

Supporting Information

Diastereoselective α -Fluorination of *N*-tert-Butanesulfinyl Imidates

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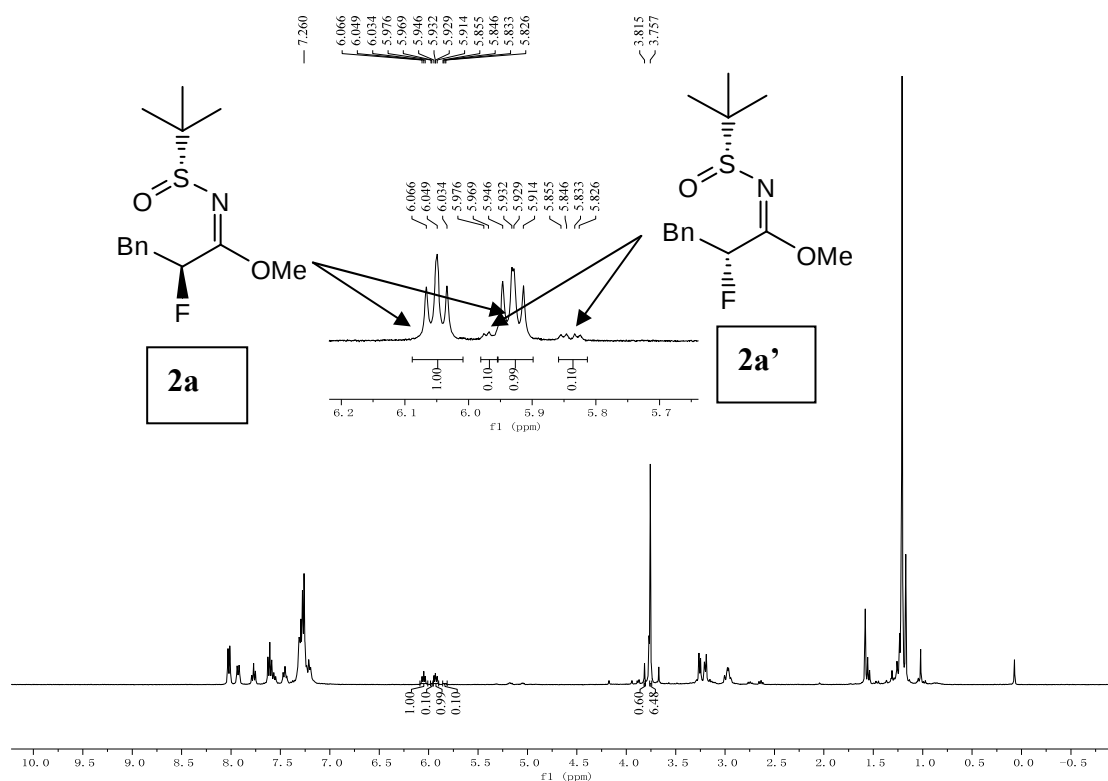
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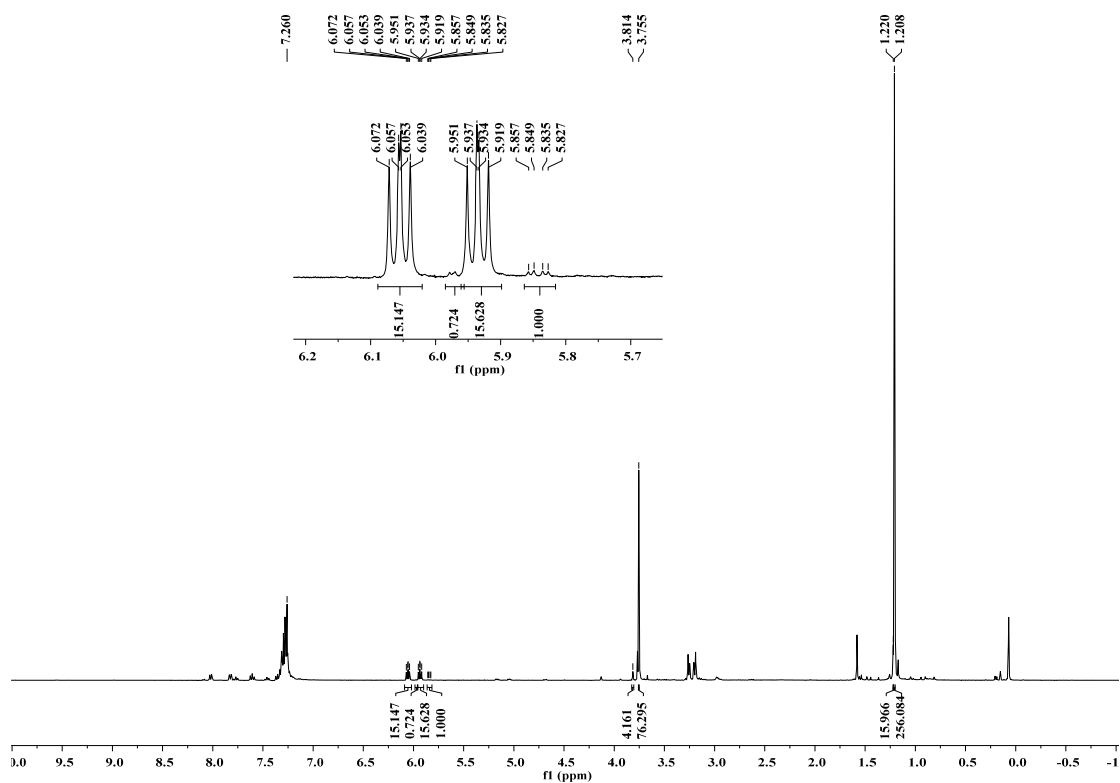
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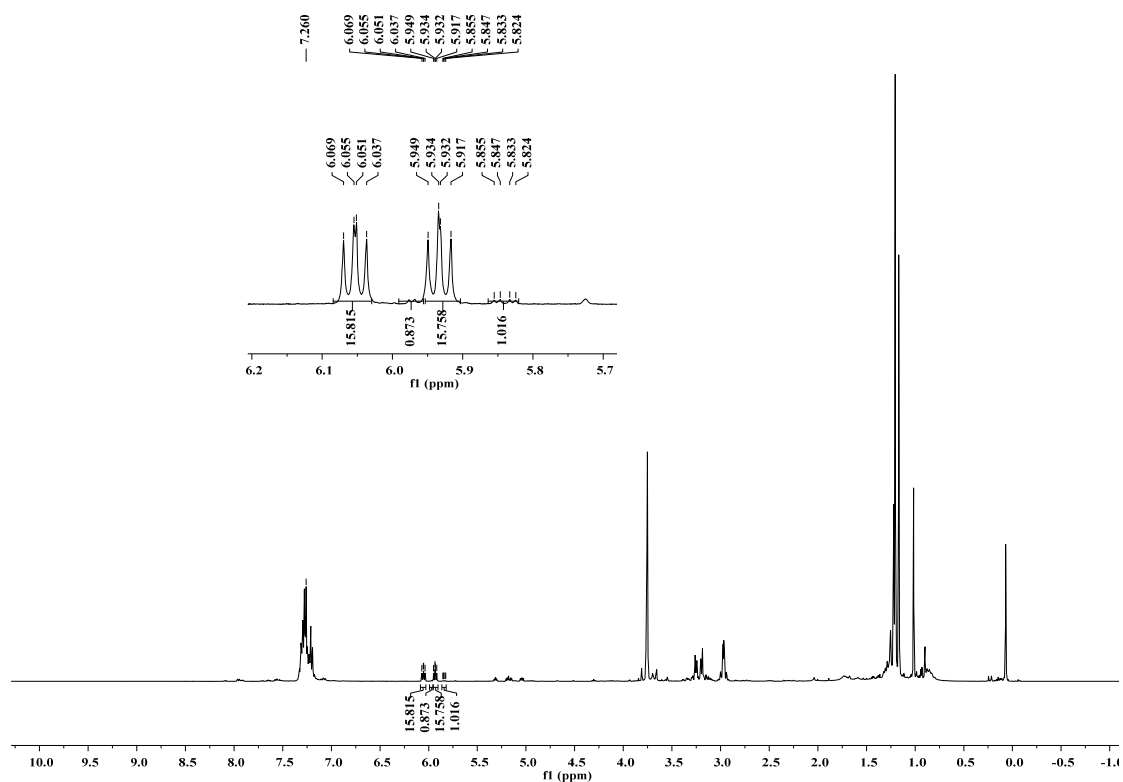
Calculation of diastereomeric ratio of **2a**



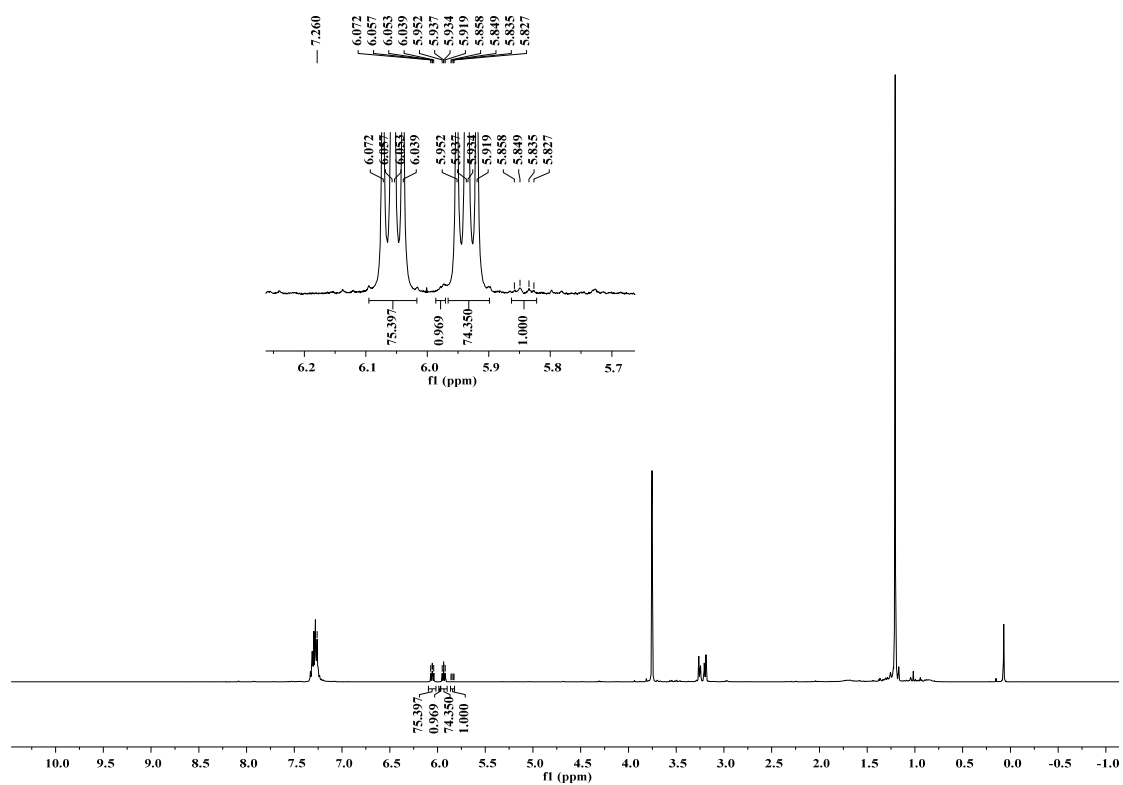
Crude ¹H NMR of **2a** prepared by using LiHMDS in THF (Table 1, entry 1, dr = 10:1)



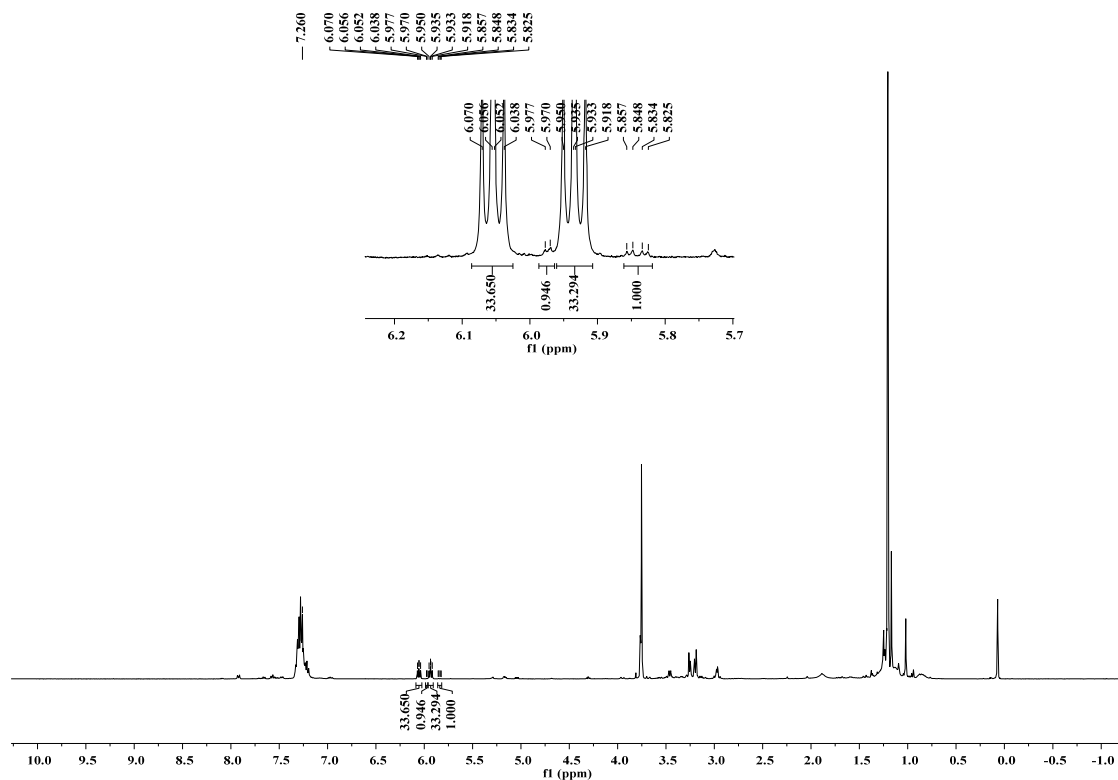
Crude ¹H NMR of **2a** prepared by using LiHMDS in CH₂Cl₂ (Table 1, entry 2, dr = 15:1)



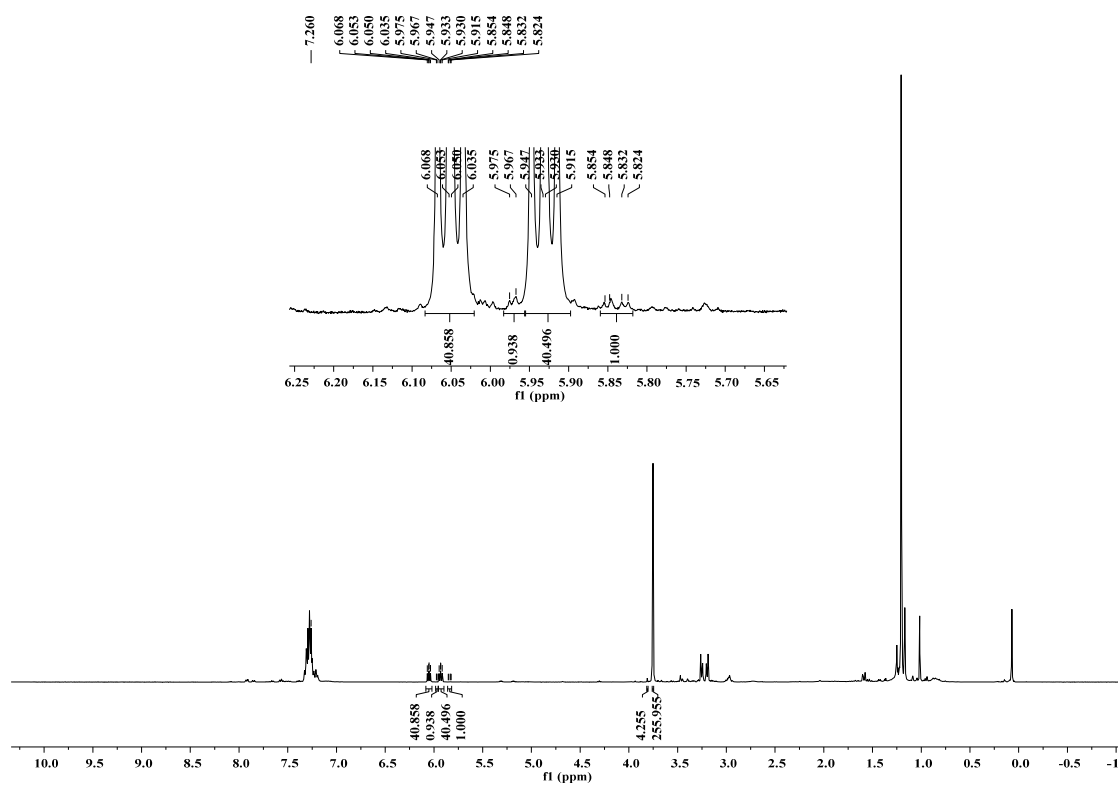
Crude ^1H NMR of **2a** prepared by using LiHMDS in Et_2O (Table 1, entry 3, dr = 15:1)



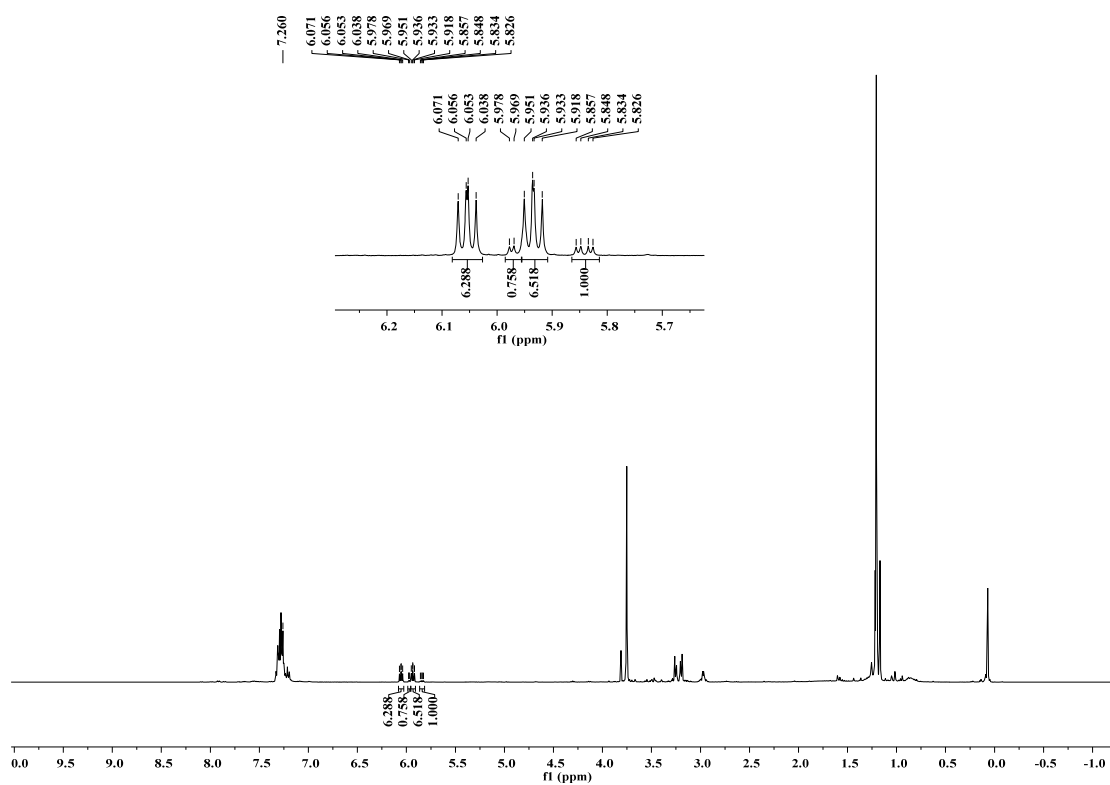
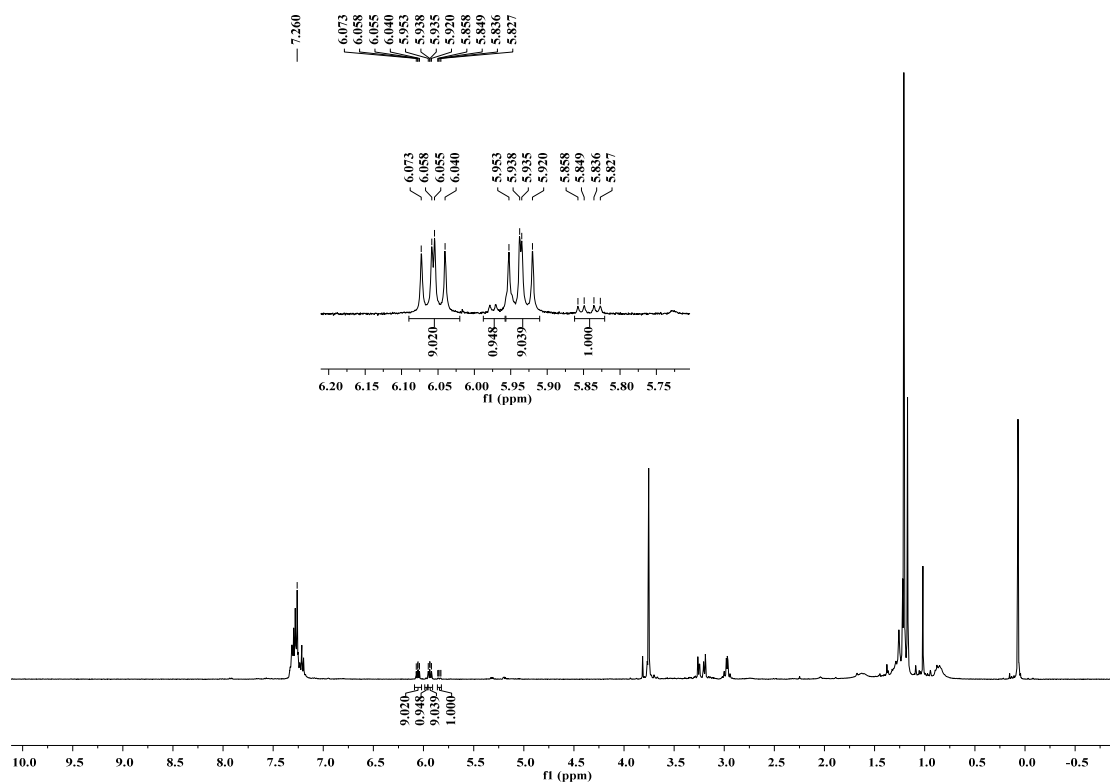
Crude ^1H NMR of **2a** prepared by using LiHMDS in toluene (Table 1, entry 4, dr > 50:1)

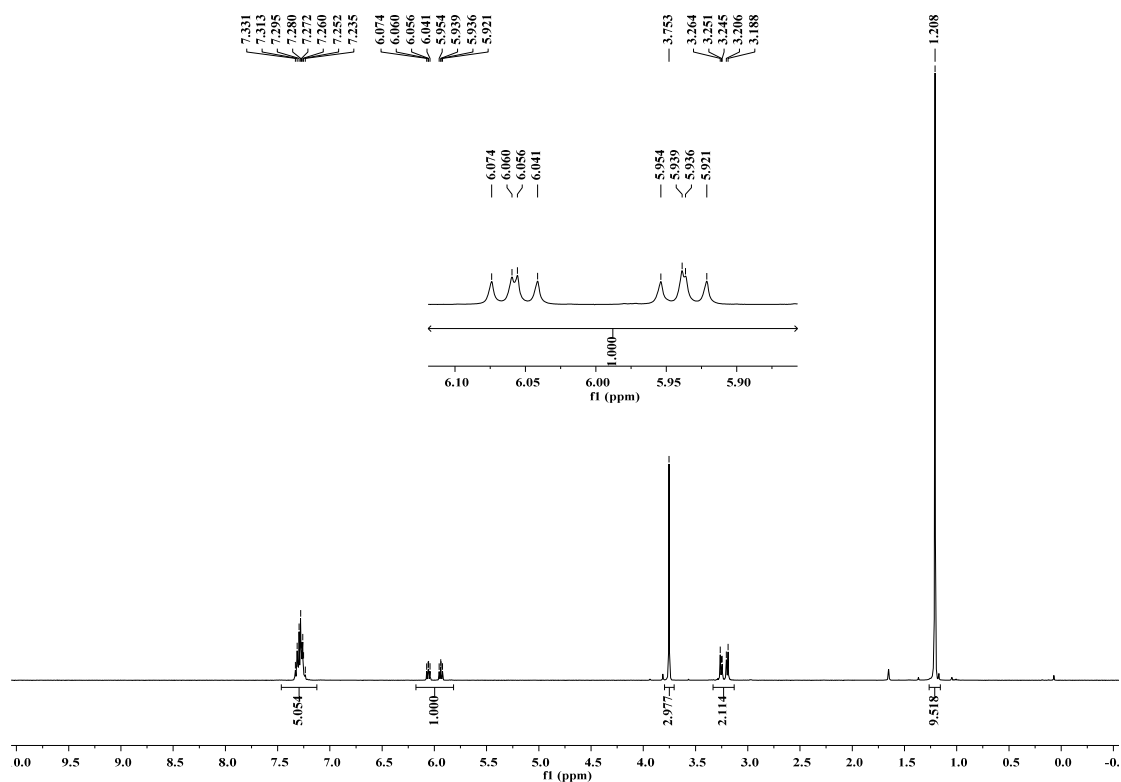


Crude ^1H NMR of **2a** prepared by using NaHMDS in THF (Table 1, entry 5, dr = 33:1)

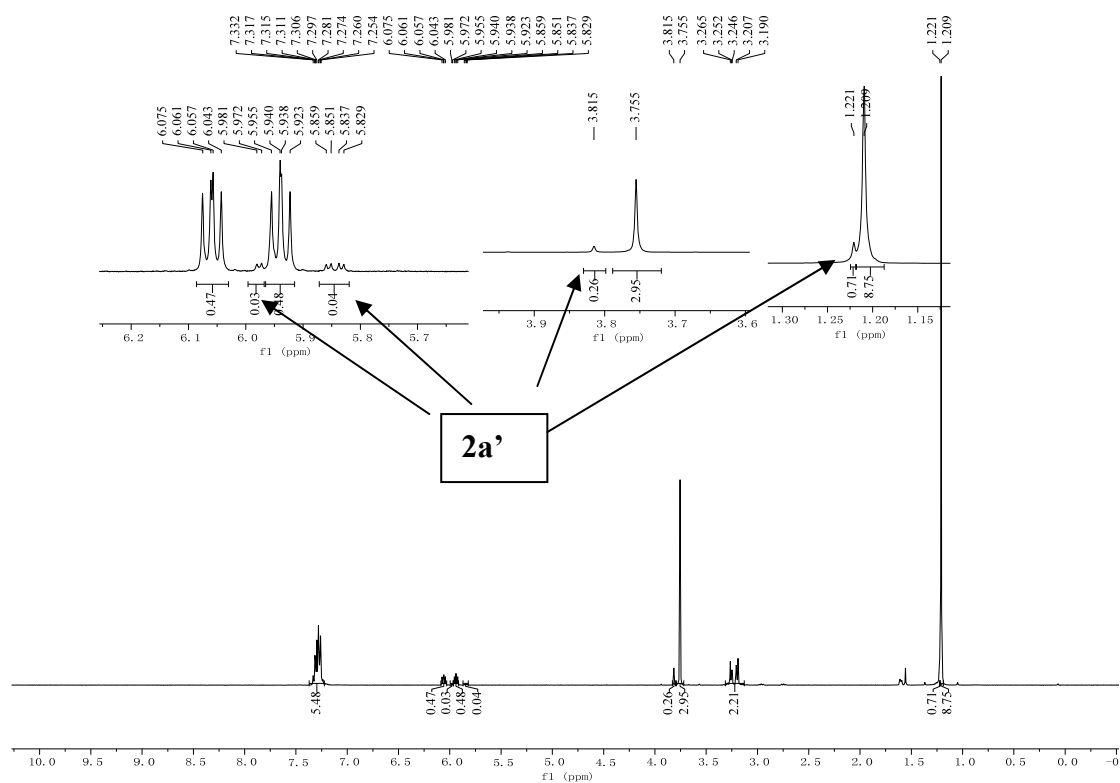


Crude ^1H NMR of **2a** prepared by using KHMDS in THF (Table 1, entry 6, dr = 40:1)



