Electrochemical 1,5-Chlorosulfonylation and 1,5-Hydrosulfonylation of Vinylcyclopropanes

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I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Solvents were degassed by bubbling Ar for 10 min before use. Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography over 300-400 mesh silica gel under a positive pressure of air. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). The Electrolysis was performed using a DJS-292B dual display potentiostat (Shanghai Xinrui Instruments Co., China). The electrochemical setup used in this research is shown in Figure S1.

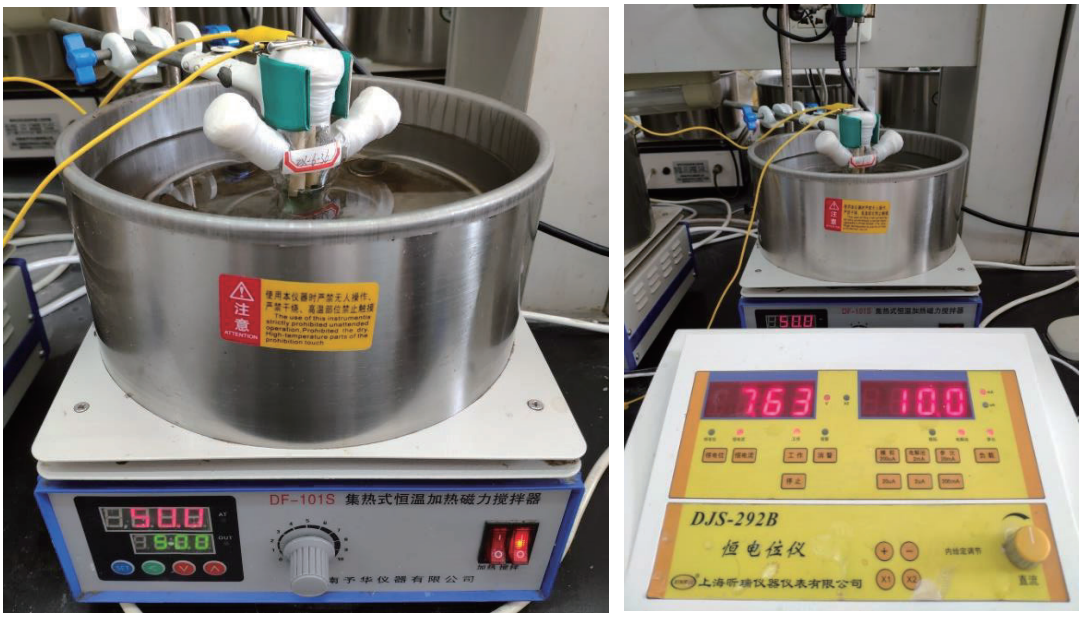
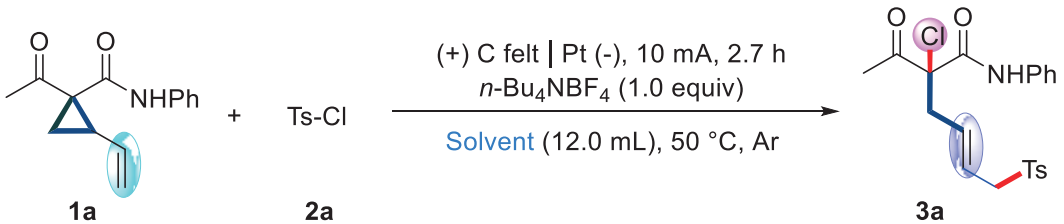


Figure S1 Electrochemical setup

II. Optimization of reaction conditions

Table S1 Solvent screening[a]



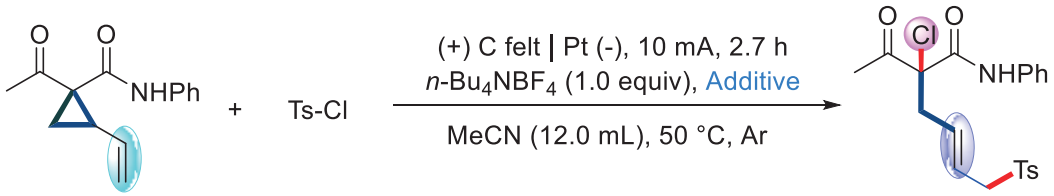
1a **2a** **3a**

Entry	Solvent	Yield (%)

1	DCE	14
2	$PhCF_3$	11
3	THF	31
4	Acetone	29
5	DMF	nr
6	DMSO	<5
7	MeOH	0
8	HFIP	<5
9	**MeCN**	**38**
10	MeCN/H_2O (9:1, v/v)	19
11	MeCN/MeOH (9:1, v/v)	17
12	MeCN/HFIP (9:1, v/v)	32

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu_4NBF_4 (0.5 mmol), solvent (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 10.0 mA, Ar, 50 ºC, 2.7 h, isolated yields.

Table S2 Additive screening[a]



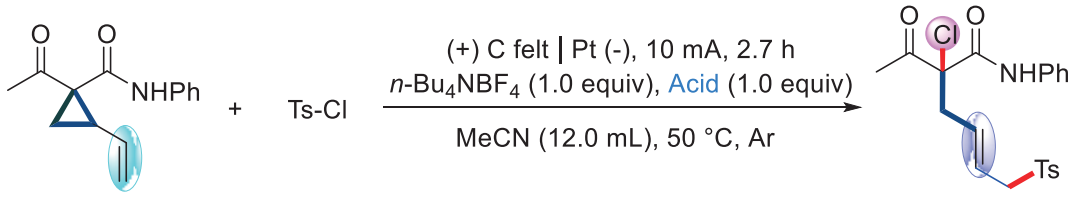
1a **2a** **3a**

Entry	Additive (equiv)	Yield (%)
1	LiCl (0.5)	10
2	NaCl (0.5)	27
3	KCl (0.5)	14
4	CsCl (0.5)	10
5	TBAC (0.5)	16
6	$AgNO_3$ (1.0)	0
7	$AgNO_3$ (2.0)	0
8	**None**	**38**

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu_4NBF_4 (0.5 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), platinum plate cathode

(15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 10.0 mA, Ar, 50 ºC, 2.7 h, isolated yields.

Table S3 Acid screening[a]

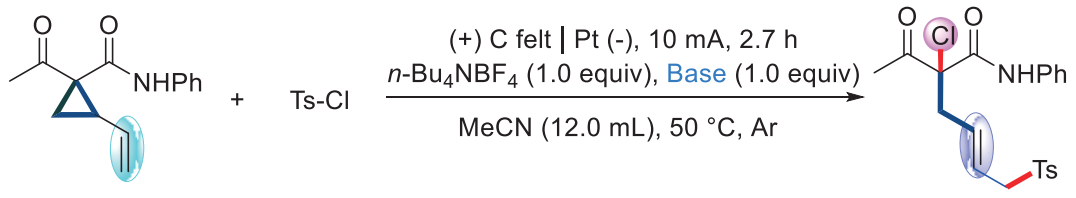


1a **2a** **3a**

Entry	Acid	Yield (%)
1	TFA (1.0)	36
2	HOAc (1.0)	34
3	**none**	**38**

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu$_4$NBF$_4$ (0.5 mmol), acid (0.5 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 10.0 mA, Ar, 50 ºC, 2.7 h, isolated yields.

Table S4 Base screening[a]



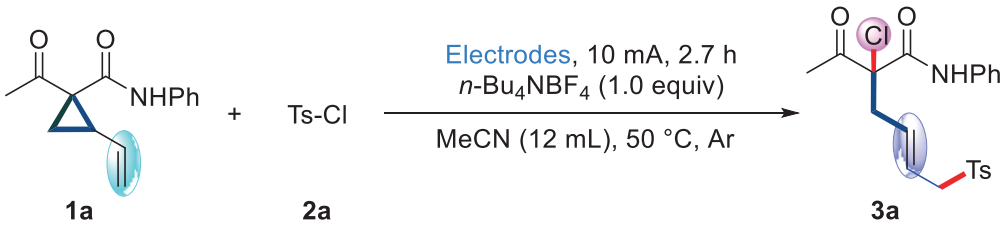
1a **2a** **3a**

Entry	Base	Yield (%)
1	*n*-Bu$_4$NOAc	15
2	Et$_3$N	14
3	K$_2$CO$_3$	<5
4	KOAc	<5
5	K$_2$HPO$_4$	<5
6	2,6-lutidine	22
7	**None**	**38**

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu$_4$NBF$_4$ (0.5 mmol), base (0.5 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), platinum plate cathode (15 mm × 15 mm × 0.3 mm), undivided cell, constant current = 10.0 mA,

Ar, 50 ºC, 2.7 h, isolated yields.

Table S5 Electrode screening[a]

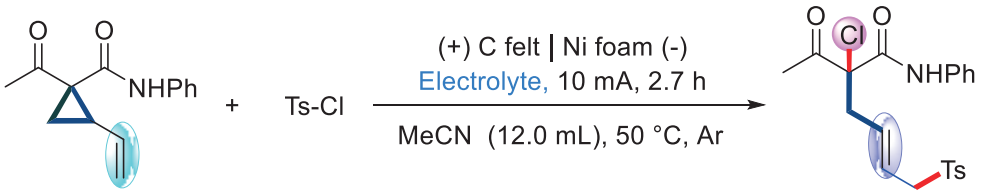


1a **2a** **3a**

Entry	Anode	Cathode	Yield (%)
1	C felt	stainless steel	30
2	C felt	Ni plate	18
3	**C felt**	**Ni foam**	**44**
4	C felt	Cu foam	<5
5	C felt	C cloth	26
6	C felt	C felt	7
7	C felt	C rod[b]	7
8	C felt	Pt plate	38
9	C cloth	Ni foam	13
10	C rod[b]	Ni foam	nr
11	Pt plate	Ni foam	19

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu_4NBF_4 (0.5 mmol), MeCN (12.0 mL), electrodes (15 mm × 15 mm), undivided cell, constant current = 10.0 mA, Ar, 50 ºC, 2.7 h, isolated yields. [b] Ø 6 mm.

Table S6 Electrolyte screening[a]



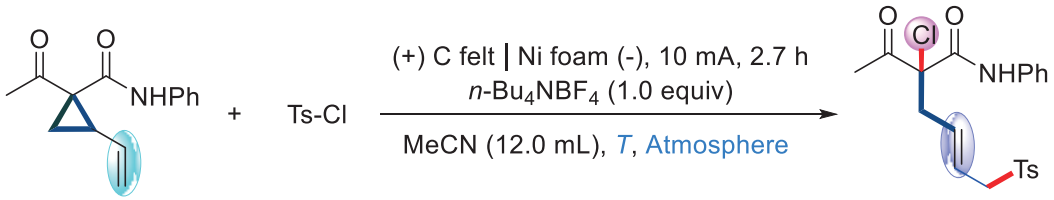
1a **2a** **3a**

Entry	Electrolyte (equiv)	Yield (%)
1	$LiClO_4$ (1.0)	29
2	*n*-Et_4NBF_4 (1.0)	32
3	*n*-Bu_4NPF_6 (1.0)	27
4	*n*-Bu_4NOAc (1.0)	25
5	*n*-Bu_4NClO_4 (1.0)	24
6	TBAI (1.0)	0

7	TBAB (1.0)	<5
8	***n*-Bu$_4$NBF$_4$ (1.0)**	**44**
9	*n*-Bu$_4$NBF$_4$ (0.3)	27
10	*n*-Bu$_4$NBF$_4$ (0.5)	35
11	*n*-Bu$_4$NBF$_4$ (1.5)	44
12	*n*-Bu$_4$NBF$_4$ (2.0)	43

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), nickel foam cathode (15 mm × 15 mm × 1.5 mm), undivided cell, constant current = 10.0 mA, Ar, 50 ºC, 2.7 h, isolated yields.

Table S7 Temperature, substrate loading and atmosphere optimization[a]

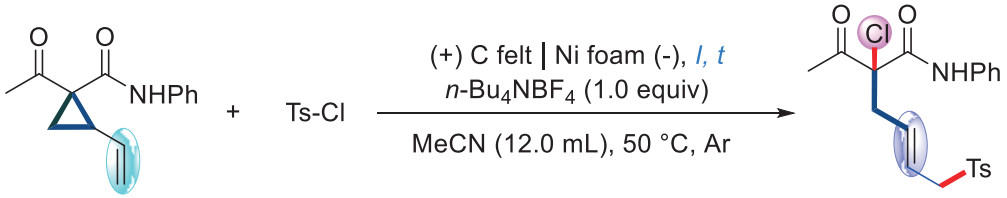


1a **2a (X equiv)** **3a**

Entry	*T* (ºC)	X (equiv)	Atmosphere	Yield (%)
1	35	1.2	Ar	40
2	**50**	**1.2**	**Ar**	**44**
3	50	1.5	Ar	42
4	50	2.0	Ar	5
5	50	1.2	in air and sealed	19

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu$_4$NBF$_4$ (0.5 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), nickel foam cathode (15 mm × 15 mm × 1.5 mm), undivided cell, constant current = 10.0 mA, 2.7 h, isolated yields.

Table S8 Current and time optimization[a]



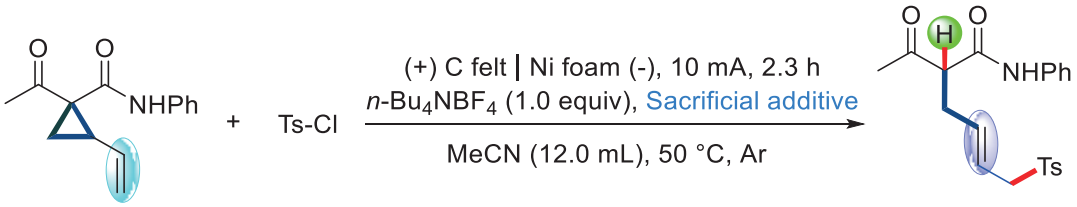
1a **2a** **3a**

Entry	*I* (mA), *t* (h)	Yield (%)
1	0, 12	0

2	5, 5.4	21
3	8, 3.4	29
4	10, 2.7	44
5	12, 2.2	43
6	15, 1.8	34
7	10, 3.5	27
8	10, 3.0	32
9	**10, 2.3**	**47**
10	10, 2.0	18
11	10, 1.7	26
12	10, 1.4	24

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu_4NBF_4 (0.5 mmol), MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), nickel foam cathode (15 mm × 15 mm × 1.5 mm), undivided cell, constant current, Ar, 50 ºC, time, isolated yields.

Table S9 Sacrificial additive screening[a]



1a **2a** **4a**

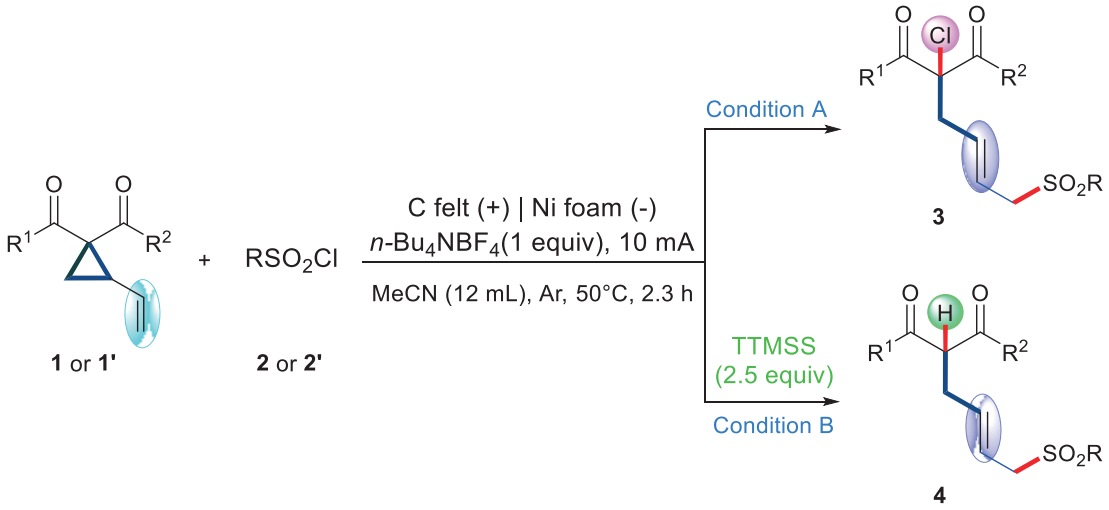
Entry	Sacrificial additive (equiv)	Yield (%)
1	HE (2.0)	64
2	TTMSS (2.0)	77
3	DIPEA (2.0)	<5
4	Et_3N (2.0)	<5
5	1,4-cyclohexadiene (2.0)	24
6	TTMSS (1.0)	67
7	TTMSS (1.5)	72
8	**TTMSS (2.5)**	**83**
9[b]	TTMSS (2.5)	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu_4NBF_4 (0.5 mmol), sacrificial additive, MeCN (12.0 mL), graphite felt anode (15 mm × 15 mm × 2 mm), nickel

foam cathode (15 mm × 15 mm × 1.5 mm), undivided cell, constant current = 10 mA, Ar, 50 ºC, 2.3 h, isolated yields. [b] No electric current, Ar, 50 ºC.

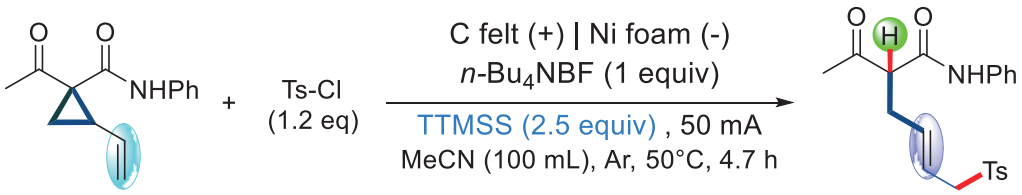
III. Experimental procedures

1. General procedure for the 1,5-chlorosulfonylation and 1,5-hydrosulfonylation of vinylcyclopropanes



Condition A: A custom-made undivided cell (Figure S1) equipped with a stir bar, a graphite felt anode (15 mm × 15 mm × 2 mm), and a nickel foam cathode (15 mm × 15 mm × 1.5 mm) was used. Under an argon atmosphere, vinylcyclopropane **1** or **1'** (0.5 mmol), electrolyte *n*-Bu_4NBF_4 (1.0 equiv, 0.5 mmol, 0.1646 g), and sulfonyl chloride (1.2 equiv, 0.6 mmol) were added to the cell (if the sulfonyl chloride is solid, dissolve it in 2.0 mL of degassed acetonitrile before adding; if it is liquid, add it directly using a microsyringe). For ***Condition B***, tris(trimethylsilyl)silane (TTMSS, 2.5 equiv, 1.25 mmol, 0.386 mL) was added at this point. Finally, degassed acetonitrile was added, bringing the total solvent volume to 12.0 mL. The mixture was electrolyzed with stirring using a constant current of 10.0 mA at 50°C (oil bath) for 2.3 hours (138 minutes). The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether−ethyl acetate) to afford products **3** or **4**.

2. Gram-scale synthesis

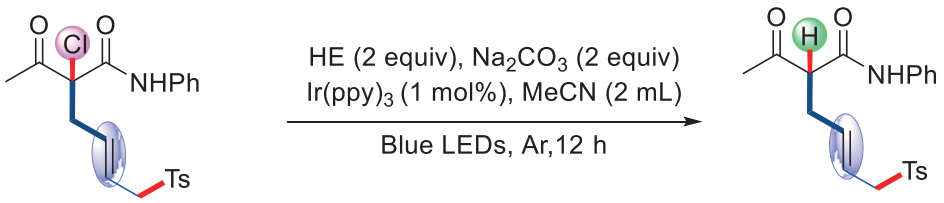


1a 5 mmol | **2a** 6 mmol | **4a** 64% yield,1.23 g

A custom-made undivided cell (Figure S2) equipped with a stir bar, a graphite felt anode (15 mm × 15 mm × 2 mm), and a nickel foam cathode (15 mm × 15 mm × 1.5 mm) was used. Under an argon atmosphere, vinylcyclopropane **1a** (5 mmol, 1.146 g), electrolyte *n*-Bu_4NBF_4 (1.0 equiv, 5 mmol, 1.646 g), *p*-toluenesulfonyl chloride **2a** (1.2 equiv, 6 mmol, 1.144 g), and tris(trimethylsilyl)silane (TTMSS, 2.5 equiv, 12.5 mmol, 3.86 mL) were added to the cell. Finally, degassed acetonitrile (100 mL) was added. The mixture was electrolyzed with stirring using a constant current of 50.0 mA at 50°C (oil bath) for 4.7 hours. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether−ethyl acetate) to afford product **4a** (1.23 g, 64% yield).

Figure S2 Setup for gram-scale synthesis

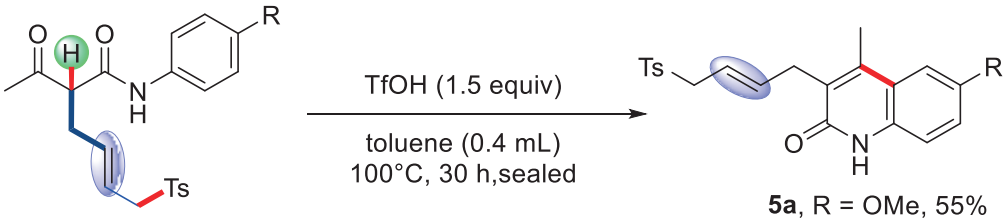
3. Transformations of the products



3a, 0.2 mmol

4a, 98%

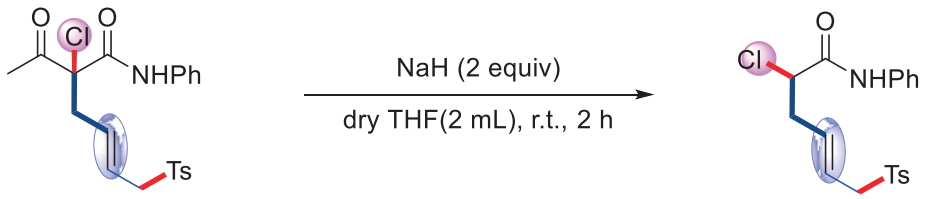
To a 10 mL reaction tube equipped with a magnetic stir bar, add **3a** (0.2 mmol, 0.0840 g), HE (Hantzsch ester, 2 equiv, 0.1023 g), Na_2CO_3 (2 equiv, 0.0424 g), and $Ir(ppy)_3$ (1 mol%, 0.0013 g) under an argon atmosphere, along with 2 mL of acetonitrile. Illuminate the reaction with blue LEDs (6 W) for 12 hours. After the reaction was completed, add 10 mL of water to quench the reaction, and extract with 10 mL of dichloromethane (repeat three times). Evaporate the solvent and purify the residue by column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) to obtain the desired product **4a** (76.3 mg, 98% yield).



3, 0.5 mmol

5a, R = OMe, 55%
5b, R = Me, 61%

To a 10 mL pressure tube equipped with a magnetic stir bar, add substrate **4** (0.2 mmol), trifluoromethanesulfonic acid (1.5 equiv, 27 μL), and toluene (0.4 mL). Seal the tube and heat at 100°C (oil bath) for 30 hours. After the reaction is complete, add 10 mL of sodium bicarbonate solution to quench the reaction, and extract with 10 mL of dichloromethane (repeat three times). Evaporate the solvent and purify the residue by column chromatography (petroleum ether/ethyl acetate/Et_3N = 50:100:1 or petroleum ether/ethyl acetate/Et_3N = 50:50:1, v/v/v) to obtain the desired product, **5a** (43.8 mg, 55% yield) or **5b** (66.3 mg, 61% yield).



3a, 0.2 mmol

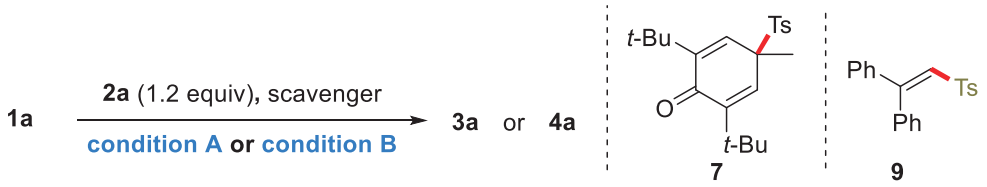
6, 57%

To a 10 mL reaction tube equipped with a magnetic stir bar, add substrate **3a** (0.2 mmol),

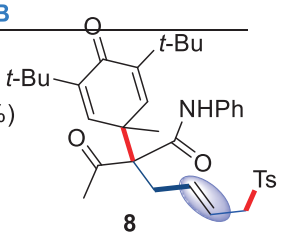
dry THF (0.4 mL), and NaH (2 equiv, 60% dispersion in mineral oil). Seal the tube and stir at room temperature for 2 hours. After the reaction is complete, add 5 mL of water to quench the reaction, and extract with 10 mL of dichloromethane (repeat three times). Evaporate the solvent and purify the residue by column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to obtain the desired product **6** (43.3 mg, 57% yield).

IV. Mechanistic investigations

1. Quenching experiments



quencher (equiv)	scavenger for	^{1}H NMR yield of **3a** (%) condition A	^{1}H NMR yield of **4a** (%) condition B
none	-	47	83
TEMPO (1)	radical	<1	<1
BHT (4)	radical	<1 (**7**, 41%; **8**, 14%)	38 (**7**, 15%)
DPE (1)	radical	<1 (**9**, 19%)	<1
*p*DNB (1)	SET	0	<1
$CuCl_2$ (1)	single electron	<1	0
CCl_4 (2)	single electron	26	65



Condition A: A custom-made undivided cell (Figure S1) equipped with a stir bar, a graphite felt anode (15 mm × 15 mm × 2 mm), and a nickel foam cathode (15 mm × 15 mm × 1.5 mm) was used. Under an argon atmosphere, vinylcyclopropane **1** (0.5 mmol), electrolyte *n*-Bu_4NBF_4 (1.0 equiv, 0.5 mmol, 0.1646 g), **a scavenger** (type and loading are shown in the table above), and sulfonyl chloride (1.2 equiv, 0.6 mmol) were added to the cell. If the sulfonyl chloride is solid, dissolve it in 2.0 mL of degassed acetonitrile before adding; if it is liquid, add it directly using a microsyringe. For ***Condition B***, tris(trimethylsilyl)silane (TTMSS, 2.5 equiv, 1.25 mmol, 0.386 mL) was added at this moment. Finally, degassed acetonitrile was added, bringing the total solvent volume to 12.0 mL. The mixture was electrolyzed with stirring using a constant current of 10.0 mA at 50°C (oil bath) for 2.3 h (138 min). The yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

2. Electricity on-off experiments

The reactions of **1a** and **2j1** (4-fluorobenzenesulfonyl chloride) were monitored for

detection purposes. Trifluorotoluene (1 equiv) was added to the reaction mixture as an internal standard before electrolysis. A 0.1 mL aliquot of the crude reaction solution was withdrawn at regular intervals using a syringe and subjected to ^{19}F NMR analysis.

	A(X)	B(Y)
Long Name	time	19F NMR yield
Units	min	%
Comments		
F(x)=		Electricity on/off
1	0	0
2	20	10
3	40	12
4	60	31
5	80	34
6	100	43
7	120	44
8	140	56
9	160	56

Figure S3 Electricity on-off experiments of condition A

	A(X)	B(Y)
Long Name	time	19F NMR Yield
Units	min	%
Comments		
F(x)=		Electricity on/off
1	0	0
2	20	59
3	40	60
4	60	70
5	80	72
6	100	81
7	120	81
8	140	89
9	160	90

Figure S4 Electricity on-off experiments of condition B

4. Reaction kinetic profiles

Benzotrifluoride (1 equiv) was added as an internal standard to the reaction mixture before electrolysis using 4-(Trifluoromethyl)benzenesulfonyl chloride as the radical precursor. 0.05 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{19}F NMR analysis.

	A(X)	B(Y)
Long Name	time	19F NMR Yield
Units	min	%
Comments		
F(x)=		
1	0	0
2	20	3
3	40	6
4	60	13
5	80	18
6	100	24
7	120	26
8	140	32
9	160	31

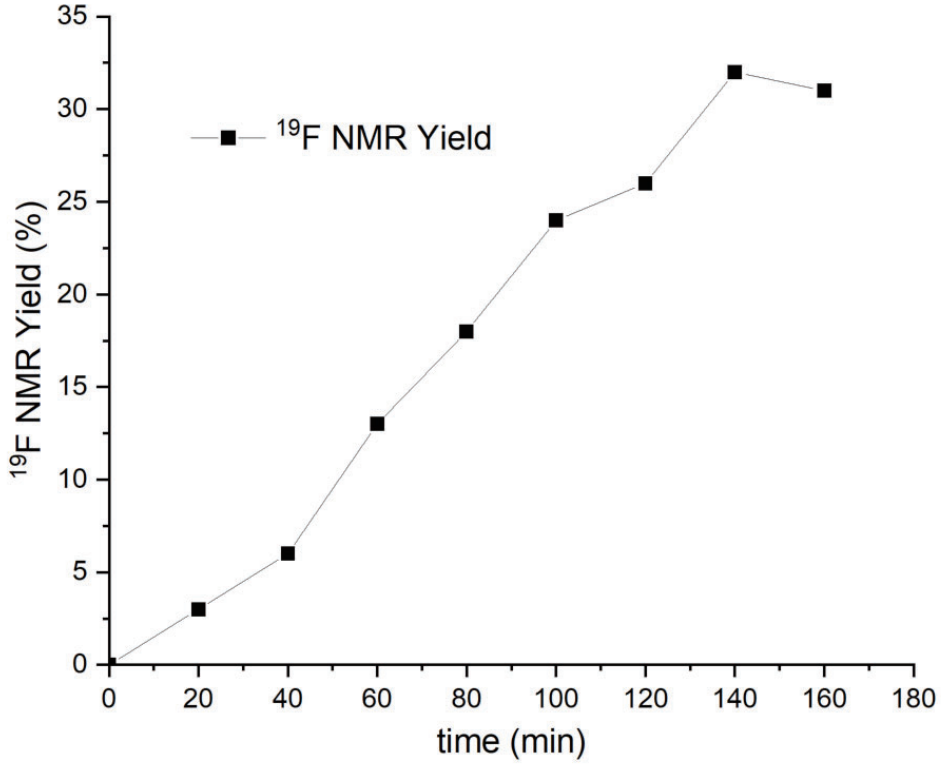


Figure S5 Reaction kinetic profiles of condition A

	A(X)	B(Y)
Long Name	time	19F NMR Yield
Units	min	%
Comments		
F(x)=		
1	0	0
2	20	73
3	40	86
4	60	87
5	80	89
6	100	91
7	120	94
8	140	95
9	160	96
10	180	96
11	200	95

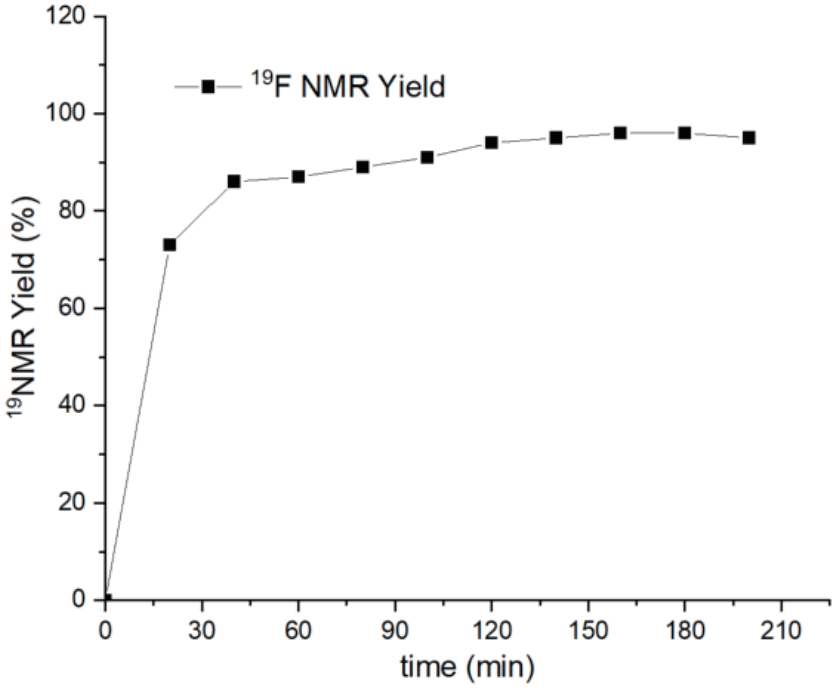


Figure S6 Reaction kinetic profiles of condition B

5. Cyclic voltammetry studies

General procedure: Cyclic voltammetries were performed in a three-electrode cell at room temperature. The working electrode was a glassy carbon (GC, d = 3 mm) disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution, and separated from

reactions by a salt bridge. 10 mL MeCN solution containing 1.0 mmol *n*-Bu_4NBF_4 was poured into the electrochemical cell in all experiments. The scan rate was 0.05 V/s.

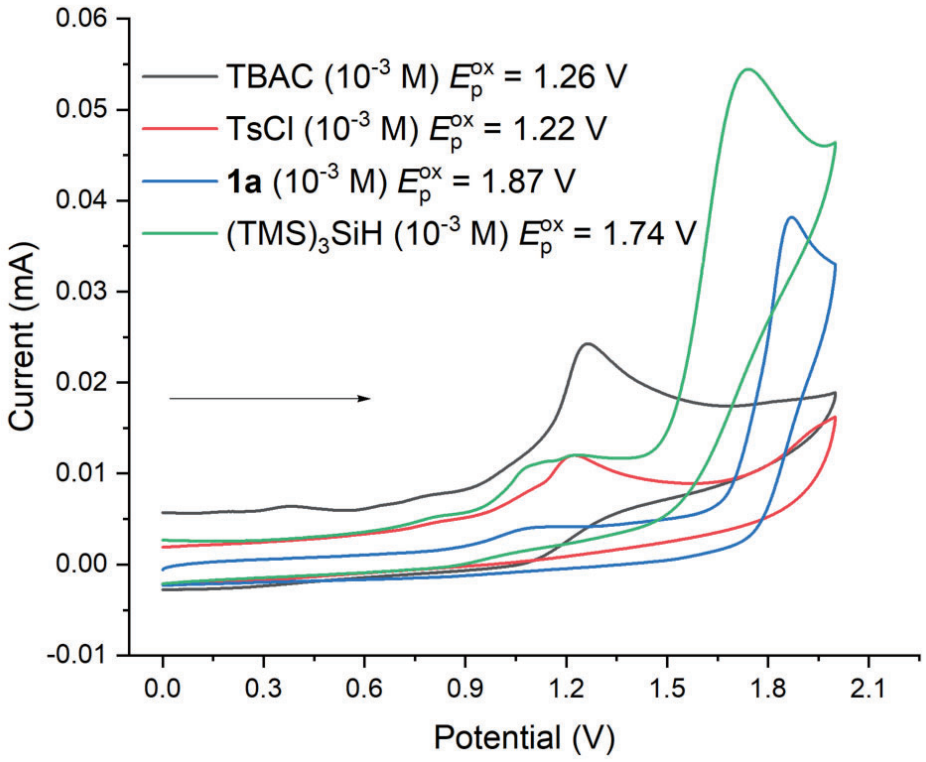


Figure S7 Anodic cyclic voltammograms of TBAC, TsCl, **1a**, or $(TMS)_3SiH$ in MeCN

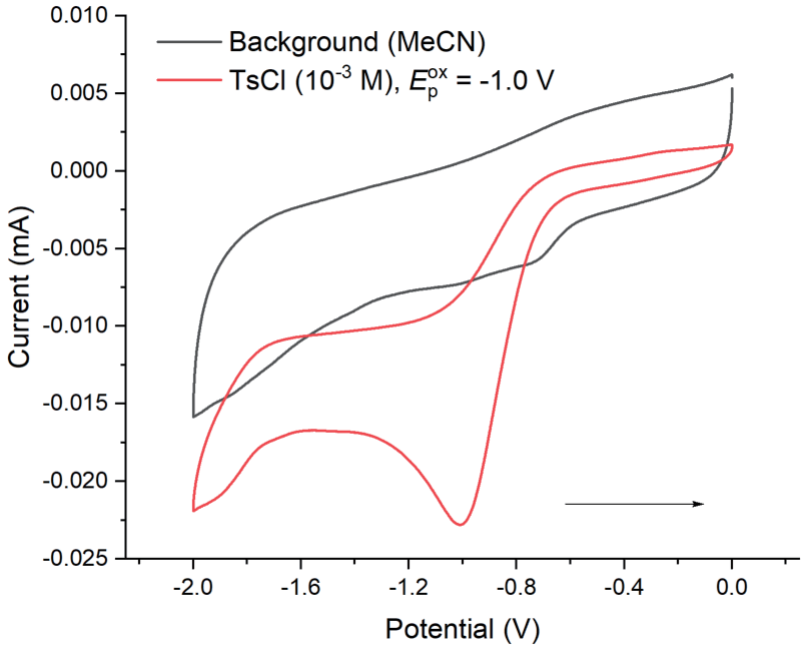
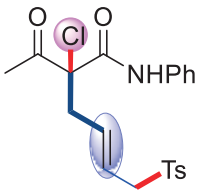
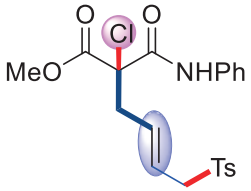


Figure S8 Cathode cyclic voltammograms of TsCl in MeCN

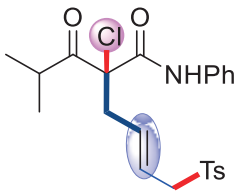
V. Spectral data of products



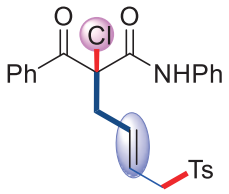
(*E*)-2-Acetyl-2-chloro-*N*-phenyl-6-tosylhex-4-enamide (**3a**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 47% yield (99.5 mg), *E/Z* = 25:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 11.0, 4.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.53 (tdd, *J* = 22.2, 14.9, 7.1 Hz, 2H), 3.65 (qd, *J* = 13.9, 7.1 Hz, 2H), 2.99 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.75 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.41, 164.49, 144.88, 136.39, 135.70, 133.30, 129.83, 129.19, 128.32, 125.68, 122.51, 120.37, 75.41, 59.93, 39.43, 25.16, 21.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_4S^+$ ($[M+H]^+$) 420.1031. Found 420.1033.



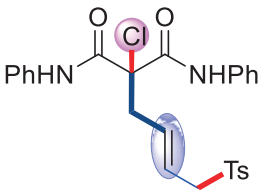
Methyl (*E*)-2-chloro-2-(phenylcarbamoyl)-6-tosylhex-4-enoate (**3a1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 25% yield (51.4 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown yellow oil, R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.74 – 7.64 (m, 2H), 7.55 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.15 (m, 1H), 5.68 – 5.55 (m, 2H), 3.83 (s, 3H), 3.78 – 3.69 (m, 2H), 3.25 – 3.15 (m, 1H), 2.99 (ddd, *J* = 14.8, 4.6, 2.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.35, 163.37, 144.84, 136.49, 135.51, 132.70, 129.79, 129.15, 128.39, 125.55, 122.91, 120.27, 70.47, 59.92, 54.10, 40.58, 21.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_5S^+$ ($[M+H]^+$) 436.0980. Found 436.0981.



(*E*)-2-Chloro-2-isobutyryl-*N*-phenyl-6-tosylhex-4-enamide (**3a2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 45% yield (101.6 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.75 – 5.47 (m, 2H), 3.74 (qd, *J* = 13.9, 7.1 Hz, 2H), 3.08 (dd, *J* = 14.7, 6.3 Hz, 1H), 2.83 (dd, *J* = 14.7, 7.7 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.44, 164.30, 144.86, 135.70, 135.49, 133.81, 133.33, 129.82, 129.67, 128.35, 122.45, 120.36, 75.41, 59.95, 39.43, 25.11, 21.65, 20.95. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_4S^+$ ($[M+H]^+$) 448.1344. Found 448.1344.

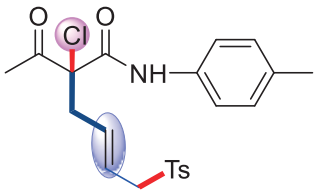


(*E*)-2-Benzoyl-2-chloro-*N*-phenyl-6-tosylhex-4-enamide (**3a3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 35% yield (83.7 mg), *E/Z* = 13:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.07 – 7.96 (m, 2H), 7.76 – 7.70 (m, 2H), 7.65 – 7.58 (m, 2H), 7.58 – 7.51 (m, 1H), 7.44 – 7.35 (m, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.17 (m, 1H), 5.81 (ddd, *J* = 8.5, 8.1, 6.7 Hz, 1H), 5.60 (ddd, *J* = 15.2, 8.4, 6.5 Hz, 1H), 3.83 (dd, *J* = 13.6, 6.4 Hz, 1H), 3.73 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.23 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.04 (dd, *J* = 14.9, 8.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.34, 165.44, 144.95, 136.48, 135.85, 133.56, 133.49, 133.23, 129.89, 129.47, 129.22, 128.58, 128.32, 125.60, 122.76, 120.43, 72.13, 60.06, 41.14, 21.68. HRMS (ESI-TOF) Calcd for $C_{26}H_{25}ClNO_4S^+$ ($[M+H]^+$) 482.1187. Found 482.1188.

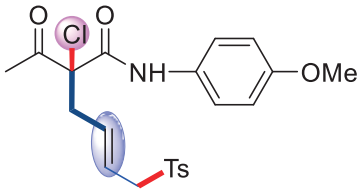


(*E*)-2-Chloro-N^1,N^3-diphenyl-2-(4-tosylbut-2-en-1-yl)malonamide (**3a4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 31% yield (78.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown solid, m.p. = 120.4-121.3 °C. R_f (petroleum ether/ethyl acetate = 4:1, v/v) 0.33. ^{1}H NMR (400 MHz,

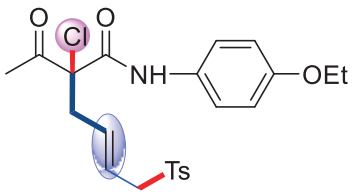
$CDCl_3$) δ 9.01 (s, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 7.9 Hz, 4H), 7.37 (t, J = 7.8 Hz, 4H), 7.30 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 7.4 Hz, 2H), 5.66 (q, J = 6.2 Hz, 2H), 3.76 (d, J = 6.0 Hz, 2H), 3.17 (d, J = 5.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.30, 144.90, 136.49, 135.56, 132.45, 129.83, 129.20, 128.36, 125.64, 123.21, 120.52, 76.12, 59.87, 44.14, 21.66. HRMS (ESI-TOF) Calcd for $C_{26}H_{26}ClN_2O_4S^+$ ($[M+H]^+$) 497.1296. Found 497.1299.



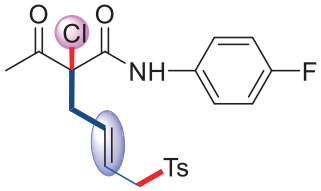
(*E*)-2-Acetyl-2-chloro-*N*-(*p*-tolyl)-6-tosylhex-4-enamide (**3b1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 9:1, v/v) in 38% yield (82.2 mg), *E*/*Z* = 17:1, which was detected by ^{1}H NMR spectroscopy. Brown oil, R_f (petroleum ether/ethyl acetate = 4:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 5.73 – 5.50 (m, 2H), 3.74 (qd, J = 13.9, 7.1 Hz, 2H), 3.08 (dd, J = 14.7, 6.3 Hz, 1H), 2.83 (dd, J = 14.7, 7.7 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.44, 164.30, 144.86, 135.70, 135.49, 133.81, 133.33, 129.82, 129.67, 128.35, 122.45, 120.36, 75.41, 59.95, 39.43, 25.11, 21.65, 20.95. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_4S^+$ ($[M+H]^+$) 434.1187. Found 434.1190.



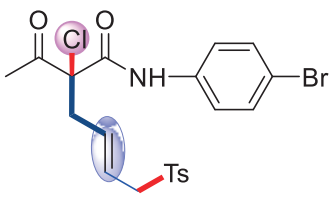
(*E*)-2-Acetyl-2-chloro-*N*-(4-methoxyphenyl)-6-tosylhex-4-enamide (**3b2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 36% yield (80.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.74 – 5.49 (m, 2H), 3.81 (s, 3H), 3.79 – 3.67 (m, 2H), 3.08 (dd, J = 14.7, 6.5 Hz, 1H), 2.83 (dd, J = 14.7, 7.8 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.47, 164.26, 157.36, 144.88, 135.72, 133.42, 129.83, 129.40, 128.34, 122.39, 122.16, 114.29, 75.37, 59.96, 55.53, 39.39, 25.10, 21.65. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_5S^+$ ($[M+H]^+$) 450.1136. Found 450.1136.



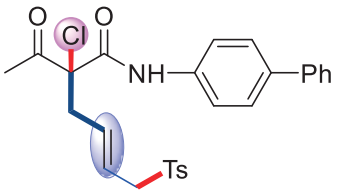
(*E*)-2-Acetyl-2-chloro-*N*-(4-ethoxyphenyl)-6-tosylhex-4-enamide (**3b3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 40% yield (93.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.78 – 5.45 (m, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.75 (qd, *J* = 13.9, 7.2 Hz, 2H), 3.08 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.83 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50, 164.22, 156.71, 144.89, 135.66, 133.43, 129.84, 129.24, 128.35, 122.40, 122.12, 114.85, 75.35, 63.75, 59.96, 39.38, 25.12, 21.68, 14.82. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_5S^+$ ($[M+H]^+$) 464.1293. Found 464.1294.



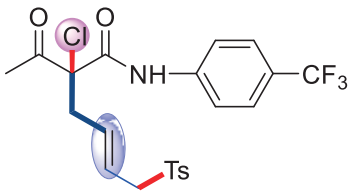
(*E*)-2-Acetyl-2-chloro-*N*-(4-fluorophenyl)-6-tosylhex-4-enamide (**3b4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 42% yield (93.0 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.55 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.02 (m, 2H), 5.71 (ddd, *J* = 14.9, 7.7, 7.0 Hz, 1H), 5.63 – 5.46 (m, 1H), 3.74 (ddd, *J* = 21.7, 13.8, 7.3 Hz, 2H), 3.09 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.94 – 2.77 (m, 1H), 2.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.36, 164.61, 164.01 (d, *J* = 246.2 Hz), 144.97, 135.79, 133.47, 132.42 (d, *J* = 3.0 Hz), 129.88, 128.26, 122.44, 122.35 (d, *J* = 8.1 Hz), 115.91 (d, *J* = 22.8 Hz), 75.32, 59.93, 39.32, 25.19, 21.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.02. HRMS (ESI-TOF) Calcd for $C_{21}H_{22}ClFNO_4S^+$ ($[M+H]^+$) 438.0937. Found 438.0938.



(*E*)-2-Acetyl-*N*-(4-bromophenyl)-2-chloro-6-tosylhex-4-enamide (**3b5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 48% yield (120.0 mg), *E*/*Z* = 17:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.75 – 5.64 (m, 1H), 5.64 – 5.49 (m, 1H), 3.78 (dd, *J* = 13.7, 6.5 Hz, 1H), 3.69 (dd, *J* = 13.8, 7.9 Hz, 1H), 3.08 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.83 (dd, *J* = 14.7, 8.0 Hz, 1H), 2.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.26, 164.68, 144.97, 135.86, 135.54, 133.42, 132.14, 129.89, 128.23, 122.49, 121.96, 118.44, 75.36, 59.92, 39.34, 25.22, 21.67. HRMS (ESI-TOF) Calcd for $C_{21}H_{22}BrClNO_4S^+$ ($[M+H]^+$) 498.0136. Found 498.0138.

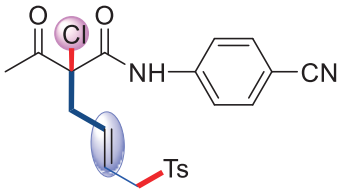


(*E*)-*N*-([1,1'-Biphenyl]-4-yl)-2-acetyl-2-chloro-6-tosylhex-4-enamide (**3b6**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 29% yield (70.9 mg), *E*/*Z* = 17:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.74 – 7.65 (m, 4H), 7.64 – 7.54 (m, 4H), 7.48 – 7.41 (m, 2H), 7.36 (dt, *J* = 9.3, 4.3 Hz, 1H), 7.32 (t, *J* = 5.4 Hz, 2H), 5.76 – 5.65 (m, 1H), 5.65 – 5.52 (m, 1H), 3.75 (qd, *J* = 13.8, 7.2 Hz, 2H), 3.11 (dd, *J* = 14.7, 6.5 Hz, 1H), 2.86 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.38, 164.53, 144.90, 140.21, 138.59, 135.79, 135.65, 133.38, 129.85, 128.88, 128.32, 127.78, 127.43, 126.94, 122.53, 120.63, 75.45, 59.96, 39.43, 25.19, 21.66. HRMS (ESI-TOF) Calcd for $C_{27}H_{27}ClNO_4S^+$ ($[M+H]^+$) 496.1344. Found 496.1345.

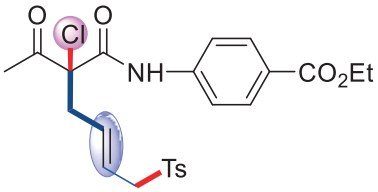


(*E*)-2-Acetyl-2-chloro-6-tosyl-*N*-(4-(trifluoromethyl)phenyl)hex-4-enamide (**3b7**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 40% yield (97.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* =

8.6 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.80 – 5.67 (m, 1H), 5.67 – 5.53 (m, 1H), 3.78 (dd, J = 13.6, 6.5 Hz, 1H), 3.69 (dd, J = 13.7, 8.1 Hz, 1H), 3.11 (dd, J = 14.6, 6.5 Hz, 1H), 2.85 (dd, J = 14.7, 8.2 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.15, 165.08, 145.02, 139.51, 135.93, 133.43, 129.91, 128.17, 127.30 (q, J = 32.9 Hz), 126.37 (q, J = 3.7 Hz), 125.70 (q, J = 272.4 Hz),122.57, 120.13, 75.34, 59.91, 39.33, 25.26, 21.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.30. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}ClF_3NO_4S^+$ ([M+H]$^+$) 488.0905. Found 488.0908.

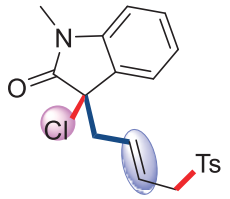


(*E*)-2-Acetyl-2-chloro-N-(4-cyanophenyl)-6-tosylhex-4-enamide (**3b8**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 36% yield (80.7 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.92 – 7.78 (m, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.90 – 5.69 (m, 1H), 5.69 – 5.48 (m, 1H), 3.78 (dd, J = 13.5, 6.5 Hz, 1H), 3.68 (dd, J = 13.6, 8.2 Hz, 1H), 3.10 (dd, J = 14.6, 6.7 Hz, 1H), 2.85 (dd, J = 14.6, 8.3 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.04, 165.31, 145.11, 140.47, 136.00, 133.51, 133.27, 129.97, 128.11, 122.59, 120.42, 118.54, 108.64, 75.29, 59.89, 39.26, 25.34, 21.68. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}ClN_2O_4S^+$ ([M+H]$^+$) 445.0983. Found 445.0984.

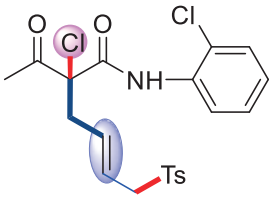


Ethyl (*E*)-4-(2-acetyl-2-chloro-6-tosylhex-4-enamido)benzoate (**3b9**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) in 38% yield (93.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.12 – 7.98 (m, 2H), 7.77 – 7.65 (m, 4H), 7.32 (d, J = 8.0 Hz, 2H), 5.80 – 5.65 (m, 1H), 5.64 – 5.50 (m, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.73 (ddd, J = 21.7, 13.7, 7.2 Hz, 2H), 3.10 (dd, J = 14.7, 6.5 Hz, 1H), 2.86 (dd, J = 14.7, 8.0 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.23, 165.88, 164.87, 144.96, 140.38, 135.85, 133.32, 130.80, 129.89, 128.23, 127.34, 122.60, 119.53, 75.43,

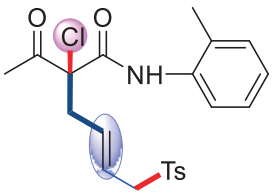
61.06, 59.91, 39.43, 25.28, 21.66, 14.35. HRMS (ESI-TOF) Calcd for $C_{24}H_{27}ClNO_6S^+$ ($[M+H]^+$) 492.1242. Found 492.1240.



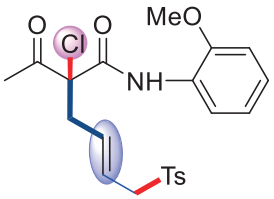
(*E*)-3-Chloro-1-methyl-3-(4-tosylbut-2-en-1-yl)indolin-2-one (**3c**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 21% yield (39.7 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown yellow oil, R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.02 (ddd, *J* = 13.3, 9.9, 4.3 Hz, 2H), 6.90 – 6.74 (m, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 5.26 (dt, *J* = 15.0, 7.4 Hz, 1H), 4.93 (dt, *J* = 15.1, 7.5 Hz, 1H), 3.58 (dd, *J* = 13.4, 6.3 Hz, 1H), 3.40 (d, *J* = 7.4 Hz, 2H), 3.08 (s, 3H), 2.94 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.38, 144.54, 143.35, 135.80, 134.97, 129.72, 128.54, 128.38, 127.39, 123.00, 121.80, 120.44, 107.80, 59.77, 55.57, 32.14, 25.82, 21.65. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_3S^+$ ($[M+H]^+$) 390.0925. Found 390.0922.



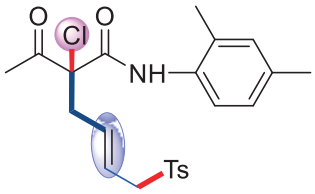
(*E*)-2-Acetyl-2-chloro-*N*-(2-chlorophenyl)-6-tosylhex-4-enamide (**3d1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 41% yield (94.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.21 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.15 (td, *J* = 7.8, 1.5 Hz, 1H), 5.65 – 5.57 (m, 2H), 3.79 – 3.71 (m, 2H), 3.16 – 3.01 (m, 1H), 2.97 – 2.84 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.16, 164.35, 144.80, 135.45, 133.14, 132.59, 129.75, 129.37, 128.41, 127.88, 126.28, 124.21, 122.82, 121.81, 75.89, 59.88, 39.72, 25.13, 21.63. HRMS (ESI-TOF) Calcd for $C_{21}H_{22}Cl_2NO_4S^+$ ($[M+H]^+$) 454.0641. Found 454.0642.



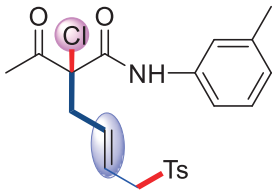
(*E*)-2-Acetyl-2-chloro-*N*-(*o*-tolyl)-6-tosylhex-4-enamide (**3d2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 44% yield (95.2 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 – 7.11 (m, 1H), 5.77 – 5.47 (m, 2H), 3.82 – 3.68 (m, 2H), 3.11 (d, *J* = 6.3 Hz, 1H), 2.97 – 2.83 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 164.27, 144.85, 135.55, 134.31, 133.03, 130.80, 129.79, 129.65, 128.39, 126.95, 126.36, 122.61, 122.57, 75.96, 59.91, 39.60, 25.06, 21.62, 17.64. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_4S^+$ ($[M+H]^+$) 434.1187. Found 434.1187.



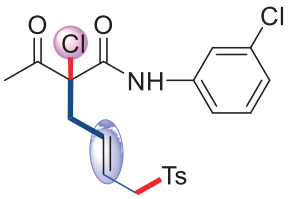
(*E*)-2-Acetyl-2-chloro-*N*-(2-methoxyphenyl)-6-tosylhex-4-enamide (**3d3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 41% yield (91.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.10 (m, 1H), 6.98 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.66 – 5.51 (m, 2H), 3.94 (s, 3H), 3.76 – 3.68 (m, 2H), 3.05 (dd, *J* = 14.8, 5.9 Hz, 1H), 2.89 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.57, 163.90, 148.66, 144.73, 135.43, 133.01, 129.72, 128.41, 126.13, 125.37, 122.41, 121.03, 119.74, 110.27, 75.81, 59.89, 55.99, 39.68, 25.05, 21.62. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_5S^+$ ($[M+H]^+$) 450.1136. Found 450.1137.



(*E*)-2-Acetyl-2-chloro-*N*-(2,4-dimethylphenyl)-6-tosylhex-4-enamide (**3e**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 39% yield (88.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 2H), 5.62 (dt, *J* = 13.4, 6.8 Hz, 2H), 3.75 (dd, *J* = 6.8, 2.8 Hz, 2H), 3.08 (dd, *J* = 14.8, 6.3 Hz, 1H), 2.94 – 2.81 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.35, 164.24, 144.83, 136.26, 135.54, 133.08, 131.64, 131.44, 129.78, 128.41, 127.45, 122.78, 122.56, 75.91, 59.94, 39.58, 25.03, 21.62, 20.93, 17.59. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_4S^+$ ($[M+H]^+$) 448.1344. Found 448.1346.

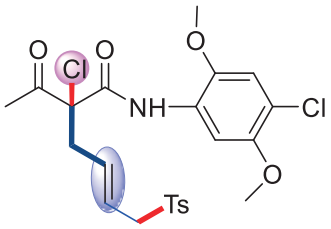


(*E*)-2-Acetyl-2-chloro-*N*-(*m*-tolyl)-6-tosylhex-4-enamide (**3f1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 45% yield (97.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 – 7.11 (m, 1H), 5.73 – 5.50 (m, 2H), 3.80 – 3.69 (m, 2H), 3.17 – 3.00 (m, 1H), 2.94 – 2.84 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 164.27, 144.85, 135.55, 134.31, 133.03, 130.80, 129.79, 129.65, 128.39, 126.95, 126.36, 122.61, 122.57, 75.96, 59.91, 39.60, 25.06, 21.62, 17.64. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_4S^+$ ($[M+H]^+$) 434.1187. Found 434.1190.

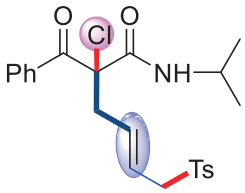


(*E*)-2-Acetyl-2-chloro-*N*-(3-chlorophenyl)-6-tosylhex-4-enamide (**3f2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 34% yield (77.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.78 (t, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.46 (ddd, *J* = 8.2, 2.0, 0.9

Hz, 1H), 7.36 – 7.28 (m, 3H), 7.18 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 5.65 (dtd, J = 22.9, 15.3, 7.9 Hz, 2H), 3.74 (ddd, J = 21.6, 13.7, 7.2 Hz, 2H), 3.09 (dd, J = 14.7, 6.4 Hz, 1H), 2.84 (dd, J = 14.7, 7.9 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.18, 164.74, 144.96, 137.53, 135.81, 134.84, 133.33, 130.16, 129.88, 128.24, 125.67, 122.57, 120.38, 118.35, 75.29, 59.95, 39.34, 25.21, 21.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{22}Cl_2NO_4S^+$ ($[M+H]^+$) 454.0641. Found 454.0645.

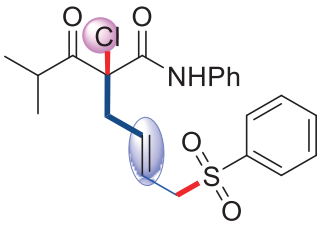


(*E*)-2-Acetyl-2-chloro-*N*-(4-chloro-2,5-dimethoxyphenyl)-6-tosylhex-4-enamide (**3g**), Isolated by flash column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) in 32% yield (82.7 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 132.6-133.6 ºC, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.11 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 5.60 (qd, J = 15.4, 8.8 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.73 (d, J = 6.3 Hz, 2H), 3.05 (dd, J = 14.7, 6.3 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.43 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.51, 164.03, 149.11, 144.79, 142.64, 135.59, 132.87, 129.75, 128.36, 125.35, 122.52, 117.60, 112.62, 104.76, 75.92, 59.84, 56.76, 56.69, 39.79, 25.19, 21.63. HRMS (ESI-TOF) Calcd for $C_{23}H_{26}Cl_2NO_6S^+$ ($[M+H]^+$) 514.0852. Found 514.0854.

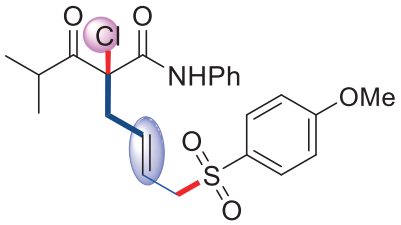


(*E*)-2-Benzoyl-2-chloro-*N*-isopropyl-6-tosylhex-4-enamide (**3h**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 36% yield (81.0 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 1H), 5.69 (dt, J = 14.8, 7.4 Hz, 1H), 5.62 – 5.49 (m, 1H), 4.07 (tt, J = 13.3, 6.6 Hz, 1H), 3.77 (ddd, J = 21.9, 13.9, 7.3 Hz, 2H), 3.11 (dd, J = 14.6, 6.7 Hz, 1H), 2.95 (dd, J = 14.7, 7.9 Hz, 1H), 2.45 (s, 3H), 1.23 (dd, J = 7.7, 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.69, 166.06, 144.89, 135.72, 133.65, 133.56, 133.33, 129.86, 129.38, 128.41, 128.31, 122.16, 72.01, 60.11, 42.57,

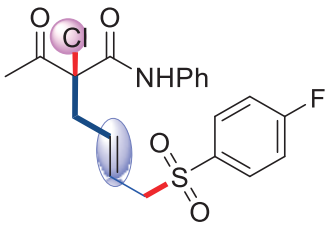
41.03, 22.35, 22.08, 21.68. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_4S^+$ ([M+H]$^+$) 448.1344. Found 448.1345.



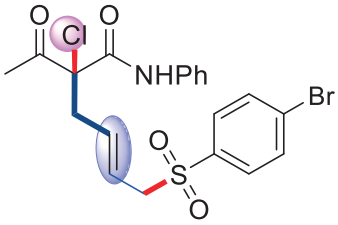
(*E*)-2-Chloro-2-isobutyryl-*N*-phenyl-6-(phenylsulfonyl)hex-4-enamide (**3i1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 7:1, v/v) in 34% yield (73.8 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.62 (dtd, *J* = 22.4, 15.1, 7.1 Hz, 2H), 3.76 (qd, *J* = 13.9, 7.2 Hz, 2H), 3.10 (dd, *J* = 14.7, 6.5 Hz, 1H), 3.02 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.83 (dd, *J* = 14.8, 7.7 Hz, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.65, 164.23, 138.62, 136.41, 133.80, 133.65, 129.20, 129.18, 128.32, 125.62, 122.15, 120.29, 75.90, 59.88, 39.49, 37.53, 21.46, 20.70, HRMS (ESI-TOF) Calcd for $C_{23}H_{25}ClNO_4S^+$ ([M+H]$^+$) 434.1187. Found 434.1190.



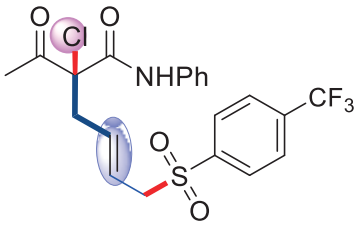
(*E*)-2-Chloro-2-isobutyryl-6-((4-methoxyphenyl)sulfonyl)-*N*-phenylhex-4-enamide (**3i2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) in 33% yield (76.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.11 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 1H), 5.60 (qd, *J* = 15.4, 8.8 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.73 (d, *J* = 6.3 Hz, 2H), 3.05 (dd, *J* = 14.7, 6.3 Hz, 1H), 2.91 (dd, *J* = 14.7, 6.4 Hz, 1H), 2.44 (d, *J* = 9.7 Hz, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.51, 164.03, 149.11, 144.79, 142.64, 135.59, 132.87, 129.75, 128.36, 125.35, 122.52, 117.60, 112.62, 104.76, 75.92, 59.84, 56.76, 56.69, 39.79, 25.19, 21.63. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_5S^+$ ([M+H]$^+$) 464.1293. Found 464.1296.



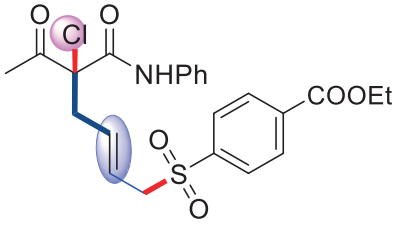
(*E*)-2-Acetyl-2-chloro-6-((4-fluorophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**3j1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 31% yield (66.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.86 – 7.76 (m, 2H), 7.64 – 7.53 (m, 2H), 7.43 – 7.33 (m, 2H), 7.24 – 7.12 (m, 3H), 5.78 – 5.64 (m, 1H), 5.64 – 5.49 (m, 1H), 3.86 – 3.65 (m, 2H), 3.10 (dd, *J* = 14.8, 6.6 Hz, 1H), 2.87 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.26, 165.83 (d, *J* = 257.7 Hz), 164.33, 136.33, 134.59 (d, *J* = 3.2 Hz), 133.81, 131.24 (d, *J* = 9.7 Hz), 129.24, 125.75, 122.07, 120.24, 116.55 (d, *J* = 22.7 Hz), 75.40, 59.97, 39.46, 25.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.03. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}ClFNO_4S^+$ ($[M+H]^+$) 424.0780. Found 424.0782.



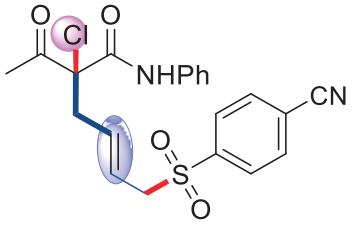
(*E*)-2-Acetyl-6-((4-bromophenyl)sulfonyl)-2-chloro-*N*-phenylhex-4-enamide (**3j2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 41% yield (98.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.65 (t, *J* = 1.9 Hz, 4H), 7.61 – 7.54 (m, 2H), 7.43 – 7.34 (m, 2H), 7.24 – 7.16 (m, 1H), 5.70 (ddd, *J* = 14.7, 7.7, 6.9 Hz, 1H), 5.63 – 5.42 (m, 1H), 3.76 (qd, *J* = 14.0, 7.3 Hz, 2H), 3.10 (dd, *J* = 14.8, 6.7 Hz, 1H), 2.86 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.24, 164.32, 137.54, 136.32, 133.96, 132.55, 129.90, 129.25, 125.76, 121.92, 120.25, 75.40, 59.85, 39.47, 25.11. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}BrClNO_4S^+$ ($[M+H]^+$) 483.9979. Found 483.9978.



(E)-2-Acetyl-2-chloro-N-phenyl-6-((4-(trifluoromethyl)phenyl)sulfonyl)hex-4-enamide (**3j3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 33% yield (77.4 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.42 – 7.35 (m, 2H), 7.24 – 7.18 (m, 1H), 5.73 (ddd, *J* = 14.7, 7.6, 6.9 Hz, 1H), 5.58 (dt, *J* = 15.2, 7.0 Hz, 1H), 3.89 – 3.68 (m, 2H), 3.10 (dd, *J* = 14.7, 6.8 Hz, 1H), 2.88 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.20, 164.27, 142.05, 136.31, 135.54 (q, *J* = 33.2 Hz), 134.37, 129.25, 129.02, 126.38 (q, *J* = 3.6 Hz), 125.78, 123.08 (q, *J* = 274.3 Hz), 121.51, 120.23, 75.37, 59.72, 39.47, 25.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}ClF_3NO_4S^+$ ($[M+H]^+$) 474.0748. Found 474.0747.

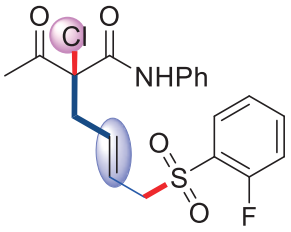


Ethyl (*E*)-4-((5-chloro-6-oxo-5-(phenylcarbamoyl)hept-2-en-1-yl)sulfonyl)benzoate (**3j4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 45% yield (108.3 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.58 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.18 (m, 1H), 5.70 (ddd, *J* = 14.7, 7.7, 6.9 Hz, 1H), 5.64 – 5.49 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.79 (qd, *J* = 14.0, 7.3 Hz, 2H), 3.09 (dd, *J* = 14.8, 6.6 Hz, 1H), 2.85 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.34 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.25, 164.96, 164.33, 142.21, 136.31, 135.34, 134.05, 130.29, 129.22, 128.42, 125.74, 121.80, 120.29, 75.35, 61.89, 59.74, 39.47, 25.10, 14.27. HRMS (ESI-TOF) Calcd for $C_{23}H_{25}ClNO_6S^+$ ($[M+H]^+$) 478.1086. Found 478.1089.

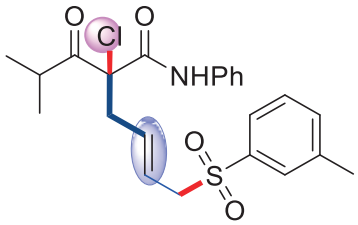


(*E*)-2-Acetyl-2-chloro-6-((4-cyanophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**3j5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in

52% yield (112.9 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.95 – 7.85 (m, 2H), 7.81 – 7.73 (m, 2H), 7.62 – 7.53 (m, 2H), 7.44 – 7.35 (m, 2H), 7.25 – 7.18 (m, 1H), 5.72 (dd, *J* = 15.0, 7.6 Hz, 1H), 5.63 – 5.47 (m, 1H), 3.87 – 3.71 (m, 2H), 3.10 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.88 (dd, *J* = 14.8, 7.5 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.13, 164.19, 142.58, 136.28, 134.60, 132.96, 129.31, 129.12, 125.86, 121.24, 120.23, 117.67, 117.06, 75.33, 59.64, 39.49, 25.06. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}ClN_2O_4S^+$ ([M+H]$^+$) 431.0827. Found 431.0827.

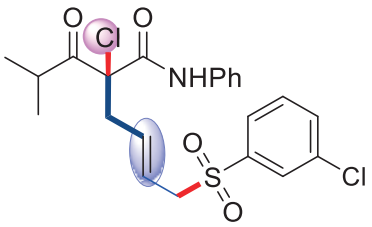


(*E*)-2-Acetyl-2-chloro-6-((2-fluorophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**3k**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 46% yield (97.3 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.83 – 7.76 (m, 1H), 7.65 – 7.60 (m, 1H), 7.58 (dt, *J* = 8.8, 1.7 Hz, 2H), 7.39 (dd, *J* = 11.3, 4.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.20 (dt, *J* = 9.4, 4.1 Hz, 2H), 5.75 (ddd, *J* = 14.8, 7.8, 6.9 Hz, 1H), 5.60 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.99 (qd, *J* = 13.9, 7.4 Hz, 2H), 3.05 (dd, *J* = 14.7, 6.7 Hz, 1H), 2.82 (dd, *J* = 14.7, 7.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.29, 164.36, 159.43 (d, *J* = 256.4 Hz), 136.34 (d, *J* = 8.4 Hz), 136.33, 133.90, 130.88, 129.22, 126.38 (d, *J* = 14.8 Hz), 125.73, 124.80 (d, *J* = 3.7 Hz), 121.77, 120.36, 117.10 (d, *J* = 15.4 Hz), 75.27, 59.15, 59.13, 39.38, 25.11. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}ClFNO_4S^+$ ([M+H]$^+$) 424.0780. Found 424.0781.

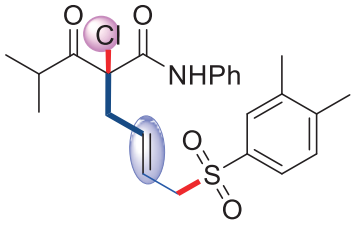


(*E*)-2-Chloro-2-isobutyryl-*N*-phenyl-6-(*m*-tolylsulfonyl)hex-4-enamide (**3l1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 60% yield (134.5 mg), *E/Z* = 16:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 114.5-115.4 °C, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.67 – 7.53 (m, 4H), 7.44 – 7.34 (m, 4H), 7.24 – 7.15

(m, 1H), 5.74 – 5.62 (m, 1H), 5.62 – 5.51 (m, 1H), 3.75 (qd, *J* = 13.9, 7.2 Hz, 2H), 3.11 (dd, *J* = 14.7, 6.4 Hz, 1H), 3.02 (dt, *J* = 13.3, 6.7 Hz, 1H), 2.83 (dd, *J* = 14.7, 7.9 Hz, 1H), 2.41 (s, 3H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.16 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.71, 164.29, 139.54, 138.51, 136.41, 134.61, 133.55, 129.19, 129.04, 128.58, 125.62, 125.47, 122.24, 120.37, 75.90, 59.89, 39.49, 37.58, 21.50, 21.33, 20.72. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_4S^+$ ($[M+H]^+$) 448.1344. Found 448.1344.

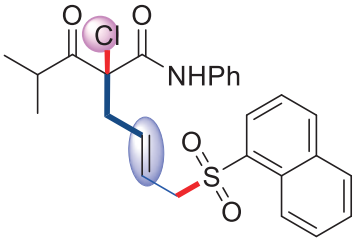


(*E*)-2-Chloro-6-((3-chlorophenyl)sulfonyl)-2-isobutyryl-*N*-phenylhex-4-enamide (**3l2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 43% yield (101.7 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.62 – 7.53 (m, 3H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 10.7, 5.2 Hz, 2H), 7.21 (dd, *J* = 11.7, 4.2 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.58 (dt, *J* = 15.2, 6.9 Hz, 1H), 3.78 (qd, *J* = 14.0, 7.2 Hz, 2H), 3.13 (dd, *J* = 14.8, 6.4 Hz, 1H), 3.03 (dt, *J* = 13.3, 6.7 Hz, 1H), 2.85 (dd, *J* = 14.7, 7.8 Hz, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.58, 164.13, 140.23, 136.34, 135.46, 134.18, 133.98, 130.50, 129.22, 128.48, 126.51, 125.67, 121.67, 120.26, 75.83, 59.83, 39.54, 37.48, 21.42, 20.70. HRMS (ESI-TOF) Calcd for $C_{22}H_{24}Cl_2NO_4S^+$ ($[M+H]^+$) 468.0798. Found 468.0799.

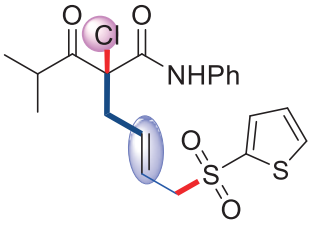


(*E*)-2-Chloro-6-((3,4-dimethylphenyl)sulfonyl)-2-isobutyryl-*N*-phenylhex-4-enamide (**3m**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 38% yield (88.7 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 129.1-130.5 °C, R_f (petroleum ether/ethyl acetate = 2.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.58 (ddd, *J* = 4.2, 3.3, 1.7 Hz, 3H), 7.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 5.74 – 5.62 (m, 1H), 5.61 – 5.48 (m, 1H), 3.73 (qd, *J* = 13.8, 7.2 Hz, 2H), 3.10 (dd, *J* = 14.7, 6.4 Hz, 1H), 3.03 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.82 (dd, *J* = 14.7, 7.9 Hz,

1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.22 (d, J = 6.7 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.75, 164.36, 143.55, 138.06, 136.44, 135.91, 133.34, 130.28, 129.18, 128.99, 125.87, 125.61, 122.47, 120.42, 75.93, 59.99, 39.49, 37.59, 21.49, 20.71, 20.04, 19.80. HRMS (ESI-TOF) Calcd for $C_{24}H_{29}ClNO_4S^+$ ($[M+H]^+$) 462.1500. Found 462.1502.

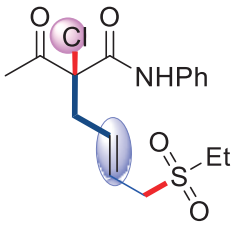


(*E*)-2-Chloro-2-isobutyryl-6-(naphthalen-1-ylsulfonyl)-*N*-phenylhex-4-enamide (**3n**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 34% yield (82.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Brown oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.5 Hz, 1H), 8.41 (s, 1H), 8.18 (dd, J = 7.3, 1.2 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.67 – 7.52 (m, 5H), 7.38 (dd, J = 10.7, 5.1 Hz, 2H), 7.20 (dd, J = 10.6, 4.2 Hz, 1H), 5.62 – 5.46 (m, 2H), 4.05 – 3.88 (m, 2H), 3.08 – 2.93 (m, 2H), 2.79 – 2.69 (m, 1H), 1.19 (d, J = 6.7 Hz, 3H), 1.13 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.65, 164.26, 136.38, 135.31, 134.14, 133.63, 133.45, 131.21, 129.30, 129.18, 128.85, 128.77, 127.04, 125.59, 124.37, 123.99, 122.14, 120.36, 75.72, 59.48, 39.40, 37.54, 21.44, 20.67. HRMS (ESI-TOF) Calcd for $C_{26}H_{27}ClNO_4S^+$ ($[M+H]^+$) 484.1344. Found 484.1347.

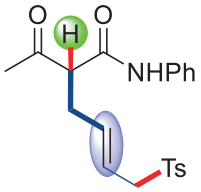


(*E*)-2-Chloro-2-isobutyryl-*N*-phenyl-6-(thiophen-2-ylsulfonyl)hex-4-enamide (**3o**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 29% yield (63.6 mg), *E*/*Z* = 17:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.66 (dd, J = 5.0, 1.3 Hz, 1H), 7.59 (ddd, J = 9.6, 6.1, 1.0 Hz, 3H), 7.42 – 7.34 (m, 2H), 7.23 – 7.17 (m, 1H), 7.10 (dd, J = 5.0, 3.8 Hz, 1H), 5.68 (tdd, J = 22.2, 15.3, 6.8 Hz, 2H), 3.85 (qd, J = 13.8, 6.9 Hz, 2H), 3.14 (dd, J = 14.6, 6.4 Hz, 1H), 3.03 (dt, J = 13.3, 6.7 Hz, 1H), 2.86 (dd, J = 14.6, 7.4 Hz, 1H), 1.22 (d, J = 6.7 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.67, 164.21, 139.41, 136.42,

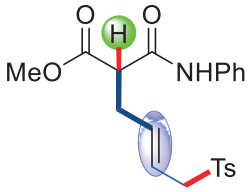
134.55, 134.23, 133.99, 129.22, 127.87, 125.64, 122.14, 120.31, 75.84, 61.13, 39.54, 37.53, 21.46, 20.71. HRMS (ESI-TOF) Calcd for $C_{20}H_{23}ClNO_4S_2^+$ ([M+H]$^+$) 440.0752. Found 440.0749.



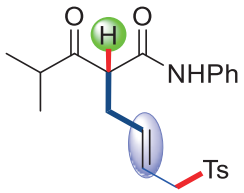
(*E*)-2-Acetyl-2-chloro-6-(ethylsulfonyl)-*N*-phenylhex-4-enamide (**3p**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 5:1, v/v) in 38% yield (67.0 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.63 – 7.55 (m, 2H), 7.38 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.89 (dt, *J* = 14.7, 7.3 Hz, 1H), 5.80 – 5.66 (m, 1H), 3.71 – 3.56 (m, 2H), 3.17 (dd, *J* = 14.6, 7.0 Hz, 1H), 2.93 (dd, *J* = 14.5, 7.4 Hz, 1H), 2.89 – 2.78 (m, 2H), 2.36 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40, 164.44, 136.37, 133.46, 129.22, 125.72, 122.42, 120.24, 75.34, 55.65, 45.85, 39.65, 25.17, 6.26. HRMS (ESI-TOF) Calcd for $C_{16}H_{21}ClNO_4S^+$ ([M+H]$^+$) 358.0874. Found 358.0874.



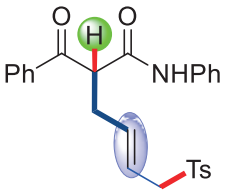
(*E*)-2-Acetyl-*N*-phenyl-6-tosylhex-4-enamide (**4a**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 83% yield (160.3 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil, R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 8.5 Hz, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.72 – 5.59 (m, 1H), 5.59 – 5.44 (m, 1H), 3.72 (d, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.90, 165.90, 144.93, 137.45, 136.59, 135.57, 129.86, 129.03, 128.29, 124.77, 120.05, 119.52, 61.07, 59.86, 32.88, 29.53, 21.64. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_4S^+$ ([M+H]$^+$) 386.1421. Found 386.1422.



Methyl (*E*)-2-(phenylcarbamoyl)-6-tosylhex-4-enoate (**4a1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 67% yield (134.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Colourless oil, R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.73 – 7.63 (m, 2H), 7.54 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.31 (dd, *J* = 11.1, 4.9 Hz, 4H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.57 (tdd, *J* = 22.5, 15.3, 7.0 Hz, 2H), 3.75 (s, 3H), 3.71 (d, *J* = 7.0 Hz, 2H), 3.42 (t, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 165.44, 144.88, 137.52, 136.51, 135.48, 129.81, 129.00, 128.34, 124.67, 120.04, 119.53, 59.87, 52.88, 52.78, 32.91, 21.64. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_5S^+$ ([M+H]$^+$) 402.1370. Found 402.1370.

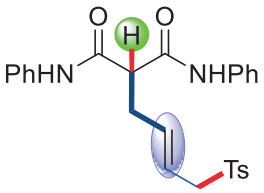


(*E*)-2-Isobutyryl-*N*-phenyl-6-tosylhex-4-enamide (**4a2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 72% yield (148.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil, R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.45 (m, 2H), 7.37 – 7.27 (m, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.69 – 5.41 (m, 2H), 3.71 (dd, *J* = 7.2, 2.5 Hz, 3H), 2.76 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.43 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.97, 165.77, 144.86, 137.37, 136.20, 135.65, 129.82, 129.03, 128.33, 124.70, 119.97, 119.80, 59.83, 58.73, 41.72, 34.53, 21.65, 17.92, 17.63. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_4S^+$ ([M+H]$^+$) 414.1734. Found 414.1735.

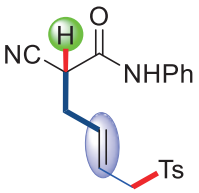


(*E*)-2-Benzoyl-*N*-phenyl-6-tosylhex-4-enamide (**4a3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 76% yield (169.2 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 123.0-123.9 °C R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.63 (dd, *J* = 18.5, 7.8 Hz, 3H), 7.49 (t, *J* = 8.0 Hz, 4H), 7.35 – 7.20 (m, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.57 (tdd, *J* = 22.6, 15.2,

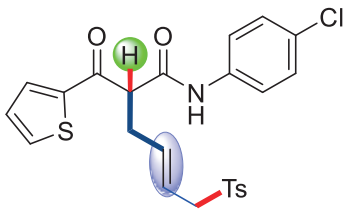
7.0 Hz, 2H), 4.44 (t, J = 7.2 Hz, 1H), 3.68 (d, J = 7.1 Hz, 2H), 2.93 – 2.67 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.04, 166.07, 144.80, 137.44, 136.25, 135.93, 135.46, 134.31, 129.76, 129.05, 128.99, 128.73, 128.34, 124.69, 120.08, 119.87, 59.83, 55.74, 34.60, 21.63. HRMS (ESI-TOF) Calcd for $C_{26}H_{26}NO_4S^+$ ($[M+H]^+$) 448.1577. Found 448.1577.



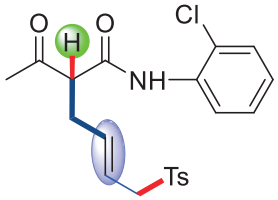
(*E*)-N^1,N^3-Diphenyl-2-(4-tosylbut-2-en-1-yl)malonamide (**4a4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 84% yield (169.2 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 164.7-165.6 ºC. R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, DMSO) δ 9.96 (s, 2H), 7.62 (dd, J = 19.0, 8.1 Hz, 6H), 7.31 (dd, J = 13.0, 5.0 Hz, 6H), 7.06 (t, J = 7.3 Hz, 2H), 5.70 – 5.37 (m, 2H), 3.98 (d, J = 7.0 Hz, 2H), 3.52 (t, J = 7.3 Hz, 1H), 2.60 (t, J = 6.7 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 167.27, 144.53, 139.40, 137.46, 136.09, 129.99, 129.23, 128.47, 123.94, 119.72, 119.49, 58.87, 54.69, 32.30, 21.43. HRMS (ESI-TOF) Calcd for $C_{26}H_{27}N_2O_4S^+$ ($[M+H]^+$) 463.1686. Found 463.1689.



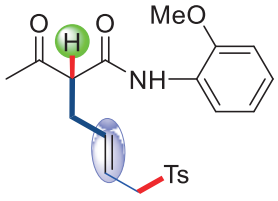
(*E*)-2-Cyano-*N*-phenyl-6-tosylhex-4-enamide (**4a5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 63% yield (116.9 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 164.5-165.4 ºC. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.7 Hz, 2H), 7.35 (dd, J = 17.7, 7.8 Hz, 4H), 7.19 (t, J = 7.4 Hz, 1H), 5.71 (t, J = 4.3 Hz, 2H), 3.79 (d, J = 5.8 Hz, 2H), 3.59 (t, J = 6.5 Hz, 1H), 2.78 (t, J = 6.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.47, 145.06, 136.50, 135.39, 134.02, 129.90, 129.19, 128.41, 125.62, 122.13, 120.45, 117.27, 59.79, 39.06, 32.74, 21.66. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}N_2O_3S^+$ ($[M+H]^+$) 369.1267. Found 369.1268.



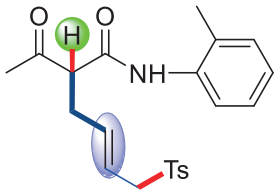
(*E*)-*N*-(4-Chlorophenyl)-2-(thiophene-2-carbonyl)-6-tosylhex-4-enamide (**4b**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 92% yield (224.8 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow solid, m.p. = 145.3-146.2 ºC. R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.86 (dd, *J* = 3.9, 0.9 Hz, 1H), 7.77 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.31 – 7.24 (m, 4H), 7.18 (dd, *J* = 4.8, 4.0 Hz, 1H), 5.71 – 5.58 (m, 1H), 5.58 – 5.41 (m, 1H), 4.26 (t, *J* = 7.2 Hz, 1H), 3.68 (d, *J* = 7.1 Hz, 2H), 2.81 (dtd, *J* = 21.3, 14.3, 7.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.73, 165.87, 144.86, 142.96, 136.48, 136.02, 135.81, 135.55, 134.14, 129.80, 129.63, 128.98, 128.92, 128.32, 121.34, 120.12, 59.78, 56.56, 35.27, 21.66. HRMS (ESI-TOF) Calcd for $C_{24}H_{23}ClNO_4S_2^+$ ($[M+H]^+$) 488.0752. Found 488.0756.



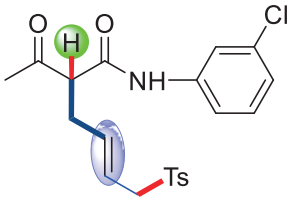
(*E*)-2-Acetyl-*N*-(2-chlorophenyl)-6-tosylhex-4-enamide (**4c1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 62% yield (129.8 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.24 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.07 (td, *J* = 7.9, 1.5 Hz, 1H), 5.66 – 5.46 (m, 2H), 3.72 (d, *J* = 6.2 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 1H), 2.71 (dd, *J* = 9.4, 4.0 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.07, 165.67, 144.84, 135.66, 135.52, 134.07, 129.79, 129.22, 128.34, 127.66, 125.32, 123.61, 121.97, 120.18, 60.86, 59.80, 33.46, 30.06, 21.63. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_4S^+$ ($[M+H]^+$) 420.1031. Found 420.1032.



(*E*)-2-Acetyl-*N*-(2-methoxyphenyl)-6-tosylhex-4-enamide (**4c2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 68% yield (141.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.27 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (td, *J* = 7.9, 1.6 Hz, 1H), 6.95 (td, *J* = 7.8, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.63 – 5.43 (m, 2H), 3.90 (s, 3H), 3.71 (d, *J* = 6.2 Hz, 2H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.73 – 2.63 (m, 2H), 2.41 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.24, 165.31, 148.21, 144.79, 136.23, 135.48, 129.77, 128.36, 127.04, 124.45, 120.98, 119.93, 119.73, 110.10, 61.72, 59.86, 55.84, 32.72, 29.33, 21.61. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_5S^+$ ($[M+H]^+$) 416.1526. Found 416.1529.

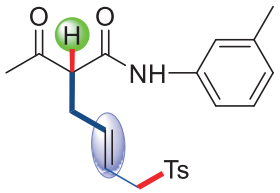


(*E*)-2-Acetyl-*N*-(o-tolyl)-6-tosylhex-4-enamide (**4c3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 71% yield (141.2 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 119.1-120.1 °C. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.15 (m, 2H), 7.09 (dd, *J* = 10.7, 4.1 Hz, 1H), 5.58 (tdd, *J* = 22.5, 15.3, 6.9 Hz, 2H), 3.72 (d, *J* = 6.9 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 1H), 2.77 – 2.63 (m, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.33, 165.62, 144.87, 136.00, 135.58, 135.23, 130.58, 129.83, 129.09, 128.33, 126.75, 125.45, 122.63, 119.94, 60.49, 59.82, 33.81, 30.18, 21.64, 17.75. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_4S^+$ ($[M+H]^+$) 400.1577. Found 400.1577.

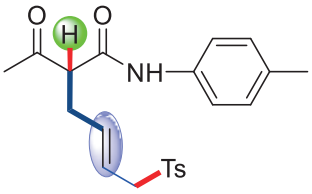


(*E*)-2-Acetyl-*N*-(3-chlorophenyl)-6-tosylhex-4-enamide (**4d1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 80% yield (167.2 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.77 – 7.57 (m, 3H), 7.37 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24

(t, J = 8.1 Hz, 1H), 7.15 – 7.05 (m, 1H), 5.73 – 5.60 (m, 1H), 5.60 – 5.47 (m, 1H), 3.72 (dd, J = 7.1, 2.1 Hz, 2H), 3.50 (t, J = 7.2 Hz, 1H), 2.68 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.07, 166.02, 144.99, 138.55, 136.40, 135.65, 134.68, 130.01, 129.90, 128.25, 124.77, 120.13, 119.74, 117.98, 60.87, 59.84, 33.11, 29.77, 21.65. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_4S^+$ ($[M+H]^+$) 420.1031. Found 420.1030.

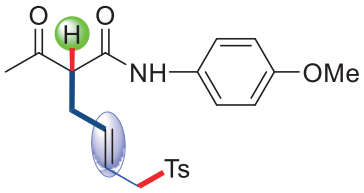


(*E*)-2-Acetyl-*N*-(*m*-tolyl)-6-tosylhex-4-enamide (**4d2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 83% yield (165.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.38 (s, 1H), 7.31 (d, J = 8.0 Hz, 3H), 7.20 (t, J = 7.8 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 5.71 – 5.59 (m, 1H), 5.58 – 5.44 (m, 1H), 3.72 (d, J = 7.0 Hz, 2H), 3.47 (t, J = 7.3 Hz, 1H), 2.68 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.10, 165.66, 144.89, 139.01, 137.27, 136.46, 135.62, 129.84, 128.87, 128.31, 125.60, 120.63, 119.65, 117.08, 61.17, 59.87, 33.03, 29.61, 21.64, 21.47. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_4S^+$ ($[M+H]^+$) 400.1577. Found 400.1575.

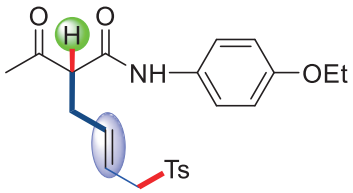


(*E*)-2-Acetyl-*N*-(*p*-tolyl)-6-tosylhex-4-enamide (**4e1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 76% yield (151.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 98.7-99.6 °C. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 5.70 – 5.58 (m, 1H), 5.58 – 5.45 (m, 1H), 3.71 (d, J = 7.1 Hz, 2H), 3.47 (t, J = 7.3 Hz, 1H), 2.67 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.03, 165.65, 144.89, 136.56, 135.59, 134.83, 134.48, 129.85, 129.51, 128.31, 120.09, 119.55, 61.08, 59.87, 32.94,

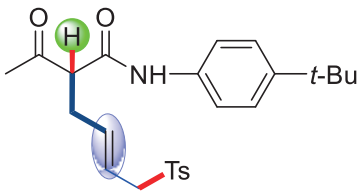
29.56, 21.64, 20.89. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_4S^+$ ([M+H]$^+$) 400.1577. Found 400.1577.



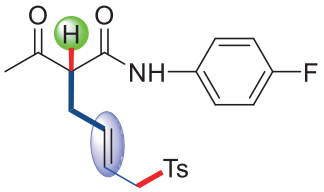
(*E*)-2-Acetyl-*N*-(4-methoxyphenyl)-6-tosylhex-4-enamide (**4e2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 68% yield (141.0 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 112.6-112.9 ºC. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.79 (m, 2H), 5.71 – 5.58 (m, 1H), 5.58 – 5.45 (m, 1H), 3.78 (s, 3H), 3.72 (d, *J* = 7.1 Hz, 2H), 3.47 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.98, 165.66, 156.71, 144.91, 136.65, 135.60, 130.51, 129.86, 128.30, 121.86, 119.48, 114.15, 60.95, 59.87, 55.50, 32.89, 29.52, 21.65. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_5S^+$ ([M+H]$^+$) 416.1526. Found 416.1523.



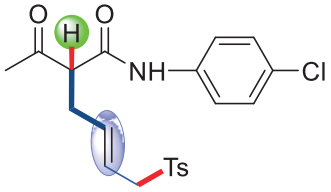
(*E*)-2-Acetyl-N-(4-ethoxyphenyl)-6-tosylhex-4-enamide (**4e3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 71% yield (151.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 131.2-132.2 ºC. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.91 – 6.75 (m, 2H), 5.63 (dd, *J* = 14.7, 7.5 Hz, 1H), 5.53 (dd, *J* = 15.0, 7.6 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 2H), 3.72 (d, *J* = 7.1 Hz, 2H), 3.46 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.26 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.03, 165.58, 156.08, 144.90, 136.63, 135.60, 130.36, 129.85, 128.31, 121.81, 119.51, 114.77, 63.72, 60.98, 59.87, 32.92, 29.54, 21.65, 14.82. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_5S^+$ ([M+H]$^+$) 430.1683. Found 430.1681.



(*E*)-2-Acetyl-*N*-(4-(*tert*-butyl)phenyl)-6-tosylhex-4-enamide (**4e4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 79% yield (173.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.37 – 7.28 (m, 4H), 5.62 (dd, *J* = 14.6, 7.6 Hz, 1H), 5.53 (dd, *J* = 14.9, 7.6 Hz, 1H), 3.72 (d, *J* = 7.1 Hz, 2H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.26 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.90, 165.71, 147.83, 144.89, 136.61, 135.58, 134.79, 129.85, 128.31, 125.86, 119.81, 119.53, 61.13, 59.87, 34.42, 32.86, 31.34, 29.48, 21.64. HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_4S^+$ ([M+H]$^+$) 422.2047. Found 422.2048.

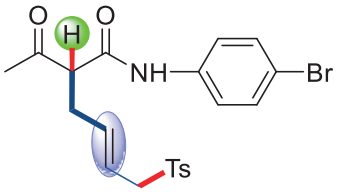


(*E*)-2-Acetyl-*N*-(4-fluorophenyl)-6-tosylhex-4-enamide (**4e5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 77% yield (155.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.44 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.93 (m, 2H), 5.74 – 5.61 (m, 1H), 5.59 – 5.46 (m, 1H), 3.72 (d, *J* = 7.3 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 1H), 2.68 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.96, 165.97, 159.64 (d, *J* = 245.1 Hz), 144.99, 136.64, 135.63, 133.46 (d, *J* = 2.8 Hz), 129.89, 128.25, 121.89 (d, *J* = 8.0 Hz), 119.50, 115.66 (d, *J* = 22.6 Hz), 60.84, 59.84, 32.94, 29.60, 21.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.33. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}FNO_4S^+$ ([M+H]$^+$) 404.1326. Found 404.1328.

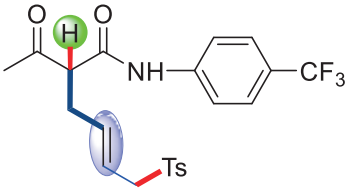


(*E*)-2-Acetyl-*N*-(4-chlorophenyl)-6-tosylhex-4-enamide (**4e6**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 80% yield (168.8

mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 101.4-102.3 °C. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 5.75 – 5.61 (m, 1H), 5.60 – 5.47 (m, 1H), 3.72 (d, *J* = 7.0 Hz, 2H), 3.51 (t, *J* = 7.2 Hz, 1H), 2.68 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.04, 165.99, 145.00, 136.54, 136.02, 135.66, 129.90, 129.72, 129.02, 128.24, 121.31, 119.60, 60.87, 59.83, 33.04, 29.71, 21.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}ClNO_4S^+$ ($[M+H]^+$) 420.1031. Found 420.1033.

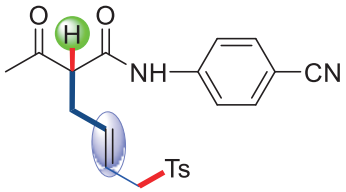


(*E*)-2-acetyl-*N*-(4-bromophenyl)-6-tosylhex-4-enamide (**4e7**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 78% yield (181.5 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.60 (m, 1H), 5.60 – 5.42 (m, 1H), 3.78 – 3.64 (m, 2H), 3.50 (t, *J* = 7.2 Hz, 1H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.11, 165.94, 144.98, 136.50, 136.47, 135.68, 131.98, 129.89, 128.23, 121.61, 119.65, 117.36, 60.88, 59.81, 33.10, 29.77, 21.65. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}BrNO_4S^+$ ($[M+H]^+$) 464.0526. Found 464.0524.

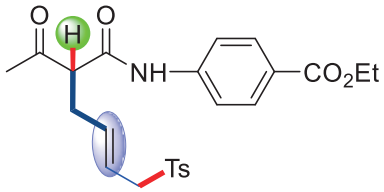


(*E*)-2-Acetyl-6-tosyl-*N*-(4-(trifluoromethyl)phenyl)hex-4-enamide (**4e8**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 85% yield (192.8 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 123.4-124.2 °C. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 4H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.76 – 5.62 (m, 1H), 5.60 – 5.48 (m, 1H), 3.74 (d, *J* = 7.4 Hz, 2H), 3.57 (t, *J* = 7.2 Hz, 1H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.80, 166.47, 145.11, 140.56, 136.61, 135.57, 129.93, 128.20, 126.40 (q, *J* = 32.9 Hz), 126.22 (q, *J* = 3.6 Hz), 124.05 (q, *J* = 272.7 Hz), 119.71,

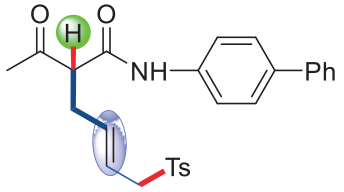
119.52. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.16. HRMS (ESI-TOF) Calcd for $C_{22}H_{23}F_3NO_4S^+$ ([M+H]$^+$) 454.1294. Found 454.1294.



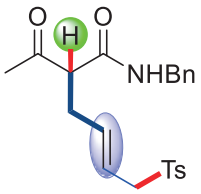
(*E*)-2-Acetyl-*N*-(4-cyanophenyl)-6-tosylhex-4-enamide (**4e9**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 77% yield (157.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.71 (dd, *J* = 11.3, 4.5 Hz, 4H), 7.65 – 7.58 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.71 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.61 – 5.48 (m, 1H), 3.72 (dd, *J* = 7.2, 2.7 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.99, 166.53, 145.08, 141.46, 136.39, 135.75, 133.24, 129.94, 128.17, 119.97, 119.76, 118.74, 107.62, 60.78, 59.78, 33.21, 29.89, 21.67. HRMS (ESI-TOF) Calcd for $C_{22}H_{23}N_2O_4S^+$ ([M+H]$^+$) 411.1373. Found 411.1376.



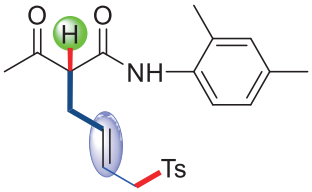
Ethyl (*E*)-4-(2-acetyl-6-tosylhex-4-enamido)benzoate (**4e10**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 74% yield (168.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 137.0-137.5 ºC. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.73 – 5.61 (m, 1H), 5.61 – 5.48 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.77 – 3.67 (m, 2H), 3.54 (t, *J* = 7.2 Hz, 1H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.10, 166.14, 166.05, 144.99, 141.46, 136.37, 135.65, 130.76, 129.90, 128.24, 126.43, 119.74, 119.14, 60.95, 59.81, 33.17, 29.83, 21.65, 14.35. HRMS (ESI-TOF) Calcd for $C_{24}H_{28}NO_6S^+$ ([M+H]$^+$) 458.1632. Found 458.1636.



(*E*)-*N*-([1,1'-Biphenyl]-4-yl)-2-acetyl-6-tosylhex-4-enamide (**4e11**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 59% yield (135.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 173.3-173.9 °C. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.73 – 7.67 (m, 2H), 7.64 – 7.59 (m, 2H), 7.59 – 7.53 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (dd, *J* = 10.8, 7.7 Hz, 3H), 5.74 – 5.61 (m, 1H), 5.61 – 5.48 (m, 1H), 3.73 (d, *J* = 7.1 Hz, 2H), 3.52 (t, *J* = 7.3 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.17, 165.84, 144.95, 140.37, 137.66, 136.67, 136.53, 135.60, 129.88, 128.83, 128.30, 127.65, 127.25, 126.88, 120.34, 119.66, 61.08, 59.86, 33.10, 29.73, 21.67. HRMS (ESI-TOF) Calcd for $C_{27}H_{28}NO_4S^+$ ($[M+H]^+$) 462.1734. Found 462.1734.

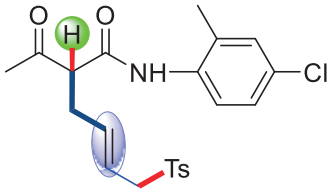


(*E*)-2-Acetyl-*N*-benzyl-6-tosylhex-4-enamide (**4f**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 54% yield (106.9 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 105.7-106.7 °C. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.24 (m, 7H), 6.46 (s, 1H), 5.51 (tdd, *J* = 22.4, 15.4, 6.9 Hz, 2H), 4.43 (ddd, *J* = 31.5, 14.7, 5.8 Hz, 2H), 3.66 (d, *J* = 6.1 Hz, 2H), 3.34 (t, *J* = 7.3 Hz, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.53, 167.50, 144.86, 137.80, 136.60, 135.69, 129.83, 128.78, 128.33, 127.82, 127.68, 119.46, 99.99, 60.45, 59.86, 43.81, 32.68, 29.42, 21.65. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_4S^+$ ($[M+H]^+$) 400.1577. Found 400.1579.

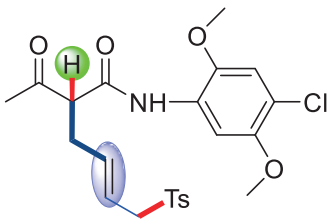


(*E*)-2-Acetyl-*N*-(2,4-dimethylphenyl)-6-tosylhex-4-enamide (**4g1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 69% yield (143.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 109.1-110.1 °C. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 2H), 5.68 – 5.47 (m, 2H), 3.72 (d, *J* = 6.8 Hz, 2H), 3.54 (t, *J* = 7.2 Hz, 1H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 6H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.23, 165.63, 144.88, 136.10, 135.53, 135.31, 132.52, 131.25,

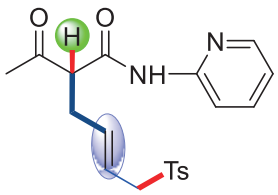
129.84, 129.43, 128.34, 127.24, 122.96, 119.86, 60.51, 59.83, 33.72, 30.12, 21.66, 20.89, 17.71. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_4S^+$ ([M+H]$^+$) 414.1734. Found 414.1737.



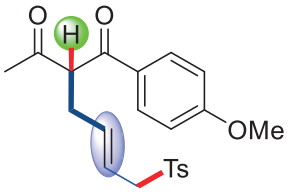
(*E*)-2-Acetyl-*N*-(4-chloro-2-methylphenyl)-6-tosylhex-4-enamide (**4g2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 64% yield (138.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.12 (m, 2H), 5.70 – 5.59 (m, 1H), 5.59 – 5.48 (m, 1H), 3.72 (d, *J* = 7.0 Hz, 2H), 3.57 (t, *J* = 7.2 Hz, 1H), 2.77 – 2.61 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.52, 165.79, 144.92, 135.89, 135.64, 133.89, 130.97, 130.32, 129.86, 128.28, 126.66, 123.81, 119.99, 60.16, 59.77, 33.94, 30.31, 21.65, 17.66. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_4S^+$ ([M+H]$^+$) 434.1187. Found 434.1188.



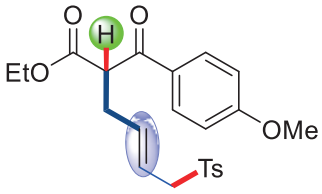
(*E*)-2-Acetyl-*N*-(4-chloro-2,5-dimethoxyphenyl)-6-tosylhex-4-enamide (**4h**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 74% yield (178.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.15 (s, 1H), 7.75 – 7.64 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.91 (s, 1H), 5.67 – 5.47 (m, 2H), 3.87 (s, 3H), 3.87 (s, 3H), 3.72 (d, *J* = 6.2 Hz, 2H), 3.50 (t, *J* = 7.3 Hz, 1H), 2.74 – 2.63 (m, 2H), 2.43 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.29, 165.50, 149.00, 144.85, 142.21, 136.01, 135.57, 129.80, 128.33, 126.31, 119.85, 116.45, 112.38, 105.02, 61.48, 59.82, 56.74, 56.54, 32.91, 29.59, 21.64. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}ClNO_6S^+$ ([M+H]$^+$) 480.1242. Found 480.1244.



(*E*)-2-Acetyl-*N*-(pyridin-2-yl)-6-tosylhex-4-enamide (**4i**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 67% yield (129.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Colourless oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.37 – 8.24 (m, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.60 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 5.67 – 5.40 (m, 2H), 3.72 (d, *J* = 6.2 Hz, 2H), 3.52 (t, *J* = 7.2 Hz, 1H), 2.76 – 2.58 (m, 2H), 2.42 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.40, 166.27, 150.84, 147.98, 144.84, 138.51, 136.05, 135.42, 129.79, 128.38, 120.37, 119.90, 114.21, 61.29, 59.81, 32.50, 29.38, 21.65. HRMS (ESI-TOF) Calcd for $C_{20}H_{23}N_2O_4S^+$ ([M+H]$^+$) 387.1373. Found 387.1374.

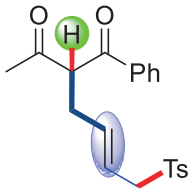


(*E*)-1-(4-Methoxyphenyl)-2-(4-tosylbut-2-en-1-yl)butane-1,3-dione (**4j1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 61% yield (121.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 5.55 – 5.47 (m, 2H), 4.36 (t, *J* = 7.1 Hz, 1H), 3.89 (s, 3H), 3.72 – 3.64 (m, 2H), 2.76 – 2.59 (m, 2H), 2.42 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.32, 193.49, 164.26, 144.72, 136.95, 135.40, 131.23, 129.72, 129.07, 128.41, 119.21, 114.19, 62.09, 59.89, 55.63, 31.68, 28.04, 21.65. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}O_5S^+$ ([M+H]$^+$) 401.1417. Found 401.1418.

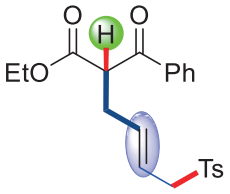


Ethyl (*E*)-2-(4-methoxybenzoyl)-6-tosylhex-4-enoate (**4j2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 70% yield (151.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f

(petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.88 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.01 – 6.88 (m, 2H), 5.65 – 5.40 (m, 2H), 4.23 (t, *J* = 7.2 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.89 (s, 3H), 3.69 (d, *J* = 6.3 Hz, 2H), 2.74 – 2.63 (m, 2H), 2.41 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.23, 169.24, 164.04, 144.67, 137.09, 135.41, 131.08, 129.67, 128.90, 128.45, 119.20, 113.99, 61.59, 59.94, 55.57, 53.26, 31.76, 21.62, 14.01. HRMS (ESI-TOF) Calcd for $C_{23}H_{27}O_6S^+$ ($[M+H]^+$) 431.1523. Found 431.1524.

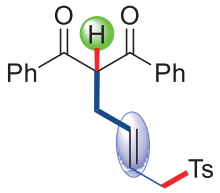


(*E*)-1-Phenyl-2-(4-tosylbut-2-en-1-yl)butane-1,3-dione (**4k1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 66% yield (121.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.80 (m, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.48 – 5.39 (m, 2H), 4.35 (t, *J* = 7.0 Hz, 1H), 3.67 – 3.56 (m, 2H), 2.69 – 2.54 (m, 2H), 2.34 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.90, 194.18, 143.70, 135.70, 135.03, 134.40, 132.98, 128.68, 127.99, 127.72, 127.36, 118.38, 61.22, 58.83, 30.59, 27.26, 20.60. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}O_4S^+$ ($[M+H]^+$) 371.1312. Found 371.1312.

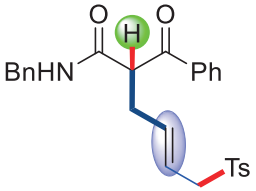


Ethyl (*E*)-2-benzoyl-6-tosylhex-4-enoate (**4k2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v) in 65% yield (131.0 mg), *E*/*Z* = 12:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.64 – 5.45 (m, 2H), 4.27 (t, *J* = 7.1 Hz, 1H), 4.12 (qd, *J* = 7.1, 2.9 Hz, 2H), 3.70 (d, *J* = 6.2 Hz, 2H), 2.71 (dd, *J* = 9.3, 4.0 Hz, 2H), 2.40 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.87, 169.02, 144.68, 136.87, 135.91, 135.40, 133.75, 129.67, 128.82, 128.64, 128.44, 119.39, 61.66, 59.90, 53.56, 31.66,

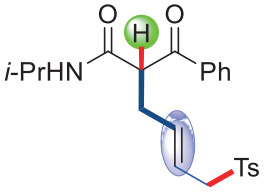
21.61, 13.96. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}O_5S^+$ ([M+H]$^+$) 401.1417. Found 401.1419.



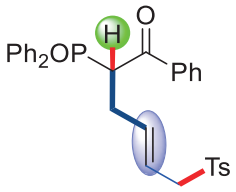
(*E*)-1,3-Diphenyl-2-(4-tosylbut-2-en-1-yl)propane-1,3-dione (**4k3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 85% yield (184.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 117.9-118.9 °C. R_f (petroleum ether/ethyl acetate = 2:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 5.70 – 5.47 (m, 1H), 5.15 (t, *J* = 6.6 Hz, 1H), 3.69 (d, *J* = 7.0 Hz, 1H), 2.80 (t, *J* = 6.6 Hz, 1H), 2.33 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.07, 144.72, 137.48, 135.63, 135.33, 133.79, 129.67, 129.03, 128.58, 128.40, 119.27, 59.87, 56.38, 32.17, 21.56. HRMS (ESI-TOF) Calcd for $C_{26}H_{25}O_4S^+$ ([M+H]$^+$) 433.1468. Found 433.1469.



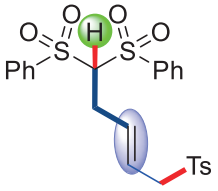
(*E*)-2-Benzoyl-*N*-benzyl-6-tosylhex-4-enamide (**4k4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 1:1, v/v) in 59% yield (136.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 104.5-105.3 °C. R_f (petroleum ether/ethyl acetate = 1:2, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.64 – 7.59 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.22 (m, 5H), 7.13 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.67 (s, 1H), 5.60 – 5.39 (m, 2H), 4.45 (dd, *J* = 14.8, 6.1 Hz, 1H), 4.35 – 4.26 (m, 2H), 3.63 (d, *J* = 6.6 Hz, 2H), 2.77 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.71 – 2.60 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.48, 167.84, 144.76, 137.84, 136.53, 136.02, 135.49, 134.10, 129.74, 128.97, 128.68, 128.35, 127.65, 127.53, 119.63, 59.83, 55.24, 43.66, 33.99, 21.65. HRMS (ESI-TOF) Calcd for $C_{27}H_{28}NO_4S^+$ ([M+H]$^+$) 462.1734. Found 462.1738.



(*E*)-2-Benzoyl-*N*-isopropyl-6-tosylhex-4-enamide (**4k5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 70% yield (144.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.48 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.12 (d, *J* = 7.9 Hz, 1H), 5.52 (q, *J* = 6.0 Hz, 2H), 4.23 (t, *J* = 7.3 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.68 (d, *J* = 6.1 Hz, 2H), 2.80 – 2.68 (m, 1H), 2.62 (dt, *J* = 12.9, 6.2 Hz, 1H), 2.40 (s, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.76, 166.98, 144.74, 136.70, 136.10, 135.43, 134.01, 129.73, 128.90, 128.61, 128.36, 119.39, 59.85, 55.49, 41.75, 34.06, 22.52, 22.35, 21.64. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_4S^+$ ([M+H]$^+$) 414.1734. Found 414.1735.

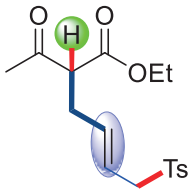


(*E*)-2-(Diphenylphosphoryl)-1-phenyl-6-tosylhex-4-en-1-one (**4l**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 24% yield (62.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 178.4-179.3 °C. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, DMSO) δ 8.00 – 7.87 (m, 2H), 7.82 – 7.72 (m, 2H), 7.68 – 7.44 (m, 8H), 7.38 (td, *J* = 7.4, 1.3 Hz, 1H), 7.29 (dt, *J* = 7.3, 5.4 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.58 – 5.40 (m, 1H), 5.36 – 5.18 (m, 1H), 5.09 (td, *J* = 12.1, 2.5 Hz, 1H), 3.84 (d, *J* = 7.3 Hz, 2H), 2.91 – 2.73 (m, 1H), 2.30 (s, 3H), 2.28 – 2.16 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 196.07 (d, $J_{C\text{-}P}$ = 3.7 Hz), 144.47, 138.19, 136.76 (d, $J_{C\text{-}P}$ = 14.3 Hz), 135.91, 133.44, 132.62 (d, $J_{C\text{-}P}$ = 2.4 Hz), 132.26 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.74 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.60 (d, $J_{C\text{-}P}$ = 98.7 Hz), 131.58 (d, $J_{C\text{-}P}$ = 98.7 Hz), 131.38 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.93, 129.23 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.94, 128.73 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.61, 128.37, 119.62, 58.77, 48.63 (d, $J_{C\text{-}P}$ = 55.5 Hz), 30.39, 21.49. ^{31}P NMR (162 MHz, DMSO) δ 27.91. HRMS (ESI-TOF) Calcd for $C_{31}H_{30}O_4PS^+$ ([M+H]$^+$) 529.1597. Found 529.1599.

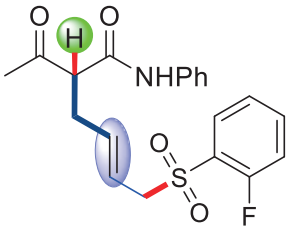


(*E*)-(5-Tosylpent-3-ene-1,1-diyldisulfonyl)dibenzene (**4m**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 1.5:1, v/v) in 46% yield (114.7 mg),

E/Z > 20:1, which was detected by ^{1}H NMR spectroscopy. Colourless oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 4H), 7.71 (t, *J* = 8.6 Hz, 4H), 7.57 (dd, *J* = 11.2, 4.4 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.66 (dt, *J* = 14.1, 6.9 Hz, 1H), 5.46 (dt, *J* = 14.9, 7.4 Hz, 1H), 4.42 – 4.32 (m, 1H), 3.68 (d, *J* = 7.3 Hz, 2H), 2.90 (t, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.98, 137.62, 135.52, 134.82, 134.45, 129.88, 129.60, 129.24, 128.36, 120.91, 82.83, 59.69, 28.75, 21.68. HRMS (ESI-TOF) Calcd for $C_{24}H_{25}O_6S_3^+$ ($[M+H]^+$) 505.0808. Found 505.0803.

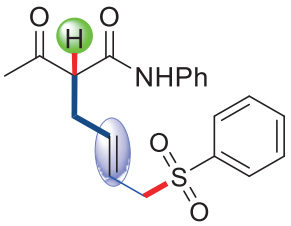


Ethyl (*E*)-2-acetyl-6-tosylhex-4-enoate (**4n**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 57% yield (106.9 mg), *E/Z* = 13:1, which was detected by ^{1}H NMR spectroscopy. White solid. m.p. = 105.7-106.7 °C. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.50 (td, *J* = 5.8, 3.9 Hz, 2H), 4.27 – 4.09 (m, 2H), 3.75 – 3.67 (m, 2H), 3.44 (t, *J* = 7.3 Hz, 1H), 2.56 (s, 2H), 2.46 (s, 3H), 2.22 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.00, 168.81, 144.79, 136.64, 135.43, 129.76, 128.44, 119.31, 61.70, 59.89, 58.65, 30.83, 29.37, 21.68, 14.10. HRMS (ESI-TOF) Calcd for $C_{17}H_{23}O_5S^+$ ($[M+H]^+$) 339.1261. Found 339.1262.

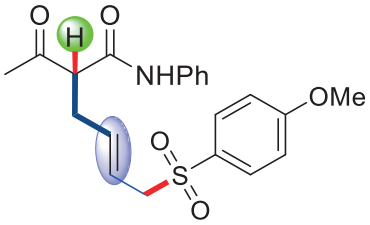


(*E*)-2-Acetyl-6-((2-fluorophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4o**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 89% yield (173.8 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.87 – 7.76 (m, 1H), 7.66 – 7.57 (m, 1H), 7.51 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.31 (ddd, *J* = 11.6, 7.6, 1.4 Hz, 3H), 7.25 – 7.18 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.74 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.56 (dt, *J* = 14.8, 7.4 Hz, 1H), 3.96 (d, *J* = 7.4 Hz, 2H), 3.44 (t, *J* = 7.3 Hz, 1H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.02, 165.59, 159.42 (d, *J* = 256.4 Hz), 137.31, 137.03, 136.34 (d, *J* = 8.9 Hz), 130.81, 129.04, 126.33 (d, *J* = 14.9 Hz), 124.82 (d, *J* = 3.0 Hz), 120.01, 118.90, 117.05 (d, *J* =

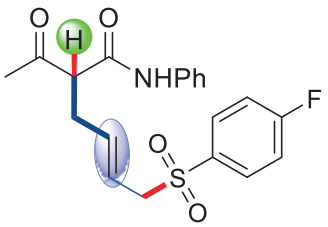
30.6 Hz), 61.03, 59.11, 59.08, 32.93, 29.54. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}FNO_4S^+$ ([M+H]$^+$) 390.1170. Found 390.1172.



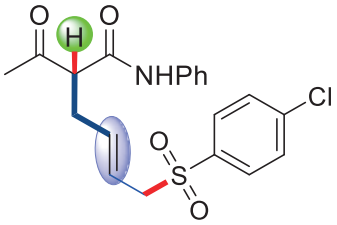
(*E*)-2-Acetyl-*N*-phenyl-6-(phenylsulfonyl)hex-4-enamide (**4p1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 78% yield (145.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.87 – 7.76 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 4H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.59 (m, 1H), 5.59 – 5.47 (m, 1H), 3.74 (d, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.89, 165.84, 138.48, 137.42, 136.78, 133.88, 129.24, 129.04, 128.28, 124.80, 120.05, 119.32, 61.05, 59.78, 32.87, 29.51. HRMS (ESI-TOF) Calcd for $C_{20}H_{22}NO_4S^+$ ([M+H]$^+$) 372.1264. Found 372.1266.



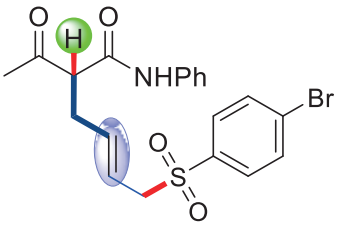
(*E*)-2-Acetyl-6-((4-methoxyphenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4p2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 77% yield (154.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Colourless oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.33 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.58 (dtd, *J* = 22.5, 15.3, 7.0 Hz, 2H), 3.86 (s, 3H), 3.71 (d, *J* = 6.8 Hz, 2H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.68 (t, *J* = 7.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.07, 165.77, 163.84, 137.39, 136.38, 130.49, 130.04, 129.05, 124.79, 120.03, 119.83, 114.40, 61.11, 60.07, 55.70, 33.01, 29.62. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_5S^+$ ([M+H]$^+$) 402.1370. Found 402.1371.



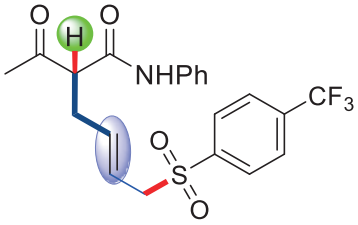
(*E*)-2-Acetyl-6-((4-fluorophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4p3**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 80% yield (156.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.87 – 7.76 (m, 2H), 7.56 – 7.47 (m, 2H), 7.34 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.73 – 5.60 (m, 1H), 5.59 – 5.45 (m, 1H), 3.74 (d, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 1H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.07, 165.90 (d, *J* = 257.8 Hz), 165.61, 137.32, 136.79, 134.50 (d, *J* = 3.1 Hz), 131.22 (d, *J* = 9.7 Hz), 129.09, 124.87, 120.01, 119.36, 116.58 (d, *J* = 22.7 Hz), 60.98, 59.91, 32.98, 29.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.01. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}FNO_4S^+$ ($[M+H]^+$) 390.1170. Found 390.1171.



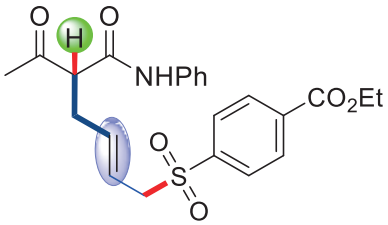
(*E*)-2-Acetyl-6-((4-methoxyphenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4p4**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 69% yield (140.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.78 – 7.69 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.74 – 5.59 (m, 1H), 5.59 – 5.47 (m, 1H), 3.74 (d, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 7.2 Hz, 1H), 2.70 (d, *J* = 7.2 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.09, 165.56, 140.68, 137.29, 136.90, 136.86, 129.82, 129.57, 129.09, 124.87, 120.00, 119.26, 60.95, 59.81, 33.00, 29.60. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_4S^+$ ($[M+H]^+$) 406.0874. Found 406.0877.



(*E*)-2-Acetyl-6-((4-bromophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4p5**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 75% yield (168.5 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.71 – 7.61 (m, 4H), 7.56 – 7.48 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.73 – 5.59 (m, 1H), 5.59 – 5.42 (m, 1H), 3.73 (d, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 7.2 Hz, 1H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.00, 165.65, 137.43, 137.33, 136.95, 132.58, 129.88, 129.30, 129.10, 124.88, 120.04, 119.18, 60.95, 59.79, 32.94, 29.56. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}BrNO_4S^+$ ([M+H]$^+$) 450.0369. Found 450.0371.

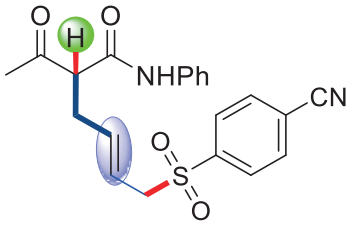


(*E*)-2-Acetyl-*N*-phenyl-6-((4-(trifluoromethyl)phenyl)sulfonyl)hex-4-enamide (**4p6**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 72% yield (158.8 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. White solid, m.p. = 141.2-141.4 °C. R_f (petroleum ether/ethyl acetate = 1:1.2, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.18 – 7.08 (m, 1H), 5.77 – 5.62 (m, 1H), 5.61 – 5.48 (m, 1H), 3.77 (d, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.17, 165.42, 141.96, 137.23, 137.11, 135.58 (q, *J* = 33.3 Hz), 129.10, 129.01, 126.38 (q, *J* = 3.6 Hz), 124.90, 123.09 (q, *J* = 274.2 Hz), 119.96, 118.97, 60.87, 59.66, 33.08, 29.67. HRMS (ESI-TOF) Calcd for $C_{21}H_{21}F_3NO_4S^+$ ([M+H]$^+$) 440.1138. Found 440.1139.

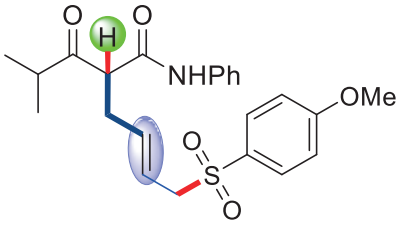


Ethyl (*E*)-4-((6-oxo-5-(phenylcarbamoyl)hept-2-en-1-yl)sulfonyl)benzoate (**4p7**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 69% yield (153.4 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 109.1-109.9 °C. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.21 – 8.12 (m, 2H), 7.94 – 7.83 (m, 2H),

7.52 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.72 – 5.58 (m, 1H), 5.58 – 5.43 (m, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.76 (d, J = 7.2 Hz, 2H), 3.48 (t, J = 7.2 Hz, 1H), 2.67 (dd, J = 11.3, 4.6 Hz, 2H), 2.26 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.64, 165.85, 165.02, 142.07, 137.41, 137.25, 135.37, 130.30, 129.04, 128.42, 124.83, 120.08, 118.85, 61.91, 60.96, 59.68, 32.70, 29.31, 14.26. HRMS (ESI-TOF) Calcd for $C_{23}H_{26}NO_6S^+$ ($[M+H]^+$) 444.1475. Found 444.1478.

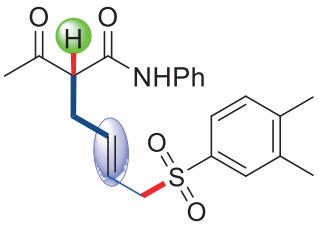


(*E*)-2-Acetyl-6-((4-cyanophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4p8**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 81% yield (161.1 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow solid, m.p. = 111.4-112.3 °C. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.98 – 7.87 (m, 2H), 7.83 – 7.71 (m, 2H), 7.59 – 7.46 (m, 2H), 7.34 (dd, J = 10.8, 5.1 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 5.79 – 5.60 (m, 1H), 5.59 – 5.44 (m, 1H), 3.77 (d, J = 7.3 Hz, 2H), 3.51 (t, J = 7.2 Hz, 1H), 2.81 – 2.56 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.81, 165.58, 142.44, 137.44, 137.31, 133.00, 129.15, 129.11, 124.99, 120.05, 118.63, 117.66, 117.08, 60.81, 59.59, 32.75, 29.40. HRMS (ESI-TOF) Calcd for $C_{21}H_{21}N_2O_4S^+$ ($[M+H]^+$) 397.1217. Found 397.1217.

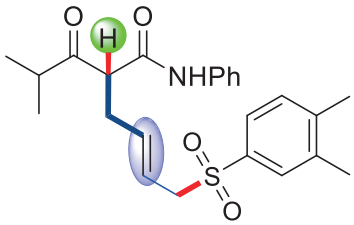


(*E*)-2-Isobutyryl-6-((4-methoxyphenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4q**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 88% yield (189.6 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.77 – 7.71 (m, 2H), 7.56 – 7.47 (m, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 5.69 – 5.42 (m, 2H), 3.86 (s, 3H), 3.69 (t, J = 6.7 Hz, 3H), 2.77 (dt, J = 13.8, 6.9 Hz, 1H), 2.65 (t, J = 6.8 Hz, 2H), 1.13 (d, J = 6.9 Hz, 3H), 1.10 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.77,

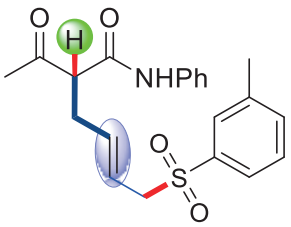
165.86, 163.83, 137.41, 136.19, 130.50, 130.07, 129.03, 124.69, 119.99, 119.90, 114.38, 60.04, 58.75, 55.70, 41.59, 34.37, 17.94, 17.71. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_5S^+$ ([M+H]$^+$) 430.1683. Found 430.1683.



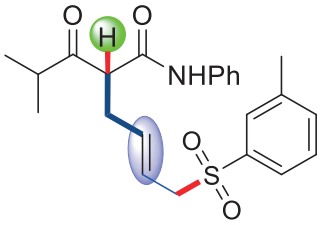
(*E*)-2-Acetyl-6-((3,4-dimethylphenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4r1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 64% yield (127.9 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.58 (d, *J* = 1.5 Hz, 1H), 7.57 – 7.45 (m, 3H), 7.33 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.73 – 5.61 (m, 1H), 5.60 – 5.45 (m, 1H), 3.78 – 3.64 (m, 2H), 3.49 (t, *J* = 7.3 Hz, 1H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.33 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.18, 165.79, 143.61, 138.13, 137.35, 136.43, 135.80, 130.30, 129.04, 128.89, 125.81, 124.78, 120.04, 119.67, 61.10, 59.85, 33.13, 29.73, 20.04, 19.79. HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_4S^+$ ([M+H]$^+$) 400.1577. Found 400.1578.



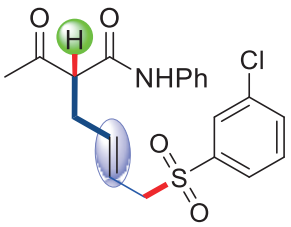
(*E*)-6-((3,4-Dimethylphenyl)sulfonyl)-2-isobutyryl-*N*-phenylhex-4-enamide (**4r2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 62% yield (132.3 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.58 (s, 1H), 7.56 – 7.46 (m, 3H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.57 (m, 1H), 5.57 – 5.44 (m, 1H), 3.69 (t, *J* = 7.1 Hz, 3H), 2.76 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.65 (dd, *J* = 12.0, 6.8 Hz, 2H), 2.33 (d, *J* = 1.3 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.90, 165.86, 143.57, 138.10, 137.38, 136.21, 135.84, 130.29, 129.02, 128.93, 125.85, 124.68, 119.99, 119.79, 59.83, 58.77, 41.72, 34.50, 20.04, 19.79, 17.92, 17.64. HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NO_4S^+$ ([M+H]$^+$) 428.1890. Found 428.1890.



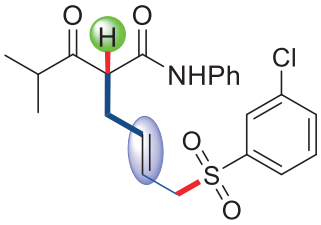
(*E*)-2-Acetyl-*N*-phenyl-6-(*m*-tolylsulfonyl)hex-4-enamide (**4s1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 72% yield (138.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.64 (s, 1H), 7.63 – 7.58 (m, 1H), 7.56 – 7.48 (m, 2H), 7.46 – 7.37 (m, 2H), 7.33 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.75 – 5.61 (m, 1H), 5.61 – 5.46 (m, 1H), 3.73 (d, *J* = 6.9 Hz, 2H), 3.49 (t, *J* = 7.3 Hz, 1H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.06, 165.81, 139.62, 138.43, 137.37, 136.67, 134.67, 129.08, 129.04, 128.48, 125.43, 124.80, 120.06, 119.42, 61.08, 59.77, 33.03, 29.66, 21.32. HRMS (ESI-TOF) Calcd for $C_{21}H_{24}NO_4S^+$ ($[M+H]^+$) 386.1421. Found 386.1423.



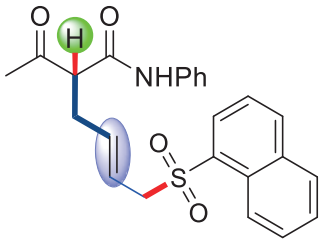
(*E*)-2-Isobutyryl-*N*-phenyl-6-(*m*-tolylsulfonyl)hex-4-enamide (**4s1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 72% yield (149.5 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.64 (s, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.57 (m, 1H), 5.57 – 5.45 (m, 1H), 3.70 (dd, *J* = 14.1, 7.1 Hz, 3H), 2.76 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.43 (s, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.69, 165.88, 139.58, 138.45, 137.40, 136.47, 134.65, 129.05, 129.01, 128.51, 125.44, 124.69, 120.01, 119.51, 59.74, 58.73, 41.58, 34.34, 21.32, 17.95, 17.72. HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_4S^+$ ($[M+H]^+$) 414.1734. Found 414.1736.



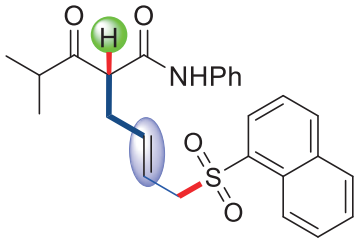
(*E*)-2-Acetyl-6-((3-chlorophenyl)sulfonyl)-*N*-phenylhex-4-enamide (**4t1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2.5:1, v/v) in 78% yield (157.3 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.84 (t, *J* = 1.8 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.59 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.52 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.34 (dd, *J* = 10.8, 5.2 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.71 – 5.61 (m, 1H), 5.59 – 5.49 (m, 1H), 3.75 (d, *J* = 6.8 Hz, 2H), 3.48 (t, *J* = 7.3 Hz, 1H), 2.70 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.08, 165.52, 140.16, 137.28, 137.10, 135.48, 134.05, 130.59, 129.08, 128.41, 126.52, 124.87, 120.00, 119.09, 61.02, 59.75, 33.03, 29.61. HRMS (ESI-TOF) Calcd for $C_{20}H_{21}ClNO_4S^+$ ($[M+H]^+$) 406.0874. Found 406.0875.



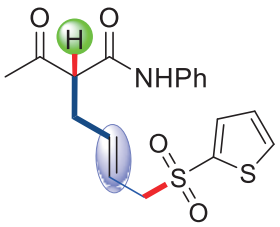
(*E*)-6-((3-Chlorophenyl)sulfonyl)-2-isobutyryl-*N*-phenylhex-4-enamide (**4t2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 87% yield (189.3 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.84 (t, *J* = 1.8 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.48 (dd, *J* = 16.6, 8.3 Hz, 3H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.58 (m, 1H), 5.58 – 5.48 (m, 1H), 3.74 (d, *J* = 7.0 Hz, 2H), 3.69 (t, *J* = 7.4 Hz, 1H), 2.76 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.67 (dd, *J* = 14.5, 8.4 Hz, 2H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.93, 165.63, 140.20, 137.31, 136.92, 135.48, 134.03, 130.56, 129.06, 128.42, 126.54, 124.75, 119.96, 119.14, 59.72, 58.64, 41.71, 34.46, 17.93, 17.66. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}ClNO_4S^+$ ($[M+H]^+$) 434.1187. Found 434.1188.



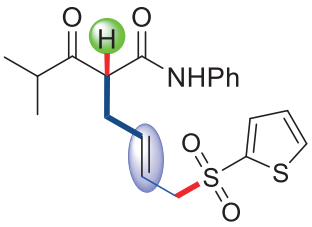
(*E*)-2-Acetyl-6-(naphthalen-1-ylsulfonyl)-*N*-phenylhex-4-enamide (**4u1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 81% yield (171.4 mg), *E*/*Z* = 20:1, which was detected by ^{1}H NMR spectroscopy. Pale yellow oil. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.7 Hz, 1H), 8.19 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.69 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.59 – 7.53 (m, 1H), 7.53 – 7.47 (m, 2H), 7.33 (dd, *J* = 10.7, 5.2 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.54 (td, *J* = 5.9, 4.1 Hz, 2H), 3.95 (dd, *J* = 5.5, 2.8 Hz, 2H), 3.36 (t, *J* = 7.3 Hz, 1H), 2.65 – 2.54 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.00, 165.69, 137.33, 136.63, 135.38, 134.14, 133.55, 131.14, 129.36, 129.05, 128.89, 128.82, 127.11, 124.80, 124.40, 124.03, 120.03, 119.39, 61.10, 59.38, 32.96, 29.60. HRMS (ESI-TOF) Calcd for $C_{24}H_{24}NO_4S^+$ ($[M+H]^+$) 422.1421. Found 422.1421.



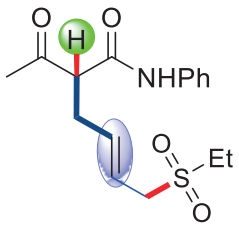
(*E*)-2-Isobutyryl-6-(naphthalen-1-ylsulfonyl)-*N*-phenylhex-4-enamide (**4u2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 81% yield (182.5 mg), *E*/*Z* = 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.20 (dd, *J* = 7.3, 1.0 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.69 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.59 – 7.52 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.57 – 5.43 (m, 2H), 3.99 – 3.87 (m, 2H), 3.58 (t, *J* = 7.4 Hz, 1H), 2.67 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.61 – 2.49 (m, 2H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.70, 165.79, 137.37, 136.41, 135.35, 134.15, 133.61, 131.15, 129.34, 129.01, 128.92, 128.79, 127.08, 124.68, 124.38, 124.06, 120.00, 119.47, 59.38, 58.74, 41.56, 34.33, 17.92, 17.65. HRMS (ESI-TOF) Calcd for $C_{26}H_{28}NO_4S^+$ ($[M+H]^+$) 450.1734. Found 450.1734.



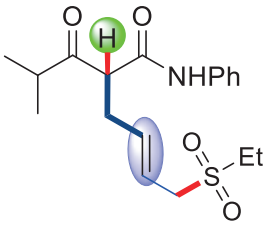
(*E*)-2-Acetyl-*N*-phenyl-6-(thiophen-2-ylsulfonyl)hex-4-enamide (**4v1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 82% yield (155.8 mg), *E*/*Z* = 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.66 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.60 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.53 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.32 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.17 – 7.07 (m, 2H), 5.75 – 5.64 (m, 1H), 5.64 – 5.52 (m, 1H), 3.83 (d, *J* = 7.0 Hz, 2H), 3.52 (t, *J* = 7.3 Hz, 1H), 2.70 (td, *J* = 7.0, 3.4 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.82, 165.86, 139.16, 137.44, 137.10, 134.59, 134.32, 129.05, 127.96, 124.81, 120.07, 119.36, 61.06, 61.02, 32.80, 29.47. HRMS (ESI-TOF) Calcd for $C_{18}H_{20}NO_4S_2^+$ ($[M+H]^+$) 378.0828. Found 378.0830.



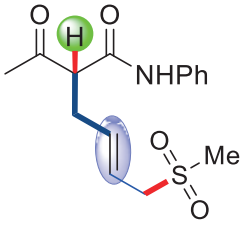
(*E*)-2-Isobutyryl-*N*-phenyl-6-(thiophen-2-ylsulfonyl)hex-4-enamide (**4v2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 87% yield (176.7 mg), *E*/*Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.59 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.09 – 6.99 (m, 2H), 5.65 – 5.44 (m, 2H), 3.75 (d, *J* = 6.9 Hz, 2H), 3.65 (t, *J* = 7.4 Hz, 1H), 2.72 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.65, 165.82, 139.25, 137.41, 136.83, 134.57, 134.28, 129.04, 127.93, 124.72, 120.01, 119.53, 60.99, 58.71, 41.53, 34.28, 17.97, 17.77. HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NO_4S_2^+$ ($[M+H]^+$) 406.1141. Found 406.1142.



(*E*)-2-Acetyl-6-(ethylsulfonyl)-*N*-phenylhex-4-enamide (**4w1**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) in 66% yield (106.8 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:1.5, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.61 – 7.48 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.86 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.74 – 5.53 (m, 1H), 3.63 (d, *J* = 7.3 Hz, 2H), 3.58 (t, *J* = 7.3 Hz, 1H), 2.89 (q, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.86, 166.00, 137.40, 136.36, 129.07, 124.84, 120.03, 119.72, 60.91, 55.62, 45.84, 32.84, 29.47, 6.32. HRMS (ESI-TOF) Calcd for $C_{16}H_{22}NO_4S^+$ ([M+H]$^+$) 324.1264. Found 324.1265.

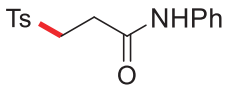


(*E*)-6-(Ethylsulfonyl)-2-isobutyryl-*N*-phenylhex-4-enamide (**4w2**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 3:1, v/v) in 73% yield (128.1 mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.84 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.76 – 5.54 (m, 1H), 3.77 (dd, *J* = 7.9, 6.9 Hz, 1H), 3.62 (d, *J* = 7.3 Hz, 2H), 2.90 (q, *J* = 7.5 Hz, 2H), 2.82 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.72 (dd, *J* = 11.6, 6.9 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.09, 165.77, 137.29, 135.83, 129.08, 124.79, 120.20, 119.96, 58.51, 55.62, 45.70, 41.71, 34.54, 17.98, 17.68, 6.34. HRMS (ESI-TOF) Calcd for $C_{18}H_{26}NO_4S^+$ ([M+H]$^+$) 352.1577. Found 352.1577.

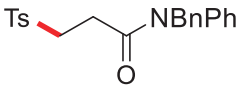


(*E*)-2-Acetyl-6-(methylsulfonyl)-*N*-phenylhex-4-enamide (**4x**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 1:1, v/v) in 83% yield (128.1

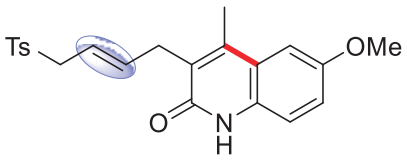
mg), *E/Z* > 20:1, which was detected by ^{1}H NMR spectroscopy. Yellow oil. R_f (petroleum ether/ethyl acetate = 1:2, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.88 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.77 – 5.59 (m, 1H), 3.65 (d, *J* = 7.4 Hz, 2H), 3.58 (t, *J* = 7.3 Hz, 1H), 2.78 (s, 3H), 2.75 (d, *J* = 7.1 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.91, 165.95, 137.35, 136.64, 129.08, 124.89, 120.08, 119.92, 60.87, 58.25, 39.27, 32.85, 29.46. HRMS (ESI-TOF) Calcd for $C_{15}H_{20}NO_4S^+$ ($[M+H]^+$) 310.1108. Found 310.1109.



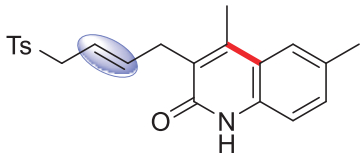
2-Methyl-*N*-phenyl-3-tosylpropanamide (**4y**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 24:1, v/v) in 75% yield (113.1 mg). White solid, m.p. = 15.4-154.1 ºC. R_f (petroleum ether/ethyl acetate = 8:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 9.9, 5.9 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.63 – 3.39 (m, 2H), 3.02 – 2.80 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.20, 145.34, 137.72, 135.55, 130.15, 128.94, 128.07, 124.43, 119.87, 52.04, 29.96, 21.67. HRMS (ESI-TOF) Calcd for $C_{16}H_{18}NO_3S^+$ ($[M+H]^+$) 304.1002. Found 304.1003. Spectra are consistent with literature report.[1]



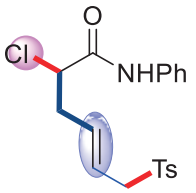
N-Benzyl-2-methyl-*N*-phenyl-3-tosylpropanamide (**4z**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v) in 45% yield (91.0 mg). White solid, m.p. = 89.1-90.0 ºC. R_f (petroleum ether/ethyl acetate = 6:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.29 (m, 5H), 7.25 (dd, *J* = 6.9, 3.5 Hz, 3H), 7.18 – 7.07 (m, 2H), 6.95 (dd, *J* = 6.3, 3.0 Hz, 2H), 4.82 (s, 2H), 3.60 – 3.31 (m, 2H), 2.66 – 2.50 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87, 144.81, 141.24, 136.91, 136.07, 129.93, 129.89, 128.83, 128.56, 128.44, 128.30, 128.00, 127.56, 53.37, 52.21, 27.60, 21.70. HRMS (ESI-TOF) Calcd for $C_{23}H_{24}NO_3S^+$ ($[M+Na]^+$) 416.1291. Found 416.1296.



(*E*)-6-Methoxy-4-methyl-3-(4-tosylbut-2-en-1-yl)quinolin-2(1*H*)-one (**5a**). Isolated by flash column chromatography (petroleum ether/ethyl acetate/Et_3N = 50:100:1, v/v) in 55% yield (43.8 mg), which was detected by ^1H NMR spectroscopy. Brown solid, m.p. = 210.0-210.4 ºC. R_f (petroleum ether/ethyl acetate = 1:3, v/v) 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 11.55 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 7.18 – 7.12 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.73 – 5.59 (m, 1H), 5.49 (dd, *J* = 15.2, 7.6 Hz, 1H), 3.90 (s, 3H), 3.72 (d, *J* = 7.3 Hz, 2H), 3.52 (d, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.48, 155.17, 144.45, 144.00, 137.83, 135.13, 131.45, 129.44, 128.42, 128.10, 121.47, 118.56, 117.16, 117.09, 106.81, 60.00, 55.79, 30.00, 21.41, 15.35. HRMS (ESI-TOF) Calcd for $C_{22}H_{24}NO_4S^+$ ($[M+H]^+$) 398.1421. Found 398.1423.

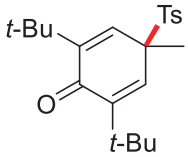


(*E*)-4,6-Dimethyl-3-(4-tosylbut-2-en-1-yl)quinolin-2(1*H*)-one (**5b**). Isolated by flash column chromatography (petroleum ether/ethyl acetate/Et_3N = 50:50:1, v/v) in 61% yield (46.3 mg), which was detected by ^1H NMR spectroscopy. Brown solid, m.p. = 221.3-221.9 ºC. R_f (petroleum ether/ethyl acetate = 1:2, v/v) 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (s, 1H), 7.32 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.64 (dt, *J* = 15.4, 6.2 Hz, 1H), 5.54 – 5.41 (m, 1H), 3.72 (d, *J* = 7.3 Hz, 2H), 3.51 (d, *J* = 6.1 Hz, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.94, 144.42, 144.38, 137.94, 135.01, 134.88, 131.98, 131.12, 129.42, 128.42, 127.52, 124.22, 120.72, 117.05, 115.93, 60.00, 29.91, 21.37, 21.35, 15.20. HRMS (ESI-TOF) Calcd for $C_{22}H_{24}NO_3S^+$ ($[M+H]^+$) 382.1471. Found 382.1474.

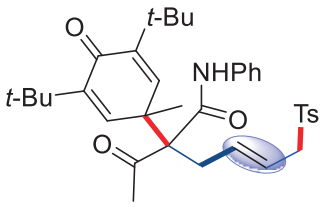


(*E*)-2-Chloro-*N*-phenyl-6-tosylhex-4-enamide (**6**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) in 57% yield (43.3 mg). White solid, m.p. = 118.4-119.2 ºC. R_f (petroleum ether/ethyl acetate = 1.5:1, v/v) 0.33. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.62 (td, *J* = 5.9, 3.5 Hz, 2H), 4.43 (dd, *J* = 7.4, 4.5 Hz, 1H), 3.83 – 3.73 (m, 2H), 2.96 – 2.72 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.82, 144.86, 136.76, 135.45, 134.43, 129.78, 129.13,

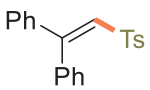
128.45, 125.25, 121.46, 120.17, 59.93, 59.73, 38.23, 21.65. HRMS (ESI-TOF) Calcd for $C_{19}H_{21}ClNO_3S^+$ ([M+H]$^+$) 378.0925. Found 378.0925.



2,6-Di-*tert*-butyl-4-methyl-4-tosylcyclohexa-2,5-dien-1-one (**7**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.64 (s, 2H), 2.37 (s, 3H), 1.82 (s, 3H), 1.10 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.70, 151.22, 145.32, 135.71, 130.59, 130.26, 128.81, 65.82, 35.20, 28.98, 21.63, 18.53. HRMS (ESI-TOF) Calcd for $C_{22}H_{30}O_3SNa^+$ ([M+Na]$^+$) 397.1808. Found 397.1814. Spectra are consistent with literature report.[2]

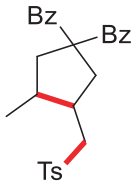


(*E*)-2-Acetyl-2-(3,5-di-*tert*-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-*N*-phenyl-6-tosylhex-4-enamide (**8**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) in 27% yield (81.2 mg). R_f (petroleum ether/ethyl acetate = 3:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 3.0 Hz, 1H), 6.25 (d, J = 3.0 Hz, 1H), 5.55 (dd, J = 15.0, 7.1 Hz, 1H), 5.49 – 5.39 (m, 1H), 3.70 (td, J = 14.1, 6.3 Hz, 2H), 3.20 (d, J = 13.7 Hz, 1H), 2.42 (t, J = 5.3 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 1.31 (s, 3H), 1.24 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.30, 185.77, 165.44, 148.37, 148.19, 144.86, 141.56, 140.54, 137.25, 136.61, 135.62, 129.83, 129.11, 128.06, 124.83, 120.35, 120.16, 67.53, 59.89, 44.76, 35.20, 35.11, 34.33, 31.96, 29.34, 29.30, 22.09, 21.52. HRMS (ESI-TOF) Calcd for $C_{36}H_{46}NO_5S^+$ ([M+H]$^+$) 604.3091. Found 604.3091.



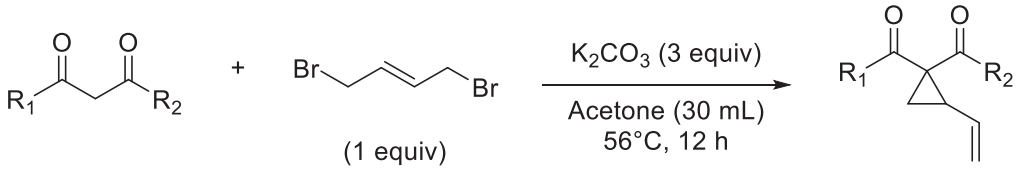
(2-Tosylethene-1,1-diyl)dibenzene (**9**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.17 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.09 (dd, J = 5.2, 3.3 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.74, 143.79, 139.24, 138.62, 135.60, 130.26, 129.79, 129.36, 128.97, 128.87, 128.60, 128.23, 127.83, 127.71, 21.59. HRMS (ESI-TOF) Calcd for

$C_{21}H_{18}NaO_2S^+$ ([M+Na^+]) 357.0925. Found 357.0916. Spectra are consistent with literature report.[3]



(3-Methyl-4-(tosylmethyl)cyclopentane-1,1-diyl)bis(phenylmethanone) (**10**). Isolated by flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v) in 72% yield (162.9 mg). Pale yellow solid, m.p. = 119-120 °C. R_f (petroleum ether/ethyl acetate = 5:1, v/v) 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.75 – 7.68 (m, 4H), 7.38 (t, J = 7.1 Hz, 2H), 7.33 – 7.23 (m, 6H), 3.21 – 3.08 (m, 2H), 2.73 (ddd, J = 13.1, 9.3, 6.8 Hz, 2H), 2.62 – 2.45 (m, 2H), 2.41 (d, J = 2.8 Hz, 3H), 2.33 (ddd, J = 13.4, 10.1, 5.7 Hz, 2H), 0.90 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.36, 197.54, 144.64, 136.69, 135.63, 135.30, 133.13, 133.07, 129.92, 129.30, 129.26, 129.21, 128.54, 128.53, 128.10, 68.56, 56.72, 41.26, 38.13, 37.70, 37.11, 21.64, 15.01. HRMS (ESI-TOF) Calcd for $C_{28}H_{29}O_4S^+$ ([M+H]$^+$) 461.1781. Found 461.1781.

