Supporting Information

Photoinduced 1,5-HAT-enabled 1,7-hydrosulfonylation of allylic ethers and amides

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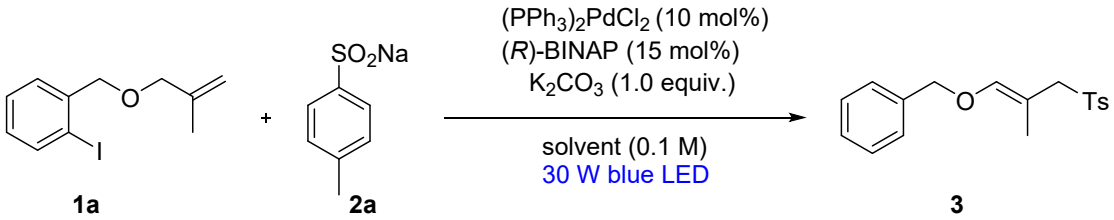
1. General Experimental Methods

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to teramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet; d = doublet; dd = doublet of doublet; t= triplet; q = quartet; *br* s = broad singlet; m = multiplet), coupling constants (Hz), integration. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^{+} Mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh, Petroleum PE/EtOAc solvent systems). Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2. Optimization of Reaction Conditions

1) Screening of Solvents[a]

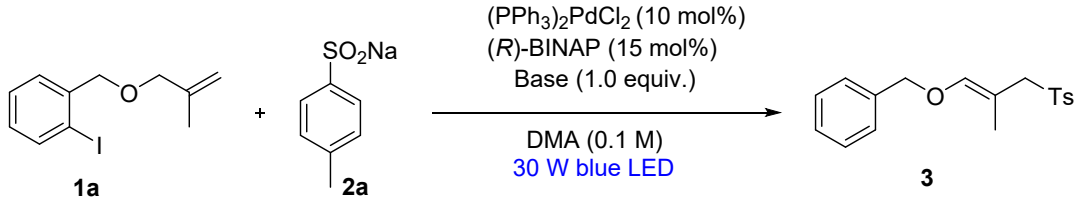


1a **2a** **3**

Entry	Pd-catalyst	Ligand	Base	Solvent	Yield (%)[b]
1	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	MeCN	16
2	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	Toluene	*trace*
3	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	DMF	*trace*
4	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	Acetone	*trace*
5	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	DMSO	*trace*
6	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	THF	27
7	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	EtOAc	*trace*
8	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	DCM	n. d.
9	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	DMA	40

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.2 mmol, 1.0 equiv.), $(PPh_3)_2PdCl_2$ (10 mol%),(*R*)-BINAP (15 mol%), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 24 h, 30 W blue LEDs; [b]Yield of the isolated product.

2) Screening of Bases[a]

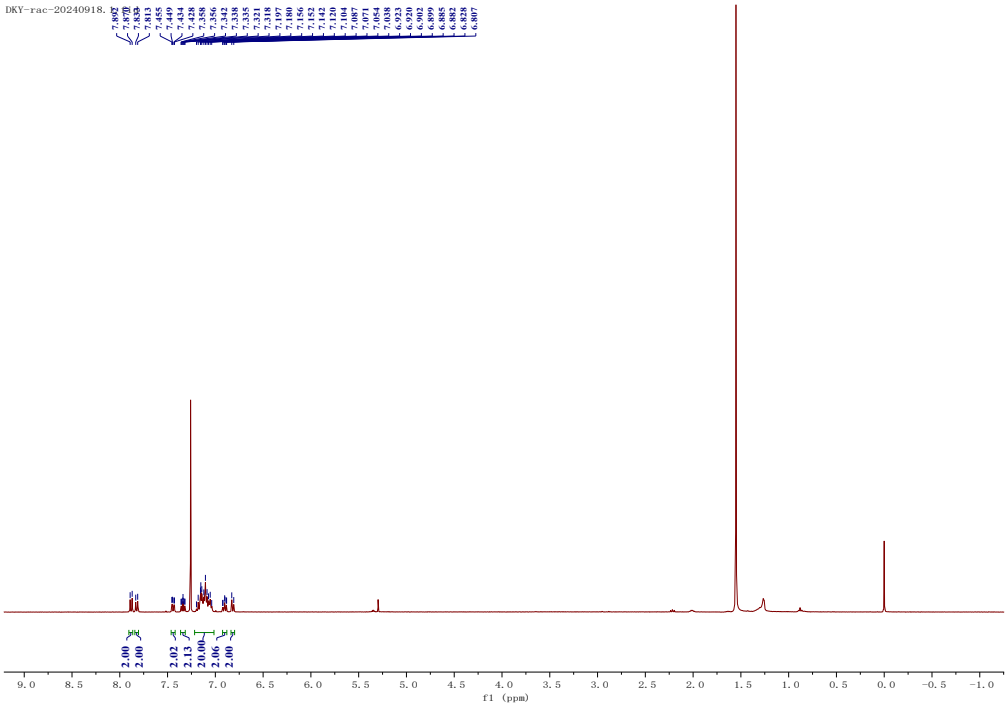


1a 2a 3

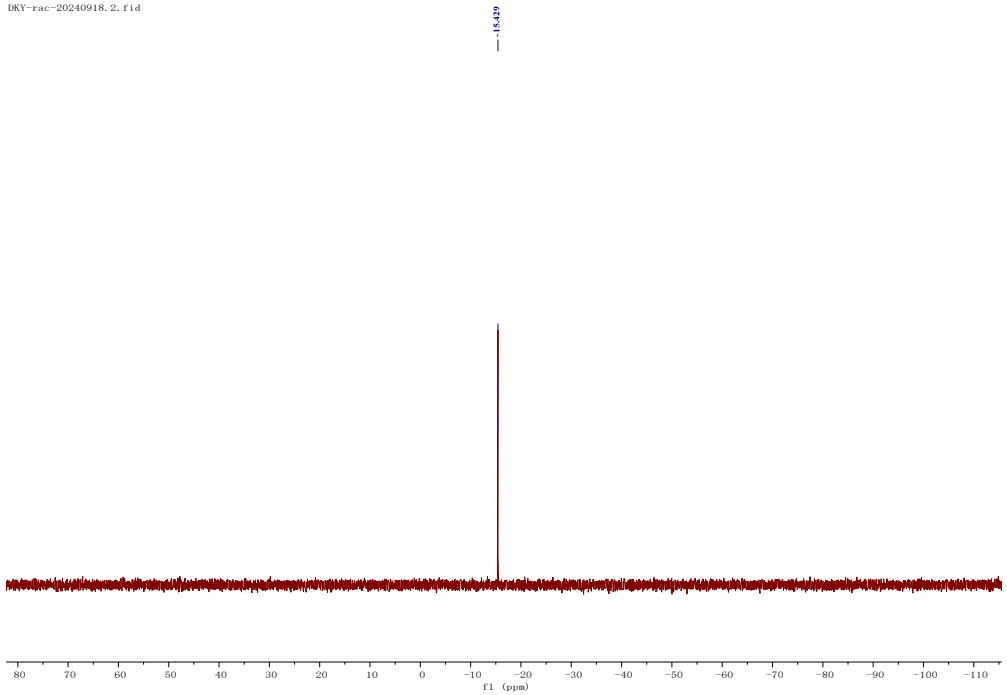
Entry	Pd-catalyst	Ligand	Base	Solvent	Yield (%)[b]
1	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	DMA	40
2	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	$CsCO_3$	DMA	16
3	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	$KHCO_3$	DMA	40
4	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	AcONa	DMA	32
5	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	DBU	DMA	11
6	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	TBAI	DMA	39
7	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	NaOH	DMA	*trace*
8	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	$K_2S_2O_5$	DMA	26
9	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	NaH_2PO_4	DMA	40
10	**$(PPh_3)_2PdCl_2$**	**(*R*)-BINAP**	**KF**	**DMA**	**62**
11[c]	-	-	KF	DMA	*trace*
12[d]	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	-	DMA	49
13[e]	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	KF	DMA	*trace*
14[f]	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	KF	DMA	*trace*
15[g]	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	KF	DMA	29
16	$(PPh_3)_2PdCl_2$	*rac*-BINAP	KF	DMA	39
17	$(PPh_3)_2PdCl_2$	*rac*-BINAP[h]	KF	DMA	37
18	$(PPh_3)_2PdCl_2$	*rac*-BINAP[i]	KF	DMA	40
19	$(PPh_3)_2PdCl_2$	(*S*)-BINAP[i]	KF	DMA	59
20	$(PPh_3)_2PdCl_2$	20 mol% *rac*-BINAP[i]	KF	DMA	38
21	$(PPh_3)_2PdCl_2$	30 mol% *rac*-BINAP[i]	KF	DMA	40
22	$(PPh_3)_2PdCl_2$	*rac*-BINAP[j]	KF	DMA	46

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.2 mmol, 1.0 equiv.), $(PPh_3)_2PdCl_2$ (10 mol%),(*R*)-BINAP (15 mol%), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 24 h, 30 W blue LEDs; [b]Yield of the isolated product; [c]no catalysts; [d]no base; [e]in the dark; [f]in the air; [g]**1a** (0.2 mmol,1.0 equiv.), **2** (0.6 mmol, 3.0 equiv.);[h]from Adamas; [i]from Energy; [j]7.5 mol%(*R*)-BINAP+7.5 mol%(*S*)-BINAP

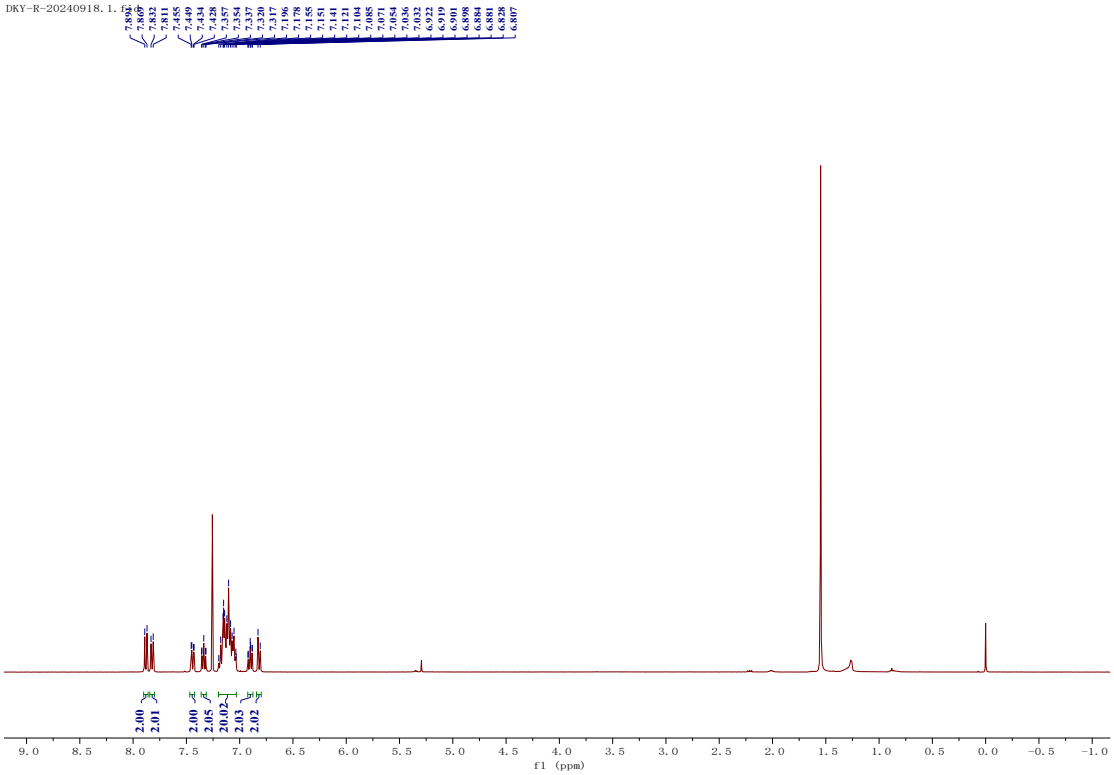
^{1}H NMR (400MHz, CDCl3) spectrum of *rac*-BINAP



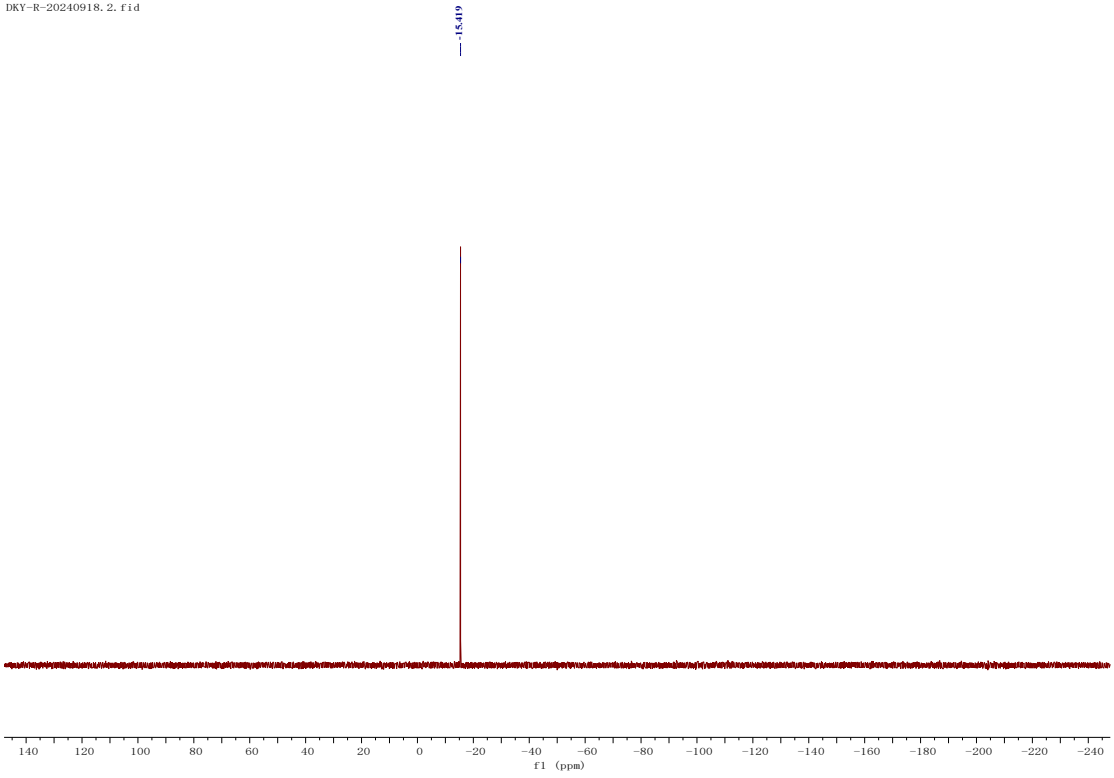
^{31}P NMR (162MHz, CDCl3) spectrum of *rac*-BINAP



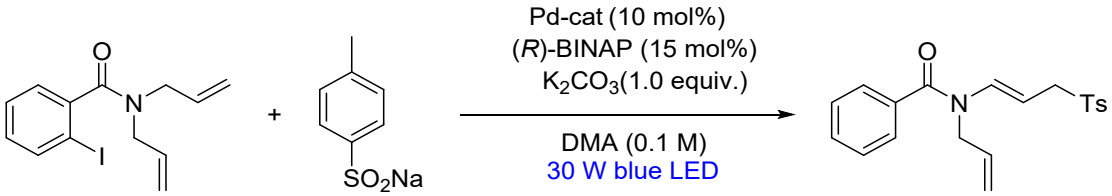
^{1}H NMR (400MHz, CDCl3) spectrum of *R*-BINAP



^{31}P NMR (162MHz, CDCl3) spectrum of *R*-BINAP



3) Screening of Pd-catalysts[a]

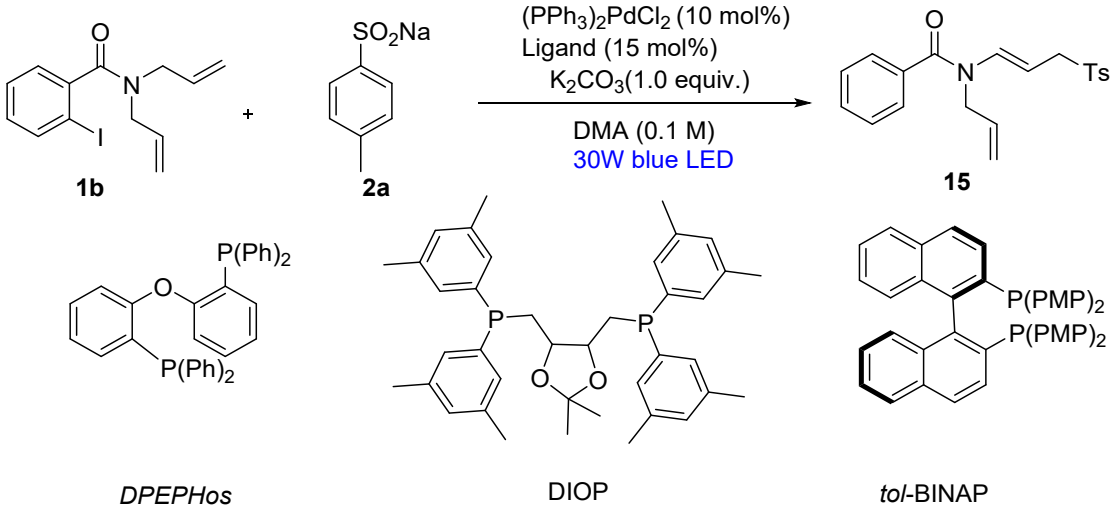


1b **2a** **15**

Entry	Pd-catalyst	Ligand	Base	Yield (%)[b]
1	$Pd(dba)_2$	(*R*)-BINAP	K_2CO_3	<10
2	$PdCl_2$	(*R*)-BINAP	K_2CO_3	23
3	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	61
4	$Pd(CN\text{-}CH_3)_2Cl_2$	(*R*)-BINAP	K_2CO_3	*trace*
5	$(PdCl\ \eta^3\text{-}C_3H_5)_2$	(*R*)-BINAP	K_2CO_3	16
6	$Pd(PPh_3)_4$	(*R*)-BINAP	K_2CO_3	48

[a]Unless otherwise noted, all reactions were carried out using **1b** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.2 mmol, 1.0 equiv.), Pd-cat (10 mol%), (*R*)-BINAP (15 mol%), DMA (2.0 mL) at ambient temperature, under Ar atmosphere for 24 h, 30 W blue LEDs; [b]Yield of the isolated product.

4) Screening of Ligands[a]

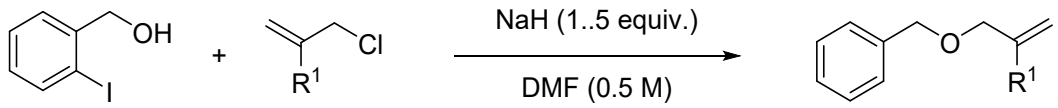


Entry	Pd-catalyst	Ligand	Base	Yield(%)[b]
1	$(PPh_3)_2PdCl_2$	*DPEPHos*	K_2CO_3	*trace*
2	$(PPh_3)_2PdCl_2$	DIOP	K_2CO_3	*trace*
3	$(PPh_3)_2PdCl_2$	*tol*-BINAP	K_2CO_3	*trace*
4	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	61
5	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	KF	32
6[c]	$(PPh_3)_2PdCl_2$	(*R*)-BINAP	K_2CO_3	15

[a]Unless otherwise noted, all reactions were carried out using **1b** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), K_2CO_3 (0.2 mmol, 1.0 equiv.), $(PPh_3)_2PdCl_2$ (10 mol%), Ligand (15 mol%), DMA (2.0 mL) at ambient temperature, under Ar atmosphere for 24 h, 30 W blue LEDs; [b]Yield of the isolated product; [c]**1b** (0.2 mmol,1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.).

3. General Procedures for the Synthesis of Compounds 1a-1e and 14

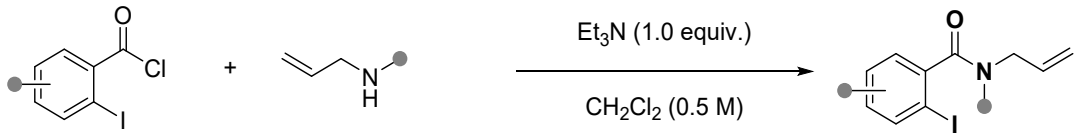
3.1 General Procedure for the Preparation of Compounds 1a-1e



1a-1e

To a two-necked flask equipped with a magnetic stirring bar, substituted or unsubstituted allyl chloride (5.0 mmol, 1.0 equiv.) and DMF (anhydrous, 0.5 M) were added under an Ar atmosphere. Then, the solution was cooled to 0 ℃ and NaH (7.5 mmol, 1.5 equiv.) stored in coal oil was added. After stirring for 30 minutes at room temperature, 2-iodobenzylalcohol (7.5 mmol, 1.5 equiv.) was added dropwise, and the mixture was stirred at room temperature overnight. Thereafter, the reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc. The combined organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the residue by column chromatography (PE/EA = 100/1) afforded the desired benzyl ether.

3.2 General Procedure for the Preparation of Compound 14

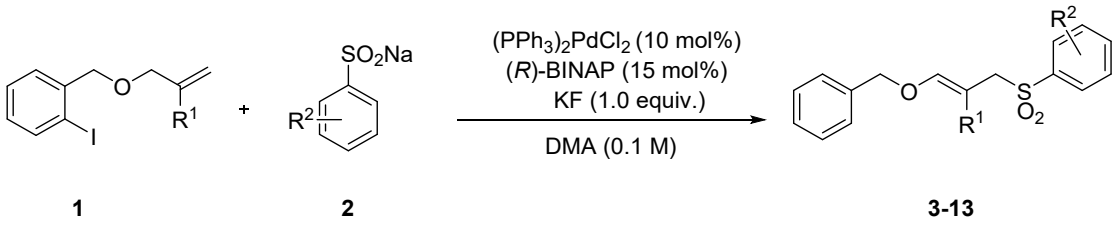


14

To a two-necked flask equipped with a magnetic stirring bar, substituted or unsubstituted allylamine (5.0 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 M) were added under an Ar atmosphere. Then, the solution was cooled to 0 ℃ and Et_3N (2.1 mL, 1.5 equiv.) stored in coal oil was added. After stirring for 30 minutes at room temperature, 2-iodobenzoyl chloride (5.5 mmol, 1.1 equiv.) was added dropwise, and the mixture was stirred at room temperature overnight. Thereafter, the reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc. The combined organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the residue by column chromatography (PE/EA = 19:1) afforded the desired *N*-allyl-acylamide.

4. General Procedure for the Preparation of Products 3-13 and 15-24

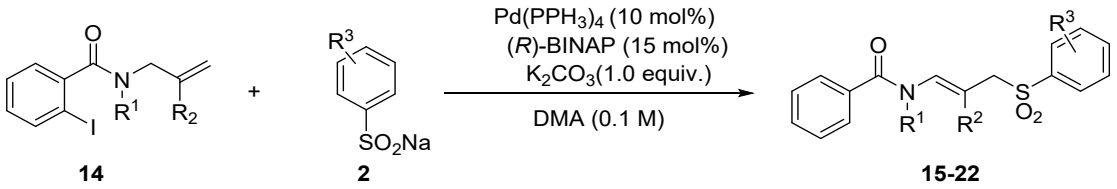
4.1 General Procedure for the Preparation of Compounds 3-13



1 **2** **3-13**

To a reaction tube equipped with a magnetic stirring bar, compound **1** (0.2 mmol, 1.0 equiv.), compound **2** (0.4 mmol, 2.0 equiv.), $(PPh_3)_2PdCl_2$ (10 mol%), (*R*)-BINAP (15 mol%), KF (0.2 mmol, 1.0 equiv.) and DMA (0.1 M) were added. The resulting mixture was charged with argon, then stirred and irradiated by a 30 W blue LED at ambient temperature for 24 h. Thereafter, the reaction was quenched with sat. aq. NaCl and extracted with EtOAc, removed under reduced pressure and then purified by column chromatography to afford the desired products **3-13**.

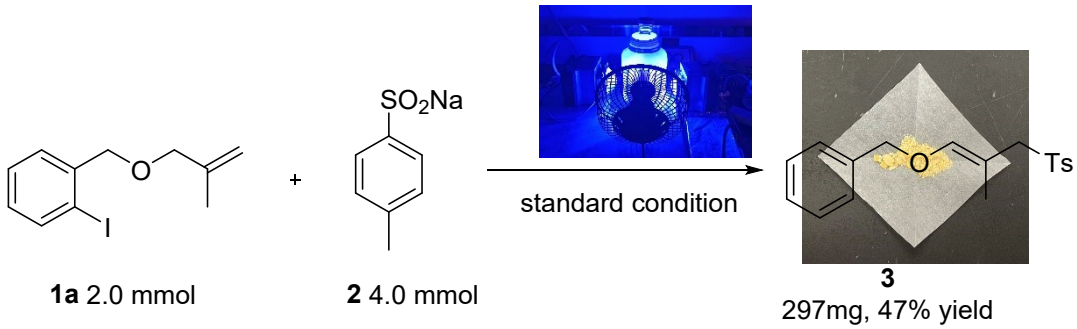
4.2 General Procedure for the Preparation of Compounds 15-24



14 **2** **15-22**

To a reaction tube equipped with a magnetic stirring bar, compound **14** (0.2 mmol, 1.0 equiv.), compound **2** (0.4 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (10 mol%), (*R*)-BINAP (15 mol%), K_2CO_3 (0.2 mmol, 1.0 equiv.) and DMA (0.1 M) were added. The resulting mixture was charged with argon, then stirred and irradiated by a 30 W blue LED at ambient temperature for 24 h. Thereafter, the reaction was quenched with sat. aq. NaCl and extracted with EtOAc, and removed under reduced pressure and then purified by column chromatography to afford the desired products **15-24**.

4.3 Scale-up Reaction

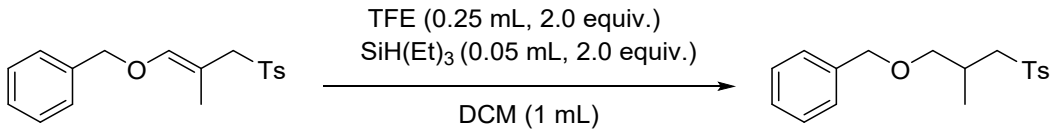


1a 2.0 mmol

2 4.0 mmol

3
297mg, 47% yield

4.4 Derivatization

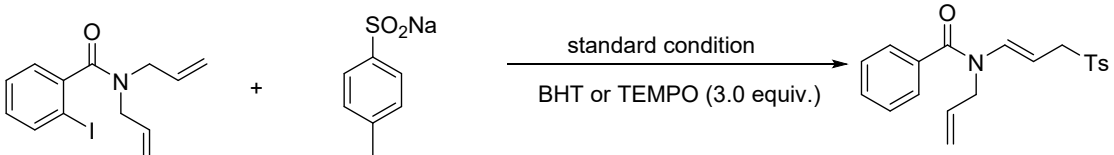


3
1.0 equiv, 0.16 mmol

3', 78%

5. Mechanistic Studies

5.1 Trapping Experiment



14 **2**

15
BHT: trace
TEMPO: trace

Radical trapping experiments between **14** and **2** were conducted under standard conditions with two trapping agents (BHT or TEMPO) to determine the putative radical. The desired product **15** was obtained trace when BHT or TEMPO was added. The corresponding coupled product between BHT/TEMPO radical and the allyl amine mixture was successfully detected by HRMS (Figure S1). HRMS (EI): $C_{28}H_{37}NNaO_2^+$, [M+Na]+ calcd: 442.2717, found: 442.2710 (BHT-adduct); HRMS (EI): $C_{22}H_{33}N_2O_2^+$, [M+Na]+ calcd: 357.2537, found: 357.2534 (TEMPO-adduct).

