Asymmetric organocatalytic sulfenylation for construction of diheteroatom-bearing tetrasubstituted carbon centre

Qingfa Tan, Qianping Chen, Zitong Zhu, Xiaohua Liu*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China.

E-mail: liuxh@scu.edu.cn

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1. General Information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification.

Column chromatography was generally performed on silica gel (300–400 mesh) and reactions were monitored with thin-layer chromatography (TLC) using 254 nm UV light and basic $KMnO_4$ aqueous.

NMR characterization data were collected on bruker ASCENDTM operating at 400 MHz and 600 MHz for ^{1}H NMR, 101 MHz and 151 MHz for ^{13}C{1H} NMR (with complete proton decoupling), and 376 MHz and 565 MHz for ^{19}F{1H} NMR (with complete proton decoupling). ^{1}H NMR chemical shifts were reported in ppm from tetramethylsilane with the TMS resonance as the internal standard (δ = 0.00). ^{13}C NMR spectra chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, $(CD_3)_2CO$, δ = 206.3, δ = 29.8). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.

Enantiomeric excesses (ee) were determined by supercritical fluid chromatography (SFC) analysis using the corresponding commercial chiral column as stated in the experimental procedures at 35 ºC.

Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]^T_D$ (c g/100 mL, in solvent).

High-resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z).

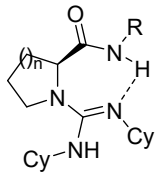
Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (ν, cm^{-1}).

All catalytic reactions were run under air conditions. Tetrahydrofuran (THF), toluene, and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Ethyl acetate (EtOAc), dichloromethane (DCM), and chloroform ($CHCl_3$) were distilled over CaH_2.

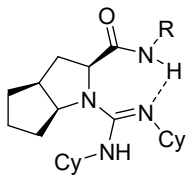
The preparation of azlactones[1-3], *N*-thiosuccinimides[4], followed the literature.

2. General procedure for the synthesis of chiral guanidines.

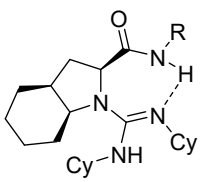
The chiral guanidines were prepared by the similar procedure in the literatures[5-6].



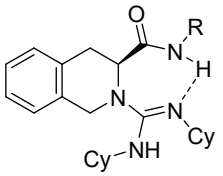
G^1-Pr-$CHPh_2$: R = $CHPh_2$, n = 1
G^1-Pi-$CHPh_2$: R = $CHPh_2$, n = 2



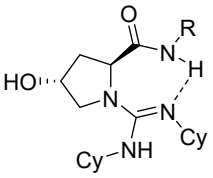
G^1-Ra-$CHPh_2$: R = $CHPh_2$



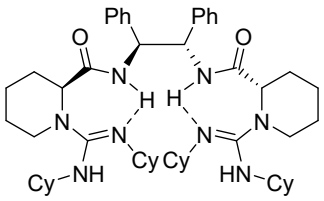
G^1-Pe-$CHPh_2$: R = $CHPh_2$



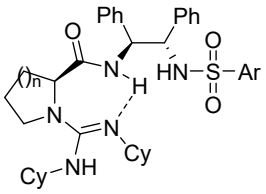
G^1-TQ-$CHPh_2$: R = $CHPh_2$



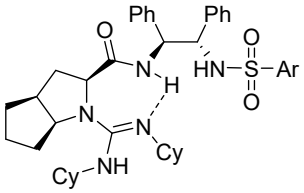
G^1-(OH)Pr-$CHPh_2$: R = $CHPh_2$



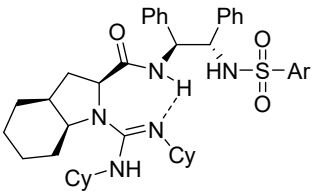
BG^1-Pi-Ph_2



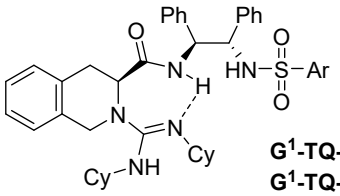
G^1-Pr-Ts: Ar = 4-MeC_6H_4, n = 1
G^1-Pr-*p*CF_3: Ar = 4-$CF_3C_6H_4$, n = 1
G^1-Pi-Ts: Ar = 4-MeC_6H_4, n = 2



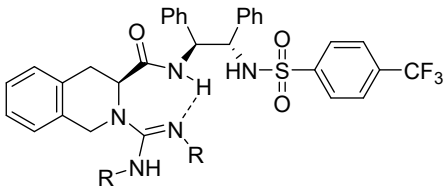
G^1-Ra-Ts: Ar = 4-MeC_6H_4
G^1-Ra-*p*CF_3: Ar = 4-$CF_3C_6H_4$



G^1-Pe-Ts: Ar = 4-MeC_6H_4
G^1-Pe-*p*CF_3: Ar = 4-$CF_3C_6H_4$

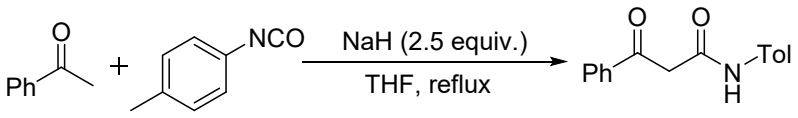


G^1-TQ-Ts: Ar = 4-MeC_6H_4
G^1-TQ-*p*CF_3: Ar = 4-$CF_3C_6H_4$
G^1-TQ-4-Br: Ar = 4-BrC_6H_4
G^1-TQ-2,4,6-iPr_3: Ar = 2,4,6-$iPr_3C_6H_2$
G^1-TQ-*p*OMe: Ar = 4-$OMeC_6H_4$
G^1-TQ-2,6-F_2: Ar = 2,6-$F_2C_6H_3$
G^1-TQ-3,5-$(CF_3)_2$: Ar = 3,5-$(CF_3)_2C_6H_3$

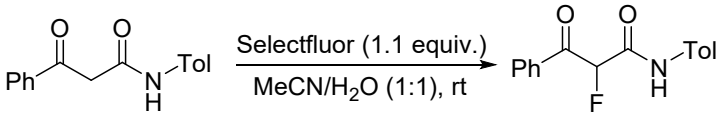


G^2-TQ-*p*CF_3: R = iPr
G^3-TQ-*p*CF_3: R =Ph

3. Typical procedure for the synthesis of β-ketoamides



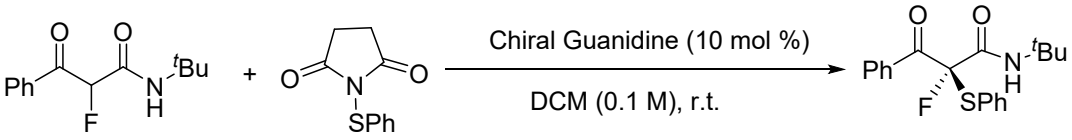
The appropriate acetophenone (10 mmol)were dissolved in dry THF at room temepreture, NaH (60% w/w dispersion in mineral oil, 25 mmol) was added to this system, then raise the temperature to 85 °C for 30 min. 1-Isocyanato-4-methylbenzene was added to the mixture for reflux 6 h. After completion, monitored by TLC (eluent: PE/AcOEt 6: 1), the mixture was cooled to 0 °C and 1 N HCl was added cautiously until the solid completely dissolved. The solution was extracted with ethyl acetate (2 x 20 mL) and the organic phase was washed with brine (20 mL), dried (Na_2SO_4) and concentrated. The resulting residue was further purified by flash column chromatography to afford the amide product.



General procedure for the synthesis of 2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide.[7] 3-Oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3 mmol) and selectfluor (3.3 mmol) were added to the solvent of CH_3CN and H_2O (v/v = 1:1, 30 mL). The mixture was sealed and then stirred at room temperature for 4 h. When the reaction was finished, the mixture was extracted by using appropriate ethyl acetate. The obtained organic phase was evaporated to remove the solvent, and the resulting residue was further purified by flash column chromatography to afford the product.

4. Optimization of reaction conditions for sulfenylation of acyclic β-ketoamides

Table S1: Screening of chiral guanidines[a].

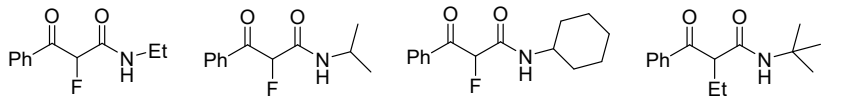


1_a **2_a** **3_a**

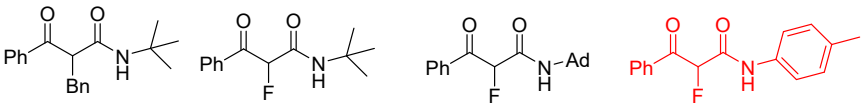
Entry[a]	Guanidine	Yield [%][b]	ee [%][c]
1	**G^1-Pr-$CHPh_2$**	64	37
2	**G^1-Pi-$CHPh_2$**	32	12
3	**G^1-(OH)Pr-$CHPh_2$**	95	9
4	**G^1-Ra-$CHPh_2$**	97	46
5	**G^1-Pe-$CHPh_2$**	98	41
6	**G^1-TQ-$CHPh_2$**	91	3
7	**G^1-Pr-Ts**	98	68
8	**G^1-Pi-Ts**	96	19
9	**G^1-Ra-Ts**	95	71
10	**G^1-Pe-Ts**	98	71
11	**G^1-Pr-*p*CF_3**	95	72
12	**G^1-TQ-*p*CF_3**	95	44
13	**G^1-TQ-*p*Br**	95	46
14	**G^1-TQ-2,4,6-iPr_3**	97	37
15	**G^1-TQ-Ts**	95	72
16	**G^1-TQ-*p*OMe**	95	29
17	**G^1-TQ-2,6-F_2**	94	50
18	**G^1-Ra-*p*CF_3**	95	74
19	**G^1-Pe-*p*CF_3**	96	70
20	**BG^1-Pi-Ph_2**	92	0

[a] Unless otherwise noted, the reactions were carried out with $\mathbf{1}_a$ (0.10 mmol), $\mathbf{2}_a$ (0.10 mmol) and the catalyst (10 mol %) in DCM (0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC.

Scheme 1: Screening of substrates[a].



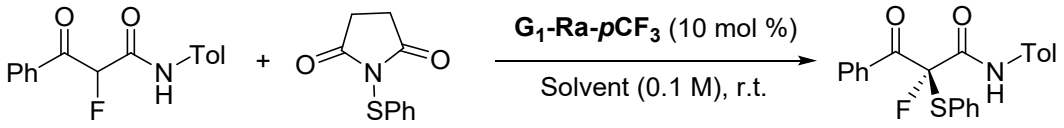
cal. pK*a* (in H_2O)	9.98	9.08	8.48	10.53
	75% yield, 73% ee	74% yield, 70% ee	57% yield, 49% ee	NR



	10.61	8.97	8.64	7.35
	NR	95% yield, 74% ee	90% yield, 78% ee	87% yield, 86% ee

[a] Unless otherwise noted, the reactions were carried out under the conditions (Table S1, entry 18), and the yield was determined by ^{1}H NMR and the ee value was determined by chiral SFC.

Table S2: Screening of solvents[a].

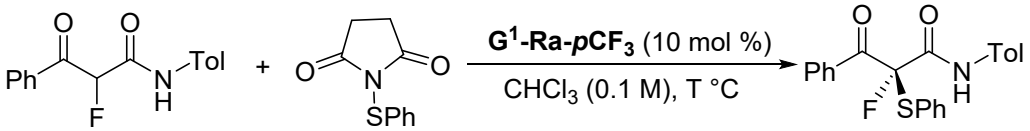


1a **2a** **3a**

Entry	Solvent	Yield [%][b]	ee [%][c]
1	DCM	87	86
2	Toluene	89	79
3	THF	91	78
4	DCE	86	84
5	1,4-dioxane	96	78
6	Et_2O	88	84
7	EtOAc	84	76
8	MTBE	96	82
9	MECN	94	34
10	$CHCl_3$	92	90

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G^1-Ra-*p*CF$_3$** (10 mol %) in solvent (0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR [c] Determined by chiral SFC.

Table S3: Screening of temperature[a].



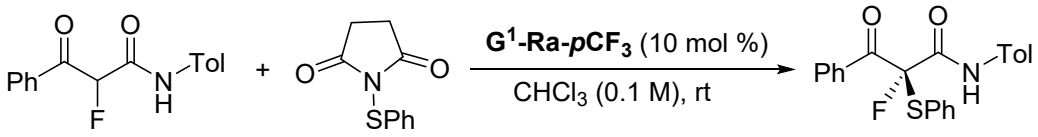
1a **2a** **3a**

Entry	T [°C]	Yield [%][b]	ee [%][c]
1[d]	-20	96	85
2	0	97	85
3	rt	90	90

4	30	93	88
5	35	88	84

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G[1]-Ra-*p*CF$_3$** (10 mol %) in $CHCl_3$ (0.1 M) at T °C for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC. [d] Reacted for 24 h.

Table S4: Screening of the substrate ratio[a].

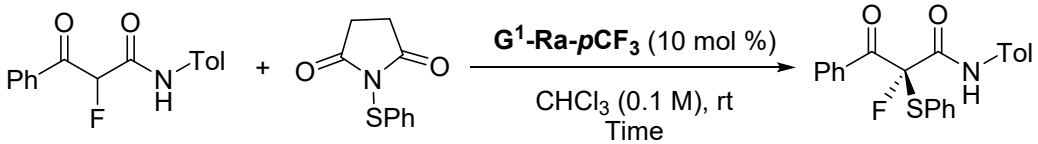


1a **2a** **3a**

Entry	**1a**: **2a**	Yield [%][b]	ee [%][c]
1	1:1.5	96	81
2	1.5:1	82	86
3	1:1	90	90
4[d]	1:1	91	86
5[e]	1:1	82	89

[a] Unless otherwise noted, the reactions were carried out with **1a**, **2a** and **G[1]-Ra-*p*CF$_3$** (10 mol %) in $CHCl_3$(0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC. [d] **G[1]-Ra-*p*CF$_3$** (5 mol %) was used. [e] **G[1]-Ra-*p*CF$_3$** (20 mol %) was used.

Table S5: Screening of the reaction time[a].



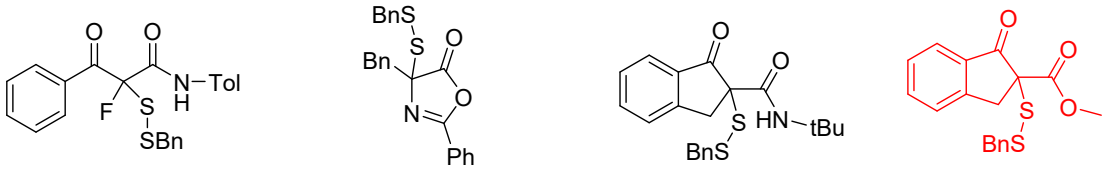
1a **2a** **3a**

Entry	Time (min)	Yield [%][b]	ee [%][c]
1	2	67	89
2	5	84	89
3	15	86	89
4	30	90	90
5	60	86	89

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol) and **G[1]-Ra-*p*CF$_3$** (10 mol %) in $CHCl_3$ (0.1 M) at rt for t minutes. [b] isolated yield. [c] Determined by chiral SFC.

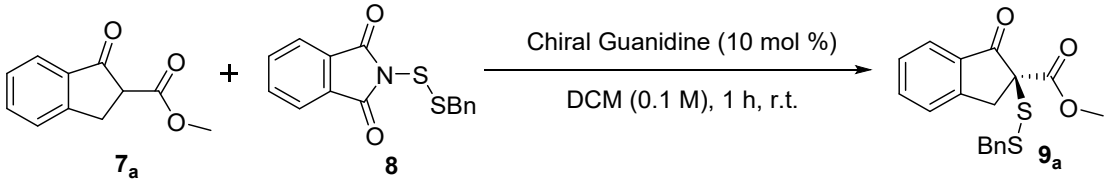
5. Optimization of reaction conditions for sulfenylation of cyclic β-ketoamides

Scheme 2: Screening of substrates[a].



[a] Unless otherwise noted, the reactions were carried out under the conditions (Table S5, entry 4), isolated yield and the ee value was determined by chiral SFC.

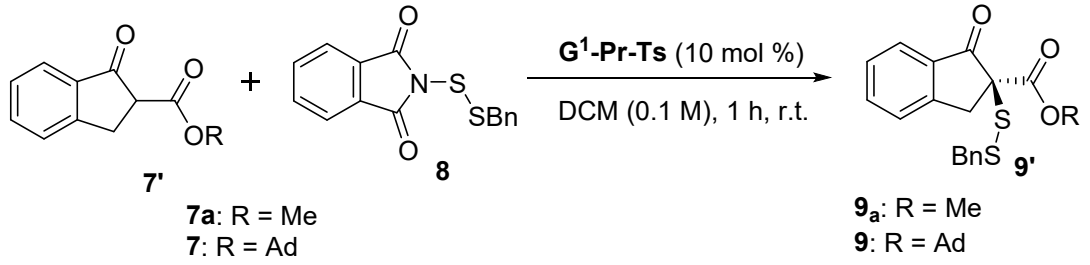
Table S6: Screening of guanidines[a].



Entry[a]	Guanidine	Yield [%][b]	ee [%][c]
1	**G^1-Pr-$CHPh_2$**	94	18
2	**G^1-Pi-$CHPh_2$**	99	16
3	**G^1-Ra-$CHPh_2$**	88	14
4	**G^1-Pe-$CHPh_2$**	99	7
5	**G^1-TQ-$CHPh_2$**	99	7
6	**G^1-Pr-Ts**	88	20
7	**G^1-Pr-2,4,6-iPr_3**	83	11
8	**G^1-Pr-*p*CF_3**	97	18
9	**G^1-Pi-Ts**	76	0
10	**G^1-Ra-Ts**	93	12
11	**G^1-TQ-Ts**	94	0
12	**BG^1-Pi-Ph_2**	88	0

[a] Unless otherwise noted, the reactions were carried out with **7_a** (0.10 mmol), **8** (0.10 mmol) and the catalyst (10 mol %) in DCM (0.1 M) at rt for 1 h. [b] Isolated yield. [c] Determined by chiral SFC.

Table S7: Screening of solvent and temperature[a].



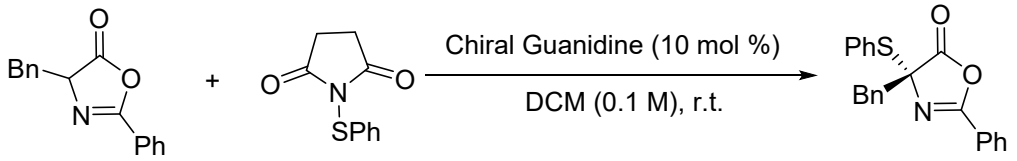
Entry	solvent	Yield [%][b]	ee [%][c]
1	DCM	88	20

2	$CHCl_3$	98	7
3	DCE	97	19
4	THF	99	14
5	1,4-dioxane	99	11
6	Toluene	88	25
7	Et_2O	87	31
8	DME	92	15
9	MTBE	94	25
10[d]	Et_2O	87	40
11[d,e]	Et_2O	trace	47
12[d,e]	Toluene	85	61
13[d,e]	Et_2O/Toluene (v/v, 1:1)	78	60

[a] Unless otherwise noted, the reactions were carried out with $\mathbf{7_a}$ (0.10 mmol), **8** (0.10 mmol) and **G[1]-Pr-Ts** (10 mol %) in solvent (0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC. [d] **7** instead of $\mathbf{7_a}$. [e] At -40 °C.

6. Optimization of reaction conditions for sulfenylation of azlactones

Table S8: Screening of guanidines[a].

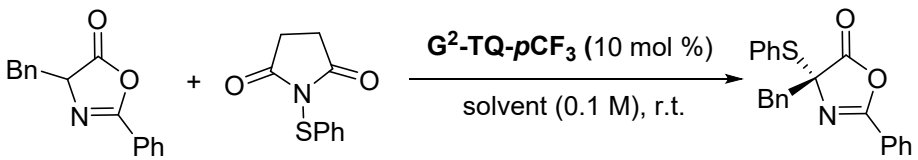


5a **2a** **6a**

Entry[a]	Guanidine	Yield [%][b]	ee [%][c]
1	**G^1-Pr-$CHPh_2$**	98	6
2	**G^1-Pi-$CHPh_2$**	94	11
3	**G^1-(OH)Pr-$CHPh_2$**	96	0
4	**G^1-Ra-$CHPh_2$**	95	＜5
5	**G^1-Pe-$CHPh_2$**	97	＜5
6	**G^1-TQ-$CHPh_2$**	96	＜5
7	**G^1-Pr-Ts**	98	25
8	**G^1-Pi-Ts**	99	10
9	**G^1-Ra-Ts**	97	25
10	**G^1-Pe-Ts**	95	23
11	**G^1-TQ-Ts**	96	43
12	**G^1-TQ-*p*Br**	97	44
13	**G^1-TQ-2,4,6-iPr_3**	97	28
14	**G^1-TQ-*p*tBu**	95	26
15	**G^1-TQ-*p*OMe**	95	40
16	**G^1-TQ-2,6-F_2**	94	42
17	**G^3-TQ-*p*CF_3**	98	0
18	**G^2-TQ-*p*CF_3**	97	49
19	**G^1-TQ-*p*CF_3**	99	45
20	**G^1-TQ-3,5-$(CF_3)_2$**	97	42
21	**G^1-Pe-*p*CF_3**	93	23
22	**BG^1-Pi-Ph_2**	98	0

[a] Unless otherwise noted, the reactions were carried out with **5a** (0.10 mmol), **2a** (0.10 mmol) and the catalyst (10 mol %) in DCM (0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC.

Table S9: Screening of solvents[a].



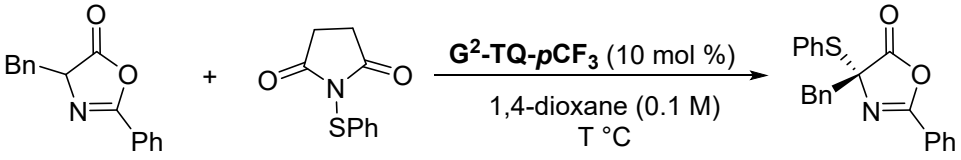
5a **2a** **6a**

Entry	Solvent	Yield [%][b]	ee [%][c]
1	DCM	96	49
2	$CHCl_3$	98	53
3	Et_2O	96	61
4	MTBE	97	64
5	1,4-dioxane	96	78

6	DME	98	60
7	DCE	99	43
8[d]	1,4-dioxane	97	69
9[e]	1,4-dioxane	96	74

[a] Unless otherwise noted, the reactions were carried out with **5a** (0.10 mmol), **2a** (0.10 mmol) and **G²-TQ-*p*CF₃** (10 mol %) in solvent (0.1 M) at rt for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC. [d] 1,4-dioxane (0.05M) .[e] 1,4-dioxane (0.2 M)

Table S10: Screening of temperature[a].

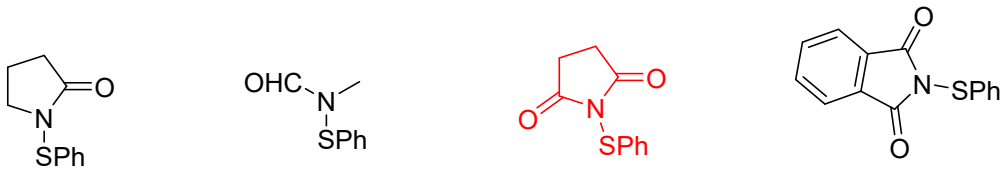


5a **2a** **6a**

Entry	T [°C]	Yield [%][b]	ee [%][c]
1	rt	96	78
2	30	98	74
3	35	98	72

[a] Unless otherwise noted, the reactions were carried out with **5a** (0.10 mmol), **2a** (0.10 mmol) and **G²-TQ-*p*CF₃** (10 mol %) in 1,4-dioxane (0.1 M) at T °C for 12 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC.

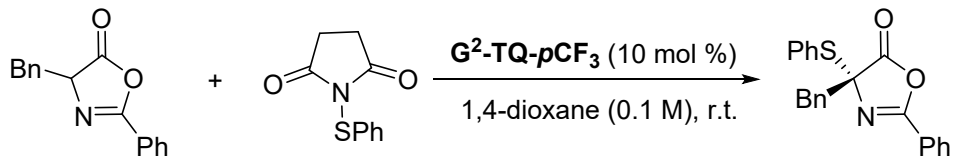
Scheme 3: Screening of sulfenyl reagents [a].



NR trace, 30% ee 96% yield, 78% ee 93% yield, 78% ee

[a] Unless otherwise noted, the reactions were carried out under the conditions (Table S10, entry 1), the yield was determined by ^{1}H NMR and the ee value was determined by chiral SFC.

Table S11: Screening of the substrate ratio and the amount of G²-TQ-4-CF₃ [a].



5a **2a** **6a**

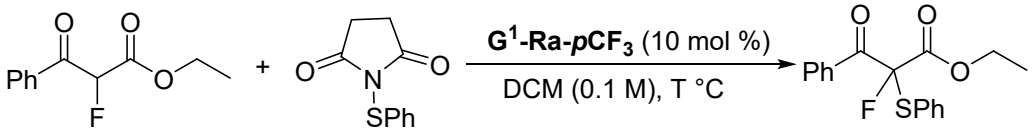
Entry	**5a** : **2a**	Yield [%][b]	ee [%][c]
1	1.2:1	99	70
2	1:1.2	99	74
3	1:1	96	78
4[d]	1:1	55	31
5[e]	1:1	99	70

6	1:1	90[f]	78
7[g]	1:1	90	78

[a] Unless otherwise noted, the reactions were carried out with **5a**, **2a** and **G²-TQ-*p*CF₃** (10 mol %) in $CHCl_3$(0.1 M) at rt for 12 h. [b] Determined by ^1H NMR. [c] Determined by chiral SFC. [d] **G²-TQ-*p*CF₃** (5 mol %) was used. [e] **G²-TQ-*p*CF₃** (20 mol %) was used. [f] Isolated yield. [g]The reaction was conducted for 3 h.

7. Optimization of reaction conditions for sulfenylation of β-ketoesters

Table S12: Screening of temperature[a].

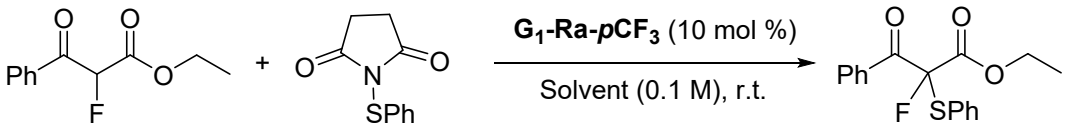


14a **2a** **15a**

Entry	T [°C]	Yield [%][b]	ee [%][c]
1[d]	-20	93	Race
2	-40	86	Race
3	-60	62	Race
4	-78	56	Race

[a] Unless otherwise noted, the reactions were carried out with **14a** (0.10 mmol), **2a** (0.10 mmol) and **G¹-Ra-*p*CF₃** (10 mol %) in $CHCl_3$ (0.1 M) at T °C for 24 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC.

Table S13: Screening of solvents[a].

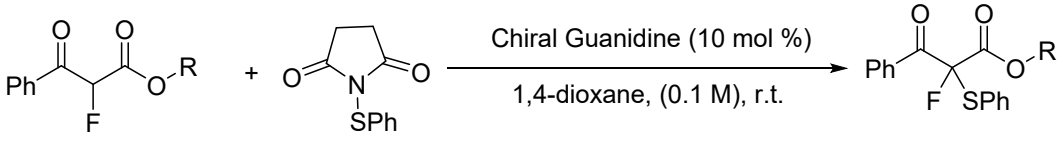


14a **2a** **15a**

Entry	Solvent	Yield [%][b]	ee [%][c]
1	DCM	99	Race
2	Toluene	87	8
3	THF	92	<5
4	1,4-dioxane	85	9
5	Et_2O	82	9
6	EtOAc	83	<5
7	MTBE	72	7
8	MECN	95	Race
9	$CHCl_3$	64	<5
10[d]	Et_2O	36	9

[a] Unless otherwise noted, the reactions were carried out with **14a** (0.10 mmol), **2a** (0.10 mmol) and **G¹-Ra-*p*CF₃** (10 mol %) in solvent (0.1 M) at rt for 4 h. [b] Determined by ^{1}H NMR [c] Determined by chiral SFC. [d] At -40°C for 24 h.

Table S14: Screening of guanidines[a].



14a: R = Et
14b: R = ^{t}Bu

2a

15a: R = Et
15b: R = ^{t}Bu

Entry[a]	Guanidine	Yield [%][b]	ee [%][c]

1	**G^1-Pr-$CHPh_2$**	78	<5
2	**G^1-Pi-$CHPh_2$**	72	<5
3	**G^1-Ra-$CHPh_2$**	81	<5
4	**G^1-TQ-$CHPh_2$**	37	<5
5	**G^1-Pr-Ts**	69	10
6	**G^1-Pi-Ts**	63	<5
7	**G^1-Ra-Ts**	76(69)[d]	11
8	**G^1-Ra-*p*CF_3**	85	9
9	**BG^1-Pi-Ph_2**	76	<5
10[e]	**G^1-Ra-Ts**	61	19

[a] Unless otherwise noted, the reactions were carried out with **14a** (0.10 mmol), **2_a** (0.10 mmol) and the catalyst (10 mol %) in 1,4-dioxane (0.1 M) at rt for 4 h. [b] Determined by ^{1}H NMR. [c] Determined by chiral SFC. [d] Isolated yield. [e] **14b** instead of **14a**.

8. General procedure for the catalytic reactions

1. General procedure for the catalytic asymmetric reaction with ketoamide (synthesis of 3a-3s, 4a-4s):

A dry reaction tube was charged with α-fluoro-β-ketoamide **1** (0.1 mmol) **G^1-Ra-*p*CF_3** (10 mol %), *N*-thiosuccinimide **2** (0.1 mmol) and $CHCl_3$ (1.0 mL). The mixture was stirred at room temperature and detected by TLC. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 4:1, as eluent) to afford the desired product. (The desired product **4t-4v** were obtained with dichloromethane as solvent).

2. General procedure for the catalytic asymmetric reaction of azlactone (synthesis of 6a-6e):

A dry reaction tube was charged with azlactone **5** (0.1 mmol), **G^2-TQ-*p*CF_3** (10 mol %), *N*-thiosuccinimide **2a** (0.1 mmol) and 1,4-dioxane (1.0 mL). The mixture was stirred at room temperature and detected by TLC. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 2:1, as eluent) to afford the desired product.

3. General procedure for the catalytic asymmetric disulfuration reaction with ketoester (synthesis of 9):

A dry reaction tube was charged with β-ketoester **7** (0.1 mmol), **G^1-Pr-Ts** (10 mol %), 2-(benzyldisulfanyl)isoindoline-1,3-dione **8** (0.1 mmol) and toluene (1.0 mL). The mixture was stirred at -40 ℃ after 24 hours. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as eluent) to afford the desired product.

4. General procedure for the catalytic asymmetric sulfenylation reaction (synthesis of 15a-15b):

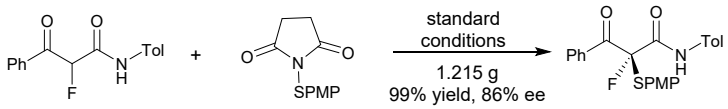
A dry reaction tube was charged with azlactone β-ketoester (0.1 mmol), **G^1-Ra-Ts** (10 mol %), *N*-thiosuccinimide **2a** (0.1 mmol) and 1,4-dioxane (1.0 mL). The mixture was stirred at room temperature and detected by TLC. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, as eluent) to afford the desired product.

5. General procedure for the synthesis of racemic products

A dry reaction tube was charged with α-fluoro-β-ketoamide **1** (0.1 mmol), 1,1,3,3-tetramethylguanidine (10 mol %), *N*-thiosuccinimide **2** (0.1 mmol) and DCM (1.0 mL). The mixture was stirred at room temperature and detected by TLC. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 4:1, as eluent) to afford the desired product (**3a-3s, 4a-4v**).

A dry reaction tube was charged with azlactone **5** (0.1 mmol), 1,1,3,3-tetramethylguanidine (10 mol %), *N*-thiosuccinimide **2a** (0.1 mmol) and 1,4-dioxane (1.0 mL). The mixture was stirred at room temperature and detected by TLC. After completion, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 2:1, as eluent) to afford the desired product (**6a-6e**).

9. Experimental Procedure for the Gram-Scale Reaction and Transformations of the Products

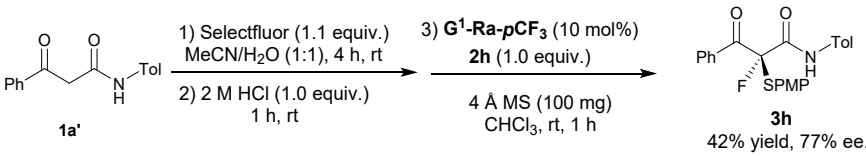


1a
3.0 mmol

2h
3.0 mmol

3h
87% yield, 99% ee.
(after recrystallization)

An over dried test tube was charged with **G[1]-Ra-*p*CF$_3$** (0.3 mmol, 10 mol%), **1a** (3.0 mmol), **2h** (3.0 mmol) and $CHCl_3$ (0.1 M). Then, the reaction mixture was stirred at room temperature for 1 hours and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the enantioenriched product **3h** (1.215 g, 99% yield, 86% ee), then recrystallized by dichloromethane/petroleum ether to afford the purified product (87% yield, 99% ee).



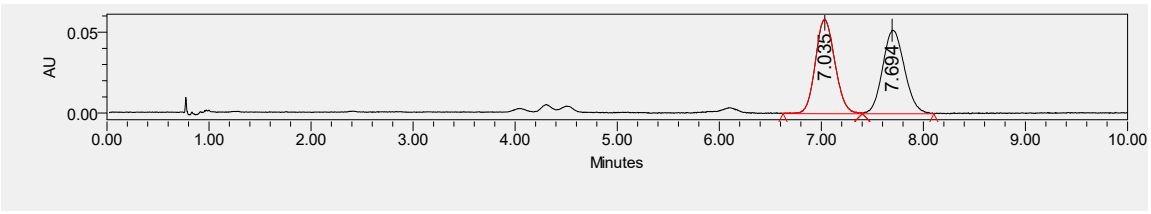
1a'

3h
42% yield, 77% ee.

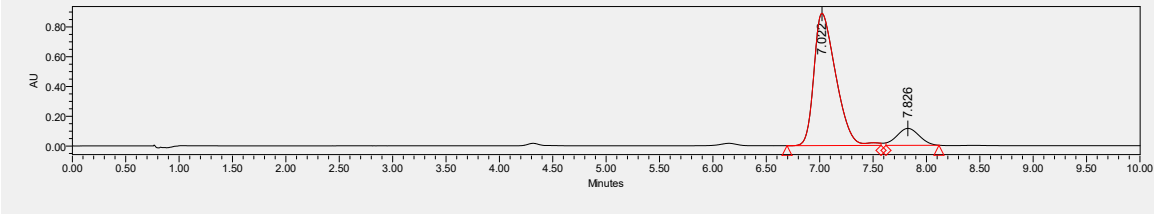
Cascade procedure for the synthesis of product 10: An over dried test tube was charged with **1a'** (0.1 mmol), selectfluor (0.11 mmol) and the solvent of CH_3CN and H_2O (v/v = 1:1, 1.0 mL). Then, the reaction mixture was stirred at room temperature for 4 hours and detected by TLC. After the reaction was completed, 2 M HCl was added to the above system for another 1 hours. The solvent was evaporated and drained, **G[1]-Ra-*p*CF$_3$** (0.01 mmol, 10 mol%), **2h** (0.1 mmol), 4 Å MS (100 mg) and $CHCl_3$ (0.1 M) were added to the tese tube for 1 hours. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the enantioenriched product **3h** (42% yield, 77% ee). (The lower result could be related to the residual water in the system)

colerless oil, 42% yield, 77% ee; $[\alpha]^{24}_D$ = -118.5 (*c* 0.33, CH_2Cl_2).

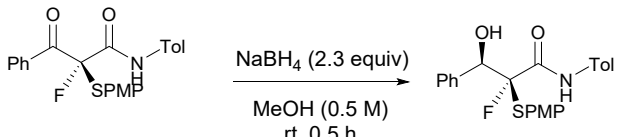
SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 7.02 min, t_2 = 7.83 min



	Retention Time	Area	% Area
1	7.035	774709	50.24
2	7.694	767208	49.76



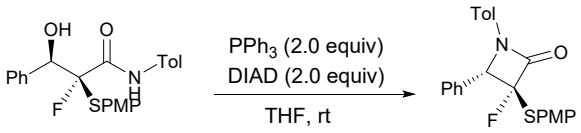
	Retention Time	Area	% Area
1	7.022	12659798	88.42
2	7.826	1657364	11.58



3h
87% yield, 99% ee.
(after recrystallization)

10
98% yield
99/99% ee, 78:22 dr.

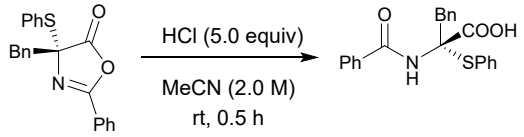
An oven-dried test tube was charged with **3h** (0.2 mmol, 81.8 mg, 99% ee) and MeOH (0.5 M) followed by adding $NaBH_4$ (2.3 equiv). The reaction mixture was stirred at room temperature for 0.5 hour and detected by TLC. After the reaction was completed, the reaction was quenched with H_2O (5 mL) and extracted with DCM (2×10 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 3:1) to afford the desired product **10** (80.2 mg, 98% yield, 99%/99% ee, 78:22 dr)



10
99%/99% ee, 78:22 dr.

11
71% yield, 99% ee
>19:1 dr.

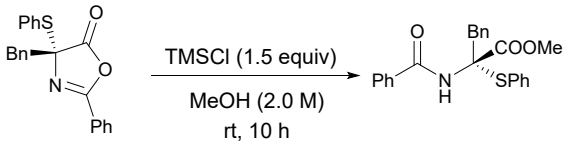
An oven-dried test tube was charged with **10** (0.1 mmol, 99%/99% ee, 78:22 dr), PPh_3 (2.0 equiv) and THF (1.0 mL) under N_2 atmosphere. After this procedure, cooling this system to 0 ℃, DIAD (2.0 equiv) in THF (1.0 ml) was added into the tube and the resulting solution was stirred at 0 ℃ for 30 min. the reaction was stirred at room temperature overnight. After the reaction was completed, the solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 8:1) to afford the desired product **11** (24.3. mg, 71% yield, 99% ee, >19:1 dr).



6a
78% ee

12
98% yield, 78% ee.

A sample vial (4.0 mL) equipped with a magnetic stirring bar was charged with CH_3CN (2.0 M) and the adduct **6a** (35.9 mg, 0.1 mmol). HCl (5.0 equiv, conc.) was then added in one portion. The stirring was maintained at room temperature until consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (PE/acetone = 1/1) to give the compound **12** as a white solid in 98% yield (35.2 mg) and 78% ee.



6a
78% ee

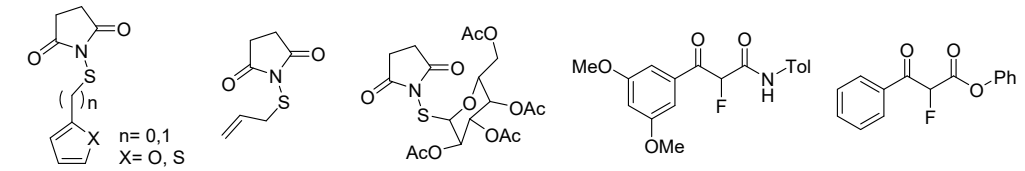
13
83% yield, 75% ee.

A sample vial (4.0 mL) equipped with a magnetic stirring bar was charged with MeOH (2.0 M) and

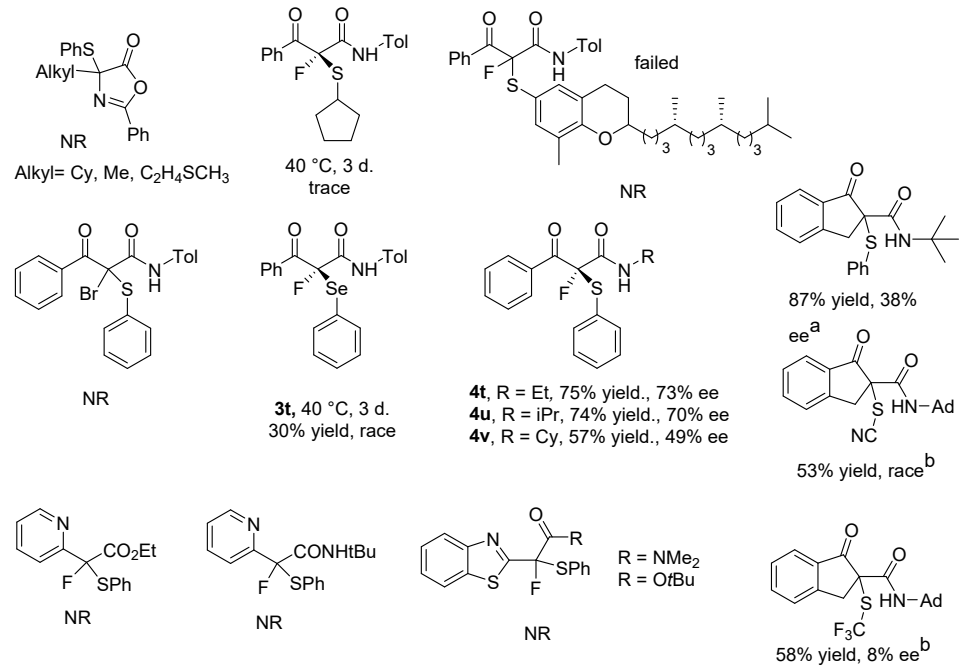
the adduct **6a** (35.9 mg, 0.1 mmol). TMSCl (1.5 equiv) was subsequently added in one portion. The stirring was maintained at room temperature until consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (PE/EtOAc = 3/1) to give compound **13** as a white solid in 83% yield (29.8 mg) and 75% ee.

10. Failed substrates and unsuccessful substrates

Failed sulfur-reagents and nucleophiles



Unsuccessful Products



[a] The reaction was carried out under the conditions (Table S1, entry 18), [b] the reactions were carried out with substrate and **G[1]-Pr-Ts** (10 mol %) in toluene (0.1 M) at -40 °C for 24 h

11. X-ray crystal data

The absolute configuration of the optically active product **3h** was determined by X-ray chromatography analysis.

Single crystal of **3h** was obtained by recrystallization in dichloromethane and petroleum ether at room temperature.

The crystal data and further details are listed in Table S12.

CCDC 2133030 (**3h**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless and block-shape crystals were selected and mounted for the single-crystal X-ray diffraction. The data set was collected by a Bruker D8 Venture Photon II at 170K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a, b, c]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[d].

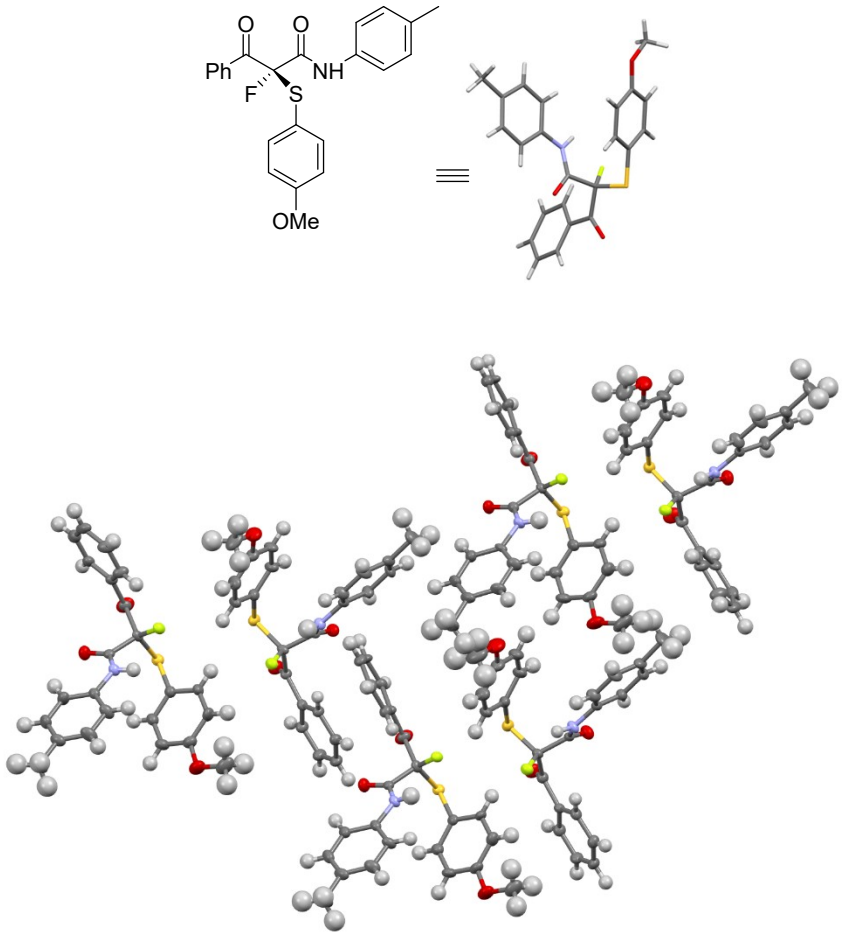


Figure S1. The thermal ellipsoid figure of **3h** with 50% probabilities

The structure of the catalyst **11** was determined by X-ray chromatography analysis.

Single crystal of **11** was obtained by recrystallization in dichloromethane and petroleum ether at room temperature.

The crystal data and further details are listed in Table S12.

CCDC 2155953 (**11**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless and plate-shape crystals were selected and mounted for the single-crystal X-ray diffraction. The data set was collected by a Bruker D8 Venture Photon II at 150(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package[a, b, c]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[d].

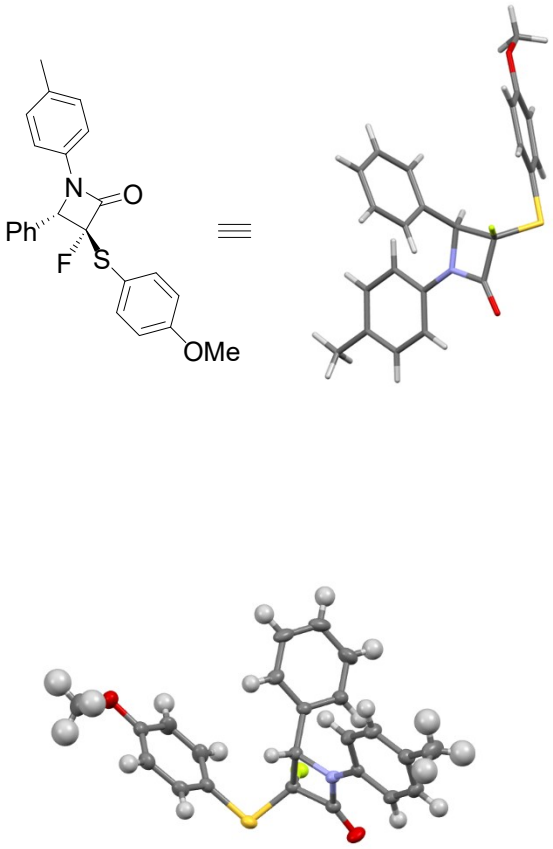


Figure S2. The thermal ellipsoid figure of **11** with 50% probabilities

The structure of product **12** was determined by X-ray chromatography analysis.

A single crystal of **12** was obtained by recrystallization in dichloromethane and petroleum ether at room temperature.

The crystal data and further details are listed in Table S12.

CCDC 2155952 (**12**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless and block-shape crystals were selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 140(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package[a, b, c]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[d].

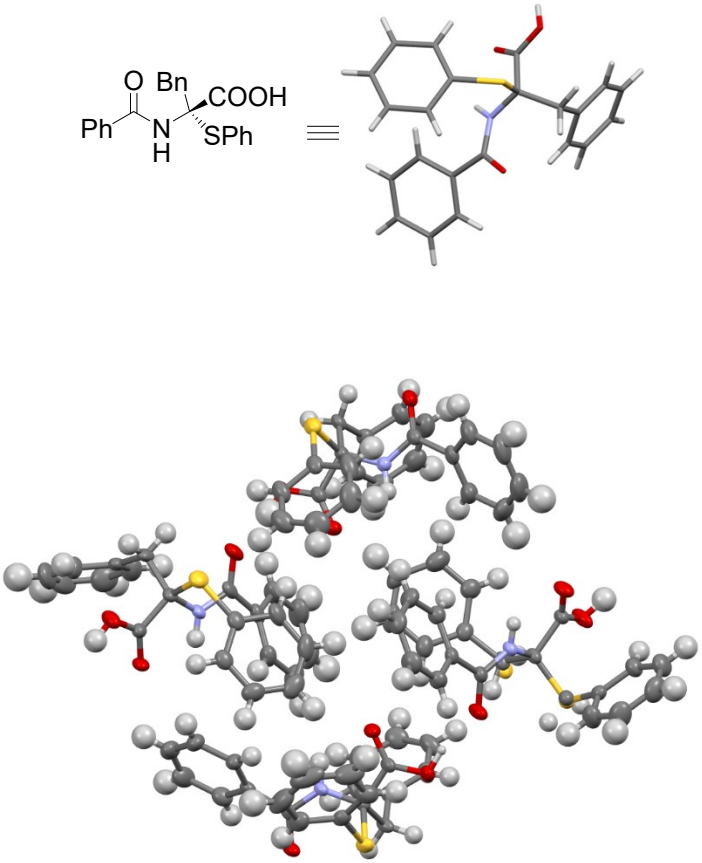


Figure S3. The thermal ellipsoid figure of **12** with 50% probabilities

Table S12. Crystallographic Data for $C_{23}H_{20}FNO_3S$ (**3h**), $C_{25}H_{22}FNO_2S$ (**11**), $C_{22}H_{19}NO_3S$ (**12**).

Formula	$C_{23}H_{20}FNO_3S$ (**3h**)	$C_{23}H_{20}FNO_2S$ (**11**)	$C_{22}H_{19}NO_3S$ (**12**)
Formula mass (amu)	409.11	393.12	377.11
Space group	P 21	P 21	P 1
a (Å)	18,3227(8)	9.7902(2)	11.3514(3)
c (Å)	6.1273(3)	8.5037(2)	13.3056(4)
c (Å)	54.463(2)	11.6291(3)	14.4521(4)
α (deg)	90	90	72.846(2)
β (deg)	92.615(2)	93.196(1)	79.748(2)
γ (deg)	90	90	68.951(2)
V (Å^3)	6108.1(5)	966.65(4)	1940.17(10)
Z	2	2	1
λ (Å)	1.54178	1.54178	1.54178
T (K)	173 K	173 K	173 K
ρ_{calcd} (g cm^{-3})	1.336	1.352	1.292
μ (mm^{-1})	1.696	1.723	1.659
Transmission factors	0.491, 1.000	0.653, 1.000	0.709, 0.879
$2\theta_{max}$ (deg)	68.377	68.272	68.413
No. of unique data, including $F_o^2 < 0$	21322	3461	13203
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	15316	2770	12237
No. of variables	1604	255	1017
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0816	0.0284	0.0359
$R_w(F_o^2)$ [b]	0.2070	0.0728	0.0787
Goodness of fit	1.045	1.050	1.066

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

References:

[a] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

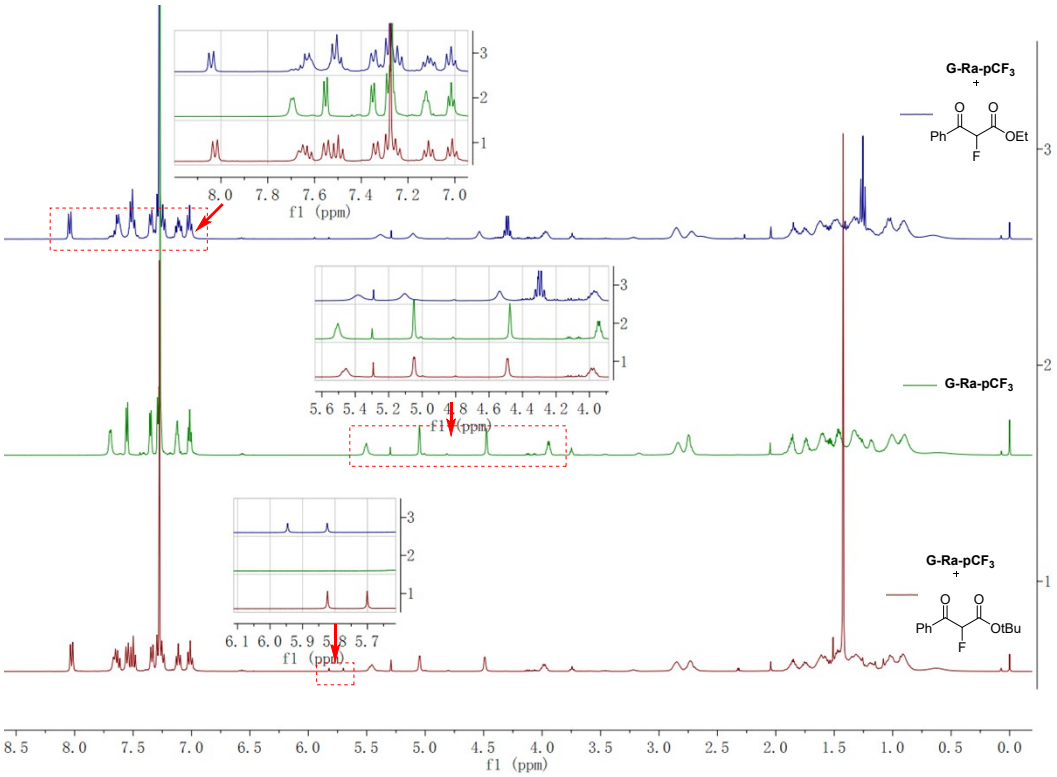
[b] Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.

[c] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3–8.

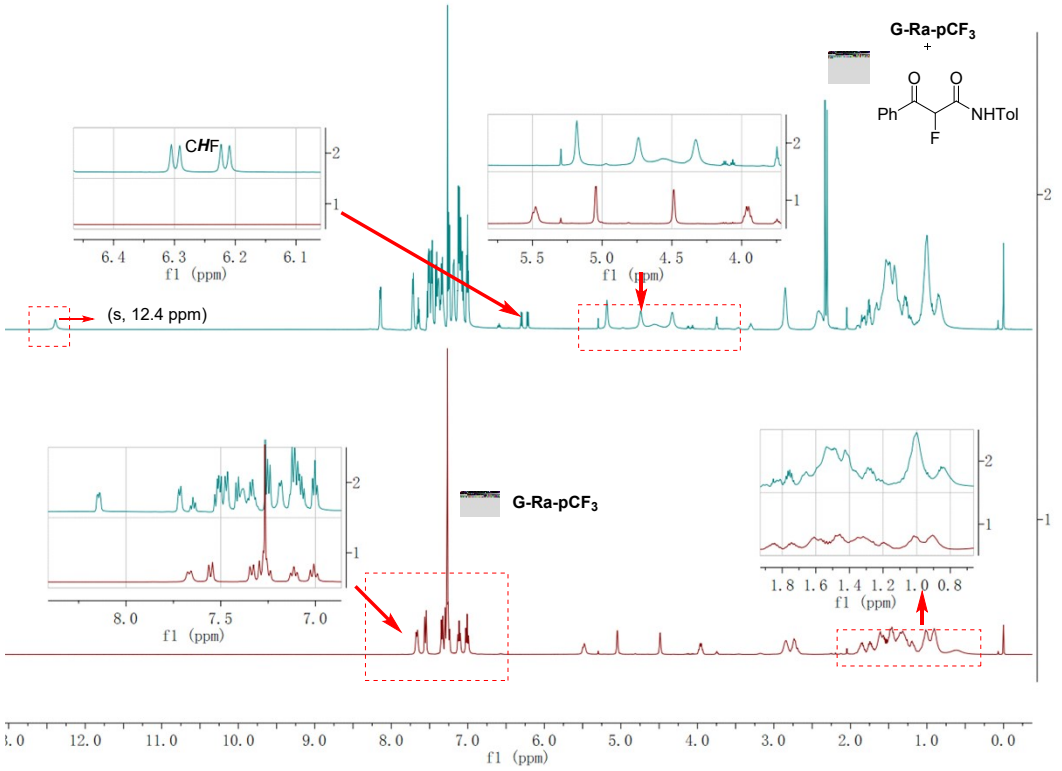
[d] Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7–13.

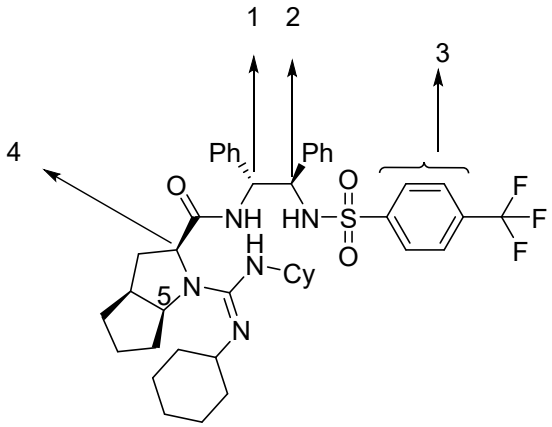
12. The NMR study of substrate and G-Ra-*p*CF_3

We performed NMR spectra analysis to probe into the decrease reactivity and enantioselectivity. And it manifested that there is less interaction of the catalyst with tert-butyl α-fluoro-β-ketoester (red vs. green), and weak interaction with ethyl α-fluoro-β-ketoester (blue vs. green), which might be the inefficiency of our catalyst system.



The interaction between α-fluoro-β-ketoamide and the catalyst is strong from the NMR analysis (green vs. red). The alkyl substitution at amidine unit has down-field shift, and protons related to stereogenic carbon centers of the catalyst also exhibit obvious chemical shift. The CHF proton shows new split and obvious NH peak at 12.4 ppm indicates strong intermolecular hydrogen-bonding.



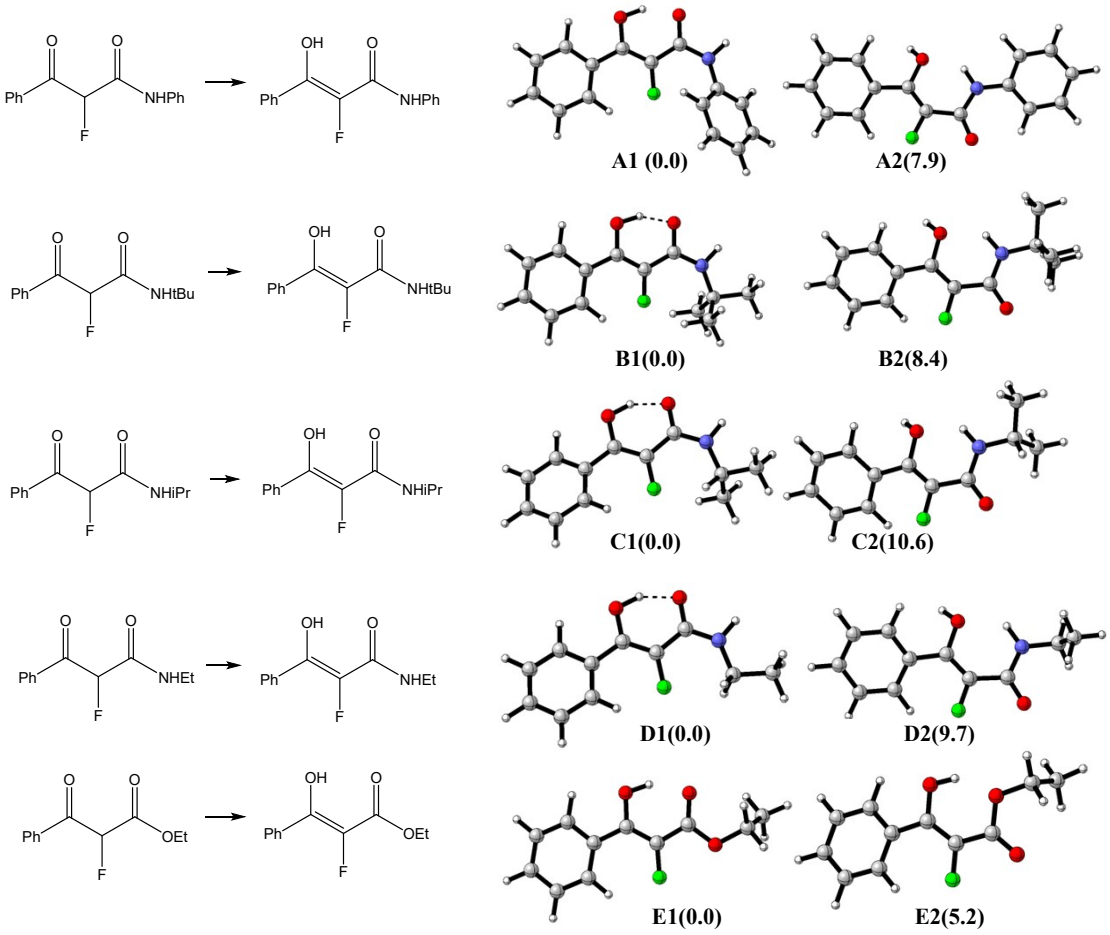


	G-Ra-*p*CF$_3$/ppm	**G-Ra-*p*CF$_3$** : OEt (1:1) / ppm	**G-Ra-*p*CF$_3$** : OtBu (1:1) / ppm	**G-Ra-*p*CF$_3$** : NHTol (1:1) / ppm
1	5.04	5.10	5.04	4.74
2	4.48	4.54	4.49	4.33
3	7.54-7.68	7.50-7.64	7.54-7.67	7.63-7.72
4	5.46-5.50	5.38	5.45-5.48	5.18
5	3.94	3.98	3.99	4.55

The changes of chemical shifts after the interaction of **G-Ra-*p*CF$_3$** with substrates in $CDCl_3$.

It indicated that the interaction between α-fluoro-β-ketoamide and the catalyst is stronger than α-fluoro-β-ketoester with the catalyst.

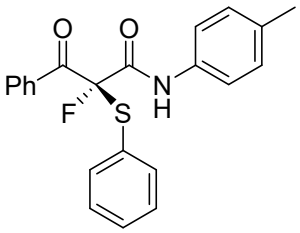
13. Comparison of enolization intermediates with different substrates



It showed that the formation of intramolecular H-bond is more stable, but the ester substituent has stronger steric hindrance closer to the carbonyl group compared with amide substituent.

14. Characterization of the products

(*S*)-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)-*N*-(*p*-tolyl)propanamide (3a):



yellow oil, 90% yield, 90% ee; $[\alpha]^{22}_D$ = -92.8 (*c* 0.61, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 5.14 min, t_2 = 5.99 min.

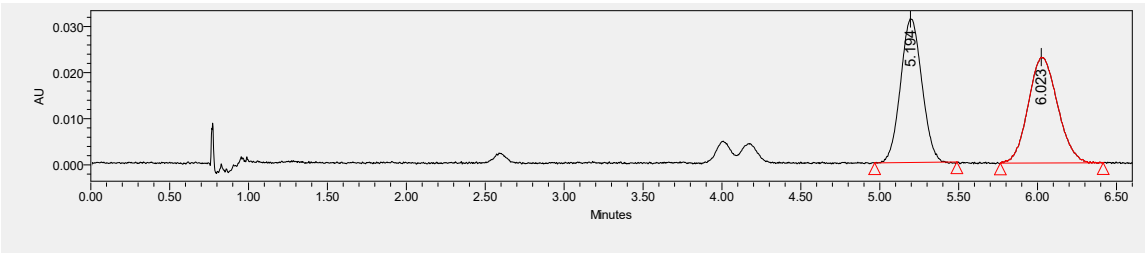
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.99 (m, 2H), 7.78 (s, 1H), 7.63 – 7.54 (m, 3H), 7.46 – 7.36 (m, 3H), 7.34 – 7.27 (m, 2H), 7.18 – 7.12 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0 (d, *J* = 25.8 Hz), 161.4 (d, *J* = 26.2 Hz), 136.5, 135.2, 134.3, 133.6, 133.3 (d, *J* = 2.8 Hz), 130.4, 130.2 (d, *J* = 4.3 Hz), 129.6, 129.3, 128.6, 127.1, 120.2, 107.2 (d, *J* = 246.5 Hz), 20.9.

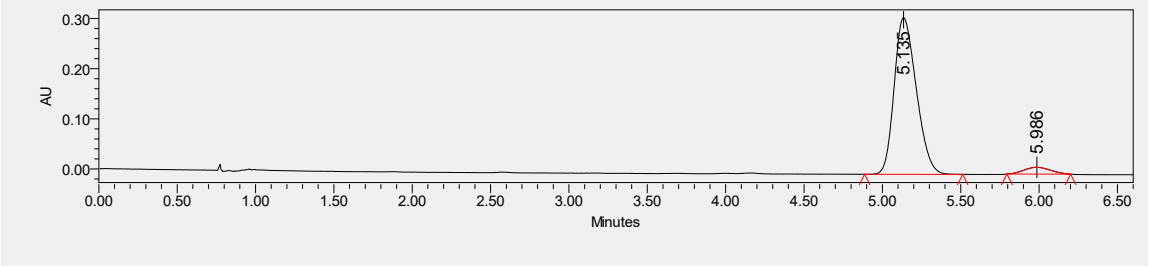
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −128.52. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{18}FNO_2S$ ([M]+Na^+) = 402.0934, Found 402.0931

IR (neat) 3324, 2922, 1697, 1597, 1522, 1446, 1407, 1317, 1249, 1186, 1028, 815, 691, 505 cm^{-1}.

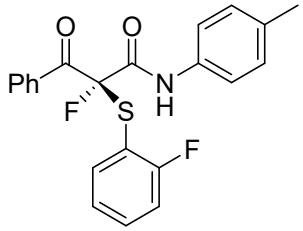


	Retention Time	Area	% Area
1	5.194	293716	49.84
2	6.023	295565	50.16



	Retention Time	Area	% Area
1	5.135	3065556	95.05
2	5.986	159687	4.95

(*S*)-2-fluoro-2-((2-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3b):



white solid, m.p. 103–106 ºC, 74% yield, 80% ee; $[\alpha]^{22}_{D}$ = -69.5 (*c* 1.21, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 11.31 min, t_2 = 12.13 min

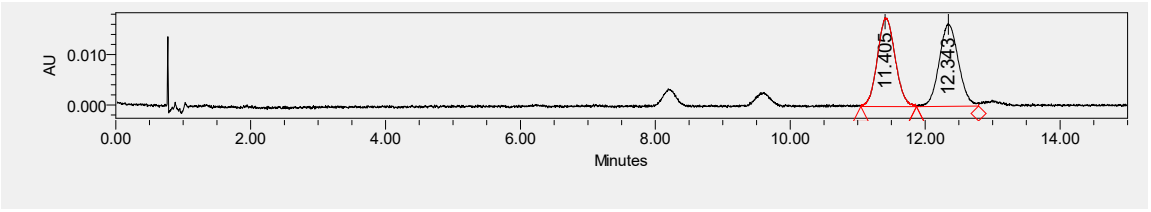
^{1}H NMR (400 MHz, $CDCl_3$) 8.02 (d, *J* = 8.5 Hz, 2H), 7.90 (s, 1H), 7.55 – 7.48 (m, 2H), 7.39 – 7.28 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.03 – 6.96 (m, 4H), 2.21 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.0 (d, *J* = 25.8 Hz), 163.6 (d, *J* = 250.5 Hz), 161.2 (d, *J* = 26.7 Hz), 139.1, 135.2, 134.5, 133.6, 133.1 (d, *J* = 8.4 Hz), 133.0 (d, *J* = 2.7 Hz), 130.3 (d, *J* = 4.4 Hz), 129.6, 128.6, 124.9 (d, *J* = 4.2 Hz), 120.2, 116.4 (d, *J* = 23.2 Hz), 114.1 (d, *J* = 18.5 Hz), 106.8 (d, *J* = 248.5 Hz), 20.9.

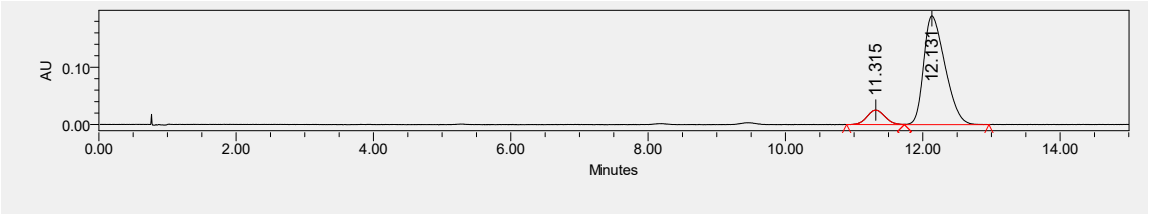
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –104.58. (s, 1F), –129.79. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{17}F_2NO_2S$ ([M]+Na^+) = 420.0840, Found 420.0837

IR (neat) 3325, 3068, 1696, 1597, 1522, 1474, 1447, 1317, 1256, 1187, 1029, 820, 692, 508 cm^{-1}.

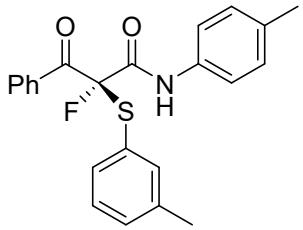


	Retention Time	Area	% Area
1	11.405	324093	49.87
2	12.343	325803	50.13



	Retention Time	Area	% Area
1	11.315	455835	10.02
2	12.131	4091497	89.98

(*S*)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-(*m*-tolylthio)propanamide (3c):



Yellow solid, m.p. 118–123 ºC, 89% yield, 89% ee; $[\alpha]^{21}_{D}$ = -88.7 (*c* 0.73, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 11.90 min, t_2 = 14.17 min

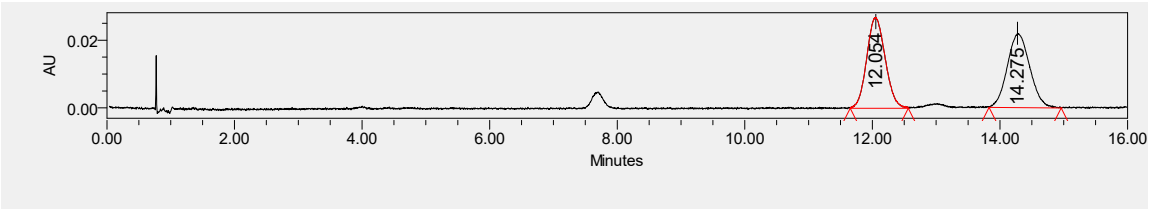
^{1}H NMR (600 MHz, $CDCl_3$) 8.07 (d, *J* = 8.5 Hz, 2H), 7.77 (s, 1H), 7.60 – 7.56 (m, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.38 (s, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 2.29 (s, 3H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.0 (d, *J* = 25.9 Hz), 161.6 (d, *J* = 27.0 Hz), 139.3, 137.2, 135.1, 134.2, 133.6, 133.5, 133.3 (d, *J* = 2.1 Hz), 131.2, 130.22 (d, *J* = 4.2 Hz), 129.5, 129.1, 128.6, 126.7, 120.2, 107.2 (d, *J* = 247.3 Hz), 21.1, 20.9.

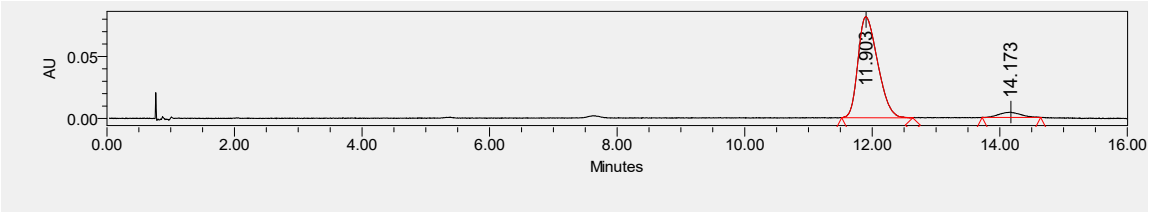
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –128.56. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{20}FNO_2S$ ([M]+Na^+) = 416.1091, Found 416.1088

IR (neat) 3329, 2921, 1681, 1596, 1519, 1475, 1407, 1245, 1186, 1029, 814, 781, 690, 507 cm^{-1}.

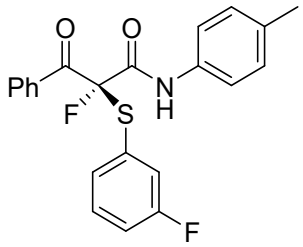


	Retention Time	Area	% Area
1	12.054	540520	50.24
2	14.275	535257	49.76



	Retention Time	Area	% Area
1	11.903	1745882	94.61
2	14.173	99413	5.39

(*S*)-2-fluoro-2-((3-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3d):



colerless oil, 49% yield, 88% ee; $[\alpha]^{18}_{D}$ = -110.3 (*c* 0.50, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 10.30 min, t_2 = 13.45 min

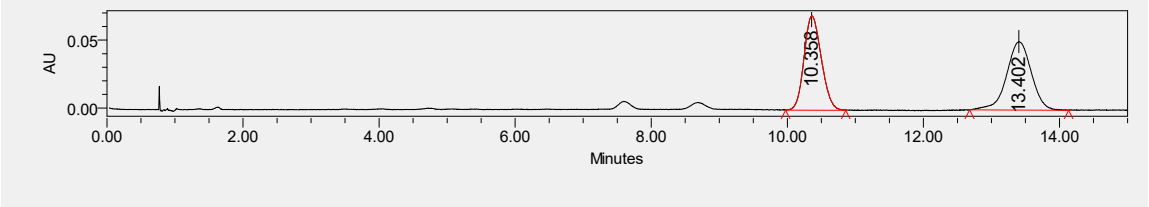
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.84 (s, 1H), 7.63 – 7.57 (m, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.40 – 7.22 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 3H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.6 (d, *J* = 25.4 Hz), 162.3 (d, *J* = 251.5 Hz), 161.1 (d, *J* = 26.4 Hz), 135.4, 134.5, 133.4, 133.1 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 3.6 Hz), 130.6, 130.5, 130.2 (d, *J* = 4.2 Hz), 129.6, 129.0 (d, *J* = 7.7 Hz), 128.7, 123.2 (d, *J* = 22.0 Hz), 120.3, 120.2, 117.6 (d, *J* = 21.0 Hz), 107.2 (d, *J* = 247.1 Hz), 20.9.

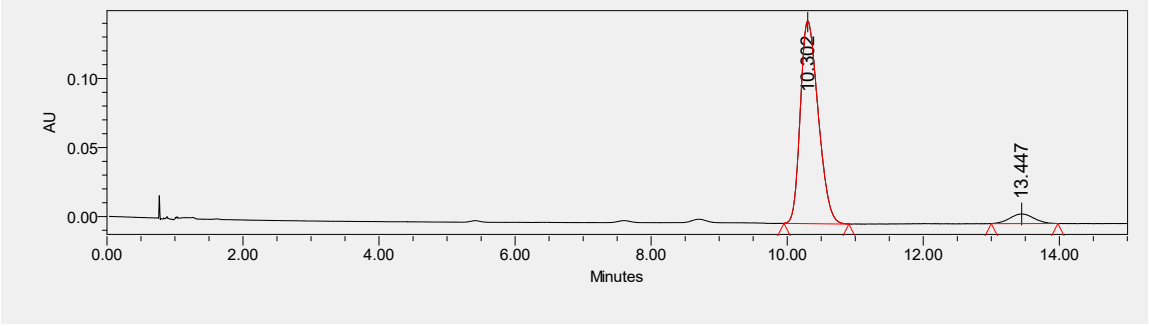
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –110.96. (s, 1F), –128.52. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{17}F_2NO_2S$ ([M]+Na^+) = 420.0840, Found 420.0836.

IR (neat) 3285, 1775, 1705, 1596, 1522, 1474, 1426, 1319, 1244, 1181, 1027, 816, 684, 511 cm^{-1}.

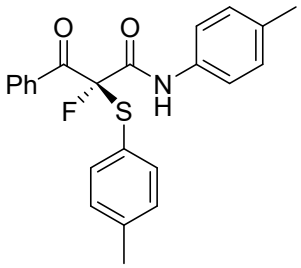


	Retention Time	Area	% Area
1	10.358	1225385	49.11
2	13.402	1269609	50.89



	Retention Time	Area	% Area
1	10.302	2672421	93.98
2	13.447	171286	6.02

(*S*)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-(*p*-tolylthio)propanamide (3e):



Colorless oil, 84% yield, 89% ee; $[\alpha]^{22}_{D}$ = -76.8 (*c* 1.17, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 14.35 min, t_2 = 16.87 min

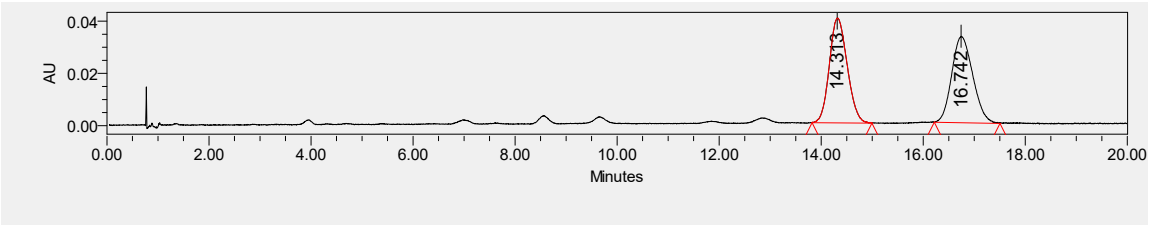
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 3.1 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.08 (dd, *J* = 15.2, 8.0 Hz, 4H), 2.31 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.2 (d, *J* = 26.1 Hz), 161.6 (d, *J* = 26.3 Hz), 140.8, 136.5, 135.1, 134.2, 133.7, 133.3 (d, *J* = 3.0 Hz), 130.3, 130.3 (d, *J* = 4.3 Hz), 129.5, 128.5, 123.4, 120.2, 107.20 (d, *J* = 246.2 Hz), 21.3, 20.9.

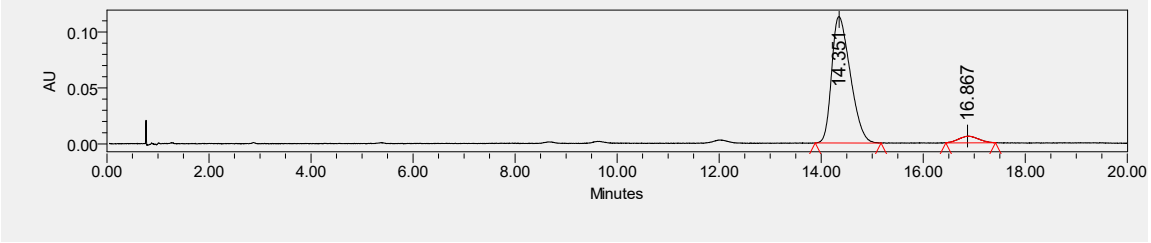
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –128.99. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{20}FNO_2S$ ([M]+Na^+) = 416.1091, Found 416.1086

IR (neat) 3331, 2921, 1681, 1597, 1519, 1448, 1405, 1244, 1185, 1025, 810, 692, 506 cm^{-1}.

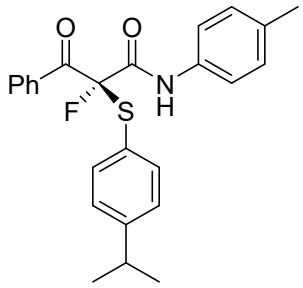


	Retention Time	Area	% Area
1	14.313	971899	50.70
2	16.742	944965	49.30



	Retention Time	Area	% Area
1	14.351	2861220	94.66
2	16.867	161312	5.34

(*S*)-2-fluoro-2-((4-isopropylphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3f):



white solid, m.p. 53–55 ºC, 96% yield, 91% ee; $[\alpha]^{21}_{D}$ = -103.6 (*c* 1.30, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 12.55 min, t_2 = 18.09 min

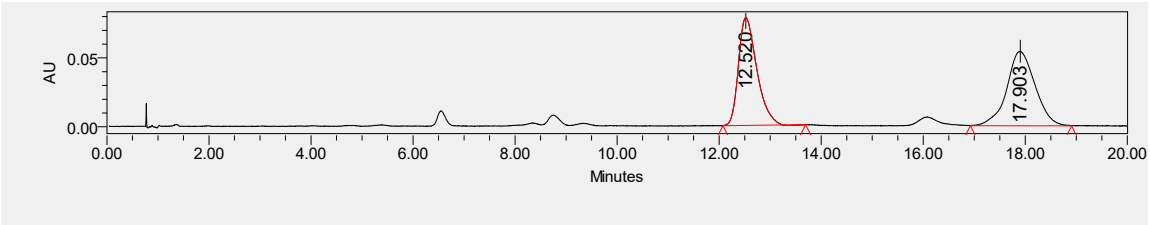
^{1}H NMR (600 MHz, $CDCl_3$)δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.72 (s, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 2.86 (p, *J* = 6.9 Hz, 1H), 2.28 (s, 3H), 1.19 (dd, *J* = 6.9, 2.8 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.0 (d, *J* = 26.1 Hz), 161.6 (d, *J* = 26.2 Hz), 151.6, 136.8, 135.1, 134.2, 133.6, 133.4 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 4.2 Hz), 130.1, 129.5, 128.6, 127.6, 123.8, 120.2, 107.3 (d, *J* = 246.4 Hz), 34.0, 23.8, 23.7, 20.9.

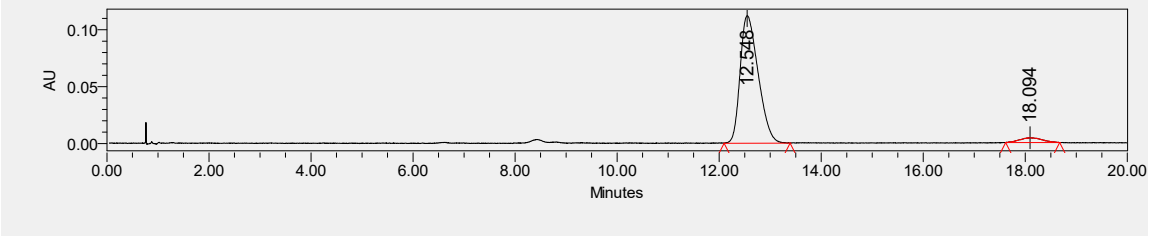
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −128.22. (s, 1F).

HRMS (ESI) Calculated for $C_{25}H_{24}FNO_2S$ ([M]+Na^+) = 444.1404, Found 444.1400

IR (neat) 3324, 2961, 1696, 1597, 1521, 1450, 1407, 1316, 1248, 1186, 1024, 821, 693, 507 cm^{-1}.