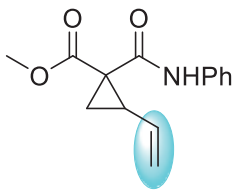
VII. General procedure for the synthesis of vinylcyclopropane substrates 1



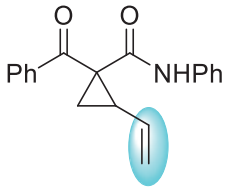
The substrate vinylcyclopropane **1** or **1'** was synthesized according to the literature procedure,[4] but some adjustments were made.

A mixture of dicarbonyl compound (10.0 mmol), 1,4-dibromo-2-butene (10.0 mmol, 1 equiv) and K_2CO_3 (30 mmol, 3 equiv) in acetone (30 mL) was stirred at 56 °C for 12 h, Then, it was quenched with water (50.0 mL) and extracted with CH_2Cl_2 (25.0 mL × 4). The residue obtained after evaporation of the solvent was purified on silica gel (petroleum ether–ethyl acetate) to afford the vinylcyclopropane **1** or **1'**.

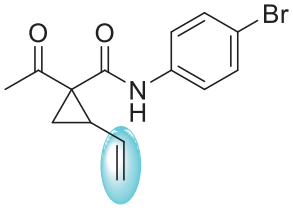
Some of the vinylcyclopropane **1** or **1'** are known, and their NMR spectra data match those previously reported in the literature.[3] The other vinylcyclopropanes listed below are all new compounds.



Methyl 1-(phenylcarbamoyl)-2-vinylcyclopropane-1-carboxylate (**1a1**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1). Major diasteroisomer: colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.64 – 7.49 (m, 2H), 7.37 – 7.27 (m, 2H), 7.15 – 7.02 (m, 1H), 5.66 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.37 (ddd, *J* = 17.1, 1.4, 0.6 Hz, 1H), 5.26 – 5.13 (m, 1H), 3.76 (s, 3H), 2.64 (dd, *J* = 17.3, 8.8 Hz, 1H), 2.20 (dd, *J* = 9.2, 4.4 Hz, 1H), 1.97 (dd, *J* = 8.1, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.25, 165.91, 138.06, 133.04, 128.96, 124.20, 120.21, 120.08, 52.36, 38.26, 34.90, 21.74. HRMS (ESI-TOF) Calcd for $C_{14}H_{16}NO_3^+$ ($[M+H]^+$) 246.1125. Found 246.1125.

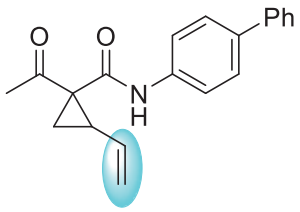


1-Benzoyl-*N*-phenyl-2-vinylcyclopropane-1-carboxamide (**1a3**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 24:1). Major diasteroisomer : minor diasteroisomer = 3:1. Major diasteroisomer: white solid, m. p.= 107-108 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.63 (s, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 10.6, 4.6 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 5.33 (dd, *J* = 16.9, 1.6 Hz, 1H), 5.27 – 5.15 (m, 1H), 5.03 (dd, *J* = 10.0, 1.5 Hz, 1H), 2.97 (dd, *J* = 16.0, 8.5 Hz, 1H), 1.89 (dd, *J* = 7.1, 4.9 Hz, 1H), 1.84 (dd, *J* = 8.8, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.93, 196.43, 166.63, 165.05, 137.60, 137.45, 136.53, 135.91, 134.00, 133.73, 133.52, 133.41, 129.27, 128.92, 128.90, 128.81, 124.60, 119.99, 118.67, 118.61, 43.78, 42.85, 32.08, 29.84, 20.38, 19.26. HRMS (ESI-TOF) Calcd for $C_{19}H_{18}NO_2^+$ ($[M+H]^+$) 292.1332. Found 292.1330.

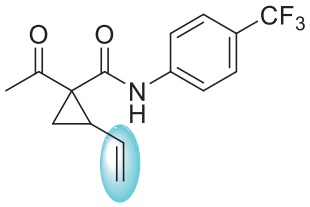


1-Acetyl-*N*-(4-bromophenyl)-2-vinylcyclopropane-1-carboxamide (**1b5**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1). Major diasteroisomer : minor diasteroisomer = 3:2. Major diasteroisomer: pale yellow solid.

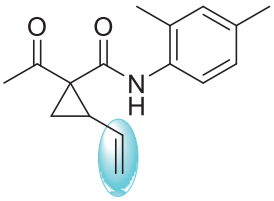
m. p.= 142-143 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 5.74 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 2.63 (d, *J* = 8.0 Hz, 1H), 2.31 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.21 (s, 3H), 1.90 (dd, *J* = 7.9, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.59, 166.32, 137.07, 132.10, 131.92, 121.65, 121.15, 116.75, 42.37, 37.04, 30.99, 21.21. HRMS (ESI-TOF) Calcd for $C_{14}H_{15}BrNO_2^+$ ($[M+H]^+$) 308.0281. Found 308.0278.



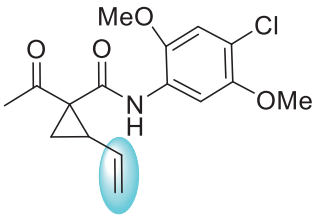
N-([1,1'-Biphenyl]-4-yl)-1-acetyl-2-vinylcyclopropane-1-carboxamide (**1b6**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 24:1). Major diasteroisomer: colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 5.73 (ddd, *J* = 17.1, 10.1, 7.2 Hz, 1H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 2.65 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.30 (dd, *J* = 9.0, 5.3 Hz, 1H), 2.23 (s, 3H), 1.90 (dd, *J* = 7.8, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.35, 166.28, 140.52, 137.28, 137.07, 132.29, 128.82, 127.61, 127.13, 126.87, 120.90, 120.41, 42.67, 36.63, 30.99, 21.05. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}NO_2^+$ ($[M+H]^+$) 306.1489. Found 306.1488.



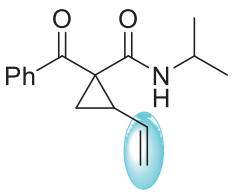
1-Acetyl-*N*-(4-(trifluoromethyl)phenyl)-2-vinylcyclopropane-1-carboxamide (**1b7**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1), Major diasteroisomer: pale yellow solid, m. p.= 101-102 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.76 (ddd, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.42 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.33 (dt, *J* = 10.2, 1.1 Hz, 1H), 2.72 – 2.59 (m, 1H), 2.35 (dd, *J* = 9.1, 5.3 Hz, 1H), 2.21 (s, 3H), 1.92 (dd, *J* = 8.0, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.58, 166.62, 141.02, 132.00, 126.22 (q, *J* = 3.1 Hz), 125.93 (q, *J* = 32.3 Hz), 124.12 (q, *J* = 272.7 Hz), 121.26, 119.73, 42.34, 37.32, 30.88, 21.35. HRMS (ESI-TOF) Calcd for $C_{15}H_{15}F_3NO_2^+$ ($[M+H]^+$) 298.1049. Found 298.1051.



1-Acetyl-*N*-(2,4-dimethylphenyl)-2-vinylcyclopropane-1-carboxamide (**1e**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1), Major diasteroisomer: pale yellow solid, m. p.= 226-227 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 2H), 5.70 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.45 – 5.32 (m, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 2.61 (dd, *J* = 16.1, 7.9 Hz, 1H), 2.27 (s, 3H), 2.27 (s, 3H), 2.23 – 2.15 (m, 4H), 1.84 (dd, *J* = 7.9, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.13, 166.26, 134.27, 133.65, 132.53, 131.09, 128.74, 127.09, 122.31, 120.49, 42.74, 36.14, 30.74, 20.98, 20.87, 17.94. HRMS (ESI-TOF) Calcd for $C_{16}H_{20}NO_2^+$ ($[M+H]^+$) 258.1489. Found 258.1492.

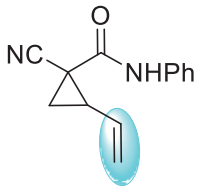


1-Acetyl-*N*-(4-(iodo-λ^2-methyl)-2,5-dimethoxyphenyl)-2-vinylcyclopropane-1-carboxamide (**1g**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1), Major diasteroisomer : minor diasteroisomer = 3:2. Major diasteroisomer: white solid, m. p.= 116-117 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.21 (s, 1H), 6.89 (s, 1H), 5.70 (ddd, *J* = 17.2, 10.2, 7.3 Hz, 1H), 5.40 (dt, *J* = 17.0, 1.1 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.62 (dd, *J* = 16.2, 7.9 Hz, 1H), 2.24 (s, 3H), 2.22 – 2.17 (m, 1H), 1.90 (dd, *J* = 7.9, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.25, 166.23, 148.78, 142.38, 132.25, 127.10, 120.67, 115.51, 112.20, 104.87, 56.52, 43.03, 36.19, 30.77, 20.82. HRMS (ESI-TOF) Calcd for $C_{16}H_{19}ClNO_4^+$ ($[M+H]^+$) 324.0997. Found 324.0999.

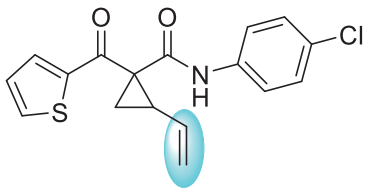


1-Benzoyl-*N*-isopropyl-2-vinylcyclopropane-1-carboxamide (**1h**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 10:1), pale yellow oil. Major diasteroisomer: white solid, m. p.= 220-221 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.88 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.60 – 5.47 (m, 1H),

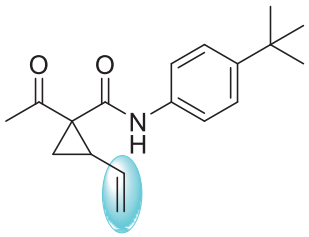
5.39 (s, 1H), 5.36 – 5.31 (m, 1H), 5.14 (dd, J = 10.2, 1.5 Hz, 1H), 4.08 – 3.85 (m, 1H), 2.67 (dd, J = 16.2, 8.9 Hz, 1H), 2.05 (dd, J = 7.1, 4.7 Hz, 1H), 1.45 (dd, J = 8.9, 4.7 Hz, 1H), 1.00 (d, J = 6.6 Hz, 3H), 0.78 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.09, 165.98, 136.35, 134.08, 133.38, 128.78, 128.62, 117.84, 43.10, 42.02, 29.01, 22.70, 21.97, 20.65. HRMS (ESI-TOF) Calcd for $C_{16}H_{20}NO_2^+$ ($[M+H]^+$) 258.1489. Found 258.1489.



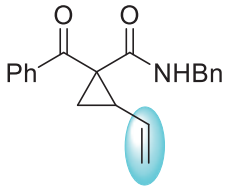
1-Cyano-*N*-phenyl-2-vinylcyclopropane-1-carboxamide (**1'a5**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1), Major diasteroisomer: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.55 – 7.45 (m, 2H), 7.39 – 7.31 (m, 2H), 7.21 – 7.11 (m, 1H), 5.68 (ddd, J = 17.0, 10.2, 8.3 Hz, 1H), 5.50 – 5.45 (m, 1H), 5.45 – 5.37 (m, 1H), 2.67 (dd, J = 16.7, 8.2 Hz, 1H), 2.10 (dd, J = 8.9, 4.9 Hz, 1H), 1.72 – 1.59 (m, 1H). Diasteroisomer *Mixture* spectrum: ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.73, 160.81, 136.91, 136.80, 132.37, 130.78, 129.14, 129.11, 125.35, 125.30, 121.12, 120.78, 120.44, 119.86, 118.25, 35.77, 33.30, 23.19, 22.35, 21.32, 21.25. HRMS (ESI-TOF) Calcd for $C_{13}H_{13}N_2O^+$ ($[M+H]^+$) 213.1022. Found 213.1020.



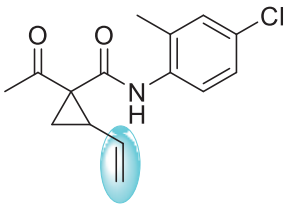
N-(4-chlorophenyl)-1-(thiophene-2-carbonyl)-2-vinylcyclopropane-1-carboxamide (**1'b**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 21:1), Major diasteroisomer : minor diasteroisomer = 3:2. Major diasteroisomer: yellow solid, m. p.= 132.0-133.0 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.97 (dd, J = 3.9, 0.9 Hz, 1H), 7.67 (dd, J = 4.9, 0.9 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.12 (dd, J = 4.8, 3.9 Hz, 1H), 5.58 (ddd, J = 17.0, 10.1, 8.9 Hz, 1H), 5.38 (dd, J = 17.0, 1.0 Hz, 1H), 5.18 (dd, J = 10.2, 1.2 Hz, 1H), 2.09 (dd, J = 7.2, 5.1 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.62 (dd, J = 8.9, 5.0 Hz, 1H). Diasteroisomer *Mixture* spectrum ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.49, 188.21, 166.37, 164.93, 143.28, 142.33, 136.42, 136.29, 135.62, 135.33, 135.05, 134.45, 133.53, 133.38, 129.61, 128.97, 128.76, 128.72, 121.26, 121.19, 118.72, 118.47, 44.12, 43.20, 31.26, 29.63, 20.26, 19.09. HRMS (ESI-TOF) Calcd for $C_{17}H_{15}ClNO_2S^+$ ($[M+H]^+$) 332.0507. Found 332.0511.



1-Acetyl-*N*-(4-(tert-butyl)phenyl)-2-vinylcyclopropane-1-carboxamide (**1'e4**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 20:1), Major diasteroisomer : minor diasteroisomer = 4:1. Major diasteroisomer: pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 5.73 – 5.62 (m, 1H), 5.37 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.28 – 5.23 (m, 1H), 2.62 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.22 (s, 3H), 2.18 – 2.13 (m, 1H), 1.84 (dd, *J* = 7.8, 5.2 Hz, 1H), 1.30 (s, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.64, 166.18, 147.31, 135.34, 132.46, 125.78, 120.40, 119.93, 43.11, 35.69, 34.39, 31.38, 30.74, 20.69. HRMS (ESI-TOF) Calcd for $C_{18}H_{24}NO_2^+$ ($[M+H]^+$) 286.1802. Found 286.1806.

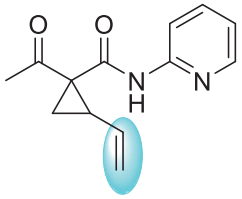


1-Benzoyl-*N*-benzyl-2-vinylcyclopropane-1-carboxamide (**1'f**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 10:1), Major diasteroisomer: white solid, m. p.= 132.0-133.0 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.63 – 7.56 (m, 1H), 7.46 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.21 – 7.11 (m, 3H), 6.92 – 6.82 (m, 2H), 5.89 (s, 1H), 5.65 – 5.50 (m, 1H), 5.36 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.16 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.33 (qd, *J* = 15.0, 5.7 Hz, 2H), 2.71 (dd, *J* = 16.3, 9.0 Hz, 1H), 2.12 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.50 (dd, *J* = 8.9, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.70, 166.95, 137.52, 136.26, 134.07, 133.51, 128.88, 128.81, 128.53, 127.41, 127.38, 118.18, 44.08, 43.05, 29.14, 20.68. HRMS (ESI-TOF) Calcd for $C_{20}H_{20}NO_2^+$ ($[M+H]^+$) 306.1489. Found 306.1490.

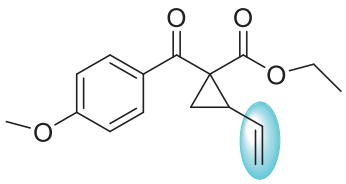


1-Acetyl-*N*-(4-chloro-2-methylphenyl)-2-vinylcyclopropane-1-carboxamide (**1'g2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1), Major diasteroisomer: white solid, m. p.= 96-97 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s,

1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 5.75 (ddd, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.40 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.31 (dt, *J* = 10.2, 1.2 Hz, 1H), 2.71 – 2.54 (m, 1H), 2.31 (s, 4H), 2.19 (s, 3H), 1.89 (dd, *J* = 8.0, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.72, 166.31, 135.04, 132.21, 130.07, 130.03, 129.14, 126.46, 122.87, 121.03, 42.31, 37.07, 30.79, 21.38, 17.90. HRMS (ESI-TOF) Calcd for $C_{15}H_{17}ClNO_2^+$ ($[M+H]^+$) 278.0942. Found 278.0942.



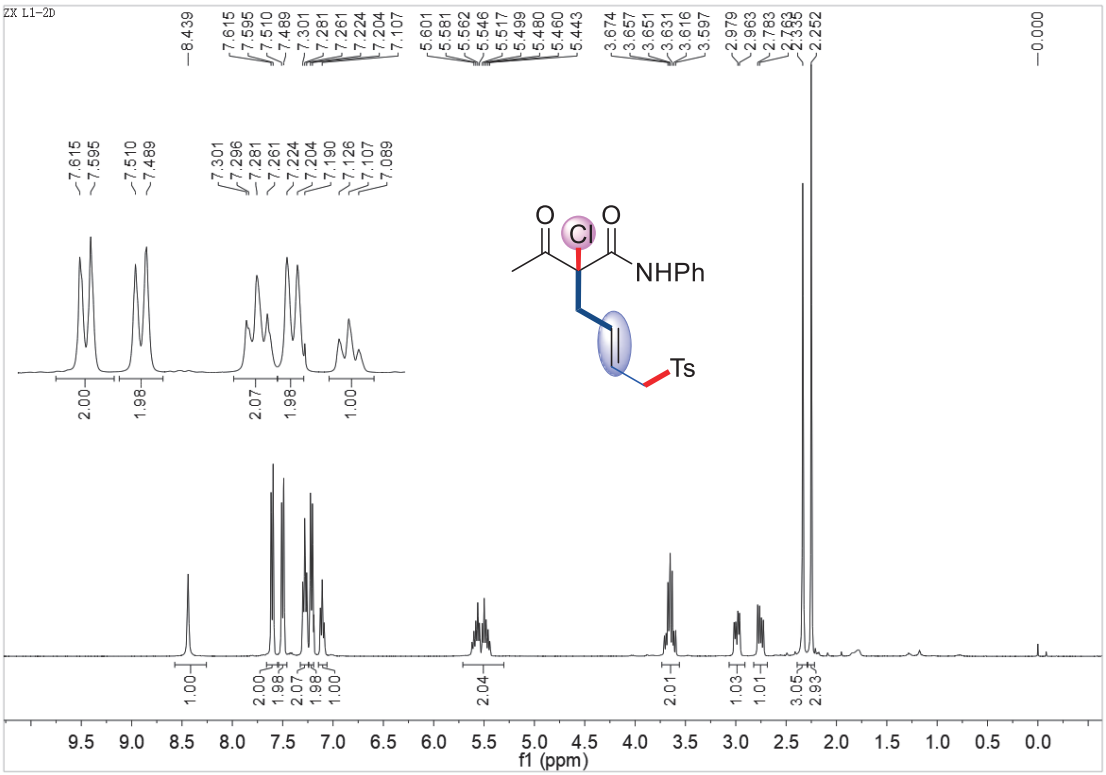
1-Acetyl-*N*-(pyridin-2-yl)-2-vinylcyclopropane-1-carboxamide (**1'i**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 30:1). Major diasteroisomer: colourless oil, m. p.= 101-102 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.31 (dd, *J* = 4.9, 1.0 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.63 (m, 1H), 7.05 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 5.62 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1H), 5.35 (d, *J* = 16.5 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 2.53 (dd, *J* = 16.7, 8.8 Hz, 1H), 2.22 (s, 3H), 2.12 (dd, *J* = 7.6, 5.3 Hz, 1H), 1.84 (dd, *J* = 9.1, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.86, 165.22, 151.26, 148.10, 138.27, 133.04, 119.99, 119.58, 114.28, 44.39, 34.97, 26.77, 21.33. HRMS (ESI-TOF) Calcd for $C_{13}H_{15}N_2O_2^+$ ($[M+H]^+$) 231.1128. Found 231.1127.



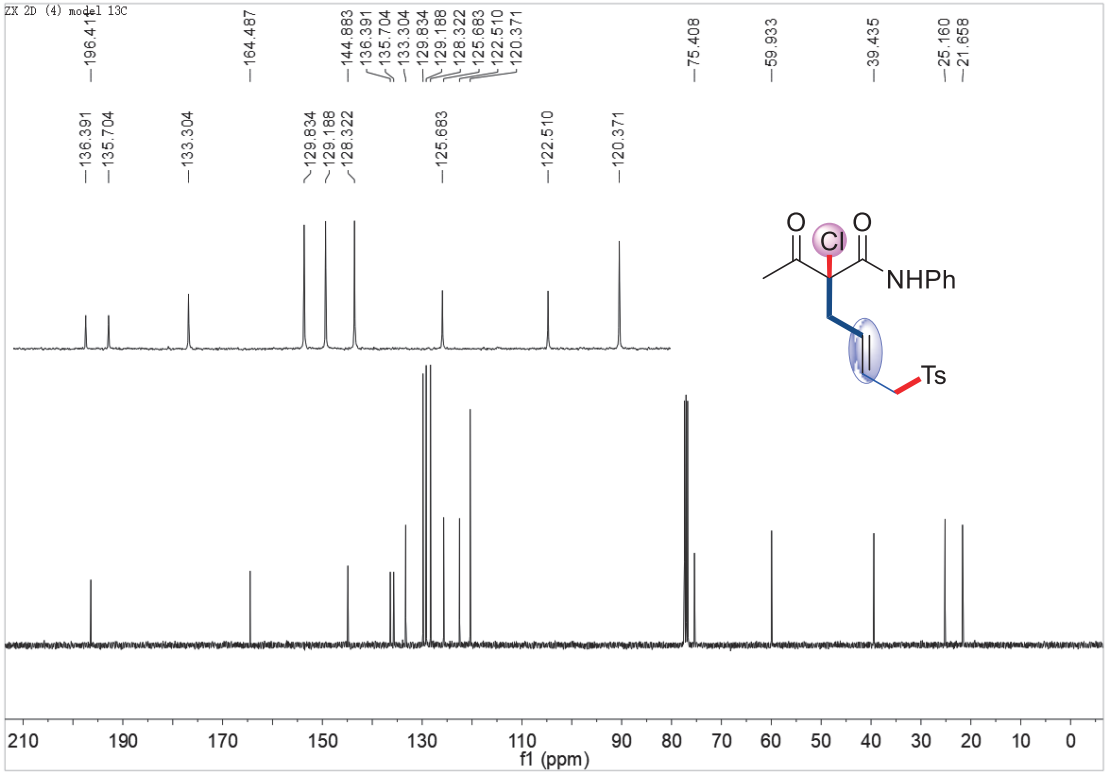
Ethyl 1-(4-methoxybenzoyl)-2-vinylcyclopropane-1-carboxylate (**1'j2**), isolated by flash column chromatography (petroleum ether/ethyl acetate = 24:1), Major diasteroisomer : minor diasteroisomer = 4:1. Major diasteroisomer: colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.78 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.38 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.68 (d, *J* = 7.7 Hz, 1H), 1.89 (dt, *J* = 7.0, 3.5 Hz, 1H), 1.63 – 1.54 (m, 5H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.63, 169.61, 163.39, 133.35, 130.73, 129.82, 118.55, 113.71, 61.36, 55.48, 40.34, 30.14, 21.15, 13.92. HRMS (ESI-TOF) Calcd for $C_{16}H_{19}O_4^+$ ($[M+H]^+$) 275.1278. Found 275.1279.