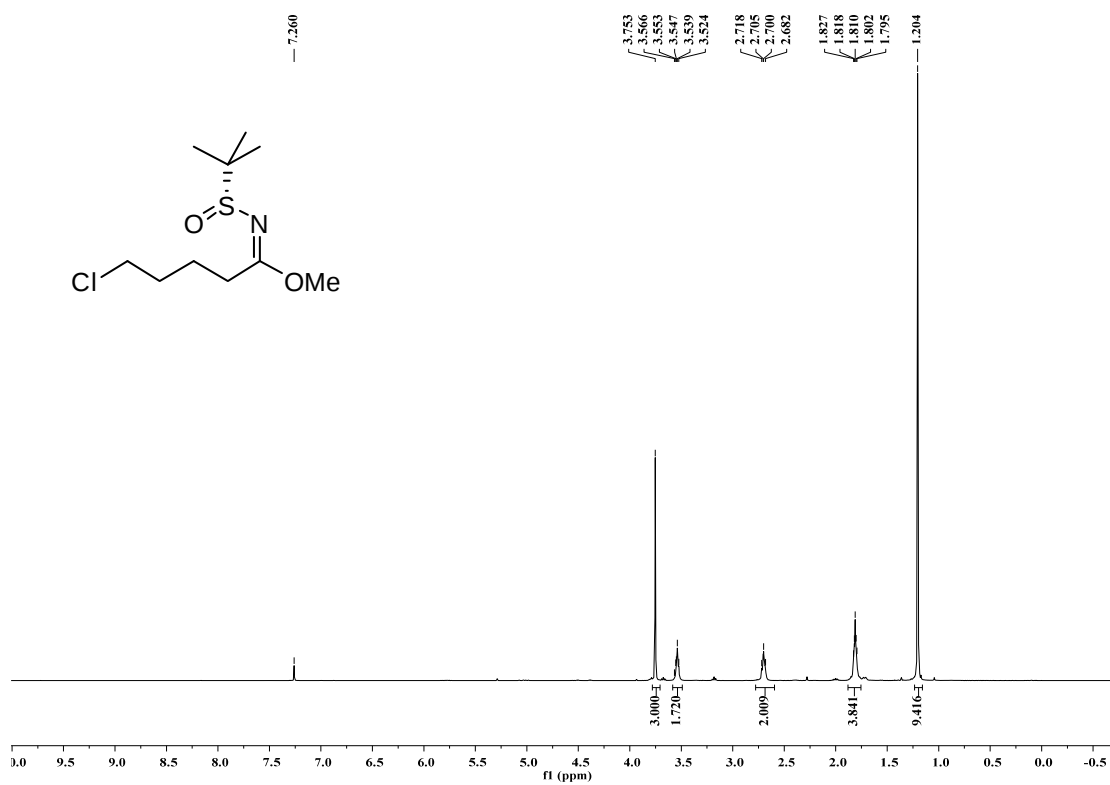


¹H NMR spectrum (CDCl₃, 400 MHz) of **2a**

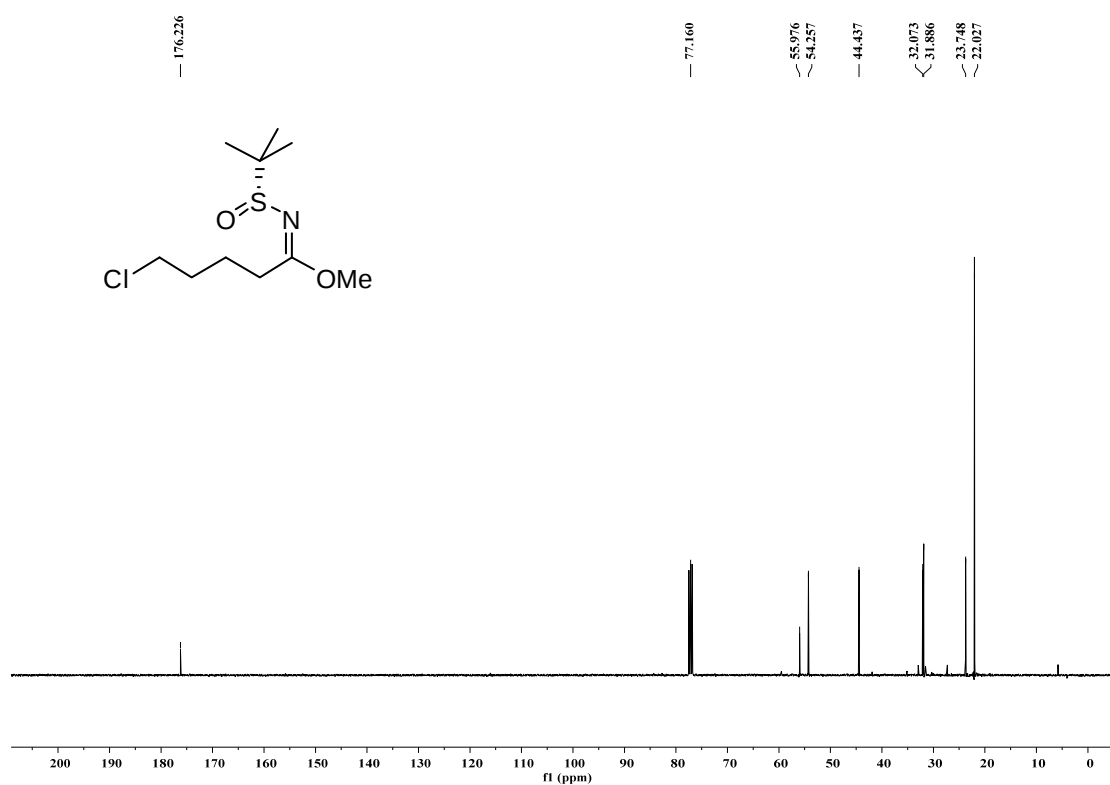


¹H NMR spectrum (CDCl₃, 400 MHz) of mixture of diastereomers **2a/2a'**

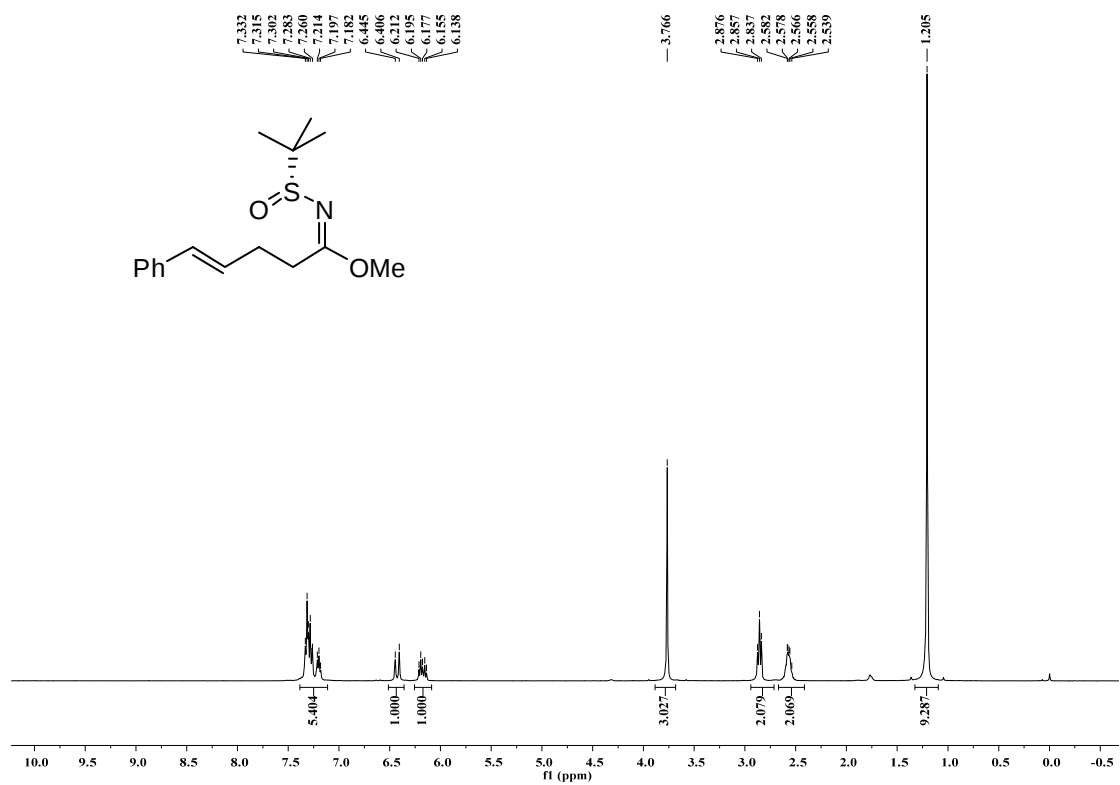
^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for all new compounds



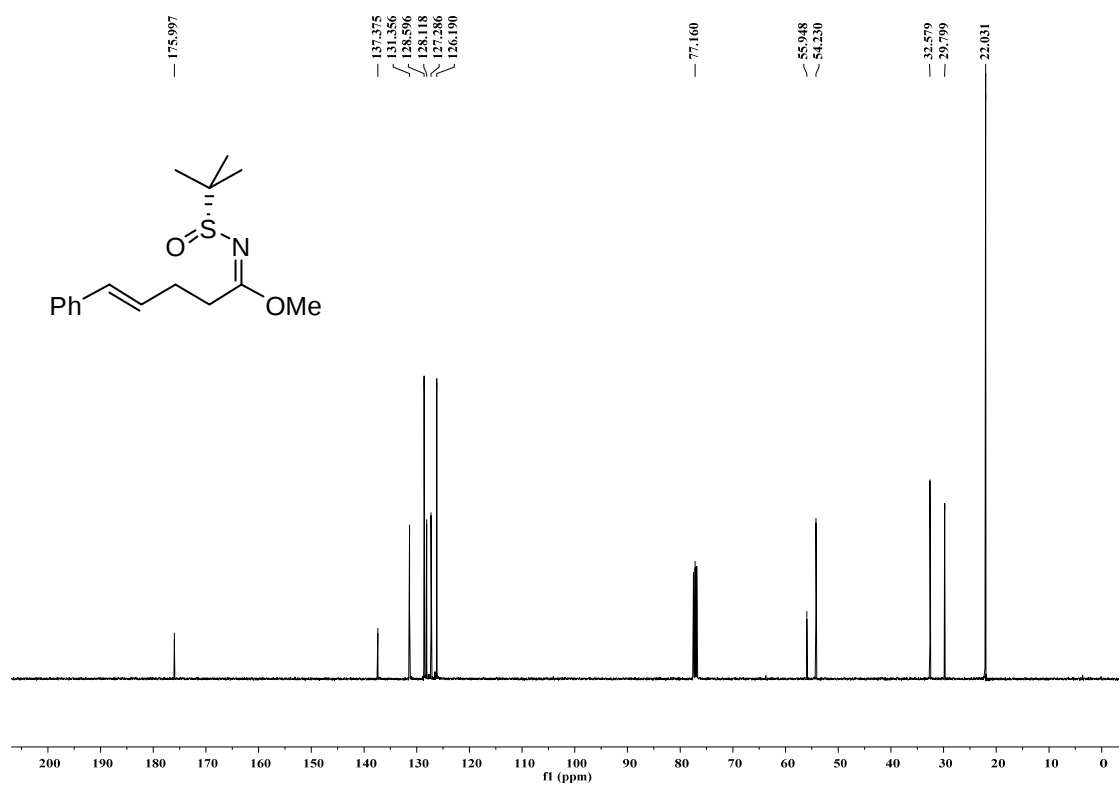
^1H NMR spectrum (CDCl_3 , 400 MHz) of **1e**



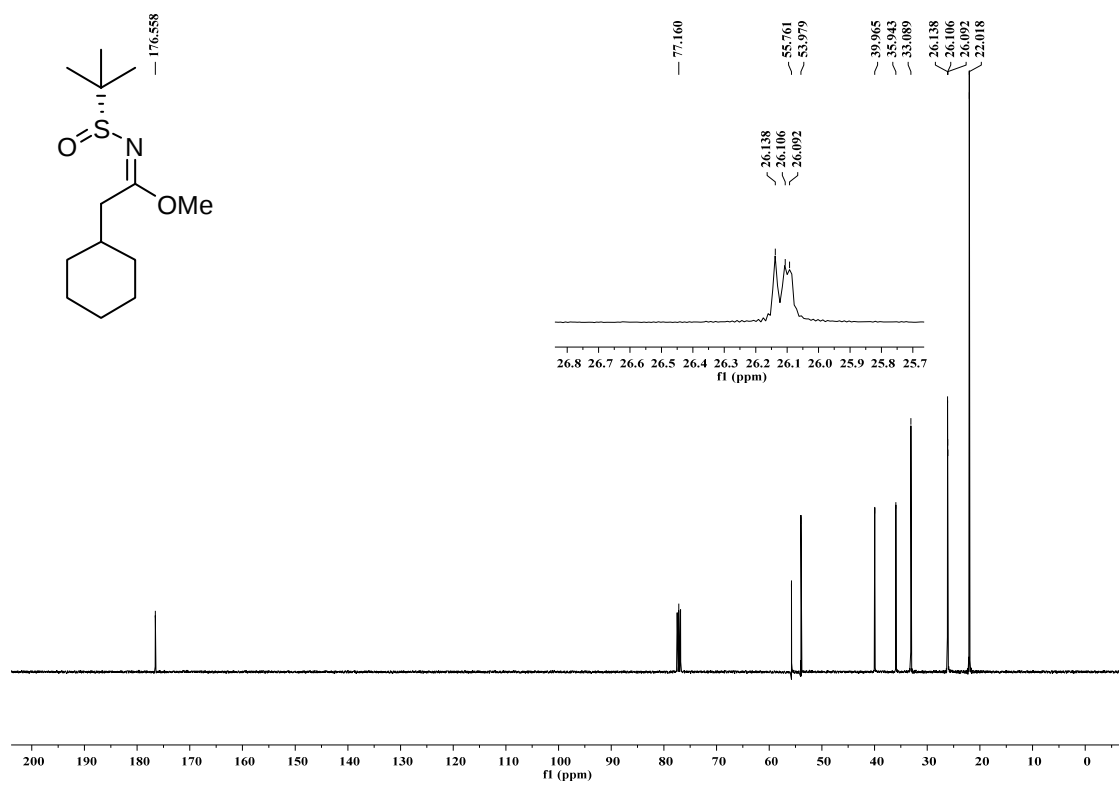
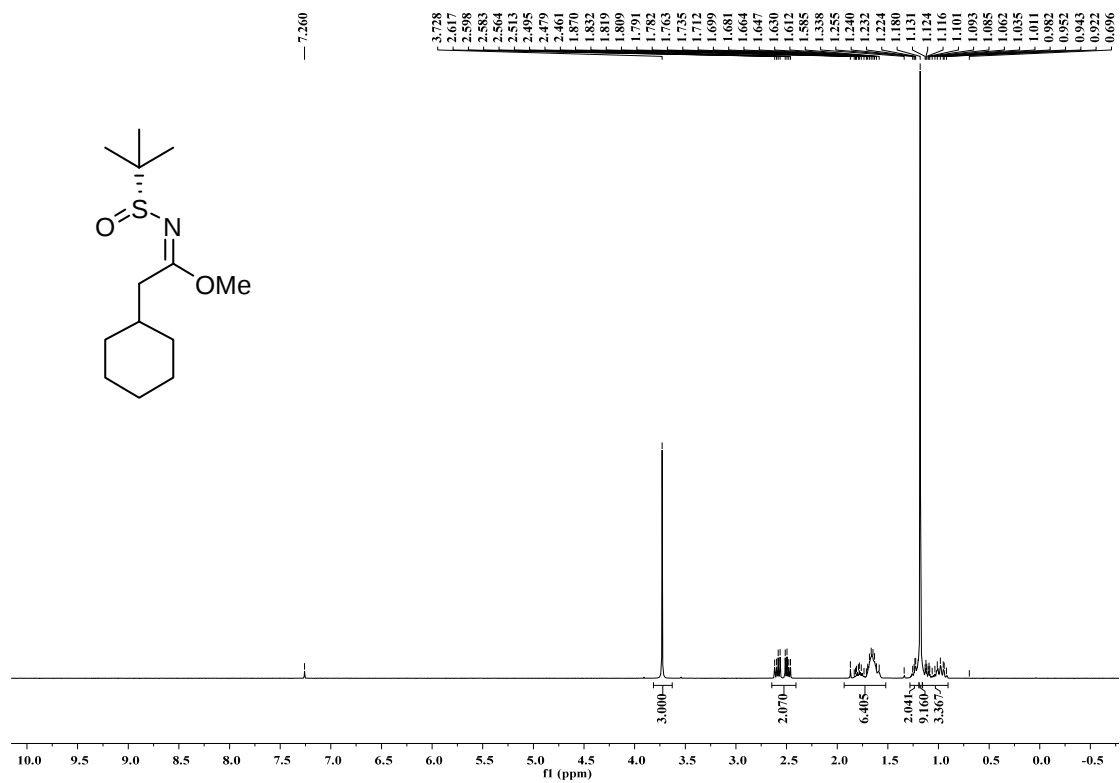
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **1e**

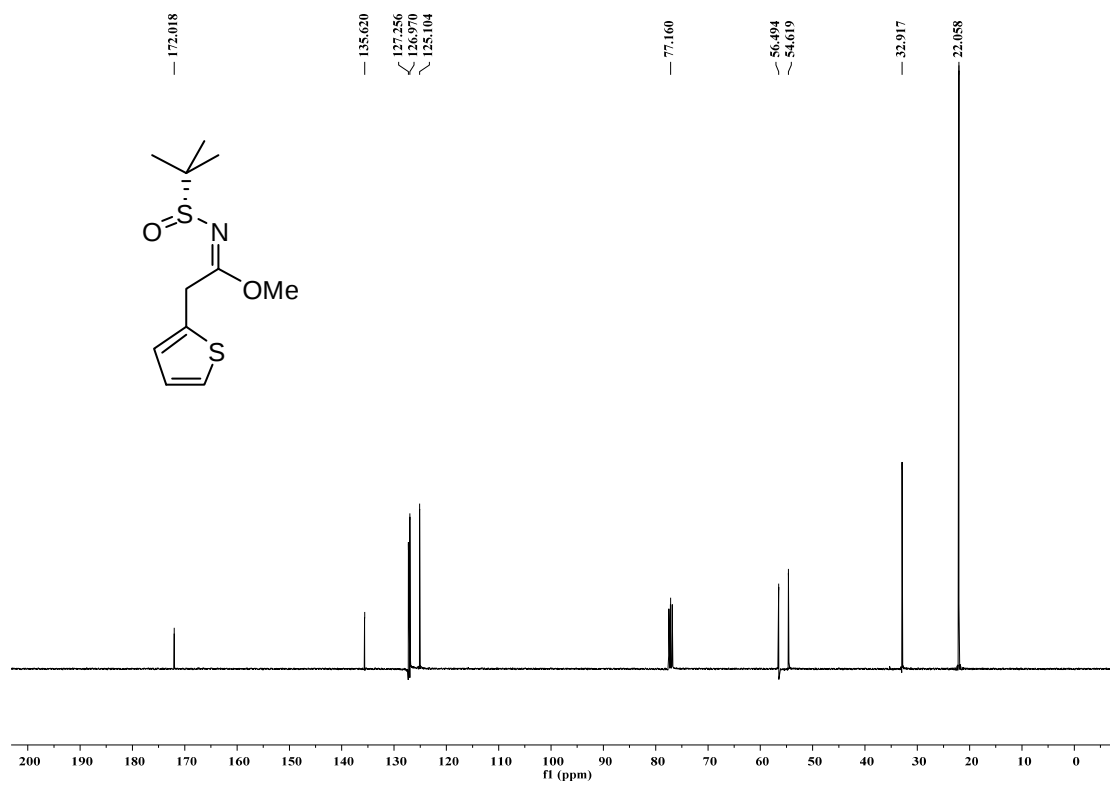
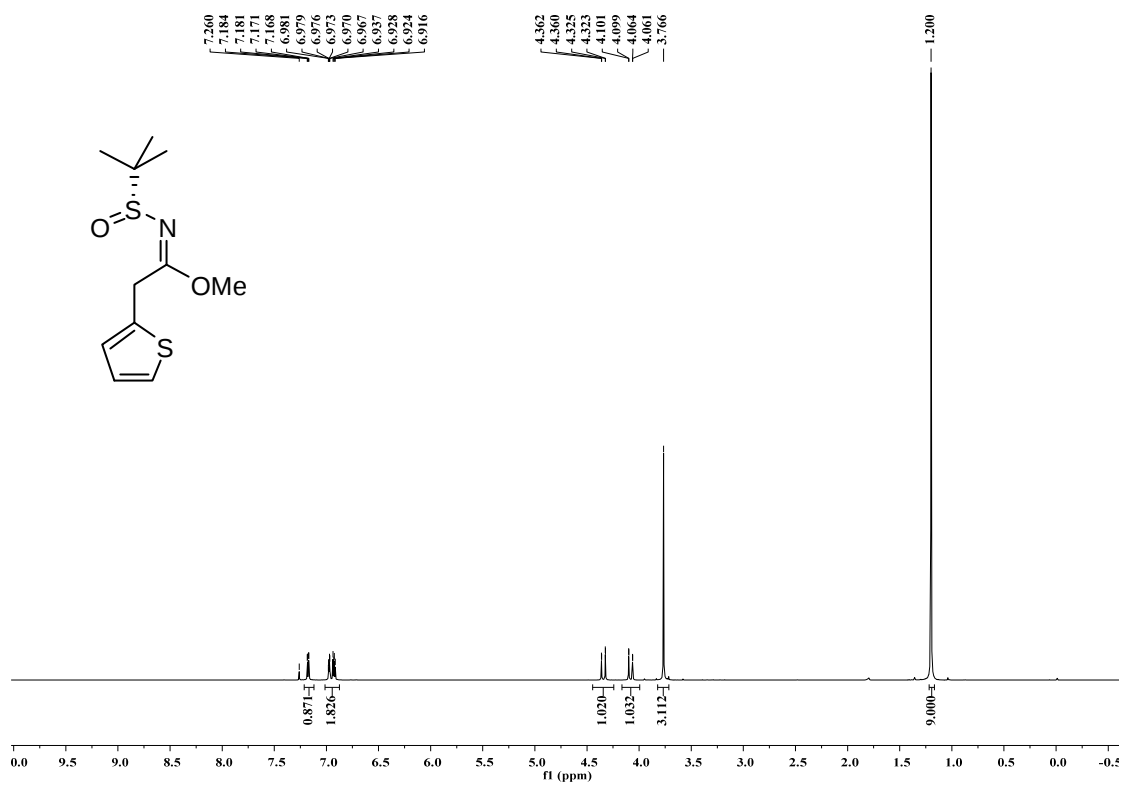


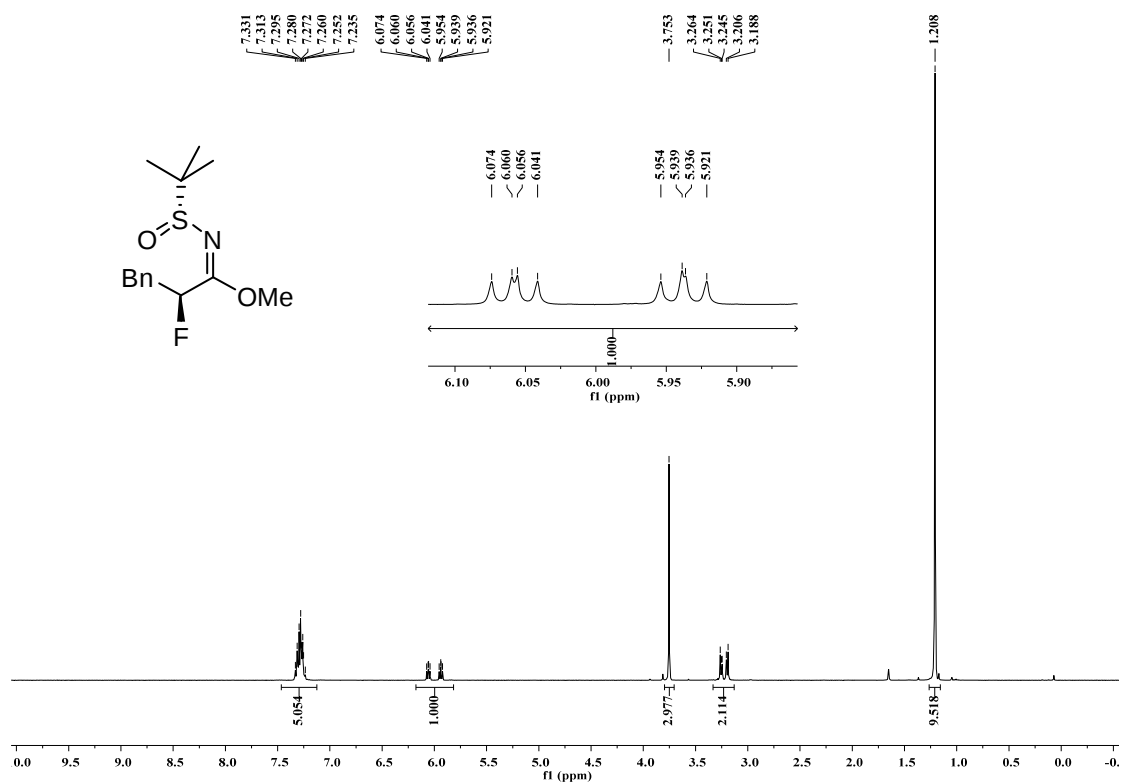
¹H NMR spectrum (CDCl₃, 400 MHz) of **1h**



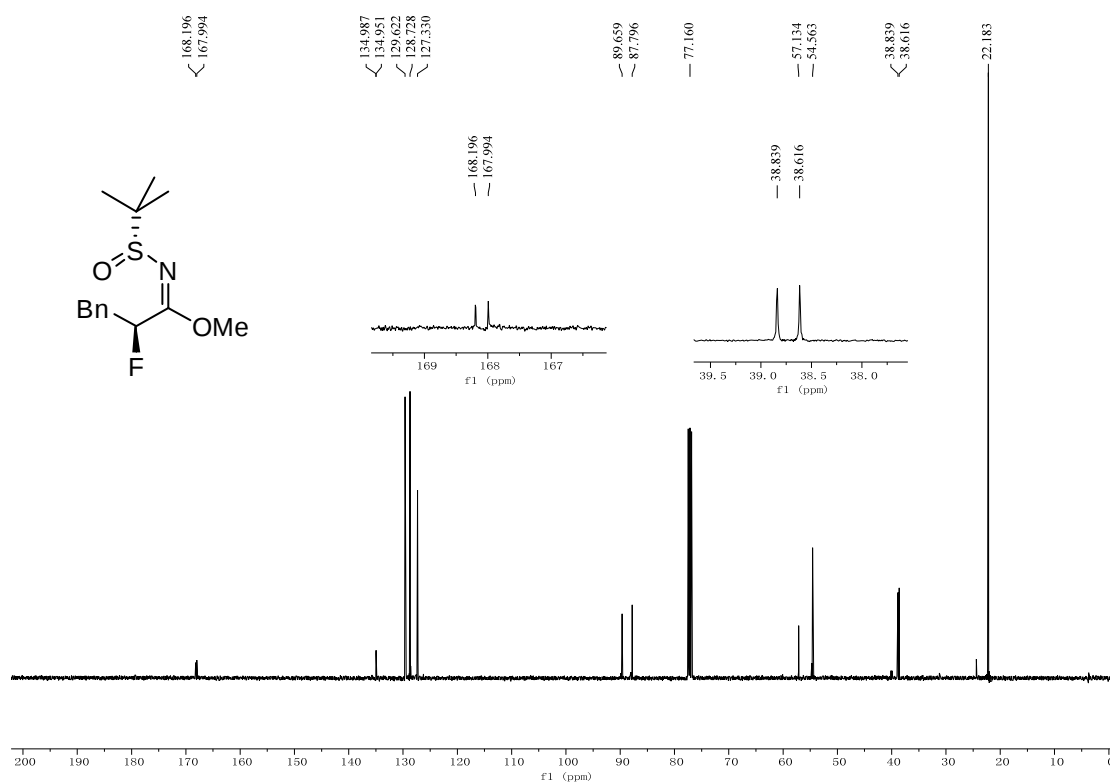
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **1h**