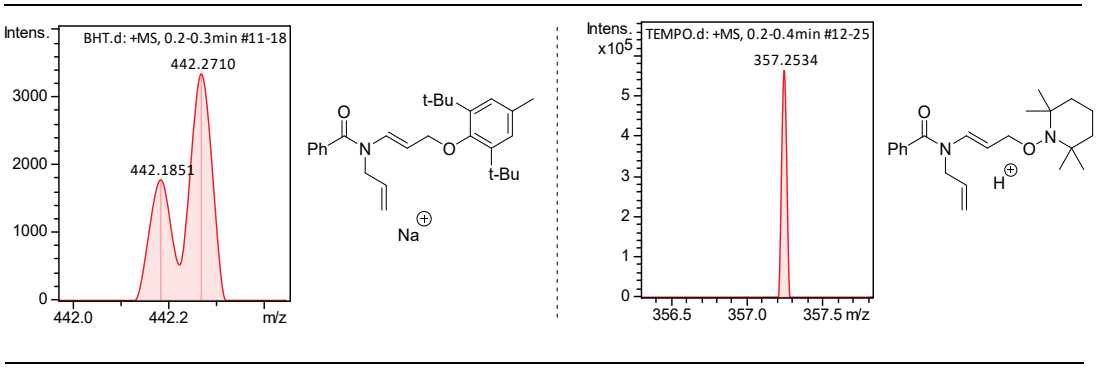


Figure S1. Crude ESI-MS of the radical-trapping experiments

5.2 UV/Vis Absorption Spectrometry

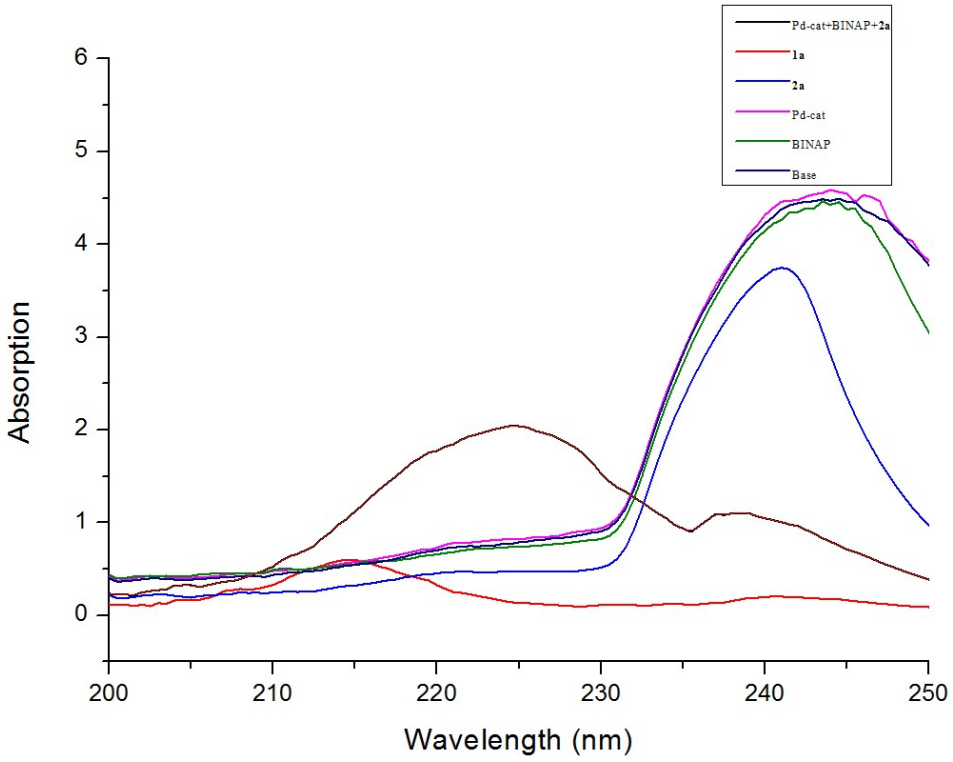
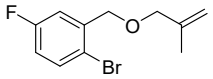


Figure S2. UV/Vis absorption spectra of **1a, 2a,** base, Pd-cat and BINAP

6. Copies of NMR Spectra

Raw material **1d** (colorless oil)



IR (neat) *v* 1283, 1158, 1097, 1026, 989, 766, 721, 624 cm^{-1};

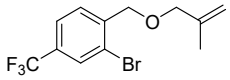
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 5.05 (s, 1H), 4.97 (s, 1H), 4.57 (s, 2H), 4.04 (s, 2H), 1.80 (s, 3H);

^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -62.59;

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 162.2 (d, $^1J_{C\text{-}F}$ = 246.4 Hz), 141.7, 140.3 (d, $^2J_{C\text{-}F}$ = 7.5 Hz), 133.5 (d, $^2J_{C\text{-}F}$ = 8.0 Hz), 115.8 (d, $^3J_{C\text{-}F}$ = 1.7 Hz), 115.5, 112.6, 74.9, 70.7, 19.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{11}H_{13}BrFO^+$ 259.0128; Found:259.0122.

Raw material **1e** (pale yellow oil)



IR (neat) *v* 1323, 1156, 1149, 1068, 975, 766, 703, 641 cm^{-1};

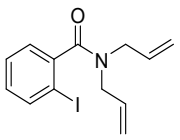
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, J = 8.7, 5.2 Hz, 1H), 7.28 (dd, J = 9.5, 3.1 Hz, 1H), 6.86 (td, J = 8.3, 3.1 Hz, 1H), 5.04 (s, 1H), 4.96 (s, 1H), 4.50 (s, 2H), 4.03 (s, 2H), 1.79 (s, 3H);

^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -114.50;

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 142.1, 141.7, 130.87 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.3 (q, $^3J_{C\text{-}F}$ = 3.9 Hz),128.7, 124.3 (q, $^3J_{C\text{-}F}$ = 3.7 Hz) 123.2 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 122.0, 112.7, 74.9, 70.7, 19.5;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{12}H_{13}BrF_3O^+$ 309.0096; Found:309.0068.

Raw material **14a** (pale yellow oil)



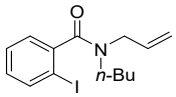
IR (neat) *v* 1390, 1128, 1054, 1001, 986, 775, 721, 662 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 7.9 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.21 (dd, J = 7.6, 1.5 Hz, 1H), 7.07 (td, J = 7.8, 1.6 Hz, 1H), 5.95 (ddt, J = 16.6, 10.1, 6.2 Hz, 1H), 5.67 (ddt, J = 16.0, 11.0, 5.7 Hz, 1H), 5.35 – 5.24 (m, 2H), 5.20 – 5.07 (m, 2H), 4.58 (d, J = 13.0 Hz, 1H), 3.78 (dd, J = 14.1, 6.4 Hz, 1H), 3.69 (t, J = 5.9 Hz, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.5, 142.2, 139.2, 132.6, 132.5, 130.2, 128.2, 127.0, 118.4, 118.2, 92.6, 50.3, 46.4;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{13}H_{14}INNaO^+$ 350.0012; Found:350.0010.

Raw material **14c** (pale yellow oil)



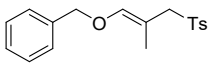
IR (neat) v 1432, 1246, 1187, 1097, 1058, 983, 755, 709, 663 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d, as a mixture of rotamers*) δ 7.88 – 7.76 (m, 1H), 7.41 – 7.33 (m, 1H), 7.24 – 7.16 (m, 1H), 7.09 – 7.03 (m, 1H), 5.97 (ddt, J = 16.6, 10.1, 6.3 Hz, 0.44H), 5.72 – 5.63 (m, 0.58H), 5.39 – 5.20 (m, 1H), 5.18 – 5.08 (m, 1H), 4.59 – 4.35 (m, 0.42H), 3.89 – 3.79 (m, 1H), 3.72 – 3.68 (m, 1H), 3.67 – 3.46 (m, 0.34H), 3.19 – 3.01 (m 1.51H), 1.77 – 1.63 (m, 1H), 1.49 – 1.38 (m, 2H), 1.15 – 1.07 (m, 1H), 0.97 (t, J = 7.3 Hz, 2H), 0.76 (t, J = 7.3 Hz, 1H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d, as a mixture of rotamers*) δ 170.5, 142.6, 139.2, 139.1, 133.1, 133.0, 130.0, 128.2, 127.2, 127.0, 118.1, 117.8, 92.7, 59.2, 51.3, 47.6, 46.9, 44.3, 30.2, 29.0, 20.4, 19.8, 13.9, 13.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{14}H_{19}INO^+$ 344.0506; Found:344.0499.

Product **3** (a pale yellow solid)



IR (neat) v 1301, 1287, 1190, 1108, 1066, 1018, 733, 681 cm^{-1};

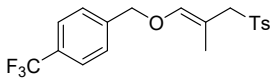
m. p. 101-102 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, J = 8.0 Hz, 2H), 7.41–7.17 (m, 7H), 5.83 (s, 1H), 4.71 (s, 2H), 3.58 (s, 2H), 2.42 (s, 3H), 1.69 (s, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 148.2, 144.4, 137.1, 135.6, 129.5, 128.6, 128.0, 127.2, 102.6, 74.0, 62.2, 21.7, 13.9;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{18}H_{20}KO_4S^+$ 333.1155; Found:333.1140.

Product **4** (yellow oil)



IR (neat) *v* 1310, 1254, 1190, 1083, 1059, 994, 749, 683 cm^{-1};

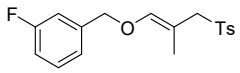
^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 5.86 (s, 1H), 4.78 (s, 2H), 3.59 (s, 2H), 2.42 (s, 3H), 1.71 (s, 3H);

$^{19}F\{^1H\}$ NMR (376 MHz, Chloroform-*d*) δ -62.61;

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 147.9, 144.5, 141.2, 135.7, 130.1(d, $^2J_{C\text{-}F}$ =44.9), 129.6, 128.5, 127.1, 125.5(q, $^4J_{C\text{-}F}$=3.81), 103.4, 73.1, 62.0, 21.6, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{19}H_{19}F_3NaO_3^+$ 407.0899; Found:407.0877.

Product **5** (yellow oil)



IR (neat) *v* 1306, 1279, 1196, 1096, 1053, 987, 740, 663 cm^{-1};

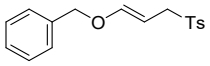
^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.62 (m, 2H), 7.33 – 7.25 (m, 3H), 7.02 – 6.97 (m, 2H), 6.93 (dt, J = 9.5, 2.1 Hz, 1H), 5.82 (s, 1H), 4.70 (s, 2H), 3.59 (s, 2H), 2.42 (s, 3H), 1.69 (d, J = 1.2 Hz, 3H);

$^{19}F\{^1H\}$ NMR (376 MHz, Chloroform-*d*) δ -112.64;

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 162.9 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 147.9, 144.4, 139.7 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 135.6, 130.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.6, 128.5, 122.5 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 114.9 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 113.9 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 103.2, 73.1 (d, $^4J_{C\text{-}F}$ = 2.0 Hz), 62.1, 21.6, 13.9;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{20}FO_3S^+$ 335.1122; Found: 335.1109.

Product **6** (a pale yellow solid)



m. p. 97-98 ℃;

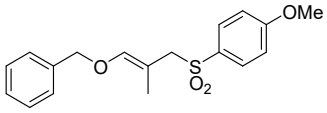
IR (neat) *v* 1190, 1108, 1066, 1018, 975, 787, 733, 681 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 7.8 Hz, 2H), 7.39 – 7.25 (m, 7H), 6.32 (d, J = 12.7 Hz, 1H), 4.82 – 4.73 (m, 1H), 4.75 (s, 2H), 3.64 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 153.1, 144.5, 136.1, 135.3, 129.7, 128.6, 128.6, 128.2, 127.5, 91.2, 71.5, 56.7, 21.6;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{17}H_{18}KO_3S^+$ 333.1155; Found:333.1140.

Product **7** (a white solid)



m. p. 101-102 ℃;

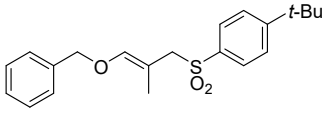
IR (neat) *v* 1309, 1297, 1185, 1042, 1018,975, 733, 681 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.8 Hz, 2H), 7.39 – 7.20 (m, 5H), 7.05 – 6.83 (m, 2H),5.84 (s, 1H), 4.72 (s, 2H), 3.86 (s, 3H), 3.58 (s, 2H), 1.68 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.6, 148.1, 137.1, 130.7, 130.1, 128.5, 128.0, 127.2, 114.1, 102.8, 74.0, 62.3, 55.6, 13.9;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{21}O_4S^+$ 333.1155; Found:333.1152.

Product **8** (a white solid)



m. p. 107-108 ℃;

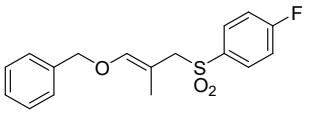
IR (neat) *v* 1306, 1190, 1094, 1032, 964, 745, 697, 662cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 2H), 7.52 – 7.47 (m, 2H), 7.38 – 7.30 (m, 3H), 7.26 – 7.23 (m, 2H), 5.84 (s, 1H), 4.69 (s, 2H), 3.59 (s, 2H), 1.70 (d, J = 1.5 Hz, 3H), 1.33 (s, 9H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 157.4, 148.2, 137.1, 135.6, 128.6, 128.4, 128.1, 127.2, 125.9, 102.6, 74.0, 62.1, 35.2, 31.1, 13.9;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{21}H_{27}O_3S^+$ 359.1675; Found: 359.1678.

Product **9** (colorless oil)



IR (neat) ν 1302, 1279, 1156, 1077, 1018, 966, 733, 681 cm^{-1};

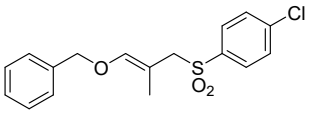
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.69 (m, 2H), 7.41 – 7.29 (m, 3H), 7.21 (dd, J = 7.4, 2.1 Hz, 2H), 7.16 – 7.04 (m, 2H), 5.79 (q, J = 1.2 Hz, 1H), 4.71 (s, 2H), 3.59 (s, 2H), 1.70 (s, 3H);

^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -103.69;

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 165.7 (d, $^1J_{C\text{-}F}$ = 255.9 Hz), 148.3, 136.9, 134.3, 131.3 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 128.6, 128.2, 127.3, 116.2 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 102.4, 74.1, 62.3, 13.8;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{17}H_{17}FKO_3S^+$ 359.0514; Found:359.0486.

Product **10** (a white solid)



m. p. 89-91 ℃;

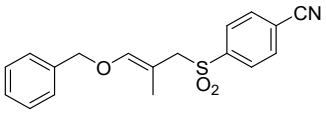
IR (neat) ν 1311, 1267, 1174, 1102, 992, 785, 733, 681 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.64 (m, 2H), 7.44 – 7.31 (m, 5H), 7.22 (d, J = 2.1 Hz, 2H), 5.80 (s, 1H), 4.72 (s, 2H), 3.60 (s, 2H), 1.71 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 148.3, 140.2, 136.9, 136.7, 130.0, 129.2, 128.6, 128.2, 127.3, 102.3, 74.1, 62.2, 13.8;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{17}H_{17}ClNaO_4S^+$ 359.0479; Found:359.0477.

Product **11** (yellow oil)



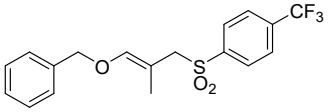
IR (neat) *v* 1301, 1290, 1186, 1103, 1054, 989, 733, 681 cm^{-1};

^{1}H NMR (400 MHz, Acetone-*d*6) δ 8.01 – 7.93 (m, 4H), 7.41 – 7.33 (m, 3H), 7.28 – 7.20 (m, 2H), 5.98 (d, *J* = 1.7 Hz, 1H), 4.74 (s, 2H), 3.87 (s, 2H), 1.72 (d, *J* = 1.3 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Acetone-*d*6) δ 149.0, 142.8, 137.5, 132.8, 129.2, 128.5, 127.9, 127.3, 117.3, 116.8, 101.6, 73.6, 60.8, 12.9;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{18}NO_3S^+$ 328.1102; Found: 328.1090.

Product **12** (yellow oil)



IR (neat) *v* 1303, 1283, 1122, 1091, 1037,991, 733, 681 cm^{-1};

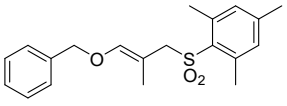
^{1}H NMR (400 MHz, Acetone-*d*6) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.25 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.02 (q, *J* = 1.2 Hz, 1H), 4.73 (s, 2H), 3.87 (s, 2H), 1.72 (s, 3H);

^{19}F{^{1}H} NMR (376 MHz, Acetone-*d*6) δ -63.091;

^{13}C{^{1}H} NMR (100 MHz, Acetone-*d*6) δ148.9, 142.9, 137.5, 134.2 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.4, 128.4, 127.9, 127.2, 126.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 101.8, 73.6, 60.9, 13.0;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{18}F_3O_3S^+$ 371.0923; Found:371.0925.

Product **13** (a white solid)



m. p. 103-104 ℃;

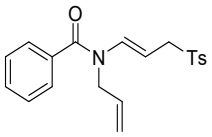
IR (neat) *v* 1317, 1296, 1277, 1180, 1104, 1018, 733, 681 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 3H), 7.25 – 7.20 (m, 2H), 6.90 (s, 2H), 5.86 (d, *J* = 1.6 Hz, 1H), 4.71 (s, 2H), 3.59 (s, 2H), 2.60 (s, 6H), 2.29 (s, 3H), 1.69 (d, *J* = 1.3 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 148.0, 143.0, 140.4, 137.1, 132.7, 132.0, 128.5, 128.0, 127.3, 102.2, 74.0, 61.6, 23.0, 21.0, 14.2;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{20}H_{25}O_3S^+$ 345.1519; Found: 345.1501.

Product **15** (yellow oil)



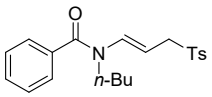
IR (neat) *v* 1636, 1586, 1318, 1144, 1064, 951, 797, 693 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.24 (m, 7H), 6.60 (s, 1H), 5.80 (ddt, J = 15.6, 10.1, 4.9 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.96 (dt, *J* = 14.7, 7.8 Hz, 1H), 4.34 (s, 2H), 3.67 (d, *J* = 7.8 Hz, 2H), 2.48 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 144.8, 135.3, 134.3, 131.6, 130.8, 129.7, 128.6, 128.4, 127.8, 58.6, 21.7;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{21}O_4S^+$ 356.1315; Found: 356.1318.

Product **16** (yellow oil)



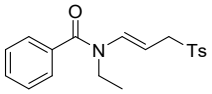
IR (neat) *v* 1441 1306,1253, 1144, 1025, 978, 766, 632 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.455 – 7.31 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 4.91 (dt, *J* = 14.8, 7.7 Hz, 1H), 3.85 – 3.57 (m, 4H), 2.49 (s, 3H), 1.60 (p, *J* = 7.3 Hz, 2H), 1.40 – 1.30 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H);

^{13}C{1H} NMR (100 MHz, Chloroform-*d*) δ 170.2, 144.7, 135.3, 134.6, 130.6, 129.7, 128.6, 128.4, 127.9, 95.1, 58.7, 43.3, 28.8, 21.7, 20.2, 13.8;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{21}H_{25}KNO_3S^+$ 410.1187; Found: 410.1157.

Product **17** (yellow oil)



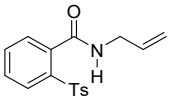
IR (neat) *v* 1498, 1322, 1163, 1070, 991, 886, 754, 663 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.38 – 7.32 (m, 4H), 7.21 (d, *J* = 7.7 Hz, 2H), 6.49 (s, 1H), 4.95 (dt, *J* = 14.8, 7.8 Hz, 1H), 3.77 (q, *J* = 7.3, 6.9 Hz, 2H), 3.67 (d, *J* = 7.7 Hz, 2H), 2.49 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ170.0, 144.8, 135.3, 134.6, 130.6, 129.8, 128.6, 128.4, 127.8, 95.1, 58.7, 38.6, 21.7, 12.0;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{19}H_{22}NO_3S^+$ 344.1315; Found: 344.1307.

Product **18** (yellow oil)



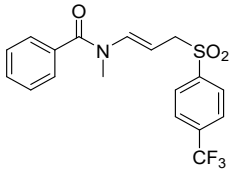
IR (neat) *v* 1620, 1589, 1325, 1163, 1058, 972, 763, 645 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.60 – 7.46 (m, 3H), 7.27 (d, *J* = 5.5 Hz, 2H), 6.32 (s, 1H), 5.97 (ddt, *J* = 16.4, 11.0, 5.8 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.05 (t, *J* = 5.9 Hz, 2H), 2.39 (s, 3H);

^{13}C{1H} NMR (100 MHz, Chloroform-*d*) δ 167.5, 144.5, 138.6, 137.7, 136.7, 133.5, 133.3, 130.01, 129.7, 129.5, 129.4, 128.2, 117.1, 42.8, 21.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{17}H_{18}O_3S^+$ 316.1002; Found: 316.0990.

Product **19** (yellow oil)



IR (neat) *v* 1457, 1318, 1265, 1124, 1058, 972, 763, 662 cm^{-1};

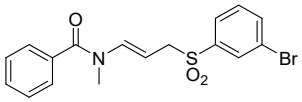
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.27 (m, 5H), 6.75 (s, 1H), 4.94 (dt, *J* = 14.6, 7.7 Hz, 1H), 3.76 (d, *J* = 7.8 Hz, 2H), 3.21 (s, 3H);

^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -63.12;

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.3, 142.0, 135.4, 134.2, 130.8, 130.8, 130.2, 129.2, 128.56, 127.9, 126.3 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.1 (q, $^{1}J_{C\text{-}F}$ = 273.1 Hz), 94.1, 58.4;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{17}F_3NO_3S^+$ 384.0876; Found: 384.0846.

Product **20** (yellow oil)



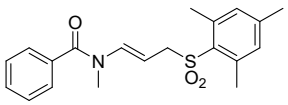
IR (neat)*v* 1436, 1327, 1129, 1025, 938, 792, 776, 683 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.72 – 7.67 (m, 1H), 7.58 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.48 – 7.34 (m, 4H), 6.69 (s, 1H), 4.99 – 4.92 (m, 1H), 3.72 (s, 2H), 3.21 (s, 3H);

^{13}C{1H} NMR (100 MHz, Chloroform-*d*) δ 170.3, 138.4, 136.8, 134.3, 133.8, 130.7, 129.2, 128.6, 128.5, 128.0, 58.4, 29.7;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{17}H_{16}BrNNaO_3S^+$ 415.9926; Found:415.9917.

Product **21** (a white solid)



m. p. 106-107 ℃;

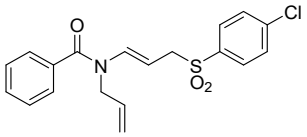
IR (neat) *v* 1448, 1329, 1137, 1064, 951, 797, 754, 693 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.27 – 7.20 (m, 2H), 6.98 (s, 2H), 6.72 (s, 1H), 5.03 – 4.96 (m, 1H), 3.72 (s, 2H), 3.19 (s, 3H), 2.62 (s, 6H), 2.34 (s, 3H);

^{13}C{1H} NMR (100 MHz, Chloroform-*d*) δ 170.3, 143.4, 140.3, 134.3, 132.2, 130.7, 128.4, 128.0, 58.2, 23.1, 21.1.;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{20}H_{24}NO_3S^+$ 358.1471; Found: 358.1465.

Product **22** (yellow oil)



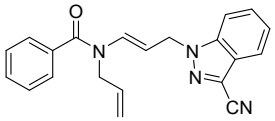
IR (neat) v 1640, 1577, 1309, 1152, 1048, 929, 786, 662 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.80 (m, 2H), 7.73 – 7.66 (m, 1H), 7.57 (t, J = 8.5 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.36 (t, J = 8.5 Hz, 2H), 7.28 (s, 1H), 6.63 (s, 1H), 5.80 (ddt, J = 17.2, 10.1, 4.9 Hz, 1H), 5.26 (d, J = 10.5 Hz, 1H), 5.16 (d, J = 17.3 Hz, 1H), 4.95 (dt, J = 14.8, 7.7 Hz, 1H), 4.34 (s, 2H), 3.69 (d, J = 7.7 Hz, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 138.3, 133.8, 131.6, 130.8, 129.1, 128.6, 128.5, 117.1, 58.6;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{19}H_{22}ClNNaO_3S^+$ 398.0588; Found: 398.0601.

