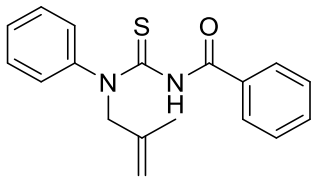
1aa

***N*-(allyl(phenyl)carbamothioyl)cyclohexanecarboxamide (1aa):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), cyclohexanecarbonyl chloride (733.6 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1aa** as white solid (751.7 mg, 50% yield). Mp:81.9-83.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.28 (dd, J = 14.2, 6.7 Hz, 1H), 7.21 (d, J = 7.7 Hz, 2H), 5.99 (m, 1H), 5.23 (dd, J = 21.8, 13.7 Hz, 2H), 4.95 – 4.70 (m, 2H), 2.18 (tt, J = 11.5, 3.4 Hz, 1H), 1.60 m, 5H), 1.22 – 0.96 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.6, 171.7, 143.6, 130.8, 128.9, 127.7, 126.1, 119.0, 59.5, 45.0, 28.6, 25.4, 25.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}N_2NaOS$ 325.1351, found 325.1336.



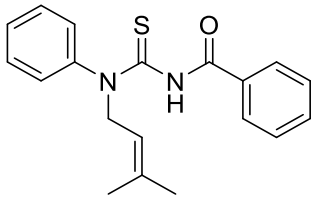
1ab

***N*-(allyl(phenyl)carbamothioyl)-2-phenylacetamide (1ab):** The general procedure from *N*-allylaniline (666.0 mg, 5 mmol), 2-phenylacetyl chloride (773.0 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1ab** as white solid (568.6 mg, 37% yield). Mp: 78.7-79.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.37 – 7.27 (m, 3H), 7.21 (q, J = 7.3 Hz, 3H), 7.11 – 6.83 (m, 4H), 5.93 (m, 1H), 5.16 (m, 2H), 4.75 (d, J = 5.6 Hz, 2H), 3.61 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 167.4, 142.3, 133.0, 130.7, 129.6, 129.2, 129.0, 128.2, 127.4, 126.2, 119.2, 58.8, 44.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{18}N_2NaOS$ 333.1032, found 333.1023.



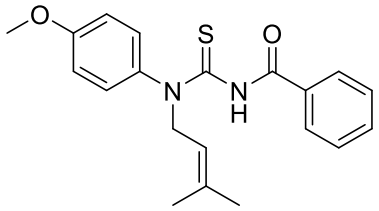
1ac

***N*-((2-methylallyl)(phenyl)carbamothioyl)benzamide (1ac):** The general procedure from *N*-(2-methylallyl)aniline (1472.2 mg, 10 mmol), benzoyl chloride (1406 mg, 10 mmol), KSCN (1943.6 mg, 20 mmol) and acetone (10 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1ac** as white solid (1770.8 mg, 57% yield). Mp: 121.1-123.4 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.50 (dt, J = 23.4, 7.5 Hz, 3H), 7.40 – 7.30 (m, 6H), 7.22 (t, J = 7.1 Hz, 1H), 5.12 (s, 1H), 4.99 (s, 1H), 4.90 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.0, 162.6, 144.0, 138.7, 132.7, 132.5, 128.9, 128.5, 127.6, 127.4, 125.3, 113.6, 62.4, 20.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{18}N_2NaOS$ 333.1032, found 333.1022.



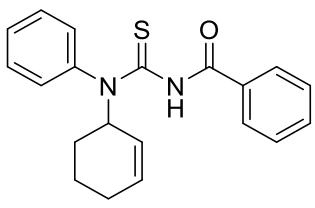
1ad

***N*-((3-methylbut-2-en-1-yl)(phenyl)carbamothioyl)benzamide (1ad):** The general procedure from N-(3-methylbut-2-en-1-yl)aniline (1612.5 mg, 10 mmol), benzoyl chloride (1406 mg, 10 mmol), KSCN (1943.6 mg, 20 mmol) and acetone (10 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1ad** as white solid (1930.2 mg, 59% yield). Mp: 112.2-113.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.47 (q, J = 8.8, 7.8 Hz, 3H), 7.40 – 7.21 (m, 7H), 5.45 (t, J = 7.2 Hz, 1H), 4.87 (s, 2H), 1.69 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.4, 162.8, 143.3, 137.7, 133.0, 132.5, 129.2, 128.6, 127.9, 127.4, 126.4, 117.3, 55.0, 25.6, 17.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{20}N_2NaOS$ 347.1189, found 347.1178.



1ae

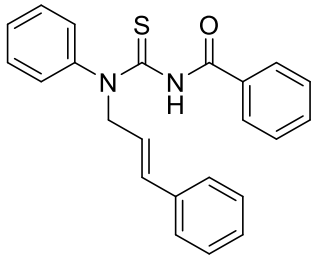
N-((4-methoxyphenyl)(3-methylbut-2-en-1-yl)carbamothioyl)benzamide (1ae): The general procedure from 4-methoxy-N-(3-methylbut-2-en-1-yl)aniline (1912.7 mg, 10 mmol), benzoyl chloride (1406 mg, 10 mmol), KSCN (1943.6 mg, 20 mmol) and acetone (10 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **1ae** as white solid (2020.7 mg, 57% yield). Mp: 112.2-113.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.48 (t, *J* = 7.2 Hz, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.44 (d, *J* = 7.9 Hz, 1H), 4.85 (d, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 1.70 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.33, 162.90, 158.78, 137.55, 135.51, 133.15, 132.39, 128.56, 128.45, 127.43, 127.36, 127.30, 114.30, 55.29, 54.88, 25.59, 17.85.



1af

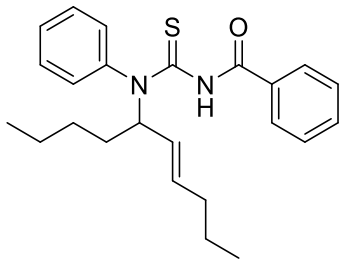
***N*-(cyclohex-2-en-1-yl(phenyl)carbamothioyl)benzamide (1af):** The general procedure from *N*-(cyclohex-2-

en-1-yl)aniline (1727.0 mg, 10 mmol), benzoyl chloride (1406 mg, 10 mmol), KSCN (1943.6 mg, 20 mmol) and acetone (10 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1af** as white solid (2007.1 mg, 60% yield). Mp: 125.5-127.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.55 – 7.16 (m, 10H), 6.30 (s, 1H), 5.83 (d, J = 14.1 Hz, 2H), 2.24 – 2.07 (m, 1H), 1.99 – 1.76 (m, 2H), 1.63 (m, 2H), 1.44 (q, J = 11.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 163.3, 139.4, 133.3, 132.3, 131.0, 129.0, 128.7, 128.5, 128.3, 127.1, 126.9, 59.0, 26.8, 24.2, 20.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{20}N_2NaOS$ 359.1189, found 359.1179.



1ag

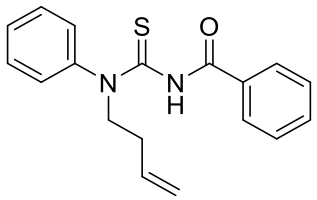
***N*-(cinnamyl(phenyl)carbamothioyl)benzamide (1ag):** The general procedure from *N*-cinnamylaniline (1465.0 mg, 7 mmol), benzoyl chloride (984.2 mg, 7 mmol), KSCN (1360.5 mg, 14 mmol) and acetone (7 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether : ethyl acetate = 10:1 to give **1ag** as white solid (1647.2 mg, 63% yield). Mp: 121.4-123.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.47 (dt, J = 15.2, 7.2 Hz, 3H), 7.30 (m, 12H), 6.61 – 6.35 (m, 2H), 5.03 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 162.8, 143.2, 136.4, 134.5, 133.0, 132.6, 129.4, 128.7, 128.5, 128.1, 127.8, 127.4, 126.5, 126.3, 122.0, 59.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{20}N_2NaOS$ 395.1189, found 395.1186.



1ah

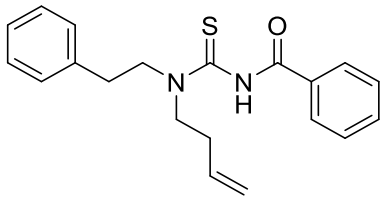
(E)-*N*-(dec-6-en-5-yl(phenyl)carbamothioyl)benzamide (1ah): The general procedure from (E)-*N*-(dec-6-en-5-yl)aniline (343.3 mg, 1.22 mmol), benzoyl isothiocyanate (199.1 mg, 1.22 mmol) and THF (12 mL) at room

temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1ah** as yellow liquid (365.4 mg, 72% yield). There is a small amount of impurities mixed in the product, but it can still be used for the next step. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.29 (m, 6H), 7.22 – 7.10 (m, 4H), 6.06 (d, J = 8.1 Hz, 1H), 5.73 (dt, J = 14.8, 6.8 Hz, 1H), 5.08 (dd, J = 15.8, 7.9 Hz, 1H), 1.91 (dq, J = 14.4, 7.8, 7.2 Hz, 2H), 1.70 (dq, J = 9.6, 4.9 Hz, 1H), 1.28 (m, 6H), 0.80 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 163.3, 139.2, 135.9, 133.4, 132.2, 128.9, 128.6, 128.5, 127.4, 127.1, 63.6, 34.4, 32.0, 28.2, 26.8, 22.4, 22.0, 13.9, 13.6.



1ai

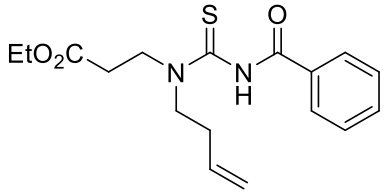
***N*-(but-3-en-1-yl(phenyl)carbamothioyl)benzamide (1ai):** The general procedure from *N*-(but-3-en-1-yl)aniline (906.9 mg, 6.16 mmol), benzoyl chloride (866.1 mg, 6.16 mmol), KSCN (1197.3 mg, 12.32 mmol) and acetone (6.2 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1ai** as white solid (1057.6 mg, 55% yield). Mp: 122.3-124.3 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.69 – 7.15 (m, 10H), 5.82 (m, 1H), 5.10 (m, 2H), 4.34 (s, 2H), 2.56 (q, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 162.7, 143.1, 134.3, 132.9, 132.5, 129.3, 128.6, 128.0, 127.4, 126.2, 117.1, 56.1, 30.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{18}N_2NaOS$ 333.1032, found 333.1022.



1aj

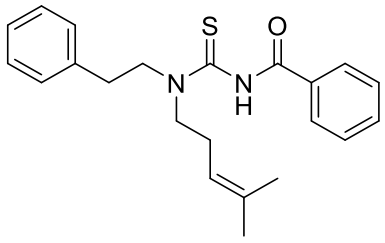
***N*-(but-3-en-1-yl(phenethyl)carbamothioyl)benzamide (1aj):** The general procedure from *N*-phenethylbut-3-en-1-amine (1752.8 mg, 10 mmol), benzoyl chloride (1406 mg, 10 mmol), KSCN (1943.6 mg, 20 mmol) and acetone (10 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1aj** as white solid (2034.5 mg, 60% yield). The spectra of this compound show more peaks because thioamide compounds are easy to isomerize. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.17 (d, J = 163.8 Hz, 1H), 7.78 (m, 2H), 7.52 (m, 3H), 7.40 – 7.01 (m, 6H), 6.03 – 5.57 (m, 1H), 5.15 (m, 2H), 4.10 (m, 2H), 3.69 (m, 2H), 3.07 (m, 2H), 2.75 – 2.31 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 180.3, 163.8, 138.3, 137.7, 134.4, 133.7, 132.8, 132.4, 128.8, 128.7, 128.5, 127.7, 126.7, 126.5, 117.9, 117.2, 55.4, 55.2, 53.4, 53.2, 34.4, 32.3, 30.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{22}N_2NaOS$ 361.1345, found 361.1335.



1ak

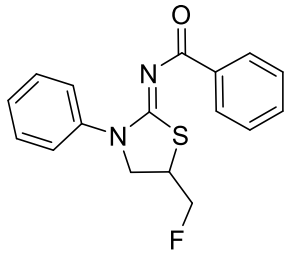
ethyl 3-(3-benzoyl-1-(but-3-en-1-yl)thioureido)propanoate (1ak): The general procedure from ethyl 3-(but-3-en-1-ylamino)propanoate (513.7 mg, 3 mmol), benzoyl isothiocyanate (489.7 mg, 3 mmol) and THF (30 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1ak** as white solid (602.4 mg, 60% yield). The spectra of this compound show more peaks because thioamide compounds are easy to isomerize. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (m, 1H), 7.98 – 7.73 (m, 2H), 7.52 (m, 3H), 6.05 – 5.56 (m, 1H), 5.30 – 4.98 (m, 2H), 4.33 – 4.07 (m, 3H), 3.91 (d, J = 40.0 Hz, 2H), 3.66 (s, 1H), 3.08 – 2.65 (m, 2H), 2.53 (d, J = 56.6 Hz, 2H), 1.40 – 1.14 (m, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 180.7, 171.5,164.4, 163.7, 134.3, 133.7, 132.8, 128.7, 127.8, 118.0, 117.3, 61.2, 60.8, 53.6, 52.3, 48.9, 48.2, 32.4, 31.4, 30.1, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}N_2NaO_3S$ 357.1243, found 357.1234.



1al

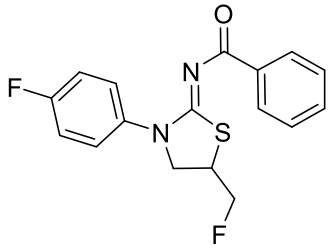
***N*-((4-methylpent-3-en-1-yl)(phenethyl)carbamothioyl)benzamide (1al):** The general procedure from 4-methyl-*N*-phenethylpent-3-en-1-amine (610.0 mg, 3 mmol), benzoyl isothiocyanate (489.7 mg, 3 mmol) and THF (30 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **1al** as white solid (844.8 mg, 83% yield). Mp: 72.1-74.2

°C.The spectra of this compound show more peaks because thioamide compounds are easy to isomerize.. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (m, 1H), 7.94 – 6.83 (m, 10H), 5.09 (m, 1H), 4.31 – 3.39 (m, 4H), 3.07 (m, 2H), 2.75 – 2.22 (m, 2H), 1.94 – 1.44 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.9, 163.6, 138.4, 135.3, 134.9, 132.7, 132.5, 128.7, 128.5, 127.6, 126.6, 126.4, 119.6, 119.1, 55.4, 55.1, 53.7, 53.5, 34.4, 32.3, 26.8, 25.6, 24.9, 17.8, 17.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{26}N_2NaOS$ 389.1658, found 389.1657.



2a

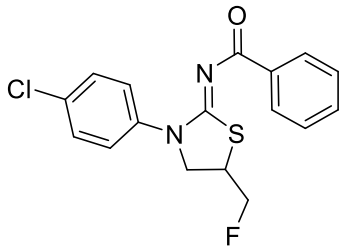
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide (2a): The general procedure from *N*-(allyl(phenyl)carbamothioyl)benzamide **1a** (59.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane = 1:2 to give **2a** as white solid (53.9 mg, 86% yield). Mp: 100-104.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 – 8.01 (m, 2H), 7.65 – 7.43 (m, 5H), 7.35 (dt, J = 16.3, 7.4 Hz, 3H), 4.59 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.51 (m, 1H), 4.43 (t, J = 9.7 Hz, 0.5H), 4.28 (dd, J = 11.1, 6.9 Hz, 1H), 4.18 (dd, J = 11.1, 2.4 Hz, 1H), 3.88 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 169.1, 140.1, 136.0, 132.2, 129.8, 129.0, 128.1, 126.9, 124.7, 82.2 (d, J = 178.9 Hz), 53.4 (d, J = 3.0 Hz), 40.2 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.77. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}FN_2NaOS$ 337.0781, found 337.0774.



2b

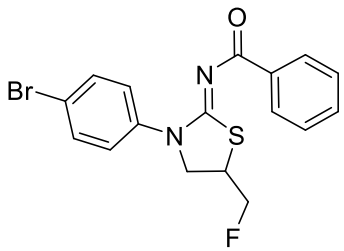
(Z)-*N*-(5-(fluoromethyl)-3-(4-fluorophenyl)thiazolidin-2-ylidene)benzamide (2b): The general procedure from *N*-(allyl(4-fluorophenyl)carbamothioyl)benzamide **1b** (51.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23

mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2b** as white solid (51.9 mg, 78% yield). Mp: 90.0-92.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.47 (m, 3H), 7.37 (dd, J = 8.3, 7.0 Hz, 2H), 7.23 – 7.13 (m, 2H), 4.55 – 4.47 (m, 0.5H), 4.41 (t, J = 9.6 Hz, 1H), 4.23 (dd, J = 11.1, 6.9 Hz, 0.5H), 4.12 (dd, J = 11.1, 2.5 Hz, 1H), 3.88 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.13, 169.32, 160.88 (d, J = 247.5 Hz), 135.98, 135.85, 132.31, 129.71, 128.08, 126.63 (d, J = 8.1 Hz), 115.89 (d, J = 22.8 Hz), 82.19 (d, J = 179.0 Hz), 53.40 (d, J = 3.0 Hz), 40.27 (d, J = 20.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.00, -212.24. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}F_2N_2NaOS$ 355.0687, found 355.0676.



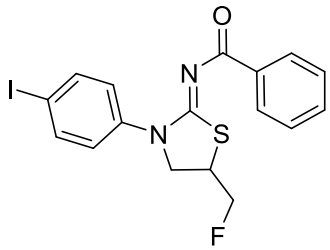
2c

(Z)-*N*-(3-(4-chlorophenyl)-5-(fluoromethyl)thiazolidin-2-ylidene)benzamide (2c): The general procedure from *N*-(allyl(4-chlorophenyl)carbamothioyl)benzamide **1c** (66.2 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2c** as white solid (51.6 mg, 74% yield). Mp: 120.5-127.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 2H), 7.53 – 7.42 (m, 5H), 7.38 (dd, J = 8.4, 7.0 Hz, 2H), 4.58 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.55 – 4.45 (m, 1H), 4.40 (t, J = 9.6 Hz, 0.5H), 4.23 (dd, J = 11.1, 7.0 Hz, 1H), 4.11 (dd, J = 11.0, 2.6 Hz, 1H), 3.87 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 169.1, 138.5, 135.8, 132.4, 132.1, 129.7, 129.0, 128.1, 125.8, 82.1 (d, J = 179.3 Hz), 53.1 (d, J = 3.1 Hz), 40.2 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.26. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}ClFN_2NaOS$ 371.0392, found 371.0386.



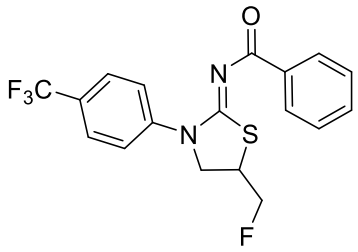
2d

(Z)-*N*-(3-(4- bromophenyl)-5-(fluoromethyl)thiazolidin-2-ylidene)benzamide (2d): The general procedure from *N*-(allyl(4-bromophenyl)carbamothioyl)benzamide **1d** (75.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2d** as white solid (56.5 mg, 72% yield). Mp: 84.9-89.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.4 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.45 – 7.33 (m, 4H), 4.59 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.49 (m, 1H), 4.40 (t, J = 9.6 Hz, 0.5H), 4.24 (dd, J = 11.0, 7.0 Hz, 1H), 4.12 (dd, J = 11.0, 2.5 Hz, 1H), 3.87 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 169.1, 139.1, 135.8, 132.4, 132.0, 129.8, 128.14 126.1, 120.0, 82.1 (d, J = 179.2 Hz), 53.0 (d, J = 3.0 Hz), 40.2 (d, J = 20.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.17. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}BrFN_2NaOS$ 414.9886, found 414.9883.



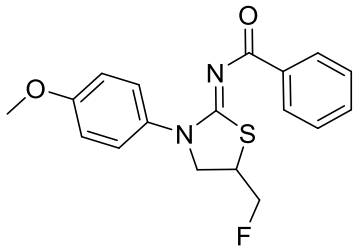
2e

(Z)-*N*-(5-(fluoromethyl)-3-(4-iodophenyl)thiazolidin-2-ylidene)benzamide (2e): The general procedure from *N*-(allyl(4-iodophenyl)carbamothioyl)benzamide **1e** (84.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2e** as white solid (74.6 mg, 85% yield). Mp: 98.1-102.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.4 Hz, 2H), 7.83 – 7.74 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 2H), 7.35 – 7.26 (m, 2H), 4.57 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.48 (m, 1H), 4.38 (t, J = 9.6 Hz, 0.5H), 4.22 (dd, J = 11.0, 7.0 Hz, 1H), 4.10 (dd, J = 11.0, 2.6 Hz, 1H), 3.92 – 3.80 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 169.0, 139.7, 137.9, 135.7, 132.4, 129.7, 128.1, 126.2, 91.1, 82.1 (d, J = 179.2 Hz), 52.9 (d, J = 3.0 Hz), 40.2 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.19. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}IFN_2NaOS$ 462.9748, found 462.9760.



2f

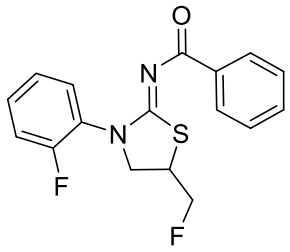
(Z)-*N*-(5-(fluoromethyl)-3-(4-(trifluoromethyl)phenyl)thiazolidin-2-ylidene)benzamide (2f): The general procedure from *N*-(allyl(4-(trifluoromethyl)phenyl)carbamothioyl)benzamide **1f** (72.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2f** as white solid (60.8 mg, 87% yield).Mp: 126.7-127.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.07 (m, 2H), 7.80 – 7.66 (m, 4H), 7.54 – 7.46 (m, 1H), 7.40 (dd, J = 8.3, 7.0 Hz, 2H), 4.59 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.50 (m, 1H), 4.40 (t, J = 9.6 Hz, 0.5H), 4.30 (dd, J = 10.9, 6.9 Hz, 1H), 4.17 (dd, J = 10.9, 2.6 Hz, 1H), 3.89 (m, Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 169.3, 143.0, 135.6, 132.6, 129.8, 128.2 (q, J = 32.8 Hz), 128.2, 126.0 (q, J = 3.7 Hz), 123.8 (q, J = 272.2 Hz), 124.3, 82.1 (d, J = 179.4 Hz), 52.8 (d, J = 3.1 Hz), 40.2 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.31, -212.45. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{14}F_4N_2NaOS$ 405.0655, found 405.0653.



2g

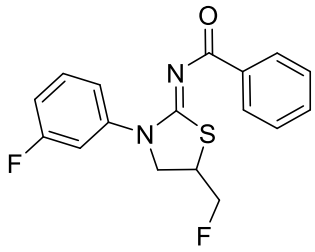
(Z)-*N*-(5-(fluoromethyl)-3-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (2g): The general procedure from *N*-(allyl(4-methoxyphenyl)carbamothioyl)benzamide **1g** (65.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2g** as yellow liquid (22.4 mg, 33% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.4 Hz, 2H), 7.83 – 7.74 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 2H), 7.35 – 7.26 (m, 2H), 4.57 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.48 (m, 1H), 4.38 (t, J = 9.6 Hz, 0.5H), 4.22

(dd, J = 11.0, 7.0 Hz, 1H), 4.10 (dd, J = 11.0, 2.6 Hz, 1H), 3.92 – 3.80 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 169.0, 139.7, 137.9, 135.7, 132.4, 129.7, 128.1, 126.2, 91.1, 82.1 (d, J = 179.2 Hz), 52.9 (d, J = 3.0 Hz), 40.2 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.19. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}IFN_2NaOS$ 462.9748, found 462.9760.



2h

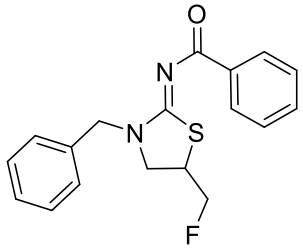
(Z)-*N*-(5-(fluoromethyl)-3-(2-fluorophenyl)thiazolidin-2-ylidene)benzamide (2h): The general procedure from *N*-(allyl(2-fluorophenyl)carbamothioyl)benzamide **1h** (62.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2h** as yellow liquid (47.5 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.3, 1.4 Hz, 2H), 7.53 – 7.36 (m, 3H), 7.36 – 7.21 (m, 4H), 4.62 – 4.54 (m, 1H), 4.53 – 4.44 (m, 1H), 4.18 (dd, J = 11.1, 6.9 Hz, 1H), 4.08 (dd, J = 11.1, 2.2 Hz, 1H), 3.92 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 169.9, 157.3 (d, J = 251.3 Hz), 135.8, 132.2, 129.8, 129.6 (d, J = 7.8 Hz), 128.8, 128.0, 127.4 (d, J = 11.8 Hz), 124.5 (d, J = 3.7 Hz), 116.8 (d, J = 19.9 Hz), 82.1 (d, J = 179.0 Hz), 52.6 (t, J = 2.9 Hz), 41.2 (d, J = 21.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.45, -211.73. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}F_2N_2NaOS$ 355.0687, found 355.0682.



2i

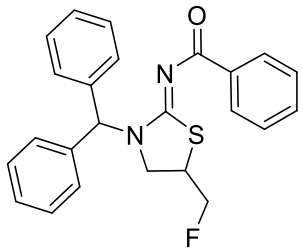
(Z)-*N*-(5-(fluoromethyl)-3-(3-fluorophenyl)thiazolidin-2-ylidene)benzamide (3i): The general procedure from *N*-(allyl(3-fluorophenyl)carbamothioyl)benzamide **1i** (62.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified

by column chromatography on silica gel using dichloromethane to give **2i** as yellow liquid (54.7 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.09 (m, 2H), 7.54 – 7.35 (m, 5H), 7.30 (dd, J = 8.2, 2.1 Hz, 1H), 7.04 (td, J = 8.2, 2.5 Hz, 1H), 4.59 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.50 (m, 1H), 4.40 (t, J = 9.6 Hz, 0.5H), 4.26 (dd, J = 11.0, 6.9 Hz, 1H), 4.16 (dd, J = 11.0, 2.5 Hz, 1H), 3.88 (m, Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.20, 169.10, 162.62 (d, J = 246.8 Hz), 141.36 (d, J = 10.0 Hz), 135.77, 132.43, 130.03 (d, J = 9.2 Hz), 129.79, 128.16, 119.64 (d, J = 3.2 Hz), 113.61 (d, J = 21.1 Hz), 112.20 (d, J = 24.9 Hz), 82.11 (d, J = 179.3 Hz), 53.10 (d, J = 3.0 Hz), 40.15 (d, J = 20.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.16, -212.12. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}F_2N_2NaOS$ 355.0687, found 355.0677.



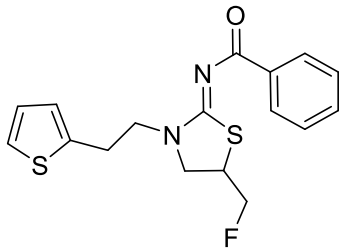
2j

(Z)-*N*-(3-benzyl-5-(fluoromethyl)thiazolidin-2-ylidene)benzamide (2j): The general procedure from *N*-(allyl(benzyl)carbamothioyl)benzamidee **1j** (62.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2j** as white solid (40.8 mg, 62% yield). Mp: 122.2-125.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 – 8.27 (m, 2H), 7.55 – 7.47 (m, 1H), 7.43 (dd, J = 8.3, 6.8 Hz, 2H), 7.40 – 7.30 (m, 5H), 5.06 – 4.94 (m, 2H), 4.41 (m, 1H), 4.25 (dt, J = 47.6, 9.6 Hz, 1H), 3.75 (m, 1H), 3.70 – 3.60 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 170.2, 136.3, 135.4, 132.1, 129.7, 129.0, 128.2, 128.2, 128.1, 82.5 (d, J = 178.8 Hz), 51.3, 50.2 (d, J = 3.1 Hz), 40.3 (d, J = 20.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.12. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaOS$ 351.0938, found 351.0935.



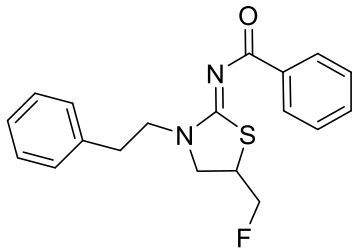
2k

(Z)-*N*-(3-benzhydryl-5-(fluoromethyl)thiazolidin-2-ylidene)benzamide (3k): The general procedure from *N*-(allyl(benzhydryl)carbamothioyl)benzamide **1k** (77.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2k** as white solid (52.8 mg, 65% yield).Mp: 122.7-124.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.15 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.26 (m, 13H), 4.48 (dd, J = 9.6, 4.9 Hz, 0.5H), 4.44 – 4.32 (m, 1H), 4.26 (t, J = 9.6 Hz, 0.5H), 3.73 (m, 1H), 3.63 (dd, J = 11.5, 2.9 Hz, 1H), 3.54 (dd, J = 11.6, 7.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 170.3, 137.8, 137.0, 136.2, 132.1, 129.7, 129.0, 128.8, 128.8, 128.2, 128.1, 128.0, 128.0, 82.4 (d, J = 179.0 Hz), 63.5, 48.0 (d, J = 2.9 Hz), 40.3 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.21. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{21}FN_2NaOS$ 427.1251, found 427.1253.



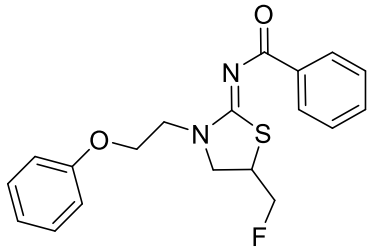
2l

(Z)-*N*-(5-(fluoromethyl)-3-(2-(thiophen-2-yl)ethyl)thiazolidin-2-ylidene)benzamide (2l): The general procedure from *N*-(allyl(2-(thiophen-2-yl)ethyl)carbamothioyl)benzamide **1l** (66.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2l** as yellow liquid (36.6 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.23 (m, 2H), 7.56 – 7.47 (m, 1H), 7.44 (dd, J = 8.2, 6.8 Hz, 2H), 7.19 (dd, J = 5.1, 1.2 Hz, 1H), 6.95 (dd, J = 5.2, 3.4 Hz, 1H), 6.89 (dd, J = 3.4, 1.2 Hz, 1H), 4.34 (m, 1H), 4.22 – 4.04 (m, 2H), 3.93 (dt, J = 13.7, 6.9 Hz, 1H), 3.74 – 3.65 (m, 1H), 3.65 – 3.59 (m, 2H), 3.31 (td, J = 7.1, 4.8 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 169.5, 140.4, 136.3, 132.1, 129.7, 128.1, 127.2, 125.8, 124.4, 82.4 (d, J = 178.7 Hz), 51.6 (d, J = 3.0 Hz), 49.5, 40.5 (d, J = 21.0 Hz), 27.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.52. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{17}FN_2NaOS_2$ 371.0659, found 371.0648.



2m

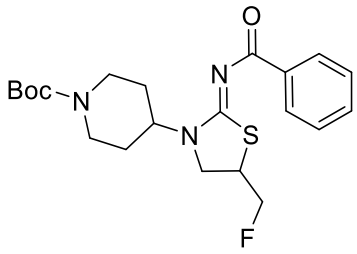
(Z)-*N*-(5-(fluoromethyl)-3-phenethylthiazolidin-2-ylidene)benzamide (2m): The general procedure from *N*-(allyl(phenethyl)carbamothioyl)benzamide **1m** (64.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2m** as white solid (47.6 mg, 70% yield).Mp: 72.8-73.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 – 8.24 (m, 2H), 7.52 (td, J = 7.1, 1.4 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.29 – 7.19 (m, 3H), 4.31 (m, 1H), 4.15 – 3.99 (m, 2H), 3.91 (m, 1H), 3.72 – 3.62 (m, 1H), 3.62 – 3.49 (m, 2H), 3.08 (dq, J = 13.4, 6.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 169.4, 138.1, 136.4, 132.0, 129.6, 128.8, 128.0, 126.8, 82.3 (d, J = 178.6 Hz), 51.5 (d, J = 2.9 Hz), 49.2, 40.3 (d, J = 20.9 Hz), 33.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.44. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{19}H_{20}FN_2OS$ 343.1275, found 343.1254.



2n

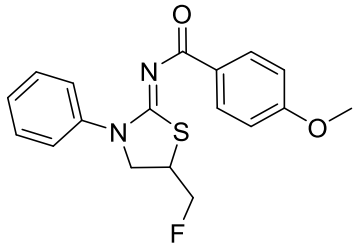
(Z)-*N*-(5-(fluoromethyl)-3-(2-phenoxyethyl)thiazolidin-2-ylidene)benzamide (2n): The general procedure from *N*-(allyl(2-phenoxyethyl)carbamothioyl)benzamide **1n** (68.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2n** as yellow liquid (59.7 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 4.48 – 4.16 (m, 5H), 4.13 – 4.01 (m, 2H), 3.98 (dd, J = 11.5, 7.1 Hz, 1H), 3.77 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 169.7, 158.1, 136.3, 132.1, 129.7,

129.7, 128.1, 121.4, 114.4, 82.3 (d, J = 178.7 Hz), 65.7, 52.7 (d, J = 2.8 Hz), 47.3, 40.8 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.51. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{19}FN_2NaO_2S$ 381.1043, found 381.1047.



2o

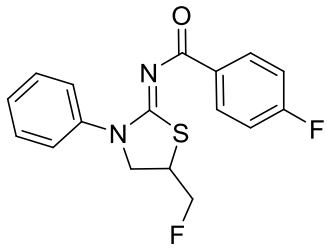
tert-butyl (Z)-4-(2-(benzoylimino)-5-(fluoromethyl)thiazolidin-3-yl)piperidine-1-carboxylate (2o): The general procedure from tert-butyl 4-(1-allyl-3-benzoylthioureido)piperidine-1-carboxylate **1o** (80.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane : methane = 100:1 to give **2o** as yellow liquid (57.6 mg, 66% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 – 8.19 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (td, J = 7.6, 1.8 Hz, 2H), 4.81 (td, J = 12.2, 4.5 Hz, 1H), 4.44 (m, 1H), 4.37 – 4.15 (m, 3H), 3.86 – 3.60 (m, 3H), 2.89 (s, 2H), 1.88 (d, J = 10.8 Hz, 2H), 1.66 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 169.5, 154.6, 136.3, 132.1, 129.6, 128.1, 82.2 (d, J = 178.6 Hz), 80.0, 54.9, 46.8, 40.2 (d, J = 20.6 Hz), 29.4, 28.7, 28.4, 27.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.04. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{28}FN_3NaO_3S$ 444.1728, found 444.1724.



2p

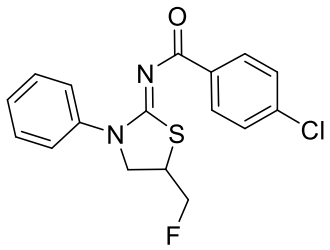
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)-4-methoxybenzamide (2p): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-4-methoxybenzamide **1p** (65.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2p** as white solid (56.1 mg, 74%

yield).Mp: 94.6-96.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 2H), 7.57 – 7.44 (m, 4H), 7.33 (tt, J = 7.1, 1.5 Hz, 1H), 6.92 – 6.79 (m, 2H), 4.59 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.54 – 4.45 (m, 1H), 4.42 (t, J = 9.7 Hz, 0.5H), 4.27 (dd, J = 11.1, 6.9 Hz, 1H), 4.16 (dd, J = 11.0, 2.4 Hz, 1H), 3.83 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 168.4, 163.0, 140.2, 131.9, 128.9, 128.8, 126.7, 124.6, 113.3, 82.2 (d, J = 179.0 Hz), 55.3, 53.2(d, J = 3.0 Hz), 40.2 (d, J = 20.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.55. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaO_2S$ 367.0887, found 367.0877.



2q

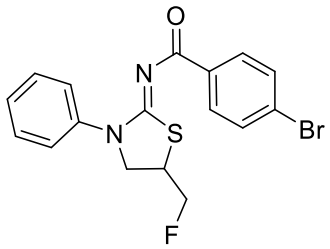
(Z)-4-fluoro-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide (2q): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-4-fluorobenzamide **1q** (62.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2q** as yellow liquid (57.5 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 – 8.19 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (td, J = 7.6, 1.8 Hz, 2H), 4.81 (td, J = 12.2, 4.5 Hz, 1H), 4.44 (m, 1H), 4.37 – 4.15 (m, 3H), 3.86 – 3.60 (m, 3H), 2.89 (s, 2H), 1.88 (d, J = 10.8 Hz, 2H), 1.66 (s, 2H), 1.49 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 169.2, 165.4 (d, J = 252.5 Hz), 140.0, 132.3 (d, J = 2.9 Hz), 132.2 (d, J = 9.2 Hz), 129.0, 127.0, 124.7, 115.0 (d, J = 21.7 Hz), 82.2 (d, J = 178.8 Hz), 53.4 (d, J = 3.0 Hz), 40.3 (d, J = 20.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.28, -212.04. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}F_2N_2NaOS$ 355.0687, found 355.0675.



2r

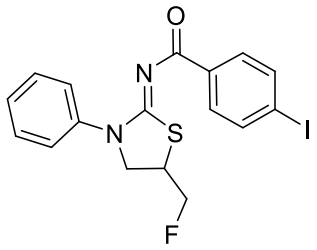
(Z)-4-chloro-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide (2r): The general procedure

from *N*-(allyl(phenyl)carbamothioyl)-4-chlorobenzamide **1r** (66.2 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2r** as yellow liquid (55.6 mg, 80% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 4.2 Hz, 4H), 7.33 (t, J = 6.6 Hz, 3H), 4.58 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.55 – 4.45 (m, 1H), 4.42 (t, J = 9.6 Hz, 0.5H), 4.27 (dd, J = 11.3, 7.0 Hz, 1H), 4.15 (dt, J = 11.3, 1.9 Hz, 1H), 3.95 – 3.81 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 169.4, 139.9, 138.4, 134.5, 131.1, 129.0, 128.3, 127.0, 124.6, 82.1 (d, J = 179.2 Hz), 53.4 (d, J = 3.1 Hz), 40.3 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.25. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}ClFN_2NaOS$ 371.0392, found 371.0370.



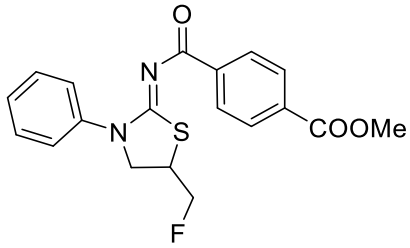
2s

(Z)-4-bromo-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide (2s): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-4-bromobenzamide **1s** (75.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2s** as yellow liquid (59.2 mg, 75% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.56 – 7.42 (m, 6H), 7.34 (dh, J = 8.7, 4.5 Hz, 1H), 4.59 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.55 – 4.46 (m, 1H), 4.42 (t, J = 9.6 Hz, 0.5H), 4.27 (dd, J = 11.2, 7.0 Hz, 1H), 4.16 (dd, J = 11.2, 2.5 Hz, 1H), 3.88 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 169.5, 139.9, 135.0, 131.3, 131.3, 129.0, 127.2, 127.0, 124.7, 82.1 (d, J = 179.0 Hz), 53.4 (d, J = 3.0 Hz), 40.3 (d, J = 20.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.24. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}BrFN_2NaOS$ 414.9886, found 414.9887.



2t

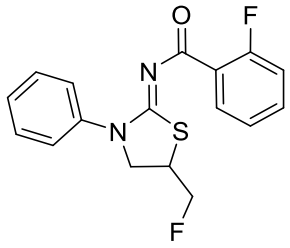
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)-4-iodobenzamide (2t): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-4-iodobenzamide **1t** (84.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane = 1:3 to give **2t** as yellow liquid (74.3 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 2H), 7.76 – 7.65 (m, 2H), 7.56 – 7.41 (m, 4H), 7.34 (m, 1H), 4.60 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.56 – 4.47 (m, 1H), 4.42 (t, J = 9.6 Hz, 0.5H), 4.28 (dd, J = 11.2, 7.0 Hz, 1H), 4.17 (dd, J = 11.2, 2.5 Hz, 1H), 3.89 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 169.5, 137.4, 135.6, 131.3, 129.0, 127.1, 124.7, 100.0, 82.2 (d, J = 178.8 Hz), 53.5(d, J = 1.5 Hz), 40.3 (d, J = 20.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.14. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}IFN_2NaOS$ 462.9748, found 462.9758.



2u

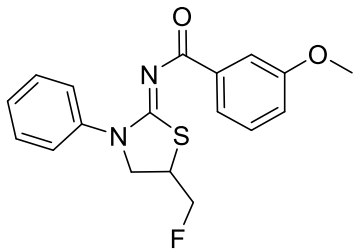
methyl (Z)-4-((5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)carbamoyl)benzoate (2u): The general procedure from methyl 4-((allyl(phenyl)carbamothioyl)carbamoyl)benzoate **1u** (70.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane : methane = 100:1 to give **2u** as white solid (56.0 mg, 79% yield). Mp:86-89.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 2H), 8.08 – 7.99 (m, 2H), 7.51 (d, J = 5.5 Hz, 4H), 7.36 (tt, J = 5.8, 2.9 Hz, 1H), 4.61 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.58 – 4.48 (m, 1H), 4.44 (t, J = 9.7 Hz, 0.5H), 4.31 (dd, J = 11.2, 7.0 Hz, 1H), 4.19 (dd, J = 11.3, 2.5 Hz, 1H), 3.91 (m,

4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 169.8, 166.7, 139.9, 139.9, 133.0, 129.6, 129.3, 129.1, 127.2, 124.7, 82.2 (d, J = 179.3 Hz), 53.5 (d, J = 2.9 Hz), 52.2, 40.3 (d, J = 21.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.29. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}FN_2NaO_3S$ 395.0836, found 395.0830.



2v

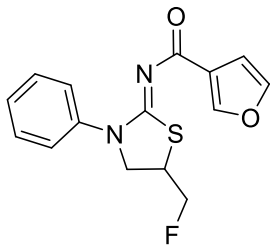
(Z)-2-fluoro-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)benzamide (2v): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-2-fluorobenzamide **1v** (62.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2v** as yellow liquid (46.7 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (td, J = 7.7, 2.0 Hz, 1H), 7.61 – 7.37 (m, 5H), 7.31 (t, J = 7.3 Hz, 1H), 7.16 – 7.02 (m, 2H), 4.59 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.55 – 4.47 (m, 1H), 4.43 (t, J = 9.7 Hz, 0.5H), 4.29 (dd, J = 11.1, 6.9 Hz, 1H), 4.17 (dd, J = 11.1, 2.5 Hz, 1H), 3.88 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 169.3, 162.4 (d, J = 259.7 Hz), 139.9, 133.5 (d, J = 9.1 Hz), 132.5, 128.9, 126.9, 124.5, 124.5 (d, J = 9.1 Hz), 123.5 (d, J = 3.8 Hz), 116.8 (d, J = 22.6 Hz), 82.1 (d, J = 179.1 Hz), 53.5 (d, J = 3.0 Hz), 40.2 (d, J = 20.9 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.80, -212.11. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{14}F_2N_2NaOS$ 355.0687, found 355.0683.



2w

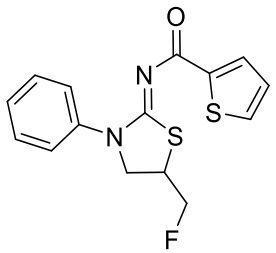
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)-3-methoxybenzamide (2w): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-3-methoxybenzamide **1w** (65.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane : methane = 200:1 to give **2w** as yellow liquid

(56.6 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 2H), 7.59 – 7.43 (m, 4H), 7.36 – 7.22 (m, 2H), 7.06 – 6.99 (m, 1H), 4.59 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.56 – 4.47 (m, 1H), 4.42 (t, J = 9.7 Hz, 0.5H), 4.28 (dd, J = 11.2, 7.0 Hz, 1H), 4.17 (dd, J = 11.1, 2.4 Hz, 1H), 3.88 (m, 1H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 169.1, 159.4, 140.1, 137.4, 129.1, 128.9, 126.9, 124.6, 122.4, 119.3, 113.6, 82.2 (d, J = 178.9 Hz), 55.2, 53.3 (d, J = 3.0 Hz), 40.2 (d, J = 20.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.85. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaO_2S$ 327.0574, found 367.0896.



2x

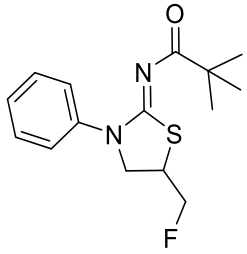
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)furan-3-carboxamide (2x): The general procedure from *N*-(allyl(phenyl)carbamothioyl)furan-3-carboxamide **1x** (57.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2x** as yellow liquid (44.3 mg, 73% yield). Mp:90-93.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.42 (m, 5H), 7.31 (td, J = 7.3, 1.3 Hz, 1H), 7.04 (d, J = 3.4 Hz, 1H), 6.43 (dd, J = 3.4, 1.7 Hz, 1H), 4.58 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.54 – 4.47 (m, 1H), 4.42 (t, J = 9.7 Hz, 0.5H), 4.28 (dd, J = 11.1, 6.9 Hz, 1H), 4.16 (dd, J = 11.1, 2.4 Hz, 1H), 3.87 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 167.2, 151.1, 146.2, 139.9, 128.9, 126.8, 124.5, 117.6, 111.7, 82.1 (d, J = 179.2 Hz), 53.4 (d, J = 2.9 Hz), 40.3 (d, J = 21.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.95. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{13}FN_2NaO_2S$ 327.0574, found 327.0563.



2y

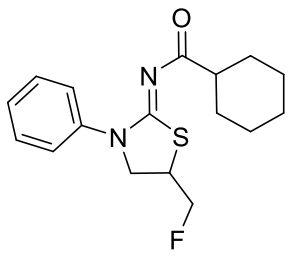
(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)thiophene-2-carboxamide (2y): The general

procedure from *N*-(allyl(phenyl)carbamothioyl)thiophene-2-carboxamide **1y** (60.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2y** as yellow liquid (48.8 mg, 76% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 3.7, 1.3 Hz, 1H), 7.59 – 7.40 (m, 5H), 7.36 – 7.27 (m, 1H), 7.04 (dd, J = 5.0, 3.7 Hz, 1H), 4.58 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.54 – 4.45 (m, 1H), 4.41 (t, J = 9.7 Hz, 0.5H), 4.28 (dd, J = 11.1, 7.0 Hz, 1H), 4.16 (dd, J = 11.1, 2.4 Hz, 1H), 3.87 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 168.3, 142.3, 139.8, 132.3, 132.2, 128.9, 127.9, 126.8, 124.5, 82.1 (d, J = 179.0 Hz), 53.3 (d, J = 3.0 Hz), 40.3 (d, J = 21.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.85. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{13}FN_2NaOS_2$ 343.0346, found 343.0334.



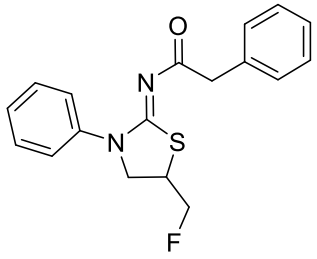
2z

(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)pivalamide (2z): The general procedure from *N*-(allyl(phenyl)carbamothioyl)pivalamide **1z** (55.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane = 1:3 to give **2z** as white solid (39.1 mg, 66% yield).Mp: 106.5-108.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.37 (m, 4H), 7.36 – 7.23 (m, 1H), 4.56 (dd, J = 9.6, 4.8 Hz, 0.5H), 4.54 – 4.45 (m, 1H), 4.39 (d, J = 9.7 Hz, 0.5H), 4.22 (dd, J = 11.0, 6.9 Hz, 1H), 4.12 (dd, J = 11.0, 2.5 Hz, 1H), 3.83 (m, 1H), 1.16 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.9, 167.9, 140.2, 128.6, 126.2, 124.1, 82.2 (d, J = 179.0 Hz), 52.9 (d, J = 2.9 Hz), 41.2, 39.9 (d, J = 21.0 Hz), 27.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.50. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{19}FN_2NaOS$ 317.1094, found 317.1085.



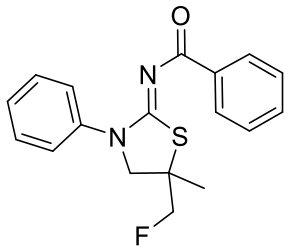
2aa

(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)cyclohexanecarboxamide (2aa): The general procedure from *N*-(allyl(phenyl)carbamothioyl)cyclohexanecarboxamide **1aa** (66.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2aa** as white solid (31.5 mg, 49% yield).Mp: 92.4-95.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 4H), 7.30 – 7.27 (m, 1H), 4.55 (dd, J = 9.5, 4.7 Hz, 0.5H), 4.49 – 4.43 (m, 1H), 4.38 (t, J = 9.8 Hz, 0.5H), 4.19 (dd, J = 11.1, 6.9 Hz, 1H), 4.10 (dd, J = 11.1, 2.4 Hz, 1H), 3.80 (m, 1H), 2.33 (tt, J = 11.3, 3.6 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.71 (dq, J = 11.9, 3.5 Hz, 2H), 1.66 – 1.52 (m, 2H), 1.38 (m, 2H), 1.24 – 1.12 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.3, 167.8, 140.1, 128.9, 126.5, 124.3, 82.2 (d, J = 178.7 Hz), 53.2 (d, J = 2.8 Hz), 47.8, 40.0 (d, J = 20.9 Hz). 29.1, 29.1, 26.0, 25.8, 25.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.53. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{21}FN_2NaOS$ 343.1251, found 334.1232.



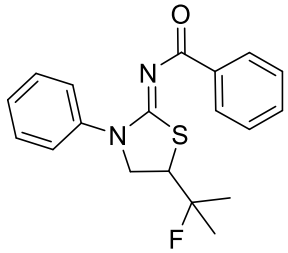
2ab

(Z)-*N*-(5-(fluoromethyl)-3-phenylthiazolidin-2-ylidene)-2-phenylacetamide (2ab): The general procedure from *N*-(allyl(phenyl)carbamothioyl)-2-phenylacetamide **1ab** (62.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ab** as yellow liquid (39.4 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.35 – 7.18 (m, 8H), 4.52 (dd, J = 9.6, 4.7 Hz, 0.5H), 4.48 – 4.39 (m, 1H), 4.34 (t, J = 9.7 Hz, 0.5H), 4.17 (dd, J = 11.2, 7.0 Hz, 1H), 4.07 (dd, J = 11.2, 2.5 Hz, 1H), 3.78 (m, 1H), 3.71 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.1, 168.4, 139.7, 135.9, 129.8, 128.9, 128.2, 126.7, 126.4, 124.4, 82.1 (d, J = 178.8 Hz), 53.3 (d, J = 3.0 Hz), 47.2, 40.0 (d, J = 20.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.91. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaOS$ 351.0938, found 351.0930.



2ac

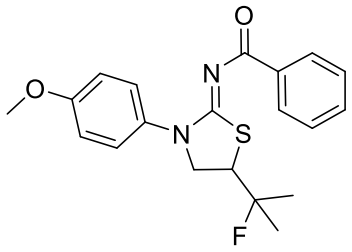
(Z)-*N*-(5-(fluoromethyl)-5-methyl-3-phenylthiazolidin-2-ylidene)benzamide (2ac): The general procedure from *N*-((2-methylallyl)(phenyl)carbamothioyl)benzamide **1ac** (77.0 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ac** as white solid (49.6 mg, 76% yield). Mp: 138.3-140.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 2H), 7.56 – 7.42 (m, 5H), 7.41 – 7.28 (m, 3H), 4.54 (dd, J = 48.2, 9.4 Hz, 1H), 4.35 (dd, J = 47.4, 9.4 Hz, 1H), 4.15 (d, J = 10.9 Hz, 1H), 3.91 (d, J = 10.9 Hz, 1H), 1.67 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 169.4, 140.2, 136.0, 132.2, 129.8, 128.9, 128.0, 126.8, 124.6, 85.4 (d, J = 183.6 Hz), 59.1 (d, J = 2.4 Hz), 48.8 (d, J = 19.0 Hz), 20.9 (d, J = 2.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -212.42. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaOS$ 351.0938, found 351.0931.



2ad

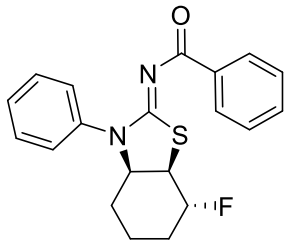
(Z)-*N*-(5-(2-fluoropropan-2-yl)-3-phenylthiazolidin-2-ylidene)benzamide (2ad): The general procedure from *N*-((3-methylbut-2-en-1-yl)(phenyl)carbamothioyl)benzamide **1ad** (64.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ad** as yellow liquid (63.9 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.07 (m, 2H), 7.59 – 7.45 (m, 5H), 7.37 (m, 3H), 4.31 – 4.18 (m, 2H), 3.81 (m, 1H), 1.54 (d, J = 9.4 Hz, 3H), 1.50 (d, J = 9.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 169.7, 140.0, 136.1, 132.1, 129.8, 129.0, 128.0, 126.8, 124.6, 96.2 (d, J = 172.5 Hz), 52.6 (d, J = 4.2 Hz), 49.3 (d, J = 25.6 Hz), 25.6 (d, J = 23.6 Hz), 21.8 (d, J = 24.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -139.70. HRMS (ESI-TOF) m/z:

[M+Na]$^+$ calculated for $C_{19}H_{19}FN_2NaOS$ 365.1094, found 365.1091.



2ae

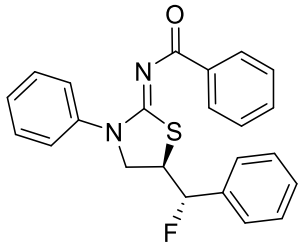
(Z)-N-(5-(2-fluoropropan-2-yl)-3-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (2ae): The general procedure from N-((4-methoxyphenyl)(3-methylbut-2-en-1-yl)carbamothioyl)benzamide **1ae** (70.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ae** as yellow liquid (61.84 mg, 83% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.38 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.03 – 6.93 (m, 2H), 4.21 – 4.08 (m, 2H), 3.85 (s, 3H), 3.75 (ddd, *J* = 10.8, 8.3, 4.0 Hz, 1H), 1.48 (dd, *J* = 21.5, 5.9 Hz, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.95, 169.65, 158.05, 136.19, 132.81, 131.97, 129.66, 127.93, 125.92, 114.09, 96.14 (d, *J* = 172.4 Hz), 55.44, 52.80, 49.35, 49.15, 25.47 (d, *J* = 23.8 Hz), 21.81 (d, *J* = 24.3 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -139.88 (d, *J* = 8.7 Hz).



2ae

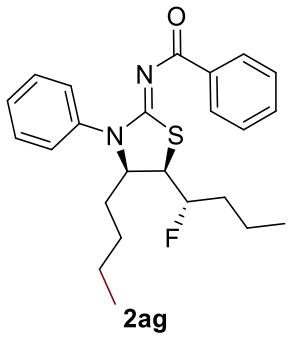
(Z)-*N*-(7-fluoro-3-phenylhexahydrobenzo[d]thiazol-2(3H)-ylidene)benzamide (2ae): The general procedure from *N*-(cyclohex-2-en-1-yl(phenyl)carbamothioyl)benzamide **1ae** (67.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ae** as white solid (56.4 mg, 80% yield). Mp: 144.1-146.3 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 2H), 7.55 – 7.27 (m, 8H), 4.88 (m, 1H), 4.42 (q, J = 6.1 Hz, 1H), 3.85 (dt, J = 14.4, 5.8 Hz, 1H), 2.06 (m, 1H), 1.93 – 1.65 (m, 3H), 1.65 – 1.45 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 170.7, 139.1, 136.2, 132.0, 129.7, 129.1, 127.9, 127.6, 126.9, 91.0 (d, J = 174.2 Hz), 62.0 (d, J = 3.5 Hz), 47.0 (d, J = 25.0 Hz), 28.1 (d, J = 19.8 Hz), 25.2, 16.8 (d, J = 6.3 Hz). ^{19}F NMR

(565 MHz, $CDCl_3$) δ -175.19. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{19}FN_2NaOS$ 377.1094, found 377.1085.



2af

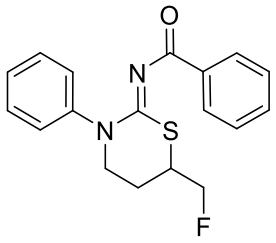
(Z)-*N*-(5-(fluoro(phenyl)methyl)-3-phenylthiazolidin-2-ylidene)benzamide (2af): The general procedure from *N*-(cinnamyl(phenyl)carbamothioyl)benzamide **1af** (74.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2af** as white solid (54.6 mg, 70% yield). Mp: 161-163.2 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 7.8 Hz, 2H), 7.70 – 7.27 (m, 13H), 5.49 (dd, J = 47.5, 9.0 Hz, 1H), 4.32 (qd, J = 11.2, 5.8 Hz, 2H), 4.15 – 3.96 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 169.4, 140.0, 136.1, 136.0, 132.2, 129.8, 129.6, 128.9, 128.8, 128.0, 126.8, 126.8, 124.7, 94.0 (d, J = 179.5 Hz), 53.6 (d, J = 4.0 Hz), 46.4 (d, J = 26.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -167.30, -167.33. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{19}FN_2NaOS$ 413.1094, found 413.1105.



2ag

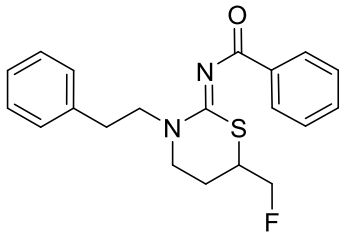
(Z)-*N*-(4-butyl-5-(1-fluorobutyl)-3-phenylthiazolidin-2-ylidene)benzamide (2ag): The general procedure from *N*-(cyclohex-2-en-1-yl(phenyl)carbamothioyl)benzamide **1ag** (67.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ag** as yellow liquid (62.6 mg, 76% yield), syn : anti = 2.2:1. ^1H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 6H), 7.49 – 7.20 (m, 26H), 4.90 – 4.73 (m, 1H), 4.58 – 4.34 (m, 6H), 4.02 (dt, J = 10.2, 7.0 Hz, 1H), 3.28 (t, J = 8.9 Hz, 2H), 1.91 – 1.32 (m, 21H),

1.31 – 1.04 (m, 14H), 0.89 (m, 10H), 0.73 (m, 10H).^{13}C NMR (151 MHz, $CDCl_3$) δ 176.3, 176.2, 169.0, 168.0, 139.7, 138.9, 136.1, 132.0, 131.9, 129.7, 129.7, 129.0, 128.8, 127.9, 127.4, 127.3, 127.0, 126.9, 93.7 (d, J = 177.8 Hz), 91.1 (d, J = 173.8 Hz), 64.9, 64.8 (d, J = 4.7 Hz), 49.9 (d, J = 24.0 Hz), 49.3 (d, J = 21.7 Hz), 36.5, 36.4, 34.7 (d, J = 20.6 Hz), 30.5, 27.7 (d, J = 12.3 Hz), 27.2, 22.7, 22.3, 18.3 (d, J = 2.5 Hz), 17.8 (d, J = 2.9 Hz), 13.8, 13.7, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -177.38, -178.64. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{29}FN_2NaOS$ 435.1877, found 435.1881.



2ah

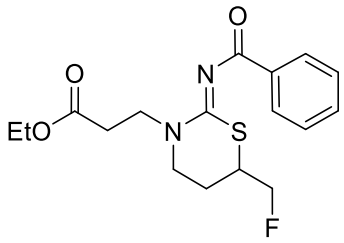
(Z)-*N*-(6-(fluoromethyl)-3-phenyl-1,3-thiazinan-2-ylidene)benzamide (2ah): The general procedure from *N*-(but-3-en-1-yl(phenyl)carbamothioyl)benzamide **1ah** (62.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane = 1:3 to give **2ah** as white solid (29.6 mg, 45% yield). Mp: 109.1-115.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.39 – 7.20 (m, 6H), 4.72 – 4.44 (m, 2H), 4.01 – 3.82 (m, 2H), 3.70 (m, 1H), 2.52 (dt, J = 15.4, 5.4 Hz, 1H), 2.30 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 164.1, 145.9, 136.8, 131.5, 129.5, 129.3, 127.8, 127.4, 126.3, 83.8 (d, J = 178.0 Hz), 49.8, 40.3 (d, J = 20.8 Hz), 26.2 (d, J = 3.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -216.29. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{17}FN_2NaOS$ 351.0938, found 351.0931.



2ai

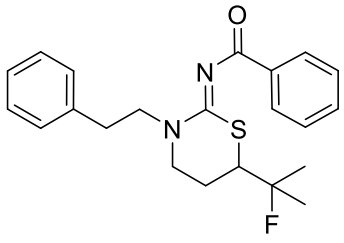
(Z)-*N*-(6-(fluoromethyl)-3-phenethyl-1,3-thiazinan-2-ylidene)benzamide (2ai): The general procedure from *N*-(but-3-en-1-yl(phenethyl)carbamothioyl)benzamide **1ai** (67.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ai** as white solid (48.6 mg, 68% yield).

Mp:84.1-85.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 – 8.19 (m, 2H), 7.54 – 7.46 (m, 1H), 7.42 (dd, J = 8.3, 6.8 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.29 – 7.19 (m, 3H), 4.50 (dd, J = 9.6, 5.1 Hz, 0.5H), 4.45 – 4.36 (m, 1H), 4.32 (t, J = 9.1 Hz, 0.5H), 4.03 (m, 2H), 3.54 – 3.43 (m, 1H), 3.33 (m, 2H), 3.10 (t, J = 7.3 Hz, 2H), 2.22 (m, 1H), 1.96 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 163.5, 138.6, 137.4, 131.5, 129.5, 128.9, 128.7, 127.9, 126.7, 83.5 (d, J = 178.3 Hz), 56.3, 47.7, 39.6 (d, J = 20.6 Hz), 33.6, 25.3(d, J = 3.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -215.93. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{21}FN_2NaOS$ 379.1251, found 379.1255.



2aj

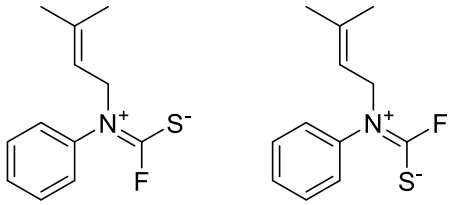
ethyl (Z)-3-(2-(benzoylimino)-6-(fluoromethyl)-1,3-thiazinan-3-yl)propanoate (2aj): The general procedure from ethyl 3-(3-benzoyl-1-(but-3-en-1-yl)thioureido)propanoate **1aj** (66.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2aj** as yellow liquid (48.7 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.45 – 7.27 (m, 3H), 4.45 (dd, J = 9.6, 5.2 Hz, 0.5H), 4.43 – 4.34 (m, 1H), 4.32 (dd, J = 9.6, 8.1 Hz, 0.5H), 4.07 (q, J = 7.1 Hz, 2H), 4.04 – 3.93 (m, 2H), 3.65 (m, 1H), 3.57 (m, 1H), 3.51 – 3.41 (m, 1H), 2.78 (td, J = 6.5, 2.8 Hz, 2H), 2.30 (m, 1H), 2.04 (m, 1H), 1.19 (t, J = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 171.9, 163.8, 137.1, 131.5, 129.4, 127.9, 83.6 (d, J = 177.9 Hz), 60.8, 50.3, 48.0, 39.8 (d, J = 20.9 Hz), 32.5, 25.6 (d, J = 3.6 Hz), 14.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ -216.31. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{21}FN_2NaO_3S$ 375.1149, found 375.1160.



2ak

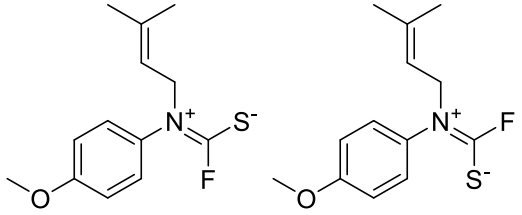
(Z)-*N*-(6-(2-fluoropropan-2-yl)-3-phenethyl-1,3-thiazinan-2-ylidene)benzamide (2ak): The general procedure from *N*-((4-methylpent-3-en-1-yl)(phenethyl)carbamothioyl)benzamide **1ak** (73.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (92.5 mg, 0.23 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 2

h, the residue was purified by column chromatography on silica gel using dichloromethane to give **2ak** as white solid (69.7 mg, 91% yield). Mp:88.4-89.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 – 8.20 (m, 2H), 7.51 – 7.45 (m, 1H), 7.42 (dd, J = 8.2, 6.7 Hz, 2H), 7.32 (td, J = 7.2, 1.6 Hz, 2H), 7.29 – 7.21 (m, 3H), 4.09 (m, 1H), 3.95 (m, 1H), 3.43 – 3.30 (m, 3H), 3.09 (m, 2H), 2.24 (dq, J = 13.7, 3.8 Hz, 1H), 1.85 (m, 1H), 1.44 (dd, J = 21.9, 13.6 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 164.4, 138.6, 137.5, 131.4, 129.5, 128.9, 128.7, 127.9, 126.7, 96.0 (d, J = 172.4 Hz), 56.0, 49.7 (d, J = 25.7 Hz), 49.7, 33.5, 25.4 (d, J = 24.1 Hz), 25.0 (d, J = 4.3 Hz), 22.6 (d, J = 24.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -137.77. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{25}FN_2NaOS$ 407.1564, found 407.1574.



3a' **3a''**

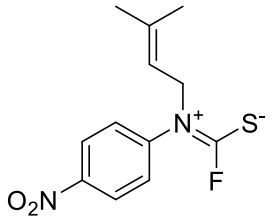
(3-methylbut-2-en-1-yl)(phenyl)carbamothioic fluoride (3a' and 3a''): The general procedure from *N*-(3-methylbut-2-en-1-yl)aniline (331.3 mg, 1.75 mmol), sulfur (224 mg, 7 mmol), KF (305 mg, 5.25 mmol), $TMSCF_3$ (1251.3 mg, 8.75 mmol) and THF (17 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 100:1 to give **3a':3a''**= 3.8:1 as yellow liquid (335.3 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.25 (m, 17H), 7.15 (m, 8H), 5.36 (tt, J = 7.2, 1.5 Hz, 4H), 5.29 (t, J = 7.5 Hz, 1H), 4.65 (d, J = 7.2 Hz, 8H), 4.37 (d, J = 7.4 Hz, 2H), 1.72 (d, J = 7.5 Hz, 15H), 1.47 (d, J = 14.2 Hz, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.8, 179.2, 142.9, 139.7, 139.0, 139.0, 129.7, 129.4, 128.6, 128.5, 126.7, 125.8, 116.7, 115.9, 55.1, 55.0, 51.9, 51.9, 25.7, 25.6, 18.0, 17.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ 23.15, 17.25. HRMS (EI-TOF) m/z: M^+ calculated for $C_{12}H_{14}FNS$ 223.0831, found 223.0835.



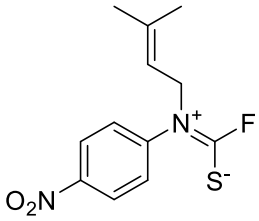
3b' **3b''**

allyl(4-methoxyphenyl)carbamothioic fluoride (3b' and 3b''): The general procedure from 4-methoxy-*N*-(3-methylbut-2-en-1-yl)aniline (688.6 mg, 3.6 mmol), sulfur (460.8 mg, 14.4 mmol), KF (627.5 mg, 10.8 mmol),

$TMSCF_3$ (2574 mg, 18 mmol) and THF (36 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3b':3b''**= 3.5:1 as yellow liquid (746.1 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.10 – 7.02 (m, 7H), 6.97 – 6.93 (m, 2H), 6.93 – 6.87 (m, 7H), 5.35 (m, 4H), 5.28 (t, J = 7.5 Hz, 1H), 4.62 (d, J = 7.2 Hz, 7H), 4.34 (d, J = 7.4 Hz, 2H), 3.82 (d, J = 4.2 Hz, 14H), 1.72 (dd, J = 6.3, 1.4 Hz, 14H), 1.48 (dd, J = 13.3, 1.4 Hz, 14H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.9, 179.8, 159.3, 159.2, 138.9, 138.9, 135.7, 132.3, 127.8, 126.9, 116.7, 115.9, 114.8, 114.5, 55.4, 55.4, 55.2, 55.1, 25.7, 25.6, 18.0, 17.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ 22.74, 17.10. HRMS (ESI-TOF) m/z: M^+ calculated for $C_{13}H_{16}FNOS$ 253.0937, found 253.0939.

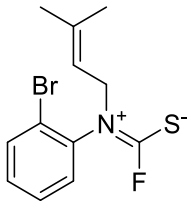


3c'

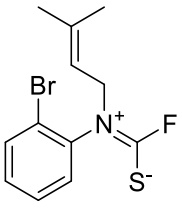


3c''

(3-methylbut-2-en-1-yl)(4-nitrophenyl)carbamothioic fluoride (3c' and 3c''): The general procedure from *N*-(3-methylbut-2-en-1-yl)-4-nitroaniline (103.1 mg, 0.5 mmol), $AgSCF_3$ (155.9 mg, 0.75 mmol), KBr (147.4 mg, 1.25 mmol) and MeCN (10 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3c':3c''**= 3:1 as yellow solid (110.1 mg, 82% yield). Mp: 55.0-55.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 4H), 7.56 – 7.23 (m, 4H), 5.25 (d, J = 13.8 Hz, 2H), 4.63 (s, 3H), 4.36 (s, 1H), 1.65 (s, 6H), 1.45 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 147.1, 144.9, 139.8, 126.9, 124.8, 115.4, 54.8, 25.6, 18.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.85, 19.01. HRMS (ESI-TOF) m/z: M^+ calculated for $C_{12}H_{13}FN_2O_2S$ 268.0682, found 268.0685.



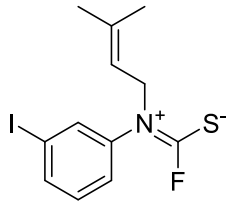
3d'



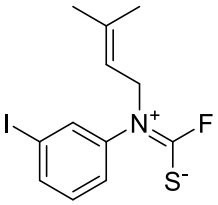
3d''

(2-bromophenyl)(3-methylbut-2-en-1-yl)carbamothioic fluoride (3d' and 3d''): The general procedure from 2-bromo-*N*-(3-methylbut-2-en-1-yl)aniline (120.1 mg, 0.5 mmol), $AgSCF_3$ (155.9 mg, 0.75 mmol), KBr (147.4 mg, 1.25 mmol) and MeCN (10 mL) at room temperature for 2 h, the residue was purified by column

chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3d':3d''**= 2.8:1 as yellow liquid (127.3 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (m, 3H), 7.30 (m, 4H), 7.20 (m, 5H), 7.07 (dd, J = 7.9, 1.6 Hz, 2H), 5.38 – 5.18 (m, 4H), 4.81 (dd, J = 14.7, 6.9 Hz, 3H), 4.62 (d, J = 7.2 Hz, 1H), 4.28 (dd, J = 14.6, 8.2 Hz, 3H), 3.94 (dd, J = 14.8, 8.2 Hz, 1H), 1.64 (d, J = 10.9 Hz, 11H), 1.37 (dd, J = 7.5, 1.4 Hz, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 139.8, 138.4, 134.0, 133.6, 130.3, 130.2, 129.8, 128.8, 128.6, 128.2, 121.4, 121.4, 116.2, 115.4, 53.7, 53.7, 50.5, 50.5, 25.7, 25.7, 17.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ 24.60, 15.51. HRMS (EI-TOF) m/z: M^+ calculated for $C_{12}H_{13}BrFNOS$ 3300.9936, found 300.9935.

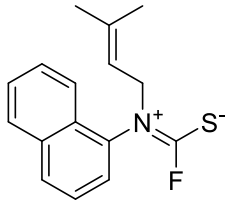


3e'

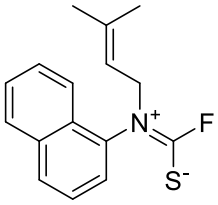


3e''

(3-iodophenyl)(3-methylbut-2-en-1-yl)carbamothioic fluoride (3e' and 3e''): The general procedure from 3-iodo-*N*-(3-methylbut-2-en-1-yl)aniline (861.3 mg, 3 mmol), sulfur (384.7 mg, 12mmol), KF (522.9 mg, 9 mmol), $TMSCF_3$ (2145 mg, 15 mmol) and THF (30 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3e':3e''**= 3.3:1 as yellow liquid (707 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.59 (m, 5H), 7.53 (s, 3H), 7.27 (d, J = 2.6 Hz, 1H), 7.22 – 7.10 (m, 8H), 5.34 (t, J = 7.2 Hz, 3H), 5.27 (t, J = 7.7 Hz, 1H), 4.62 (d, J = 7.2 Hz, 7H), 4.34 (d, J = 7.4 Hz, 2H), 1.74 (d, J = 5.6 Hz, 13H), 1.50 (d, J = 16.9 Hz, 13H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.2, 179.1, 143.8, 140.6, 139.6, 139.5, 137.6, 137.6, 135.8, 134.9, 131.1, 130.8, 126.4, 125.4, 116.5, 115.6, 93.9, 93.8, 55.0, 54.9, 51.9, 25.7, 25.7, 18.1, 17.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.13, 17.81. HRMS (EI-TOF) m/z: M^+ calculated for $C_{12}H_{13}FINS$ 348.9797, found 348.9801.



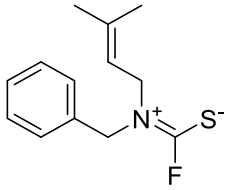
3f'



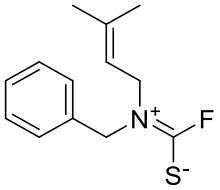
3f''

(3-methylbut-2-en-1-yl)(naphthalen-1-yl)carbamothioic fluoride (3f' and 3f''): The general procedure from *N*-(3-methylbut-2-en-1-yl)naphthalen-1-amine (676.0 mg, 3 mmol), sulfur (384.7 mg, 12 mmol), KF (522.9 mg,

9 mmol), $TMSCF_3$ (2145 mg, 15 mmol) and THF (30 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3f':3f''**= 4.2:1 as yellow liquid (606.9 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dt, J = 9.9, 7.8 Hz, 10H), 7.71 (dd, J = 8.3, 1.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 4H), 7.57 – 7.30 (m, 17H), 7.24 – 7.14 (m, 5H), 5.41 – 5.25 (m, 5H), 4.90 (dd, J = 14.4, 6.9 Hz, 4H), 4.62 (dd, J = 14.6, 7.1 Hz, 1H), 4.42 (dd, J = 14.3, 7.9 Hz, 4H), 4.12 (dd, J = 14.5, 8.1 Hz, 1H), 1.64 – 1.60 (m, 3H), 1.60 – 1.53 (m, 13H), 1.25 (d, J = 1.5 Hz, 16H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.2, 182.5, 181.1, 180.3, 139.5, 139.5, 138.9, 136.0, 134.6, 134.3, 129.4, 129.3, 128.8, 128.7, 128.5, 128.0, 127.5, 127.3, 126.8, 126.7, 125.6, 125.2, 125.2, 124.1, 122.0, 122.0, 116.9, 115.8, 54.8, 54.8, 51.7, 51.7, 25.7, 25.6, 17.9, 17.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.17, 17.15. HRMS (EI-TOF) m/z: M^+ calculated for $C_{16}H_{16}FNS$ 273.0987, found 273.0990.

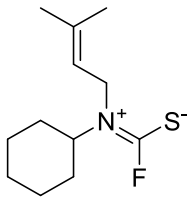


3g'

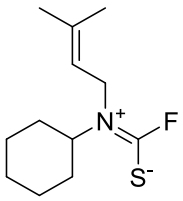


3g''

benzyl(3-methylbut-2-en-1-yl)carbamothioic fluoride (3g' and 32g''): The general procedure from *N*-benzyl-3-methylbut-2-en-1-amine (771.2 mg, 4.4 mmol), sulfur (563.2 mg, 17.6 mmol), KF (766.9 mg, 13.2 mmol), $TMSCF_3$ (3146 mg, 22 mmol) and THF (44 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3g':3g''**= 1.1:1 as yellow liquid (884.2 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 9H), 7.13 (dd, J = 7.2, 1.6 Hz, 2H), 5.20 (m, 1H), 5.05 (m, 1H), 4.88 (s, 2H), 4.54 (s, 2H), 4.23 (d, J = 7.1 Hz, 2H), 3.90 (d, J = 7.2 Hz, 2H), 1.67 (dd, J = 14.9, 1.4 Hz, 7H), 1.53 (dd, J = 26.9, 1.4 Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.8, 182.6, 181.3, 180.0, 139.2, 138.8, 134.4, 129.0, 128.8, 128.3, 128.0, 127.6, 116.8, 116.1, 55.9, 55.9, 51.4, 51.4, 50.7, 50.7, 46.3, 46.2, 25.7, 25.7, 18.2, 17.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ 15.07, 14.69. HRMS (EI-TOF) m/z: M^+ calculated for $C_{13}H_{16}FNS$ 237.0989, found 237.0989.

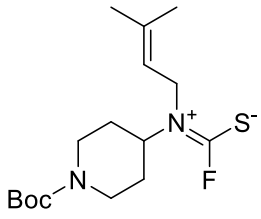


3h'

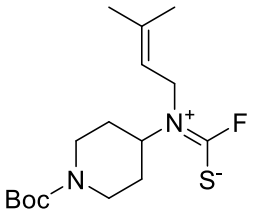


3h''

cyclohexyl(3-methylbut-2-en-1-yl)carbamothioic fluoride (3h' and 3h''): The general procedure from *N*-(3-methylbut-2-en-1-yl)cyclohexanamine (836.5 mg, 5 mmol), sulfur (641.2 mg, 20 mmol), KF (871.5 mg, 20 mmol), $TMSCF_3$ (3554.8 mg, 25 mmol) and THF (50 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3h':3h''**= 1.3:1 as yellow liquid (822.5 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.15 (t, J = 6.4 Hz, 1H), 4.99 (t, J = 6.7 Hz, 1H), 4.54 (tt, J = 11.6, 4.1 Hz, 1H), 4.24 (d, J = 6.4 Hz, 2H), 3.97 – 3.77 (m, 4H), 1.93 – 1.70 (m, 11H), 1.69 – 1.54 (m, 18H), 1.53 – 1.15 (m, 12H), 1.05 (tt, J = 13.0, 3.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 182.9, 180.4, 180.3, 136.0, 135.8, 119.3, 118.3, 62.9, 62.8, 60.7, 60.6, 49.1, 49.0, 43.3, 43.2, 31.0, 29.6, 25.8, 25.7, 25.5, 25.3, 25.1, 18.3, 17.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ 19.39, 14.51. HRMS (EI-TOF) m/z: M^+ calculated for $C_{12}H_{20}FNS$ 229.1300, found 229.1304.



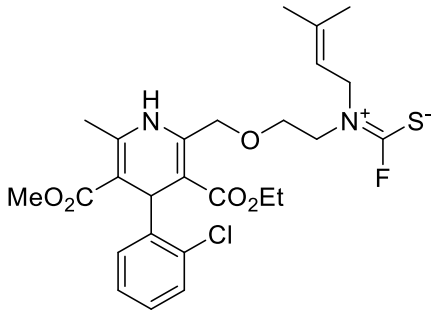
3i'



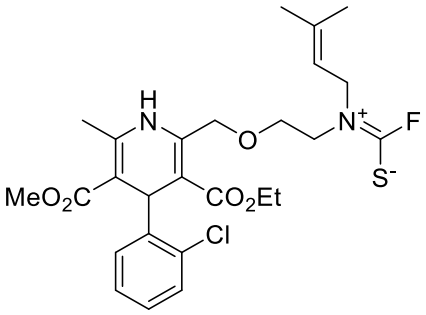
3i''

tert-butyl 4-((fluorocarbonothioyl)(3-methylbut-2-en-1-yl)amino)piperidine-1-carboxylate (3i' and 3i''): The general procedure from tert-butyl 4-((3-methylbut-2-en-1-yl)amino)piperidine-1-carboxylate (805.2 mg, 3 mmol), sulfur (384 mg, 12 mmol), KF (522.9 mg, 9 mmol), $TMSCF_3$ (2145 mg, 15 mmol) and THF (30 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **3i':3i''**= 2:1 as yellow liquid (708.6 mg, 71% yield). Mp: 55.0-56.7 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (m, 1H), 5.01 – 4.92 (m, 2H), 4.72 (tq, J = 12.3, 4.1 Hz, 2H), 4.31 – 4.03 (m, 8H), 3.99 (tt, J = 11.7, 4.3 Hz, 1H), 3.91 – 3.81 (m, 4H), 2.68 (d, J = 40.1 Hz, 6H), 1.83 (m, 4H), 1.70 – 1.58 (m, 24H), 1.54 – 1.44 (m, 5H), 1.40 (d, J = 2.8 Hz, 28H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 182.9, 182.6, 180.8, 154.6, 154.5, 136.6, 136.5, 118.8, 117.9, 80.1, 80.0, 61.0, 61.0, 58.6, 58.5, 49.0, 48.9, 43.4, 43.4, 30.1, 28.6, 28.4, 28.4, 25.7,

18.3, 18.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ 19.91, 15.35. HRMS (EI-TOF) m/z: M^+ calculated for $C_{16}H_{27}FN_2O_2S$ 330.1777, found 330.1783.

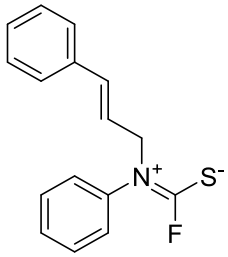


3j'

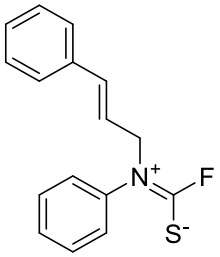


3j''

3-ethyl 5-methyl 4-(2-chlorophenyl)-2-((2-((fluorocarbonothioyl)(3-methylbut-2-en-1-yl)amino)ethoxy)methyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (3j' and 3j''): The general procedure from 3-ethyl 5-methyl 4-(2-chlorophenyl)-6-methyl-2-((2-((3-methylbut-2-en-1-yl)amino)ethoxy)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (231.5 mg, 0.5 mmol), $AgSCF_3$ (155.9 mg, 0.75 mmol), KBr (147.4 mg, 1.25 mmol) and MeCN (10 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **3j':3j''**= 1.2:1 as white solid (222.0 mg, 85% yield). Mp: 85.5-87.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, J = 7.8, 1.7 Hz, 2H), 7.16 (dt, J = 7.9, 1.4 Hz, 2H), 7.07 (m, 4H), 6.97 (tt, J = 7.4, 1.9 Hz, 3H), 6.83 (s, 1H), 5.34 (s, 2H), 5.27 – 5.04 (m, 2H), 4.71 (dd, J = 15.8, 2.8 Hz, 2H), 4.62 (dd, J = 15.8, 6.9 Hz, 2H), 4.43 – 4.29 (m, 2H), 4.08 (d, J = 7.2 Hz, 3H), 4.04 – 3.88 (m, 8H), 3.85 – 3.73 (m, 3H), 3.70 – 3.60 (m, 4H), 3.54 (d, J = 1.2 Hz, 8H), 2.29 (d, J = 1.9 Hz, 7H), 1.77 – 1.60 (m, 15H), 1.11 (t, J = 7.1 Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.6, 181.1, 167.9, 167.9, 167.1, 167.1, 145.7, 145.6, 144.6, 144.3, 144.1, 143.9, 139.3, 139.0, 132.3, 132.2, 131.4, 129.2, 129.2, 127.4, 127.3, 126.9, 126.9, 116.8, 116.2, 104.0, 104.0, 101.6, 101.4, 68.4, 68.1, 67.6, 67.4, 59.8, 59.8, 52.4, 52.3, 51.7, 51.7, 50.8, 50.7, 48.1, 48.0, 47.8, 47.8, 37.0, 37.0, 25.7, 25.7, 19.4, 19.4, 18.2, 17.9, 14.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ 17.58, 16.11. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{32}ClFN_2NaO_5S$ 561.1597, found 561.1600.

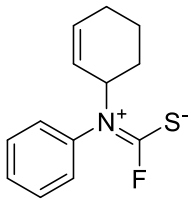


3k'

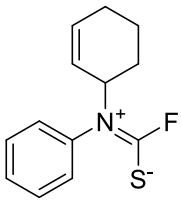


3k''

cinnamyl(phenyl)carbamothioic fluoride (3k' and 3k''): The general procedure from *N*-cinnamylaniline (248.7 mg, 1.15 mmol), sulfur (147.2 mg, 4.6 mmol), KF (200.4 mg, 3.45 mmol), $TMSCF_3$ (822.3 mg, 5.75 mmol) and THF (12 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3k':3k''**= 4.3:1 as yellow liquid (247.4 mg, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.13 (m, 51H), 6.51 (m, 5H), 6.36 (dt, J = 16.0, 6.8 Hz, 4H), 6.24 (dt, J = 15.8, 6.7 Hz, 1H), 4.80 (d, J = 6.8 Hz, 9H), 4.53 (d, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.8, 179.7, 142.9, 139.7, 136.0, 135.7, 135.6, 135.3, 129.9, 129.6, 128.8, 128.7, 128.7, 128.6, 128.4, 128.2, 126.8, 126.6, 125.9, 121.1, 120.3, 59.4, 59.3, 56.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.03, 18.31. HRMS (EI-TOF) m/z: M^+ calculated for $C_{16}H_{14}FNS$ 271.0831, found 271.0827.



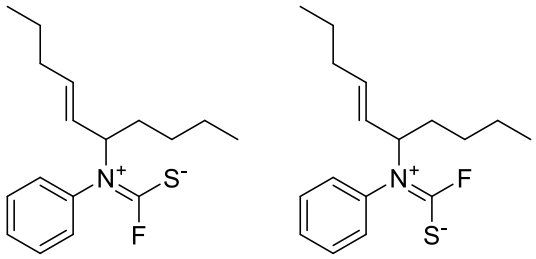
3l'



3l''

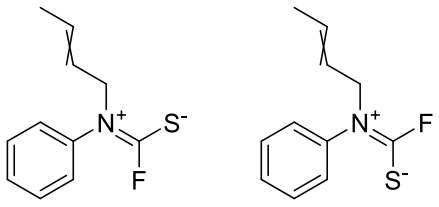
cyclohex-2-en-1-yl(phenyl)carbamothioic fluoride (3l' and 3l''): The general procedure from *N*-(cyclohex-2-en-1-yl)aniline (545.8 mg, 3.15 mmol), sulfur (403.2 mg, 12.6 mmol), KF (549 mg, 9.45 mmol), $TMSCF_3$ (2252.3 mg, 15.75 mmol) and THF (12 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3l':3l''**= 4.3:1 as white solid (519.9 mg, 70% yield). Mp: 84.7-86.6 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 3H), 7.17 – 6.99 (m, 2H), 5.83 – 5.72 (m, 1H), 5.69 (dt, J = 10.4, 2.1 Hz, 1H), 5.63 – 5.52 (m, 1H), 2.07 – 1.90 (m, 1H), 1.90 – 1.81 (m, 1H), 1.76 (m, 1H), 1.62 – 1.46 (m, 2H), 1.41 – 1.26 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 182.2, 180.1, 136.6, 132.2, 131.9, 129.5, 129.2, 129.0, 128.8, 128.3, 127.6, 125.8, 125.4, 61.1, 61.0, 58.8, 28.0, 26.5, 24.2, 24.1, 20.8, 20.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ 28.36, 17.33. HRMS (EI-TOF) m/z: M^+ calculated for $C_{13}H_{14}FNS$

235.0831, found 235.0835.



3m' **3m''**

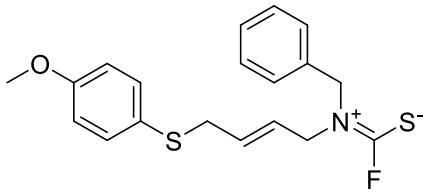
(E)-dec-6-en-5-yl(phenyl)carbamothioic fluoride (3m' and 3m''): The general procedure from (E)-*N*-(dec-6-en-5-yl)aniline (140.7 mg, 0.5 mmol), $AgSCF_3$ (155.9 mg, 0.75 mmol), KBr (147.4 mg, 1.25 mmol) and MeCN (10 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3m':3m''**= 2.8:1 as yellow liquid (99.6 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 10H), 7.11 (dd, J = 7.4, 1.6 Hz, 2H), 7.04 – 6.97 (m, 5H), 5.77 (dt, J = 15.3, 6.8 Hz, 3H), 5.63 (m, 1H), 5.36 (m, 3H), 5.19 – 5.09 (m, 1H), 5.04 (m, 3H), 4.66 (q, J = 7.9 Hz, 1H), 2.06 – 1.83 (m, 7H), 1.73 – 1.57 (m, 4H), 1.52 – 1.22 (m, 29H), 0.82 (m, 22H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.8, 179.7, 140.4, 136.9, 136.4, 136.3, 129.4, 129.0, 128.9, 128.7, 128.3, 127.9, 126.9, 126.3, 66.3, 66.2, 65.4, 34.4, 34.2, 33.1, 31.6, 28.4, 28.2, 22.3, 22.2, 22.0, 22.0, 13.9, 13.9, 13.6, 13.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ 27.97, 17.11. HRMS (EI-TOF) m/z: M^+ calculated for $C_{17}H_{14}FNS$ 293.1614, found 293.1609.



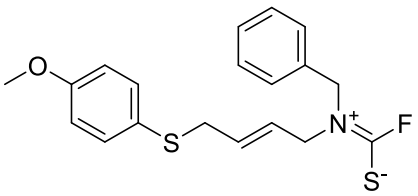
3n' **3n''**

but-2-en-1-yl(phenyl)carbamothioic fluoride (3n' and 3n''): The general procedure from *N*-(but-2-en-1-yl)aniline (368.1 mg, 2.5 mmol, trans and cis mixture), sulfur (320 mg, 10 mmol), KF (435.8 mg, 7.5 mmol), $TMSCF_3$ (1787.5 mg, 12.5 mmol) and THF (25 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 100:1 to give **3n:3n''=** 4:1 as yellow liquid (407.0 mg, 78% yield, trans: cis = 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.25 (m, 35H), 7.22 (d, J = 6.7 Hz, 5H), 7.15 – 7.04 (m, 24H), 6.59 (dd, J = 17.4, 7.8 Hz, 9H), 5.76 – 5.29 (m, 31H), 4.64 (d, J = 7.0 Hz, 4H), 4.49 (d, J = 5.1 Hz, 15H), 4.35 (d, J = 7.1 Hz, 1H), 4.22 (d, J = 6.5 Hz, 4H), 3.83 – 3.68 (m, 12H), 1.72 – 1.54

(m, 37H), 1.41 (m, 7H).^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 132.4, 130.3, 129.7, 129.5, 129.4, 129.0, 128.6, 128.6, 127.7, 127.1, 126.7, 126.7, 125.9, 125.8, 122.1, 116.1, 112.4, 59.2, 59.1, 56.0, 51.8, 51.5, 17.7, 17.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ 23.92, 23.29, 17.88, 17.61. HRMS (EI-TOF) m/z: M^+ calculated for $C_{11}H_{172}FNS$ 209.0674, found 209.0676.

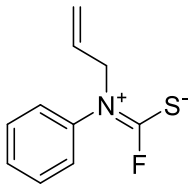


3o'

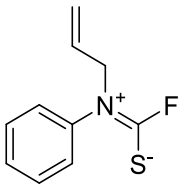


3o''

(E)-benzyl(4-((4-methoxyphenyl)thio)but-2-en-1-yl)carbamothioic fluoride (3o' and 3o''): The general procedure from (E)-*N*-benzyl-4-((4-methoxyphenyl)thio)but-2-en-1-amine (149.7 mg, 0.5 mmol), $AgSCF_3$ (155.9 mg, 0.75 mmol), KBr (147.4 mg, 1.25 mmol) and MeCN (10 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **3o':3o''**= 1:1 as yellow liquid (157.8 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 10H), 7.21 – 7.15 (m, 2H), 7.08 – 7.01 (m, 2H), 6.86 – 6.75 (m, 4H), 5.68 – 5.49 (m, 2H), 5.38 – 5.27 (m, 1H), 5.21 – 5.04 (m, 1H), 4.68 (s, 2H), 4.29 (s, 2H), 4.08 (d, J = 6.5 Hz, 2H), 3.74 (dd, J = 21.8, 7.6 Hz, 8H), 3.41 – 3.26 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.6, 181.1, 159.4, 159.4, 134.7, 134.4, 134.1, 134.0, 132.1, 131.7, 129.0, 128.9, 128.4, 128.1, 127.7, 124.8, 124.7, 124.5, 124.0, 114.6, 114.5, 55.6, 55.6, 55.4, 55.3, 53.8, 53.7, 51.1, 51.0, 49.4, 49.3, 37.8, 37.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ 27.97, 17.11. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{20}FNNaOS_2$ 384.0863, found 384.0857.



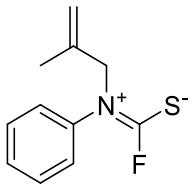
3p'



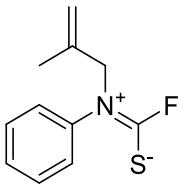
3p''

allyl(phenyl)carbamothioic fluoride (3p' and 3p''): The general procedure from *N*-allylaniline (1688.9 mg, 12.68 mmol), sulfur (1623 mg, 50.72 mmol), KF (2206.7 mg, 38.04 mmol), $TMSCF_3$ (9066.2 mg, 63.4 mmol) and THF (127 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3p':3p''**= 4.3:1 as yellow liquid (1992.5 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.31 (m, 9H), 7.20 (dd, J = 7.5, 2.0 Hz, 4H), 5.96 (m, 3H), 5.36 – 5.20 (m, 5H), 4.67 (dq, J = 6.4, 1.2 Hz, 4H), 4.44 – 4.36 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.0, 180.8, 179.4, 142.9, 139.7, 130.4, 129.7, 129.5, 129.4, 128.7, 128.6, 126.6, 125.7, 120.3, 119.9, 59.6, 59.6, 56.5, 56.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ 23.95, 18.51. HRMS (EI-TOF) m/z: M^+ calculated for $C_{10}H_{10}FNS$ 195.0518, found 195.0520.

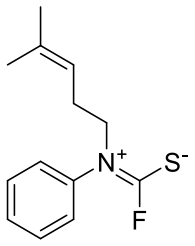


3q'

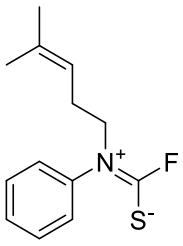


3q''

allyl(phenyl)carbamothioic fluoride (3q' and 3q''): The general procedure from *N*-(2-methylallyl)aniline (611 mg, 4.15 mmol), sulfur (531.2 mg, 16.6 mmol), KF (723.3 mg, 12.45 mmol), $TMSCF_3$ (2967.2 mg, 20.75 mmol) and THF (42 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3q':3q''**= 3.4:1 as yellow liquid (831.1 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 14H), 7.22 – 7.14 (m, 6H), 4.98 (s, 1H), 4.93 (t, J = 1.5 Hz, 3H), 4.87 – 4.81 (m, 4H), 4.67 (s, 6H), 4.34 (s, 2H), 1.81 (s, 13H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 182.4, 180.3, 143.0, 139.6, 138.2, 137.7, 129.6, 129.4, 128.6, 128.5, 126.5, 125.5, 114.9, 114.8, 62.6, 62.5, 59.7, 59.6, 20.3, 20.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.93, 18.89. HRMS (EI-TOF) m/z: M^+ calculated for $C_{11}H_{12}FNS$ 209.0674, found 209.0677.



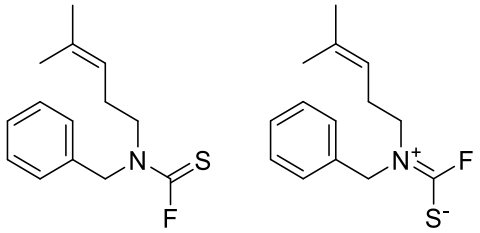
3r'



3r''

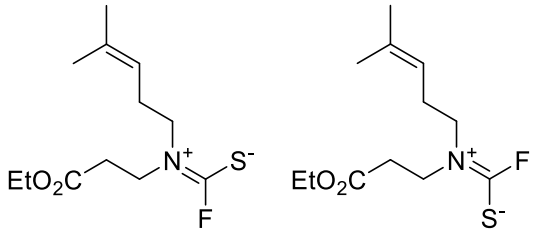
(4-methylpent-3-en-1-yl)(phenyl)carbamothioic fluoride (3r' and 3r''): The general procedure from *N*-(4-methylpent-3-en-1-yl)aniline (280.4 mg, 1.6 mmol), sulfur (204.8 mg, 6.4 mmol), KF (278.9 mg, 4.8 mmol), $TMSCF_3$ (1144 mg, 8 mmol) and THF (16 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3r':3r''**= 4.1:1 as yellow liquid (157.8 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 8H), 7.22 (dd, J = 7.5, 1.8 Hz, 1H),

7.10 (dd, J = 7.5, 1.8 Hz, 4H), 4.96 (m, 2H), 4.00 – 3.90 (m, 4H), 3.72 (td, J = 7.5, 1.6 Hz, 1H), 2.35 (q, J = 7.6 Hz, 4H), 2.27 (q, J = 7.5 Hz, 1H), 1.61 (dd, J = 10.5, 1.5 Hz, 8H), 1.52 (d, J = 1.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.8, 179.3, 139.8, 135.5, 129.8, 129.5, 128.7, 128.6, 126.8, 125.8, 119.0, 118.7, 56.7, 56.6, 53.6, 53.6, 26.9, 25.7, 25.7, 24.8, 17.8, 17.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ 24.59, 17.15. HRMS (EI-TOF) m/z: M^+ calculated for $C_{13}H_{16}FNS$ 237.0987, found 237.0981.



3s' **3s''**

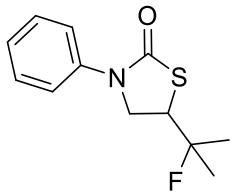
benzyl(4-methylpent-3-en-1-yl)carbamothioic fluoride (3s' and 3s''): The general procedure from *N*-benzyl-4-methylpent-3-en-1-amine (378.6 mg, 2 mmol), sulfur (256 mg, 8 mmol), KF (348.6 mg, 6 mmol), $TMSCF_3$ (1430 mg, 10 mmol) and THF (20 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **3s':3s''**= 1.3:1 as yellow liquid (443.5 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 9H), 7.17 – 7.11 (m, 2H), 4.99 (tt, J = 7.3, 1.5 Hz, 1H), 4.93 (d, J = 3.9 Hz, 4H), 4.58 (s, 2H), 3.60 – 3.48 (m, 2H), 3.28 (td, J = 7.7, 1.9 Hz, 2H), 2.33 (q, J = 7.6 Hz, 2H), 2.18 (q, J = 7.5 Hz, 3H), 1.62 (dd, J = 3.0, 1.5 Hz, 7H), 1.55 (d, J = 1.3 Hz, 3H), 1.50 (d, J = 1.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.8 (d, J = 321.3 Hz), 181.1 (d, J = 321.1 Hz), 135.8, 135.5, 134.4, 134.4, 129.0, 128.9, 128.3, 128.0, 127.6, 119.1, 118.7, 57.1, 57.0, 53.2, 53.2, 53.0, 52.9, 48.6, 48.6, 26.7, 25.7, 24.3, 17.7, 17.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ 15.36, 15.31. HRMS (EI-TOF) m/z: M^+ calculated for $C_{14}H_{18}FNS$ 251.1144, found 251.1148.



3t' **3t''**

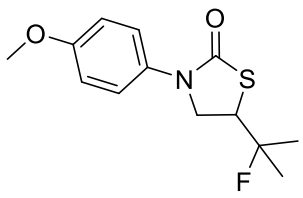
ethyl 3-((fluorocarbonothioyl)(4-methylpent-3-en-1-yl)amino)propanoate (3t' and 3t''): The general

procedure from ethyl 3-((4-methylpent-3-en-1-yl)amino)propanoate (299.0 mg, 1.5 mmol), sulfur (192 mg, 6 mmol), KF (261.5 mg, 4.5 mmol), $TMSCF_3$ (1072.5 mg, 7.5 mmol) and THF (15 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 20:1 to give **3t':3t''**= 1.6:1 as yellow liquid (290.3 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 – 5.01 (m, 1H), 4.98 (t, J = 7.6 Hz, 1H), 4.09 (qd, J = 7.1, 1.5 Hz, 5H), 3.84 (t, J = 7.0 Hz, 3H), 3.73 – 3.54 (m, 4H), 3.52 – 3.37 (m, 3H), 2.77 (t, J = 7.0 Hz, 3H), 2.58 (t, J = 7.1 Hz, 2H), 2.38 (q, J = 7.6 Hz, 2H), 2.25 (q, J = 7.4 Hz, 3H), 1.64 (s, 8H), 1.59 (s, 3H), 1.56 (s, 5H), 1.21 (t, J = 7.2 Hz, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.4 (d, J = 322.0 Hz), 181.3 (d, J = 321.5 Hz), 171.2, 170.4, 135.8, 135.6, 119.0, 118.6, 61.0, 60.9, 54.2, 54.1, 50.8, 50.8, 49.6, 49.5, 45.9, 45.8, 33.1, 30.7, 30.6, 27.0, 25.6, 24.6, 17.7, 17.5, 14.0, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ 16.84, 15.29. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{20}FNNaO_2S$ 284.1091, found 284.1091.



4a

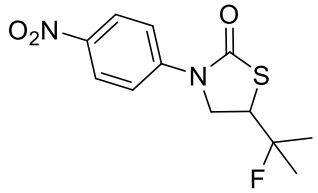
5-(2-fluoropropan-2-yl)-3-phenylthiazolidin-2-one (4a): The general procedure from (3-methylbut-2-en-1-yl)(phenyl)carbamothioic fluoride **2a** (44.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4a** as white solid (43.2 mg, 90% yield). Mp: 72.9-74.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.20 (m, 1H), 4.22 (m, 1H), 4.09 (m, 1H), 3.85 (m, 1H), 1.49 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 138.5, 129.1, 125.7, 122.0, 96.12 (d, J = 172.7 Hz), 51.17 (d, J = 5.0 Hz), 48.05 (d, J = 27.2 Hz), 25.15 (d, J = 23.7 Hz), 22.13 (d, J = 24.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.41. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{14}FNNaOS$ 262.0672, found 262.0679.



4b

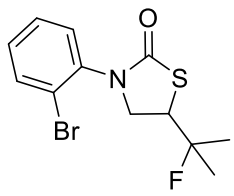
5-(2-fluoropropan-2-yl)-3-(4-methoxyphenyl)thiazolidin-2-one (4b): The general procedure from (4-

methoxyphenyl)(3-methylbut-2-en-1-yl)carbamothioic fluoride **2b** (50.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4b** as yellow liquid (43.8 mg, 81% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.87 – 6.80 (m, 2H), 4.09 (dd, J = 10.8, 8.0 Hz, 1H), 3.95 (dd, J = 10.8, 3.9 Hz, 1H), 3.81 – 3.67 (m, 4H), 1.42 (t, J = 21.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 157.6, 131.4, 124.1, 114.4, 96.17 (d, J = 172.4 hz), 55.4, 51.59 (d, J = 5.0 Hz), 48.06 (d, J = 27.1 Hz), 25.14 (d, J = 23.7 Hz), 22.13 (d, J = 24.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.46. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{16}FNNaO_2S$ 292.0778, found 292.0770.



4c

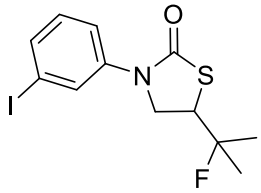
5-(2-fluoropropan-2-yl)-3-(4-nitrophenyl)thiazolidin-2-one (4c): The general procedure from (3-methylbut-2-en-1-yl)(4-nitrophenyl)carbamothioic fluoride **2c** (53.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4c** as white solid (52 mg, 91% yield). Mp: 75.3-79.0 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.20 (m, 2H), 7.72 – 7.60 (m, 2H), 4.29 (dd, J = 10.6, 7.9 Hz, 1H), 4.20 (dd, J = 10.6, 4.3 Hz, 1H), 3.94 (m, 1H), 1.53 (d, J = 2.7 Hz, 3H), 1.49 (d, J = 2.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 143.9, 143.9, 124.7, 120.4, 95.7 (d, J = 173.7 Hz), 50.5 (d, J = 5.0 Hz), 47.9 (d, J = 27.1 Hz), 25.2 (d, J = 23.9 Hz), 22.4 (d, J = 24.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -142.36. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{13}FN_2NaO_3S$ 307.1523, found 307.1532.



4d

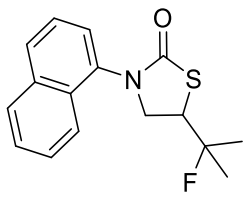
3-(2-bromophenyl)-5-(2-fluoropropan-2-yl)thiazolidin-2-one (4d): The general procedure from (2-bromophenyl)(3-methylbut-2-en-1-yl)carbamothioic fluoride **2d** (60.4 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was

purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4d** as yellow liquid (57 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.1, 1.4 Hz, 1H), 7.31 (td, J = 7.6, 1.4 Hz, 1H), 7.24 (dd, J = 7.9, 1.7 Hz, 1H), 7.17 (td, J = 7.7, 1.7 Hz, 1H), 4.05 (d, J = 10.7 Hz, 1H), 3.97 (m, 1H), 3.92 – 3.79 (m, 1H), 1.53 (d, J = 21.2 Hz, 3H), 1.43 (d, J = 21.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 137.5, 133.9, 130.1, 129.6, 128.7, 122.5, 95.8 (d, J = 172.7 Hz), 51.1 (d, J = 5.3 Hz), 49.5 (d, J = 26.3 Hz), 25.25 (d, J = 23.7 Hz), 23.05 (d, J = 24.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -142.01. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{13}BrFNNaOS$ 339.9777, found 339.9778.



4e

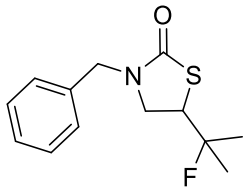
5-(2-fluoropropan-2-yl)-3-(3-iodophenyl)thiazolidin-2-one (4e): The general procedure from (3-iodophenyl)(3-methylbut-2-en-1-yl)carbamothioic fluoride **2e** (69.8 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4e** as yellow liquid (67.6 mg, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.46 (m, 1H), 7.37 – 7.32 (m, 1H), 7.03 (t, J = 8.0 Hz, 1H), 4.11 (dd, J = 10.7, 7.9 Hz, 1H), 3.99 (dd, J = 10.7, 3.9 Hz, 1H), 3.78 (m, 1H), 1.41 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 139.6, 134.6, 130.5, 130.3, 121.0, 96.0 (d, J = 173.0 Hz), 94.1, 50.9 (d, J = 5.0 Hz), 48.0 (d, J = 27.2 Hz), 25.2 (d, J = 23.8 Hz), 22.2 (d, J = 24.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.65. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{13}FINNaOS$ 387.9639, found 387.9650.



4f

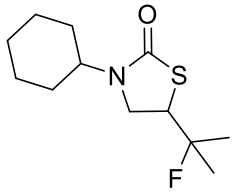
5-(2-fluoropropan-2-yl)-3-(naphthalen-1-yl)thiazolidin-2-one (4f): The general procedure from (3-methylbut-2-en-1-yl)(naphthalen-1-yl)carbamothioic fluoride **2f** (54.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was

purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4f** as white solid (55.3 mg, 96% yield). Mp: 118.2-119.4 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (m, 3H), 7.54 – 7.36 (m, 3H), 7.32 (d, J = 7.3 Hz, 1H), 4.11 (t, J = 9.4 hz, 1H), 3.95 (d, J = 34.1 Hz, 2H), 1.53 (d, J = 21.2 Hz, 3H), 1.42 (d, J = 21.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.30, 135.00, 134.59, 129.64, 128.95, 128.61, 127.09, 126.52, 125.53, 125.10, 124.15, 122.71, 122.28, 95.60 (d, J = 173.2 Hz), 52.80, 49.54, 25.01 (d, J = 24.0 Hz), 23.29. ^{19}F NMR (565 MHz, $CDCl_3$) δ -142.51, -144.47. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{16}FNNaOS$ 312.0829, found 312.0826.



4g

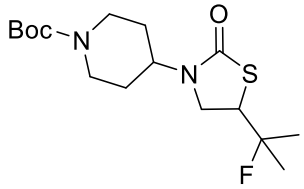
3-benzyl-5-(2-fluoropropan-2-yl)thiazolidin-2-one (4g): The general procedure from benzyl(3-methylbut-2-en-1-yl)carbamothioic fluoride **2g** (47.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: dichloromethane = 1:2 to give **4g** as yellow liquid (45 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 4.39 (s, 2H), 3.67 (m, 1H), 3.47 (dd, J = 11.0, 8.4 Hz, 1H), 3.40 (dd, J = 10.9, 4.3 Hz, 1H), 1.27 (t, J = 21.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.40, 135.45, 128.81, 128.34, 128.00, 96.10 (d, J = 171.9 Hz), 48.60, 48.36 (d, J = 5.0 Hz), 48.18 (d, J = 27.0 Hz), 25.12 (d, J = 24.0 Hz), 22.00 (d, J = 24.4 hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.43. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{16}FNNaOS$ 276.0829, found 276.0827.



4h

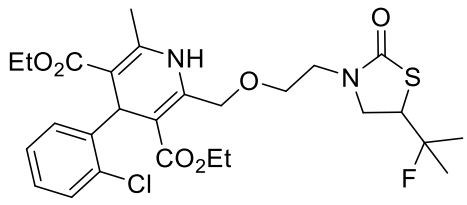
3-cyclohexyl-5-(2-fluoropropan-2-yl)thiazolidin-2-one (4h): The general procedure from cyclohexyl(3-methylbut-2-en-1-yl)carbamothioic fluoride **2h** (43.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 20:1 to give **4h** as white solid (39

mg, 79% yield). Mp: 48.6-49.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (tt, J = 11.9, 3.8 Hz, 1H), 3.74 (m, 1H), 3.66 (m, 2H), 1.90 – 1.73 (m, 4H), 1.73 – 1.65 (m, 1H), 1.52 – 1.32 (m, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 96.7 (d, J = 171.7 Hz), 53.6, 48.2 (d, J = 26.4 hz), 45.0 (d, J = 5.0 Hz), 30.3 (d, J = 27.2 Hz), 25.6, 25.5, 25.5 (d, J = 23.9 Hz), 25.4, 21.8, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -140.86. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{20}FNNaOS$ 268.1142, found 268.1151.



4i

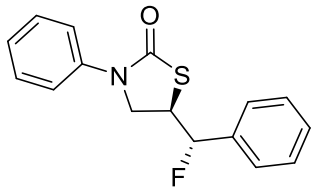
tert-butyl 4-(5-(2-fluoropropan-2-yl)-2-oxothiazolidin-3-yl)piperidine-1-carboxylate (4i): The general procedure from tert-butyl 4-((fluorocarbonothioyl)(3-methylbut-2-en-1-yl)amino)piperidine-1-carboxylate **2i** (66.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4i** as white solid (60.4 mg, 87% yield). Mp: 69.1-72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 – 3.98 (m, 3H), 3.68 (m, 1H), 3.60 – 3.50 (m, 2H), 2.70 (s, 2H), 1.70 – 1.61 (m, 2H), 1.55 (m, 2H), 1.44 – 1.29 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.98, 154.44, 96.26 (d, J = 172.3 Hz), 79.83, 51.77, 48.28 (d, J = 27.2 Hz), 44.90 (d, J = 5.0 Hz), 43.0, 29.19 (d, J = 29.3 Hz), 28.35, 25.33 (d, J = 23.9 Hz), 21.98, 21.82. ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.25, 141.66. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{27}FN_2NaO_3S$ 369.1619, found 369.1618.



4j

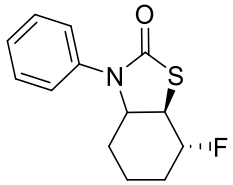
3-ethyl 5-methyl 4-(2-chlorophenyl)-2-((2-(5-(2-fluoropropan-2-yl)-2-oxothiazolidin-3-yl)ethoxy)methyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (4j): The general procedure from 3-ethyl 5-methyl 4-(2-chlorophenyl)-2-((2-((fluorocarbonothioyl)(3-methylbut-2-en-1-yl)amino)ethoxy)methyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate **2j** (105.0 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7

mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 1:1 to give **4j** as yellow liquid (74.5 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.28 – 7.22 (m, 2H), 7.15 (m, 1H), 7.10 – 7.03 (m, 1H), 5.42 (s, 1H), 4.86 – 4.63 (m, 2H), 4.11 – 4.01 (m, 2H), 3.87 – 3.70 (m, 5H), 3.70 – 3.50 (m, 5H), 2.39 (s, 3H), 1.54 – 1.41 (m, 6H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 171.2, 168.0, 167.2, 145.9, 144.9, 144.9, 144.6, 144.6, 132.3, 131.5, 131.5, 129.2, 127.3, 126.9, 126.8, 103.8, 103.8, 101.4, 101.3, 96.9, 95.5, 68.1, 68.1, 67.8, 67.6, 59.8, 50.8, 49.4, 49.4, 49.3, 49.2, 48.5, 48.5, 48.3, 48.3, 44.4, 44.4, 37.0, 37.0, 29.7, 25.5, 25.5, 25.3, 25.3, 22.0, 22.0, 21.8, 21.8, 19.1, 19.1, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -142.13, -142.19. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{32}ClFN_2NaO_6S$ 577.1546, found 577.1535.



4k

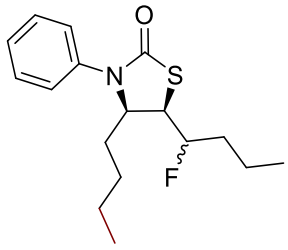
5-(fluoro(phenyl)methyl)-3-phenylthiazolidin-2-one (4k): The general procedure from cinnamyl(phenyl)carbamothioic fluoride **2k** (54.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4k** as white solid (43.2 mg, 75% yield). Mp: 107.7-111.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 9H), 7.21 (tt, J = 5.5, 3.0 Hz, 1H), 5.50 (dd, J = 47.2, 9.1 Hz, 1H), 4.30 (m, 2H), 4.07 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, Chloroform-d) δ 169.0, 138.6, 136.1, 135.9, 129.7, 129.6, 129.1, 128.7, 126.8, 126.7, 125.8, 122.0, 93.96 (d, J = 180.3 Hz), 52.12 (d, J = 3.8 Hz), 45.16 (d, J = 28.7 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -168.37. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{14}FNNaOS$ 310.0672, found 310.0675.



4l

7-fluoro-3-phenylhexahydrobenzo[d]thiazol-2(3H)-one (4l): The general procedure from cyclohex-2-en-1-yl(phenyl)carbamothioic fluoride **2l** (47.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg,

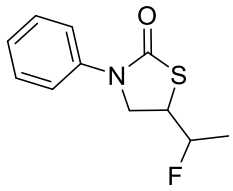
0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4l** as white solid (42.1 mg, 84% yield). Mp: 112.4-113.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.26 – 7.20 (m, 1H), 7.20 – 7.14 (m, 2H), 4.77 (m, 1H), 4.37 (m, 1H), 3.80 (dt, J = 13.8, 6.1 Hz, 1H), 2.04 (m, 1H), 1.87 – 1.76 (m, 1H), 1.72 – 1.57 (m, 2H), 1.57 – 1.33 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, Chloroform-d) δ 171.27, 137.55, 129.37, 127.30, 125.98, 92.14 (d, J = 175.3 Hz), 61.48 (d, J = 4.7 Hz), 47.14 (d, J = 25.4 Hz), 28.72 (d, J = 19.3 Hz), 25.98, 17.08 (d, J = 7.6 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -176.14. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{14}FNNaOS$ 274.0668, found 274.0668.



4m

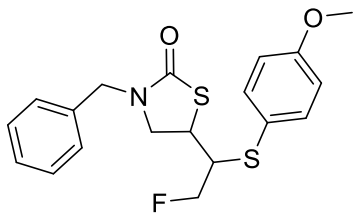
5-butyl-5-(1-fluorobutyl)-3-phenylthiazolidin-2-one (4m): The general procedure from (E)-dec-6-en-5-yl(phenyl)carbamothioic fluoride **2m** (58.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 50:1 to give anti-**4m** and syn-**4m** as yellow liquid (anti-**4m**: 36.2 mg, 58% yield; syn-**4m**: 13.7 mg, 22% yield). anti-**4m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.18 (tt, J = 6.9, 1.4 hz, 1H), 4.54 (m, 1H), 4.33 (dd, J = 9.2, 3.4 hz, 1H), 3.30 (dd, J = 9.4, 8.0 Hz, 1H), 1.85 – 1.68 (m, 2H), 1.67 – 1.50 (m, 3H), 1.43 (m, 1H), 1.32 – 1.19 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H), 0.78 (td, J = 8.5, 7.0, 4.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 137.6, 129.3, 126.7, 125.2, 93.9 (d, J = 177.4 Hz), 63.6 (d, J = 4.7 Hz), 48.3 (d, J = 23.4 hz), 34.7, 34.5, 31.1, 27.1, 22.3, 18.2 (d, J = 2.7 Hz), 13.8 (d, J = 8.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -179.22. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{24}FNNaOS$ 332.1446, found 332.1445. syn-**4n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 1H), 4.95 – 4.75 (m, 1H), 4.47 (q, J = 6.1 Hz, 1H), 4.28 (dt, J = 9.8, 6.7 Hz, 1H), 1.89 – 1.60 (m, 5H), 1.53 (m, 1H), 1.40 – 1.15 (m, 4H), 1.01 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 138.3, 129.3, 126.8, 125.5, 91.0 (d, J = 173.6 Hz), 64.0 (d, J = 1.9 Hz), 49.5 (d, J = 25.8 Hz), 36.5 (d, J =

21.1 Hz), 28.4 (d, J = 1.8 Hz), 27.7 (d, J = 2.2 Hz), 22.8, 17.9 (d, J = 3.1 Hz), 13.8 (d, J = 6.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -179.54. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{24}FNNaOS$ 332.1455, found 332.1445.



4n

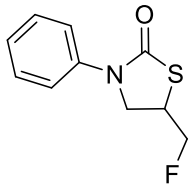
5-(1-fluoroethyl)-3-phenylthiazolidin-2-one (4n): The general procedure from but-2-en-1-yl(phenyl)carbamothioic fluoride **2n** (41.9 mg, 0.2 mmol, trans : cis = 4:1), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 50:1 to give **4n** as yellow liquid (anti-**4n**: 26.9 mg, 60% yield, syn-**4n**: 10.6 mg, 24% yield). anti-**4n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 4H), 7.14 (qt, J = 5.5, 2.9 Hz, 1H), 4.70 (ddq, J = 48.5, 9.1, 6.1 Hz, 1H), 4.18 (ddd, J = 10.7, 7.0, 1.1 Hz, 1H), 4.08 (dd, J = 10.6, 3.4 Hz, 1H), 3.62 (dtd, J = 9.1, 7.2, 3.4 Hz, 1H), 1.41 (dd, J = 24.0, 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 138.6, 129.1, 125.8, 122.0, 90.5 (d, J = 175.1 Hz), 52.2 (d, J = 5.3 Hz), 45.0 (d, J = 24.4 Hz), 18.8 (d, J = 22.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -170.47. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{11}H_{12}FNNaOS$ 248.0516, found 248.0522. syn-**4n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.14 (dq, J = 8.6, 4.0 Hz, 1H), 4.78 (dqd, J = 46.9, 6.3, 4.9 Hz, 1H), 4.15 (dd, J = 10.5, 7.8 Hz, 1H), 3.94 (dd, J = 10.4, 4.7 Hz, 1H), 3.87 (ddt, J = 14.8, 7.8, 4.9 Hz, 1H), 1.41 (dd, J = 23.6, 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.39, 138.53, 129.13, 125.82, 122.09, δ 90.50 (d, J = 174.8 Hz), 51.39 (d, J = 4.4 hz), 44.56 (d, J = 23.3 Hz), 17.05 (d, J = 22.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -175.30. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{11}H_{12}FNNaOS$ 248.0516, found 248.0519.



4o

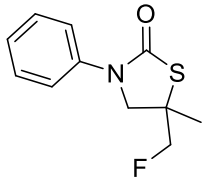
5-(fluoro(phenyl)methyl)-3-phenylthiazolidin-2-one (4o): The general procedure from (E)-benzyl(4-((4-methoxyphenyl)thio)but-2-en-1-yl)carbamothioic fluoride **2o** (63.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4

mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4o** as yellow liquid (32.4 mg, 43% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 7H), 6.80 – 6.70 (m, 2H), 4.65 – 4.40 (m, 3H), 4.34 (d, J = 14.8 Hz, 1H), 3.74 (s, 3H), 3.70 – 3.59 (m, 3H), 3.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.41, 160.34, 136.37, 135.75, 128.88, 128.27, 127.95, 121.90, 114.95, 82.85 (d, J = 175.3 Hz), 55.37, 54.07 (d, J = 18.3 Hz), 51.68, 48.58, 42.09 (d, J = 2.9 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ –221.57. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{20}FNNaO_2S_2$ 400.0812, found 400.0811.



4p

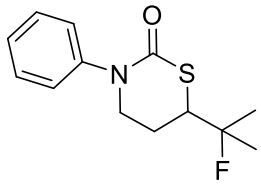
5-(fluoromethyl)-3-phenylthiazolidin-2-one (4p): The general procedure from allyl(phenyl)carbamothioic fluoride **2p** (39.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4p** as yellow liquid (21.1 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 4H), 7.24 (m, 1H), 4.62 (d, J = 7.2 Hz, 1H), 4.52 (d, J = 7.3 Hz, 1H), 4.31 (dd, J = 10.7, 6.7 Hz, 1H), 4.10 (dd, J = 10.6, 2.6 Hz, 1H), 3.96 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.97, 138.58, 129.11, 125.86, 122.04, 82.49 (d, J = 179.2 Hz), 51.76 (d, J = 3.4 hz), 39.06 (d, J = 22.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -211.10. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{10}H_{10}FNNaOS$ 234.0359, found 234.0362.



4q

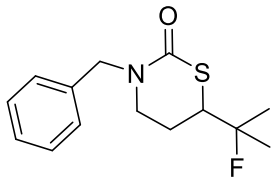
5-(fluoromethyl)-5-methyl-3-phenylthiazolidin-2-one (4q): The general procedure from (2-methylallyl)(phenyl)carbamothioic fluoride **2q** (41.9 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4q** as white solid (17.5 mg, 39% yield). Mp: 124.9-131.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (m, 4H), 7.25 – 7.18 (m, 1H), 4.59 (dd,

J = 48.1, 9.3 Hz, 1H), 4.36 (dd, J = 47.1, 9.1 Hz, 1H), 4.07 (d, J = 10.4 Hz, 1H), 3.90 (d, J = 10.4 hz, 1H), 1.66 (d, J = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.28, 138.70, 129.12, 125.85, 122.12, 85.60 (d, J = 184.2 Hz), 57.80 (d, J = 2.9 Hz), 48.56 (d, J = 19.8 Hz), 21.94 (d, J = 2.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -210.89. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{11}H_{12}FNNaOS$ 248.0516, found 248.0519.



4r

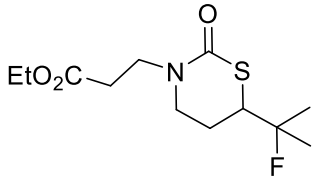
6-(2-fluoropropan-2-yl)-3-phenyl-1,3-thiazinan-2-one (4r): The general procedure from (4-methylpent-3-en-1-yl)(phenyl)carbamothioic fluoride **2r** (47.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **4r** as white solid (33.4 mg, 70% yield). Mp: 95.1-97.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.7 Hz, 2H), 7.25 – 7.09 (m, 3H), 3.86 – 3.63 (m, 3H), 2.33 (m, 1H), 2.03 (m, 1H), 1.42 (dd, J = 21.6, 13.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 143.0, 129.2, 127.0, 125.8, 95.8 (d, J = 172.0 Hz), 52.8 (d, J = 25.0 Hz), 51.1, 26.2 (d, J = 4.4 Hz), 24.6 (d, J = 24.3 Hz), 23.2 (d, J = 24.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ –138.79. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{16}FNNaOS$ 276.0829, found 276.0828.



4s

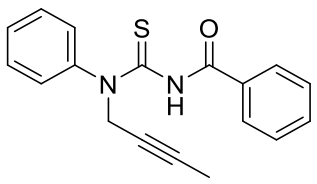
3-benzyl-6-(2-fluoropropan-2-yl)-1,3-thiazinan-2-one (4s): The general procedure from benzyl(4-methylpent-3-en-1-yl)carbamothioic fluoride **2s** (50.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4s** as yellow liquid (27.9 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.13 (m, 5H), 4.66 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 3.57 (m, 1H), 3.36 – 3.17 (m, 2H), 2.16 (m, 1H), 1.78 (m, 1H), 1.36 (dd, J = 21.7, 9.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 136.3, 128.7, 128.1, 127.7, 95.7 (d, J = 172.1 Hz), 52.5 (d, J = 25.3 Hz), 51.9,

46.9, 25.7 (d, J = 4.4 Hz), 24.7 (d, J = 24.1 Hz), 23.1 (d, J = 24.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.74. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{14}H_{18}FNNaOS$ 290.0985, found 290.0978.



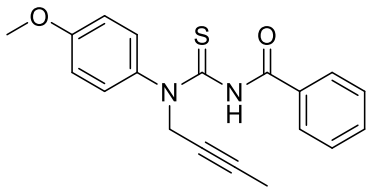
4t

ethyl 3-(6-(2-fluoropropan-2-yl)-2-oxo-1,3-thiazinan-3-yl)propanoate (4t): The general procedure from ethyl 3-((fluorocarbonothioyl)(4-methylpent-3-en-1-yl)amino)propanoate **2t** (52.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol), $Et_3N{\cdot}3HF$ (96.7 mg, 0.6 mmol) and PhMe (3 mL) at room temperature for 4 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4t** as yellow liquid (28.2 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 3.80 – 3.45 (m, 5H), 2.65 (q, J = 6.4 Hz, 2H), 2.30 (m, 1H), 1.91 (m, 1H), 1.44 (dd, J = 21.7, 12.2 Hz, 6H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.88, 165.07, 95.72 (d, J = 172.0 Hz), 60.74, 52.50 (d, J = 25.2 Hz), 48.96, 45.99, 32.90, 25.96 (d, J = 4.3 Hz), 24.58 (d, J = 24.1 Hz), 23.12 (d, J = 24.3 Hz), 14.14. ^{19}F NMR (471 MHz, $CDCl_3$) δ -138.68. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{12}H_{20}FNNaO_3S$ 300.1040, found 300.1033.



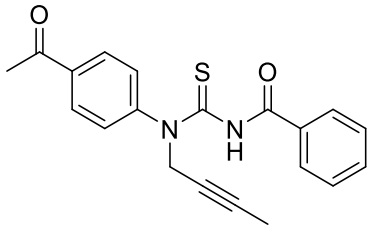
5a

***N*-(but-2-yn-1-yl(phenyl)carbamothioyl)benzamide (5a):** The general procedure from *N*-(but-2-yn-1-yl)aniline (1036.4 mg, 5 mmol), benzoyl isothiocyanate (816.0 mg, 5 mmol) and THF (50 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **5a** as white solid (1249.3 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.43 (m, 10H), 5.00 (s, 2H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 162.9, 142.6, 133.0, 132.6, 129.5, 128.7, 128.5, 127.4, 126.5, 81.5, 72.3, 46.6, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{16}N_2NaOS$ 331.0876, found 331.0670. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{16}N_2NaOS$ 331.0876, found 331.0670.



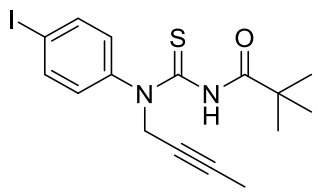
5b

***N*-(but-2-yn-1-yl(4-methoxyphenyl)carbamothioyl)benzamide (5b):** The general procedure from *N*-(but-2-yn-1-yl)-4-methoxyaniline (876.2 mg, 5 mmol), benzoyl isothiocyanate (816.0 mg, 5 mmol) and THF (50 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **5b** as white solid (1397.0 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.61 – 7.28 (m, 7H), 6.93 (d, J = 8.9 Hz, 2H), 4.97 (s, 2H), 3.79 (s, 3H), 1.80 (t, J = 2.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 159.3, 134.7, 133.2, 132.6, 128.7, 127.8, 127.4, 114.7, 72.5, 55.4, 46.6, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}N_2NaO_2S$ 361.0981, found 361.0973. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}N_2NaO_2S$ 361.0981, found 361.0973.



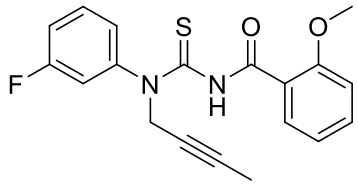
5c

***N*-((4-acetylphenyl)(but-2-yn-1-yl)carbamothioyl)benzamide (5c):** The general procedure from 1-(4-(but-2-yn-1-ylamino)phenyl)ethan-1-one (505.5 mg, 2.7 mmol), benzoyl isothiocyanate (440.6 mg, 2.7 mmol) and THF (27 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **5c**as yellow solid (1397.0 mg, 70% yield). The product was very unstable; therefore, we didn't get pure **5c**. The product was immediately put into the next step. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.02 – 7.88 (m, 2H), 7.64 – 7.43 (m, 5H), 7.34 (t, J = 7.8 Hz, 2H), 5.00 (q, J = 2.4 Hz, 2H), 2.53 (s, 3H), 1.78 (t, J = 2.4 Hz, 3H). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{18}N_2NaO_2S$ 373.0981, found 373.0985.



5d

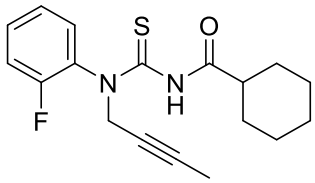
***N*-(but-2-yn-1-yl(4-iodophenyl)carbamothioyl)pivalamide (5d):** The general procedure from *N*-(but-2-yn-1-yl)-4-iodoaniline (964.6 mg, 8 mmol), pivaloyl chloride (2168.8 mg, 8 mmol), KSCN (1554.9 mg, 18 mmol) and acetone (8 mL) at room temperature for 5 h, the residue was washed with petroleum ether without additional purification to give **5d** as white solid (2.9412 g, 89% yield). The product contained a small amount of impurities, which was directly put into the next reaction. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 4.89 (s, 2H), 1.79 (t, J = 2.4 Hz, 3H), 0.97 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 173.1, 142.8, 138.1, 137.6, 128.5, 125.7, 93.2, 72.0, 47.0, 39.6, 26.7, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{19}N_2NaOS$ 437.0155, found 437.0160.



5e

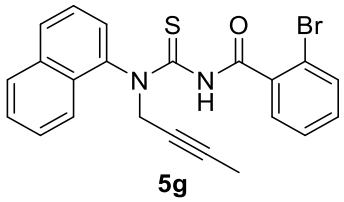
***N*-(but-2-yn-1-yl(3-fluorophenyl)carbamothioyl)-2-methoxybenzamide (5e):** The general procedure from *N*-(but-2-yn-1-yl)-3-fluoroaniline (887.1 mg, 5.2 mmol), 2-methoxybenzoyl chloride (848.6 mg, 5.2 mmol), KSCN (1010.7 mg, 10.4 mmol) and acetone (8 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **5e** as white solid (1241.1 g, 67% yield). Isomerism is unconspicuous in the ^{1}H NMR spectrum, but it is obvious in the ^{13}C NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.01 (dd, J = 8.0, 1.9 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.22 – 7.12 (m, 2H), 7.08 (td, J = 8.3, 2.5 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 4.97 (q, J = 2.5 Hz, 2H), 3.68 (s, 3H), 1.79 (t, J = 2.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.3, 176.1, 167.3, 163.6, 161.6, 161.3, 159.6, 156.9, 144.2 (d, J = 9.4 Hz), 141.2 (d, J = 10.5 Hz), 134.0, 132.9, 132.8, 132.4, 130.6 (d, J = 9.1 Hz), 129.7 (d, J = 9.1 Hz), 129.0, 125.7, 122.7 (d, J = 3.2 Hz), 121.6, 120.4, 119.8, 118.8 (d, J = 3.1 Hz), 117.2, 115.3 (d, J = 20.9 Hz), 114.4 (d, J = 23.0 Hz), 113.0 (d, J = 21.3 Hz), 112.0, 111.8 (d, J = 4.2 Hz), 111.4, 81.5, 72.4, 55.9, 55.7, 46.0,

15.4, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}FN_2NaO_2S$ 379.0887, found 379.0892.



5f

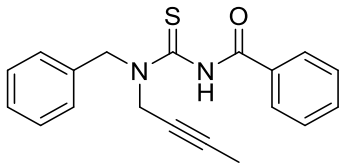
***N*-(but-2-yn-1-yl(2-fluorophenyl)carbamothioyl)cyclohexanecarboxamide (5f):** The general procedure from *N*-(but-2-yn-1-yl)-2-fluoroaniline (1387.2 mg, 8.5 mmol), cyclohexanecarbonyl chloride (1246.2 mg, 8.5 mmol), KSCN (1652.1 mg, 17 mmol) and acetone (8.5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **5f** as white solid (1.72 g, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.42 – 7.28 (m, 2H), 7.23 – 7.07 (m, 2H), 5.12 (s, 1H), 4.88 – 4.53 (m, 1H), 2.18 (d, J = 12.0 Hz, 1H), 1.75 (q, J = 2.4 Hz, 3H), 1.70 – 1.43 (m, 5H), 1.11 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 171.9, 156.5 (d, J = 251.9 Hz), 130.2, 129.9 (d, J = 7.9 Hz), 128.8, 124.2, 124.2, 116.5 (d, J = 19.9 Hz)., 81.5, 71.8, 46.1, 45.1, 28.7, 28.6, 25.4, 25.1, 3.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{21}FN_2NaOS$ 355.1251, found 355.1251.



5g

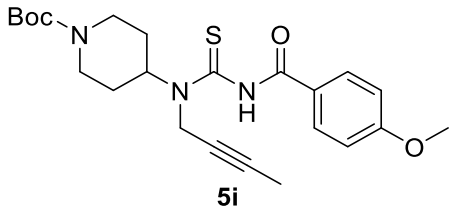
2-bromo-*N*-(but-2-yn-1-yl(naphthalen-1-yl)carbamothioyl)benzamide (5g): The general procedure from *N*-(but-2-yn-1-yl)naphthalen-1-amine (976.4 mg, 5 mmol), 2-bromobenzoyl chloride (1097.3 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **5g** as white solid (1.5092 g, 69% yield). The product contained a small amount of impurities, which was directly put into the next reaction.^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.02 – 7.93 (m, 2H), 7.88 (d, J = 8.2 Hz, 1H), 7.68 – 7.56 (m, 4H), 7.38 (dd, J = 7.8, 1.3 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.14 (dd, J = 7.5, 1.9 Hz, 1H), 5.40 (dt, J = 16.9, 2.4 Hz, 1H), 4.79 (dt, J = 16.9, 2.4 Hz, 1H), 1.73 (t, J = 2.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 165.5, 137.1, 136.41 134.7, 133.1, 131.6, 130.1, 129.8, 129.4, 128.6, 127.9, 127.3, 127.1, 126.0, 125.7, 122.4, 118.7, 81.9,

72.4, 45.7, 3.5. . HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{17}BrN_2NaOS$ 459.0137, found 459.0140.



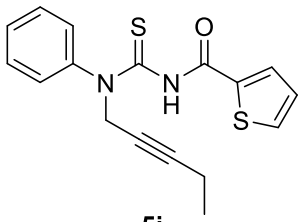
5h

***N*-(benzyl(but-2-yn-1-yl)carbamothioyl)benzamide (5h):** The general procedure from *N*-benzylbut-2-yn-1-amine (640.1 mg, 4 mmol), benzoyl isothiocyanate (656.1 mg, 4 mmol) and THF (40 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **5h** as purple liquid (1097.3 mg, 81% yield). The product contained a small amount of impurities, which was directly put into the next reaction. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.79 (d, J = 63.9 Hz, 2H), 7.62 – 7.08 (m, 8H), 5.46 (s, 1H), 5.20 – 4.54 (m, 2H), 4.22 (d, J = 17.0 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.9, 163.7, 133.0, 132.5, 128.8, 128.7, 128.0, 127.8, 71.9, 56.1, 42.2, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}N_2NaOS$ 345.1032, found 345.1032.



