Supporting Information

Deoxygenation of Allyl Arylsulfones to Allyl Arylthioethers via "Cut-Sew" Strategy: Phosphines as Bifunctional Reagents

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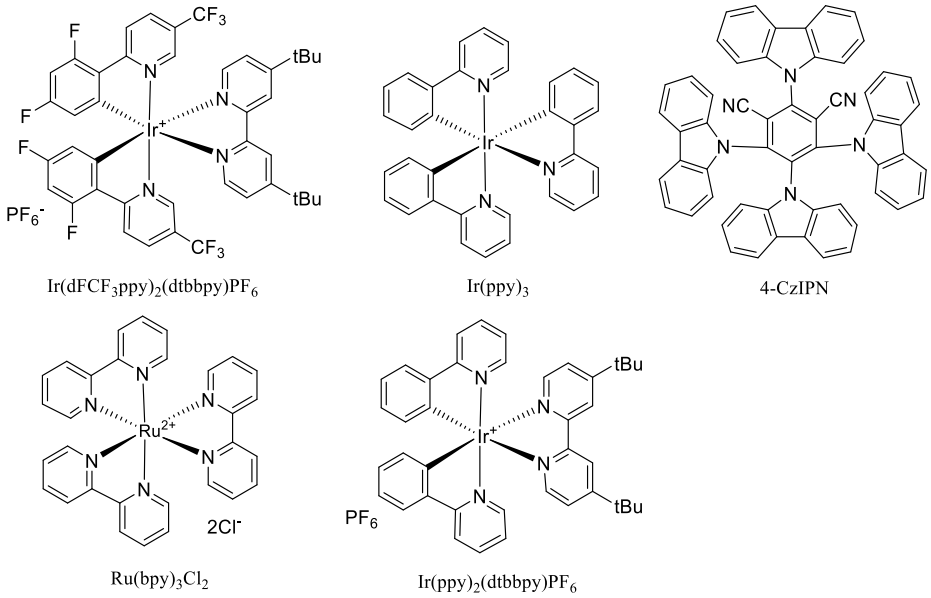
1. General Information

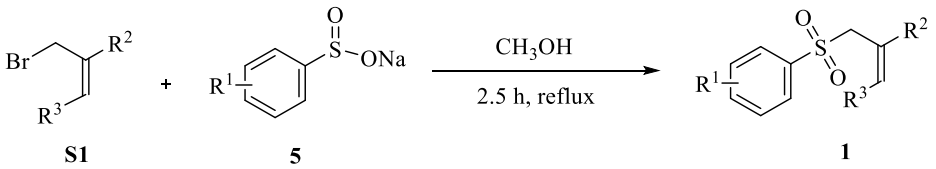
Unless otherwise noted, all reactions via general procedure were carried out under an atmosphere of argon. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance-III-HD (500 MHz). ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. The structures of known compounds were further corroborated by comparing their ^{1}H NMR and ^{13}C NMR data with those in literature. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (J) are in Hertz (Hz). A commercially available blue LED (25 W, luminous flux is not less than 3200 lm) was purchased from Chinese Taobao. All irradiation reactions were carried out in borosilicate glass vessel. The distance from the light source to the irradiation vessel is around 3-4 cm. The photocatalyst $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$, $Ir(ppy)_3$ were prepared follow literature procedures[1, 2]. Other reagents and solvents were purchased from *Energy Chemical.*



Scheme S1 The structure of photocatalysts

2. Substrate preparation

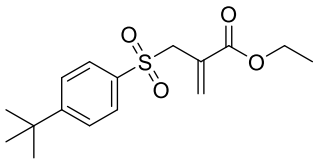
2.1 General procedure A



To a solution of **S1** (10.4 mmol) in dry methanol (25 mL), corresponding sodium aryl sulfinate (15.2 mmol) was added. After refluxing for 2.5 h, the mixture was concentrated under reduced pressure. The residue obtained was dissolved in EtOAc, and the mixture was washed with water, brine, dried over Na_2SO_4, and purified by flash column chromatography.[3]

The compounds **1a**, **1b**, **1d**, **1f**, **1r**, **1s**, **1u** and **1v-y** were known compounds. The new compounds **1c**, **1e**, **1g-1q** and **1aa** can be synthesized according to the method described above.

2.2 Analytical data of starting materials



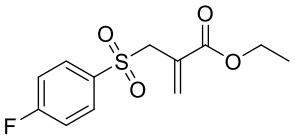
Ethyl 2-(((4-(tert-butyl)phenyl)sulfonyl)methyl)acrylate (1c)

According to the general procedure **A**, compound **1c** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 6.51 (s, 1H), 5.94 (s, 1H), 4.14 (s, 2H), 3.97 (q, J = 7.1 Hz, 2H), 1.33 (s, 9H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 157.8, 135.4, 133.3, 129.2, 128.6, 126.0, 61.3, 57.5, 35.2, 31.0, 14.0.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{22}O_4S$ $[M+H]^+$: 311.1311, found: 311.1308.



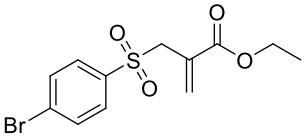
Ethyl 2-(((4-fluorophenyl)sulfonyl)methyl)acrylate (1e)

According to the general procedure **A**, compound **1e** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.24 – 7.16 (m, 2H), 6.52 (s, 1H), 5.95 (s, 1H), 4.16 (s, 2H), 4.04 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (d, J_1 = 256.7 Hz), 164.7, 134.4 (d, J_3 = 3.3 Hz), 133.5, 131.7 (d, J_3 = 9.6 Hz), 129.0, 116.3 (d, J_2 = 22.6 Hz), 61.5, 57.6, 14.0.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}FO_4S$ $[M+H]^+$: 273.0591, found: 273.0588.



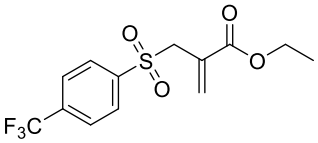
Ethyl 2-(((4-bromophenyl)sulfonyl)methyl)acrylate (1g)

According to the general procedure **A**, compound **1g** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.57 (m, 4H), 6.52 (s, 1H), 5.95 (s, 1H), 4.15 (s, 2H), 4.05 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 137.3, 133.5, 132.3, 130.3, 129.3, 128.9, 61.6, 57.5, 14.0.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}BrO_4S$ $[M+H]^+$: 332.9790, found: 332.9785.



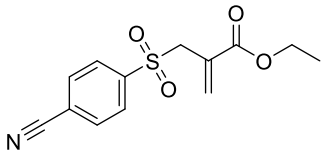
Ethyl 2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)acrylate (1h)

According to the general procedure **A**, compound **1h** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 6.54 (s, 1H), 5.99 (s, 1H), 4.19 (s, 2H), 4.00 (q, J = 7.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 141.8, 135.5 (q, J_2 = 33.2 Hz), 133.8, 129.5, 128.6, 126.1 (q, J_3 = 3.7 Hz), 123.0 (q, J_1 = 273.1 Hz), 61.6, 57.5, 13.9.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{13}F_3O_4S$ $[M+H]^+$: 323.0559, found: 323.0555.



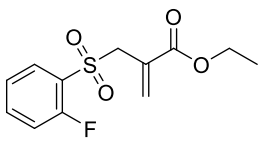
Ethyl 2-(((4-cyanophenyl)sulfonyl)methyl)acrylate (1i)

According to the general procedure **A**, compound **1i** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 6.55 (s, 1H), 6.00 (s, 1H), 4.19 (s, 2H), 4.04 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 142.5, 134.0, 132.7, 129.5, 128.5, 117.6, 117.0, 61.7, 57.4, 14.0.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{13}NO_4S$ $[M+H]^+$: 280.0638, found: 280.0634.



Ethyl 2-(((2-fluorophenyl)sulfonyl)methyl)acrylate (1j)

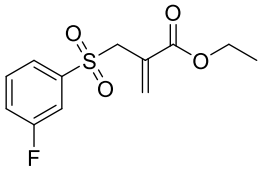
According to the general procedure **A**, compound **1j** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.67 – 7.58 (m, 1H), 7.32 – 7.18

(m, 2H), 6.48 (s, 1H), 5.92 (s, 1H), 4.34 (s, 2H), 4.06 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 159.9 (d, J_1 = 256.8 Hz), 136.3 (d, J_2 = 8.5 Hz), 133.7, 131.2, 128.6, 126.2 (d, J_2 = 14.5 Hz), 124.5 (d, J_3 = 3.9 Hz), 117.0 (d, J_2 = 21.3 Hz), 61.5, 56.9 (d, J_3 = 2.2 Hz), 13.9.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}FO_4S$ $[M+H]^+$: 273.0591, found: 273.0588.



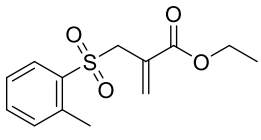
Ethyl 2-(((3-fluorophenyl)sulfonyl)methyl)acrylate (1k)

According to the general procedure **A**, compound **1k** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.34 (td, J = 8.3, 1.6 Hz, 1H), 6.53 (s, 1H), 5.95 (s, 1H), 4.17 (s, 2H), 4.05 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 162.3 (d, J_1 = 252.5 Hz), 140.4 (d, J_3 = 6.5 Hz), 133.6, 130.9 (d, J_3 = 7.4 Hz), 128.8, 124.6 (d, J_3 = 3.5 Hz), 121.1 (d, J_2 = 21.1 Hz), 116.1 (d, J_2 = 24.3 Hz), 61.6, 57.4, 13.9.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}FO_4S$ $[M+H]^+$: 273.0591, found: 273.0588.



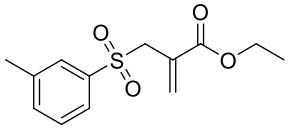
Ethyl 2-((o-tolylsulfonyl)methyl)acrylate (1l)

According to the general procedure **A**, compound **1l** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.4 Hz, 2H), 6.49 (s, 1H), 5.96 (s, 1H), 4.18 (s, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.74 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 138.8, 136.4, 133.8, 133.4, 132.6, 131.0, 128.8, 126.2, 61.4, 56.5, 20.5, 13.9.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{16}O_4S$ $[M+H]^+$: 269.0842, found: 269.0838.



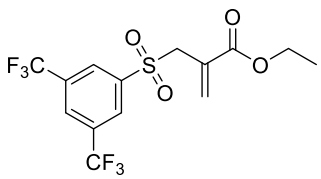
Ethyl 2-((m-tolylsulfonyl)methyl)acrylate (1m)

According to the general procedure **A**, compound **1m** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 9.0 Hz, 2H), 7.49 – 7.36 (m, 2H), 6.50 (s, 1H), 5.91 (s, 1H), 4.14 (s, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 139.3, 138.3, 134.6, 133.2, 129.1, 128.9, 128.9, 125.8, 61.4, 57.5, 21.2, 13.9.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{16}O_4S$ $[M+H]^+$: 269.0842, found: 269.0839.



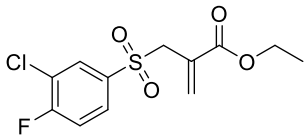
Ethyl 2-(((3,5-bis(trifluoromethyl)phenyl)sulfonyl)methyl)acrylate (1n)

According to the general procedure **A**, compound **1n** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 2H), 8.14 (s, 1H), 6.61 (s, 1H), 6.10 (s, 1H),

4.24 (s, 2H), 4.00 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 141.2, 134.5, 132.9 (q, J_2 = 34.8 Hz), 129.2 (d, J_3 = 3.8 Hz), 128.3, 127.7 – 127.2 (m), 122.3(q, J_1 = 273.4 Hz), 61.8, 57.6, 13.8.



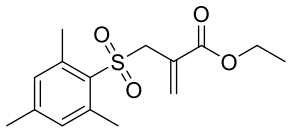
Ethyl 2-(((3-chloro-4-fluorophenyl)sulfonyl)methyl)acrylate (1o)

According to the general procedure **A**, compound **1o** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 6.7, 2.3 Hz, 1H), 7.76 (ddd, J = 8.6, 4.4, 2.3 Hz, 1H), 7.30 (t, J = 8.5 Hz, 1H), 6.55 (s, 1H), 5.99 (s, 1H), 4.17 (s, 2H), 4.06 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 161.4 (d, J_1 = 258.9 Hz), 135.4 (d, J_3 = 3.9 Hz), 133.8, 131.7, 129.4 (d, J_3 = 8.7 Hz), 128.7, 122.5 (d, J_2 = 18.8 Hz), 117.4 (d, J_2 = 22.3 Hz), 61.7, 57.6, 14.0.

HRMS (ESI, m/z) calcd for $C_{12}H_{12}ClFO_4S$ $[M+H]^+$: 307.0201, found: 307.0198.

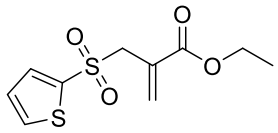


Ethyl 2-((mesitylsulfonyl)methyl)acrylate (1p)

According to the general procedure **A**, compound **1p** was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.48 (s, 1H), 5.93 (s, 1H), 4.14 (s, 2H), 4.02 (q, J = 7.2 Hz, 2H), 2.64 (s, 6H), 2.28 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 143.5, 140.6, 133.1, 132.5, 132.0, 128.7, 61.4, 57.1, 23.0, 21.0, 13.9.



Ethyl 2-((thiophen-2-ylsulfonyl)methyl)acrylate (1q)

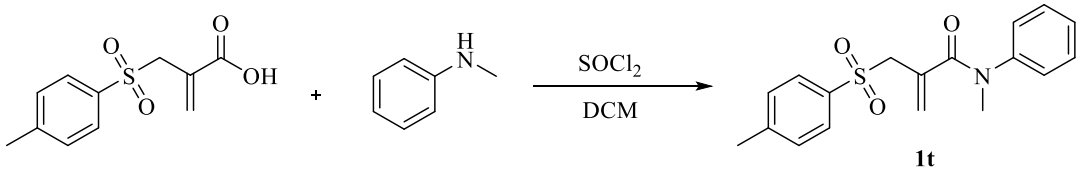
According to the general procedure **A**, compound **1q** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 5.0, 1.3 Hz, 1H), 7.62 (dd, J = 3.8, 1.4 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 6.55 (s, 1H), 5.95 (s, 1H), 4.25 (s, 2H), 4.08 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 139.1, 135.0, 134.5, 133.5, 129.1, 127.7, 61.5, 58.6, 14.0.

HRMS (ESI, m/z) calcd for $C_{10}H_{13}O_4S_2$ $[M+H]^+$: 261.0249, found: 261.0243.

Synthesis of *N*-methyl-*N*-phenyl-2-(tosylmethyl)acrylamide (1t)



1t

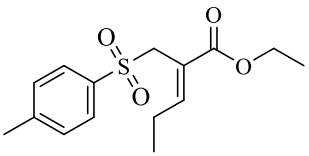
The 2-(tosylmethyl)acrylic acid (3 mmol, 0.68 g) was dissolved in excess $SOCl_2$ (96 mmol, 11.3 g) and heated under reflux for 4 h, then the excess $SOCl_2$ was removed, the remaining acid chloride was dissolved in 10 equivalents of DCM, then *N*-methylaniline (19 mmol, 2.03 g) was added to the acid chloride system in an ice-water bath, and then stirred at room temperature for 16 h. After the reaction was completed, the product was concentrated, absorbed with Et_2O, washed with 5%HCl, washed with saturated aqueous Na_2CO_3, washed with brine and dried over anhydrous Na_2SO_4 to give the product **1t** (0.414 g, 42 % yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.33

– 7.26 (m, 5H), 5.34 (s, 1H), 5.29 (s, 1H), 3.93 (s, 2H), 3.35 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 144.8, 144.2, 135.8, 132.1, 129.6, 129.5, 128.3, 127.2, 126.8, 60.1, 38.8, 21.6, 1.8.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{20}NO_3S$ $[M+H]^+$: 330.1158, found: 330.1151.



Ethyl 2-(tosylmethyl)pent-2-enoate (1aa)

According to the general procedure **A**, compound **1aa** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 4.18 (s, 2H), 3.90 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 2.18 (p, J = 7.6 Hz, 2H), 1.09 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H).

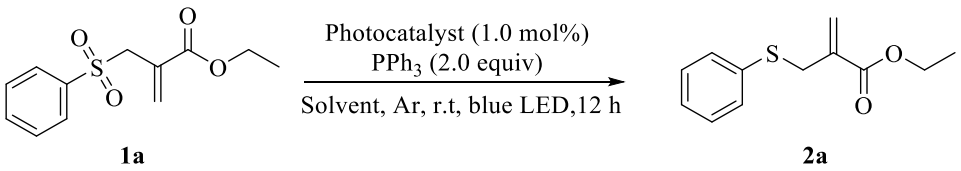
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 152.6, 144.6, 136.0, 129.5, 128.7, 120.3, 61.0, 53.9, 23.0, 21.6, 14.0, 12.6.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{18}O_4S[M+H]^+$: 283.0998, found: 283.0993.

3. Reaction condition optimization

3.1 Deoxygenation reaction condition optimization

Table S1. Screening Lewis base, photoredox catalysts and solvent.[a]

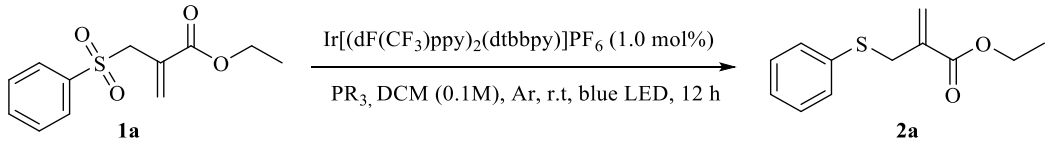


1a **2a**

Entry	PC	Solvent	Yield/%[b]
1[c]	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.1 M)	17
2[d]	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.1 M)	6
3[e]	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.1 M)	28
4	**$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$**	**DCM (0.1 M)**	**51**
5	$Ru(bpy)_3Cl_2$	DCM (0.1 M)	19
6	4-CzIPN	DCM (0.1 M)	21
7	*fac*-$Ir(ppy)_3$	DCM (0.1 M)	18
8	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF (0.1 M)	35
9	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	CH_3CN (0.1 M)	42
10	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DMSO (0.1 M)	10
11	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCE (0.1 M)	50
12	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	$PhCF_3$ (0.1 M)	39
13	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.05 M)	43
14	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.2 M)	49
15[f]	-	DCM (0.1 M)	trace
16[g]	$Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM (0.1 M)	N. R.

[a]Reaction condition: **1a** (0.2 mmol), Solvent (varied), PPh_3 (0.4 mmol), photoredox catalyst (1 mol%) under Ar atmosphere. Stirred at room temperature under blue LEDs (25 W). [b]Isolated yield. [c]additional addition of Et_3N (1.0 equiv). [d]additional addition of DABCO (1.0 equiv). [e]additional addition of DBU (1.0 equiv). N.R.= not reaction. [f]Without photocatalyst. [g]In the dark.

Table S2. Screening phosphides source[a].

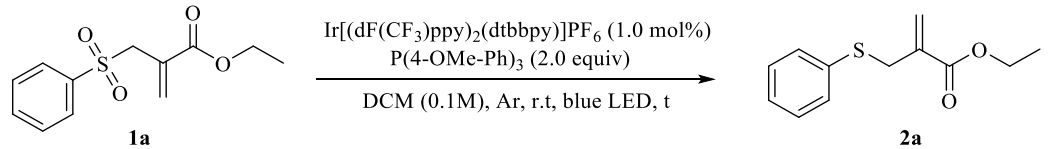


1a **2a**

Entry	PR_3	Yield/%[b]
1	PPh_3 (1.5 equiv)	34
2	PPh_3 (2.0 equiv)	51
3	PPh_3 (2.5 equiv)	50
4	PPh_3 (3.0 equiv)	42
5	PPh_3 (4.0 equiv)	36
6	$P(4\text{-F-Ph})_3$ (2.0 equiv)	trace
7	**$P(4\text{-OMe-Ph})_3$ (2.0 equiv)**	**55**

[a]Reaction condition: **1a** (0.2 mmol), DCM (0.1 M), $Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1.0 mol%) under Ar atmosphere. Stirred at room temperature under blue LEDs (25 W). [b]Isolated yield.

Table S3. Screening reaction time[a]



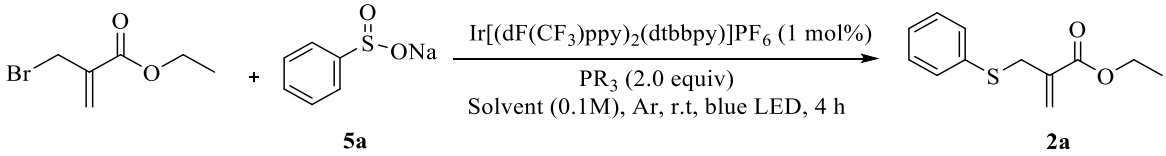
1a **2a**

Entry	t (h)	Yield/%[b]
1	12	55
2	6	59
3	**4**	**71**
4	3	60

[a]Reaction condition: **1a** (0.2 mmol), DCM (0.1 M), $Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%), $P(4\text{-OMe-Ph})_3$ (0.4 mmol) under Ar atmosphere. Stirred at room temperature under blue LEDs (25 W). [b]Isolated yield.

3.2 Deoxyallylation Reaction Condition optimization

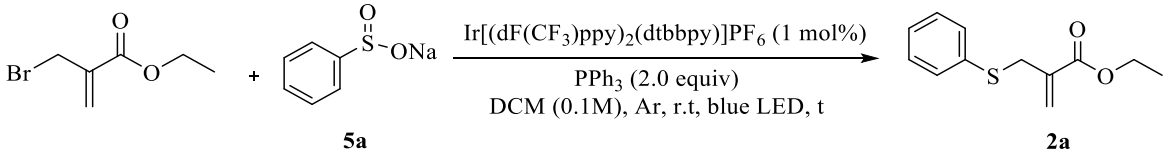
Table S4. Screening of solvents and triarylphosphines.[a]



Entry	PR_3	Solvent	Yield/%[b]
1	**PPh_3 (2.0 equiv)**	**DCM (0.1 M)**	**39**
2	P(Ph-OMe)$_3$ (2.0 equiv)	DCM (0.1 M)	trace
3	P(Ph-F)$_3$ (2.0 equiv)	DCM (0.1 M)	15
4	PPh_3 (2.0 equiv)	CH_3CN (0.1 M)	35
5	PPh_3 (2.0 equiv)	PhMe (0.1 M)	8
6	PPh_3 (2.0 equiv)	THF (0.1 M)	12
7	PPh_3 (2.0 equiv)	DCE (0.1 M)	30

[a]Reaction condition: ethyl 2-(bromomethyl)acrylate (0.2 mmol), **5a** (0.2 mmol), Ir[(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (1 mol%), PR_3 (2.0 equiv), Solvent (0.1 M) under Ar atmosphere. Stirred at room temperature under blue LEDs (25 W). [b]Isolated yield.

Table S5. Screening reaction time and base.[a]

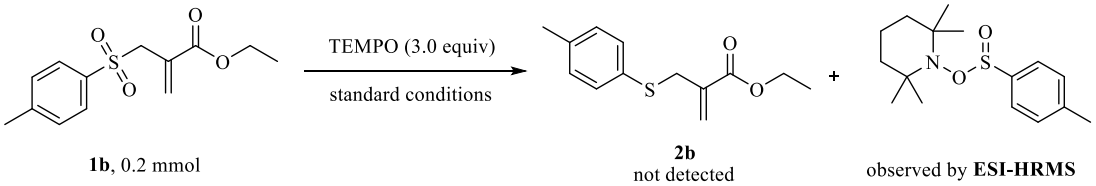


Entry	t (h)	base	Yield/%[b]
1	4	/	39
2	**12**	**/**	**54**
3	14	/	53
4	12	Cs_2CO_3 (1.0 equiv)	52
5	12	K_3PO_4 (1.0 equiv)	45
6	12	K_2HPO_4 (1.0 equiv)	28

[a]Reaction condition: ethyl 2-(bromomethyl)acrylate (0.2 mmol), **5a** (0.2 mmol), $Ir[(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%), PPh_3 (0.4 mmol), DCM (0.1 M) under Ar atmosphere. Stirred at room temperature under blue LEDs (25 W). [b]Isolated yield.