Product **23** (yellow oil)



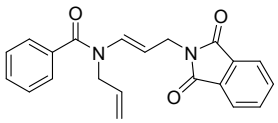
IR (neat) v 1639, 1218, 1085, 950, 769, 746, 720, 699 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.2 Hz, 1H), 7.52 – 7.34 (m, 8H), 6.81 (s, 1H), 5.82 – 5.73 (m, 1H), 5.31 – 5.24 (m, 1H), 5.20 – 5.14 (m, 2H), 5.02 (s, 2H), 4.31 (s, 2H);

^{13}C NMR {1H} (100 MHz, Chloroform-*d*) δ 170.4, 139.2, 134.6, 131.6, 130.7, 128.5, 127.8, 126.9, 125.7, 123.7, 119.8, 117.9, 117.1, 113.5, 110.3, 50.7, 42.5;

HRMS (ESI) m/z: [M+H]+ Calcd for: $C_{21}H_{19}N_4O^+$ 343.1553; Found: 343.1526

Product **24** (yellow oil)



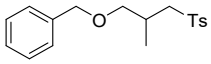
IR (neat) *v* 1699, 1345, 1127, 1064, 989, 768, 681, 633cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.76 – 7.67 (m, 2H), 7.54 – 7.36 (m, 5H), 6.89 (s, 1H), 5.80 (ddt, *J* = 15.0, 9.8, 4.4 Hz, 1H), 5.28 – 5.02 (m, 3H), 4.34 (s, 2H), 4.20 (s, 2H);

^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 170.2, 167.8, 134.8, 134.0, 132.1, 131.9, 130.5, 128.4, 128.1, 123.3, 116.9, 37.9, 29.7;

HRMS (ESI) m/z: [M+H]+ Calcd for: $C_{21}H_{19}N_2O_3^+$ 347.1390; Found: 347.1367

Product **3'** (white oil)



IR (neat) *v* 1603, 1288, 1145, 1021, 991, 751, 667, 631cm^{-1};

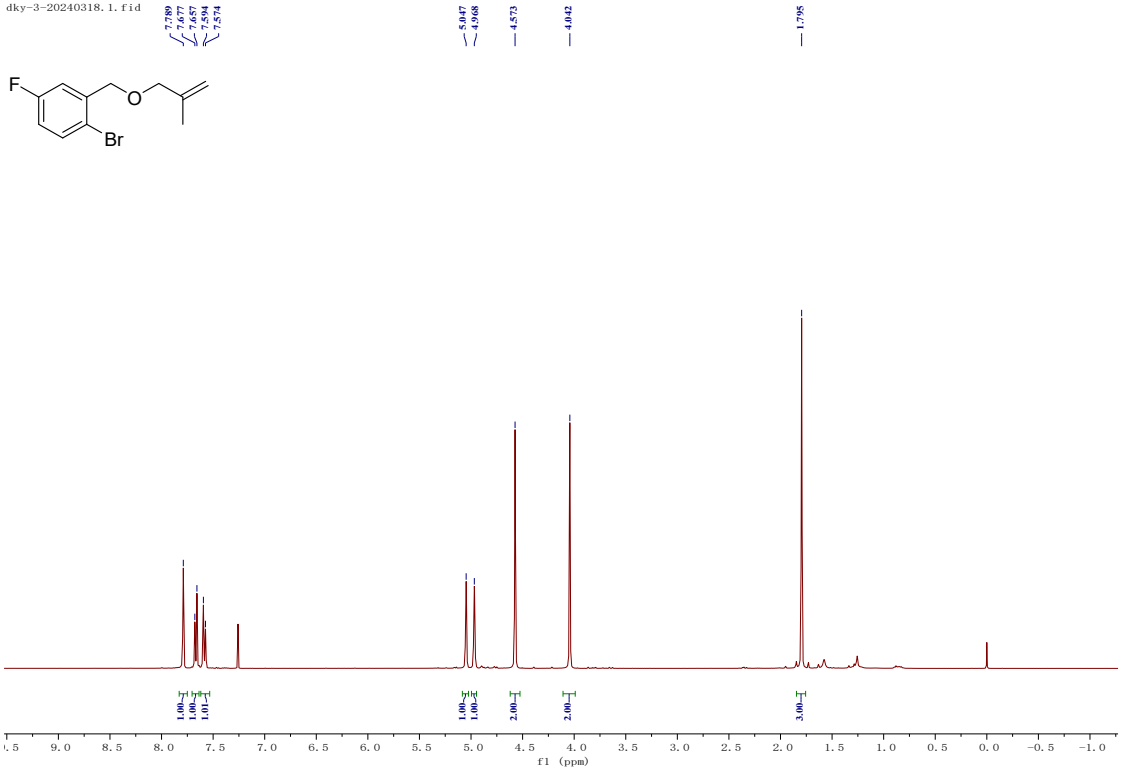
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.25 (m, 7H), 4.44 (s, 2H), 3.47 – 3.38 (m, 2H), 3.33 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.94 (dd, *J* = 14.2, 7.9 Hz, 1H), 2.46 (s, 3H), 2.44 – 2.34 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 144.5, 138.1, 137.1, 129.9, 128.4, 127.9, 127.7, 127.5, 73.6, 72.9, 59.4, 29.5, 21.7, 17.2;

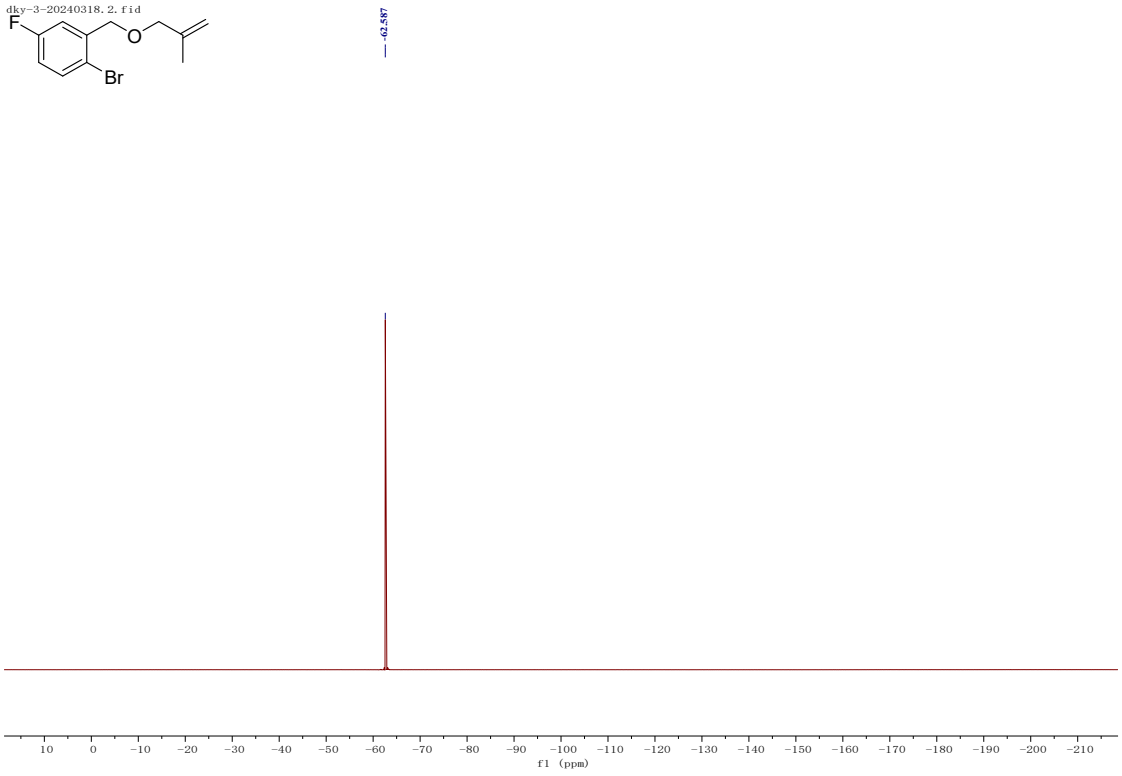
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{23}O_3S^+$ 319.1362; Found: 319.1359.

7. NMR Spectra of Compounds of 1d-1e, 14a, 14c, 3-13, 15-24, 3’

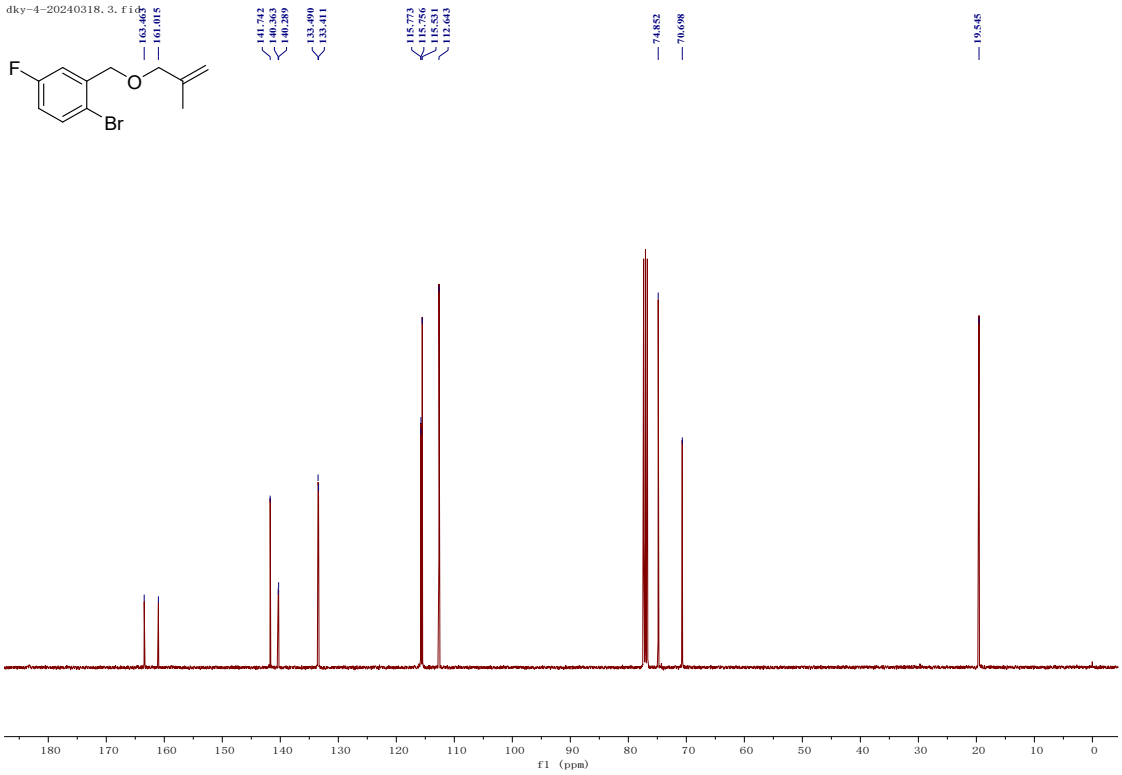
^{1}H NMR (400MHz, $CDCl_3$) spectrum of raw material 1d



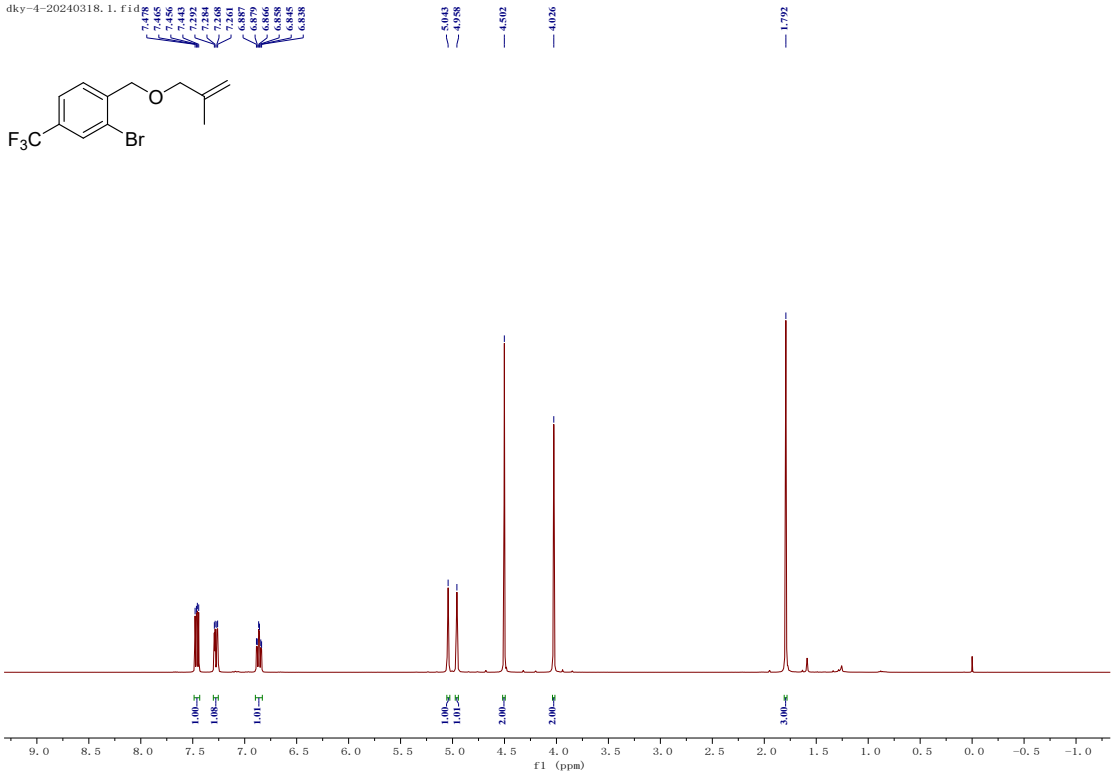
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 1d


dky-3-20240318_2.fid
F
O
Br
-62.587
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

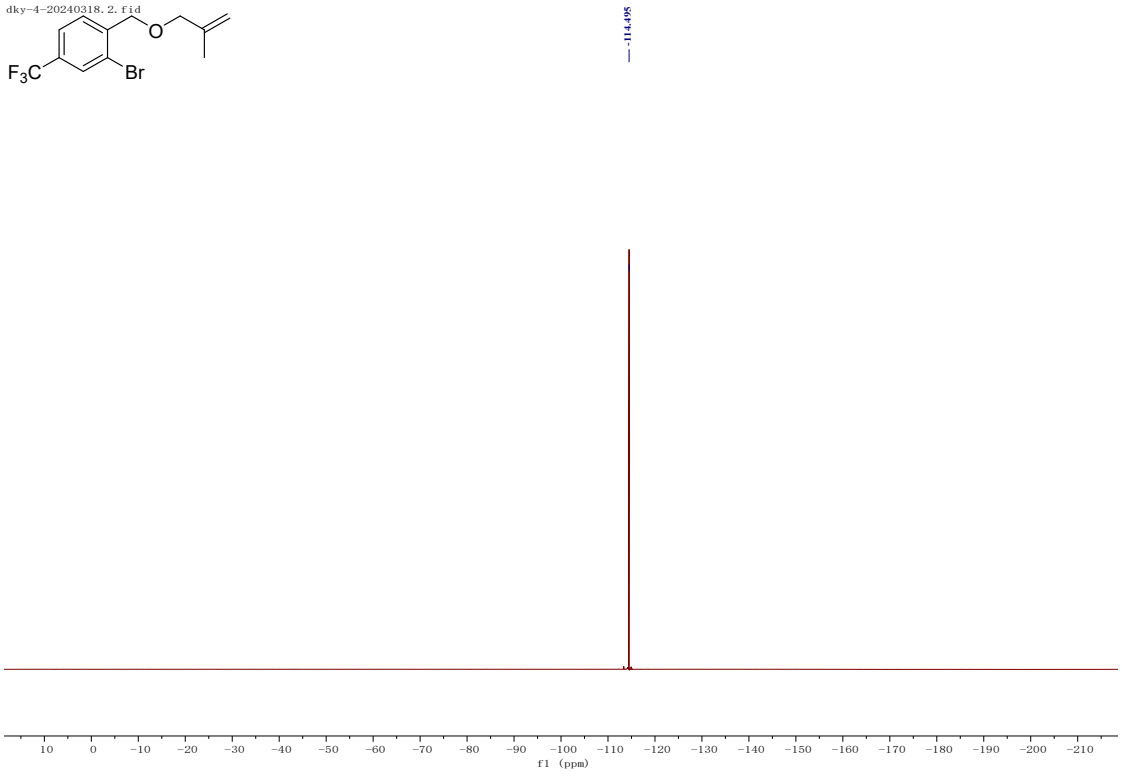
^{13}C NMR (400MHz, $CDCl_3$) spectrum of raw material 1d



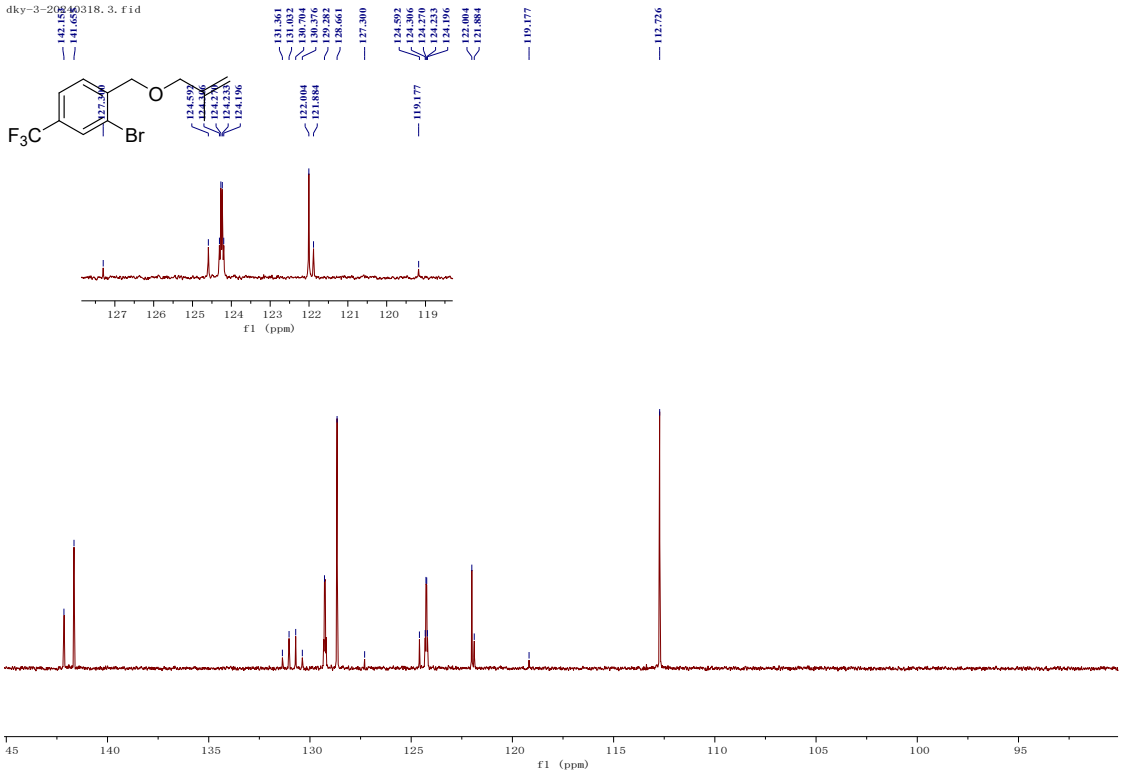
^{1}H NMR (400MHz, $CDCl_3$) spectrum of raw material 1e



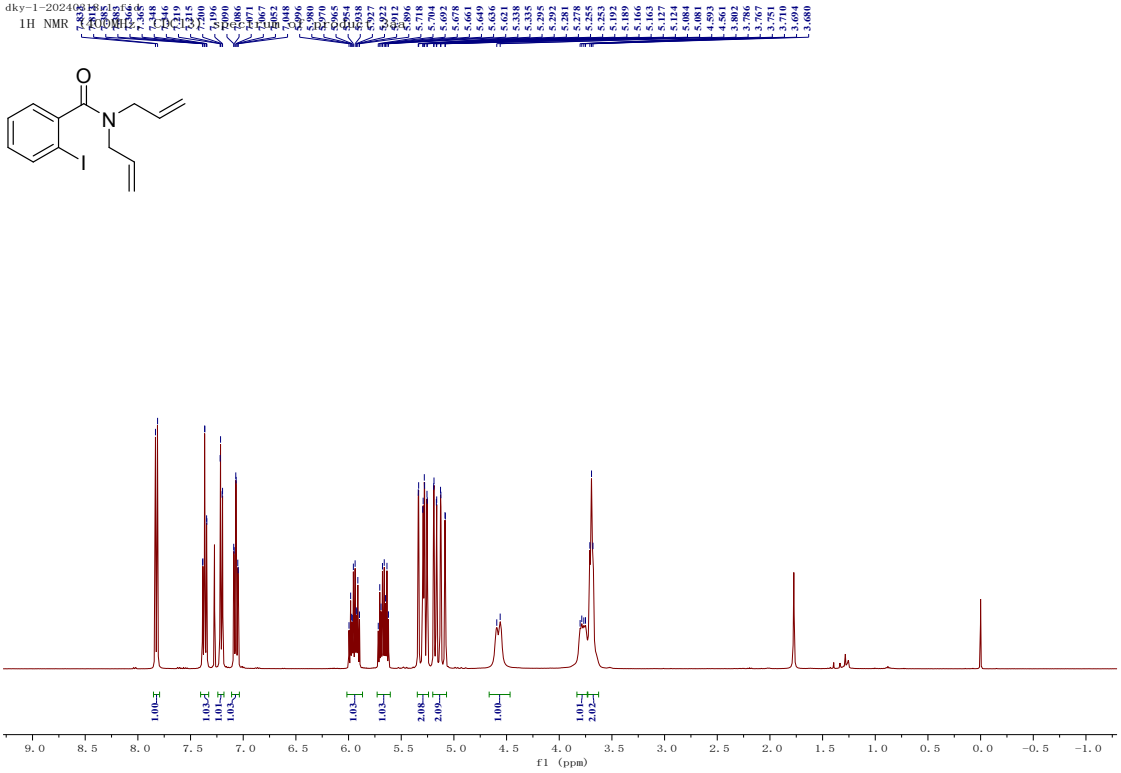
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 1e



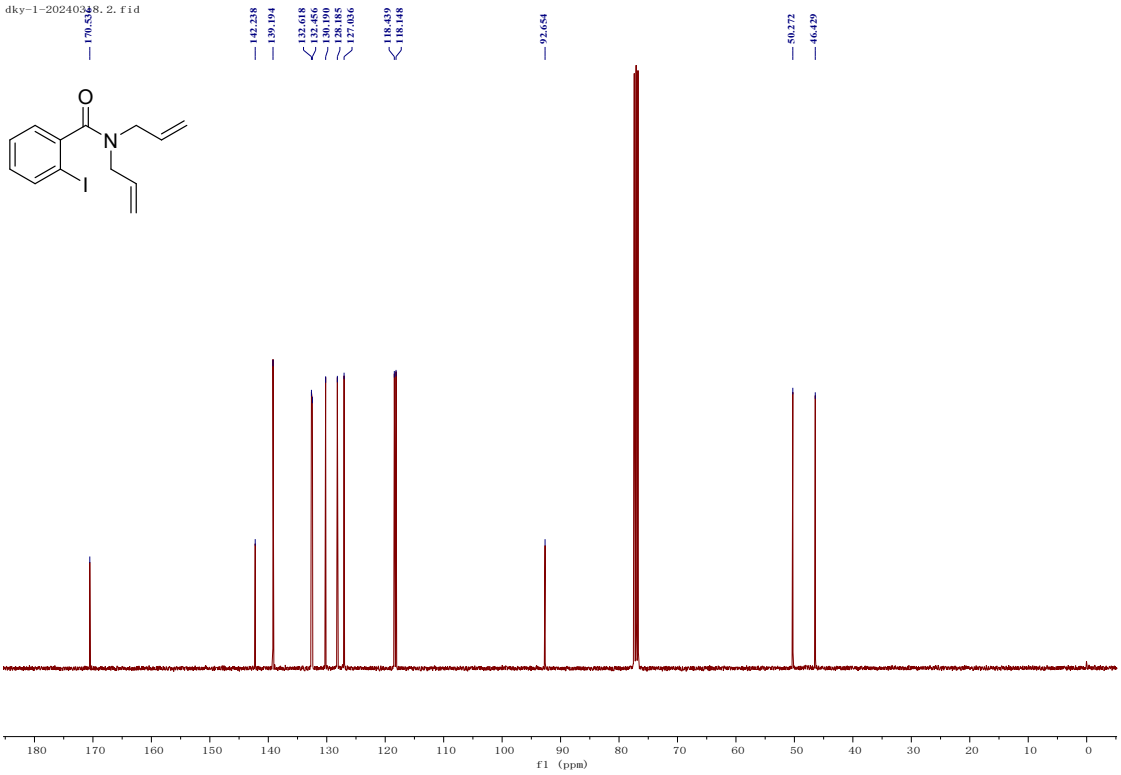
^{13}C NMR (400MHz, $CDCl_3$) spectrum of raw material 1e



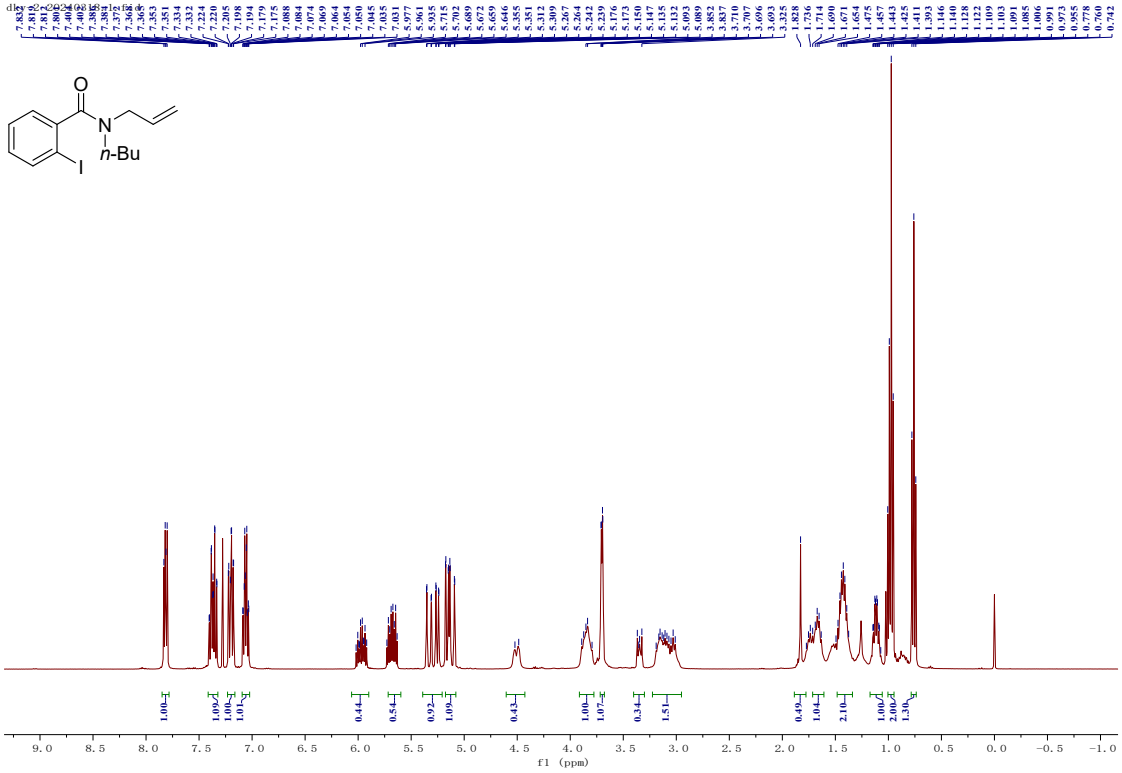
^{1}H NMR (400MHz, $CDCl_3$) spectrum of raw material 14a



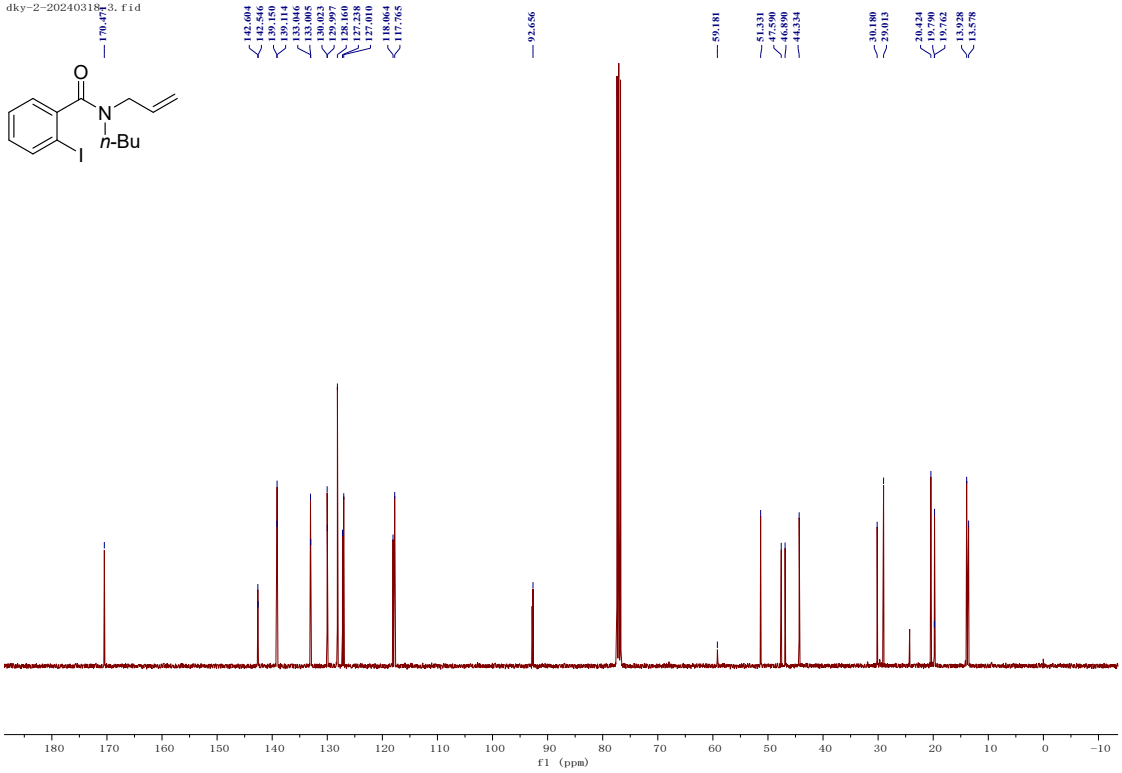
^{13}C NMR (400MHz, $CDCl_3$) spectrum of raw material 14a