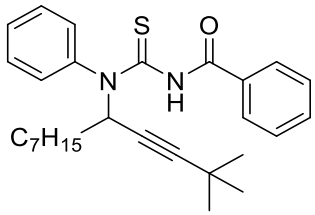
5i

tert-butyl 4-(1-(but-2-yn-1-yl)-3-(4-methoxybenzoyl)thioureido)piperidine-1-carboxylate (5i): The general procedure from tert-butyl 4-(but-2-yn-1-ylamino)piperidine-1-carboxylate (1261.8 mg, 5 mmol), 4-methoxybenzoyl chloride (938.2 mg, 5 mmol), KSCN (971.8 mg, 10 mmol) and acetone (5 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 3:1 to give **5i** as white solid (1.9237 g, 86% yield). The product are easy to isomerize, therefore, there are more peaks in the ^{1}H NMR and ^{13}C NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 5.22 (s, 1H), 4.66 – 4.00 (m, 4H), 3.87 (s, 3H), 2.81 (s, 2H), 2.03 (d, J = 12.2 Hz, 2H), 1.82 (s, 5H), 1.47 (s, 9H), 1.25 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 163.3, 154.5, 129.9, 125.0, 114.0, 79.7, 73.2, 61.1, 55.5, 37.4, 28.8, 28.3, 3.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{31}N_3NaO_4S$ 468.1927, found 468.1931.



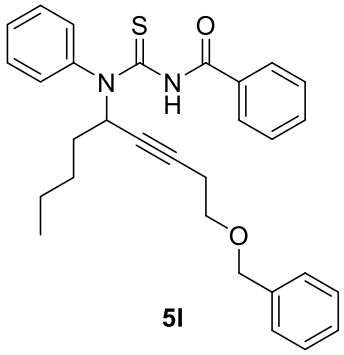
5j

***N*-(pent-2-yn-1-yl(phenyl)carbamothioyl)thiophene-2-carboxamidee (5j):** The general procedure from *N*-(pent-2-yn-1-yl)aniline (1242.0 mg, 7.8 mmol), thiophene-2-carbonyl chloride (1143.5 mg, 7.8 mmol), KSCN (971.8 mg, 15.6 mmol) and acetone (7.8 mL) at room temperature for 5 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **5j** as white solid (1804.3 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.55 – 7.31 (m, 6H), 7.20 (d, J = 5.6 Hz, 1H), 6.98 (t, J = 4.4 Hz, 1H), 4.99 (s, 2H), 2.25 – 2.08 (m, 2H), 1.06 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 178.4, 157.1, 142.1, 137.5, 132.3, 129.7, 129.6, 128.7, 127.9, 126.8, 87.6, 72.5, 46.1, 13.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{16}N_2NaOS_2$ 351.0596, found 351.0600.



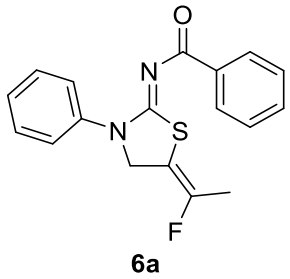
5k

***N*-((2,2-dimethyldodec-3-yn-5-yl)(phenyl)carbamothioyl)benzamide (5k):** The general procedure from *N*-(2,2-dimethyldodec-3-yn-5-yl)aniline (1541.6 mg, 5.4 mmol), benzoyl isothiocyanate (881.3 mg, 5.4 mmol) and THF (54 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **5k** as brown liquid (1.042 mg, 43% yield). The product contained a small amount of impurities, which was directly put into the next reaction. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.58 – 7.18 (m, 10H), 6.45 (s, 1H), 1.97 – 1.90 (m, 1H), 1.63 – 1.40 (m, 4H), 1.40 – 1.25 (m, 11H), 1.09 (s, 9H), 0.88 (t, J = 6.7 Hz, 5H). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{28}H_{36}N_2NaOS$ 471.2441, found 471.2452.



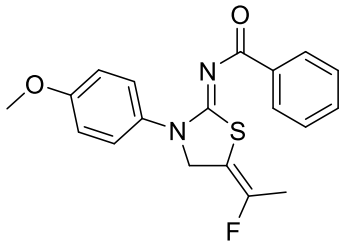
5l

***N*-((8-(benzyloxy)oct-5-yn-4-yl)(phenyl)carbamothioyl)benzamide (5l):** The general procedure from *N*-(8-(benzyloxy)oct-5-yn-4-yl)aniline (3043.7 mg, 9.9 mmol), benzoyl isothiocyanate (1615.7 mg, 9.9 mmol) and THF (54 mL) at room temperature for 2 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **5l** as brown liquid (2.4688 g, 53% yield). The product contained a small amount of impurities, which was directly put into the next reaction. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.08 (dt, J = 8.4, 1.7 Hz, 1H), 7.49 – 7.29 (m, 14H), 6.56 (s, 1H), 4.54 (s, 2H), 3.52 (t, J = 7.0 Hz, 2H), 2.48 (td, J = 7.2, 3.9 Hz, 2H), 1.85 (d, J = 6.5 Hz, 1H), 1.63 – 1.46 (m, 3H), 0.99 (t, J = 7.1 Hz, 3H). HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{29}H_{30}FN_2NaO_2S$ 493.1920, found 493.1923.



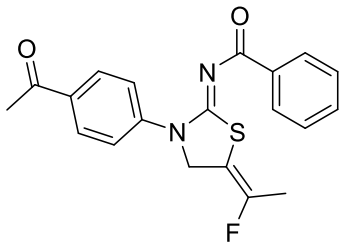
6a

***N*-((2Z,5E)-5-(1-fluoroethylidene)-3-phenylthiazolidin-2-ylidene)benzamide (6a):** The general procedure from *N*-(but-2-yn-1-yl(phenyl)carbamothioyl)benzamide **5a** (61.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6a** as white solid (53.6 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.41 (dt, J = 13.5, 7.5 Hz, 3H), 7.28 (q, J = 7.9 Hz, 3H), 4.74 (m, 2H), 1.99 (dt, J = 17.0, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 167.9, 148.1 (d, J = 252.8 Hz), 139.8, 135.9, 132.3, 129.8, 129.1, 128.1, 127.1, 124.8, 108.1 (d, J = 25.9 Hz), 52.0 (d, J = 6.4 Hz), 16.3 (d, J = 27.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.00. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{15}FN_2NaOS$ 349.0781, found 349.0779.



6b

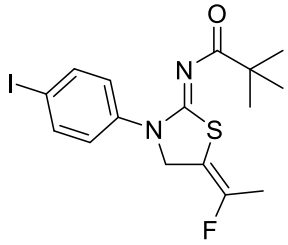
***N*-((2Z,5E)-5-(1-fluoroethylidene)-3-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (6b):** The general procedure from *N*-(but-2-yn-1-yl(4-methoxyphenyl)carbamothioyl)benzamide **5b** (67.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6b** as white solid (52.6 mg, 74% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.3, 1.4 Hz, 2H), 7.51 – 7.40 (m, 3H), 7.36 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 4.73 (dq, J = 4.5, 2.4 Hz, 2H), 3.86 (s, 3H), 2.04 (dt, J = 17.0, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 167.8, 158.3, 147.9 (d, J = 252.7 Hz), 136.0, 132.6, 132.1, 129.7, 128.0, 126.2, 114.1, 108.2 (d, J = 26.0 Hz), 55.5, 52.2 (d, J = 6.3 Hz), 16.3 (d, J = 27.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.15. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}FN_2NaO_2S$ 379.0887, found 379.0885.



6c

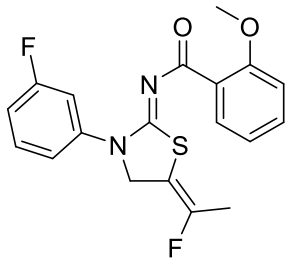
***N*-((2Z,5E)-3-(4-acetylphenyl)-5-(1-fluoroethylidene)thiazolidin-2-ylidene)benzamide (6c):** The general procedure from *N*-((4-acetylphenyl)(but-2-yn-1-yl)carbamothioyl)benzamide **5c** (70.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **6c** as white solid (58.1 mg, 79% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.03 (m, 4H), 7.78 (d, J = 8.6 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 4.86 (t, J = 2.7 Hz, 2H), 2.66 (s, 3H), 2.08 (dt, J = 17.0, 2.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 176.1, 167.9, 148.5 (d, J = 253.8 Hz), 143.7, 135.6, 134.8, 132.6, 129.8, 129.2, 128.3, 123.8, 107.5 (d, J = 26.1 Hz), 51.3 (d, J = 6.6 Hz), 26.6, 16.3 (d, J = 27.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.16. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{17}FN_2NaO_2S$ 391.0887,

found 391.0894.



6d

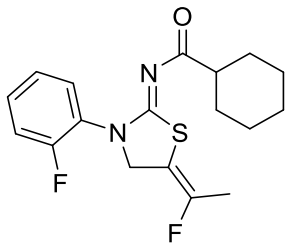
***N*-((2Z,5E)-5-(1-fluoroethylidene)-3-(4-iodophenyl)thiazolidin-2-ylidene)pivalamide (6d):** The general procedure from *N*-(but-2-yn-1-yl(4-iodophenyl)carbamothioyl)pivalamide **5d** (82.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6d** as white solid (44.9 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.9 Hz, 2H), 7.43 – 7.30 (m, 2H), 4.78 – 4.61 (m, 2H), 2.02 (dt, J = 17.0, 2.2 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.81, 166.68, 148.07 (d, J = 253.0 Hz), 139.57, 137.74, 125.71, 107.71 (d, J = 25.6 Hz), 90.65, 50.97 (d, J = 6.7 Hz), 41.22, 27.18, 16.23 (d, J = 27.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.15. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{18}FIN_2NaOS$ 455.0061, found 455.0070.



6e

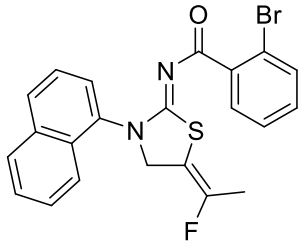
***N*-((2Z,5E)-5-(1-fluoroethylidene)-3-(3-fluorophenyl)thiazolidin-2-ylidene)-2-methoxybenzamide (6e):** The general procedure from *N*-(but-2-yn-1-yl(3-fluorophenyl)carbamothioyl)-2-methoxybenzamide **5e** (71.3 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **6e** as white solid (58.8 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.7, 1.8 Hz, 1H), 7.66 (dt, J = 10.8, 2.3 Hz, 1H), 7.47 – 7.34 (m, 2H), 7.31 (dd, J = 8.6, 1.7 Hz, 1H), 7.04 – 6.87 (m, 3H), 4.77 (m, 2H), 3.92 (s, 3H), 2.04 (dt, J = 16.9, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 167.1, 162.6 (d, J = 246.0 Hz), 159.8, 148.1 (d, J = 253.5 Hz), 141.2 (d, J = 10.7 Hz), 133.2, 132.5, 129.9 (d, J = 9.2 Hz), 125.3,

120.0, 118.9 (d, J = 3.0 Hz), 113.4 (d, J = 21.1 Hz), 112.1 (d, J = 25.6 Hz), 111.9, 107.9 (d, J = 25.4 Hz), 55.8, 51.5 (d, J = 6.6 Hz), 16.3 (d, J = 27.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.96, -111.04. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{16}F_2N_2NaO_2S$ 397.0793, found 397.0798.



6f

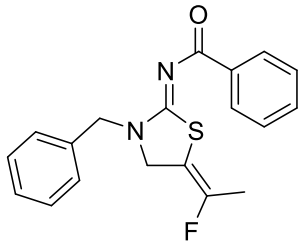
***N*-((2Z,5E)-5-(1-fluoroethylidene)-3-(2-fluorophenyl)thiazolidin-2-ylidene)cyclohexanecarboxamide (6f):** The general procedure from *N*-(but-2-yn-1-yl(2-fluorophenyl)carbamothioyl) cyclohexanecarboxamide **5f** (66.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6f** as white solid (48.5 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.25 – 7.15 (m, 2H), 4.61 (dt, J = 4.6, 2.3 Hz, 2H), 2.26 (tt, J = 11.1, 3.6 Hz, 1H), 2.02 (dt, J = 16.9, 2.3 Hz, 3H), 1.82 (m, 2H), 1.67 (dt, J = 12.6, 3.4 Hz, 2H), 1.62 – 1.54 (m, 1H), 1.41 – 1.08 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.2, 167.7, 157.4 (d, J = 252.3 Hz), 147.8 (d, J = 252.7 Hz), 129.7 (d, J = 7.9 Hz), 128.8 (d, J = 1.8 Hz), 127.2 (d, J = 12.1 Hz), 124.5 (d, J = 3.7 Hz), 116.8 (d, J = 19.8 Hz), 108.7 (d, J = 25.9 Hz), 51.0 (d, J = 6.6 Hz), 47.5, 29.0, 26.0, 25.7, 16.3 (d, J = 27.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.30, -118.77. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{20}F_2N_2NaOS$ 373.1157, found 373.1159.



6g

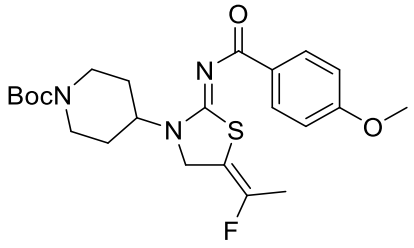
2-bromo-*N*-((2Z,5E)-5-(1-fluoroethylidene)-3-(naphthalen-1-yl)thiazolidin-2-ylidene)benzamide (6g): The general procedure from 2-bromo-*N*-(but-2-yn-1-yl(naphthalen-1-yl)carbamothioyl)benzamide **5g** (87.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether:

ethyl acetate = 10:1 to give **6g** as white solid (54.2 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 7.83 (m, 2H), 7.71 (dt, J = 6.3, 3.6 Hz, 1H), 7.64 – 7.38 (m, 6H), 7.03 (m, 2H), 4.84 (m, 1H), 4.80 – 4.66 (m, 1H), 2.11 (dt, J = 16.9, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 169.7, 148.3 (d, J = 253.3 Hz), 136.7, 136.3, 134.6, 134.1, 132.1, 131.5, 129.3, 129.1, 128.7, 127.2, 126.6, 126.6, 125.6, 125.1, 122.4, 122.0, 108.7 (d, J = 26.6 Hz), 53.0 (d, J = 6.0 Hz), 16.4 (d, J = 27.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.16. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{16}BrFN_2NaO_2S$ 477.0043, found 477.0074.



6h

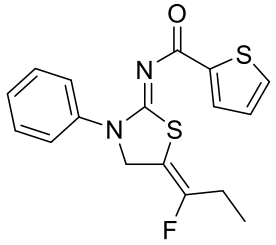
***N*-((2Z,5E)-3-benzyl-5-(1-fluoroethylidene)thiazolidin-2-ylidene)benzamide (6h):** The general procedure from *N*-(benzyl(but-2-yn-1-yl)carbamothioyl)benzamide **5h** (64.5 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6h** as white solid (40.9 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 – 8.25 (m, 2H), 7.57 – 7.47 (m, 1H), 7.43 (dd, J = 8.2, 6.7 Hz, 2H), 7.40 – 7.28 (m, 5H), 5.02 (s, 2H), 4.26 (dd, J = 3.6, 2.3 Hz, 2H), 1.99 (dt, J = 17.0, 2.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 168.8, 148.0 (d, J = 252.3 Hz), 136.2, 135.1, 132.1, 129.7, 129.0, 128.3, 128.2, 128.1, 108.5 (d, J = 26.1 Hz), 51.2, 49.2 (d, J = 6.4 Hz), 16.4 (d, J = 27.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.23. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}FN_2NaOS$ 363.0938, found 363.0931.



6i

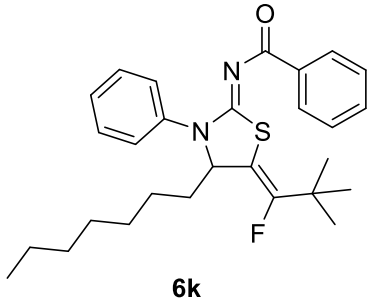
tert-butyl 4-((2Z,5E)-5-(1-fluoroethylidene)-2-((4-methoxybenzoyl)imino)thiazolidin-3-yl)piperidine-1-carboxylate (6i): The general procedure from tert-butyl 4-(1-(but-2-yn-1-yl)-3-(4-methoxybenzoyl)thioureido)piperidine-1-carboxylate **5i** (89.1 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21

mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 5:1 to give **6i** as white solid (51.1 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 4.80 (tt, J = 12.2, 4.0 Hz, 1H), 4.33 (t, J = 2.9 Hz, 4H), 3.86 (s, 3H), 2.88 (s, 2H), 2.00 (dt, J = 17.0, 2.4 Hz, 3H), 1.95 – 1.87 (m, 2H), 1.73 (qd, J = 12.2, 4.5 Hz, 2H), 1.49 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 167.5, 162.9, 154.5, 147.9 (d, J = 252.0 Hz), 131.5, 128.9, 113.3, 108.6 (d, J = 25.4 Hz), 79.9, 55.2 (d, J = 29.7 Hz), 45.8, 45.8, 43.2, 28.8, 28.4, 16.4 (d, J = 27.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.56. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{30}FN_3NaO_4S$ 486.1833, found 486.1826.



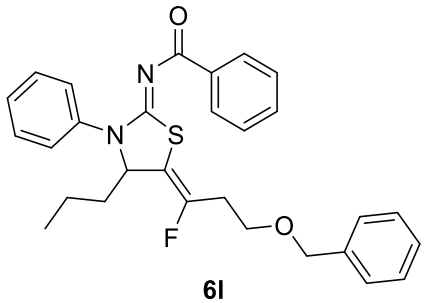
6j

***N*-((2Z,5E)-5-(1-fluoropropylidene)-3-phenylthiazolidin-2-ylidene)thiophene-2-carboxamide (6j):** The general procedure from *N*-(pent-2-yn-1-yl(phenyl)carbamothioyl)thiophene-2-carboxamidee **5j** (65.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6j** as white solid (54.1 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, J = 3.8, 1.3 Hz, 1H), 7.67 – 7.53 (m, 2H), 7.53 – 7.42 (m, 3H), 7.32 (t, J = 7.4 Hz, 1H), 7.04 (dd, J = 5.0, 3.7 Hz, 1H), 4.80 (dt, J = 3.4, 1.7 Hz, 2H), 2.45 – 2.24 (m, 2H), 1.16 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.75, 167.09, 152.45 (d, J = 256.3 Hz), 142.28, 139.51, 132.24, 132.15, 128.88, 127.86, 126.95, 124.59, 106.90 (d, J = 26.9 Hz), 51.93 (d, J = 6.5 Hz), 24.14 (d, J = 26.0 Hz), 10.14. ^{19}F NMR (471 MHz, $CDCl_3$) δ -101.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{15}N_2NaOS_2$ 369.0502, found 369.0506.



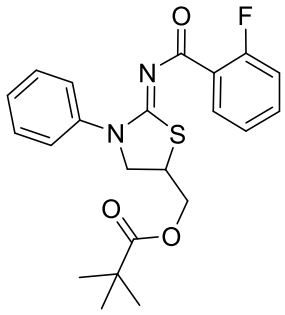
6k

***N*-((2Z,5E)-5-(1-fluoro-2,2-dimethylpropylidene)-4-heptyl-3-phenylthiazolidin-2-ylidene)benzamide (6k):** The general procedure from *N*-((2,2-dimethyldodec-3-yn-5-yl)(phenyl)carbamothioyl)benzamide **5k** (65.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **6k** as white solid (73.5 mg, 79% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.54 – 7.45 (m, 4H), 7.45 – 7.29 (m, 4H), 5.28 (q, J = 3.8 Hz, 1H), 1.77 (m, 1H), 1.68 – 1.56 (m, 1H), 1.32 (d, J = 1.6 Hz, 10H), 1.22 (dd, J = 24.9, 5.2 Hz, 8H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 168.0, 157.7 (d, J = 256.5 Hz), 138.6, 136.2, 131.9, 129.7, 129.0, 127.9, 127.5, 126.9, 110.8 (d, J = 29.1 Hz), 64.5 (d, J = 7.3 Hz), 36.3 (d, J = 24.5 Hz), 32.2 (d, J = 2.4 Hz), 31.6, 29.3, 28.9, 27.7 (d, J = 3.7 Hz), 22.8, 22.5, 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.55. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{28}H_{35}FN_2NaOS$ 489.2346, found 489.2353.



6l

***N*-((2Z,5E)-5-(3-(benzyloxy)-1-fluoropropylidene)-3-phenyl-4-propylthiazolidin-2-ylidene)benzamide (6l):** The general procedure from *N*-((8-(benzyloxy)oct-5-yn-4-yl)(phenyl)carbamothioyl)benzamide **5l** (97.7 mg, 0.2 mmol), $PhI(OPiv)_2$ (85.3 mg, 0.21 mmol), $Et_3N{\cdot}3HF$ (117 mg, 0.7 mmol) and dioxane (3 mL) at room temperature for 3 h, the residue was purified by column chromatography on silica gel using petroleum ether: ethyl acetate = 30:1 to give **6l** as colorless liquid (65.3 mg, 67% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.53 – 7.30 (m, 12H), 7.27 (m, 1H), 5.26 (dt, J = 6.1, 3.1 Hz, 1H), 4.56 (d, J = 2.2 Hz, 2H), 3.70 (t, J = 6.5 Hz, 2H), 2.82 – 2.58 (m, 2H), 1.82 – 1.70 (m, 1H), 1.69 – 1.61 (m, 1H), 1.40 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 167.6, 149.1 (d, J = 256.6 Hz), 138.6, 138.0, 136.1, 132.0, 129.7, 129.1, 128.4, 128.0, 127.6, 127.6, 127.6, 126.9, 114.3 (d, J = 24.0 Hz), 72.9, 65.7, 63.1 (d, J = 2.3 Hz), 31.7 (d, J = 25.6 Hz), 31.8, 31.6, 16.6, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -100.46. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{29}H_{29}FN_2NaO_2S$ 511.1826, found 511.1830.



7a

(Z)-(2-((2-fluorobenzoyl)imino)-3-phenylthiazolidin-5-yl)methyl pivalate (7a): ^{1}H NMR (600 MHz , $CDCl_3$) δ 7.96 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.43 – 7.37 (m, 1H), 7.31 (td, *J* = 7.3, 1.3 Hz, 1H), 7.16 – 7.02 (m, 2H), 4.54 – 4.18 (m, 3H), 3.99 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.89 (qd, *J* = 7.2, 3.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.05, 174.18, 174.15, 169.83, 163.28, 161.56, 139.93, 133.41, 133.35, 132.49, 128.92, 126.82, 124.56, 123.49, 116.84, 116.69, 64.68, 54.26, 40.25, 38.84, 27.10.

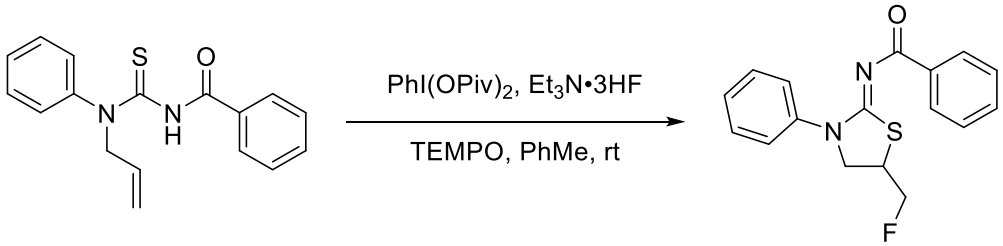
Reference

[1] Liu, S.; Jiang, L. Copper-Catalyzed Multicomponent Reactions of Intramolecular and Intermolecular Thiotrifluoromethylation of Alkenes: Access to CF3–Containing 2-Iminothiazolidines and Isothioureas. *Org. Lett.* **2022**, 39, 7157-7162.

7. Mechanism study.

7.1 Radical trapping experiment

Adding 2.0 equiv of TEMPO to the reaction system of 1b to give 3b

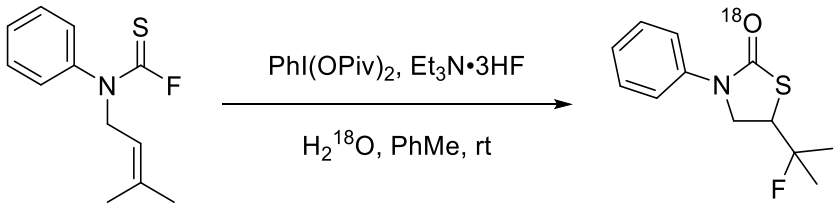


1a **2a**

A solution of $PhI(OPiv)_2$ (0.23 mmol, 1.2 eq) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in PhMe (3 mL) was stirred at room temperature for 5 minutes, then TEMPO (0.4 mmol, 2 eq) and alkenyl thioureas **1b** (0.2 mmol, 1 eq)

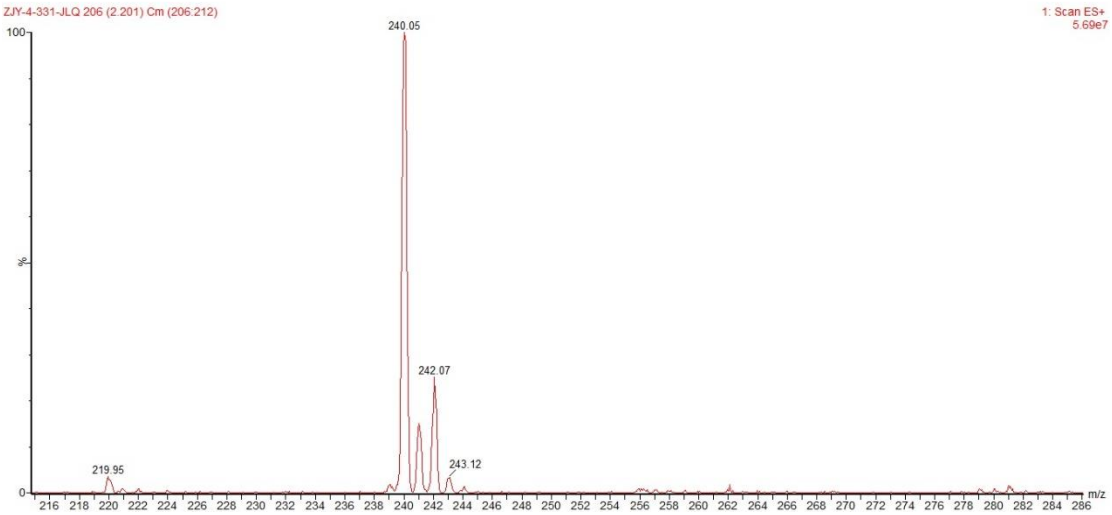
was added. The mixture was stirred at the room temperature for 2 h until alkenyl thioureas **1b** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The yield of the **1b** was 79% through ^1H NMR spectrum with CH_2Br_2 as internal standard.

7.2 Isotope labeling experiment ($H_2{}^{18}O$)

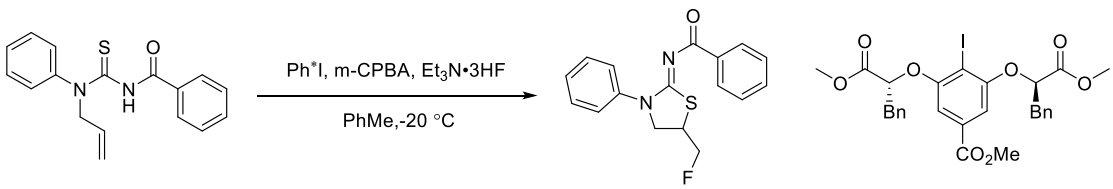


3a **4a'**

A solution of $PhI(OPiv)_2$ (162.5 mg, 0.4 mmol) and $Et_3N{\cdot}3HF$ (98.2 mg, 0.6 mmol) in PhMe (3 mL) was stirred at room temperature for 5 minutes, then $H_2{}^{18}O$ (8 mg, 0.4 mmol) and (3-methylbut-2-en-1-yl)(phenyl)carbamothioic fluoride **3a** (44.7 mg, 0.2 mmol) was added. The mixture was stirred at the room temperature for 4 h until thiocarbamoyl fluorides **3a** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was analyzed by LC-MS.

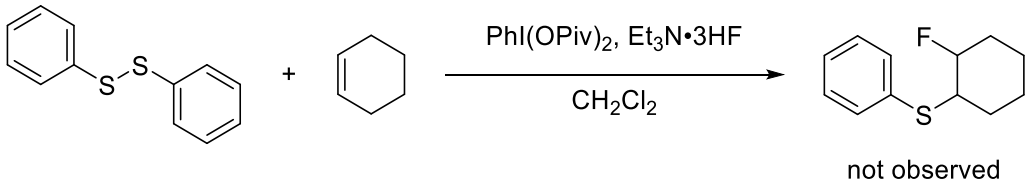


7.3 Chiral regulation experiment



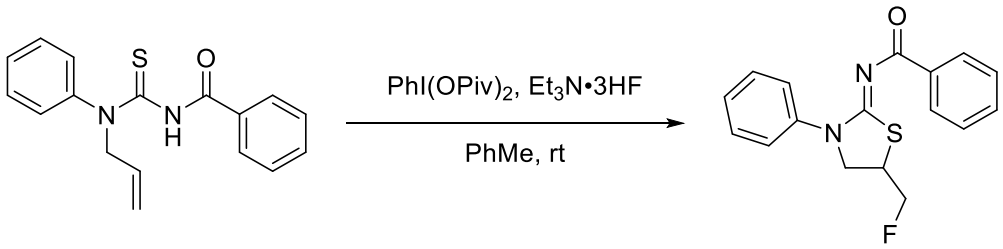
A solution of $PhI(OPiv)_2$ (0.23 mmol, 1.2 eq) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in PhMe (3 mL) was stirred at room temperature for 5 minutes, then alkenyl thioureas **1r** (0.2 mmol, 1 eq) was added. The mixture was stirred at the room temperature for 2 h until alkenyl thioureas **1r** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The yield of the **1r** was 53% by analyzing ^1H NMR spectrum with CH_2Br_2 as internal standard.and the residue was analyzed by HPLC, which showed the reaction is not stereoselective.

7.4 Experiment of disulfide as a sulfur source



A solution of $PhI(OPiv)_2$ (0.4 mmol,2 eq) and $Et_3N{\cdot}3HF$ (0.6 mmol, 3 eq) in CH_2Cl_2 (3 mL) was stirred at room temperature for 5 minutes, then cyclohexene (0.4 mmol, 2 eq) and diphenyl disulfide (0.2 mmol, 1 eq) was added. The mixture was stirred at the room temperature for 10 h. TLC monitoring showed that a large amount of raw materials remained and few new products were produced.

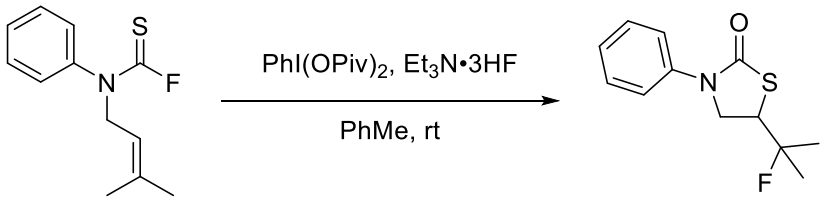
8. The 4 mmol scale of procedures for 2a.



1a **2a**

A solution of $PhI(OPiv)_2$ (1950 mg, 4.8 mmol) and $Et_3N{\cdot}3HF$ (2006.5 mg, 12 mmol) in PhMe (60 mL) was stirred at room temperature for 20 minutes, then *N*-(allyl(phenyl)carbamothioyl)benzamide **1a** (1185.6 mg, 4 mmol) was added. The mixture was stirred at the room temperature for 2 h until alkenyl thioureas **1a** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether: dichloromethane = 1:2 to give **3a** as yellow liquid (872.3 mg, 69%).

9. The 10 mmol scale of procedures for 4a.

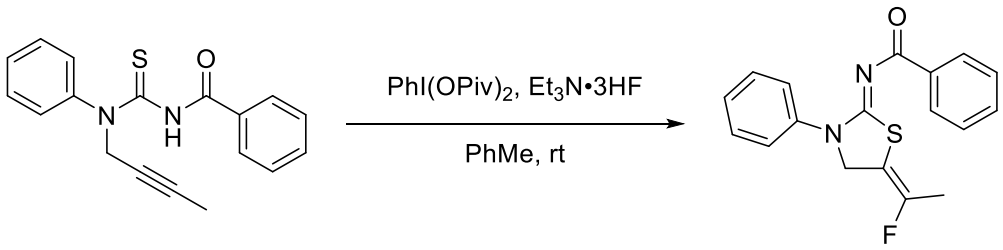


3a **4a**

A solution of $PhI(OPiv)_2$ (8125.2 mg, 20 mmol) and $Et_3N{\cdot}3HF$ (5016.3 mg, 30 mmol) in PhMe (100 mL) was stirred at room temperature for 10 minutes, then (3-methylbut-2-en-1-yl)(phenyl)carbamothioic fluoride **3a** (2233.1 mg, 10 mmol) was added. The mixture was stirred at the room temperature for 4 h until thiocarbamoyl fluorides **3a** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **4a** as white solid

(1923.9 mg, 80%).

10. The 4.6 mmol scale of procedures for 6a.

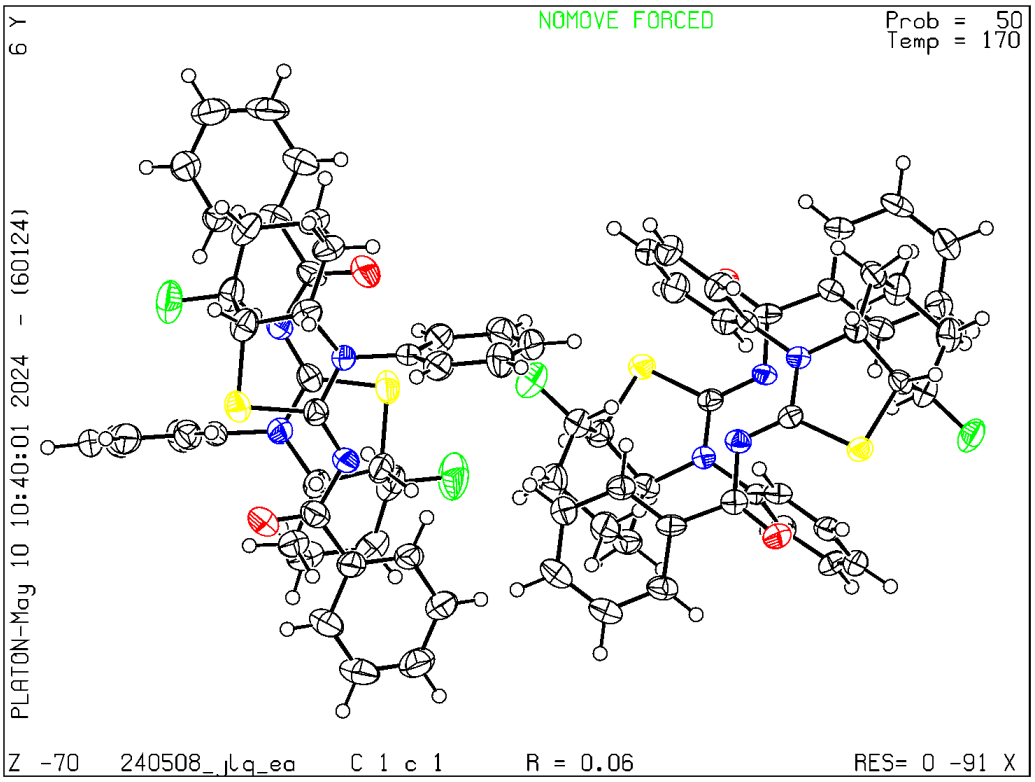


5a **6a**

A solution of $PhI(OPiv)_2$ (1962.2 mg, 4.83 mmol) and $Et_3N{\cdot}3HF$ (2692.1 mg, 16.1 mmol) in dioxane (69 mL) was stirred at room temperature for 10 minutes, then N-(but-2-yn-1-yl(phenyl)carbamothioyl)benzamide **5a** (1418.6 mg, 4.6 mmol) was added. The mixture was stirred at the room temperature for 4 h until alkynyl thioureas **5a** was consumed. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution, extracted with EA, and the combined organic phases were washed with brine, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether: ethyl acetate = 10:1 to give **6a** as white solid (766.2 mg, 51%).

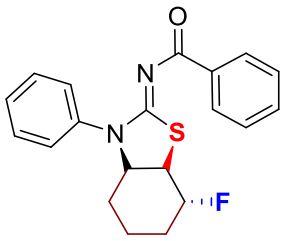
11. The X-ray crystallographic analysis for 2af (CCDC 2364347)

With 50% ellipsoid:


NOMOVE FORCED
Prob = 50
Temp = 170
6 Y
PLATON-May 10 10:40:01 2024 - (60124)
Z -70 240508_jlq_ea C 1 c 1 R = 0.06 RES= 0 -91 X

|||

four of

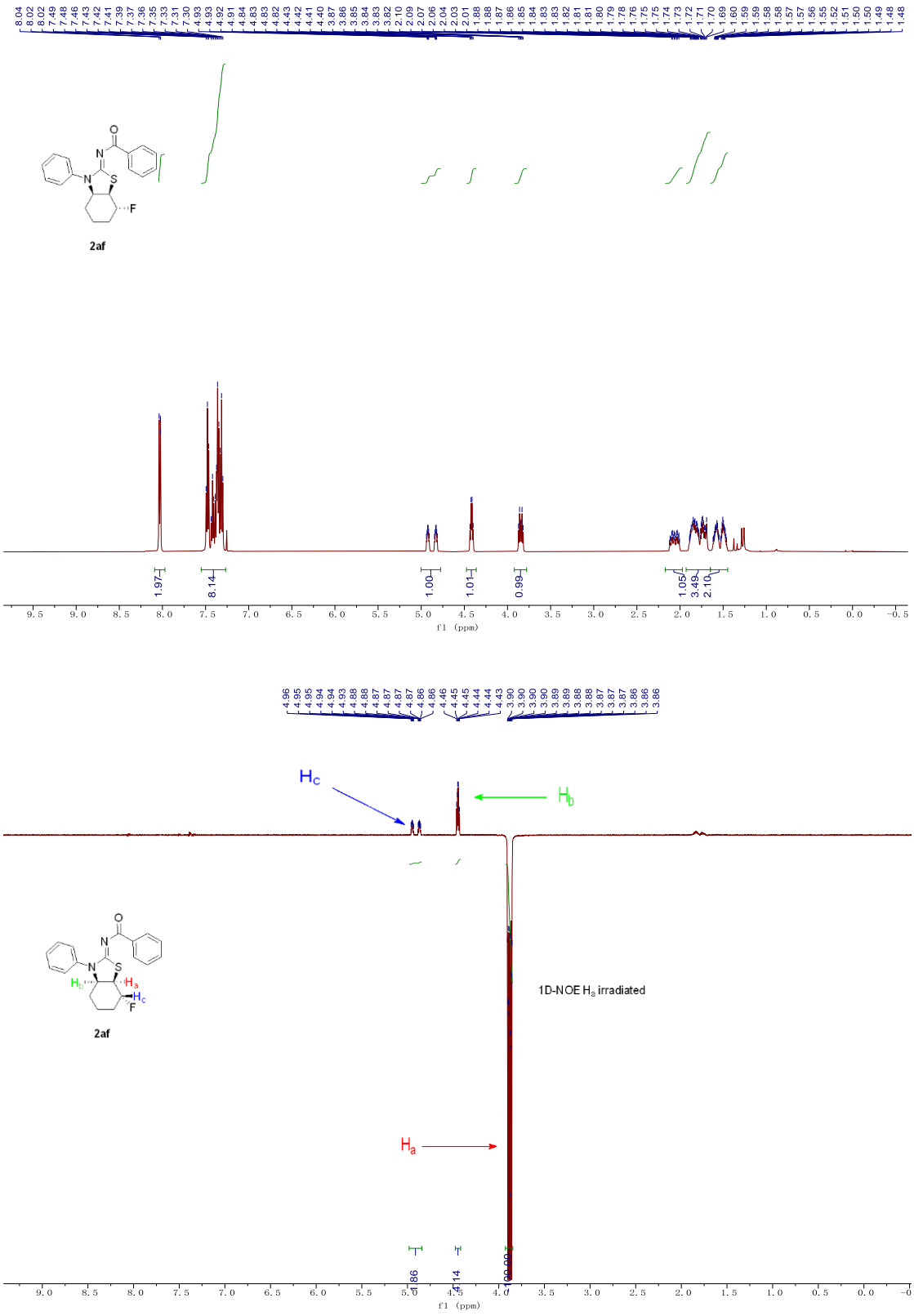

O
N
N
S
F

2af

```
Bond precision:   C-C = 0.0091 A          Wavelength=1.34139

Cell:             a=20.6128(9)     b=9.2353(4)          c=37.9915(19)
                  alpha=90         beta=103.249(2)      gamma=90
Temperature:      170 K

                  Calculated                  Reported
Volume            7039.8(6)                   7039.8(6)
Space group       C c                         C 1 c 1
Hall group        C -2yc                      C -2yc
Moiety formula    C20 H19 F N2 O S            C20 H19 F N2 O S
Sum formula       C20 H19 F N2 O S            C20 H19 F N2 O S
Mr                354.43                      354.43
Dx,g cm-3         1.338                       1.338
Z                 16                          16
Mu (mm-1)         1.177                       1.177
F000              2976.0                      2976.0
F000'             2986.94
h,k,lmax          26,12,49                    26,12,49
Nref              16200[ 8103]                15342
Tmin,Tmax         0.932,0.954                 0.674,0.752
Tmin'             0.910

Correction method= # Reported T Limits: Tmin=0.674 Tmax=0.752
AbsCorr = MULTI-SCAN

Data completeness= 1.89/0.95        Theta(max)= 60.739

R(reflections)= 0.0566( 12785)                wR2(reflections)=
                                              0.1495( 15342)
S = 1.077                Npar= 902
```

12. 1D NOESY spectra.

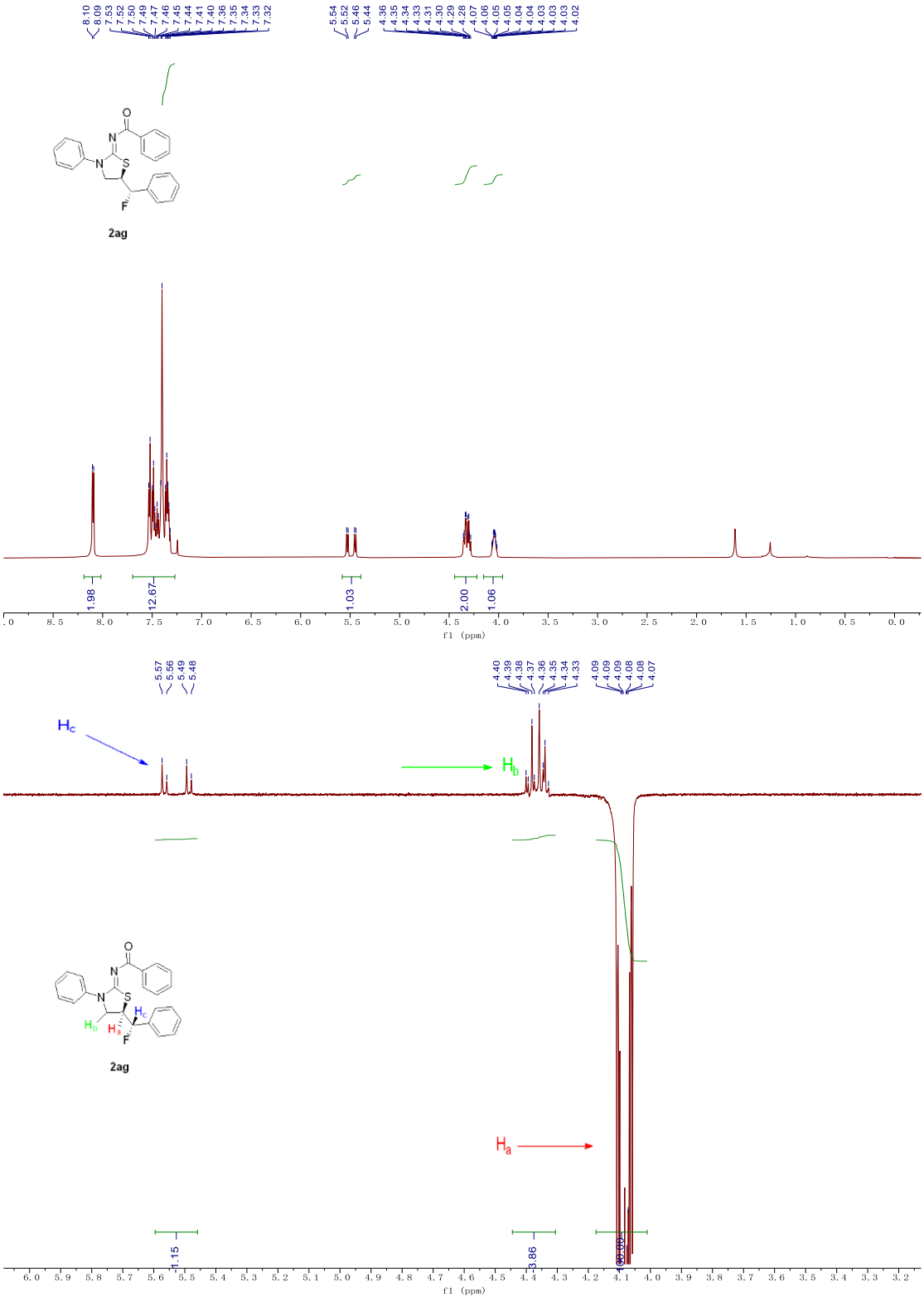
12.1 1D NOESY spectra of 2af



NOE (H_b) enhancement = 4.1%, NOE(H_c) enhancement = 1.9%

1D NOESY spectra of **2af** is shown as above. When the hydrogen H_a of the methine attached to sulfur was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached to nitrogen is 4.1%. The NOE enhancement of H_c of the methine attached to fluorine is 1.9%.

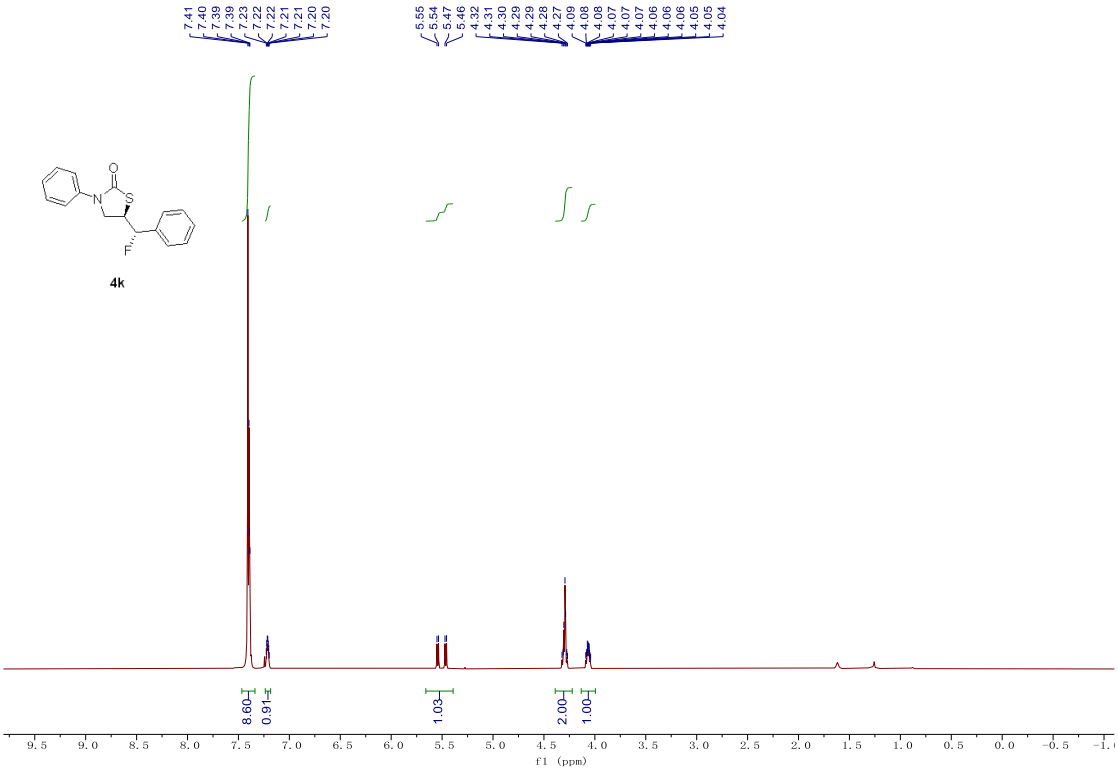
12.2 1D NOESY spectra of 2ag

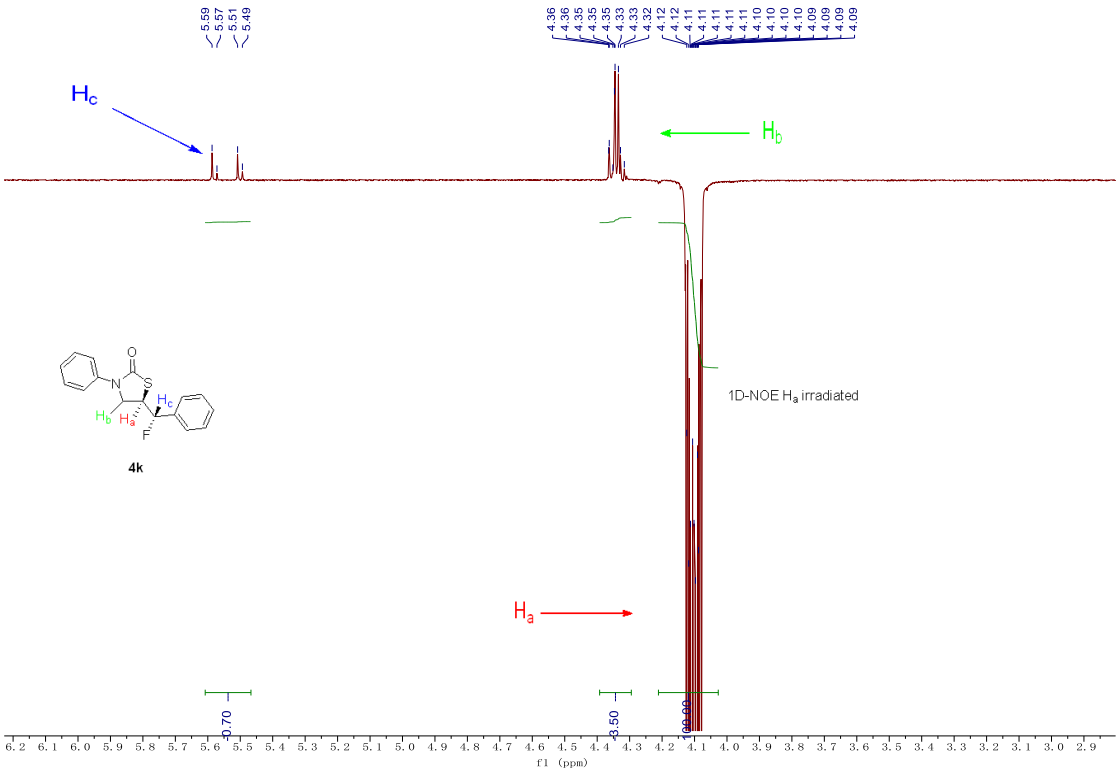


NOE (H_b) enhancement = 3.9%, NOE(H_c) enhancement = 1.2%

1D NOESY spectra of **2ag** is shown as above. When the hydrogen H_a of the methine attached to sulfur was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached to nitrogen is 3.9%. The NOE enhancement of H_c of the methine attached to fluorine is 1.2%.

12.3 1D NOESY spectra of 4k

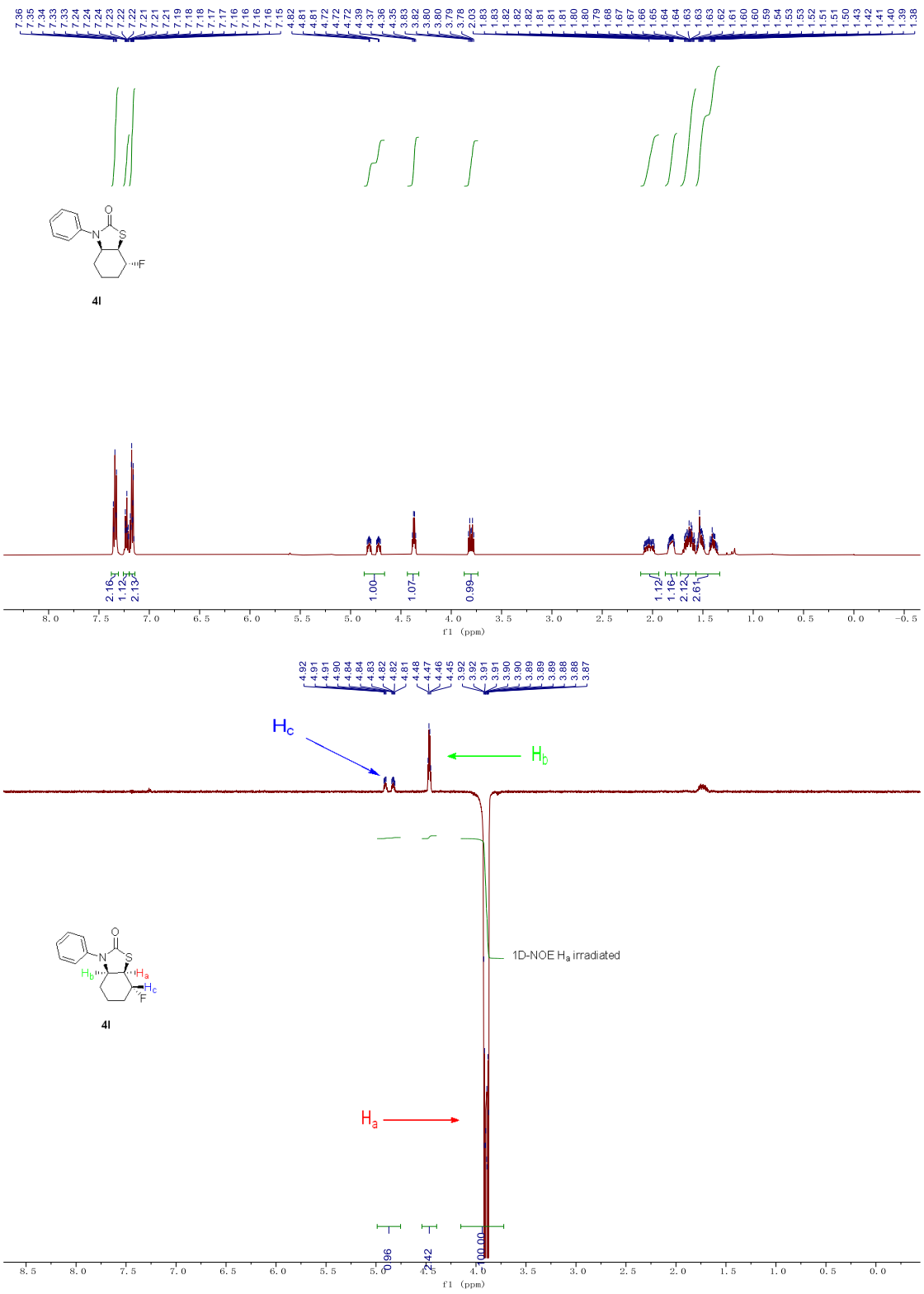




NOE (H_b) enhancement = 3.5%, NOE(H_c) enhancement = 0.7%

1D NOESY spectra of **4k** is shown as above. When the hydrogen H_a of the methine attached to sulfur was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached to nitrogen is 3.5%. The NOE enhancement of H_c of the methine attached to fluorine is 0.7%.

12.4 1D NOESY spectra of 4l

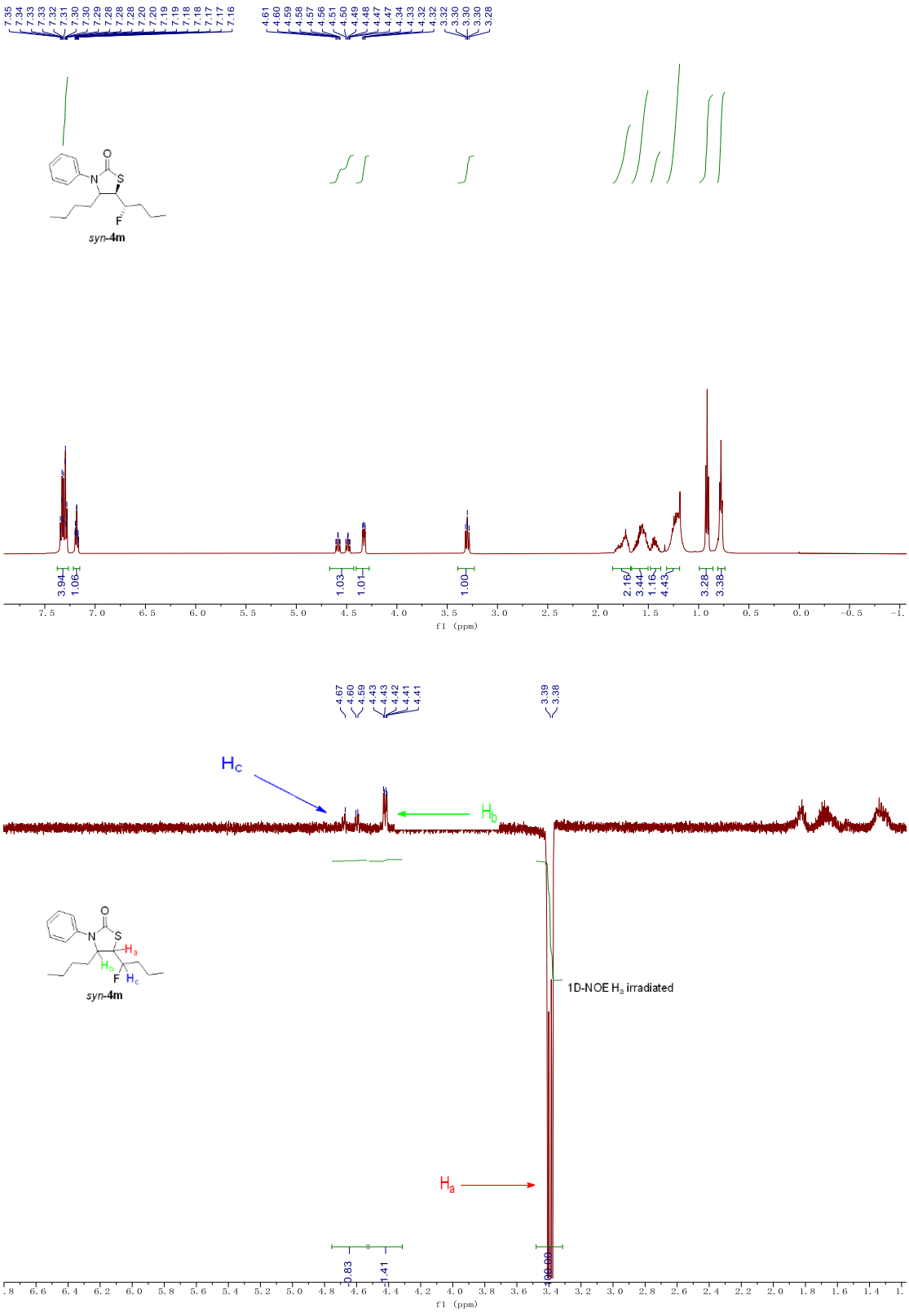


NOE (H_b) enhancement = 2.4%, NOE(H_c) enhancement = 1.0%

1D NOESY spectra of **4k** is shown as above. When the hydrogen H_a of the methine attached to sulfur was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached

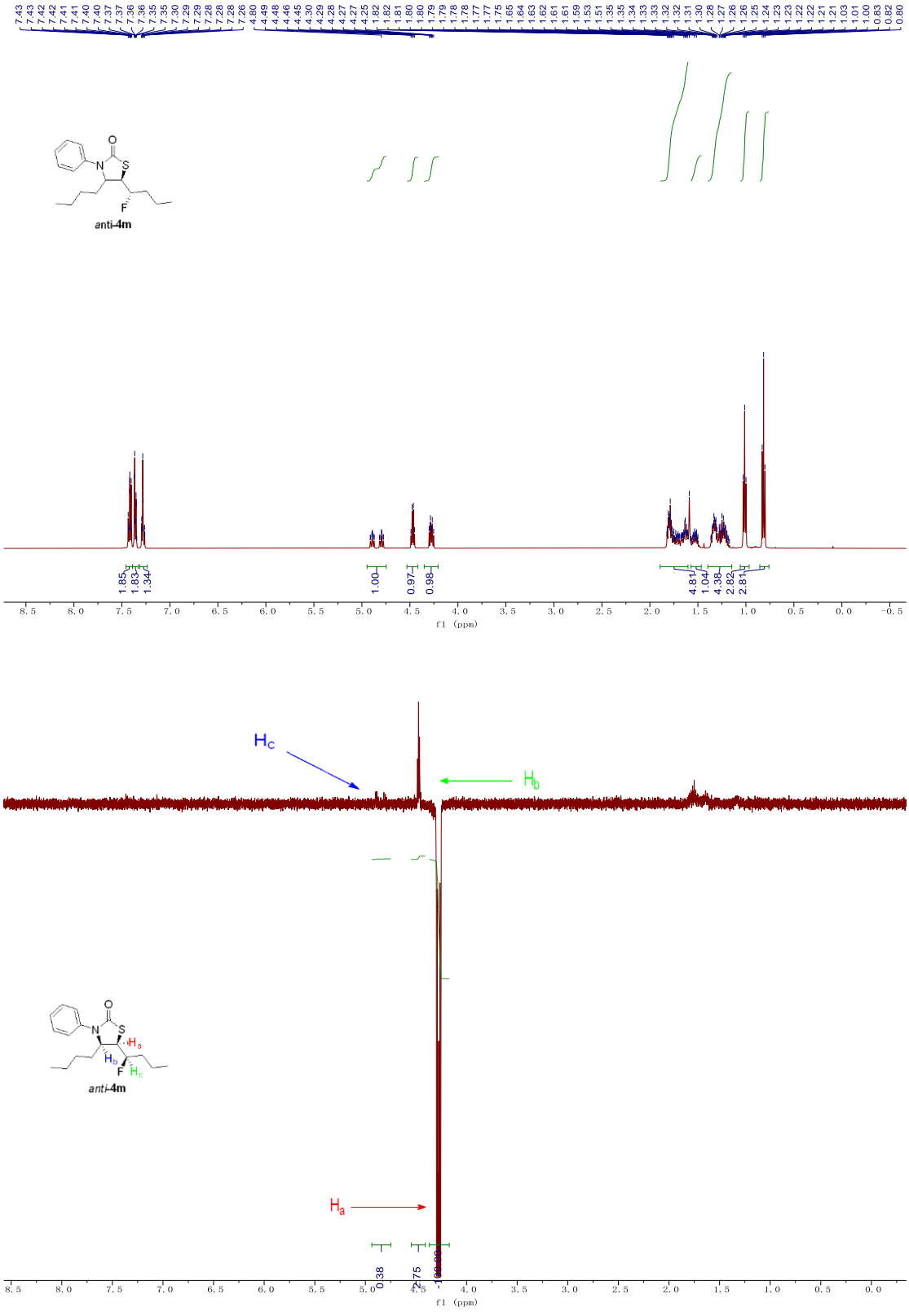
to nitrogen is 2.4%. The NOE enhancement of H_c of the methine attached to fluorine is 1.0%.

12.5 1D NOESY spectra of 4m



NOE (H_b) enhancement = 1.4%, NOE(H_c) enhancement = 0.8%

1D NOESY spectra of anti-**4n** is shown as above. When the hydrogen H_a of the methine attached to sulfur was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached to nitrogen is 1.4%. The NOE enhancement of H_c of the methine attached to fluorine is 0.8%.

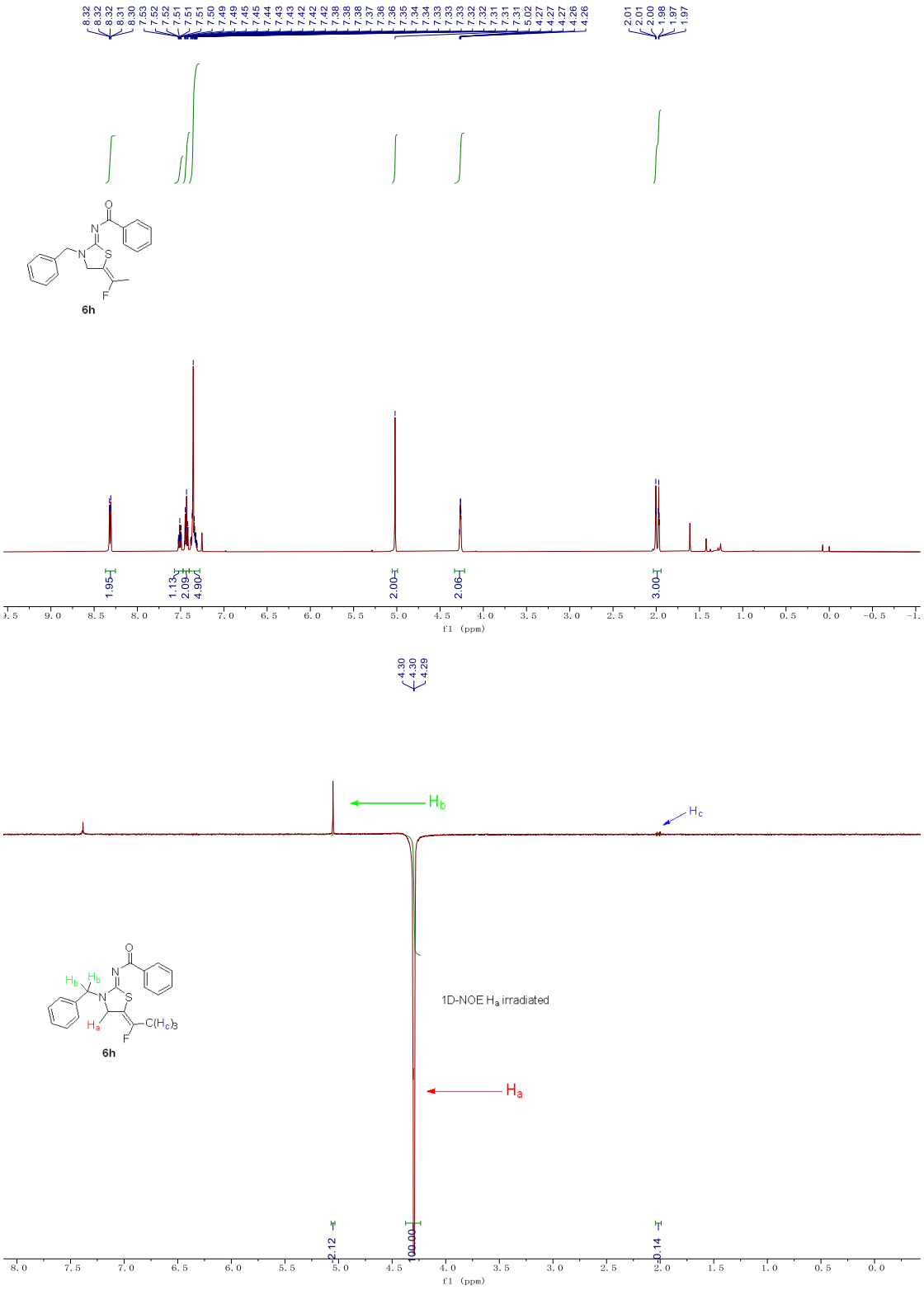


NOE (H_b) enhancement = 2.8%, NOE(H_c) enhancement = 0.4%

1D NOESY spectra of syn-**4n** is shown as above. When the hydrogen H_a of the methine attached to sulfur

was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_b of the methine attached to nitrogen is 2.8%. The NOE enhancement of H_c of the methine attached to fluorine is 0.4%.

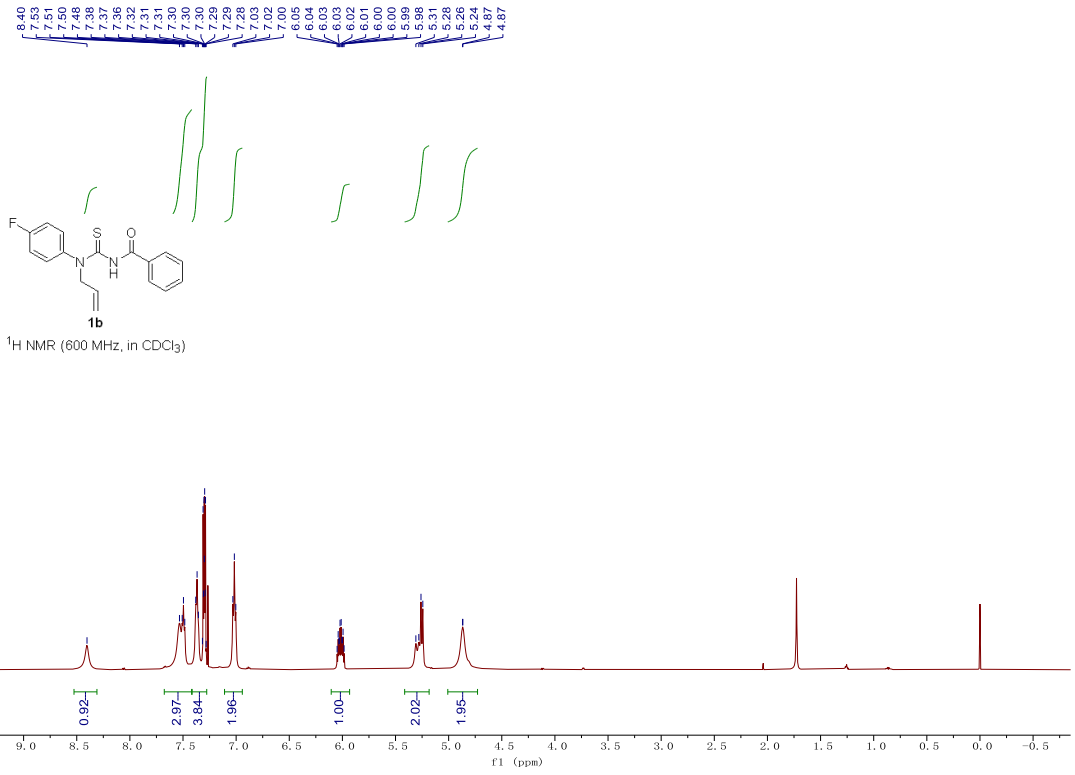
12.6 1D NOESY spectra of 6h

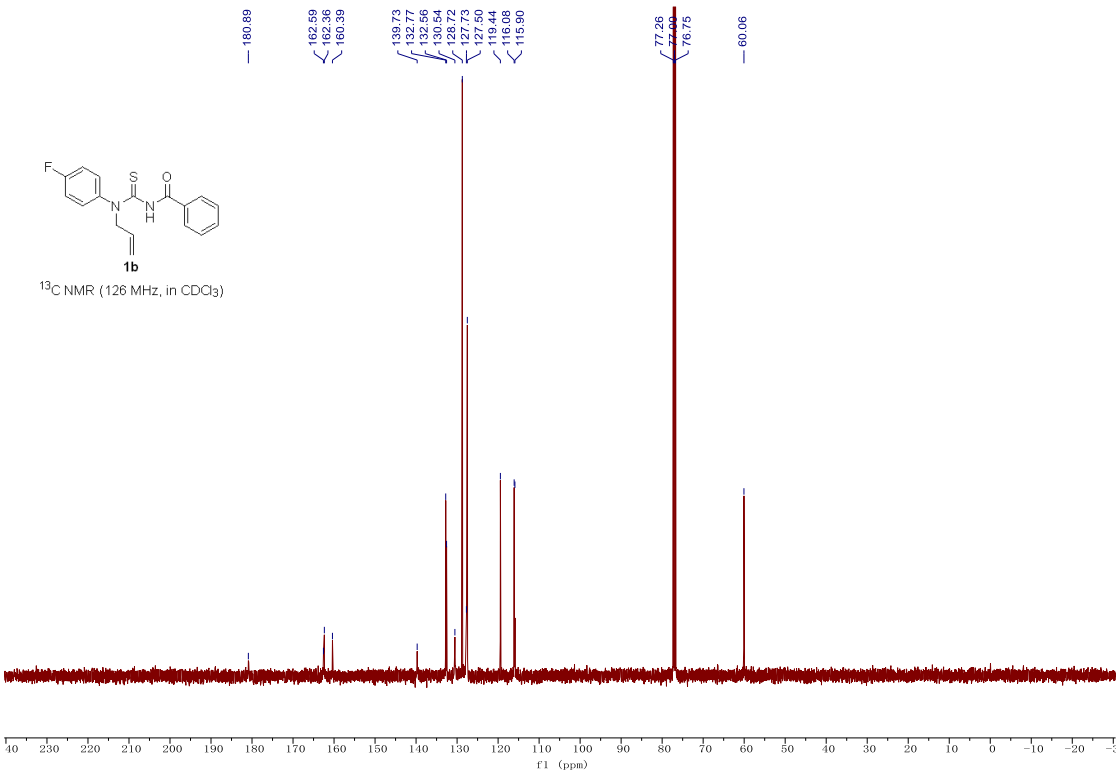


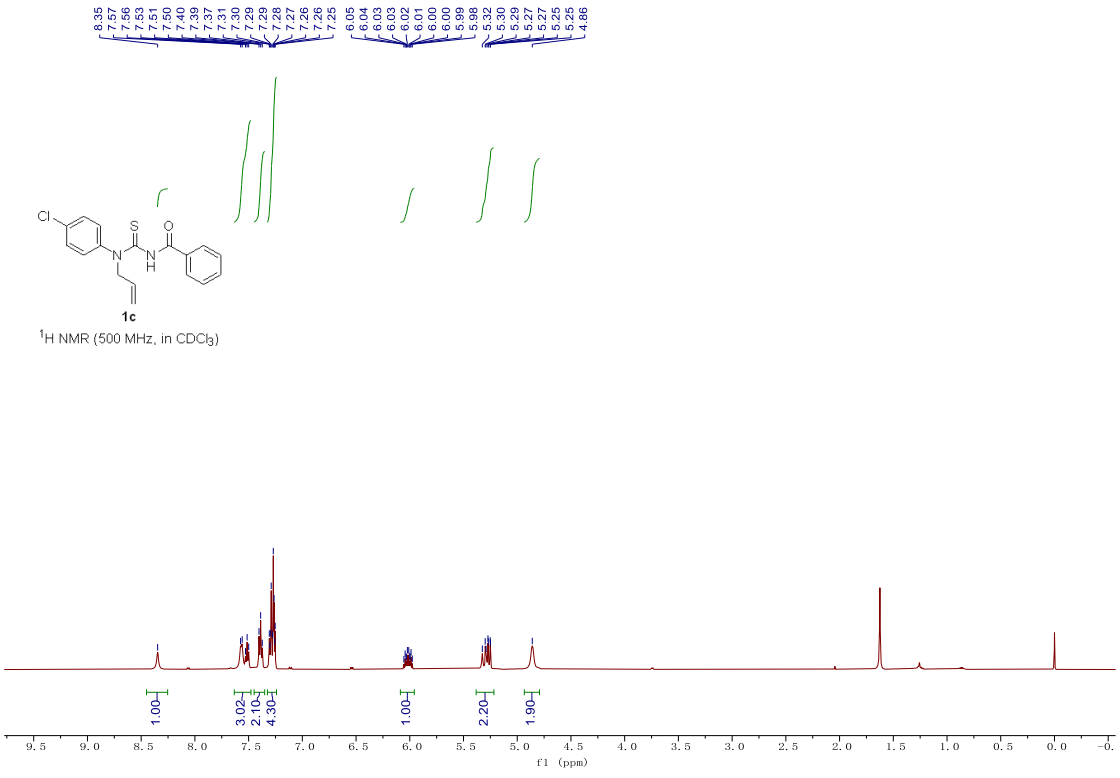
NOE(H_c) enhancement = 0.1%

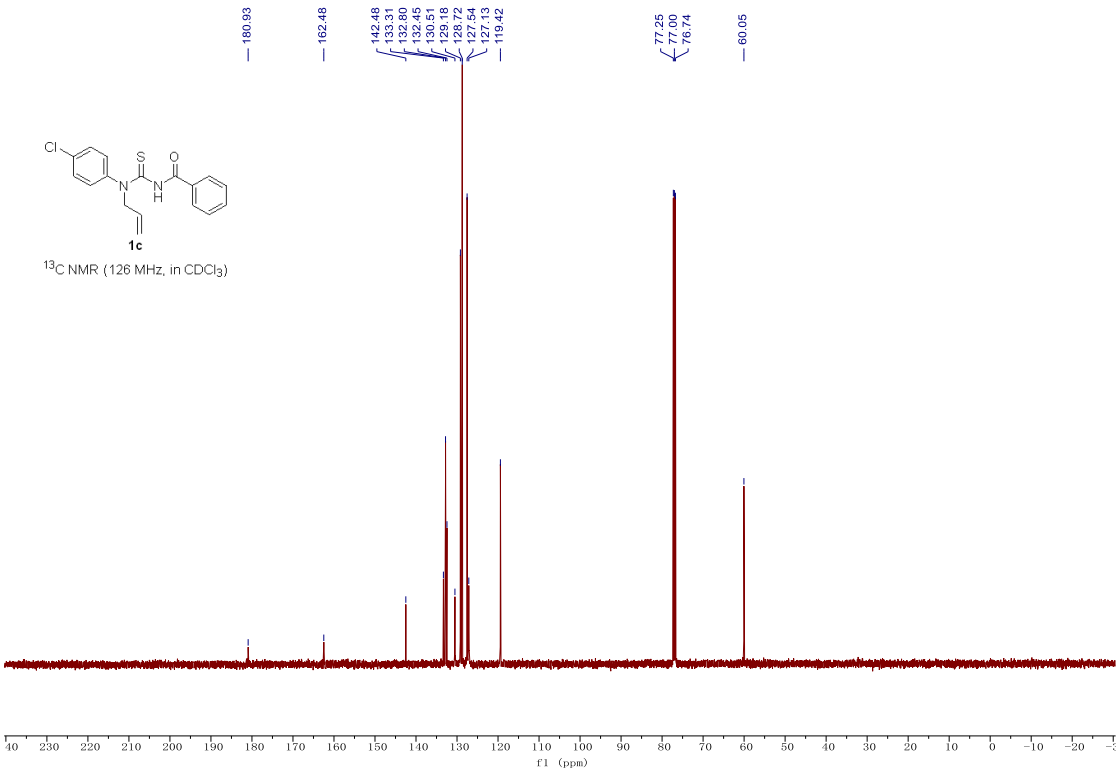
1D NOESY spectra of **6h** is shown as above. When the hydrogen H_a of the methine attached to N-atom was irradiated, the 1D NOESY spectra shows that the NOE enhancement of H_c of the methine attached to double bond is 0.1%.

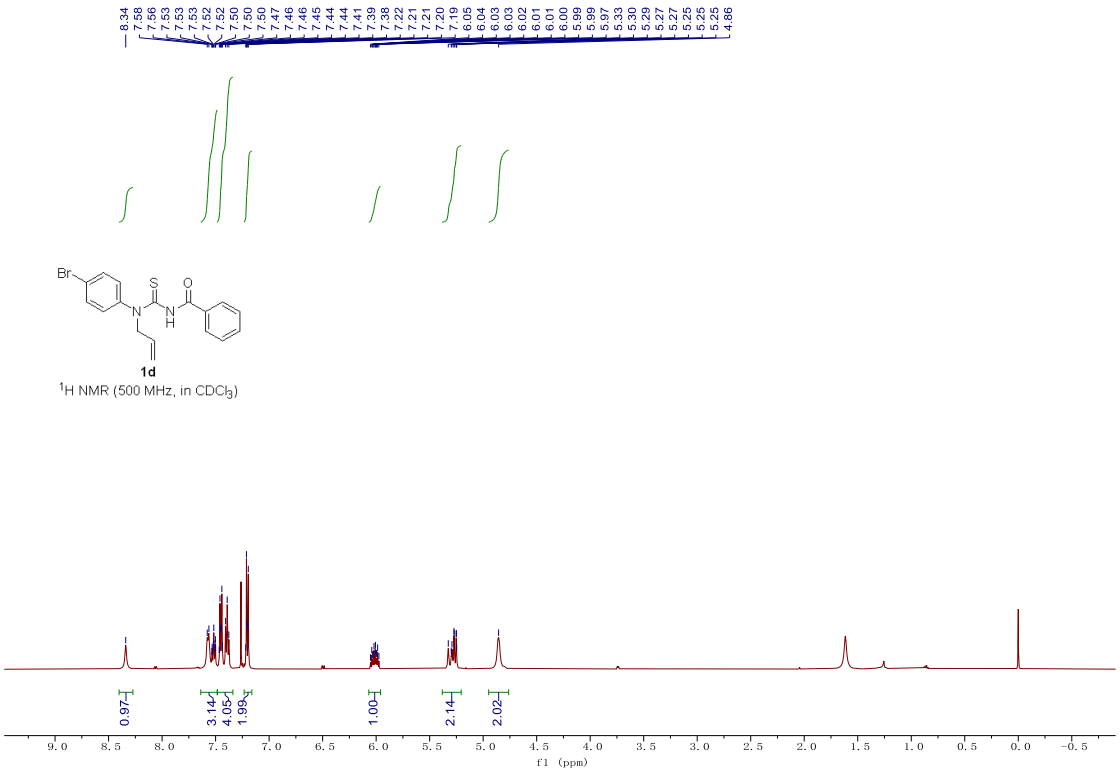
13. NMR spectra.

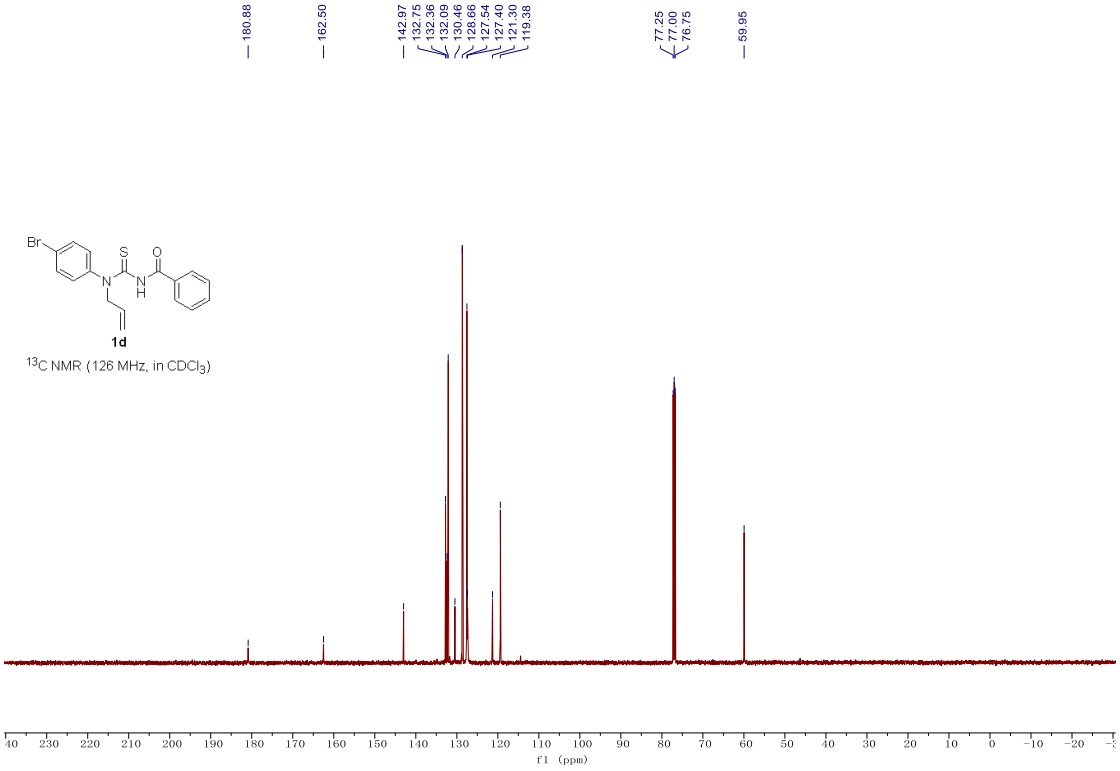


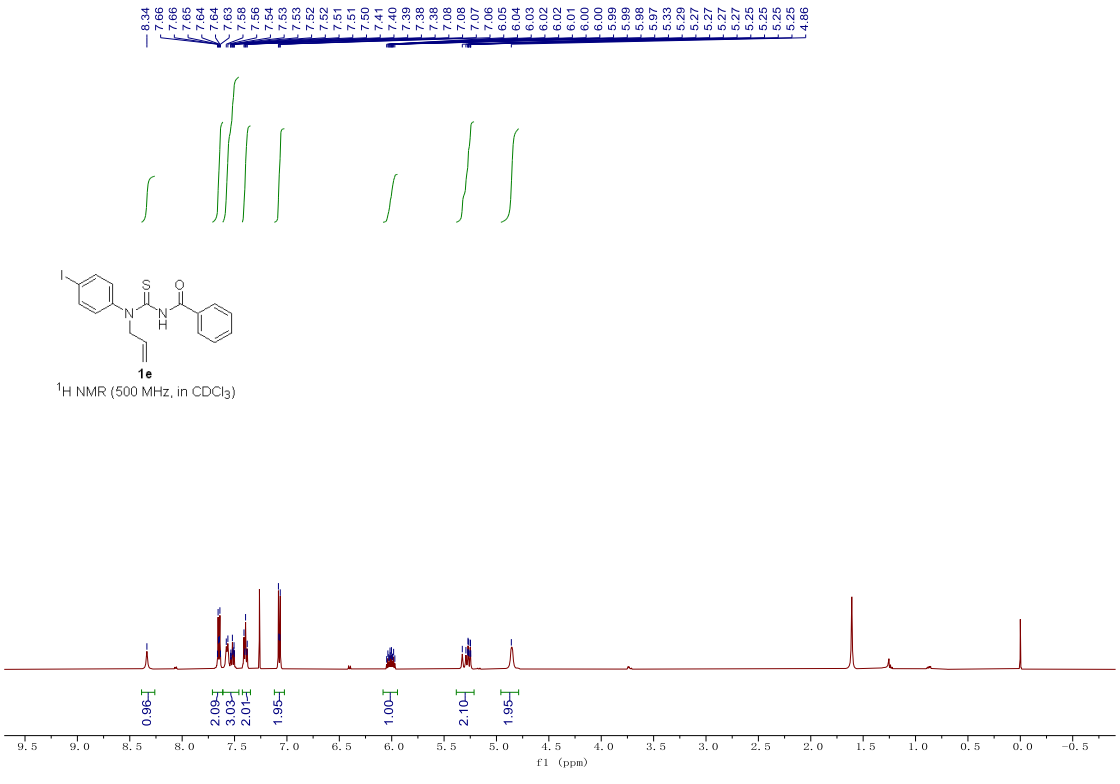

180.89
162.59
162.36
160.39
139.73
132.77
132.56
130.54
128.72
127.73
127.50
119.44
116.08
115.90
77.26
77.00
76.75
60.06
F
S
O
N
N
H
1b
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

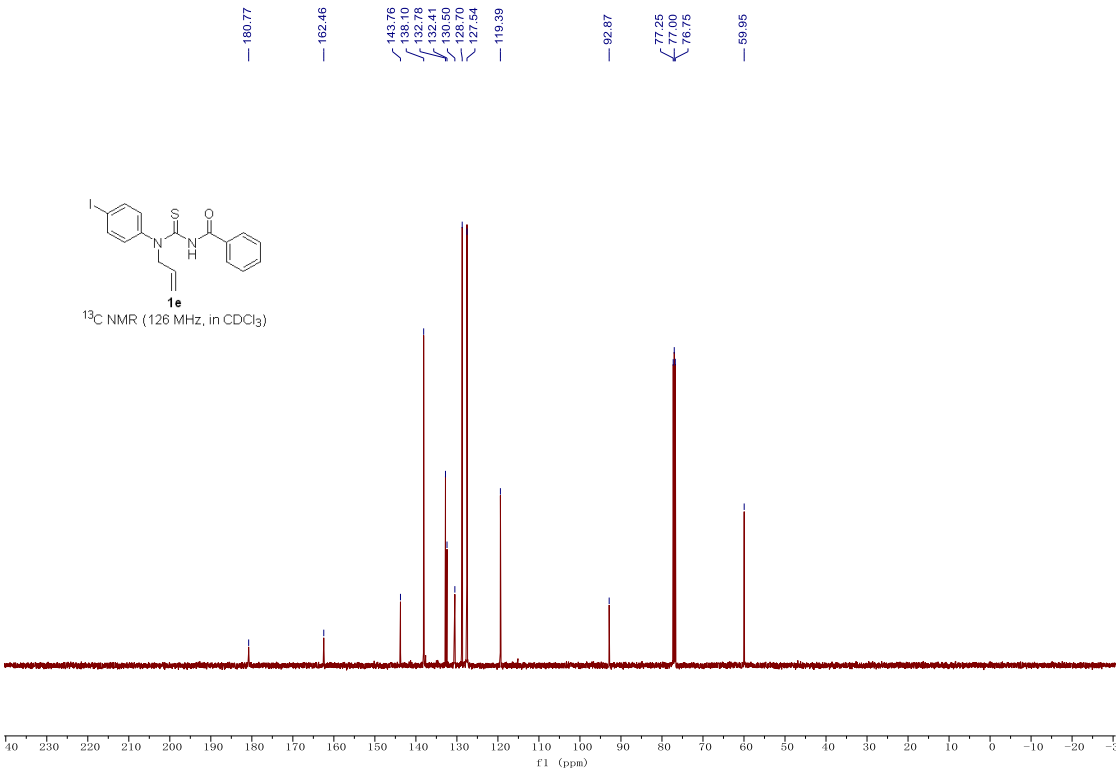

8.35
7.57
7.56
7.53
7.51
7.50
7.40
7.39
7.37
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
6.05
6.04
6.03
6.03
6.02
6.01
6.00
6.00
5.99
5.98
5.32
5.30
5.29
5.27
5.27
5.25
5.25
4.86
Cl
S
O
N
N
H
1c
1H NMR (500 MHz, in CDCl3)
1.00
3.02
2.10
4.30
1.00
2.20
1.90
f1 (ppm)

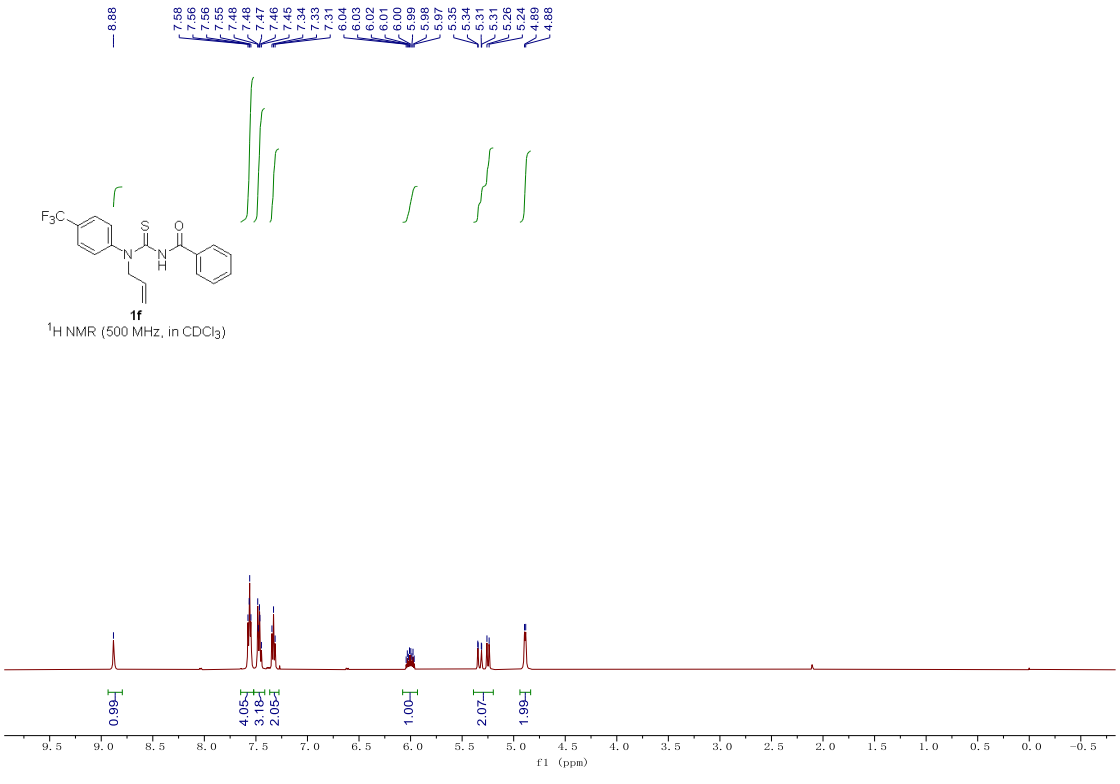

180.93
162.48
142.48
133.31
132.80
132.45
130.51
129.18
128.72
127.54
127.13
119.42
77.25
77.00
76.74
60.05
Cl
S
O
N
N
H
1c
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

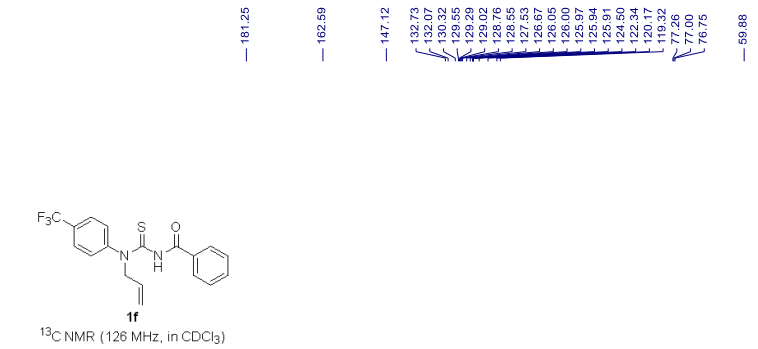

8.34
7.58
7.56
7.53
7.53
7.53
7.52
7.52
7.50
7.50
7.50
7.47
7.46
7.46
7.45
7.44
7.44
7.41
7.39
7.38
7.22
7.21
7.21
7.20
7.19
6.05
6.04
6.03
6.03
6.02
6.01
6.01
6.00
5.99
5.99
5.97
5.33
5.30
5.29
5.27
5.25
5.25
5.25
4.86
Br
S
O
N
N
H
1d
1H NMR (500 MHz, in CDCl3)
0.97
3.14
4.05
1.99
1.00
2.14
2.02
f1 (ppm)


180.88
162.50
142.97
132.75
132.36
132.09
130.46
128.66
127.54
127.40
121.30
119.38
77.25
77.00
76.75
59.95
Br
S
O
N
N
H
1d
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.34
7.66
7.66
7.65
7.64
7.64
7.63
7.58
7.56
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.41
7.40
7.39
7.38
7.38
7.08
7.08
7.07
7.06
6.05
6.04
6.03
6.02
6.02
6.01
6.00
6.00
5.99
5.99
5.98
5.97
5.33
5.29
5.27
5.27
5.27
5.25
5.25
5.25
5.25
4.86
I
S
O
N
N
H
1e
1H NMR (500 MHz, in CDCl3)
0.96
2.09
3.03
2.01
1.95
1.00
2.10
1.95
f1 (ppm)

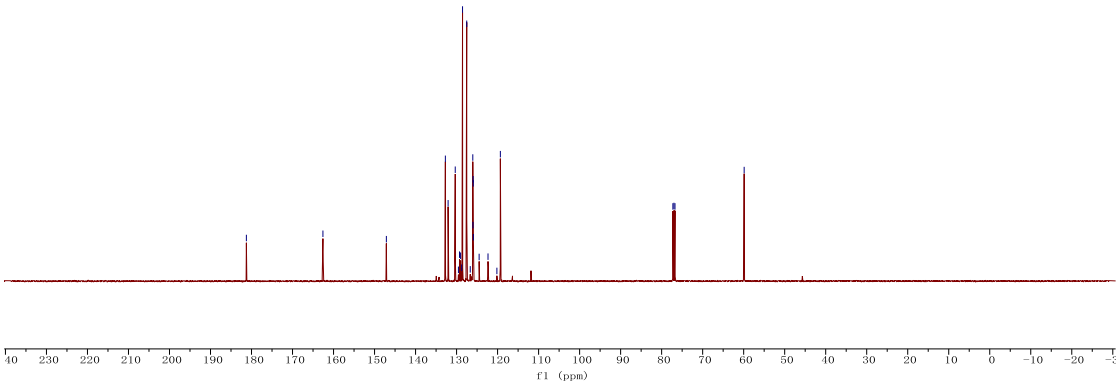

180.77
162.46
143.76
138.10
132.78
132.41
130.50
128.70
127.54
119.39
92.87
77.25
77.00
76.75
59.95
I
S
O
N
H
1e
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

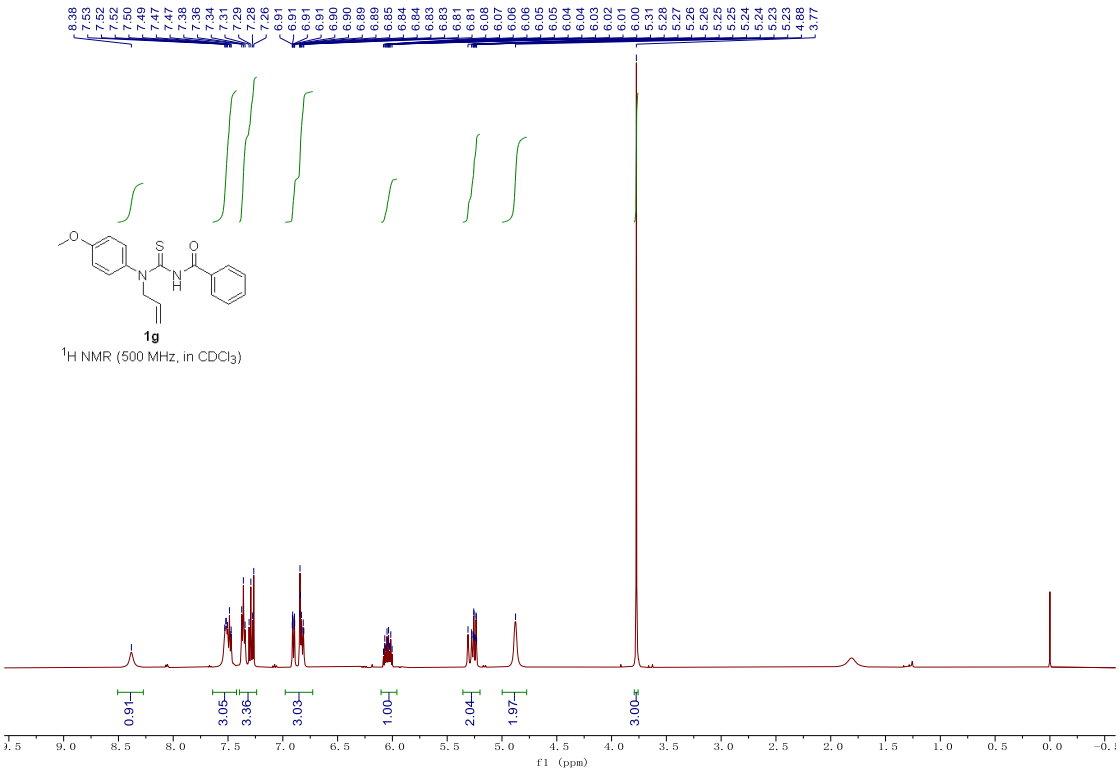

8.88
7.58
7.56
7.56
7.55
7.48
7.47
7.46
7.45
7.34
7.33
7.31
6.04
6.03
6.02
6.01
6.00
5.99
5.98
5.97
5.35
5.34
5.31
5.31
5.26
5.24
4.89
4.88
F3C
S
O
N
H
1f
1H NMR (500 MHz, in CDCl3)
0.99
4.05
3.18
2.05
1.00
2.07
1.99
f1 (ppm)



1f

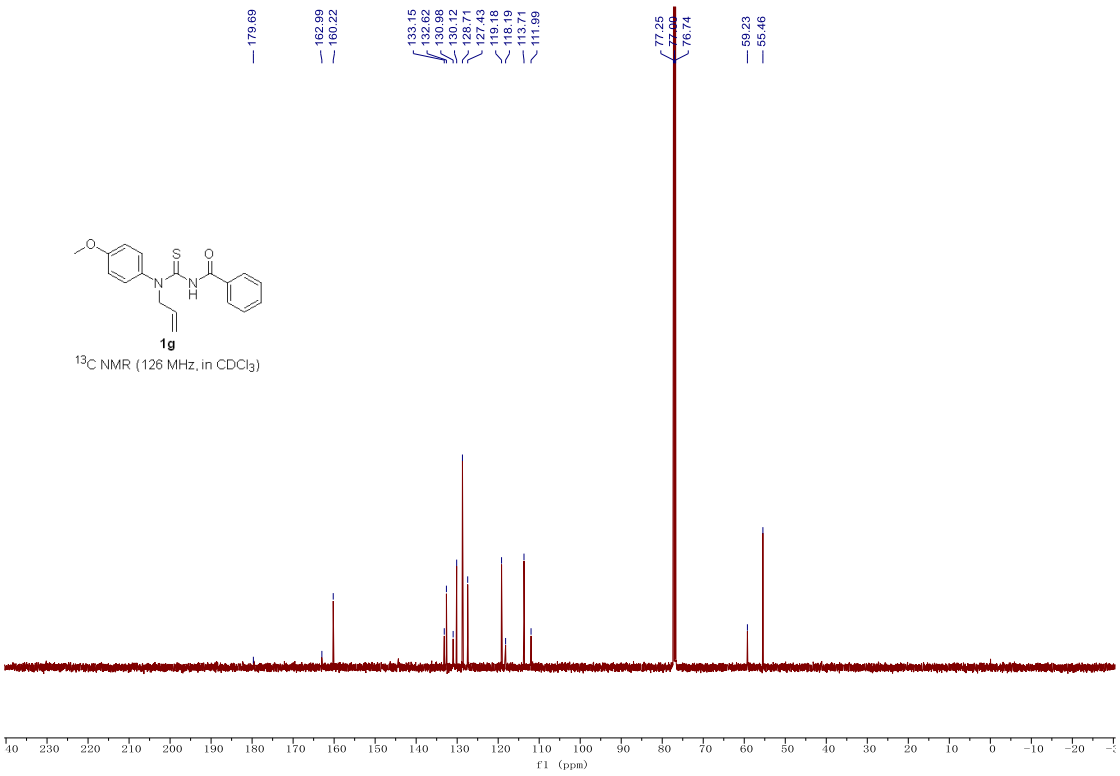
^{13}C NMR (126 MHz, in $CDCl_3$)

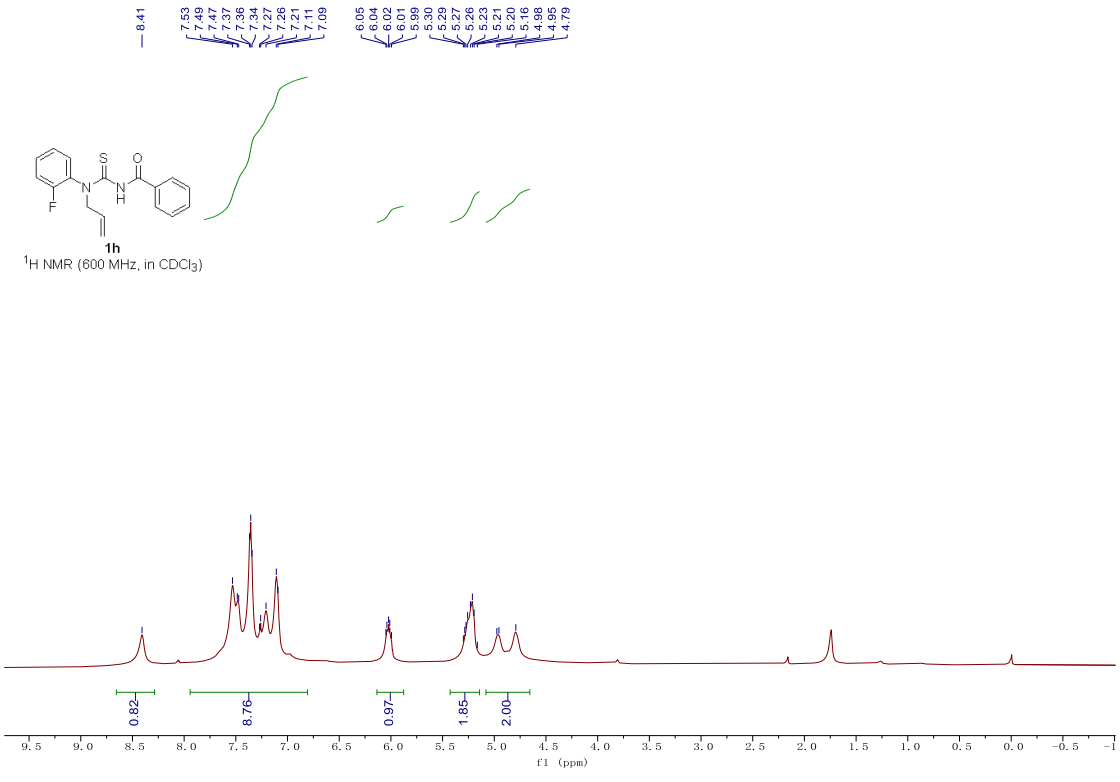


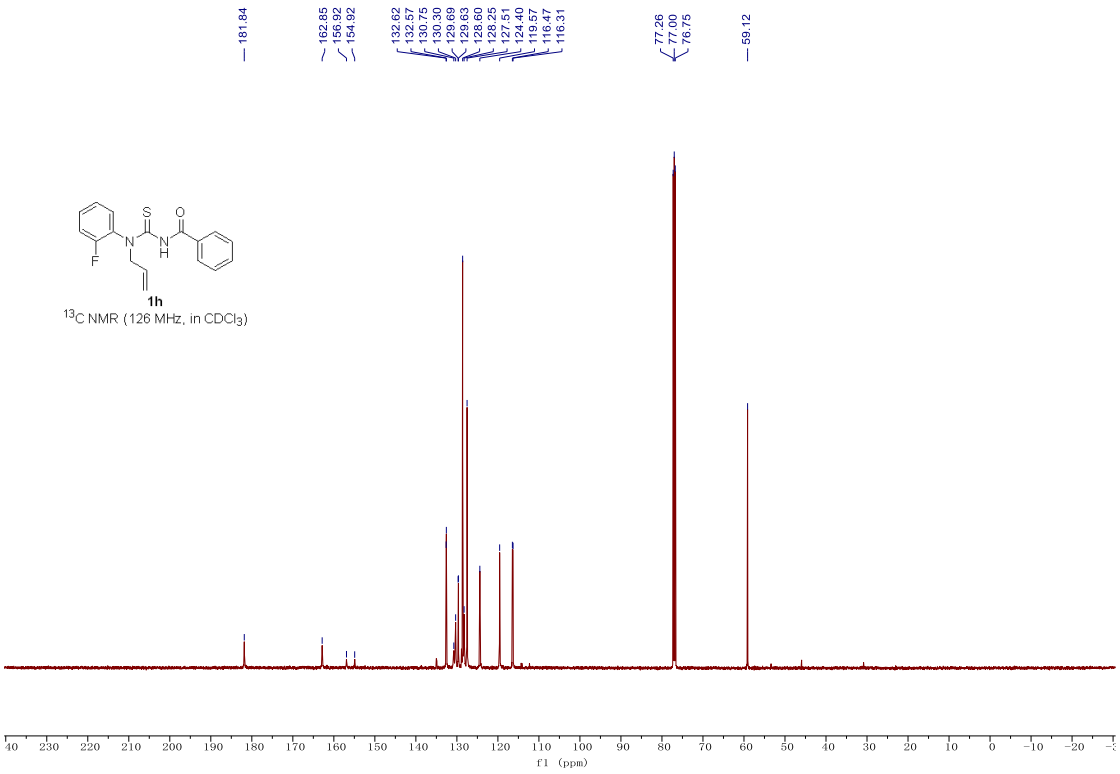


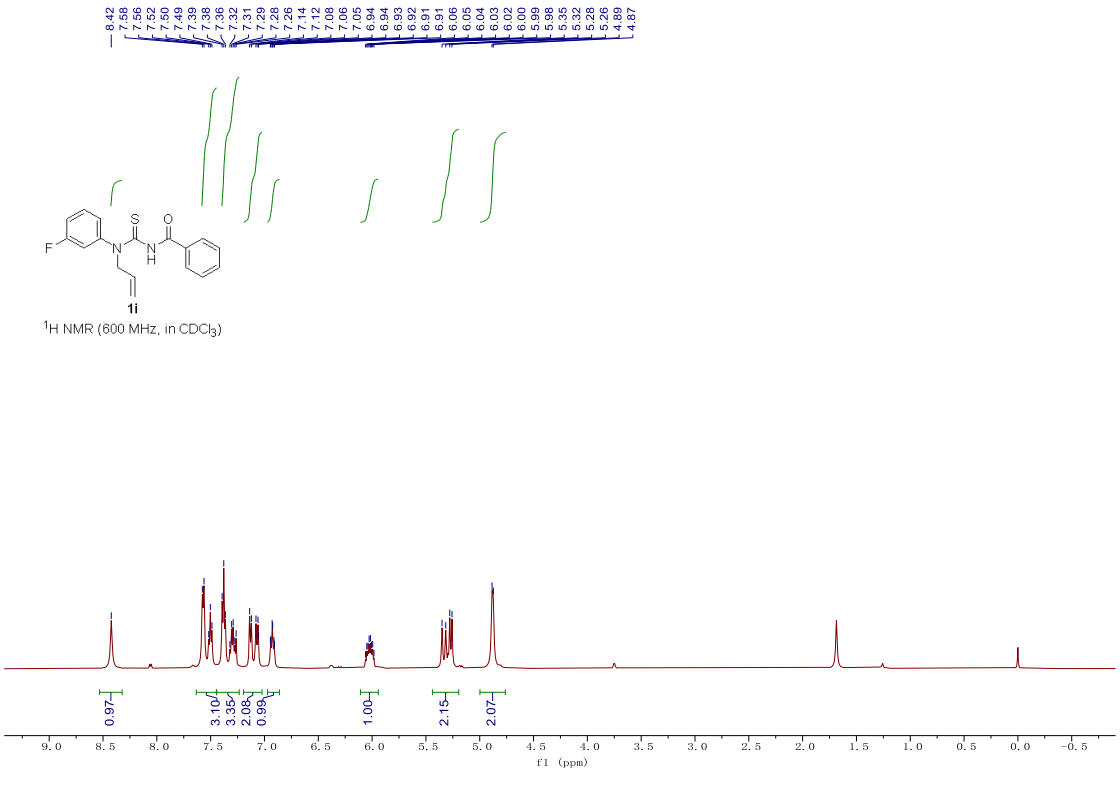
1g

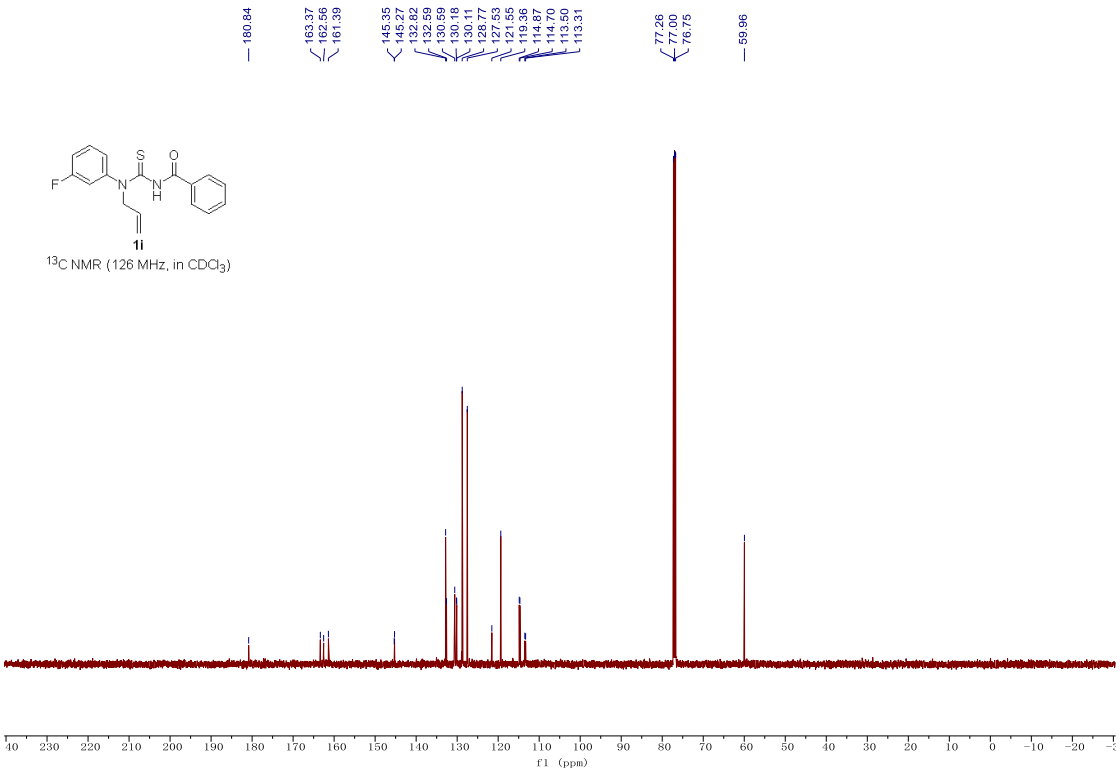
^{1}H NMR (500 MHz, in $CDCl_3$)

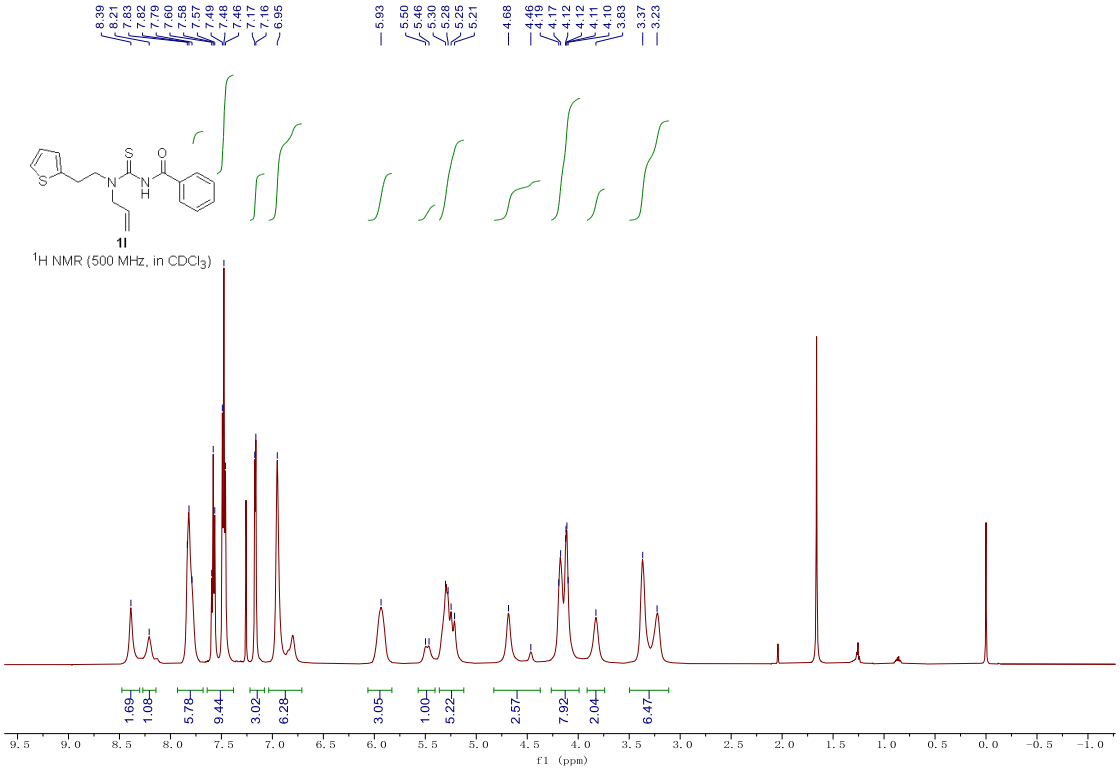

179.69
162.99
160.22
133.15
132.62
130.98
130.12
128.71
127.43
119.18
118.19
113.71
111.99
77.25
77.00
76.74
59.23
55.46
1g
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

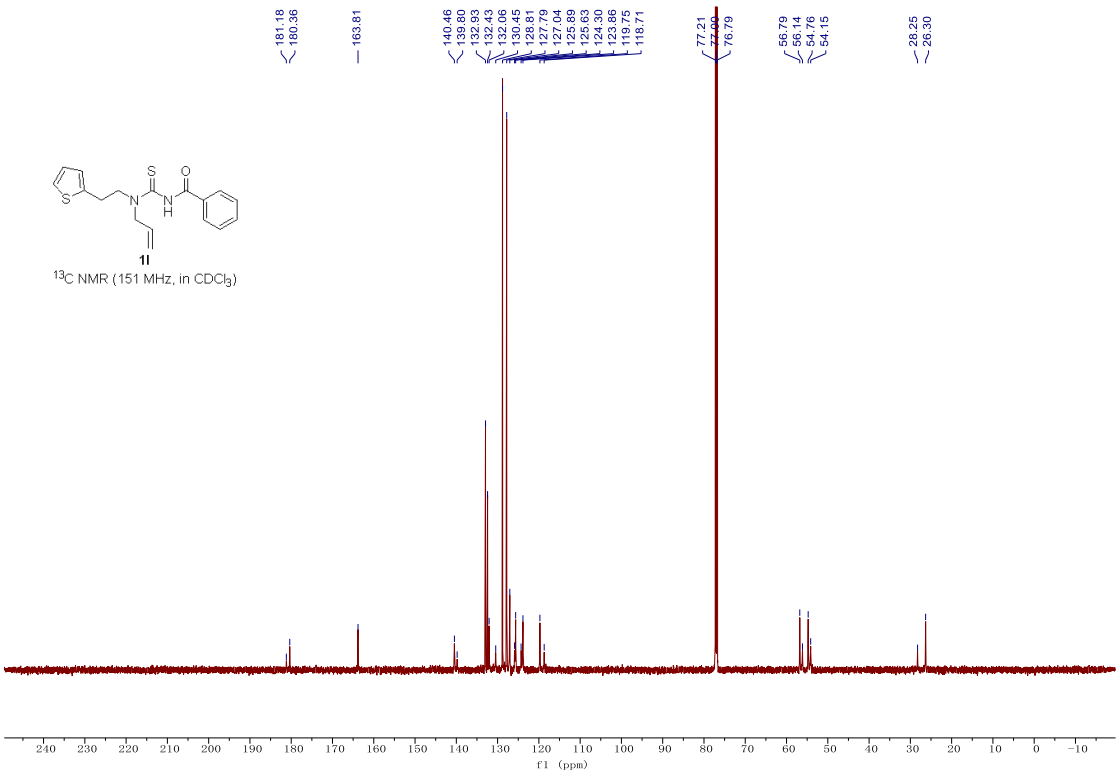

8.41
7.53
7.49
7.47
7.37
7.36
7.34
7.27
7.26
7.21
7.11
7.09
6.05
6.04
6.02
6.01
5.99
5.30
5.29
5.27
5.26
5.23
5.21
5.20
5.16
4.98
4.95
4.79
1h
1H NMR (600 MHz, in CDCl3)
0.82
8.76
0.97
1.85
2.00
f1 (ppm)

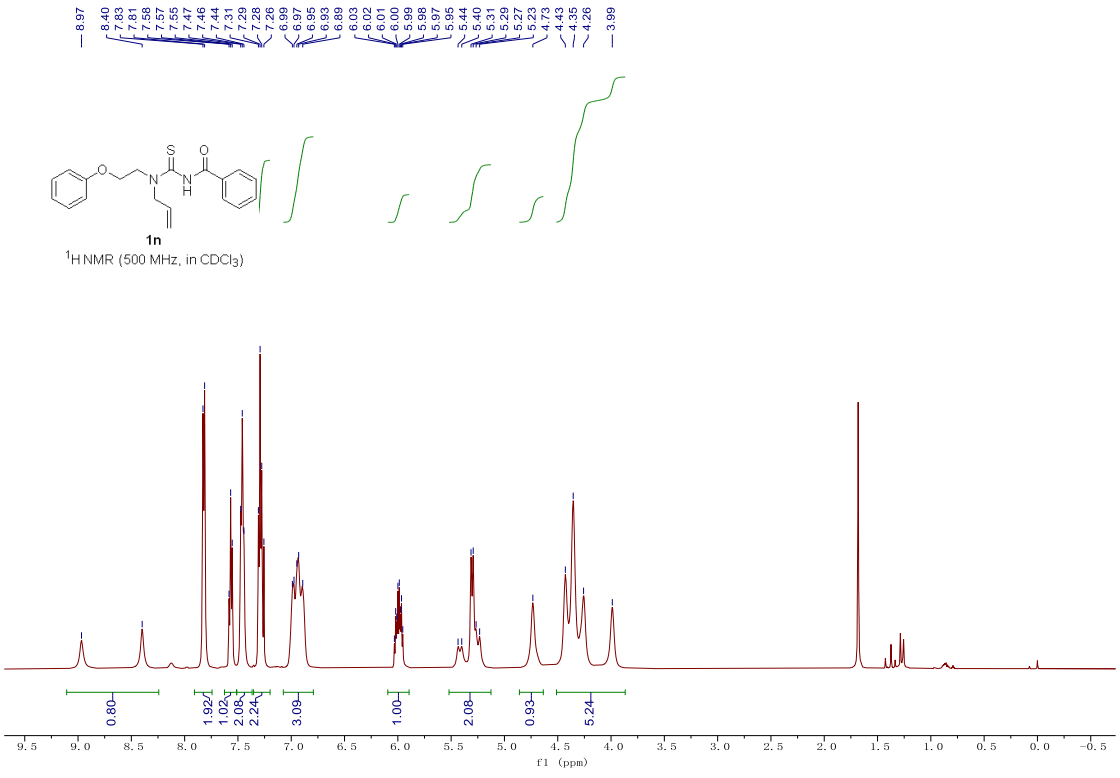

181.84
162.85
156.92
154.92
132.62
132.57
130.75
130.30
129.69
129.63
128.60
128.25
127.51
124.40
119.57
116.47
116.31
77.26
77.00
76.75
59.12
F
S
O
N
H
1h
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

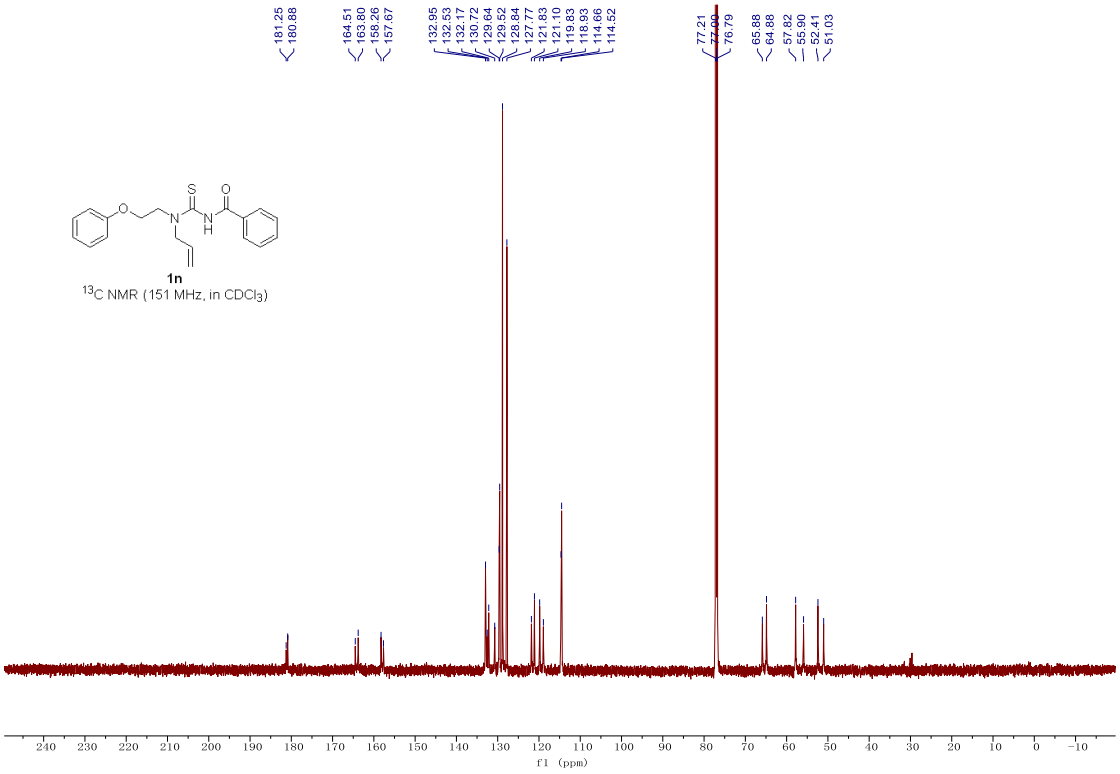

8.42
7.58
7.56
7.52
7.50
7.49
7.39
7.38
7.36
7.32
7.31
7.29
7.28
7.26
7.14
7.12
7.08
7.06
7.05
6.94
6.94
6.93
6.92
6.91
6.91
6.06
6.05
6.04
6.03
6.02
6.00
5.99
5.98
5.35
5.32
5.28
5.26
4.89
4.87
F
S
O
N
H
1i
1H NMR (600 MHz, in CDCl3)
0.97
3.10
3.35
2.08
0.99
1.00
2.15
2.07
f1 (ppm)

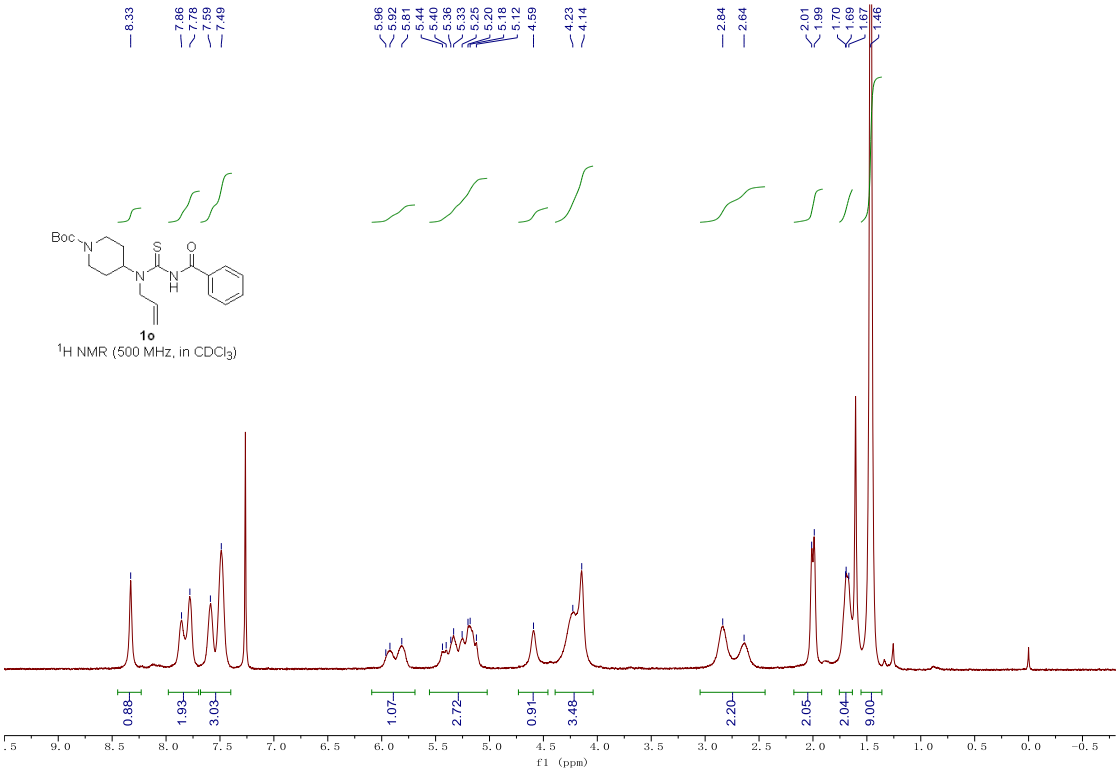

180.84
163.37
162.56
161.39
145.35
145.27
132.82
132.59
130.59
130.18
130.11
128.77
127.53
121.55
119.36
114.87
114.70
113.50
113.31
77.26
77.00
76.75
59.96
F
S
O
N
H
N
1i
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

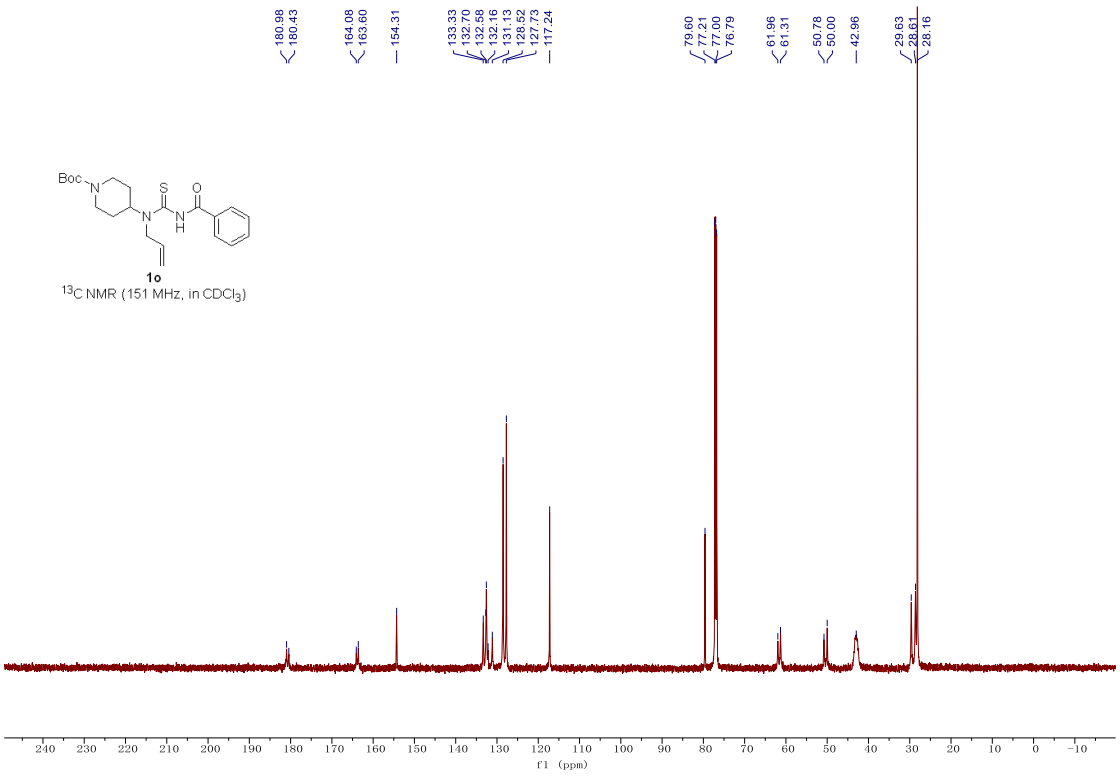

8.39
8.21
7.83
7.82
7.79
7.60
7.58
7.57
7.49
7.48
7.46
7.17
7.16
6.95
5.93
5.50
5.46
5.30
5.28
5.25
5.21
4.68
4.46
4.19
4.17
4.12
4.12
4.11
4.10
3.83
3.37
3.23
S
O
N
H
1l
1H NMR (500 MHz, in CDCl3)
1.69
1.08
5.78
9.44
3.02
6.28
3.05
1.00
5.22
2.57
7.92
2.04
6.47
f1 (ppm)


181.18
180.36
163.81
140.46
139.80
132.93
132.43
132.06
130.45
128.81
127.79
127.04
125.89
125.63
124.30
123.86
119.75
118.71
77.21
77.00
76.79
56.79
56.14
54.76
54.15
28.25
26.30
1l
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


8.97
8.40
7.83
7.81
7.58
7.57
7.55
7.47
7.46
7.44
7.31
7.29
7.28
7.26
6.99
6.97
6.95
6.93
6.89
6.03
6.02
6.01
6.00
5.99
5.98
5.97
5.95
5.44
5.40
5.31
5.29
5.27
5.23
4.73
4.43
4.35
4.26
3.99
1n
1H NMR (500 MHz, in CDCl3)
0.80
1.92
1.02
2.08
2.24
3.09
1.00
2.08
0.93
5.24
f1 (ppm)

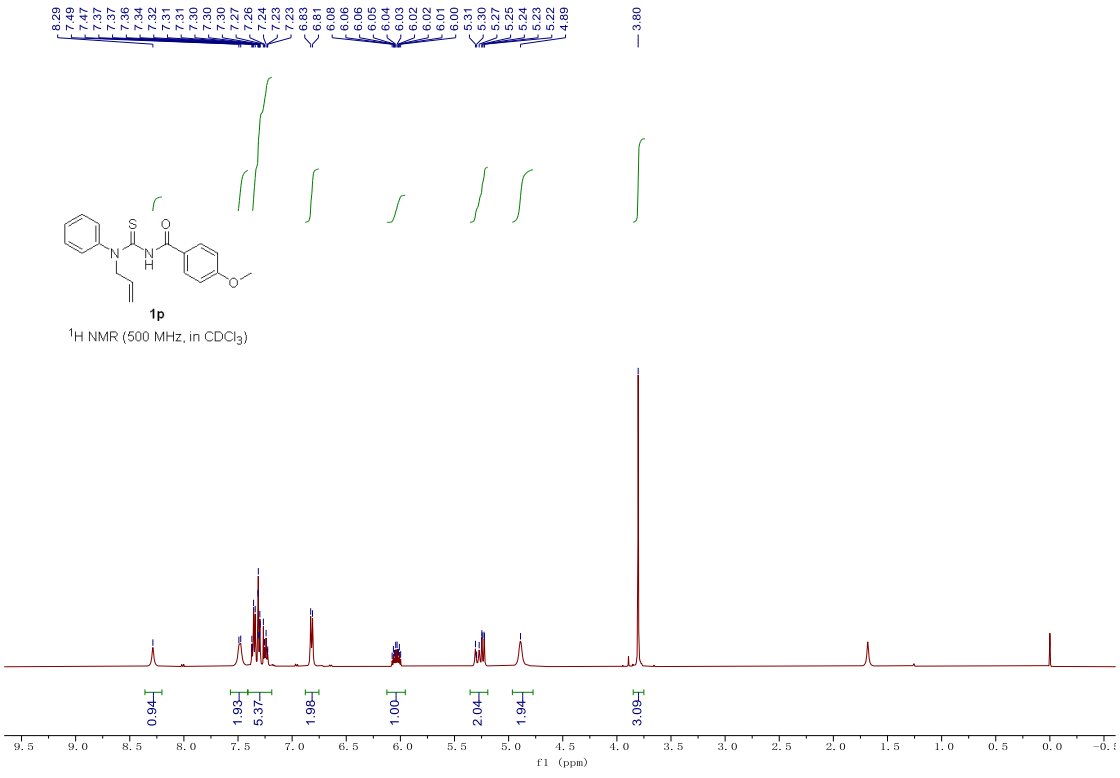

181.25
180.88
164.51
163.80
158.26
157.67
132.95
132.53
132.17
130.72
129.64
129.52
128.84
127.77
121.83
121.10
119.83
118.93
114.66
114.52
77.21
77.00
76.79
65.88
64.88
57.62
55.90
52.41
51.03
1n
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


8.33
7.86
7.78
7.59
7.49
5.96
5.92
5.81
5.44
5.40
5.36
5.33
5.25
5.20
5.18
5.12
4.59
4.23
4.14
2.84
2.64
2.01
1.99
1.70
1.69
1.67
1.46
Boc
1o
1H NMR (500 MHz, in CDCl3)
0.88
1.93
3.03
1.07
2.72
0.91
3.48
2.20
2.05
2.04
9.00
f1 (ppm)