4. Mechanistic studies

4.1 Radical trapping experiment



Under an argon atmosphere, allyl sulfone **1b** (0.2 mmol, 53.6 mg), triarylphosphine (0.4 mmol, 140.8 mg), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%), and TEMPO (0.6 mmol, 93.6 mg) were added to the reaction tube, followed by DCM as the solvent. The reaction was allowed to proceed under blue light irradiation for 4 hours. The mixture was passed through a short pad of Celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure. Product **2b** was not detected, but the TEMPO adduct was captured by ESI. Based on these results, we speculate that the reaction is a radical-involved reaction, in which sulfoxide radicals are generated during the reaction process.

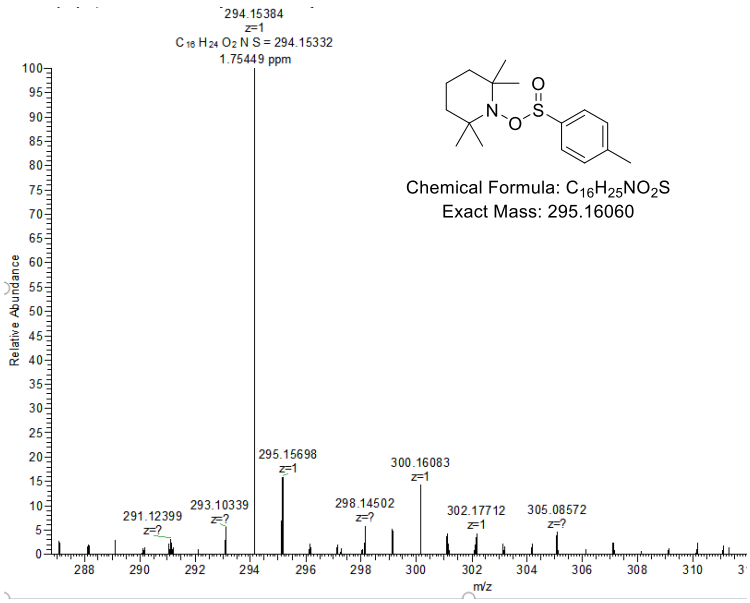


Figure S1 ESI spectrum of the TEMPO-adduct

4.2 Stern-Volmer quenching experiments

Formulation solution: Sodium benzenesulfite (164.2 mg) was dissolved in methanol in a 10 mL reaction flask to obtain a concentration to be 0.1 M. P(4-OMe-Ph)$_3$ (352 mg) was dissolved in DCM in a 25 mL volumetric flask to set the concentration to be 0.1 M. Ethyl 2-(bromomethyl)acrylate (14 μL) was dissolved in DCM in a 25 mL volumetric flask to set the concentration to be 0.1 M. **1a** (256 mg) was dissolved in DCM in a 5 mL volumetric flask to set the concentration to be 0.1 M. Photocatalyst [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (3.8 mg) was dissolved in DCM (25 mL) to set the concentration to be 0.1 mM. (2-(Ethoxycarbonyl)allyl)tris(4-methoxyphenyl)phosphonium bromide (544 mg) was dissolved in DCM in a 10 mL reaction flask to obtain a concentration to be 0.1 M. Ethyl 2-(tosylmethyl)acrylate (1.0 equiv) and P(4-OMe-Ph)$_3$ (1.0 equiv) were stirred in DCM for one hour, and the mixture solution was prepared in 0.1M.

Experimental procedure: For the fluorescence quenching experiments, stock solutions of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) solutions (2.5×10^{-5} M), Sodium benzenesulfite (0.5×10^{-3} M), P(4-OMe-Ph)$_3$ (0.5×10^{-3} M), ethyl 2-(bromomethyl)acrylate (0.5×10^{-3} M), **1a** (0.5×10^{-3} M), (2-(ethoxycarbonyl)allyl)tris(4-methoxyphenyl)phosphonium bromide (0.5×10^{-3} M) and Reaction mixture of **1a** and P(4-OMe-Ph)$_3$ (0.5×10^{-3} M) were prepared in DCM in a 3 mL quartz cuvette. Samples were obtained by mixing a fixed volume of the stock solution of the photocatalyst ([Ir]PF$_6$) and variable amount of the quencher. Before the measurements, argon gas was bubbled into the solutions for 1-2 minutes. Thereafter, the emission spectra were recorded for each sample from a wavelength of 410 nm to 700 nm, as shown in the following figures.

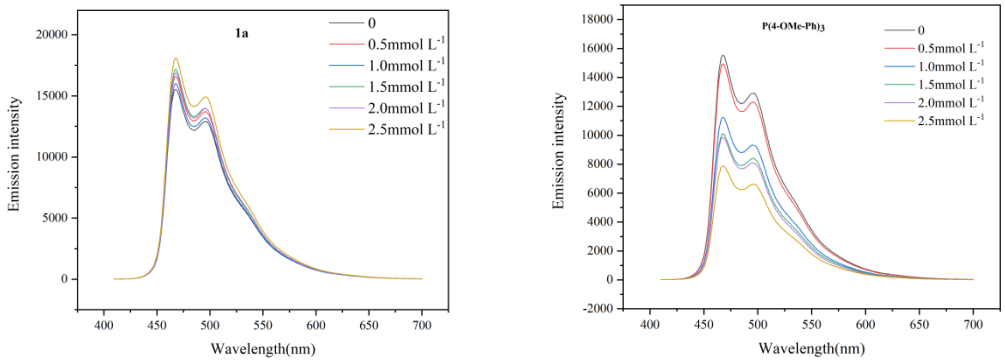


Figure S2 Fluorescence quenching of $[Ir]PF_6$ with **1a** and $P(4\text{-}OMe\text{-}Ph)_3$

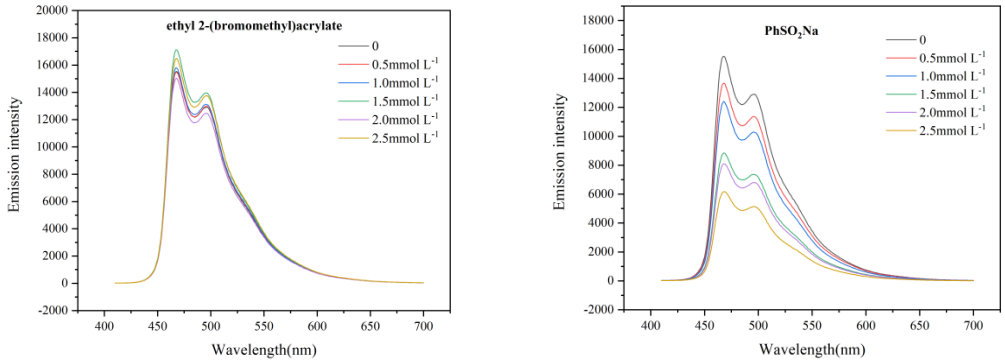


Figure S3 Fluorescence quenching of $[Ir]PF_6$ with ethyl 2-(bromomethyl)acrylate and $PhSO_2Na$

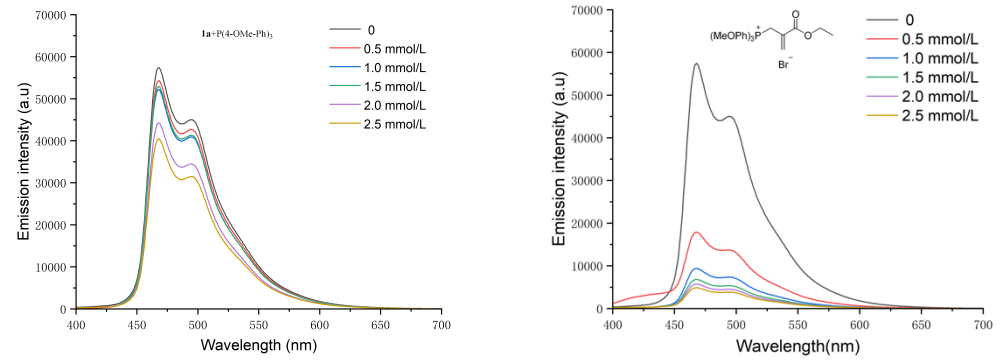


Figure S4 Fluorescence quenching of $[Ir]PF_6$ with Reaction mixture of **1a** and $P(4\text{-}OMe\text{-}Ph)_3$, (2-(ethoxycarbonyl)allyl)tris(4-methoxyphenyl)phosphonium bromide **4**.

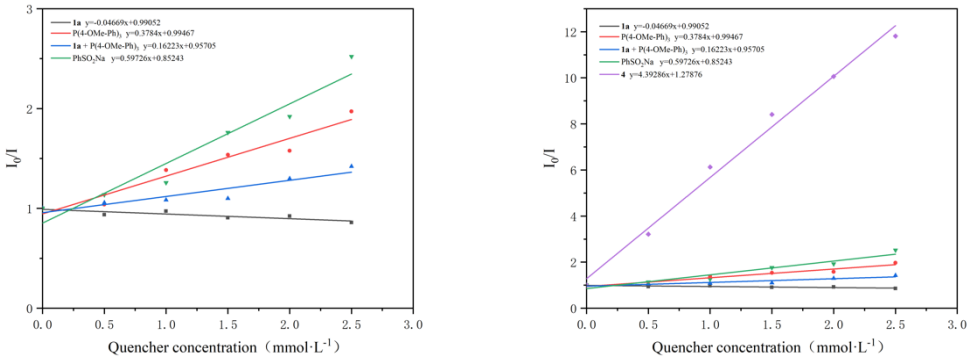
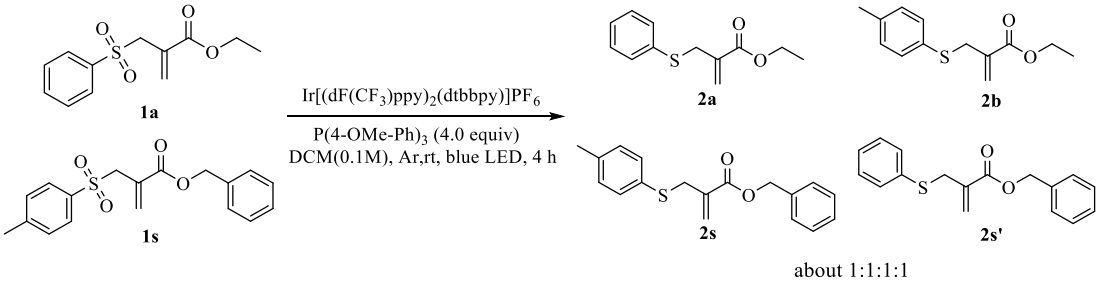


Figure S5 Stern-Volmer plots of reaction substrates.

4.3 Cross-over experiment



Under an argon atmosphere, allyl sulfone **1a** (0.2 mmol, 50.8 mg), allyl sulfone **1s** (0.2 mmol, 66.0 mg), triaryl phosphine (0.8 mmol, 281.6 mg), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%), and DCM as the solvent were added to the reaction tube. The reaction was stirred at room temperature under 25W blue LEDs for 4 h. Then, the mixture was passed through a short pad of celite and rinsed with EtOAc. The filtrate was evaporated to dryness under reduced pressure, and the crude residue was directly identified by NMR. Products **2a**, **2b**, **2s**, and **2s'** were detected. Based on the obtained products, we can infer that the reaction is actually an intermolecular reaction, that is, allyl sulfone undergoes bond cleavage during the reaction to generate two different active species. According to the NMR spectrum, the ratio of the four product groups is close to 1:1:1:1.

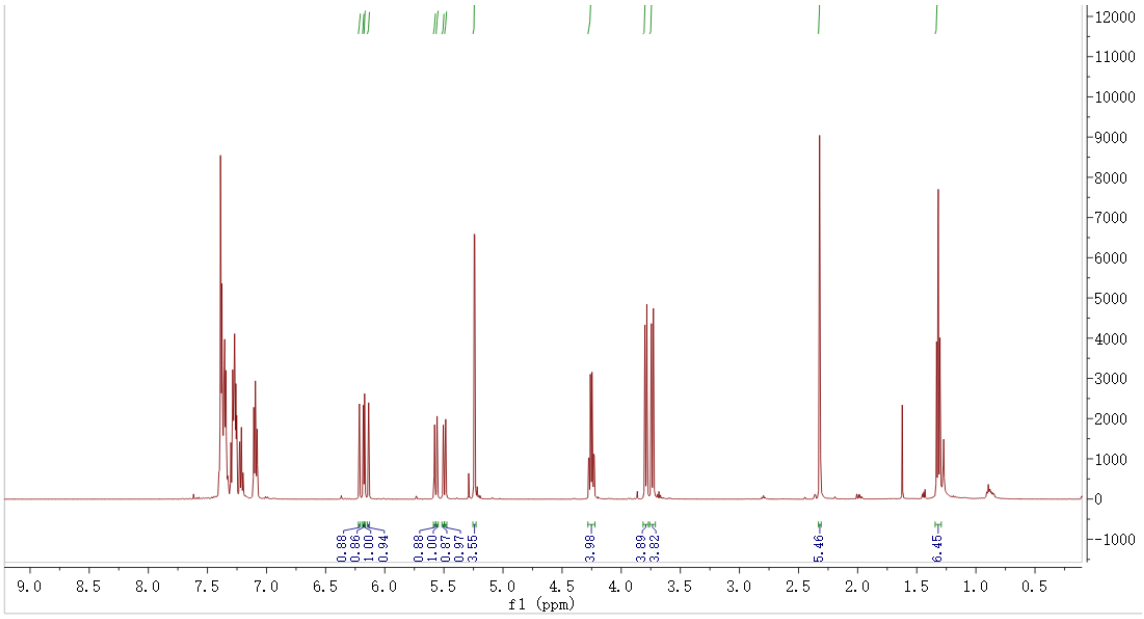
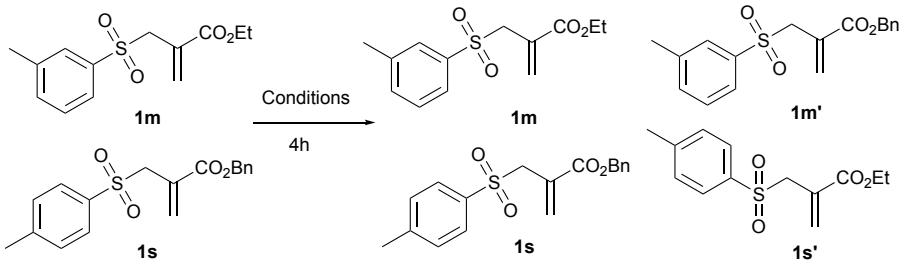


Figure S6 Crude ^{1}H NMR of crossover experimental products

4.4 Experiments to Probe C-S deconstruction



	PC, *hv*	P(4-OMe-Ph)$_3$ (5 mol%)	4-Me-PhSO$_2$Na (5 mol%)	Distribution of allyl sulfones
Entry 1	✔	✘	✘	**1m** + **1s**
Entry 2	✘	✘	✔	**1m** + **1s**
Entry 3	✔	✘	✔	**1m** + **1m'** + **1s** + **1s'**
Entry 4	✔	✔	✘	**1m** + **1m'** + **1s** + **1s'**
Entry 5	✘	✔	✘	**1m** + **1m'** + **1s** + **1s'**

To figure out how this sp^3 C-S bond deconstructed, control experiments using **1m** and **1s** were carried out. Under an argon atmosphere, allyl sulfone 1**m** (0.1 mmol, 26.8 mg), allyl sulfone **1s** (0.08 mmol, 26.4 mg), and $CDCl_3$ as the solvent were added to the NMR tube. Other reagents and reaction conditions were selectively added according to different reaction conditions. The ^{1}H NMR spectra were recorded after 4h.

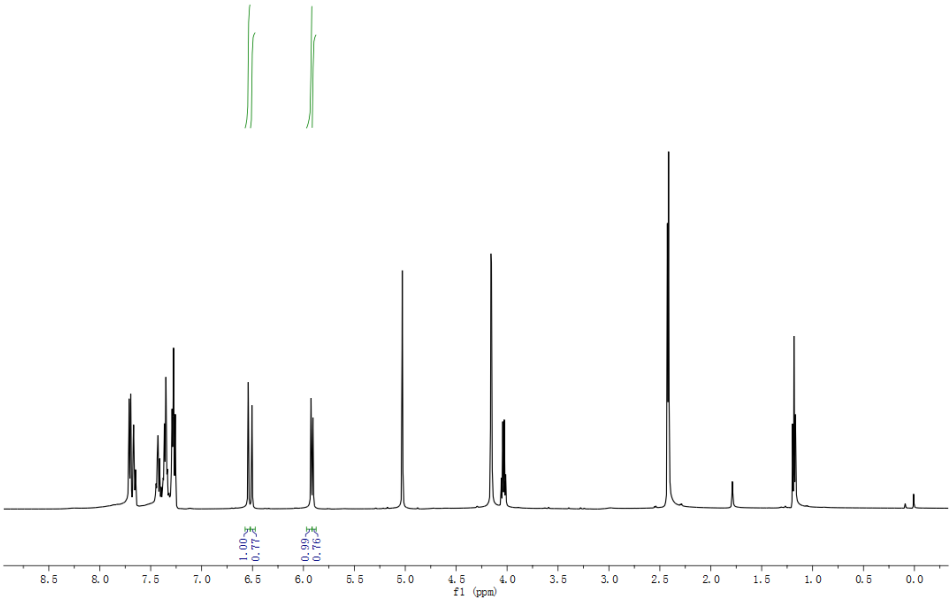


Figure S7 ^{1}H NMR of Entry 2

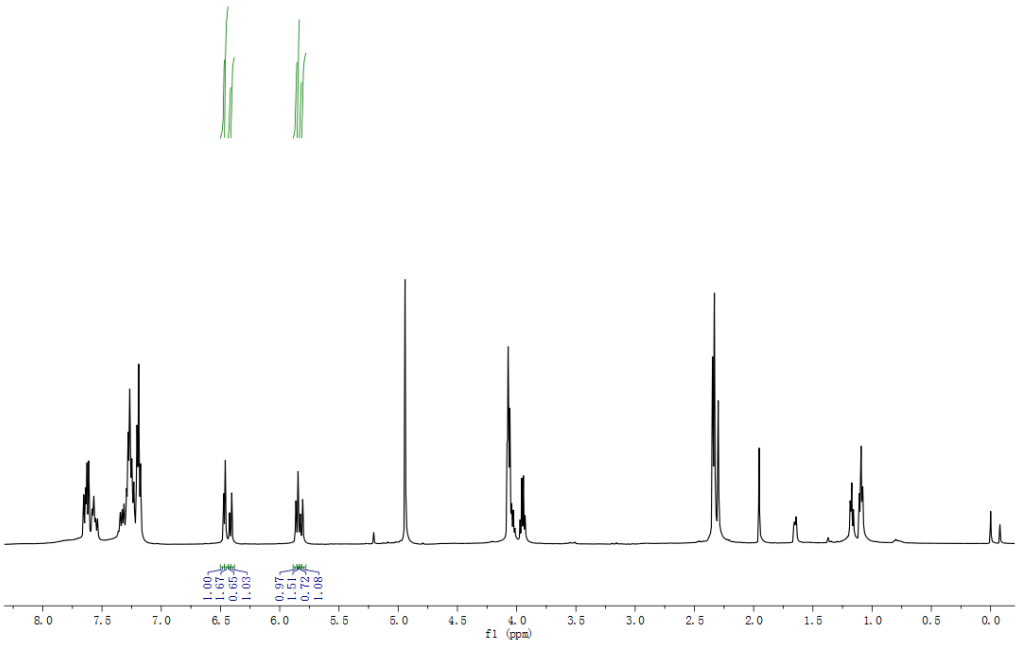


Figure S8 ^{1}H NMR of Entry 3

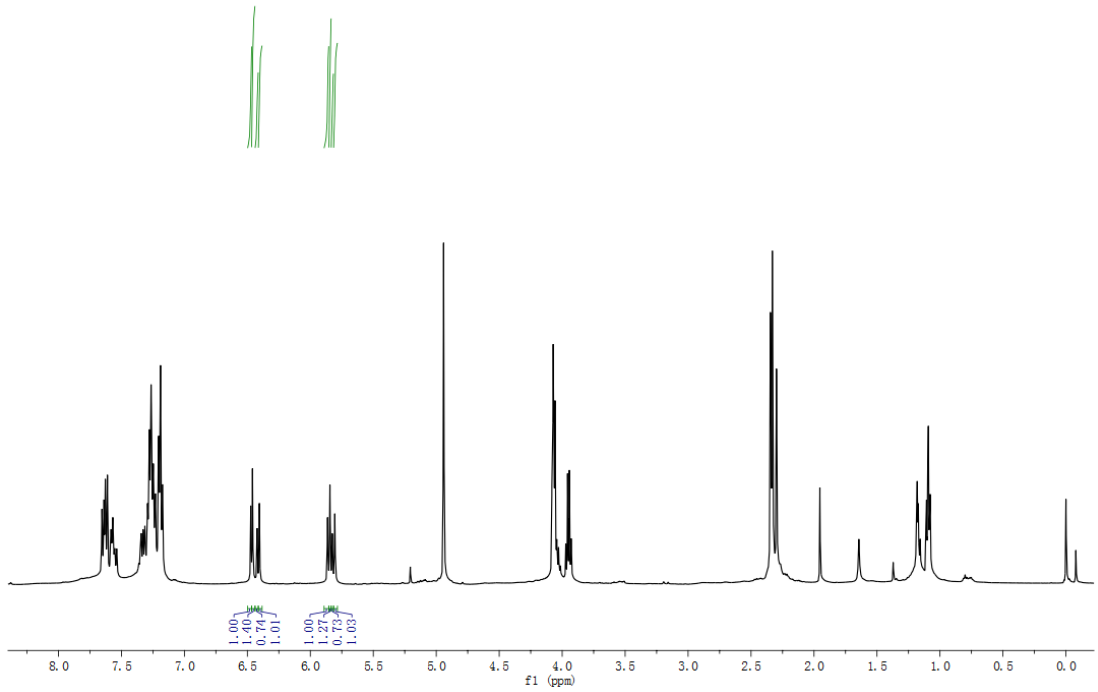


Figure S9 ^{1}H NMR of Entry 4

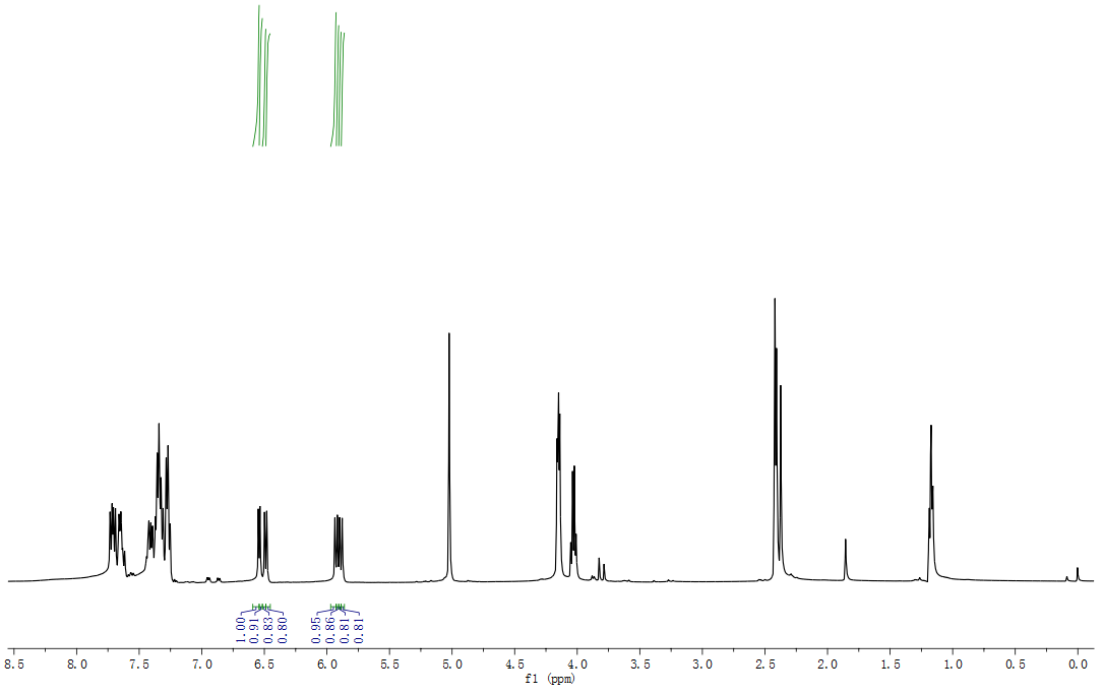


Figure S10 ^{1}H NMR of Entry 5

4.5 The Quantum Yield Measurements

According to the literature,[7] The photon flux of the reaction photoreactor was 7.39 $\times 10^{-9}$ einstein s^{-1}, measured by the ferrioxalate actinometry. A cuvette was charged with allyl sulfone **1a** (0.1 mmol, 1 equiv), P(4-OMe-Ph)$_3$ (0.2 mmol, 2 equiv), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (2.2 mg, 1 mol%) and 2.0 mL DCM. The cuvette was then degassed with Ar for 5 mins and irradiated by blue LED (λ = 460 nm, 1 cm distance) for 1800 s (0.5 h). Then the product yield was determined by **1H NMR** in 24% yield using dibromomethane as an internal standard. The absorbance of Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ in DCM (1×10^{-3} M) was measured and the absorbance at 460 nm is 0.51. The quantum yield was calculated using Equation S1 to be 6.1.