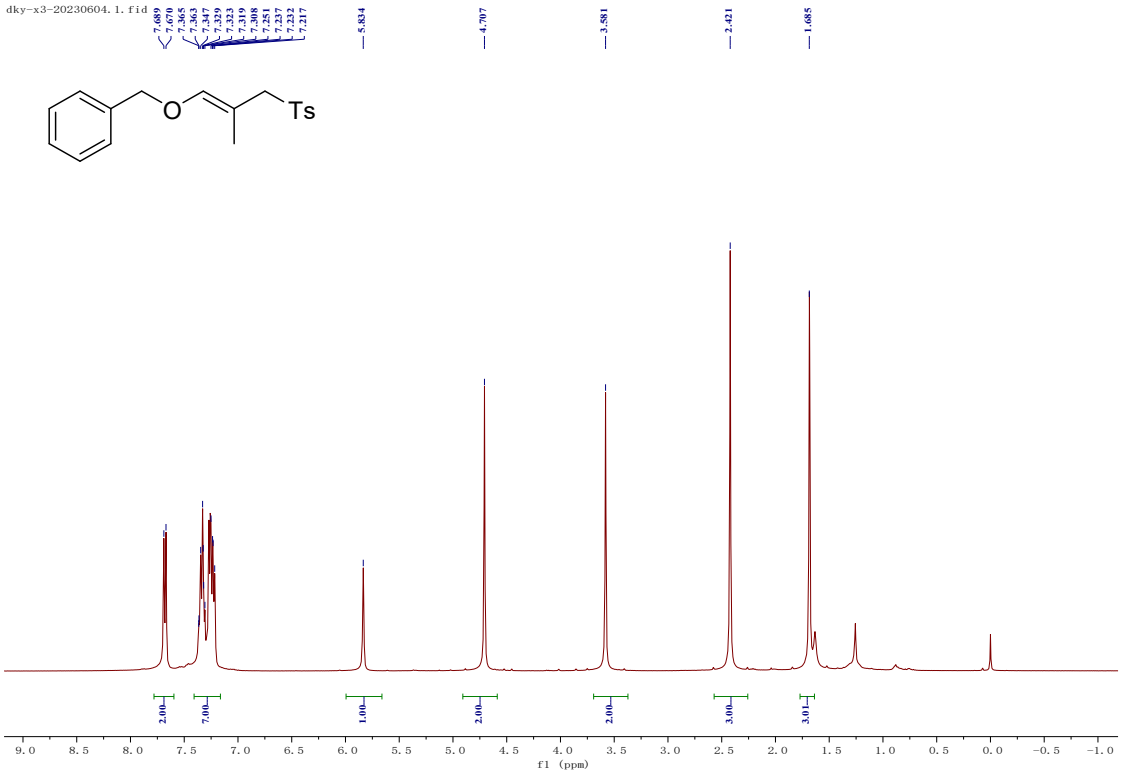
^{1}H NMR (400MHz, $CDCl_3$) spectrum of raw material 14c



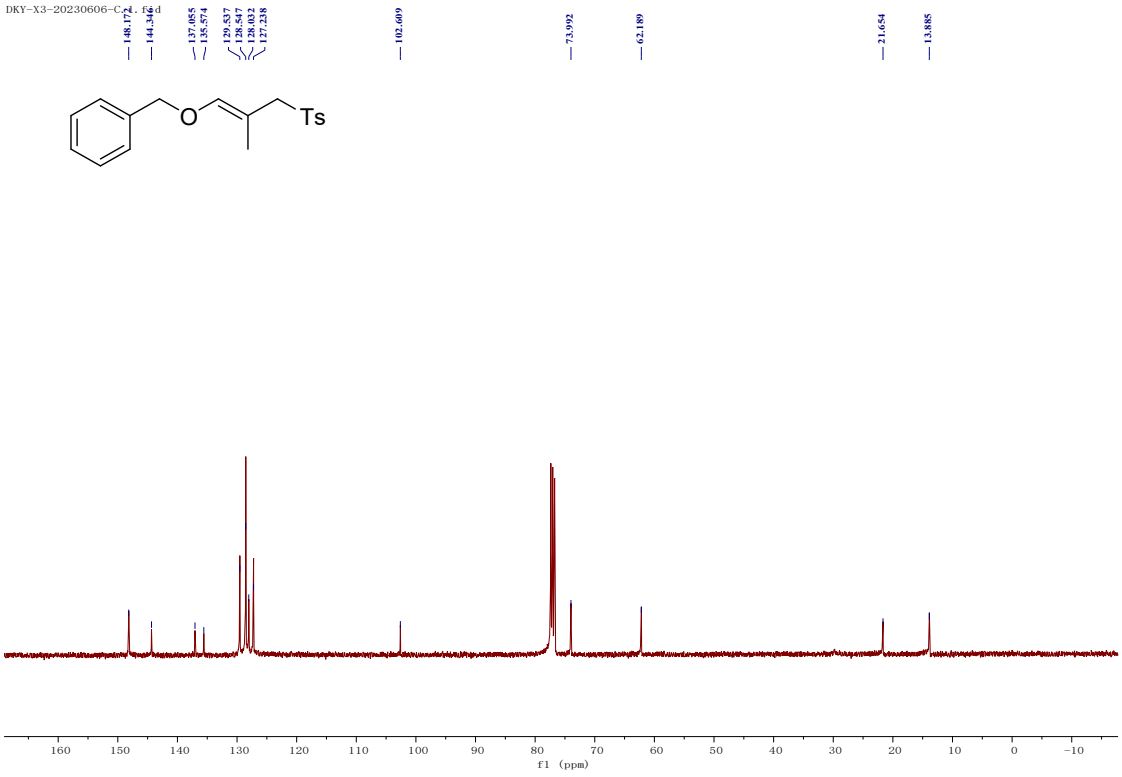
^{13}C NMR (400MHz, $CDCl_3$) spectrum of raw material 14c



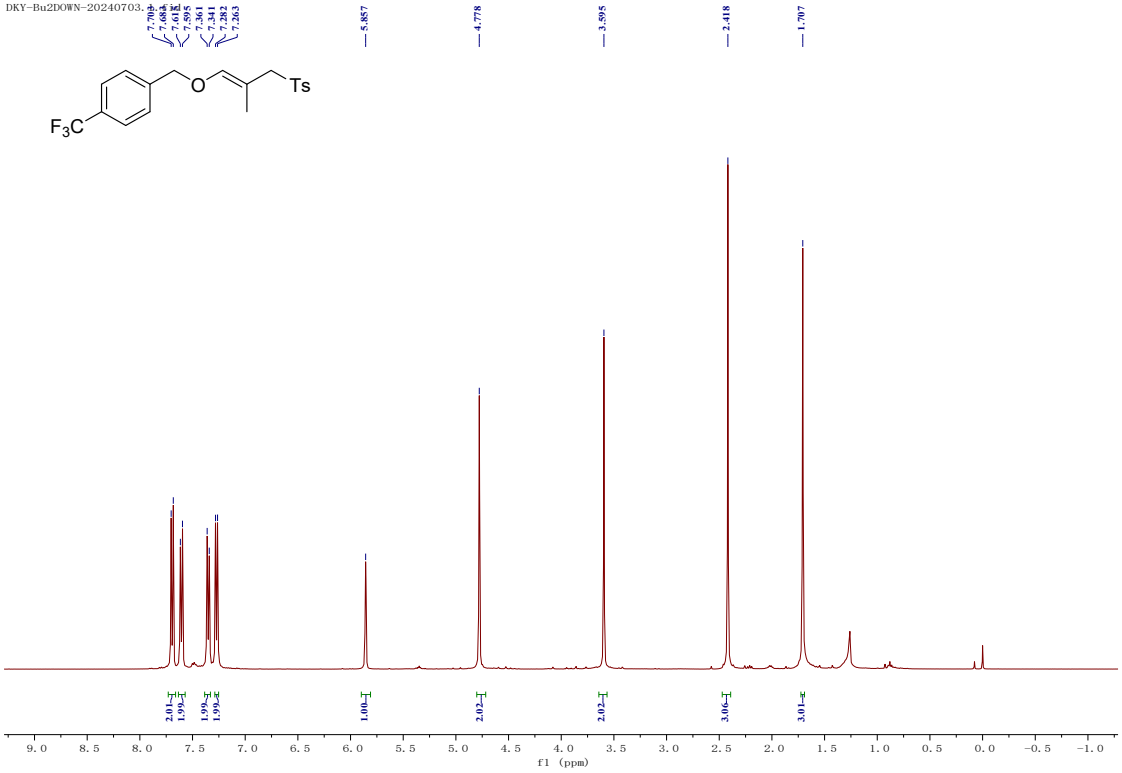
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3



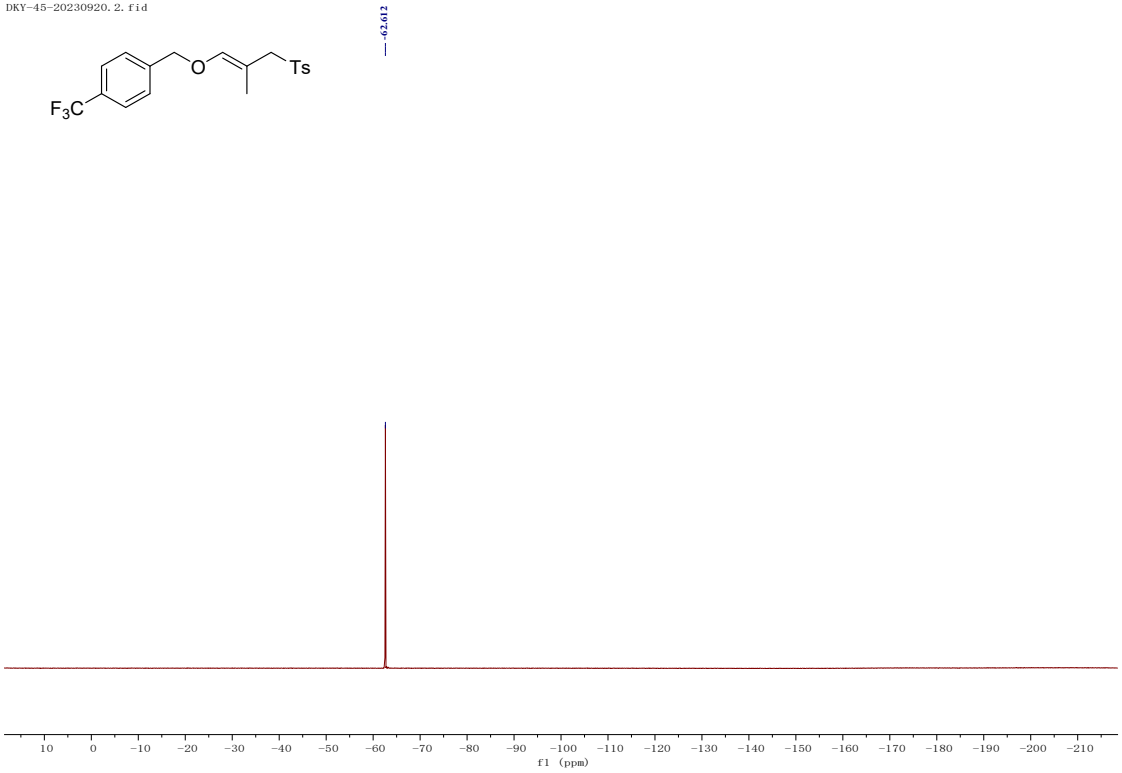
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3



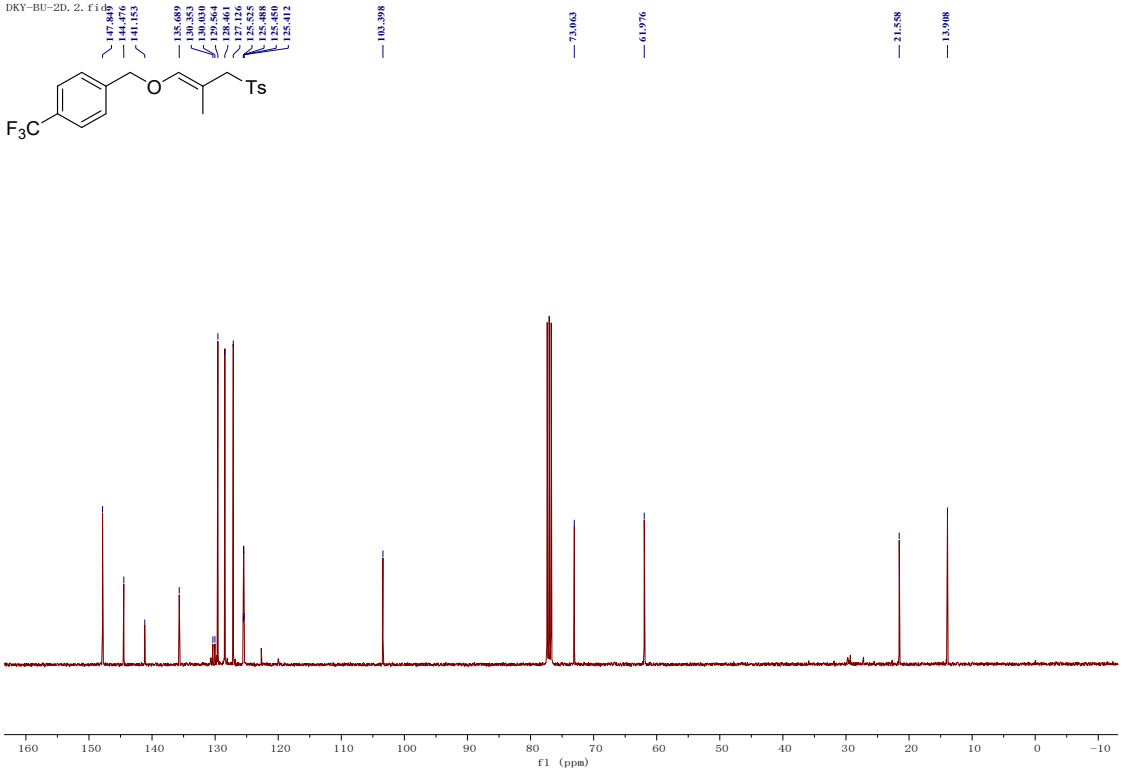
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 4



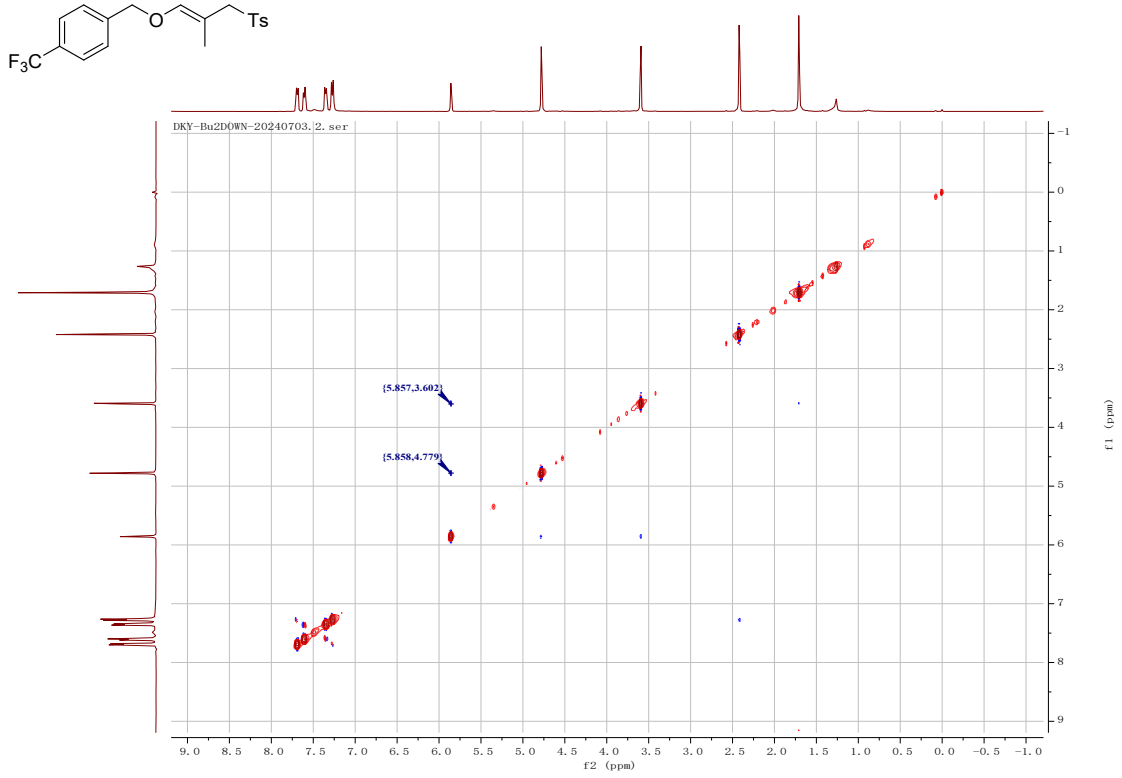
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 4



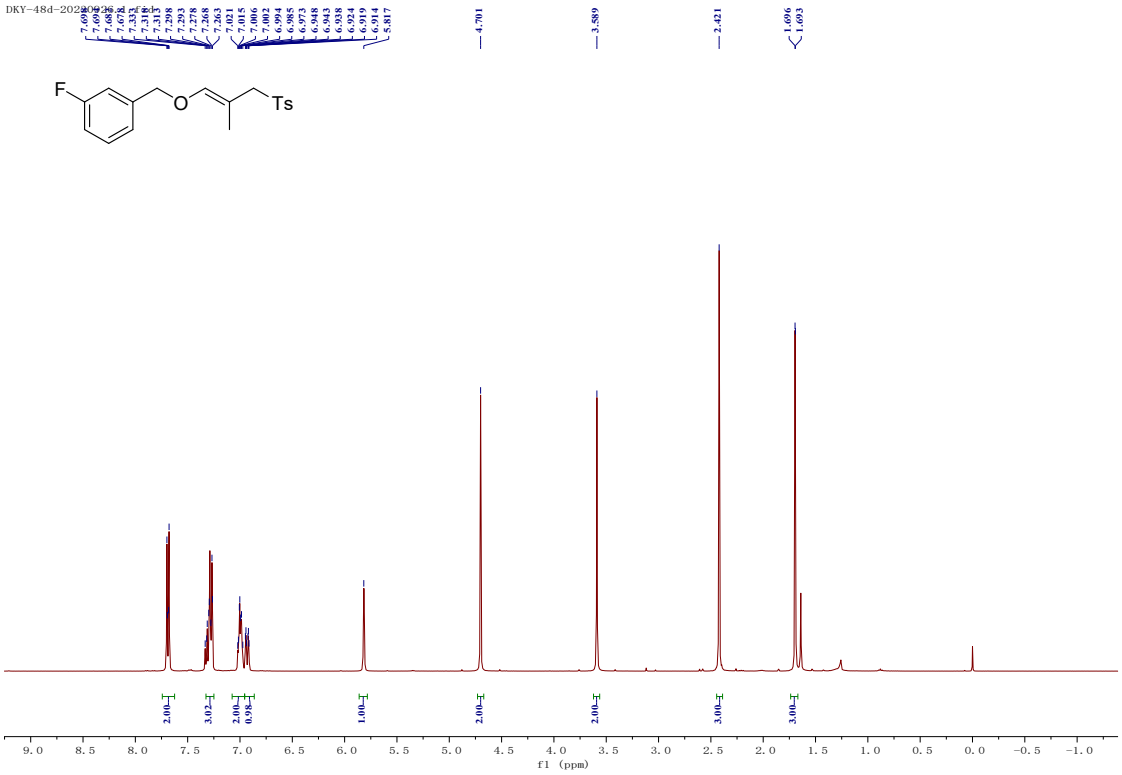
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 4



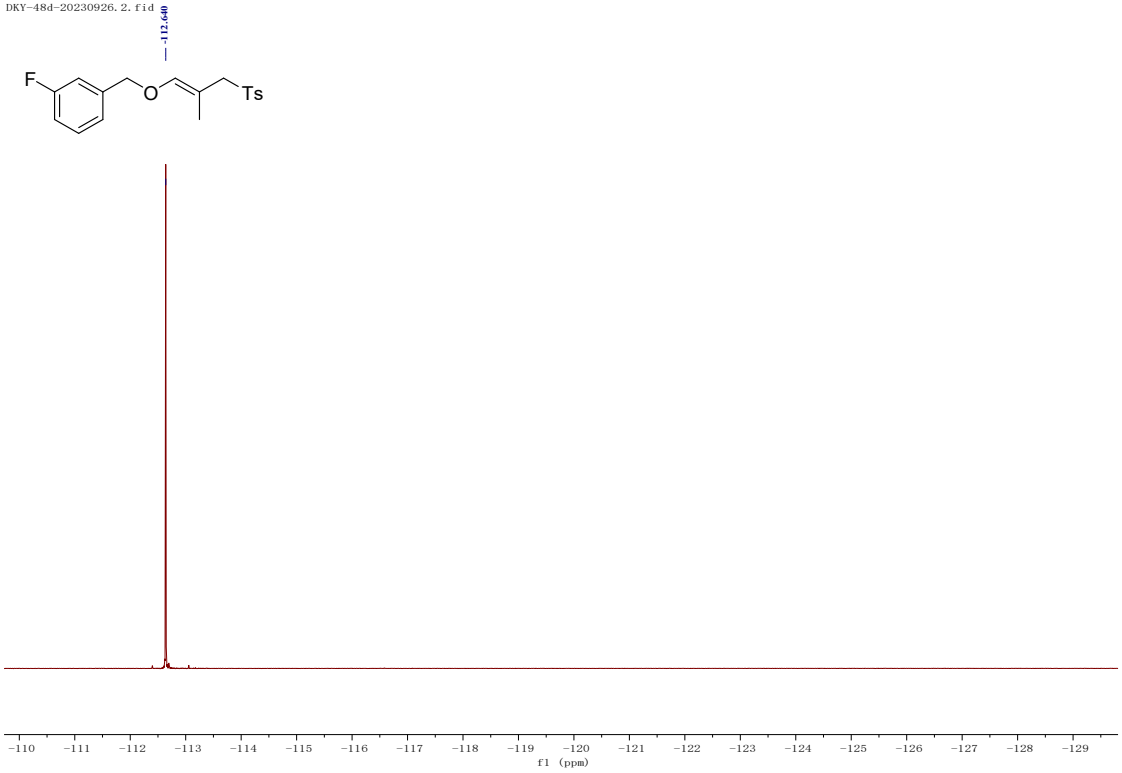
NOE NMR (400MHz, $CDCl_3$) spectrum of product 4



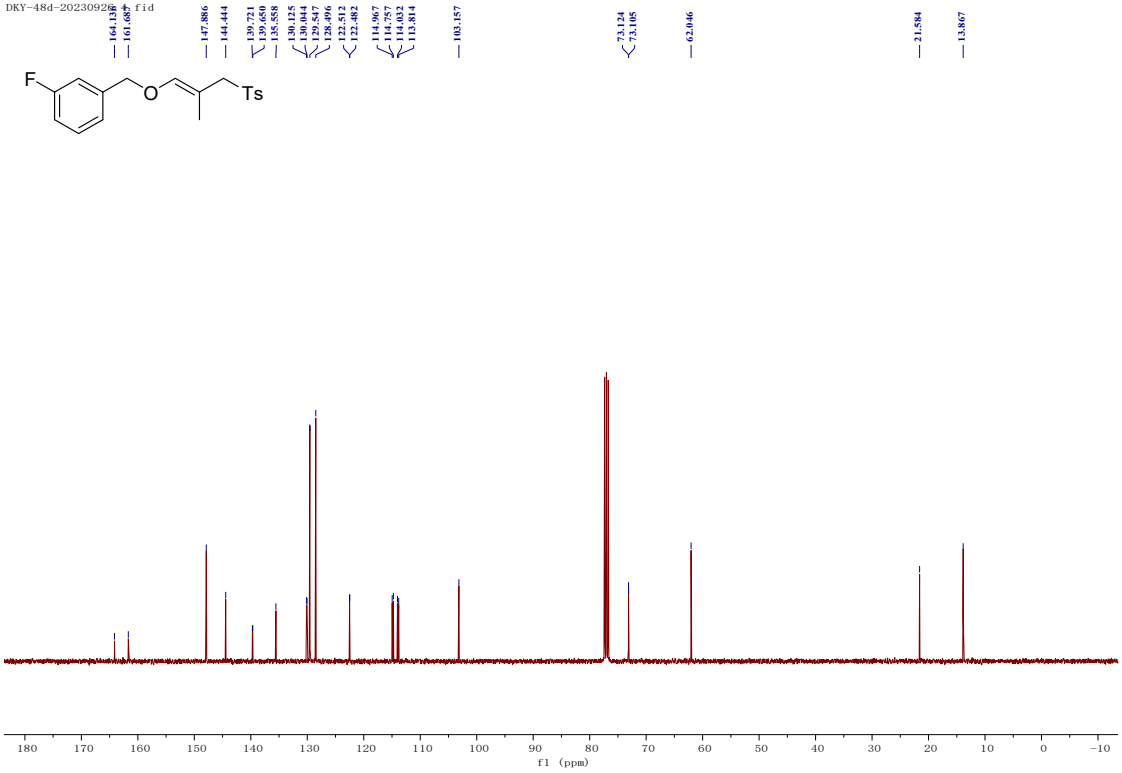
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 5



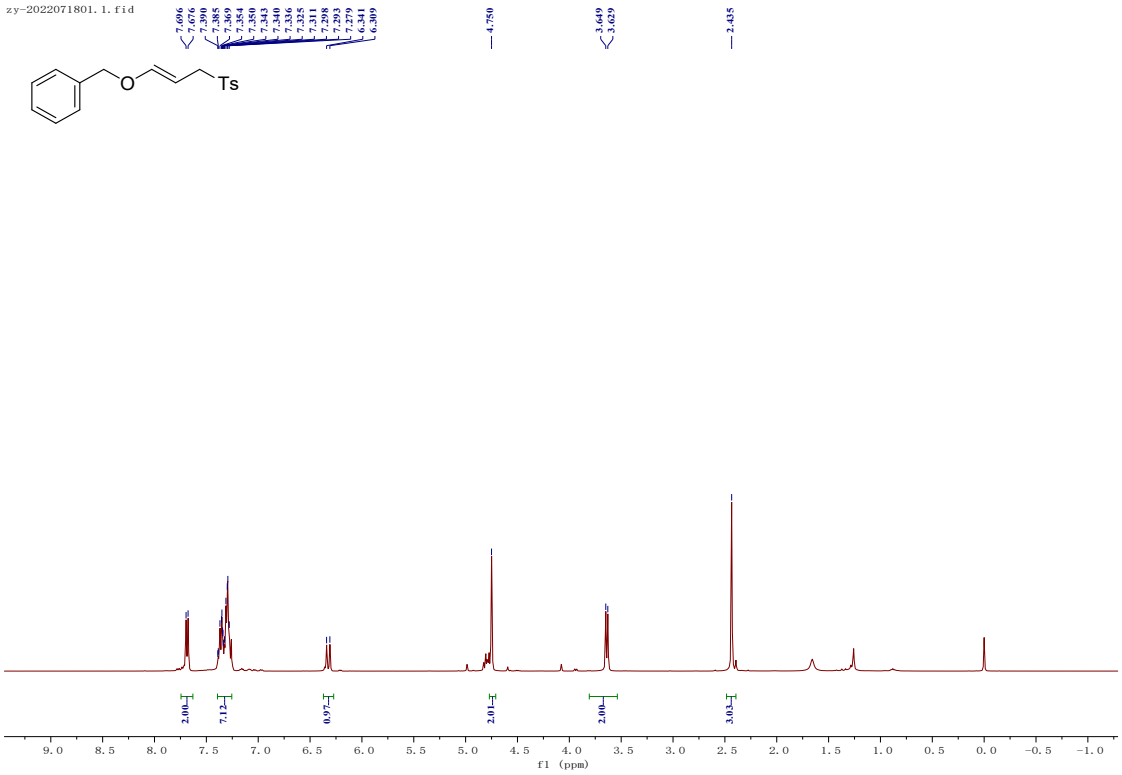
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 5