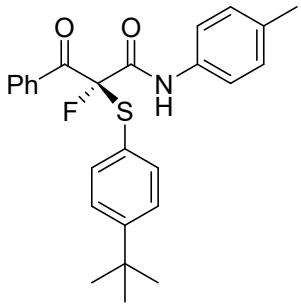


	Retention Time	Area	% Area
1	12.520	1960128	48.53
2	17.903	2078707	51.47



	Retention Time	Area	% Area
1	12.548	2754040	95.58
2	18.094	127467	4.42

(*S*)-2-((4-(tert-butyl)phenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3g):



white solid, m.p. 50–54 ºC, 99% yield, 91% ee; $[\alpha]^{19}_{D}$ = -132.6 (*c* 0.47, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 11.73 min, t_2 = 16.00 min

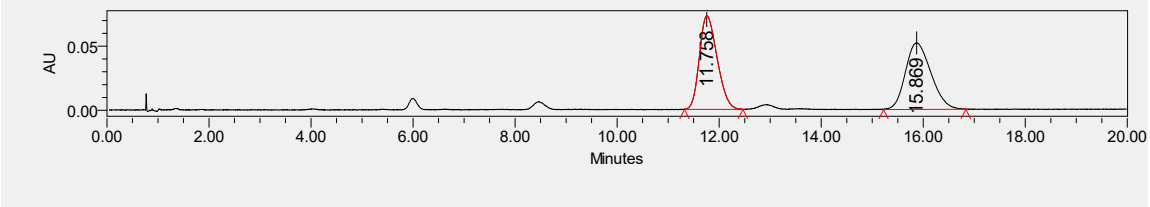
^{1}H NMR (600 MHz, $CDCl_3$) 8.04 (d, *J* = 8.6 Hz, 2H), 7.69 (s, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 1.26 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 189.9 (d, *J* = 26.1 Hz), 161.7 (d, *J* = 26.2 Hz), 153.9, 136.5, 135.1, 134.2, 133.6, 133.3 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 4.3 Hz), 129.5, 128.6, 126.5, 123.6, 120.3, 107.36 (d, *J* = 246.4 Hz), 34.8, 31.2, 20.9.

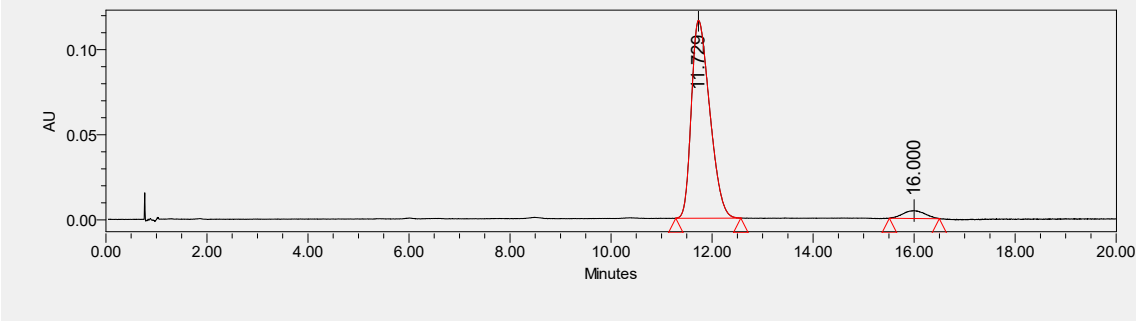
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –128.05. (s, 1F).

HRMS (ESI) Calculated for $C_{26}H_{26}FNO_2S$ ([M]+Na^+) = 458.1560, Found 458.1557.

IR (neat) 3323, 2962, 1699, 1598, 1524, 1451, 1406, 1317, 1250, 1187, 1022, 820, 693, 508 cm^{-1}.

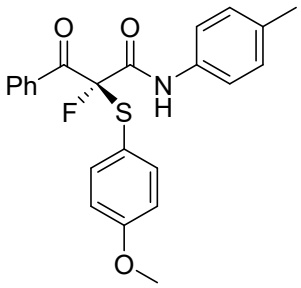


	Retention Time	Area	% Area
1	11.758	1762611	49.50
2	15.869	1798538	50.50



	Retention Time	Area	% Area
1	11.729	2936439	95.41
2	16.000	141354	4.59

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3h):



colerless oil, 99% yield, 87% ee; $[\alpha]^{22}_{D}$ = -78.4 (*c* 1.30, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 7.00 min, t_2 = 7.75 min

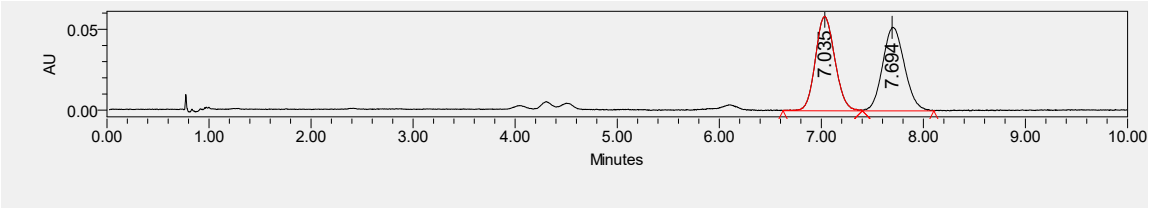
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.85 (s, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.3 8 (d, *J* = 26.1 Hz), 161.6 (d, *J* = 26.3 Hz), 161.5, 138.3, 135.1, 134.2, 133.7, 133.4 (d, *J* = 2.2 Hz), 130.2 (d, *J* = 3.9 Hz), 129.5, 128.6, 120.2, 107.2 (d, *J* = 245.4 Hz), 55.4, 20.9.

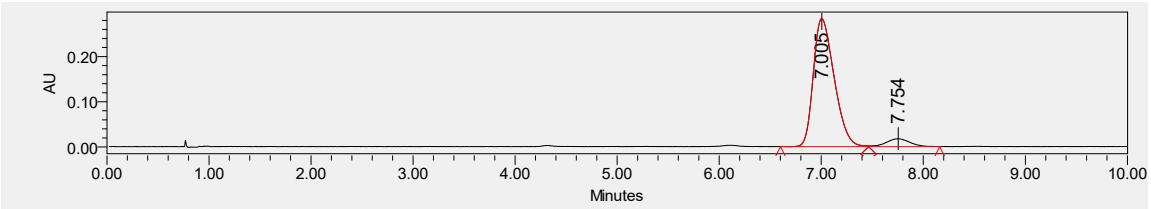
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –129.59 (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{20}FNO_3S$ ([M]+Na+) = 432.1040, Found 432.1037.

IR (neat) 3322, 2923, 1681, 1592, 1519, 1493, 1406, 1291, 1246, 1177, 1027, 826, 691, 506 cm^{-1}.

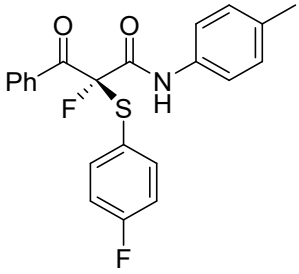


	Retention Time	Area	% Area
1	7.035	774709	50.24
2	7.694	767208	49.76



	Retention Time	Area	% Area
1	7.005	4021355	93.47
2	7.754	281124	6.53

(*S*)-2-fluoro-2-((4-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3i):



colerless oil, 91% yield, 88% ee; $[\alpha]^{21}_{D}$ = -90.9 (*c* 1.37, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 10.32 min, t_2 = 12.07 min

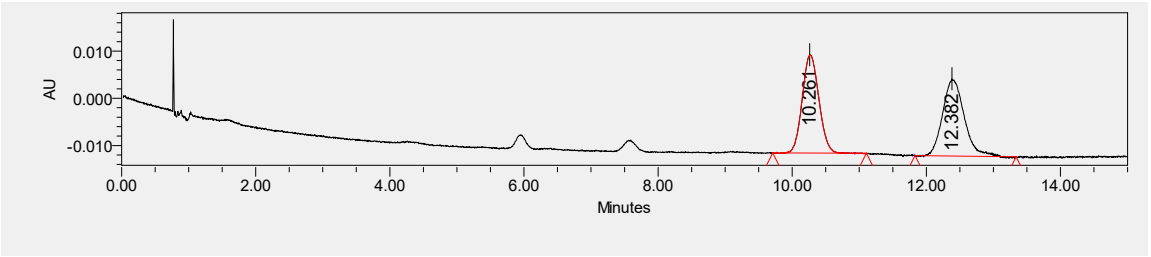
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.80 (s, 1H), 7.52 – 7.44 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 2.21 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 189.9 (d, *J* = 25.6 Hz), 164.3 (d, *J* = 252.0 Hz), 161.3 (d, *J* = 26.2 Hz), 138.8 (d, *J* = 8.8 Hz), 135.3, 134.4, 133.5, 133.2 (d, *J* = 2.6 Hz), 130.2 (d, *J* = 3.9 Hz), 129.6, 128.6, 122.3 (d, *J* = 3.4 Hz), 120.1, 116.7, 116.5, 107.2 (d, *J* = 246.7 Hz), 20.9.

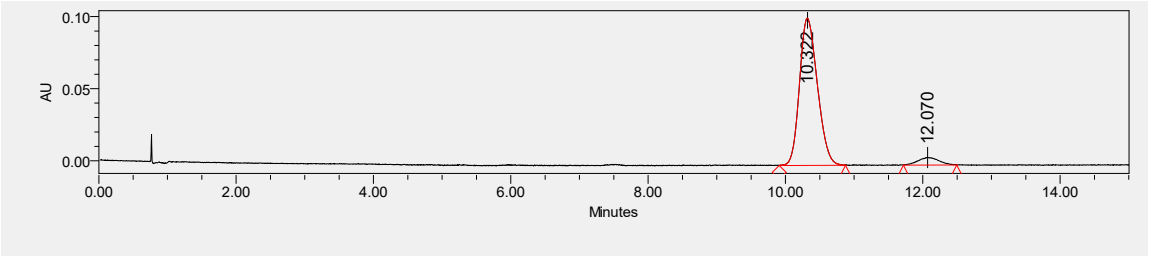
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –109.35. (s, 1F), –129.27. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{17}F_2NO_2S$ ([M]+Na^+) = 420.0840, Found 420.0836

IR (neat) 3319, 2922, 1696, 1592, 1522, 1489, 1449, 1317, 1233, 1158, 1030, 817, 630, 507 cm^{-1}.

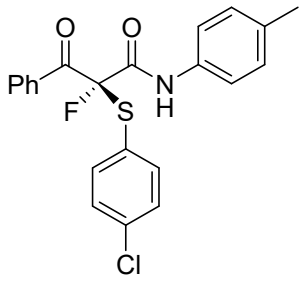


	Retention Time	Area	% Area
1	10.261	358180	49.54
2	12.382	364877	50.46



	Retention Time	Area	% Area
1	10.322	1845818	94.20
2	12.070	113629	5.80

(*S*)-2-((4-chlorophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3j):



colerless oil, 59% yield, 88% ee; $[\alpha]^{23}_{D}$ = -86.0 (*c* 0.83, CH_2Cl_2).

SFC Chiralcel OJ-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.41 min, t_2 = 4.82 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.86 (s, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H).

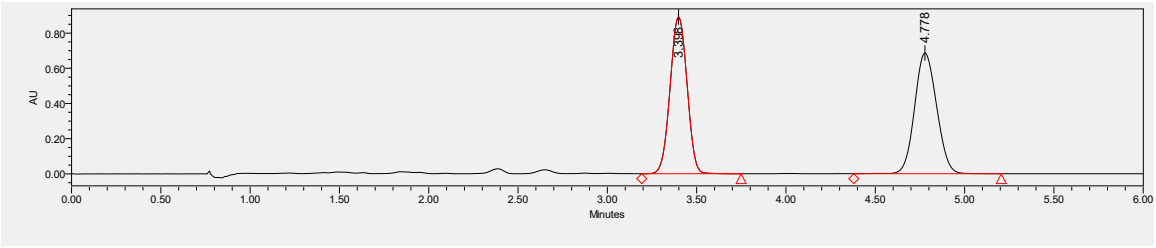
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)δ 189.8 (d, *J* = 26.0 Hz), 161.2 (d, *J* = 26.2 Hz), 137.7, 137.1, 136.1, 135.4, 134.5, 133.5, 133.1 (d, *J* = 2.2 Hz), 130.3 (d, *J* = 4.2 Hz), 129.7, 129.6, 128.6, 125.5, 120.4, 120.2, 107.1 (d, *J* = 246.5 Hz), 20.9.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –128.99. (s, 1F).

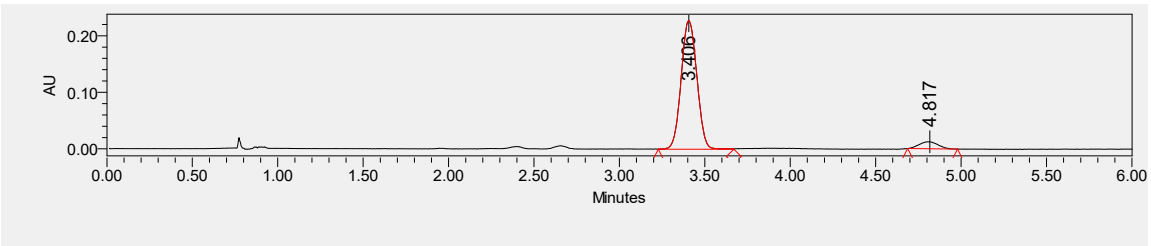
HRMS (ESI) Calculated for $C_{22}H_{17}{}^{35}ClFNO_2S$ ([M]+Na^+) = 436.0545, Found 436.0545.

HRMS (ESI) Calculated for $C_{22}H_{17}{}^{37}ClFNO_2S$ ([M]+Na^+) = 438.0515, Found 438.0514.

IR (neat) 3316, 2923, 1680, 1598, 1521, 1475, 1407, 1317, 1250, 1186, 1094, 1016, 818, 691, 506 cm^{-1}.

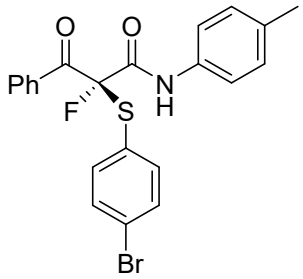


	Retention Time	Area	% Area
1	3.398	5873390	49.95
2	4.778	5885917	50.05



	Retention Time	Area	% Area
1	3.406	1455255	93.83
2	4.817	95760	6.17

(*S*)-2-((4-bromophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3k):



white solid, m.p. 104–108 ºC, 64% yield, 89% ee; $[\alpha]^{22}_{D}$ = -85.6 (*c* 1.05, CH_2Cl_2).

SFC Chiralcel **IC**-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 5.81 min, t_2 = 6.34 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.78 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.34 (s, 6H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.22 (s, 3H).

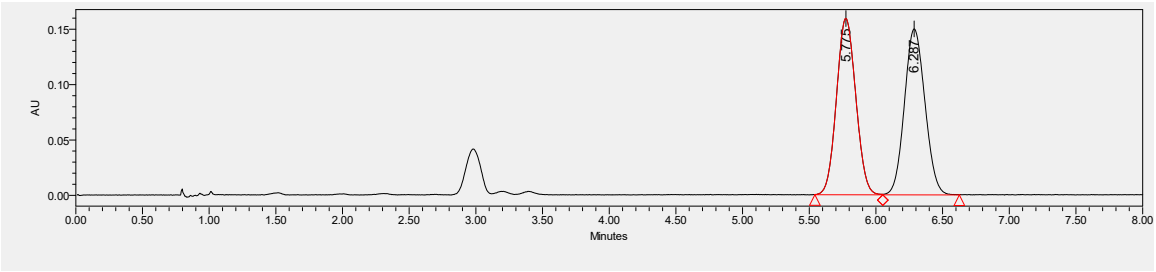
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.7 (d, *J* = 25.5 Hz), 161.2 (d, *J* = 26.5 Hz), 137.9, 135.4, 134.5, 133.5, 133.1 (d, *J* = 2.2 Hz), 132.5, 130.2 (d, *J* = 3.8 Hz), 129.6, 128.7, 126.2, 125.5, 120.2, 107.1 (d, *J* = 247.0 Hz), 21.0.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −128.85. (s, 1F).

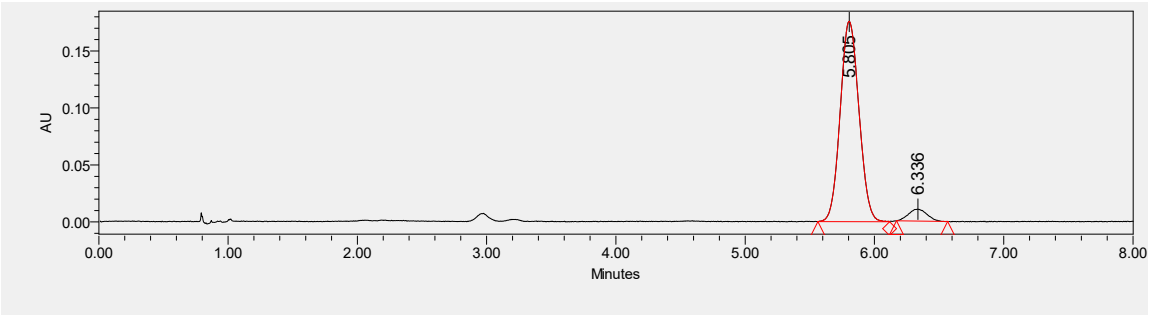
HRMS (ESI) Calculated for $C_{22}H_{17}{}^{79}BrFNO_2S$ ([M]+Na^+) = 480.0040, Found 480.0039.

HRMS (ESI) Calculated for $C_{22}H_{17}{}^{81}BrFNO_2S$ ([M]+Na^+) = 482.0019, Found 482.0017.

IR (neat) 3319, 2923, 1697, 1597, 1522, 1472, 1449, 1316, 1251, 1186, 1010, 815, 691, 507 cm^{-1}.

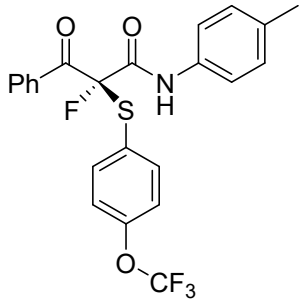


	Retention Time	Area	% Area
1	5.775	1602414	49.96
2	6.287	1605043	50.04



	Retention Time	Area	% Area
1	5.805	1772143	94.42
2	6.336	104802	5.58

(S)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-((4-(trifluoromethoxy)phenyl)thio)propanamide (3l):



colerless oil, 70% yield, 89% ee; $[\alpha]^{22}_{D}$ = -81.0 (*c* 0.68, CH_2Cl_2).

HPLC: Chiralcel ADH, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 30.59 min, t_{r2} = 33.02 min

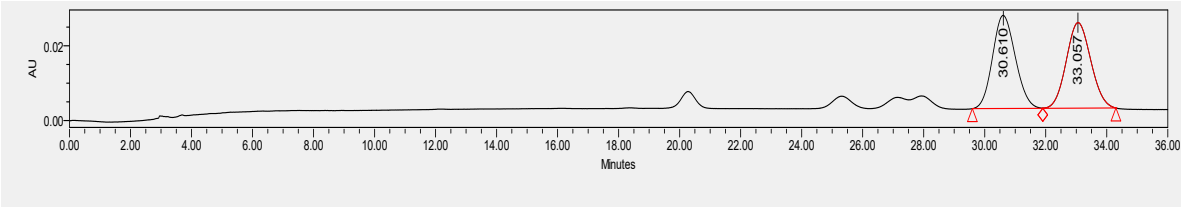
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.80 (s, 1H), 7.60 (dd, *J* = 11.5, 8.1 Hz, 3H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.6 (d, *J* = 25.5 Hz), 161.2 (d, *J* = 25.8 Hz), 150.9, 138.2, 135.4, 134.5, 133.4, 133.1 (d, *J* = 2.7 Hz), 130.2 (d, *J* = 3.9 Hz), 129.6, 128.7, 121.6, 120.3 (q, *J* = 259.3 Hz), 107.2 (d, *J* = 247.4 Hz), 20.9.

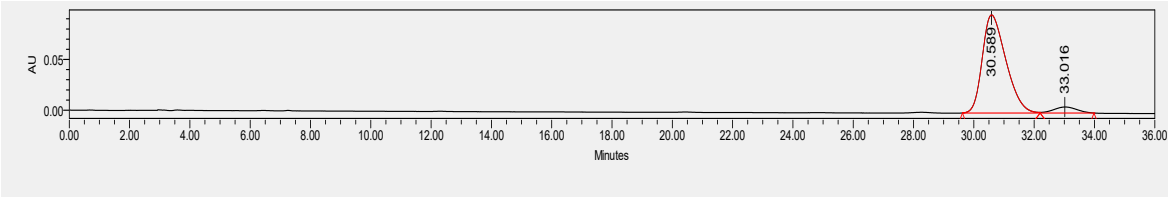
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −57.77. (s, 1F), −128.78. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{17}F_4NO_3S$ ([M]+Na^+) = 486.0757, Found 486.0756

IR (neat) 3306, 1697, 1597, 1522, 1449, 1407, 1252, 1166, 1023, 809, 692, 507 cm^{-1}.

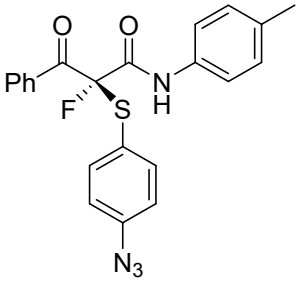


	Retention Time	Area	% Area
1	30.610	1292926	50.32
2	33.057	1276656	49.68



	Retention Time	Area	% Area
1	30.589	5245804	94.32
2	33.016	316089	5.68

(*S*)-2-((4-azidophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3m):



yellow oil, 55% yield, 89% ee; $[\alpha]^{23}_{D}$ = -86.0 (*c* 0.83, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 85/15, 1.5 mL/min, λ = 280 nm, t_1 = 13.57 min, t_2 = 15.10 min

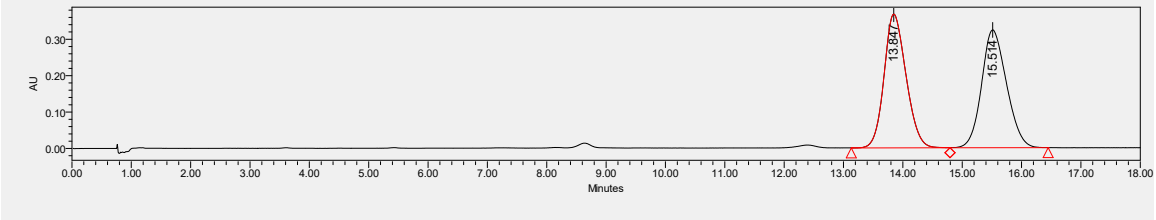
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.89 (s, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.0 (d, *J* = 26.0 Hz), 161.2 (d, *J* = 26.3 Hz), 142.7, 138.1, 135.3, 134.4, 133.6, 133.2 (d, *J* = 2.4 Hz), 130.3 (d, *J* = 4.2 Hz), 129.6, 128.6, 122.8, 120.3, 120.1, 119.9, 119.8, 107.2 (d, *J* = 246.4 Hz), 20.9.

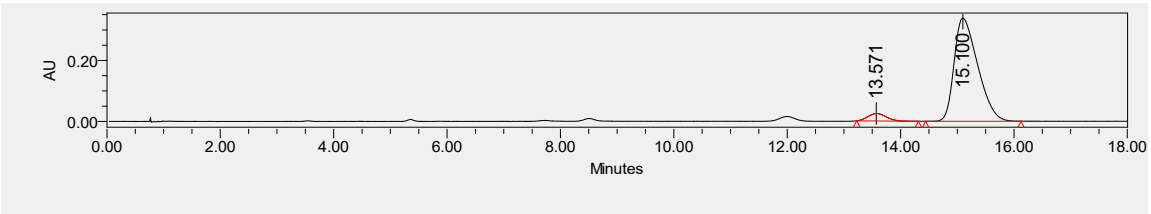
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –129.36. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{17}FN_4O_2S$ ([M]+Na+) = 443.0948, Found 443.0945

IR (neat) 3328, 2922, 2126, 2094, 1696, 1592, 1522, 1487, 1406, 1293, 1250, 1128, 1028, 816, 693, 508 cm^{-1}.

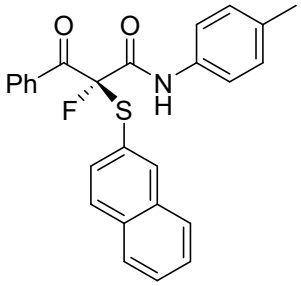


	Retention Time	Area	% Area
1	13.847	9432886	50.00
2	15.514	9431326	50.00



	Retention Time	Area	% Area
1	13.571	550556	5.34
2	15.100	9767350	94.66

(*S*)-2-fluoro-2-(naphthalen-2-ylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3n):



yelow solid, m.p. 110–114 ºC, 88% yield, 90% ee; $[\alpha]^{22}_{D}$ = -82.6 (*c* 0.75, CH_2Cl_2).

HPLC: Chiralcel ADH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, t_{r1} = 19.60 min, t_{r2} = 24.62 min

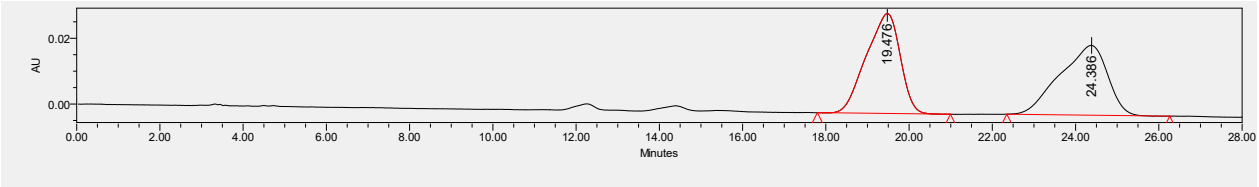
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 3H), 7.80 (d, *J* = 6.9 Hz, 2H), 7.74 (t, *J* = 8.1 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.57 – 7.53 (m, 1H), 7.53 – 7.45 (m, 2H), 7.42 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.05 – 6.90 (m, 4H), 2.25 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.0 (d, *J* = 25.5 Hz), 161.5 (d, *J* = 26.2 Hz), 137.0, 135.1, 134.3, 133.7, 133.5, 133.4, 133.3 (d, *J* = 2.4 Hz), 132.2, 130.3 (d, *J* = 3.8 Hz), 129.5, 128.9, 128.6, 128.1, 127.7, 127.6, 126.8, 124.2, 120.2, 107.3 (d, *J* = 246.5 Hz), 20.9.

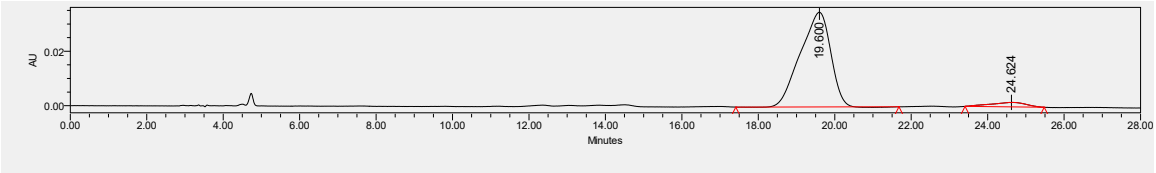
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −128.58. (s, 1F).

HRMS (ESI) Calculated for $C_{26}H_{20}FNO_2S$ ([M]+Na^+) = 452.1091, Found 452.1089

IR (neat) 3328, 2922, 1696, 1597, 1521, 1449, 1407, 1317, 1249, 1187, 1027, 815, 692, 507 cm^{-1}.

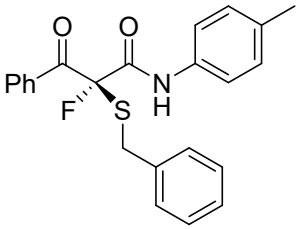


	Retention Time	Area	% Area
1	19.476	1716245	50.39
2	24.386	1689822	49.61



	Retention Time	Area	% Area
1	19.600	1929242	94.87
2	24.624	104388	5.13

(*S*)-2-(benzylthio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3o):



white solid, m.p. 147–152 ºC, 67% yield, 93% ee; $[\alpha]^{21}_{D}$ = -88.7 (*c* 0.73, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 16.40 min, t_2 = 17.84 min

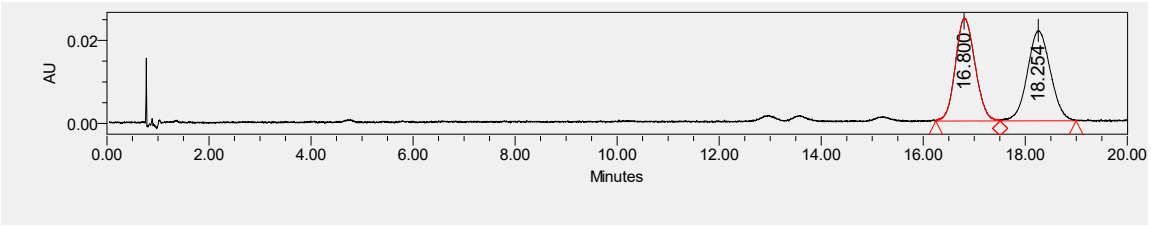
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.47 – 7.43 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.27 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.05 – 3.98 (m, 2H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.2 (d, *J* = 26.2 Hz), 161.5 (d, *J* = 27.3 Hz), 135.4, 135.2, 134.4, 133.9, 133.2 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 4.4 Hz), 129.6, 129.3, 128.7, 128.5, 127.8, 120.1, 106.2 (d, *J* = 243.1 Hz), 34.1, 21.0.

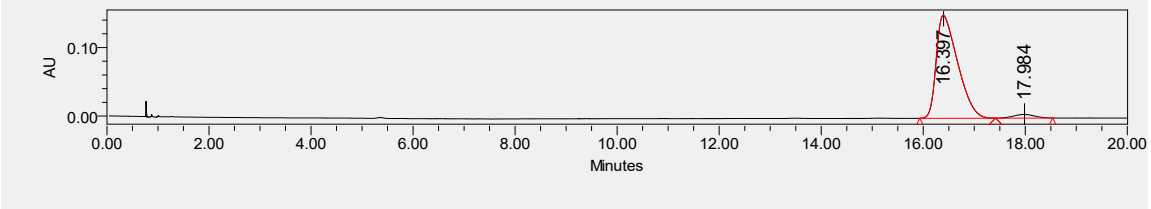
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –134.59. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{20}FNO_2S$ ([M]+Na+) = 416.1091, Found 416.1087

IR (neat) 3319, 2922, 1680, 1597, 1521, 1450, 1407, 1317, 1242, 1186, 1026, 813, 694, 508 cm^{-1}.

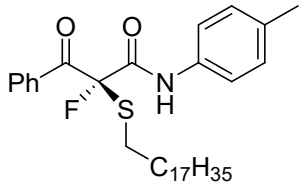


	Retention Time	Area	% Area
1	16.800	661291	49.37
2	18.254	678095	50.63



	Retention Time	Area	% Area
1	16.397	4365243	96.62
2	17.984	152712	3.38

(*S*)-2-fluoro-2-(octadecylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3p):



white solid, m.p. 65–68 ºC, 91% yield, 91% ee; $[\alpha]^{22}_{D}$ = -92.8 (*c* 0.61, CH_2Cl_2).

SFC Chiralcel ID-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.23 min, t_2 = 3.66 min

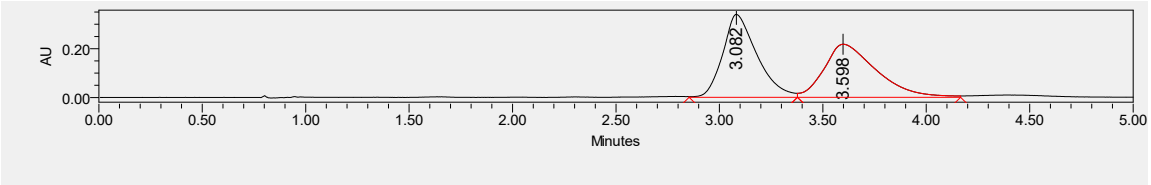
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.22 – 8.17 (m, 2H), 7.62 – 7.57 (m, 1H), 7.48 – 7.41 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.78 (qd, *J* = 7.7, 1.7 Hz, 2H), 2.31 (s, 3H), 1.65 – 1.59 (m, 2H), 1.24 (d, *J* = 14.0 Hz, 30H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.6 (d, *J* = 26.8 Hz), 161.8 (d, *J* = 28.1 Hz), 135.1, 134.3, 134.0, 133.3 (d, *J* = 2.5 Hz), 130.6 (d, *J* = 4.4 Hz), 129.7, 128.5, 120.0, 106.3 (d, *J* = 242.1 Hz), 32.0, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.4, 29.0, 29.0, 28.8, 22.7, 20.9 14.2.

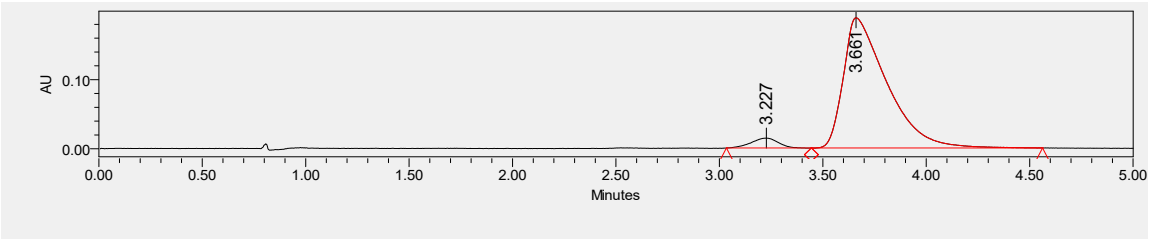
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –134.40. (s, 1F).

HRMS (ESI) Calculated for $C_{34}H_{50}FNO_2S$ ([M]+Na+) = 578.3438, Found 578.3435

IR (neat) 3333, 2922 1685, 1598, 1524, 1451, 1407, 1316, 1241, 1187, 1025, 813, 691, 507 cm^{-1}.

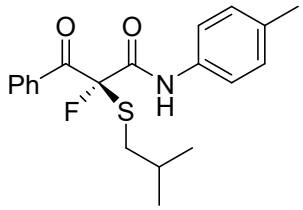


	Retention Time	Area	% Area
1	3.082	3914932	50.59
2	3.598	3823710	49.41



	Retention Time	Area	% Area
1	3.227	130311	4.52
2	3.661	2753404	95.48

(*S*)-2-fluoro-2-(isobutylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3q):



white solid, m.p. 83–86 ºC, 73% yield, 88% ee; $[\alpha]^{22}_{D}$ = -21.9 (*c* 1.03, CH_2Cl_2).

SFC Chiralcel ID-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 280 nm, t_1 = 5.49 min, t_2 = 6.19 min

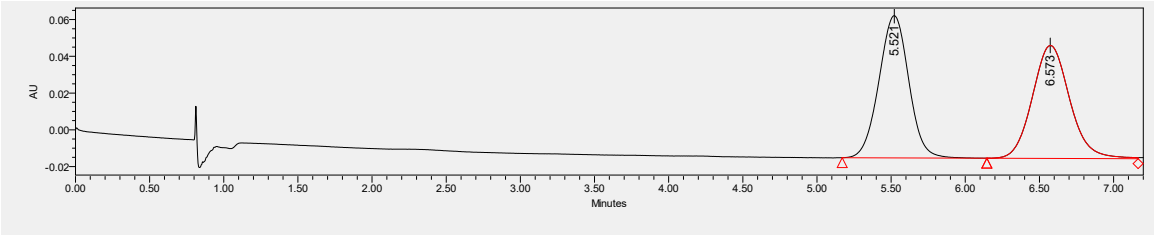
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 2.64 – 2.60 (m, 1H), 2.56 (dd, *J* = 11.0, 7.2 Hz, 1H), 2.23 (s, 3H), 1.80 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.6 (d, *J* = 26.3 Hz), 161.8 (d, *J* = 27.4 Hz), 135.1, 134.4, 134.0, 133.3 (d, *J* = 1.9 Hz), 130.6 (d, *J* = 4.4 Hz), 129.7, 128.5, 120.0, 106.2 (d, *J* = 242.1 Hz), 38.0, 28.3, 22.0, 21.9, 20.9.

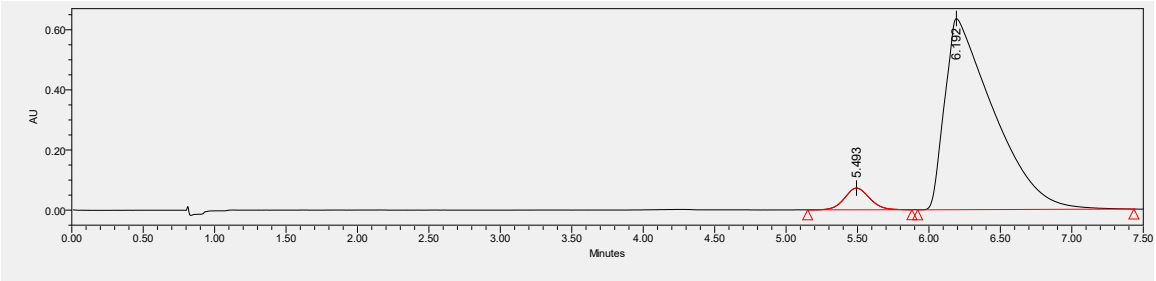
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −134.63. (s, 1F).

HRMS (ESI) Calculated for $C_{20}H_{22}FNO_2S$ ([M]+Na+) = 382.1247, Found 382.1243.

IR (neat) 3329, 2925, 1681, 1597, 1521, 1449, 1317, 1240, 1186, 1025, 813, 690, 508 cm^{-1}.

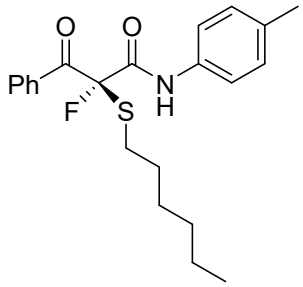


	Retention Time	Area	% Area
1	5.521	1082423	50.21
2	6.573	1073172	49.79



	Retention Time	Area	% Area
1	5.493	880309	5.51
2	6.192	15094748	94.49

(*S*)-2-fluoro-2-(hexylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3r):



colerless oil, 84% yield, 90% ee; $[\alpha]^{21}_{D}$ = -22.7 (*c* 1.23, CH_2Cl_2).

SFC Chiralcel ID-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 280 nm, t_1 = 7.55 min, t_2 = 8.57 min

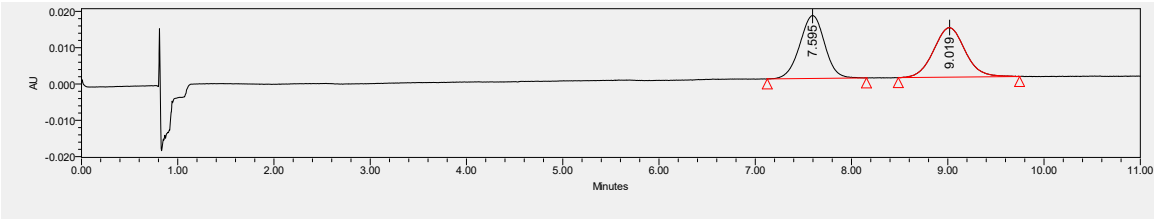
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 14.4, 8.2 Hz, 4H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.74 – 2.66 (m, 2H), 2.23 (s, 3H), 1.54 (p, *J* = 7.6, 7.1 Hz, 2H), 1.30 – 1.25 (m, 2H), 1.19 – 1.13 (m, 4H), 0.77 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 191.6 (d, *J* = 27.1 Hz), 161.8 (d, *J* = 27.4 Hz), 135.1, 134.4, 134.0, 133.3 (d, *J* = 1.8 Hz), 130.6 (d, *J* = 4.3 Hz), 129.7, 128.5, 120.0, 106.4 (d, *J* = 242.0 Hz), 31.2, 29.6, 29.0, 28.4, 22.5, 20.9, 14.0.

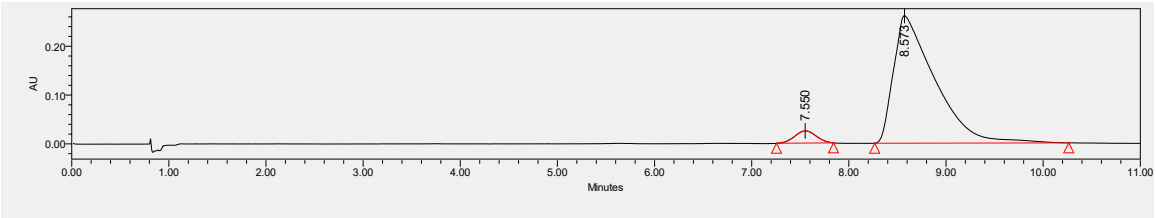
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –134.26. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{26}FNO_2S$ ([M]+Na^+) = 410.1560, Found 410.1559

IR (neat) 3328, 2926, 1681, 1598, 1521, 1449, 1406, 1316, 1240, 1186, 1025, 813, 690, 508 cm^{-1}.

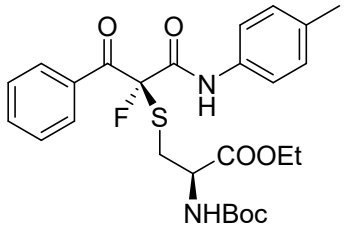


	Retention Time	Area	% Area
1	7.595	311284	50.10
2	9.019	310084	49.90



	Retention Time	Area	% Area
1	7.550	382785	4.74
2	8.573	7690887	95.26

ethyl *N*-(tert-butoxycarbonyl)-*S*-((*S*)-2-fluoro-1,3-dioxo-1-phenyl-3-(*p*-tolylamino)propan-2-yl)-L-cysteinate (3s):



colerless oil, 78% yield, >19:1 dr, $[\alpha]^{22}_{D}$ = -35.5 (*c* 0.39, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.12 (m, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.14 (d, *J* = 8.3 Hz, 2H), 4.56 (s, 1H), 4.18 (qd, *J* = 7.2, 4.8 Hz, 2H), 3.41 (d, *J* = 9.4 Hz, 1H), 3.23 (d, *J* = 12.8 Hz, 1H), 2.32 (s, 3H), 1.43 (d, *J* = 8.0 Hz, 10H), 1.26 (dt, *J* = 12.1, 7.1 Hz, 4H).

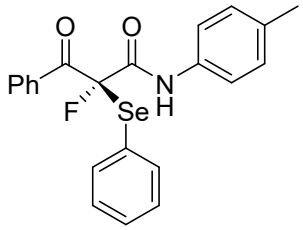
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.2 (d, *J* = 25.7 Hz), 170.0, 161.5 (d, *J* = 24.8 Hz), 155.3, 135.3, 134.5, 133.9, 132.9 (d, *J* = 2.3 Hz), 130.5 (d, *J* = 3.9 Hz), 129.7, 129.6, 128.6, 120.3, 120.1, 106.1 (d, *J* = 243.0 Hz), 80.4, 62.2, 53.0, 31.7, 28.3, 20.9, 14.1.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −130.89. (s, 1F).

HRMS (ESI) Calculated for $C_{26}H_{31}FN_2O_6S$ ([M]+Na+) = 541.1780, Found 541.1776

IR (neat) 3342, 2979, 1700, 1599, 1519, 1450, 1369, 1317, 1247, 1164, 1025, 816, 693, 509 cm^{-1}.

(*S*)-2-fluoro-3-oxo-3-phenyl-2-(phenylselanyl)-*N*-(*p*-tolyl)propanamide (3t):



yellow oil, 30% yield, race;

SFC Chiralcel IC-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 6.01 min, t_2 = 6.54 min

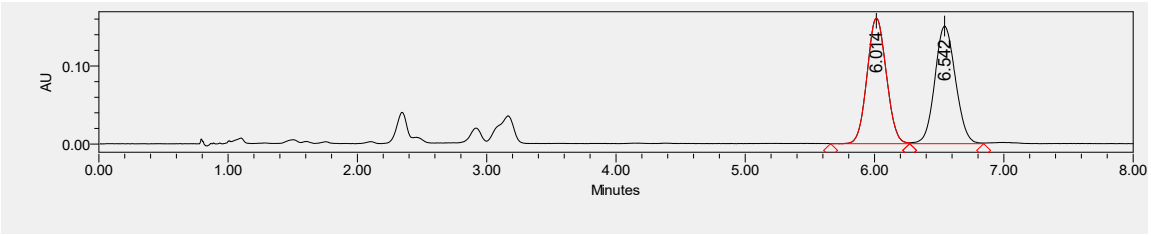
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 8.6, 1.6 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.65 – 7.56 (m, 2H), 7.46 – 7.38 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.05 (m, 4H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0 (d, *J* = 23.8 Hz), 162.6 (d, *J* = 24.2 Hz), 137.9, 135.1, 134.2, 133.6, 133.0 (d, *J* = 2.6 Hz), 130.2, 130.1 (d, *J* = 4.3 Hz), 129.5, 129.4, 128.7, 124.5, 120.0, 104.0 (d, *J* = 258.4 Hz), 20.3.

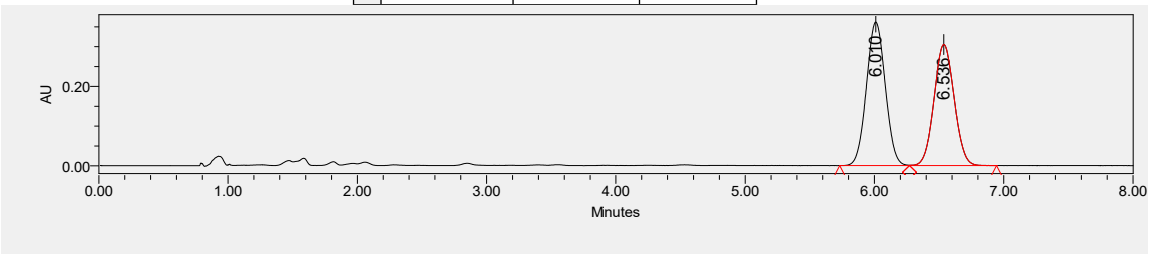
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −133.98. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{18}FNO_2Se$ ([M]+Na+) = 444.0439, Found 444.0441

IR (neat) 3328, 2923, 1693, 1597, 1523, 1447, 1407, 1316, 1253, 1186, 1031, 815, 691, 506 cm^{-1}.

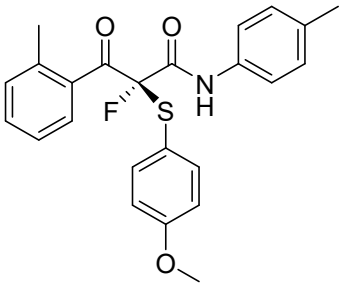


	Retention Time	Area	% Area
1	6.014	1661516	49.82
2	6.542	1673541	50.18



	Retention Time	Area	% Area
1	6.010	3659765	52.62
2	6.536	3294876	47.38

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-(*o*-tolyl)-*N*-(*p*-tolyl)propanamide (4a):



colerless oil, 99% yield, 89% ee; $[\alpha]^{22}_{D}$ = -65.9 (*c* 1.48, CH_2Cl_2).

SFC Chiralcel OD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.17 min, t_2 = 3.85 min

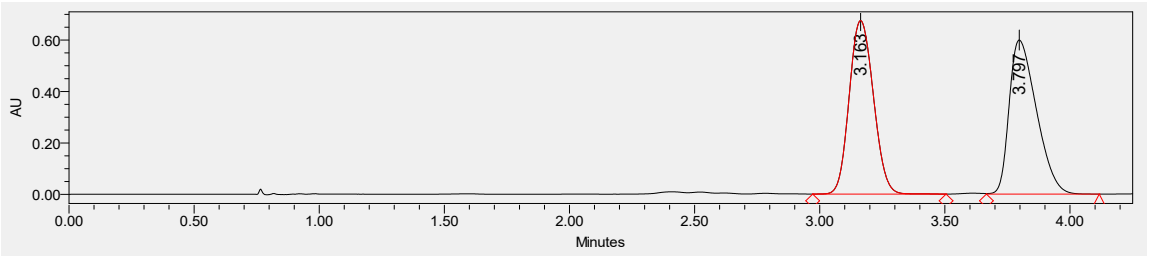
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.60 (dd, *J* = 6.5, 3.1 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.88 – 6.75 (m, 2H), 3.75 (s, 3H), 2.31 (d, *J* = 14.6 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.1 (d, *J* = 28.3 Hz), 161.6, 161.2 (d, *J* = 26.9 Hz), 138.8, 138.3, 135.1, 134.4 (d, *J* = 2.3 Hz), 133.8, 132.0, 131.6, 129.6, 128.7 (d, *J* = 6.5 Hz), 125.3, 120.2, 117.5, 114.9, 107.1 (d, *J* = 246.3 Hz), 55.4, 20.9, 20.5.

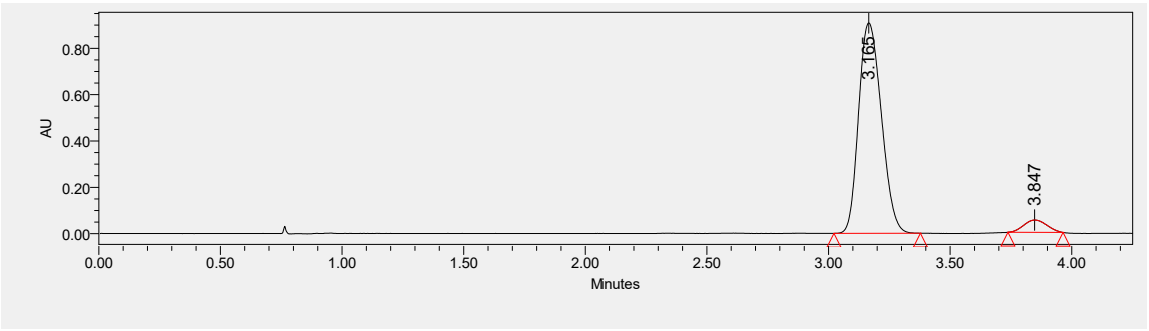
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –131.32. (s, 1F).

HRMS (ESI) Calculated for $C_{24}H_{22}FNO_3S$ ([M]+Na^+) = 446.1196, Found 446.1195

IR (neat) 3345, 2927, 1687, 1592, 1519, 1492, 1458, 1291, 1245, 1176, 1028, 830, 629, 507 cm^{-1}.

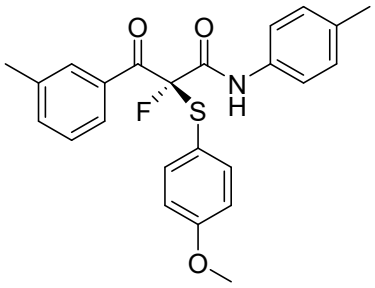


	Retention Time	Area	% Area
1	3.163	4543750	50.08
2	3.797	4530012	49.92



	Retention Time	Area	% Area
1	3.165	5893675	94.39
2	3.847	350143	5.61

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-(*m*-tolyl)-*N*-(*p*-tolyl)propanamide (4b):



colerless oil, 98% yield, 89% ee; $[\alpha]^{23}_{D}$ = -75.0 (*c* 1.33, CH_2Cl_2).

SFC Chiralcel OD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.25 min, t_2 = 3.64 min

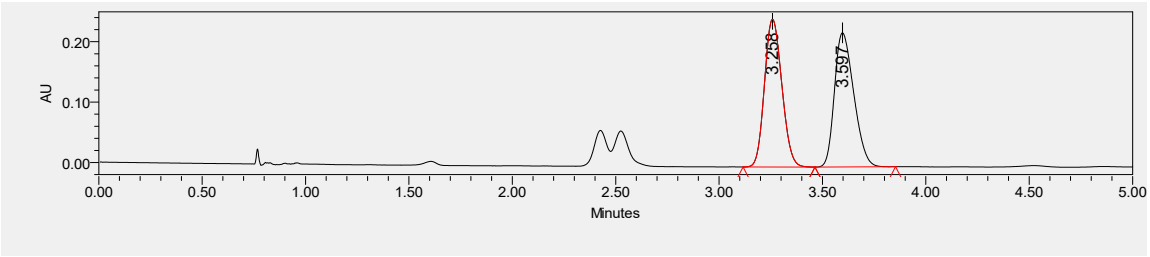
^{1}H NMR (600 MHz, $CDCl_3$)δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.74 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 3.66 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.6 (d, *J* = 25.9 Hz), 161.7 (d, *J* = 26.3 Hz), 161.5, 138.4, 138.4, 135.1, 133.8, 133.4 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 4.4 Hz), 129.5, 128.6, 128.4, 127.4, 127.4, 120.2, 117.4, 114.9, 107.2 (d, *J* = 246.2 Hz), 55.4, 21.4, 20.9.

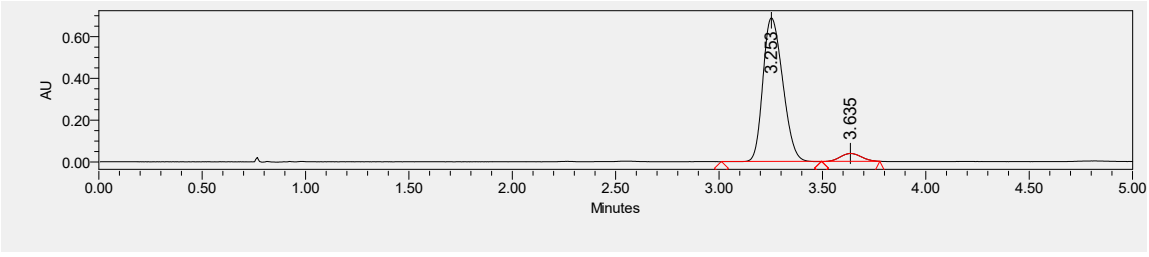
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –129.69. (s, 1F).

HRMS (ESI) Calculated for $C_{24}H_{22}FNO_3S$ ([M]+Na^+) = 446.1197, Found 446.1193

IR (neat) 3336, 2923, 1694, 1593, 1522, 1493, 1459, 1291, 1250, 1178, 1029, 830, 630, 509 cm^{-1}.

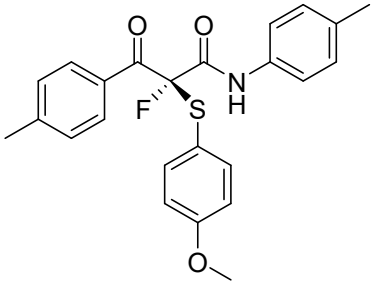


	Retention Time	Area	% Area
1	3.258	1427588	49.80
2	3.597	1439035	50.20



	Retention Time	Area	% Area
1	3.253	4567860	94.55
2	3.635	263244	5.45

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*,3-di-ptolylpropanamide (4c):



colerless oil, 99% yield, 89% ee; $[\alpha]^{23}_{D}$ = -61.5 (*c* 1.34, CH_2Cl_2).

SFC Chiralcel OD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.61 min, t_2 = 4.16 min

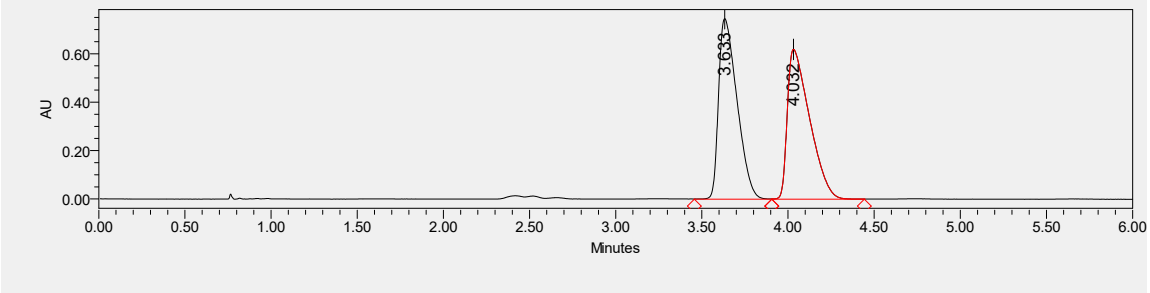
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.87 (s, 1H), 7.51 – 7.46 (m, 2H), 7.20 (dd, *J* = 14.5, 8.5 Hz, 4H), 7.10 – 7.02 (m, 2H), 6.86 – 6.74 (m, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.7 (d, *J* = 25.4 Hz), 161.7 (d, *J* = 26.5 Hz), 161.5, 145.5, 138.3, 135.0, 133.8, 130.8 (d, *J* = 2.8 Hz), 130.4(d, *J* = 4.3 Hz), 129.5, 129.5, 129.3, 120.2, 117.4, 114.9, 107.2 (d, *J* = 245.6 Hz), 55.4, 21.8, 20.9.

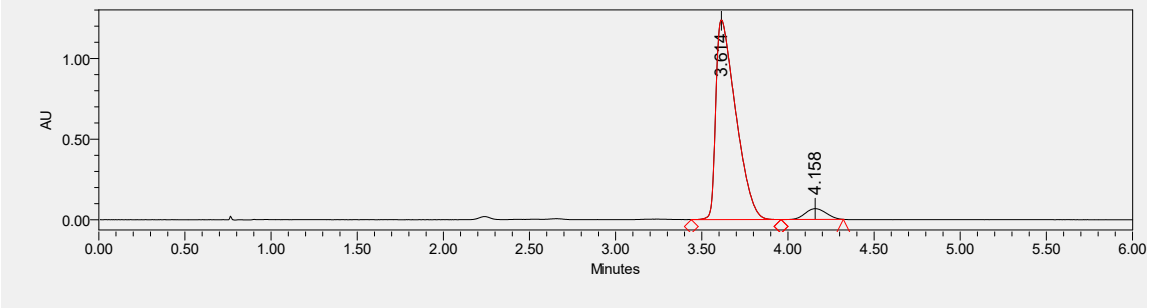
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –129.48. (s, 1F).

HRMS (ESI) Calculated for $C_{24}H_{22}FNO_3S$ ([M]+Na^+) = 446.1197, Found 446.1194

IR (neat) 3335, 2922, 1681, 1595, 1520, 1493, 1459, 1291, 1247, 1181, 1027, 830, 639, 506 cm^{-1}.

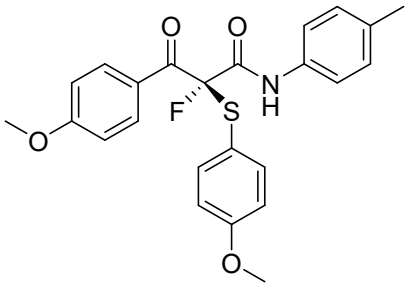


	Retention Time	Area	% Area
1	3.633	5539989	50.02
2	4.032	5536340	49.98



	Retention Time	Area	% Area
1	3.614	9925817	94.64
2	4.158	562384	5.36

(*S*)-2-fluoro-3-(4-methoxyphenyl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4d):



colerless oil, 99% yield, 87% ee; $[\alpha]^{22}_{D}$ = -36.7 (*c* 1.27, CH_2Cl_2).

SFC Chiralcel IC-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 9.78 min, t_2 = 12.07 min

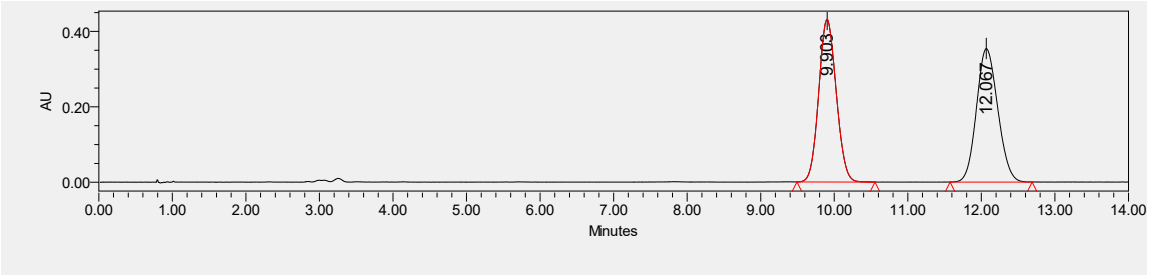
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 9.0, 1.5 Hz, 2H), 7.92 (d, *J* = 3.0 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 2.28 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 188.4 (d, *J* = 25.0 Hz), 164.5, 161.8 (d, *J* = 26.7 Hz), 161.5, 138.3, 135.0, 133.8, 133.0 (d, *J* = 4.4 Hz), 129.5, 126.0 (d, *J* = 2.2 Hz), 120.2, 117.5, 114.8, 113.9, 107.3 (d, *J* = 245.3 Hz), 55.6, 55.4, 20.9.

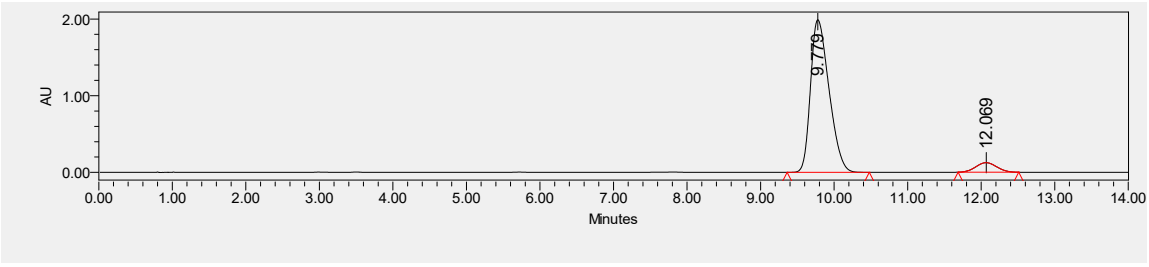
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –129.30. (s, 1F).

HRMS (ESI) Calculated for $C_{24}H_{22}FNO_4S$ ([M]+Na^+) = 463.1146, Found 462.1142

IR (neat) 3335, 2936, 1690, 1595, 1516, 1494, 1460, 1291, 1250, 1175, 1027, 831, 602, 510 cm^{-1}.

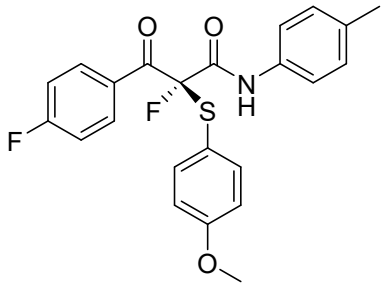


	Retention Time	Area	% Area
1	9.903	7119246	50.02
2	12.067	7114613	49.98



	Retention Time	Area	% Area
1	9.779	34762130	93.37
2	12.069	2467659	6.63

(*S*)-2-fluoro-3-(4-fluorophenyl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4e):



colerless oil, 89% yield, 89% ee; $[\alpha]^{22}_{D}$ = -68.8 (*c* 1.39, CH_2Cl_2).

SFC Chiralcel IA-3, CO_2/MeOH = 85/15, 1.5 mL/min, λ = 280 nm, t_1 = 5.08 min, t_2 = 5.57 min

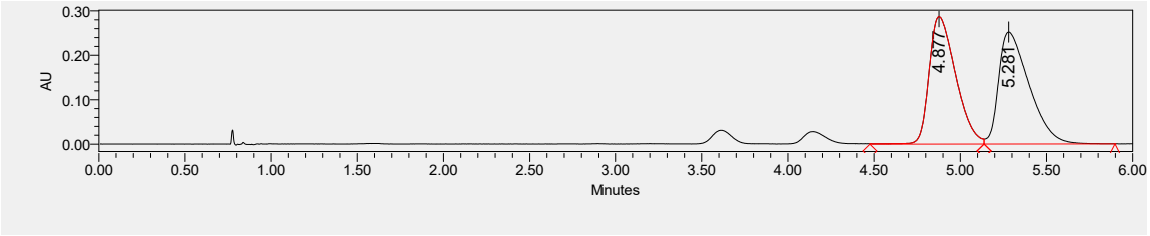
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (ddt, *J* = 6.7, 5.4, 1.3 Hz, 2H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.12 – 7.05 (m, 4H), 6.83 – 6.77 (m, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 188.6 (d, *J* = 25.2 Hz), 166.3 (d, *J* = 258.0 Hz), 161.6, 161.4 (d, *J* = 26.3 Hz), 138.3, 135.2, 133.6, 133.4 (dd, *J* = 9.8, 4.3 Hz), 129.6, 120.2, 117.1, 115.8 (d, *J* = 22.0 Hz), 114.9, 107.1 (d, *J* = 245.3 Hz), 55.4, 20.9.

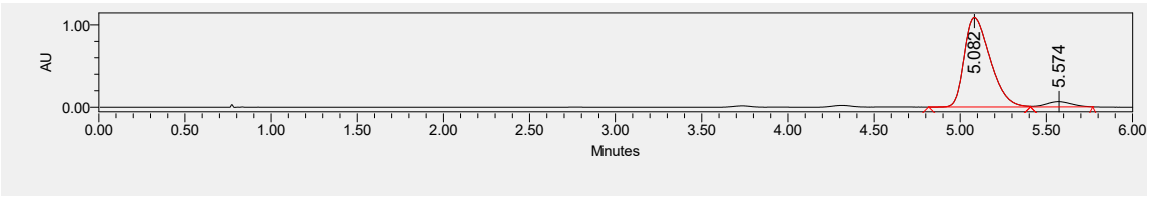
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –102.26. (s, 1F), –129.43. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{19}F_2NO_3S$ ([M]+Na+) = 450.0946, Found 450.0943

IR (neat) 3328, 2940, 1682, 1593, 1520, 1494, 1461, 1292, 1242, 1161, 1028, 829, 643, 508 cm^{-1}.

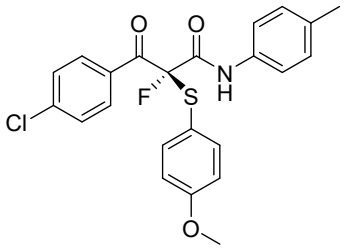


	Retention Time	Area	% Area
1	4.877	3072167	49.80
2	5.281	3096585	50.20



	Retention Time	Area	% Area
1	5.082	11324535	94.55
2	5.574	652287	5.45

(*S*)-3-(4-chlorophenyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4f):



colerless oil, 93% yield, 87% ee; $[\alpha]^{23}_{D}$ = -29.7 (*c* 1.37, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 12.00 min, t_2 = 14.01 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.87 (s, 1H), 7.48 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.82 – 6.79 (m, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

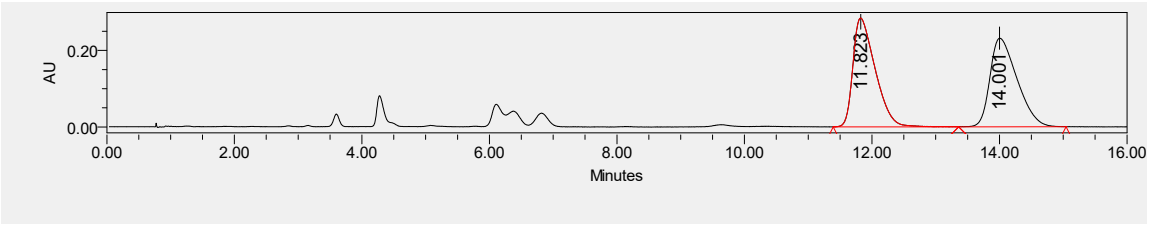
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.1 (d, *J* = 25.8 Hz), 161.6, 161.3 (d, *J* = 26.2 Hz), 140.9, 138.3, 135.2, 133.6, 131.8 (d, *J* = 4.2 Hz), 131.6 (d, *J* = 2.4 Hz), 129.6, 129.5, 128.9, 120.4, 120.2, 117.0, 114.9, 114.8, 107.1 (d, *J* = 244.9 Hz), 55.4, 20.9.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –129.55. (s, 1F).

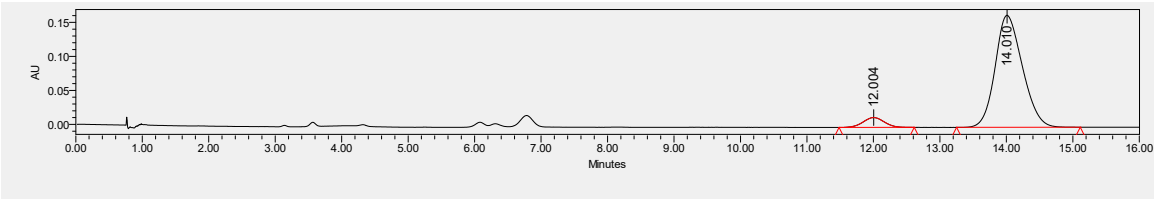
HRMS (ESI) Calculated for $C_{23}H_{19}{}^{35}ClFNO_3S$ ([M]+Na^+) = 466.0650, Found 466.0652.

HRMS (ESI) Calculated for $C_{23}H_{19}{}^{37}ClFNO_3S$ ([M]+Na^+) = 468.0621, Found 468.0620.

IR (neat) 3326, 2940, 1680, 1589, 1520, 1492, 1460, 1291, 1247, 1178, 1029, 830, 643, 507 cm^{-1}.

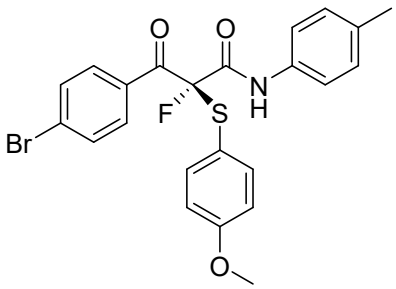


	Retention Time	Area	% Area
1	11.823	6895131	50.26
2	14.001	6822625	49.74



	Retention Time	Area	% Area
1	12.004	320077	6.40
2	14.010	4683343	93.60

(*S*)-3-(4-bromophenyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4g):



colerless oil, 90% yield, 89% ee; $[\alpha]^{21}_{D}$ = -38.0 (*c* 1.54, CH_2Cl_2).

SFC Chiralcel IB-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.90 min, t_2 = 4.17 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.88 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

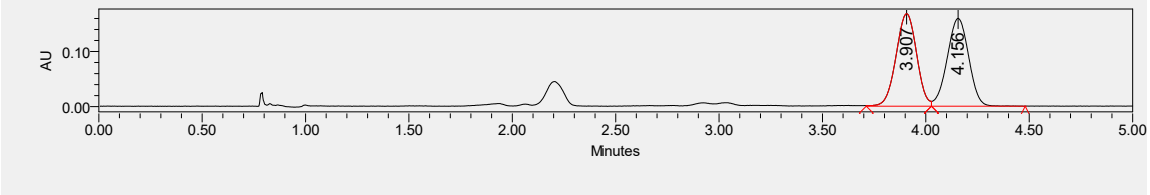
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.3 (d, *J* = 26.1 Hz), 161.6, 161.3 (d, *J* = 26.5 Hz), 138.3, 135.2, 133.6, 132.1 (d, *J* = 2.4 Hz), 131.9, 131.8 (d, *J* = 4.1 Hz), 129.8, 129.6, 120.2, 117.0, 114.9, 107.1 (d, *J* = 245.5 Hz), 55.4, 20.9.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −129.50. (s, 1F).

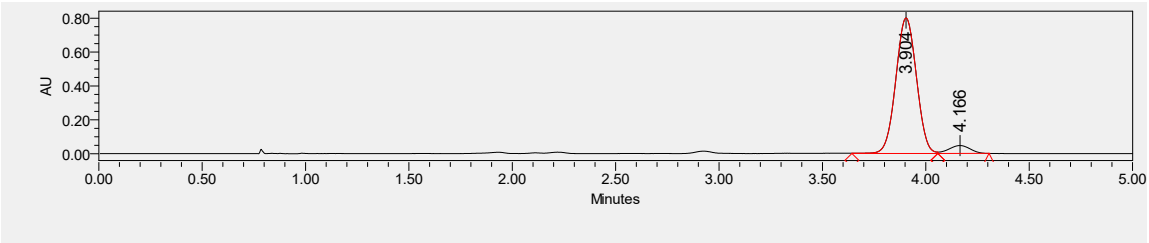
HRMS (ESI) Calculated for $C_{23}H_{19}{}^{79}BrFNO_3S$ ([M]+Na^+) = 510.0145, Found 510.0146.

HRMS (ESI) Calculated for $C_{23}H_{19}{}^{81}BrFNO_3S$ ([M]+Na^+) = 510.0125, Found 510.0125.

IR (neat) 3324, 2923, 1682, 1586, 1521, 1493, 1460, 1291, 1248, 1176, 1029, 829, 641, 507 cm^{-1}.

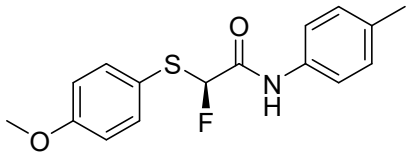


	Retention Time	Area	% Area
1	3.907	1158737	50.19
2	4.156	1150156	49.81



	Retention Time	Area	% Area
1	3.904	5531706	94.39
2	4.166	328755	5.61

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-*N*-(*p*-tolyl)acetamide (4h):



white solid, m.p. 118–123 ºC, 41% yield, 26% ee; $[\alpha]^{22}_{D}$ = -57.6 (*c* 0.50, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.39 min, t_2 = 6.36 min

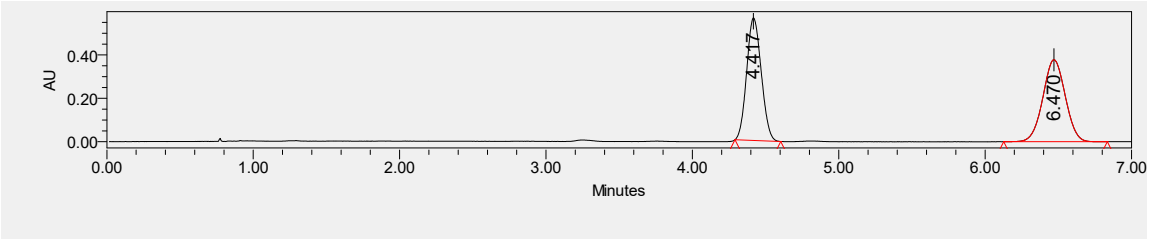
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.13 (s, 1H), 6.05 (s, 1H), 3.76 (s, 3H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 163.0 (d, *J* = 23.0 Hz), 161.1, 137.2, 135.0, 133.6, 129.5, 120.4, 119.1, 114.8, 97.9 (d, *J* = 236.8 Hz), 55.4, 20.9.

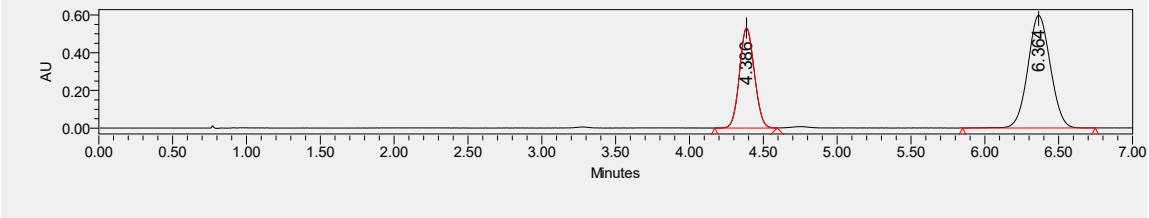
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −155.50. (s, 1F).

HRMS (ESI) Calculated for $C_{16}H_{16}FNO_2S$ ([M]+Na+) = 328.0780, Found 328.0775

IR (neat) 3392, 2924, 1677, 1594, 1529, 1494, 1460, 1289, 1248, 1177, 1028, 821, 640, 510 cm^{-1}.

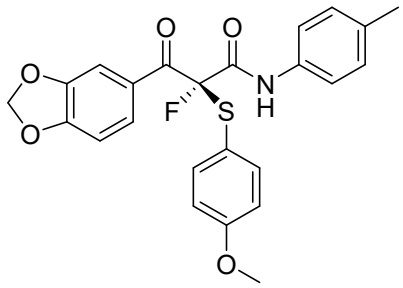


	Retention Time	Area	% Area
1	4.417	3911463	49.38
2	6.470	4009519	50.62



	Retention Time	Area	% Area
1	4.386	3698533	36.92
2	6.364	6318330	63.08

(*S*)-3-(benzo[d][1,3]dioxol-5-yl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4i):



colerless oil, 99% yield, 88% ee; $[\alpha]^{21}_{D}$ = -38.0 (*c* 1.54, CH_2Cl_2).

SFC Chiralcel IA-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 7.41 min, t_2 = 8.05 min

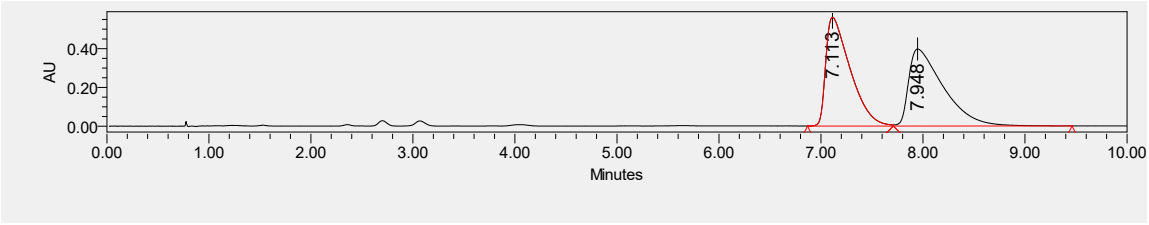
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 1.4 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 3H), 6.02 (s, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 187.9 (d, *J* = 25.0 Hz), 161.8 (d, *J* = 27.1 Hz), 161.5, 152.9, 148.0, 138.3, 135.0, 133.8, 129.5, 127.6, 127.55 (d, *J* = 3.0 Hz)., 120.2, 117.4, 114.9, 110.0 (d, *J* = 3.4 Hz), 108.1, 107.3 (d, *J* = 245.2 Hz), 102.1, 55.4, 20.9.

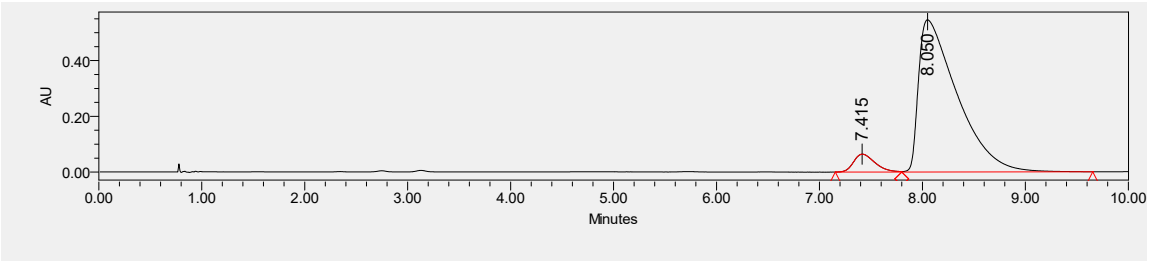
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –128.80. (s, 1F).

HRMS (ESI) Calculated for $C_{24}H_{20}FNO_5S$ ([M]+Na^+) = 476.0938, Found 476.0936

IR (neat) 3337, 2910, 1687, 1593, 1520, 1491, 1442, 1284, 1249, 1177, 1032, 813, 625, 508 cm^{-1}.

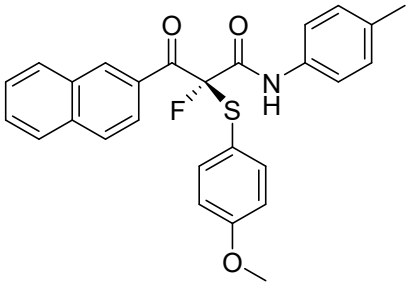


	Retention Time	Area	% Area
1	7.113	9294896	49.78
2	7.948	9375897	50.22



	Retention Time	Area	% Area
1	7.415	925243	6.12
2	8.050	14203808	93.88

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-(naphthalen-2-yl)-3-oxo-*N*-(*p*-tolyl)propanamide (4j):



white solid, m.p. 52–57 ºC, 95% yield, 40% ee; $[\alpha]^{22}_{D}$ = -2.3 (*c* 0.78, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.35 min, t_2 = 6.09 min

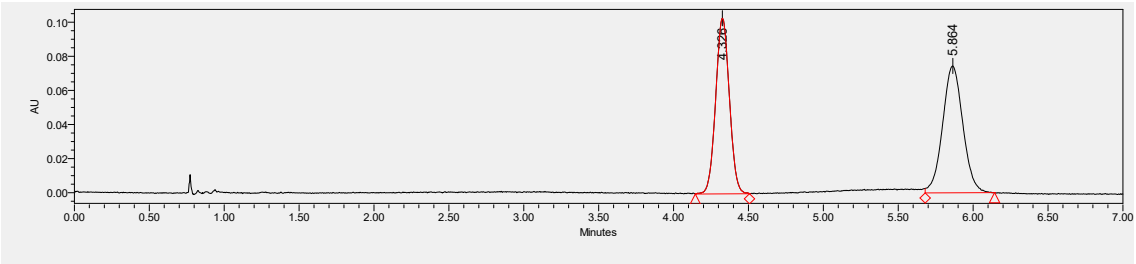
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.84 (dd, *J* = 8.5, 3.8 Hz, 2H), 7.61 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.24 – 7.18 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.3 (d, *J* = 25.9 Hz), 161.6 (d, *J* = 27.9 Hz), 161.5, 138.3, 137.2, 135.9, 135.1, 133.7, 133.1 (d, *J* = 6.2 Hz), 132.2, 130.6 (d, *J* = 2.7 Hz), 130.2, 129.6, 129.5, 129.3, 128.4, 127.7, 126.9, 125.1, 125.0, 120.3, 120.2, 117.3, 114.9, 114.8, 107.3 (d, *J* = 245.5 Hz), 55.4, 20.9.

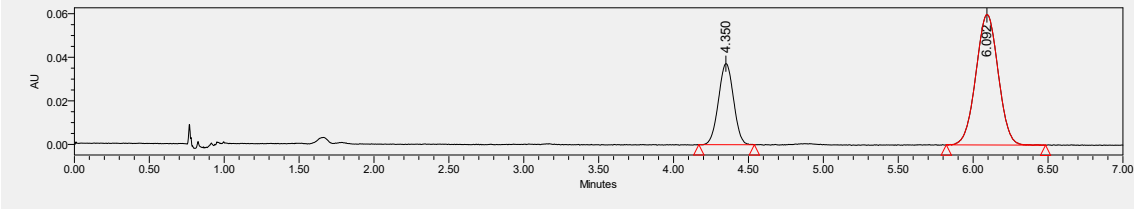
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –129.43. (s, 1F).

HRMS (ESI) Calculated for $C_{27}H_{22}FNO_3S$ ([M]+Na^+) = 482.1197, Found 482.1197

IR (neat) 3332, 2923, 1691, 1593, 1522, 1494, 1407, 1285, 1250, 1178, 1029, 815, 761, 508 cm^{-1}.

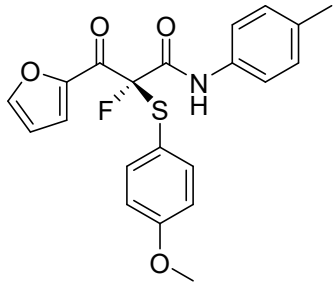


	Retention Time	Area	% Area
1	4.326	655080	48.38
2	5.864	698822	51.62



	Retention Time	Area	% Area
1	4.350	260066	29.63
2	6.092	617501	70.37

(*S*)-2-fluoro-3-(furan-2-yl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4k):



white solid, m.p. 137–140 ºC, 99% yield, 87% ee; $[\alpha]^{23}_{D}$ = -18.8 (*c* 1.23, CH_2Cl_2).