$$\Phi = \frac{mol\ product}{flux*t*f} = \frac{5.6*10^{-5}\ mol}{7.39*10^{-9}\ einstein\ s^{-1}*1800\ s*0.694} = 6.1 \quad \textbf{Equation S1}$$

$$f = 1 - 10^{-A} = 1 - 10^{-0.514} = 0.694$$

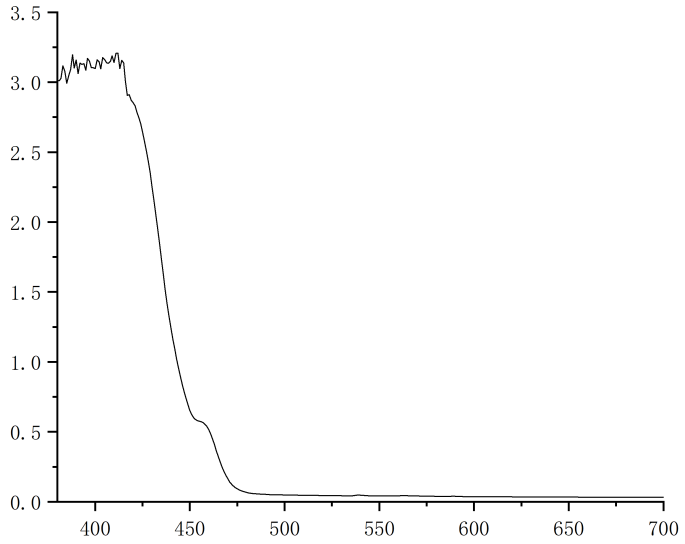


Figure S11: Absorption spectrum of Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ 0.001M

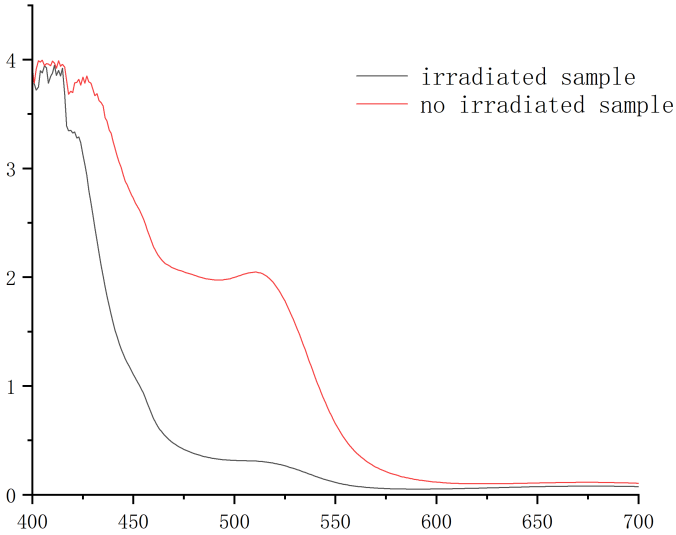
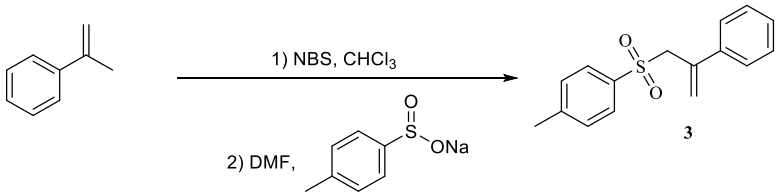


Figure S12: Absorption spectra of irradiation and non-irradiation experiments

4.6 Other control experiments

Synthesis of 1-methyl-4-((2-phenylallyl)sulfonyl)benzene (3)



A solution of *α*-methyl styrene (8.3 mL, 64 mmol) and *N*-bromosuccinimide (NBS, 15.0 g, 84 mmol) in chloroform (15 mL) was heated to reflux for 3 h. The mixture was cooled down after reflux and the filtrated was evaporated and purified by chromatography (100% hexanes) to afford 1-bromo-2-phenyl-2-propene (4.58 g, 36% yield).

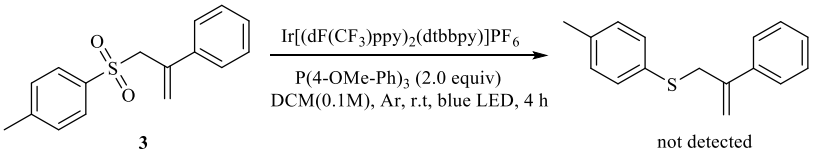
To a solution of the 1-bromo-2-phenyl-2-propene (2.61 g, 13.2 mmol) in dry DMF (40 mL) was added sodium *p*-toluenesulfonate. This mixture was heated to 80 ℃ for 4 h, cooled, and diluted with EtOAc (100 mL). The mixture was washed with water (3 x 50

mL), brine, dried with Na_2SO_4, filtered and the filtrate was evaporated and purified by chromatography (20% hexane/EtOAc) afforded **3** as a white solid (2.72 g, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.28 – 7.19 (m, 7H), 5.59 (s, 1H), 5.22 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H).

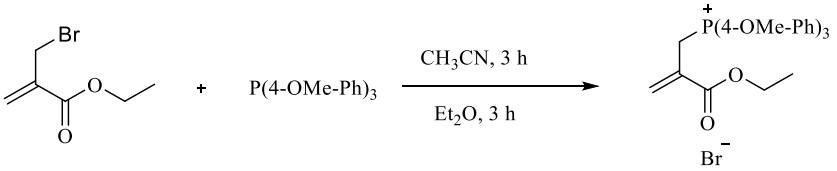
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 138.9, 136.6, 135.6, 129.4, 128.6, 128.3, 127.8, 126.2, 121.6, 62.2, 21.5.

(a) Experiment with *β*-Ph ally sulfone 3



Under an argon atmosphere, allyl sulfone **3** (54.4 mg, 0.2 mmol), triaryl phosphine (140.8 mg, 0.4 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%), and DCM (2.0 mL, 0.1 M) as the solvent were added to the reaction tube. The reaction was stirred at room temperature under 25 W blue LEDs for 4 h. However, no deoxygenated product was obtained, and most of substrate allyl sulfone remained.

(b) Synthesis of phosphonium 4



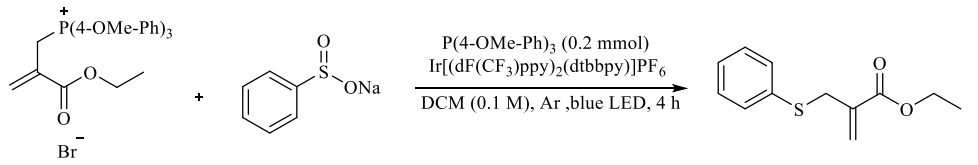
According to relevant literature,[4] the corresponding triarylphosphine (1.76 g, 5 mmol) and ethyl 2-(bromomethyl)acrylate (1.34 g, 7 mmol) were added to the reaction flask, followed by acetonitrile (16.7 mL, 0.3 M) as the solvent. The reaction mixture was stirred at room temperature for 3 hours. Upon completion, acetonitrile was removed, followed by the addition of Et_2O (16.7 mL, 0.3 M), and the mixture was stirred for 3

hours. Then, the product **4** (2.72 g, 90% yield) was filtered and obtained (2.72g, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 6H), 7.10 (dd, J = 9.0, 2.6 Hz, 6H), 6.42 (d, J = 5.6 Hz, 1H), 6.25 (d, J = 5.4 Hz, 1H), 4.77 (d, J = 14.9 Hz, 2H), 3.86 (s, 9H), 3.82 (q, J = 7.2 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 165.3, 164.6, 164.6, 136.0, 135.9, 134.7, 134.6, 128.3, 128.3, 115.9, 115.8, 108.8, 108.0, 61.5, 61.4, 55.9, 55.8, 27.2, 26.7, 13.9.

(c) Possible intermediate experiments



4. 0.2 mmol **5**. 0.2 mmol with $P(4\text{-OMe-Ph})_3$ 22 % yield

Under an argon atmosphere, pre-prepared **4** (109 mg, 0.2 mmol), sodium sulfinate (32.8 mg, 0.2 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%), and the relevant triarylphosphine (70.4 mg, 0.2 mmol) were added into the reaction flask, followed by the addition of DCM (2 mL, 0.1 M). The mixture was then stirred under light (460 nm) for 8 hours. After the reaction was completed, the solvent was concentrated, and the product was purified by column chromatography, yielding 22% of **2a**.

(d) In situ generation of phosphonium salts

Under an argon atmosphere, allyl sulfone **1a** (0.1 mmol, 25.4 mg), $P(4\text{-OMe-Ph})_3$ (0.2 mmol, 70.4 mg), mesitylene (0.1 mmol, 14 uL) as internal standard and $CDCl_3$ (0.5 mL) as the solvent were added to the NMR tube. The ^{1}H NMR spectra were recorded after 5 min and 3 h respectively.

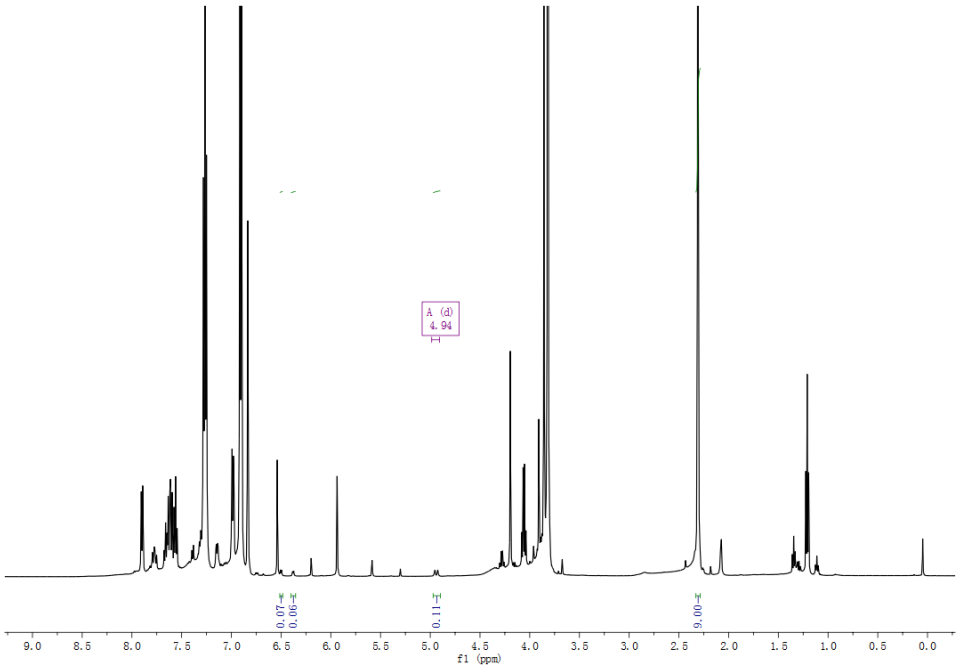


Figure S11 ^{1}H NMR of the mixture of **1a** and P(4-OMe-Ph)$_3$ after 5 min

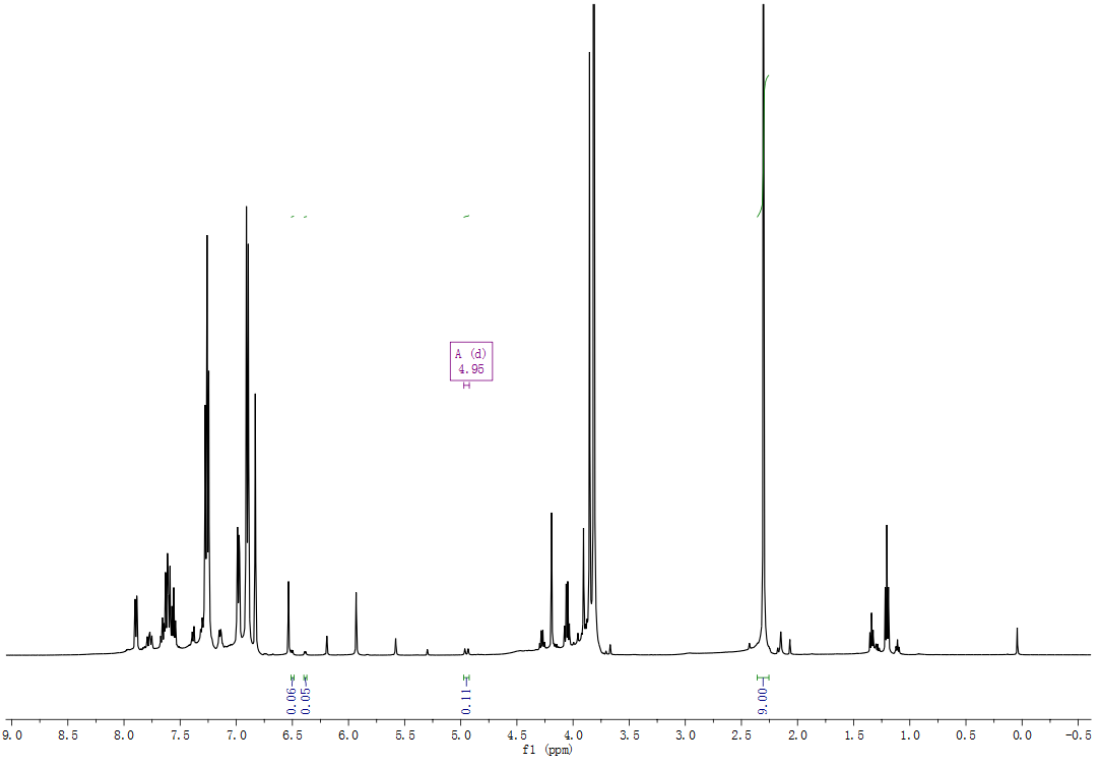


Figure S12 ^{1}H NMR of the mixture of **1a** and P(4-OMe-Ph)$_3$ after 3 h

The substrate **1z** with exclusive (*Z*)-selectivity as evidenced by extensive NMR

studies.[5, 6] In addition, we conducted relevant NOESY experiments to determine the configuration of the product **2z**. From the NOESY spectrum results, it can be seen that the methyl substituted on the olefin has an interaction with the adjacent methylene; Secondly, the chemical shift of H on the olefin on the product sulfide does not change significantly from the chemical shift of the substrate allyl sulfone. Combining together, we judge that the product 2z is in *Z*-form.

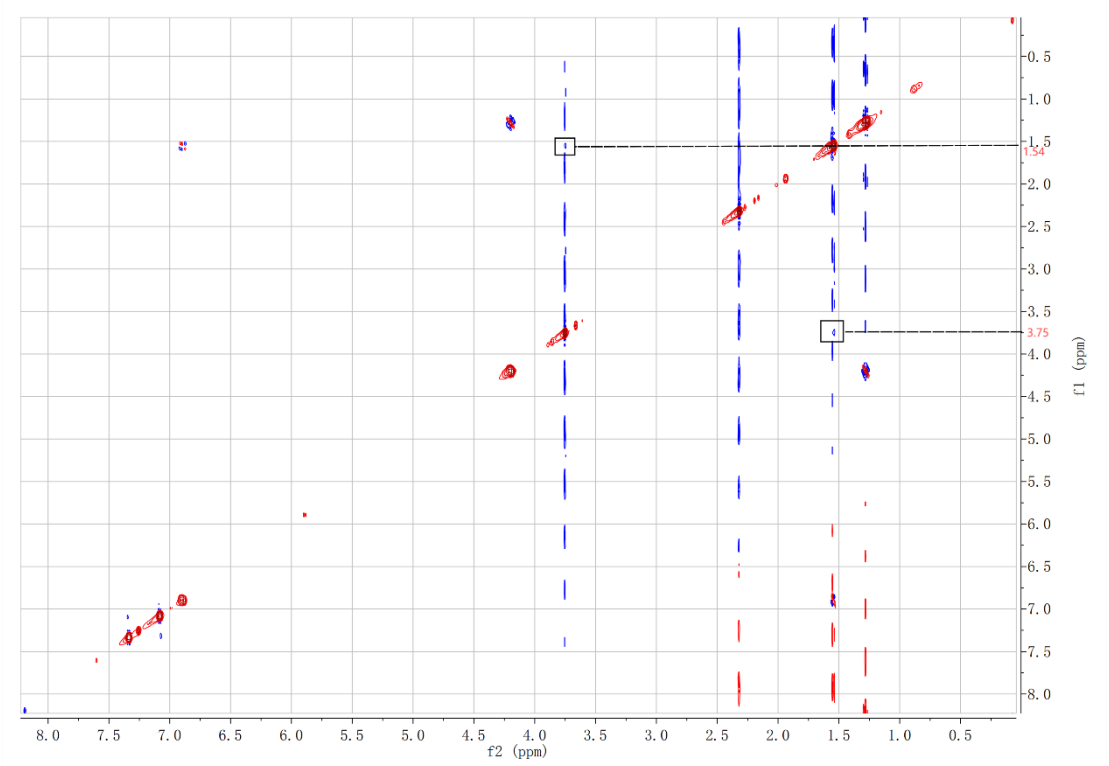
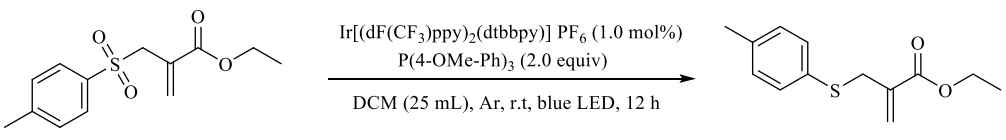


Figure S13: NOESY spectrum of product **2z**

5. Scale-up reaction and product derivatization

5.1. Gram-scale synthesis of compound 2b



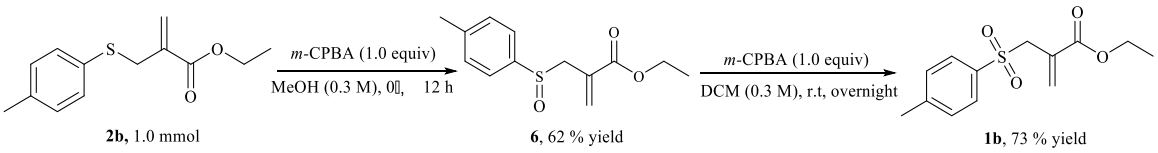
1b, 7.5mmol

2b, 1.04g, 58% yield

Under argon atmosphere, to a 50-mL glass bottle charged with allyl sulfone **1b** (2.1 g, 7.5 mmol), P(4-OMe-Ph)$_3$ (5.28 g, 15 mmol) and Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (90 mg, 1 mol%), was added DCM (25 mL). The reaction mixture was stirred and irradiated with a blue LED for 12 hours. After the reaction was completed, the solvent was evacuated, and the target product **2b** was obtained by flash column chromatography (1.04 g, 58%).

5.2. Transformations of the products

(a) Stepwise oxidation

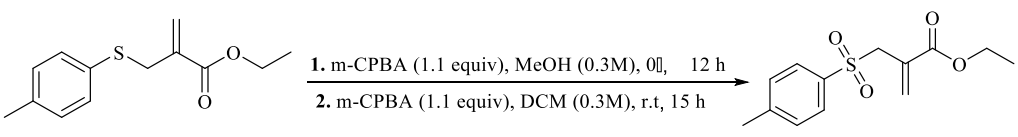


2b, 1.0 mmol — **6**, 62 % yield — **1b**, 73 % yield

A 50-mL glass bottle was charged with allyl sulfone **2b** (472 mg, 1.0 mmol) and methanol (0.3 M). Then, *m*-chloroperoxybenzoic acid (*m*-CPBA, 172.5 mg, 1.0 mmol) was added to the reaction system at 0 °C. It was stirred 0 °C for 12 hours. After the reaction was completed, the reaction mixture was quenched with saturated Na_2CO_3 aqueous solution and extracted with ethyl acetate. Subsequent flash column chromatography yielded the sulfoxide product in 62% yield.

To the solution of sulfoxide **6** in DCM (3 mL) was added *m*-CPBA (172.5 mg, 1.0 mmol), then it was stirred at room temperature overnight. After the sulfoxide reaction was completed, quench the reaction with a saturated Na_2CO_3 aqueous solution, and extract with ethyl acetate. After concentration and flash column chromatography, **1b** was finally isolated in 73% yield.

(b) One-pot method



2b, 1.0 mmol — **1b,** 71 % yield

To the solution of allyl sulfone **2b** (472 mg, 1.0 mmol) in methanol (3 mL) was

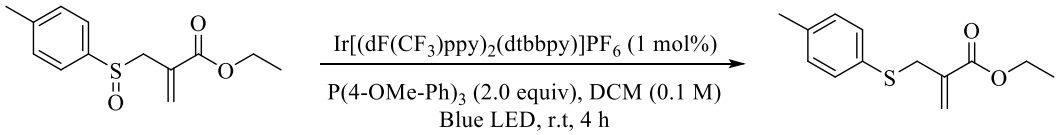
added *m*-chloroperoxybenzoic acid (*m*-CPBA, 189.7 mg, 1.1 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 12 hours. After the consumption of **2b** by TLC, the solvent was evacuated and *m*-CPBA (189.7 mg, 1.1mmol) in DCM (15 mL) was added, then it reacted at room temperature for 15 hours. Once the reaction is completed, quench the reaction mixture with saturated Na_2CO_3. It was extracted with ethyl acetate for 3 times, dried over Na_2SO_4, concentrated, and purified by flash column chromatography. Finally, **1b** was isolated in 71% yield.

ethyl 2-((*p*-tolylsulfinyl)methyl)acrylate (6)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 6.42 (s, 1H), 5.74 (s, 1H), 4.10 (m, 1H), 3.83 – 3.68 (m, 2H), 2.39 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 141.6, 139.8, 131.7, 129.6, 129.5, 124.3, 61.2, 59.5, 21.3, 14.0.