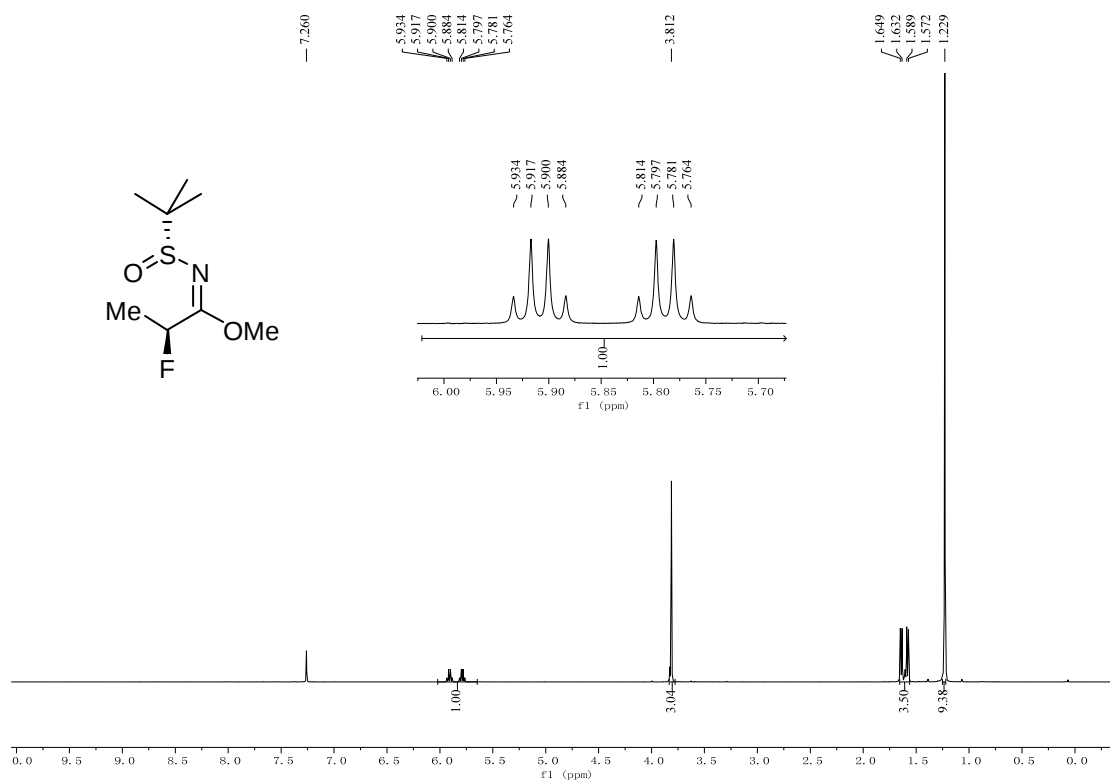




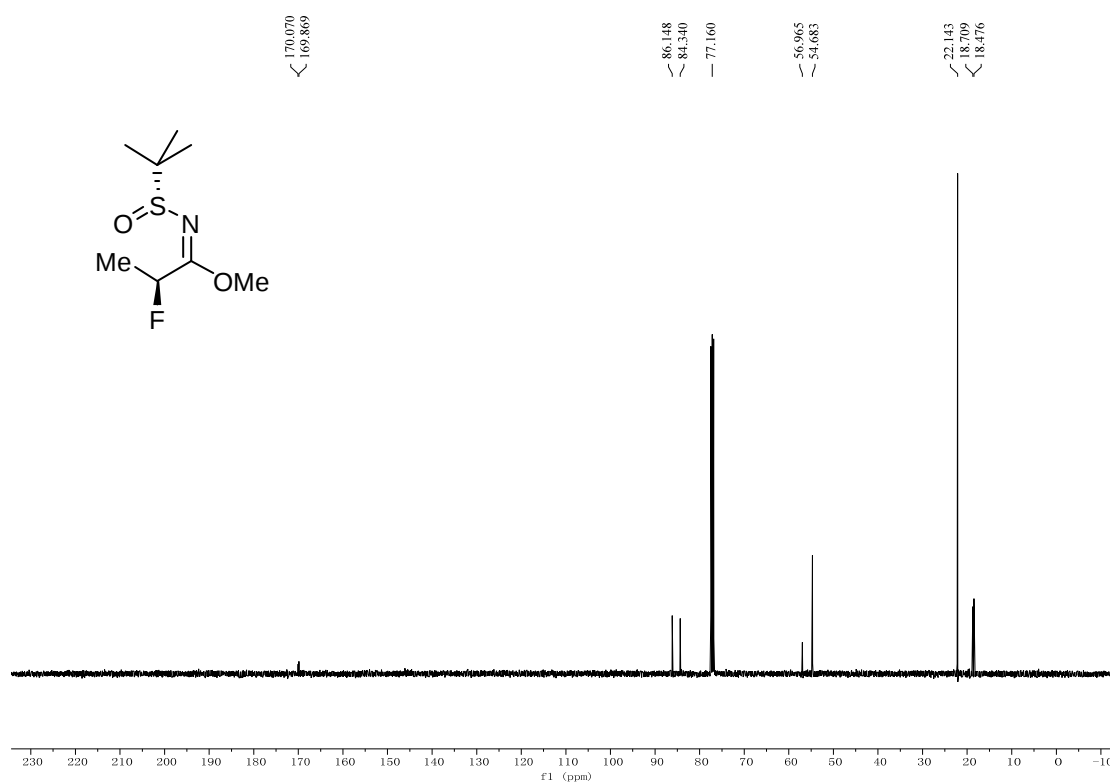
¹H NMR spectrum (CDCl₃, 400 MHz) of **2a**



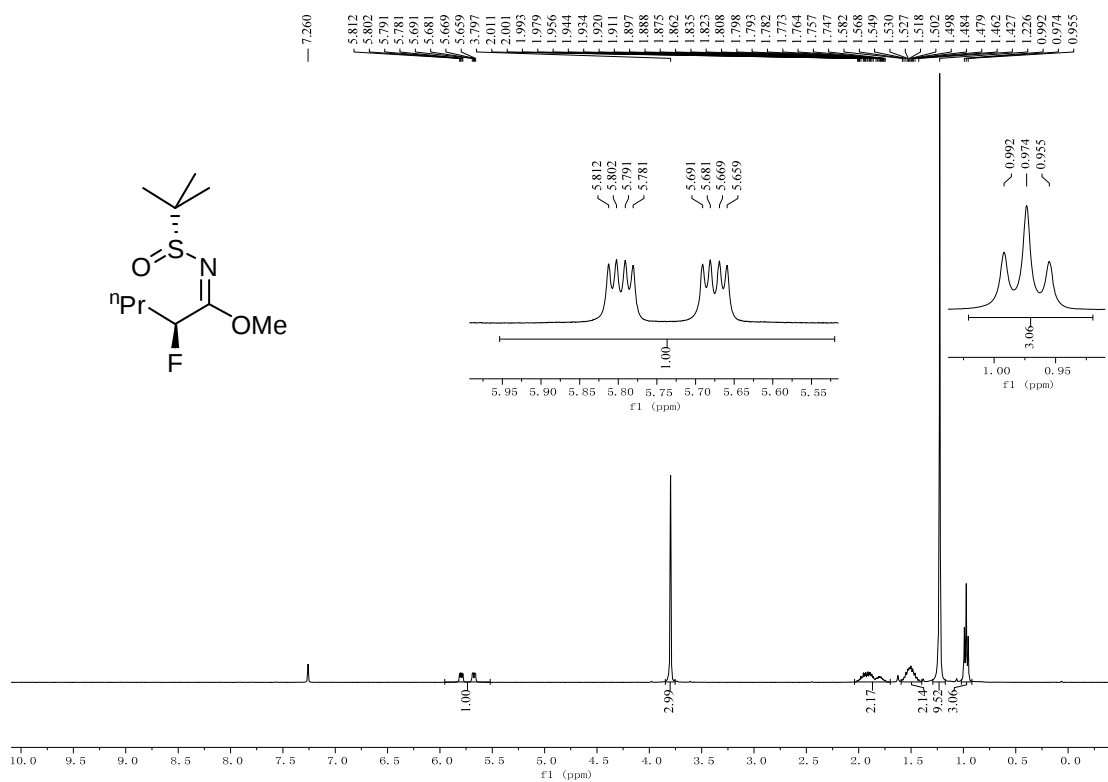
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2a**



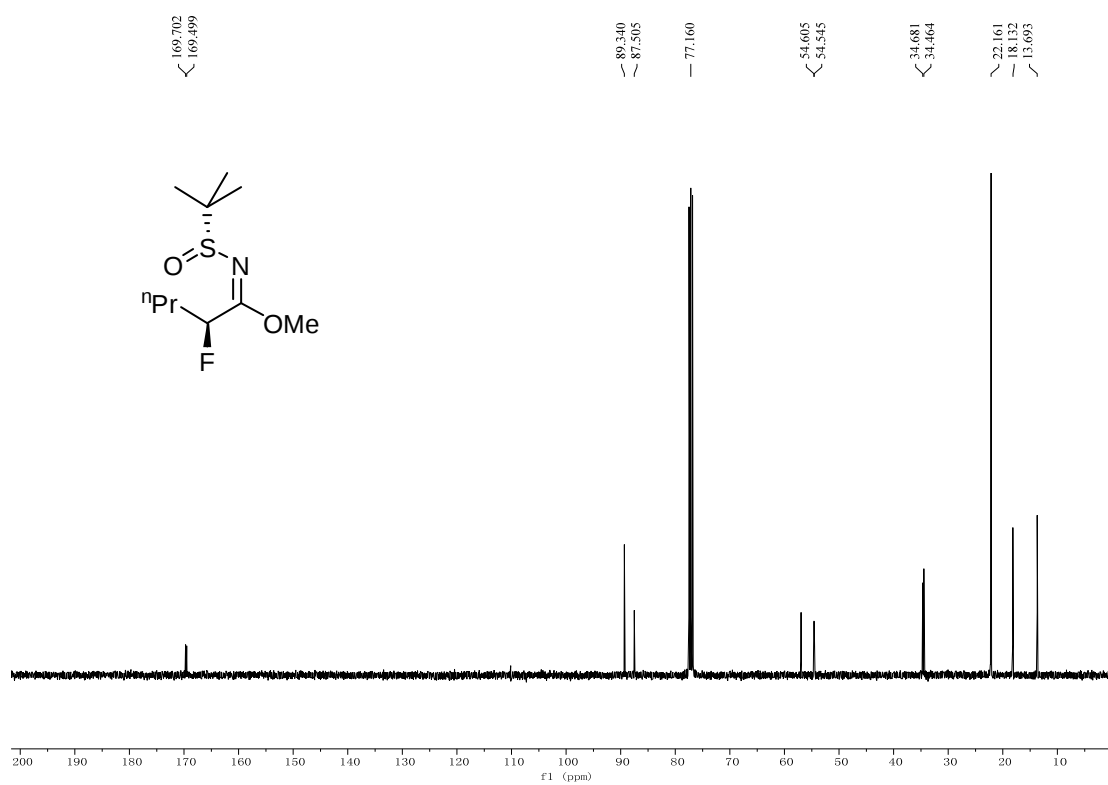
¹H NMR spectrum (CDCl₃, 400 MHz) of **2b**



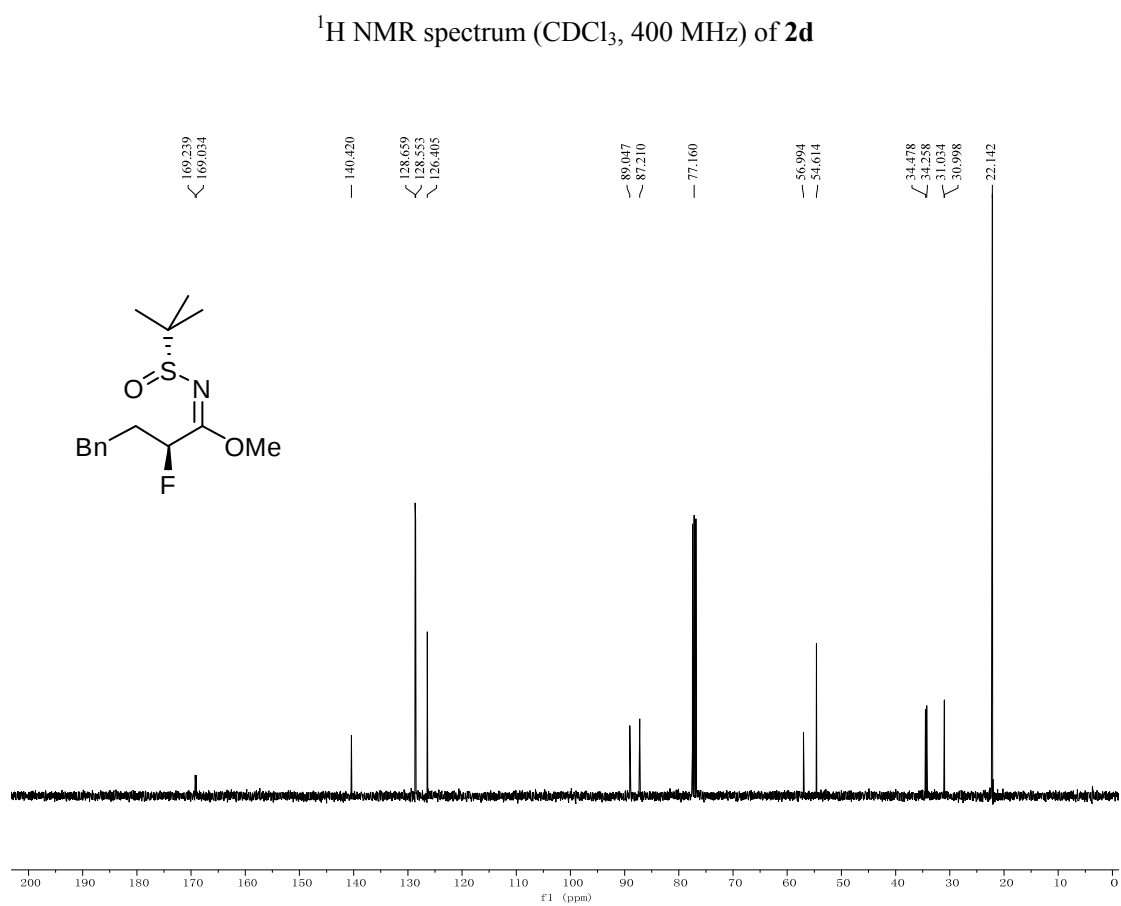
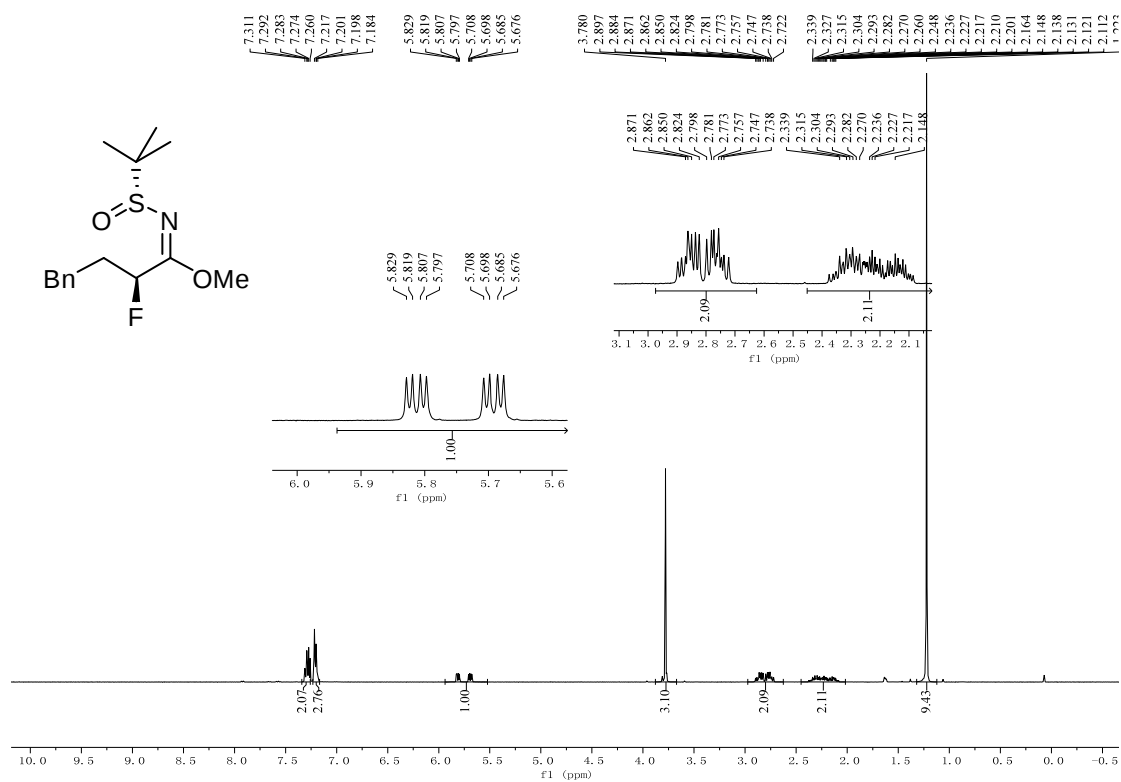
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2b**

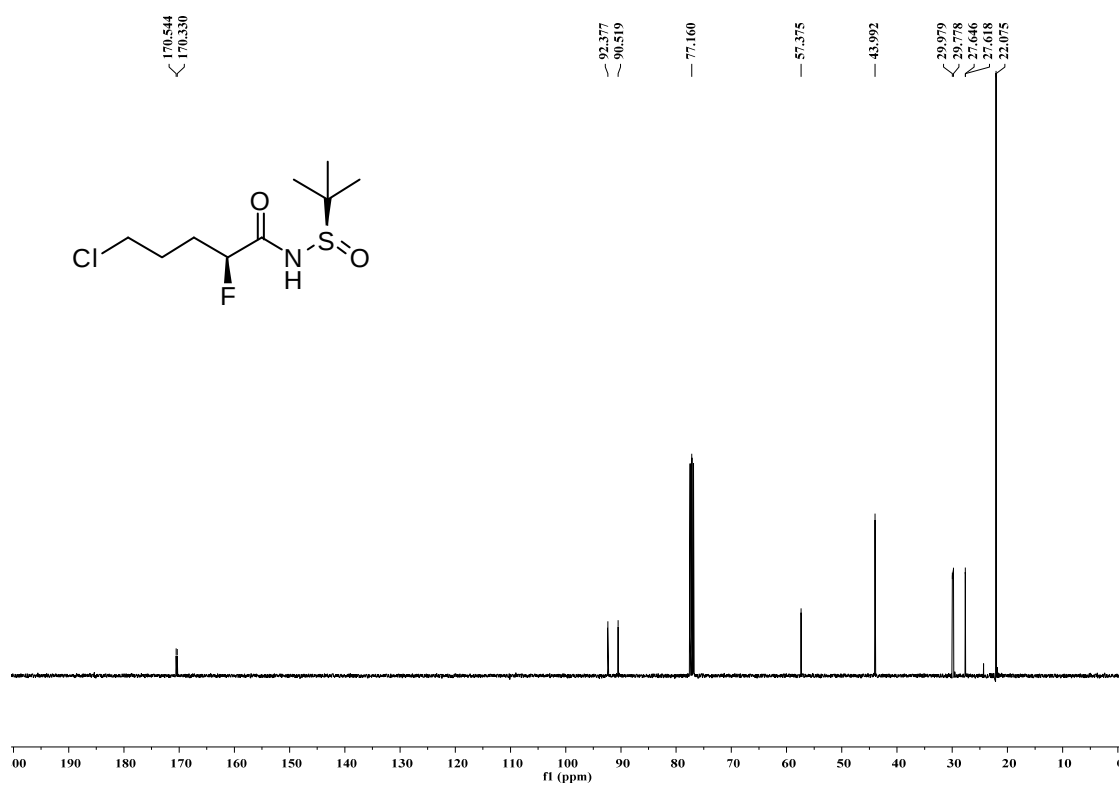
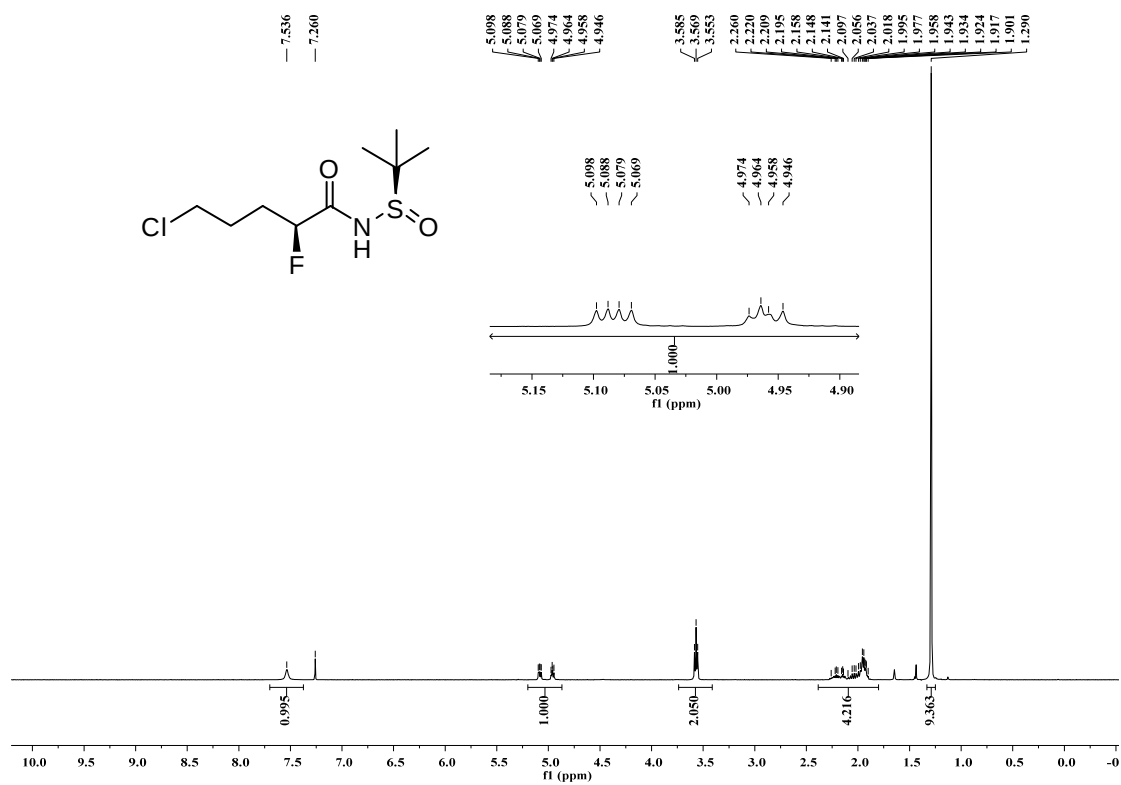


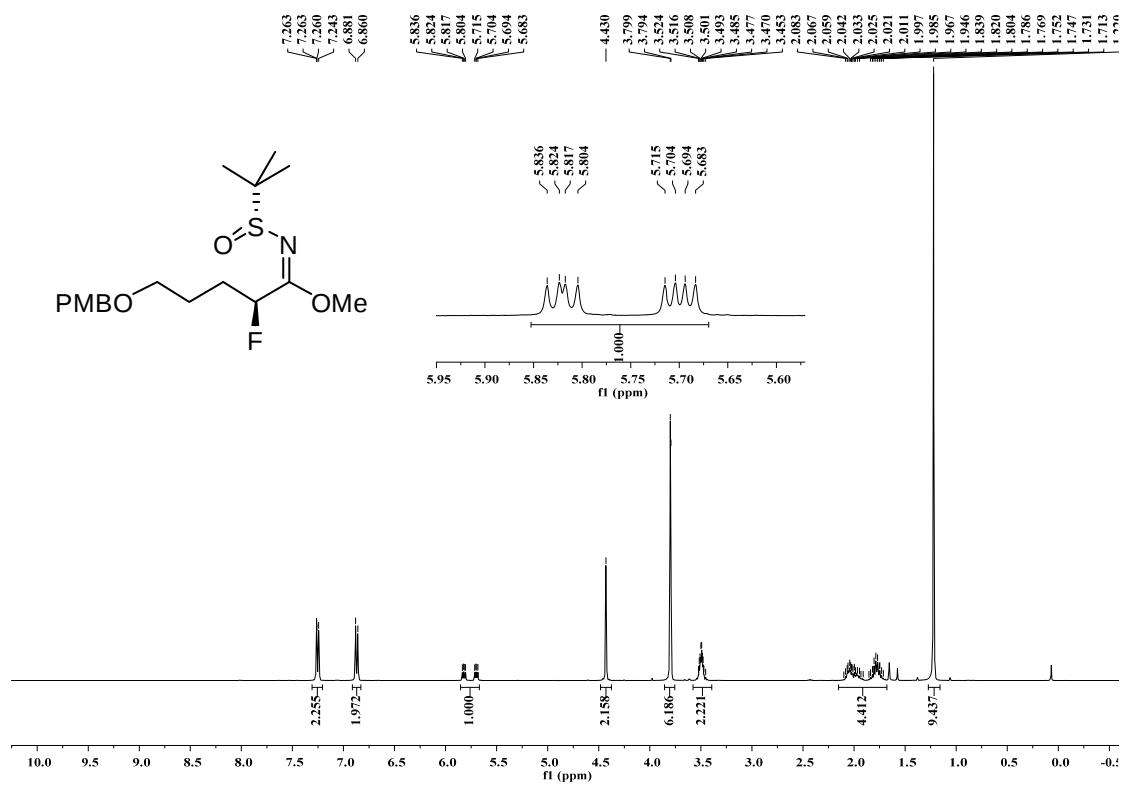
¹H NMR spectrum (CDCl₃, 400 MHz) of **2c**



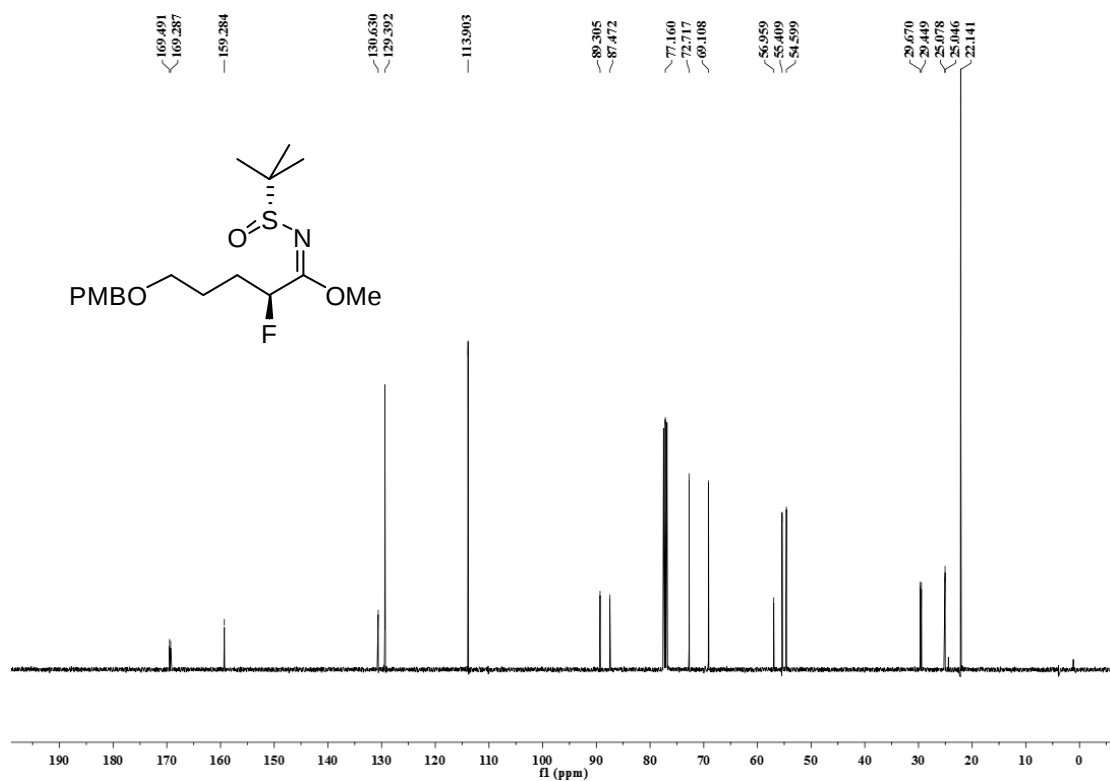
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2c**



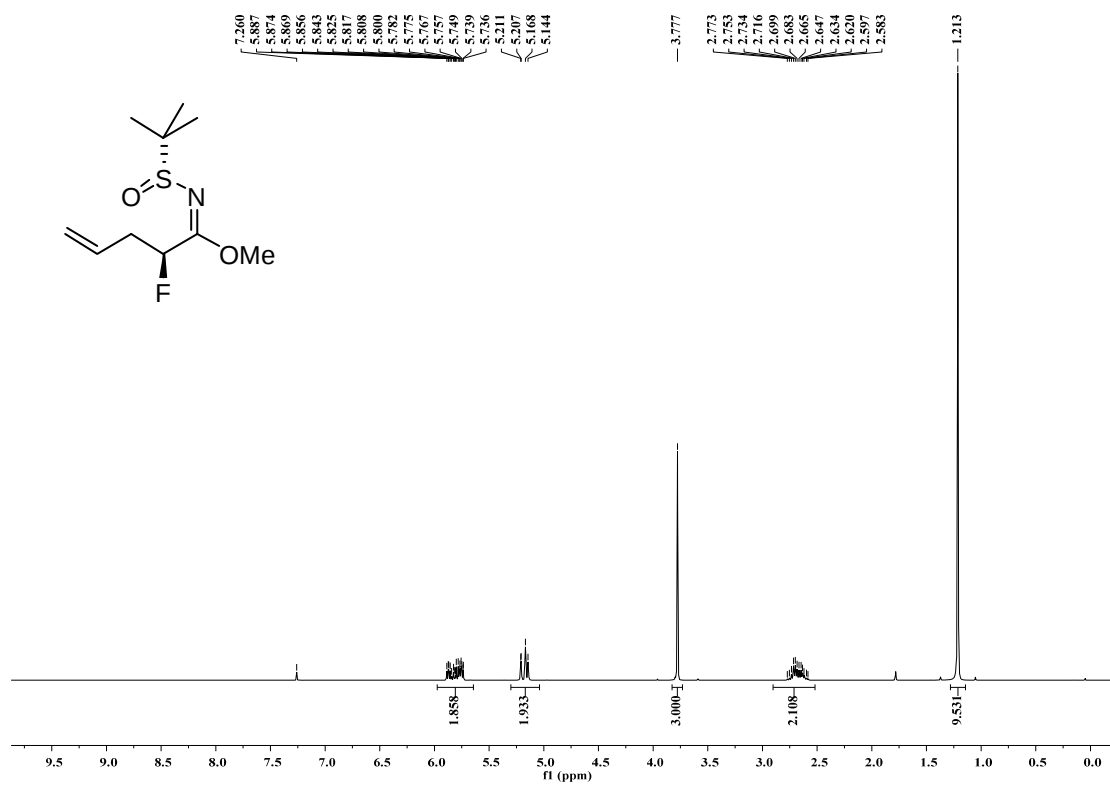




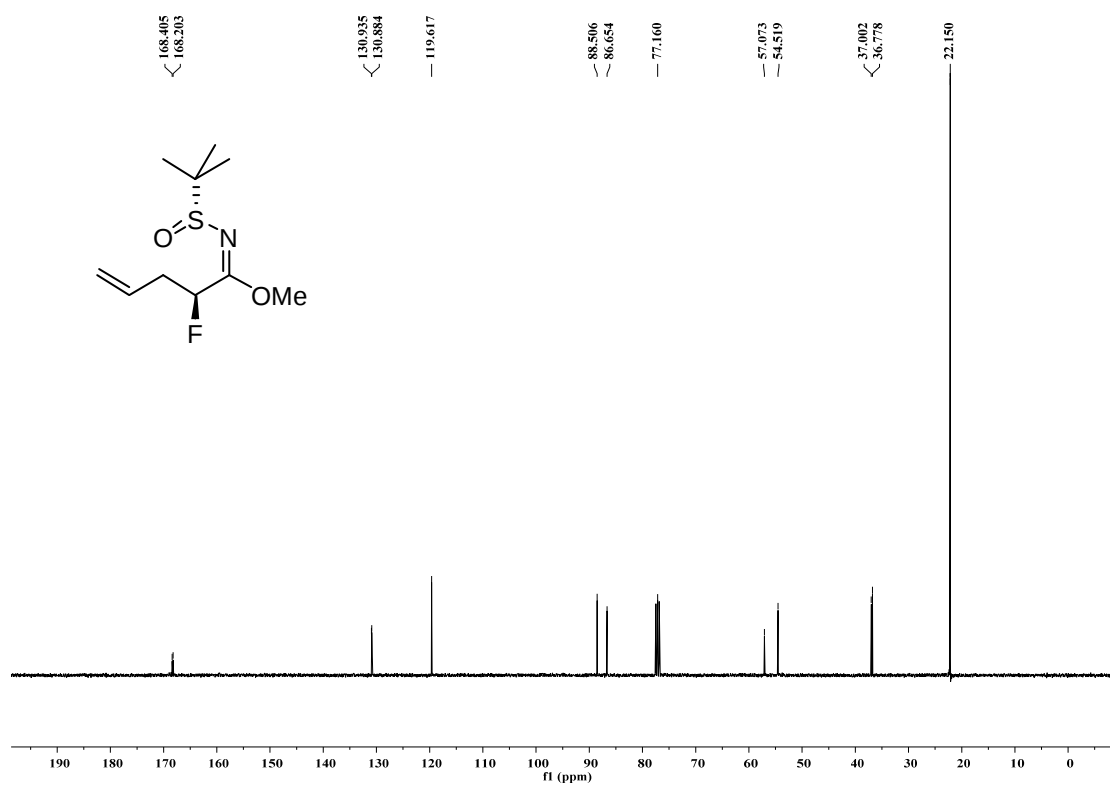
¹H NMR spectrum (CDCl₃, 400 MHz) of **2f**