VI. Copies of ^{1}H, ^{19}F, ^{13}C and DEPT NMR spectra

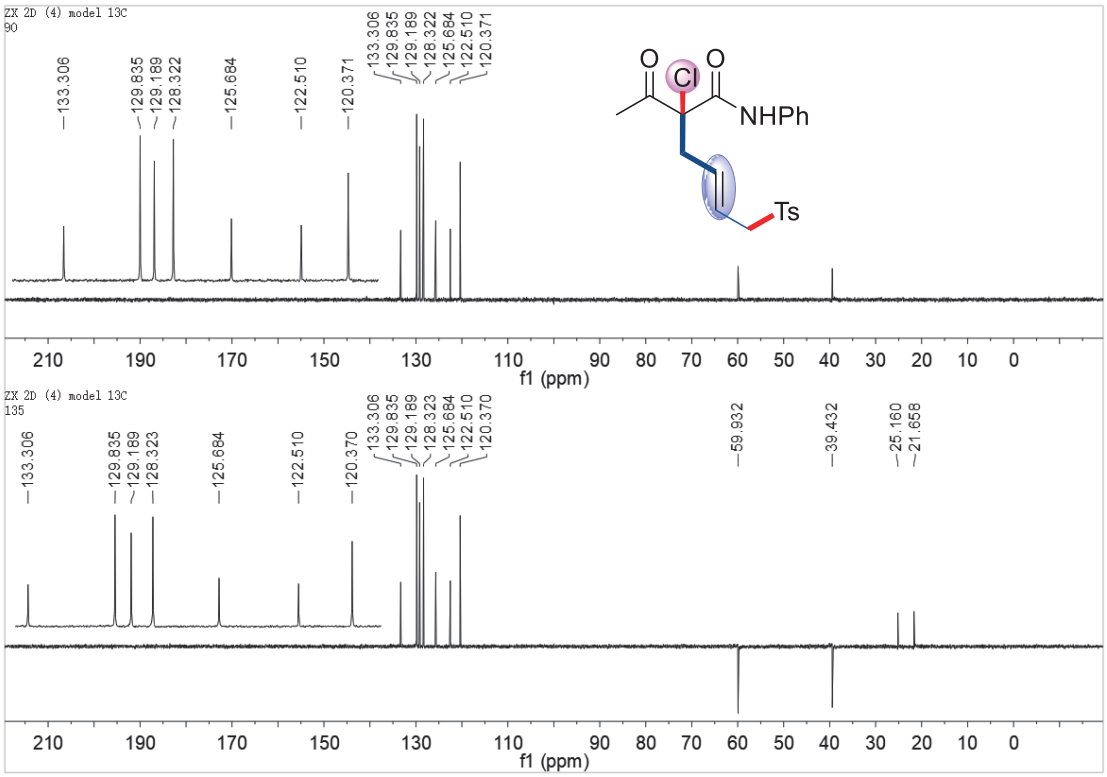
3a, ^{1}H NMR



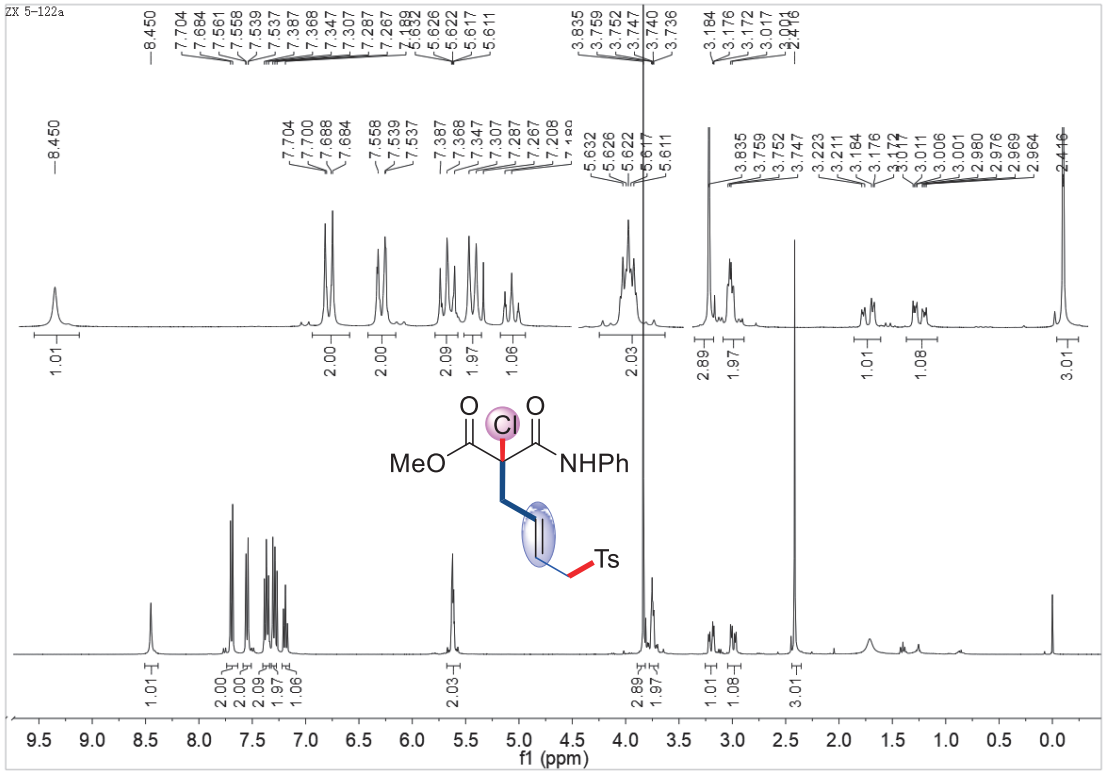
3a, ^{13}C NMR



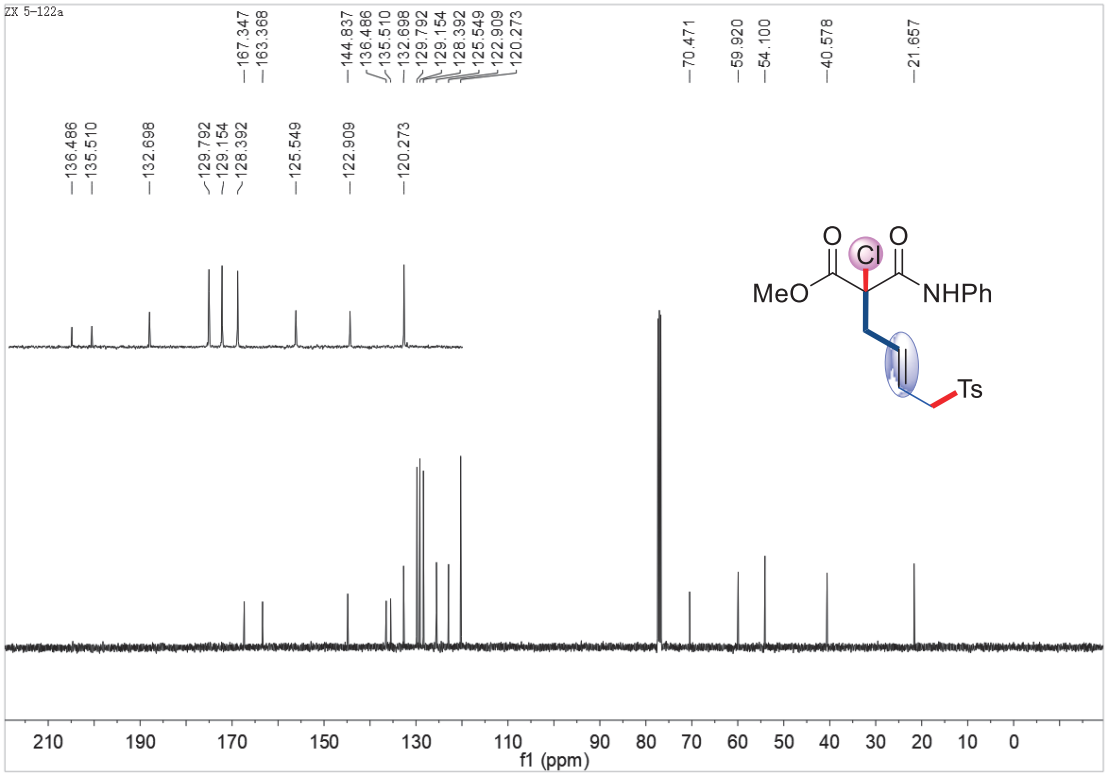
3a, DEPT 90 and DEPT 135



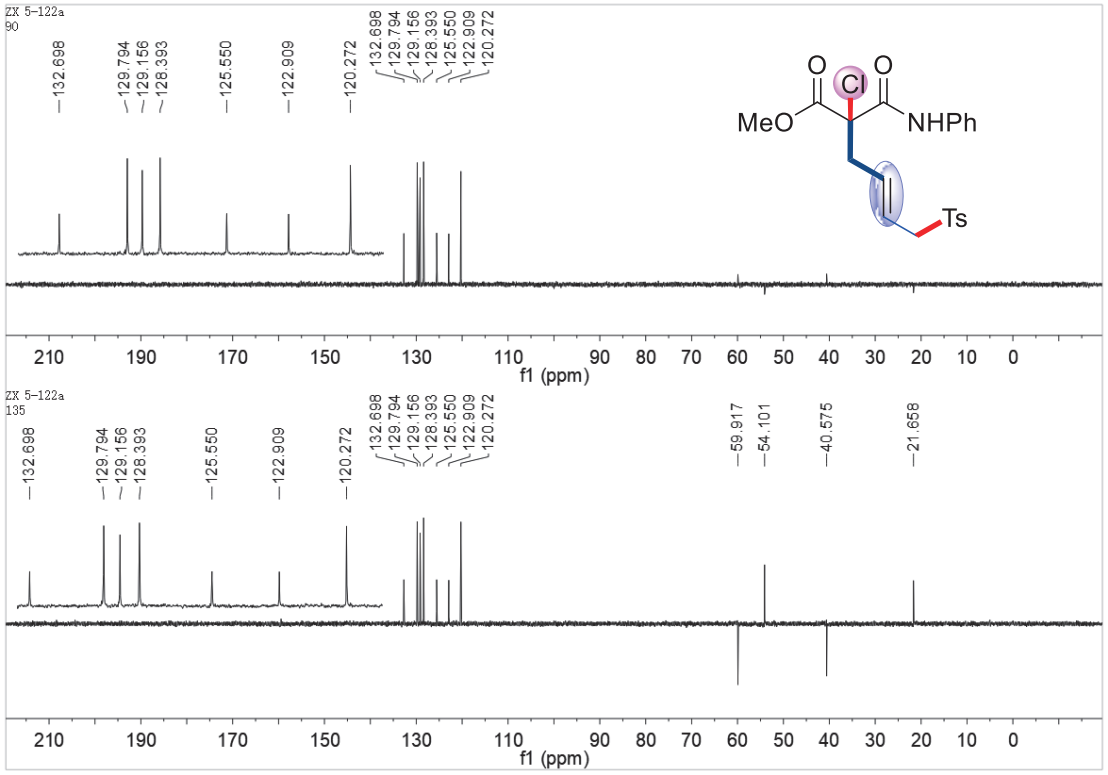
3a1, ^{1}H NMR



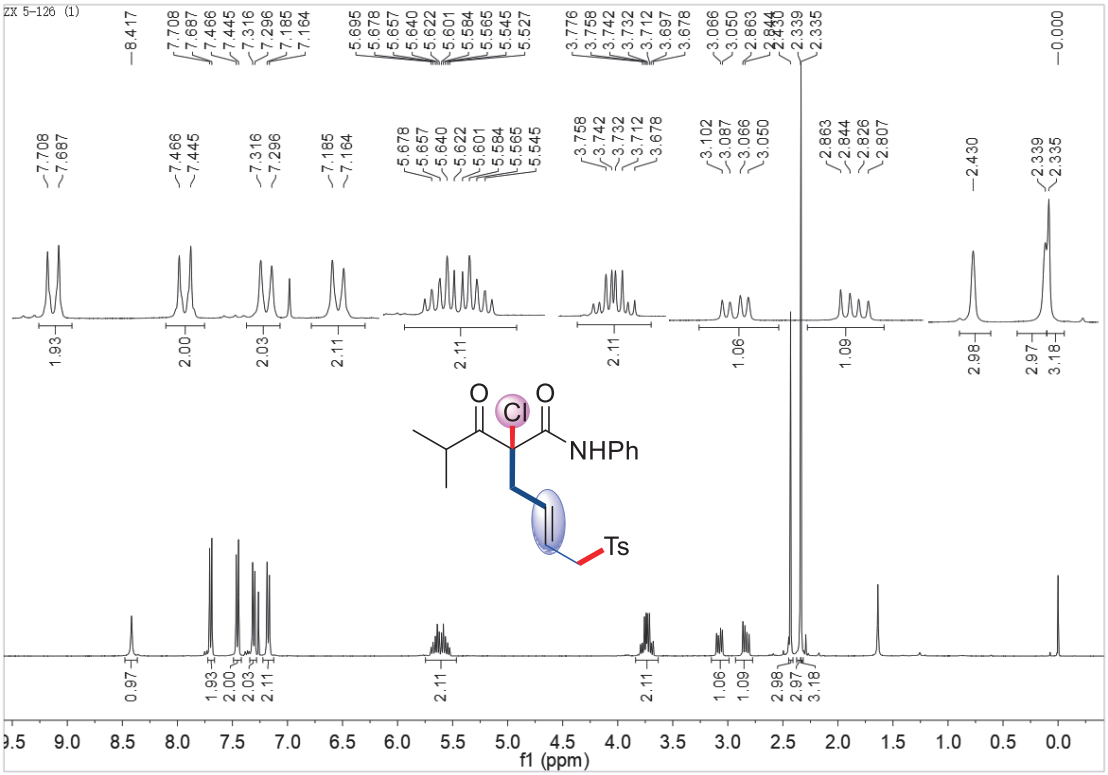
3a1, ^{13}C NMR



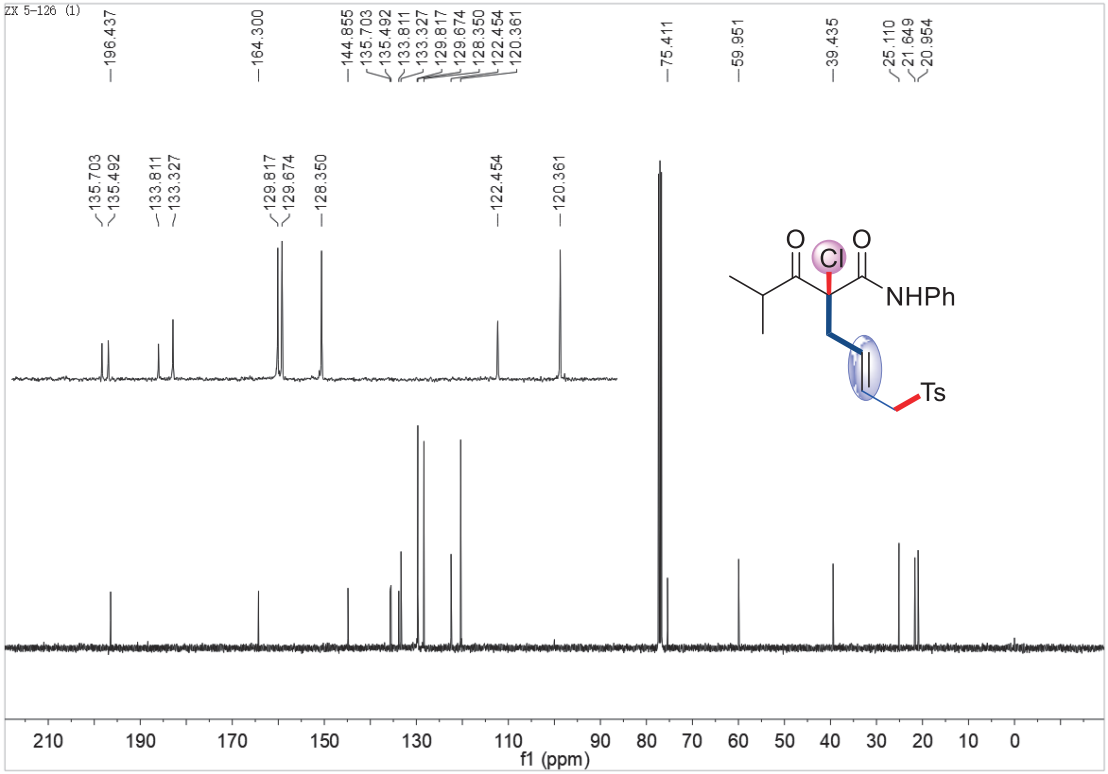
3a1, DEPT 90 and DEPT 135



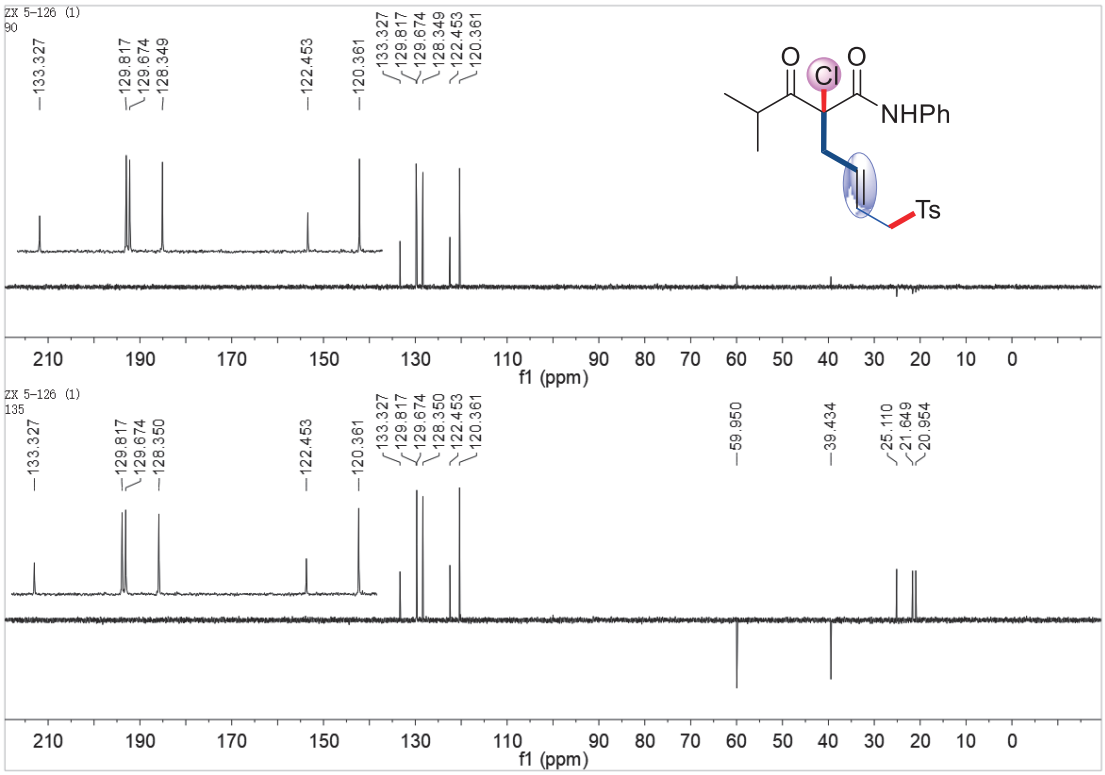
3a2, ^{1}H NMR



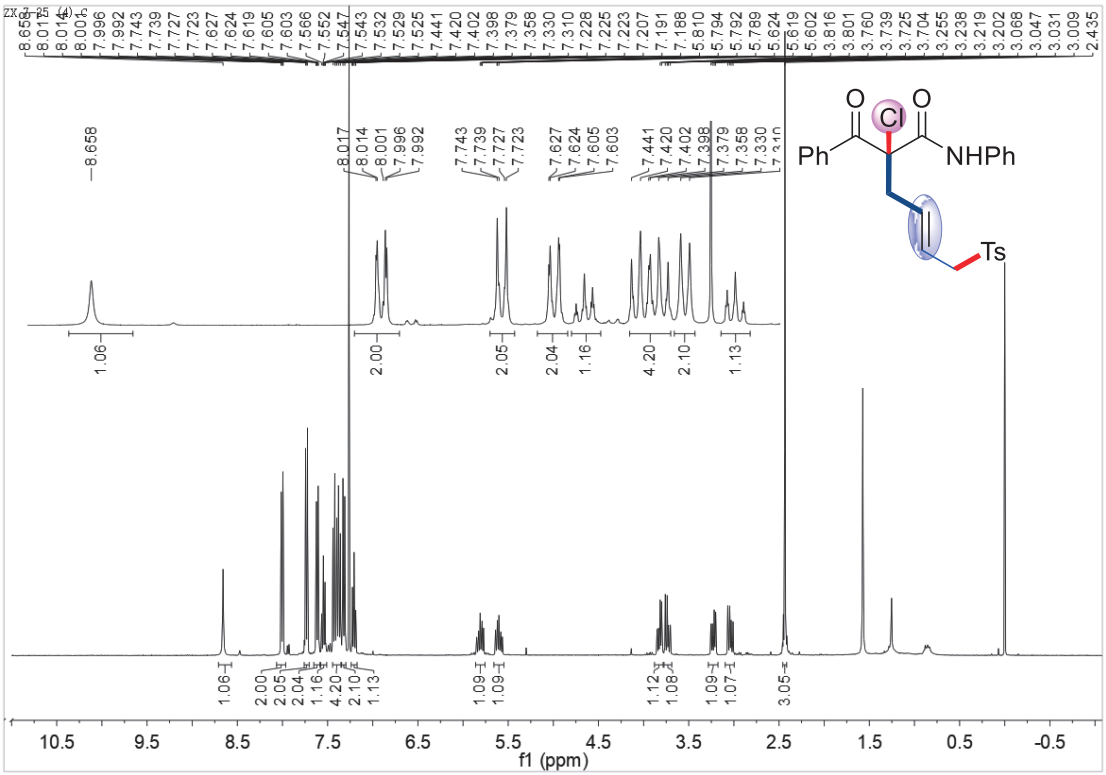
3a2, ^{13}C NMR



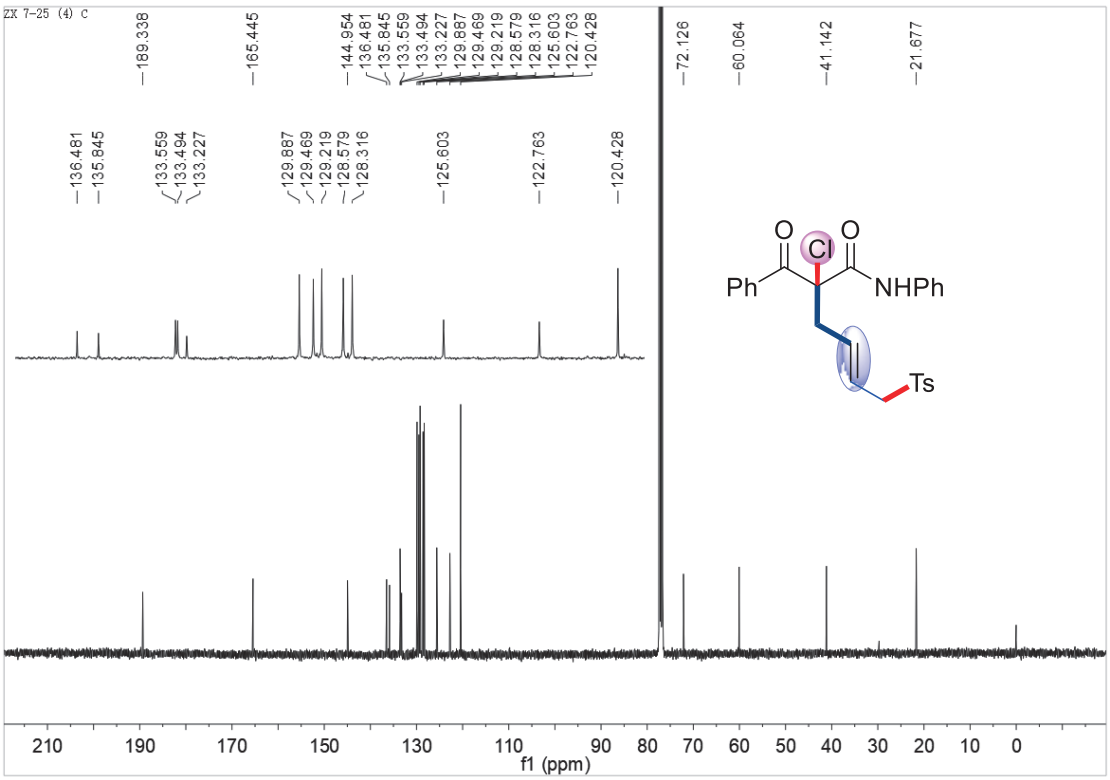
3a2 DEPT 90 and DEPT 135



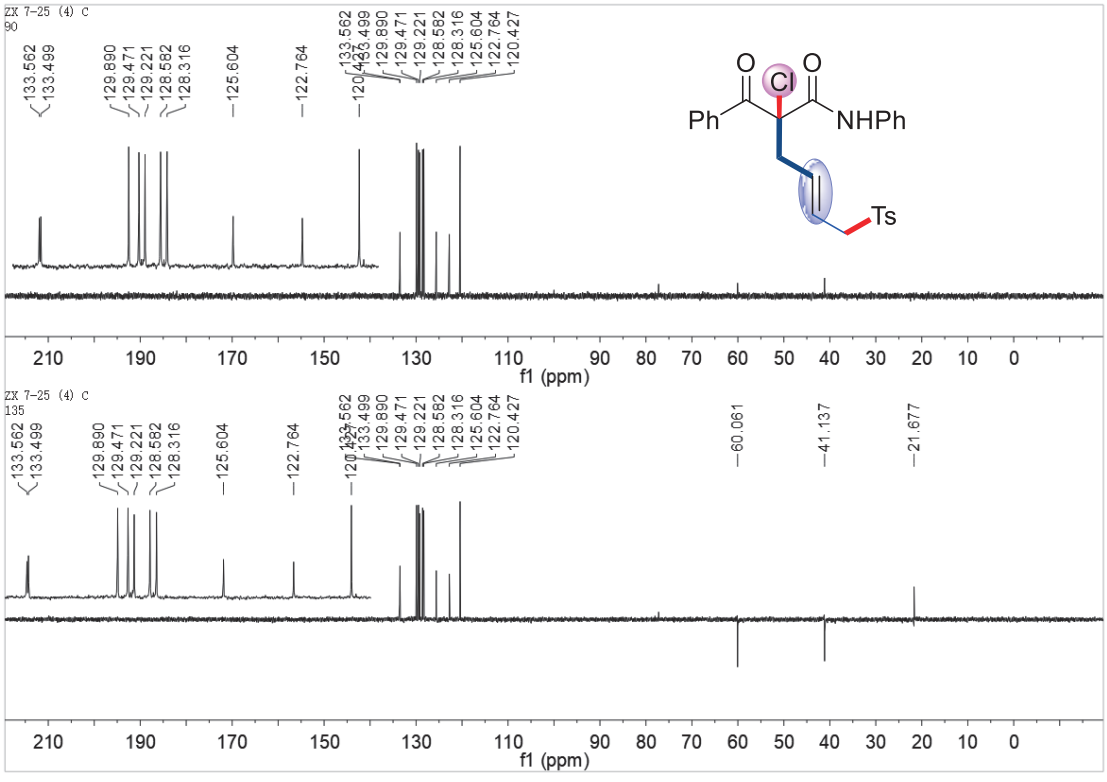
3a3, ^{1}H NMR



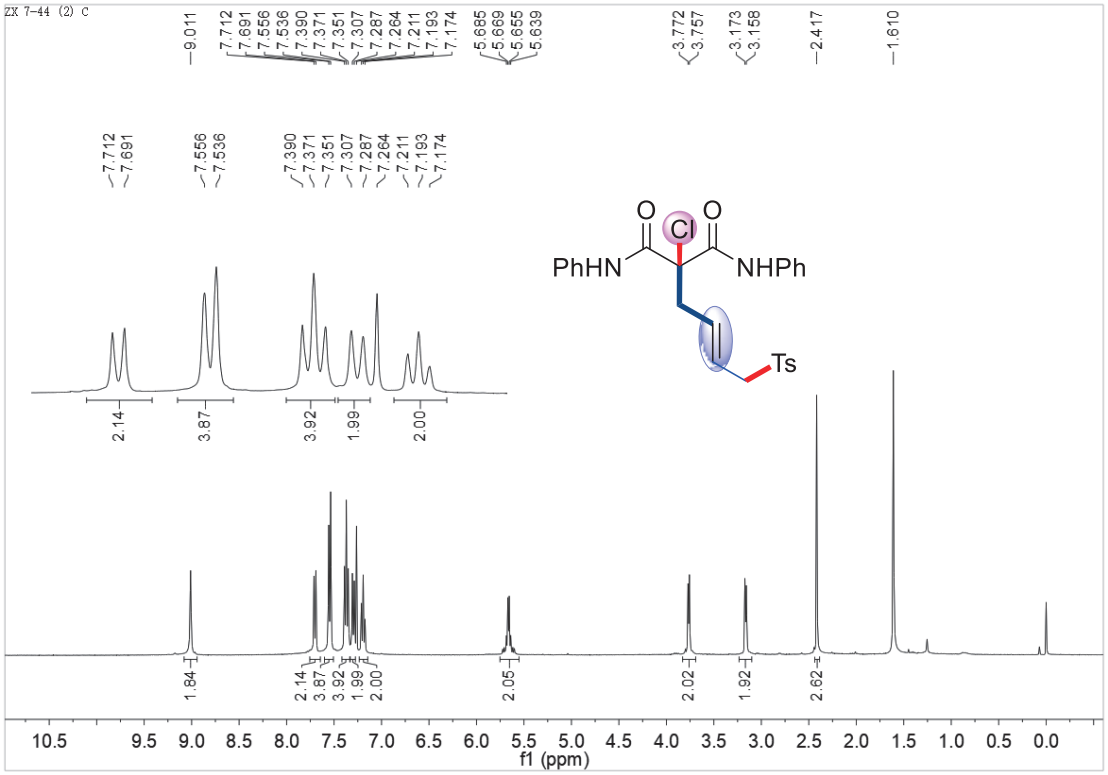
3a3, ^{13}C NMR



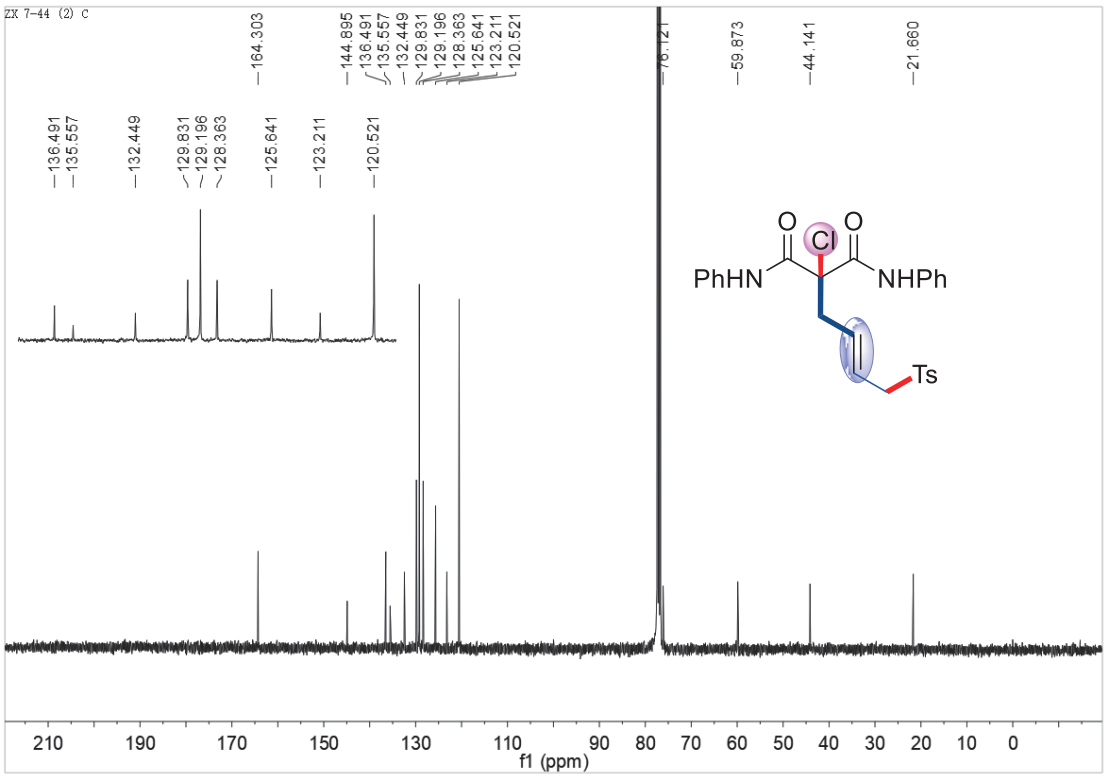
3a3 DEPT 90 and DEPT 135



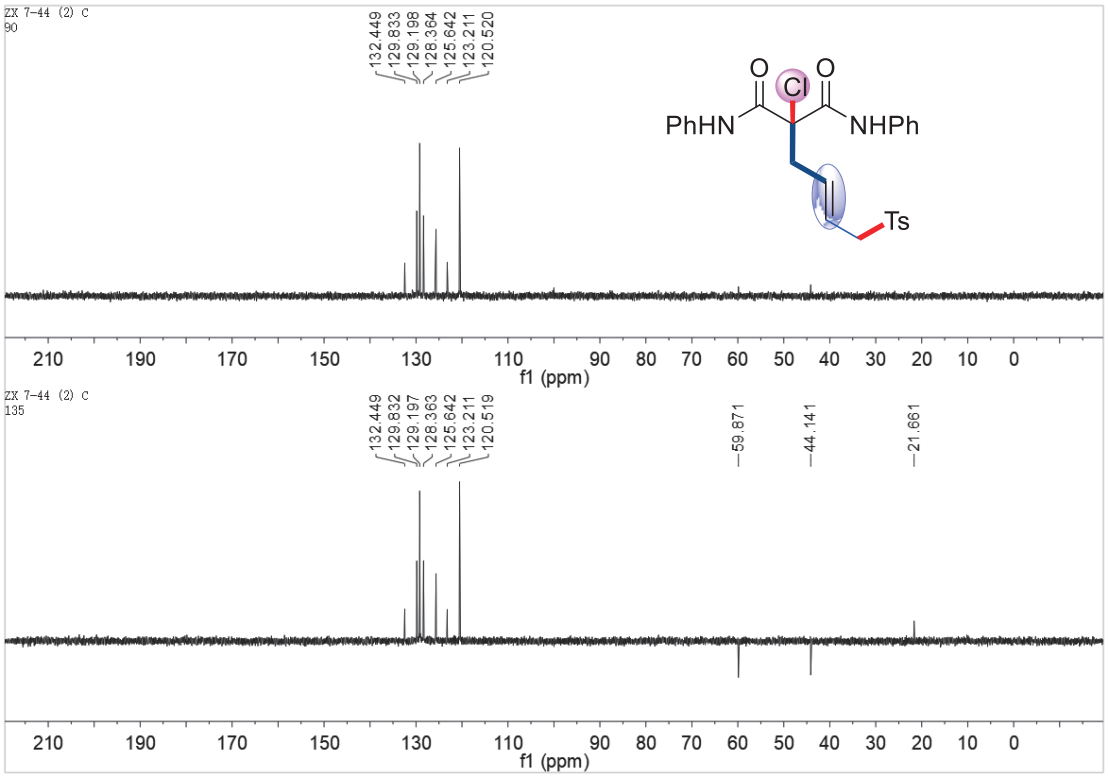
3a4, ^{1}H NMR



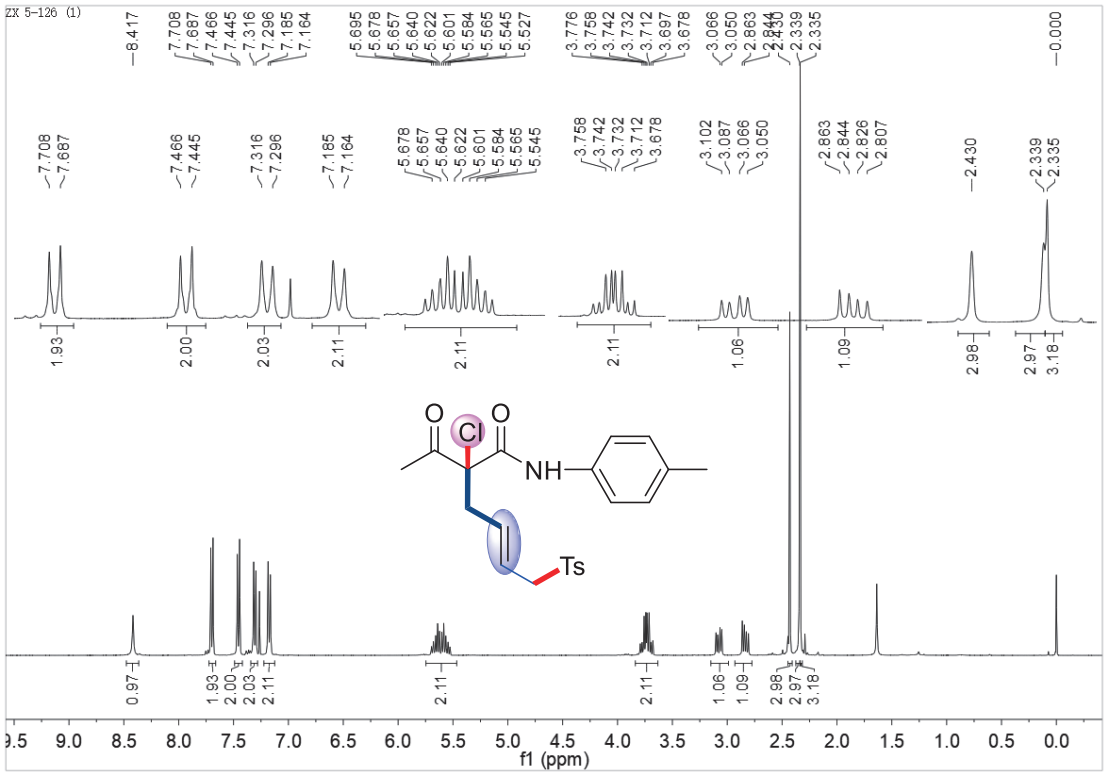
3a4, ^{13}C NMR



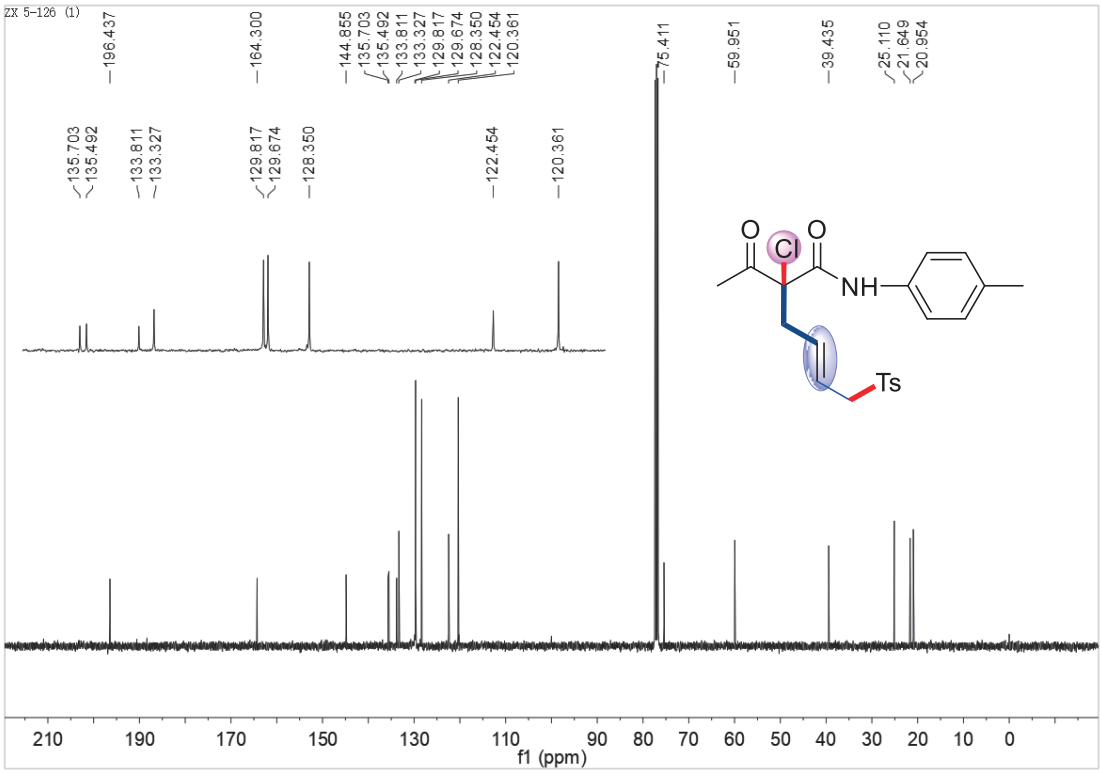
3a4 DEPT 90 and DEPT 135



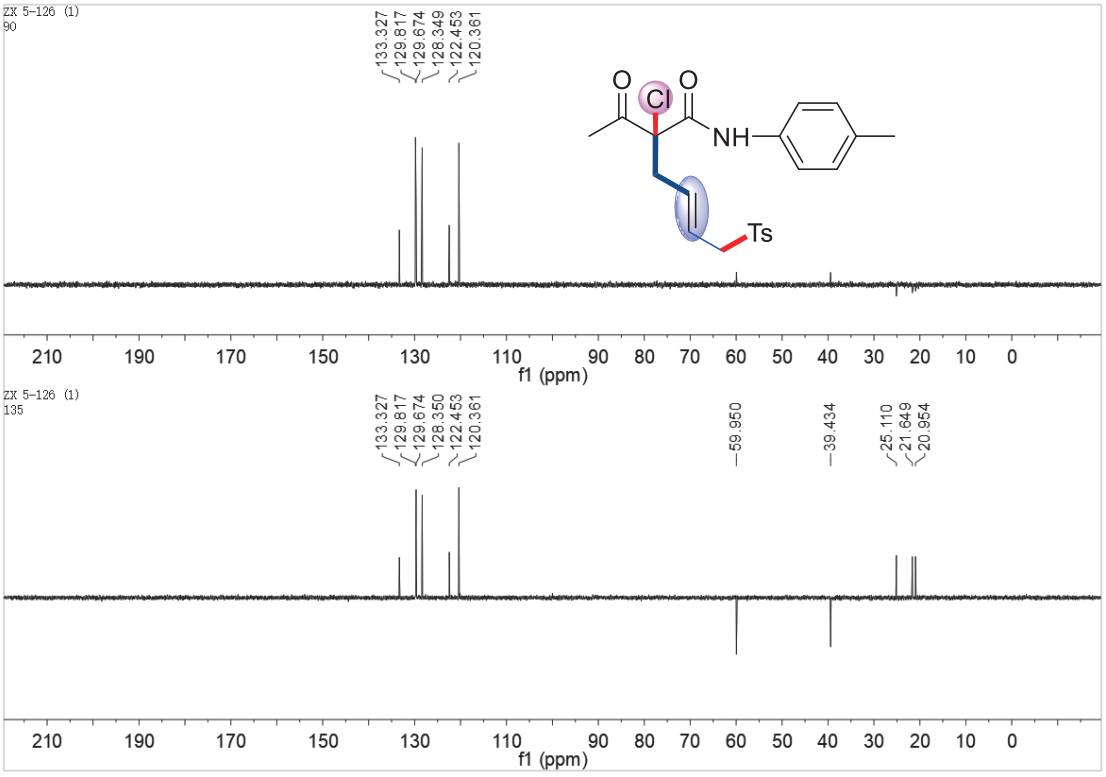
3b1, ^{1}H NMR



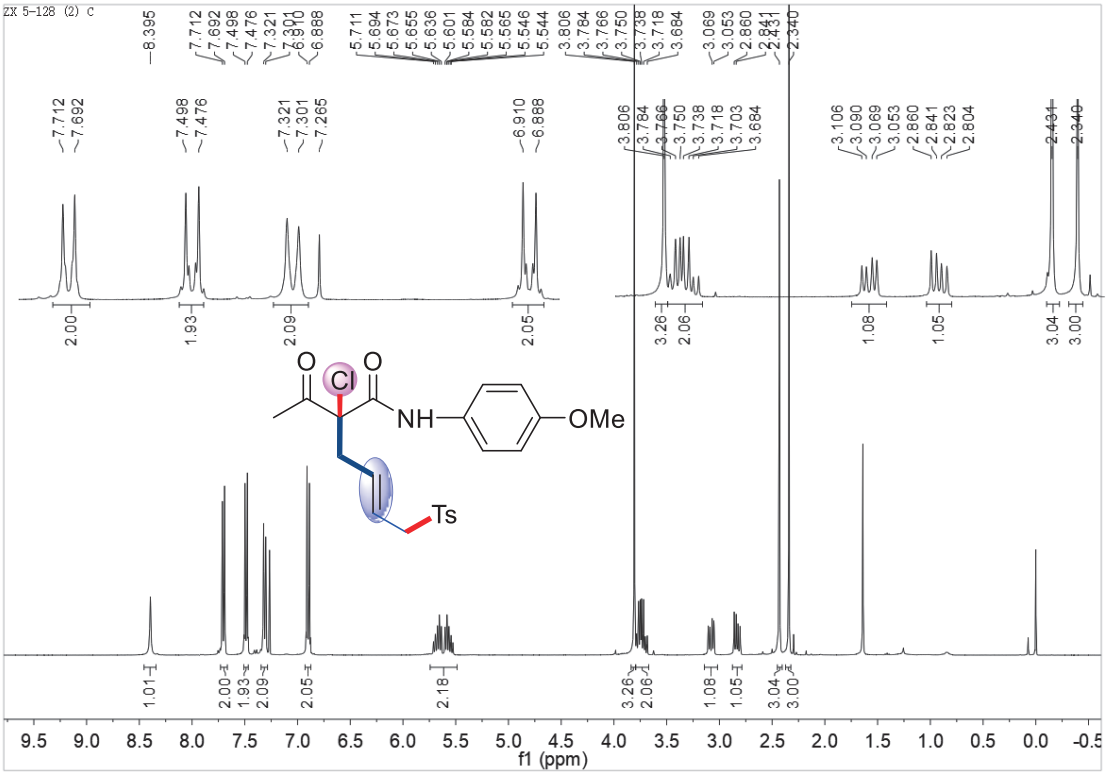
3b1, ^{13}C NMR



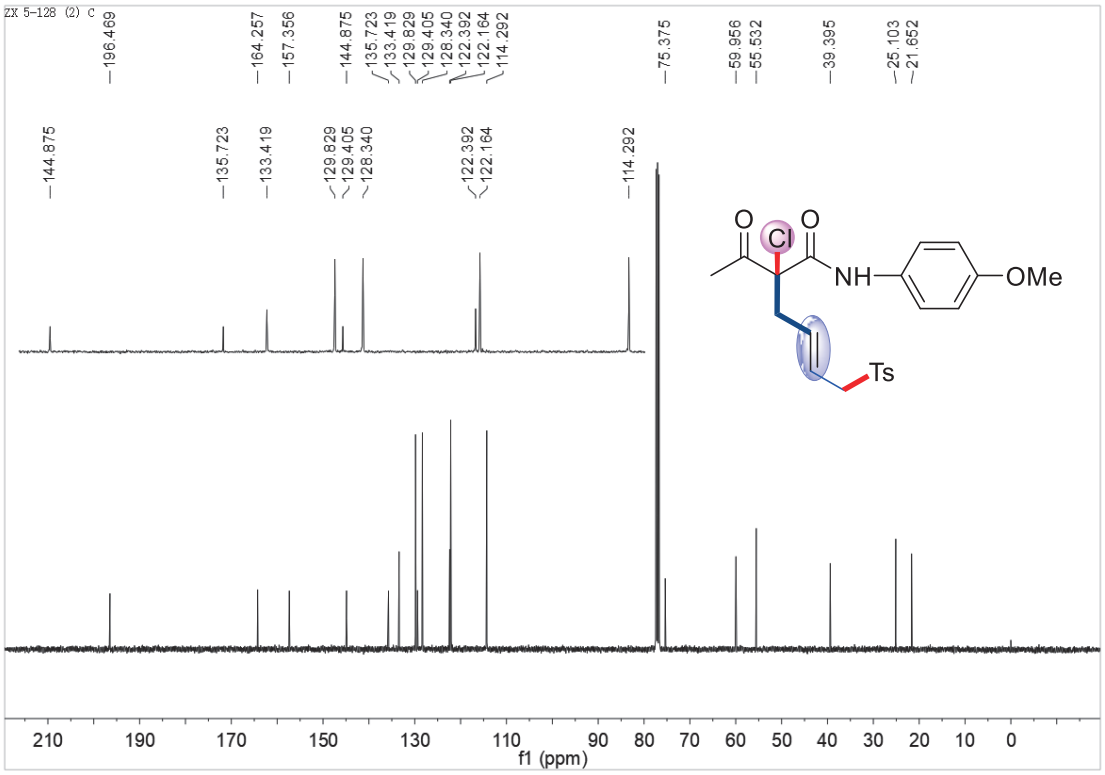
3b1 DEPT 90 and DEPT 135



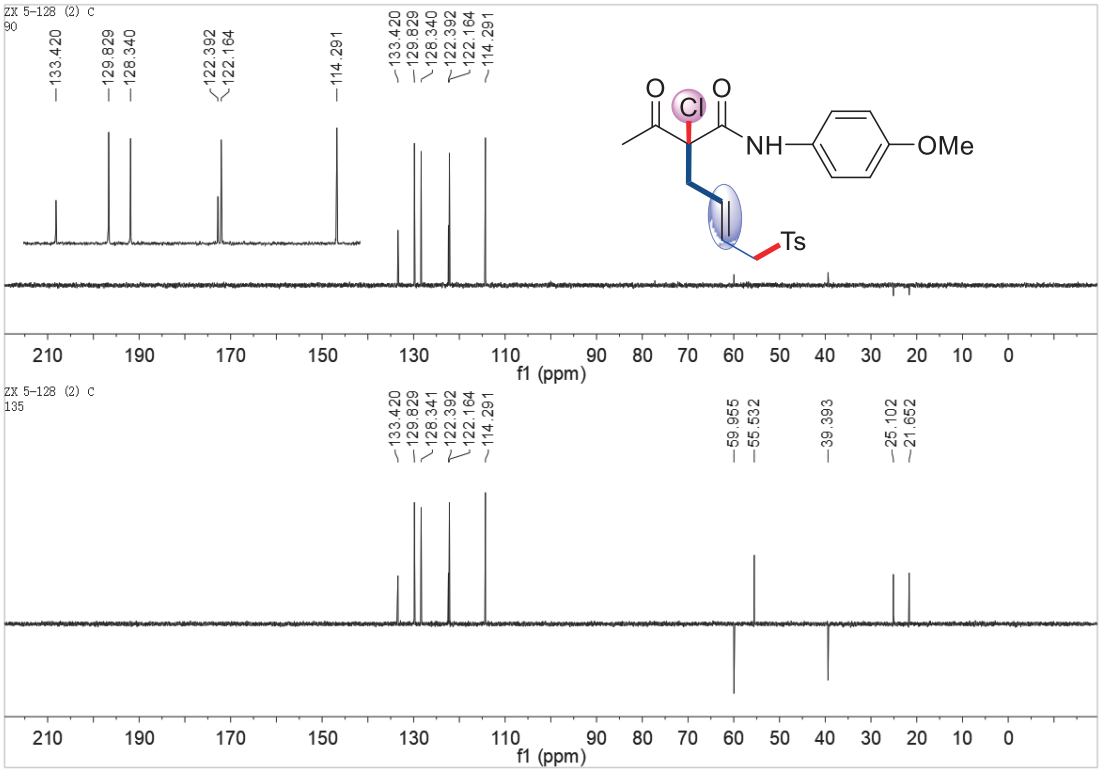
3b2, ^{1}H NMR



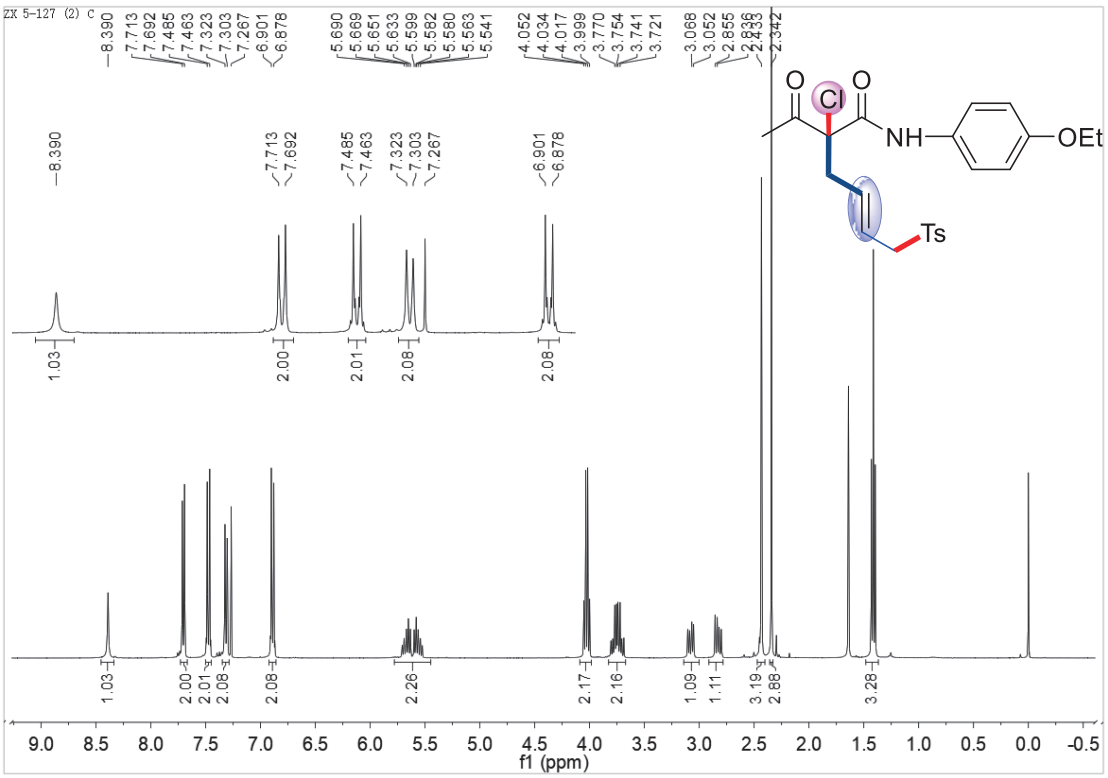
3b2, ^{13}C NMR



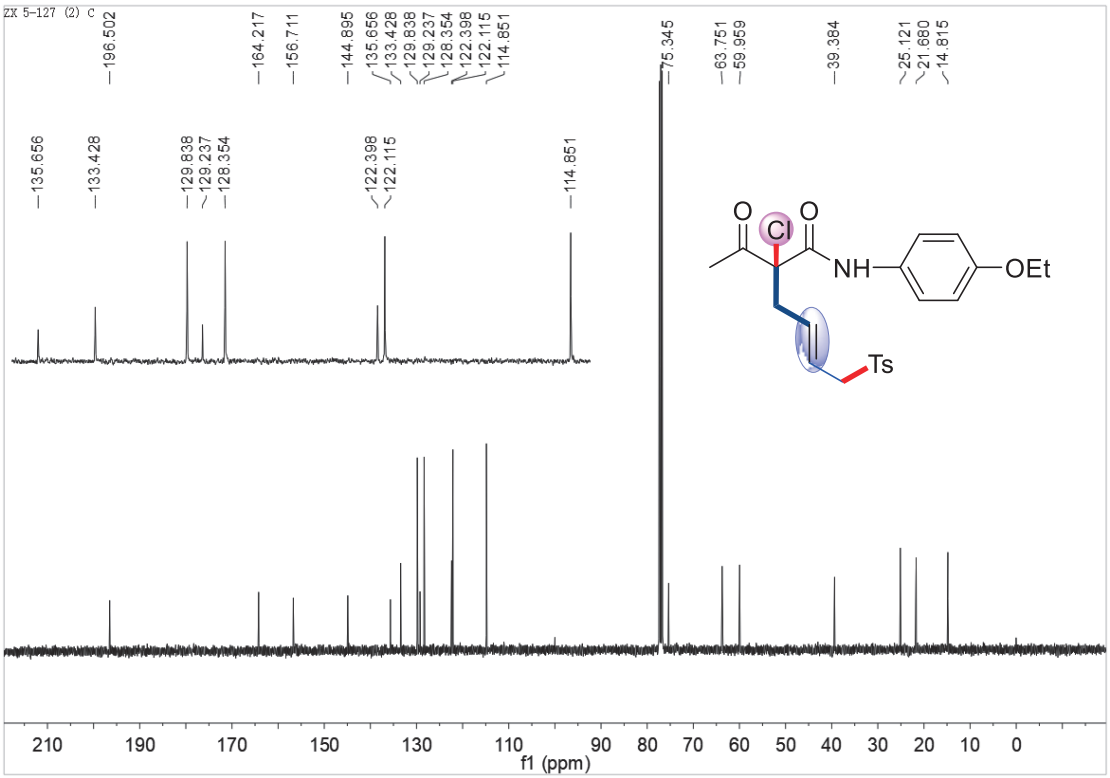
3b2 DEPT 90 and DEPT 135



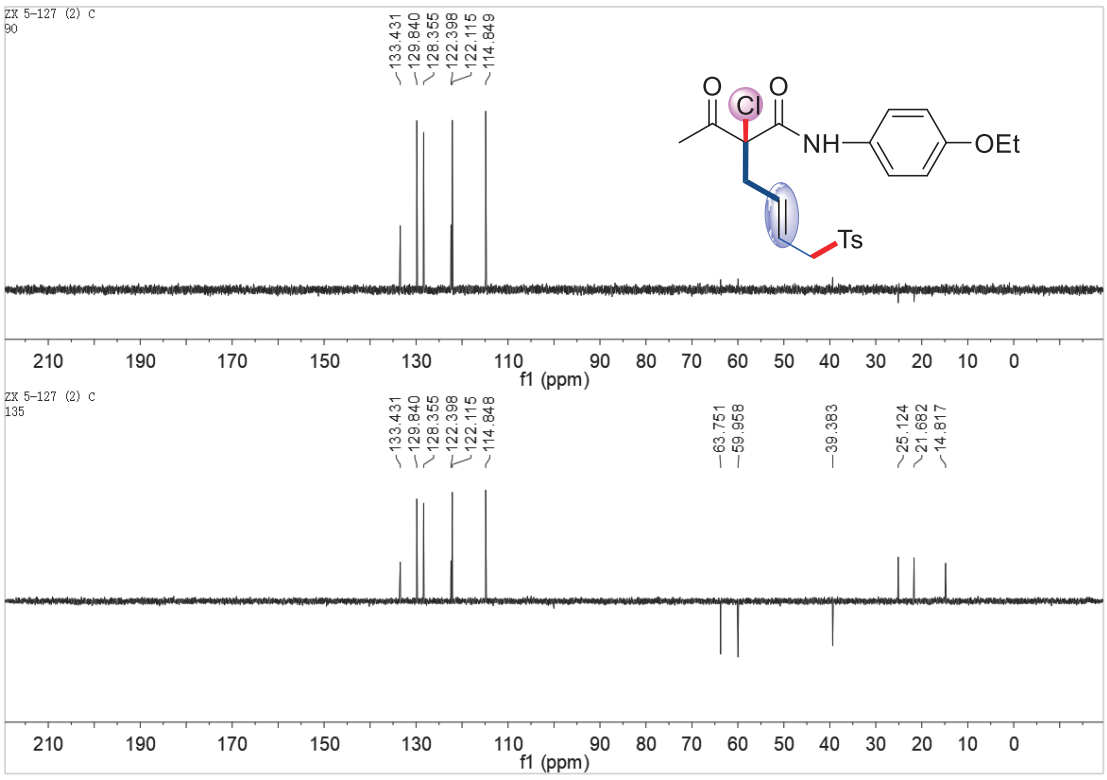
3b3, ^{1}H NMR



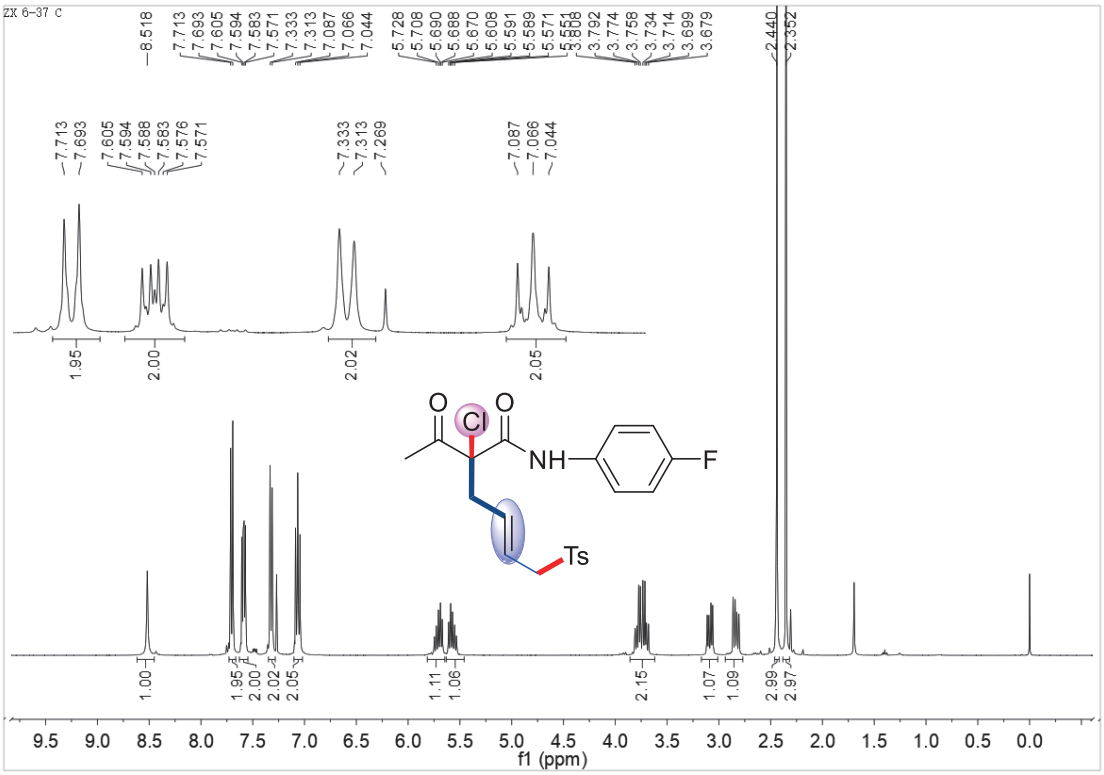
3b3, ^{13}C NMR



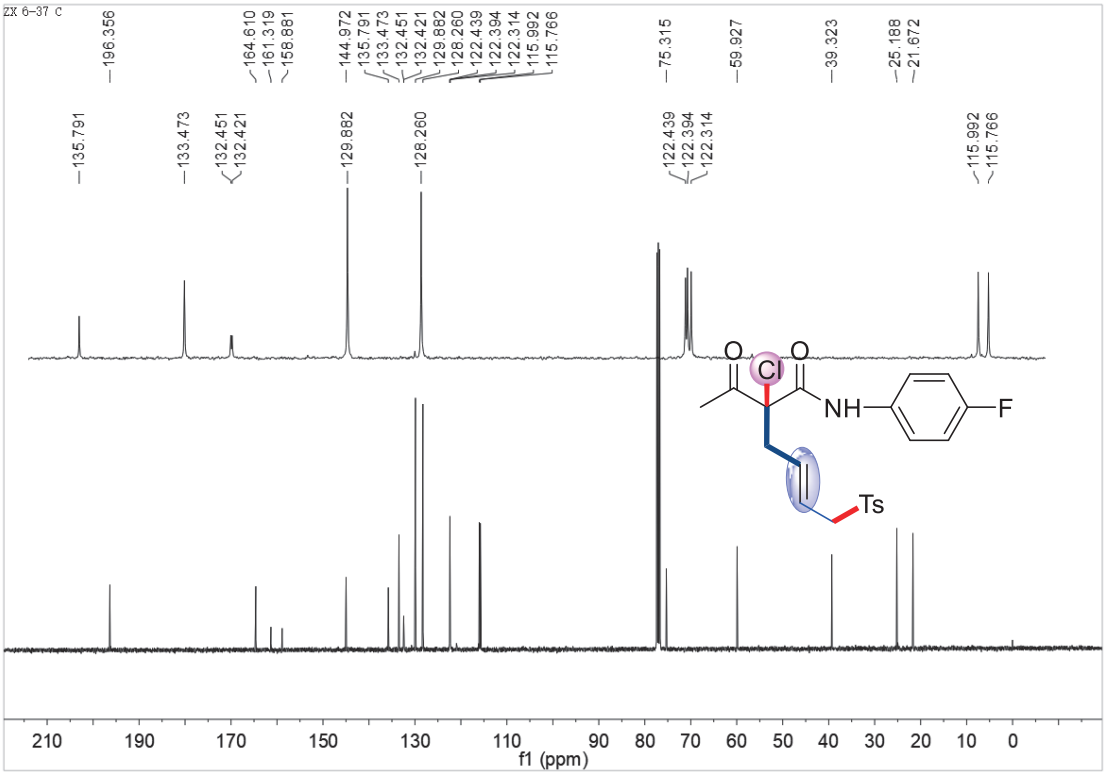
3b3 DEPT 90 and DEPT 135



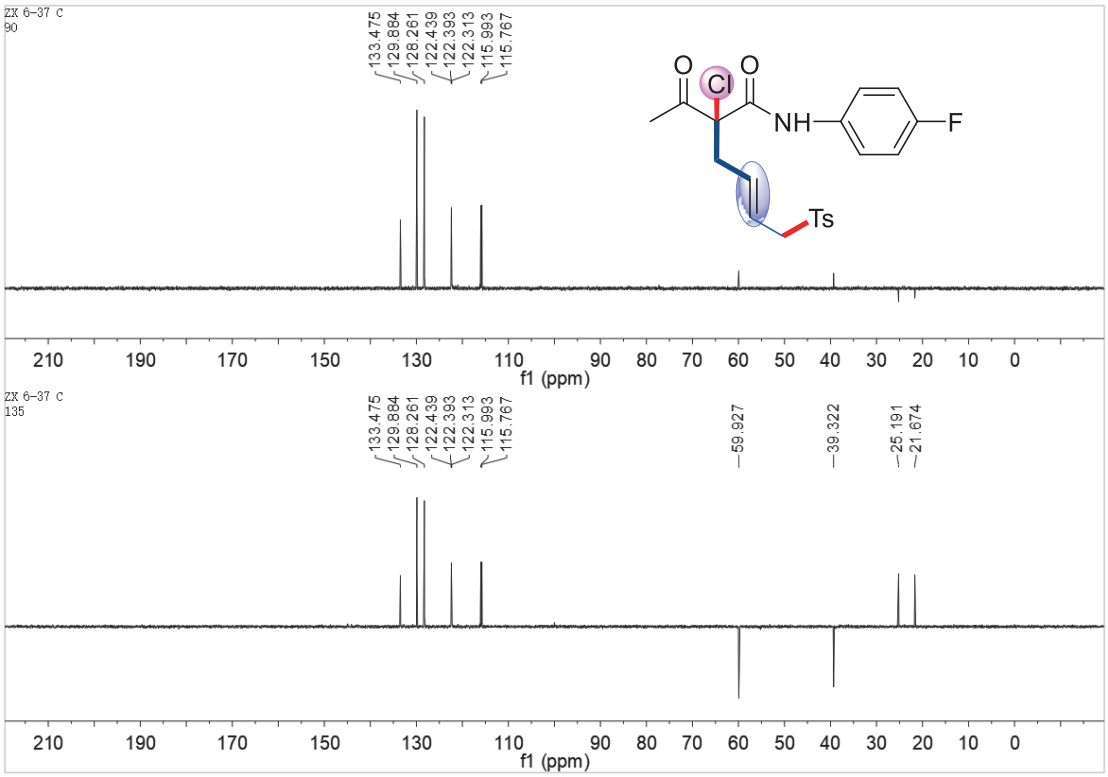
3b4, ^{1}H NMR



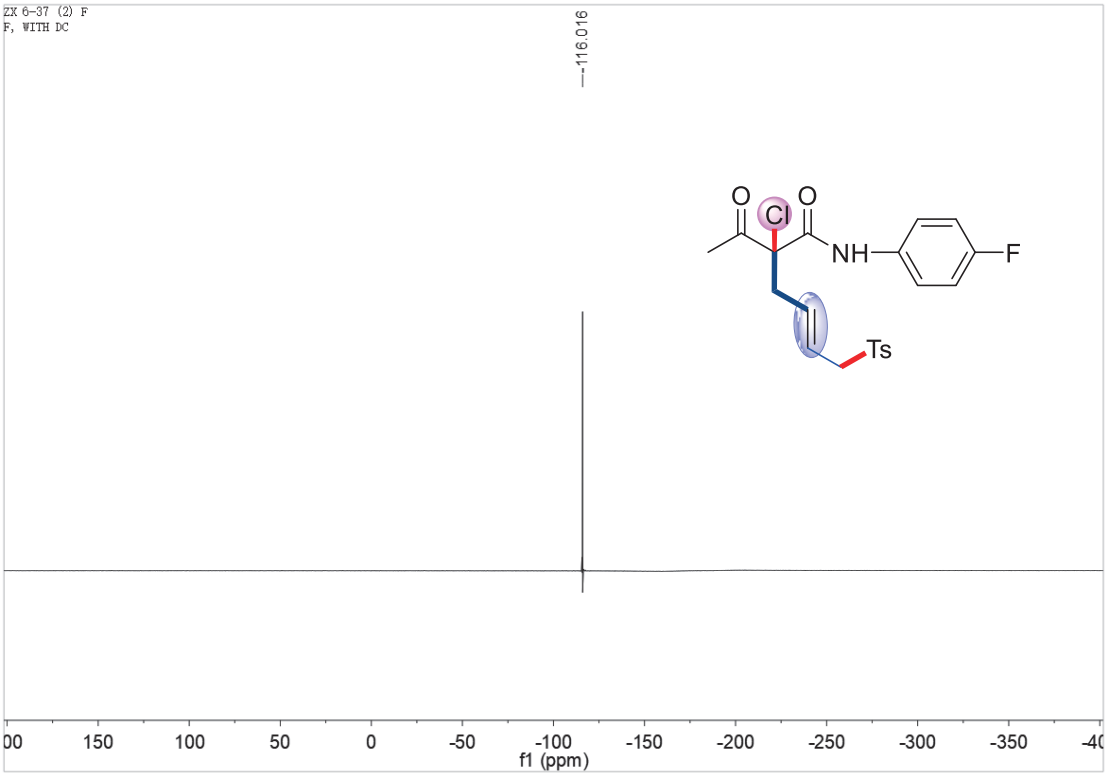
3b4, ^{13}C NMR



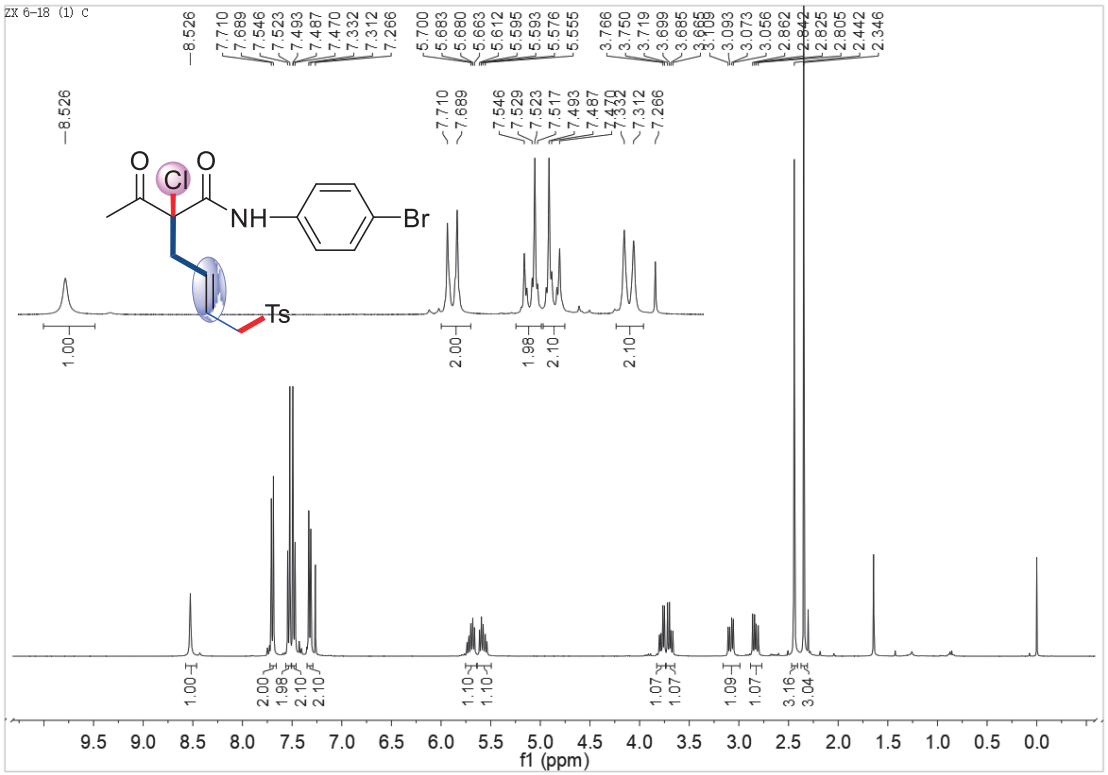
3b4 DEPT 90 and DEPT 135



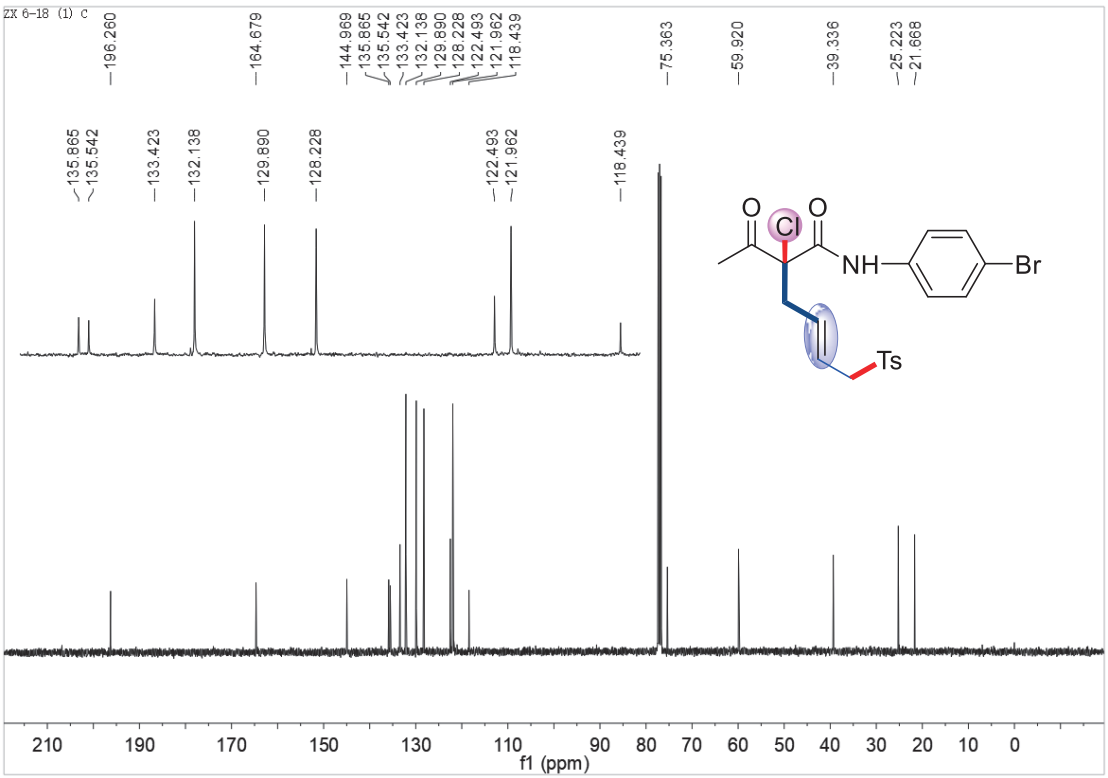
3b4 ^{19}F NMR



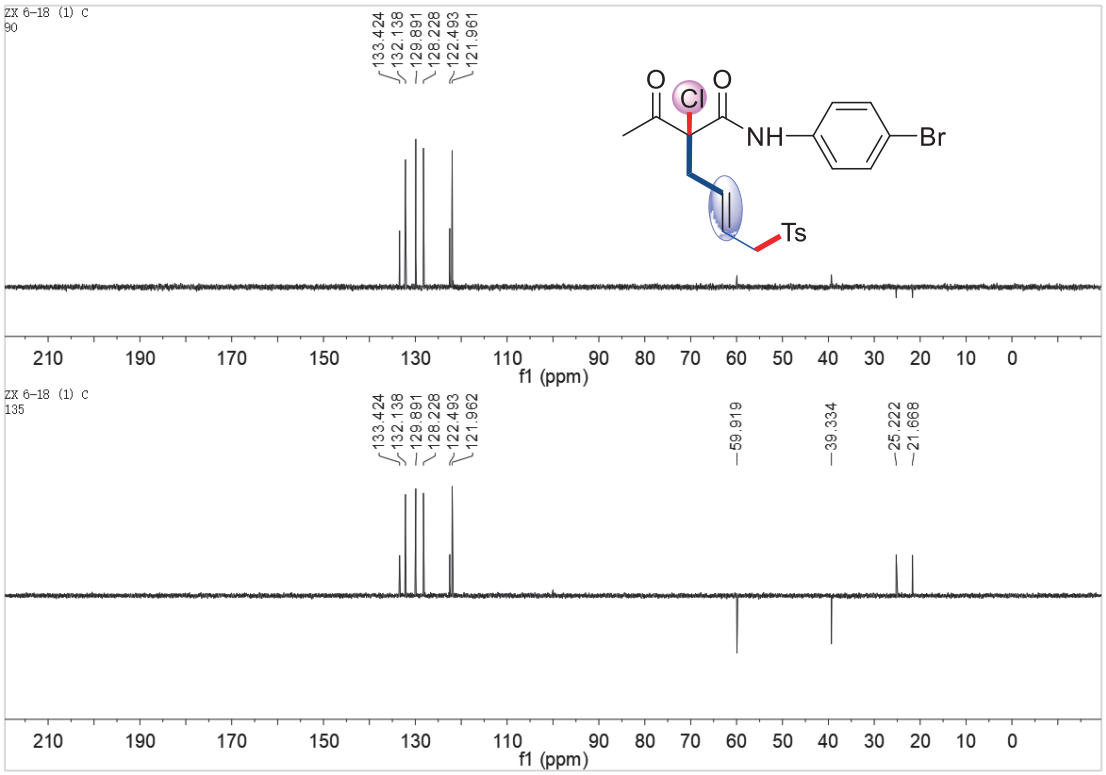
3b5, ^{1}H NMR



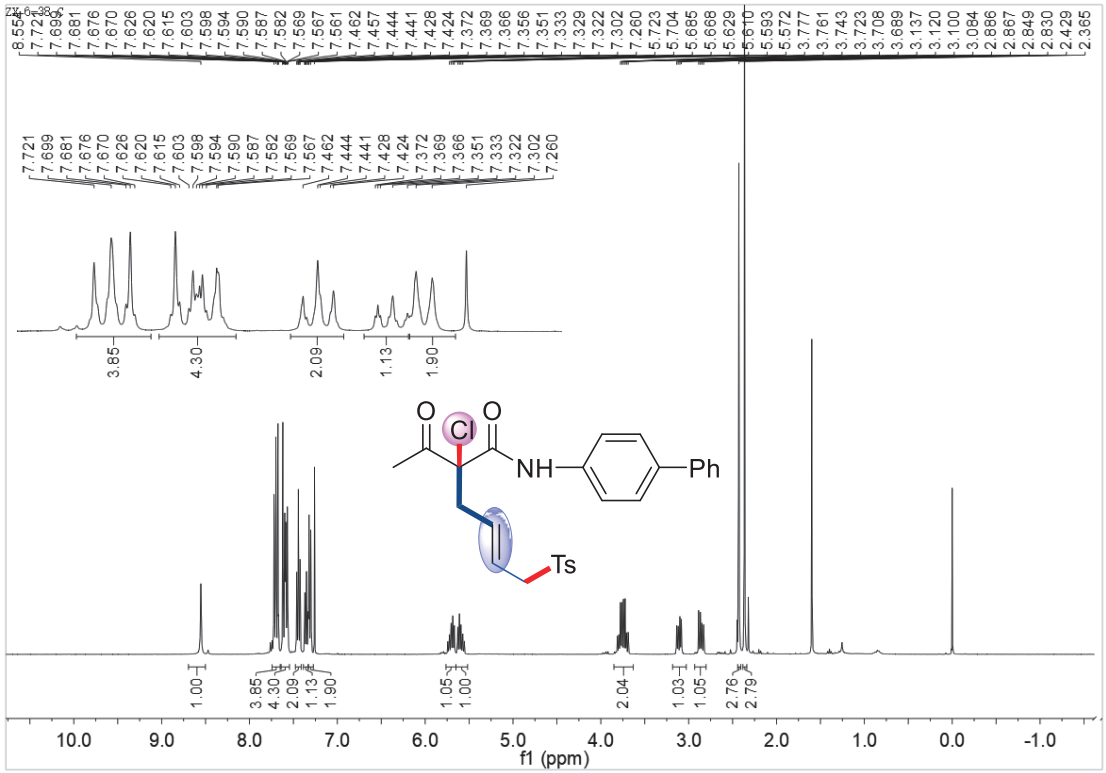
3b5, ^{13}C NMR



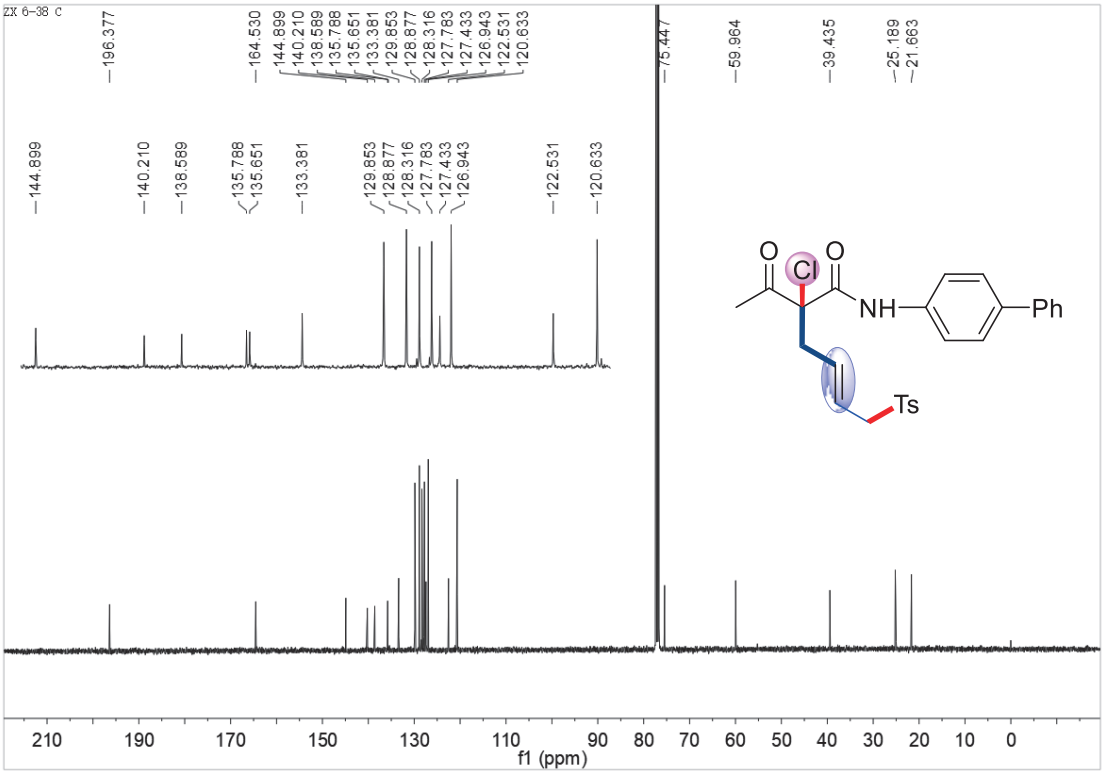
3b5 DEPT 90 and DEPT 135



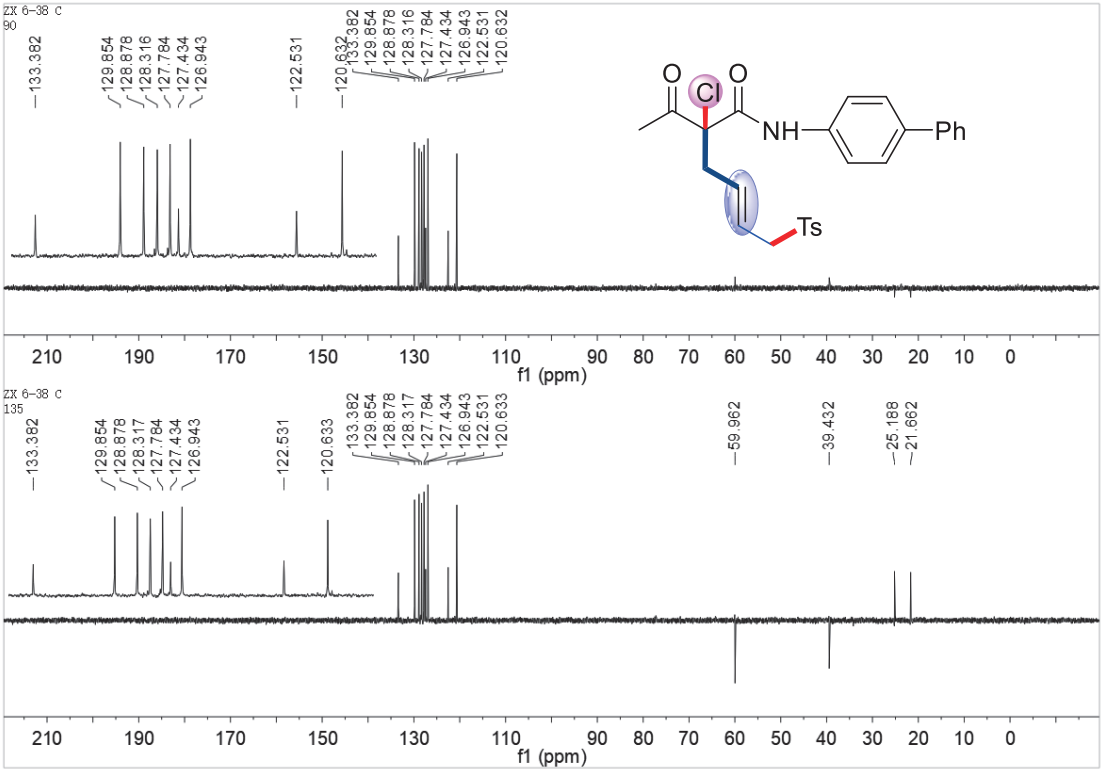
3b6, ^{1}H NMR



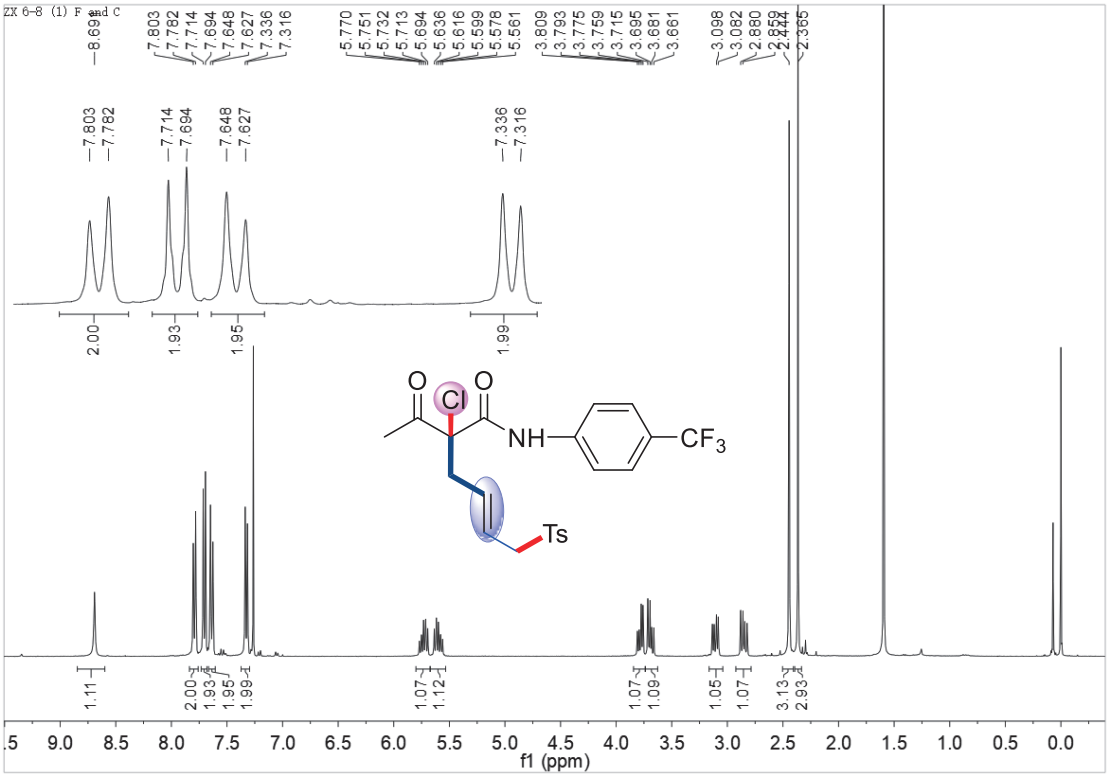
3b6, ^{13}C NMR



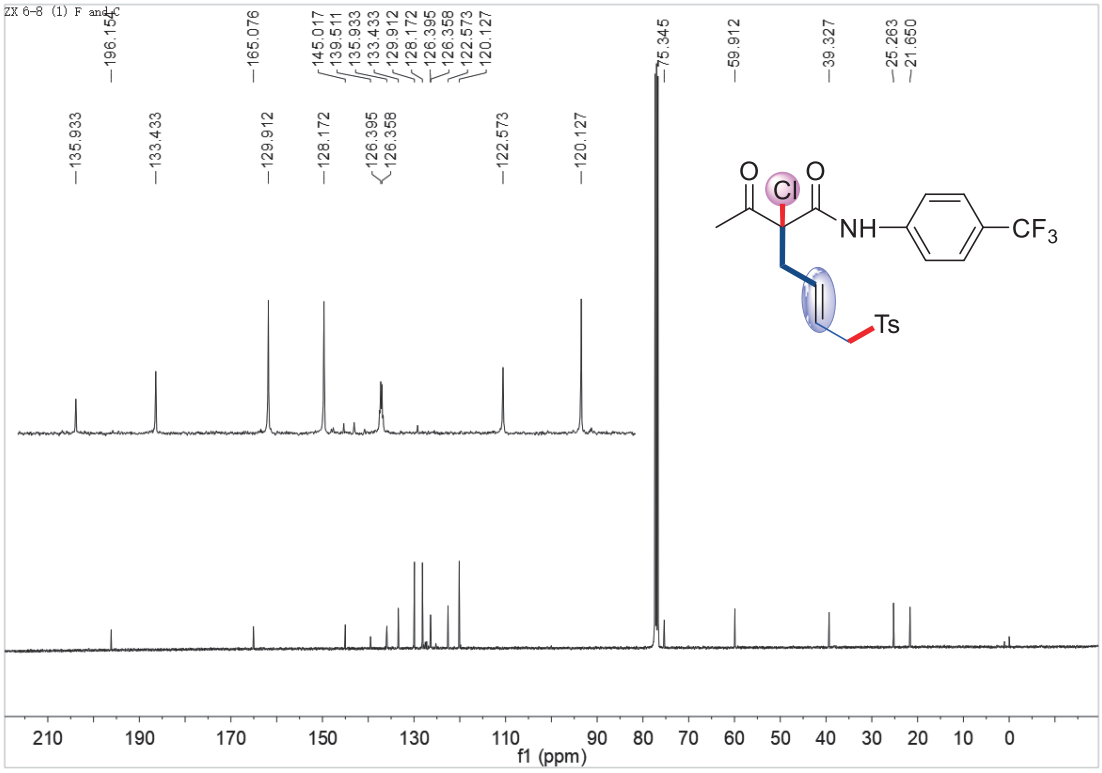
3b6 DEPT 90 and DEPT 135



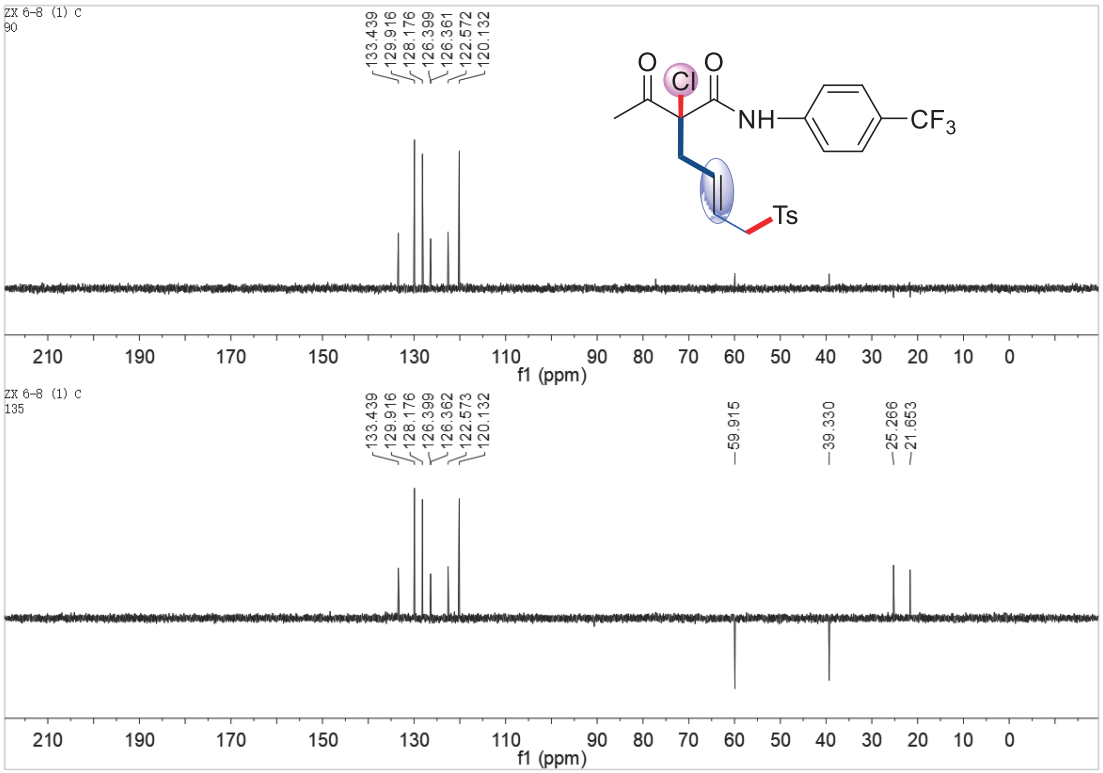
3b7, ^{1}H NMR



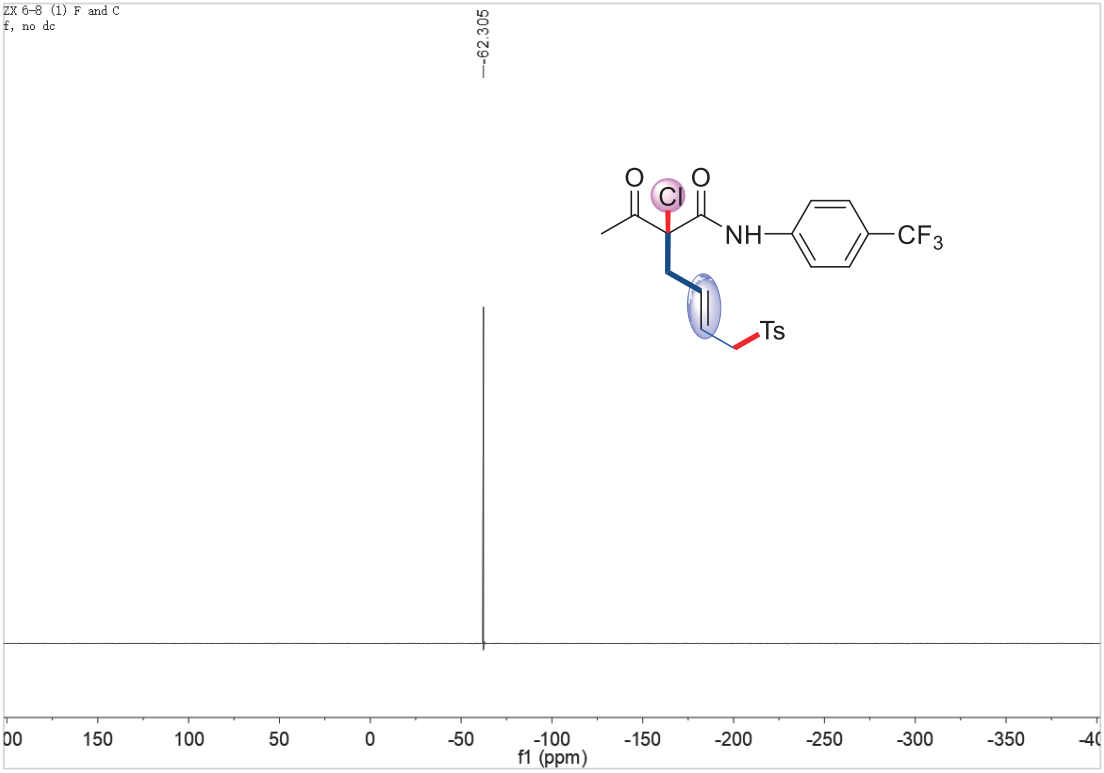
3b7, ^{13}C NMR



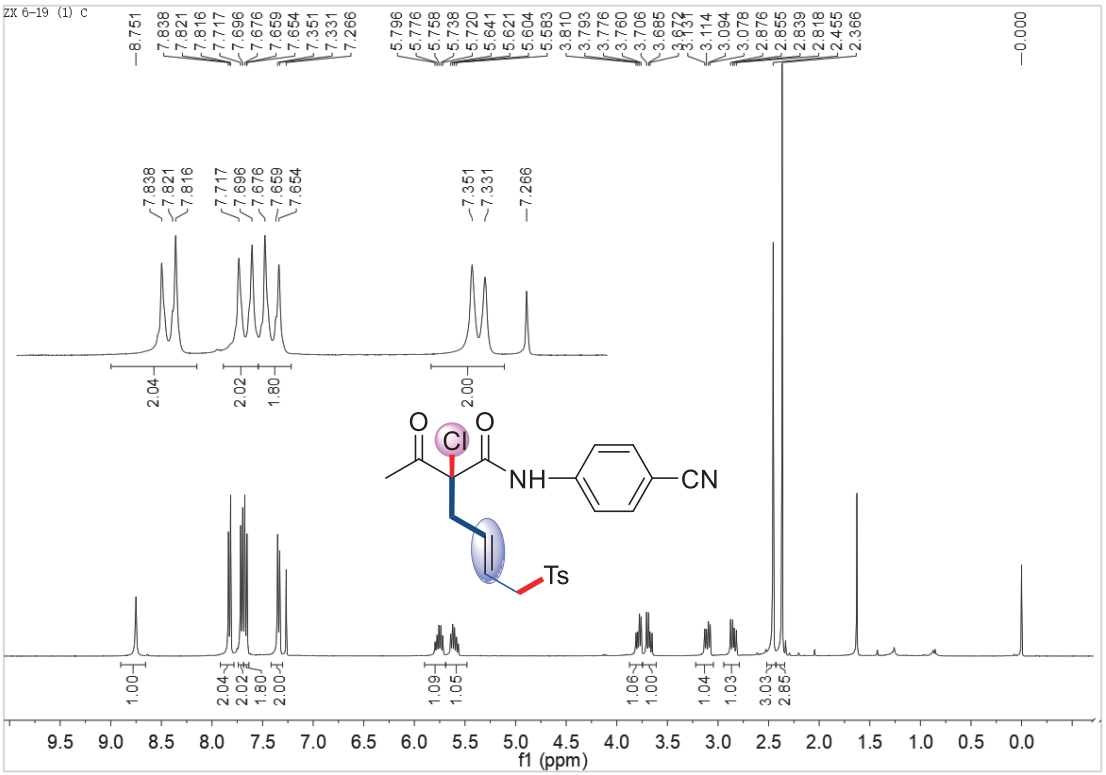
3b7 DEPT 90 and DEPT 135



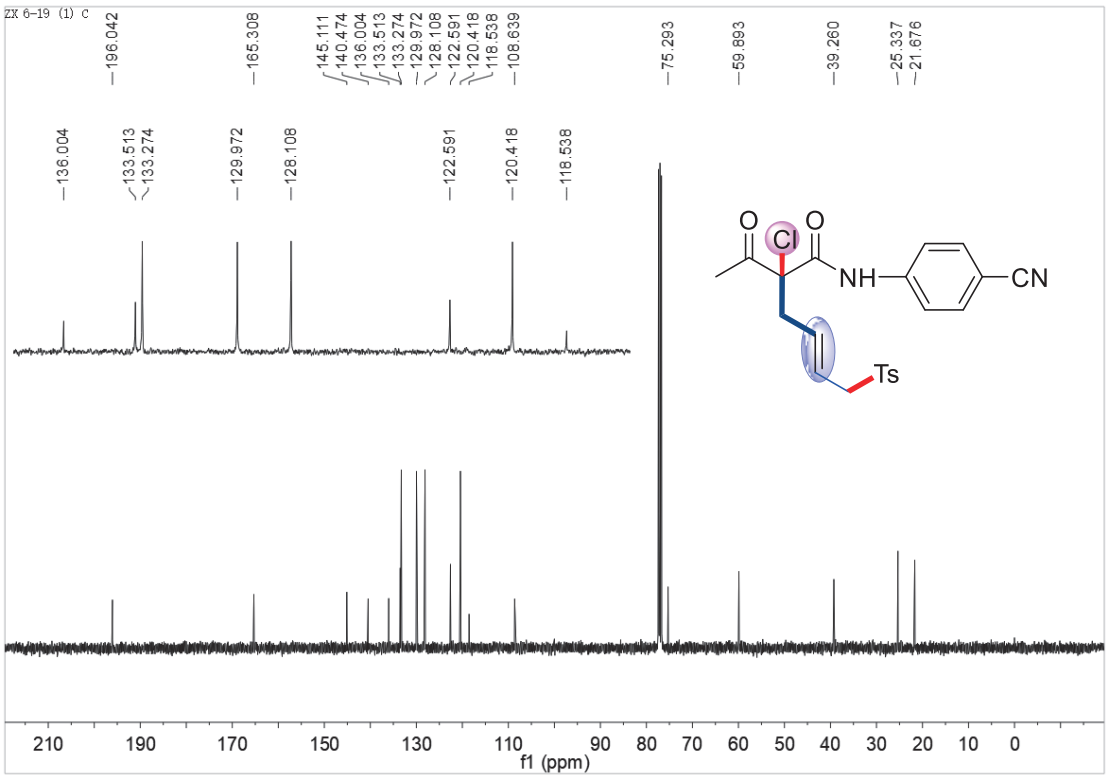
3b7 ^{19}F NMR



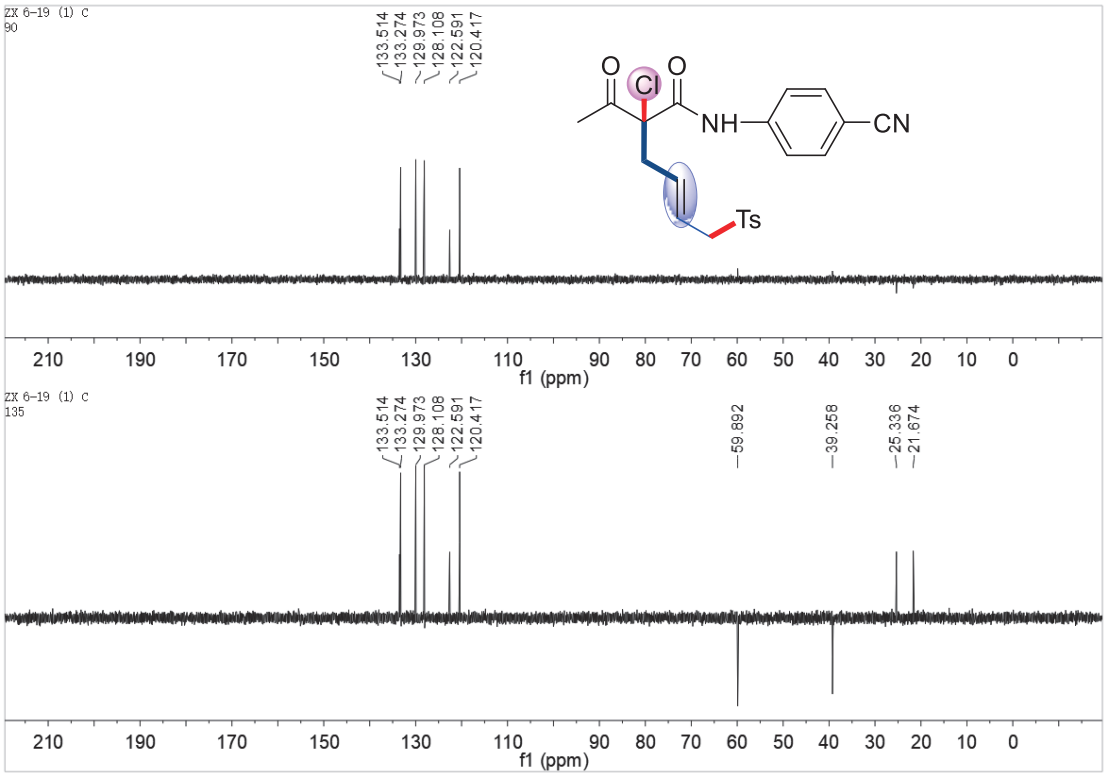
3b8, ^{1}H NMR



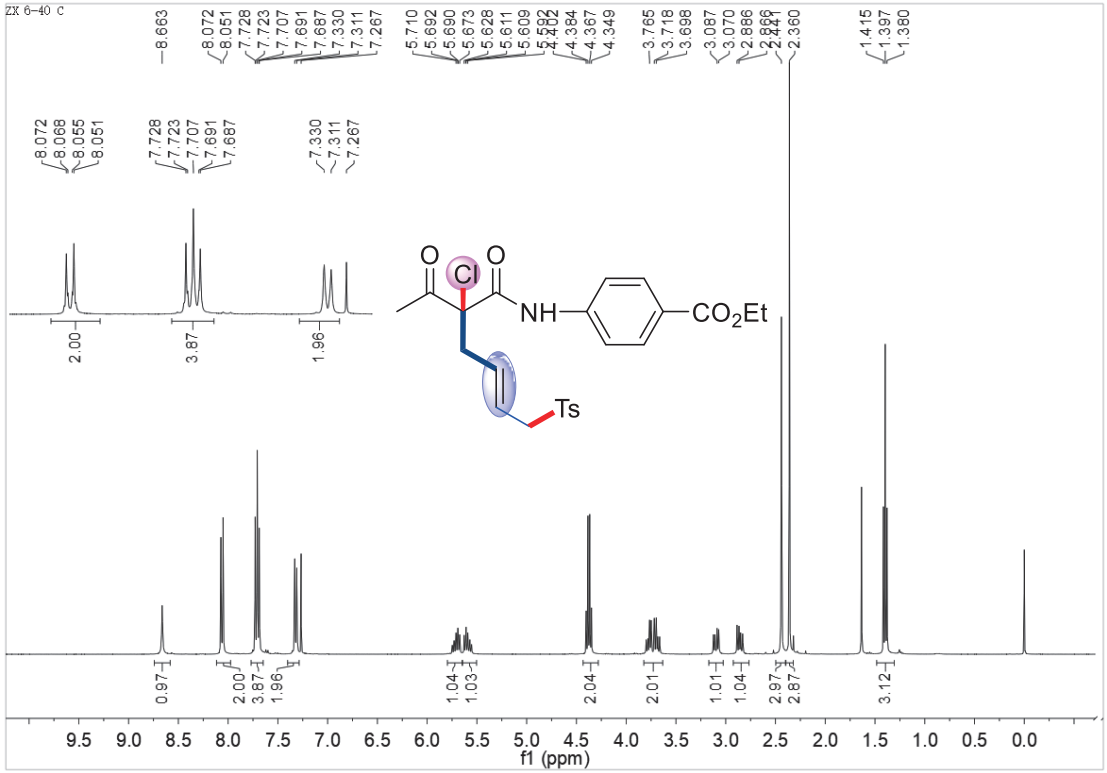
3b8, ^{13}C NMR



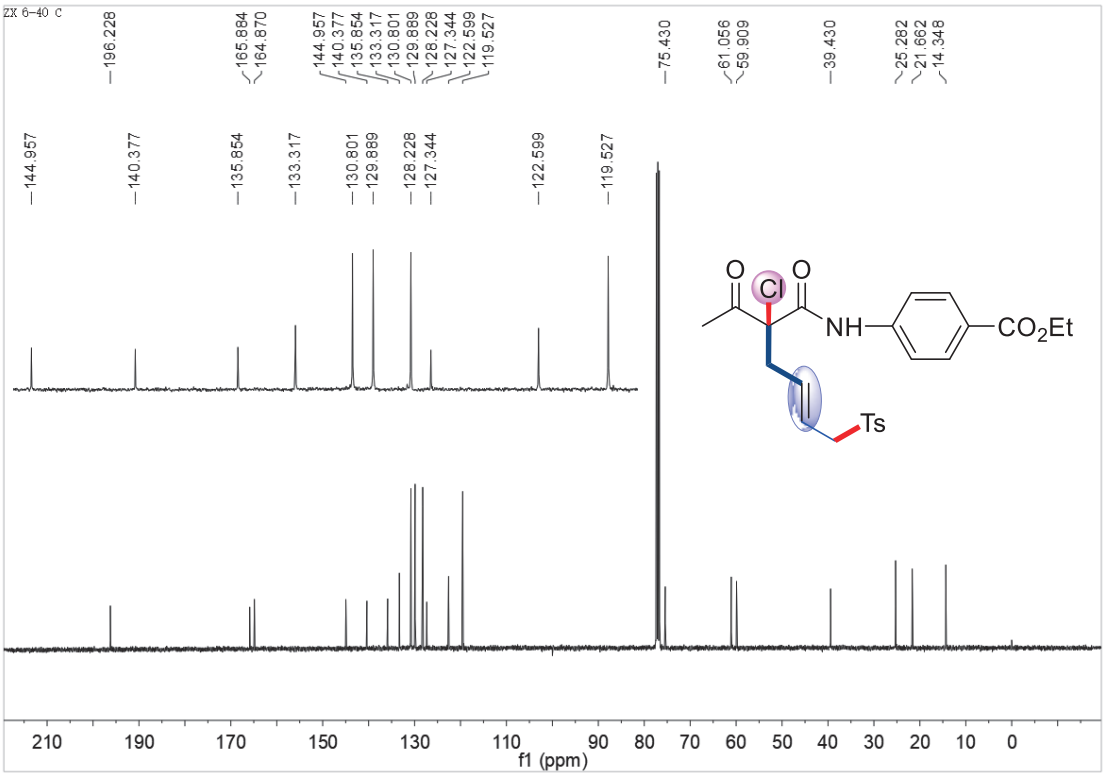
3b8 DEPT 90 and DEPT 135



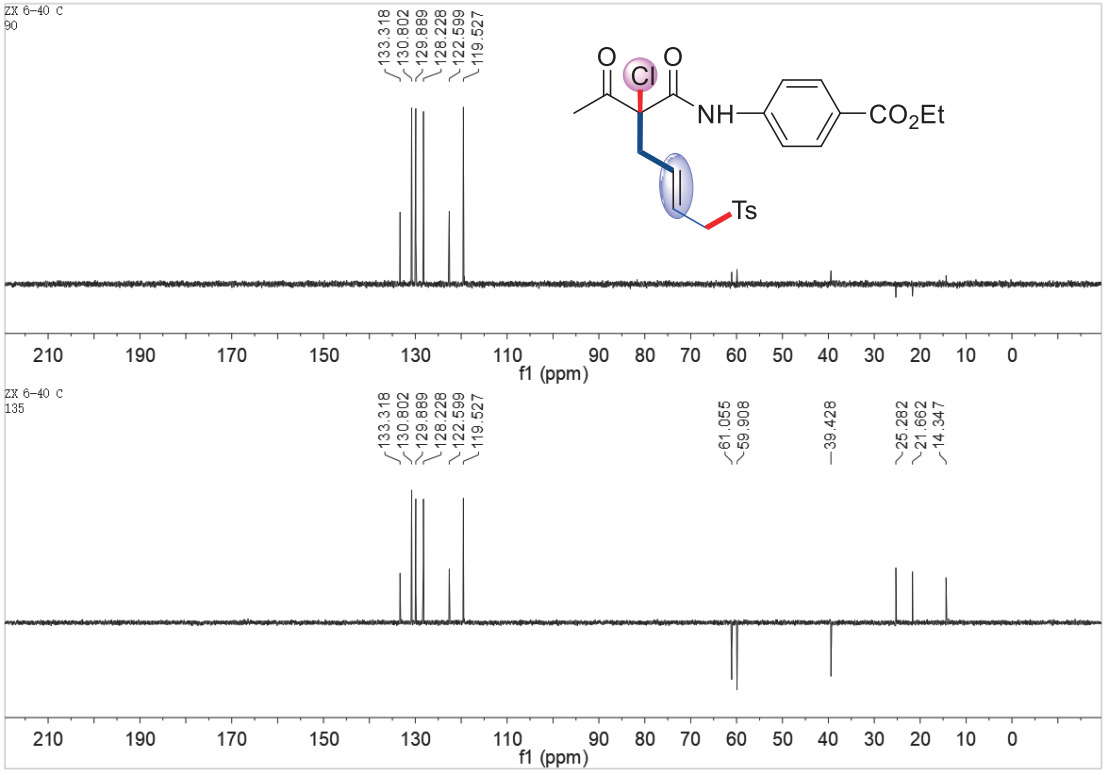
3b9, ^{1}H NMR



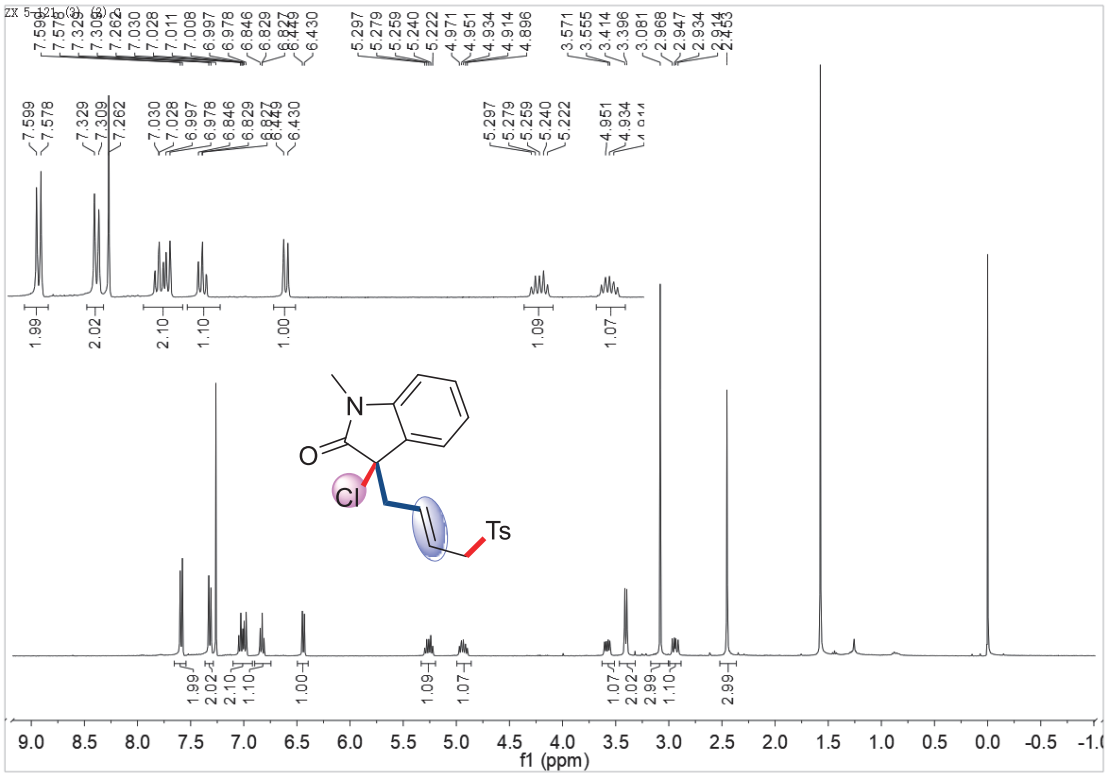
3b9, ^{13}C NMR



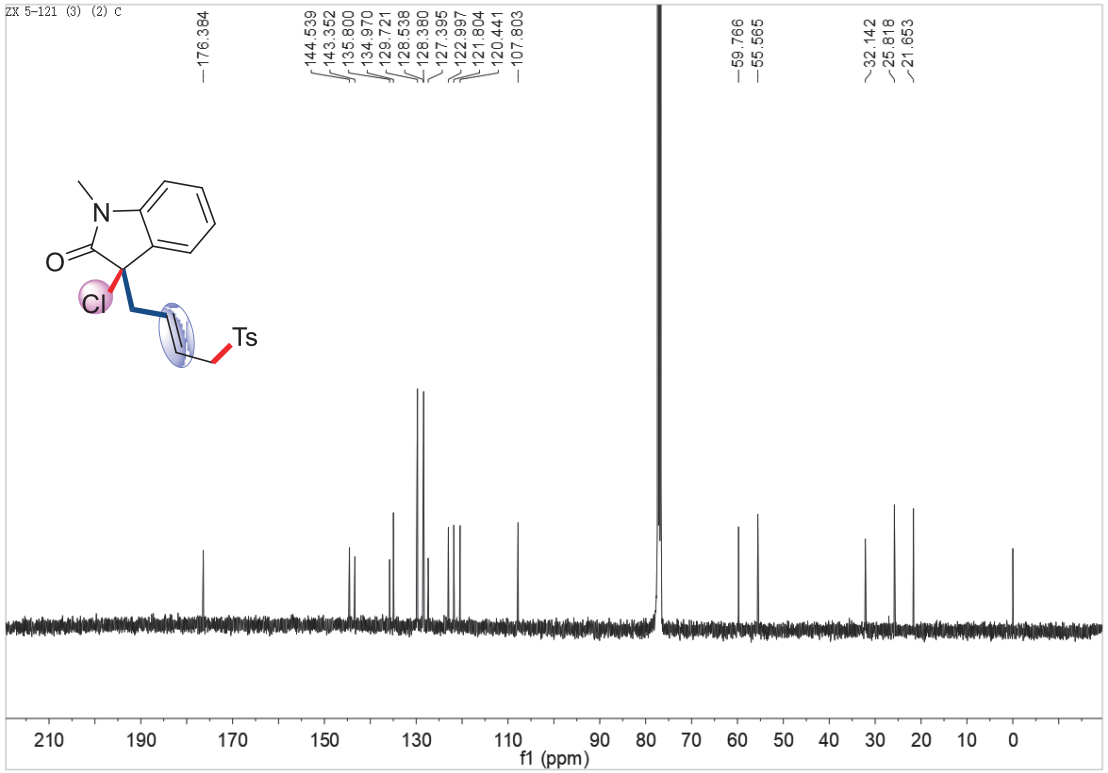
3b9 DEPT 90 and DEPT 135



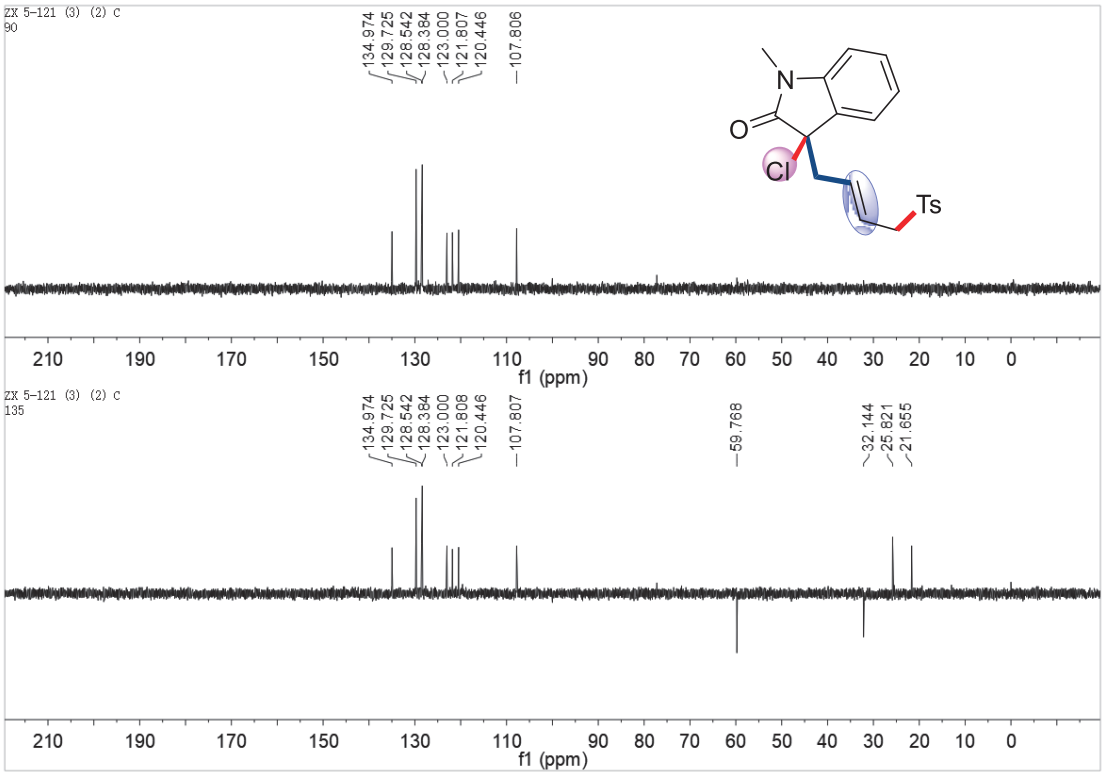
3c, ^{1}H NMR



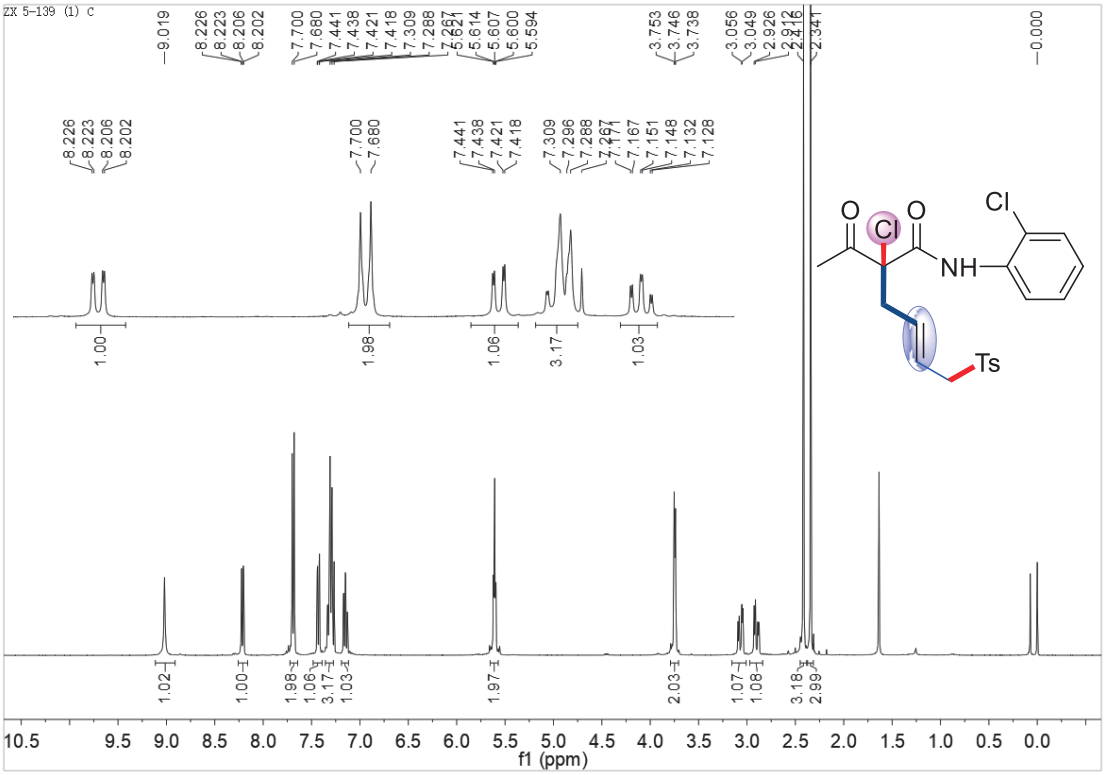
3c, ^{13}C NMR



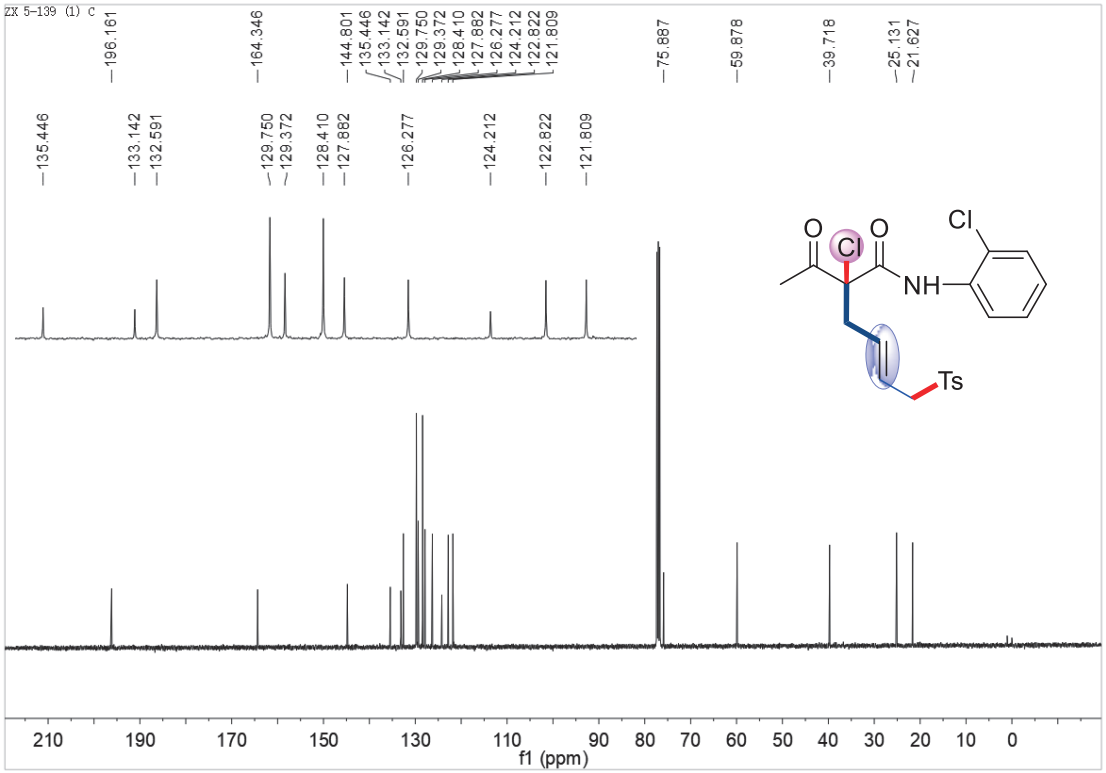
3c DEPT 90 and DEPT 135



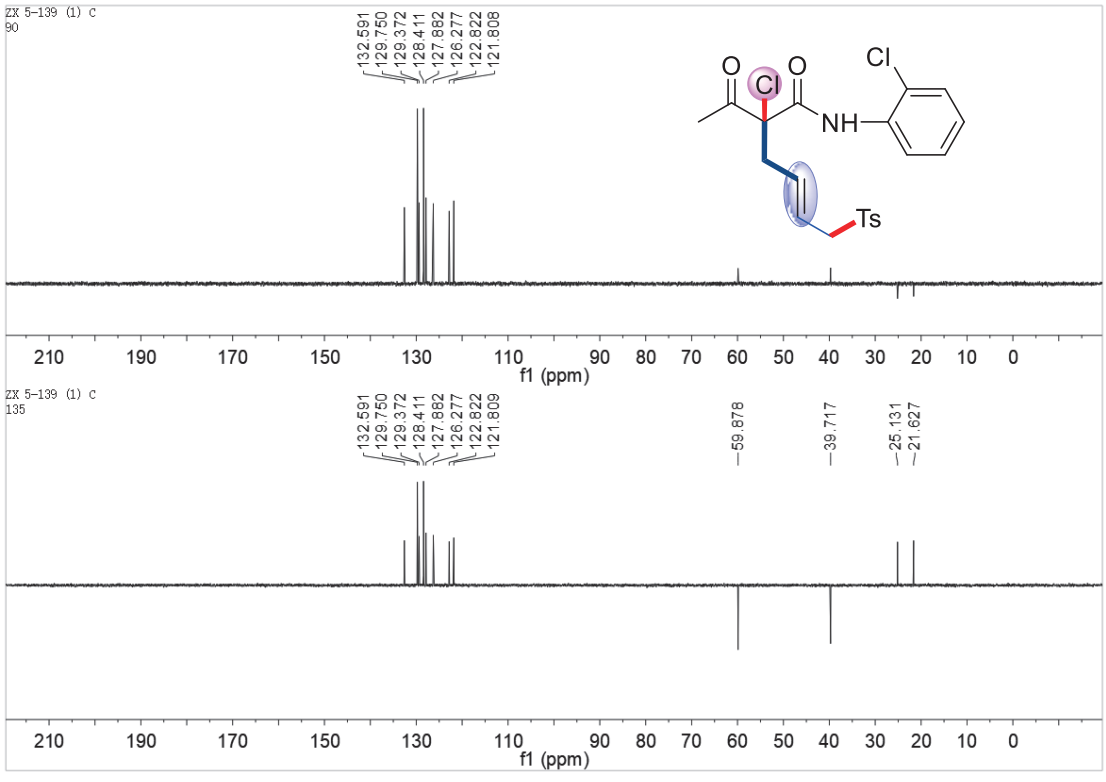
3d1, ^{1}H NMR



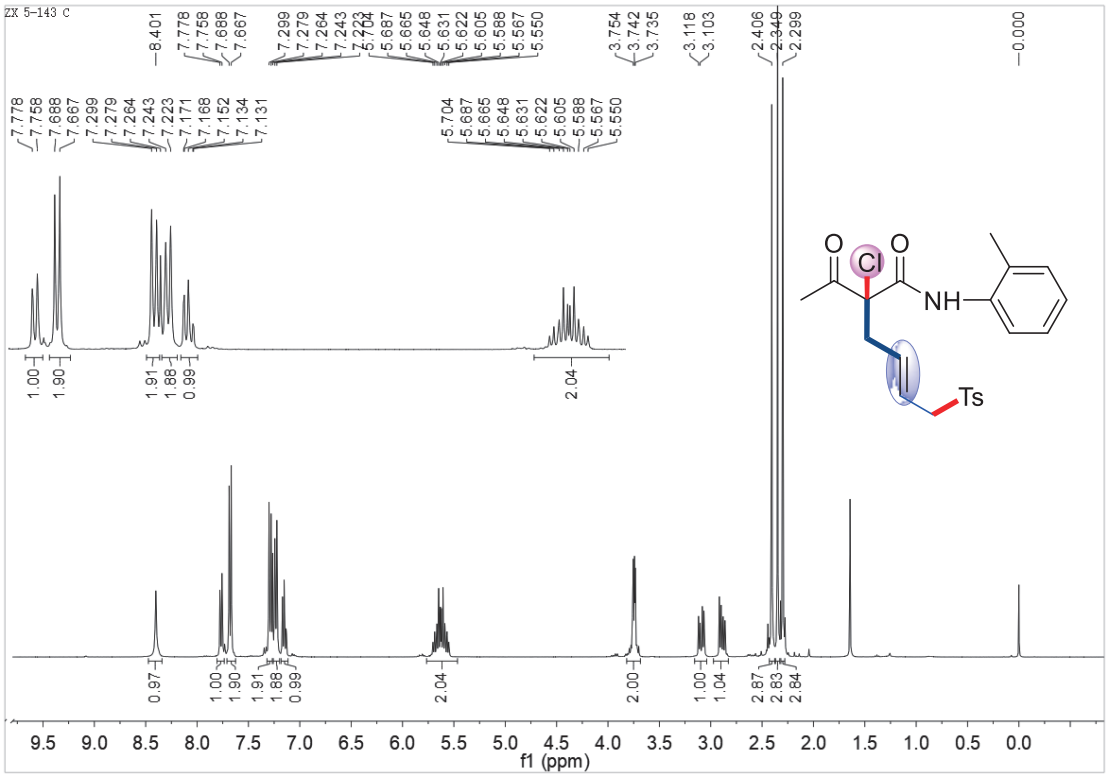
3d1, ^{13}C NMR



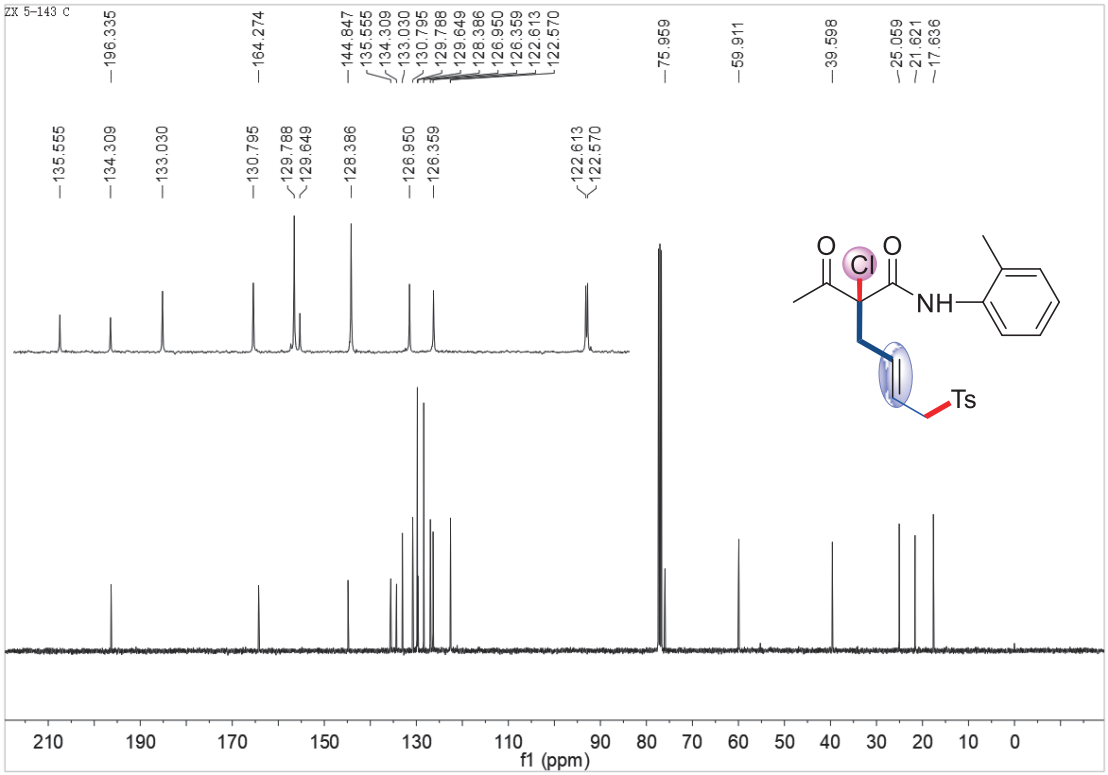
3d1 DEPT 90 and DEPT 135



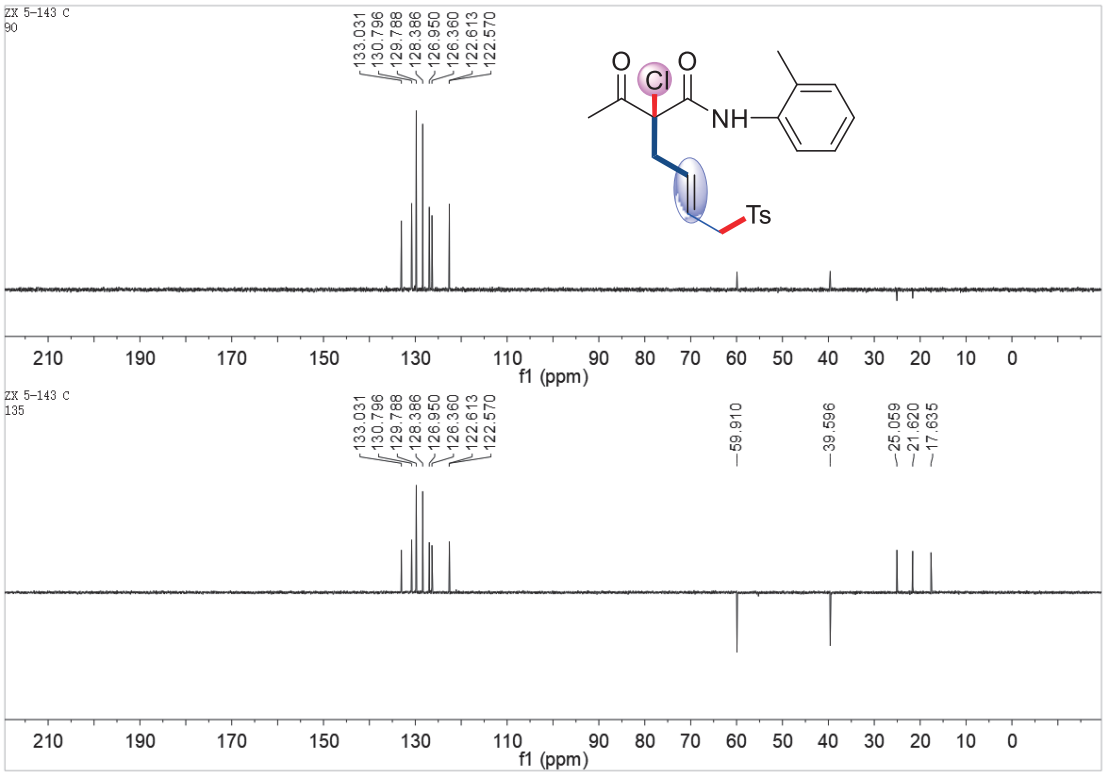
3d2, ^{1}H NMR



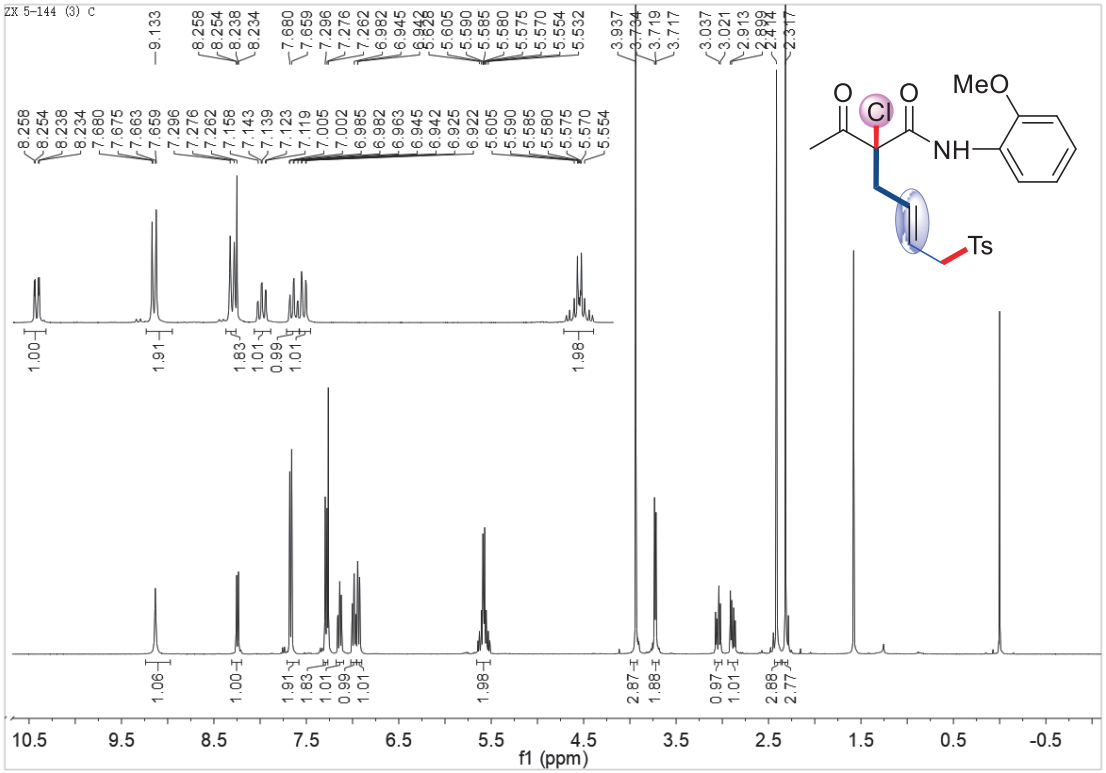
3d2, ^{13}C NMR



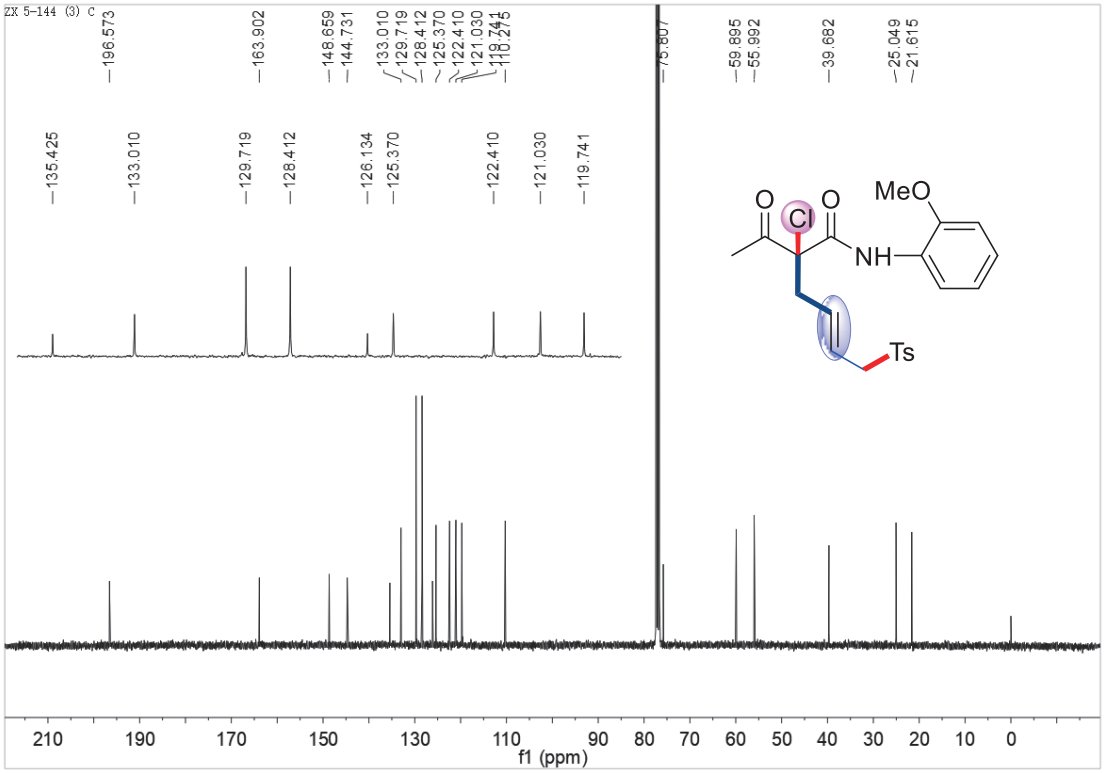
3d2 DEPT 90 and DEPT 135



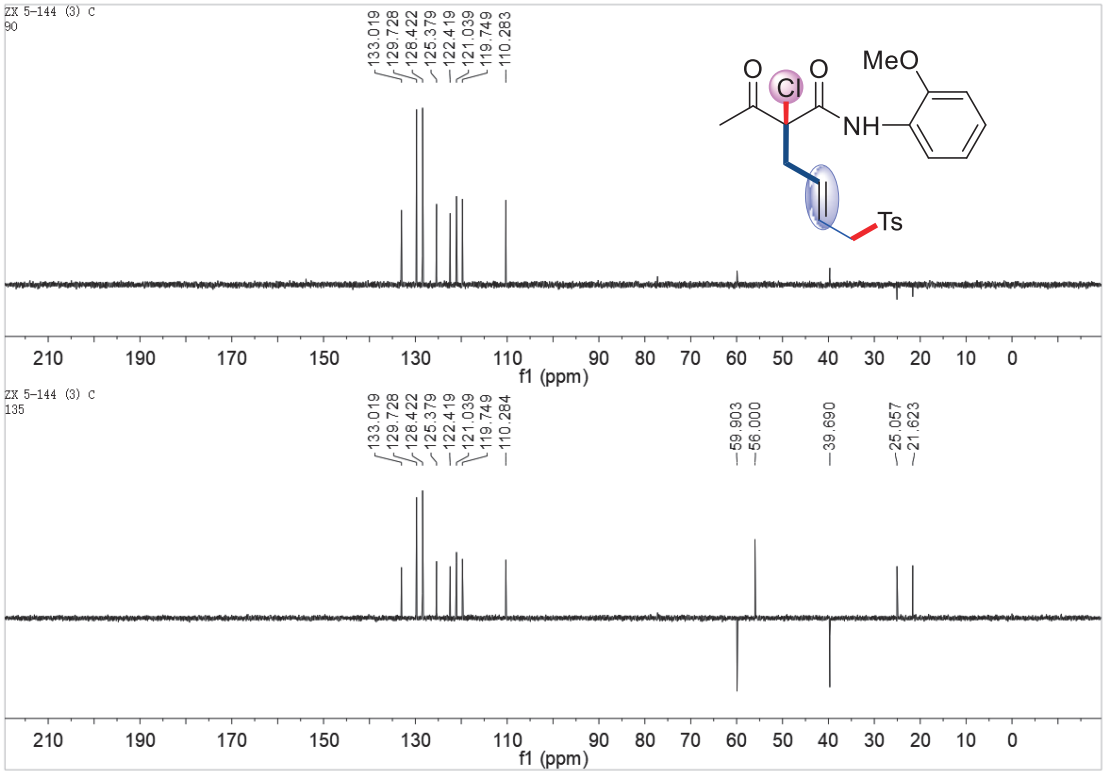
3d3, ^{1}H NMR



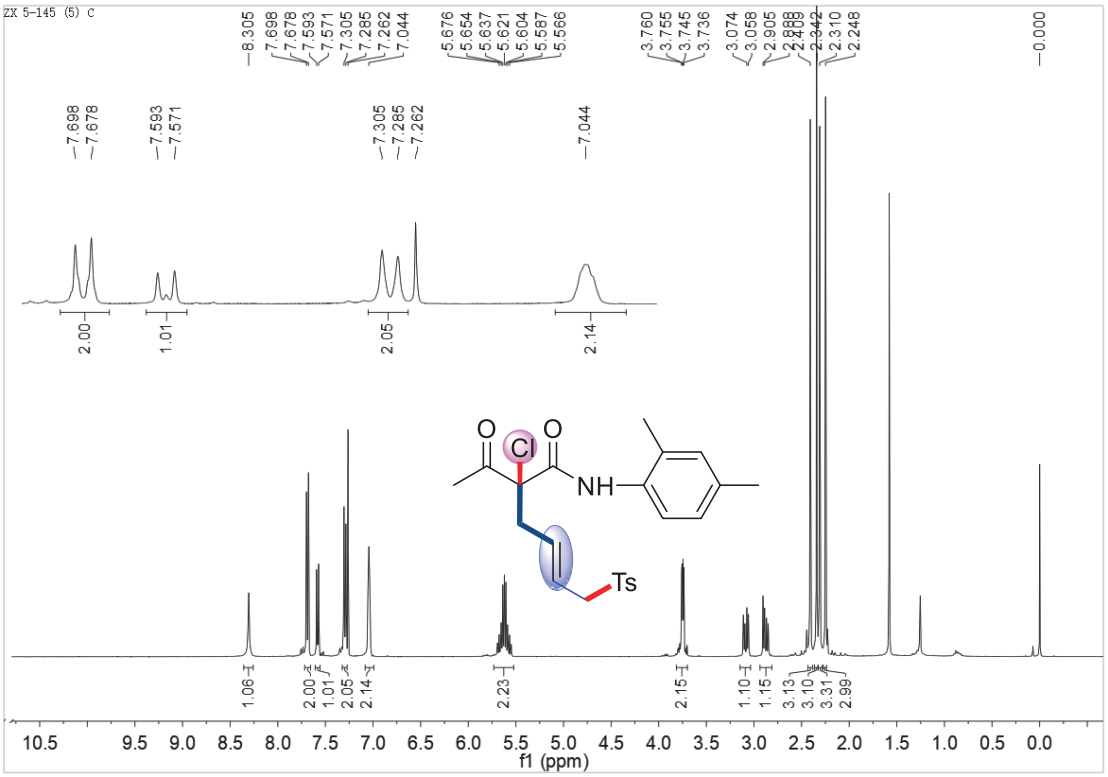
3d3, ^{13}C NMR



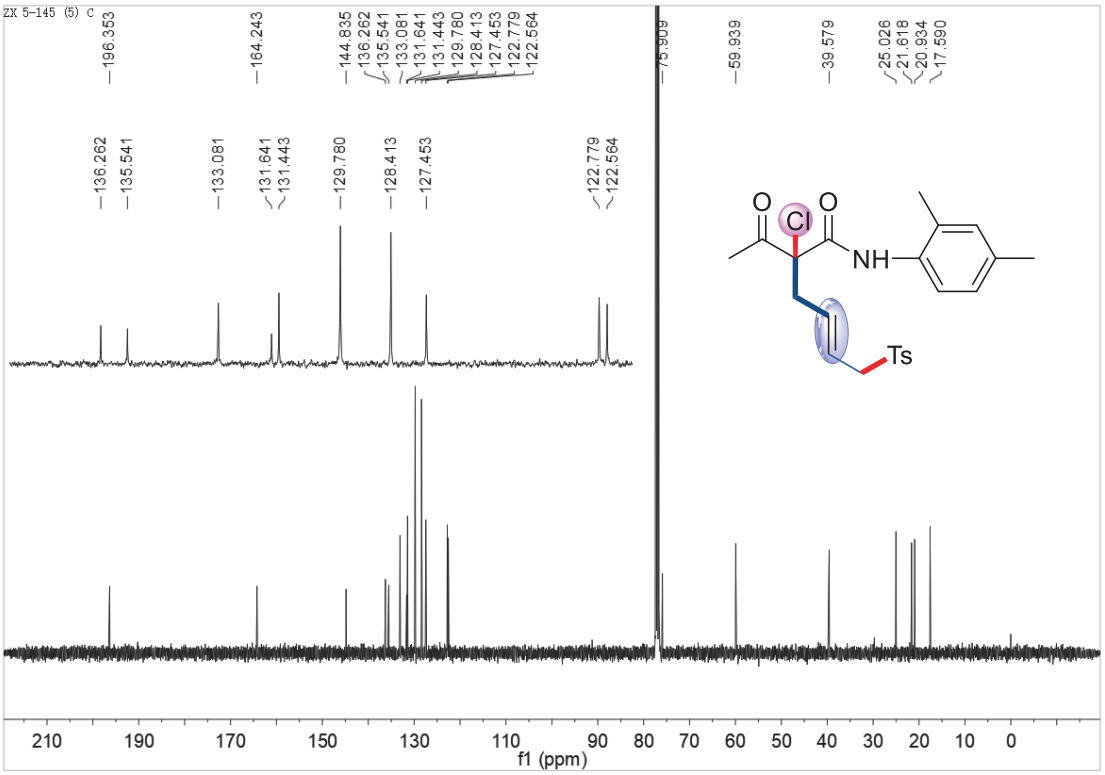
3d3 DEPT 90 and DEPT 135



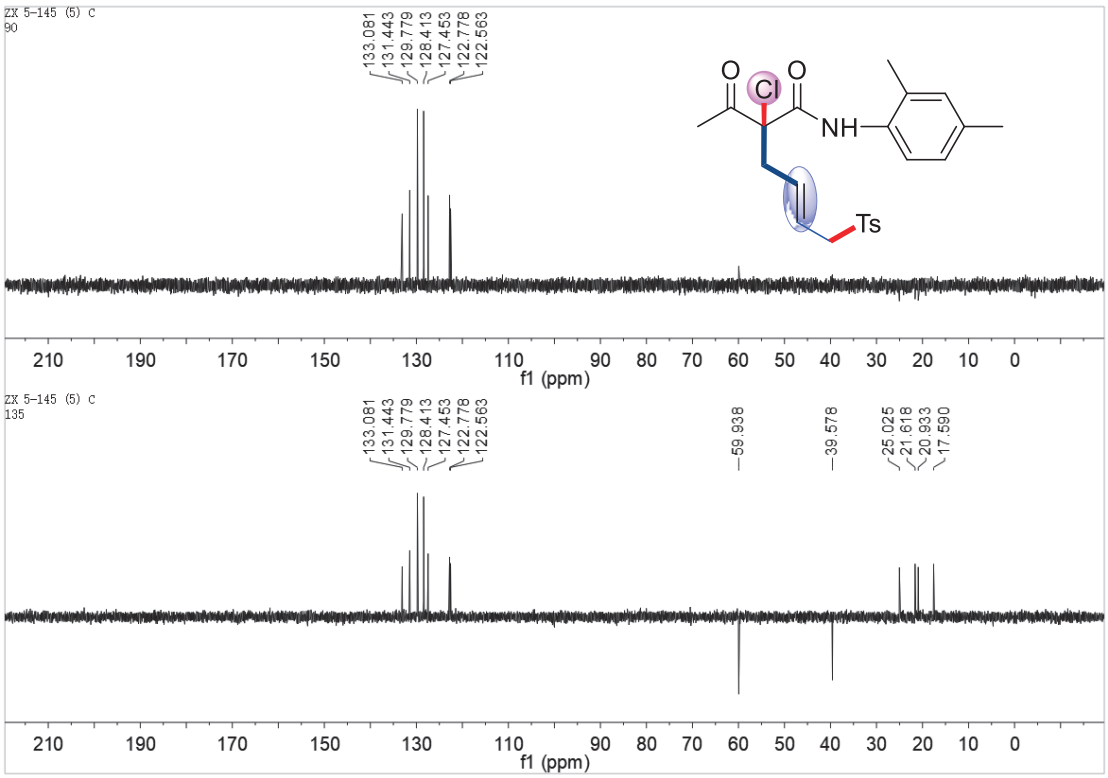
3e, ^{1}H NMR



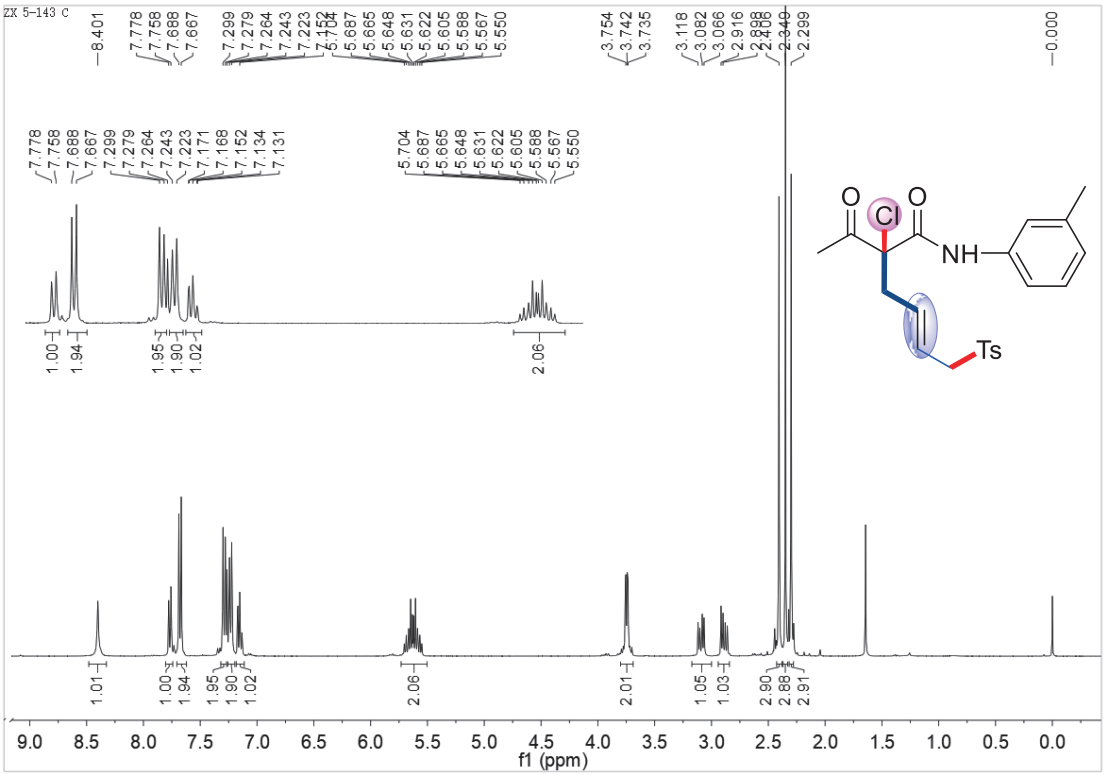
3e, ^{13}C NMR



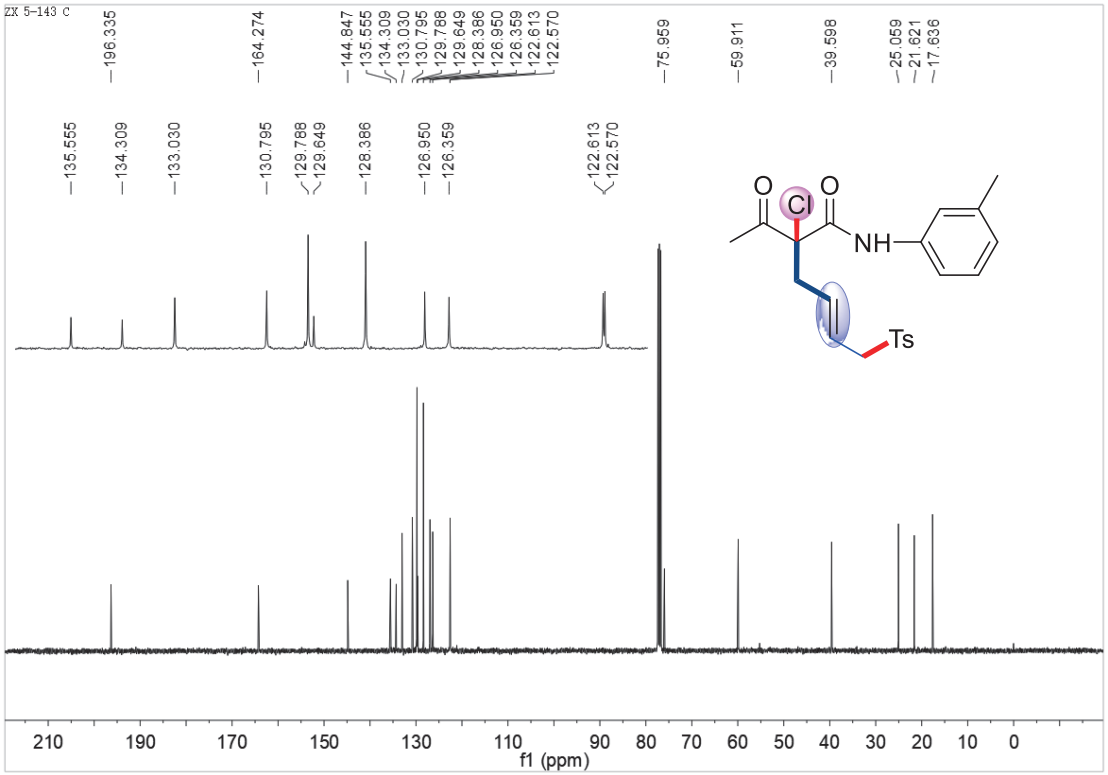
3e DEPT 90 and DEPT 135



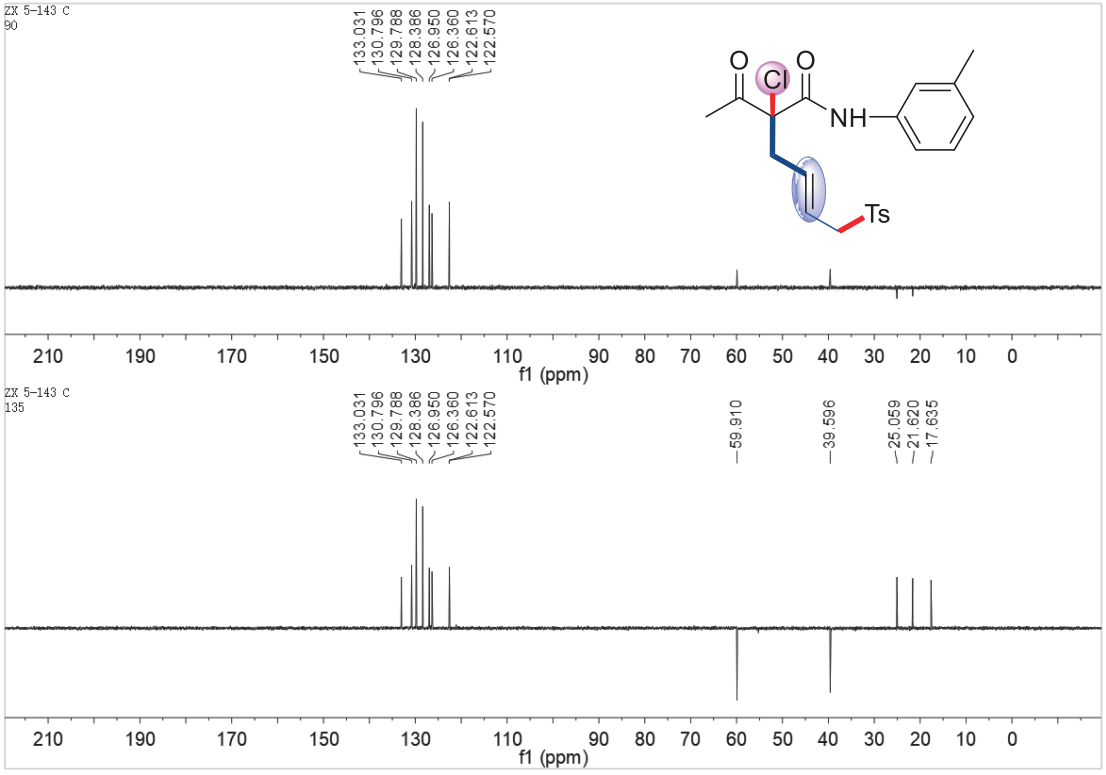
3f1, ^{1}H NMR



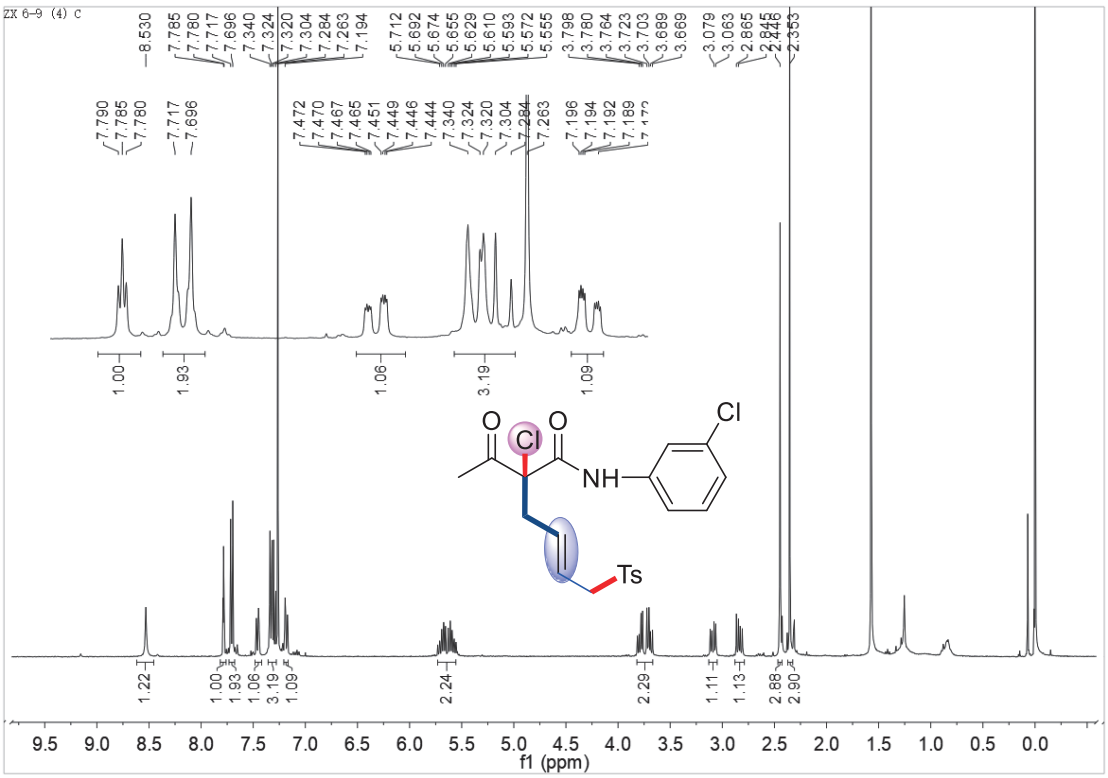
3f1, ^{13}C NMR



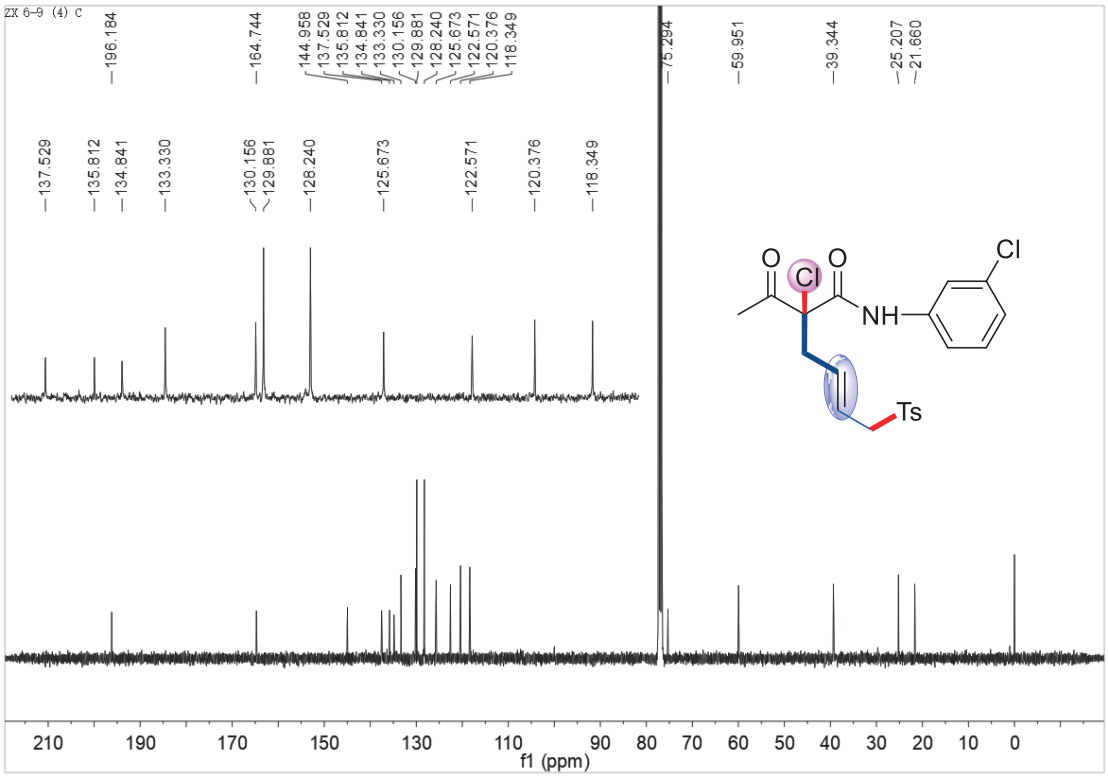
3f1, DEPT 90 and DEPT 135