(c) Sulfoxide deoxygenation reaction



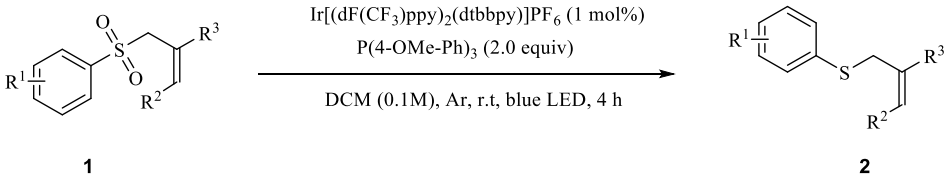
6, 0.2 mmol

1b, 57 % yield

At room temperature, to a 10-mL glass bottle charged with sulfoxide **6** (50.4 mg, 0.2 mmol), P(4-OMe-Ph)$_3$ (140.8 mg, 0.4 mmol), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (2.2 mg, 1 mol%) was added DCM (2 mL). The reaction was stirred and irradiated with blue LED for 4 hours under an argon atmosphere. After the reaction was completed, the solvent was evacuated, and the target product **1b** (26.9 mg, 57%) was obtained by flash column chromatography.

6. Experimental and analytical data of products

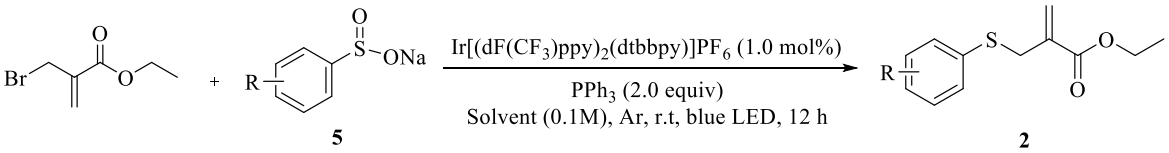
6.1 Method A



1 2

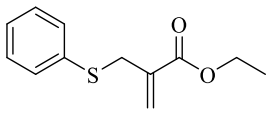
At room temperature, to a 10-mL glass bottle charged with allyl sulfone **1** (0.2 mmol), $P(4\text{-OMe-Ph})_3$ (140.8 mg, 0.4 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) was added DCM (2 mL). The reaction mixture was stirred and irradiated with a Blue LED for 4 hours under an argon atmosphere. Upon completion, the solvent was evacuated, and the target product **2** was obtained by flash column chromatography.

6.2 Method B



5 2

At room temperature, to a 10-mL glass bottle charged with ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (0.4 mmol), triphenylphosphine (140.8 mg, 0.4 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) was added DCM (2 mL). The reaction mixture was stirred and irradiated with a blue LED for 12 hours under an argon atmosphere. Upon completion, the solvent was evacuated, and the target product **2** was obtained by flash column chromatography.



Ethyl 2-((phenylthio)methyl)acrylate (2a)

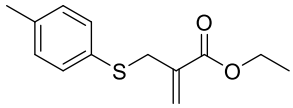
2a was prepared as a colorless oil from ethyl 2-((phenylsulfonyl)methyl)acrylate **1a** (50.8 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50), in 71% yield (31.5 mg).

2a could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (65.6 mg, 0.4 mmol), and triphenylphosphine (104.8 mg, 0.40 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50), in 54% yield (23.9 mg).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, J = 7.2 Hz, 2H), 7.27 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.16 (s, 1H), 5.55 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.77 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 136.5, 135.5, 130.8, 128.8, 126.7, 126.5, 61.0, 35.7, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{15}O_2S$ $[M+H]^+$: 223.0787, found: 223.0787.



Ethyl 2-((p-tolylthio)methyl)acrylate (2b)

2b was prepared as a colorless oil from ethyl 2-(tosylmethyl)acrylate **1b** (53.6 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol) according to the method A (overnight, eluent:Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50), in 67% yield (31.6 mg).

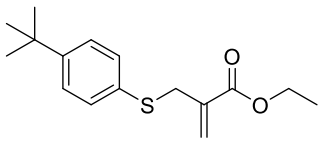
2b could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (71.2 mg, 0.4 mmol),

and triphenylphosphine (104.8 mg, 0.40 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50), in 40% yield (18.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.15 (s, 1H), 5.50 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.74 (s, 2H), 2.34 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 137.0, 136.6, 131.7, 129.6, 126.3, 60.9, 36.4, 21.0, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0943, found: 237.0945.



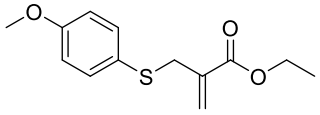
Ethyl 2-(((4-(tert-butyl)phenyl)thio)methyl)acrylate (2c)

2c was prepared as a colorless oil from ethyl 2-(((4-(tert-butyl)phenyl)sulfonyl)methyl)acrylate **1c** (62 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to the method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 69% yield (38.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 4H), 6.16 (s, 1H), 5.55 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.75 (s, 2H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 150.0, 136.7, 131.9, 130.9, 126.5, 125.9, 61.0, 36.0, 34.5, 31.2, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{23}O_2S$ $[M+H]^+$: 279.1413, found: 279.1410.



Ethyl 2-(((4-methoxyphenyl)thio)methyl)acrylate (2d)

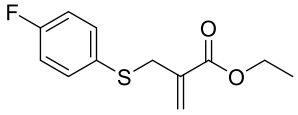
2d was prepared as a colorless oil from ethyl 2-(((4-methoxyphenyl)sulfonyl)methyl)acrylate **1d** (56.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.30), in 52% yield (26.2 mg).

2d could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (77.6 mg, 0.4 mmol), triphenylphosphine (104.8 mg, 0.40 mmol), tris(4-methoxyphenyl)phosphine (70.4 mg, 0.20 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) under argon according to method B (eluent: Petroleum ether/EtOAc = 15:0, TLC R_f = 0.30), in 52% yield (27.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.10 (s, 1H), 5.35 (s, 1H), 4.26 (q, J = 7.3 Hz, 2H), 3.81 (s, 3H), 3.66 (s, 2H), 1.33 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 159.4, 136.7, 134.8, 126.1, 126.1, 125.5, 114.4, 60.9, 55.3, 55.2, 37.8, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{17}O_3S$ $[M+H]^+$: 253.0892, found: 253.0892.



Ethyl 2-(((4-fluorophenyl)thio)methyl)acrylate (2e)

2e was prepared as a colorless oil from ethyl 2-(((4-fluorophenyl)sulfonyl)methyl)acrylate **1e** (54.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent:

Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 62% yield (29.7 mg).

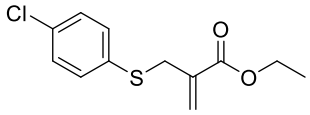
2e could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (72.4 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 54% yield (25.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.11 (s, 1H), 5.40 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.69 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 163.2, 161.3, 136.5, 134.2 (d, J_2 = 8.2 Hz), 130.2 (d, J_3 = 3.5 Hz), 126.4, 116.0 (d, J_1 = 21.8 Hz), 61.0, 37.1, 14.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.36.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{14}FO_2S$ $[M+H]^+$: 241.0693, found: 241.0690.



Ethyl 2-(((4-chlorophenyl)thio)methyl)acrylate (2f)

2f was prepared as a colorless oil from ethyl 2-(((4-chlorophenyl)sulfonyl)methyl)acrylate **1f** (57.6 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 78% yield (39.9 mg).

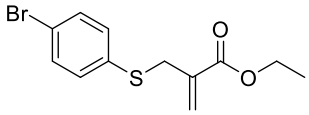
2f could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (78.8 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 59% yield (30.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.16 (m, 4H), 6.16 (s, 1H), 5.52 (s, 1H), 4.24 (q,

J = 7.1 Hz, 2H), 3.74 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 136.2, 136.2, 133.9, 132.9, 132.3, 129.0, 126.6, 61.1, 36.0, 14.1.

HRMS (ESI, m/z) calcd for $C_{12}H_{14}ClO_2S$ $[M+H]^+$: 257.0397, found: 257.0394.



Ethyl 2-(((4-bromophenyl)thio)methyl)acrylate (2g)

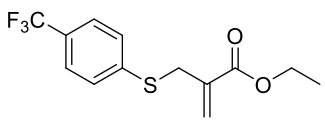
2g was prepared as a colorless oil from ethyl 2-(((4-bromophenyl)sulfonyl)methyl)acrylate **1g** (66.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 68% yield (40.8 mg).

2g could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (96.4 mg, 0.4 mmol), and triphenylphosphine (104.8 mg, 0.40 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 48% yield (28.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.19 (s, 1H), 5.56 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.77 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 136.2, 134.7, 132.3, 131.9, 126.7, 120.8, 61.1, 35.8, 14.1.

HRMS (ESI, m/z) calcd for $C_{12}H_{13}BrO_2S$ $[M+H]^+$: 300.9892, found: 300.9891.



Ethyl 2-(((4-(trifluoromethyl)phenyl)thio)methyl)acrylate (2h)

2h was prepared as a colorless oil from ethyl 2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)acrylate **1h** (64.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 75% yield (43.5 mg).

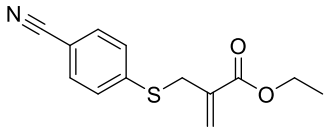
2h could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (92.4 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 56% yield (32.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 6.24 (s, 1H), 5.70 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.85 (s, 2H), 1.31 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 141.1, 135.8, 128.7, 128.1 (q, J_2 = 32.7 Hz), 127.1, 125.6 (q, J_3 = 3.8 Hz), 124.0 (q, J_1 = 271.8 Hz), 61.2, 34.2, 14.1.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.53.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{14}F_3O_2S$ $[M+H]^+$: 291.0661, found: 291.0659.



Ethyl 2-(((4-cyanophenyl)thio)methyl)acrylate (2i)

2i was prepared as a colorless oil from ethyl 2-(((4-cyanophenyl)sulfonyl)methyl)acrylate **1i** (55.8 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.35), in 62% yield (30.6 mg).

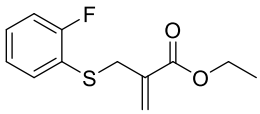
2i could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol), the corresponding sodium aryl sulfinate (75.2 mg, 0.4 mmol), and triphenylphosphine (104.8 mg, 0.40 mmol), according to method B (eluent: Petroleum

ether/EtOAc = 15:1, TLC R_f = 0.35), in 41% yield (20.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.28 (s, 1H), 5.77 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.87 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 143.5, 135.4, 132.2, 127.9, 127.4, 118.6, 109.0, 61.3, 33.5, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{13}NO_2S$ $[M+H]^+$: 248.0739, found: 248.0738.



Ethyl 2-(((2-fluorophenyl)thio)methyl)acrylate (2j)

2j was prepared as a colorless oil from ethyl 2-(((2-fluorophenyl)sulfonyl)methyl)acrylate **1j** (54.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 76% yield (36.4 mg).

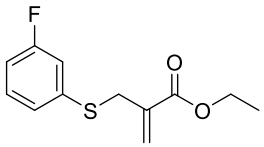
2j could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (72.4 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 59% yield (28.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, J = 7.6 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.06 (dd, J = 9.8, 7.9 Hz, 2H), 6.11 (d, J = 1.0 Hz, 1H), 5.46 (d, J = 1.1 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.75 (d, J = 1.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 , 162.1 (d, J = 245.9 Hz), 136.5 , 134.2 (d, J = 1.7 Hz), 129.4 (d, J = 7.9 Hz), 126.5 , 124.4 (d, J = 3.9 Hz), 122.0 (d, J = 17.7 Hz), 115.7 (d, J = 22.7 Hz), 61.0 , 35.0 (d, J = 2.9 Hz), 14.1 .

^{19}F NMR (471 MHz, Chloroform-*d*) δ -108.36.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}FO_2S$ $[M+H]^+$: 241.0693, found: 241.0691.



Ethyl 2-(((3-fluorophenyl)thio)methyl)acrylate (2k)

2k was prepared as a colorless oil from ethyl 2-(((3-fluorophenyl)sulfonyl)methyl)acrylate **1k** (54.4 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 55% yield (26.4 mg).

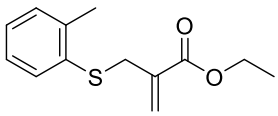
2k could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (72.4 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 51% yield (24.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.04 (dt, J = 9.3, 2.1 Hz, 1H), 6.89 (td, J = 8.4, 1.6 Hz, 1H), 6.21 (s, 1H), 5.63 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.80 (s, 2H), 1.32 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 162.7 (d, J_1 = 248.3 Hz), 138.0 (d, J_3 = 7.7 Hz), 136.1, 130.1 (d, J_3 = 8.6 Hz), 126.9, 125.5 (d, J_3 = 3.0 Hz), 116.7 (d, J_2 = 23.0 Hz), 113.5 (d, J_2 = 21.2 Hz), 61.1, 35.1, 14.1

^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.30.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{14}FO_2S$ $[M+H]^+$: 241.0693, found: 241.0690.



Ethyl 2-((o-tolylthio)methyl)acrylate (2l)

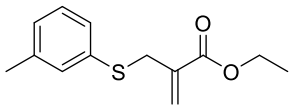
2l was prepared as a colorless oil from ethyl 2-((o-tolylsulfonyl)methyl)acrylate **1l**

(53.6 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50), in 77% yield (36.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.18 (dd, J = 6.2, 2.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.16 (s, 1H), 5.54 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.75 (s, 2H), 2.40 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 138.9, 136.3, 134.6, 130.4, 130.1, 126.6, 126.6, 126.3, 61.0, 34.9, 20.5, 14.2.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0943, found: 237.0941.



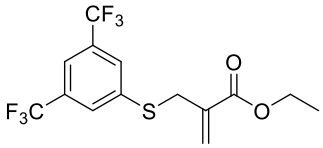
Ethyl 2-((m-tolylthio)methyl)acrylate (2m)

2m was prepared as a colorless oil from ethyl 2-((m-tolylsulfonyl)methyl)acrylate **1m** (53.6 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol) according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.50) in 68% yield (30.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 3H), 7.02 (d, J = 6.7 Hz, 1H), 6.17 (s, 1H), 5.58 (s, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.77 (s, 2H), 2.32 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 138.6, 136.5, 135.2, 131.2, 128.7, 127.6, 127.5, 126.5, 61.0, 35.5, 21.2, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{17}O_2S$ $[M+H]^+$: 237.0943, found: 237.0943.



Ethyl 2-(((3,5-bis(trifluoromethyl)phenyl)thio)methyl)acrylate (2n)

2n was prepared as a colorless oil from ethyl 2-(((3,5-bis(trifluoromethyl)phenyl)sulfonyl)methyl)acrylate **1n** (78 mg, 0.2 mmol), and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 80% yield (57.2 mg).

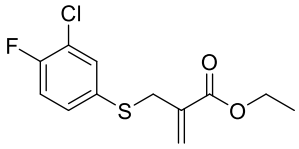
2n could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (120 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 62% yield (44.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.67 (s, 1H), 6.26 (s, 1H), 5.68 (s, 1H), 4.26 (q, J = 7.2 Hz, 2H), 3.89 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 139.6, 135.6, 132.1 (q, J_2 = 33.4 Hz), 129.0 (t, J_3 = 3.9 Hz), 127.4, 122.9 (q, J_1= 273.0 Hz), 119.9 (p, J_3 = 3.9 Hz), 61.3, 34.7, 14.0.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.12.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{11}F_6O_2S$ $[M-H]^+$: 357.0389, found: 357.0383.



Ethyl 2-(((3-chloro-4-fluorophenyl)thio)methyl)acrylate (2o)

2o was prepared as a colorless oil from ethyl 2-(((3-chloro-4-fluorophenyl)sulfonyl)methyl)acrylate **1o** (61.2 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent:

Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 76% yield (41.6 mg).

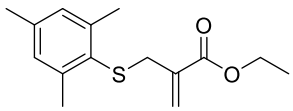
2o could also be prepared as a colorless oil from ethyl 2-(bromomethyl)acrylate (38.4 mg, 0.2 mmol) and the corresponding sodium aryl sulfinate (86 mg, 0.4 mmol), according to method B (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.65), in 50% yield (27.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 6.9, 2.3 Hz, 1H), 7.23 (m, J = 8.6, 4.5, 2.3 Hz, 1H), 7.06 (t, J = 8.7 Hz, 1H), 6.16 (s, 1H), 5.49 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.72 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 157.4 (d, J_1 = 249.9 Hz), 136.2, 133.6, 131.8 (d, J_3 = 4.1 Hz), 131.6 (d, J_3 = 7.0 Hz), 126.7, 121.3 (d, J_2 = 18.2 Hz), 116.9 (d, J_2 = 21.5 Hz), 61.1, 36.7, 14.1.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -116.84.

HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{13}ClFO_2S$ $[M+H]^+$: 275.0303, found: 275.0301.



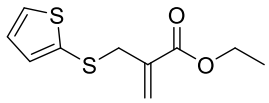
Ethyl 2-((mesitylthio)methyl)acrylate (2p)

2p was prepared as a colorless oil from ethyl 2-((mesitylsulfonyl)methyl)acrylate **1p** (59.2 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), according to method A (eluent: Petroleum ether/EtOAc = 15:1, TLC R_f = 0.60), in 63% yield (33.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 5.98 (s, 1H), 5.18 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.48 (s, 2H), 2.45 (s, 6H), 2.25 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 143.3, 138.2, 137.0, 129.1, 128.9, 125.9, 60.9, 36.2, 21.8, 21.0, 14.1.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{21}O_2S$ $[M+H]^+$: 265.1256, found: 265.1254.



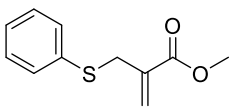
Ethyl 2-((thiophen-2-ylthio)methyl)acrylate (2q)

2q was prepared as a colorless oil from ethyl 2-((thiophen-2-ylsulfonyl)methyl)acrylate **1q** (52.0 mg, 0.2 mmol), the corresponding triphenylphosphine (140.8 mg, 0.4 mmol), and 4-CzIPN (2.2 mg, 1 mol%) in DCM (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 4 h. The mixture was directly subjected to silica gel column chromatography (eluent: Petroleum ether/EtOAc = 10:1, TLC R_f = 0.60) to afford the desired product **2q** in 51% yield (23.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 5.4, 1.2 Hz, 1H), 7.08 (dd, J = 3.5, 1.2 Hz, 1H), 6.96 (dd, J = 5.3, 3.6 Hz, 1H), 6.11 (s, 1H), 5.29 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 136.3, 135.1, 133.4, 130.1, 127.5, 126.7, 61.0, 40.4, 14.2.

HRMS (ESI, *m*/*z*) calcd for $C_{10}H_{12}O_2S_2$ $[M+H]^+$: 229.0351, found: 229.0350.



Methyl 2-((phenylthio)methyl)acrylate (2r)

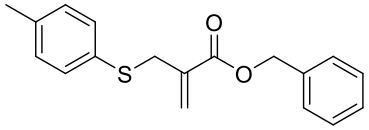
2r was prepared as a colorless oil from methyl 2-((phenylsulfonyl)methyl)acrylate **1r** (48.0 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol)

according to the method A (eluent:Petroleum ether/EtOAc = 15:1, TLC R_f = 0.5), in 60 % yield (24.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.0 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 6.16 (s, 1H), 5.55 (s, 1H), 3.79 (s, 3H), 3.77 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 136.1, 135.3, 130.9, 128.9, 126.8, 126.8, 52.1, 35.7.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{13}O_2S$ $[M+H]^+$: 209.0630, found: 209.0628.



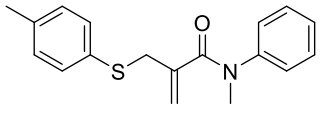
Benzyl 2-((p-tolylthio)methyl)acrylate (2s)

2s was prepared as a colorless oil from benzyl 2-(tosylmethyl)acrylate **1s** (66.0 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol) according to the method A (eluent:Petroleum ether/EtOAc = 15:1, TLC R_f = 0.55), in 61 % yield (36.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 7.26 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.19 (s, 1H), 5.51 (s, 1H), 5.24 (s, 2H), 3.75 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 137.1, 136.3, 135.8, 131.8, 131.5, 129.6, 128.5, 128.2, 128.0, 126.9, 66.7, 36.5, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{19}O_2S$ $[M+H]^+$: 299.1100, found: 299.1096.



N-methyl-N-phenyl-2-((p-tolylthio)methyl)acrylamide (2t)

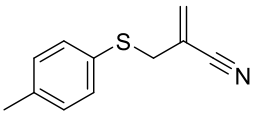
2t was prepared as a colorless oil from *N*-methyl-*N*-phenyl-2-

(tosylmethyl)acrylamide **1t** (65.8 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol) in CH_3CN (2.0 mL, 0.1 M) using $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) as a catalyst. The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 20 h. After completion, the mixture was subjected to silica gel column chromatography using Petroleum ether/EtOAc = 10:0 as the eluent (TLC R_f = 0.50). The reaction yielded **2t** in 54% (32.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (q, J = 9.0, 8.0 Hz, 3H), 7.16 (t, J = 9.1 Hz, 4H), 7.06 (d, J = 7.9 Hz, 2H), 5.23 (s, 1H), 5.02 (s, 1H), 3.64 (s, 2H), 3.36 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 144.3, 140.1, 136.1, 132.3, 129.6, 129.6, 129.2, 126.9, 126.7, 38.1, 37.6, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{20}NOS$ $[M+H]^+$: 298.1260, found: 298.1254.



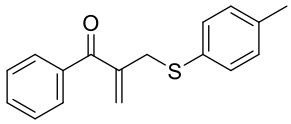
2-((p-tolylthio)methyl)acrylonitrile (2u)

2u was prepared as a colorless oil from 2-(tosylmethyl)acrylonitrile **1u** (44.2 mg, 0.2 mmol) and tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), following method A. The eluent used for chromatography was Petroleum ether/EtOAc = 15:1, and the TLC R_f value was 0.55. The reaction yielded **2u** in 61% yield (23.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.78 (s, 1H), 5.55 (s, 1H), 3.56 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 132.8, 131.5, 129.9, 129.4, 119.9, 117.7, 39.4, 21.1.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{12}NS$ $[M+H]^+$:190.0685, found: 190.0684.



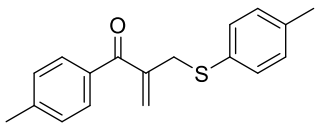
1-phenyl-2-((p-tolylthio)methyl)prop-2-en-1-one (2v)

2v was prepared as a colorless oil from 1-phenyl-2-(tosylmethyl)prop-2-en-1-one **1v** (60.0 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 12 h. After completion, the mixture was subjected to chromatography using Petroleum ether/EtOAc = 10:1 as the eluent (TLC R_f = 0.60). The reaction yielded **2v** in 44% yield (23.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 6.8 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.84 (s, 1H), 5.59 (s, 1H), 3.94 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 143.5, 137.4, 136.8, 132.4, 131.1, 129.7, 129.6, 128.1, 127.0, 36.2, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{17}OS$ $[M+H]^+$: 269.0994, found: 269.0990.