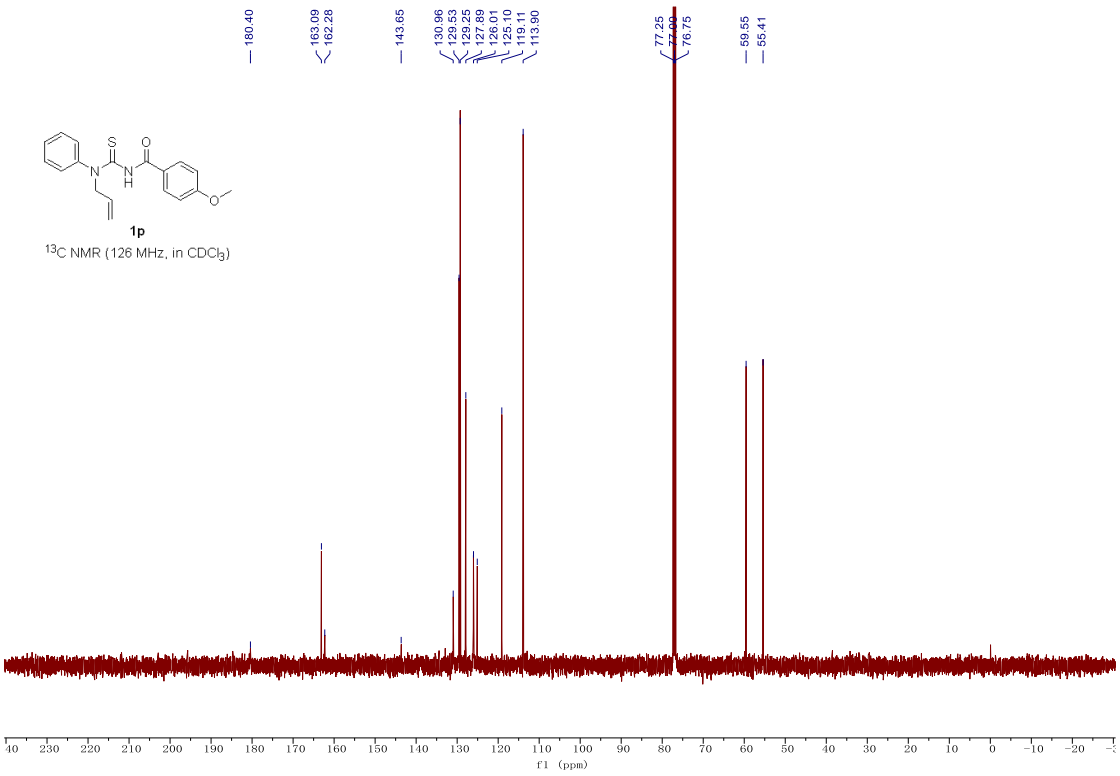
1o

^{13}C NMR (151 MHz, in $CDCl_3$)



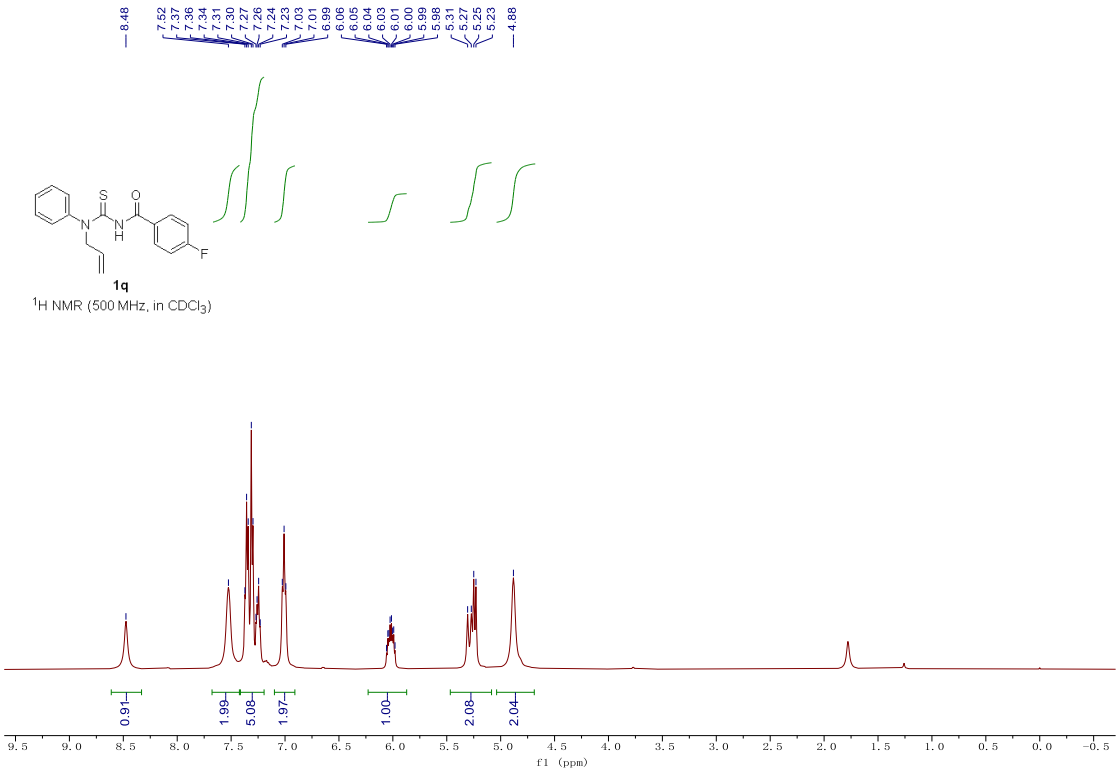
1p

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



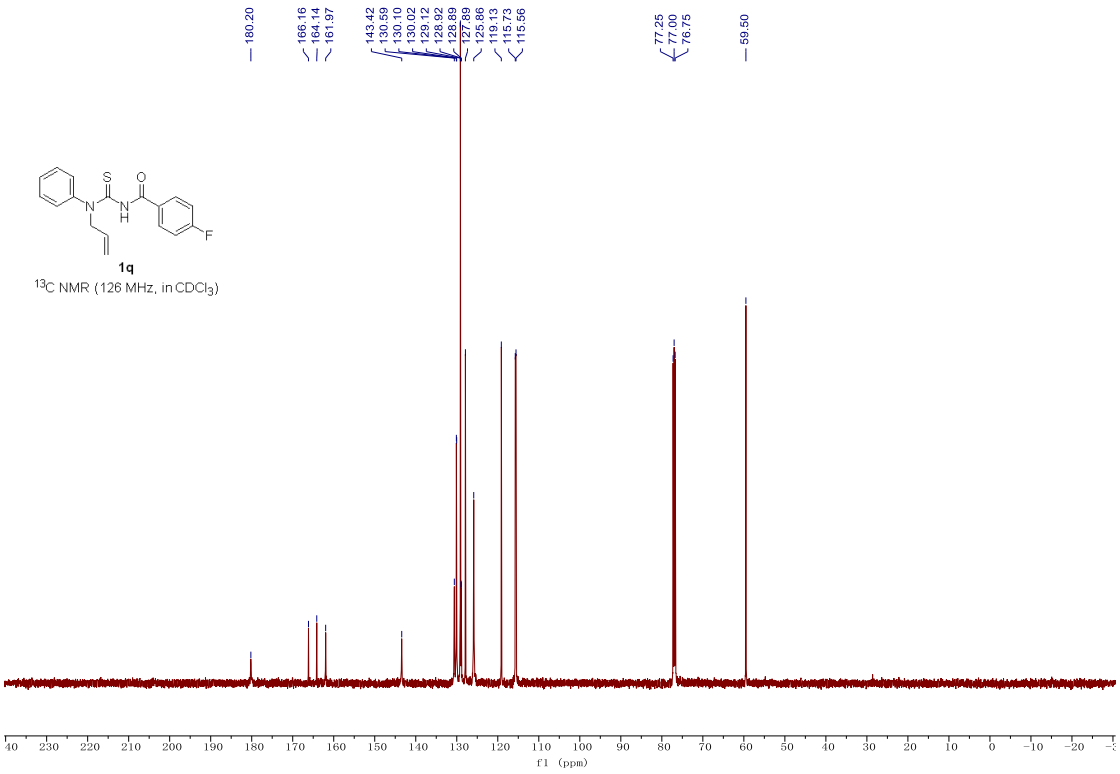
1p

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



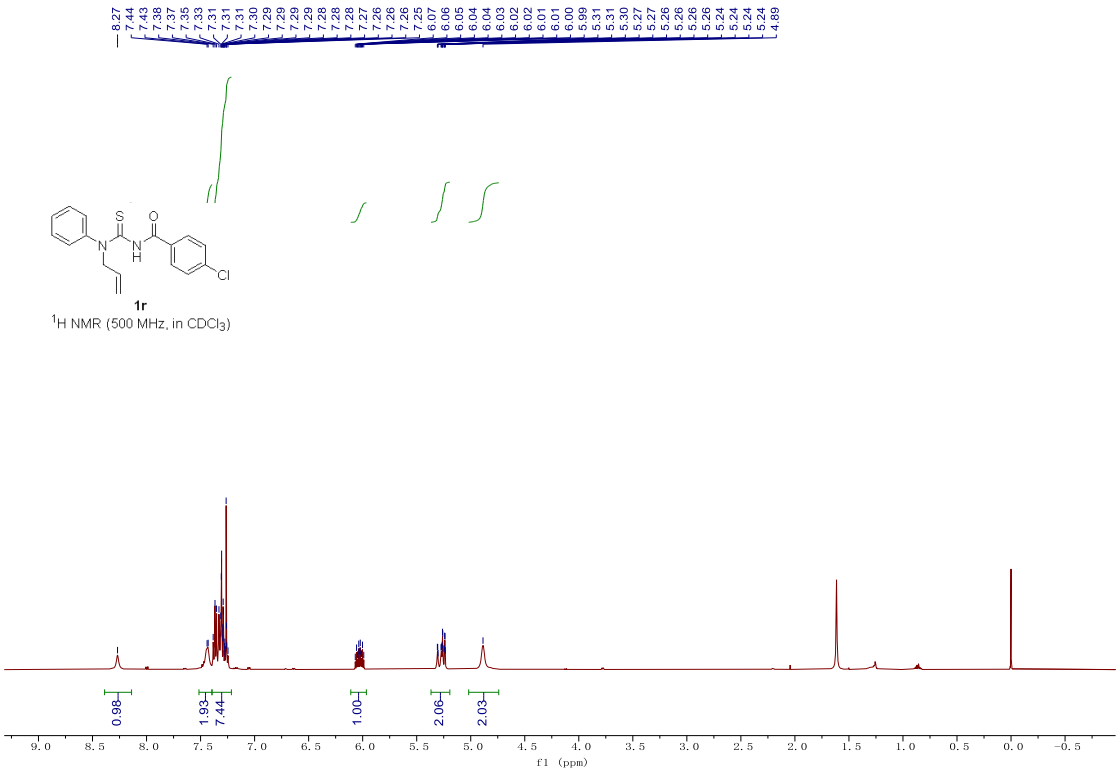
1q

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



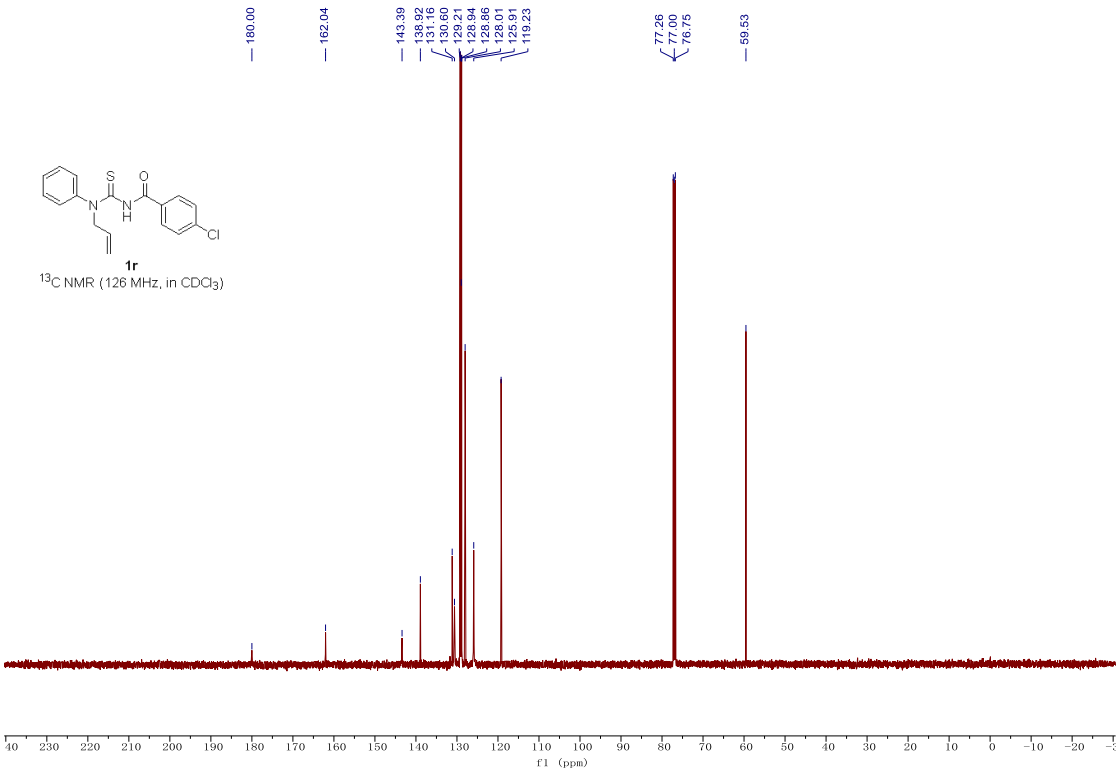
1q

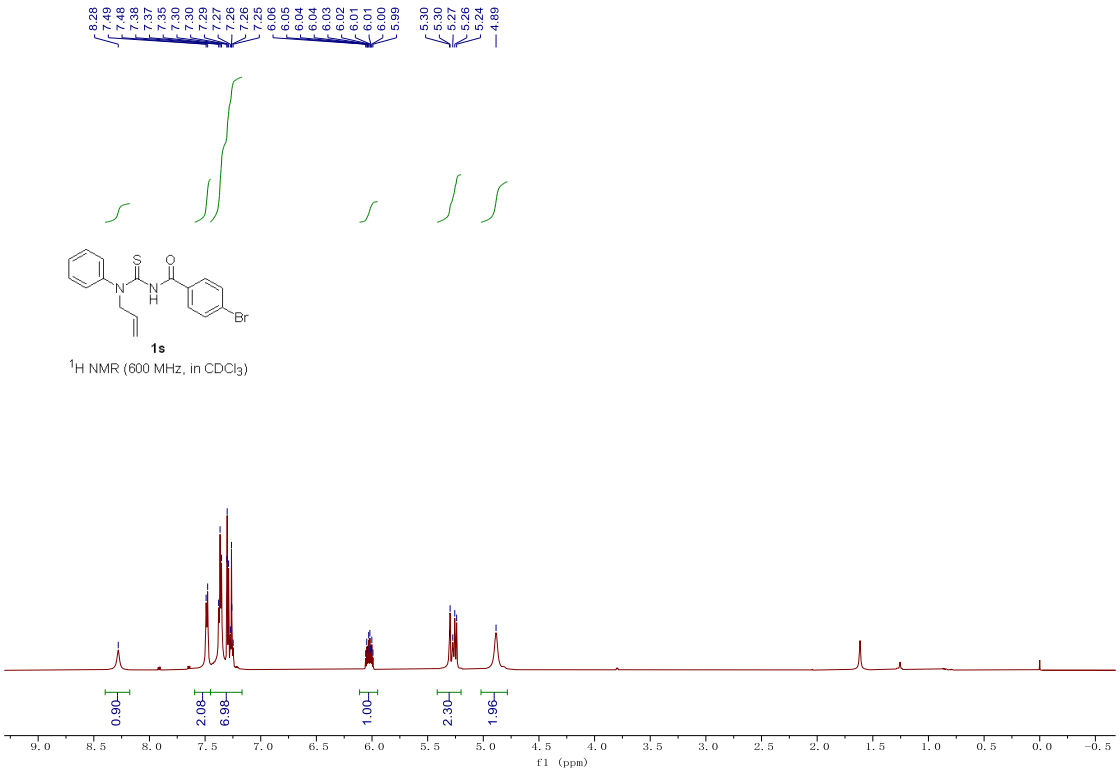
^{13}C NMR (126 MHz, in $CDCl_3$)

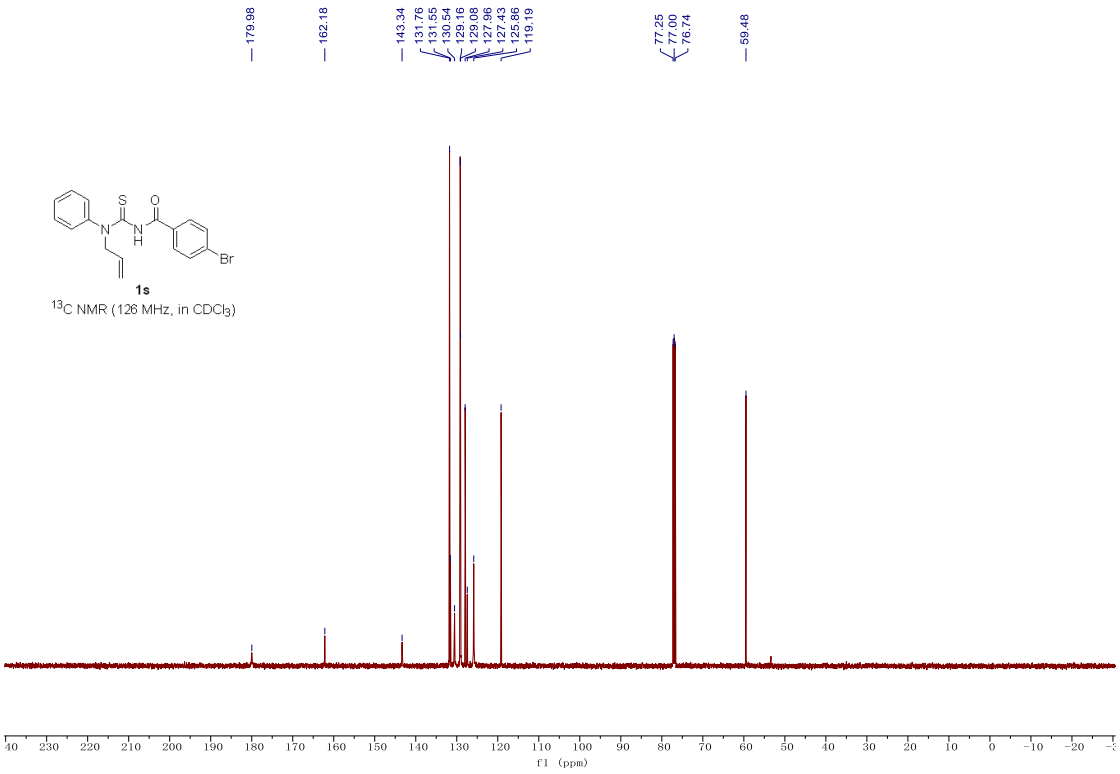


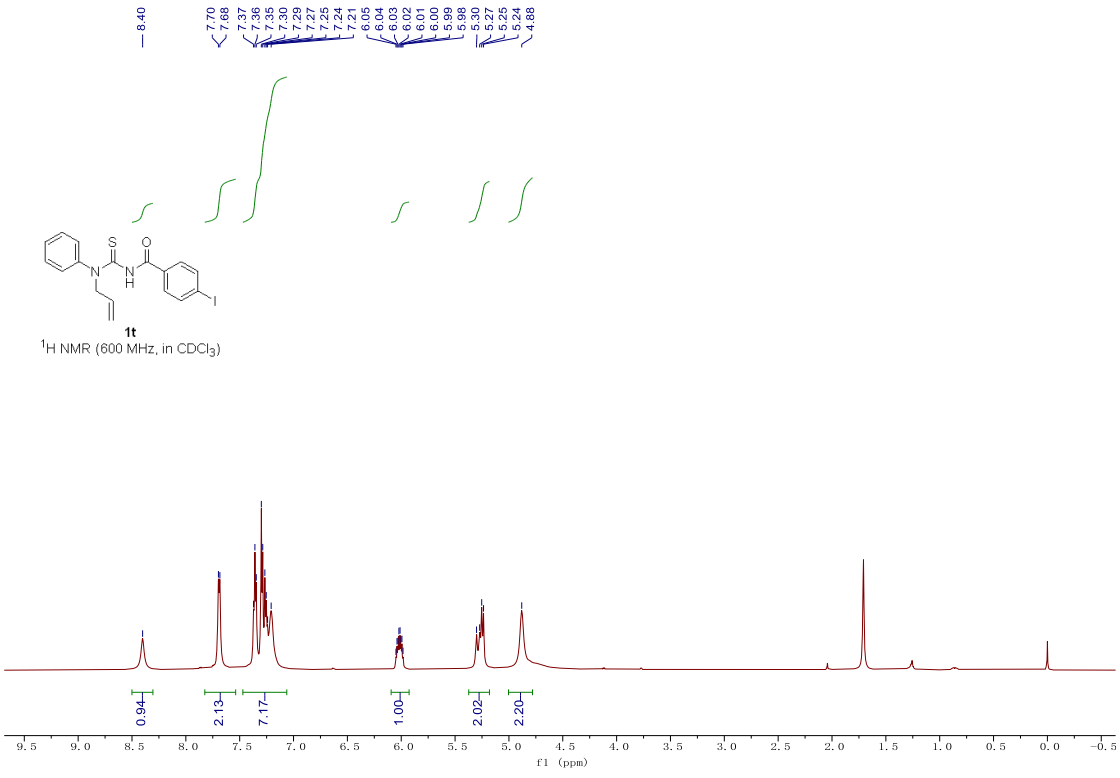
1r

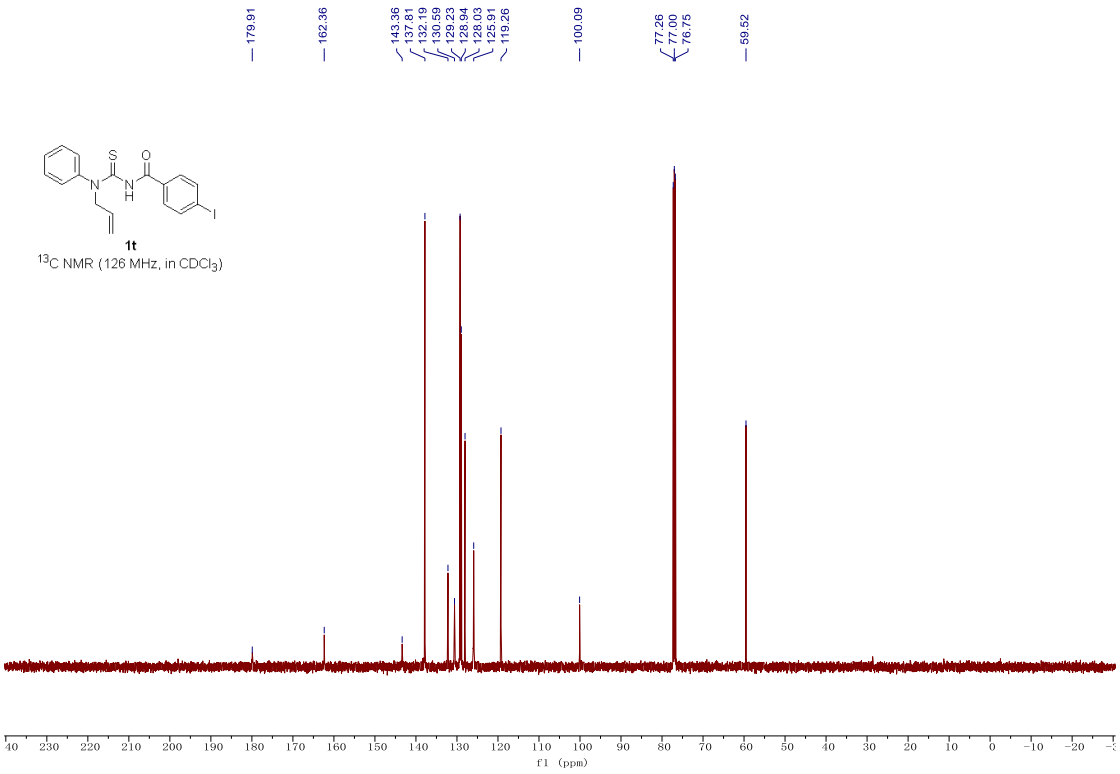
^{1}H NMR (500 MHz, in $CDCl_3$)

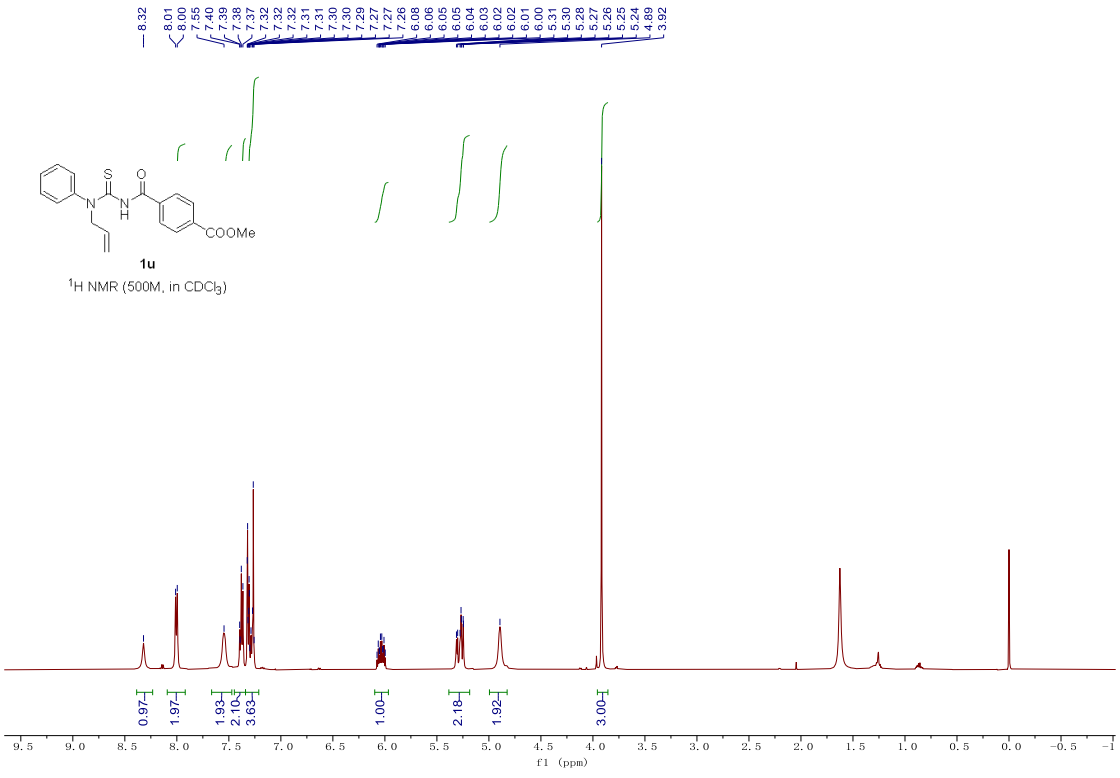

180.00
162.04
143.39
138.92
131.16
130.60
129.21
128.94
128.86
128.01
125.91
119.23
77.26
77.00
76.75
59.53
S
O
N
H
N
Cl
1r
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

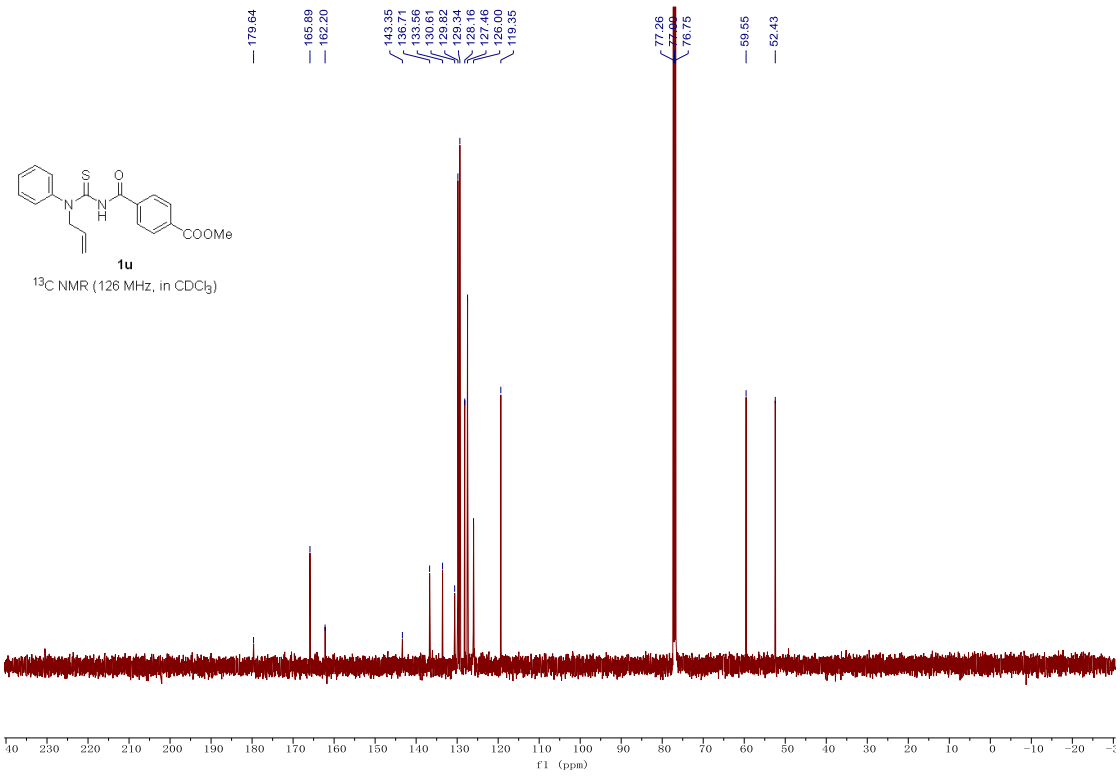

8.28
7.49
7.48
7.38
7.37
7.35
7.30
7.30
7.29
7.27
7.26
7.26
7.25
6.06
6.05
6.04
6.04
6.03
6.02
6.01
6.01
6.00
5.99
5.30
5.30
5.27
5.26
5.24
4.89
S
O
N
H
Br
1s
1H NMR (600 MHz, in CDCl3)
0.90
2.08
6.98
1.00
2.30
1.96
f1 (ppm)


179.98
162.18
143.34
131.76
131.55
130.54
129.16
129.08
127.96
127.43
125.86
119.19
77.25
77.00
76.74
59.48
Br
1s
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.40
7.70
7.68
7.37
7.36
7.35
7.30
7.29
7.27
7.25
7.24
7.21
6.05
6.04
6.03
6.02
6.01
6.00
5.99
5.98
5.30
5.27
5.25
5.24
4.88
I
1t
1H NMR (600 MHz, in CDCl3)
0.94
2.13
7.17
1.00
2.02
2.20
f1 (ppm)

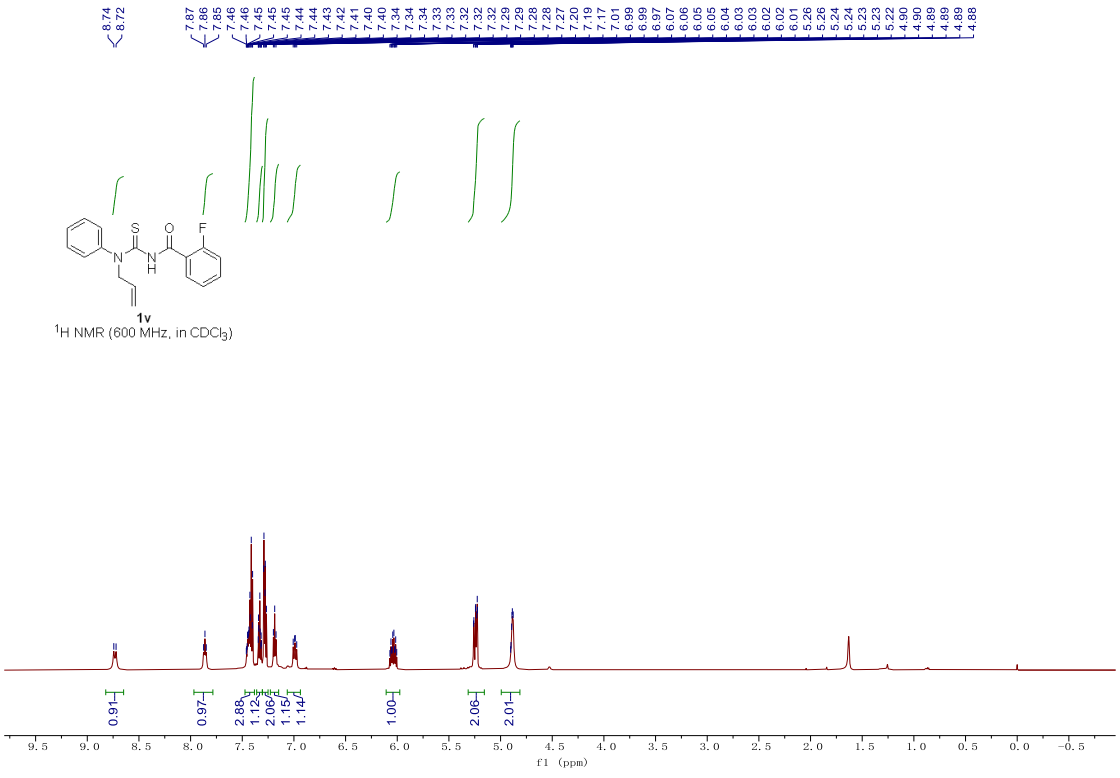

179.91
162.36
143.36
137.81
132.19
130.59
129.23
128.94
128.03
125.91
119.26
100.09
77.26
77.00
76.75
59.52
1t
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.32
8.01
8.00
7.55
7.40
7.39
7.38
7.37
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.27
7.27
7.26
6.08
6.06
6.05
6.05
6.04
6.03
6.02
6.02
6.01
6.00
5.31
5.30
5.28
5.27
5.26
5.25
5.24
4.89
3.92
COOMe
1u
1H NMR (500M, in CDCl3)
0.97
1.97
1.93
2.10
3.63
1.00
2.18
1.92
3.00
f1 (ppm)



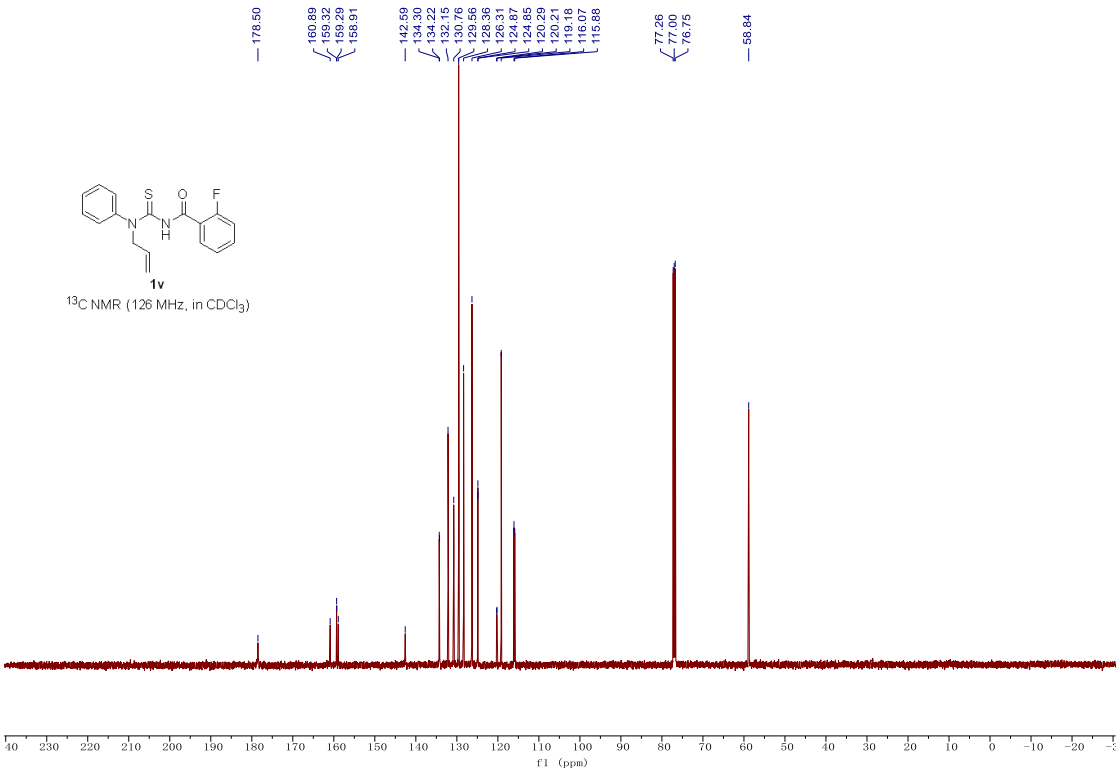
1u

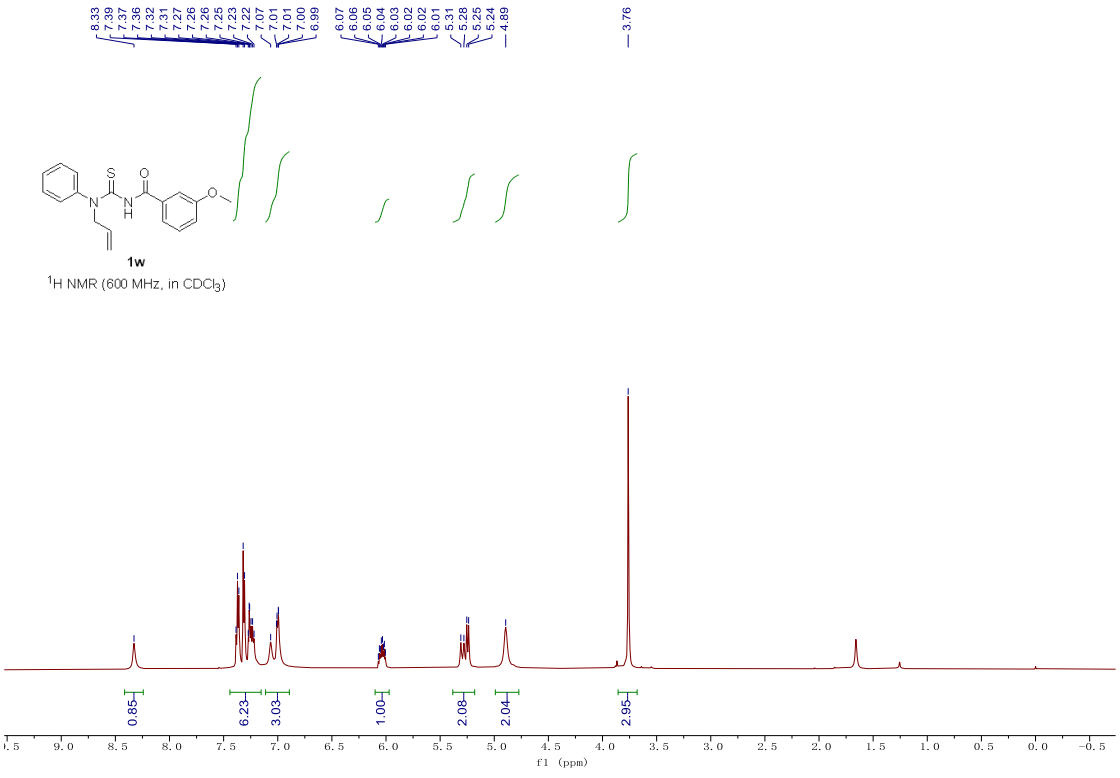
^{13}C NMR (126 MHz, in $CDCl_3$)

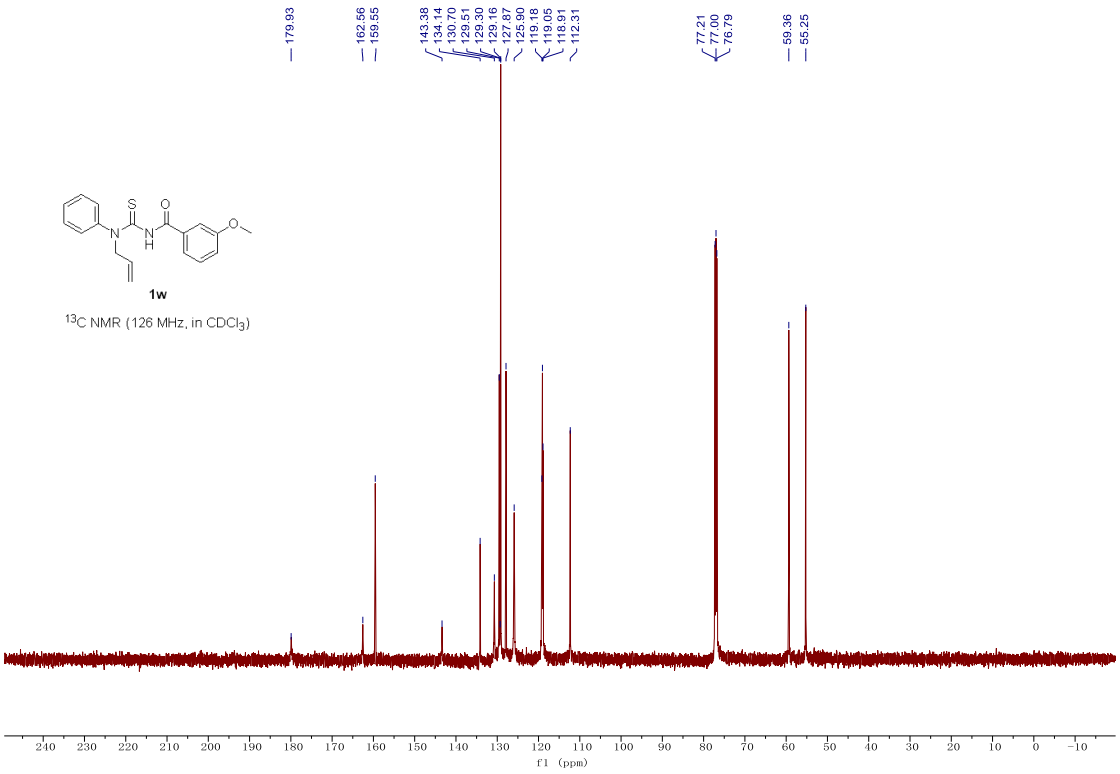


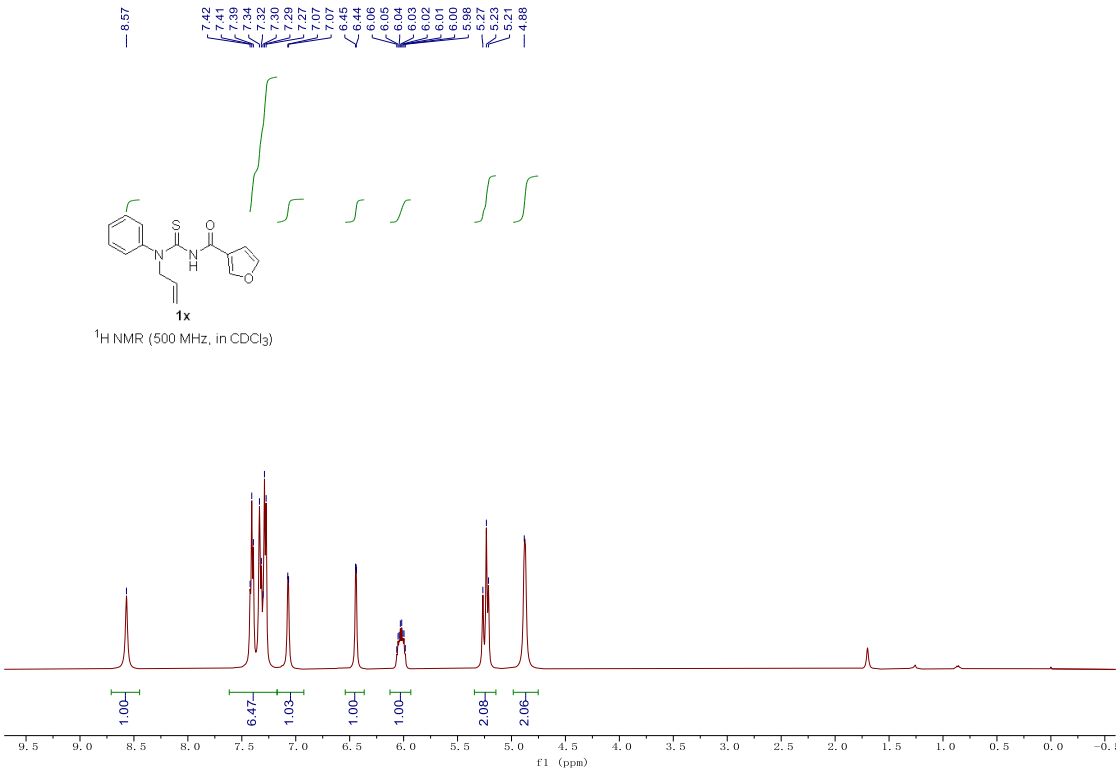
1v

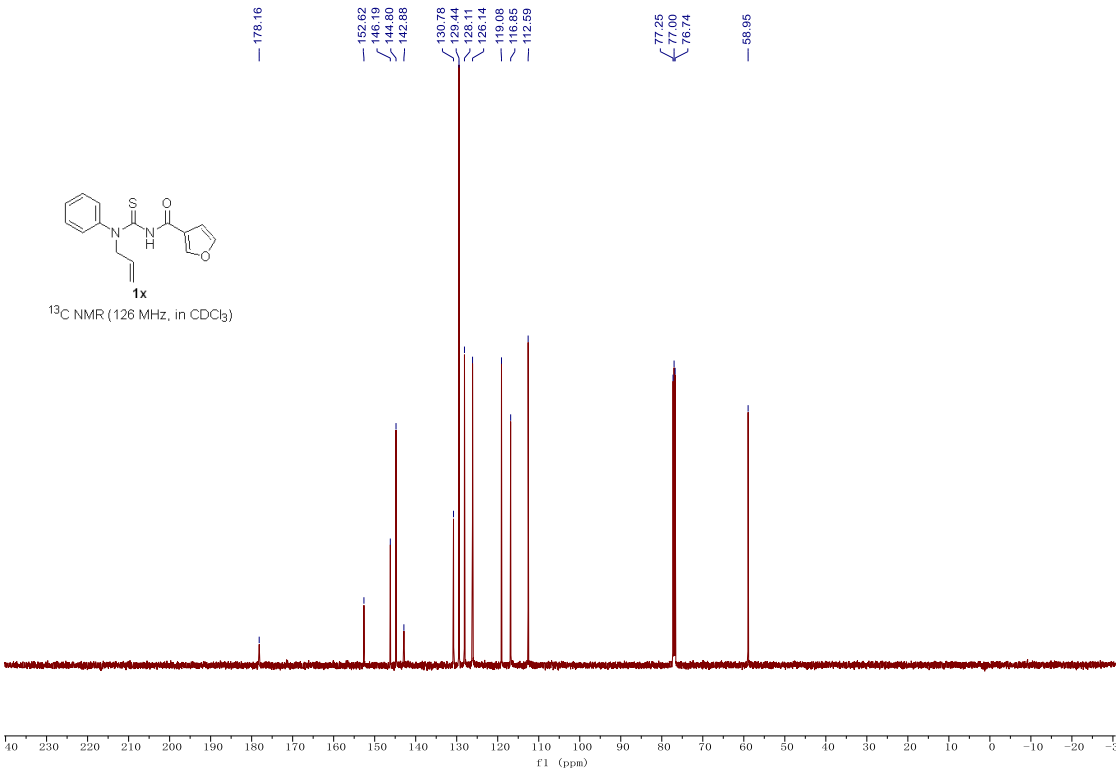
^{1}H NMR (600 MHz, in $CDCl_3$)

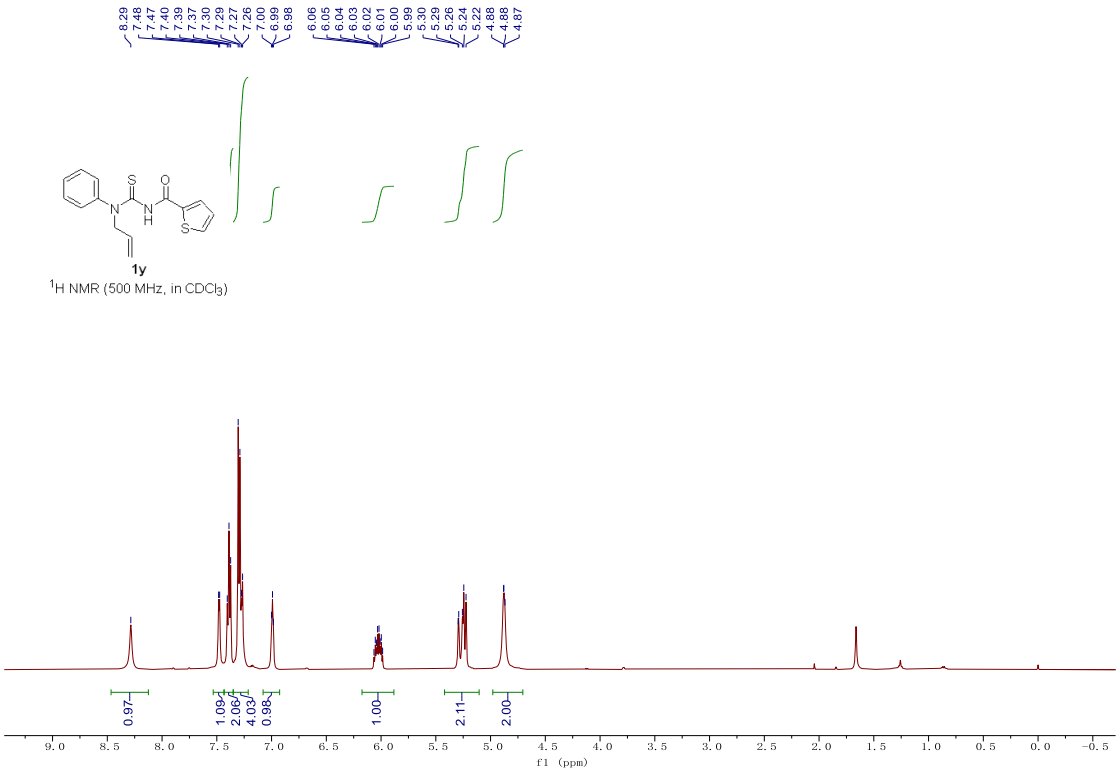

178.50
160.89
159.32
159.29
158.91
142.59
134.30
134.22
132.15
130.76
129.56
128.36
126.31
124.87
124.85
120.29
120.21
119.18
116.07
115.88
77.26
77.00
76.75
58.84
S
O
F
N
H
1v
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

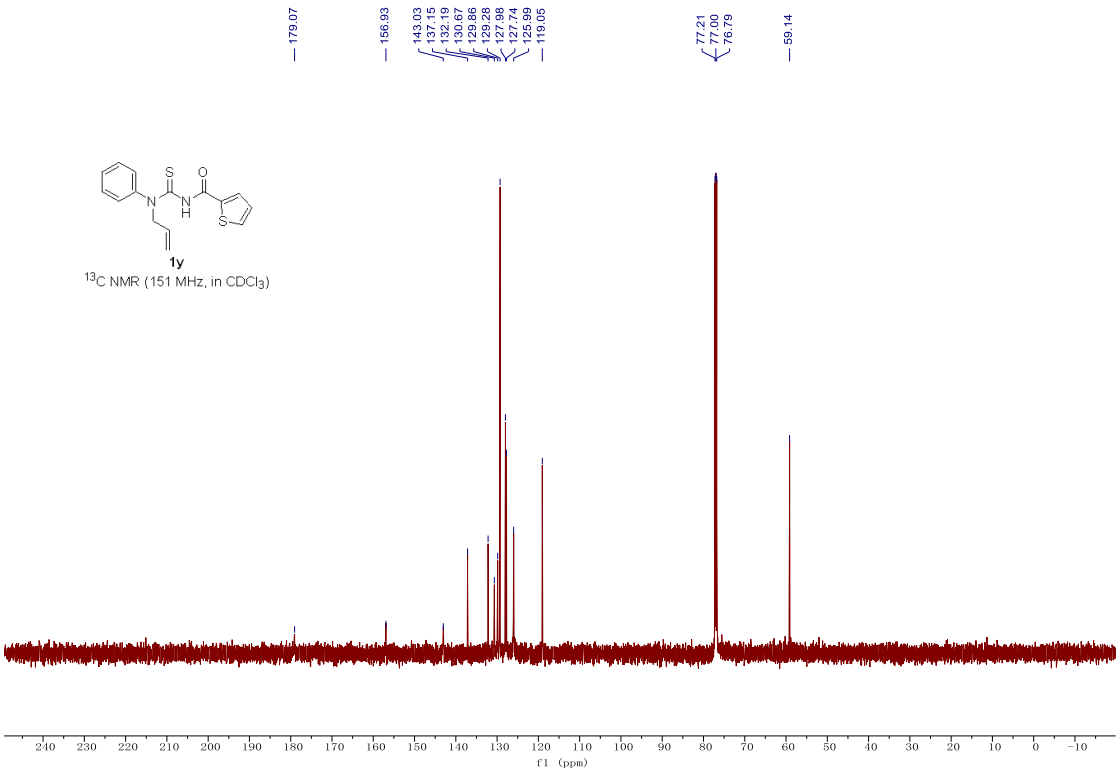

8.33
7.39
7.37
7.36
7.32
7.31
7.27
7.26
7.26
7.25
7.23
7.22
7.07
7.01
7.01
7.00
6.99
6.07
6.06
6.05
6.04
6.03
6.02
6.02
6.01
5.31
5.28
5.25
5.24
4.89
3.76
S
O
N
H
O
1w
1H NMR (600 MHz, in CDCl3)
0.85
6.23
3.03
1.00
2.08
2.04
2.95
f1 (ppm)

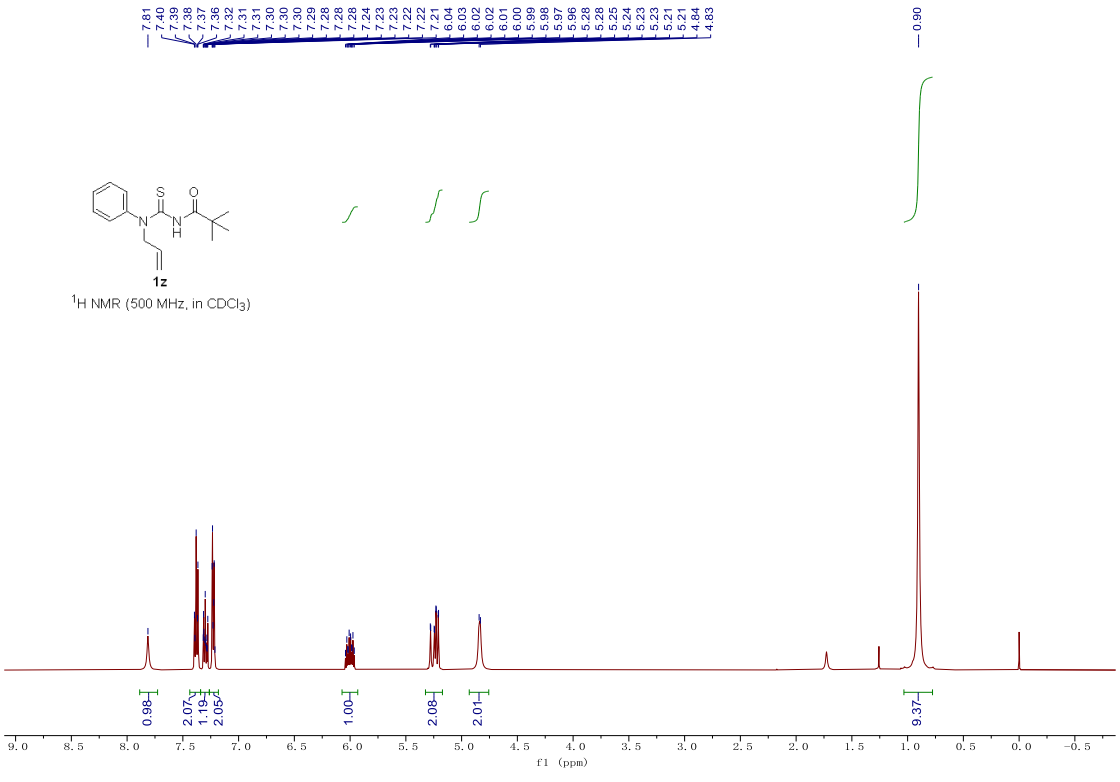

179.93
162.56
159.55
143.38
134.14
130.70
129.51
129.30
129.16
127.87
125.90
119.18
119.05
118.91
112.31
77.21
77.00
76.79
59.36
55.25
1w
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

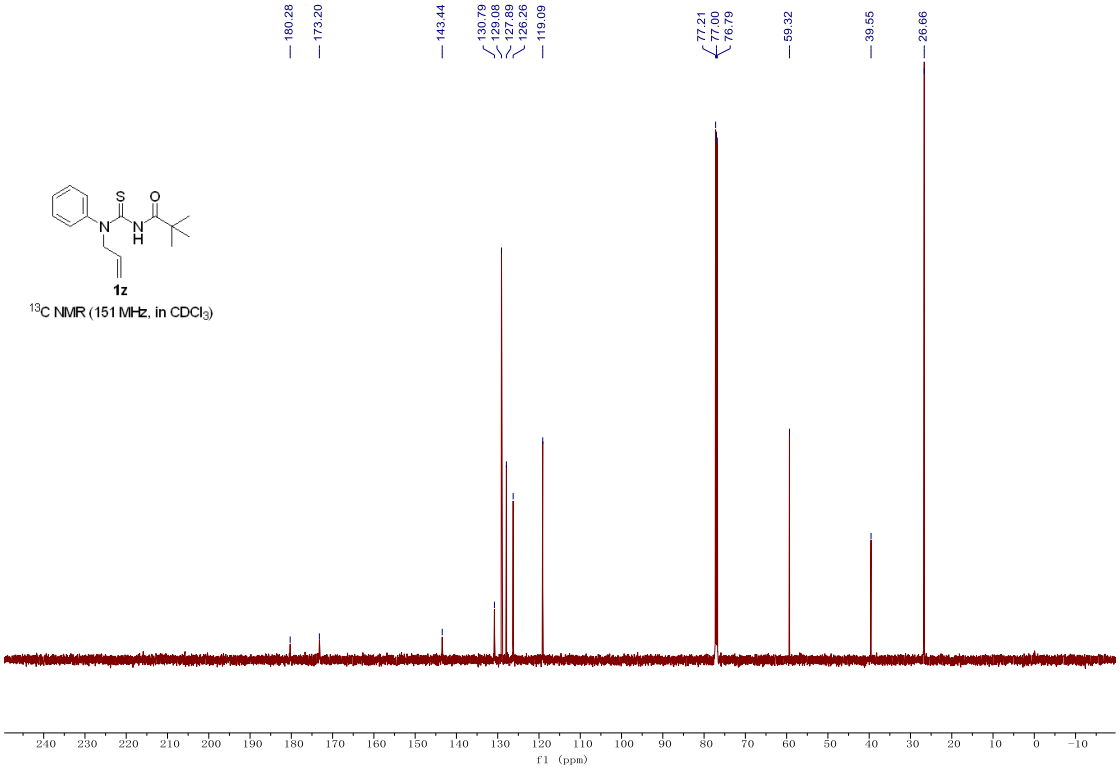

8.57
7.42
7.41
7.39
7.34
7.32
7.30
7.29
7.27
7.07
7.07
6.45
6.44
6.06
6.05
6.04
6.03
6.02
6.01
6.00
5.98
5.27
5.23
5.21
4.88
1x
1H NMR (500 MHz, in CDCl3)
1.00
6.47
1.03
1.00
1.00
2.08
2.06
f1 (ppm)


178.16
152.62
146.19
144.80
142.88
130.78
129.44
128.11
126.14
119.08
116.85
112.59
77.25
77.00
76.74
58.95
1x
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.29
7.48
7.47
7.40
7.39
7.37
7.30
7.29
7.27
7.26
7.00
6.99
6.98
6.06
6.05
6.04
6.03
6.02
6.01
6.00
5.99
5.30
5.29
5.26
5.24
5.22
4.88
4.88
4.87
1y
1H NMR (500 MHz, in CDCl3)
0.97
1.09
2.06
4.03
0.98
1.00
2.11
2.00
f1 (ppm)

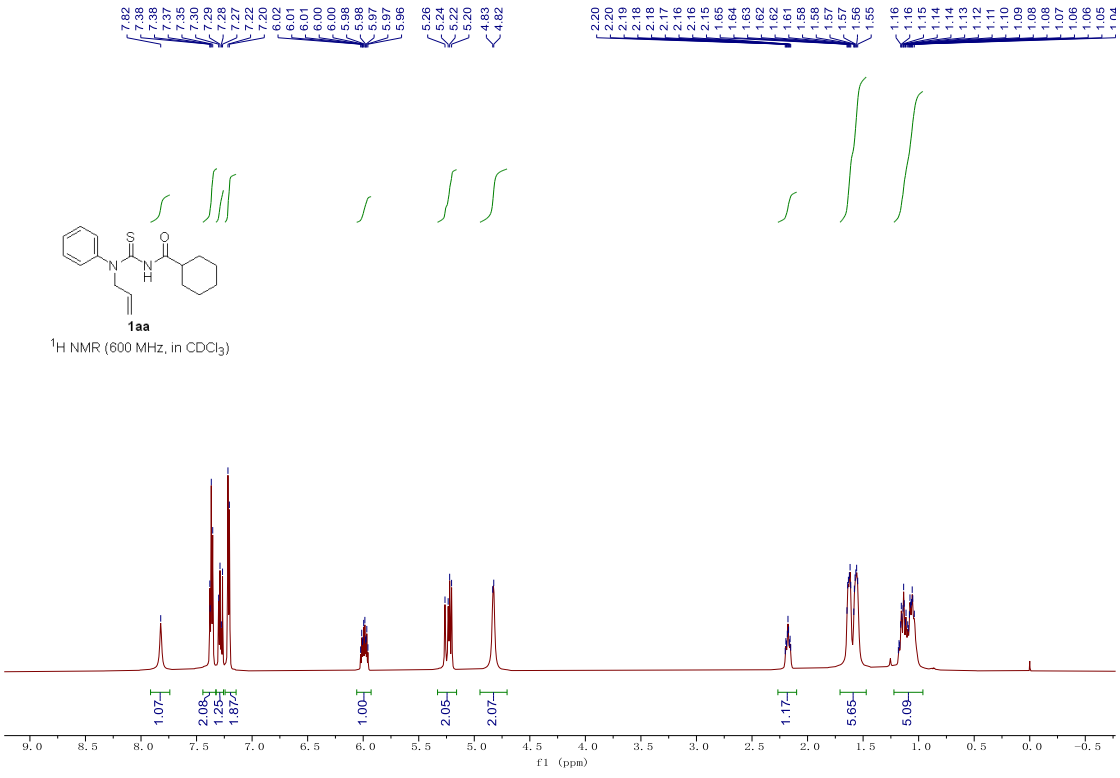

179.07
156.93
143.03
137.15
132.19
130.67
129.86
129.28
127.98
127.74
125.99
119.05
77.21
77.00
76.79
59.14
1y
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


7.81
7.40
7.39
7.38
7.37
7.36
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.28
7.24
7.23
7.23
7.22
7.21
6.04
6.03
6.02
6.02
6.01
6.00
5.99
5.98
5.97
5.96
5.28
5.28
5.25
5.24
5.23
5.23
5.21
5.21
4.84
4.83
0.90
1z
1H NMR (500 MHz, in CDCl3)
0.98
2.07
1.19
2.05
1.00
2.08
2.01
9.37
f1 (ppm)



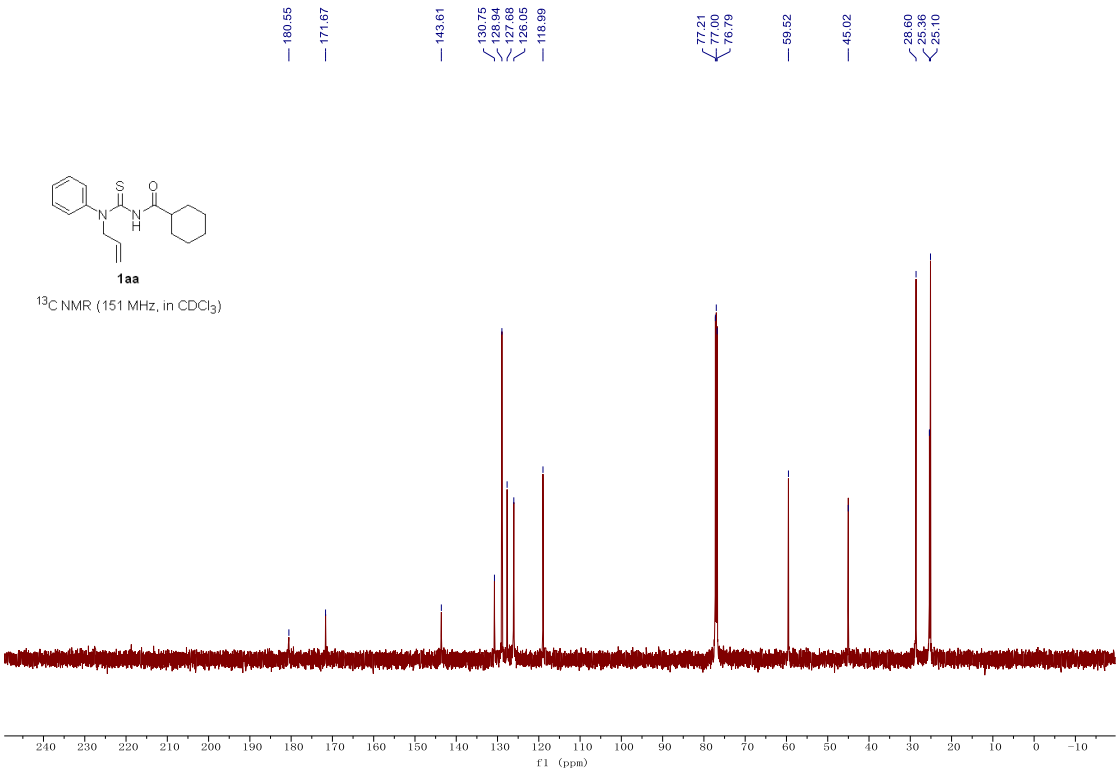
1z

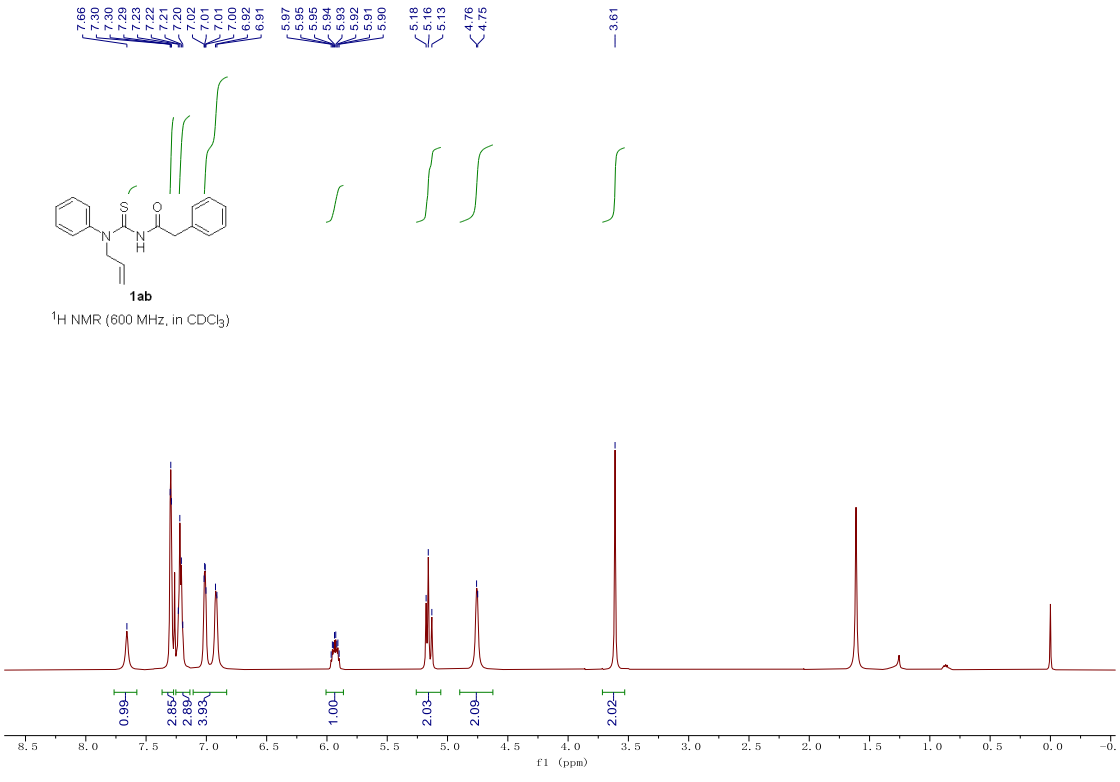
^{13}C NMR (151 MHz, in $CDCl_3$)

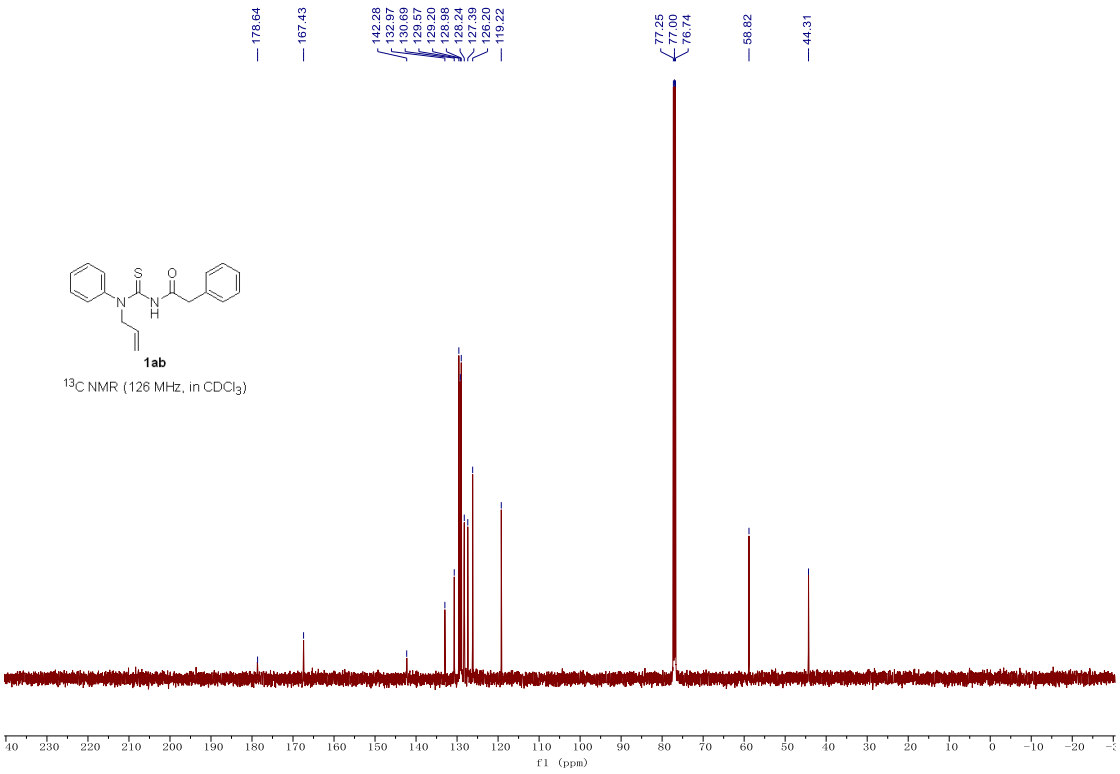


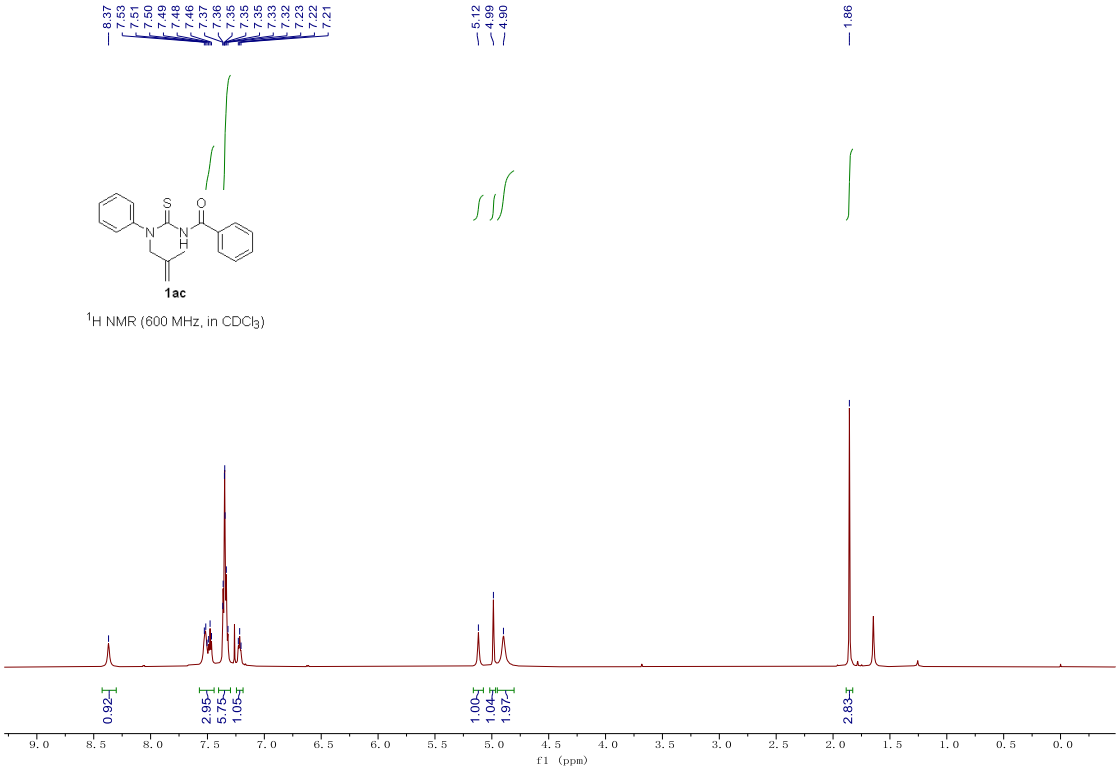
1aa

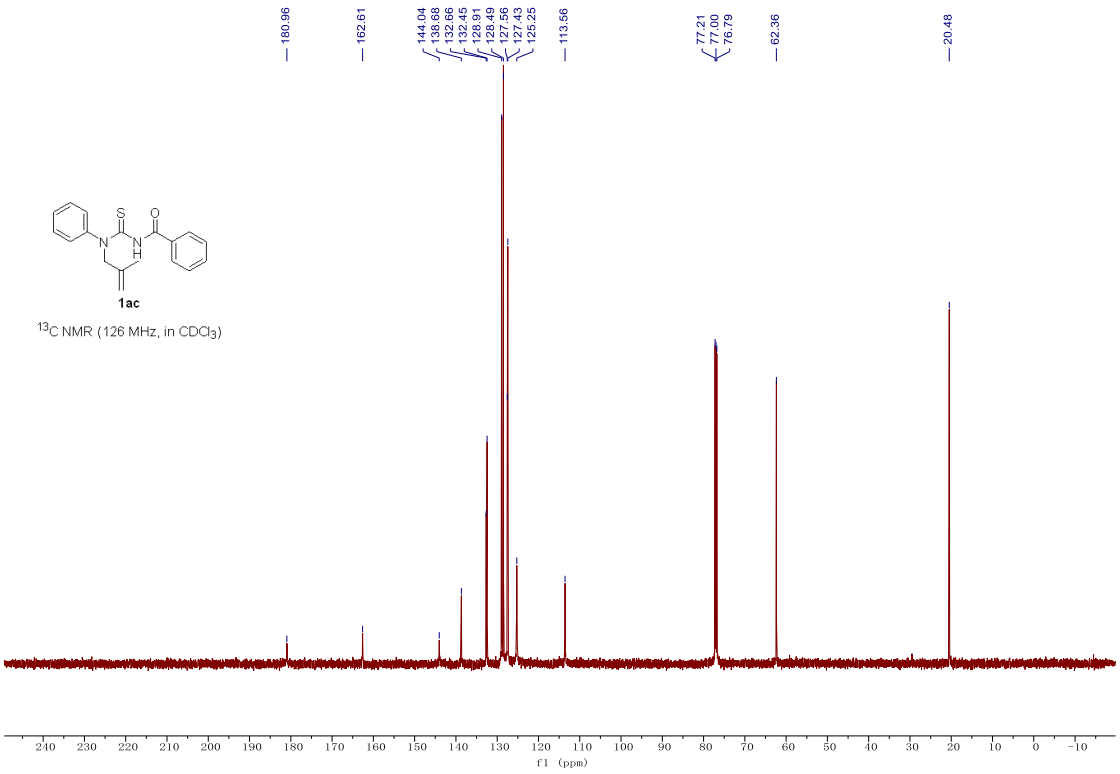
^{1}H NMR (600 MHz, in $CDCl_3$)

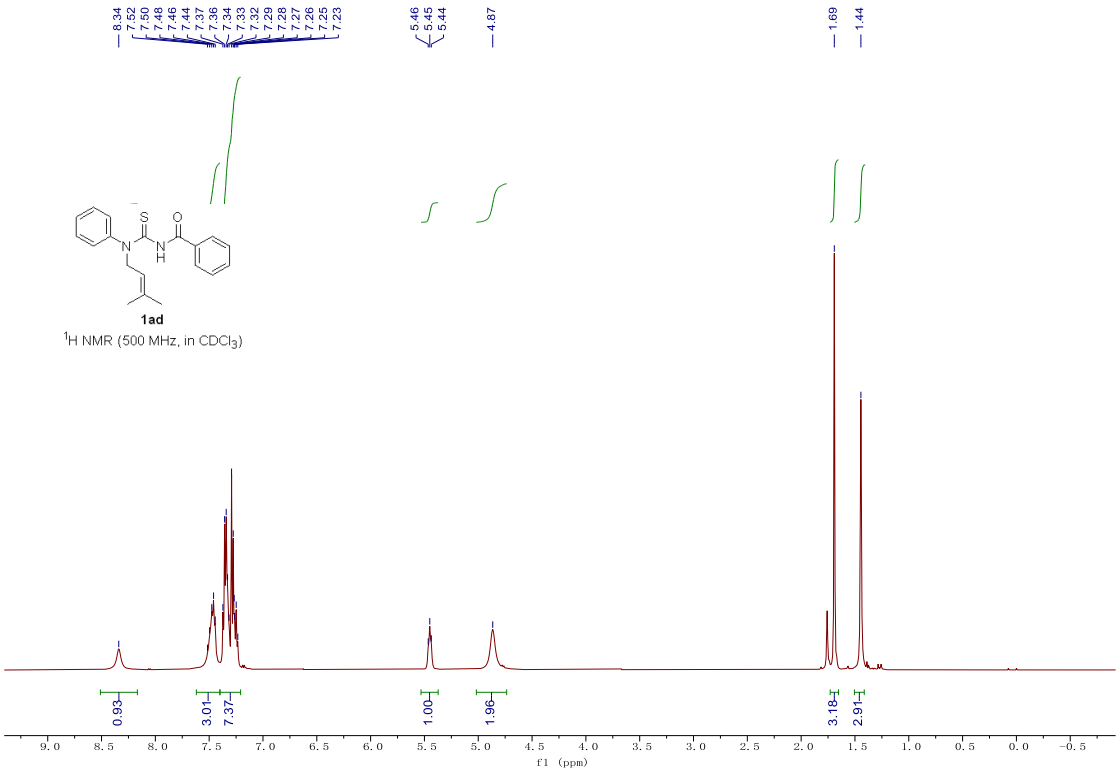

180.55
171.67
143.61
130.75
128.94
127.68
126.05
118.99
77.21
77.00
76.79
59.52
45.02
28.60
25.36
25.10
1aa
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

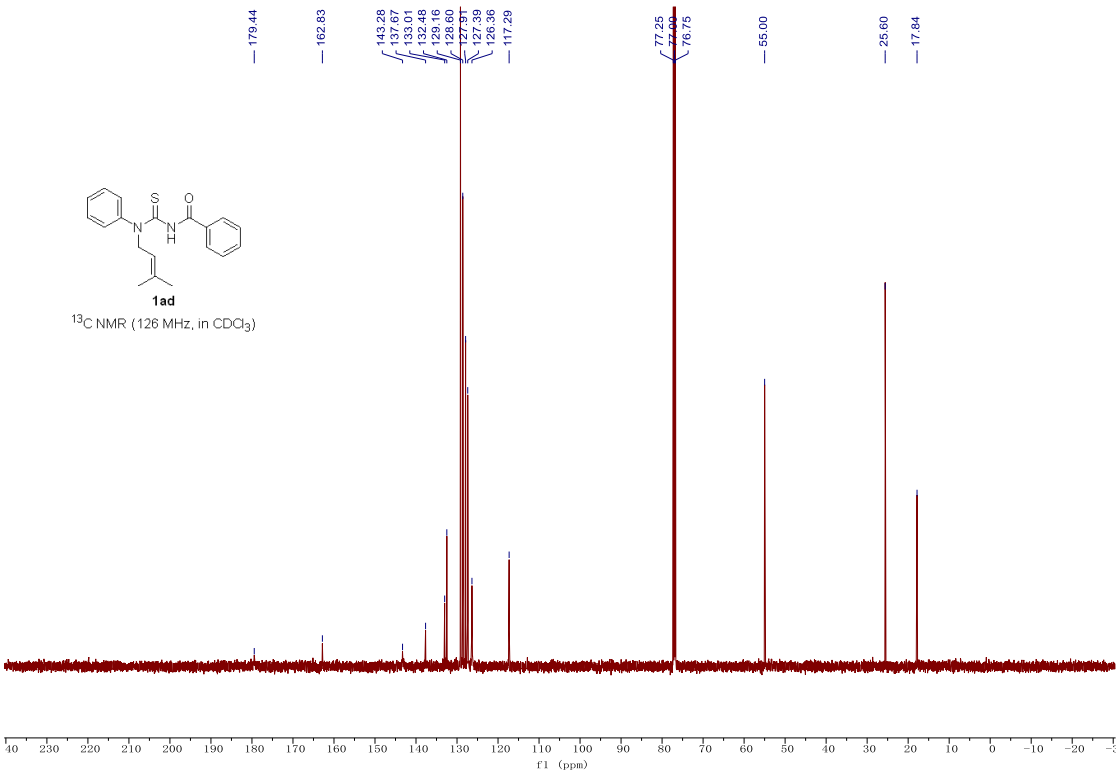

7.66
7.30
7.30
7.29
7.23
7.22
7.21
7.20
7.02
7.01
7.01
7.00
6.92
6.91
5.97
5.95
5.95
5.94
5.93
5.92
5.91
5.90
5.18
5.16
5.13
4.76
4.75
3.61
1ab
1H NMR (600 MHz, in CDCl3)
0.99
2.85
2.89
3.93
1.00
2.03
2.09
2.02
f1 (ppm)

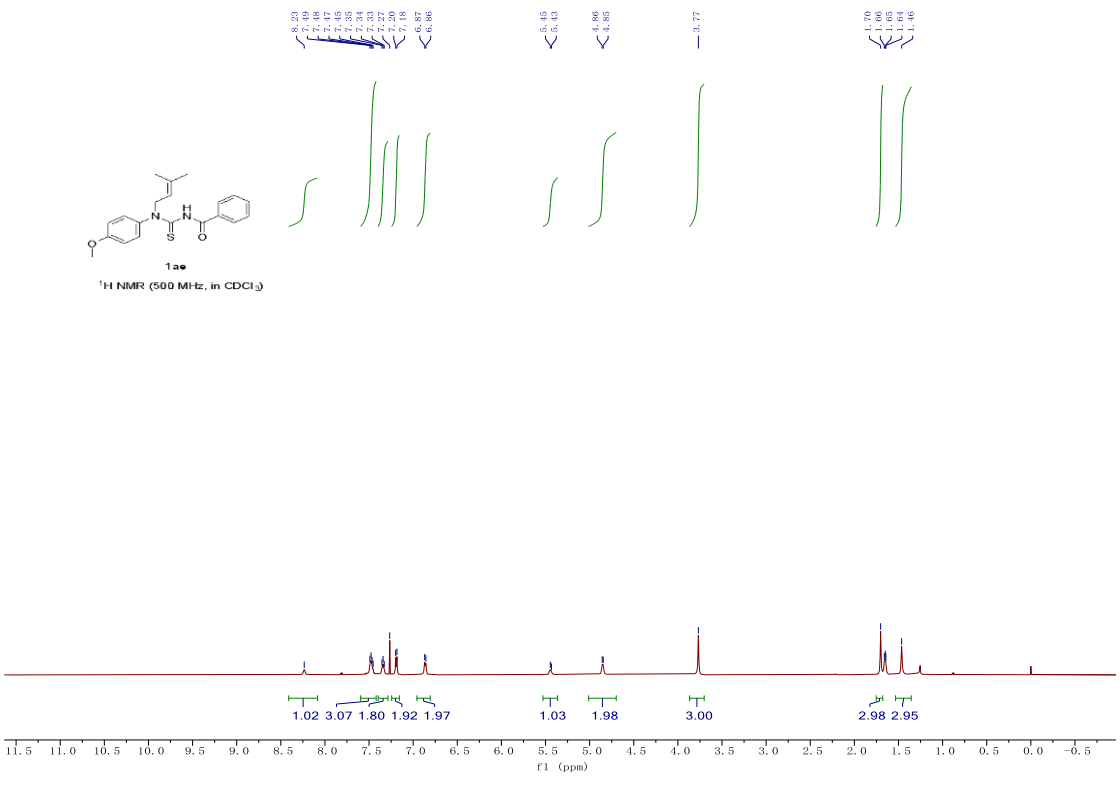

178.64
167.43
142.28
132.97
130.69
129.57
129.20
128.98
128.24
127.39
126.20
119.22
77.25
77.00
76.74
58.82
44.31
1ab
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

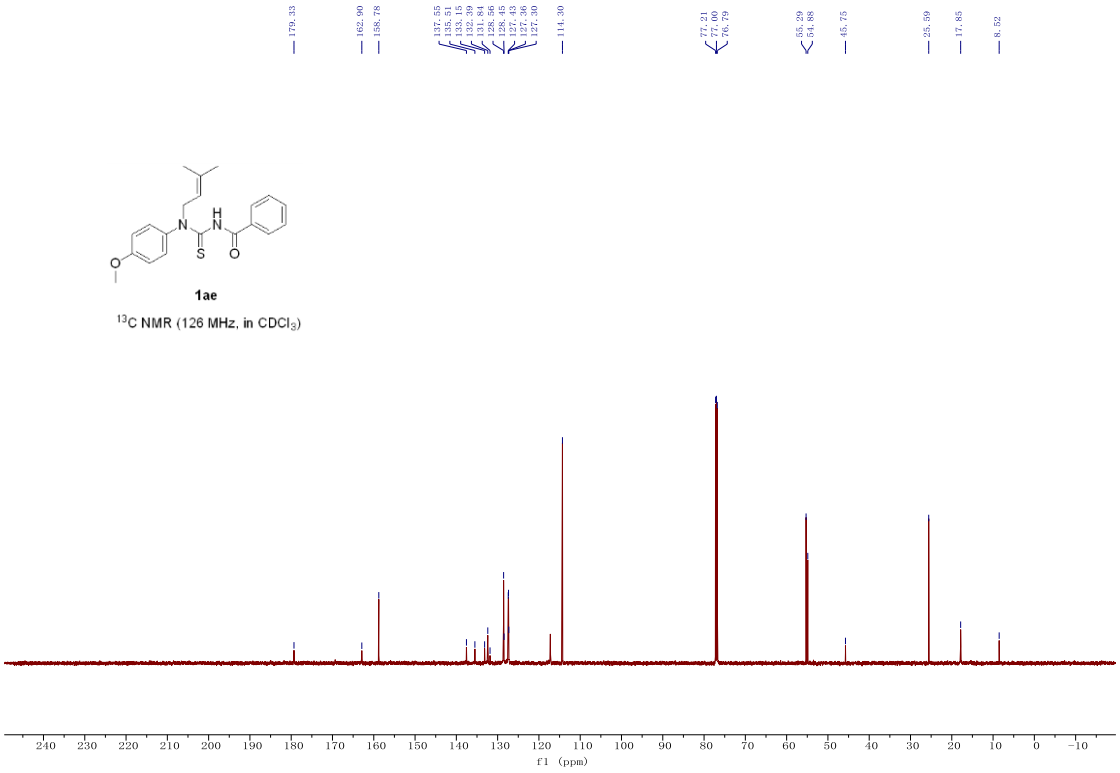

8.37
7.53
7.51
7.50
7.49
7.48
7.46
7.37
7.36
7.35
7.35
7.35
7.33
7.32
7.23
7.22
7.21
5.12
4.99
4.90
1.86
1ac
1H NMR (600 MHz, in CDCl3)
0.92
2.95
5.75
1.05
1.00
1.04
1.97
2.83
f1 (ppm)


180.96
162.61
144.04
138.68
132.66
132.45
128.91
128.49
127.56
127.43
125.25
113.56
77.21
77.00
76.79
62.36
20.48
1ac
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.34
7.52
7.50
7.48
7.46
7.44
7.37
7.36
7.34
7.33
7.32
7.29
7.28
7.27
7.26
7.25
7.23
5.46
5.45
5.44
4.87
1.69
1.44
1ad
1H NMR (500 MHz, in CDCl3)
0.93
3.01
7.37
1.00
1.96
3.18
2.91
f1 (ppm)


179.44
162.83
143.28
137.67
133.01
132.48
129.16
128.60
127.91
127.39
126.36
117.29
77.25
77.00
76.75
55.00
25.60
17.84
S
O
N
H
N
1ad
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.23
7.49
7.48
7.47
7.45
7.35
7.34
7.33
7.27
7.20
7.18
6.87
6.86
5.45
5.43
4.86
4.85
3.77
1.70
1.66
1.65
1.64
1.46
O
N
H
N
S
O
1ae
1H NMR (500 MHz, in CDCl3)
1.02 3.07 1.80 1.92 1.97
1.03
1.98
3.00
2.98 2.95
f1 (ppm)


179.33
162.90
158.78
137.55
135.51
133.15
132.39
131.84
128.56
128.45
127.43
127.36
127.30
114.30
77.21
77.00
76.79
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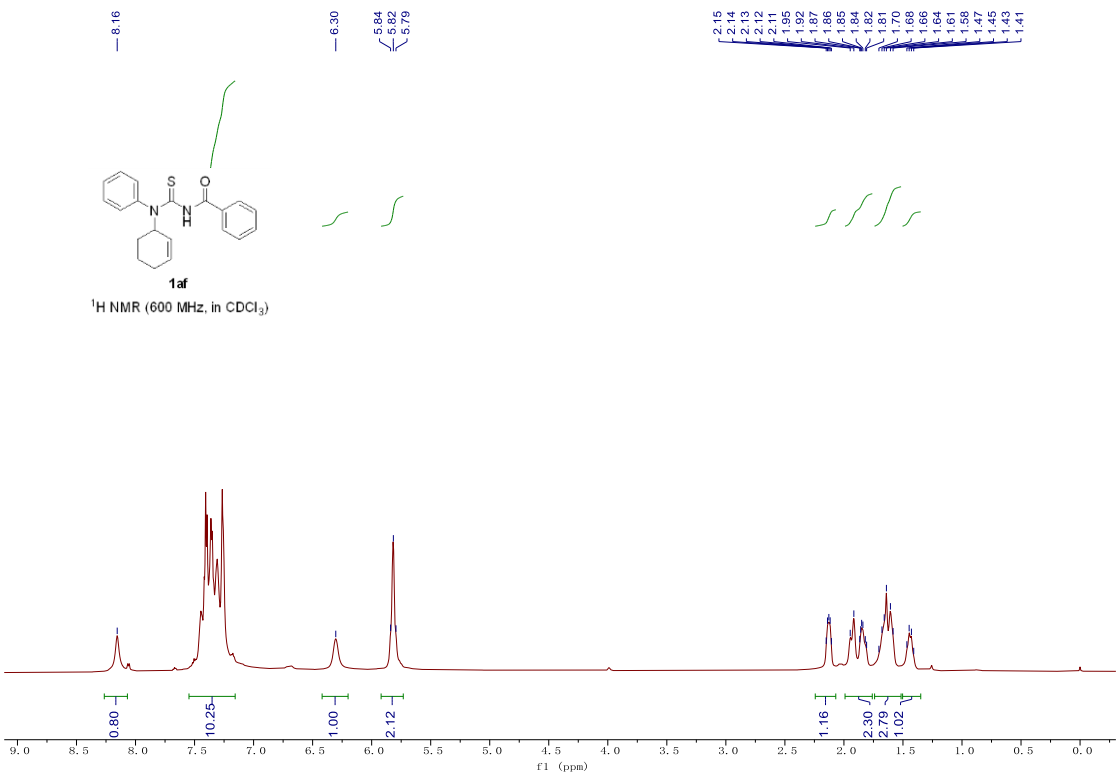
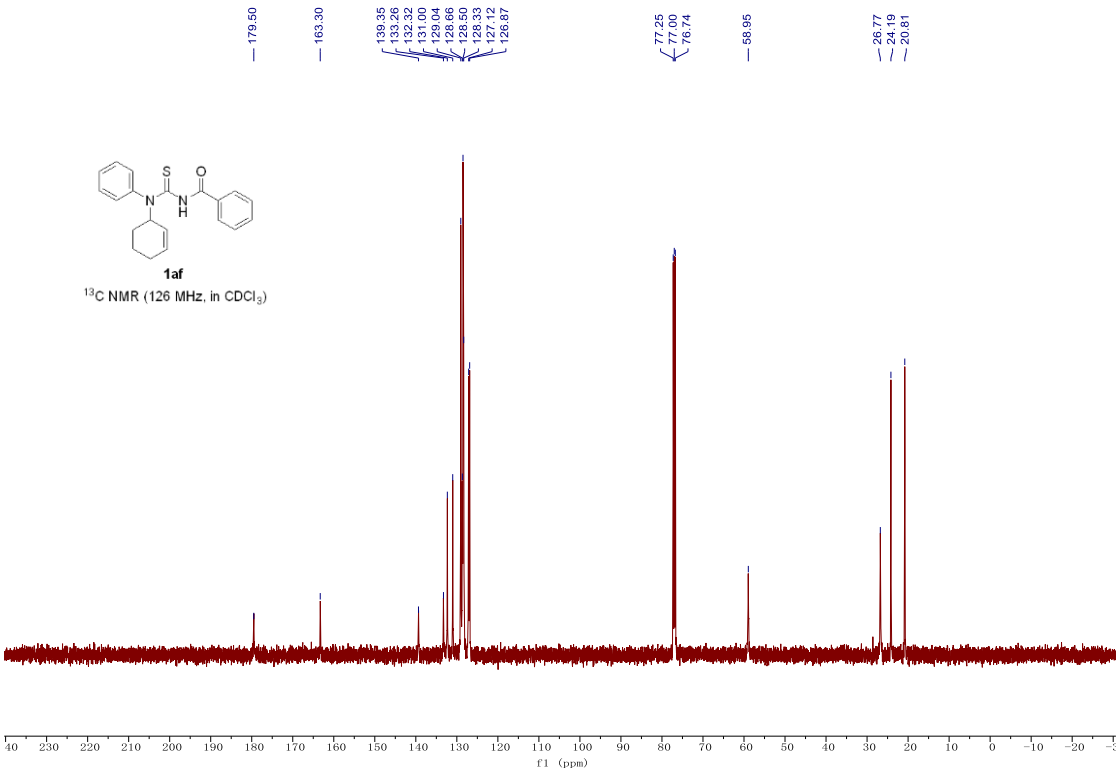
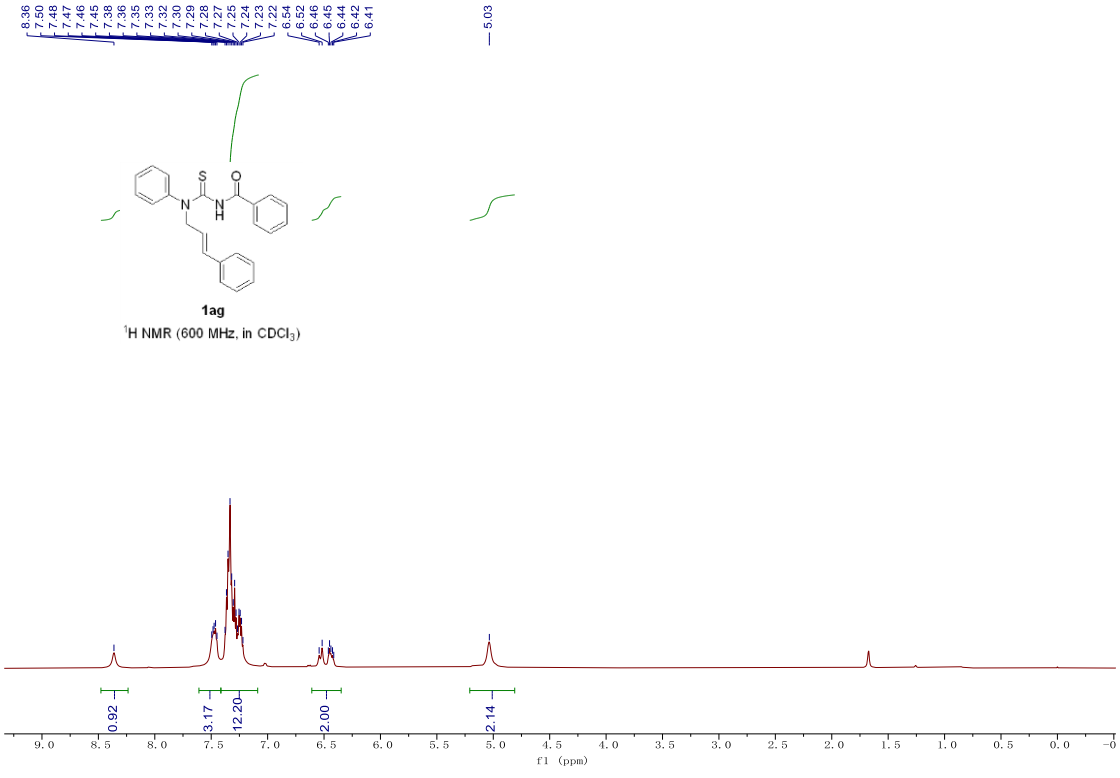
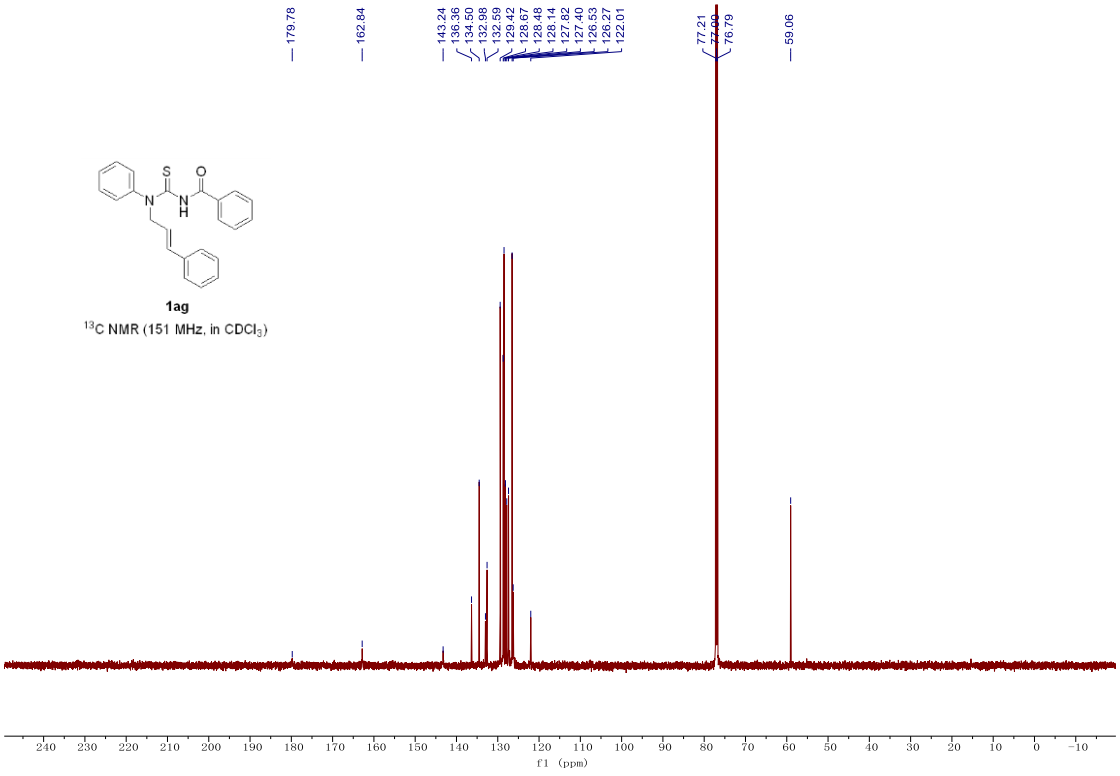
45.75
25.59
17.85
8.52
1ae
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.16
6.30
5.84
5.82
5.79
2.15
2.14
2.13
2.12
2.11
1.95
1.92
1.87
1.86
1.85
1.84
1.82
1.81
1.70
1.68
1.66
1.64
1.61
1.58
1.47
1.45
1.43
1.41
1af
1H NMR (600 MHz, in CDCl3)
0.80
10.25
1.00
2.12
1.16
2.30
2.79
1.02
f1 (ppm)

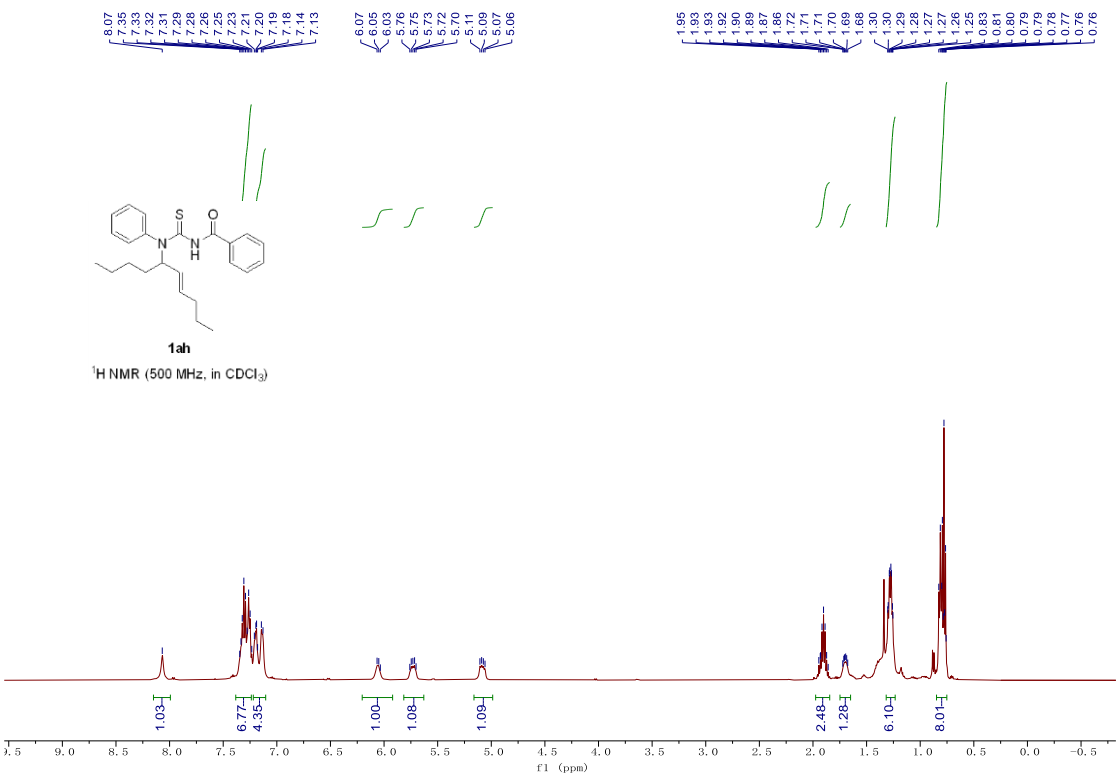

179.50
163.30
139.35
133.26
132.32
131.00
129.04
128.66
128.56
128.33
127.12
126.87
77.25
77.00
76.74
58.95
26.77
24.19
20.81
1af
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.36
7.50
7.48
7.47
7.46
7.45
7.38
7.36
7.35
7.33
7.32
7.30
7.29
7.28
7.27
7.25
7.24
7.23
7.22
6.54
6.52
6.46
6.45
6.44
6.42
6.41
5.03
1ag
1H NMR (600 MHz, in CDCl3)
0.92
3.17
12.20
2.00
2.14
f1 (ppm)



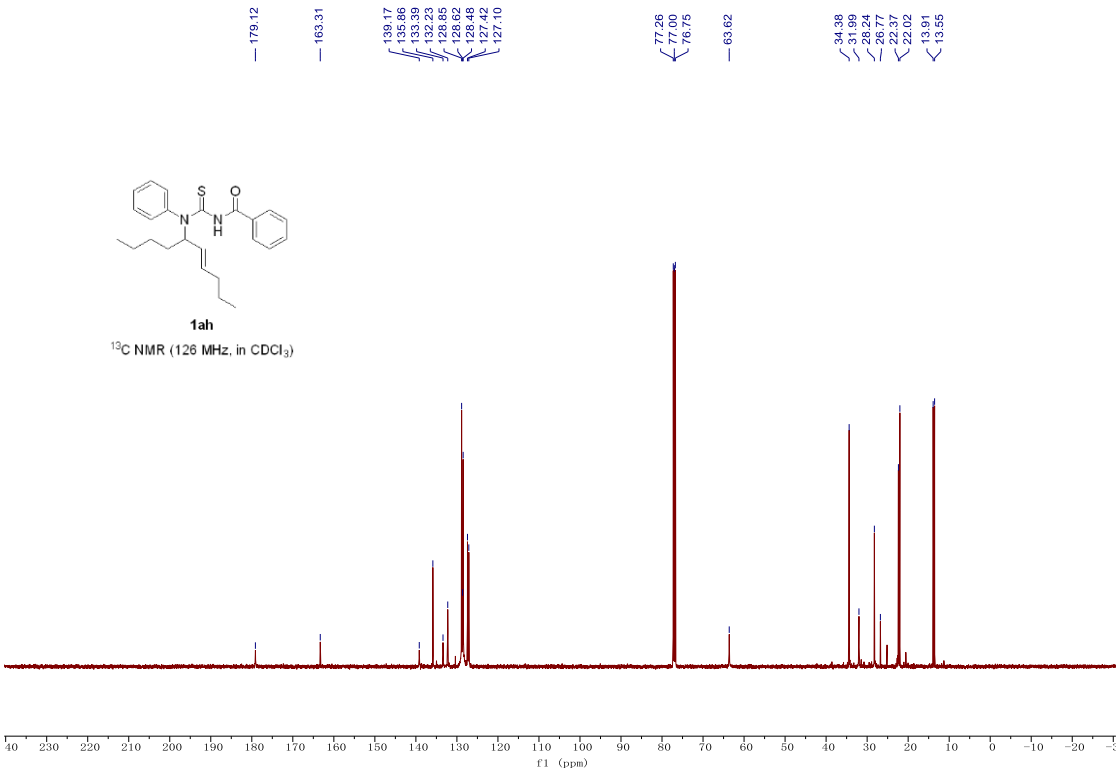
1ag

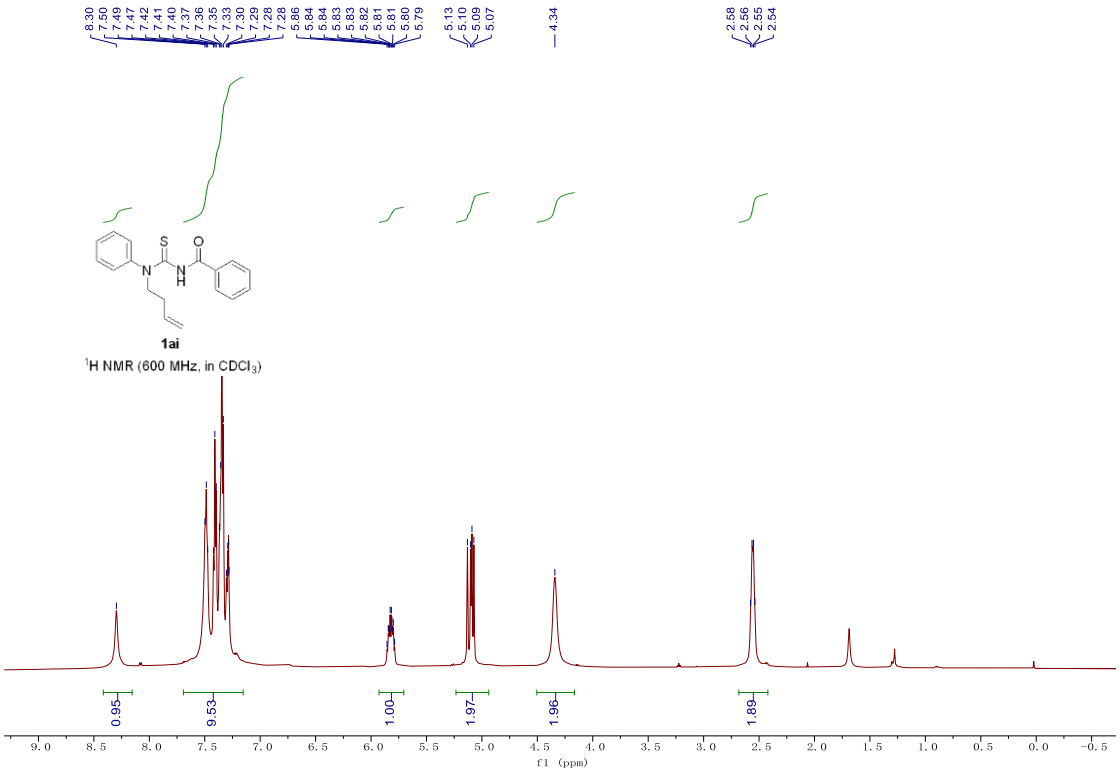
^{13}C NMR (151 MHz, in $CDCl_3$)

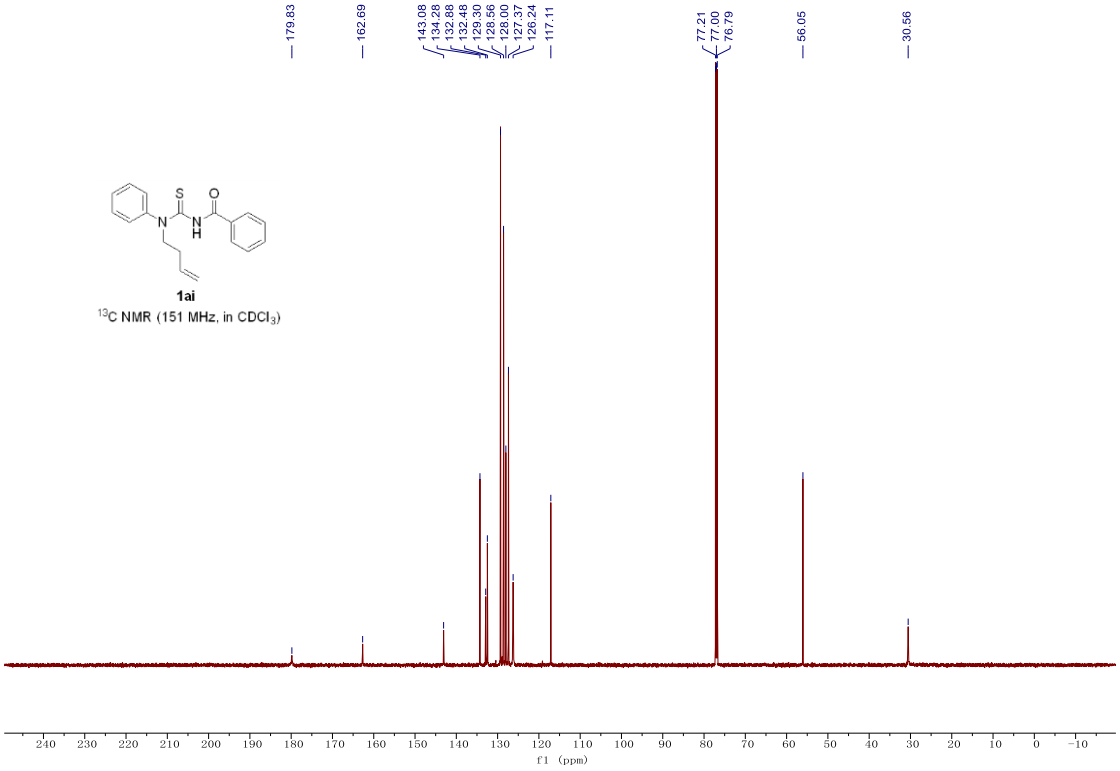


1ah

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

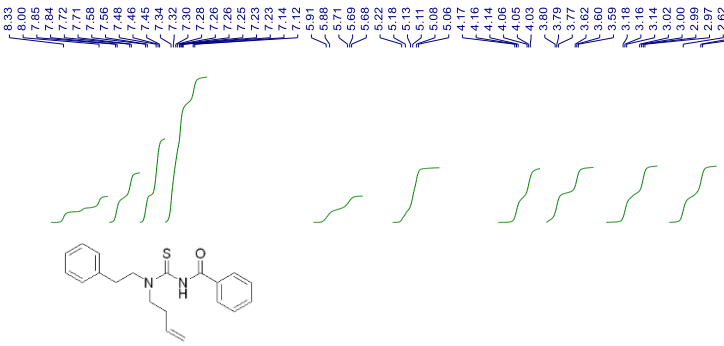

179.12
163.31
139.17
135.86
133.39
132.23
128.85
128.62
128.48
127.42
127.10
77.26
77.00
76.75
63.62
34.38
31.99
28.24
26.77
22.37
22.02
13.91
13.55
1ah
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.30
7.50
7.49
7.47
7.42
7.41
7.40
7.37
7.36
7.35
7.33
7.30
7.29
7.28
5.86
5.84
5.84
5.83
5.83
5.82
5.81
5.81
5.80
5.79
5.13
5.10
5.09
5.07
4.34
2.58
2.56
2.55
2.54
1ai
1H NMR (600 MHz, in CDCl3)
0.95
9.53
1.00
1.97
1.96
1.89
f1 (ppm)



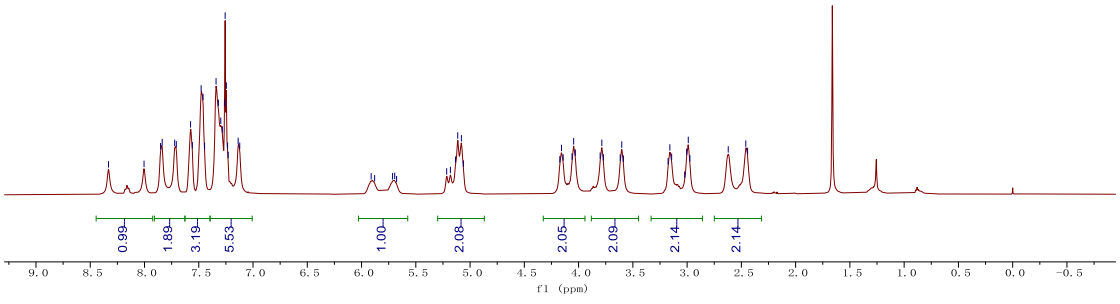
1ai

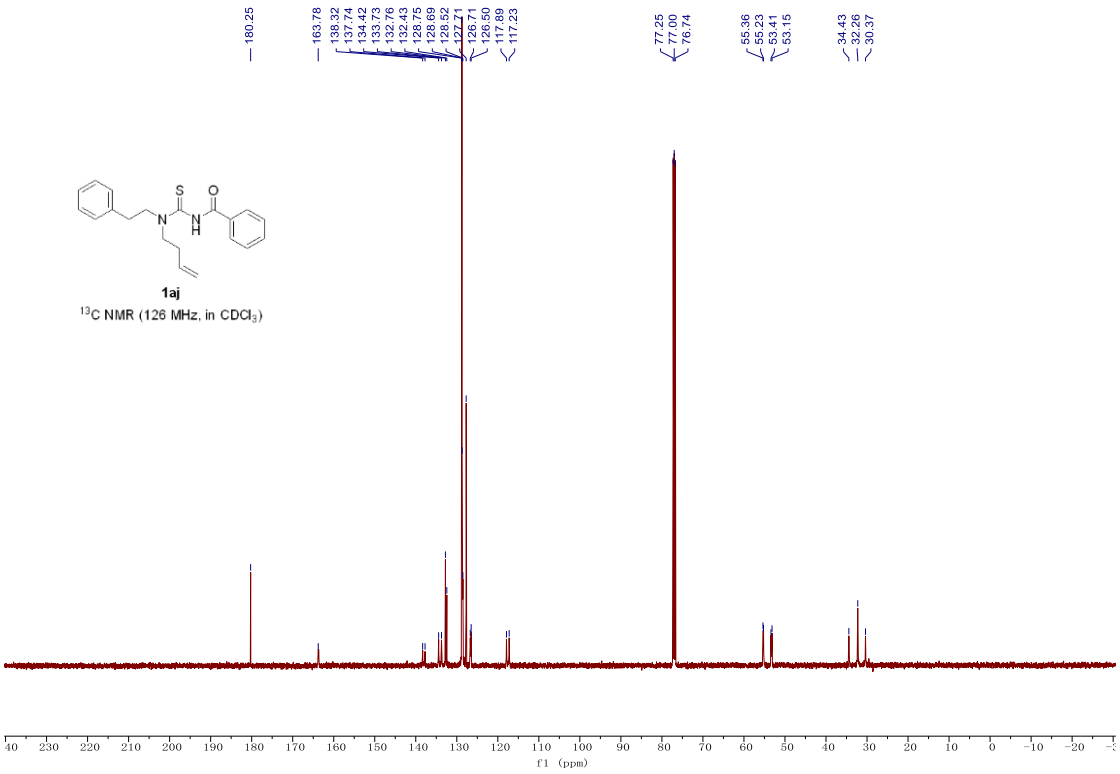
^{13}C NMR (151 MHz, in $CDCl_3$)

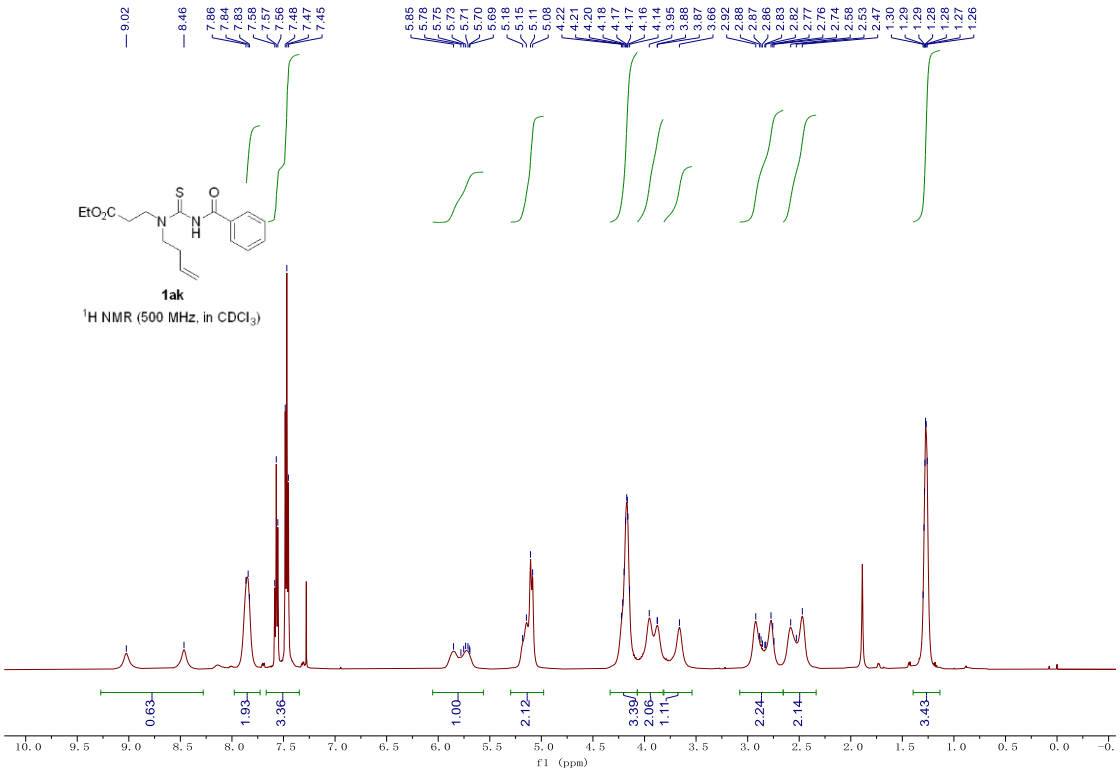


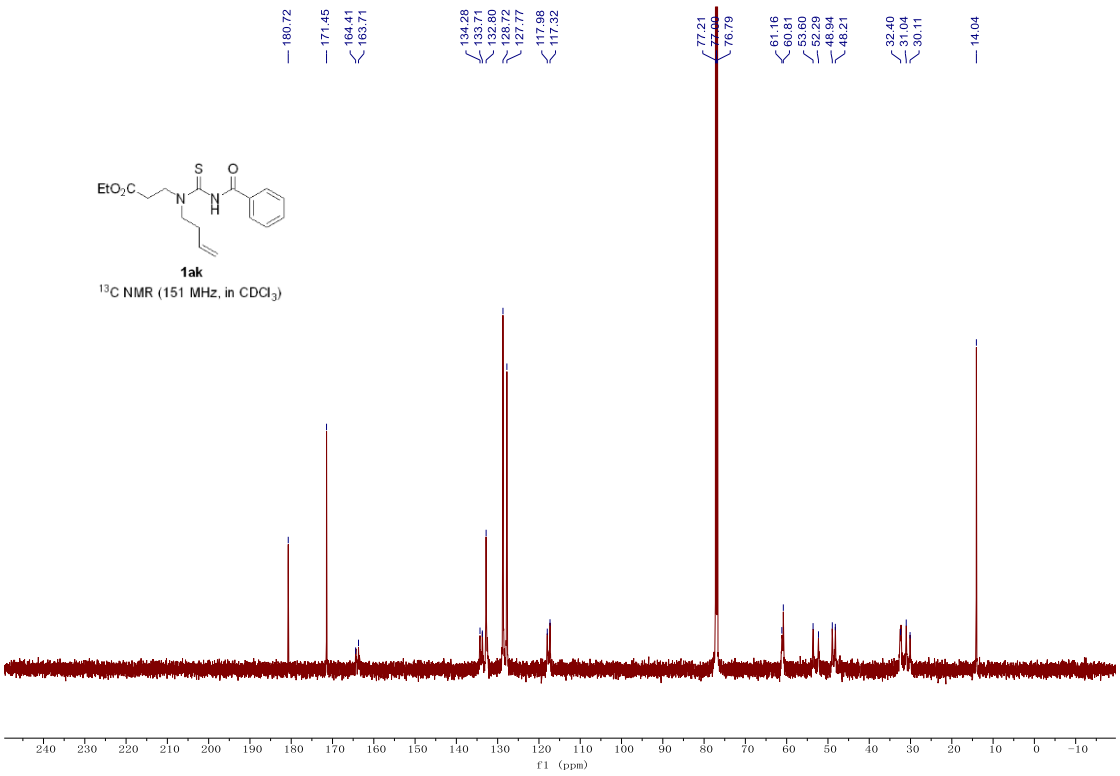
1aj

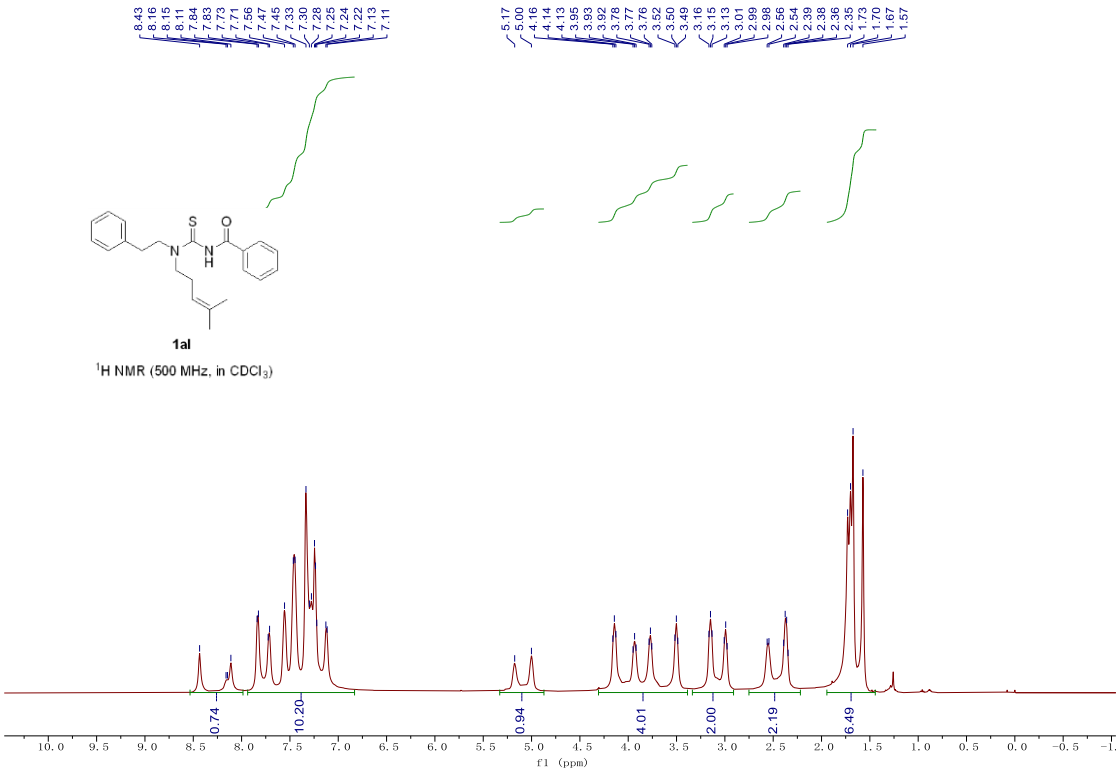
^{1}H NMR (500 MHz, in $CDCl_3$)

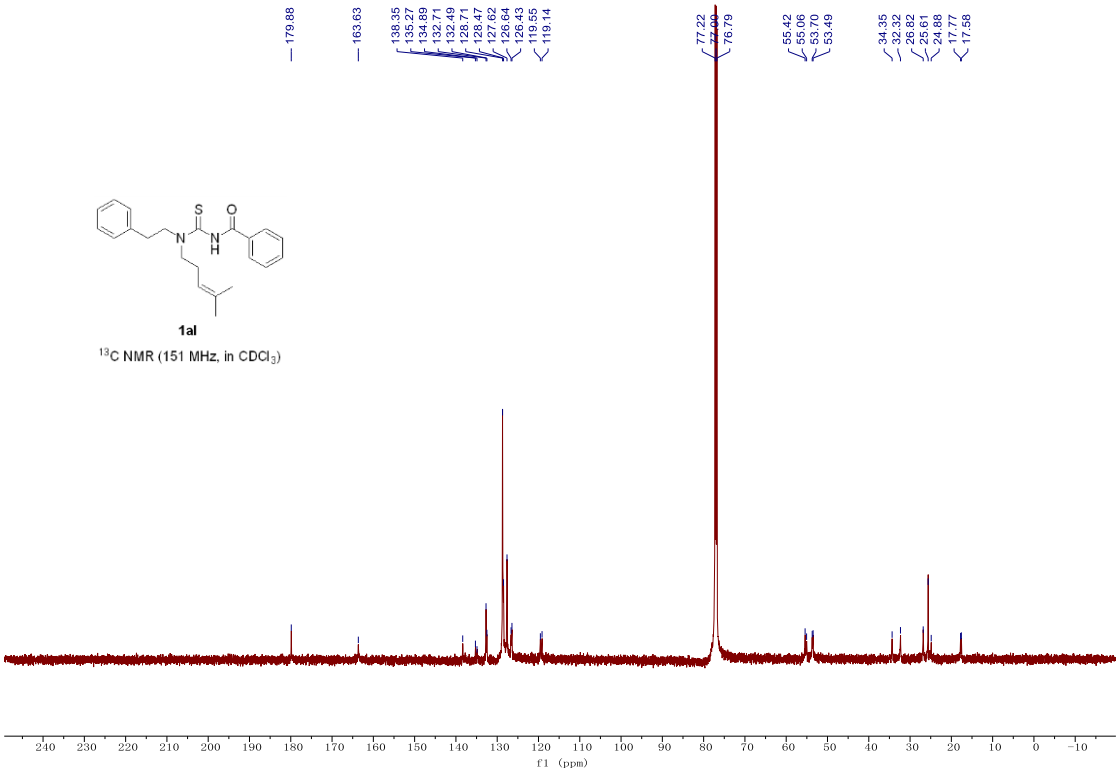



180.25
163.78
138.32
137.74
134.42
133.73
132.76
132.43
128.75
128.69
128.52
127.71
126.71
126.50
117.89
117.23
77.25
77.00
76.74
55.36
55.23
53.41
53.15
34.43
32.26
30.37
1aj
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


9.02
8.46
7.86
7.84
7.83
7.58
7.57
7.56
7.48
7.47
7.45
5.85
5.78
5.75
5.73
5.71
5.70
5.69
5.18
5.15
5.11
5.08
4.22
4.21
4.20
4.18
4.17
4.17
4.16
4.14
3.95
3.88
3.87
3.66
2.92
2.88
2.87
2.86
2.83
2.82
2.77
2.76
2.74
2.58
2.53
2.47
1.30
1.29
1.29
1.28
1.28
1.27
1.26
EtO2C
1ak
1H NMR (500 MHz, in CDCl3)
0.63
1.93
3.36
1.00
2.12
3.39
2.06
1.11
2.24
2.14
3.43
f1 (ppm)

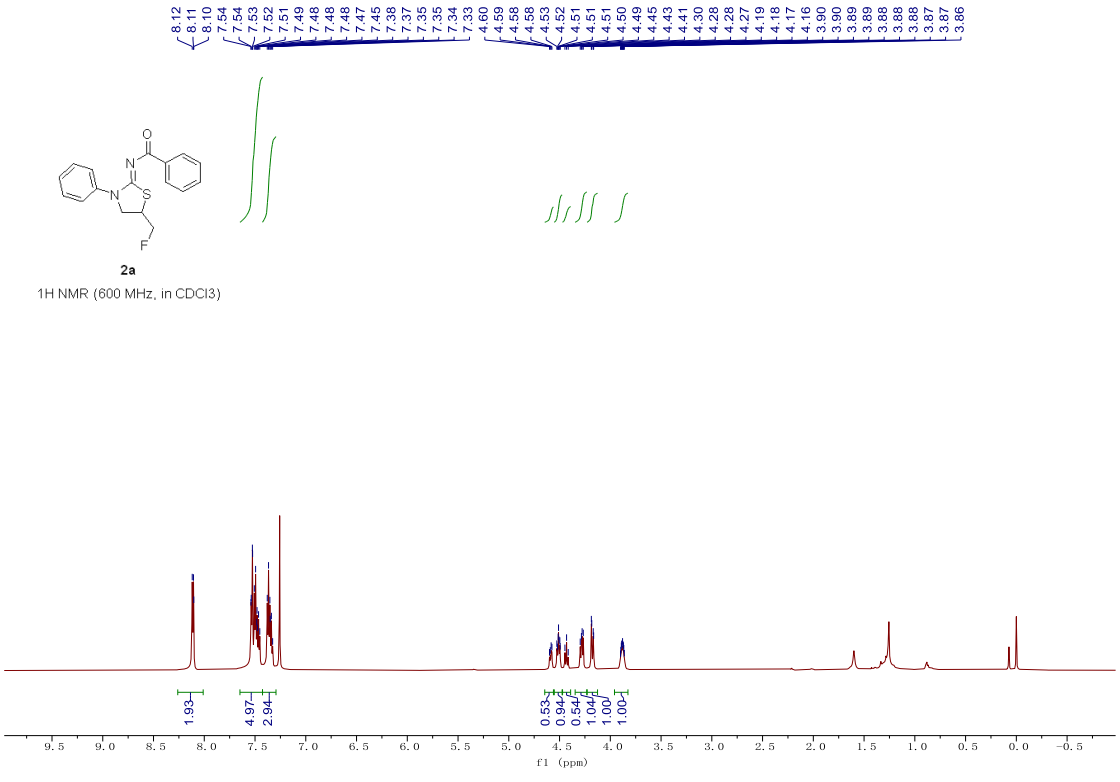

180.72
171.45
164.41
163.71
134.28
133.71
132.80
128.72
127.77
117.98
117.32
77.21
77.00
76.79
61.16
60.81
53.60
52.29
48.94
48.21
32.40
31.04
30.11
14.04
EtO2C
S
O
N
N
H
1ak
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


8.43
8.16
8.15
8.11
7.84
7.83
7.73
7.71
7.56
7.47
7.45
7.33
7.30
7.28
7.25
7.24
7.22
7.13
7.11
5.17
5.00
4.16
4.14
4.13
3.95
3.93
3.92
3.78
3.77
3.76
3.52
3.50
3.49
3.16
3.15
3.13
3.01
2.99
2.98
2.56
2.54
2.39
2.38
2.36
2.35
1.73
1.70
1.67
1.57
S
O
N
N
H
1al
1H NMR (500 MHz, in CDCl3)
0.74
10.20
0.94
4.01
2.00
2.19
6.49
f1 (ppm)



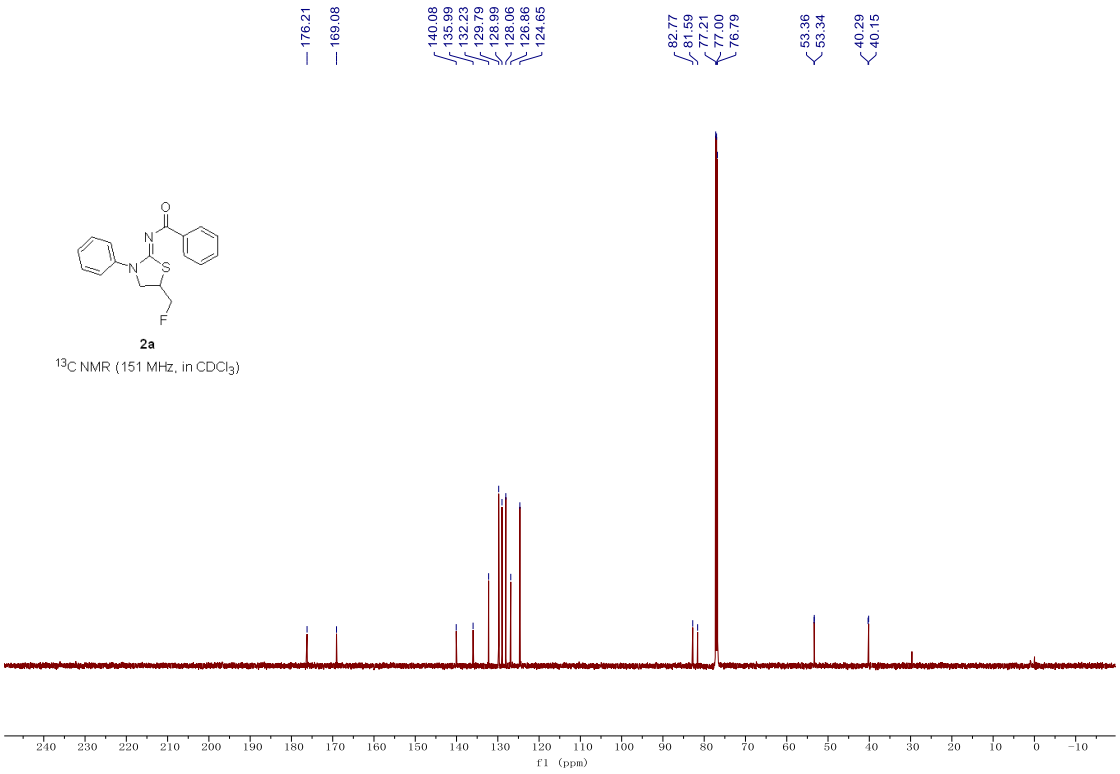
1al

^{13}C NMR (151 MHz, in $CDCl_3$)