SFC Chiralcel IA-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.25 min, t_2 = 4.64 min

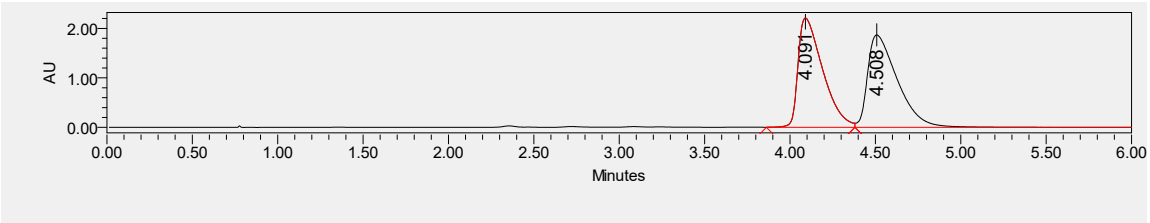
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.54 (t, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.46 (dd, *J* = 3.8, 1.6 Hz, 1H), 3.67 (s, 3H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 178.3 (d, *J* = 28.2 Hz), 160.7 (d, *J* = 26.3 Hz), 160.6, 149.0, 148.7 (d, *J* = 3.2 Hz), 138.3, 135.0, 133.8, 129.5, 129.4, 124.7 (d, *J* = 10.5 Hz), 120.2, 116.9, 114.9, 113.0, 105.7 (d, *J* = 244.2 Hz), 55.4, 20.9.

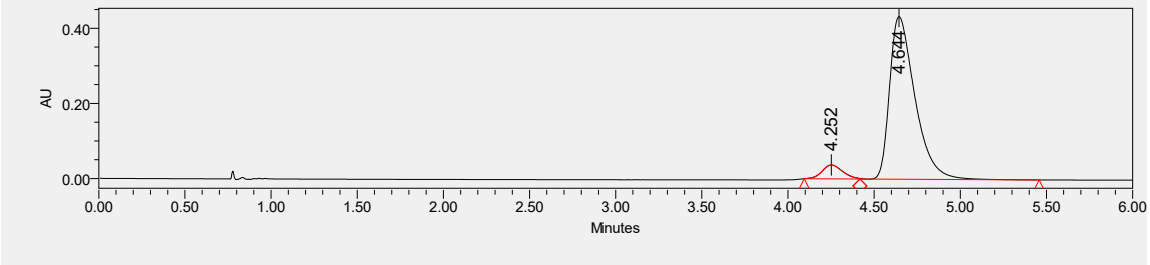
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –136.30. (s, 1F).

HRMS (ESI) Calculated for $C_{21}H_{18}FNO_4S$ ([M]+Na^+) = 422.0833, Found 422.0827

IR (neat) 3334, 2923, 1690, 1592, 1520, 1493, 1457, 1289, 1249, 1175, 1027, 813, 643, 509 cm^{-1}.

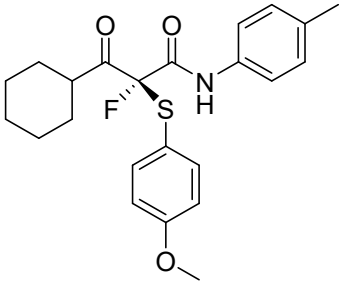


	Retention Time	Area	% Area
1	4.091	22152918	49.40
2	4.508	22695015	50.60



	Retention Time	Area	% Area
1	4.252	304022	6.43
2	4.644	4421562	93.57

(*S*)-3-cyclohexyl-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4l):



colerless oil, 95% yield, 86% ee; $[\alpha]^{22}_{D}$ = -45.9 (*c* 1.27, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.79 min, t_2 = 5.97 min

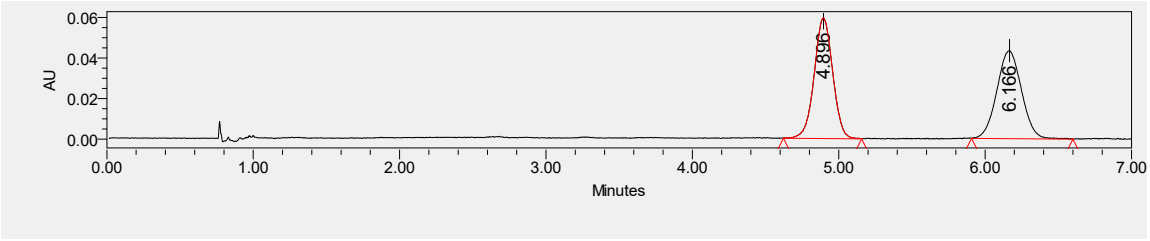
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.30 (s, 3H), 1.86 – 1.82 (m, 1H), 1.74 (s, 2H), 1.64 (d, *J* = 13.1 Hz, 2H), 1.32 – 1.13 (m, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 205.2 (d, *J* = 27.2 Hz), 161.5, 160.6 (d, *J* = 26.3 Hz), 138.2, 134.9, 133.9, 129.6, 120.1, 117.2, 114.9, 105.9 (d, *J* = 245.1 Hz), 55.4, 46.8, 28.5, 28.2, 25.6, 25.5, 25.3, 20.9.

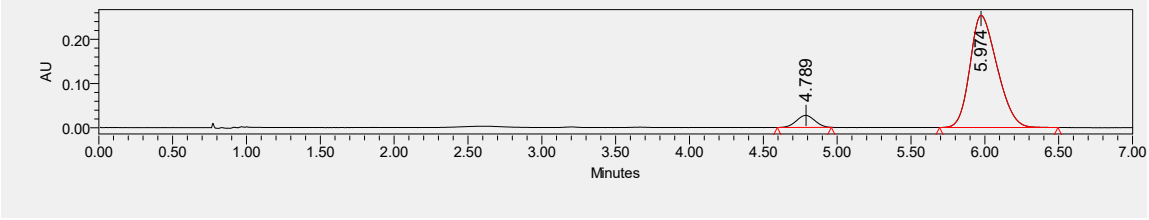
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –142.09. (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{26}FNO_3S$ ([M]+Na+) = 438.1510, Found 438.1507

IR (neat) 3343, 2930, 1689, 1593, 1522, 1494, 1448, 1292, 1249, 1177, 1028, 830, 643, 509 cm^{-1}.

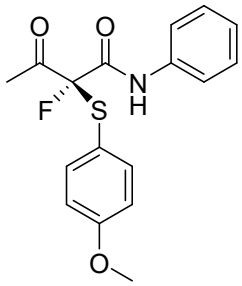


	Retention Time	Area	% Area
1	4.896	523149	50.73
2	6.166	508133	49.27



	Retention Time	Area	% Area
1	4.789	234778	6.78
2	5.974	3229118	93.22

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-phenylbutanamide (4m):



colorless oi; 75% yield, 87% ee; $[\alpha]^{22}_{D}$ = -64.5 (*c* 0.81, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 2.97 min, t_2 = 3.85 min

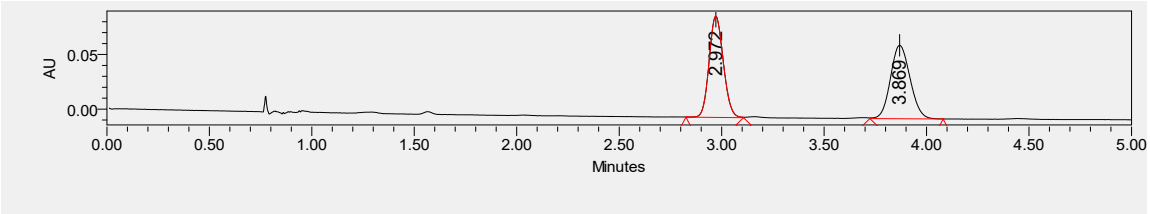
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 2.36 (d, *J* = 3.3 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 198.9 (d, *J* = 28.3 Hz), 161.6, 160.6 (d, *J* = 25.1 Hz), 138.0, 136.3, 129.1, 125.4, 120.2, 116.8, 115.0, 105.9 (d, *J* = 244.3 Hz), 55.4, 26.8.

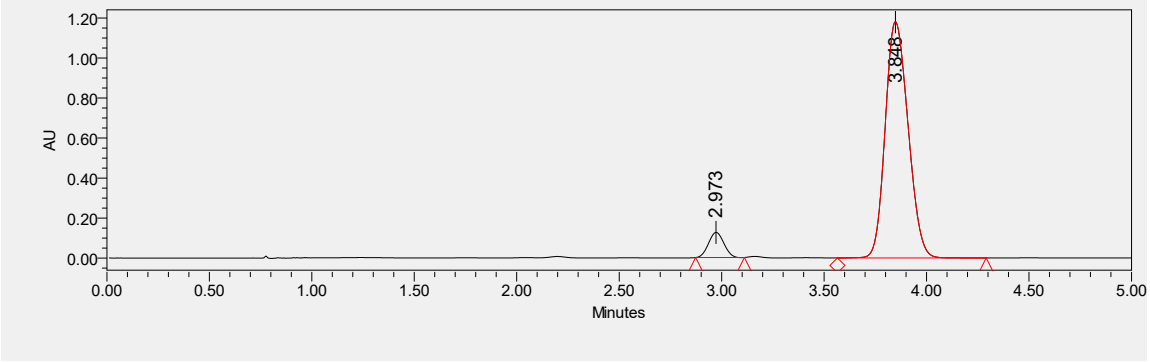
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −139.00. (s, 1F).

HRMS (ESI) Calculated for $C_{17}H_{16}FNO_3S$ ([M]+Na^+) = 356.0727, Found 356.0724

IR (neat) 3339, 2939, 1690, 1594, 1532, 1494, 1443, 1292, 1249, 1178, 1028, 831, 692, 502 cm^{-1}.

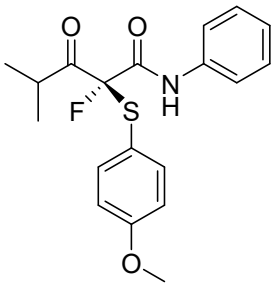


	Retention Time	Area	% Area
1	2.972	445048	49.94
2	3.869	446131	50.06



	Retention Time	Area	% Area
1	2.973	655176	6.68
2	3.848	9158453	93.32

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-4-methyl-3-oxo-*N*-phenylpentanamide (4n):



colorless oil;, 97% yield, 89% ee; $[\alpha]^{21}_{D}$ = -43.7 (*c* 0.65, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 2.33 min, t_2 = 2.74 min

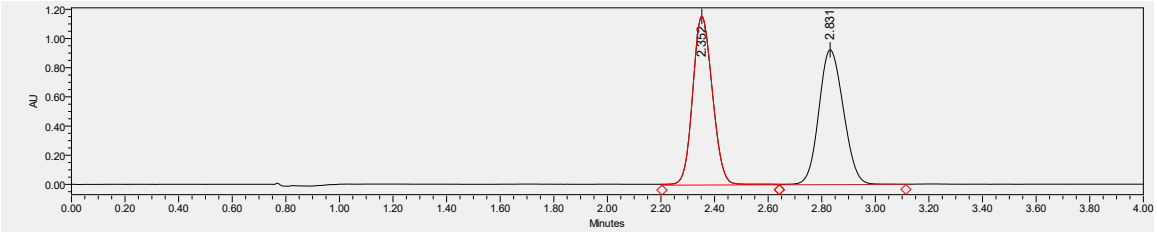
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.87 – 6.81 (m, 2H), 3.78 (s, 3H), 3.16 (pd, *J* = 6.8, 2.6 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.6 (d, *J* = 27.6 Hz), 161.6, 160.6 (d, *J* = 26.6 Hz), 138.2, 136.4, 129.1, 125.2, 120.0, 117.1, 114.9, 105.8 (d, *J* = 244.9 Hz), 55.4, 37.2, 18.3, 18.3, 18.0.

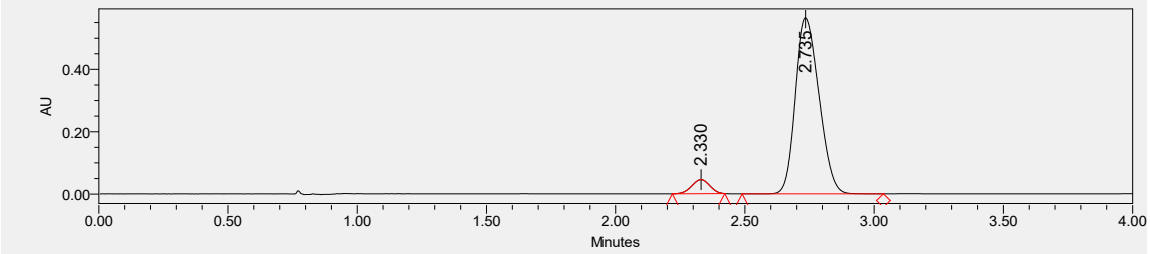
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –142.55. (s, 1F).

HRMS (ESI) Calculated for $C_{20}H_{22}FNO_3S$ ([M]+Na+) = 398.1197, Found 398.1195

IR (neat) 3345, 2975, 2937, 1719, 1691, 1595, 1532, 1495, 1443, 1292, 1250, 1177, 1028, 832, 692, 502 cm^{-1}.

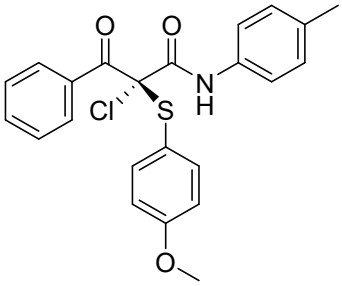


	Retention Time	Area	% Area
1	2.352	5929950	50.14
2	2.831	5895801	49.86



	Retention Time	Area	% Area
1	2.330	216694	5.65
2	2.735	3618224	94.35

(*R*)-2-chloro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (4o):



white solid, m.p. 47–52 ºC, 94% yield, 93% ee; $[\alpha]^{21}_{D}$ = -97.0 (*c* 1.48, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 7.48 min, t_2 = 10.81 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.72 (s, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 2.30 (s, 3H).

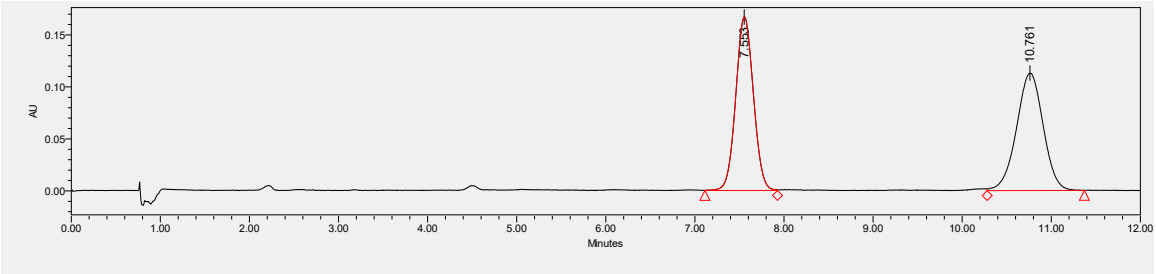
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 187.6, 162.6, 161.8, 139.1, 135.3, 133.9, 133.7, 132.5, 130.0, 129.6, 128.6, 120.1, 118.3, 114.8, 83.9, 55.4, 21.0.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –136.30. (s, 1F).

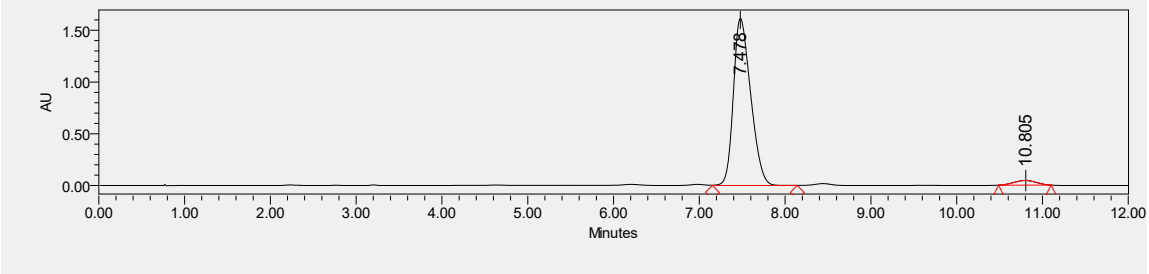
HRMS (ESI) Calculated for $C_{23}H_{20}{}^{34.9689}ClNO_3S$ ([M]+H^+) = 426.0925, Found 429.0932.

HRMS (ESI) Calculated for $C_{23}H_{20}{}^{36.9659}ClNO_3S$ ([M]+H^+) = 428.0896, Found 428.0881.

IR (neat) 3336, 2939, 1676, 1592, 1517, 1493, 1447, 1292, 1247, 1177, 1024, 809, 656, 506 cm^{-1}.

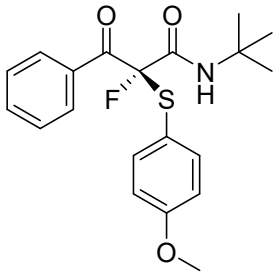


	Retention Time	Area	% Area
1	7.553	2299679	49.49
2	10.761	2347389	50.51



	Retention Time	Area	% Area
1	7.478	22598468	96.54
2	10.805	810249	3.46

(*S*)-N-(tert-butyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4p):



white solid, m.p. 101–105 ºC, 83% yield, 82% ee; $[\alpha]^{21}_{D}$ = -58.7 (*c* 1.26, CH_2Cl_2).

SFC Chiralcel IC-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.13 min, t_2 = 3.93 min

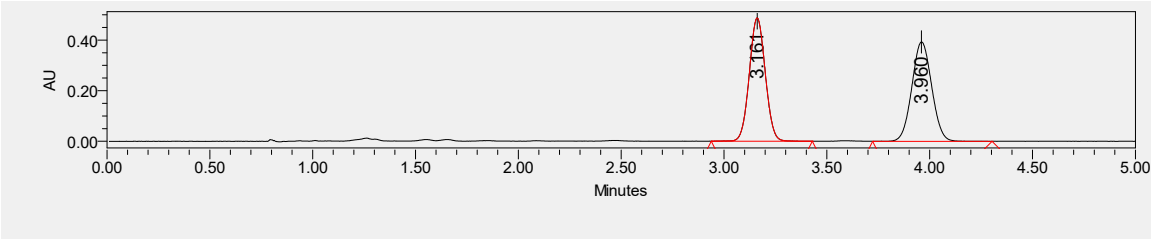
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 8.6, 1.3 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.51 – 7.47 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.89 – 6.85 (m, 2H), 5.91 (s, 1H), 3.81 (s, 3H), 1.18 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.0 (d, *J* = 26.0 Hz), 162.6 (d, *J* = 25.1 Hz), 162.7, 162.5, 161.3, 138.3, 133.9, 133.5 (d, *J* = 2.7 Hz), 130.1 (d, *J* = 3.6 Hz), 128.4, 118.0, 114.7, 107.1 (d, *J* = 244.9 Hz), 55.4, 52.1, 28.3.

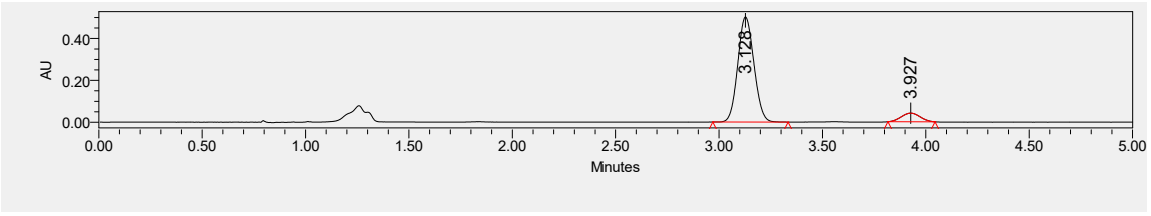
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −126.26. (s, 1F).

HRMS (ESI) Calculated for $C_{20}H_{22}FNO_3S$ ([M]+Na^+) = 398.1197, Found 398.1194

IR (neat) 3371, 2970, 1683, 1592, 1518, 1494, 1454, 1287, 1249, 1179, 1028, 826, 641, 529 cm^{-1}.

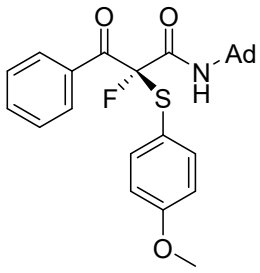


	Retention Time	Area	% Area
1	3.161	2634263	50.02
2	3.960	2632126	49.98



	Retention Time	Area	% Area
1	3.128	2722062	91.28
2	3.927	260082	8.72

(*S*)-*N*-((3*R*,5*R*,7*R*)-adamantan-1-yl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4q):



white solid, m.p. 52–58 ºC, 76% yield, 83% ee; $[\alpha]^{21}_{D}$ = -48.4 (*c* 1.87, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.54 min, t_2 = 6.12 min

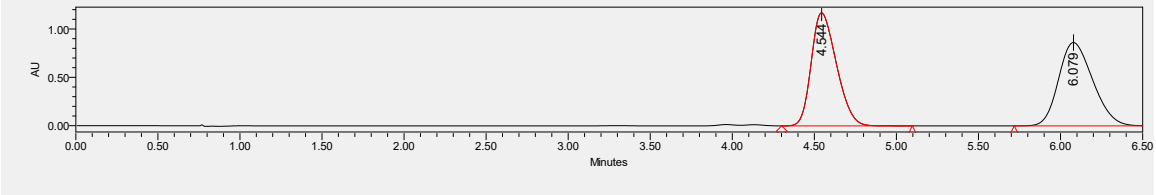
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 8.5, 1.3 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.90 – 6.85 (m, 2H), 5.77 (d, *J* = 3.3 Hz, 1H), 3.81 (s, 3H), 2.01 (s, 3H), 1.83 – 1.76 (m, 6H), 1.61 (dt, *J* = 6.4, 3.0 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.0 (d, *J* = 25.5 Hz), 162.3 (d, *J* = 25.2 Hz), 161.3, 138.3, 133.9, 133.4 (d, *J* = 2.2 Hz), 130.1 (d, *J* = 3.6 Hz), 128.4, 118.0, 114.7,114.6, 107.0 (d, *J* = 244.8 Hz), 55.5, 52.8, 41.0, 36.1, 29.3.

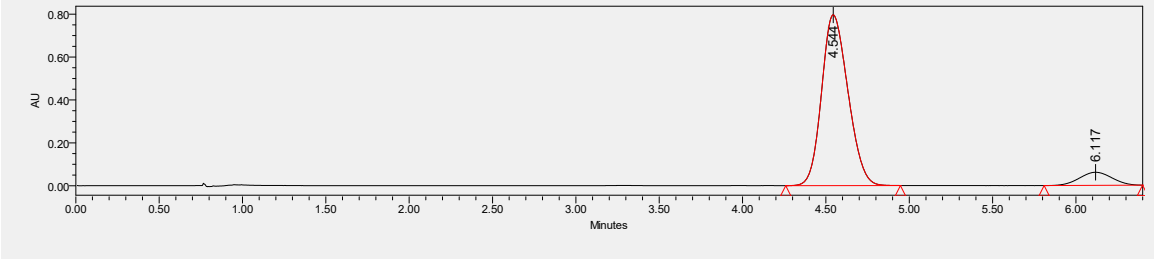
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –125.89. (s, 1F).

HRMS (ESI) Calculated for $C_{26}H_{28}FNO_3S$ ([M]+Na^+) = 476.1666, Found 476.1664

IR (neat) 3417, 2906, 1682, 1592, 1517, 1450, 1360, 1248, 1178, 1028, 828, 693, 528 cm^{-1}.

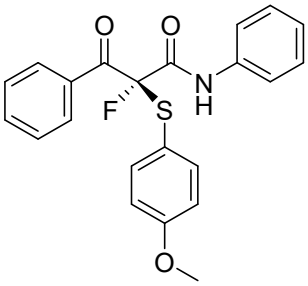


	Retention Time	Area	% Area
1	4.544	12463524	50.00
2	6.079	12465489	50.00



	Retention Time	Area	% Area
1	4.544	8746430	91.39
2	6.117	824329	8.61

(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*,3-diphenylpropanamide (4r):



white solid, m.p. 126–128 ºC, 96% yield, 90% ee; $[\alpha]^{22}_{D}$ = -75.4 (*c* 1.21, CH_2Cl_2).

SFC Chiralcel IC-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 4.78 min, t_2 = 5.22 min

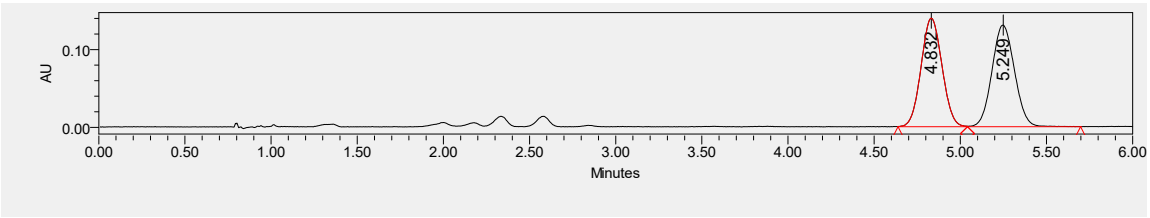
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.92 (s, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.42 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.32 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.3 (d, *J* = 26.1 Hz), 161.7 (d, *J* = 26.5 Hz), 161.6, 138.3, 136.3, 134.3, 133.4 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 4.3 Hz), 129.1, 128.6, 125.3, 120.3, 120.1, 117.2, 114.9, 107.2 (d, *J* = 245.3 Hz), 55.4.

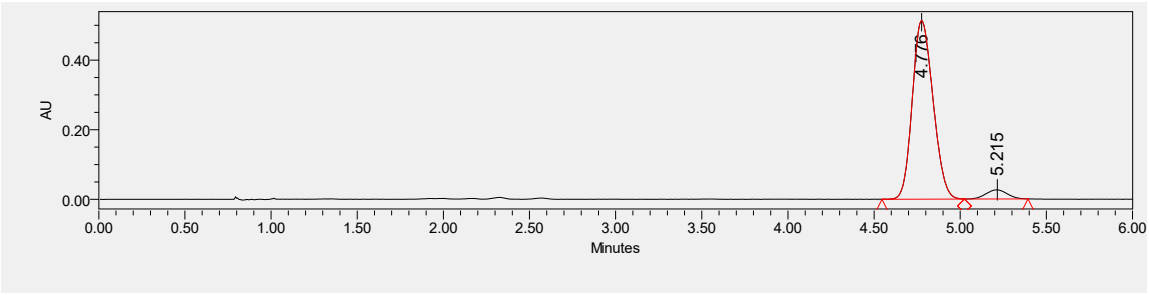
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –129.78. (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{18}FNO_3S$ ([M]+Na^+) = 418.0884, Found 418.0880

IR (neat) 3336, 3063, 1697, 1595, 1532, 1495, 1445, 1292, 1250, 1178, 1028, 833, 637, 502 cm^{-1}.

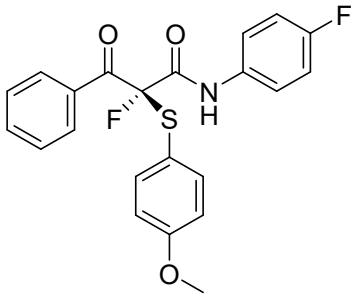


	Retention Time	Area	% Area
1	4.832	1175295	49.80
2	5.249	1184750	50.20



	Retention Time	Area	% Area
1	4.776	4297211	94.95
2	5.215	228551	5.05

(*S*)-2-fluoro-*N*-(4-fluorophenyl)-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4s):



colorless oil, 89% yield, 90% ee; $[\alpha]^{21}_{D}$ = -71.1 (*c* 1.24, CH_2Cl_2).

SFC Chiralcel IC-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.52 min, t_2 = 3.84 min

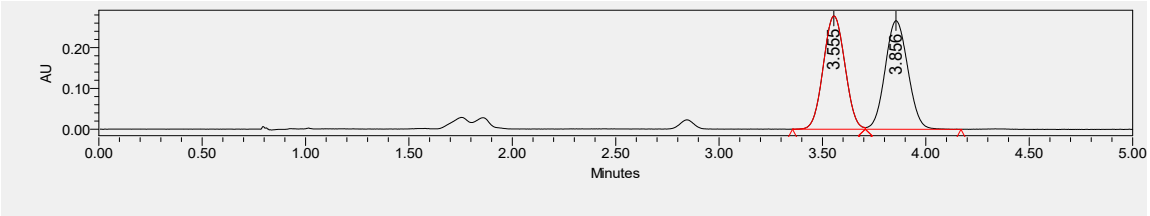
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.99 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.43 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.27 (dd, *J* = 9.1, 4.7 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 190.3 (d, *J* = 26.1 Hz), 161.8 (d, *J* = 26.5 Hz), 161.6, 159.9 (d, *J* = 245.1 Hz), 138.3, 134.3, 133.3 (d, *J* = 2.2 Hz), 132.3 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 4.3 Hz), 128.6, 122.0 (d, *J* = 7.7 Hz), 117.2, 115.8 115.7, 114.9, 107.1 (d, *J* = 245.3 Hz), 55.4.

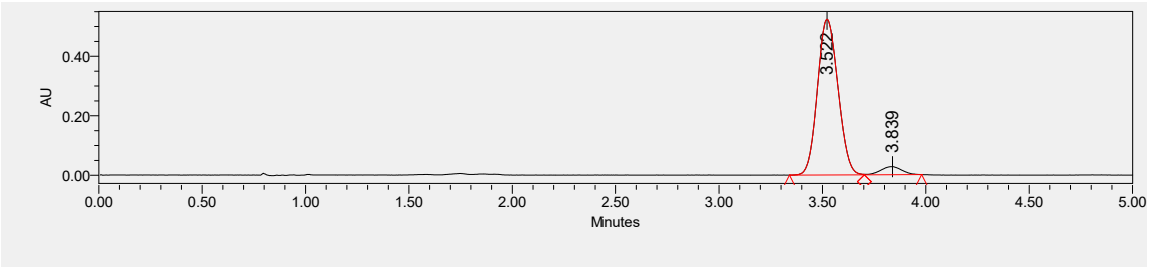
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –116.38 (s, 1F), 129.99 (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{17}F_2NO_3S$ ([M]+Na^+) = 436.0789, Found 436.0788

IR (neat) 3325, 3070, 1696, 1592, 1511, 1447, 1291, 1250, 1178, 1029, 831, 627, 516 cm^{-1}.

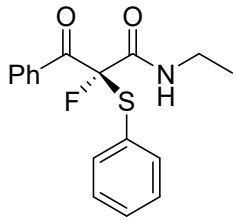


	Retention Time	Area	% Area
1	3.555	2015196	49.80
2	3.856	2031255	50.20



	Retention Time	Area	% Area
1	3.522	3606910	94.95
2	3.839	191762	5.05

(S)-*N*-ethyl-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanamide (4t):



white solid, m.p. 92–94 ºC, 75% yield, 73% ee; $[\alpha]^{30}_{D}$ = -49.2 (*c* 0.24, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 4.29 min, t_2 = 4.64 min

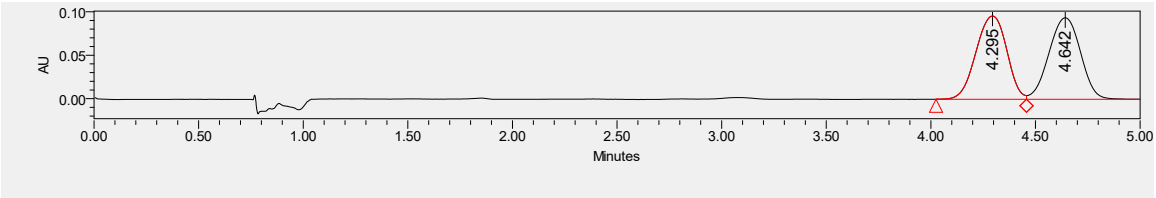
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.98 (m, 2H), 7.57 (d, *J* = 7.4 Hz, 3H), 7.42 (q, *J* = 7.7 Hz, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 6.17 (d, *J* = 6.1 Hz, 1H), 3.15 (m, *J* = 17.3, 7.0 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.8 (d, *J* = 25.9 Hz), 163.4 (d, *J* = 26.2 Hz), 136.4, 134.1, 133.4 (d, *J* = 2.2 Hz), 130.2 (d, *J* = 2.0 Hz), 130.1, 129.2, 128.4, 127.5, 107.5 (d, *J* = 245.0 Hz), 34.9, 14.3.

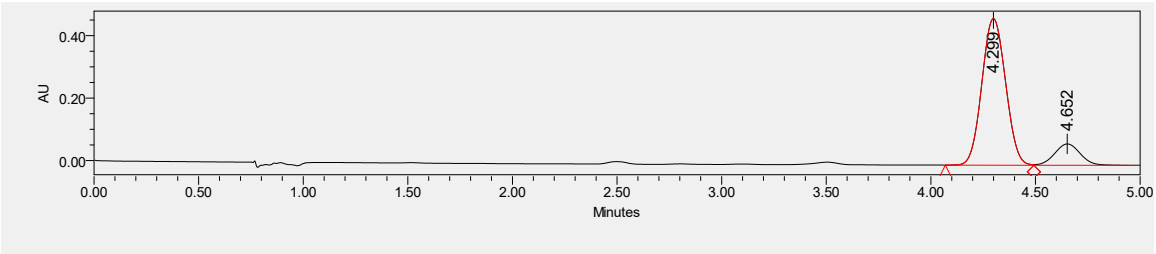
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ −128.23. (s, 1F).

HRMS (ESI) Calculated for $C_{17}H_{16}FNO_2S$ ([M]+Na^+) = 340.0778, Found 340.0775

IR (neat) 3325, 2932, 2855, 1699, 1666, 1526, 1187, 993, 840, 747, 632 cm^{-1}.

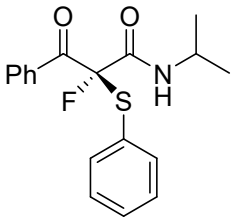


	Retention Time	Area	% Area
1	4.295	976023	49.77
2	4.642	985210	50.23



	Retention Time	Area	% Area
1	4.299	3692183	86.36
2	4.652	583088	13.64

***(S)*-2-fluoro-N-isopropyl-3-oxo-3-phenyl-2-(phenylthio)propanamide (4u):**



white solid, m.p. 127–129 ºC, 74% yield, 70% ee; $[\alpha]^{31}_{D}$ = -118.7 (*c* 0.24, CH_2Cl_2).

HPLC: Chiralcel ADH, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 280 nm, t_1 = 6.16 min, t_2 = 7.10 min

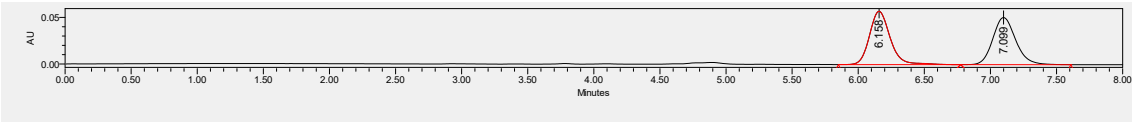
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, *J* = 8.5, 1.4 Hz, 2H), 7.63 – 7.55 (m, 3H), 7.48 – 7.38 (m, 3H), 7.34 (dd, *J* = 8.3, 6.6 Hz, 2H), 6.07 – 5.82 (m, 1H), 4.02 – 3.77 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ δ 189.5 (d, *J* = 25.5 Hz), 162.7 (d, *J* = 26.2 Hz), 136.4, 134.1, 133.3 (d, *J* = 2.2 Hz), 130.1, 130.1, 129.2, 128.4, 127.6, 107.5 (d, *J* = 244.8 Hz), 42.1, 22.3, 22.0.

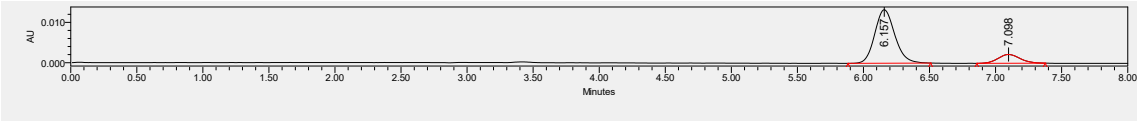
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -127.40. (s, 1F).

HRMS (ESI) Calculated for $C_{18}H_{18}FNO_2S$ ([M]+Na^+) = 354.0934, Found 354.0931

IR (neat) 3319, 2974, 1697, 1663, 1540, 1451, 1252, 1155, 991, 806, 691 cm^{-1}.

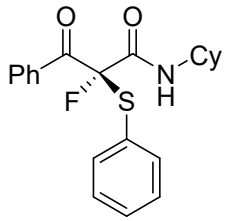


	Retention Time	Area	% Area
1	6.158	620624	50.47
2	7.099	609156	49.53



	Retention Time	Area	% Area
1	6.157	139991	84.75
2	7.098	25187	15.25

***(S)-N*-cyclohexyl-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanamide (4v):**



white solid, m.p. 128–131 ºC, 57% yield, 49% ee; $[\alpha]^{30}_{D}$ = -86.7 (*c* 0.23, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 6.16 min, t_2 = 7.10 min

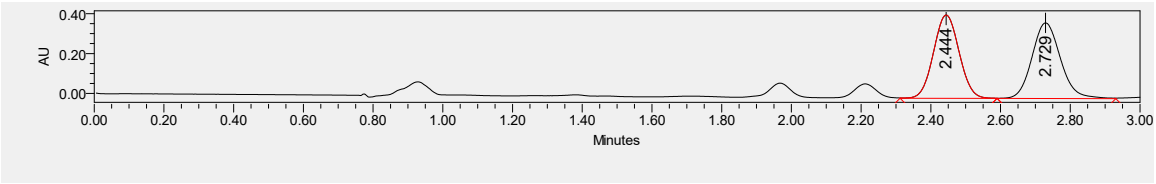
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.96 (m, 2H), 7.57 (m, *J* = 7.0, 6.1, 1.3 Hz, 3H), 7.47 – 7.38 (m, 3H), 7.34 (m, *J* = 8.3, 6.5 Hz, 2H), 6.10 – 5.91 (m, 1H), 3.58 (m, *J* = 11.1, 8.2, 4.0 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.67 – 1.53 (m, 3H), 1.46 (m, *J* = 10.4, 3.8, 1.9 Hz, 1H), 1.25 (m, *J* = 11.7, 9.9, 3.3 Hz, 2H), 1.08 (m, *J* = 22.5, 15.3, 10.5, 3.7 Hz, 2H), 0.82 (qd, *J* = 11.6, 3.5 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.6 (d, *J* = 25.3 Hz), 162.0 (d, *J* = 26.2 Hz), 136.4, 134.1, 133.3 (d, *J* = 2.2 Hz), 130.2, 130.1 (d, *J* = 2.4 Hz), 129.2, 128.4, 127.6, 107.5 (d, *J* = 244.9 Hz), 48.7, 32.6, 32.2, 25.3, 24.6.

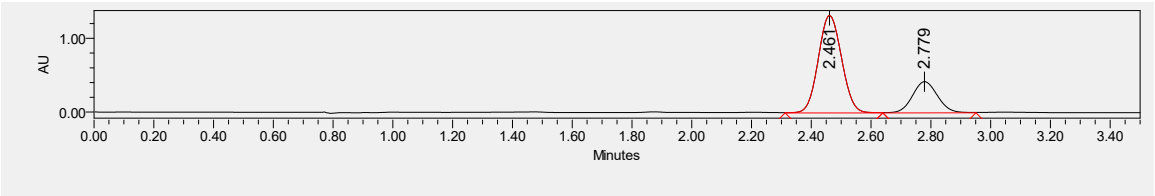
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -127.37. (s, 1F).

HRMS (ESI) Calculated for $C_{21}H_{22}FNO_2S$ ([M]+Na^+) = 394.1247, Found 394.1245

IR (neat) 3325, 2931, 2855, 1698, 1665, 1597, 1448, 1187, 747, 632 cm^{-1}.

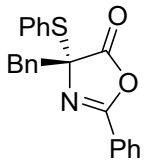


	Retention Time	Area	% Area
1	2.444	2130033	49.66
2	2.729	2159012	50.34



	Retention Time	Area	% Area
1	2.461	7163659	74.32
2	2.779	2475066	25.68

(*R*)-4-benzyl-2-phenyl-4-(phenylthio)oxazol-5(4H)-one (6a):



white solid, m.p. 93–96 ºC, 92% yield, 78% ee; $[\alpha]^{22}_{D}$ = 24.1 (*c* 0.63, CH_2Cl_2).

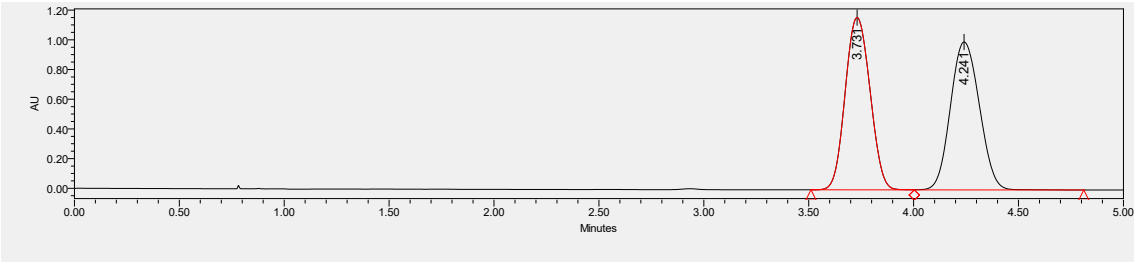
SFC Chiralcel AD-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 280 nm, t_1 = 3.70 min, t_2 = 4.25 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.55 – 7.45 (m, 3H), 7.35 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.22 – 7.12 (m, 5H), 3.52 (q, *J* = 13.5 Hz, 2H).

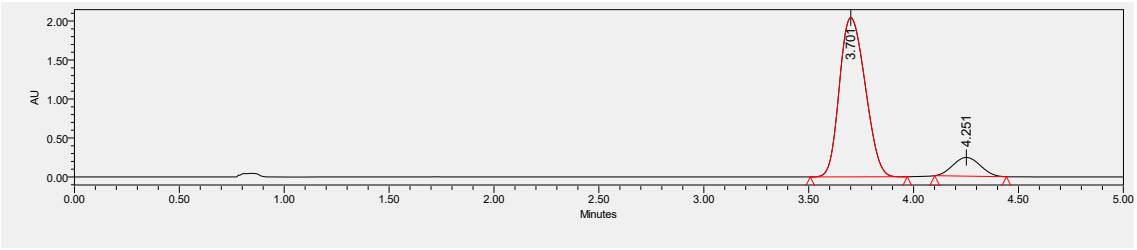
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.5, 160.8, 137.1, 133.7, 132.9, 130.3, 129.0, 128.6, 128.4, 128.0, 127.8, 127.6, 125.0, 80.1, 41.5.

HRMS (ESI) Calculated for $C_{22}H_{17}NO_2S$ ([M]+Na^+) = 382.0872, Found 382.0867

IR (neat) 3061, 2925, 1817, 1643, 1579, 1494, 1451, 1321, 1239, 1176, 1026, 748, 695, 508 cm^{-1}.

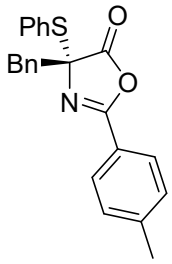


	Retention Time	Area	% Area
1	3.731	9547872	50.00
2	4.241	9547459	50.00



	Retention Time	Area	% Area
1	3.701	17427438	88.94
2	4.251	2166603	11.06

(*R*)-4-benzyl-4-(phenylthio)-2-(p-tolyl)oxazol-5(4H)-one (6b):



colorless oil, 86% yield, 75% ee; $[\alpha]^{22}_{D}$ = 11.8 (*c* 0.64, CH_2Cl_2).

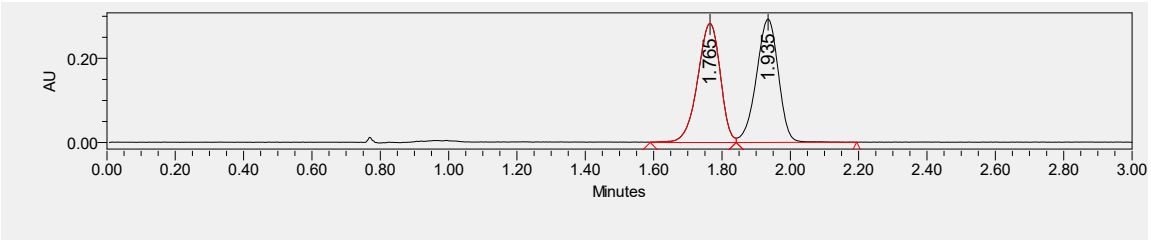
SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 254 nm, t_1 = 1.76 min, t_2 = 1.93 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.20 – 7.13 (m, 7H), 3.55 – 3.46 (m, 2H), 2.36 (s, 3H).

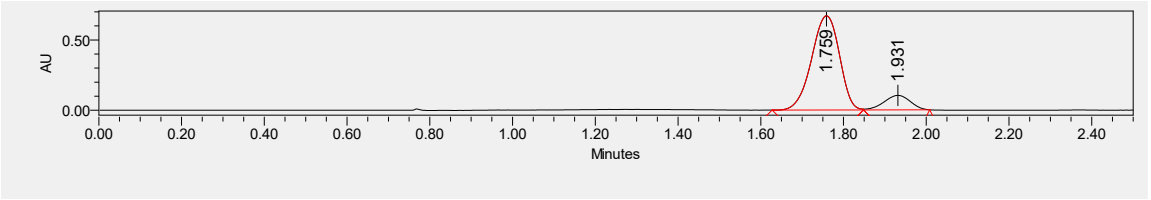
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.6, 160.9, 143.7, 137.1, 133.7, 130.3, 130.3, 129.4, 129.0, 128.4, 128.1, 127.8, 127.5, 127.2, 122.2, 80.1, 41.6, 21.7.

HRMS (ESI) Calculated for $C_{23}H_{19}NO_2S$ ([M]+Na^+) = 396.1029, Found 396.1025

IR (neat) 3033, 2924, 1817, 1641, 1573, 1511, 1437, 1316, 1296, 1237, 1180, 1062, 828, 697, 488 cm^{-1}.

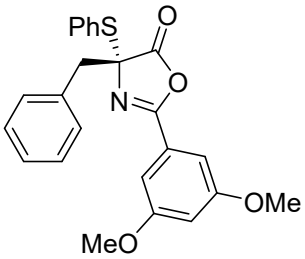


	Retention Time	Area	% Area
1	1.765	1304497	49.82
2	1.935	1313713	50.18



	Retention Time	Area	% Area
1	1.759	3125717	87.33
2	1.931	453532	12.67

(*R*)-4-benzyl-2-(3,5-dimethoxyphenyl)-4-(phenylthio)oxazol-5(4H)-one (6c):



colorless oil, 95% yield, 74% ee; $[\alpha]^{22}_{D}$ = 16.0 (*c* 0.69, CH_2Cl_2).

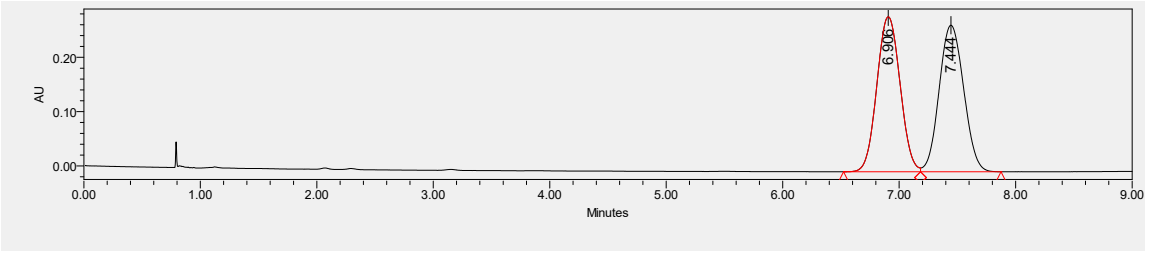
SFC Chiralcel OD-3, CO_2/MeOH = 95/5, 1.5 mL/min, λ = 254 nm, t_1 = 6.93 min, t_2 = 7.49 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.31 – 7.16 (m, 9H), 6.80 (d, *J* = 2.3 Hz, 2H), 6.56 (t, *J* = 2.3 Hz, 1H), 3.76 (s, 6H), 3.51 (q, *J* = 13.5 Hz, 2H).

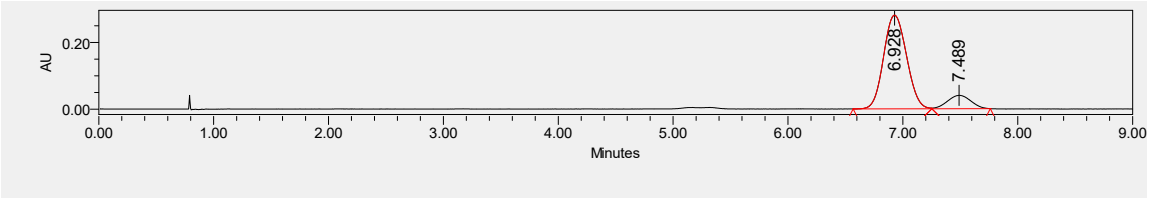
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.4, 160.7, 160.7 137.1, 133.6, 130.4, 130.3, 129.6, 129.1, 128.5, 128.4, 128.0, 127.6, 127.3, 126.6, 105.7, 105.4, 80.1, 55.6, 41.6.

HRMS (ESI) Calculated for $C_{24}H_{21}NO_4S$ ([M]+H^+) = 420.1264, Found 420.1264

IR (neat) 2936, 2840, 1821, 1643, 1595, 1458, 1427, 1315, 1232, 1158, 1045, 847, 698, 615 cm^{-1}.

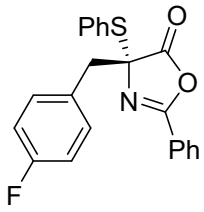


	Retention Time	Area	% Area
1	6.906	3947822	50.00
2	7.444	3947328	50.00



	Retention Time	Area	% Area
1	6.928	3885845	87.29
2	7.489	565687	12.71

(*R*)-4-(4-fluorobenzyl)-2-phenyl-4-(phenylthio)oxazol-5(4H)-one (6d):



colorless oil, 70% yield, 74% ee; $[\alpha]^{22}_{D}$ = 24.9 (*c* 0.55, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 254 nm, t_1 = 1.46 min, t_2 = 1.74 min

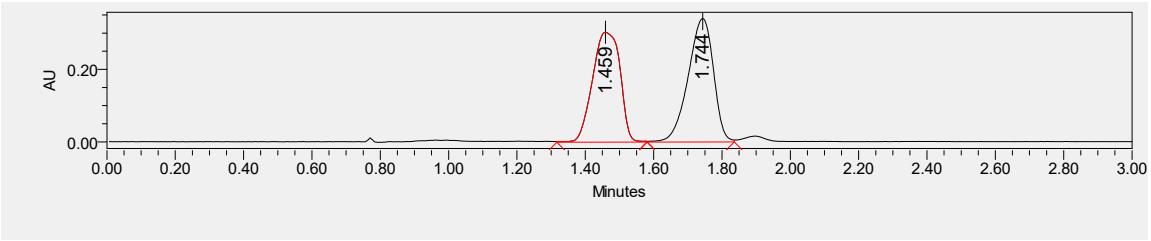
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 3H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.09 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.45 – 3.37 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.5, 162.2 (d, *J* = 246.1 Hz), 160.9, 137.1, 133.0, 131.9 (d, *J* = 7.7 Hz), 130.4, 129.4 (d, *J* = 3.6 Hz), 129.0, 128.7, 127.8, 127.8, 124.8, 115.3 (d, *J* = 20.9 Hz), 80.0, 40.7.

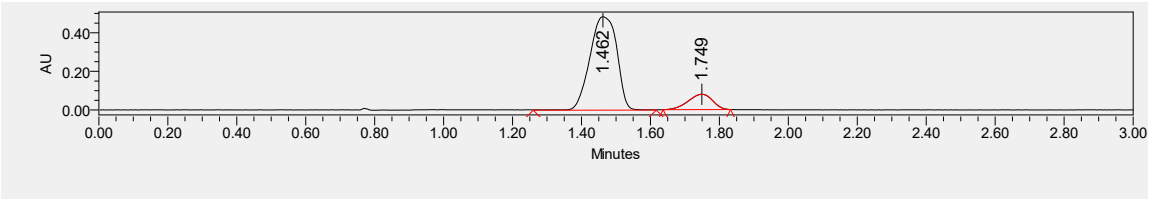
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −114.69 (s, 1F).

HRMS (ESI) Calculated for $C_{22}H_{16}FNO_2S$ ([M]+H^+) = 378.0959, Found 378.0954

IR (neat) 3063, 2927, 1818, 1643, 1579, 1509, 1447, 1321, 1293, 1225, 1159, 1066, 834, 694, 487 cm^{-1}.

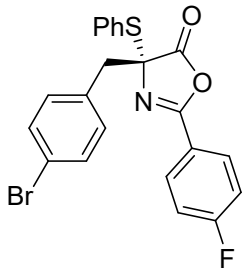


	Retention Time	Area	% Area
1	1.459	1699946	49.21
2	1.744	1754622	50.79



	Retention Time	Area	% Area
1	1.462	2638376	87.06
2	1.749	392270	12.94

(*R*)-4-(4-bromobenzyl)-2-(4-fluorophenyl)-4-(phenylthio)oxazol-5(4H)-one (6e):



colorless oil, 82% yield, 82% ee; $[\alpha]^{22}_{D}$ = 19.3 (*c* 0.67, CH_2Cl_2).

SFC Chiralcel AD-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 254 nm, t_1 = 2.03 min, t_2 = 2.60 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 3.50 – 3.41 (m, 2H).

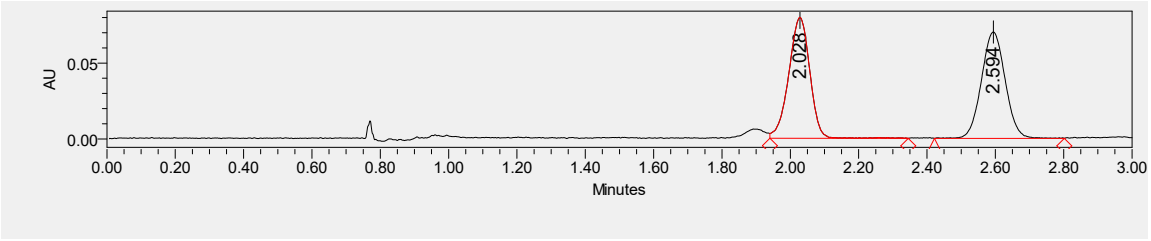
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.2, 165.6 (d, *J* = 255.9 Hz), 160.1, 137.2, 132.6, 132.0, 131.6, 130.5, 130.3 (d, *J* = 8.9 Hz), 129.0, 127.7, 121.9, 121.0 (d, *J* = 3.2 Hz), 116.1 (d, *J* = 21.9 Hz), 79.7, 40.8.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −104.36 (s, 1F).

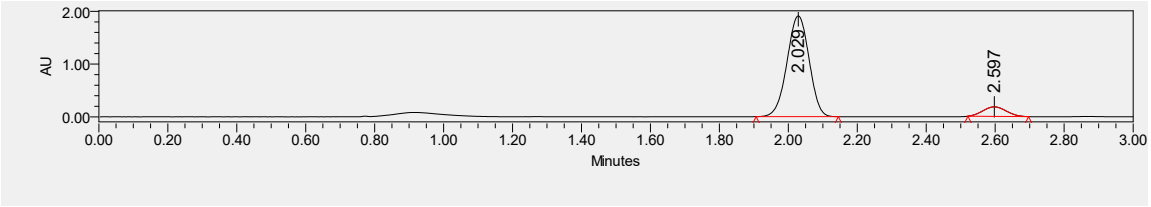
HRMS (ESI) Calculated for $C_{22}H_{15}{}^{78.9183}BrFNO_2S$ ([M]+H^+) = 456.0064, Found 456.0066.

HRMS (ESI) Calculated for $C_{22}H_{15}{}^{80.9163}BrFNO_2S$ ([M]+H^+) = 458.0043, Found 458.0040.

IR (neat) 2927, 1819, 1644, 1602, 1508, 1438, 1412, 1295, 1234, 1157, 1069, 847, 694, 505 cm^{-1}.

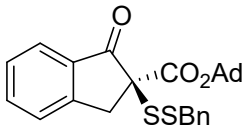


	Retention Time	Area	% Area
1	2.028	342105	50.18
2	2.594	339705	49.82



	Retention Time	Area	% Area
1	2.029	8490121	90.89
2	2.597	850977	9.11

(3*S*)-adamantan-1-yl (2*S*)-2-((*S*)-benzylsulfinothioyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (9):



colorless oil, 85% yield, 61% ee; $[\alpha]^{23}_{D}$ = -5.19 (*c* 0.42, CH_2Cl_2).

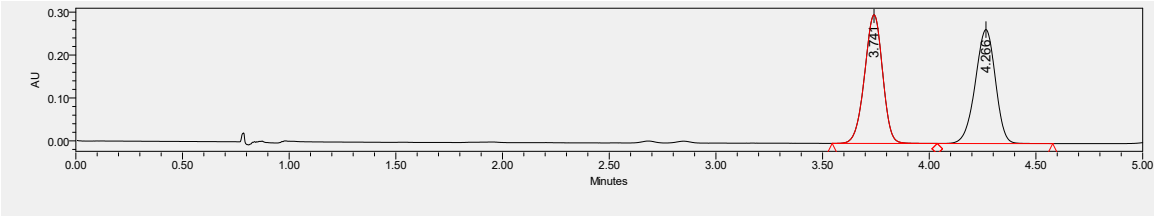
SFC Chiralcel IB-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 3.74 min, t_2 = 4.27.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 6.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.27 – 7.20 (m, 3H), 7.10 (dd, *J* = 7.6, 1.9 Hz, 2H), 3.92 – 3.83 (m, 2H), 3.75 (d, *J* = 12.0 Hz, 1H), 3.47 (d, *J* = 18.0 Hz, 1H), 2.19 – 2.08 (m, 10H), 1.63 (d, *J* = 3.0 Hz, 7H).

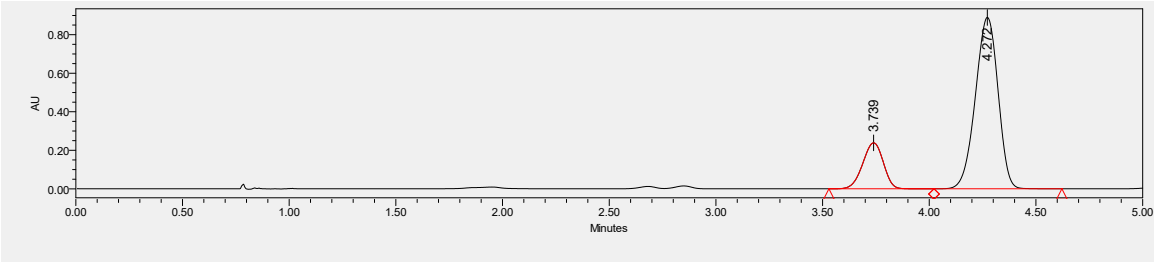
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 167.0, 151.9, 136.5, 135.6, 134.9, 129.4, 128.5, 128.1, 127.5, 126.2, 125.0, 83.9, 65.1, 43.9, 41.1, 39.3, 36.0, 30.9.

HRMS (ESI) Calculated for $C_{27}H_{28}O_3S_2$ ([M]+Na^+) = 487.1372, Found 487.1369

IR (neat) 2910, 1710, 1605, 1494, 1457, 1423, 1351, 1238, 1179, 1047, 761, 699, 470 cm^{-1}.

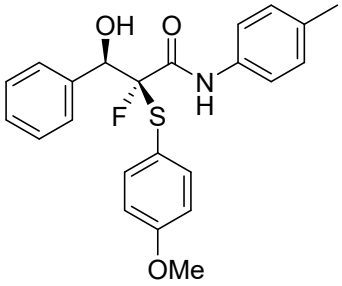


	Retention Time	Area	% Area
1	3.741	1752304	50.25
2	4.266	1734932	49.75



	Retention Time	Area	% Area
1	3.739	1603919	19.65
2	4.272	6557269	80.35

(2*S*,3*R*)-2-fluoro-3-hydroxy-2-((4-methoxyphenyl)thio)-3-phenyl-N-(p-tolyl)propanamide (10):



white solid, m.p. 147-149 ºC, 98% yield, 99% ee/99% ee, 78:22 dr; $[\alpha]^{21}_D$ = -15.3 (*c* 0.69, CH_2Cl_2).

SFC Chiralcel OX-3, CO_2/MeOH = 82/18, 1.5 mL/min, λ = 280 nm, t_1 = 10.34 min, t_2 = 11.55 min, t_3 = 13.30 min

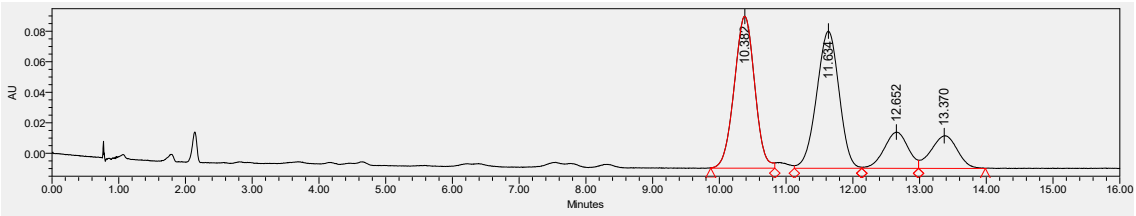
^{1}H NMR (400 MHz, $CDOD_3$) δ 7.53 – 7.48 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.33 – 7.23 (m, 3H), 7.01 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 5.44 (d, *J* = 23.0 Hz, 1H), 3.69 (s, 3H), 2.20 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDOD_3$) δ 165.3 (d, *J* = 25.3 Hz), 161.2, 138.5, 137.9, 134.8, 133.5, 128.5, 128.4, 127.7 (d, *J* = 25.3 Hz), 127.6, 122.0, 119.4, 114.1, 111.0 (d, *J* = 246.3 Hz), 76.00 (d, *J* = 19.7 Hz), 54.4, 19.5.

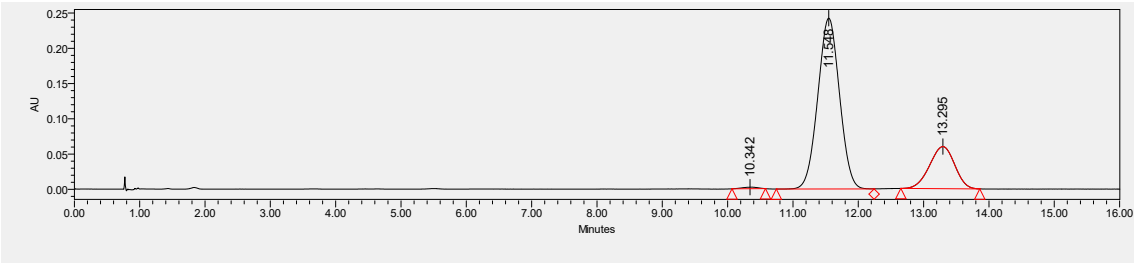
^{19}F{^{1}H} NMR (377 MHz, $CDOD_3$) δ –150.32 (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{22}FNO_3S$ ([M]+Na^+) = 434.1198, Found 434.1197

IR (neat) 3414, 2922, 1664, 1591, 1517, 1437, 1401, 1289, 1249, 1177, 1028, 829, 701, 507 cm^{-1}.

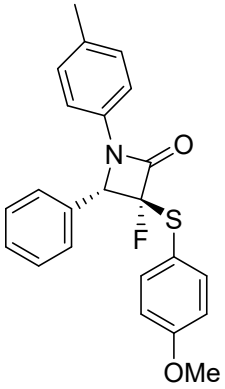


	Retention Time	Area	% Area
1	10.382	2111006	39.26
2	11.634	2090137	38.87
3	12.652	589987	10.97
4	13.370	585694	10.89



	Retention Time	Area	% Area
1	10.342	36728	0.51
2	11.548	5578626	77.41
3	13.295	1591171	22.08

(3*S*,4*S*)-3-fluoro-3-((4-methoxyphenyl)thio)-4-phenyl-1-(*p*-tolyl)azetidin-2-one (11):



white solid, m.p. 164-168 ºC, 71% yield, 99% ee, >19:1 dr; $[\alpha]^{18}_{D}$ = 349.3 (*c* 0.14, CH_2Cl_2).

SFC Chiralcel IA-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 254 nm, t_1 = 3.03 min, t_2 = 3.89 min.

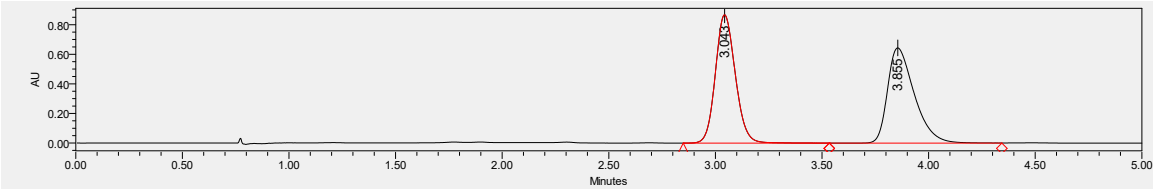
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.30 (dd, J = 11.4, 7.1 Hz, 3H), 7.18 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 7.3 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 5.20 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.2, 159.3 (d, J = 29.5 Hz), 137.2, 134.8, 134.1 (d, J = 3.1 Hz), 131.6, 129.8, 129.2, 128.8, 127.5, 118.3, 117.7, 114.9, 105.0 (d, J = 276.8 Hz), 68.3 (d, J = 26.4 Hz), 55.5, 21.0.

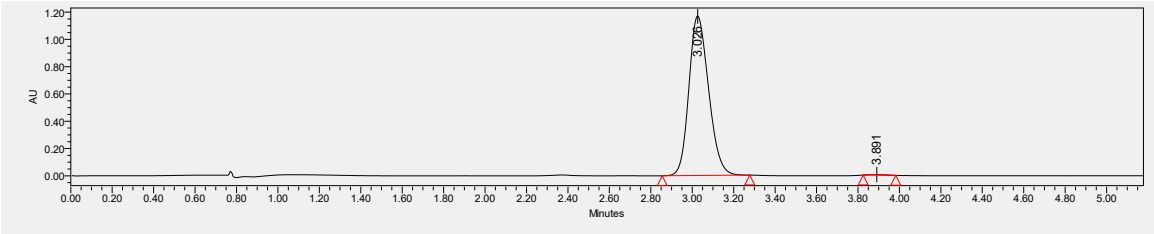
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –141.13 (s, 1F).

HRMS (ESI) Calculated for $C_{23}H_{20}FNO_2S$ ([M]+Na^+) = 416.1091, Found 416.1089

IR (neat) 2923, 2855, 1759, 1590, 1515, 1493, 1458, 1385, 1290, 1249, 1163, 1129, 1104, 1029, 985, 825, 700, 511 cm^{-1}.

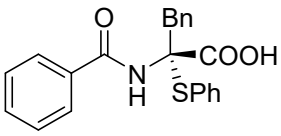


	Retention Time	Area	% Area
1	3.043	5630658	50.05
2	3.855	5620154	49.95



	Retention Time	Area	% Area
1	3.026	7721148	99.70
2	3.891	23105	0.30

(*R*)-2-benzamido-3-phenyl-2-(phenylthio)propanoic acid (12):



white solid, m.p. 148-152 ºC, 98% yield, 78% ee; $[\alpha]^{21}_{D}$ = -199.5 (*c* 0.85, CH_3COCH_3).

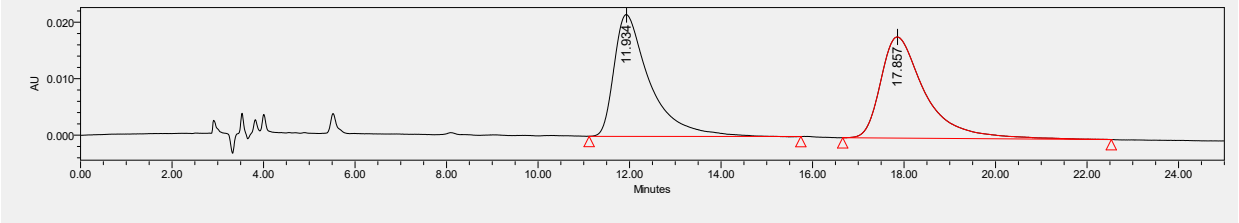
HPLC: Chiralcel ADH, hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, t_1 = 12.70 min, t_2 = 18.38 min.

^{1}H NMR (400 MHz, CD_3COCD_3) δ 7.60 – 7.35 (m, 8H), 7.33 – 7.25 (m, 4H), 7.25 – 7.14 (m, 4H), 4.43 (d, *J* = 13.3 Hz, 1H), 3.59 (d, *J* = 13.3 Hz, 1H).

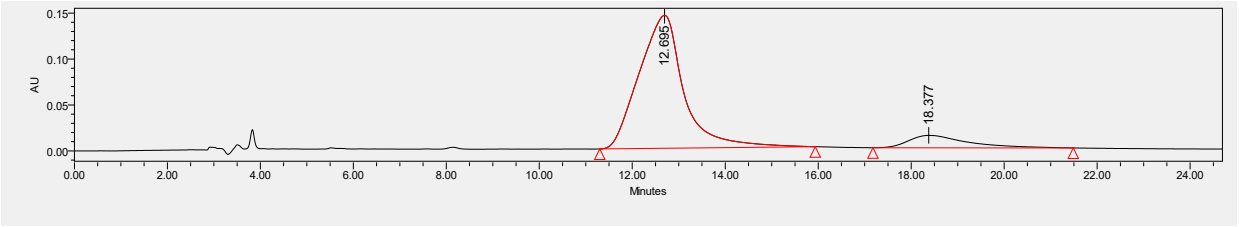
^{13}C{^{1}H} NMR (101 MHz, CD_3COCD_3) δ 171.0, 165.4, 136.9, 135.9, 135.3, 131.6, 130.6, 130.0, 129.9, 129.0, 128.6, 128.2, 127.1, 126.6, 71.3, 38.7.

HRMS (ESI) Calculated for $C_{22}H_{19}NO_3S$ ([M]+Na^+) = 400.0978, Found 400.0974

IR (neat) 3357, 3059, 1629, 1579, 1508, 1437, 1382, 1213, 1111, 1027, 695, 501 cm^{-1}.

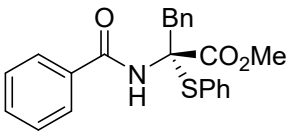


	Retention Time	Area	% Area
1	11.934	1170902	49.20
2	17.857	1208875	50.80



	Retention Time	Area	% Area
1	12.695	9659297	89.10
2	18.377	1181226	10.90

methyl (*R*)-2-benzamido-3-phenyl-2-(phenylthio)propanoate (13):



colorless oil, 83% yield, 75% ee; $[\alpha]^{21}_{D}$ = -183.0 (*c* 0.73, CH_2Cl_2).

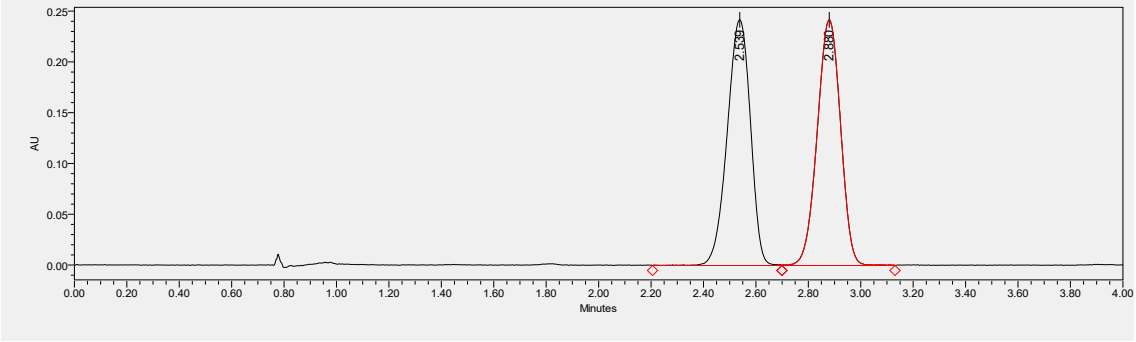
SFC Chiralcel OX-3, CO_2/MeOH = 80/20, 1.5 mL/min, λ = 280 nm, t_1 = 2.54 min, t_2 = 2.89 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.32 (m, 5H), 7.28 – 7.23 (m, 2H), 7.22 – 7.12 (m, 5H), 7.06 (s, 1H), 4.49 (d, *J* = 13.6 Hz, 1H), 3.83 (s, 3H), 3.58 (d, *J* = 13.7 Hz, 1H).

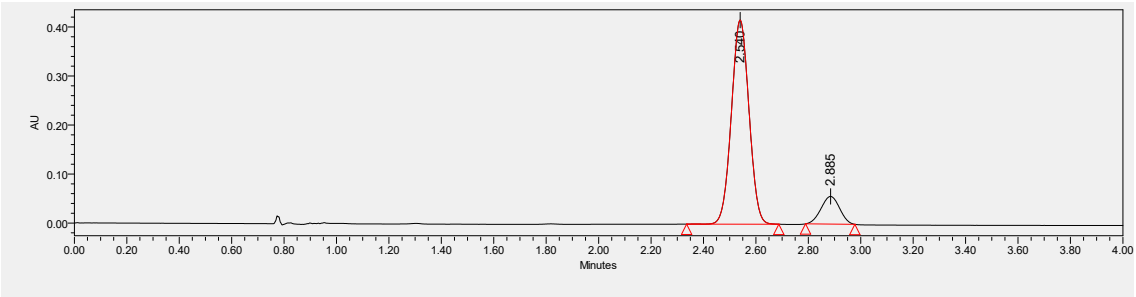
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.8, 166.3, 137.0, 135.5, 135.0, 131.8, 130.0, 129.9, 129.0, 128.7, 128.4, 127.3, 126.8, 72.0, 53.2, 39.0.

HRMS (ESI) Calculated for $C_{23}H_{21}NO_3S$ ([M]+Na^+) = 414.1134, Found 414.1130

IR (neat) 3340, 2951, 1728, 1674, 1601, 1507, 1481, 1440, 1308, 1255, 1081, 1040, 824, 700, 499 cm^{-1}.

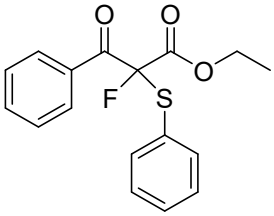


	Retention Time	Area	% Area
1	2.539	1489681	49.92
2	2.880	1494710	50.08



	Retention Time	Area	% Area
1	2.540	1942149	87.48
2	2.885	278070	12.52

ethyl 2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanoate (15a):



colorless oil, 69% yield, 11% ee; $[\alpha]^{27}_{D}$ = 19.5 (*c* 0.21, CH_2Cl_2).

SFC Chiralcel OJ-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 254 nm, t_1 = 4.20 min, t_2 = 6.35 min.

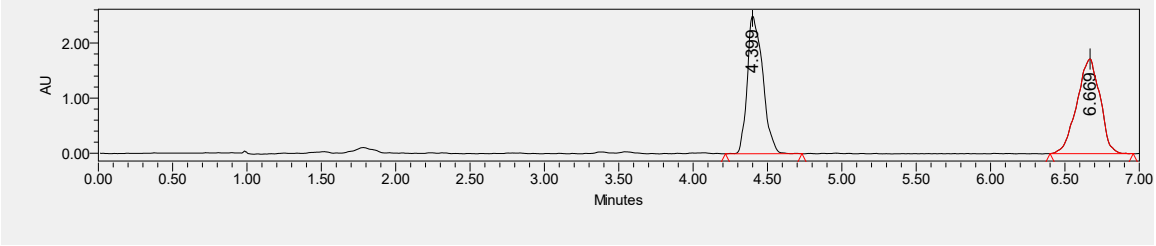
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 7.97 (m, 2H), 7.61 – 7.55 (m, 3H), 7.47 – 7.41 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 4.14 – 4.05 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 187.3 (d, *J* = 25.7 Hz), 164.5 (d, *J* = 30.5 Hz), 136.3, 134.4, 132.8 (d, *J* = 2.9 Hz), 130.2, 129.9 (d, *J* = 4.1 Hz), 129.2, 128.7, 127.2, 105.9 (d, *J* = 242.1 Hz), 63.2, 13.8.

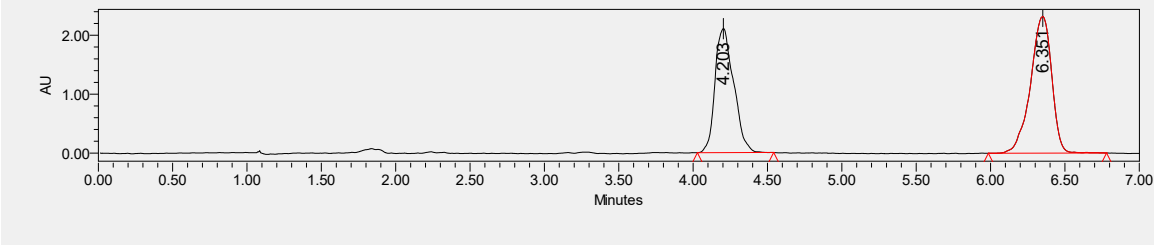
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ −127.16. (s, 1F).

HRMS (ESI) Calculated for $C_{17}H_{15}FO_3S$ ([M]+Na^+) = 341.0618, Found 341.0613.

IR (neat) 2984, 2361, 1756, 1700, 1597, 1474, 1446, 1264, 1229, 1046, 843, 691 639 cm^{-1}.

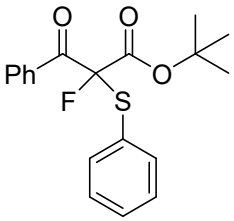


	Retention Time	Area	% Area
1	4.399	18085172	49.42
2	6.669	18511843	50.58



	Retention Time	Area	% Area
1	4.203	18421349	44.50
2	6.351	22974891	55.50

tert-butyl 2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanoate (15b):



colorless oil, 61% yield, 19% ee; $[\alpha]^{29}_{D}$ = -18.5 (*c* 0.21, CH_2Cl_2).

SFC Chiralcel OJ-3, CO_2/MeOH = 90/10, 1.5 mL/min, λ = 280 nm, t_1 = 1.83 min, t_2 = 4.26 min

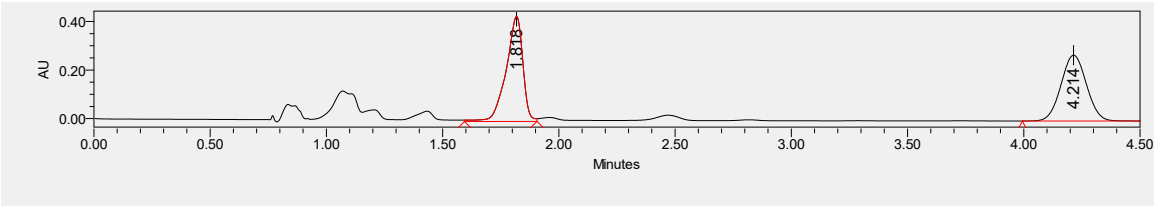
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m *J* = 8.6, 1.3 Hz, 2H), 7.59 (m, *J* = 5.0, 1.4 Hz, 3H), 7.48 – 7.42 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 2H), 1.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 187.5 (d, *J* = 25.4 Hz), 163.2 (d, *J* = 29.8 Hz), 136.1, 134.1, 133.1 (d, *J* = 2.7 Hz), 133.0, 129.9, 129.8 (d, *J* = 3.7 Hz), 129.7, 129.0, 128.6, 127.6, 105.46 (d, *J* = 242.2 Hz), 85.0, 27.5.

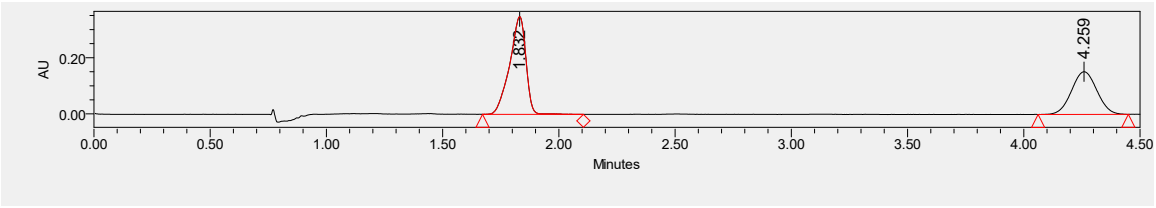
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -125.60. (s, 1F).

HRMS (ESI) Calculated for $C_{19}H_{19}FO_3S$ ([M]+Na^+) = 369.0931, Found 369.0927

IR (neat) 2988, 2358, 2339, 1754, 1701, 1281, 1155, 843, 754, 686 cm^{-1}.