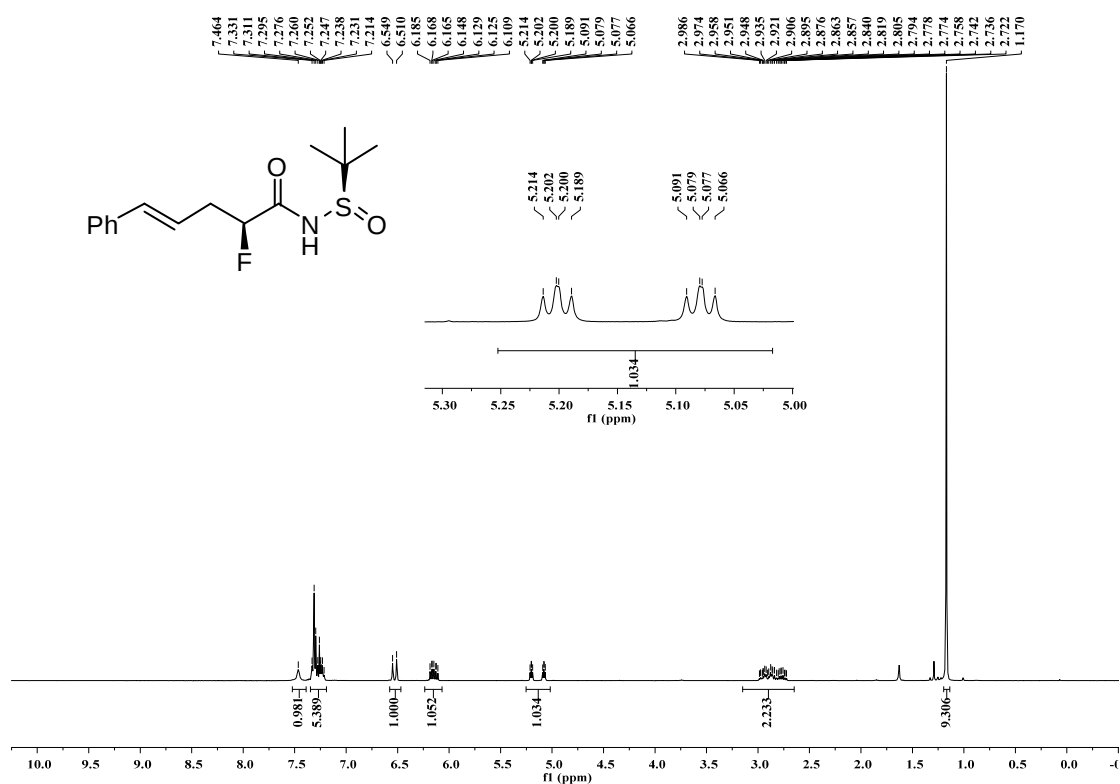
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2f**



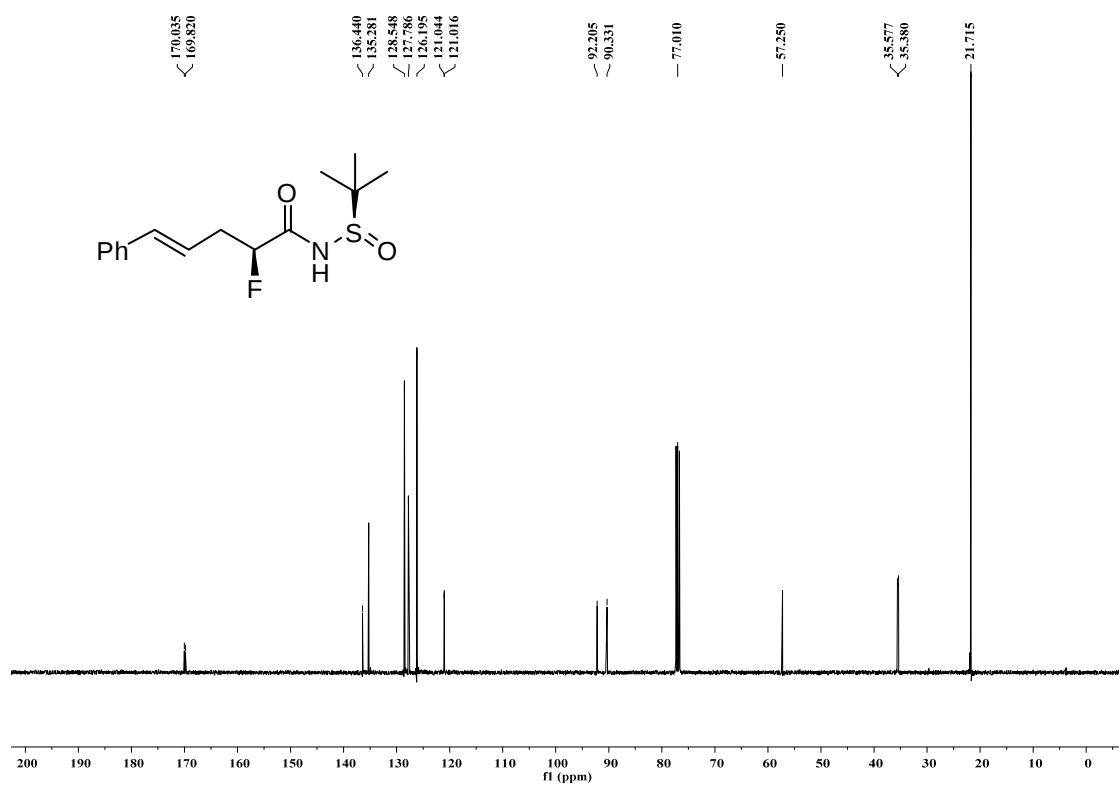
¹H NMR spectrum (CDCl₃, 400 MHz) of **2g**



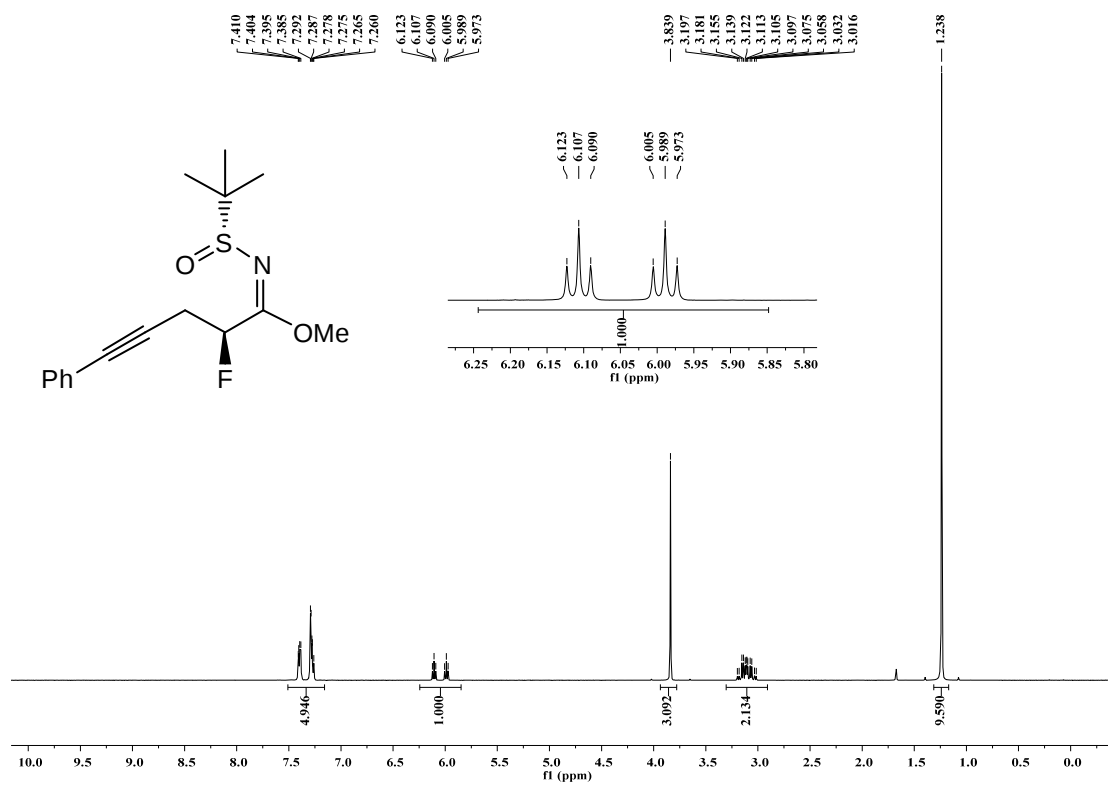
¹³C {¹H} NMR spectrum (CDCl₃, 100 MHz) of **2g**



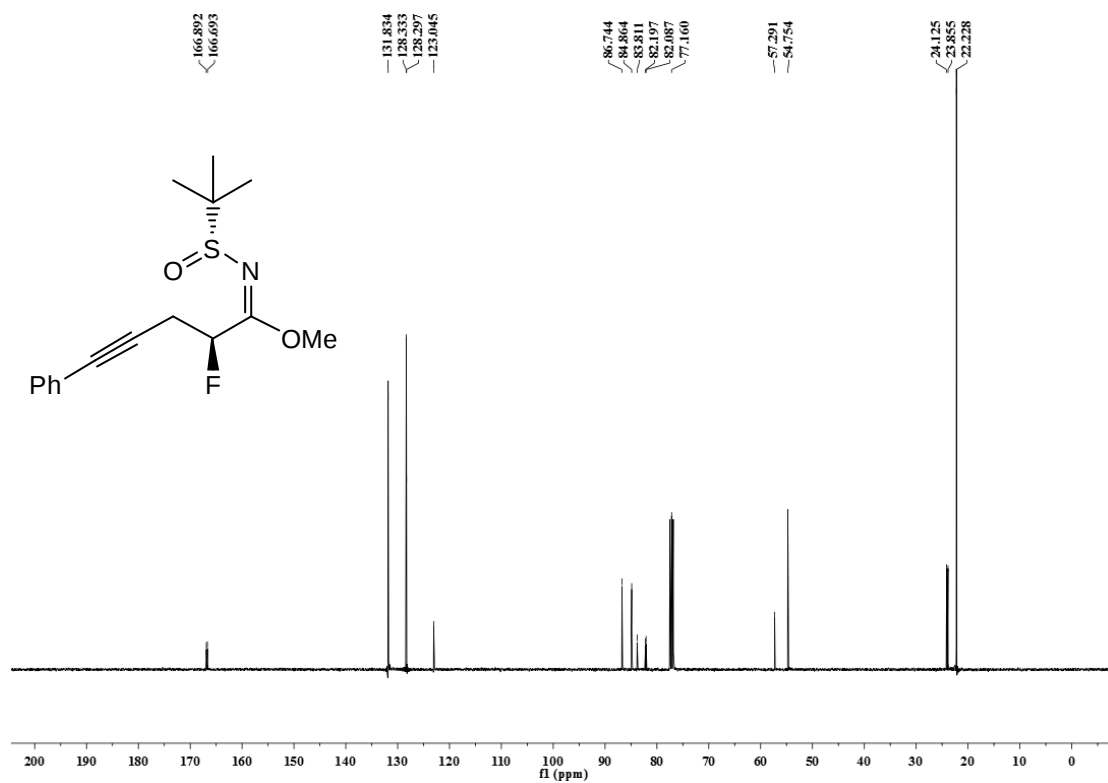
¹H NMR spectrum (CDCl₃, 400 MHz) of **2h**



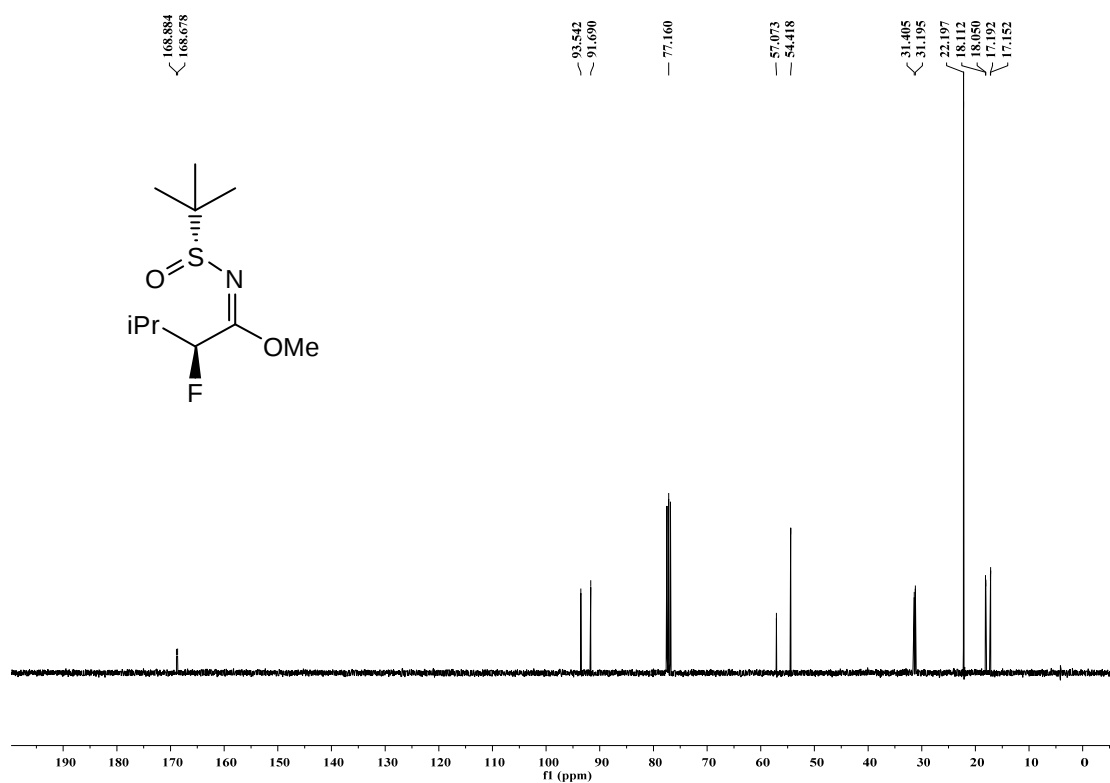
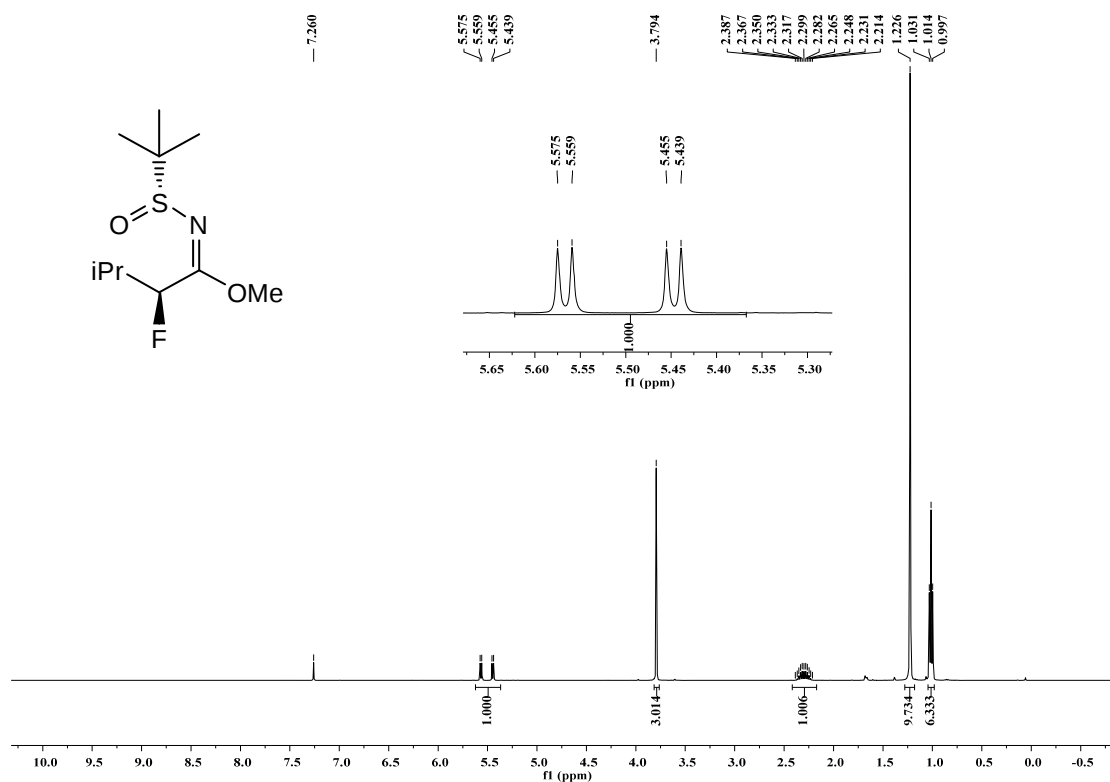
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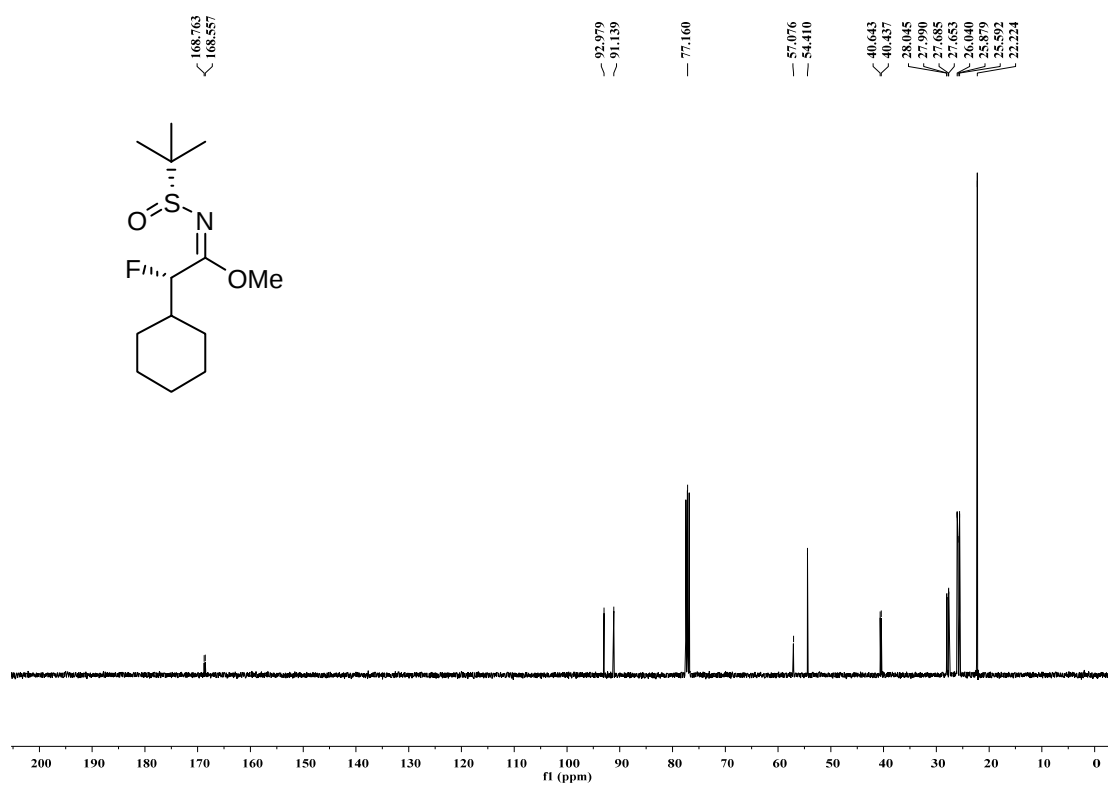
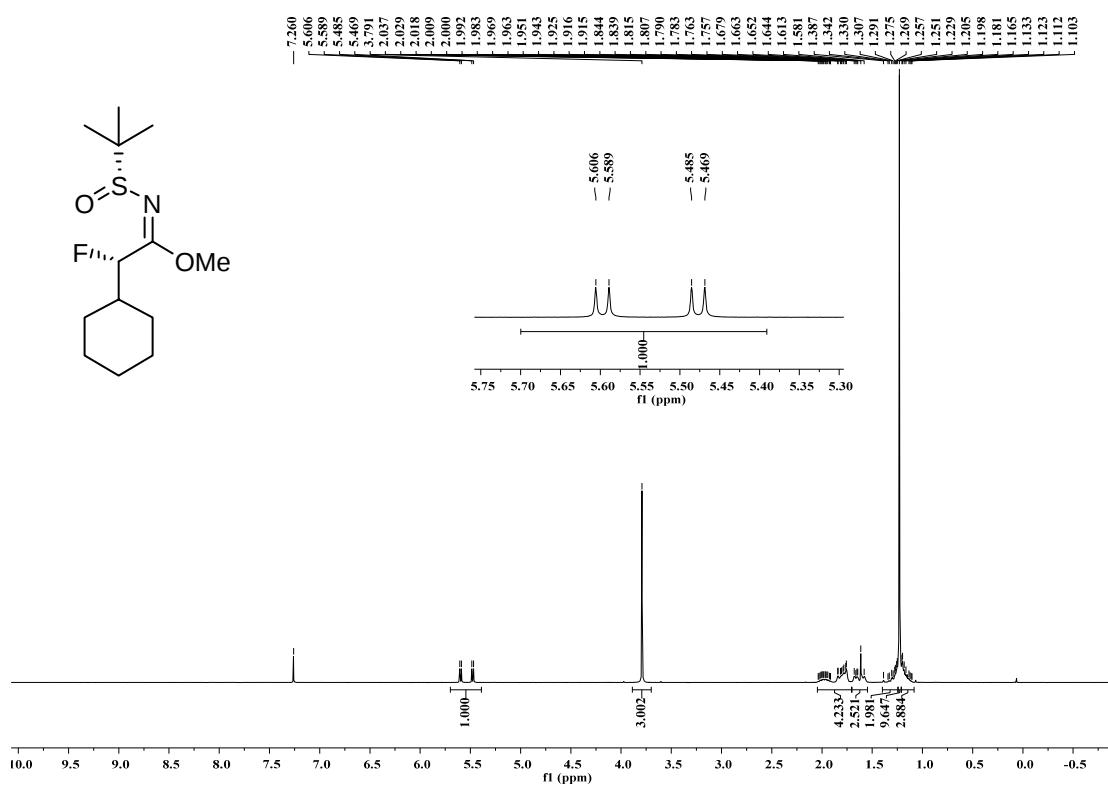


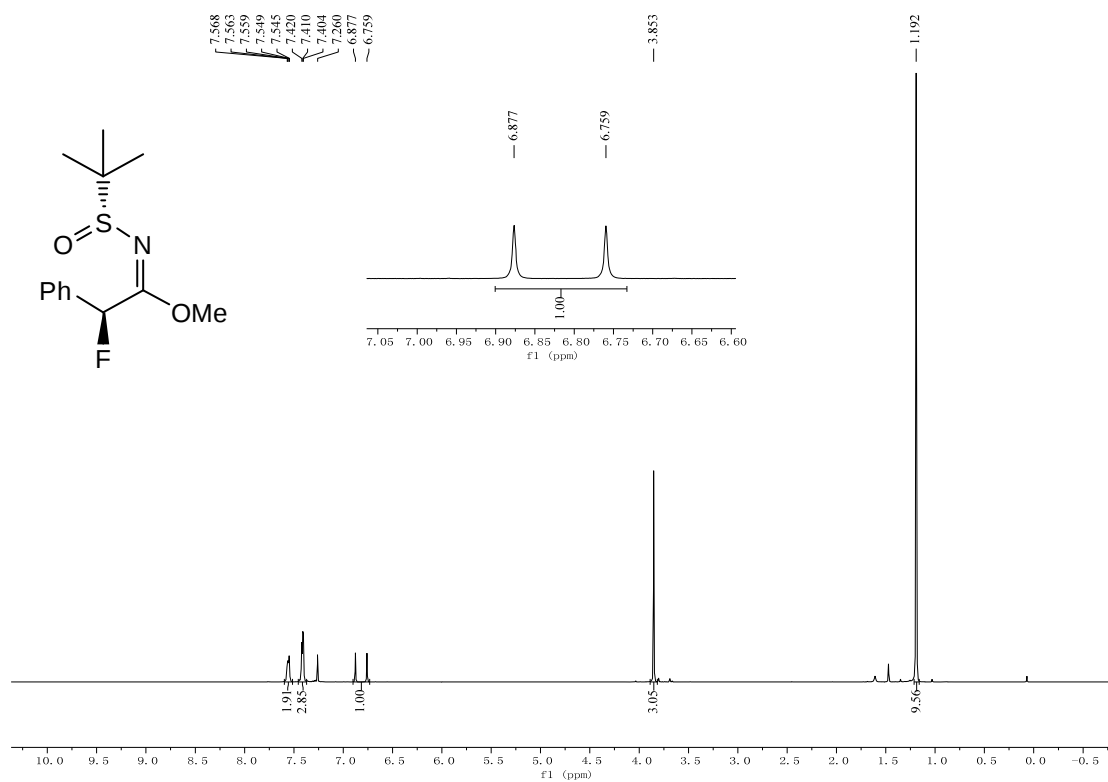
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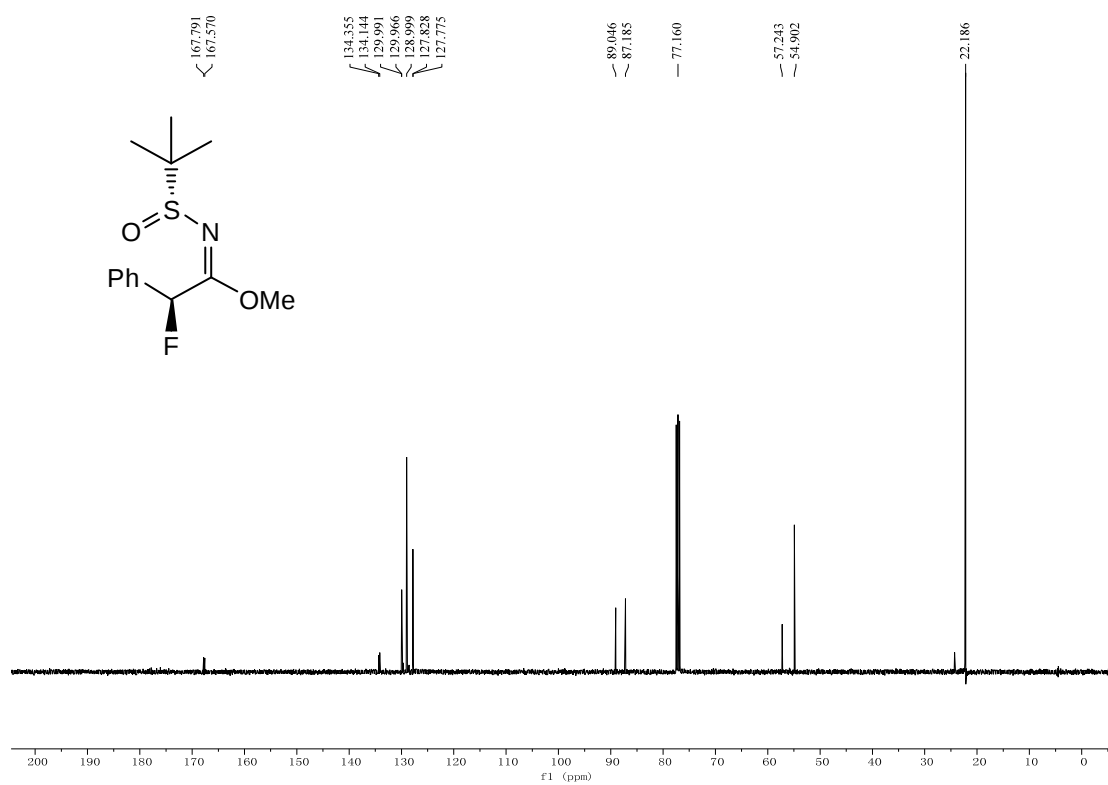
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2i**