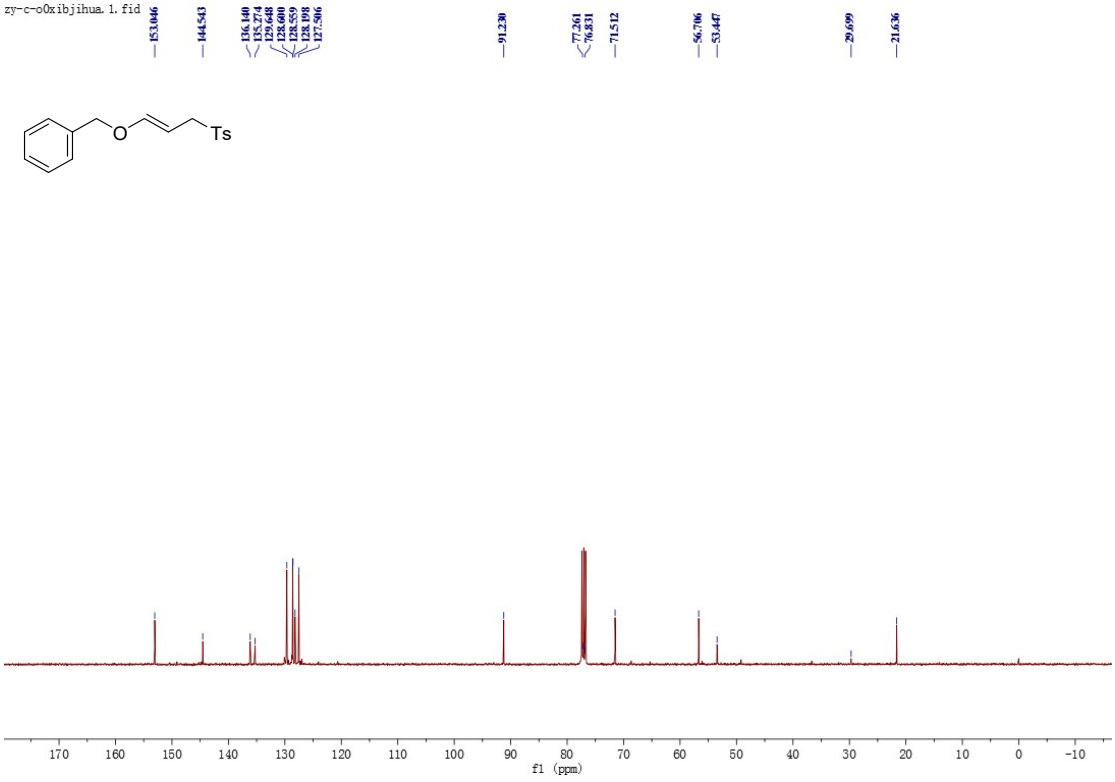
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 5



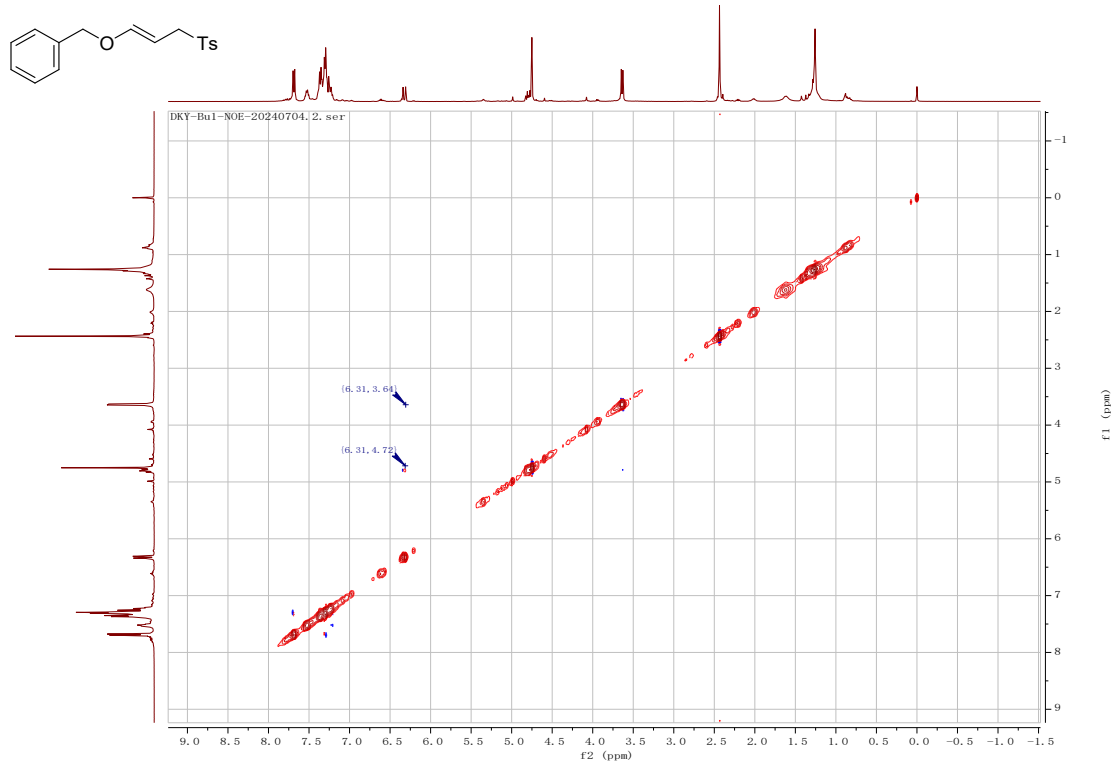
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 6



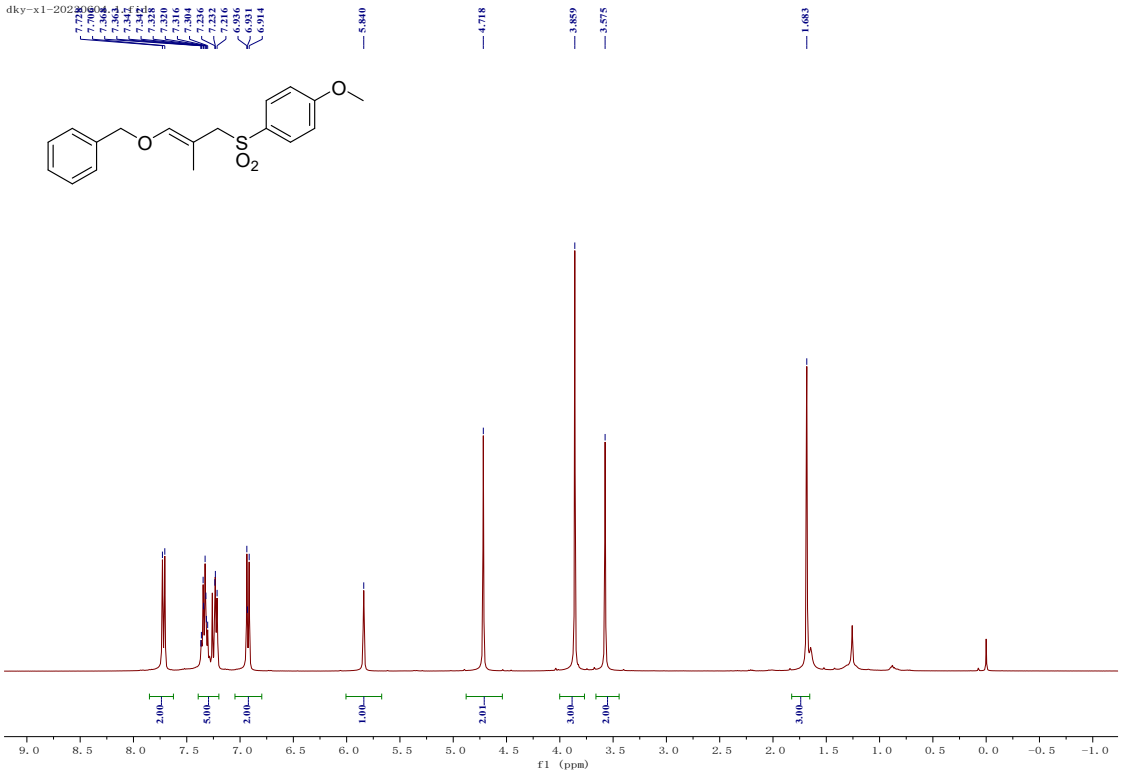
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 6



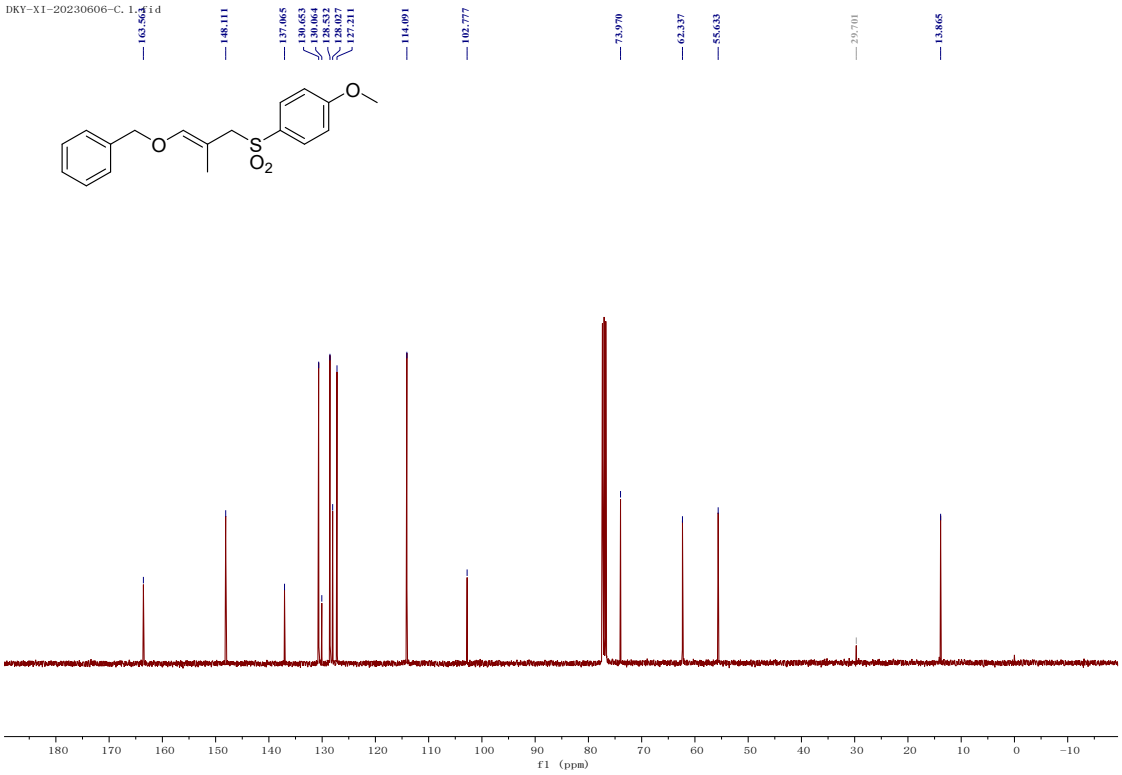
NOE NMR (400MHz, $CDCl_3$) spectrum of product 6



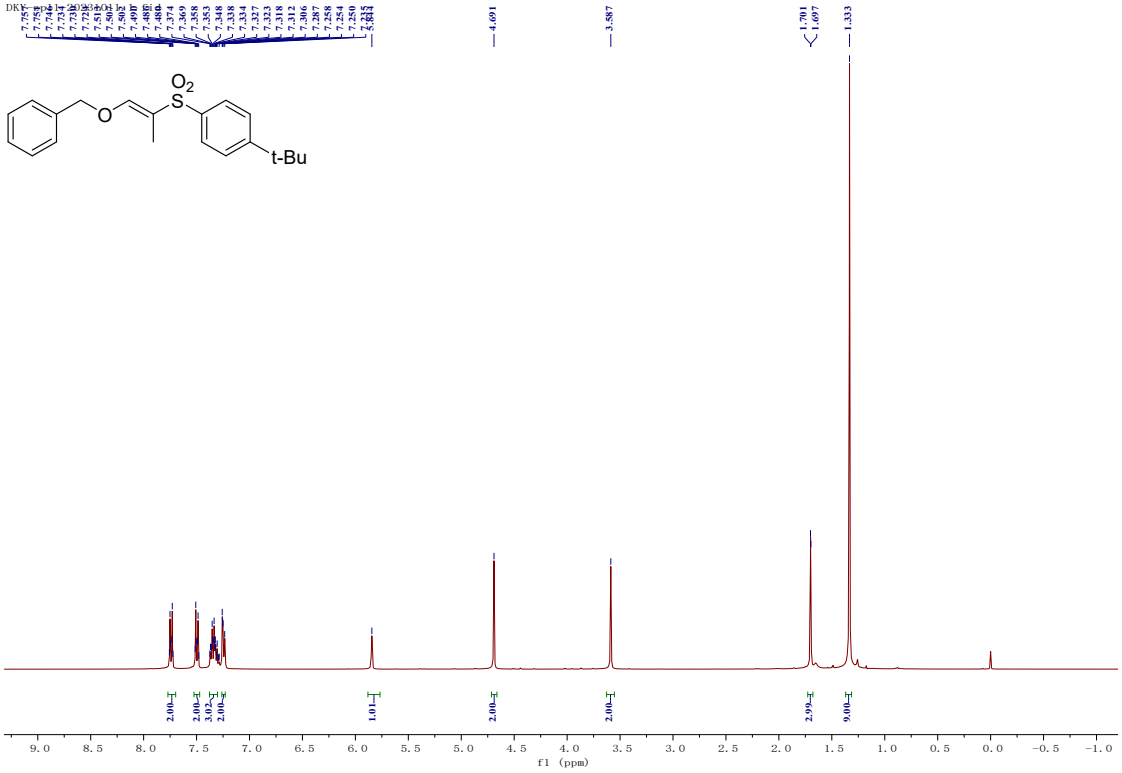
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 7



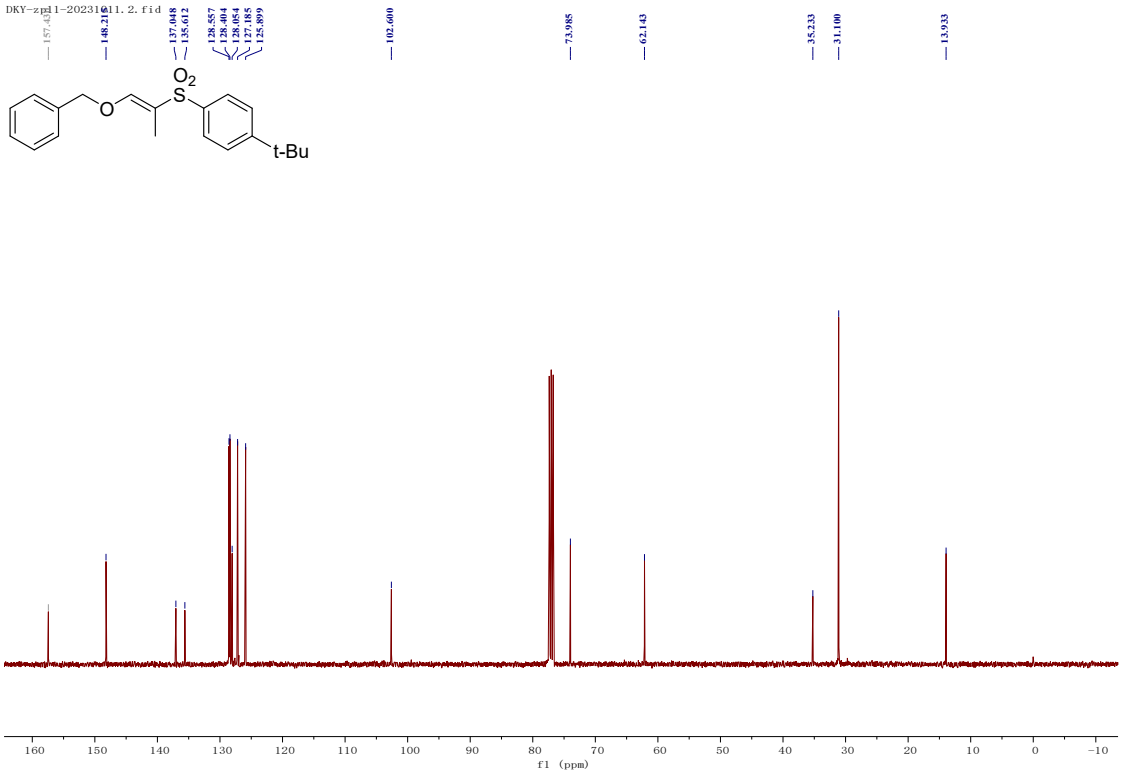
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 7



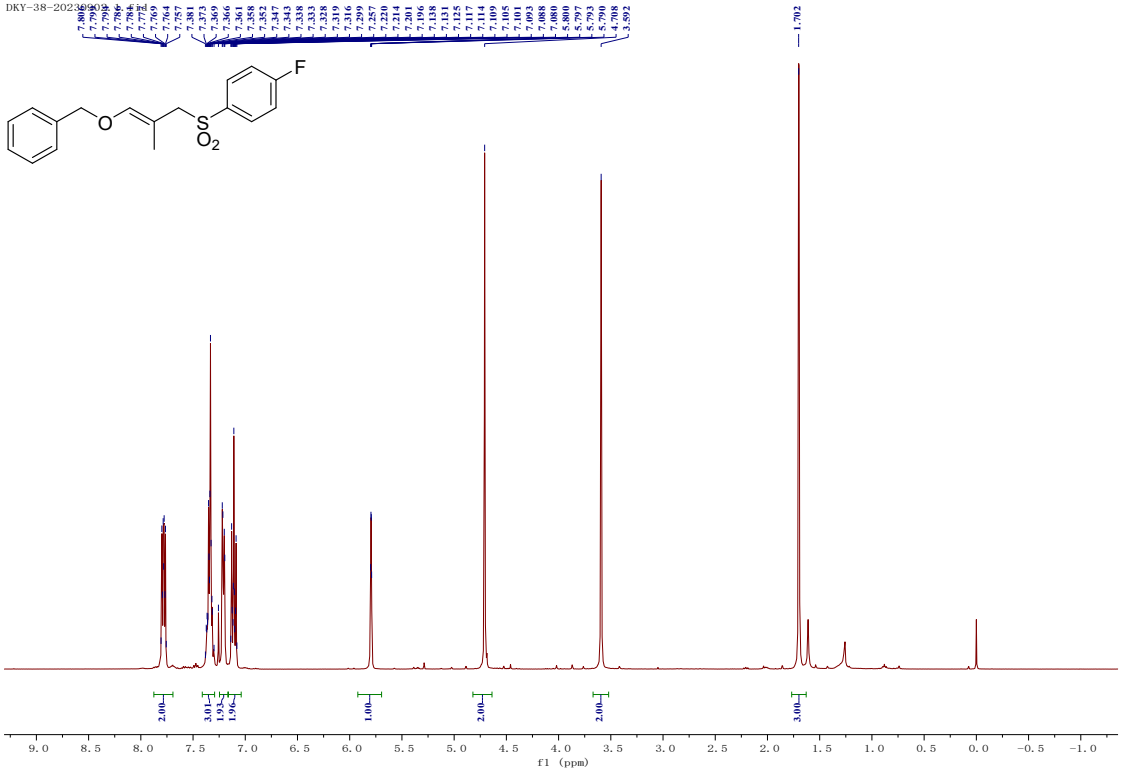
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 8



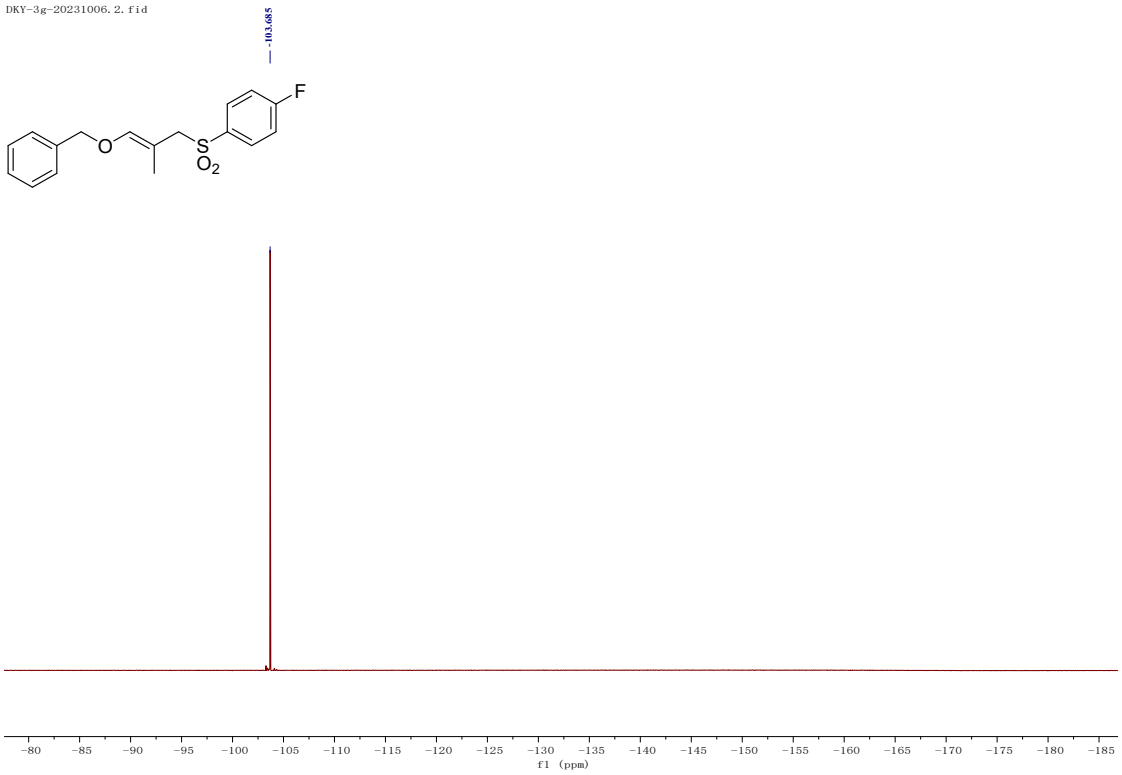
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 8



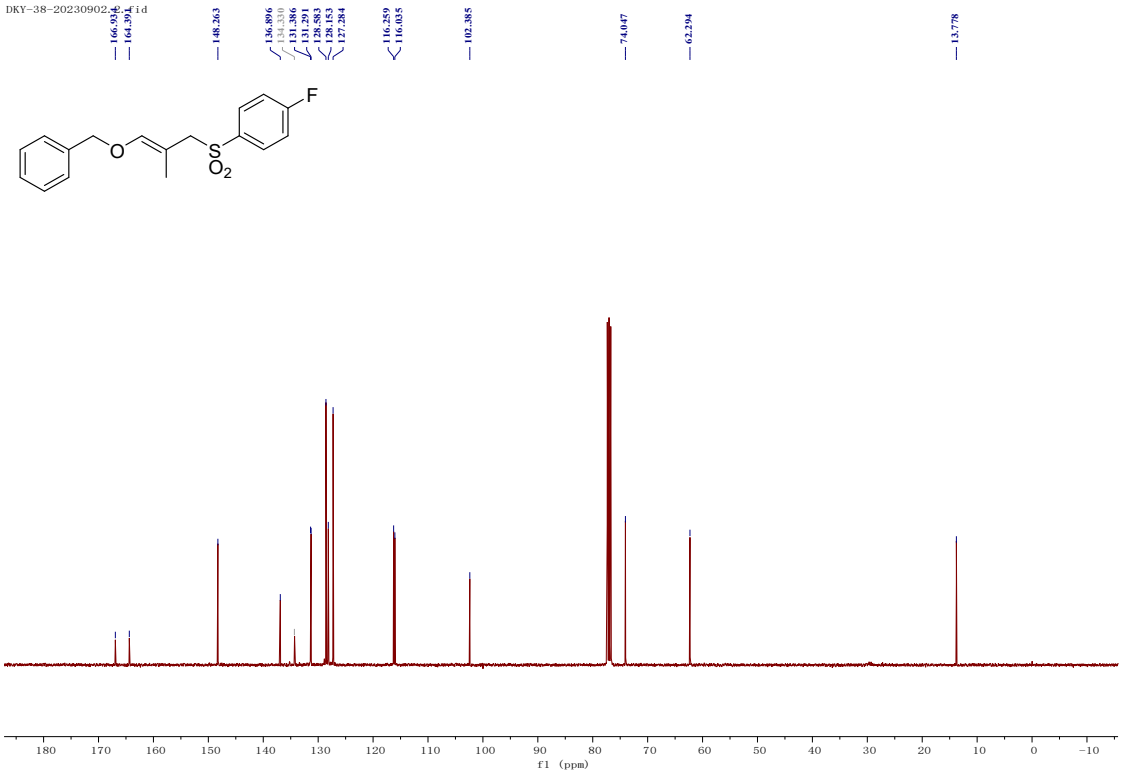
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 9



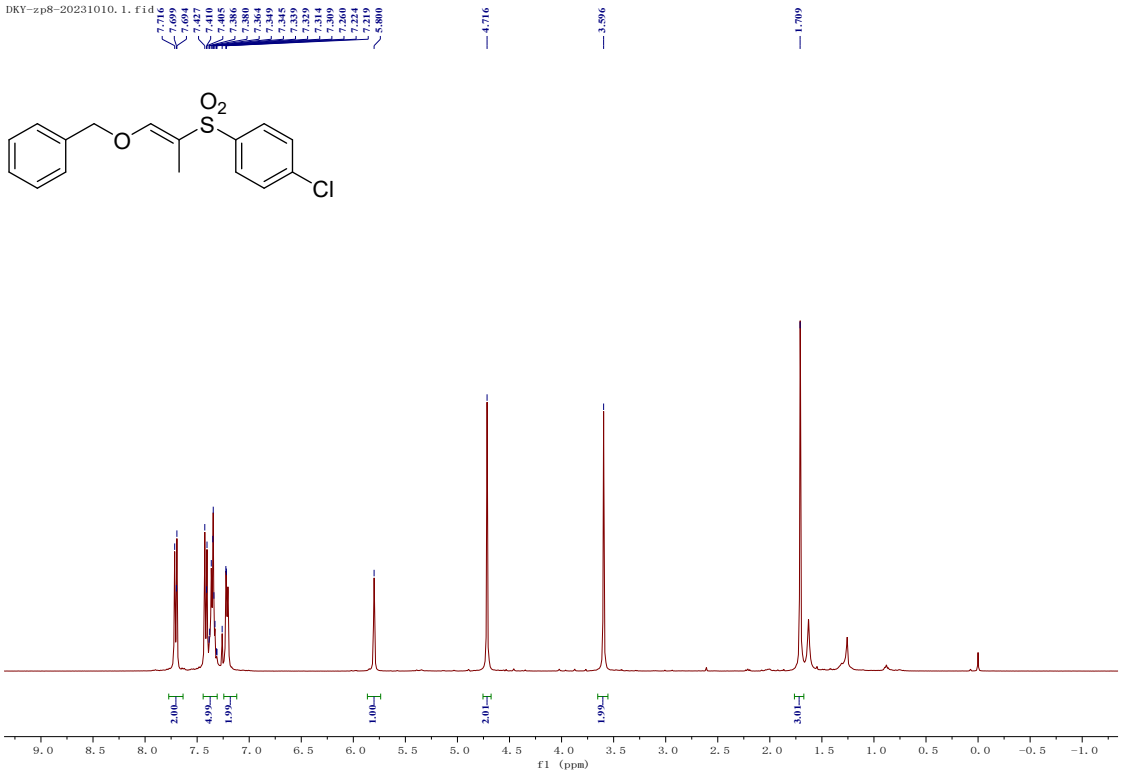
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 9