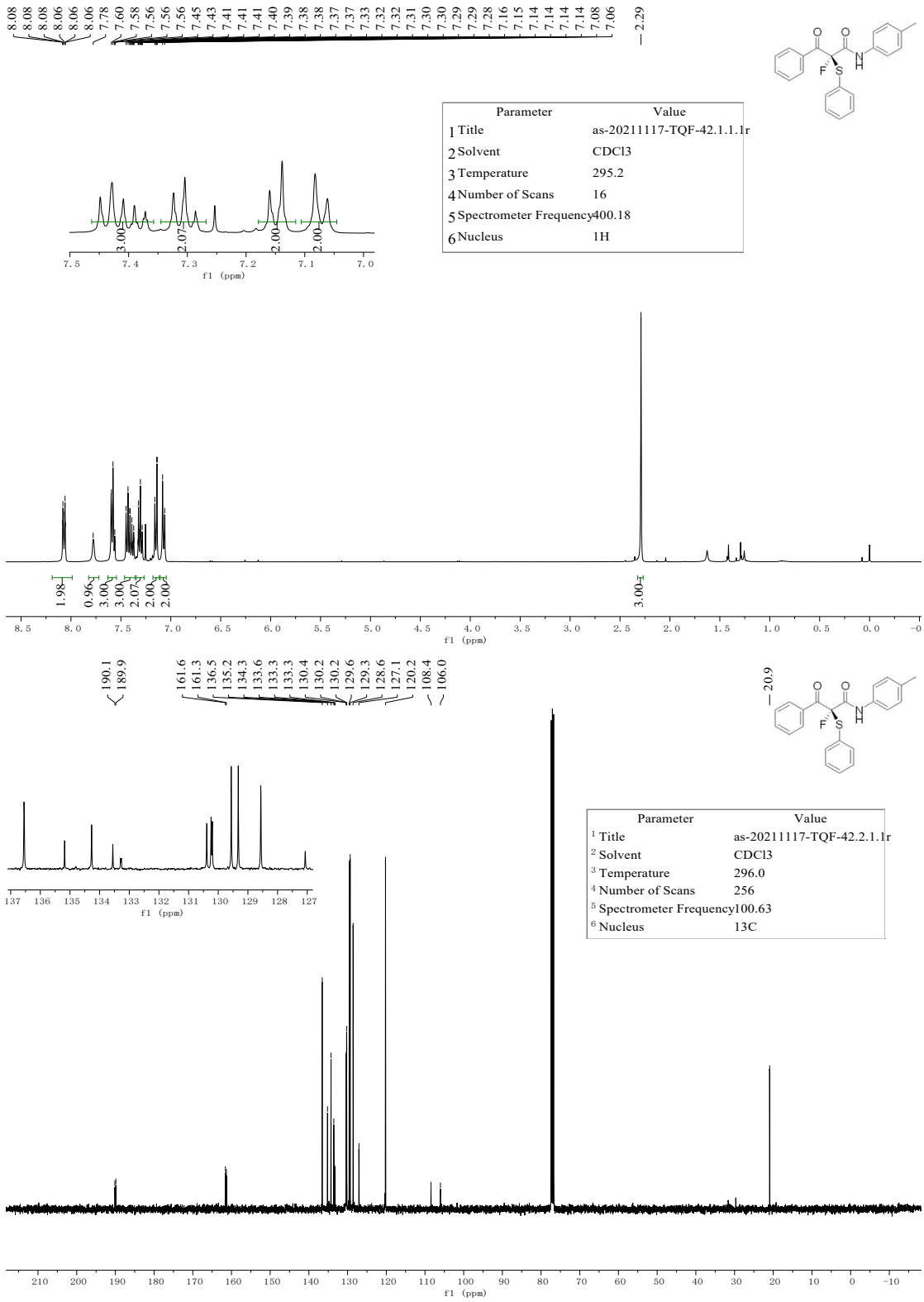
	Retention Time	Area	% Area
1	1.818	2160058	51.12
2	4.214	2065791	48.88

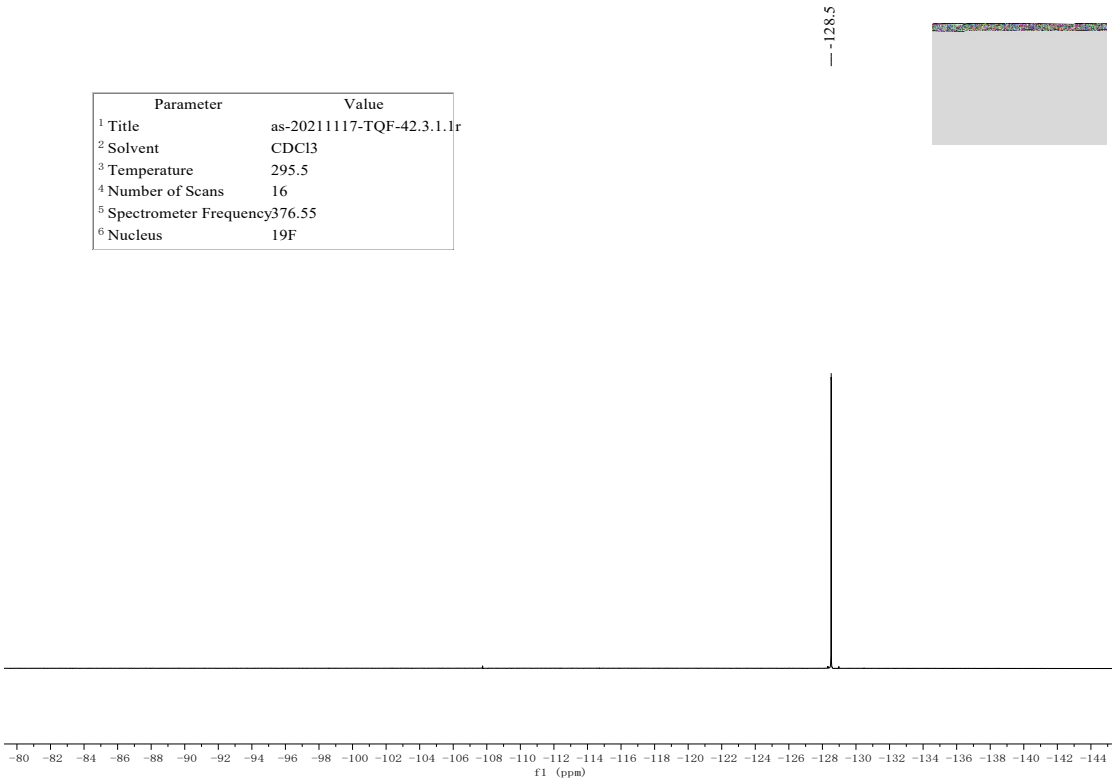


	Retention Time	Area	% Area
1	1.832	1681809	59.25
2	4.259	1156520	40.75

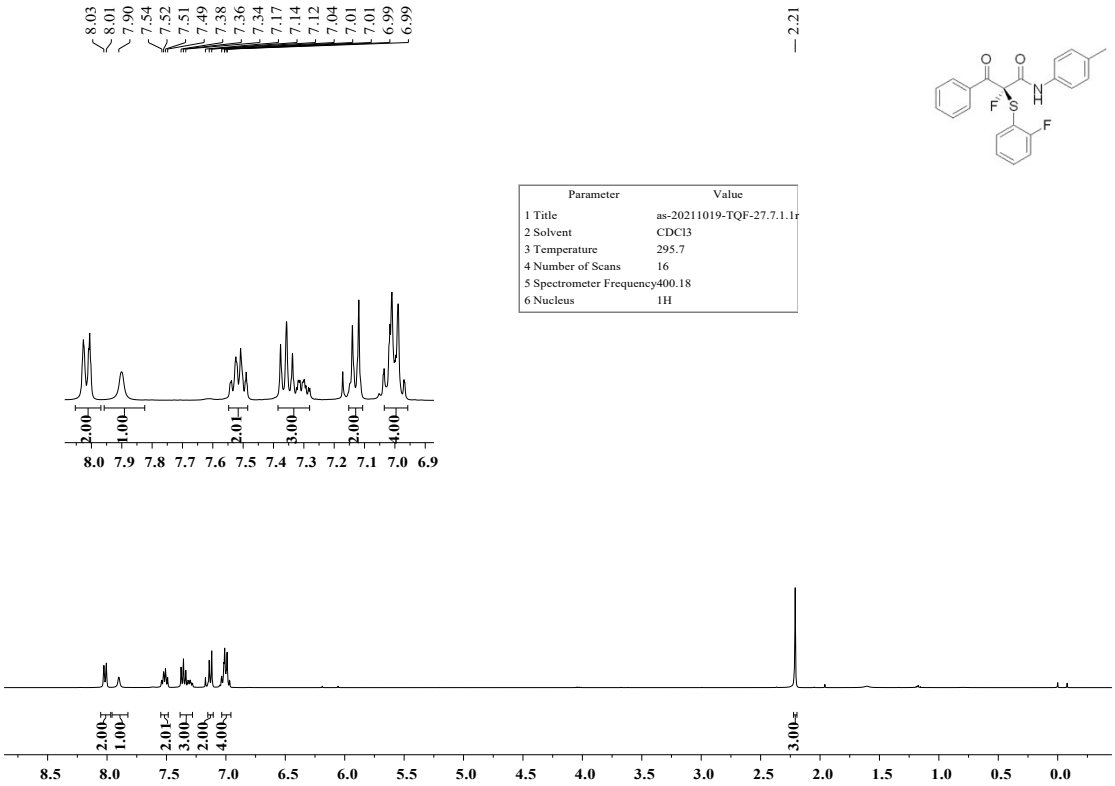
15. Copies of NMR spectra for products

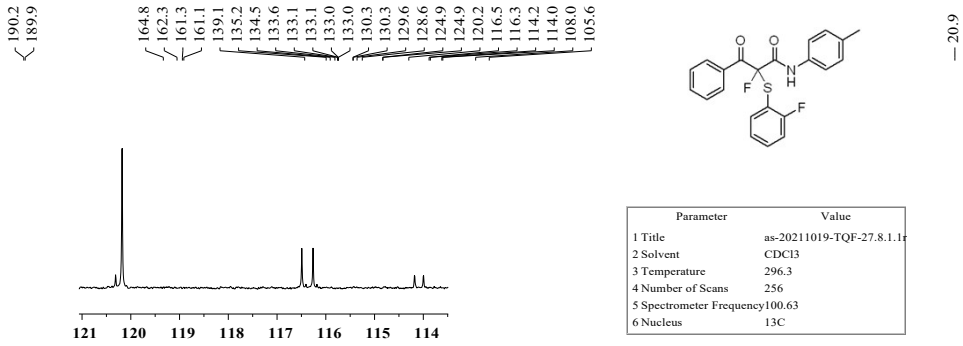
(S)-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)-*N*-(*p*-tolyl)propanamide (3a):



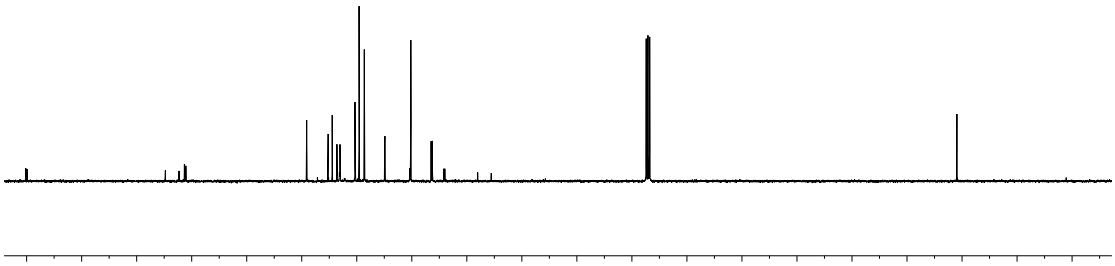


(*S*)-2-fluoro-2-((2-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3b):

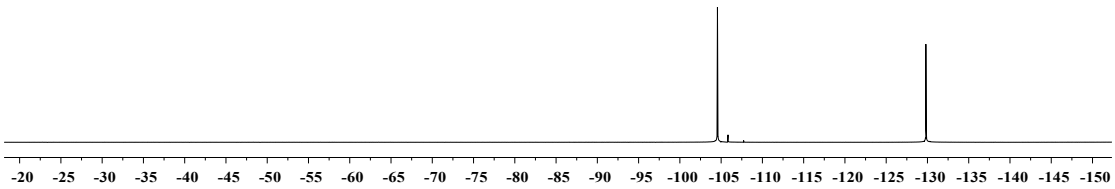




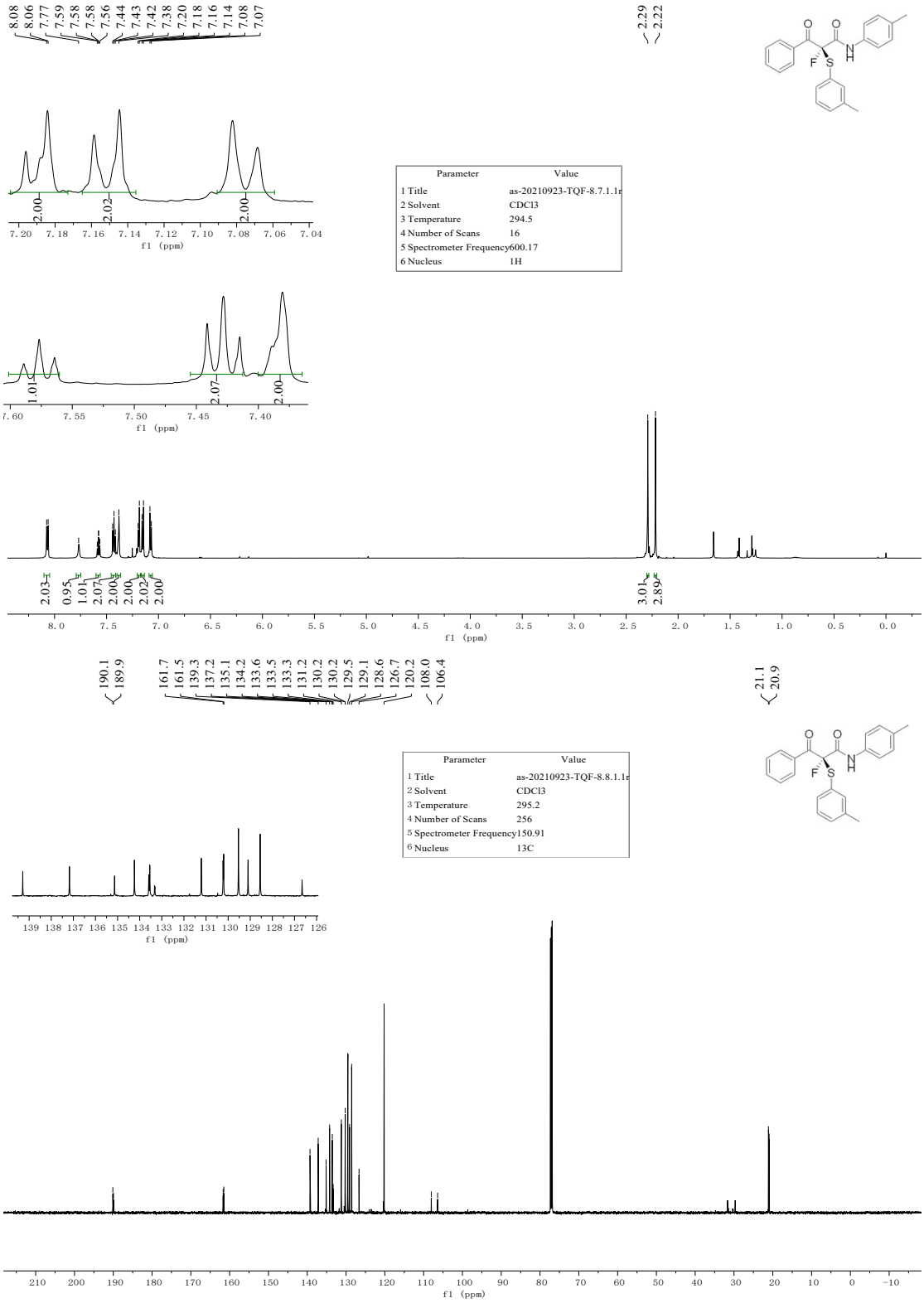
Parameter	Value
1 Title	as-20211019-TQF-27.8.1.1r
2 Solvent	CDCl3
3 Temperature	296.3
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C



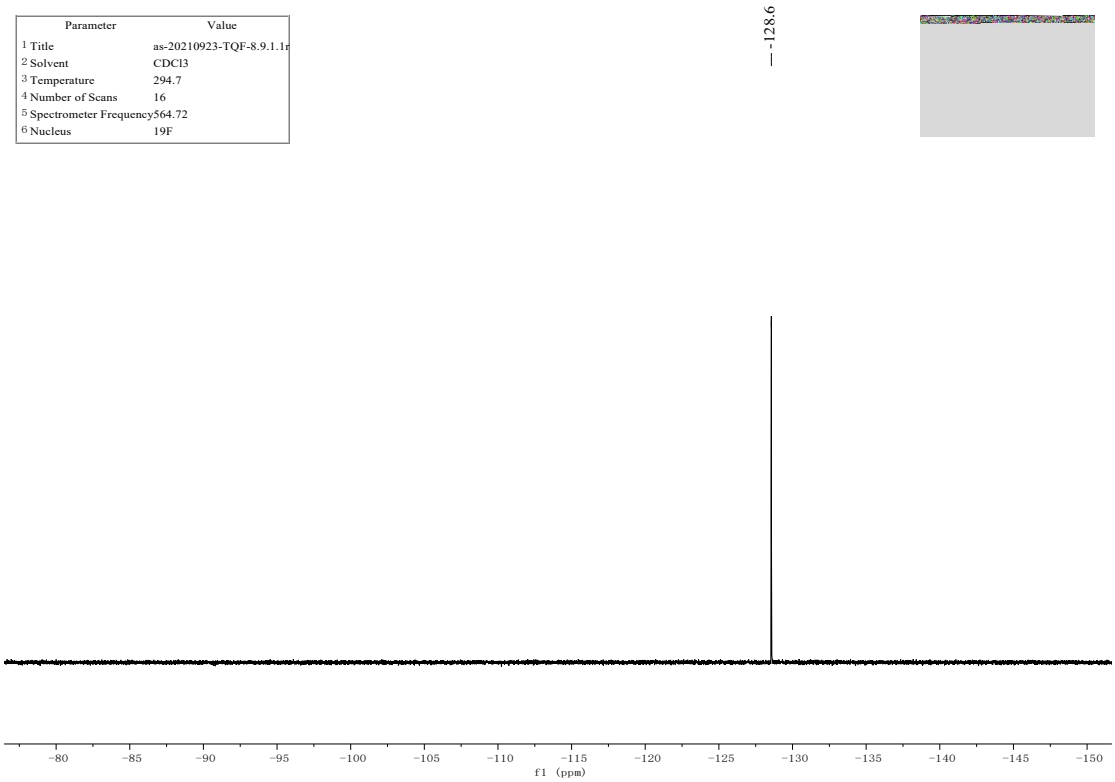
Parameter	Value
1 Title	as-20211019-TQF-27.9.1.1r
2 Solvent	CDCl3
3 Temperature	295.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



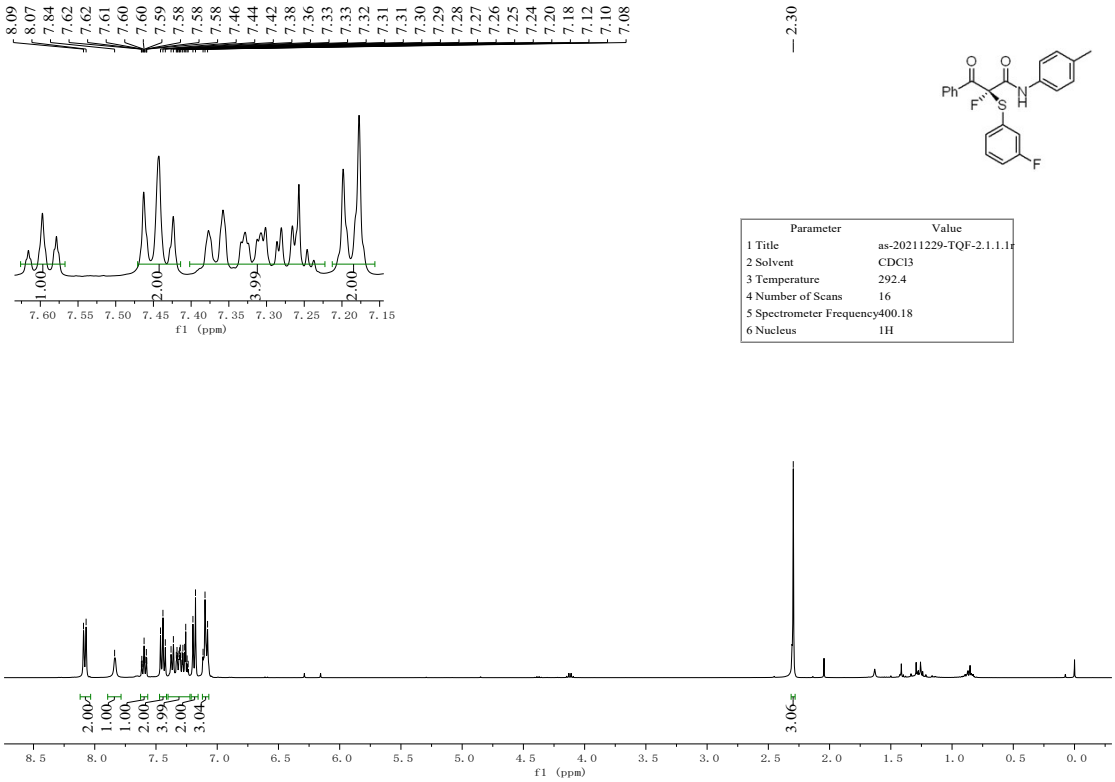
(*S*)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-(*m*-tolylthio)propanamide (3c):



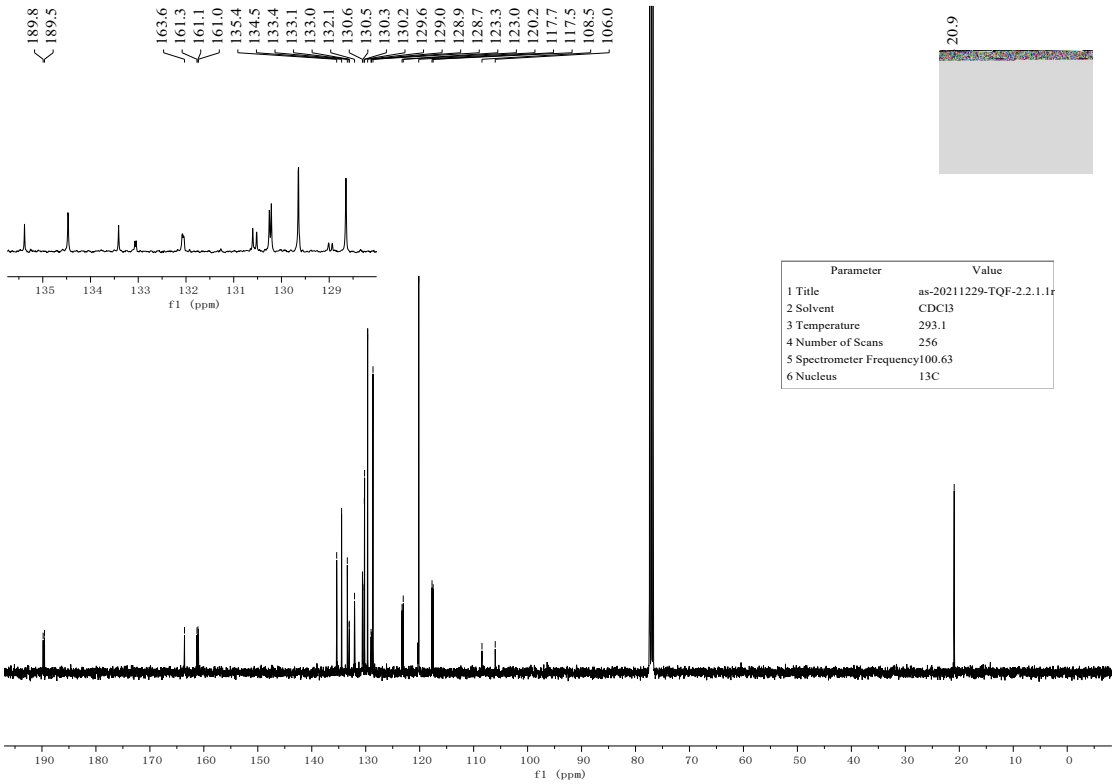
Parameter	Value
1 Title	as-20210923-TQF-8.9.1.1r
2 Solvent	CDCl3
3 Temperature	294.7
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

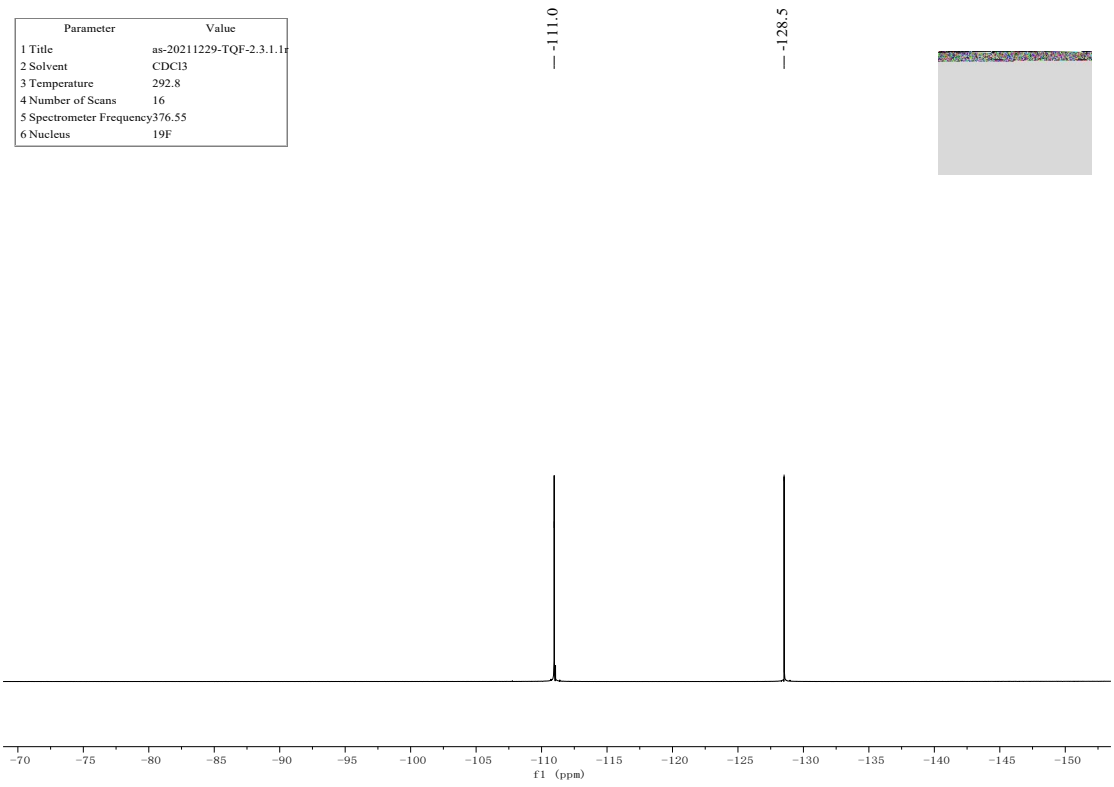


(S)-2-fluoro-2-((3-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3d):

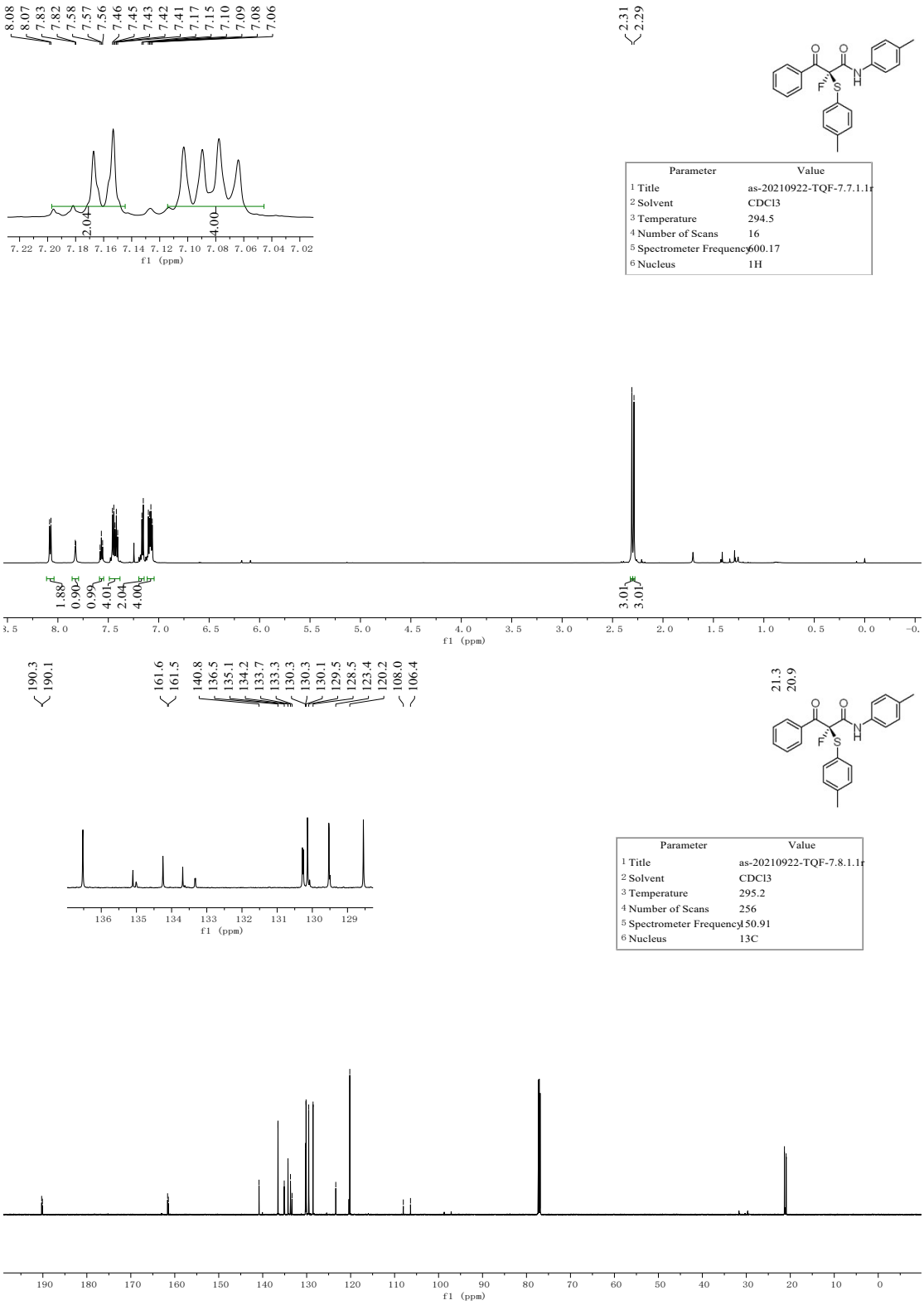


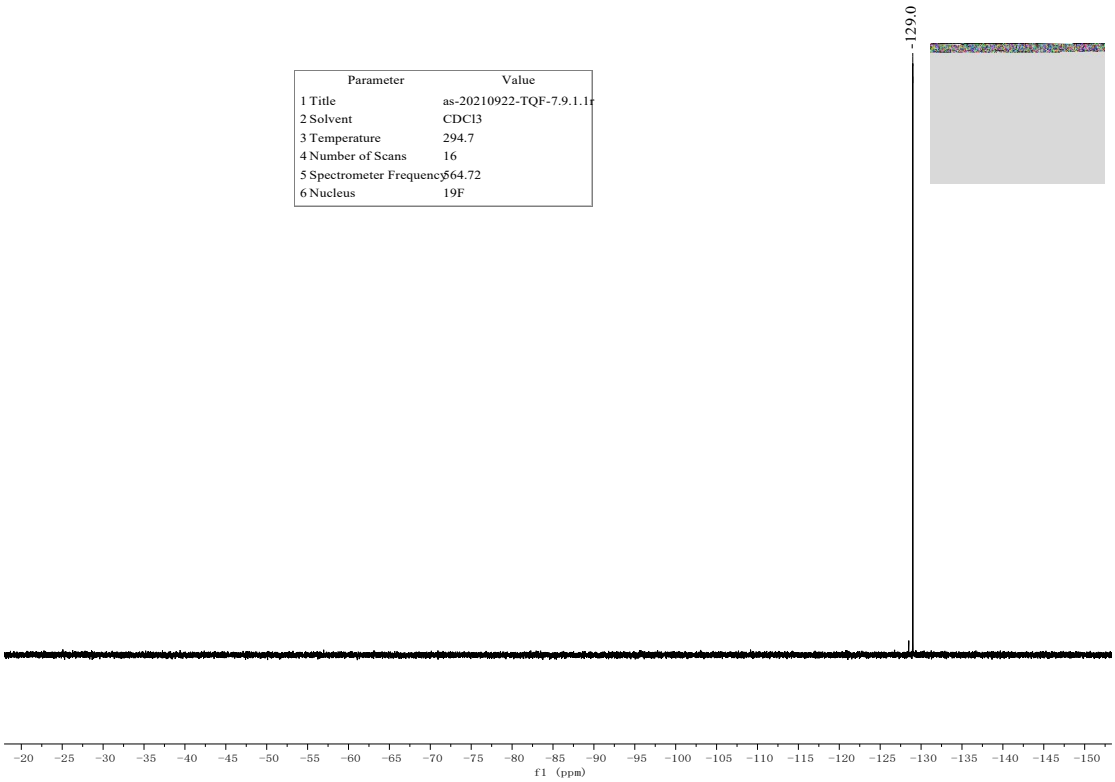
Parameter	Value
1 Title	as-20211229-TQF-2.1.1.1r
2 Solvent	CDCl3
3 Temperature	292.4
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H


189.8
189.5
163.6
161.3
161.1
161.0
135.4
134.5
133.4
133.1
133.0
132.1
130.6
130.5
130.3
130.2
129.6
129.0
128.9
128.7
123.3
123.0
120.2
117.7
117.5
108.5
106.0
20.9
135 134 133 132 131 130 129
f1 (ppm)
Parameter Value
1 Title as-20211229-TQF-2.2.1.1r
2 Solvent CDCl3
3 Temperature 293.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

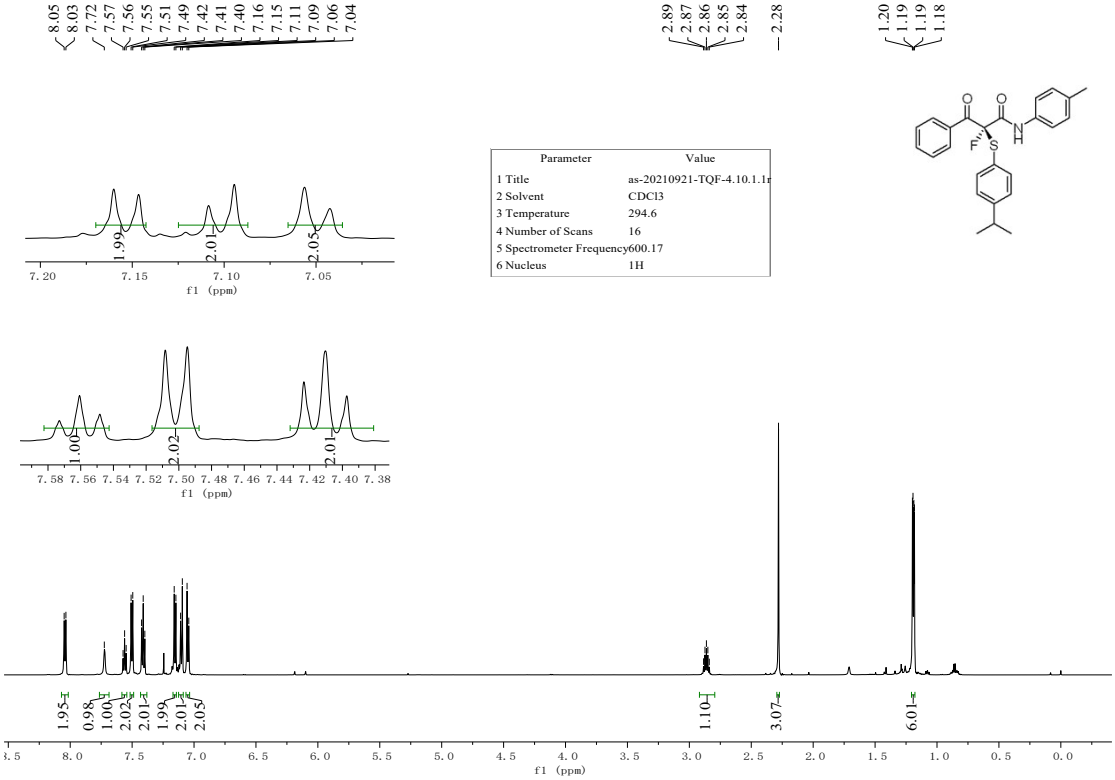

Parameter Value
1 Title as-20211229-TQF-2.3.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-111.0
-128.5
−70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150
f1 (ppm)

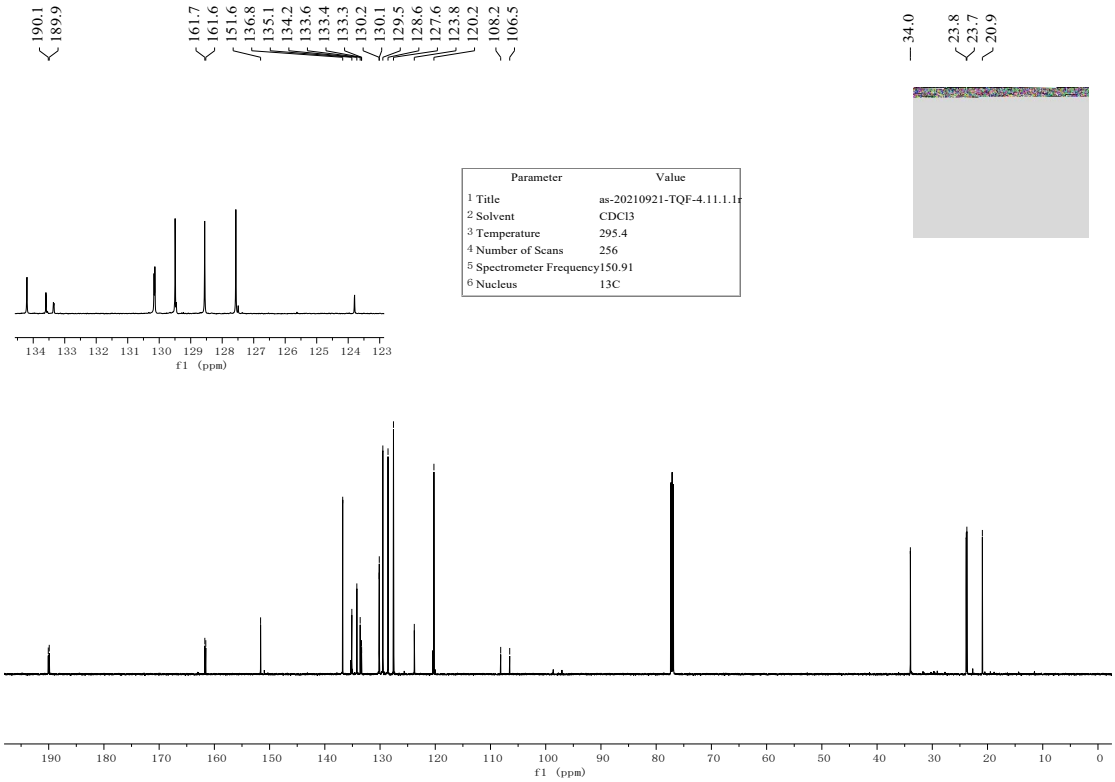
(*S*)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-(*p*-tolylthio)propanamide (3e):

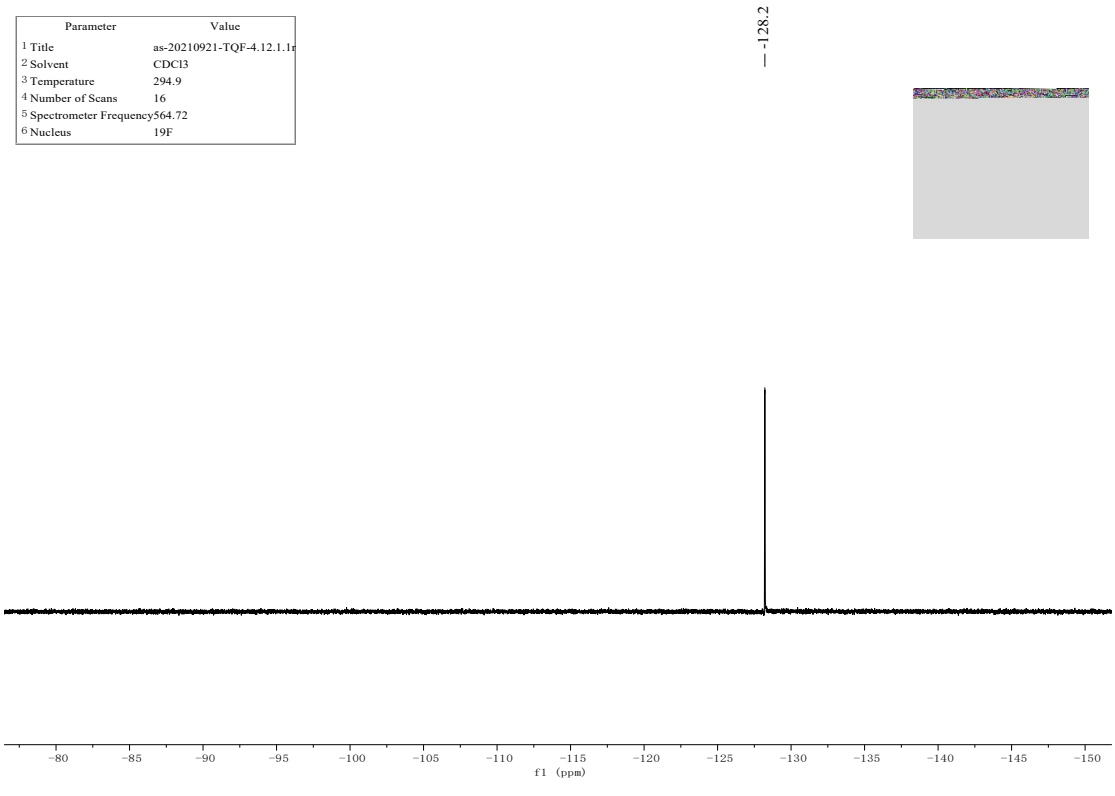




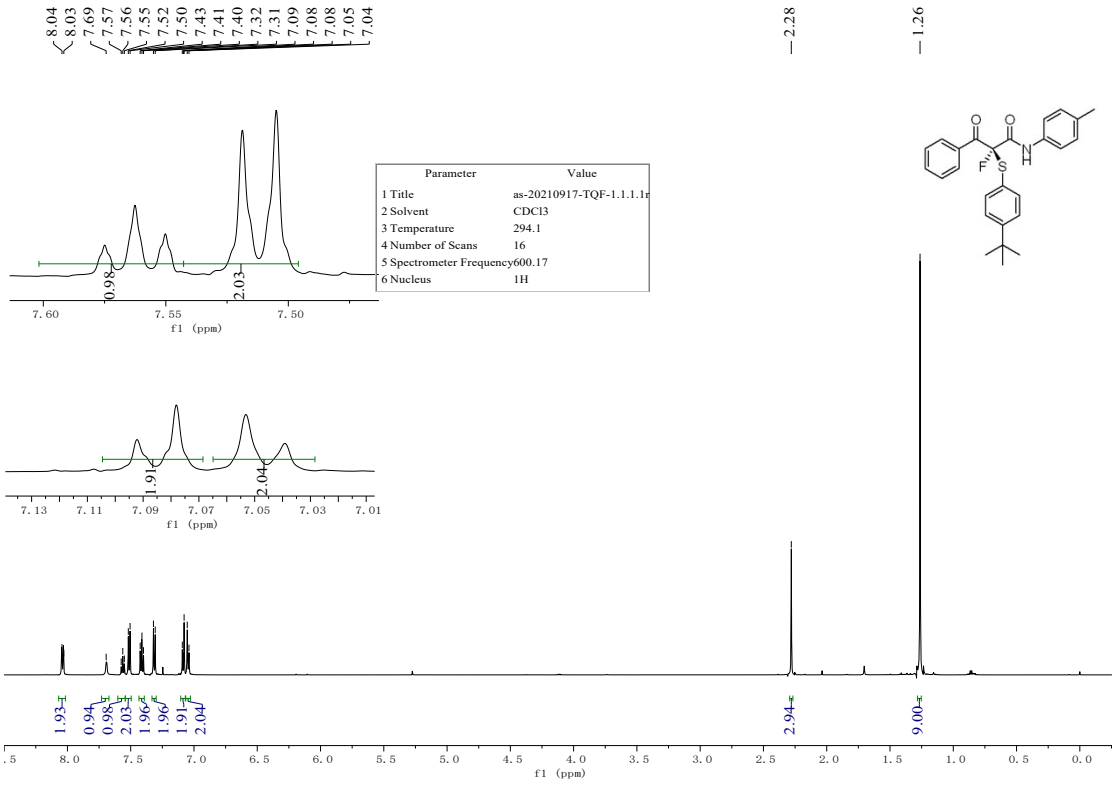
(*S*)-2-fluoro-2-((4-isopropylphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3f):

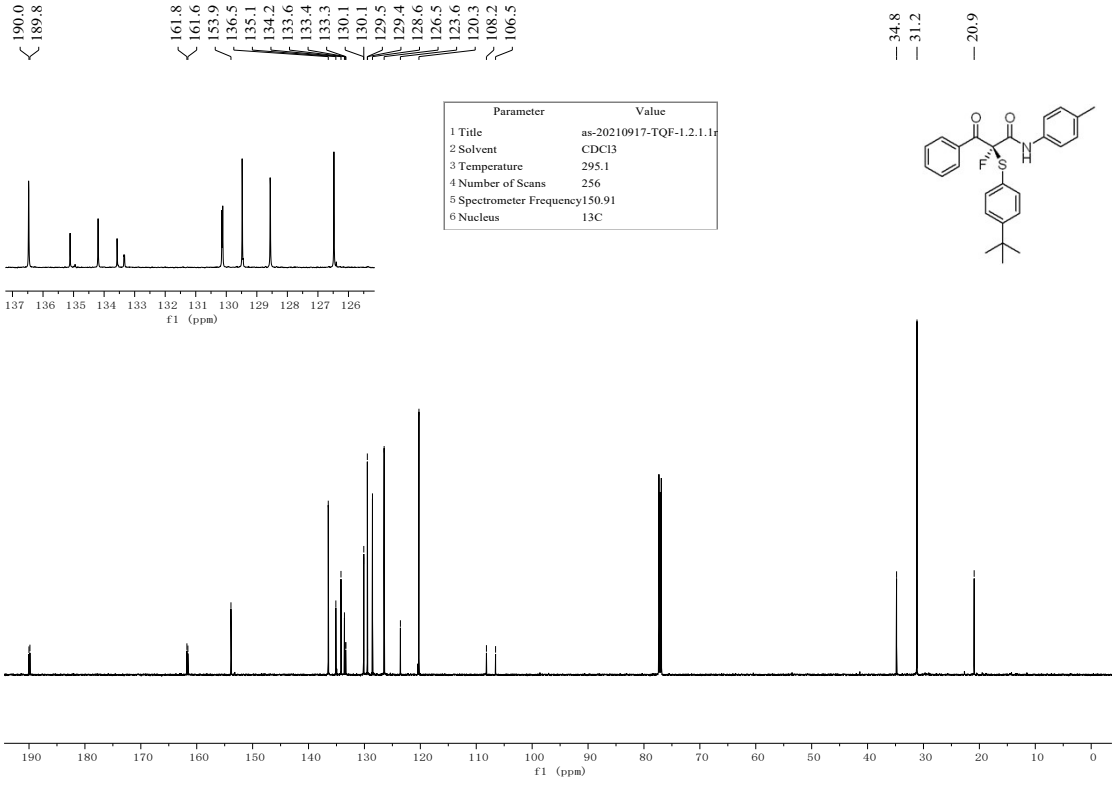


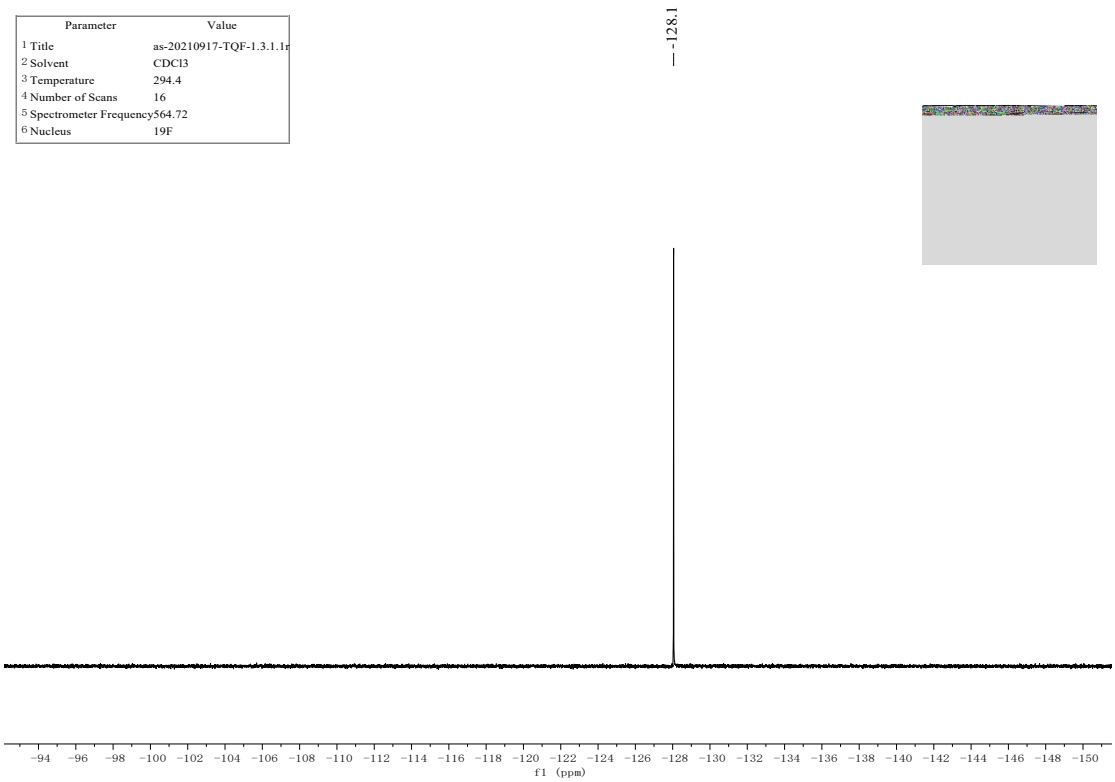

190.1
189.9
161.7
161.6
151.6
136.8
135.1
134.2
133.6
133.4
133.3
130.2
130.1
129.5
128.6
127.6
123.8
120.2
108.2
106.5
34.0
23.8
23.7
20.9
Parameter Value
1 Title as-20210921-TQF-4.11.1.1r
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
134 133 132 131 130 129 128 127 126 125 124 123
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-128.2
Parameter Value
1 Title as-20210921-TQF-4.12.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
−80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150
f1 (ppm)

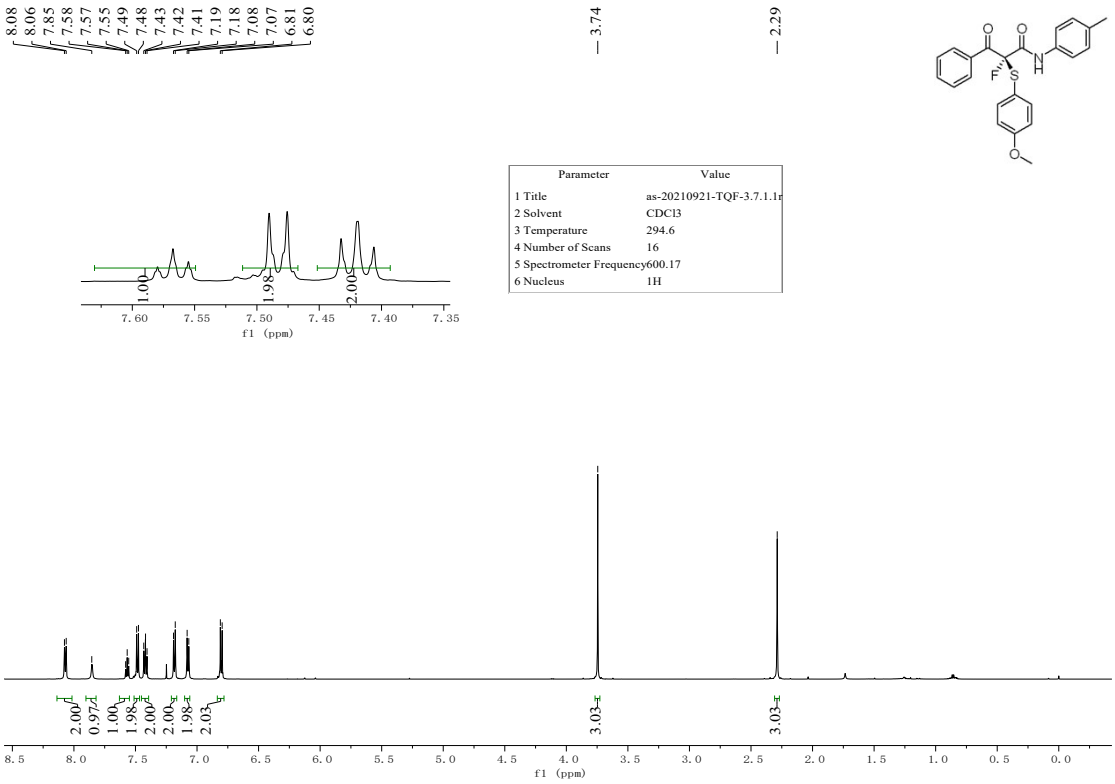
(*S*)-2-((4-(tert-butyl)phenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3g):

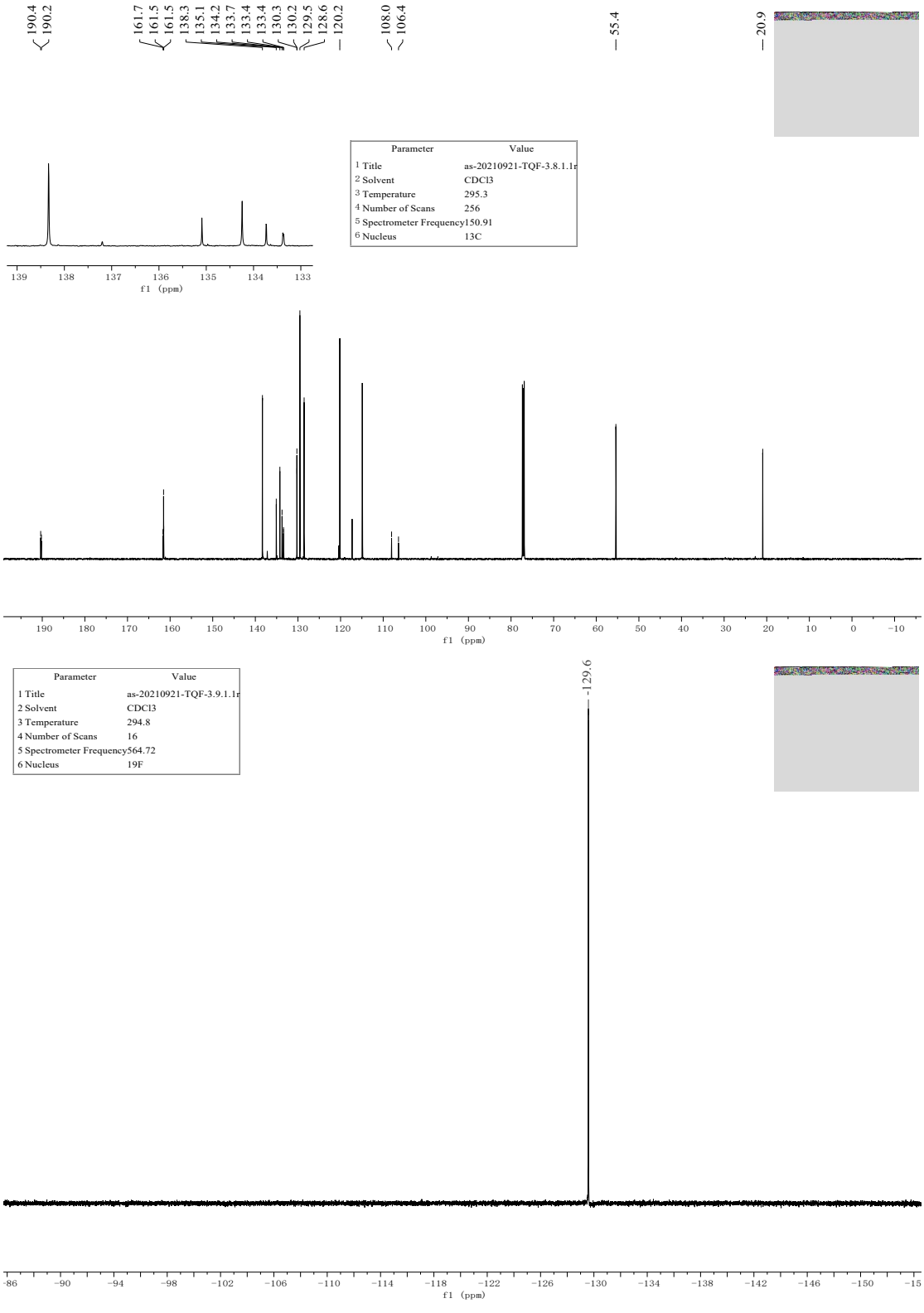




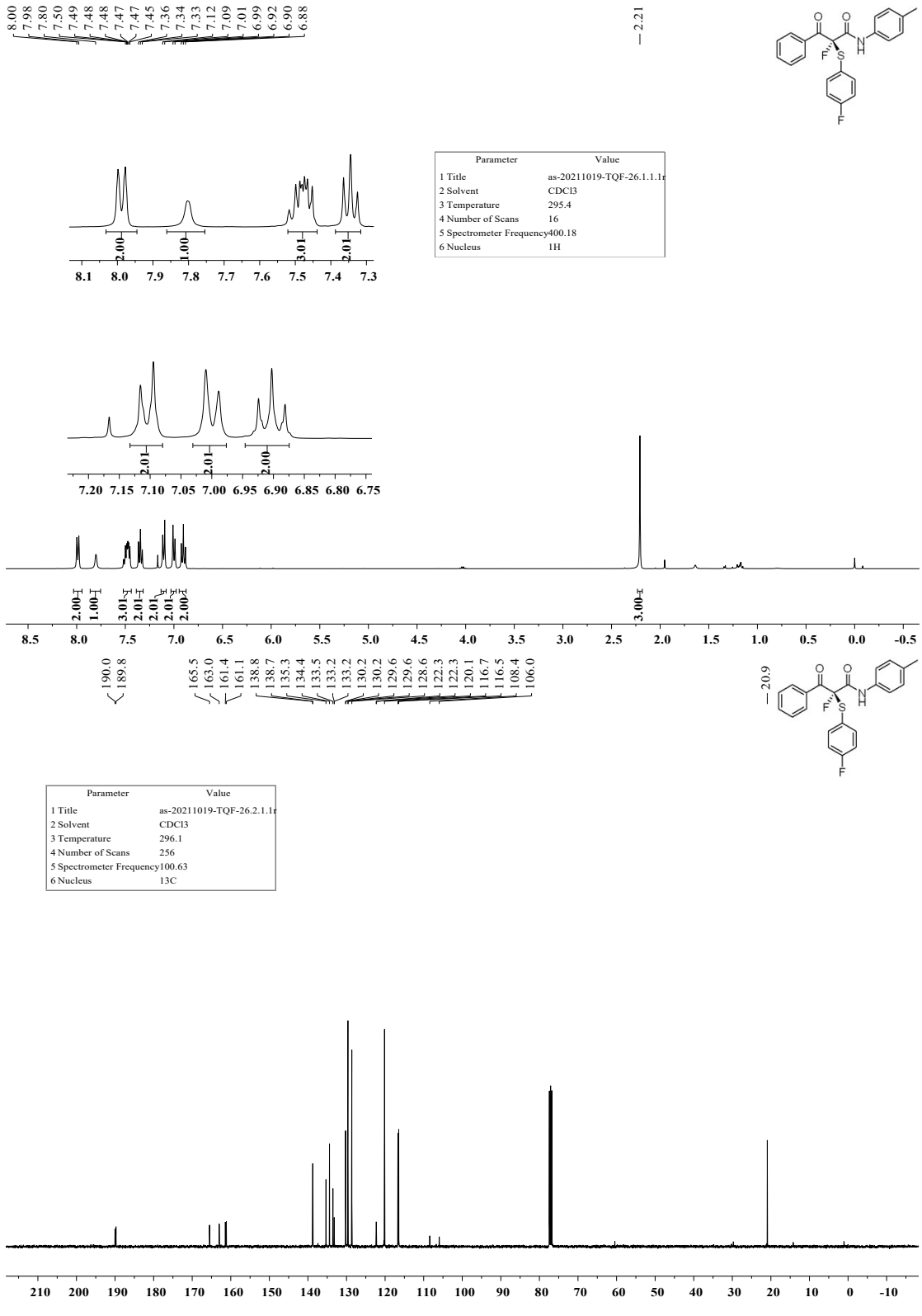


(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3h):

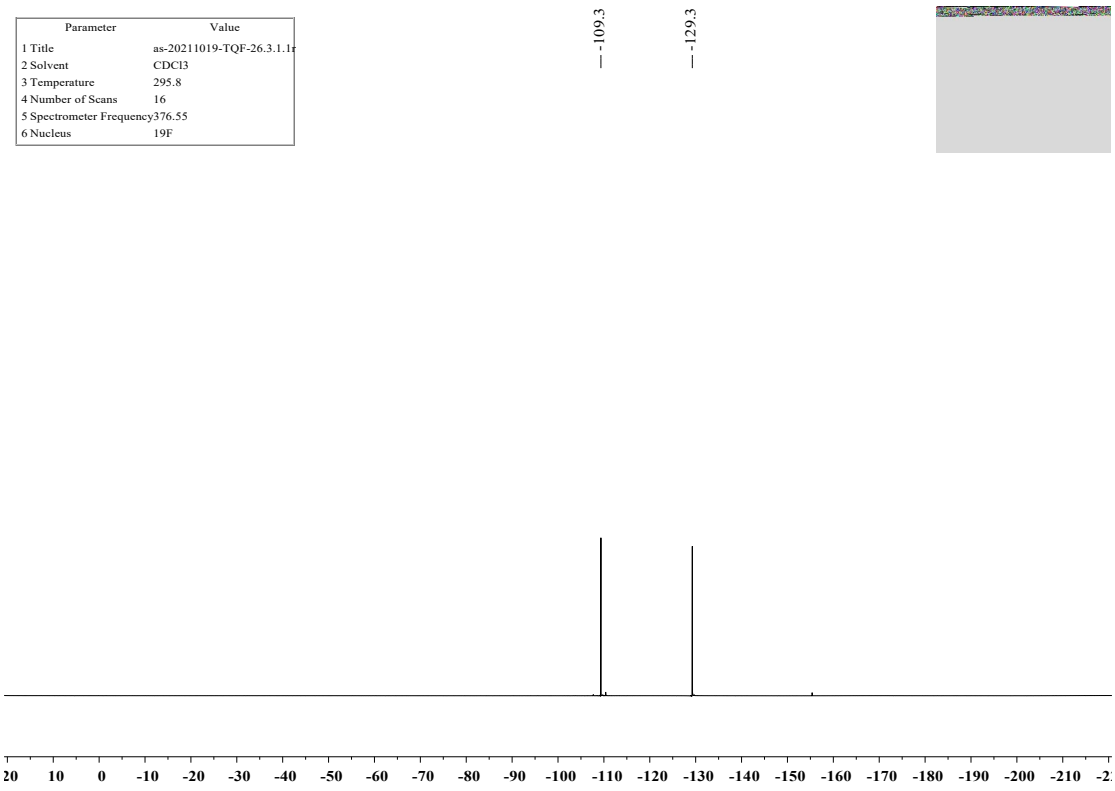



190.4
190.2
161.7
161.5
161.5
138.3
135.1
134.2
133.7
133.4
133.4
130.3
130.2
129.5
128.6
120.2
108.0
106.4
55.4
20.9
Parameter Value
1 Title as-20210921-TQF-3.8.1.1r
2 Solvent CDCl3
3 Temperature 295.3
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)
Parameter Value
1 Title as-20210921-TQF-3.9.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-129.6
f1 (ppm)

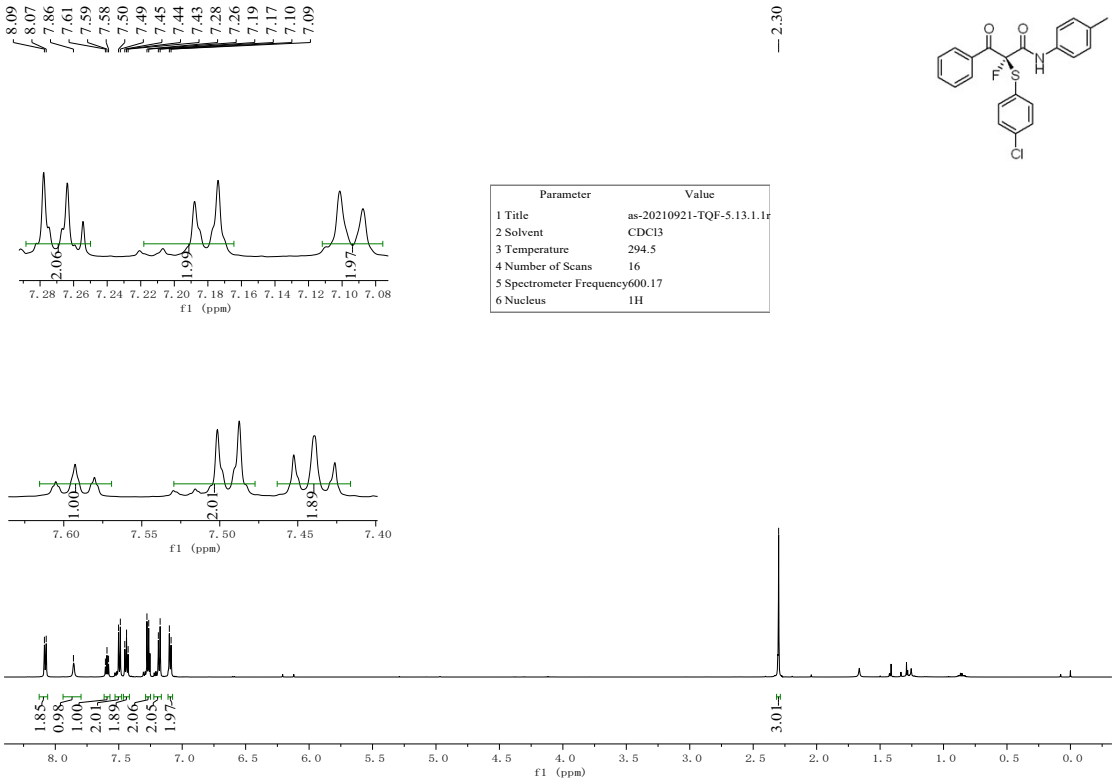
(*S*)-2-fluoro-2-((4-fluorophenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3i):



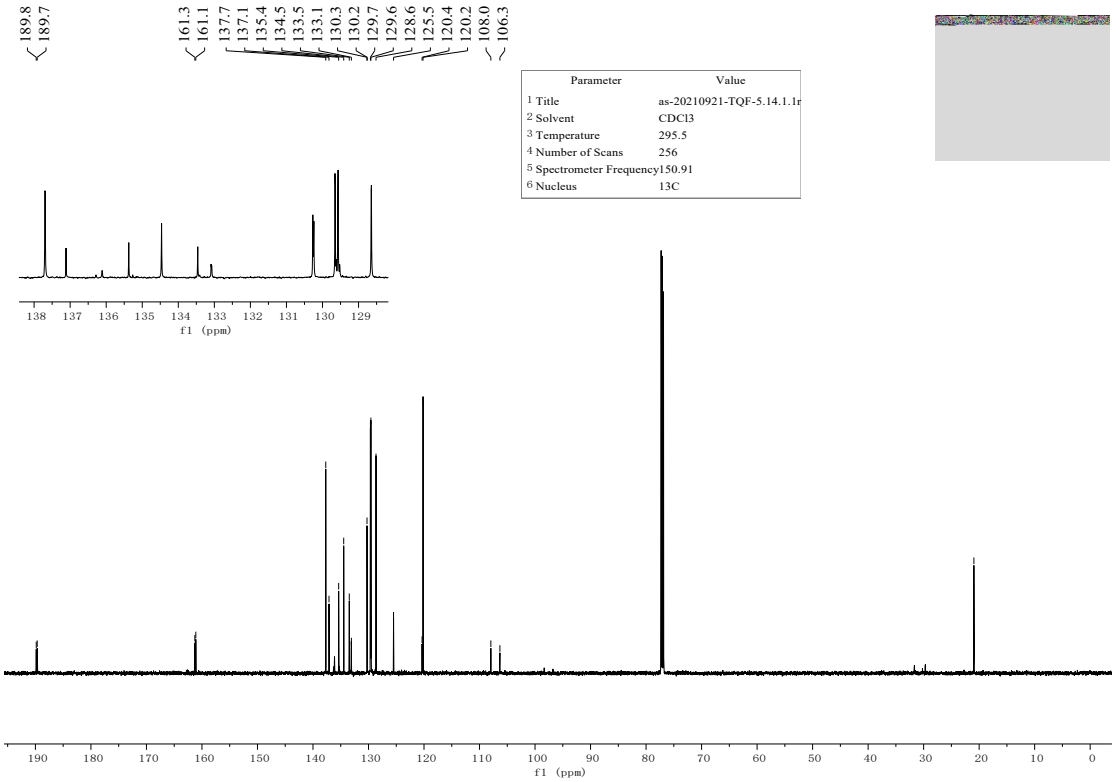
Parameter	Value
1 Title	as-20211019-TQF-26.3.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

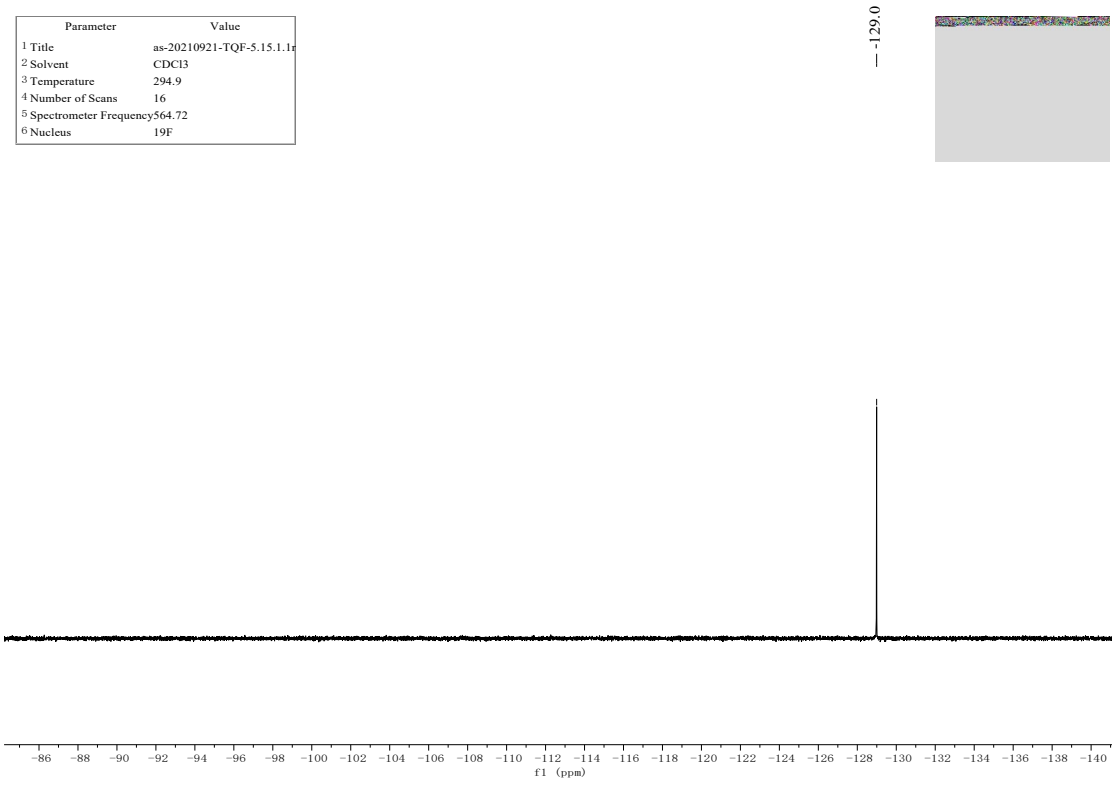


(*S*)-2-((4-chlorophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3j):

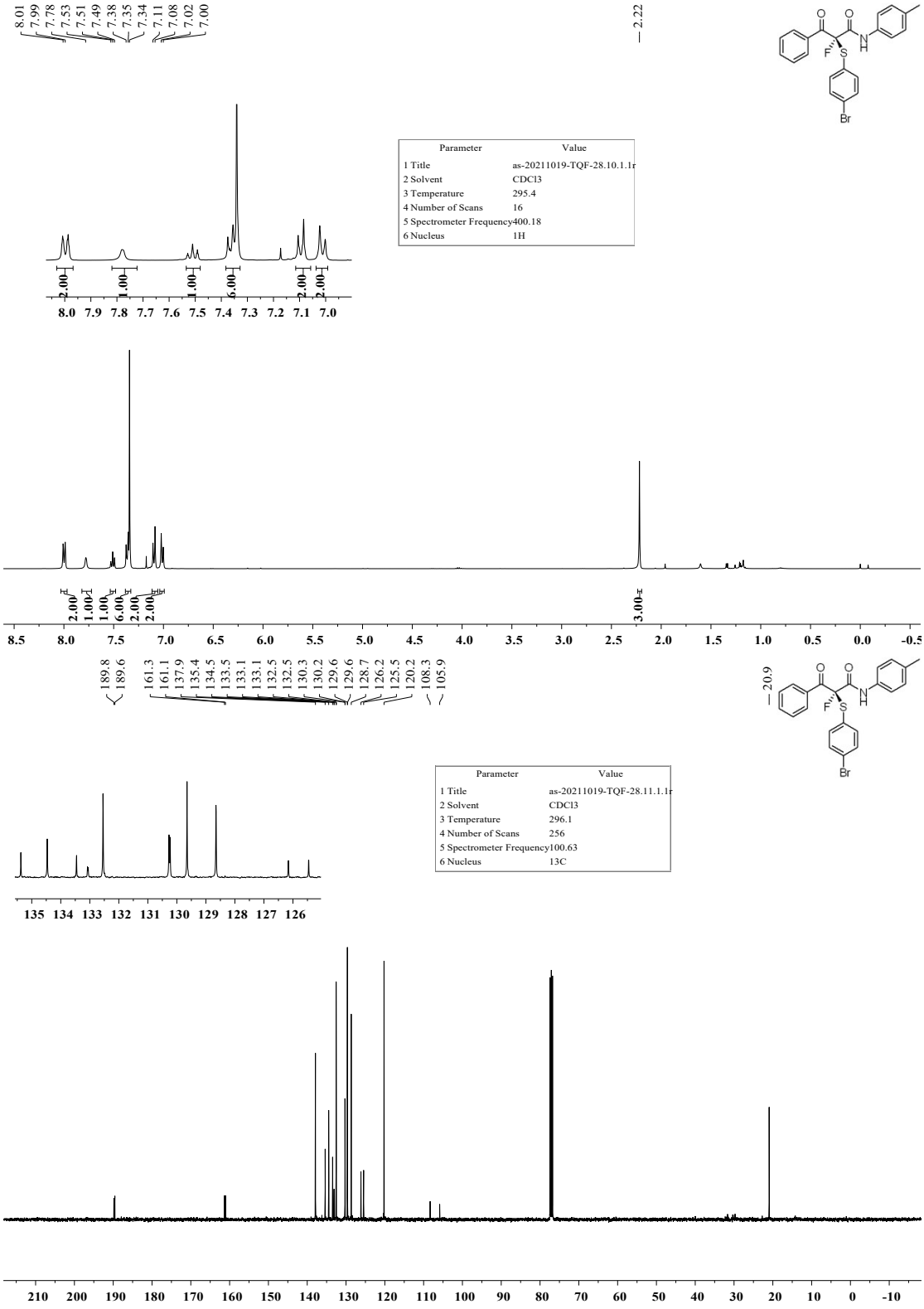


Parameter	Value
1 Title	as-20210921-TQF-5.13.1.1r
2 Solvent	CDCl3
3 Temperature	294.5
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

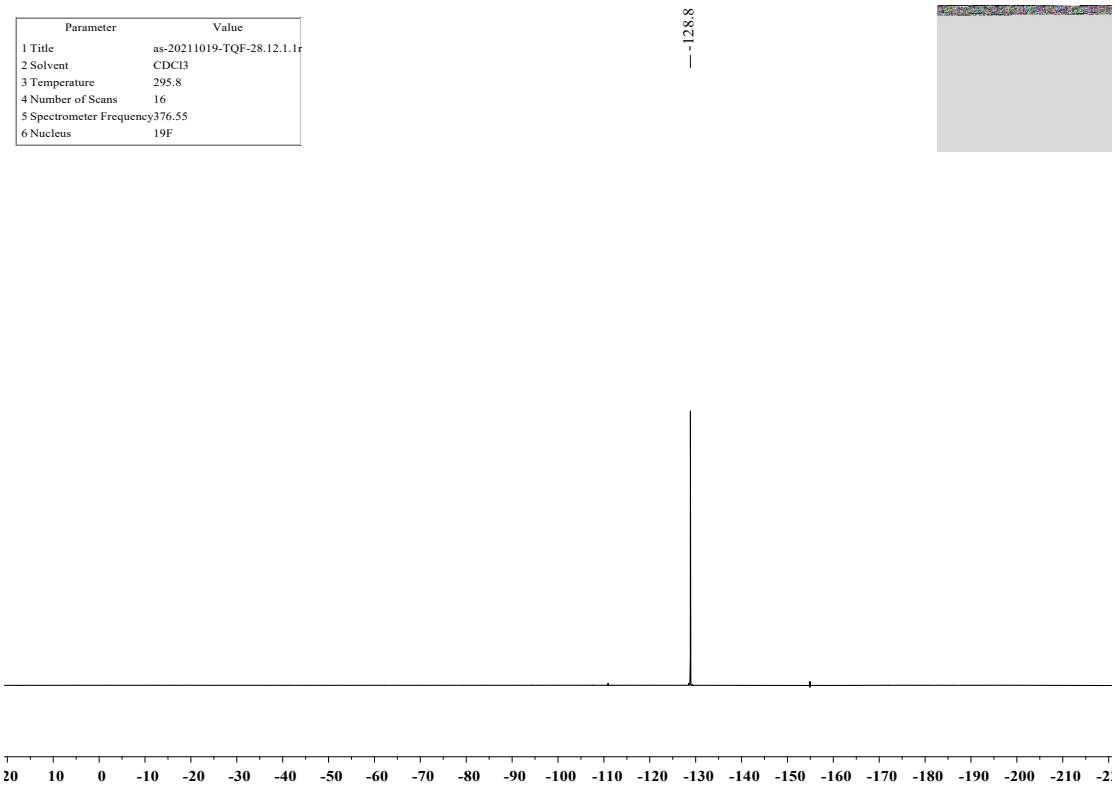

189.8
189.7
161.3
161.1
137.7
137.1
135.4
134.5
133.5
133.1
130.3
130.2
129.7
129.6
128.6
125.5
120.4
120.2
108.0
106.3
Parameter Value
1 Title as-20210921-TQF-5.14.1.1r
2 Solvent CDCl3
3 Temperature 295.5
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
138 137 136 135 134 133 132 131 130 129
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameter Value
1 Title as-20210921-TQF-5.15.1.1r
2 Solvent CDCl3
3 Temperature 294.9
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-129.0
−86 −88 −90 −92 −94 −96 −98 −100 −102 −104 −106 −108 −110 −112 −114 −116 −118 −120 −122 −124 −126 −128 −130 −132 −134 −136 −138 −140
f1 (ppm)

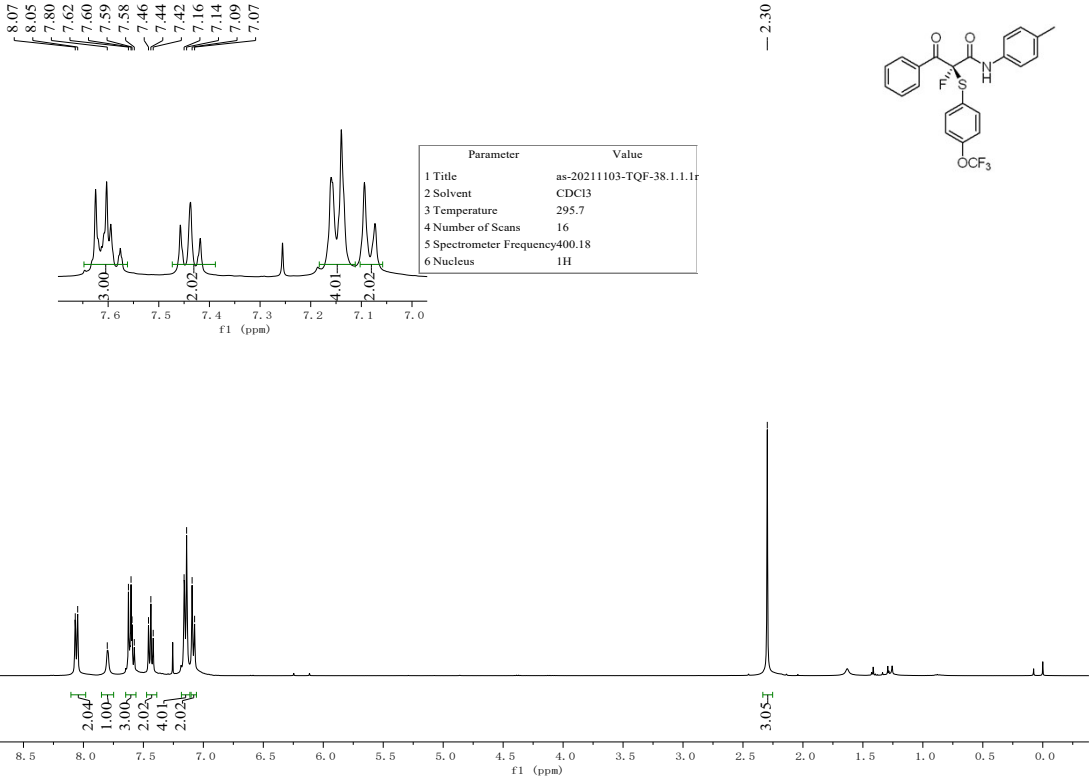
(*S*)-2-((4-bromophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3k):