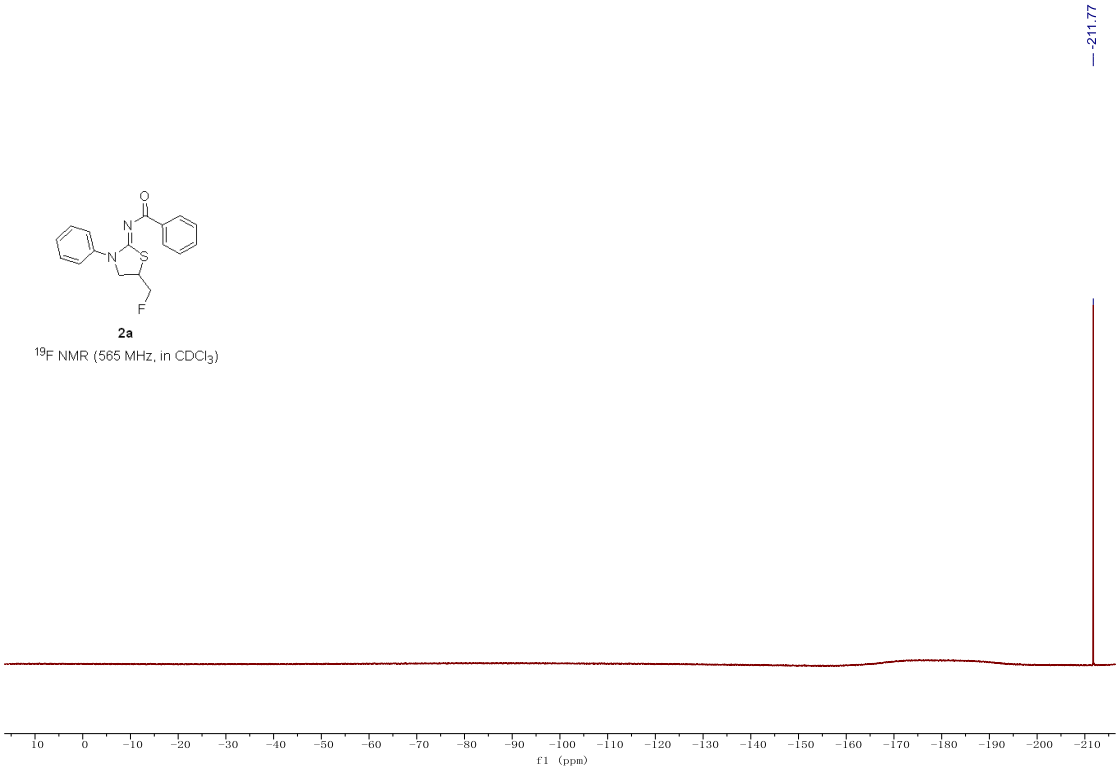
2a

1H NMR (600 MHz, in CDCl3)



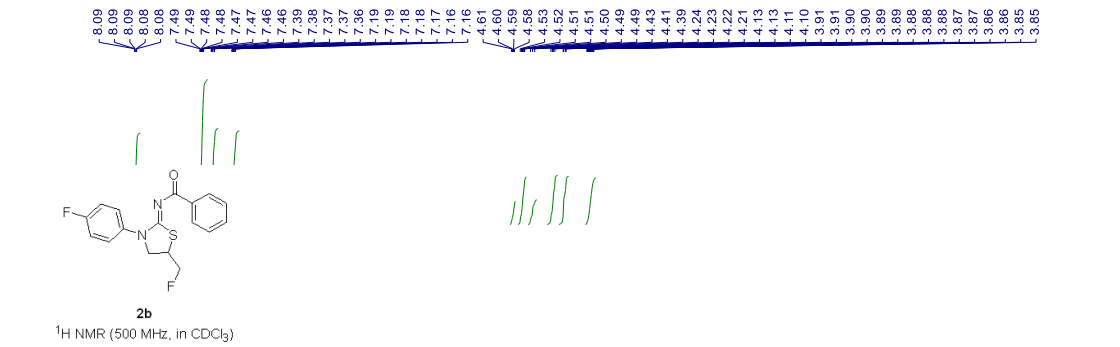
2a

^{13}C NMR (151 MHz, in $CDCl_3$)



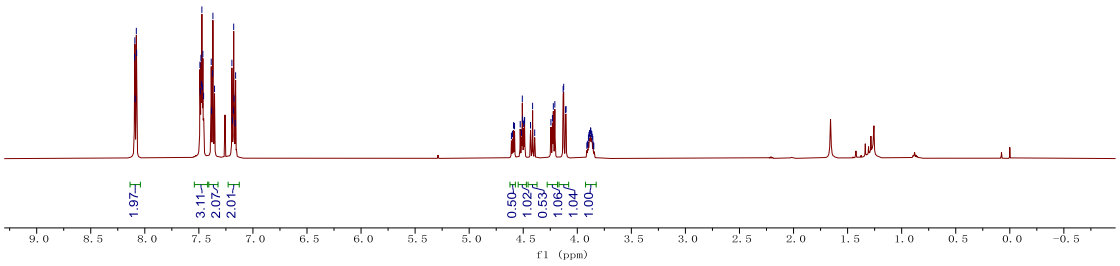
2a

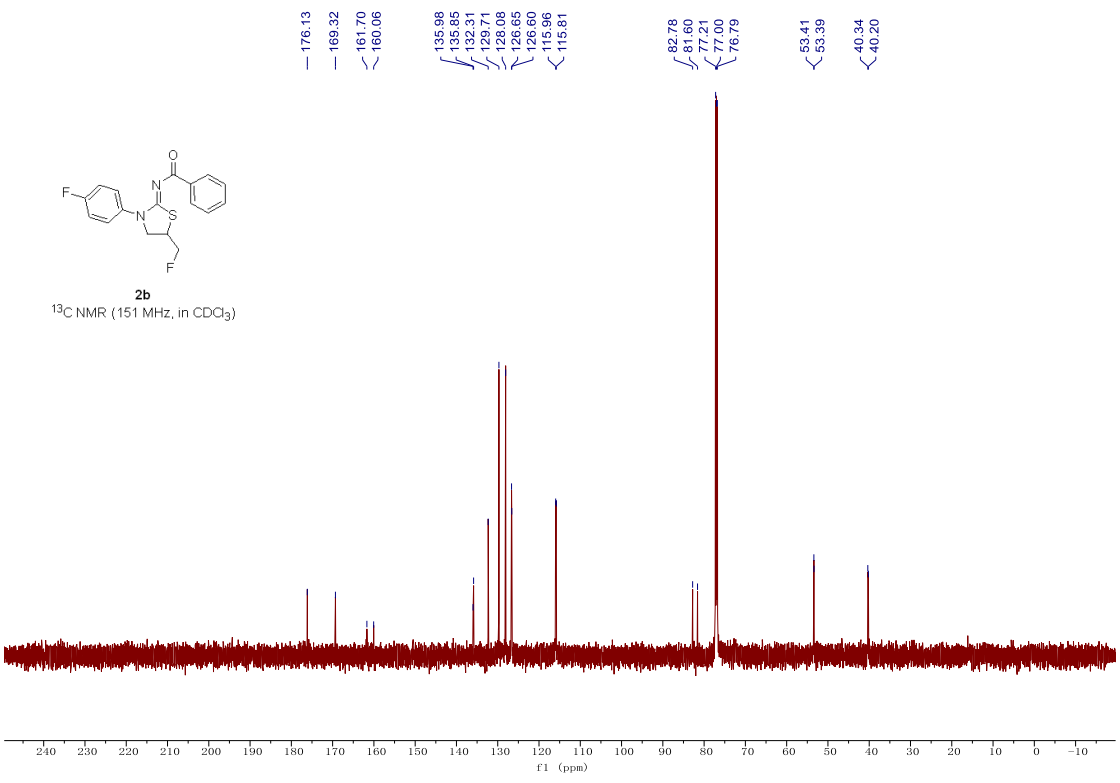
^{19}F NMR (565 MHz, in $CDCl_3$)



2b

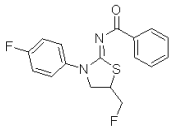
^{1}H NMR (500 MHz, in $CDCl_3$)





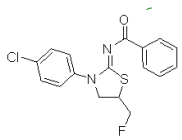
2b

^{13}C NMR (151 MHz, in $CDCl_3$)



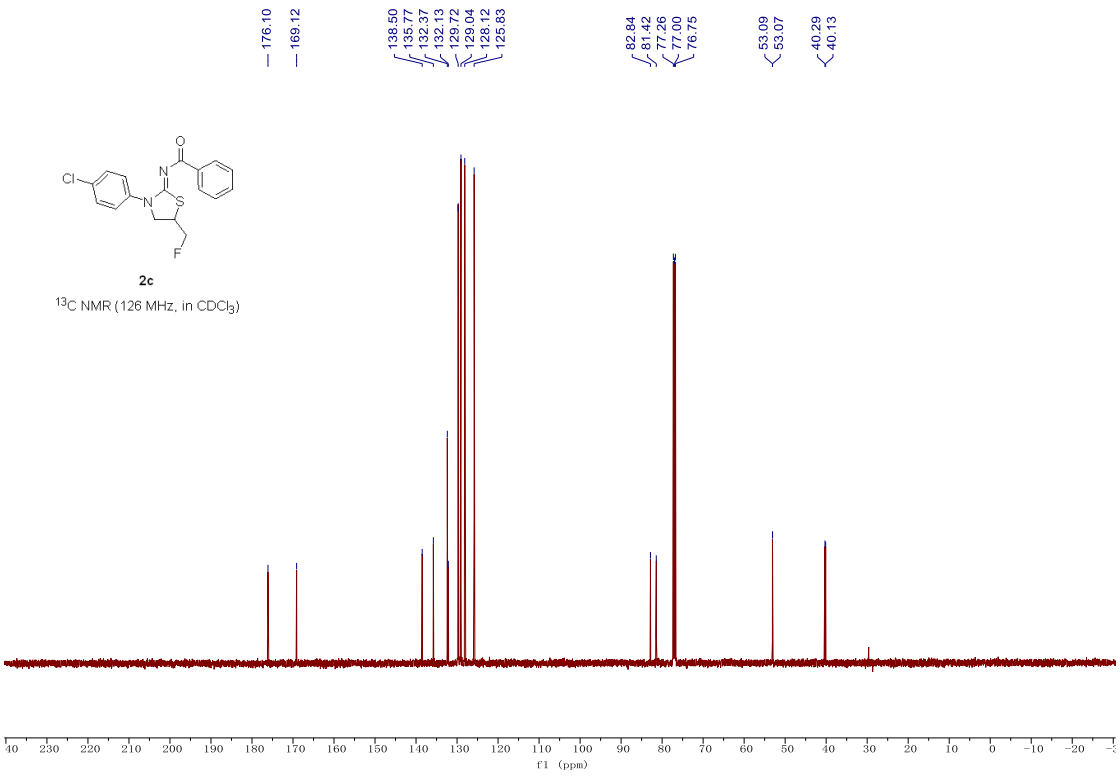
2b

^{19}F NMR (565 MHz, in $CDCl_3$)



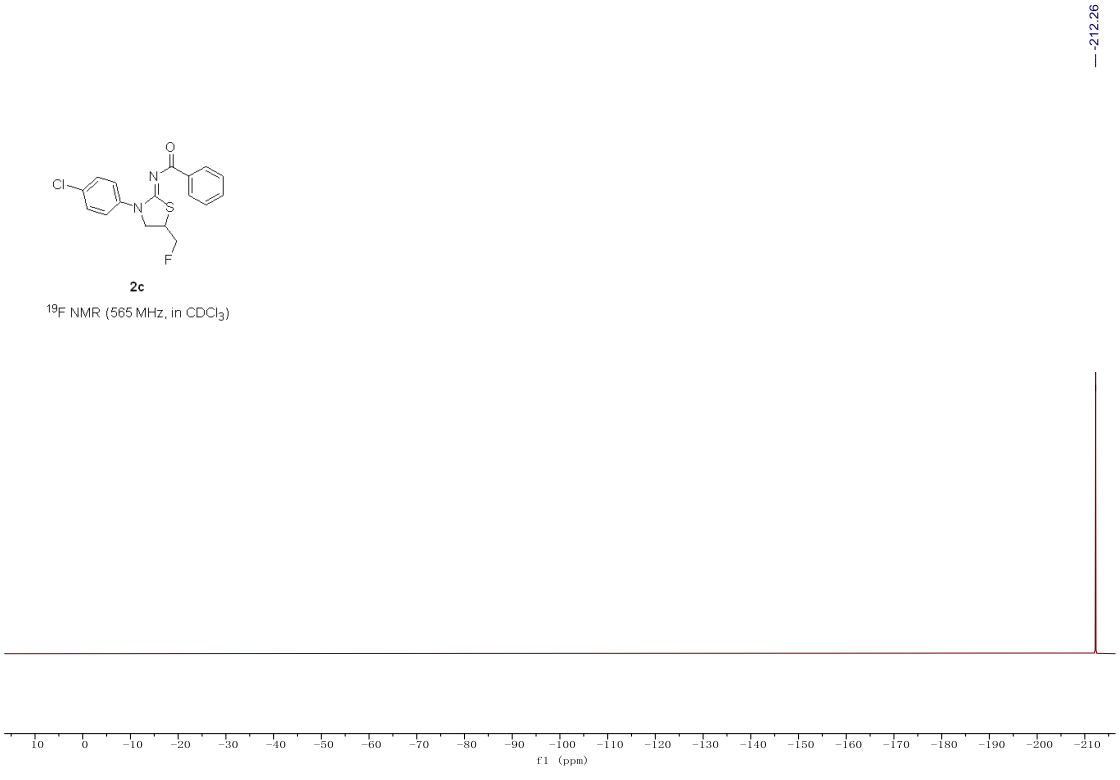
2c

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



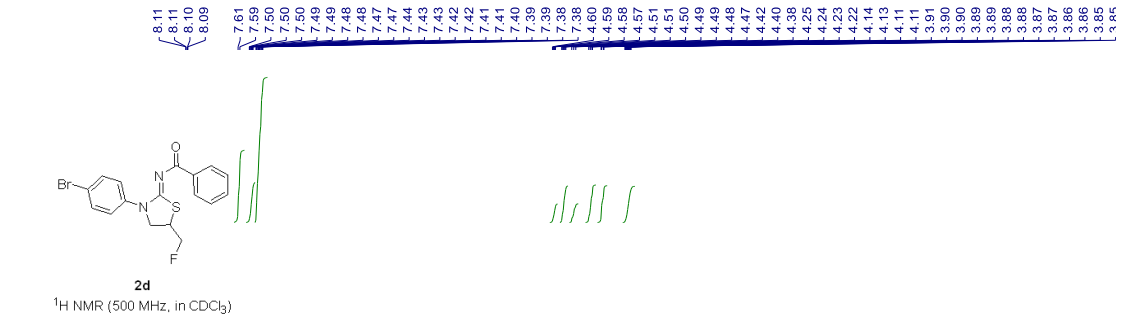
2c

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



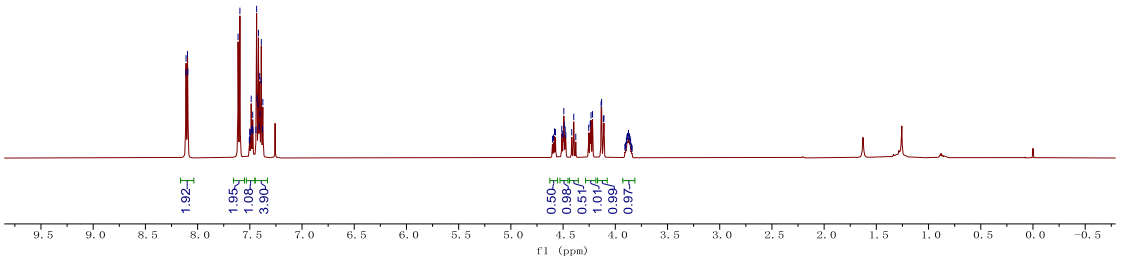
2c

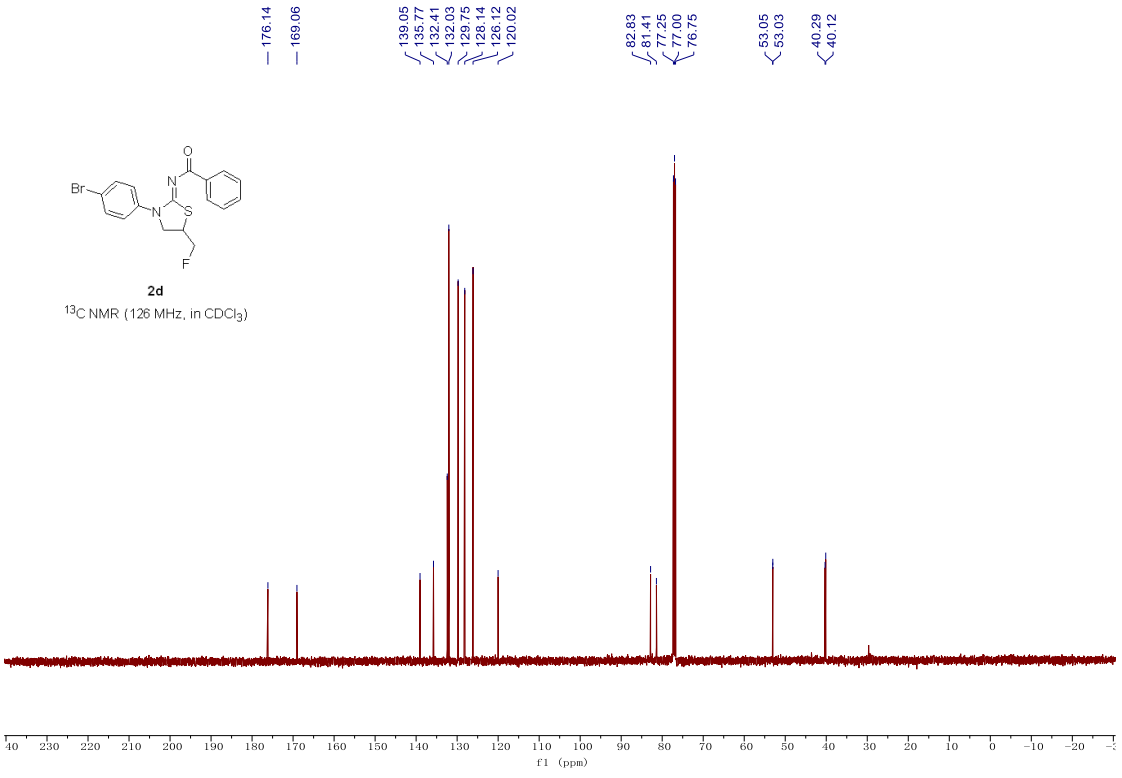
^{19}F NMR (565 MHz, in $CDCl_3$)



2d

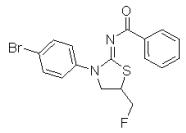
^{1}H NMR (500 MHz, in $CDCl_3$)





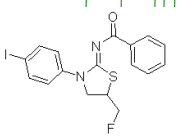
2d

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



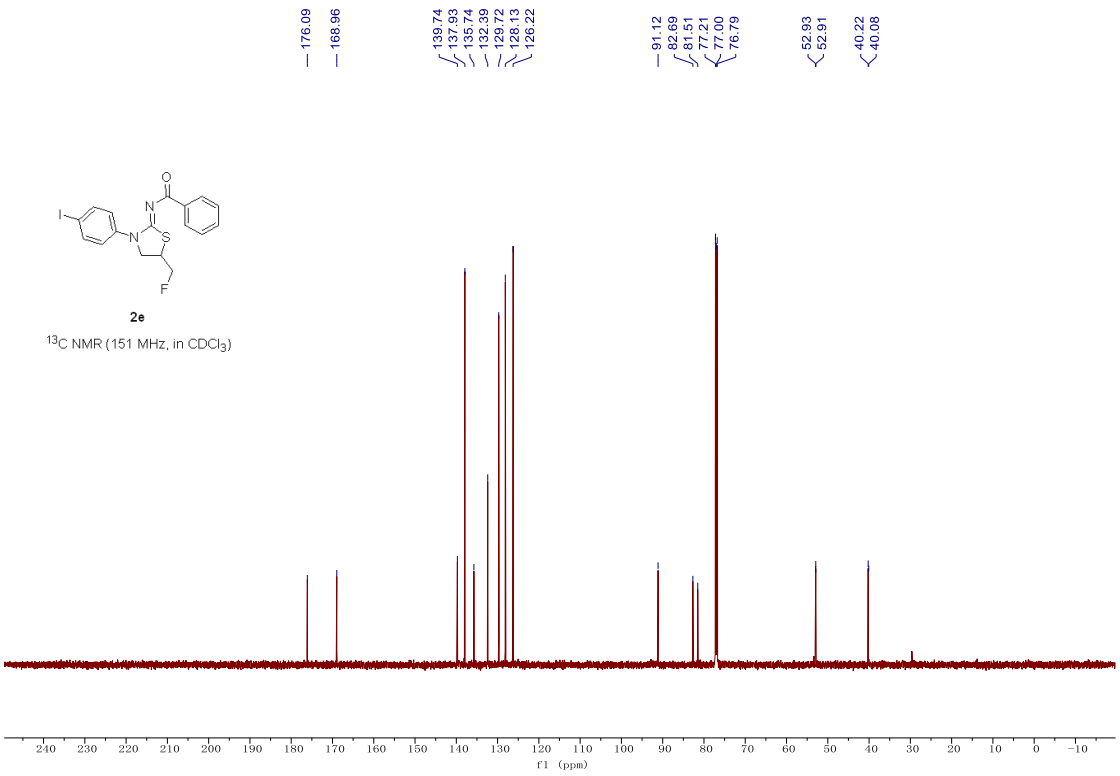
2d

^{19}F NMR (565 MHz, in $CDCl_3$)



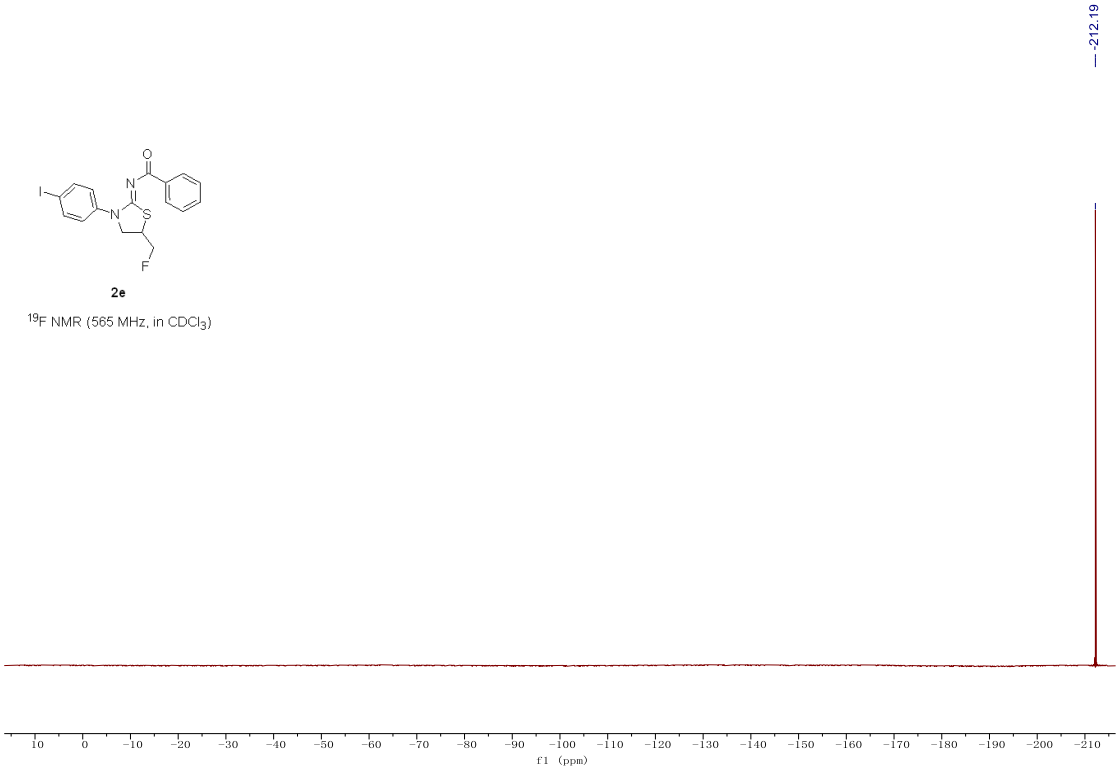
2e

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



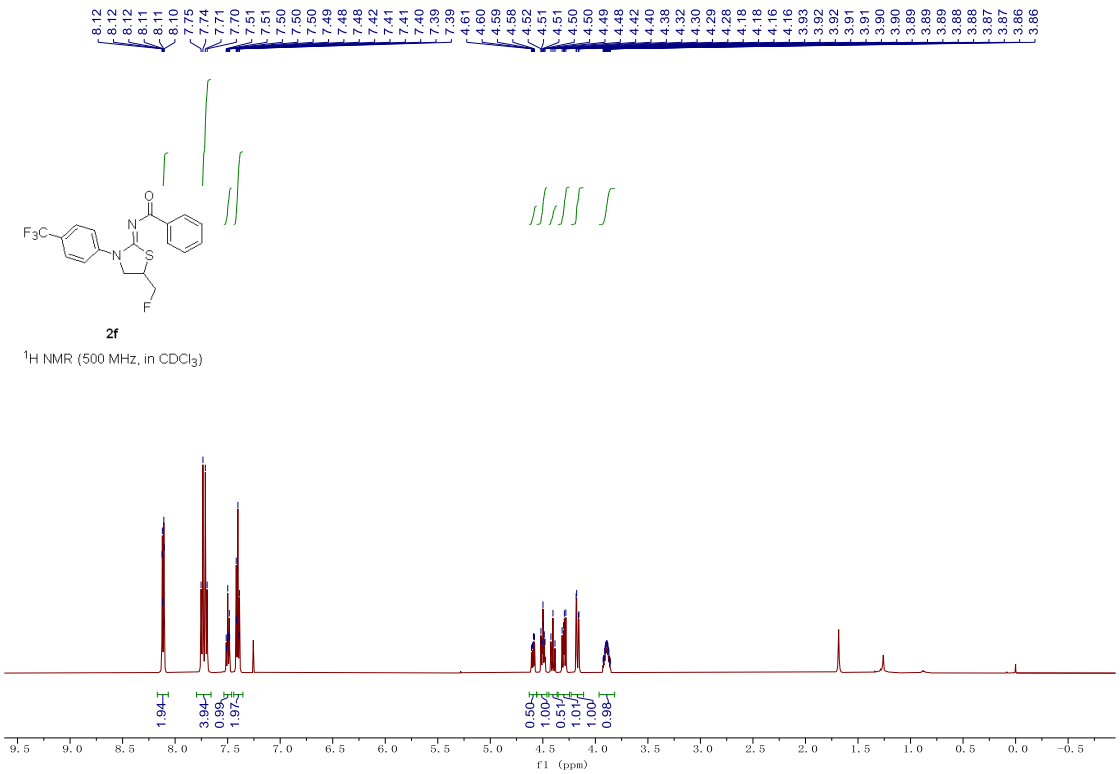
2e

^{13}C NMR (151 MHz, in $CDCl_3$)



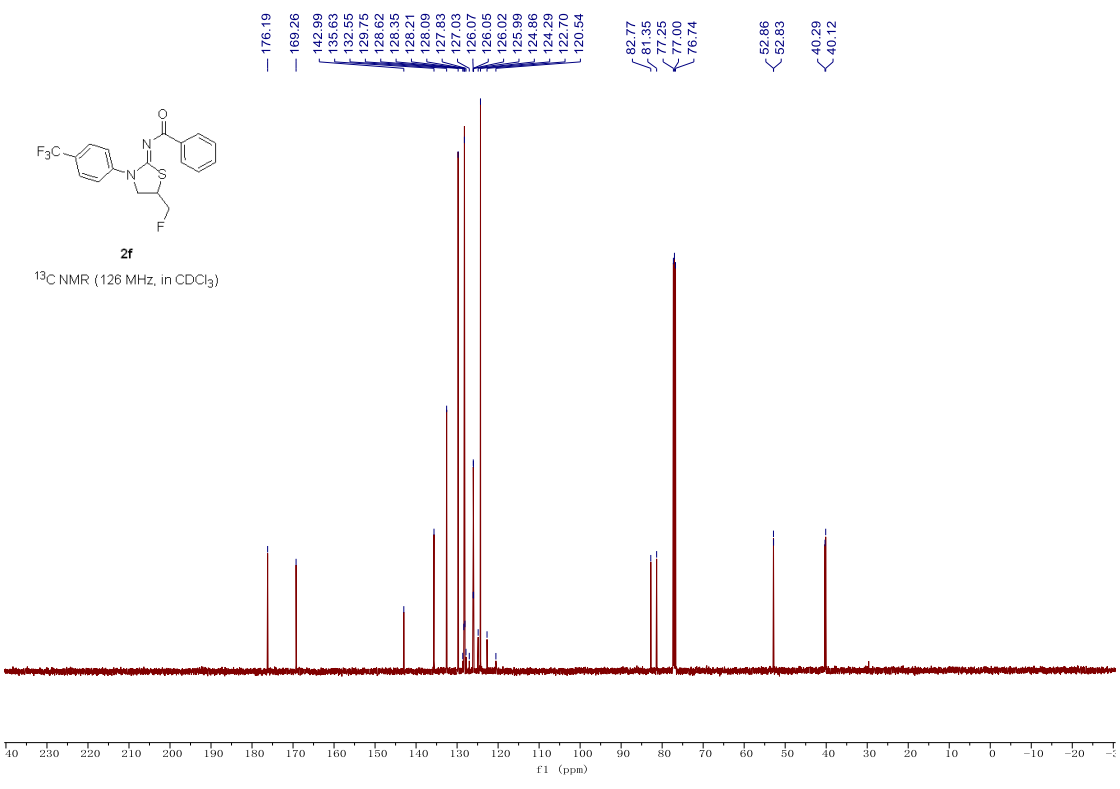
2e

^{19}F NMR (565 MHz, in $CDCl_3$)



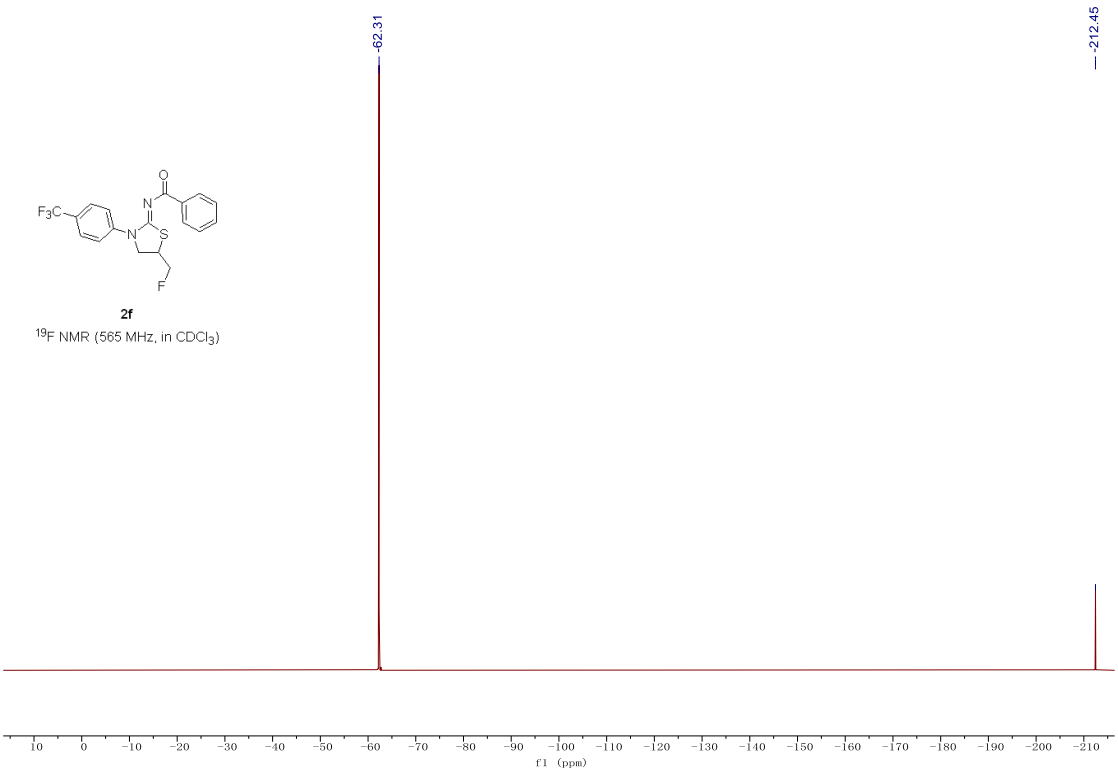
2f

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



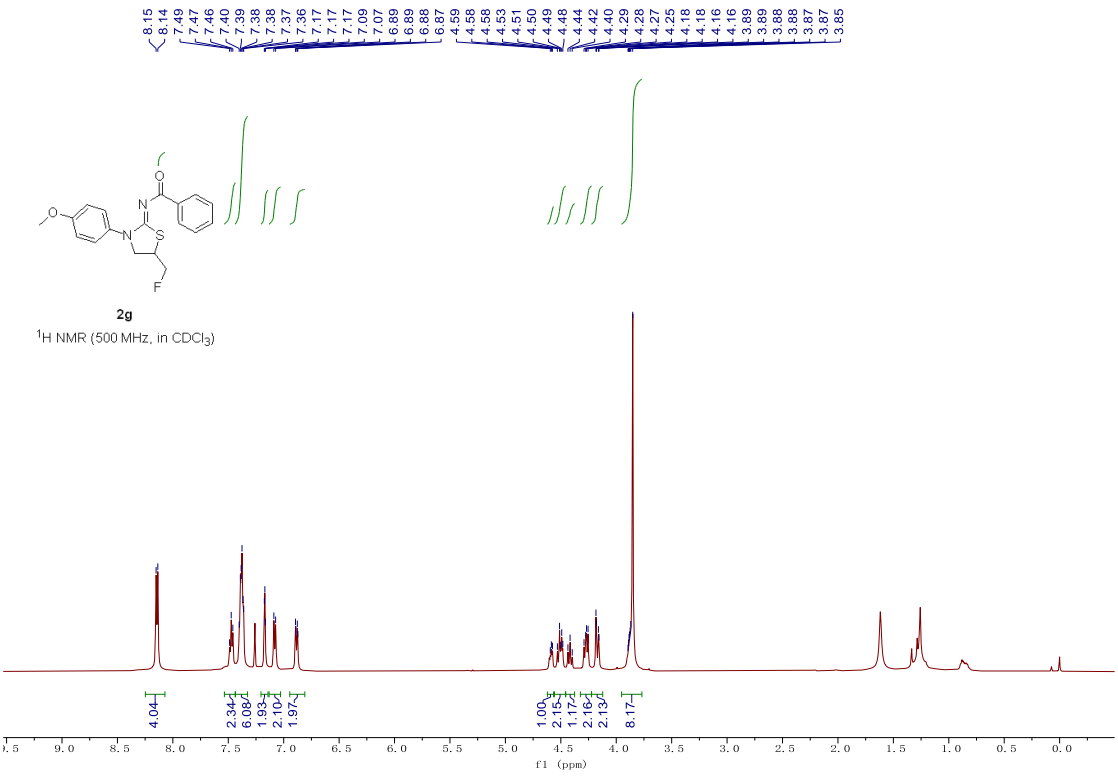
2f

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



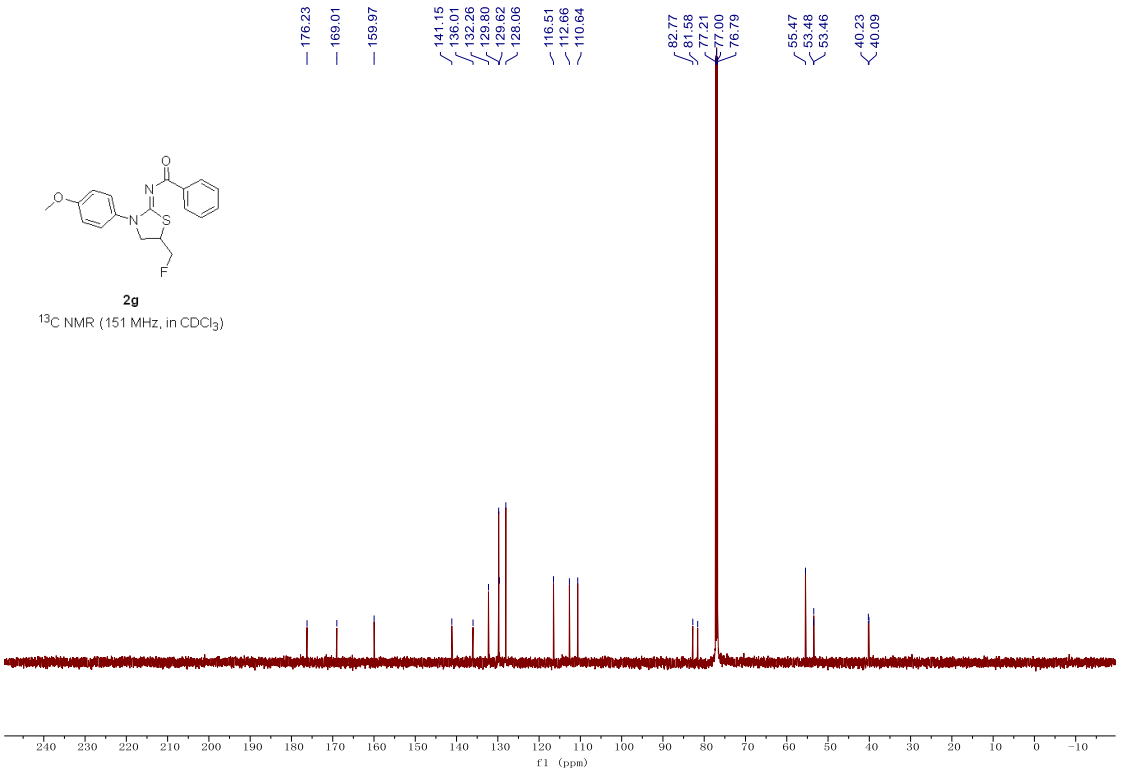
2f

^{19}F NMR (565 MHz, in $CDCl_3$)



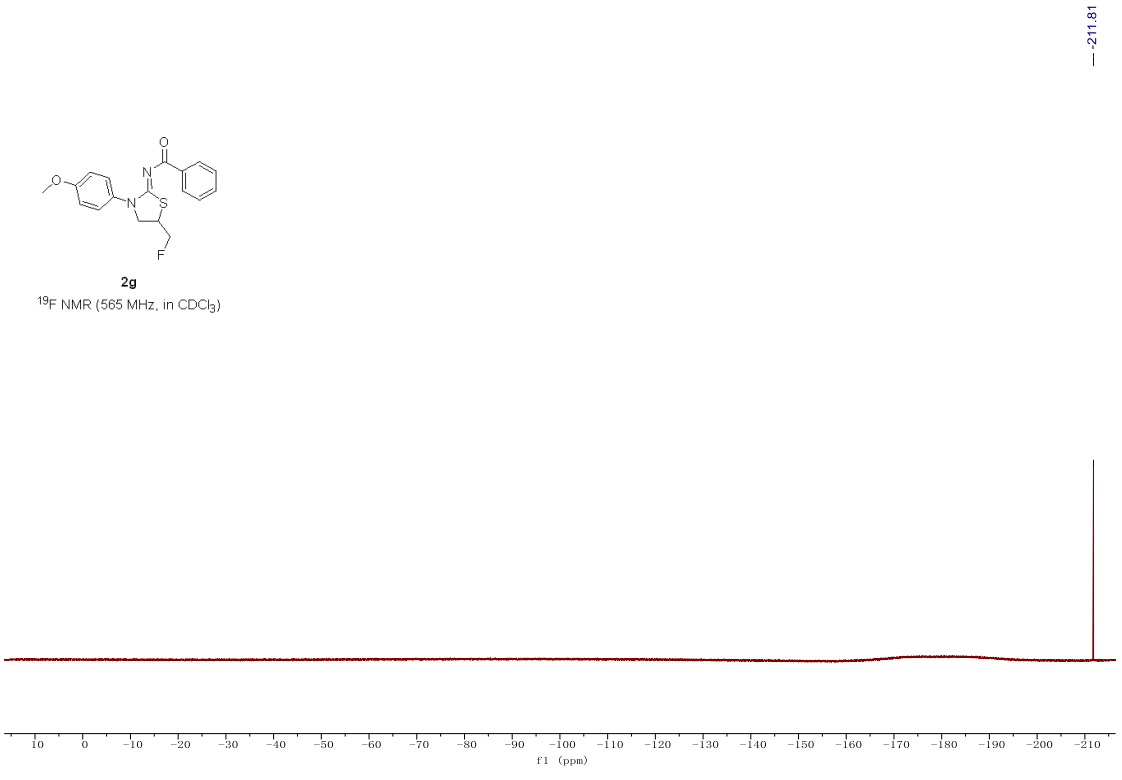
2g

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



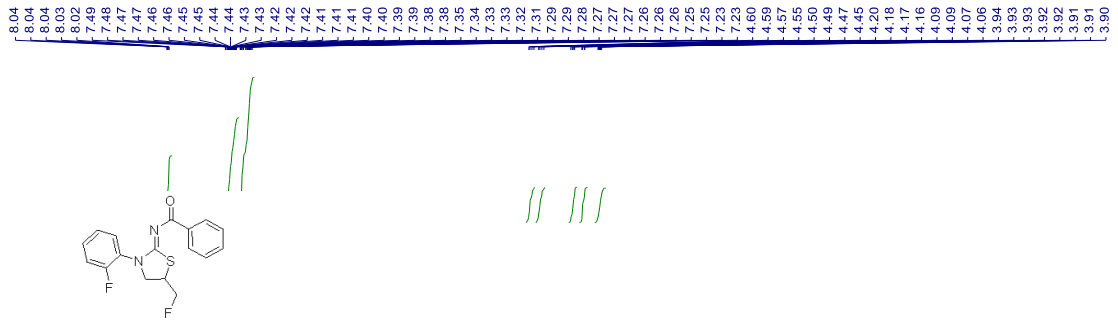
2g

^{13}C NMR (151 MHz, in $CDCl_3$)



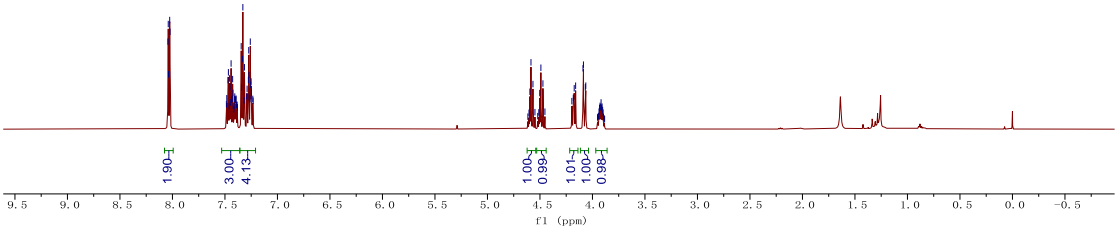
2g

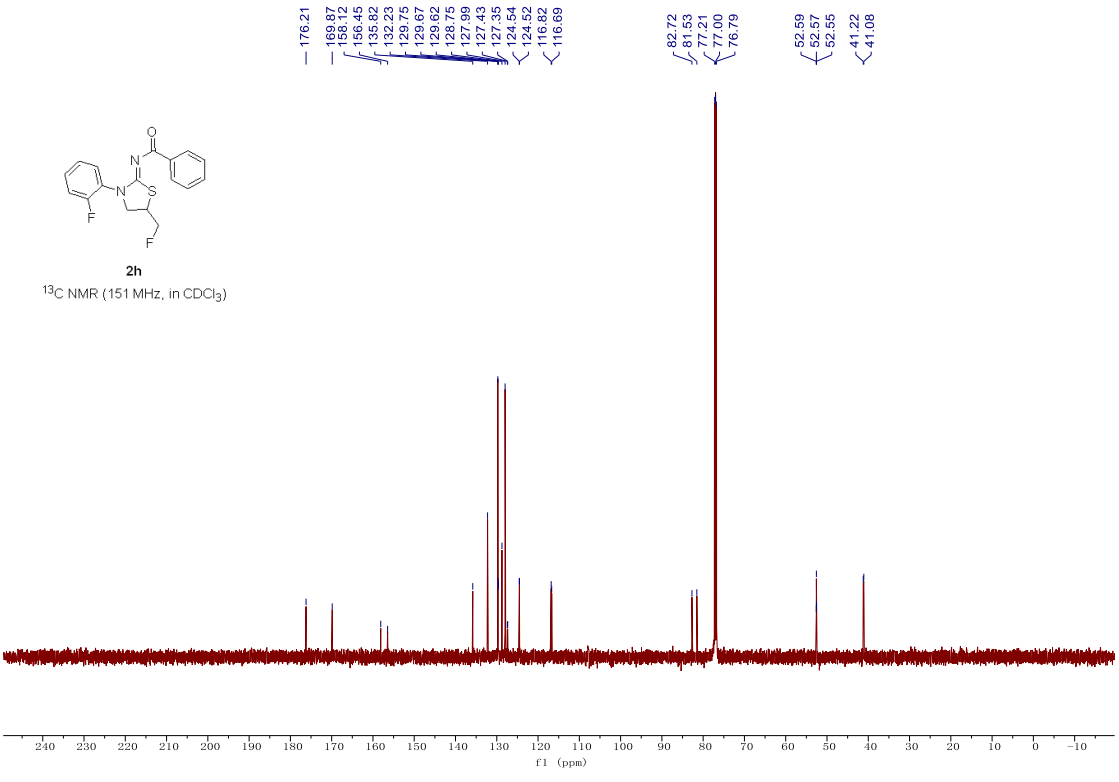
^{19}F NMR (565 MHz, in $CDCl_3$)



2h

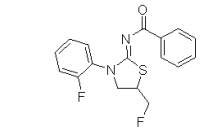
^{1}H NMR (500 MHz, in $CDCl_3$)





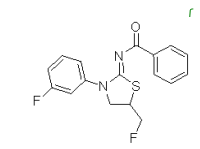
2h

^{13}C NMR (151 MHz, in $CDCl_3$)



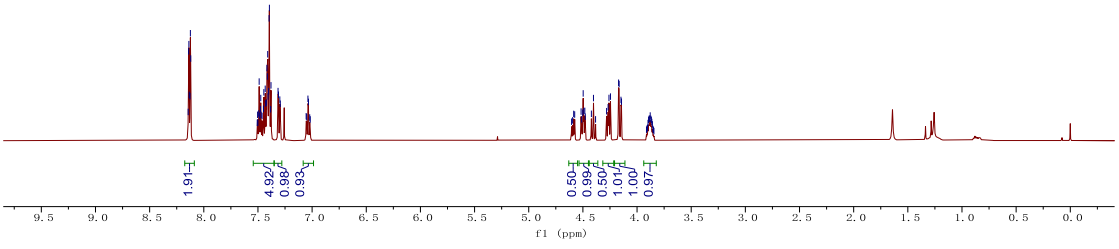
2h

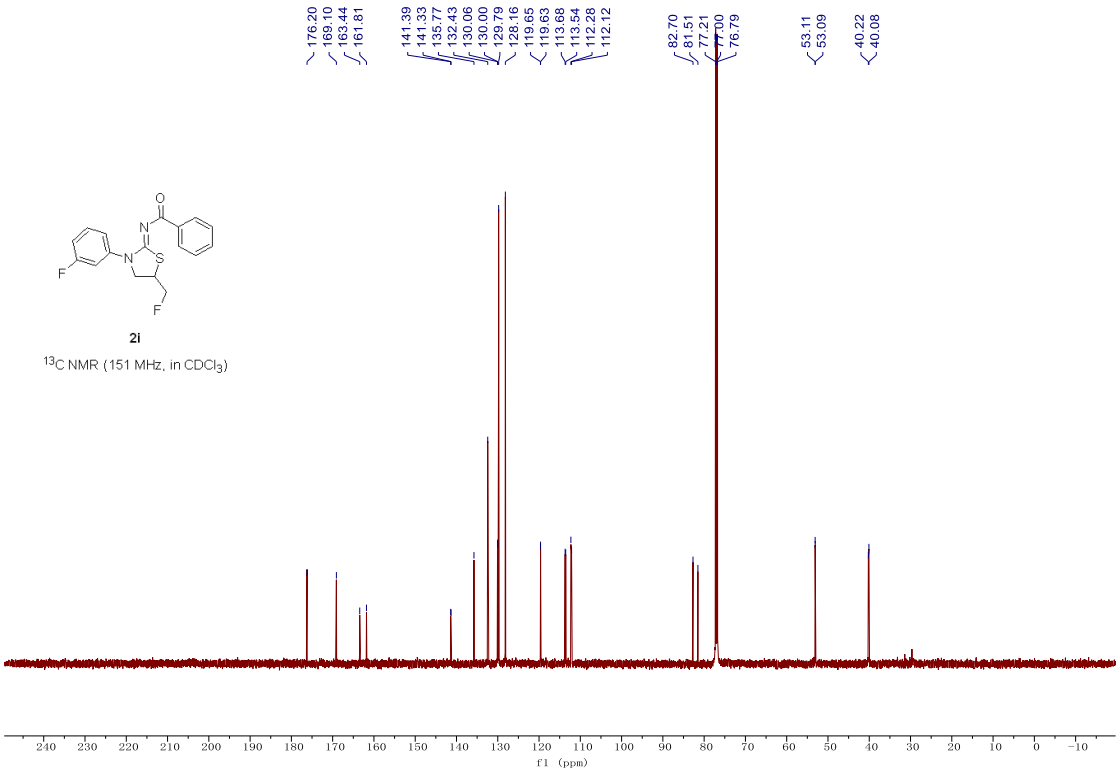
^{19}F NMR (565 MHz, in $CDCl_3$)



2i

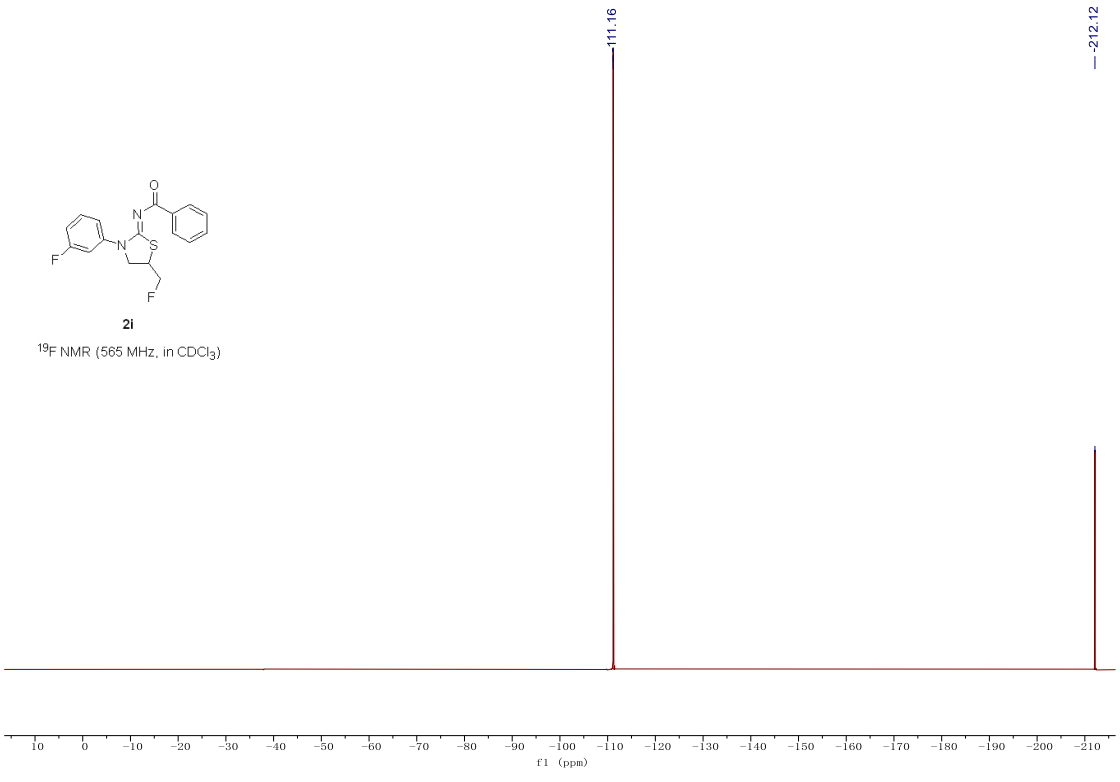
^{1}H NMR (500 MHz, in $CDCl_3$)





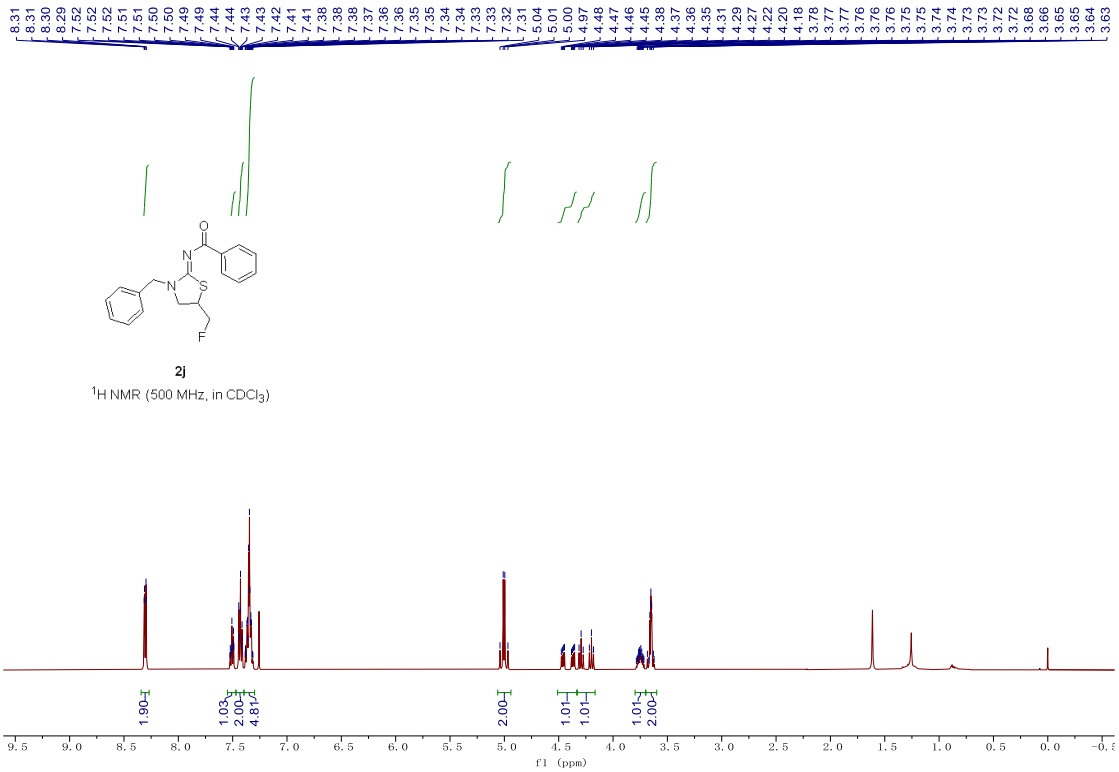
2i

^{13}C NMR (151 MHz, in $CDCl_3$)



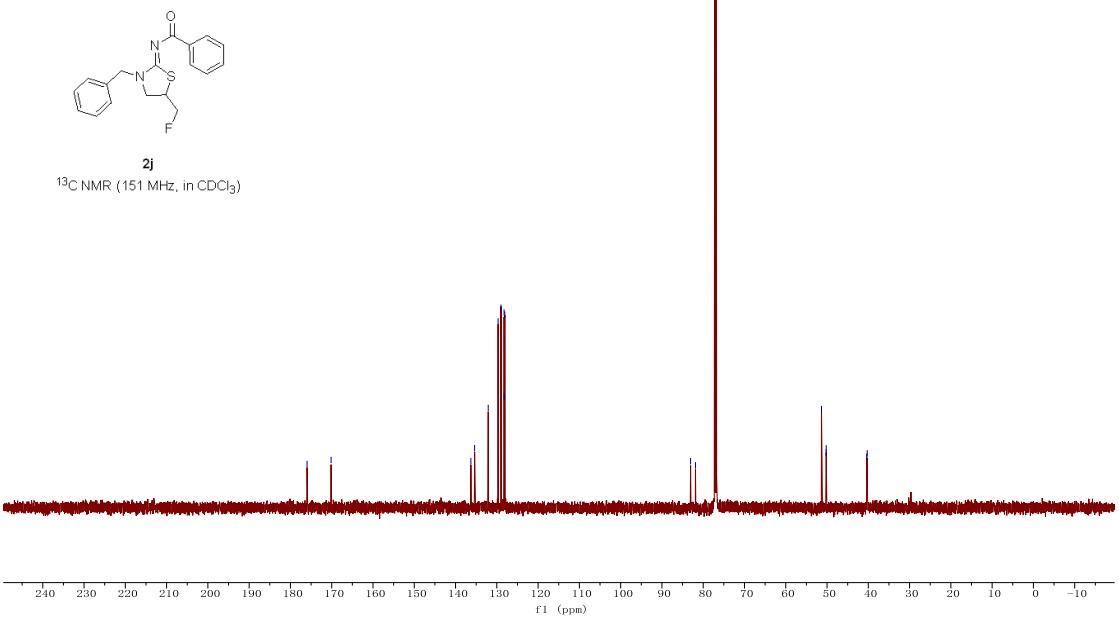
2i

^{19}F NMR (565 MHz, in $CDCl_3$)



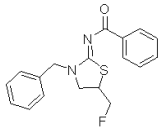
2j

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



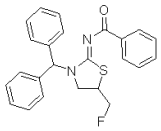
2j

^{13}C NMR (151 MHz, in $CDCl_3$)



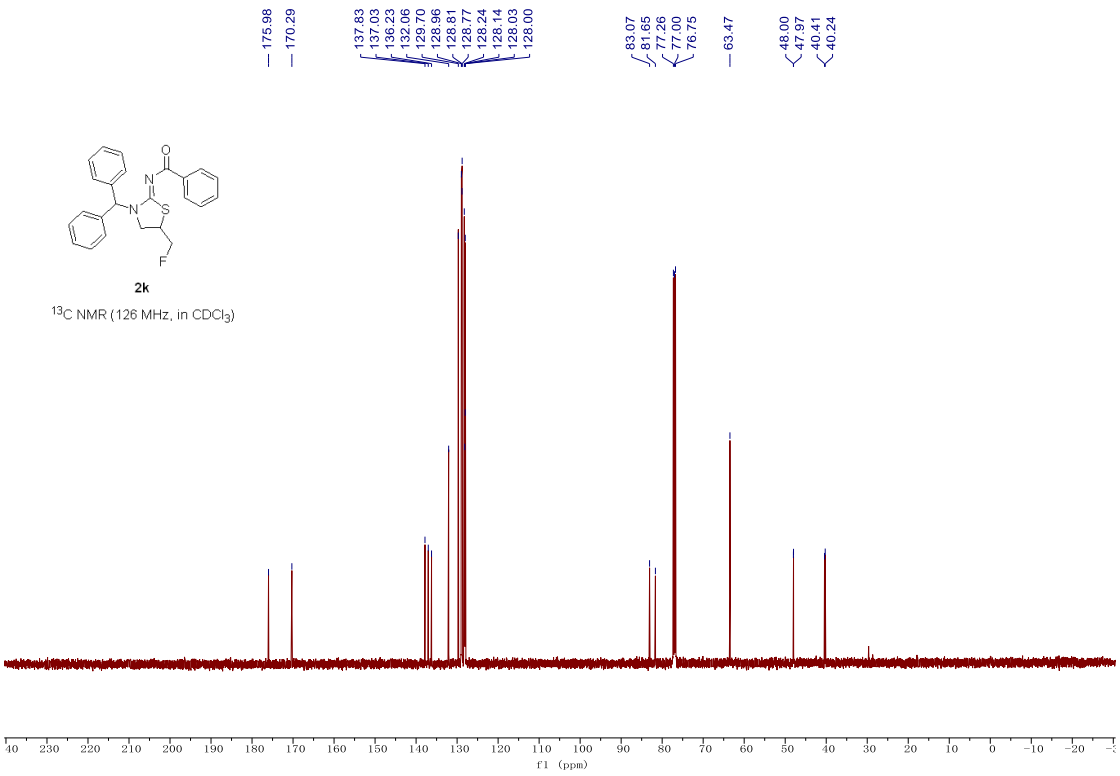
2j

^{19}F NMR (565 MHz, in $CDCl_3$)



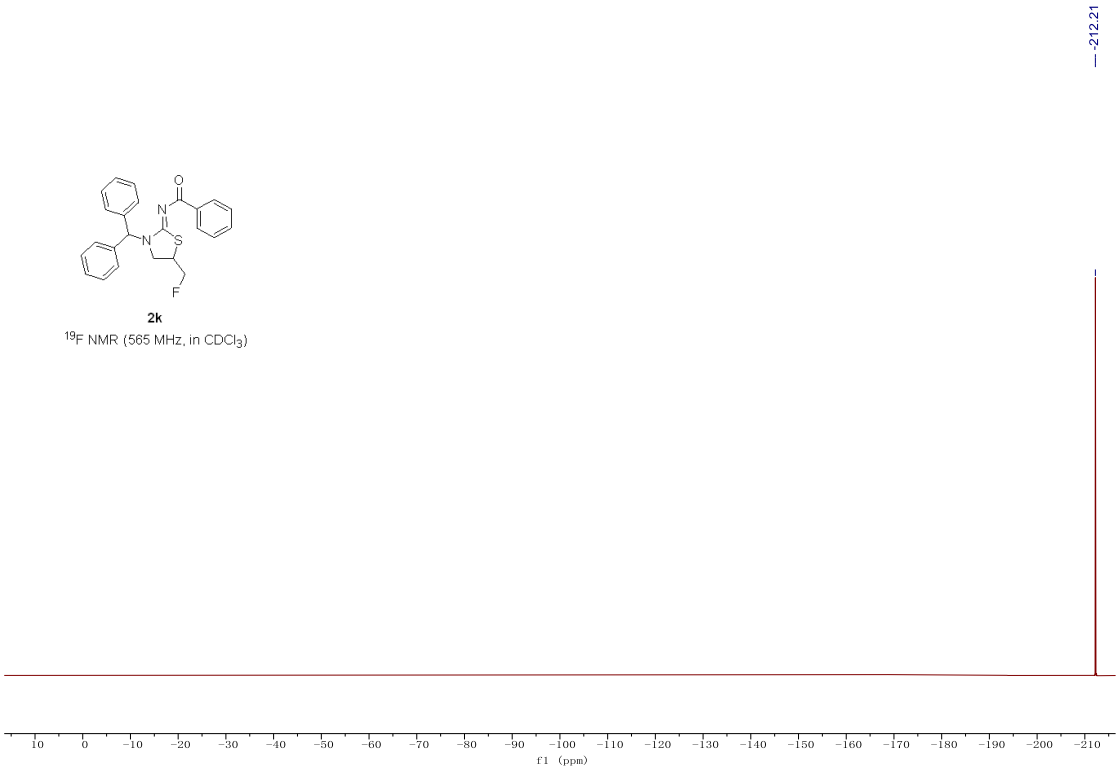
2k

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



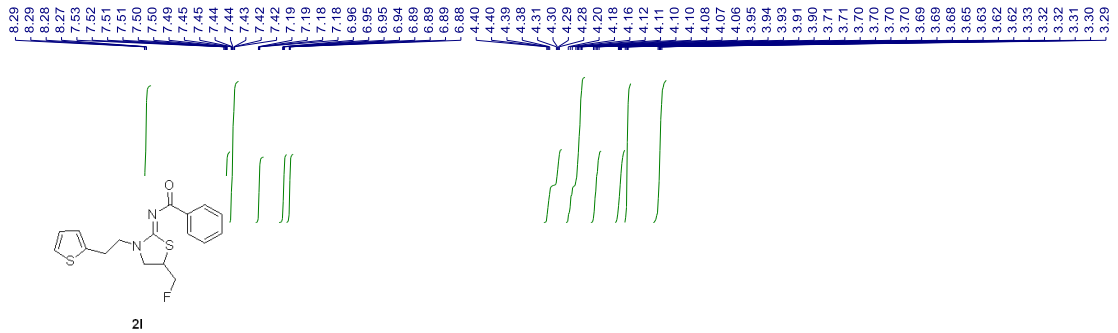
2k

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



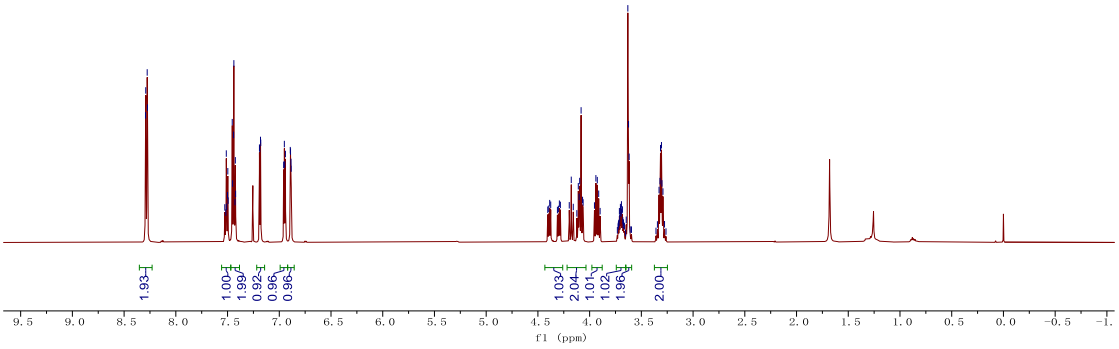
2k

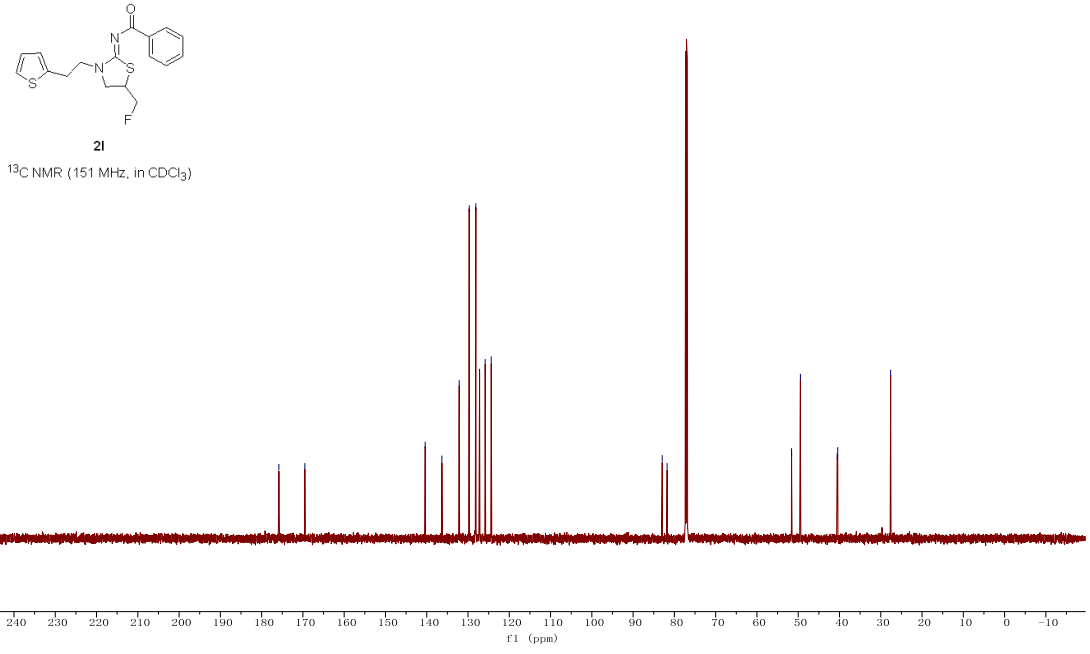
^{19}F NMR (565 MHz, in $CDCl_3$)



2l

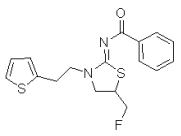
^{1}H NMR (500 MHz, in $CDCl_3$)





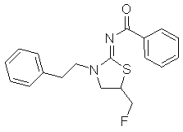
2l

^{13}C NMR (151 MHz, in $CDCl_3$)



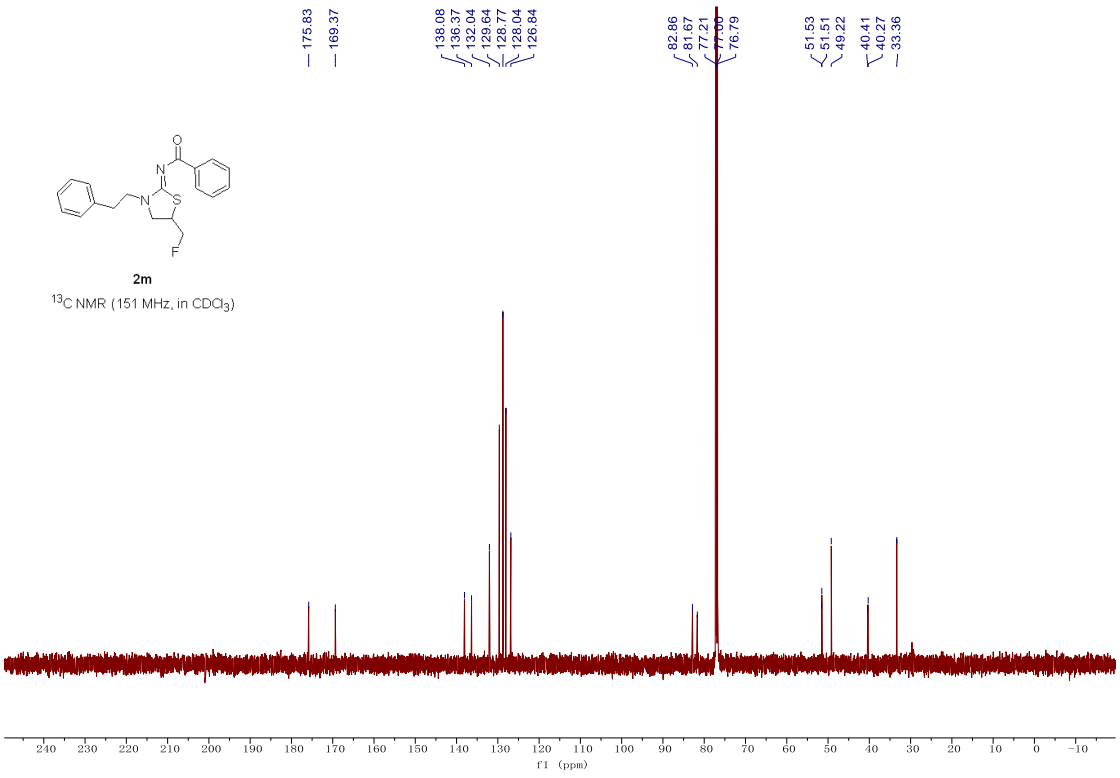
2l

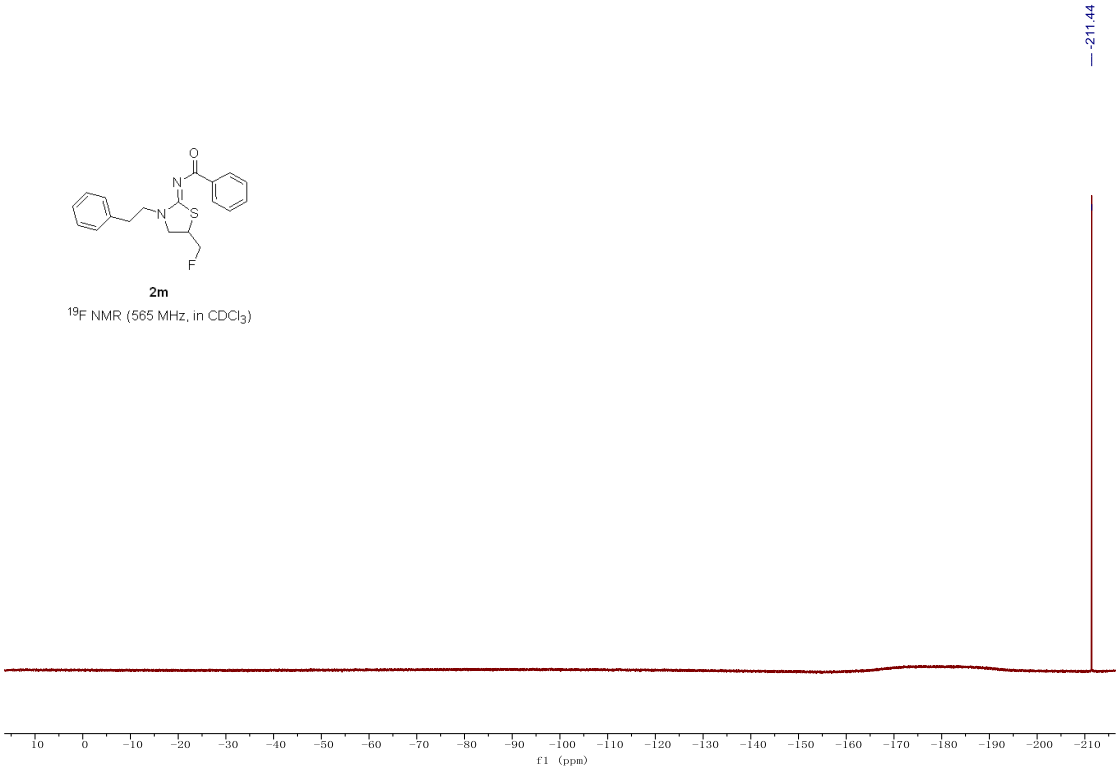
^{19}F NMR (565 MHz, in $CDCl_3$)

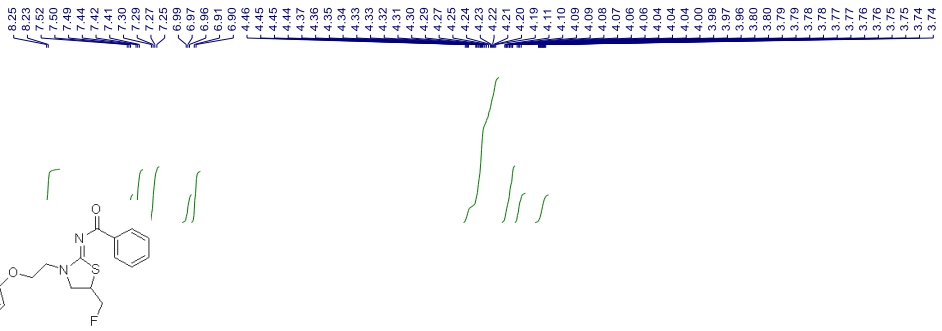


2m

^{1}H NMR (600 MHz, in $CDCl_3$)

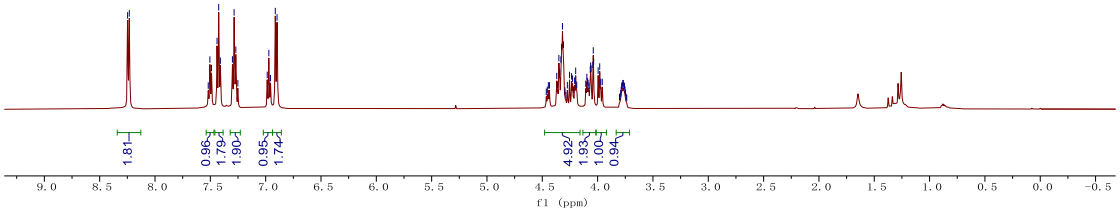

175.83
169.37
138.08
136.37
132.04
129.64
128.77
128.04
126.84
82.86
81.67
77.21
77.00
76.79
51.53
51.51
49.22
40.41
40.27
33.36
O
N
S
N
F
2m
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

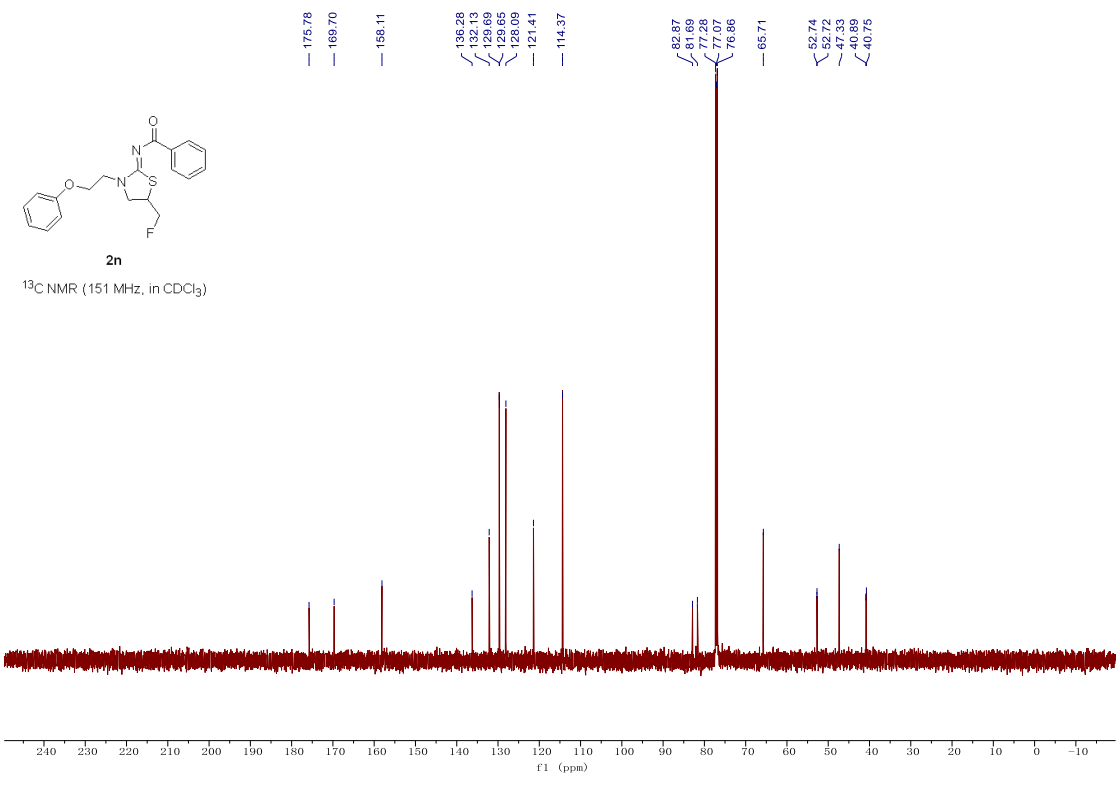

-211.44
O
N
S
N
F
2m
19F NMR (565 MHz, in CDCl3)
f1 (ppm)



2n

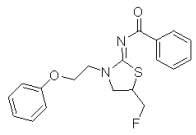
^{1}H NMR (500 MHz, in $CDCl_3$)





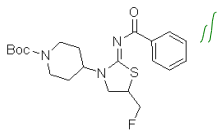
2n

^{13}C NMR (151 MHz, in $CDCl_3$)



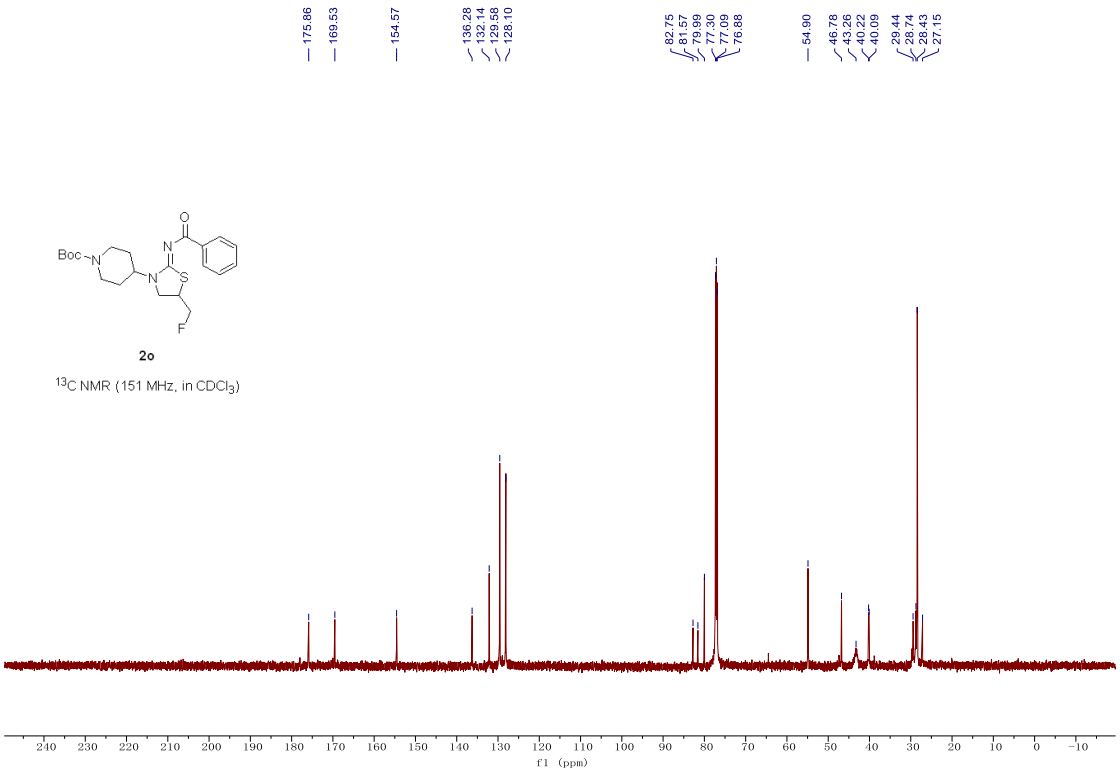
2n

^{19}F NMR (565 MHz, in $CDCl_3$)



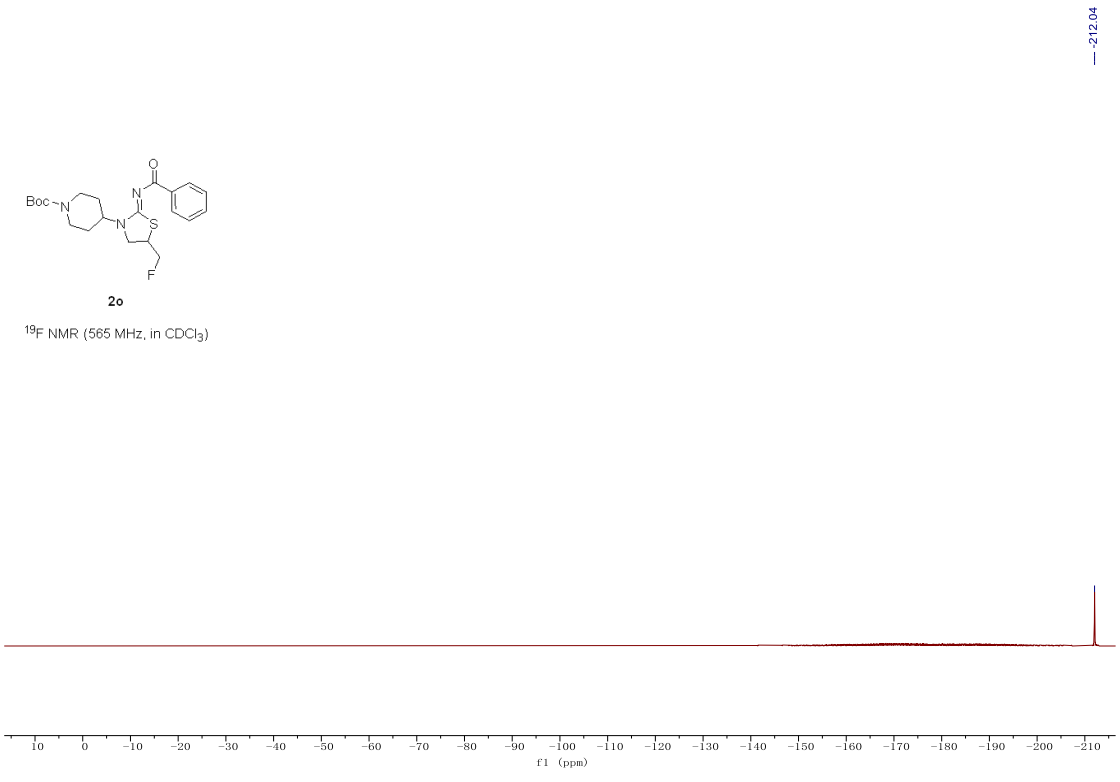
2o

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



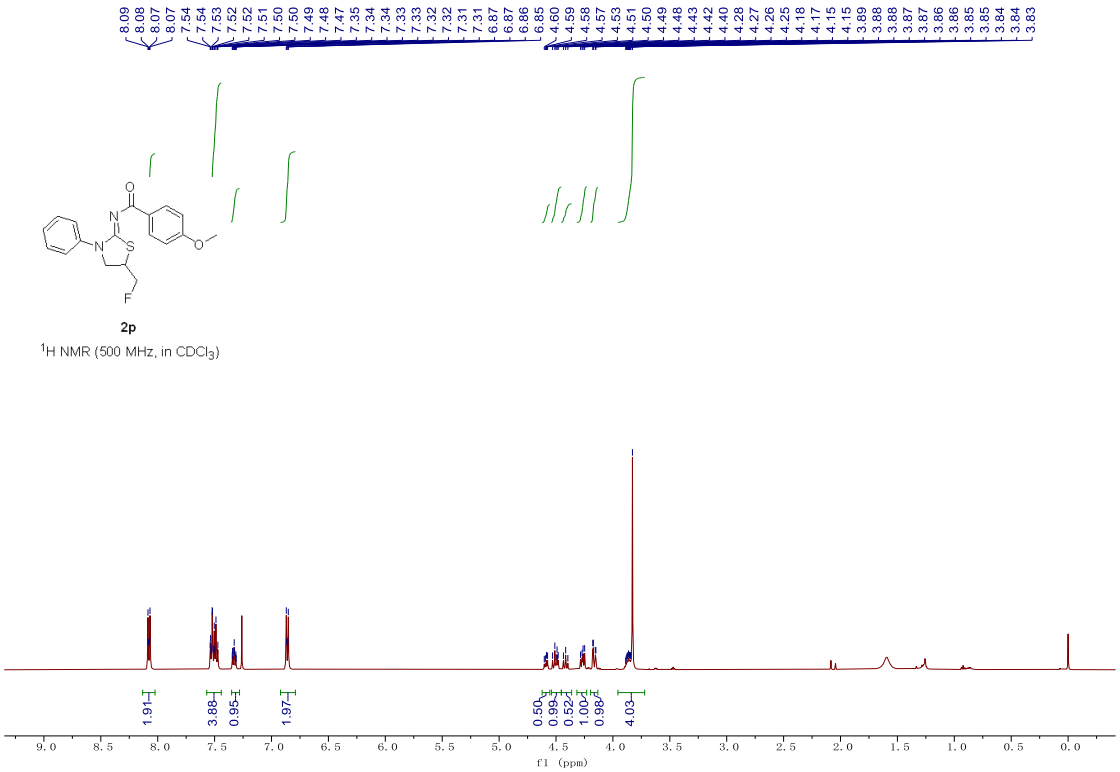
2o

^{13}C NMR (151 MHz, in $CDCl_3$)



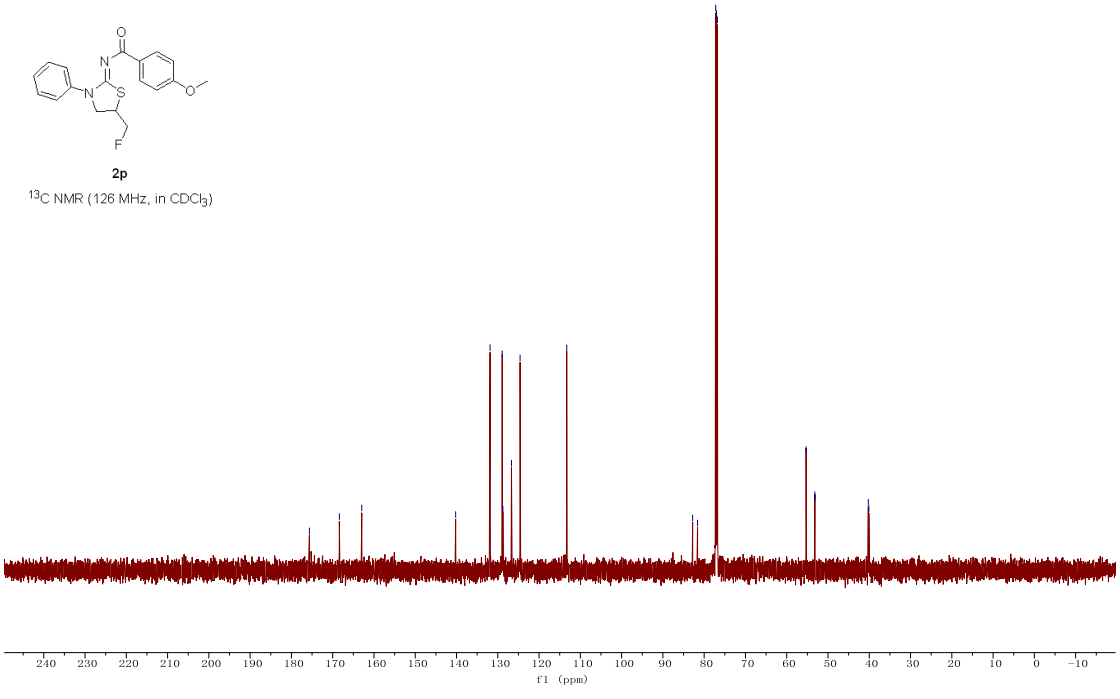
2o

^{19}F NMR (565 MHz, in $CDCl_3$)



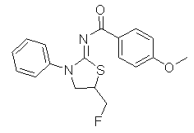
2p

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



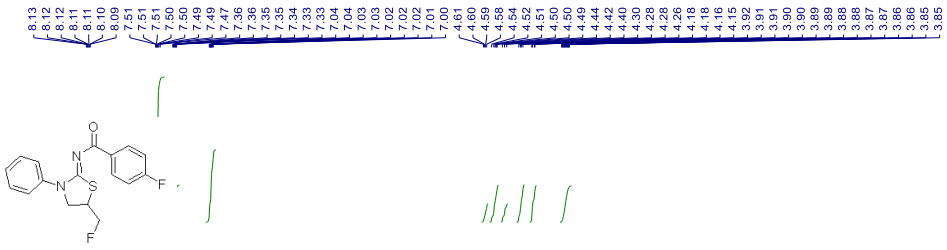
2p

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



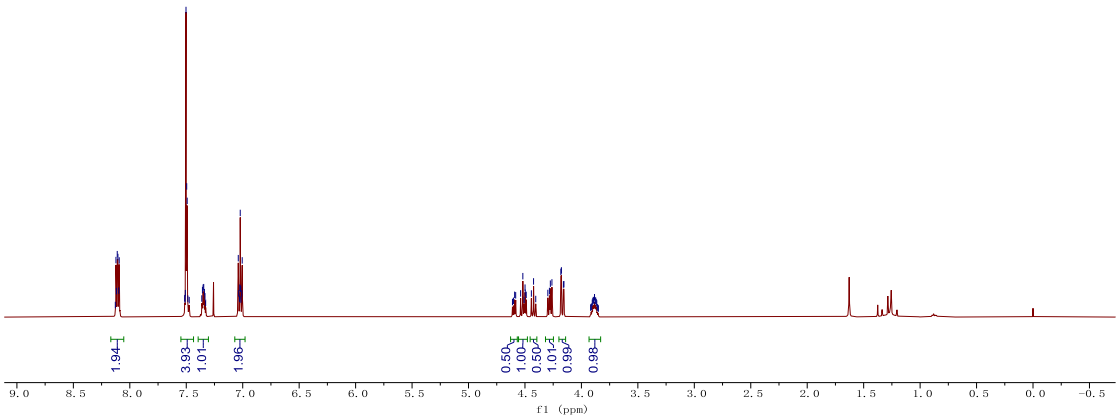
2p

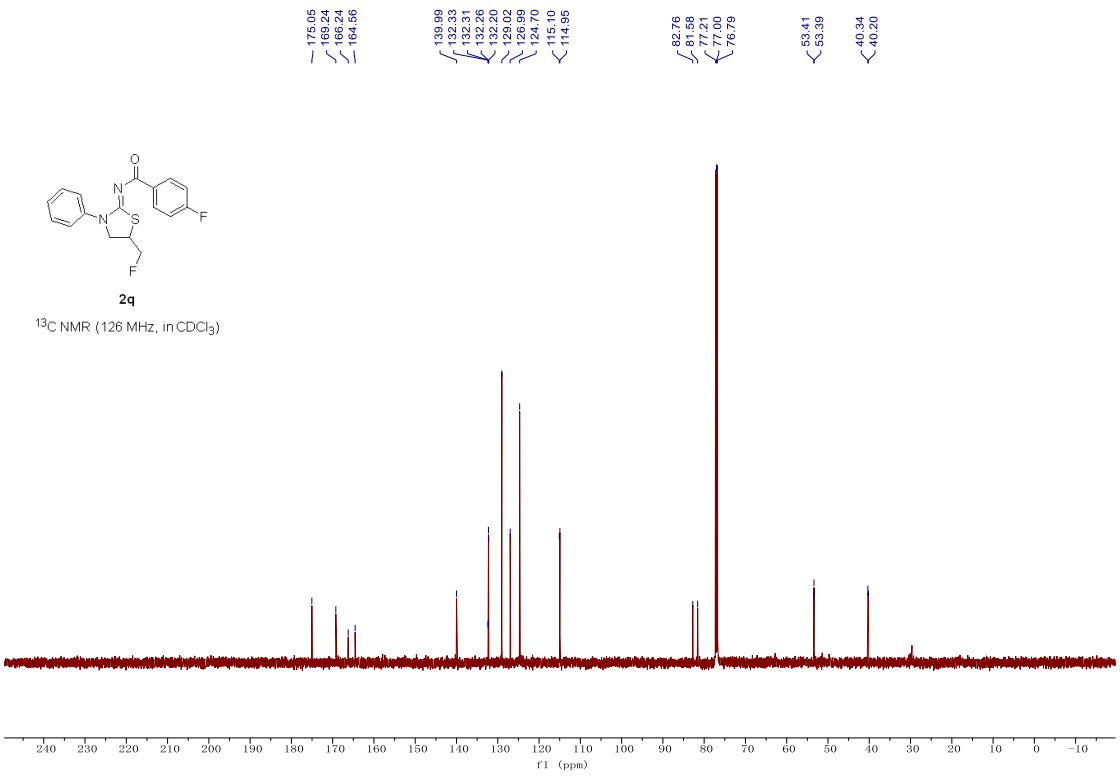
^{19}F NMR (565 MHz, in $CDCl_3$)



2q

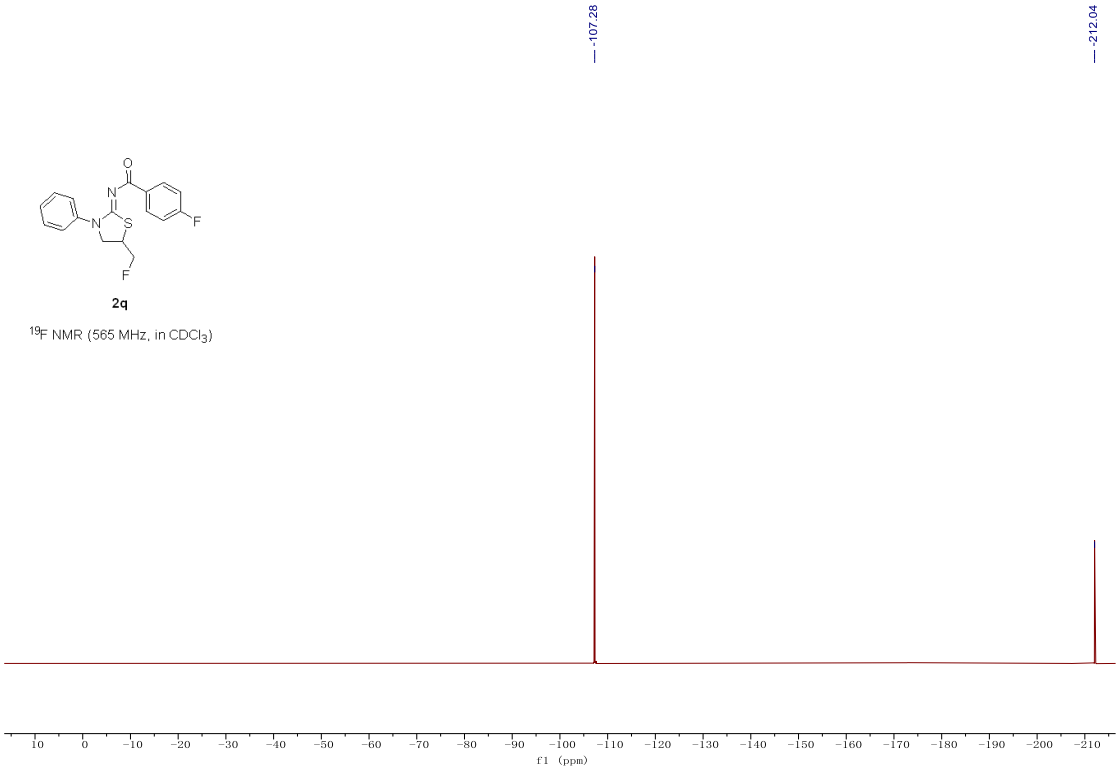
^{1}H NMR (500 MHz, in $CDCl_3$)





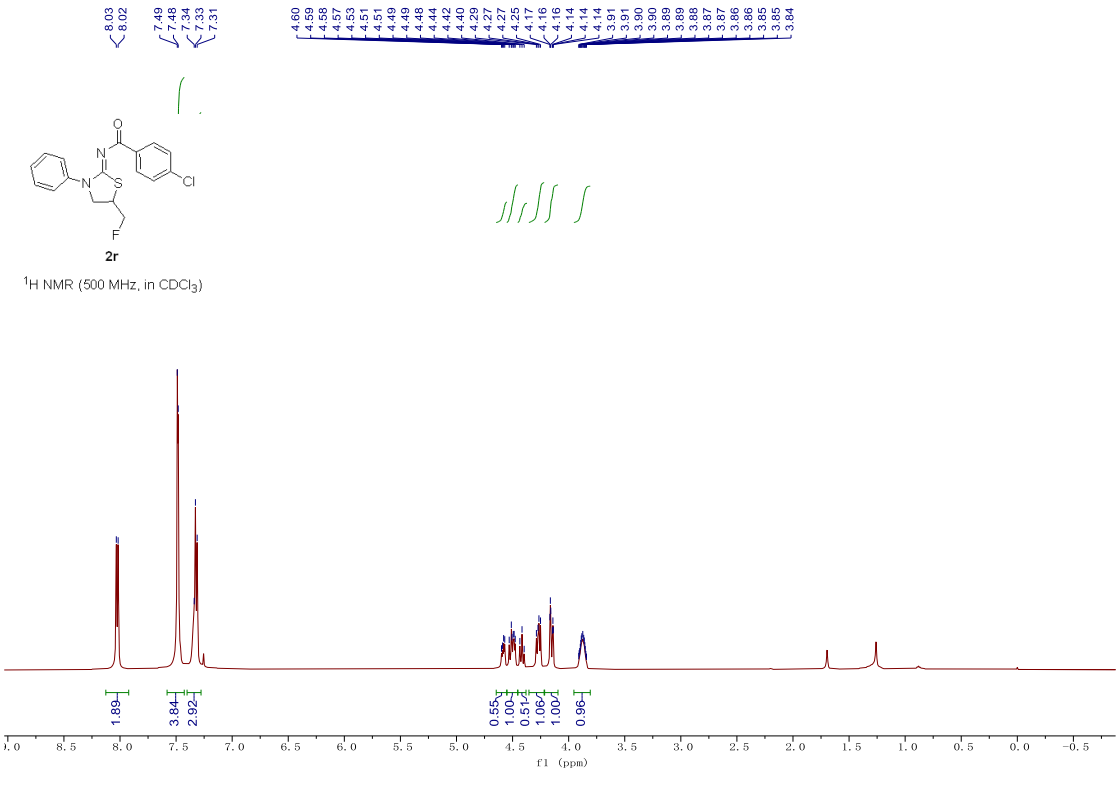
2q

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



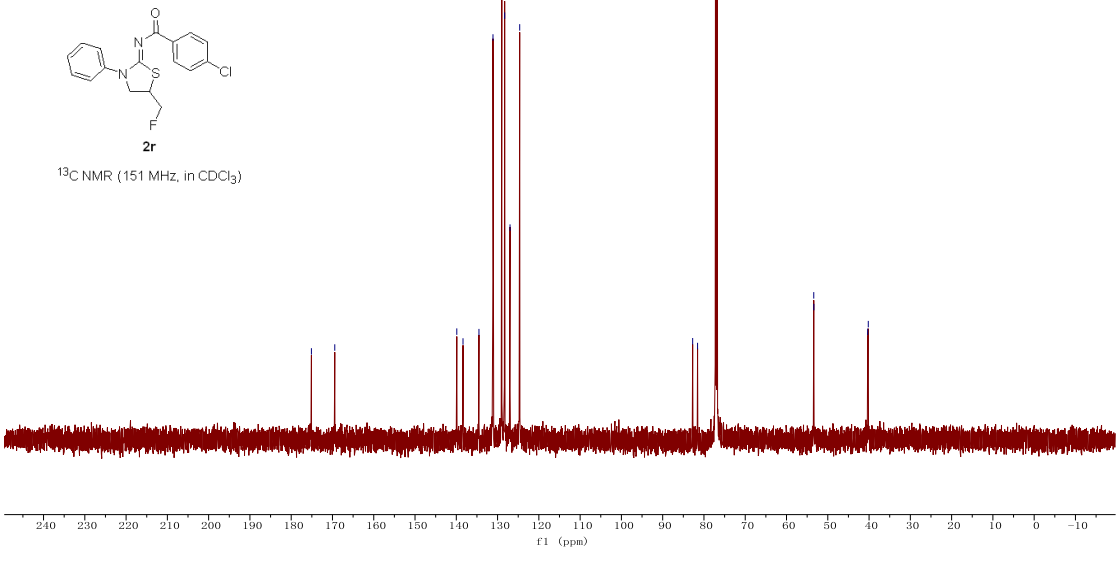
2q

^{19}F NMR (565 MHz, in $CDCl_3$)



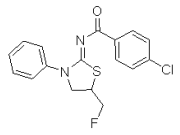
2r

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



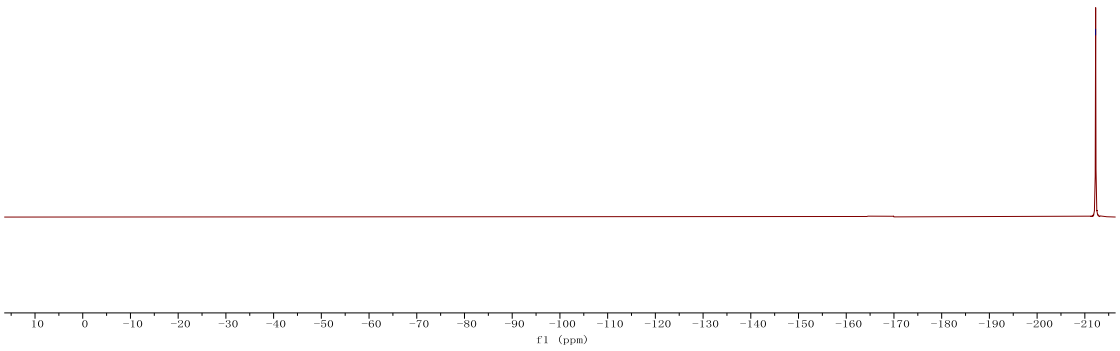
2r

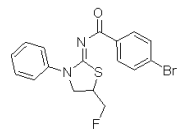
^{13}C NMR (151 MHz, in $CDCl_3$)



2r

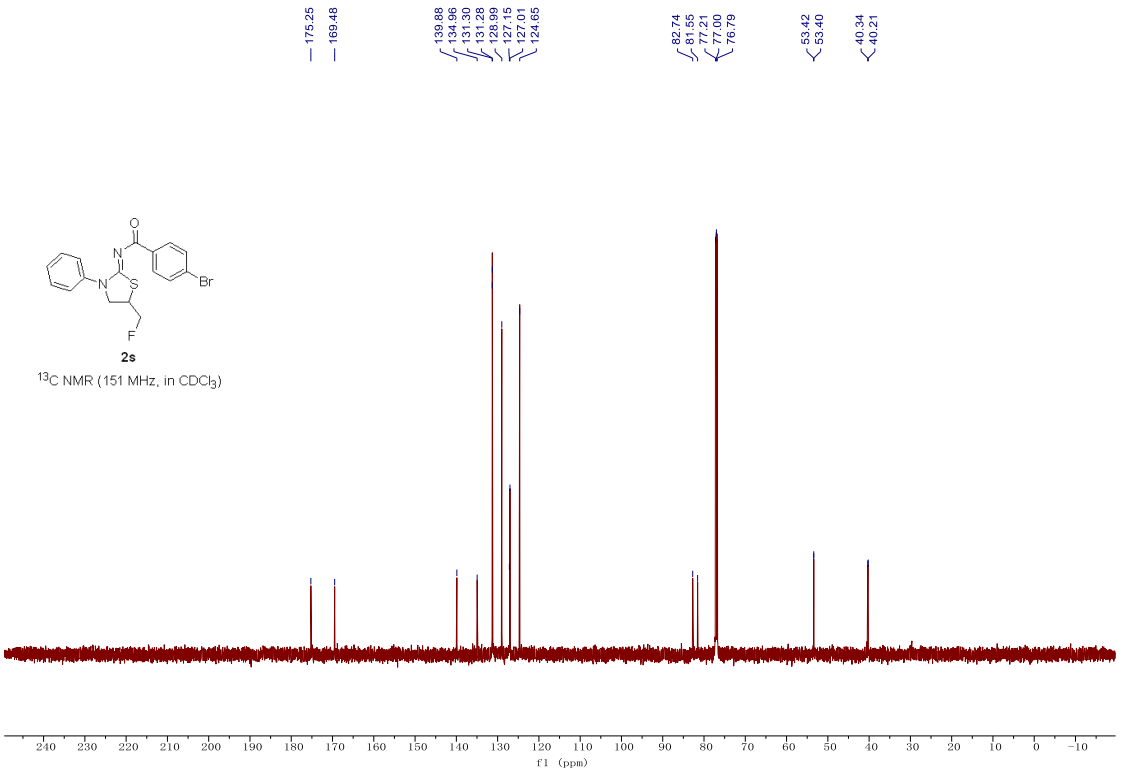
^{19}F NMR (565 MHz, in $CDCl_3$)





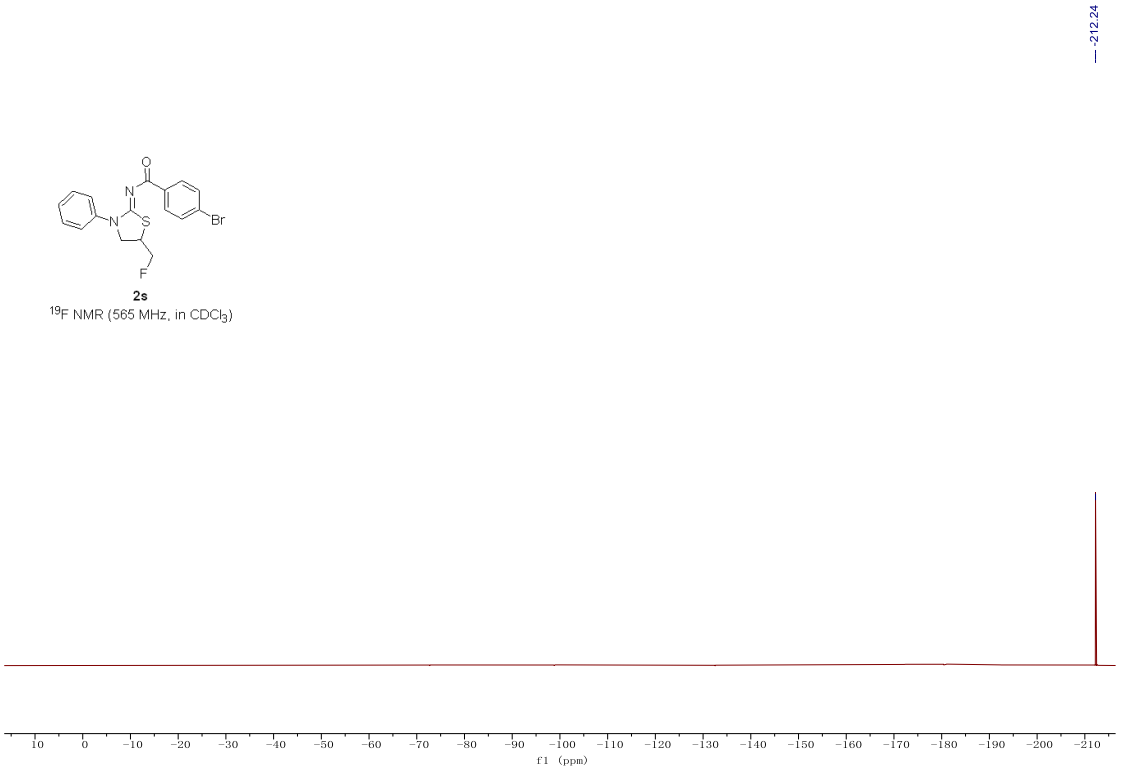
2s

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



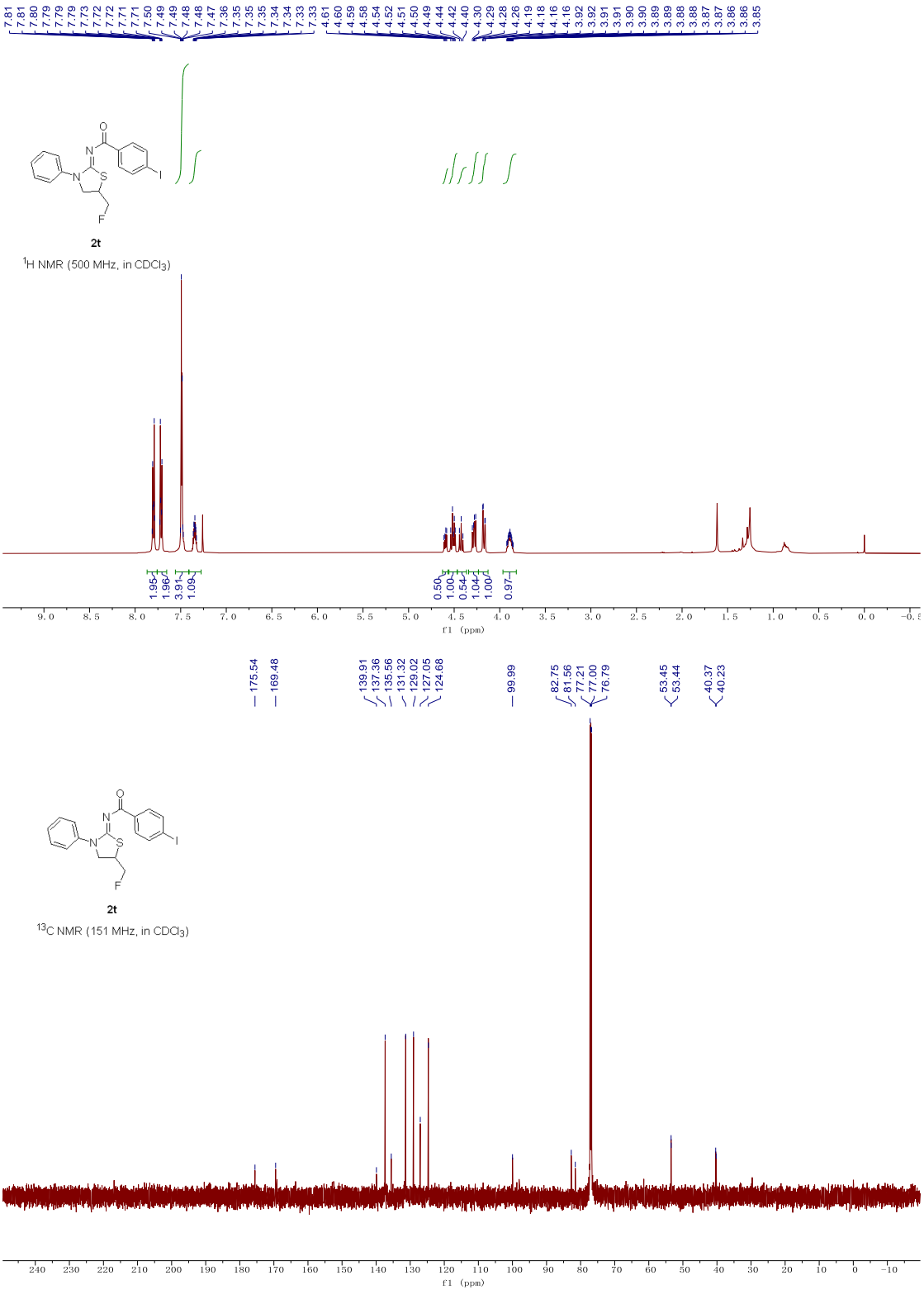
2s

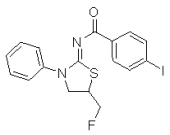
^{13}C NMR (151 MHz, in $CDCl_3$)



2s

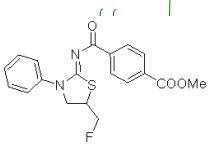
^{19}F NMR (565 MHz, in $CDCl_3$)


7.81 7.81 7.80 7.79 7.79 7.79 7.73 7.72 7.72 7.71 7.71 7.50 7.49 7.49 7.48 7.48 7.47 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33
4.61 4.60 4.59 4.58 4.54 4.52 4.51 4.50 4.49 4.44 4.42 4.40 4.30 4.29 4.28 4.26 4.19 4.18 4.16 4.16 3.92 3.92 3.91 3.91 3.90 3.90 3.89 3.89 3.88 3.88 3.87 3.87 3.86 3.86 3.85
O
N
S
I
F
2t
1H NMR (500 MHz, in CDCl3)
1.95 1.96 3.91 1.09 0.50 1.00 0.54 1.04 1.00 0.97
f1 (ppm)
175.54 169.48 139.91 137.36 135.56 131.32 129.02 127.05 124.68 99.99 82.75 81.56 77.21 77.00 76.79 53.45 53.44 40.37 40.23
2t
13C NMR (151 MHz, in CDCl3)
f1 (ppm)



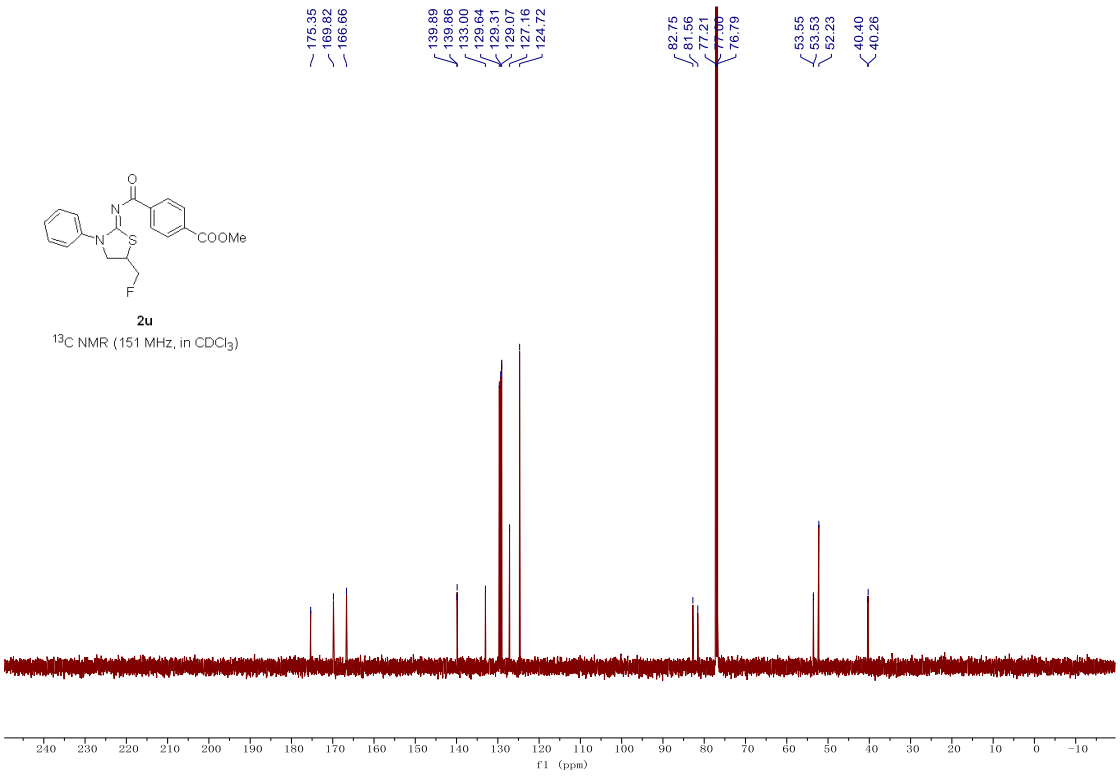
2t

^{19}F NMR (565 MHz, in $CDCl_3$)



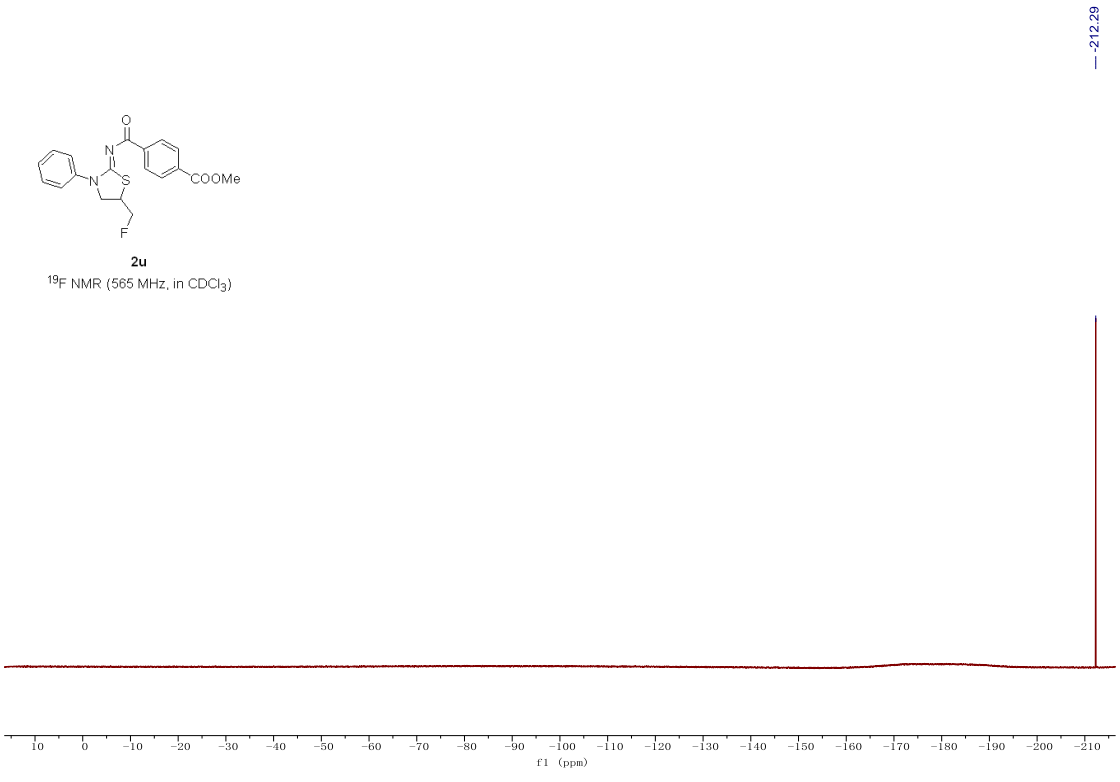
2u

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



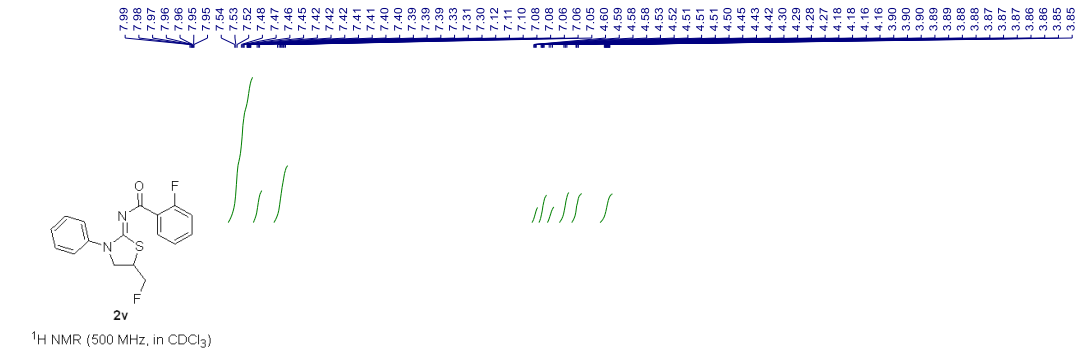
2u

^{13}C NMR (151 MHz, in $CDCl_3$)



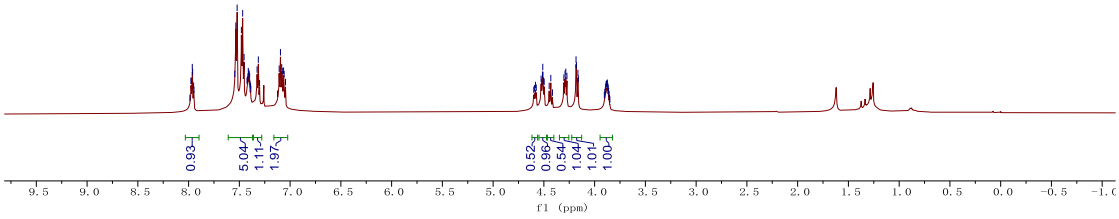
2u

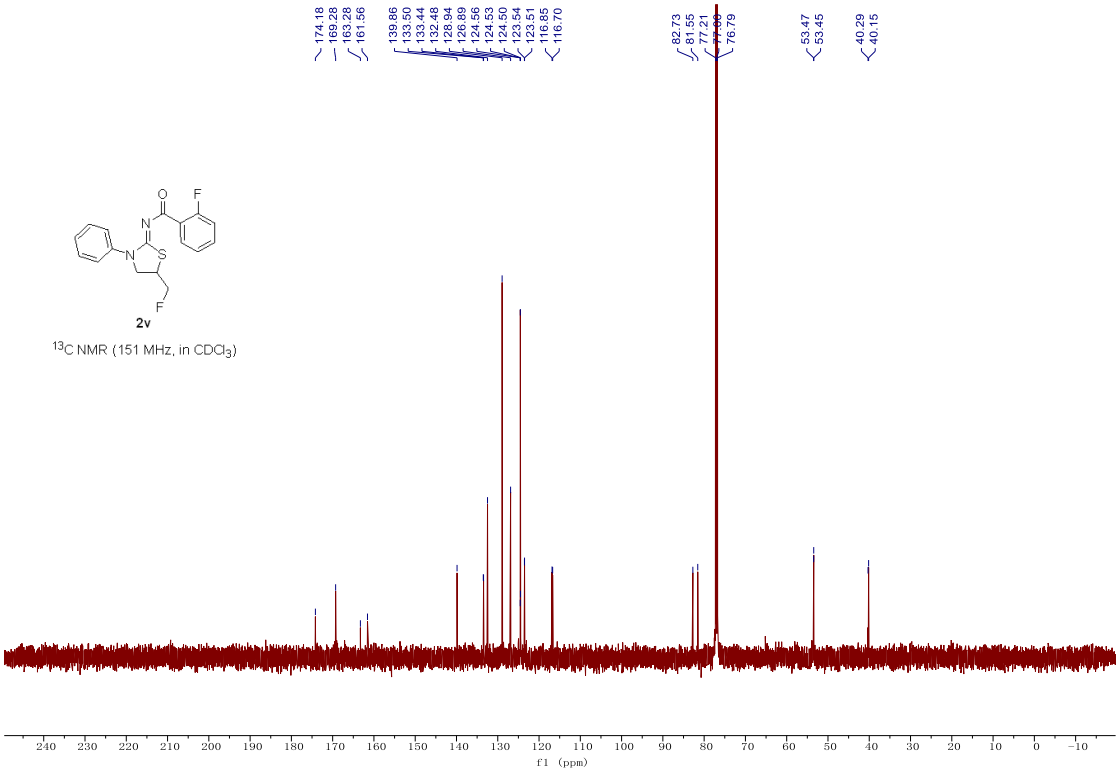
^{19}F NMR (565 MHz, in $CDCl_3$)



2v

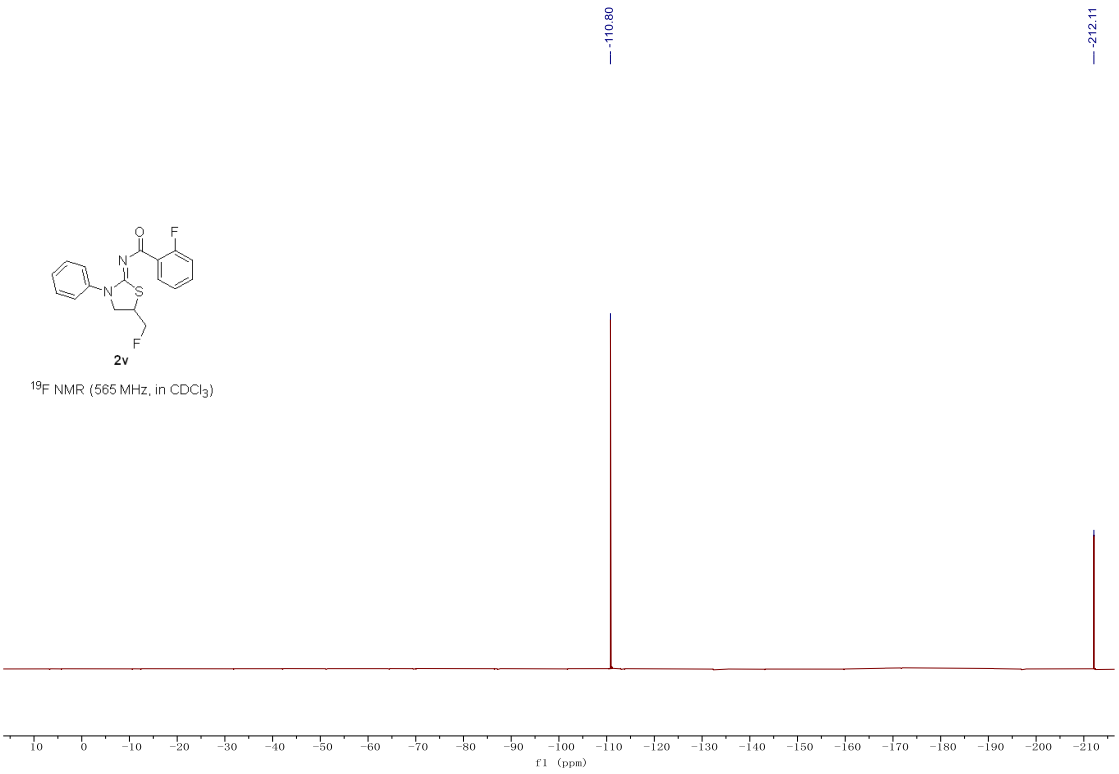
^{1}H NMR (500 MHz, in $CDCl_3$)

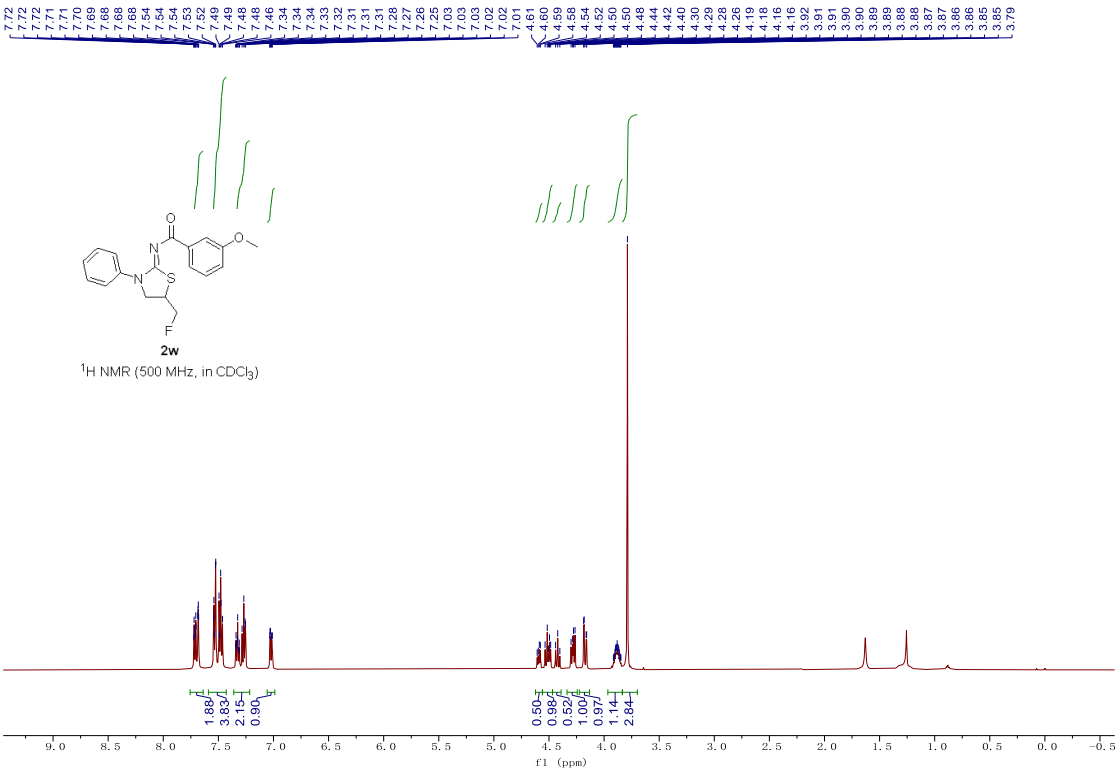


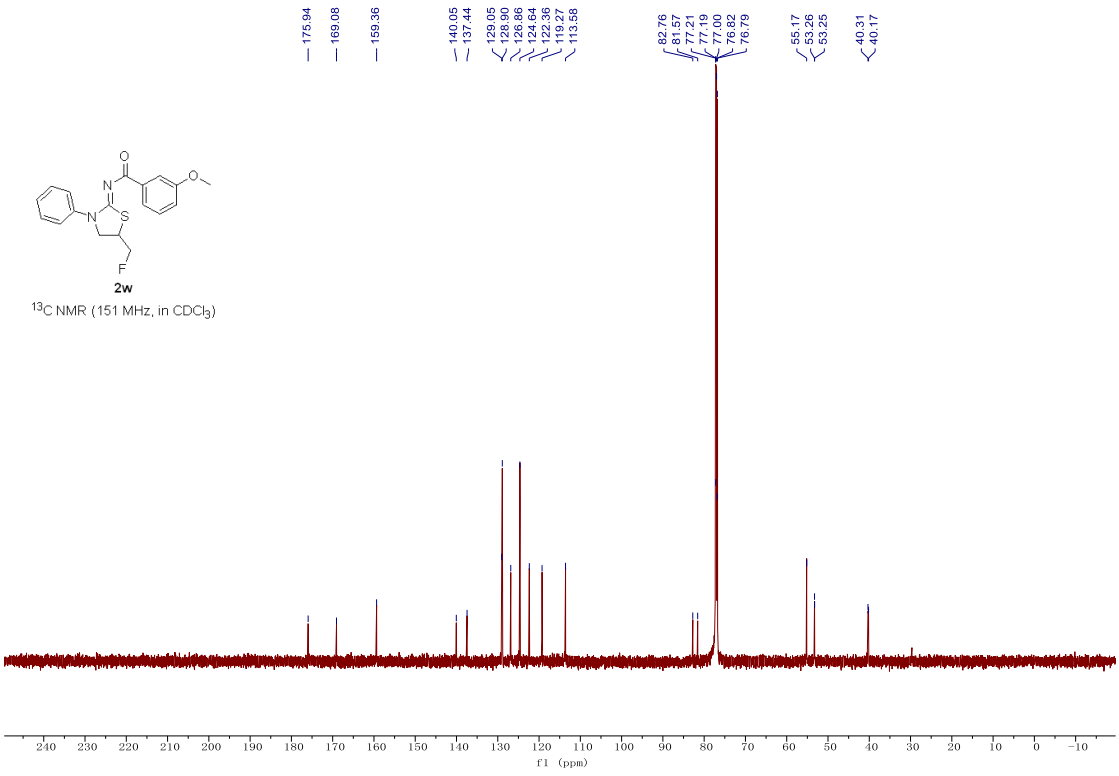


2v

^{13}C NMR (151 MHz, in $CDCl_3$)

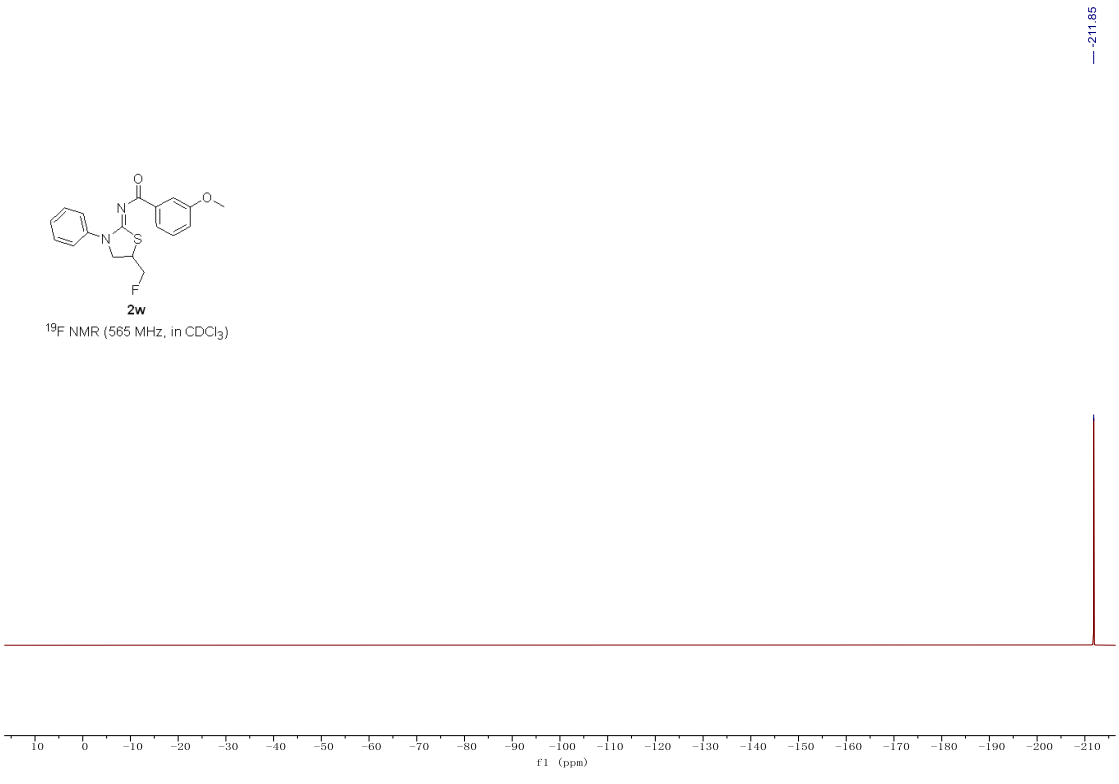

-110.80
-212.11
2v
19F NMR (565 MHz, in CDCl3)
f1 (ppm)


2w
1H NMR (500 MHz, in CDCl3)
1.88
3.83
2.15
0.90
0.50
0.98
0.52
1.00
0.97
1.14
2.84
f1 (ppm)



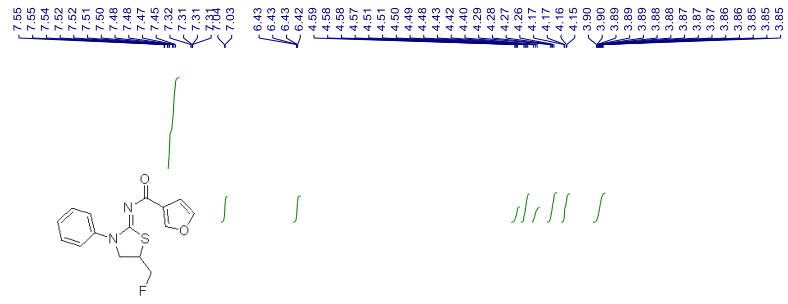
2w

^{13}C NMR (151 MHz, in $CDCl_3$)