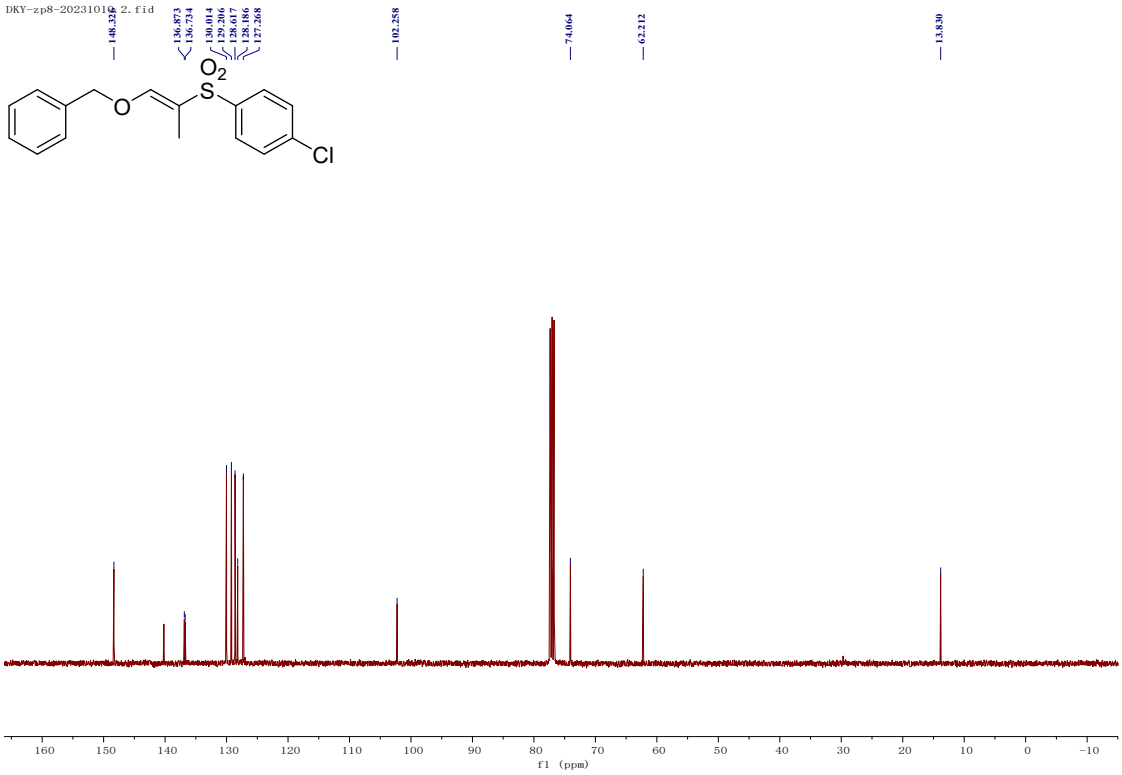
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 9



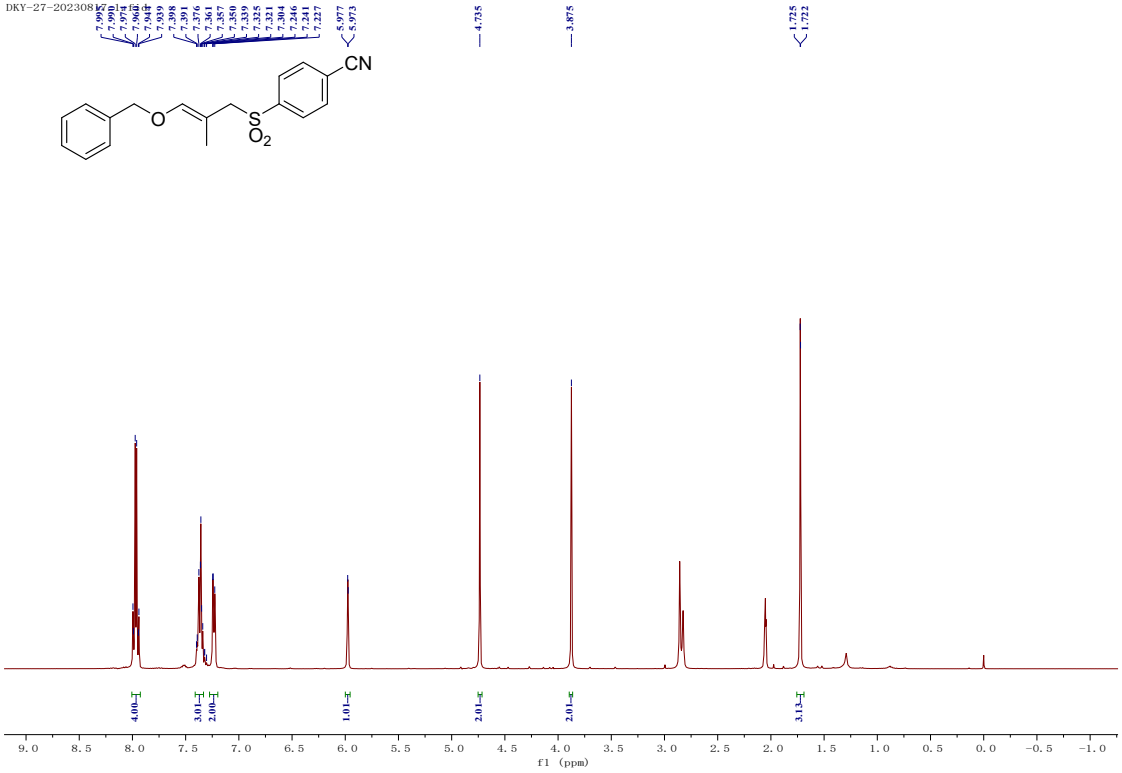
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 10



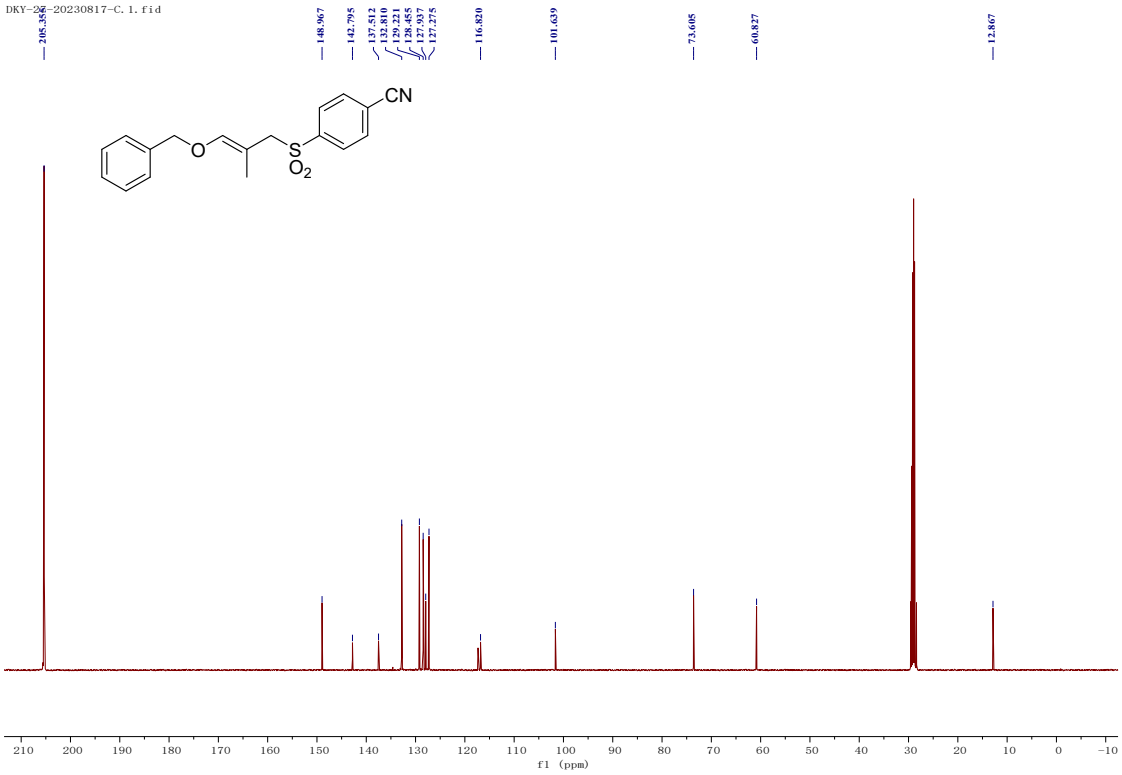
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 10



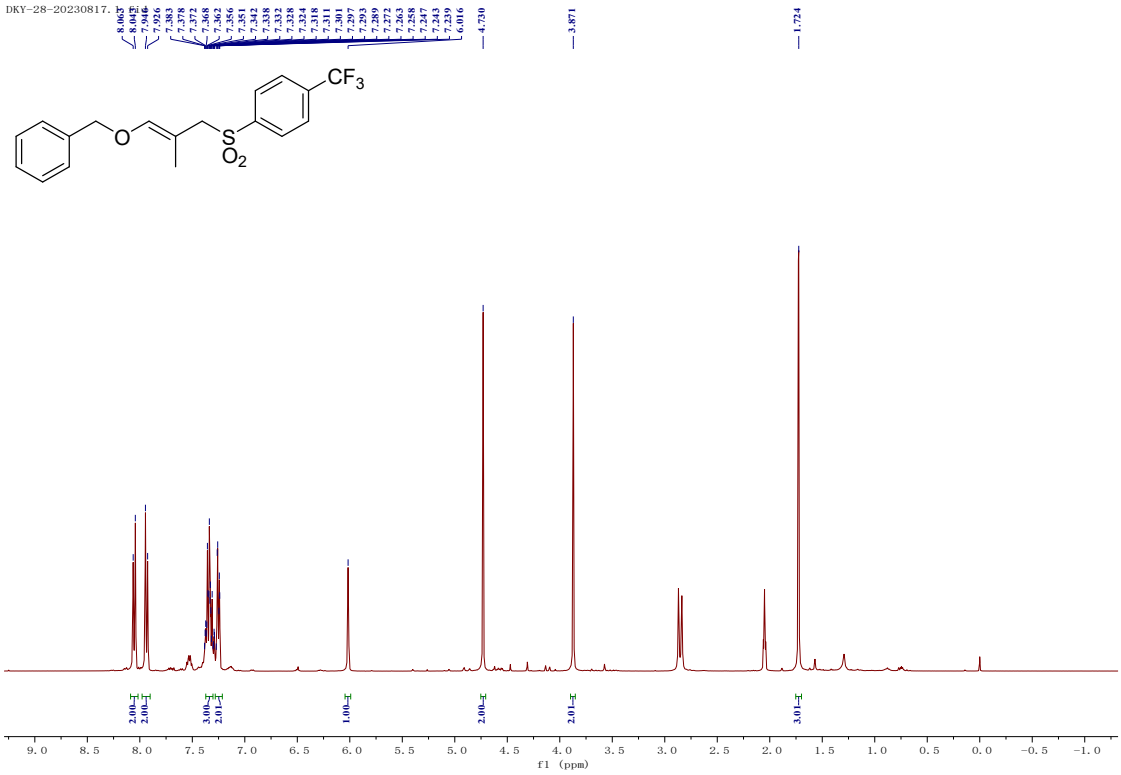
^{1}H NMR (400MHz, Acetone-*d*6) spectrum of product 11



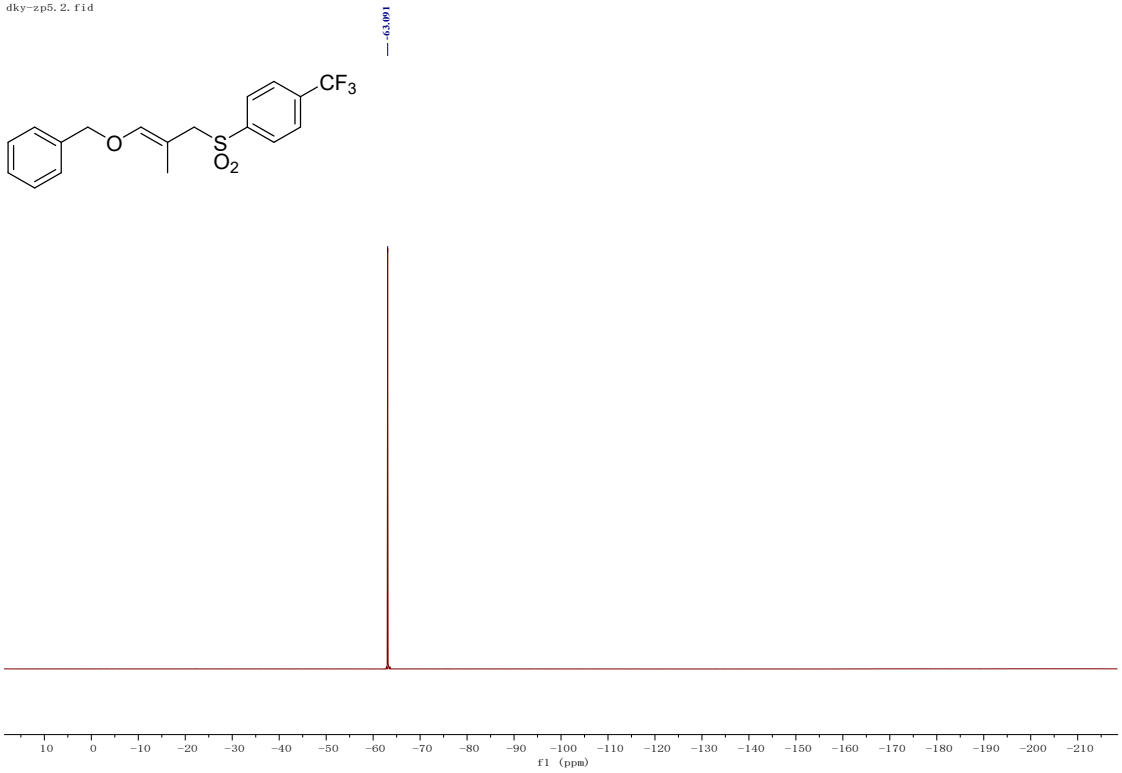
^{13}C NMR (400MHz, Acetone-*d*6) spectrum of product 11



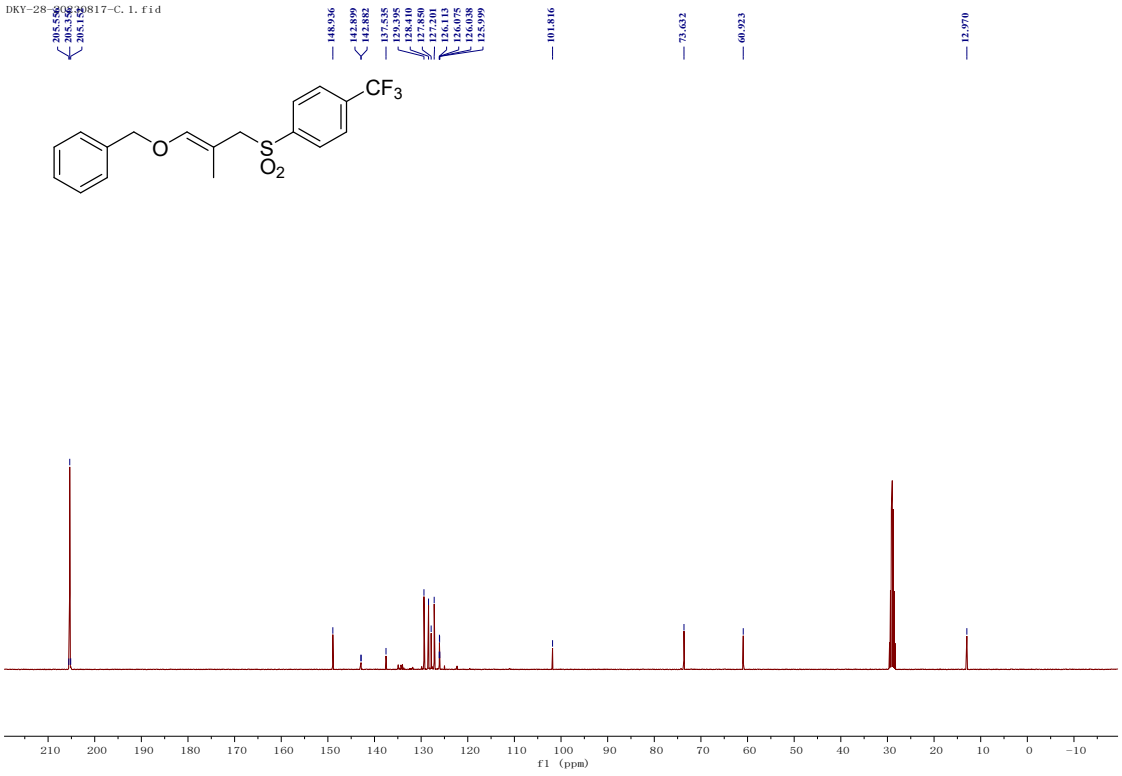
^{1}H NMR (400MHz, Acetone-*d*6) spectrum of product 12



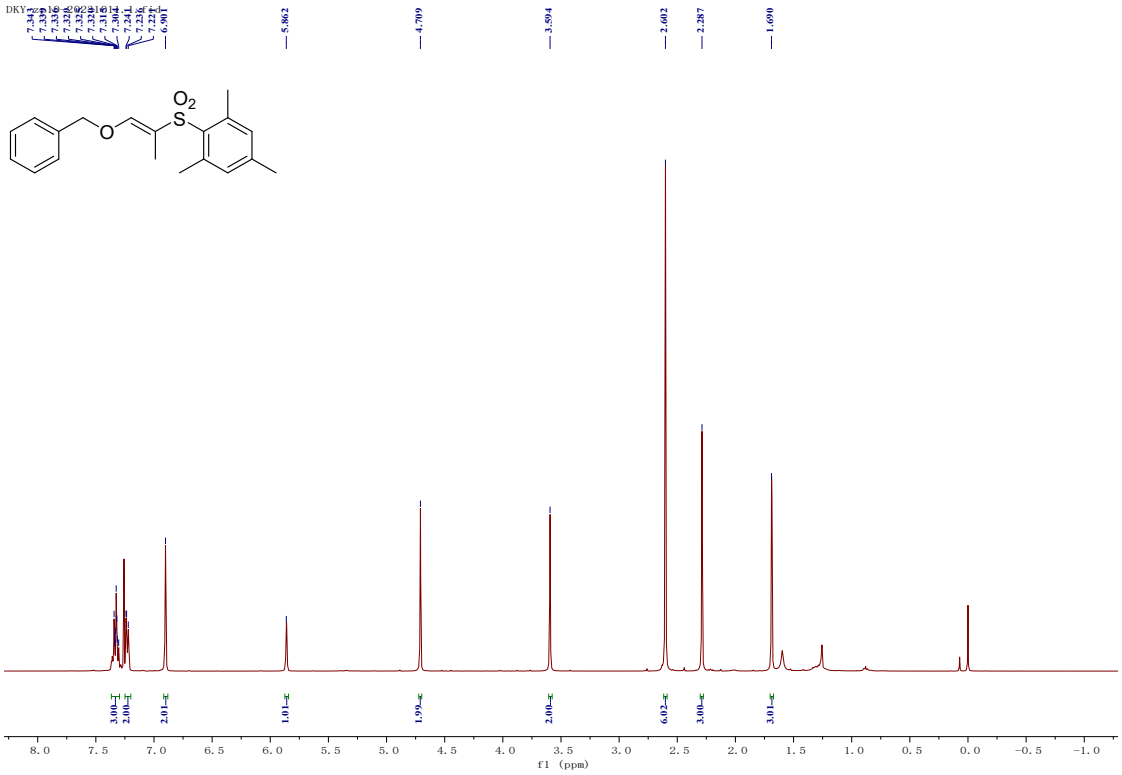
^{19}F NMR (376MHz, Acetone-*d*6) spectrum of product 12



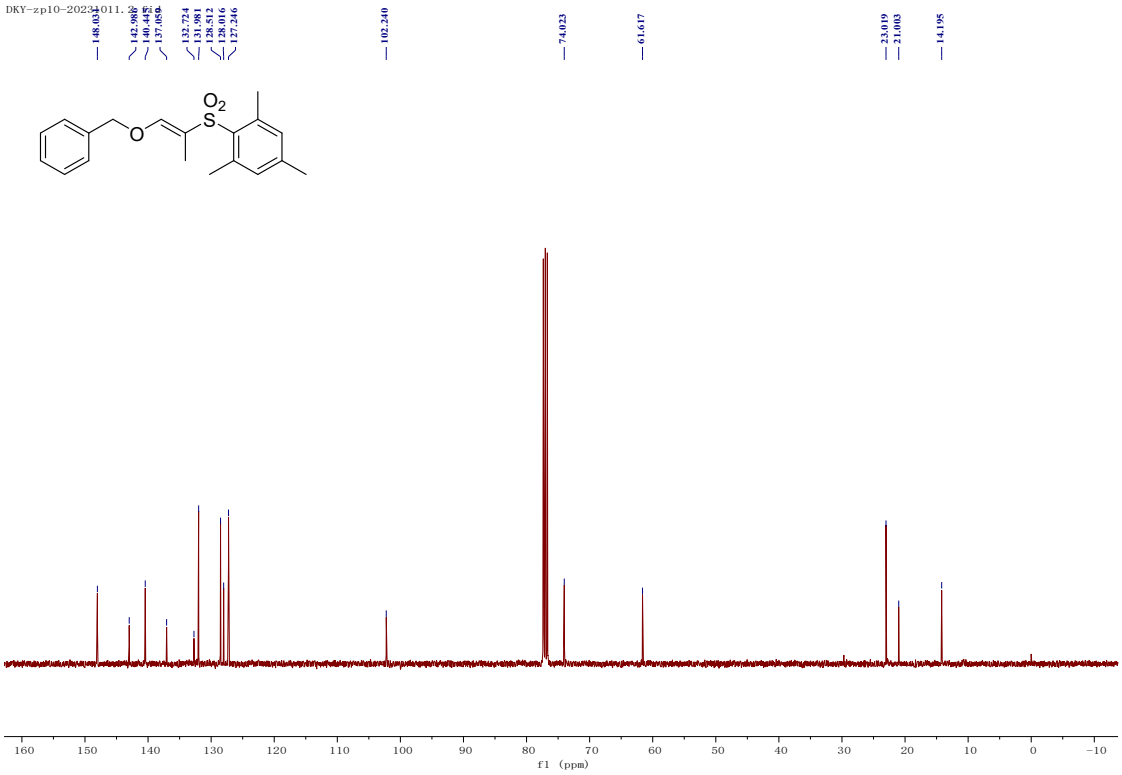
^{13}C NMR (400MHz, Acetone-*d*6) spectrum of product 12



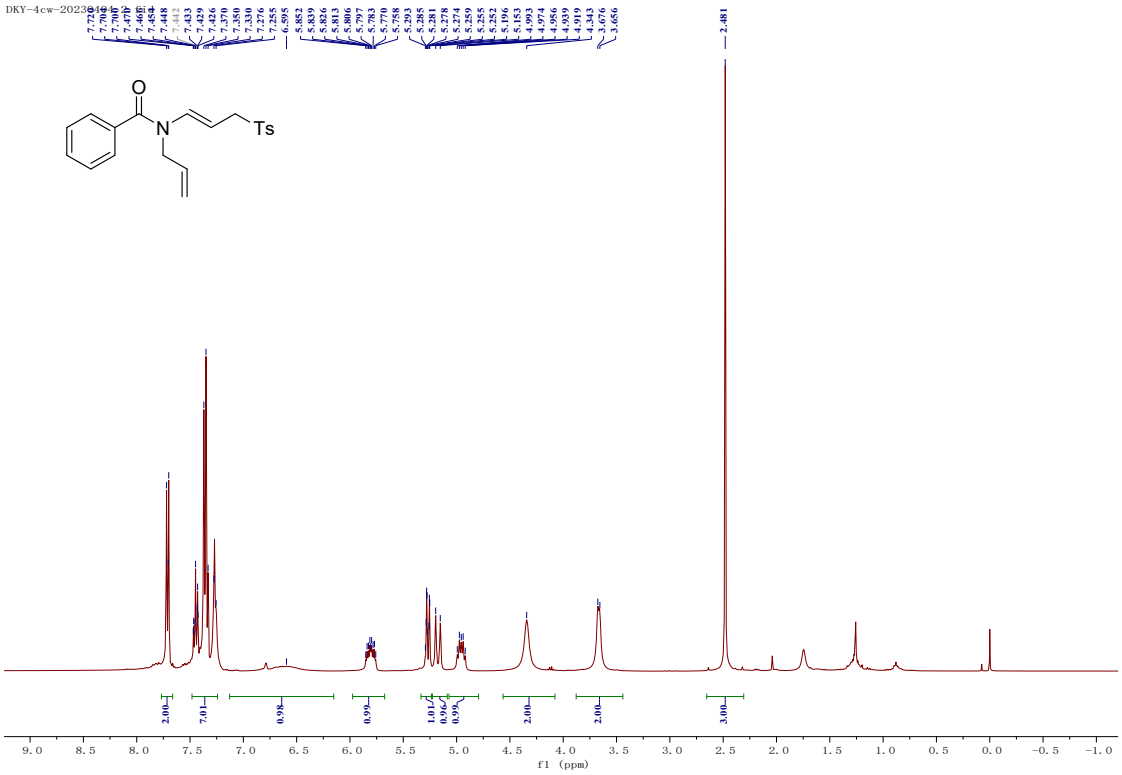
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 13



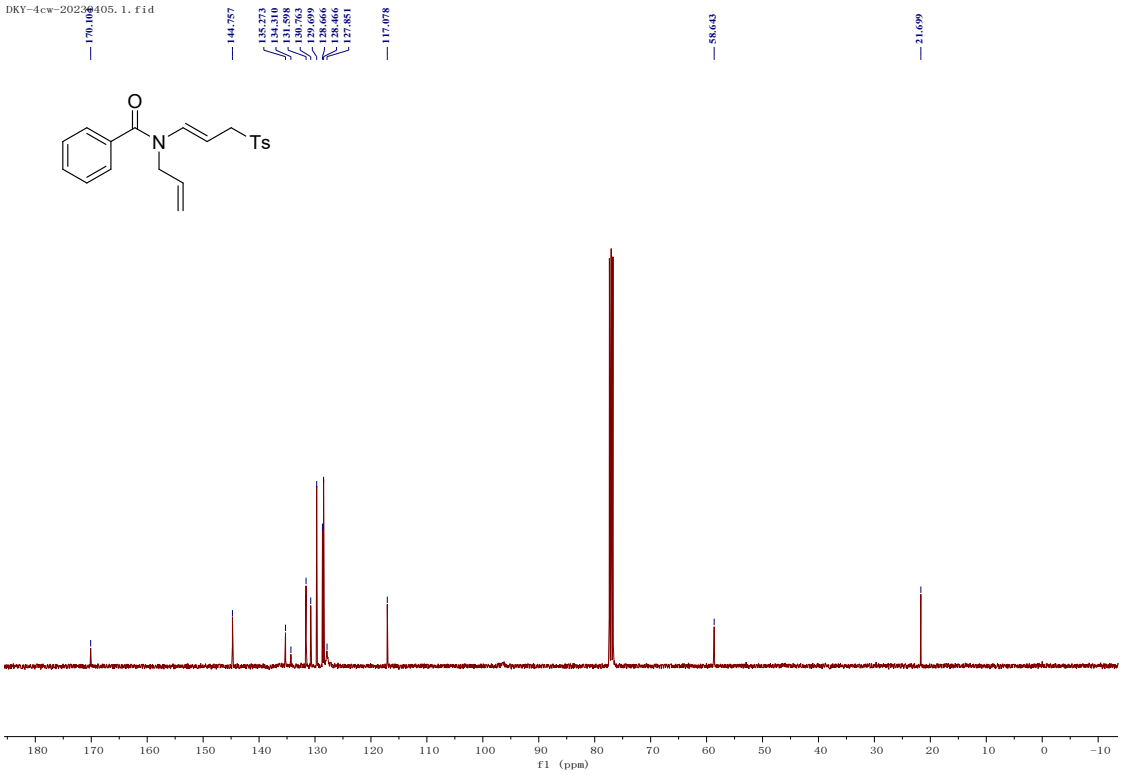
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 13