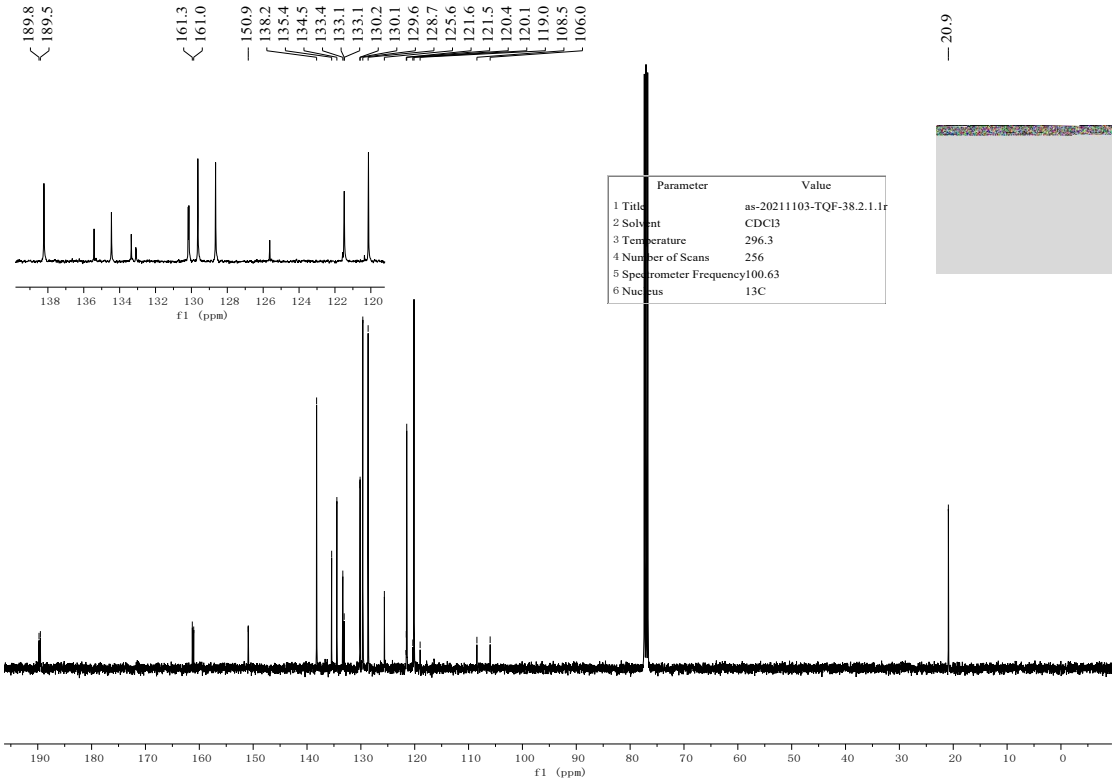
Parameter	Value
1 Title	as-20211019-TQF-28.12.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

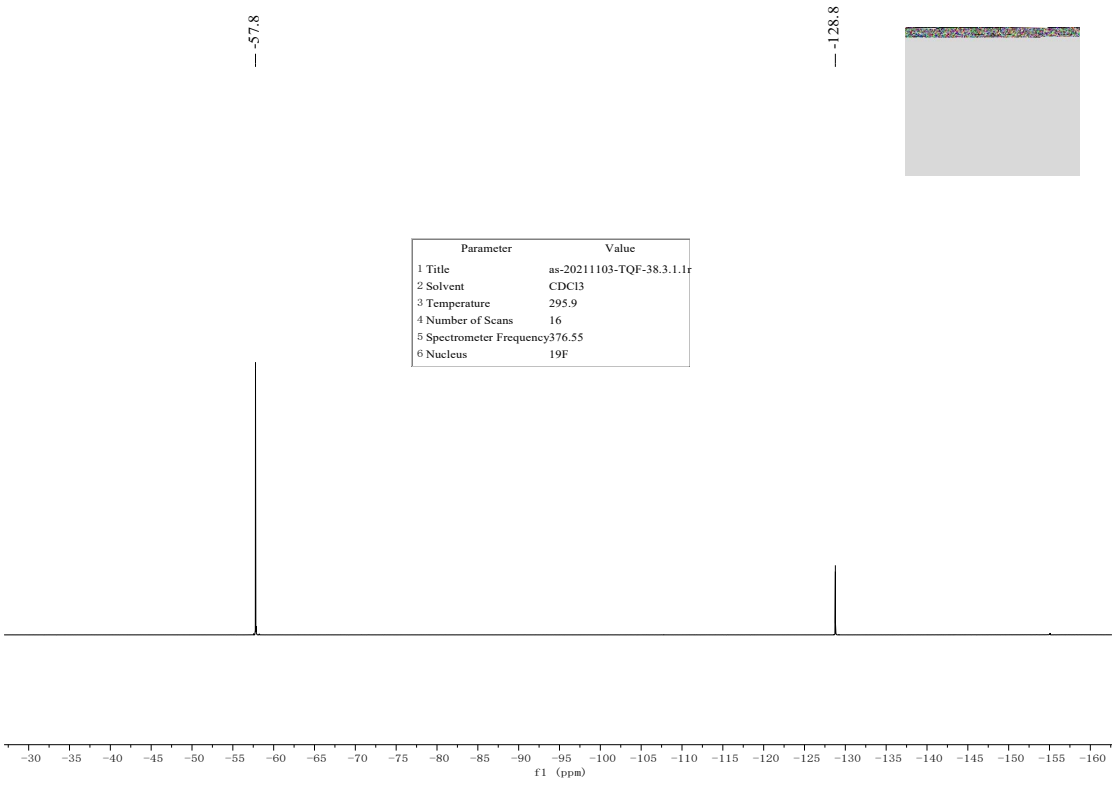


(*S*)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)-2-((4-(trifluoromethoxy)phenyl)thio)propanamide (3l):

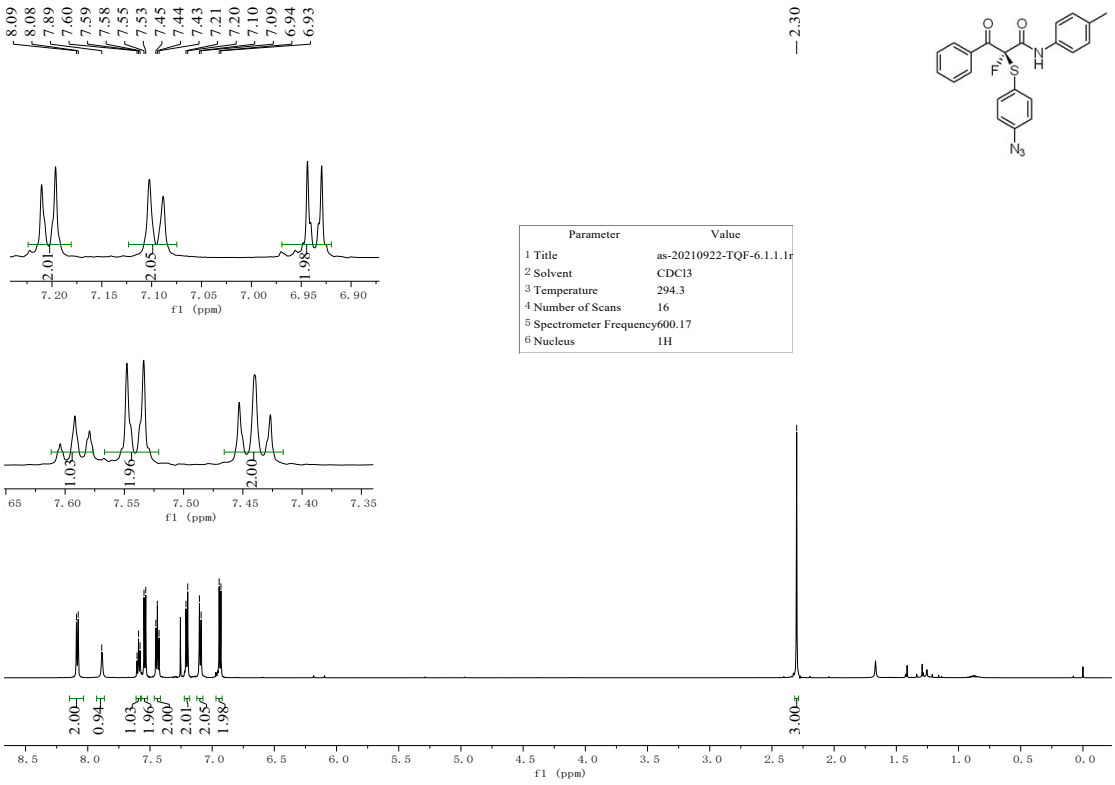


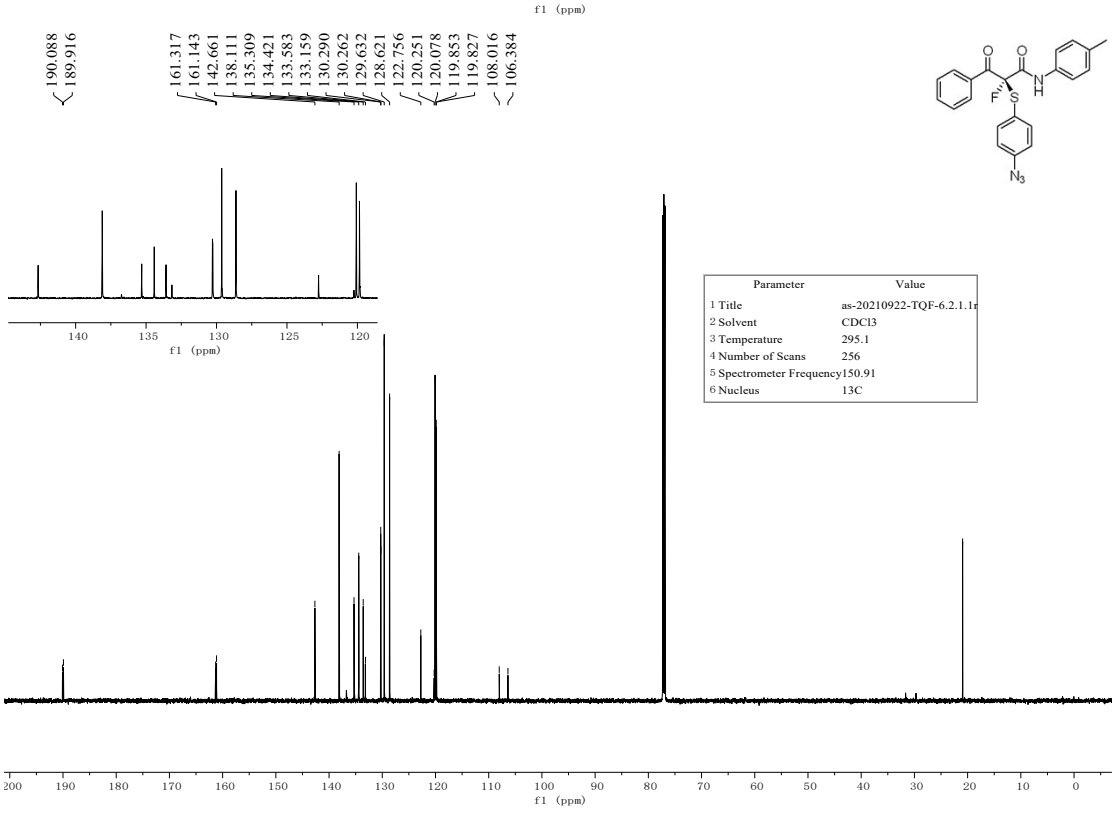
Parameter	Value
1 Title	as-20211103-TQF-38.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H


189.8
189.5
161.3
161.0
150.9
138.2
135.4
134.5
133.4
133.1
133.1
130.2
130.1
129.6
128.7
125.6
121.6
121.5
120.4
120.1
119.0
108.5
106.0
20.9
Parameter Value
1 Title as-20211103-TQF-38.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

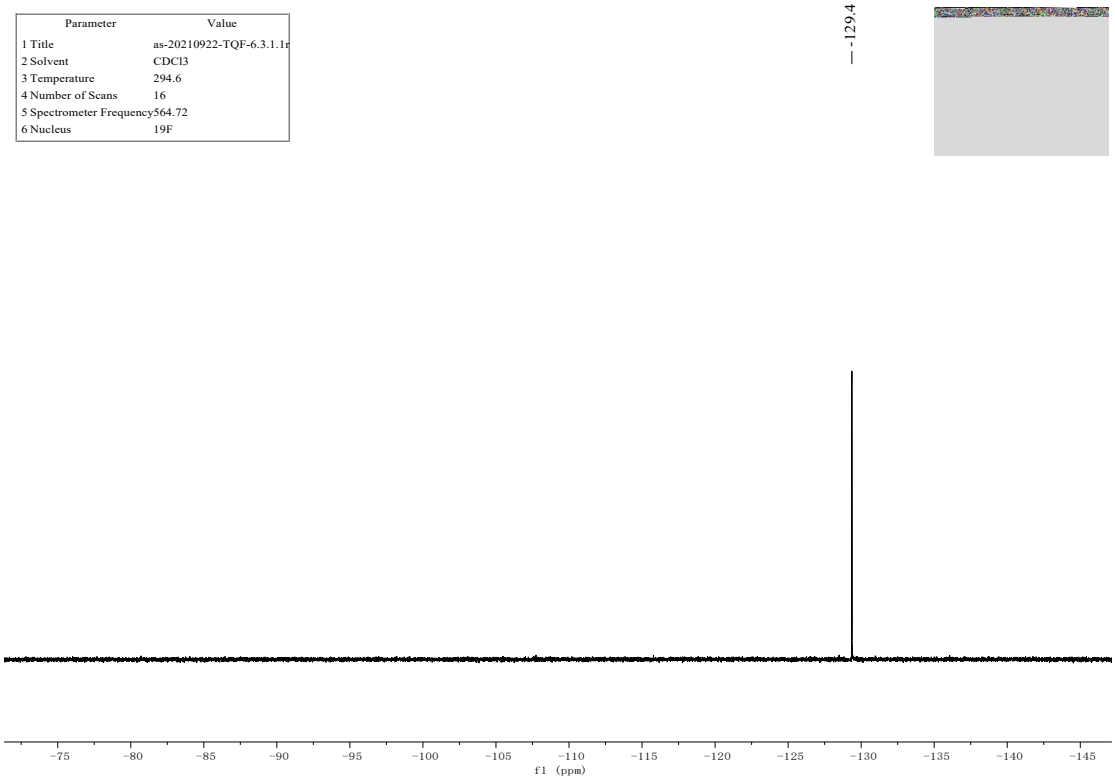

-57.8
-128.8
Parameter Value
1 Title as-20211103-TQF-38.3.1.1r
2 Solvent CDCl3
3 Temperature 295.9
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
f1 (ppm)

(*S*)-2-((4-azidophenyl)thio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3m):

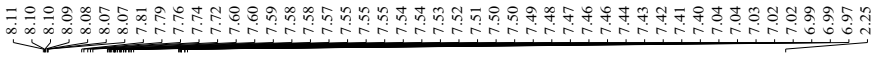


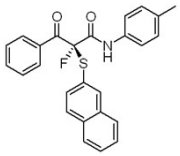


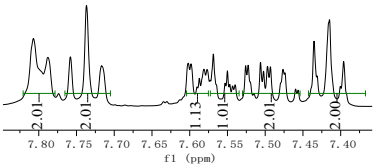
Parameter	Value
1 Title	as-20210922-TQF-6.3.1.1r
2 Solvent	CDCl3
3 Temperature	294.6
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F



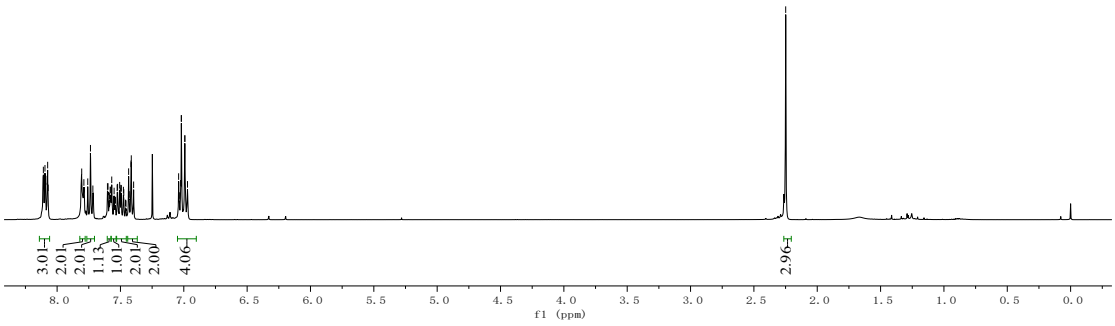
(*S*)-2-fluoro-2-(naphthalen-2-ylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3n):

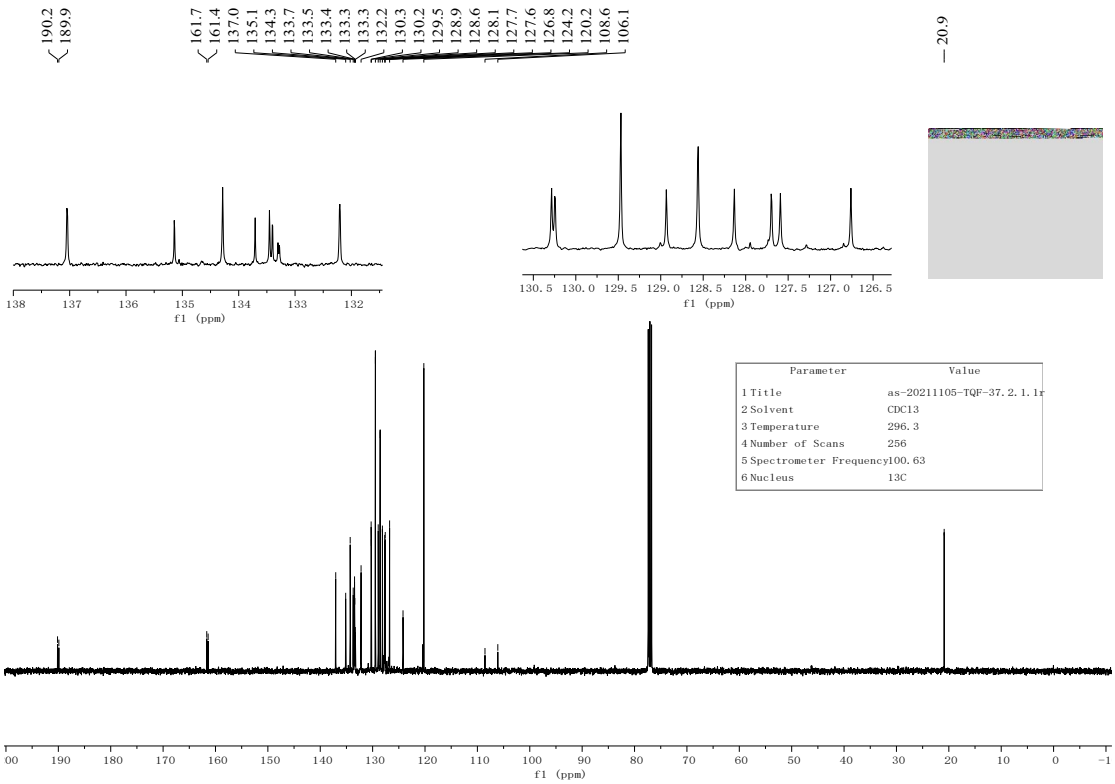


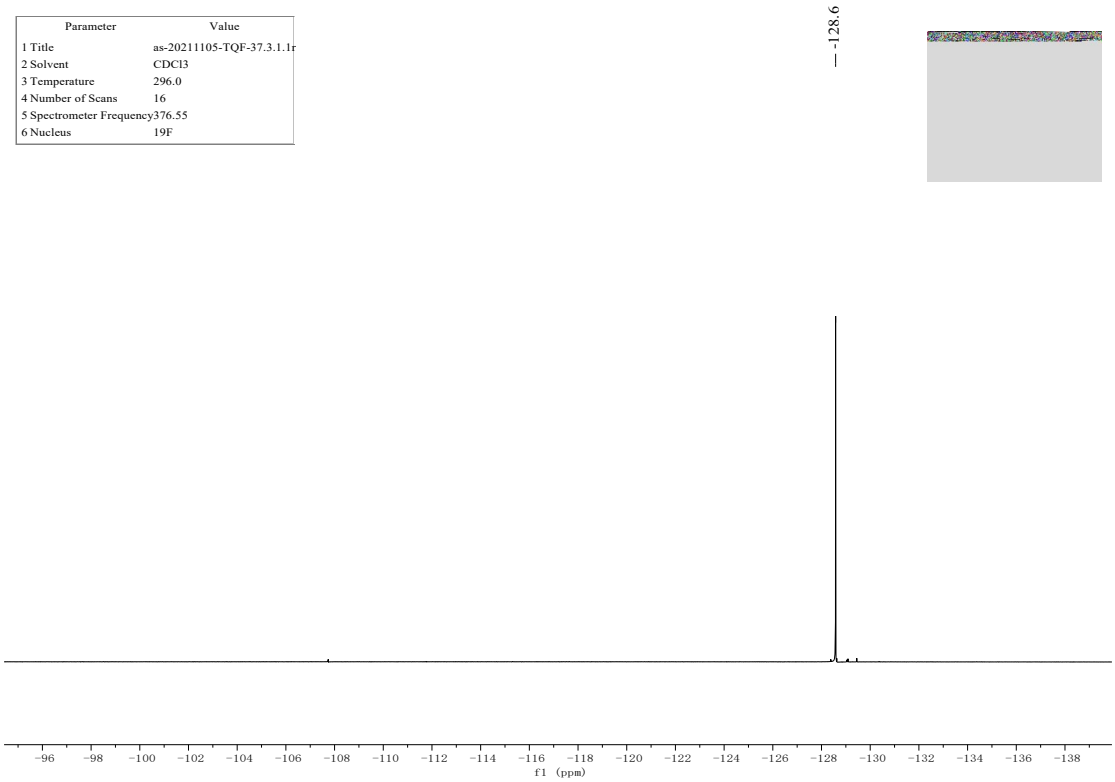




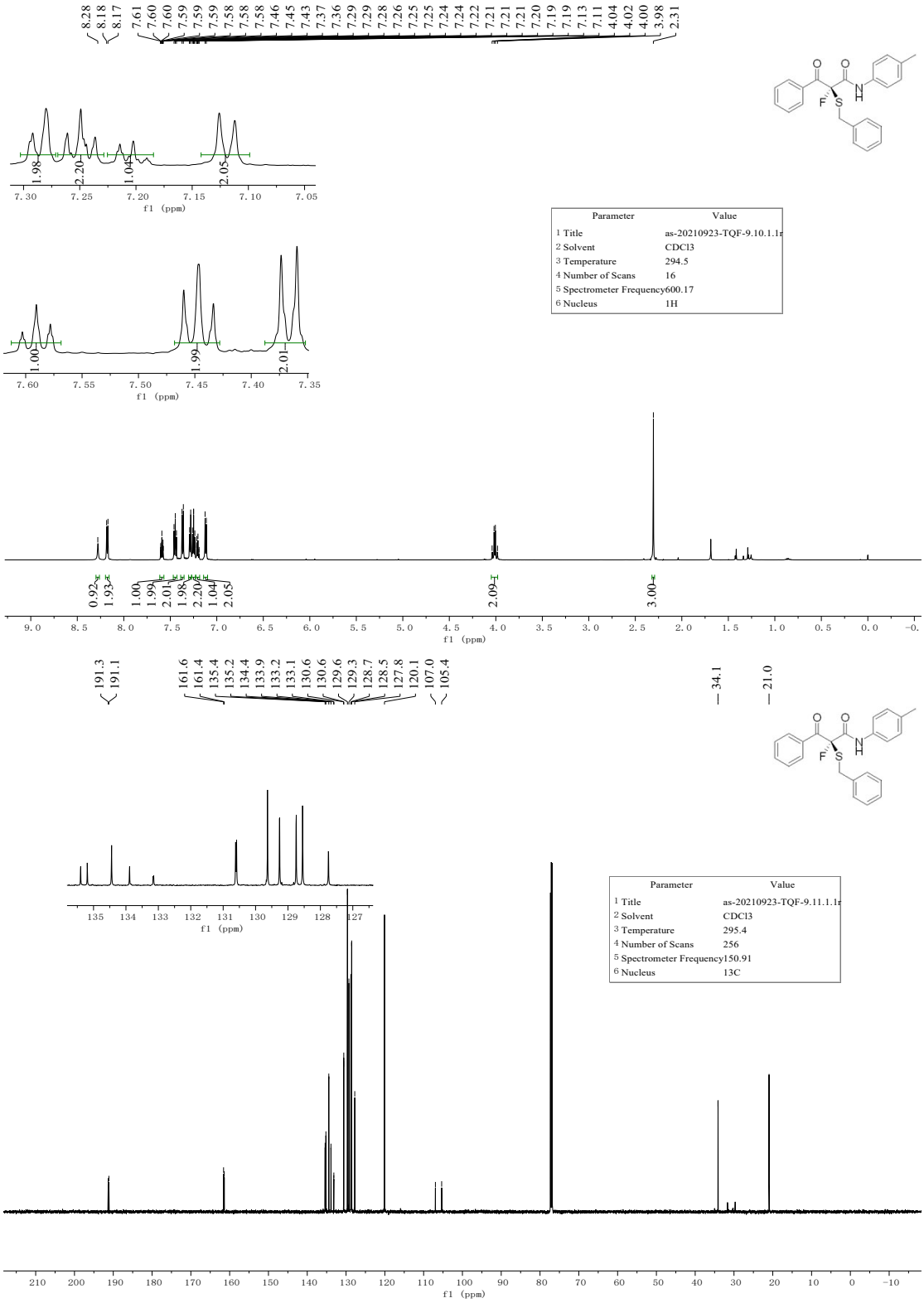
Parameter	Value
1 Title	as-20211105-TQF-37.1.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

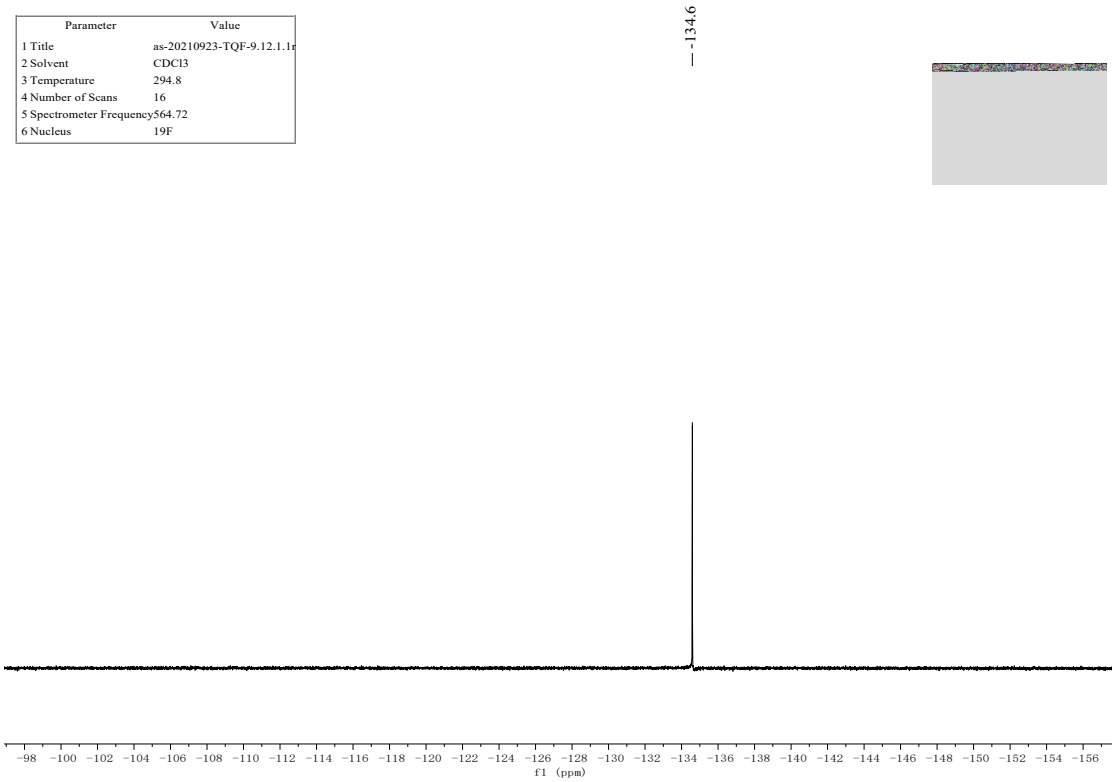



190.2
189.9
161.7
161.4
137.0
135.1
134.3
133.7
133.5
133.4
133.3
133.3
132.2
130.3
130.2
129.5
128.9
128.6
128.1
127.7
127.6
126.8
124.2
120.2
108.6
106.1
20.9
f1 (ppm)
Parameter Value
1 Title as-20211105-TQF-37.2.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C

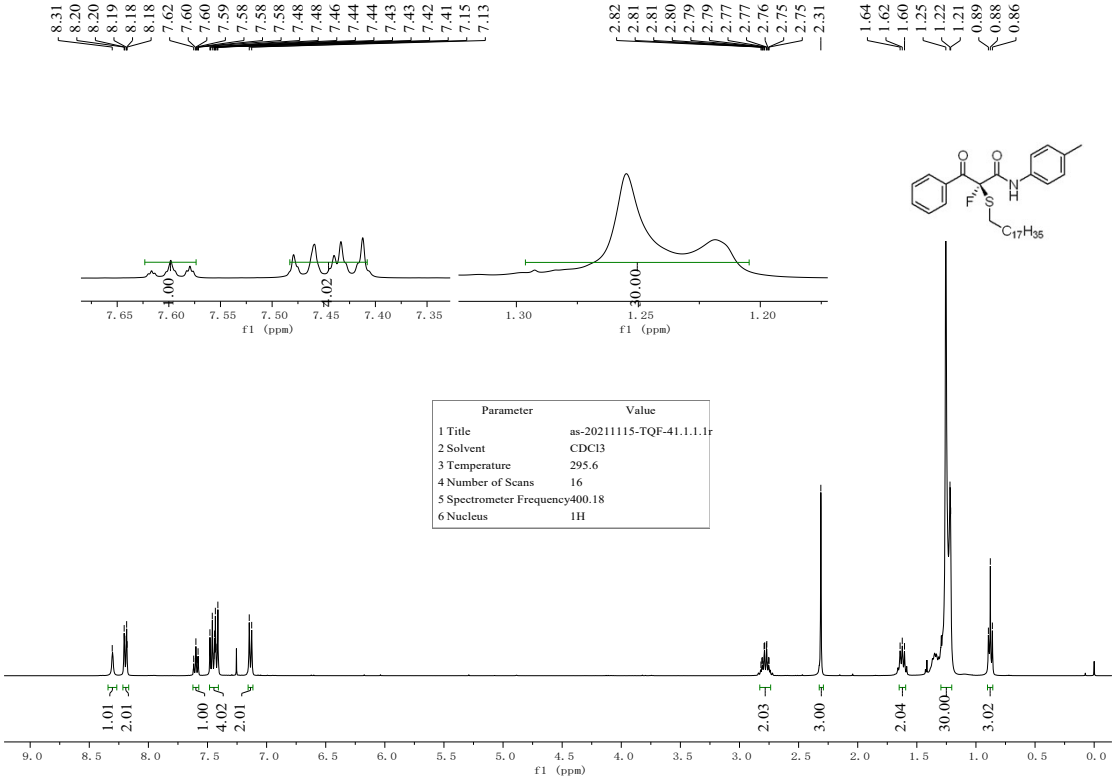

Parameter Value
1 Title as-20211105-TQF-37.3.1.1r
2 Solvent CDCl3
3 Temperature 296.0
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-128.6
f1 (ppm)

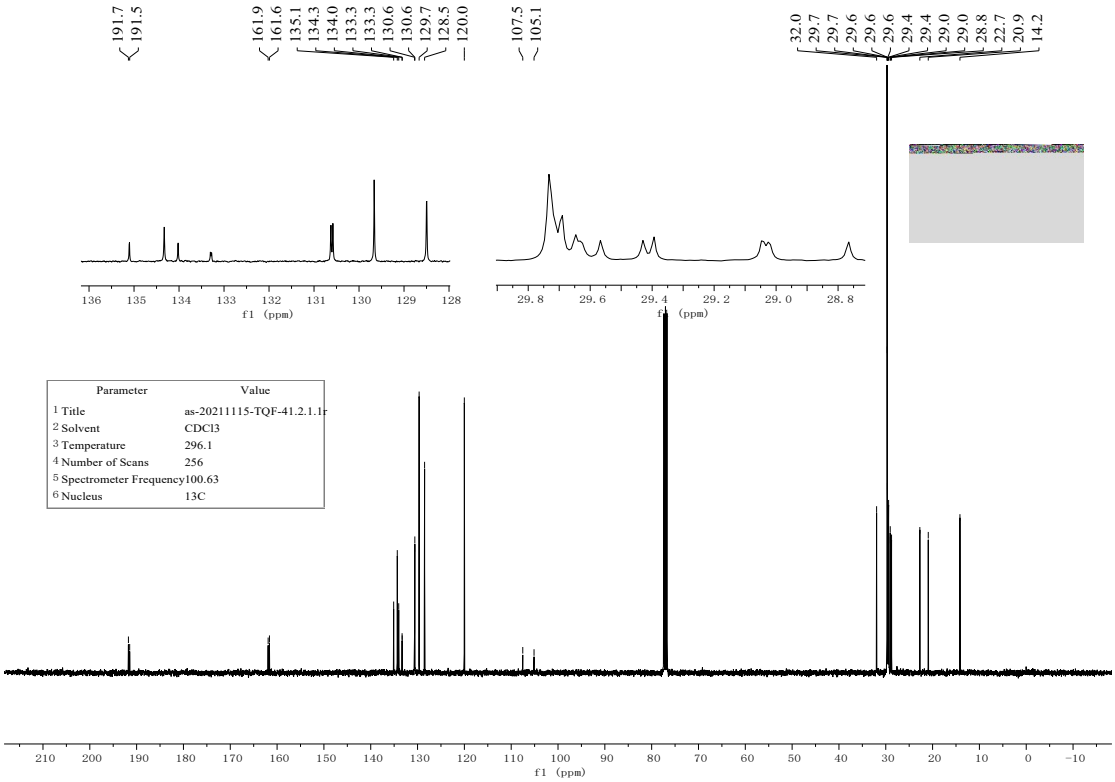
(*S*)-2-(benzylthio)-2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3o):

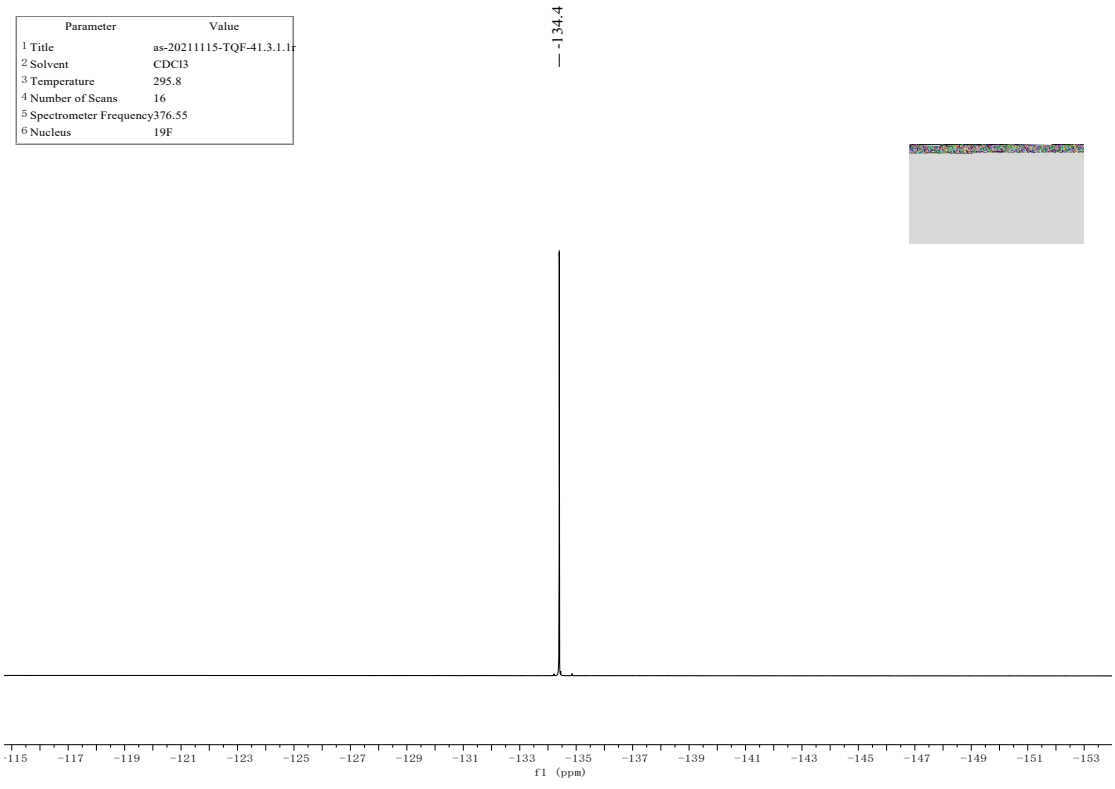




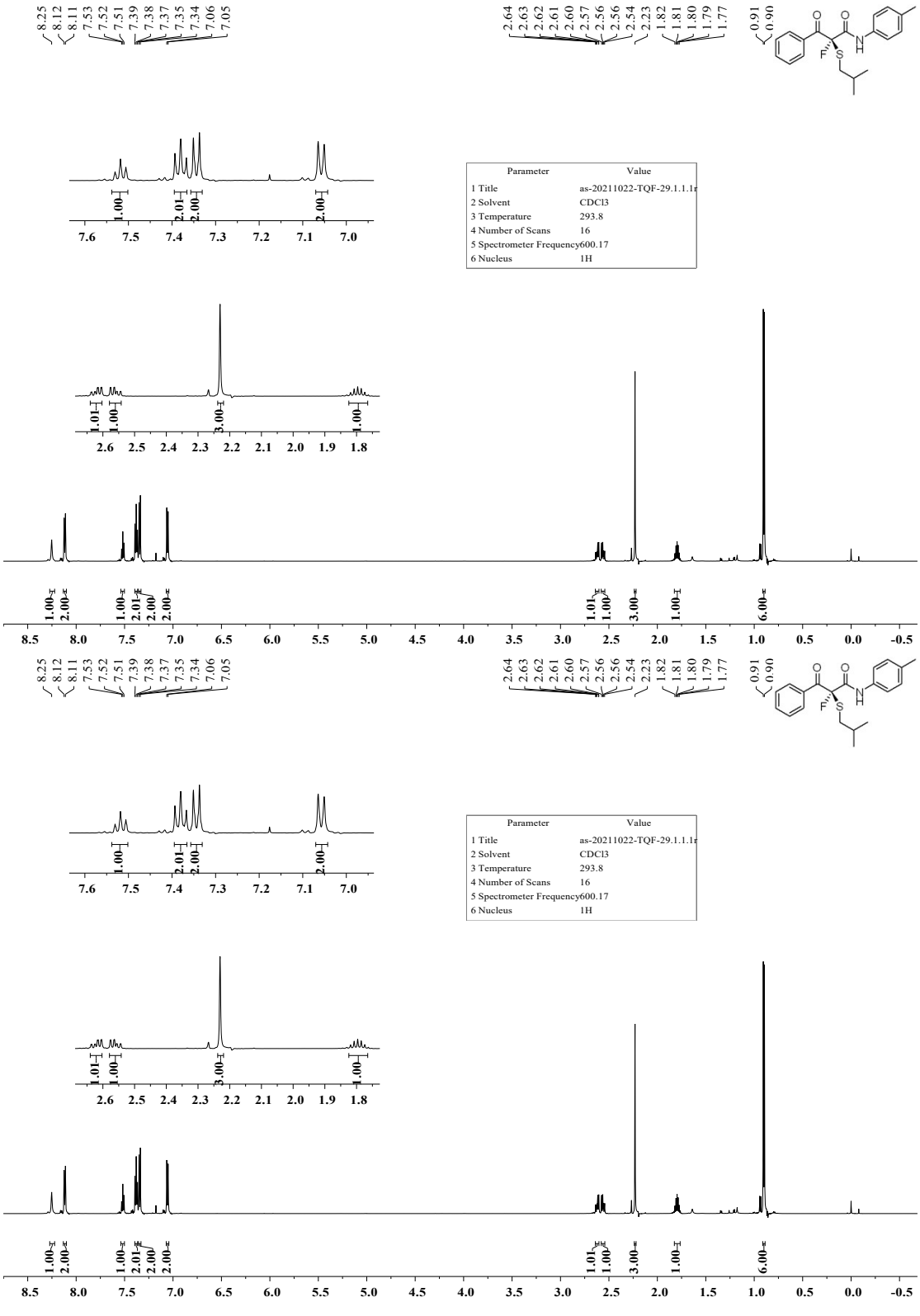
(*S*)-2-fluoro-2-(octadecylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3p):

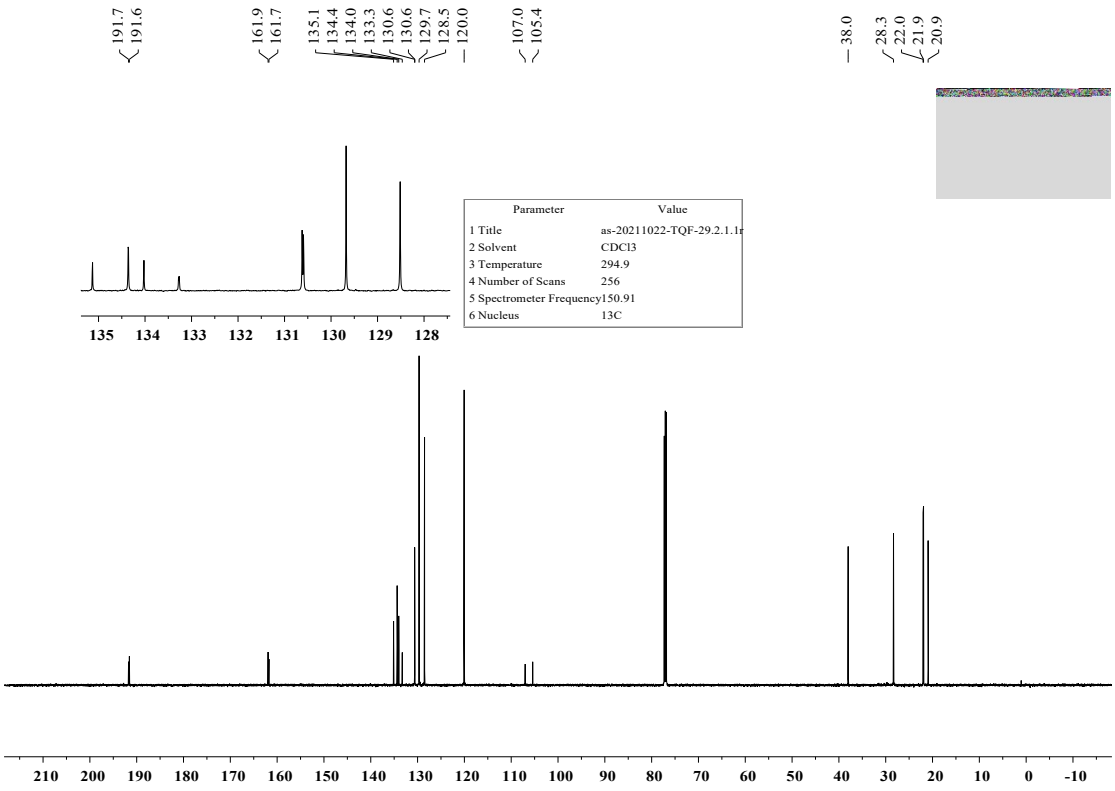



191.7
191.5
161.9
161.6
135.1
134.3
134.0
133.3
133.3
130.6
130.6
129.7
128.5
120.0
107.5
105.1
32.0
29.7
29.7
29.6
29.6
29.6
29.4
29.4
29.0
29.0
28.8
22.7
20.9
14.2
136 135 134 133 132 131 130 129 128
f1 (ppm)
29.8 29.6 29.4 29.2 29.0 28.8
f1 (ppm)
Parameter Value
1 Title as-20211115-TQF-41.2.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
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)

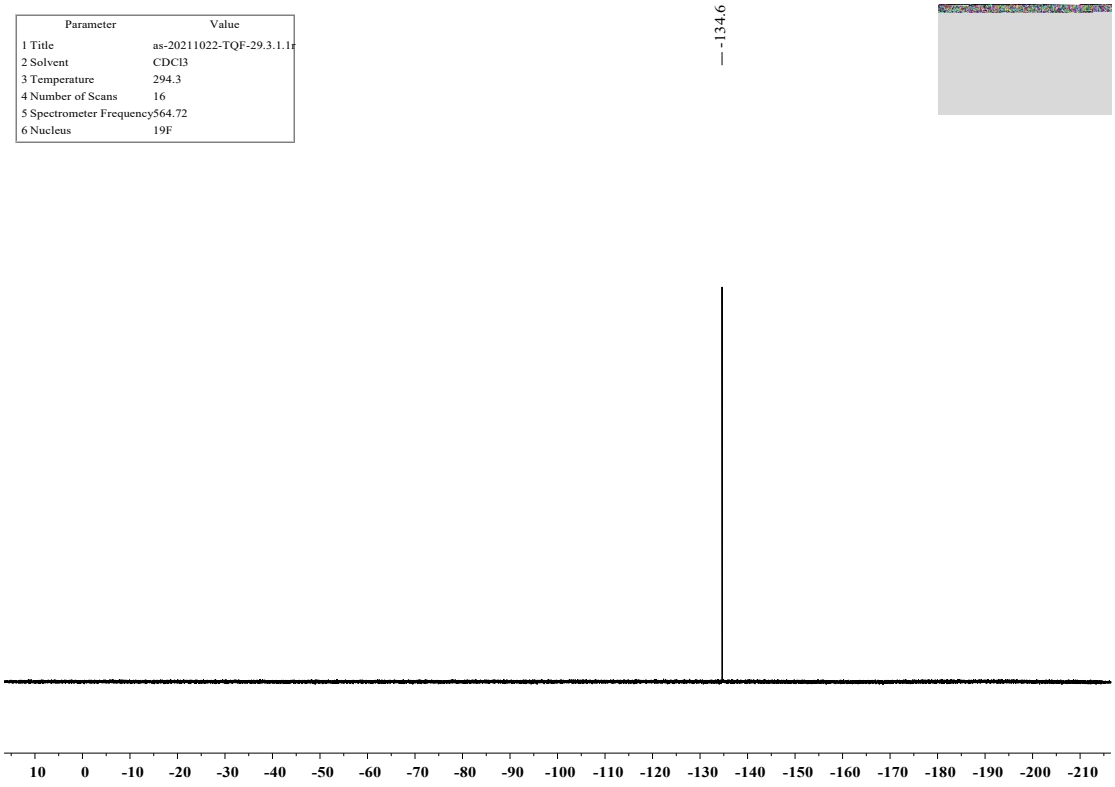

Parameter Value
1 Title as-20211115-TQF-41.3.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-134.4
-115 -117 -119 -121 -123 -125 -127 -129 -131 -133 -135 -137 -139 -141 -143 -145 -147 -149 -151 -153
f1 (ppm)

(*S*)-2-fluoro-2-(isobutylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3q):



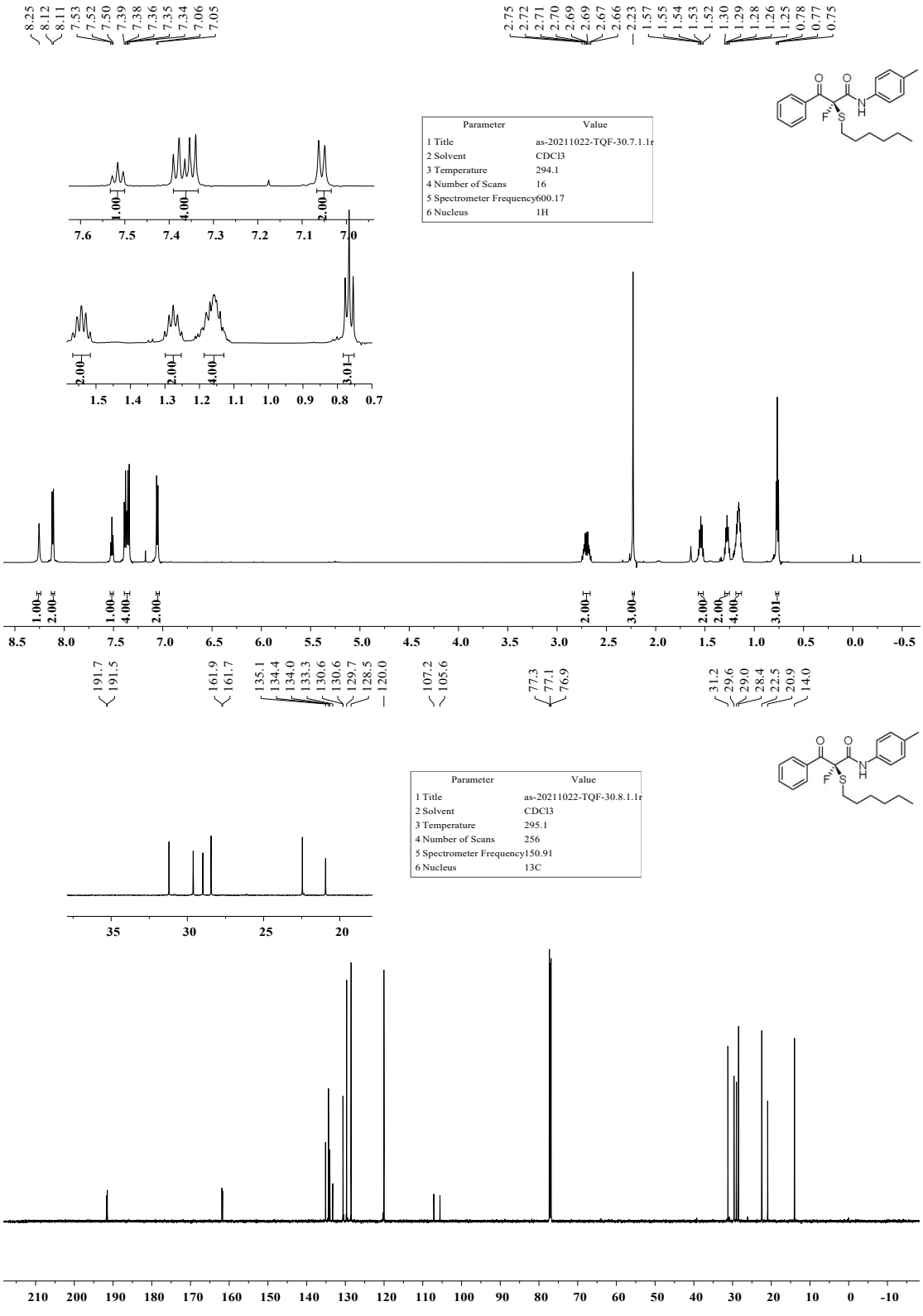


Parameter	Value
1 Title	as-20211022-TQF-29.2.1.1r
2 Solvent	CDCl3
3 Temperature	294.9
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C

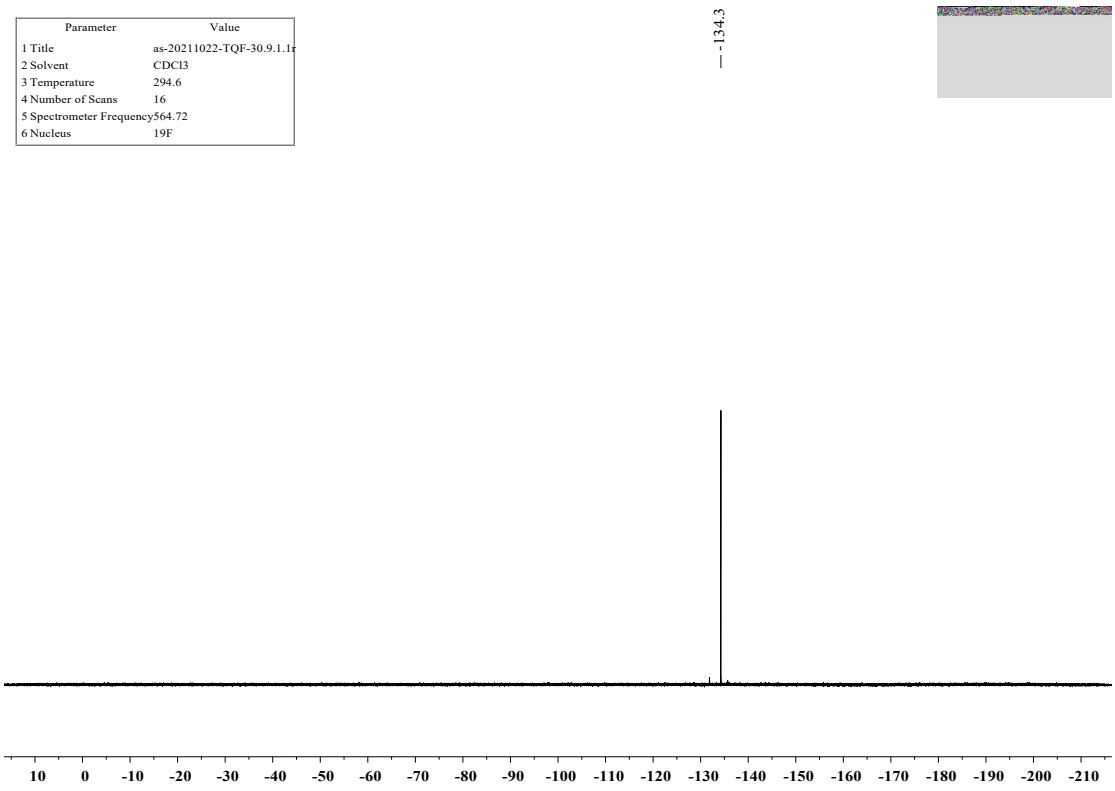


Parameter	Value
1 Title	as-20211022-TQF-29.3.1.1r
2 Solvent	CDCl3
3 Temperature	294.3
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

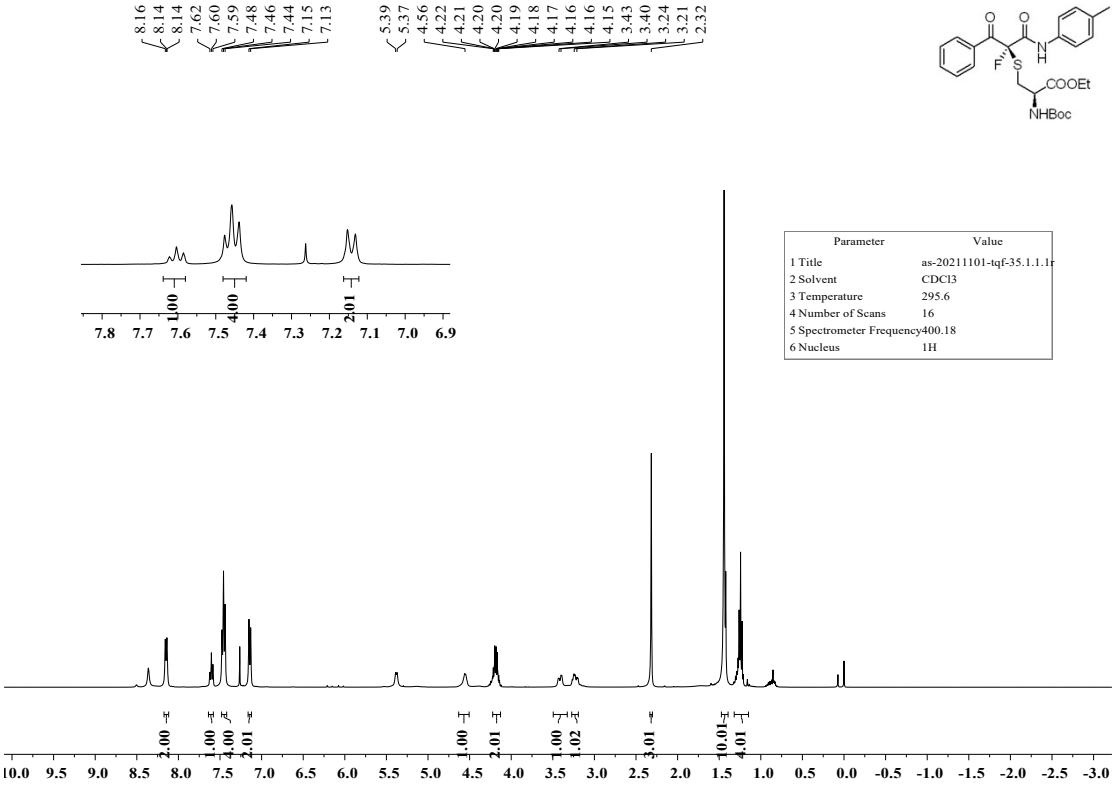
(*S*)-2-fluoro-2-(hexylthio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (3r):

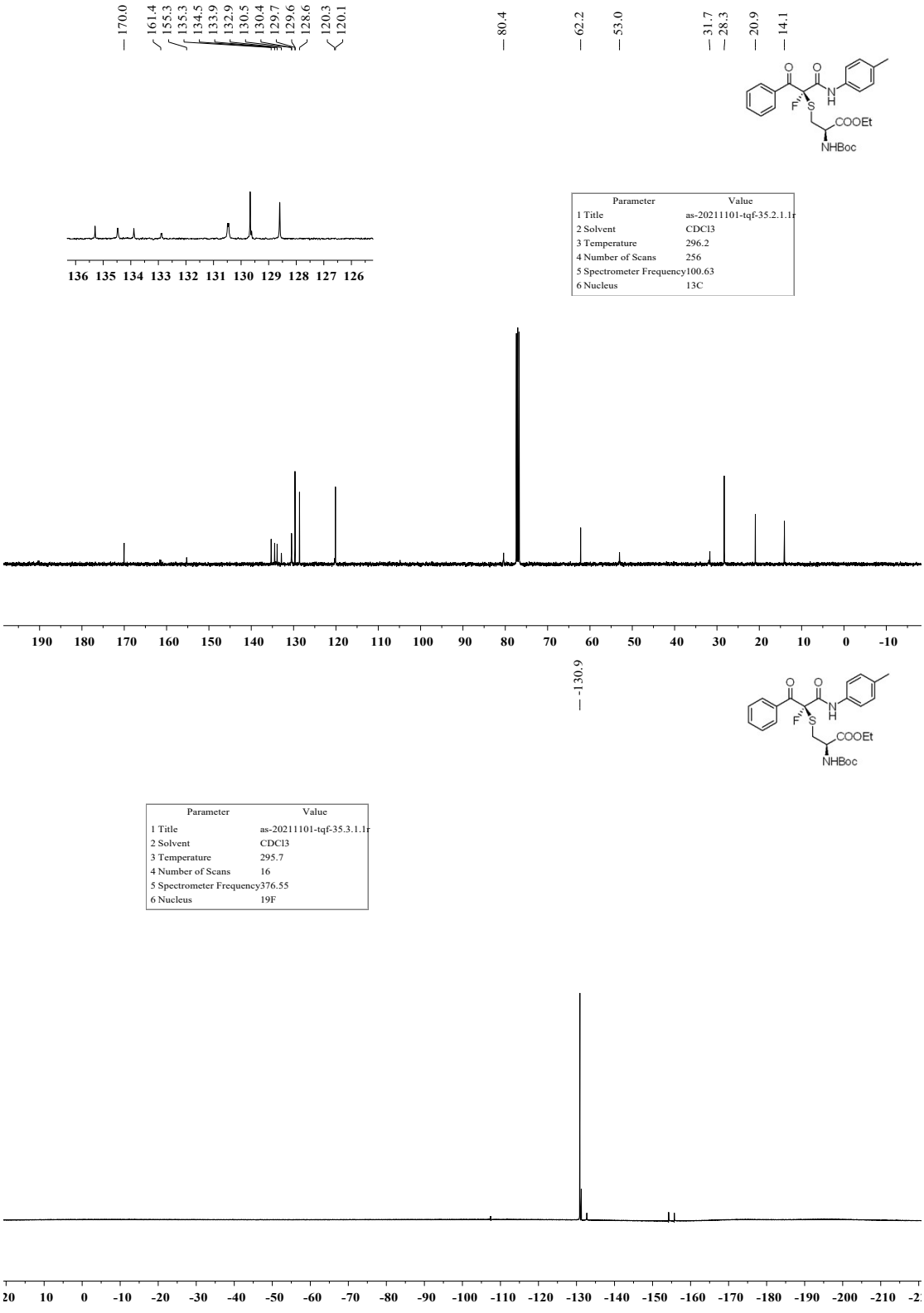


Parameter	Value
1 Title	as-20211022-TQF-30.9.1.1r
2 Solvent	CDCl3
3 Temperature	294.6
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

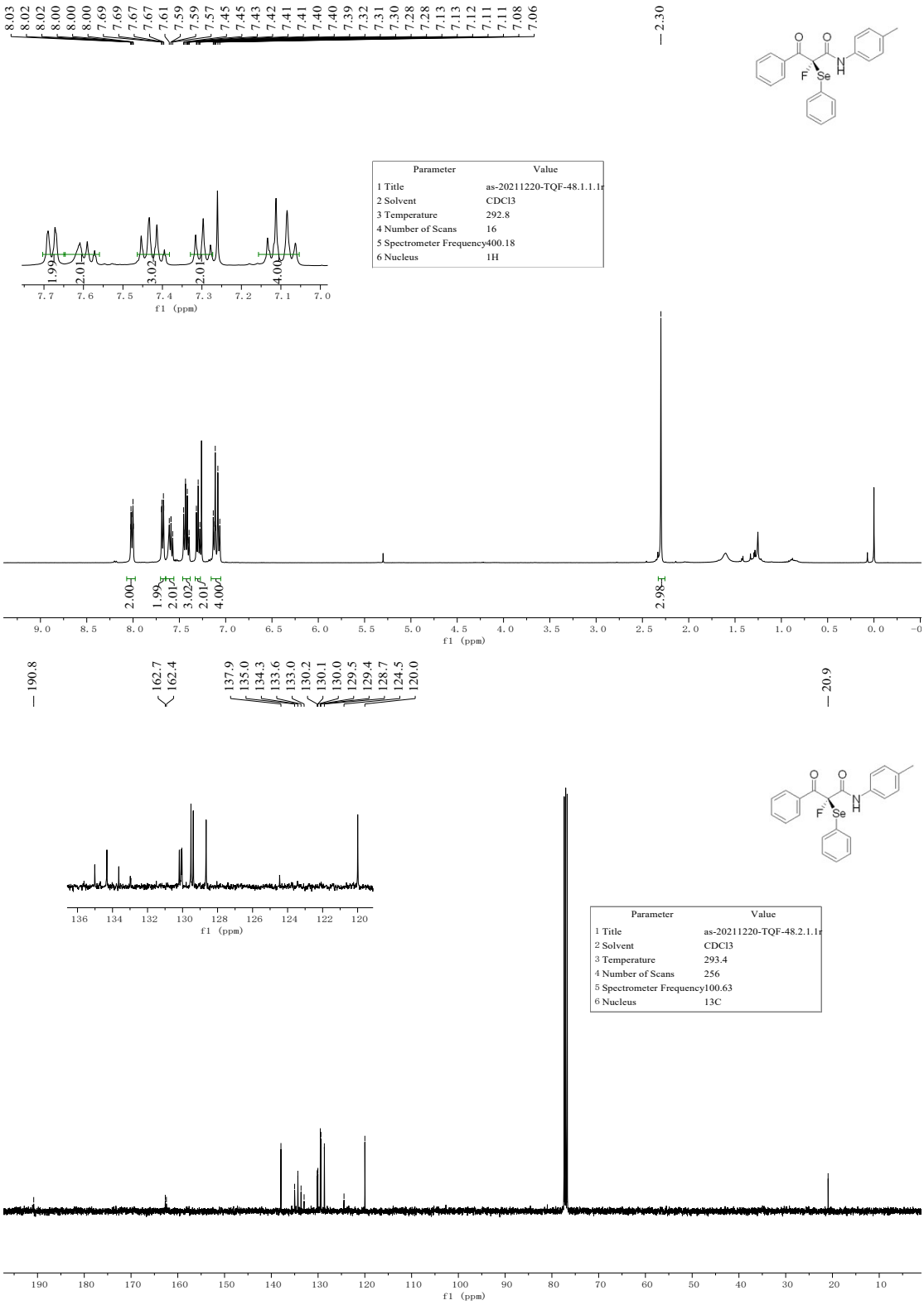


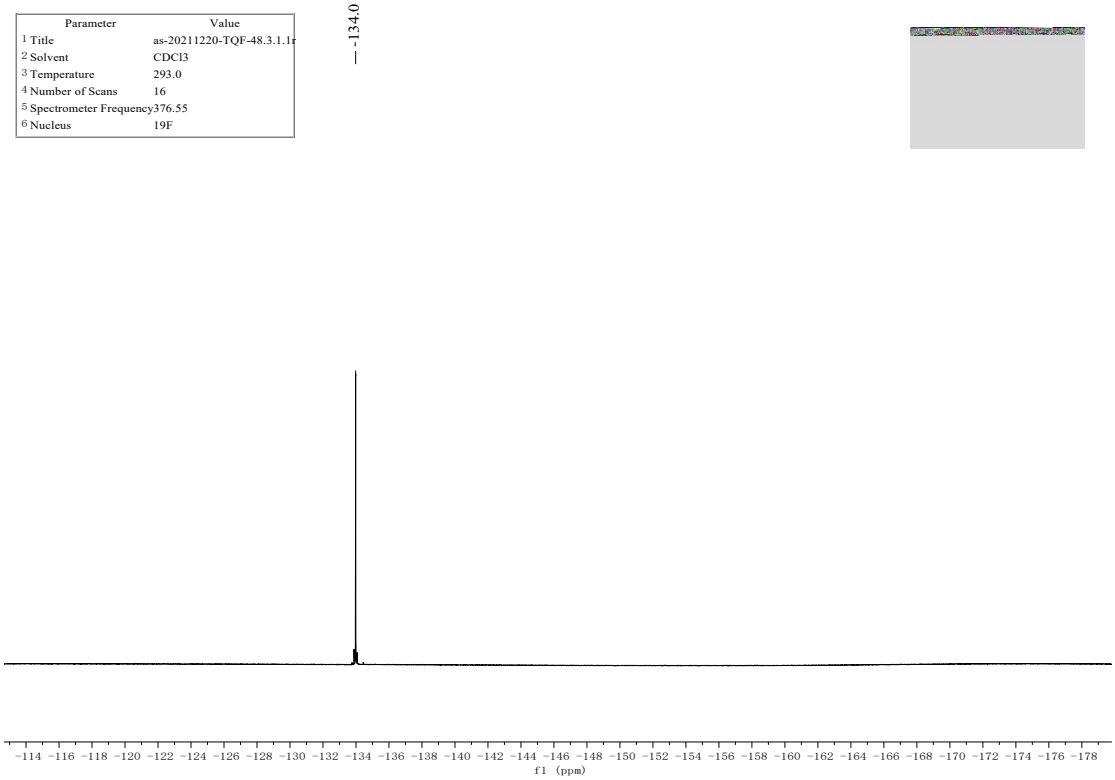
Ethyl *N*-(tert-butoxycarbonyl)-*S*-((*S*)-2-fluoro-1,3-dioxo-1-phenyl-3-(*p*-tolylamino)propan-2-yl)-L-cysteinate (3s):



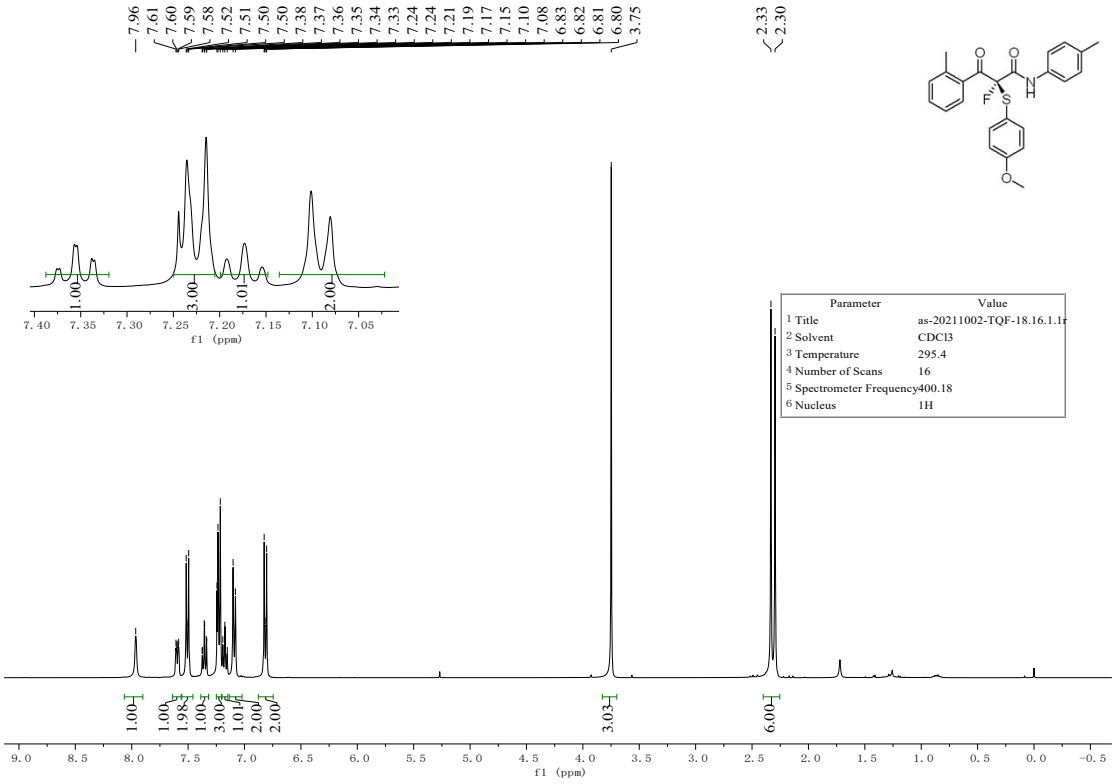

170.0
161.4
155.3
135.3
134.5
133.9
132.9
130.5
130.4
129.7
129.6
128.6
120.3
120.1
80.4
62.2
53.0
31.7
28.3
20.9
14.1
136 135 134 133 132 131 130 129 128 127 126
Parameter Value
1 Title as-20211101-tqf-35.2.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
-130.9
Parameter Value
1 Title as-20211101-tqf-35.3.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

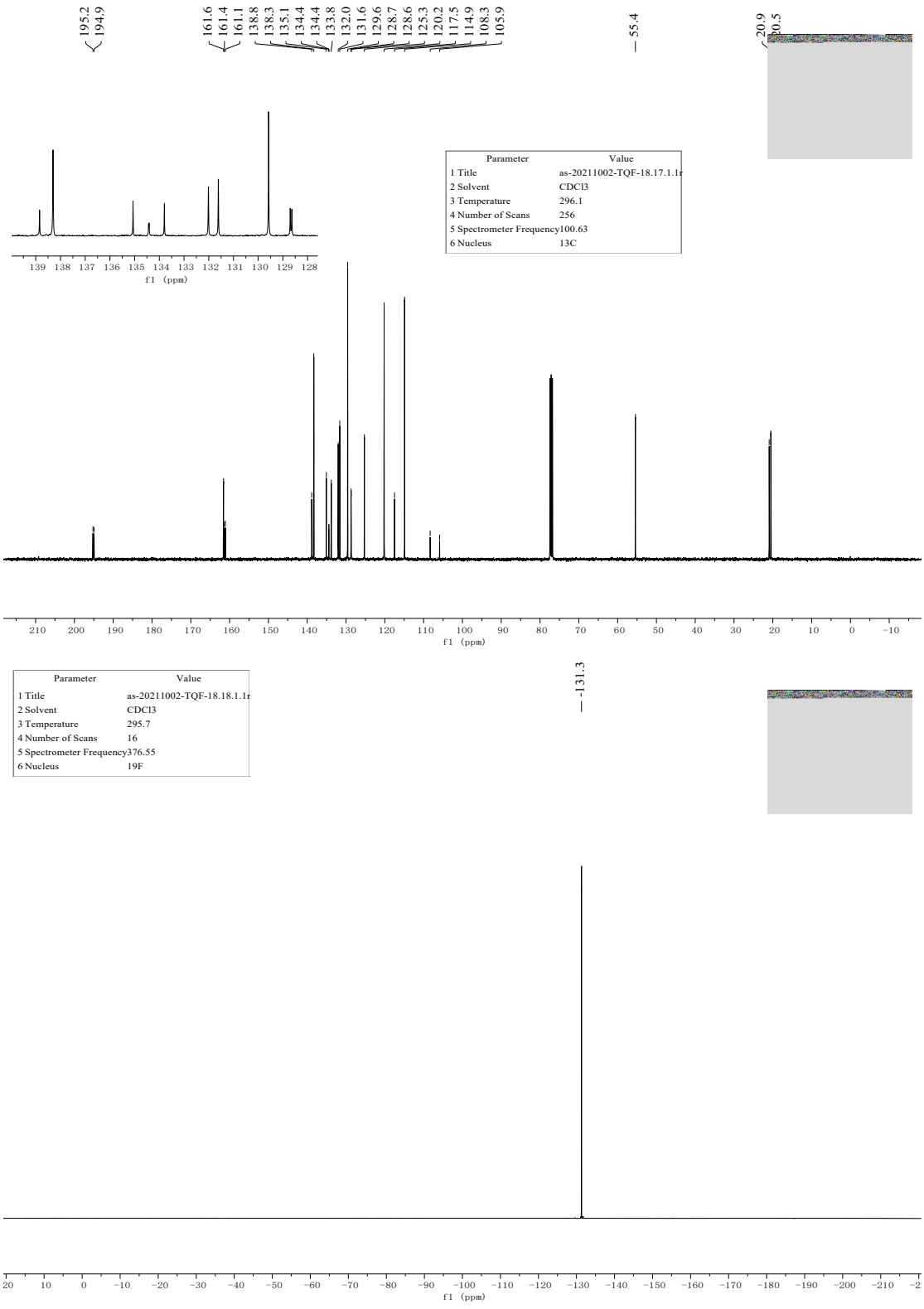
(*S*)-2-fluoro-3-oxo-3-phenyl-2-(phenylselanyl)-*N*-(*p*-tolyl)propanamide (3t):



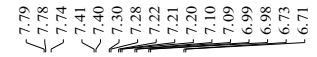


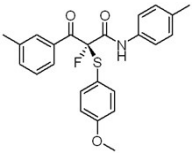
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-(*o*-tolyl)-*N*-(*p*-tolyl)propanamide (4a):

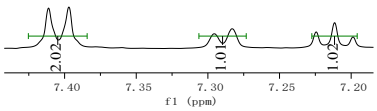




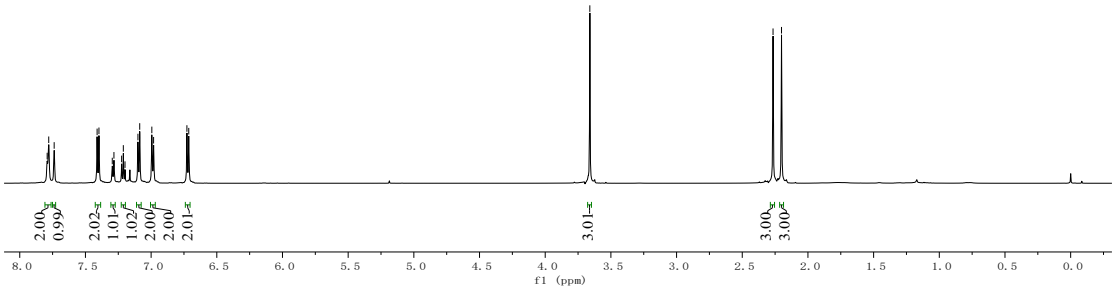
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-(*m*-tolyl)-*N*-(*p*-tolyl)propanamide (4b):

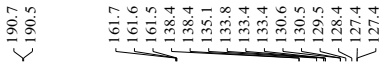


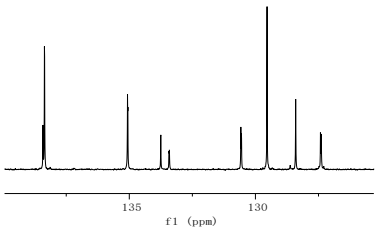


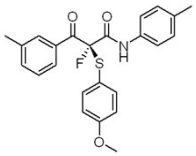


Parameter	Value
1 Title	as-20211001-TQF-13-1.1.1.1r
2 Solvent	CDCl3
3 Temperature	294.3
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

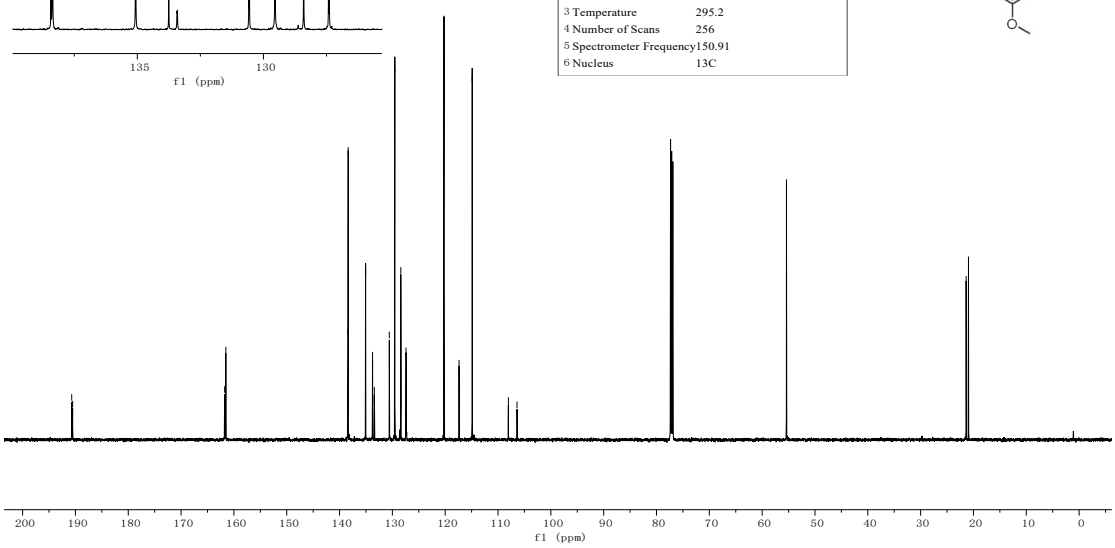




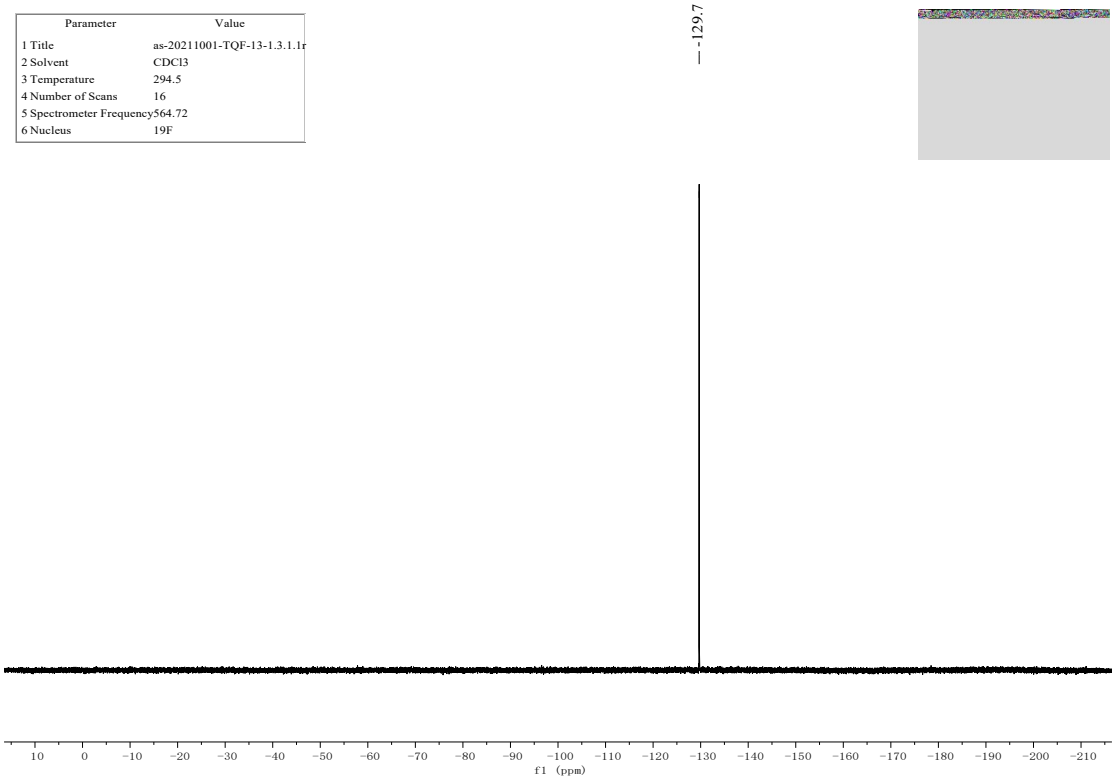




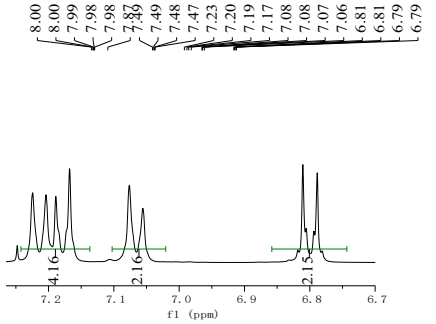
Parameter	Value
1 Title	as-20211001-TQF-13-1.2.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	256
5 Spectrometer Frequency	150.91
6 Nucleus	13C

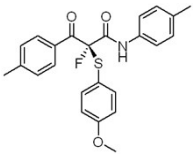


Parameter	Value
1 Title	as-20211001-TQF-13-1.3.1.1r
2 Solvent	CDCl3
3 Temperature	294.5
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