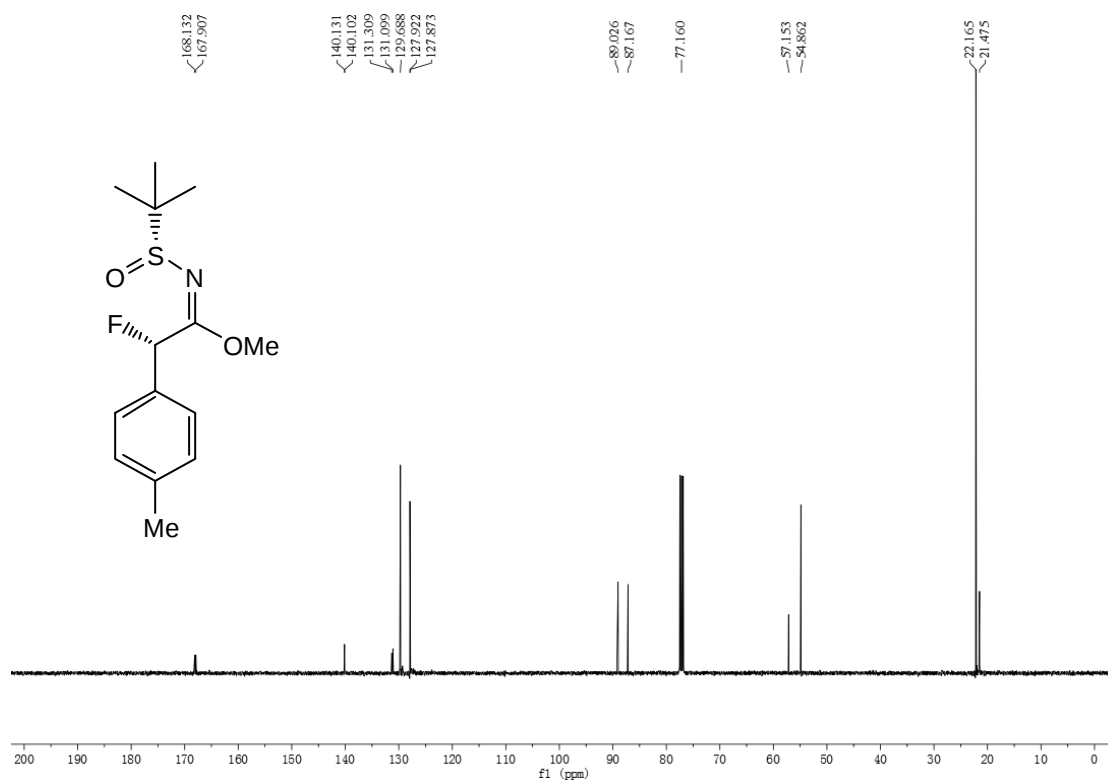
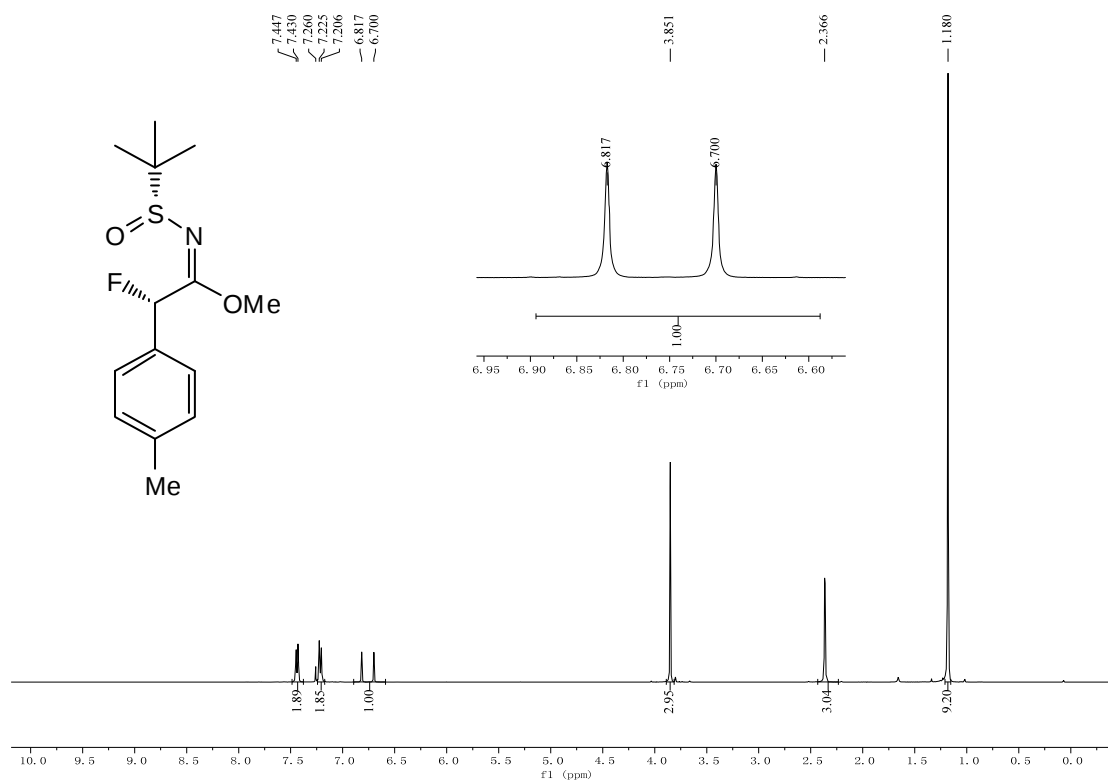


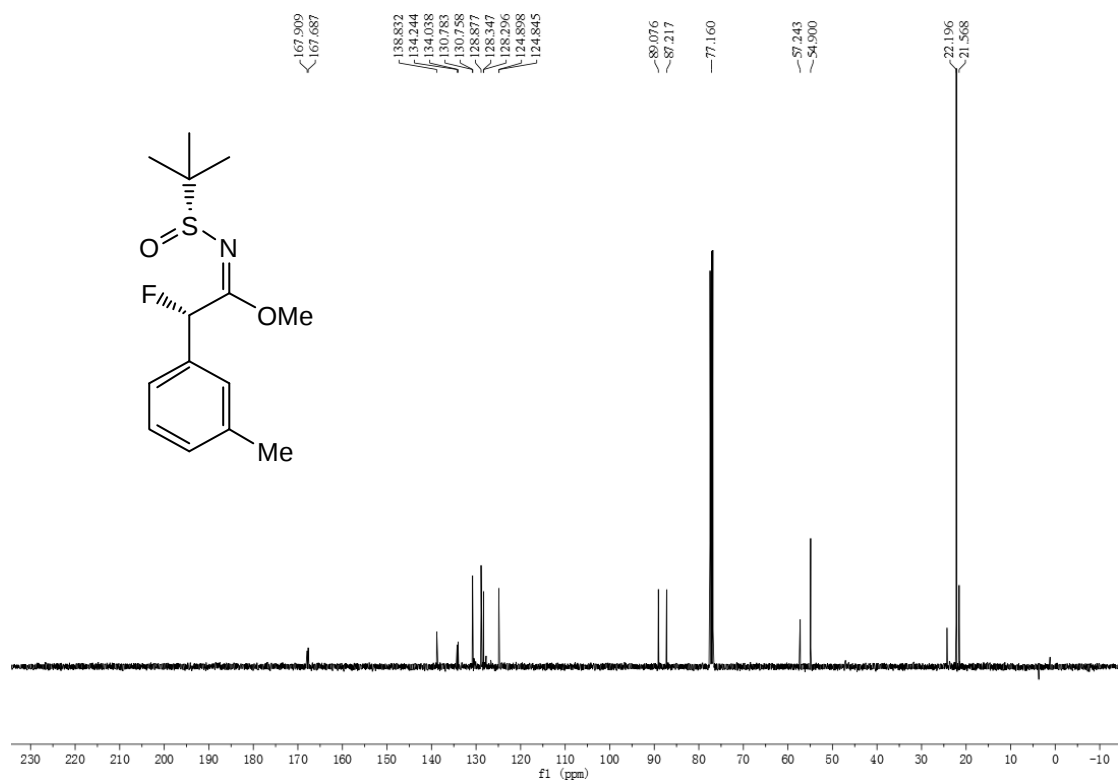
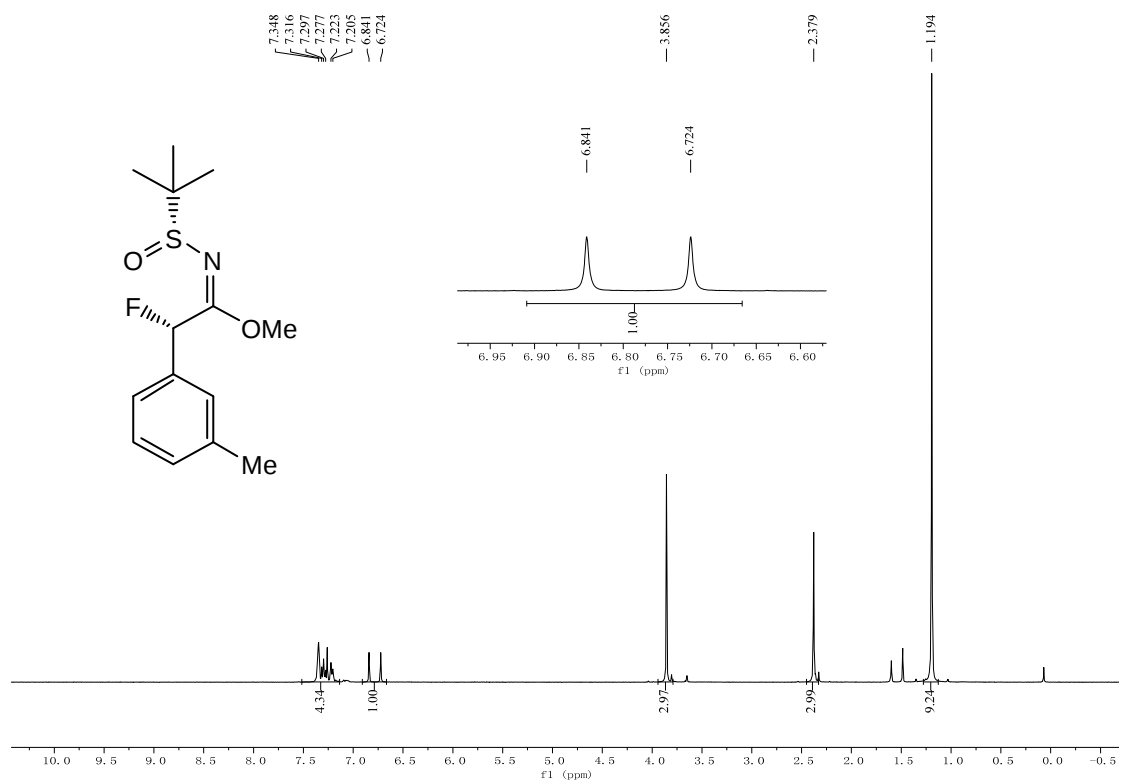


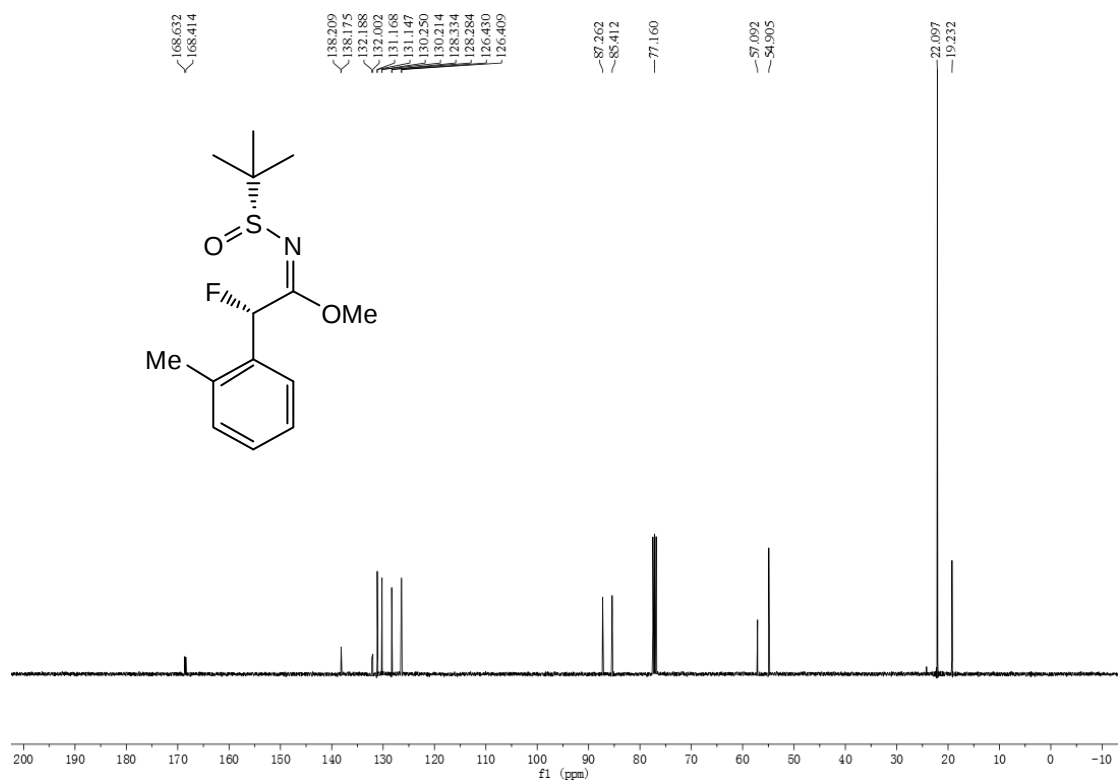
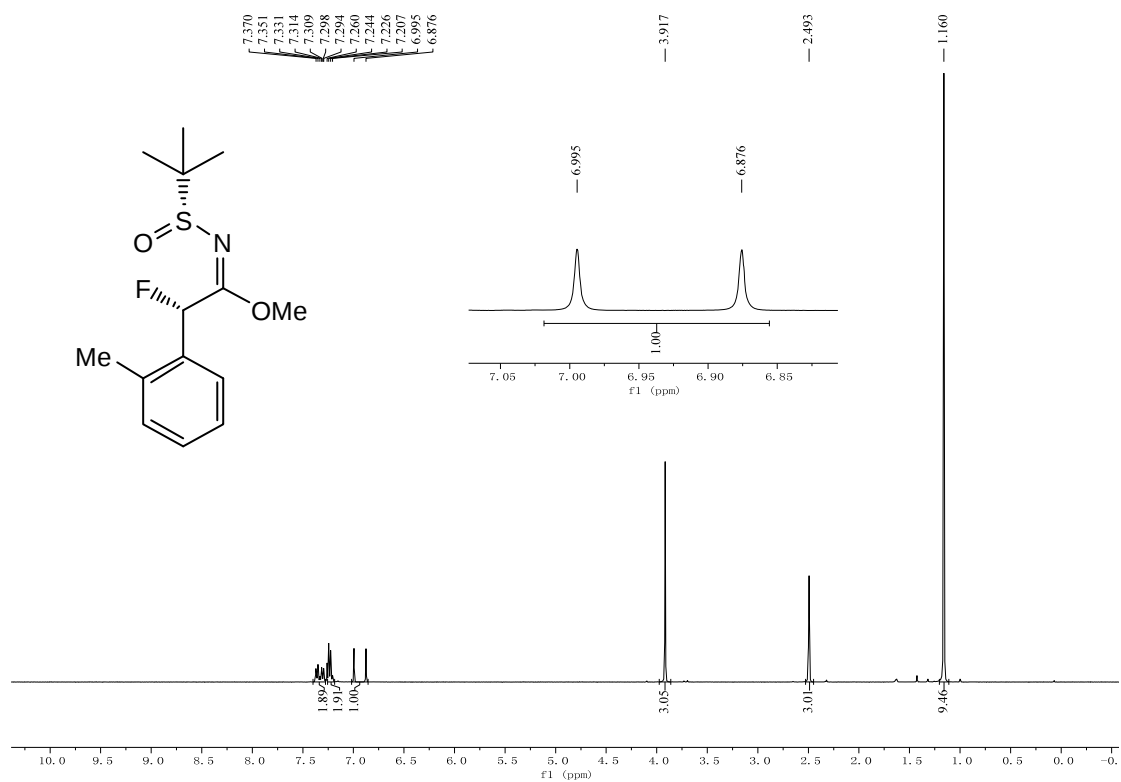
^1H NMR spectrum (CDCl_3 , 400 MHz) of **2I**

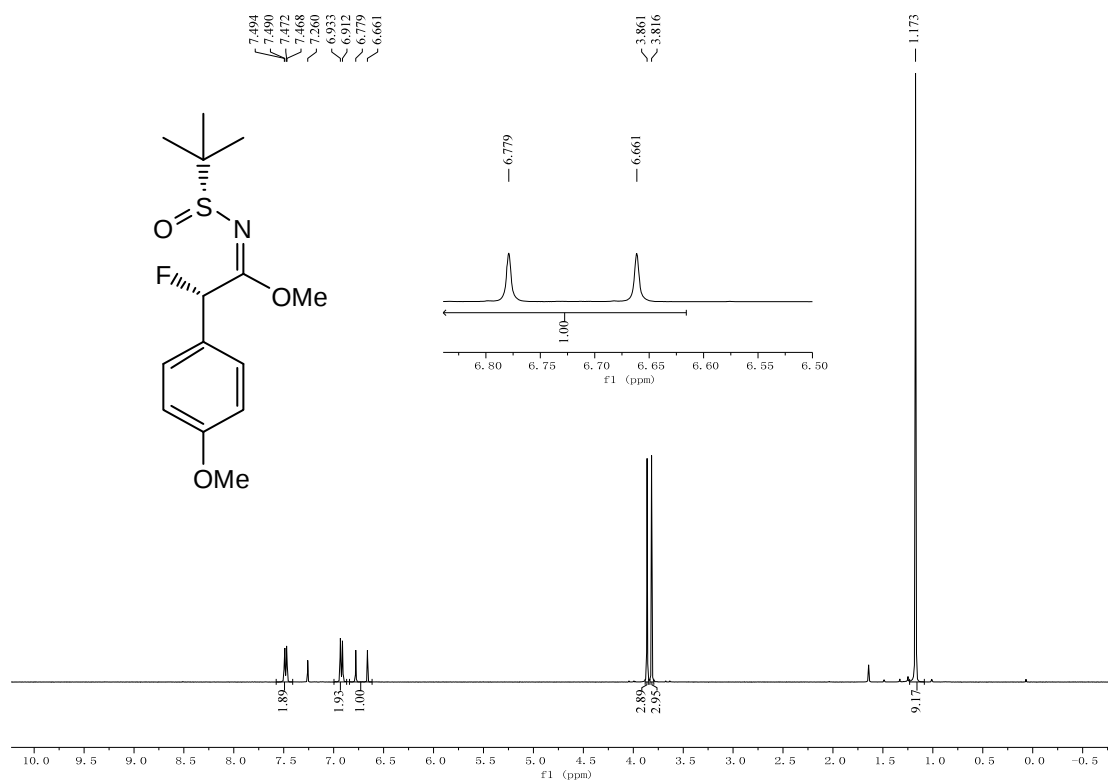


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **2I**

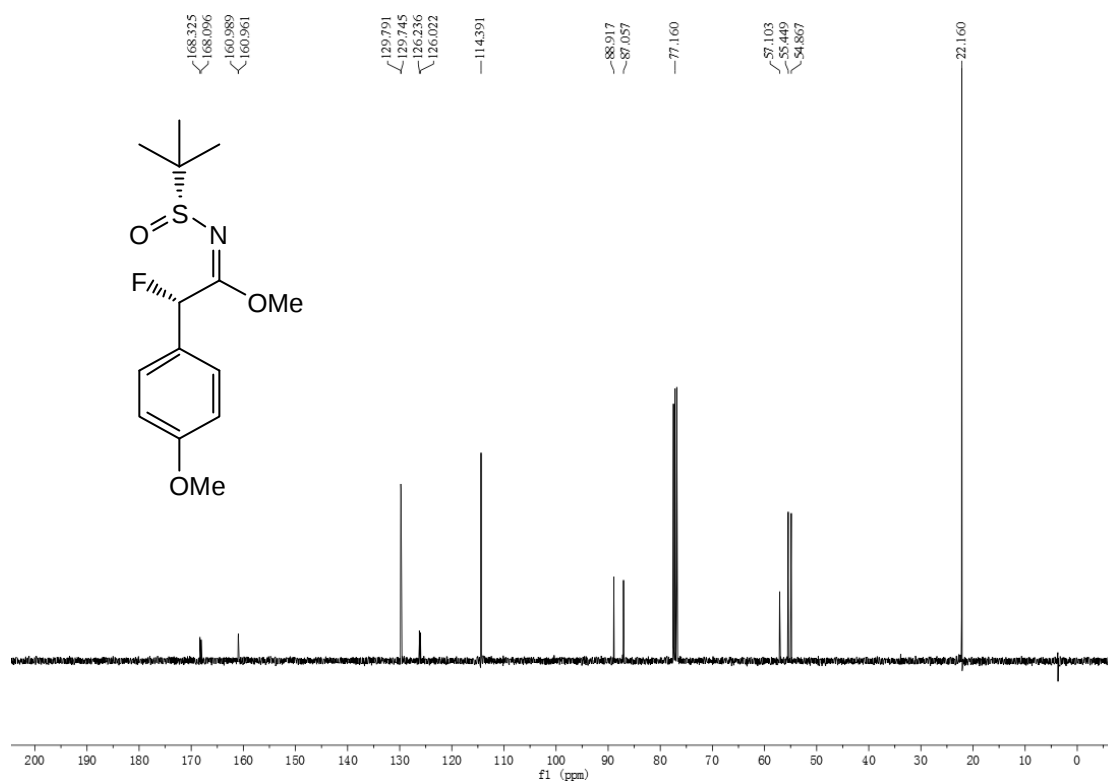




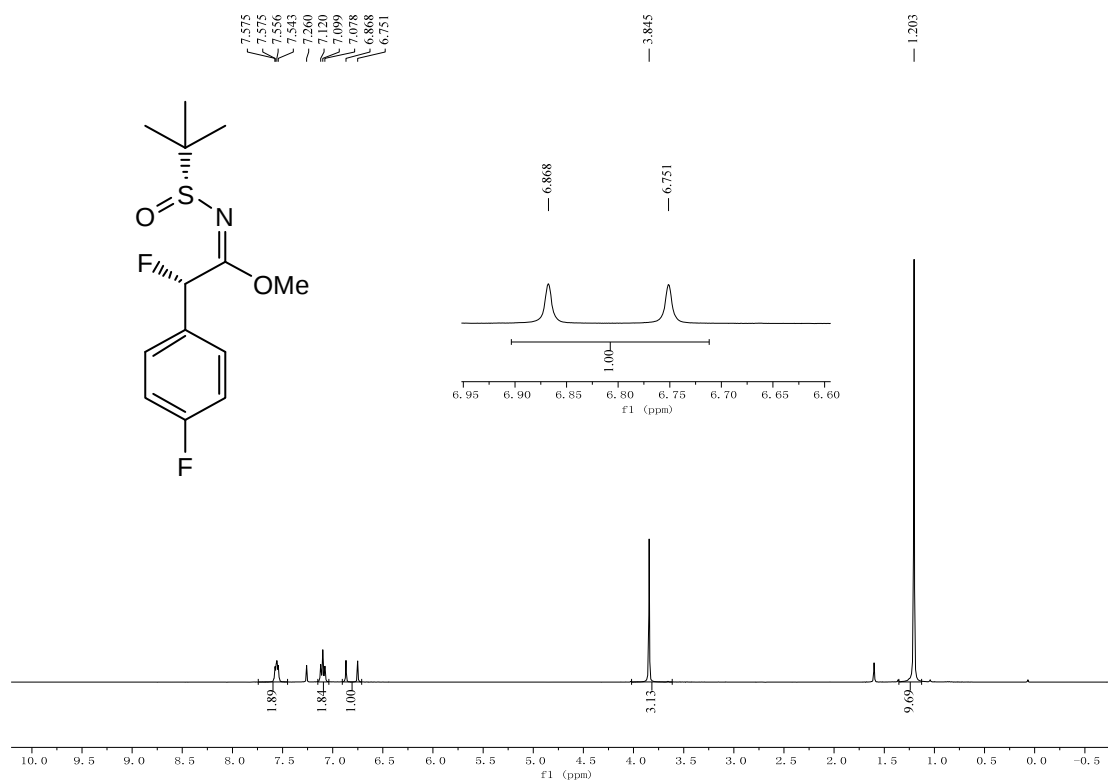




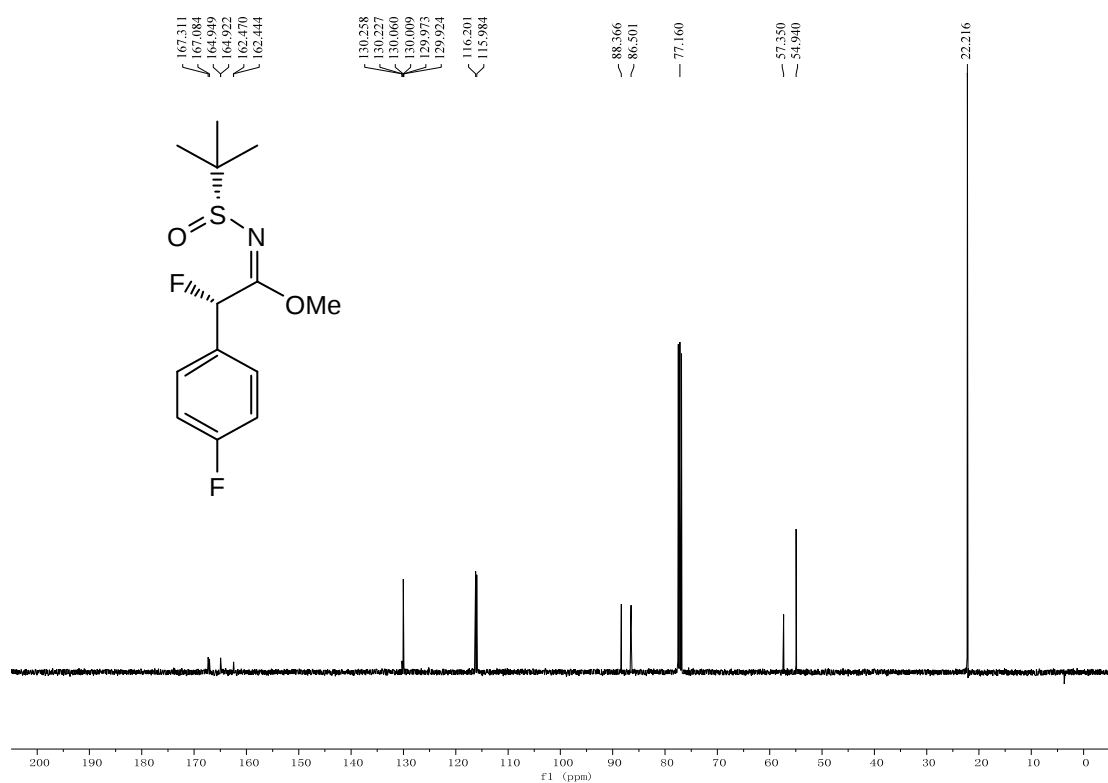
¹H NMR spectrum (CDCl₃, 400 MHz) of **2p**