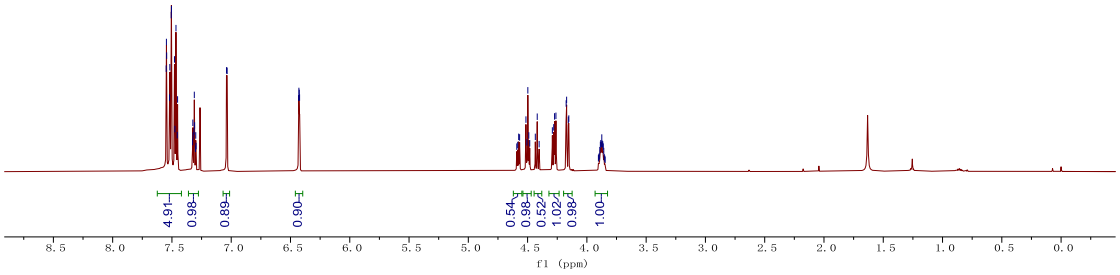
2w

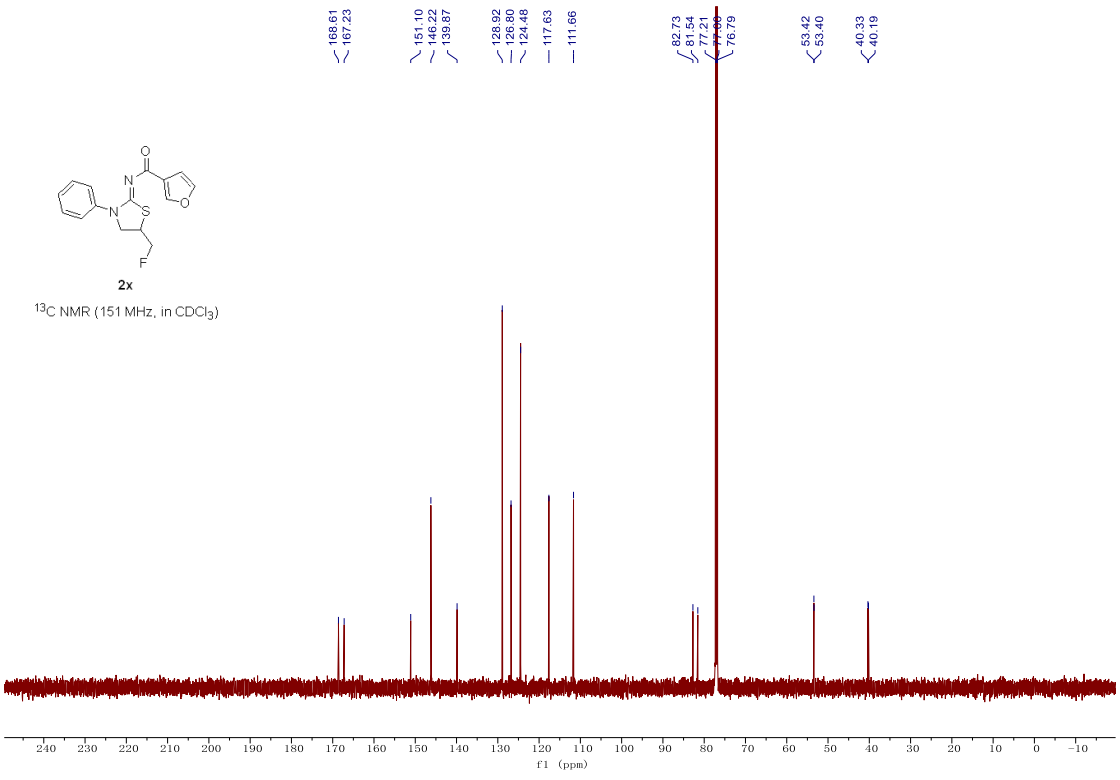
^{19}F NMR (565 MHz, in $CDCl_3$)



2x

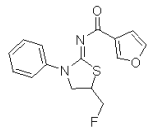
^{1}H NMR (500 MHz, in $CDCl_3$)





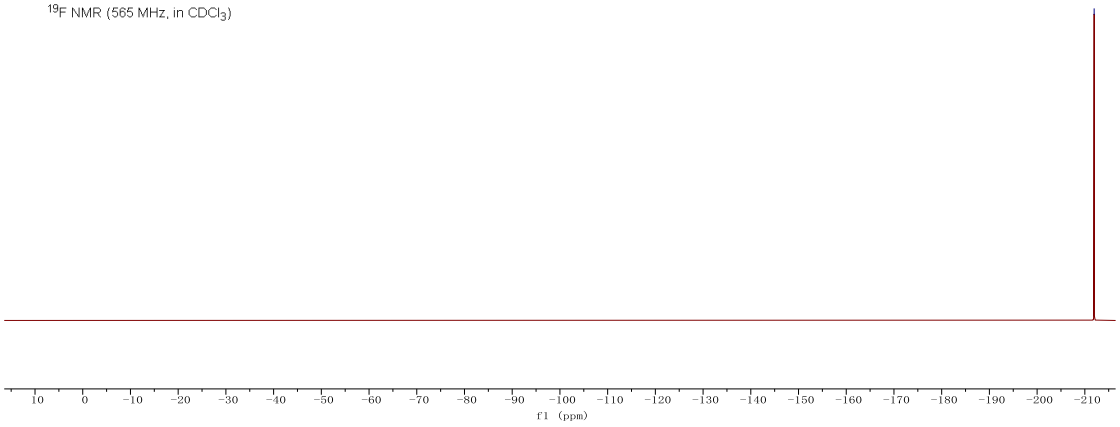
2x

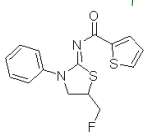
^{13}C NMR (151 MHz, in $CDCl_3$)



2x

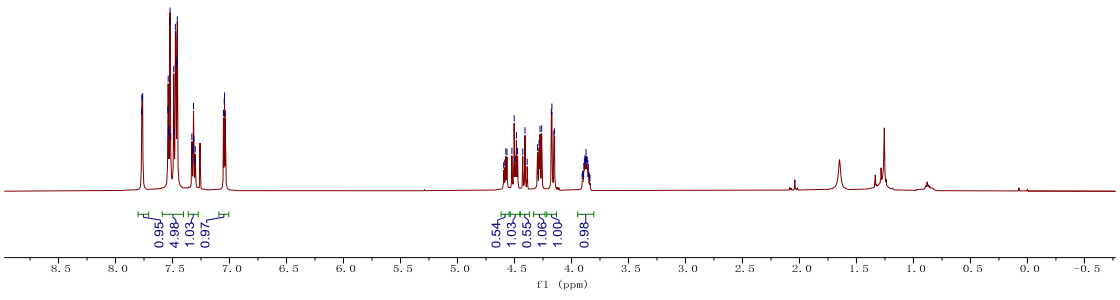
^{19}F NMR (565 MHz, in $CDCl_3$)

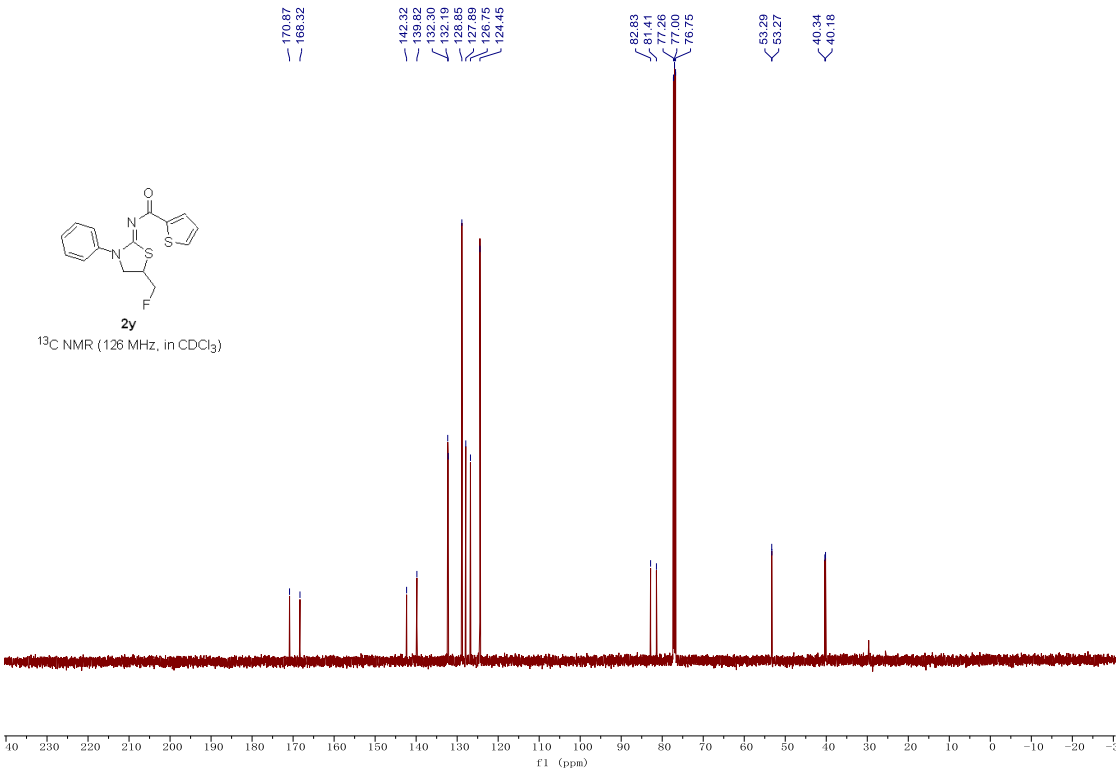




2y

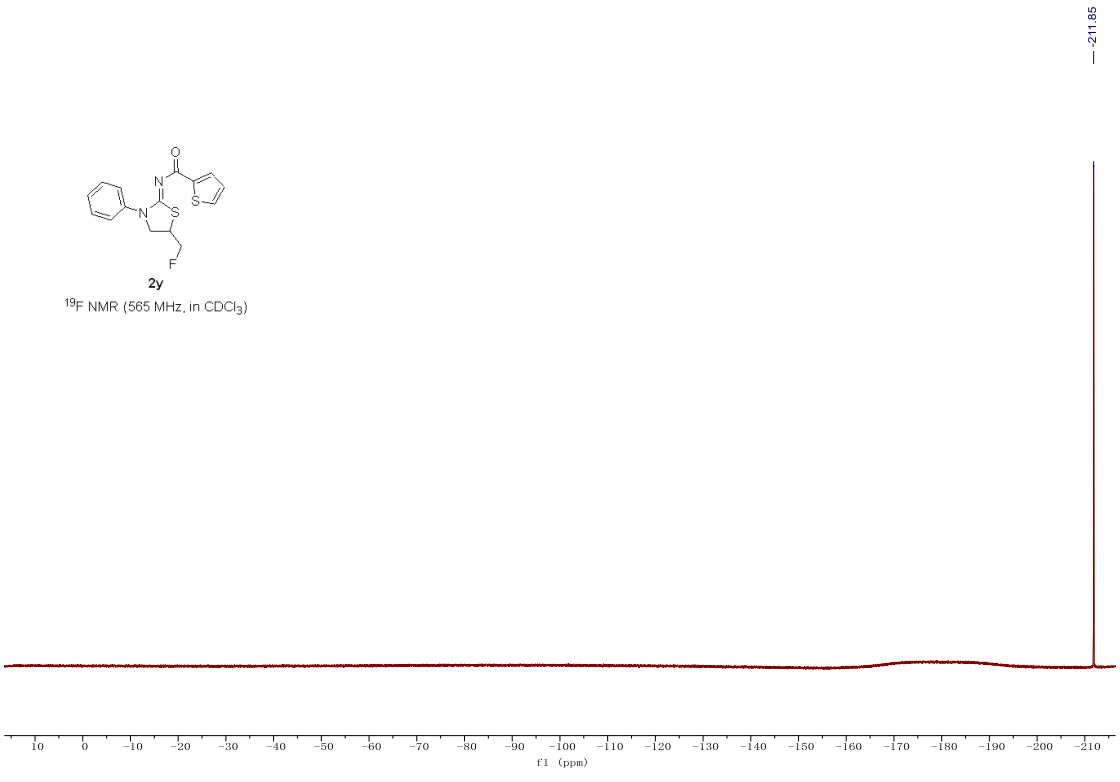
^{1}H NMR (500 MHz, in $CDCl_3$)





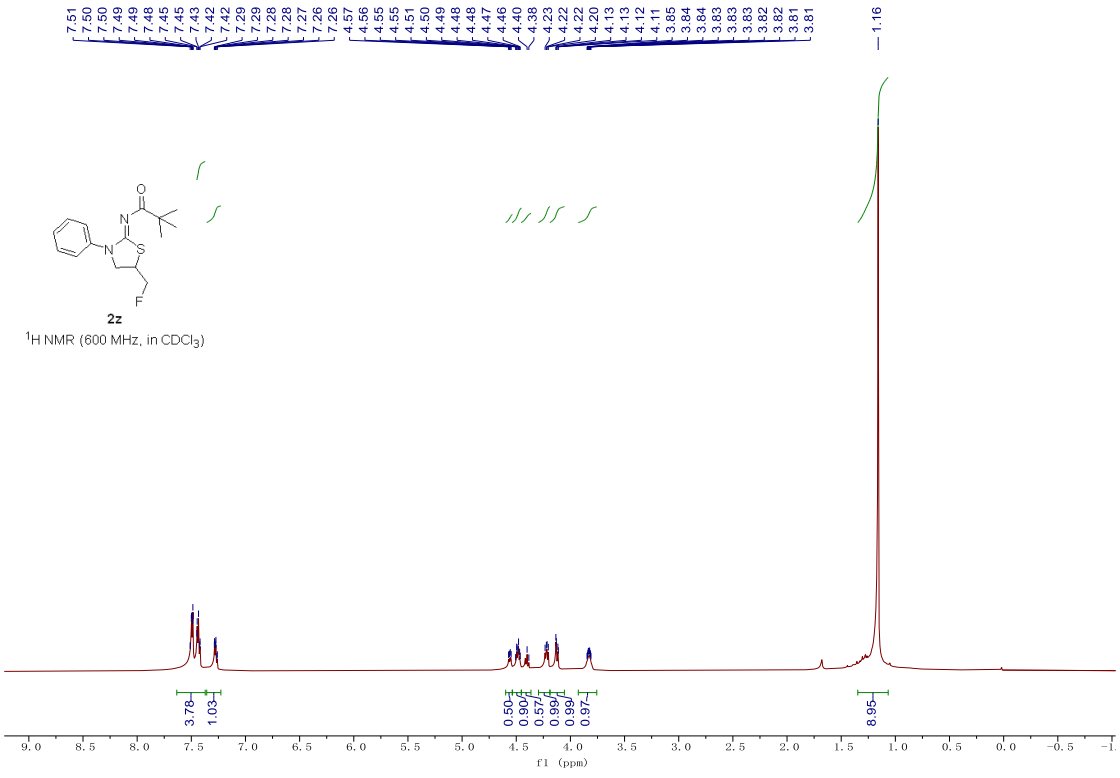
2y

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



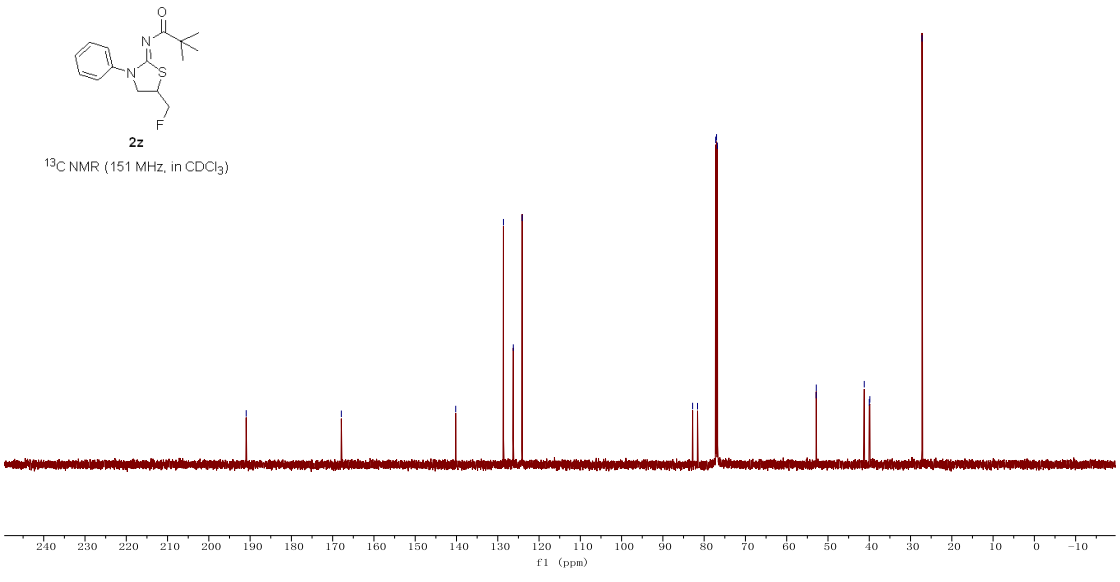
2y

^{19}F NMR (565 MHz, in $CDCl_3$)



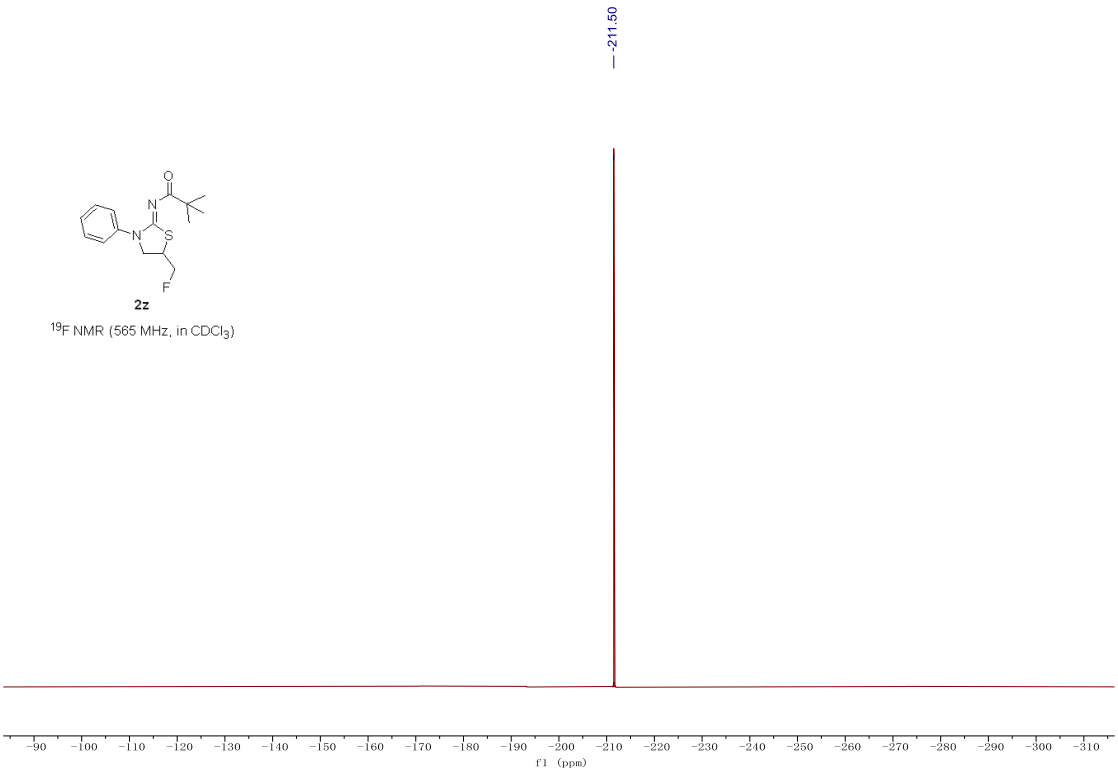
2z

^{1}H NMR (600 MHz, in $CDCl_3$)



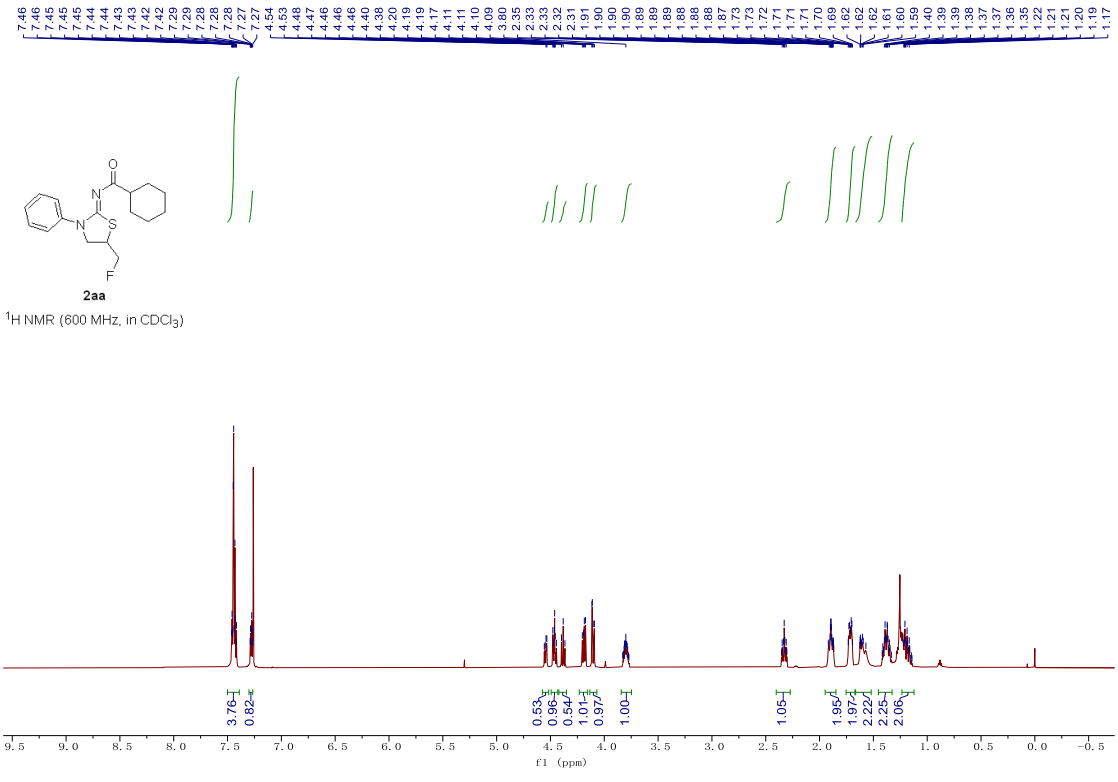
2z

^{13}C NMR (151 MHz, in $CDCl_3$)



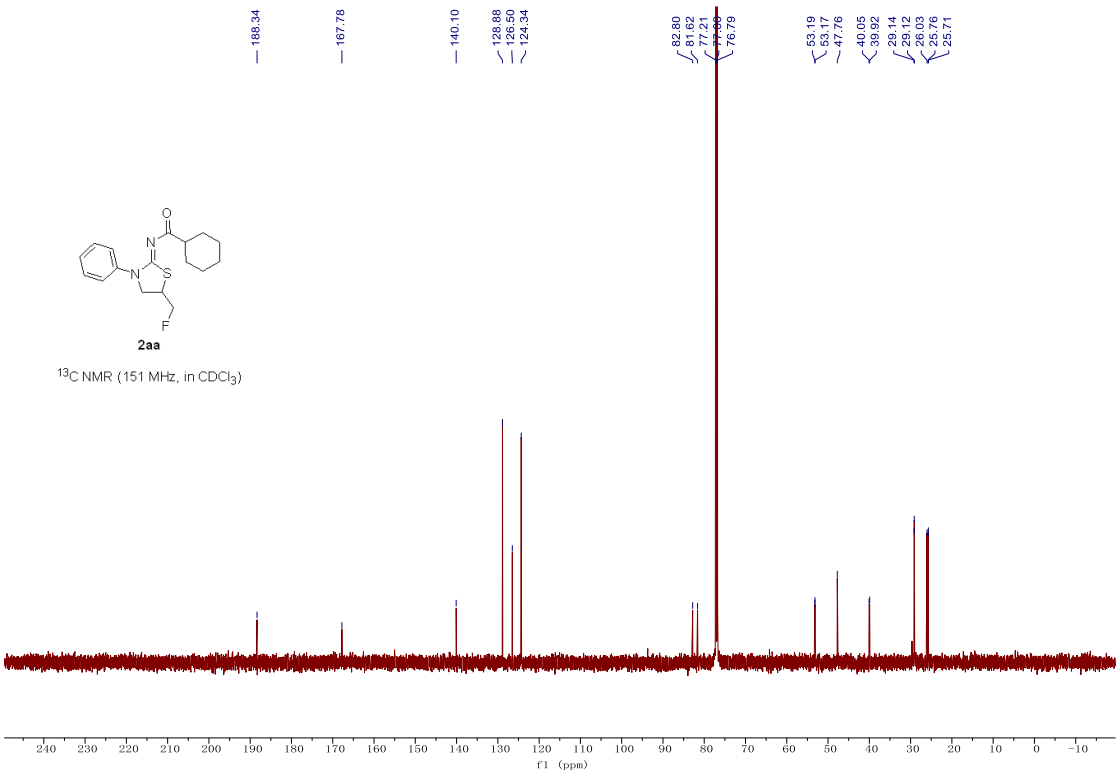
2z

^{19}F NMR (565 MHz, in $CDCl_3$)



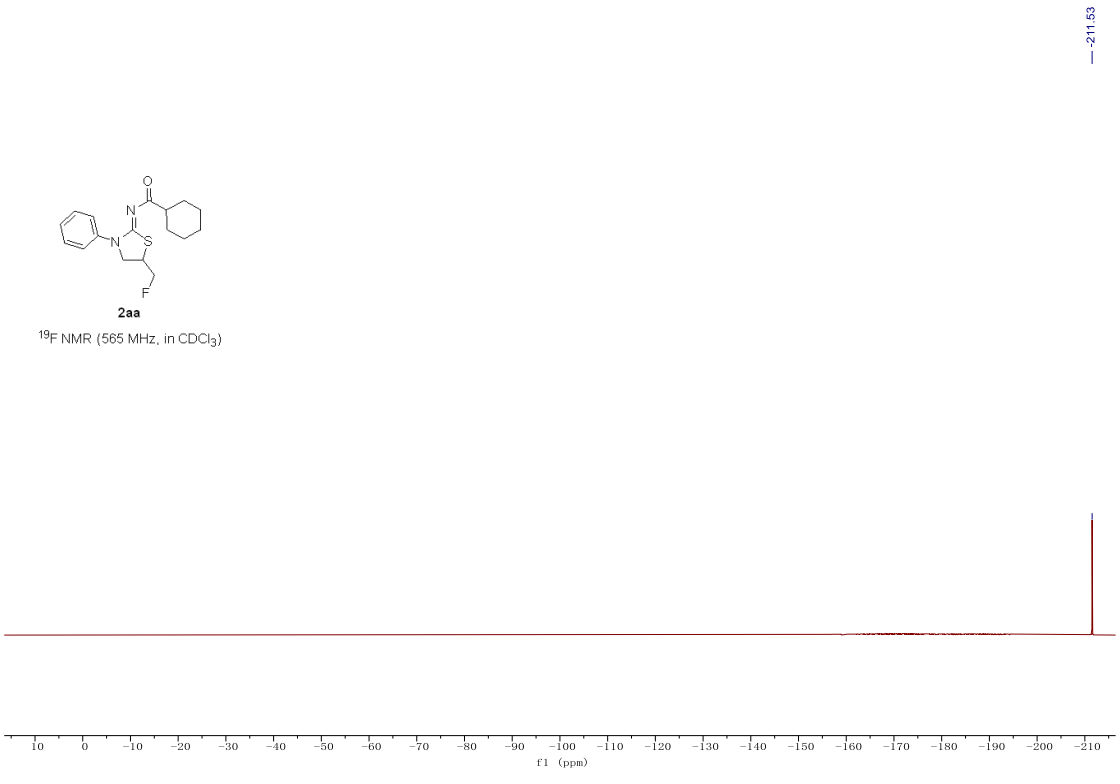
2aa

^{1}H NMR (600 MHz, in $CDCl_3$)



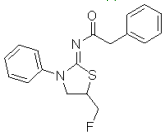
2aa

^{13}C NMR (151 MHz, in $CDCl_3$)



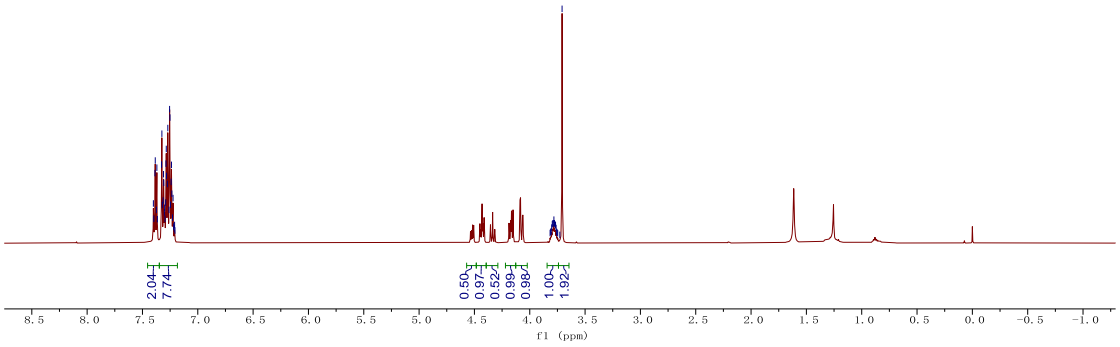
2aa

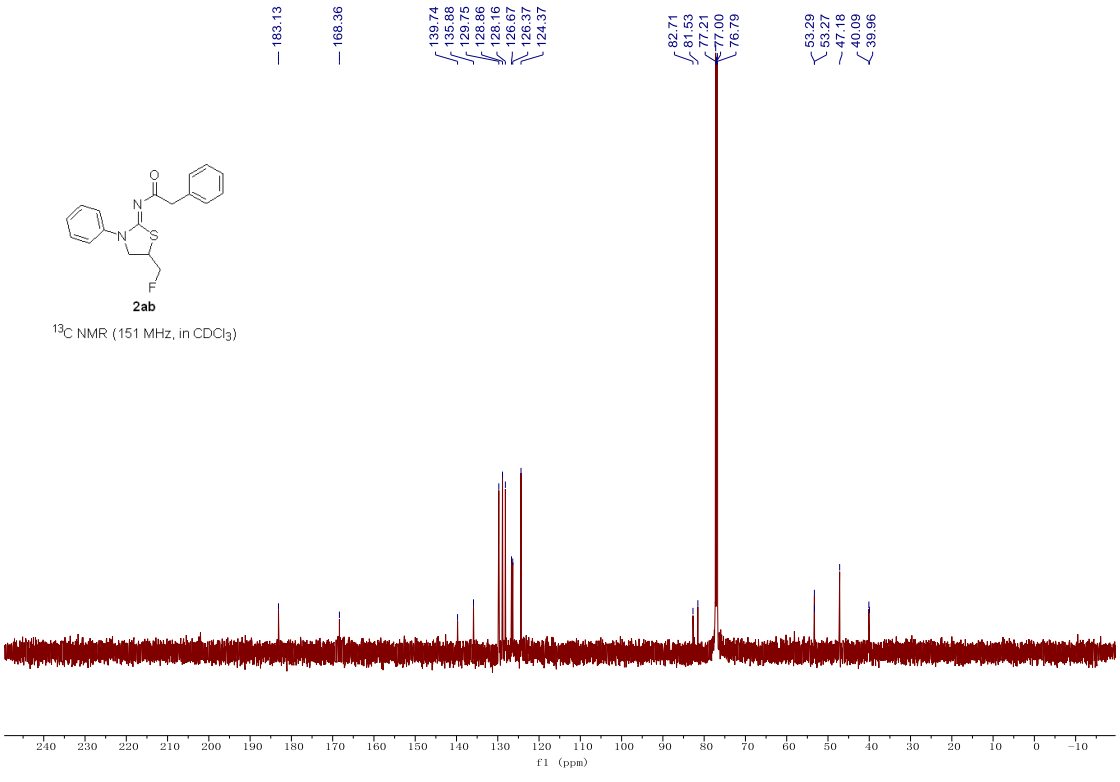
^{19}F NMR (565 MHz, in $CDCl_3$)



2ab

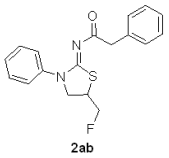
^{1}H NMR (500 MHz, in $CDCl_3$)





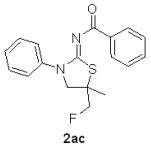
2ab

^{13}C NMR (151 MHz, in $CDCl_3$)



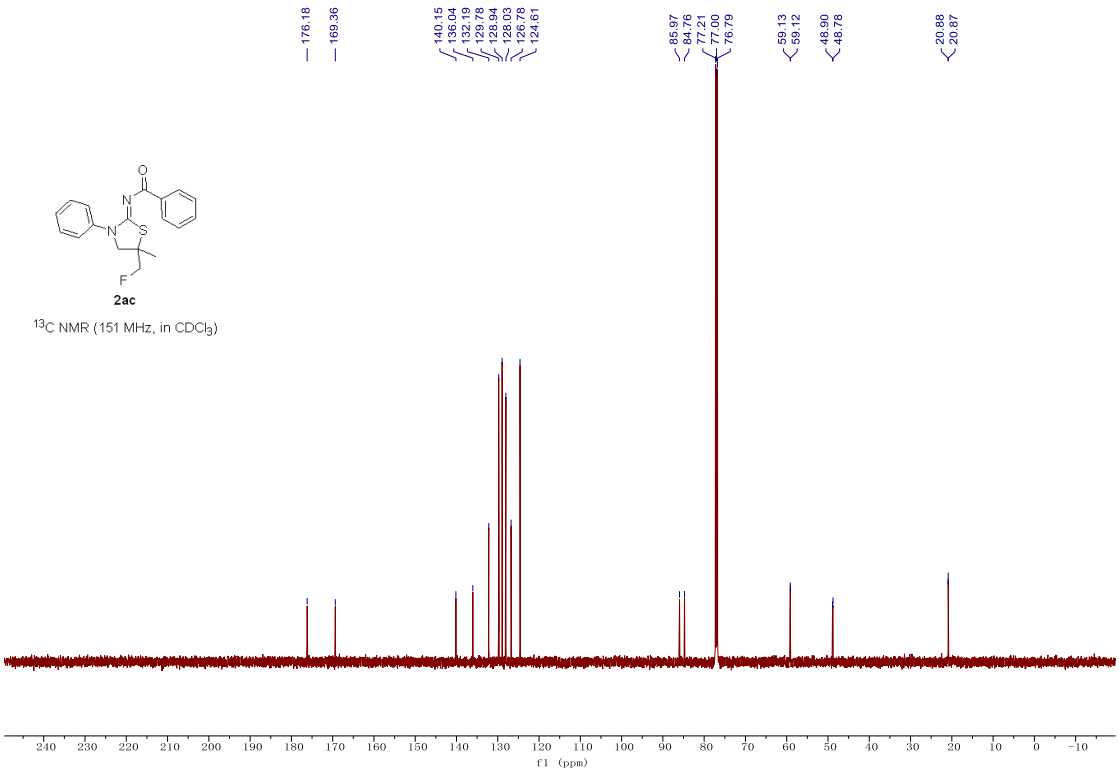
2ab

^{19}F NMR (565 MHz, in $CDCl_3$)



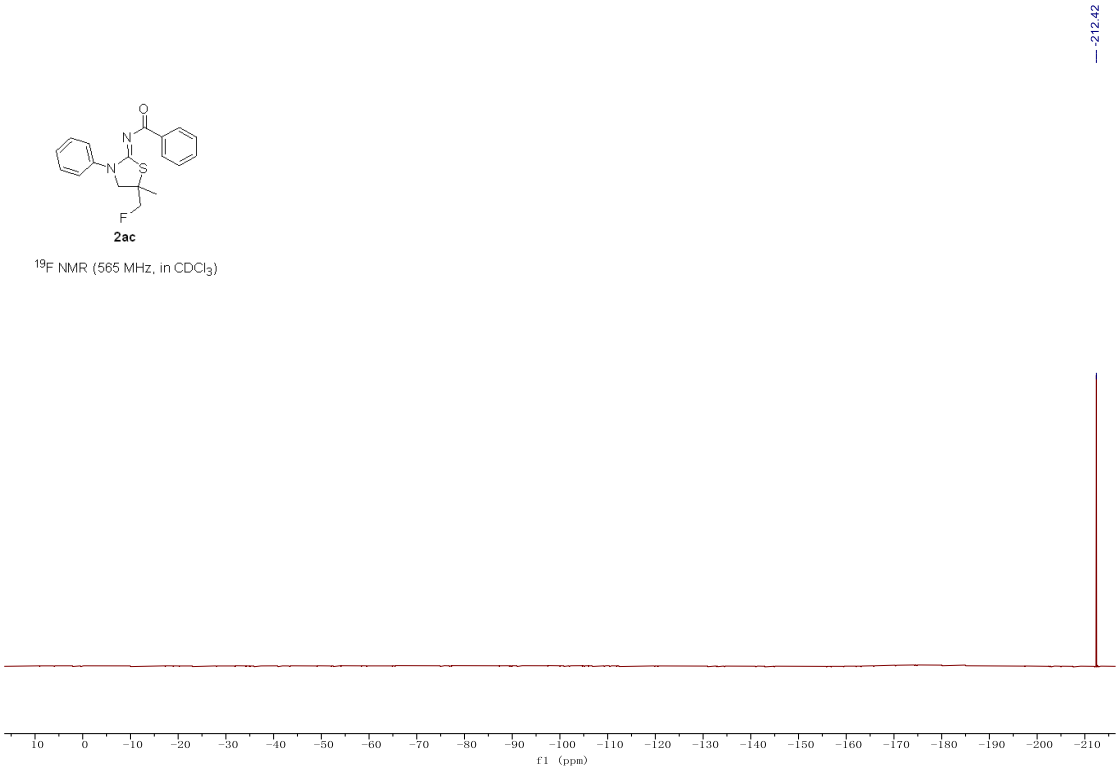
2ac

^{1}H NMR (600 MHz, in $CDCl_3$)



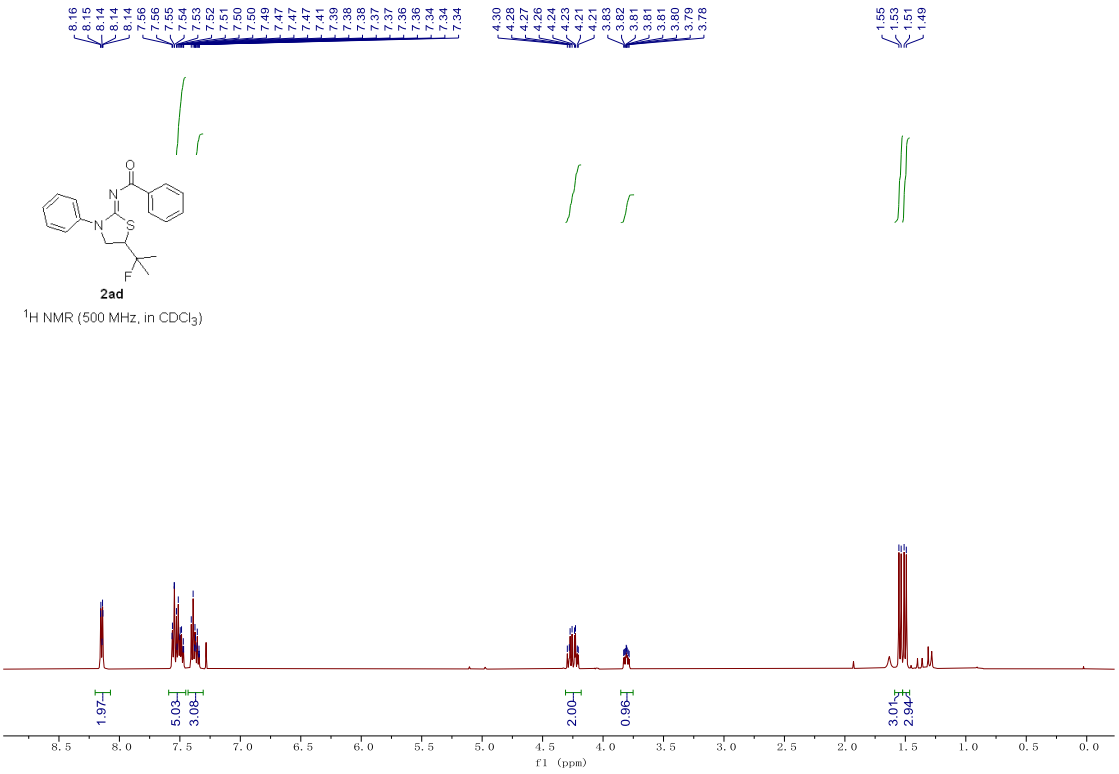
2ac

^{13}C NMR (151 MHz, in $CDCl_3$)



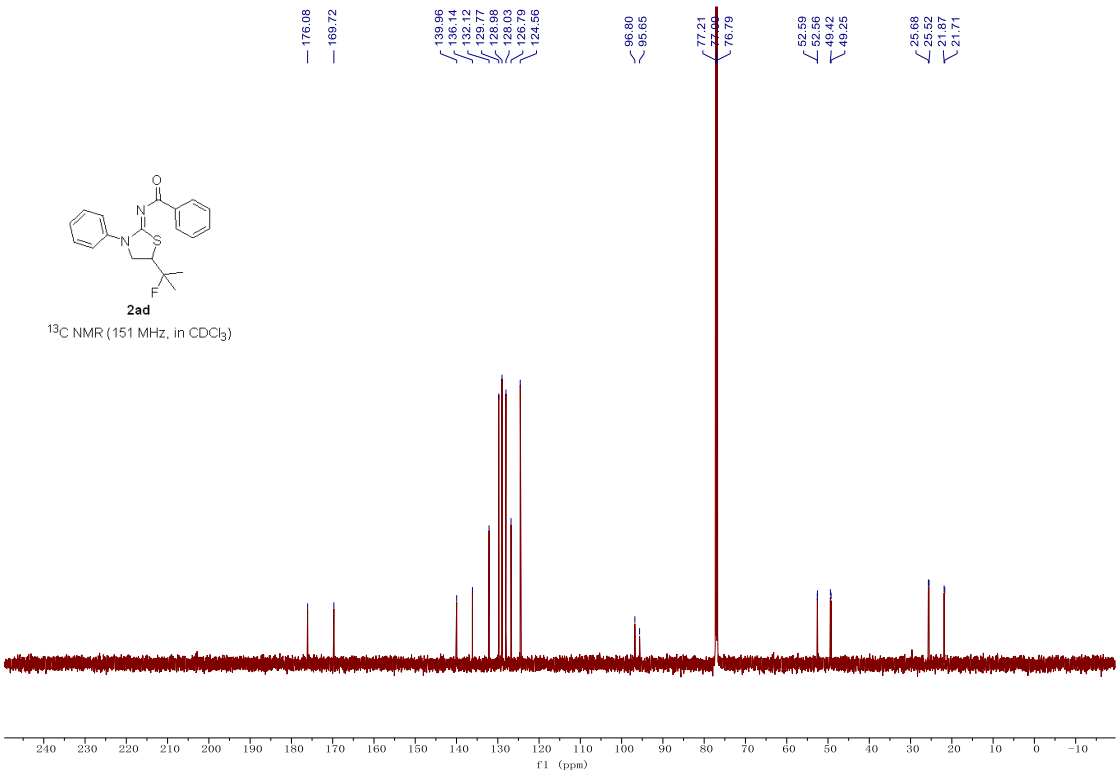
2ac

^{19}F NMR (565 MHz, in $CDCl_3$)



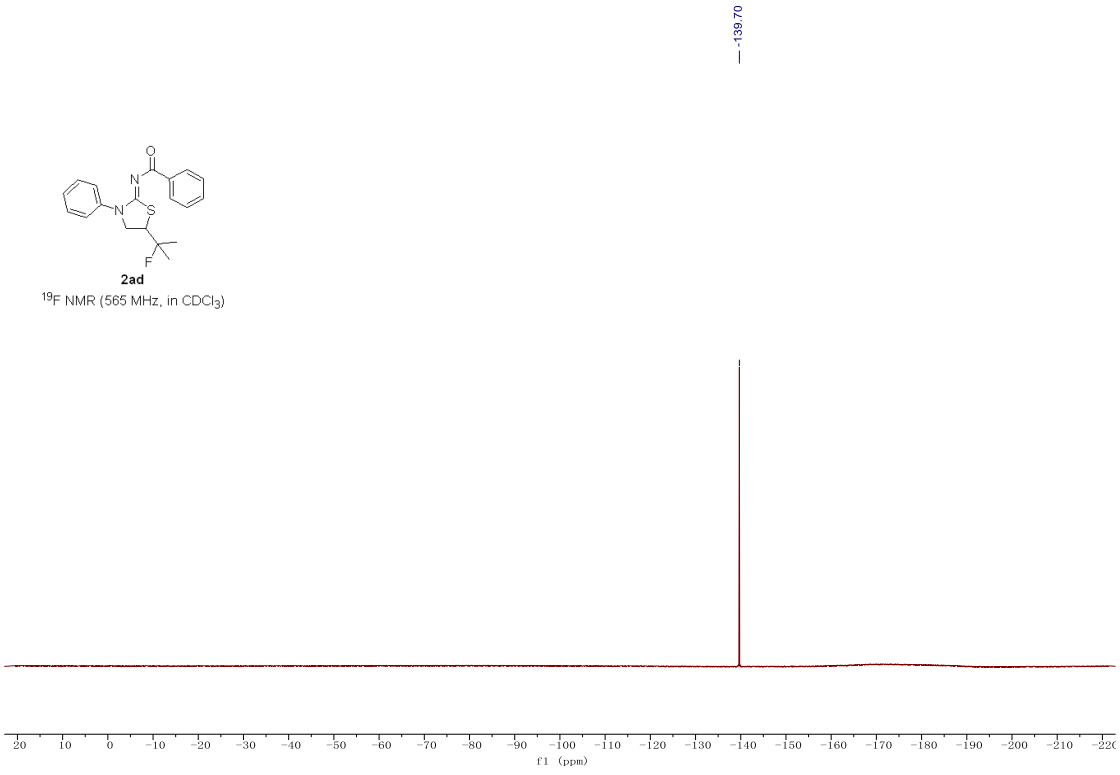
2ad

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



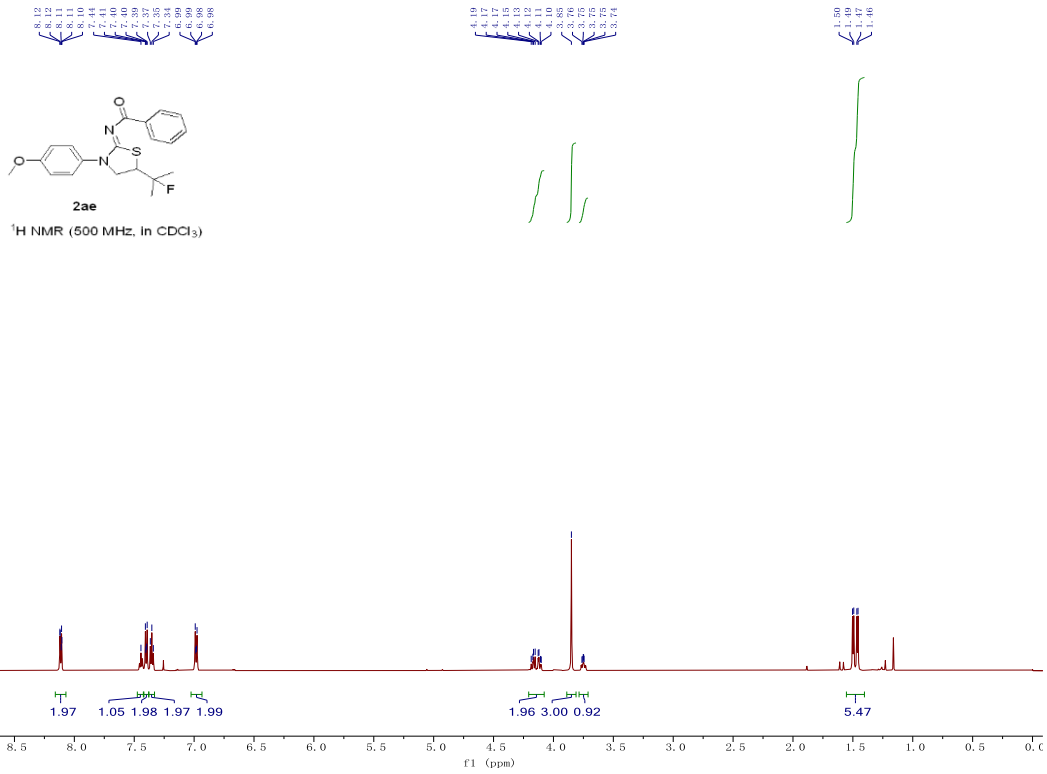
2ad

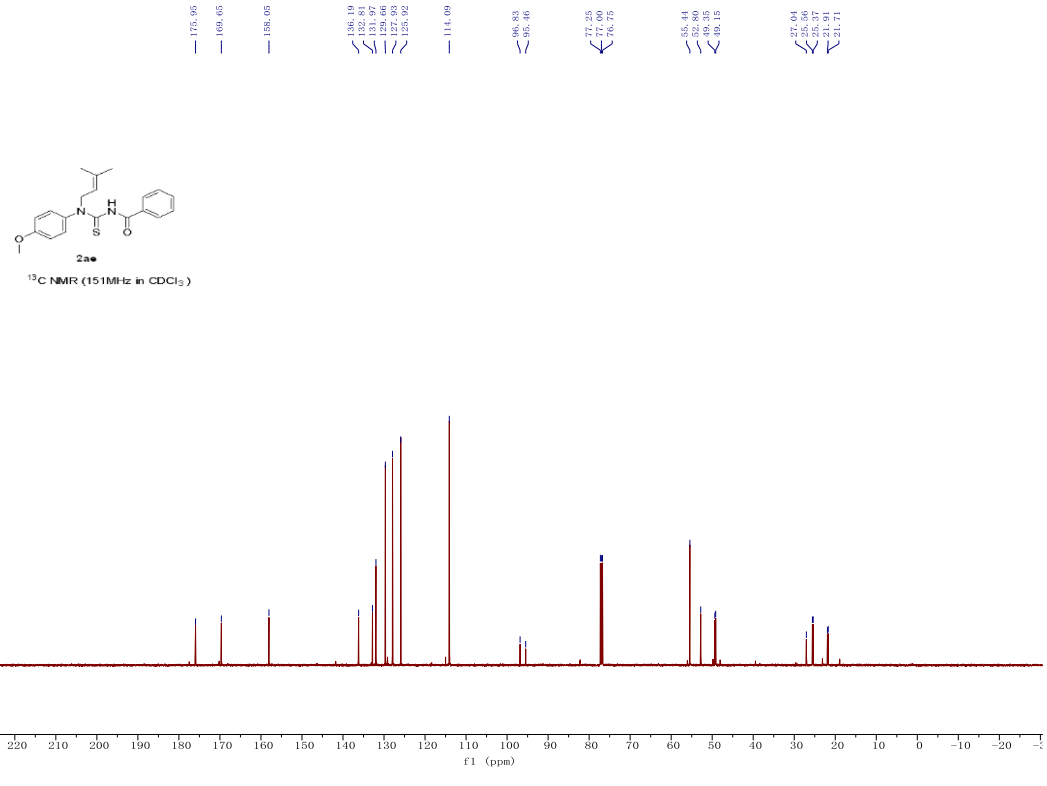
^{13}C NMR (151 MHz, in $CDCl_3$)

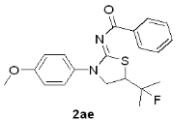


2ad

^{19}F NMR (565 MHz, in $CDCl_3$)

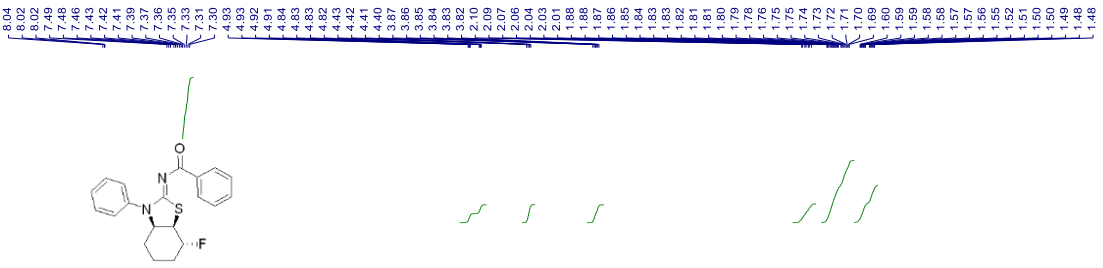

2ae
1H NMR (500 MHz, In CDCl3)
1.97
1.05 1.98 1.97 1.99
1.96 3.00 0.92
5.47
f1 (ppm)


2ae
13C NMR (151MHz in CDCl3)
f1 (ppm)



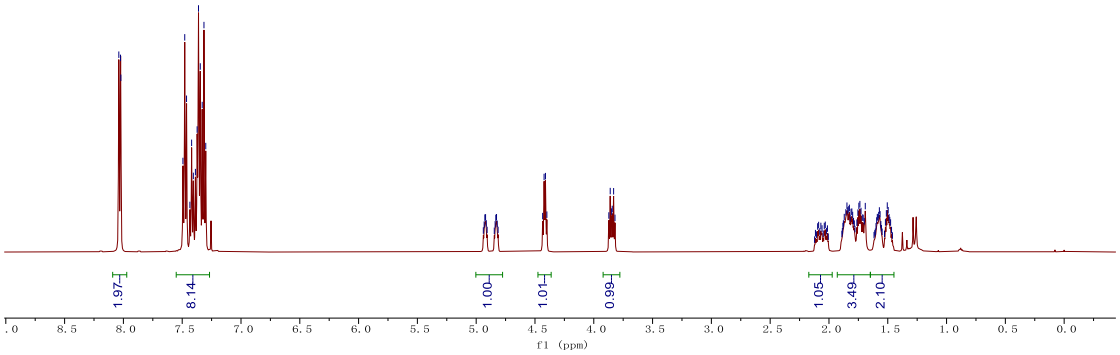
2ae

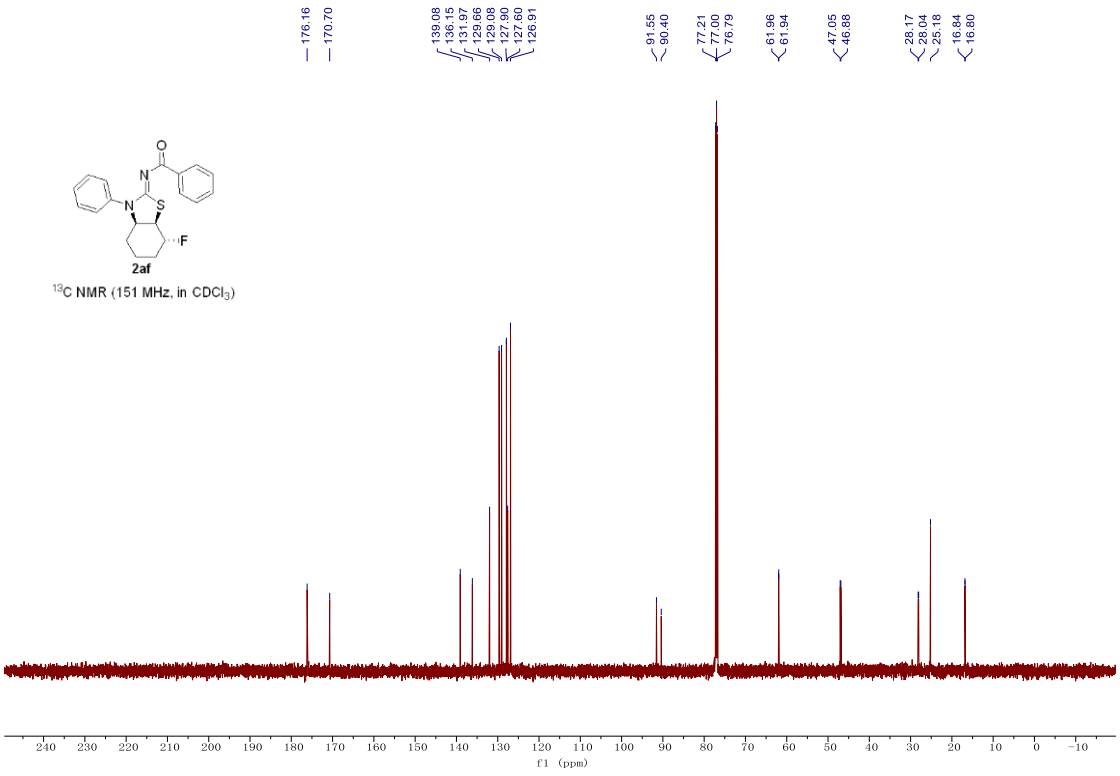
^{19}F NMR (565 MHz, in $CDCl_3$)

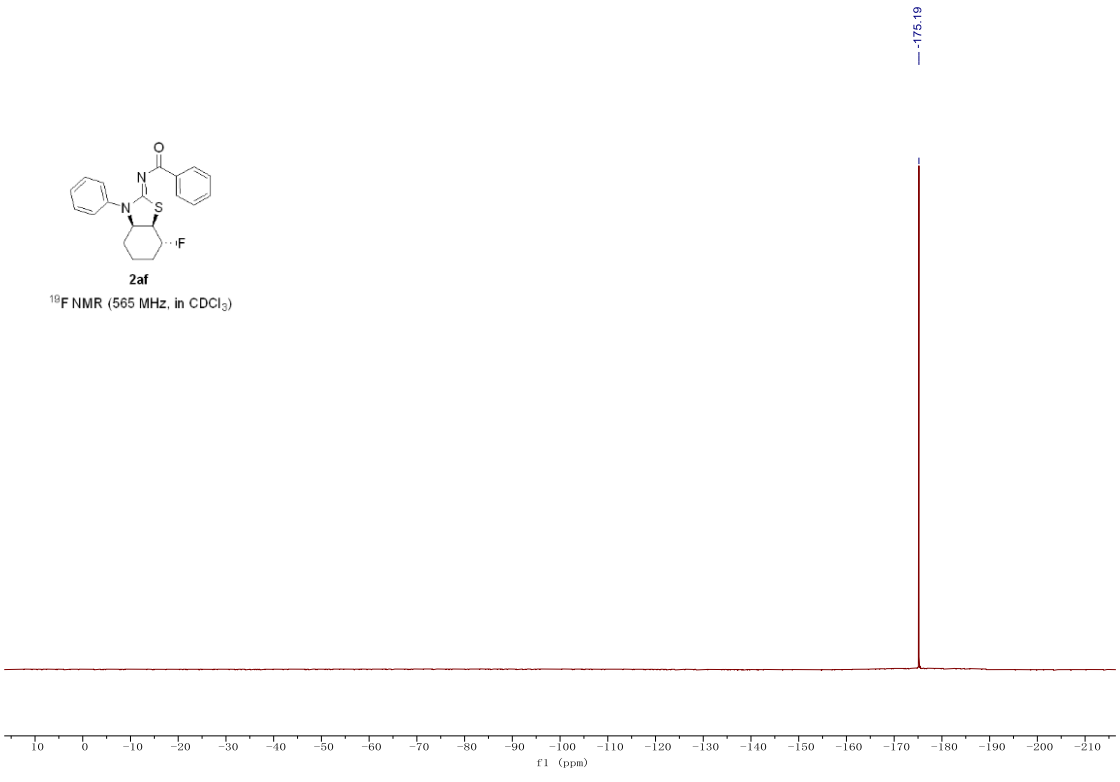


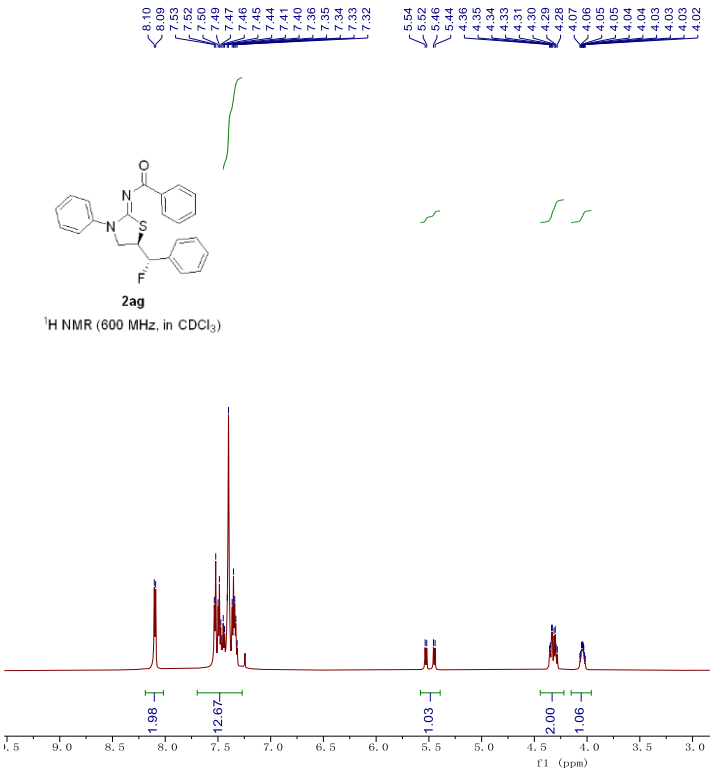
2af

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



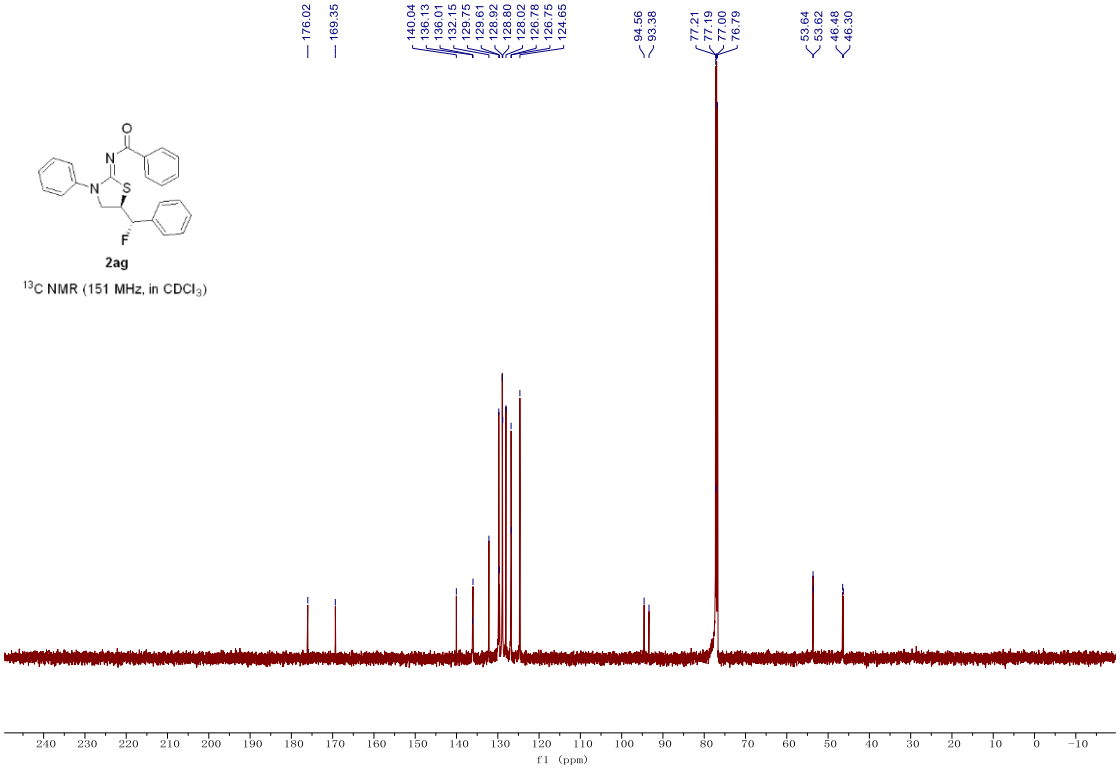

176.16
170.70
139.08
136.15
131.97
129.66
129.08
127.90
127.60
126.91
91.55
90.40
77.21
77.00
76.79
61.96
61.94
47.05
46.88
28.17
28.04
25.18
16.84
16.80
O
N
N
S
F
2af
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


-175.19
O
N
N
S
F
2af
19F NMR (565 MHz, in CDCl3)
f1 (ppm)



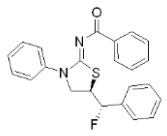
2ag

^{1}H NMR (600 MHz, in $CDCl_3$)



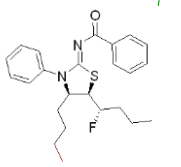
2ag

^{13}C NMR (151 MHz, in $CDCl_3$)



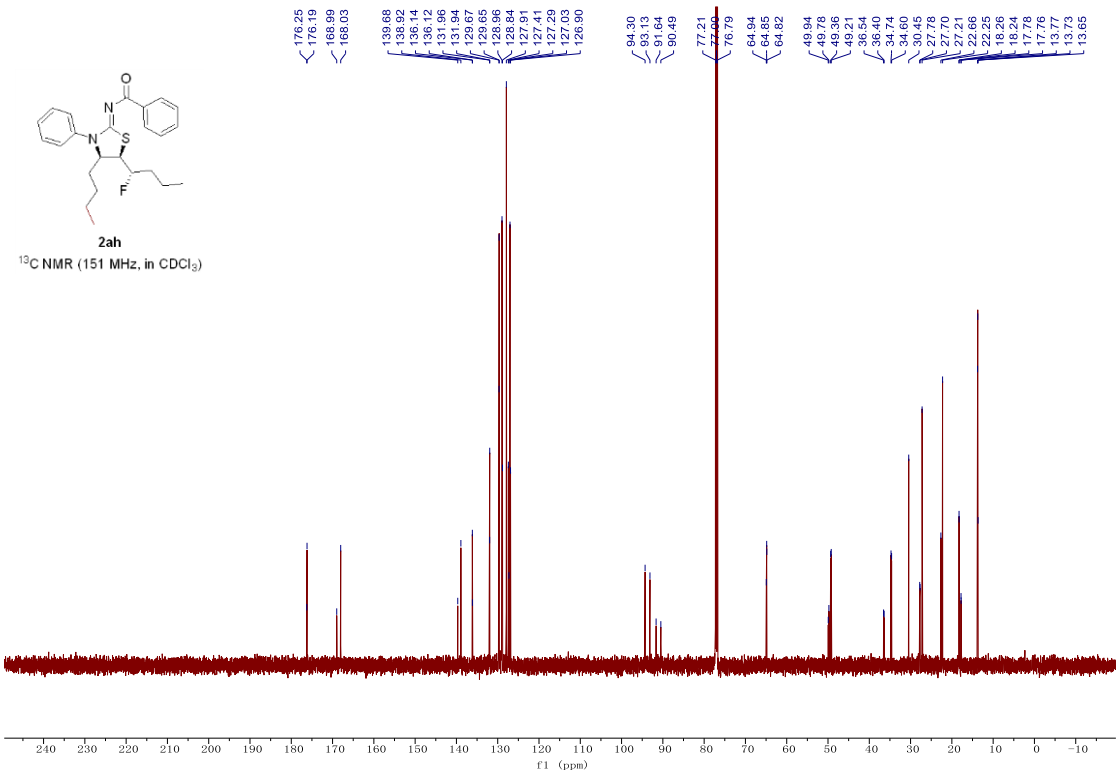
2ag

^{19}F NMR (565 MHz, in $CDCl_3$)



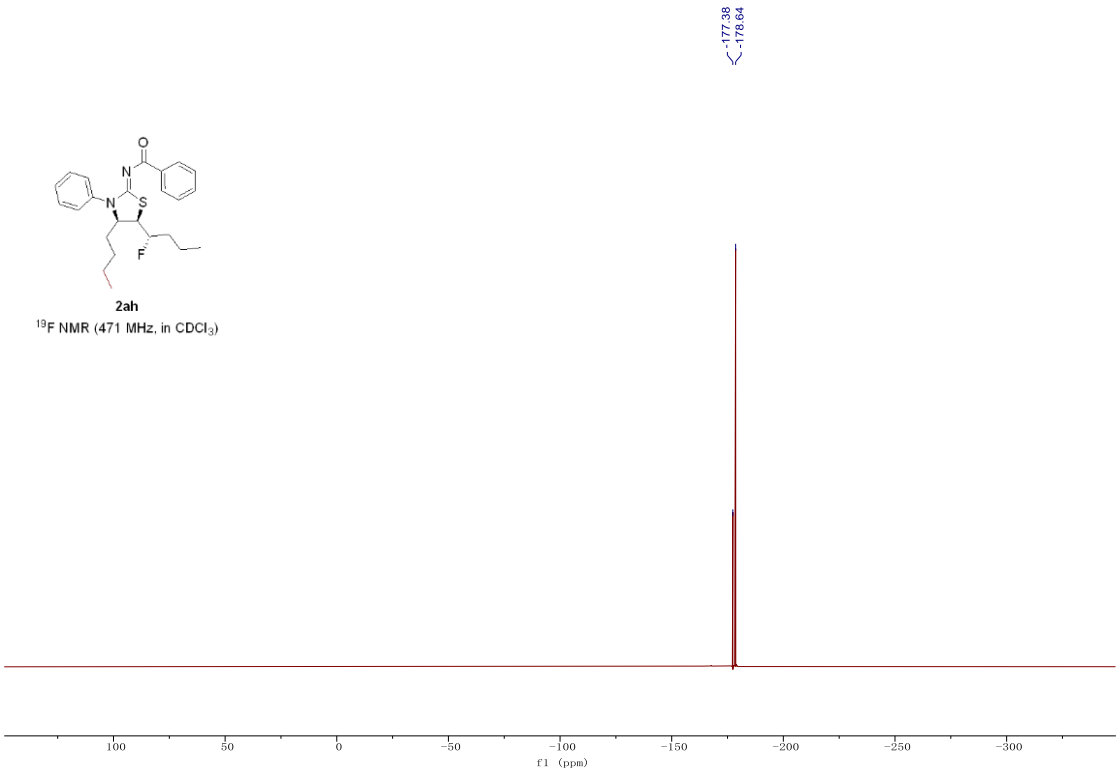
2ah

^{1}H NMR (600 MHz, in $CDCl_3$)



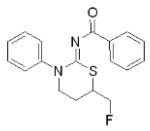
2ah

^{13}C NMR (151 MHz, in $CDCl_3$)



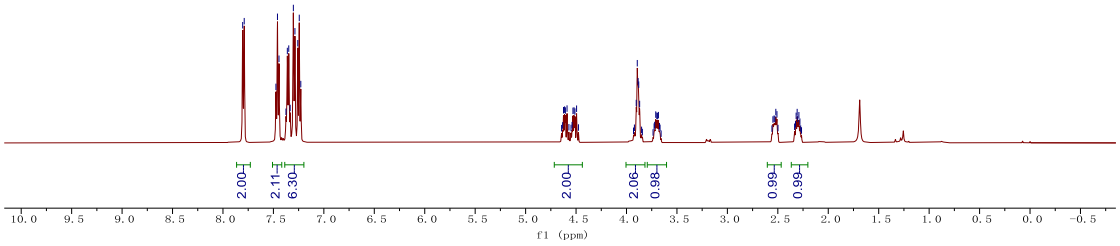
2ah

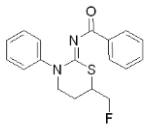
^{19}F NMR (471 MHz, in $CDCl_3$)



2ai

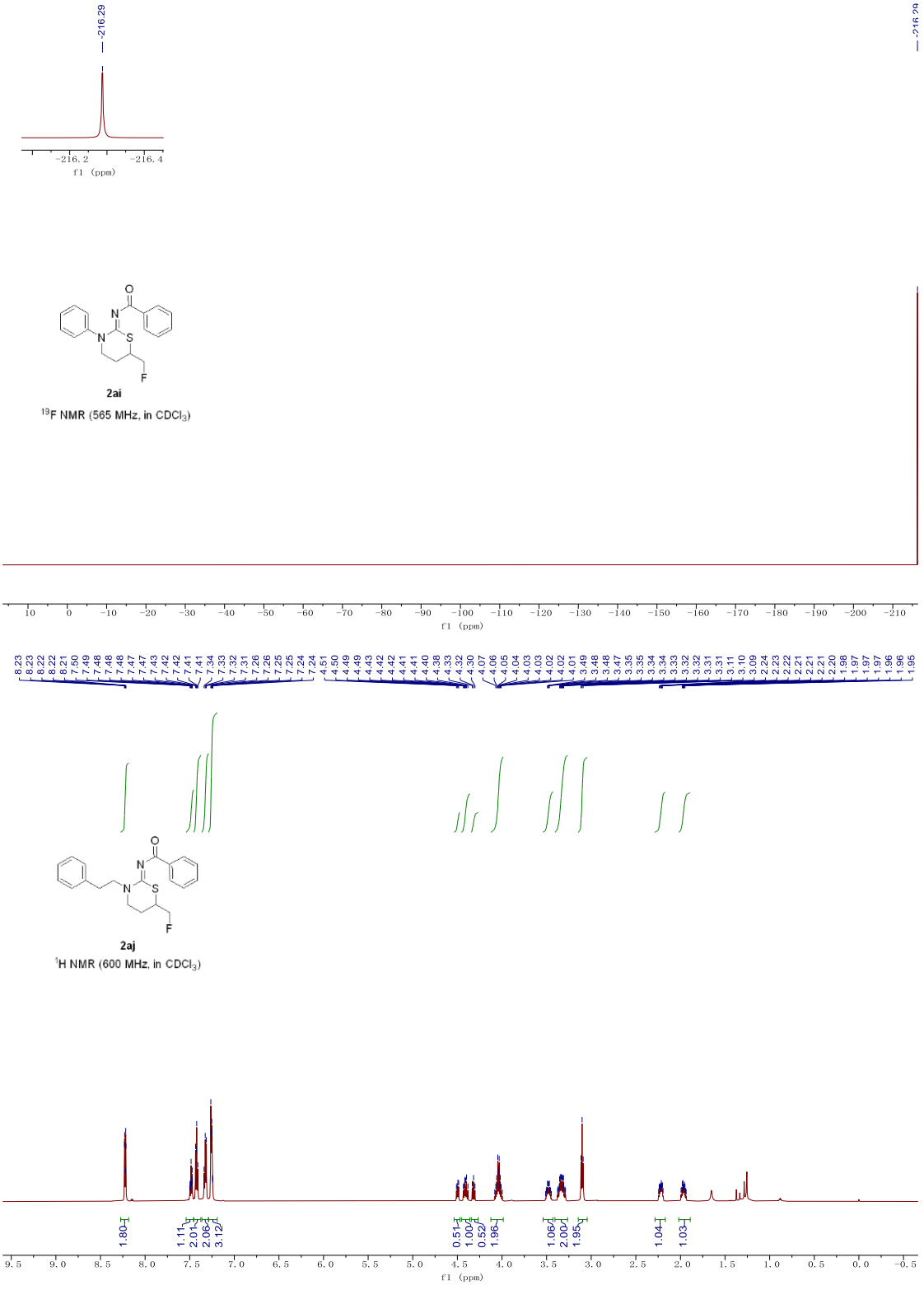
^{1}H NMR (500 MHz, in $CDCl_3$)

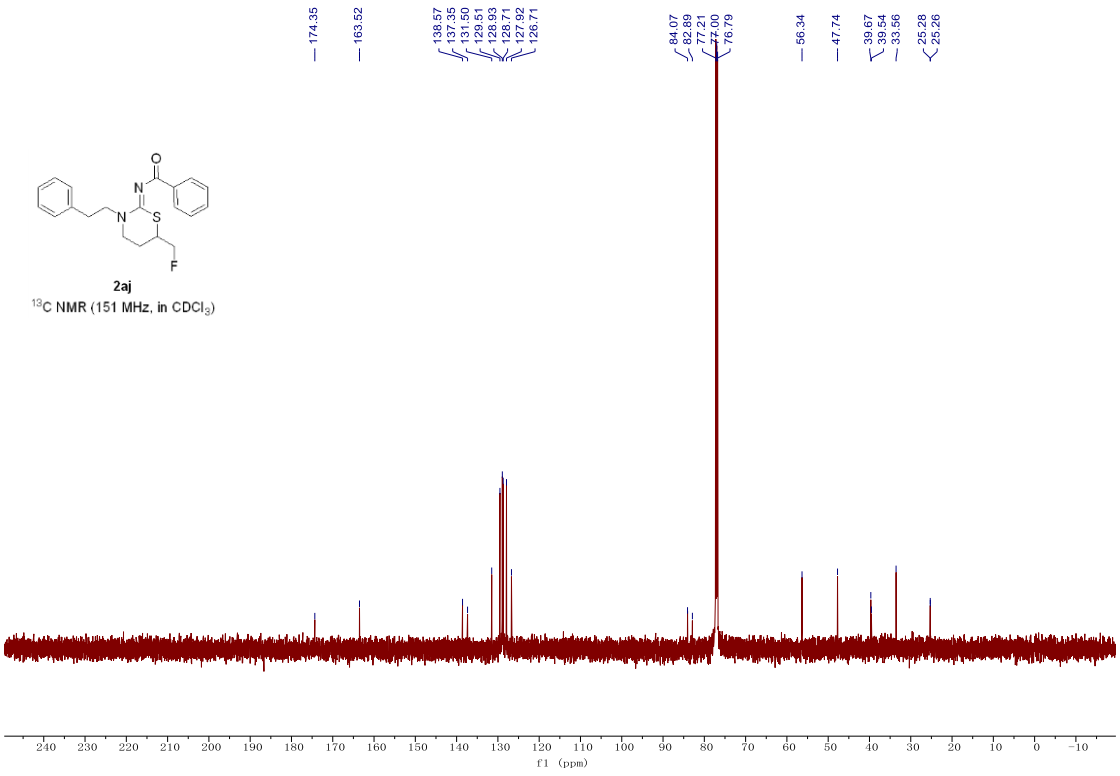




2ai

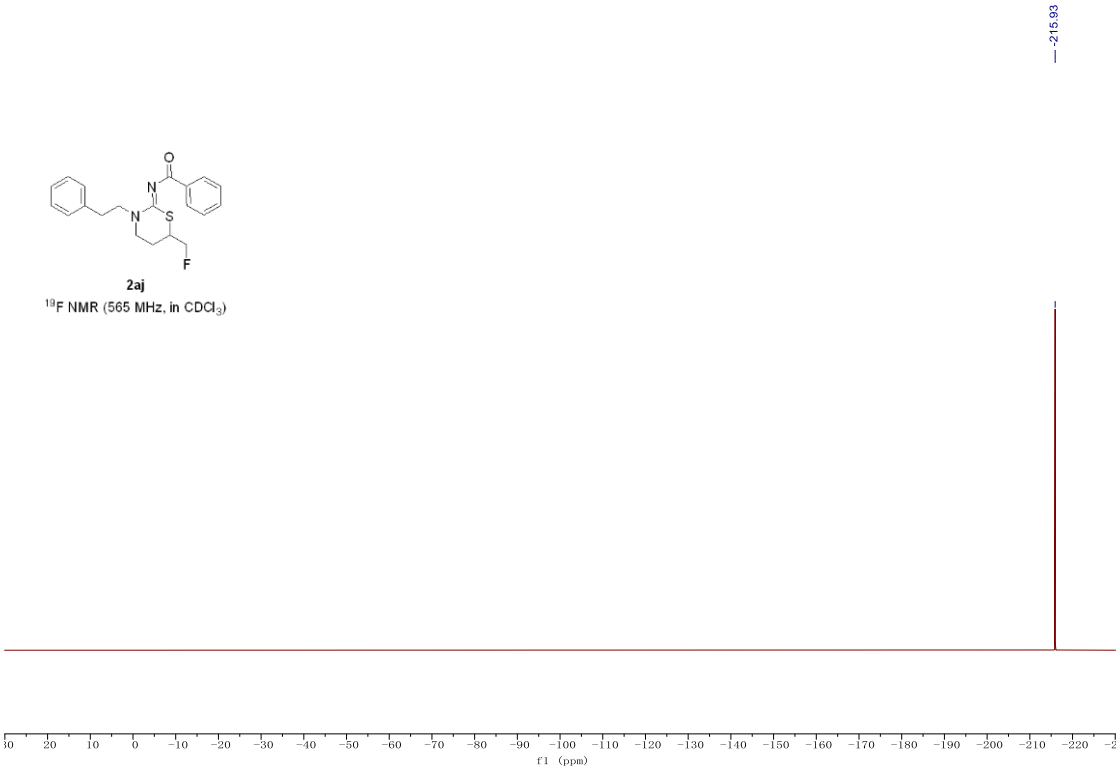
^{13}C NMR (126 MHz, in $CDCl_3$)


-216.29
-216.2
-216.4
f1 (ppm)
2ai
19F NMR (565 MHz, in CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
8.23 8.23 8.22 8.22 8.21 7.50 7.49 7.48 7.48 7.48 7.47 7.47 7.43 7.42 7.42 7.41 7.41 7.34 7.33 7.32 7.31 7.26 7.26 7.25 7.25 7.24 7.24 4.51 4.50 4.49 4.49 4.43 4.42 4.42 4.41 4.41 4.40 4.38 4.33 4.32 4.30 4.07 4.06 4.05 4.04 4.03 4.03 4.02 4.02 4.01 3.49 3.48 3.48 3.47 3.35 3.35 3.34 3.34 3.33 3.32 3.32 3.31 3.31 3.11 3.10 3.09 2.24 2.23 2.22 2.21 2.21 2.20 1.98 1.97 1.97 1.97 1.96 1.96 1.95
2aj
1H NMR (600 MHz, in CDCl3)
1.80 1.11 2.01 2.06 3.12 0.51 1.00 0.52 1.96 1.06 2.00 1.95 1.04 1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



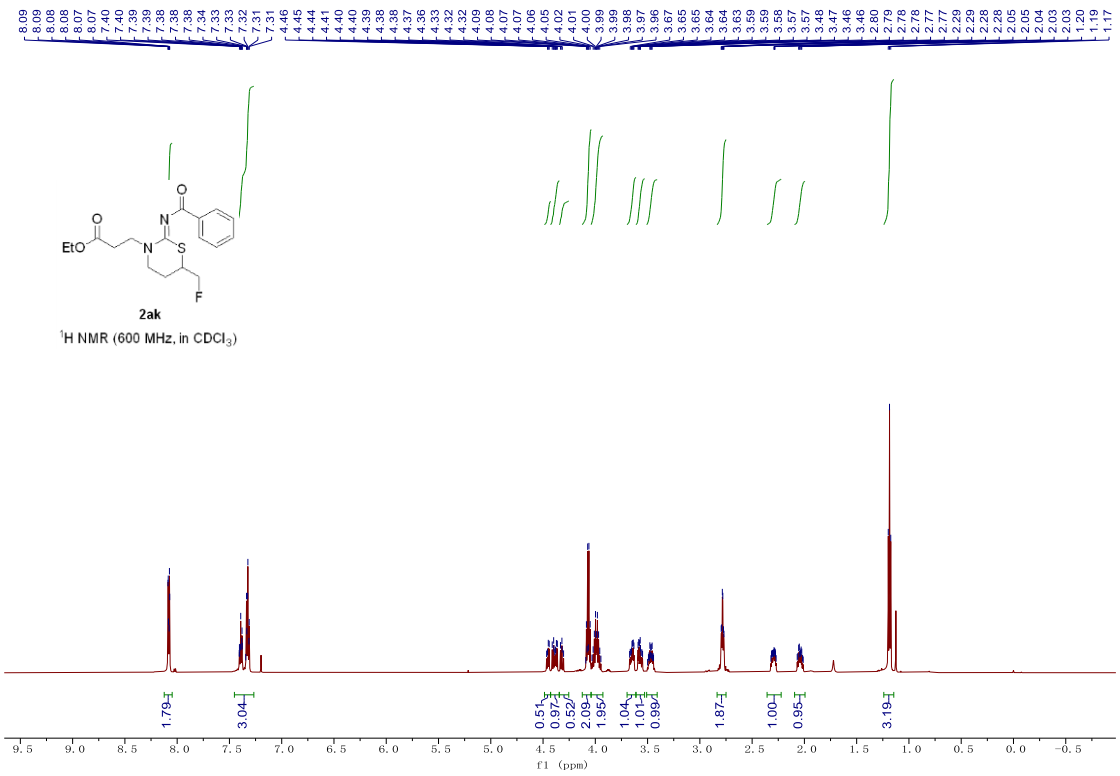
2aj

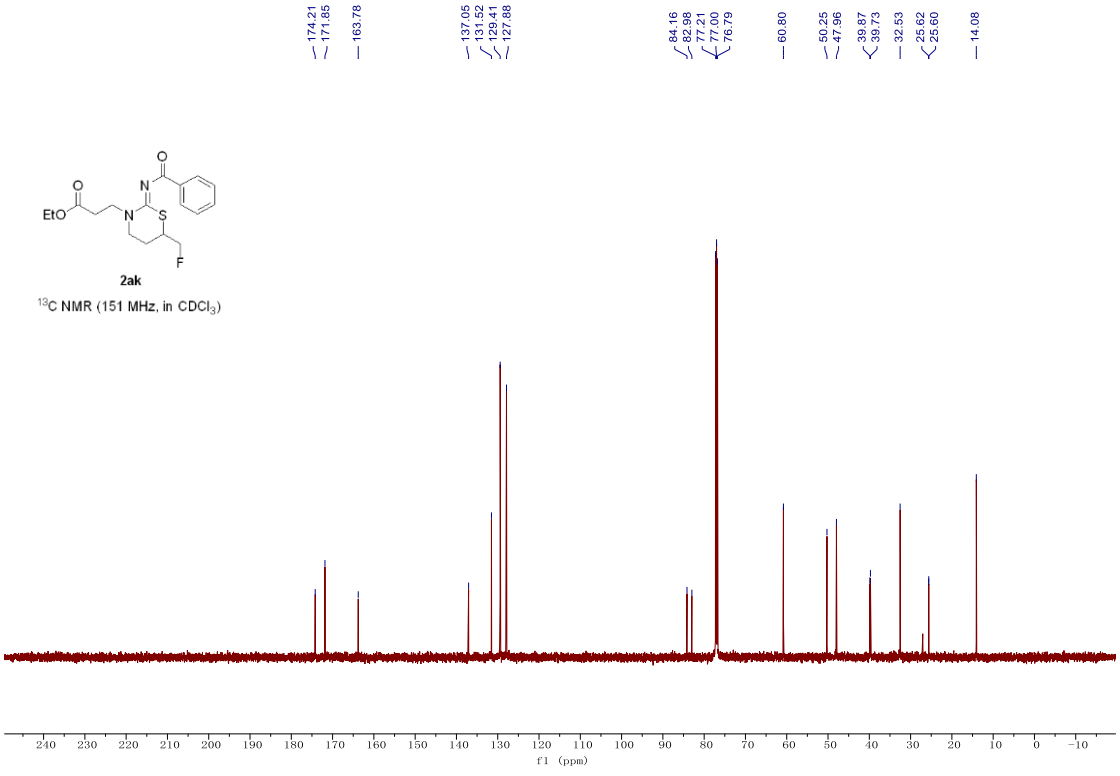
^{13}C NMR (151 MHz, in $CDCl_3$)

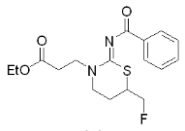


2aj

^{19}F NMR (565 MHz, in $CDCl_3$)

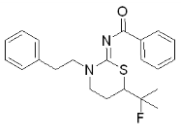

8.09 8.09 8.08 8.08 8.07 8.07 7.40 7.40 7.39 7.39 7.38 7.38 7.34 7.33 7.33 7.32 7.31 7.31
4.46 4.45 4.44 4.41 4.40 4.40 4.39 4.38 4.38 4.37 4.36 4.33 4.32 4.32 4.09 4.08 4.07 4.07 4.06 4.05 4.02 4.01 4.00 3.99 3.99 3.98 3.97 3.96 3.67 3.65 3.65 3.64 3.64 3.63 3.59 3.59 3.58 3.57 3.57 3.48 3.47 3.46 3.46 2.80 2.79 2.78 2.78 2.77 2.77 2.29 2.29 2.28 2.28 2.05 2.05 2.04 2.03 2.03 1.20 1.19 1.17
O
N
O
EtO
N
S
F
2ak
1H NMR (600 MHz, in CDCl3)
1.79 3.04 0.51 0.97 0.52 2.09 1.95 1.04 1.01 0.99 1.87 1.00 0.95 3.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


174.21 171.85 163.78 137.05 131.52 129.41 127.88 84.16 82.98 77.21 77.00 76.79 60.80 50.25 47.96 39.87 39.73 32.53 25.62 25.60 14.08
O
N
O
EtO
N
S
F
2ak
13C NMR (151 MHz, in CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



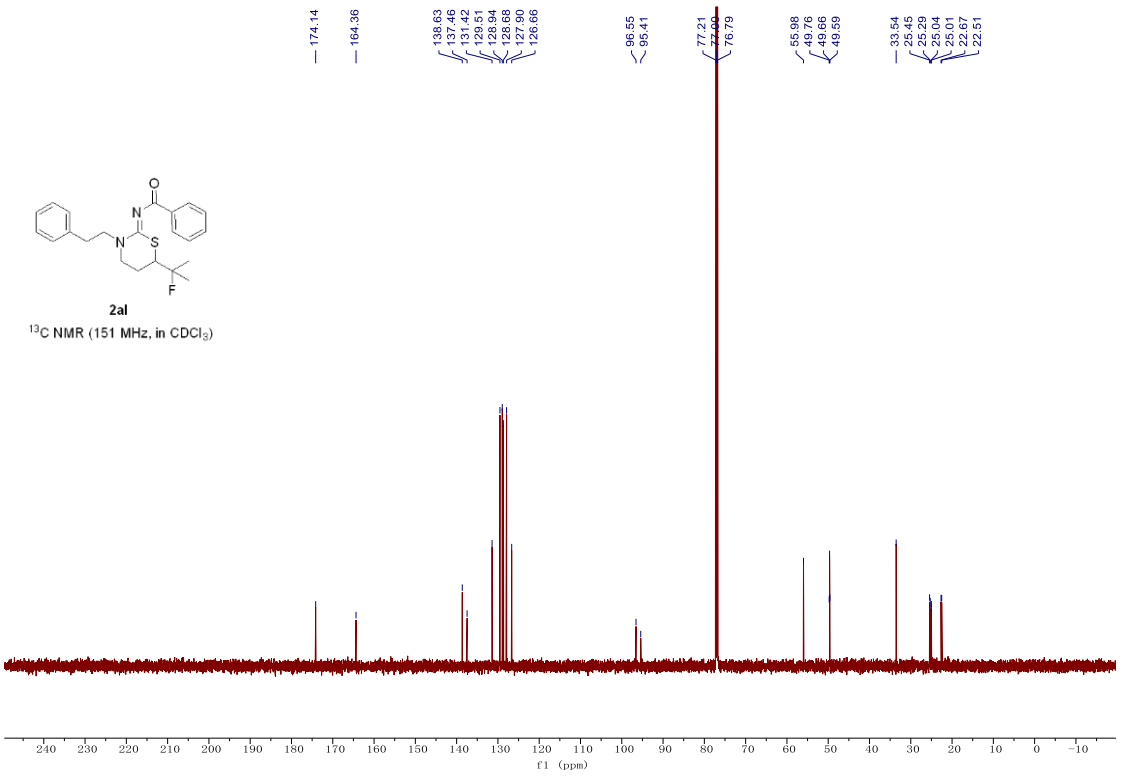
2ak

^{19}F NMR (565 MHz, in $CDCl_3$)



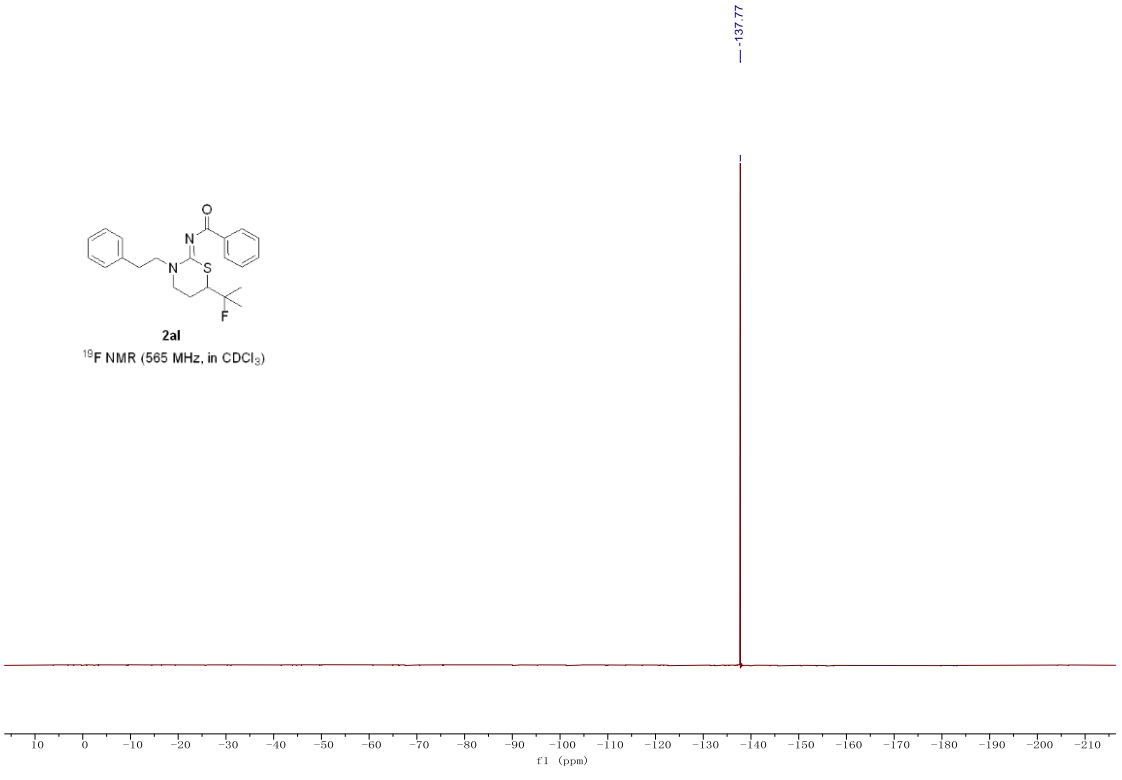
2al

^{1}H NMR (600 MHz, in $CDCl_3$)



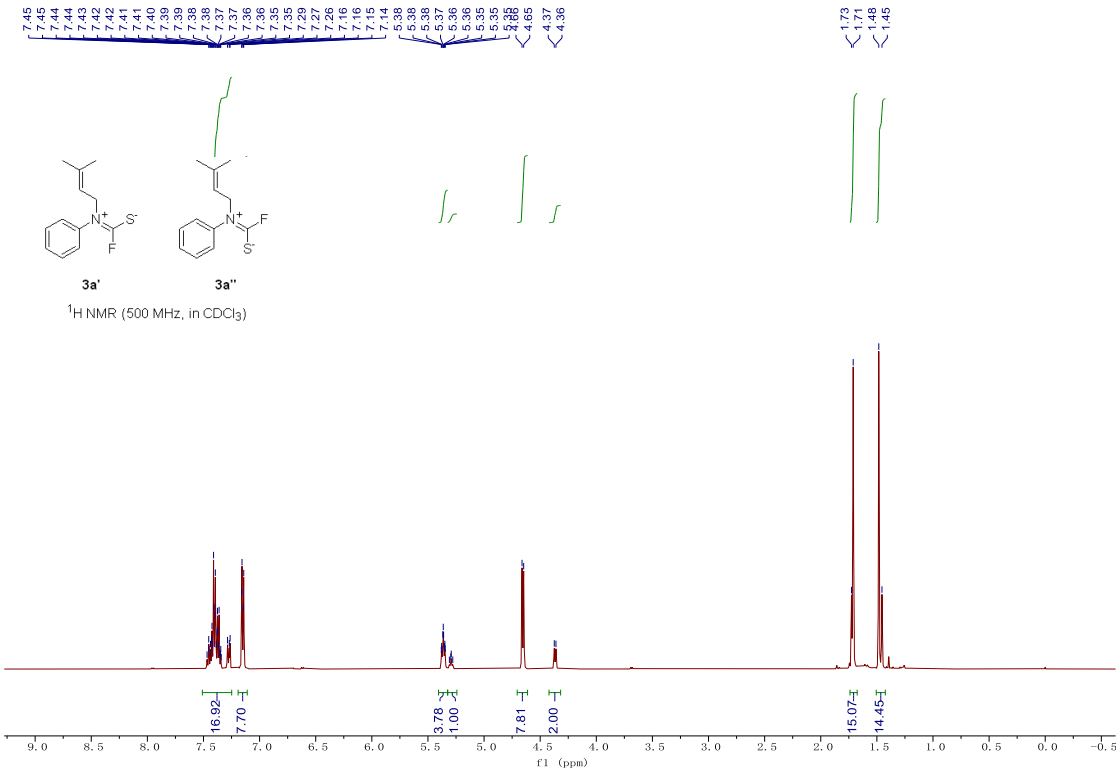
2al

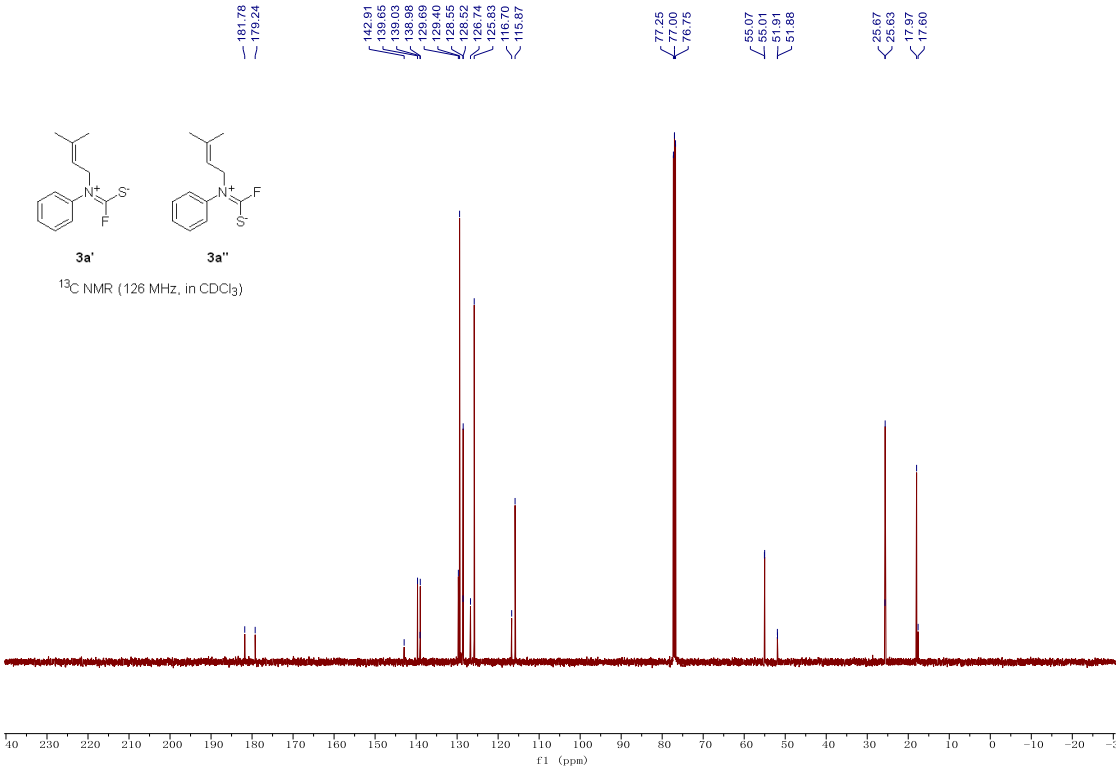
^{13}C NMR (151 MHz, in $CDCl_3$)

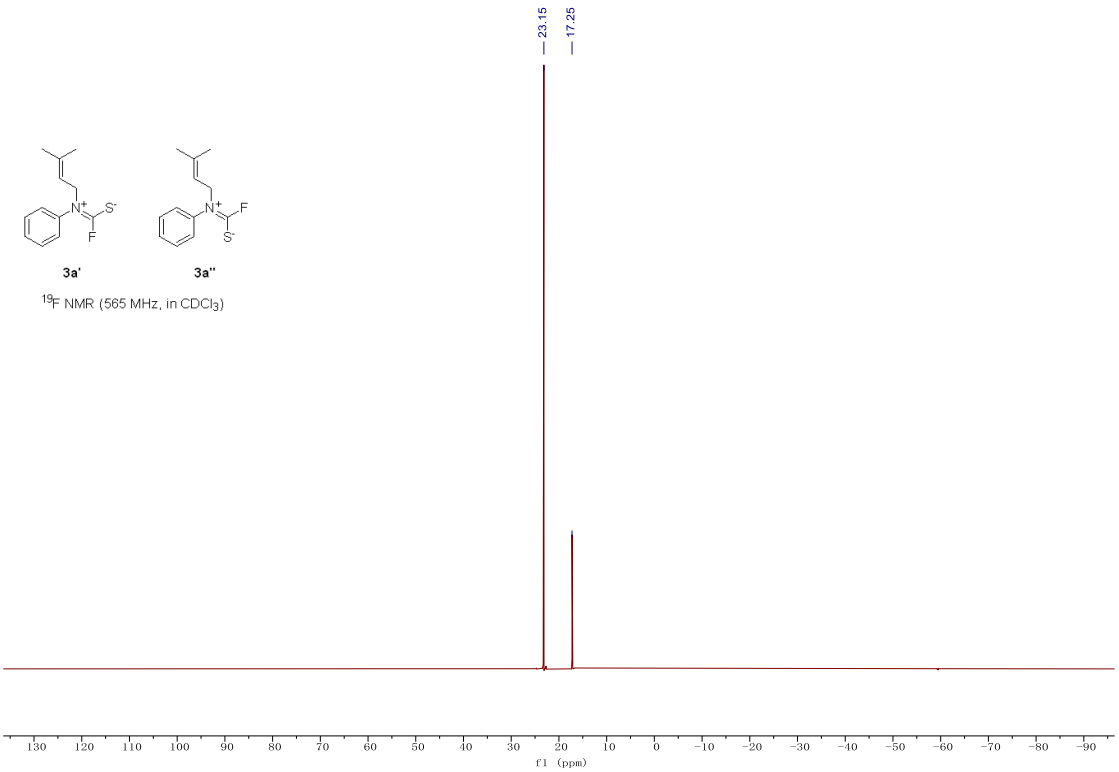


2al

^{19}F NMR (565 MHz, in $CDCl_3$)

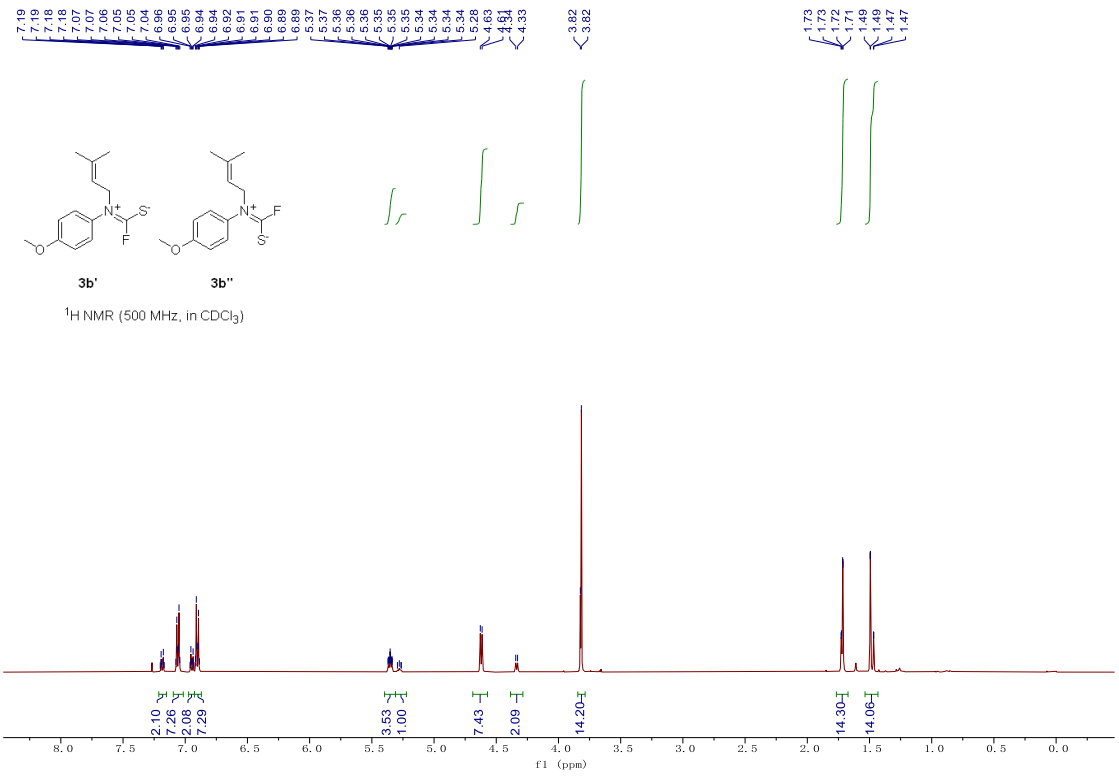

3a'
3a''
1H NMR (500 MHz, in CDCl3)
f1 (ppm)


3a'
3a''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)



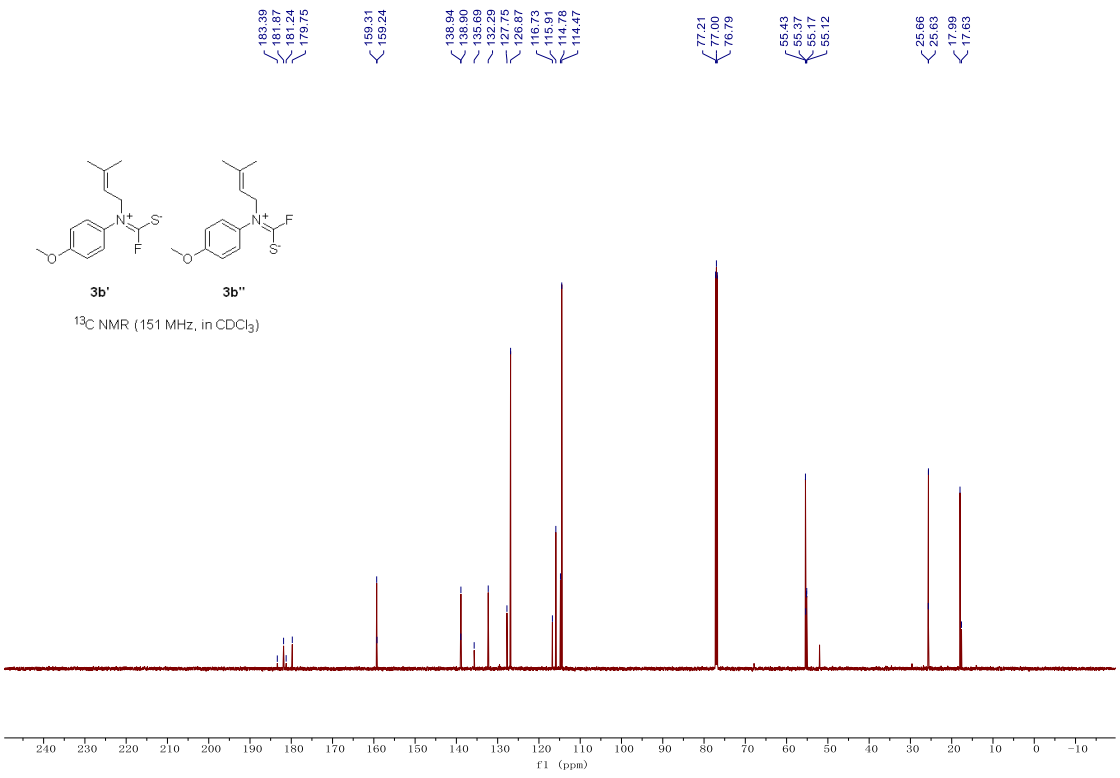
3a' **3a''**

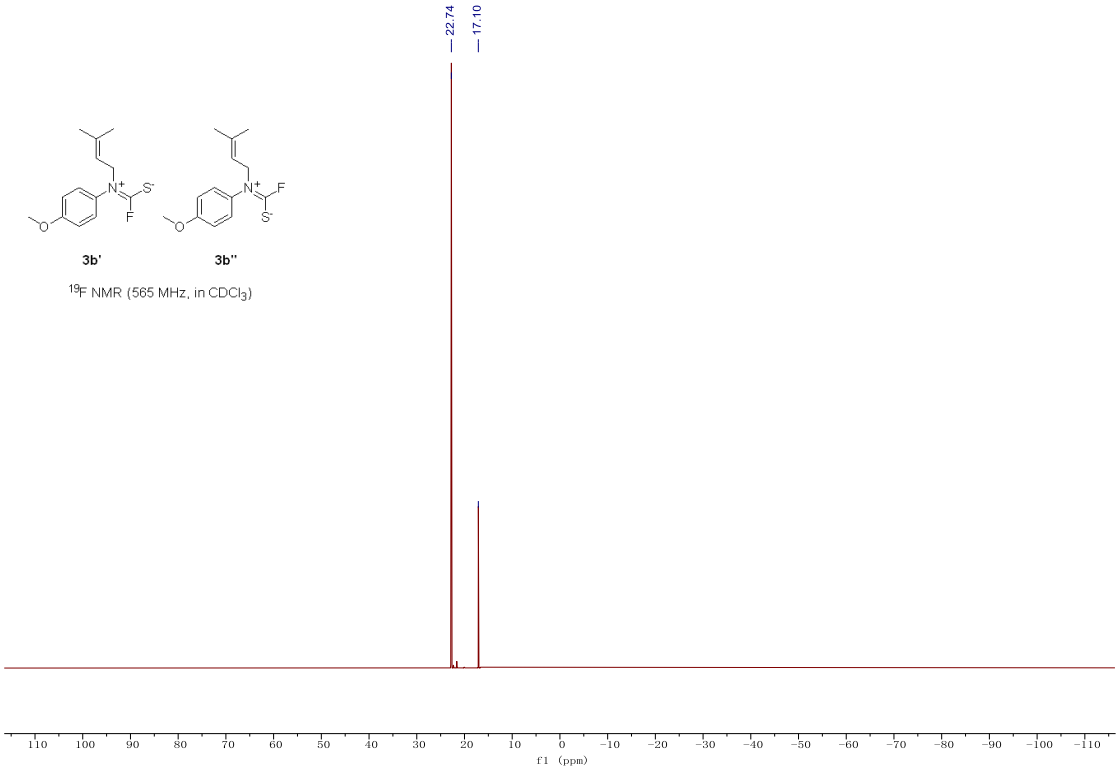
^{19}F NMR (565 MHz, in $CDCl_3$)

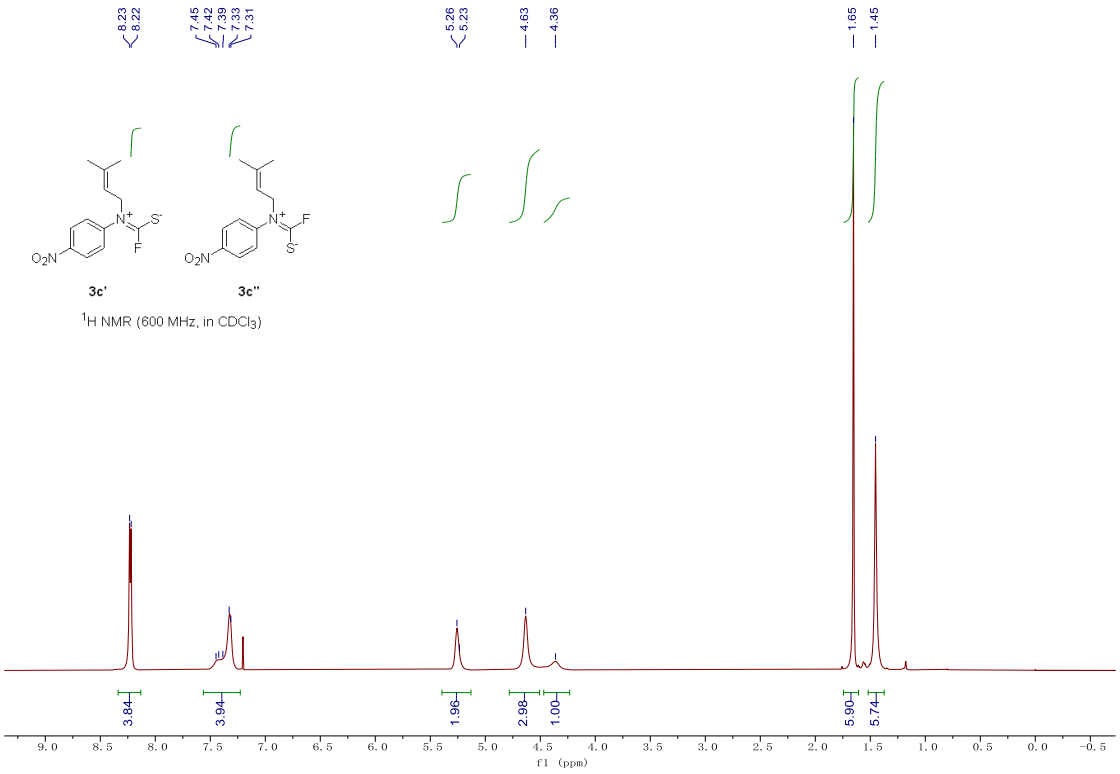


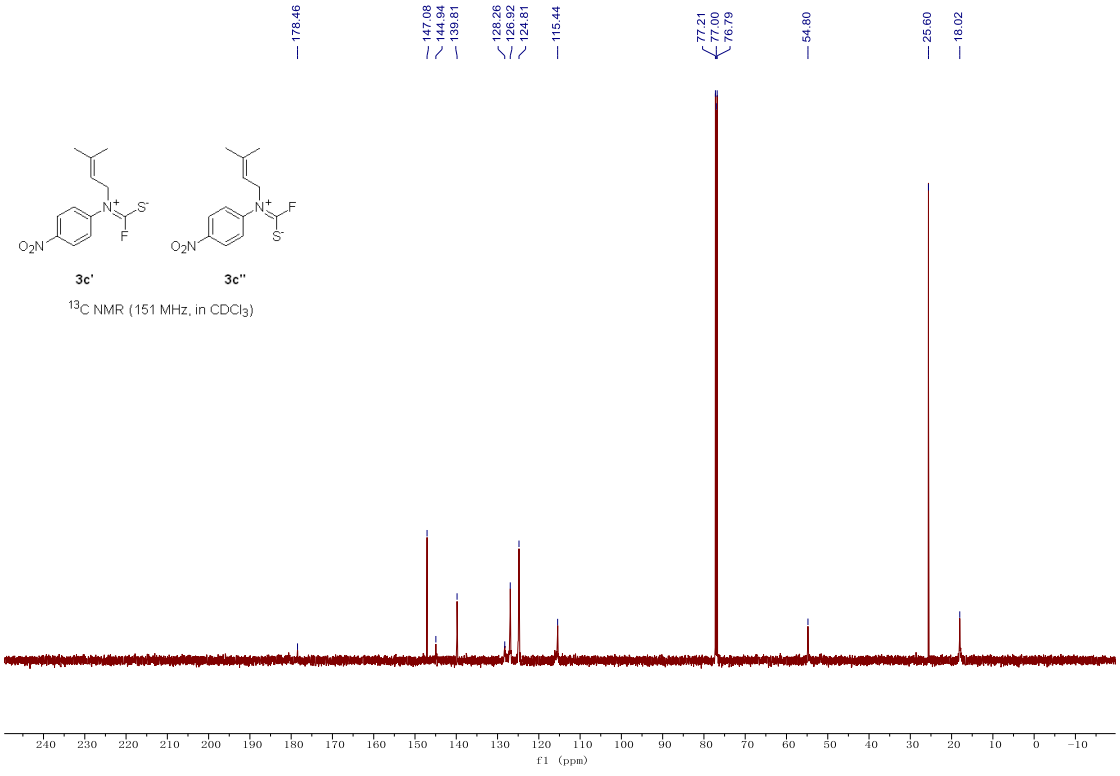
3b' **3b''**

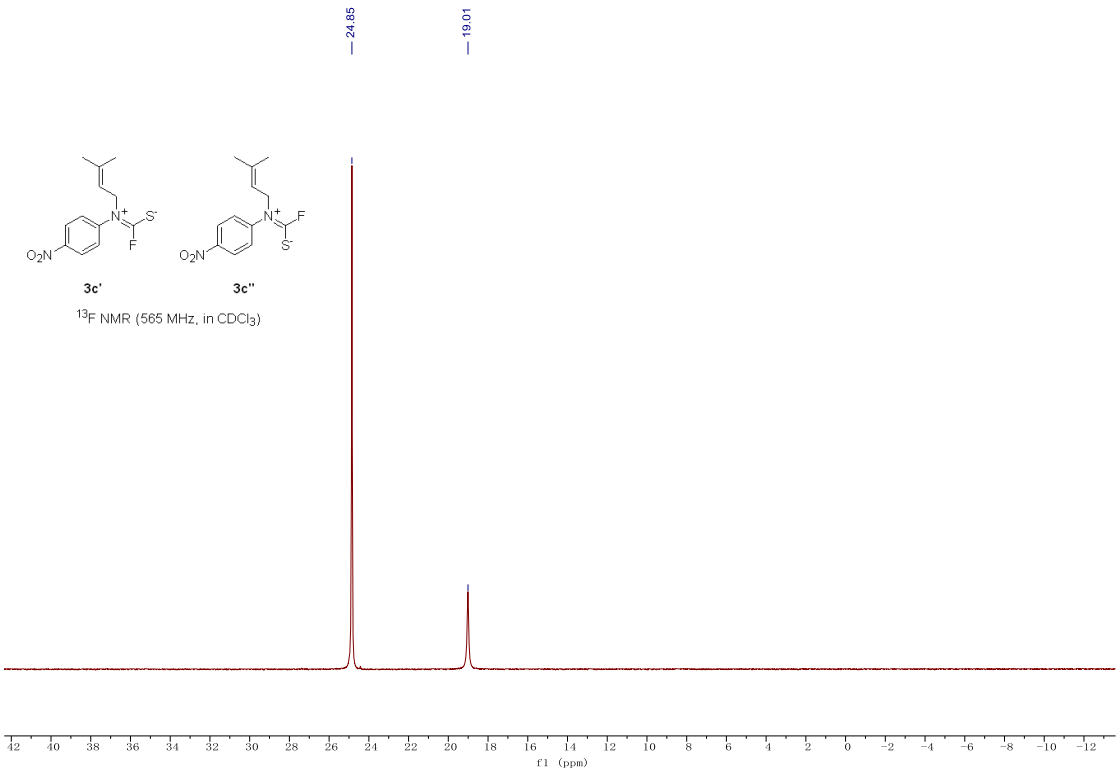
^{1}H NMR (500 MHz, in $CDCl_3$)

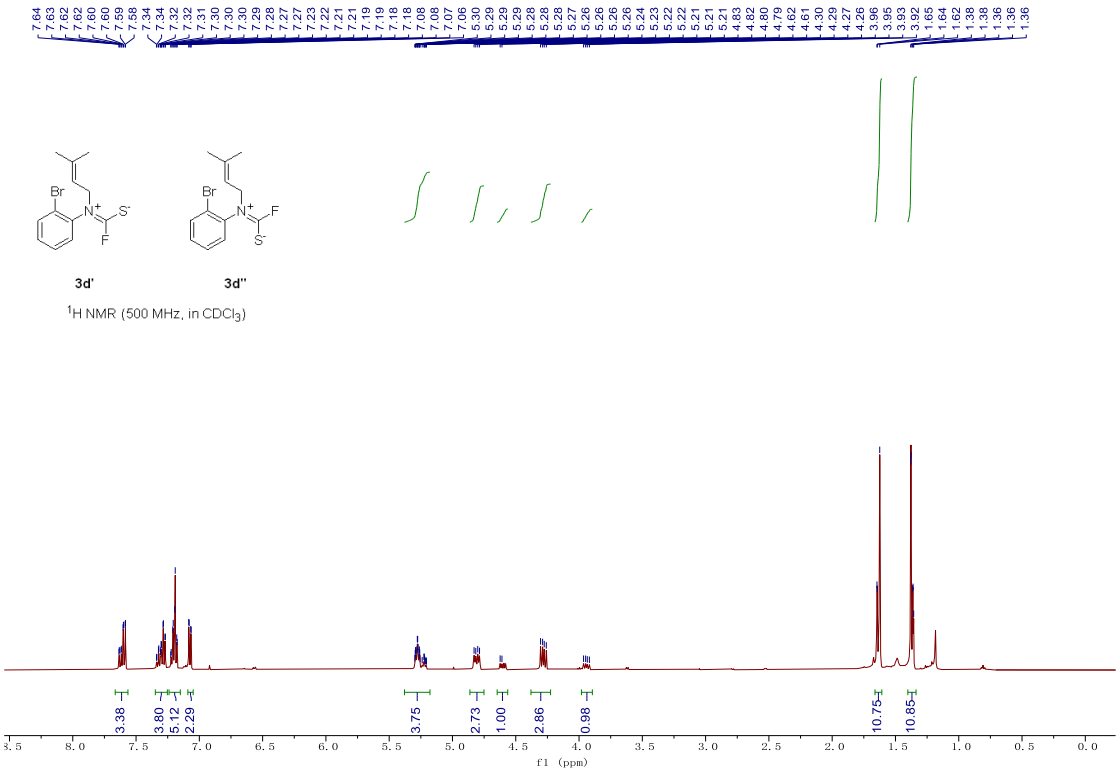

183.39
181.87
181.24
179.75
159.31
159.24
138.94
138.90
135.69
132.29
127.75
126.87
116.73
115.91
114.78
114.47
77.21
77.00
76.79
55.43
55.37
55.17
55.12
25.66
25.63
17.99
17.63
3b'
3b''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

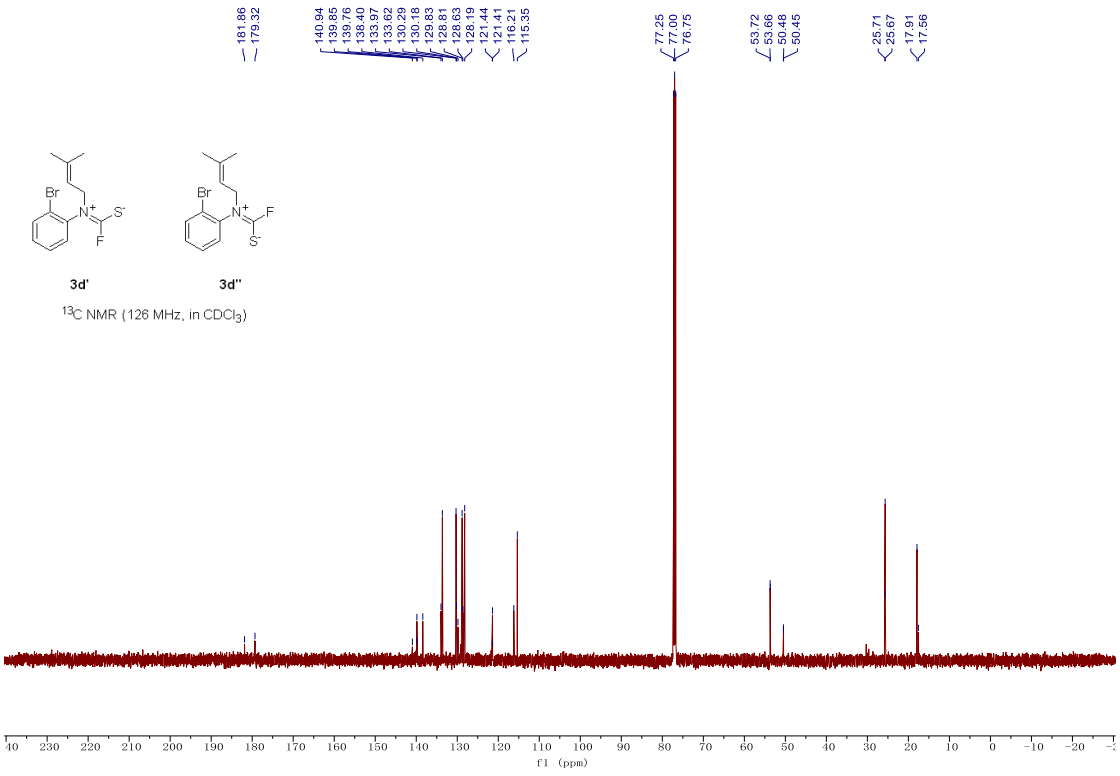

22.74
17.10
3b'
3b''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

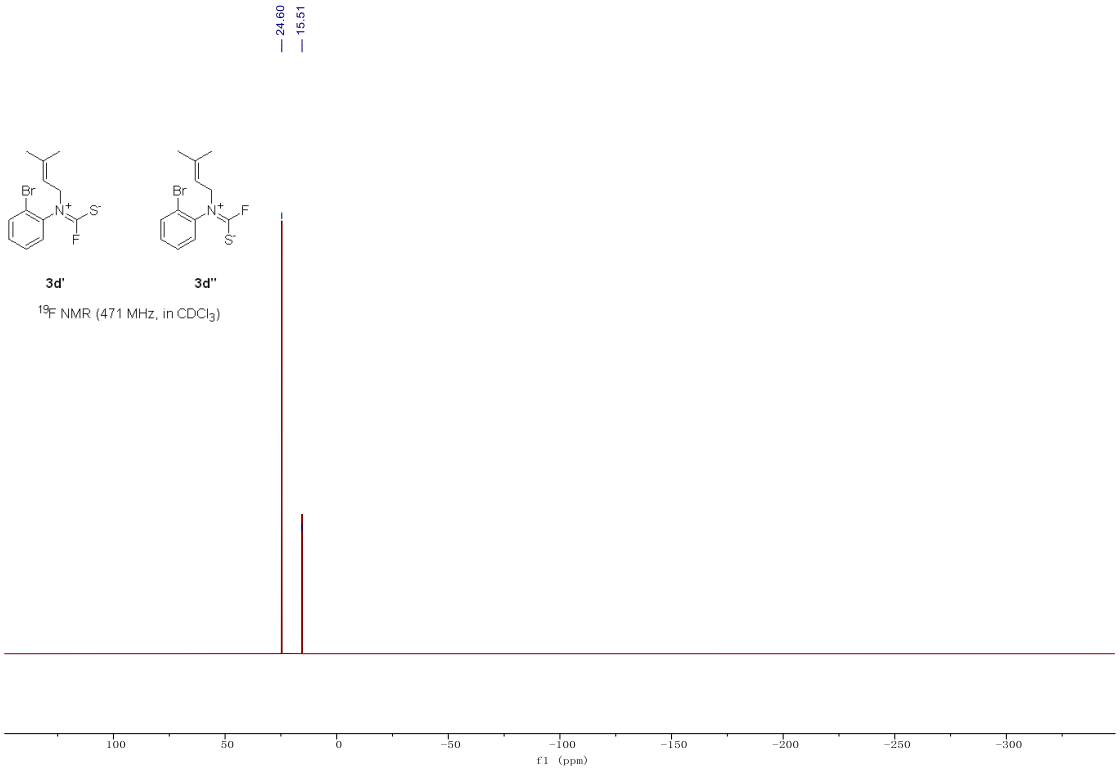

8.23
8.22
7.45
7.42
7.39
7.33
7.31
5.26
5.23
4.63
4.36
1.65
1.45
3c'
3c''
^{1}H NMR (600 MHz, in CDCl$_3$)
3.84
3.94
1.96
2.98
1.00
5.90
5.74
f1 (ppm)

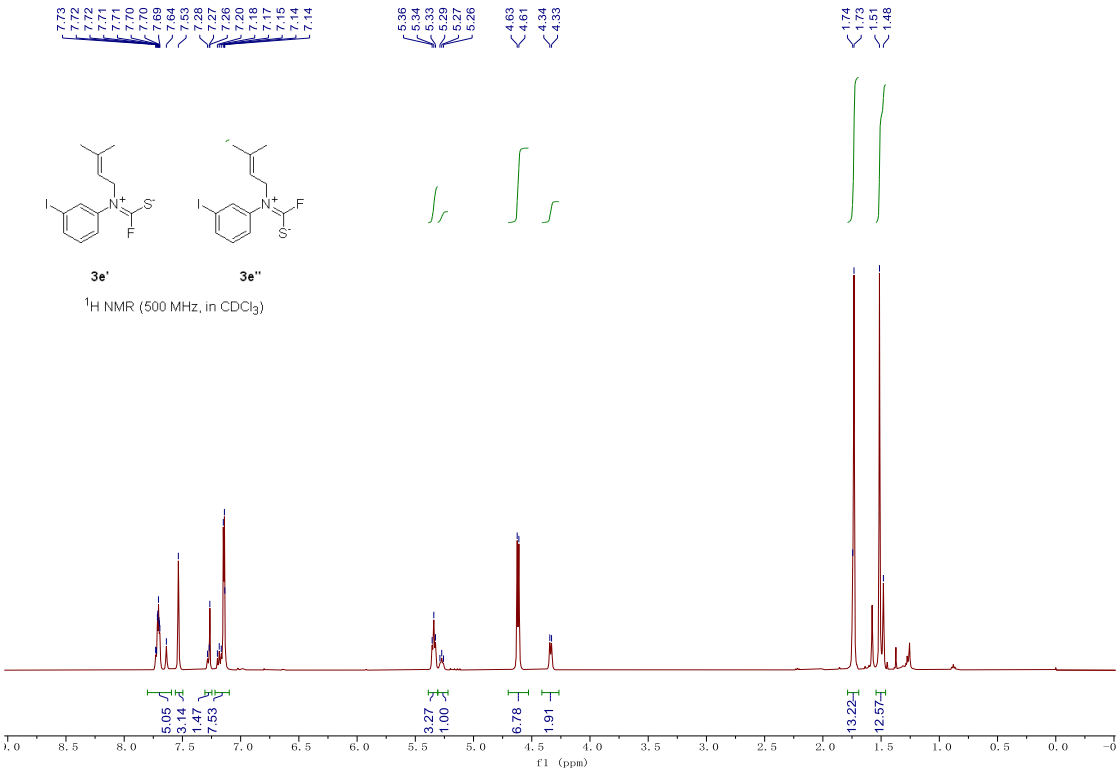

178.46
147.08
144.94
139.81
128.26
126.92
124.81
115.44
77.21
77.00
76.79
54.80
25.60
18.02
3c'
3c''
^{13}C NMR (151 MHz, in CDCl$_3$)
f1 (ppm)

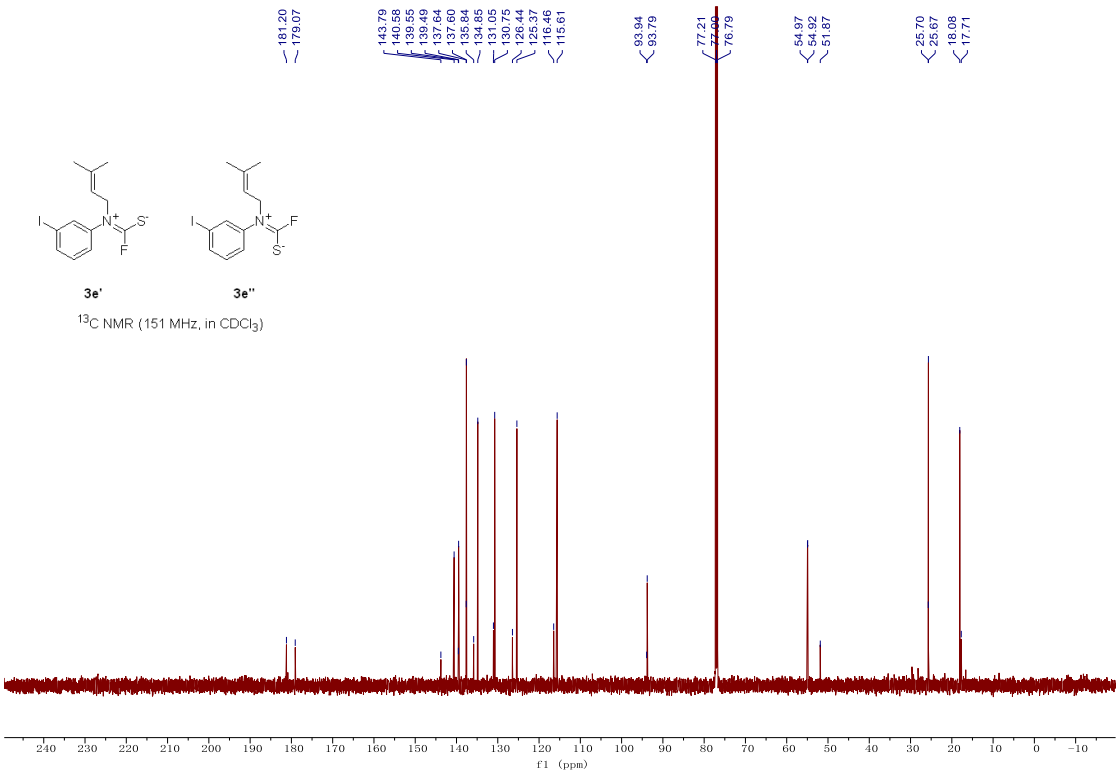

— 24.85
— 19.01
3c'
3c''
^{13}F NMR (565 MHz, in CDCl$_3$)
f1 (ppm)

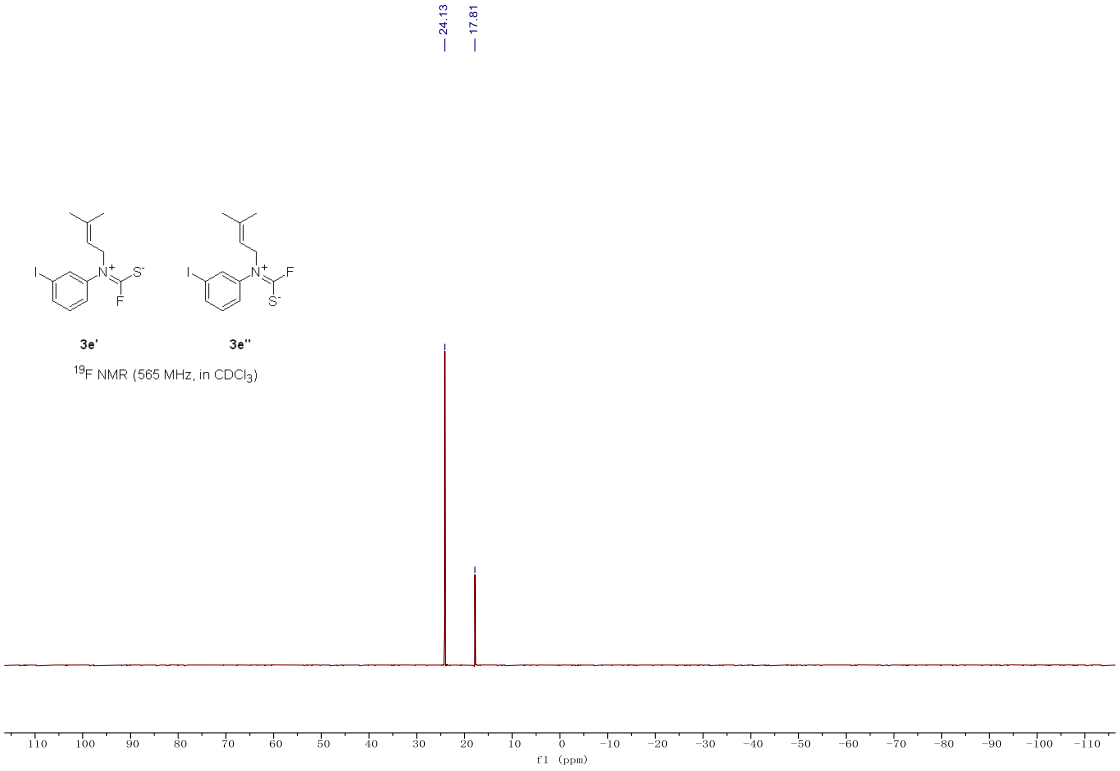

3d'
3d''
^{1}H NMR (500 MHz, in CDCl$_3$)
3.38
3.80
5.12
2.29
3.75
2.73
1.00
2.86
0.98
10.75
10.85
f1 (ppm)