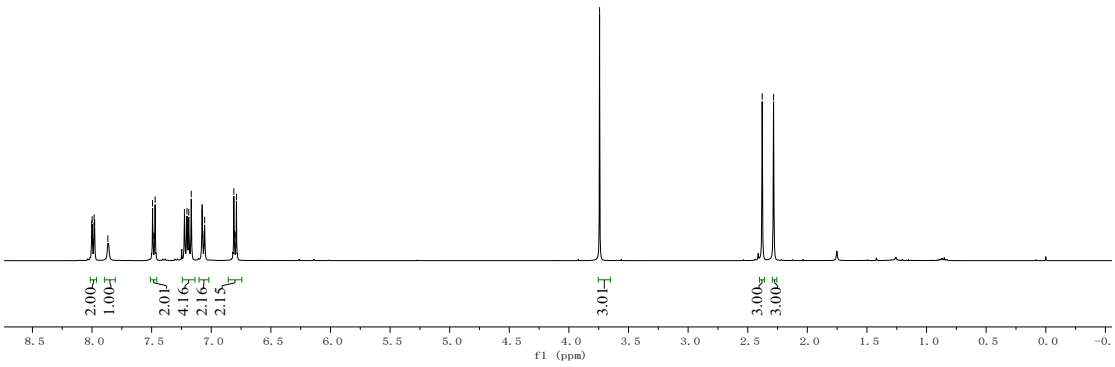


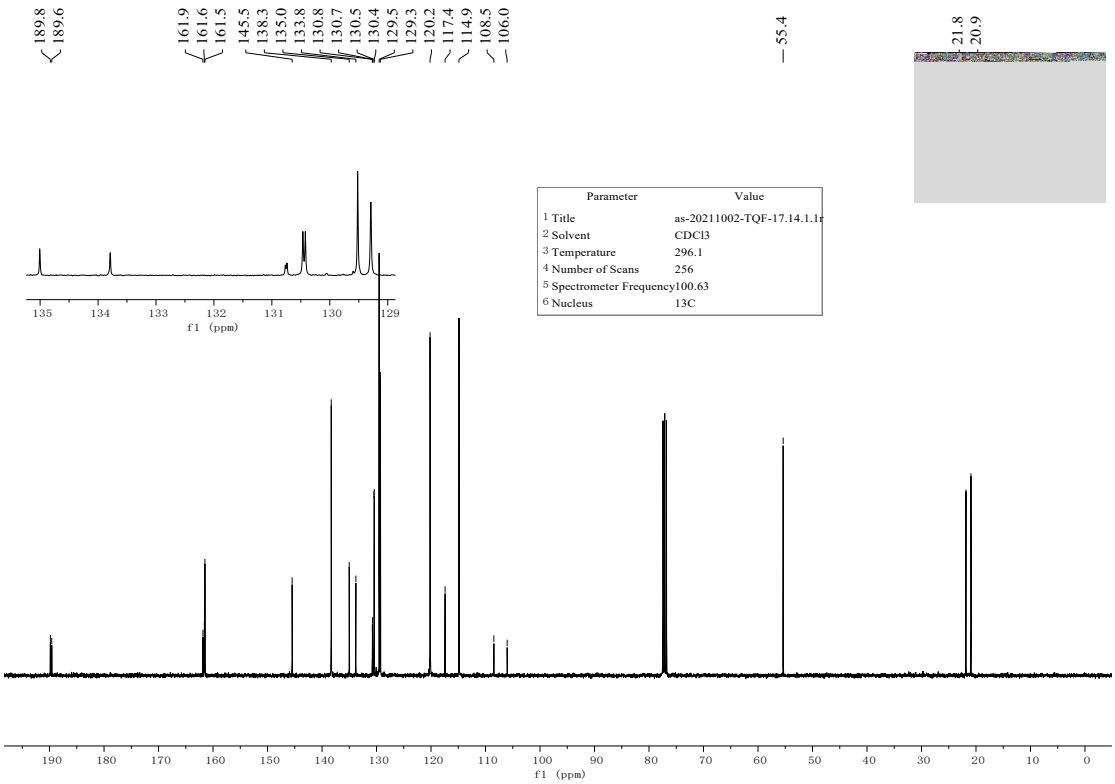
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*,3-di-ptolylpropanamide (4c):

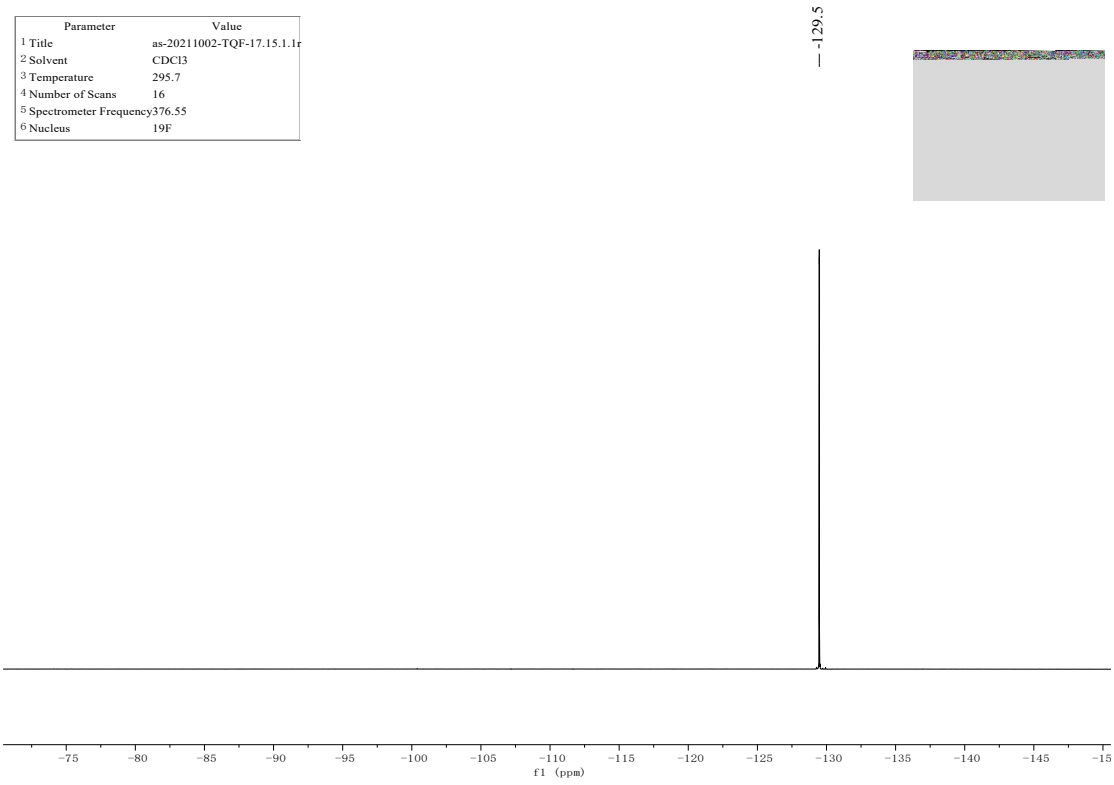




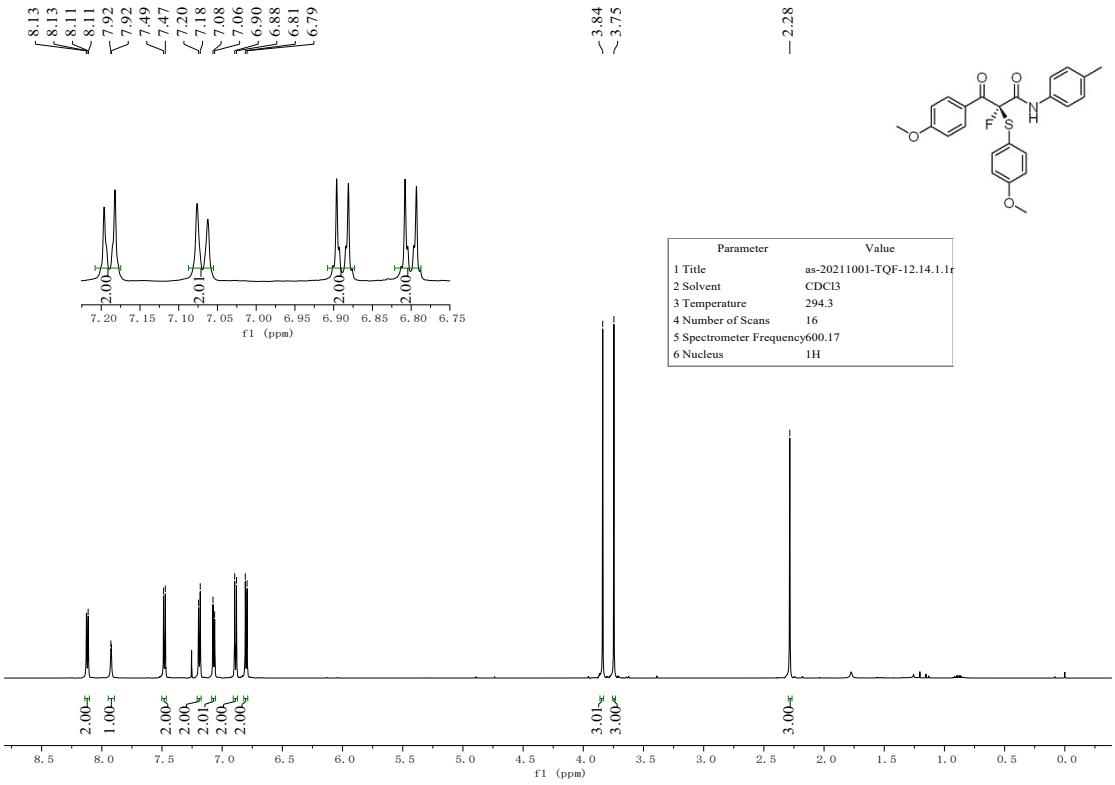
Parameter	Value
1 Title	as-20211002-TQF-17.13.1.1r
2 Solvent	CDCl3
3 Temperature	295.4
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

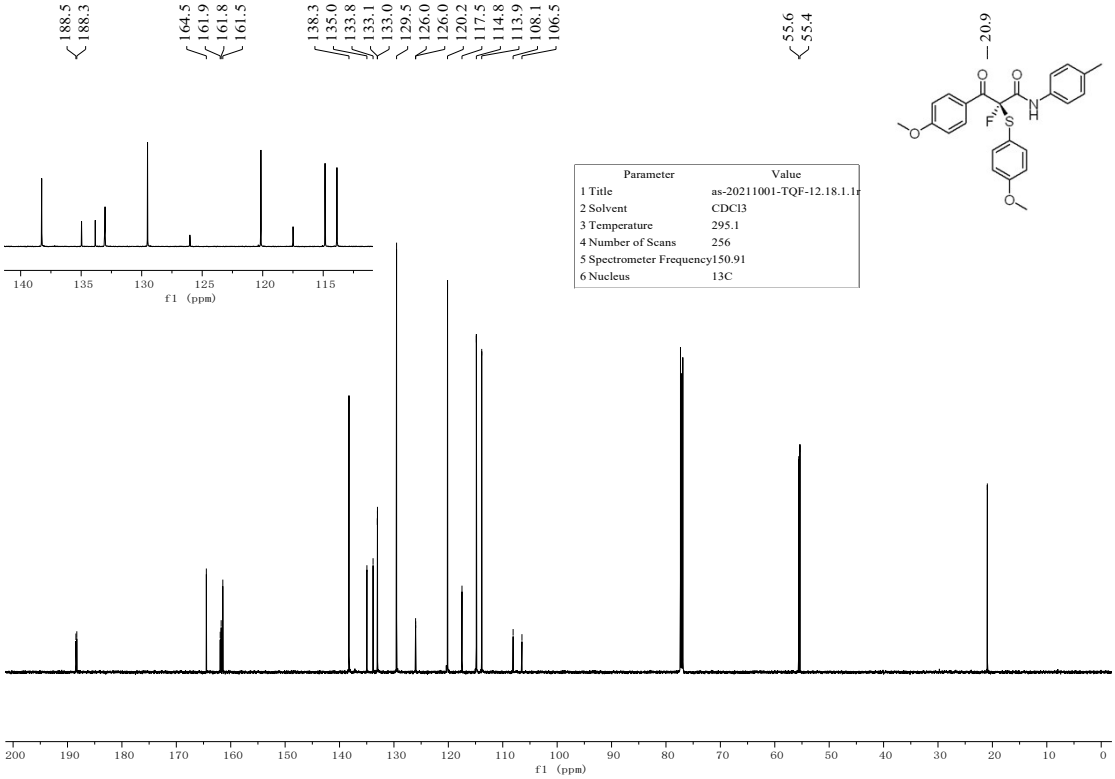



189.8
189.6
161.9
161.6
161.5
145.5
138.3
135.0
133.8
130.8
130.7
130.5
130.4
129.5
129.3
120.2
117.4
114.9
108.5
106.0
55.4
21.8
20.9
Parameter Value
1 Title as-20211002-TQF-17.14.1.1r
2 Solvent CDCl3
3 Temperature 296.1
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

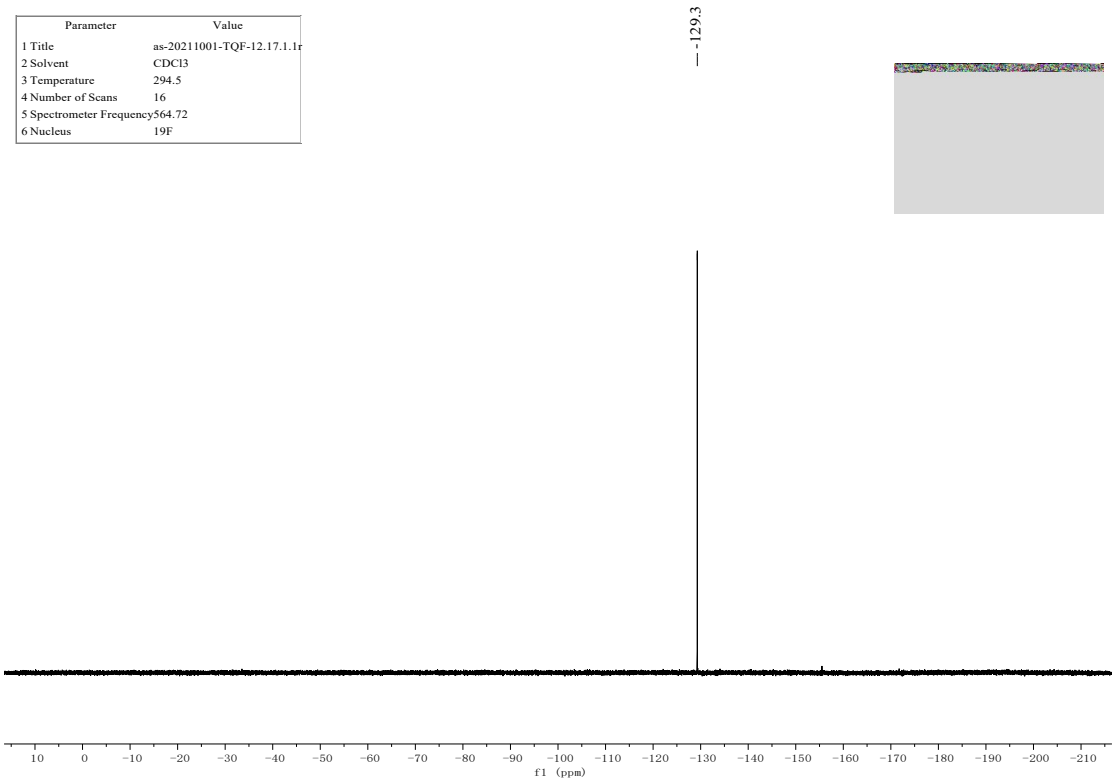

Parameter Value
1 Title as-20211002-TQF-17.15.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-129.5
f1 (ppm)

(*S*)-2-fluoro-3-(4-methoxyphenyl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4d):

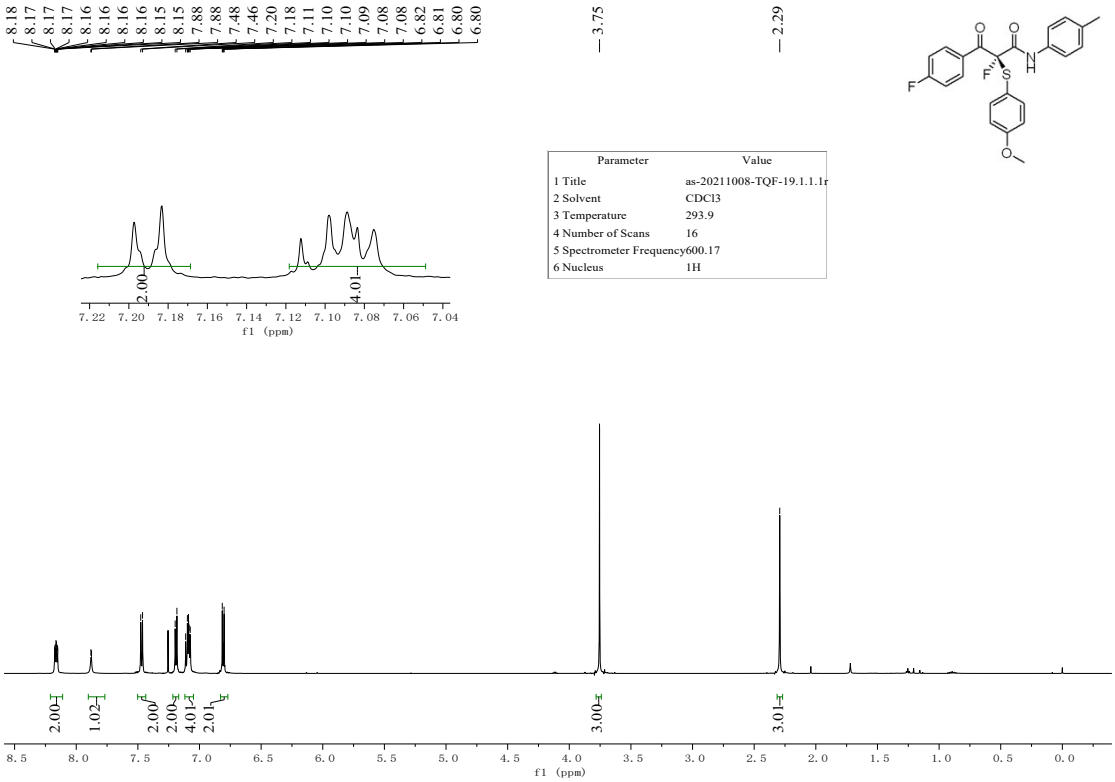




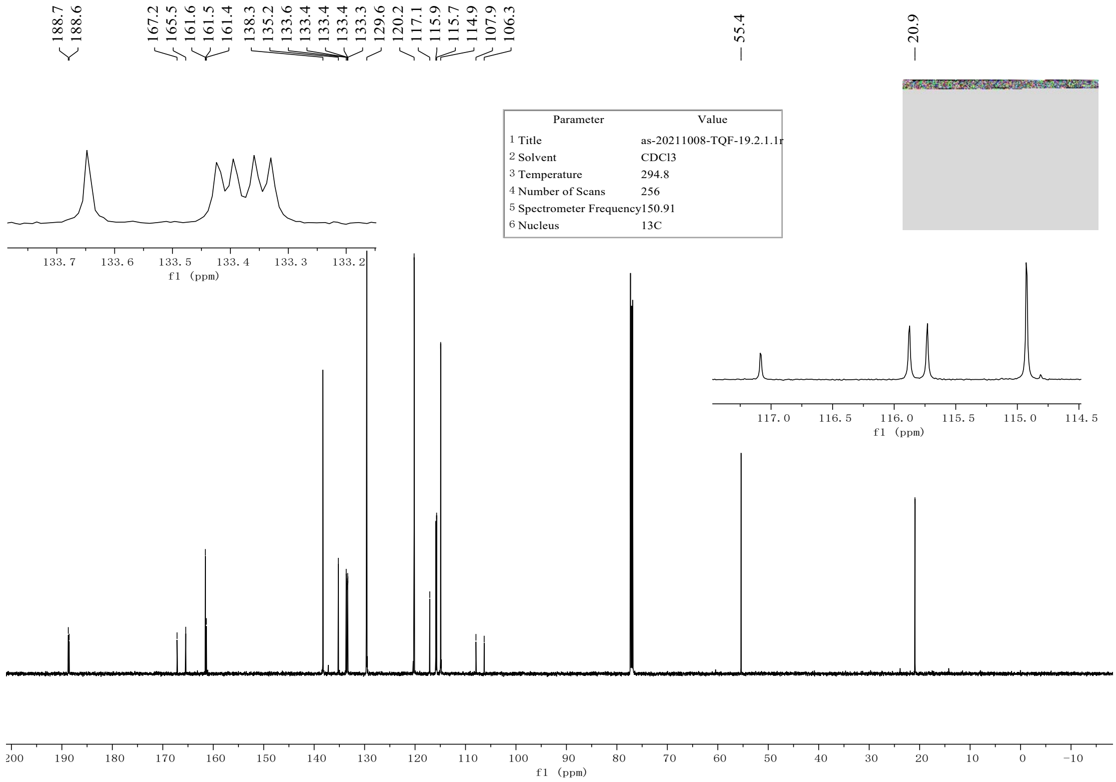
Parameter	Value
1 Title	as-20211001-TQF-12.17.1.1r
2 Solvent	CDCl3
3 Temperature	294.5
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

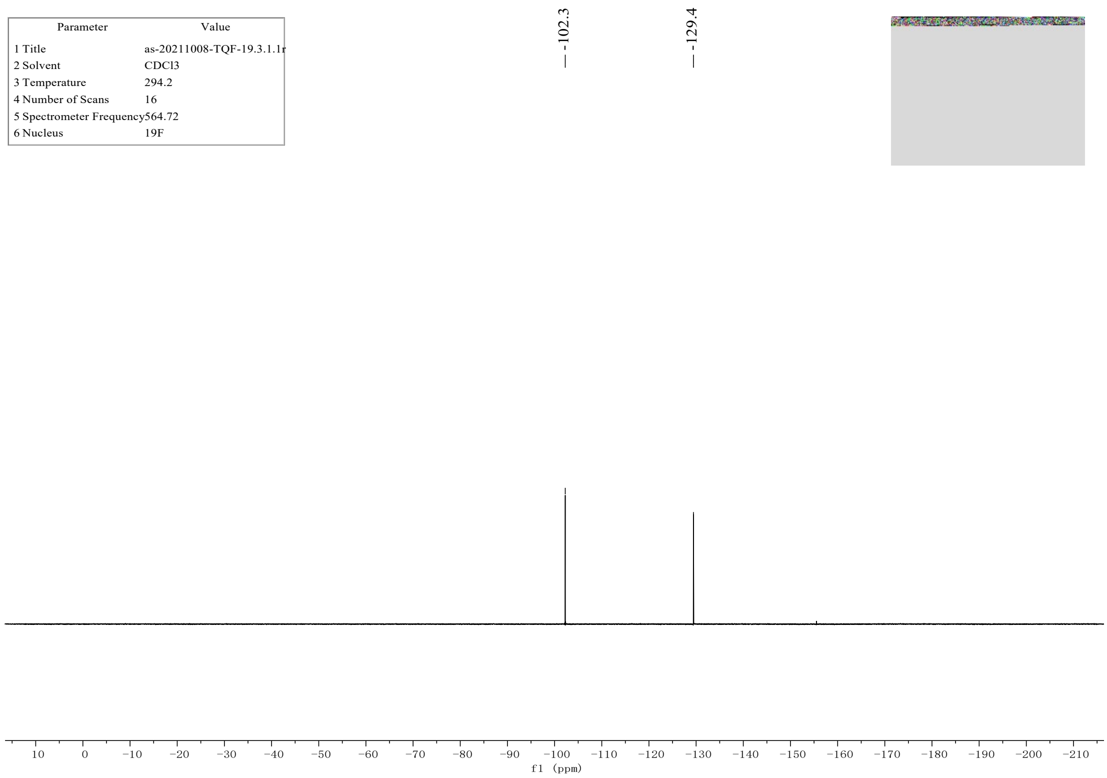


(*S*)-2-fluoro-3-(4-fluorophenyl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4e):

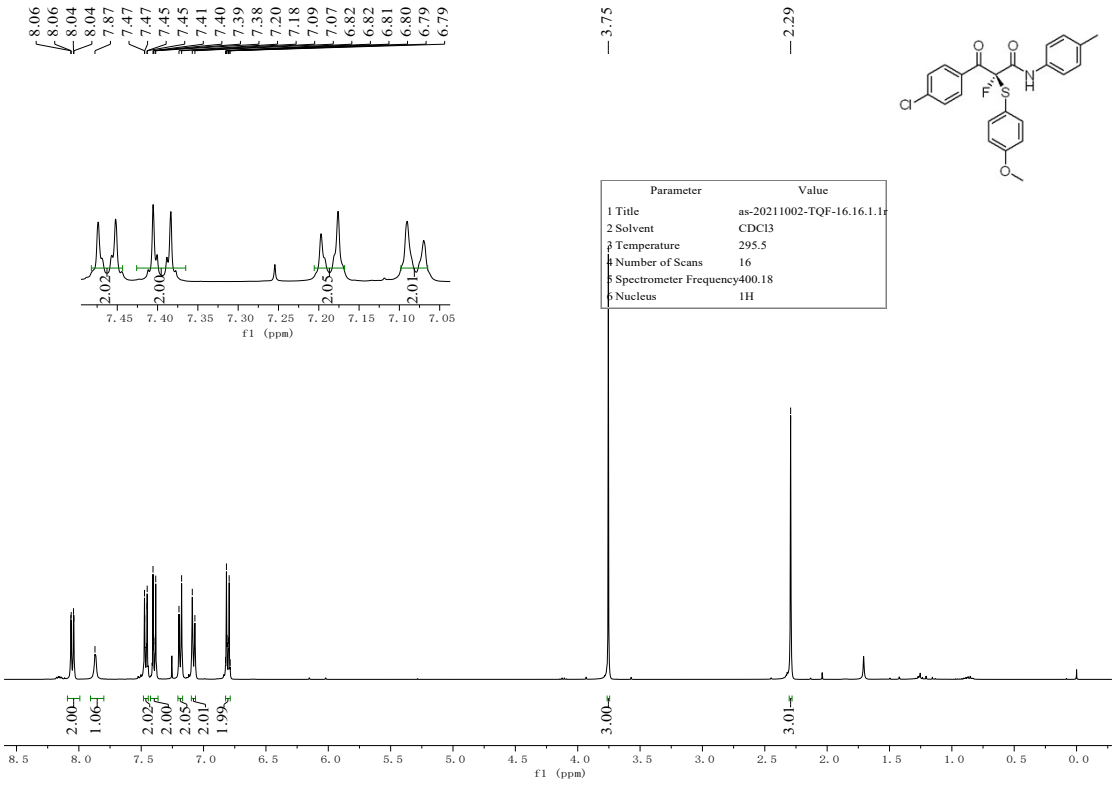


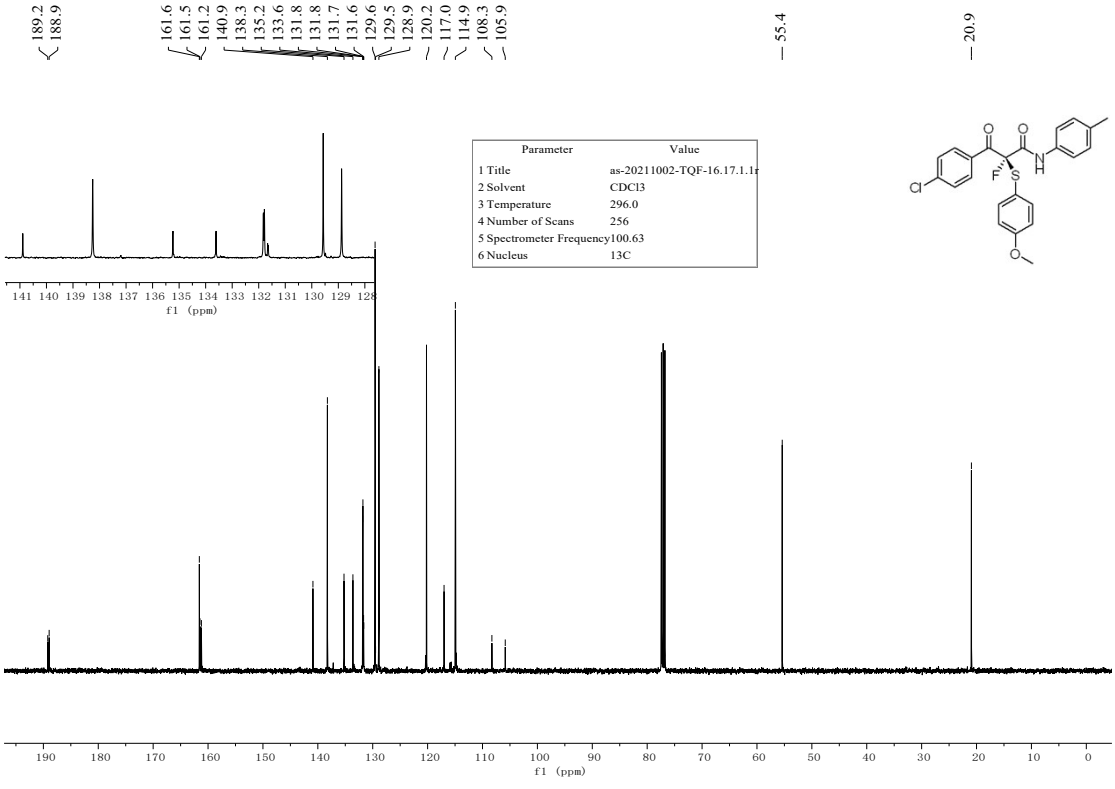
Parameter	Value
1 Title	as-20211008-TQF-19.1.1.1r
2 Solvent	CDCl3
3 Temperature	293.9
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H


188.7
188.6
167.2
165.5
161.6
161.5
161.4
138.3
135.2
133.6
133.4
133.4
133.4
133.3
129.6
120.2
117.1
115.9
115.7
114.9
107.9
106.3
55.4
20.9
Parameter Value
1 Title as-20211008-TQF-19.2.1.1r
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)

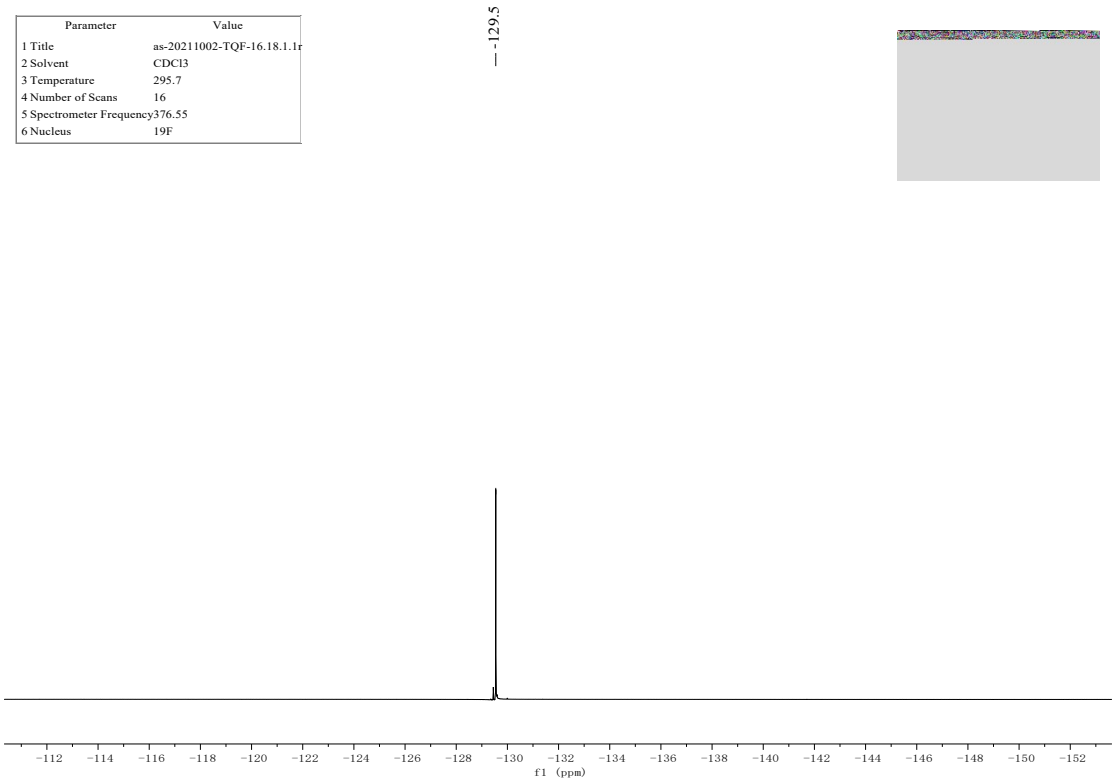

Parameter Value
1 Title as-20211008-TQF-19.3.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-102.3
-129.4
f1 (ppm)

(*S*)-3-(4-chlorophenyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4f):

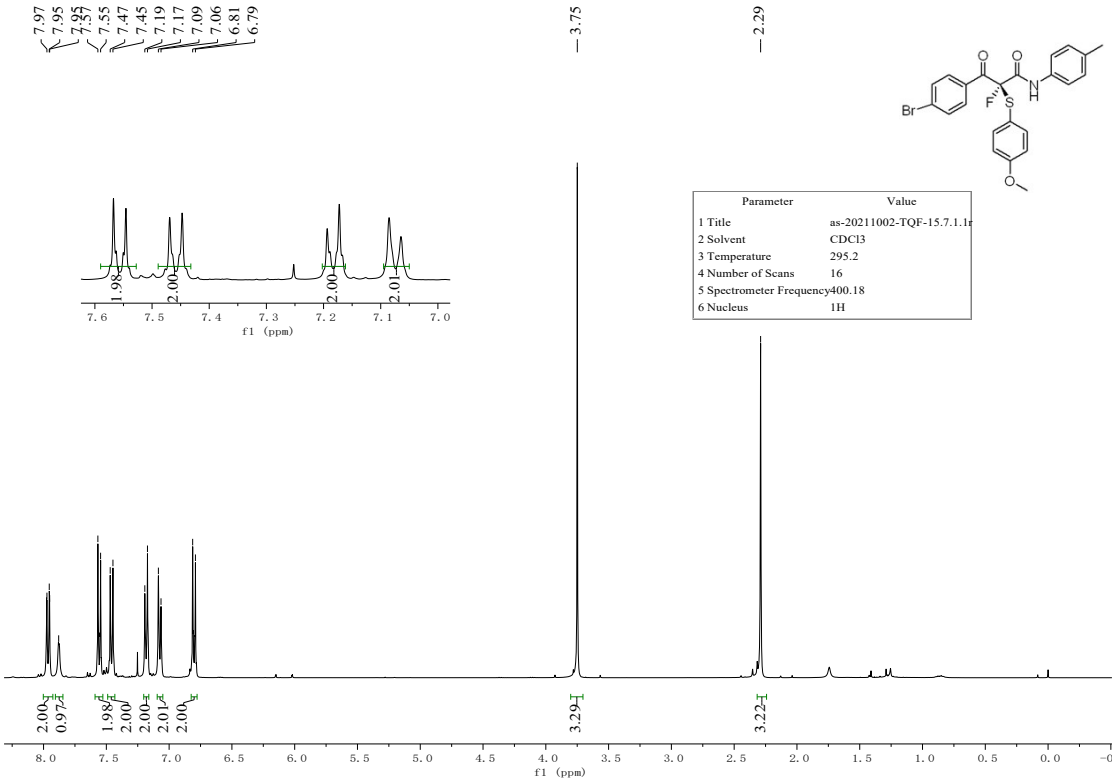




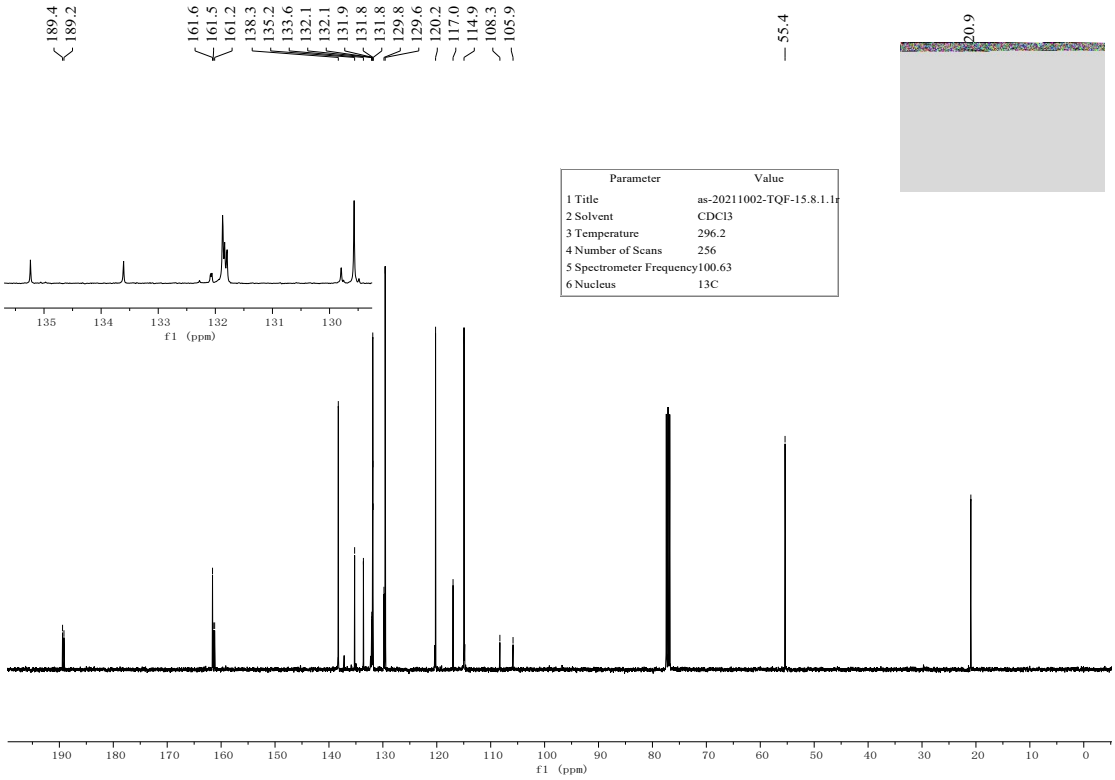
Parameter	Value
1 Title	as-20211002-TQF-16.18.1.1r
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

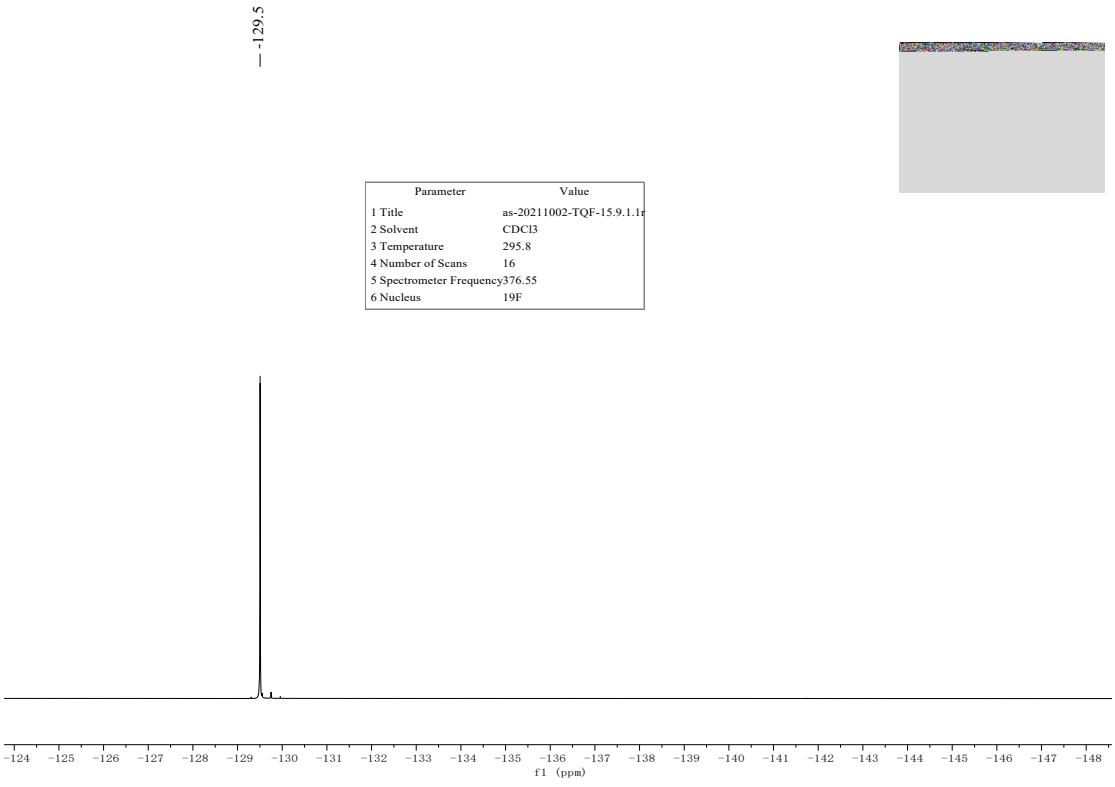


(*S*)-3-(4-bromophenyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4g):

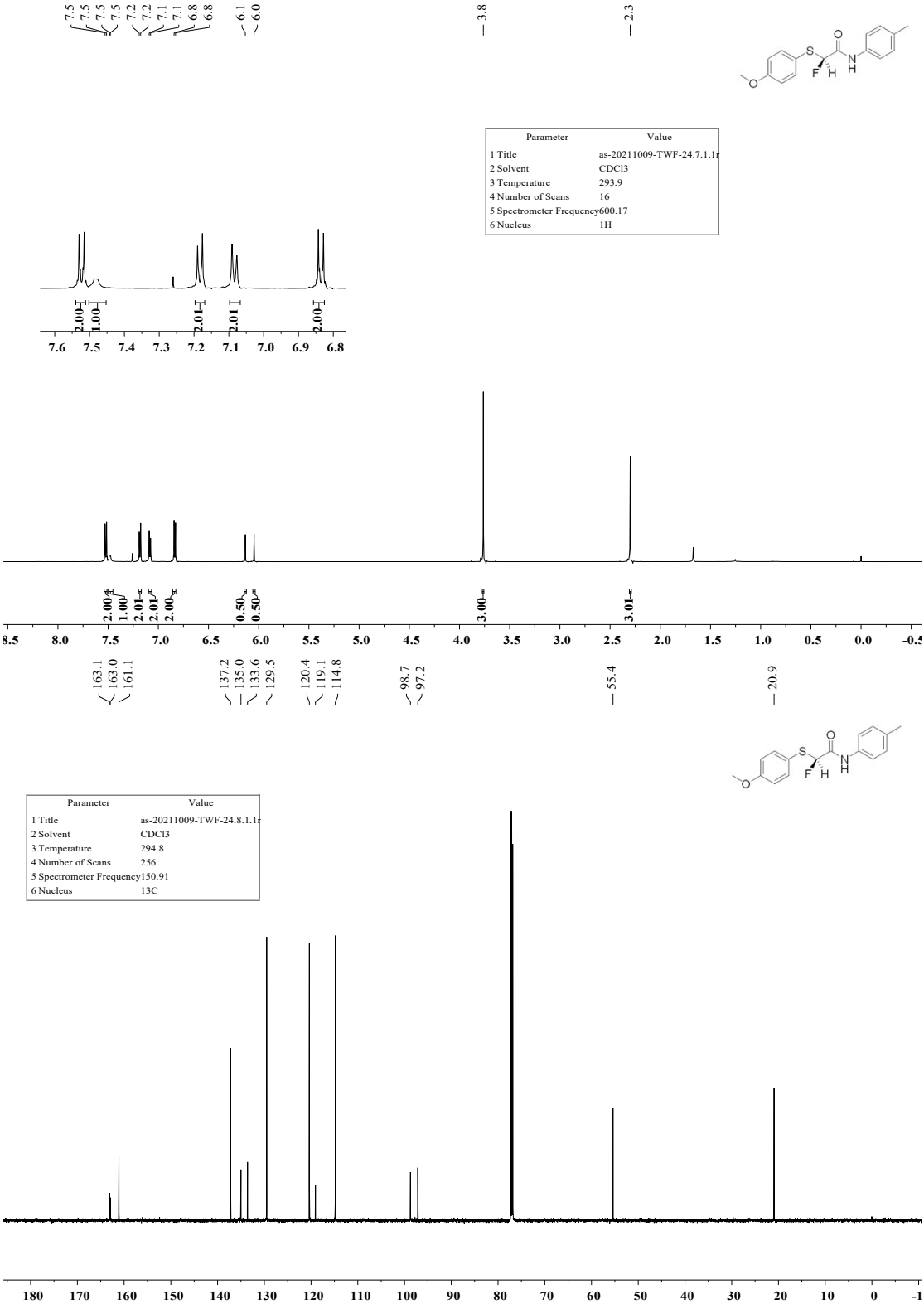


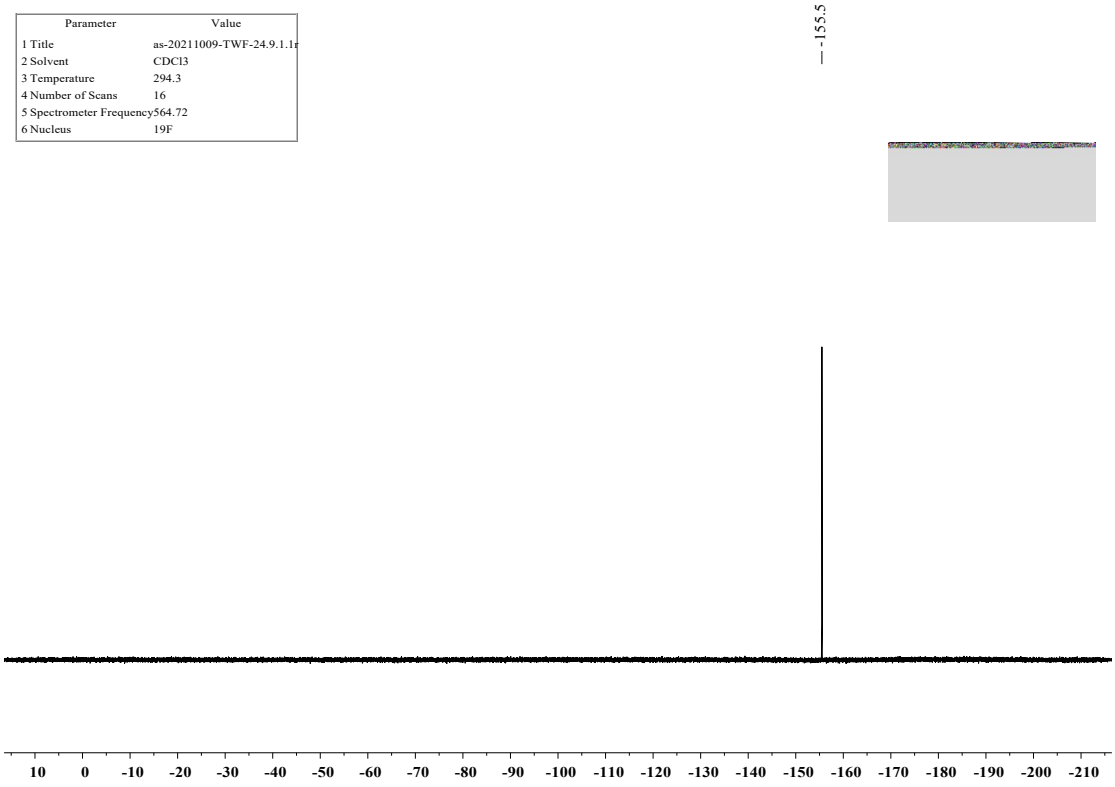
Parameter	Value
1 Title	as-20211002-TQF-15.7.1.1r
2 Solvent	CDCl3
3 Temperature	295.2
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H


189.4
189.2
161.6
161.5
161.2
138.3
135.2
133.6
132.1
132.1
131.9
131.8
131.8
129.8
129.6
120.2
117.0
114.9
108.3
105.9
55.4
20.9
Parameter Value
1 Title as-20211002-TQF-15.8.1.1r
2 Solvent CDCl3
3 Temperature 296.2
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

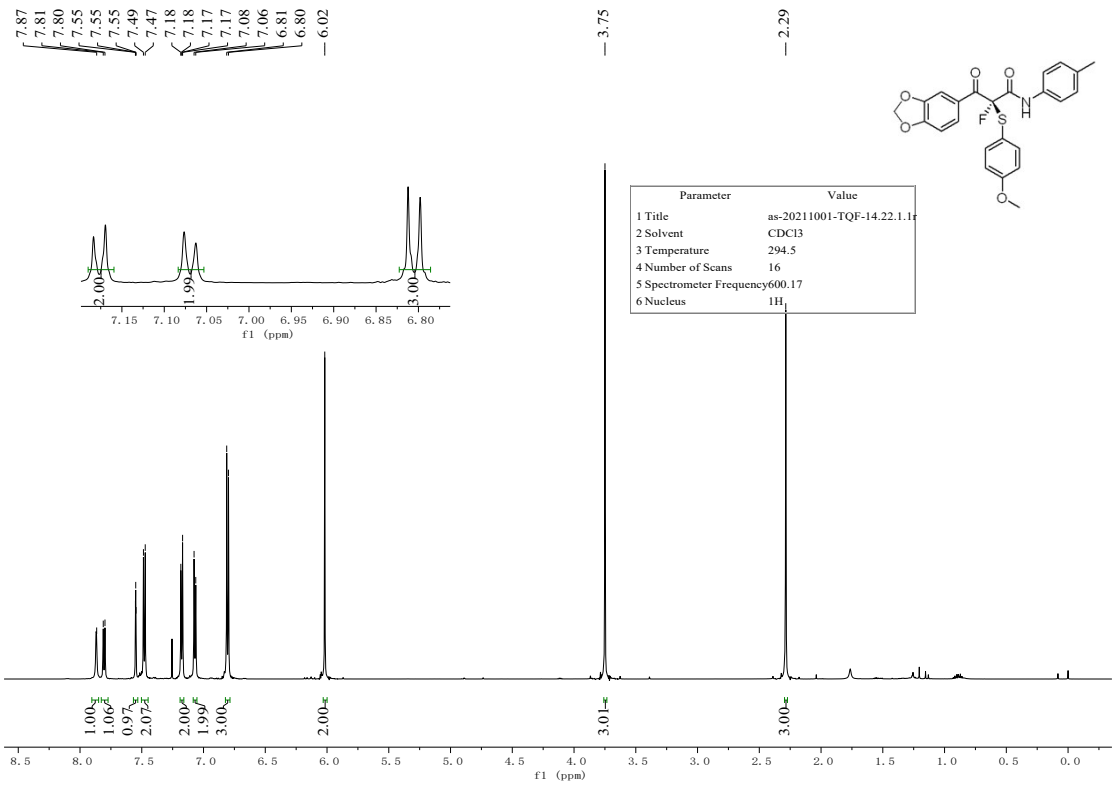

-129.5
Parameter Value
1 Title as-20211002-TQF-15.9.1.1r
2 Solvent CDCl3
3 Temperature 295.8
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
f1 (ppm)

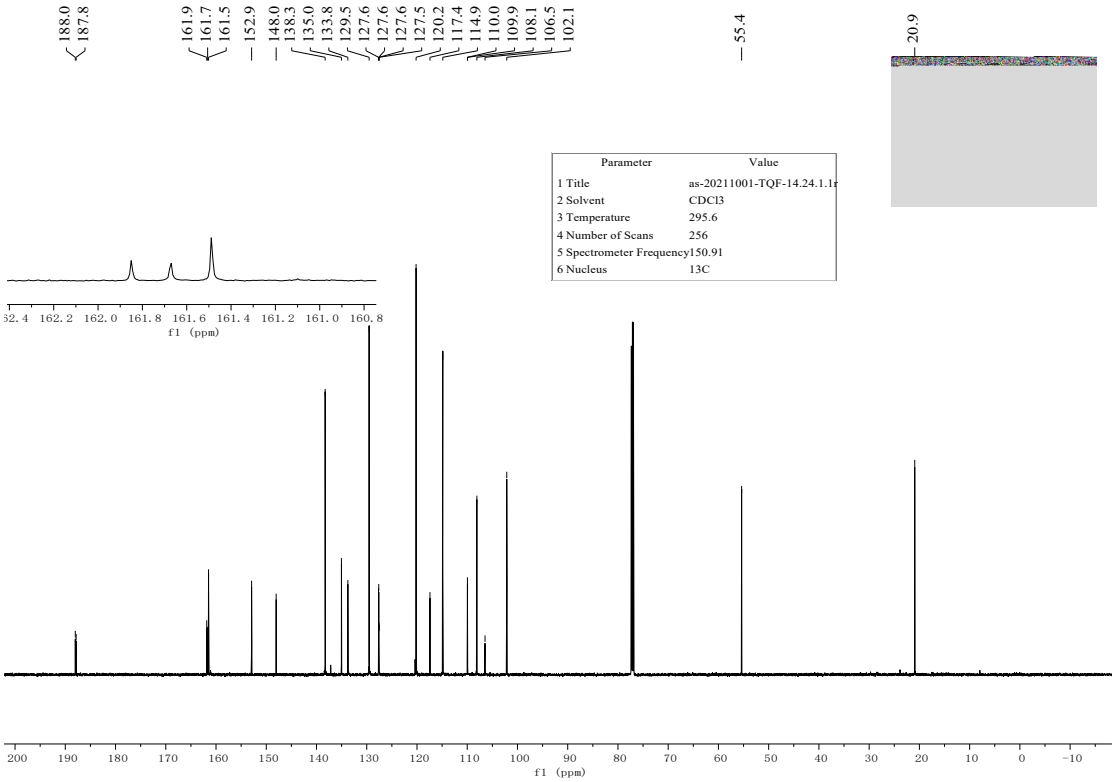
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-*N*-(*p*-tolyl)acetamide (4h):

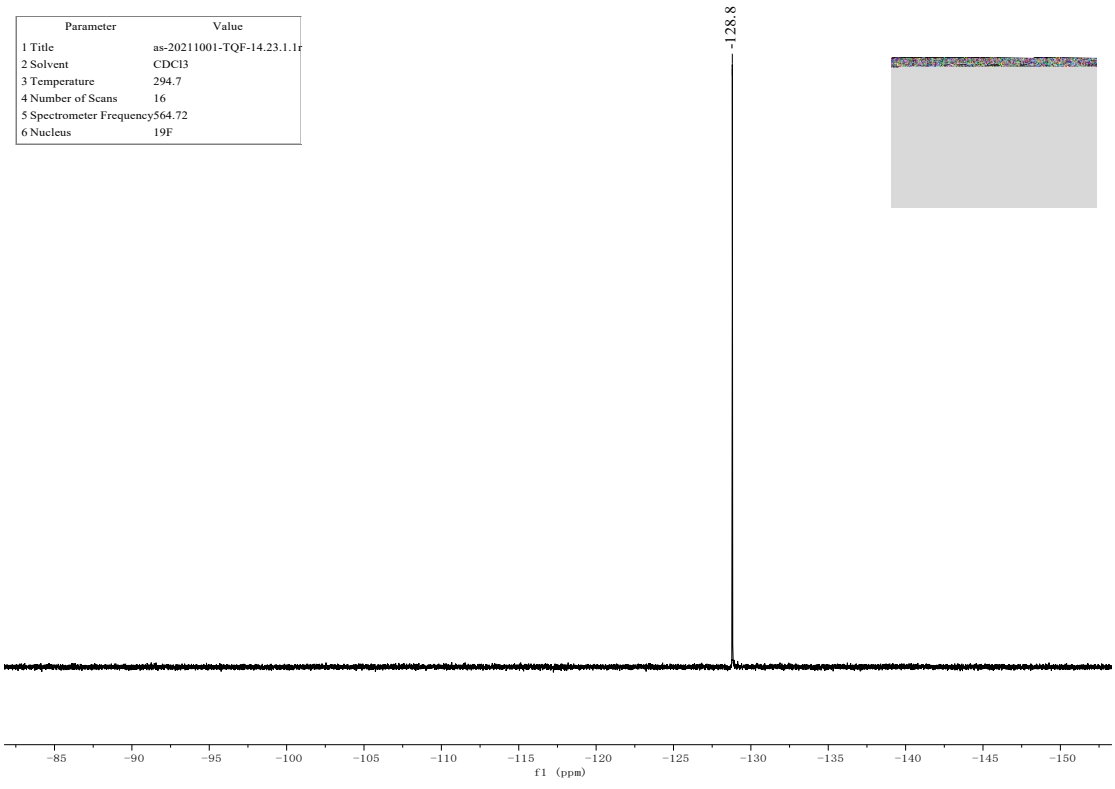




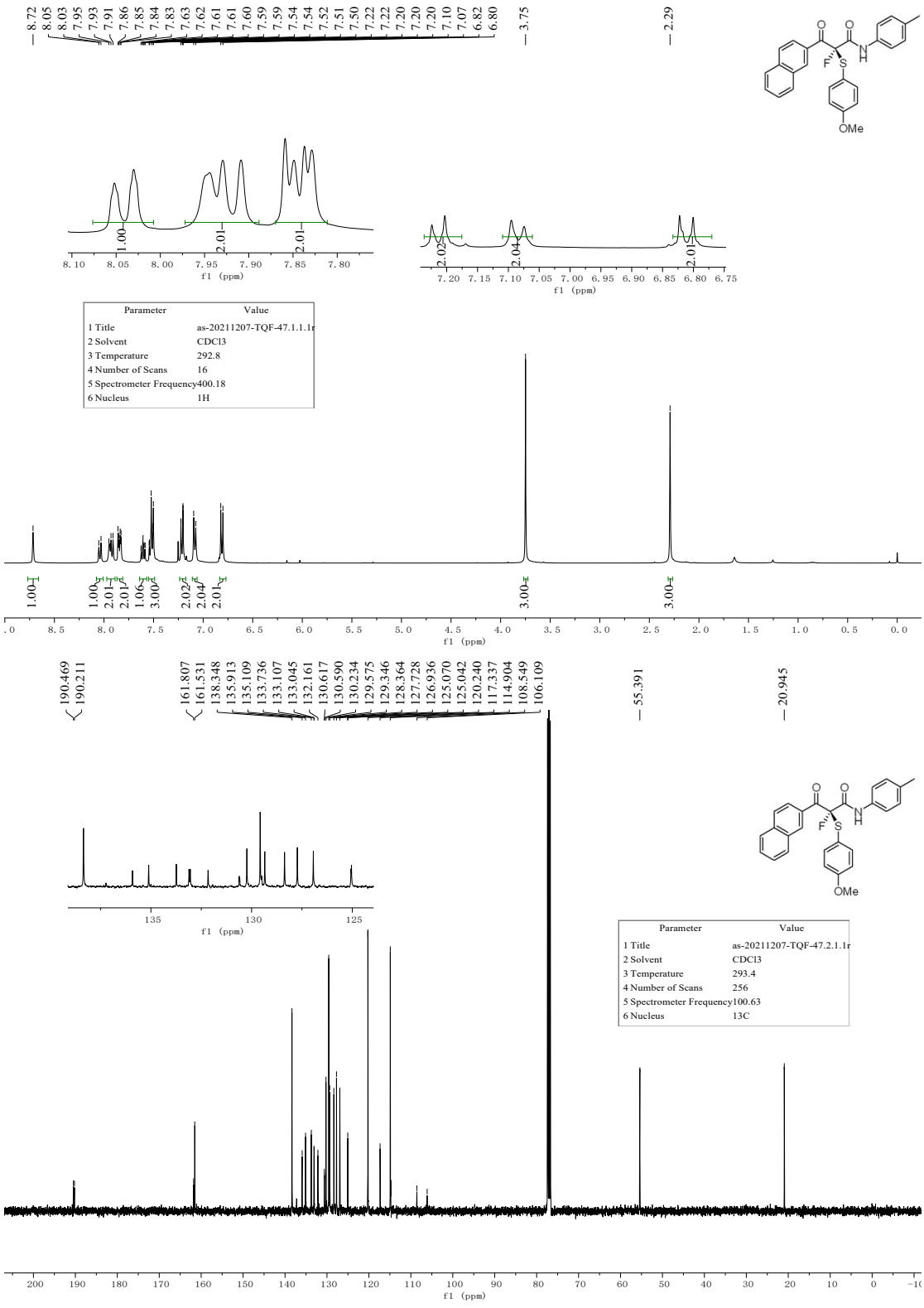
(*S*)-3-(benzo[d][1,3]dioxol-5-yl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4i):

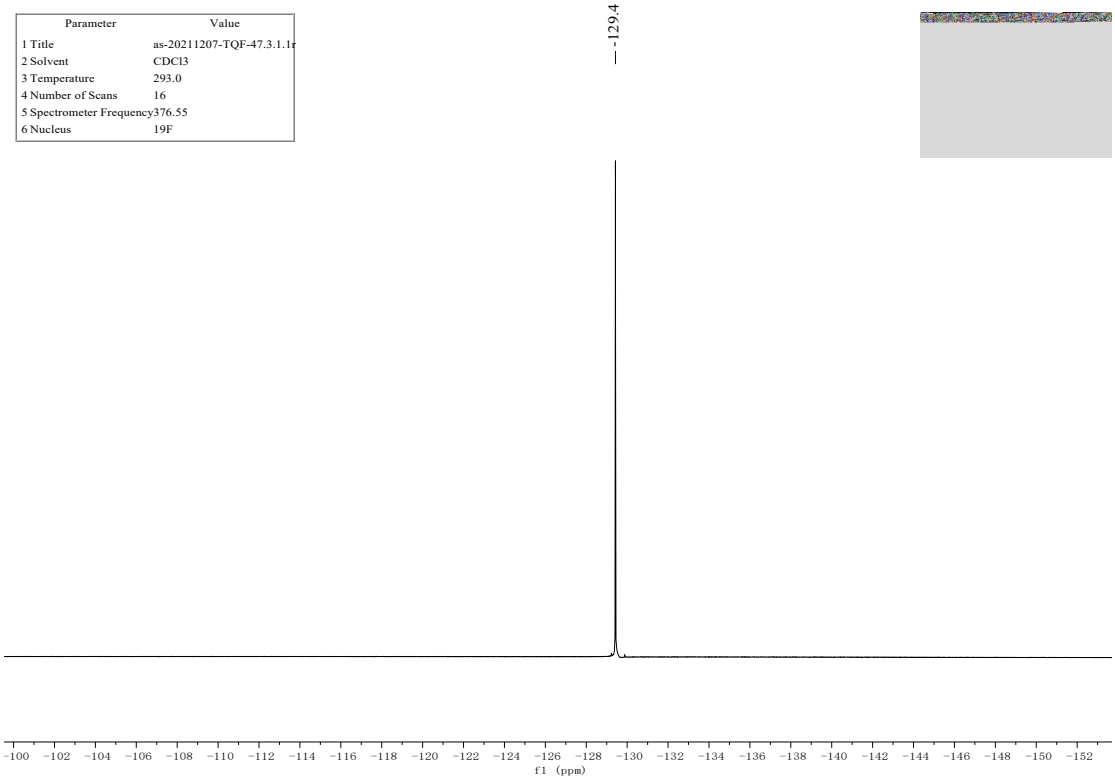




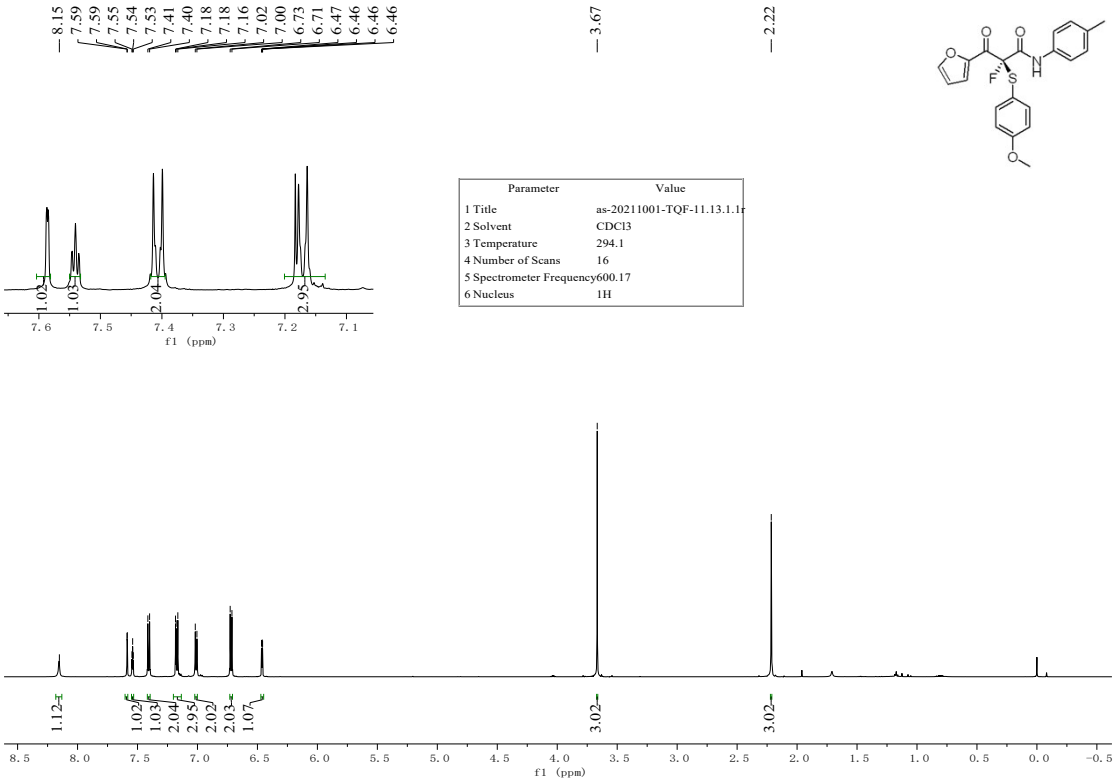


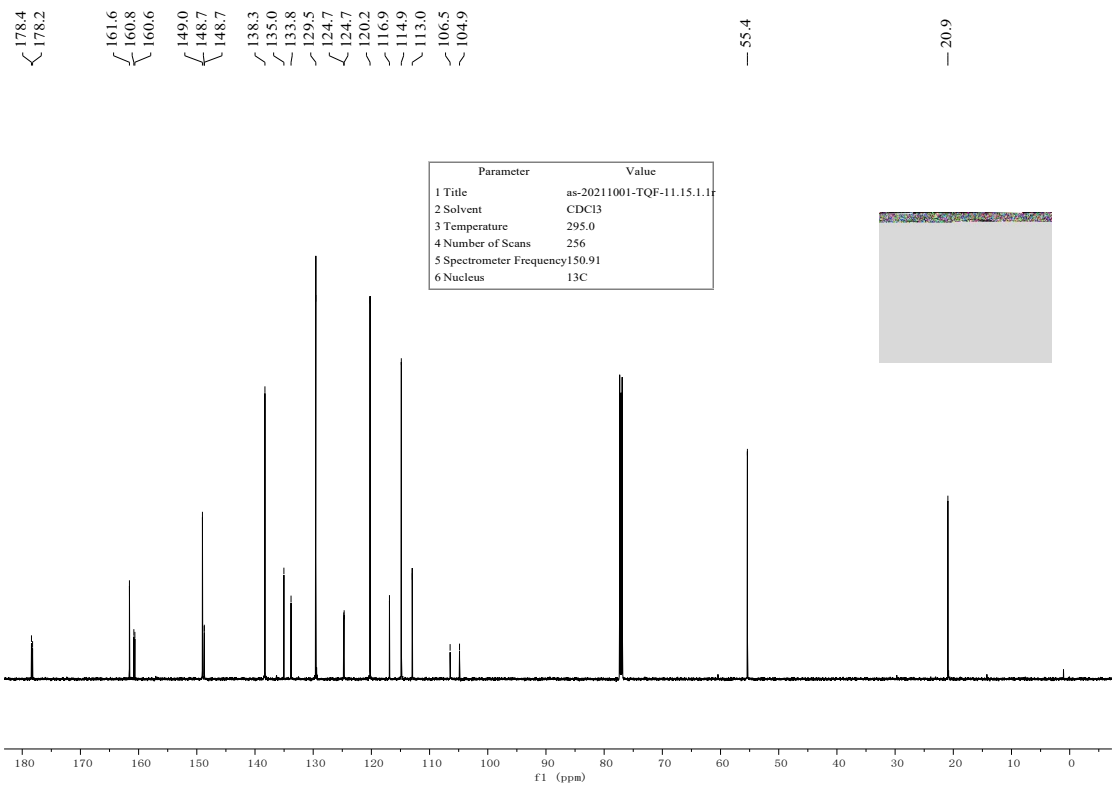
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-(naphthalen-2-yl)-3-oxo-*N*-(*p*-tolyl)propanamide (4j):

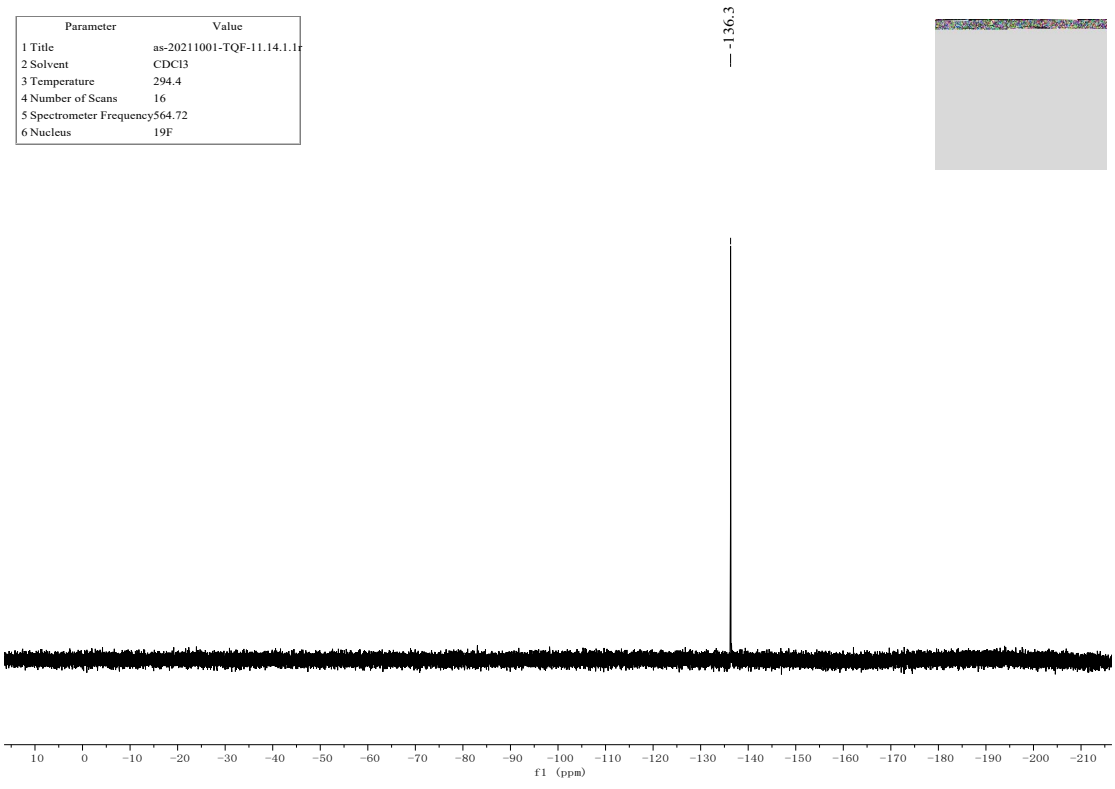

8.72 8.05 8.03 7.95 7.93 7.91 7.86 7.85 7.84 7.83 7.63 7.62 7.61 7.61 7.60 7.59 7.59 7.54 7.54 7.52 7.51 7.50 7.22 7.20 7.20 7.20 7.10 7.07 6.82 6.80
3.75
2.29
OMe
1.00 2.01 2.01
8.10 8.05 8.00 7.95 7.90 7.85 7.80
f1 (ppm)
2.02 2.04 2.01
7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)
Parameter Value
1 Title as-20211207-TQF-47.1.1.1r
2 Solvent CDCl3
3 Temperature 292.8
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
1.00 1.00 2.01 2.01 1.06 3.00 2.02 2.04 2.01 3.00 3.00
f1 (ppm)
190.469 190.211
161.807 161.531 138.348 135.913 135.109 133.736 133.107 133.045 132.161 130.617 130.590 130.234 129.575 129.346 128.364 127.728 126.936 125.070 125.042 120.240 117.337 114.904 108.549 106.109
55.391
20.945
OMe
135 130 125
f1 (ppm)
Parameter Value
1 Title as-20211207-TQF-47.2.1.1r
2 Solvent CDCl3
3 Temperature 293.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)



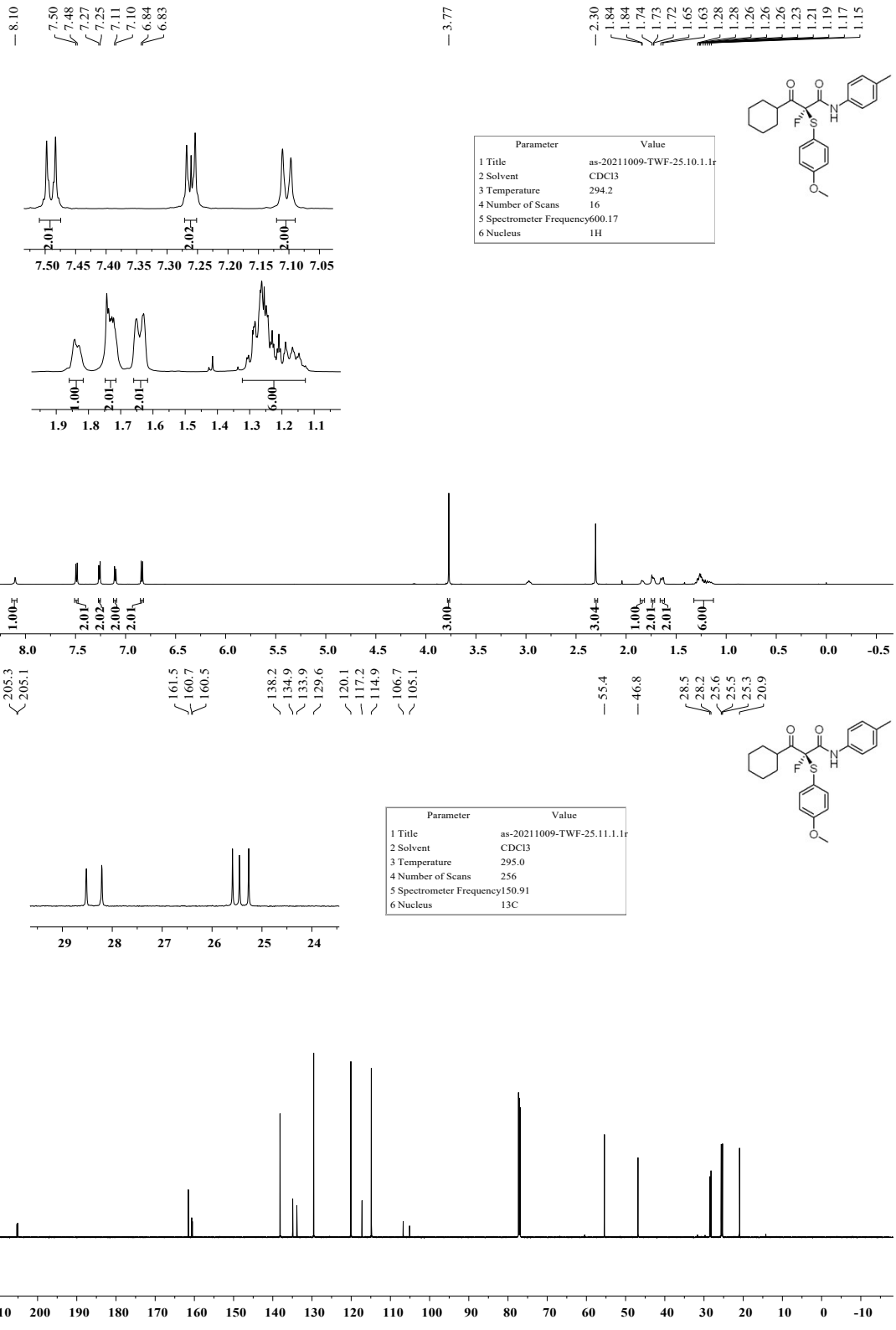
(*S*)-2-fluoro-3-(furan-2-yl)-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4k):

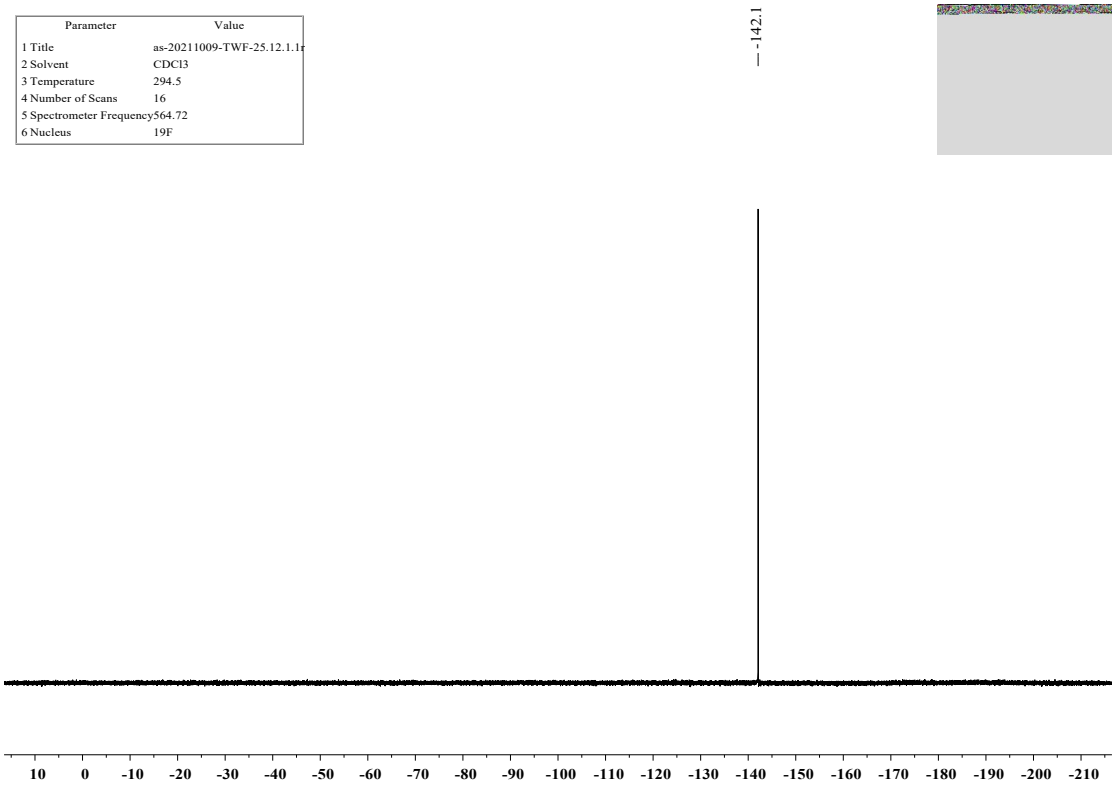




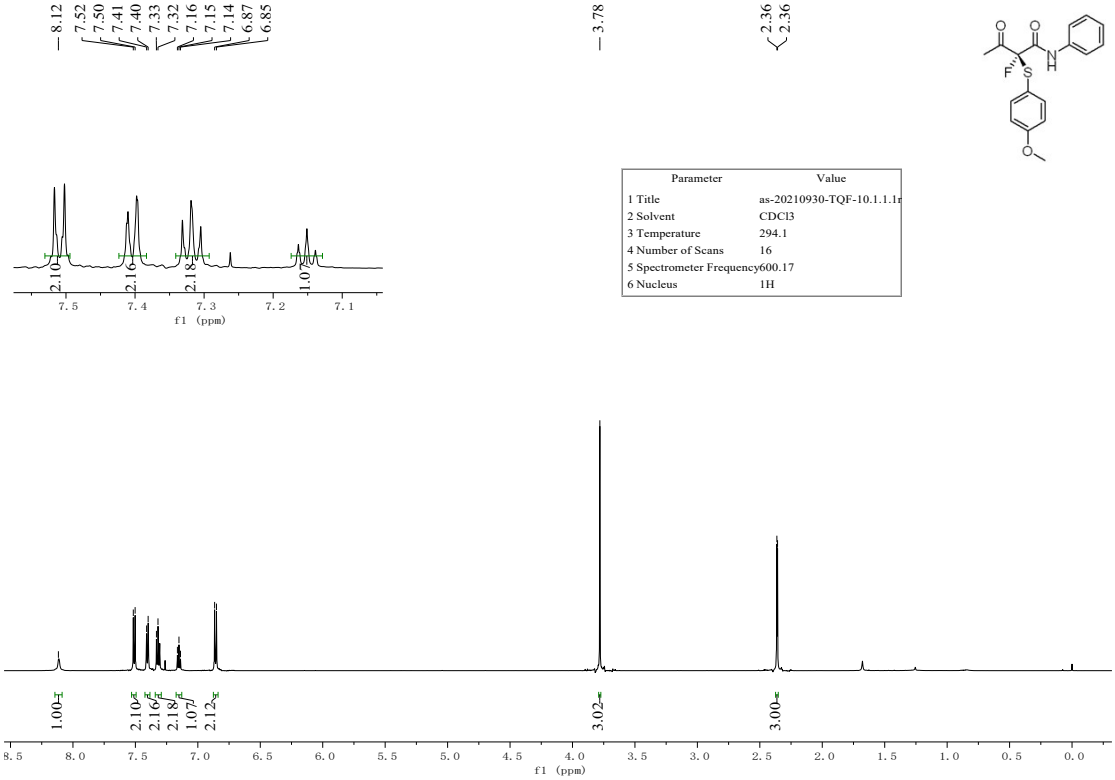


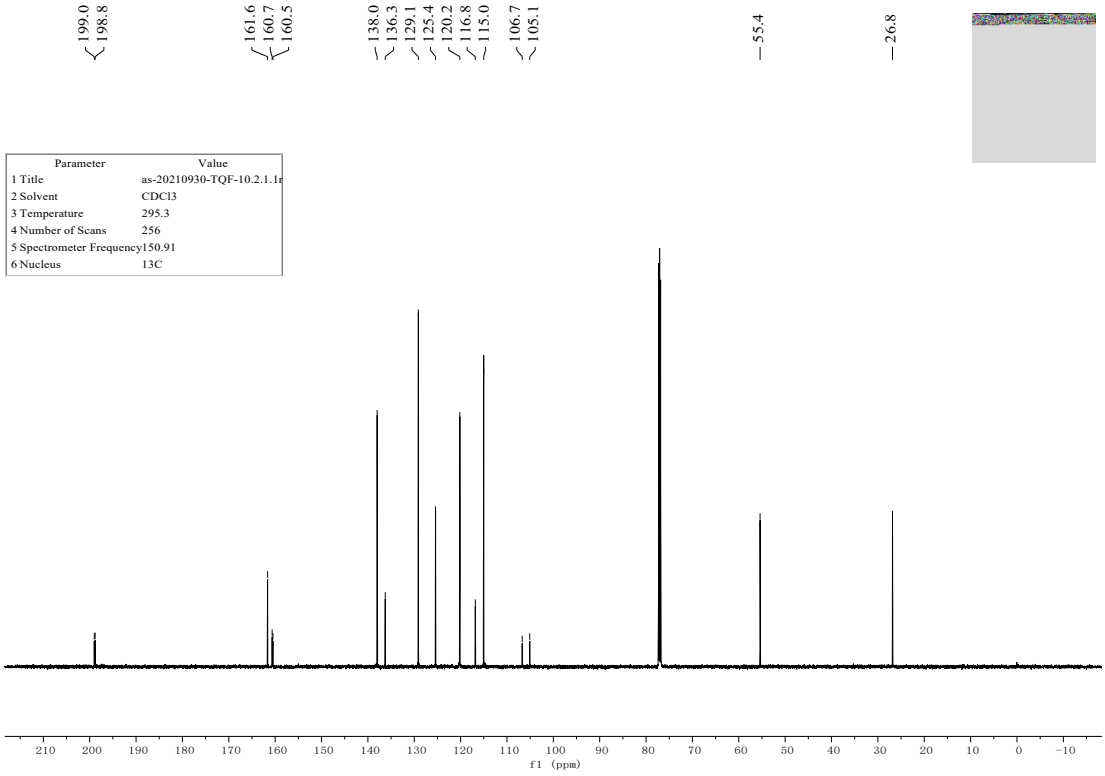
(*S*)-3-cyclohexyl-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-(*p*-tolyl)propanamide (4l):