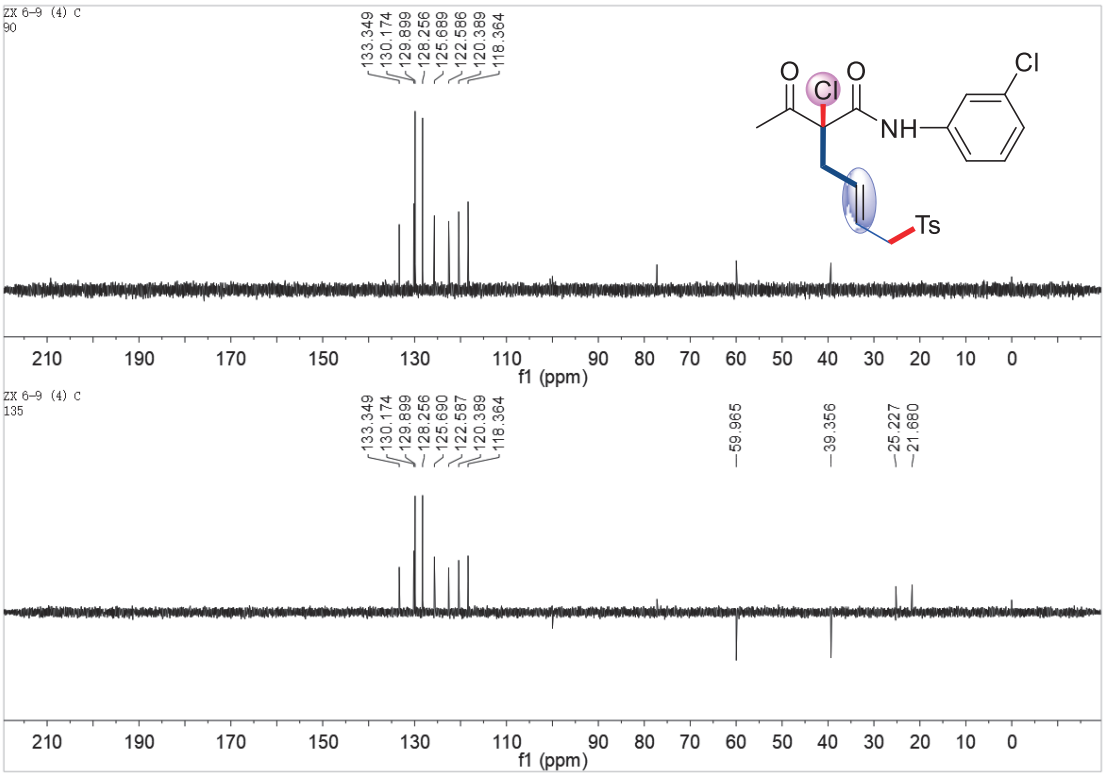
3f2, ^{1}H NMR



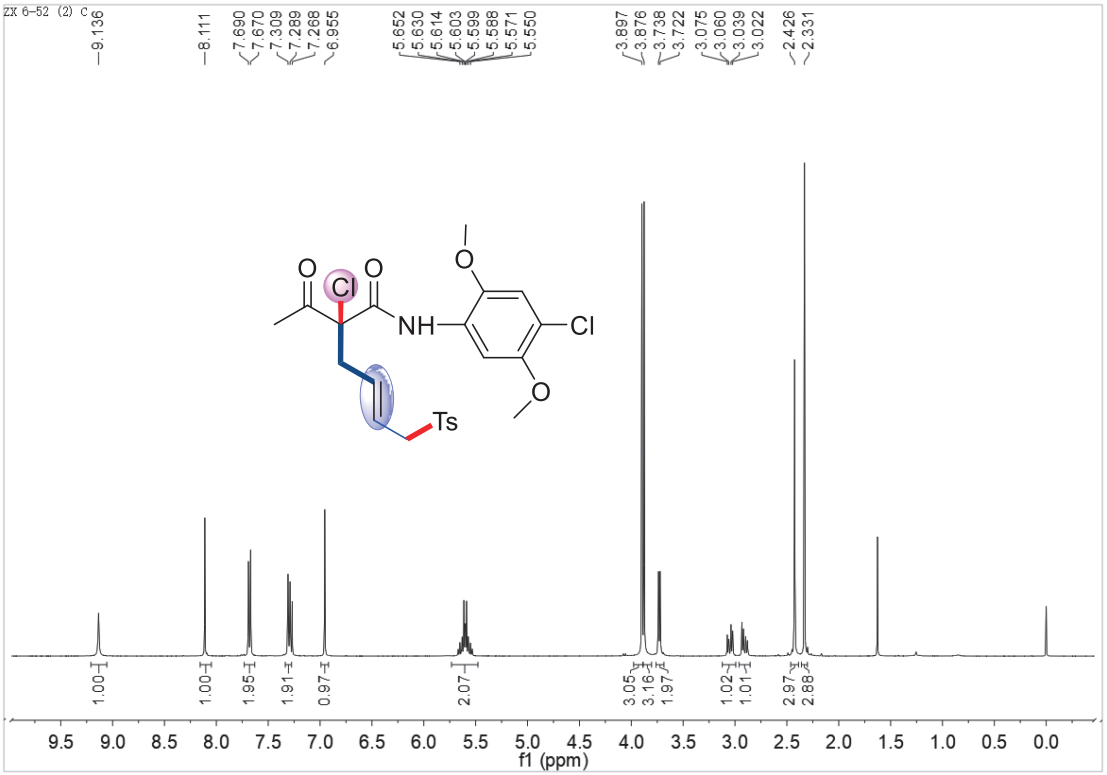
3f2, ^{13}C NMR



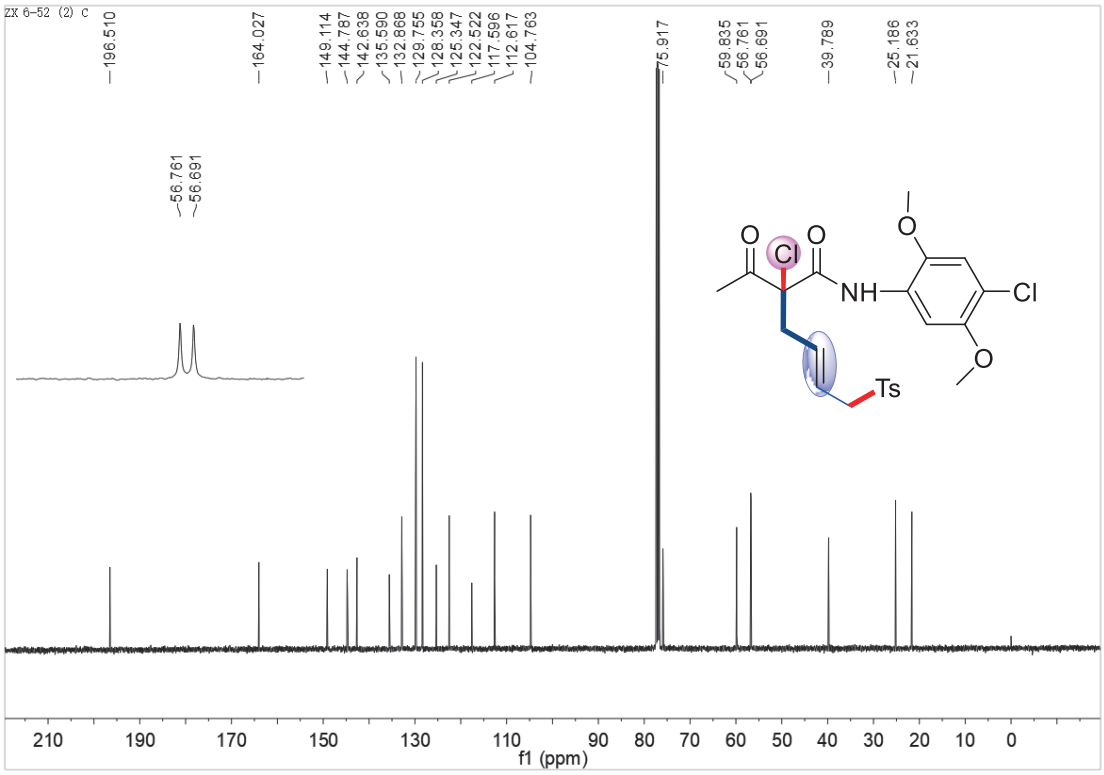
3f2, DEPT 90 and DEPT 135



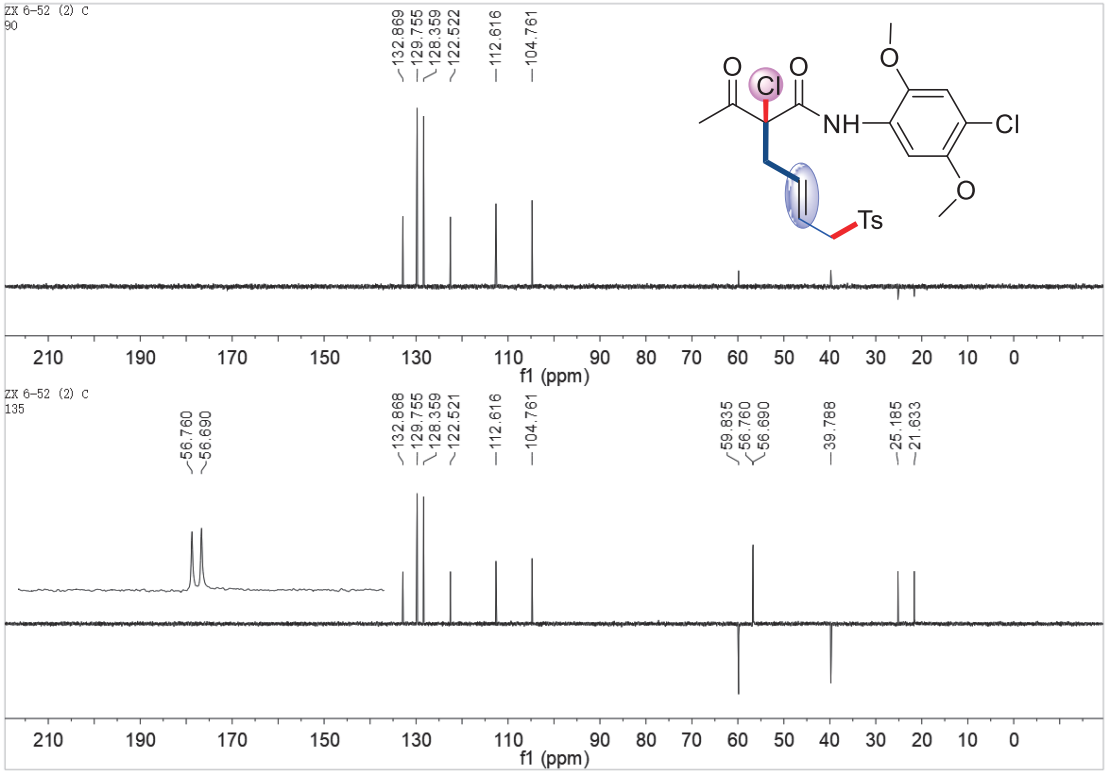
3g, ^{1}H NMR



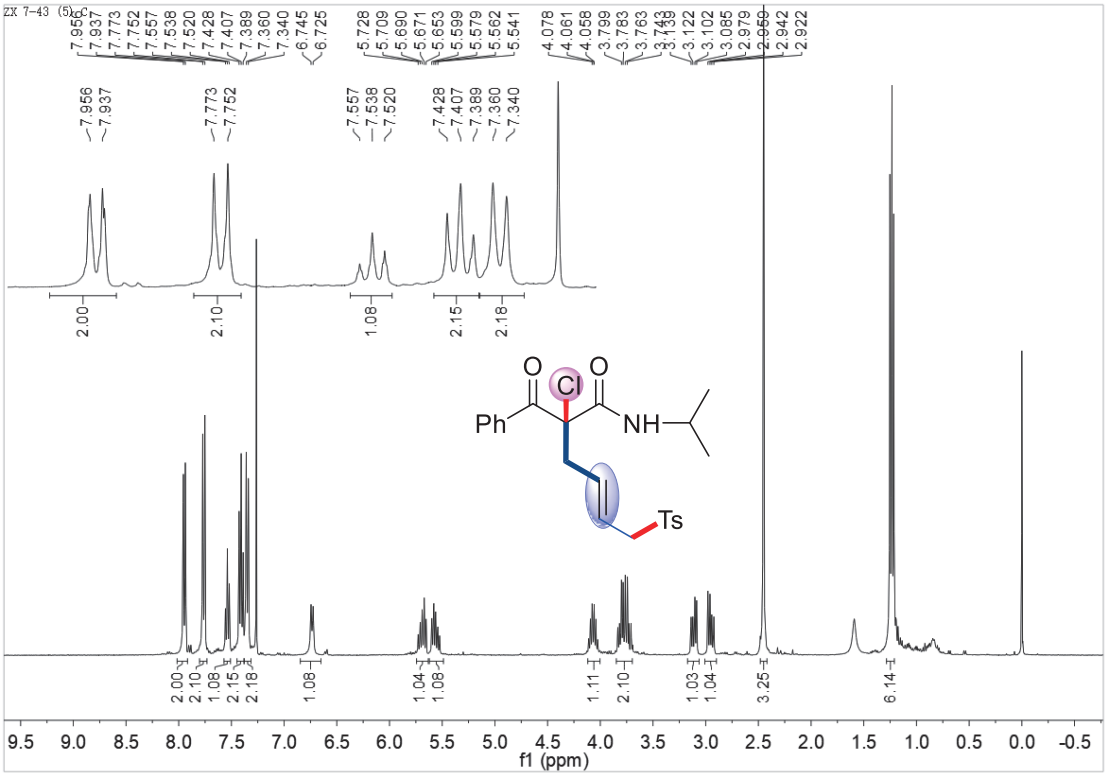
3g, ^{13}C NMR



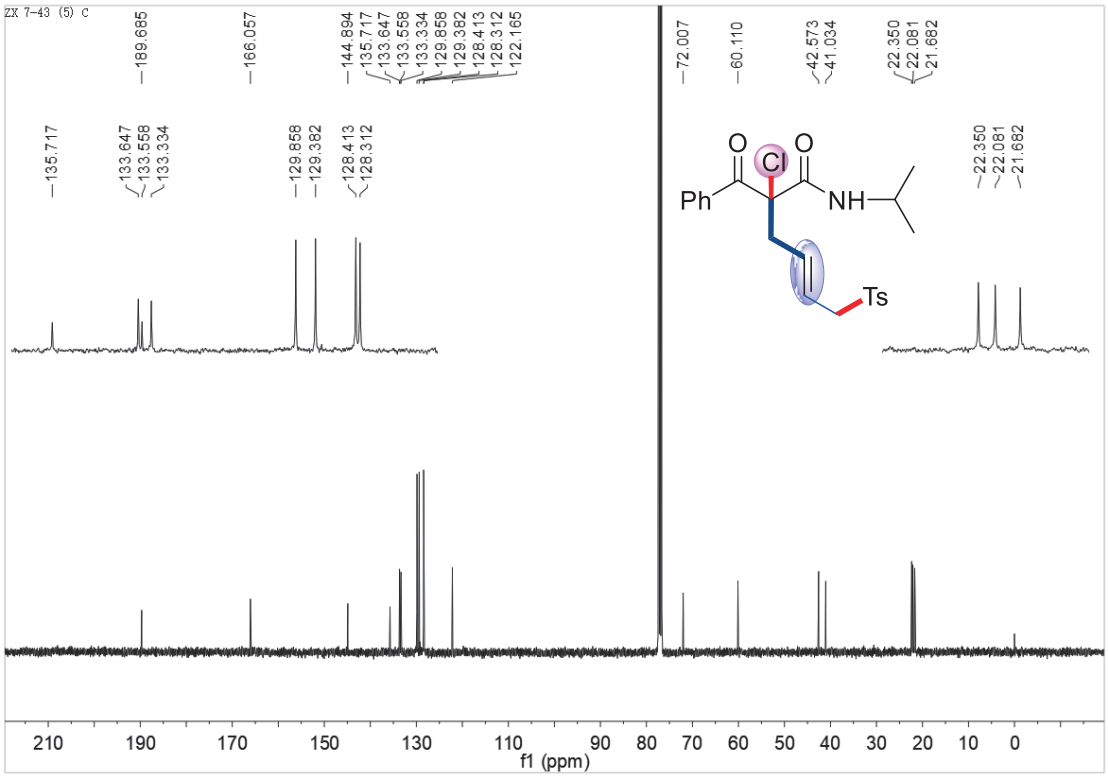
3g, DEPT 90 and DEPT 135



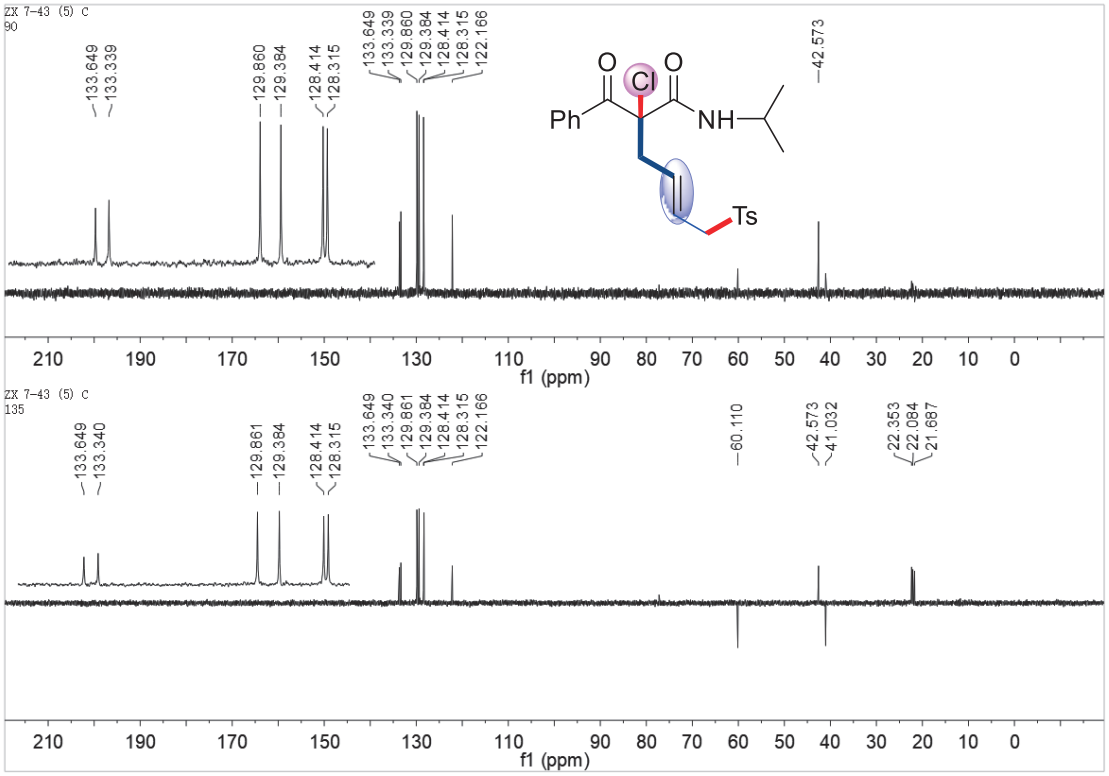
3h, ^{1}H NMR



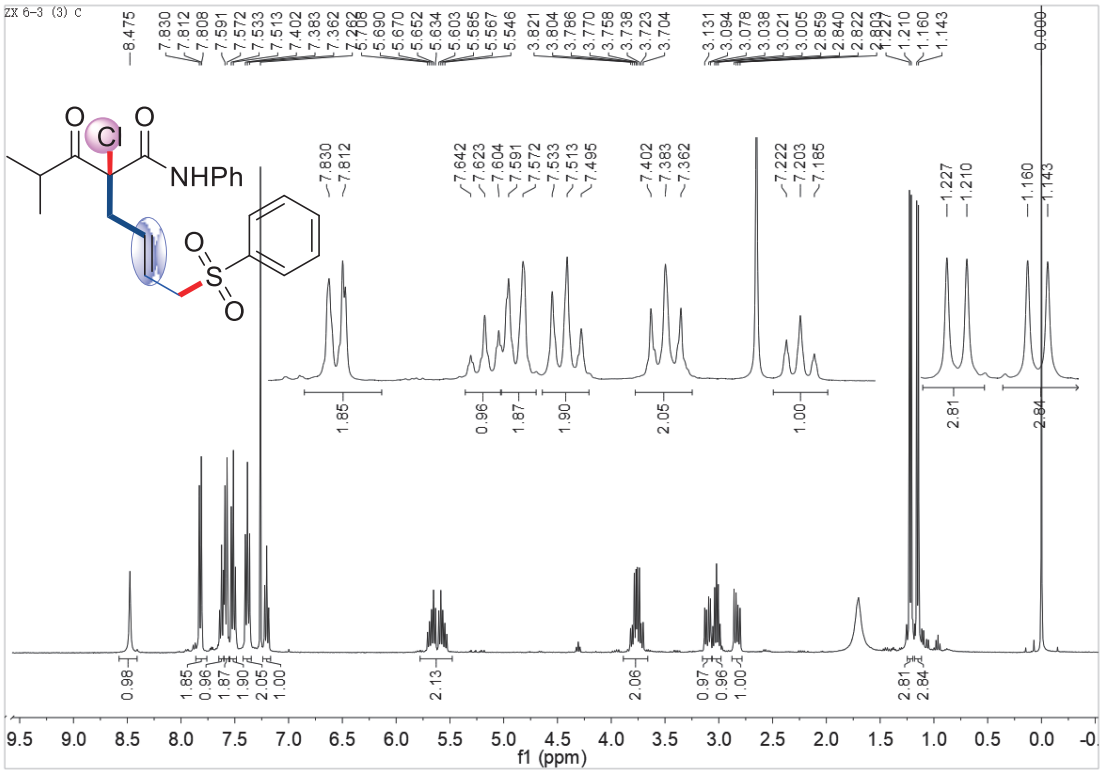
3h, ^{13}C NMR



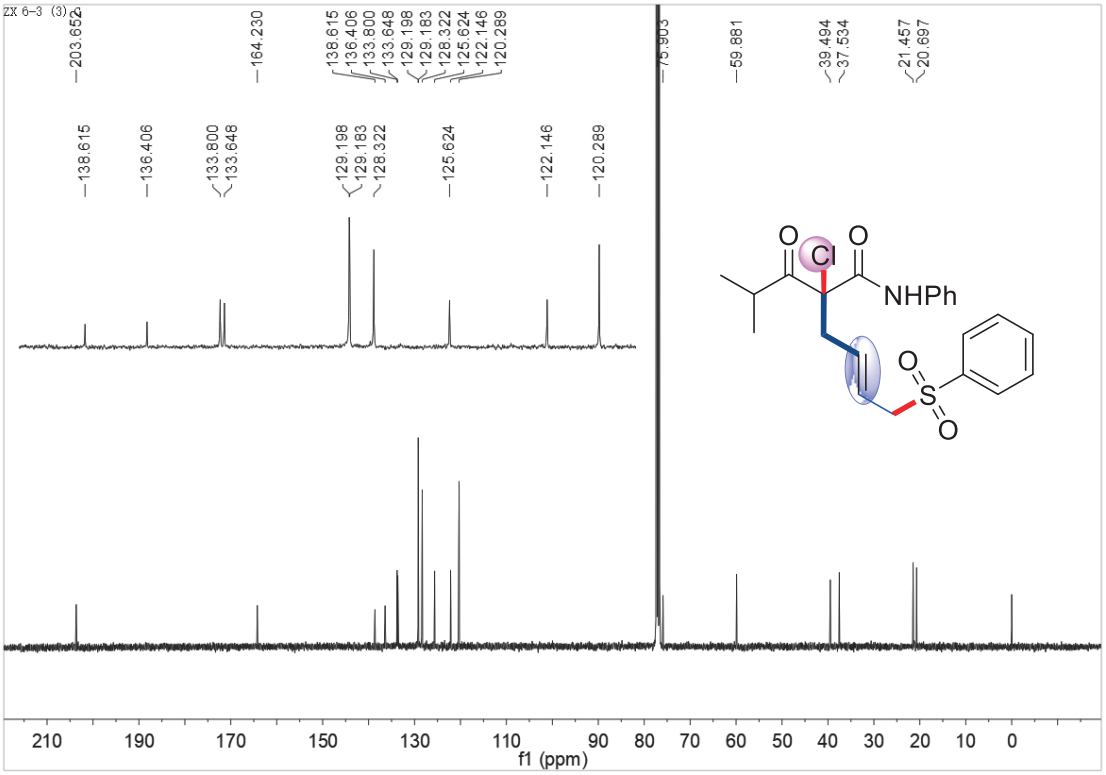
3h, DEPT 90 and DEPT 135



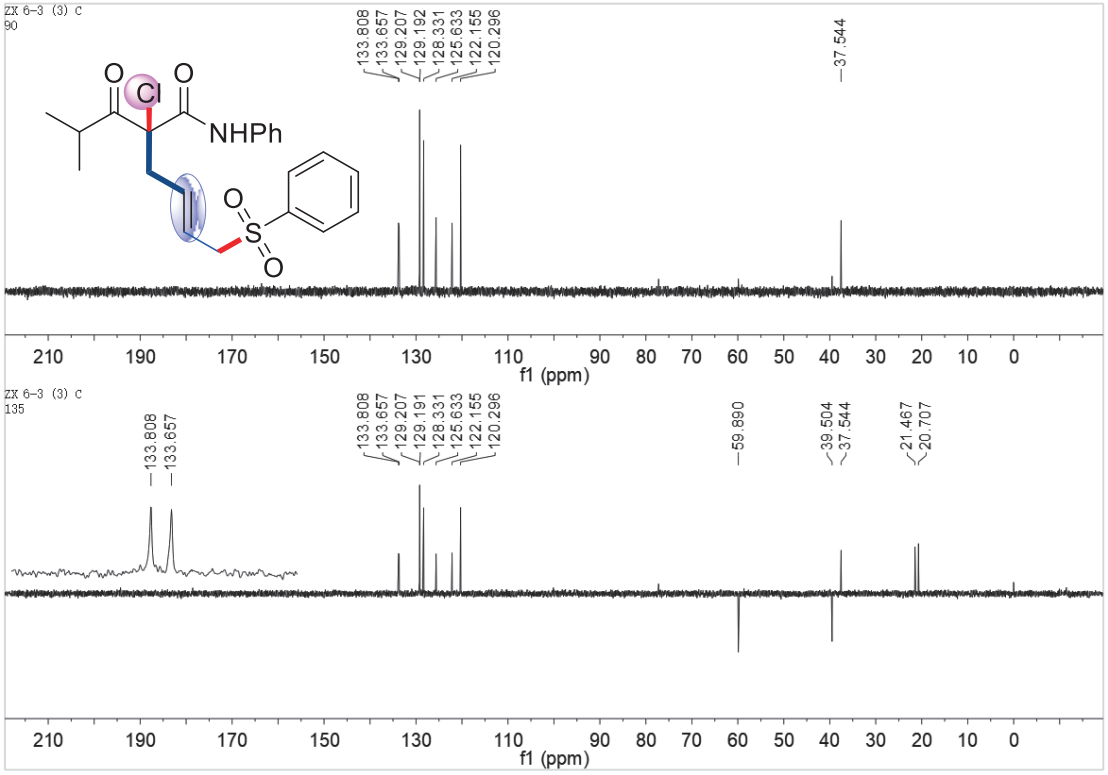
3i1, ^{1}H NMR



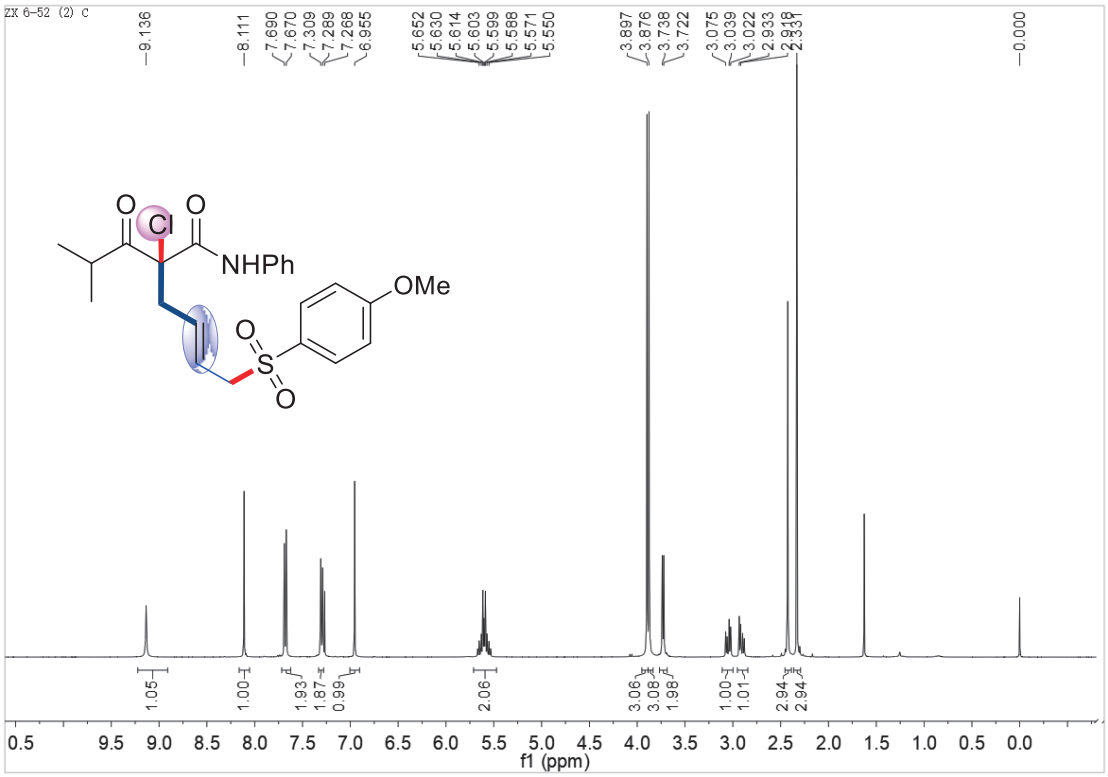
3i1, ^{13}C NMR



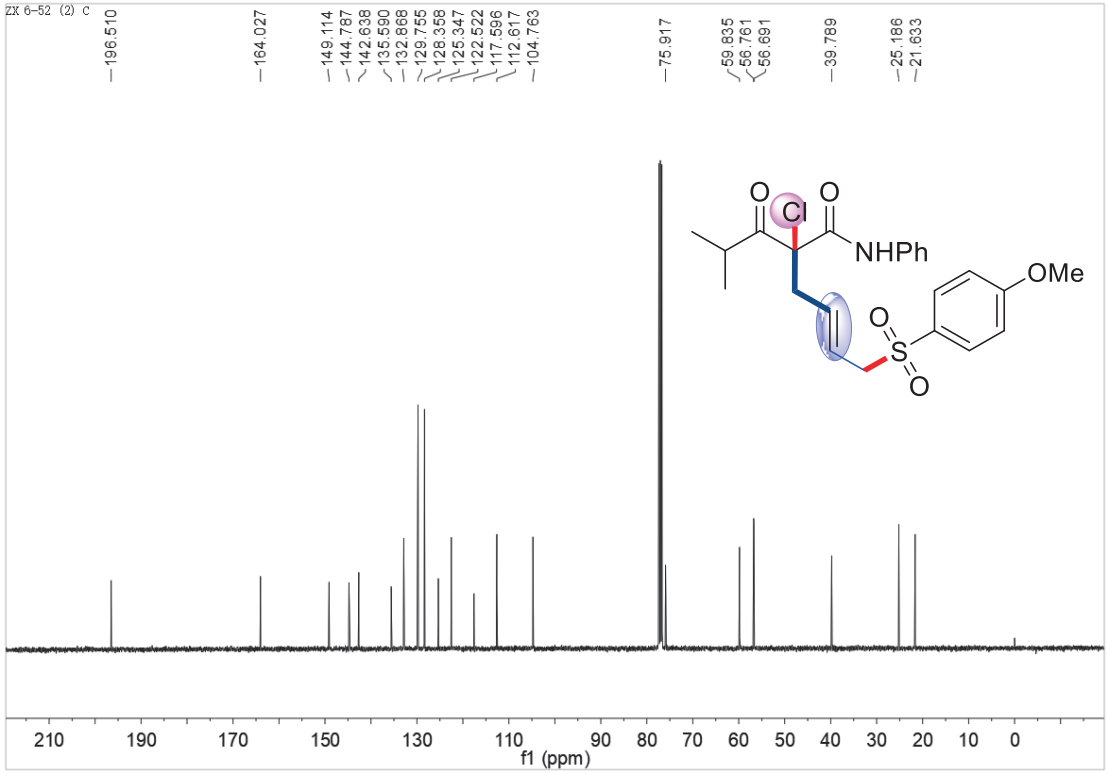
3i1, DEPT 90 and DEPT 135



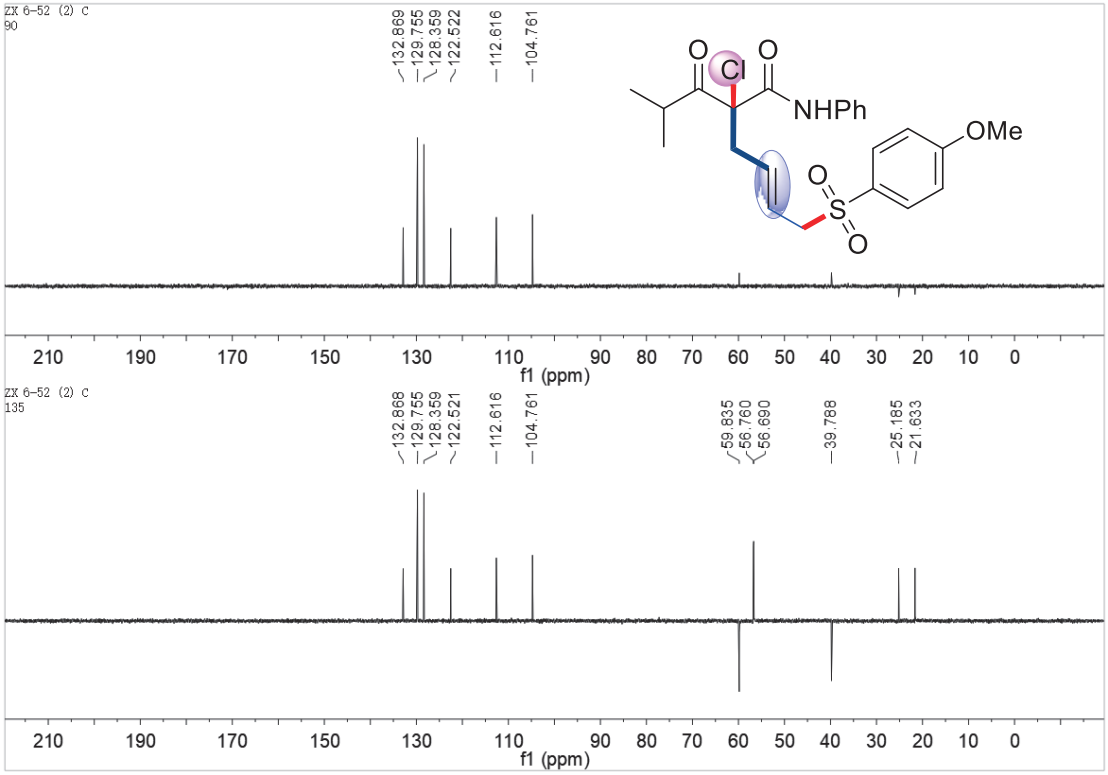
3i2, ^{1}H NMR



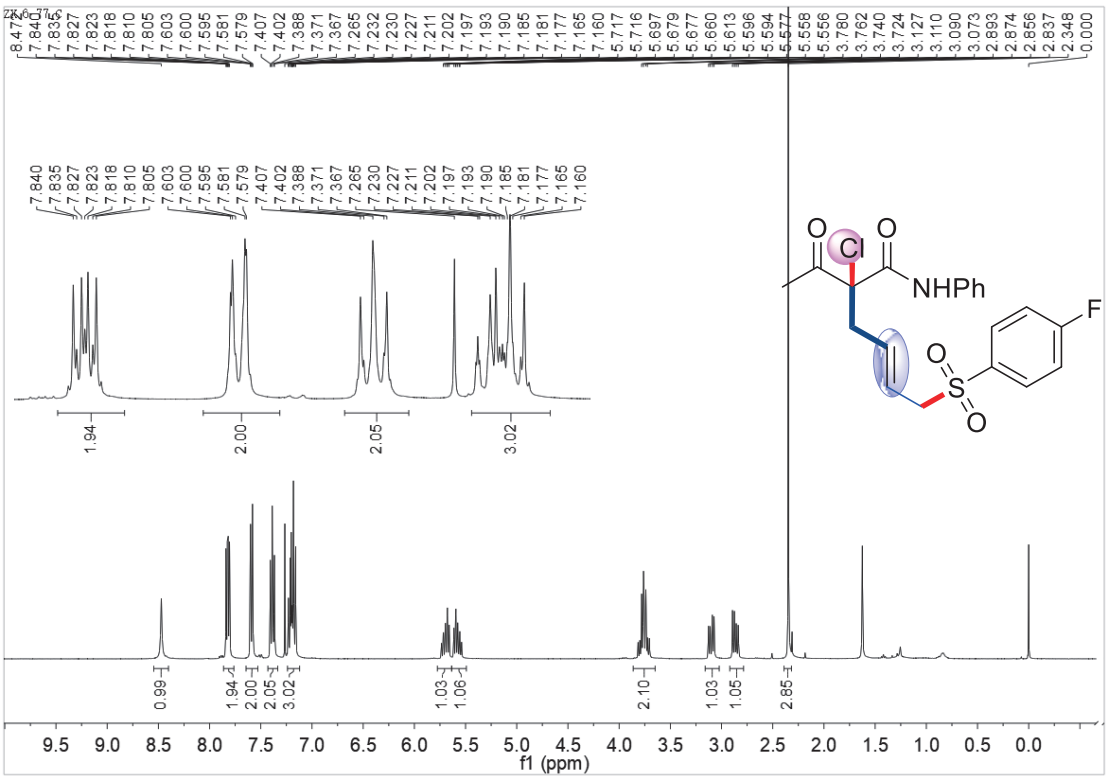
3i2, ^{13}C NMR



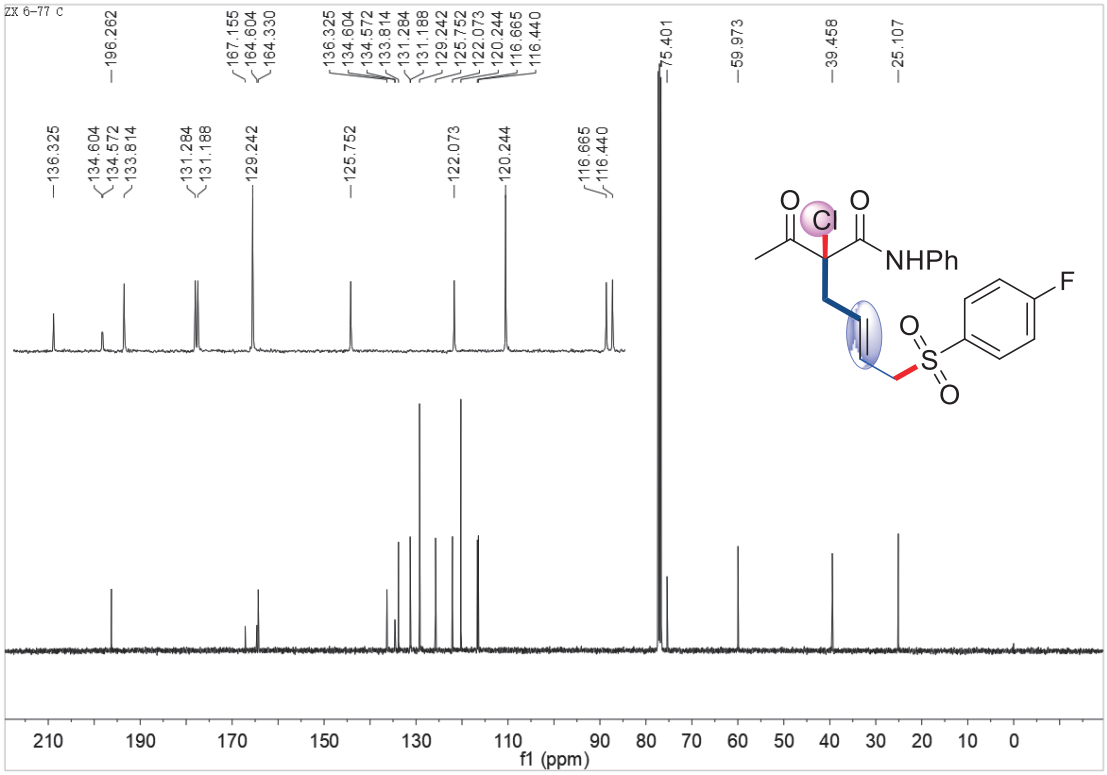
3i2 DEPT 90 and DEPT 135



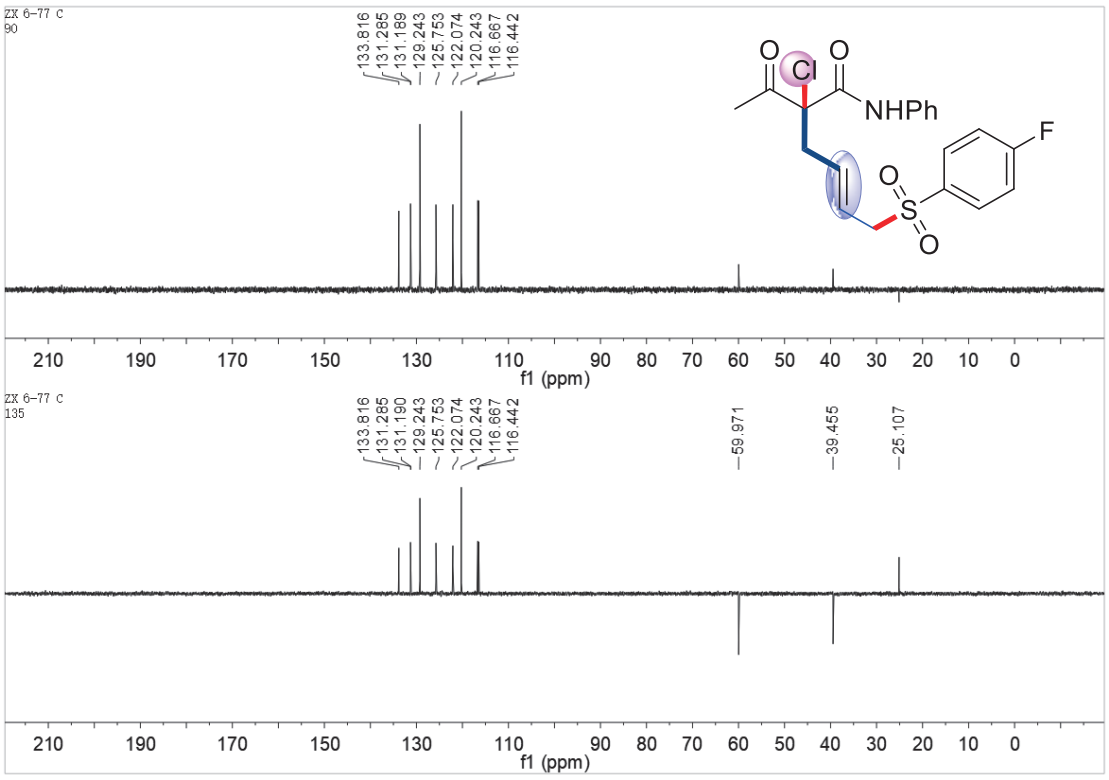
3j1, ^{1}H NMR



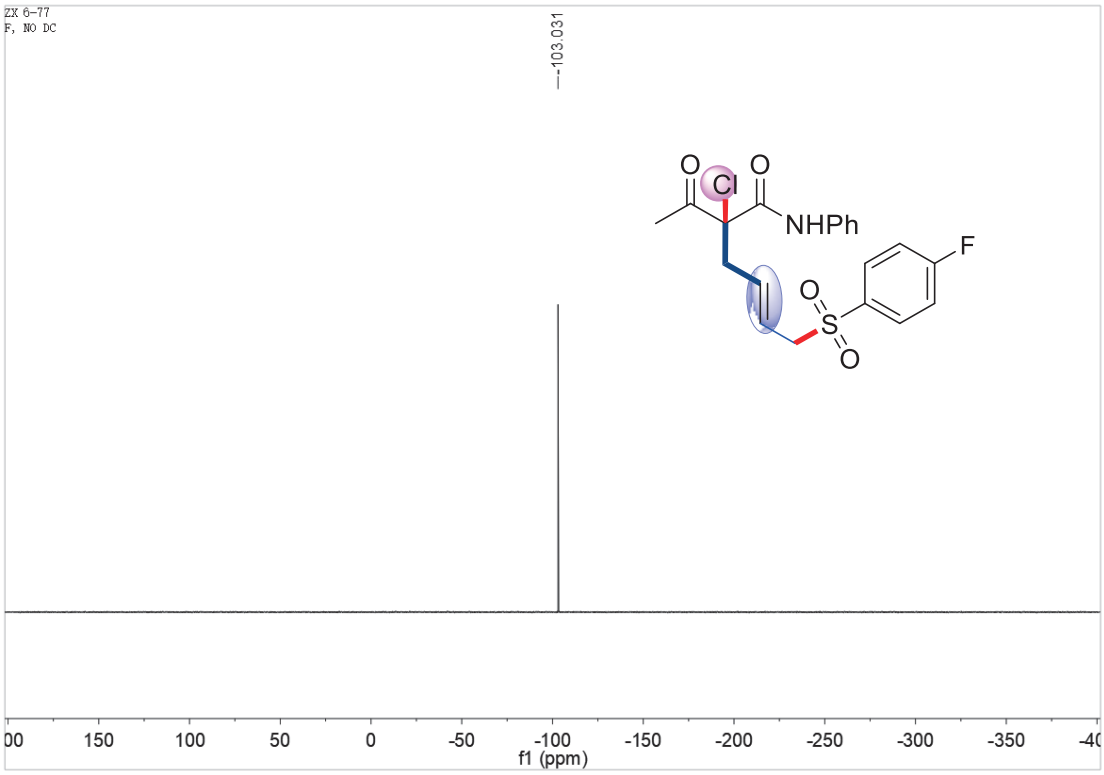
3j1, ^{13}C NMR



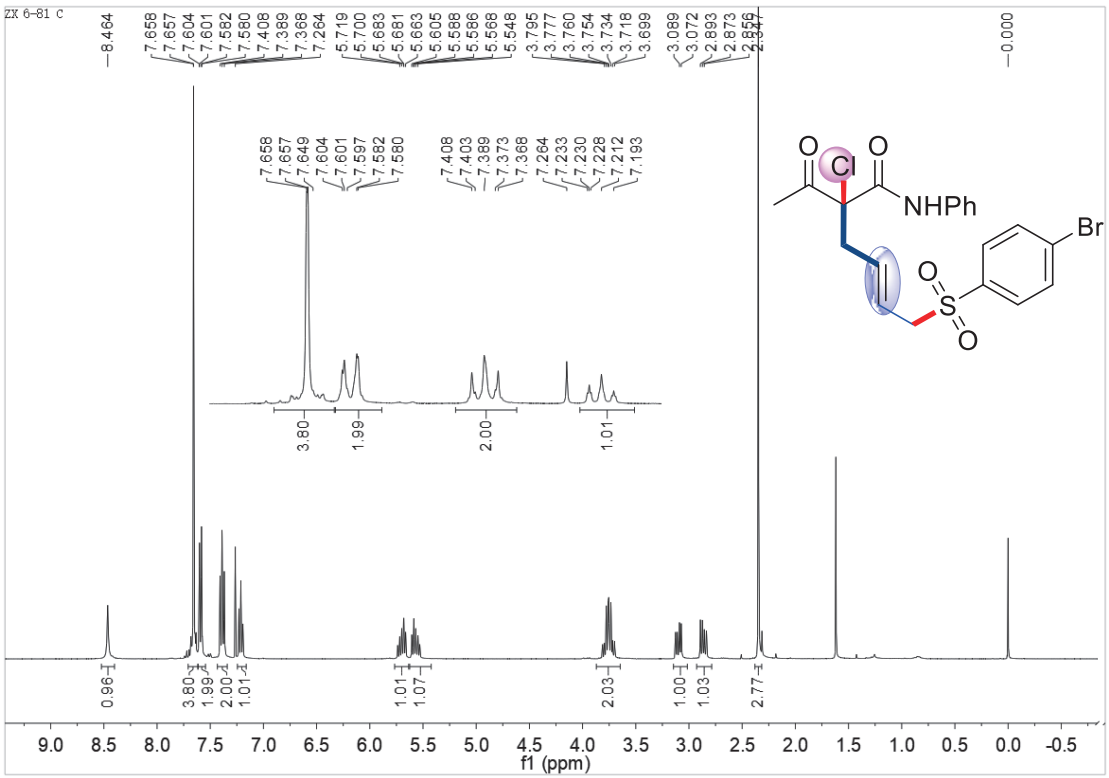
3j1, DEPT 90 and DEPT 135



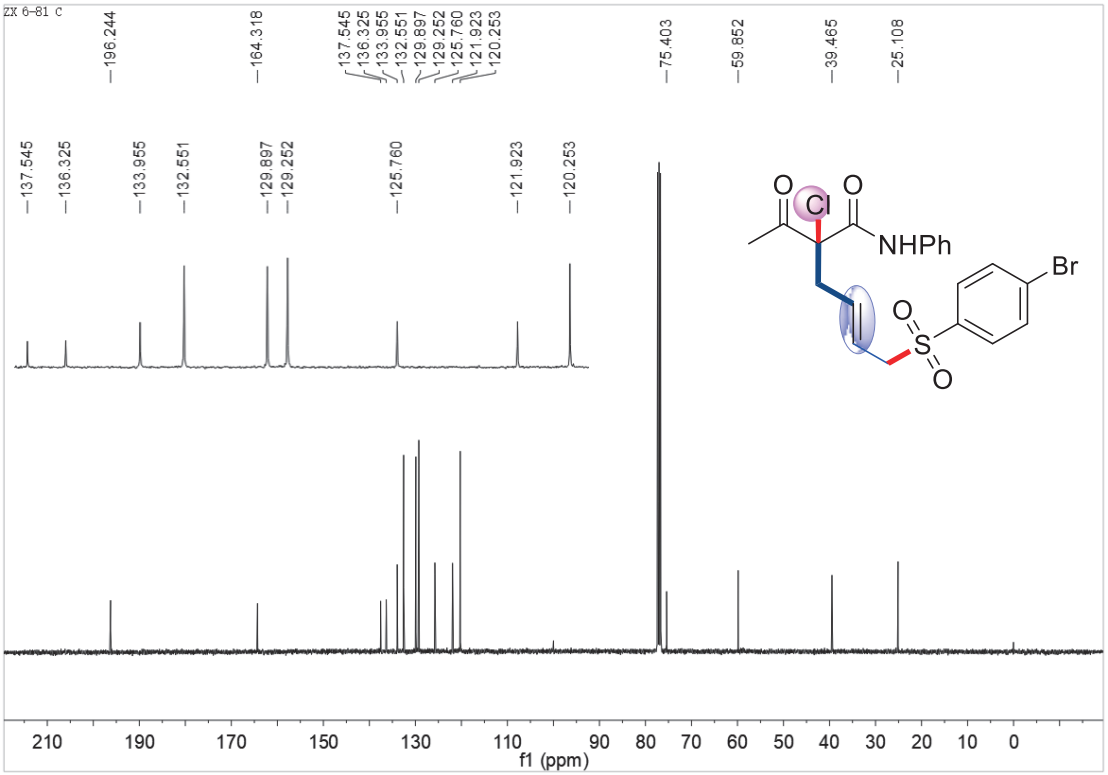
3j1, ^{19}F NMR



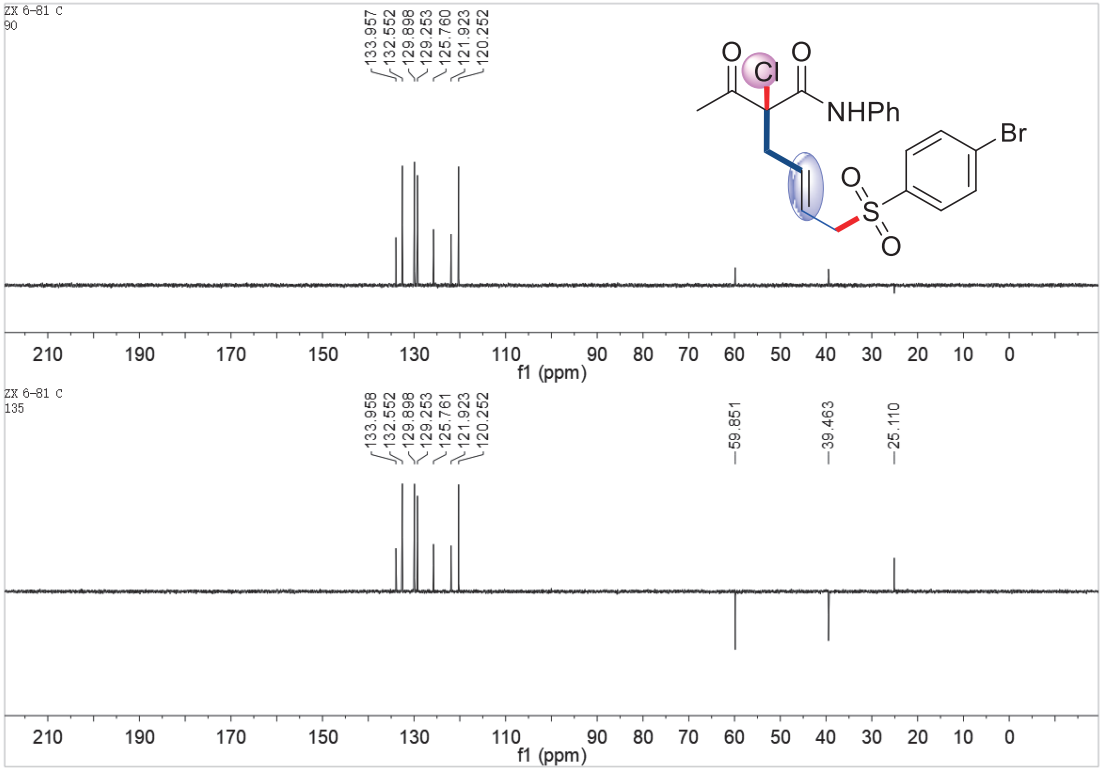
3j2, ^{1}H NMR



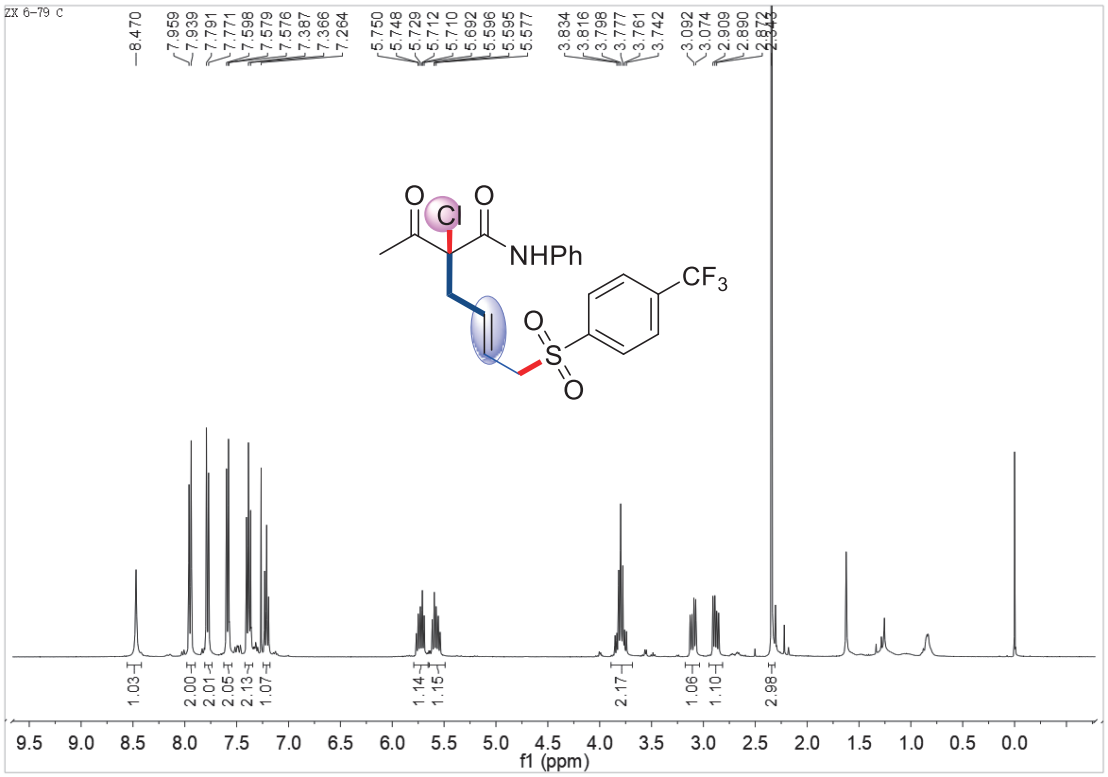
3j2, ^{13}C NMR



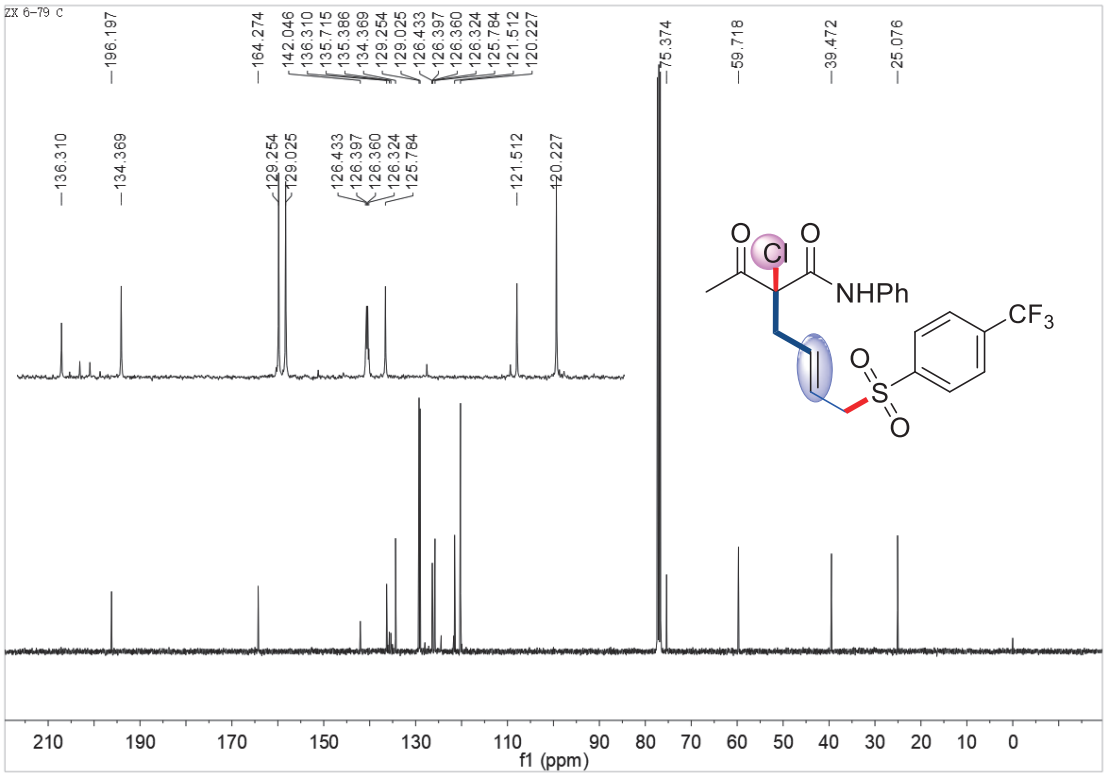
3j2 DEPT 90 and DEPT 135



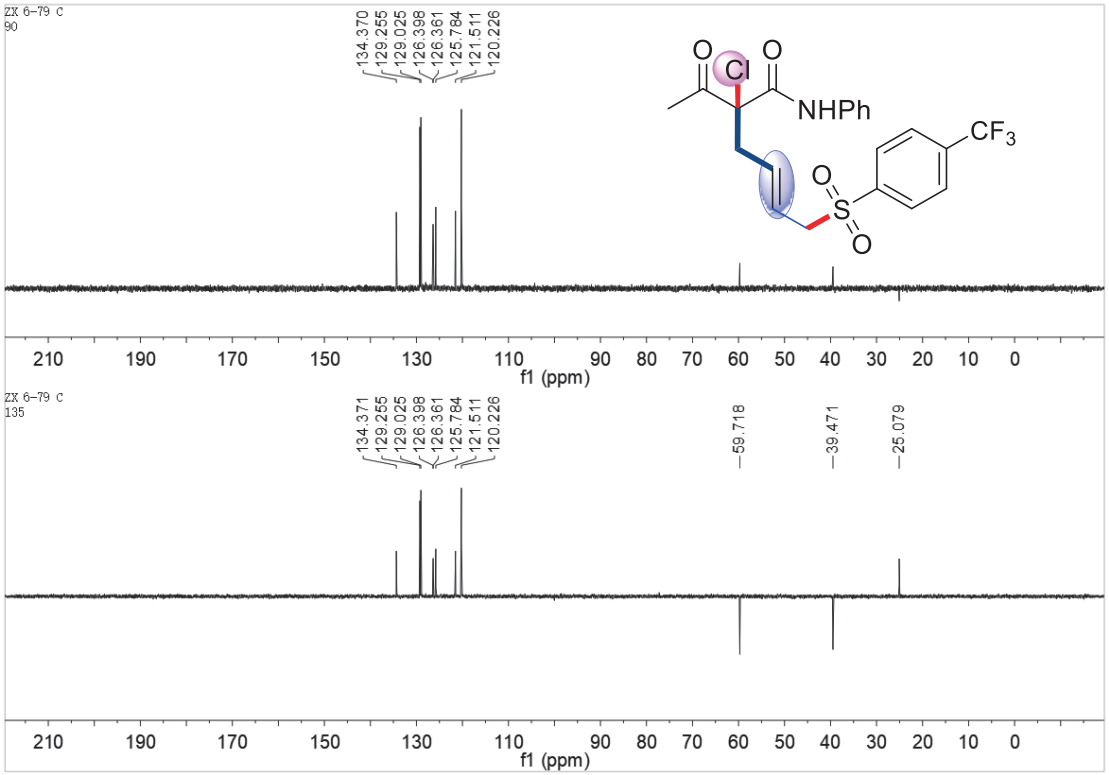
3j3, ^{1}H NMR



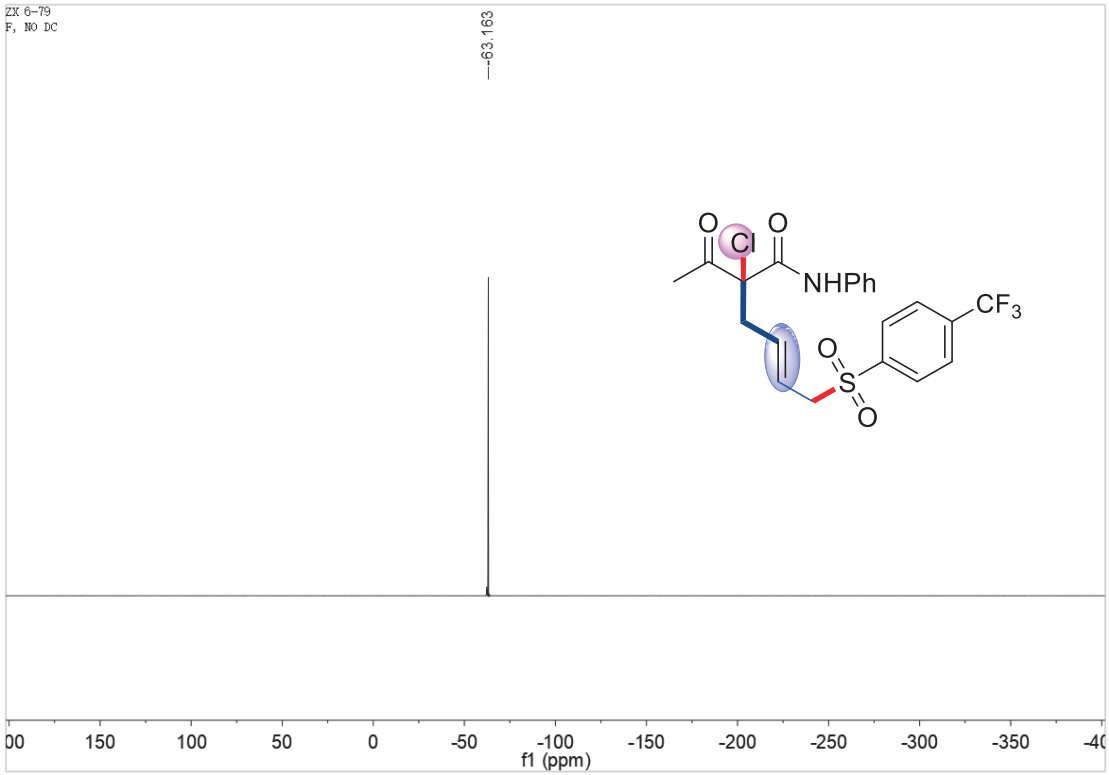
3j3, ^{13}C NMR



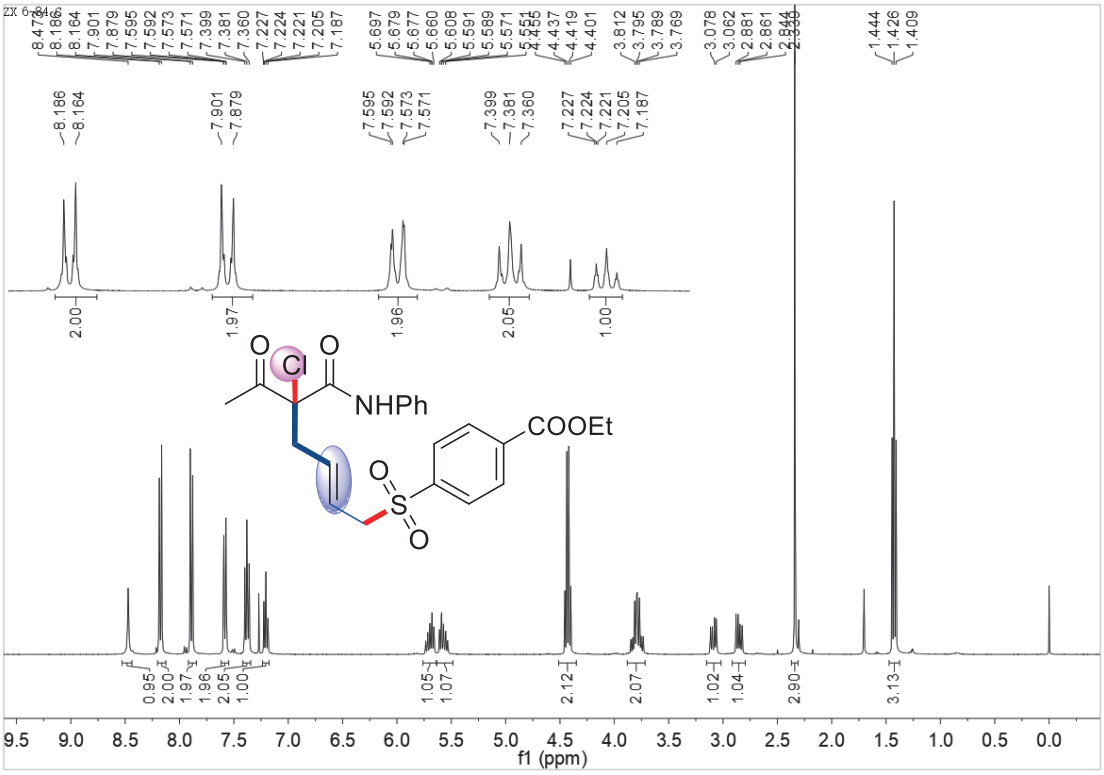
3j3 DEPT 90 and DEPT 135



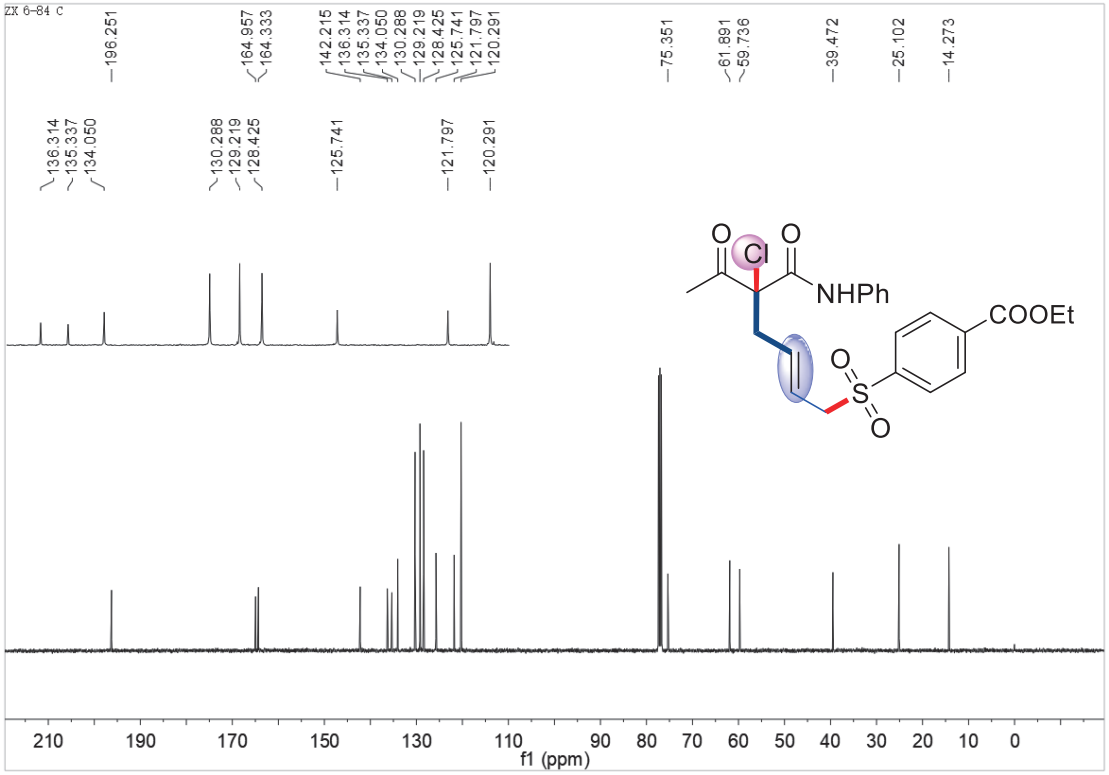
3j3 ^{19}F NMR



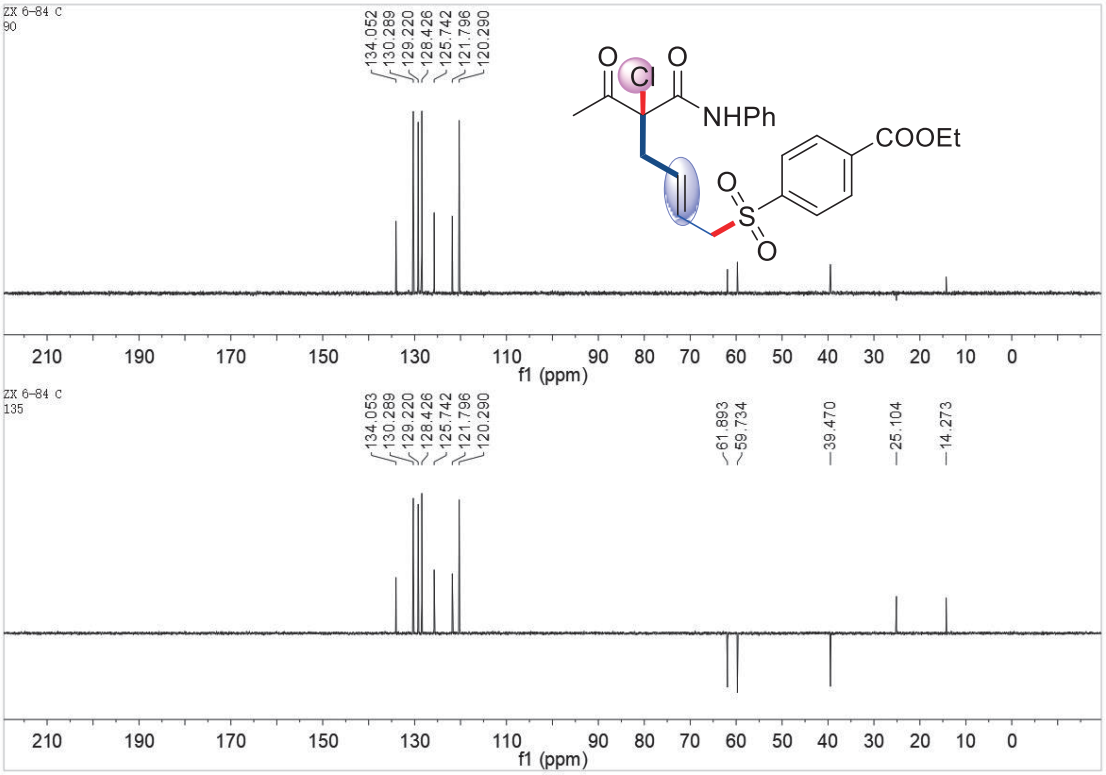
3j4, ^{1}H NMR



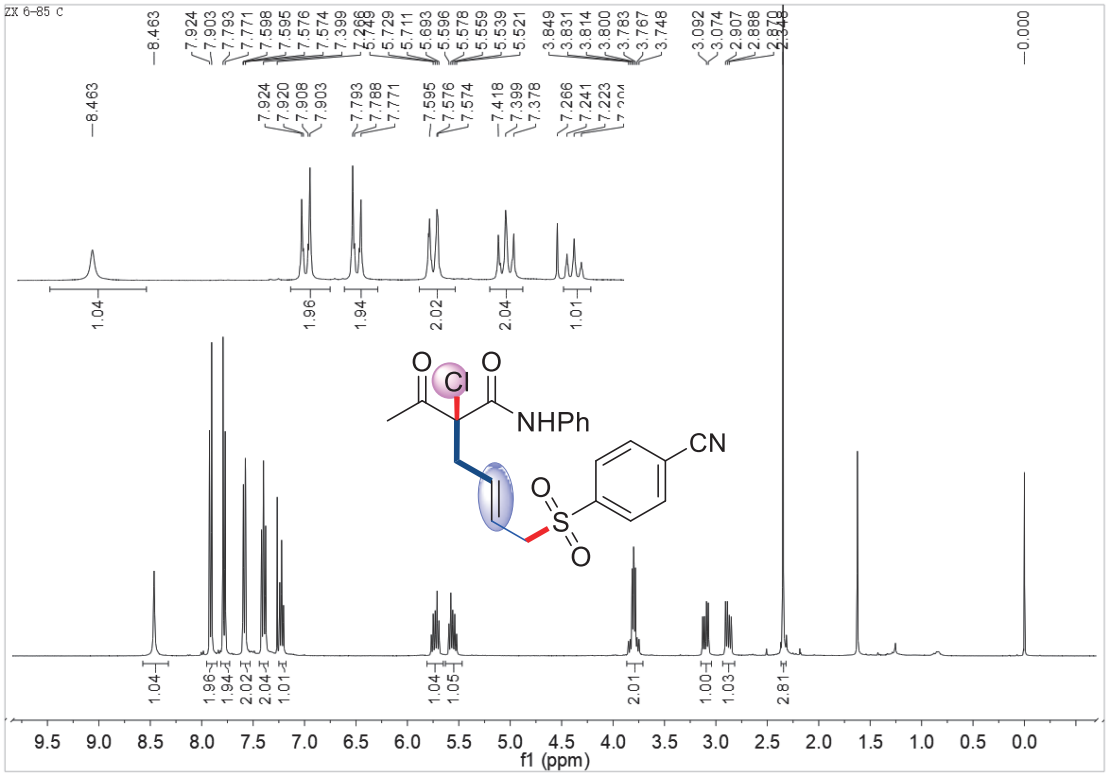
3j4, ^{13}C NMR



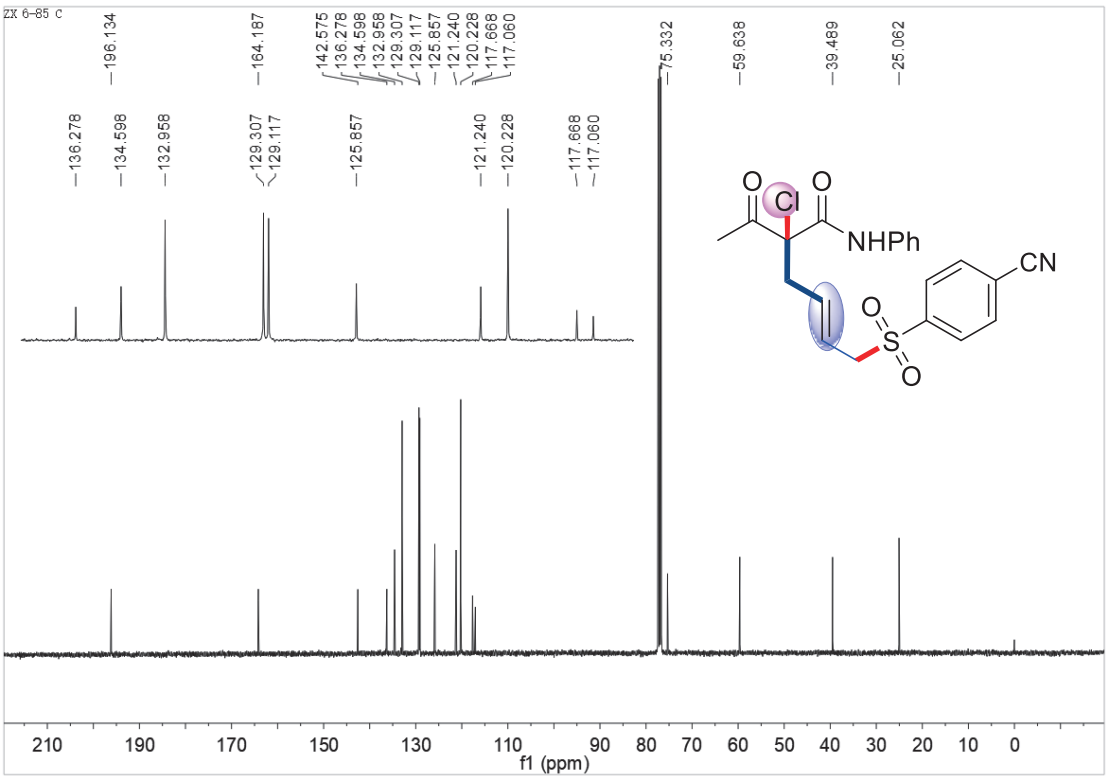
3j4 DEPT 90 and DEPT 135



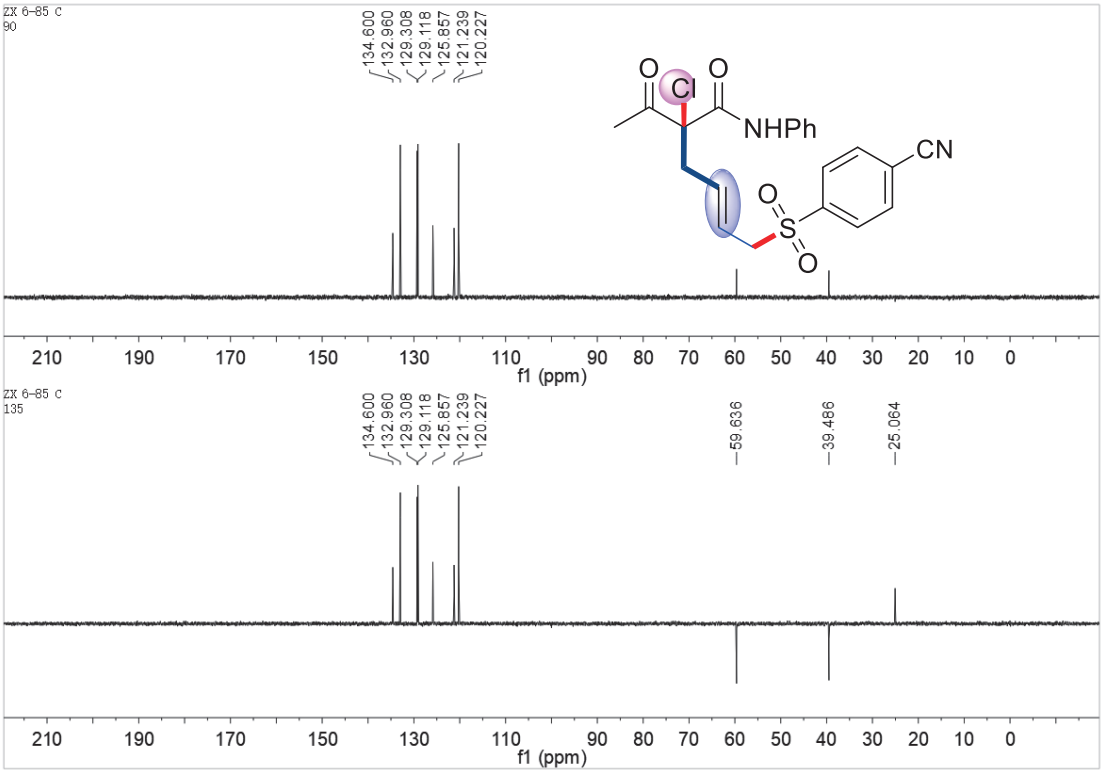
3j5, ^{1}H NMR



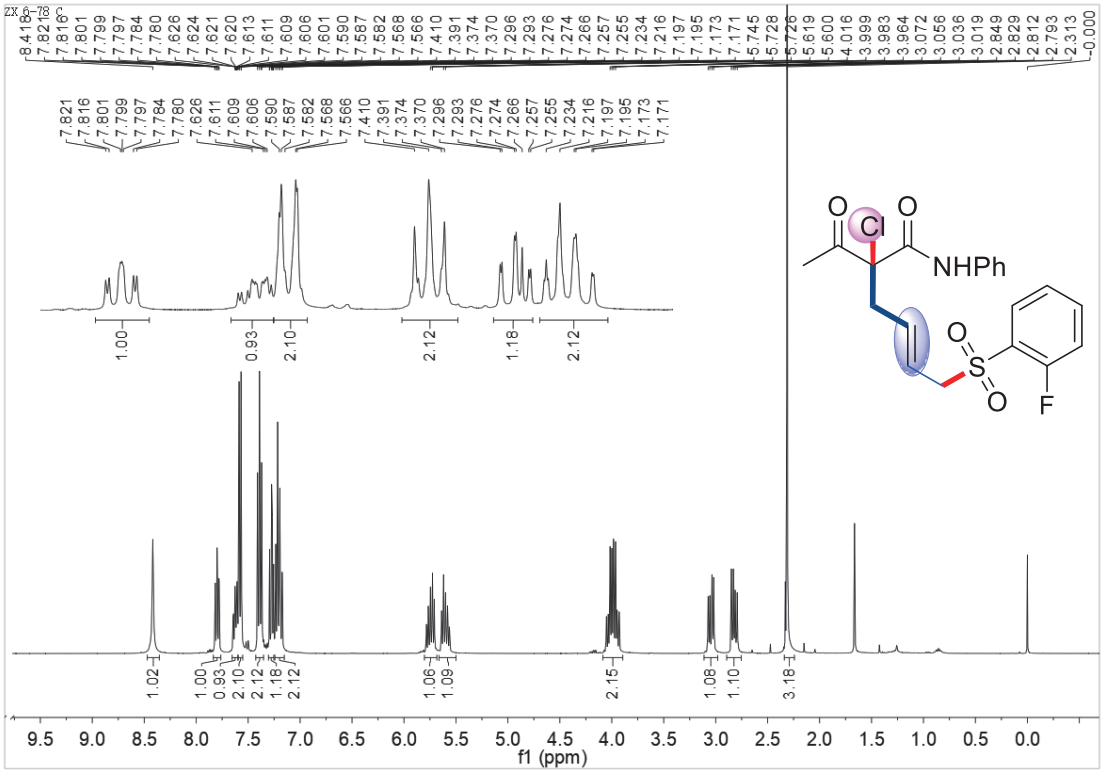
3j5, ^{13}C NMR



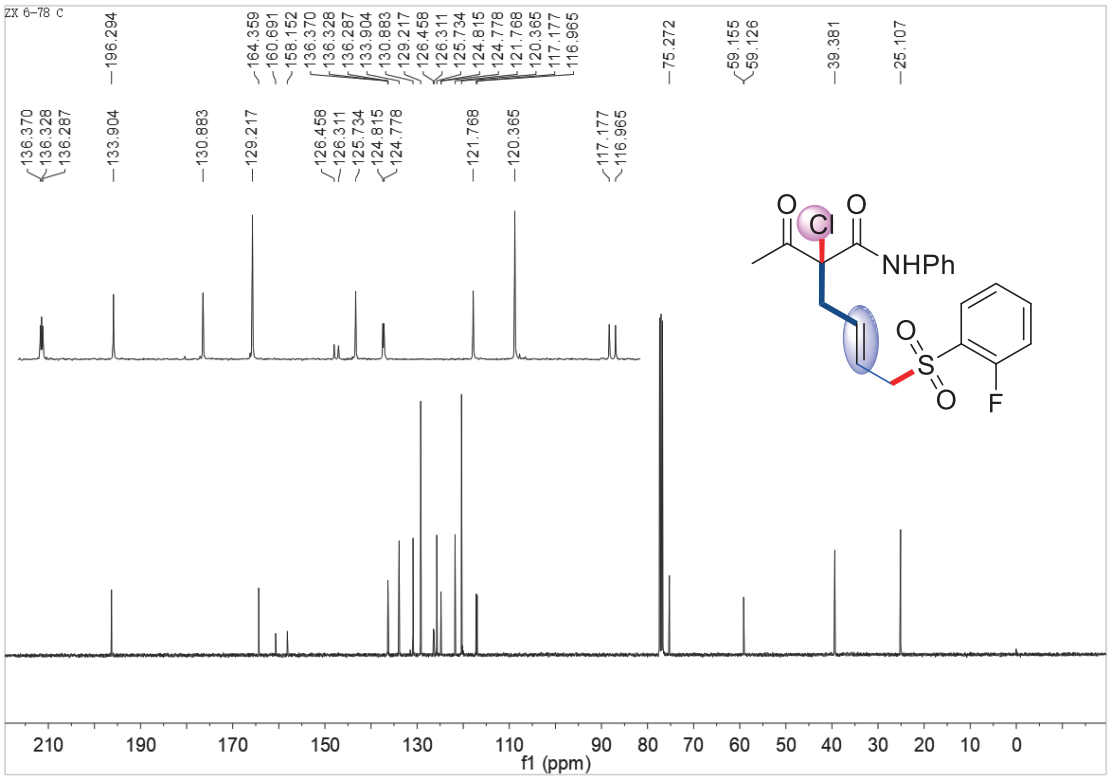
3j5, DEPT 90 and DEPT 135



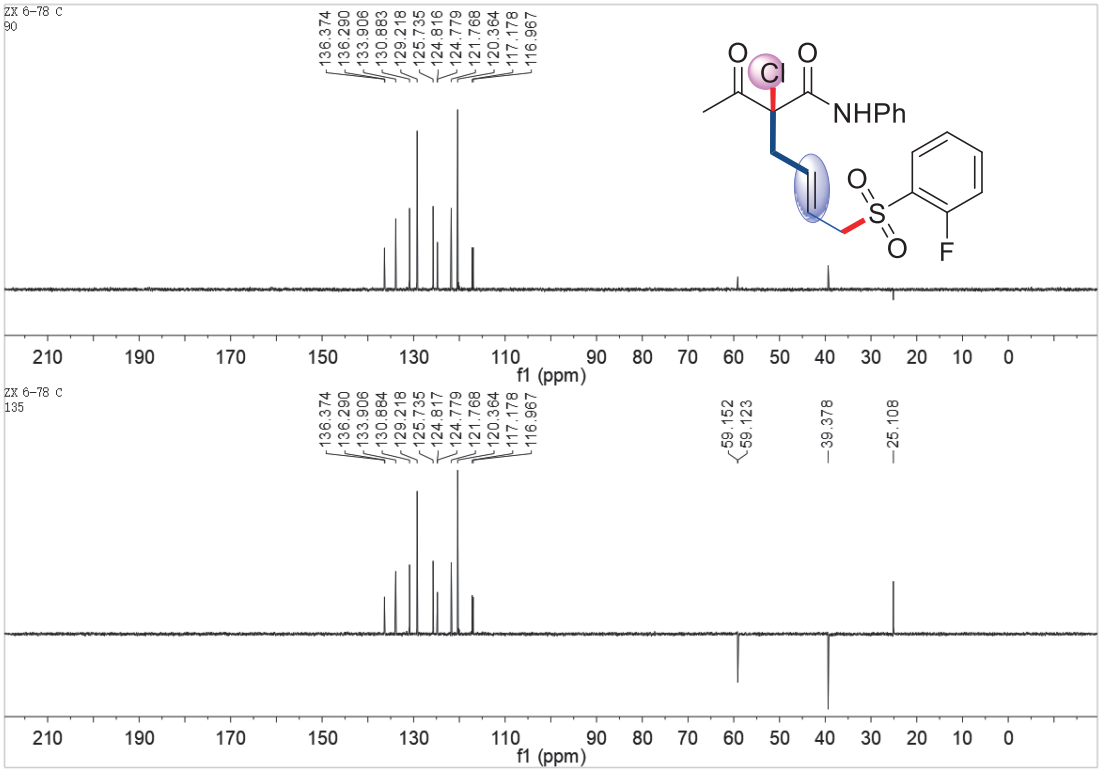
3k, ^{1}H NMR



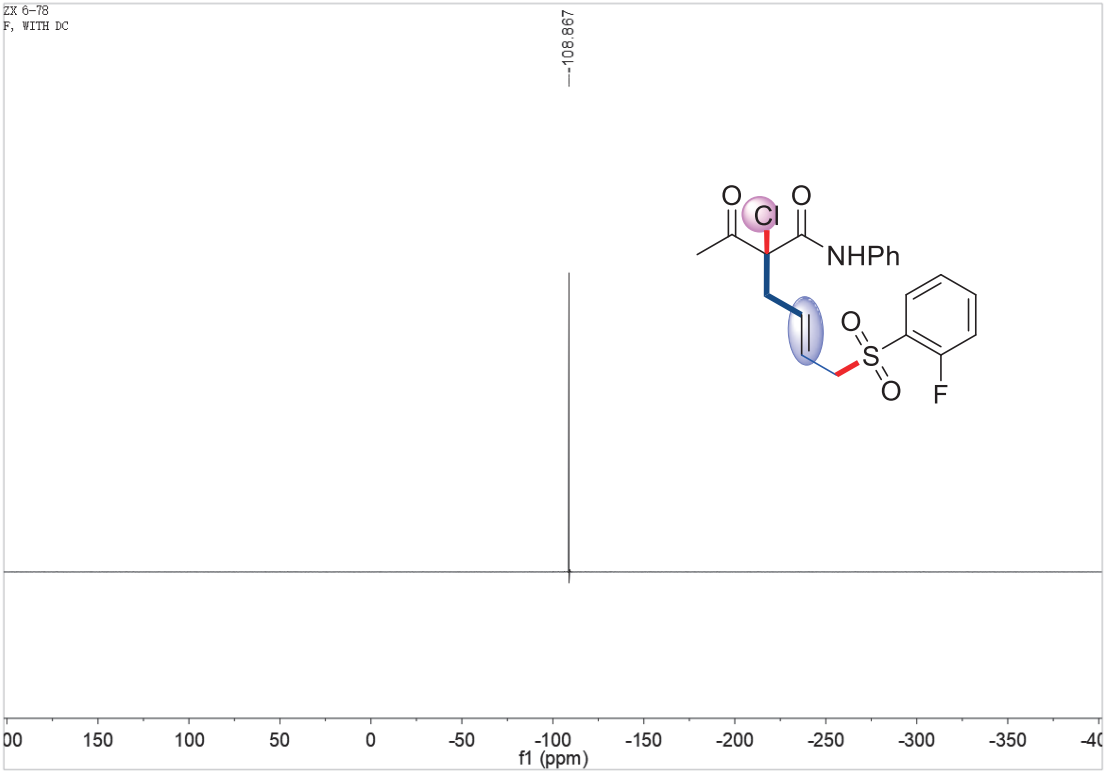
3k, ^{13}C NMR



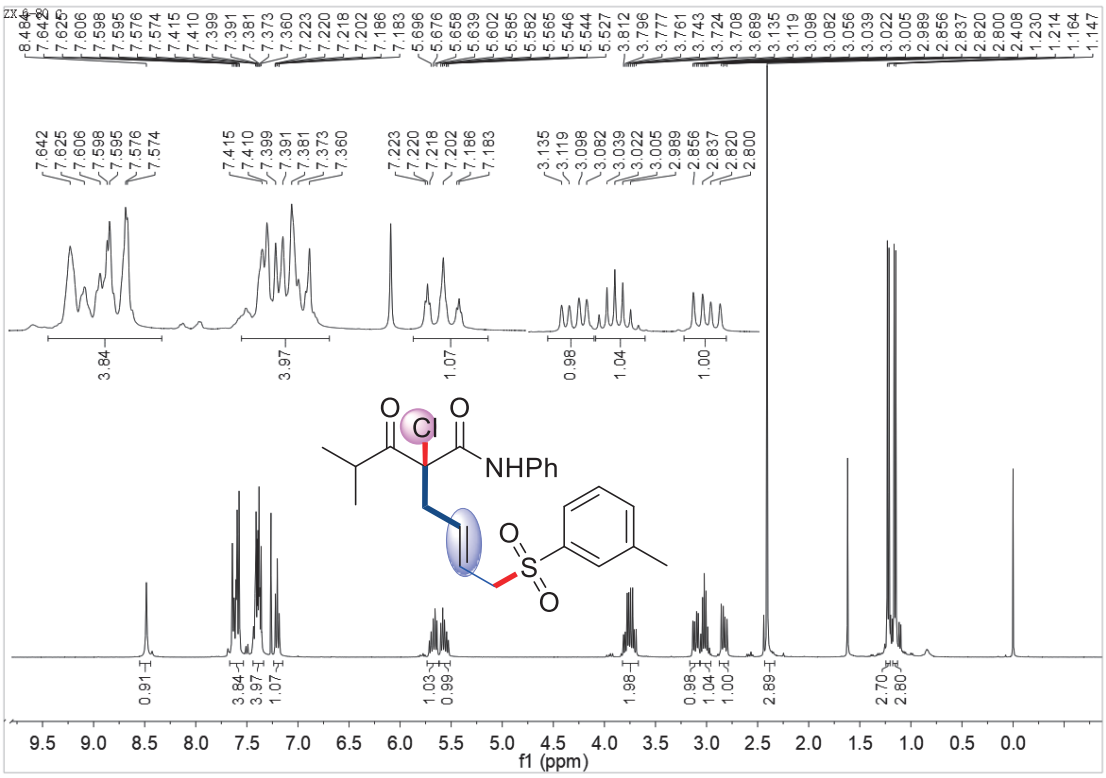
3k DEPT 90 and DEPT 135



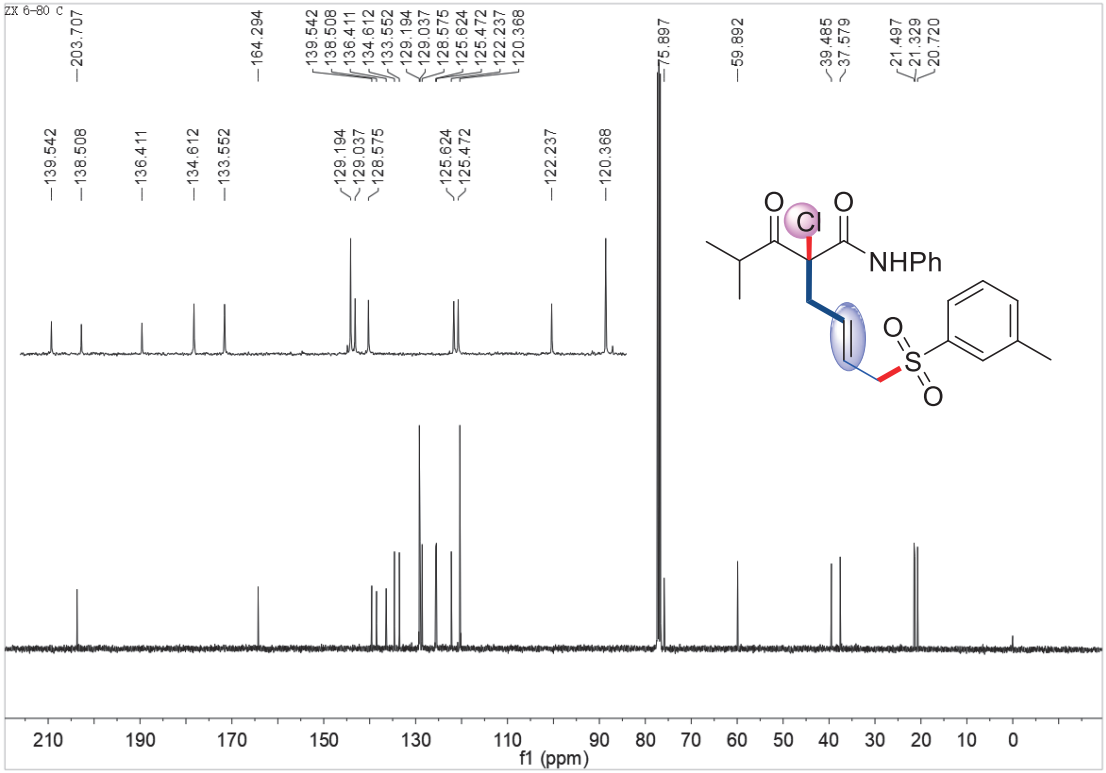
3k ^{19}F NMR



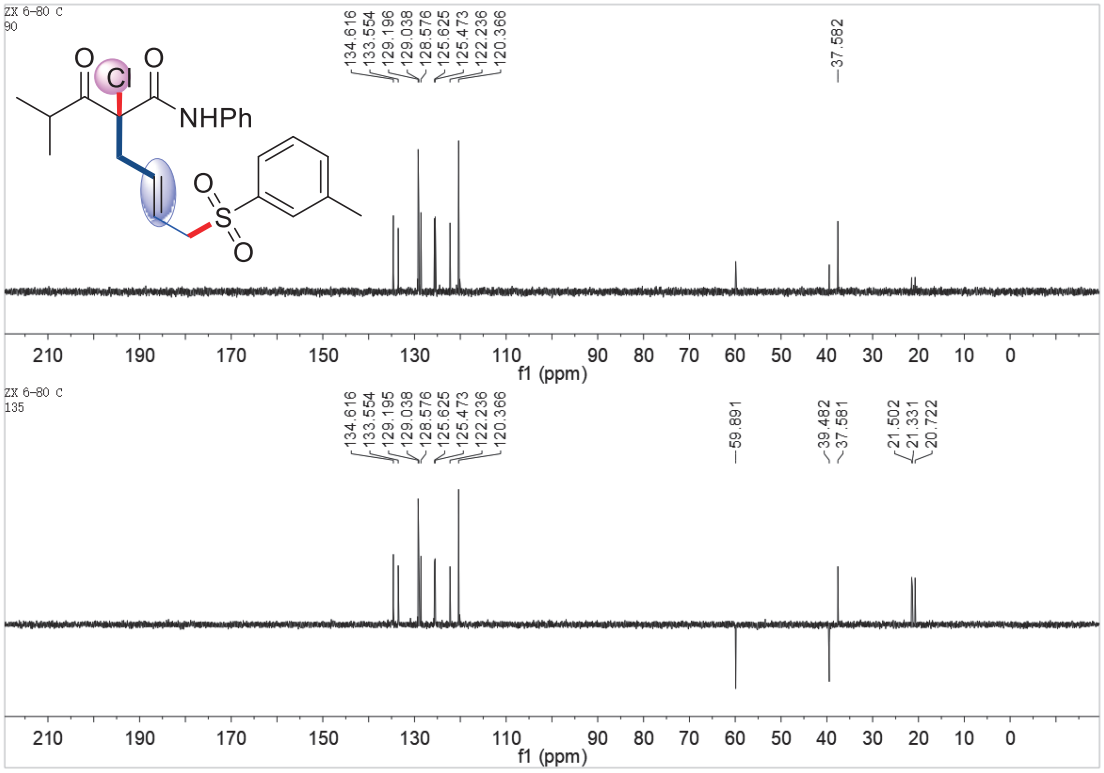
3l1, ^{1}H NMR



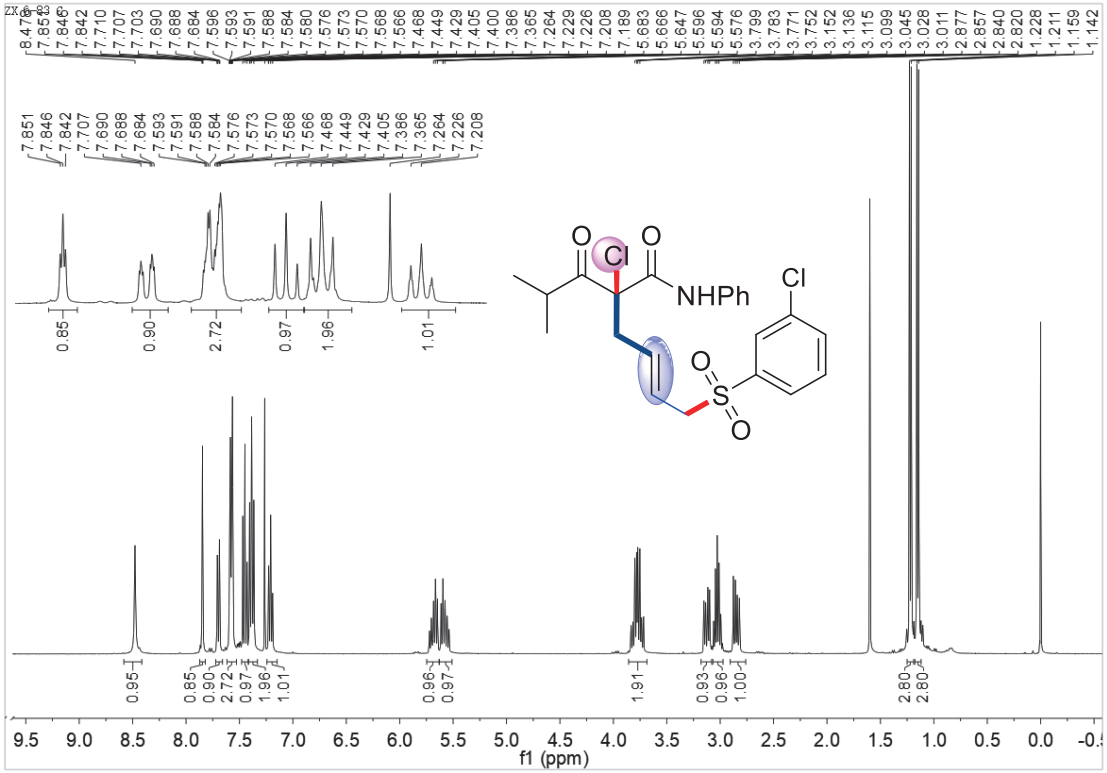
3l1, ^{13}C NMR



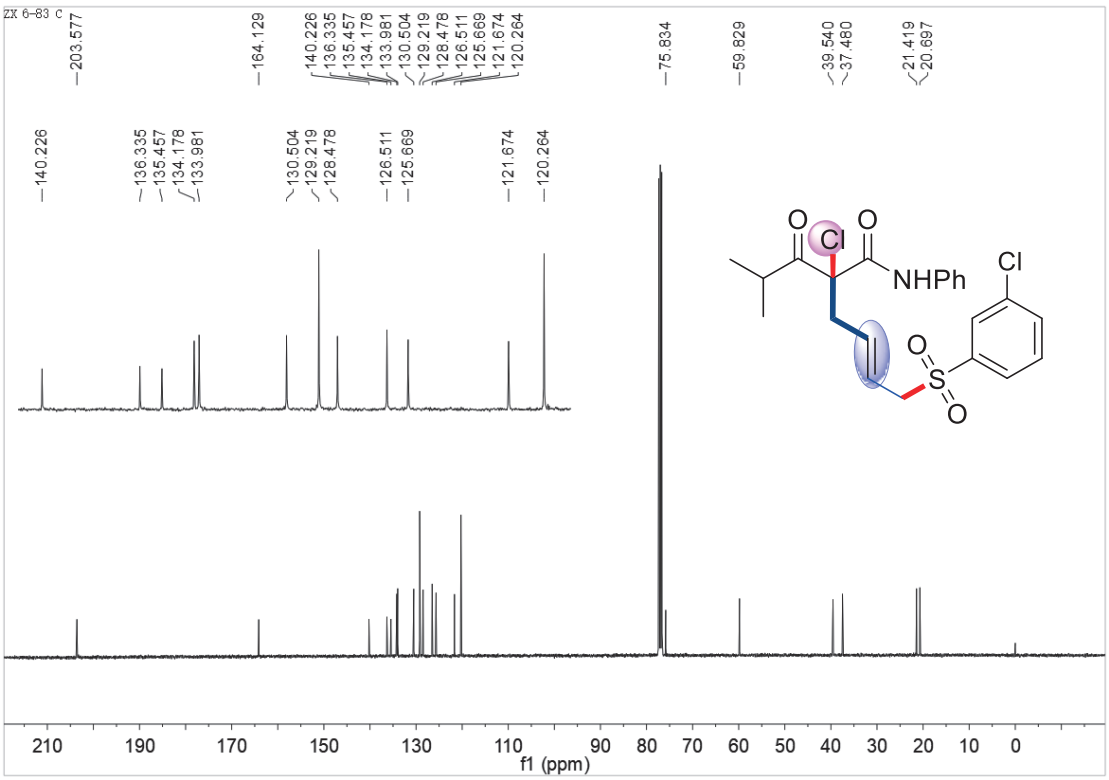
3l1, DEPT 90 and DEPT 135



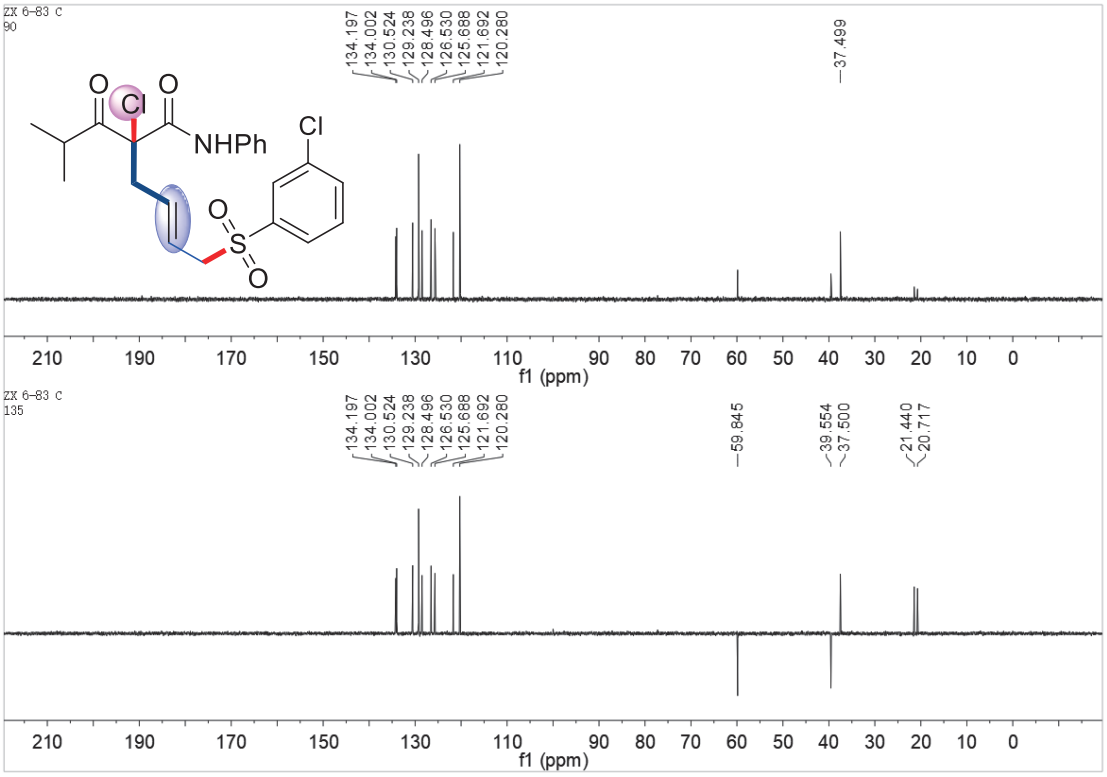
3l2, ^{1}H NMR



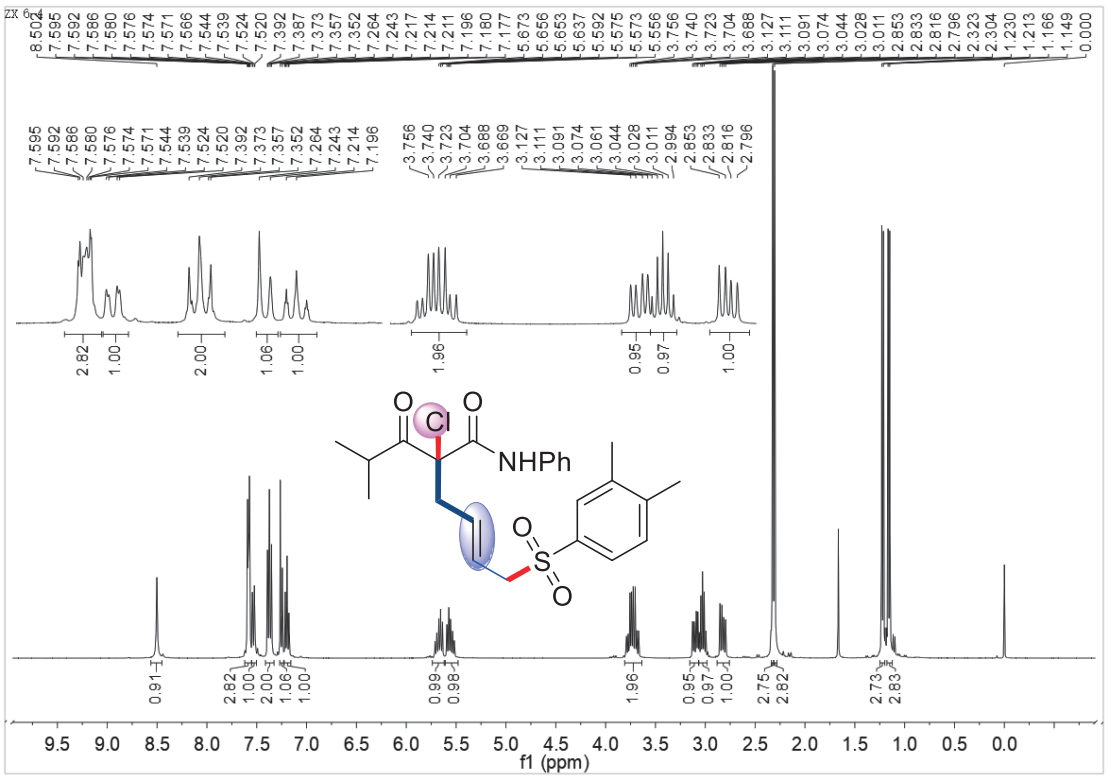
3l2, ^{13}C NMR



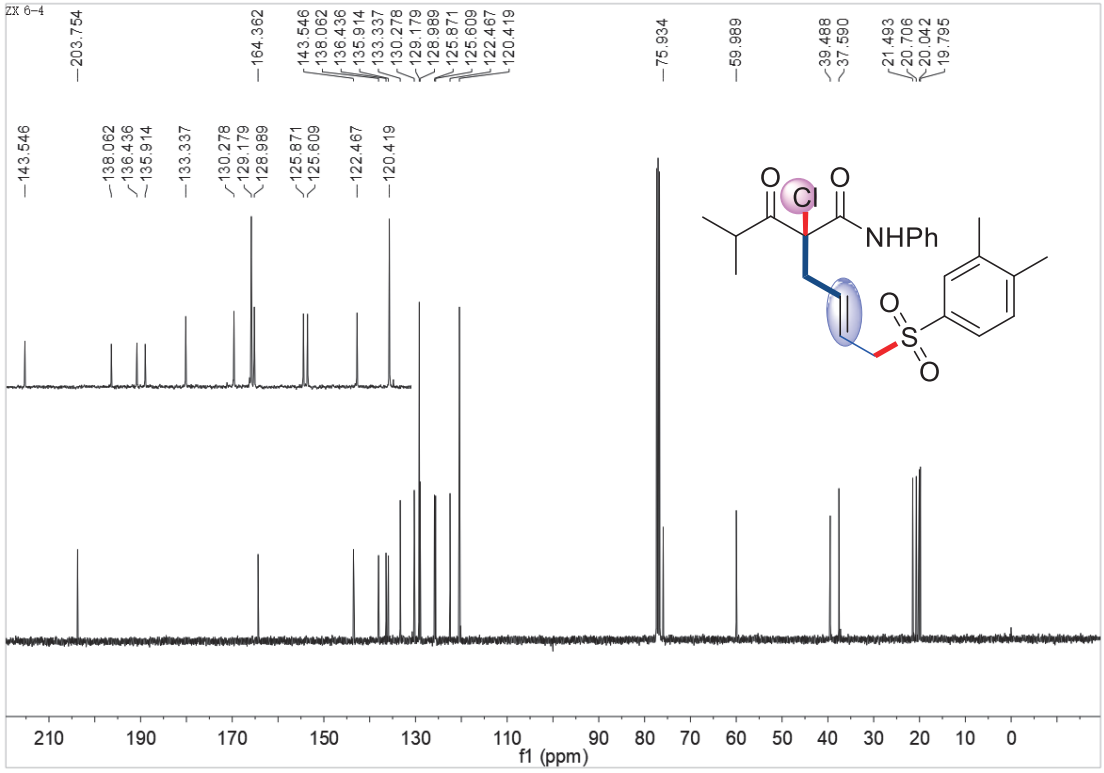
3l2 DEPT 90 and DEPT 135



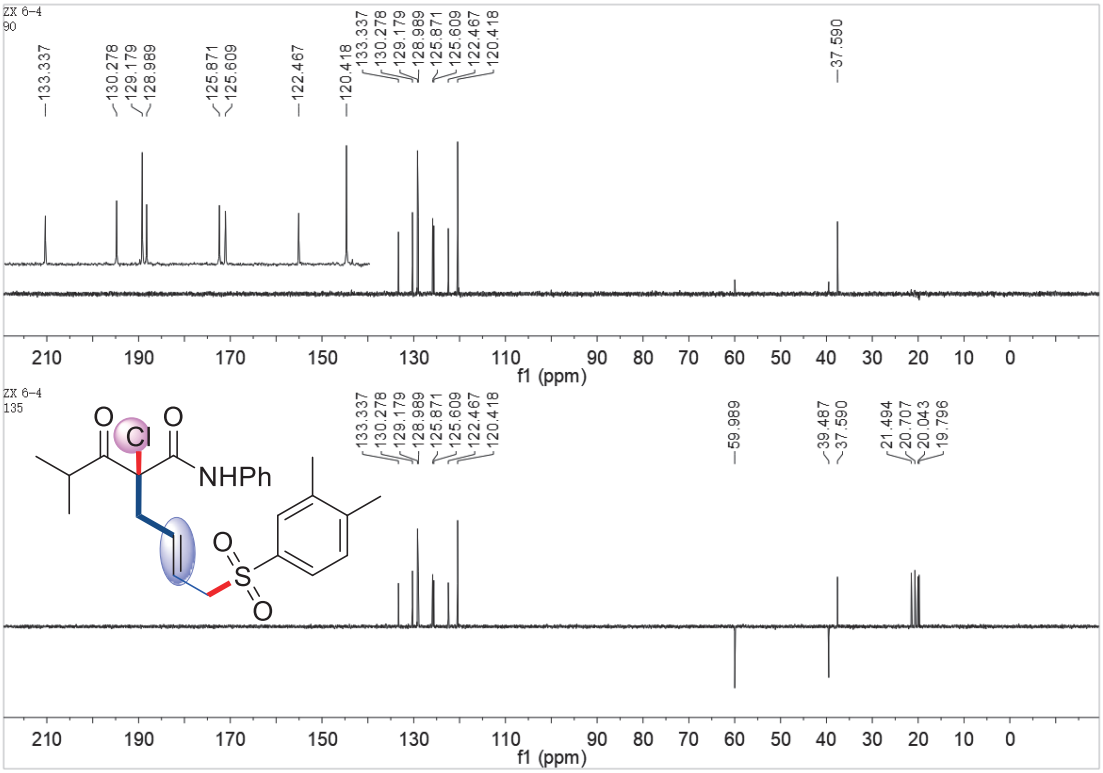
3m, ^{1}H NMR



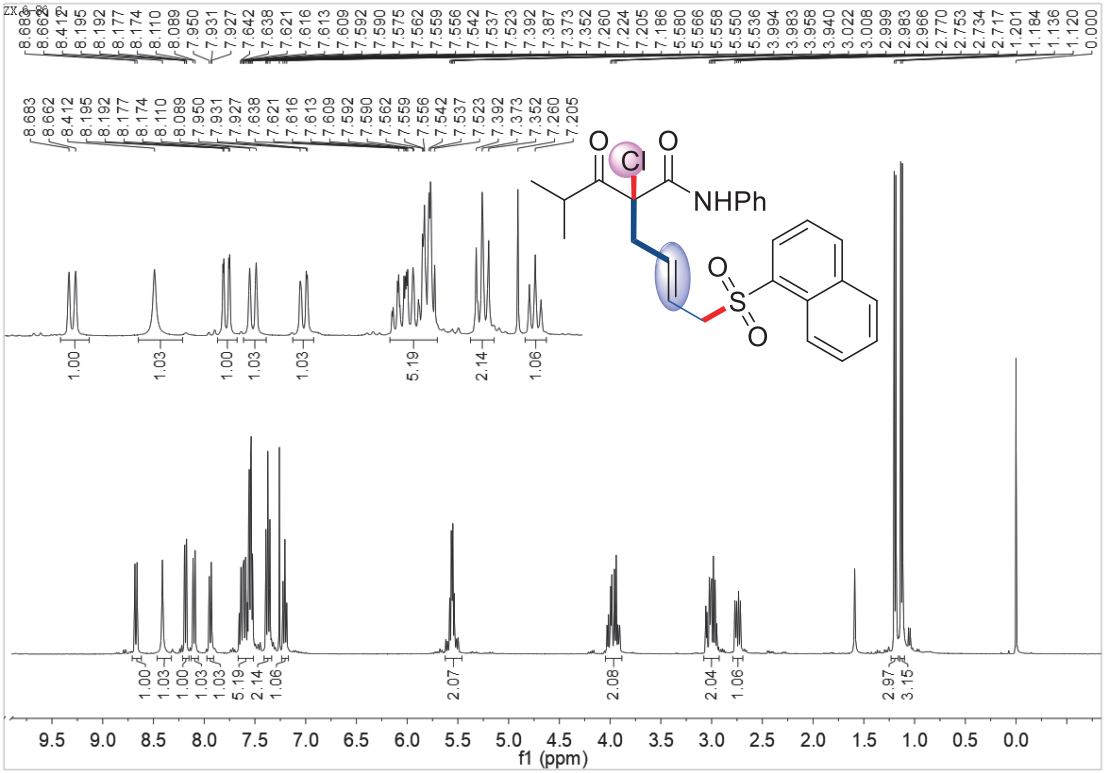
3m, ^{13}C NMR



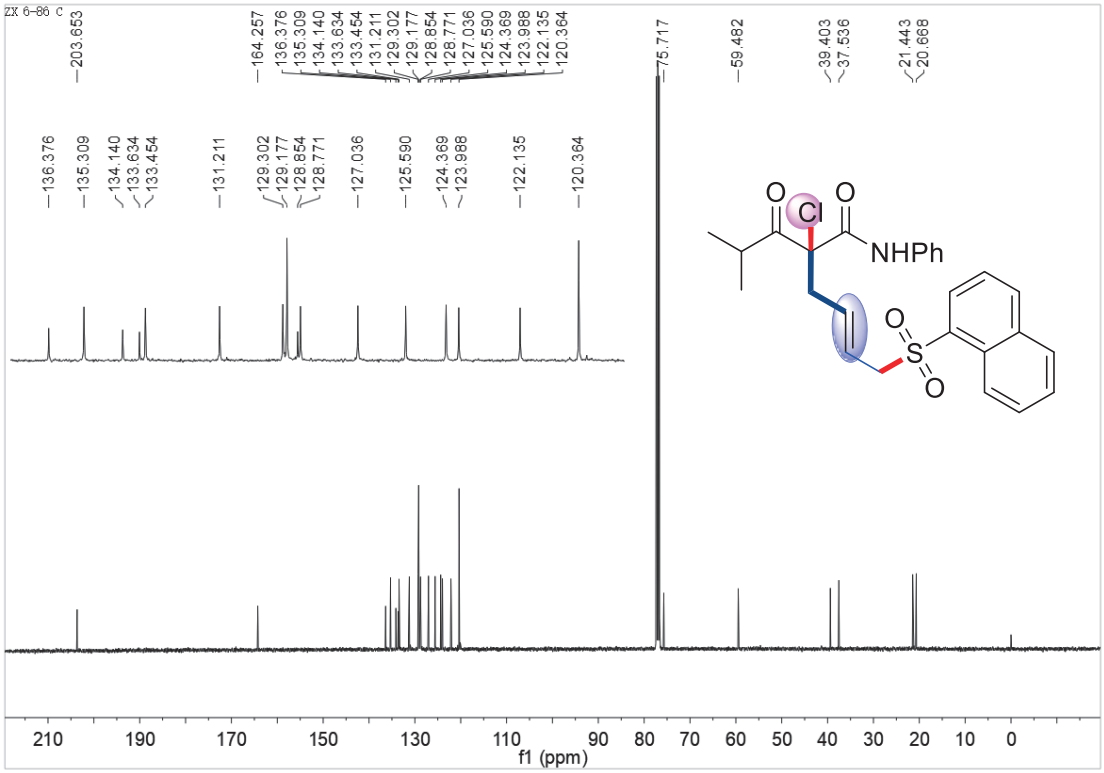
3m, DEPT 90 and DEPT 135



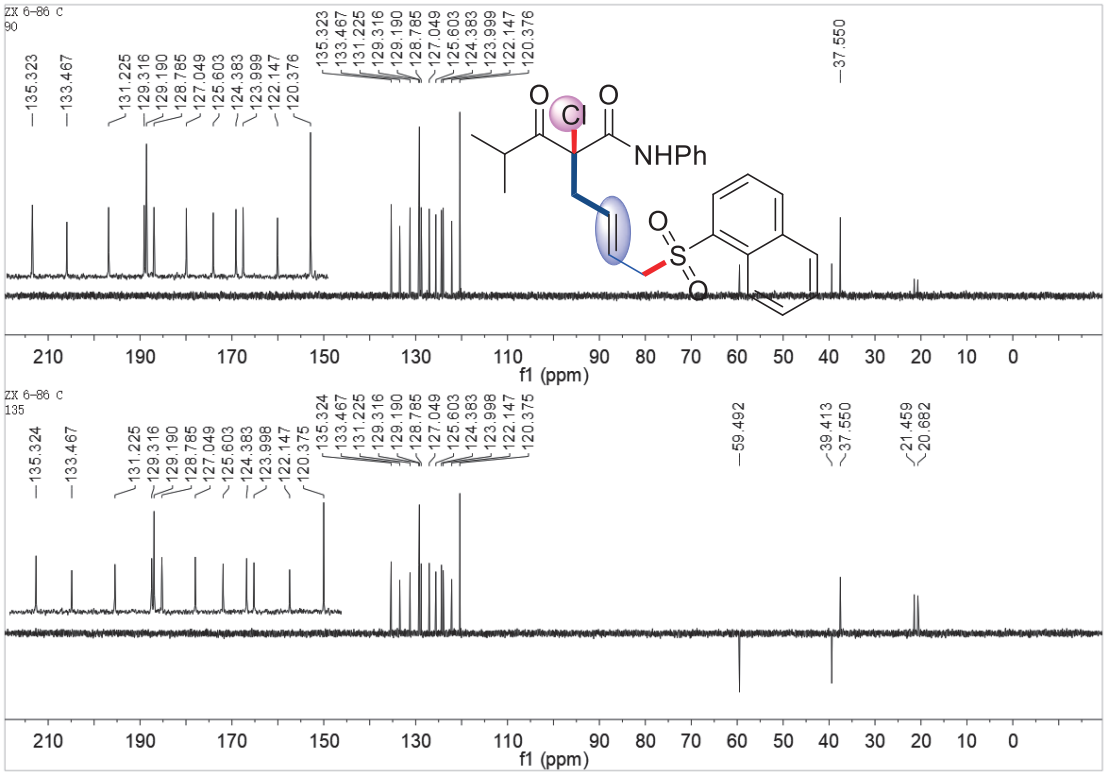
3n, ^{1}H NMR



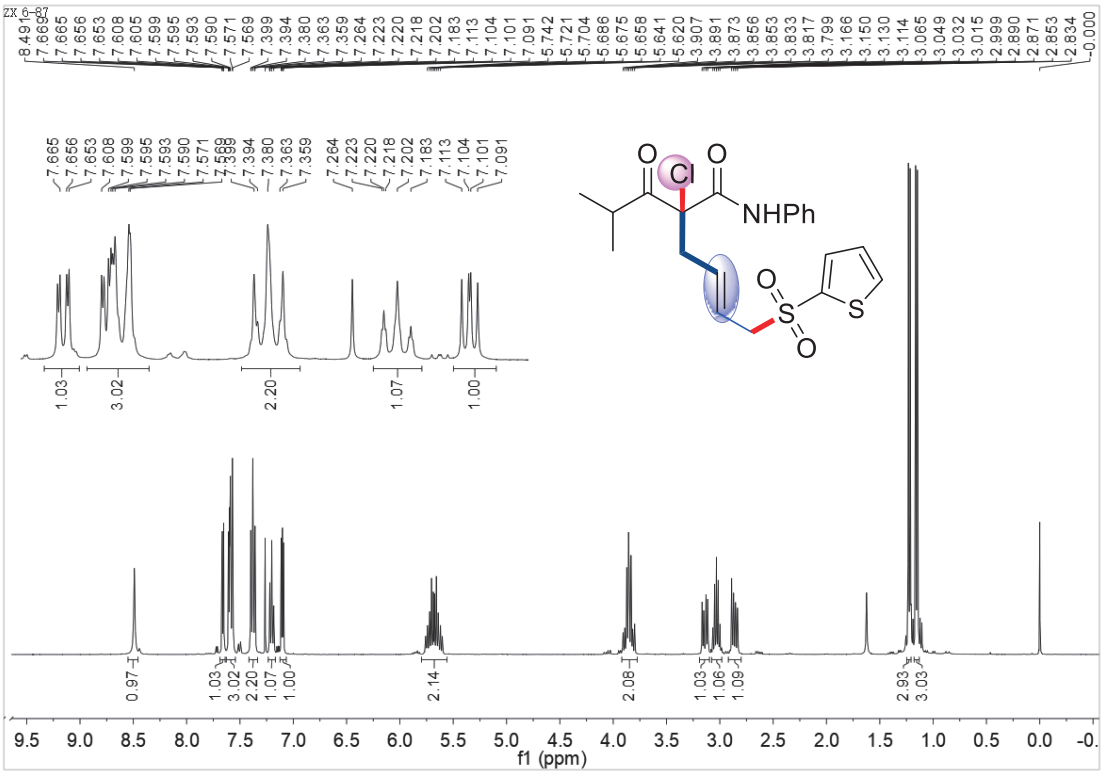
3n, ^{13}C NMR



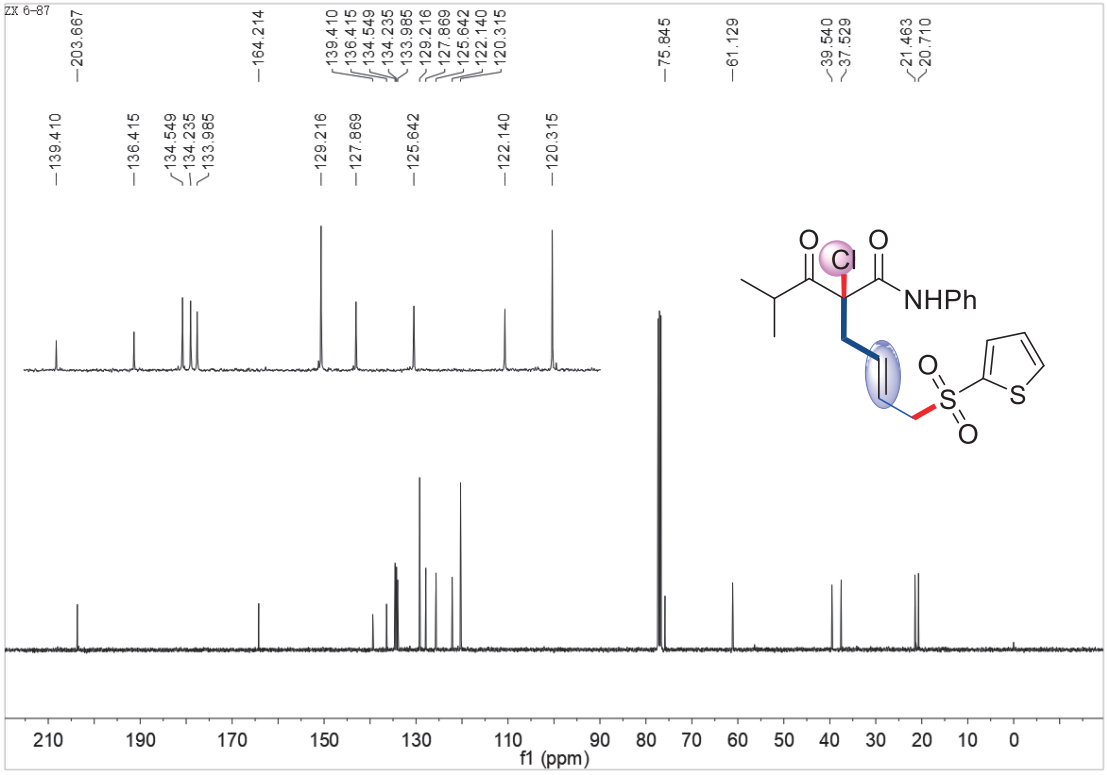
3n, DEPT 90 and DEPT 135



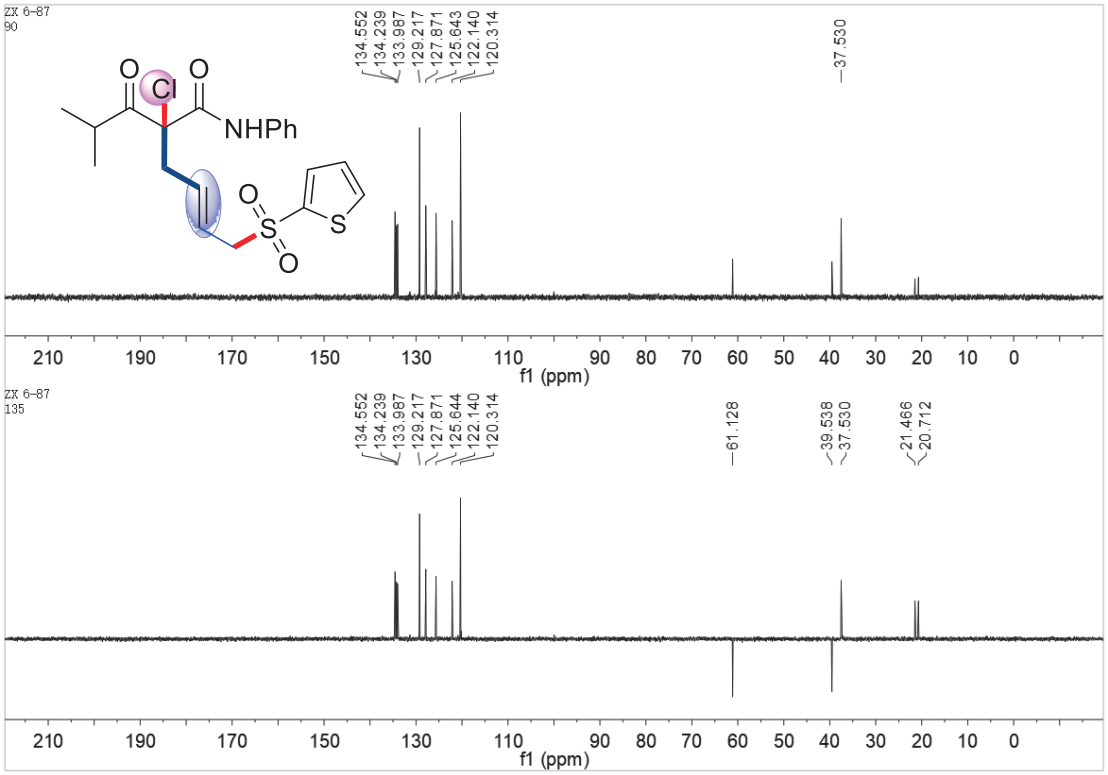
3o, ^{1}H NMR



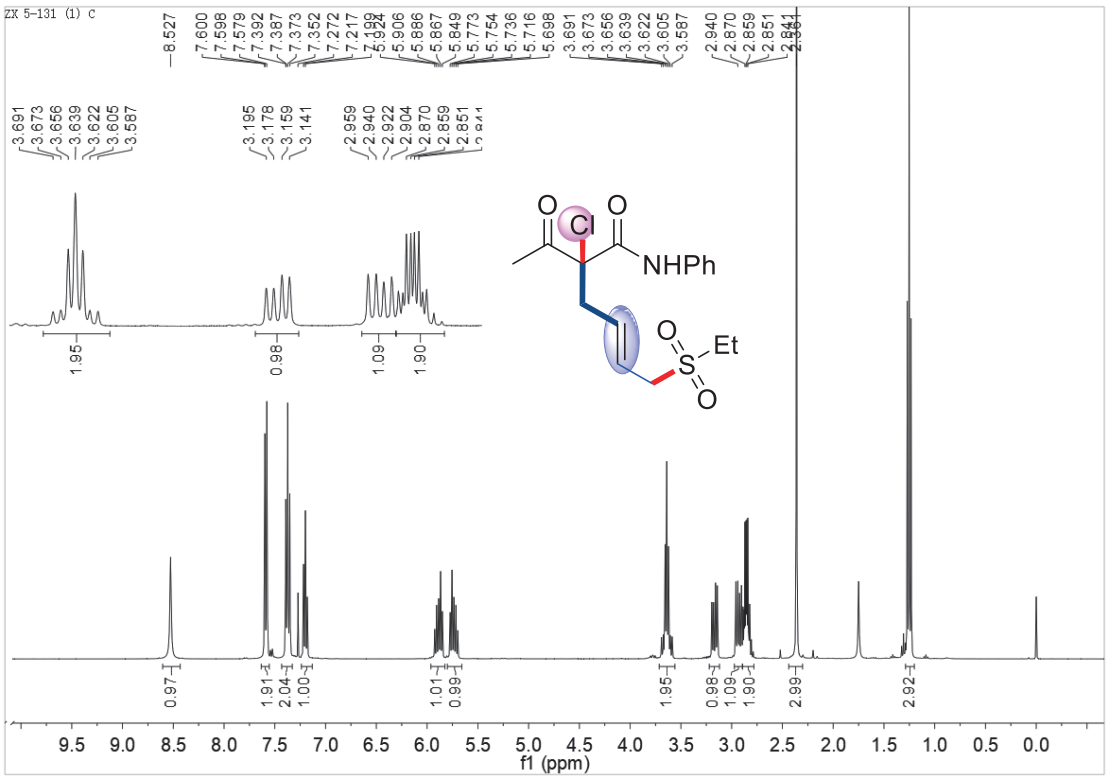
3o, ^{13}C NMR



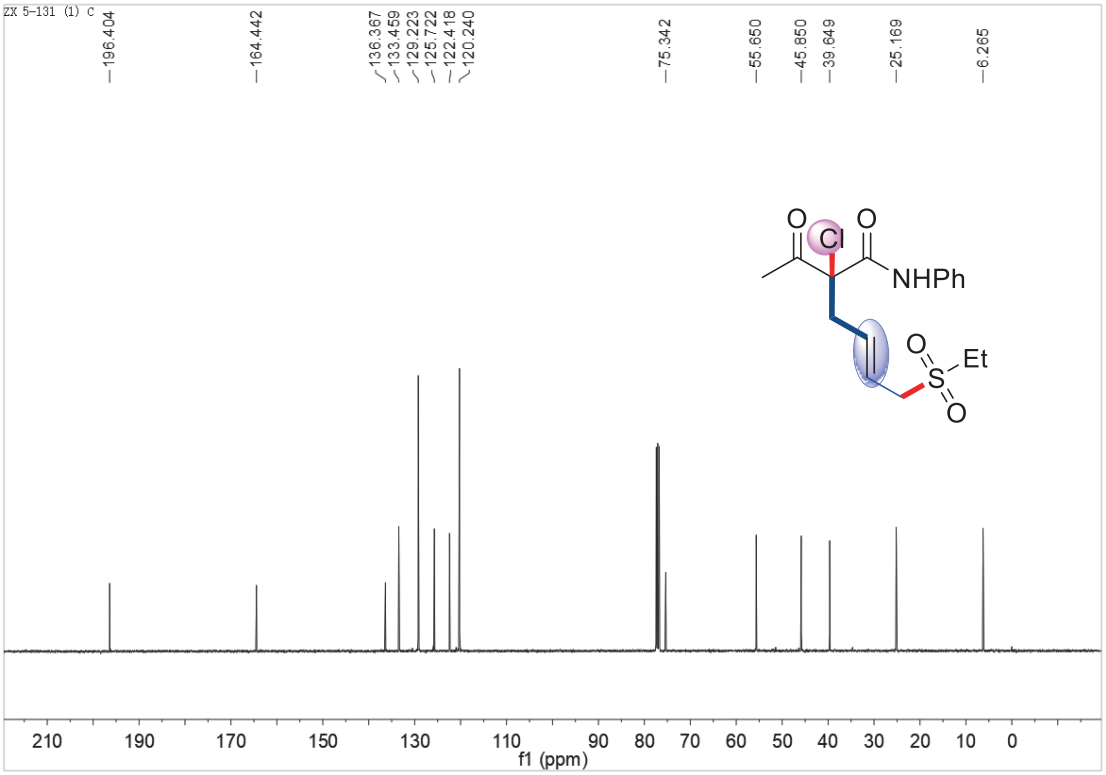
3o DEPT 90 and DEPT 135



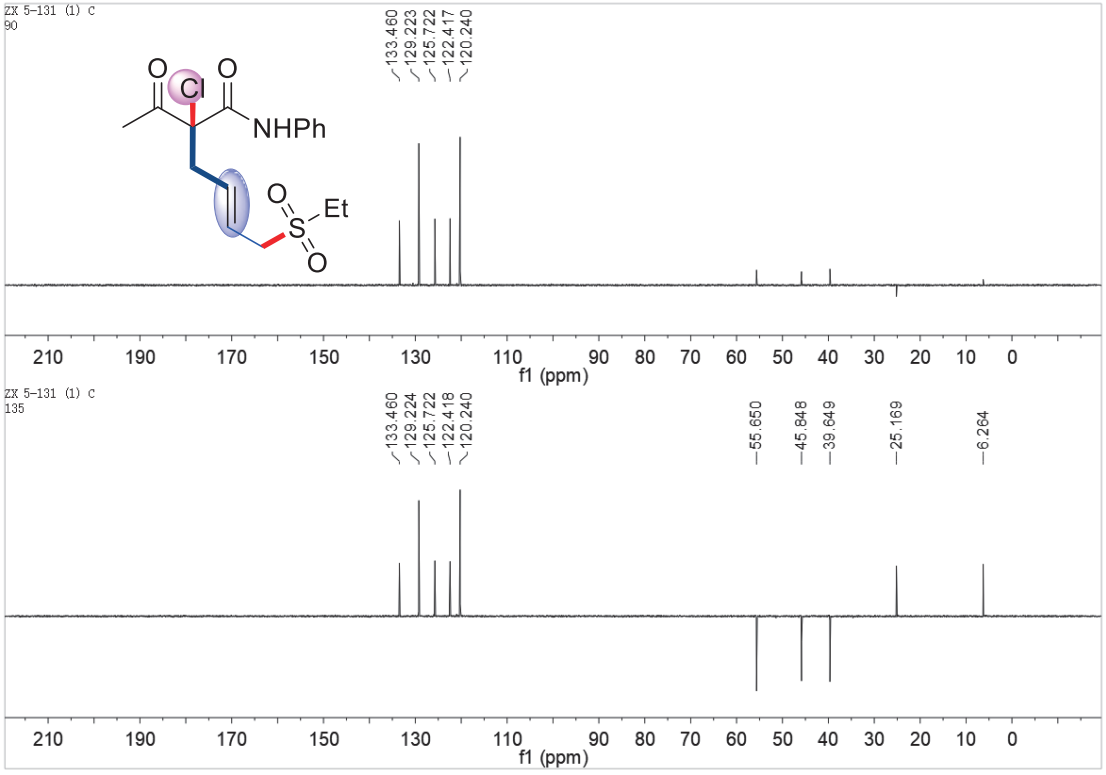
3p, ^{1}H NMR



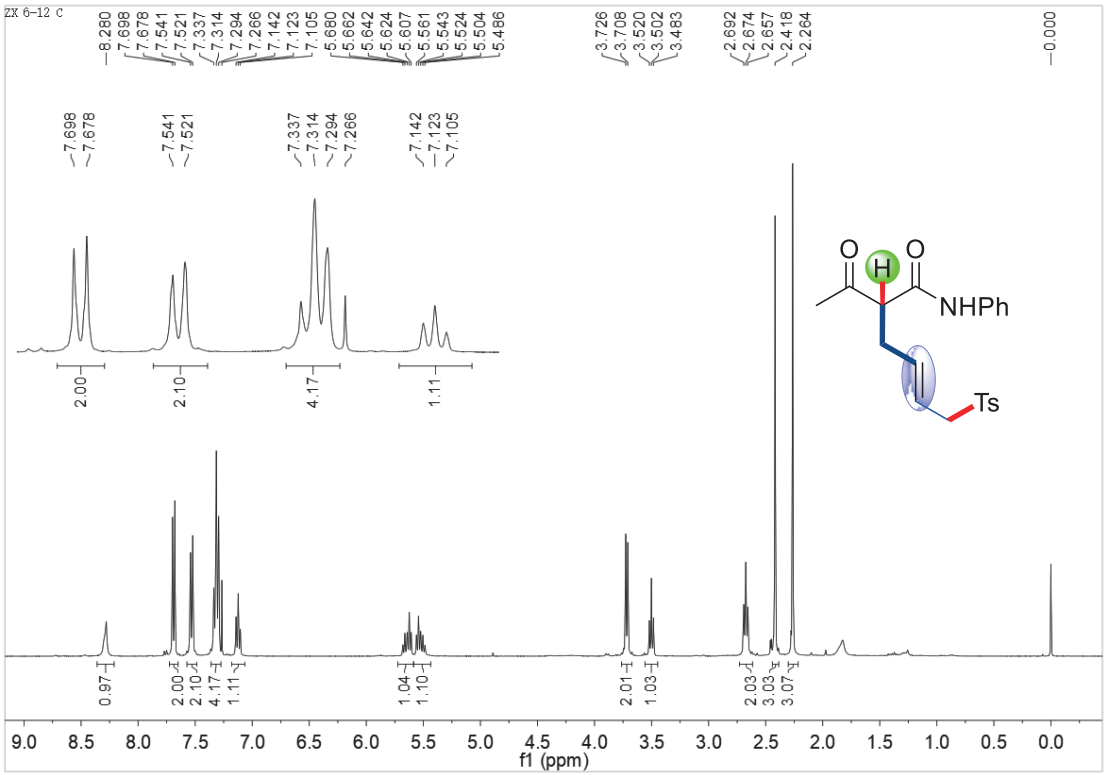
3p, ^{13}C NMR



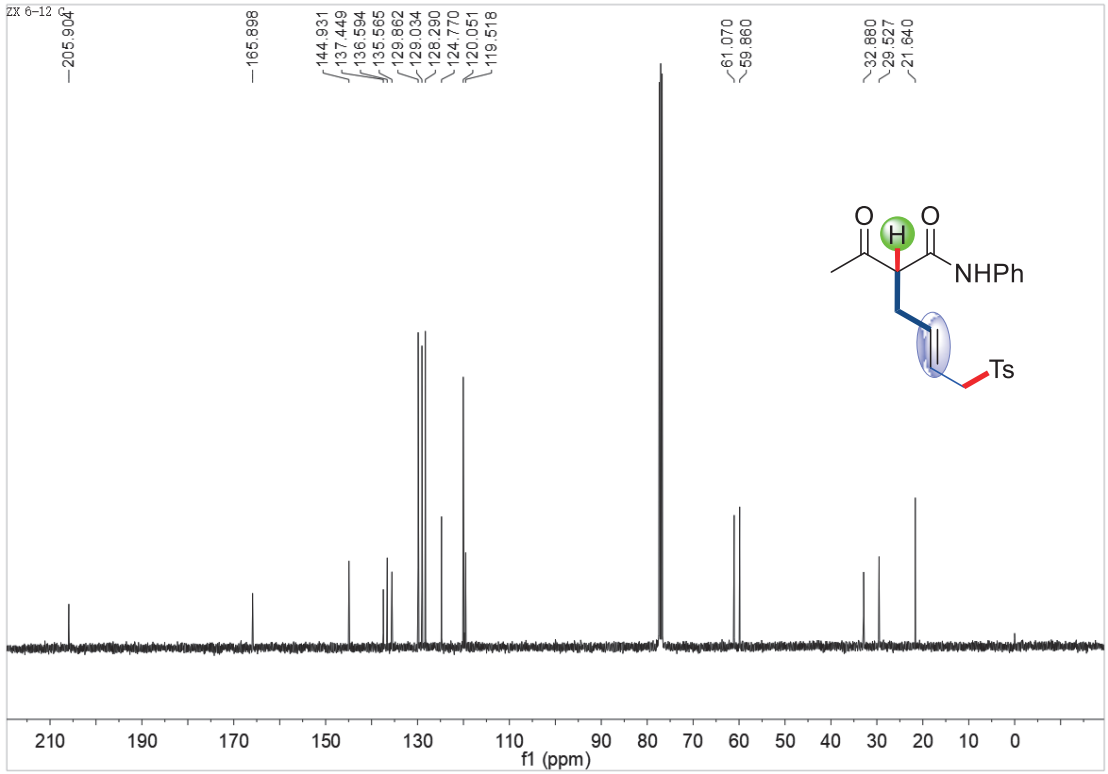
3p, DEPT 90 and DEPT 135



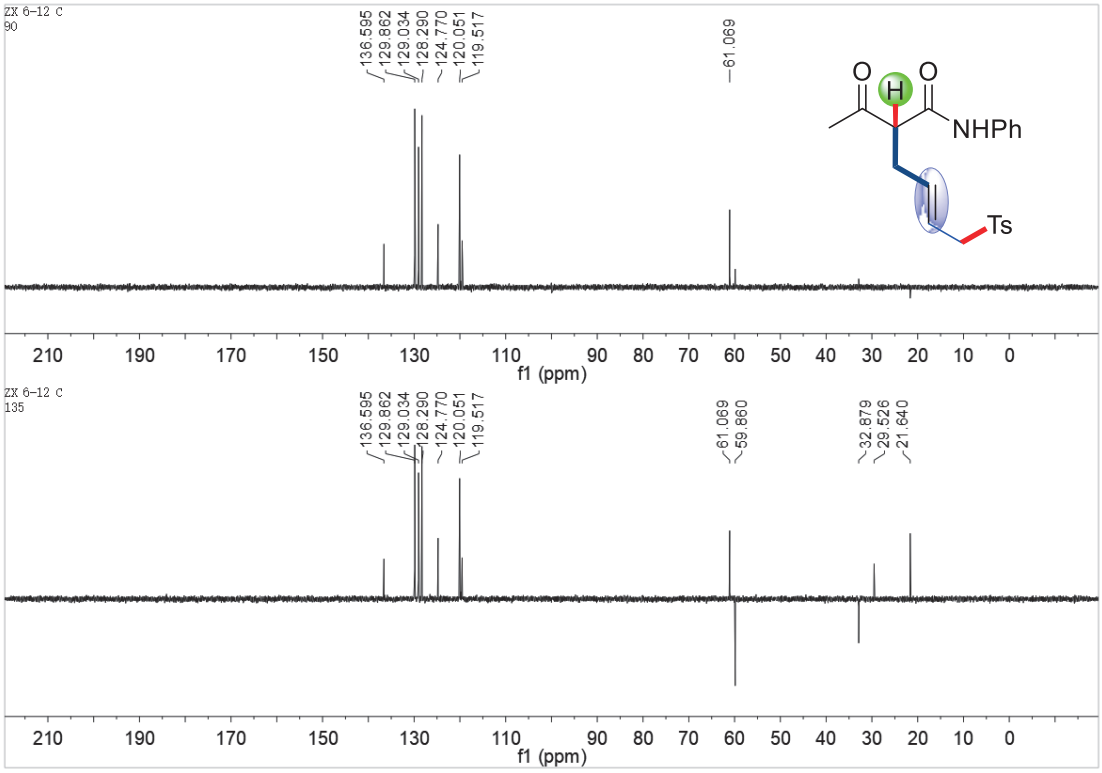
4a, ^{1}H NMR



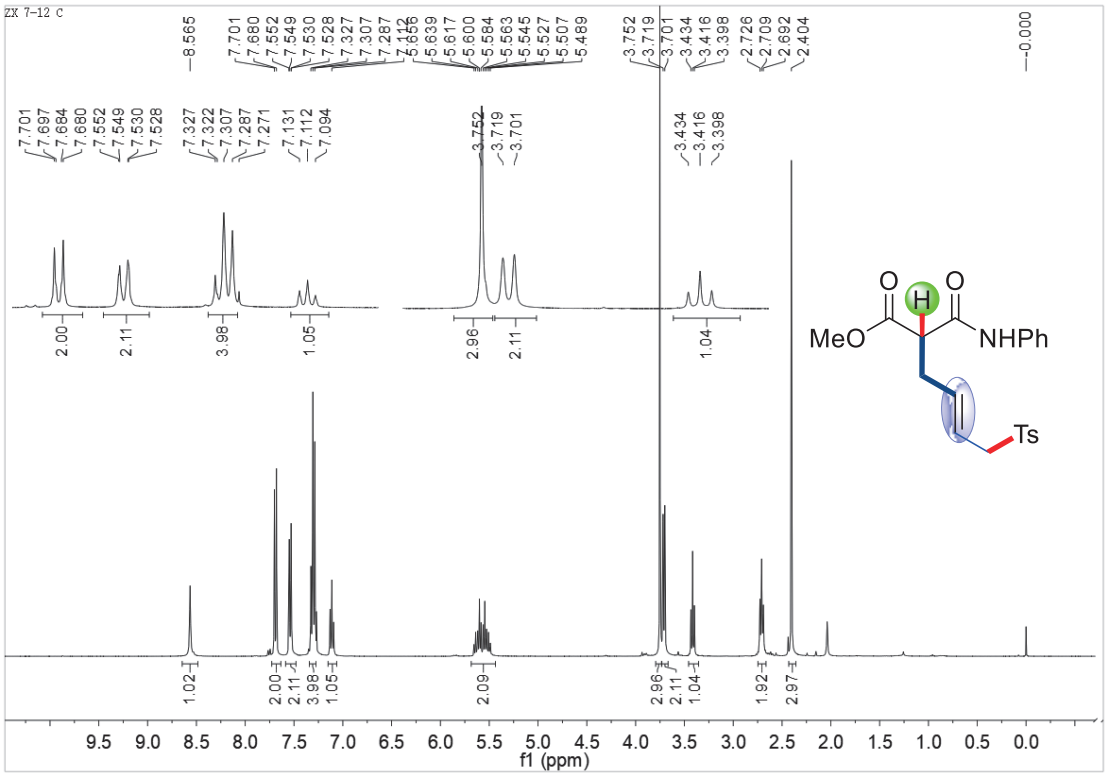
4a, ^{13}C NMR



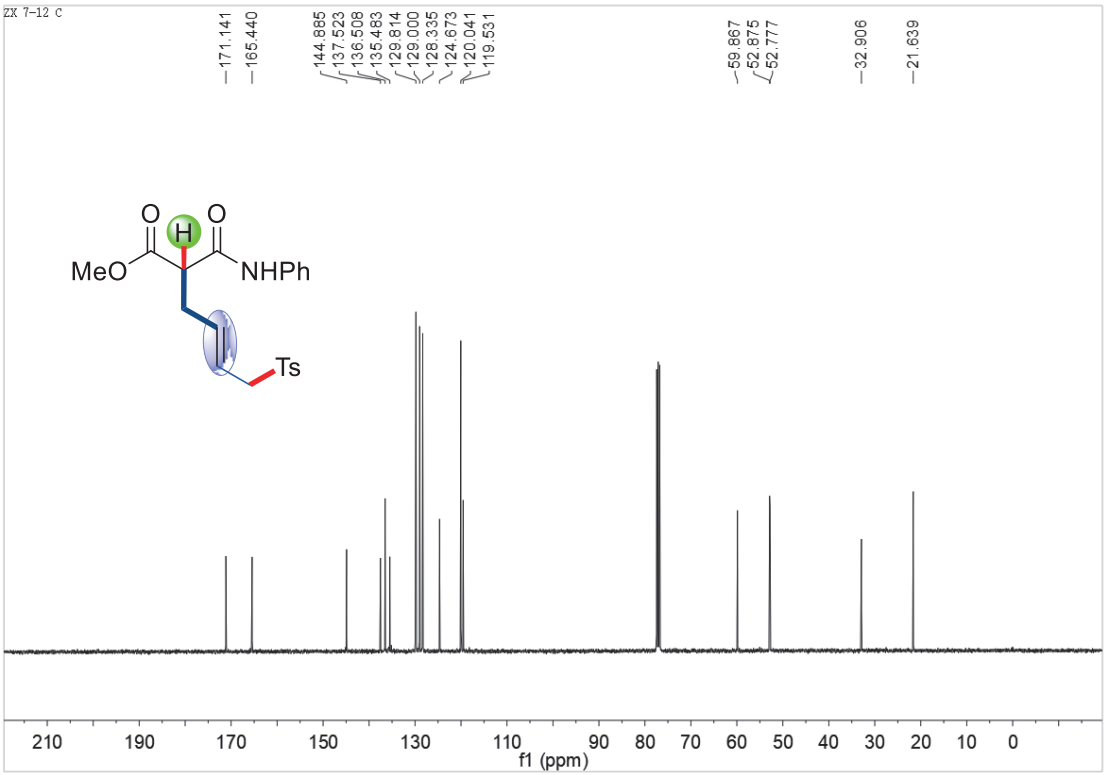
4a, DEPT 90 and DEPT 135



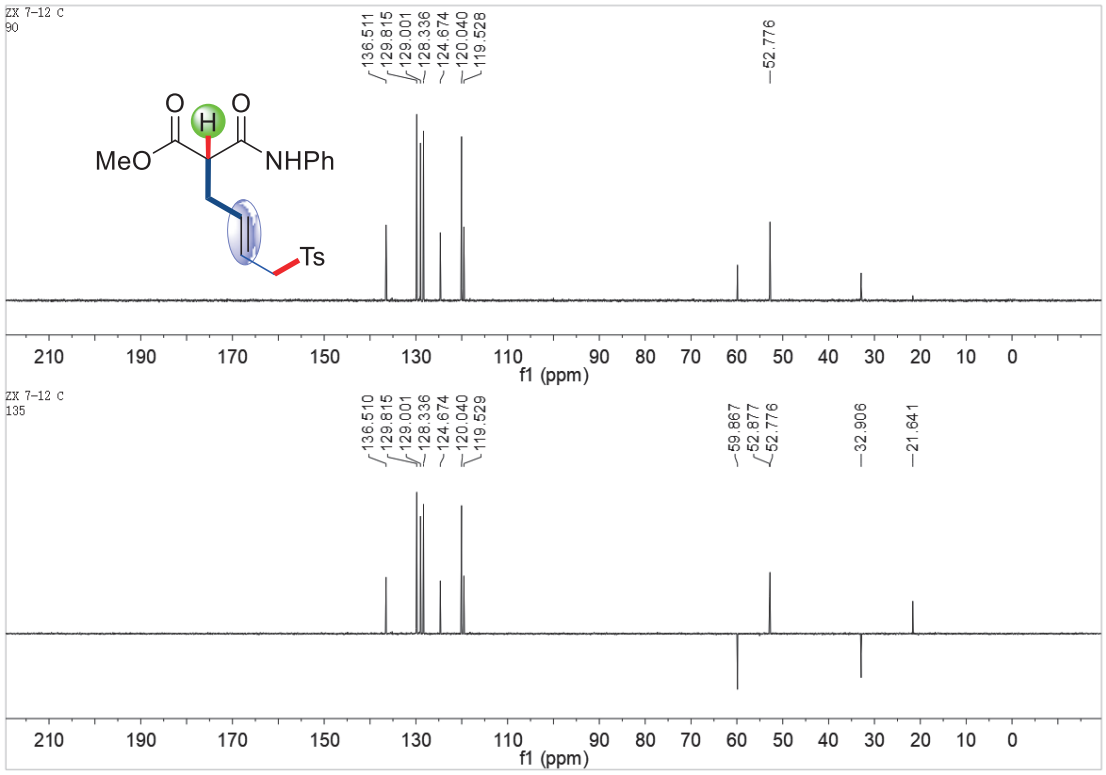
4a1, ^{1}H NMR



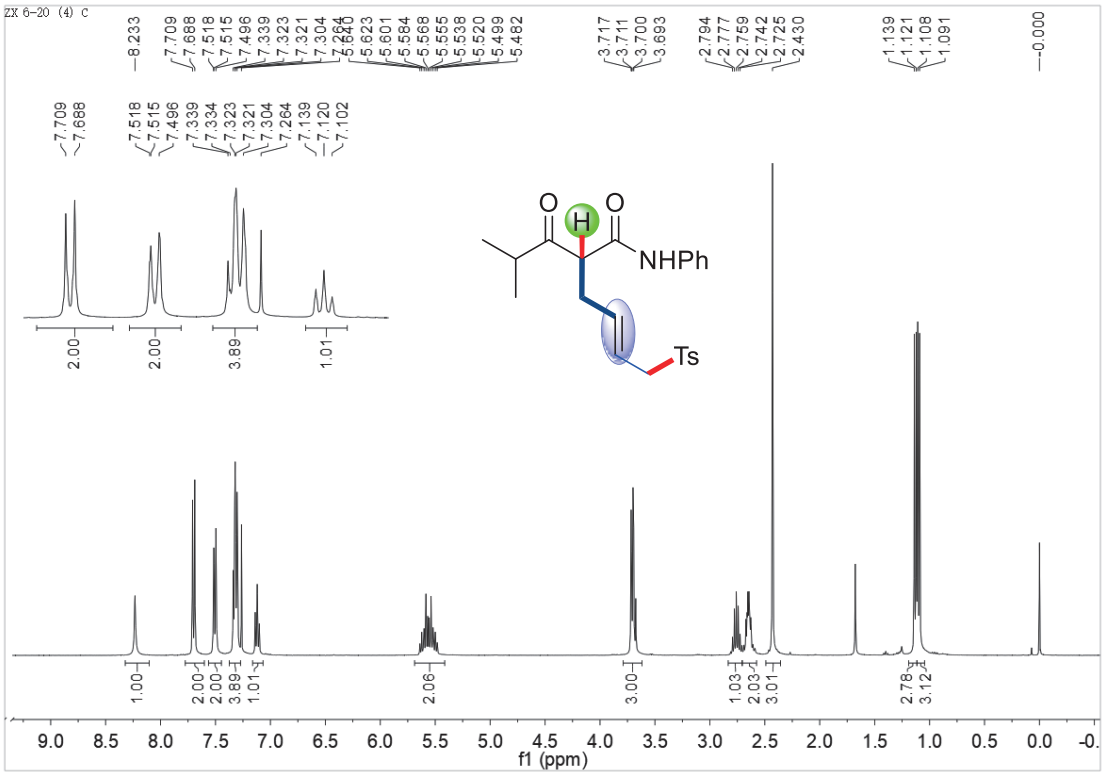
4a1, ^{13}C NMR



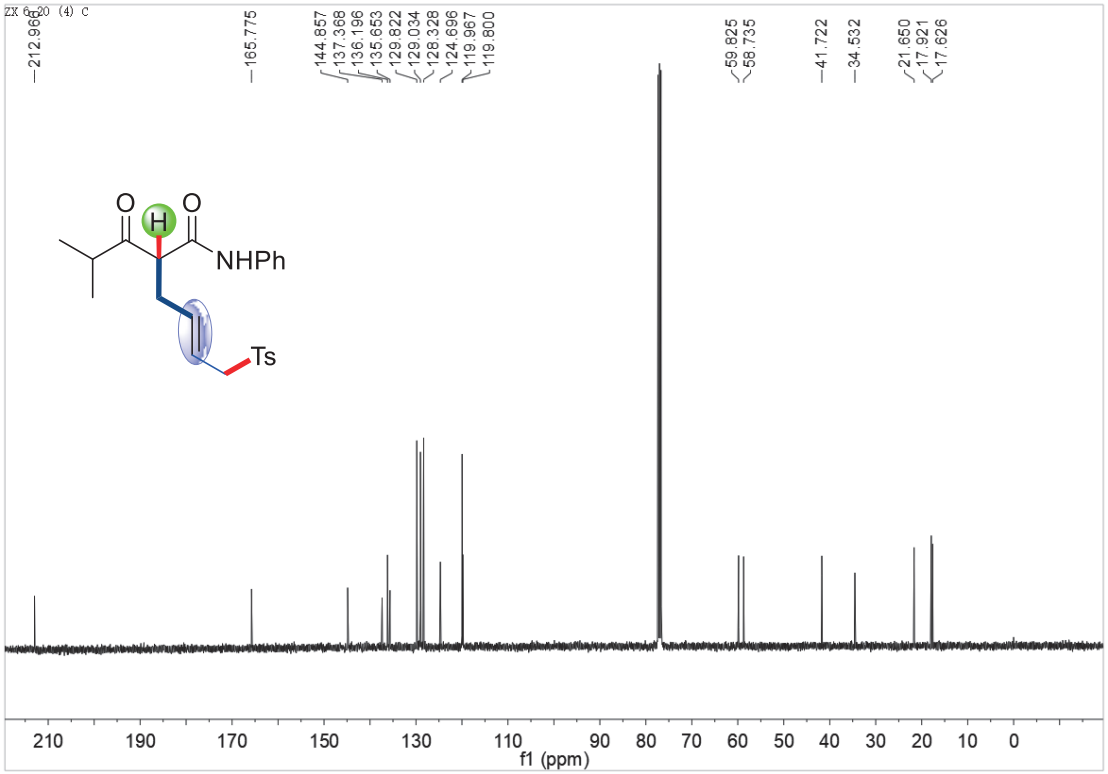
4a1, DEPT 90 and DEPT 135



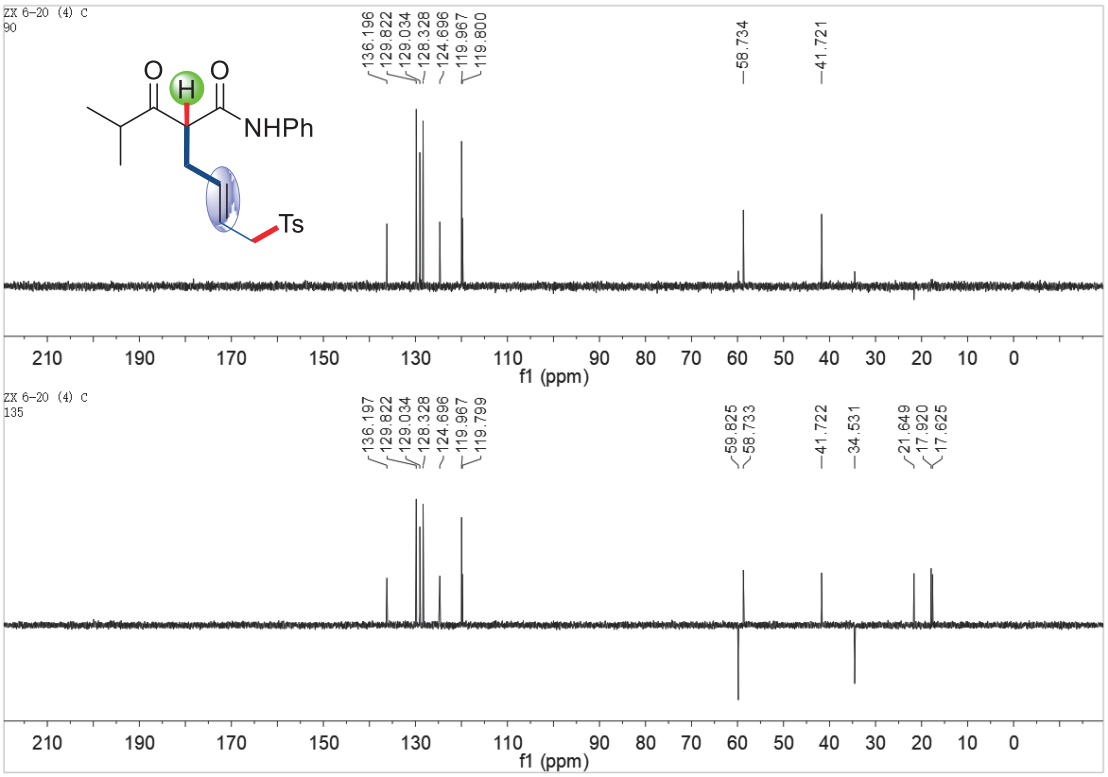
4a2, ^{1}H NMR



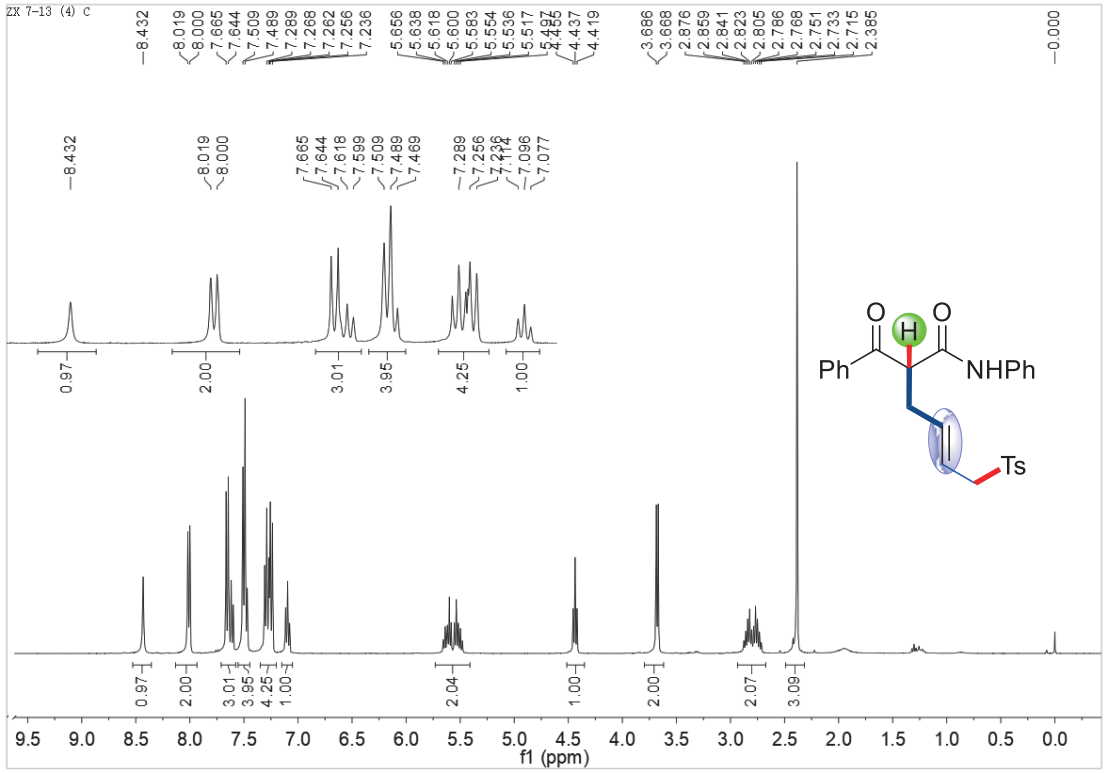
4a2, ^{13}C NMR



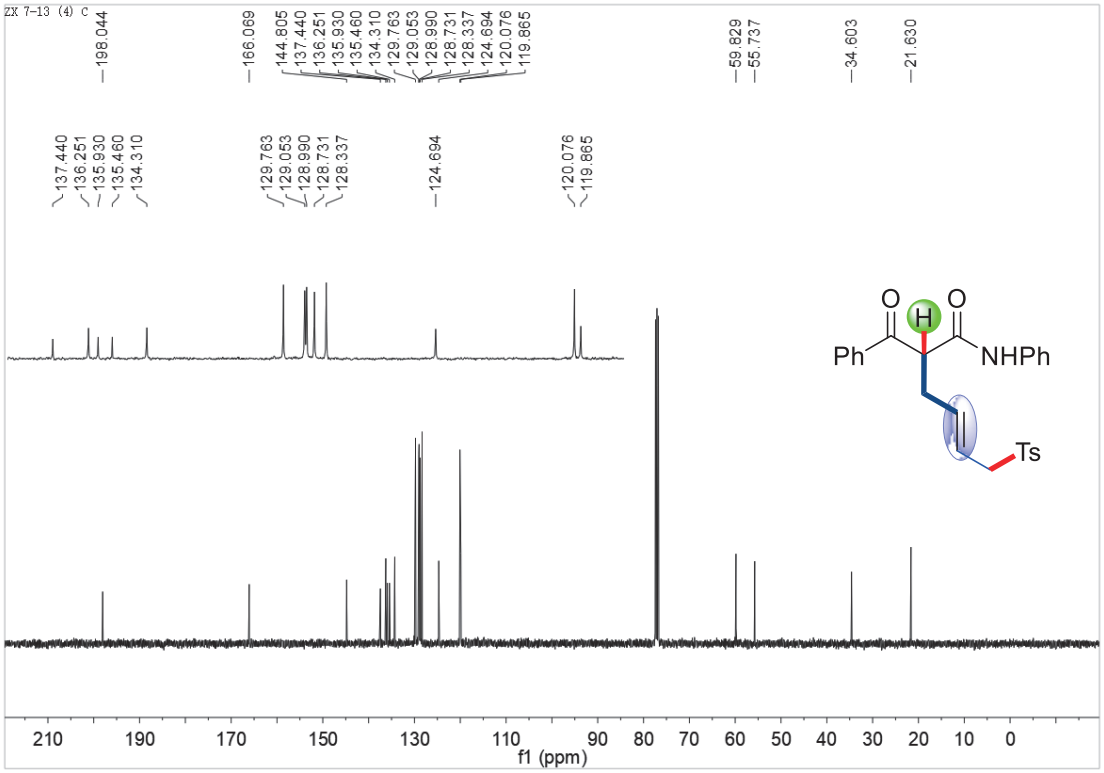
4a2, DEPT 90 and DEPT 135



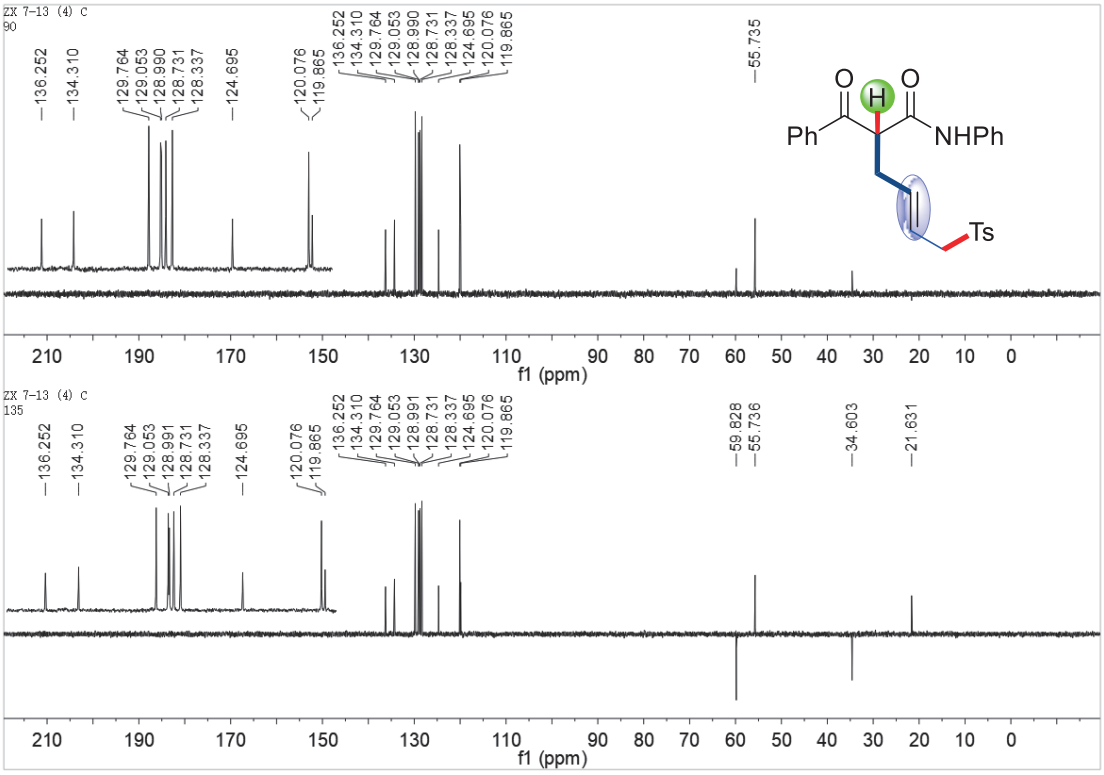