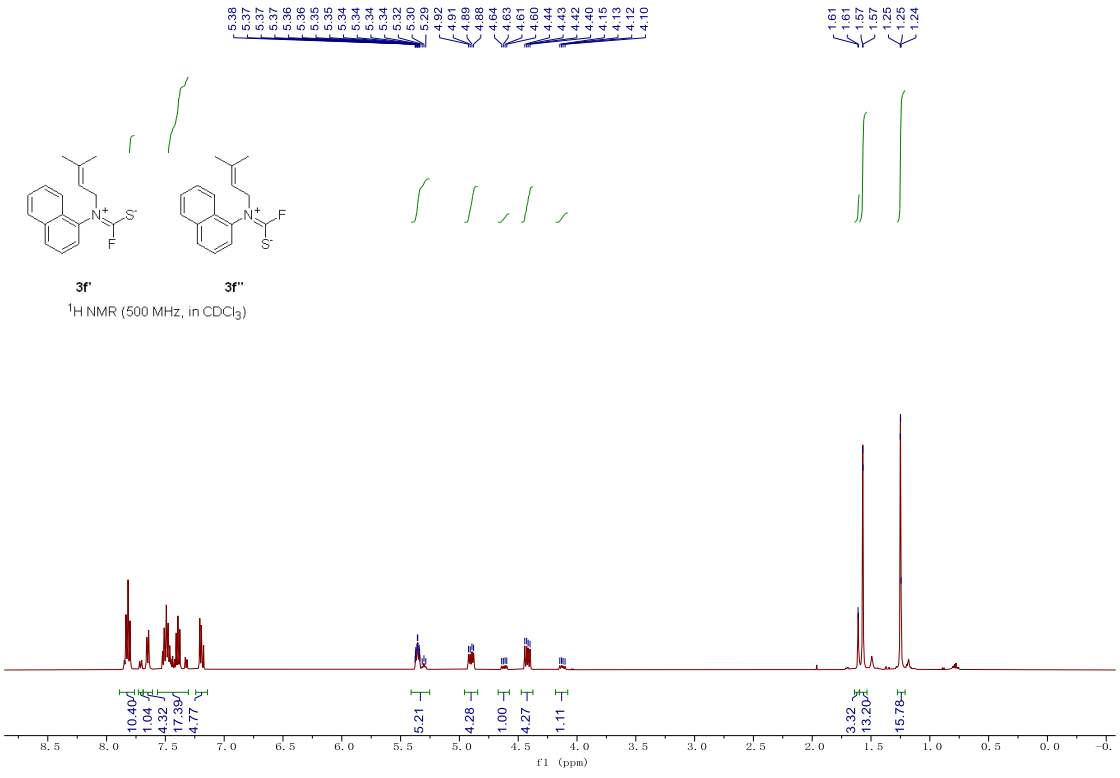

181.86
179.32
140.94
139.85
139.76
138.40
133.97
133.62
130.29
130.18
129.83
128.81
128.63
128.19
121.44
121.41
116.21
115.35
77.25
77.00
76.75
53.72
53.66
50.48
50.45
25.71
25.67
17.91
17.56
Br
N+
S-
F
3d'
3d''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

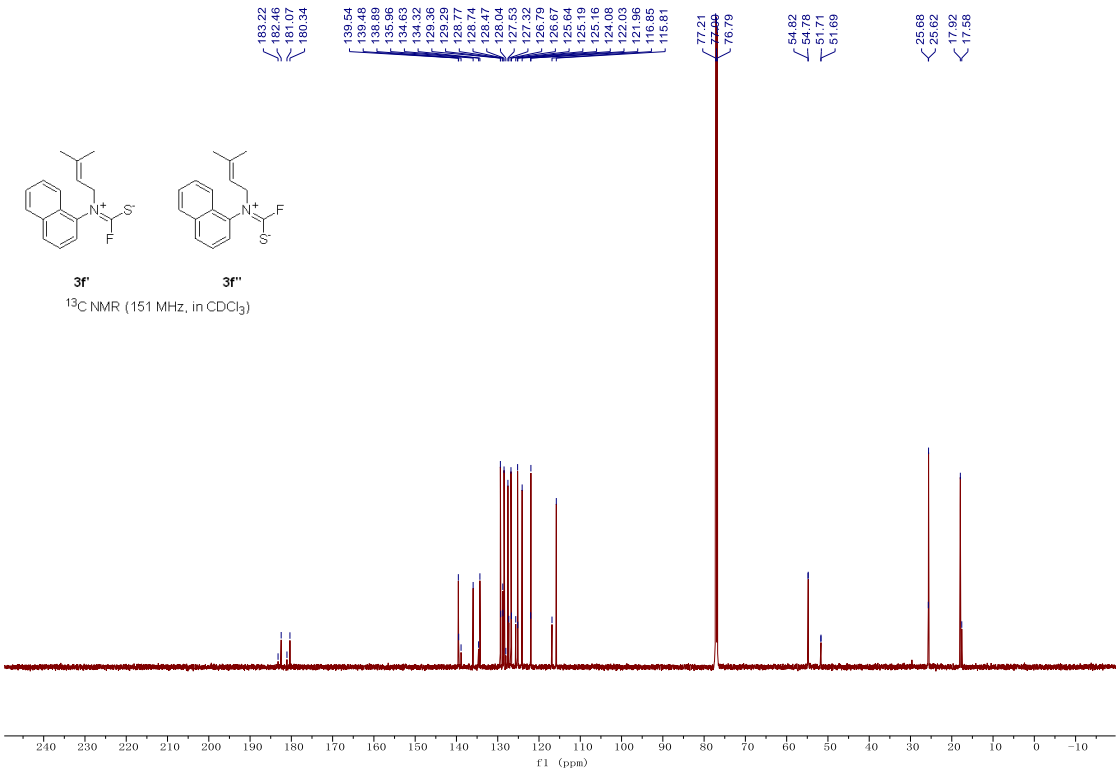

24.60
15.51
Br
N+
S-
F
3d'
3d''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)


7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.69
7.64
7.53
7.28
7.27
7.26
7.20
7.18
7.17
7.15
7.14
7.14
5.36
5.34
5.33
5.29
5.27
5.26
4.63
4.61
4.34
4.33
1.74
1.73
1.51
1.48
3e'
3e''
1H NMR (500 MHz, in CDCl3)
5.05
3.14
1.47
7.53
3.27
1.00
6.78
1.91
13.22
12.57
f1 (ppm)


181.20
179.07
143.79
140.58
139.55
139.49
137.64
137.60
135.64
134.65
131.05
130.75
126.44
125.37
116.46
115.61
93.94
93.79
77.21
77.00
76.79
54.97
54.92
51.87
25.70
25.67
18.08
17.71
3e'
3e''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

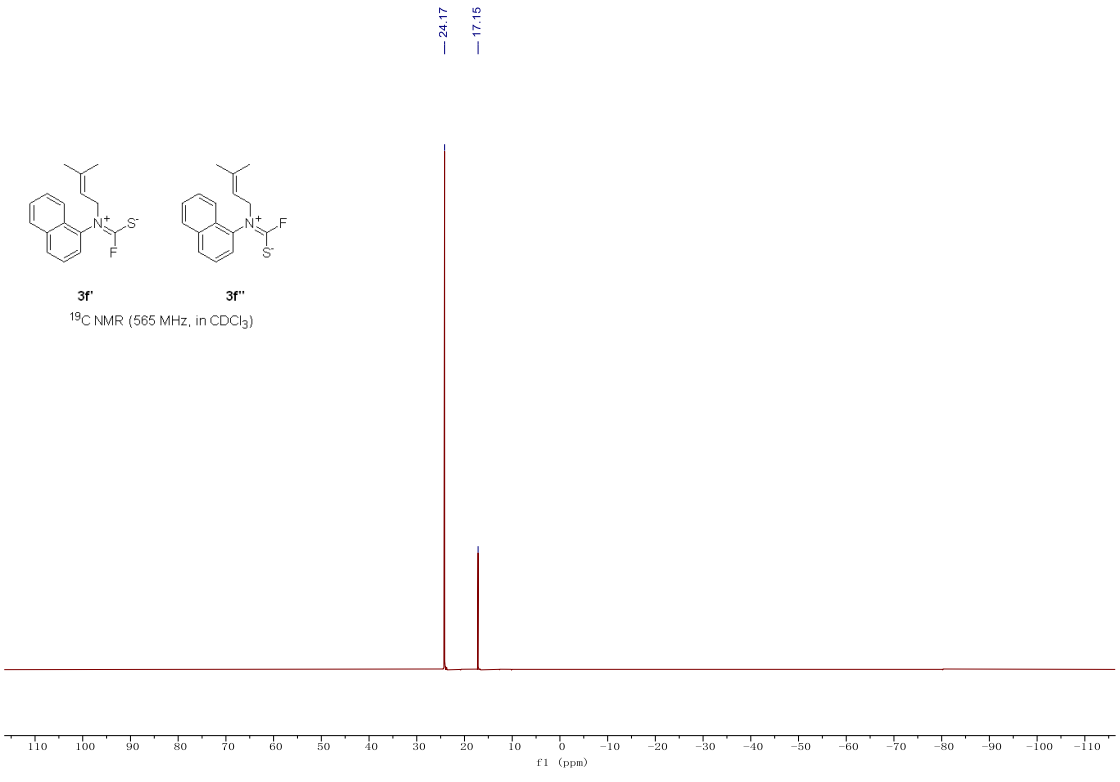

24.13
17.81
3e'
3e''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)


3f'
3f''
1H NMR (500 MHz, in CDCl3)
10.40
1.04
4.32
17.39
4.77
5.21
4.28
1.00
4.27
1.11
3.32
13.20
15.78
f1 (ppm)



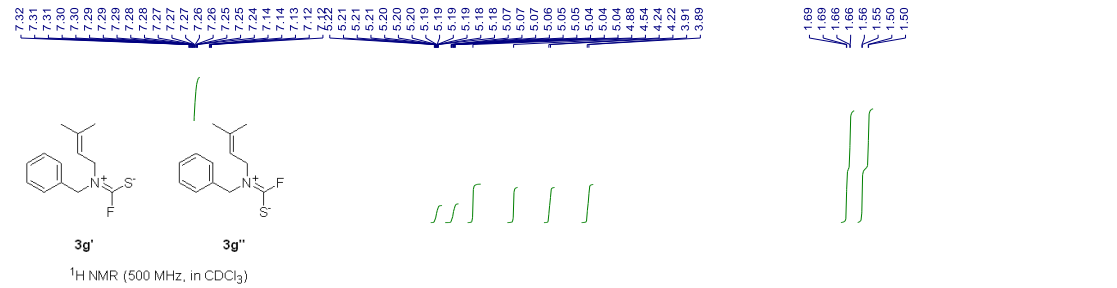
3f' **3f''**

^{13}C NMR (151 MHz, in $CDCl_3$)



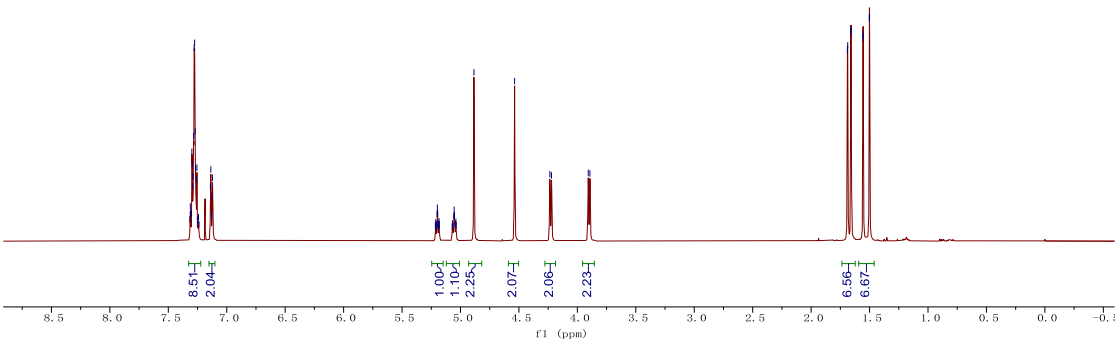
3f' **3f''**

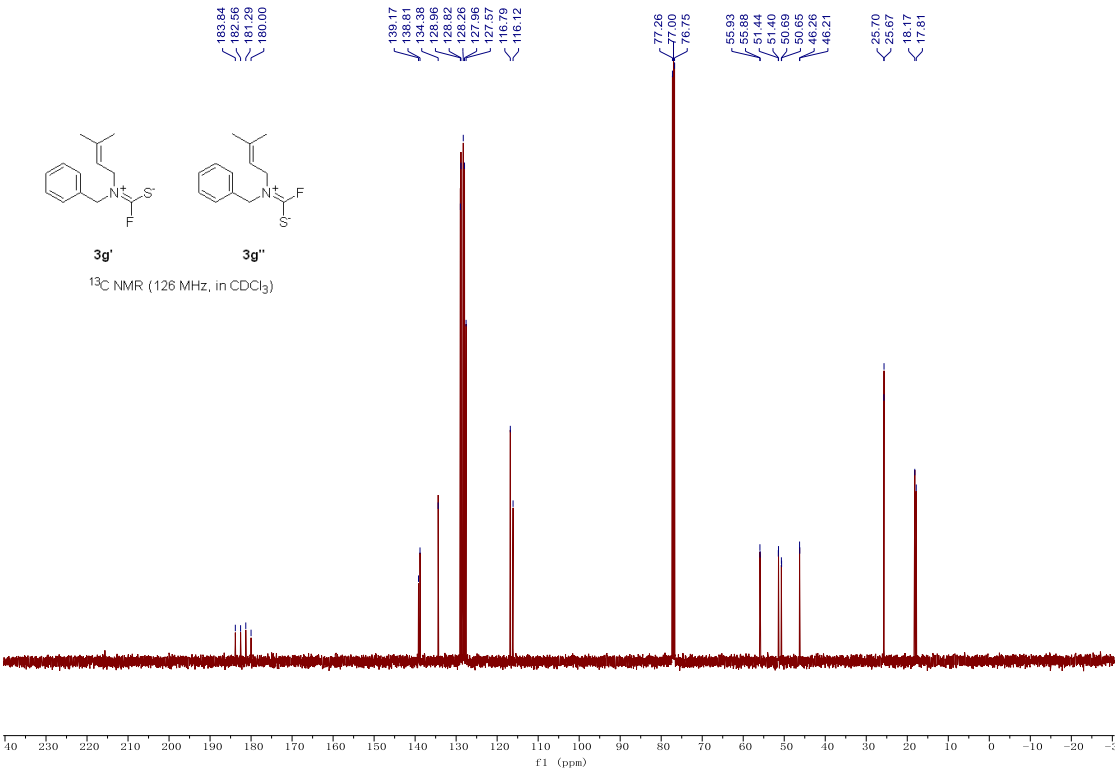
^{19}C NMR (565 MHz, in $CDCl_3$)



3g' 3g''

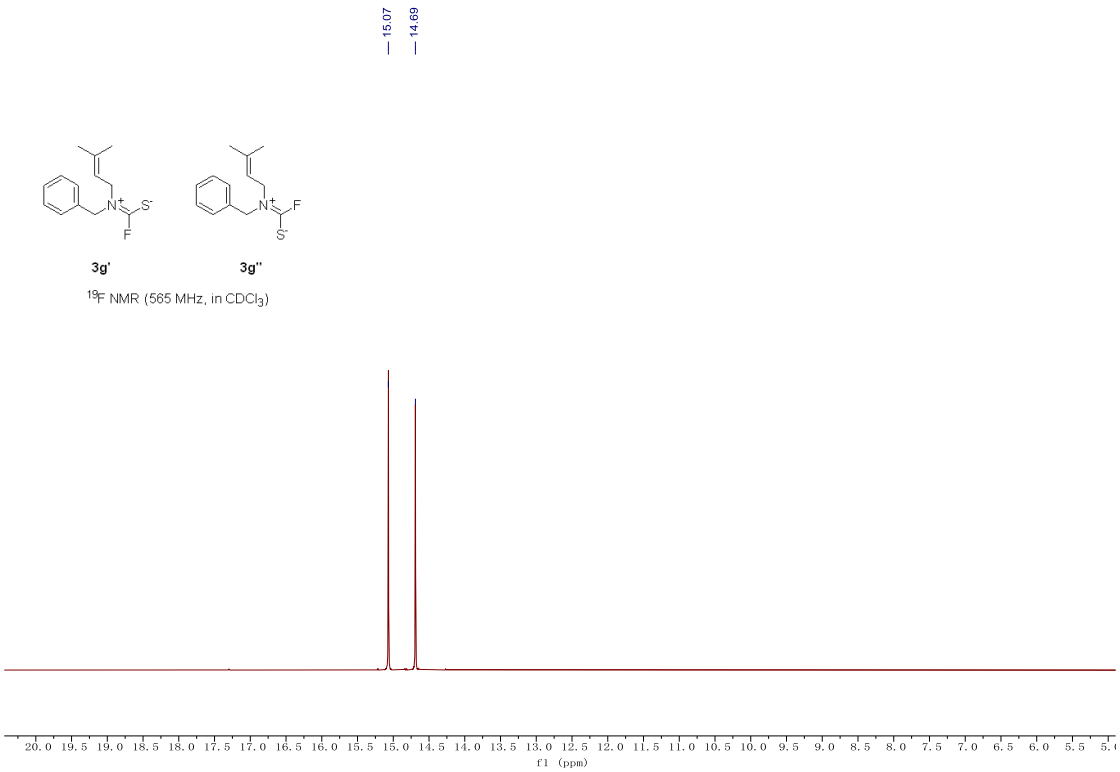
^{1}H NMR (500 MHz, in $CDCl_3$)

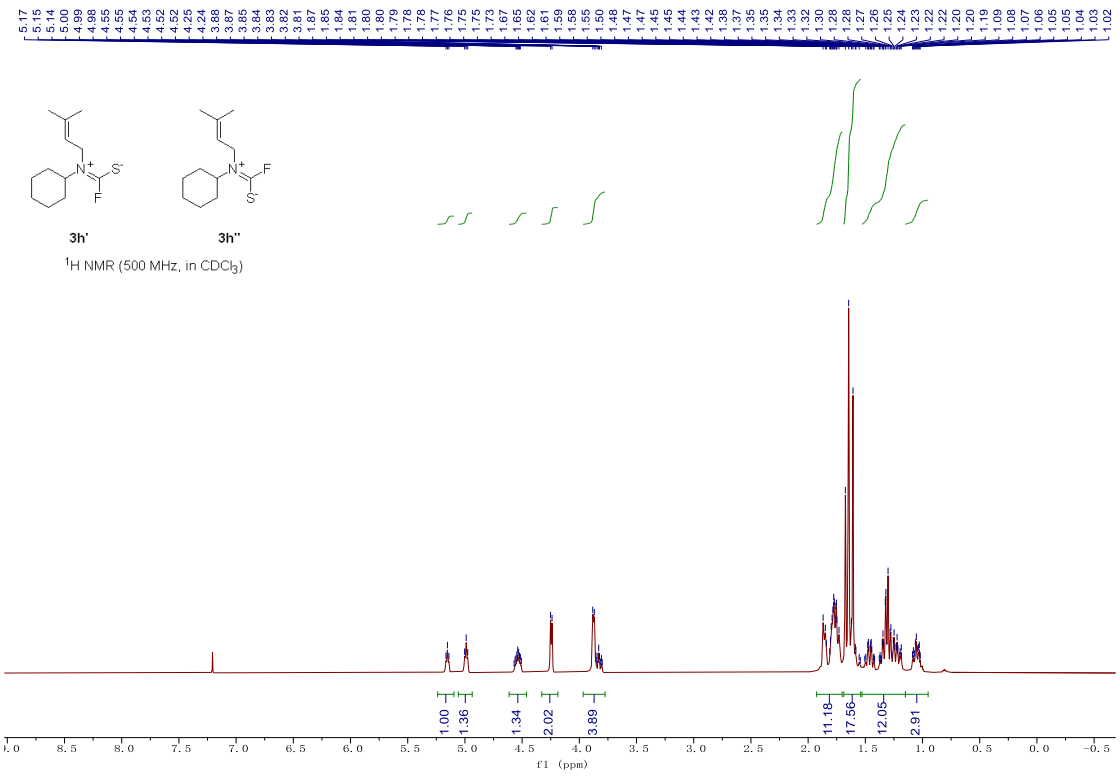


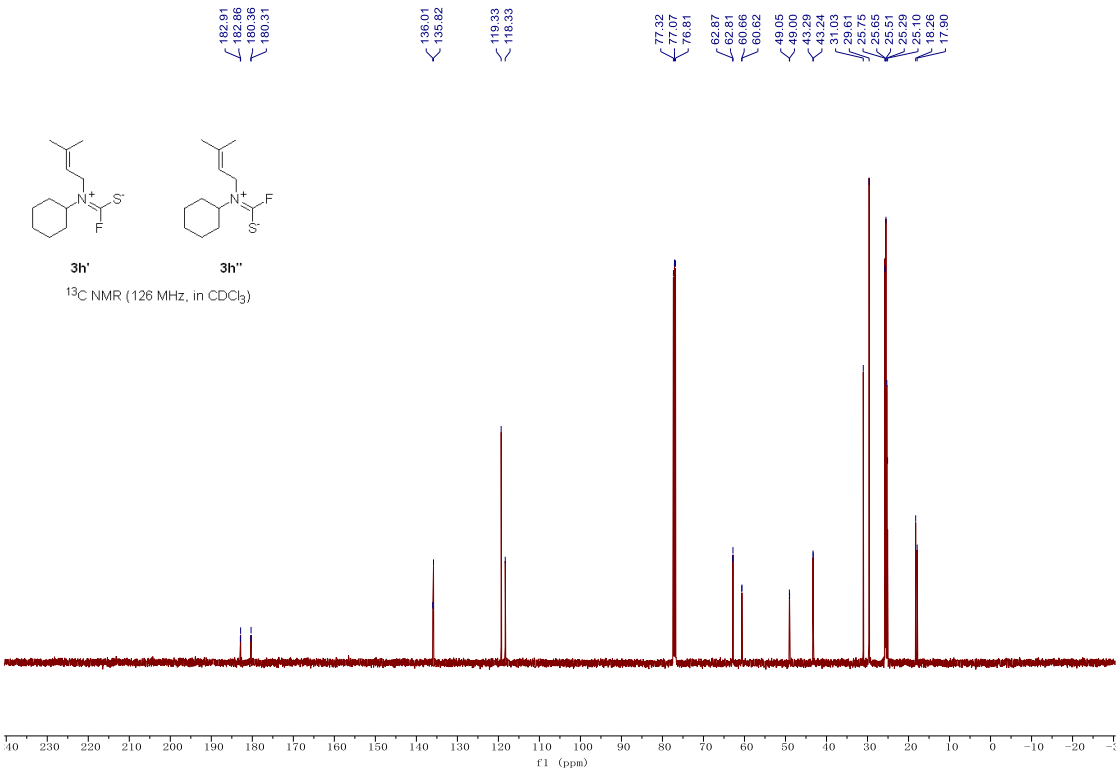


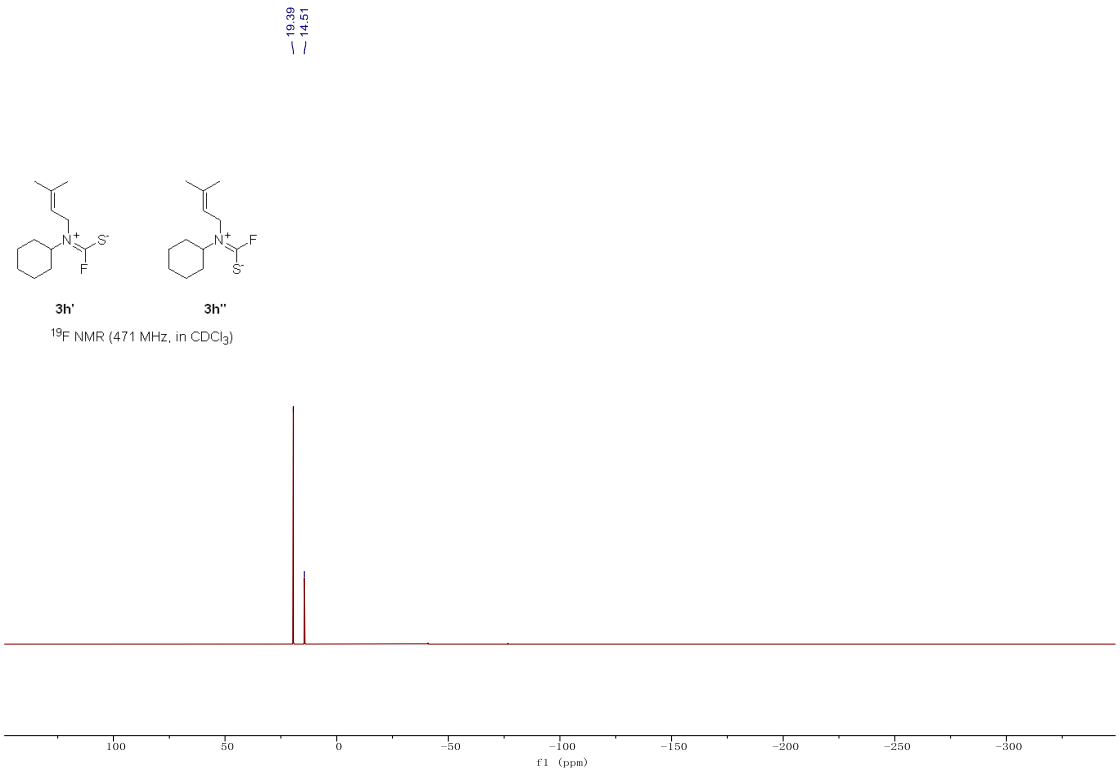
3g' 3g''

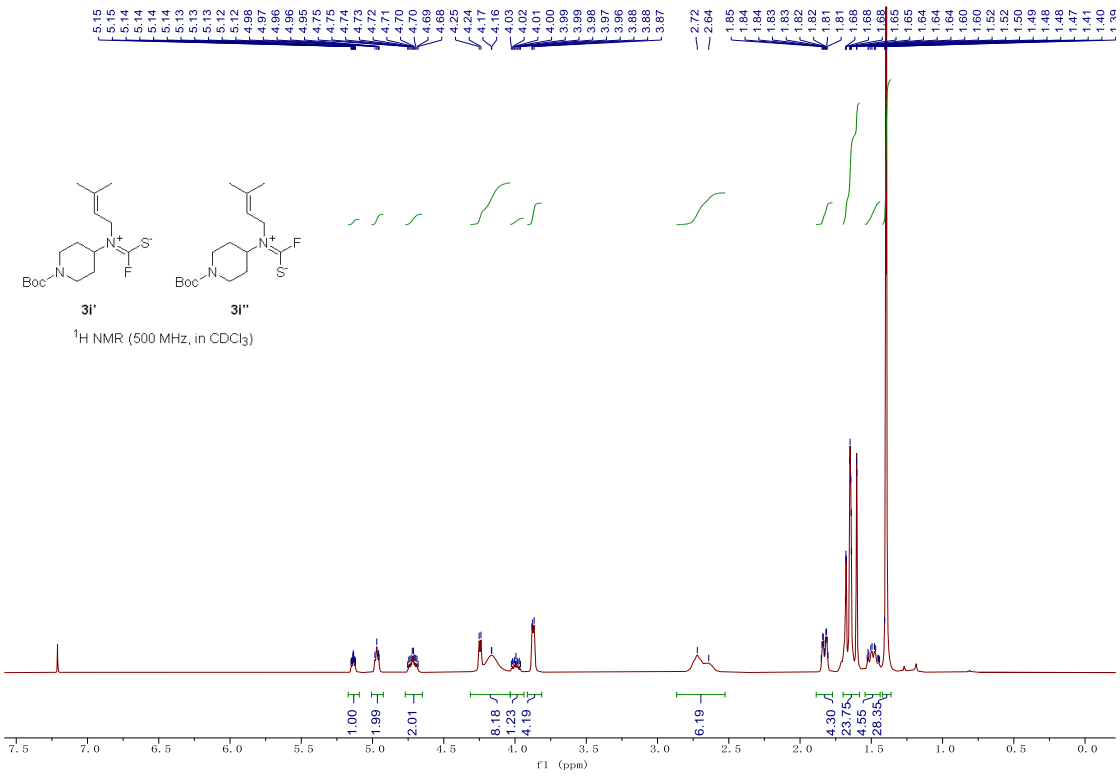
^{13}C NMR (126 MHz, in $CDCl_3$)

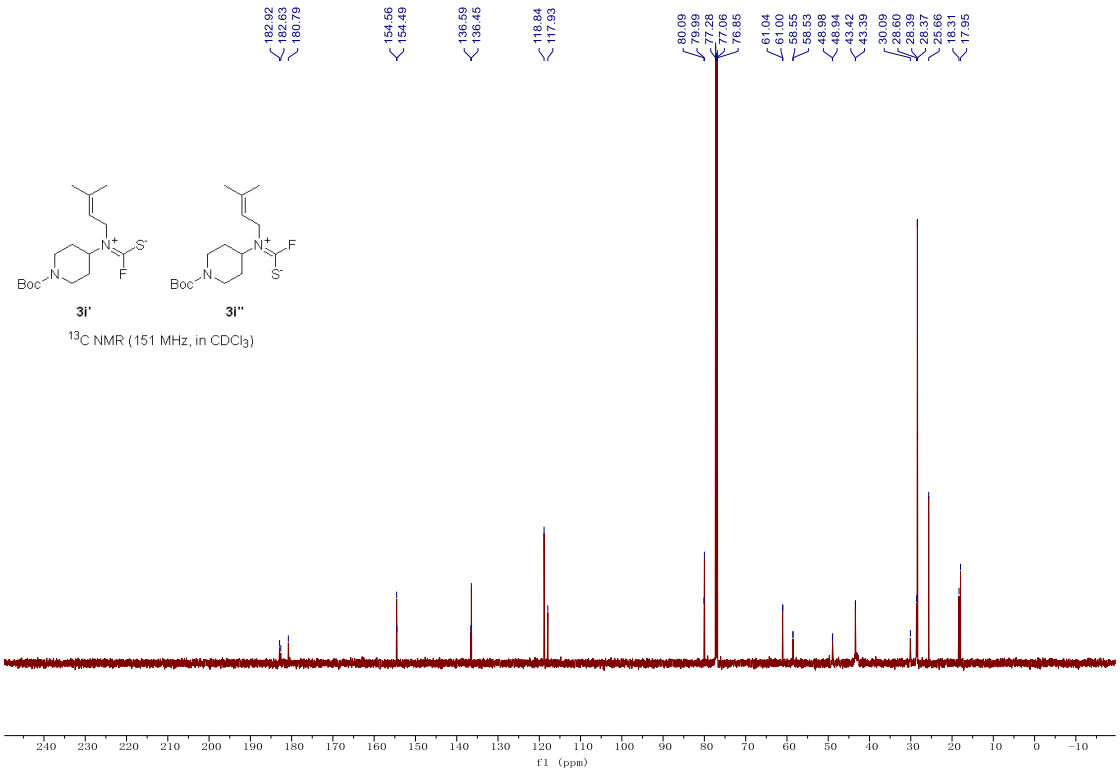

15.07
14.69
3g'
3g''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

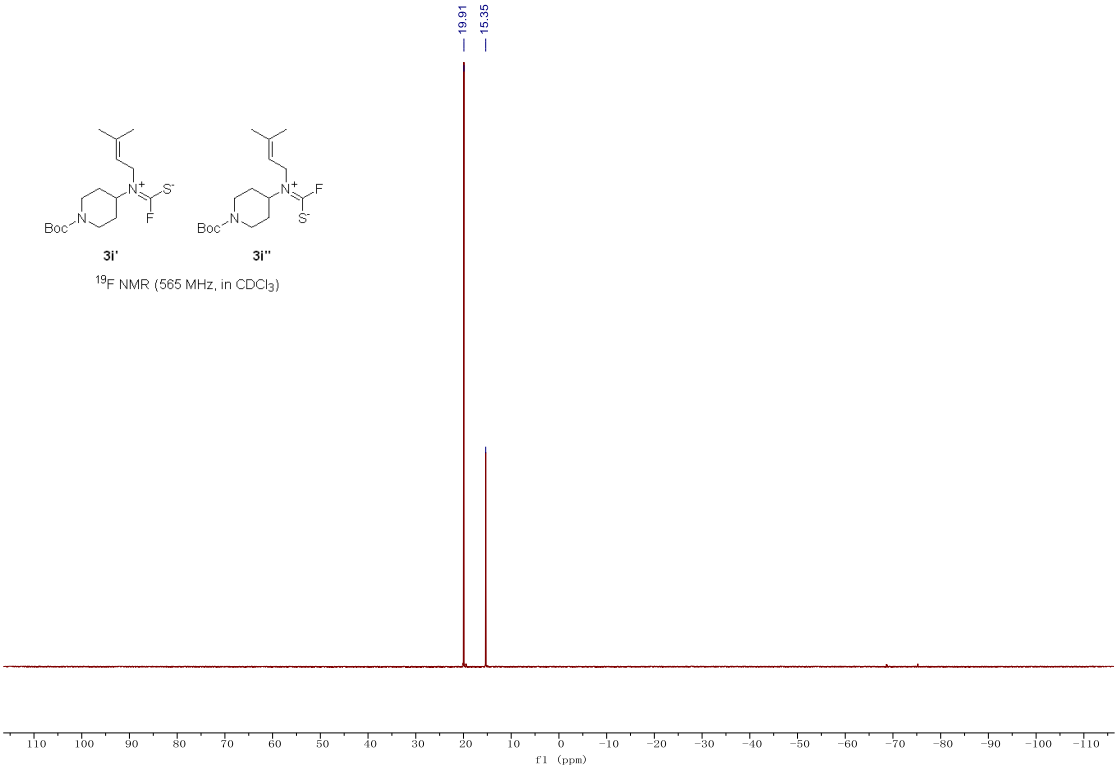

3h'
3h''
1H NMR (500 MHz, in CDCl3)
1.00
1.36
1.34
2.02
3.89
11.18
17.56
12.05
2.91
f1 (ppm)

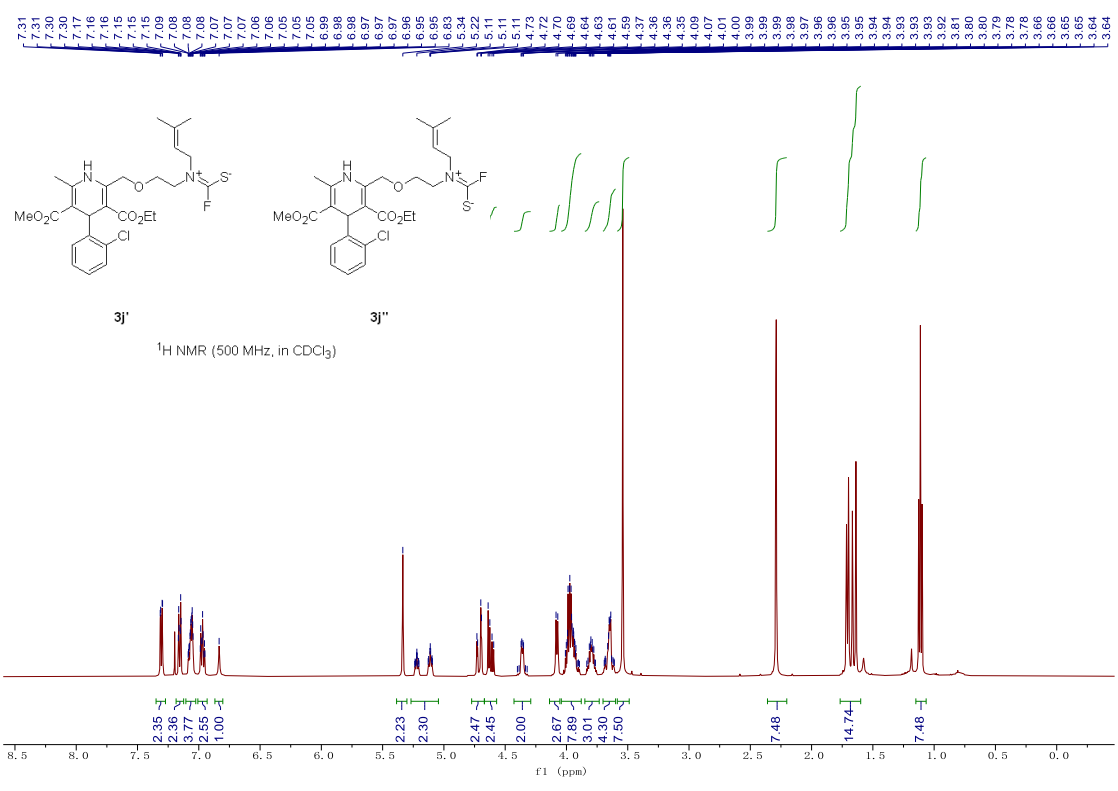

182.91
182.86
180.36
180.31
136.01
135.82
119.33
118.33
77.32
77.07
76.81
62.87
62.81
60.66
60.62
49.05
49.00
43.29
43.24
31.03
29.61
25.75
25.65
25.51
25.29
25.10
18.26
17.90
3h'
3h''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

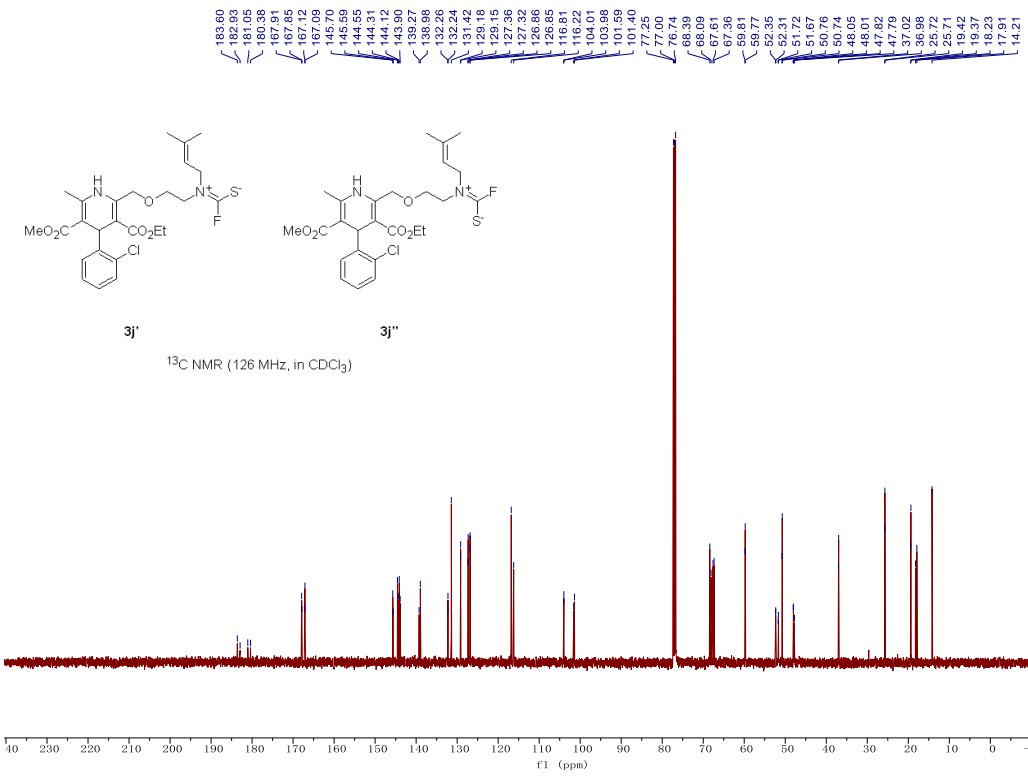

19.39
14.51
3h'
3h''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)

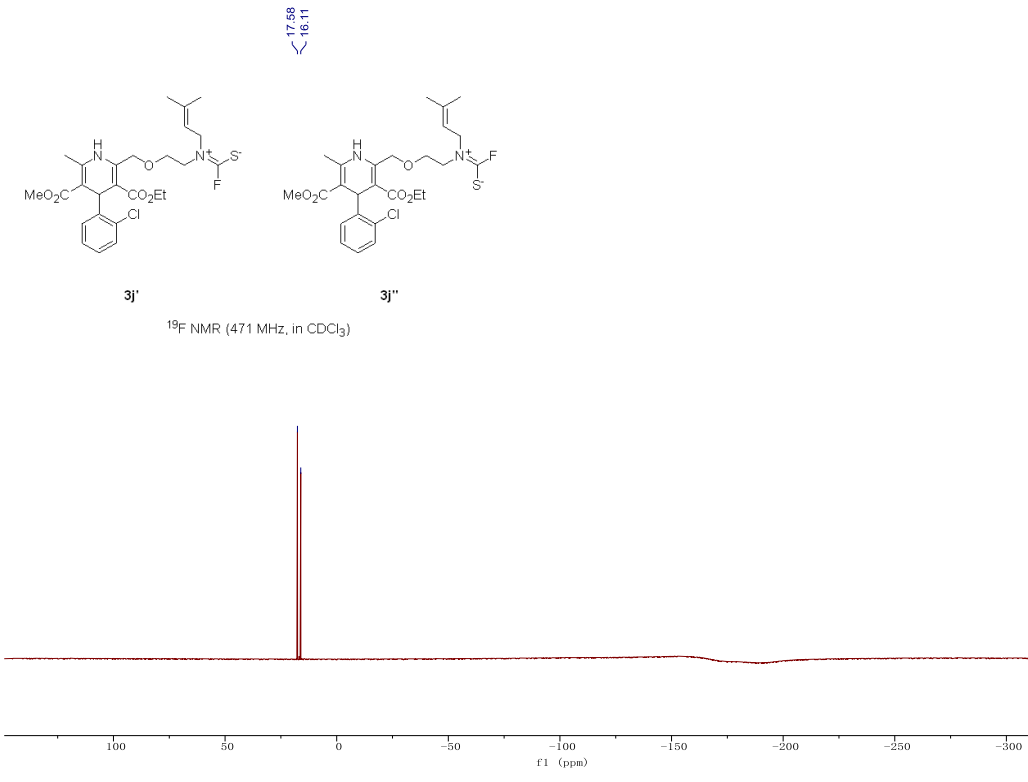

3i'
3i''
1H NMR (500 MHz, in CDCl3)
f1 (ppm)

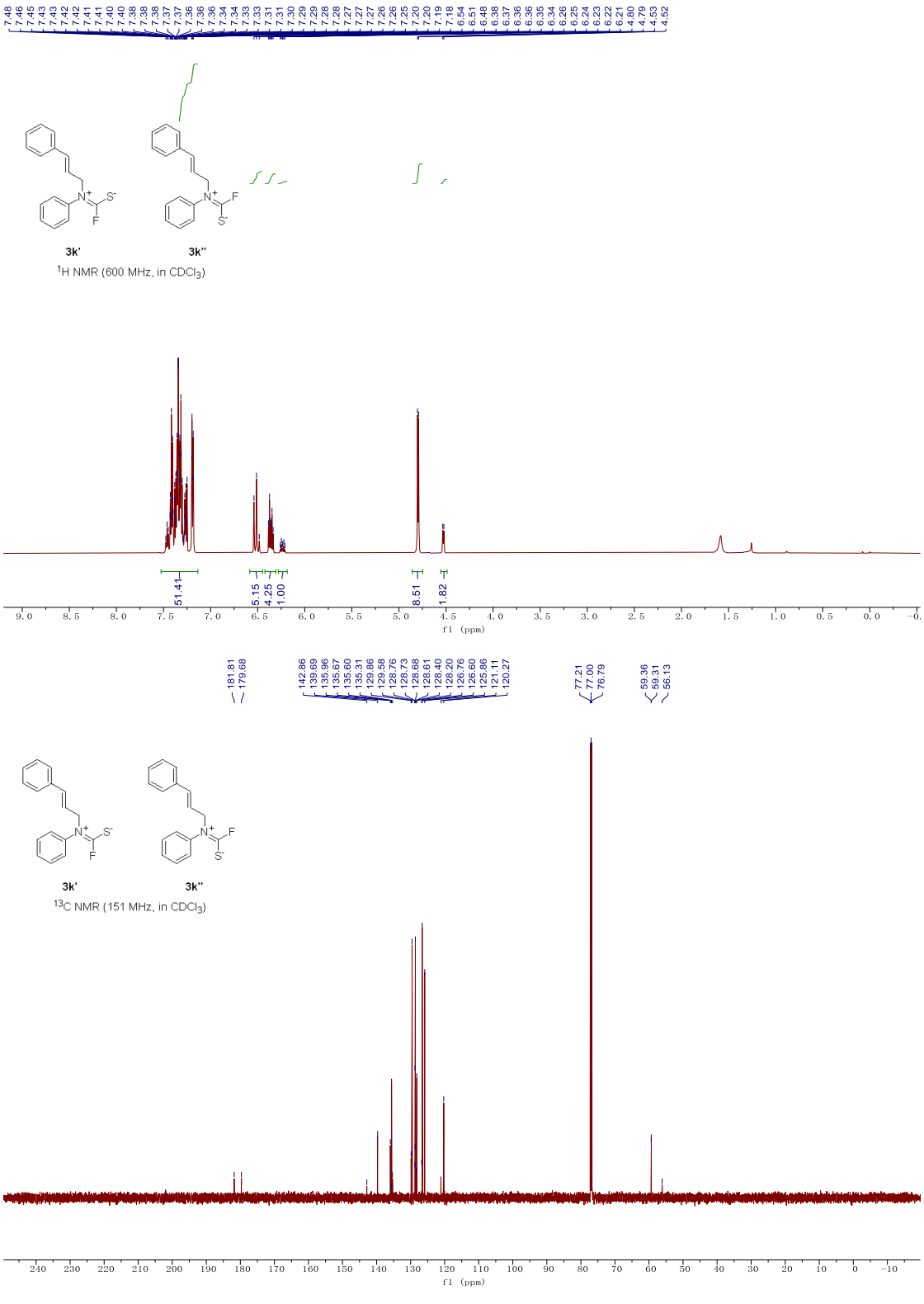

3i'
3i''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

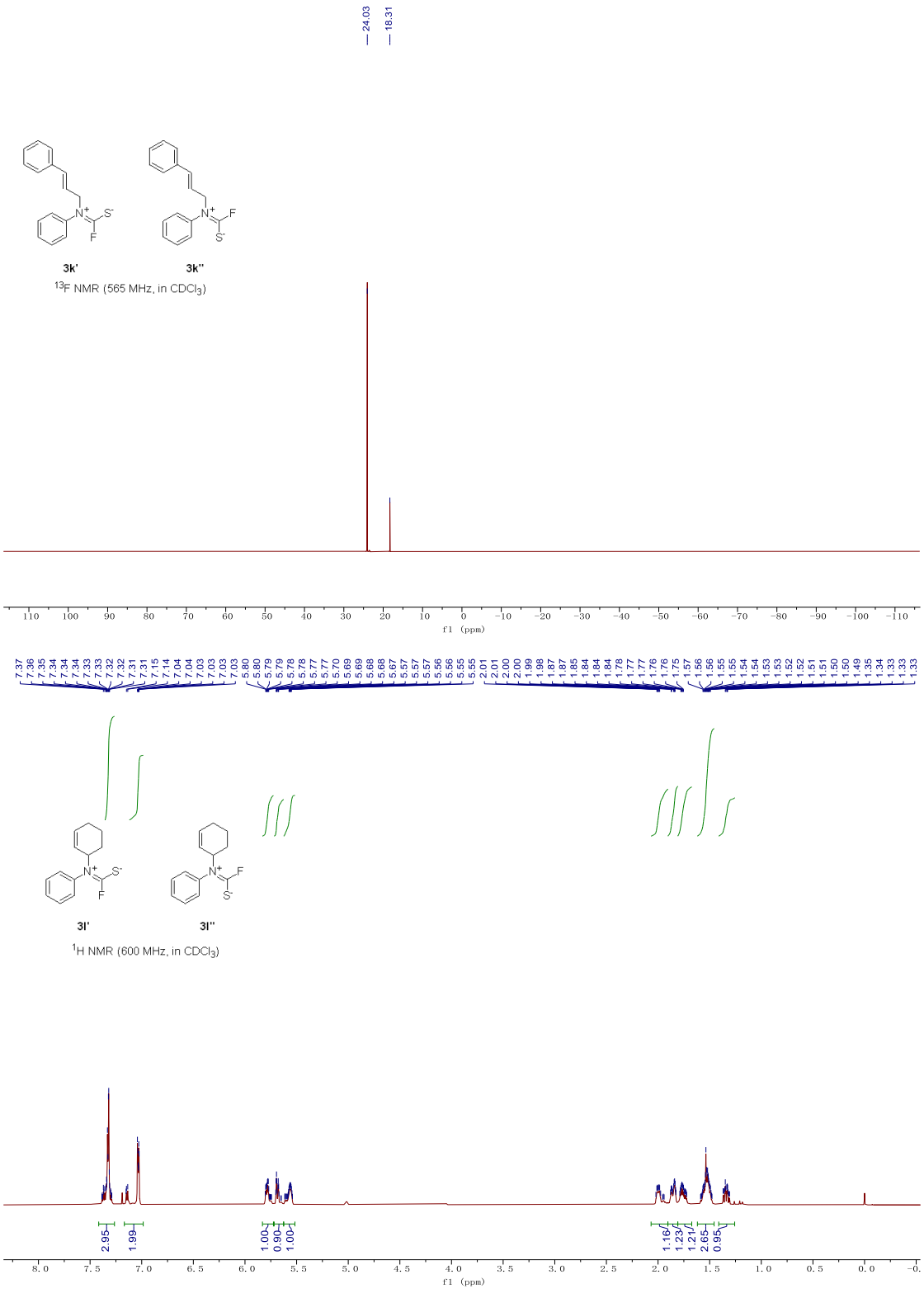

19.91
15.35
Boc
Boc
3i'
3i''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

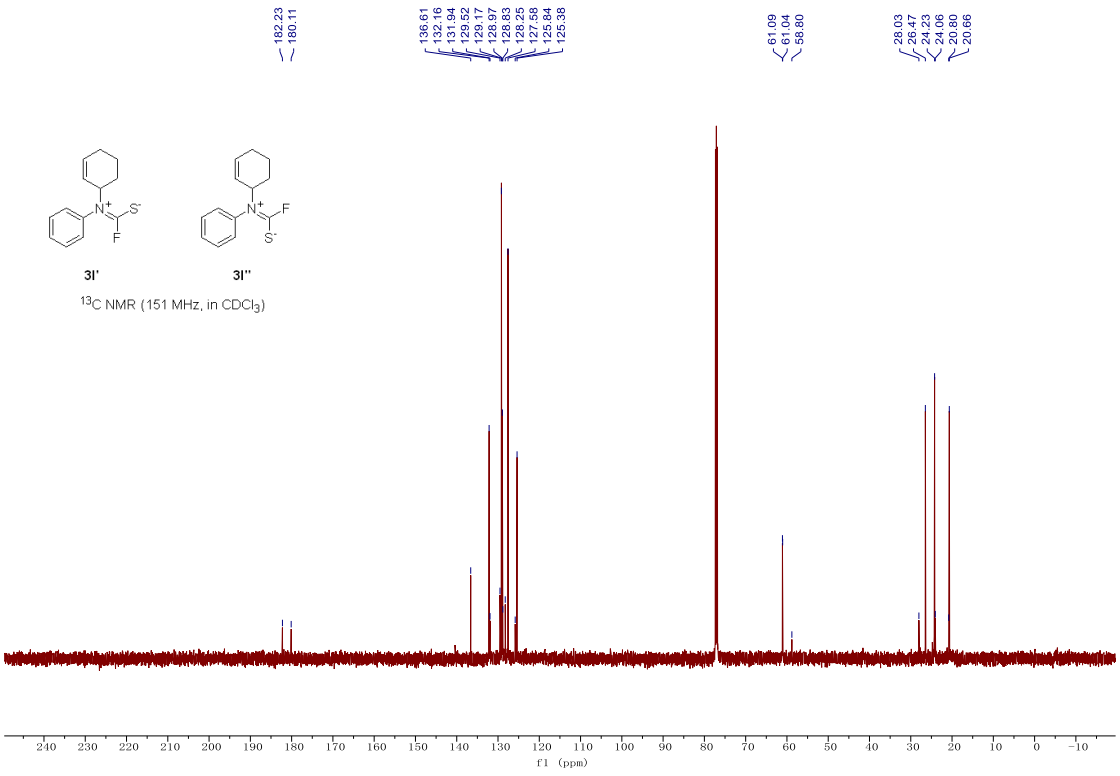

MeO2C
CO2Et
Cl
MeO2C
CO2Et
Cl
3j'
3j''
1H NMR (500 MHz, in CDCl3)
2.35
2.36
3.77
2.55
1.00
2.23
2.30
2.47
2.45
2.00
2.67
7.89
3.01
4.30
7.50
7.48
14.74
7.48
f1 (ppm)

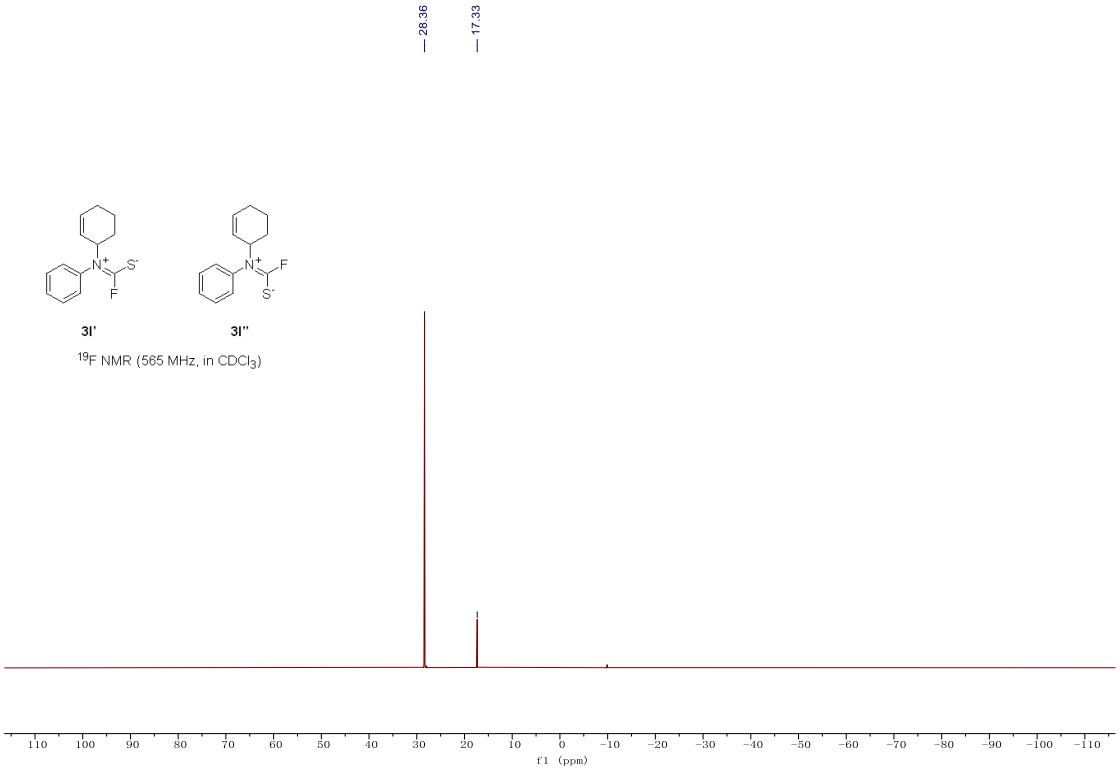

183.60
182.93
181.05
180.38
167.91
167.85
167.12
167.09
145.70
145.59
144.55
144.31
144.12
143.90
139.27
138.98
132.26
132.24
131.42
129.18
129.15
127.36
127.32
126.86
126.85
116.81
116.22
104.01
103.98
101.59
101.40
77.25
77.00
76.74
68.39
68.09
67.61
67.36
59.81
59.77
52.35
52.31
51.72
51.67
50.76
50.74
48.05
48.01
47.82
47.79
37.02
36.98
25.72
25.71
19.42
19.37
18.23
17.91
14.21
MeO2C
CO2Et
Cl
3j'
3j''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

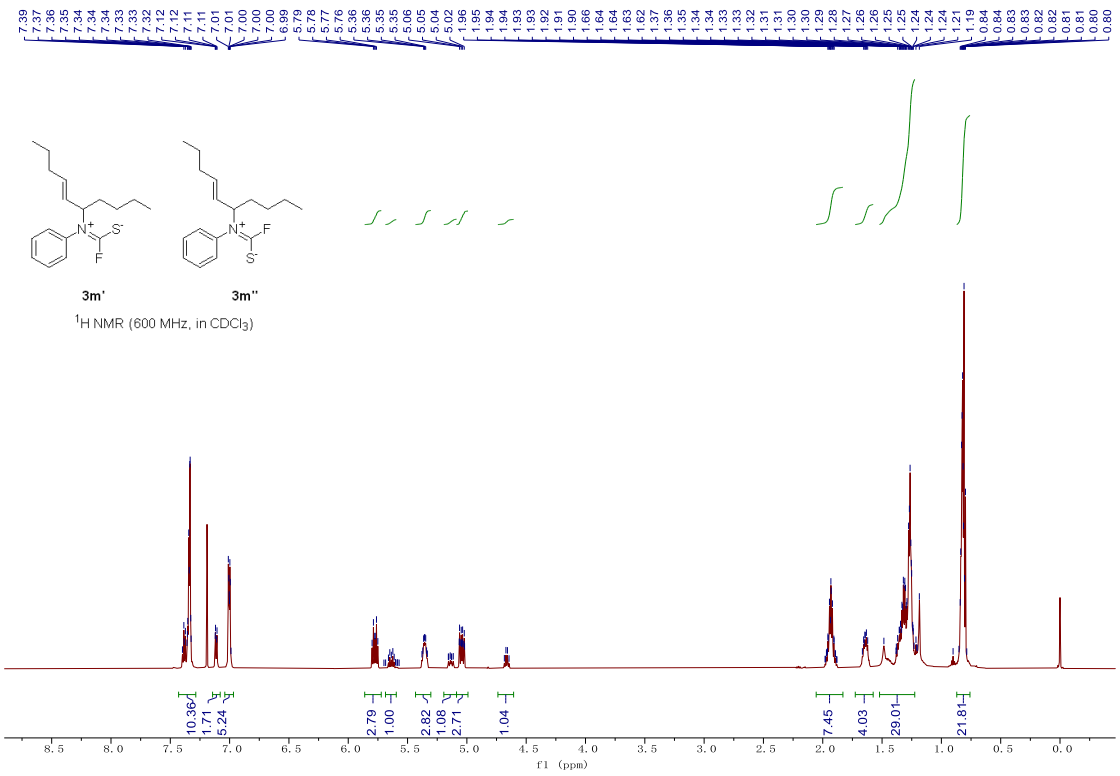

17.58
16.11
MeO2C
CO2Et
Cl
3j'
3j''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)

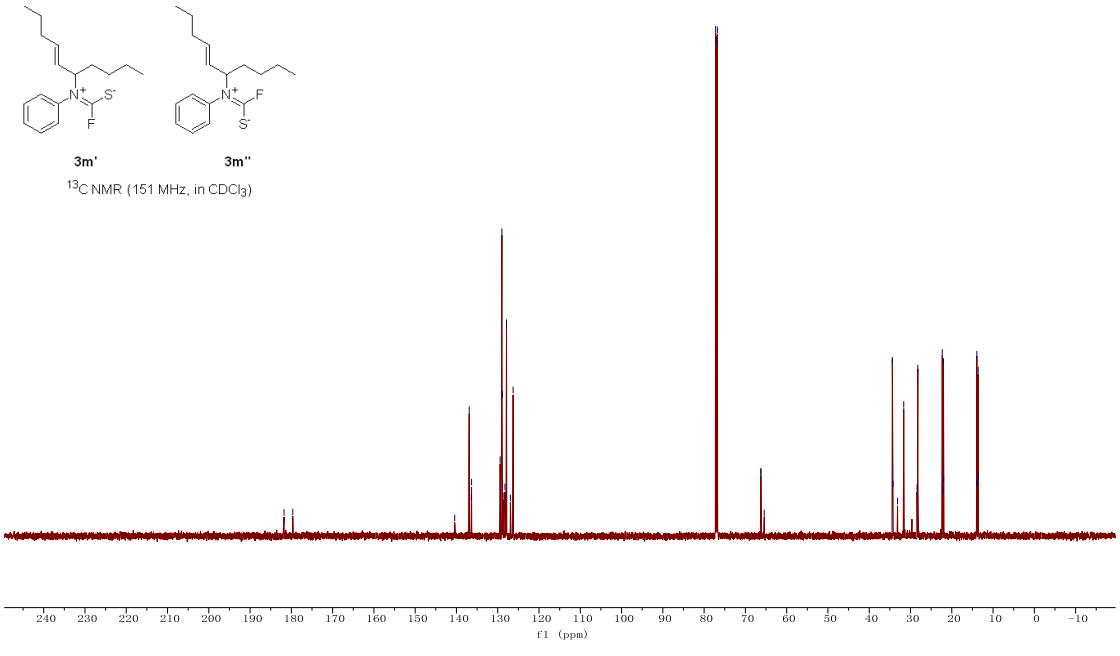

3k'
3k''
1H NMR (600 MHz, in CDCl3)
51.41
5.15
4.25
1.00
8.51
1.82
f1 (ppm)
3k'
3k''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

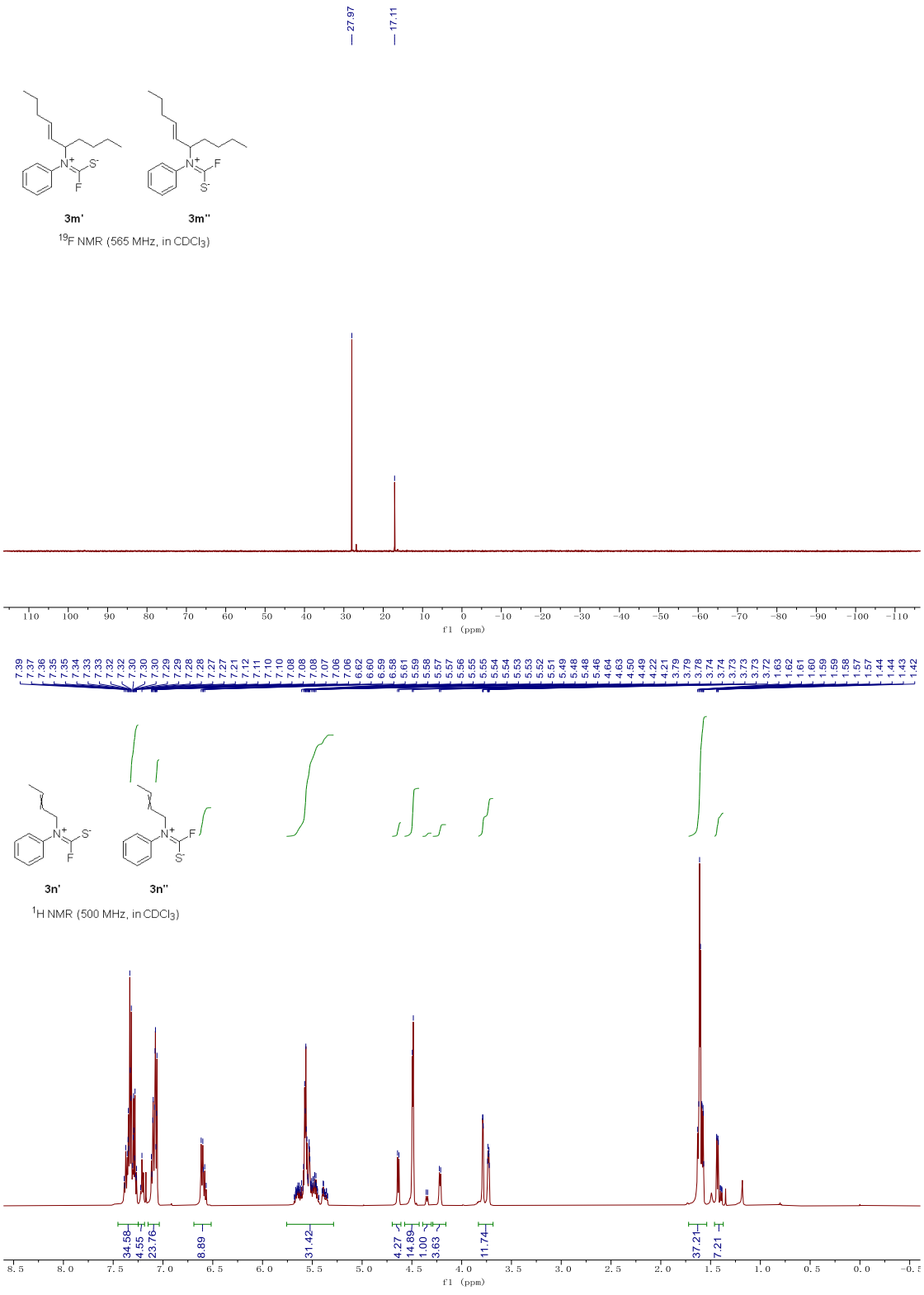

24.03
18.31
3k'
3k''
^{13}F NMR (565 MHz, in CDCl$_3$)
f1 (ppm)
3l'
3l''
^{1}H NMR (600 MHz, in CDCl$_3$)
2.95
1.99
1.00
0.90
1.00
1.16
1.23
1.21
2.65
0.95
f1 (ppm)

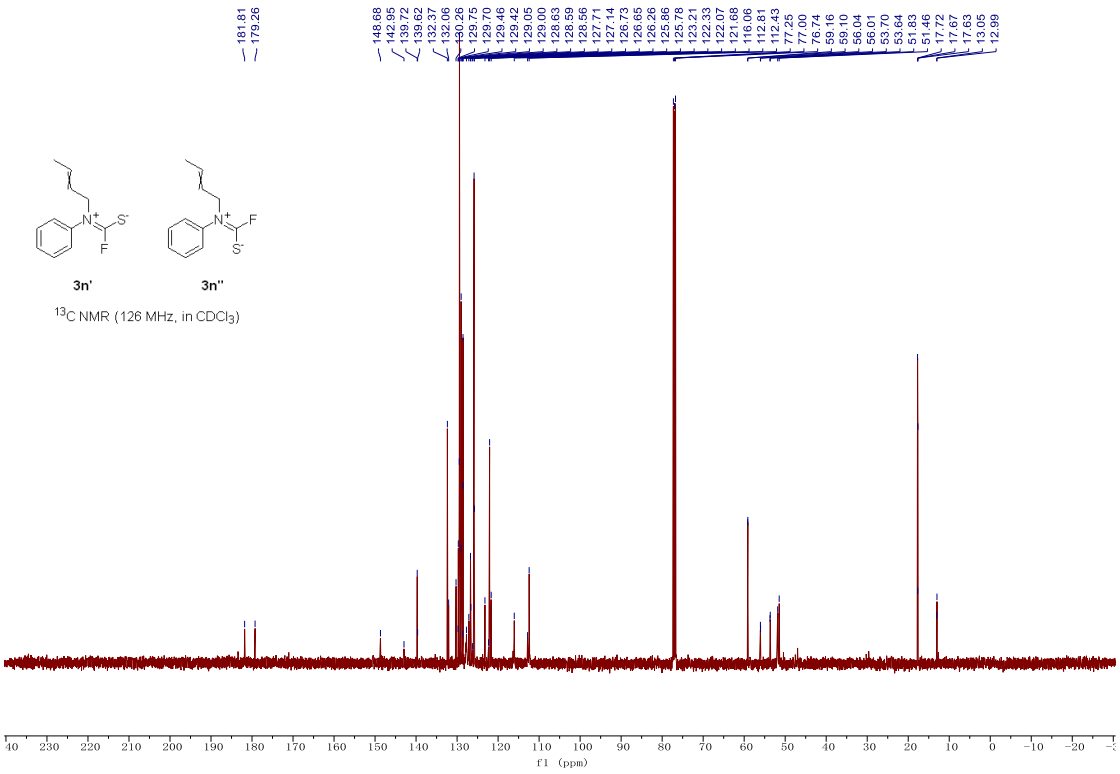

182.23
180.11
136.61
132.16
131.94
129.52
129.17
128.97
128.63
128.25
127.68
125.84
125.38
61.09
61.04
58.80
28.03
26.47
24.23
24.06
20.80
20.66
3l'
3l''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)

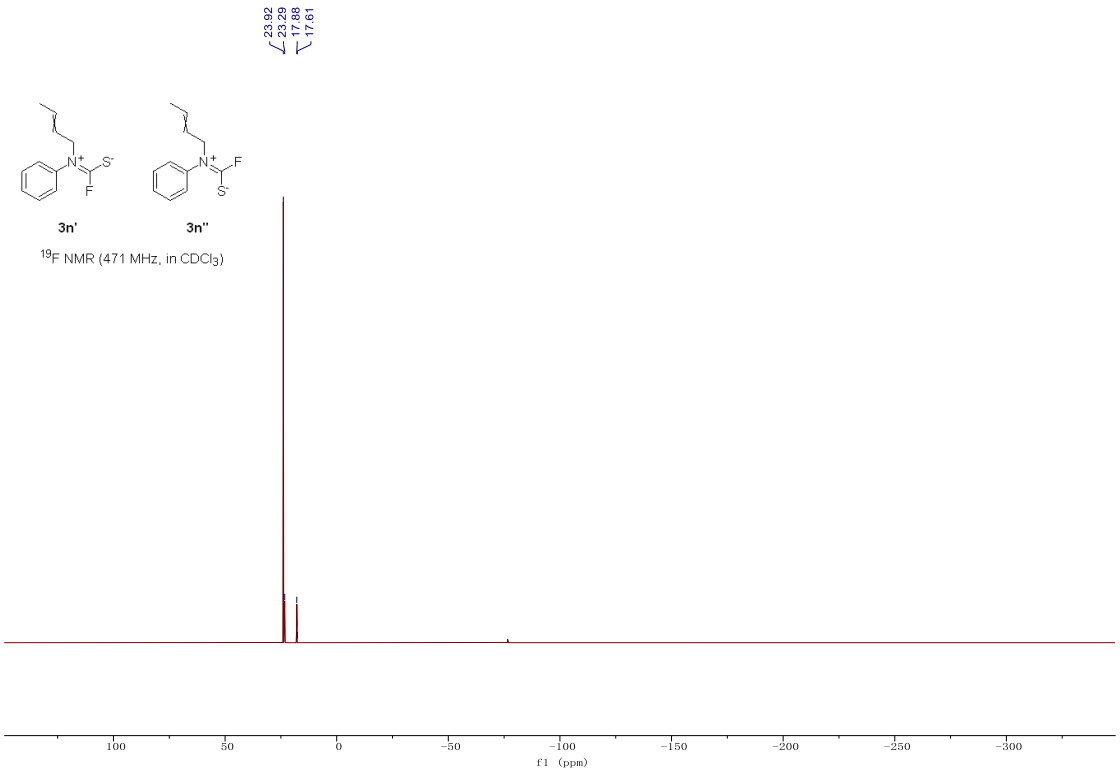

28.36
17.33
3l'
3l''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

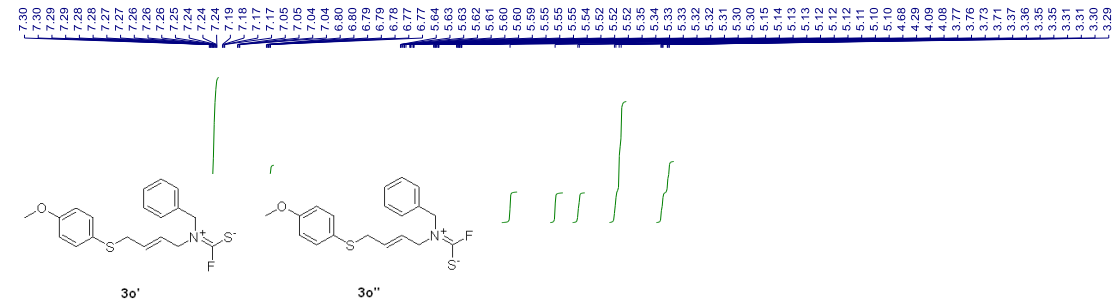

3m'
3m''
1H NMR (600 MHz, in CDCl3)
f1 (ppm)


3m'
3m''
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


— 27.97
— 17.11
3m'
3m''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)
3n'
3n''
1H NMR (500 MHz, in CDCl3)
34.58
4.55
23.76
8.89
31.42
4.27
14.89
1.00
3.63
11.74
37.21
7.21
f1 (ppm)

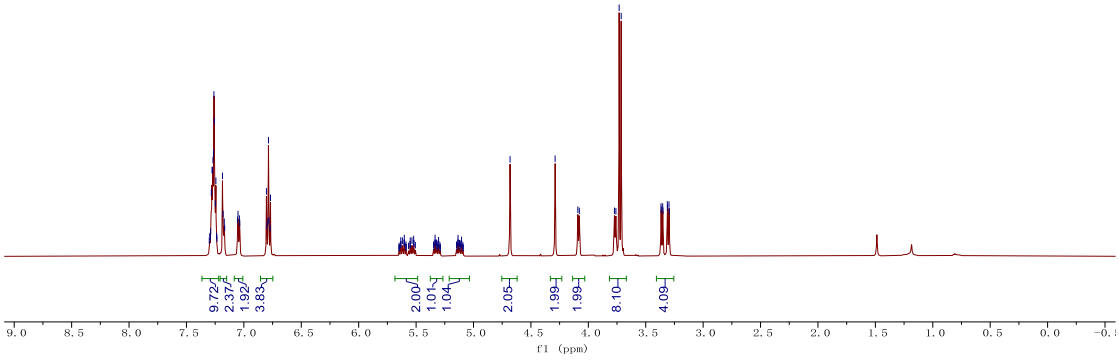

181.81
179.26
148.68
142.95
139.72
139.62
132.37
132.06
130.26
129.75
129.70
129.46
129.42
129.05
129.00
128.63
128.59
128.56
127.71
127.14
126.73
126.65
126.26
125.86
125.78
123.21
122.33
122.07
121.68
116.06
112.81
112.43
77.25
77.00
76.74
59.16
59.10
56.04
56.01
53.70
53.64
51.83
51.46
17.72
17.67
17.63
13.05
12.99
3n'
3n''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

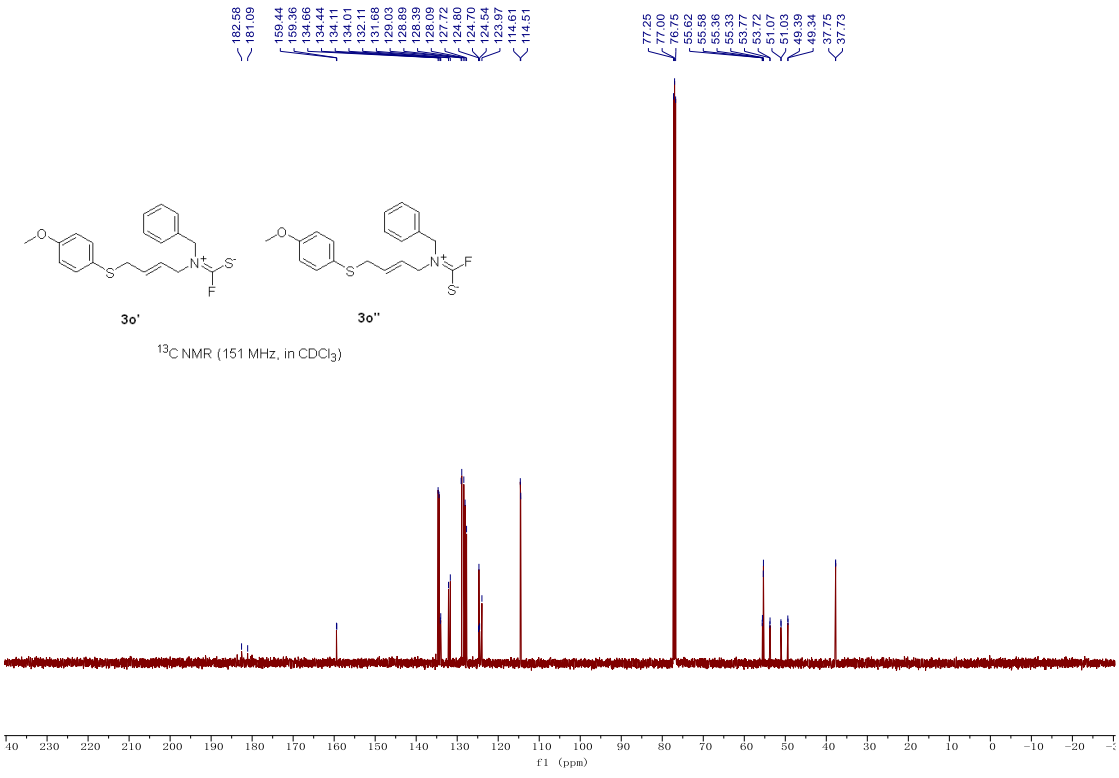

23.92
23.89
17.88
17.61
3n'
3n''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)



3o' **3o''**

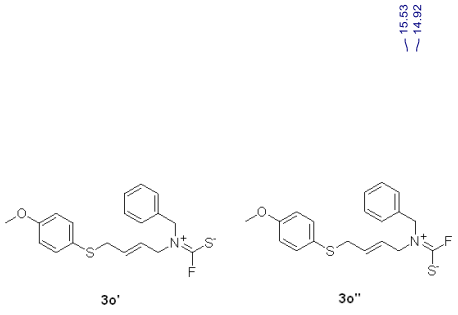
^{1}H NMR (500 MHz, in $CDCl_3$)





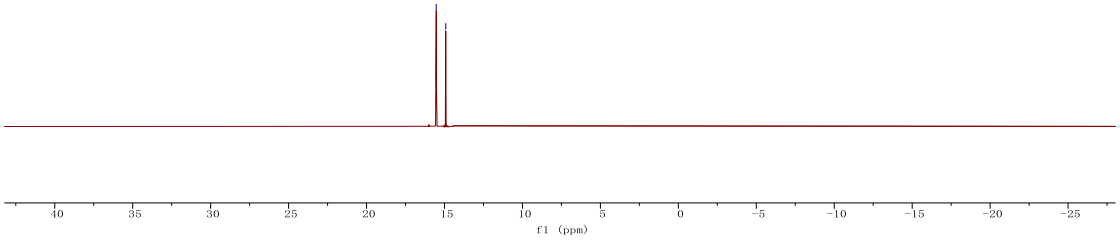
3o' **3o''**

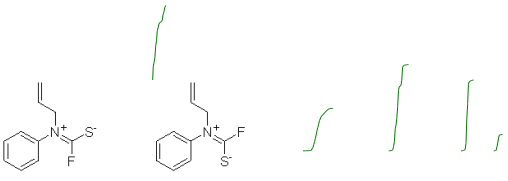
^{13}C NMR (151 MHz, in $CDCl_3$)



3o' **3o''**

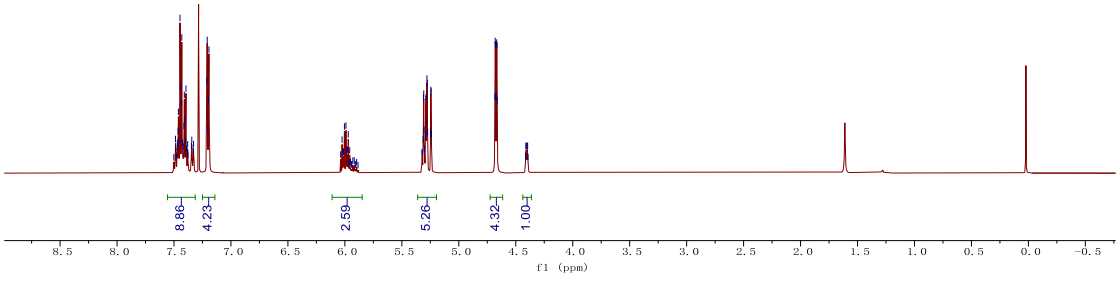
^{19}F NMR (565 MHz, in $CDCl_3$)

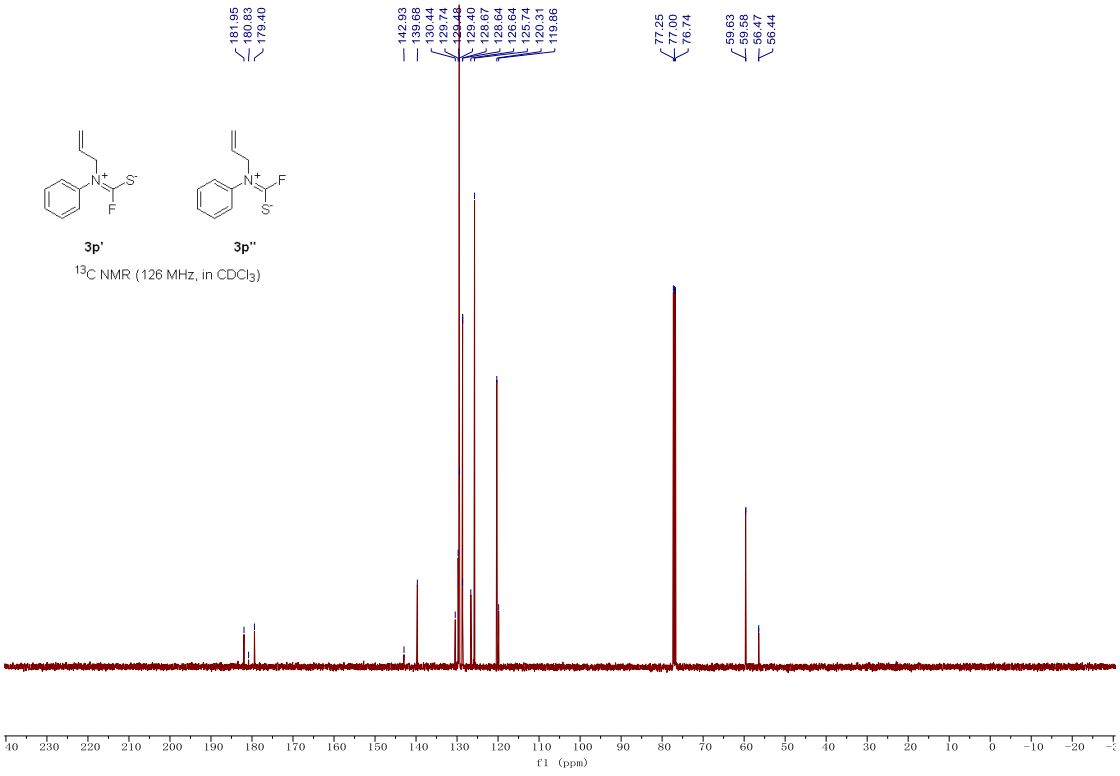


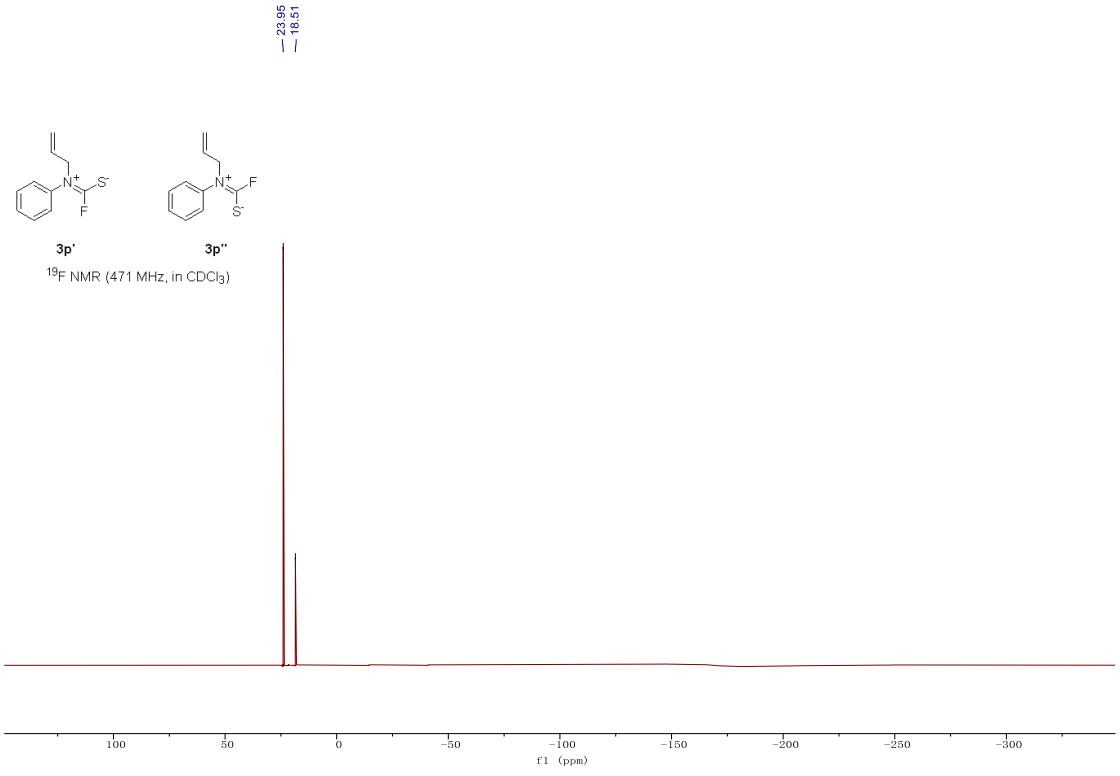


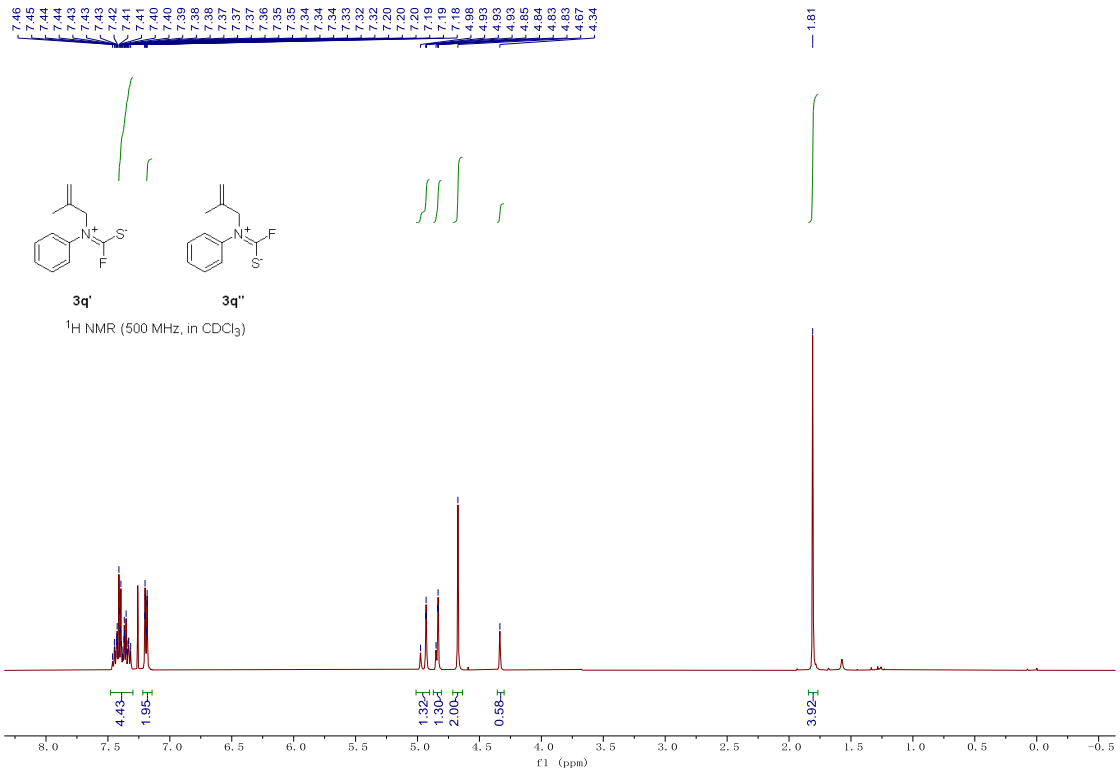
3p' **3p''**

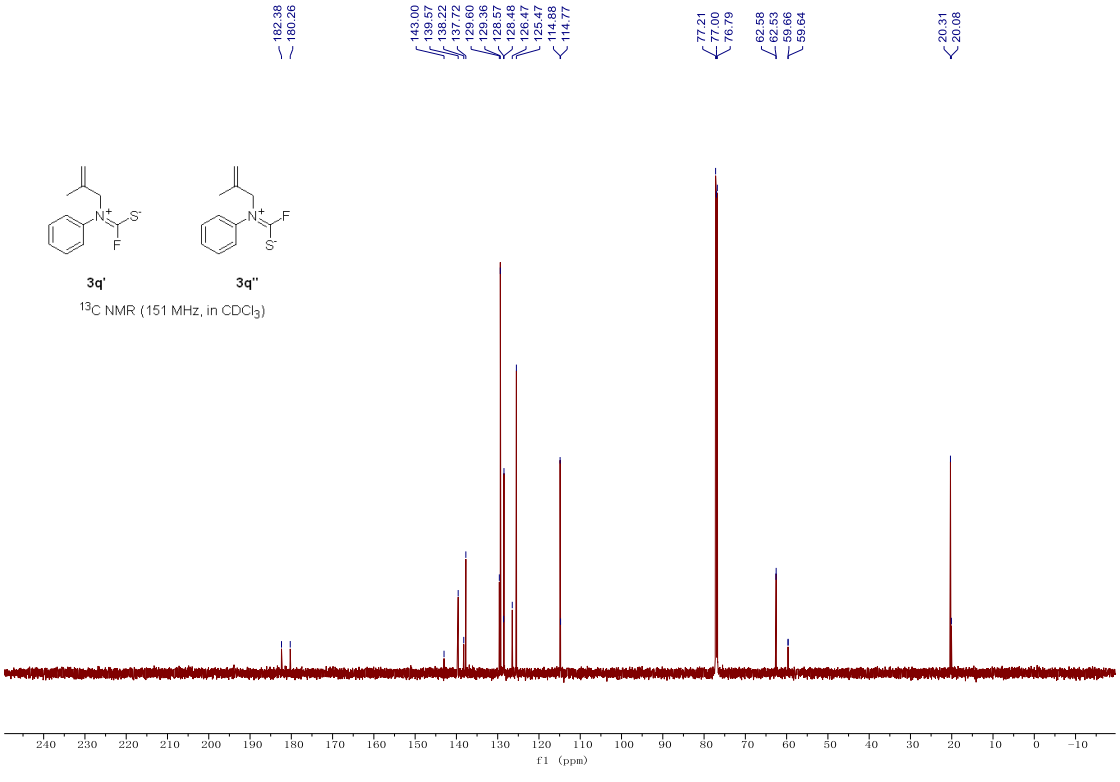
^{1}H NMR (500 MHz, in $CDCl_3$)

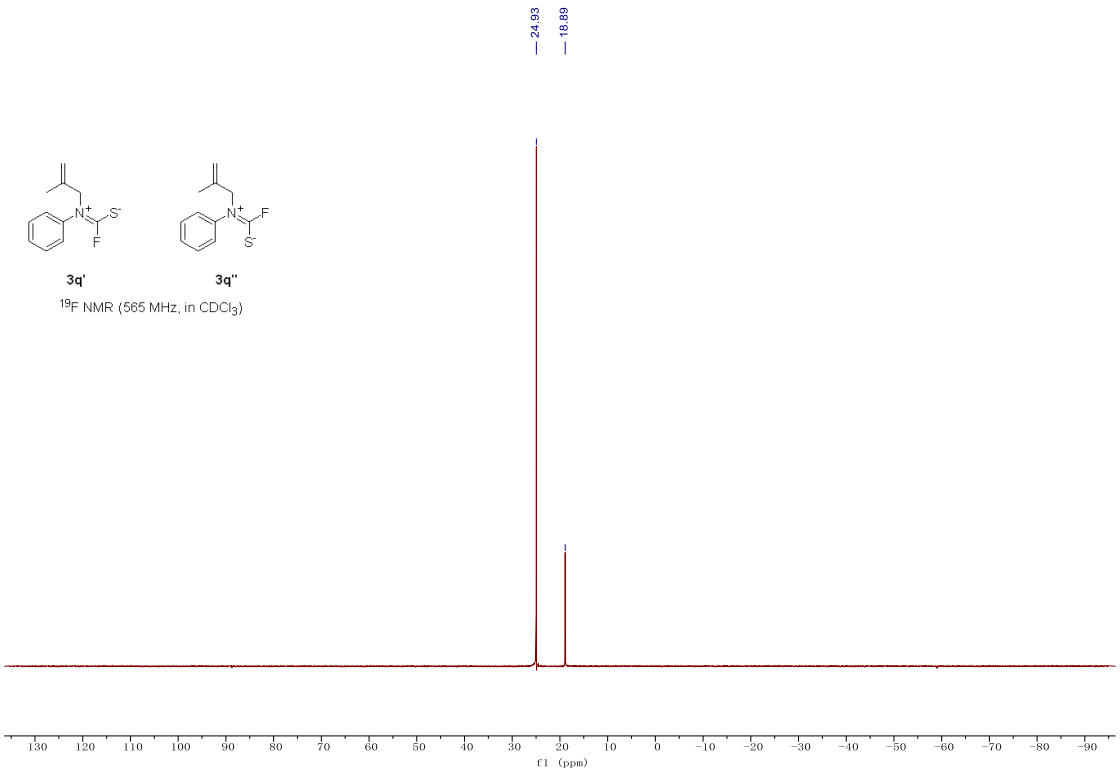


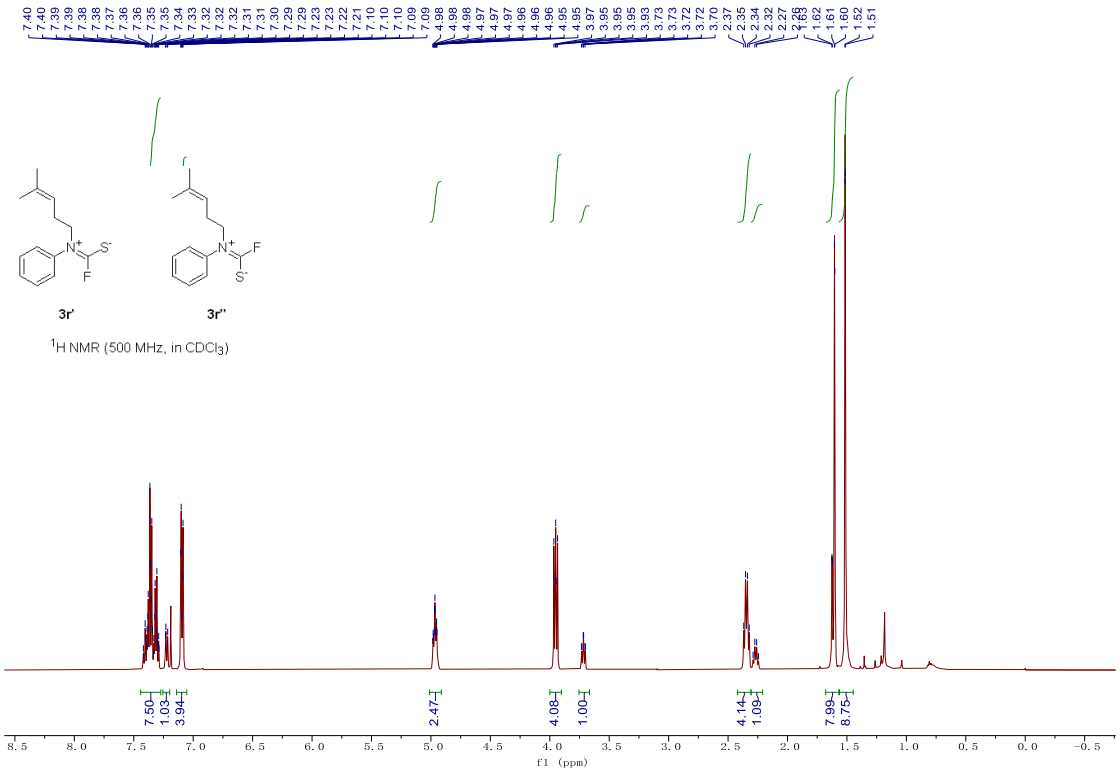

181.95
180.83
179.40
142.93
139.68
130.44
129.74
129.40
128.67
128.64
126.64
125.74
120.31
119.86
77.25
77.00
76.74
59.63
59.58
58.47
56.44
3p'
3p''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

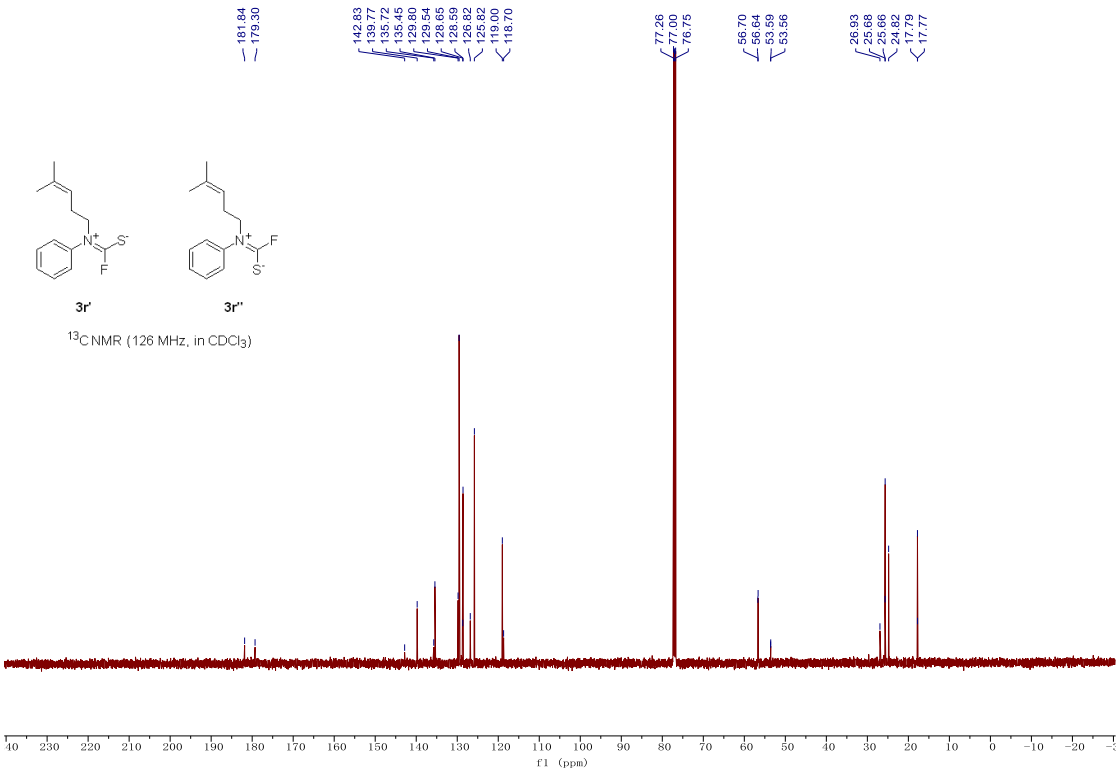

23.95
18.51
3p'
3p''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)

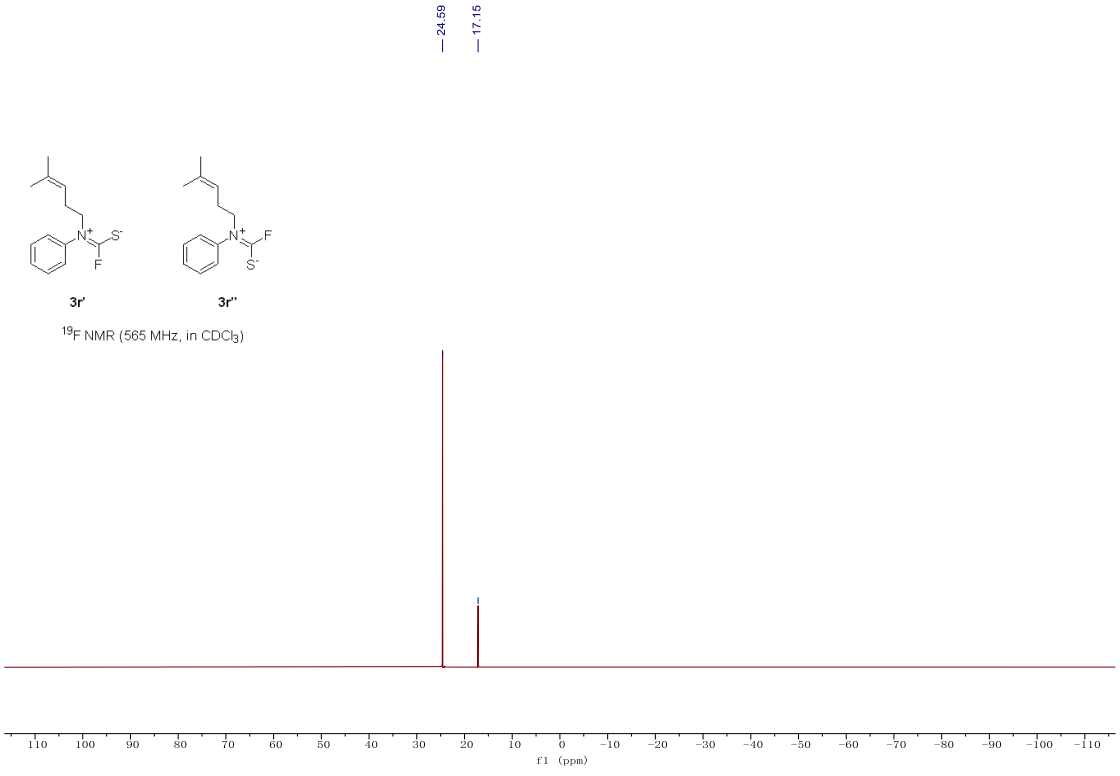

7.46 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.20 7.20 7.20 7.19 7.19 7.18 4.98 4.93 4.93 4.85 4.84 4.83 4.83 4.67 4.34
1.81
3q'
3q''
^{1}H NMR (500 MHz, in $CDCl_3$)
4.43 1.95 1.32 1.30 2.00 0.58 3.92
f1 (ppm)

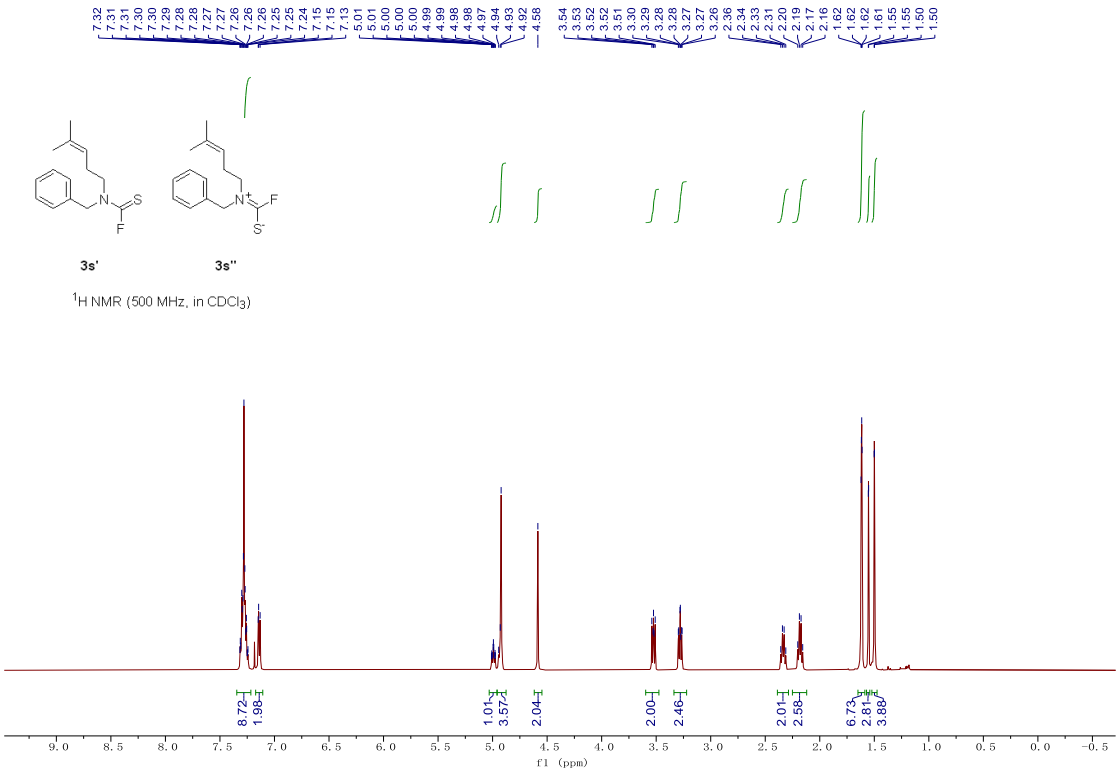

182.38 180.26 143.00 139.57 138.22 137.72 129.60 129.36 128.57 128.48 126.47 125.47 114.88 114.77 77.21 77.00 76.79 62.58 62.53 59.66 59.64 20.31 20.08
3q'
3q''
^{13}C NMR (151 MHz, in $CDCl_3$)
f1 (ppm)

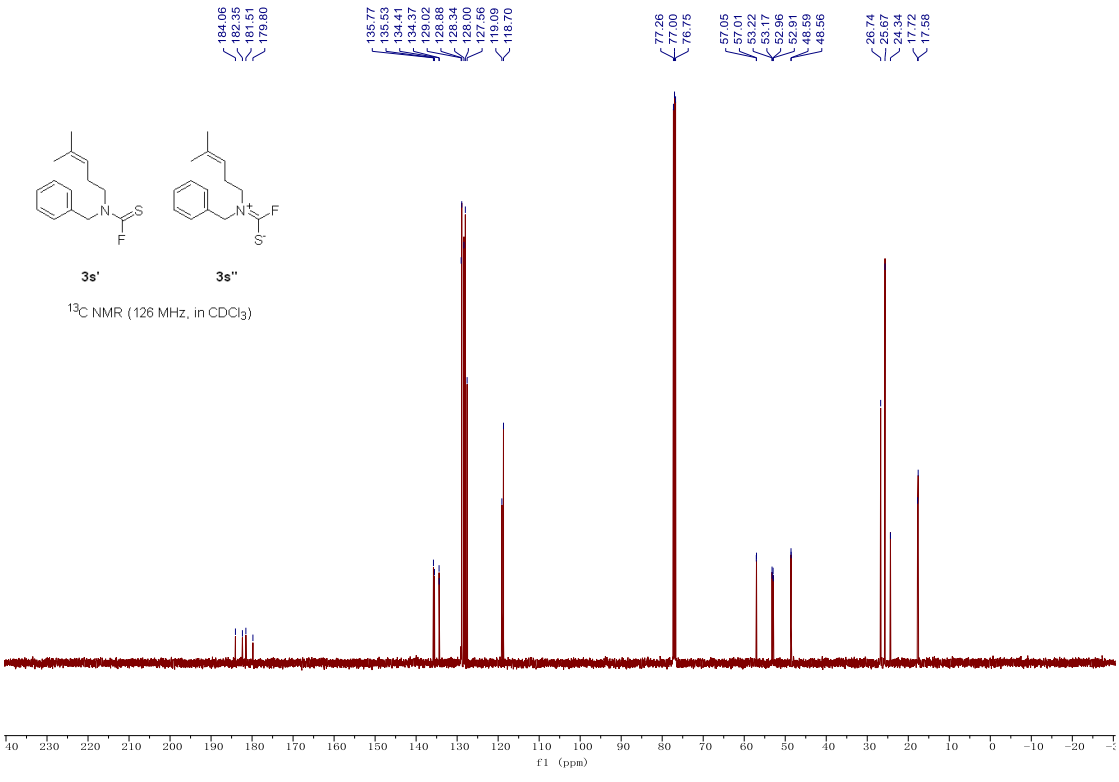

24.93
18.89
3q'
3q''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

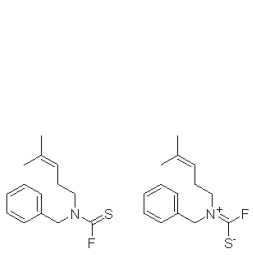

3r'
3r''
1H NMR (500 MHz, in CDCl3)
7.50
1.03
3.94
2.47
4.08
1.00
4.14
1.09
7.99
8.75
f1 (ppm)


181.84
179.30
142.83
139.77
135.72
135.45
129.80
129.54
128.65
128.59
126.82
125.82
119.00
118.70
77.26
77.00
76.75
56.70
56.64
53.59
53.56
26.93
25.68
25.66
24.82
17.79
17.77
3r'
3r''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


24.59
17.15
3r'
3r''
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

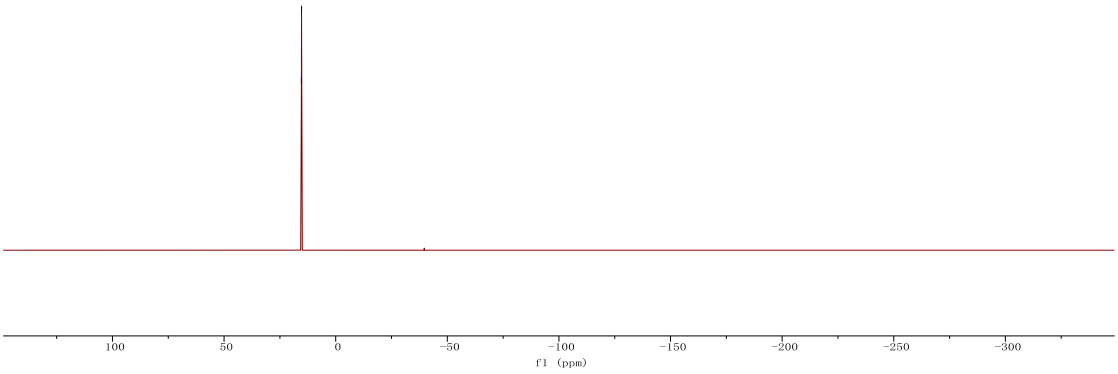

3s'
3s''
^{1}H NMR (500 MHz, in $CDCl_3$)
f1 (ppm)

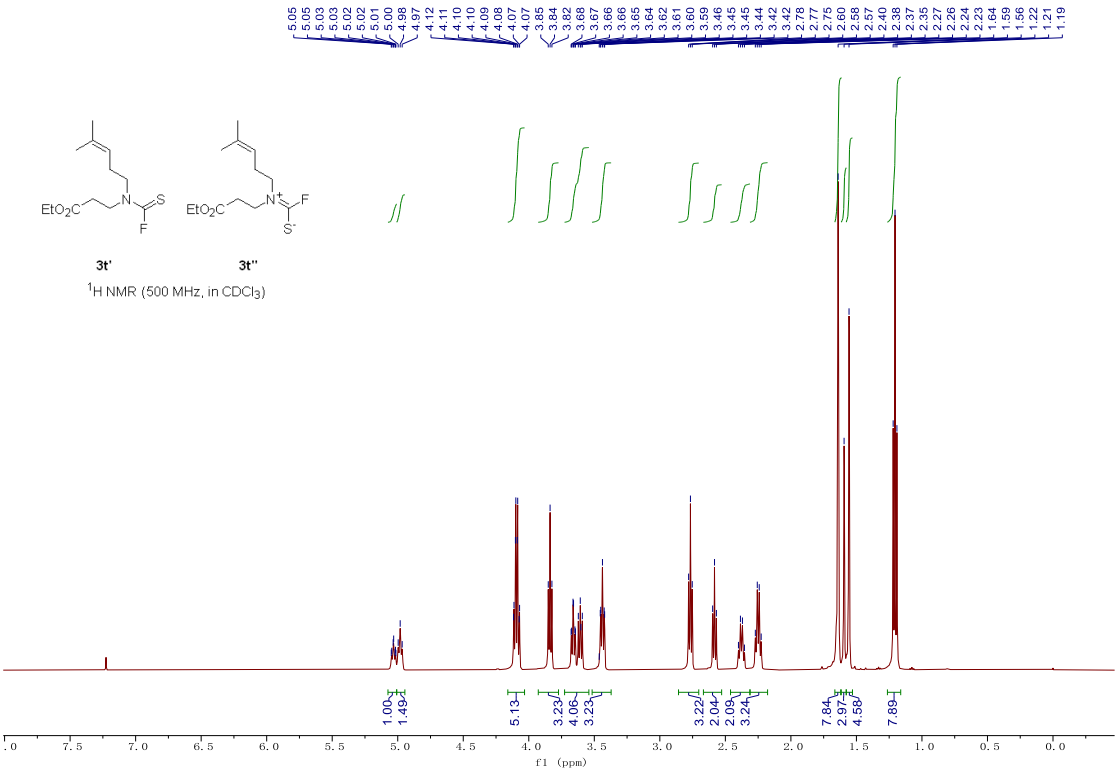

3s'
3s''
^{13}C NMR (126 MHz, in $CDCl_3$)
f1 (ppm)



3s' **3s''**

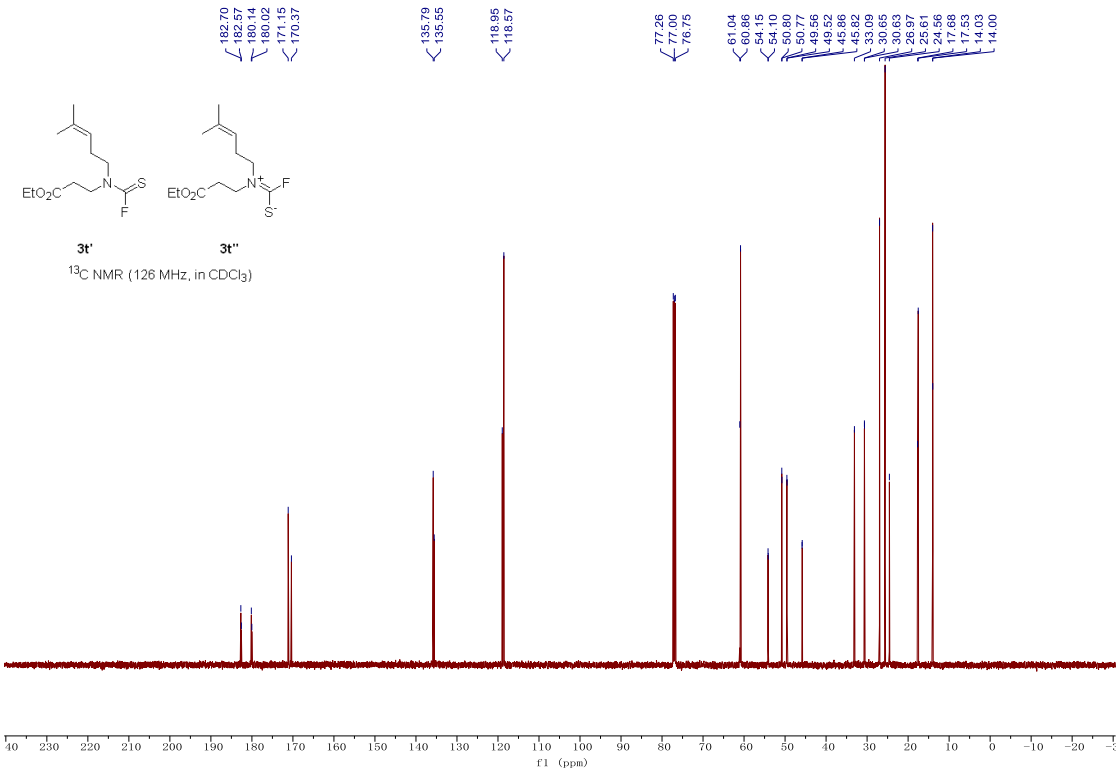
^{19}F NMR (471 MHz, in $CDCl_3$)

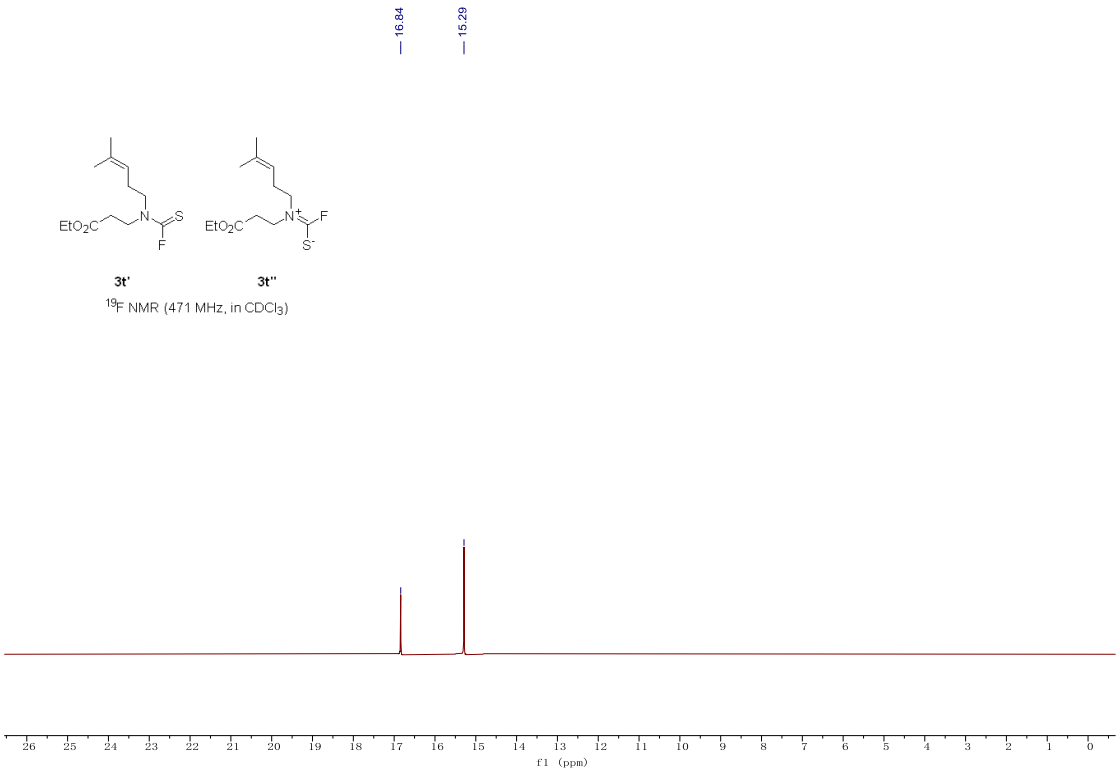


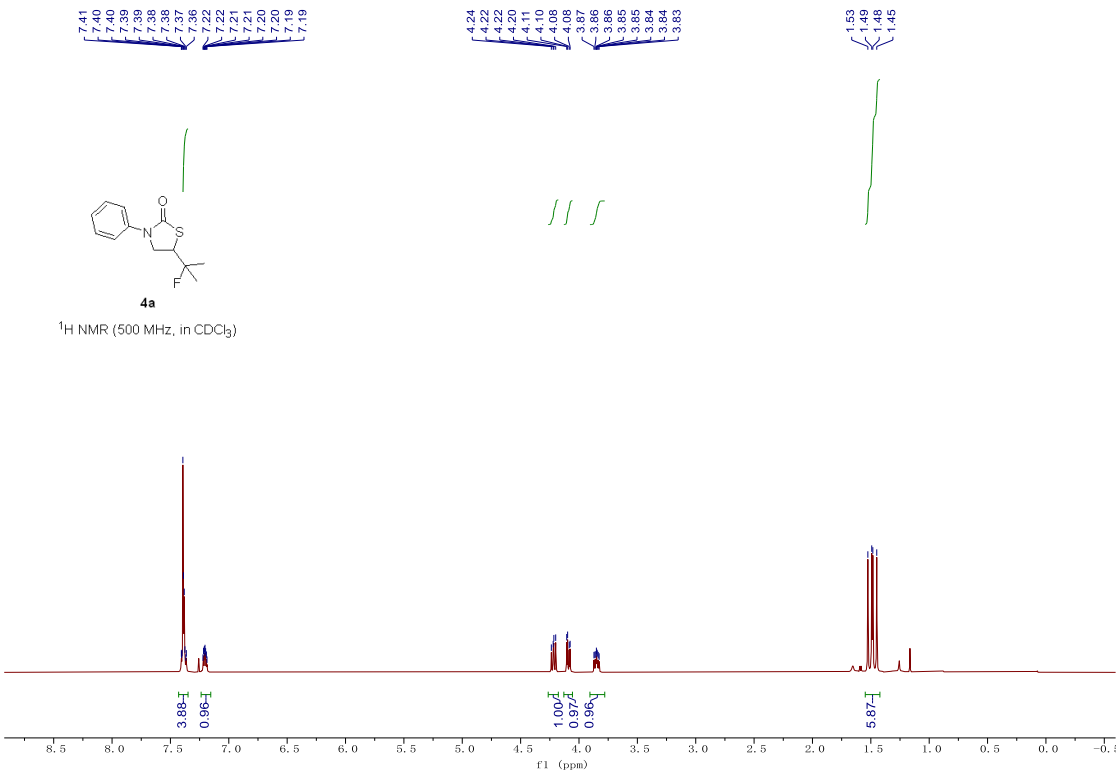


3t' **3t''**

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

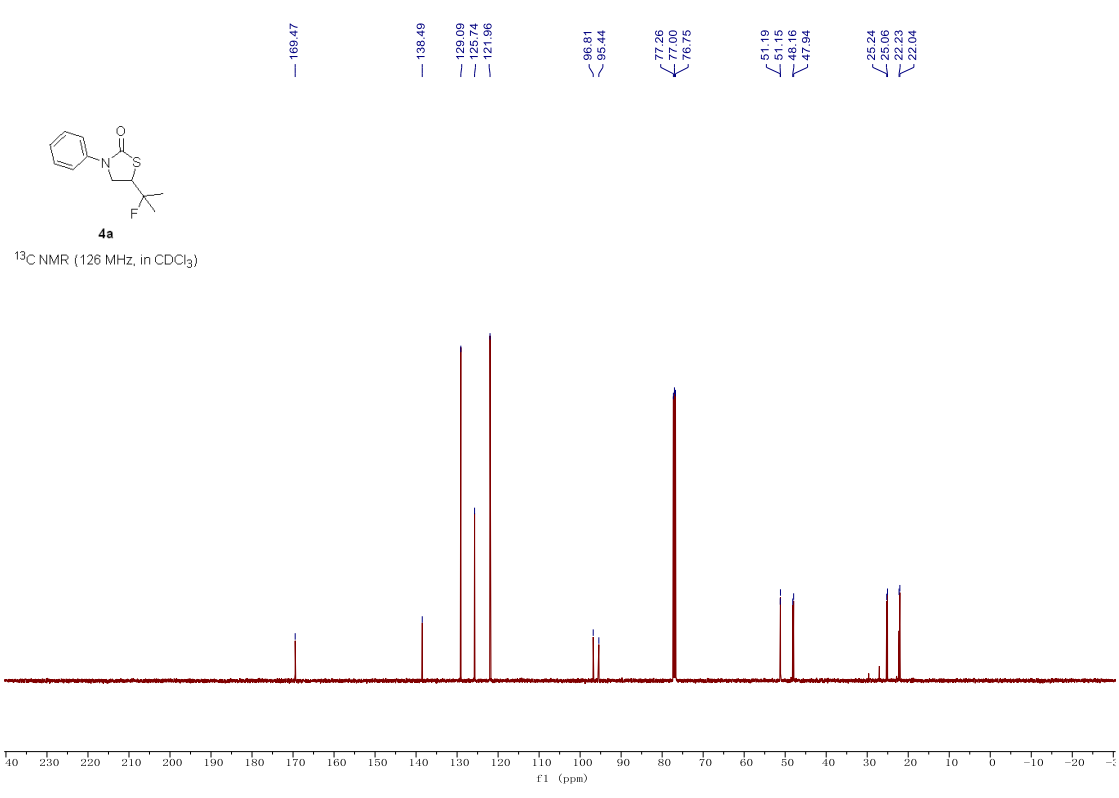

182.70
182.57
180.14
180.02
171.15
170.37
135.79
135.55
118.95
118.57
77.26
77.00
76.75
61.04
60.86
54.15
54.10
50.80
50.77
49.56
49.32
45.86
45.82
33.09
30.65
30.63
26.97
25.61
24.56
17.68
17.53
14.03
14.00
EtO2C
N
S
F
EtO2C
N+
F
S-
3t'
3t''
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


16.84
15.29
EtO2C
N
S
F
EtO2C
N+
F
S-
3t'
3t''
19F NMR (471 MHz, in CDCl3)
f1 (ppm)



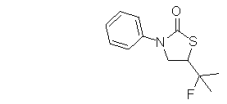
4a

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



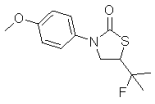
4a

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



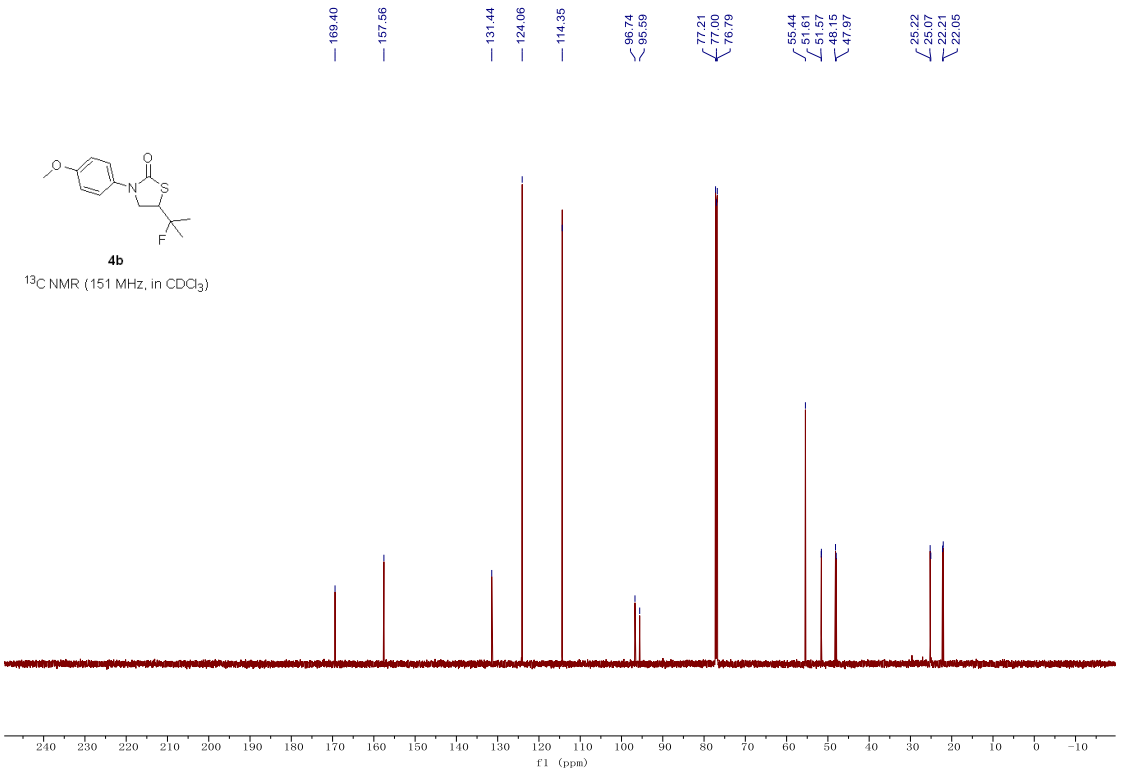
4a

^{19}F NMR (565 MHz, in $CDCl_3$)



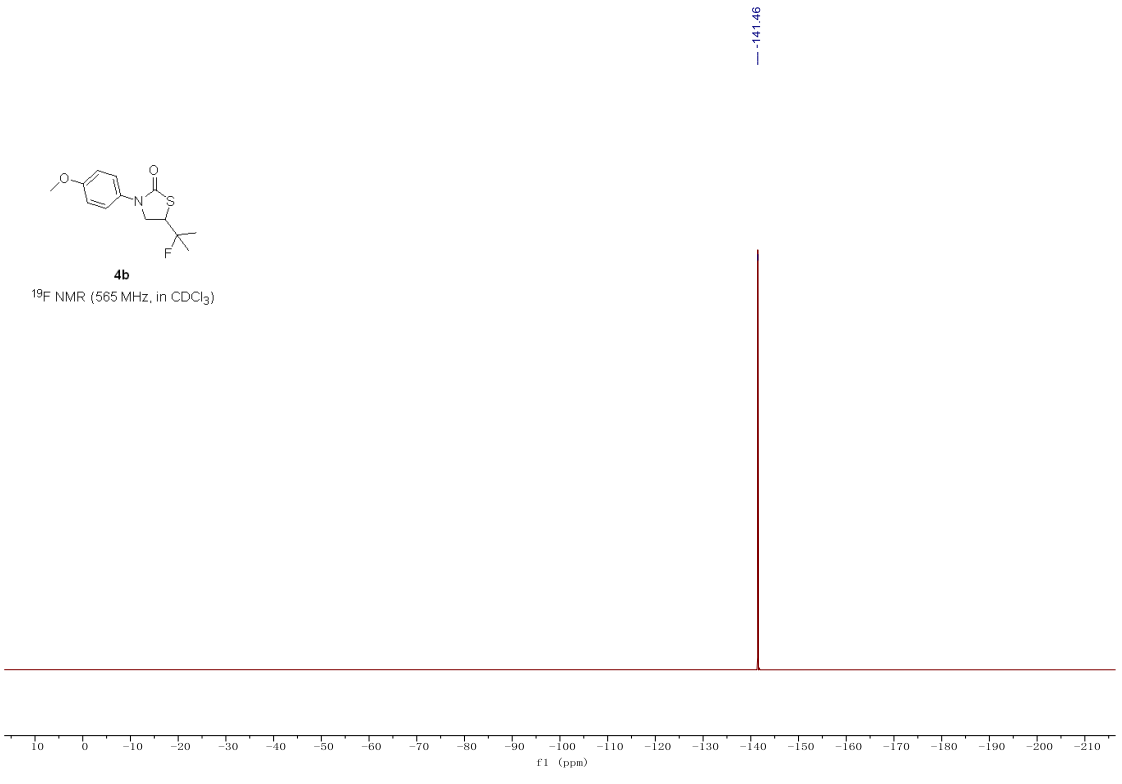
4b

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



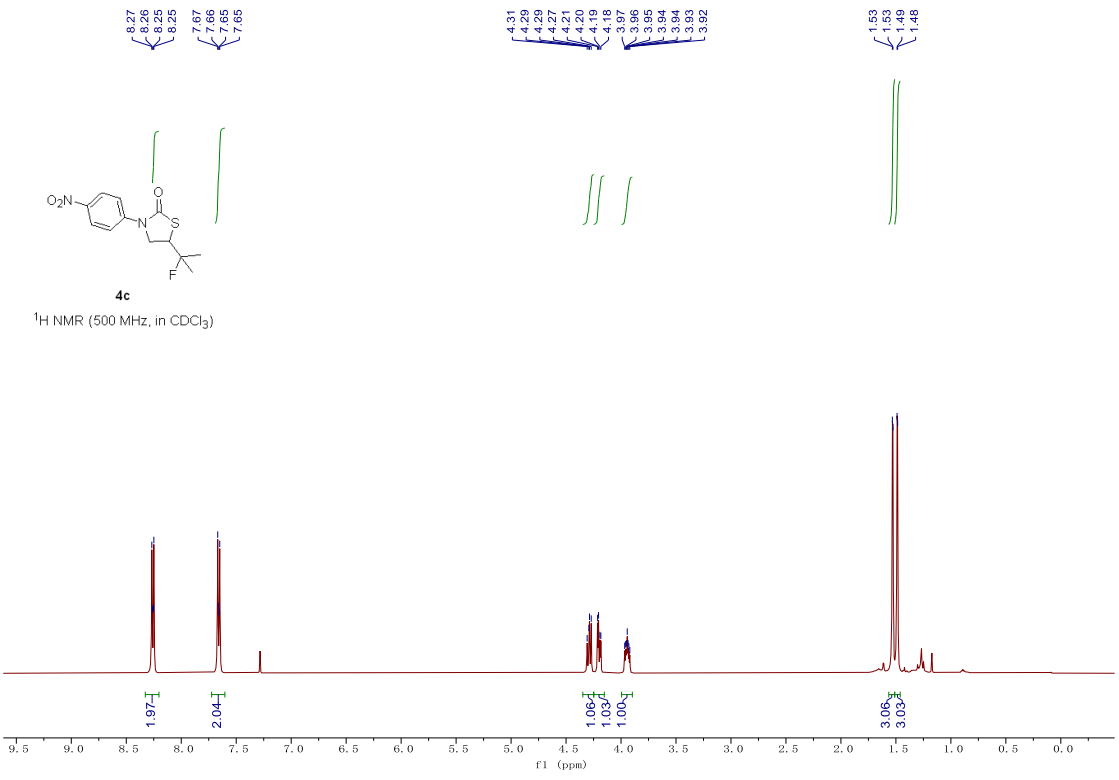
4b

^{13}C NMR (151 MHz, in $CDCl_3$)



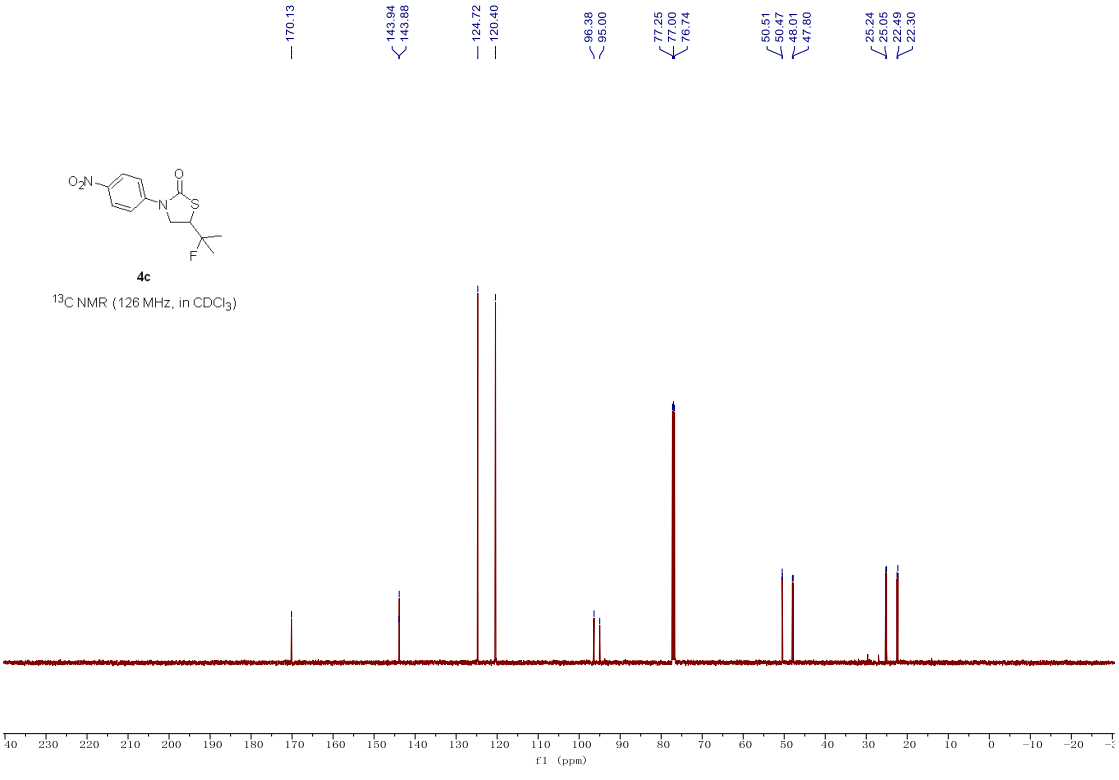
4b

^{19}F NMR (565 MHz, in $CDCl_3$)