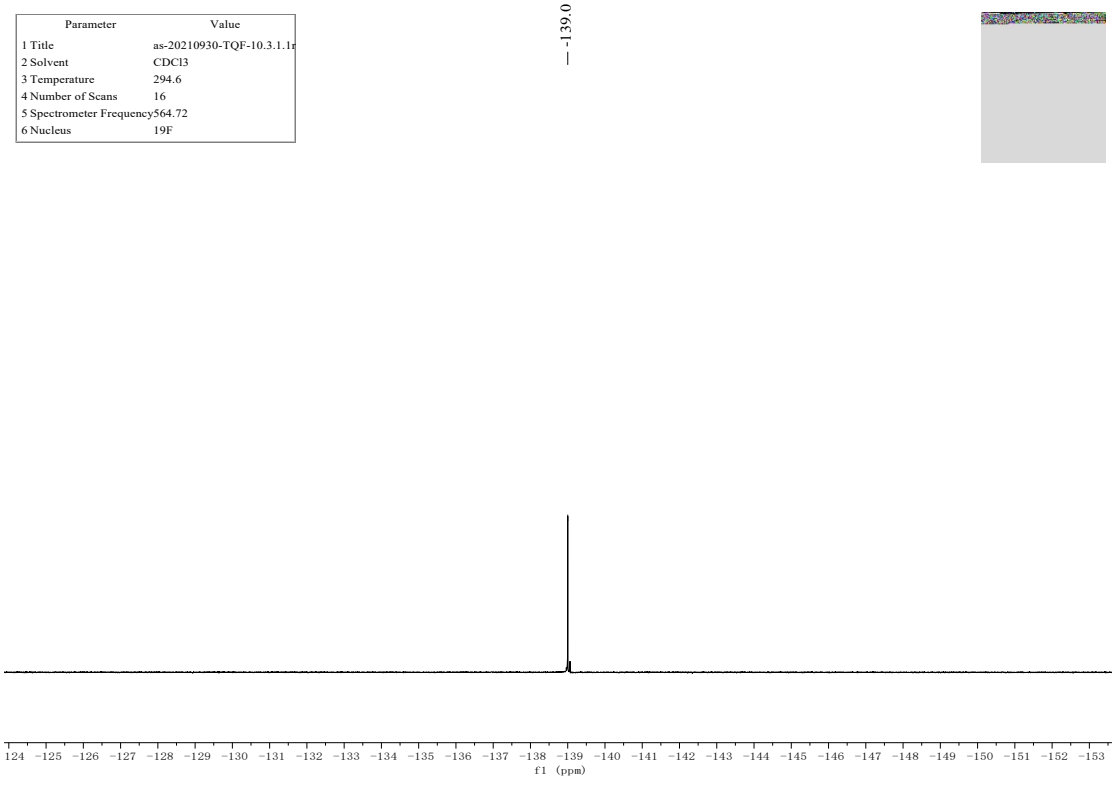

8.10
7.50
7.48
7.27
7.25
7.11
7.10
6.84
6.83
3.77
2.30
1.84
1.84
1.74
1.73
1.72
1.65
1.63
1.28
1.28
1.26
1.26
1.26
1.23
1.21
1.19
1.17
1.15
Parameter Value
1 Title as-20211009-TWF-25.10.1.1r
2 Solvent CDCl3
3 Temperature 294.2
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
205.3
205.1
161.5
160.7
160.5
138.2
134.9
133.9
129.6
120.1
117.2
114.9
106.7
105.1
55.4
46.8
28.5
28.2
25.6
25.5
25.3
20.9
Parameter Value
1 Title as-20211009-TWF-25.11.1.1r
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C



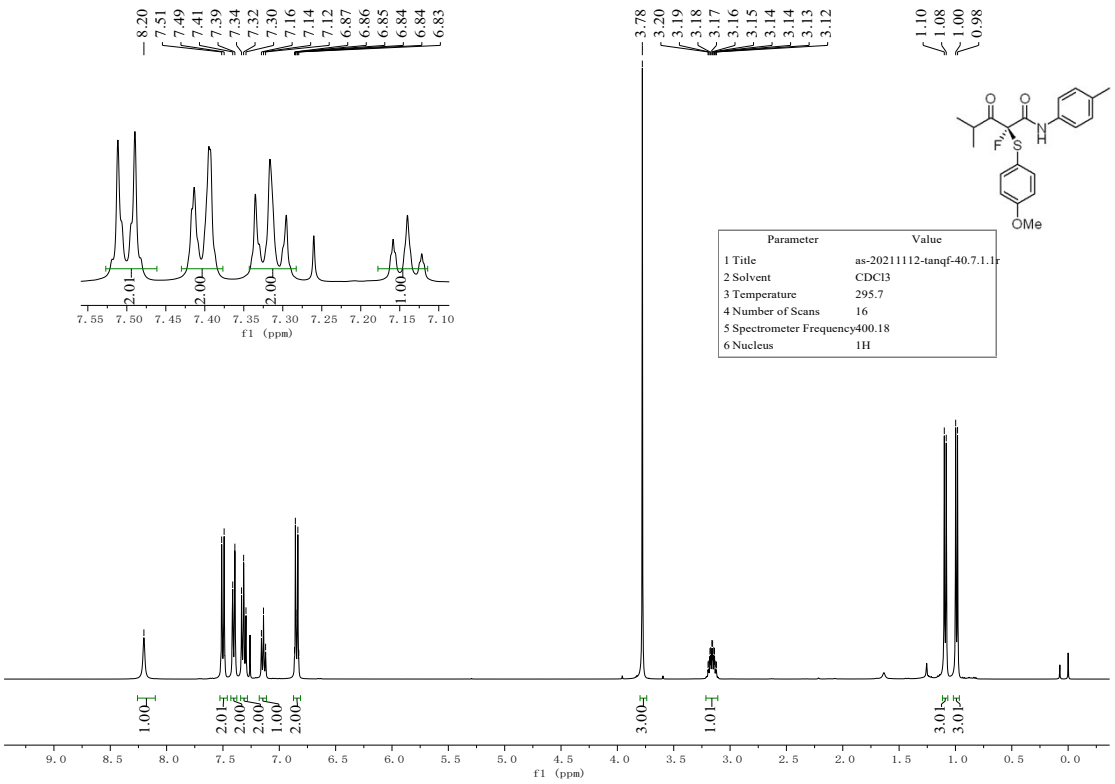
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*-phenylbutanamide (4m):

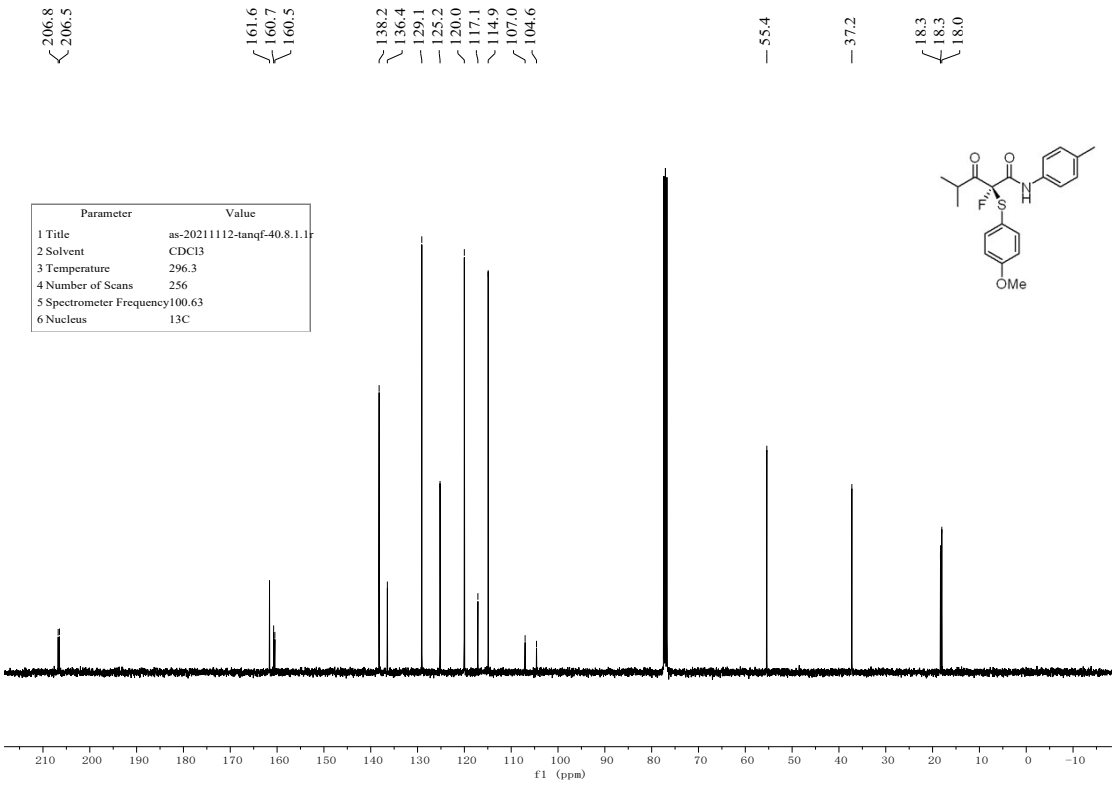




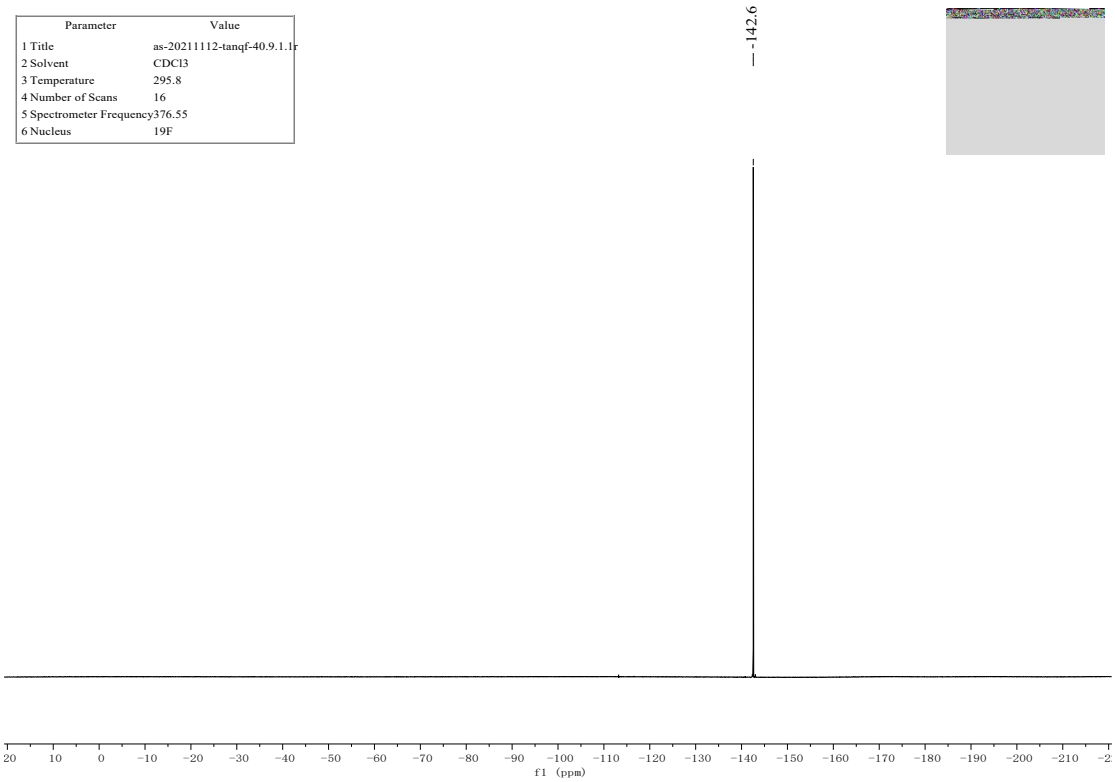


(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-4-methyl-3-oxo-*N*-phenylpentanamide (4n):

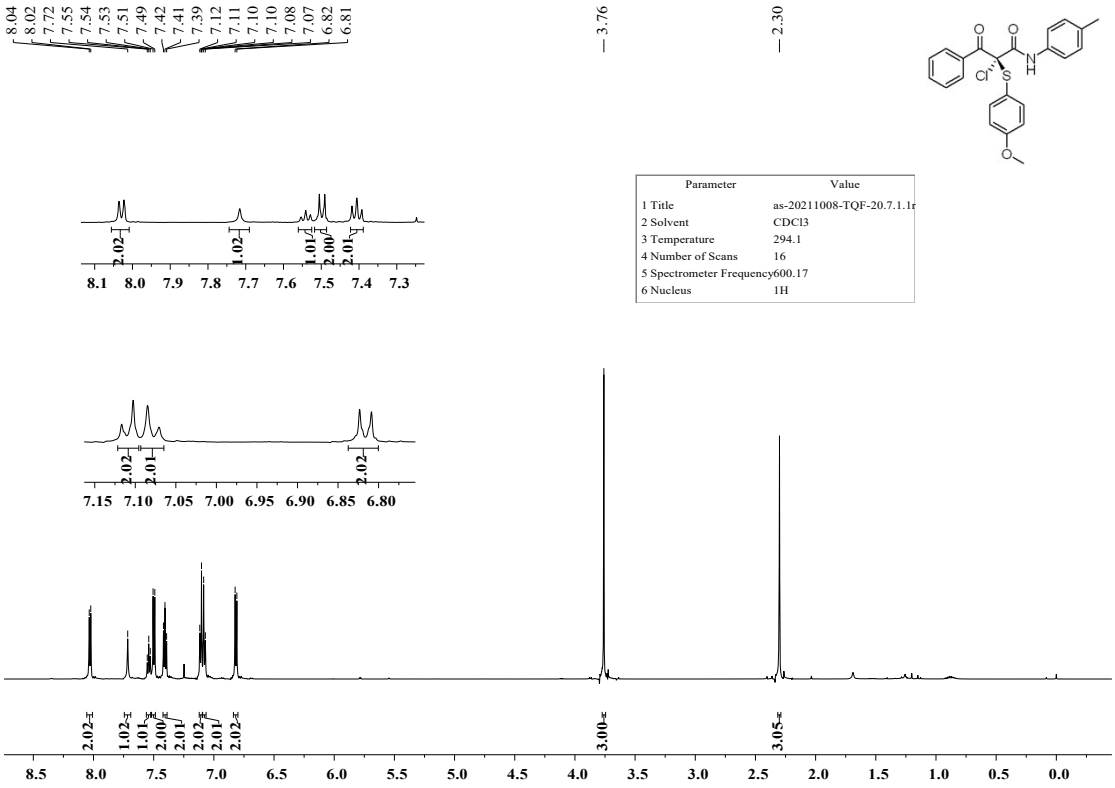

8.20
7.51
7.49
7.41
7.39
7.34
7.32
7.30
7.16
7.14
7.12
6.87
6.86
6.85
6.84
6.84
6.83
3.78
3.20
3.19
3.18
3.17
3.16
3.15
3.14
3.14
3.13
3.12
1.10
1.08
1.00
0.98
2.01
2.00
2.00
1.00
f1 (ppm)
OMe
Parameter Value
1 Title as-20211112-tanqf-40.7.1.1r
2 Solvent CDCl3
3 Temperature 295.7
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
1.00
2.01
2.00
2.00
1.00
2.00
3.00
1.01
3.01
3.01
f1 (ppm)


206.8
206.5
161.6
160.7
160.5
138.2
136.4
129.1
125.2
120.0
117.1
114.9
107.0
104.6
55.4
37.2
18.3
18.3
18.0
OMe
Parameter Value
1 Title as-20211112-tanqf-40.8.1.1r
2 Solvent CDCl3
3 Temperature 296.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)

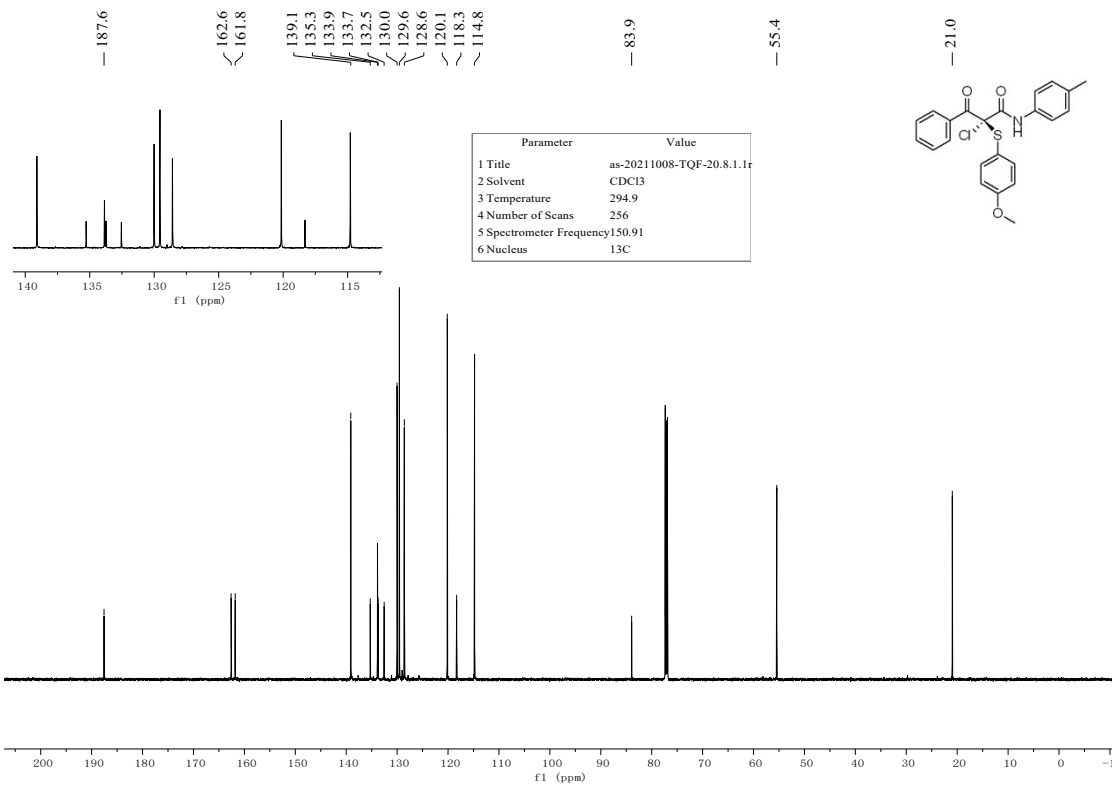
Parameter	Value
1 Title	as-20211112-tanqf-40.9.1.1r
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



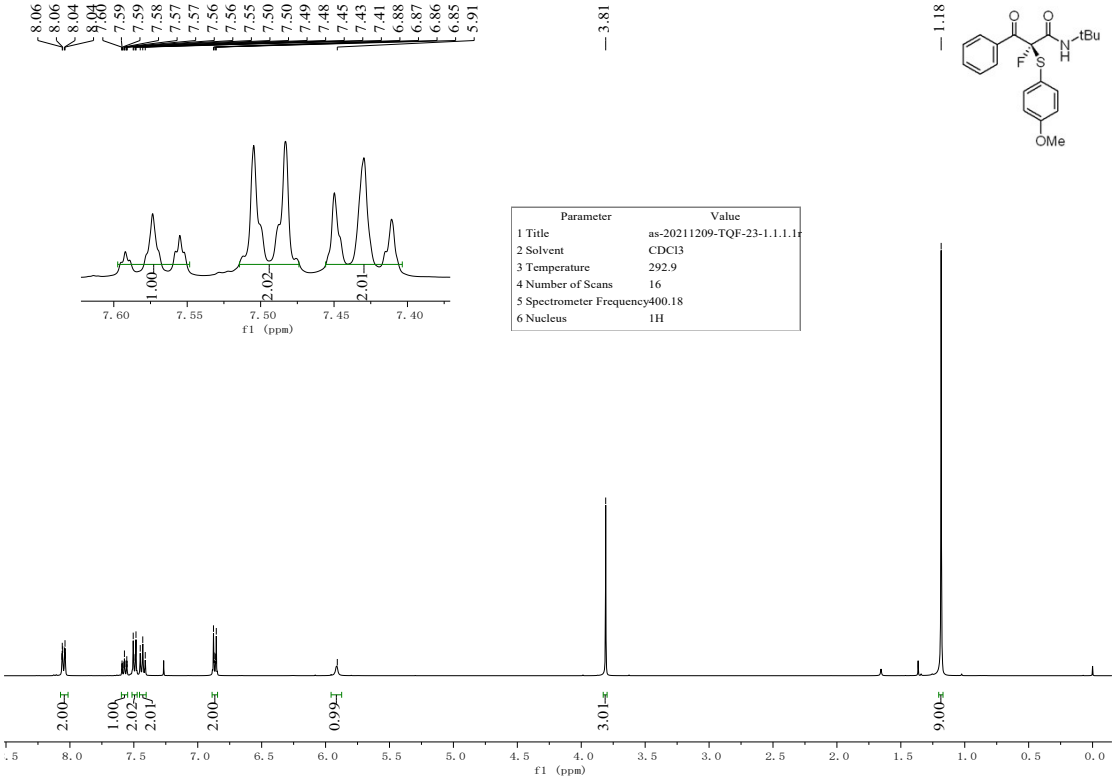
(*R*)-2-chloro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanamide (4o):

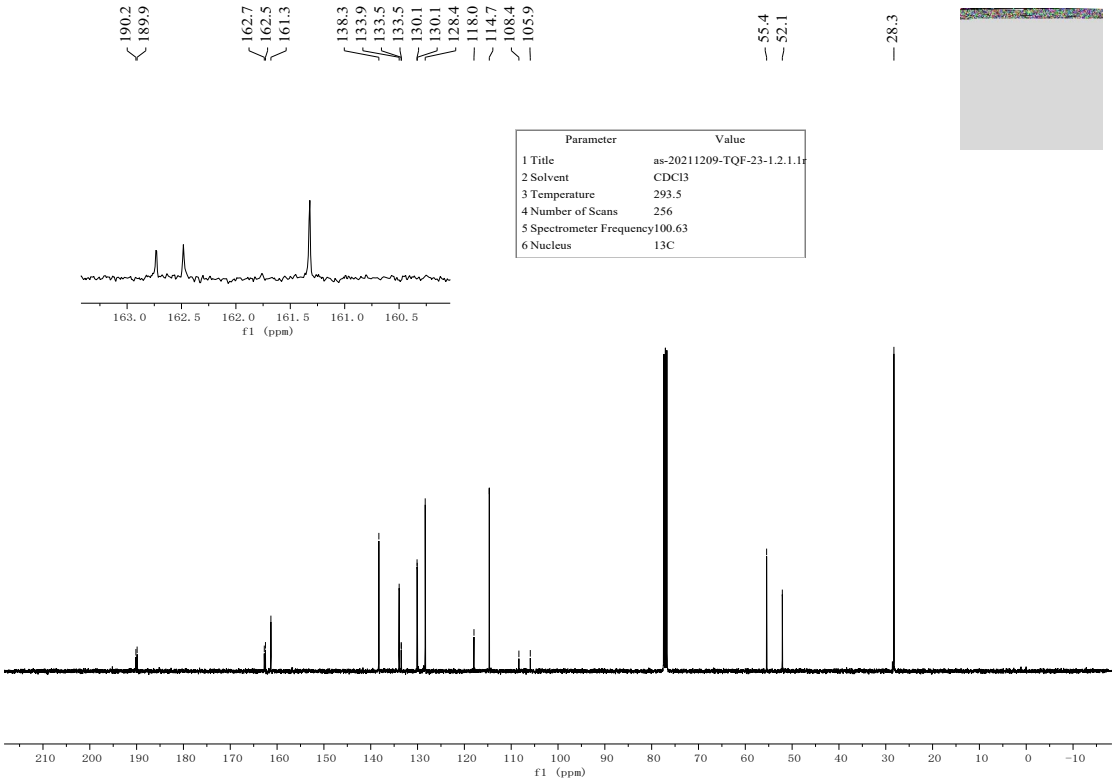


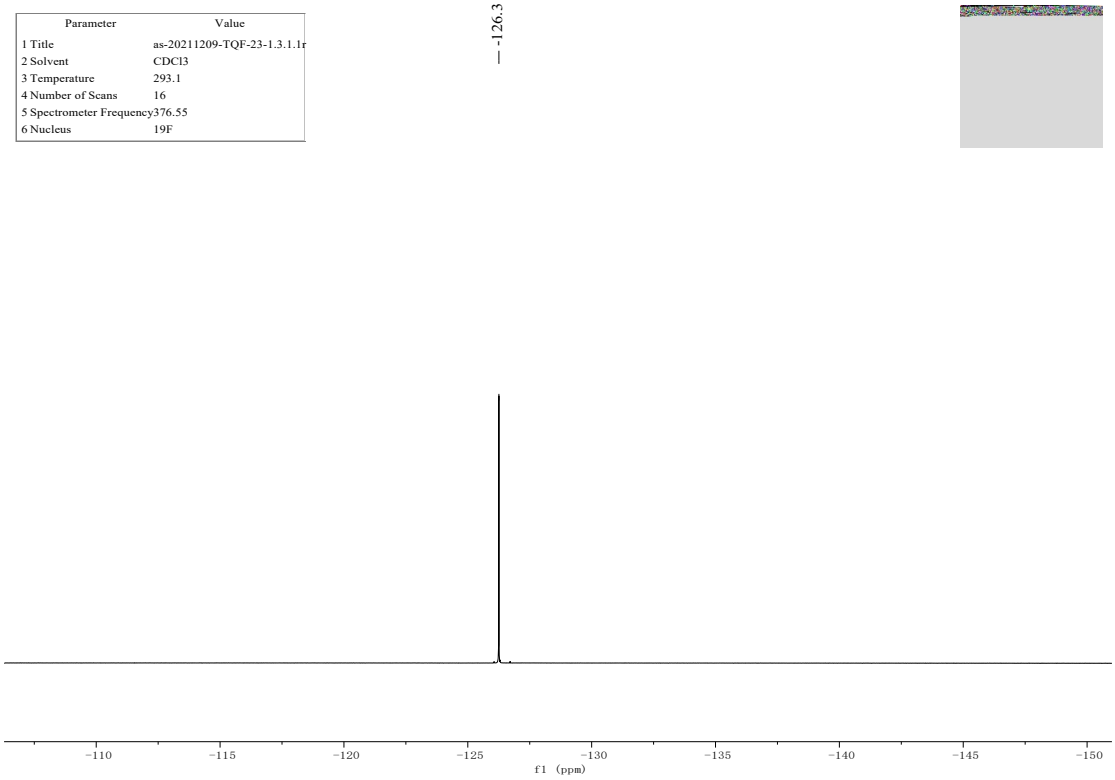
Parameter	Value
1 Title	as-20211008-TQF-20.7.1.1r
2 Solvent	CDCl3
3 Temperature	294.1
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H



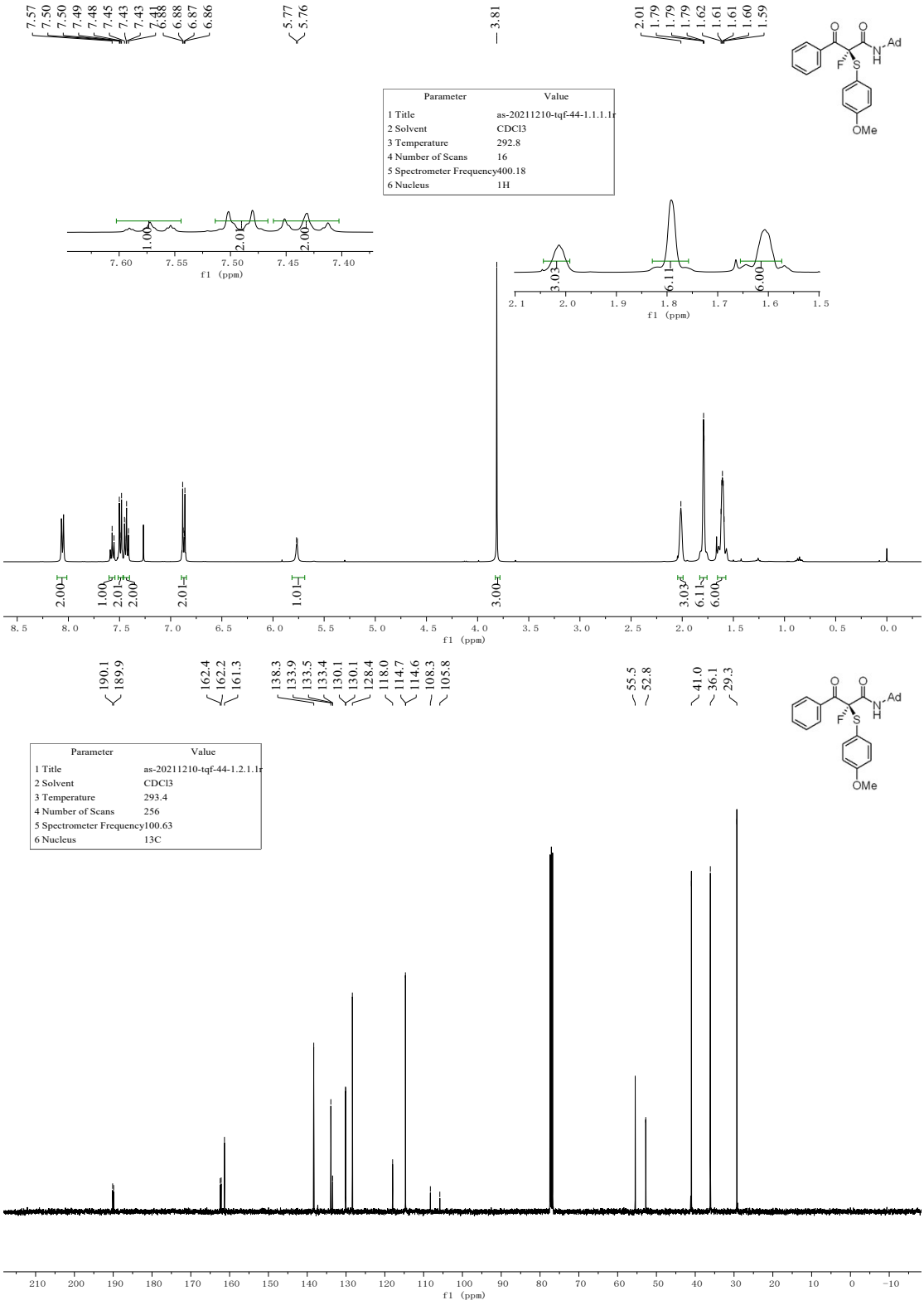
(*S*)-*N*-(tert-butyl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4p):



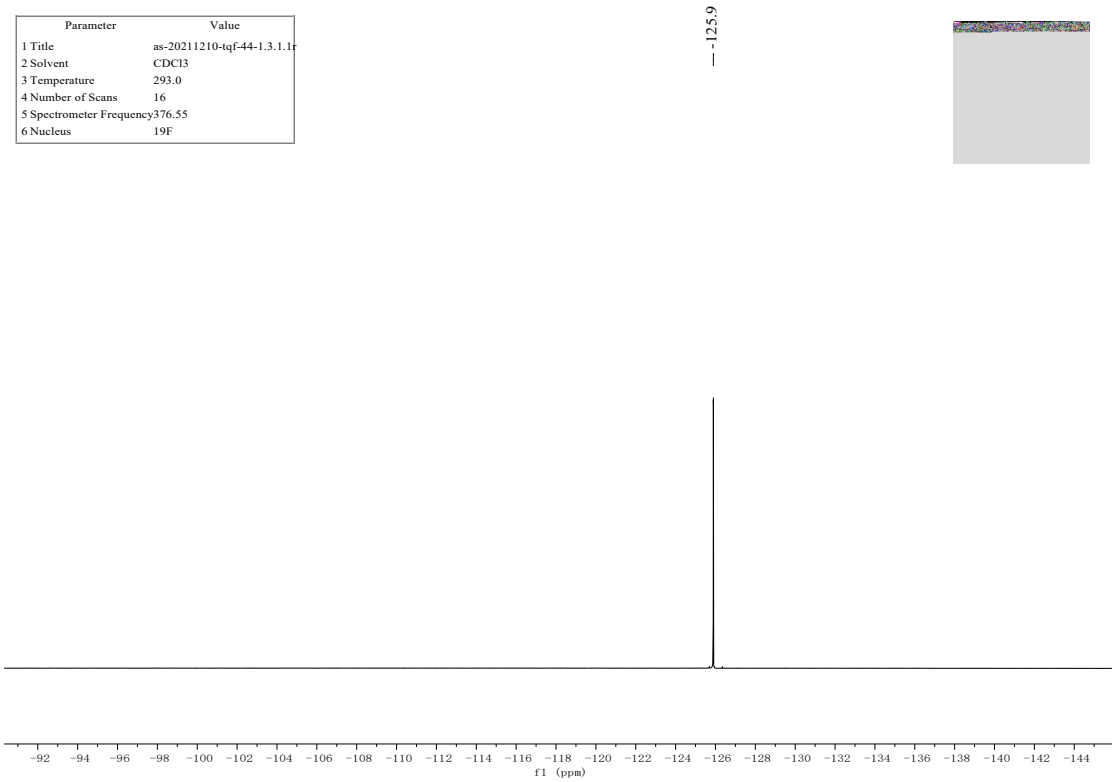

190.2
189.9
162.7
162.5
161.3
138.3
133.9
133.5
133.5
130.1
130.1
128.4
118.0
114.7
108.4
105.9
55.4
52.1
28.3
Parameter Value
1 Title as-20211209-TQF-23-1.2.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
163.0 162.5 162.0 161.5 161.0 160.5
f1 (ppm)
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)


Parameter Value
1 Title as-20211209-TQF-23-1.3.1.1r
2 Solvent CDCl3
3 Temperature 293.1
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
-126.3
-110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

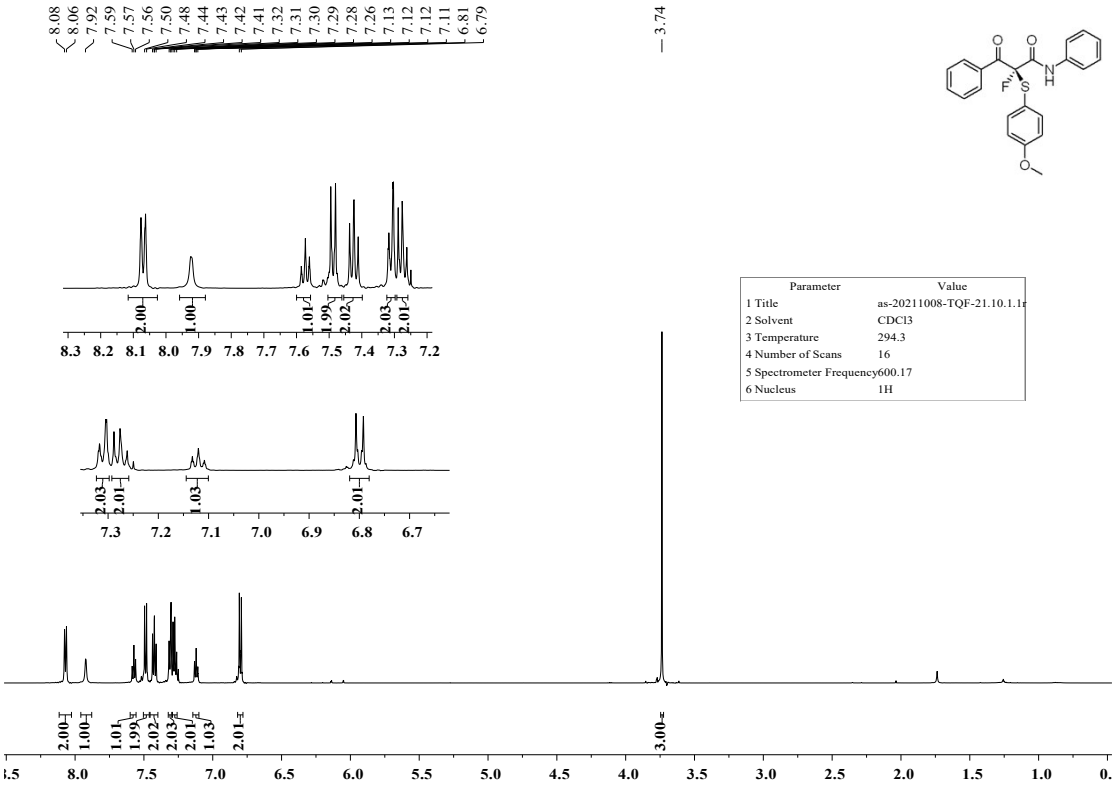
(*S*)-*N*-((3*R*,5*R*,7*R*)-adamantan-1-yl)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4q):



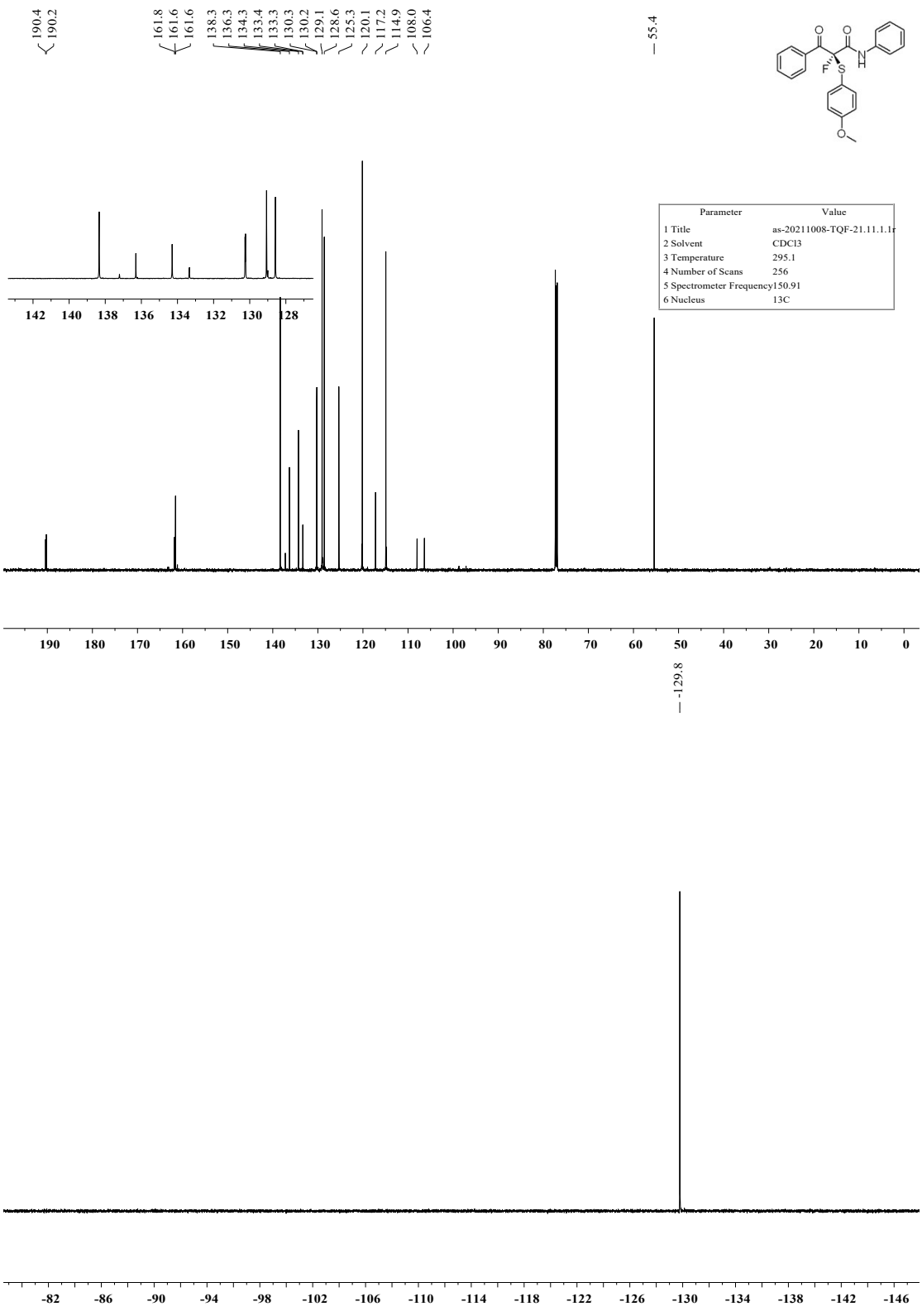
Parameter	Value
1 Title	as-20211210-tqf-44-1.3.1.1r
2 Solvent	CDCl3
3 Temperature	293.0
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F



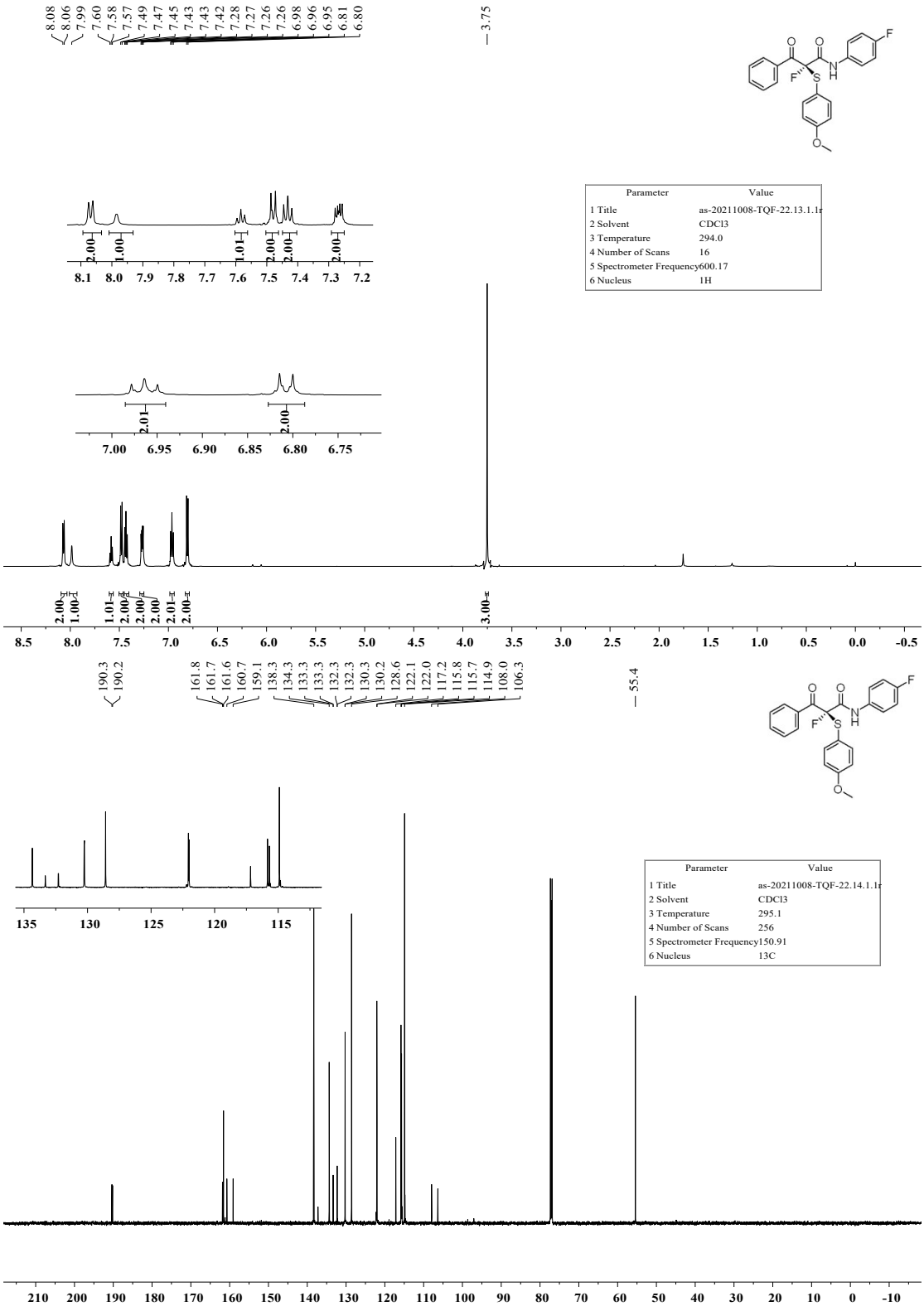
(*S*)-2-fluoro-2-((4-methoxyphenyl)thio)-3-oxo-*N*,3-diphenylpropanamide (4r):

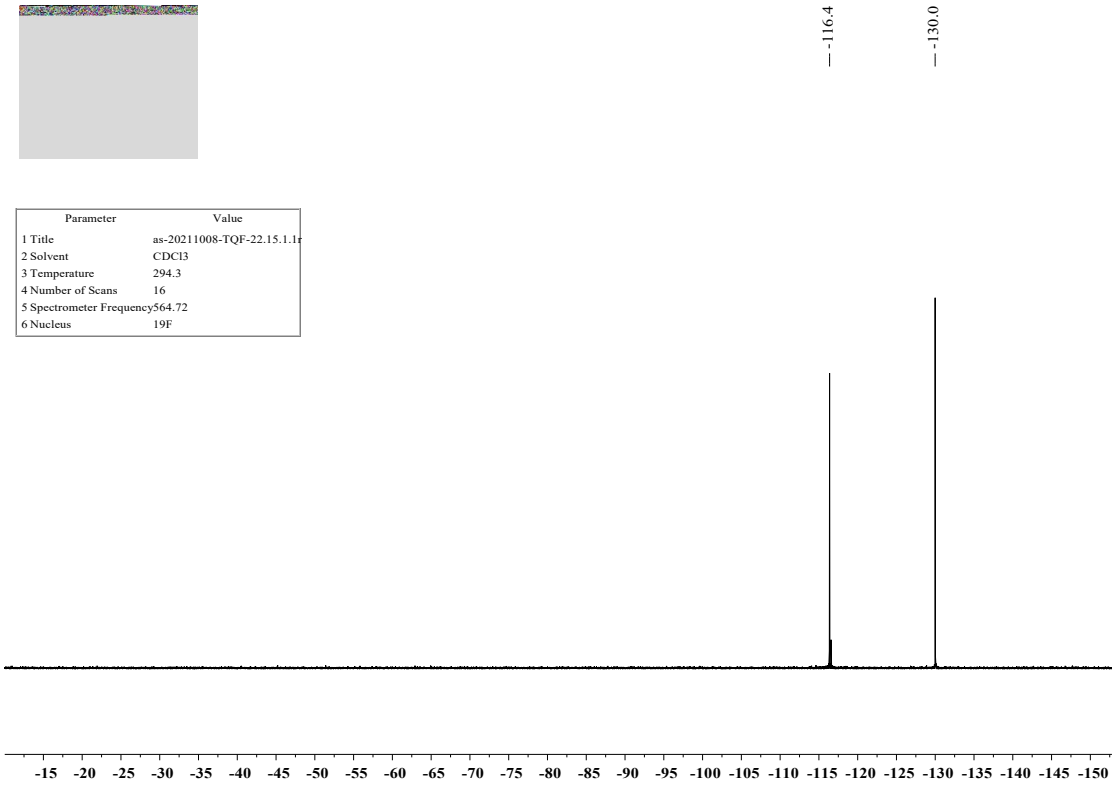


Parameter	Value
1 Title	as-20211008-TQF-21.10.1.1r
2 Solvent	CDCl3
3 Temperature	294.3
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

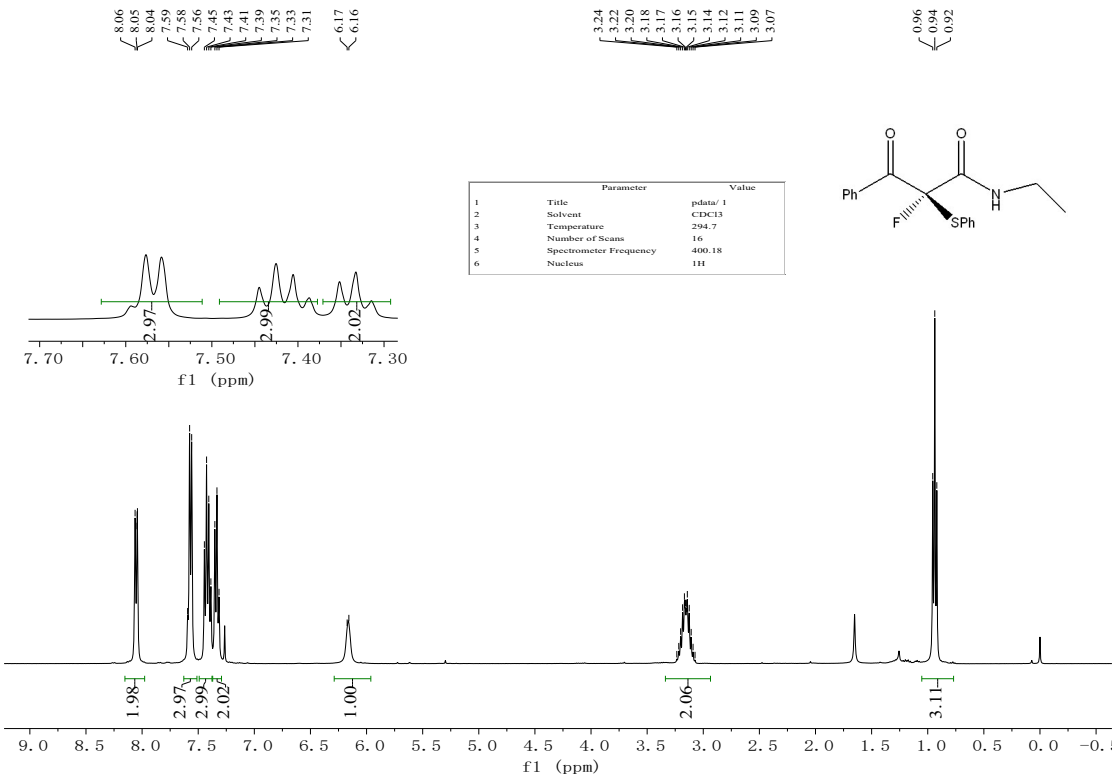

190.4
190.2
161.8
161.6
161.6
138.3
136.3
134.3
133.4
133.3
130.3
130.2
129.1
128.6
125.3
120.1
117.2
114.9
108.0
106.4
55.4
Parameter Value
1 Title as-20211008-TQF-21.11.1.1r
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
142 140 138 136 134 132 130 128
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-129.8
-82 -86 -90 -94 -98 -102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146

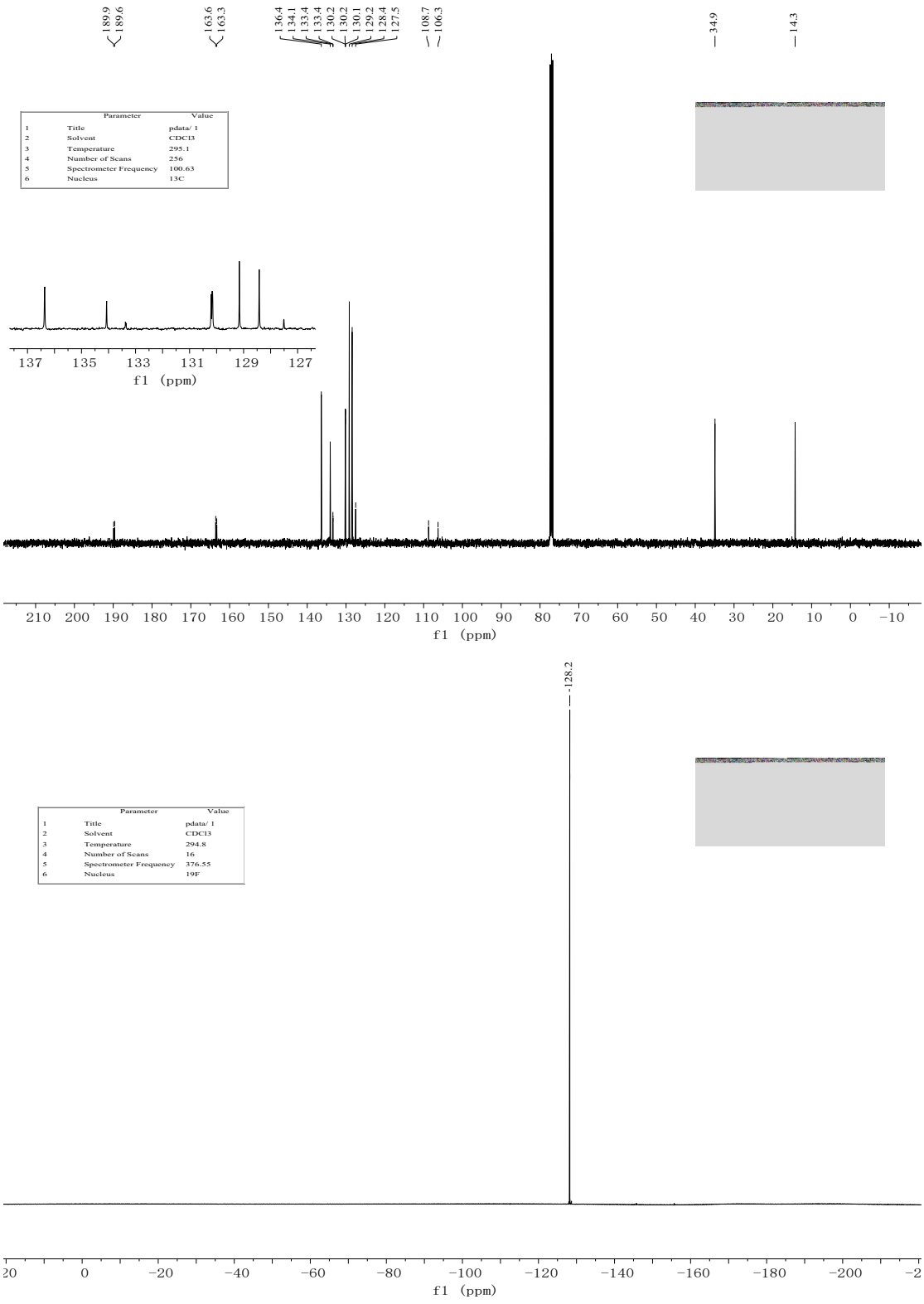
(*S*)-2-fluoro-*N*-(4-fluorophenyl)-2-((4-methoxyphenyl)thio)-3-oxo-3-phenylpropanamide (4s):



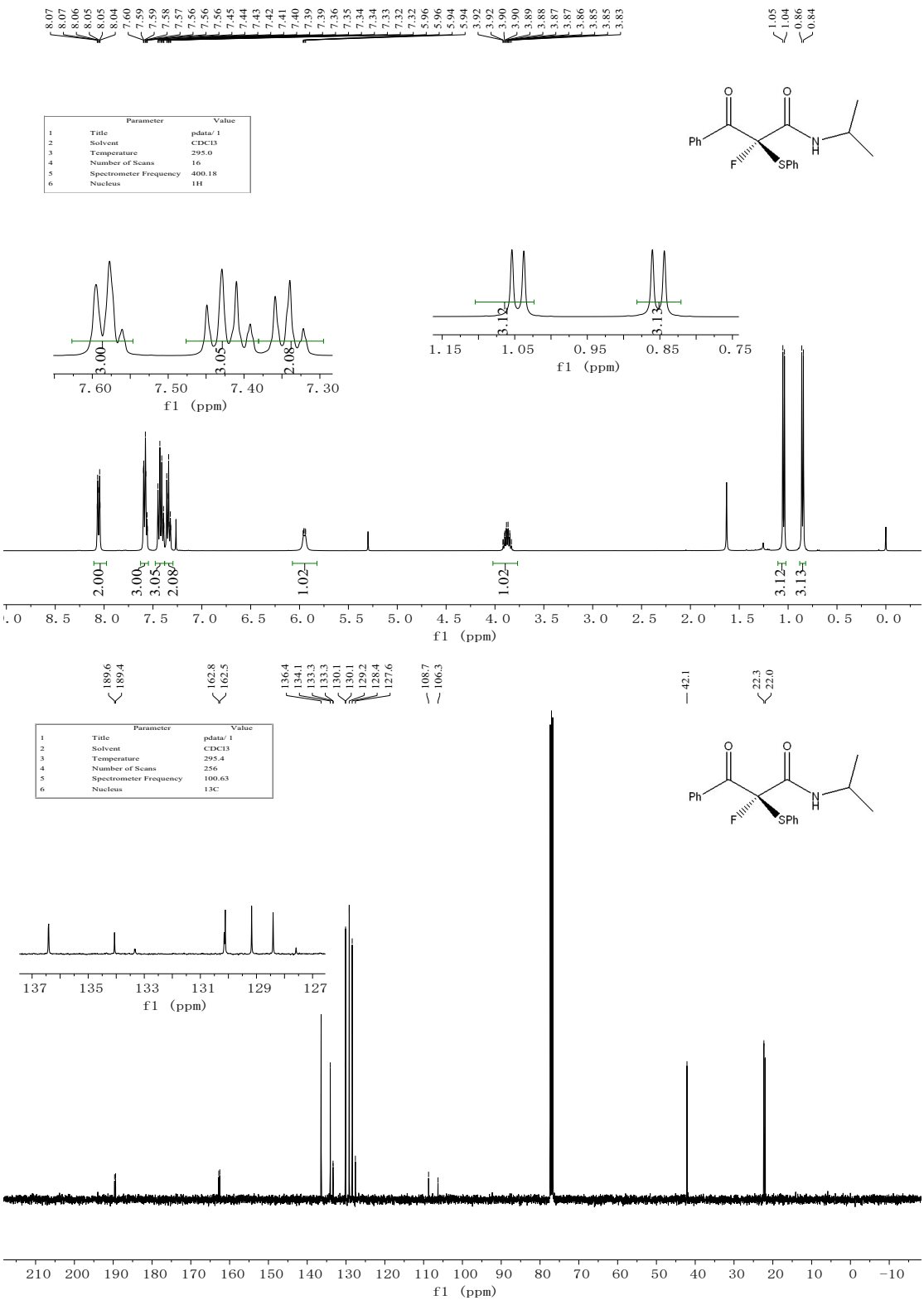


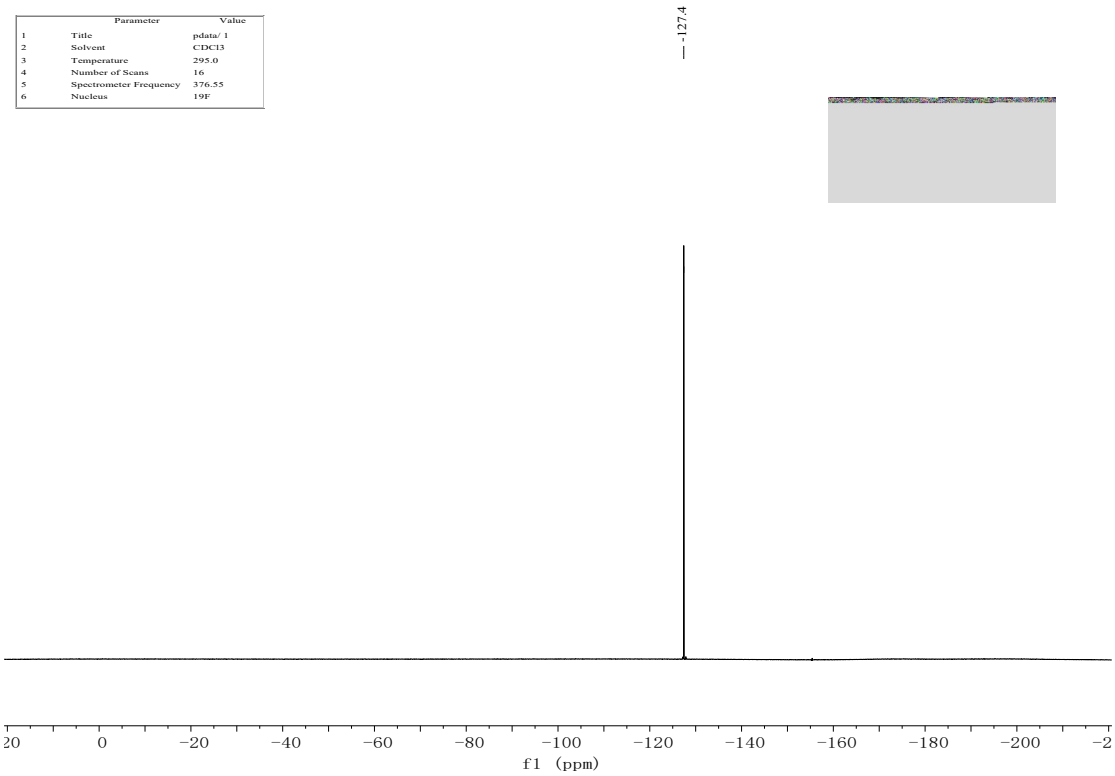
(S)-*N*-ethyl-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanamide (4t)：



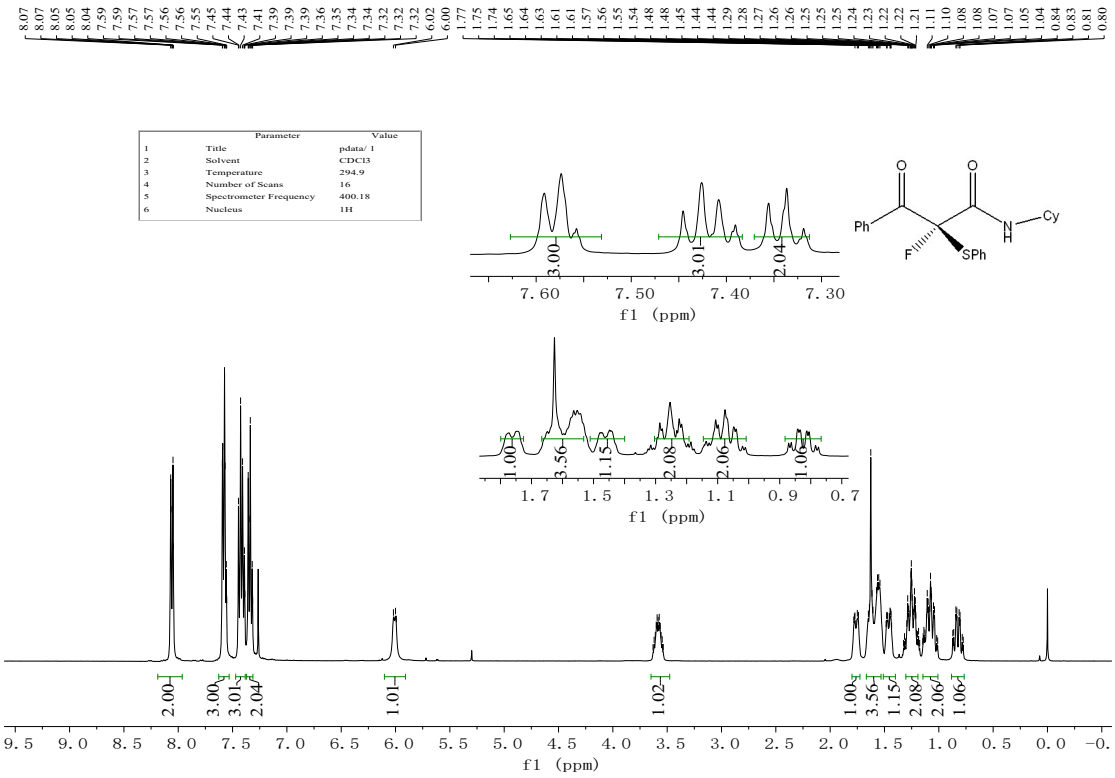


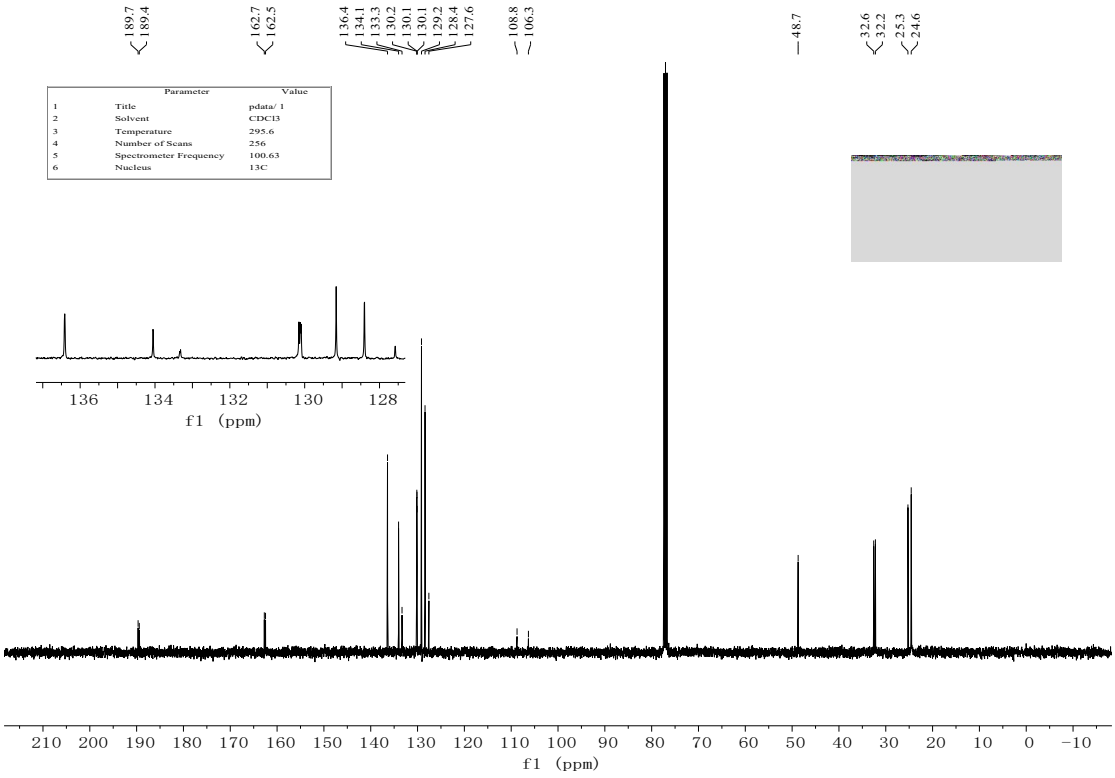
***(S)*-2-fluoro-N-isopropyl-3-oxo-3-phenyl-2-(phenylthio)propanamide (4u):**

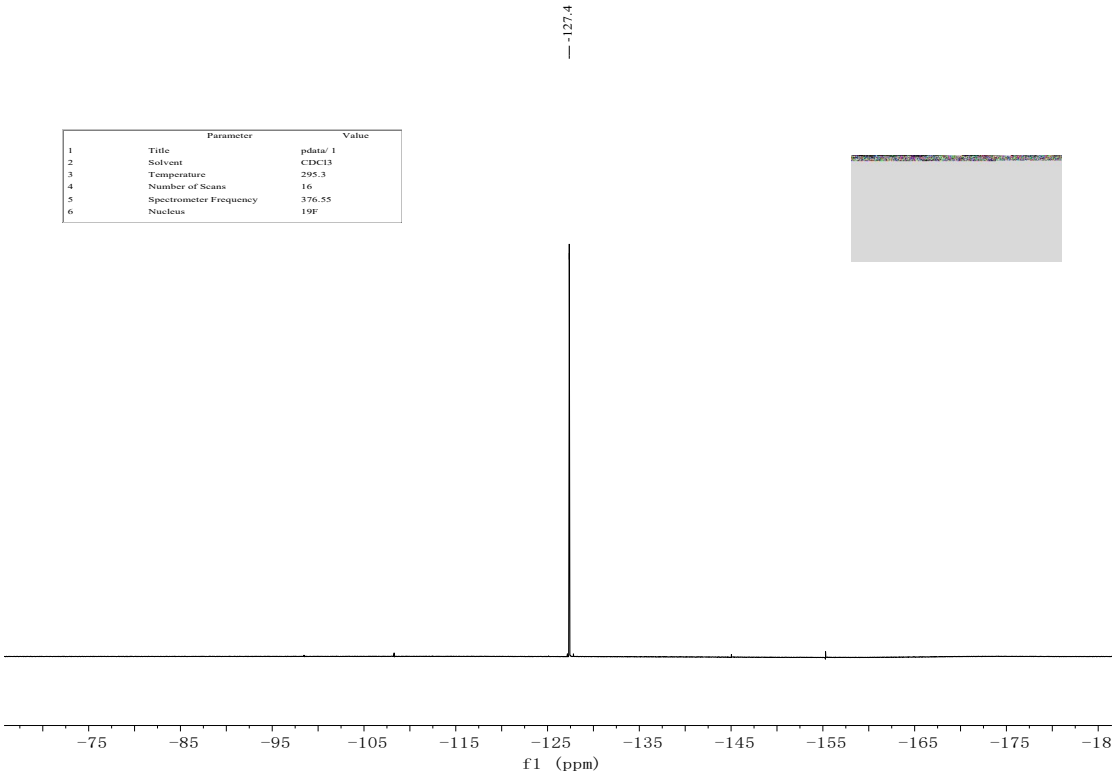

8.07 8.07 8.06 8.05 8.05 8.04 7.60 7.59 7.59 7.58 7.57 7.56 7.56 7.56 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.39 7.36 7.35 7.34 7.34 7.33 7.32 5.96 5.94 5.94 3.92 3.92 3.90 3.90 3.89 3.88 3.87 3.87 3.86 3.85 3.85 3.83
1.05 1.04 0.86 0.84
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
Ph F SPh N H O O
3.00 3.05 2.08
7.60 7.50 7.40 7.30
f1 (ppm)
3.12 3.13
1.15 1.05 0.95 0.85 0.75
f1 (ppm)
2.00 3.00 3.05 2.08 1.02 1.02 3.12 3.13
f1 (ppm)
189.6 189.4 162.8 162.5 136.4 134.1 133.3 133.3 130.1 130.1 129.2 128.4 127.6 108.7 106.3 42.1 22.3 22.0
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 295.4
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
137 135 133 131 129 127
f1 (ppm)
f1 (ppm)



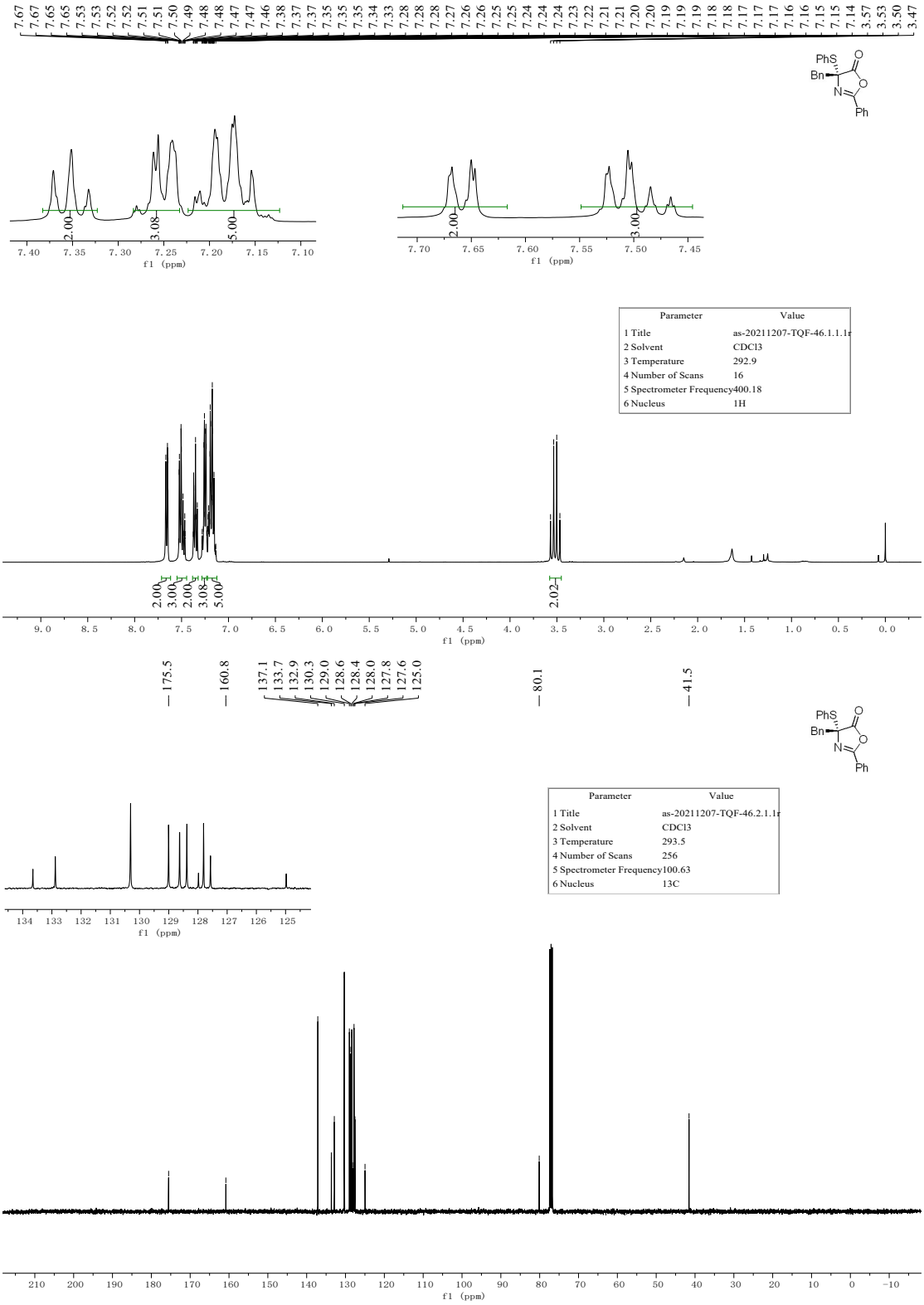
***(S)*-*N*-cyclohexyl-2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanamide (4v):**



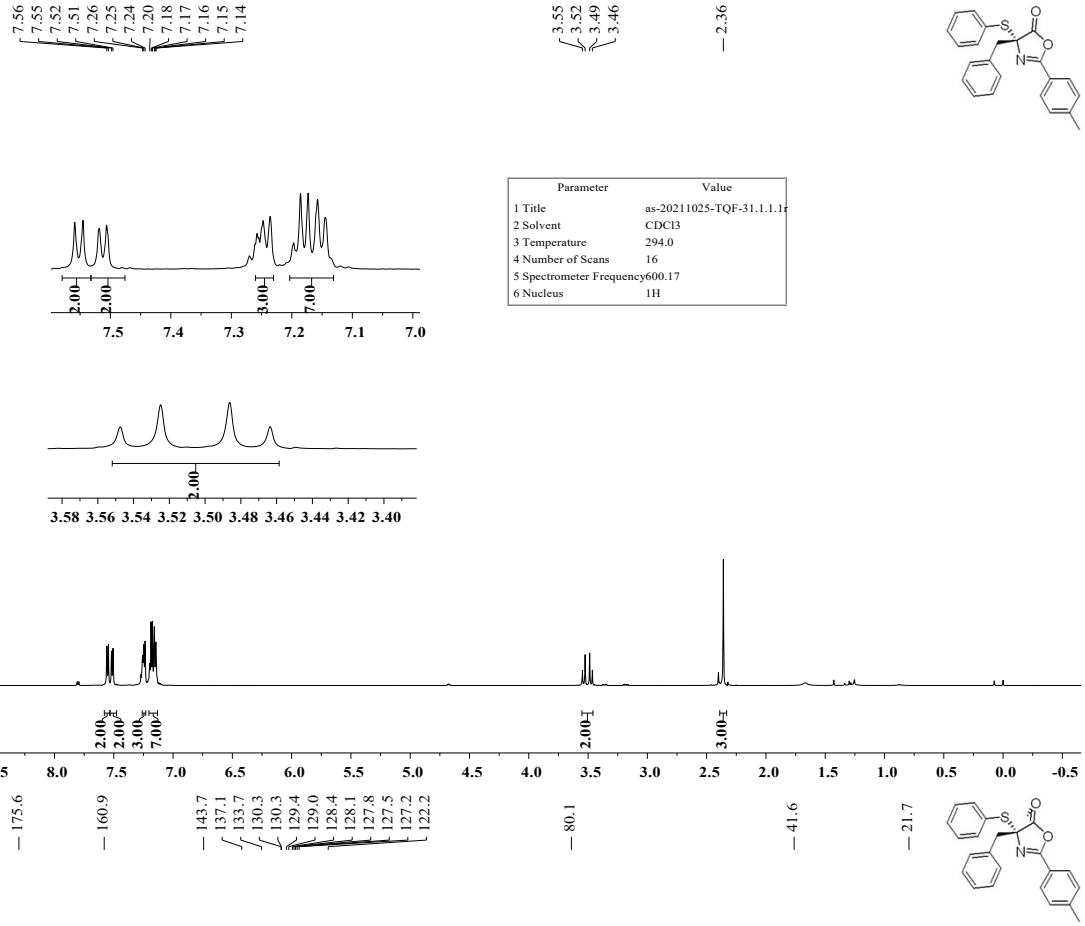




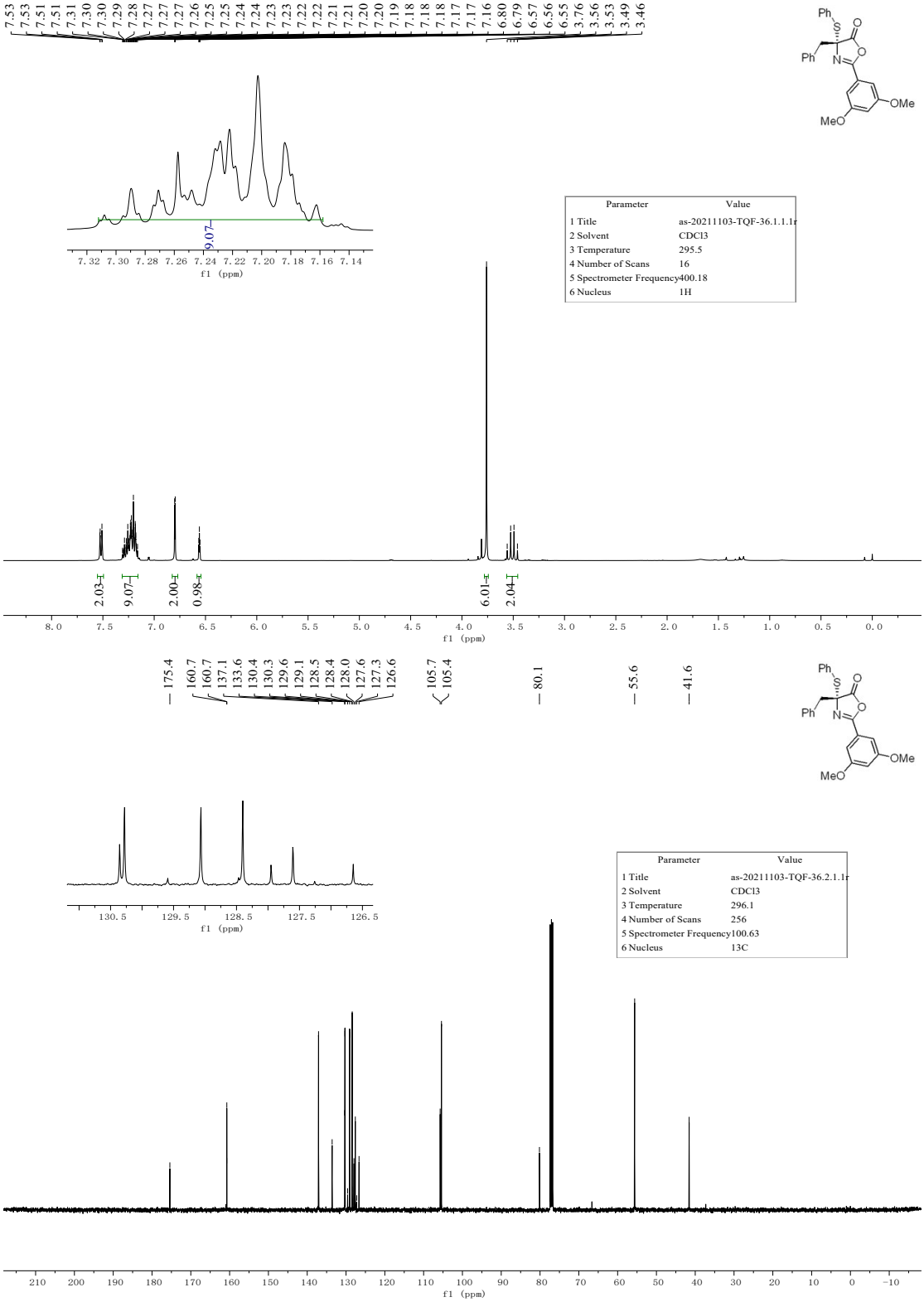
(*R*)-4-benzyl-2-phenyl-4-(phenylthio)oxazol-5(4H)-one (6a):


7.67 7.67 7.65 7.65 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.49 7.48 7.48 7.47 7.47 7.46 7.38 7.37 7.37 7.35 7.35 7.34 7.33 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.15 7.15 7.14 3.57 3.53 3.50 3.47
PhS
Bn
O
O
N
Ph
2.00
3.08
5.00
2.00
3.00
f1 (ppm)
Parameter Value
1 Title as-20211207-TQF-46.1.1.1r
2 Solvent CDCl3
3 Temperature 292.9
4 Number of Scans 16
5 Spectrometer Frequency 400.18
6 Nucleus 1H
2.00
3.00
2.00
3.08
5.00
2.02
f1 (ppm)
175.5
160.8
137.1
133.7
132.9
130.3
129.0
128.6
128.4
128.0
127.8
127.6
125.0
80.1
41.5
PhS
Bn
O
O
N
Ph
Parameter Value
1 Title as-20211207-TQF-46.2.1.1r
2 Solvent CDCl3
3 Temperature 293.5
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
f1 (ppm)
f1 (ppm)