4a3, ^{1}H NMR



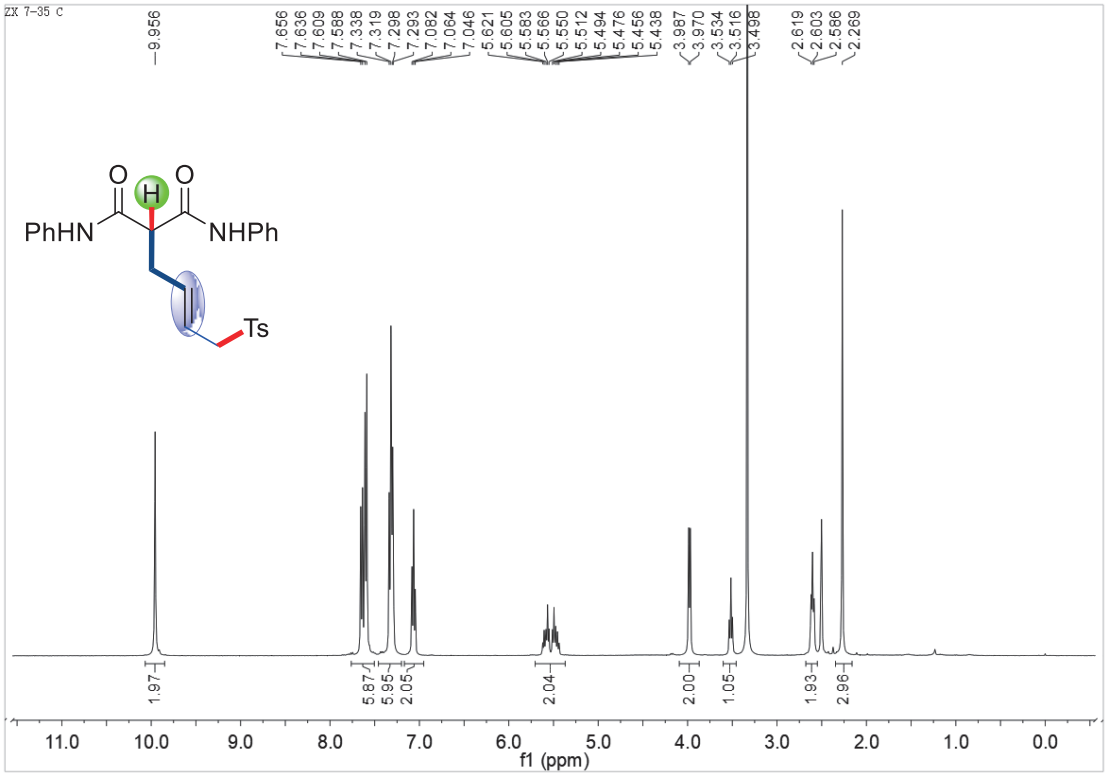
4a3, ^{13}C NMR



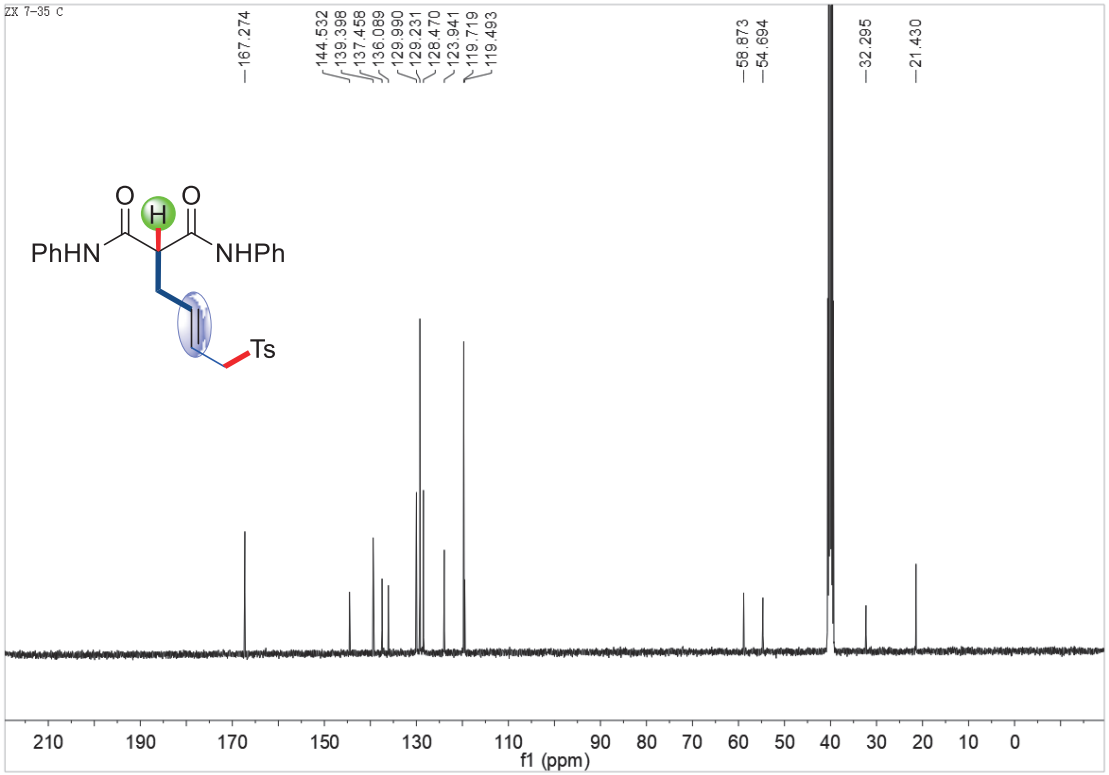
4a3, DEPT 90 and DEPT 135



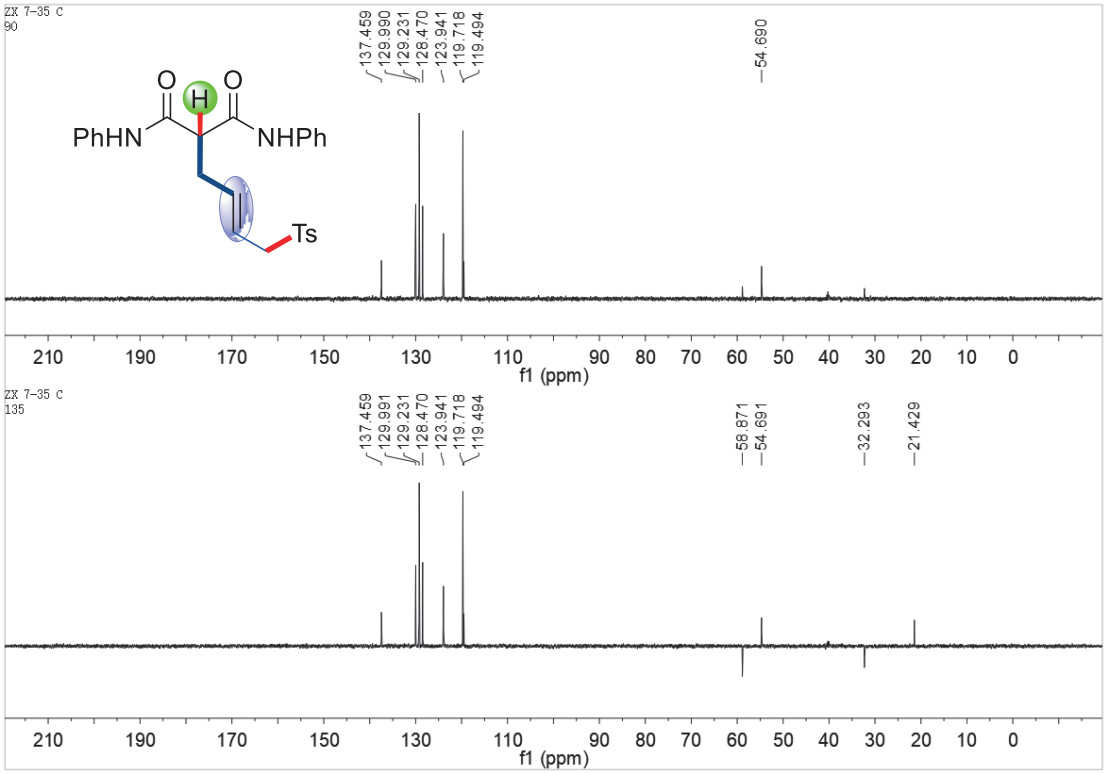
4a4, ^{1}H NMR



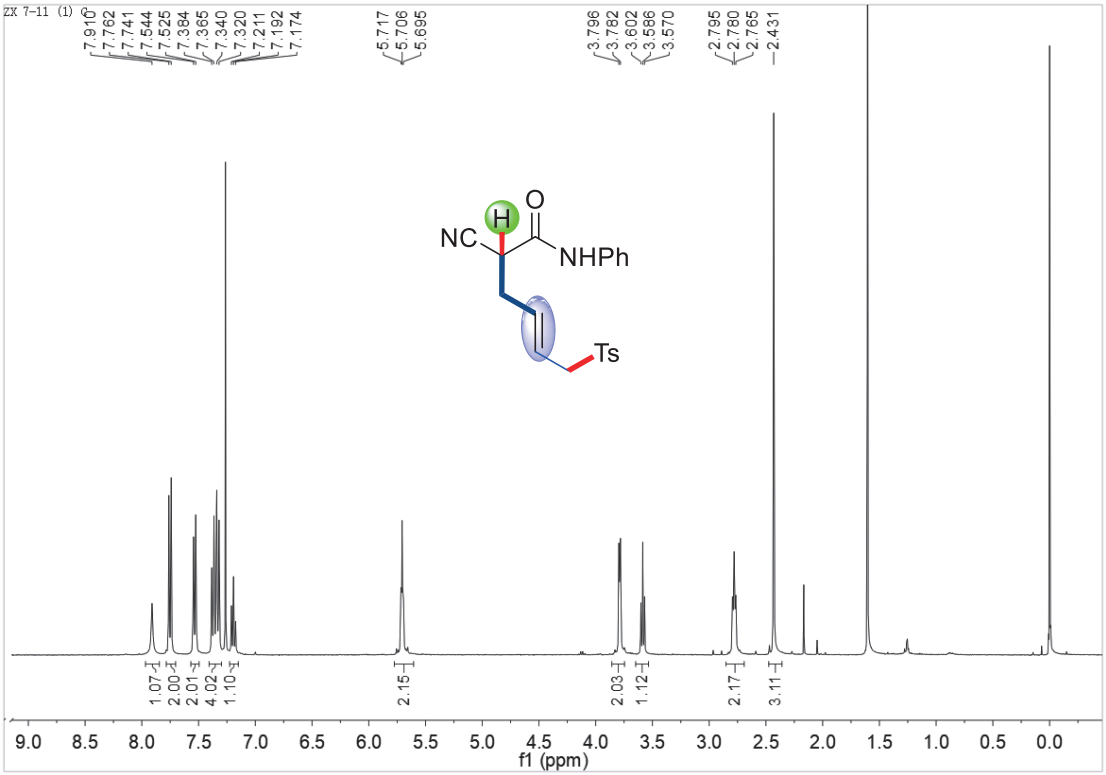
4a4, ^{13}C NMR



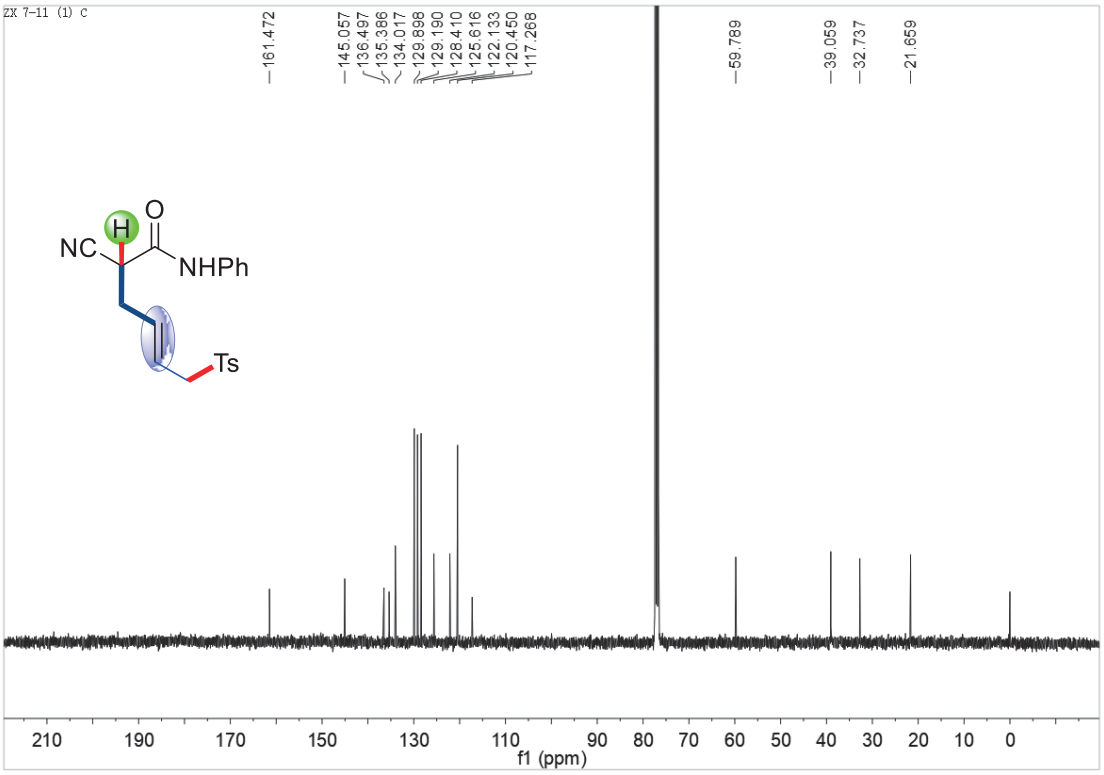
4a4, DEPT 90 and DEPT 135



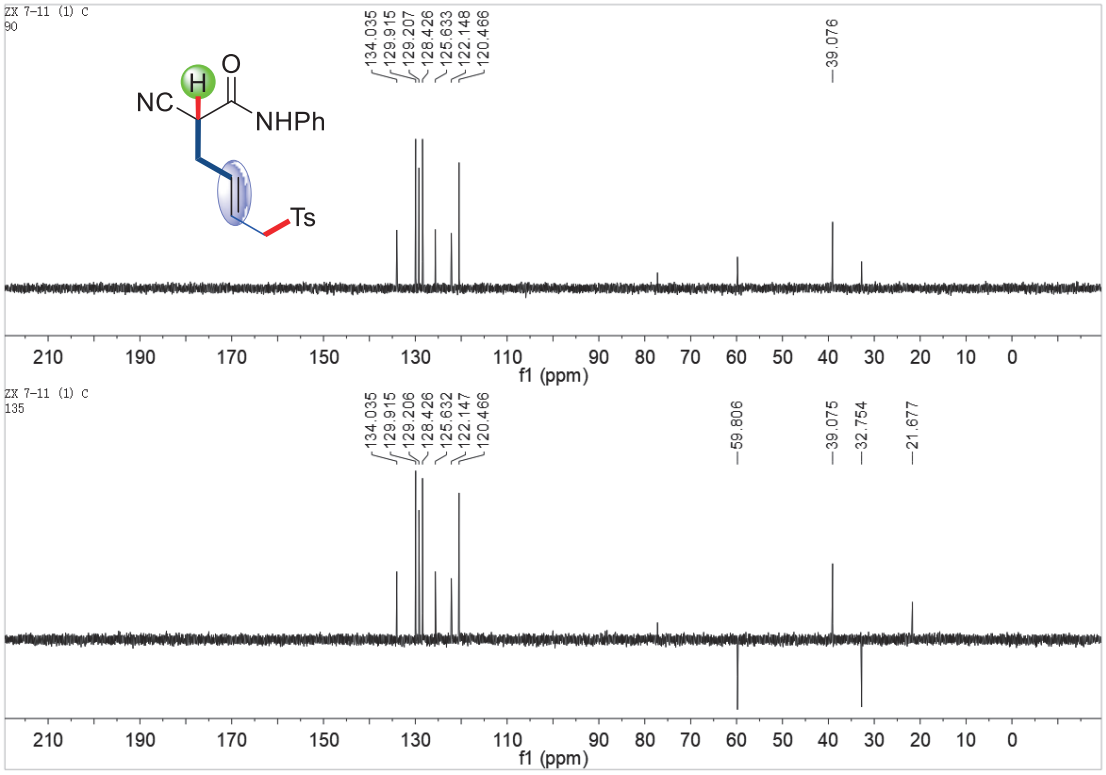
4a5, ^{1}H NMR



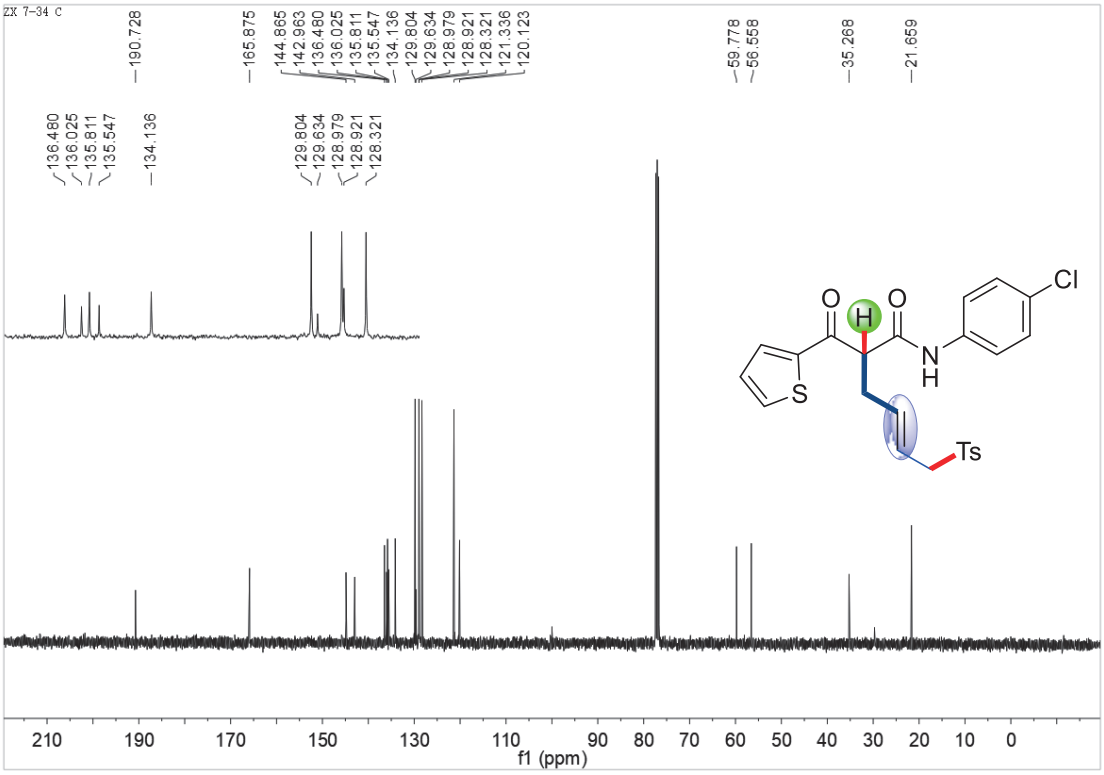
4a5, ^{13}C NMR



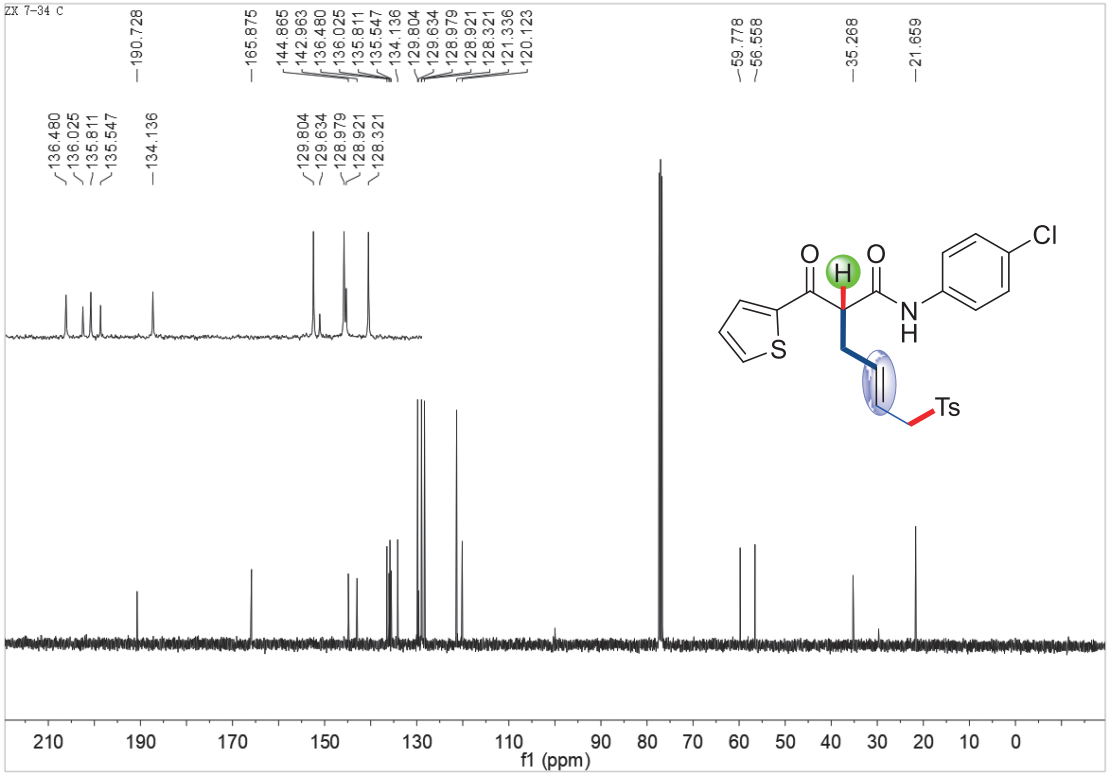
4a5, DEPT 90 and DEPT 135



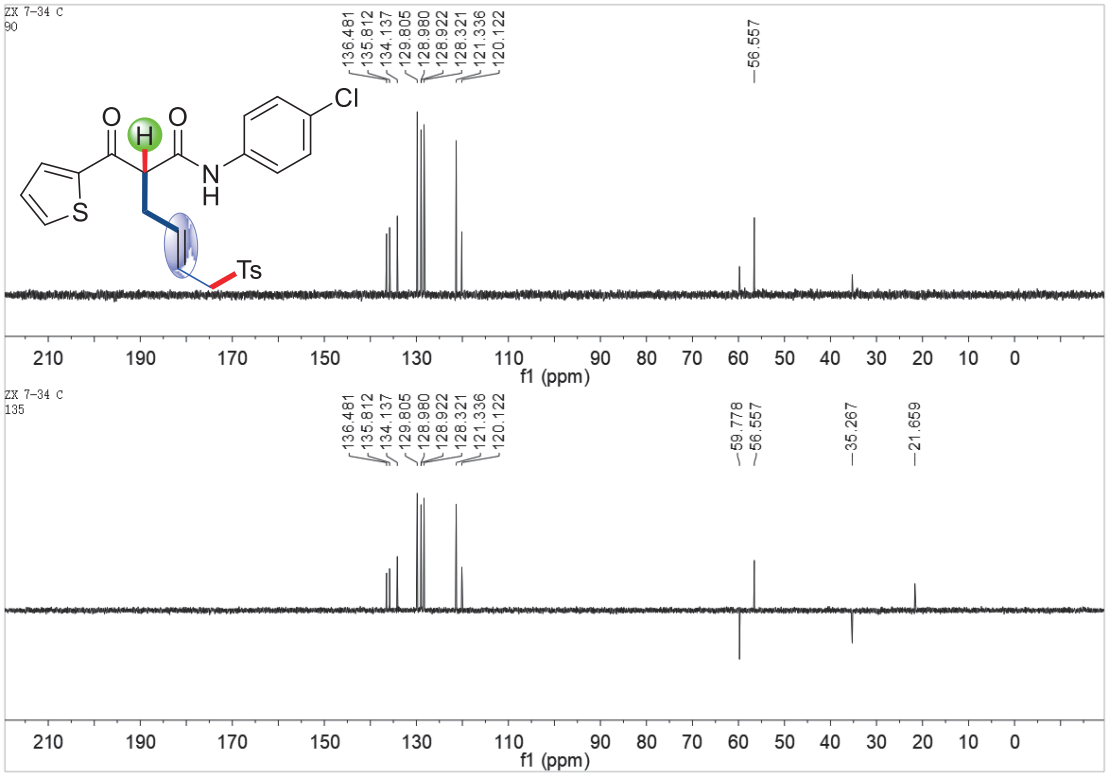
4b, ^{1}H NMR



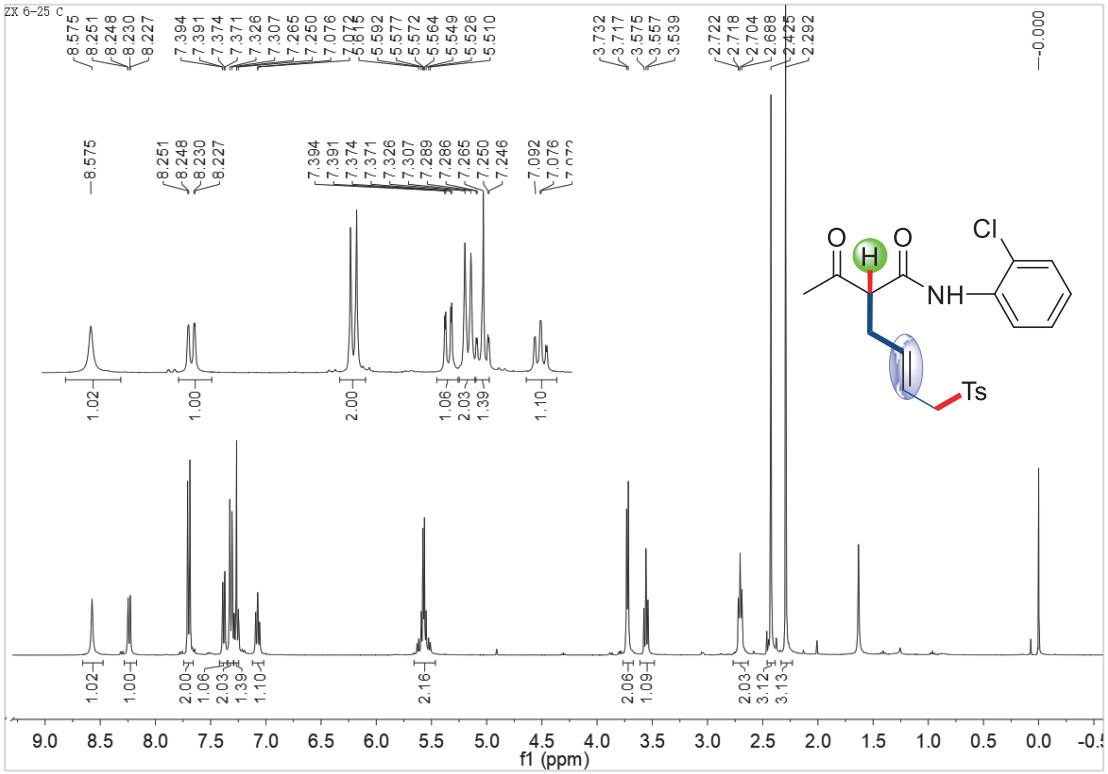
4b, ^{13}C NMR



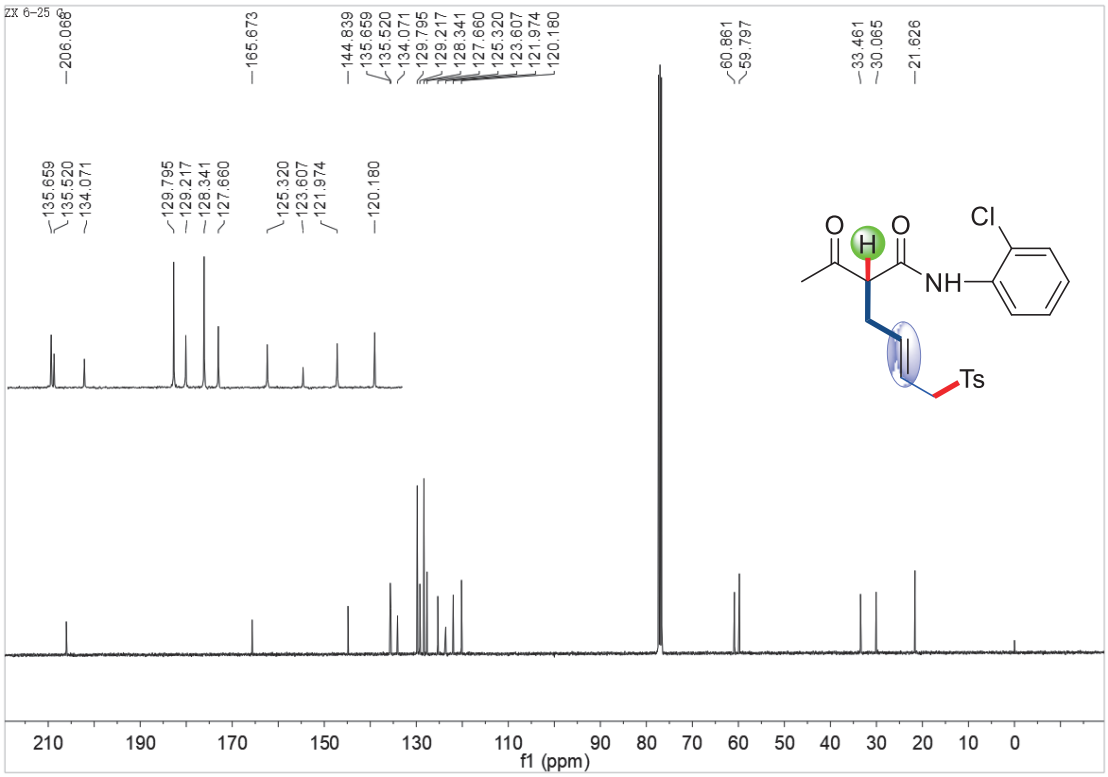
4b, DEPT 90 and DEPT 135



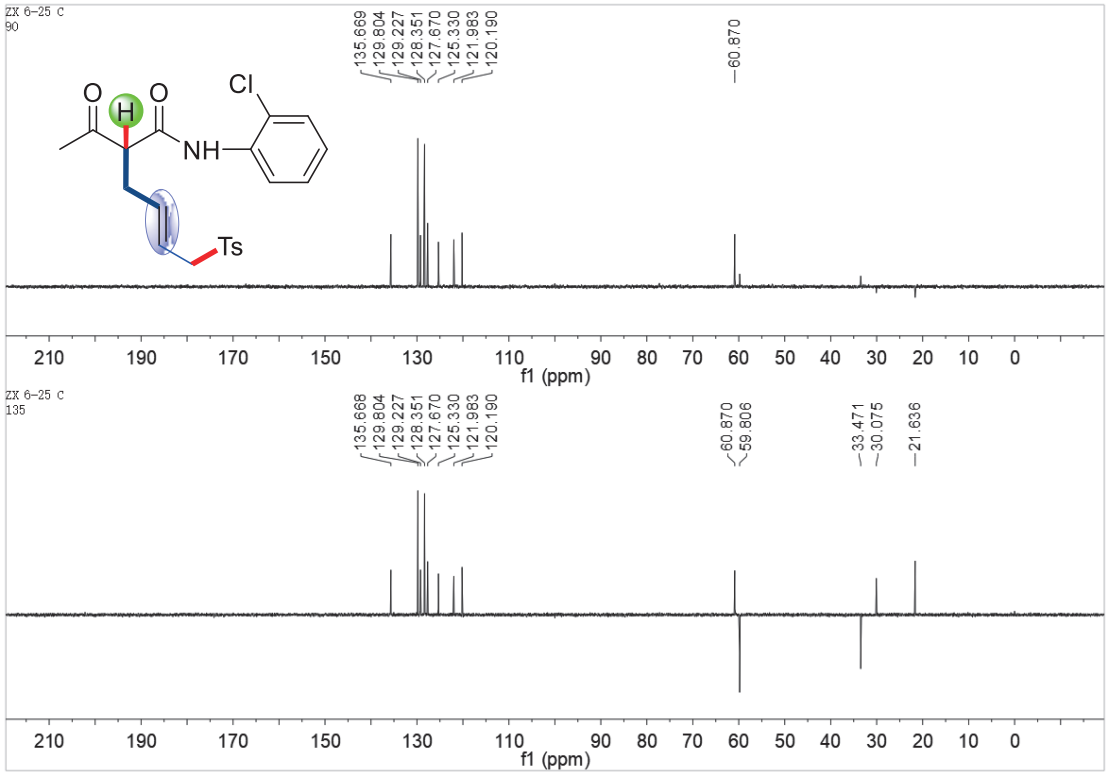
4c1, ^{1}H NMR



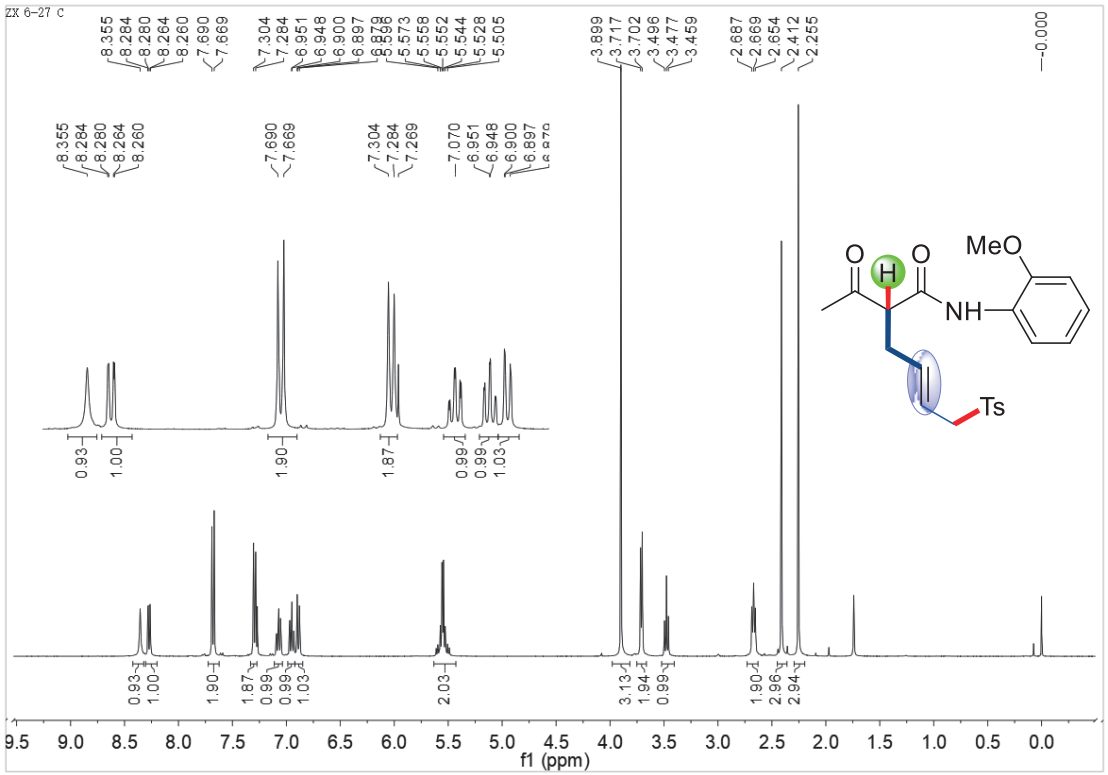
4c1, ^{13}C NMR



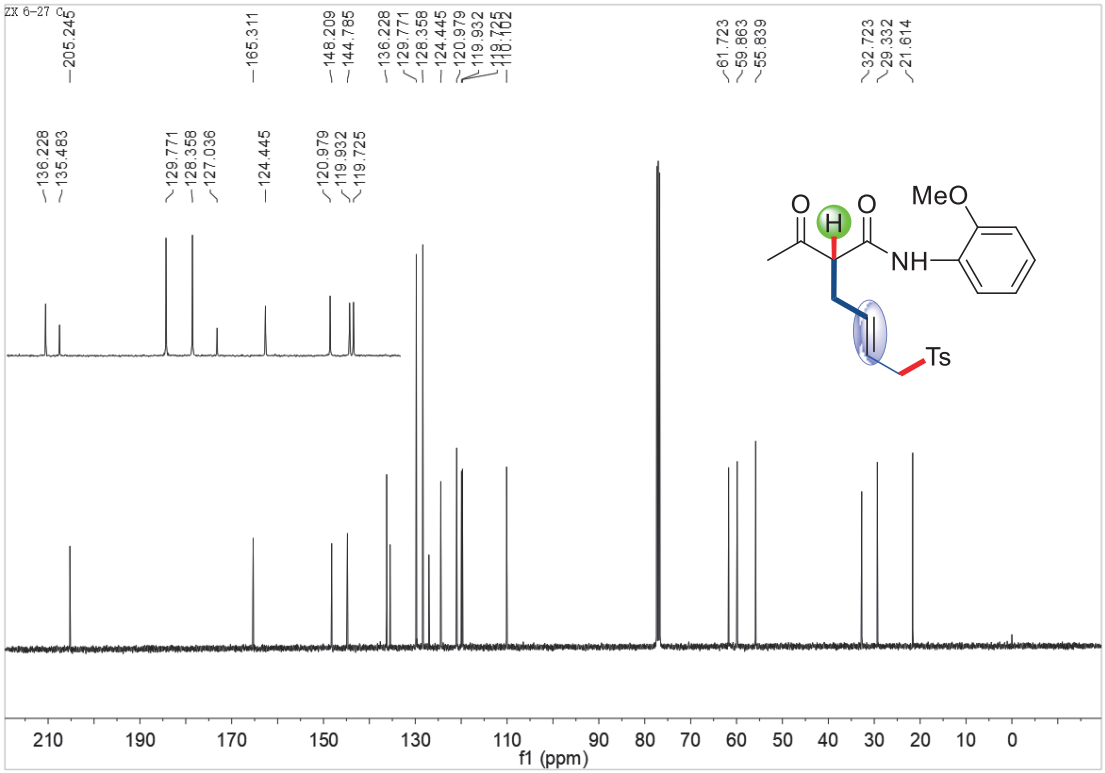
4c1, DEPT 90 and DEPT 135



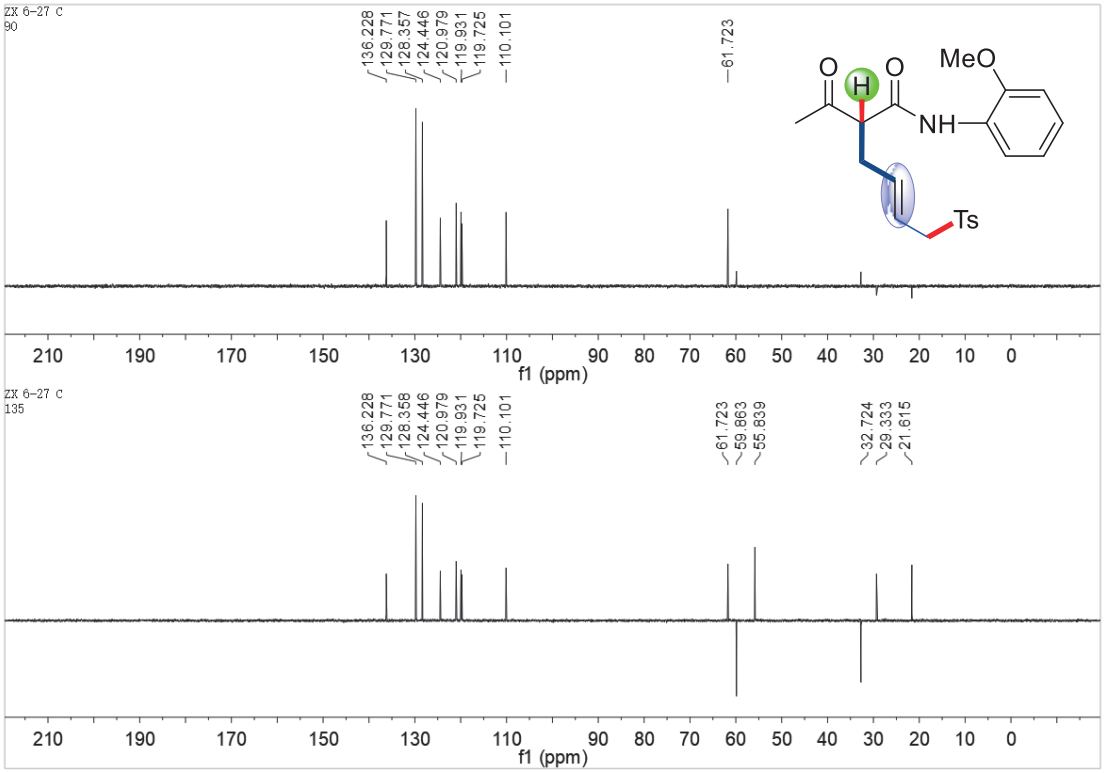
4c2, ^{1}H NMR



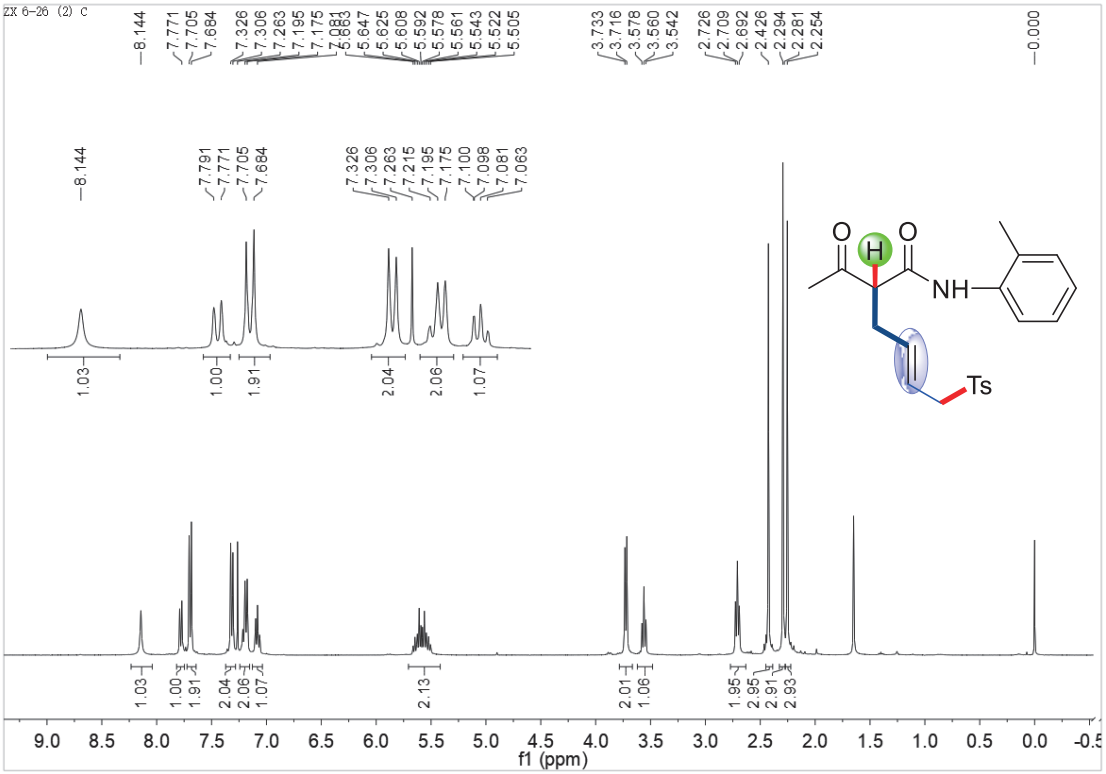
4c2, ^{13}C NMR



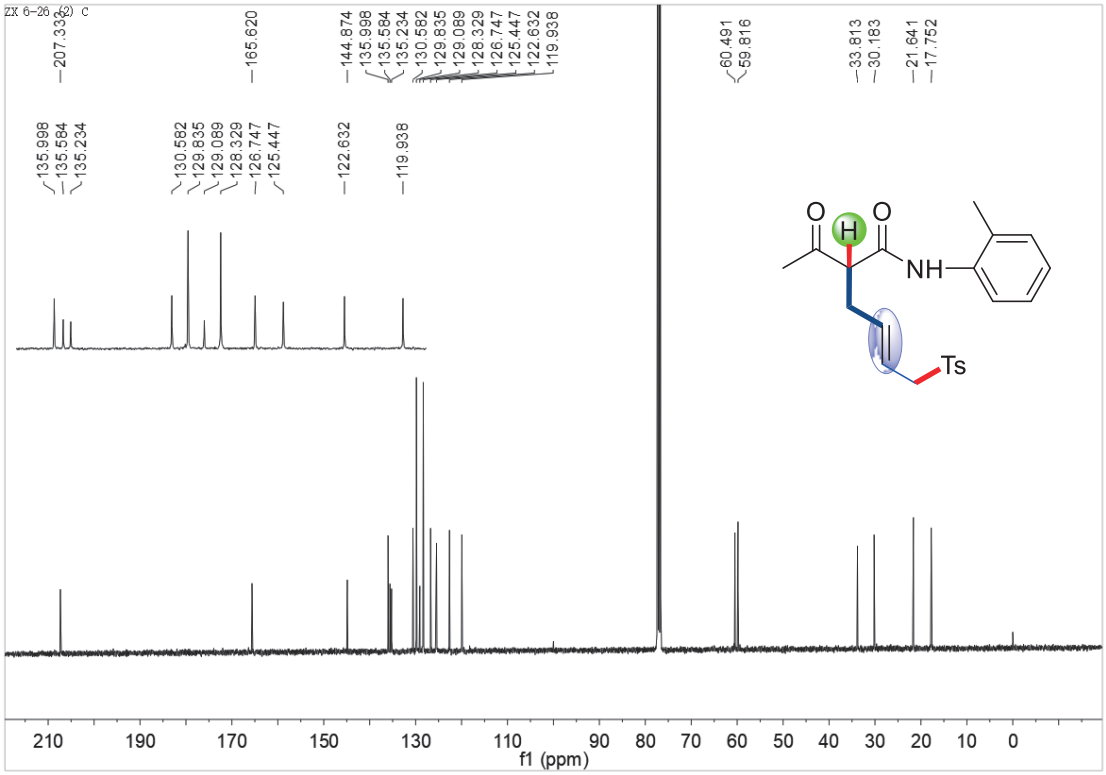
4c2, DEPT 90 and DEPT 135



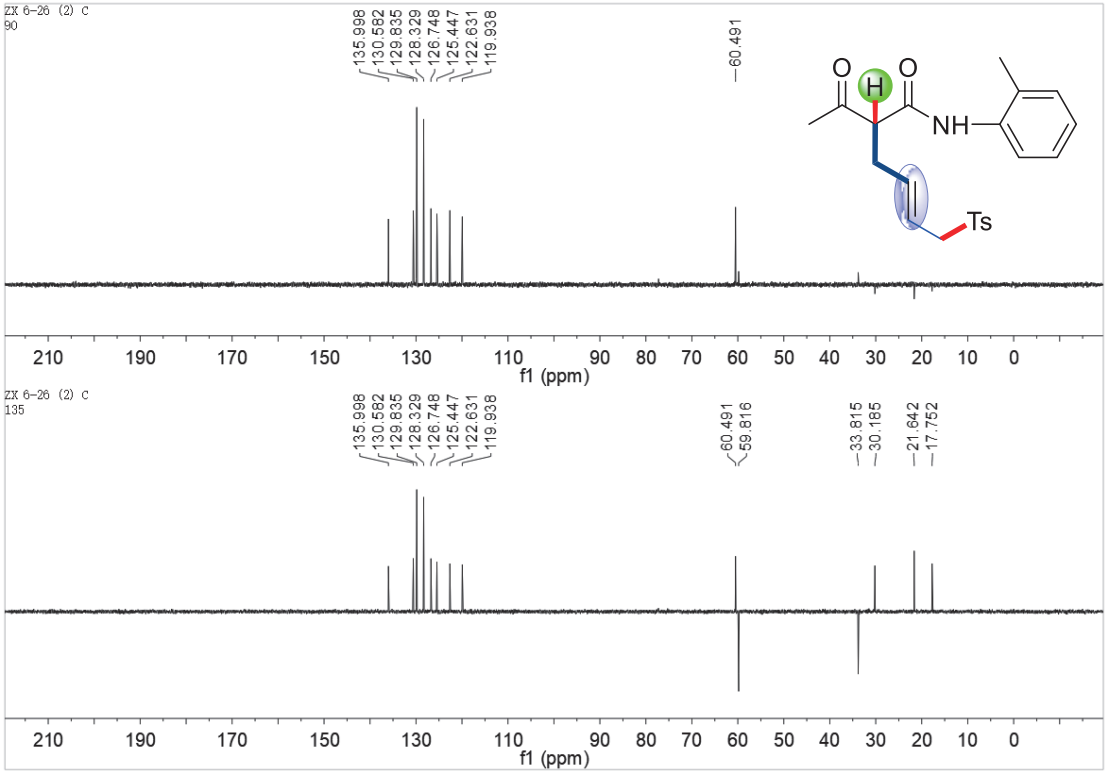
4c3, ^{1}H NMR



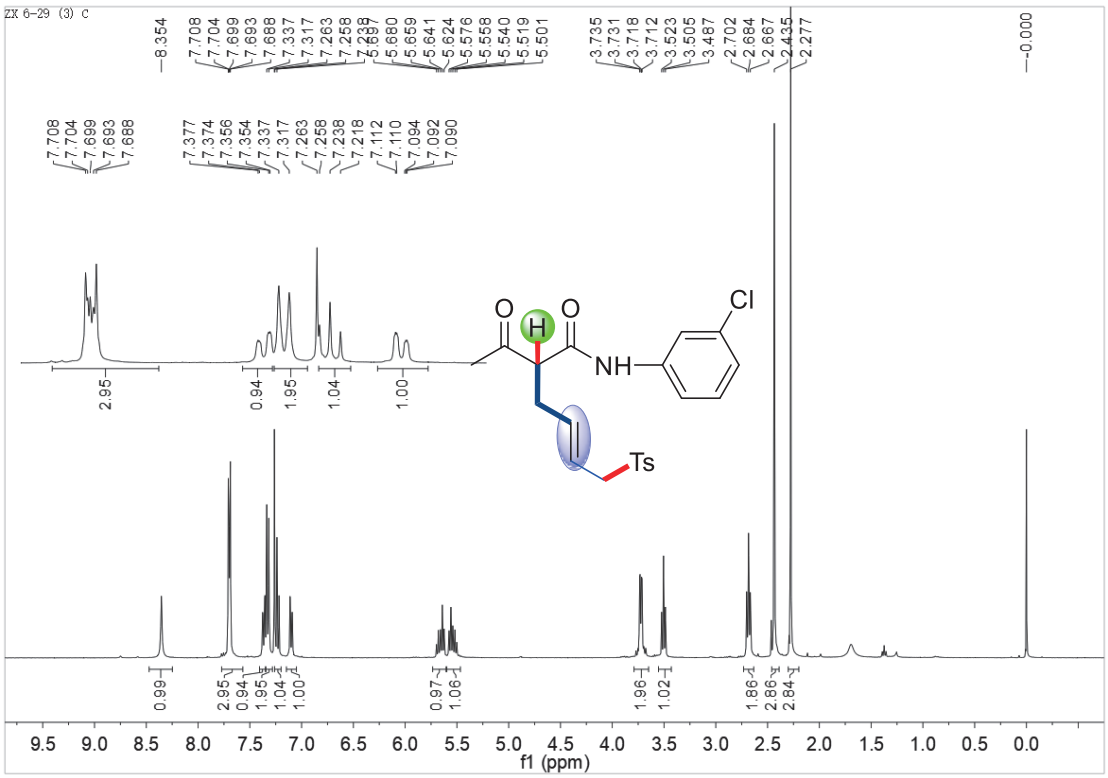
4c3, ^{13}C NMR



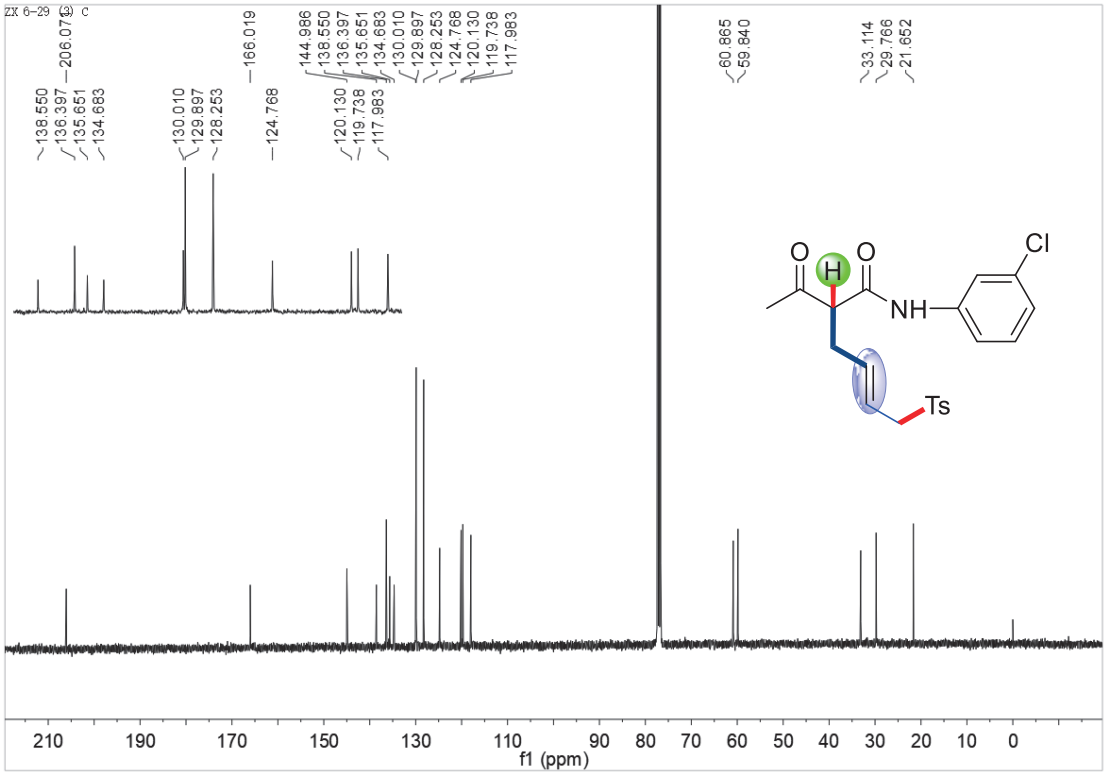
4c3, DEPT 90 and DEPT 135



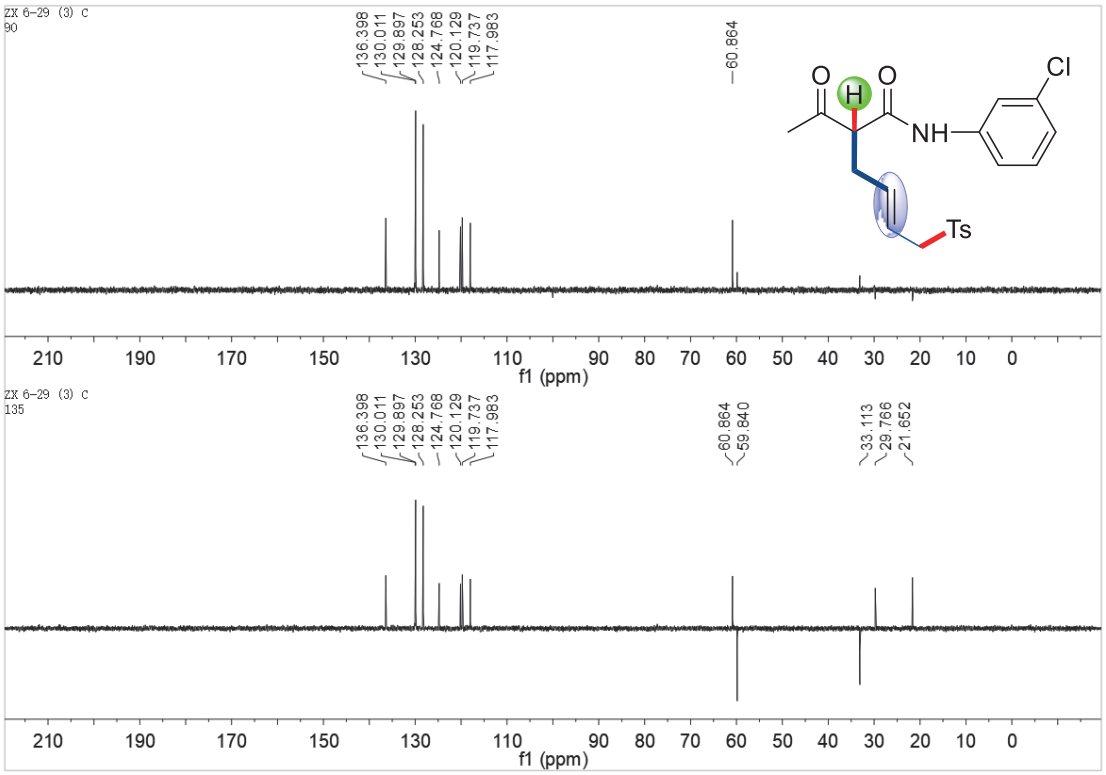
4d1, ^{1}H NMR



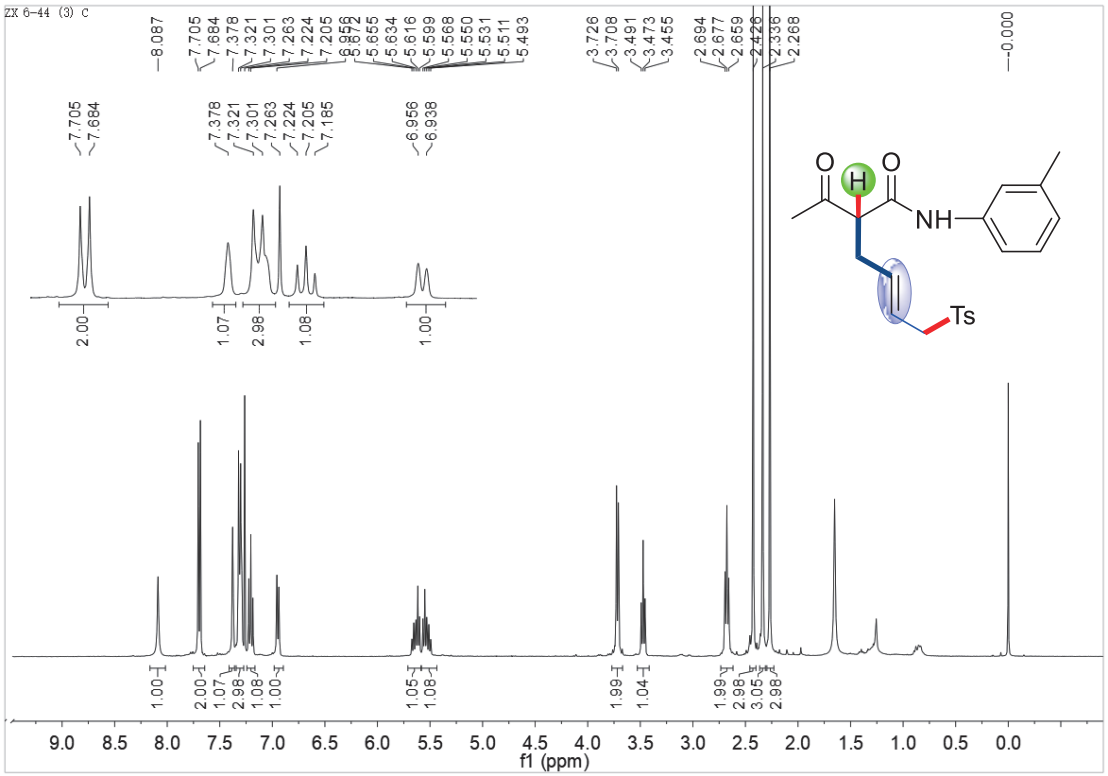
4d1, ^{13}C NMR



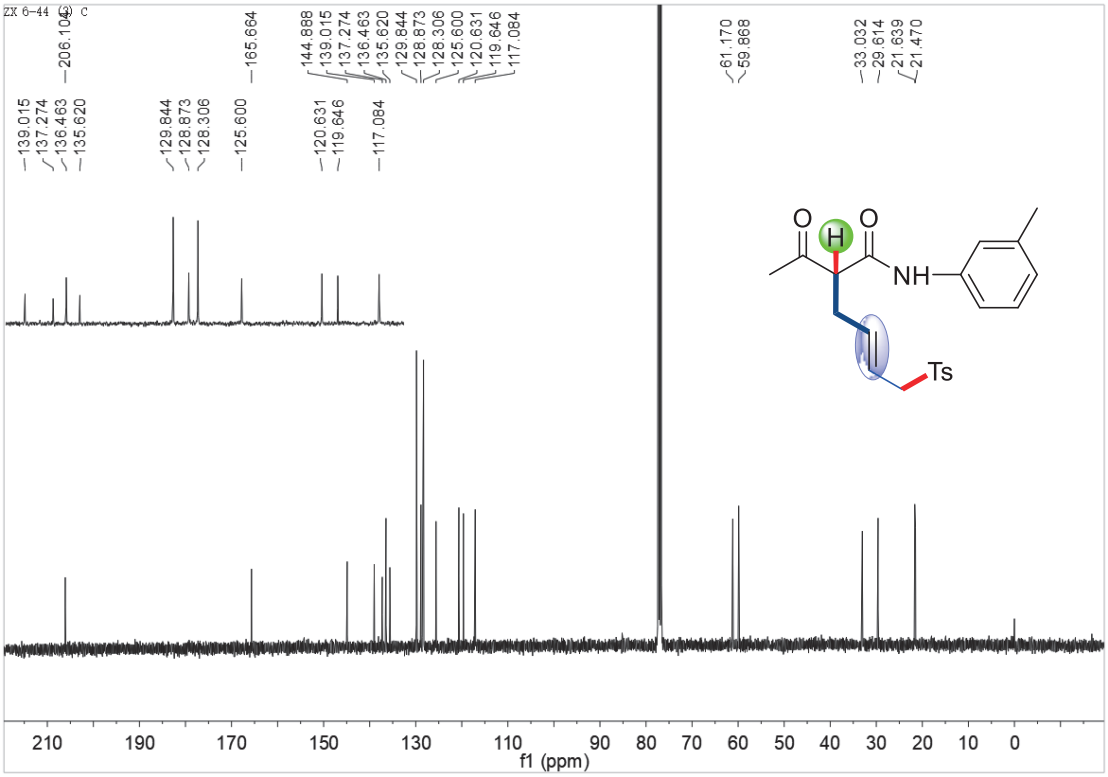
4d1, DEPT 90 and DEPT 135



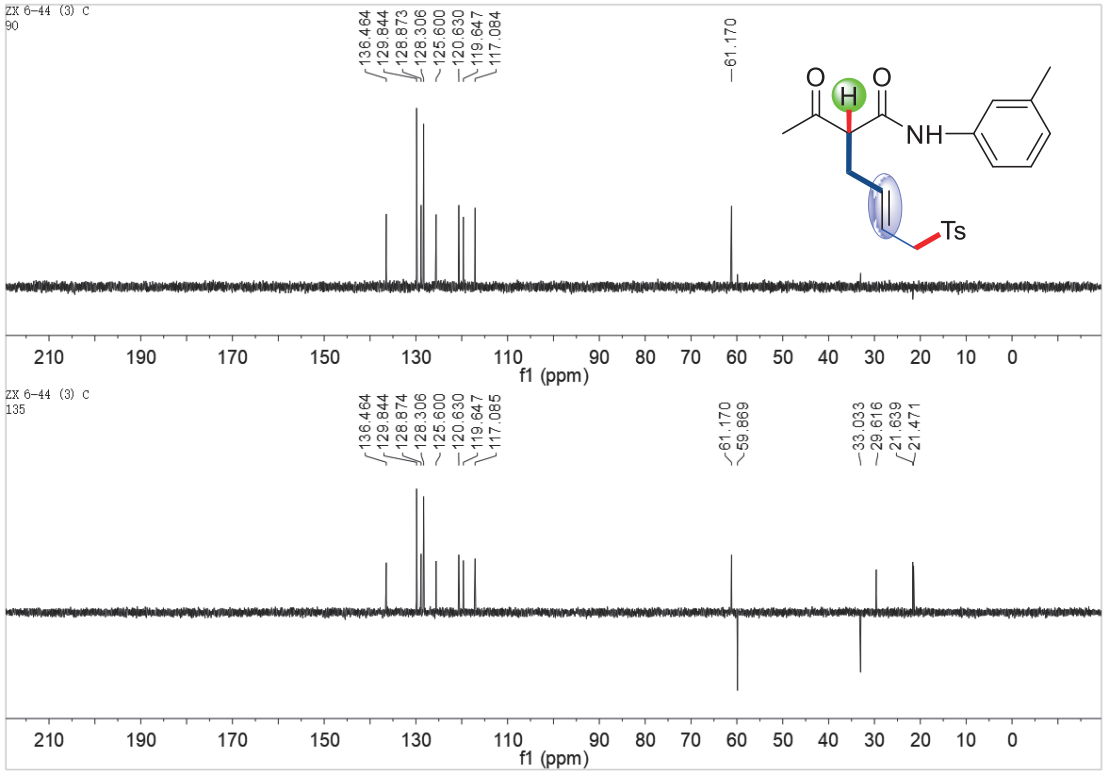
4d2, ^{1}H NMR



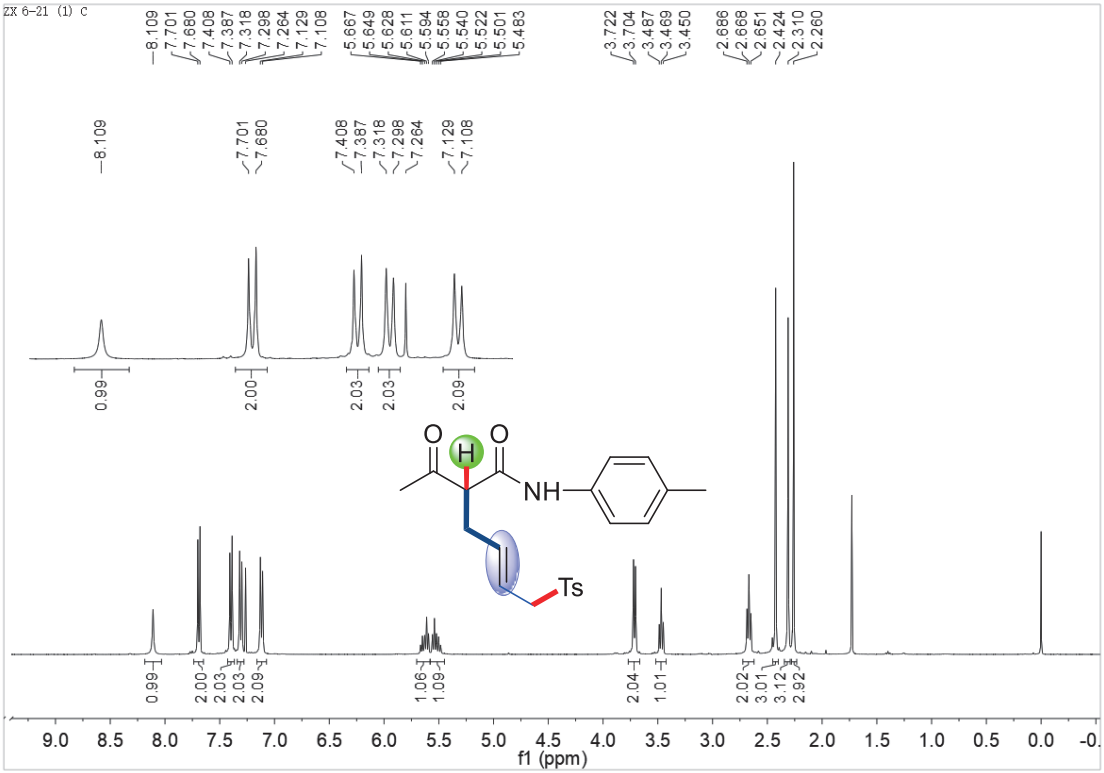
4d2, ^{13}C NMR



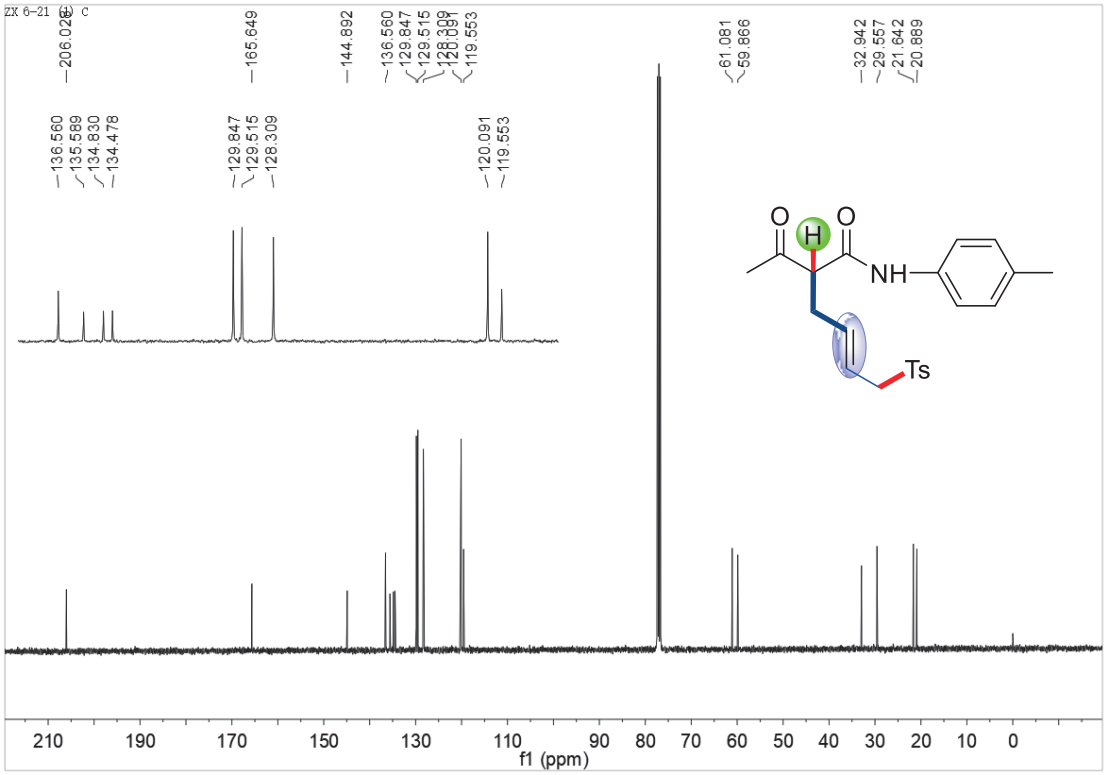
4d2, DEPT 90 and DEPT 135



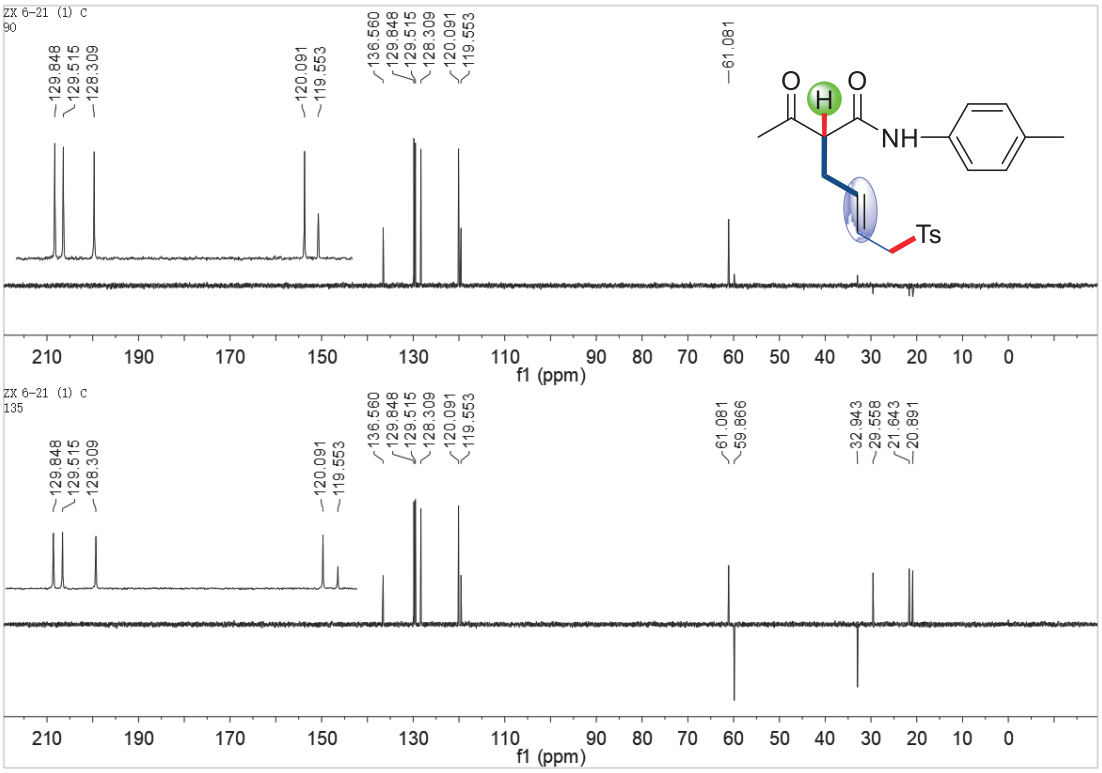
4e1, ^{1}H NMR



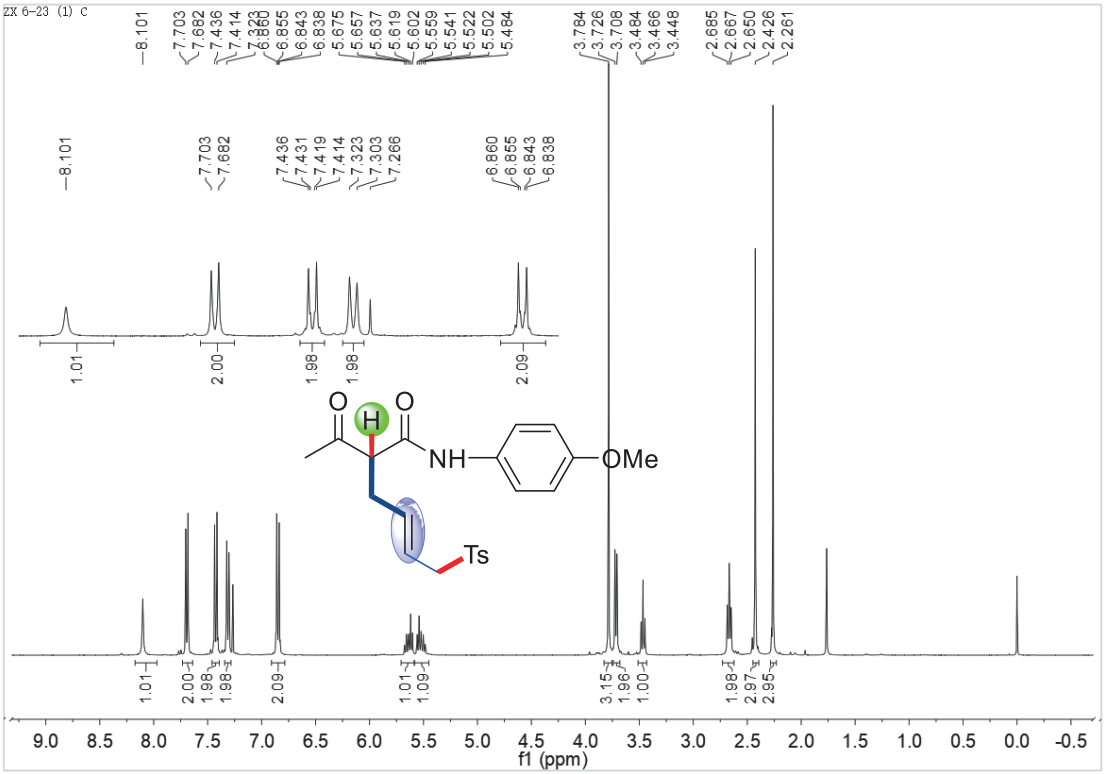
4e1, ^{13}C NMR



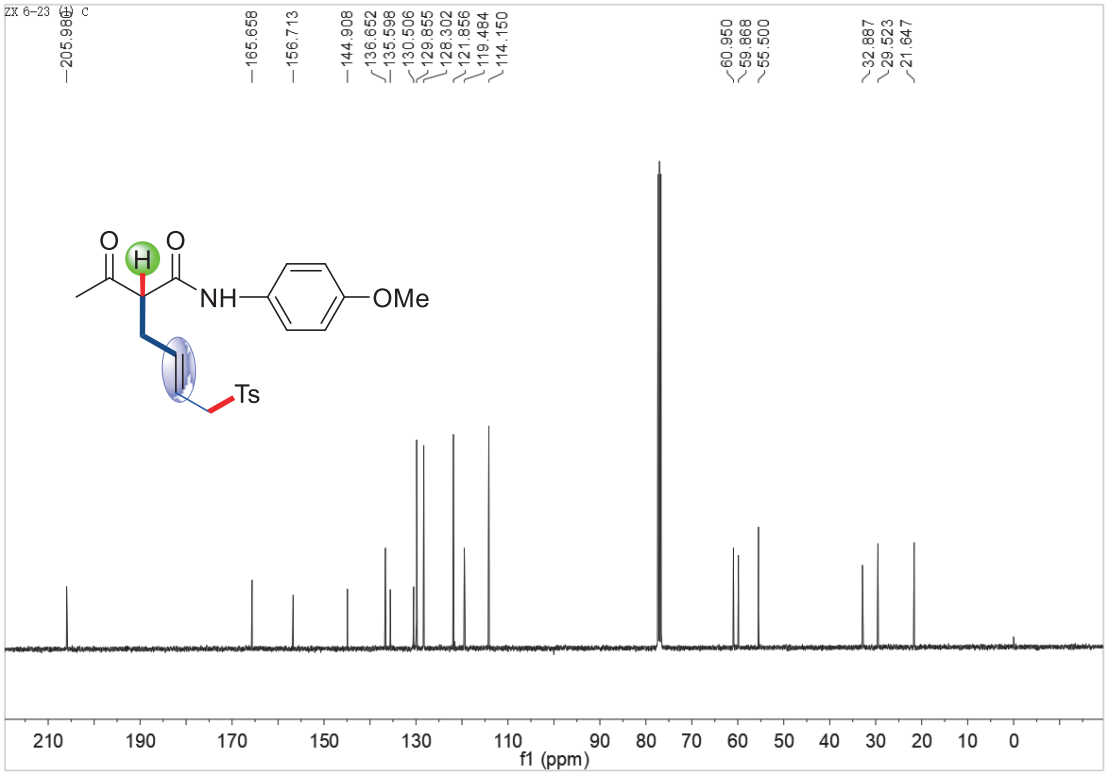
4e1, DEPT 90 and DEPT 135



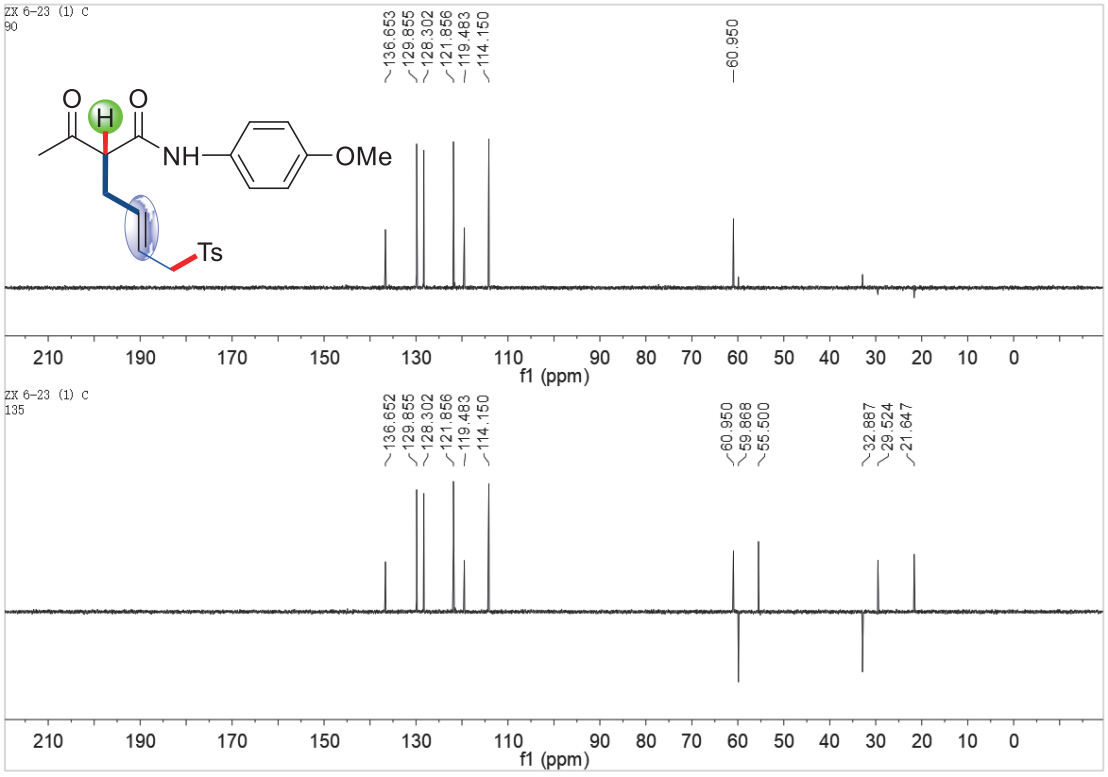
4e2, ^{1}H NMR



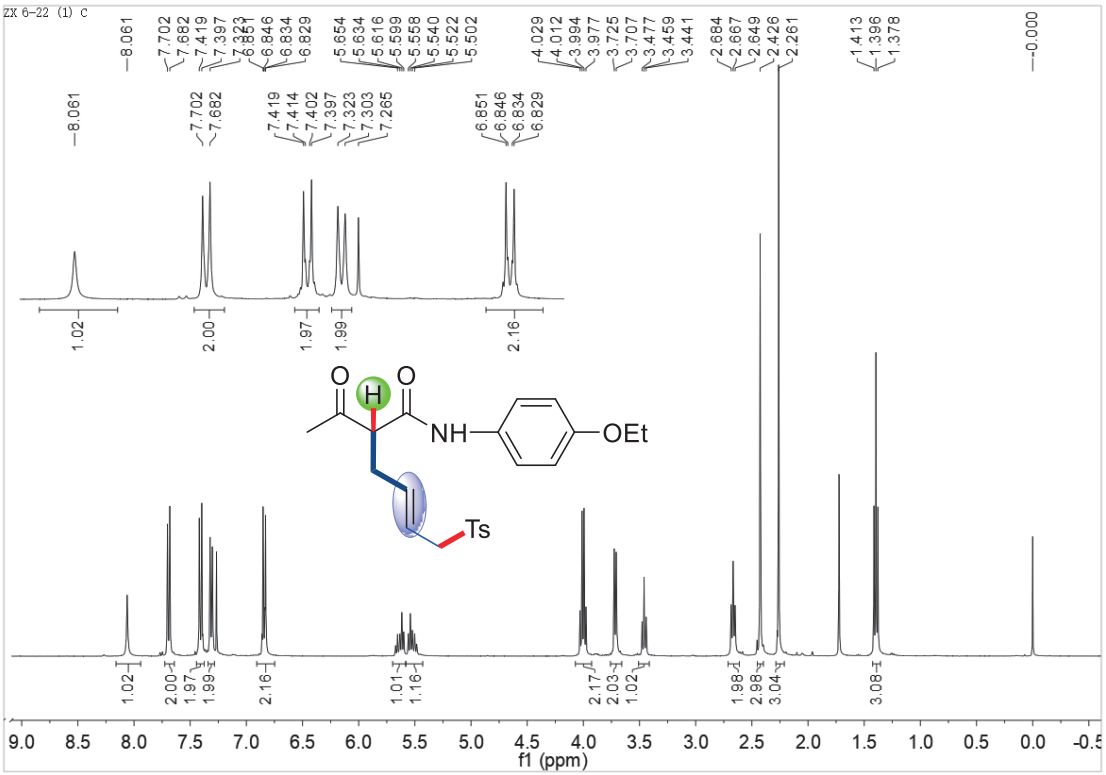
4e2, ^{13}C NMR



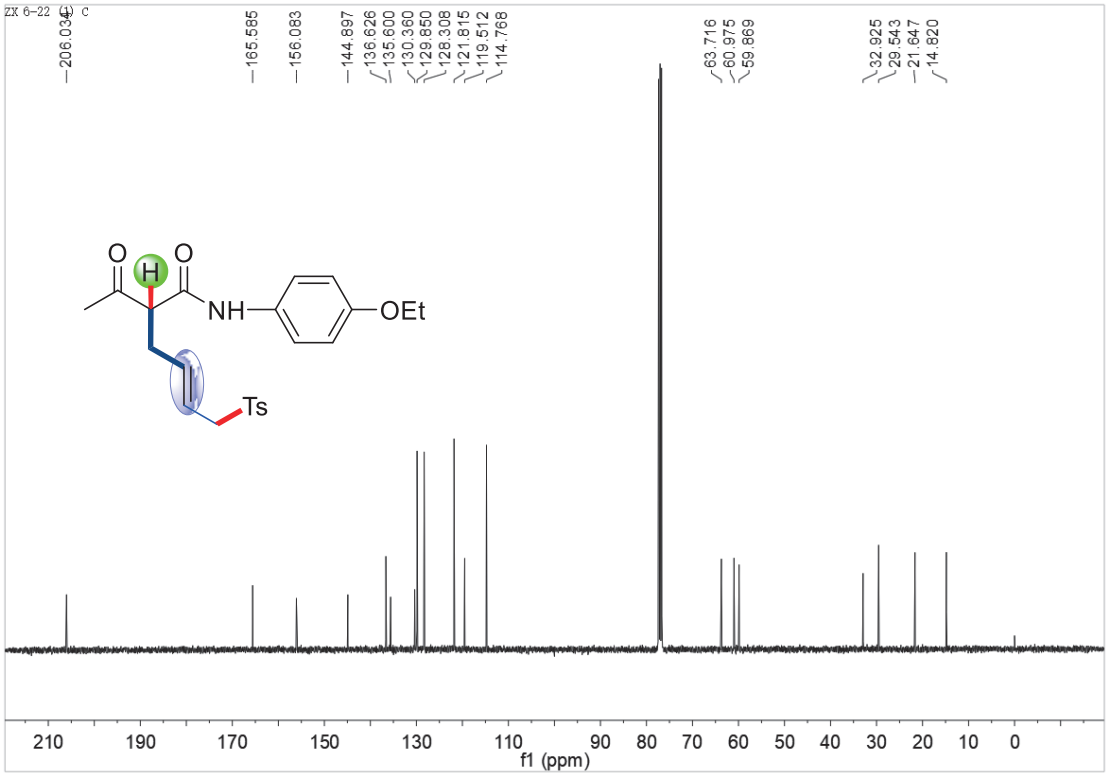
4e2, DEPT 90 and DEPT 135



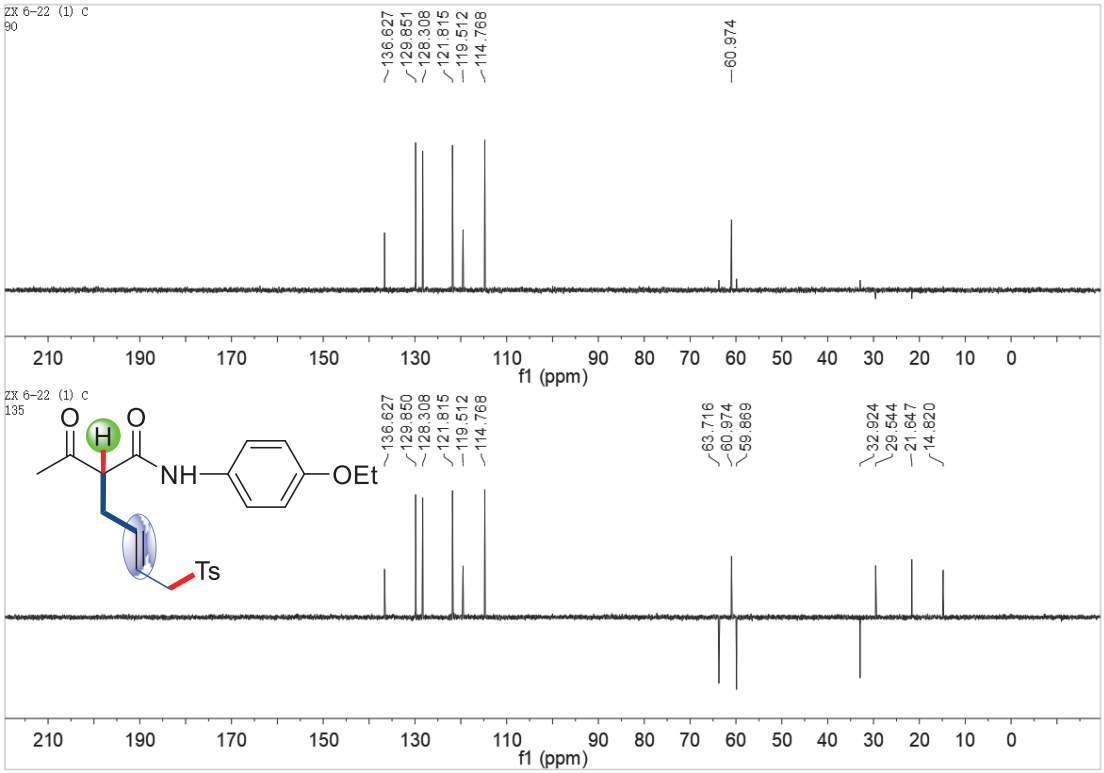
4e3, ^{1}H NMR



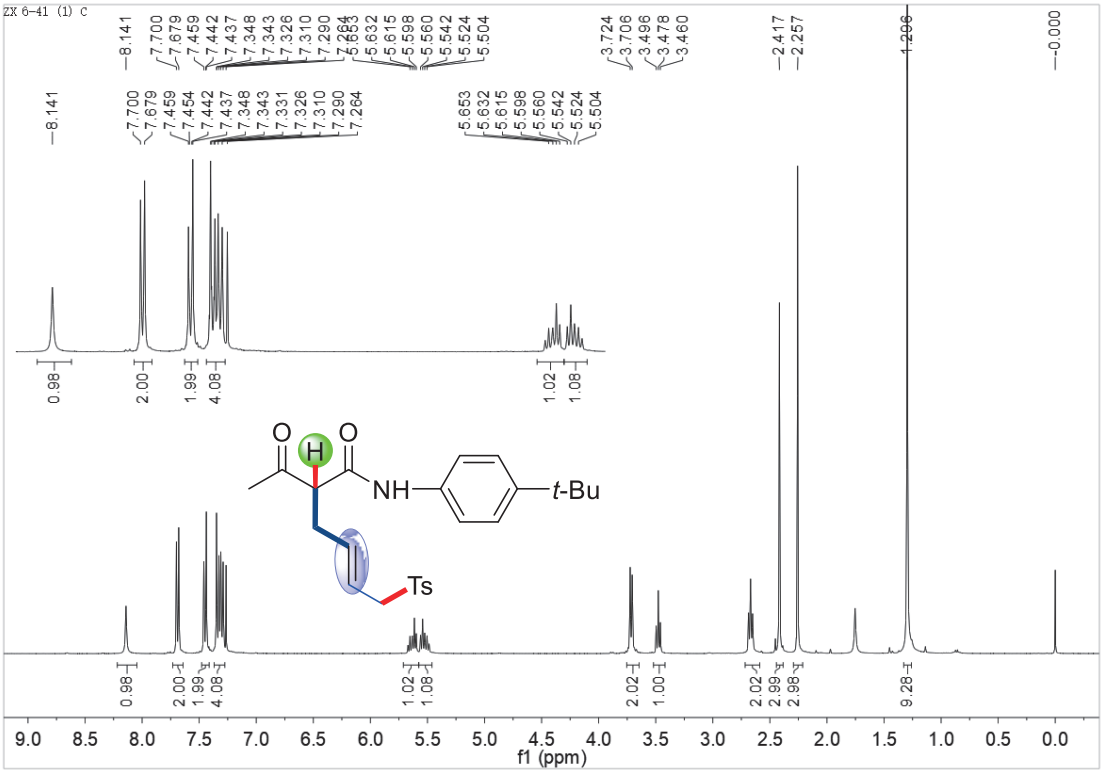
4e3, ^{13}C NMR



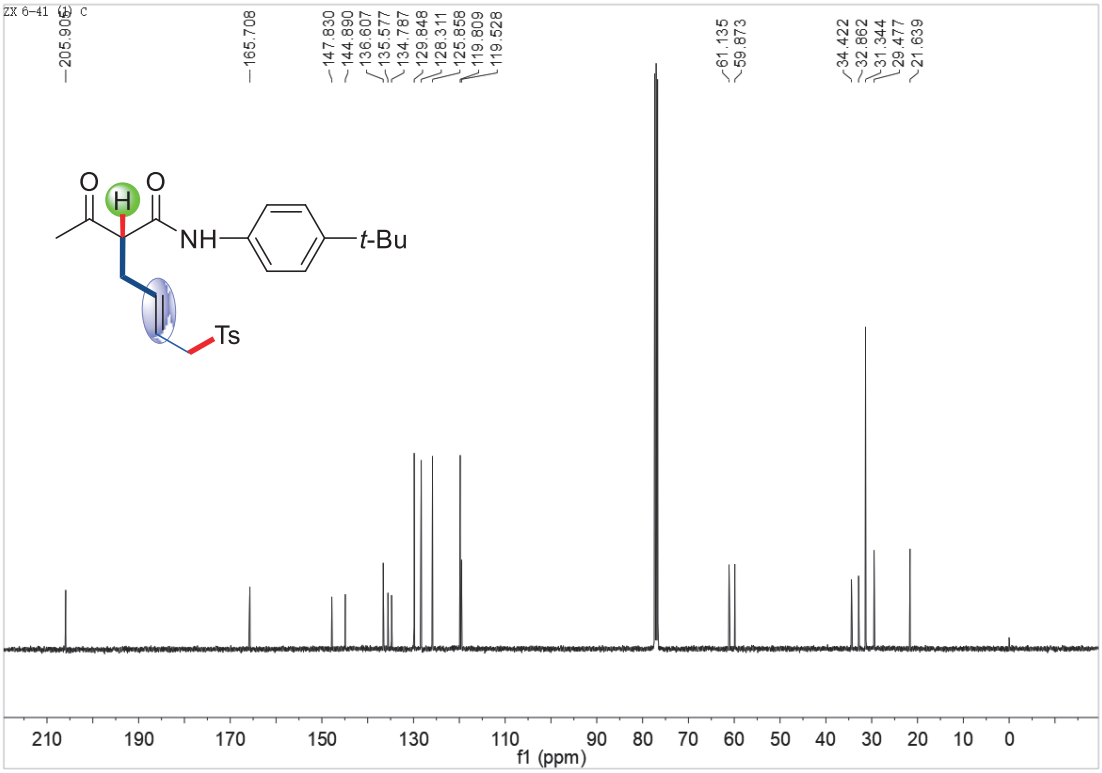
4e3, DEPT 90 and DEPT 135



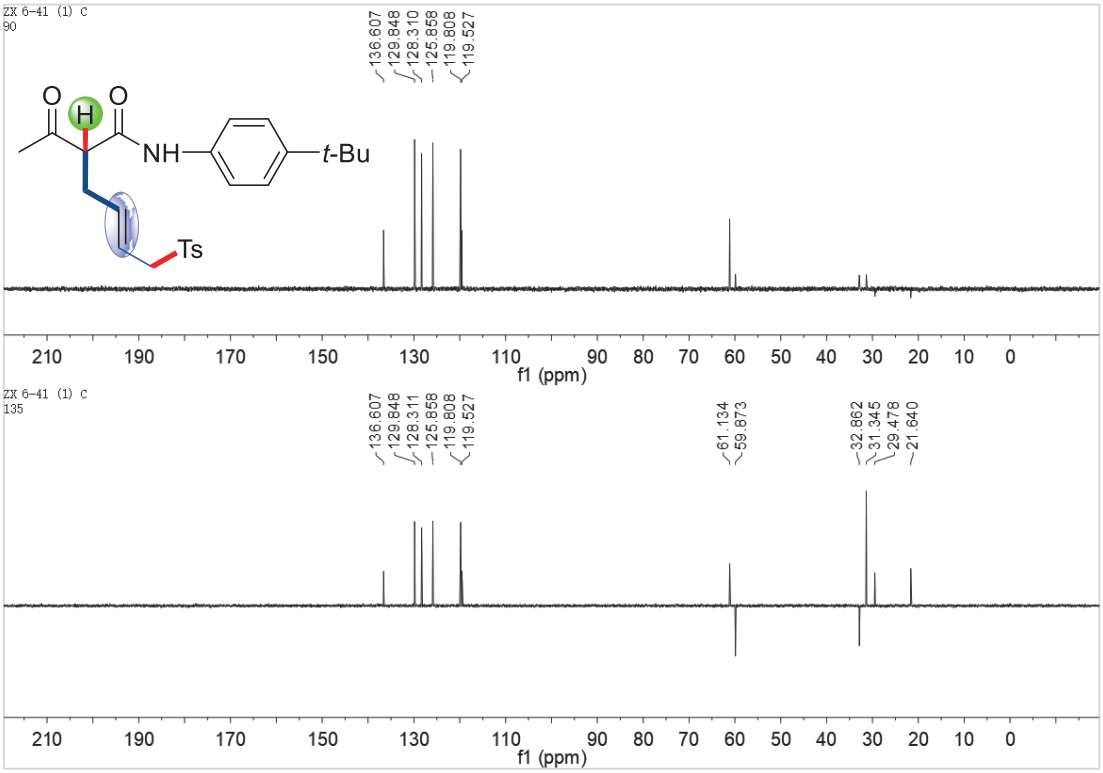
4e4, ^{1}H NMR



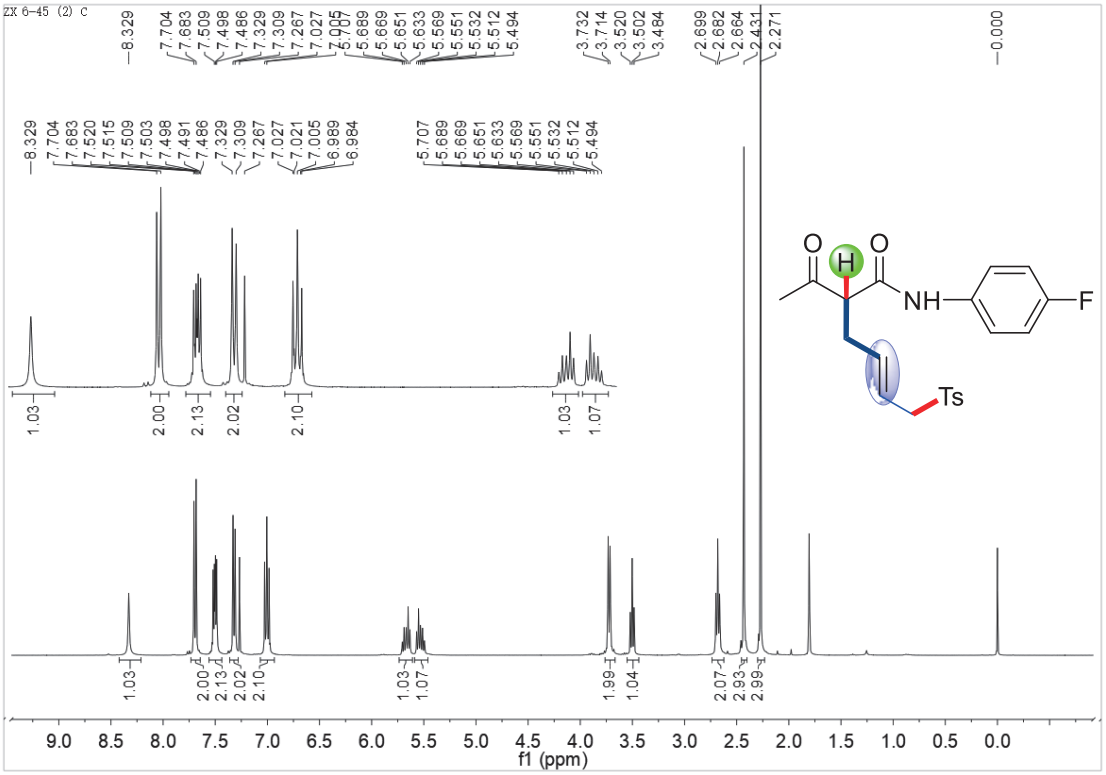
4e4, ^{13}C NMR



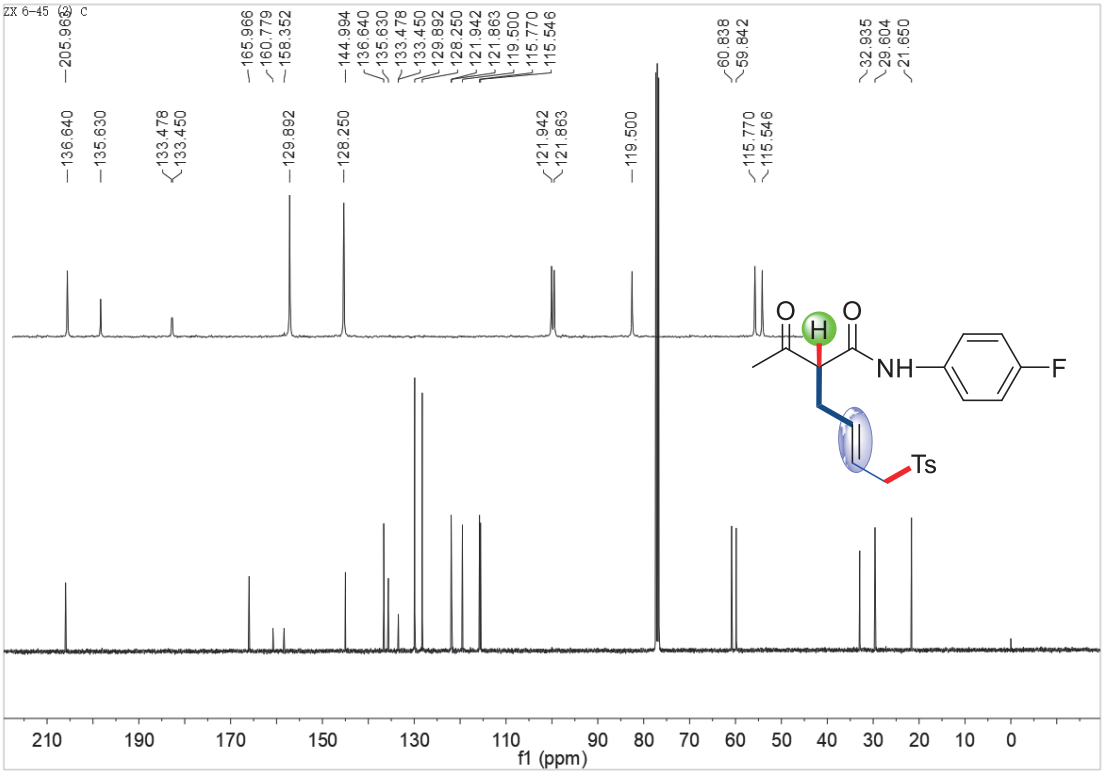
4e4, DEPT 90 and DEPT 135



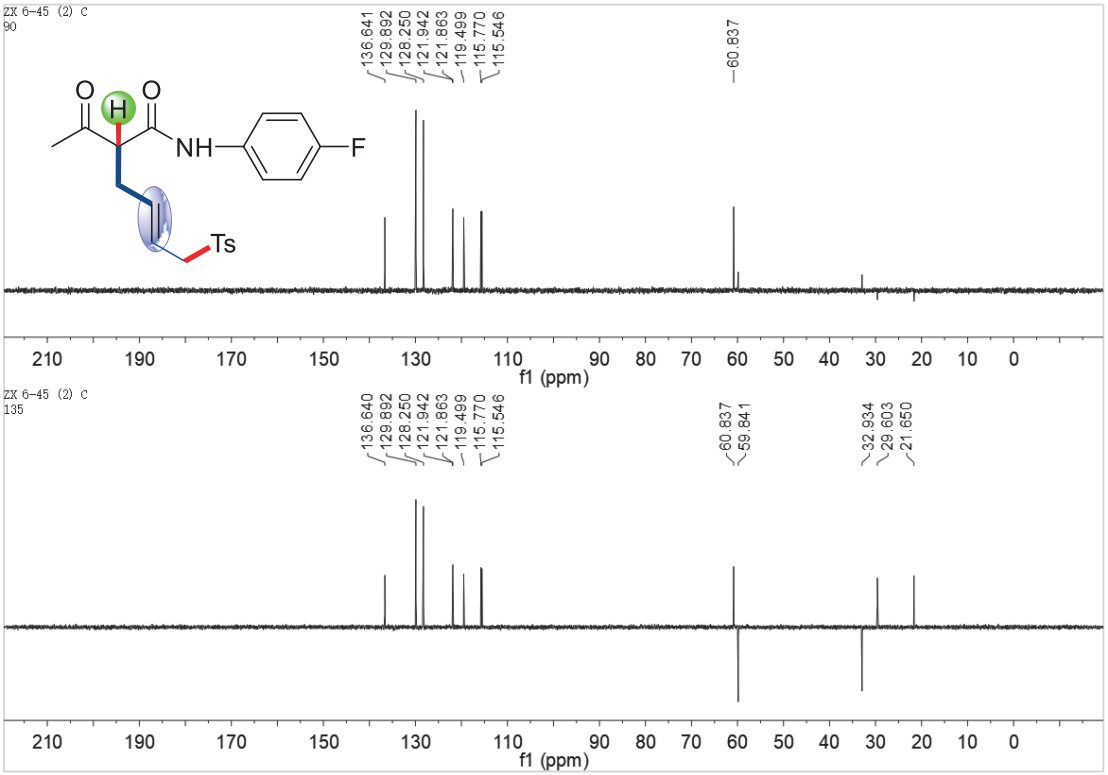
4e5, ^{1}H NMR



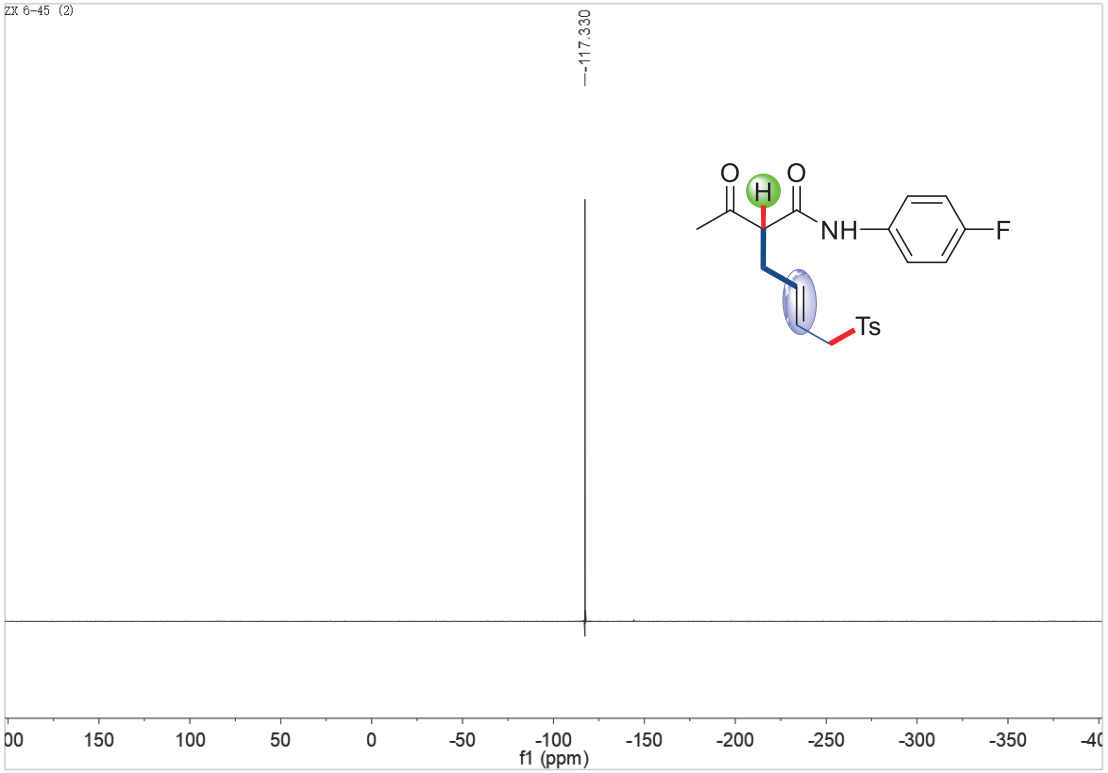
4e5, ^{13}C NMR



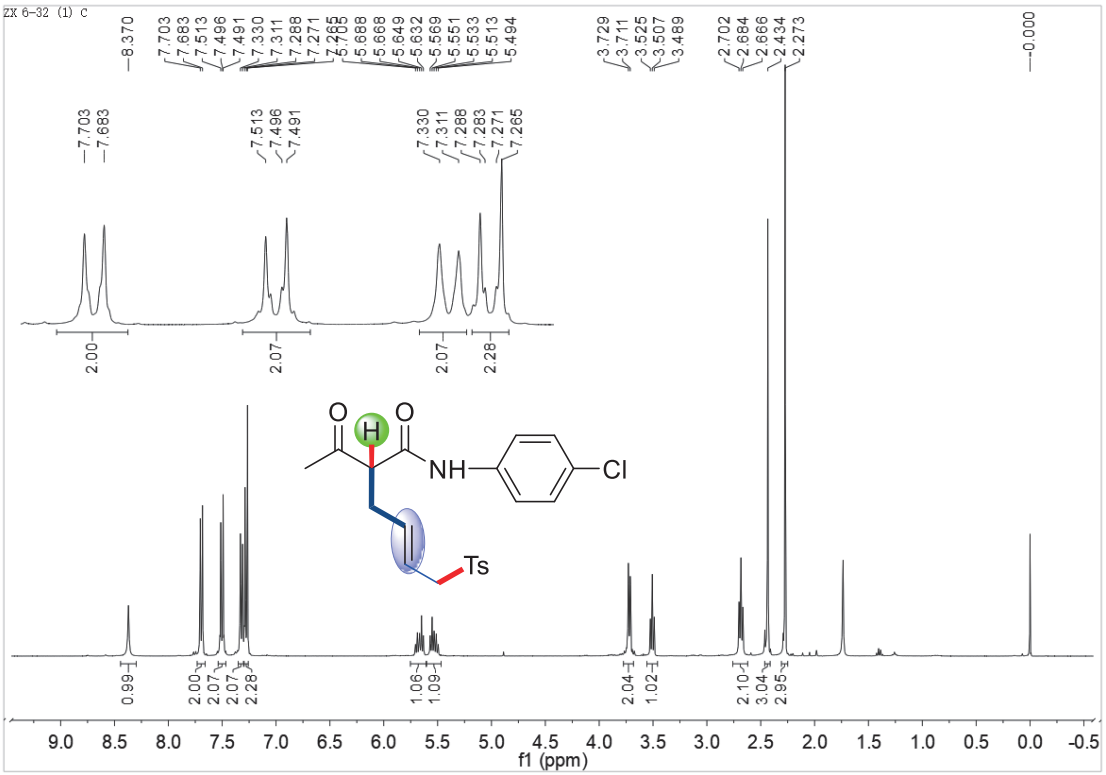
4e5, DEPT 90 and DEPT 135



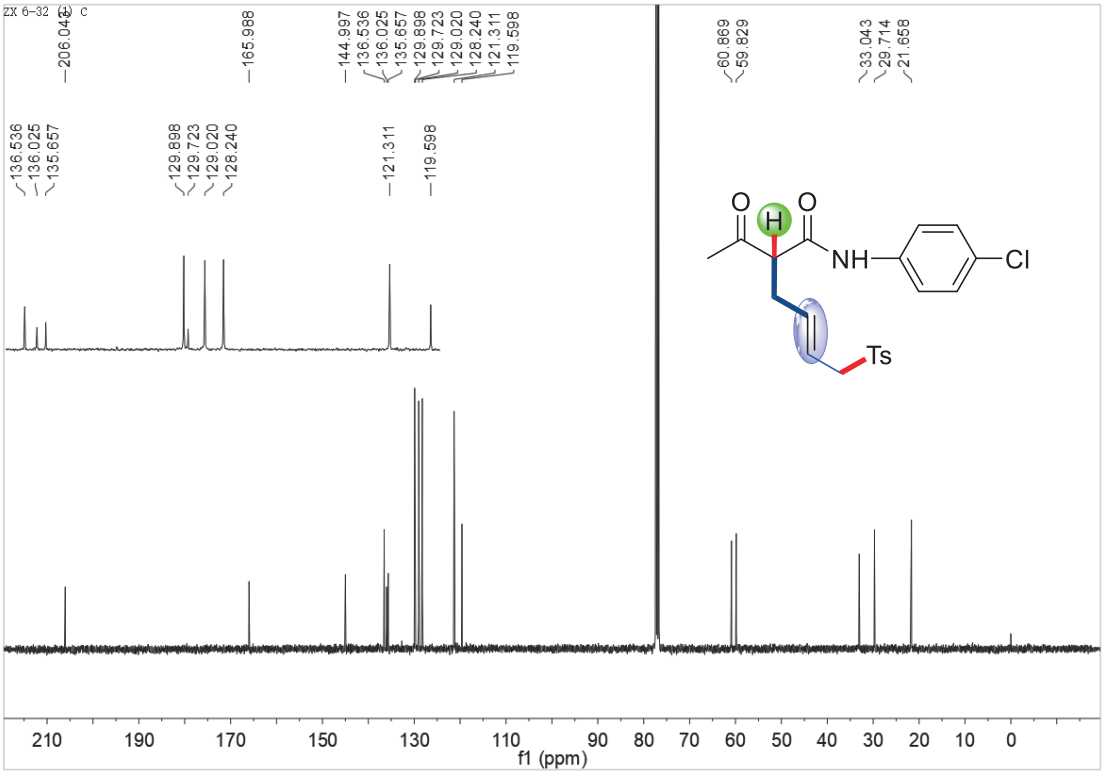
4e5, ^{19}F NMR



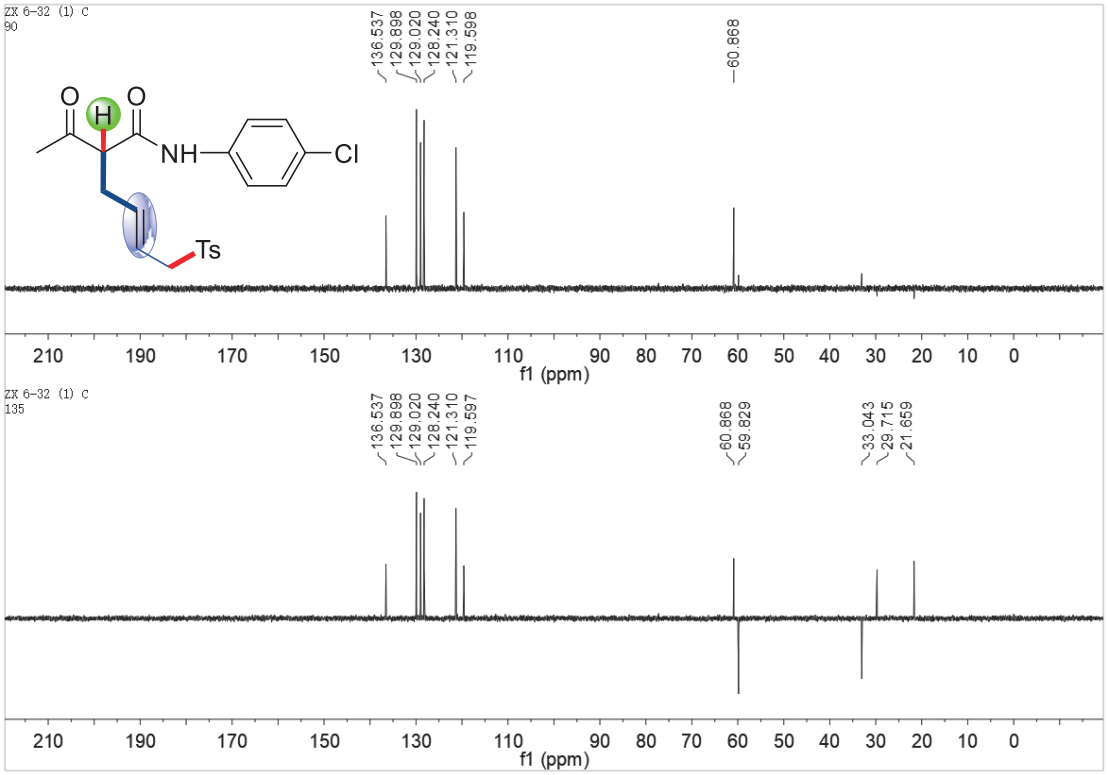
4e6, ^{1}H NMR



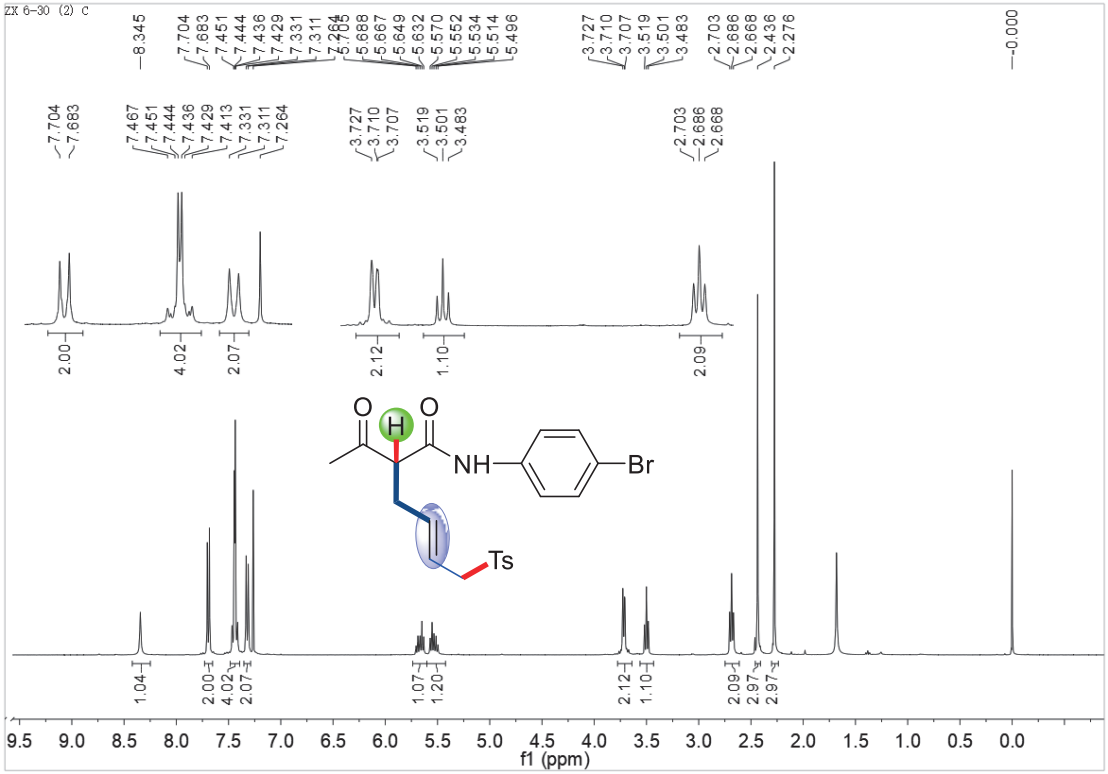
4e6, ^{13}C NMR



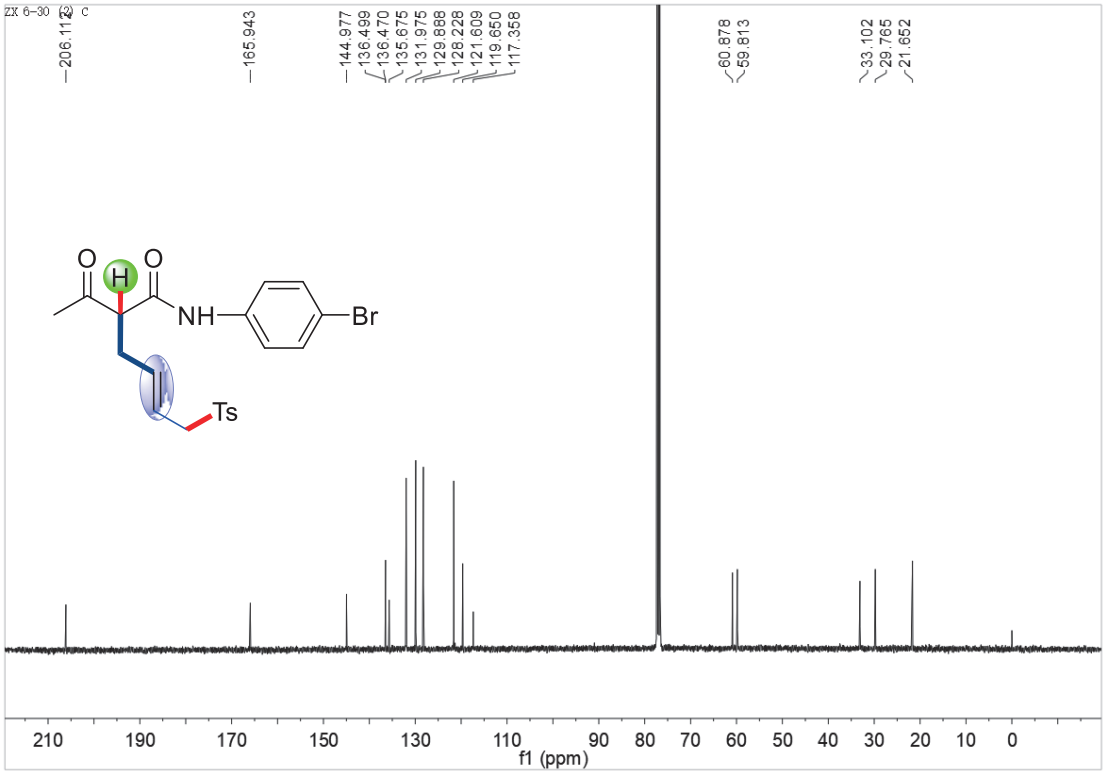
4e6, DEPT 90 and DEPT 135



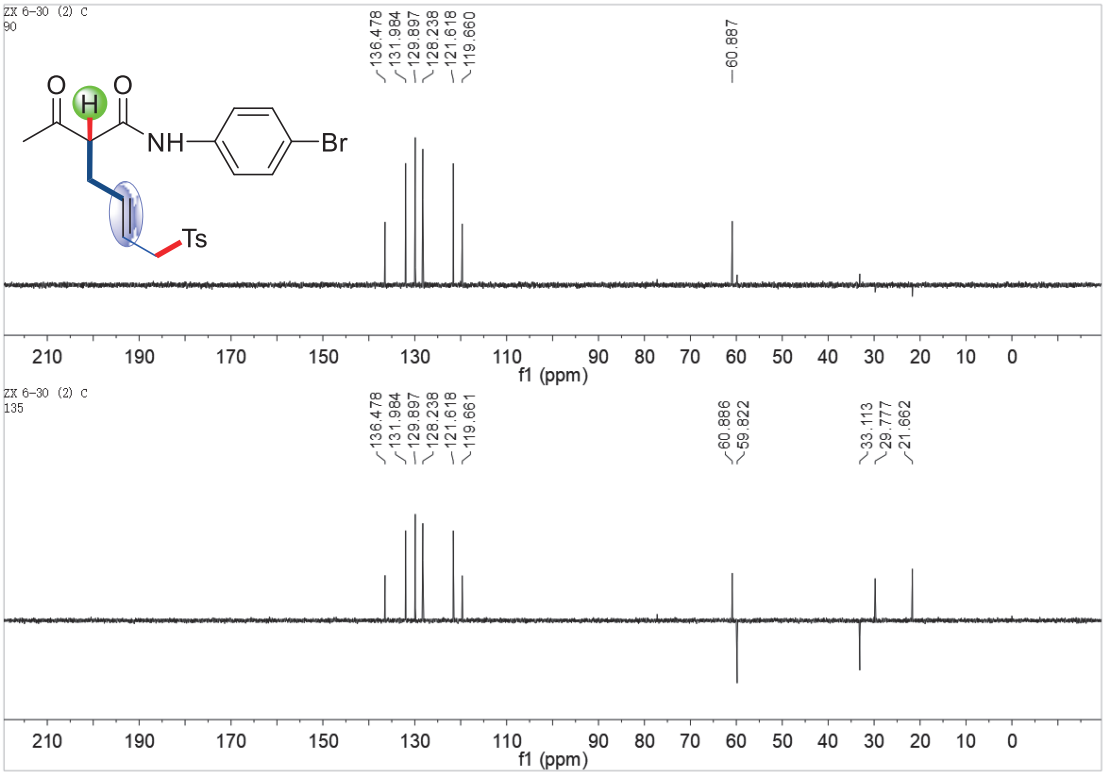
4e7, ^{1}H NMR



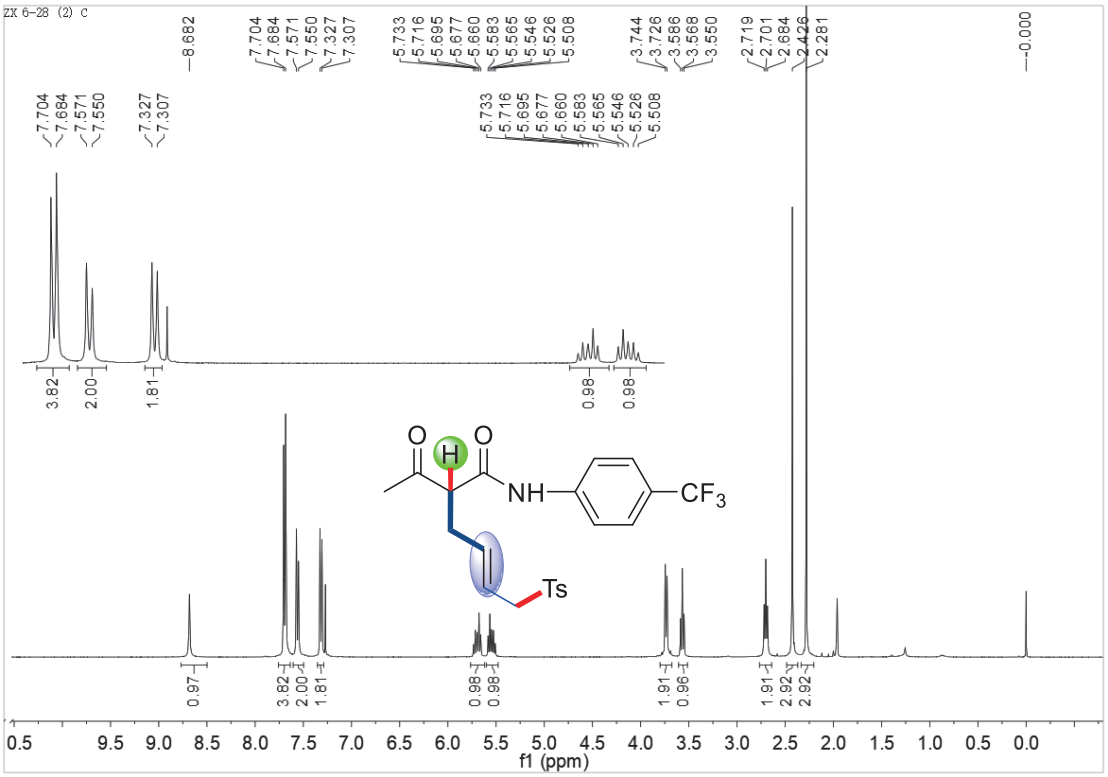
4e7, ^{13}C NMR



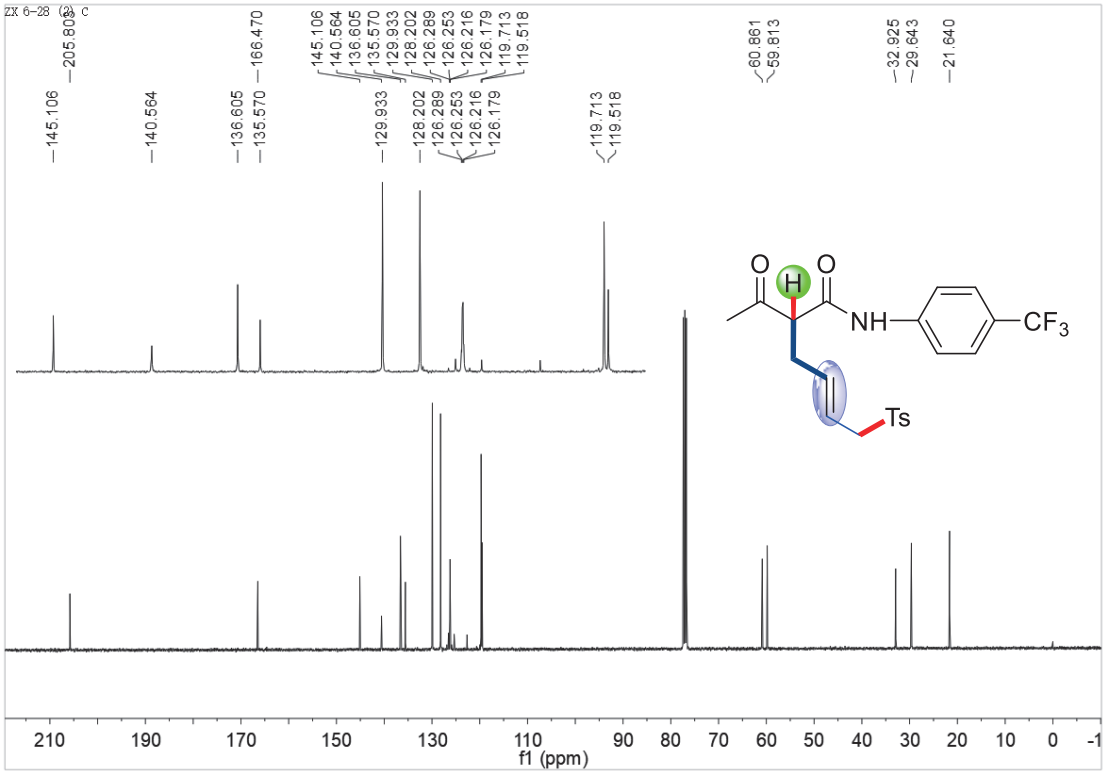
4e7, DEPT 90 and DEPT 135



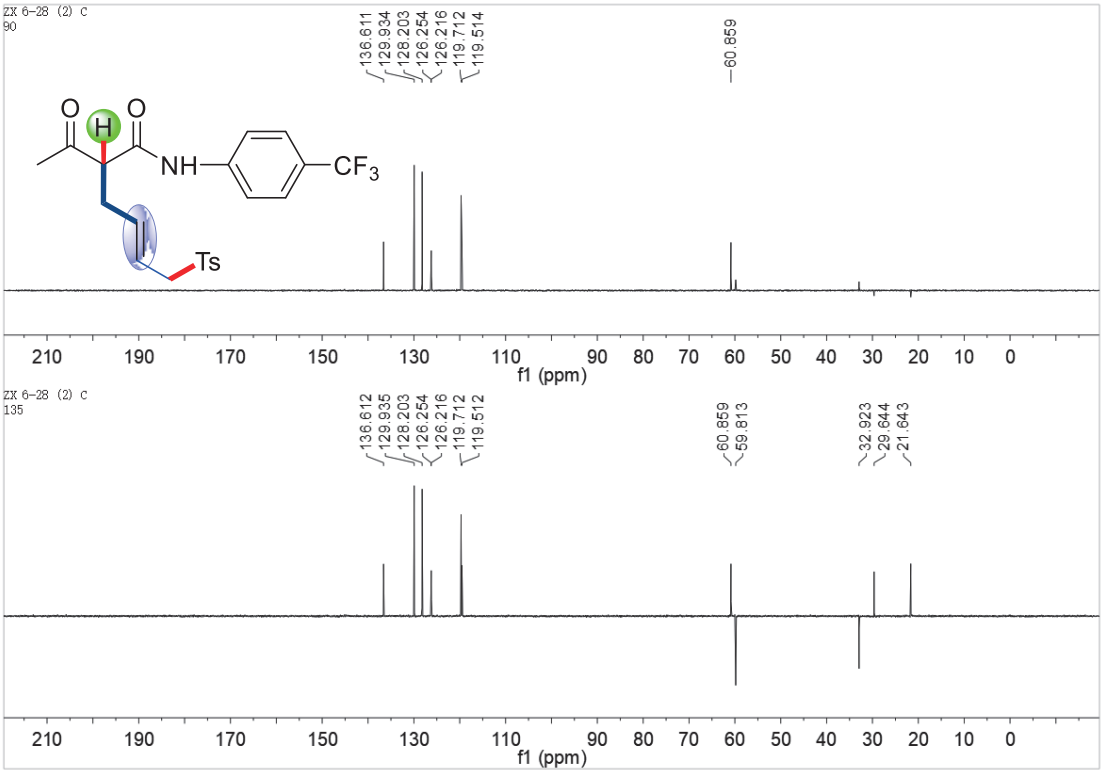
4e8, ^{1}H NMR



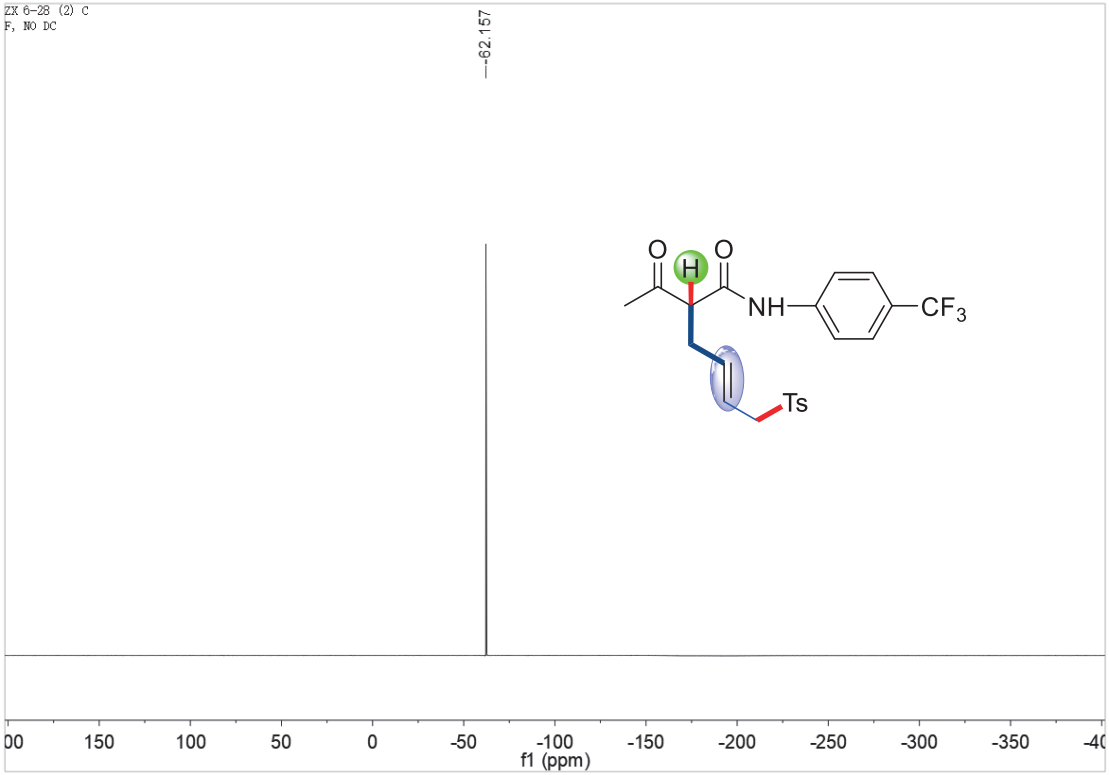
4e8, ^{13}C NMR



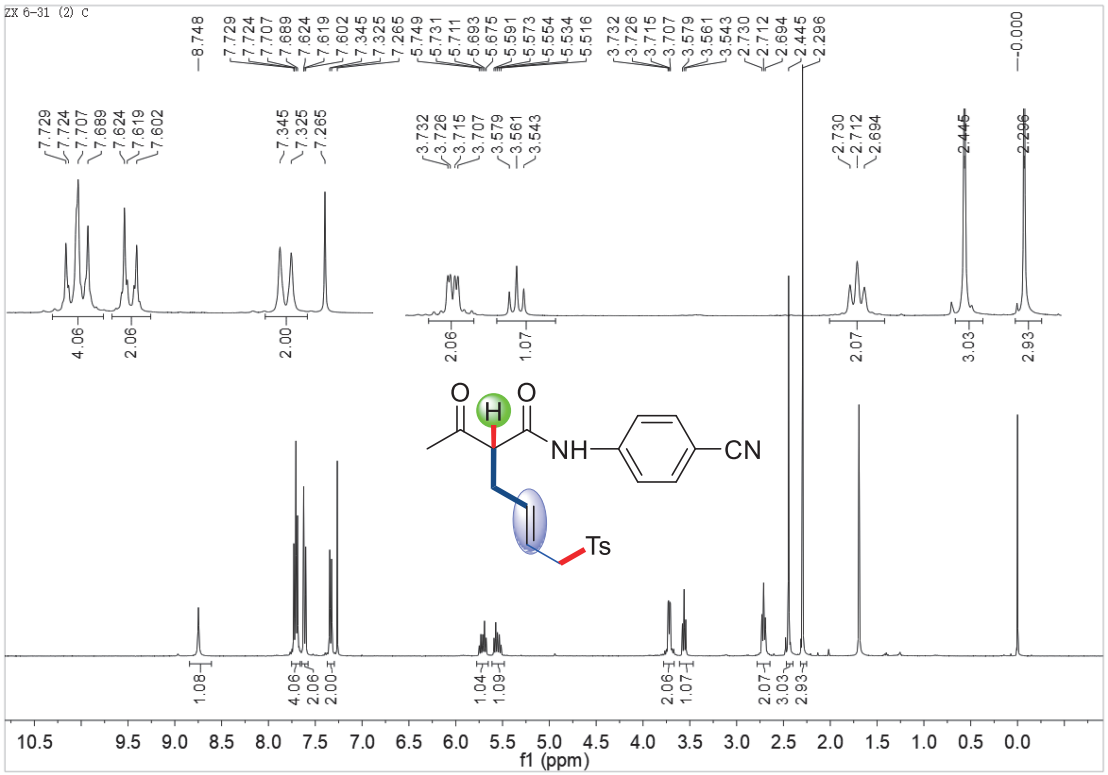
4e8, DEPT 90 and DEPT 135



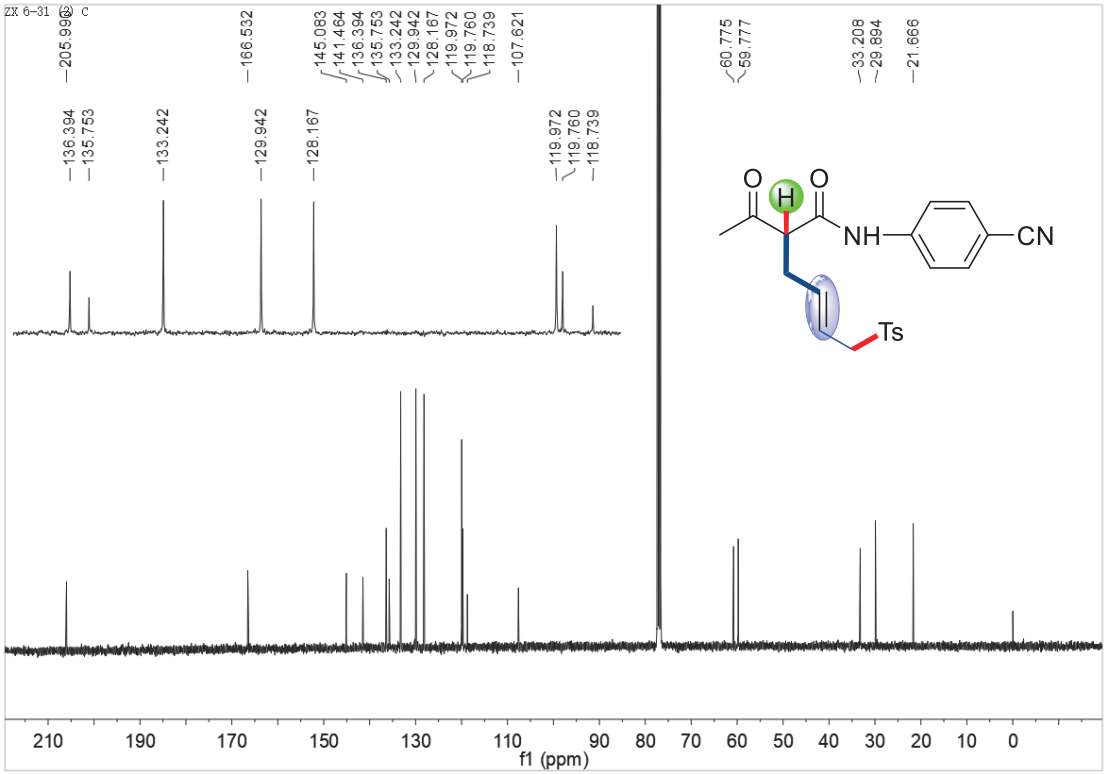
4e8, ^{19}F NMR



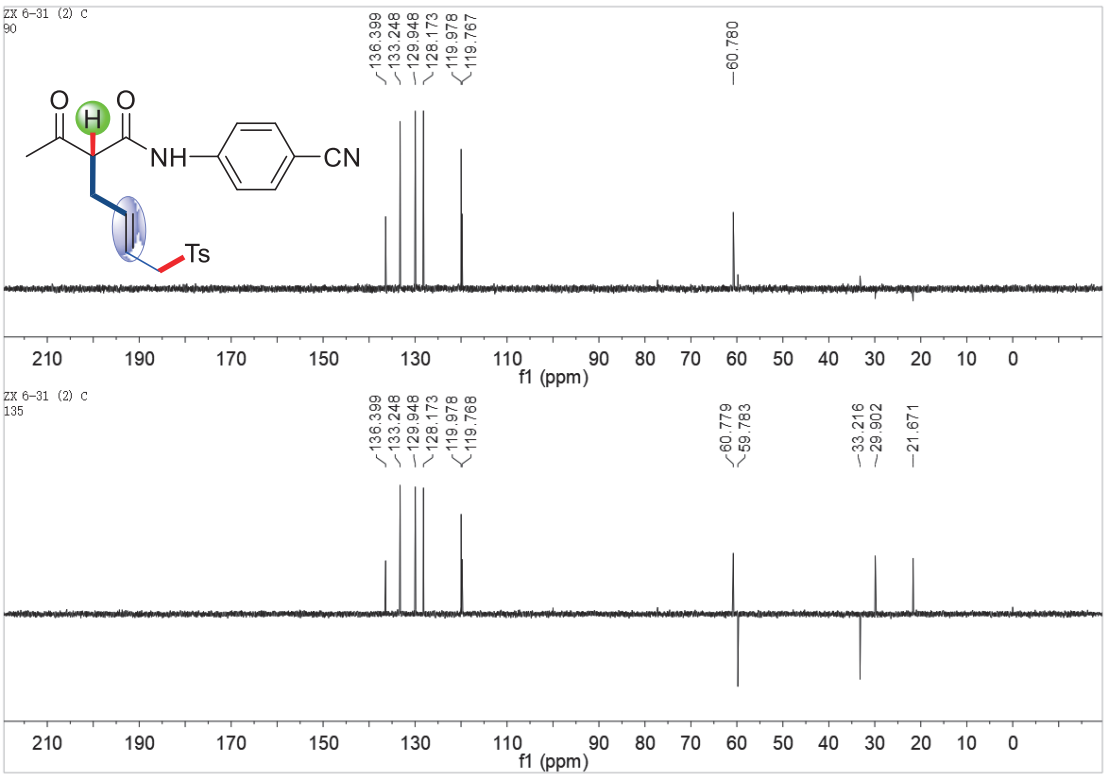
4e9, ^{1}H NMR



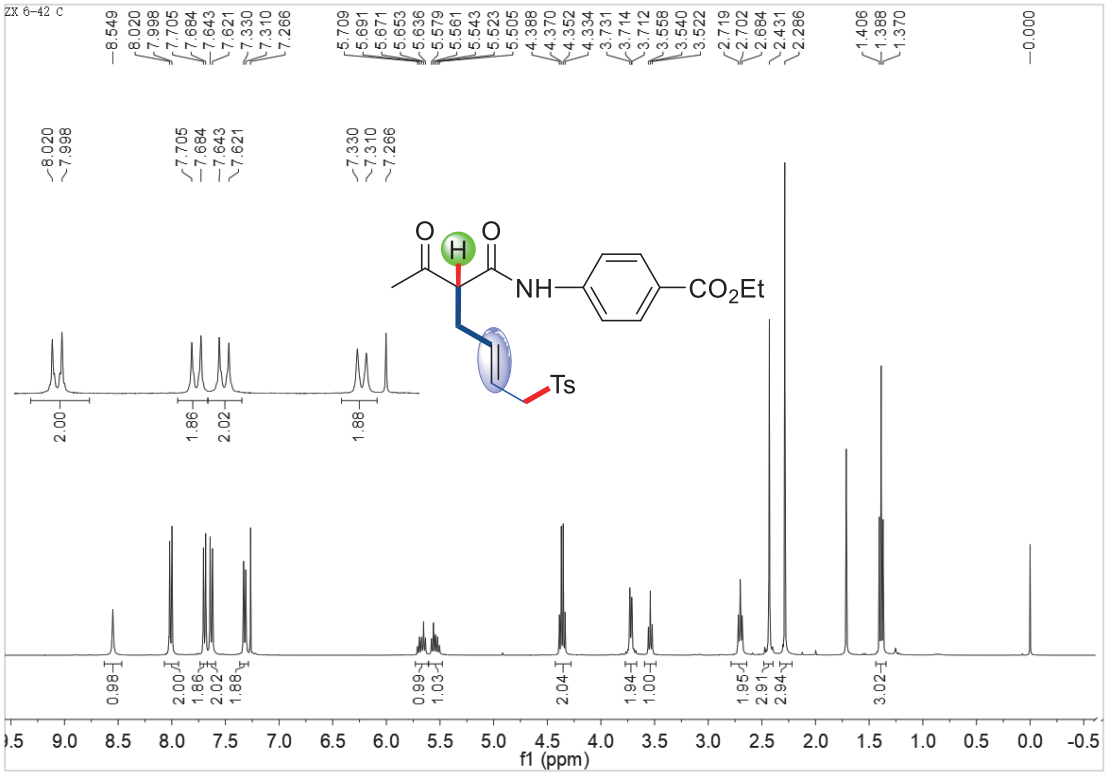
4e9, ^{13}C NMR



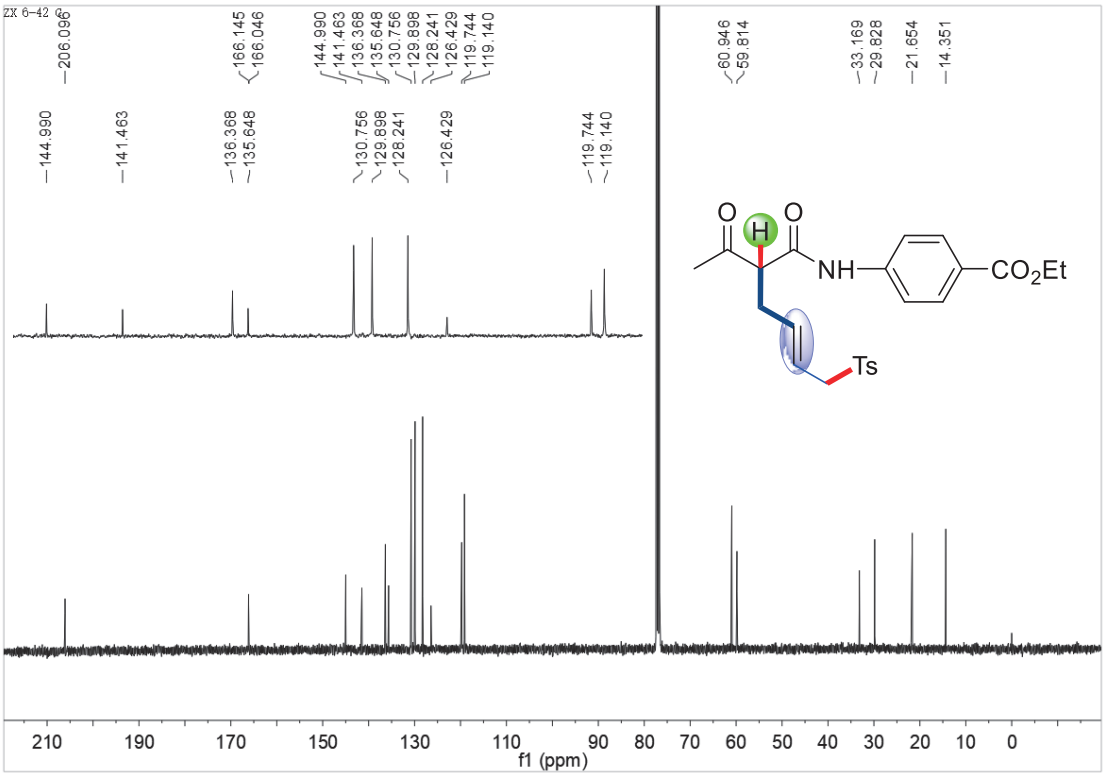
4e9, DEPT 90 and DEPT 135



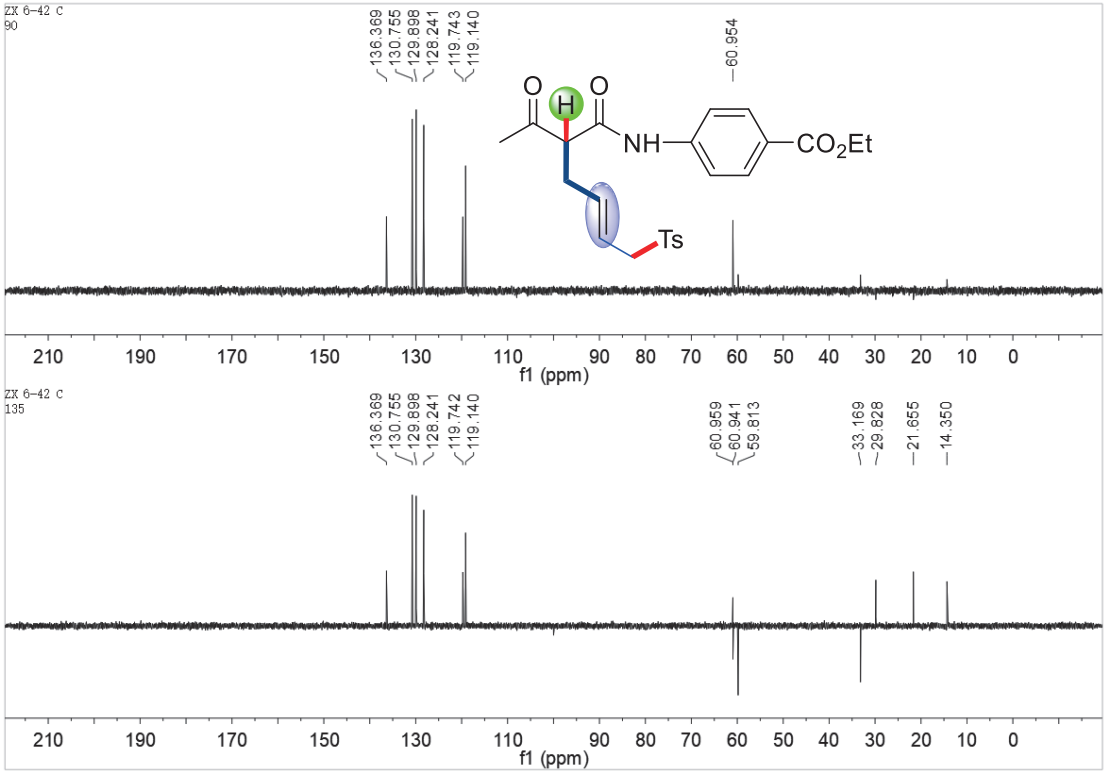
4e10, ^{1}H NMR



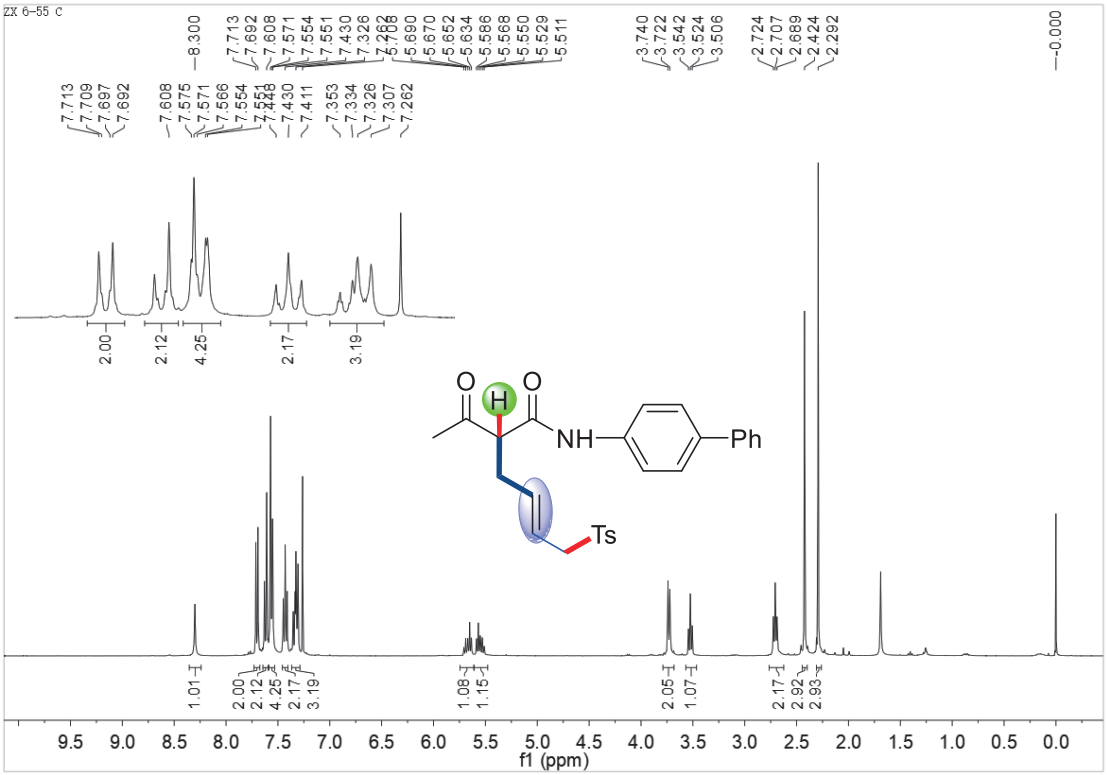
4e10, ^{13}C NMR



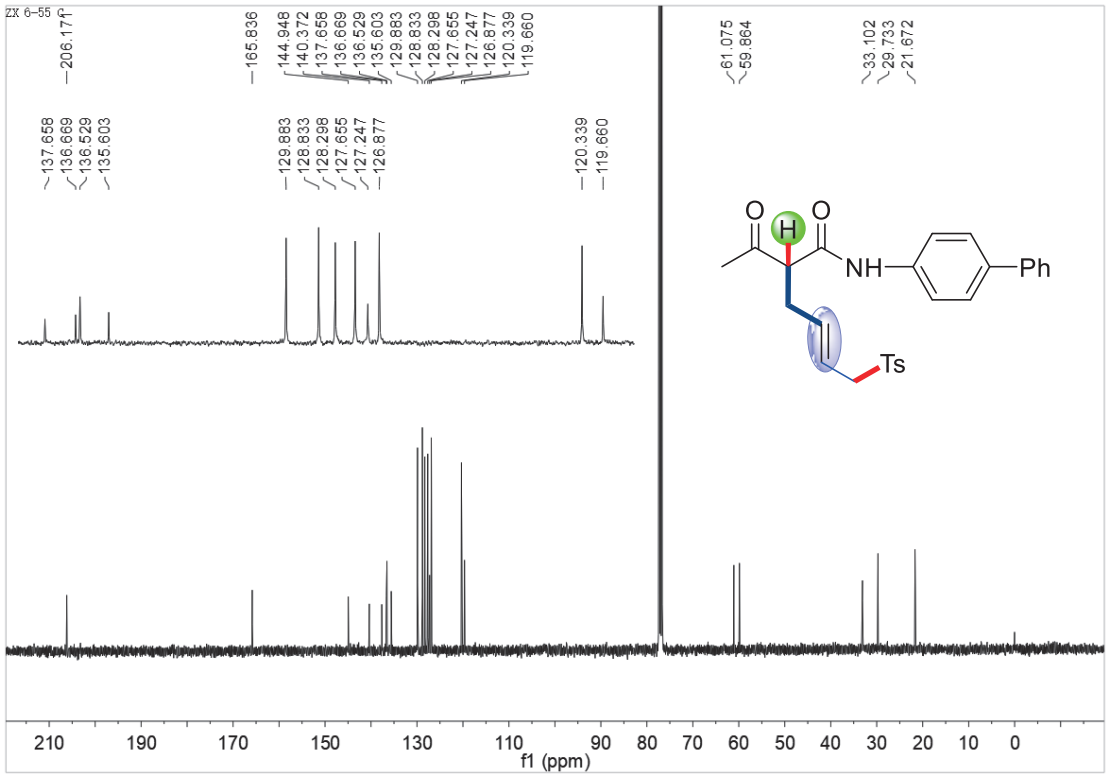
4e10, DEPT 90 and DEPT 135



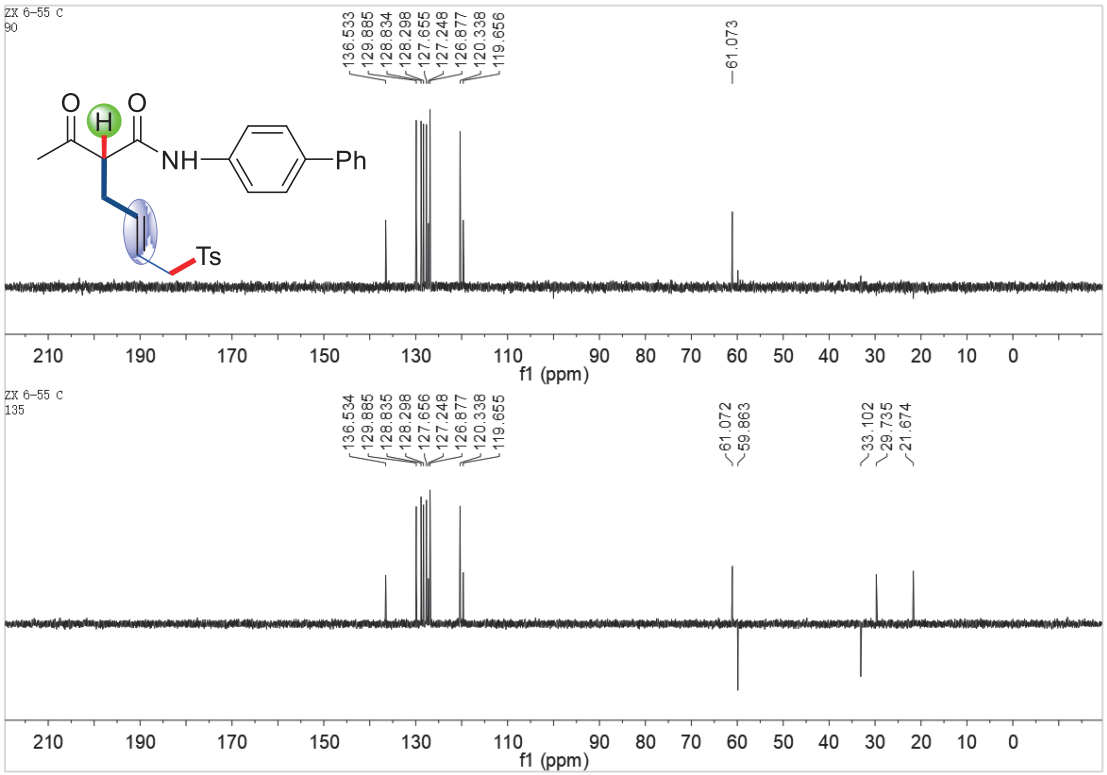
4e11, ^{1}H NMR



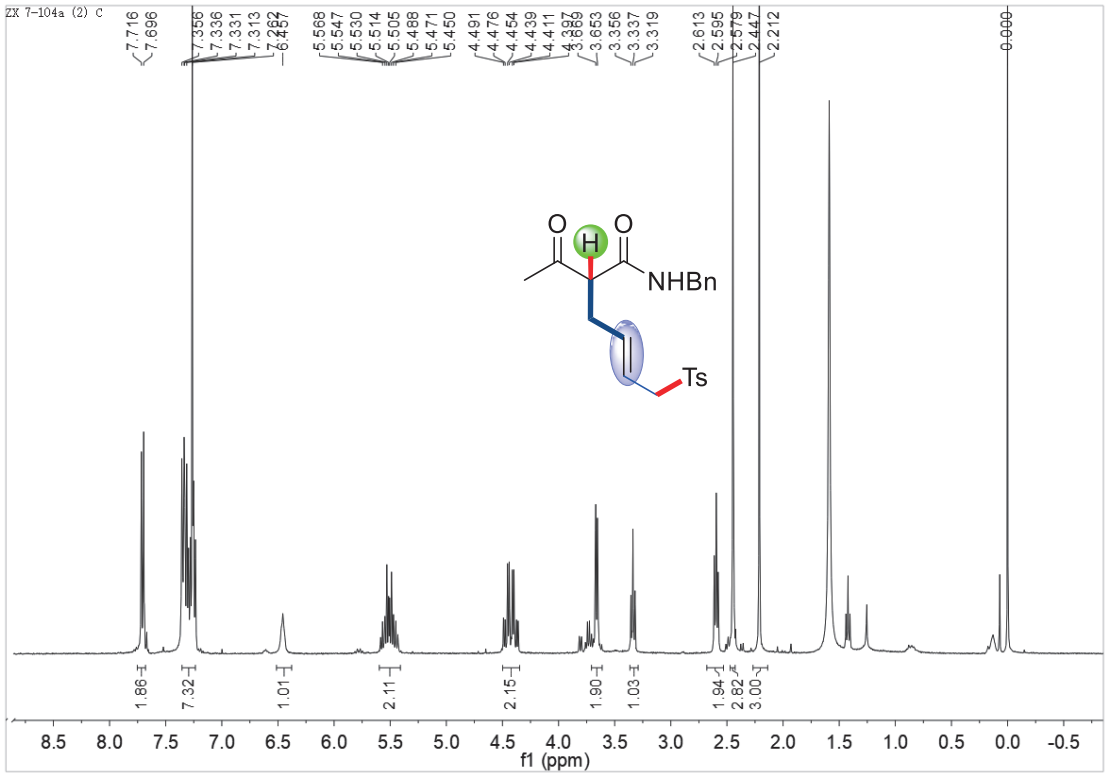
4e11, ^{13}C NMR



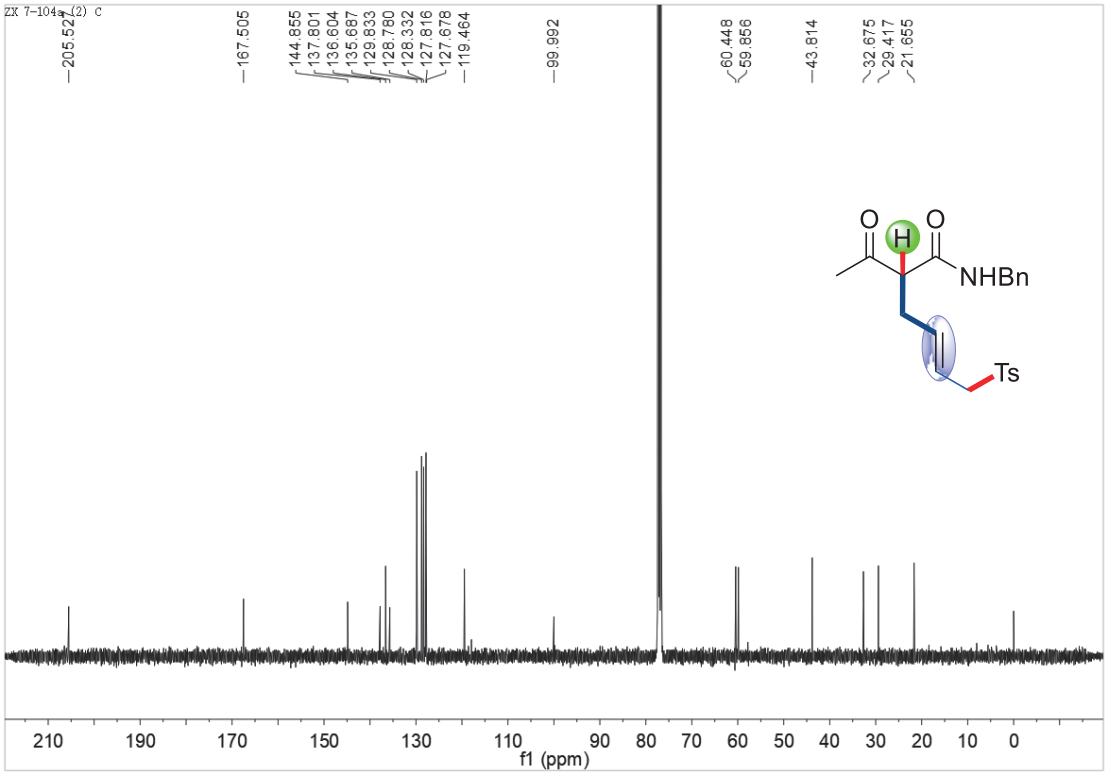
4e11, DEPT 90 and DEPT 135



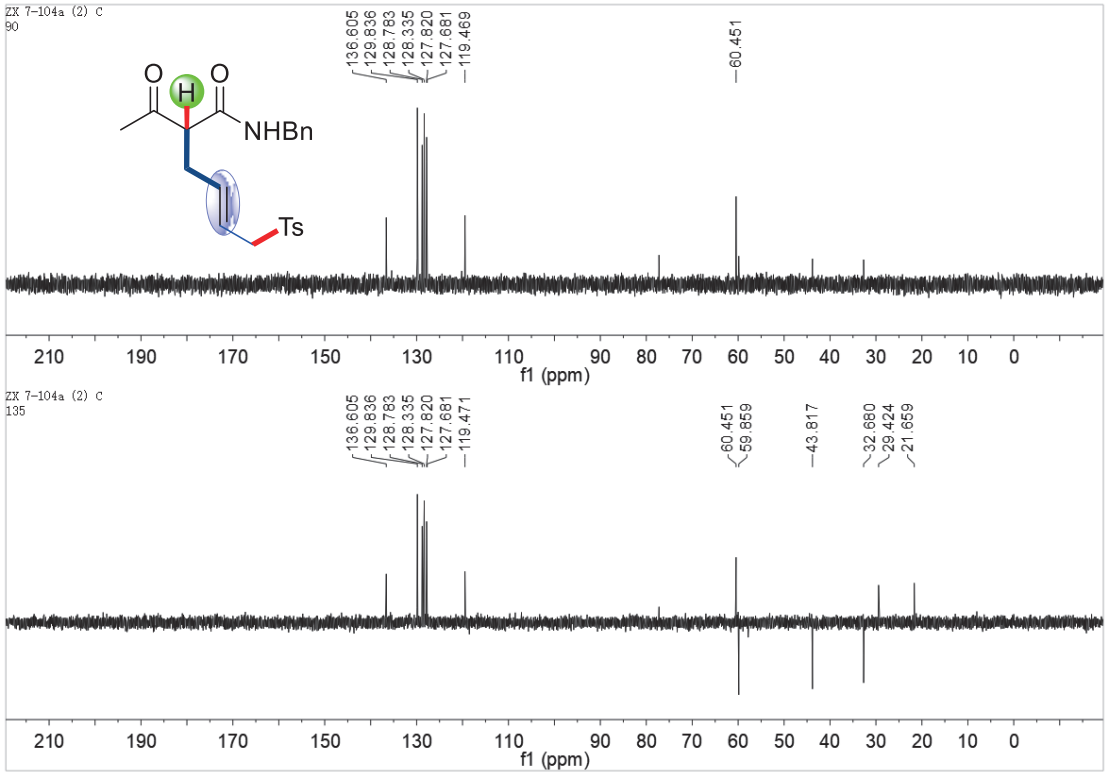
4f, ^{1}H NMR