1-(p-tolyl)-2-((p-tolylthio)methyl)prop-2-en-1-one (2w)

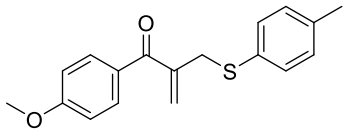
2w was prepared as a colorless oil from 1-(*p*-tolyl)-2-(tosylmethyl)prop-2-en-1-one **1w** (62.8 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar.

The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 12 h. After completion, the mixture was purified by chromatography using Petroleum ether/EtOAc = 10:1 as the eluent (TLC R_f = 0.60). The reaction yielded **2w** in 49% yield (27.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 5.80 (s, 1H), 5.55 (s, 1H), 3.93 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 143.5, 143.2, 136.7, 134.7, 131.7, 131.0, 129.8, 129.7, 128.9, 126.1, 36.3, 21.6, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{19}OS$ $[M+H]^+$: 283.1151, found: 283.1146.



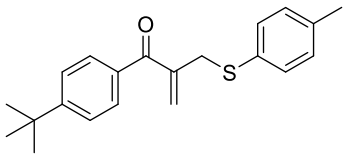
1-(4-methoxyphenyl)-2-((p-tolylthio)methyl)prop-2-en-1-one (2x)

2x was prepared as a colorless oil from 1-(4-methoxyphenyl)-2-(tosylmethyl)prop-2-en-1-one **1x** (66.0 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 12 h. After completion, the crude product was purified by chromatography using Petroleum ether/EtOAc (10:1) as the eluent (TLC R_f = 0.50). The reaction yielded **2x** in 41% yield (24.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 5.76 (s, 1H), 5.50 (s, 1H), 3.93 (s, 2H), 3.87 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 163.3, 143.6, 136.7, 132.1, 131.7, 131.0, 129.9, 129.6, 125.0, 113.4, 55.4, 36.6, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{19}O_2S$ $[M+H]^+$: 299.1100, found: 299.1094.



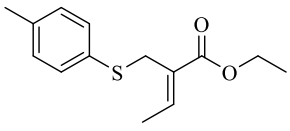
1-(4-(tert-butyl)phenyl)-2-((p-tolylthio)methyl)prop-2-en-1-one (2y)

2y was prepared as a colorless oil from 1-(4-(tert-butyl)phenyl)-2-(tosylmethyl)prop-2-en-1-one **1y** (71.2 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at room temperature under 25 W blue LEDs for 12 h. After completion, the crude product was purified by chromatography using Petroleum ether/EtOAc (10:1) as the eluent (TLC R_f = 0.50). The reaction yielded **2y** in 44% yield (28.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.80 (s, 1H), 5.58 (s, 1H), 3.93 (s, 2H), 2.33 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 156.2, 143.5, 136.7, 134.6, 131.7, 131.1, 129.6, 126.2, 125.1, 36.3, 35.0, 31.1, 21.0.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{25}OS$ $[M+H]^+$: 325.1620, found: 325.1614.



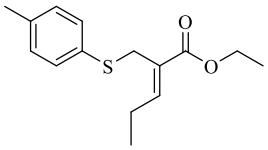
Ethyl 2-((p-tolylthio)methyl)but-2-enoate (2z)

2z was prepared as a colorless oil from ethyl 2-(tosylmethyl)but-2-enoate 1z (56.4 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at 60 °C under 25 W blue LEDs for 12 h. After completion, the crude product was purified by chromatography using Petroleum ether/EtOAc (10:1) as the eluent (TLC R_f = 0.50). The reaction yielded **2z** in 51% yield (25.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.90 (q, *J* = 7.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 2H), 2.32 (s, 3H), 1.54 (d, *J* = 7.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 166.6, 139.8, 137.4, 133.0, 131.9, 129.7, 129.5, 60.7, 31.7, 21.1, 14.2.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{19}O_2S$ $[M+H]^+$: 251.1100, found: 251.1094.



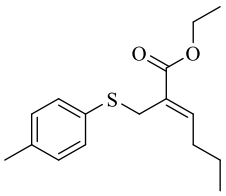
Ethyl 2-((p-tolylthio)methyl)pent-2-enoate (2aa)

2aa was prepared as a colorless oil from ethyl 2-(tosylmethyl)pent-2-enoate 1aa (59.2 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at 60 ℃ under 25 W blue LEDs for 12 h. After the reaction was complete, the crude product was purified by chromatography using Petroleum ether/EtOAc (10:1) as the eluent (TLC R_f = 0.50). The reaction yielded **2aa** in 49% yield (25.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.78 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.75 (s, 2H), 2.32 (s, 3H), 1.95 (p, J = 7.5 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 146.5, 137.3, 132.8, 132.0, 129.5, 128.0, 60.7, 31.9, 22.0, 21.0, 14.2, 13.0.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{21}O_2S$ $[M+H]^+$: 265.1256, found: 165.1251.



Ethyl 2-((p-tolylthio)methyl)hex-2-enoate (2ab)

2ab was prepared as a colorless oil from ethyl 2-(tosylmethyl)pent-2-enoate **1ab** (62.0 mg, 0.2 mmol), tris(4-methoxyphenyl)phosphine (140.8 mg, 0.40 mmol), and $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2.2 mg, 1 mol%) in CH_3CN (2.0 mL, 0.1 M) under Ar. The reaction tube was then capped, and the resulting mixture was stirred at 60 ℃ under 25 W blue LEDs for 12 h. After the reaction was complete, the crude product was purified by chromatography using Petroleum ether/EtOAc (10:1) as the eluent (TLC R_f = 0.50). The reaction yielded **2ab** in 30% yield (16.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.80 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.75 (s, 2H), 2.32 (s, 3H), 1.91 (q, J = 7.5 Hz, 2H), 1.29 (td, J = 7.2, 4.3 Hz, 5H), 0.84 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 145.1, 137.2, 132.7, 132.1, 129.5, 128.6, 60.7, 32.0, 30.6, 21.8, 21.0, 14.2, 13.8.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{23}O_2S$ $[M+H]^+$: 279.1413, found: 279.1407.

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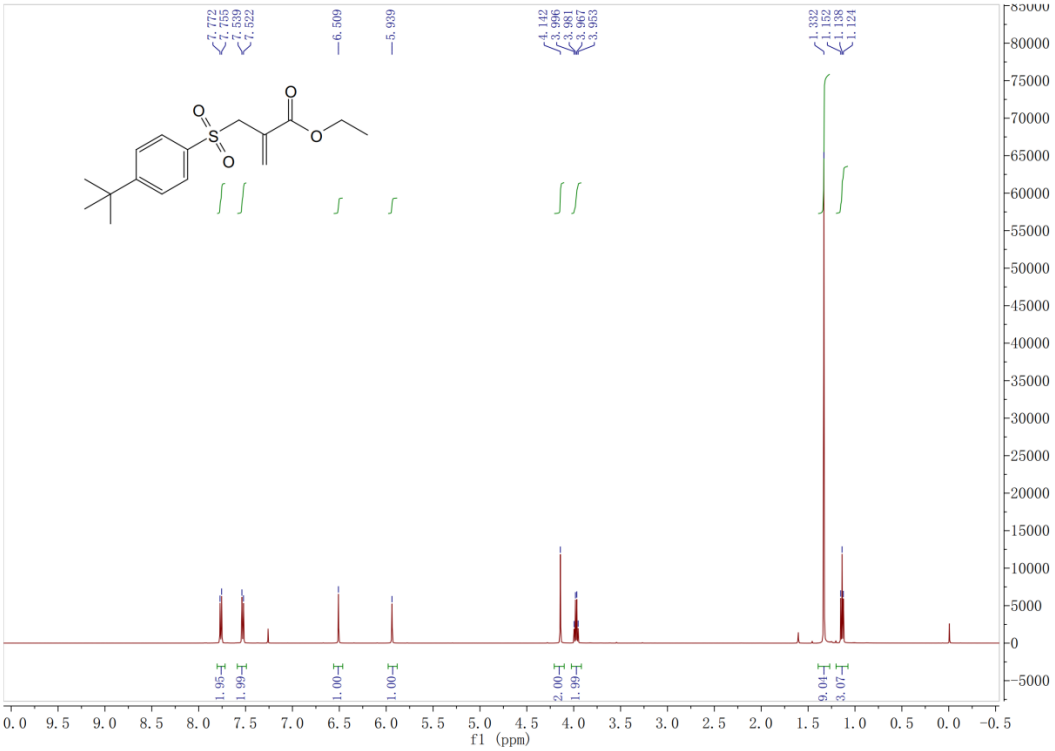
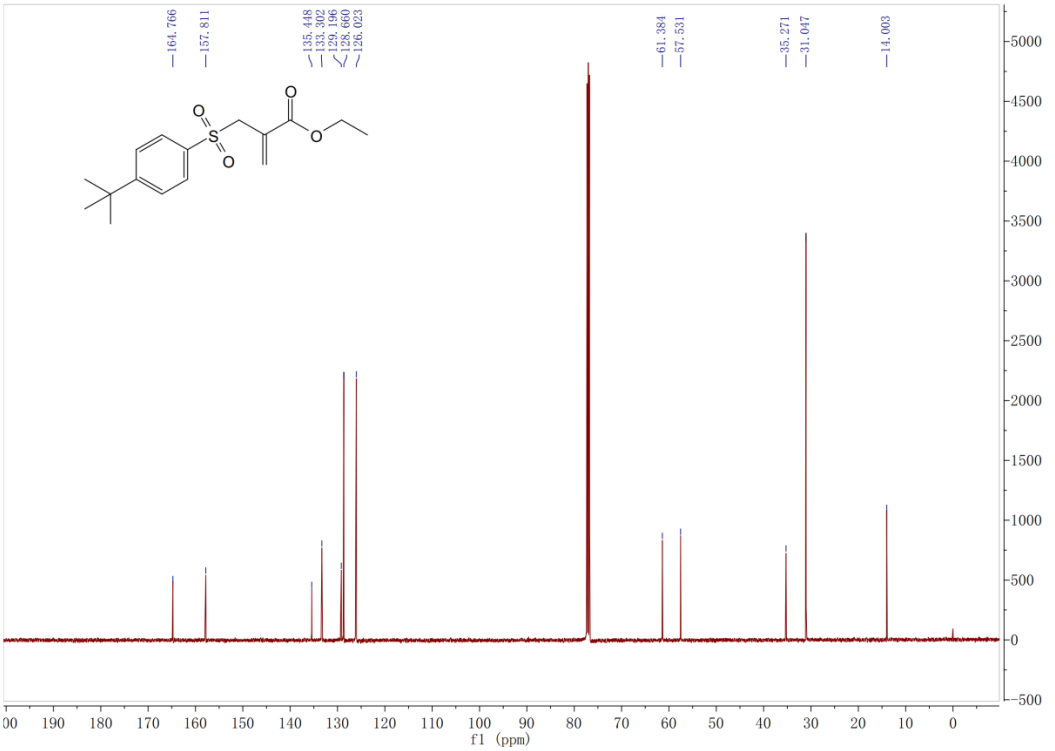
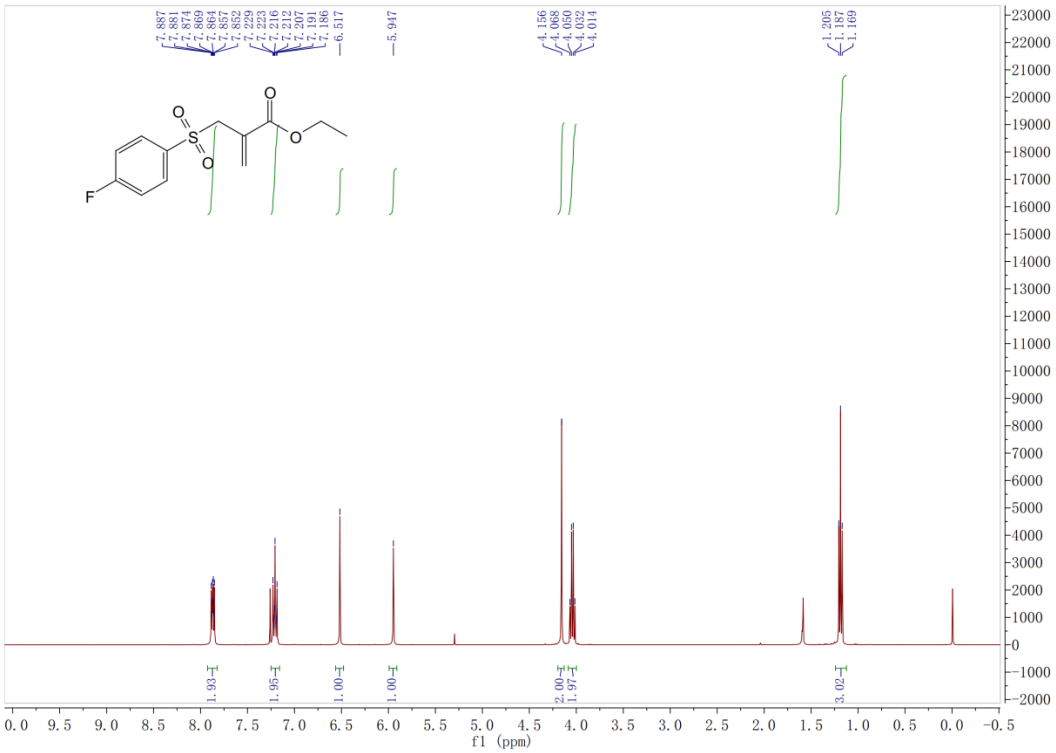
8. ^{1}H, ^{19}F and ^{13}C NMR spectra of structurally novel compounds

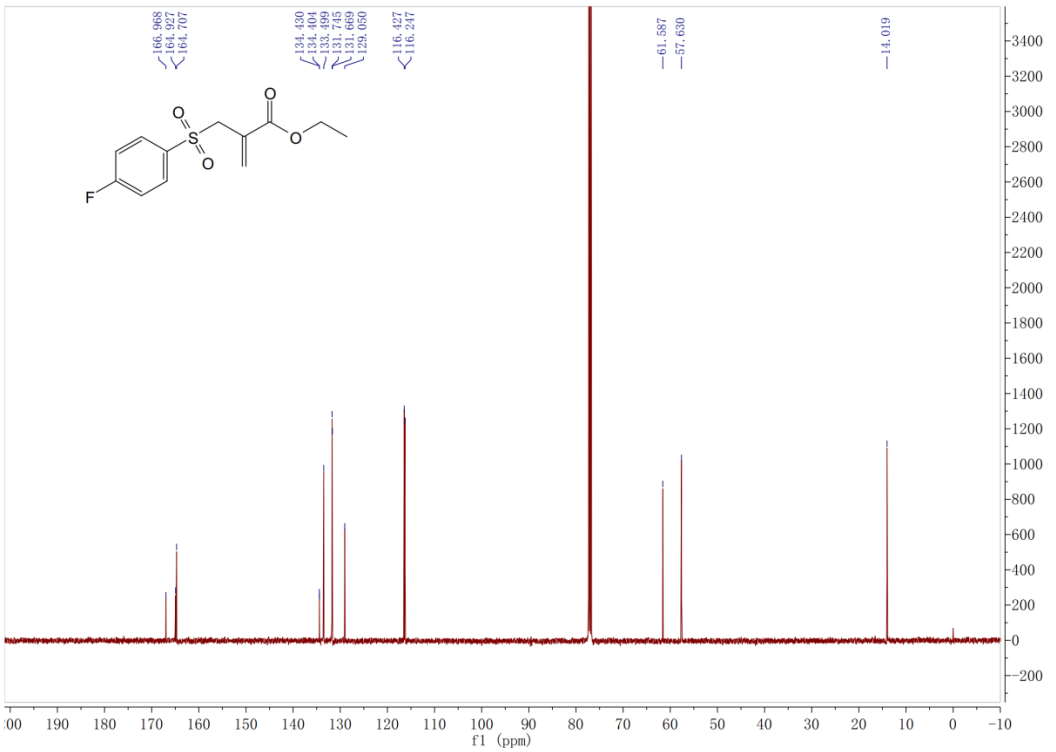
1c; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



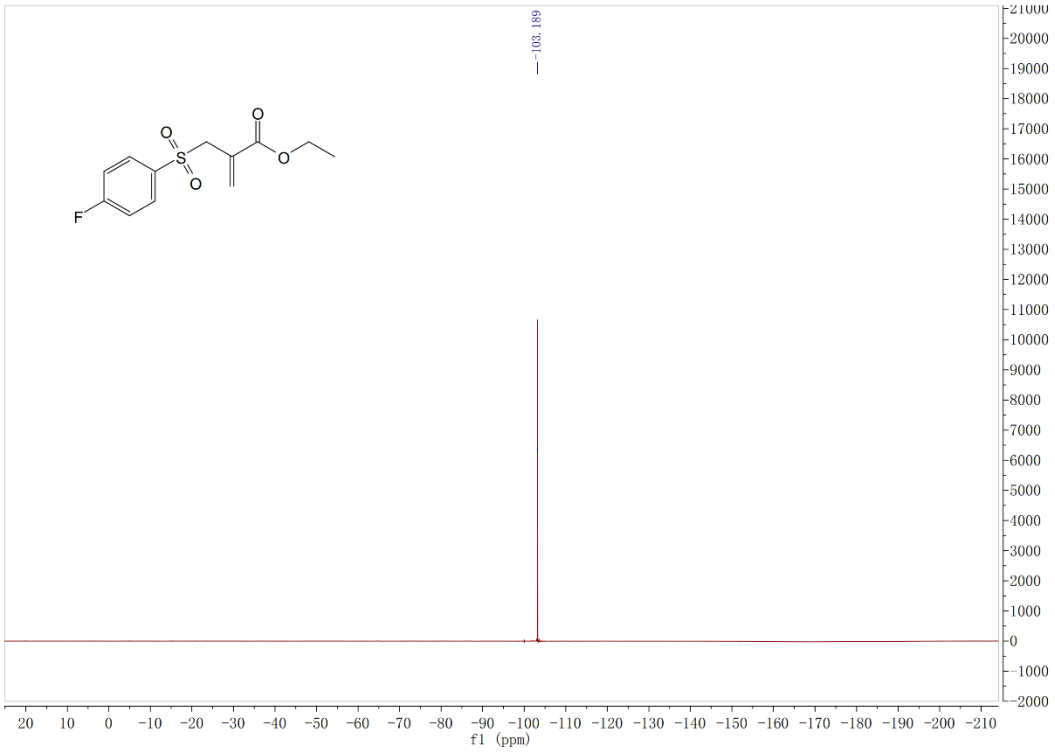


1e; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

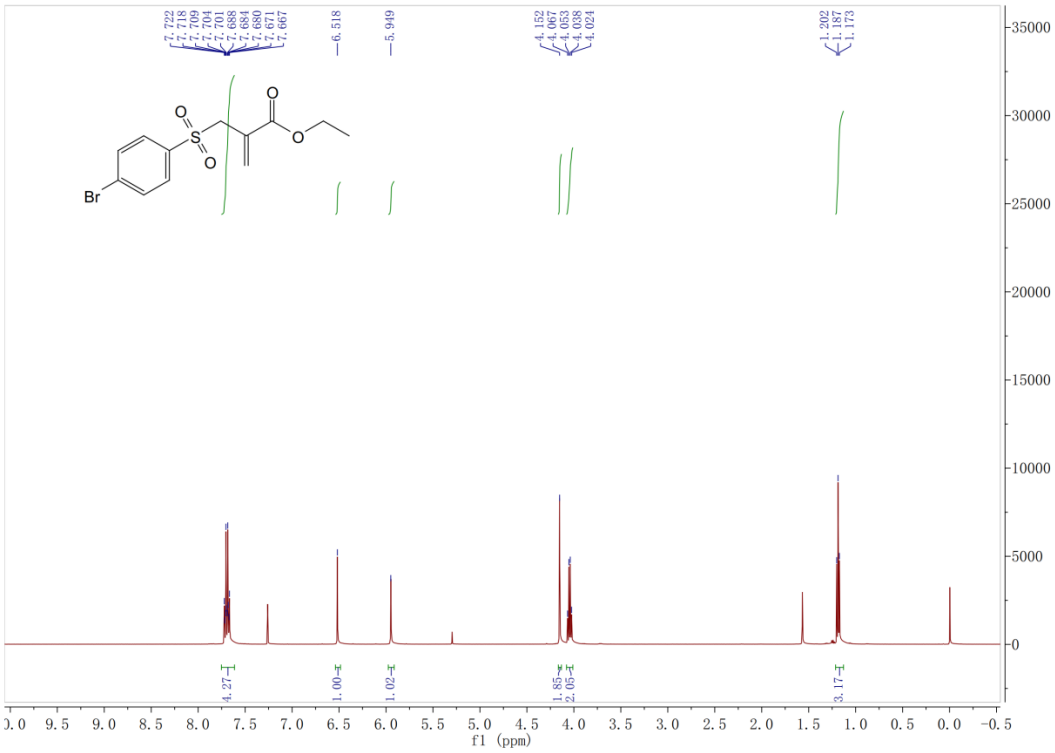


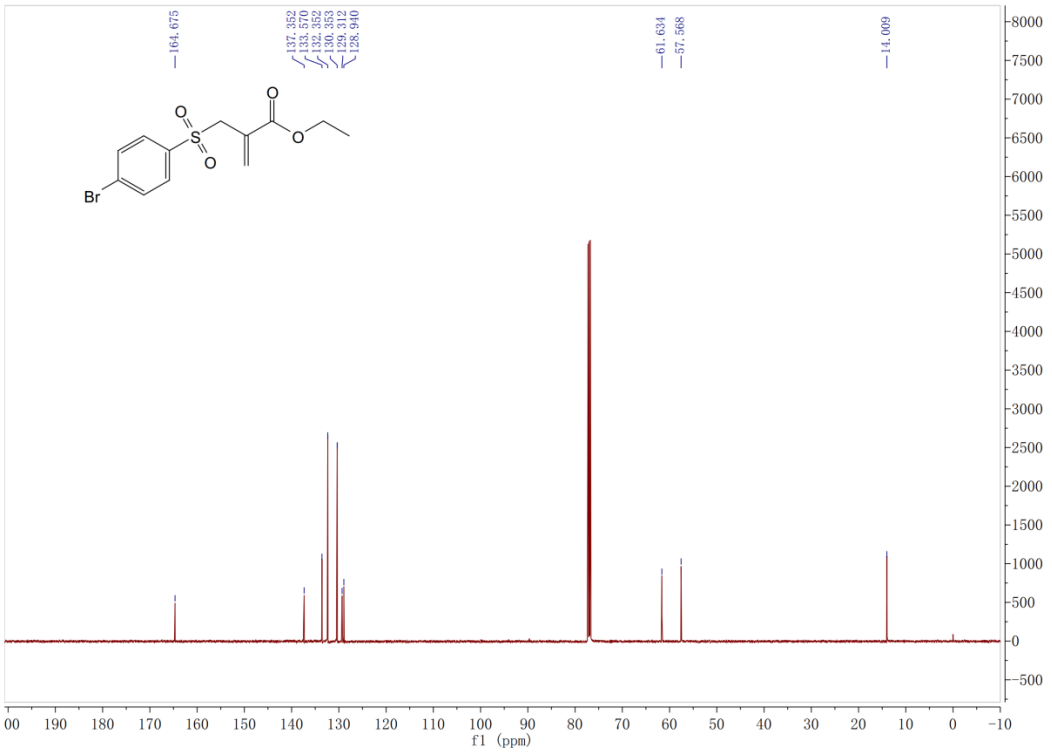


1e; ^{19}F NMR (471 MHz, $CDCl_3$)