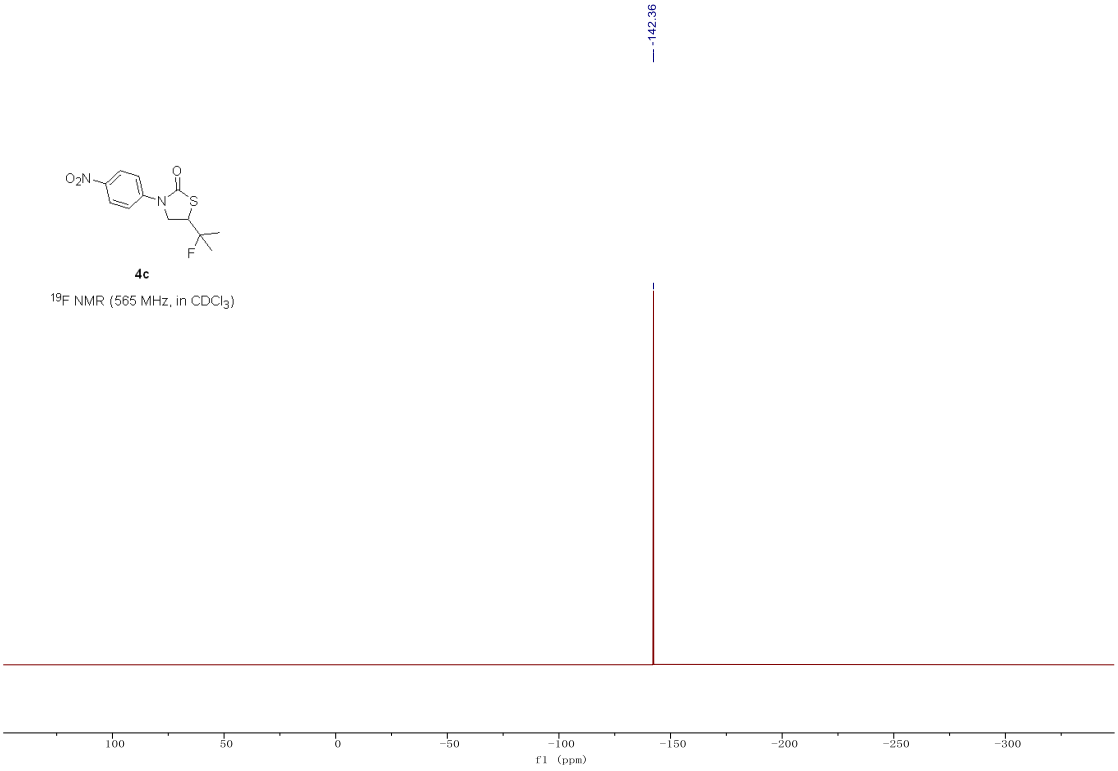
4c

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



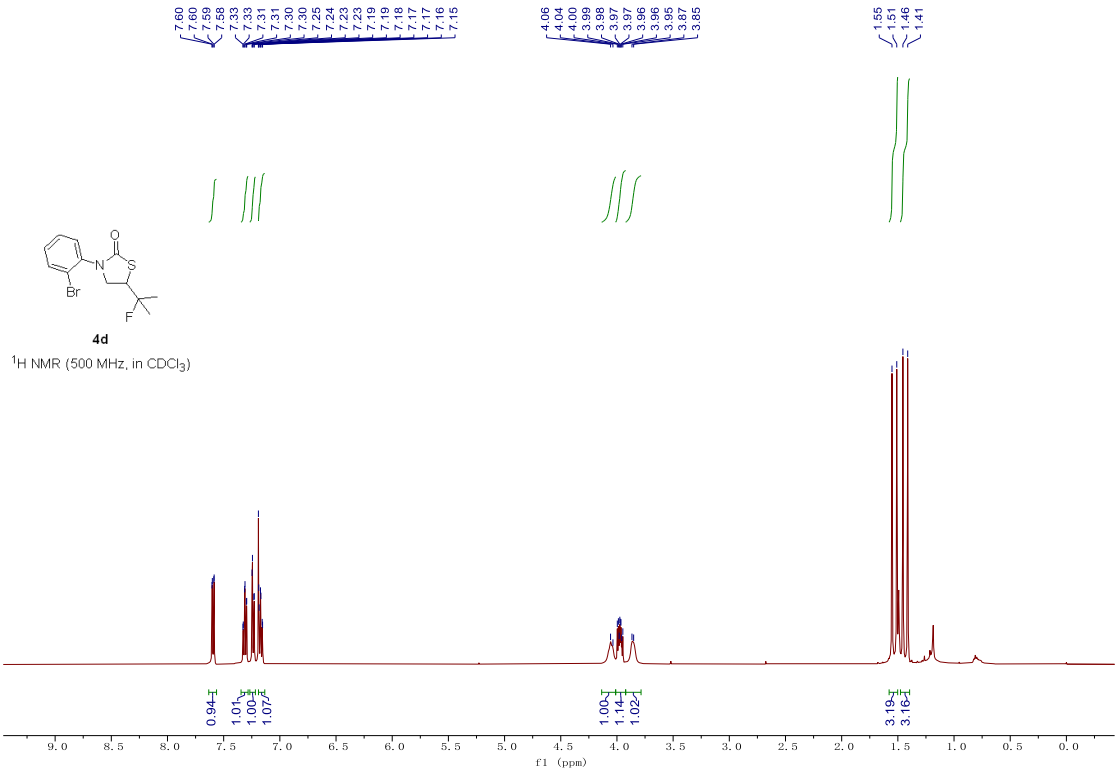
4c

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



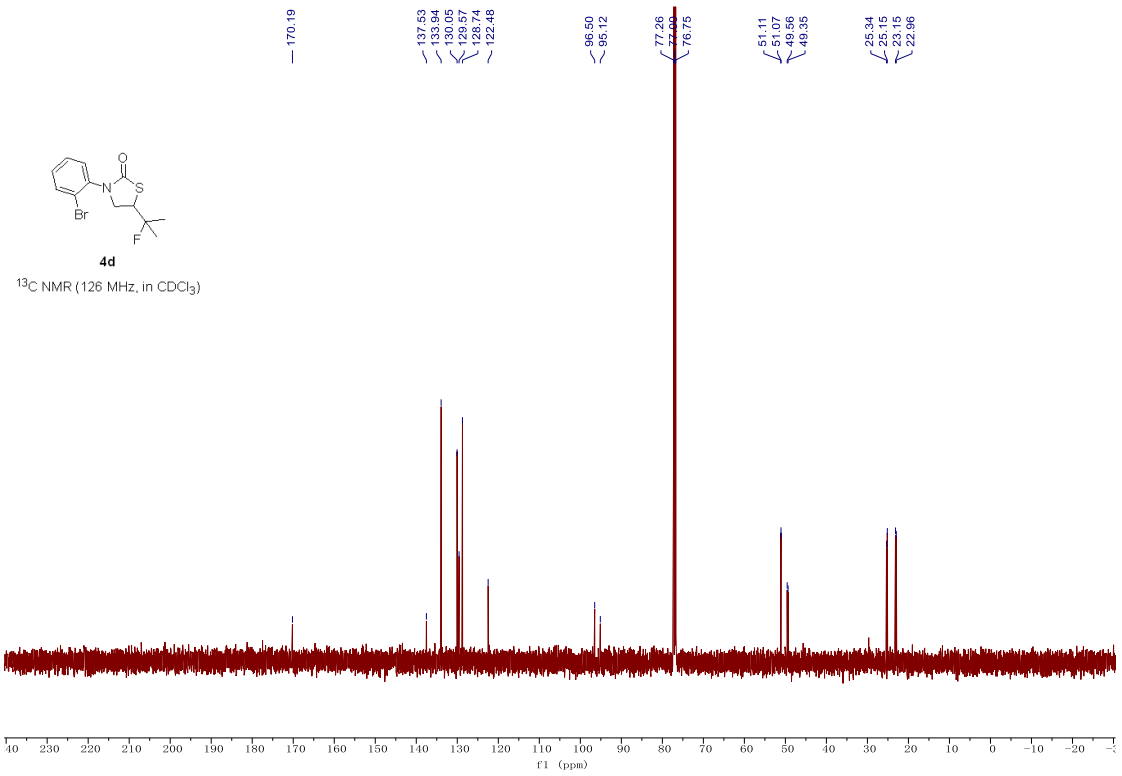
4c

^{19}F NMR (565 MHz, in $CDCl_3$)



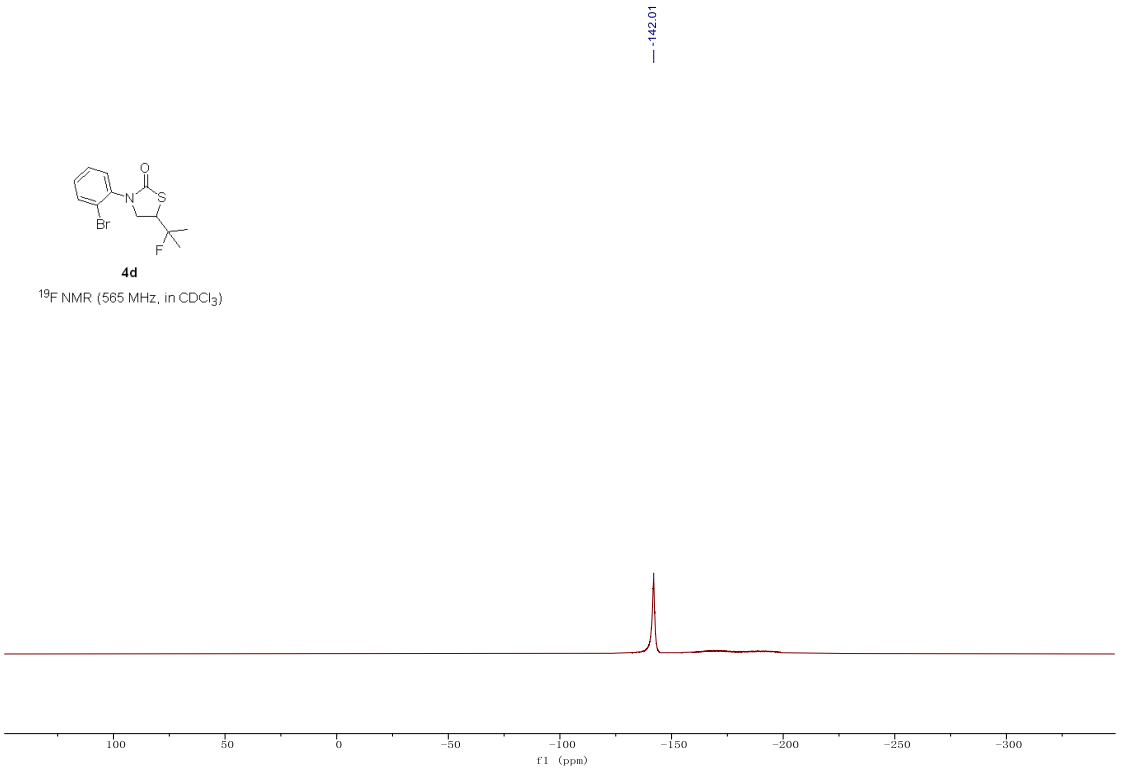
4d

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



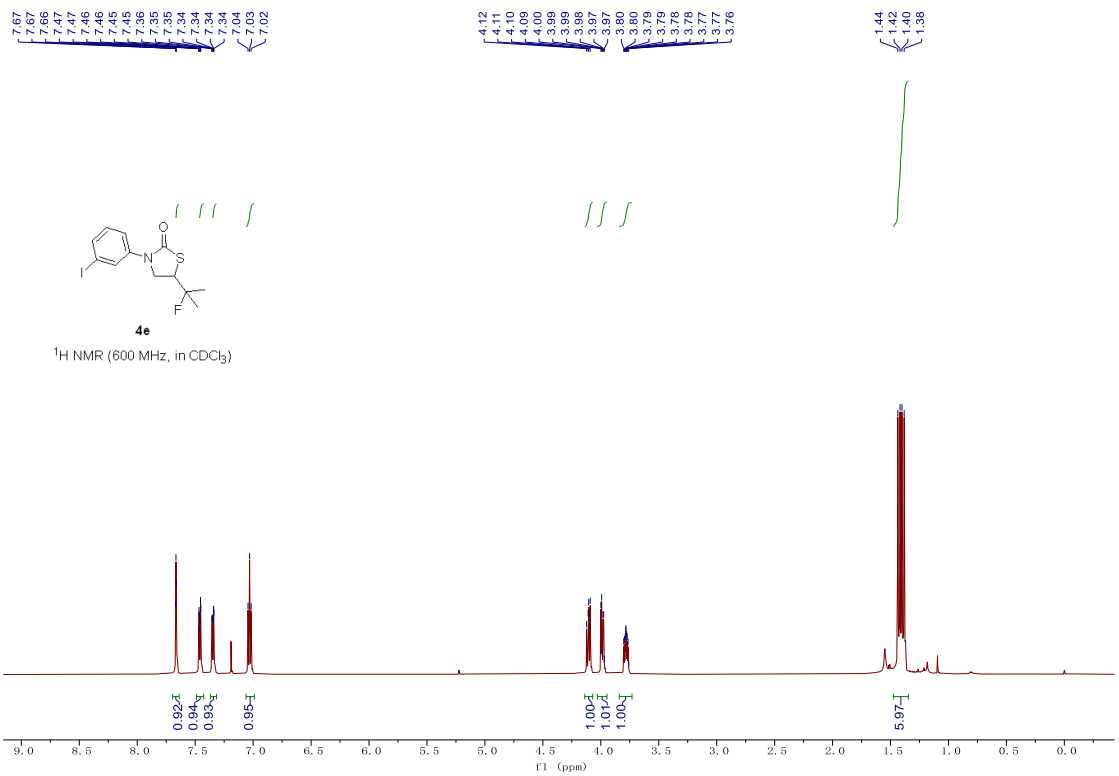
4d

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



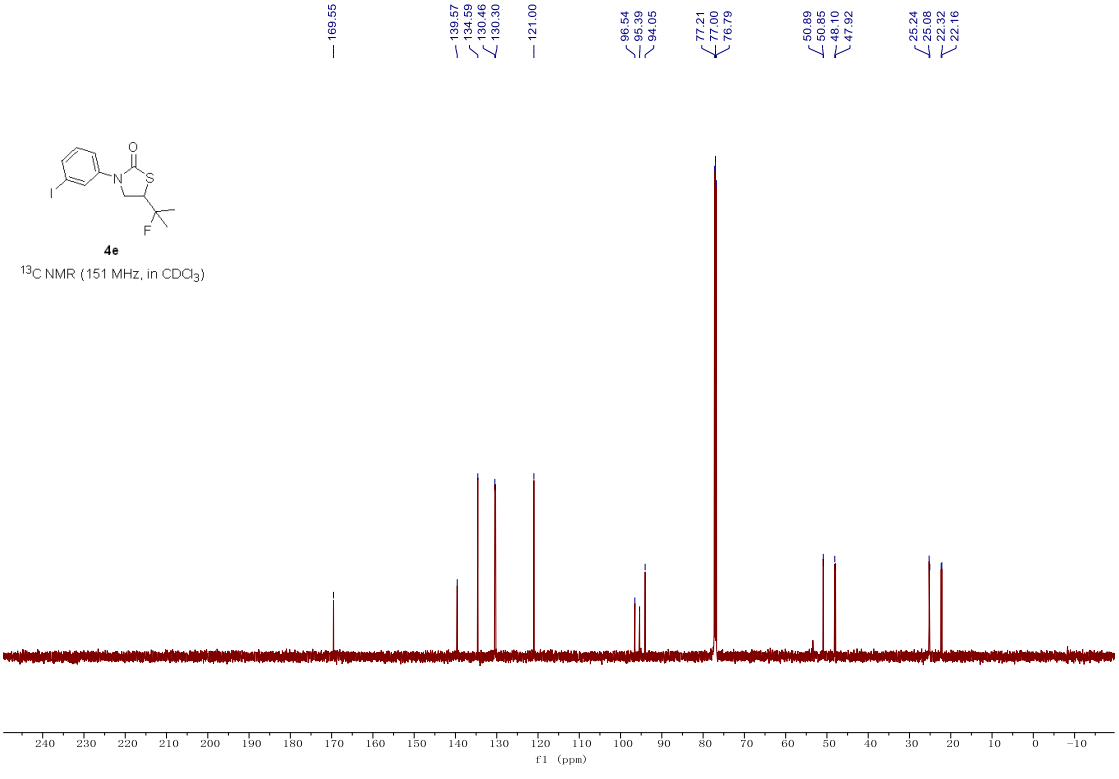
4d

^{19}F NMR (565 MHz, in $CDCl_3$)



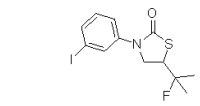
4e

^{1}H NMR (600 MHz, in $CDCl_3$)



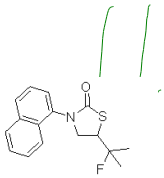
4e

^{13}C NMR (151 MHz, in $CDCl_3$)



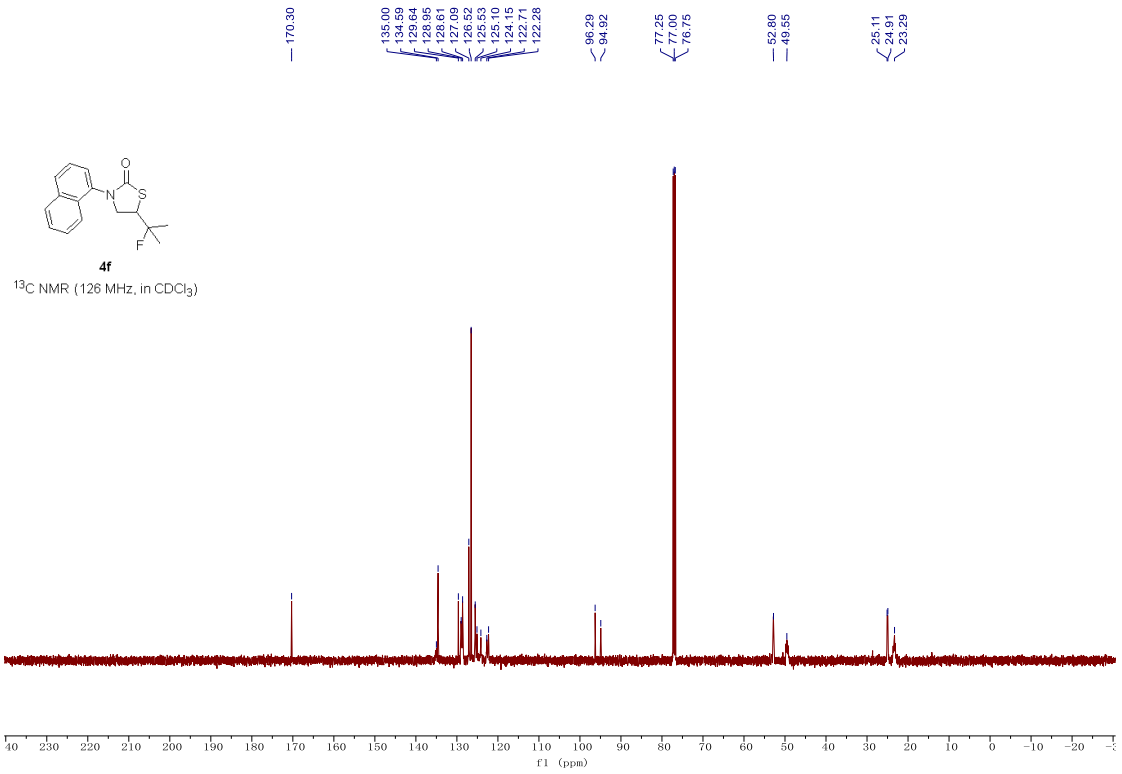
4e

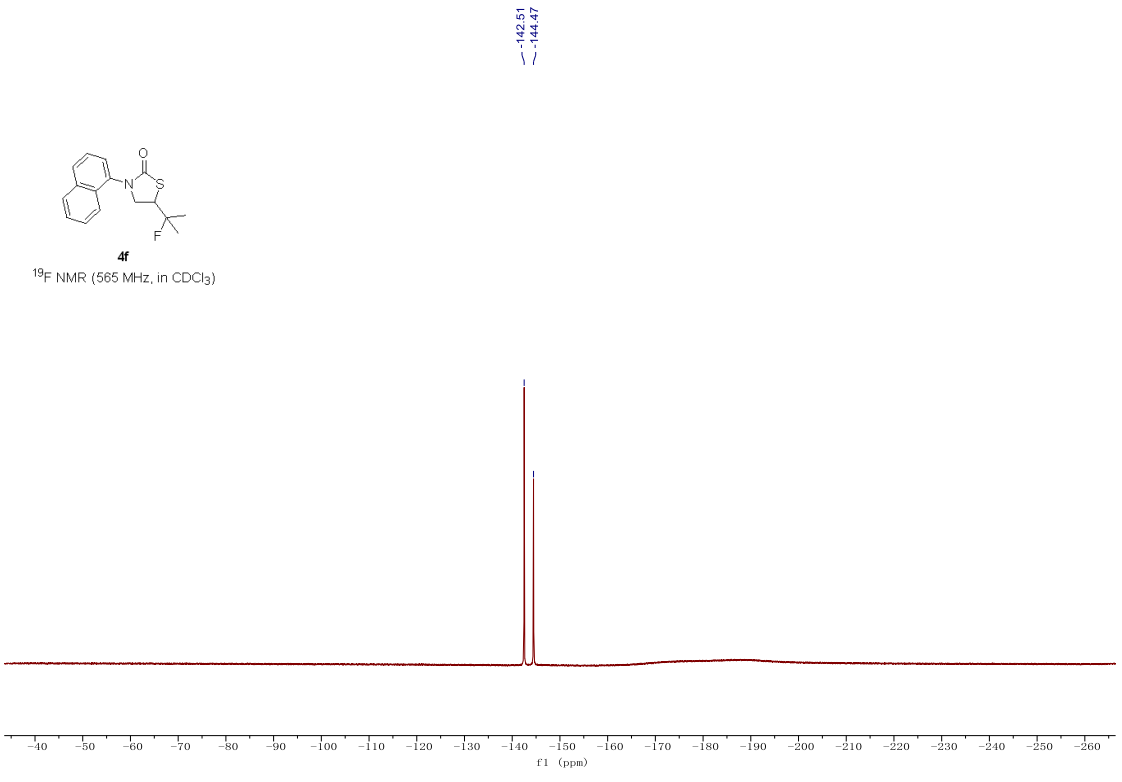
^{19}F NMR (565 MHz, in $CDCl_3$)

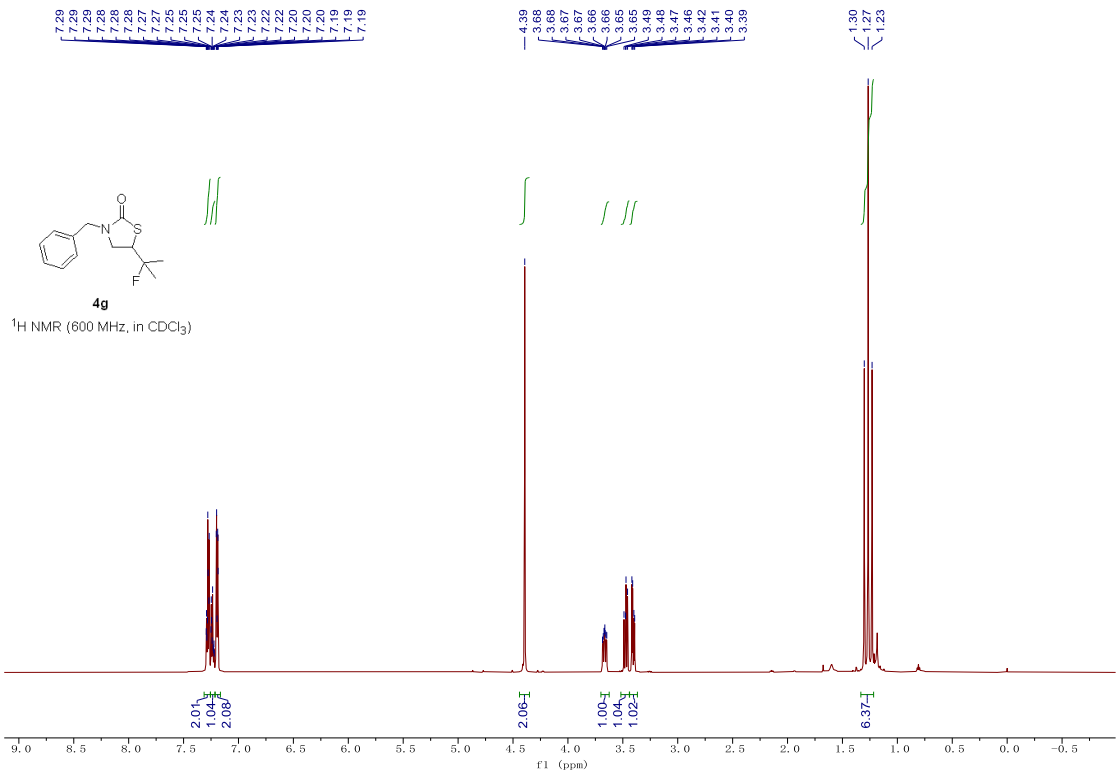


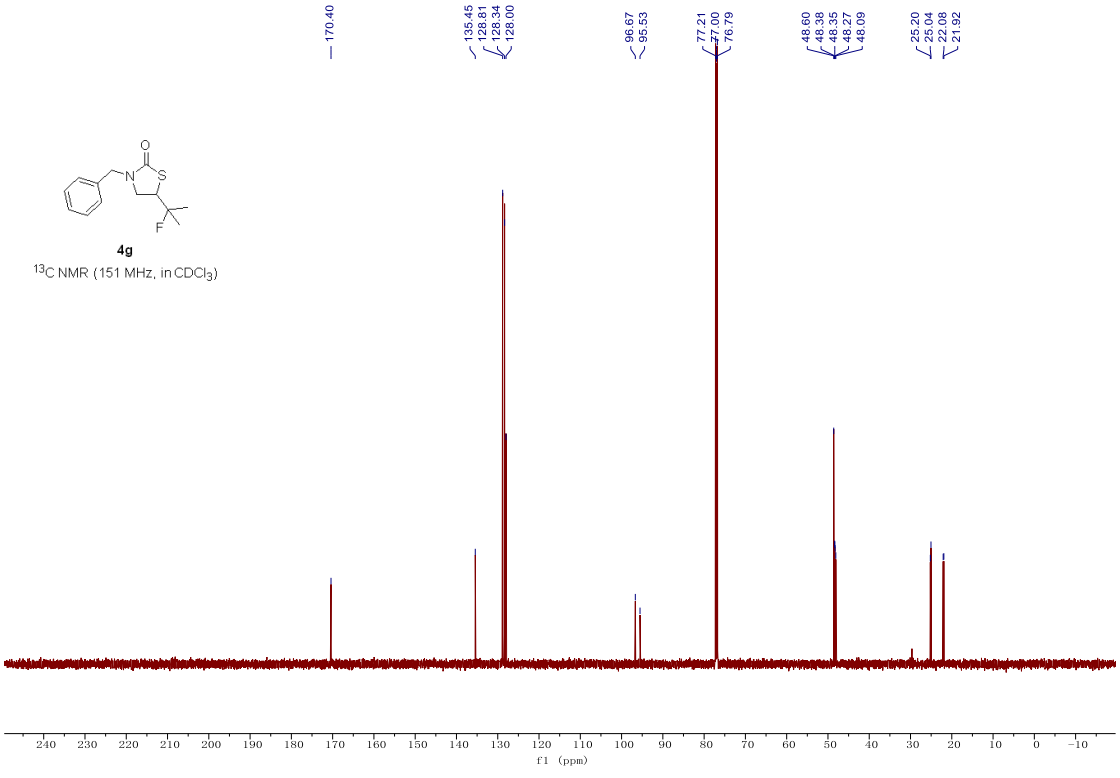
4f

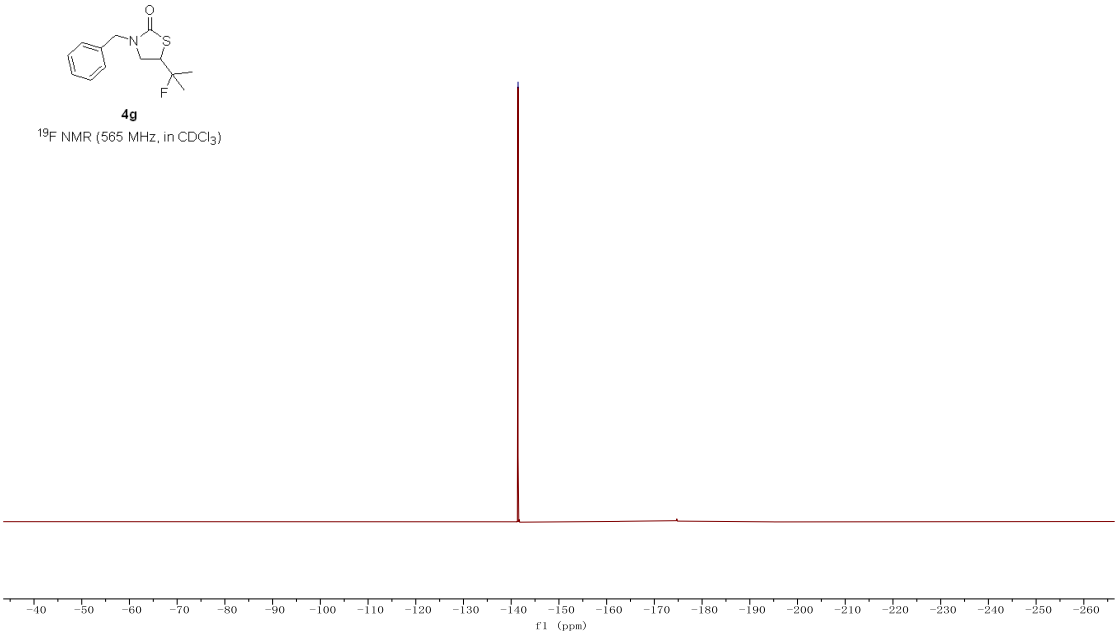
^{1}H NMR (500 MHz, in $CDCl_3$)


170.30
135.00
134.59
129.64
128.95
128.61
127.09
126.52
125.53
125.10
124.15
122.71
122.28
96.29
94.92
77.25
77.00
76.75
52.80
49.55
25.11
24.91
23.29
O
N
S
F
4f
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


-142.51
-144.47
O
N
S
F
4f
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

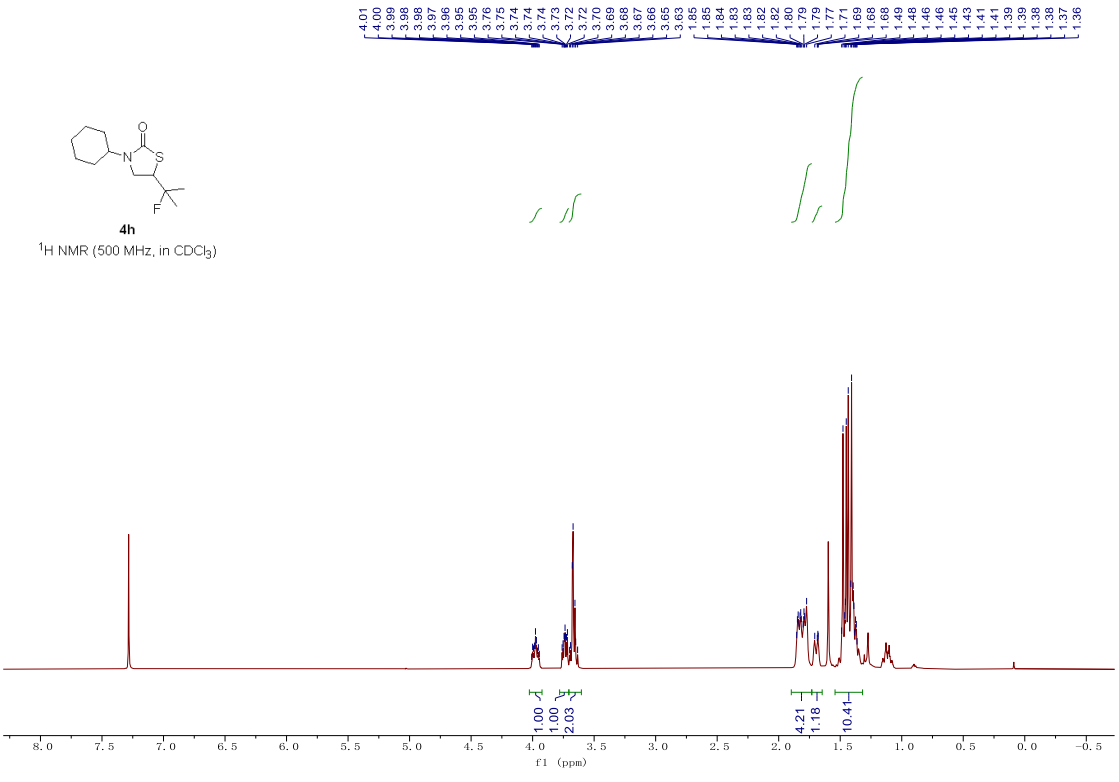

4g
1H NMR (600 MHz, in CDCl3)
f1 (ppm)


4g
13C NMR (151 MHz, in CDCl3)
f1 (ppm)



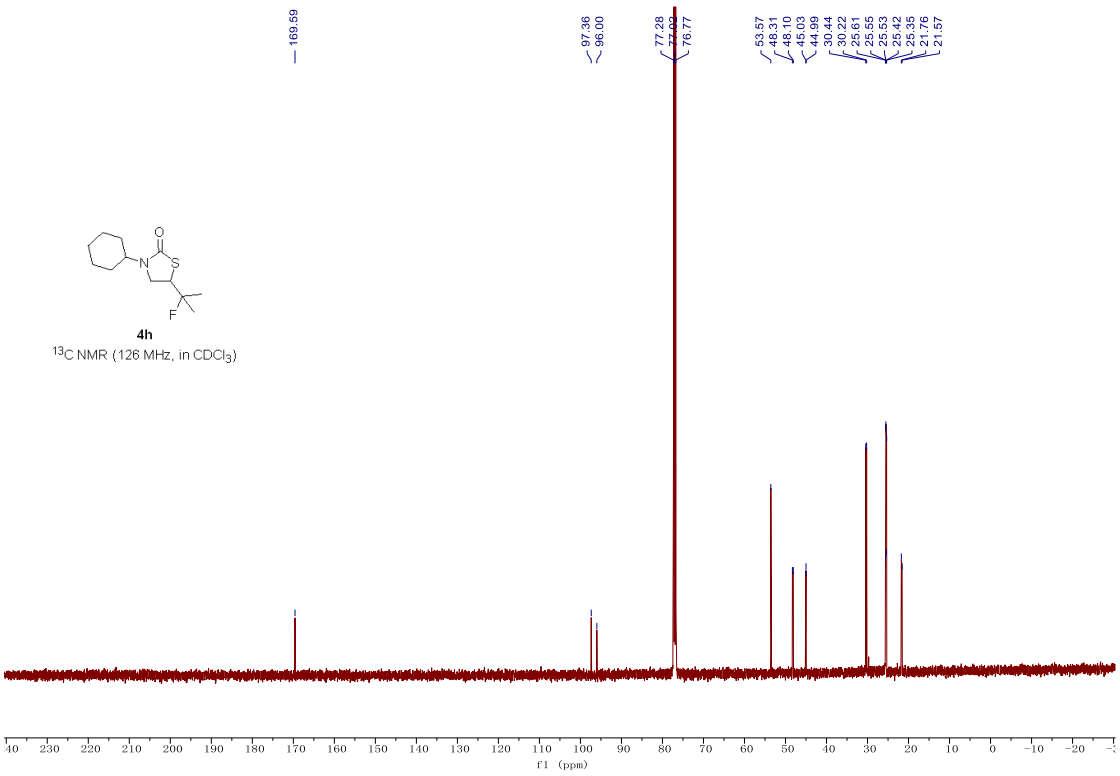
4g

^{19}F NMR (565 MHz, in $CDCl_3$)



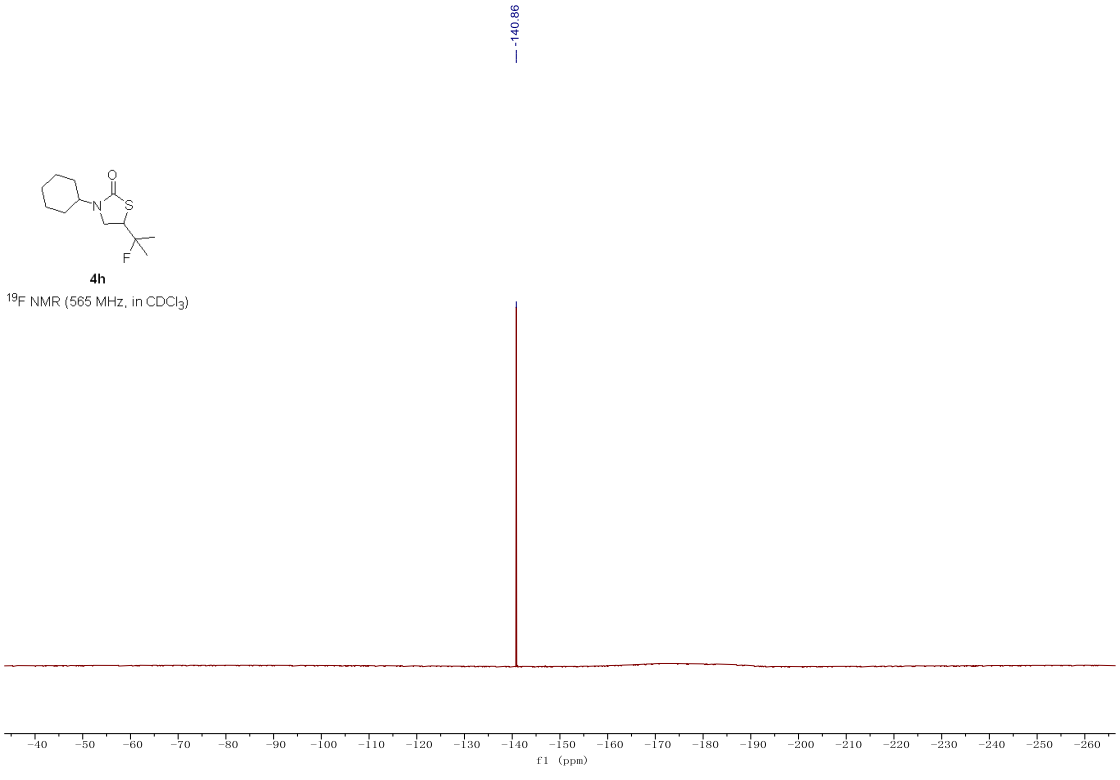
4h

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



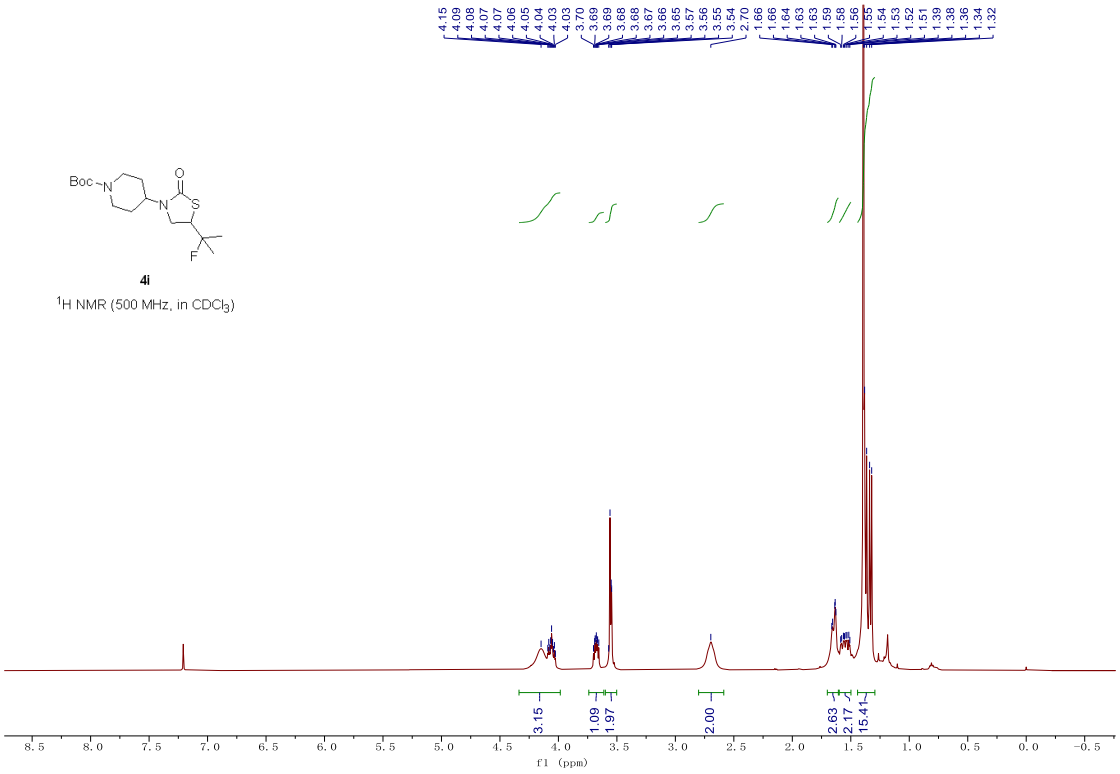
4h

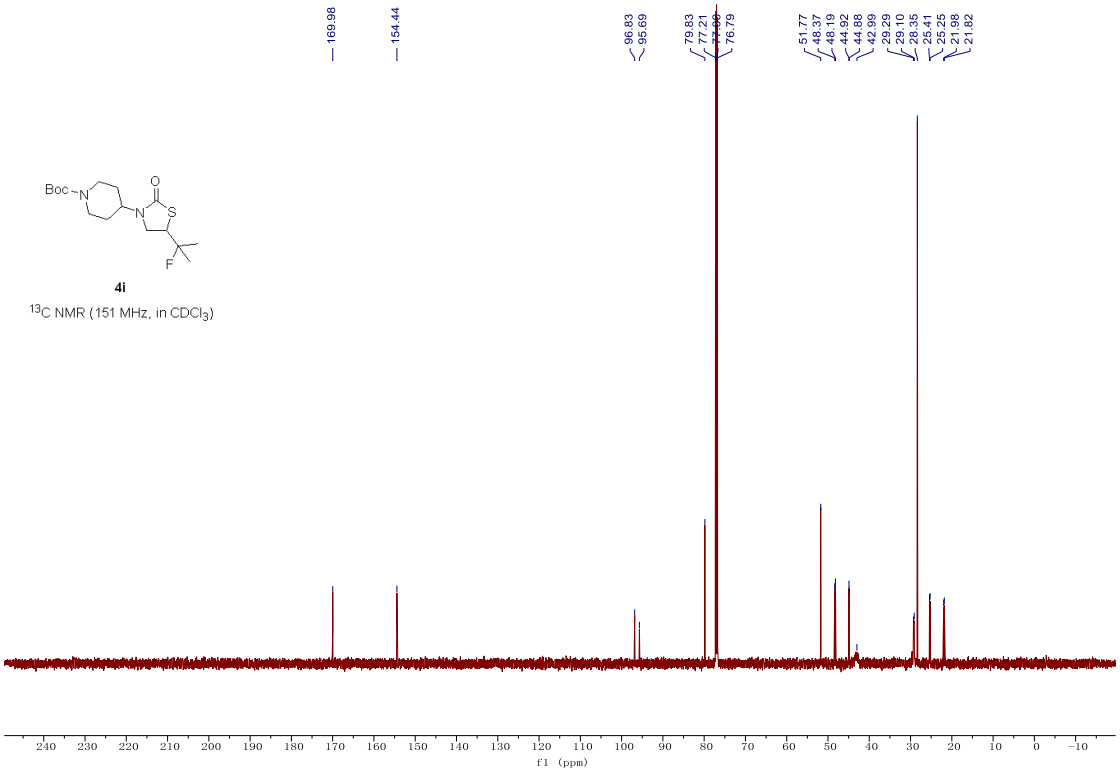
^{13}C NMR (126 MHz, in $CDCl_3$)

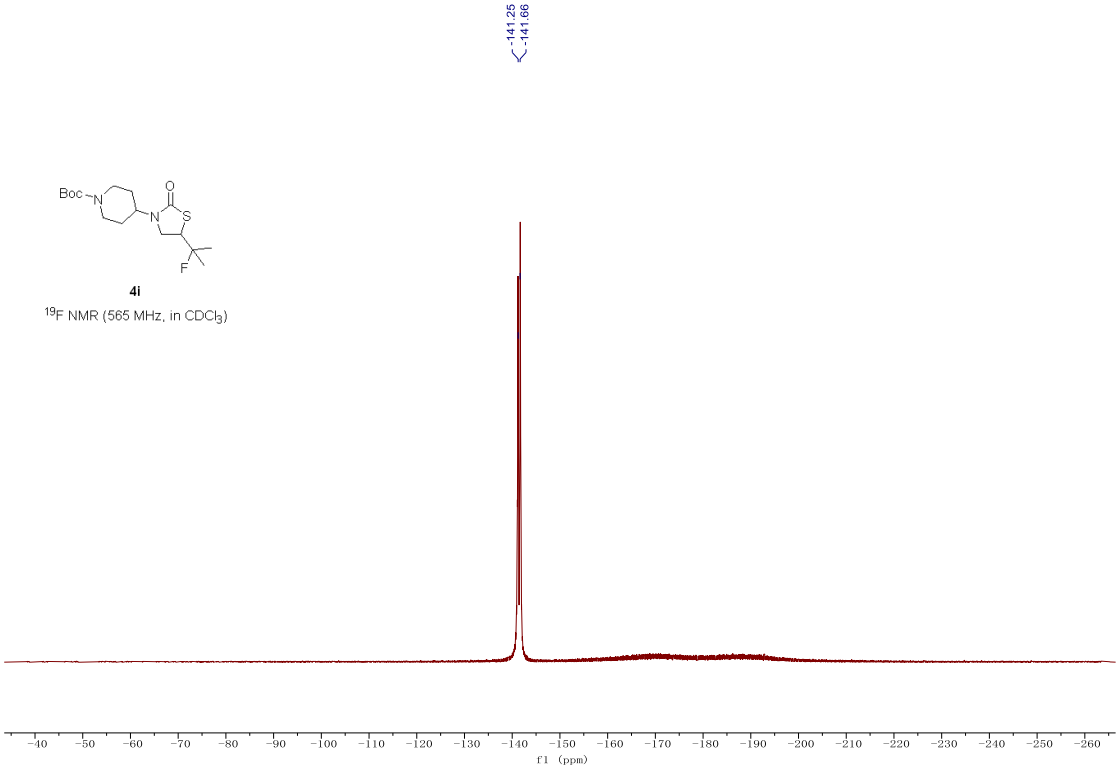


4h

^{19}F NMR (565 MHz, in $CDCl_3$)

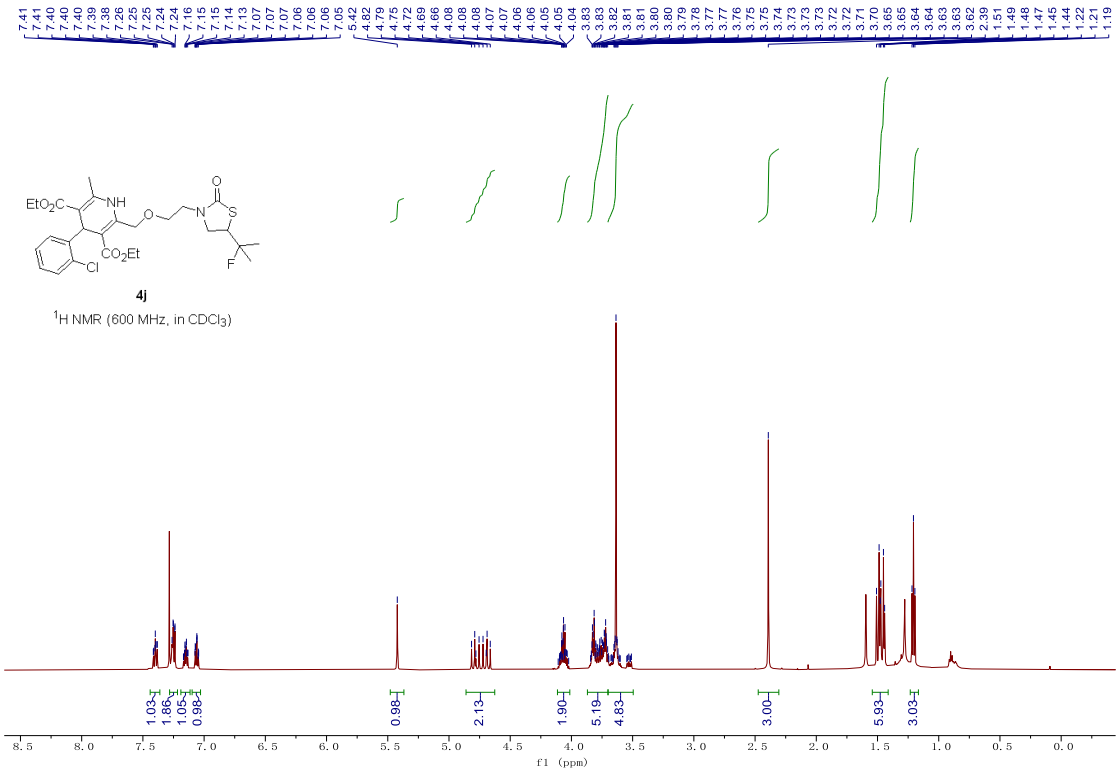

4.15
4.09
4.08
4.07
4.07
4.06
4.05
4.04
4.03
4.03
3.70
3.69
3.69
3.68
3.68
3.67
3.66
3.65
3.57
3.56
3.55
3.54
2.70
1.66
1.66
1.64
1.63
1.59
1.58
1.56
1.55
1.54
1.53
1.52
1.51
1.39
1.38
1.36
1.34
1.32
Boc
N
O
N
S
F
4i
1H NMR (500 MHz, in CDCl3)
3.15
1.09
1.97
2.00
2.63
2.17
15.41
f1 (ppm)


169.98
154.44
96.83
95.69
79.83
77.21
77.00
76.79
51.77
48.37
48.19
44.92
44.88
42.99
29.29
29.10
28.35
25.41
25.25
21.98
21.82
Boc
N
O
N
S
F
4i
13C NMR (151 MHz, in CDCl3)
f1 (ppm)



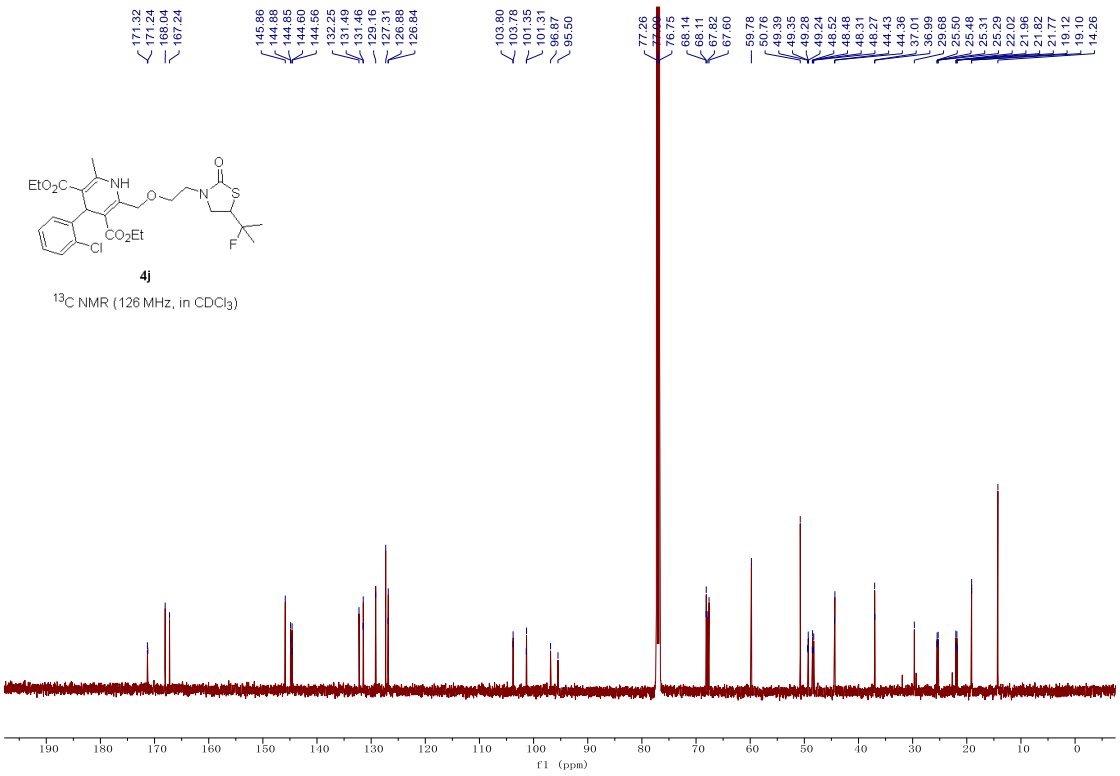
4i

^{19}F NMR (565 MHz, in $CDCl_3$)



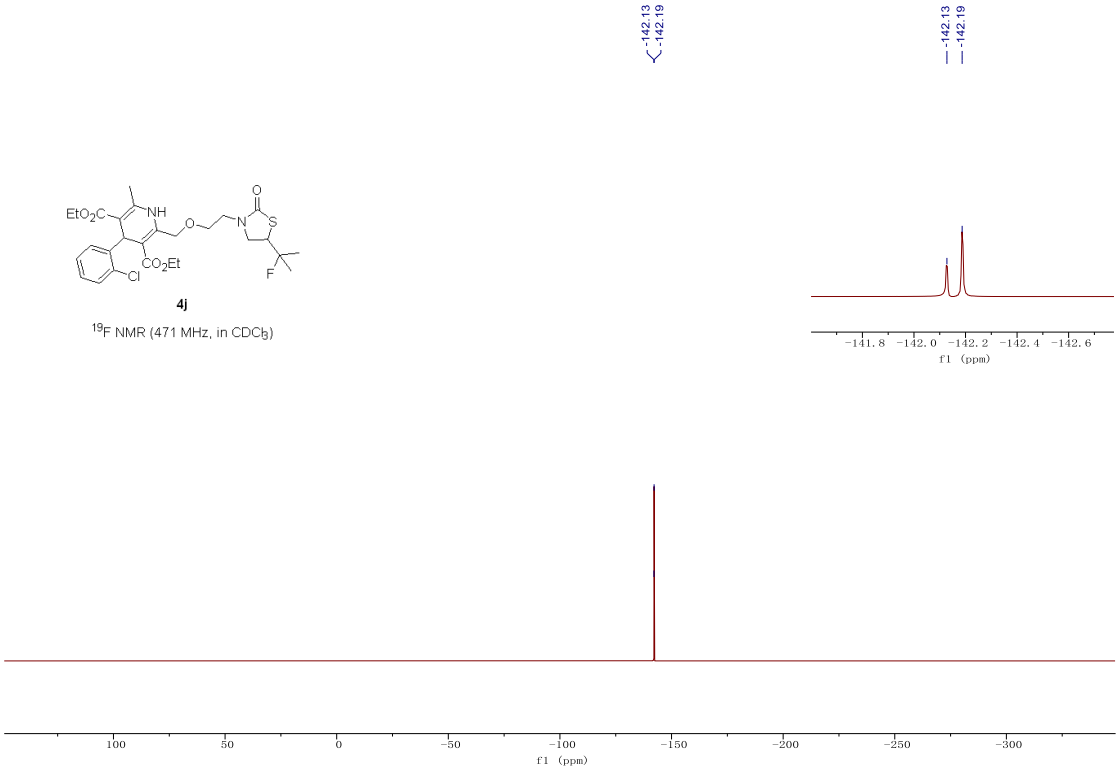
4j

^{1}H NMR (600 MHz, in $CDCl_3$)



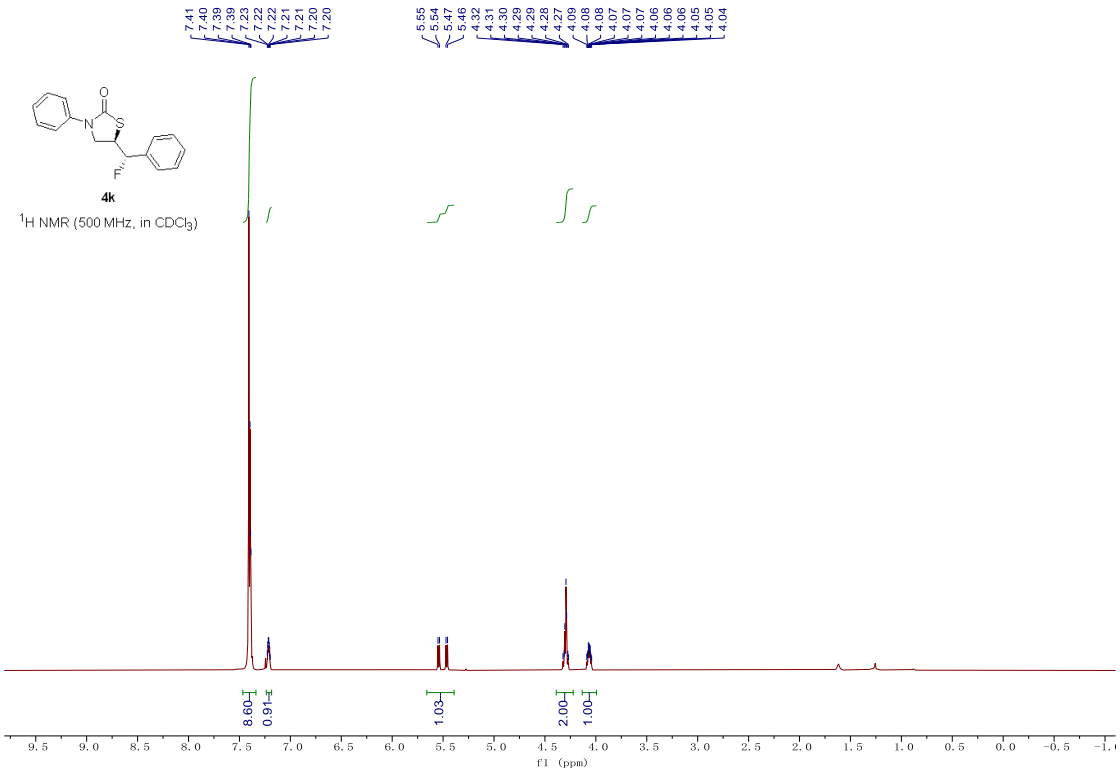
4j

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



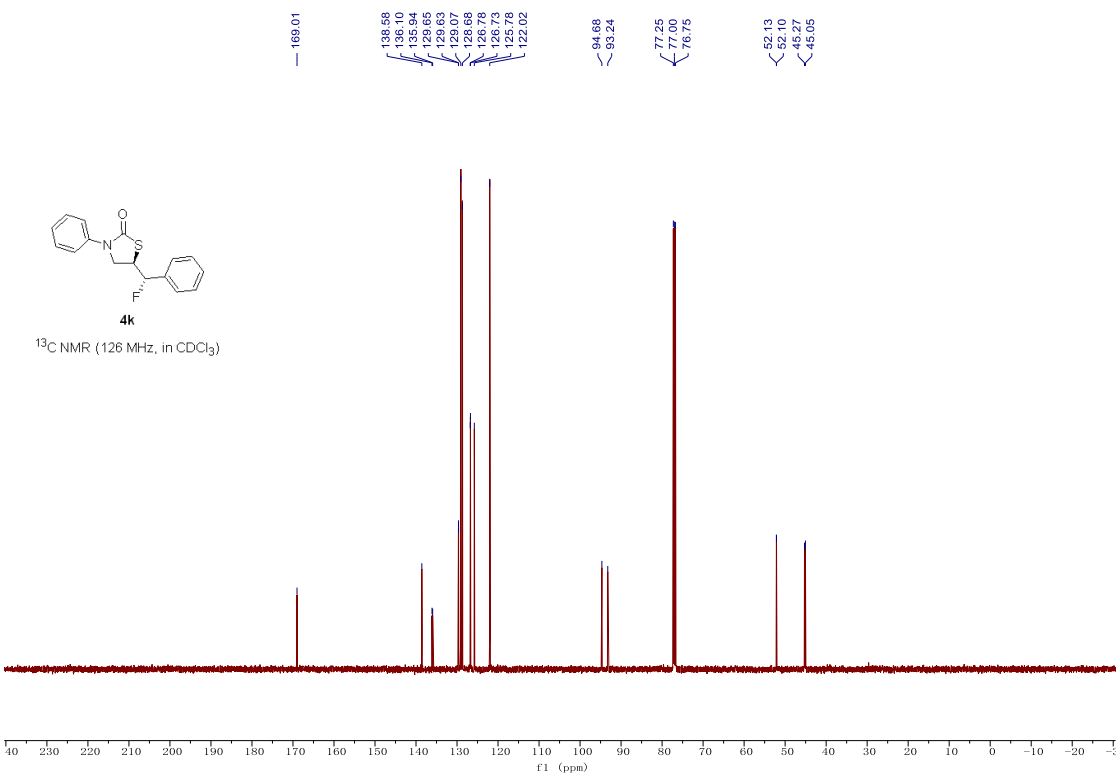
4j

^{19}F NMR (471 MHz, in $CDCl_3$)



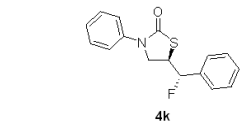
4k

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



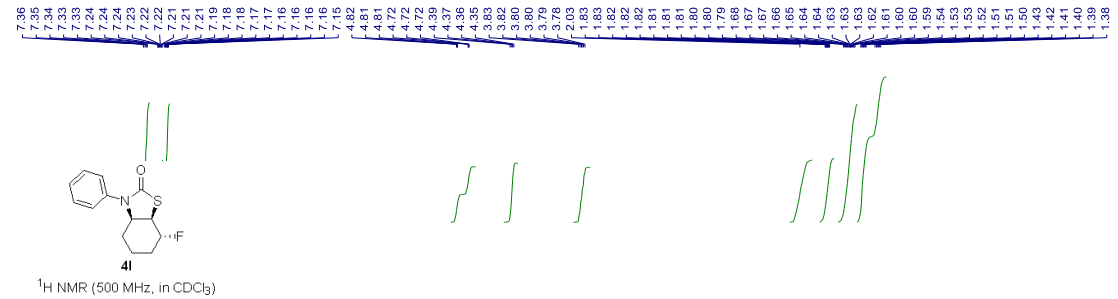
4k

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



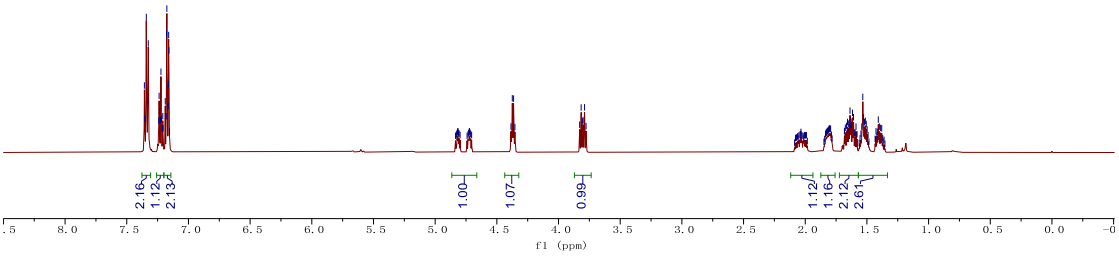
4k

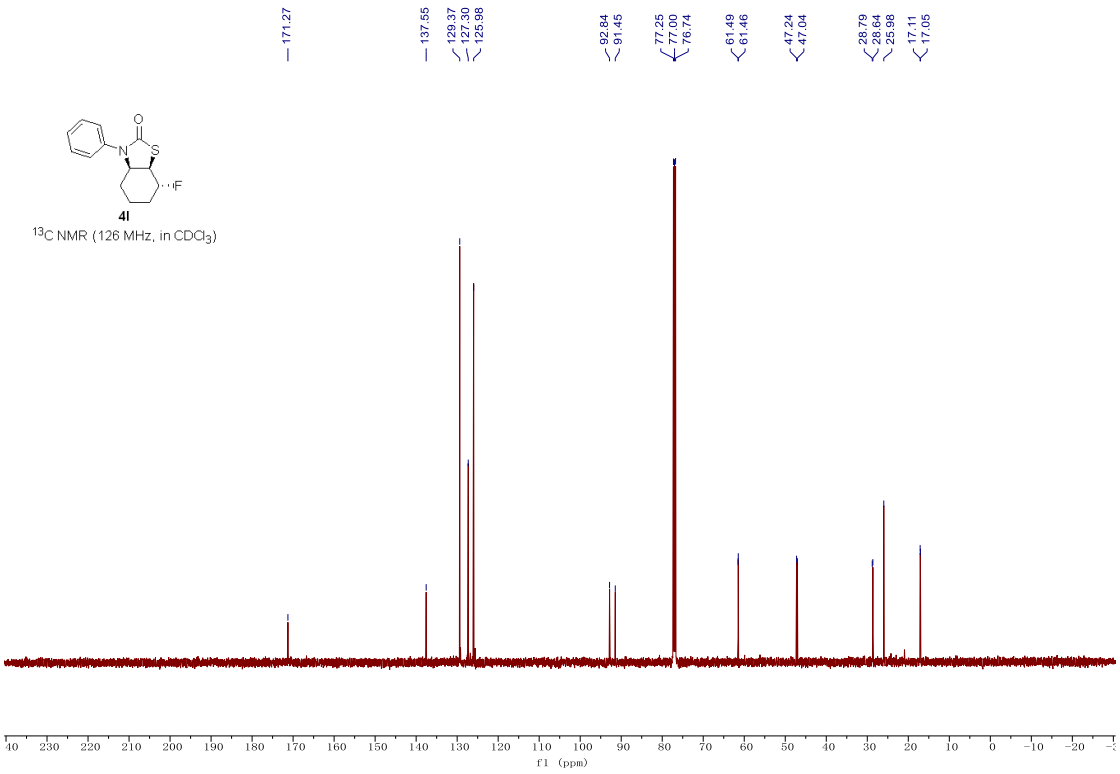
^{19}F NMR (565 MHz, in $CDCl_3$)



4l

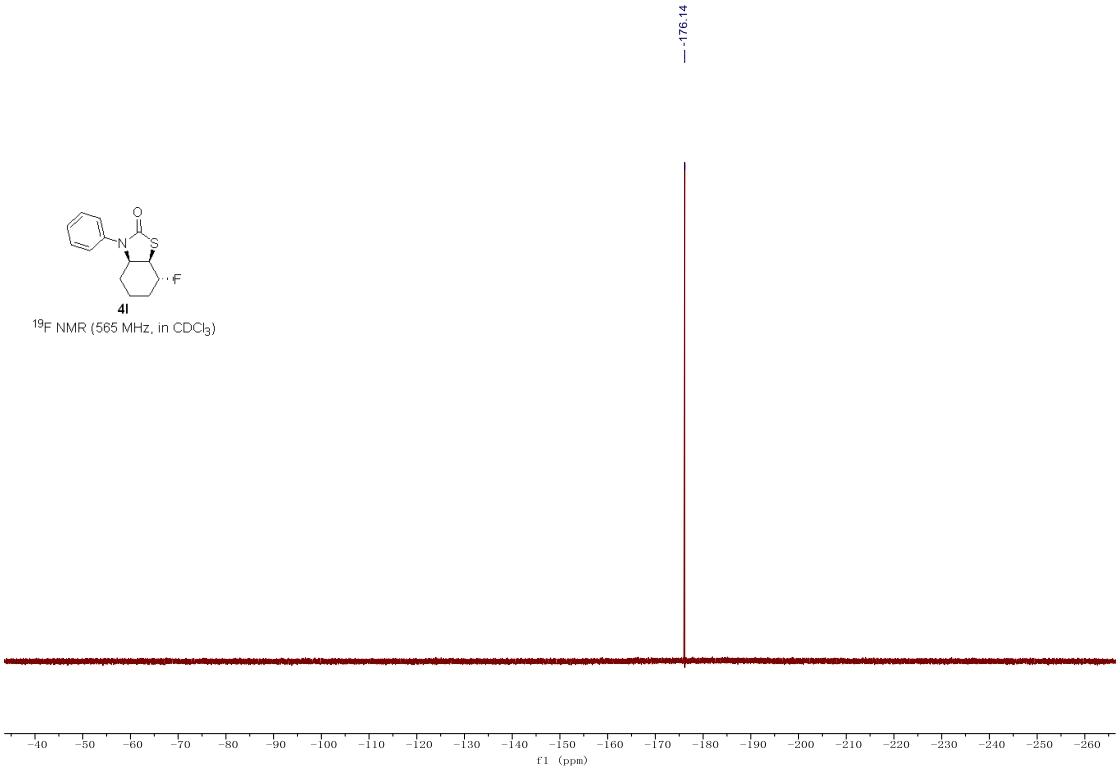
^{1}H NMR (500 MHz, in $CDCl_3$)





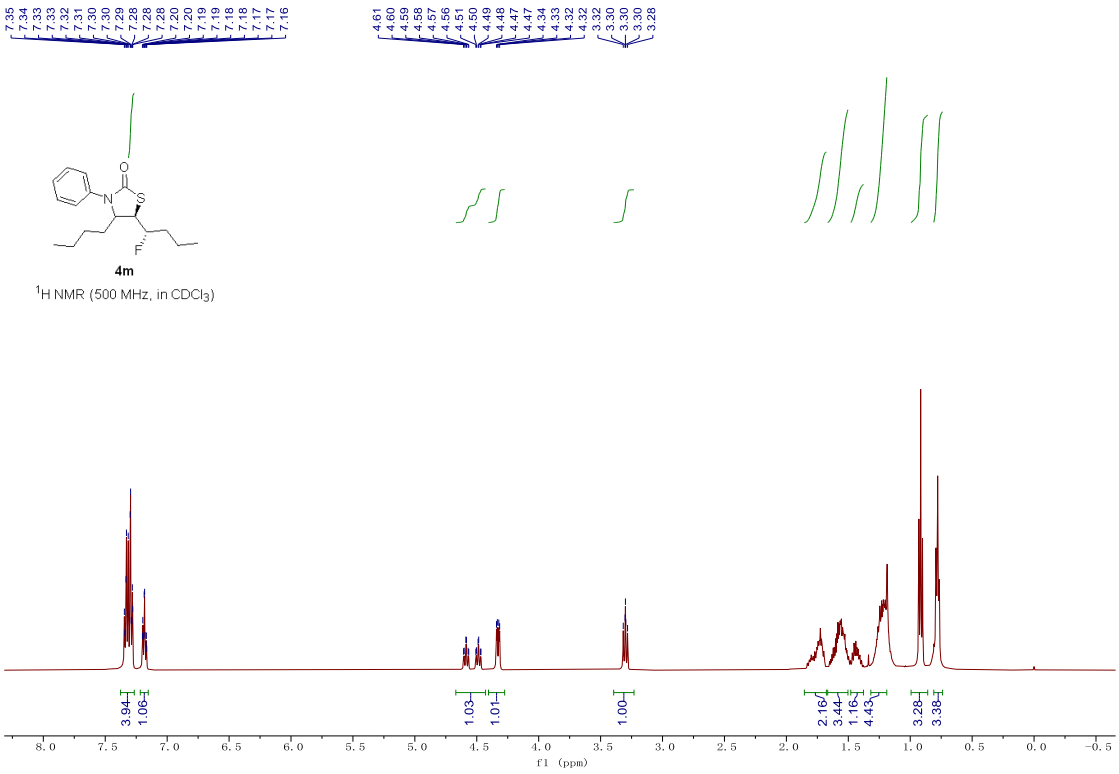
4l

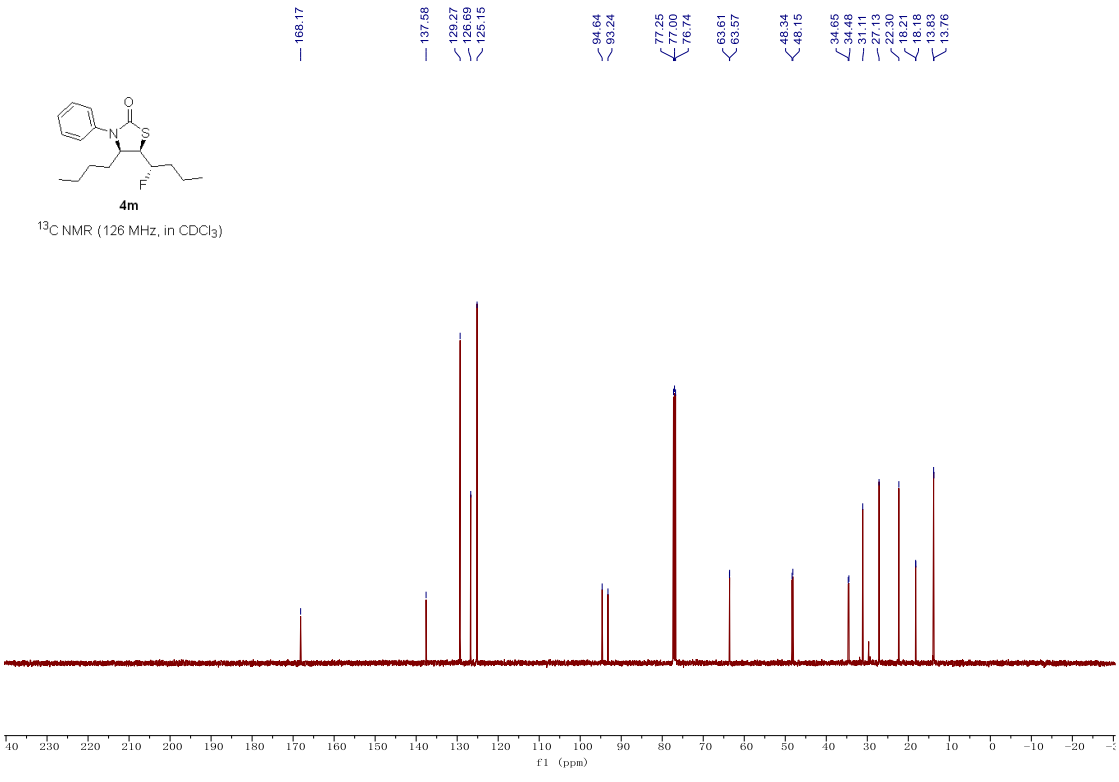
^{13}C NMR (126 MHz, in $CDCl_3$)

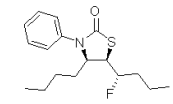


4l

^{19}F NMR (565 MHz, in $CDCl_3$)

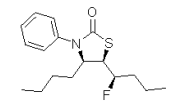

7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.28 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16
4.61 4.60 4.59 4.58 4.57 4.56 4.51 4.50 4.49 4.48 4.47 4.47 4.34 4.33 4.32 4.32 3.32 3.30 3.30 3.30 3.28
O
N
S
F
4m
1H NMR (500 MHz, in CDCl3)
3.94 1.06 1.03 1.01 1.00 2.16 3.44 1.16 4.43 3.28 3.38
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


168.17
137.58
129.27
126.69
125.15
94.64
93.24
77.25
77.00
76.74
63.61
63.57
48.34
48.15
34.65
34.48
31.11
27.13
22.30
18.21
18.18
13.83
13.76
O
N
S
F
4m
13C NMR (126 MHz, in CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



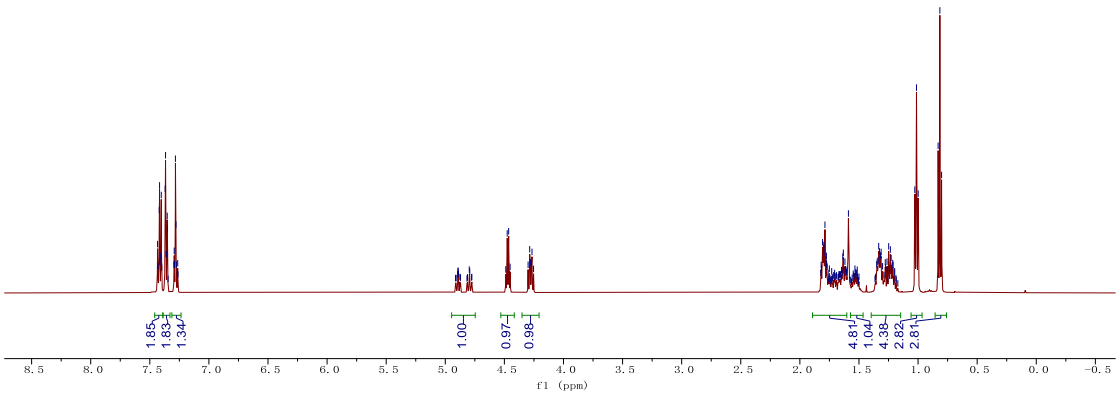
4m

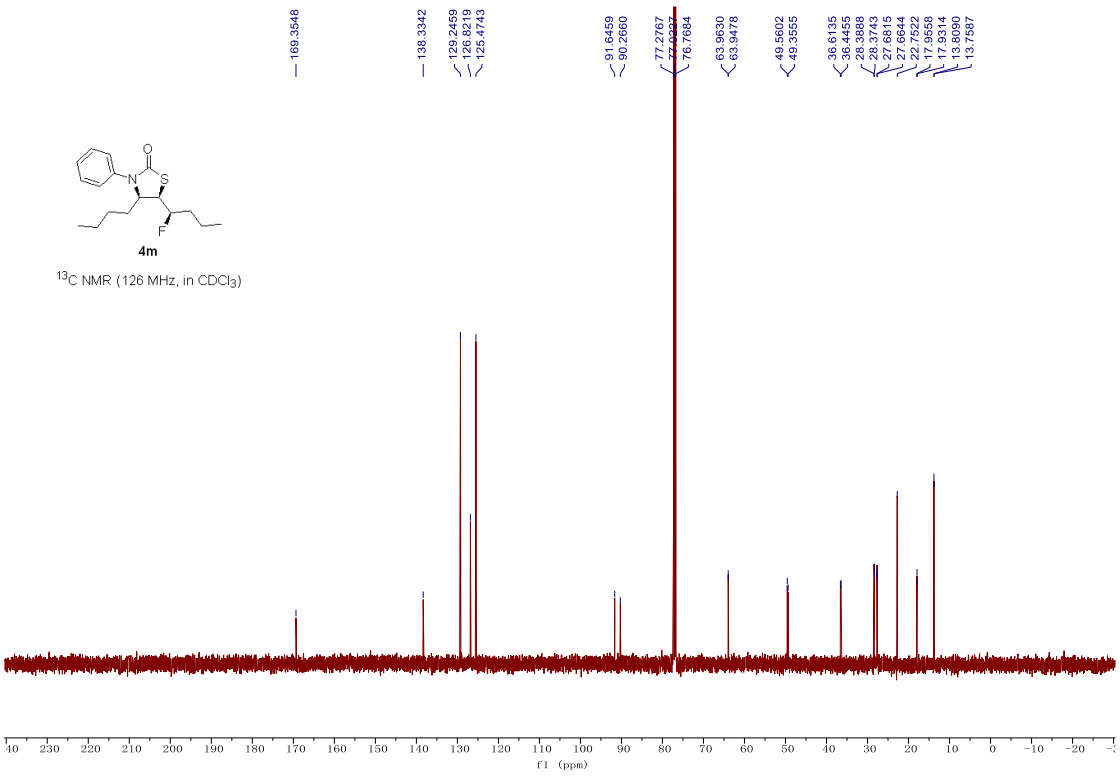
^{19}F NMR (471 MHz, in $CDCl_3$)



4m

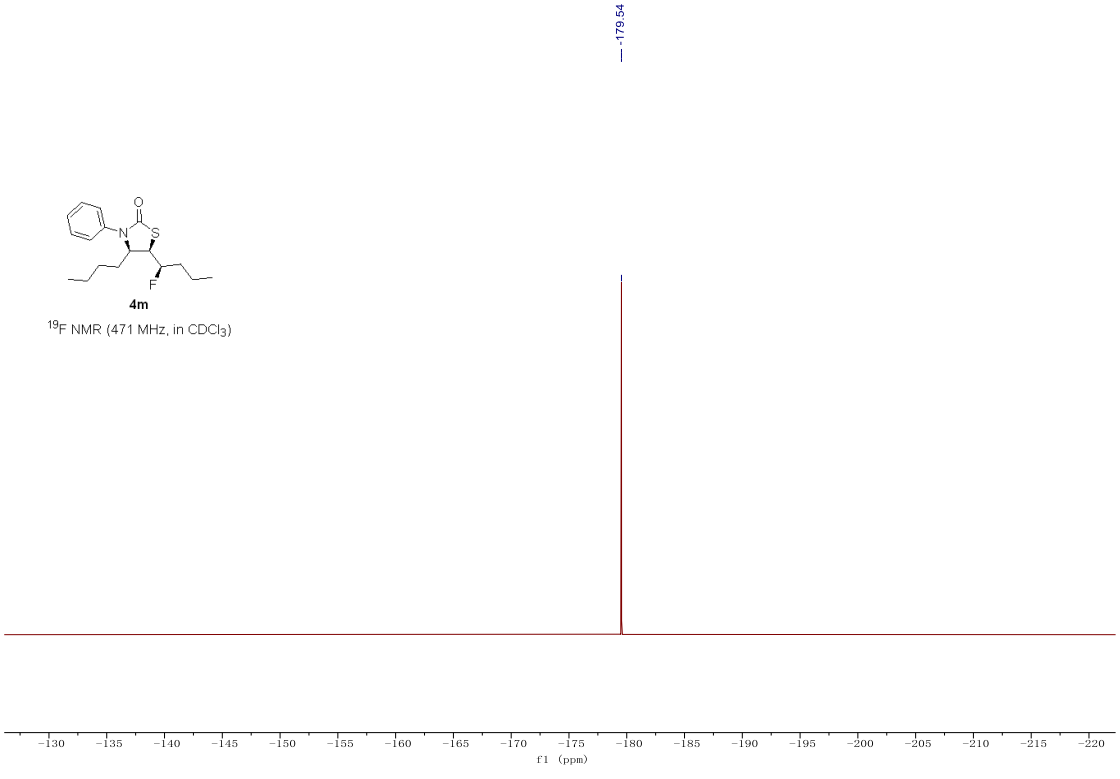
^{1}H NMR (500 MHz, in $CDCl_3$)





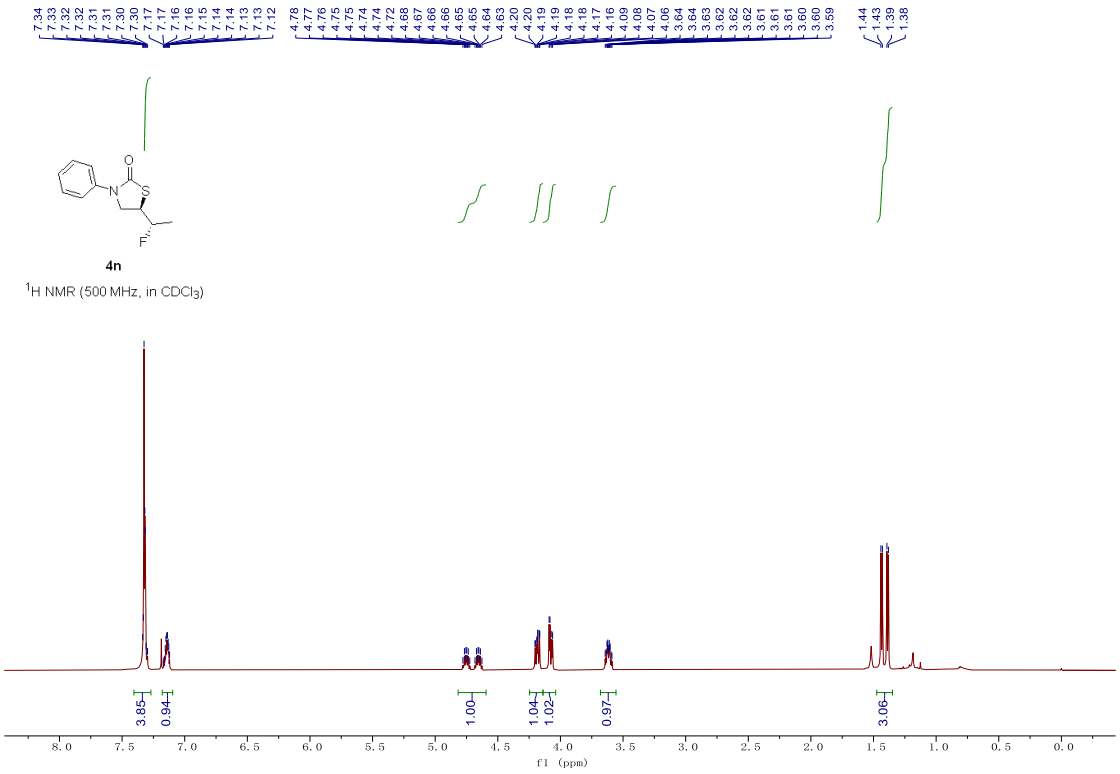
4m

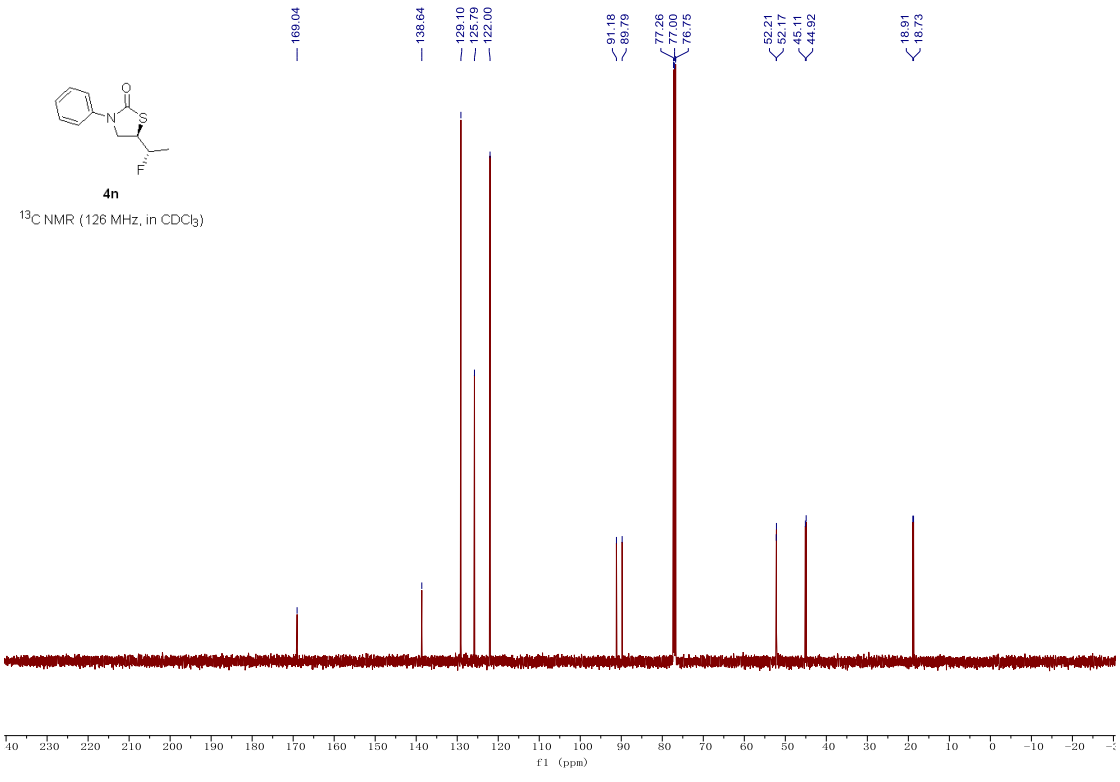
^{13}C NMR (126 MHz, in $CDCl_3$)

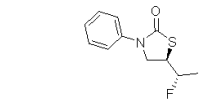


4m

^{19}F NMR (471 MHz, in $CDCl_3$)

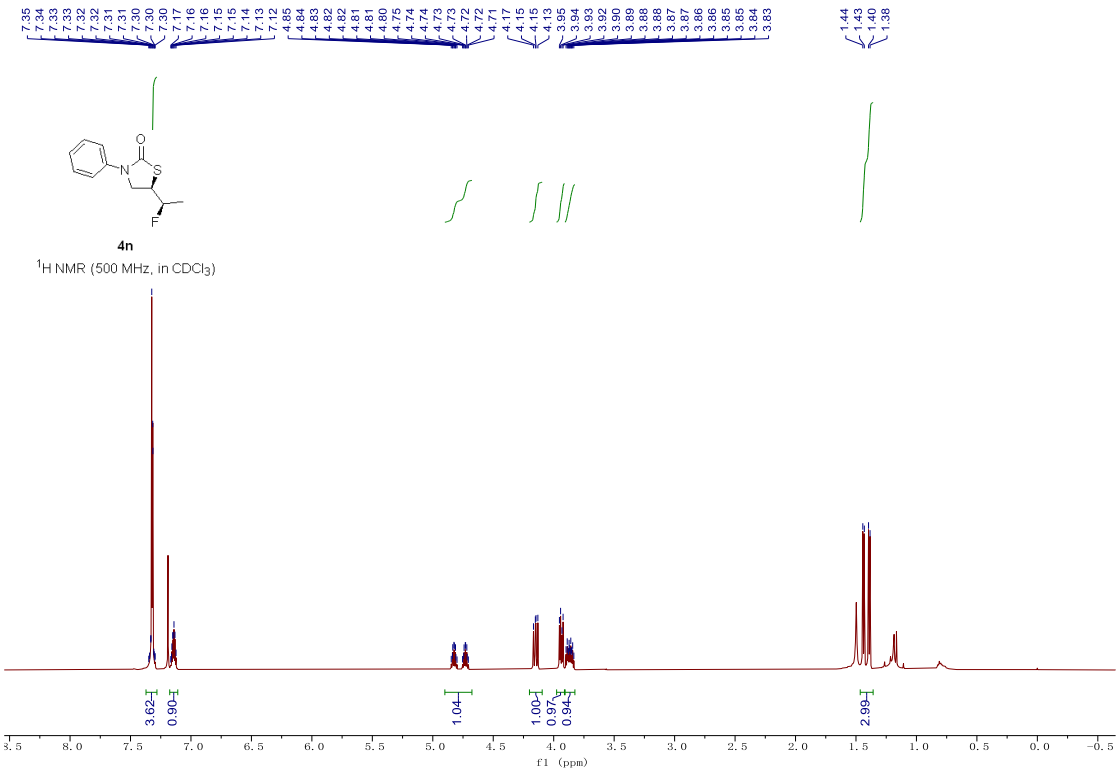

7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.13 7.12
4.78 4.77 4.76 4.75 4.75 4.74 4.74 4.72 4.68 4.67 4.66 4.66 4.65 4.65 4.64 4.63
4.20 4.20 4.19 4.19 4.18 4.18 4.17 4.16 4.09 4.08 4.07 4.06 3.64 3.64 3.63 3.62 3.62 3.61 3.61 3.60 3.60 3.59
1.44 1.43 1.39 1.38
O
N
S
F
4n
1H NMR (500 MHz, in CDCl3)
3.85 0.94 1.00 1.04 1.02 0.97 3.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.04
138.64
129.10
125.79
122.00
91.18
89.79
77.26
77.00
76.75
52.21
52.17
45.11
44.92
18.91
18.73
O
N
S
F
4n
13C NMR (126 MHz, in CDCl3)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



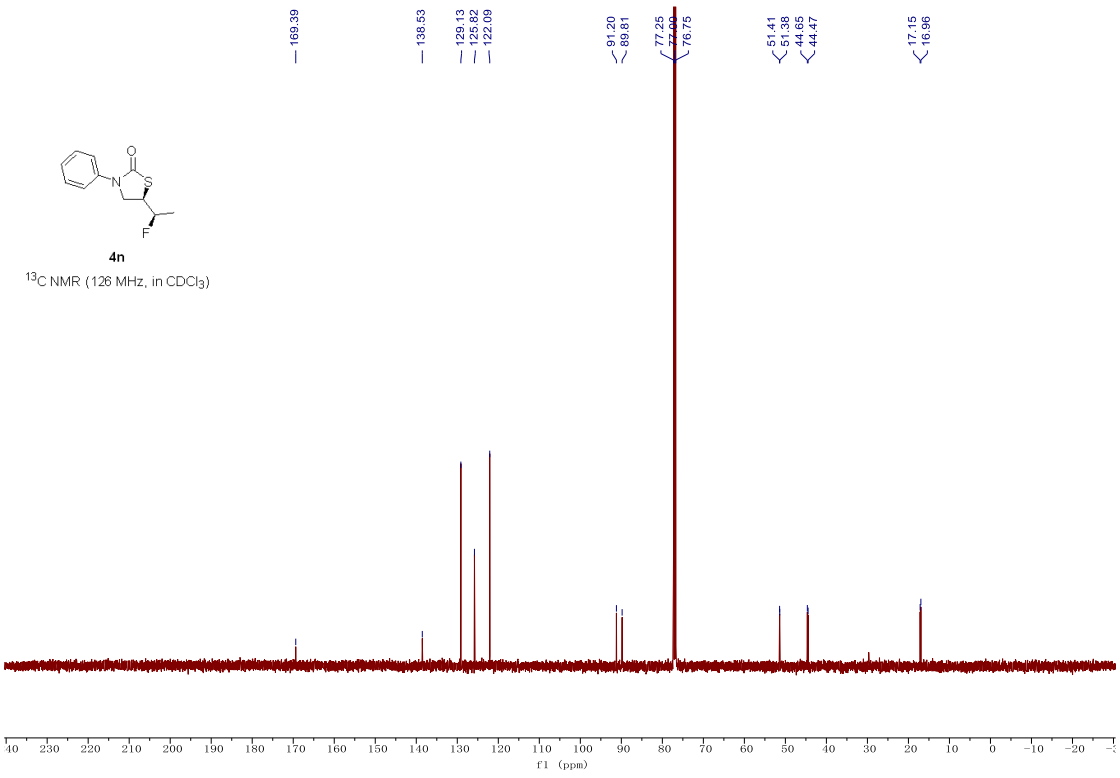
4n

^{19}F NMR (471 MHz, in $CDCl_3$)



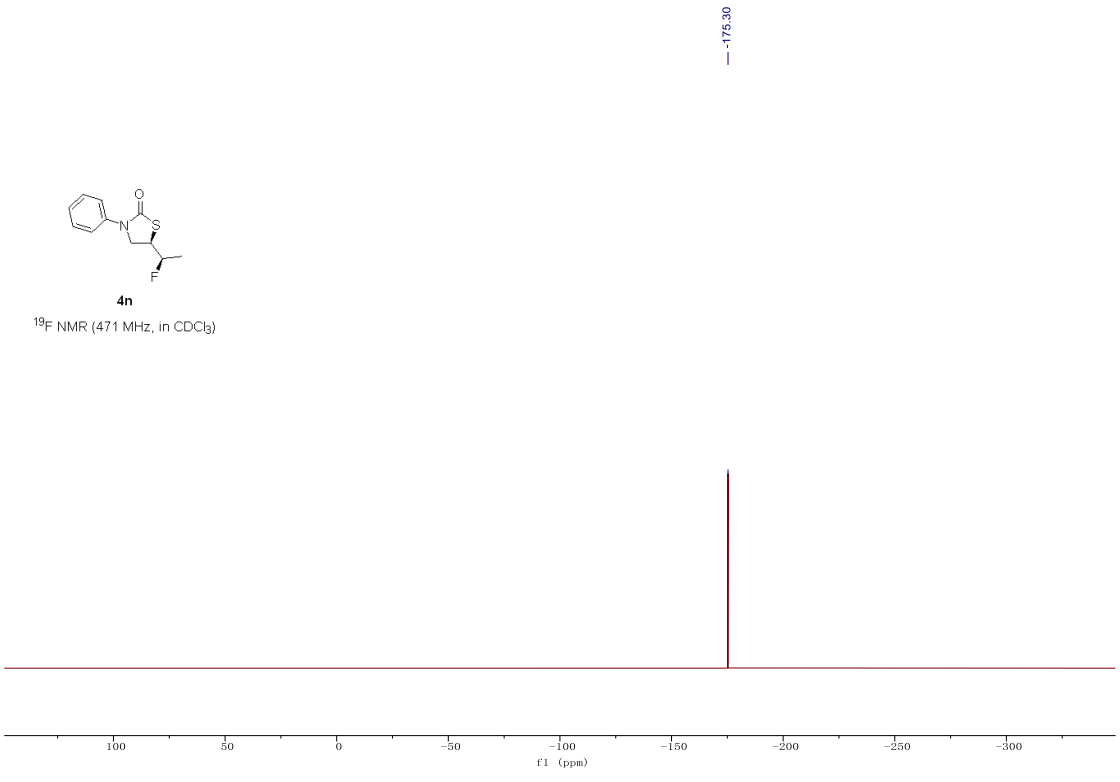
4n

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



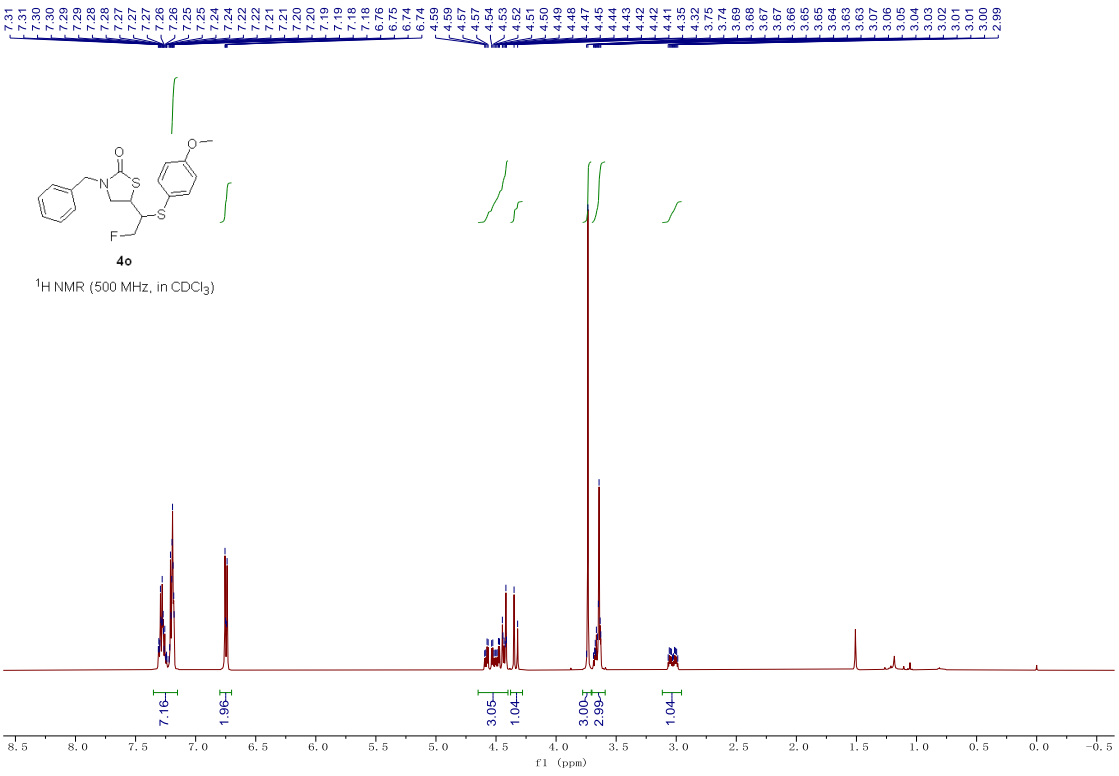
4n

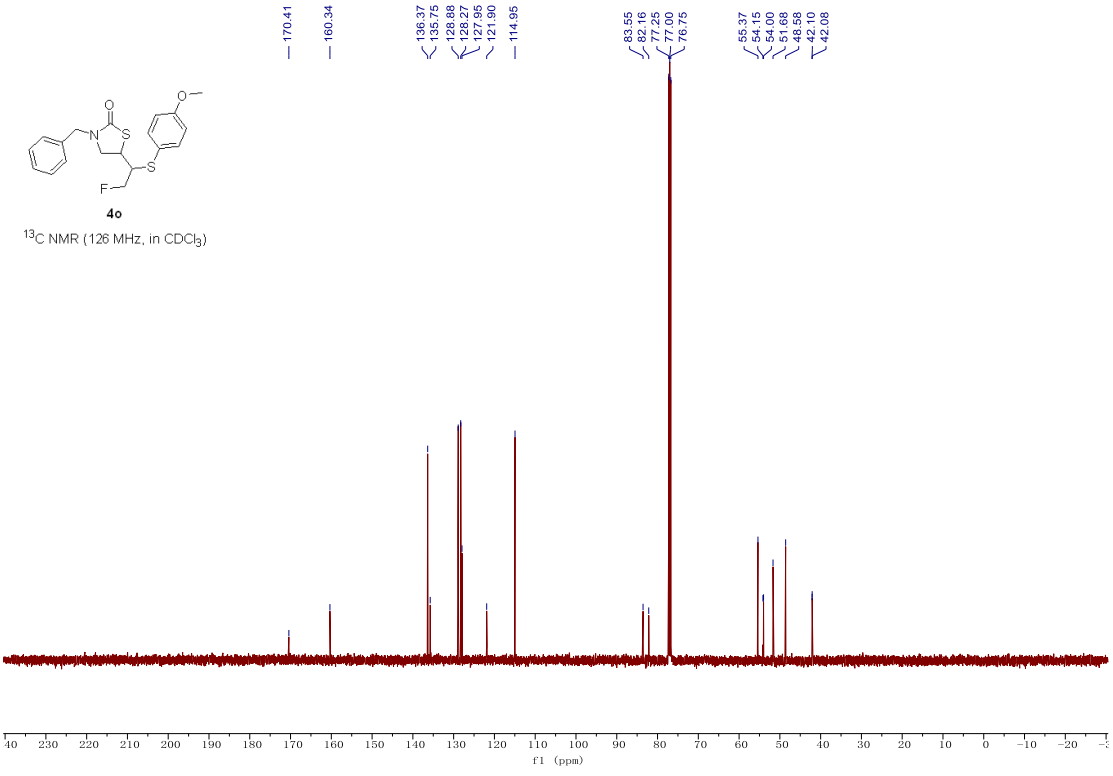
^{13}C NMR (126 MHz, in $CDCl_3$)

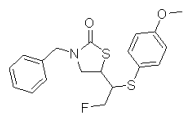


4n

^{19}F NMR (471 MHz, in $CDCl_3$)

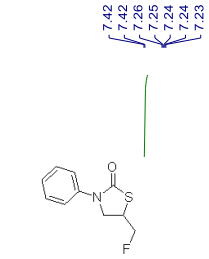

4o
1H NMR (500 MHz, in CDCl3)
f1 (ppm)


4o
13C NMR (126 MHz, in CDCl3)
f1 (ppm)



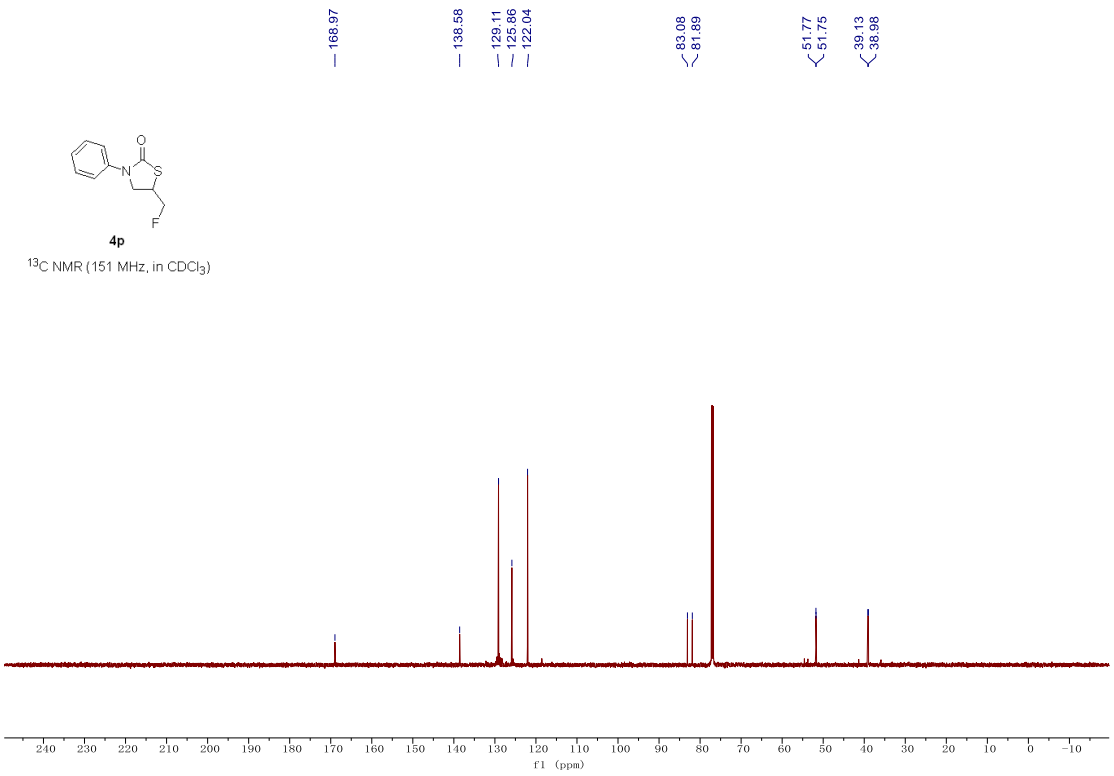
4o

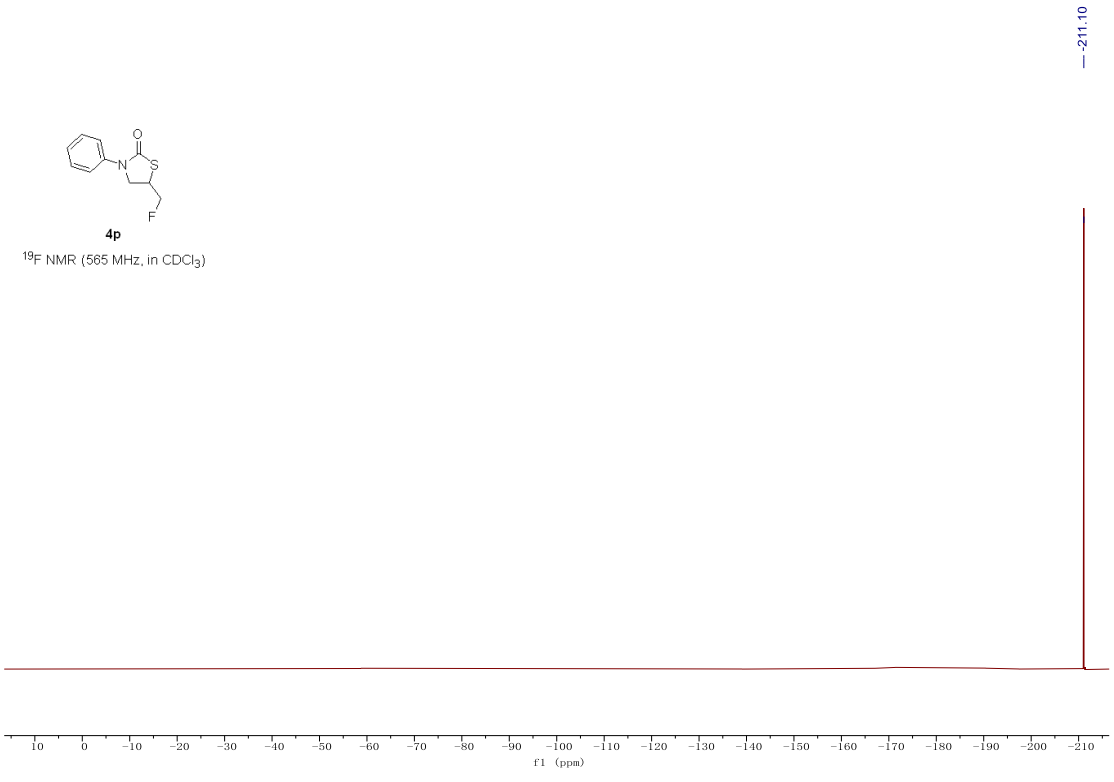
^{19}F NMR (471 MHz, in $CDCl_3$)

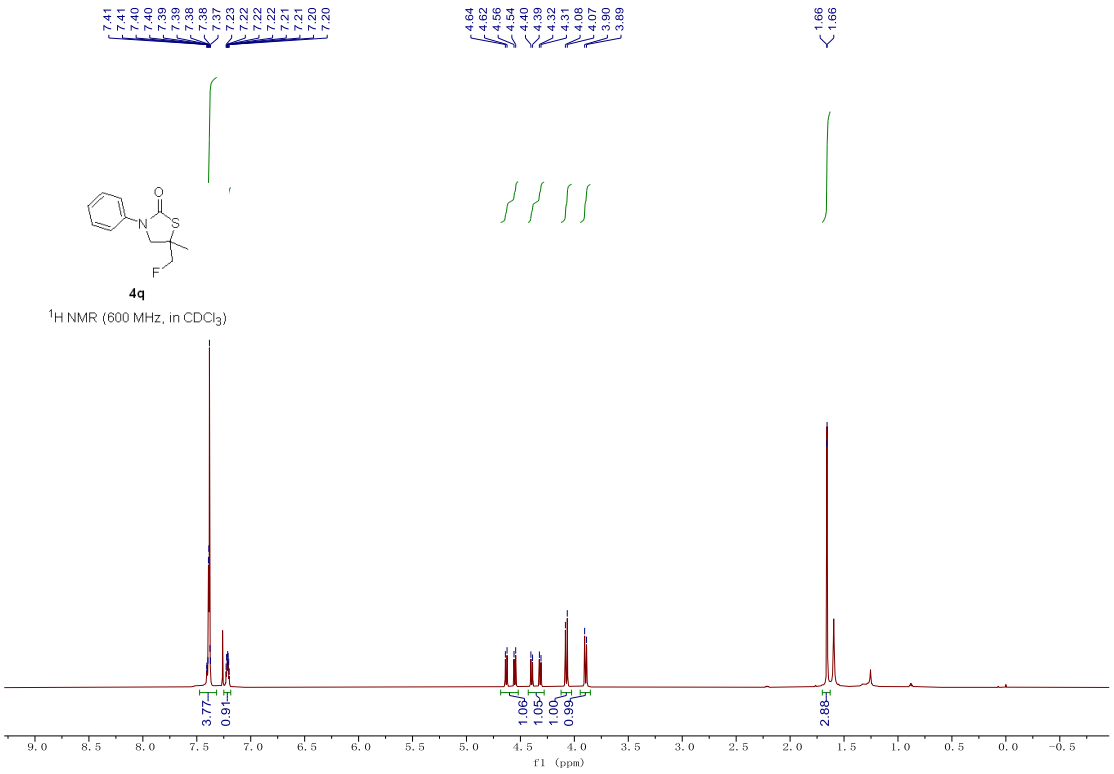


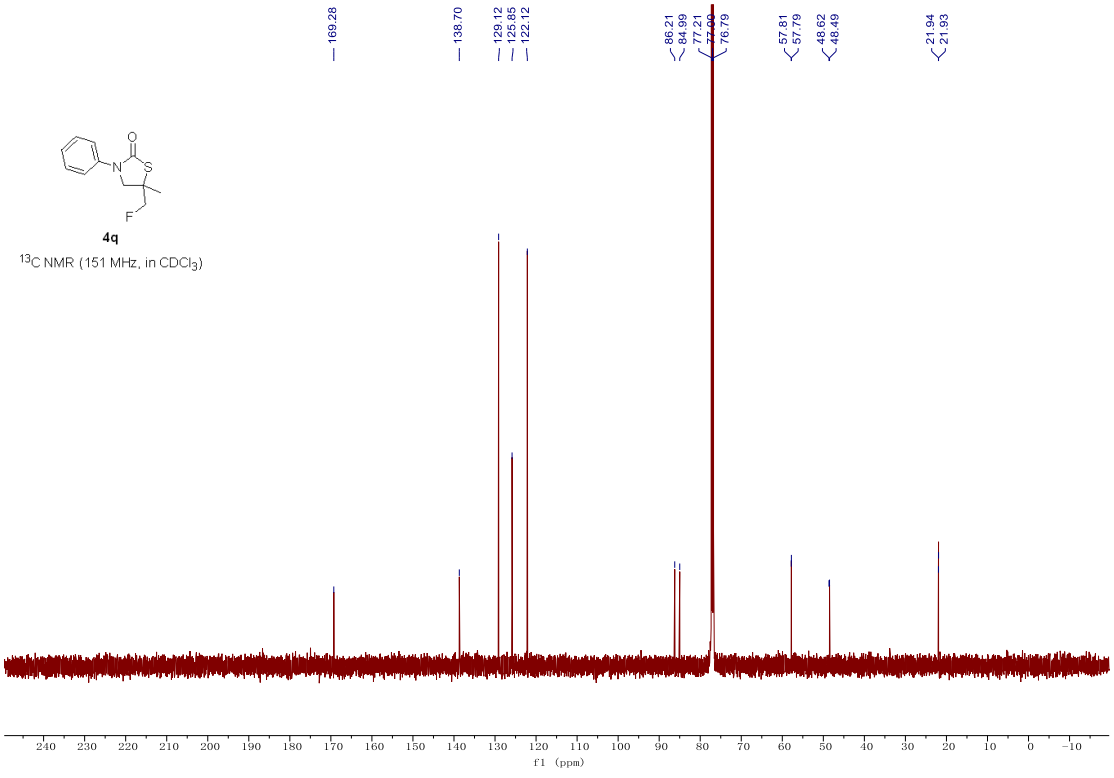
4p

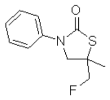
^{1}H NMR (500 MHz, in $CDCl_3$)


168.97
138.58
129.11
125.86
122.04
83.08
81.89
51.77
51.75
39.13
38.98
O
N
S
F
4p
13C NMR (151 MHz, in CDCl3)
f1 (ppm)


-211.10
O
N
S
F
4p
19F NMR (565 MHz, in CDCl3)
f1 (ppm)

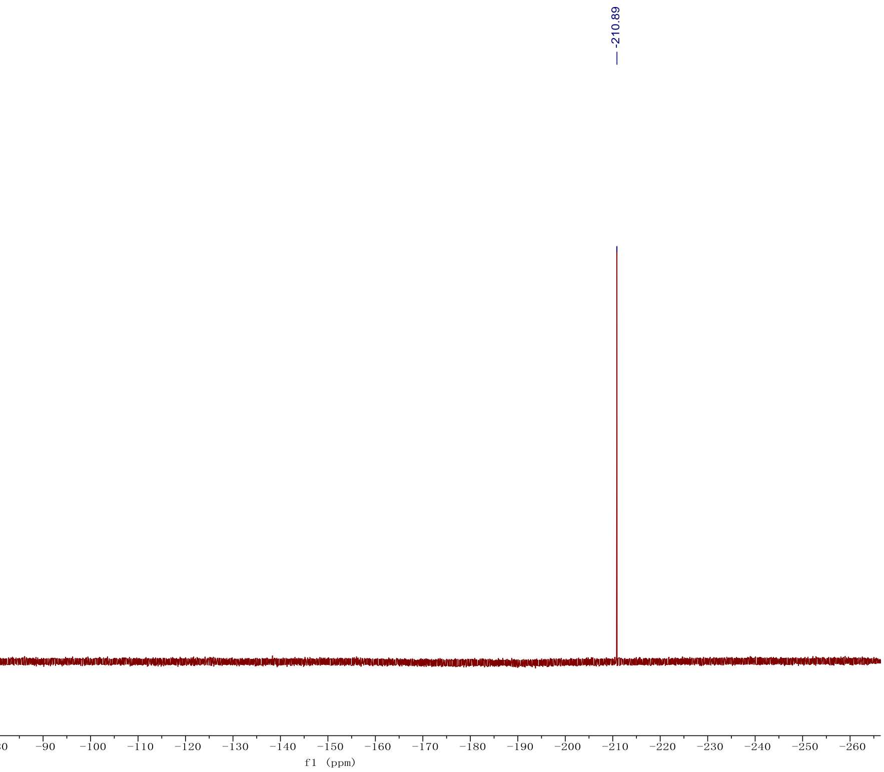

7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.20
4.64
4.62
4.56
4.54
4.40
4.39
4.32
4.31
4.08
4.07
3.90
3.89
1.66
1.66
O
N
S
F
4q
1H NMR (600 MHz, in CDCl3)
3.77
0.91
1.06
1.05
1.00
0.99
2.88
f1 (ppm)

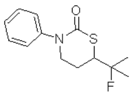

169.28
138.70
129.12
125.85
122.12
86.21
84.99
77.21
77.00
76.79
57.81
57.79
48.62
48.49
21.94
21.93
O
N
S
F
4q
13C NMR (151 MHz, in CDCl3)
f1 (ppm)



4q

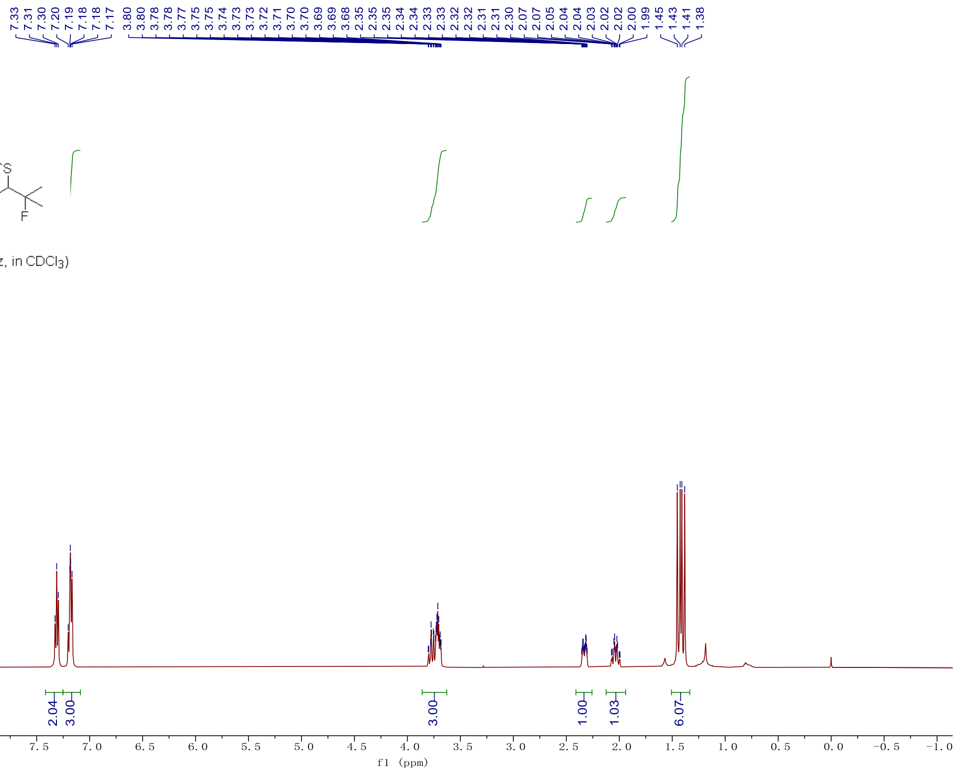
^{19}F NMR (565 MHz, in $CDCl_3$)

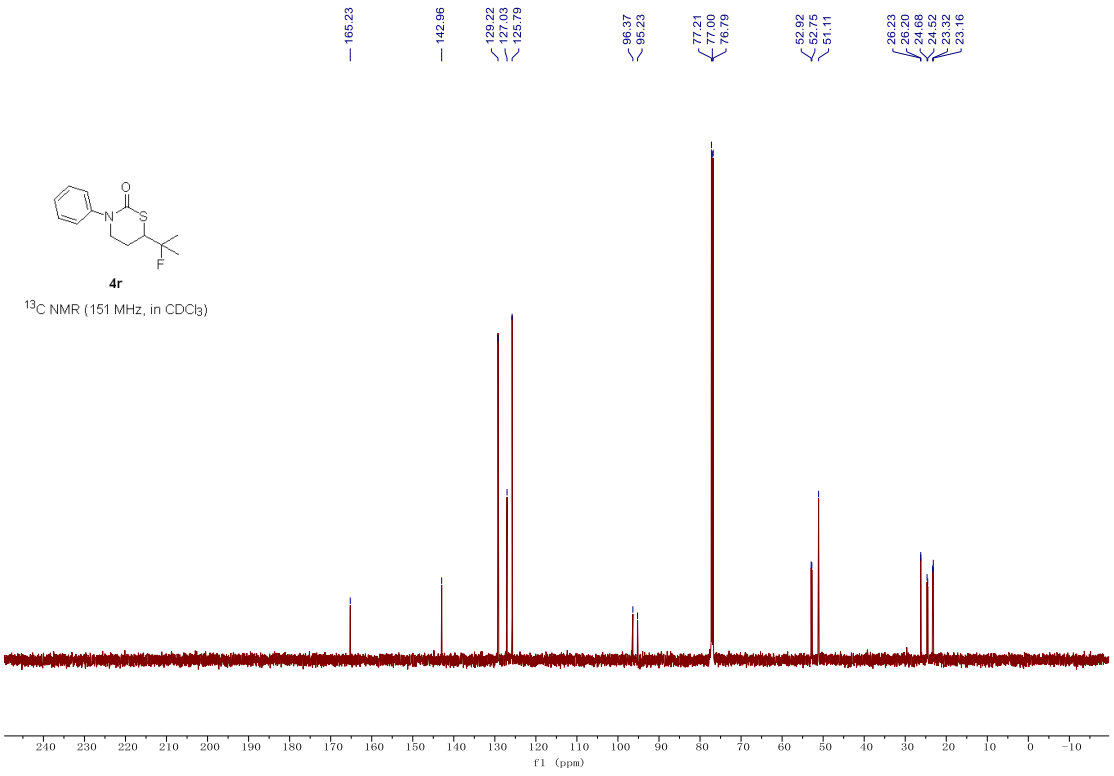




4r

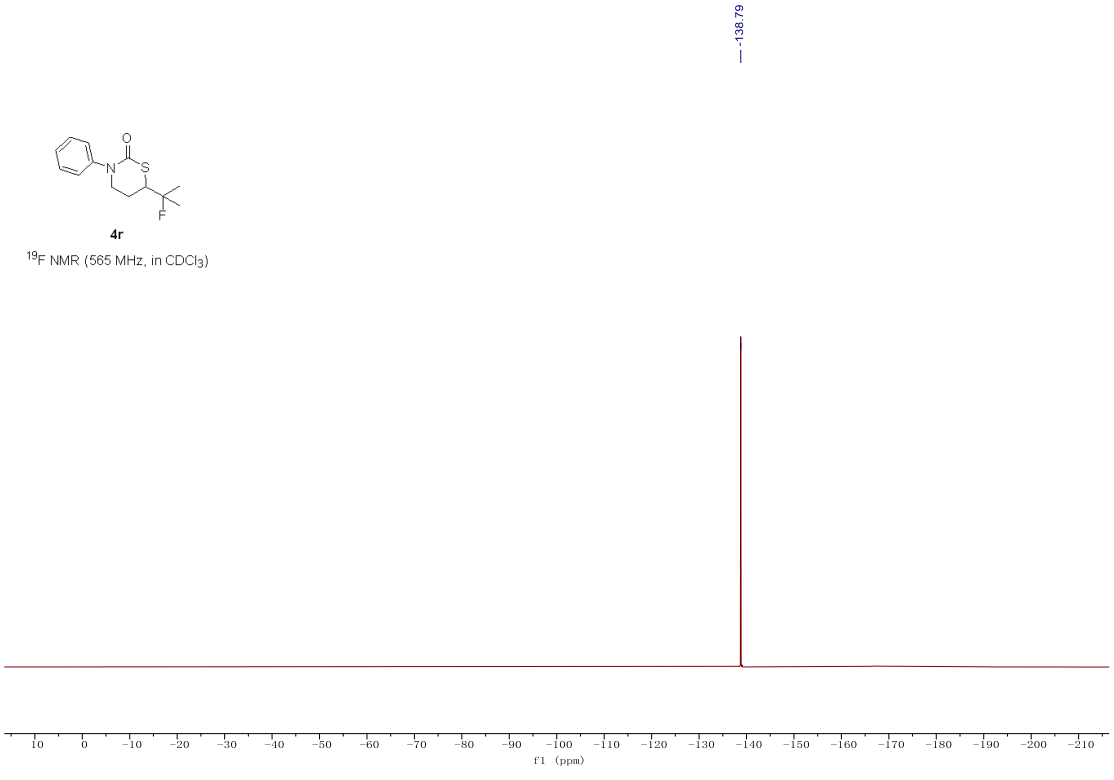
^{1}H NMR (500 MHz, in $CDCl_3$)





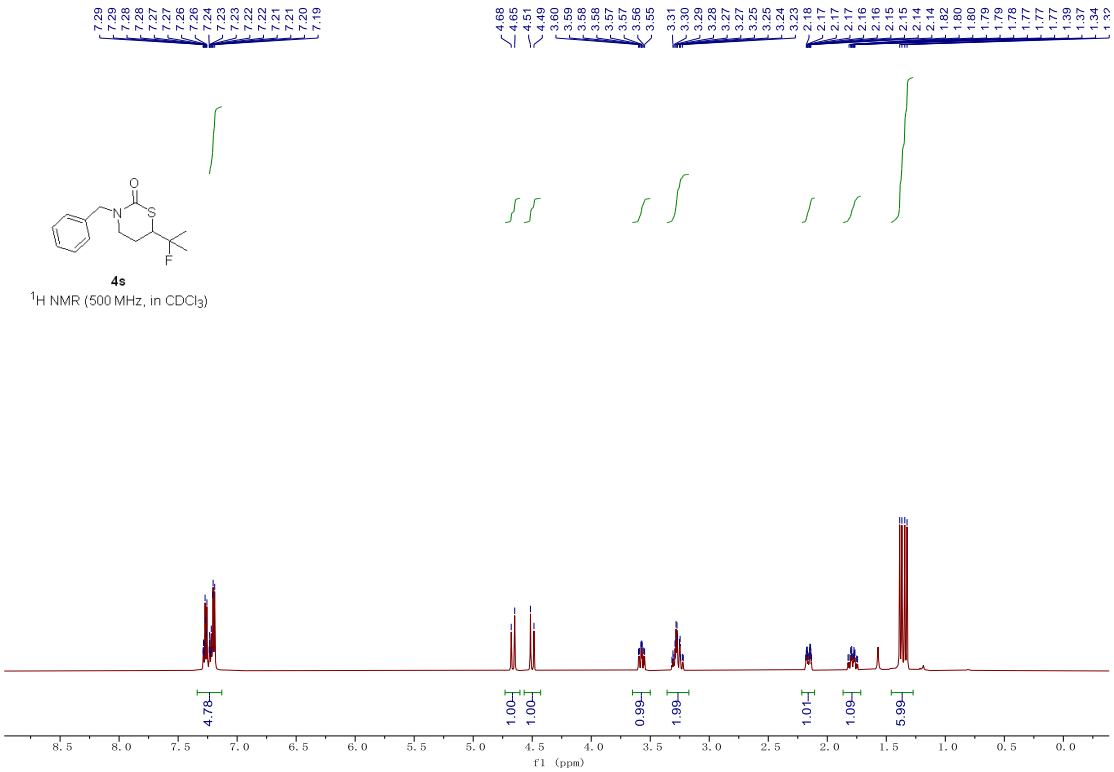
4r

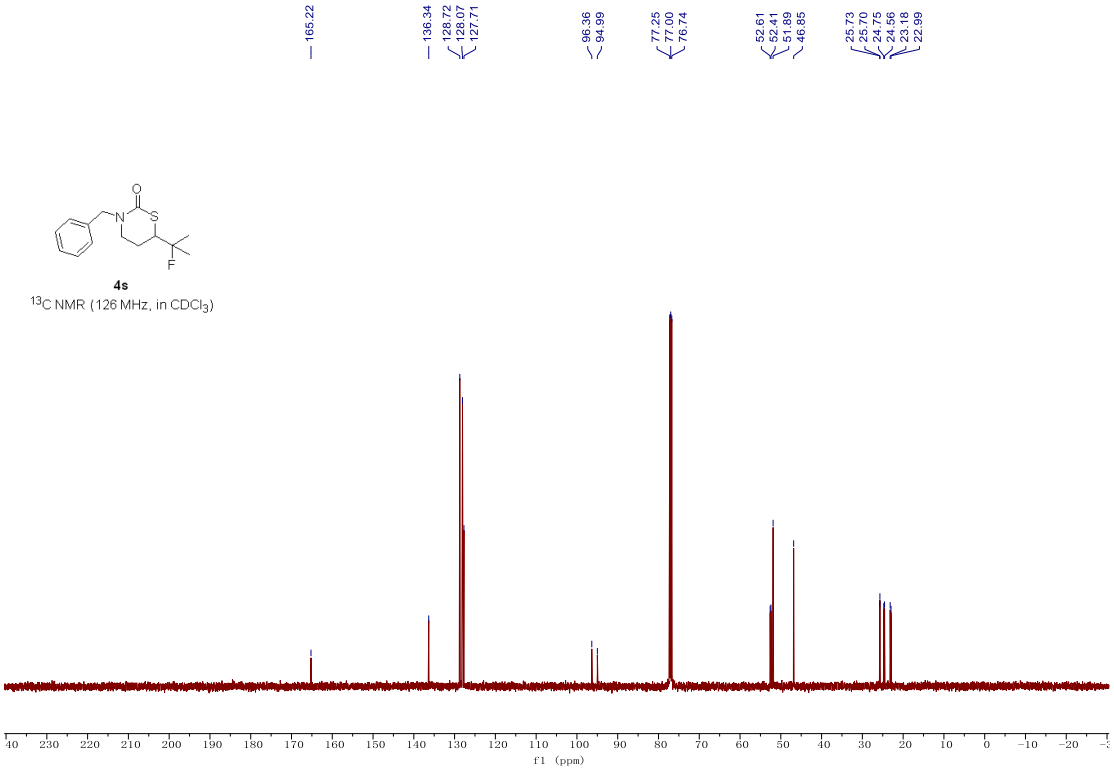
^{13}C NMR (151 MHz, in $CDCl_3$)

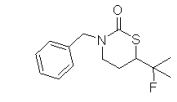


4r

^{19}F NMR (565 MHz, in $CDCl_3$)

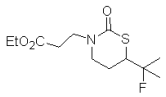

4s
1H NMR (500 MHz, in CDCl3)
4.78
1.00
1.00
0.99
1.99
1.01
1.09
5.99
f1 (ppm)


4s
13C NMR (126 MHz, in CDCl3)
f1 (ppm)



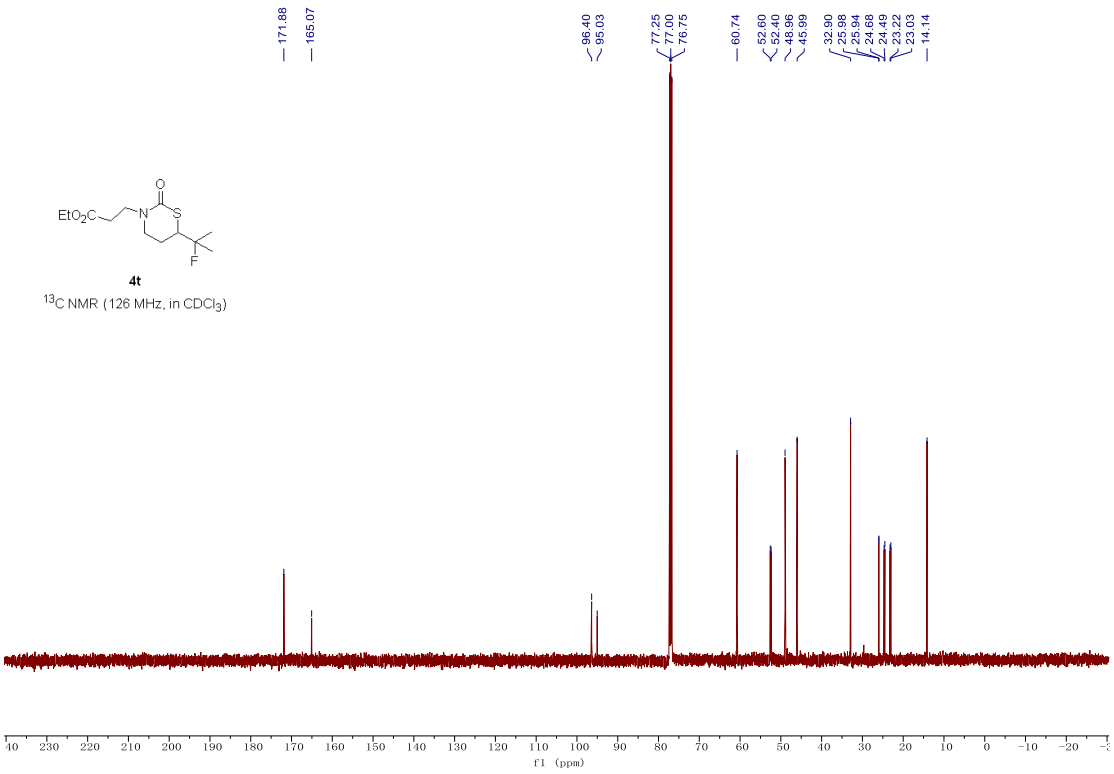
4s

^{19}F NMR (471 MHz, in $CDCl_3$)



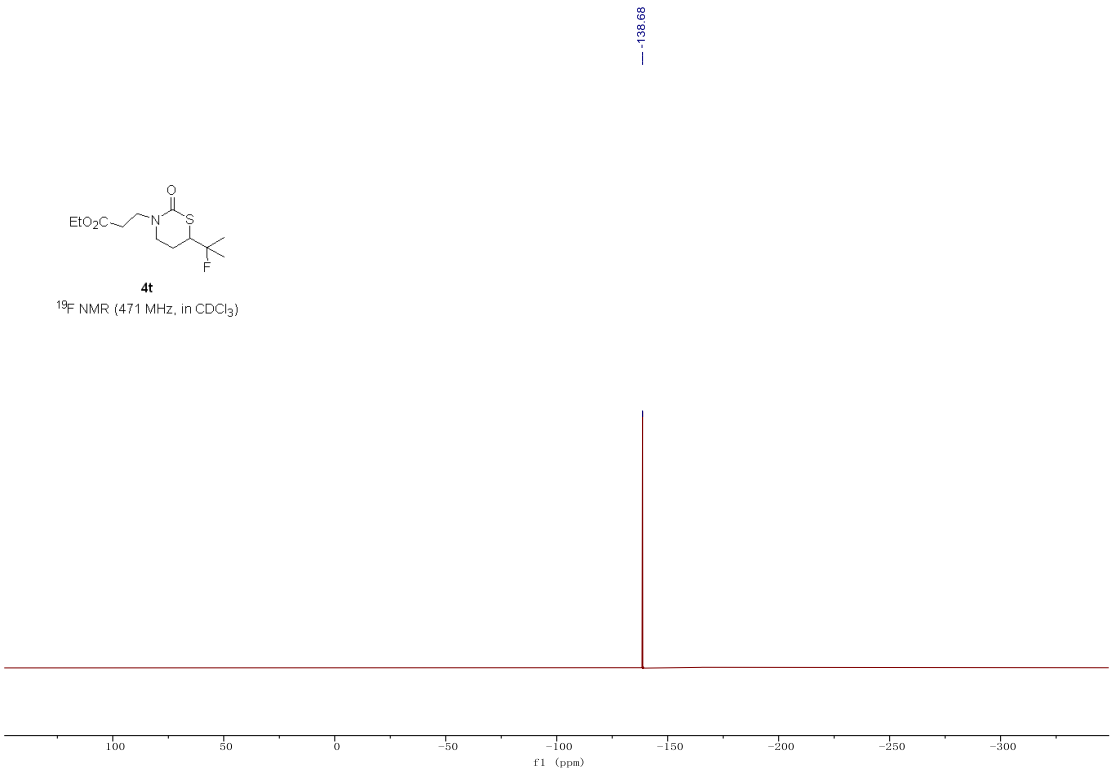
4t

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



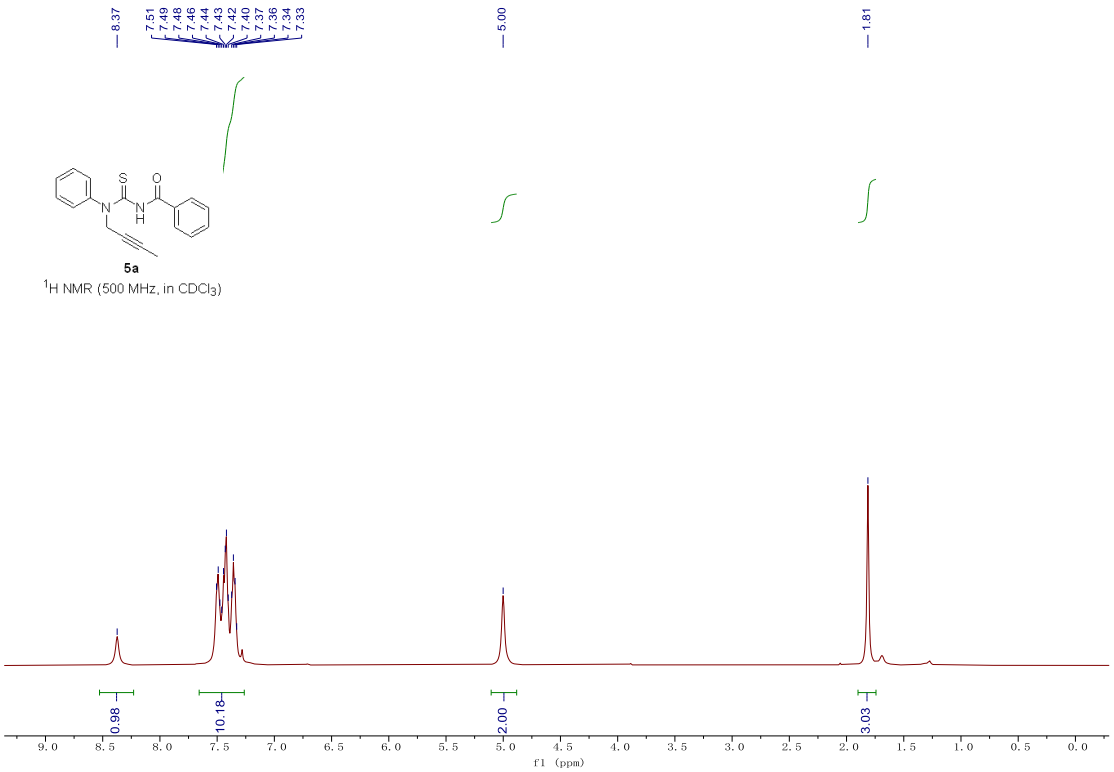
4t

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



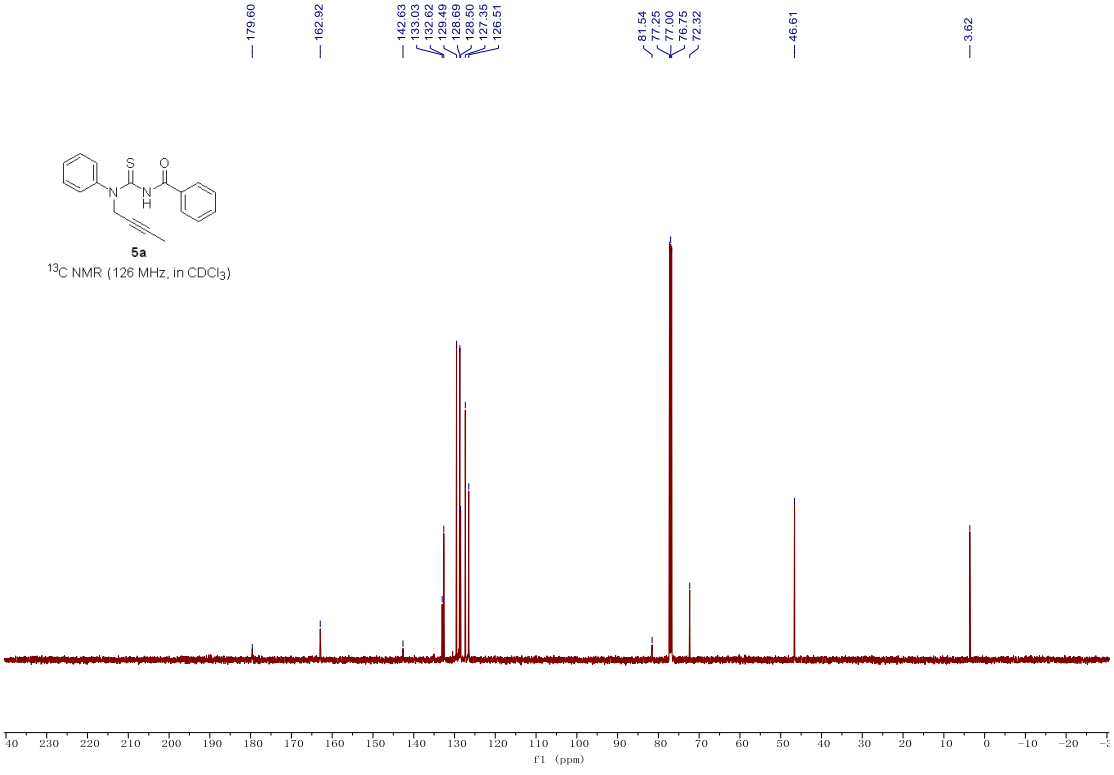
4t

^{19}F NMR (471 MHz, in $CDCl_3$)