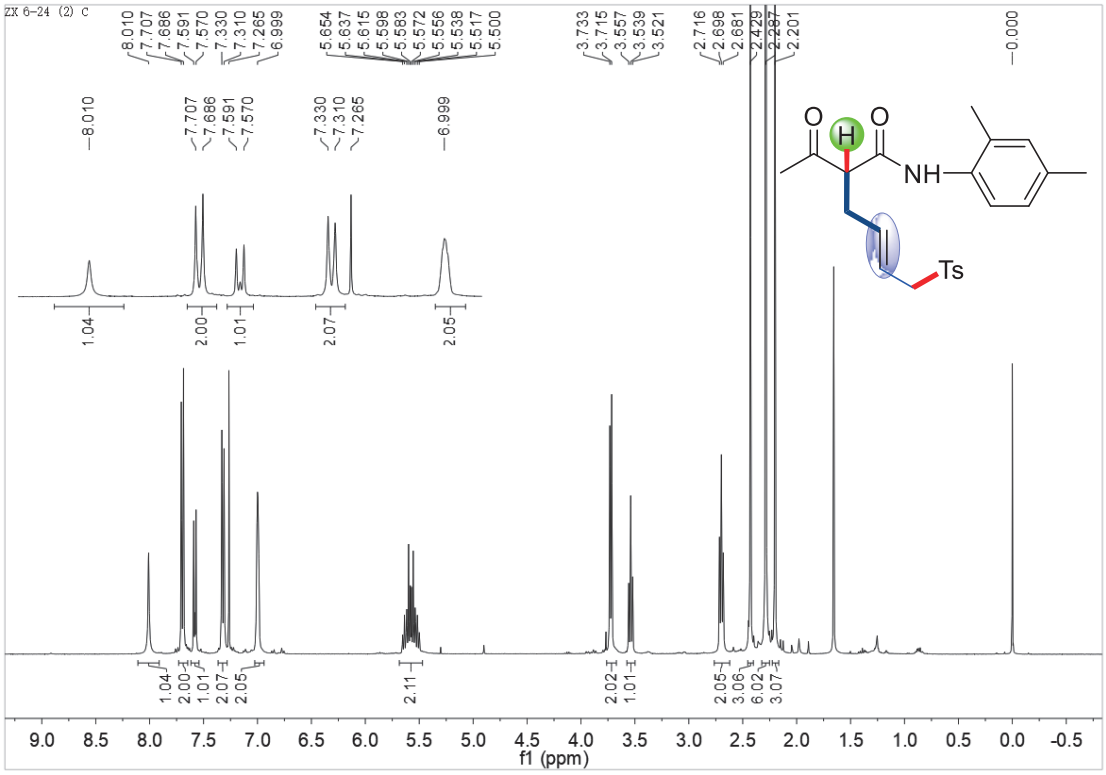
4f, ^{13}C NMR



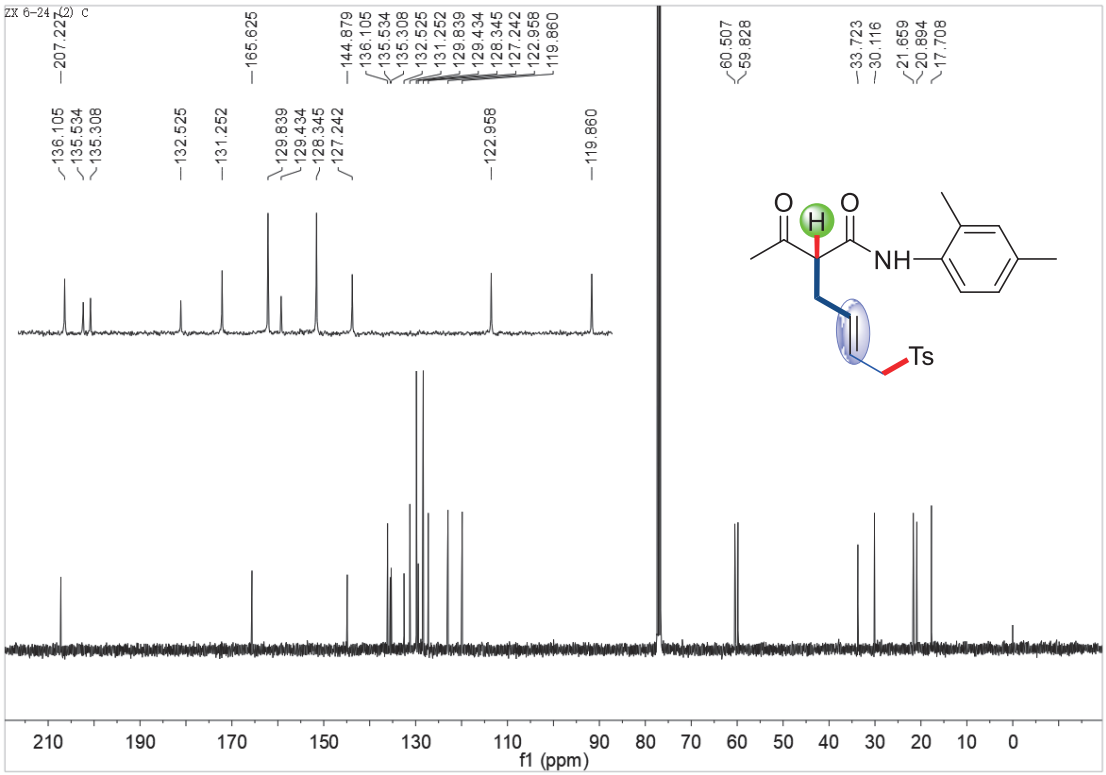
4f, DEPT 90 and DEPT 135



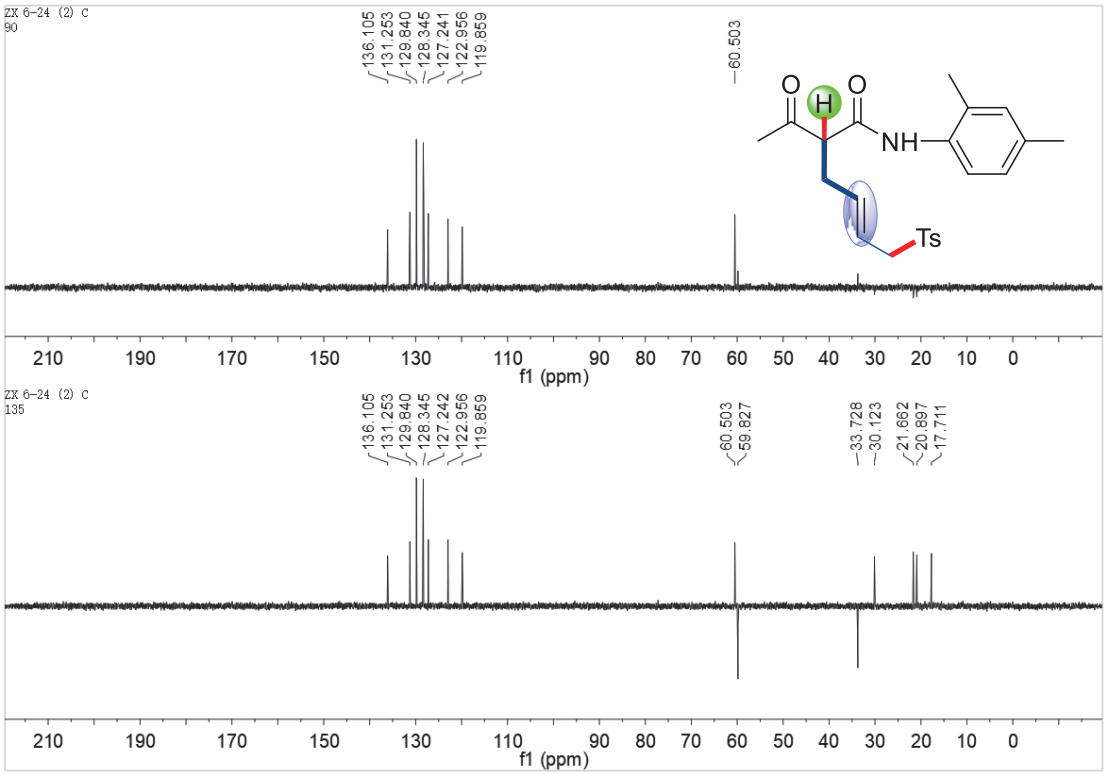
4g1, ^{1}H NMR



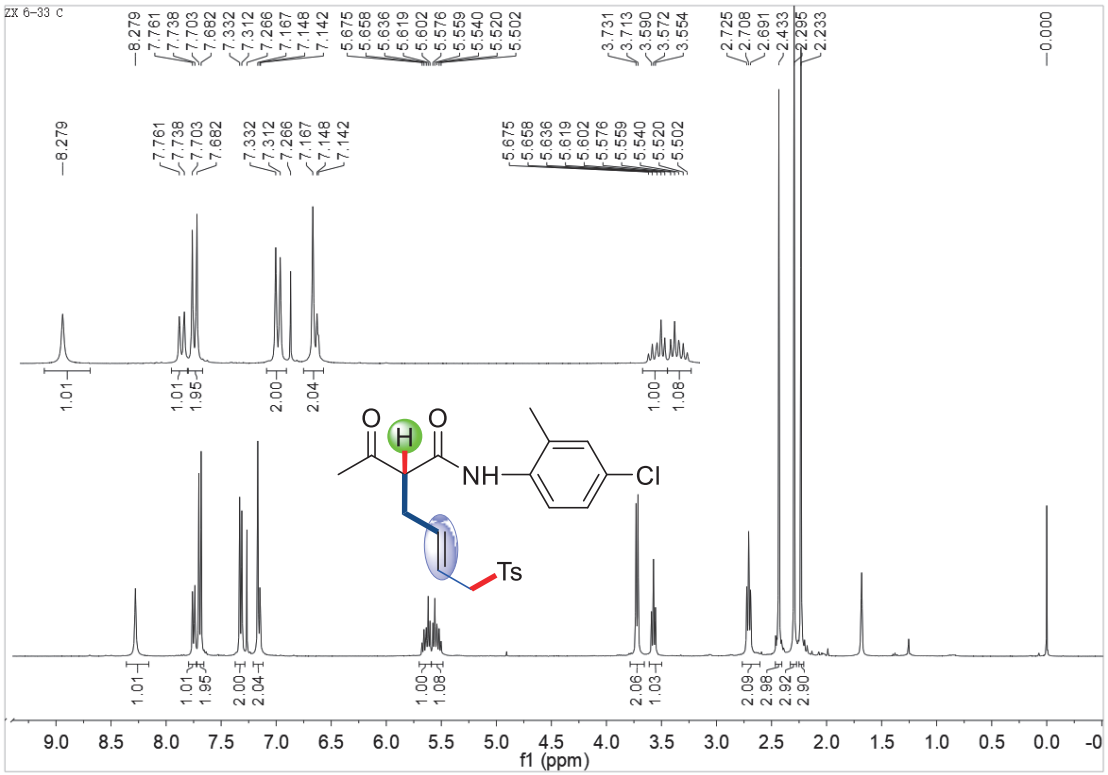
4g1, ^{13}C NMR



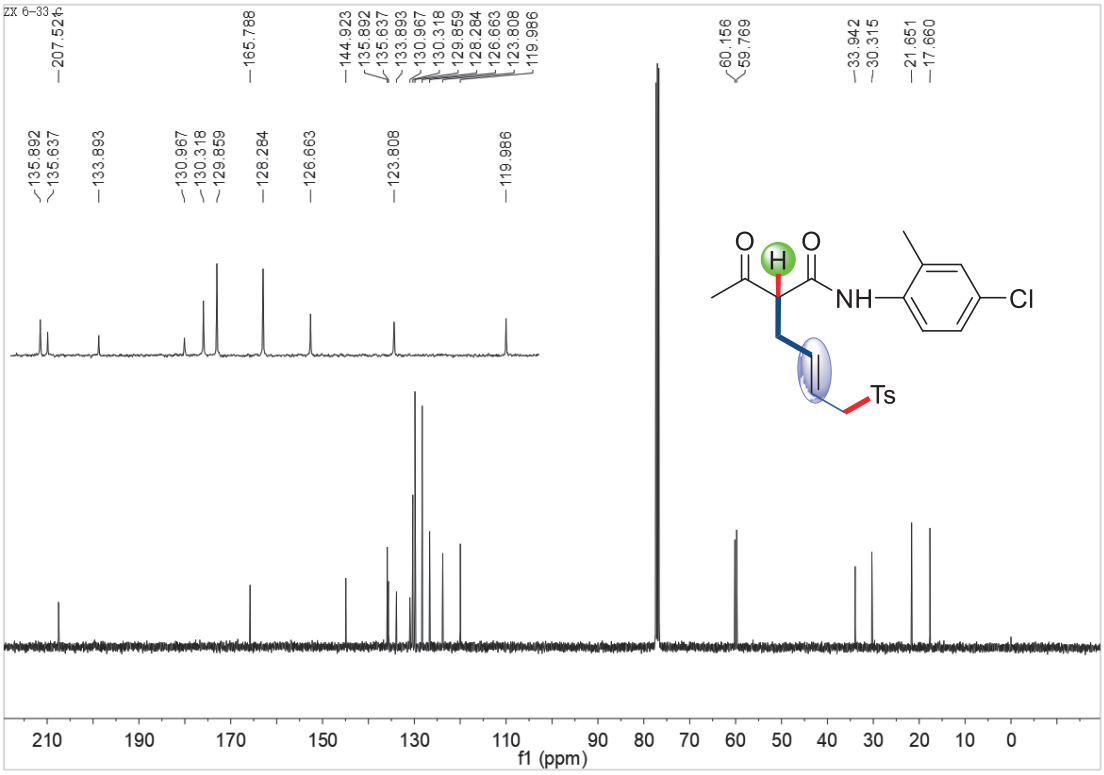
4g1, DEPT 90 and DEPT 135



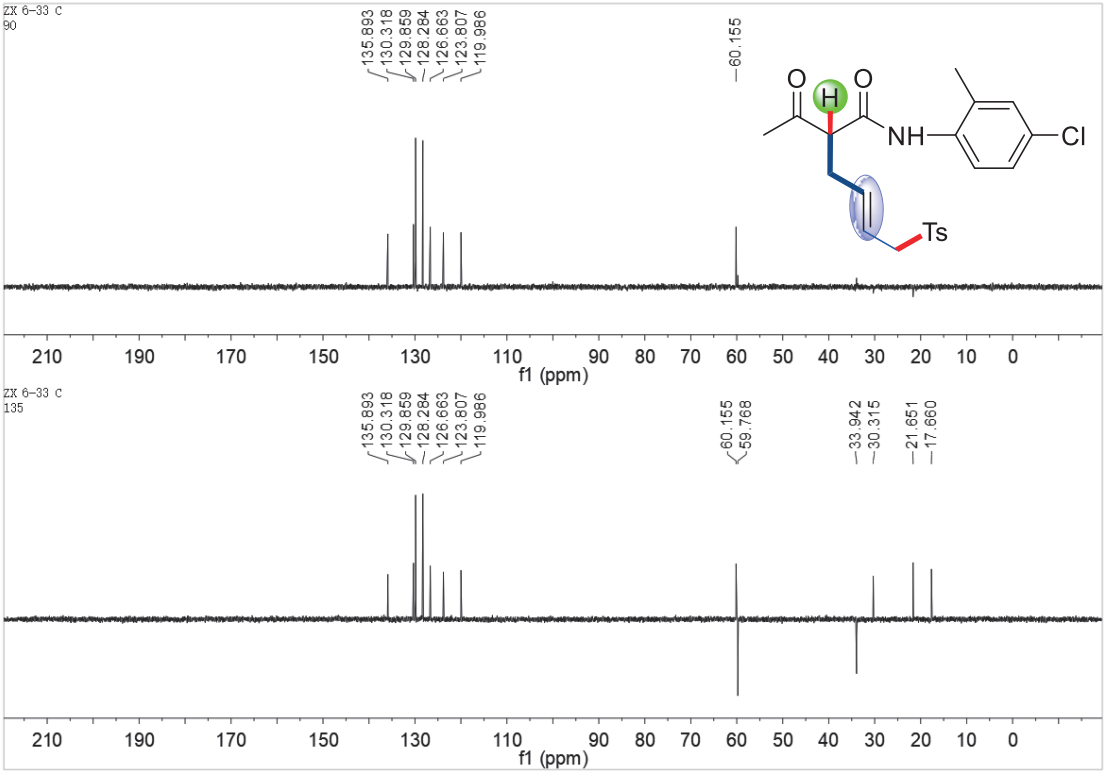
4g2, ^{1}H NMR



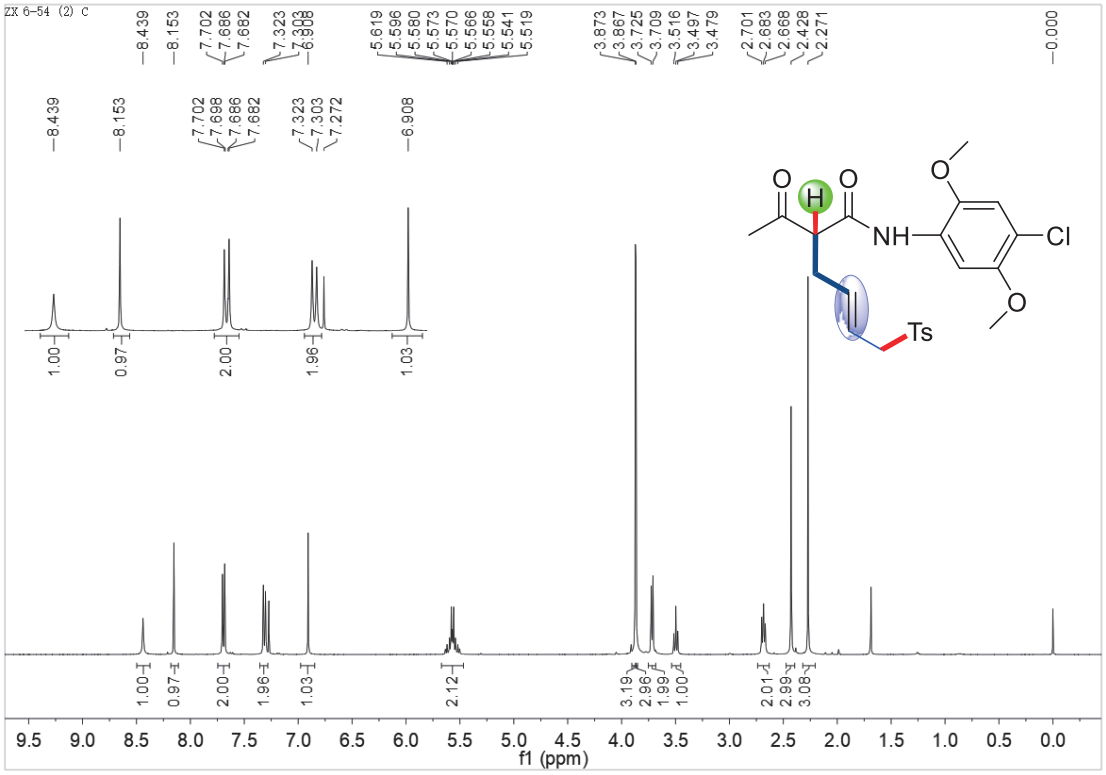
4g2, ^{13}C NMR



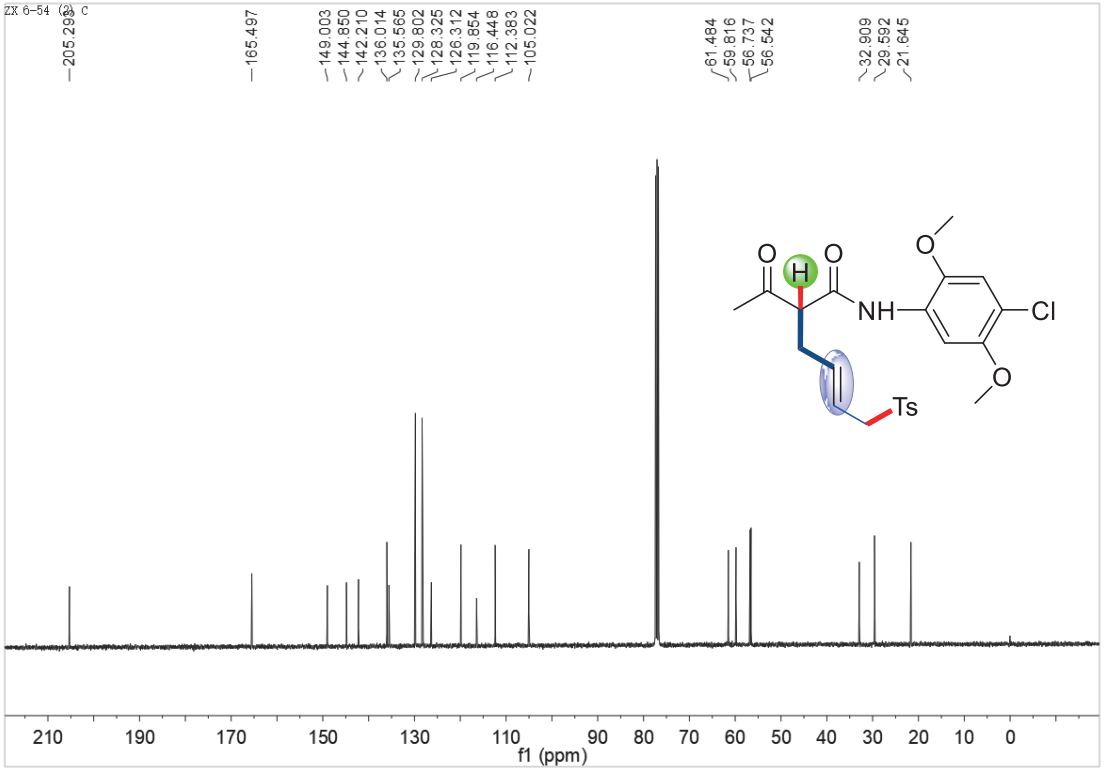
4g2, DEPT 90 and DEPT 135



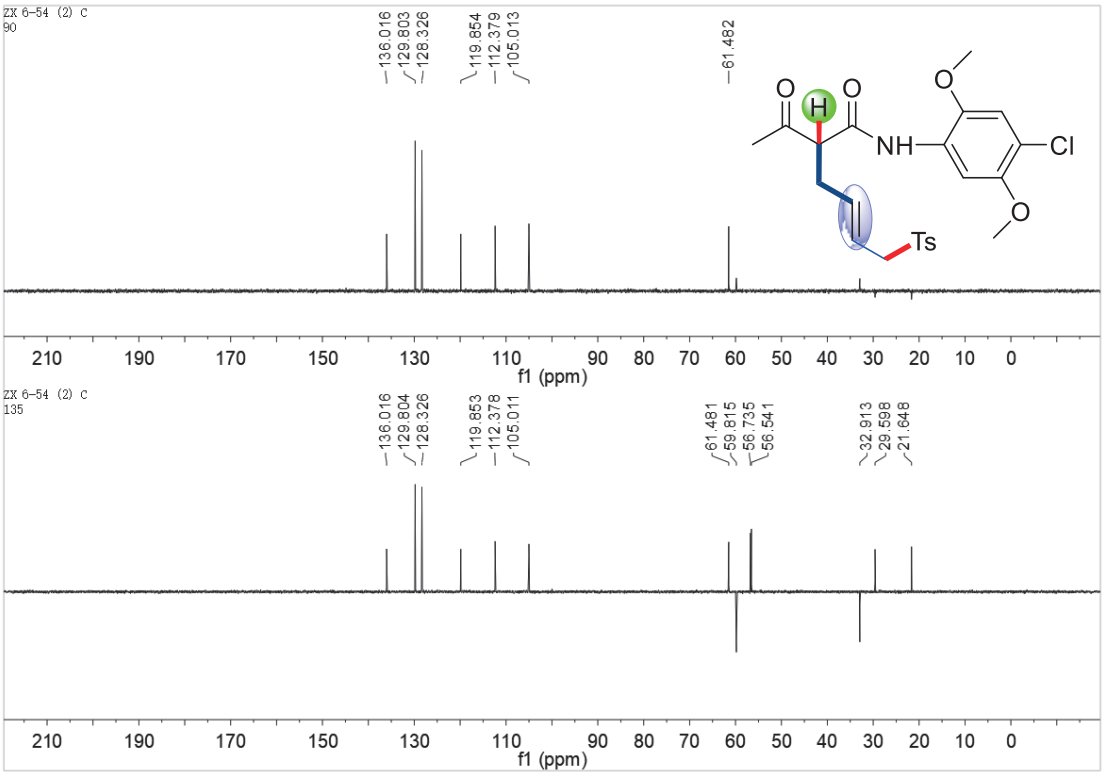
4h, ^{1}H NMR



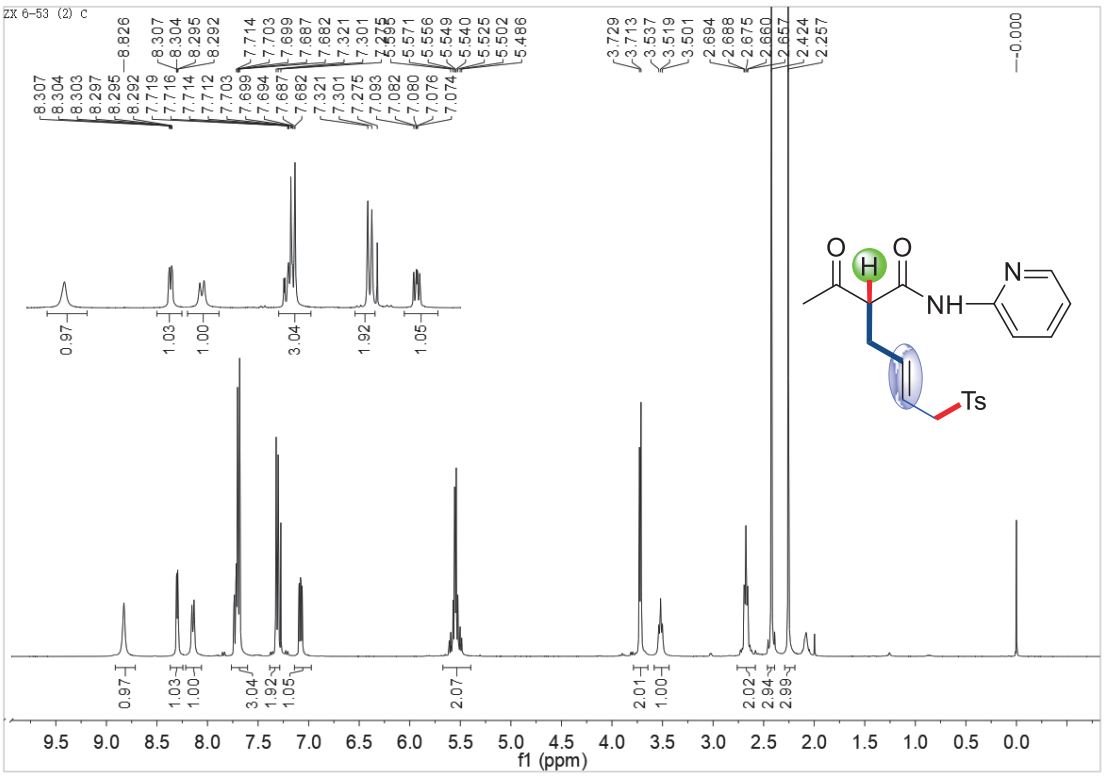
4h, ^{13}C NMR



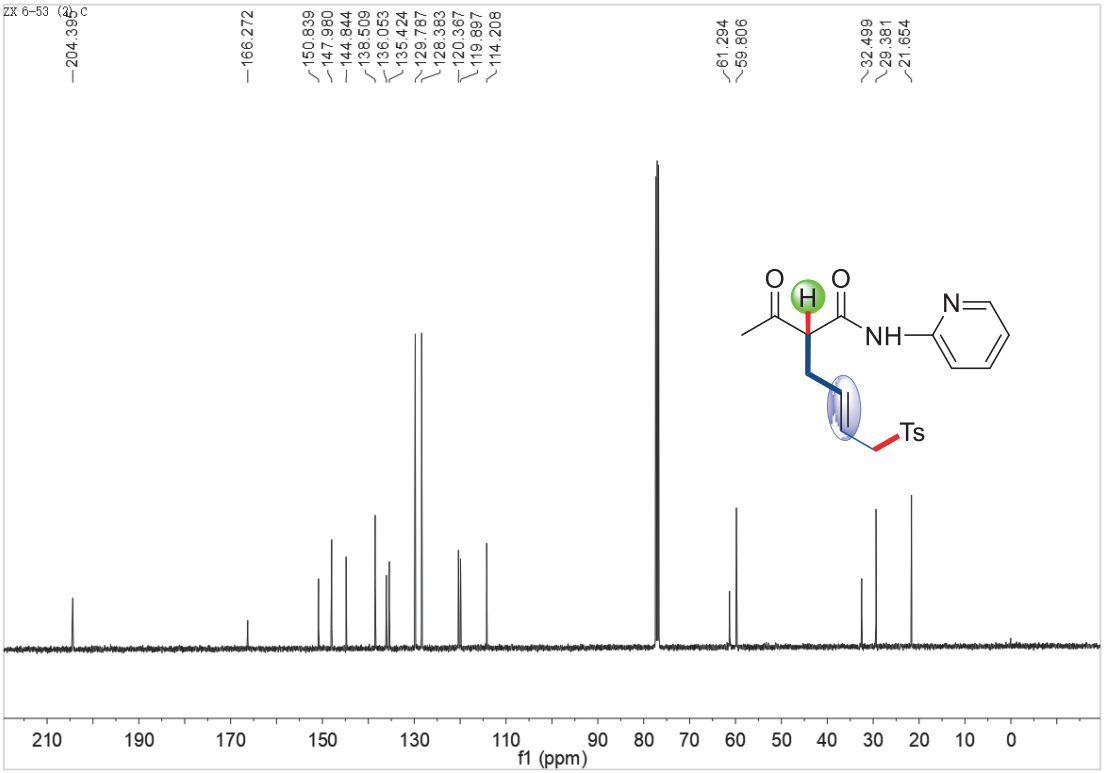
4h, DEPT 90 and DEPT 135



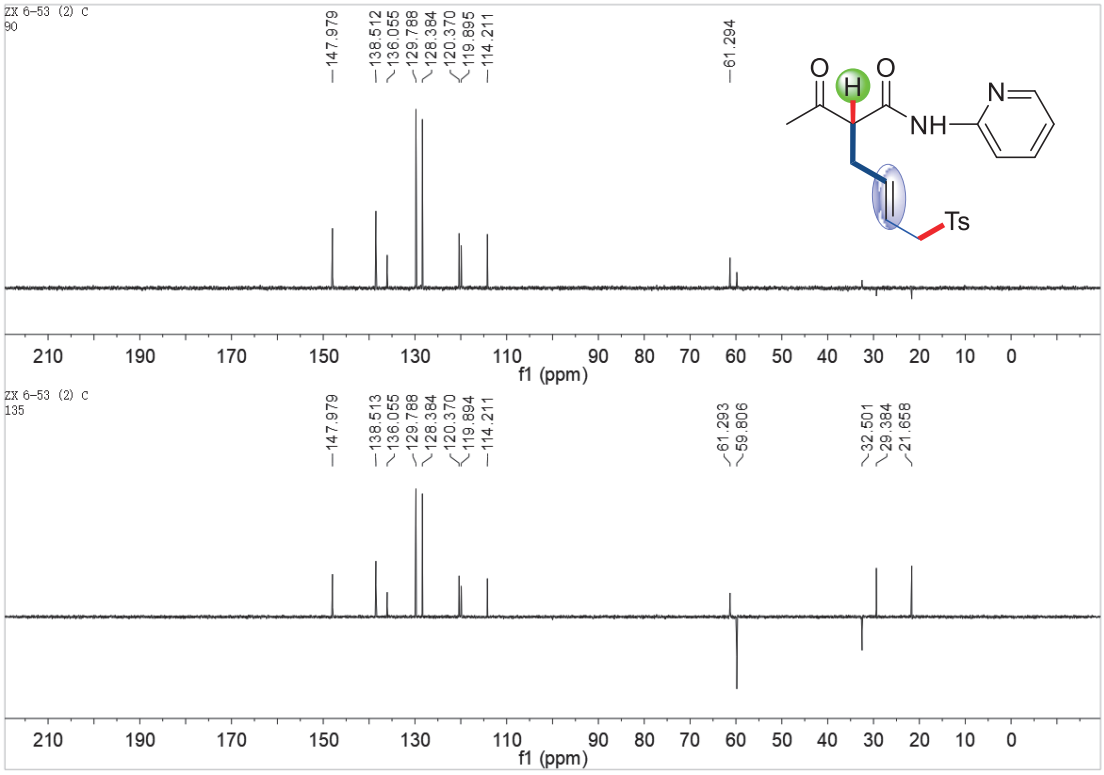
4i, ^{1}H NMR



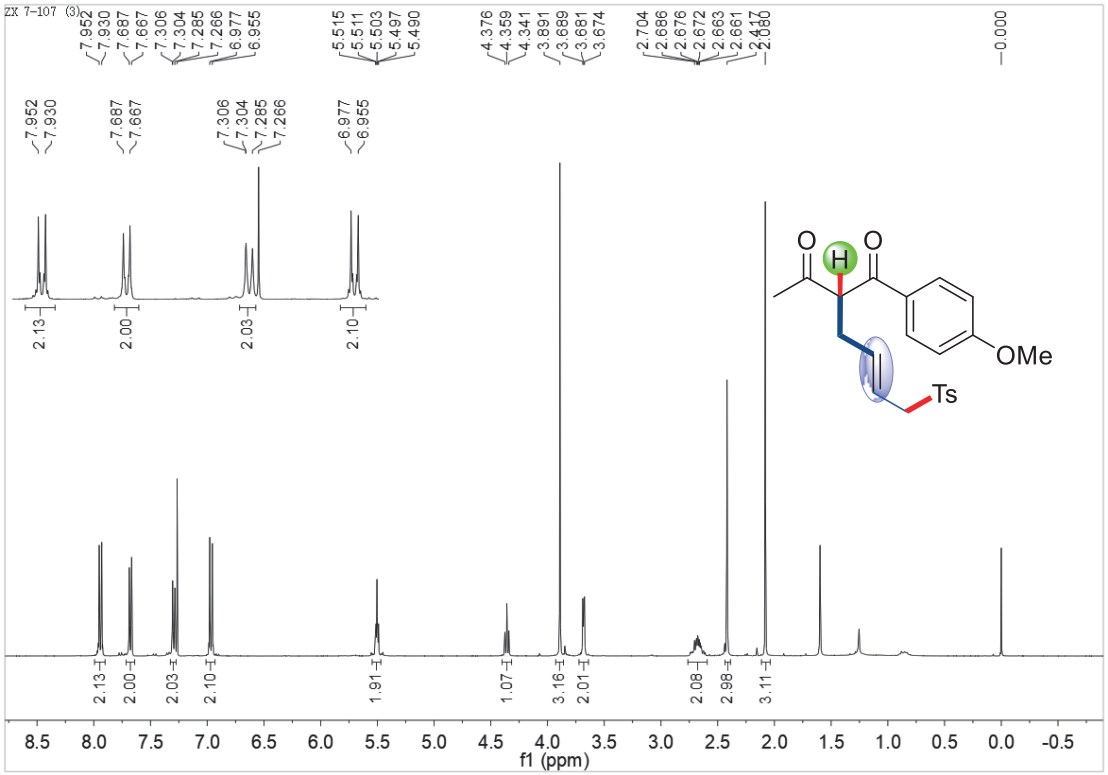
4i, ^{13}C NMR



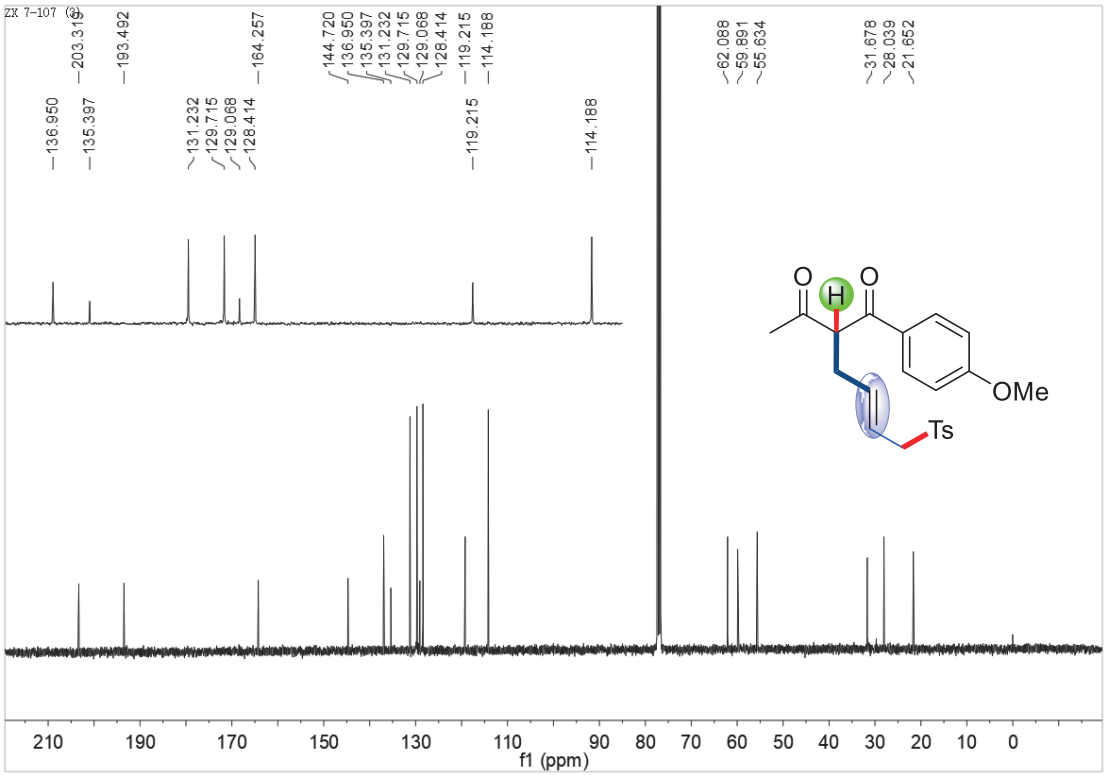
4i, DEPT 90 and DEPT 135



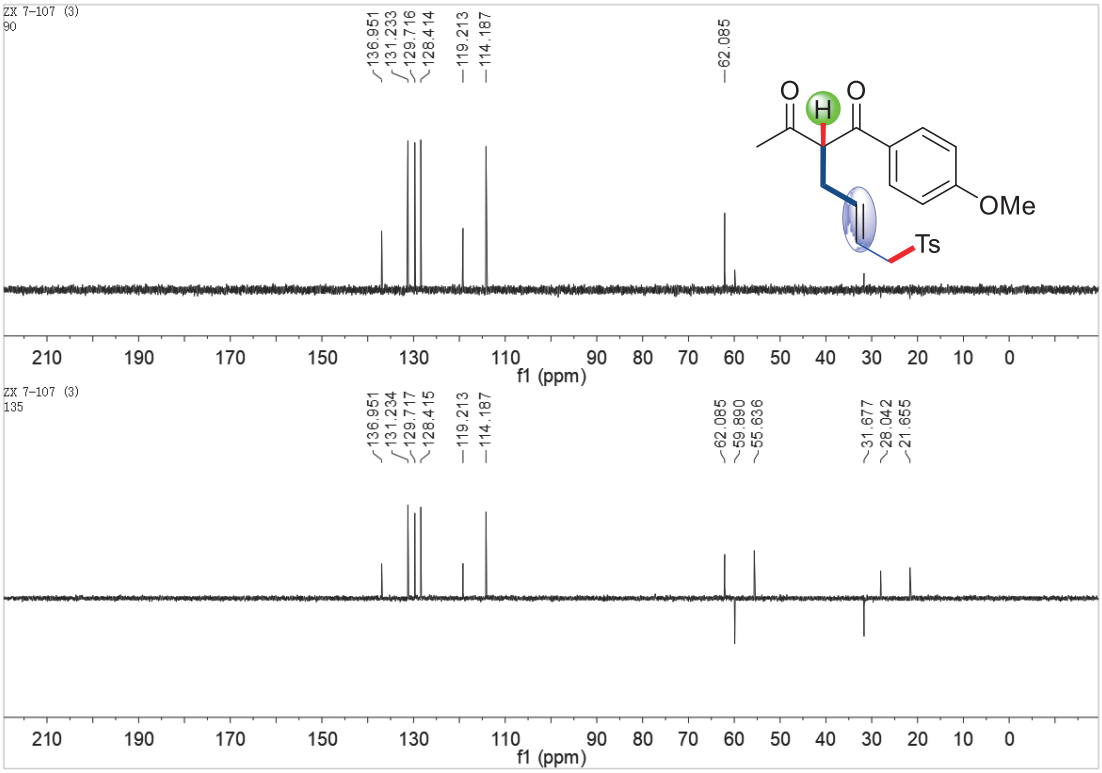
4j1, ^{1}H NMR



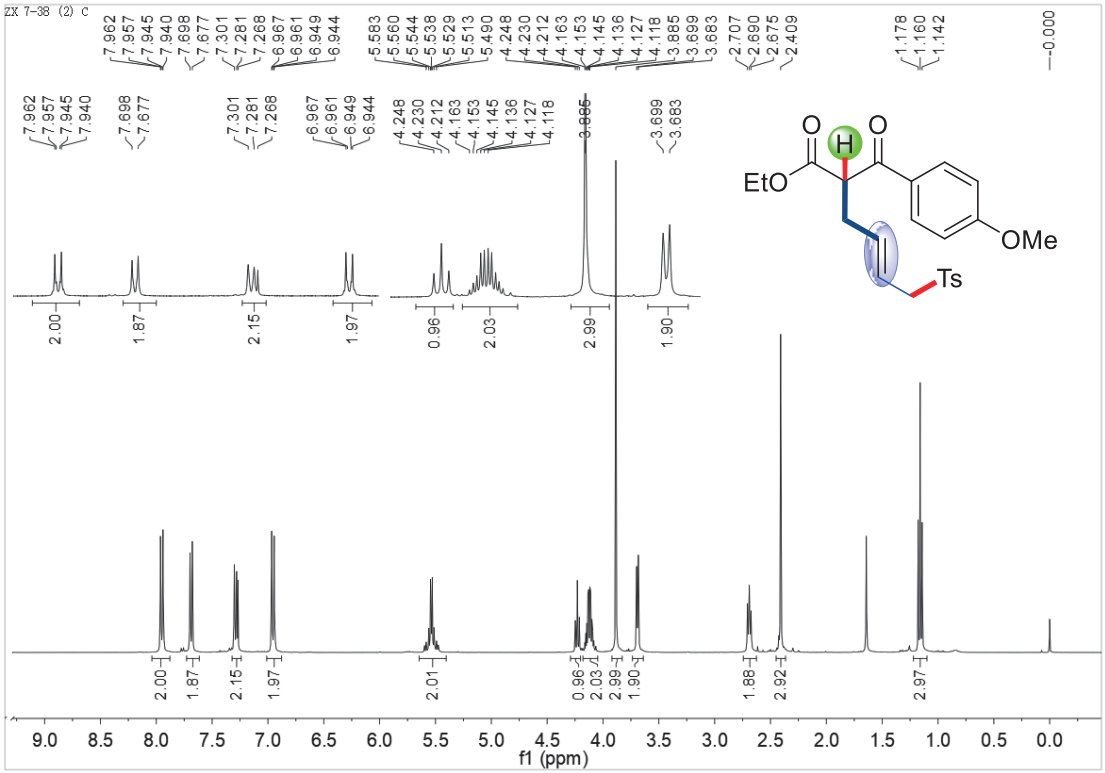
4j1, ^{13}C NMR



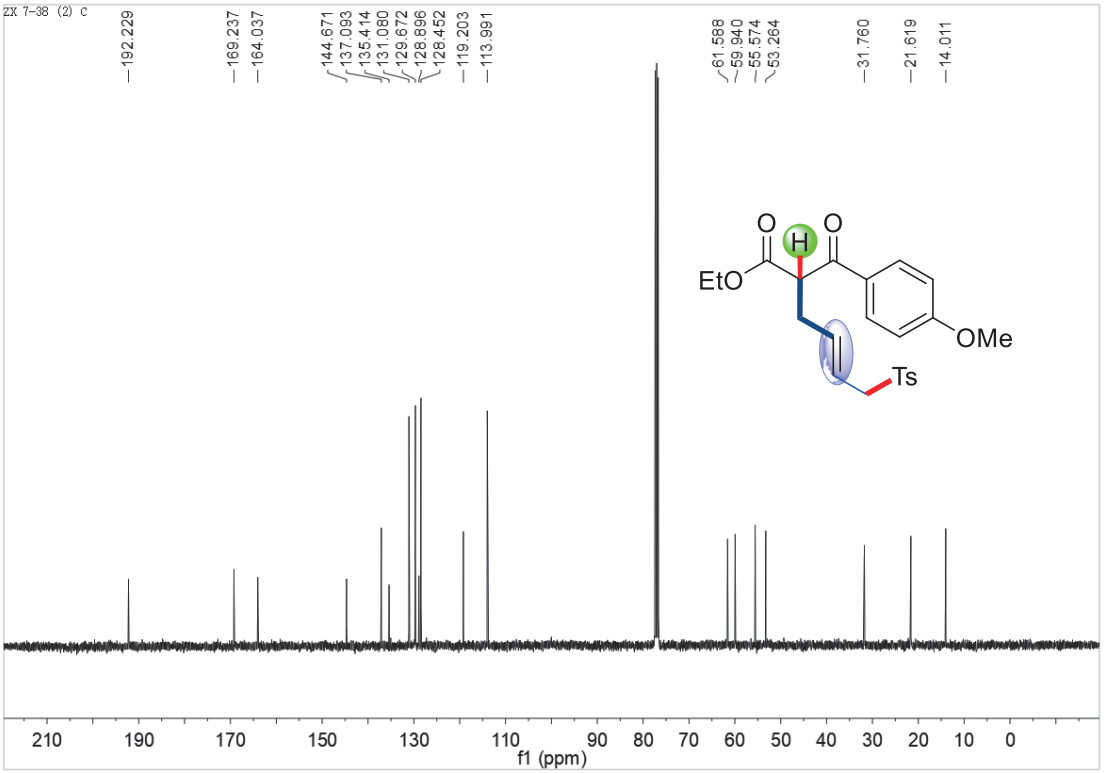
4j1, DEPT 90 and DEPT 135



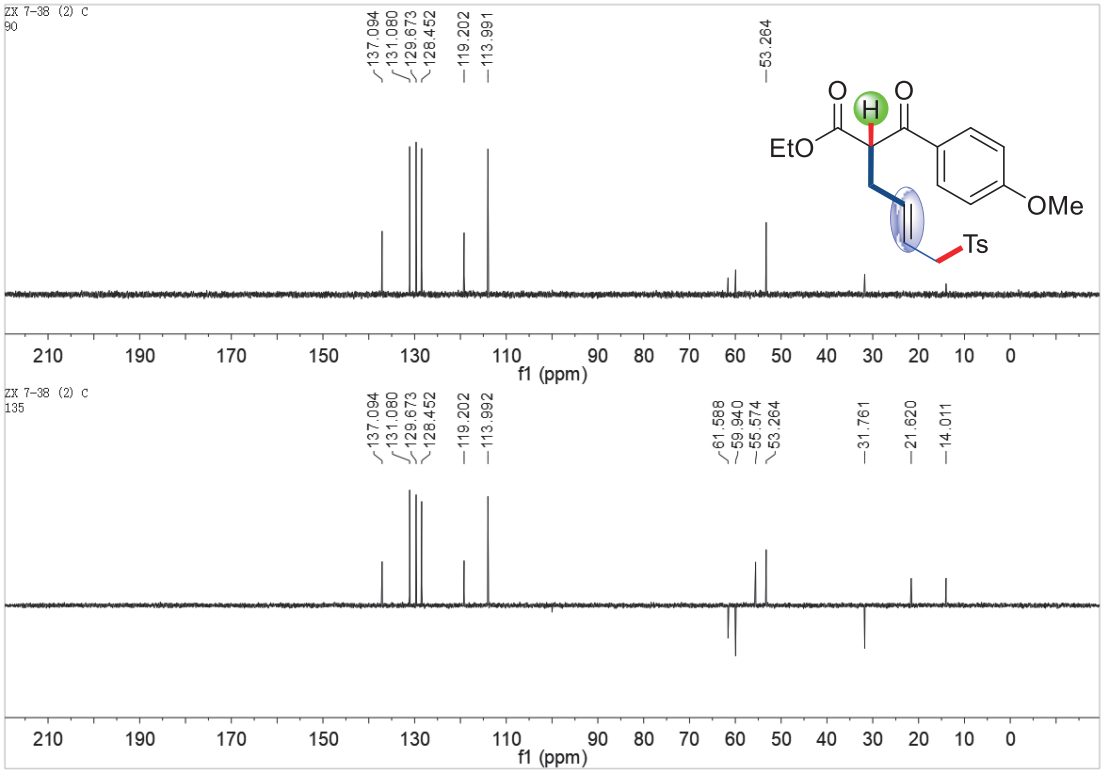
4j2, ^{1}H NMR



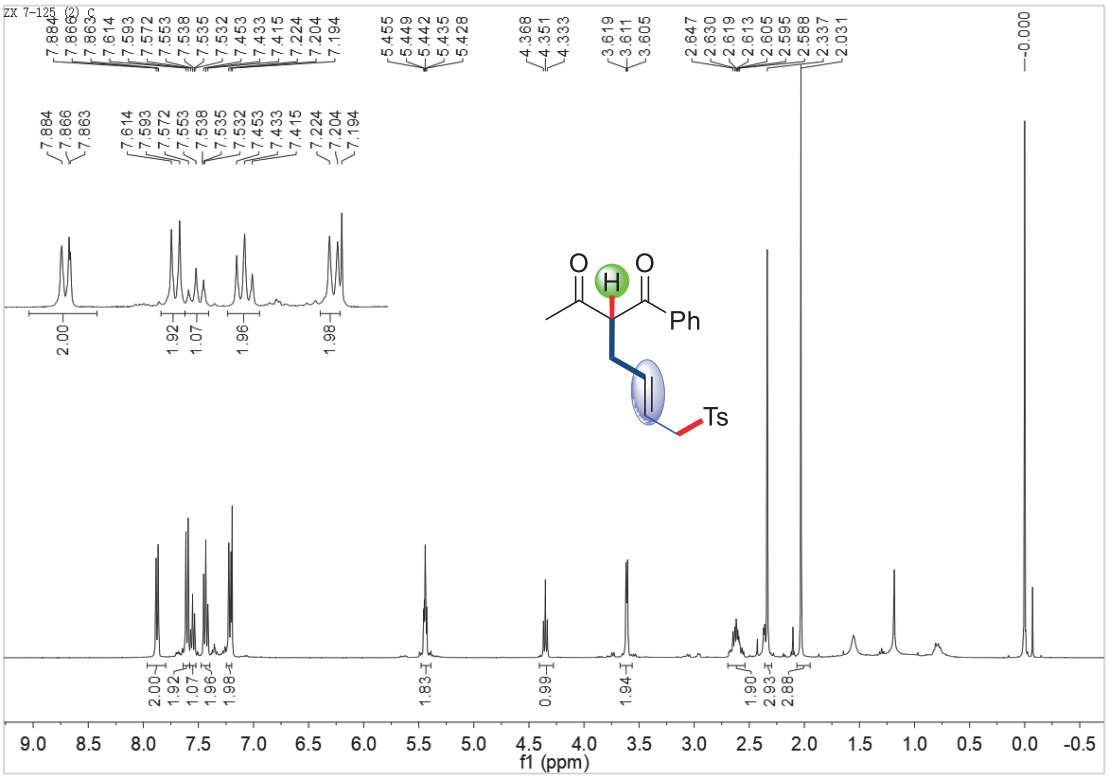
4j2, ^{13}C NMR



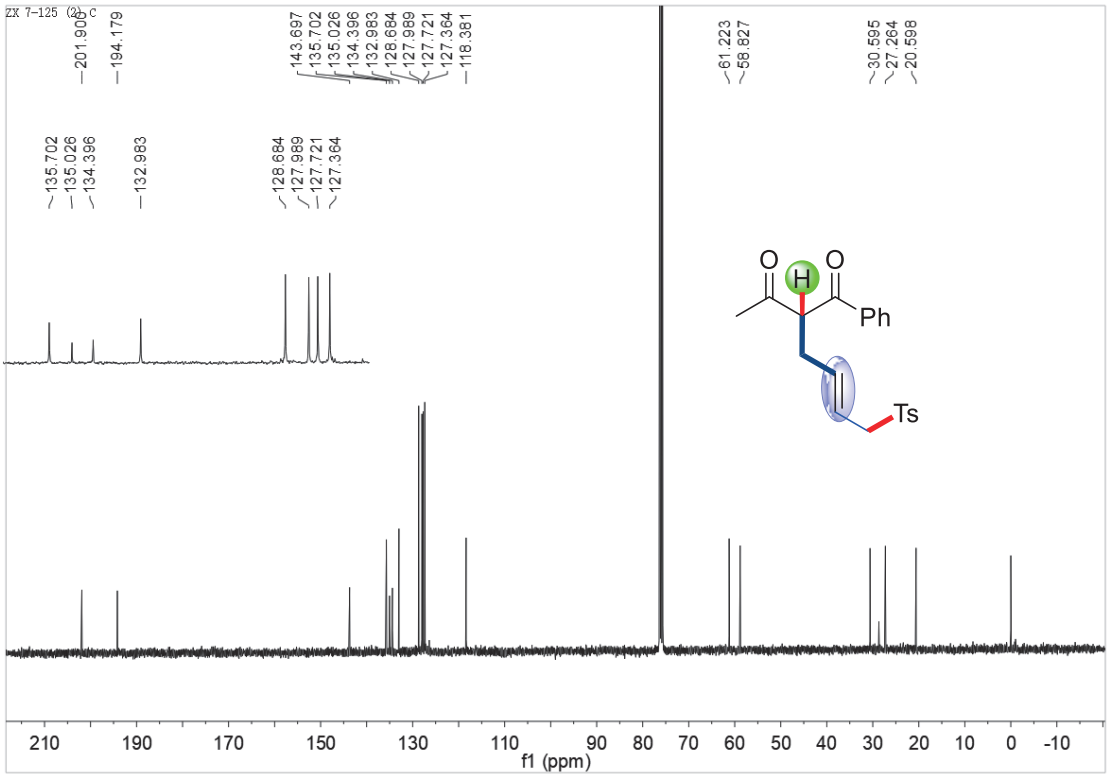
4j2, DEPT 90 and DEPT 135



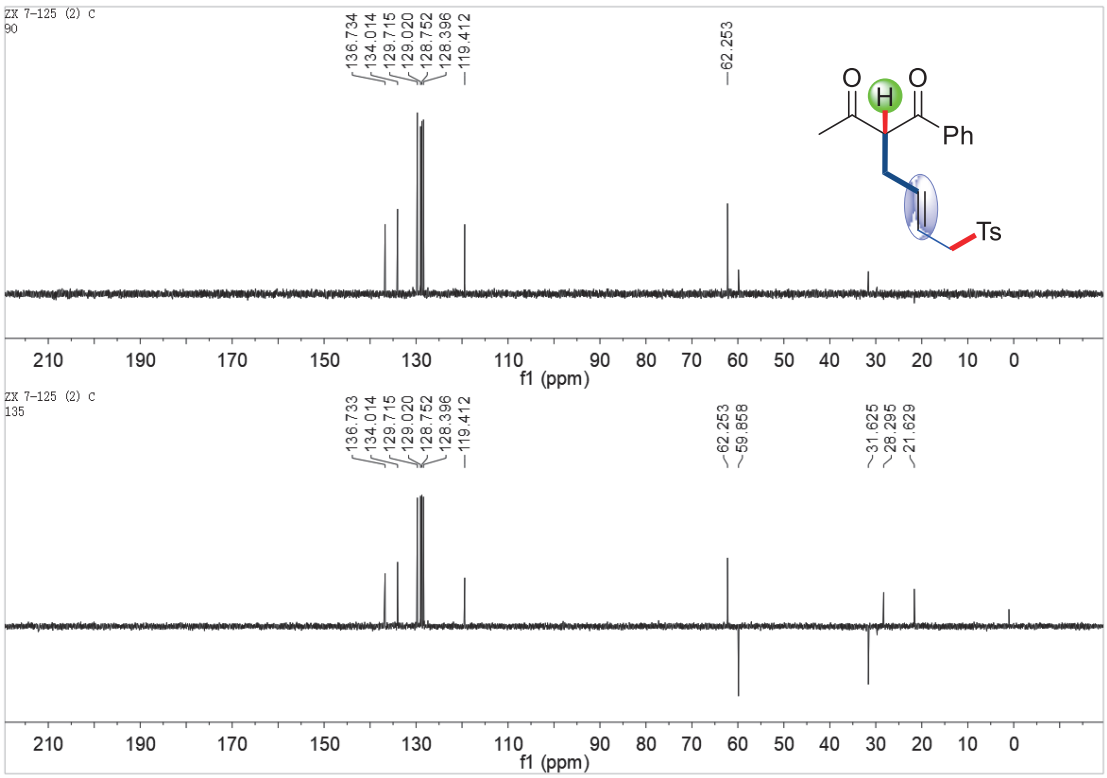
4k1, ^{1}H NMR



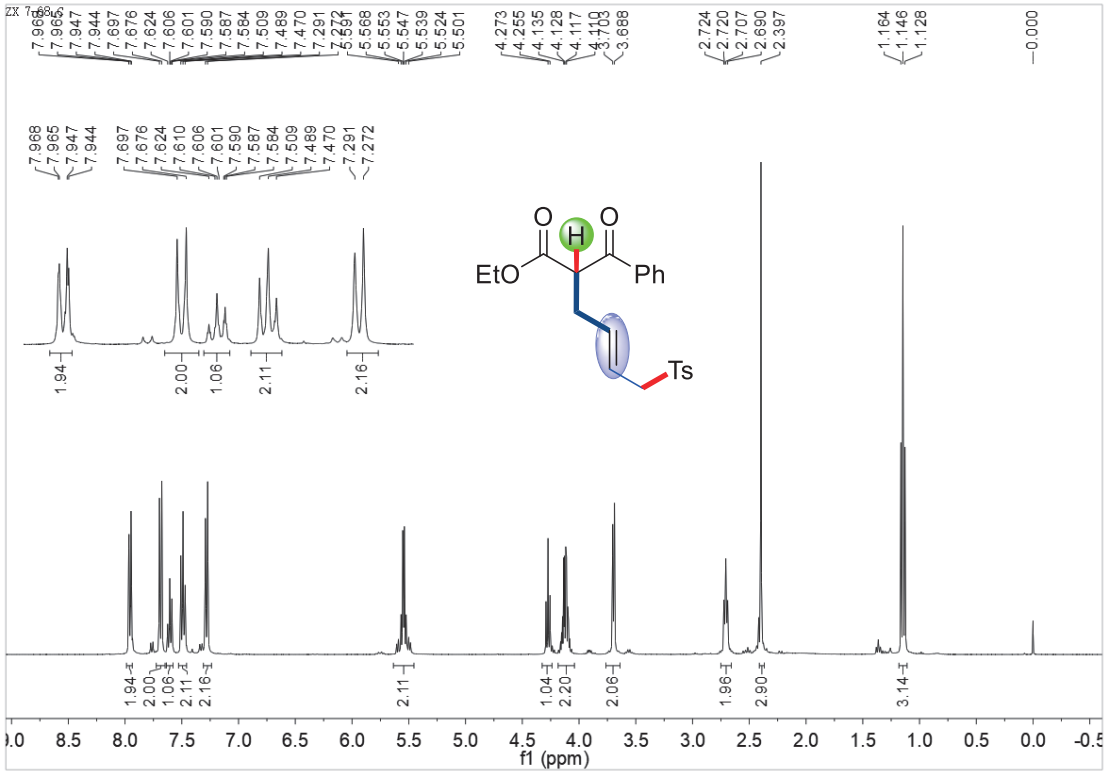
4k1, ^{13}C NMR



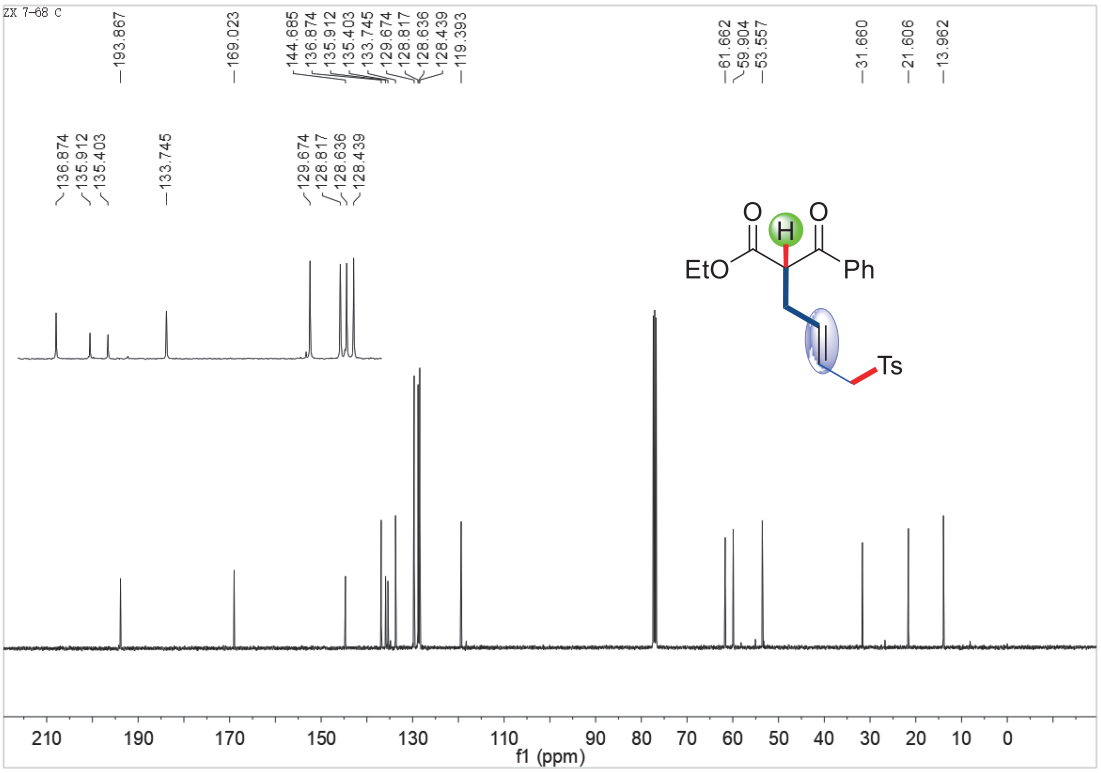
4k1, DEPT 90 and DEPT 135



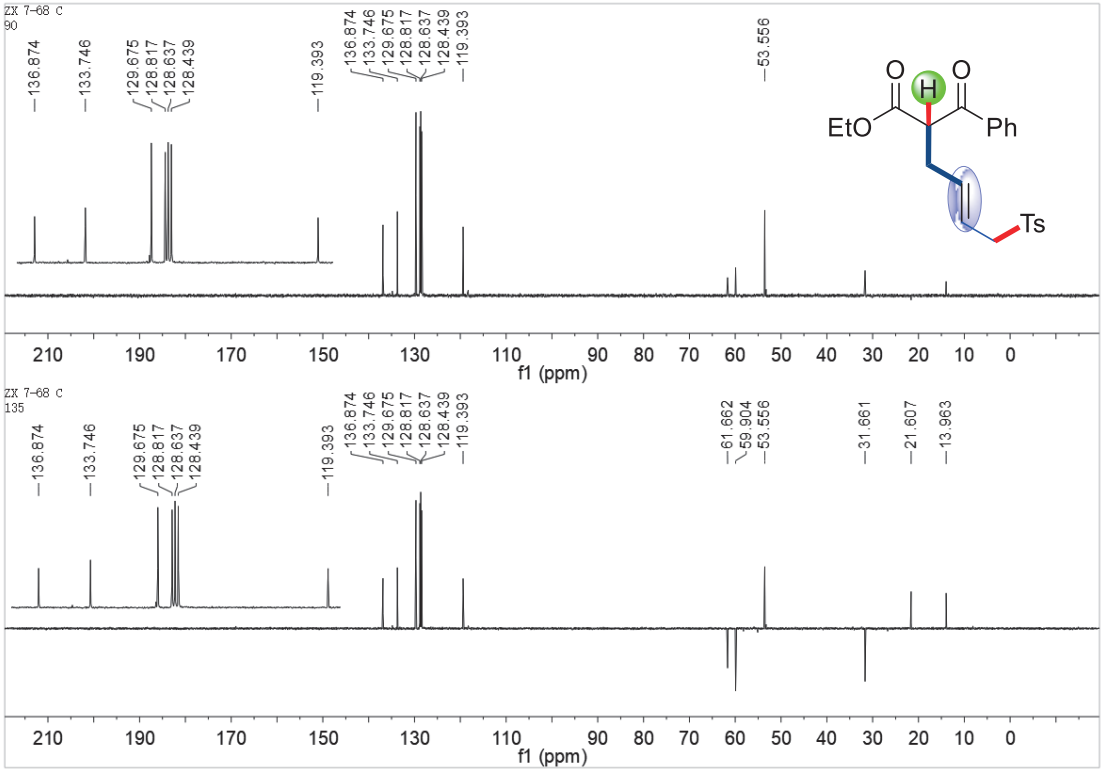
4k2, ^{1}H NMR



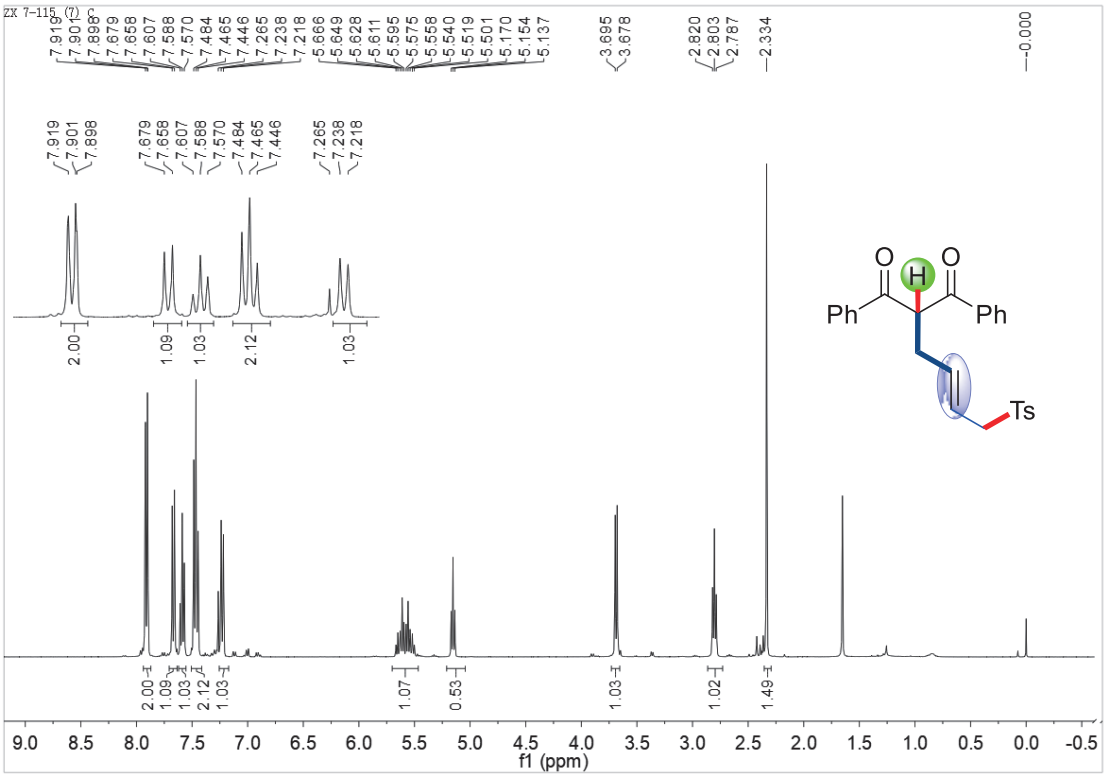
4k2, ^{13}C NMR



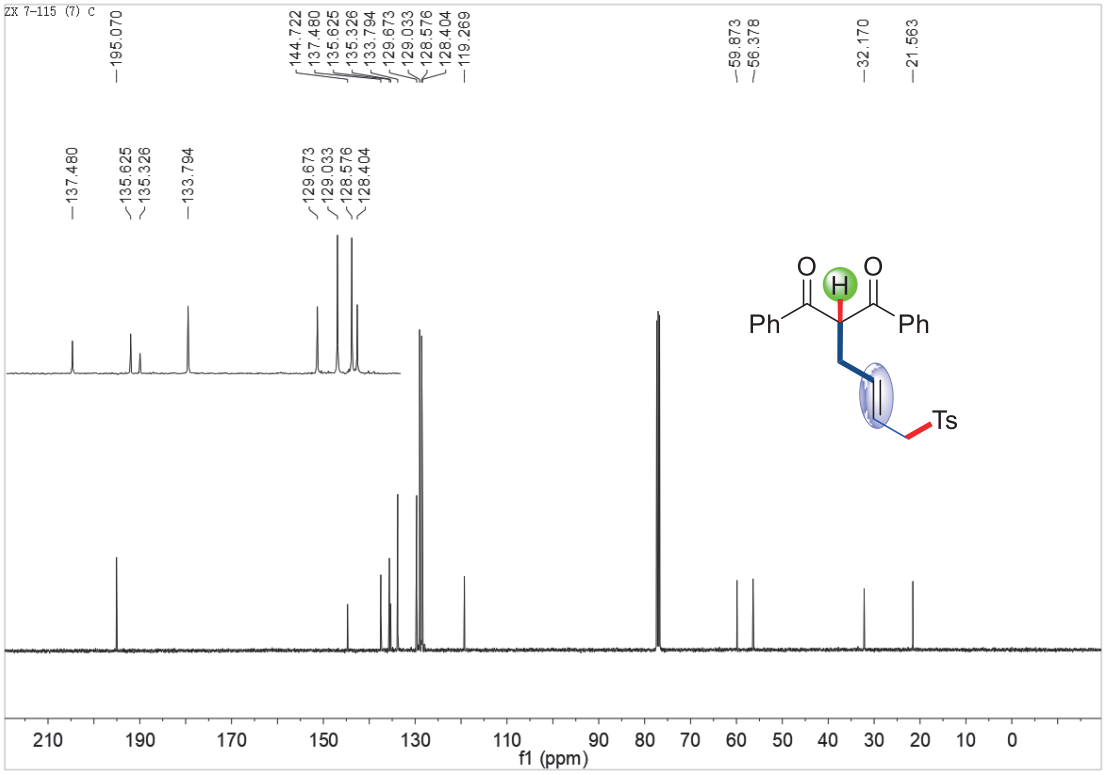
4k2, DEPT 90 and DEPT 135



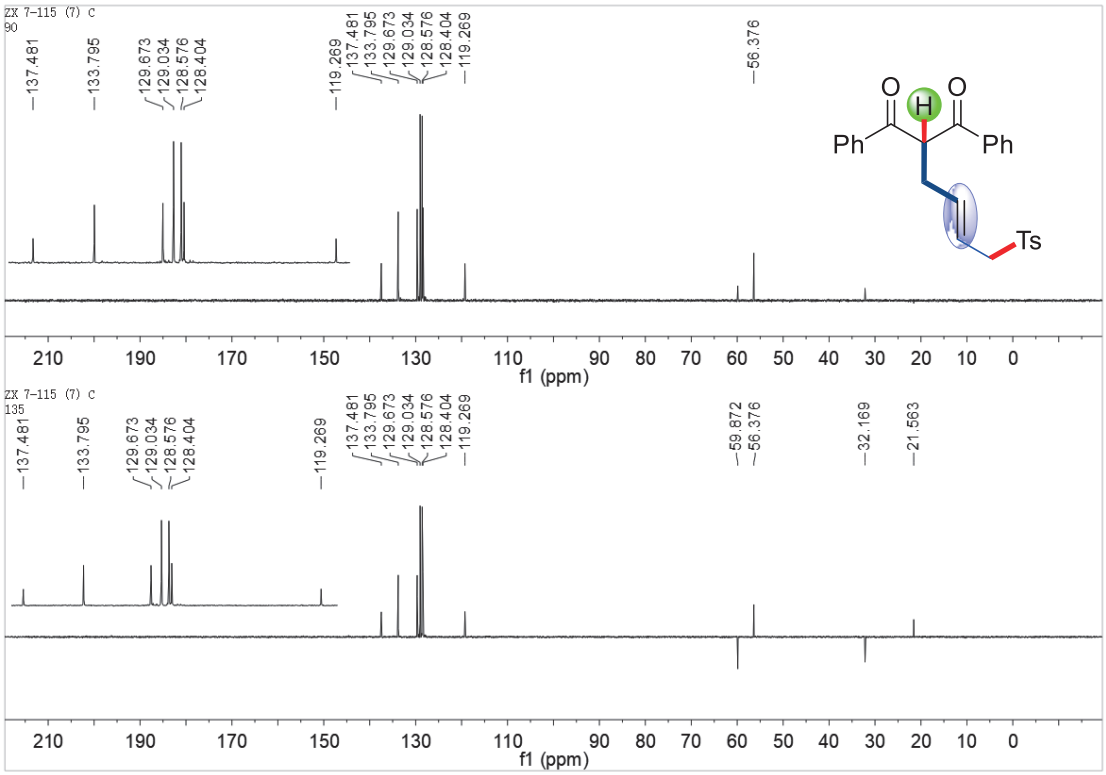
4k3, ^{1}H NMR



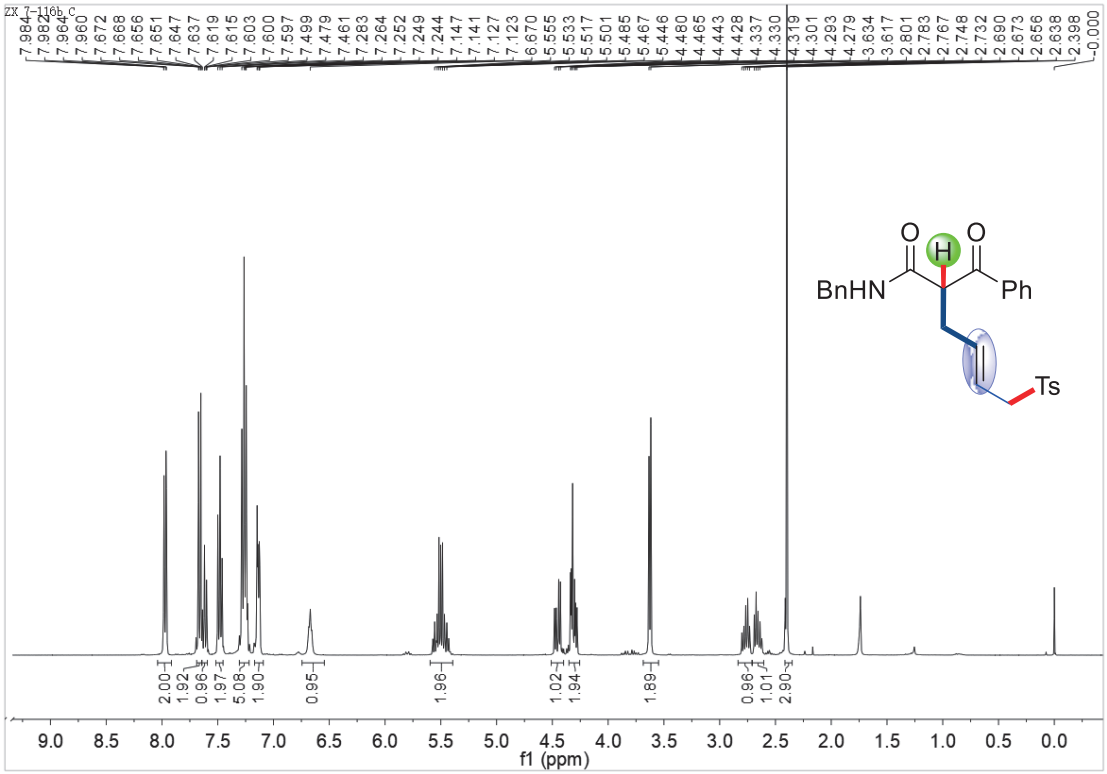
4k3, ^{13}C NMR



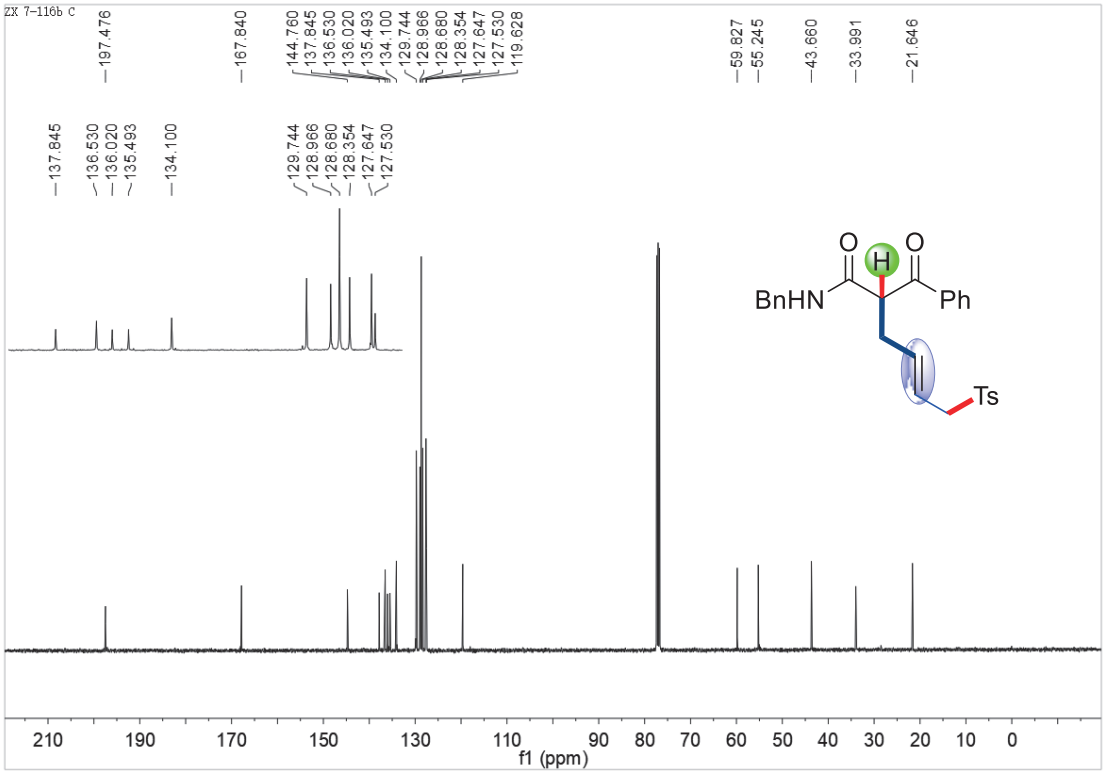
4k3, DEPT 90 and DEPT 135



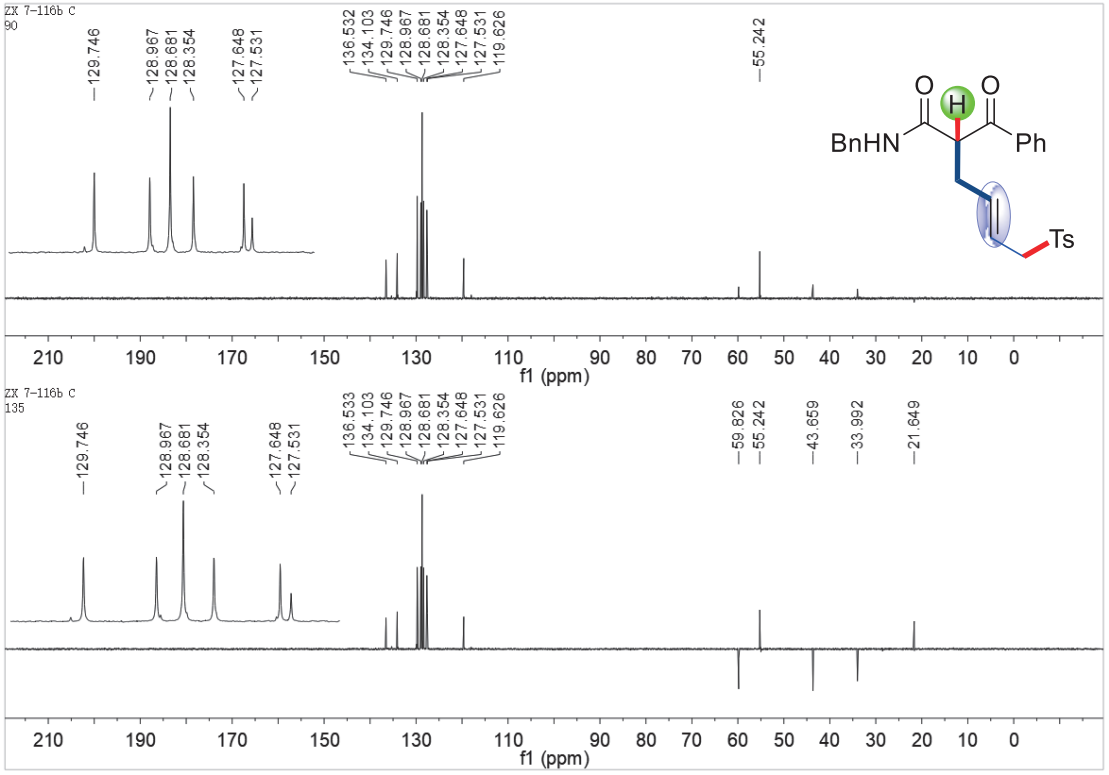
4k4, ^{1}H NMR



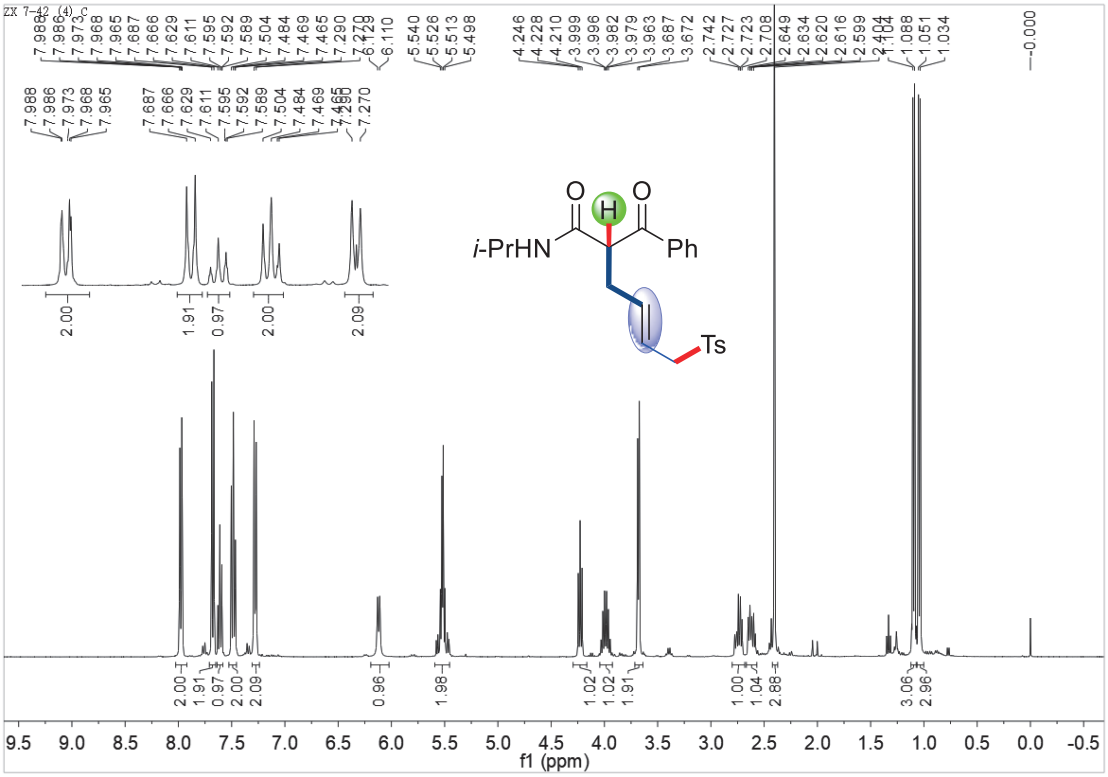
4k4, ^{13}C NMR



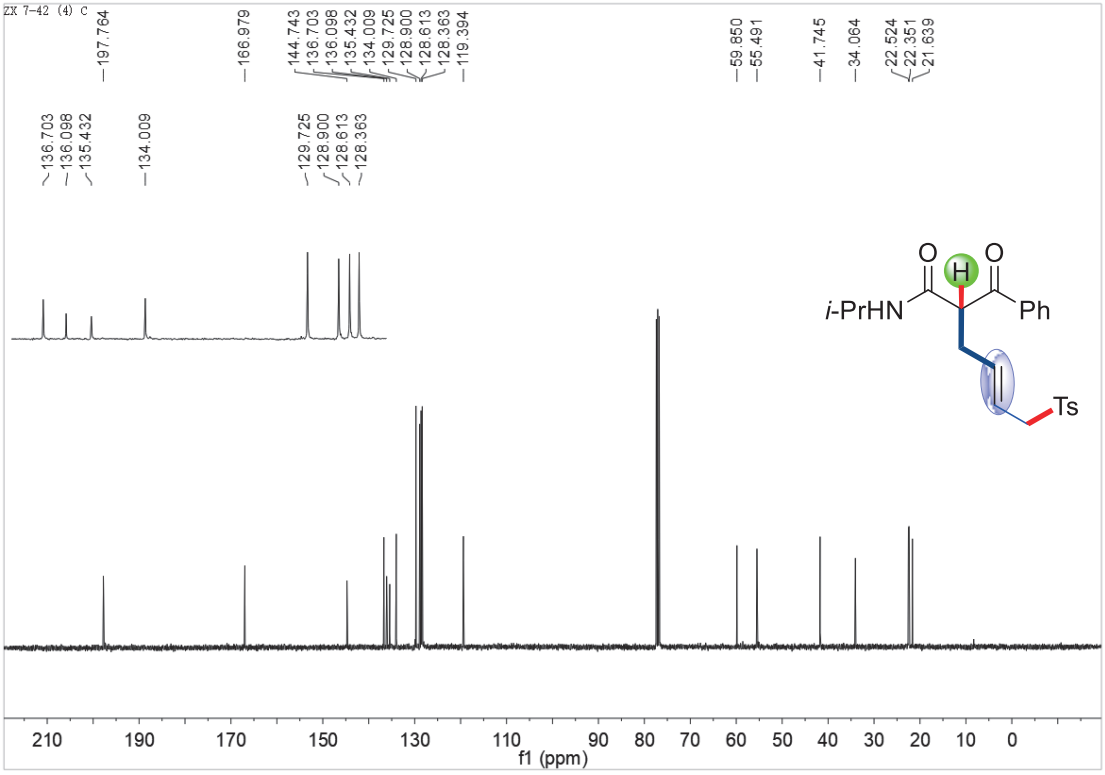
4k4, DEPT 90 and DEPT 135



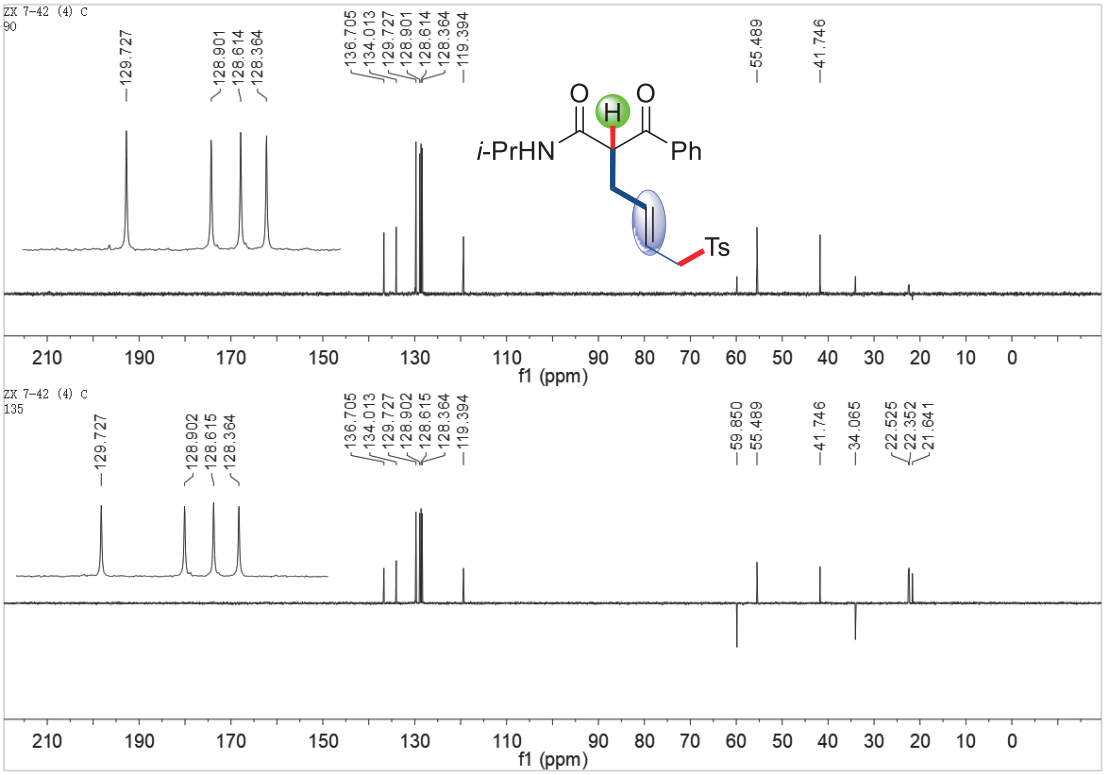
4k5, ^{1}H NMR



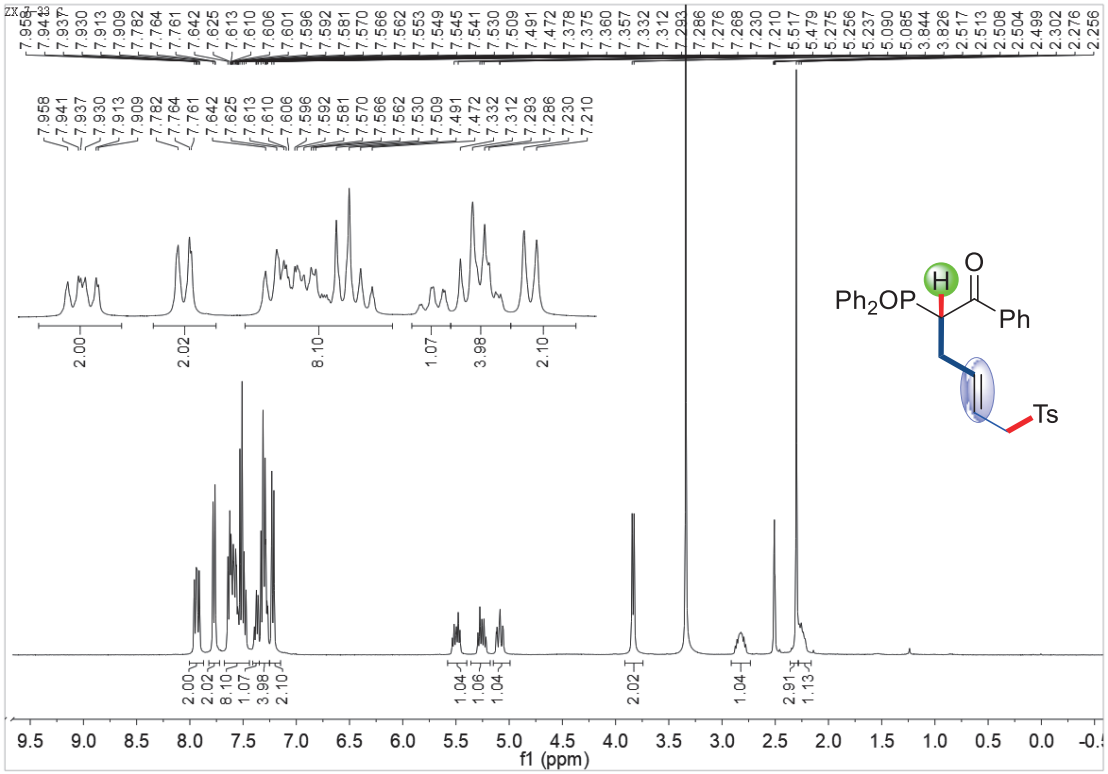
4k5, ^{13}C NMR



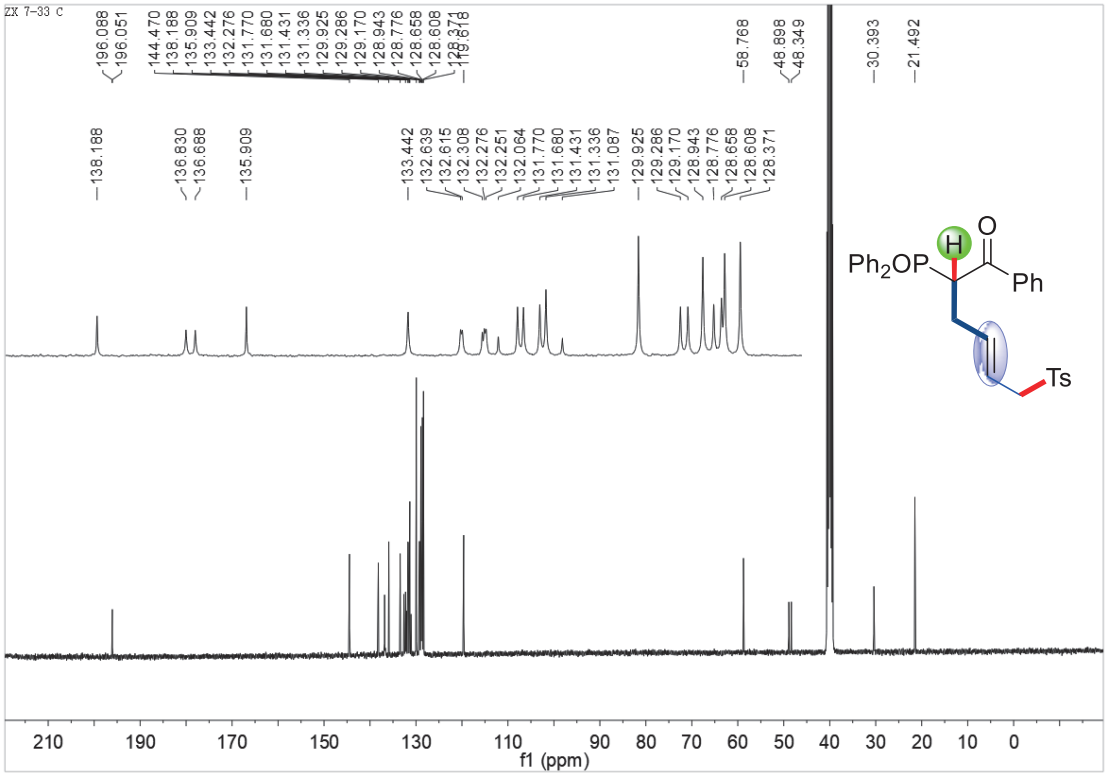
4k5, DEPT 90 and DEPT 135



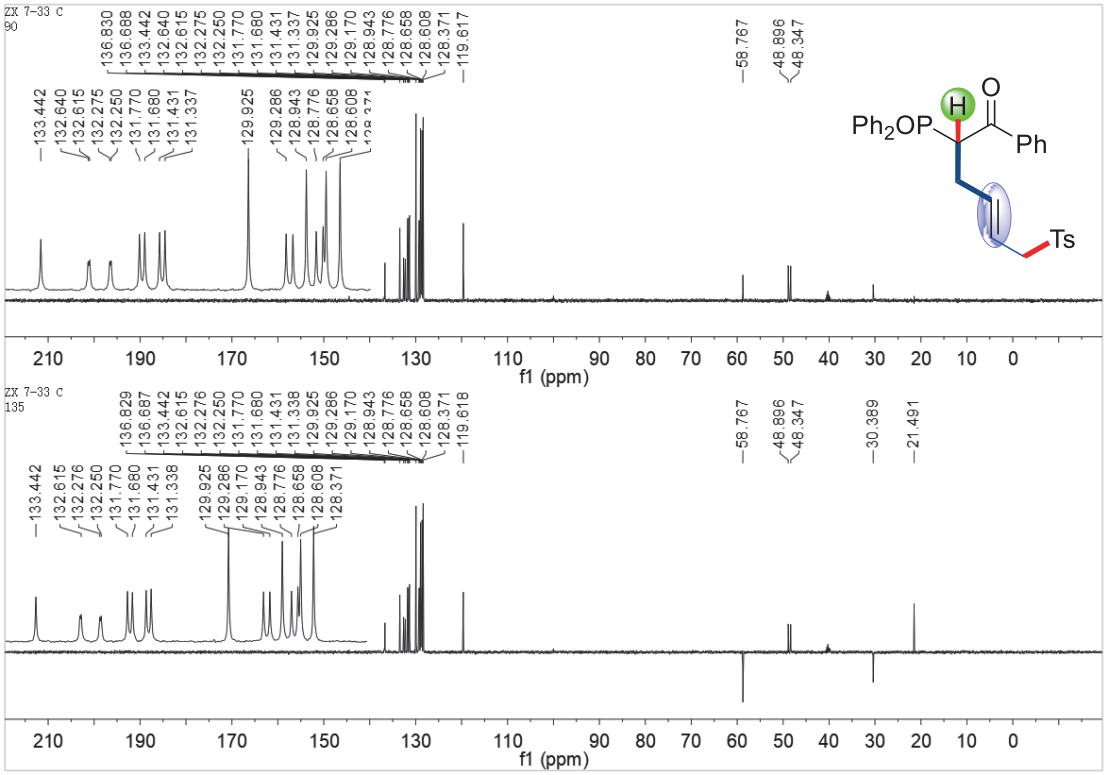
4l, ^{1}H NMR



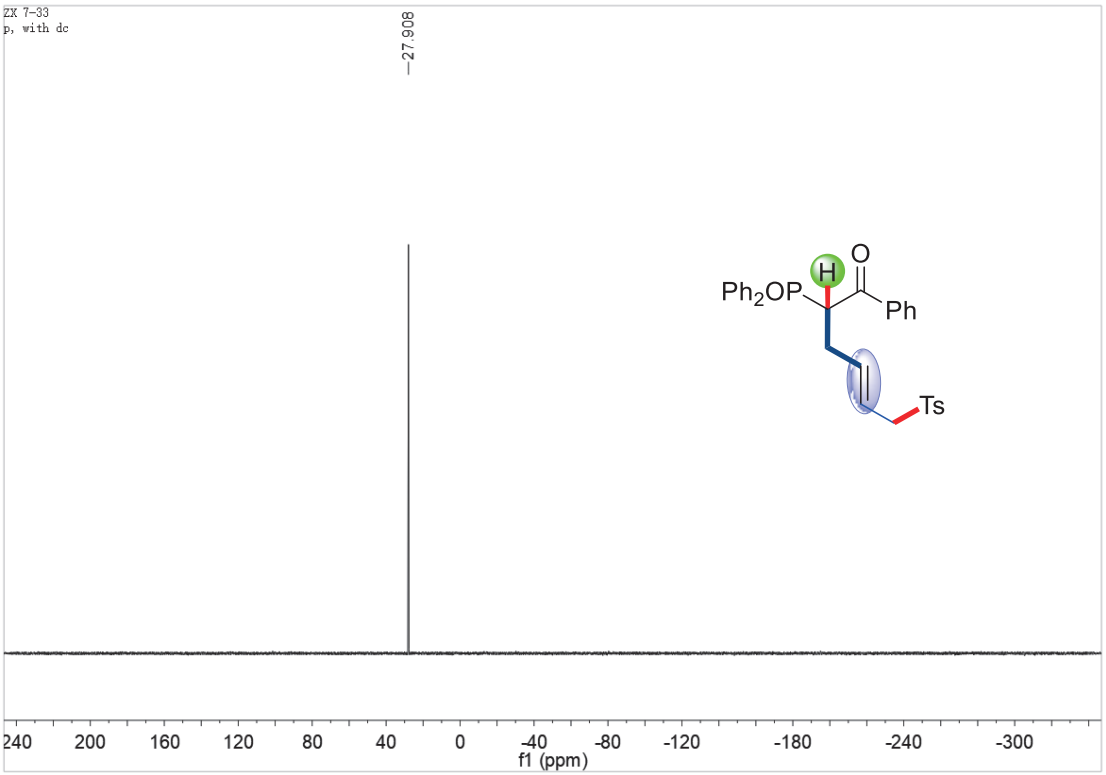
4l, ^{13}C NMR



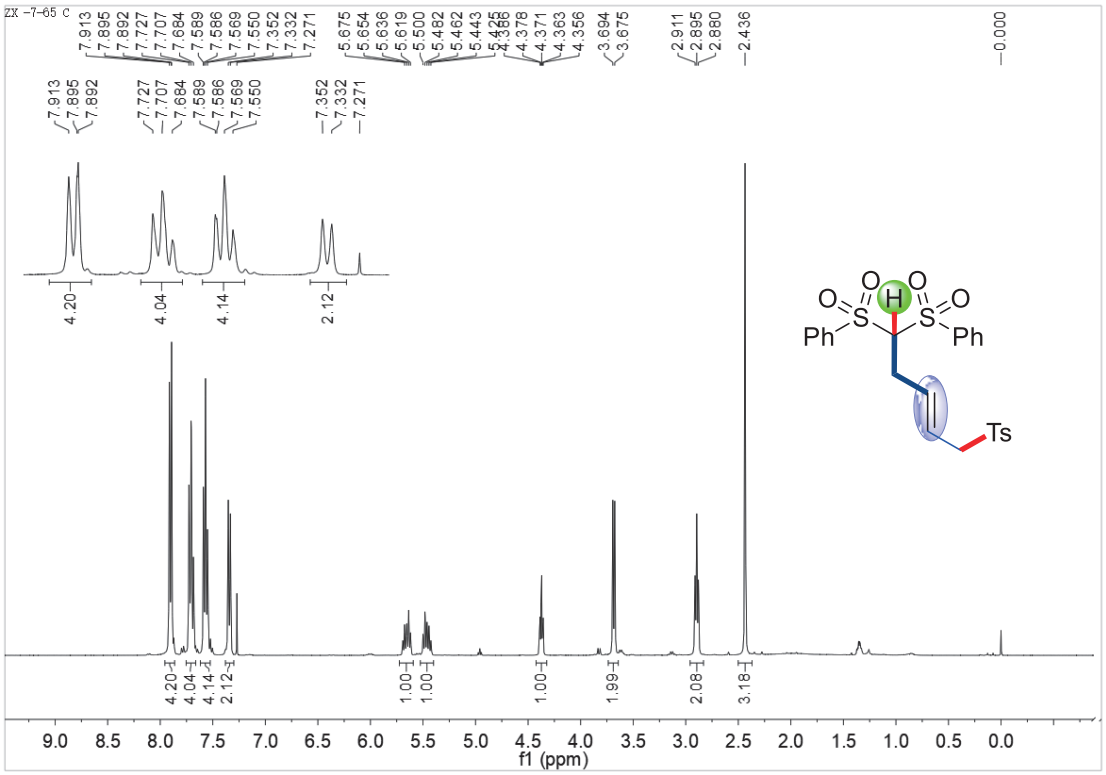
4l, DEPT 90 and DEPT 135



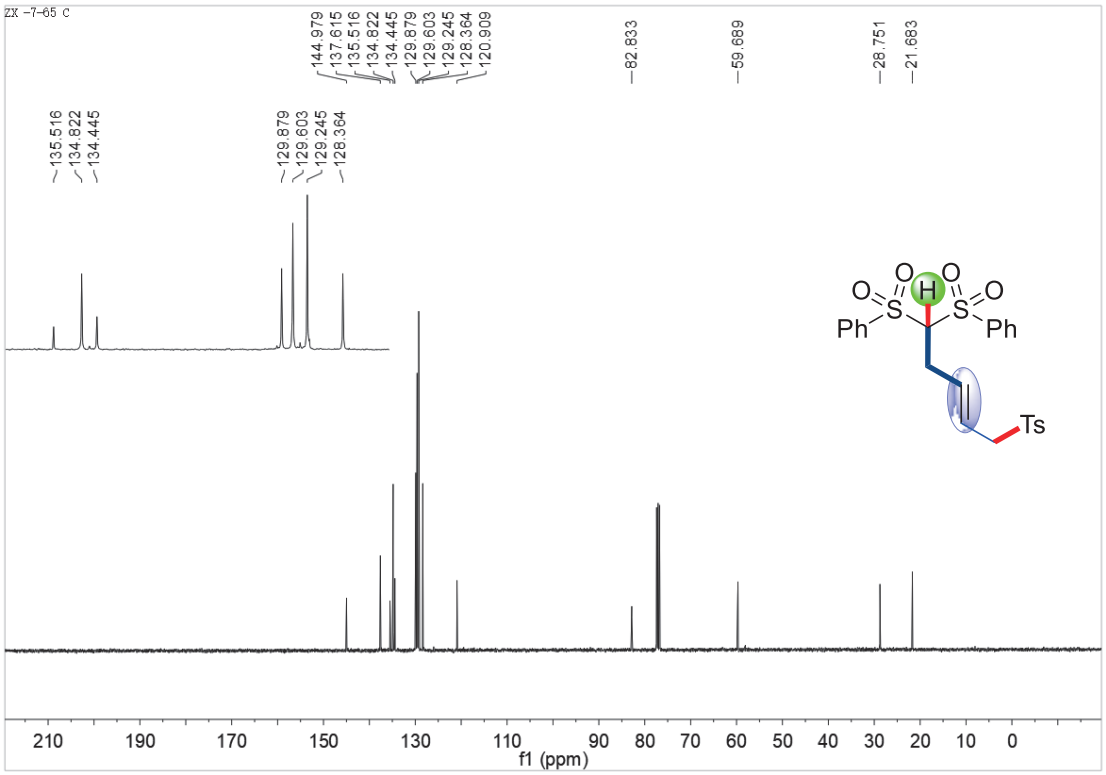
4l, ^{31}P NMR



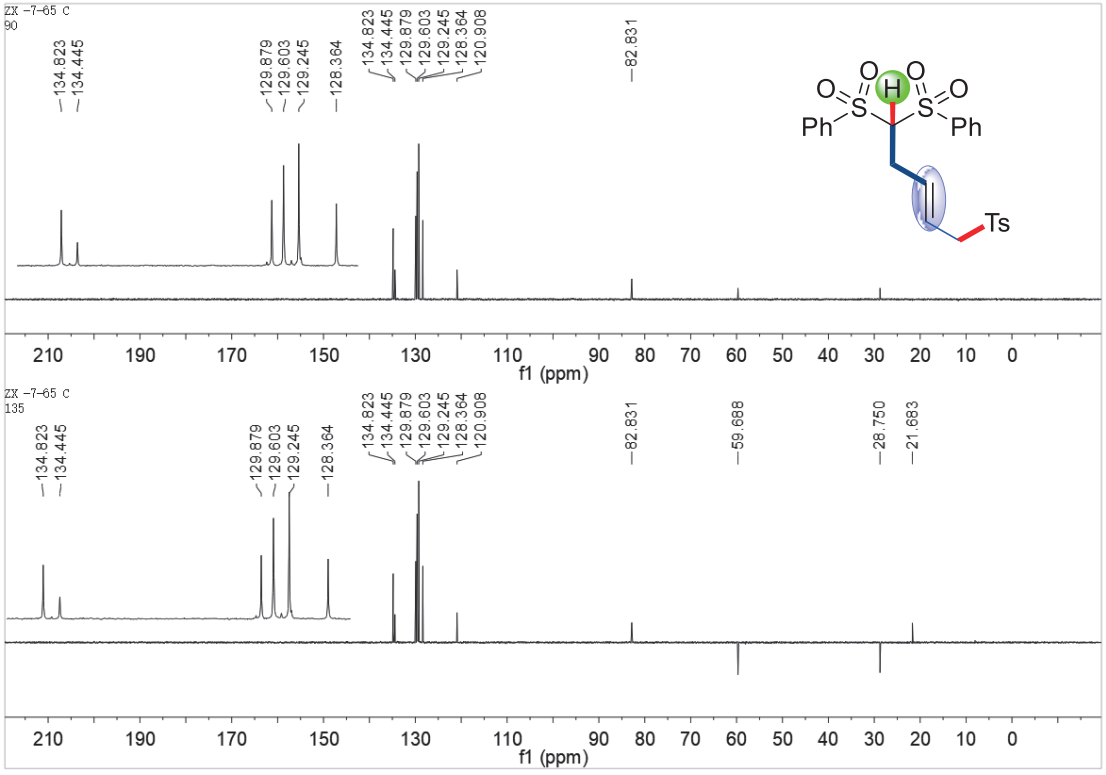
4m, ^{1}H NMR



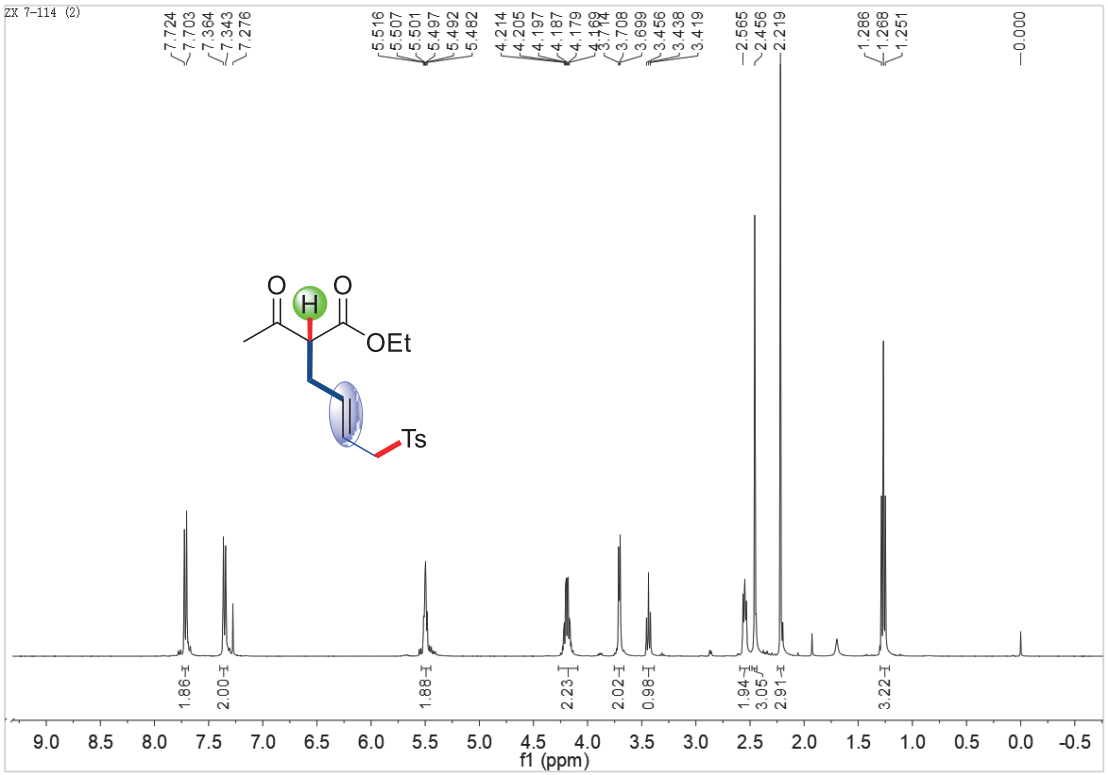
4m, ^{13}C NMR



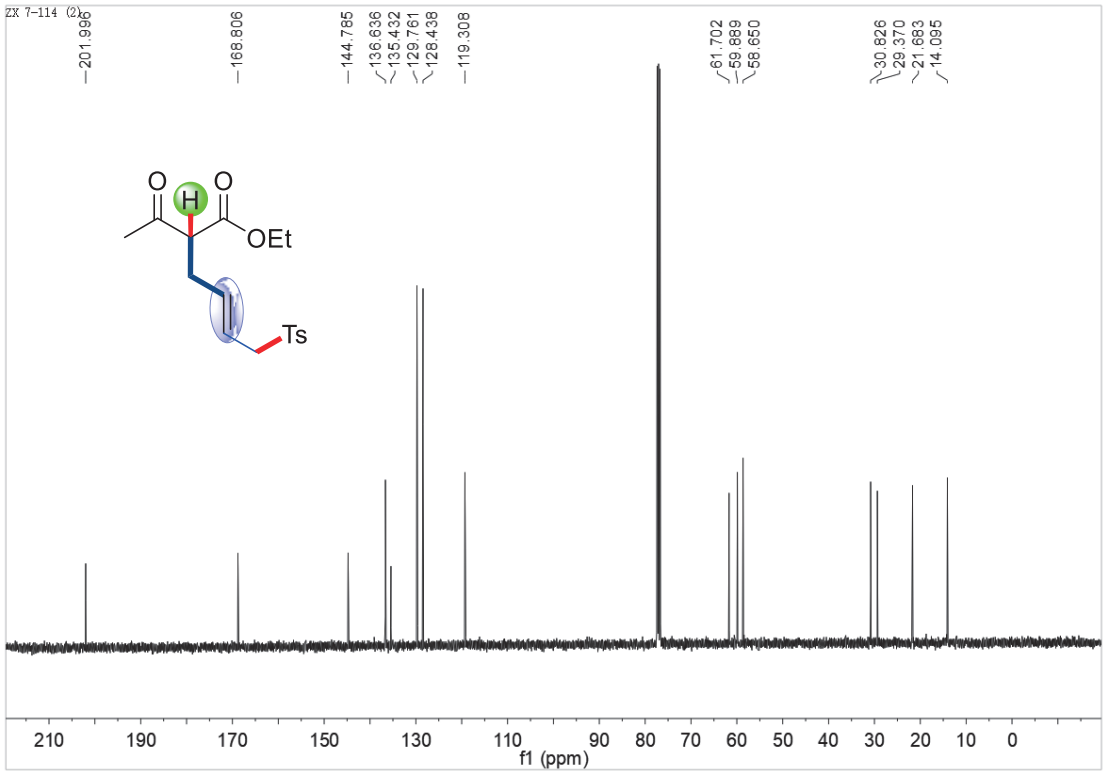
4m, DEPT 90 and DEPT 135



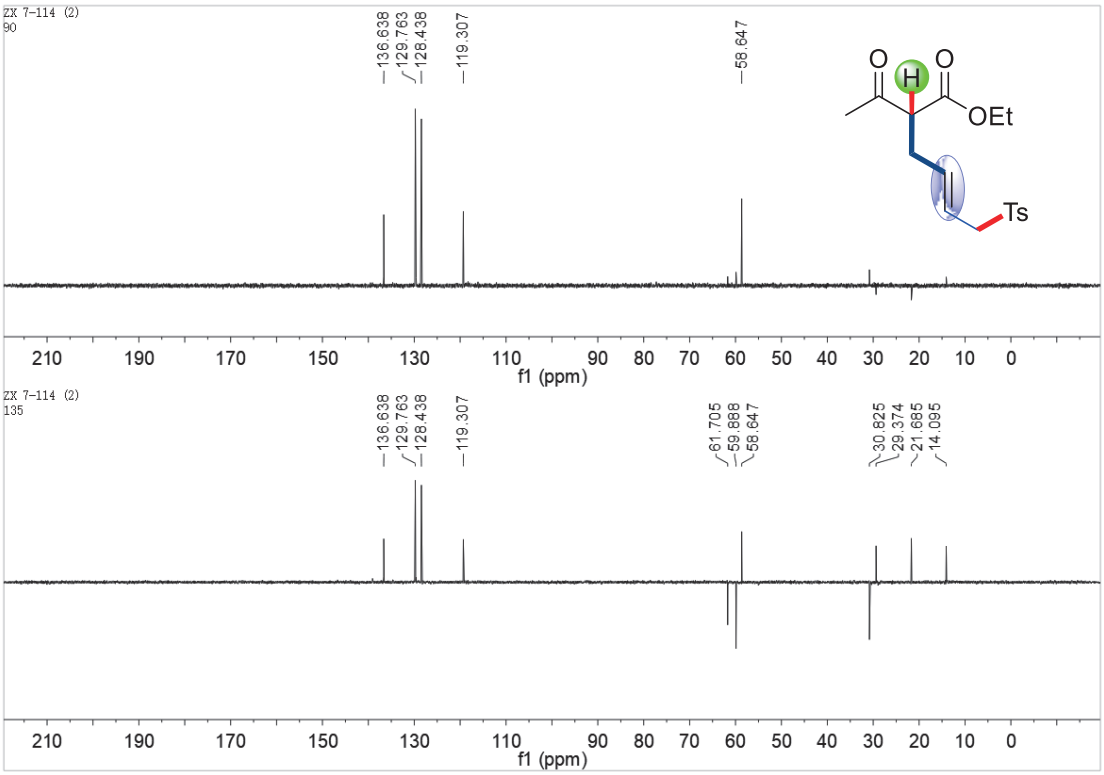
4n, ^{1}H NMR



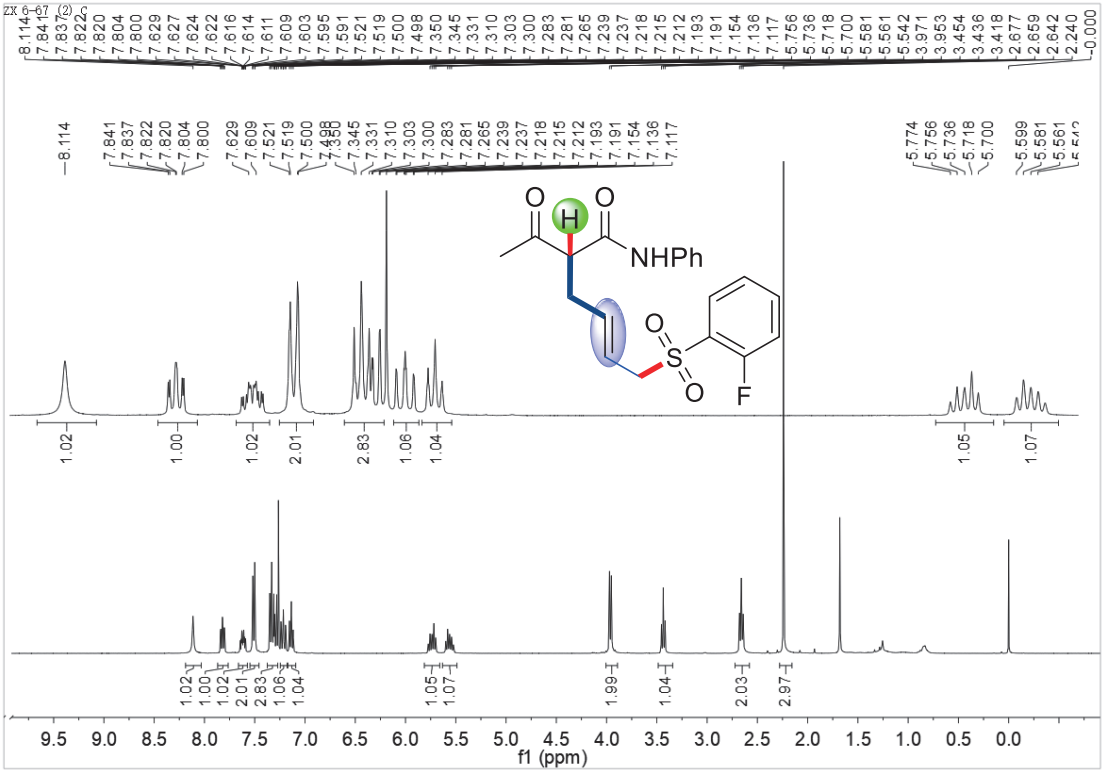
4n, ^{13}C NMR



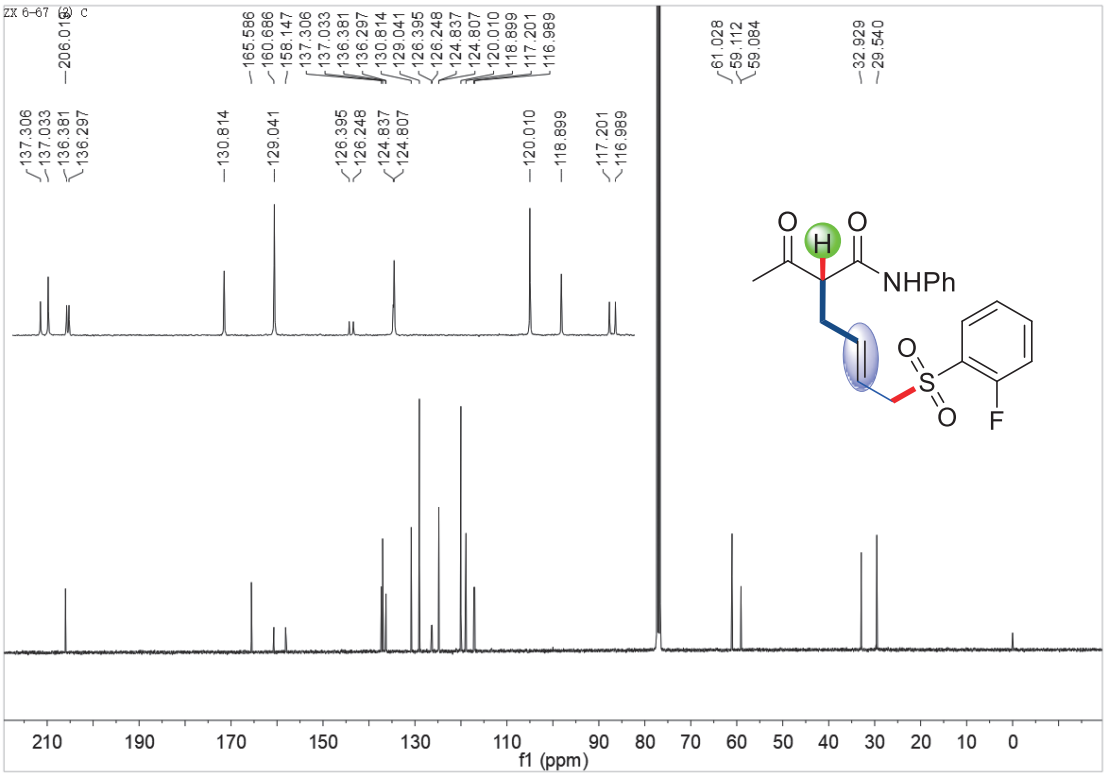
4n, DEPT 90 and DEPT 135



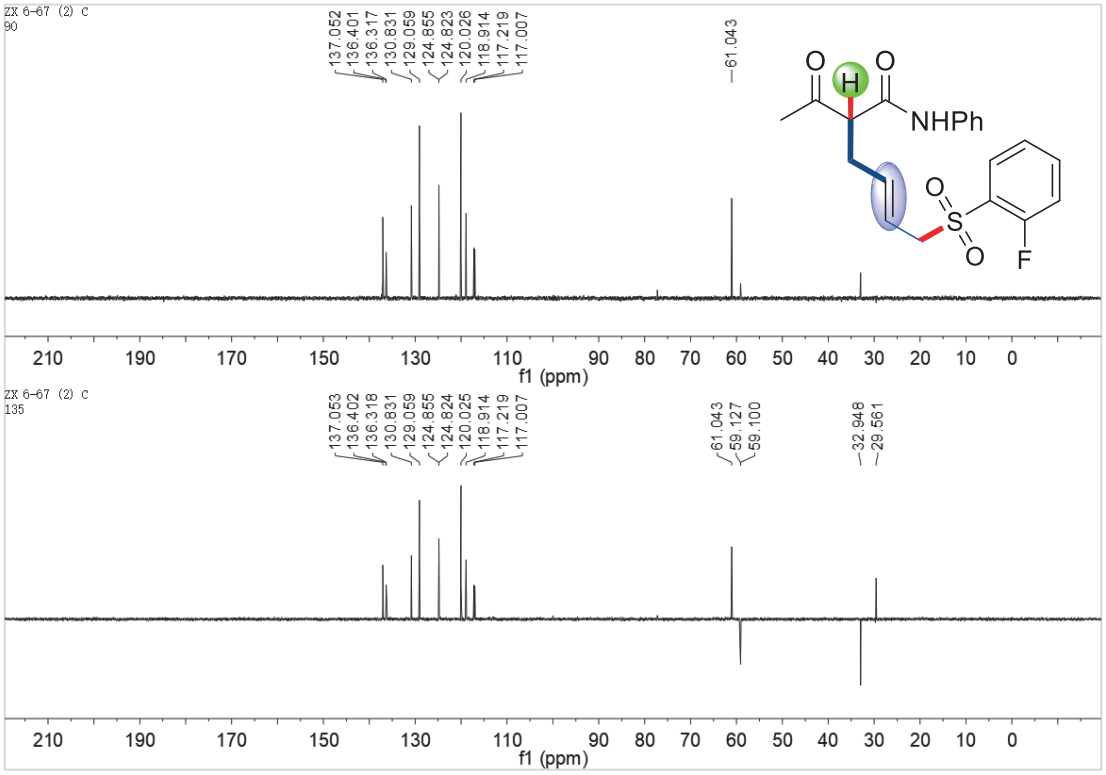
4o, ^{1}H NMR



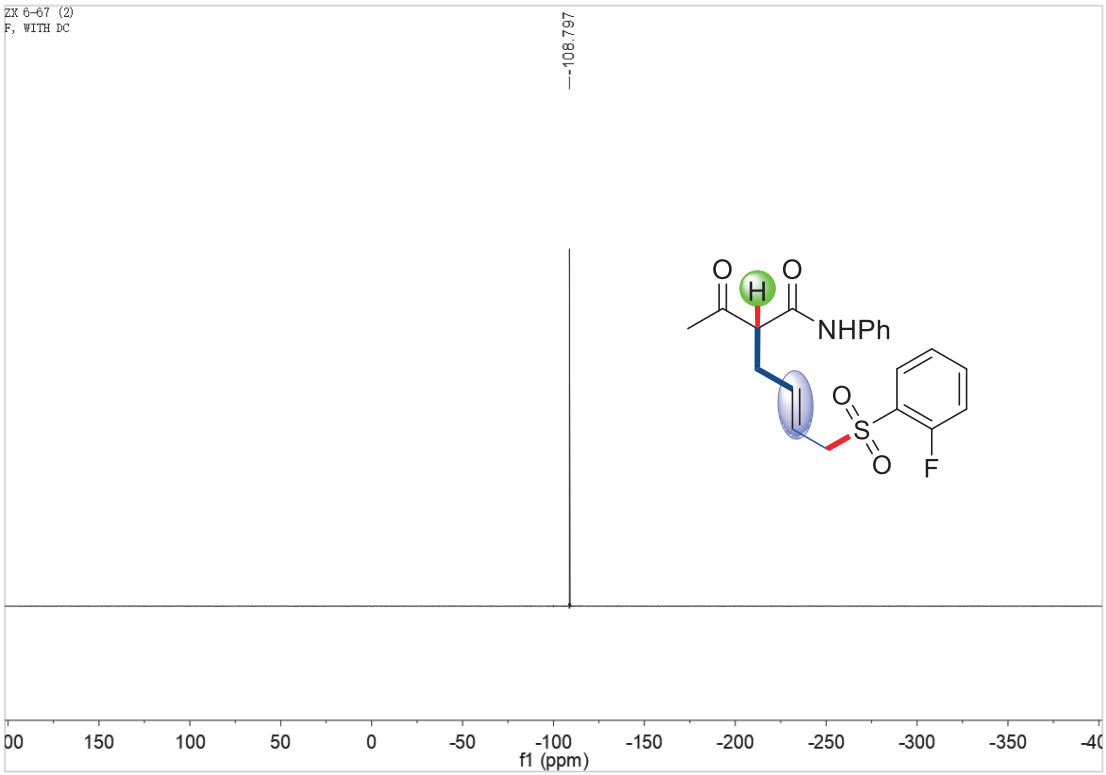
4o, ^{13}C NMR



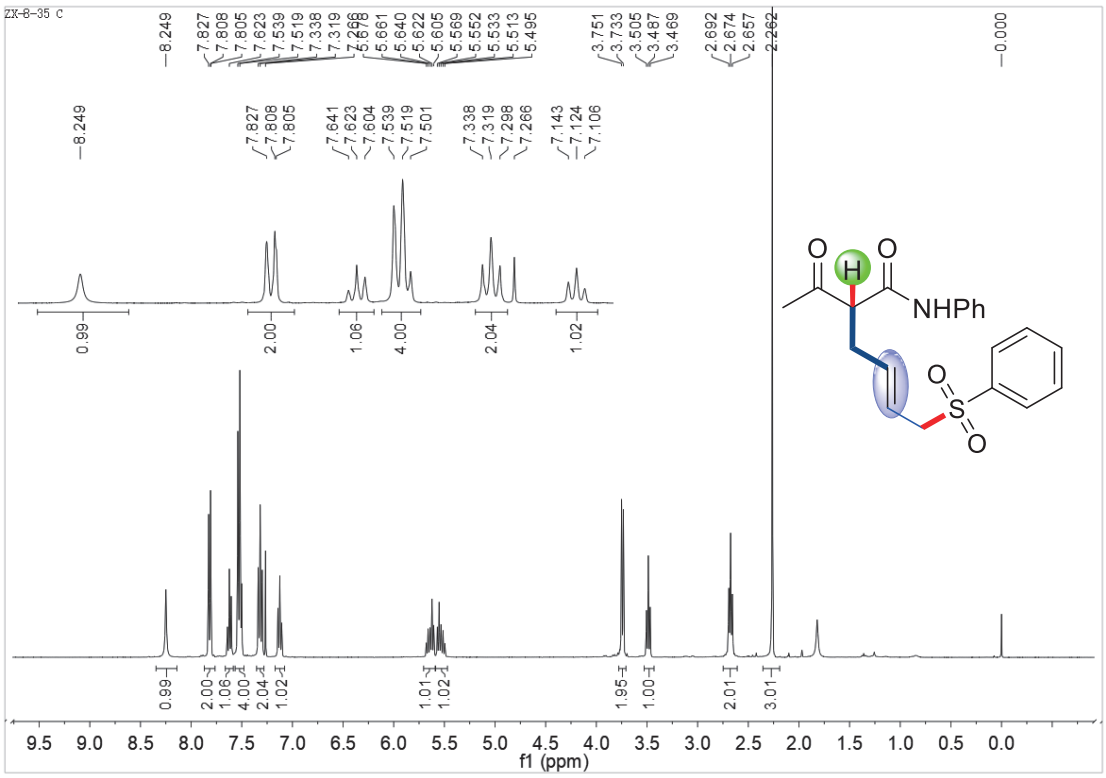
4o, DEPT 90 and DEPT 135



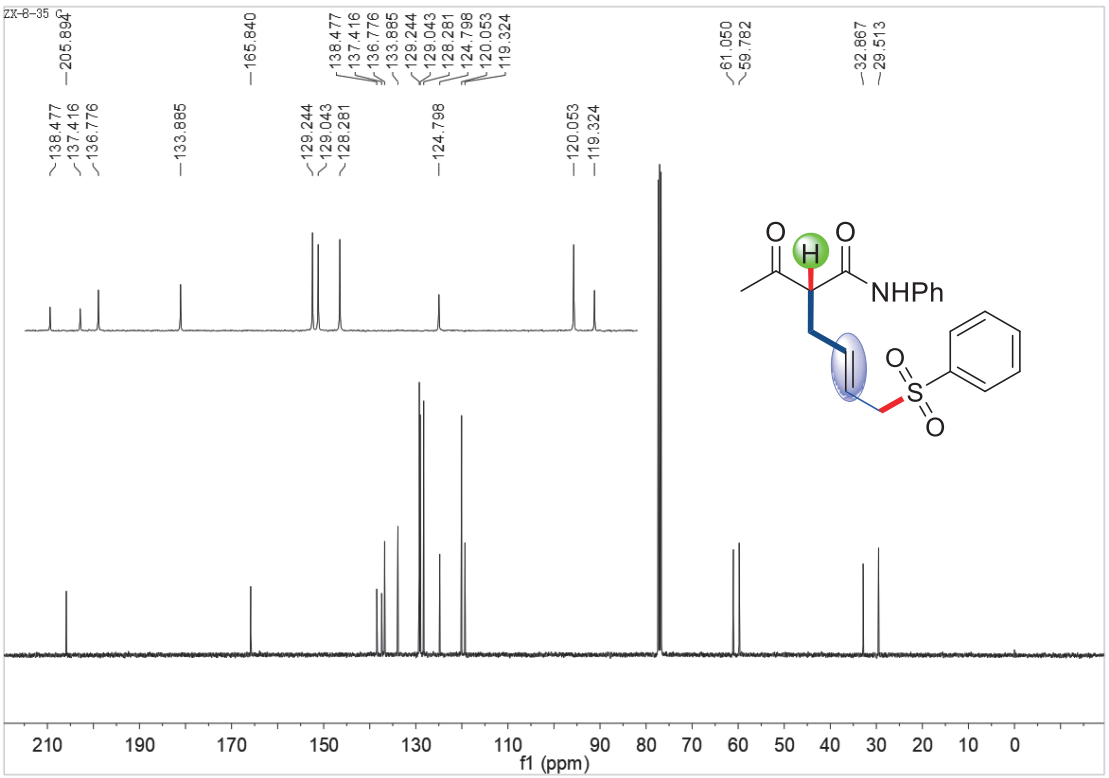
4o, ^{19}F NMR



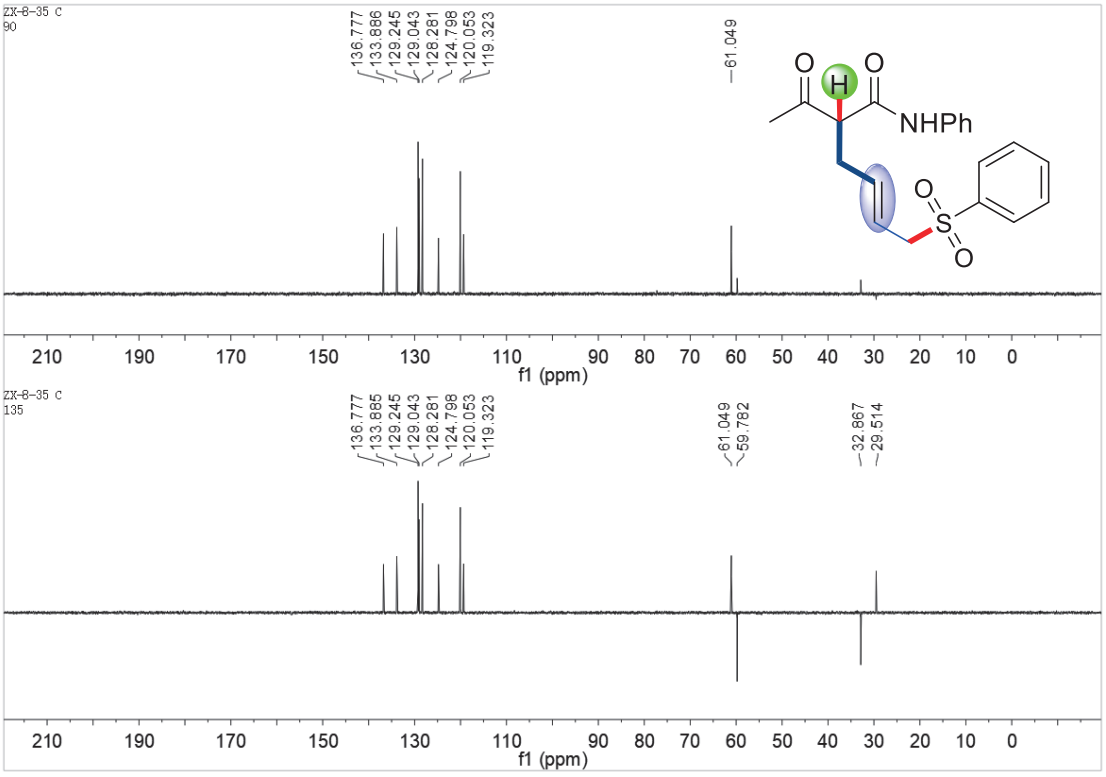
4p1, ^{1}H NMR



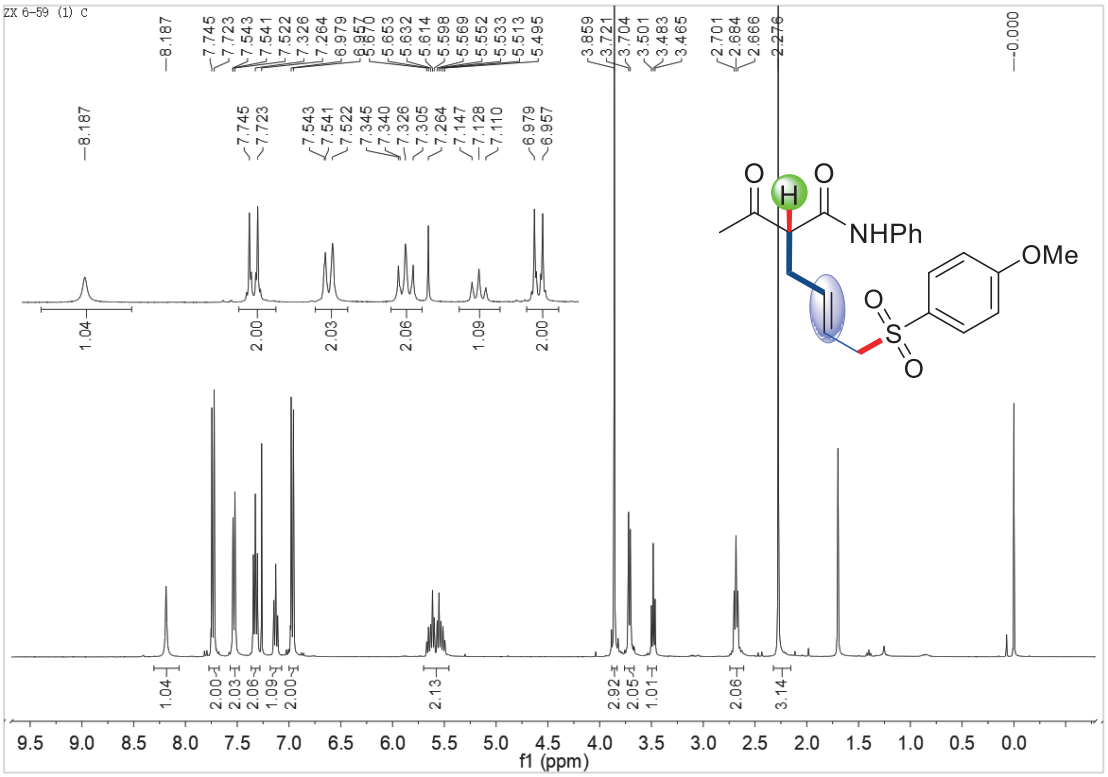
4p1, ^{13}C NMR



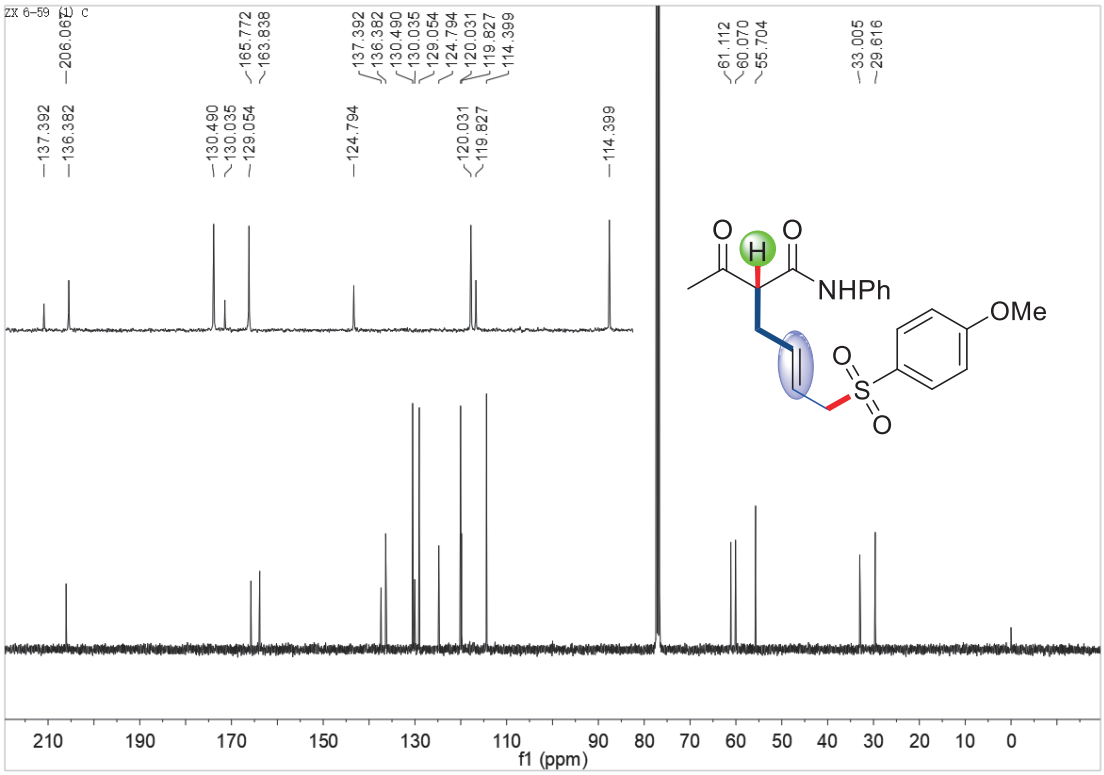
4p1, DEPT 90 and DEPT 135



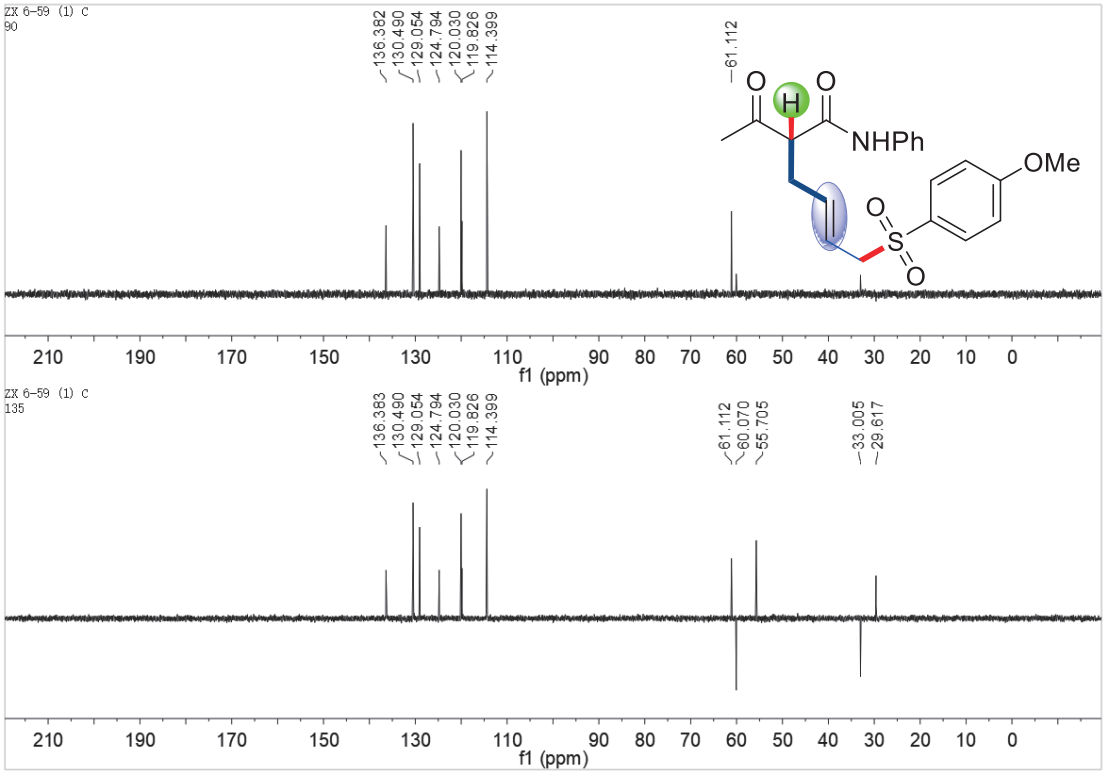
4p2, ^{1}H NMR



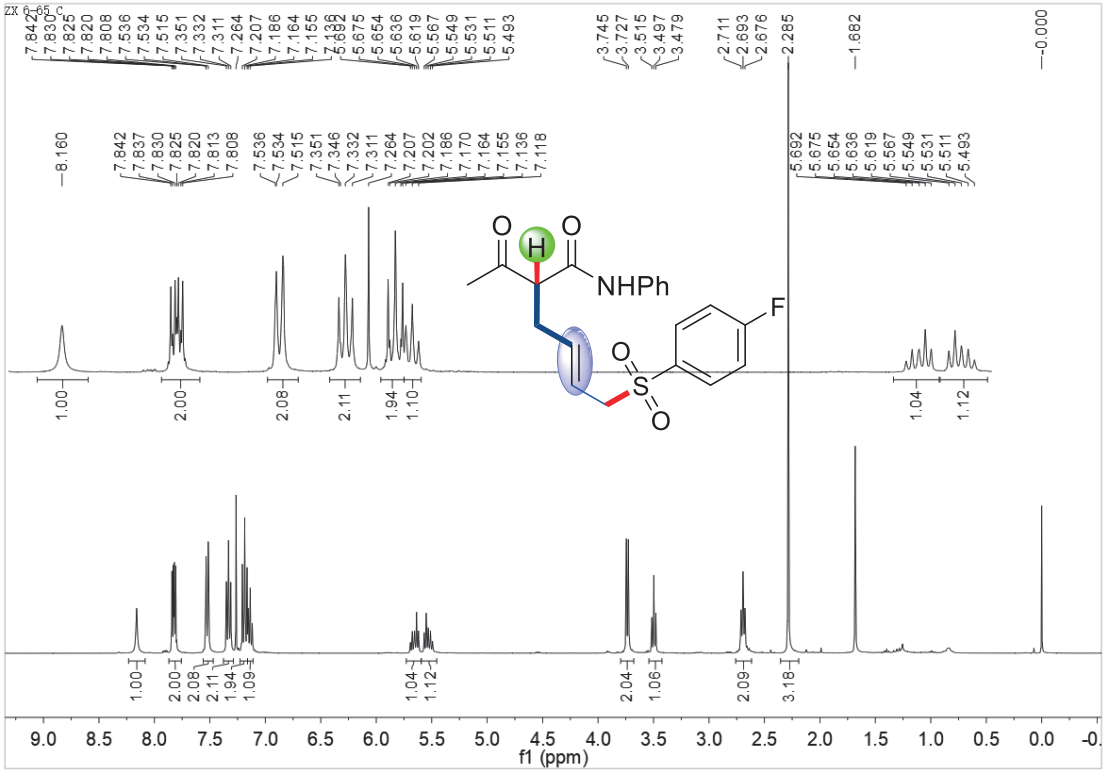
4p2, ^{13}C NMR



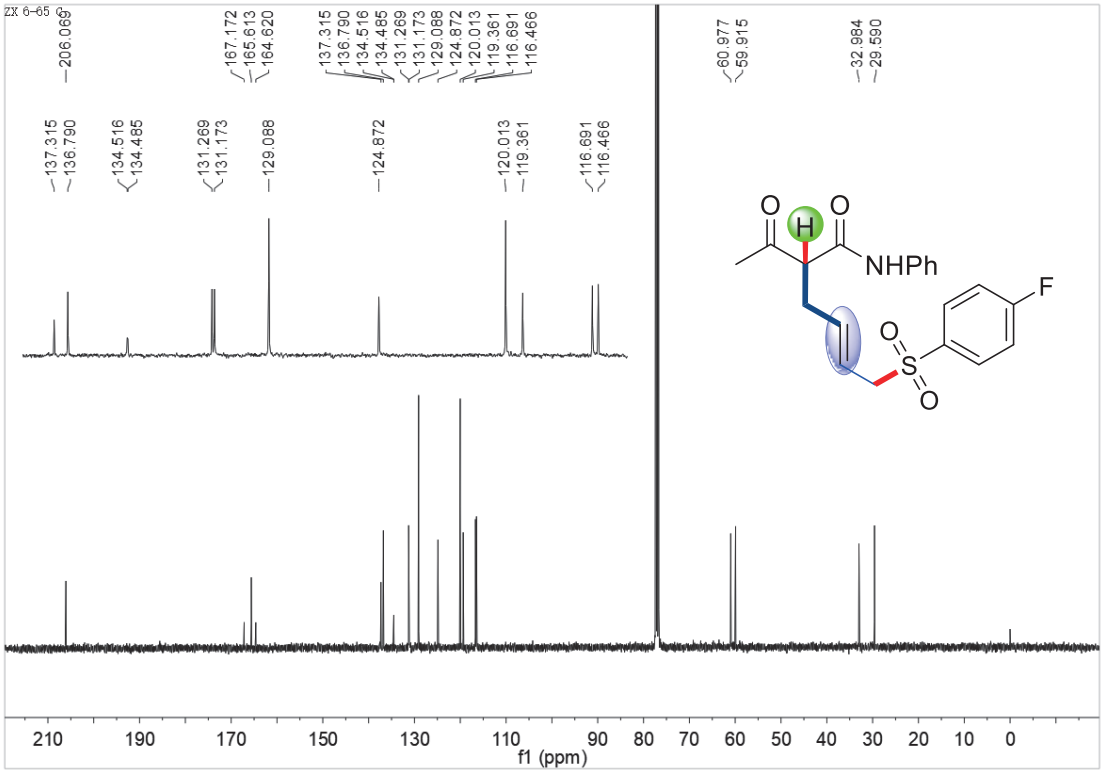
4p2, DEPT 90 and DEPT 135



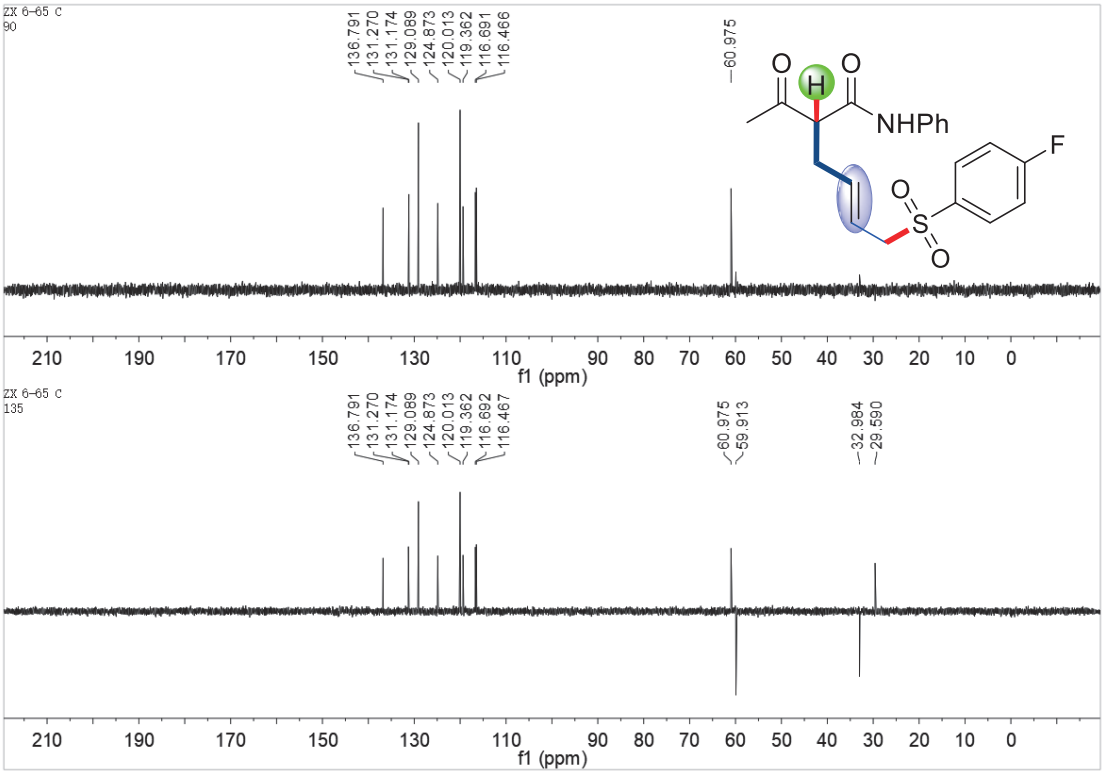
4p3, ^{1}H NMR



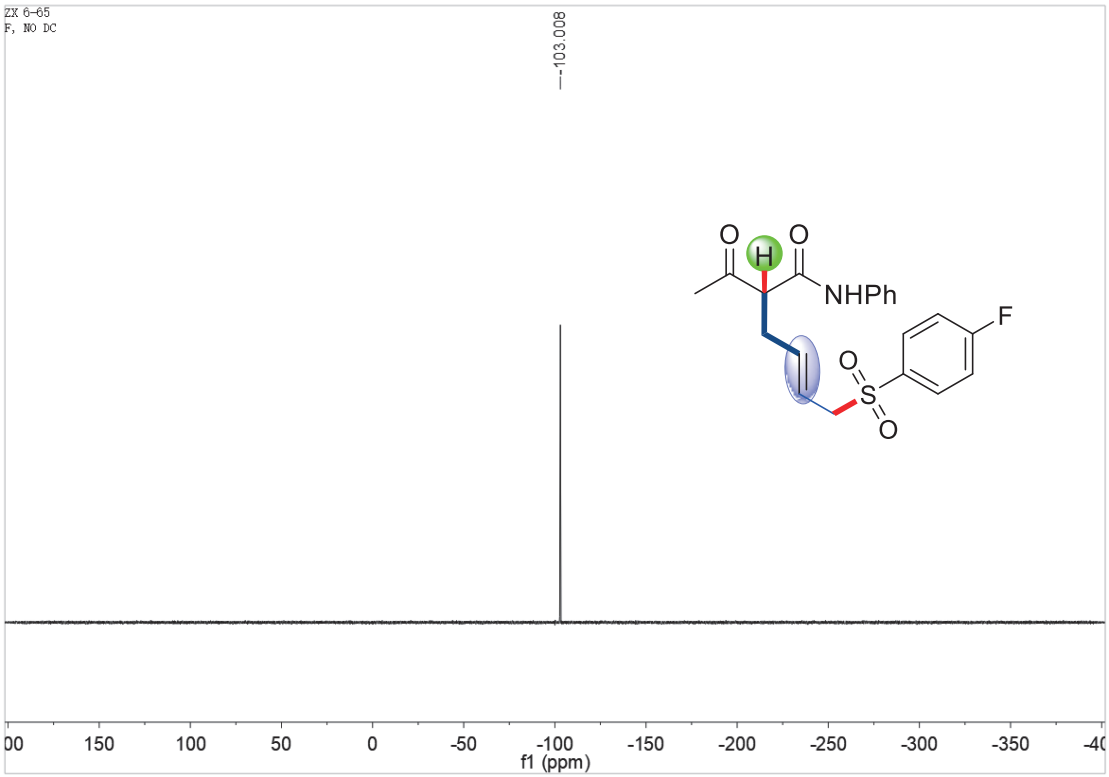
4p3, ^{13}C NMR



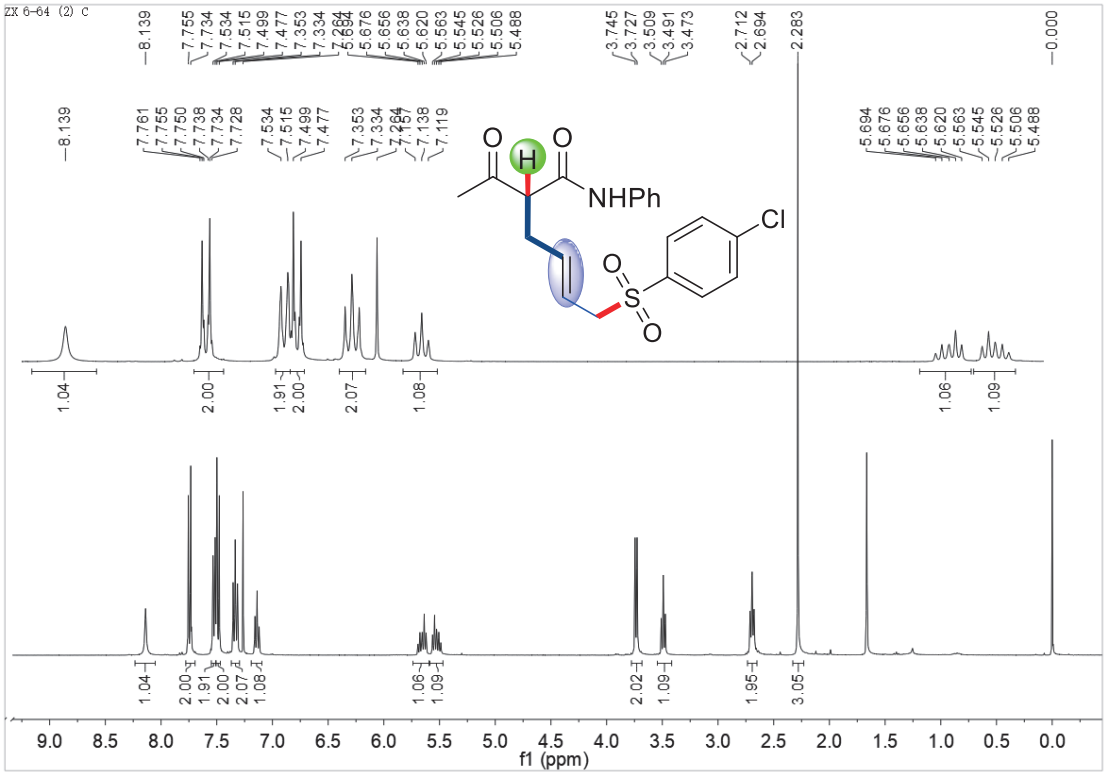
4p3, DEPT 90 and DEPT 135



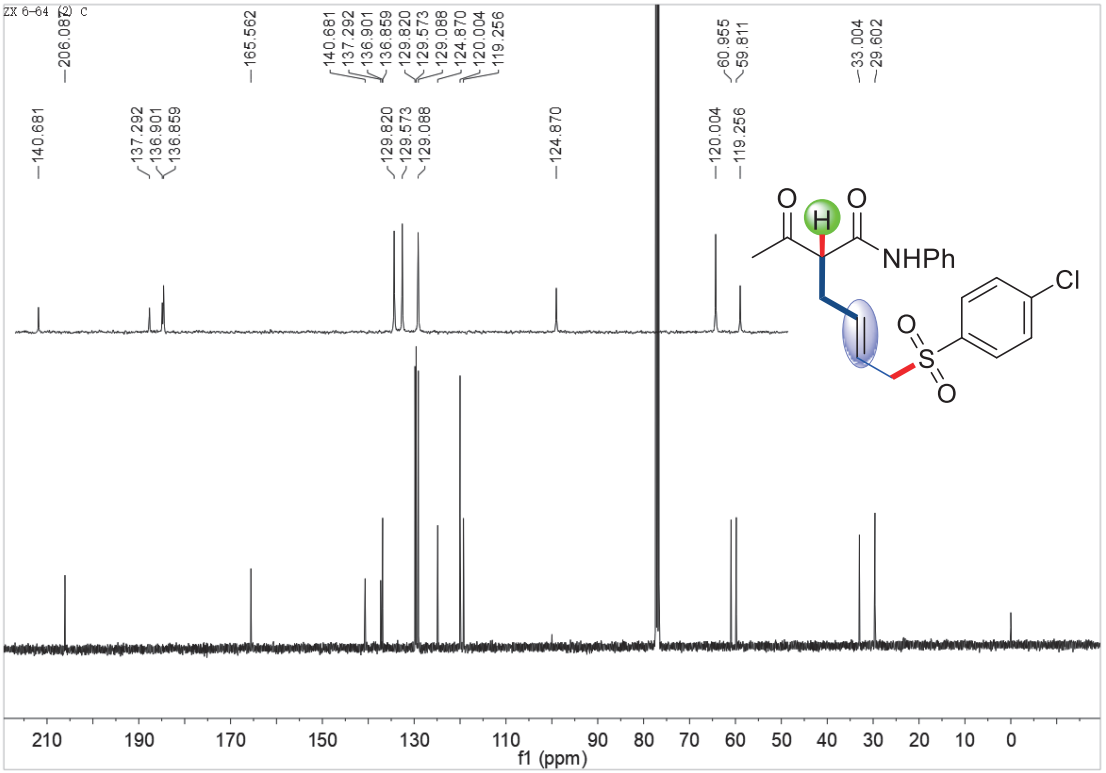
4p3, ^{19}F NMR



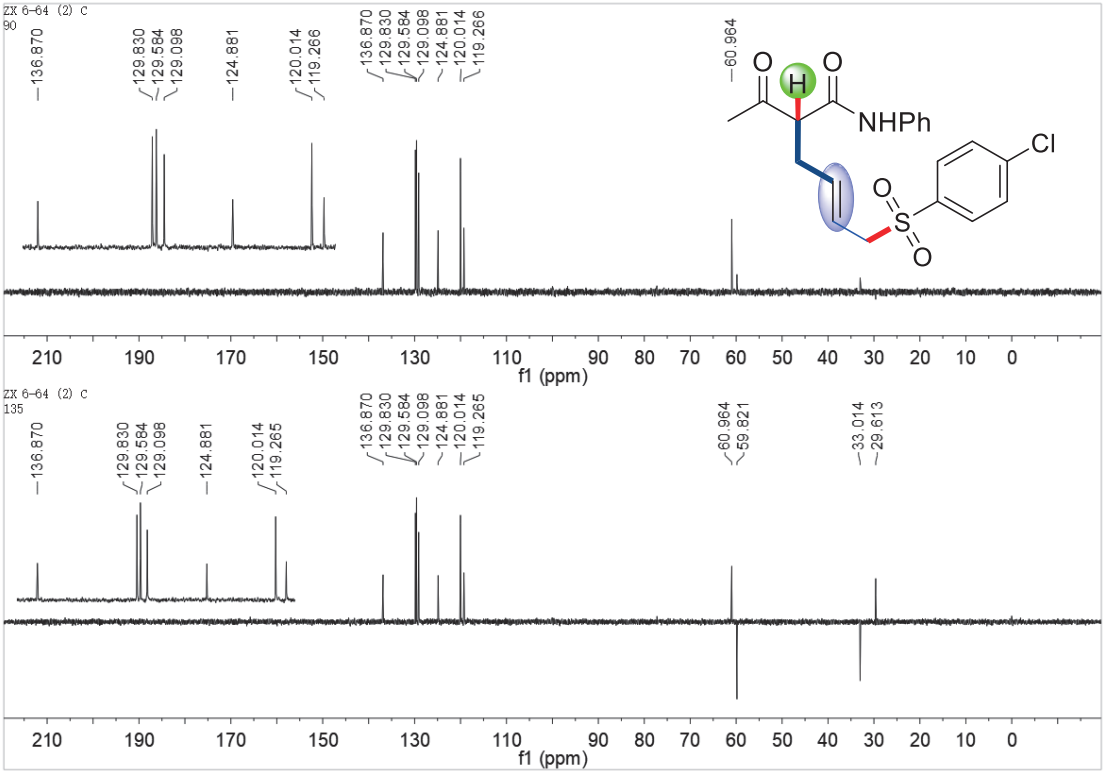
4p4, ^{1}H NMR



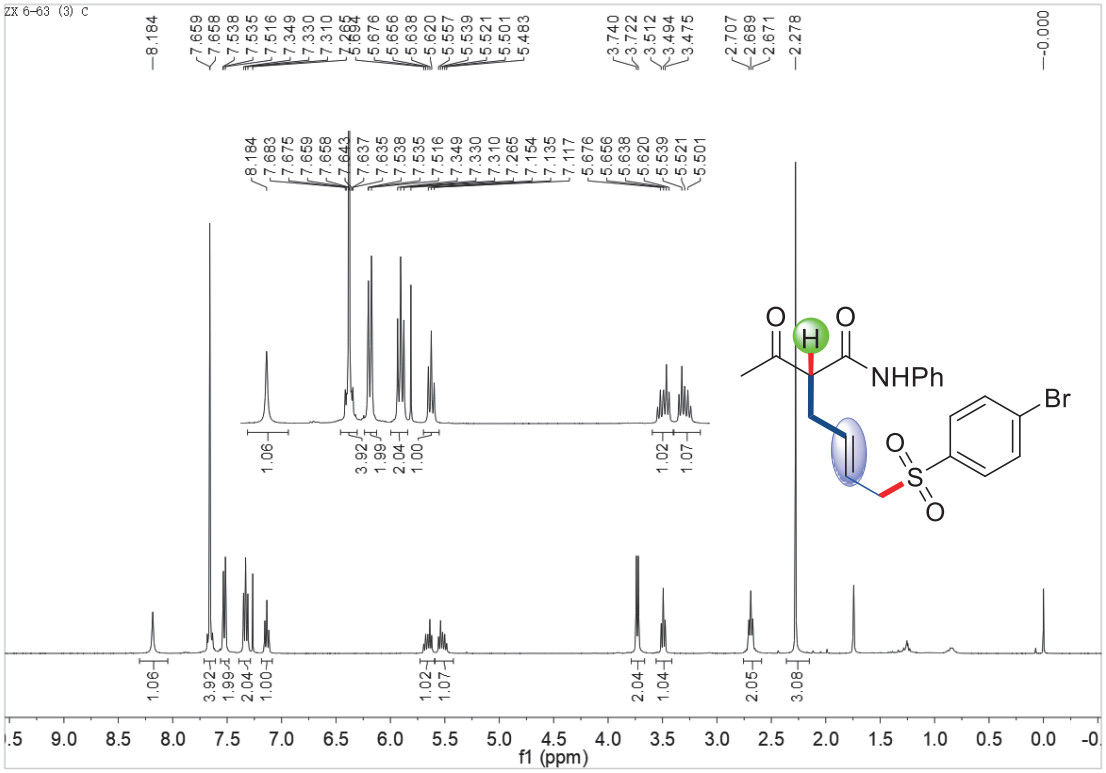
4p4, ^{13}C NMR



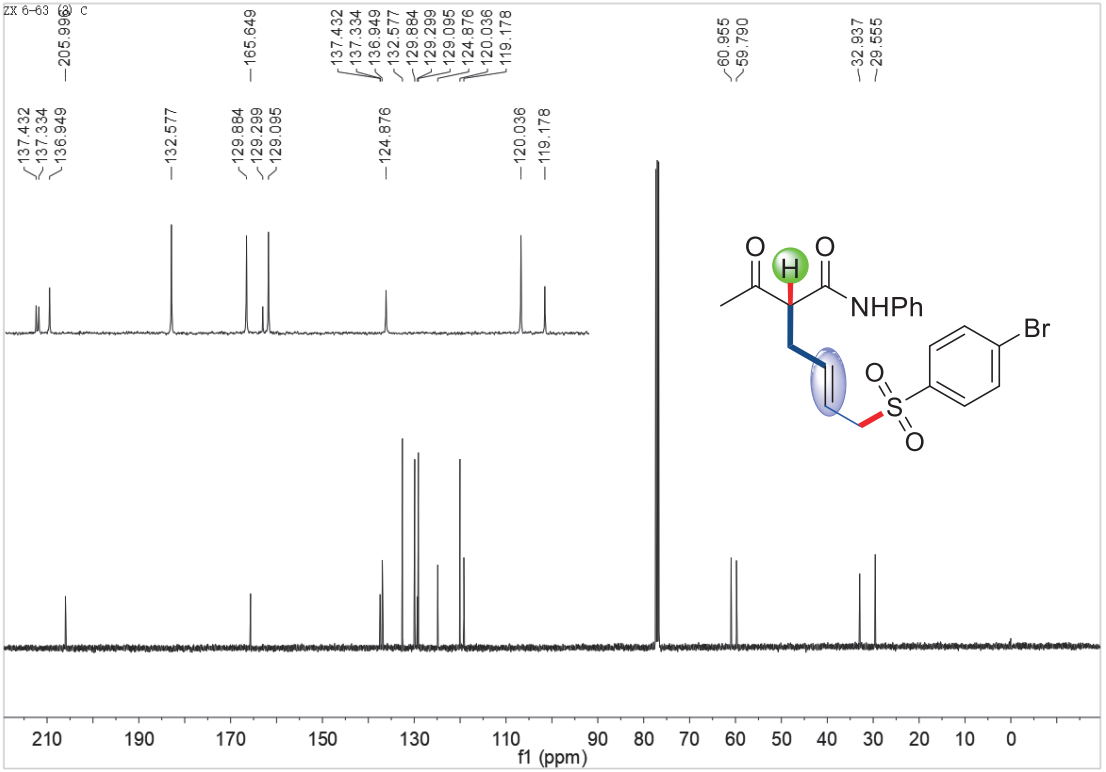
4p4, DEPT 90 and DEPT 135



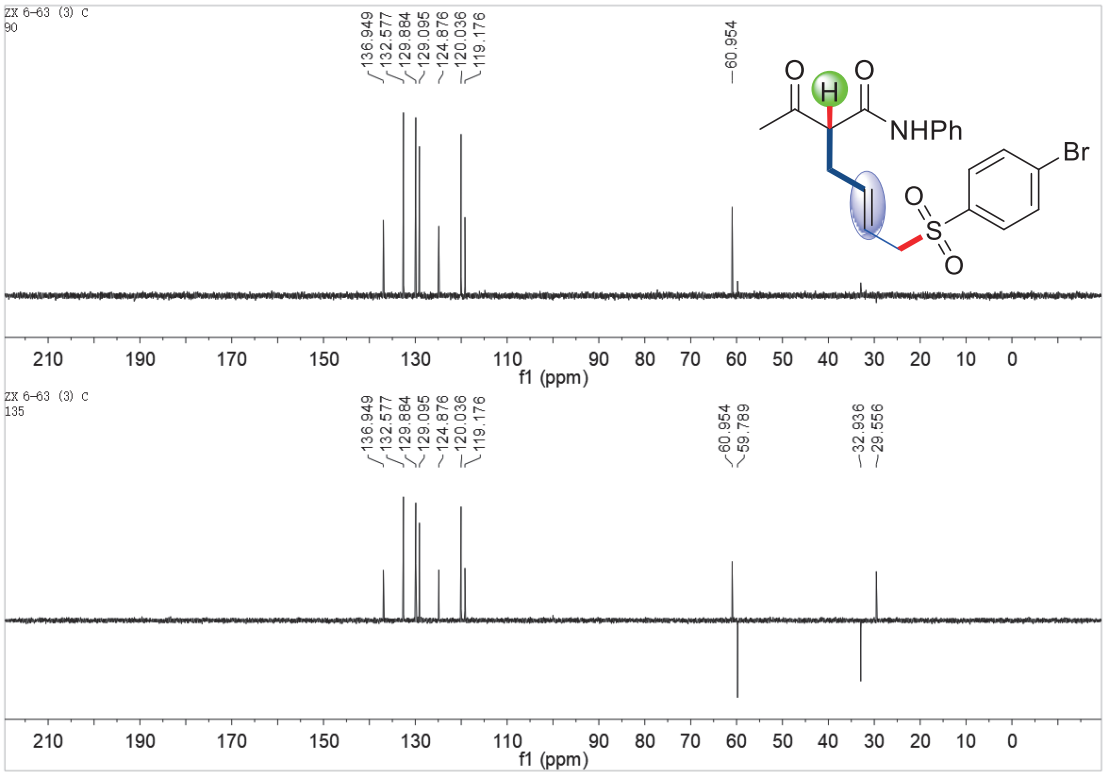
4p5, ^{1}H NMR