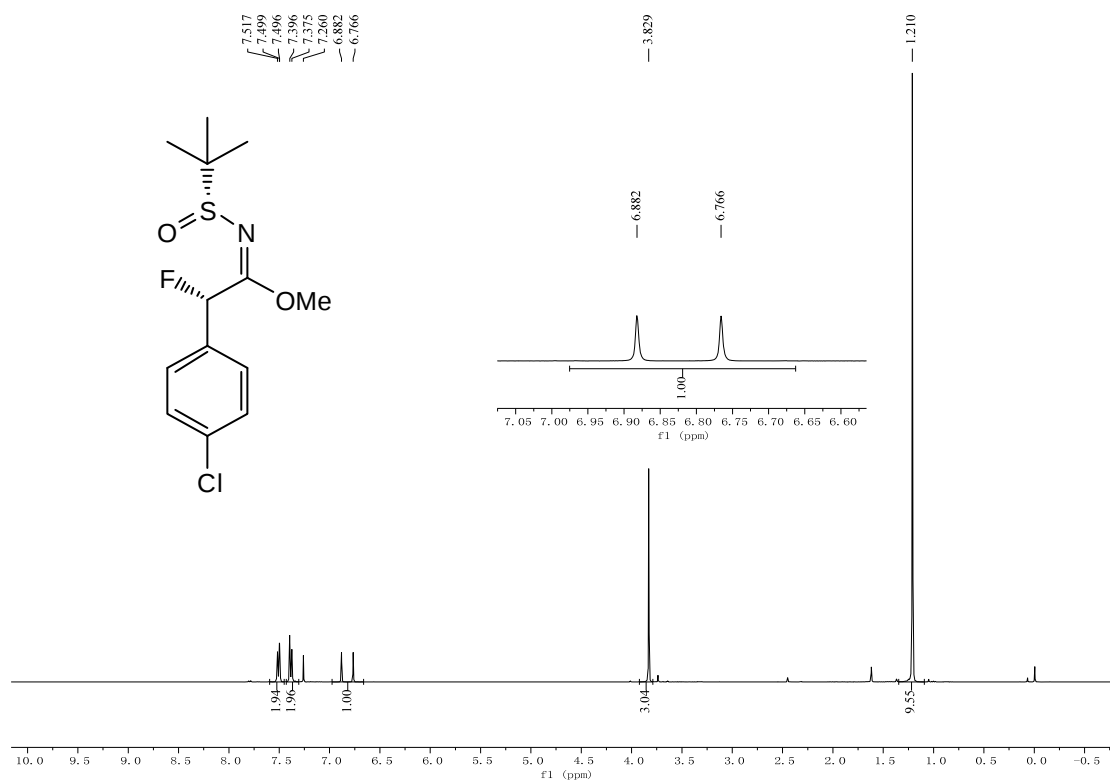
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2p**



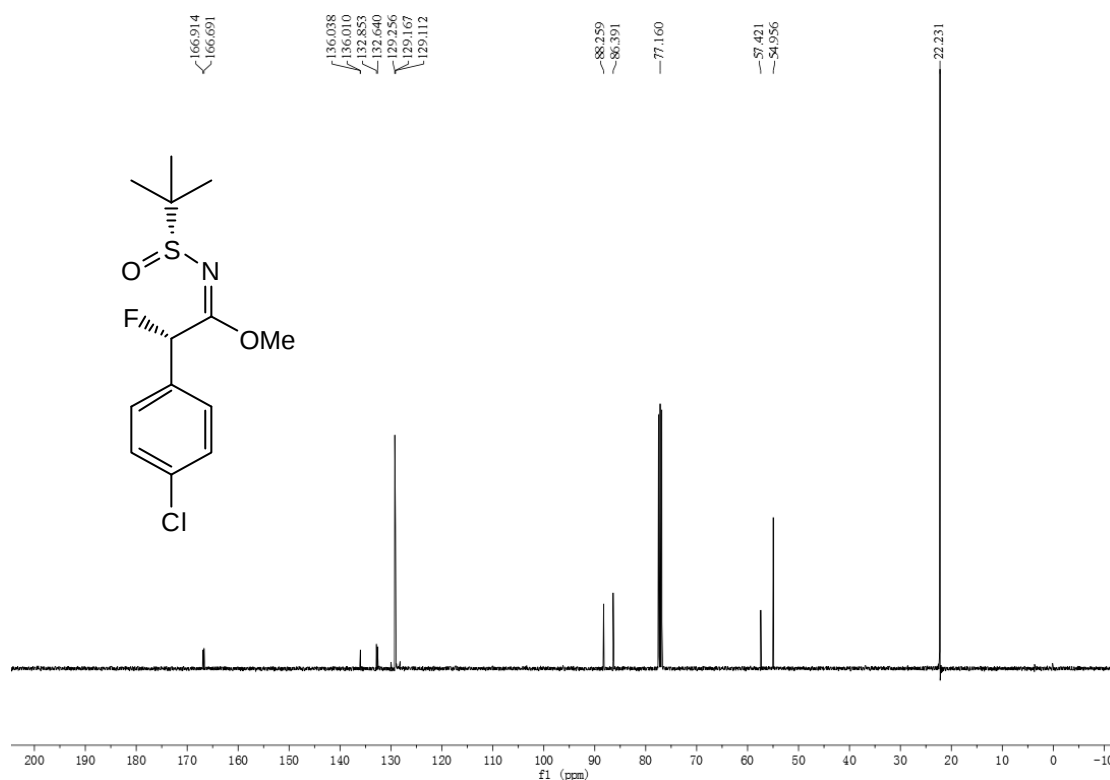
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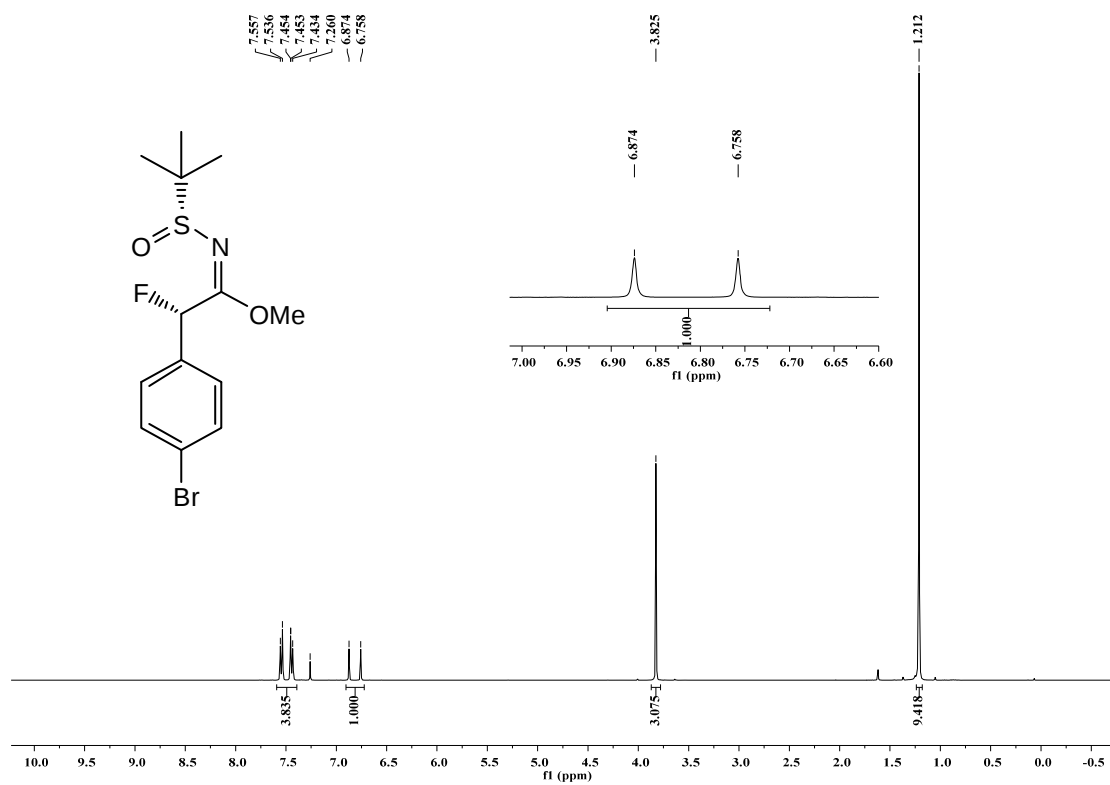
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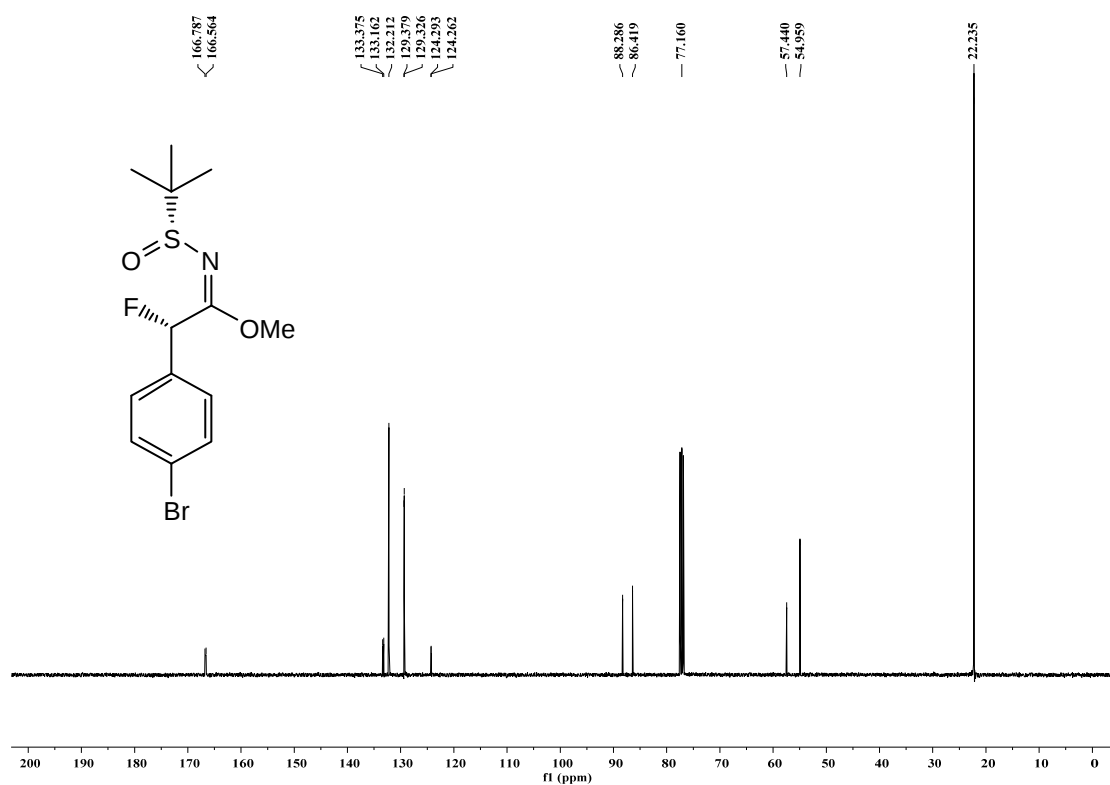
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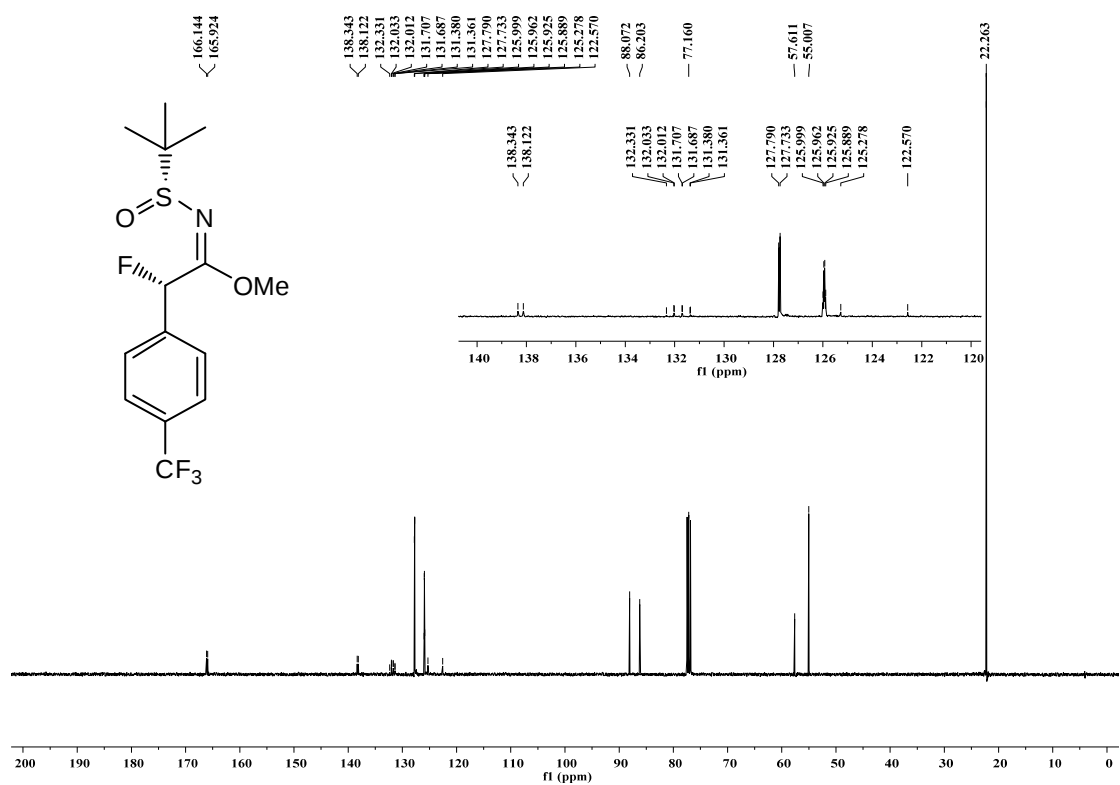
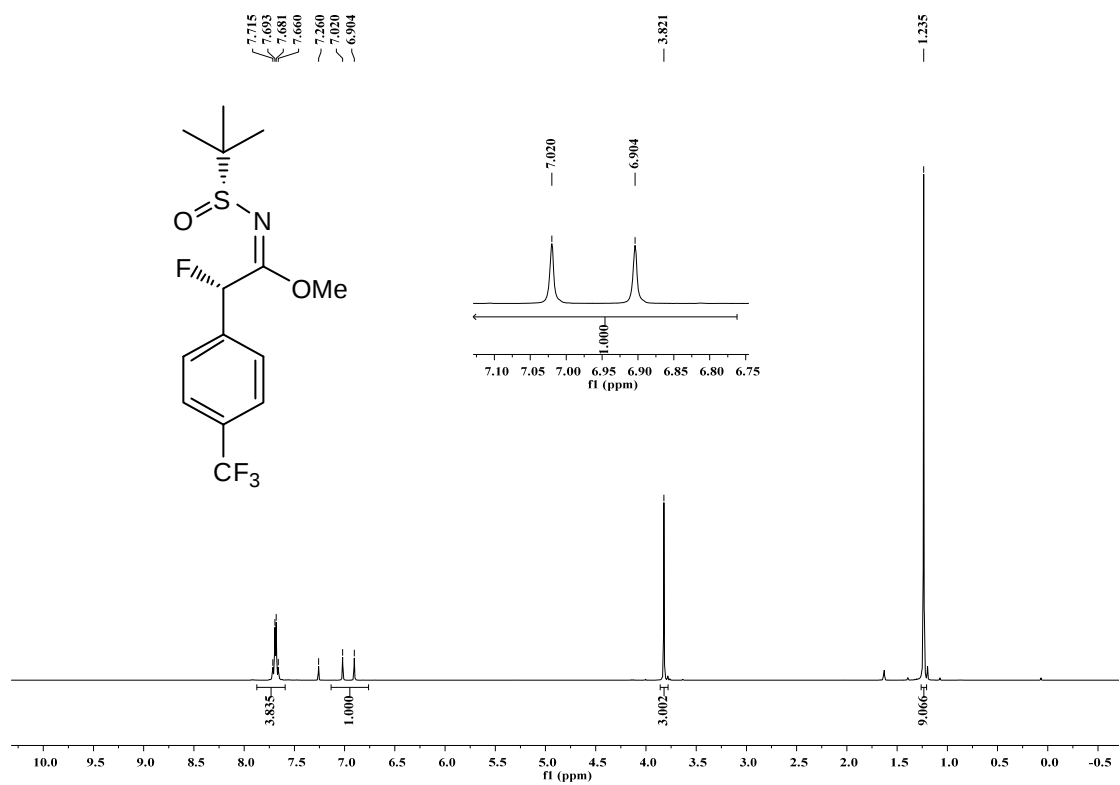
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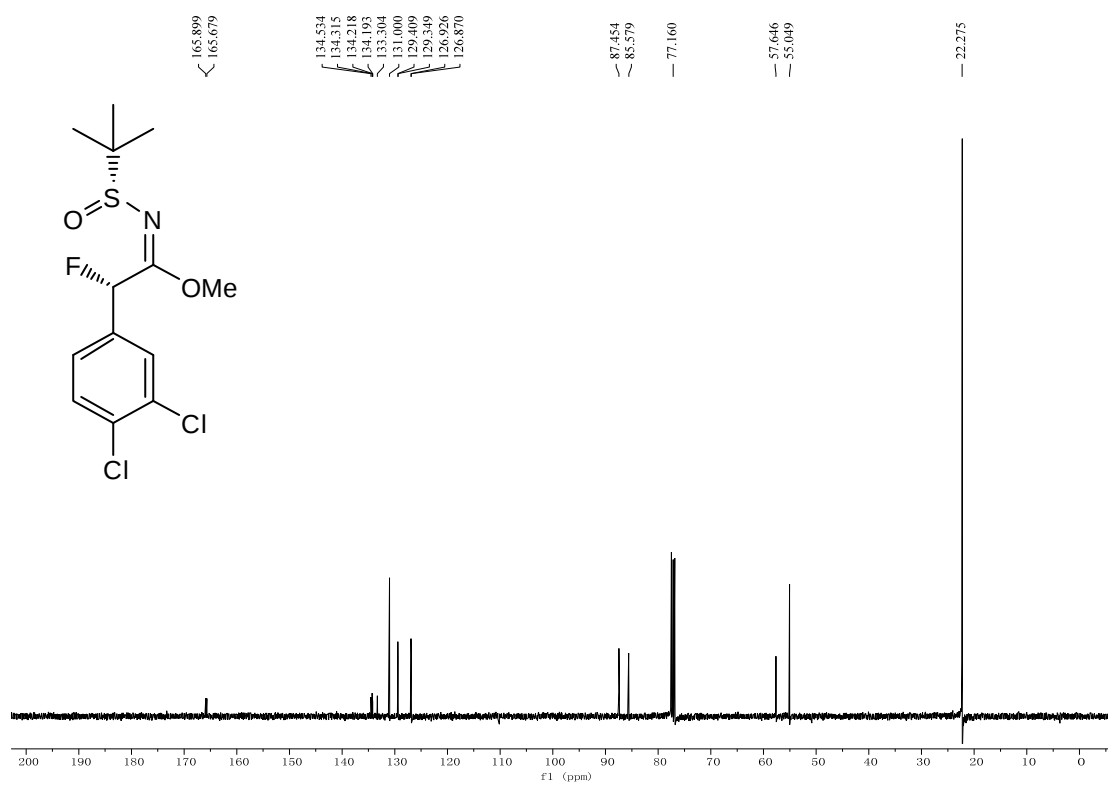
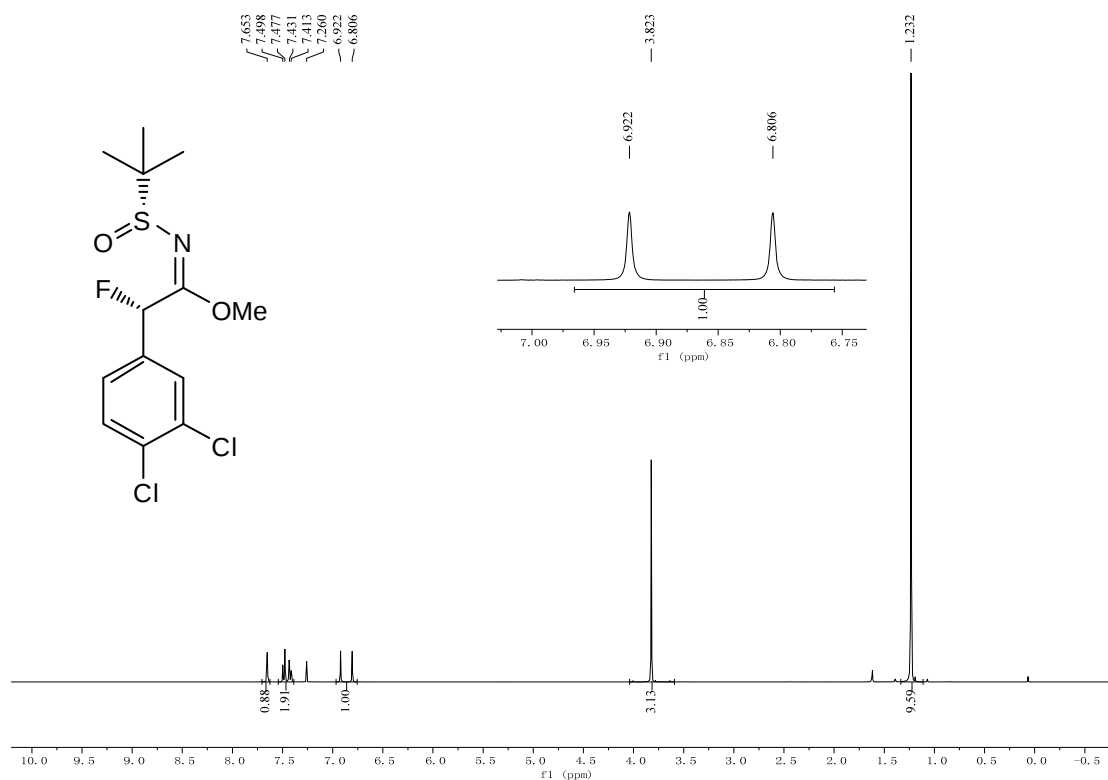


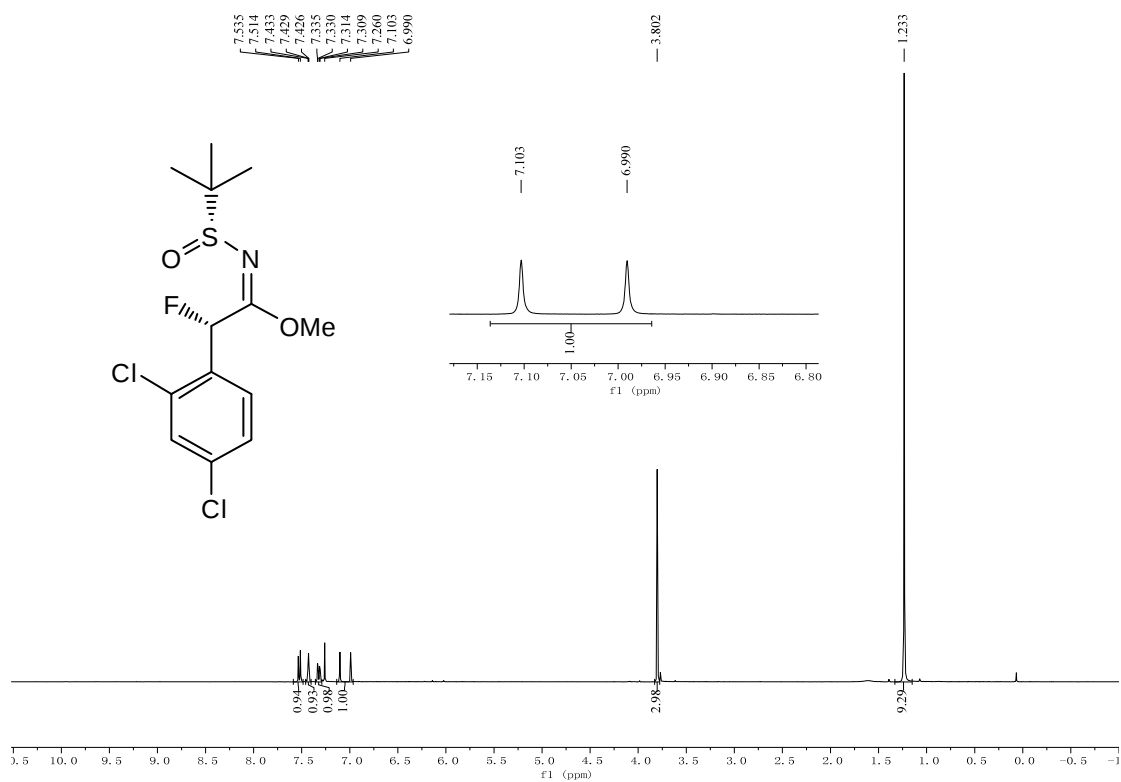
¹H NMR spectrum (CDCl₃, 400 MHz) of **2s**



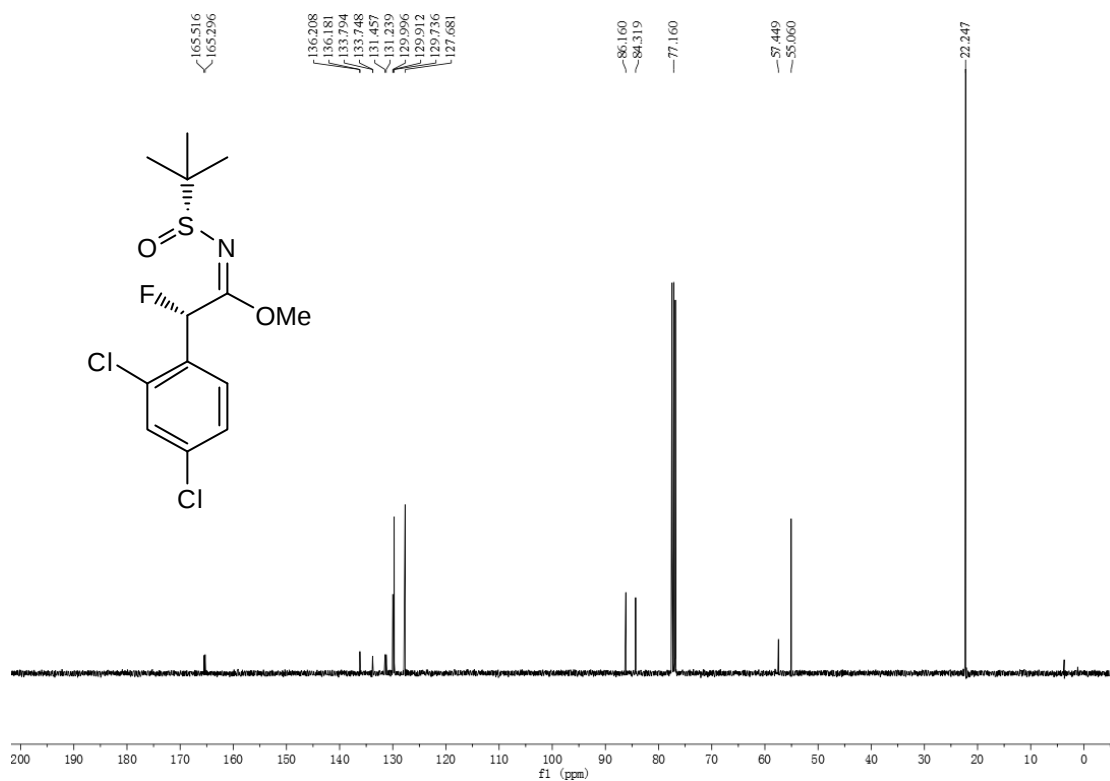
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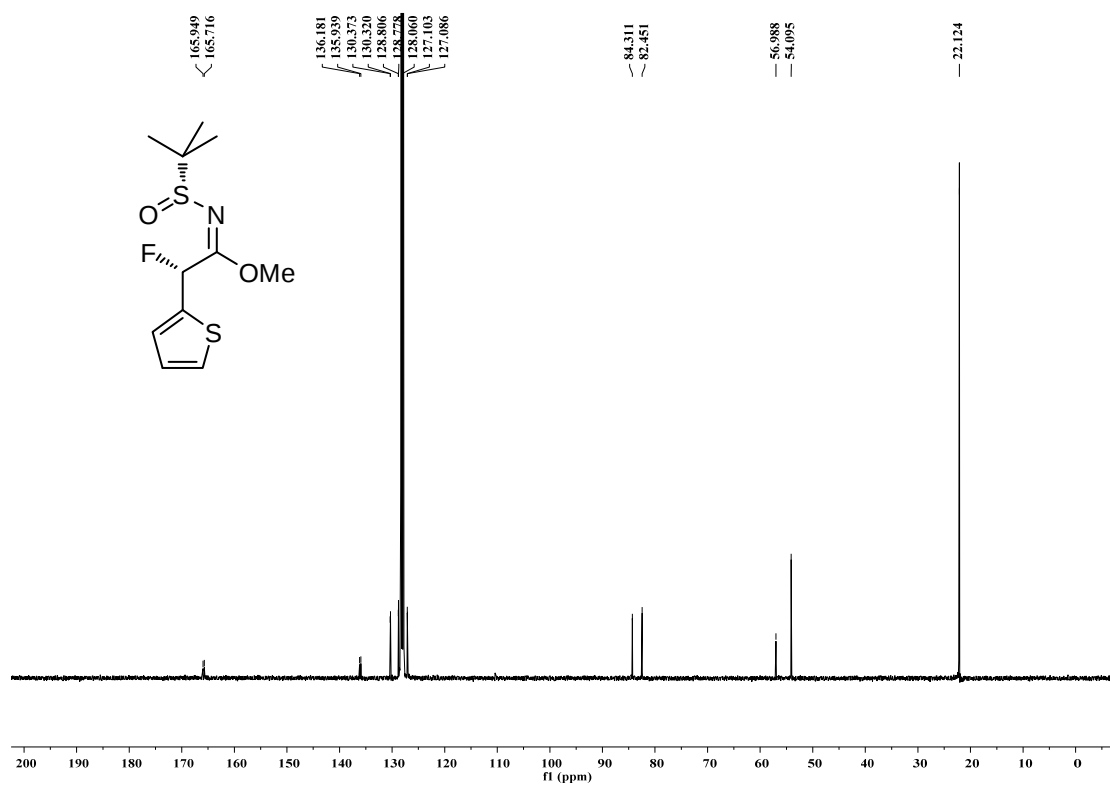
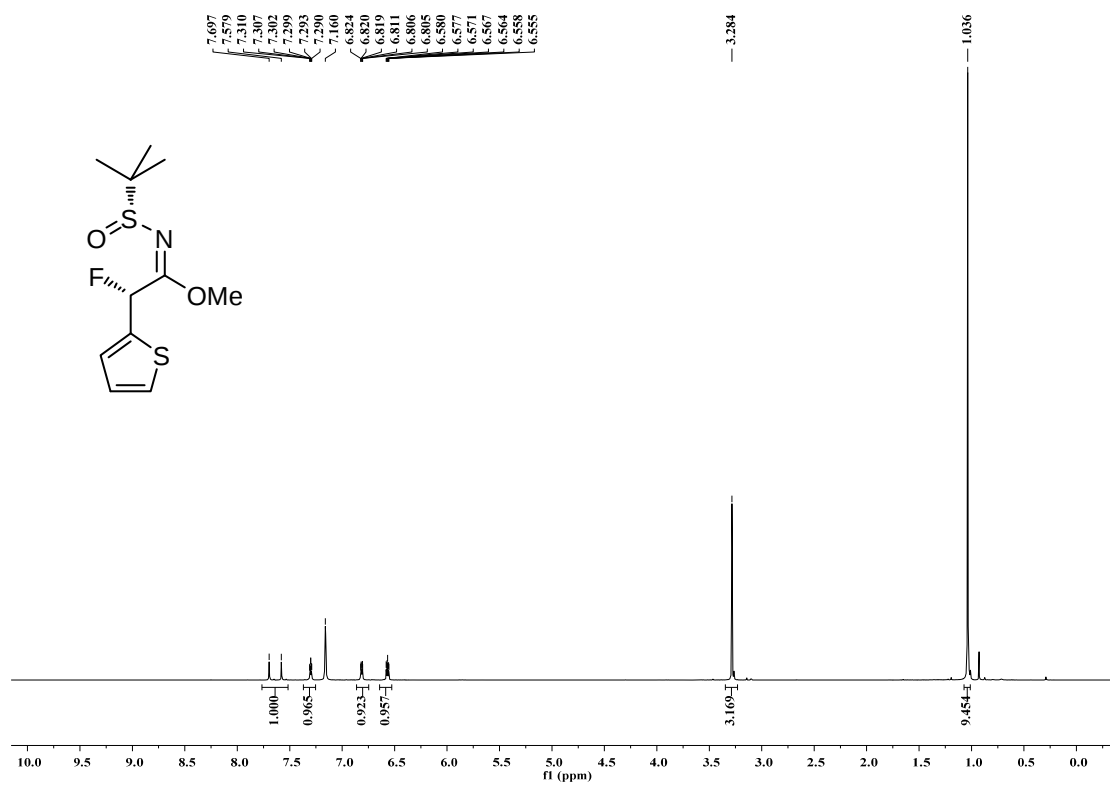