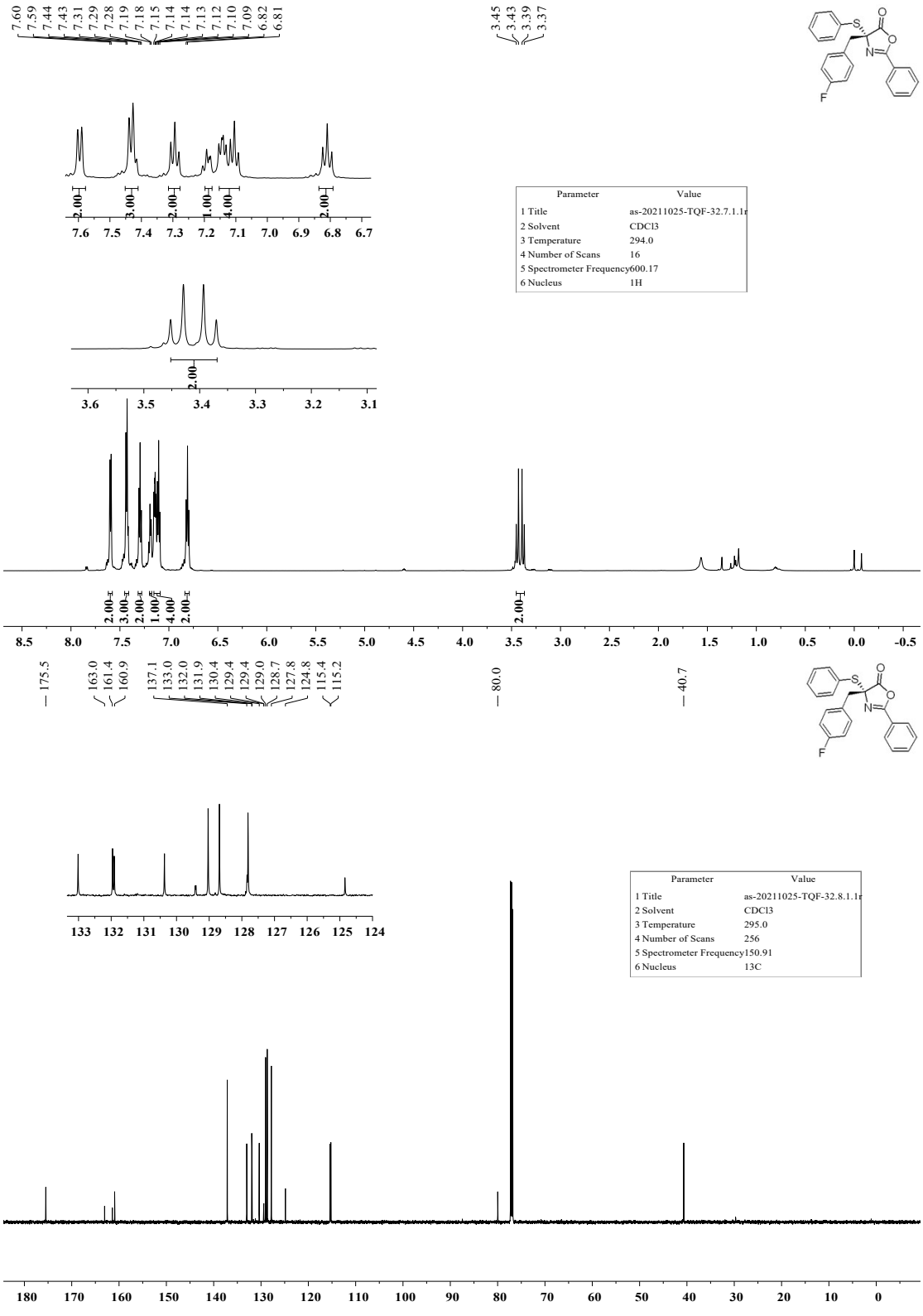
(*R*)-4-benzyl-4-(phenylthio)-2-(*p*-tolyl)oxazol-5(4H)-one (6b):



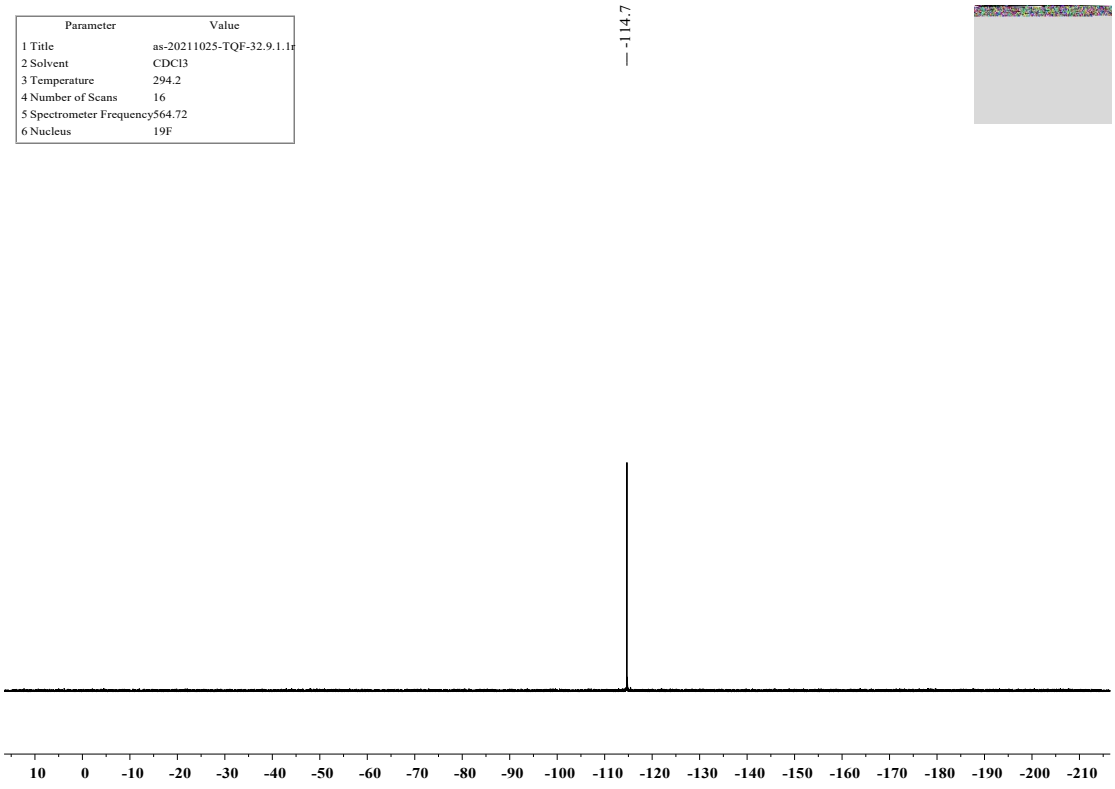
(*R*)-4-benzyl-2-(3,5-dimethoxyphenyl)-4-(phenylthio)oxazol-5(4H)-one (6c):



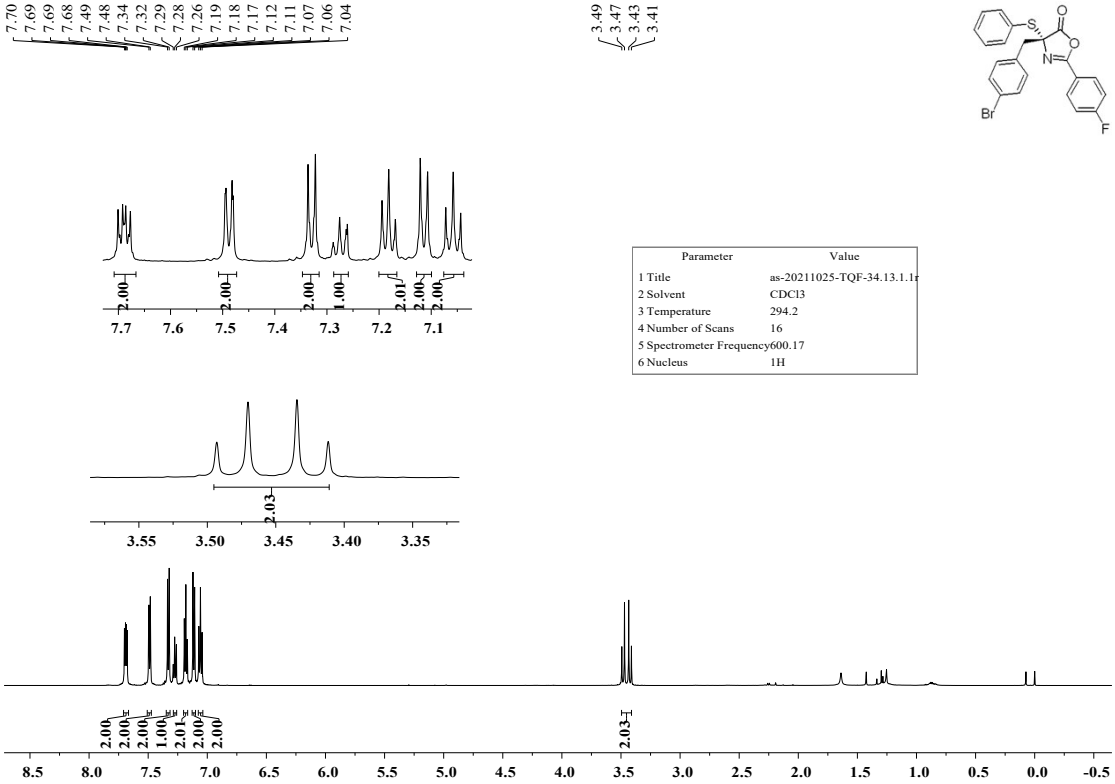
(*R*)-4-(4-fluorobenzyl)-2-phenyl-4-(phenylthio)oxazol-5(4H)-one (6d):



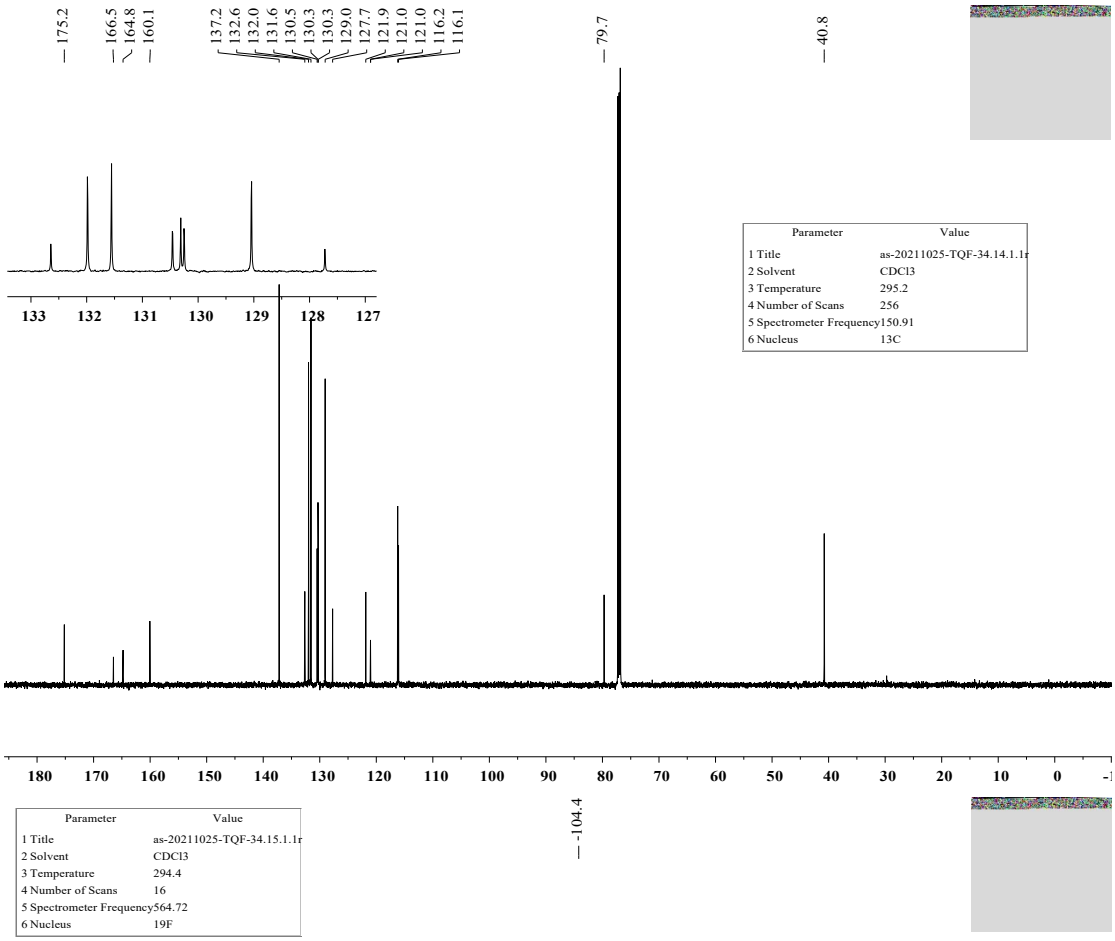
Parameter	Value
1 Title	as-20211025-TQF-32.9.1.1r
2 Solvent	CDCl3
3 Temperature	294.2
4 Number of Scans	16
5 Spectrometer Frequency	564.72
6 Nucleus	19F

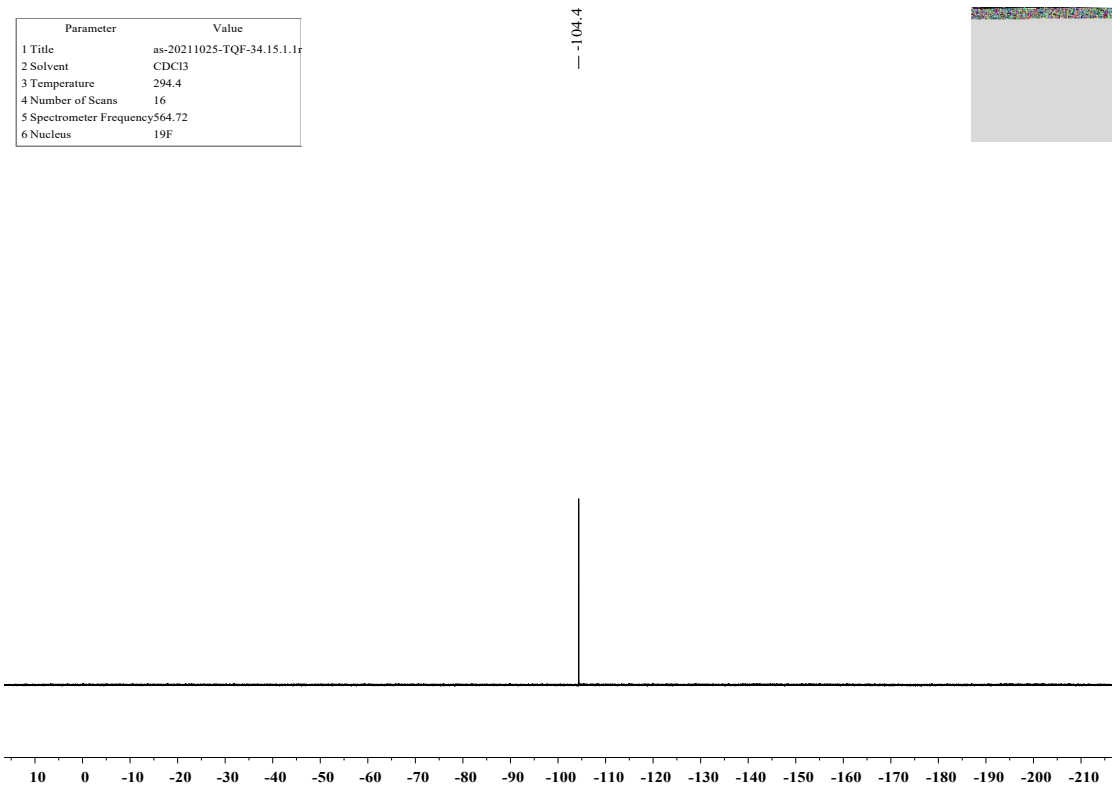


(*R*)-4-(4-bromobenzyl)-2-(4-fluorophenyl)-4-(phenylthio)oxazol-5(4H)-one (6e):

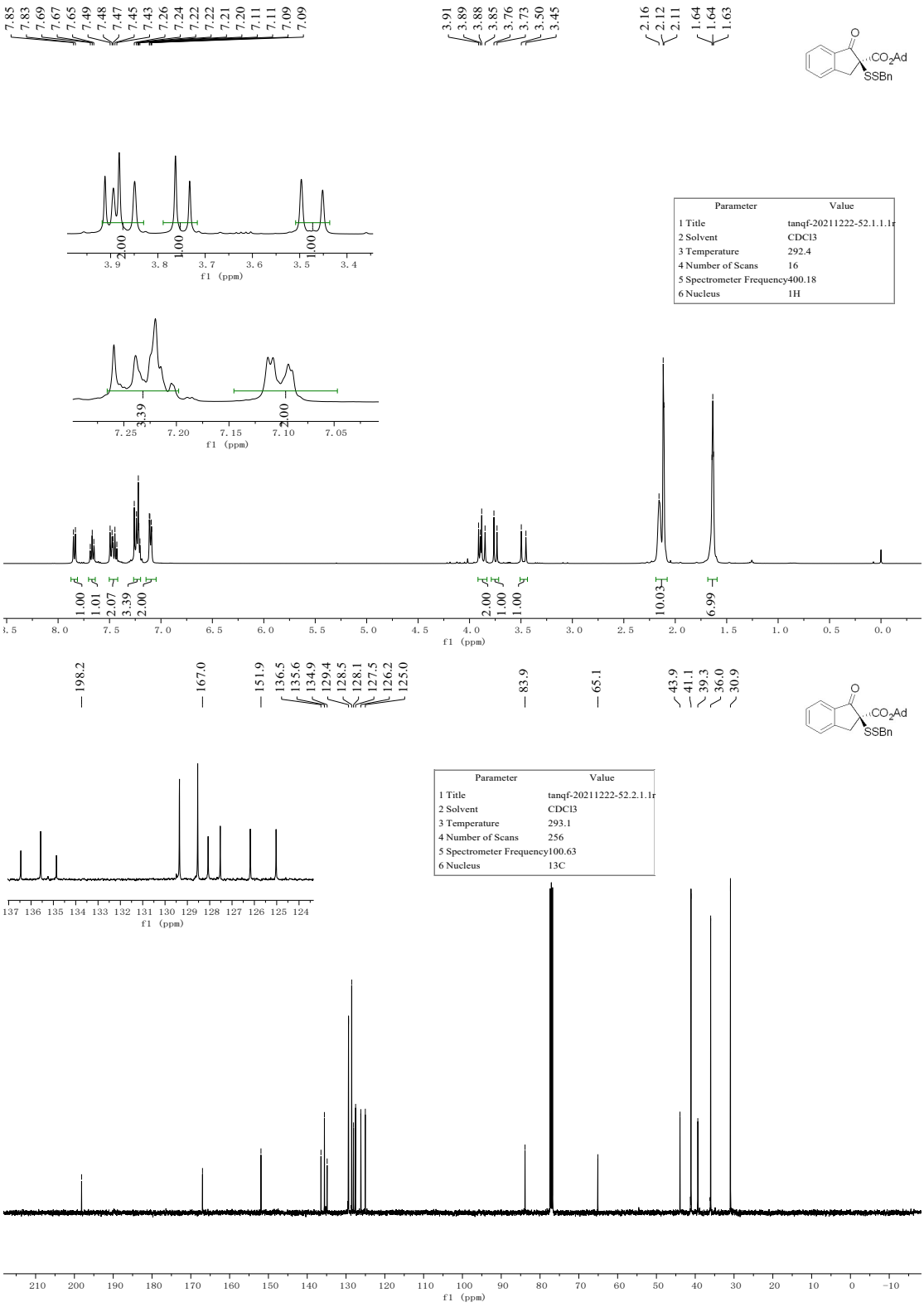


Parameter	Value
1 Title	as-20211025-TQF-34.13.1.1r
2 Solvent	CDCl3
3 Temperature	294.2
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

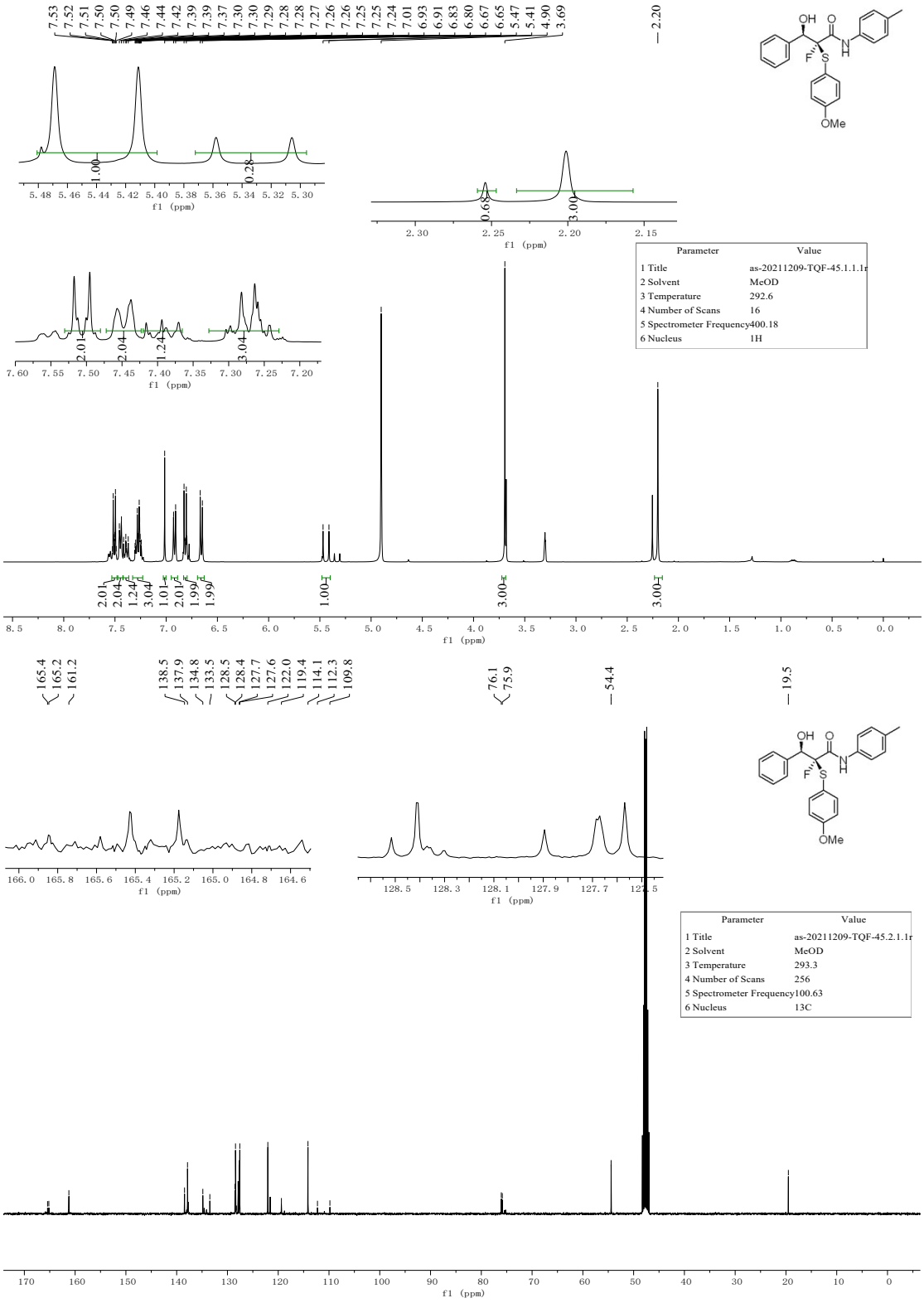

175.2
166.5
164.8
160.1
137.2
132.6
132.0
131.6
130.5
130.3
130.3
129.0
127.7
121.9
121.0
121.0
116.2
116.1
79.7
40.8
133 132 131 130 129 128 127
Parameter Value
1 Title as-20211025-TQF-34.14.1.1r
2 Solvent CDCl3
3 Temperature 295.2
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Parameter Value
1 Title as-20211025-TQF-34.15.1.1r
2 Solvent CDCl3
3 Temperature 294.4
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-104.4
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

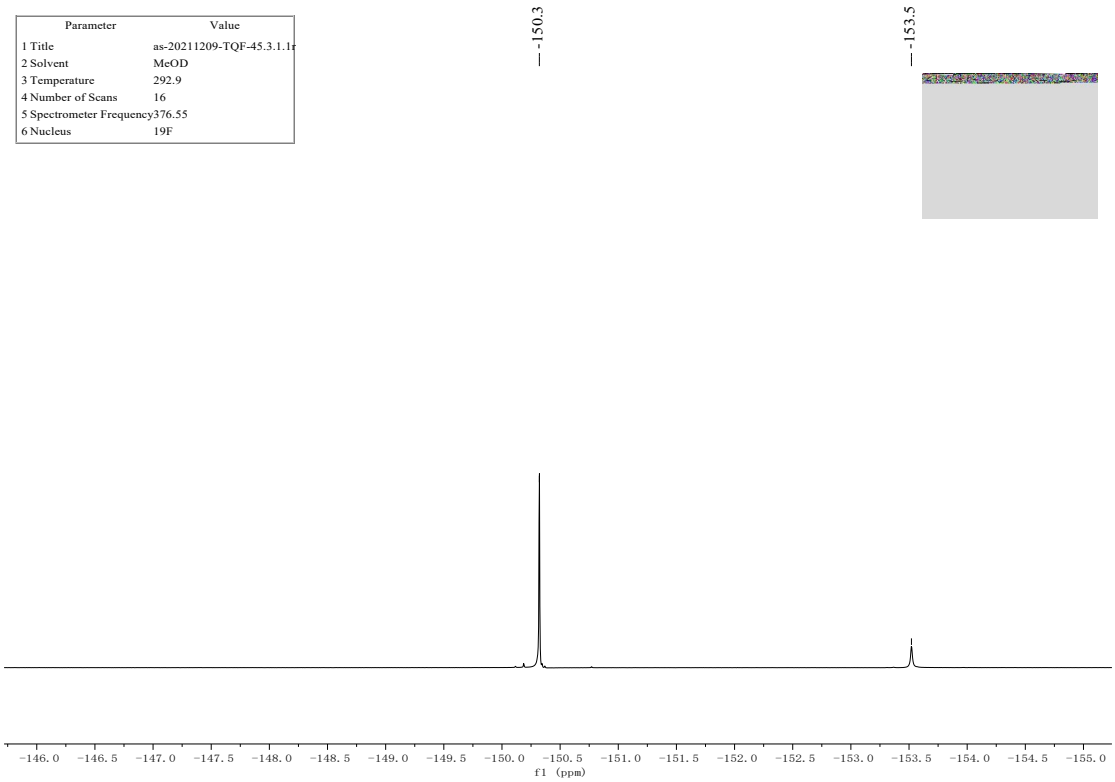
(3*S*)-adamantan-1-yl (2*S*)-2-((*S*)-benzylsulfinothioyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (9):



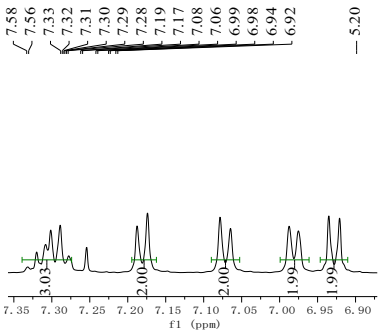
(2*S*,3*R*)-2-fluoro-3-hydroxy-2-((4-methoxyphenyl)thio)-3-phenyl-*N*-(*p*-tolyl)propanamide (10):



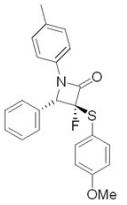
Parameter	Value
1 Title	as-20211209-TQF-45.3.1.1r
2 Solvent	MeOD
3 Temperature	292.9
4 Number of Scans	16
5 Spectrometer Frequency	376.55
6 Nucleus	19F

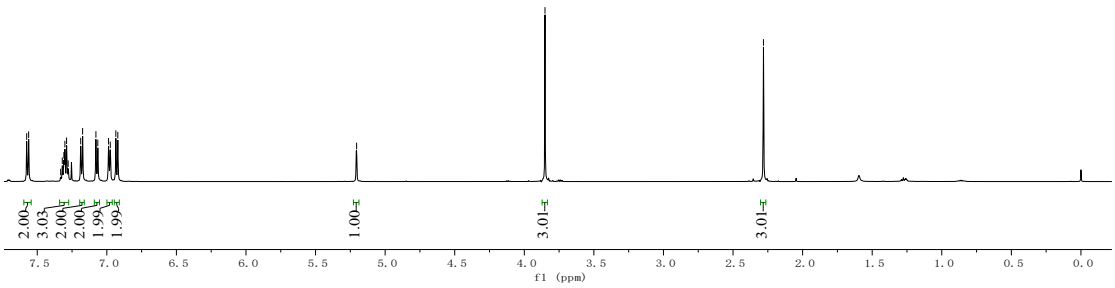


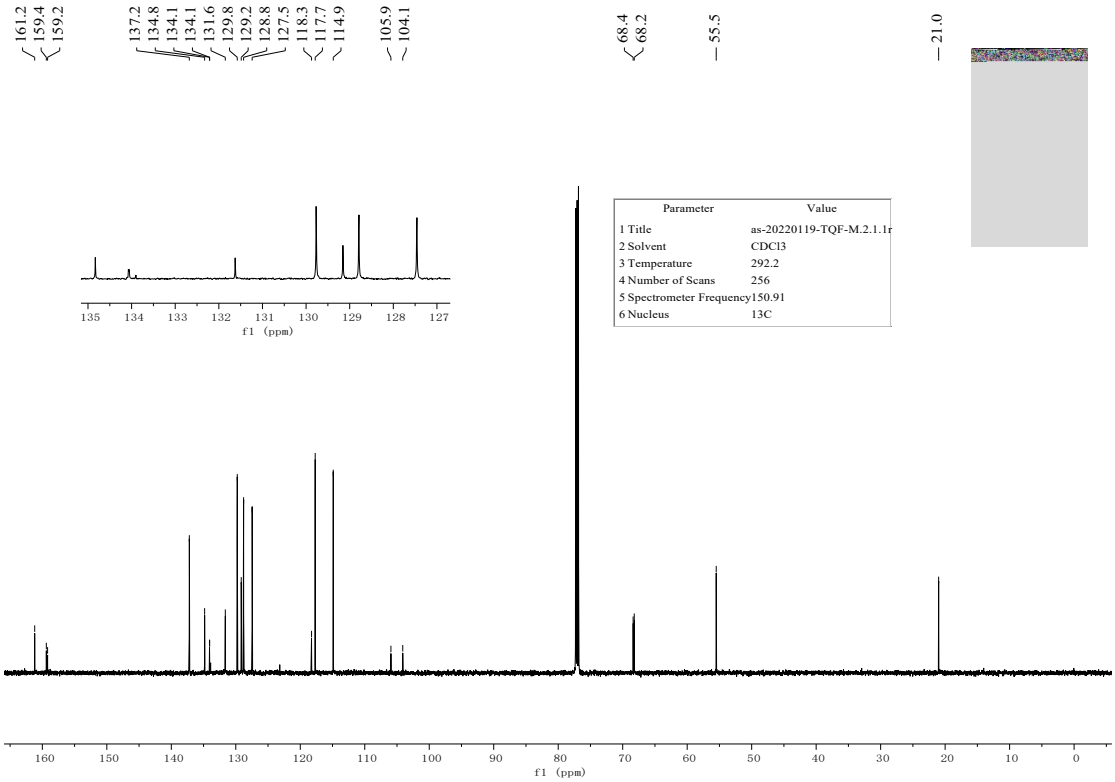
(3*S*,4*S*)-3-fluoro-3-((4-methoxyphenyl)thio)-4-phenyl-1-(*p*-tolyl)azetidin-2-one (11):

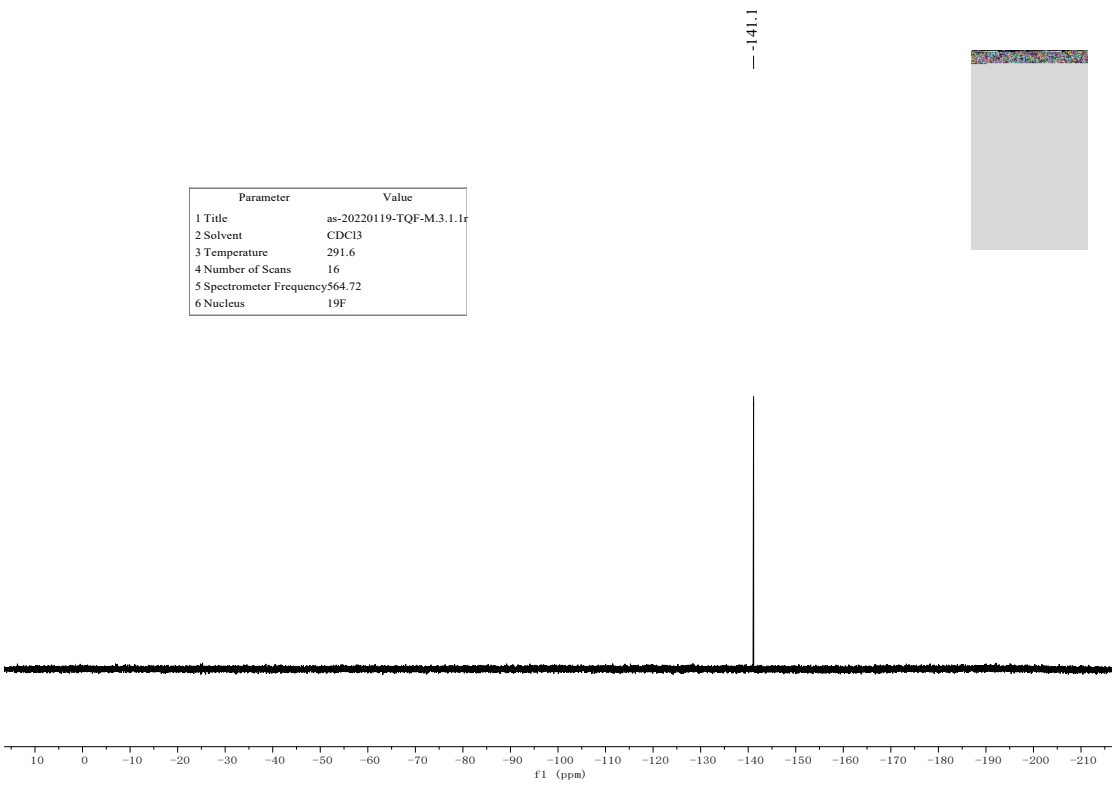


Parameter	Value
1 Title	as-20220119-TQF-M.1.1.1r
2 Solvent	CDCl3
3 Temperature	291.2
4 Number of Scans	16
5 Spectrometer Frequency	600.17
6 Nucleus	1H

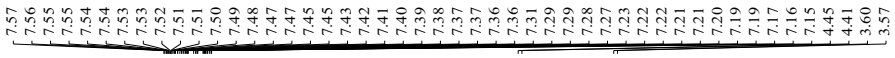


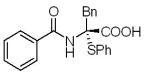


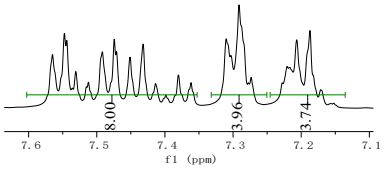

161.2
159.4
159.2
137.2
134.8
134.1
134.1
131.6
129.8
129.2
128.8
127.5
118.3
117.7
114.9
105.9
104.1
68.4
68.2
55.5
21.0
Parameter Value
1 Title as-20220119-TQF-M.2.1.1r
2 Solvent CDCl3
3 Temperature 292.2
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)


-141.1
Parameter Value
1 Title as-20220119-TQF-M.3.1.1r
2 Solvent CDCl3
3 Temperature 291.6
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
f1 (ppm)

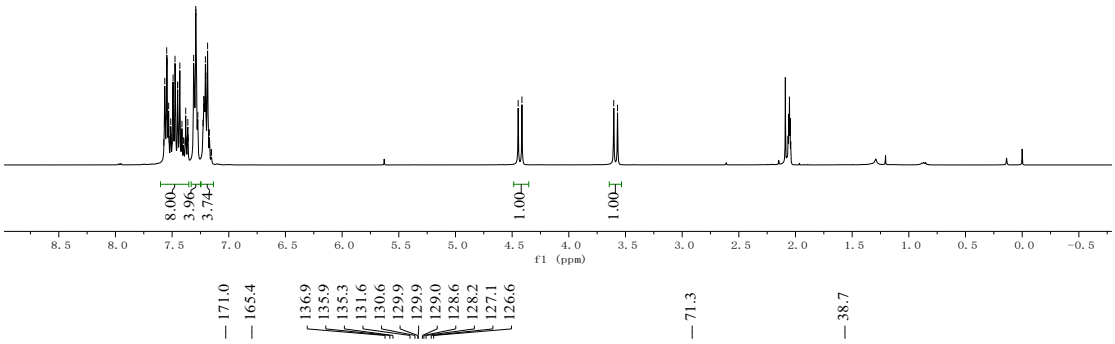
(*R*)-2-benzamido-3-phenyl-2-(phenylthio)propanoic acid (12):

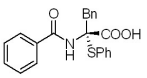


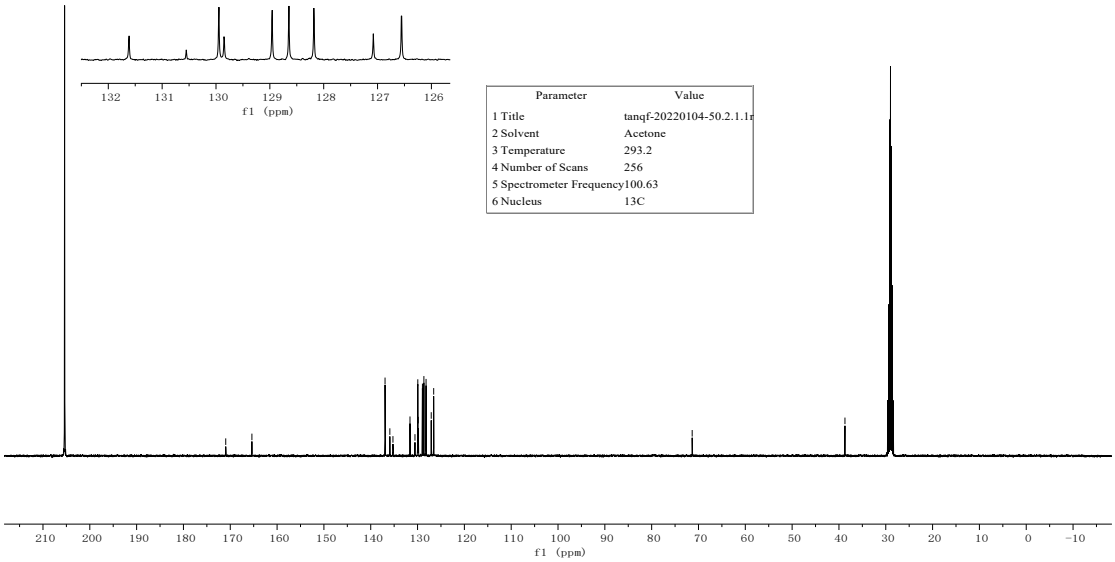




Parameter	Value
1 Title	tanqf-20220104-50.1.1.1r
2 Solvent	Acetone
3 Temperature	292.6
4 Number of Scans	16
5 Spectrometer Frequency	400.18
6 Nucleus	1H

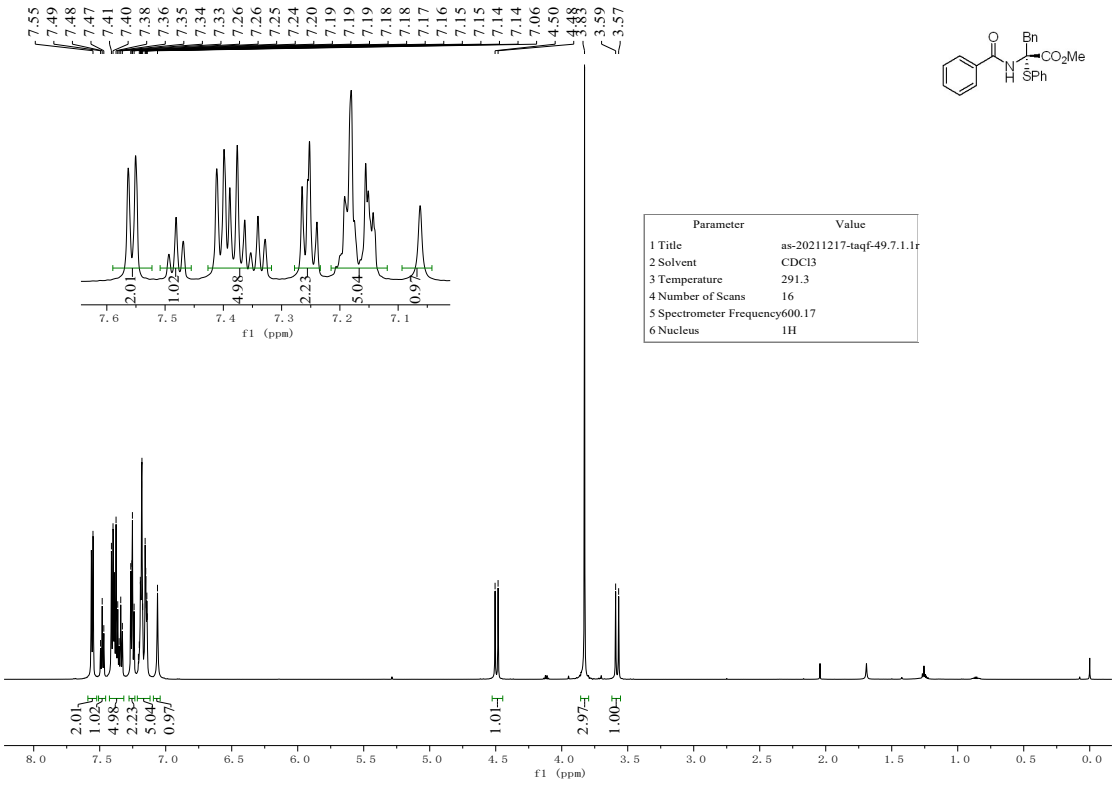


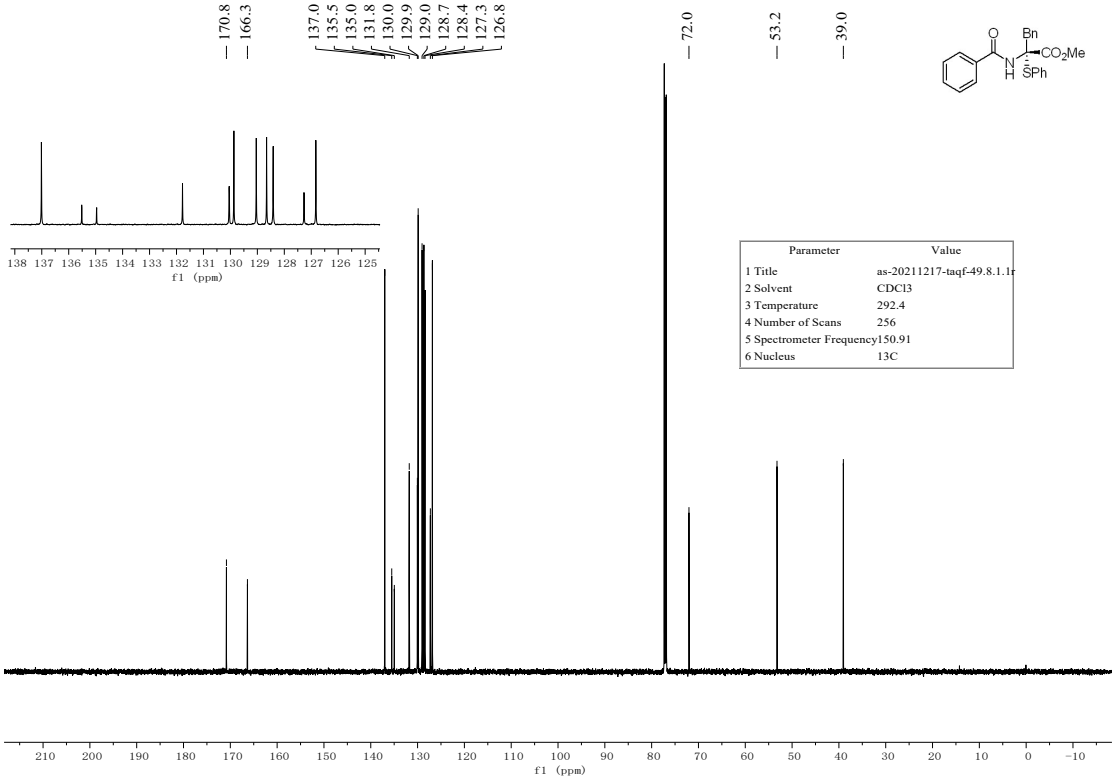




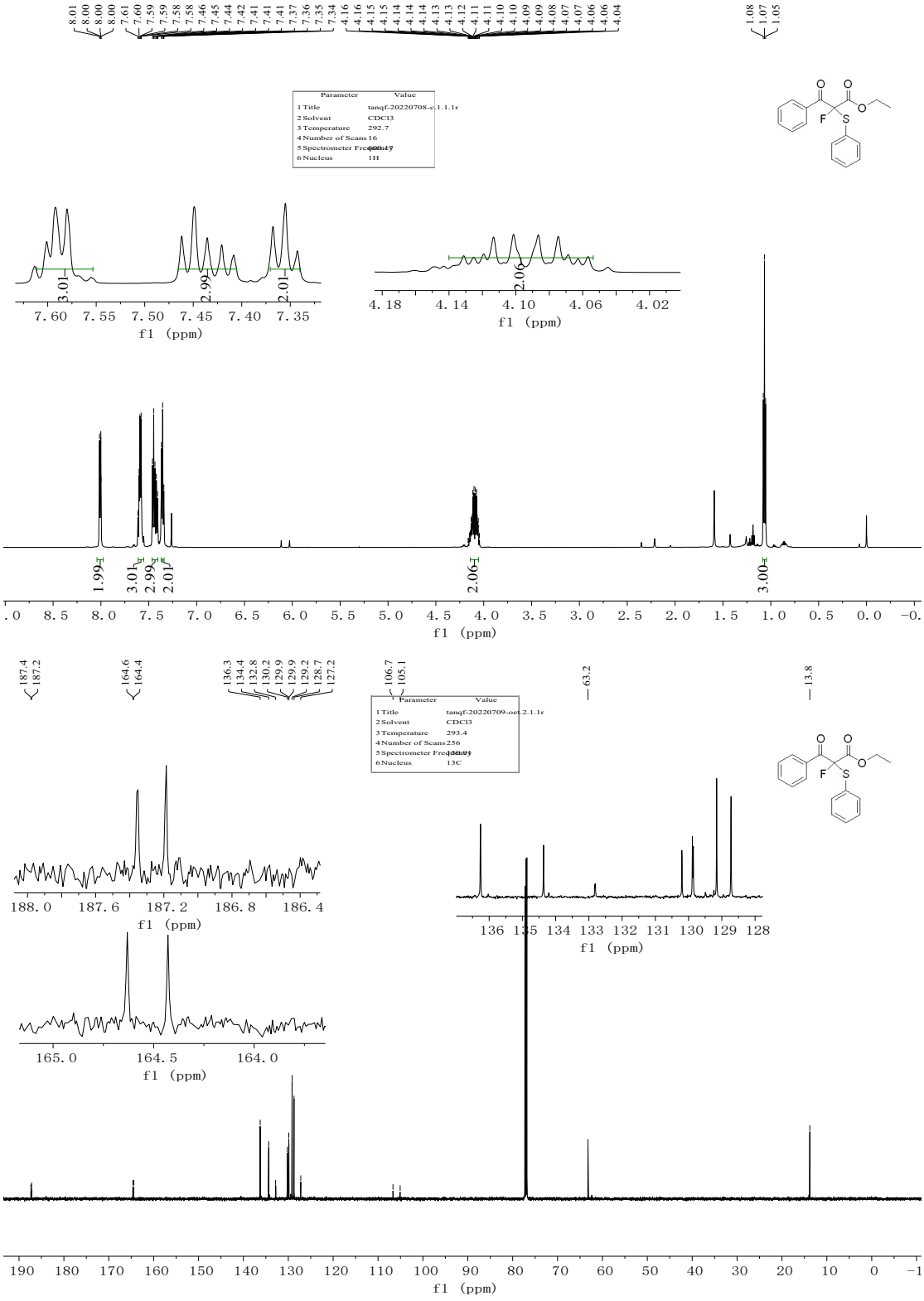
Parameter	Value
1 Title	tanqf-20220104-50.2.1.1r
2 Solvent	Acetone
3 Temperature	293.2
4 Number of Scans	256
5 Spectrometer Frequency	100.63
6 Nucleus	13C

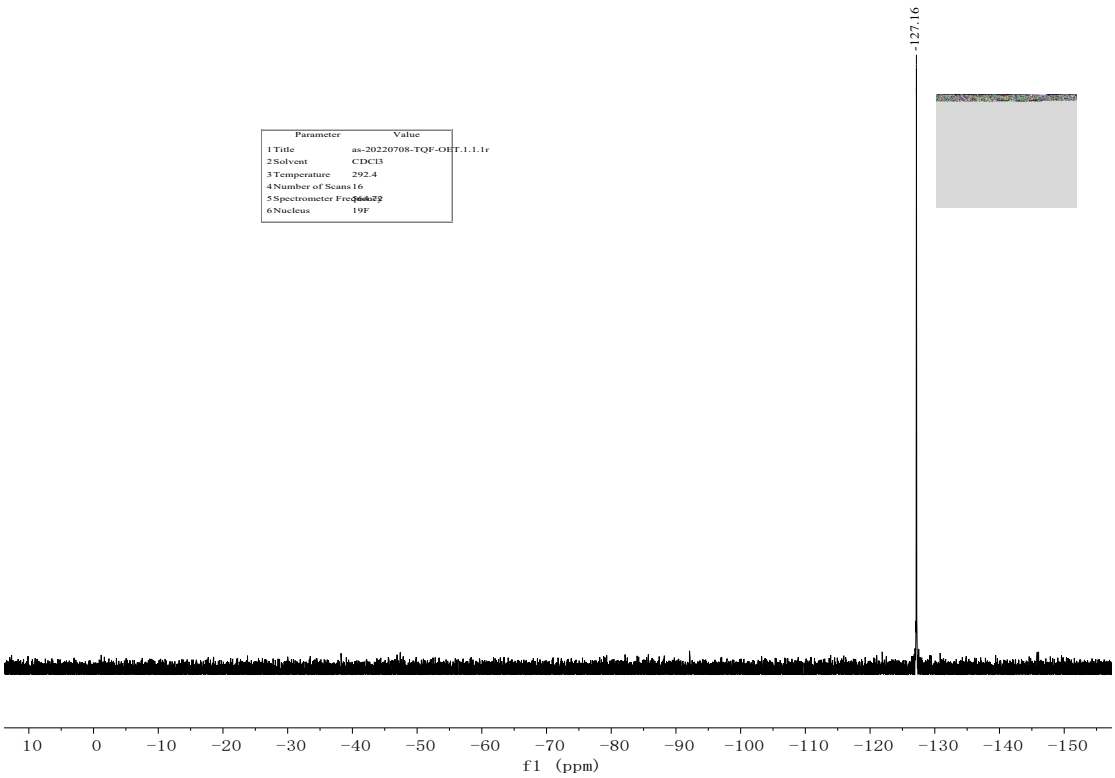
Methyl (*R*)-2-benzamido-3-phenyl-2-(phenylthio)propanoate (13):



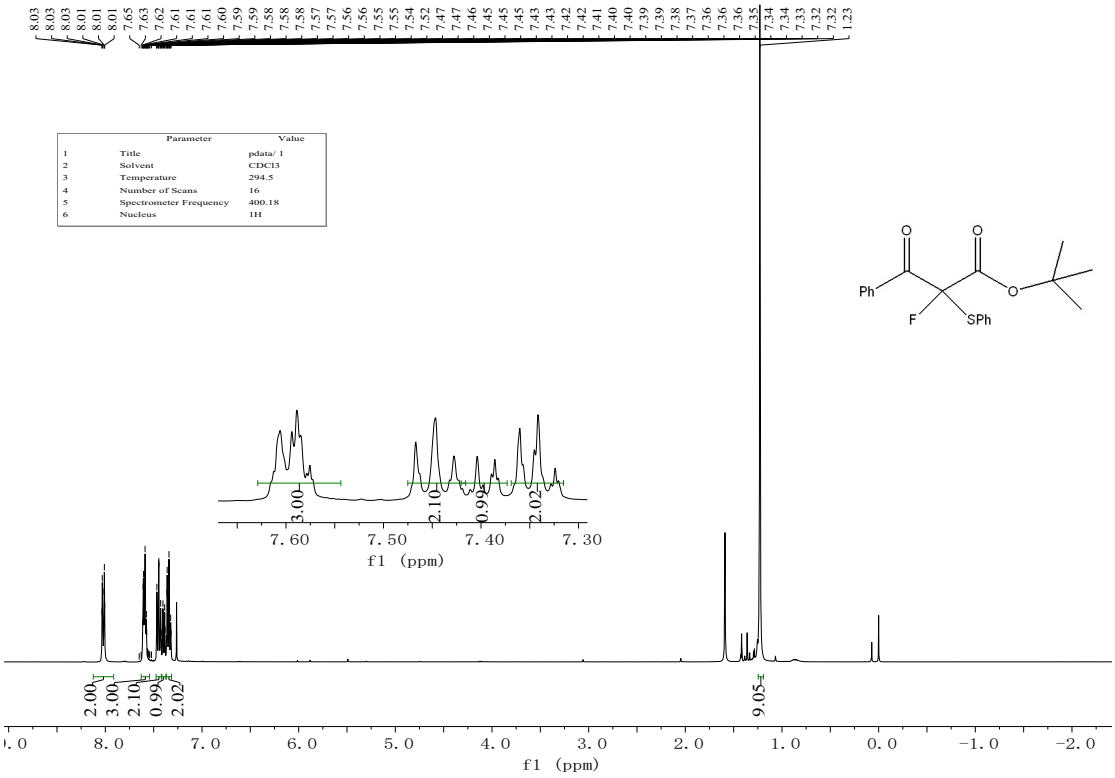


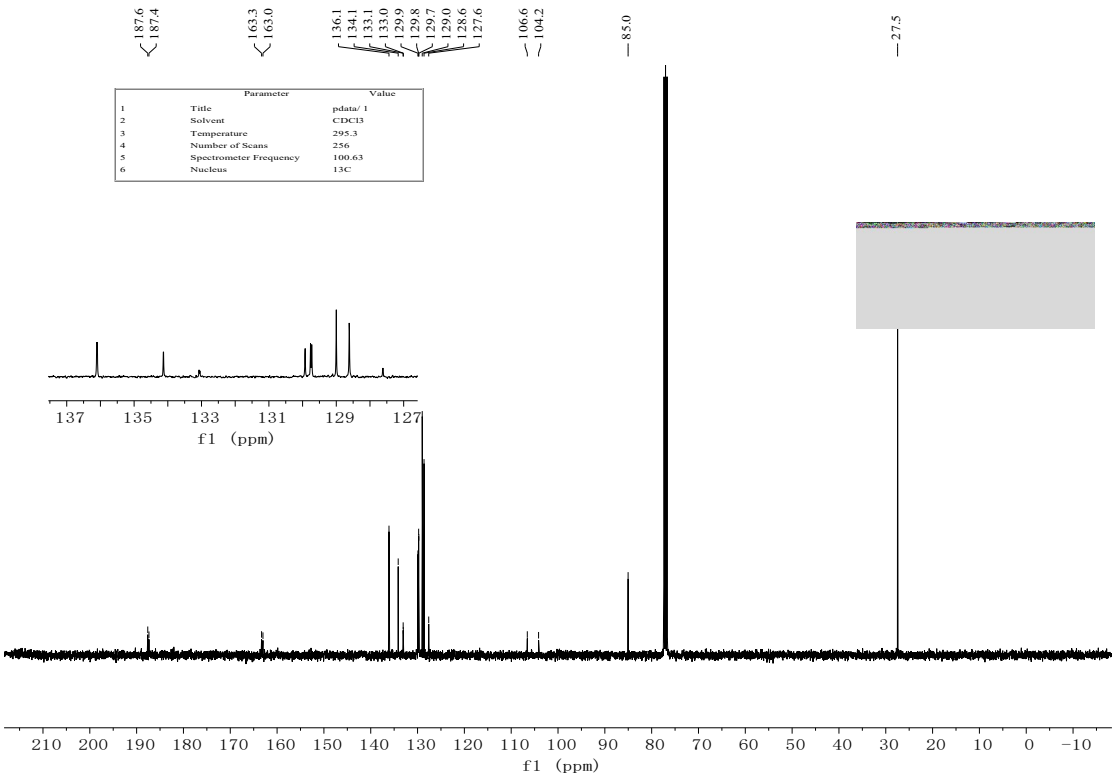
ethyl 2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanoate (15a):

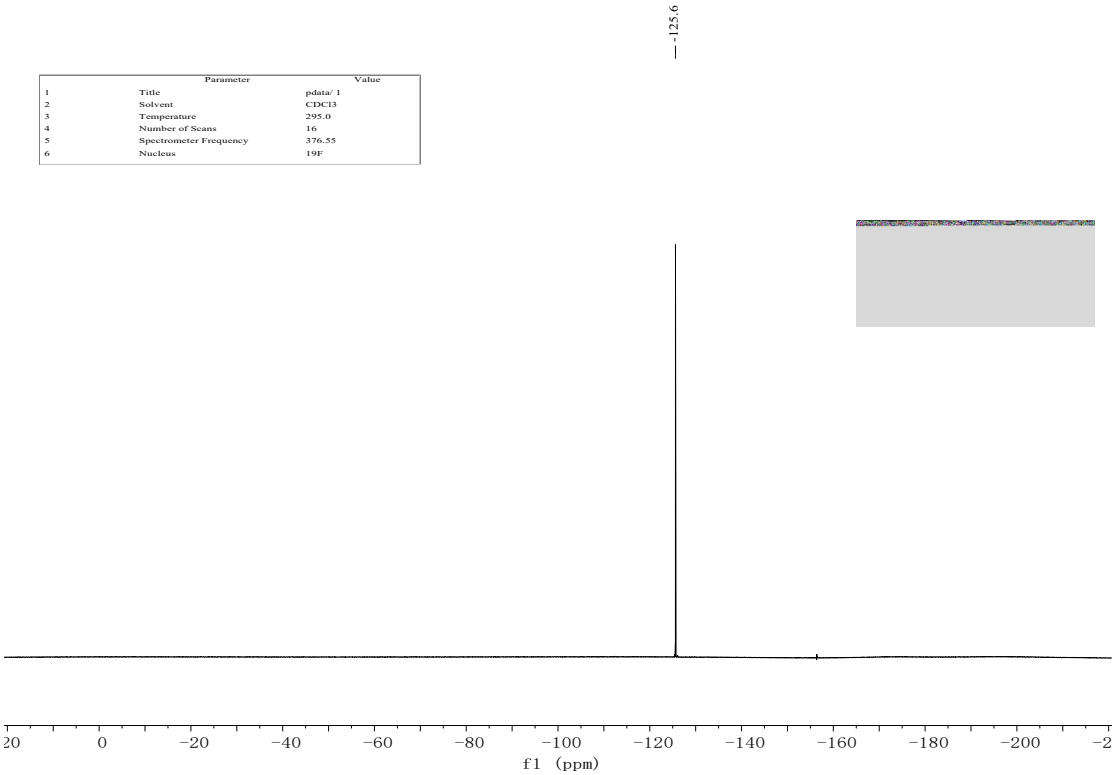




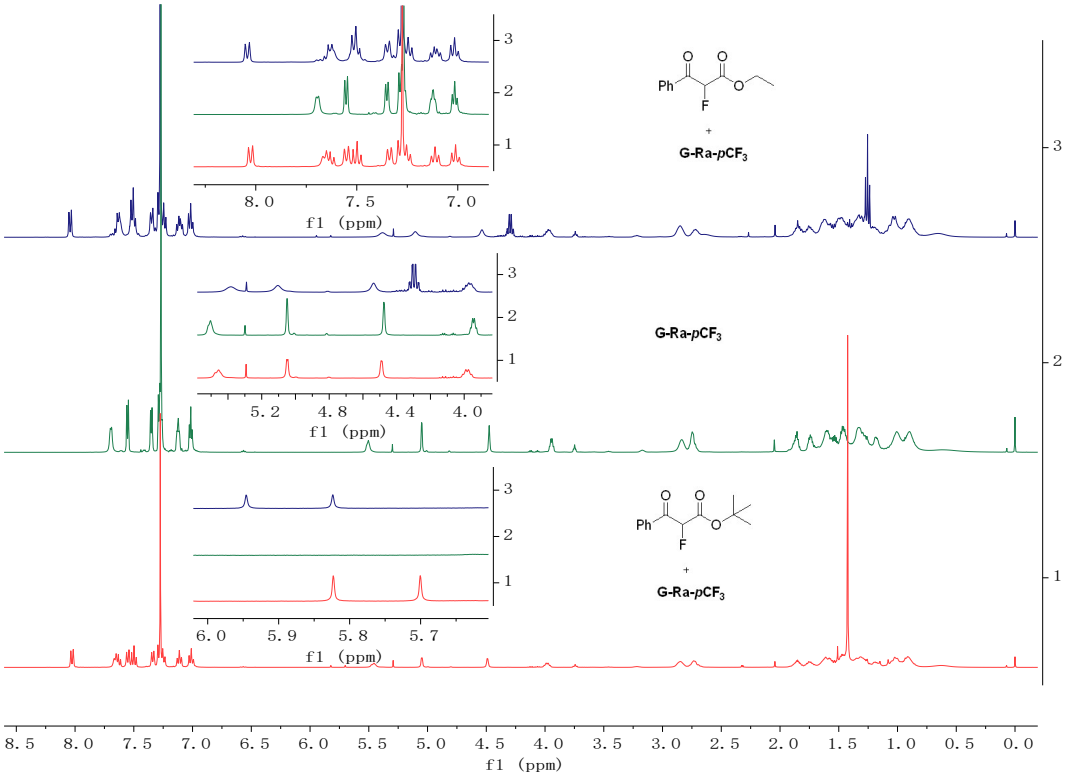
tert-butyl 2-fluoro-3-oxo-3-phenyl-2-(phenylthio)propanoate (15b):

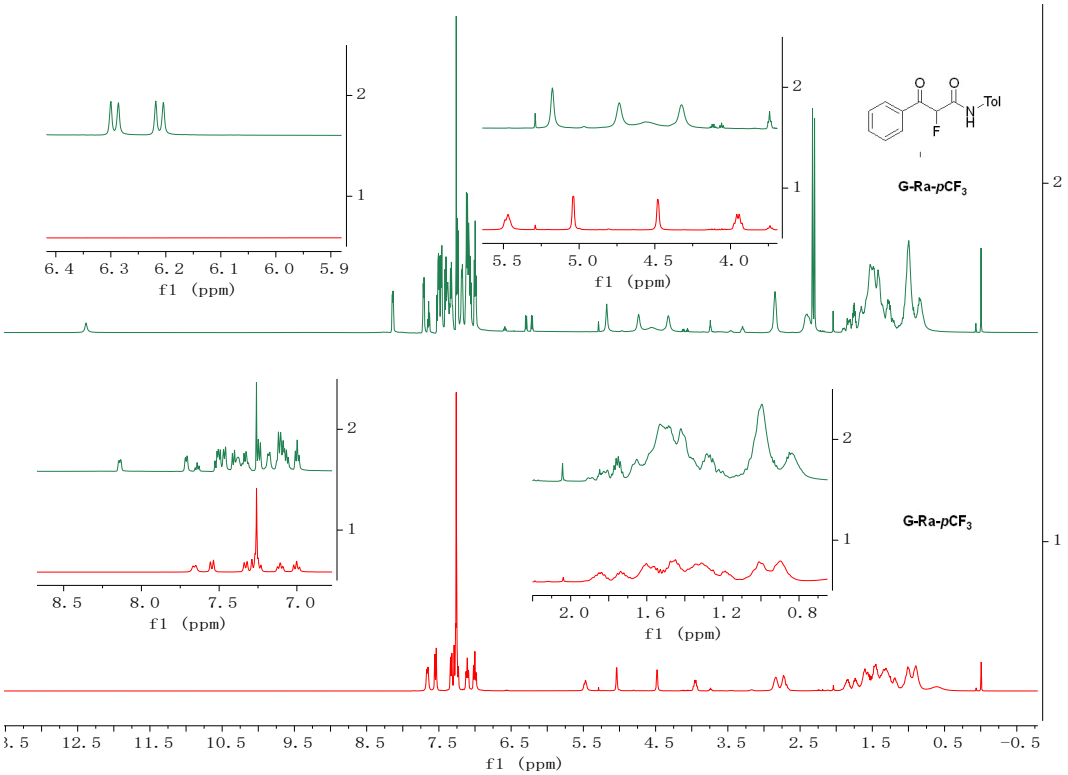



187.6
187.4
163.3
163.0
136.1
134.1
133.1
133.0
129.9
129.8
129.7
129.0
128.6
127.6
106.6
104.2
85.0
27.5
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 295.3
4 Number of Scans 256
5 Spectrometer Frequency 100.63
6 Nucleus 13C
137 135 133 131 129 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

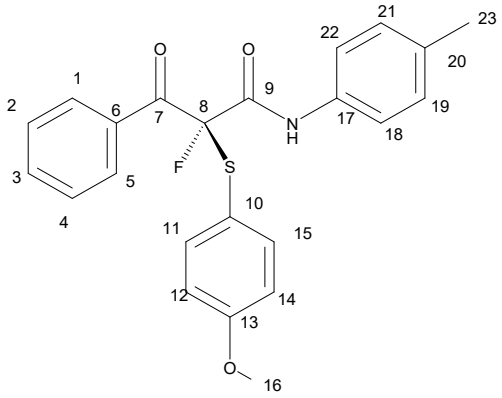

-125.6
Parameter Value
1 Title pdata/ 1
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 376.55
6 Nucleus 19F
20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −2
f1 (ppm)

16. Copies of NMR spectra for the NMR study of substrate and G-Ra-*p*CF_3

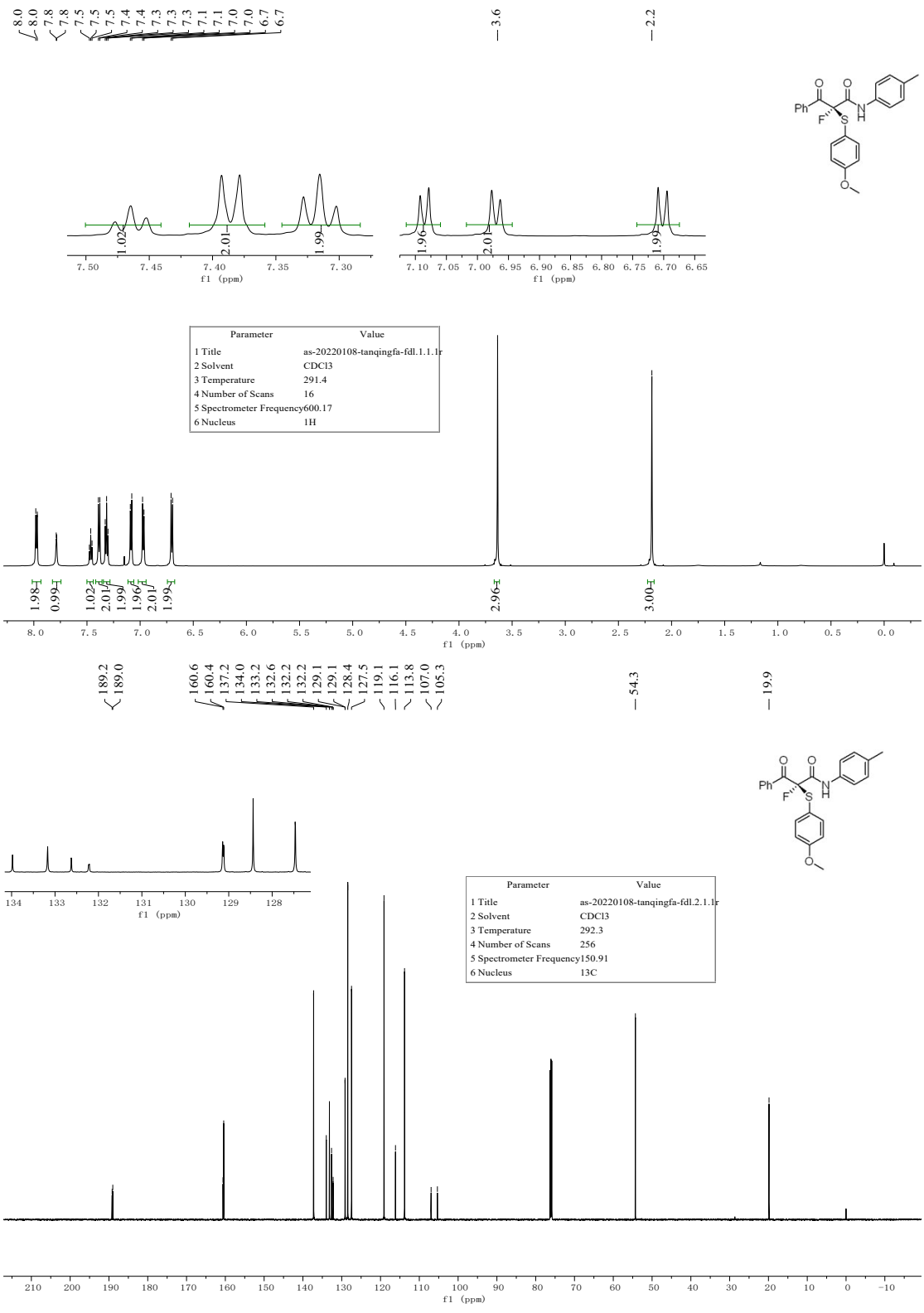


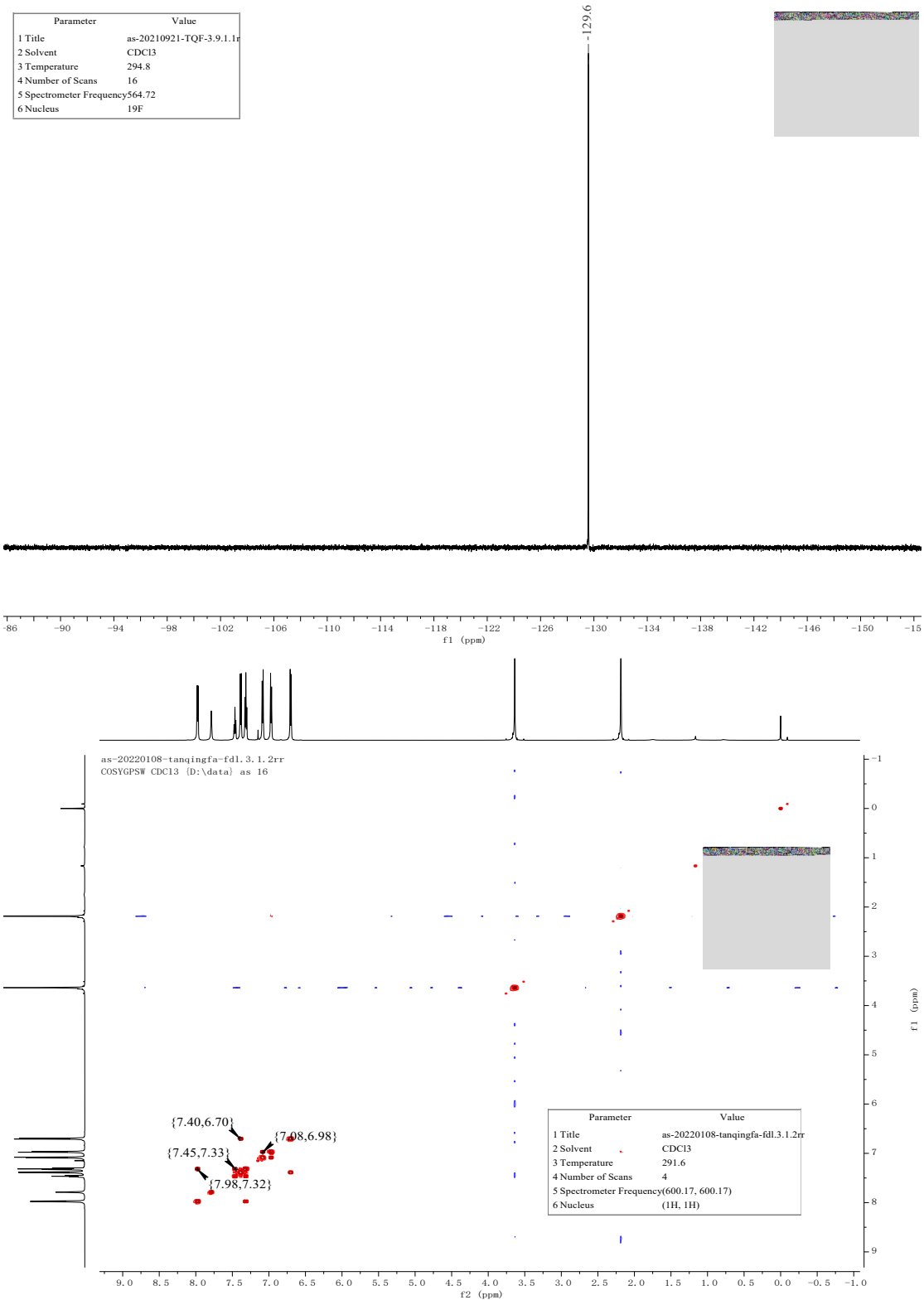


17. Analysis Results of 2D NMR Spectra of the Product 3h (After Recrystallization)



Number of atom	H (ppm)	C (ppm)	Number of atom	H (ppm)	C (ppm)
1	**8.0**	**129.1**	**13**	**-**	**160.4**
2	**7.3**	**127.5**	**14**	**6.7**	**113.8**
3	**7.5**	**133.2**	**15**	**7.4**	**137.3**
4	**7.3**	**127.5**	**16**	**3.6**	**54.3**
5	**8.0**	**129.1**	**17**	**-**	**132.6**
6	**-**	**132.2**	**18**	**7.1**	**119.2**
7	**-**	**(189.2, 189.0)**	**19**	**7.0**	**128.5**
8	**-**	**(105.3, 107.0)**	**20**	**-**	**134.0**
9	**-**	**(160.6, 160.4)**	**21**	**7.0**	**128.5**
10	**-**	**116.1**	**22**	**7.1**	**119.2**
11	**7.4**	**137.3**	**23**	**2.2**	**19.9**
12	**6.7**	**113.8**	**-**	**-**	**-**


8.0
8.0
7.8
7.8
7.5
7.5
7.5
7.4
7.4
7.3
7.3
7.3
7.1
7.1
7.0
7.0
6.7
6.7
3.6
2.2
Ph
O
O
N
H
F
S
O
1.02
2.01
1.99
1.96
2.01
1.99
f1 (ppm)
Parameter Value
1 Title as-20220108-tanqingfa-fdl.1.1.1r
2 Solvent CDCl3
3 Temperature 291.4
4 Number of Scans 16
5 Spectrometer Frequency 600.17
6 Nucleus 1H
1.98
0.99
1.02
2.01
1.99
1.96
2.01
1.99
2.96
3.00
f1 (ppm)
189.2
189.0
160.6
160.4
137.2
134.0
133.2
132.6
132.2
132.2
129.1
129.1
128.4
127.5
119.1
116.1
113.8
107.0
105.3
54.3
19.9
f1 (ppm)
Parameter Value
1 Title as-20220108-tanqingfa-fdl.2.1.1r
2 Solvent CDCl3
3 Temperature 292.3
4 Number of Scans 256
5 Spectrometer Frequency 150.91
6 Nucleus 13C
f1 (ppm)


Parameter Value
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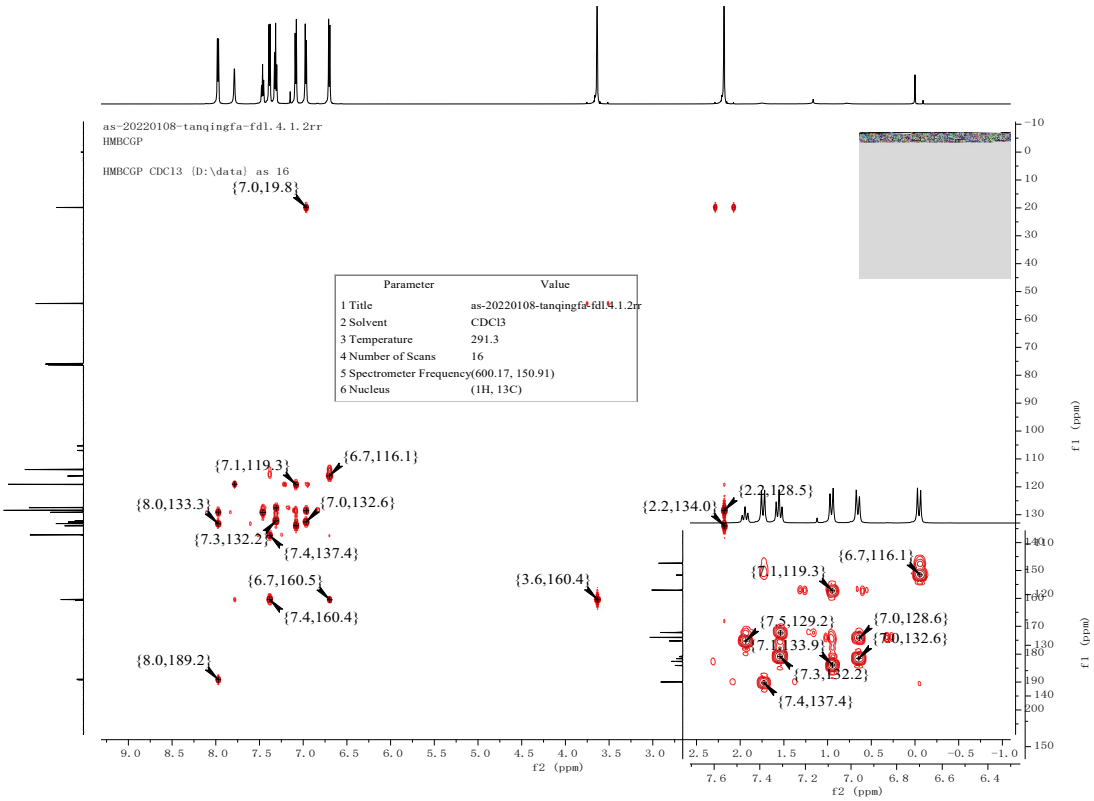
2 Solvent CDCl3
3 Temperature 294.8
4 Number of Scans 16
5 Spectrometer Frequency 564.72
6 Nucleus 19F
-129.6
f1 (ppm)
as-20220108-tanqingfa-fdl.3.1.2rr
COSYGPSW CDCl3 {D:\data} as 16
{7.40,6.70}
{7.08,6.98}
{7.45,7.33}
{7.98,7.32}
Parameter Value
1 Title as-20220108-tanqingfa-fdl.3.1.2rr
2 Solvent CDCl3
3 Temperature 291.6
4 Number of Scans 4
5 Spectrometer Frequency (600.17, 600.17)
6 Nucleus (1H, 1H)
f2 (ppm)
f1 (ppm)


as-20220108-tanqingfa-fdl.4.1.2rr
HMBCGP
HMBCGP CDC13 {D:\data} as 16
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Parameter Value
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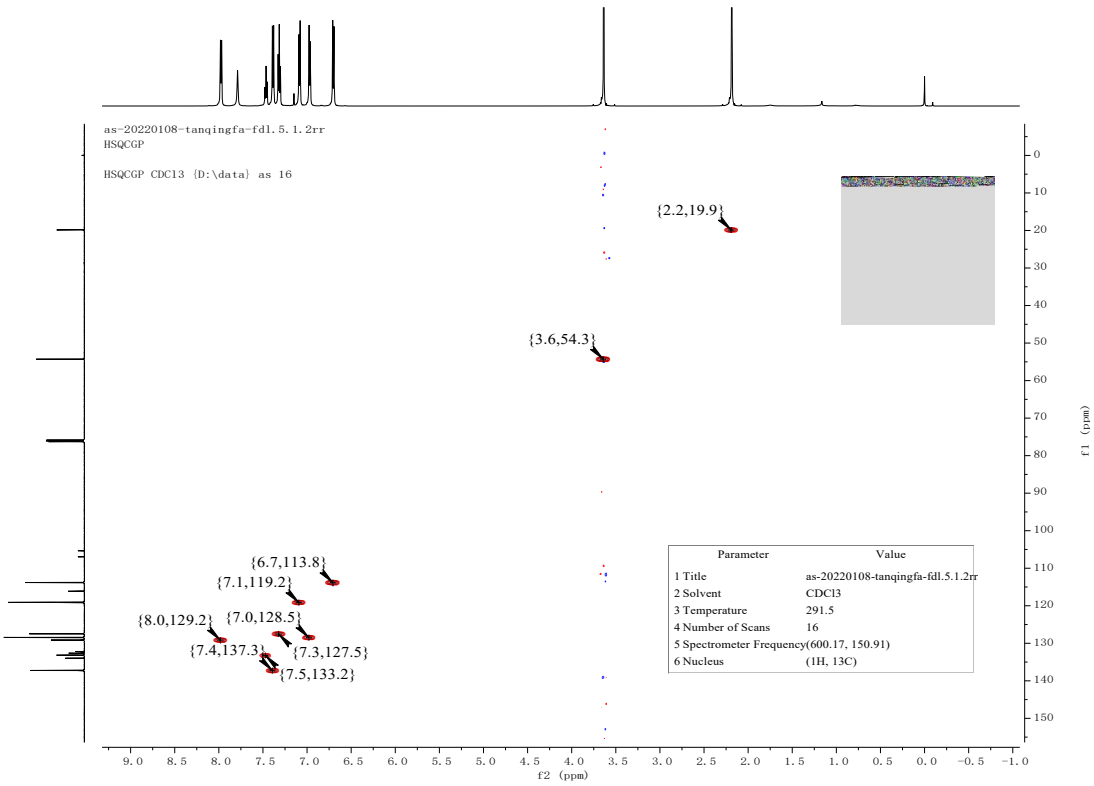
2 Solvent CDCl3
3 Temperature 291.3
4 Number of Scans 16
5 Spectrometer Frequency (600.17, 150.91)
6 Nucleus (1H, 13C)
{7.1,119.3}
{6.7,116.1}
{8.0,133.3}
{7.0,132.6}
{7.3,132.2}
{7.4,137.4}
{6.7,160.5}
{7.4,160.4}
{3.6,160.4}
{8.0,189.2}
{2.2,134.0}
{2.2,128.5}
{6.7,116.1}
{7.1,119.3}
{7.5,129.2}
{7.0,128.6}
{7.1,133.9}
{7.0,132.6}
{7.3,132.2}
{7.4,137.4}
f2 (ppm)
f1 (ppm)


as-20220108-tanqingfa-fdl.5.1.2rr
HSQCGP
HSQCGP CDC13 {D:\data} as 16
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{3.6,54.3}
{6.7,113.8}
{7.1,119.2}
{8.0,129.2}
{7.0,128.5}
{7.4,137.3}
{7.3,127.5}
{7.5,133.2}
Parameter Value
1 Title as-20220108-tanqingfa-fdl.5.1.2rr
2 Solvent CDCl3
3 Temperature 291.5
4 Number of Scans 16
5 Spectrometer Frequency (600.17, 150.91)
6 Nucleus (1H, 13C)
f2 (ppm)
f1 (ppm)

18. References

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19. Author Contributions

Q.F.T conducted the experiments, analyzed the results, wrote the Supporting Information and manuscript. Q.P.C. synthesized some starting materials and catalysts. Z.T.Z. repeated some experiments. X.H.L. helped with modifying the Supporting Information and manuscript.