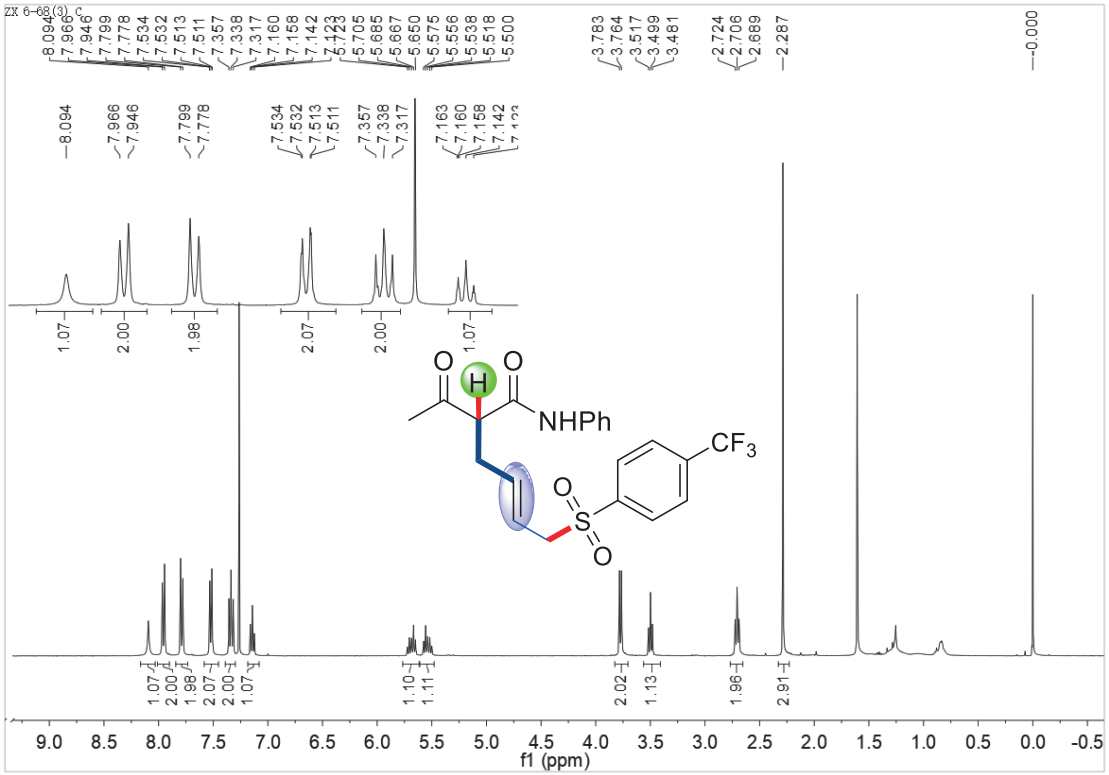
4p5, ^{13}C NMR



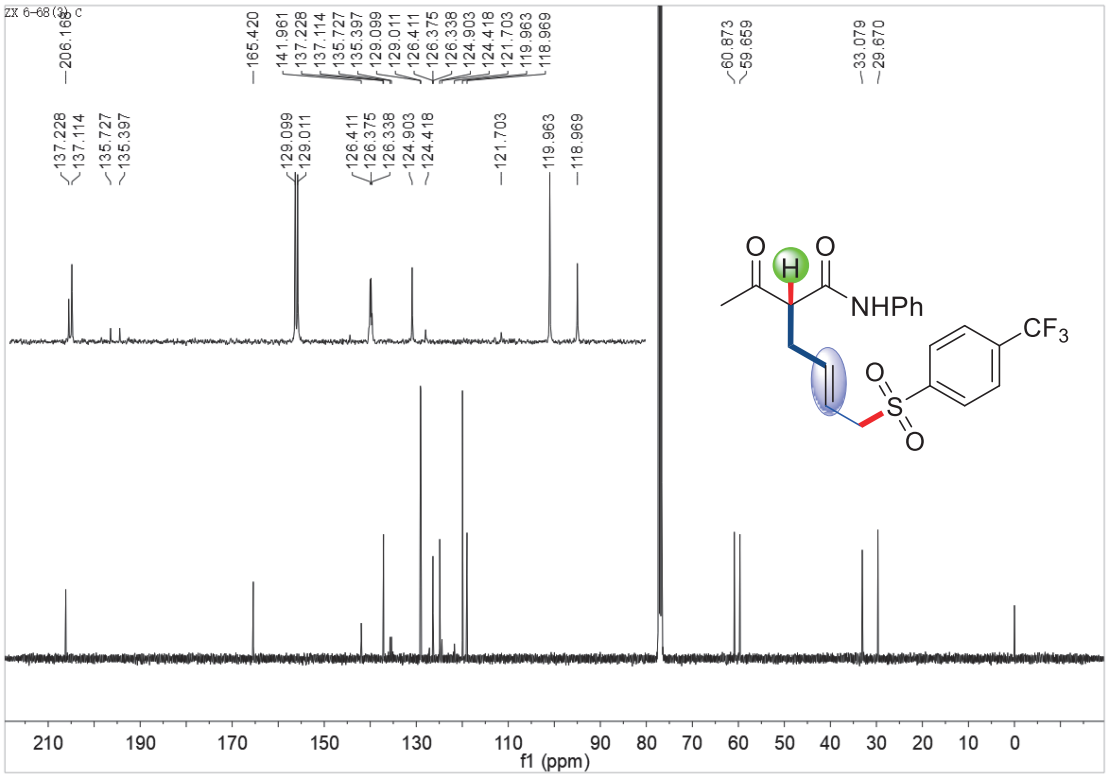
4p5, DEPT 90 and DEPT 135



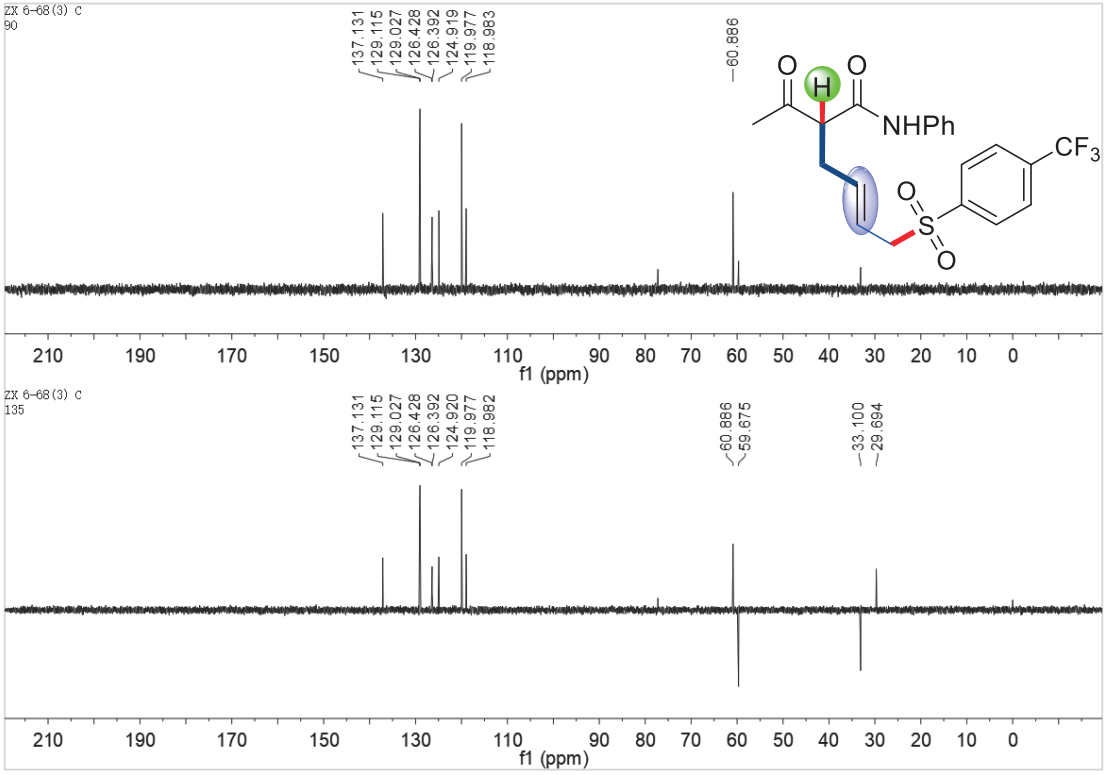
4p6, ^{1}H NMR



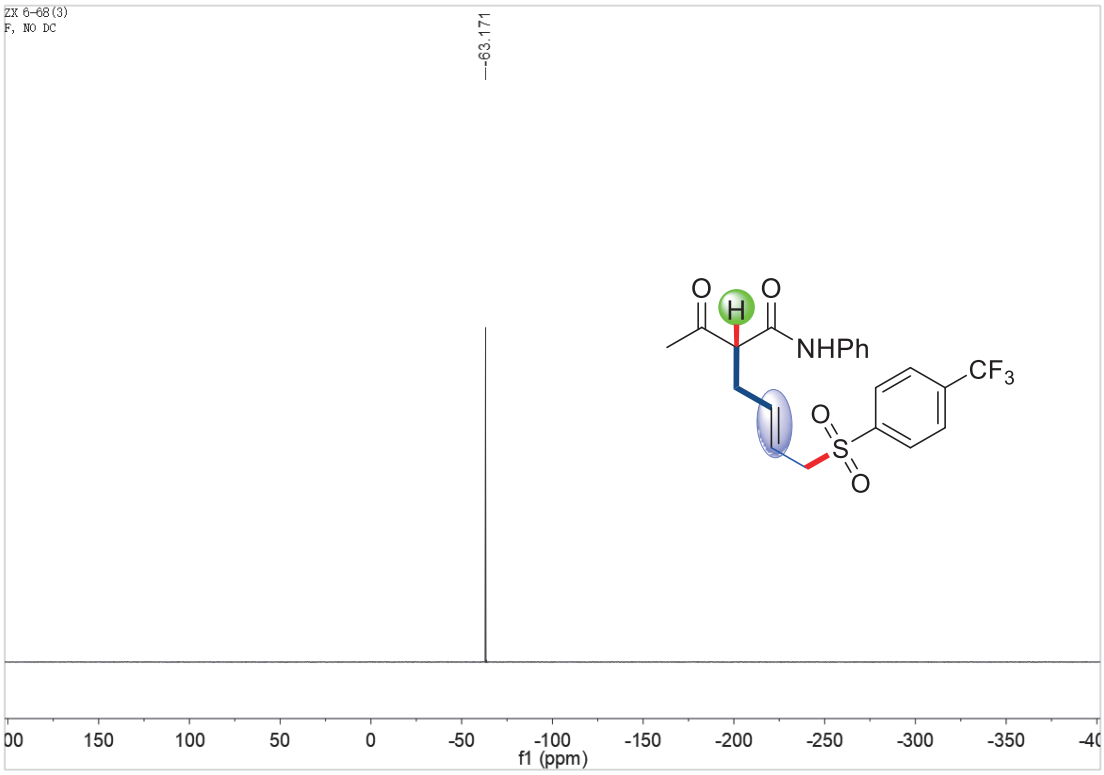
4p6, ^{13}C NMR



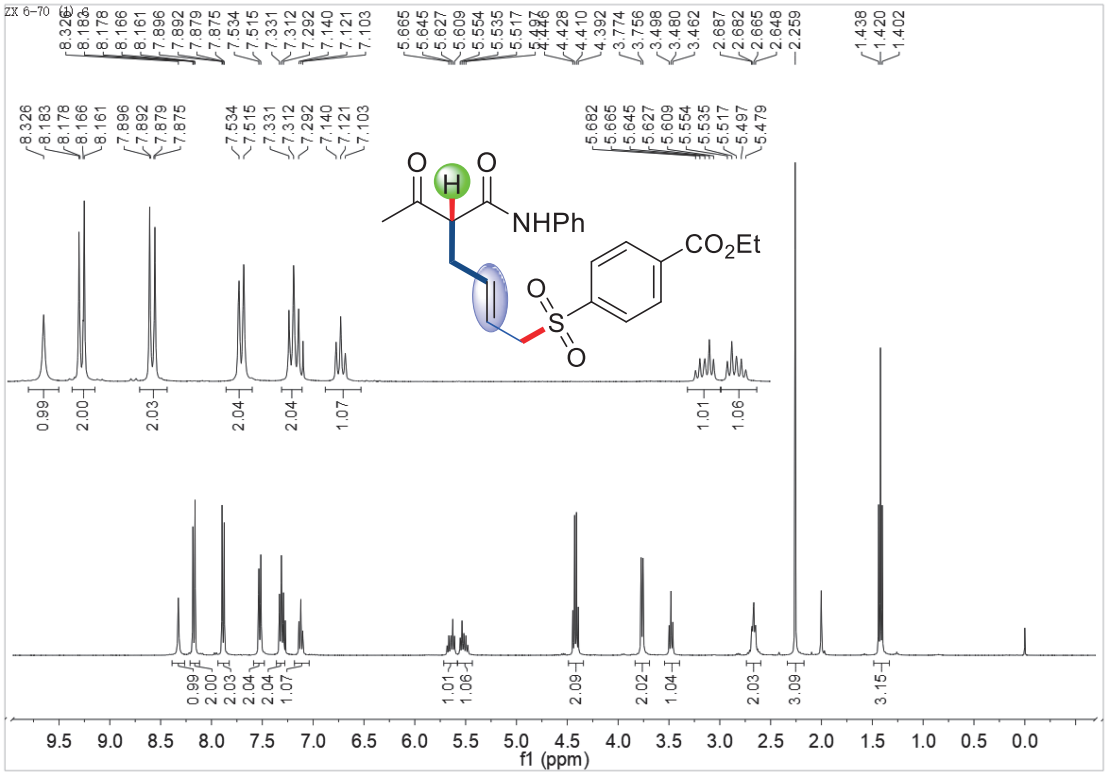
4p6, DEPT 90 and DEPT 135



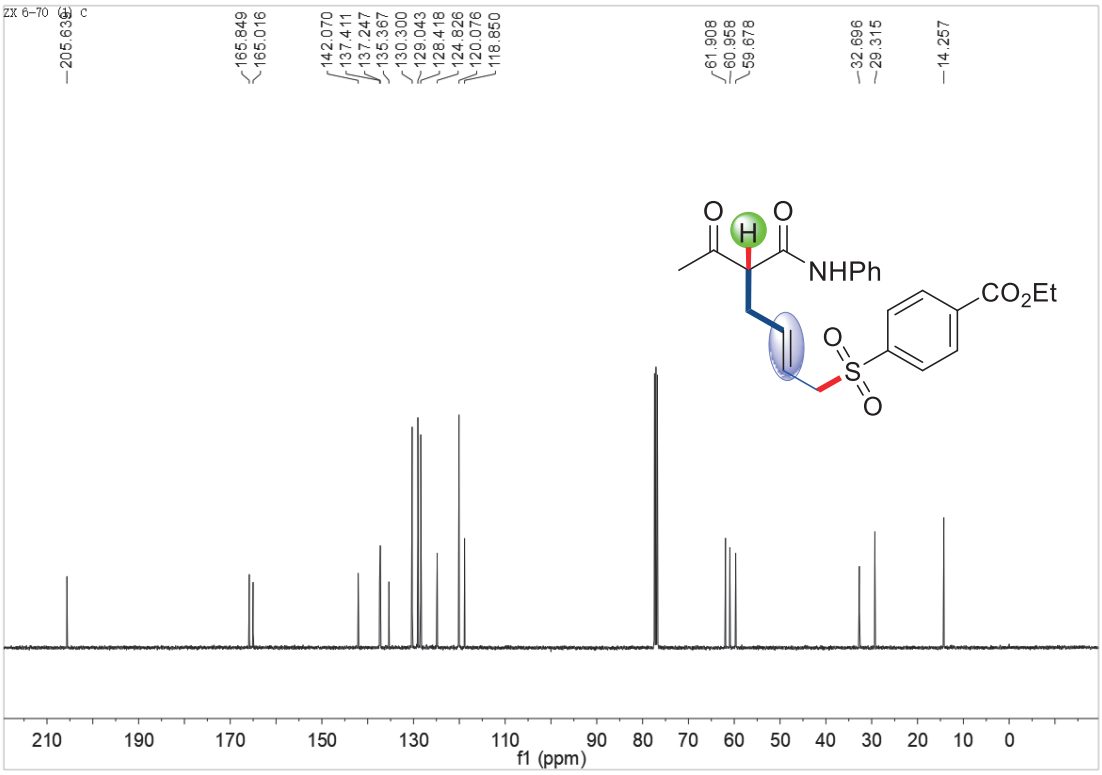
4p6, ^{19}F NMR



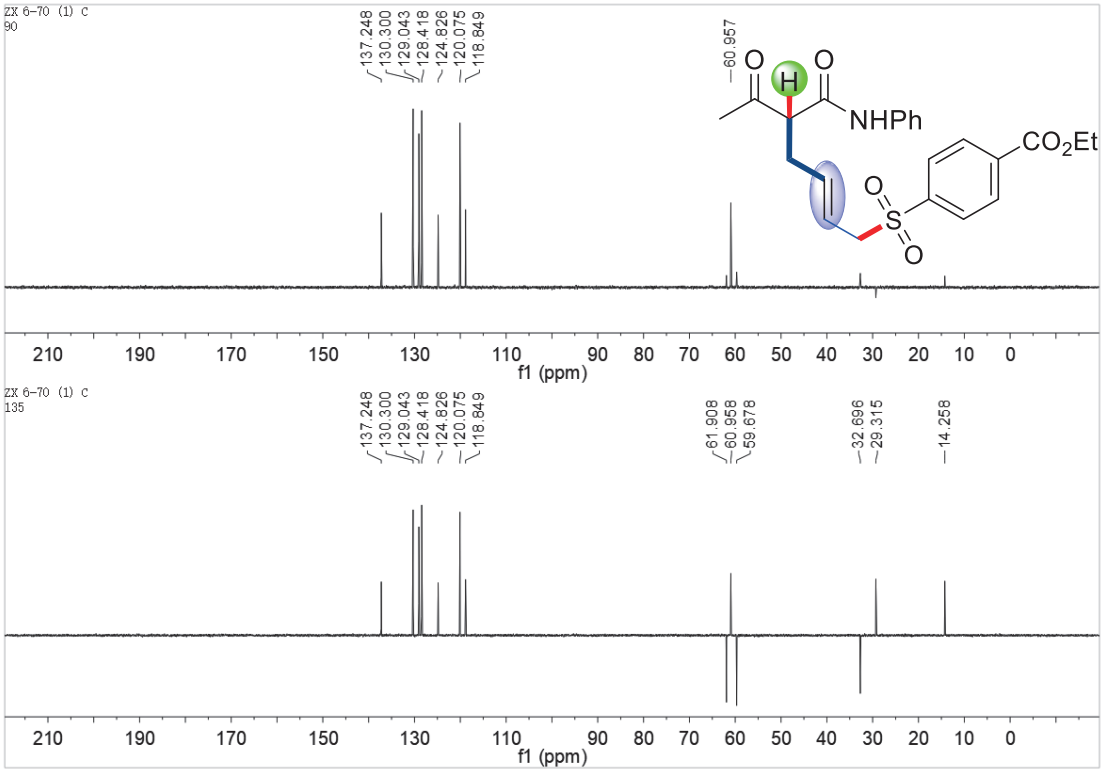
4p7, ^{1}H NMR



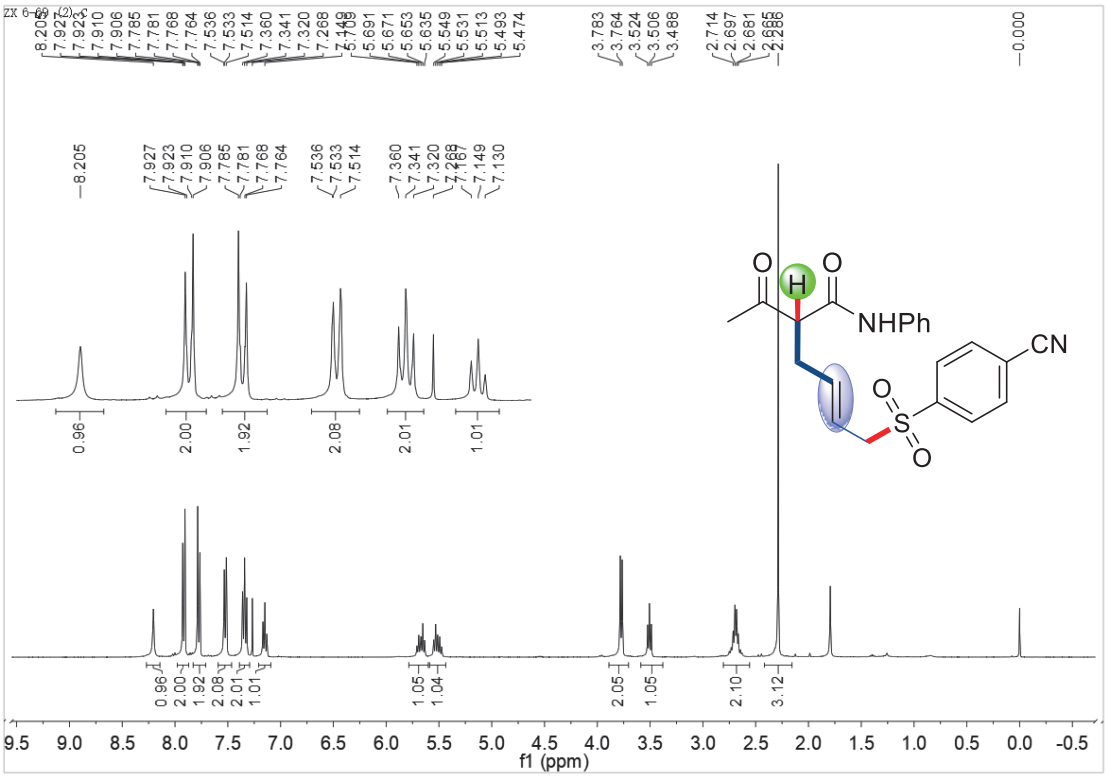
4p7, ^{13}C NMR



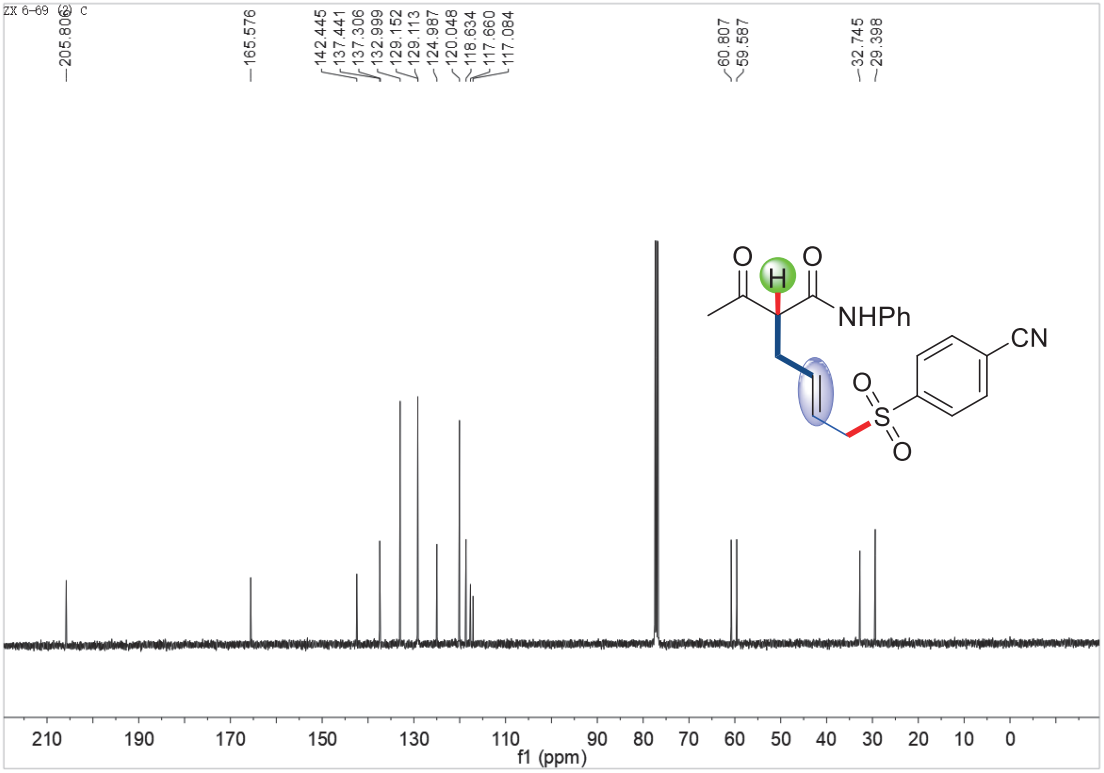
4p7, DEPT 90 and DEPT 135



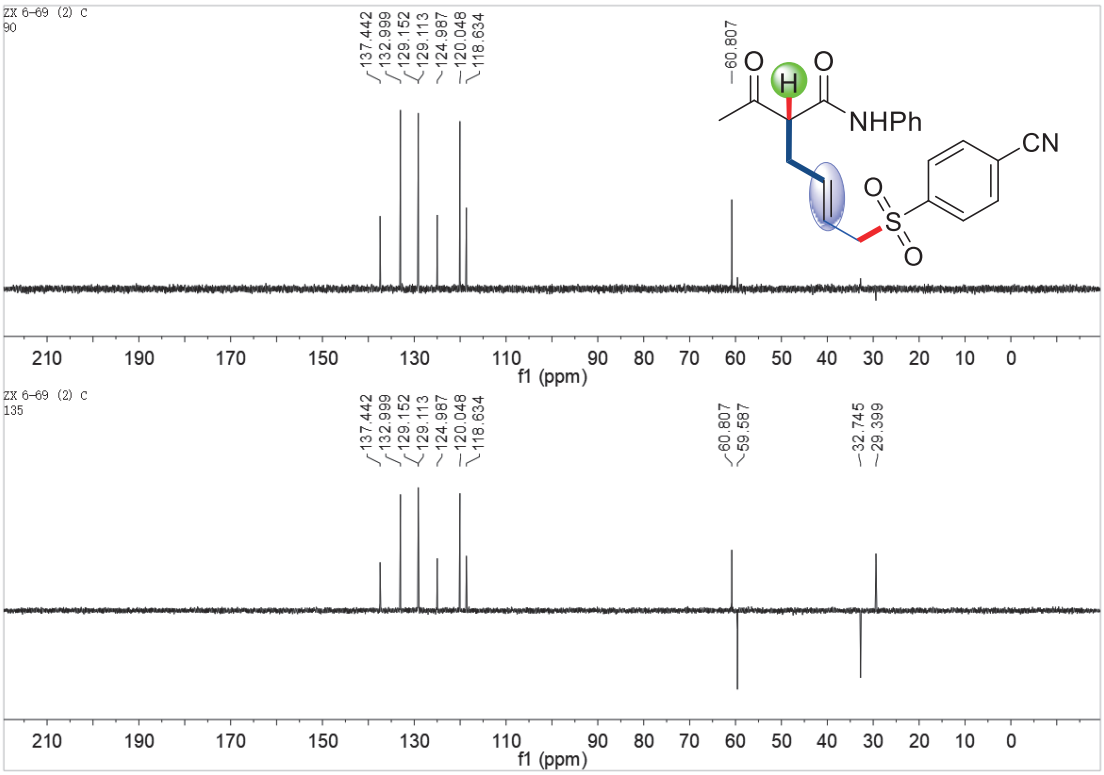
4p8, ^{1}H NMR



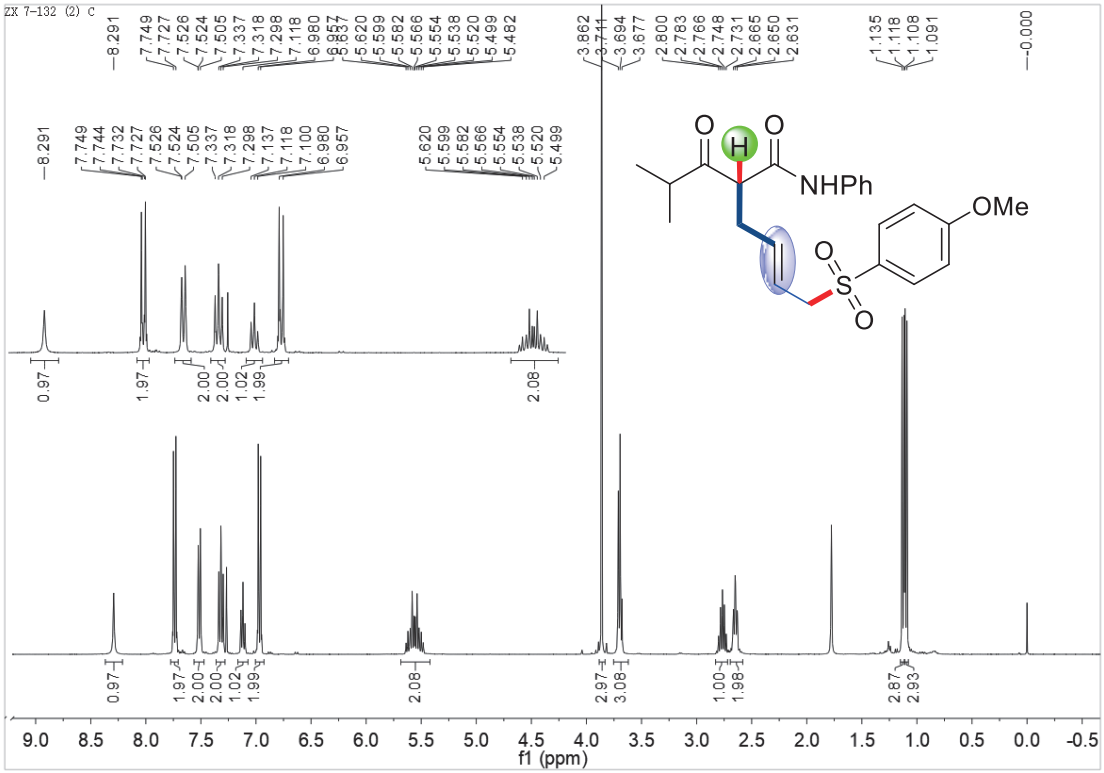
4p8, ^{13}C NMR



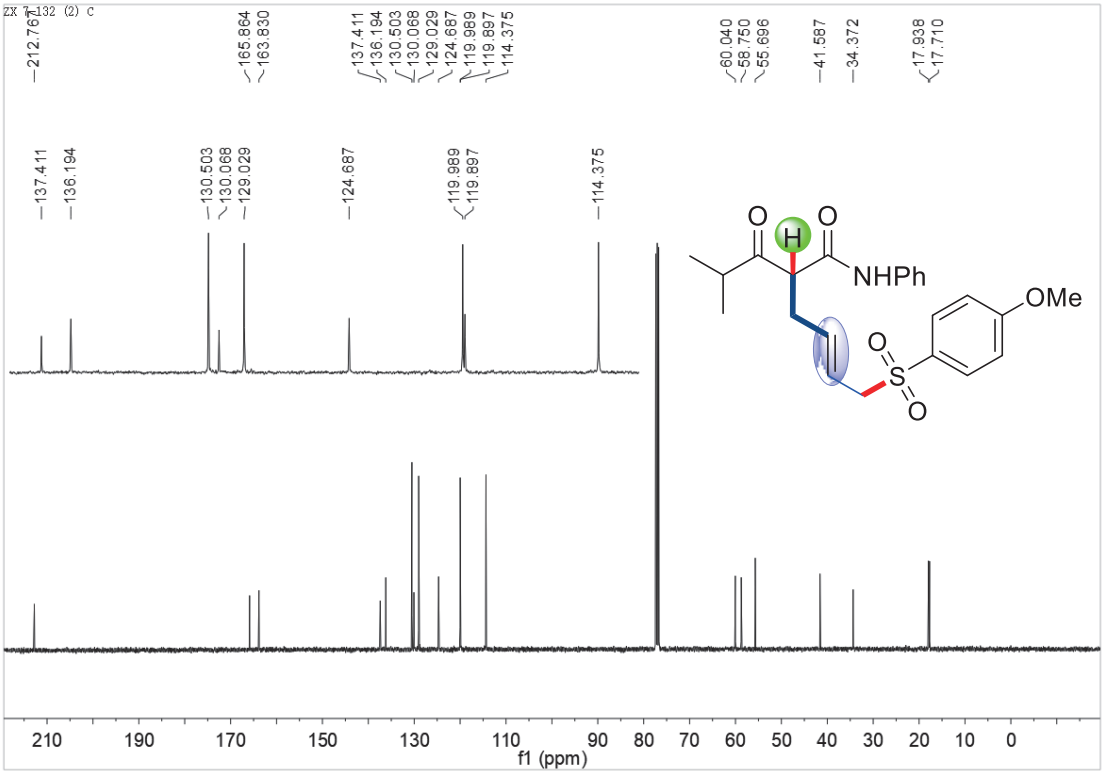
4p8, DEPT 90 and DEPT 135



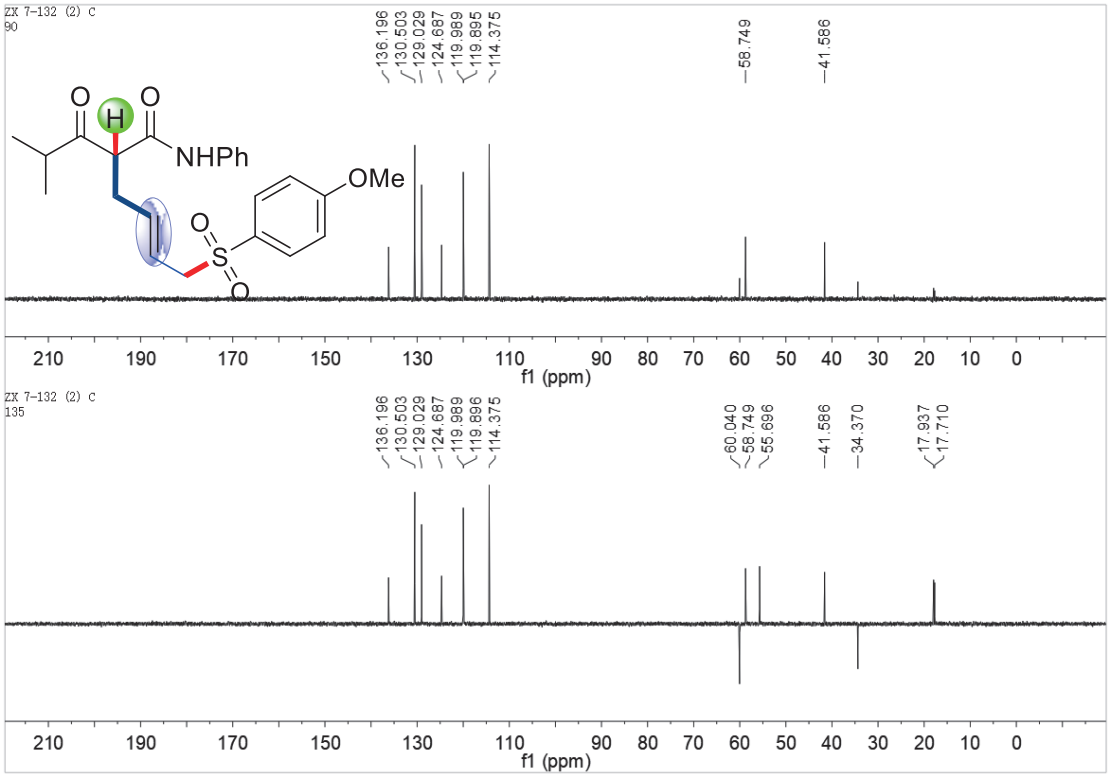
4q, ^{1}H NMR



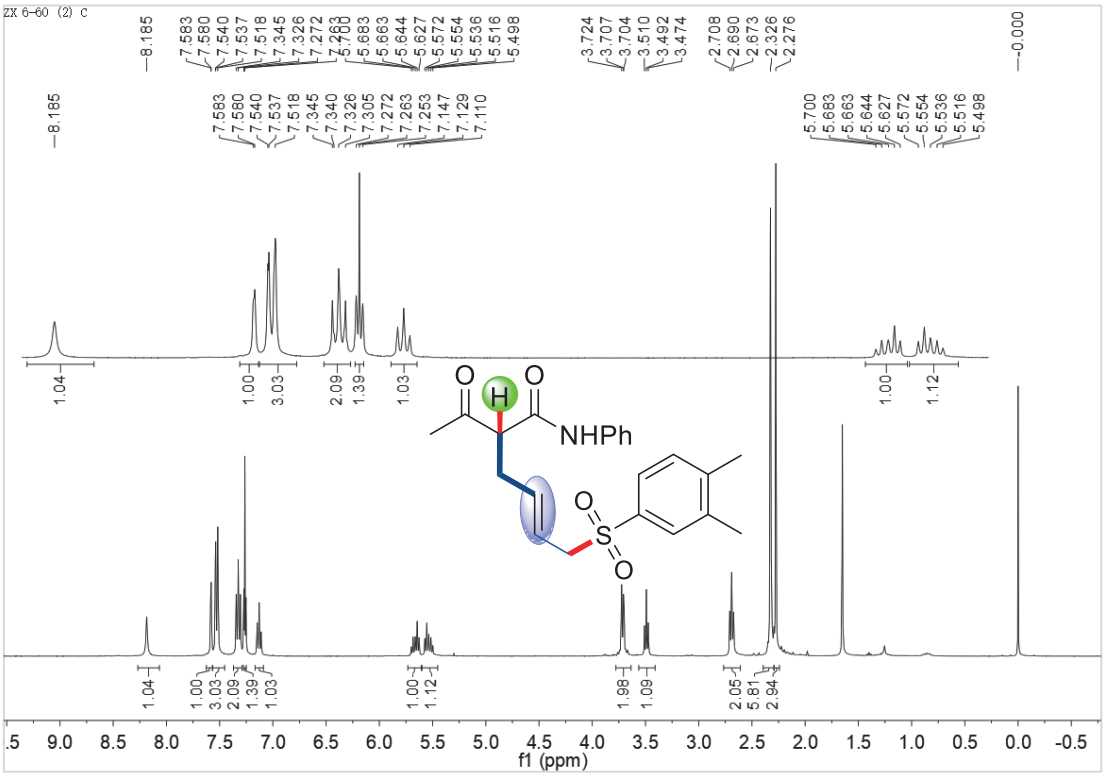
4q, ^{13}C NMR



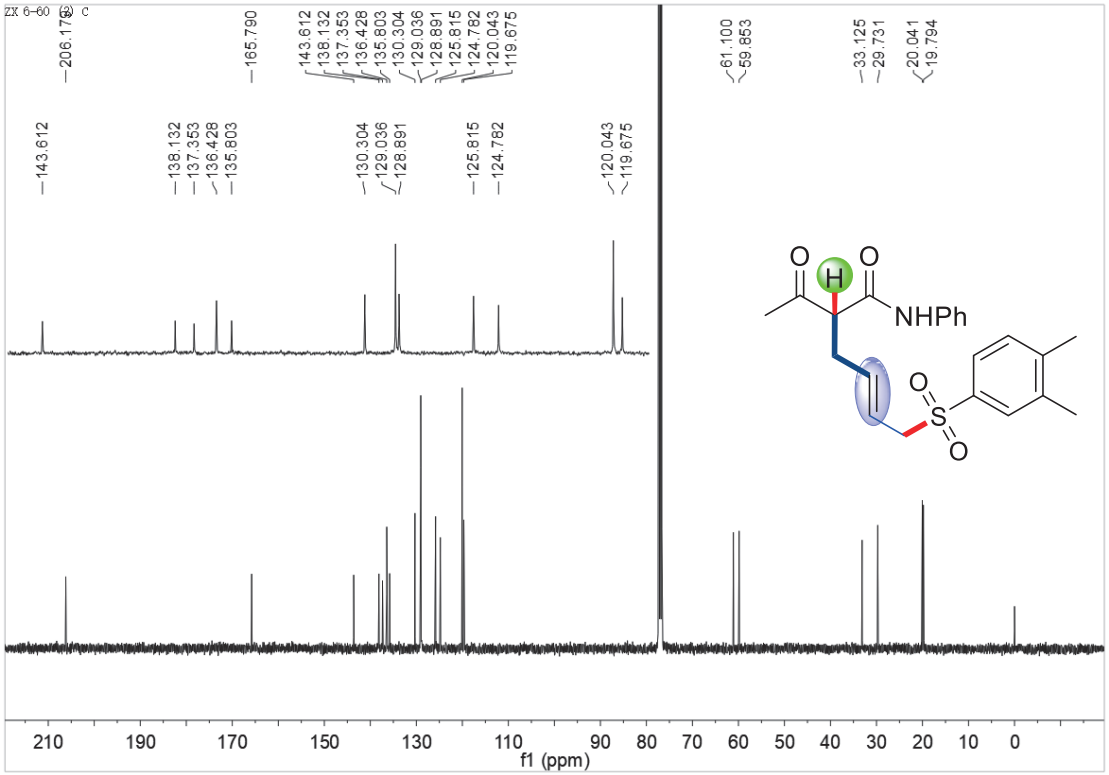
4q, DEPT 90 and DEPT 135



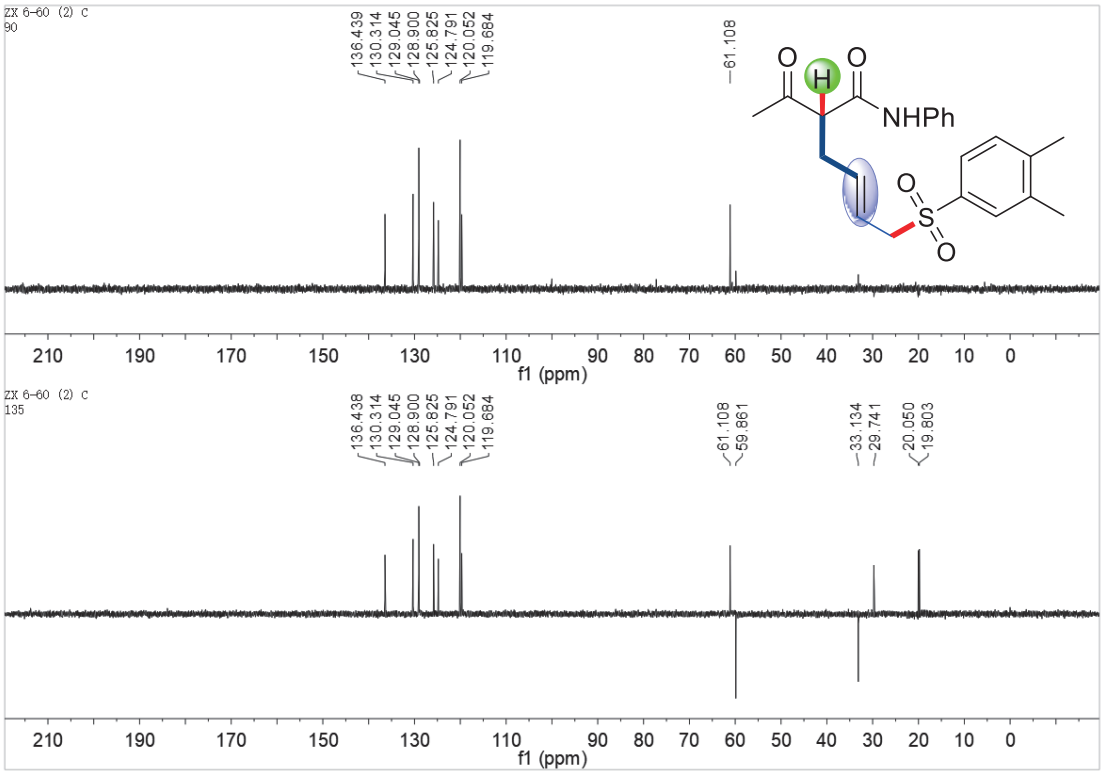
4r1, ^{1}H NMR



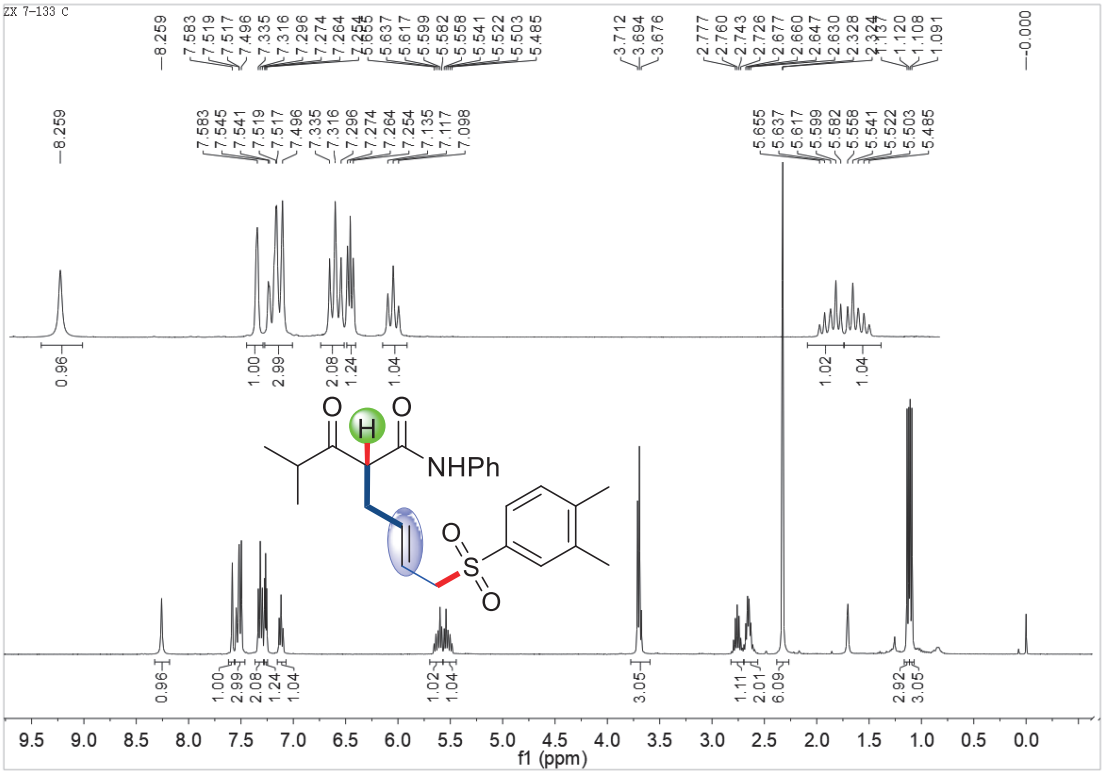
4r1, ^{13}C NMR



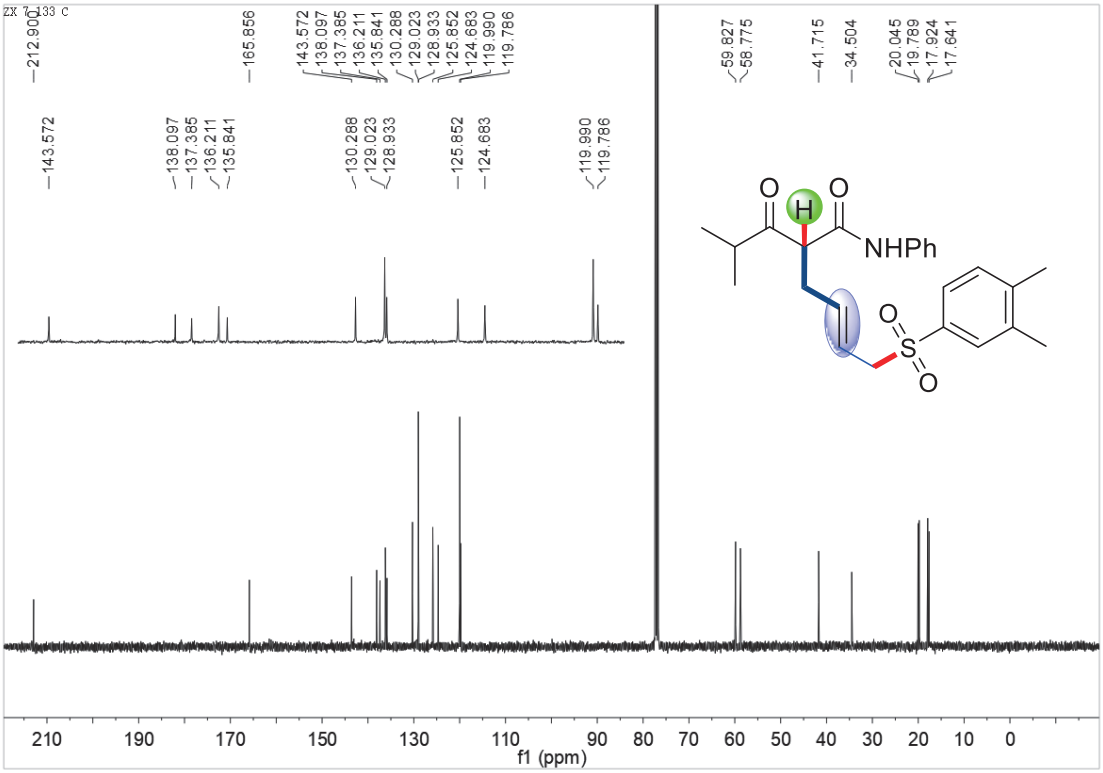
4r1, DEPT 90 and DEPT 135



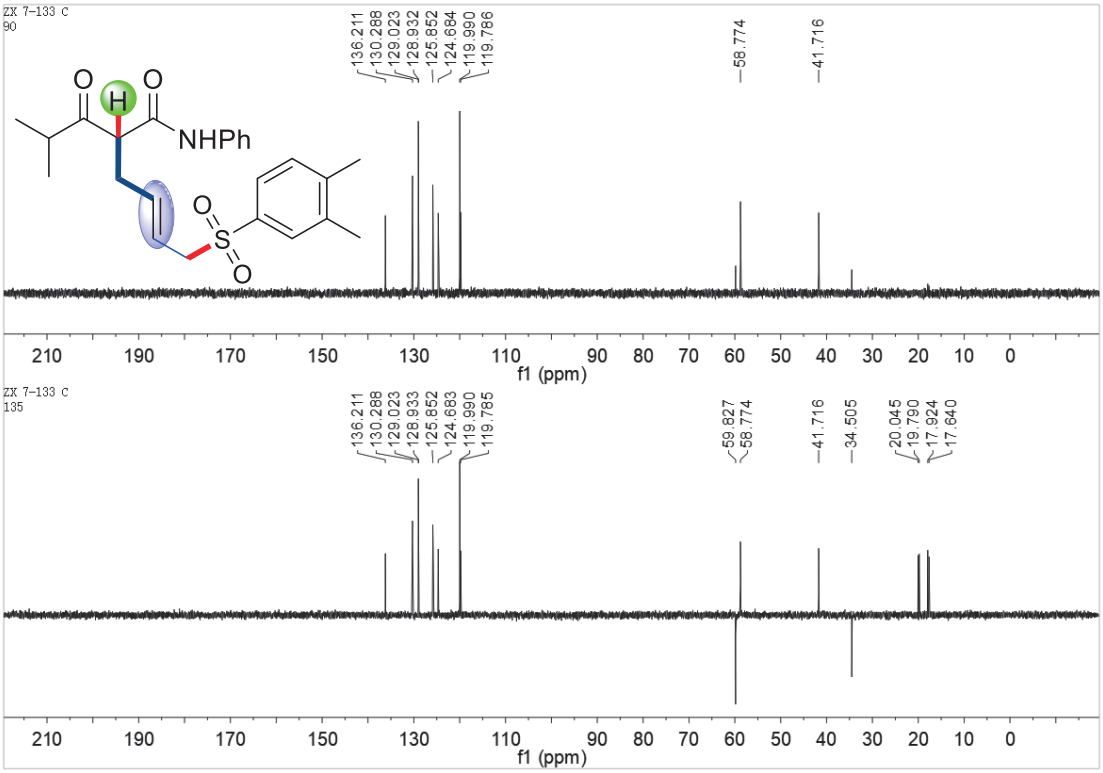
4r2, ^{1}H NMR



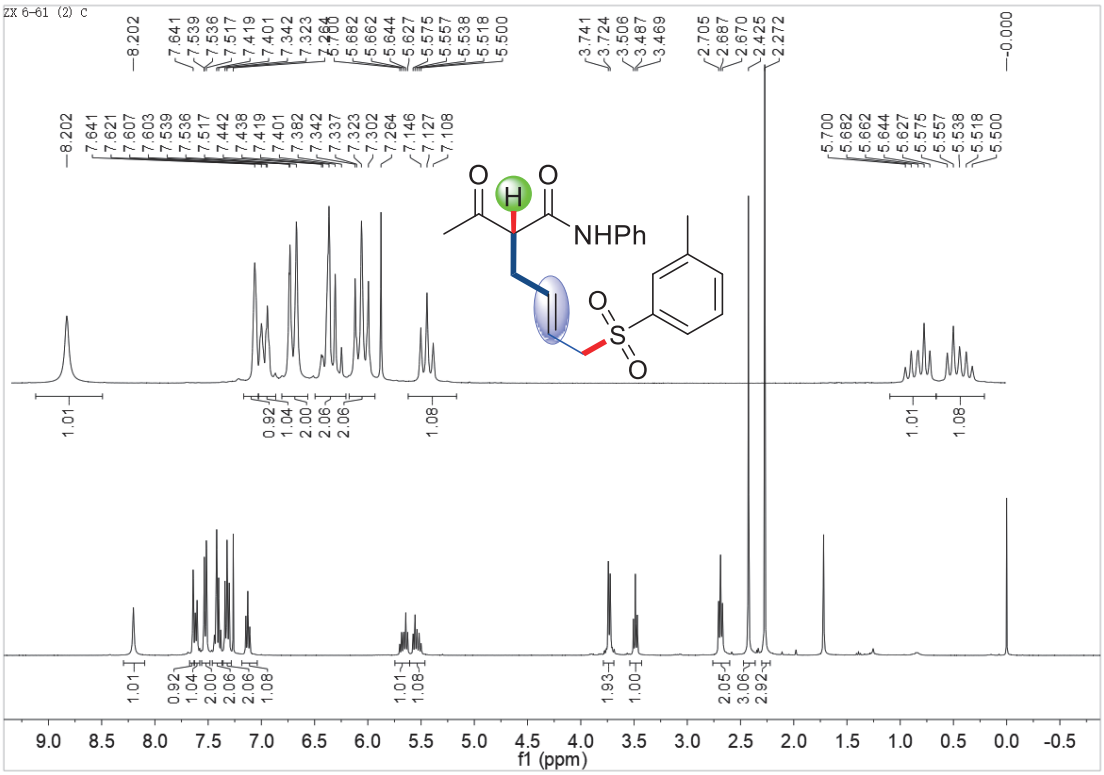
4r2, ^{13}C NMR



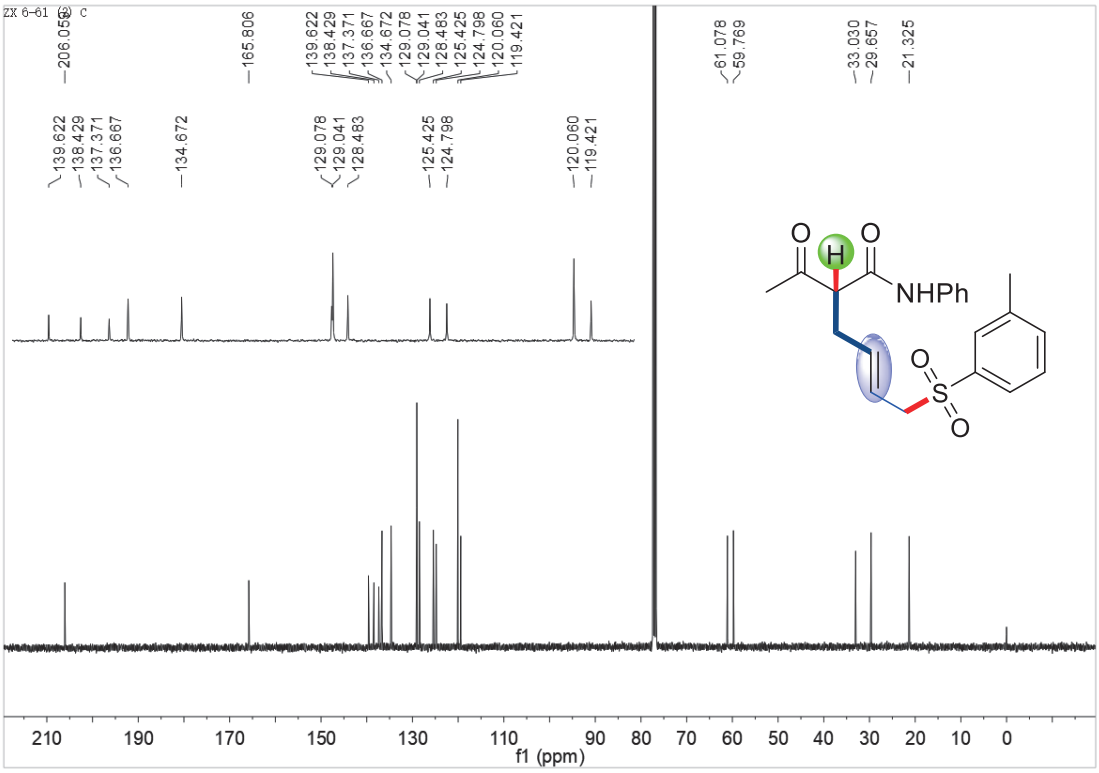
4r2, DEPT 90 and DEPT 135



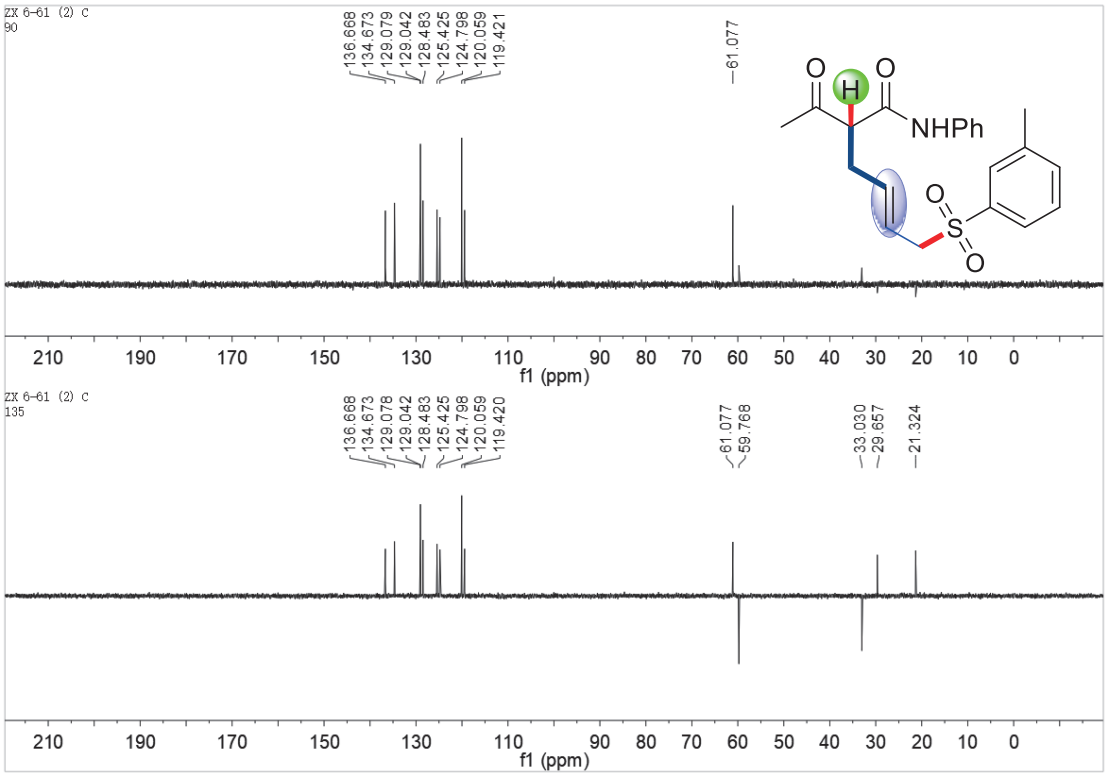
4s1, ^{1}H NMR



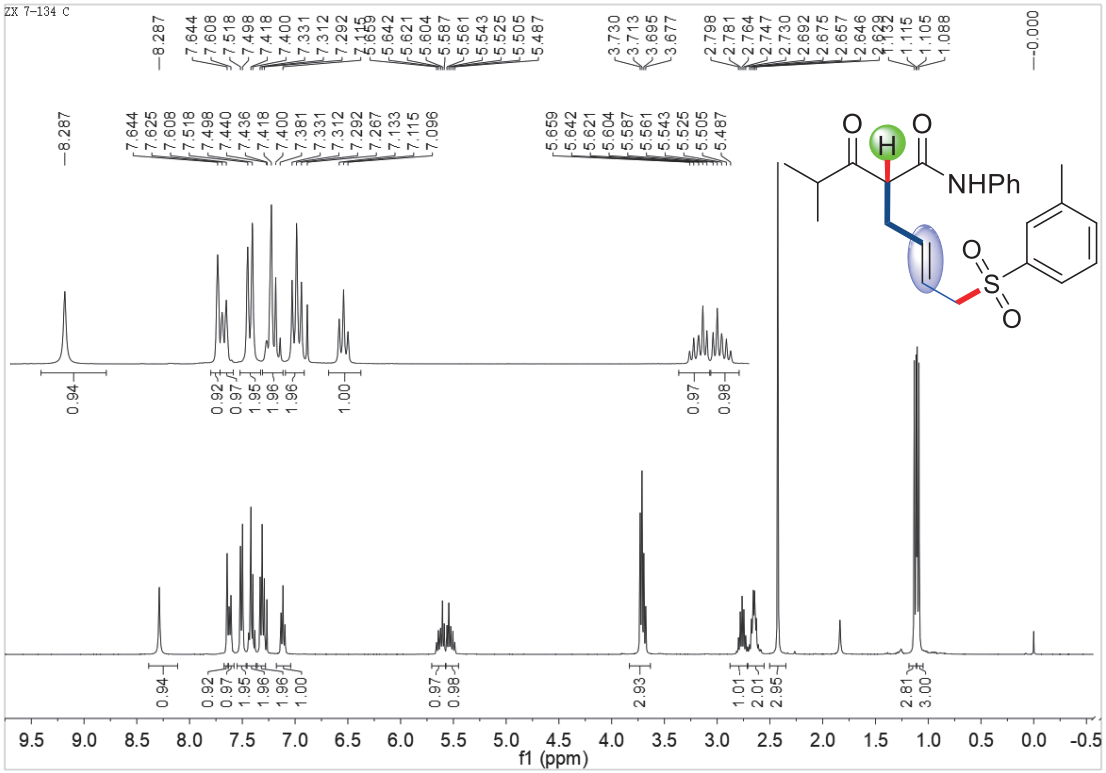
4s1, ^{13}C NMR



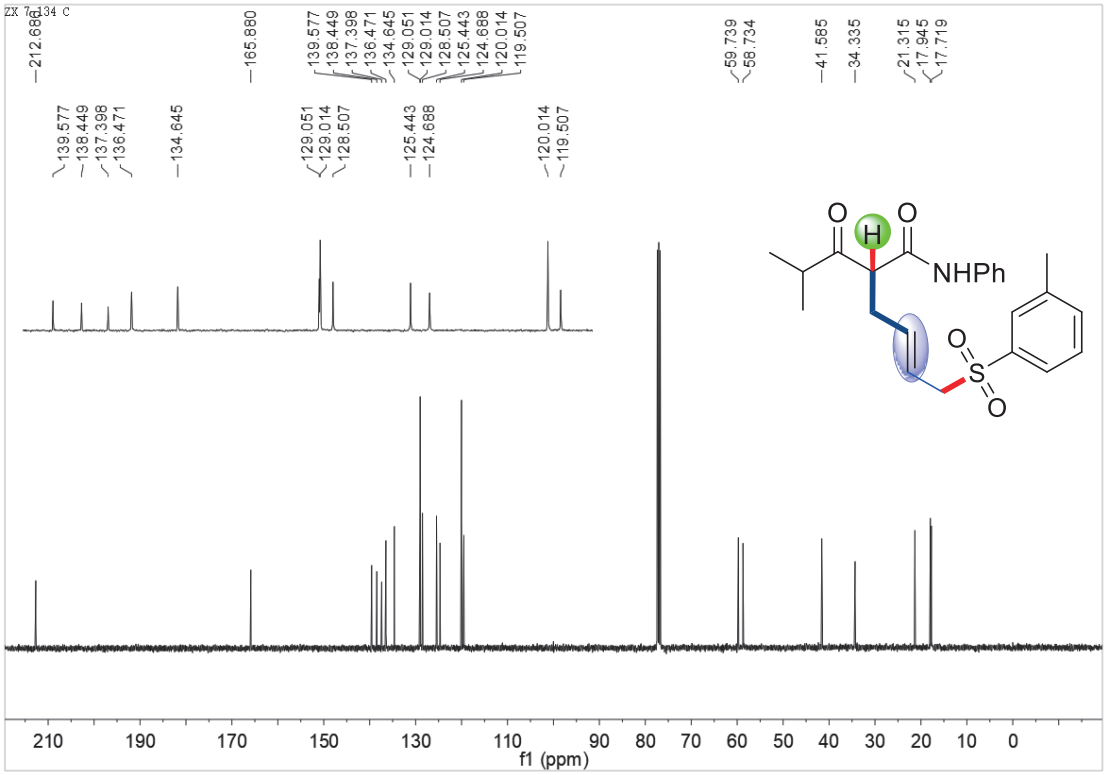
4s1, DEPT 90 and DEPT 135



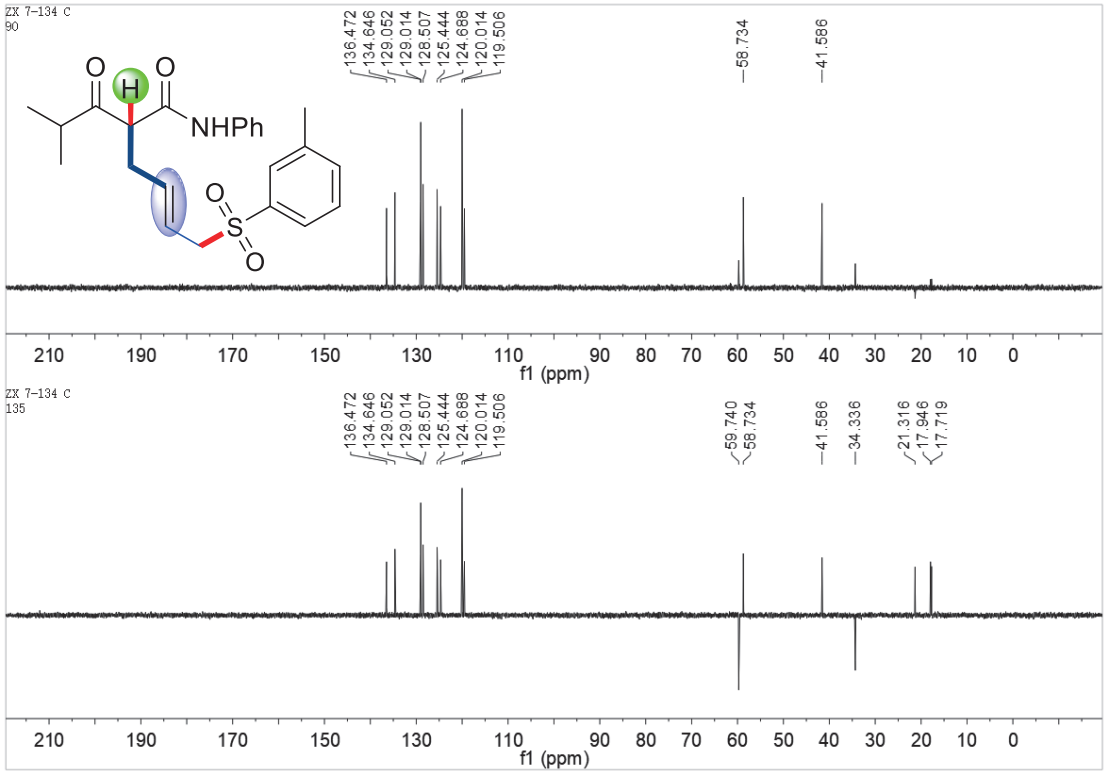
4s2, ^{1}H NMR



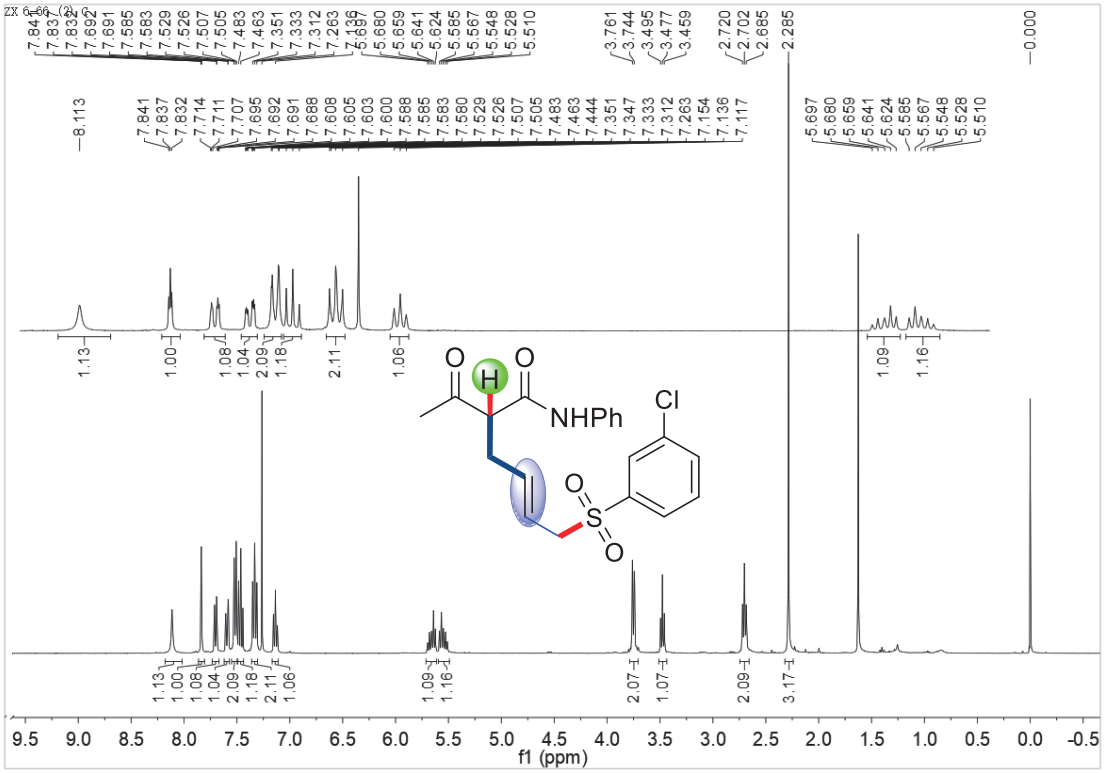
4s2, ^{13}C NMR



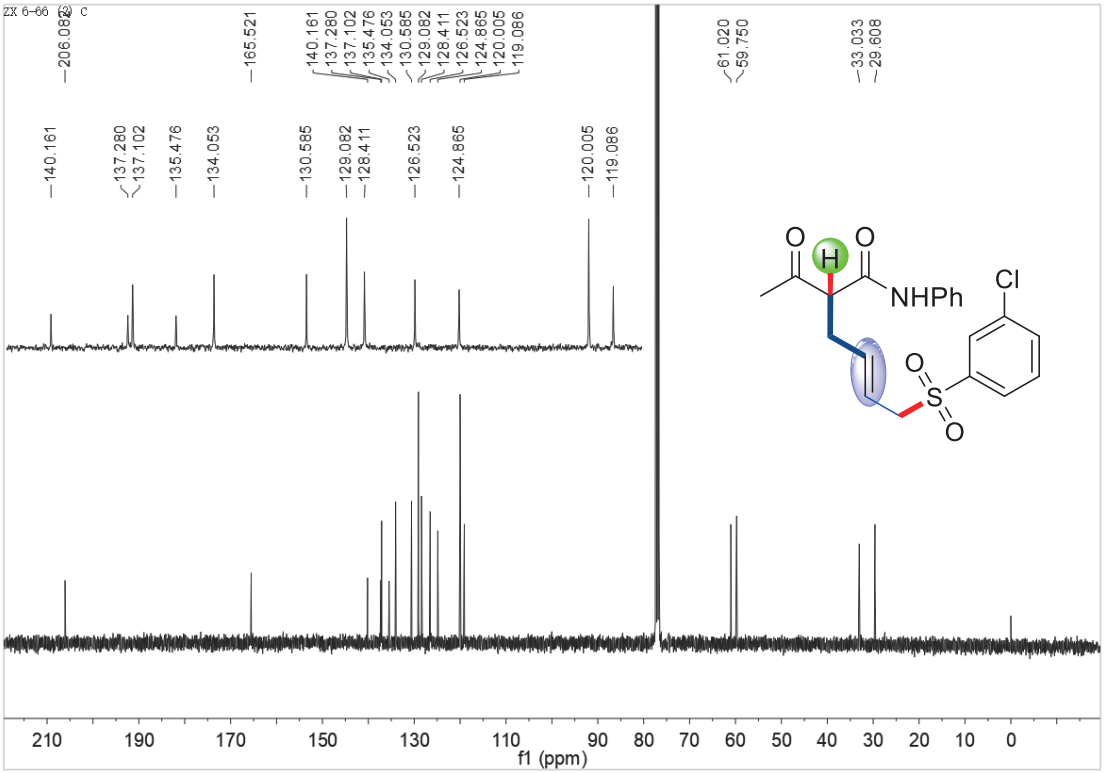
4s2, DEPT 90 and DEPT 135



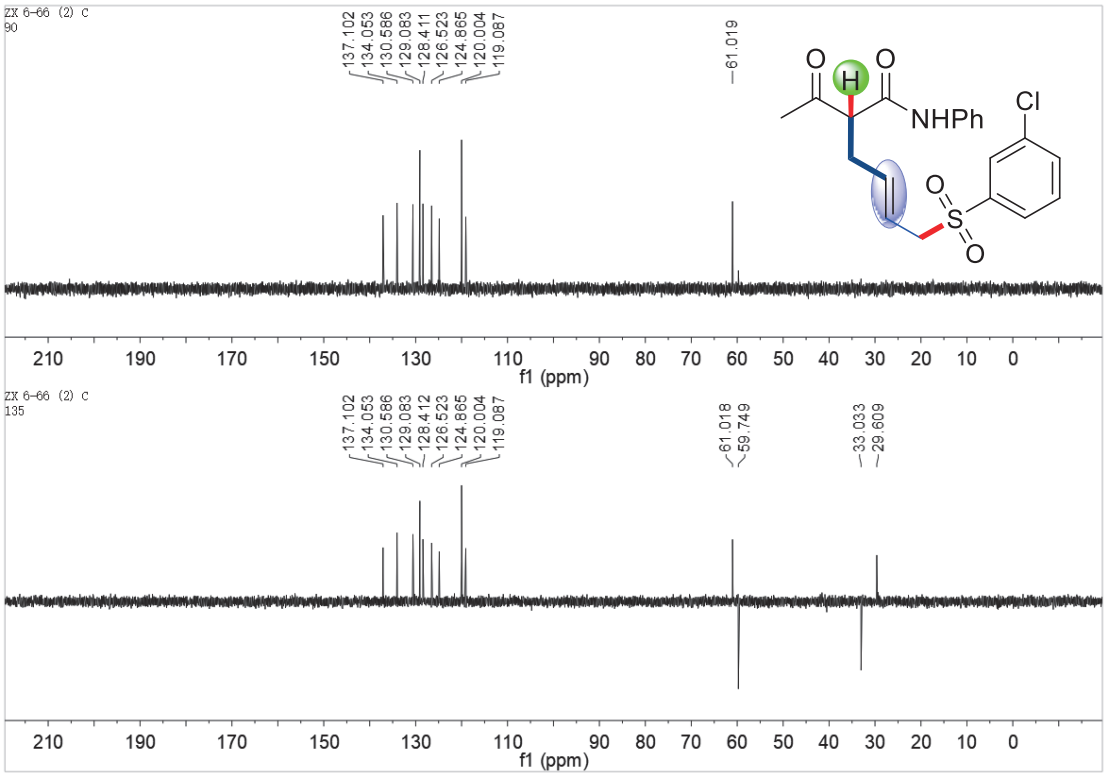
4t1, ^{1}H NMR



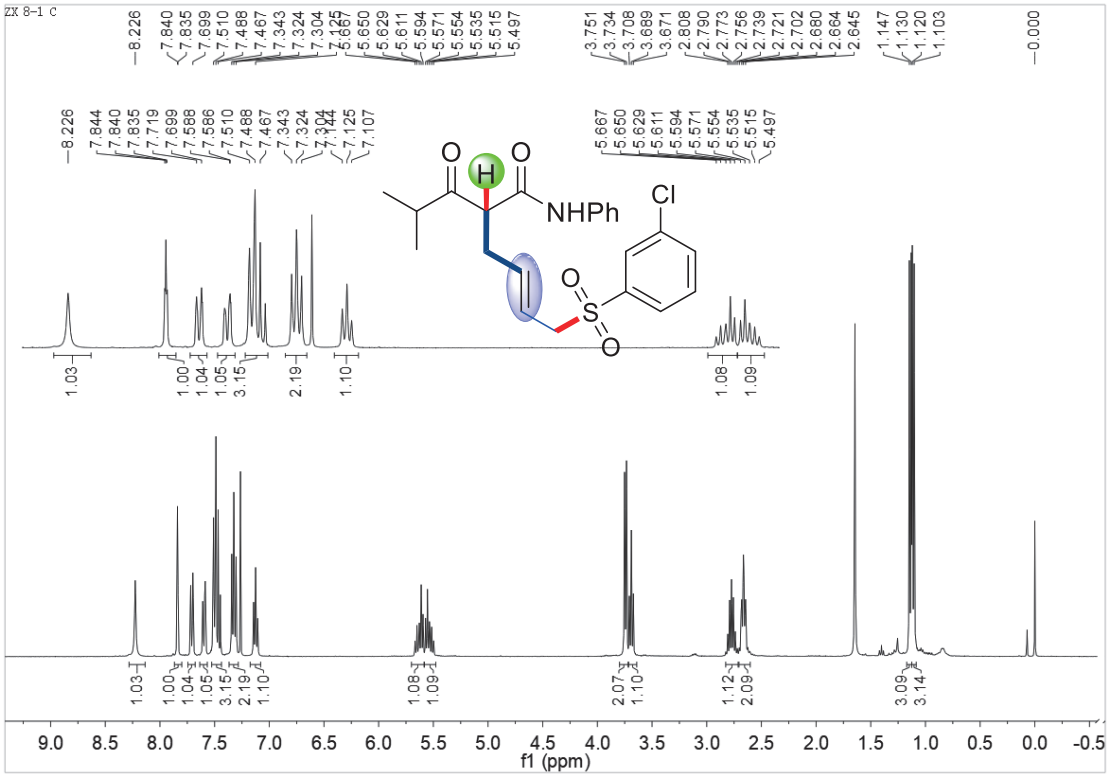
4t1, ^{13}C NMR



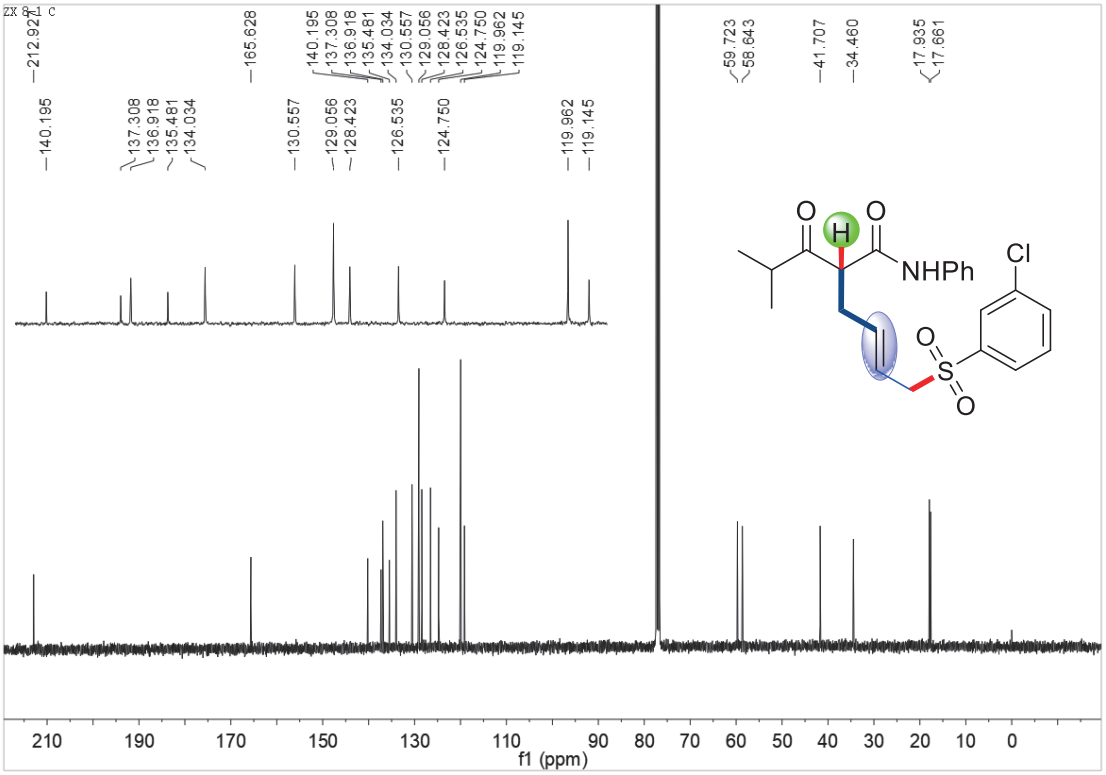
4t1, DEPT 90 and DEPT 135



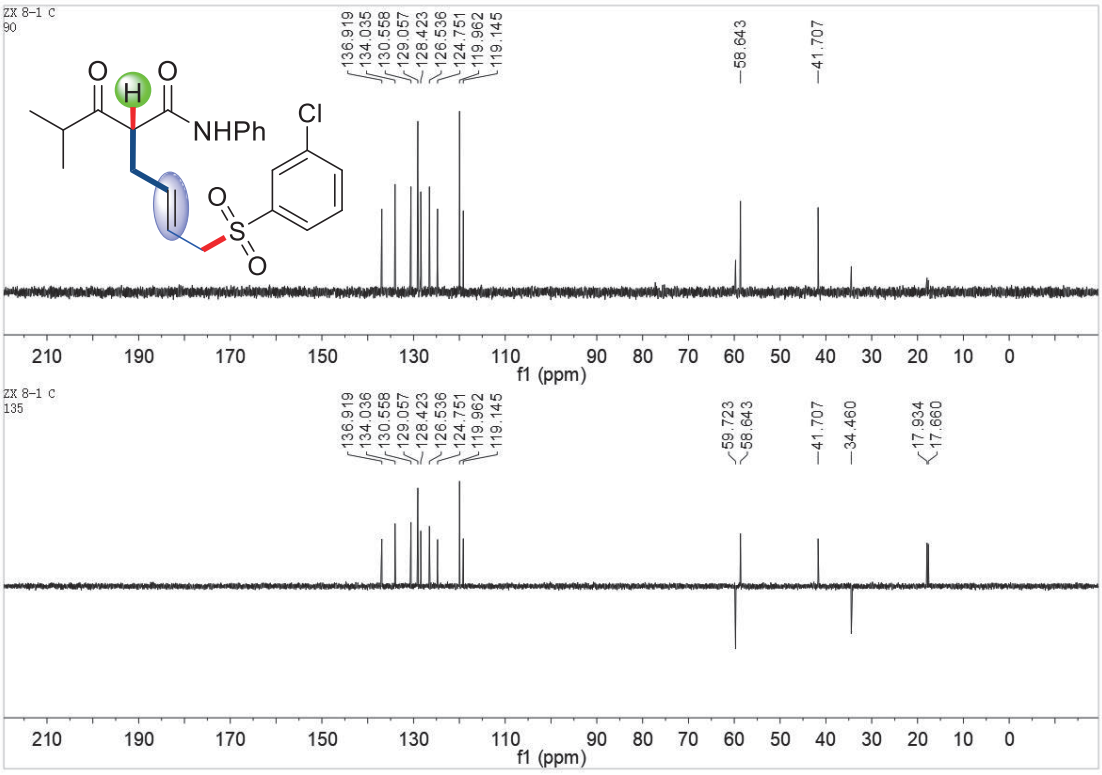
4t2, ^{1}H NMR



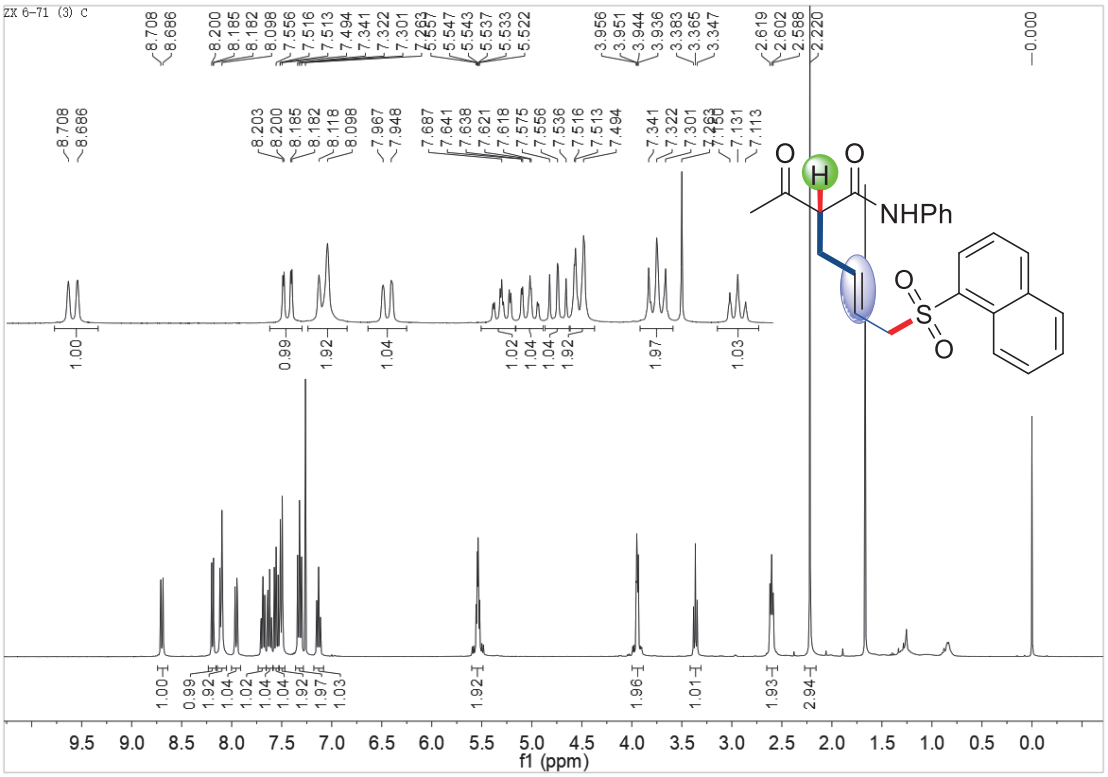
4t2, ^{13}C NMR



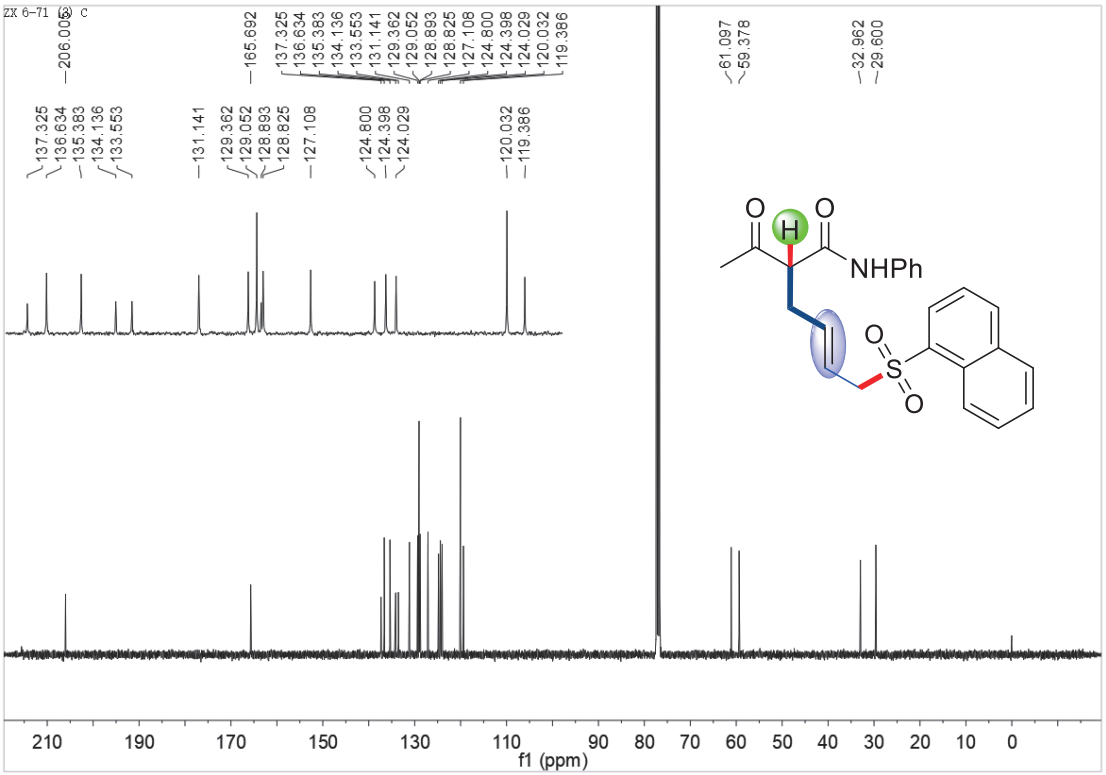
4t2, DEPT 90 and DEPT 135



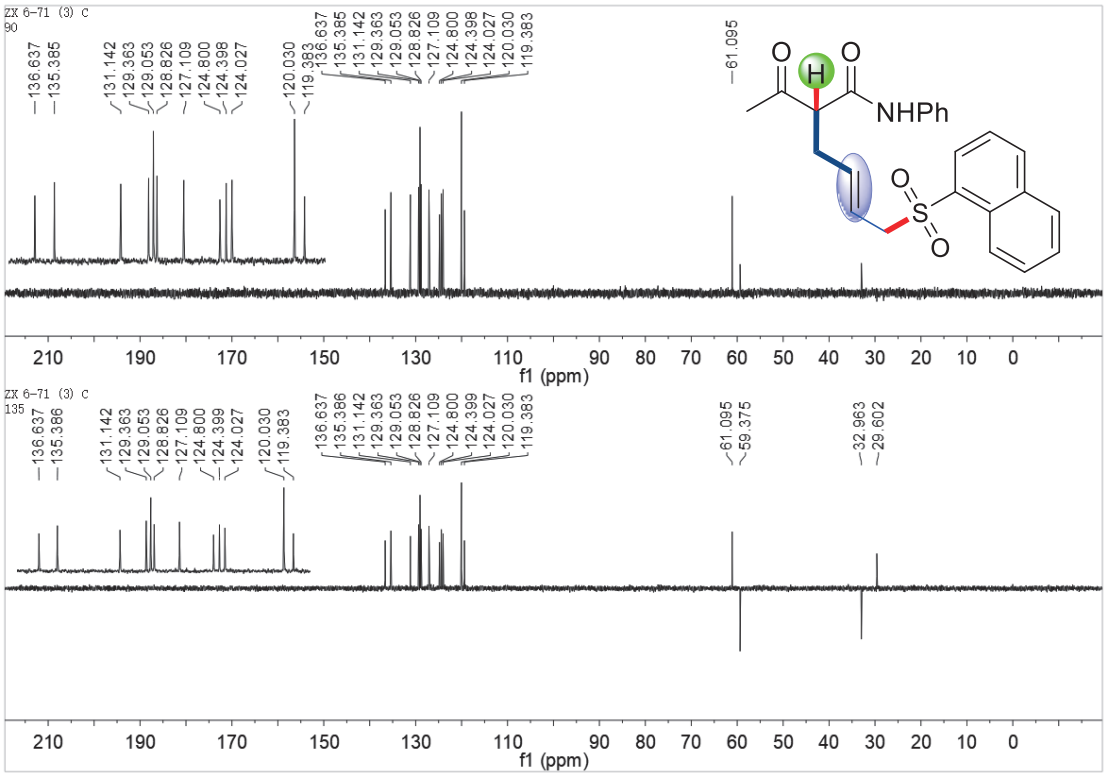
4u1, ^{1}H NMR



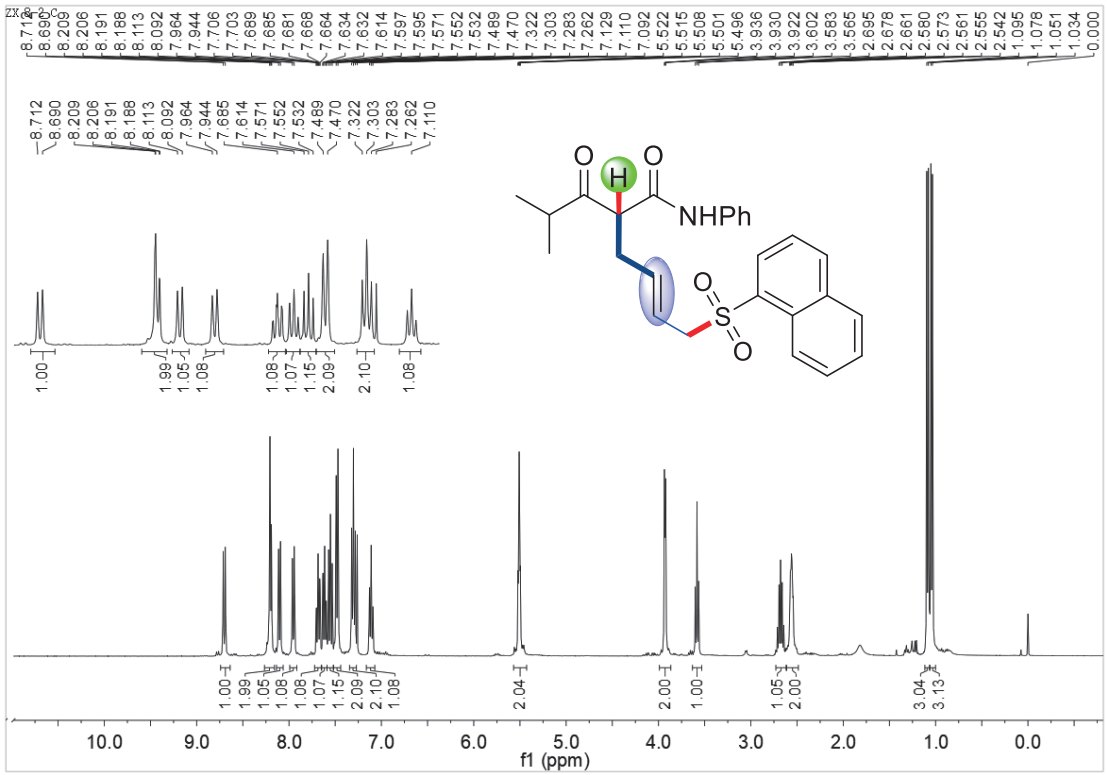
4u1, ^{13}C NMR



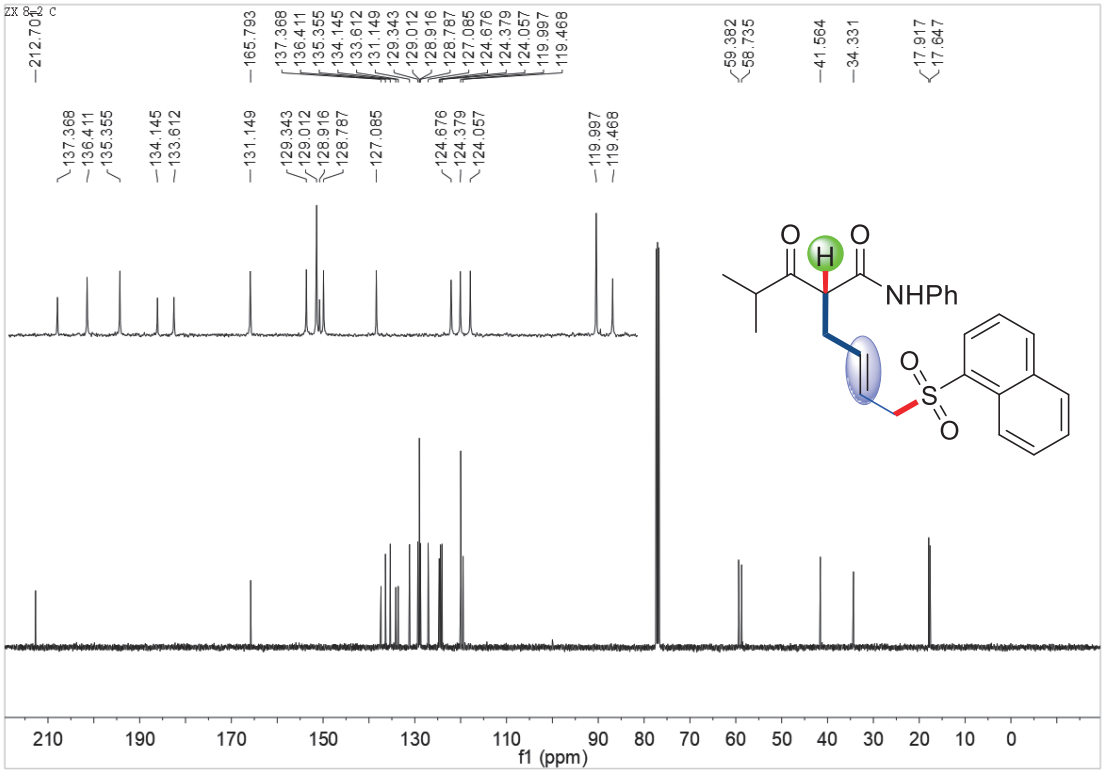
4u1, DEPT 90 and DEPT 135



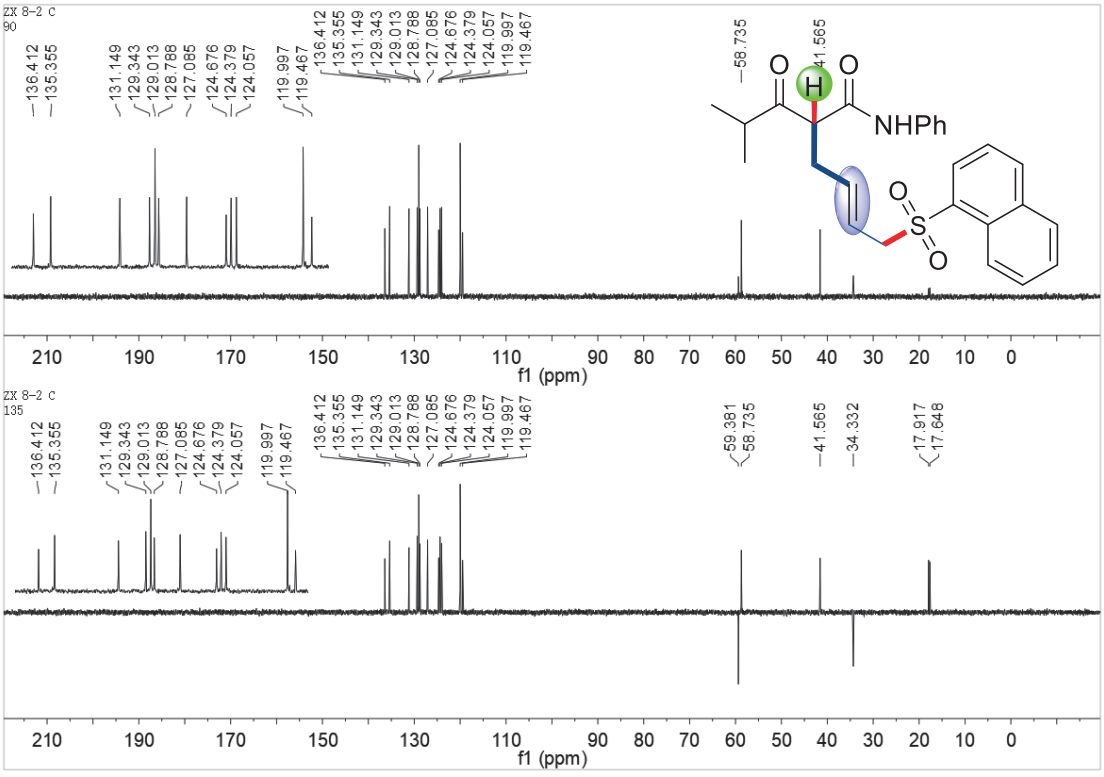
4u2, ^{1}H NMR



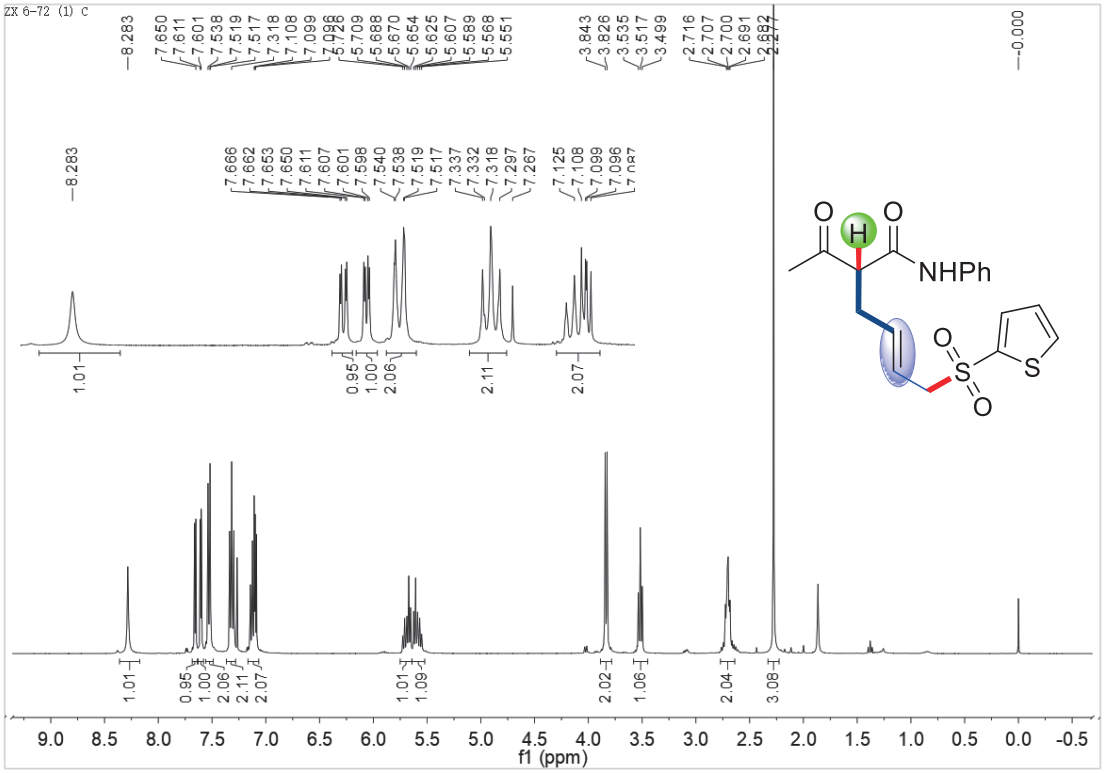
4u2, ^{13}C NMR



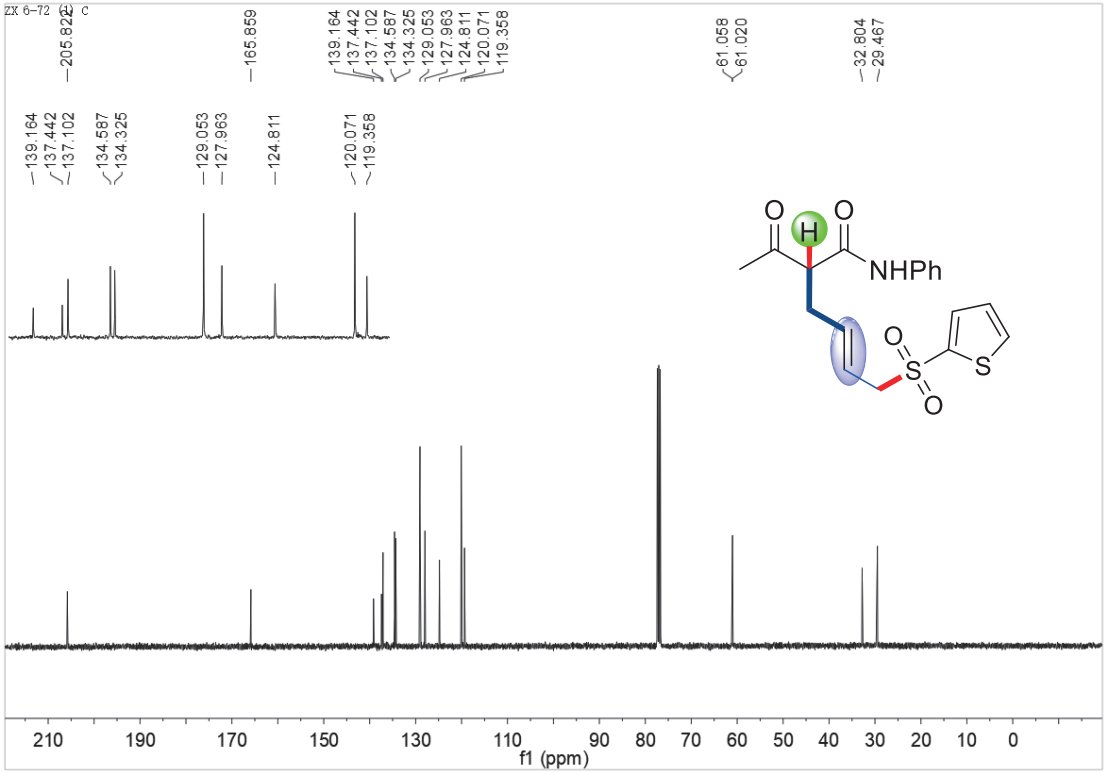
4u2, DEPT 90 and DEPT 135



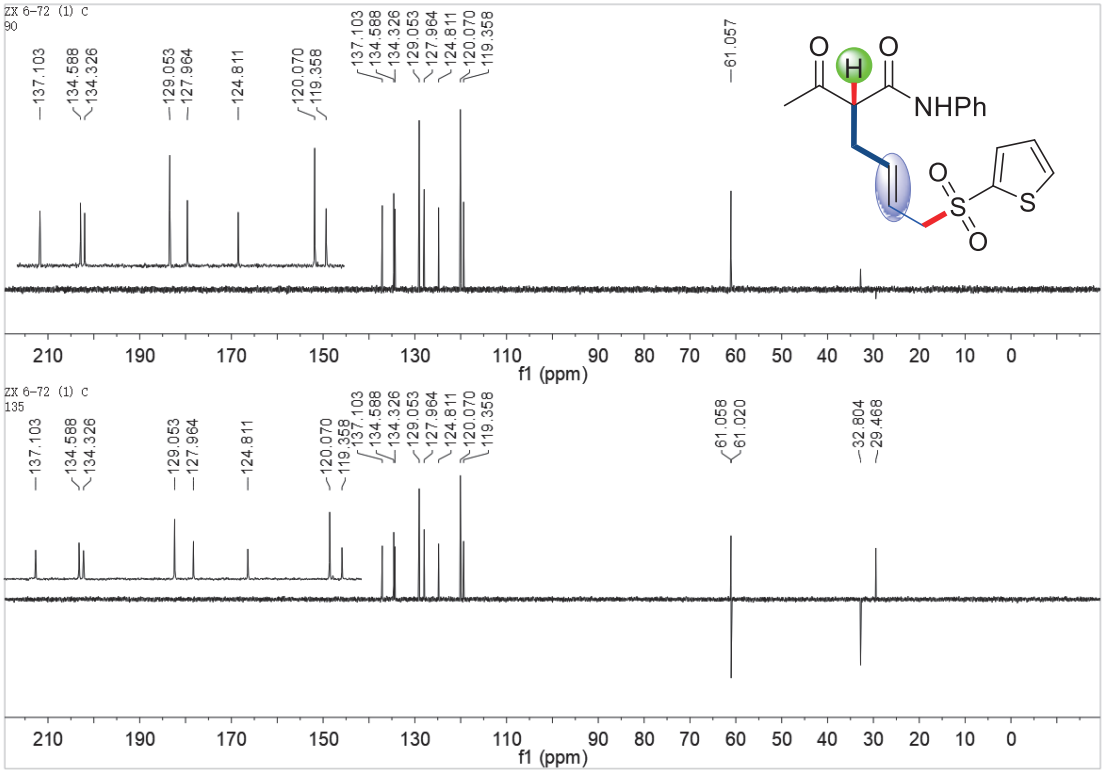
4v1, ^{1}H NMR



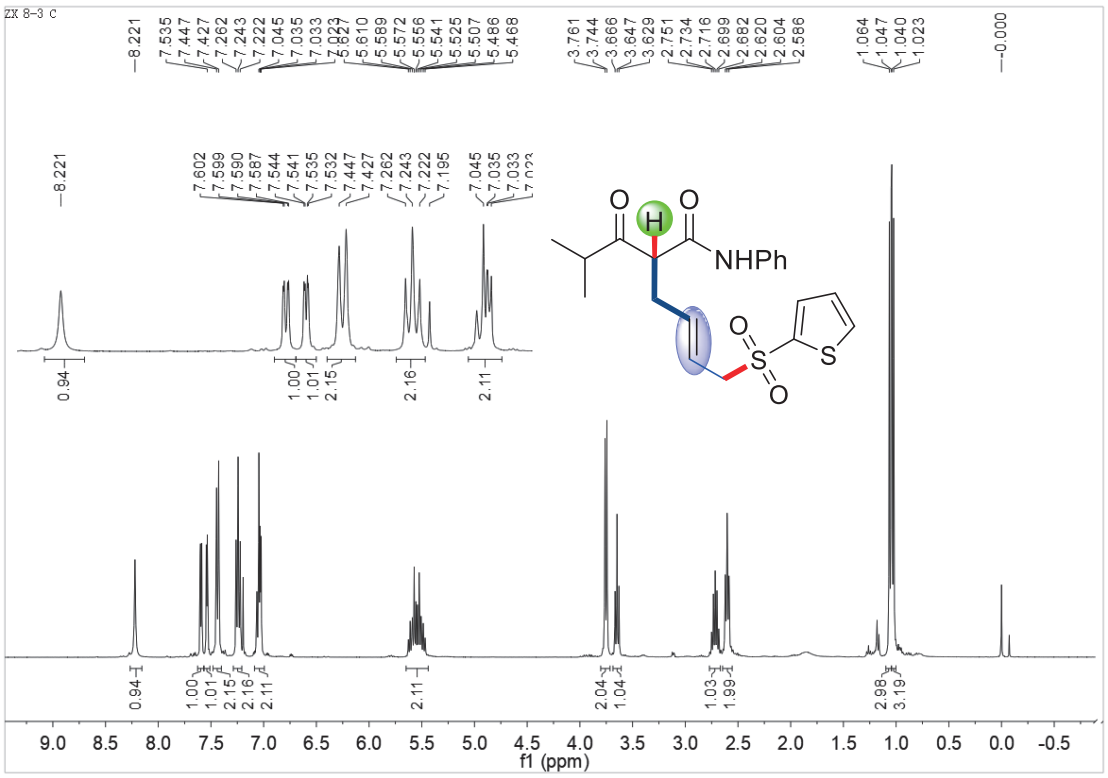
4v1, ^{13}C NMR



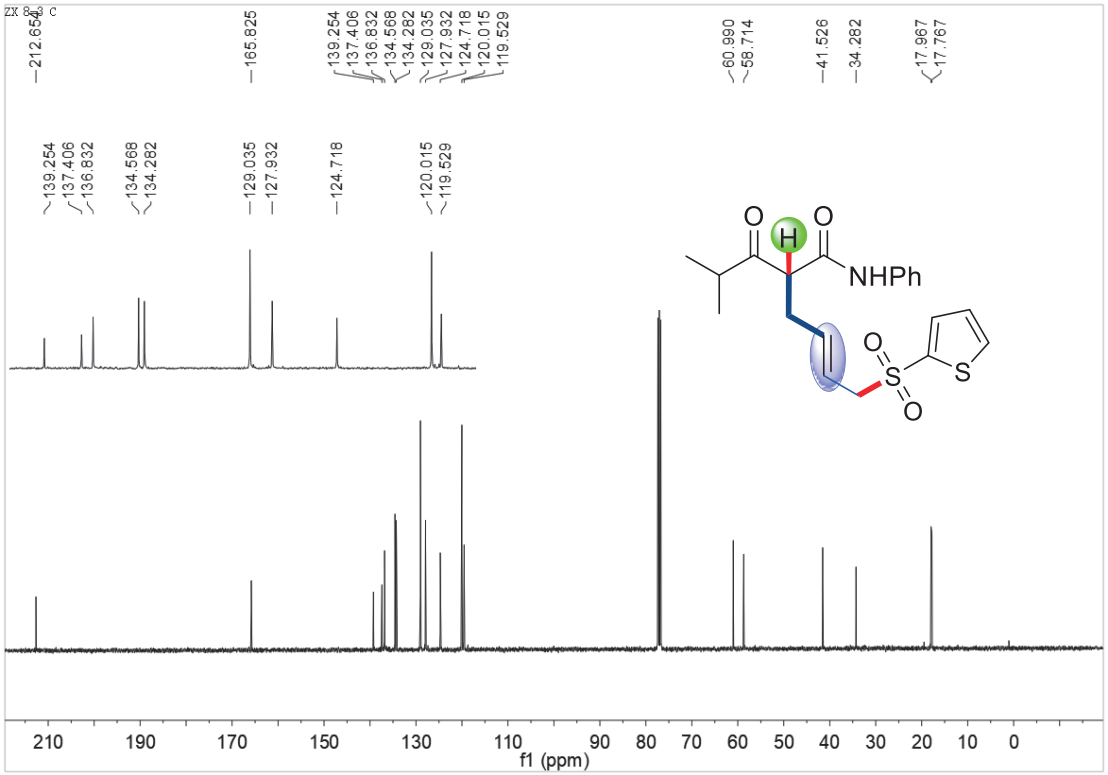
4v1, DEPT 90 and DEPT 135



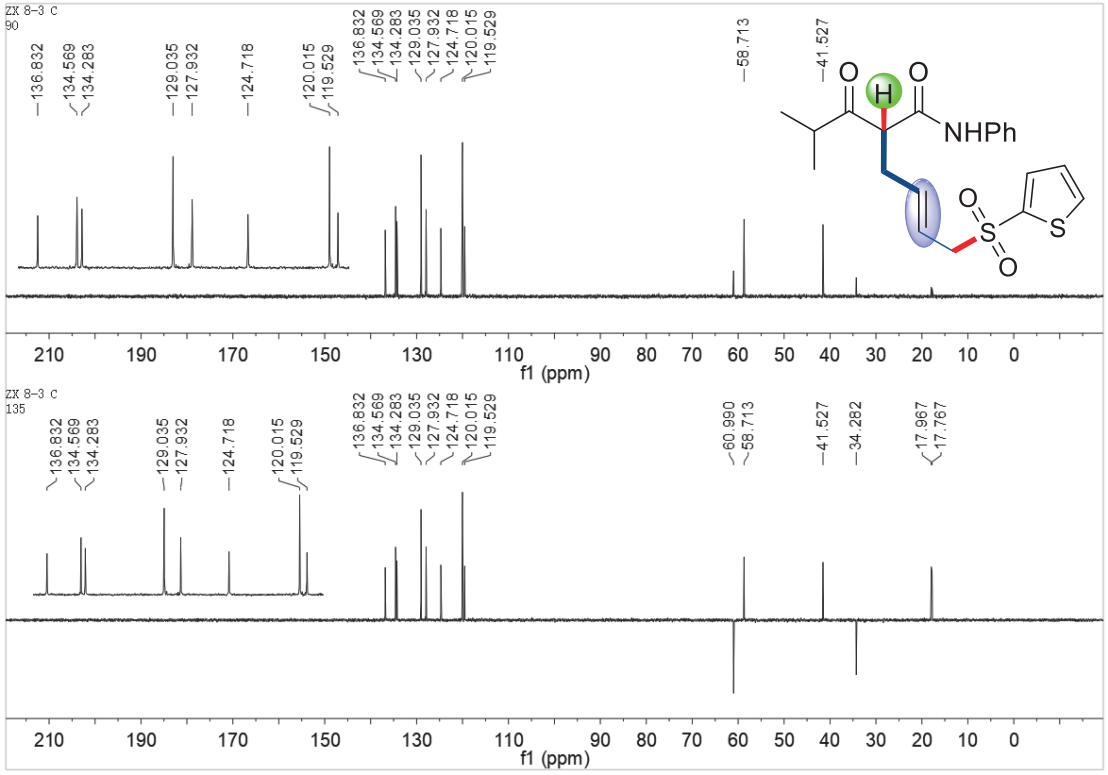
4v2, ^{1}H NMR



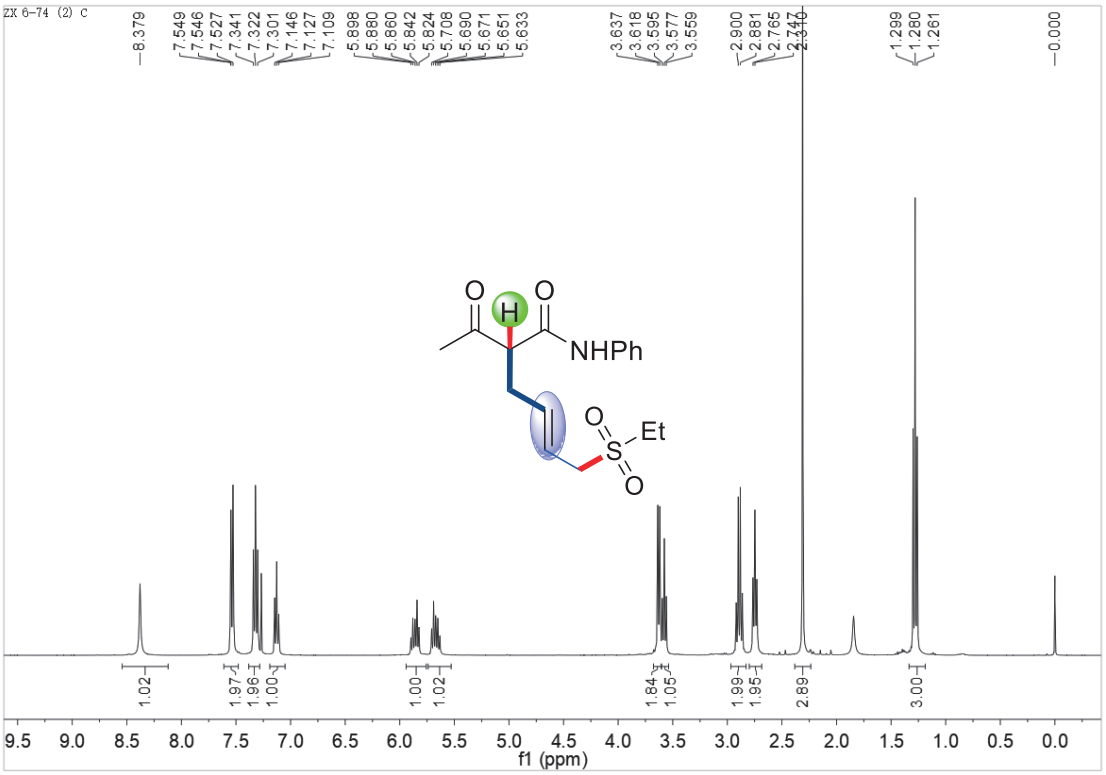
4v2, ^{13}C NMR



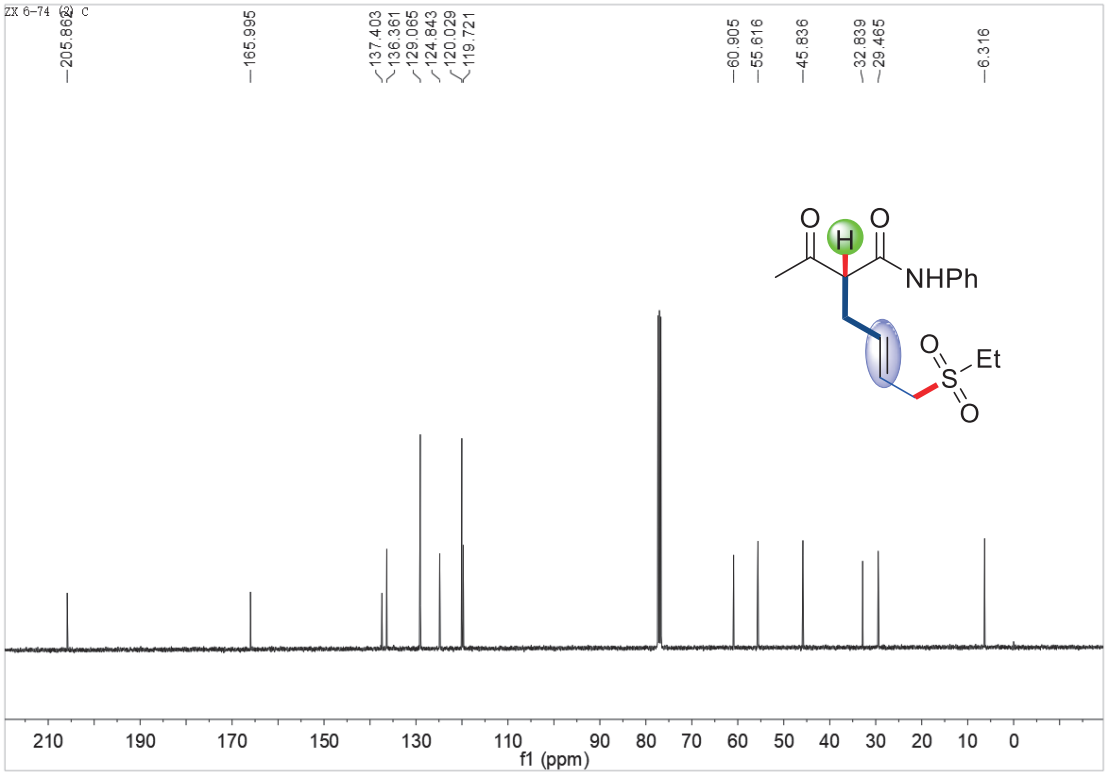
4v2, DEPT 90 and DEPT 135



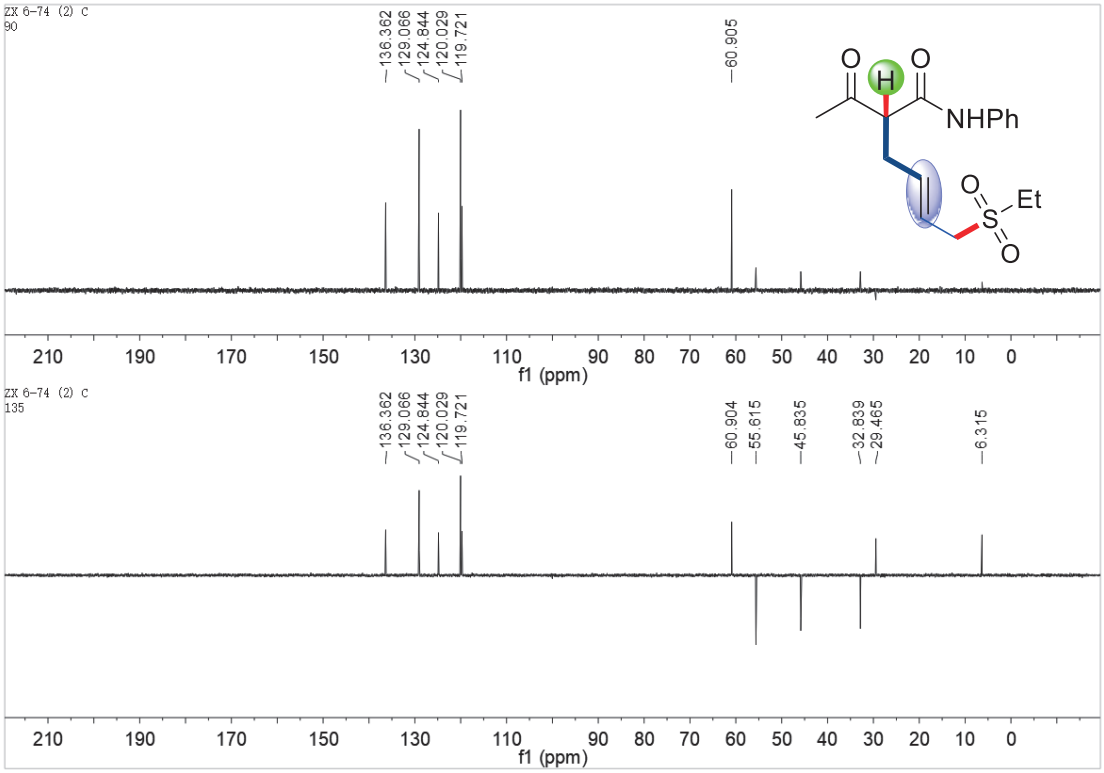
4w1, ^{1}H NMR



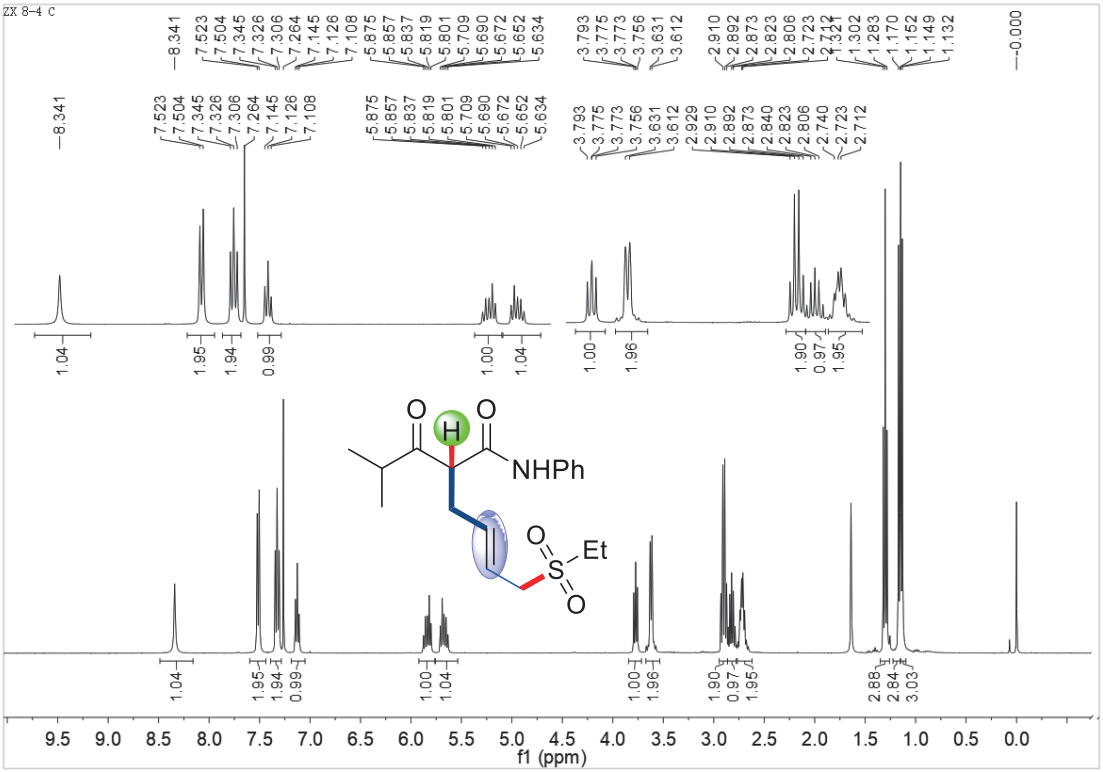
4w1, ^{13}C NMR



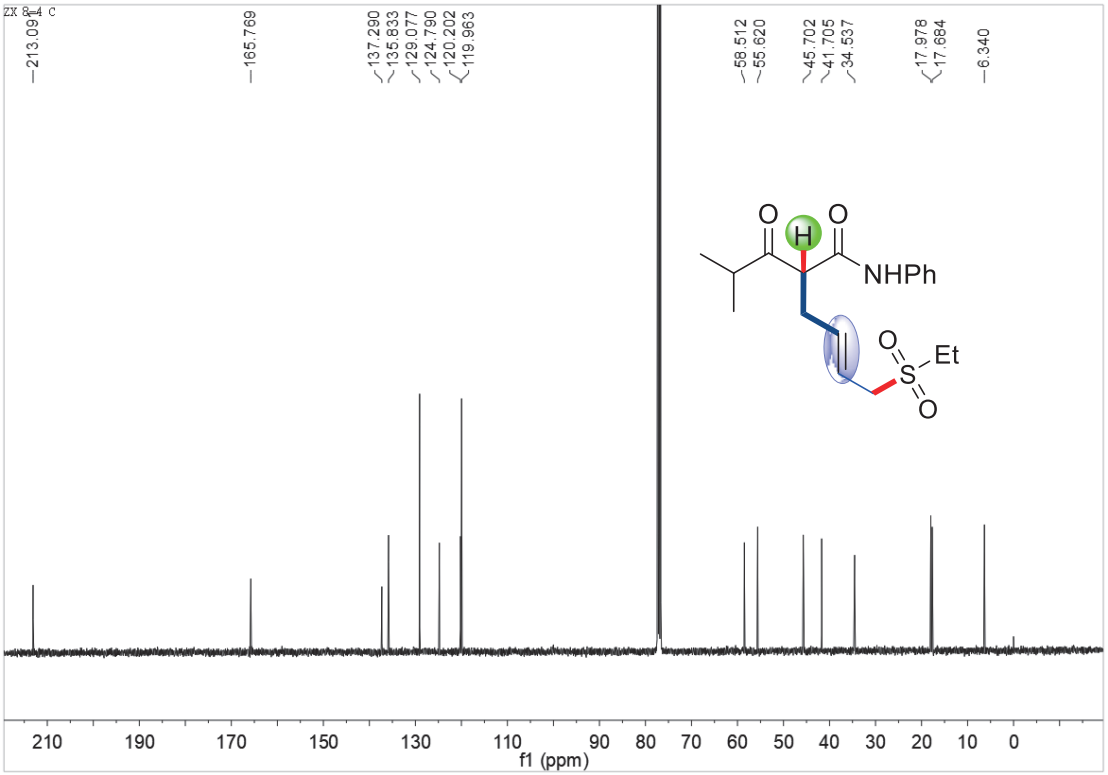
4w1, DEPT 90 and DEPT 135



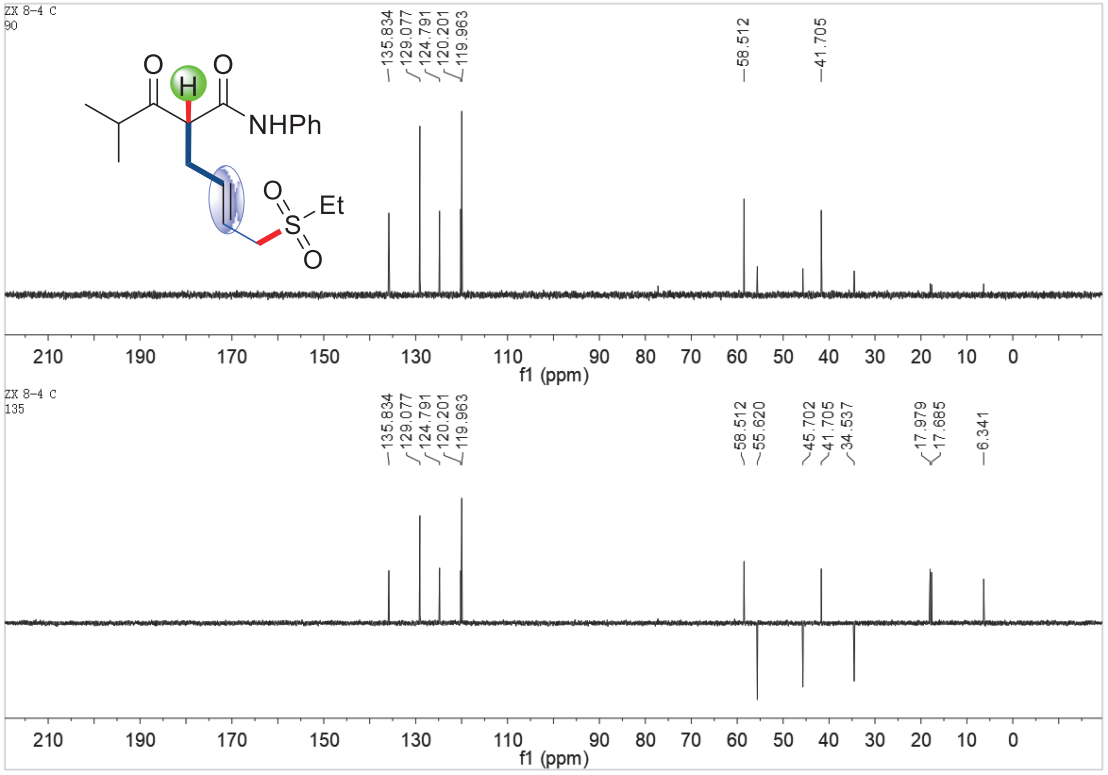
4w2, ^{1}H NMR



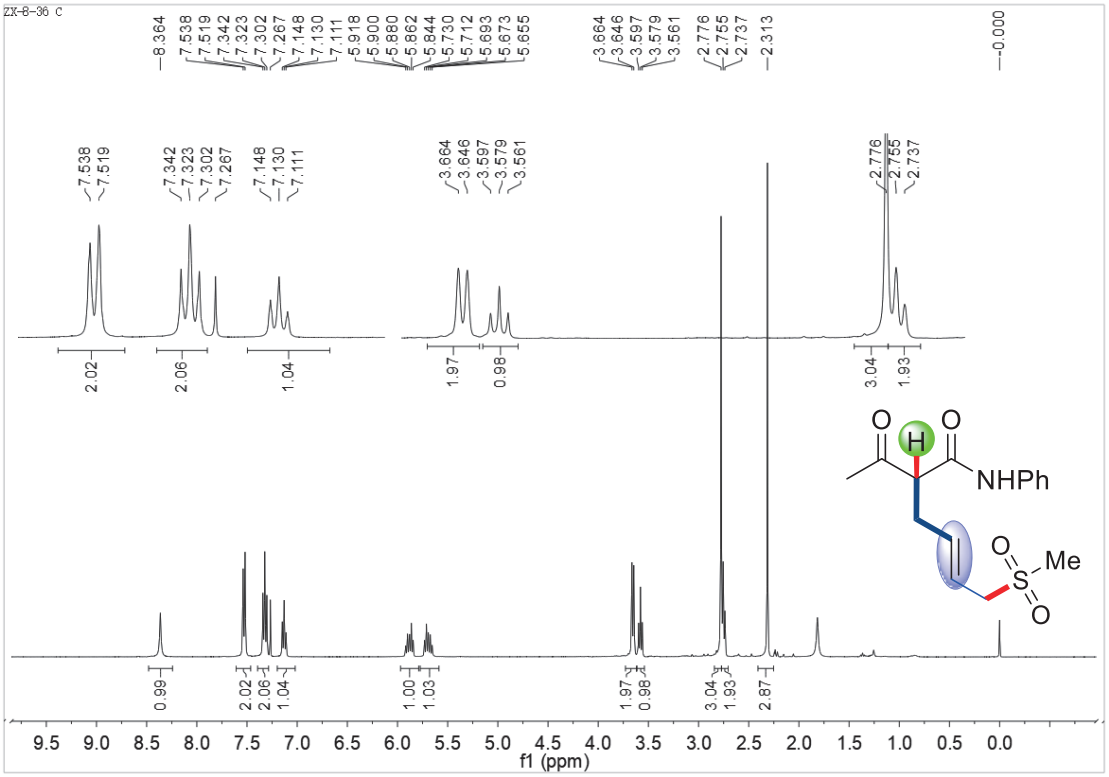
4w2, ^{13}C NMR



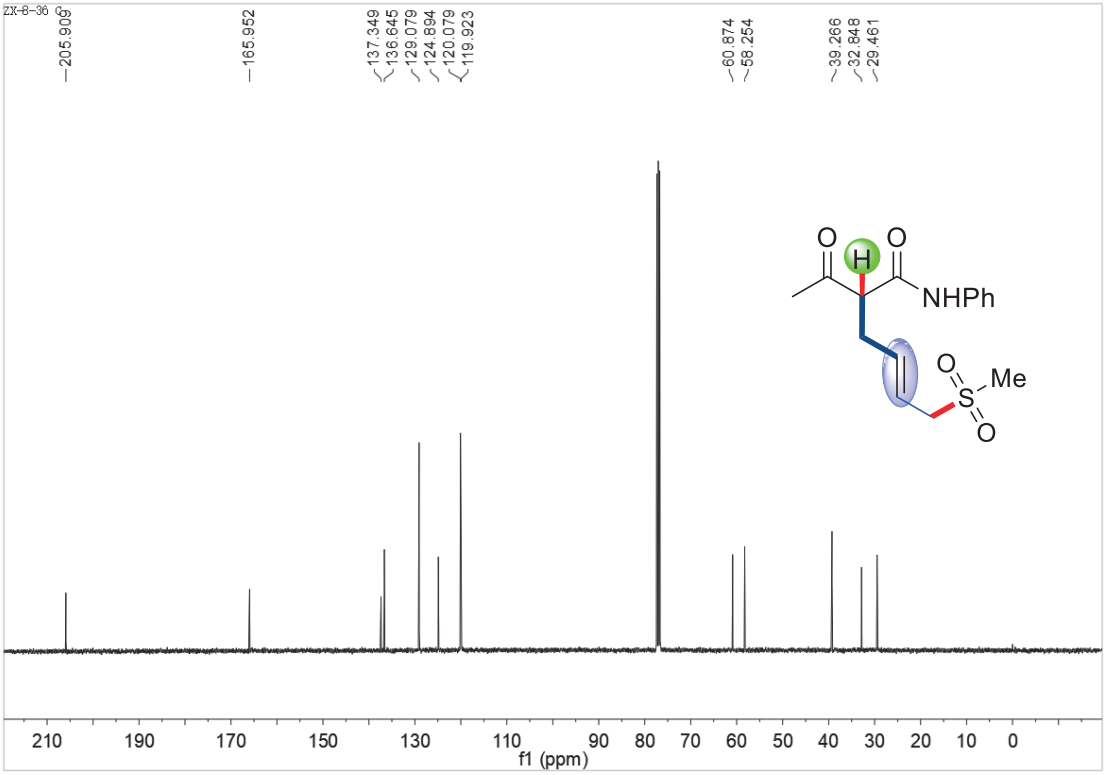
4w2, DEPT 90 and DEPT 135



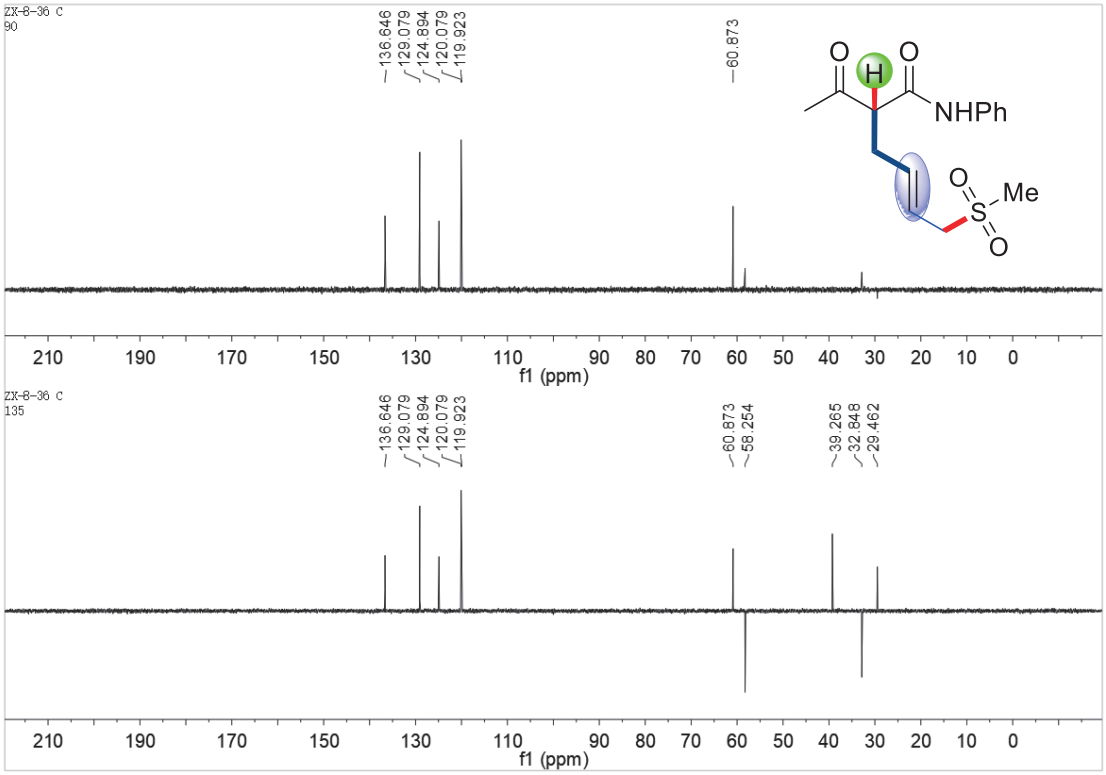
4x, ^{1}H NMR



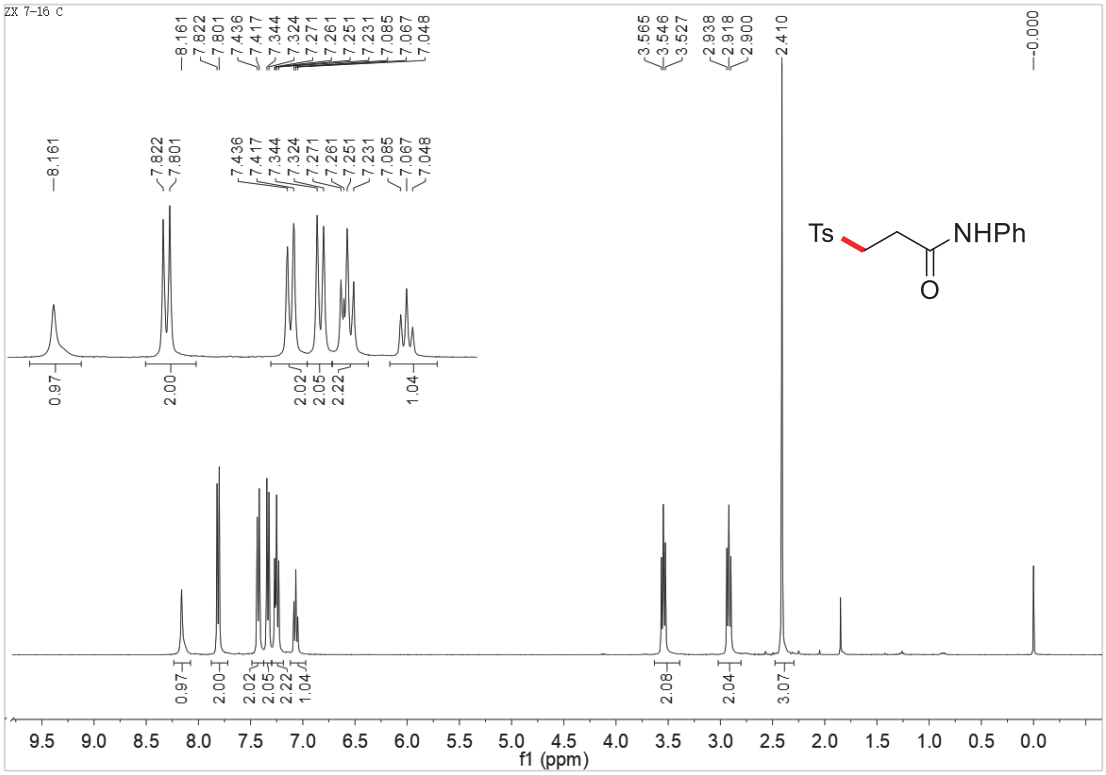
4x, ^{13}C NMR



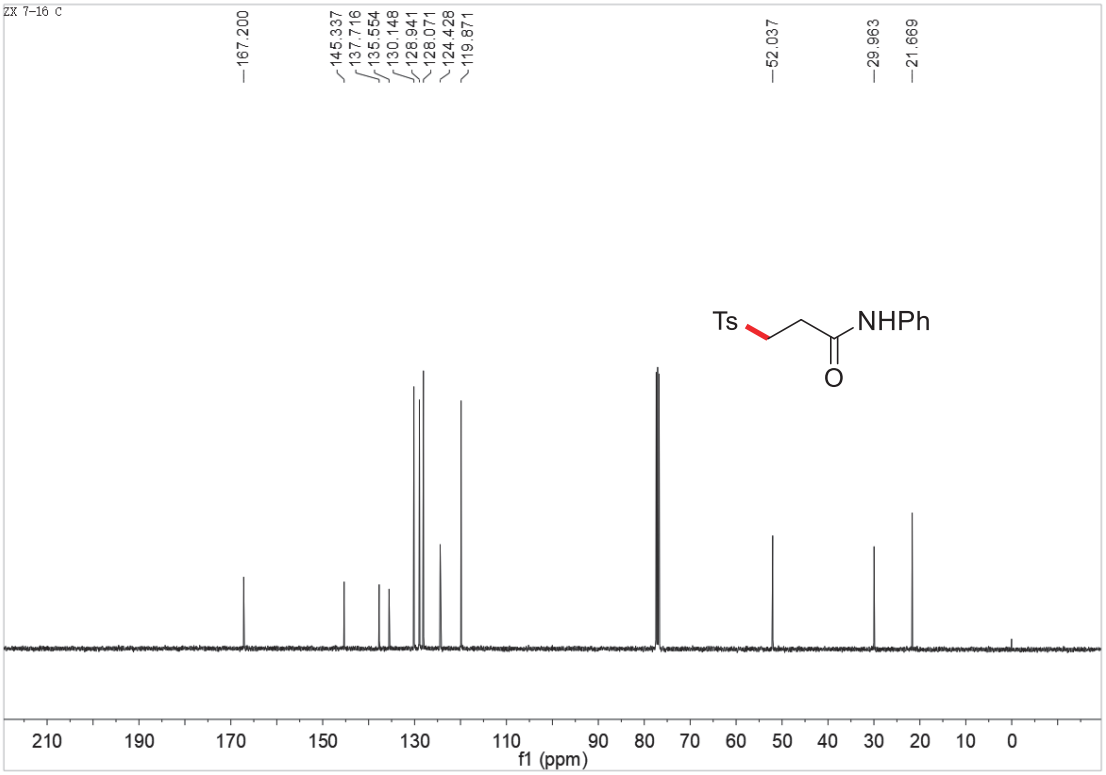
4x, DEPT 90 and DEPT 135



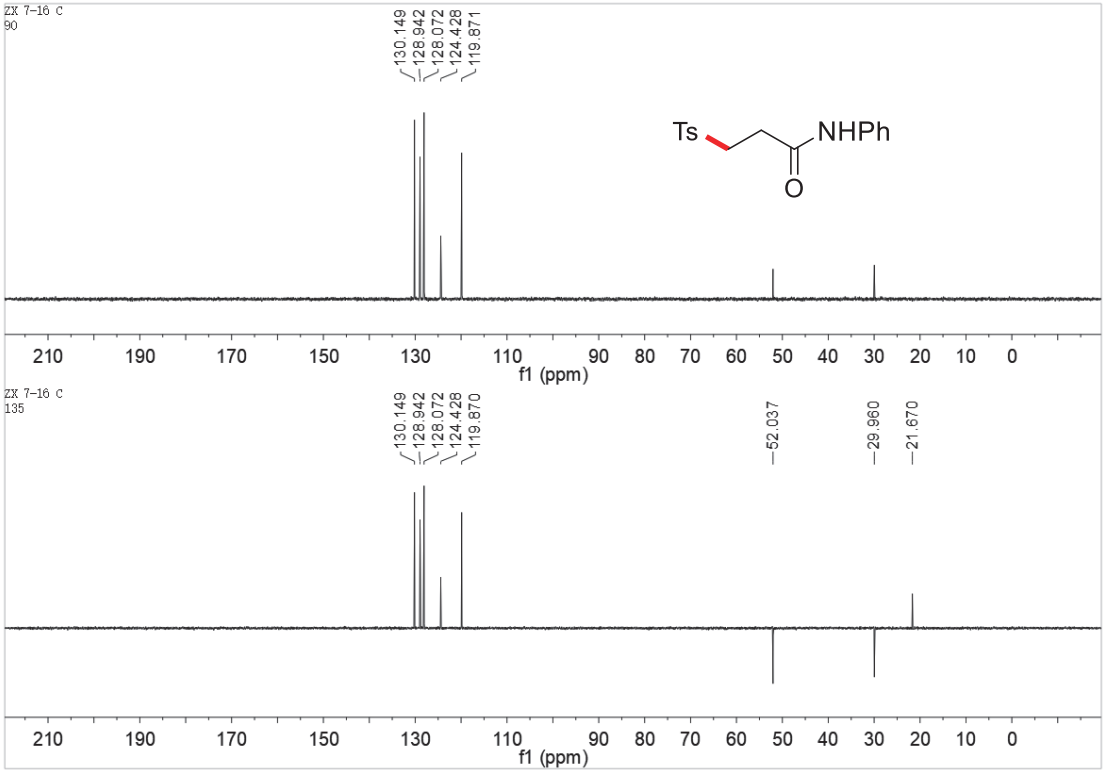
4y, ^{1}H NMR



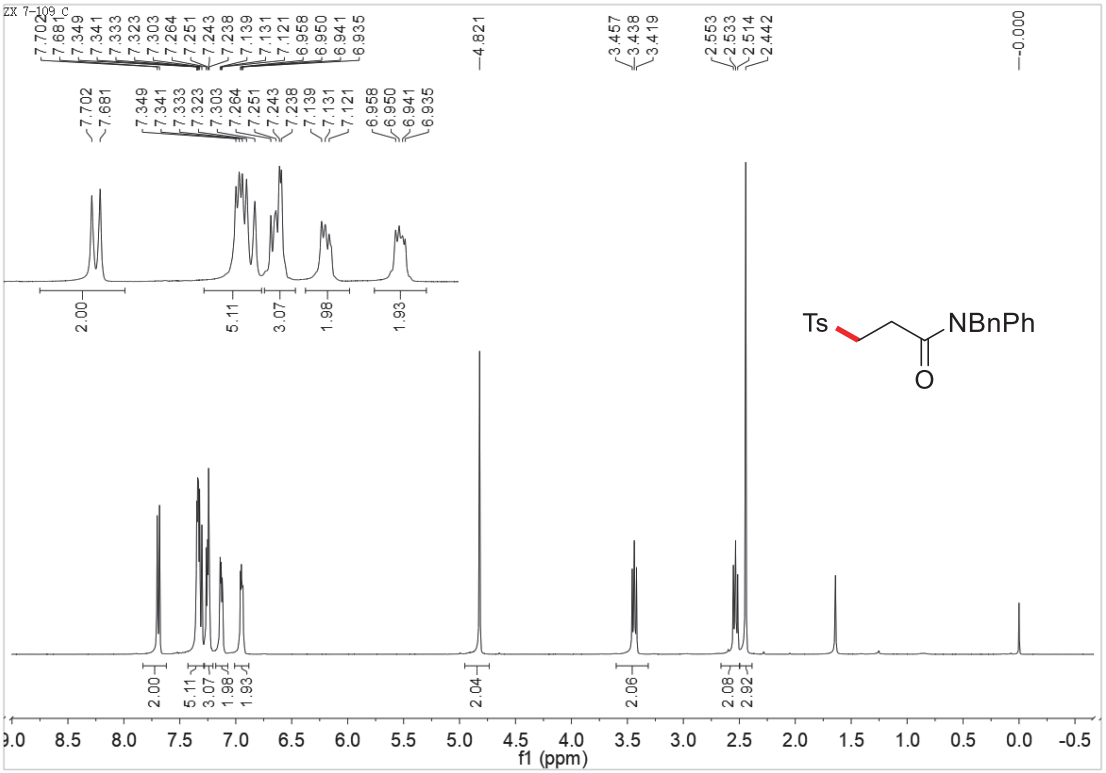
4y, ^{13}C NMR



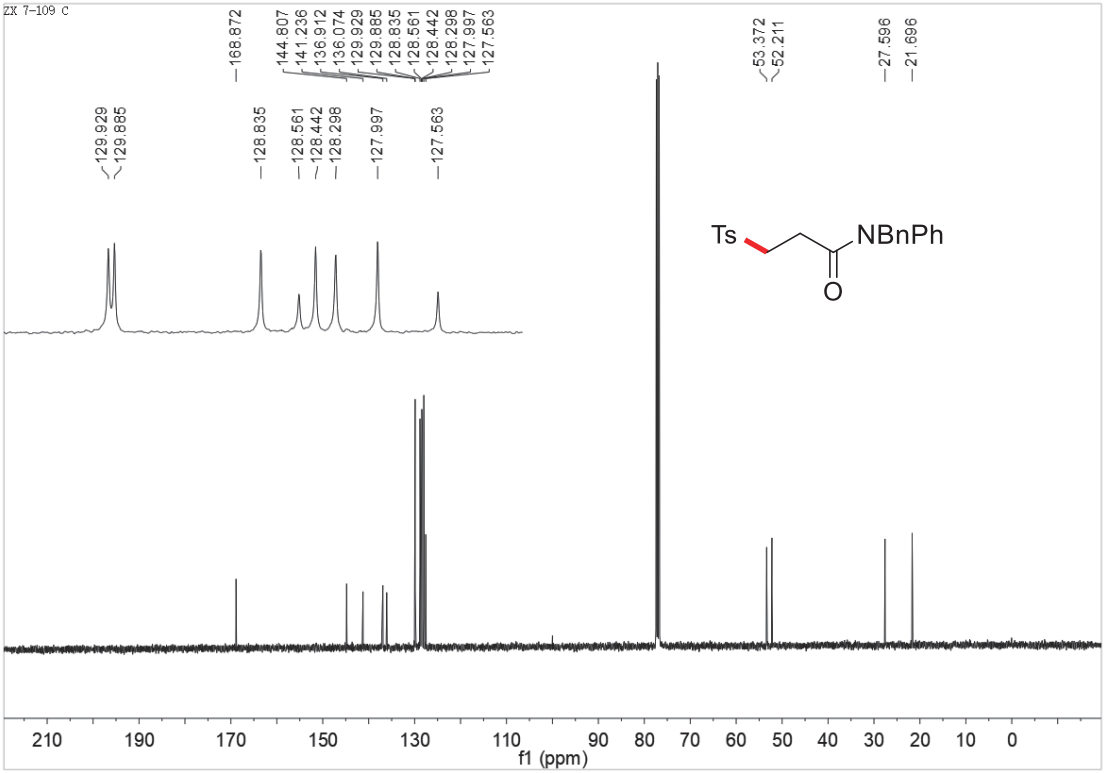
4y, DEPT 90 and DEPT 135



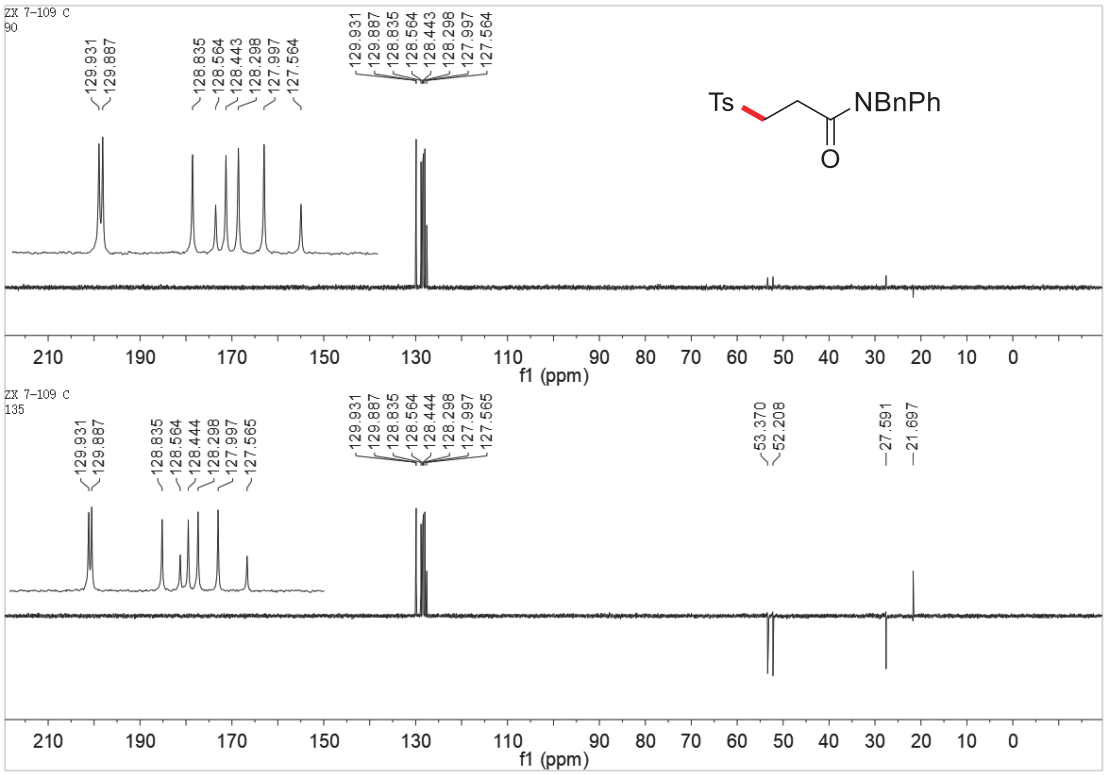
4z, ^{1}H NMR



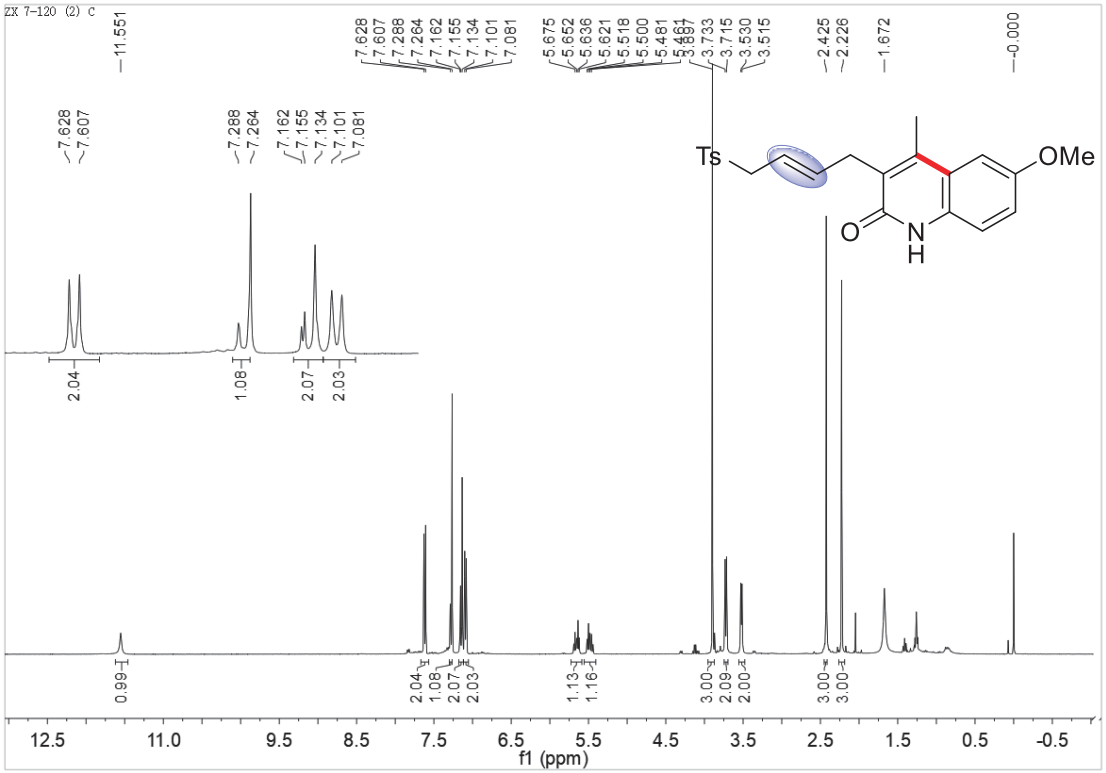
4z, ^{13}C NMR



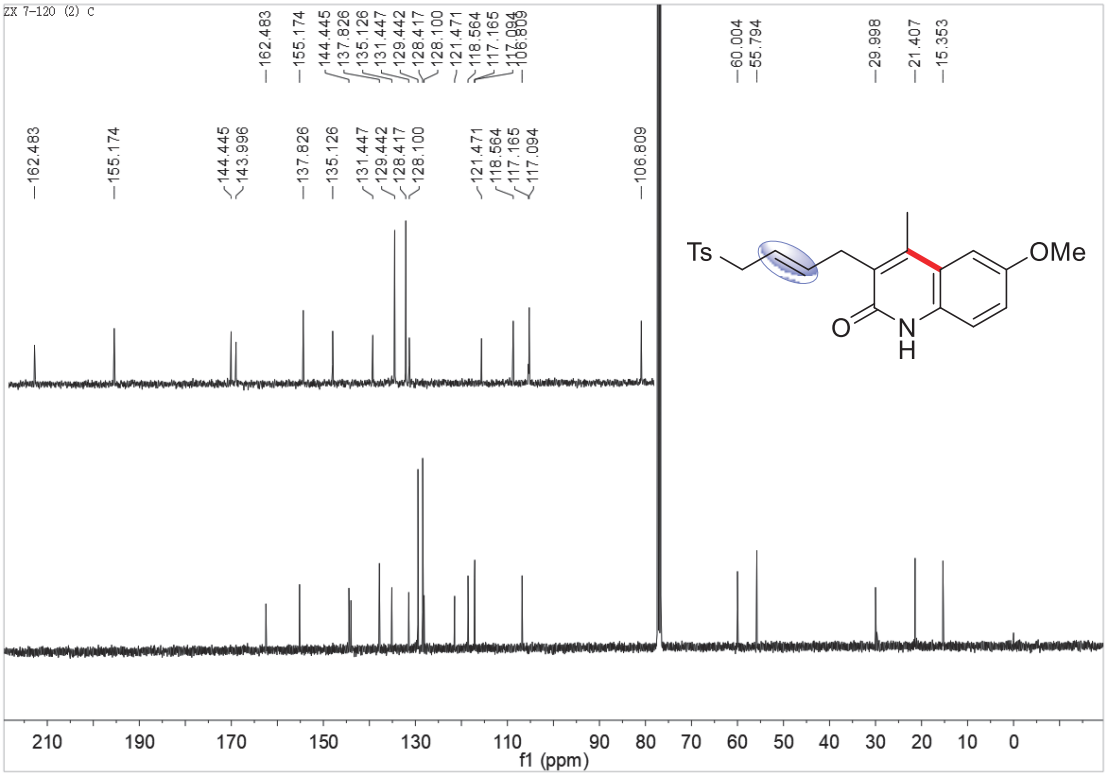
4z, DEPT 90 and DEPT 135



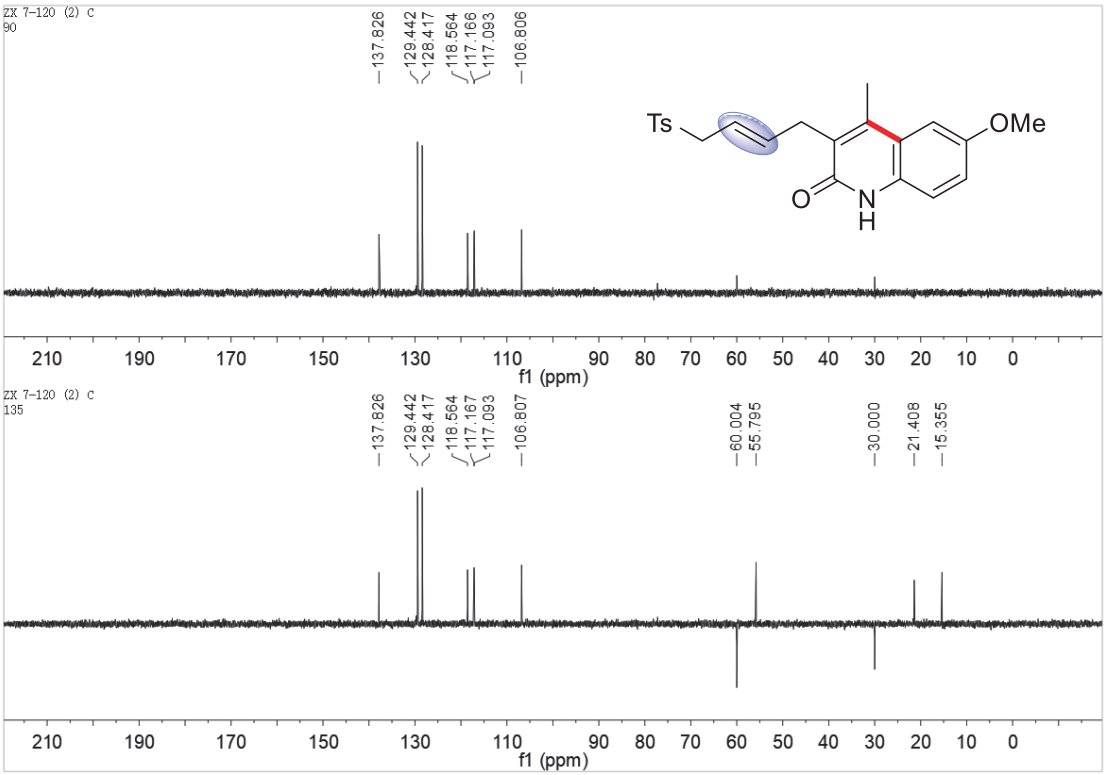
5a, ^{1}H NMR



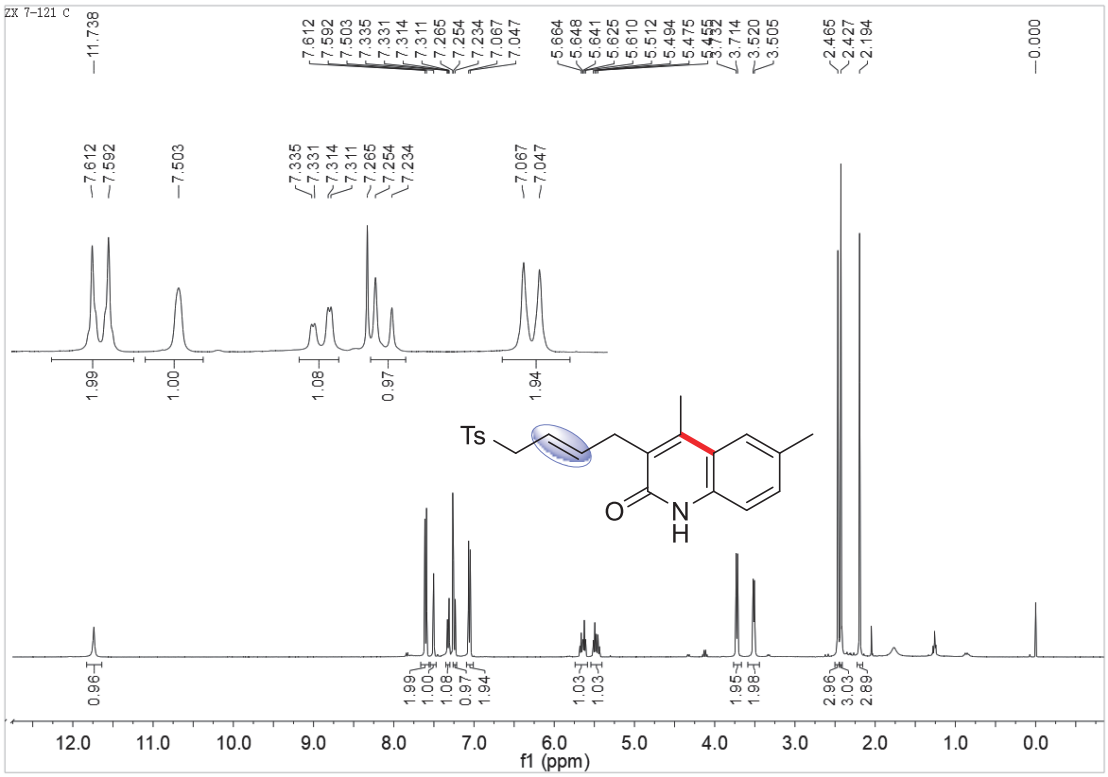
5a, ^{13}C NMR



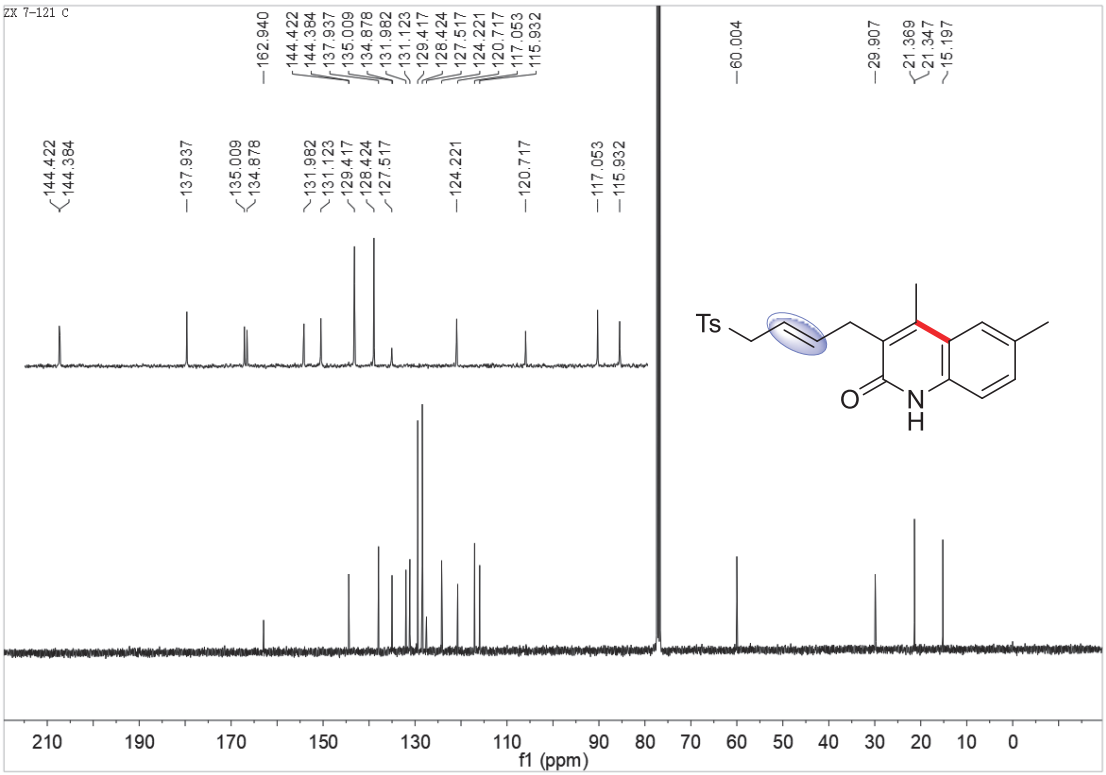
5a, DEPT 90 and DEPT 135