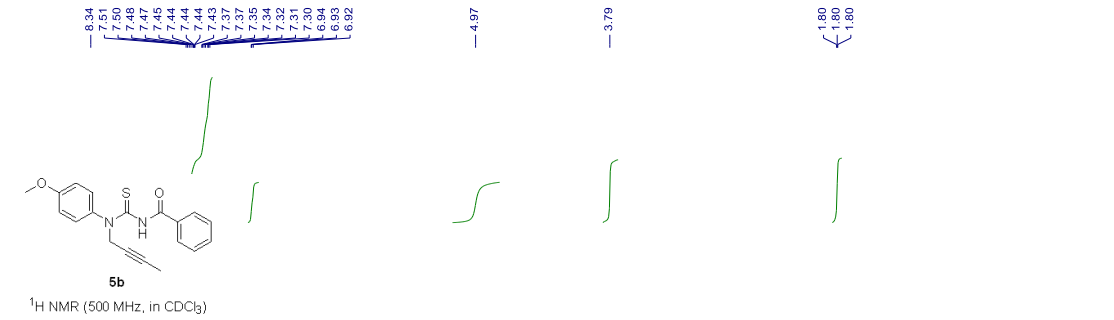
5a

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



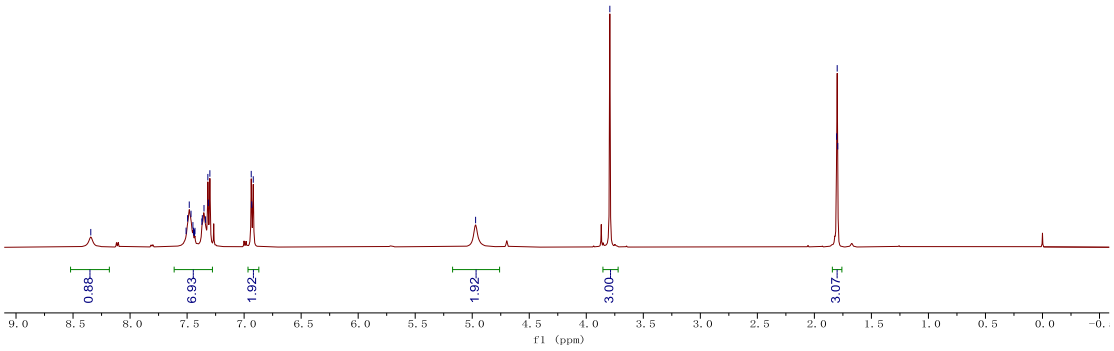
5a

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



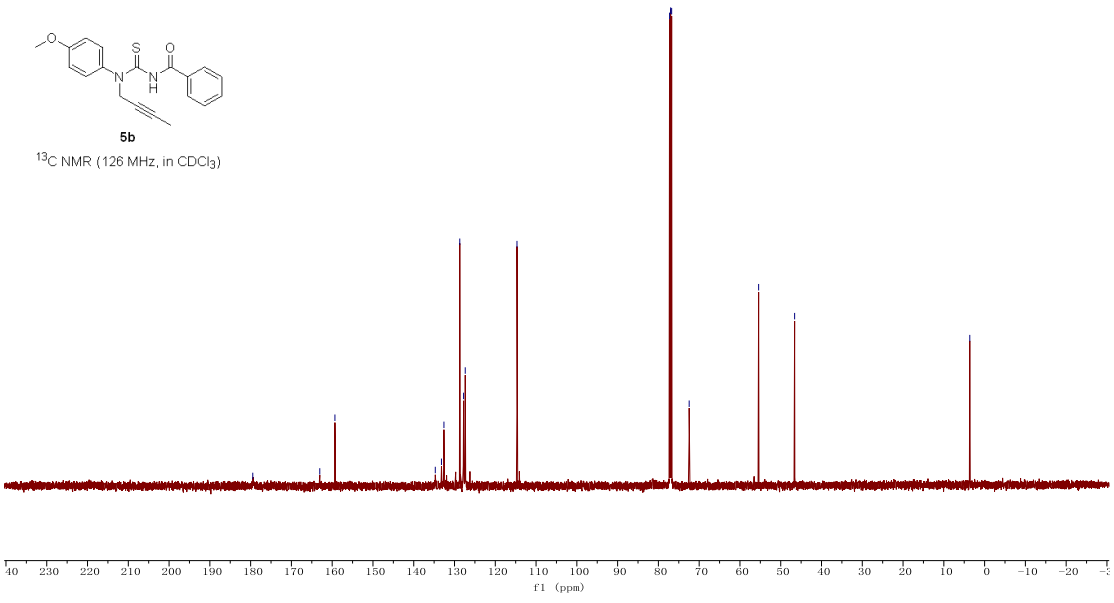
5b

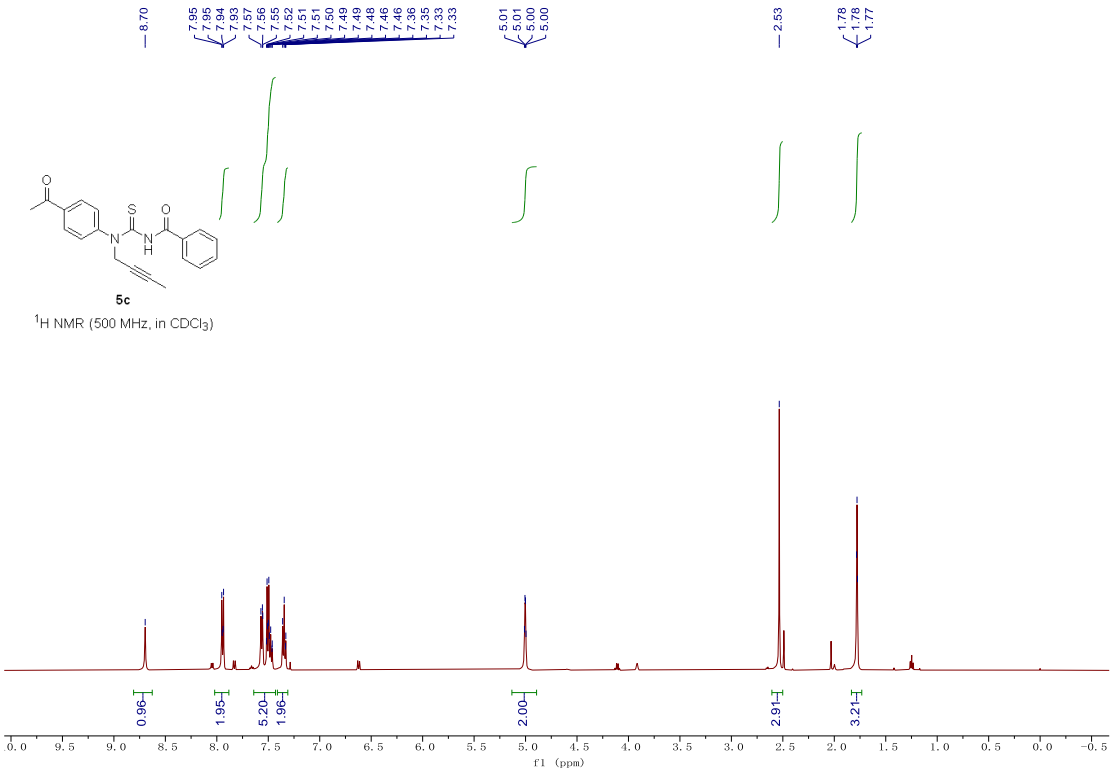
^{1}H NMR (500 MHz, in $CDCl_3$)



5b

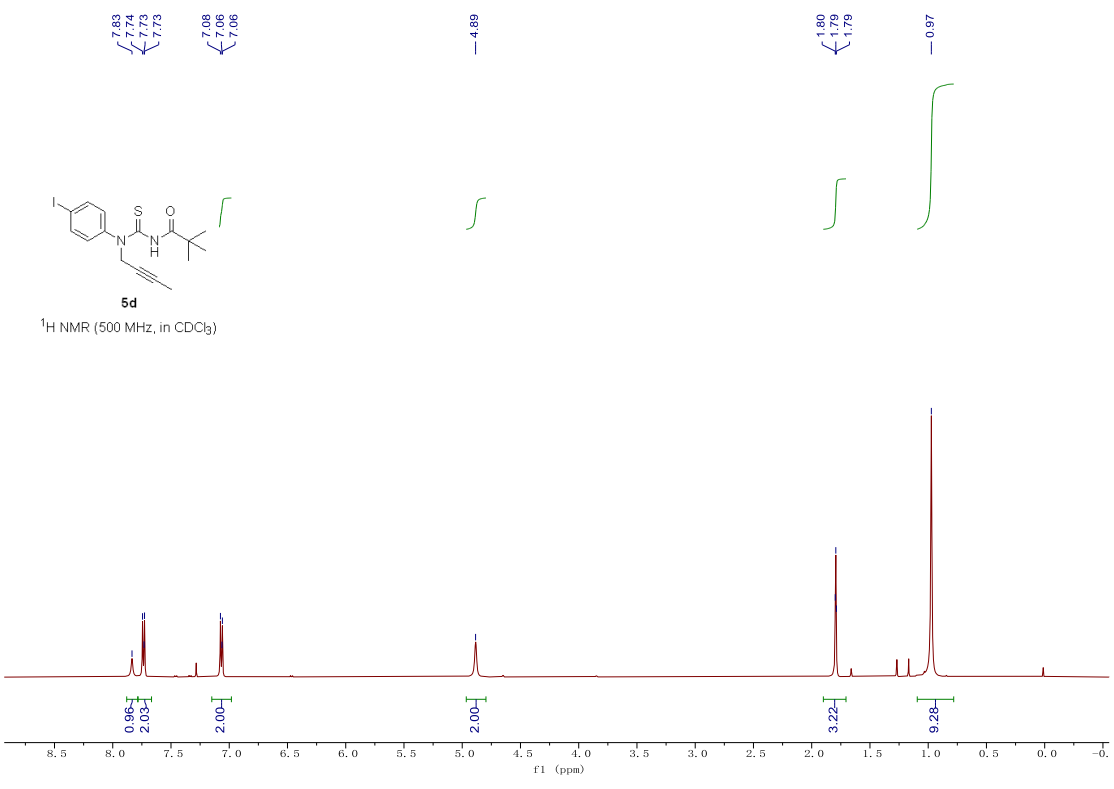
^{13}C NMR (126 MHz, in $CDCl_3$)





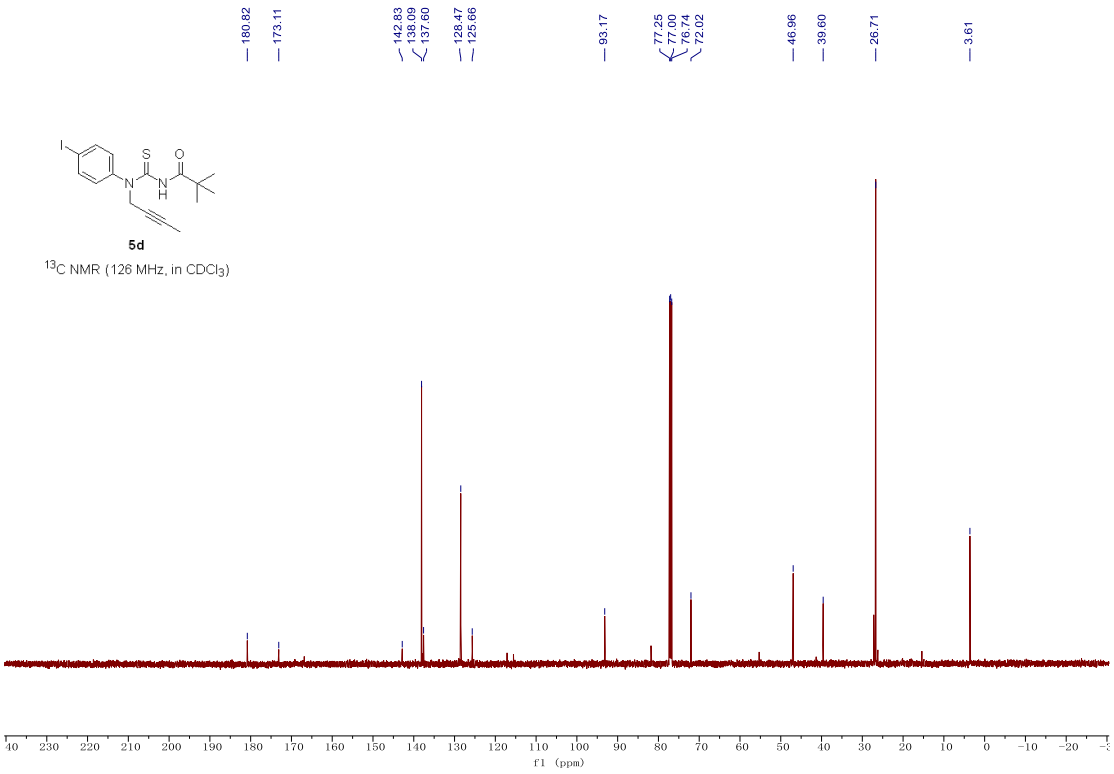
5c

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



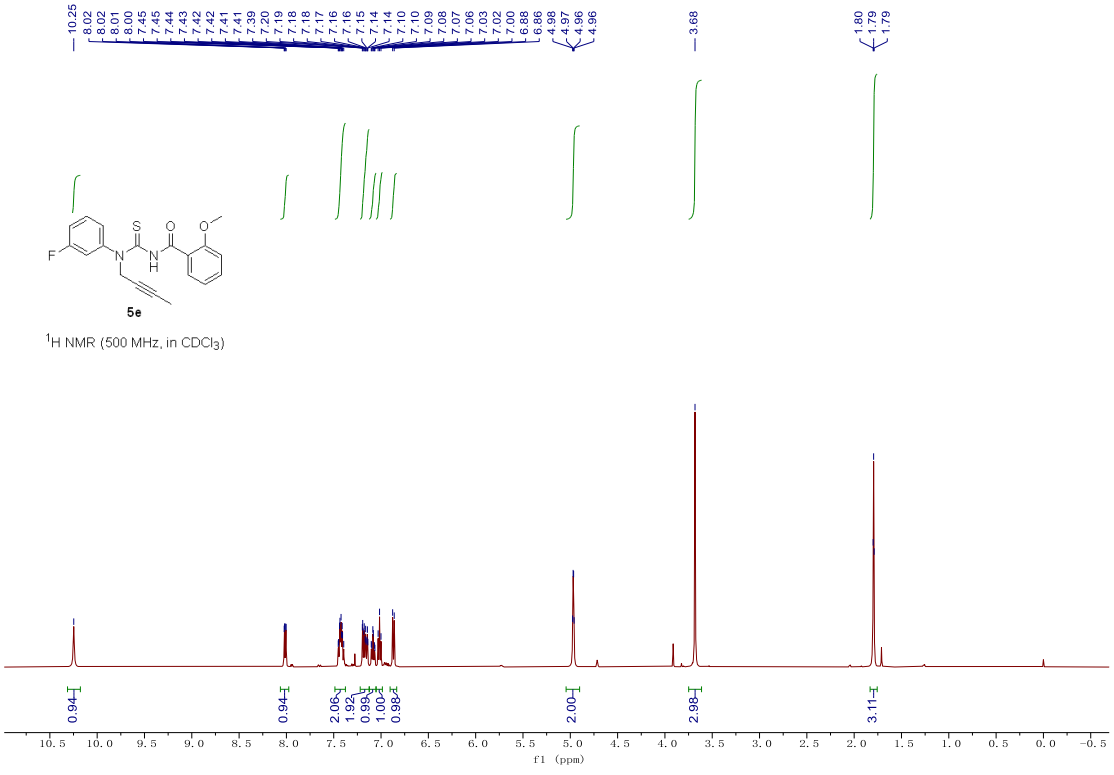
5d

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



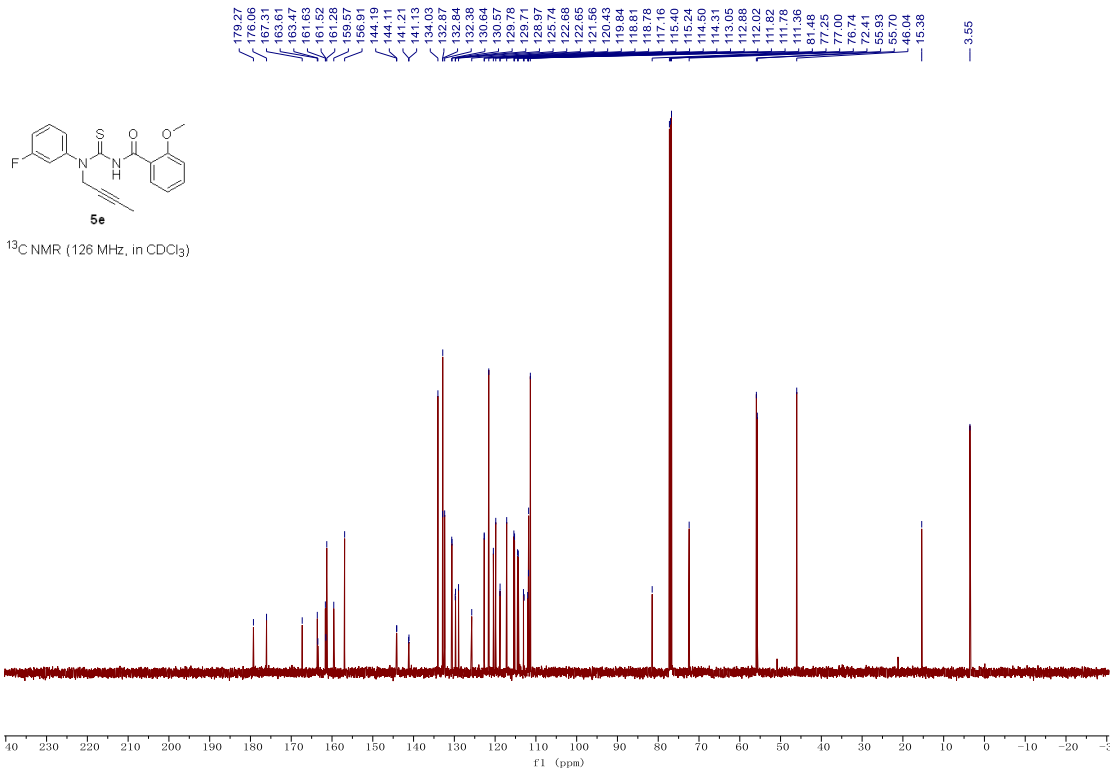
5d

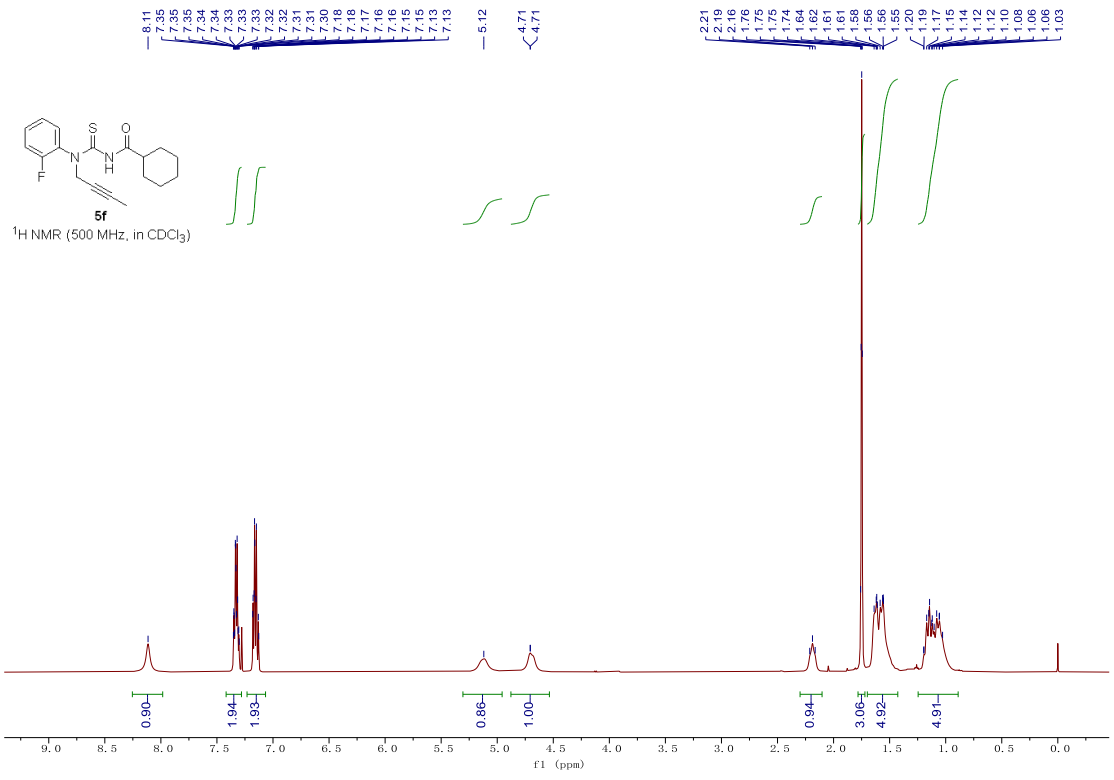
^{13}C NMR (126 MHz, in $CDCl_3$)

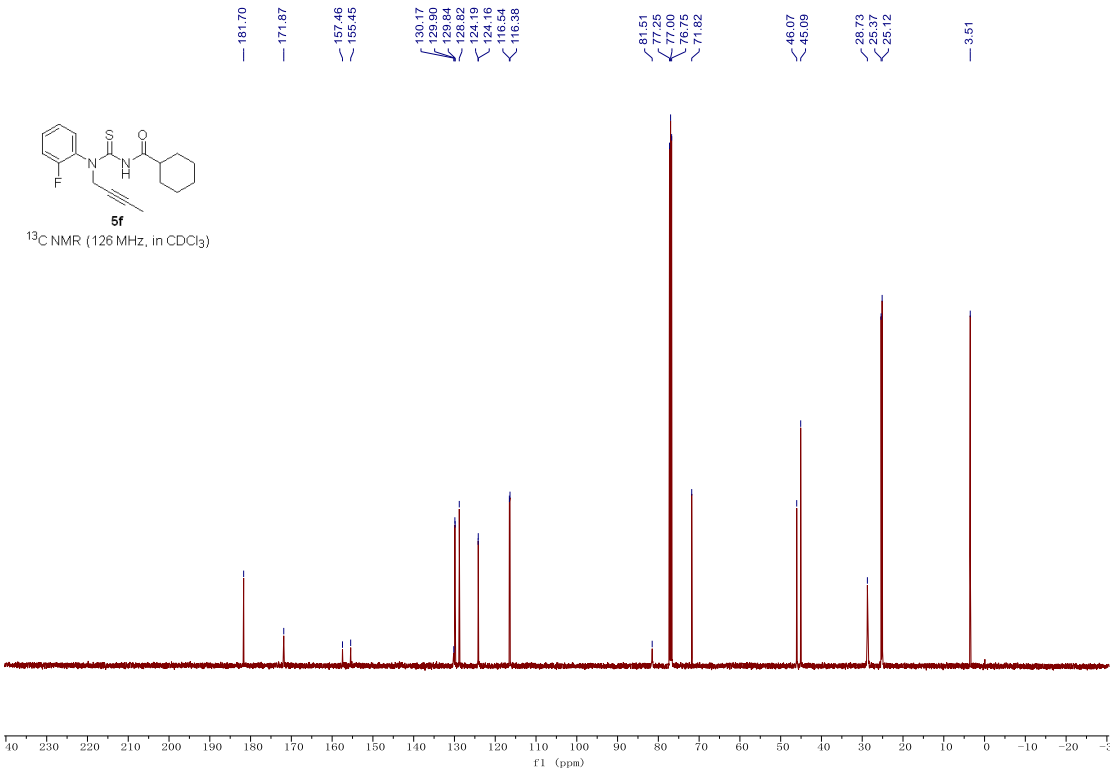


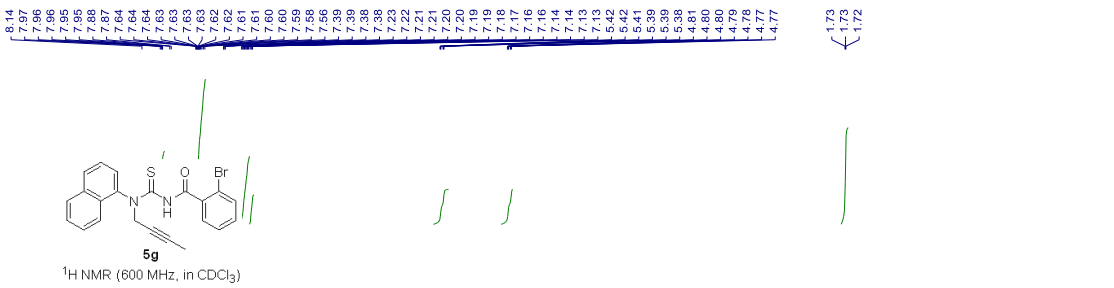
5e

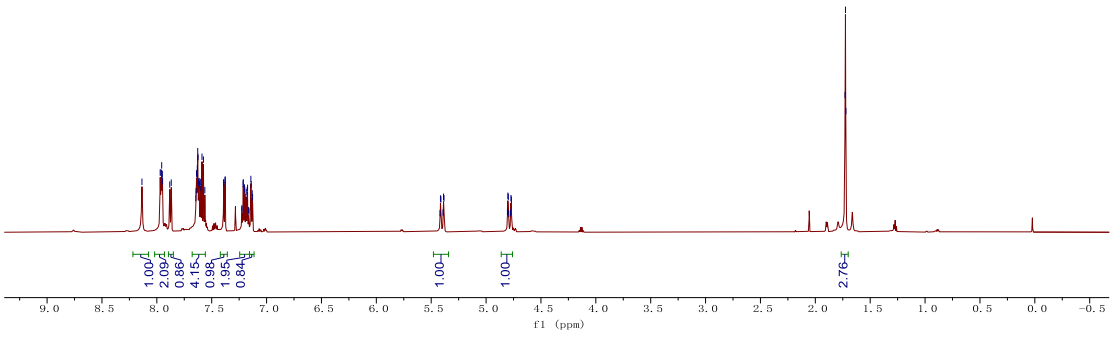
^{1}H NMR (500 MHz, in $CDCl_3$)

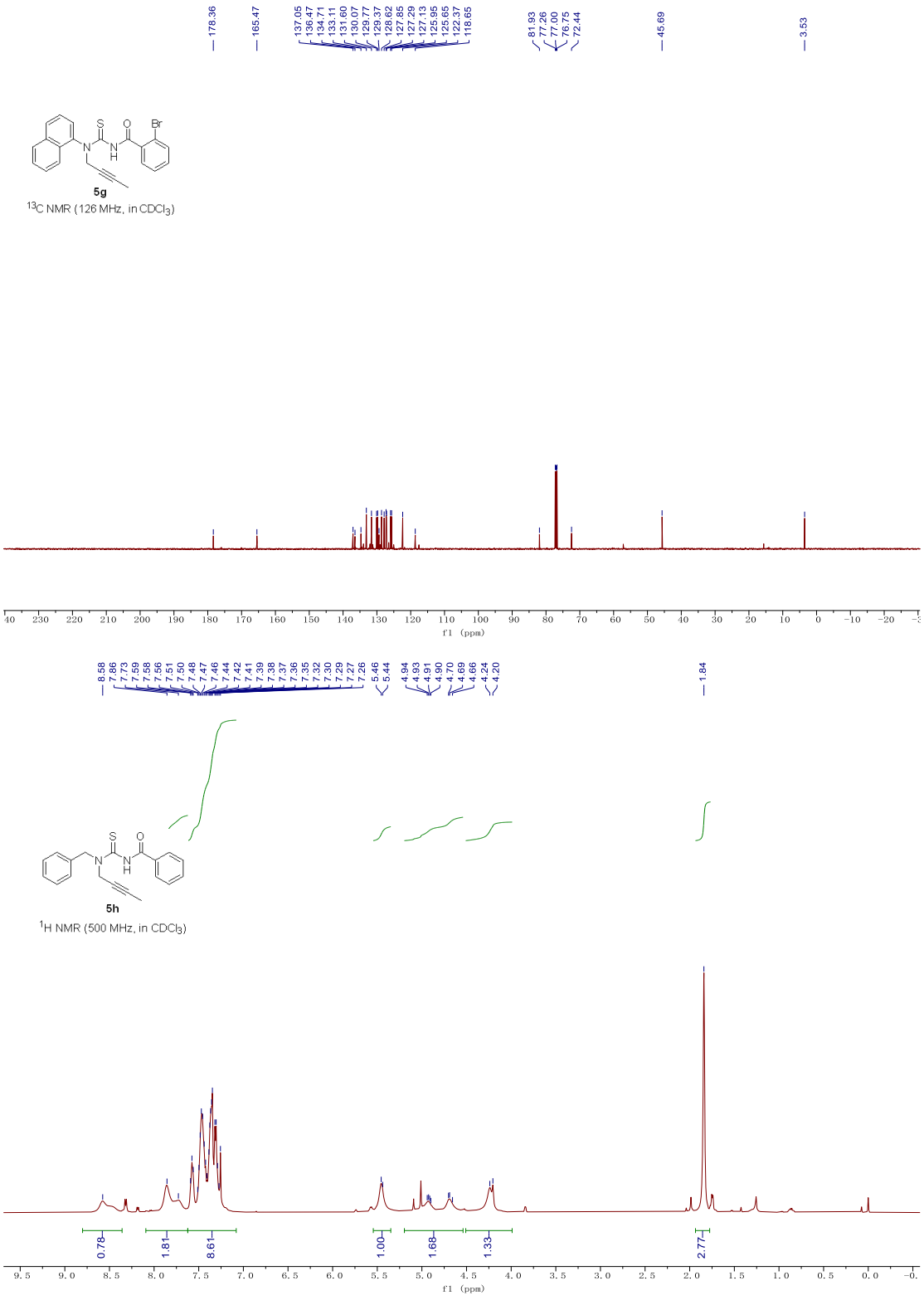

5e
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

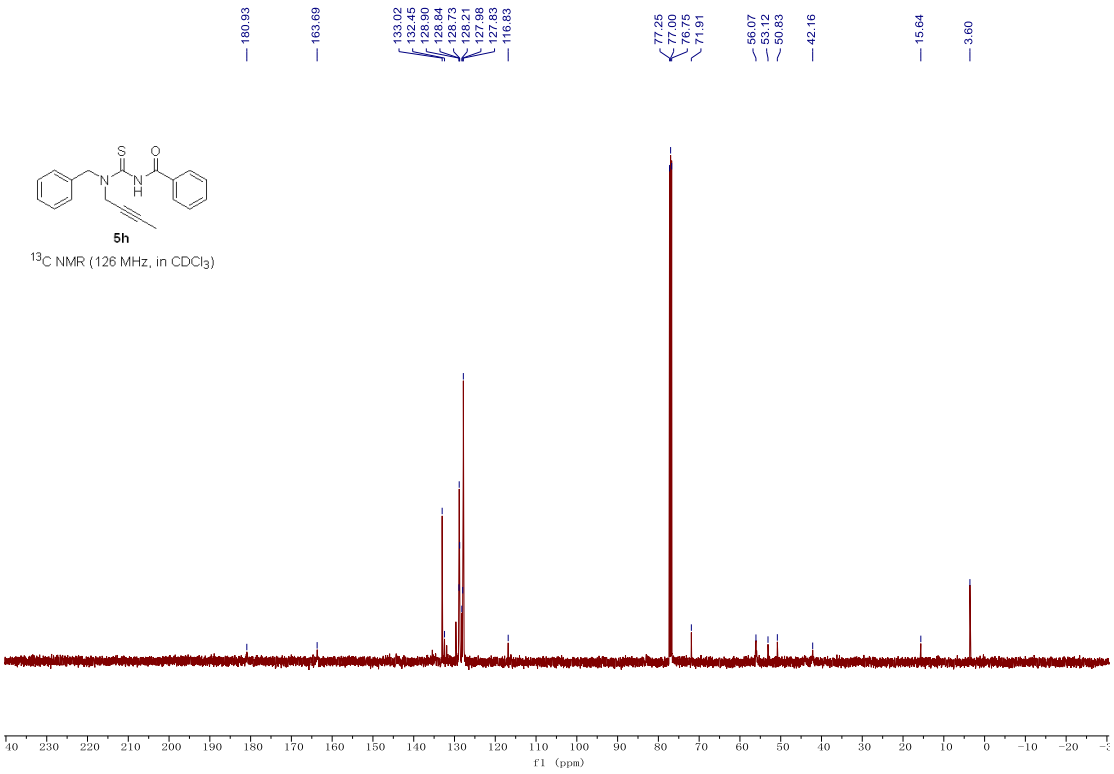

5f
1H NMR (500 MHz, in CDCl3)
f1 (ppm)

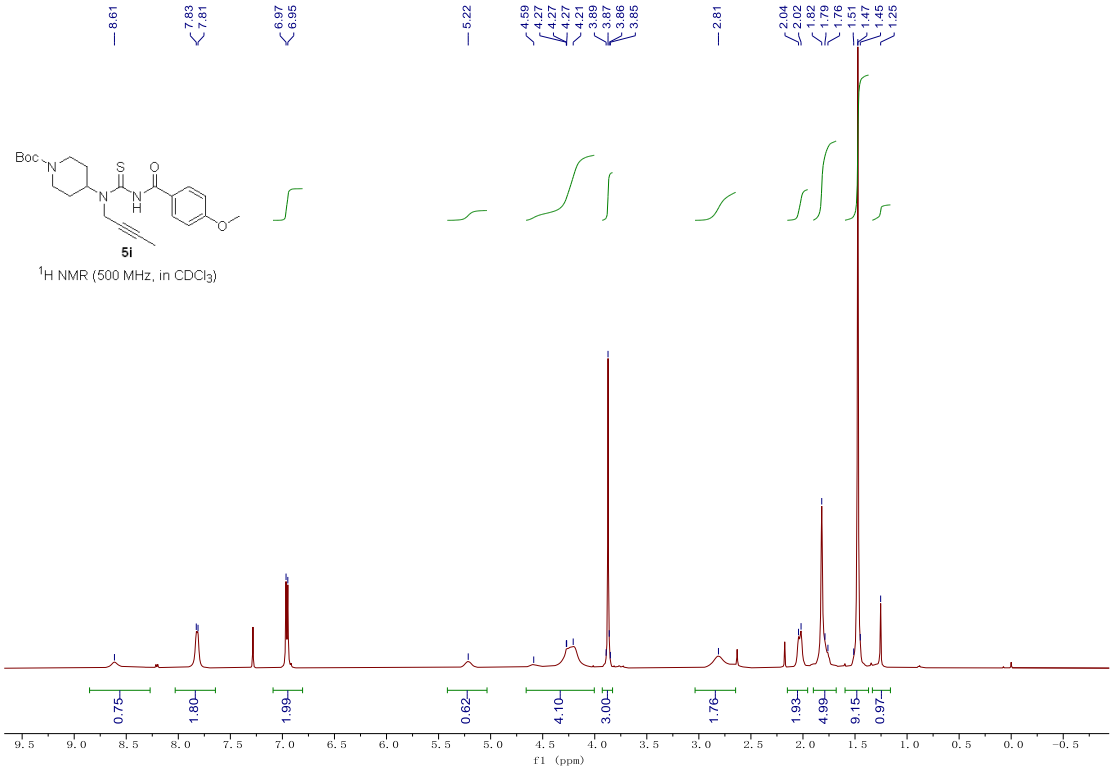

181.70
171.87
157.46
155.45
130.17
129.90
129.84
128.82
124.19
124.16
116.54
116.38
81.51
77.25
77.00
76.75
71.82
46.07
45.09
28.73
25.37
25.12
3.51
F
S
O
N
H
5f
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

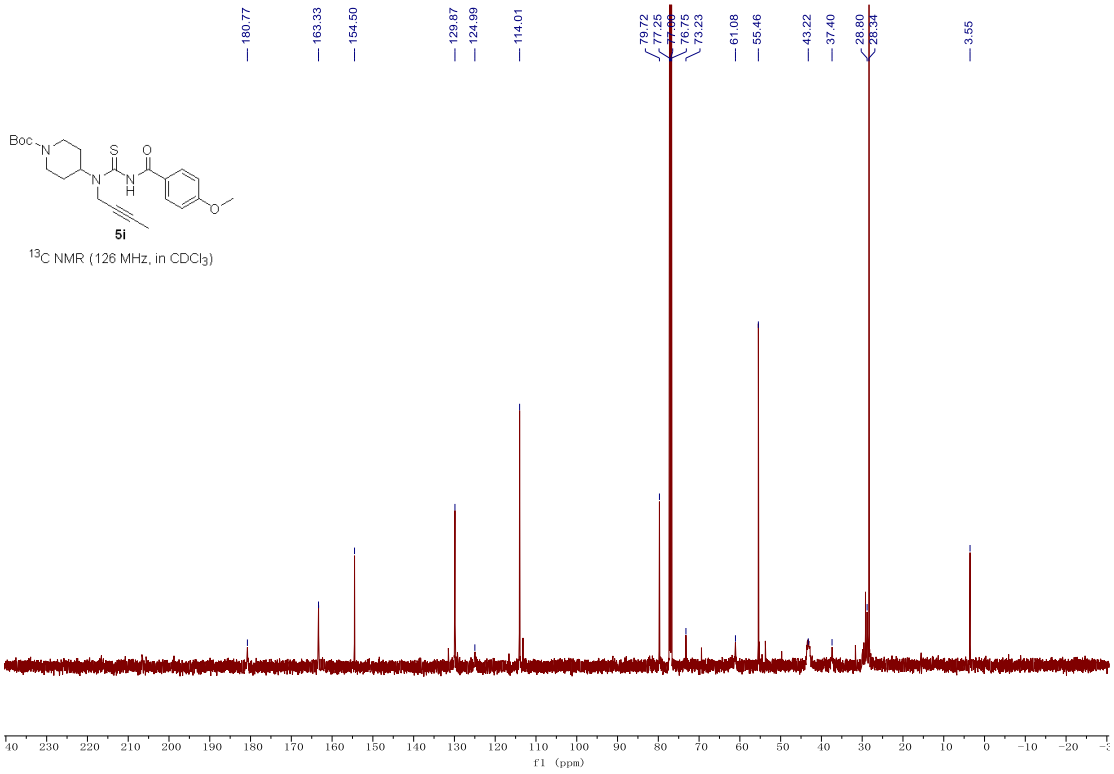

8.14
7.97
7.96
7.96
7.95
7.95
7.88
7.87
7.64
7.64
7.63
7.63
7.63
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.56
7.39
7.39
7.38
7.38
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.14
7.14
7.13
5.42
5.42
5.41
5.39
5.39
5.38
4.81
4.80
4.80
4.79
4.78
4.77
4.77
1.73
1.73
1.72
S
O
Br
N
H
5g
1H NMR (600 MHz, in CDCl3)


1.00
2.09
0.86
4.15
0.98
1.95
0.84
1.00
1.00
2.76
f1 (ppm)


178.36
165.47
137.05
136.47
134.71
133.11
131.60
130.07
129.77
129.37
128.62
127.85
127.29
127.13
125.95
125.65
122.37
118.65
81.93
77.26
77.00
76.75
72.44
45.69
3.53
Br
5g
13C NMR (126 MHz, in CDCl3)
f1 (ppm)
8.58
7.86
7.73
7.59
7.58
7.56
7.51
7.50
7.48
7.47
7.46
7.44
7.42
7.41
7.39
7.38
7.37
7.36
7.35
7.32
7.30
7.29
7.27
7.26
5.46
5.44
4.94
4.93
4.91
4.90
4.70
4.69
4.66
4.24
4.20
1.84
5h
1H NMR (500 MHz, in CDCl3)
0.78
1.81
8.61
1.00
1.68
1.33
2.77
f1 (ppm)

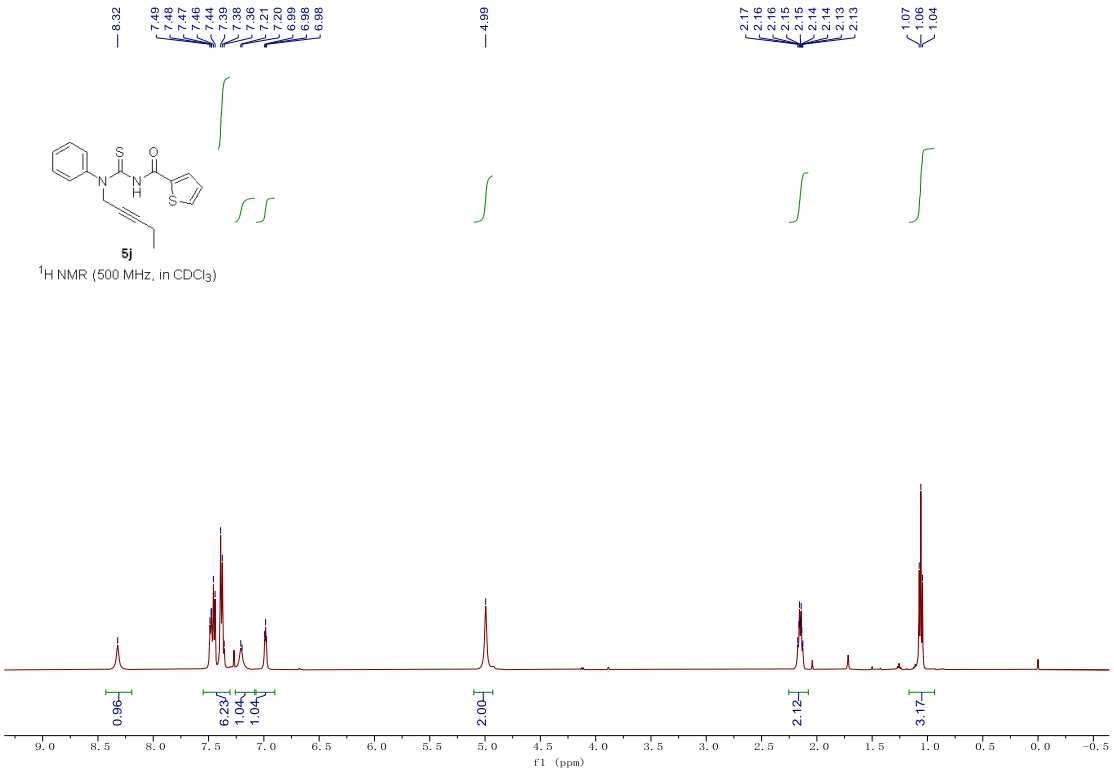

180.93
163.69
133.02
132.45
128.90
128.84
128.73
128.21
127.98
127.83
116.83
77.25
77.00
76.75
71.91
56.07
53.12
50.83
42.16
15.64
3.60
5h
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


8.61
7.83
7.81
6.97
6.95
5.22
4.59
4.27
4.27
4.27
4.21
3.89
3.87
3.86
3.85
2.81
2.04
2.02
1.82
1.79
1.76
1.51
1.47
1.45
1.25
Boc
5i
1H NMR (500 MHz, in CDCl3)
0.75
1.80
1.99
0.62
4.10
3.00
1.76
1.93
4.99
9.15
0.97
f1 (ppm)



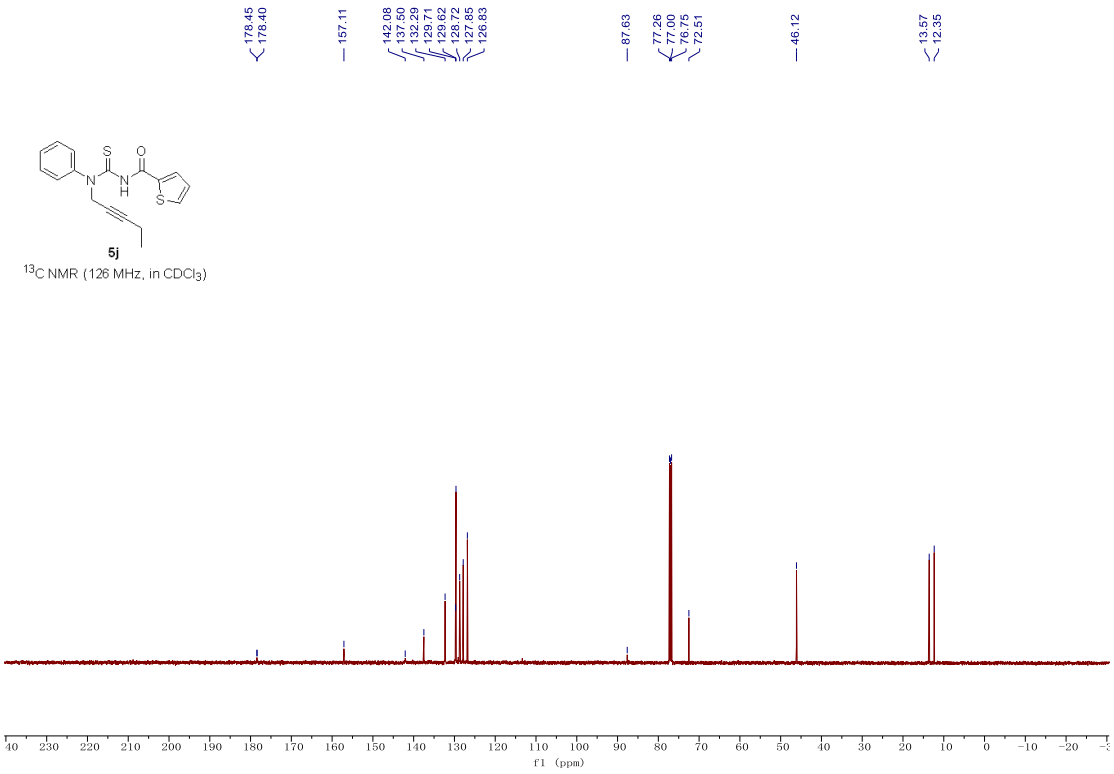
5i

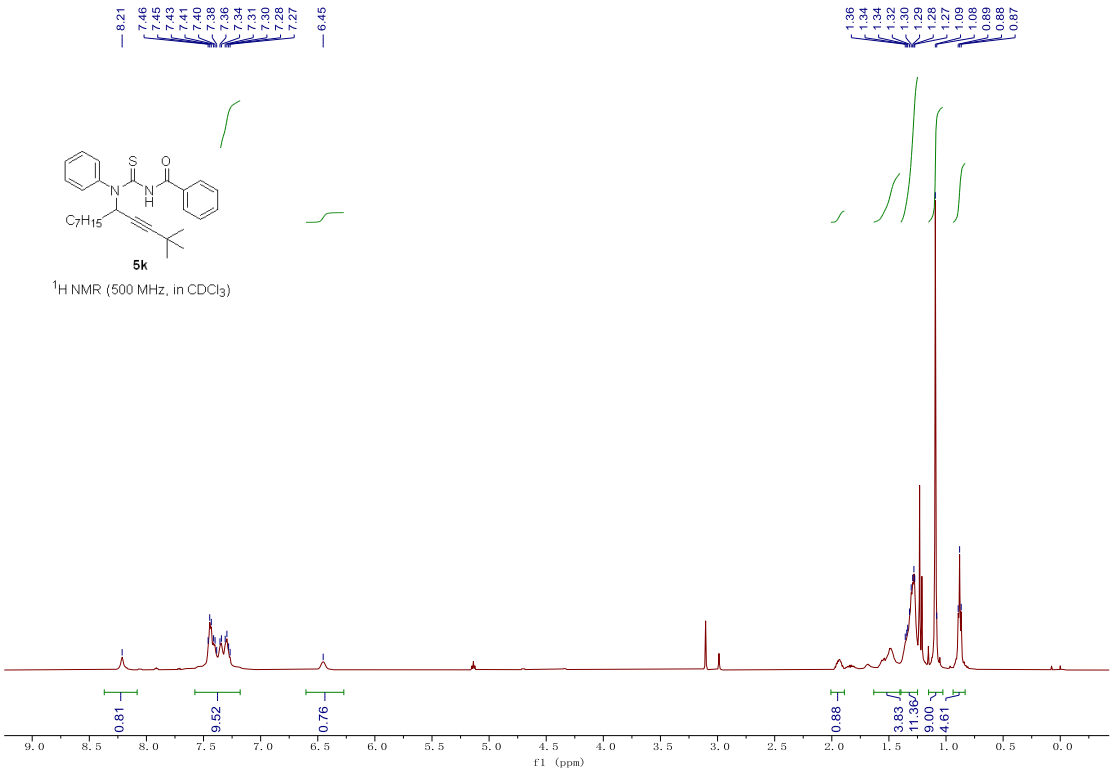
^{13}C NMR (126 MHz, in $CDCl_3$)

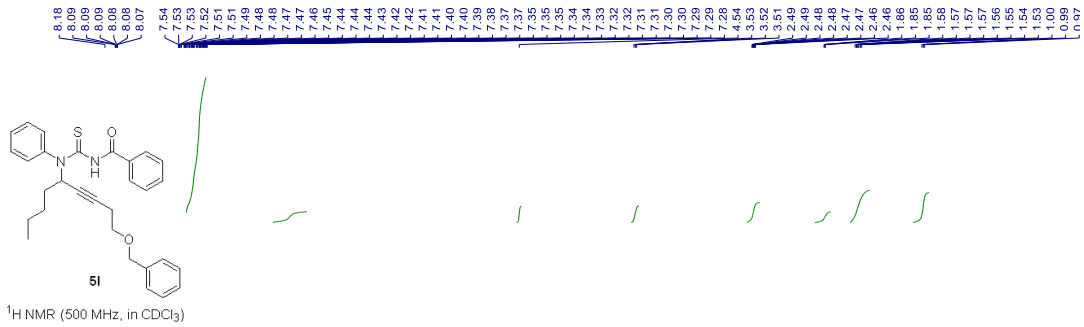


5j

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

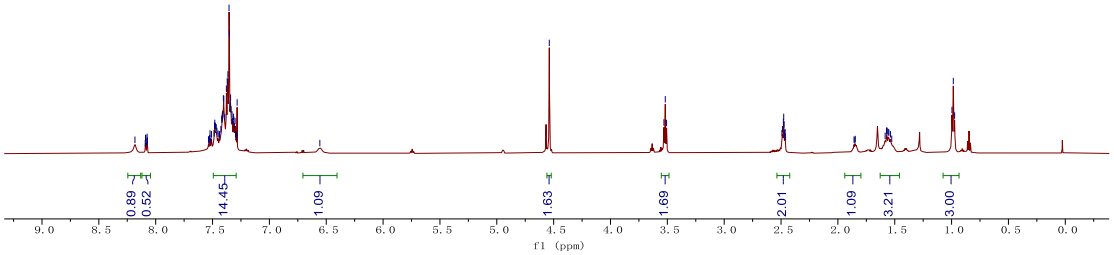

178.45
178.40
157.11
142.08
137.50
132.29
129.71
129.62
128.72
127.85
126.83
87.63
77.26
77.00
76.75
72.51
46.12
13.57
12.35
5j
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

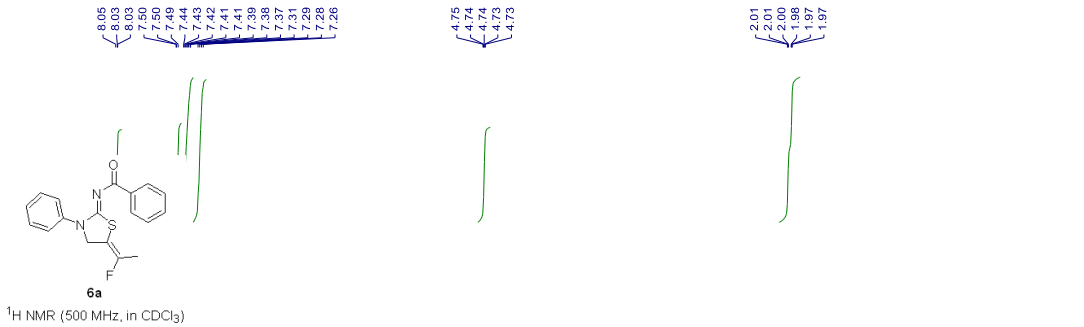

8.21
7.46
7.45
7.43
7.41
7.40
7.38
7.36
7.34
7.31
7.30
7.28
7.27
6.45
1.36
1.34
1.34
1.32
1.30
1.29
1.28
1.27
1.09
1.08
0.89
0.88
0.87
C7H15
5k
1H NMR (500 MHz, in CDCl3)
0.81
9.52
0.76
0.88
3.83
11.36
9.00
4.61
f1 (ppm)



5l

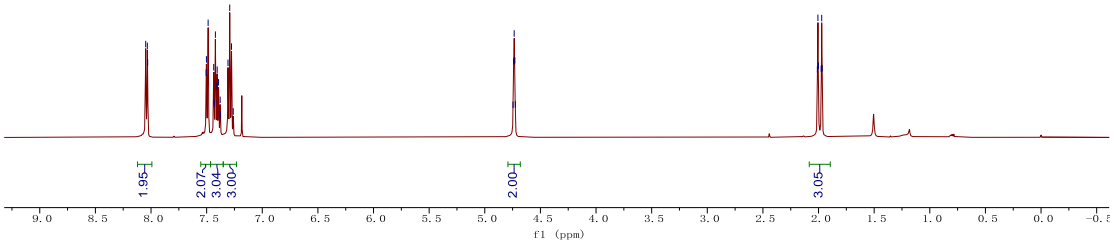
^{1}H NMR (500 MHz, in $CDCl_3$)

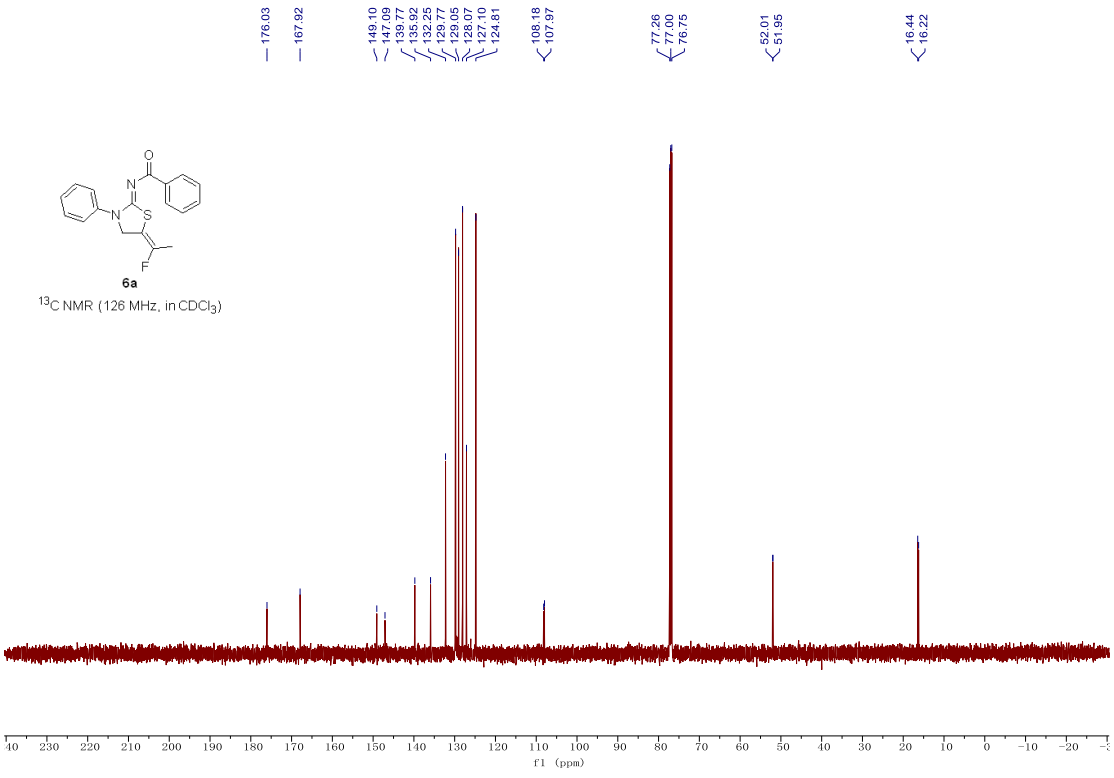


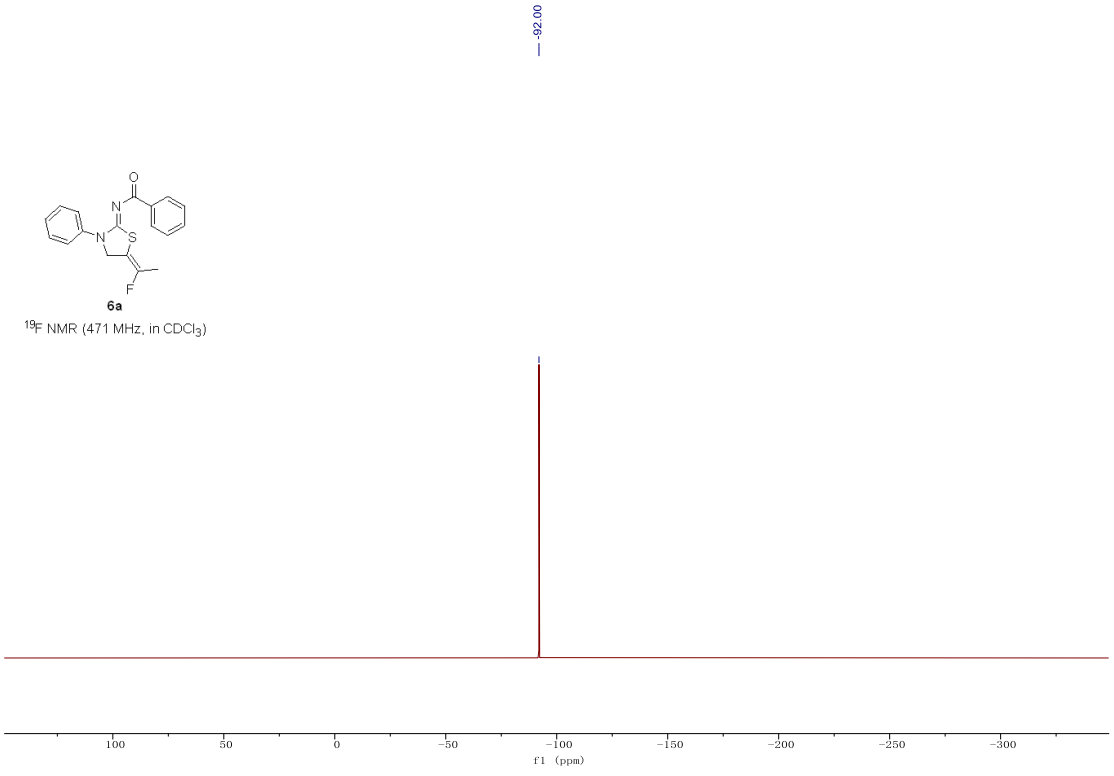


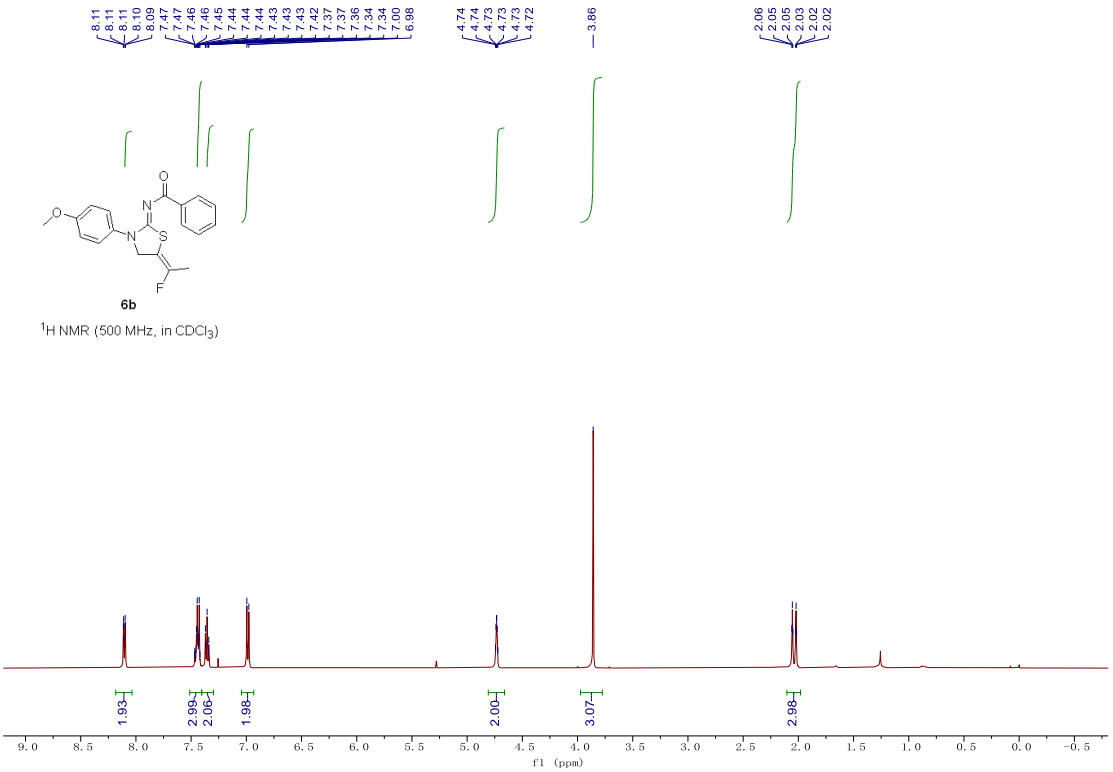
6a

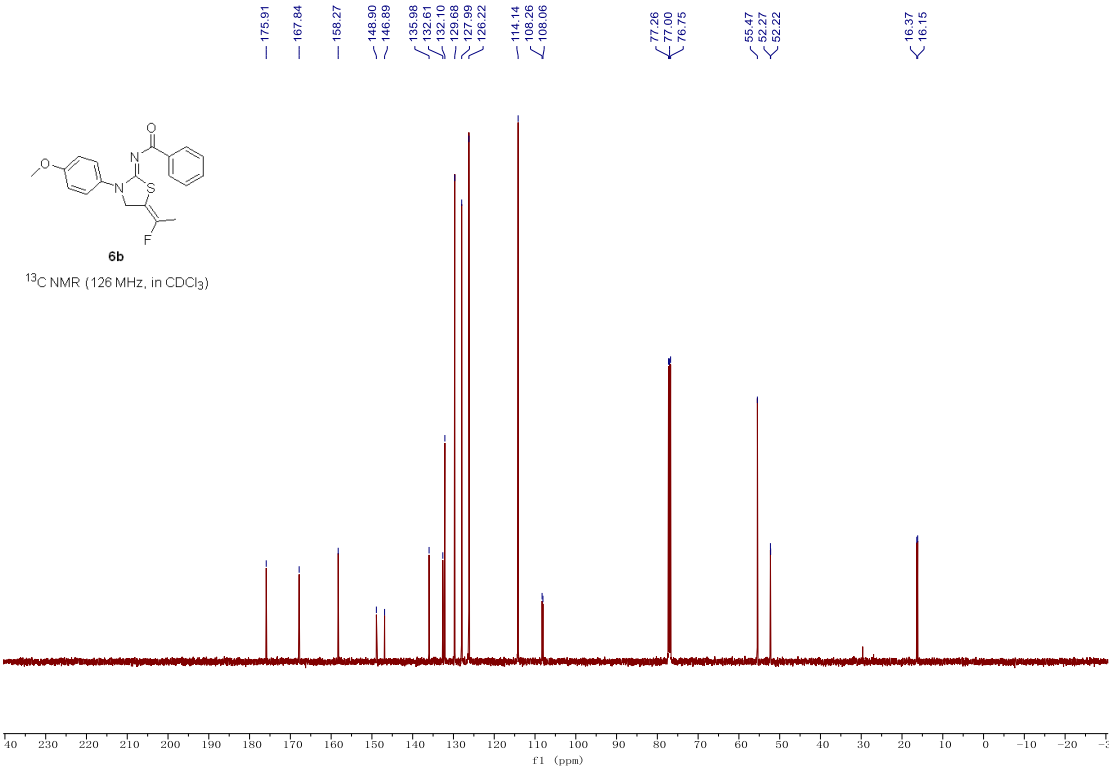
^{1}H NMR (500 MHz, in $CDCl_3$)

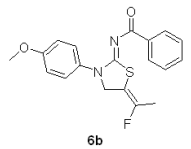



176.03
167.92
149.10
147.09
139.77
135.92
132.25
129.77
129.05
128.07
127.10
124.81
108.18
107.97
77.26
77.00
76.75
52.01
51.95
16.44
16.22
6a
13C NMR (126 MHz, in CDCl3)
f1 (ppm)


-92.00
6a
19F NMR (471 MHz, in CDCl3)
f1 (ppm)

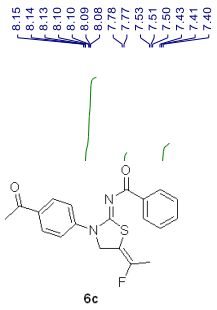

8.11
8.11
8.11
8.10
8.09
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.37
7.37
7.36
7.34
7.34
7.00
6.98
4.74
4.74
4.73
4.73
4.73
4.72
3.86
2.06
2.05
2.05
2.03
2.02
2.02
O
N
S
O
N
F
6b
1H NMR (500 MHz, in CDCl3)
1.93
2.99
2.06
1.98
2.00
3.07
2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


175.91
167.84
158.27
148.90
146.89
135.98
132.61
132.10
129.68
127.99
126.22
114.14
108.26
108.06
77.26
77.00
76.75
55.47
52.27
52.22
16.37
16.15
O
N
S
O
N
F
6b
13C NMR (126 MHz, in CDCl3)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



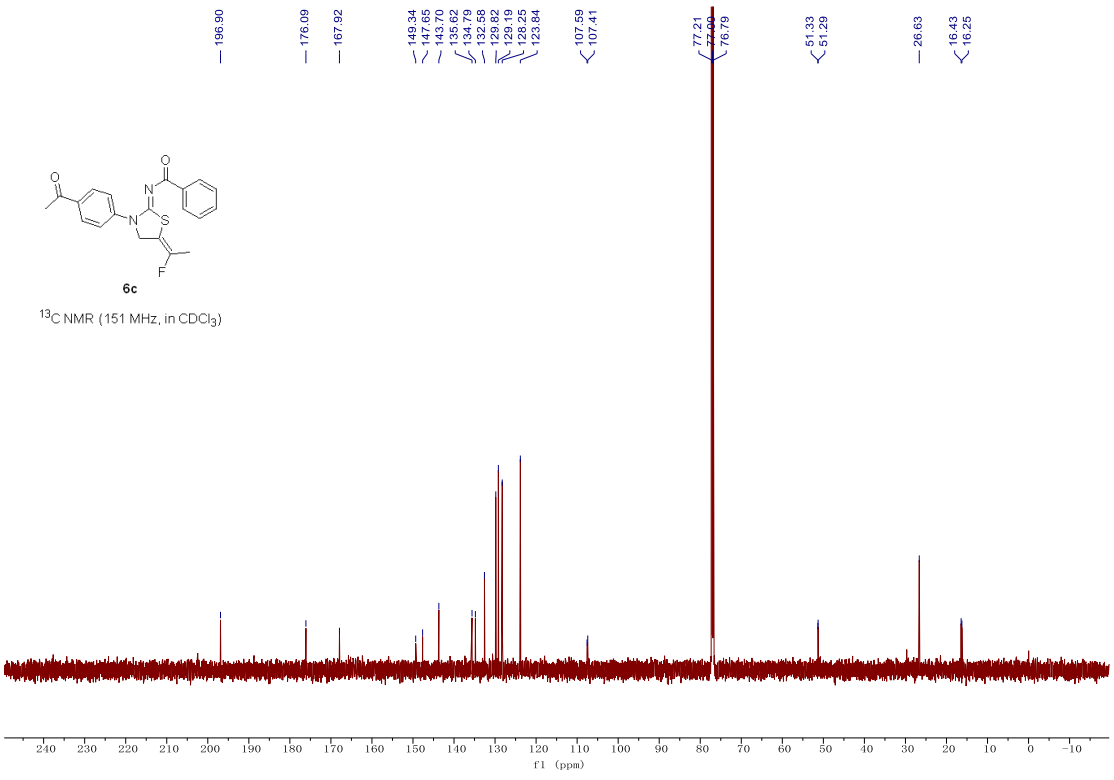
6b

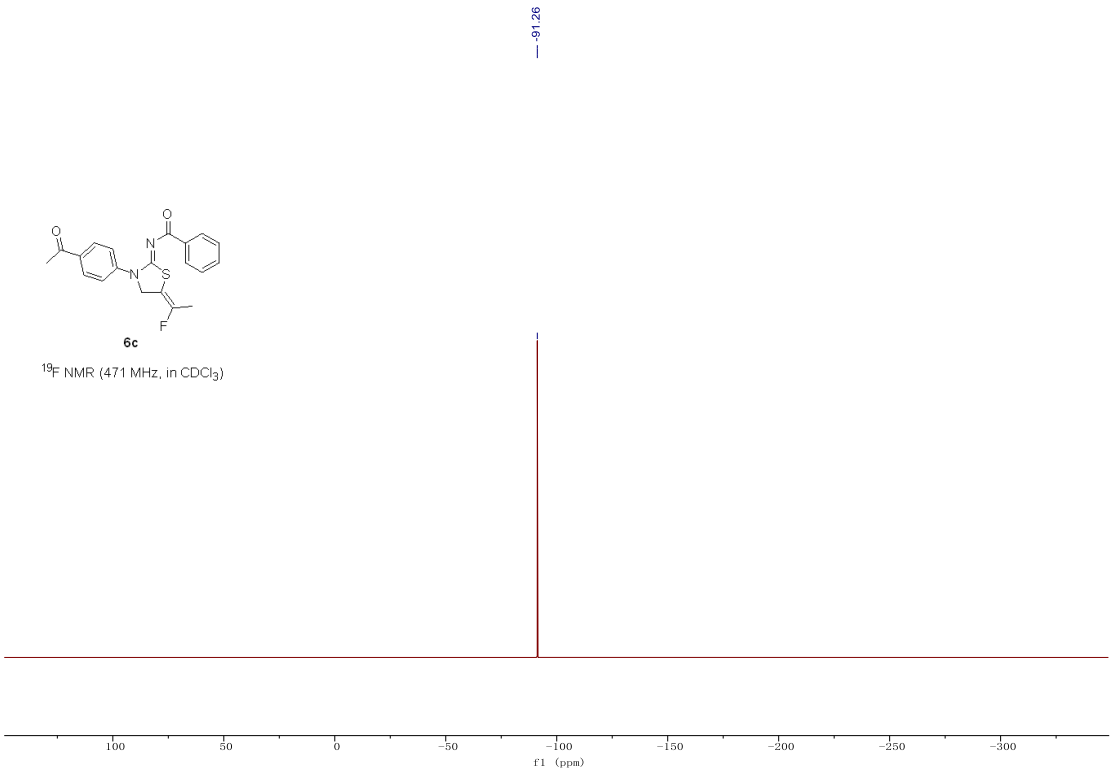
^{19}F NMR (471 MHz, in $CDCl_3$)

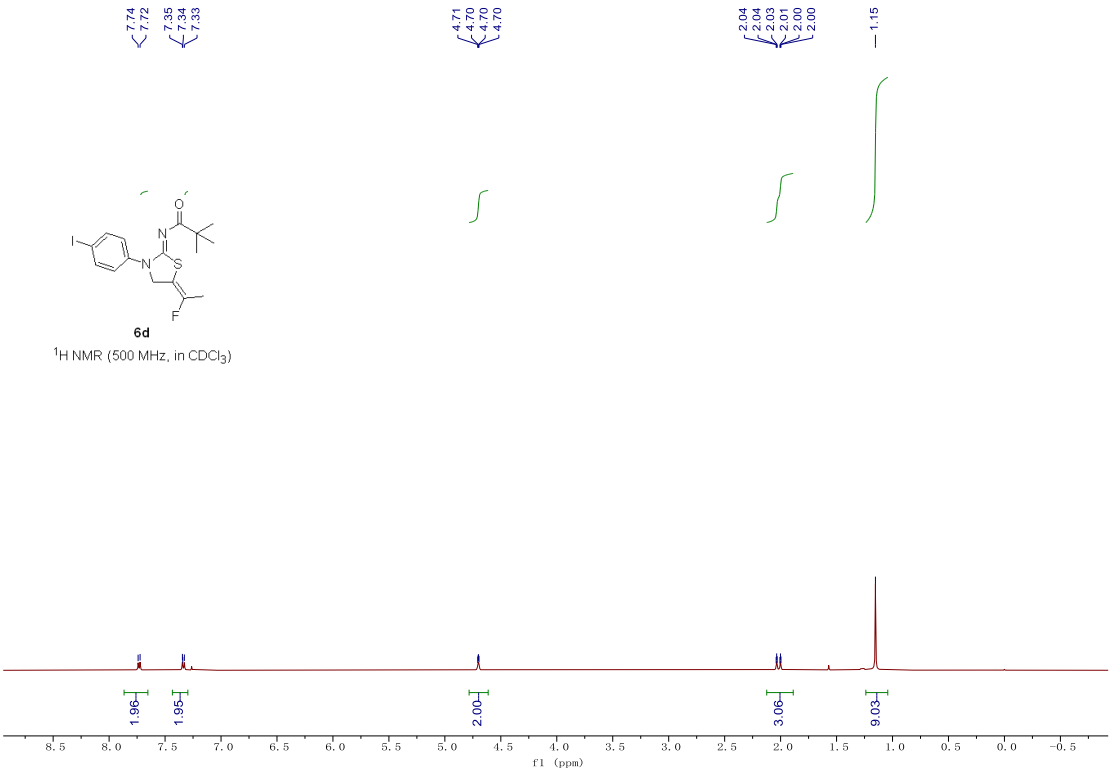


6c

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

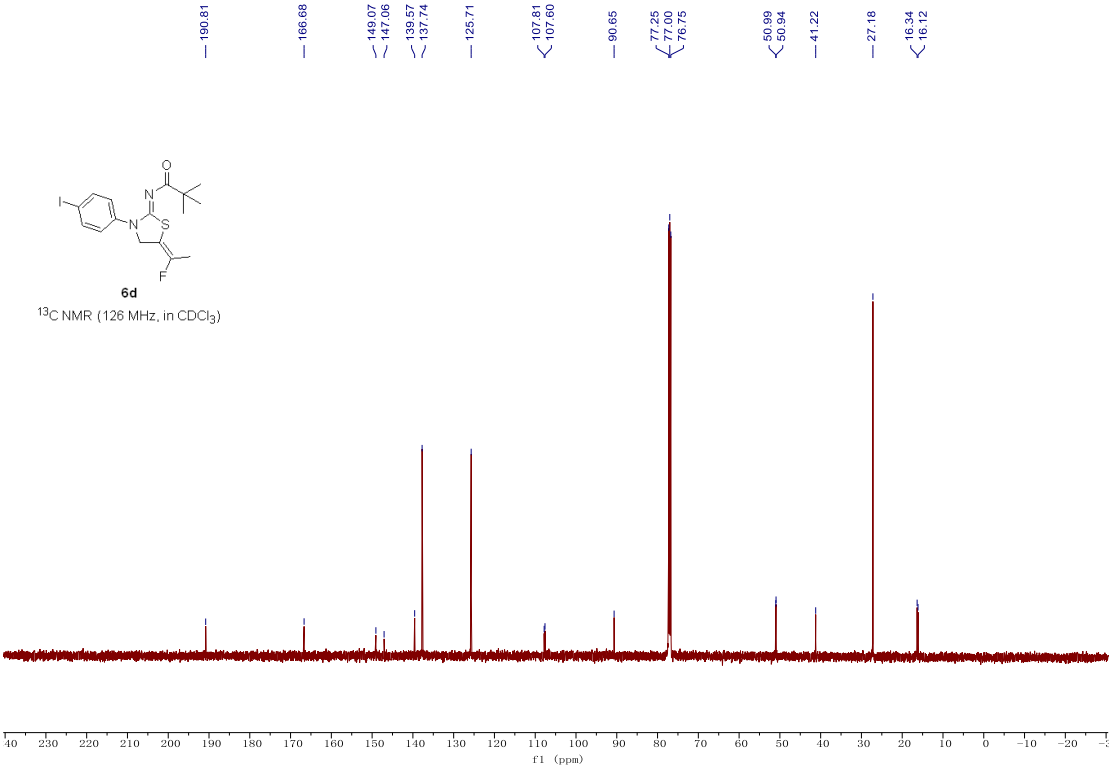

196.90
176.09
167.92
149.34
147.65
143.70
135.62
134.79
132.58
129.82
129.19
128.25
123.84
107.59
107.41
77.21
77.00
76.79
51.33
51.29
26.63
16.43
16.25
O
N
O
N
S
F
6c
13C NMR (151 MHz, in CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-91.26
O
N
O
N
S
F
6c
19F NMR (471 MHz, in CDCl3)
100 50 0 −50 −100 −150 −200 −250 −300
f1 (ppm)



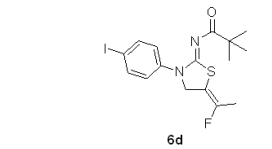
6d

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



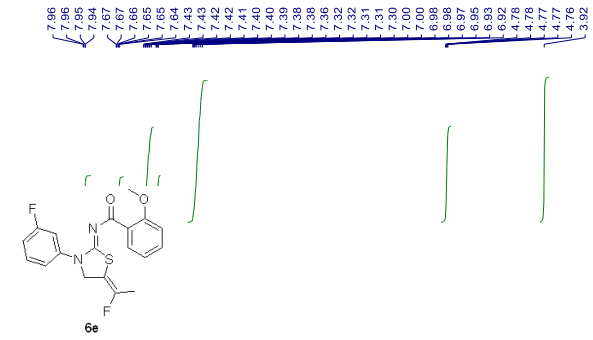
6d

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



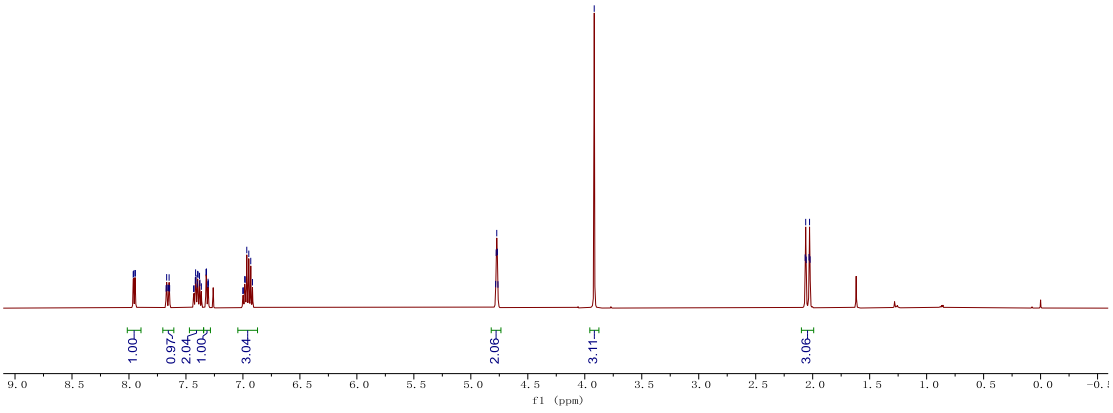
6d

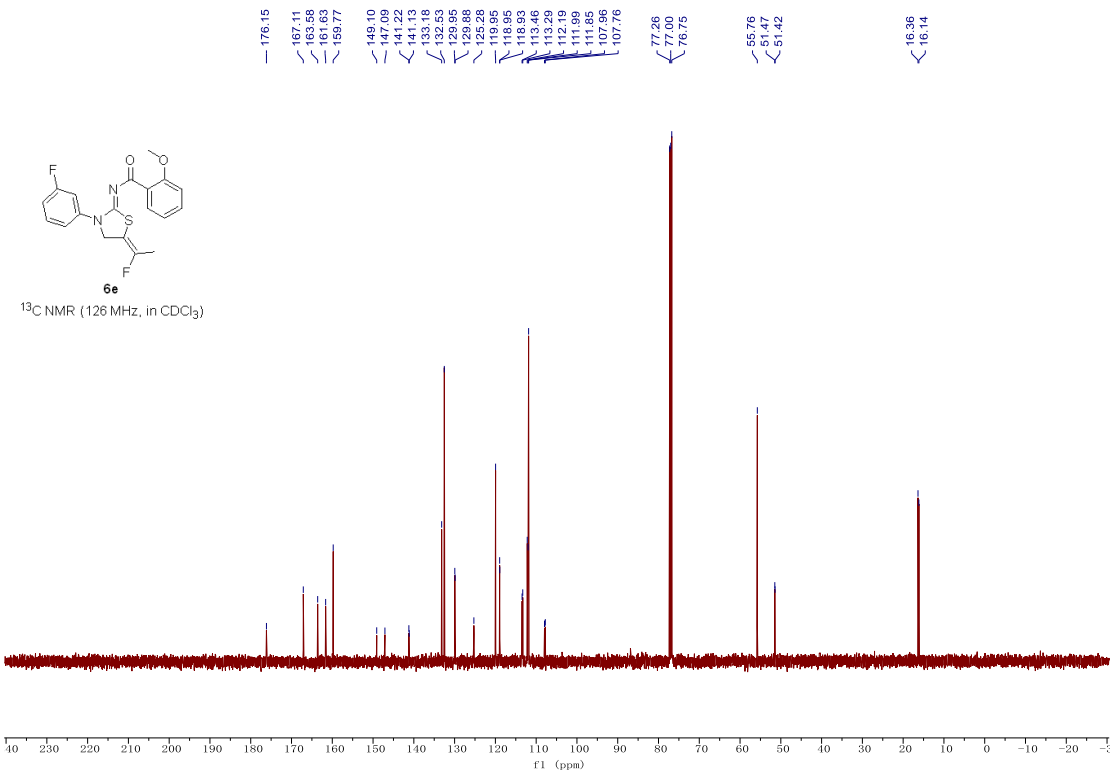
^{19}F NMR (471 MHz, in $CDCl_3$)

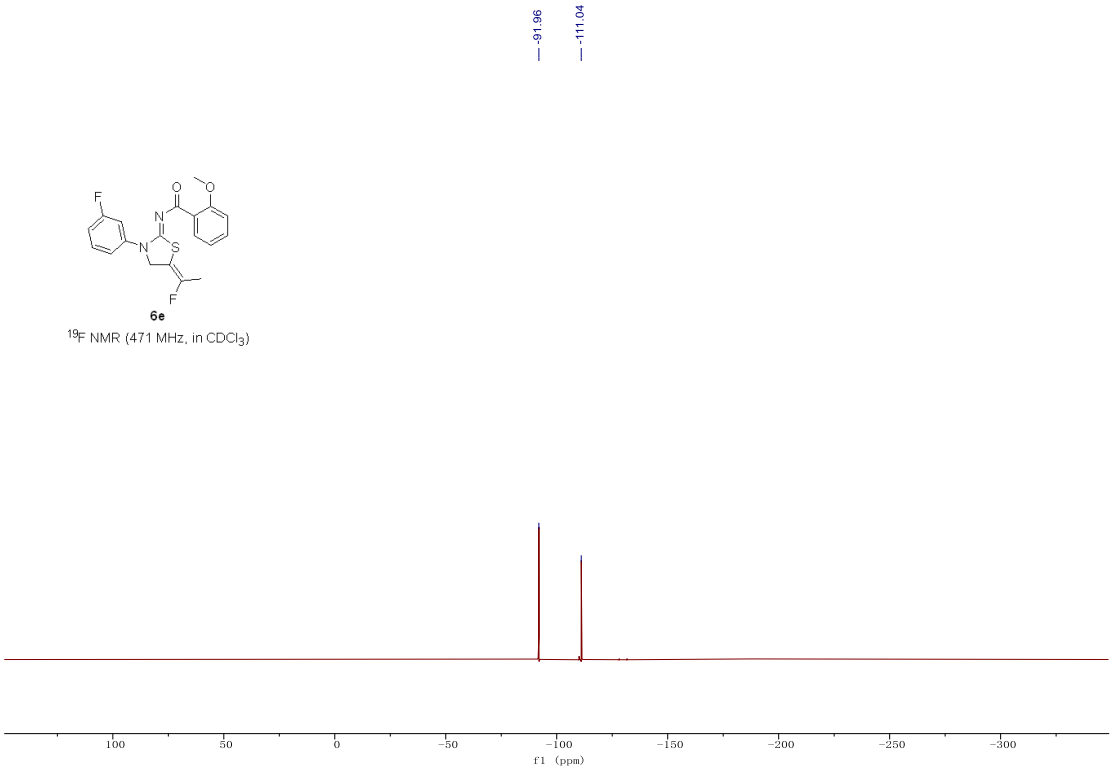


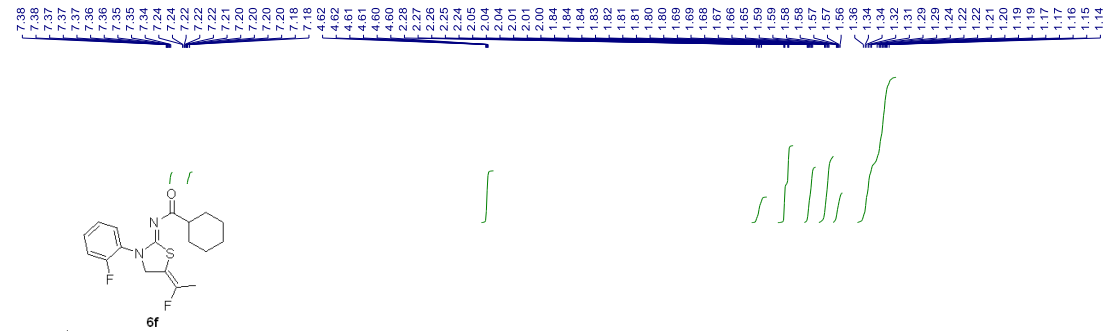
6e

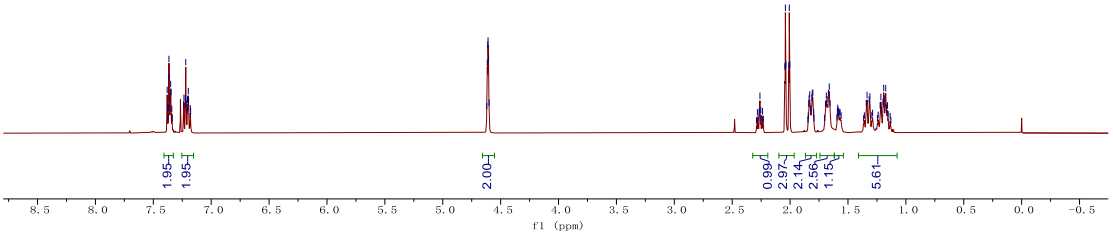
^{1}H NMR (500 MHz, in $CDCl_3$)




176.15
167.11
163.58
161.63
159.77
149.10
147.09
141.22
141.13
133.18
132.53
129.95
129.88
125.28
119.95
116.95
116.93
113.46
113.29
112.19
111.99
111.85
107.96
107.76
77.26
77.00
76.75
55.76
51.47
51.42
16.36
16.14
F
O
O
N
N
S
F
6e
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

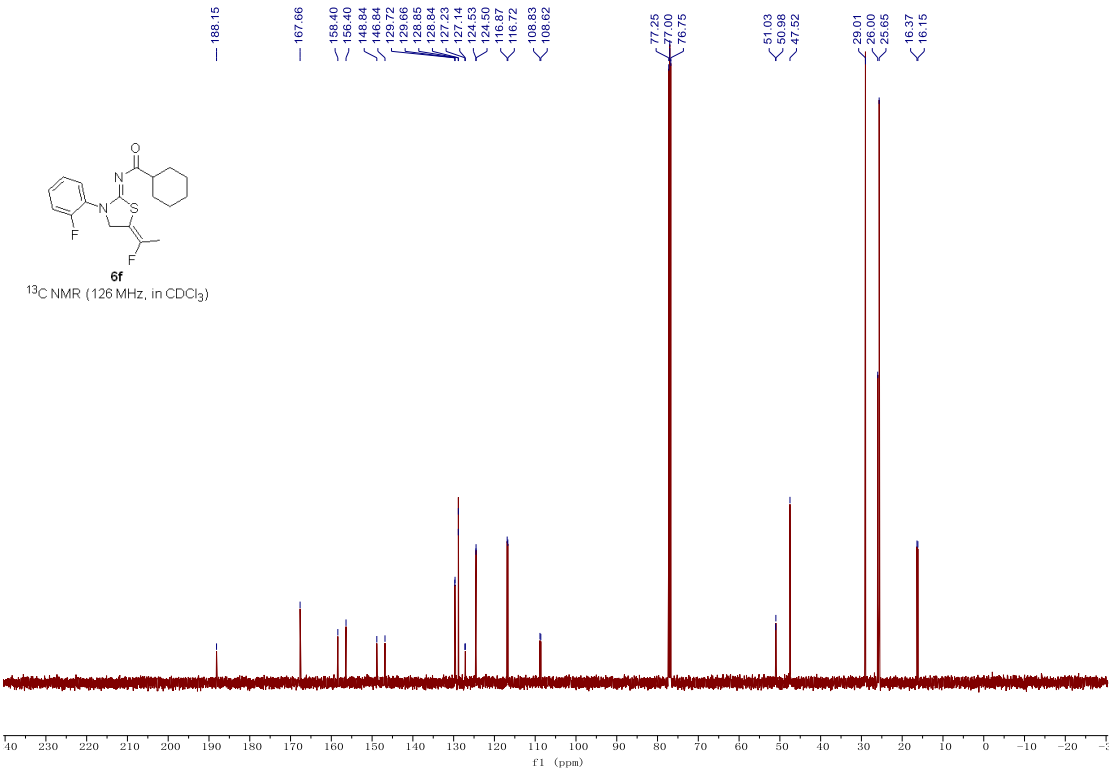

-91.96
-111.04
F
O
O
N
N
S
F
6e
19F NMR (471 MHz, in CDCl3)
f1 (ppm)





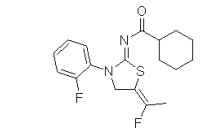
6f

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



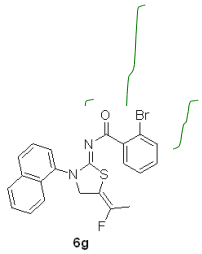
6f

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



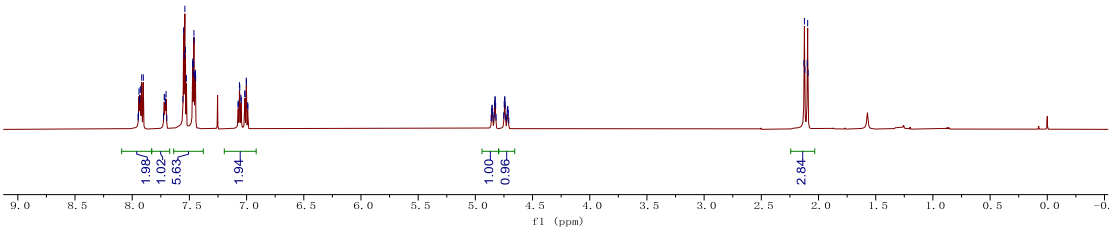
6f

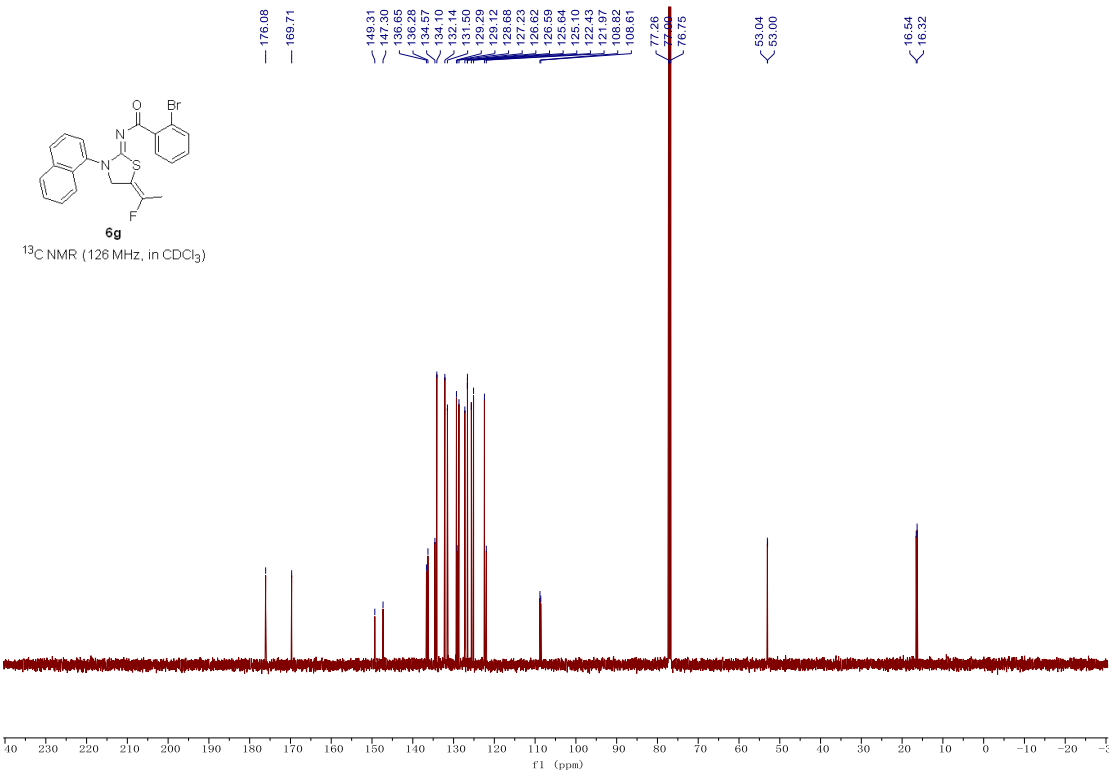
^{19}F NMR (471 MHz, in $CDCl_3$)



6g

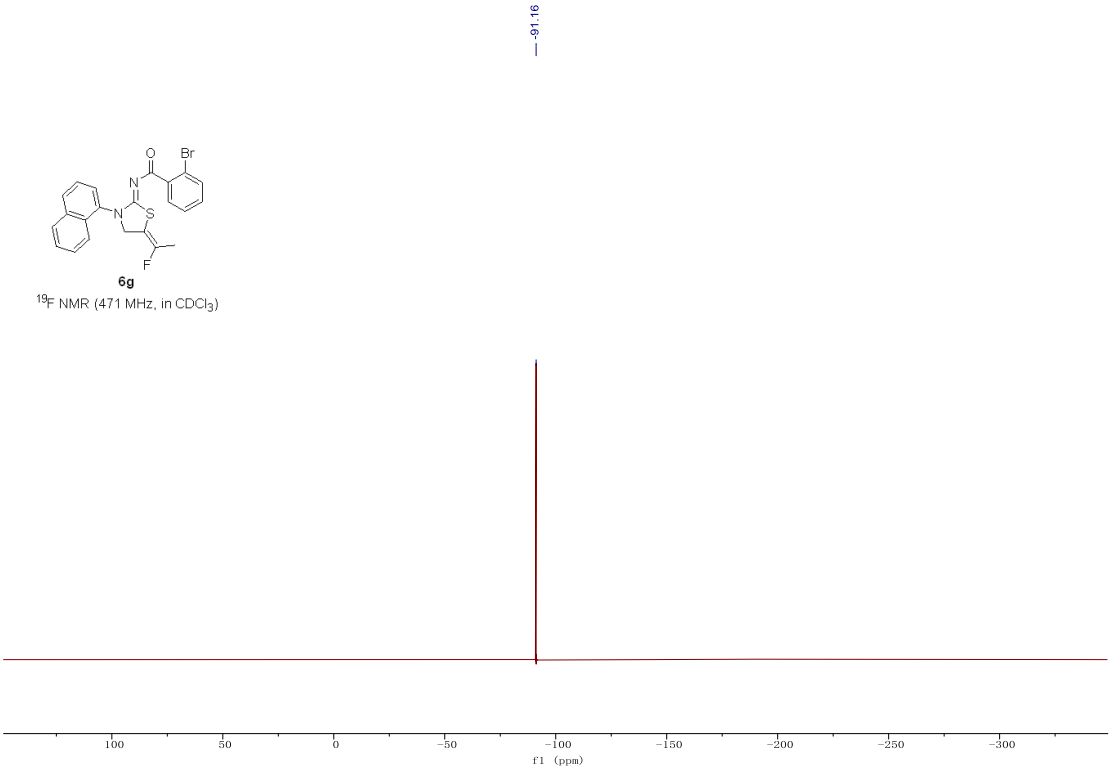
^{1}H NMR (600 MHz, in $CDCl_3$)





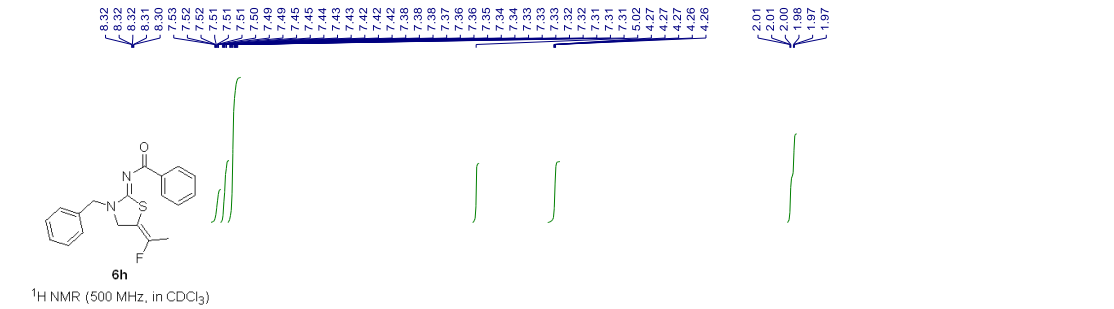
6g

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



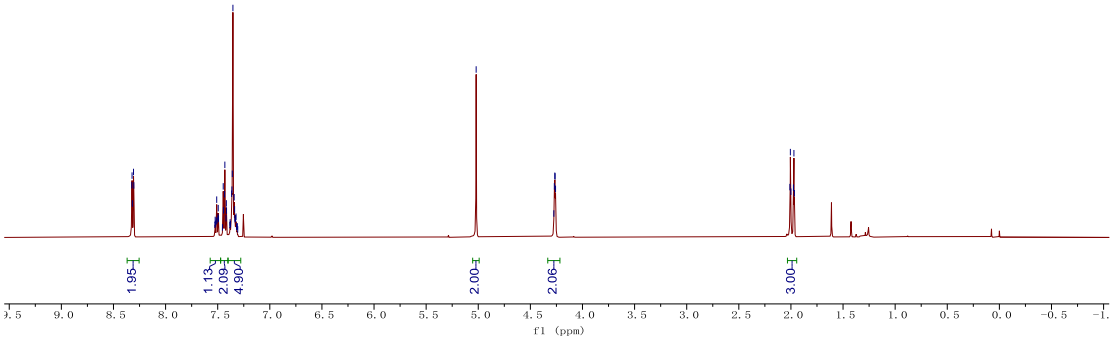
6g

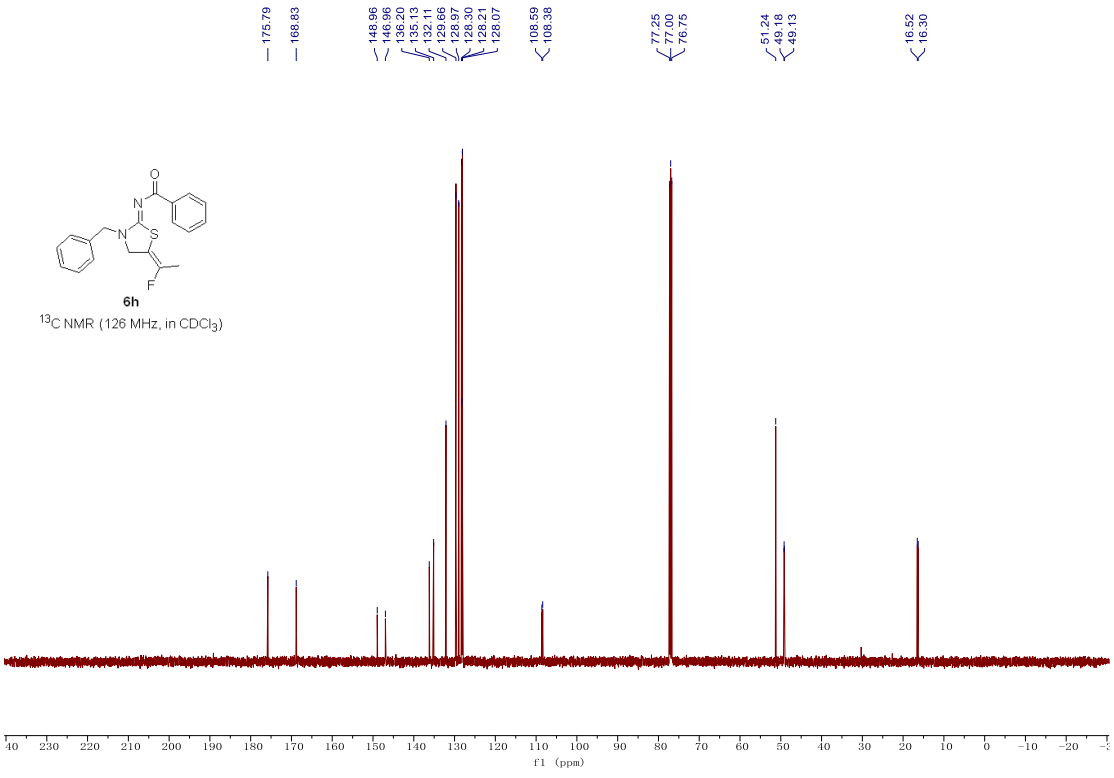
^{19}F NMR (471 MHz, in $CDCl_3$)



6h

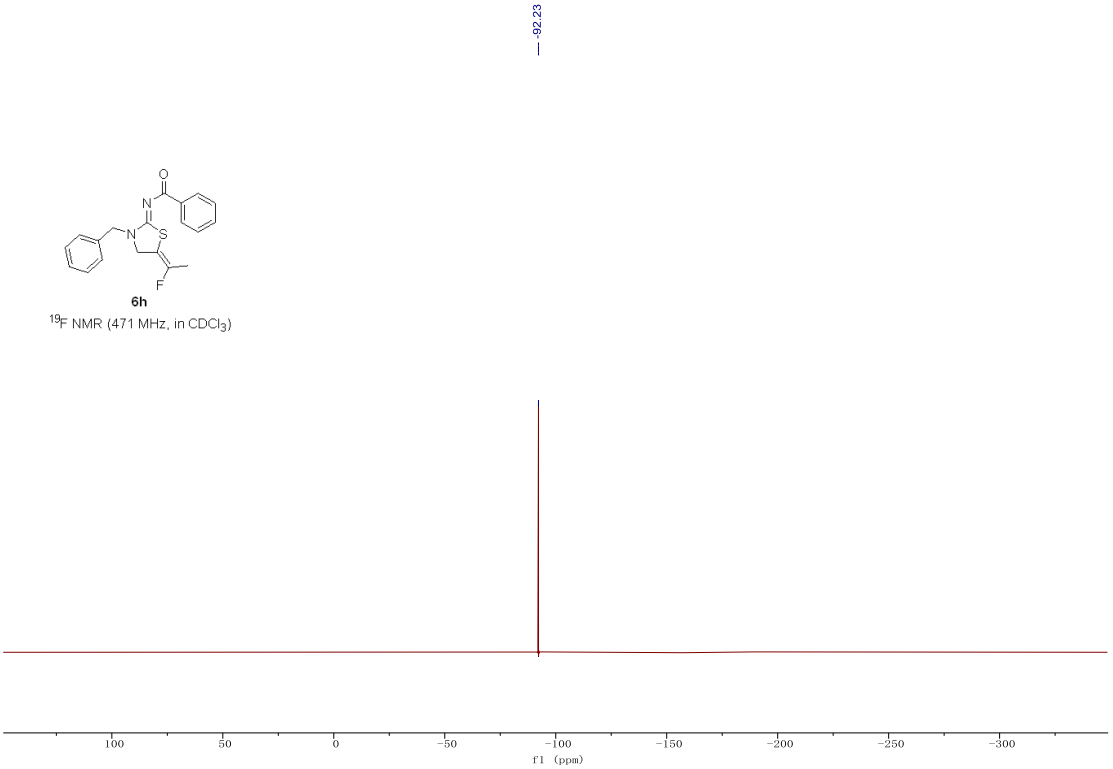
^{1}H NMR (500 MHz, in $CDCl_3$)

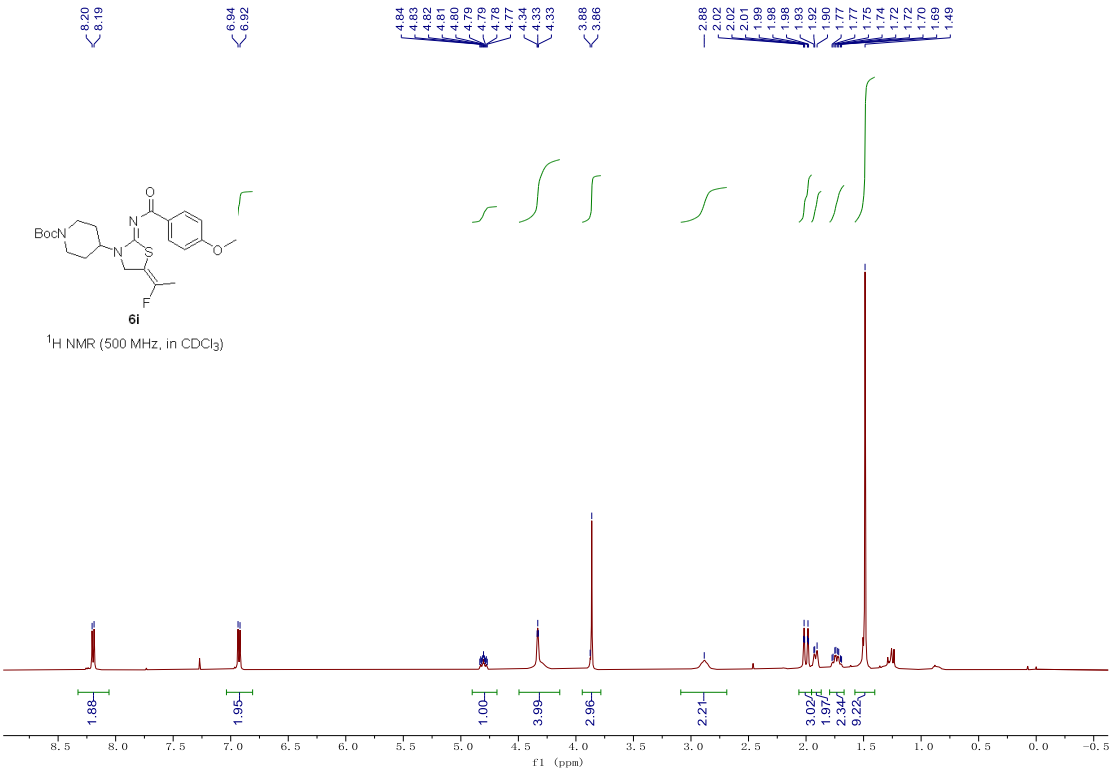


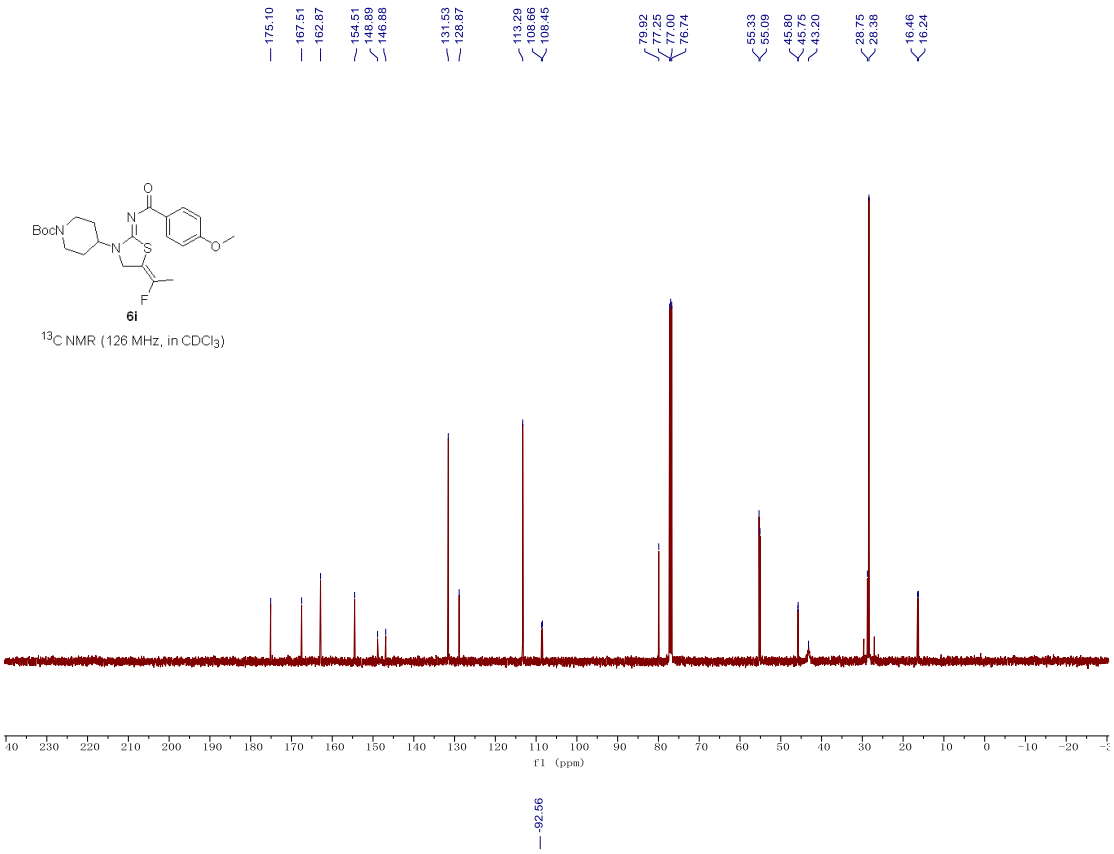


6h

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

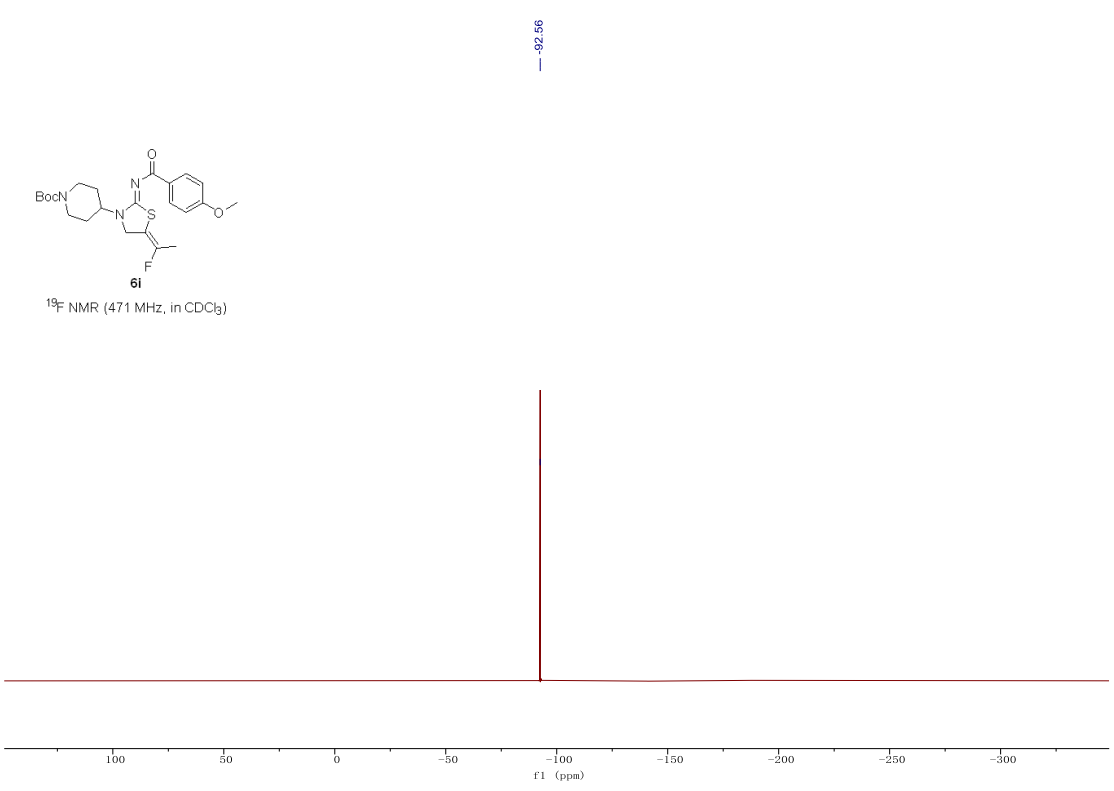

-92.23
6h
19F NMR (471 MHz, in CDCl3)
f1 (ppm)


8.20
8.19
6.94
6.92
4.84
4.83
4.82
4.81
4.80
4.79
4.79
4.78
4.77
4.34
4.33
4.33
3.88
3.86
2.88
2.02
2.02
2.01
1.99
1.98
1.98
1.93
1.92
1.90
1.77
1.77
1.75
1.74
1.72
1.72
1.70
1.69
1.49
BocN
6i
1H NMR (500 MHz, in CDCl3)
1.88
1.95
1.00
3.99
2.96
2.21
3.02
1.97
2.34
9.22
f1 (ppm)



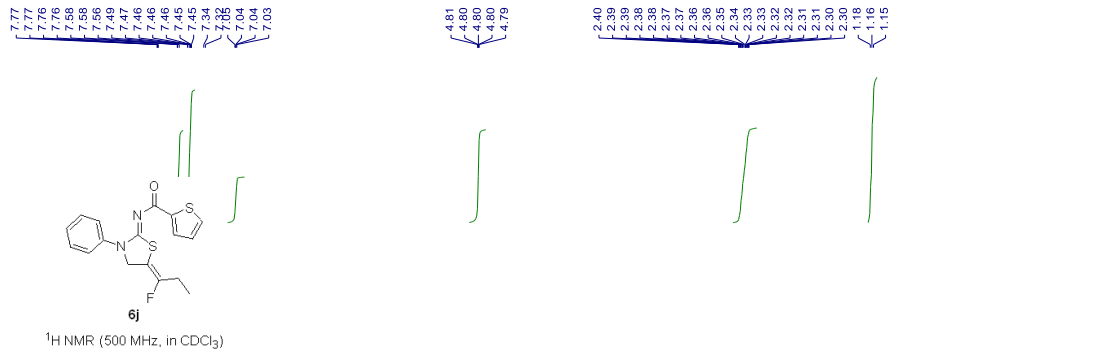
6i

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

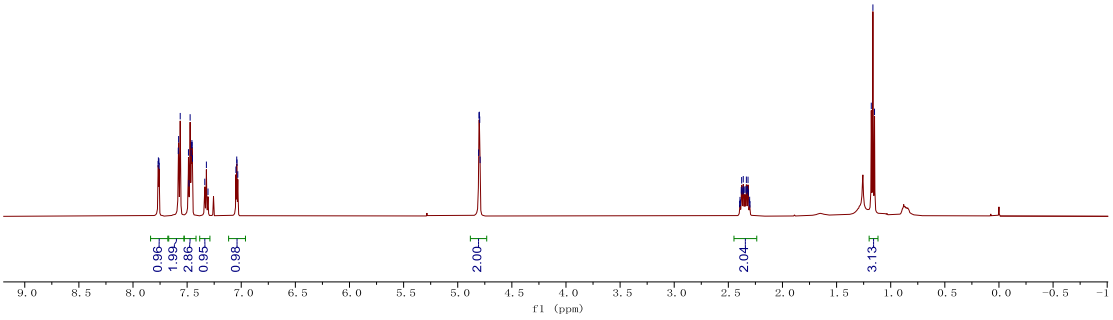


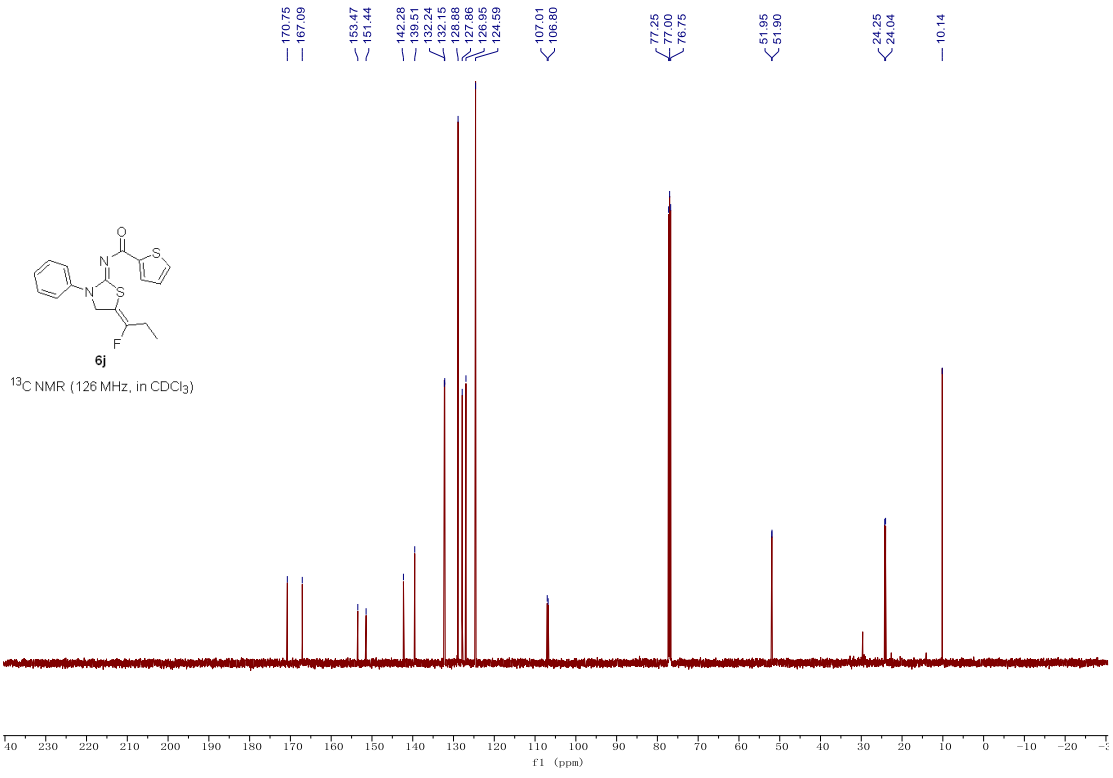
6i

^{19}F NMR (471 MHz, in $CDCl_3$)

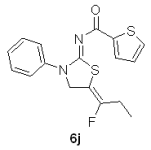


^{1}H NMR (500 MHz, in $CDCl_3$)



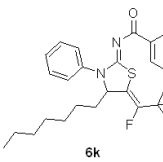


^{13}C NMR (126 MHz, in $CDCl_3$)



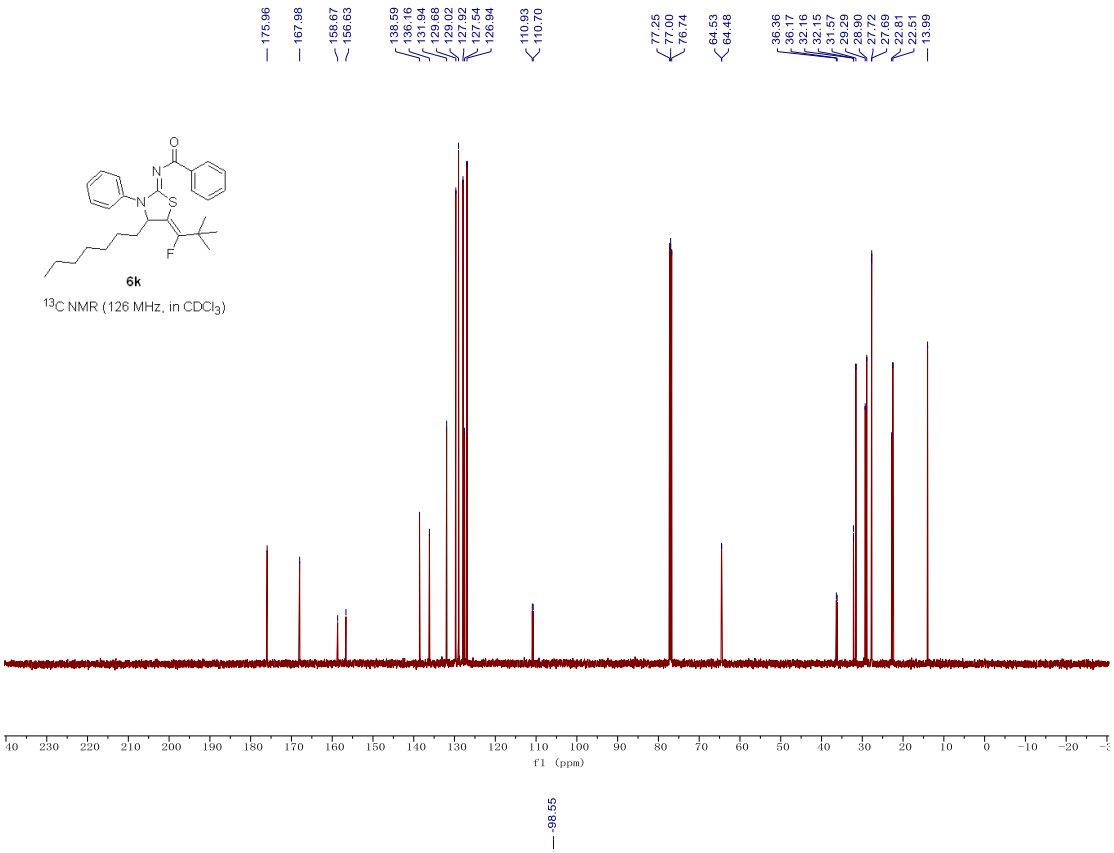
6j

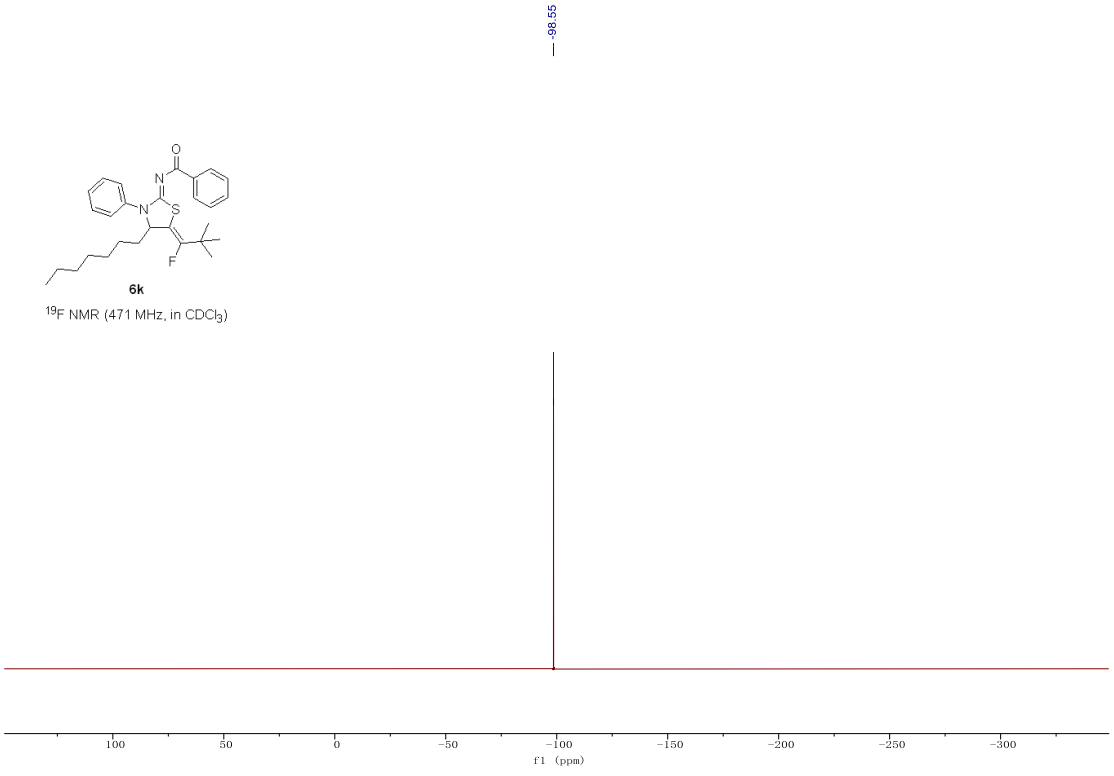
^{19}F NMR (471 MHz, in $CDCl_3$)

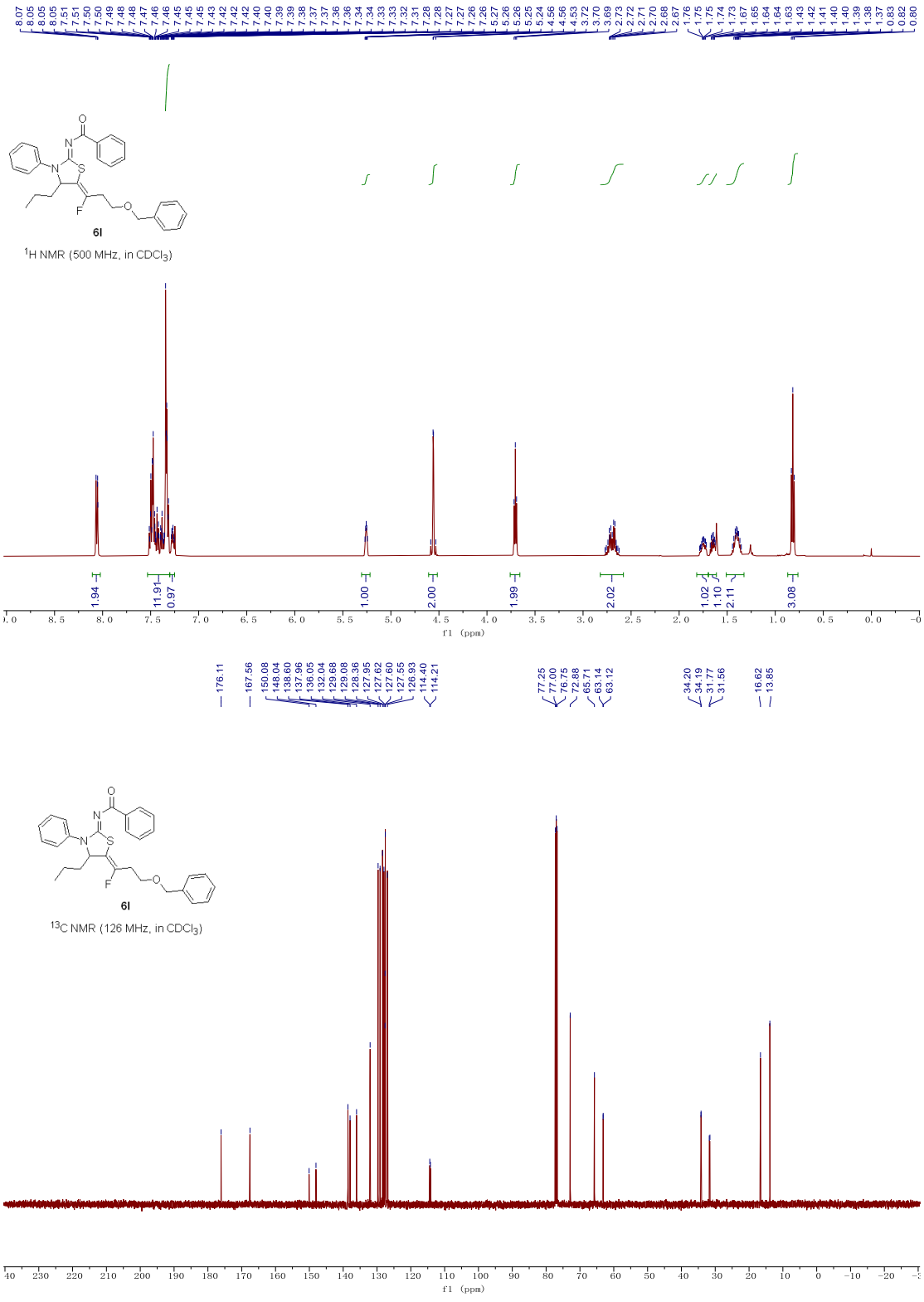


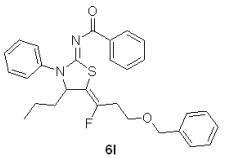
6k

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


175.96
167.98
158.67
156.63
138.59
136.16
131.94
129.68
129.02
127.92
127.54
126.94
110.93
110.70
77.25
77.00
76.74
64.53
64.48
36.36
36.17
32.16
32.15
31.57
29.29
28.90
27.72
27.69
22.61
22.51
13.99
6k
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

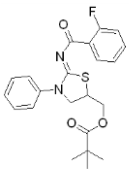

-98.55
6k
19F NMR (471 MHz, in CDCl3)
f1 (ppm)


6l
1H NMR (500 MHz, in CDCl3)
1.94
11.91
0.97
1.00
2.00
1.99
2.02
1.02
1.10
2.11
3.08
f1 (ppm)
6l
13C NMR (126 MHz, in CDCl3)
f1 (ppm)

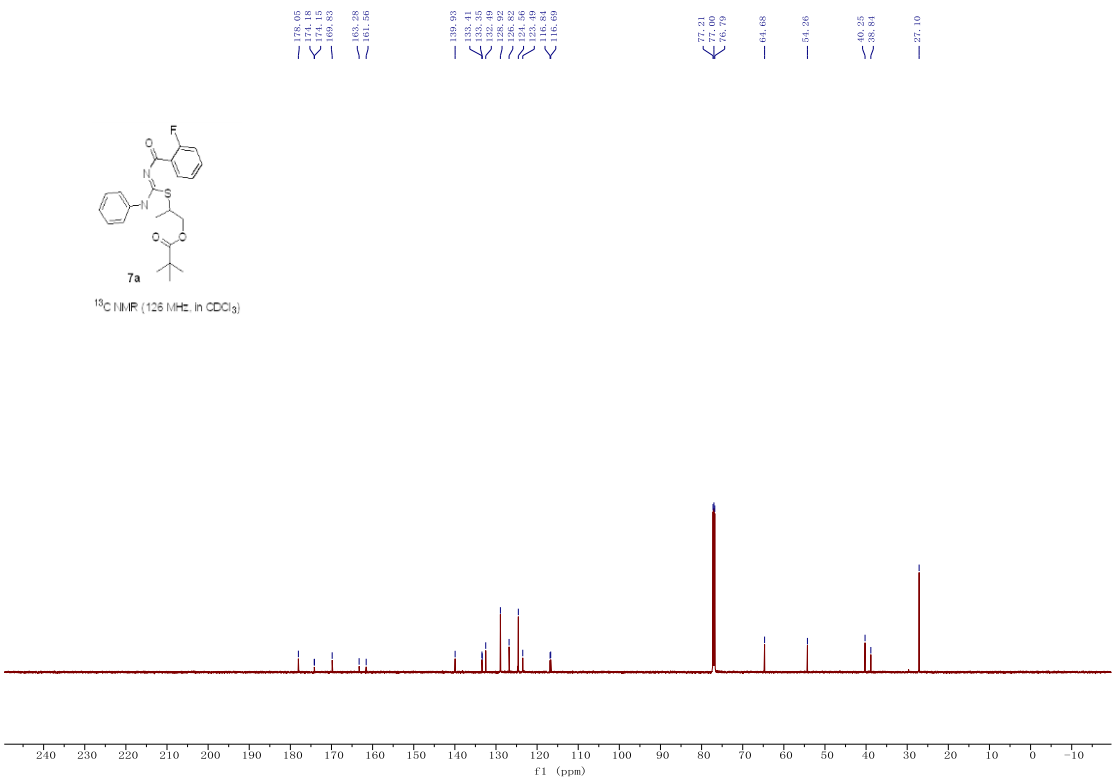


6l

^{19}F NMR (471 MHz, in $CDCl_3$)



7a (^{1}H NMR, in $CDCl_3$)


178.05
171.15
171.15
169.83
163.28
161.56
139.93
133.41
132.35
131.49
128.92
126.82
124.56
123.49
116.84
116.69
77.21
77.00
76.79
64.68
54.26
40.25
38.84
27.10
F
O
N
S
N
O
O
7a
13C NMR (126 MHz, in CDCl3)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)