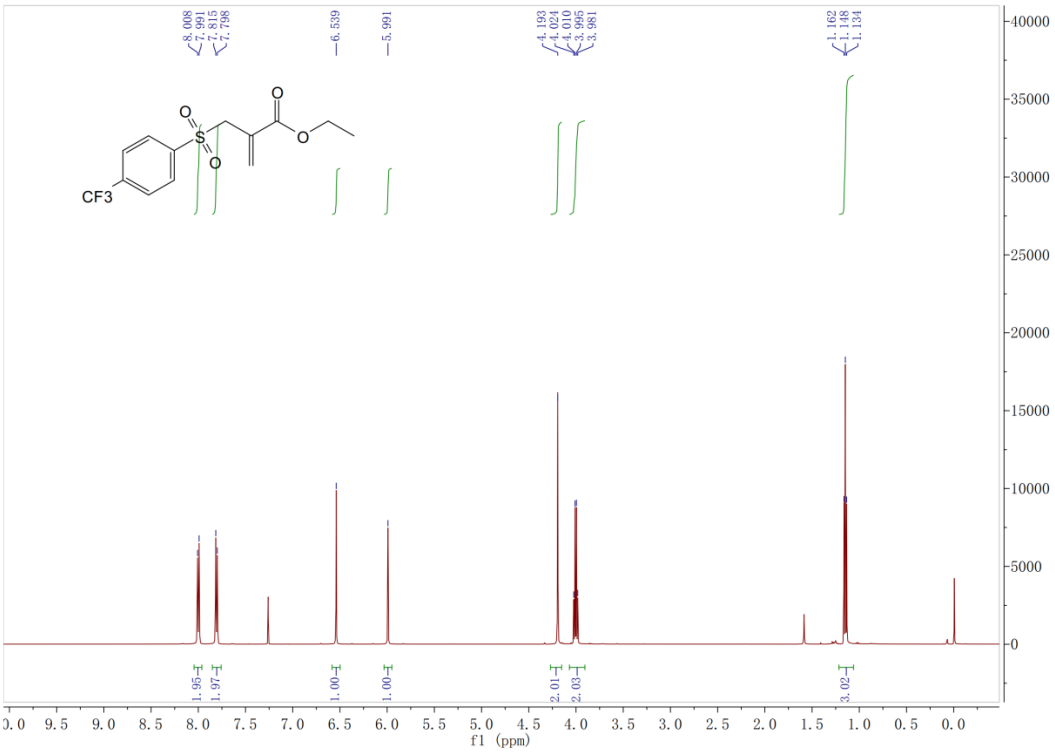


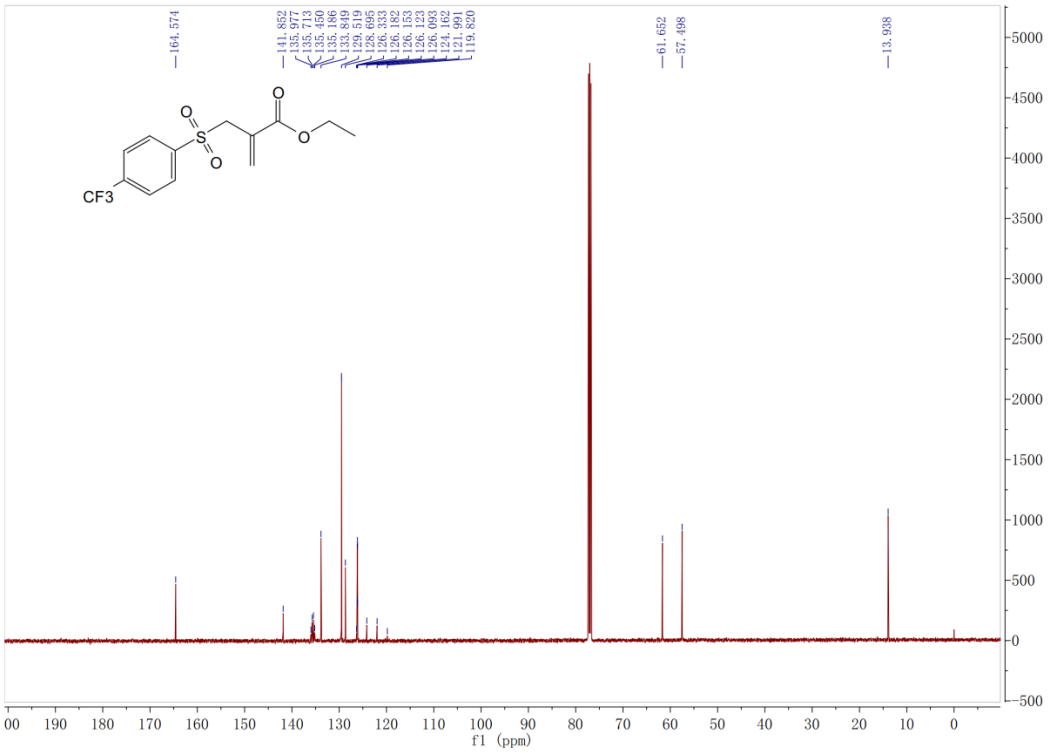
1g; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



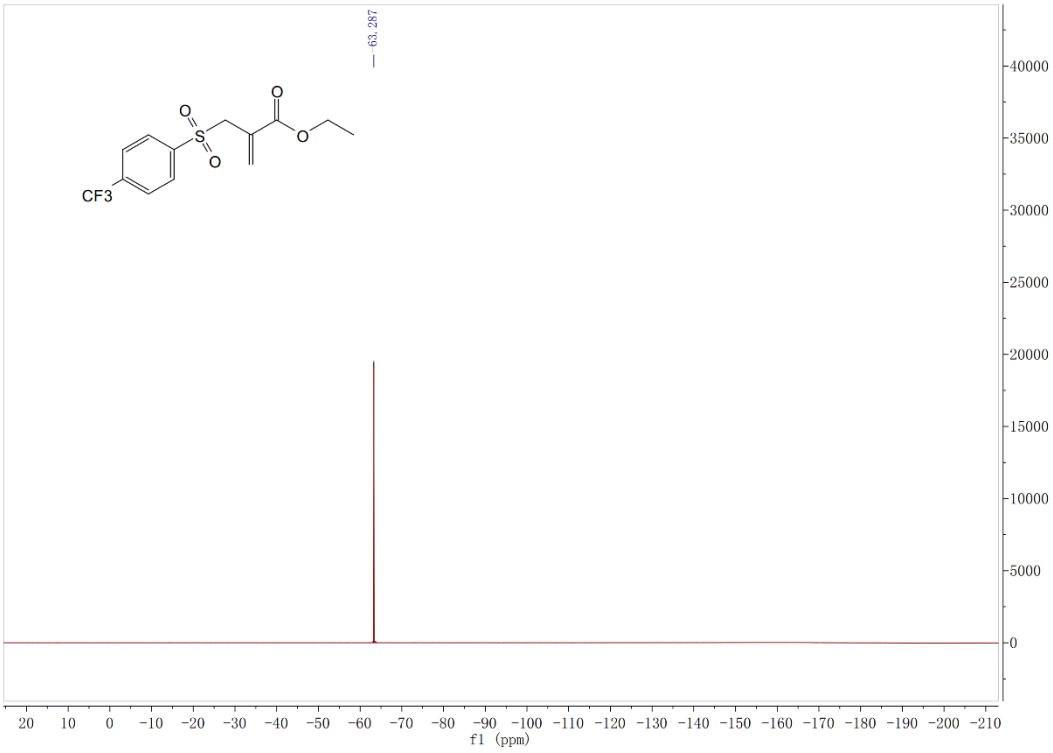


1h; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

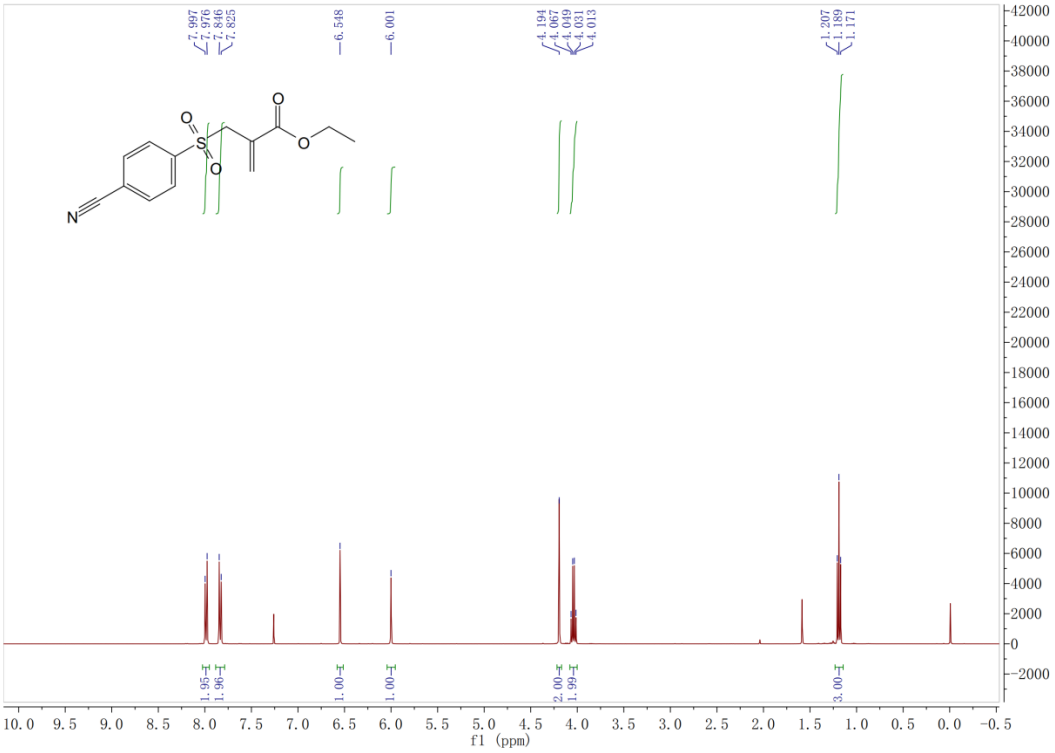


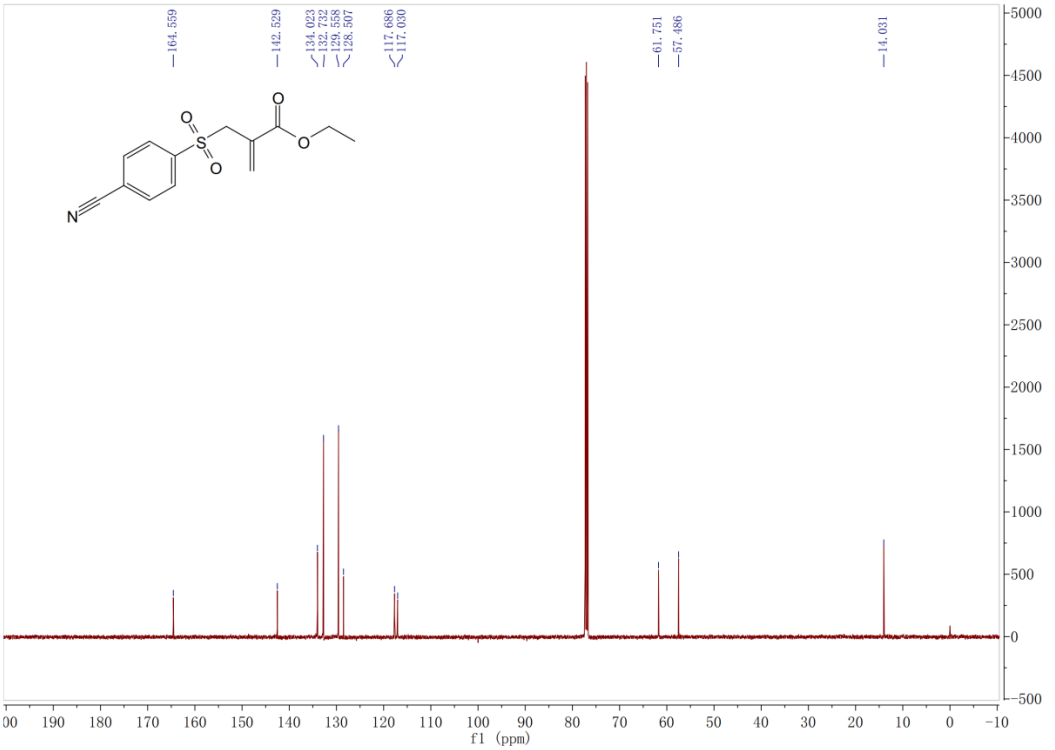


1h; **^{19}F NMR (471 MHz, $CDCl_3$)**

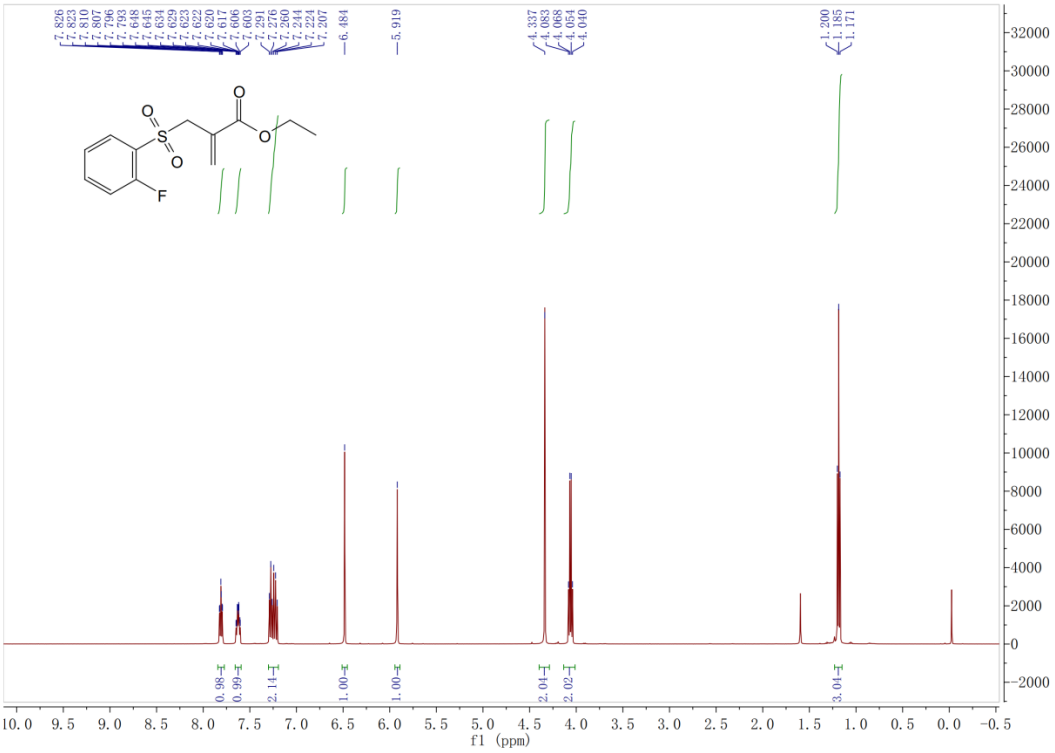


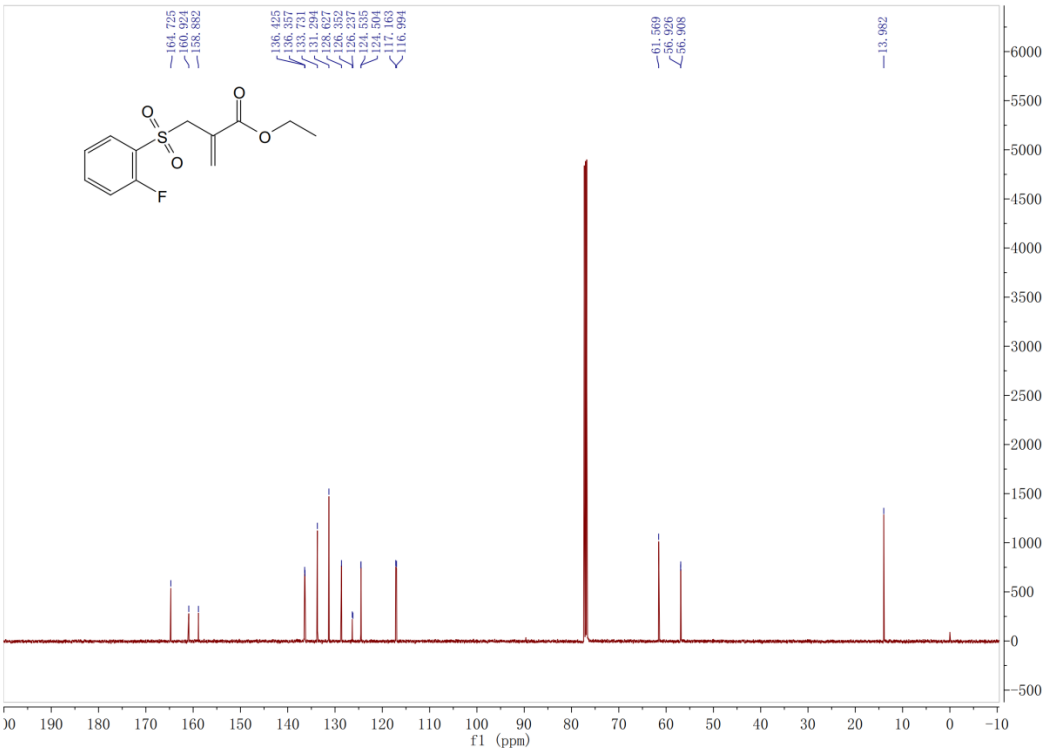
1i; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



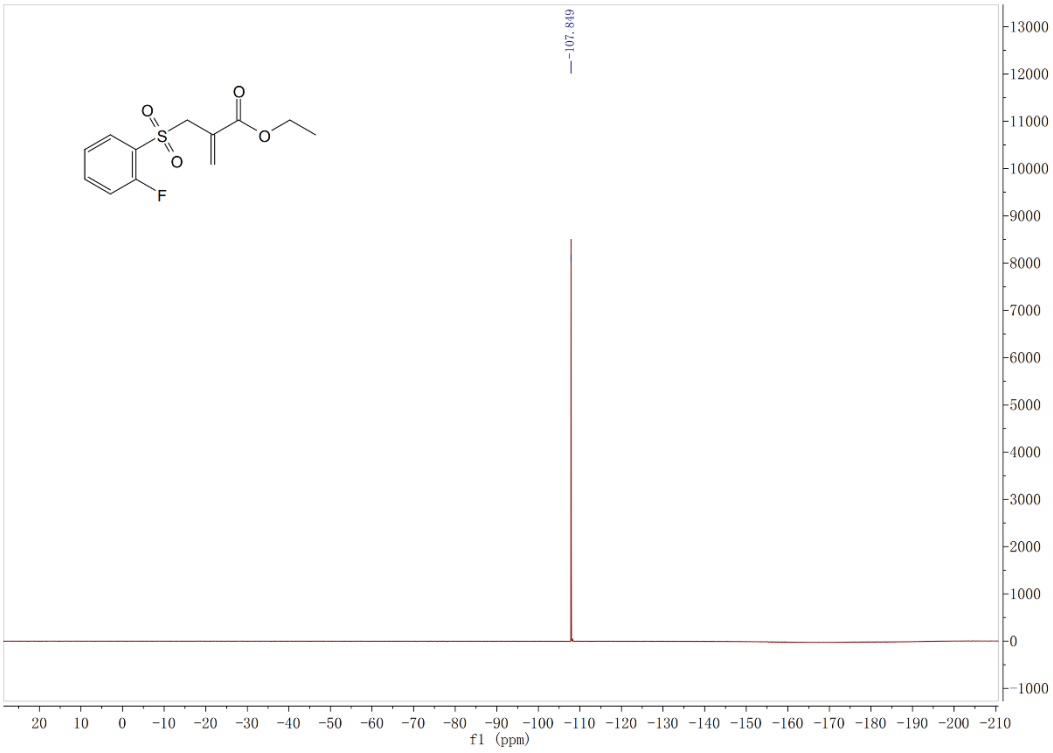


1j; ^{1}**H NMR (500 MHz, CDCl$_3$);** ^{13}**C NMR (126 MHz, CDCl$_3$)**

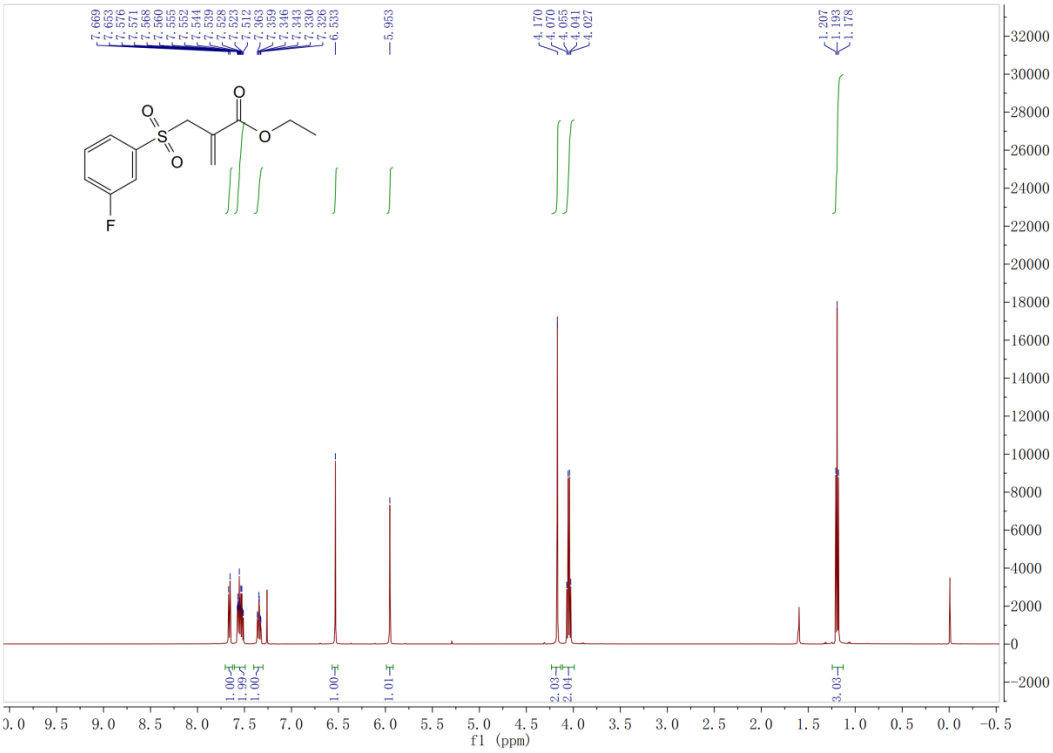


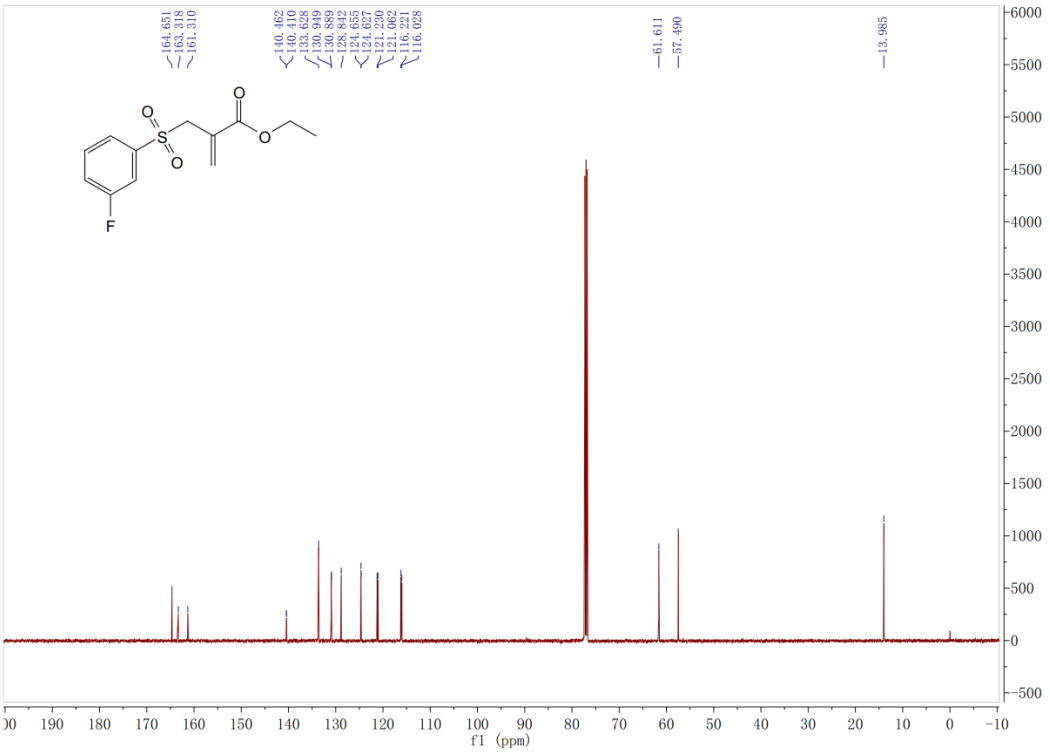


1j; ^{19}F NMR (471 MHz, $CDCl_3$)