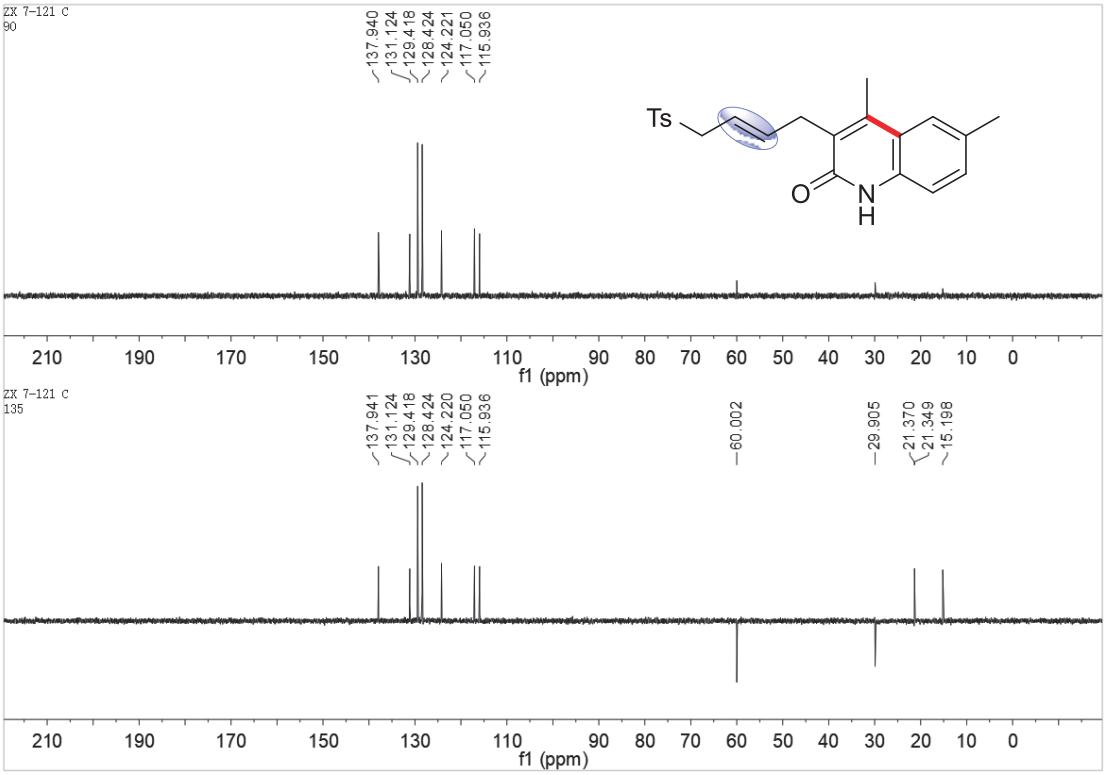
5b, ^{1}H NMR



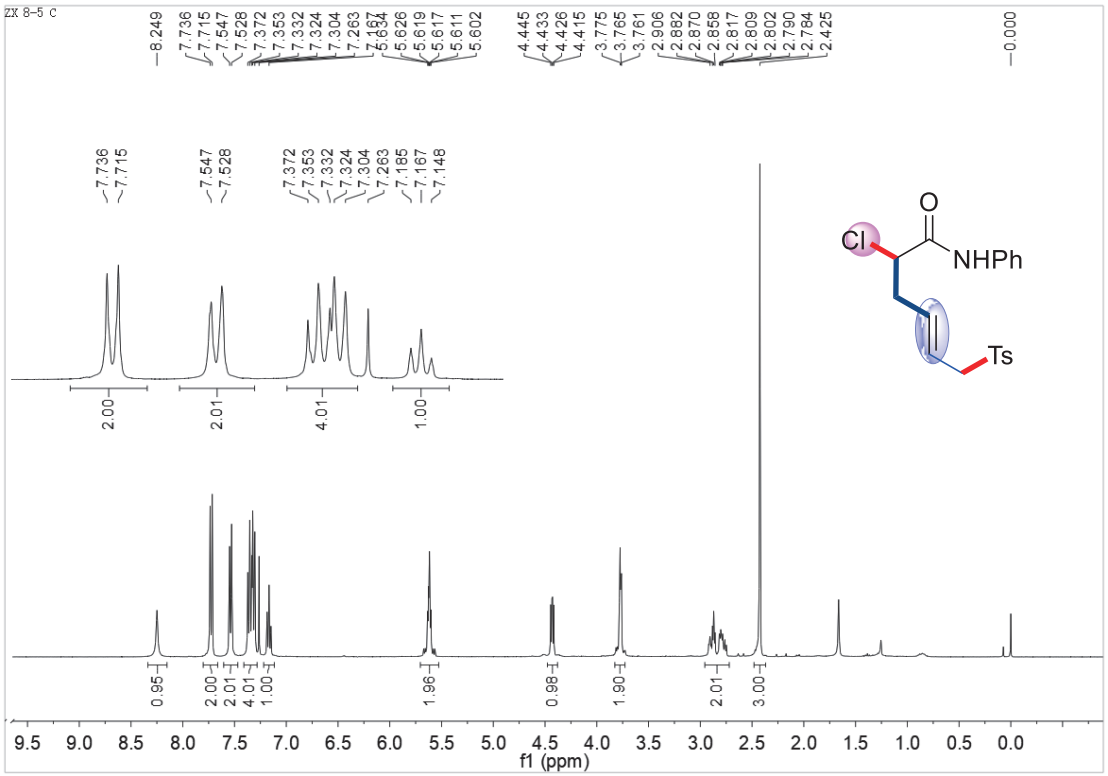
5b, ^{13}C NMR



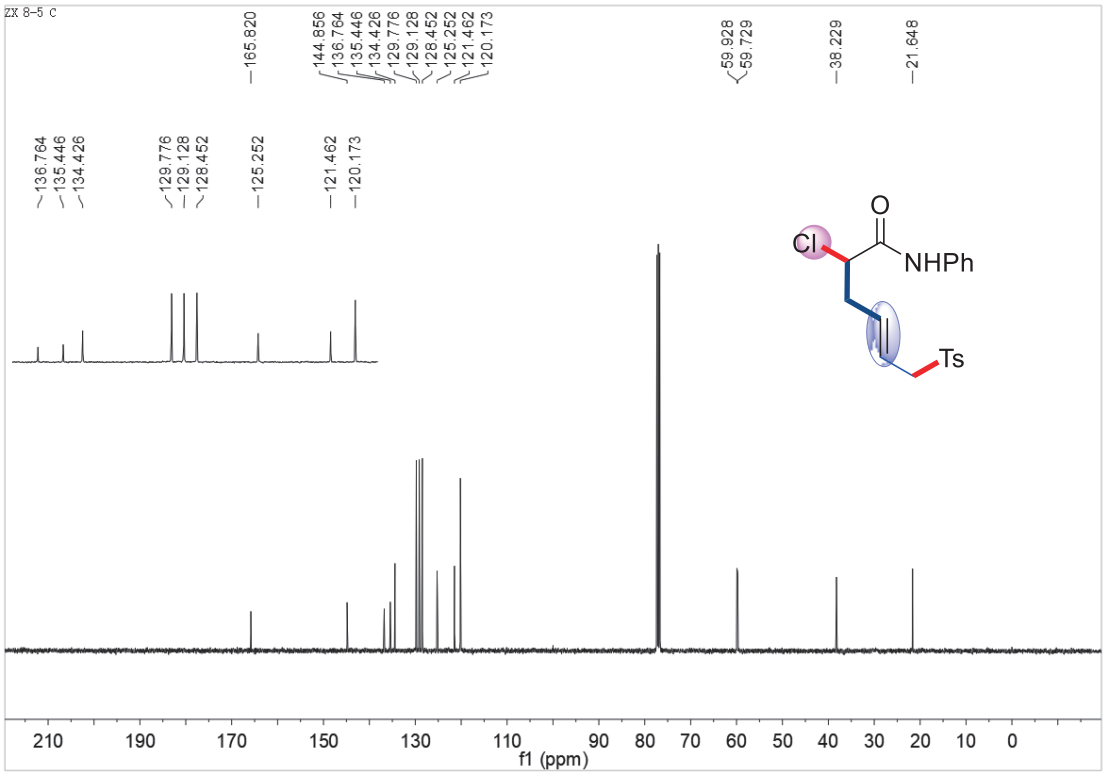
5b, DEPT 90 and DEPT 135



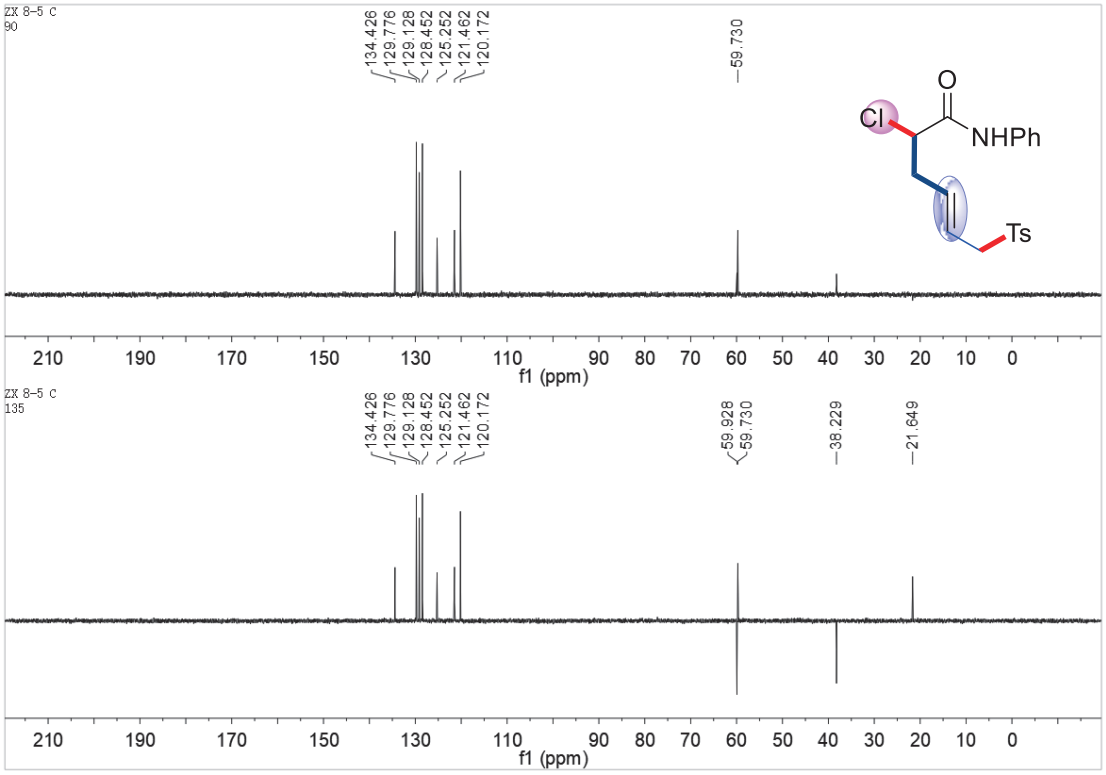
6, ^{1}H NMR



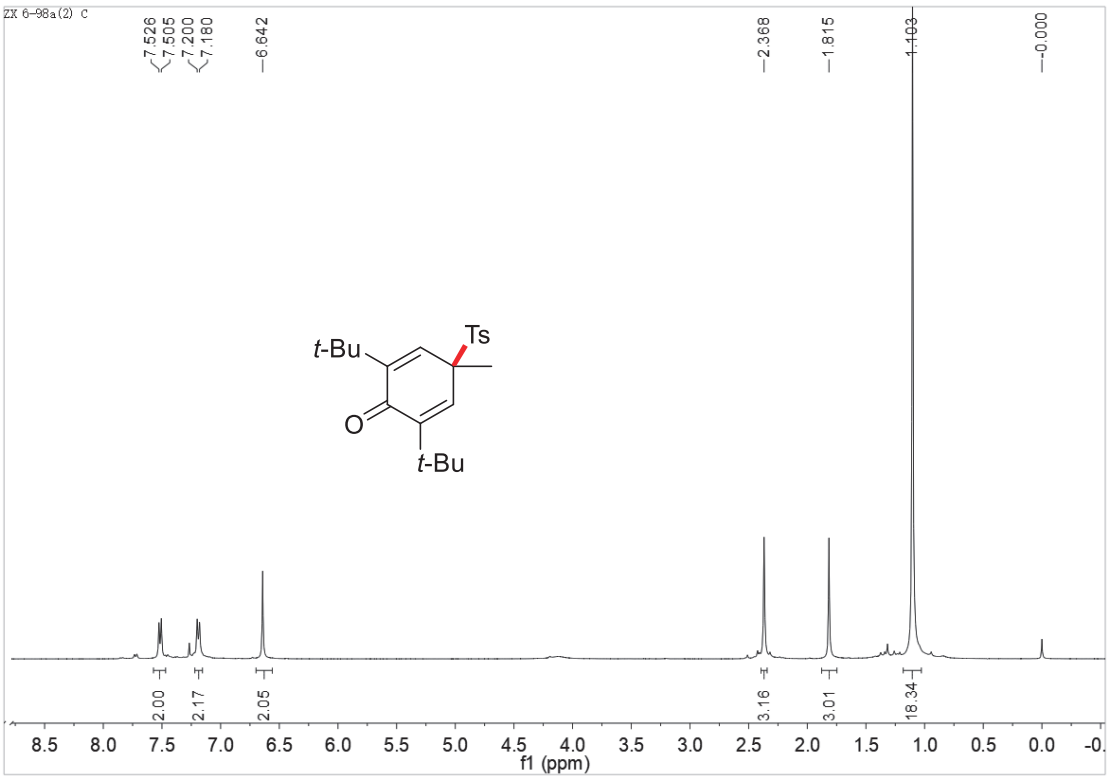
6, ^{13}C NMR



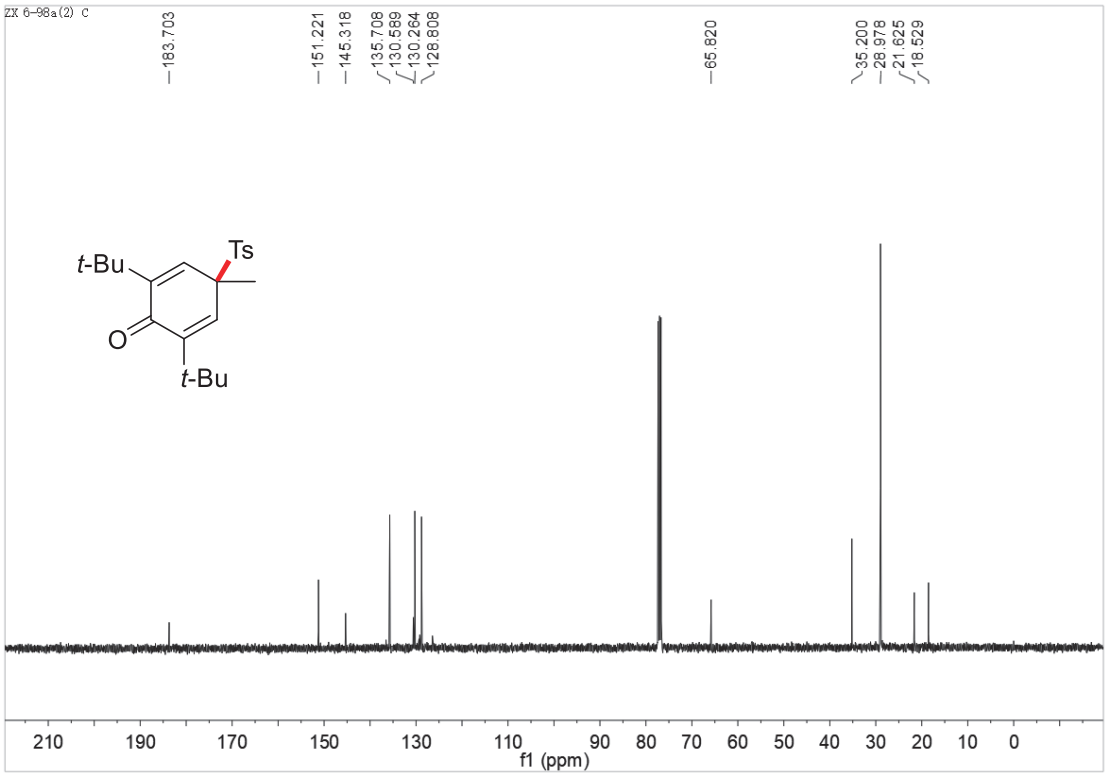
6, DEPT 90 and DEPT 135



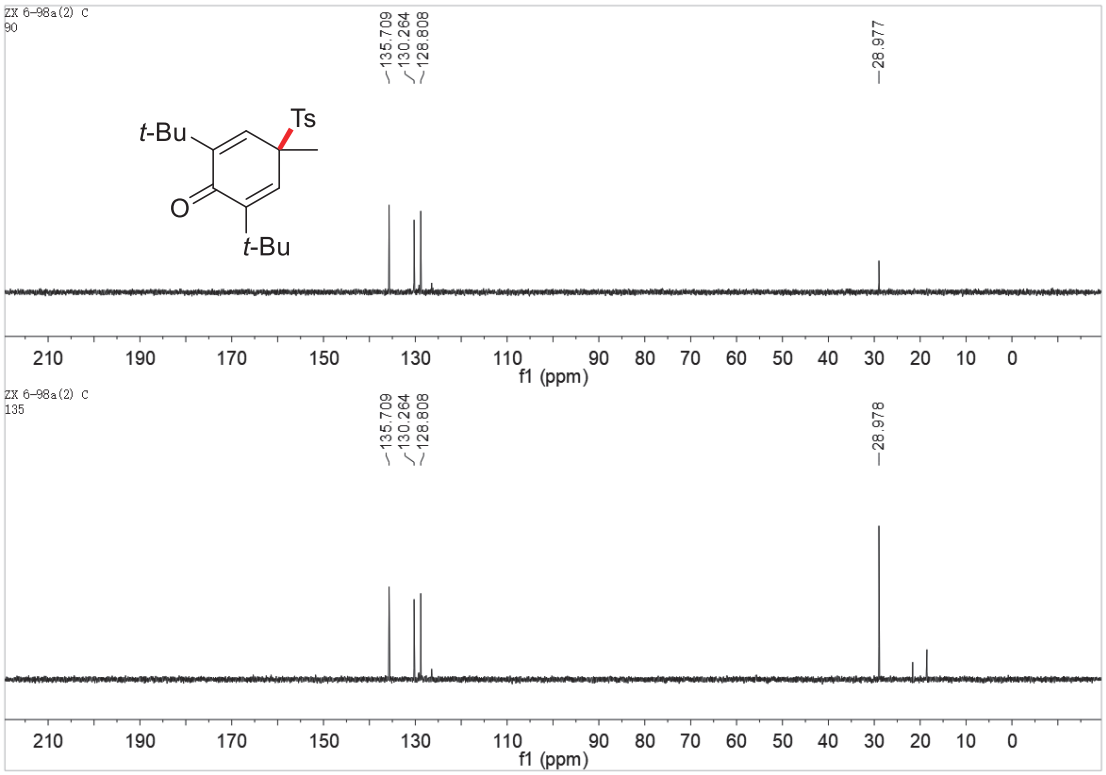
7, ^{1}H NMR



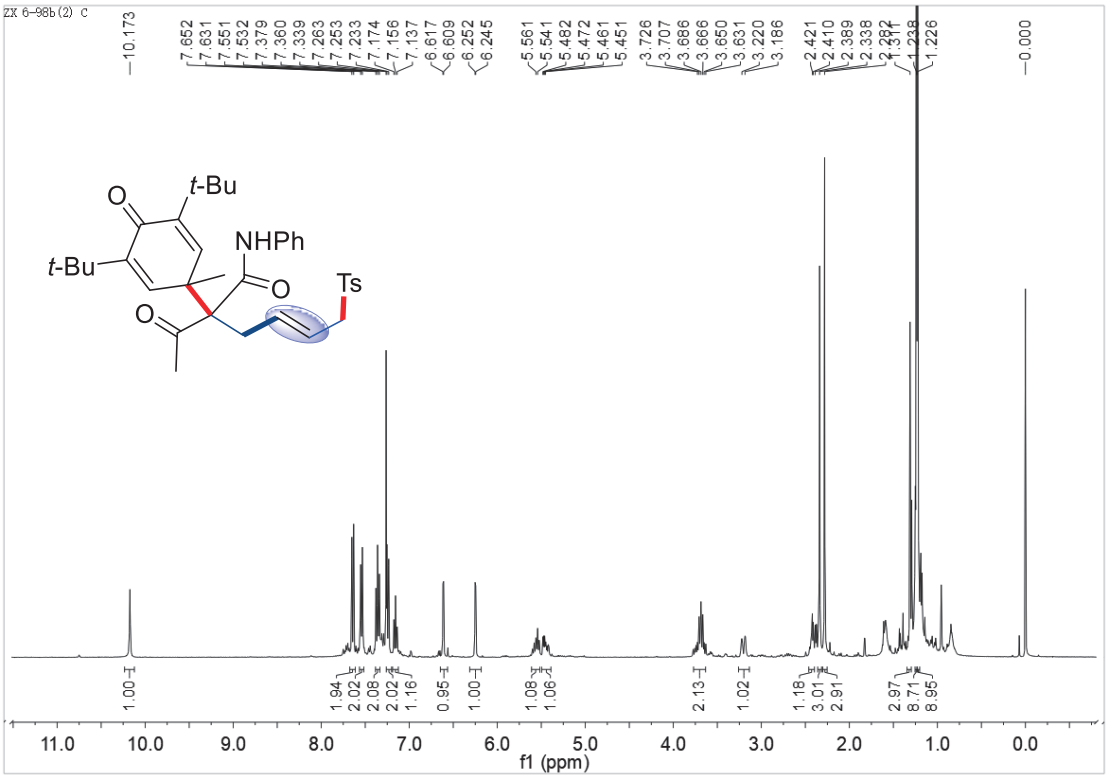
7, ^{13}C NMR



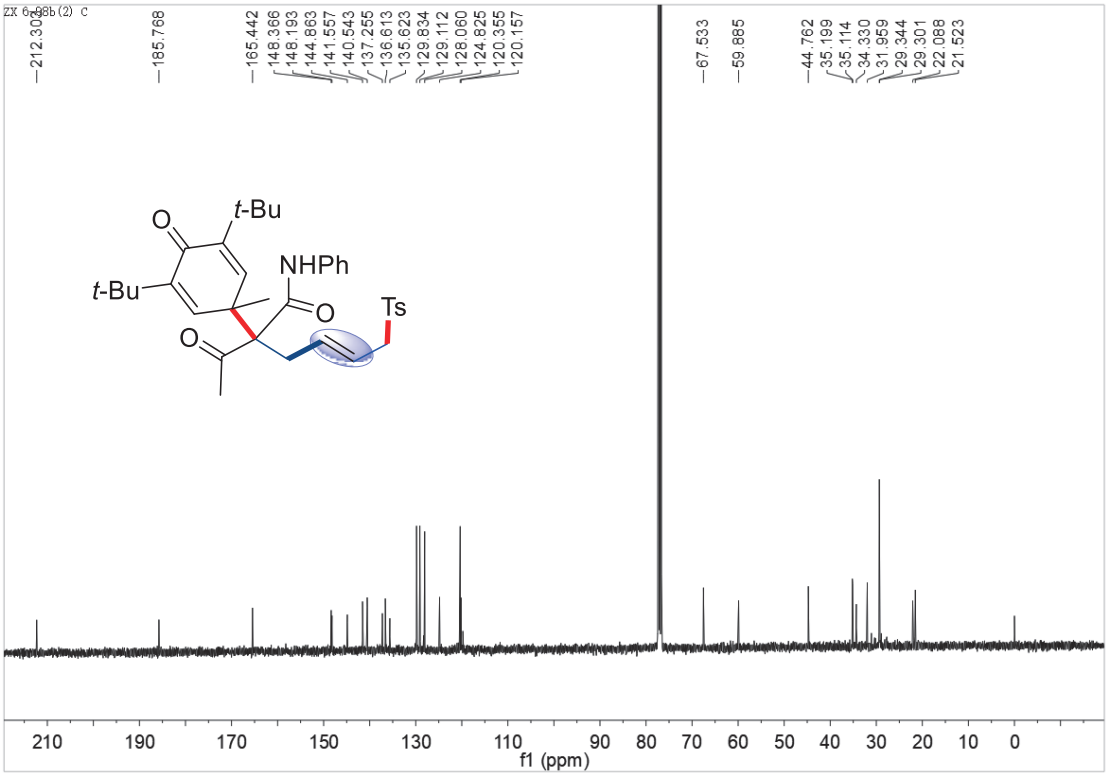
7, DEPT 90 and DEPT 135



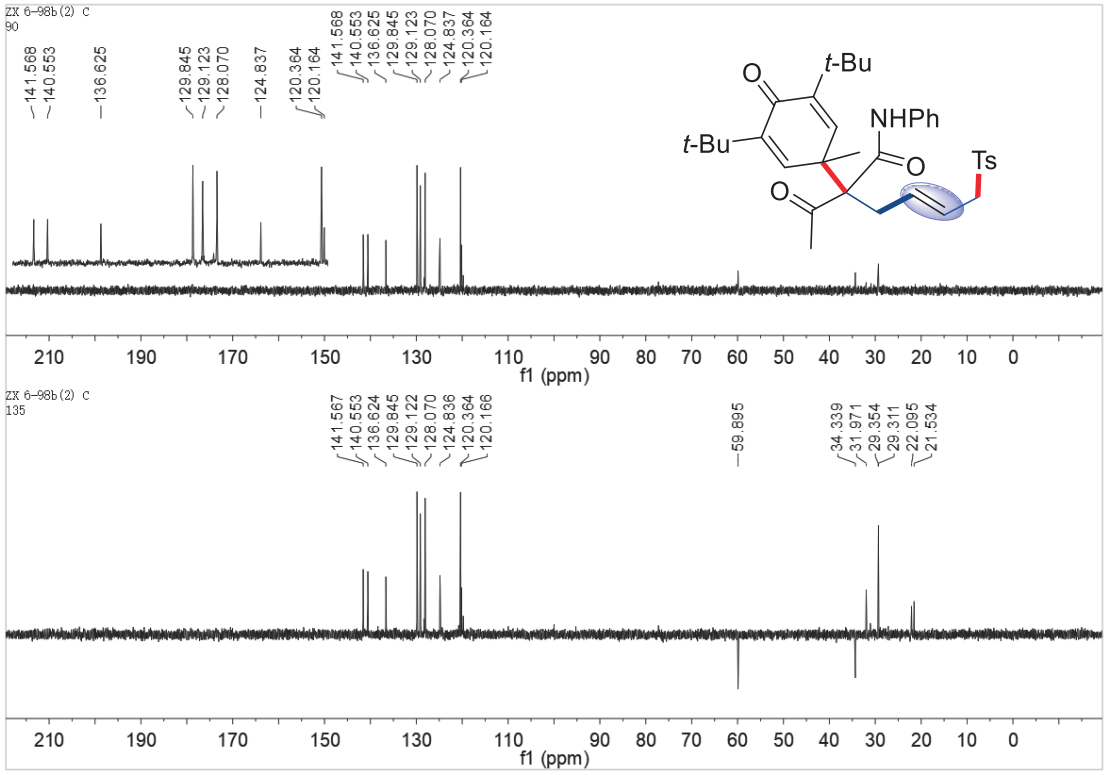
8, ^{1}H NMR



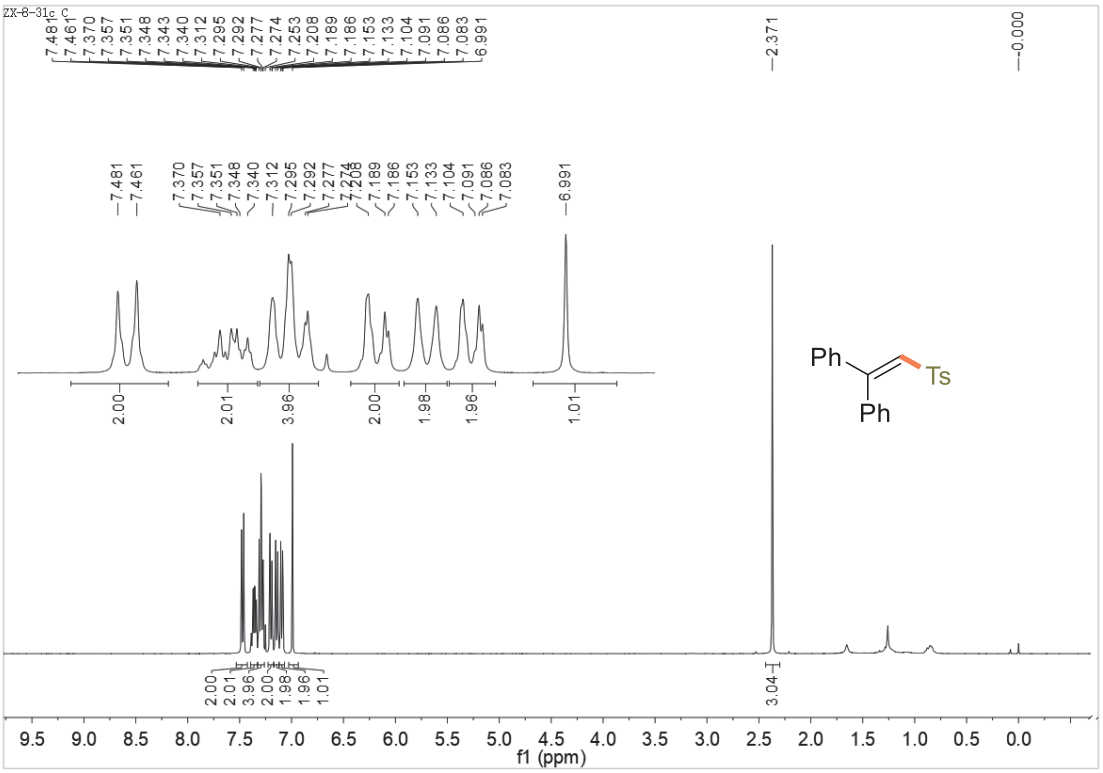
8, ^{13}C NMR



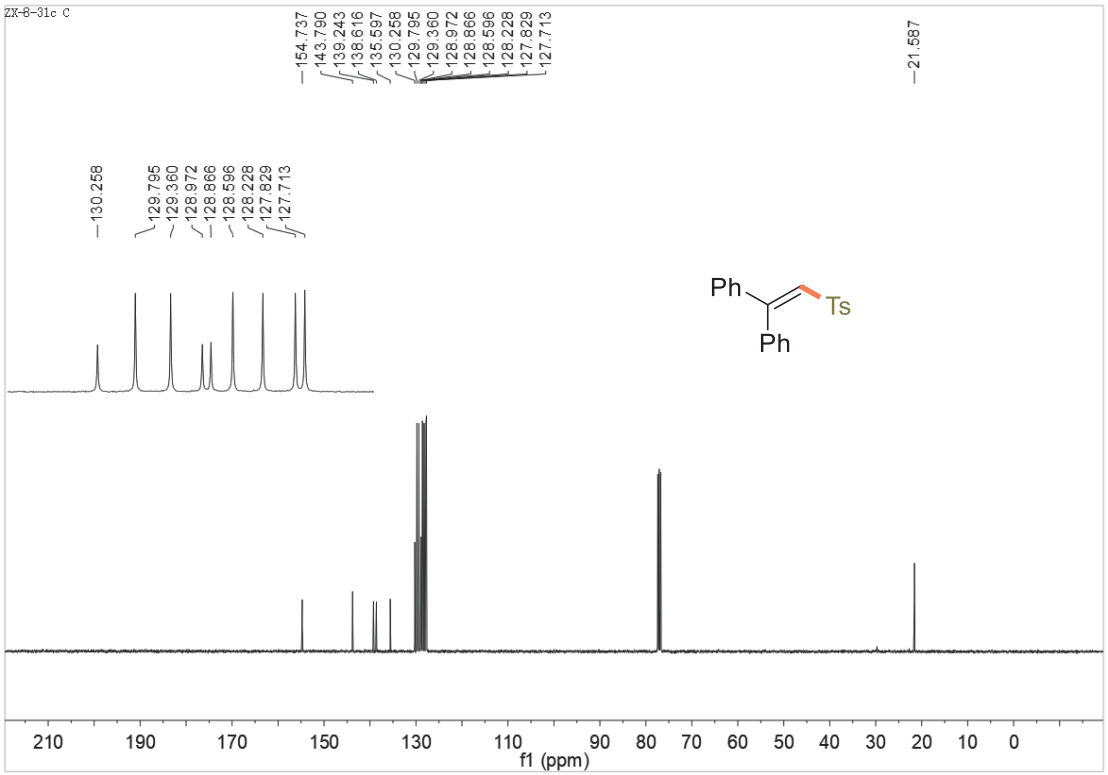
8, DEPT 90 and DEPT 135



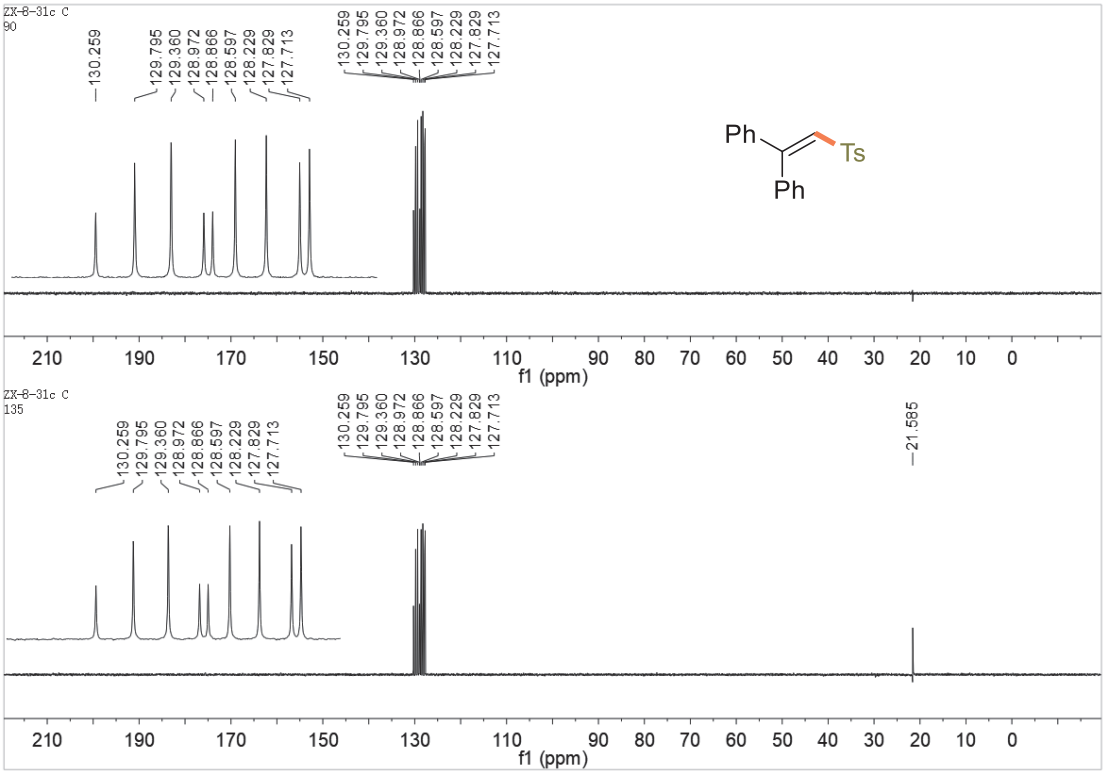
9, ^{1}H NMR



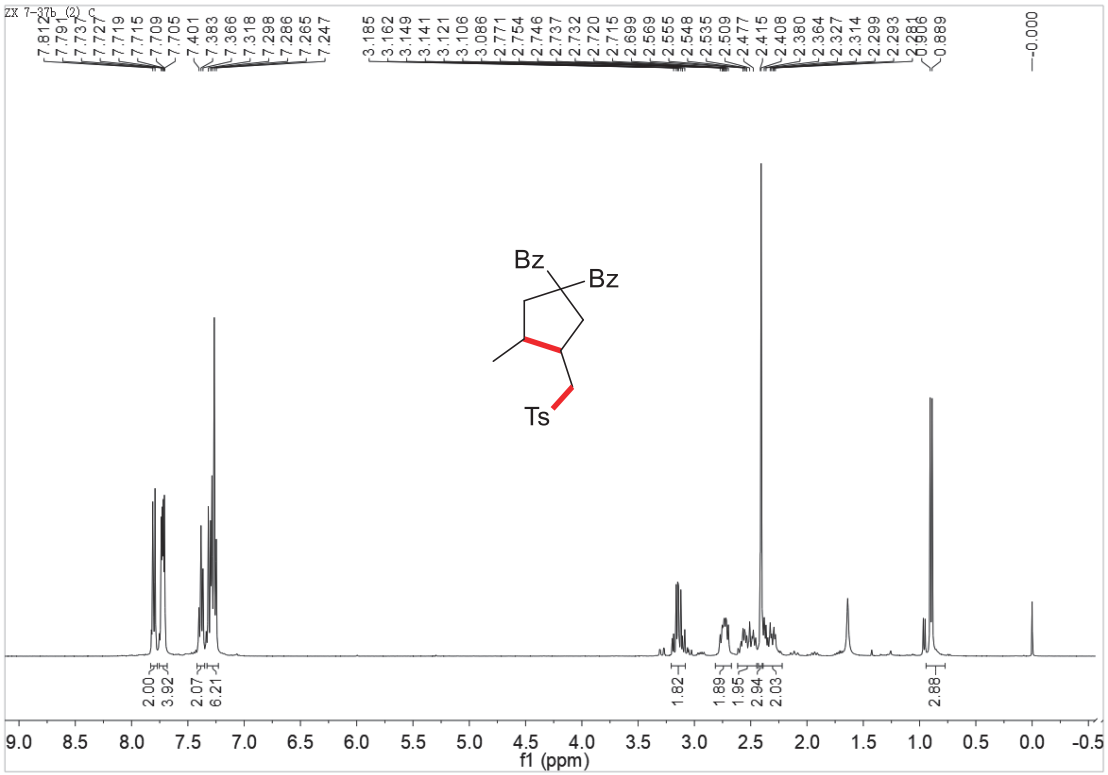
9, ^{13}C NMR



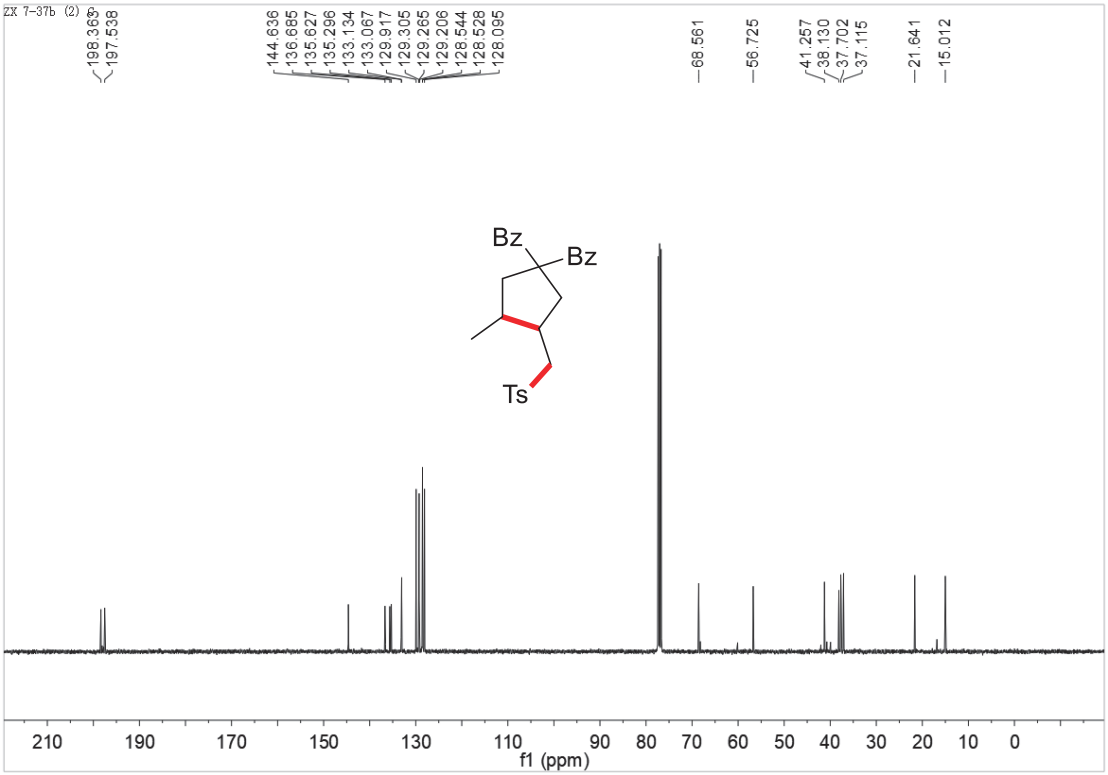
9, DEPT 90 and DEPT 135



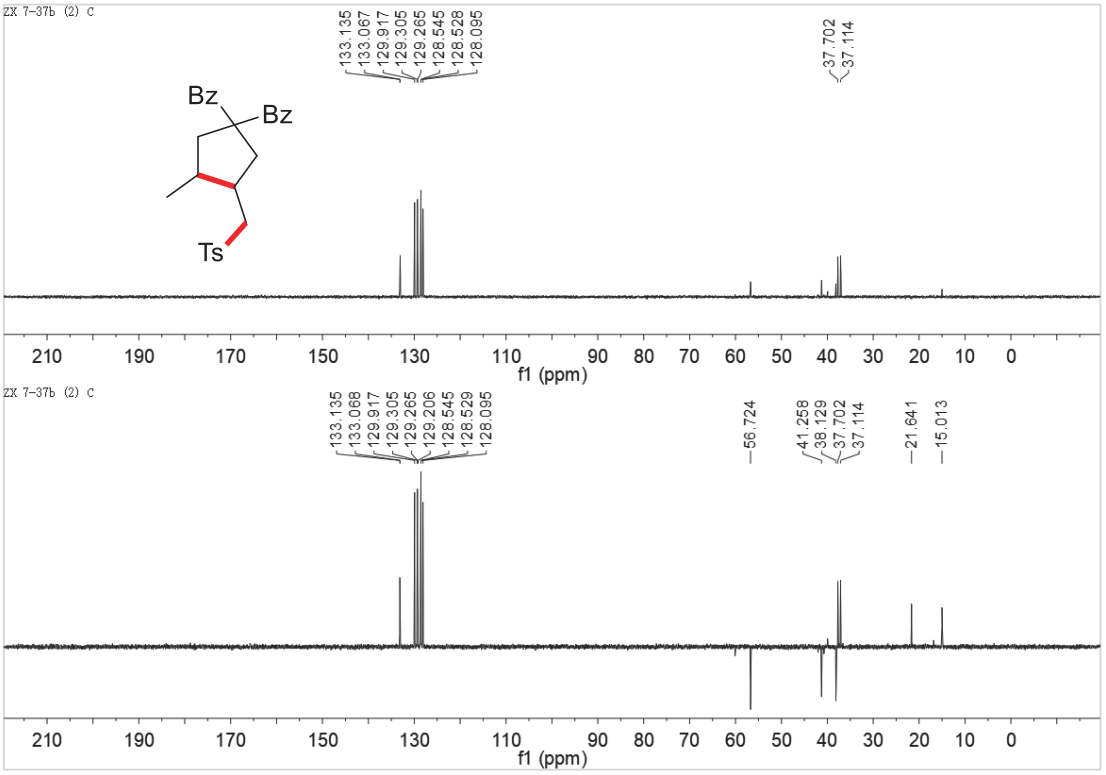
10, ^{1}H NMR



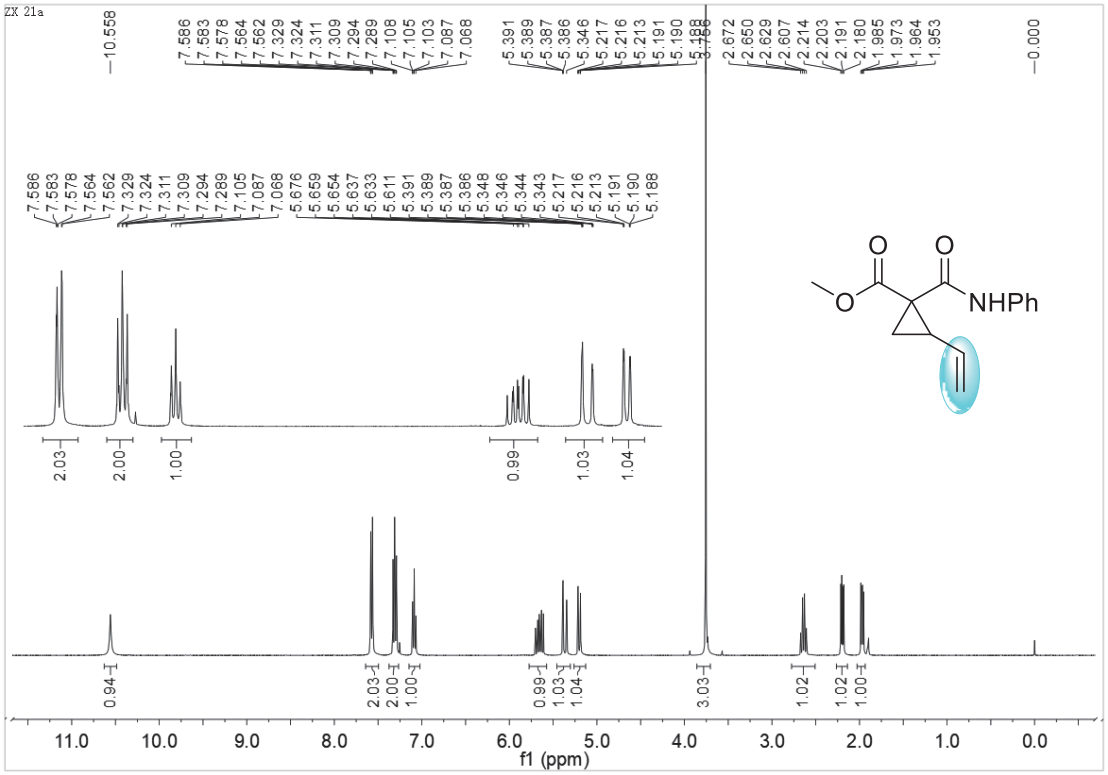
10, ^{13}C NMR



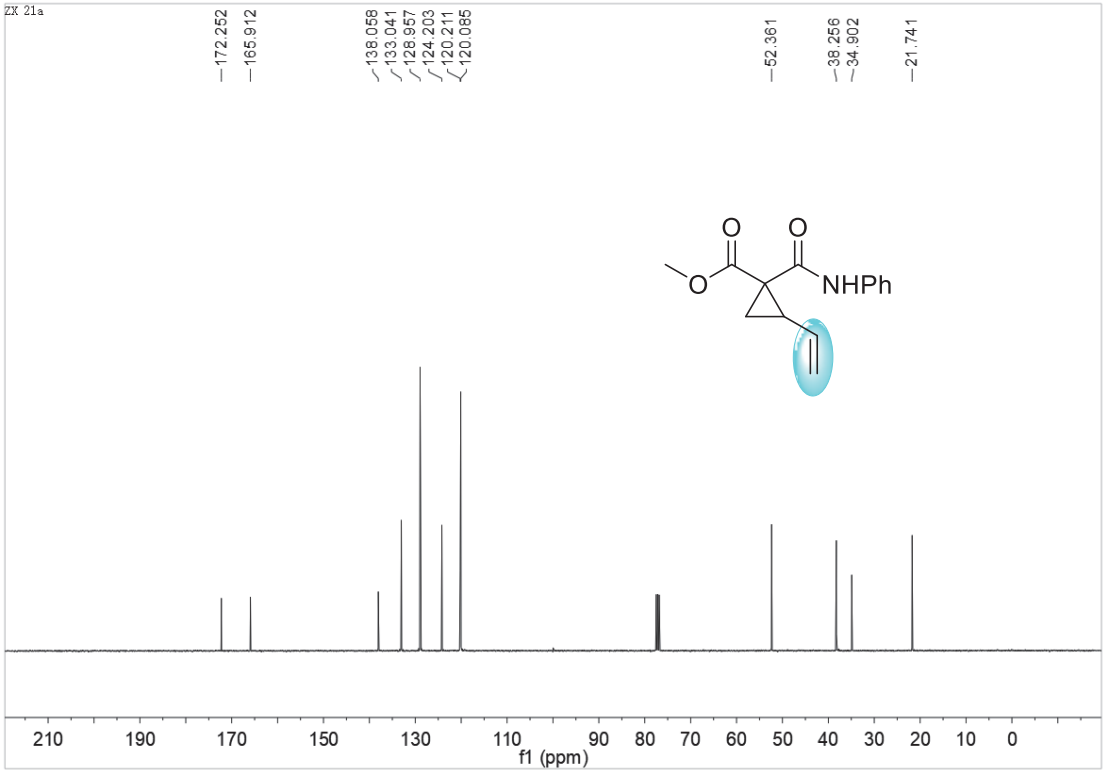
10, DEPT 90 and DEPT 135



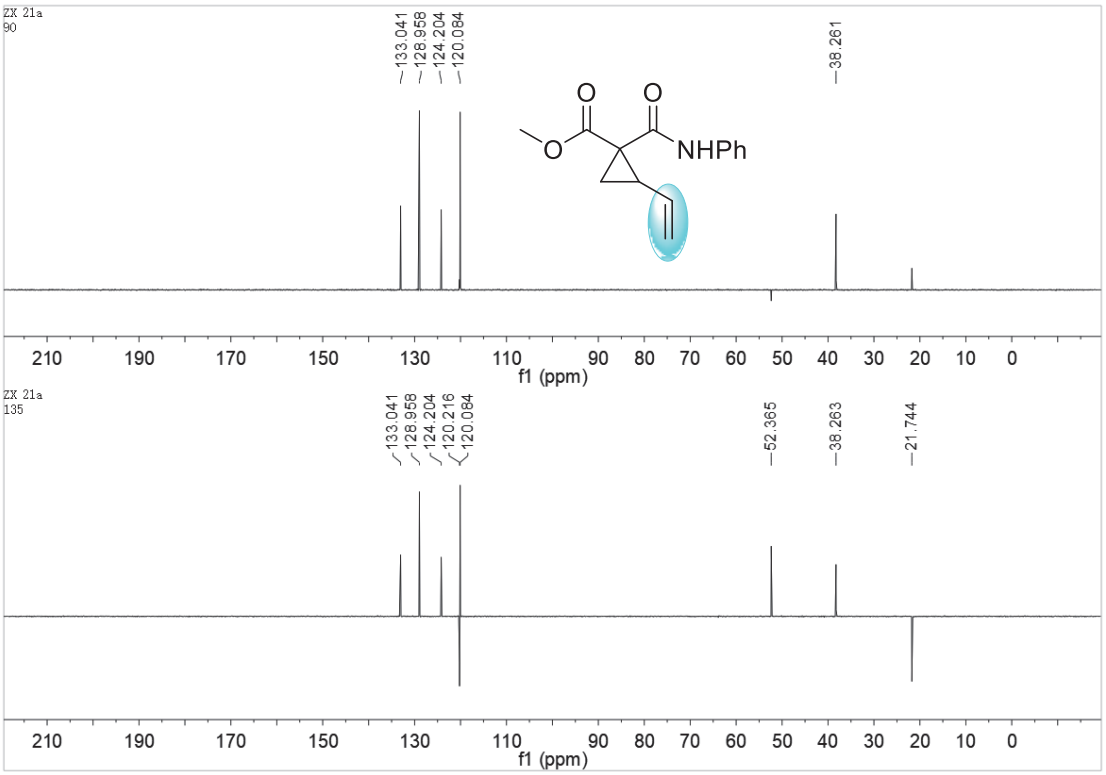
1a1, ^{1}H NMR



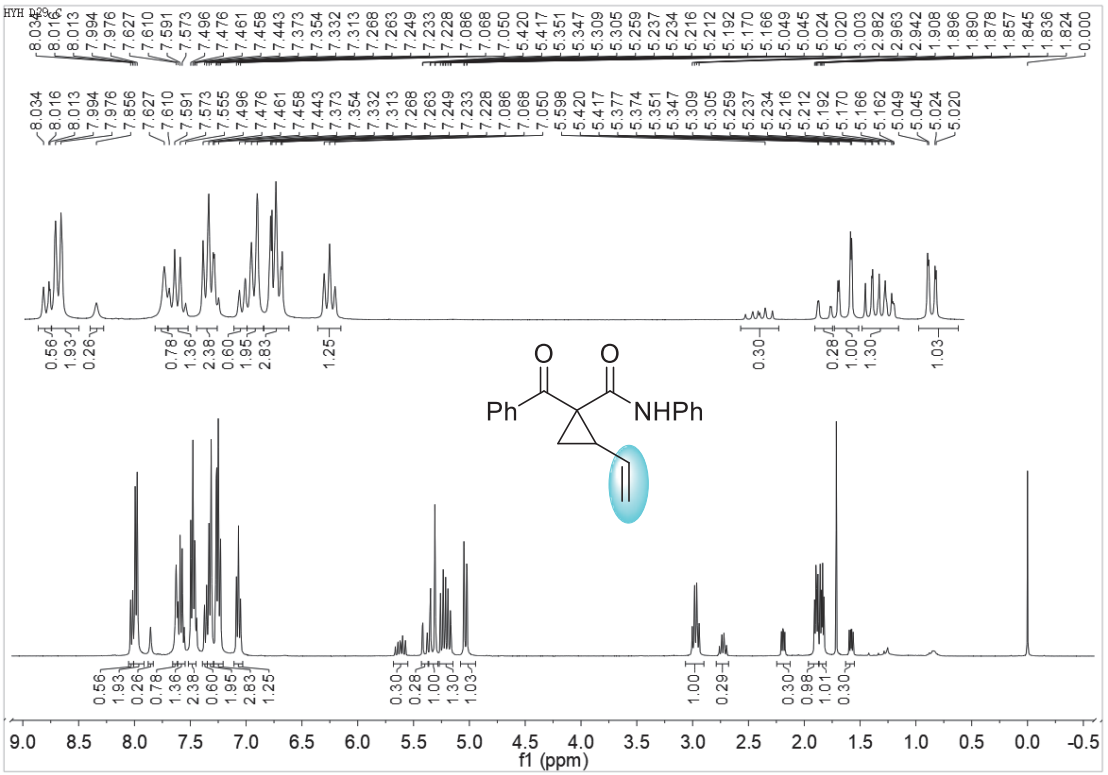
1a1, ^{13}C NMR



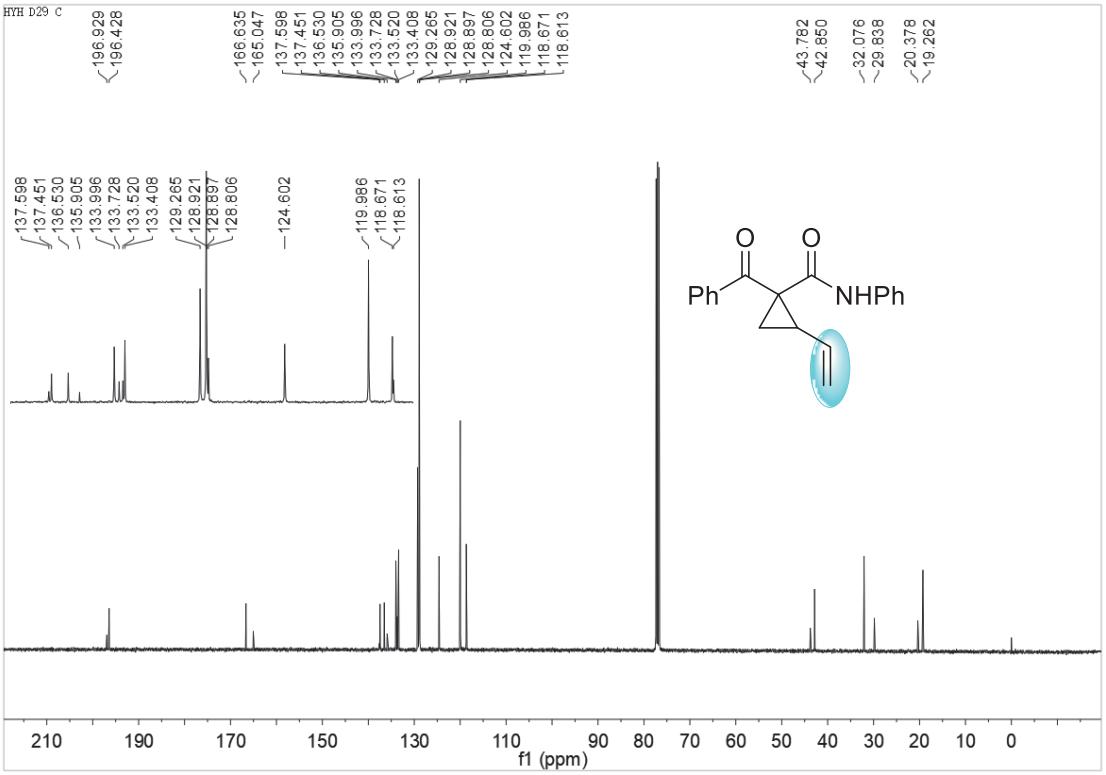
1a1, DEPT 90 and DEPT 135



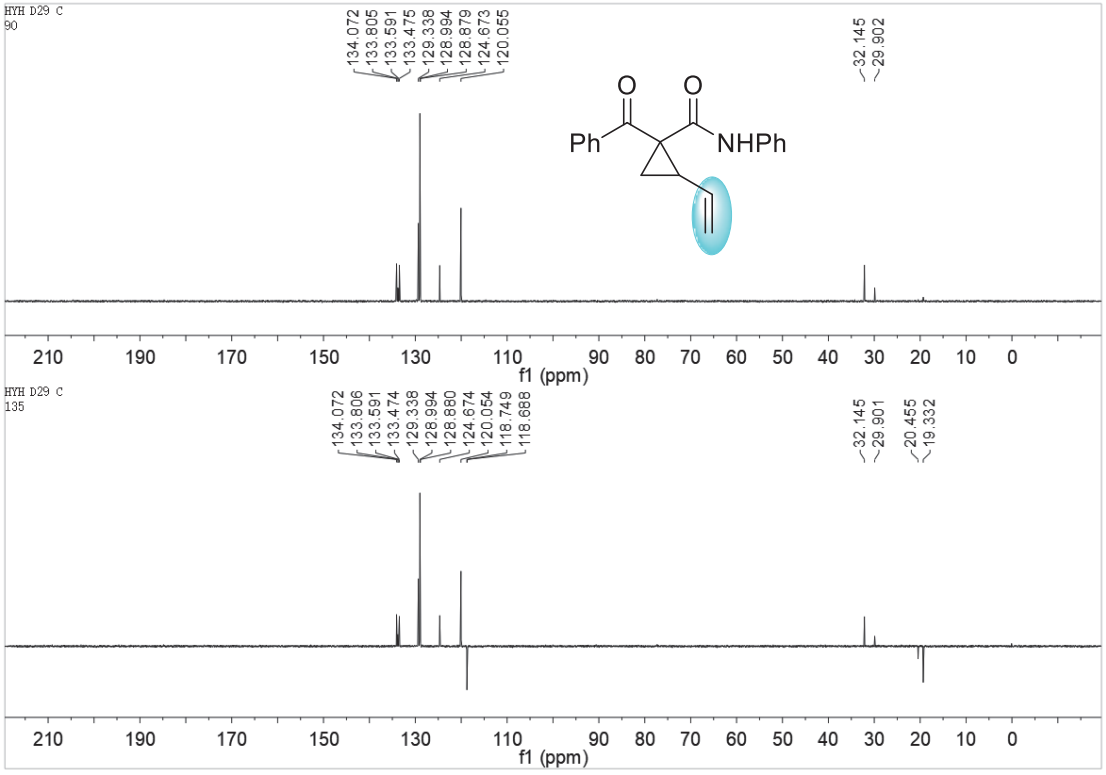
1a3, ^{1}H NMR



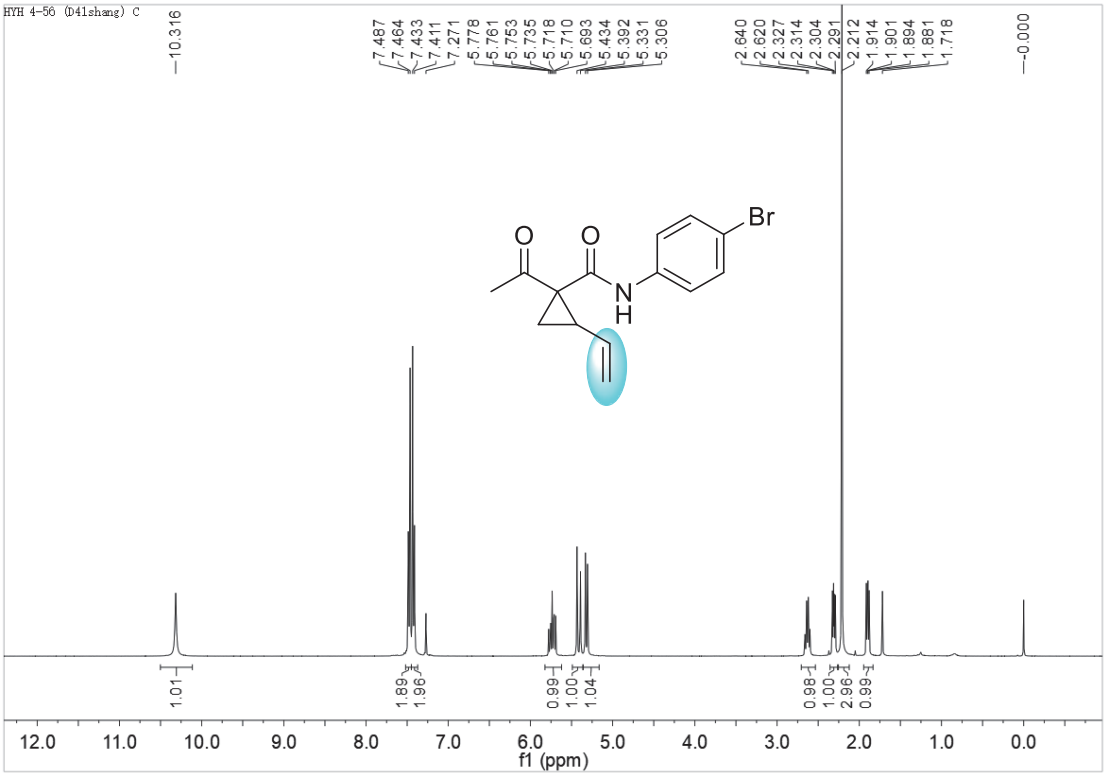
1a3, ^{13}C NMR



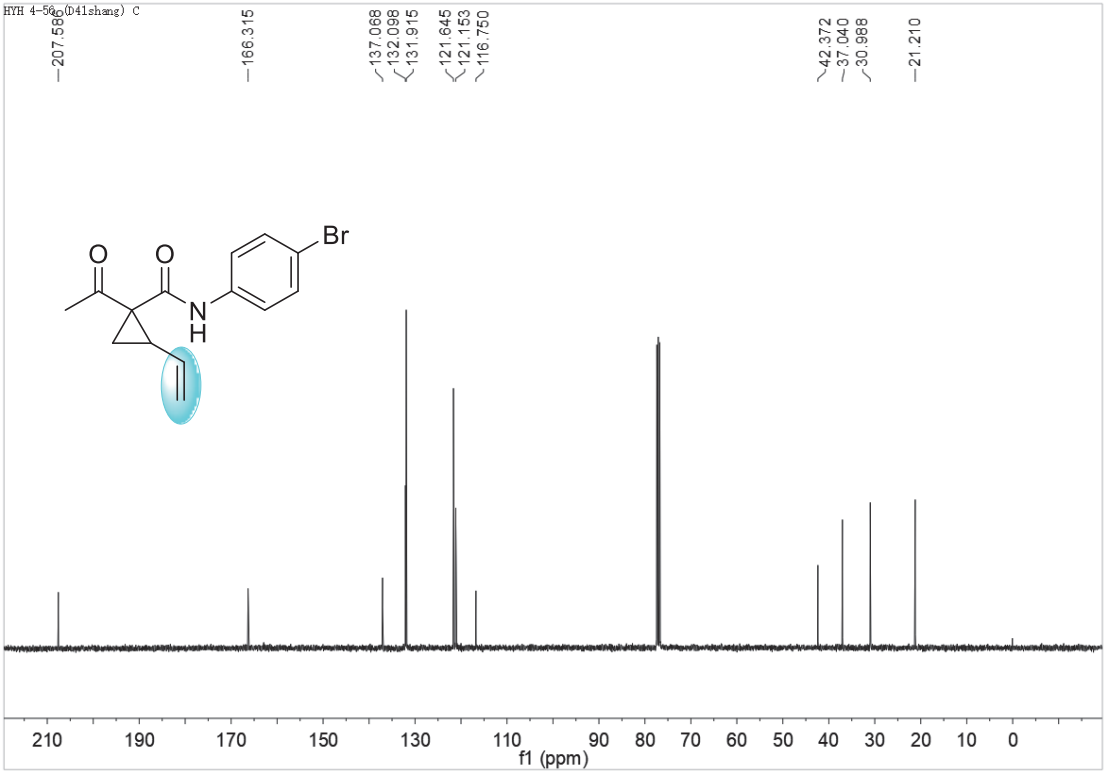
1a3, DEPT 90 and DEPT 135



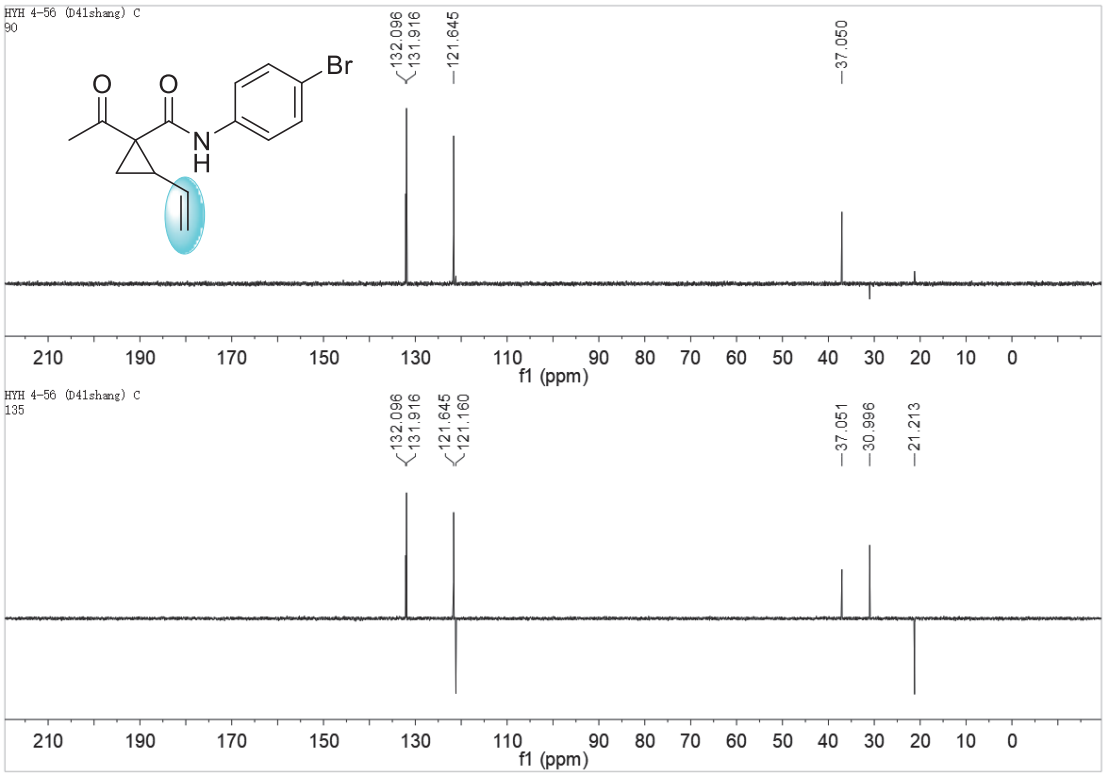
1b5, ^{1}H NMR



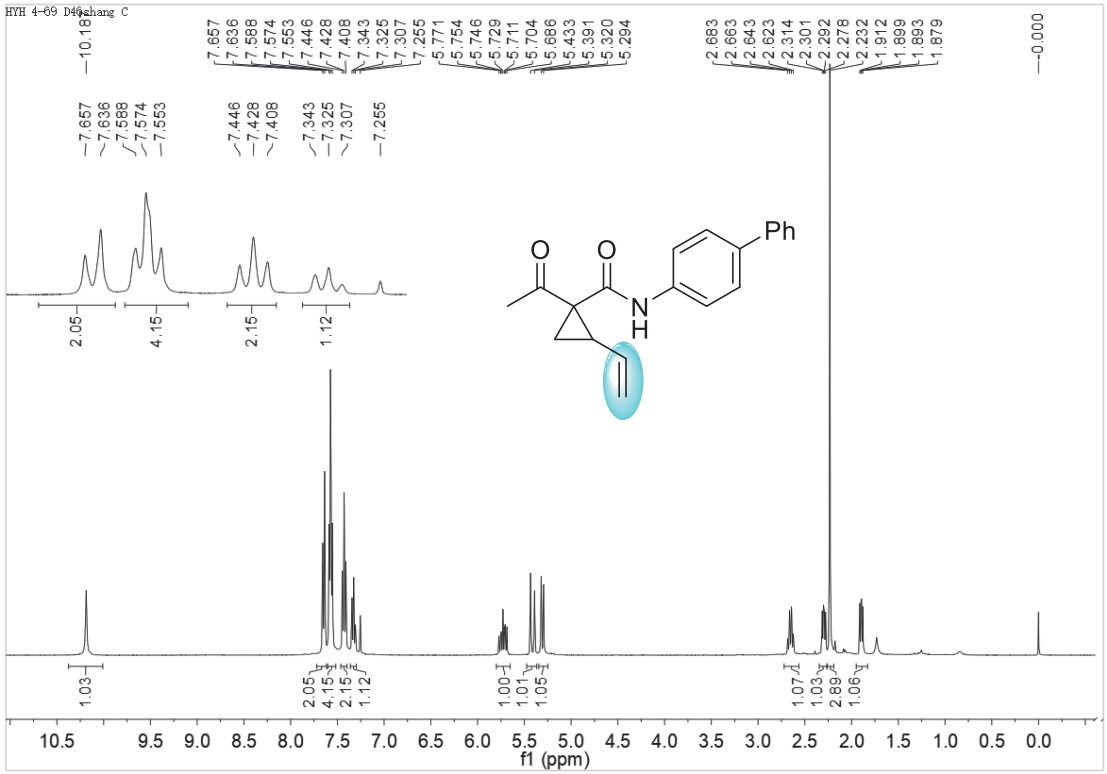
1b5, ^{13}C NMR



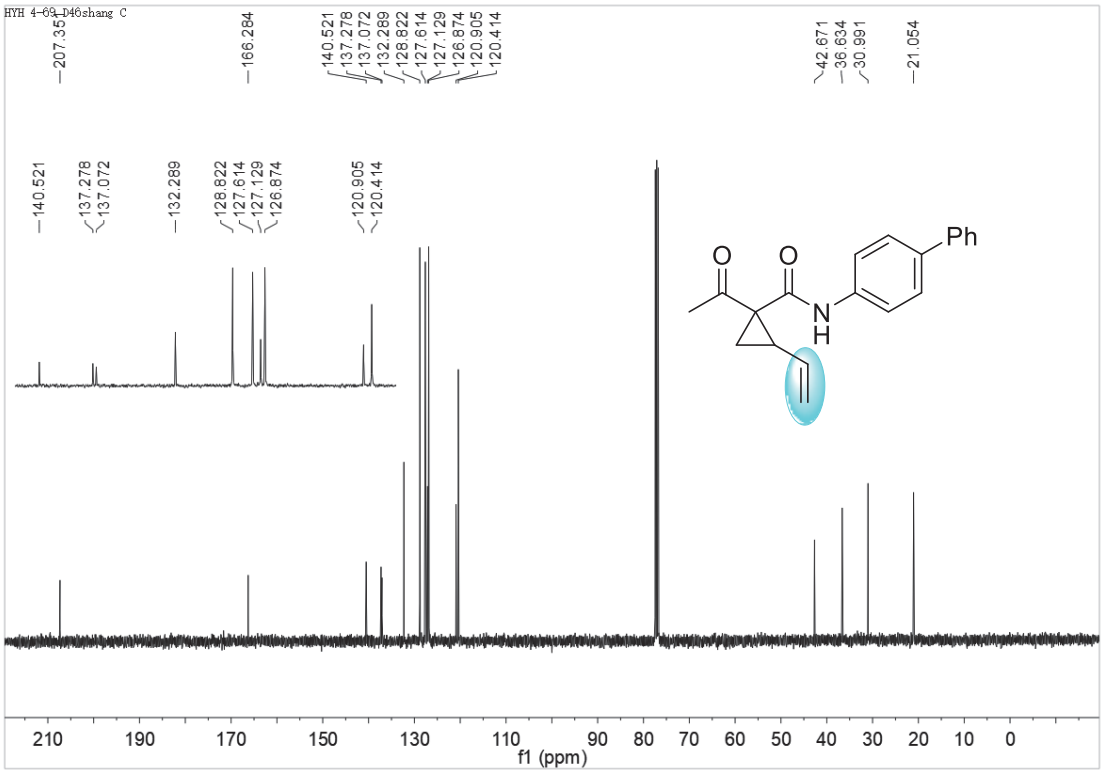
1b5, DEPT 90 and DEPT 135



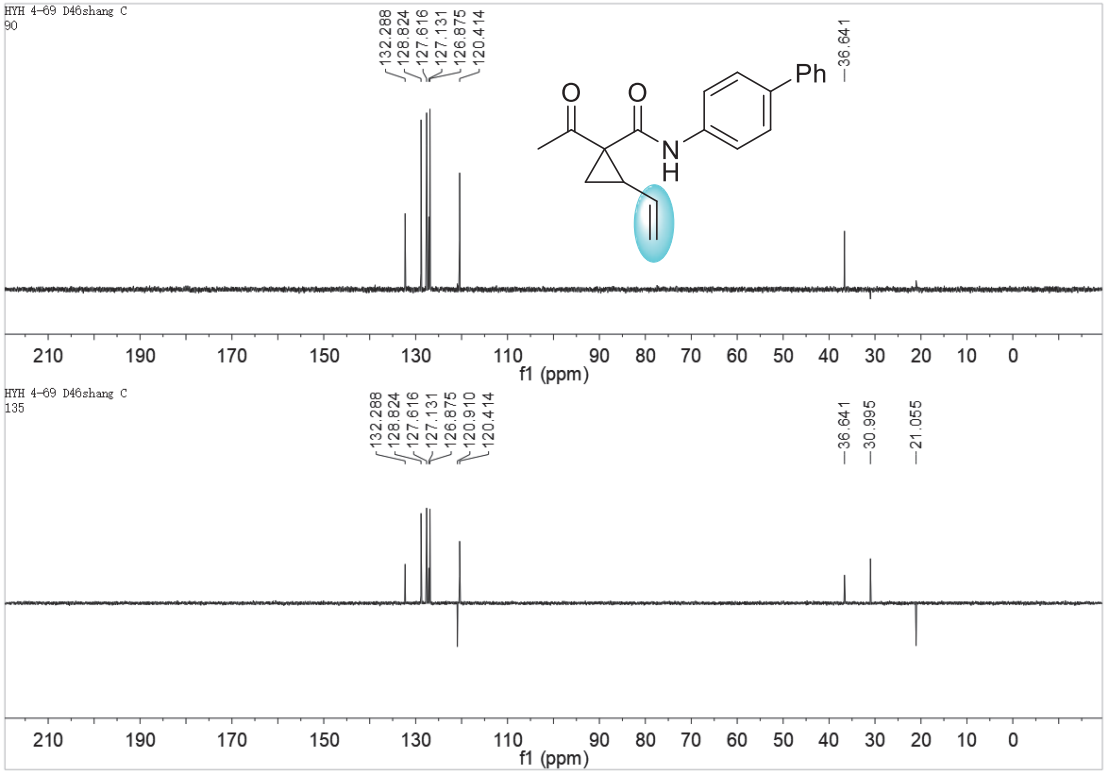
1b6, ^{1}H NMR



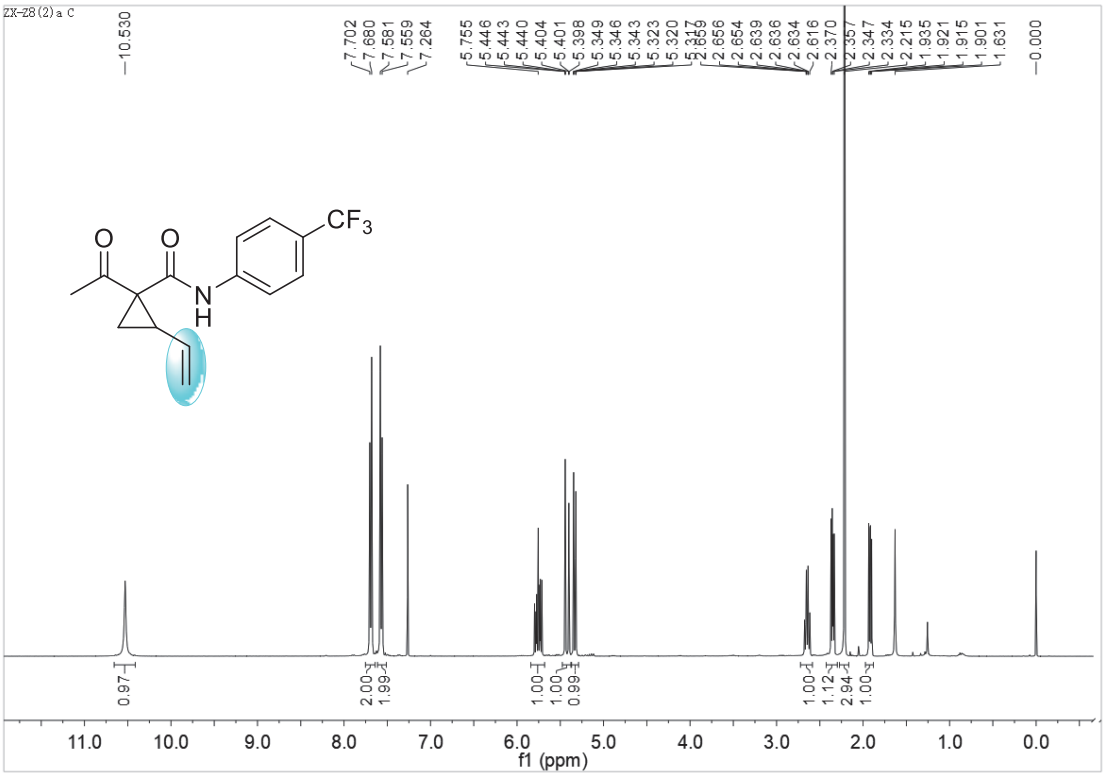
1b6, ^{13}C NMR



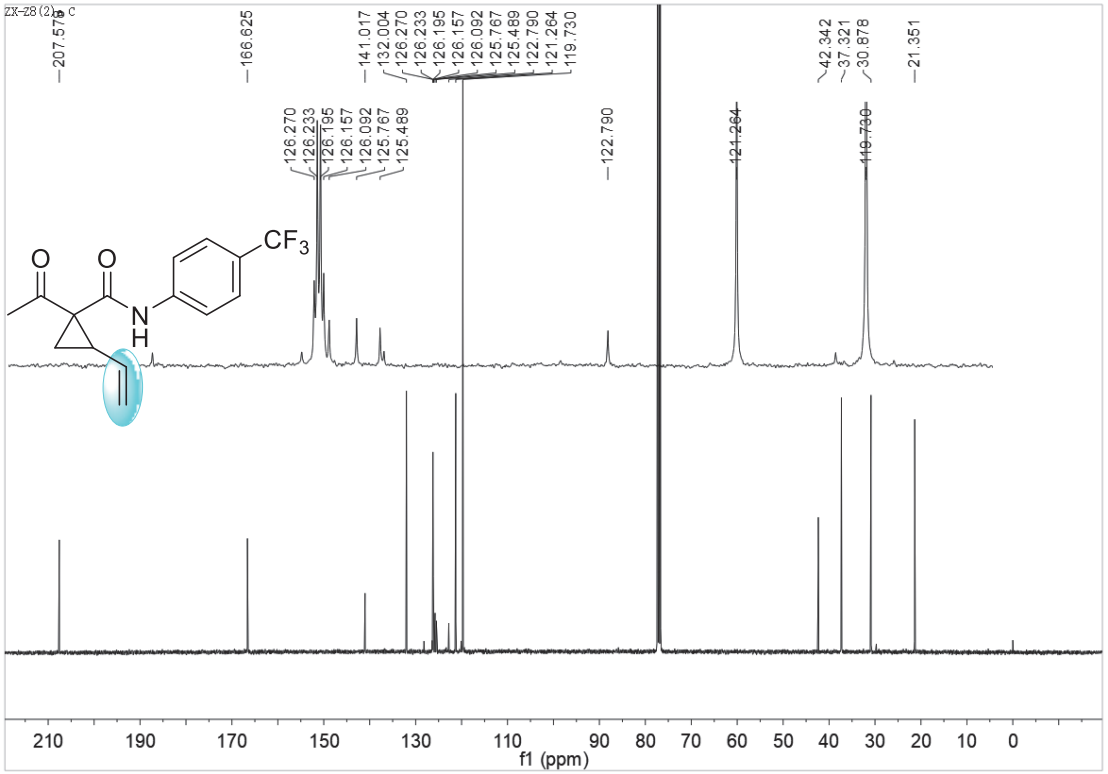
1b6, DEPT 90 and DEPT 135



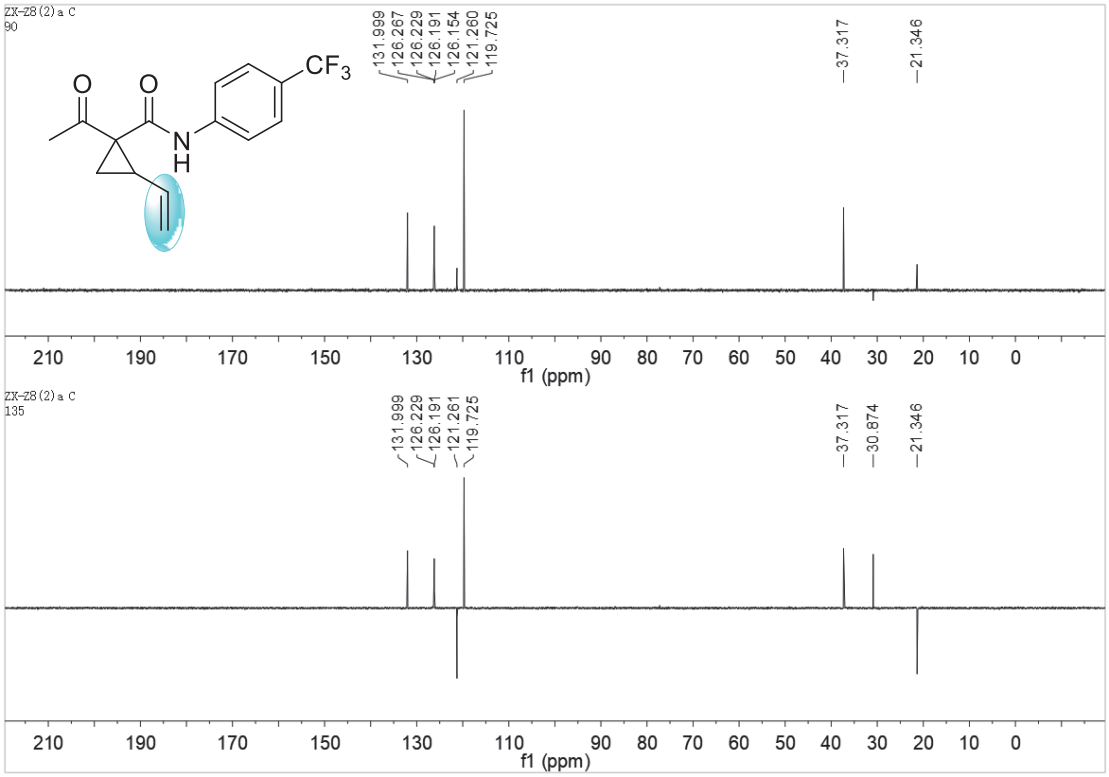
1b7, ^{1}H NMR



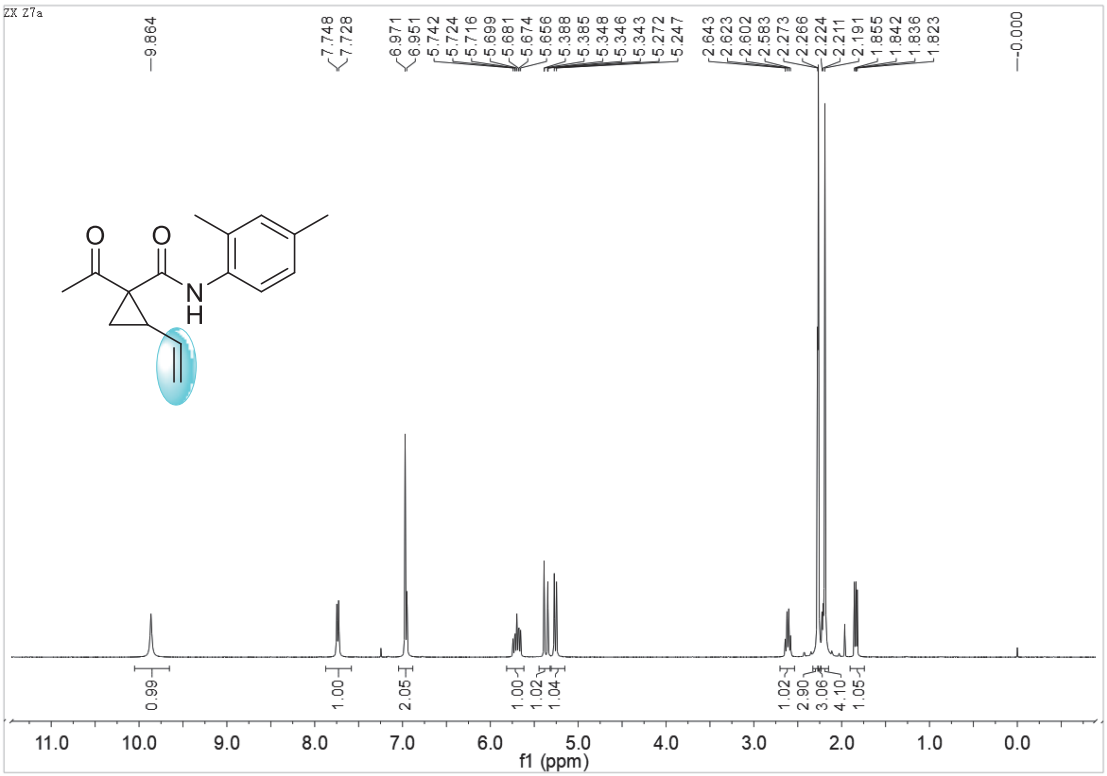
1b7, ^{13}C NMR



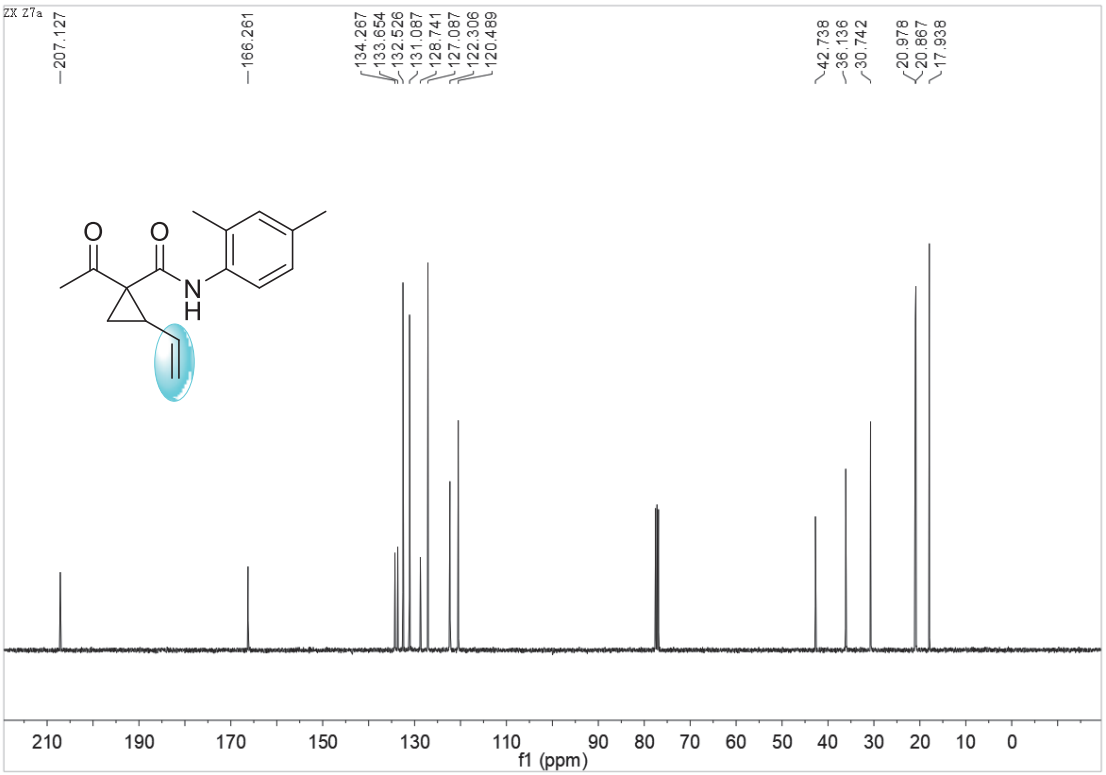
1b7, DEPT 90 and DEPT 135



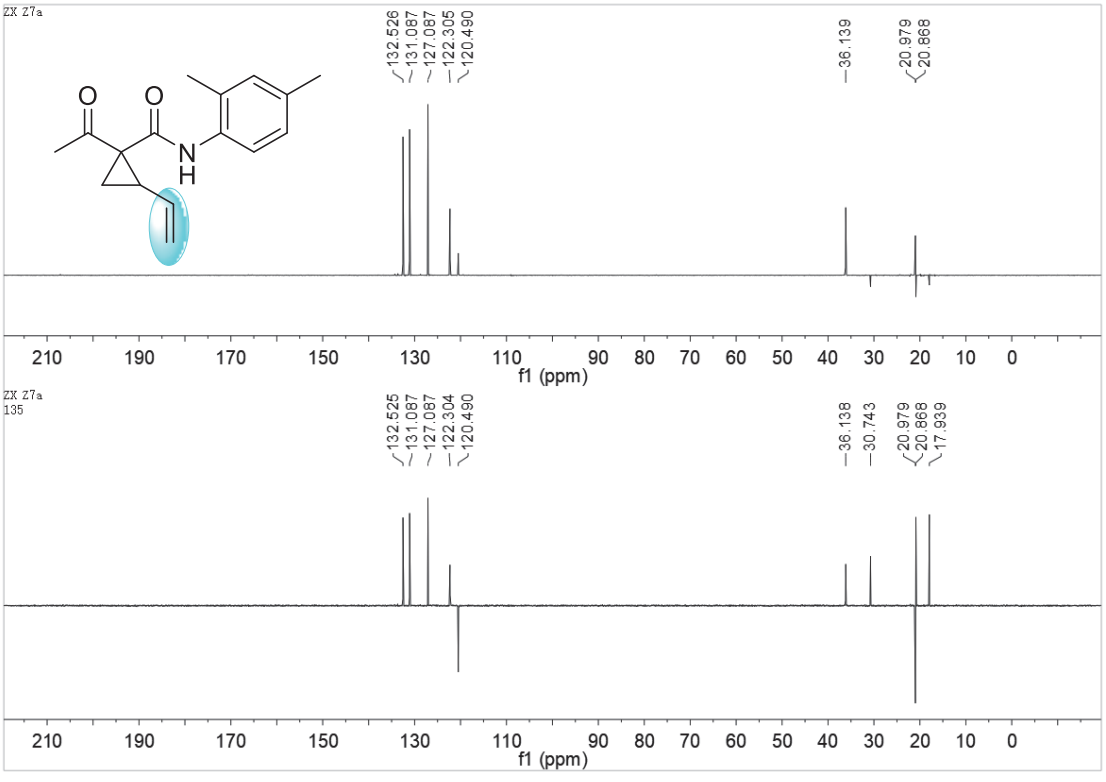
1e, ^{1}H NMR



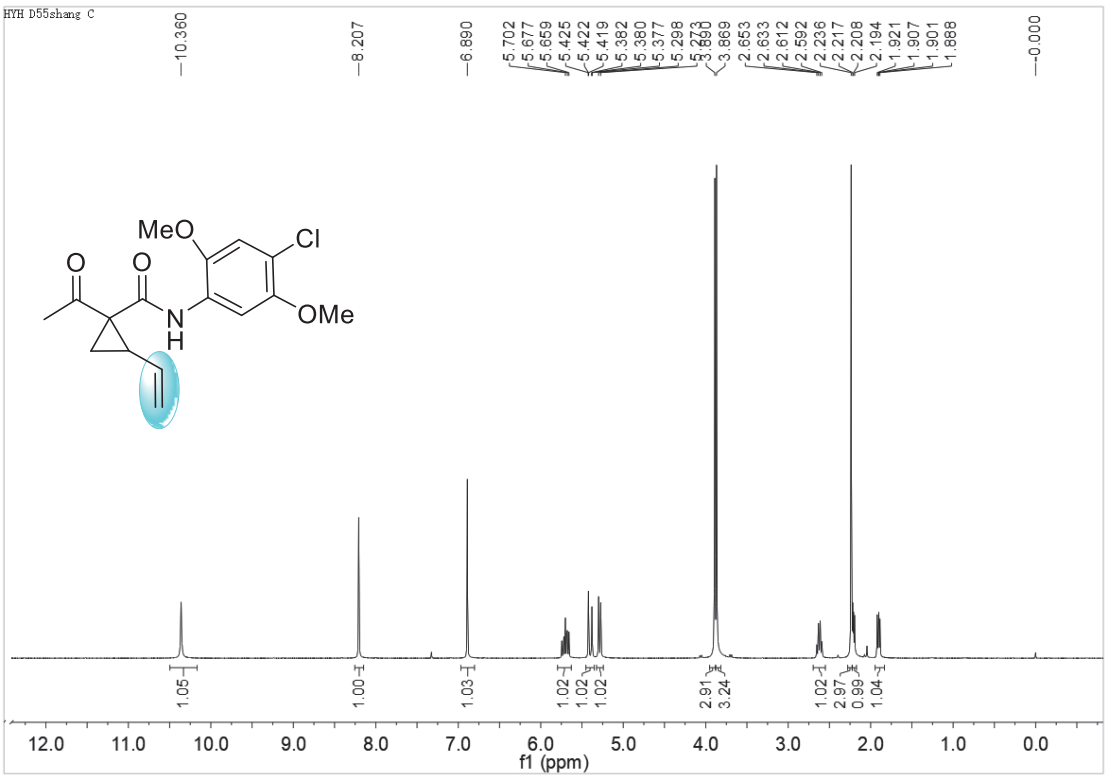
1e, ^{13}C NMR



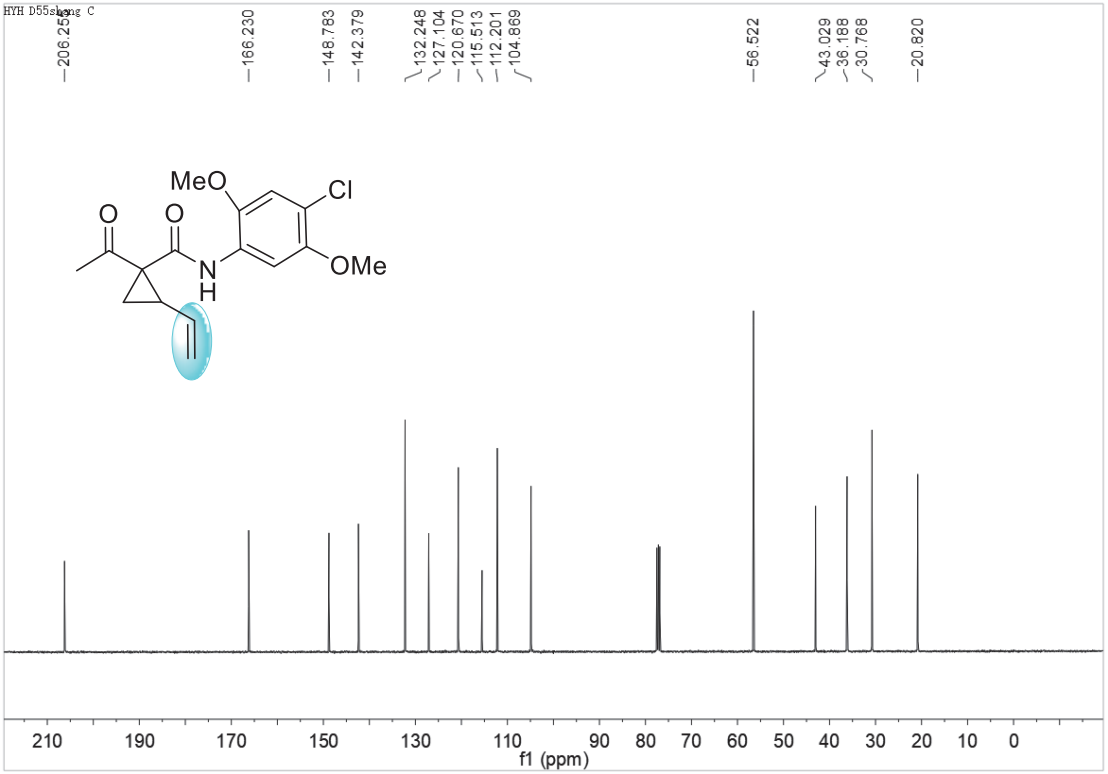
1e, DEPT 90 and DEPT 135



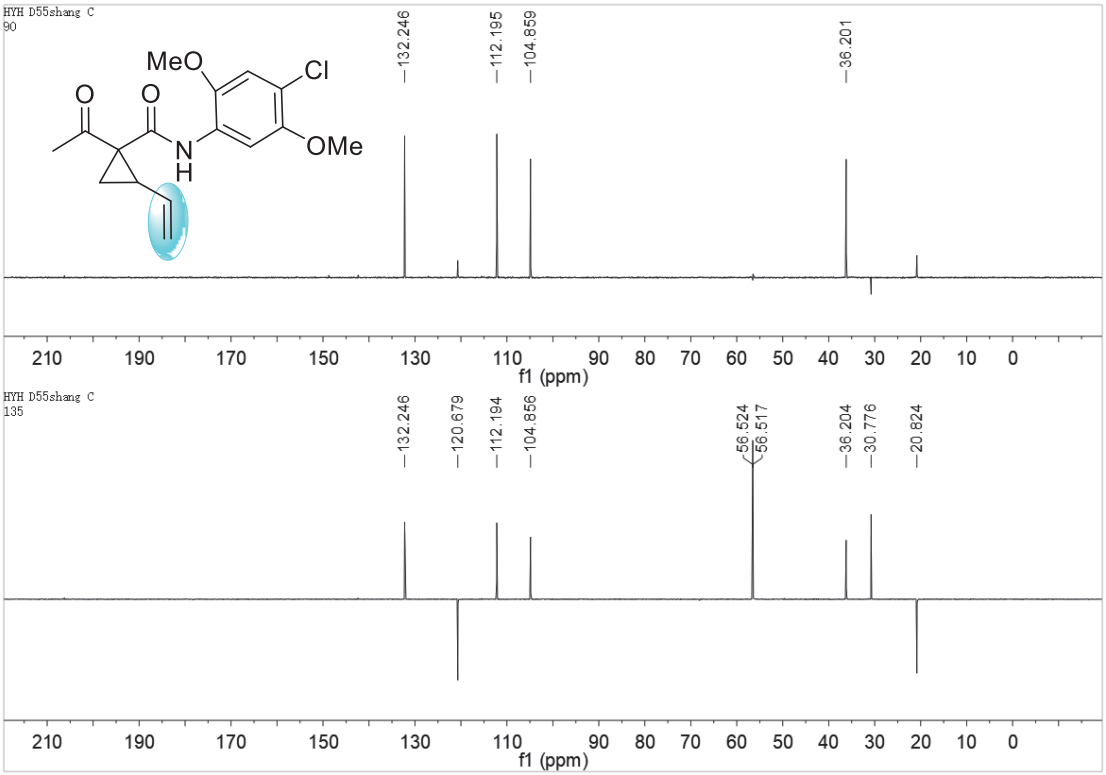
1g, ^{1}H NMR



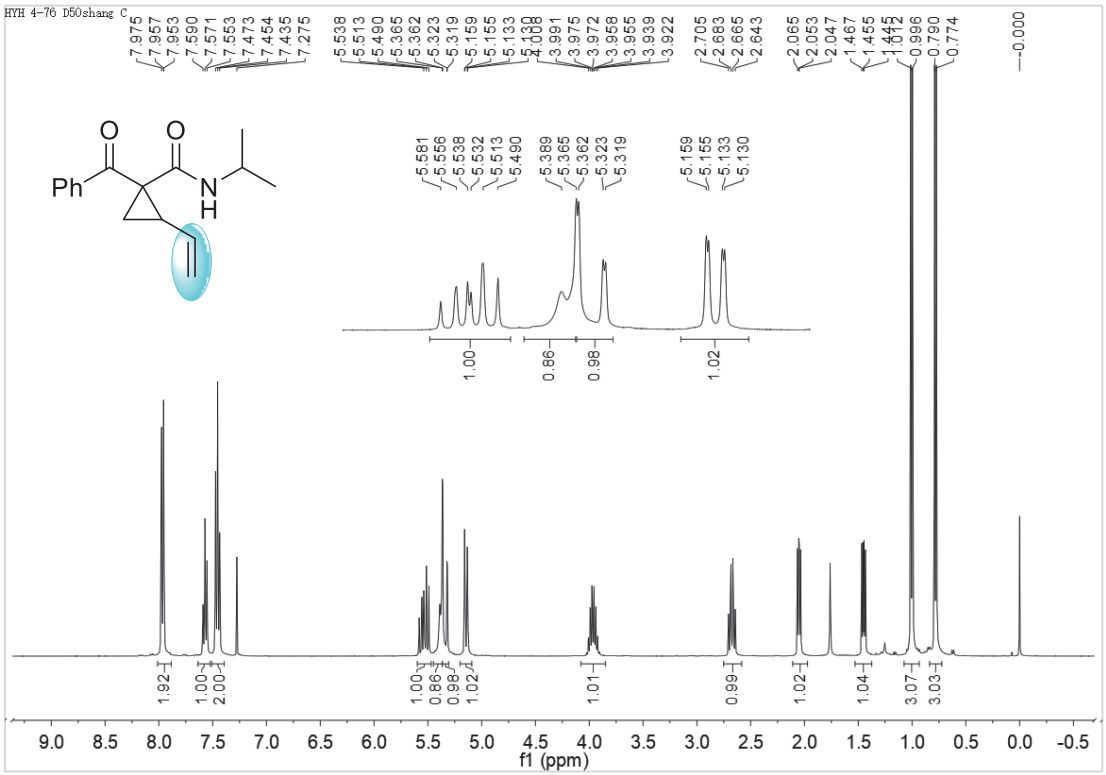
1g, ^{13}C NMR



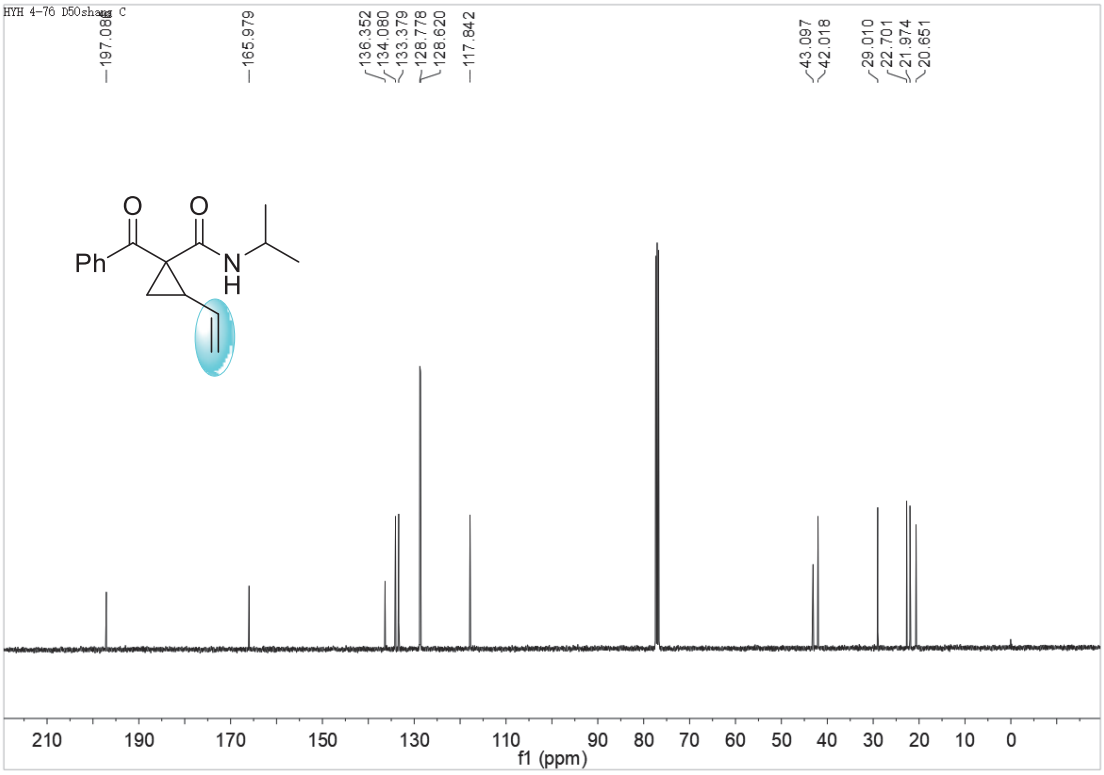
1g, DEPT 90 and DEPT 135



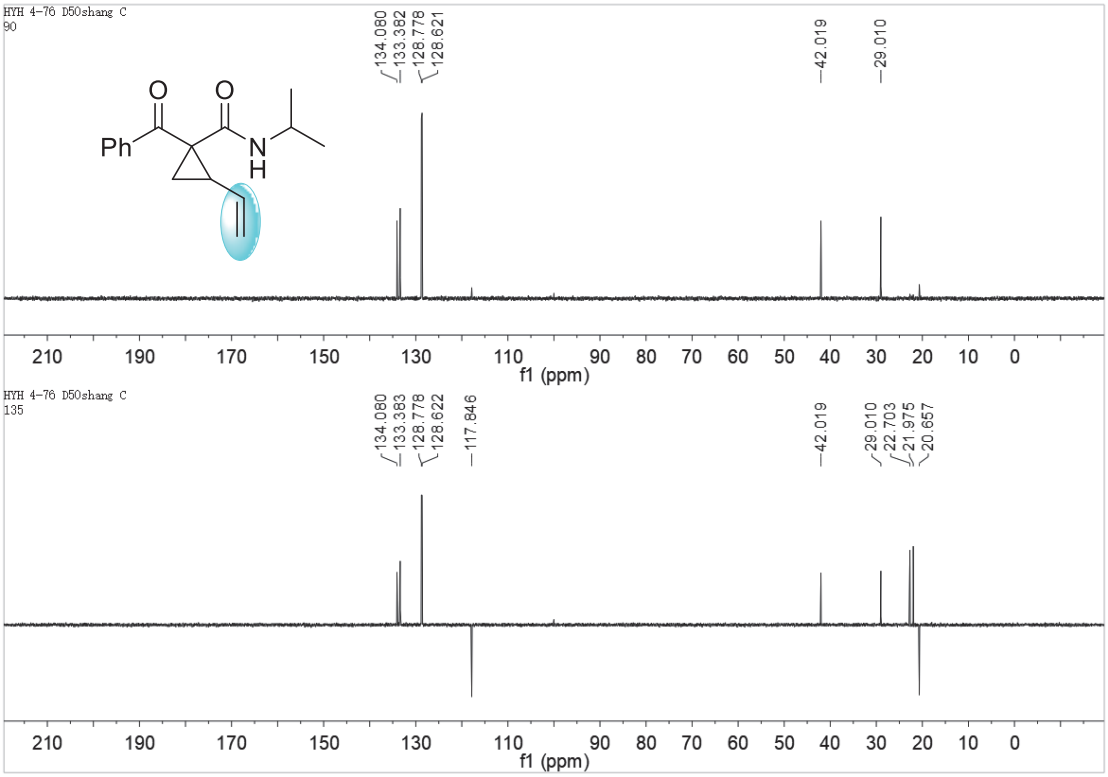
1h, ^{1}H NMR



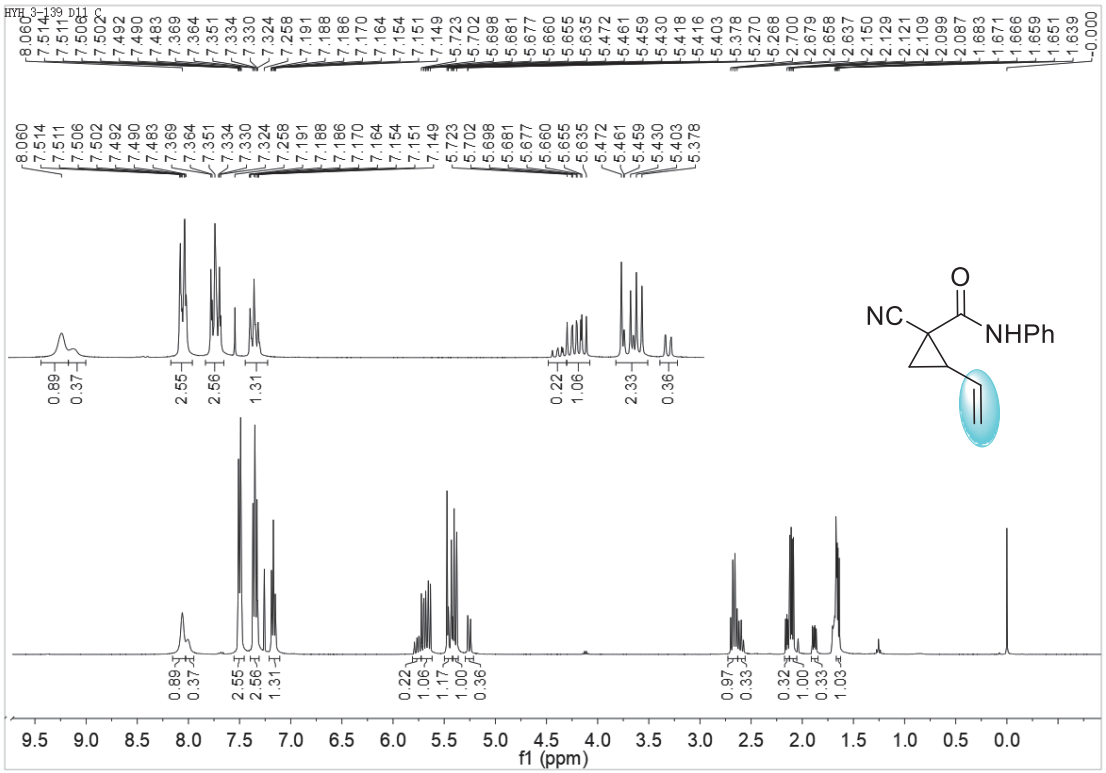
1h, ^{13}C NMR



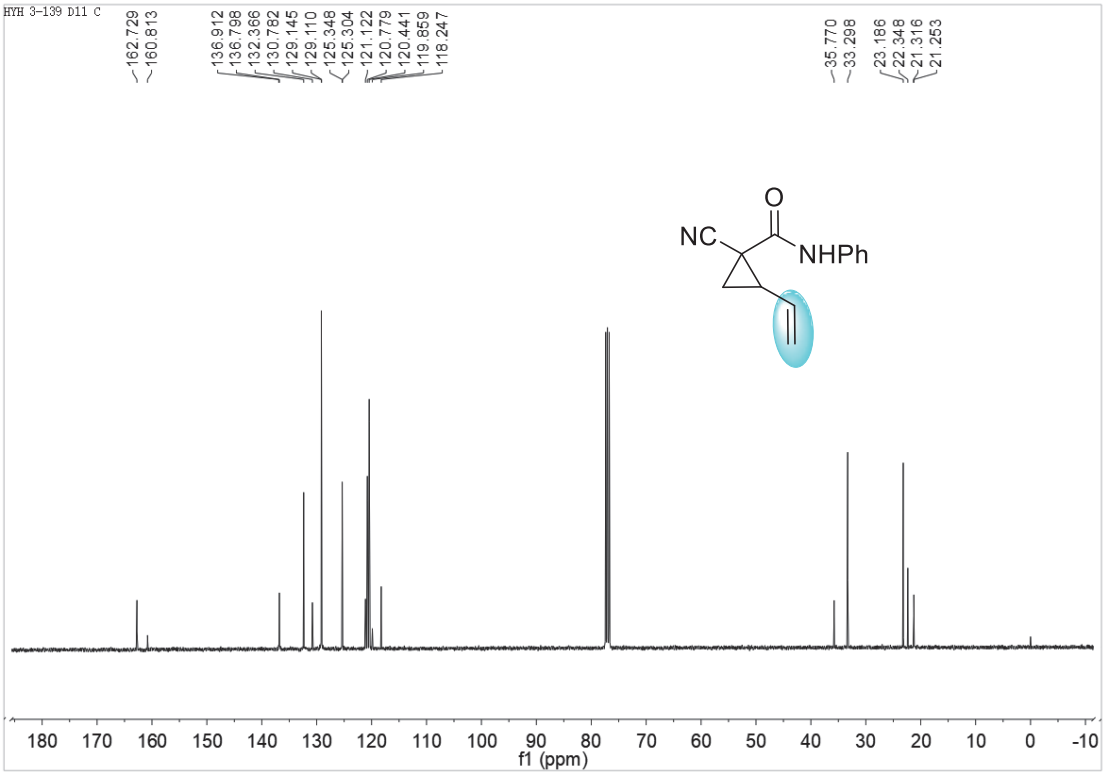
1h, DEPT 90 and DEPT 135



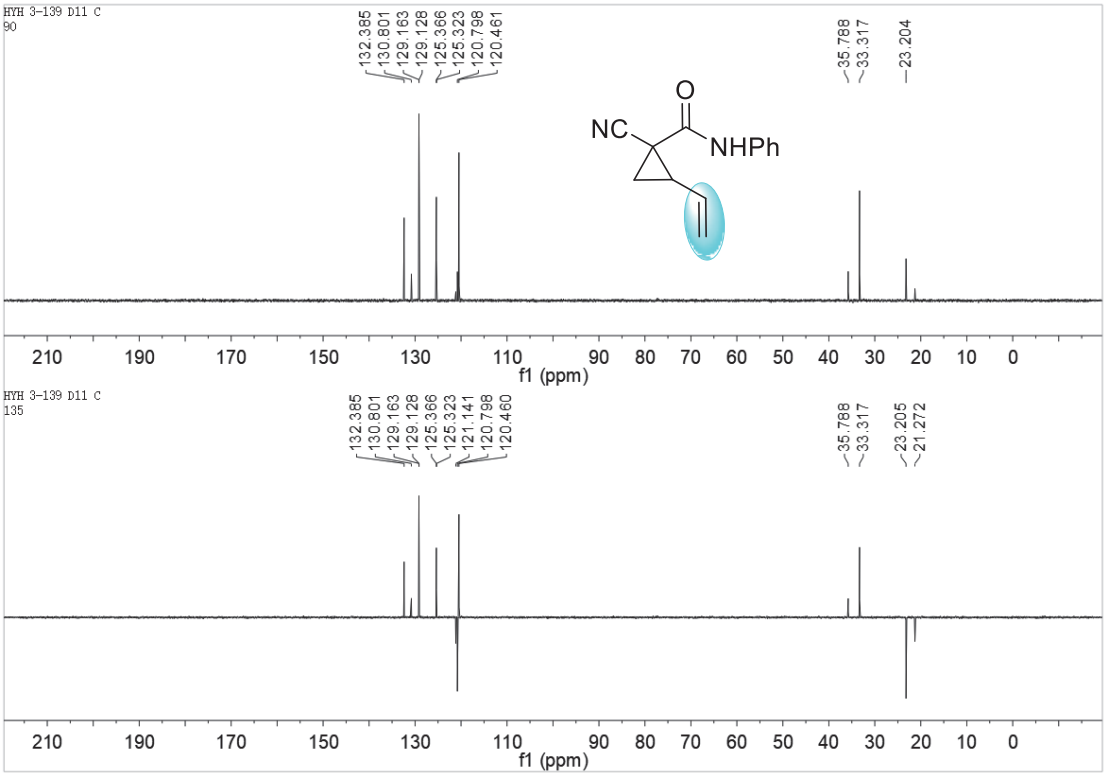
1'a5, ^{1}H NMR



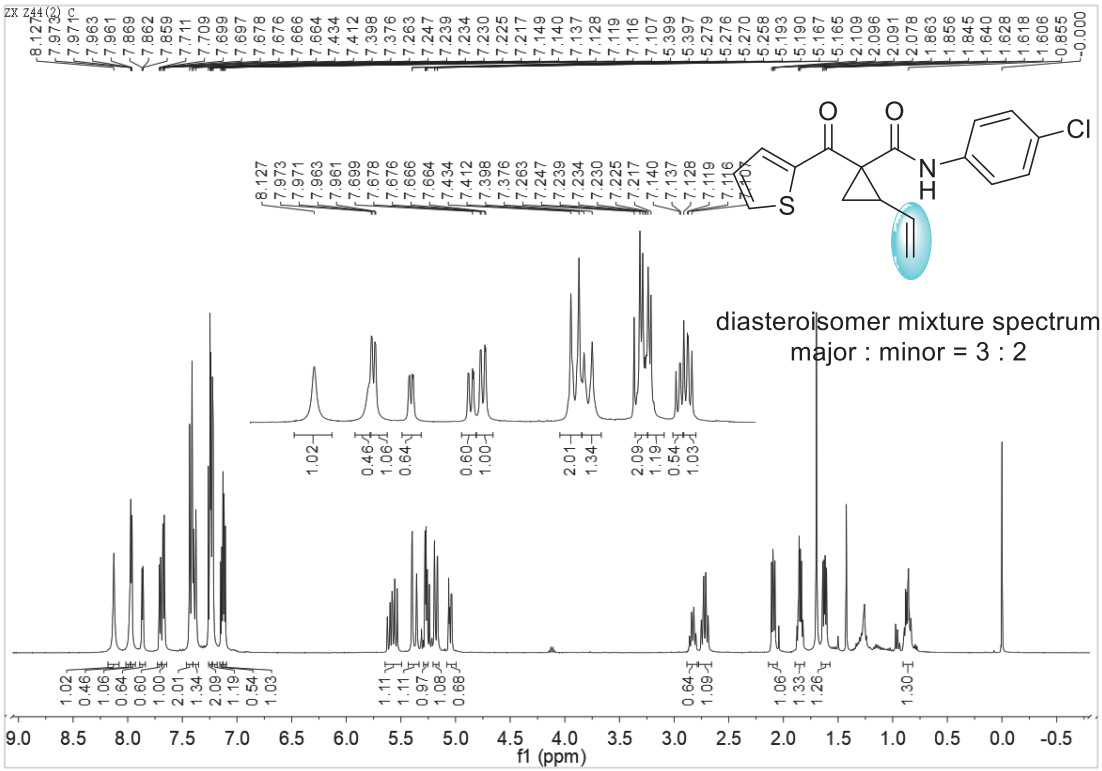
1'a5, ^{13}C NMR



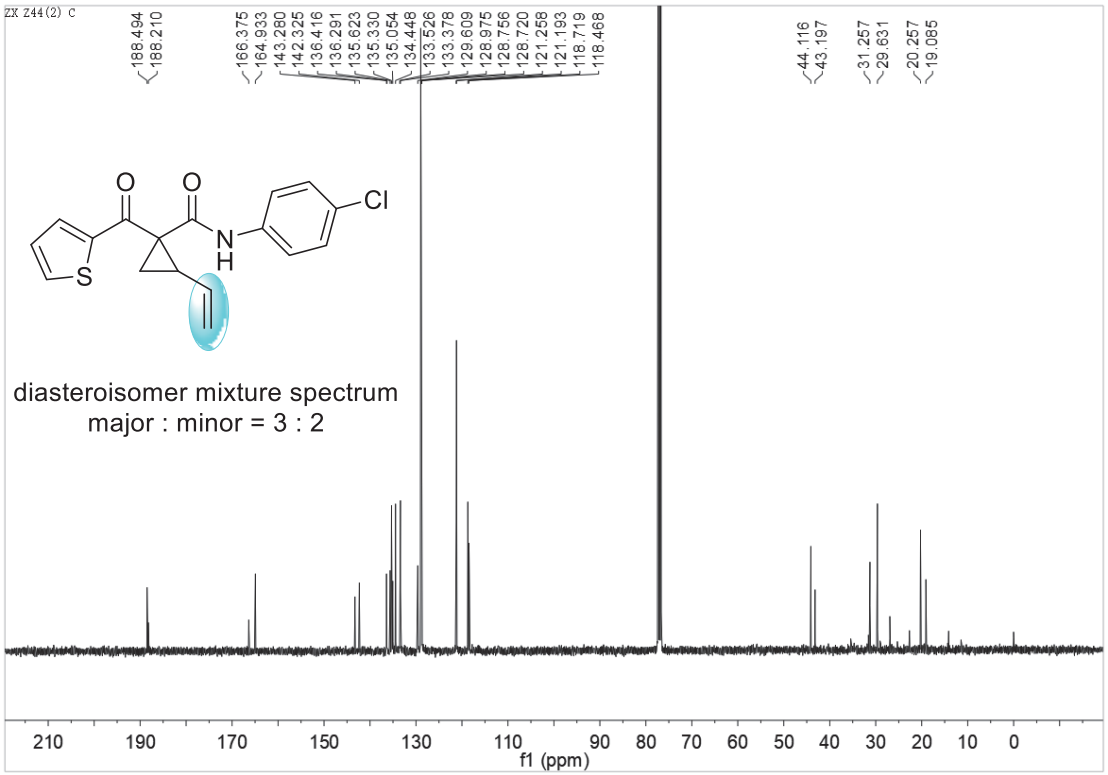
1'a5, DEPT 90 and DEPT 135



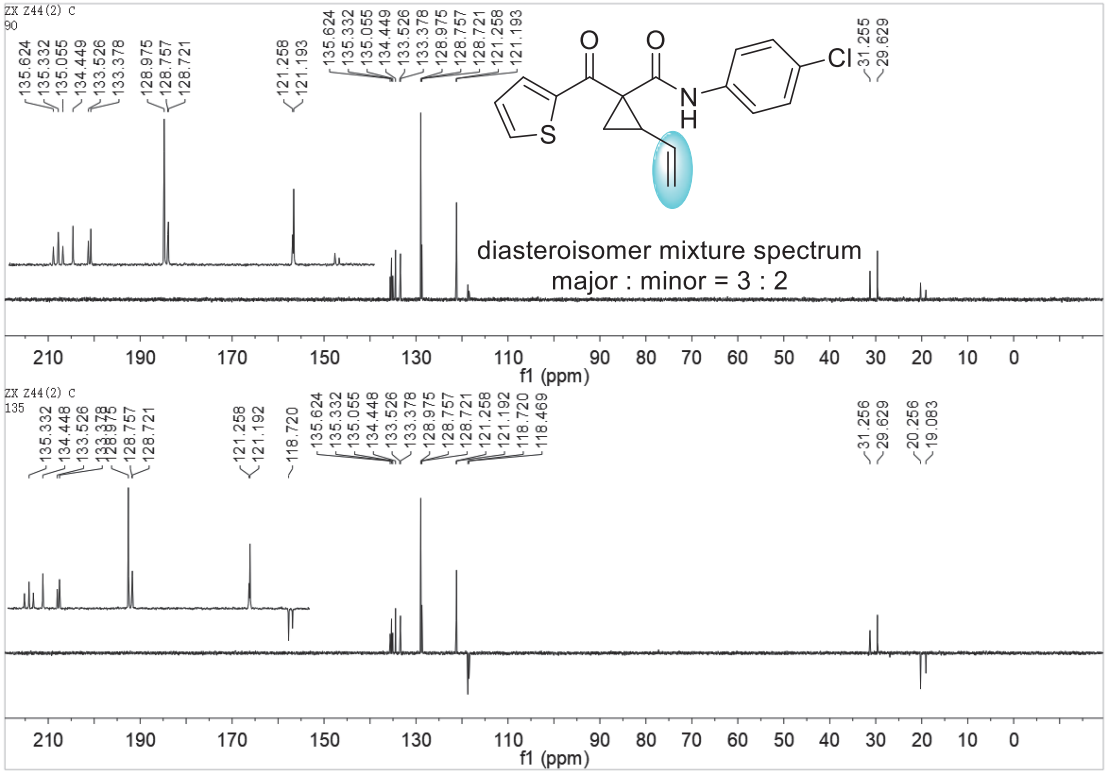
1'b, ^{1}H NMR



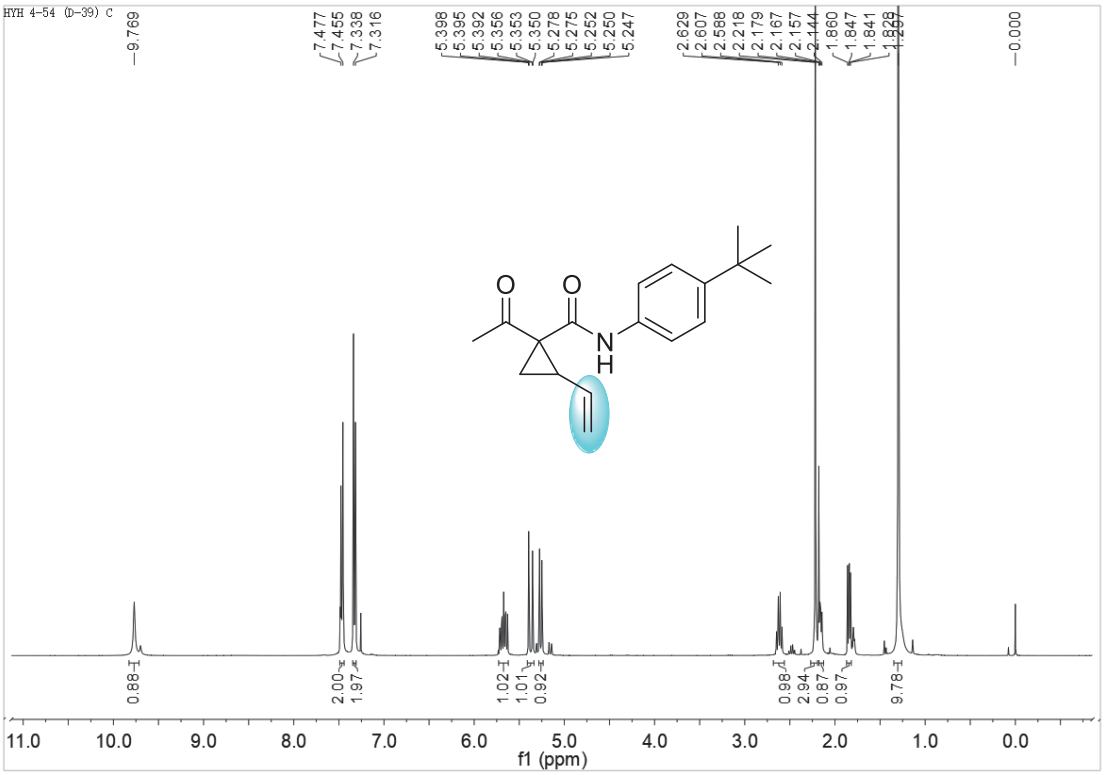
1'b, ^{13}C NMR



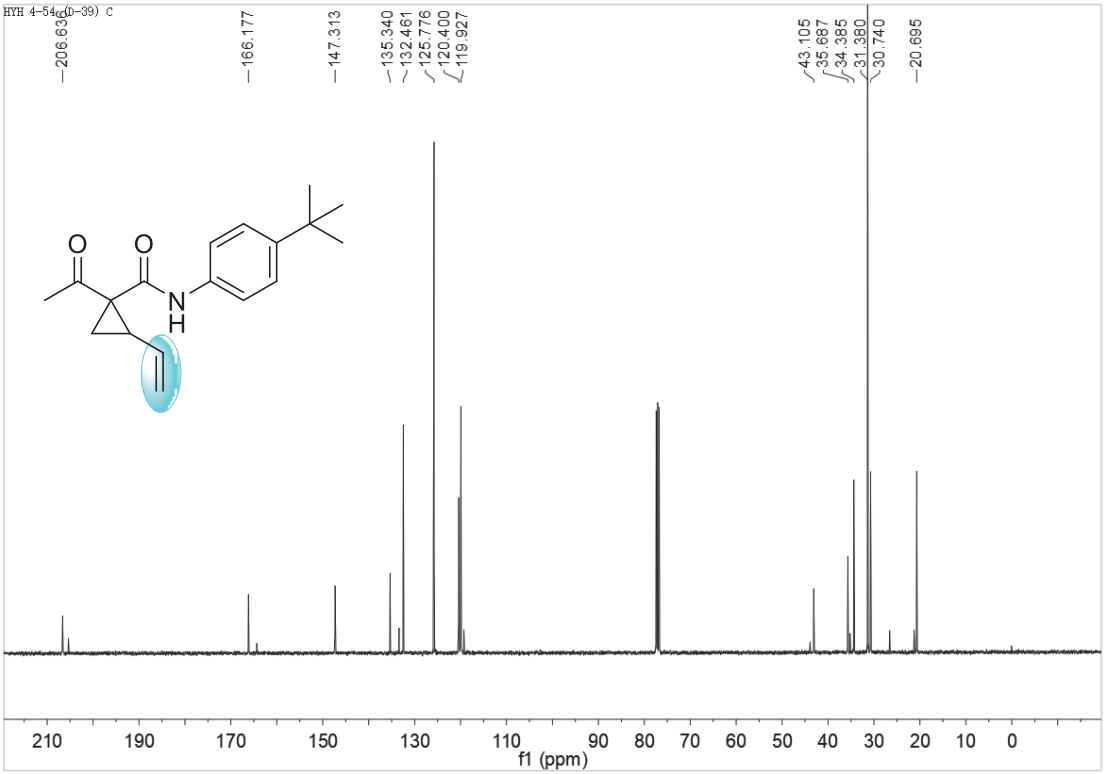
1'b, DEPT 90 and DEPT 135



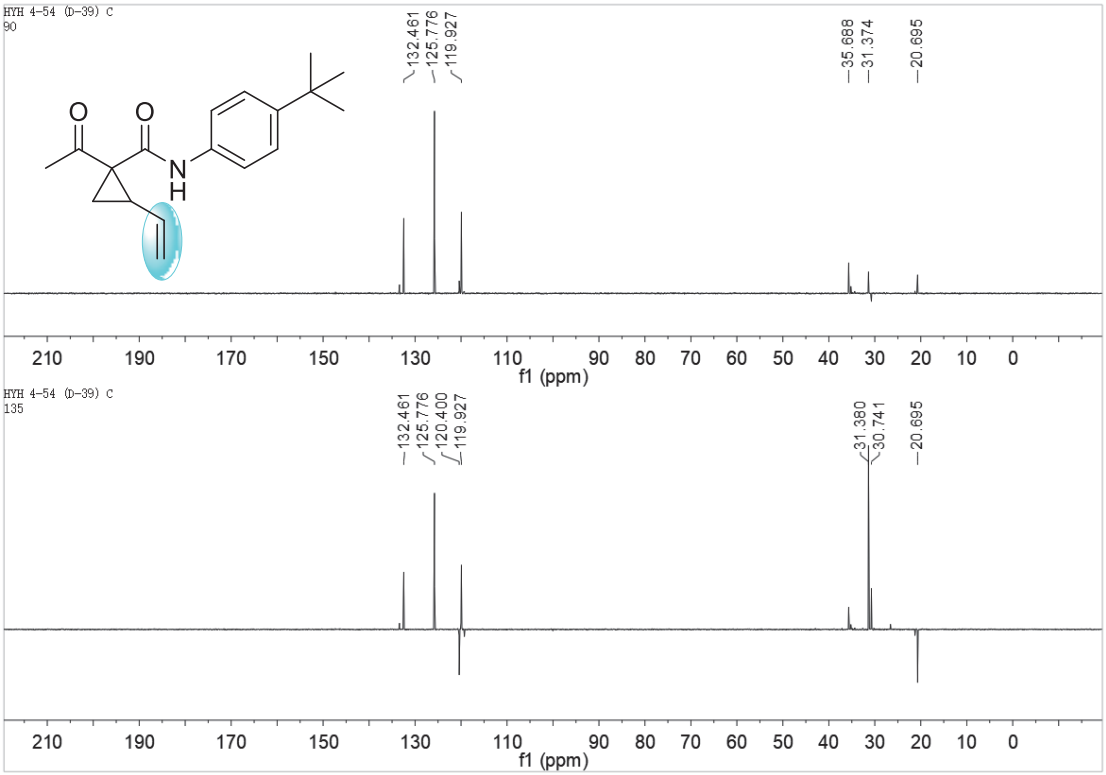
1'e4, ^{1}H NMR



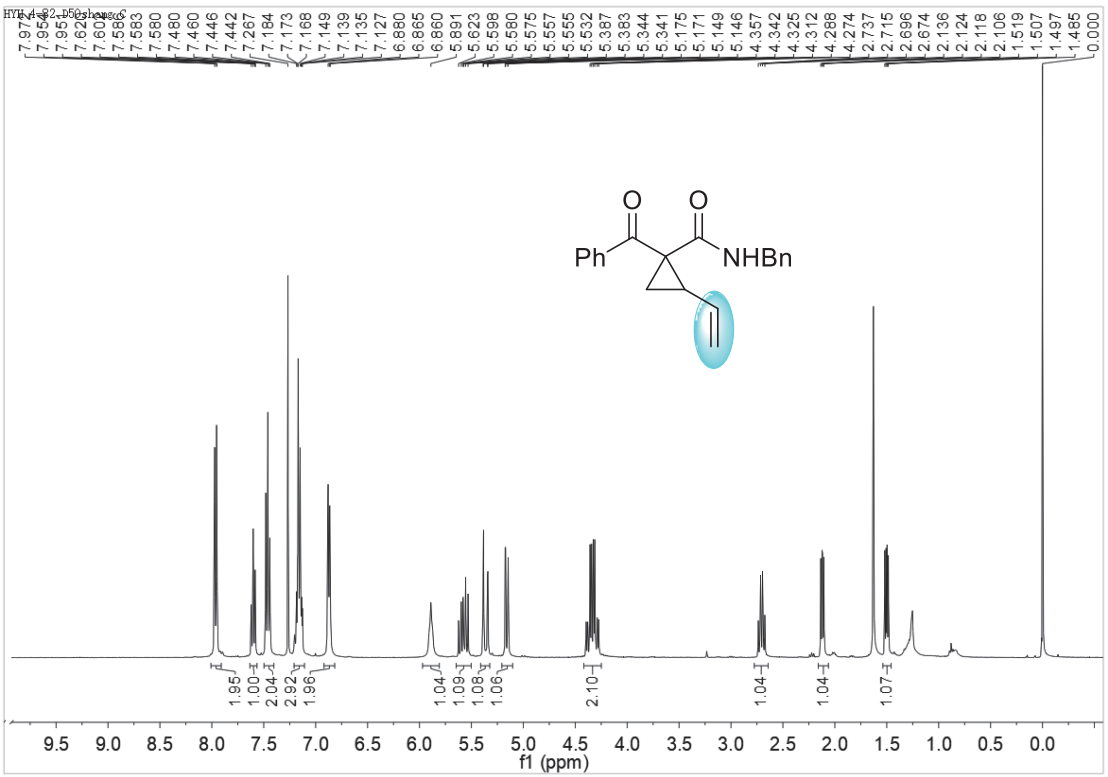
1'e4, ^{13}C NMR



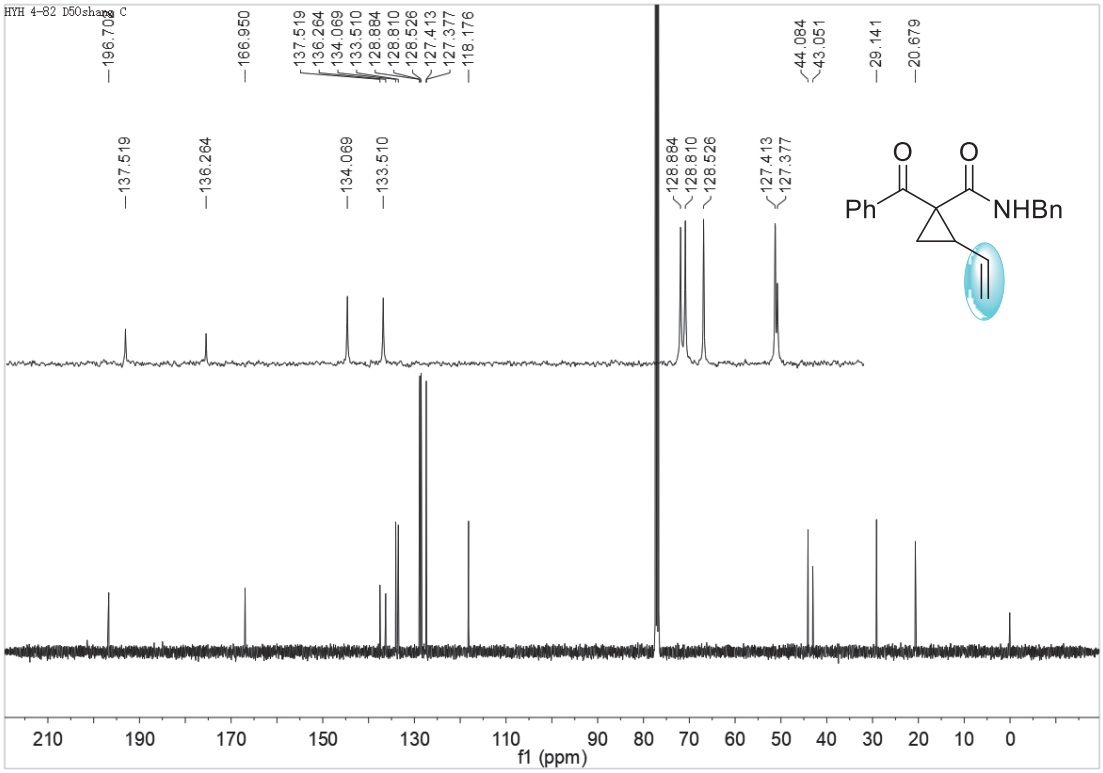
1'e4, DEPT 90 and DEPT 135



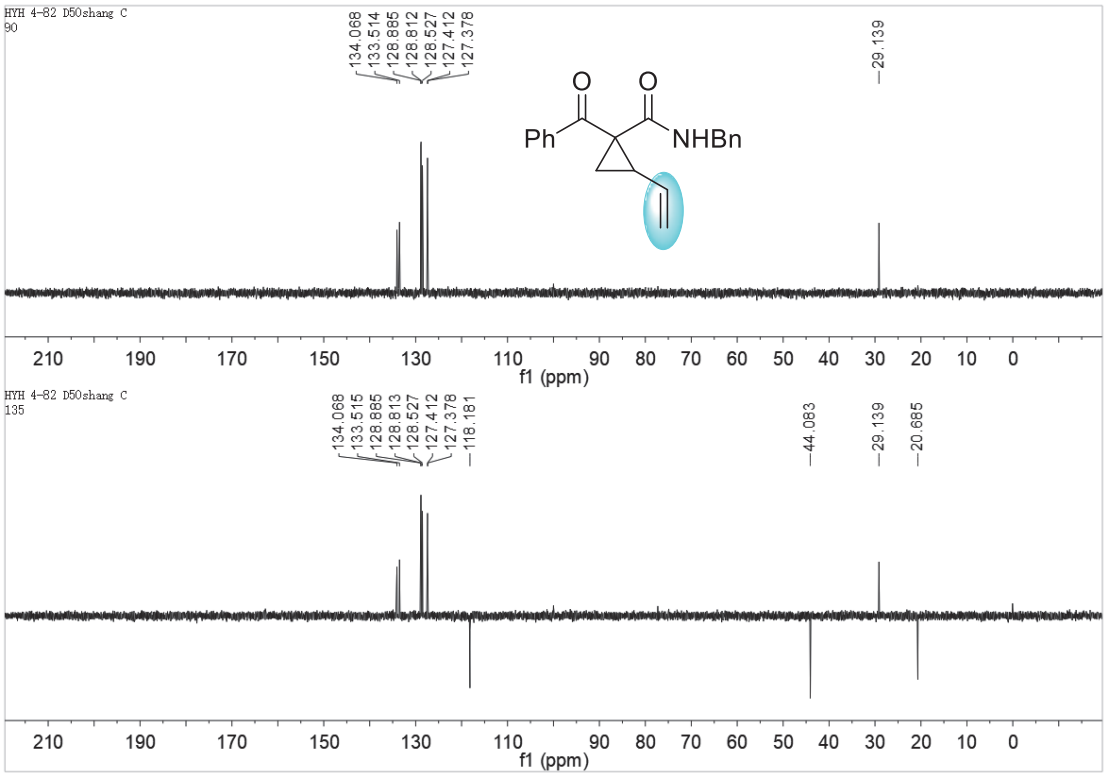
1'f, ^{1}H NMR



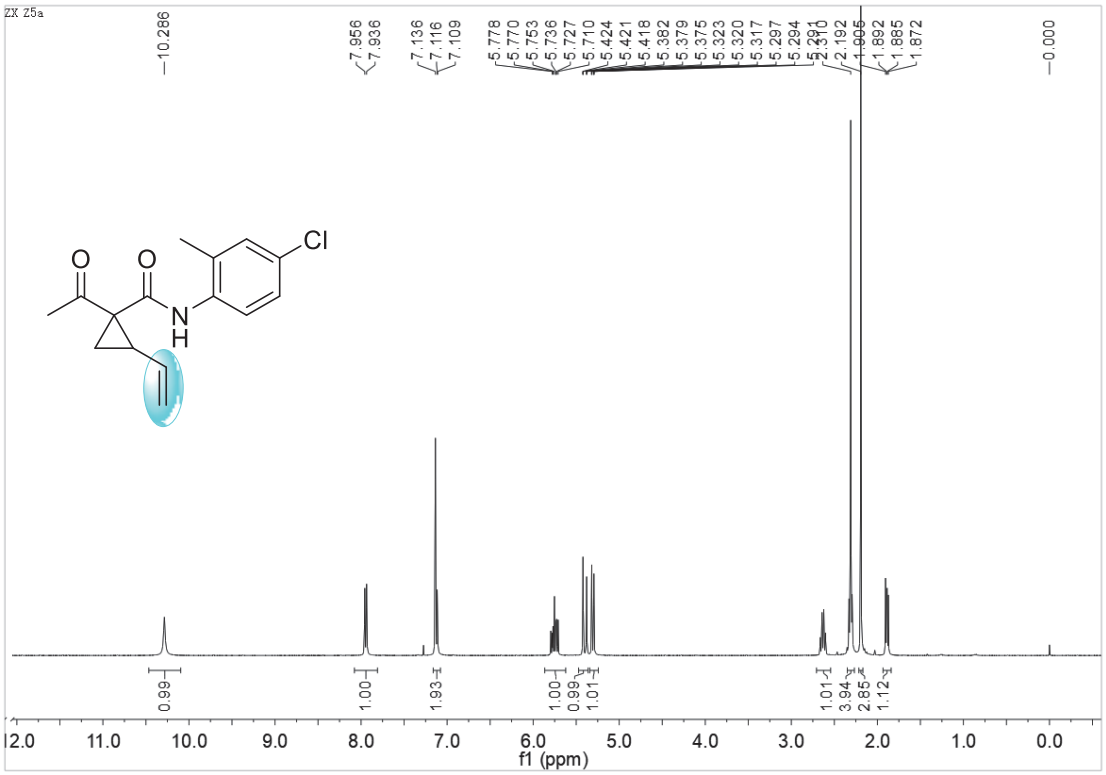
1'f, ^{13}C NMR



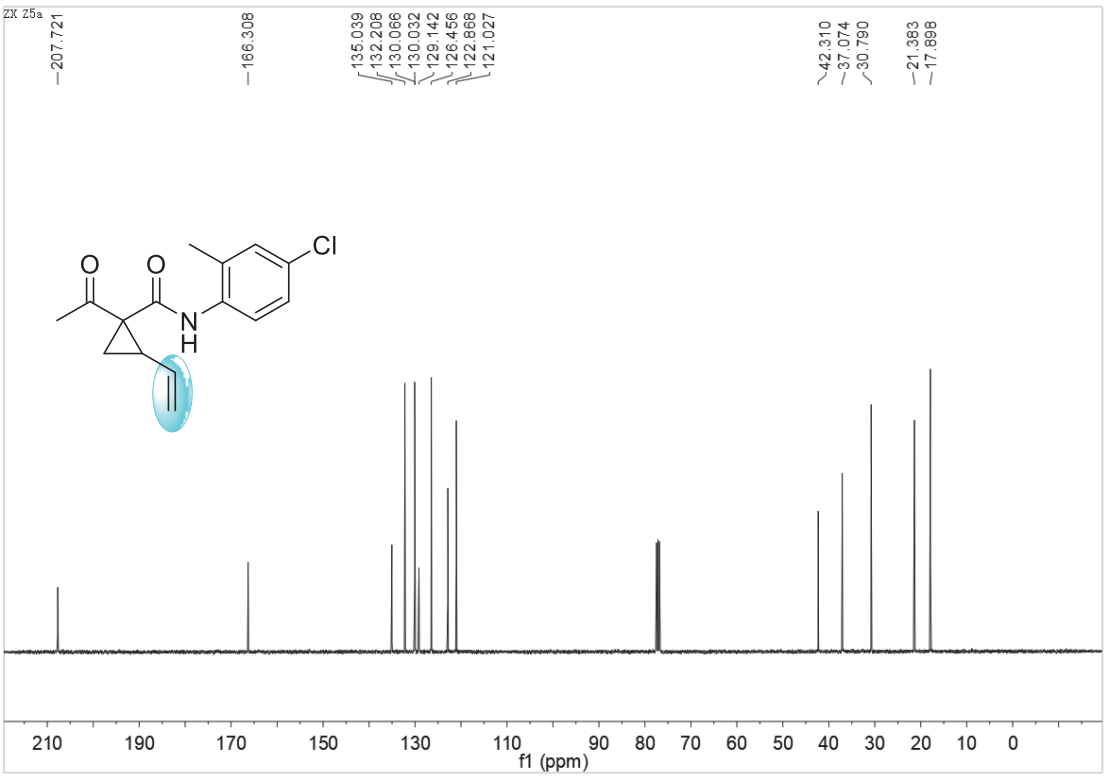
1'f, DEPT 90 and DEPT 135



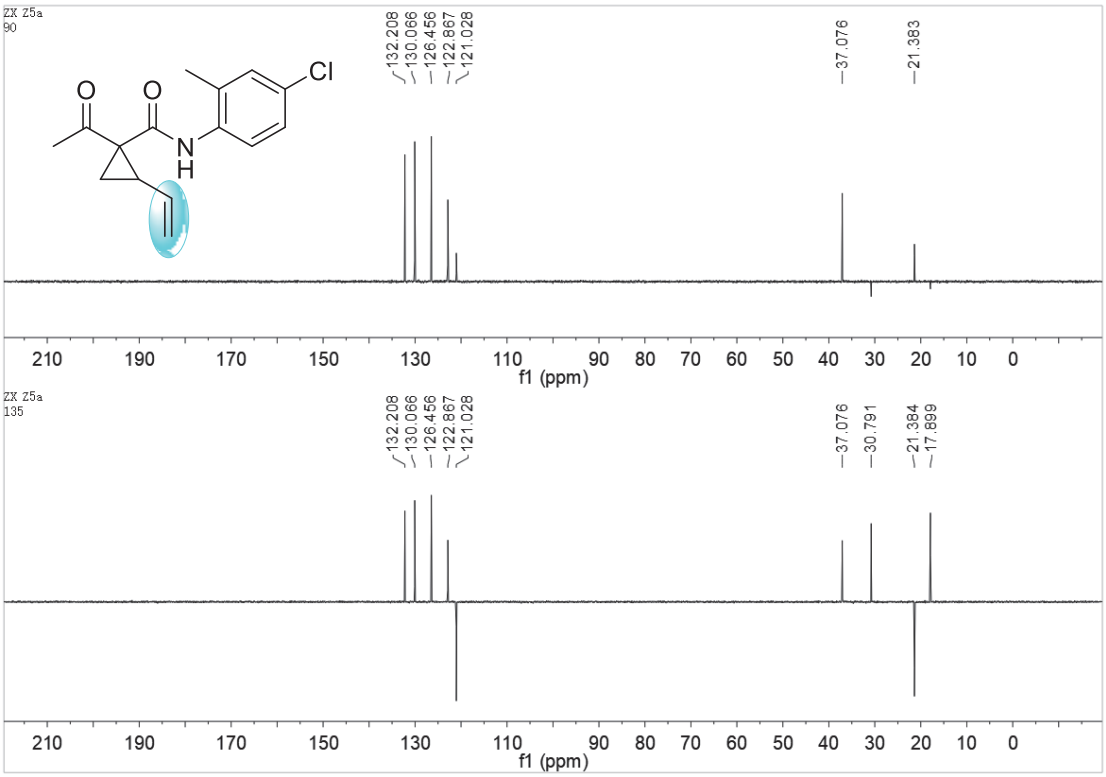
1'g2, ^{1}H NMR



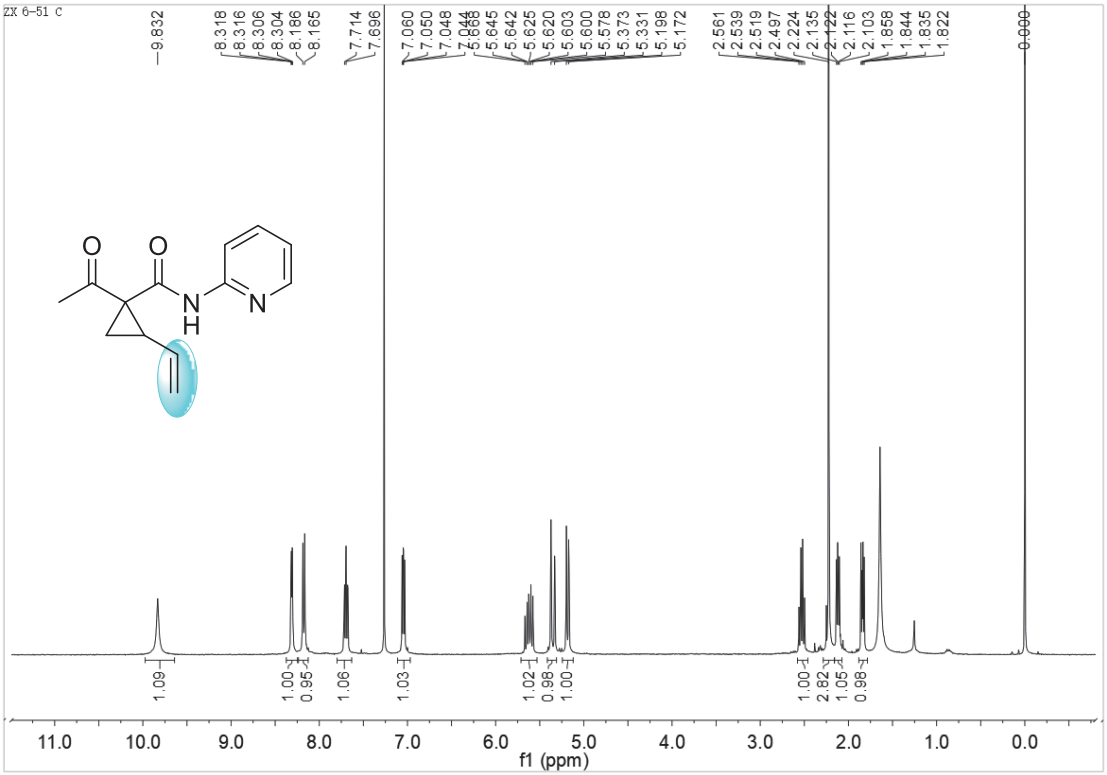
1'g2, ^{13}C NMR



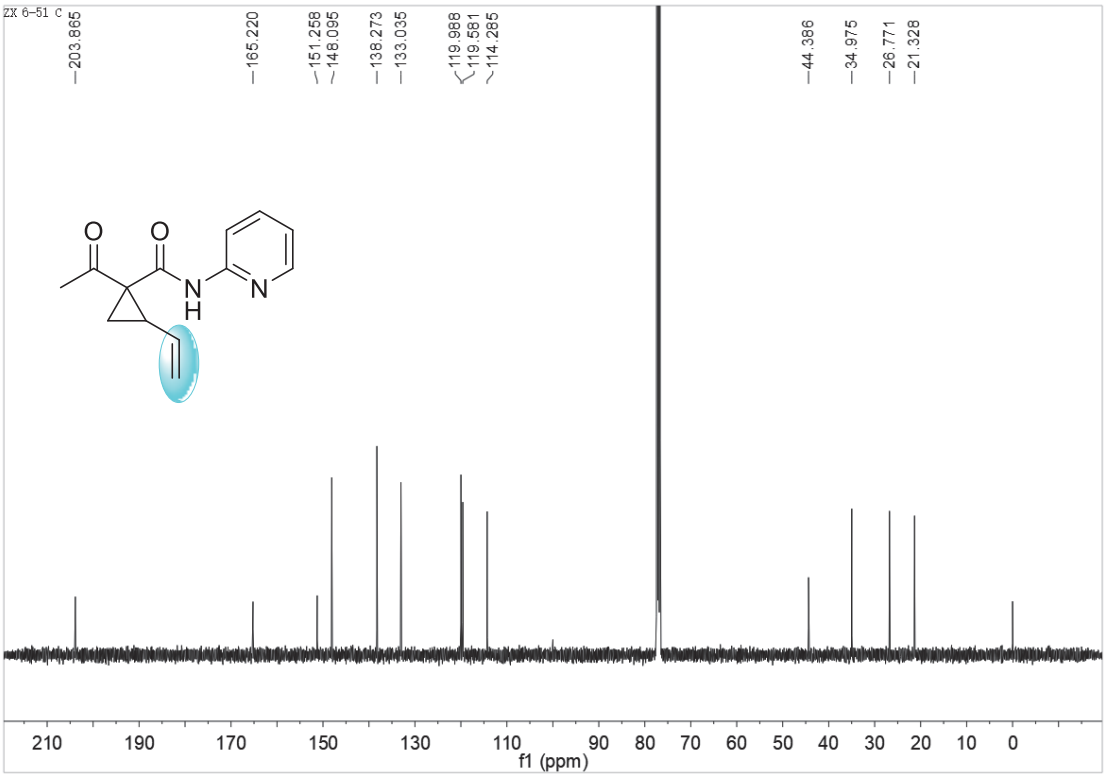
1'g2, DEPT 90 and DEPT 135



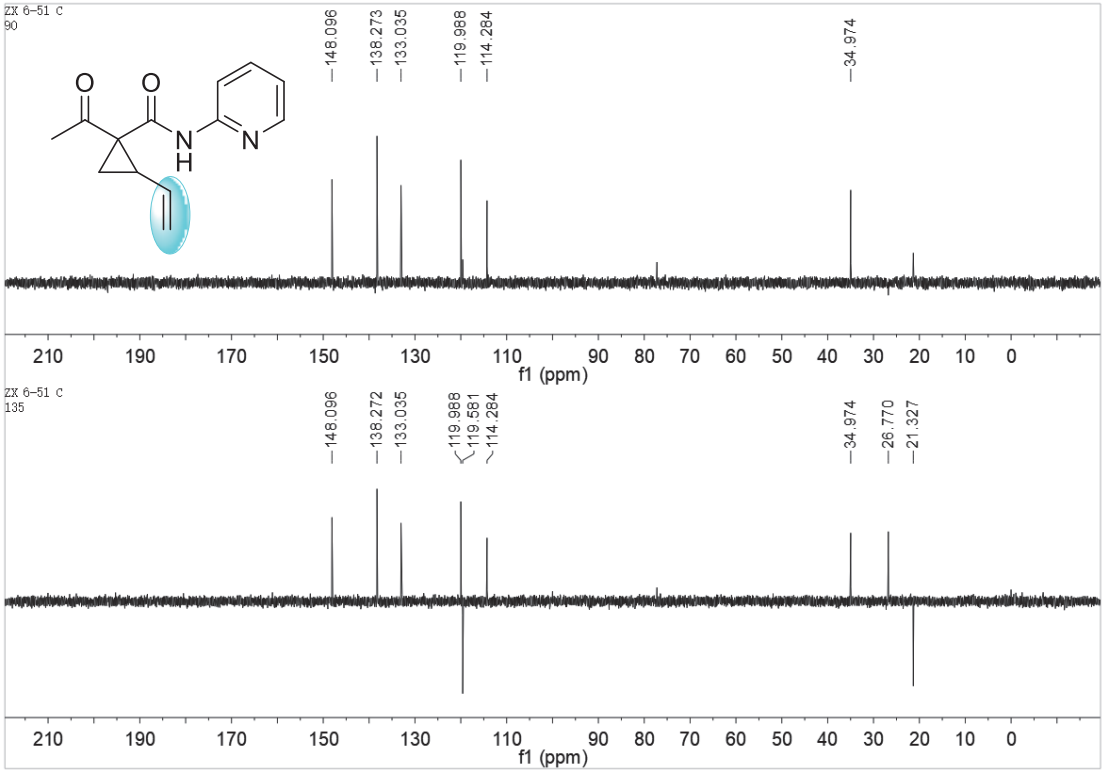
1'i, ^{1}H NMR



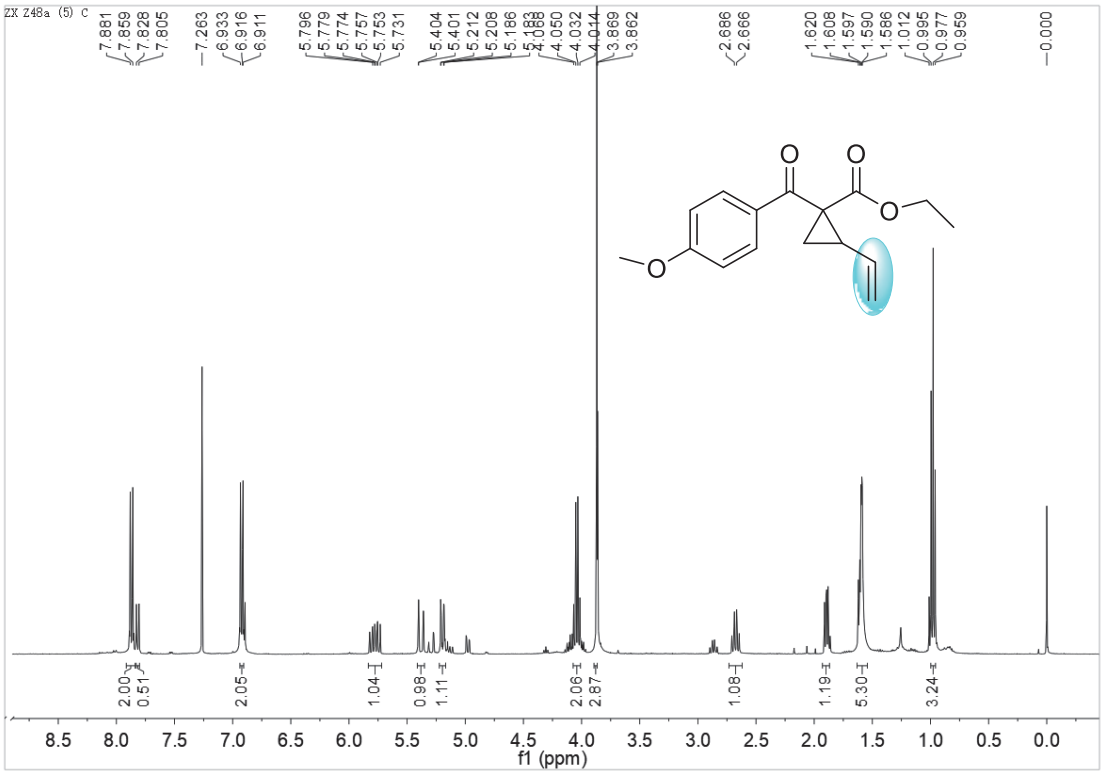
1'i, ^{13}C NMR



1'i, DEPT 90 and DEPT 135



1'j2, ^{1}H NMR



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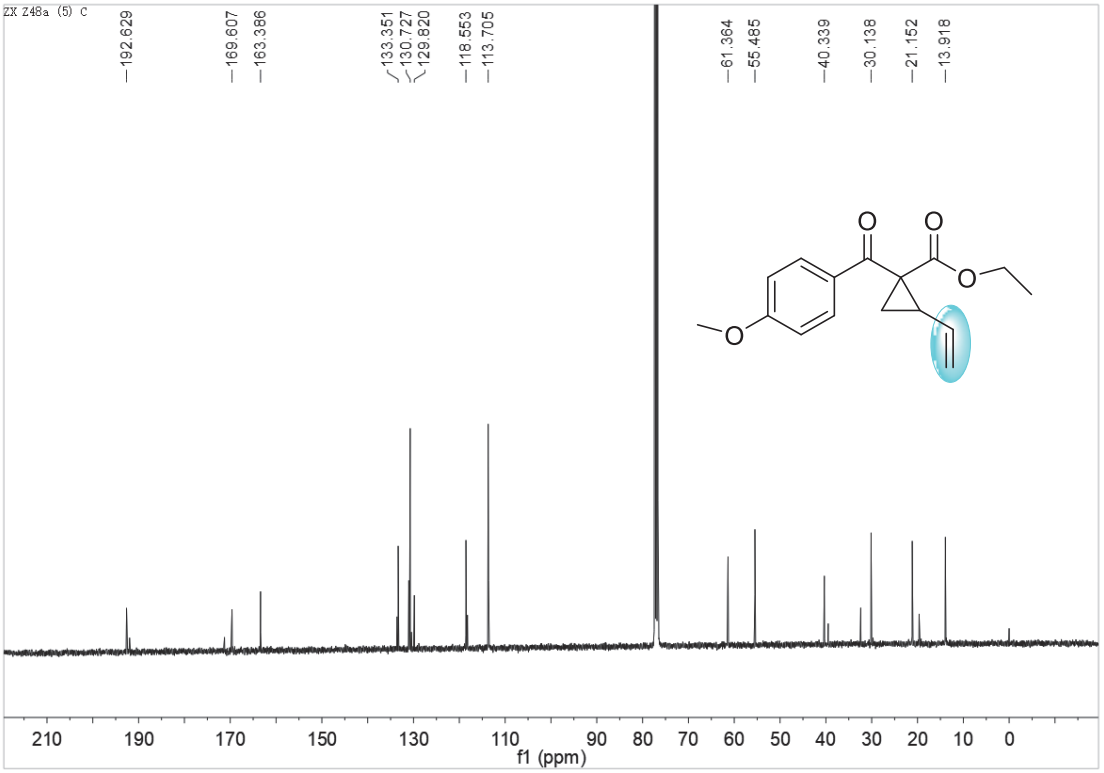
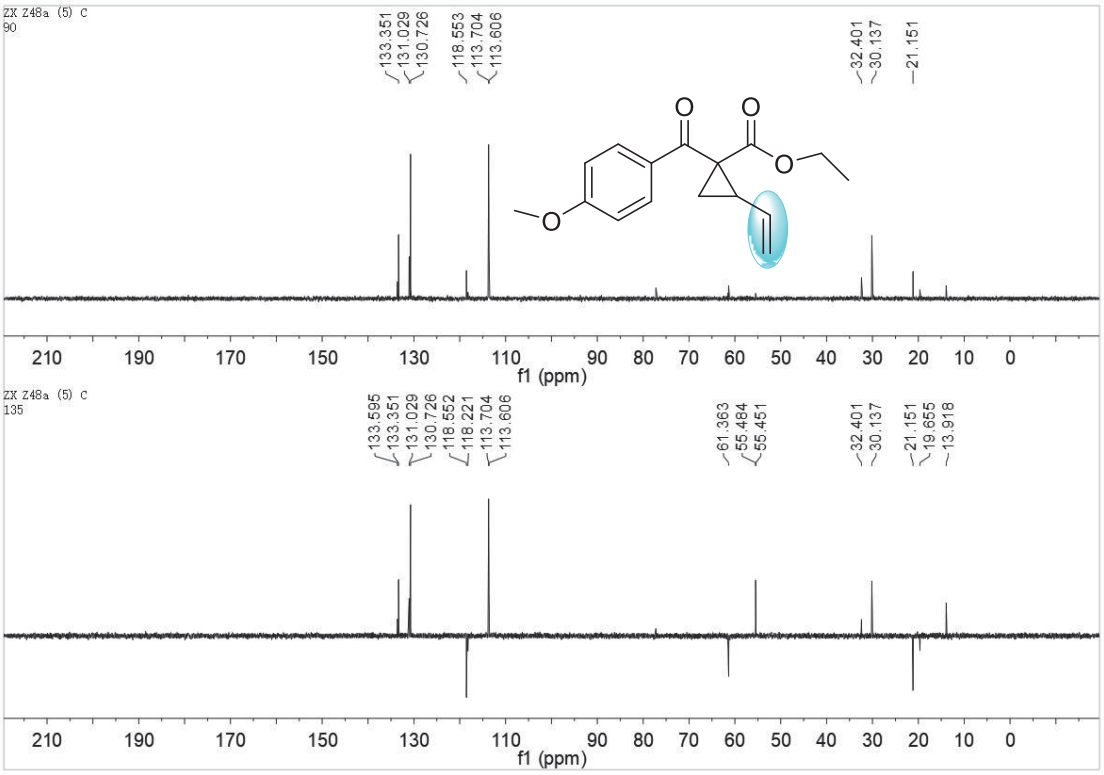


1'j2, DEPT 90 and DEPT 135



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