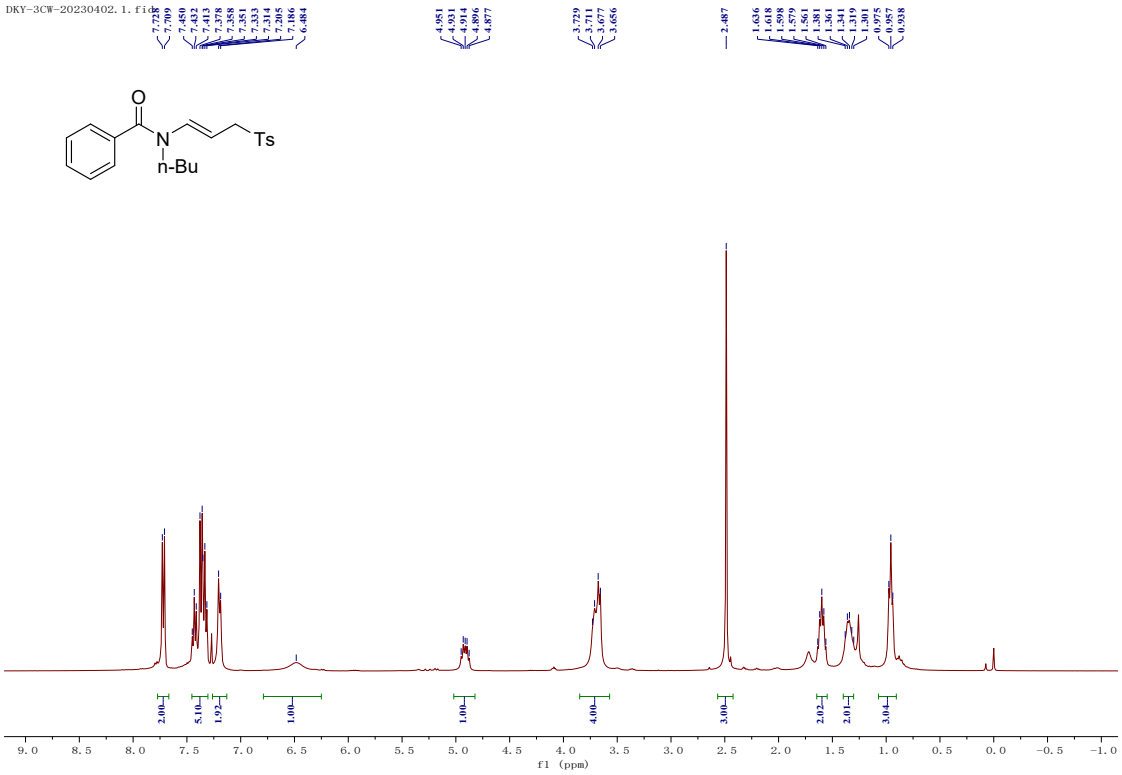
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 15



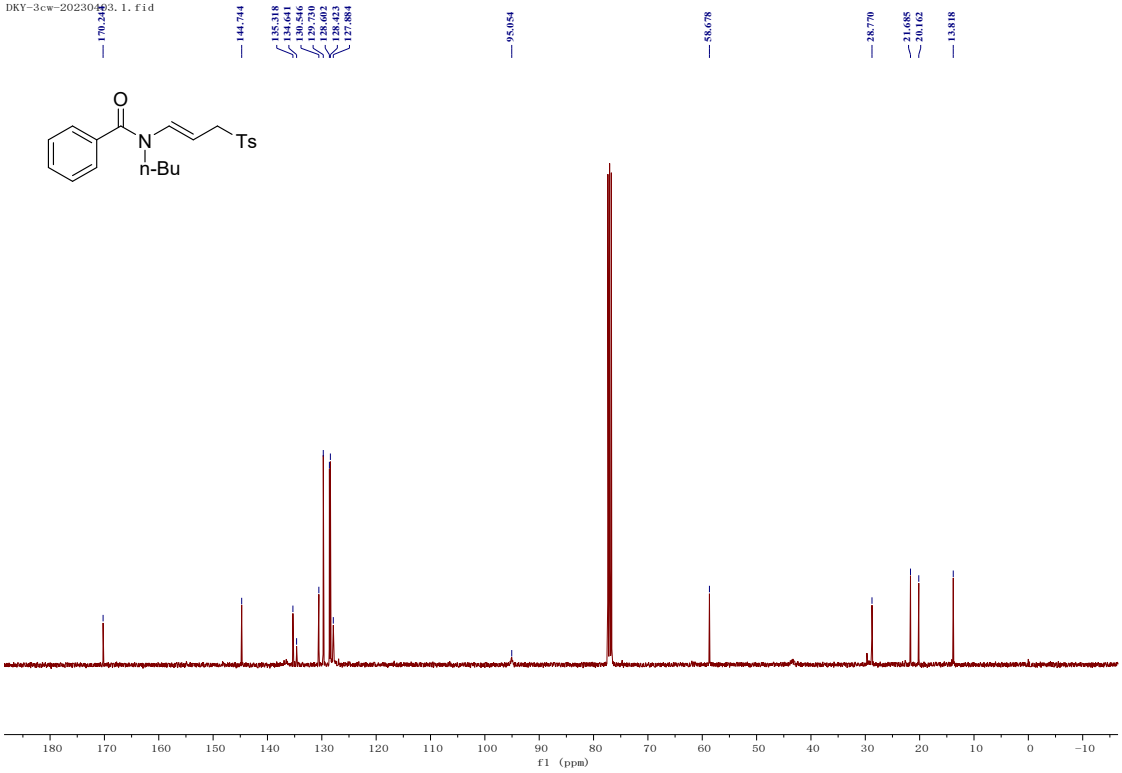
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 15



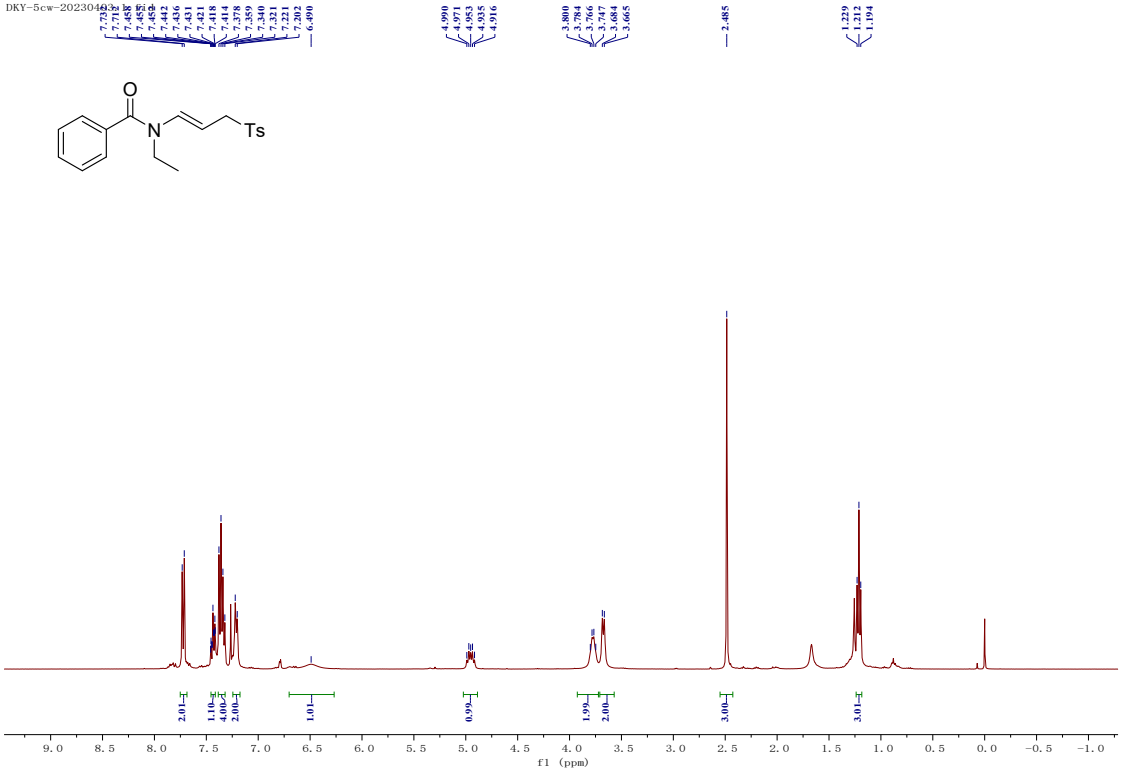
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 16



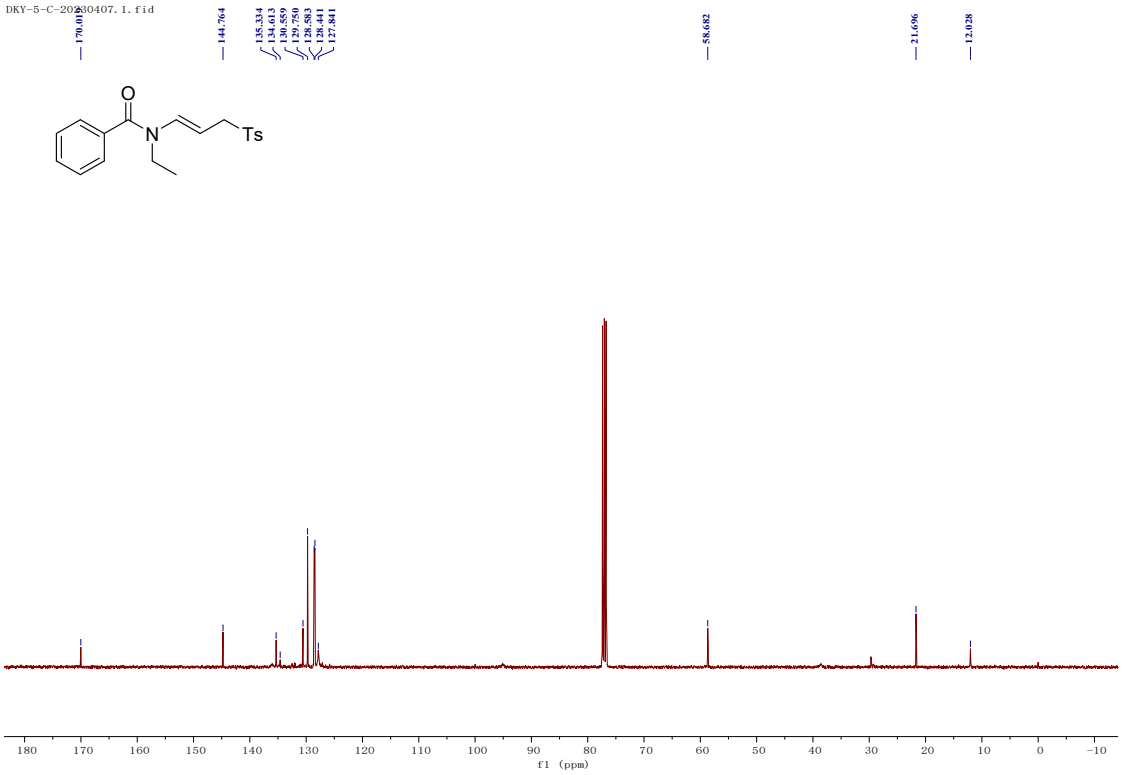
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 16



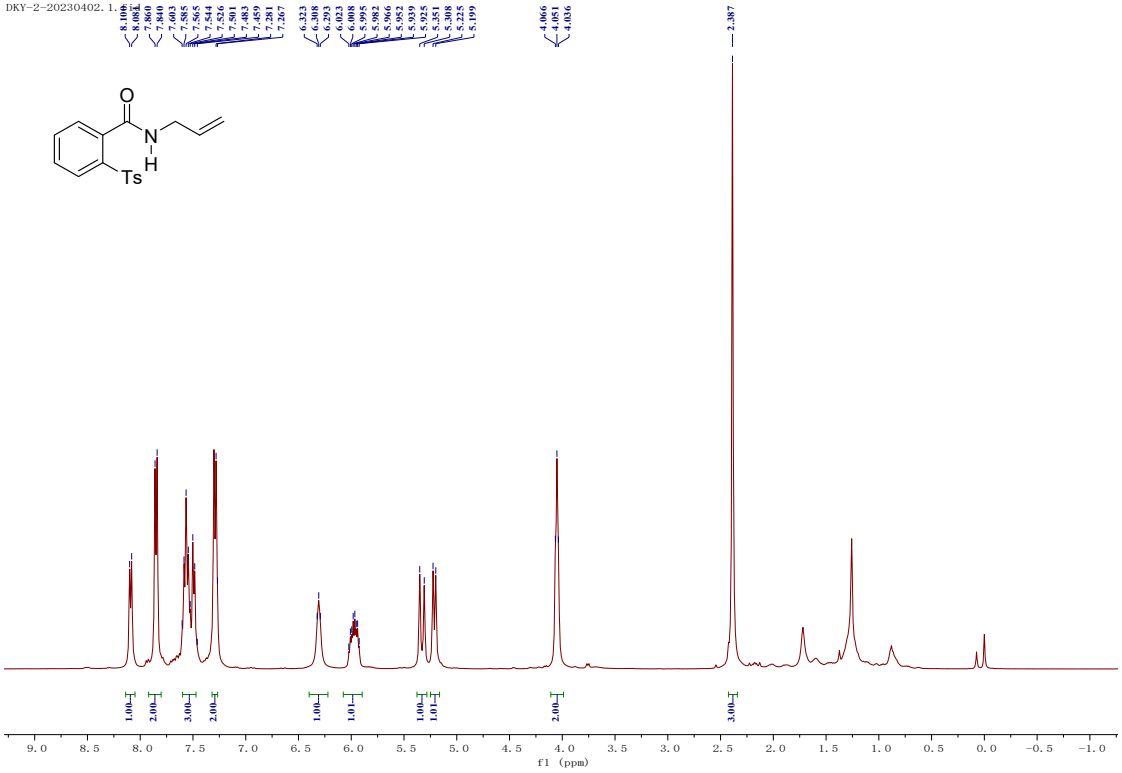
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 17



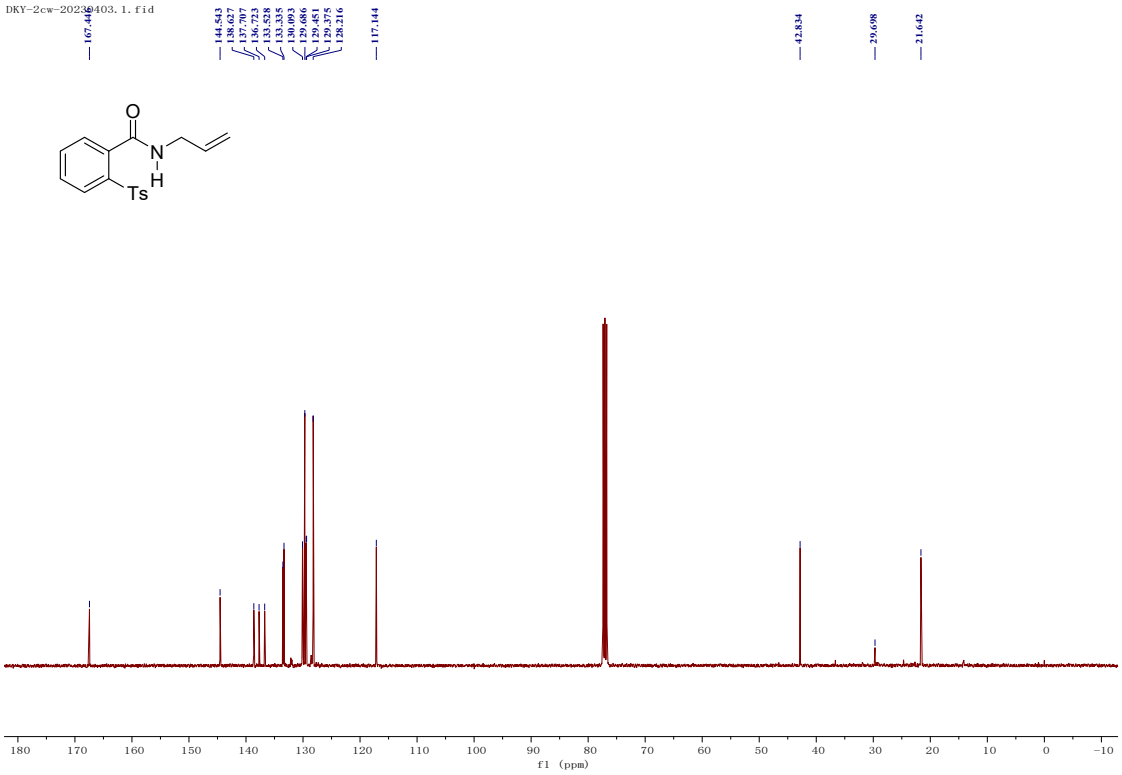
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 17



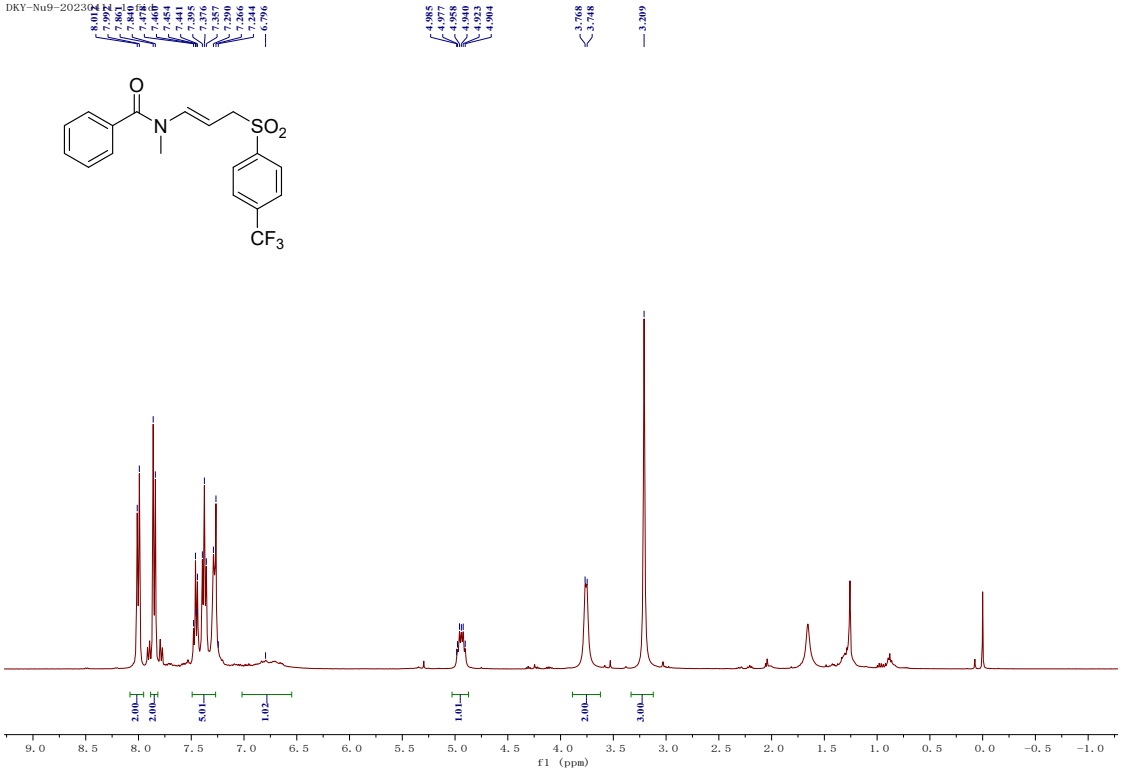
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 18



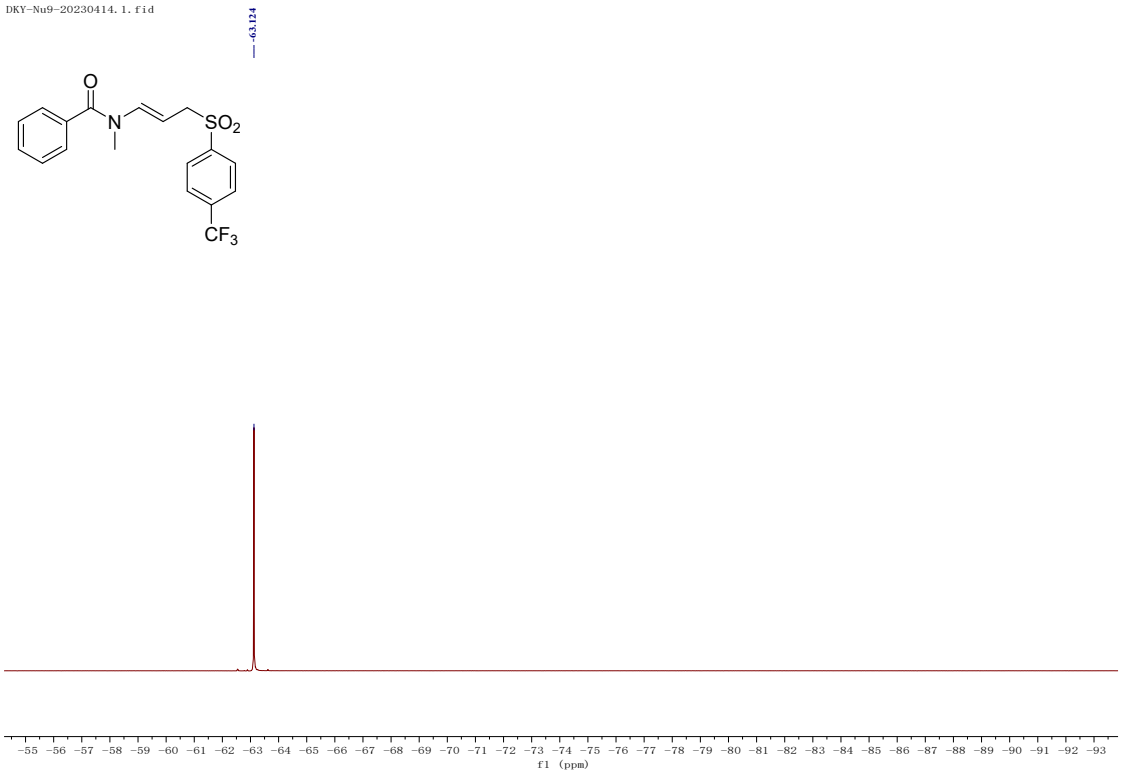
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 18



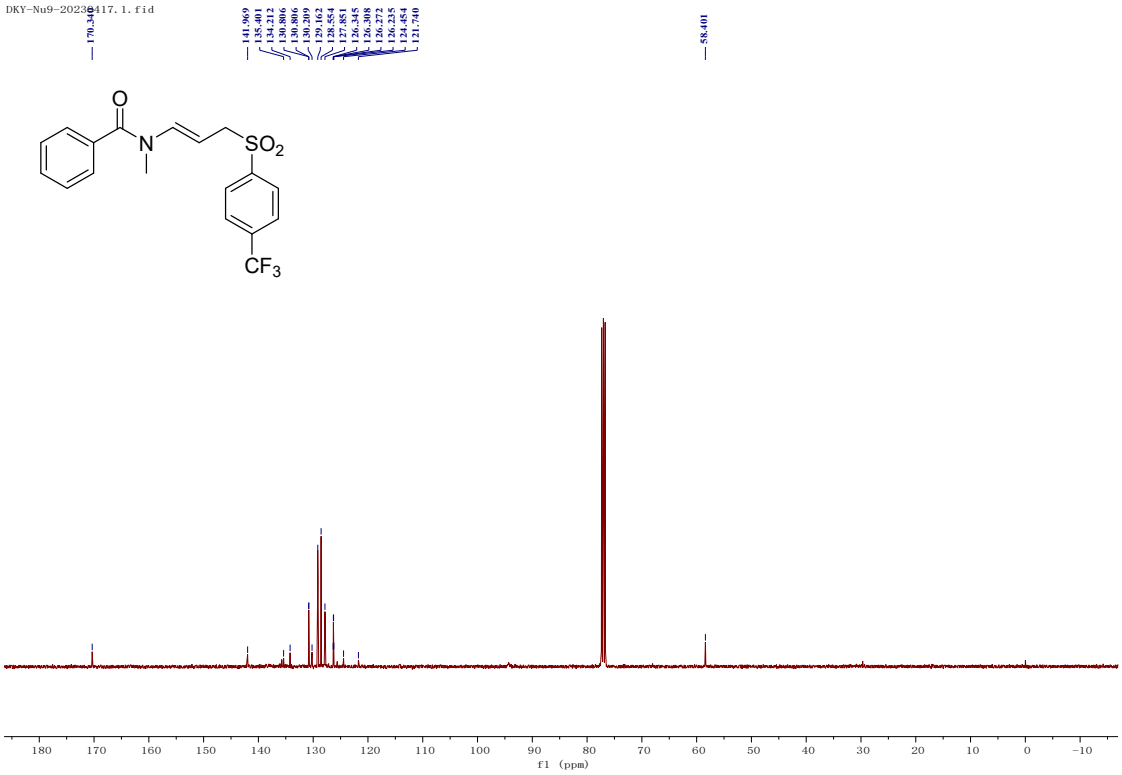
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 19



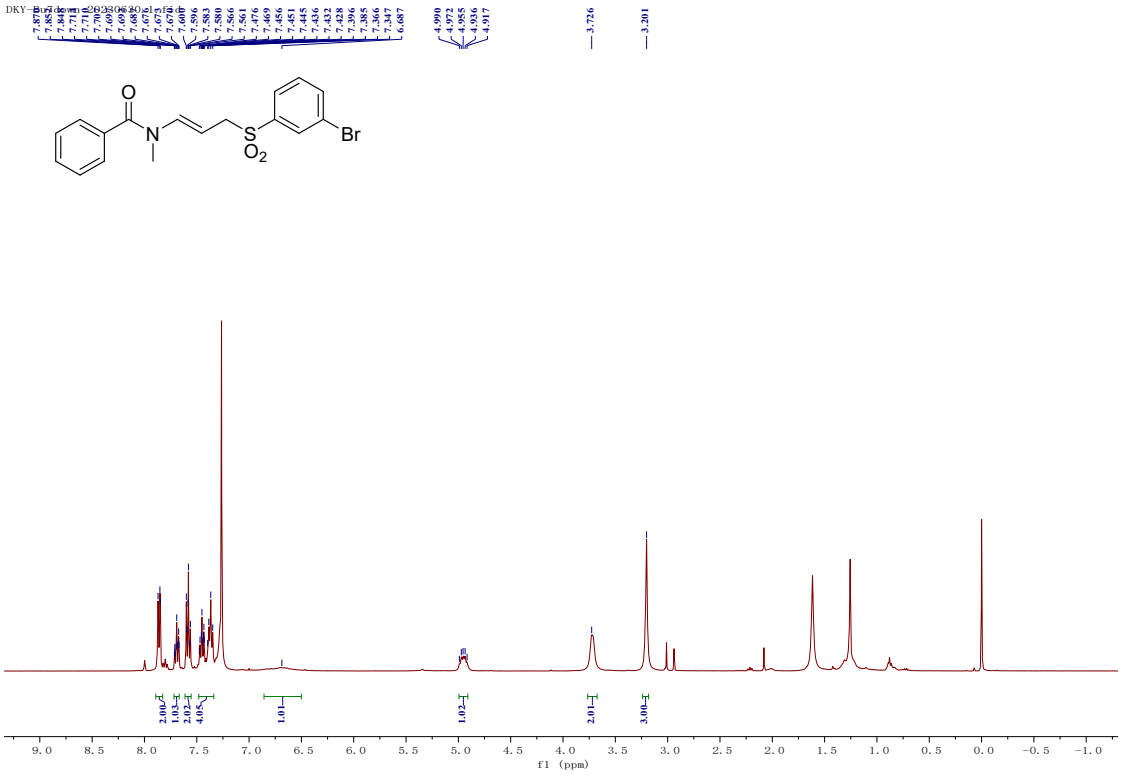
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 19