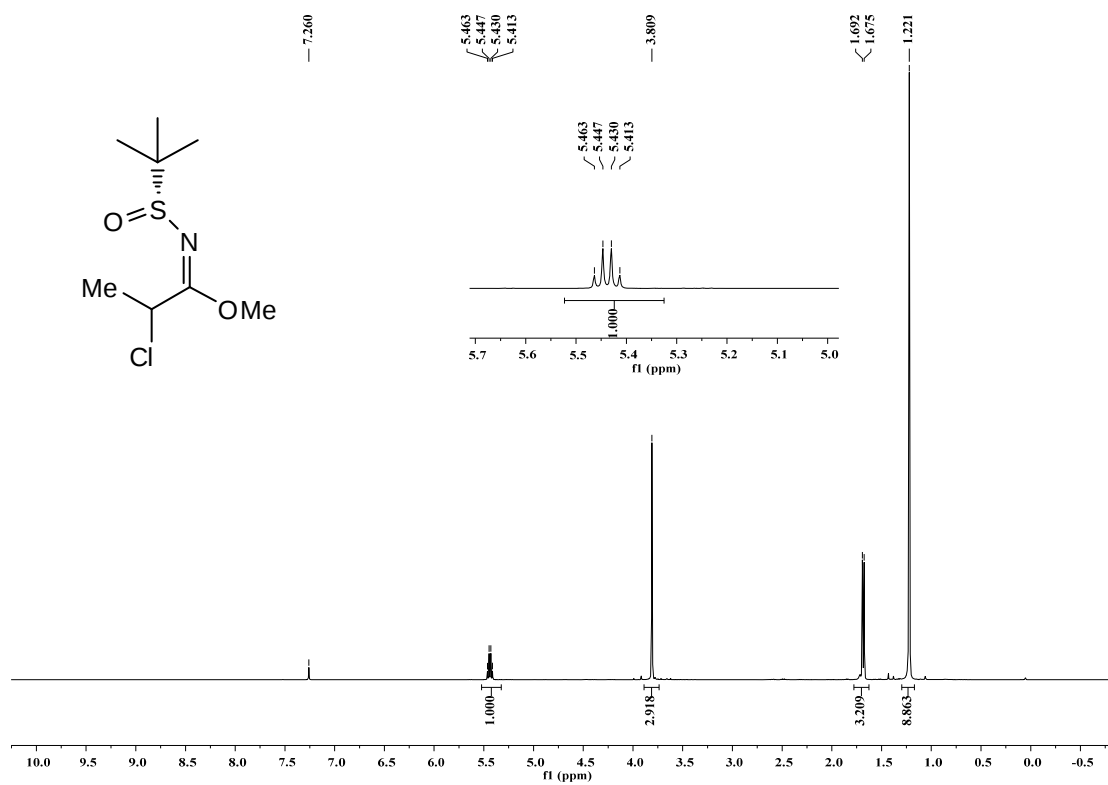


¹H NMR spectrum (CDCl₃, 400 MHz) of **2v**

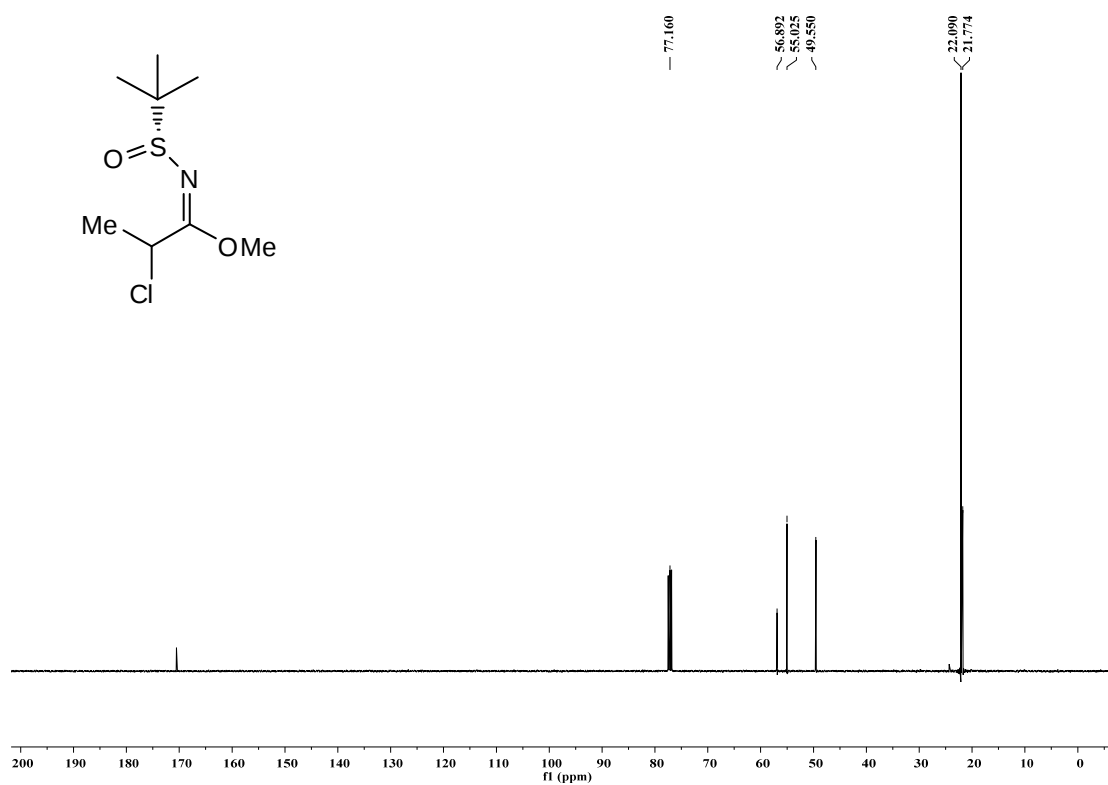


¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **2v**

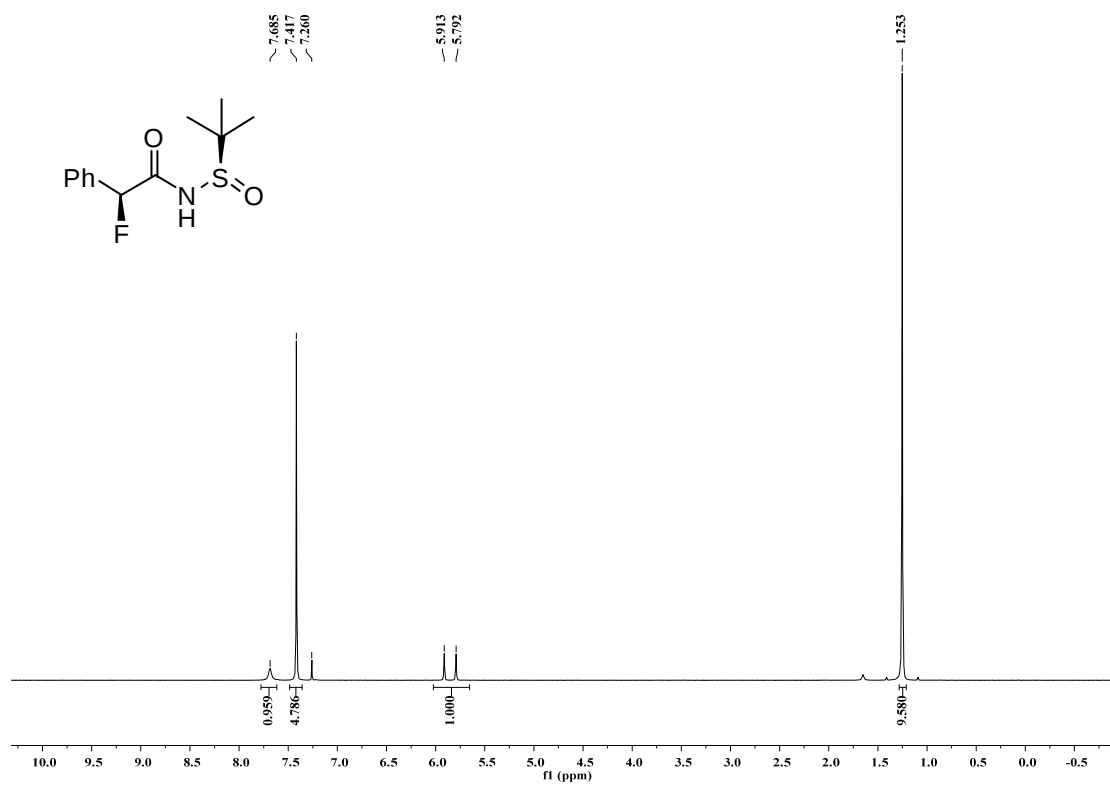




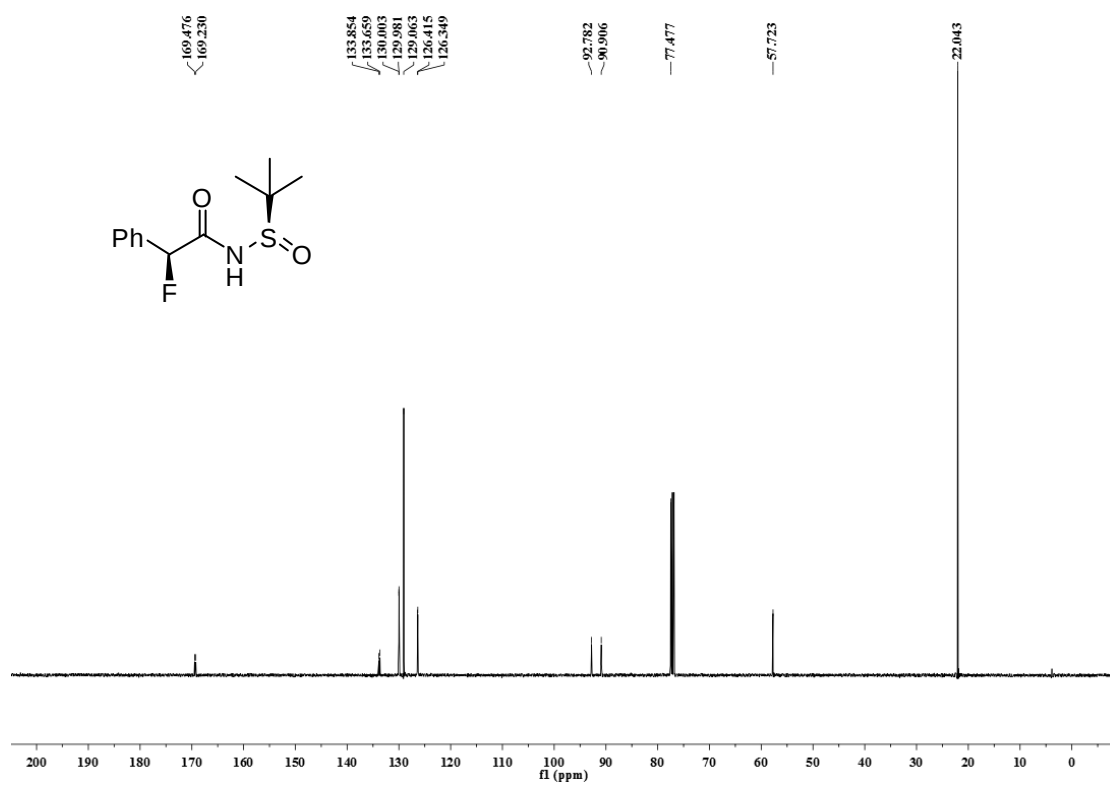
^1H NMR spectrum (CDCl_3 , 400 MHz) of **3**



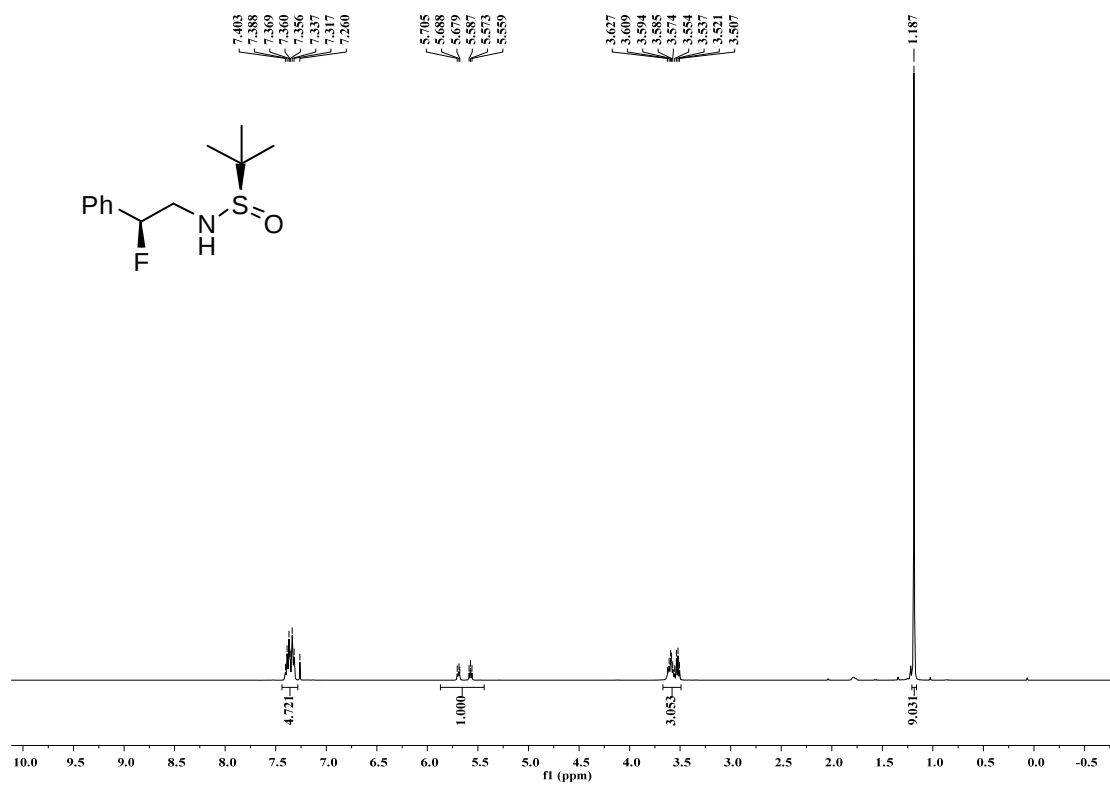
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **3**



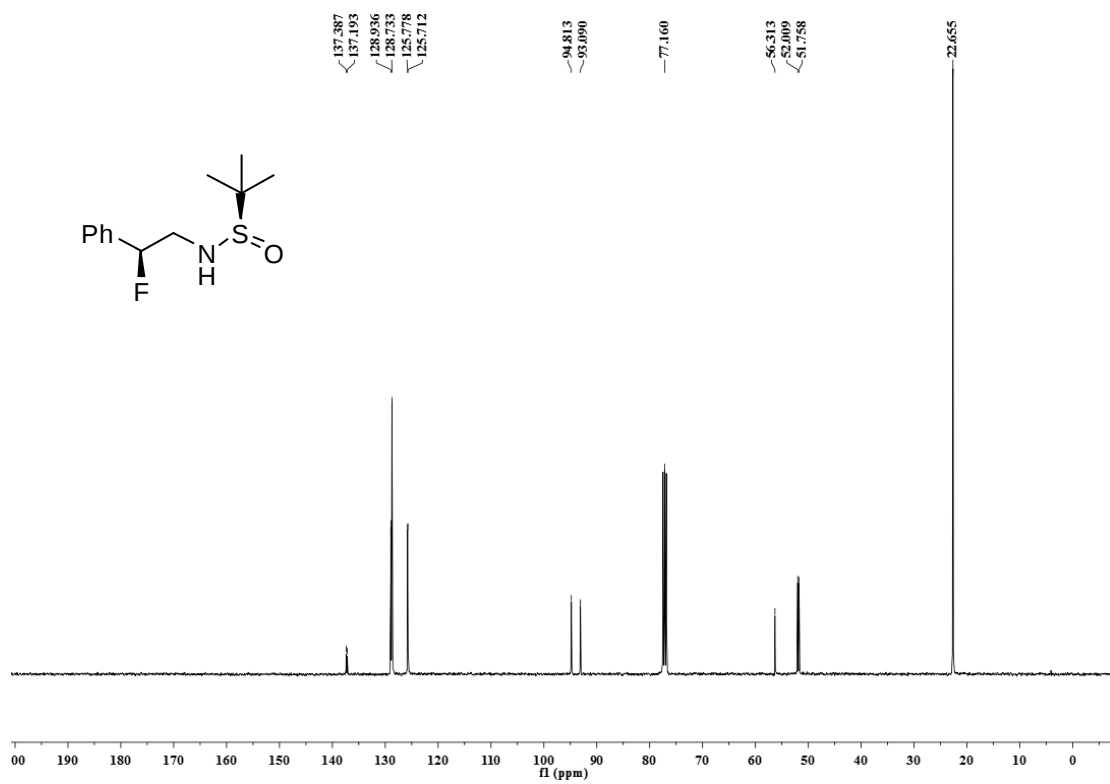
^1H NMR spectrum (CDCl_3 , 400 MHz) of **4**



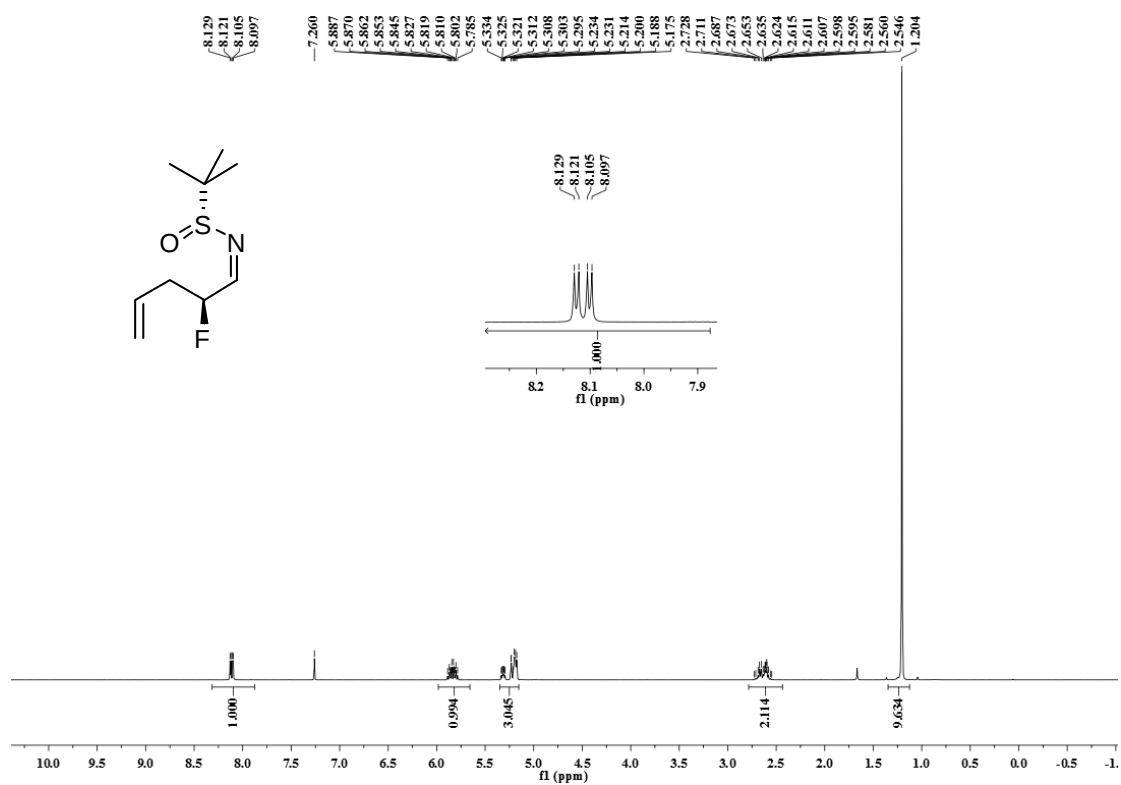
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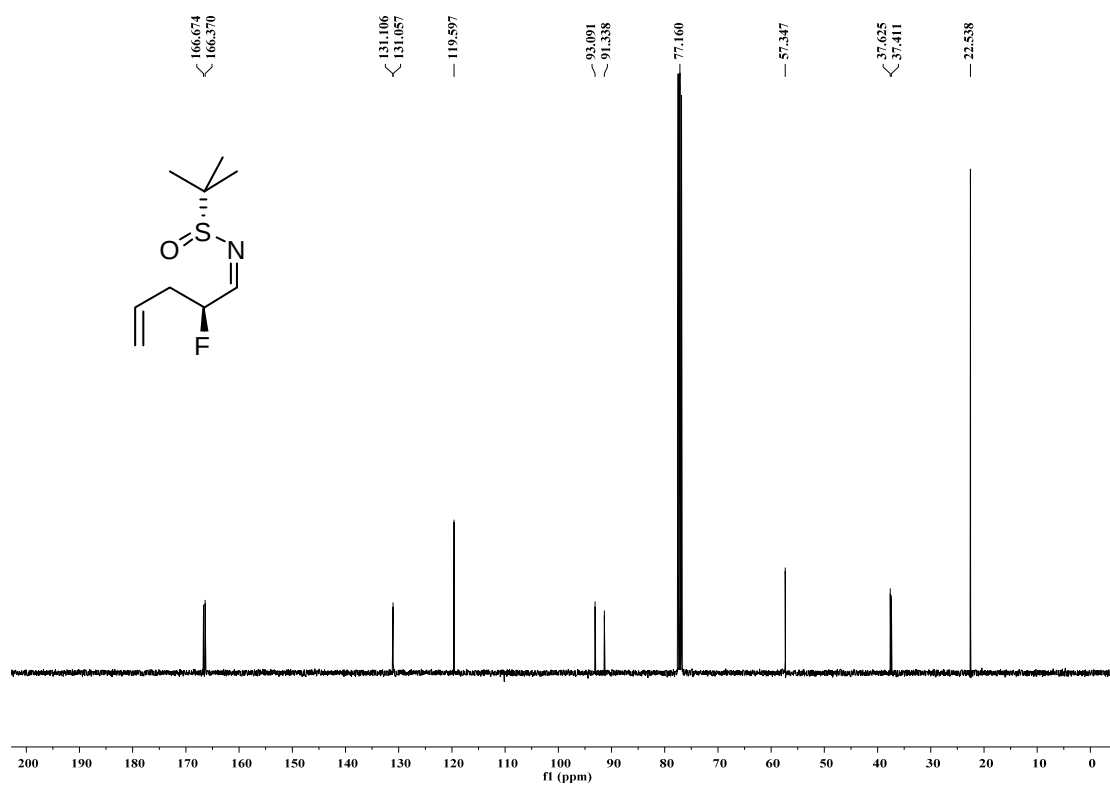
^1H NMR spectrum (CDCl_3 , 400 MHz) of **5**



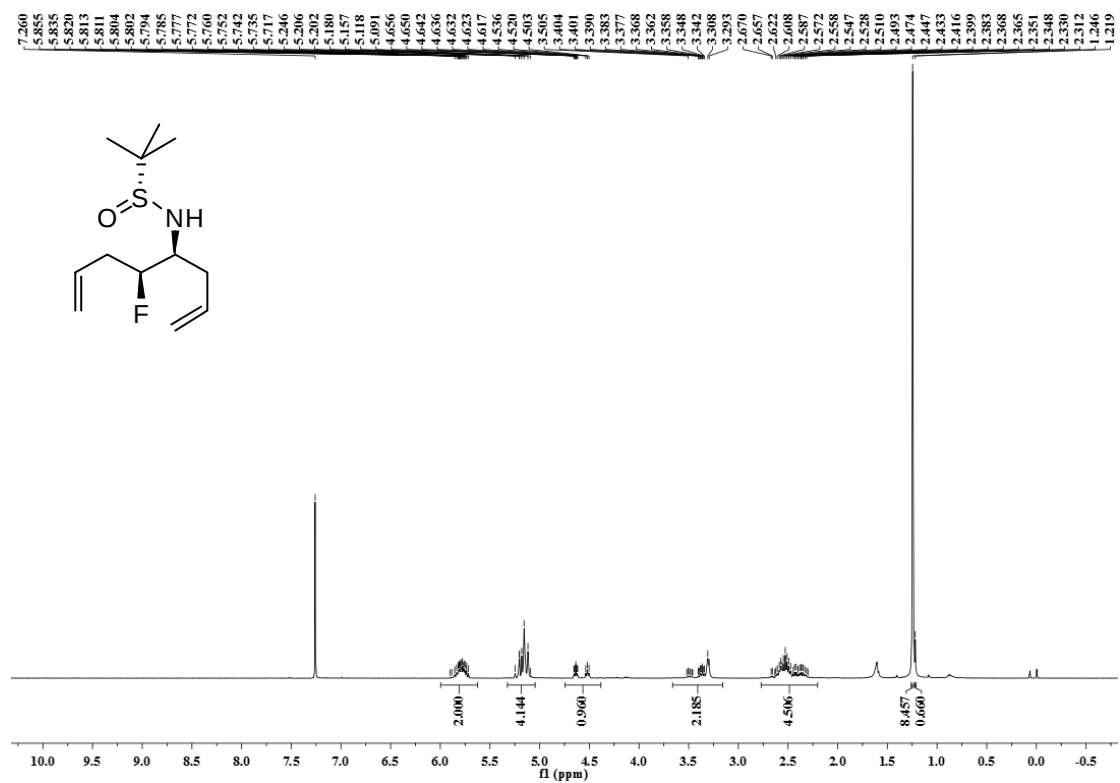
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **5**