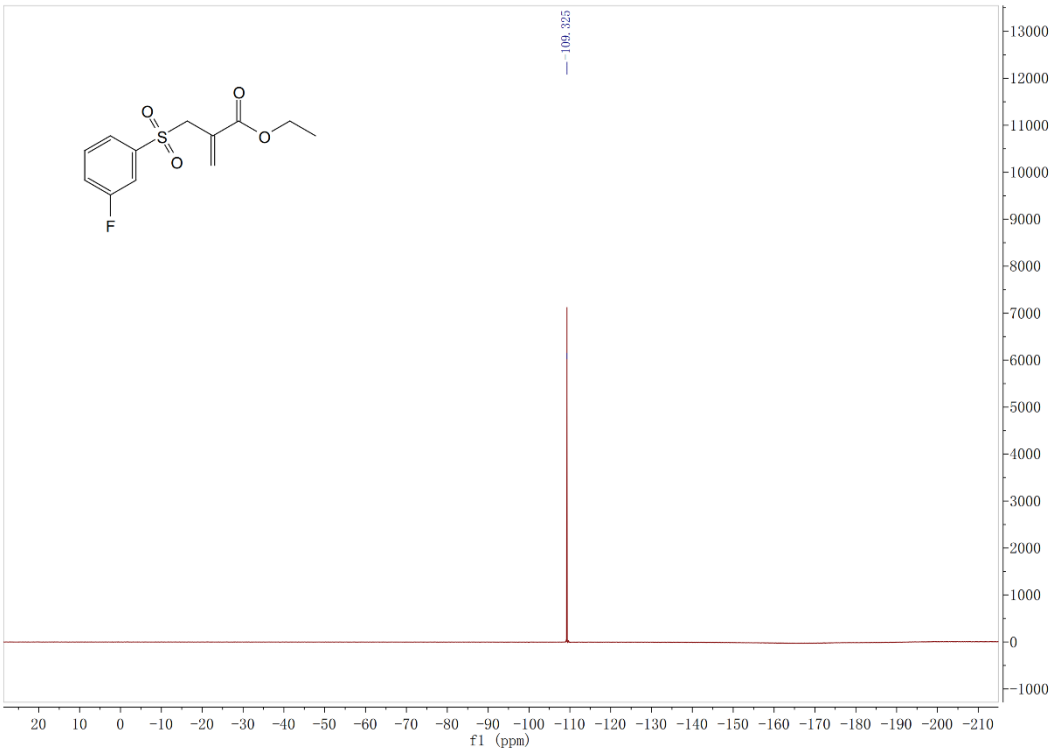


1k; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

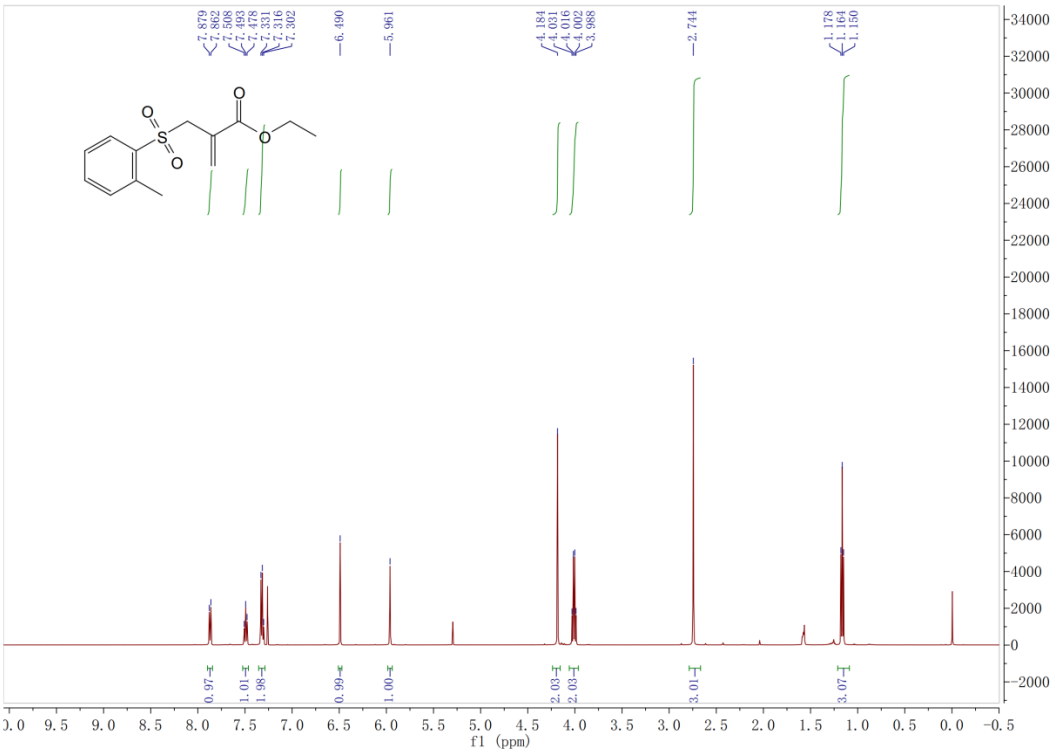


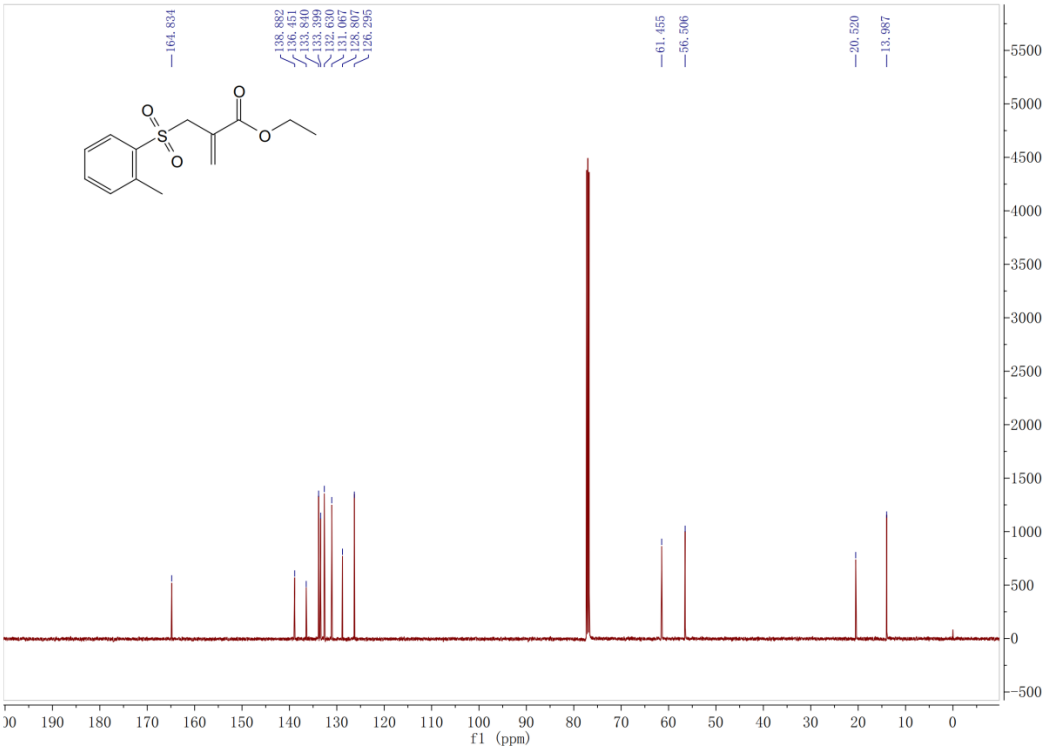


1k; **^{19}F NMR (471 MHz, $CDCl_3$)**

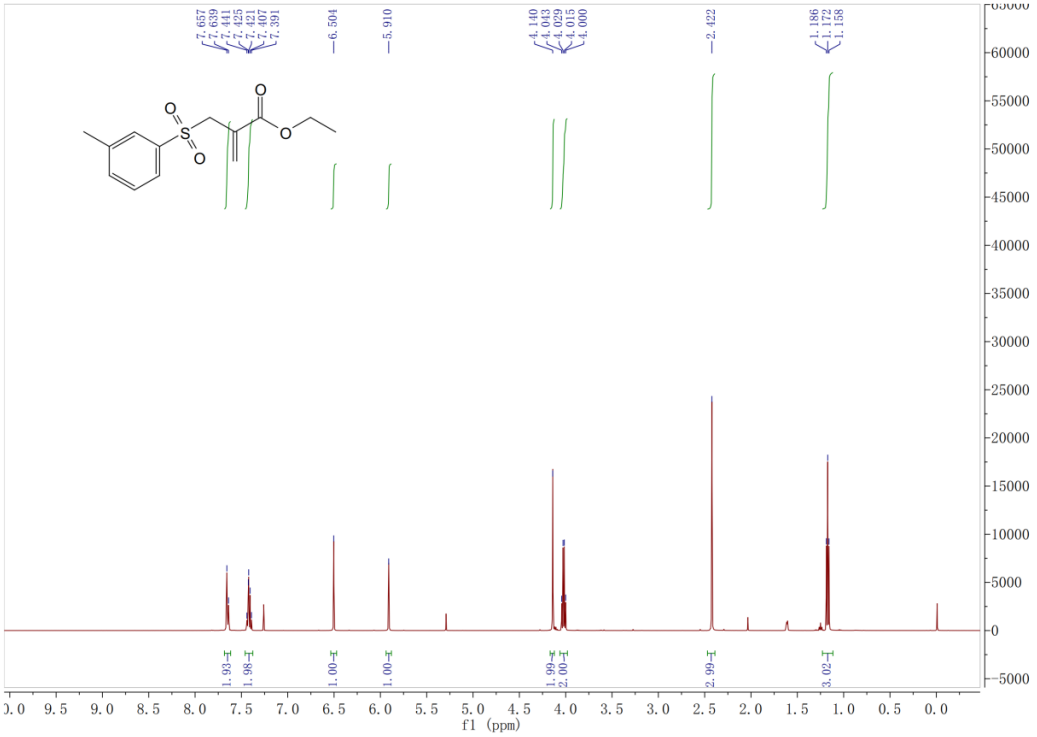


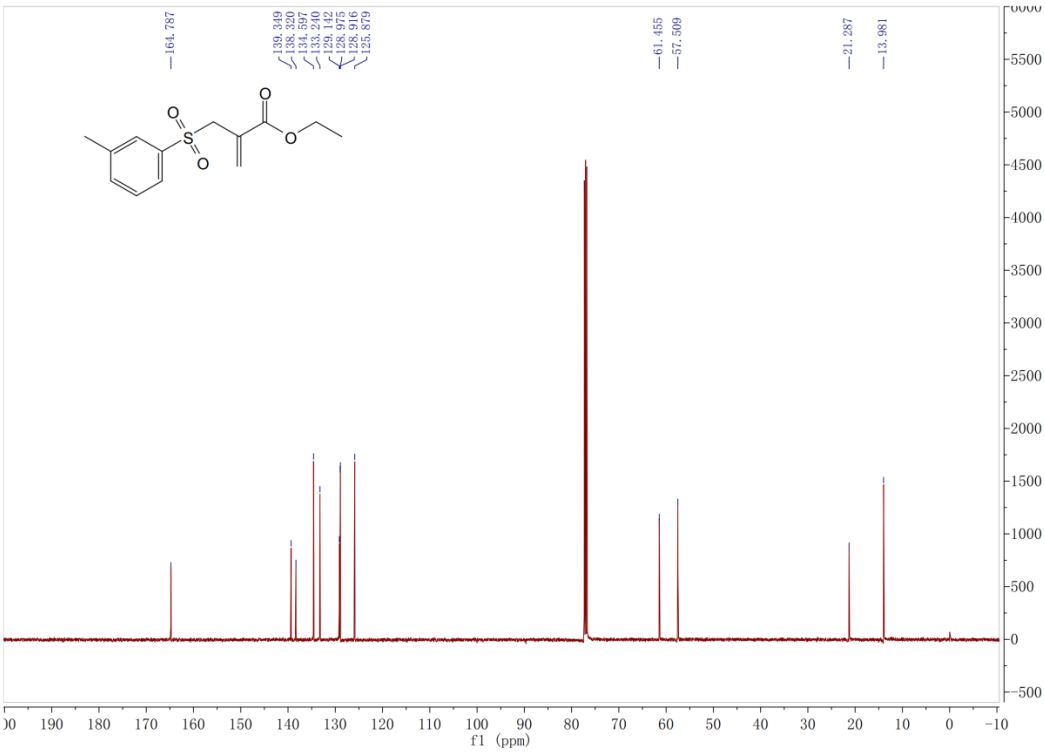
1l; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



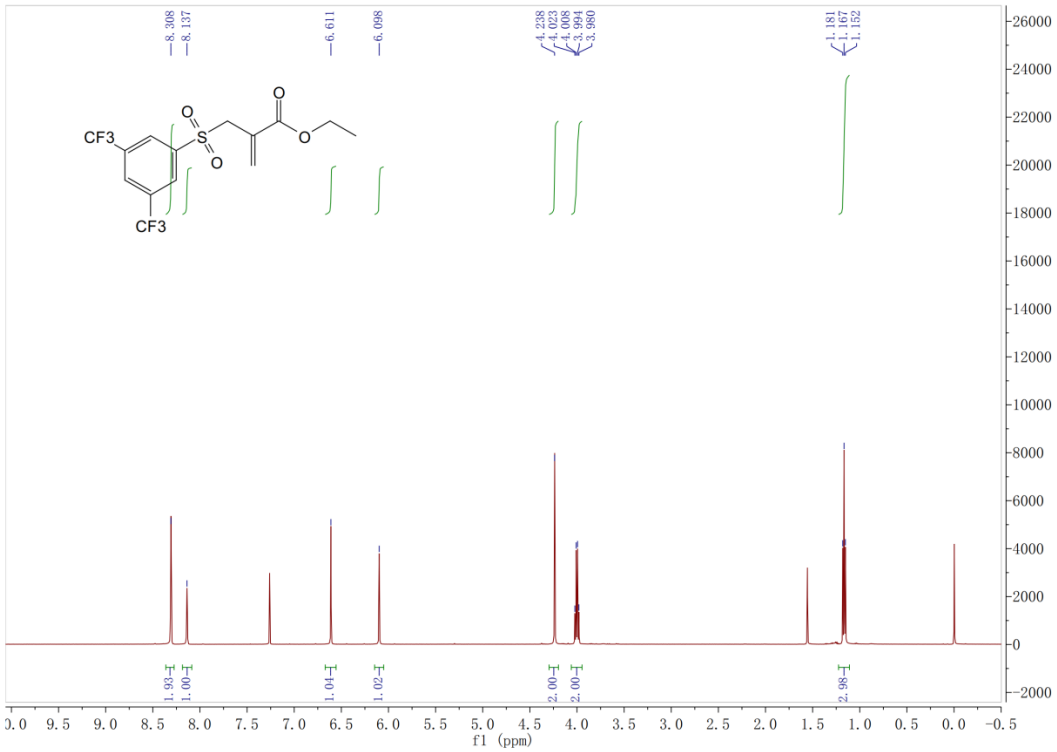


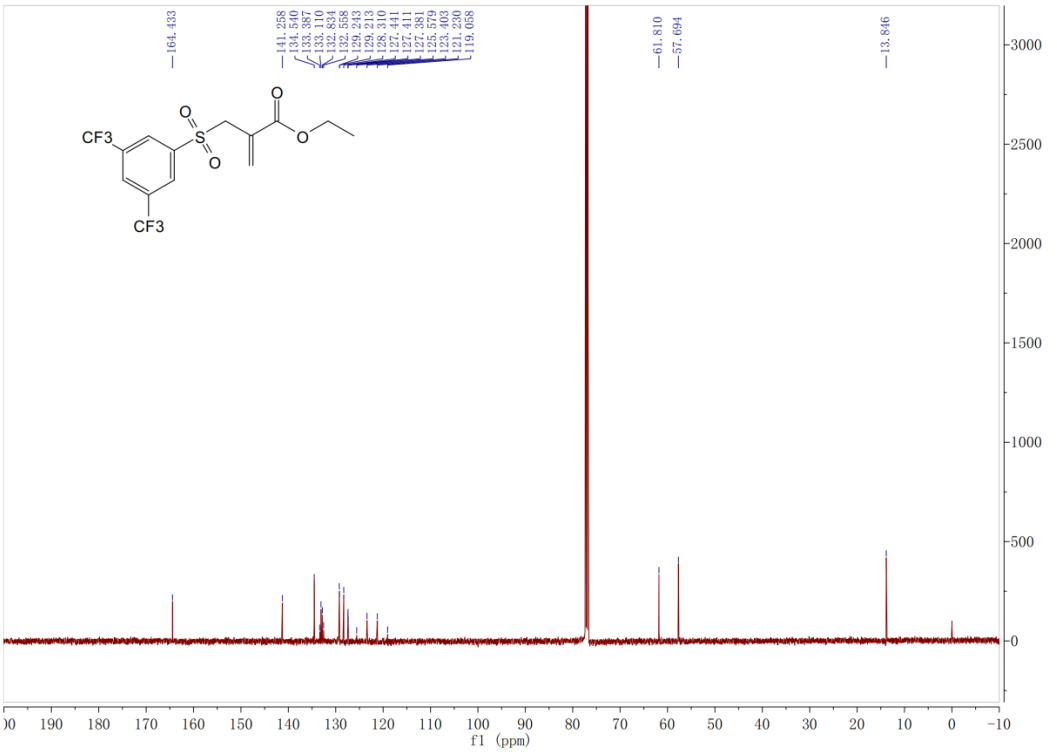
1m; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



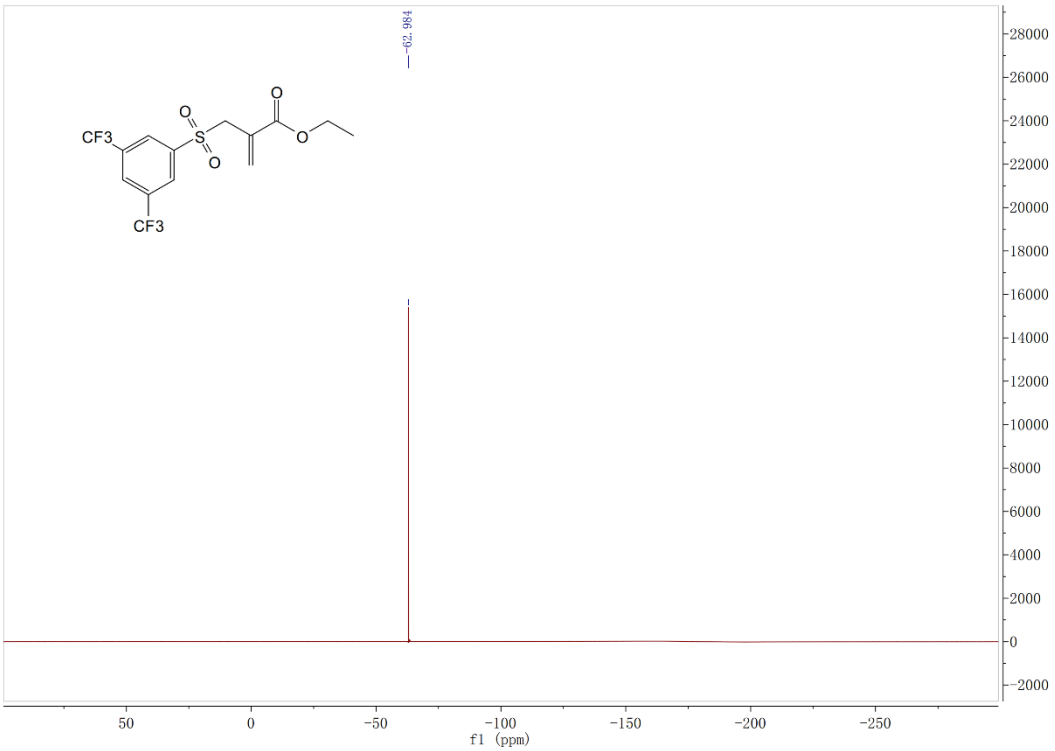


1n; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**

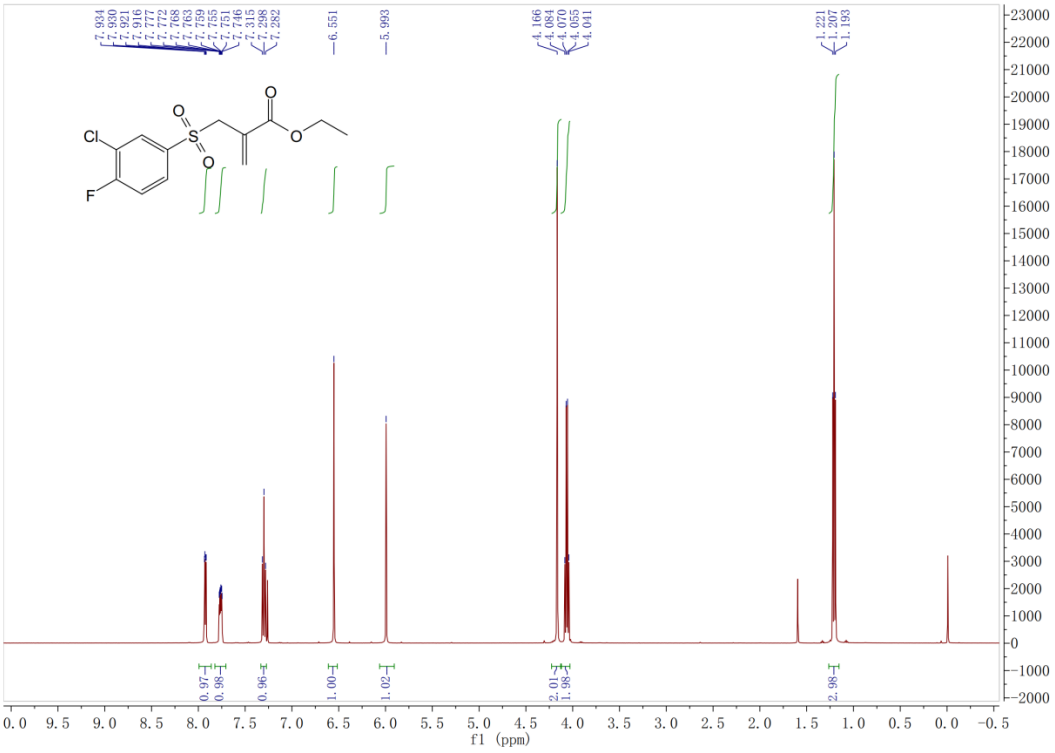


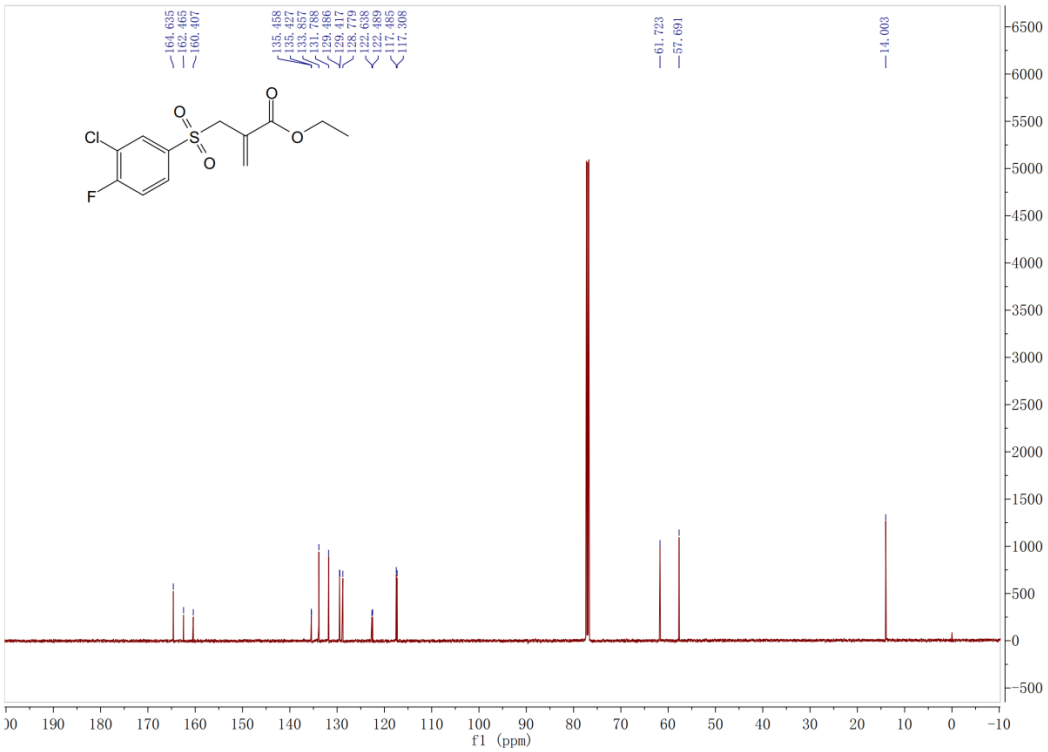


1n; ^{19}F NMR (471 MHz, $CDCl_3$)