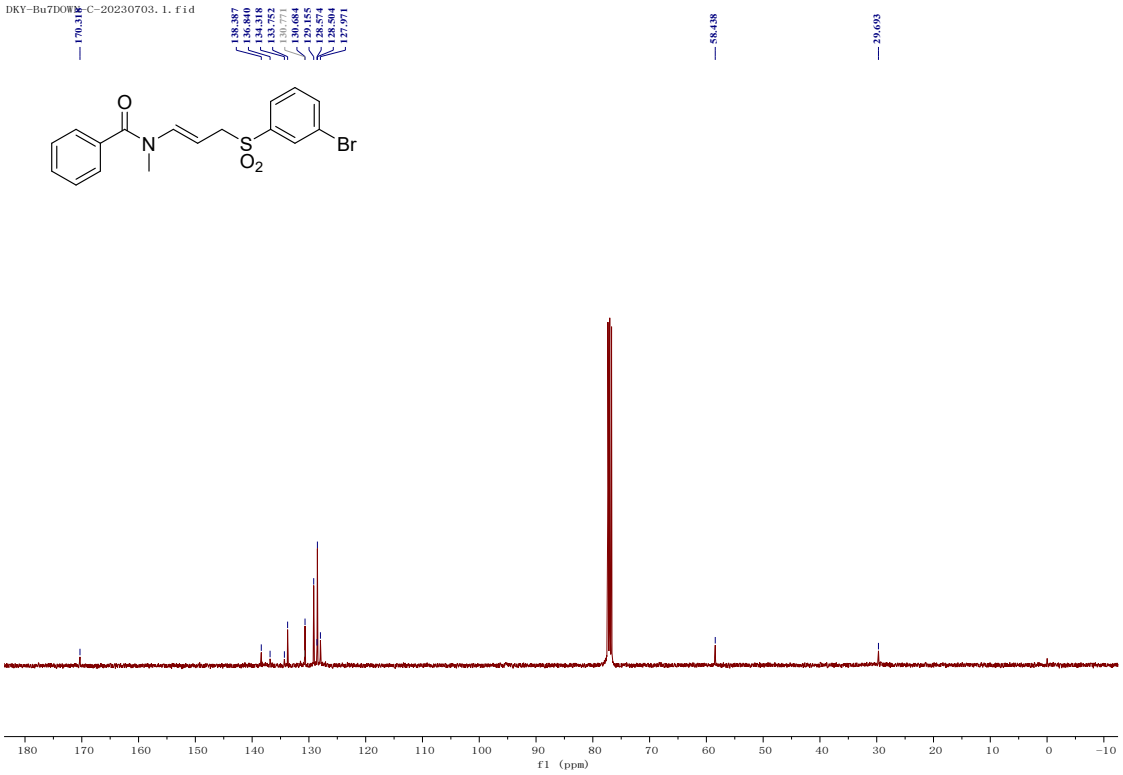
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 19



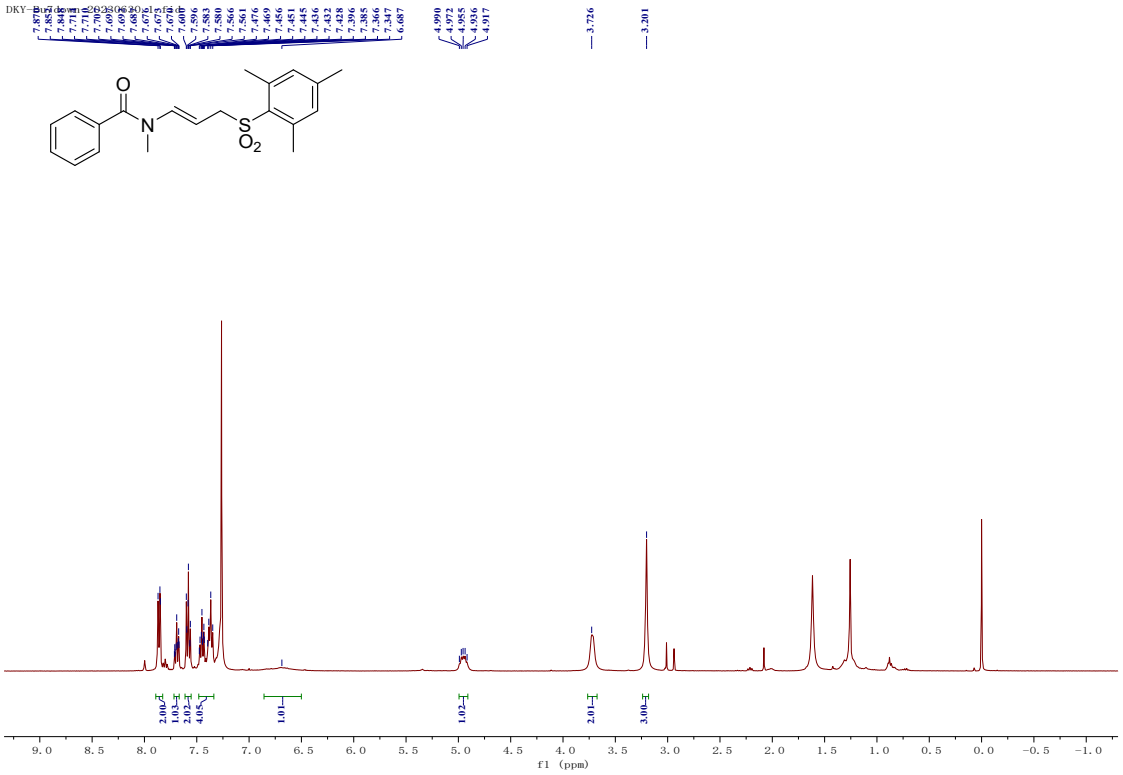
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 20



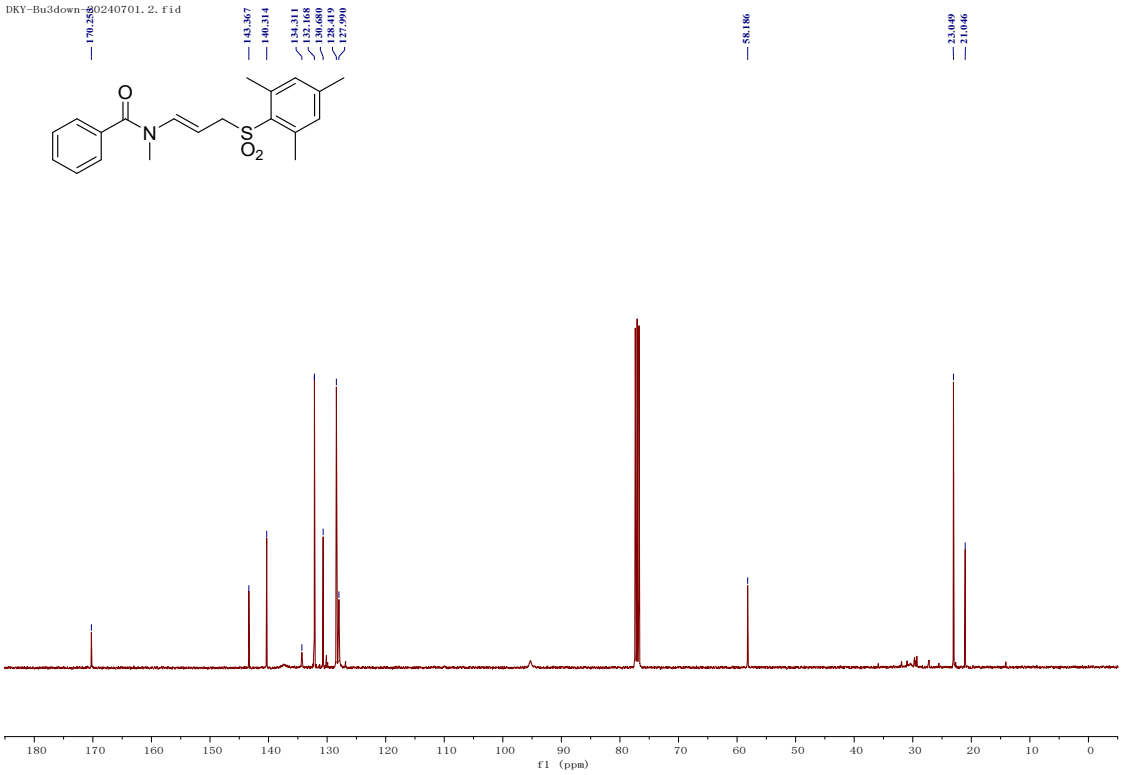
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 20



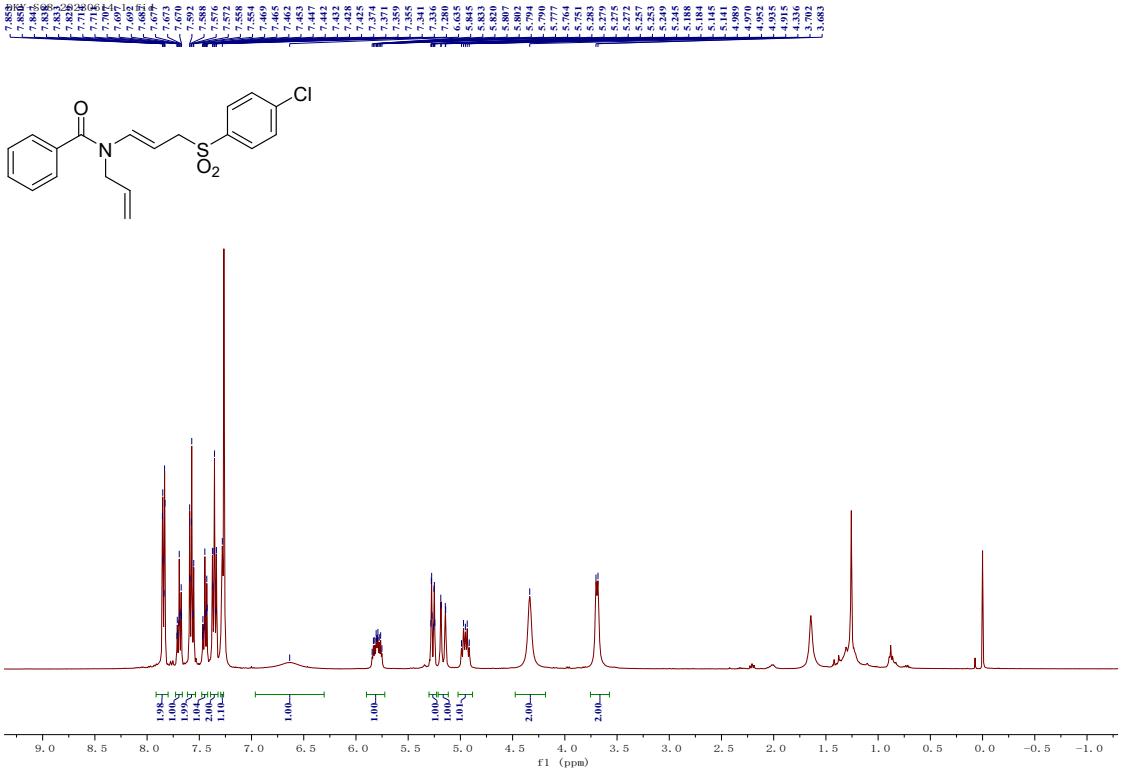
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 21



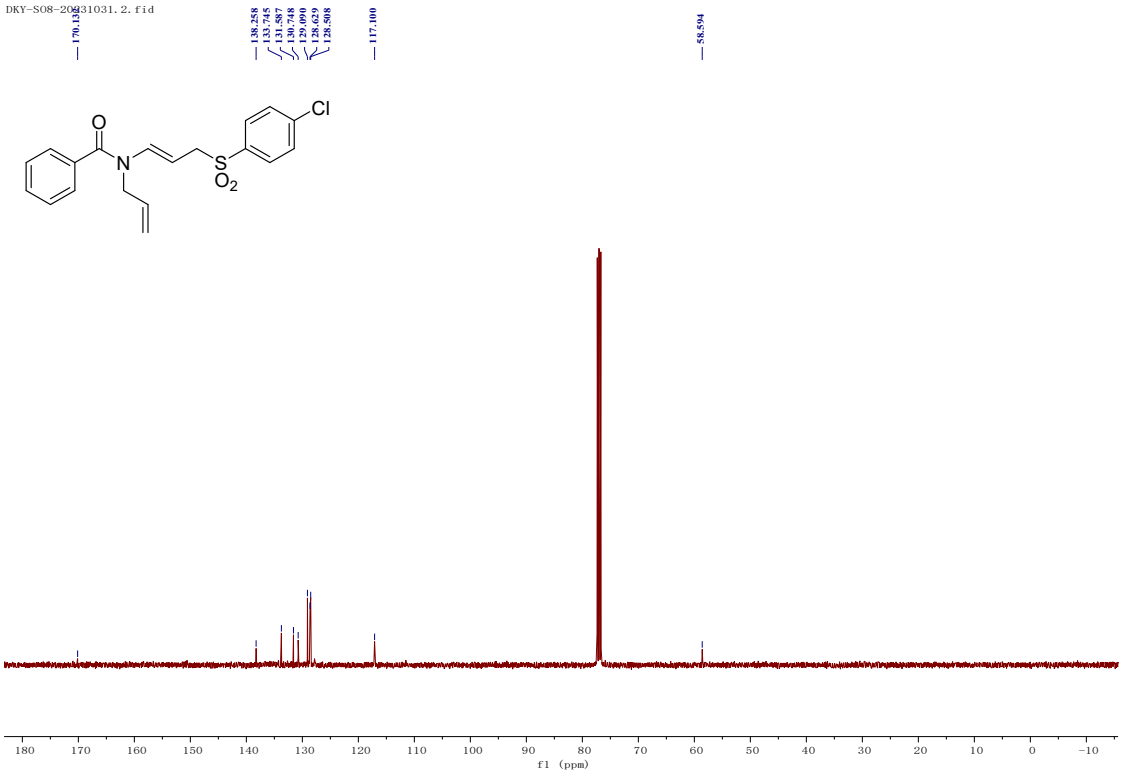
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 21



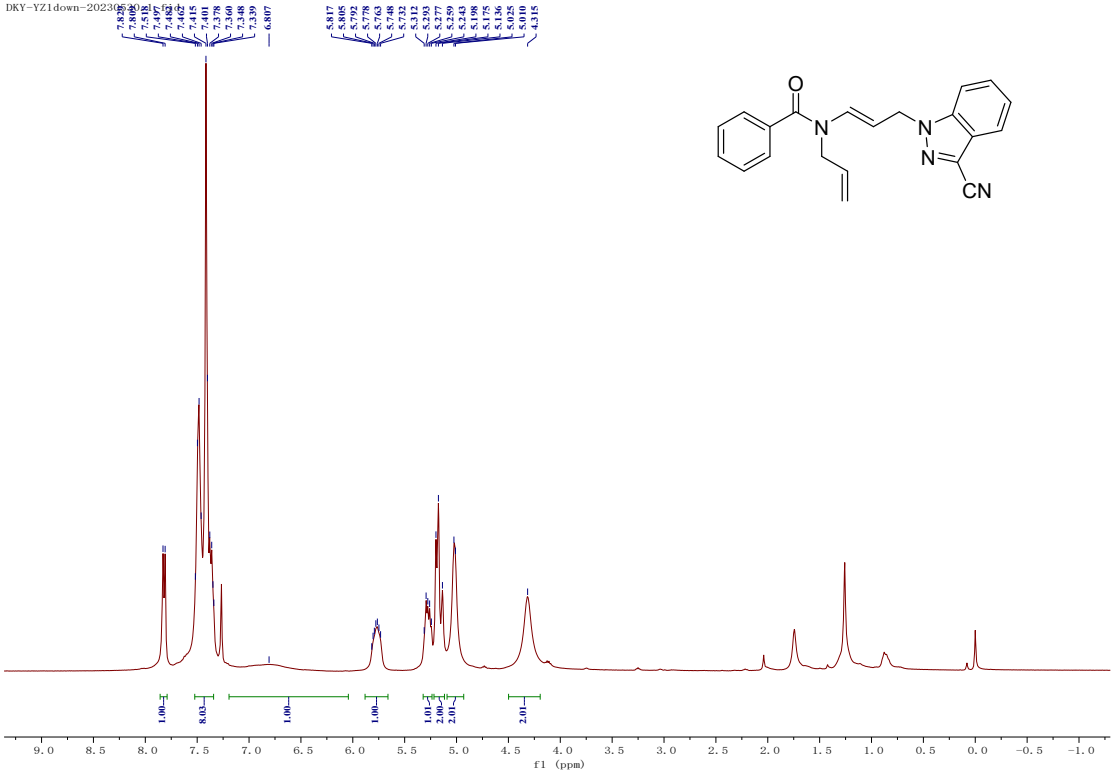
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 22



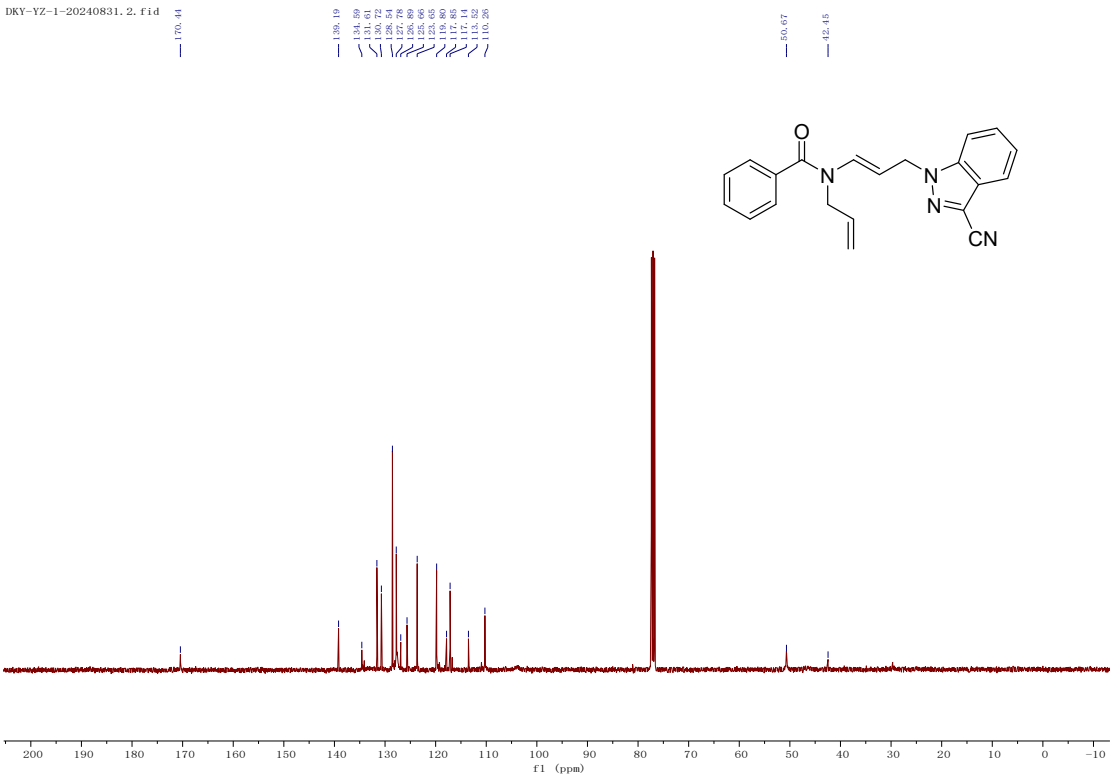
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 22



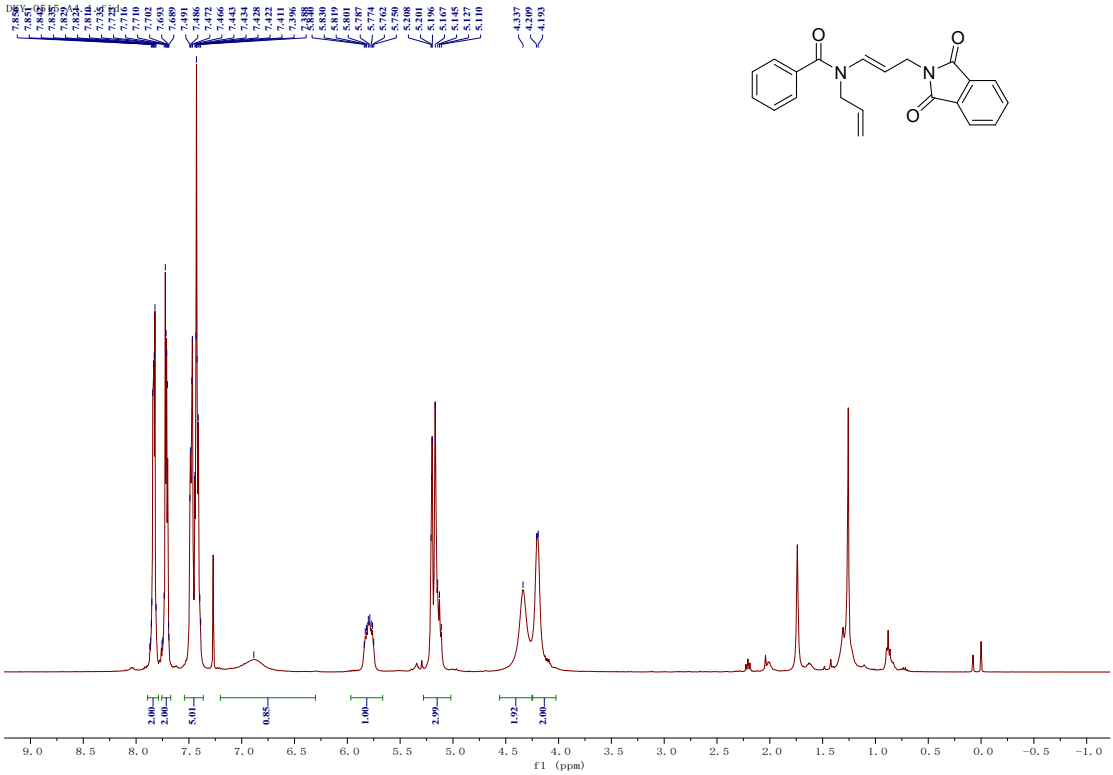
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 23



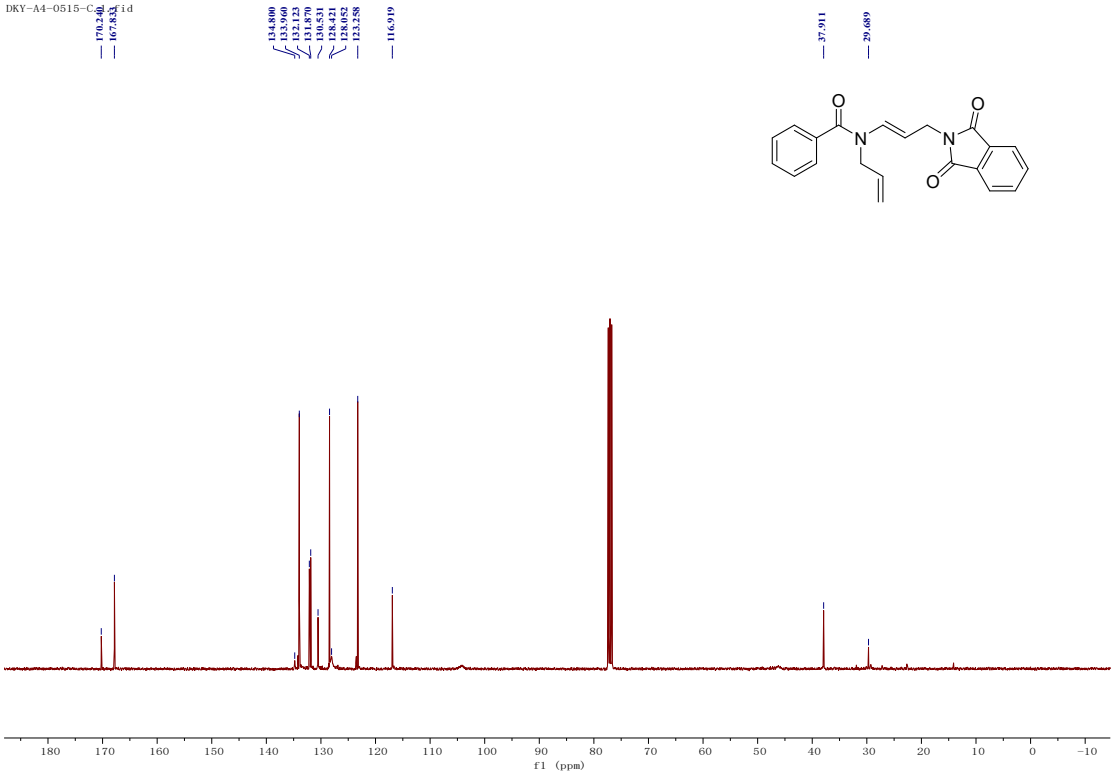
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 23



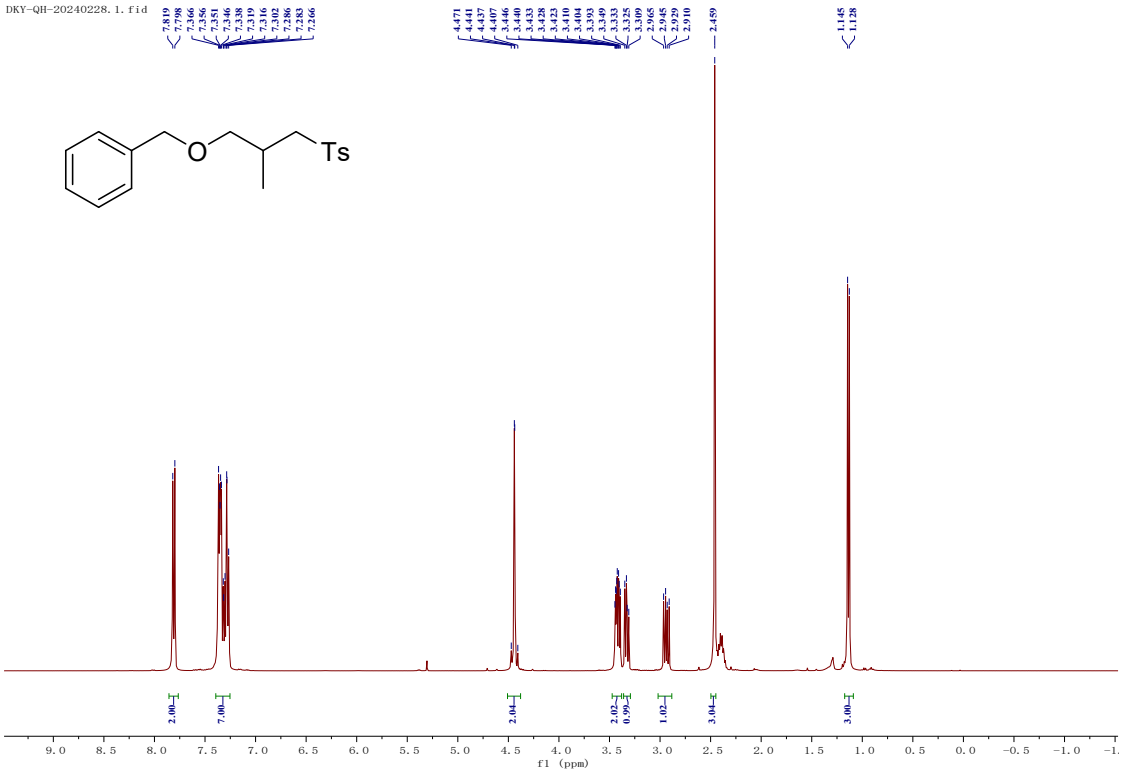
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 24



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 24



^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3’



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3’