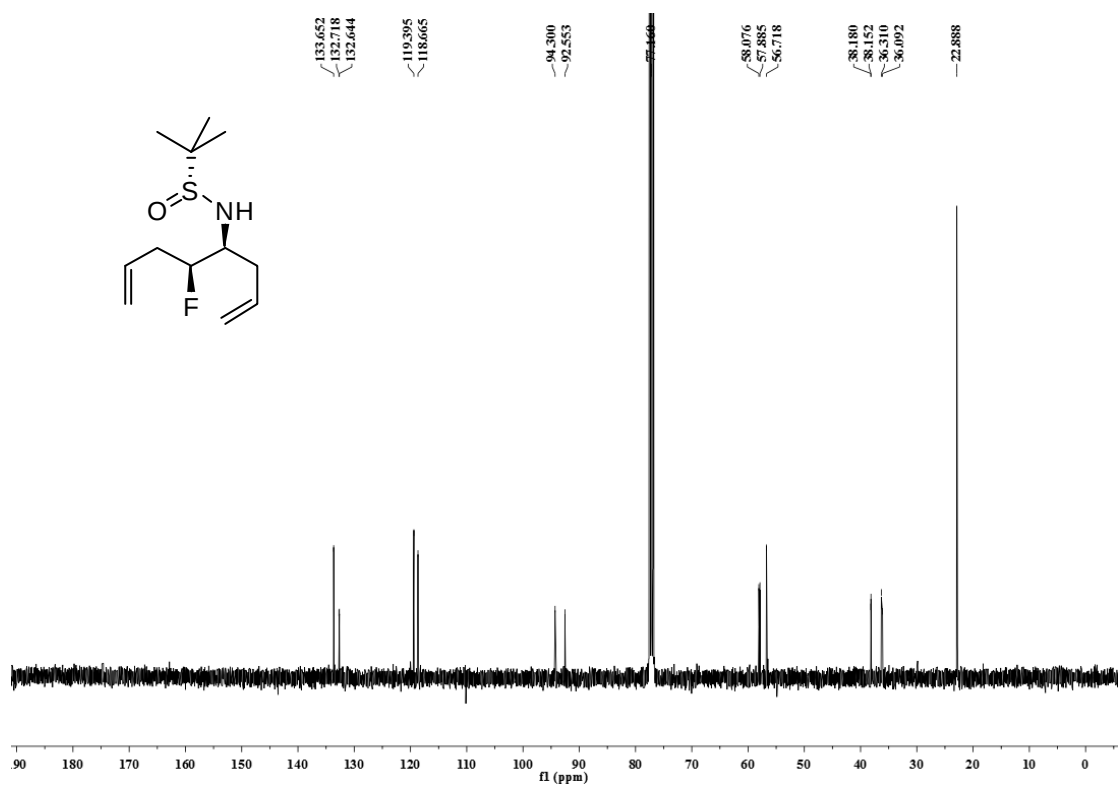
¹H NMR spectrum (CDCl₃, 400 MHz) of 6



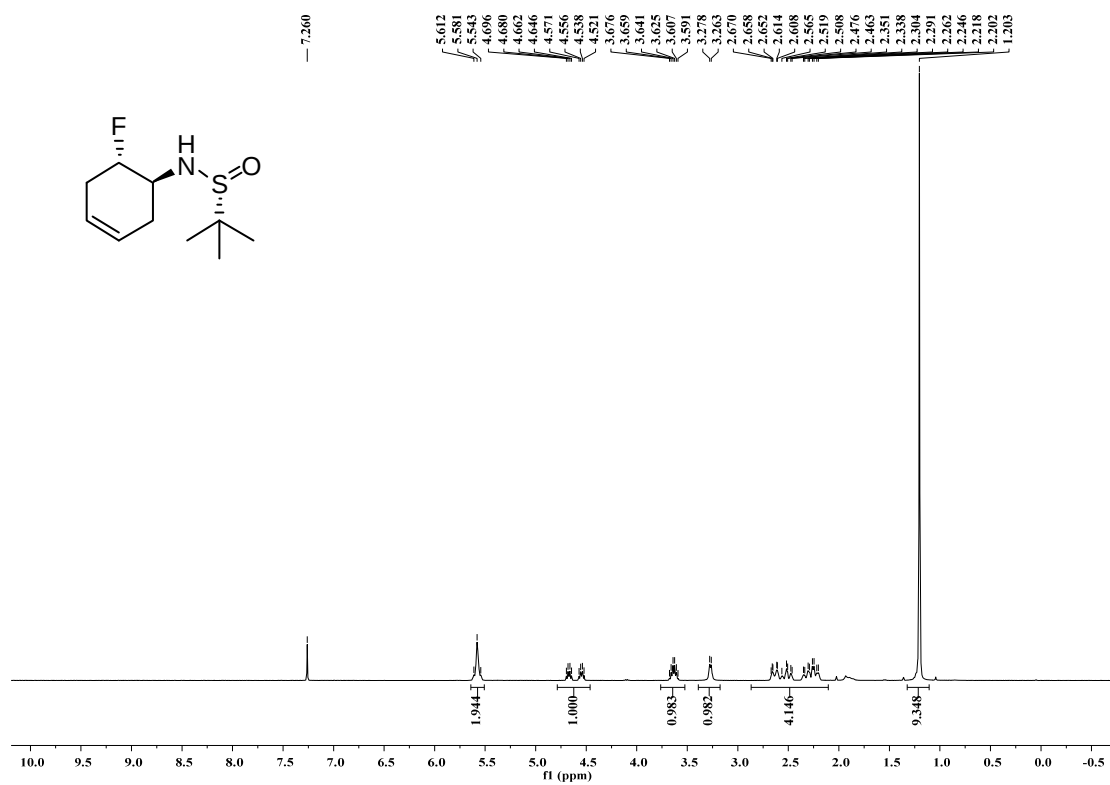
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of 6



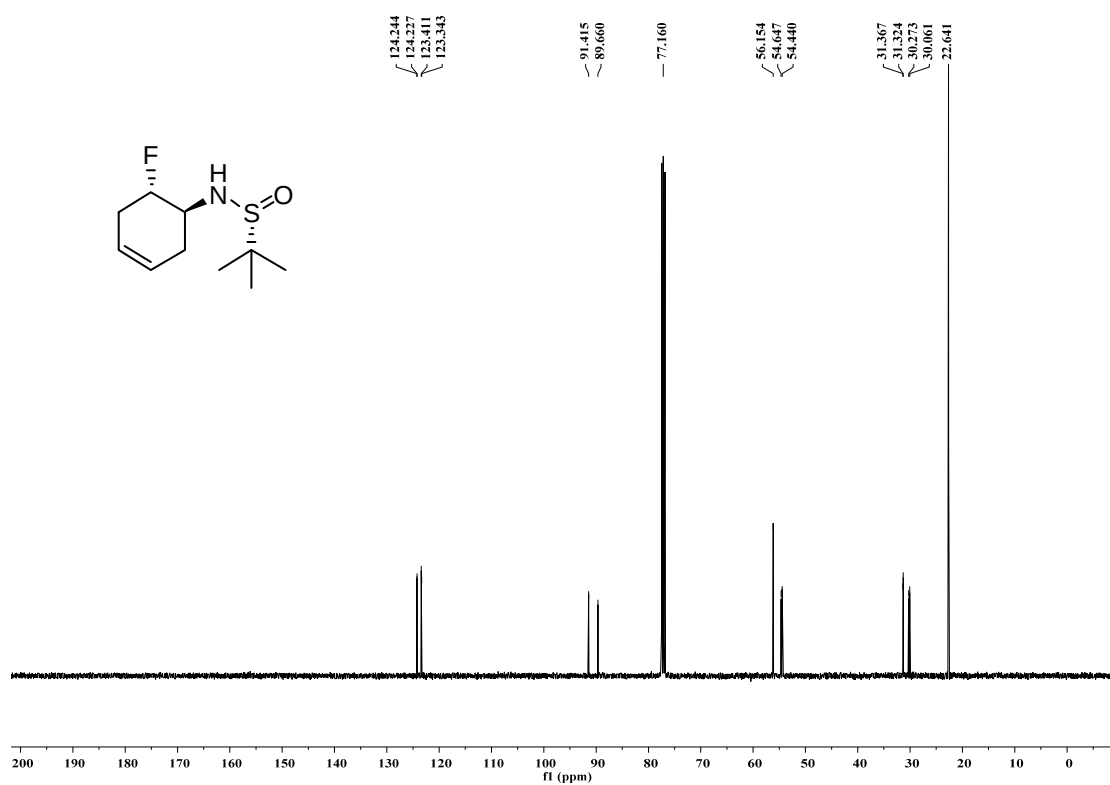
¹H NMR spectrum (CDCl₃, 400 MHz) of **7**



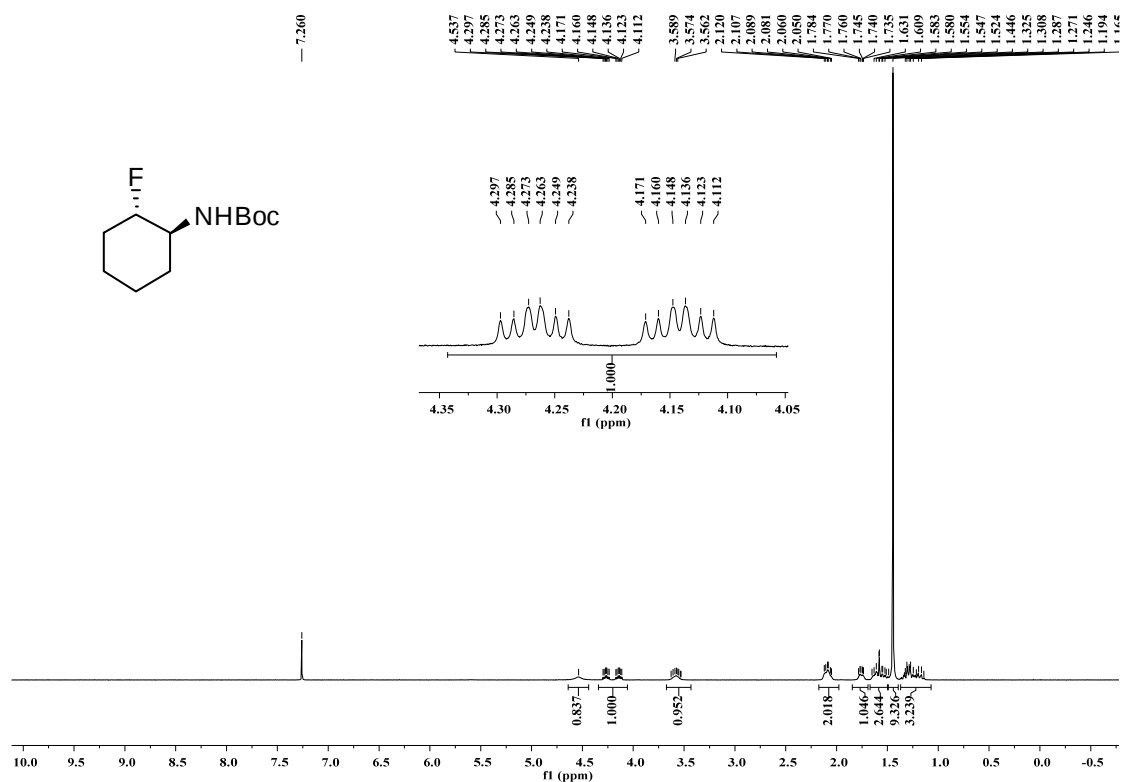
¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz) of **7**



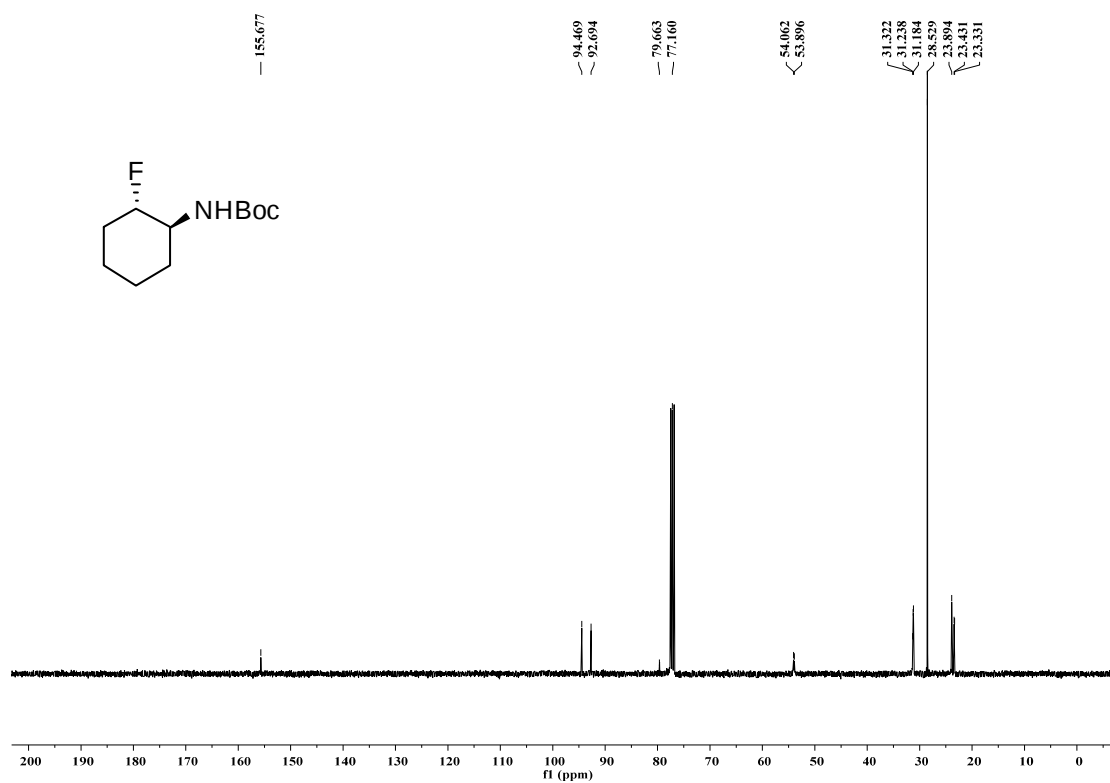
^1H NMR spectrum (CDCl_3 , 400 MHz) of **8**



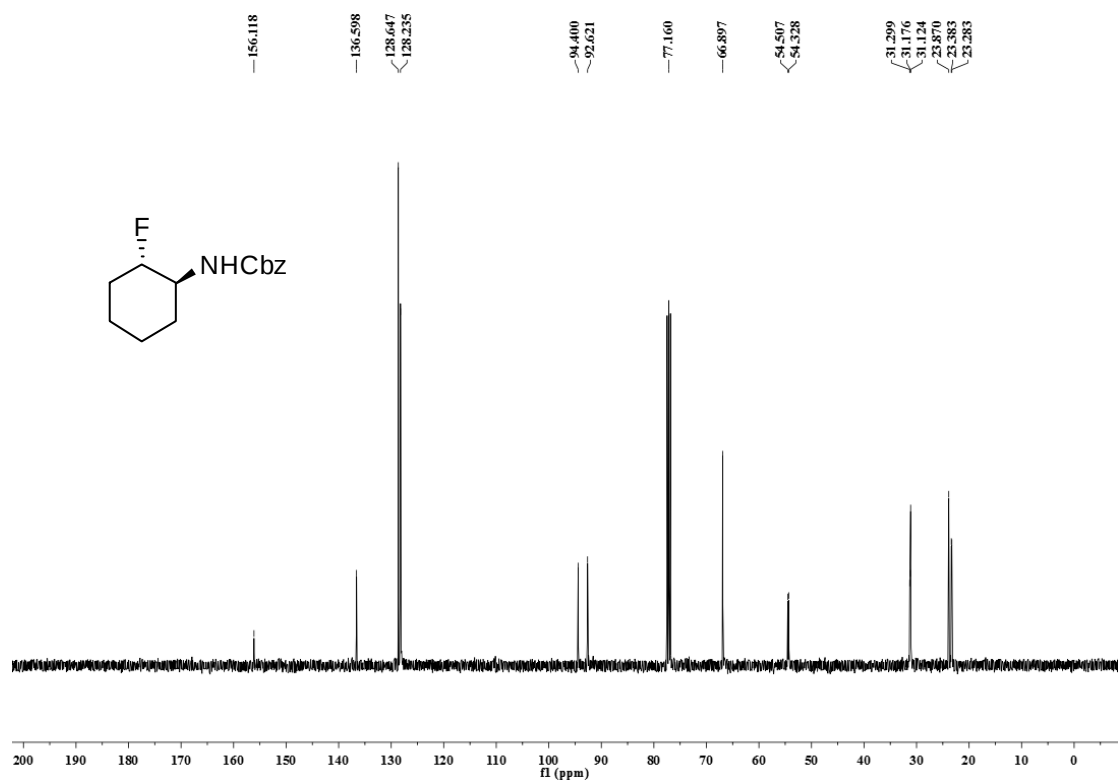
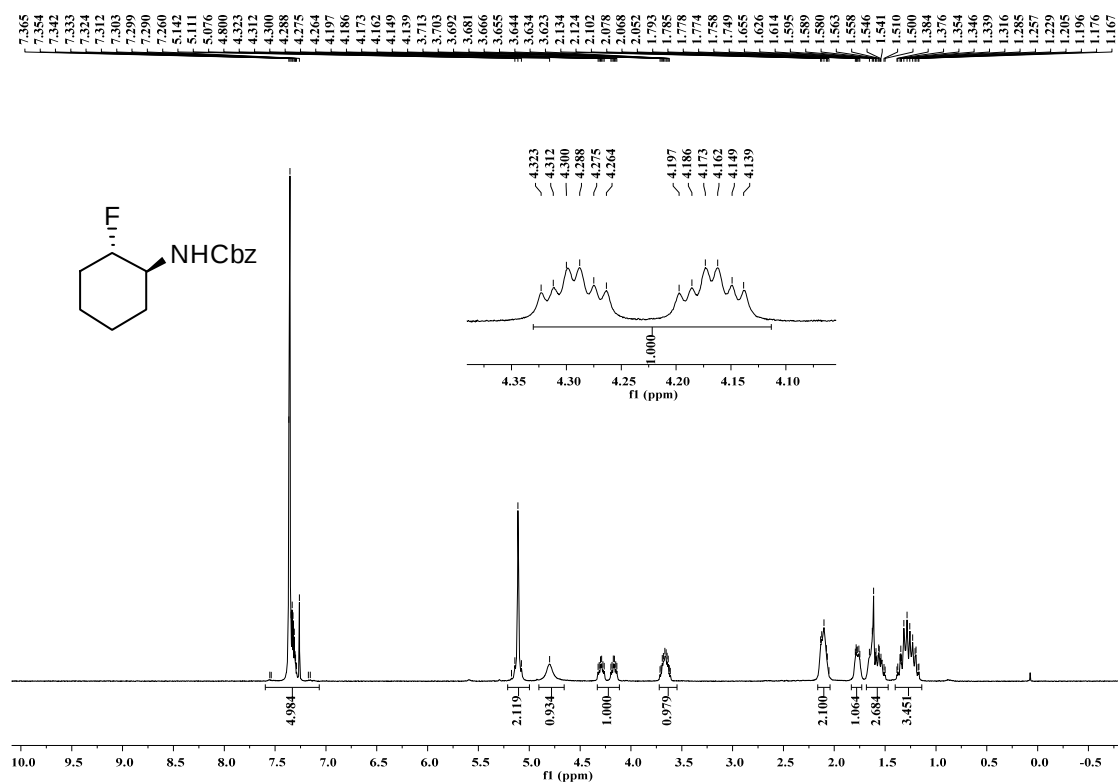
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **8**



^1H NMR spectrum (CDCl_3 , 400 MHz) of **9**



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz) of **9**



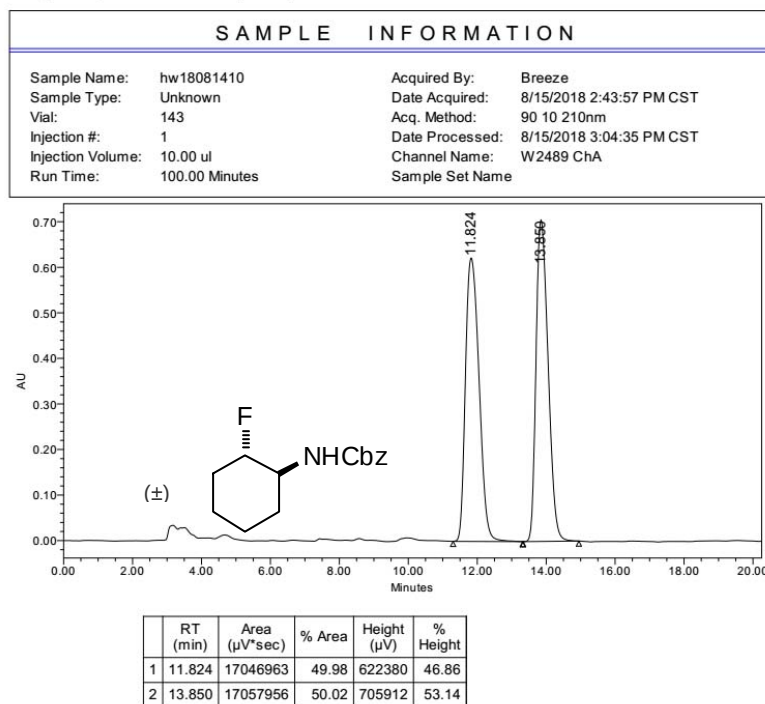
Chiral HPLC analysis of **10**

The er (> 99.5:0.5) of compound **10** was determined by chiral HPLC (Daicel Chirapak OD-3, hexane / *iso*-propanol = 90:10, flow rate 1.0 mL/min, 210 nm). Racemic **10** was prepared accordingly using racemic *tert*-butanesulfinamide as starting material.

XJTIPC

Project Name Lu
Reported by User: Breeze user (Breeze)

Breeze 2
HPLC System



XJTIPC

Project Name Lu
Reported by User: Breeze user (Breeze)

Breeze 2
HPLC System

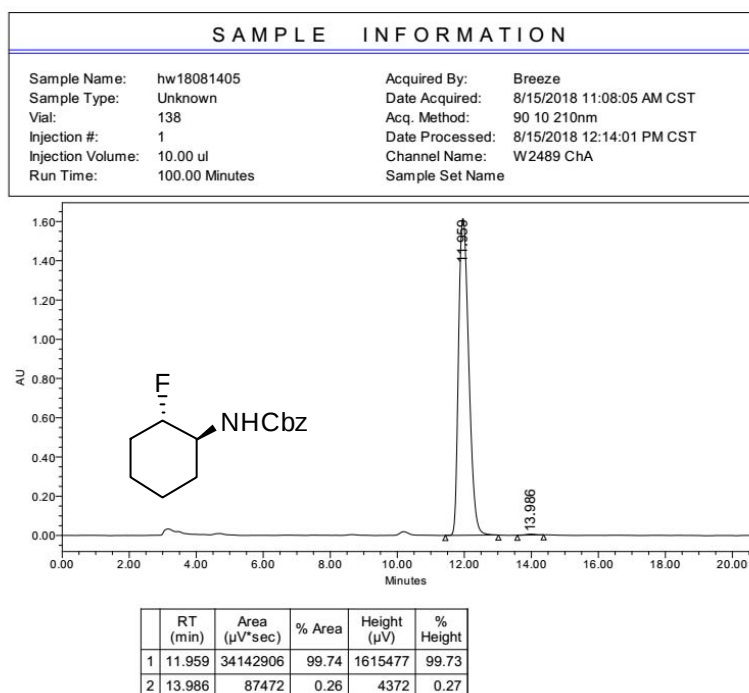


Figure S1. X-Ray crystal structure of the compound 4

Crystals of the compound 4 for X-ray structure studies were obtained by evaporation its solution (CH_2Cl_2 /petroleum ether) at room temperature.

X-Ray crystal structure (ORTEP) of compound 4 with the thermal ellipsoids shown at a 50% probability level.

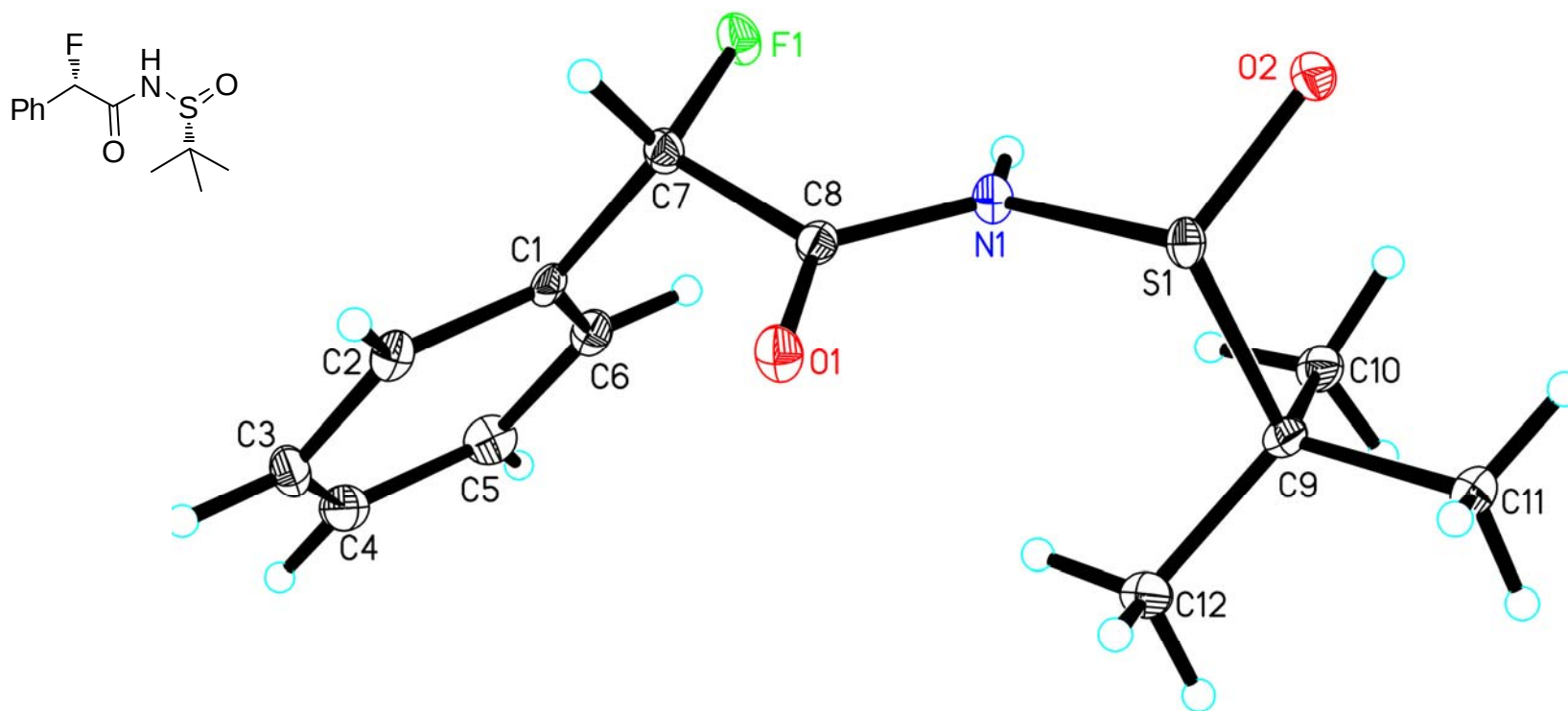


Table S1 Crystal data and structure refinement for 4.

Identification code	4
Empirical formula	C ₁₂ H ₁₆ FNO ₂ S
Formula weight	257.32
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.3373(7)
b/Å	10.0709(8)
c/Å	17.0758(16)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1261.8(2)
Z	4
ρ _{calc} /cm ³	1.355
μ/mm ⁻¹	0.259
F(000)	544.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.696 to 49.992
Index ranges	-8 ≤ h ≤ 6, -10 ≤ k ≤ 11, -20 ≤ l ≤ 15
Reflections collected	8072
Independent reflections	2216 [R _{int} = 0.0427, R _{sigma} = 0.0434]
Data/restraints/parameters	2216/0/157
Goodness-of-fit on F ²	1.013
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0363, wR ₂ = 0.0783
Final R indexes [all data]	R ₁ = 0.0399, wR ₂ = 0.0803
Largest diff. peak/hole / e Å ⁻³	0.32/-0.26
Flack parameter	0.14(6)

Table S2 Bond Lengths for 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	O(2)	1.486(2)	C(2)	C(3)	1.382(5)
S(1)	N(1)	1.700(3)	C(7)	C(8)	1.526(5)
S(1)	C(9)	1.842(3)	C(10)	C(9)	1.518(5)
F(1)	C(7)	1.394(4)	C(3)	C(4)	1.377(5)
O(1)	C(8)	1.211(4)	C(9)	C(11)	1.528(5)
N(1)	C(8)	1.364(4)	C(9)	C(12)	1.520(4)
C(1)	C(2)	1.391(4)	C(6)	C(5)	1.382(5)
C(1)	C(7)	1.508(4)	C(5)	C(4)	1.380(5)
C(1)	C(6)	1.388(5)			

Table S3 Bond Angles for 4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O(2)	S(1)	N(1)	104.39(14)	O(1)	C(8)	N(1)	123.9(3)
O(2)	S(1)	C(9)	106.28(13)	O(1)	C(8)	C(7)	119.8(3)
N(1)	S(1)	C(9)	100.51(15)	N(1)	C(8)	C(7)	116.3(3)
C(8)	N(1)	S(1)	119.4(2)	C(10)	C(9)	S(1)	110.0(2)
C(2)	C(1)	C(7)	119.6(3)	C(10)	C(9)	C(11)	111.1(3)
C(2)	C(1)	C(6)	119.7(3)	C(10)	C(9)	C(12)	113.1(3)
C(6)	C(1)	C(7)	120.7(3)	C(11)	C(9)	S(1)	103.9(2)
C(3)	C(2)	C(1)	119.8(3)	C(12)	C(9)	S(1)	107.2(2)
F(1)	C(7)	C(1)	109.9(3)	C(12)	C(9)	C(11)	111.1(3)
F(1)	C(7)	C(8)	110.0(2)	C(5)	C(6)	C(1)	119.7(3)
C(1)	C(7)	C(8)	112.1(2)	C(4)	C(5)	C(6)	120.6(3)
C(4)	C(3)	C(2)	120.5(3)	C(3)	C(4)	C(5)	119.7(3)