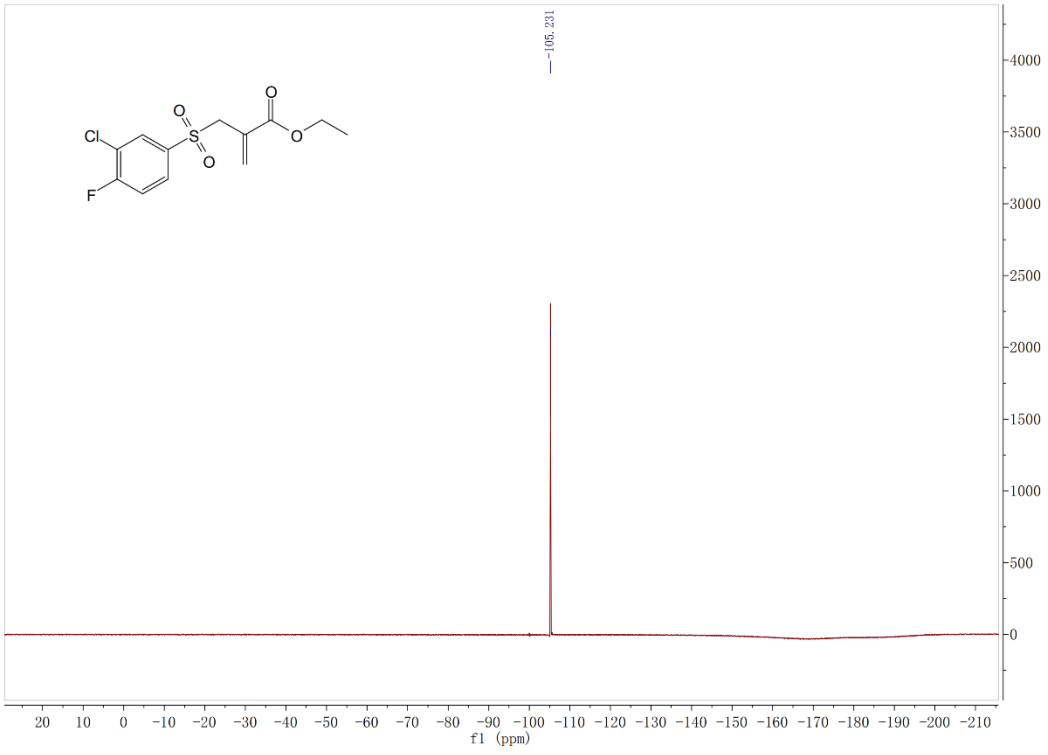


1o; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

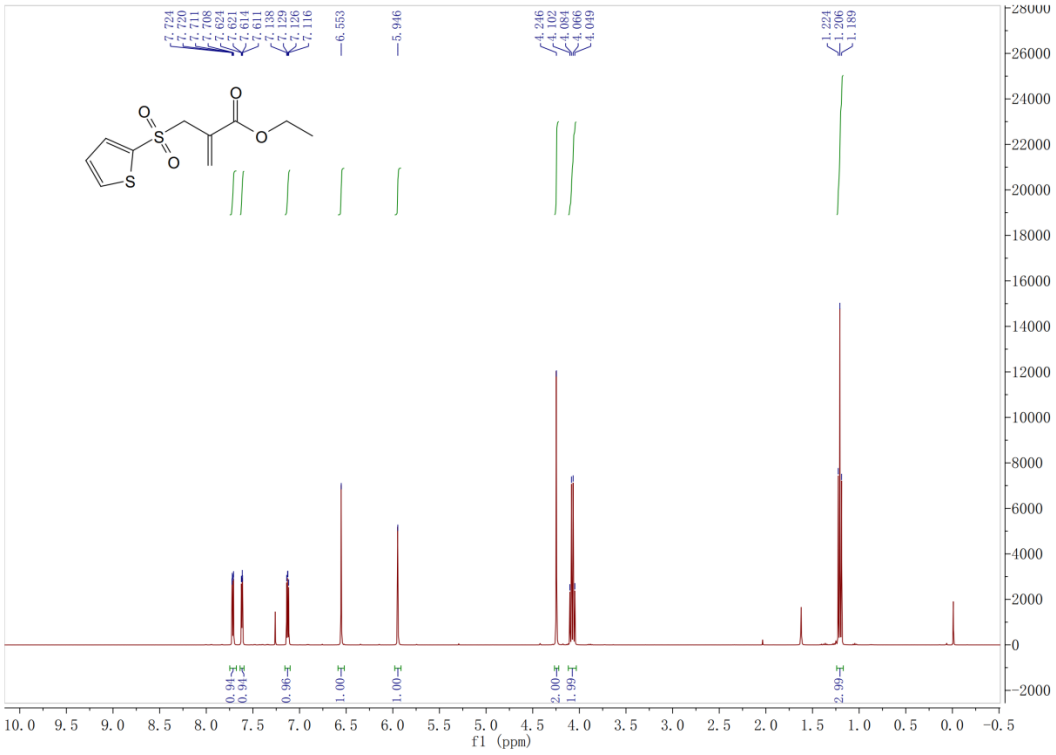


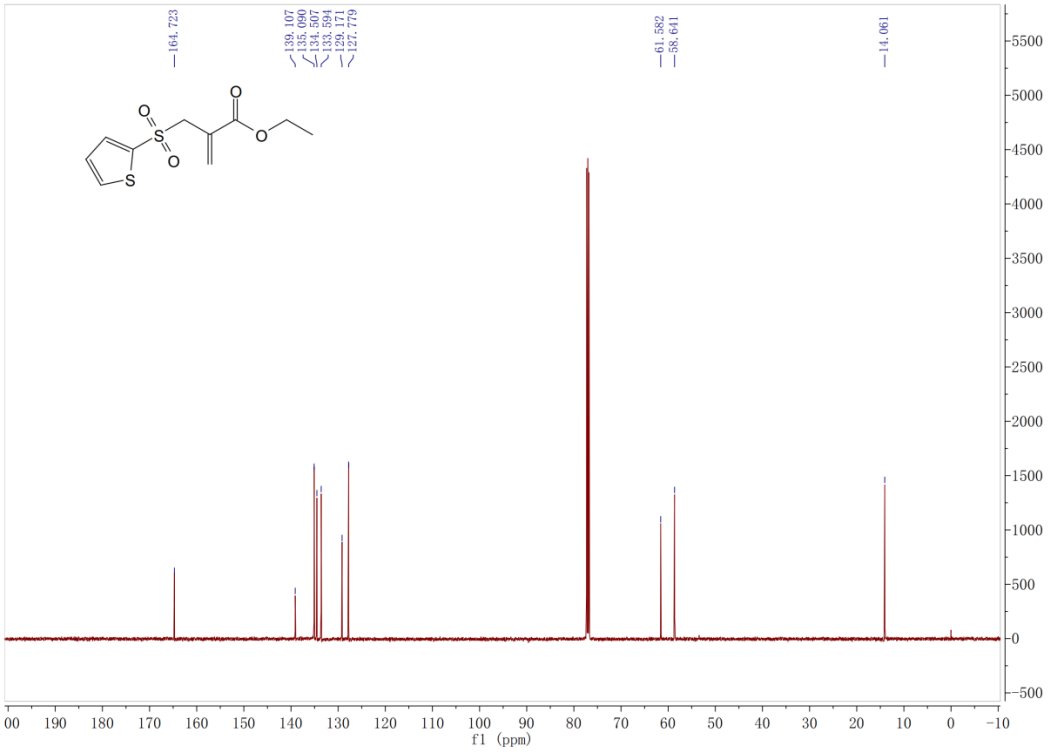


1o; **^{19}F NMR (471 MHz, $CDCl_3$)**

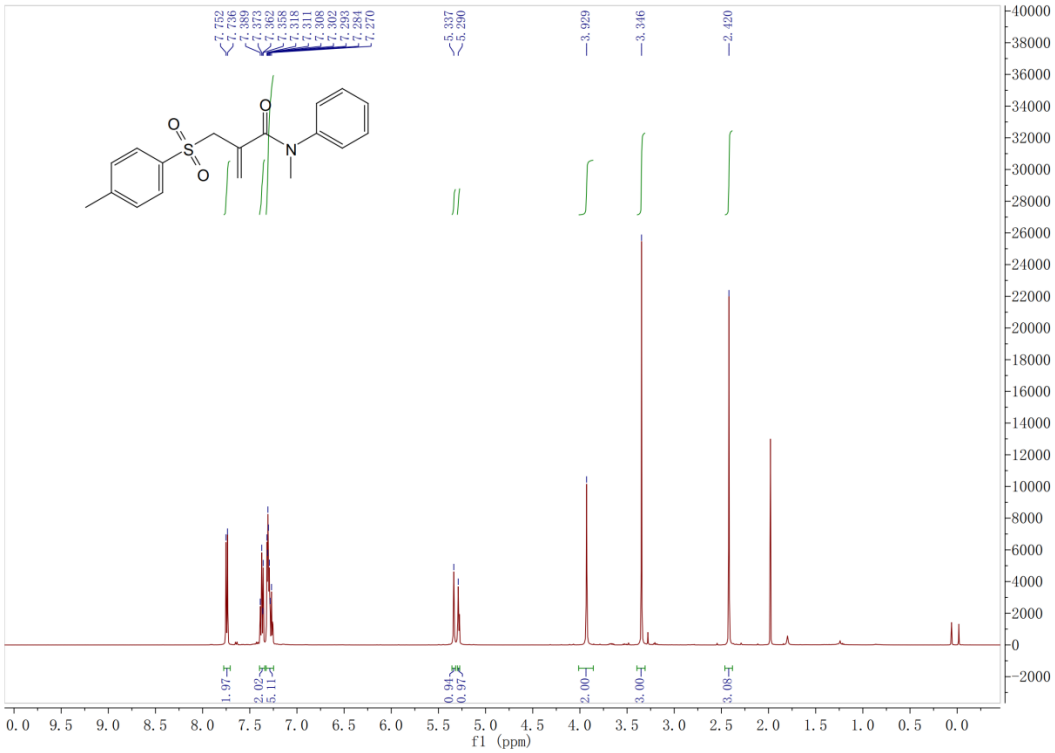


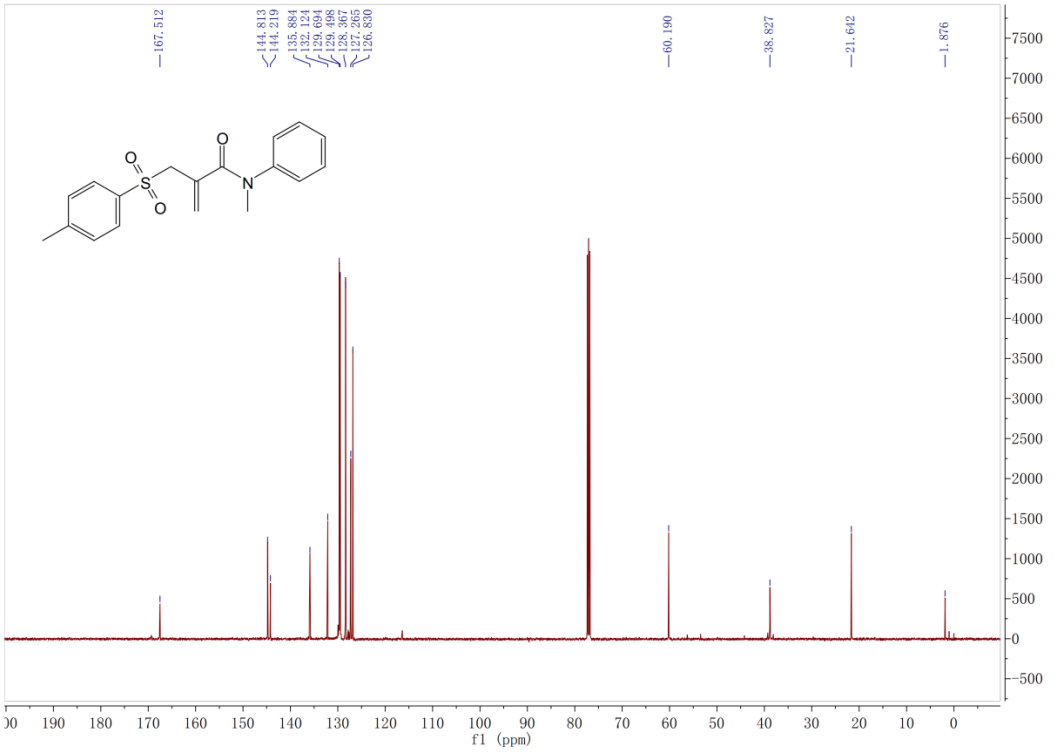
1q; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



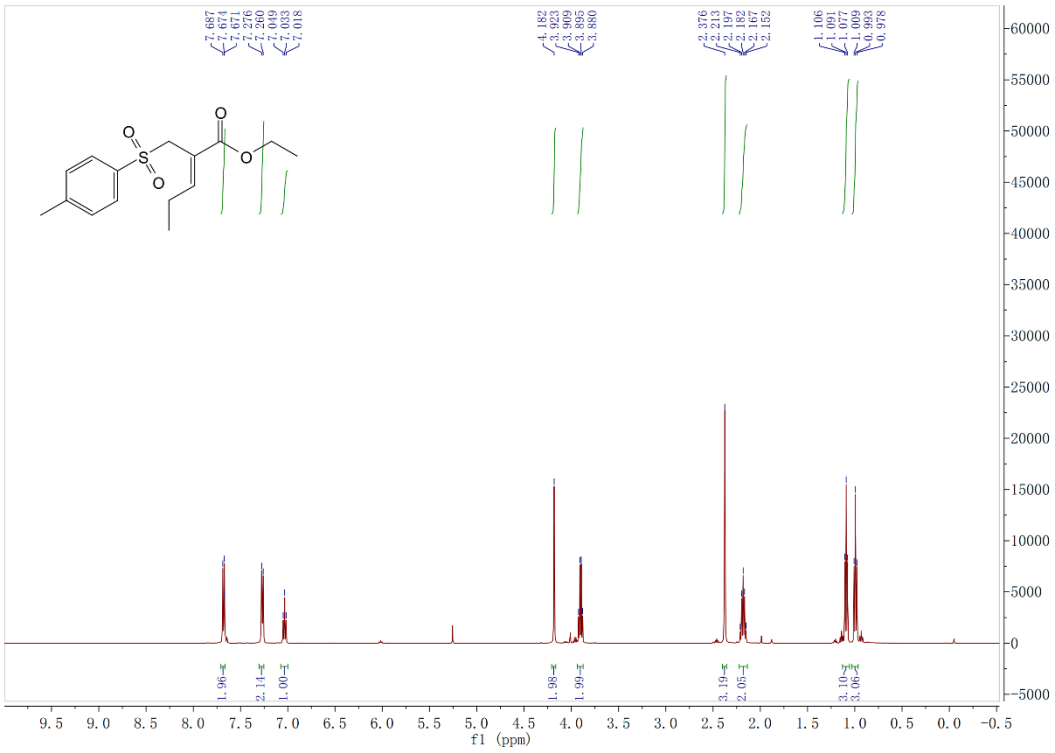


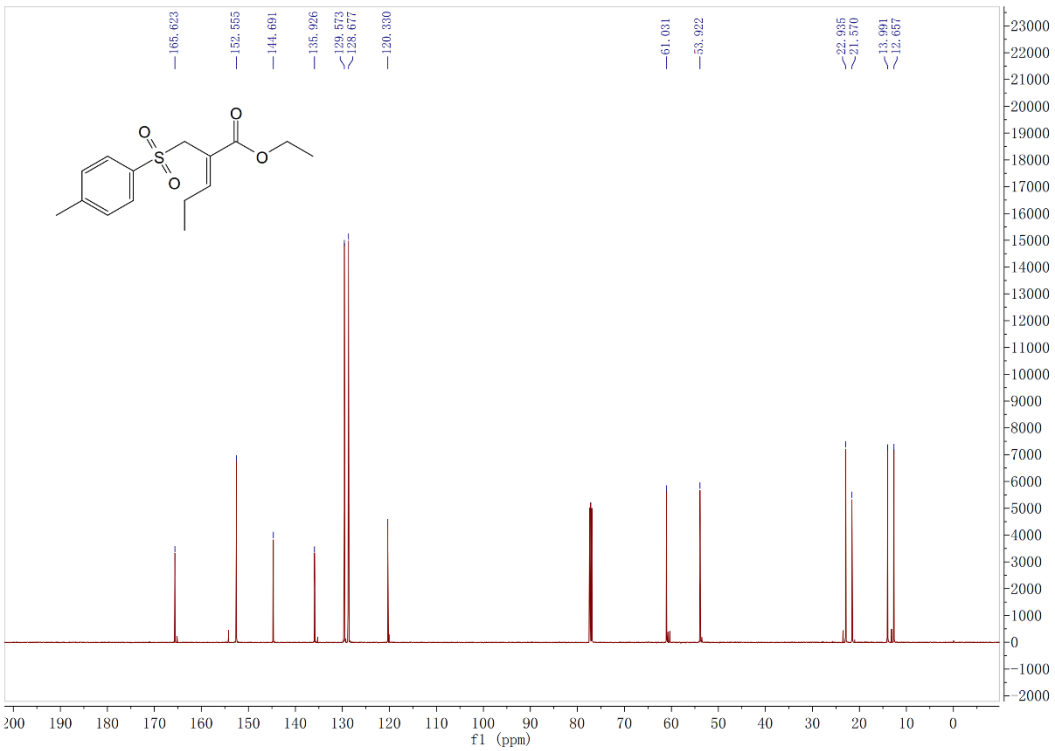
1t; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



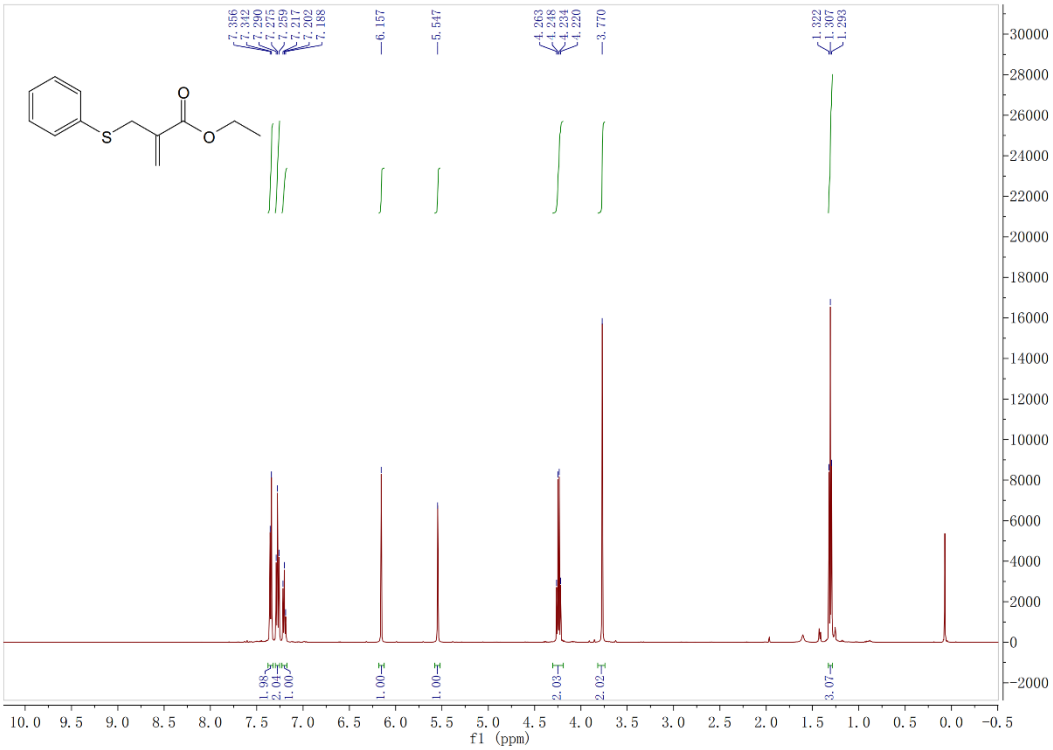


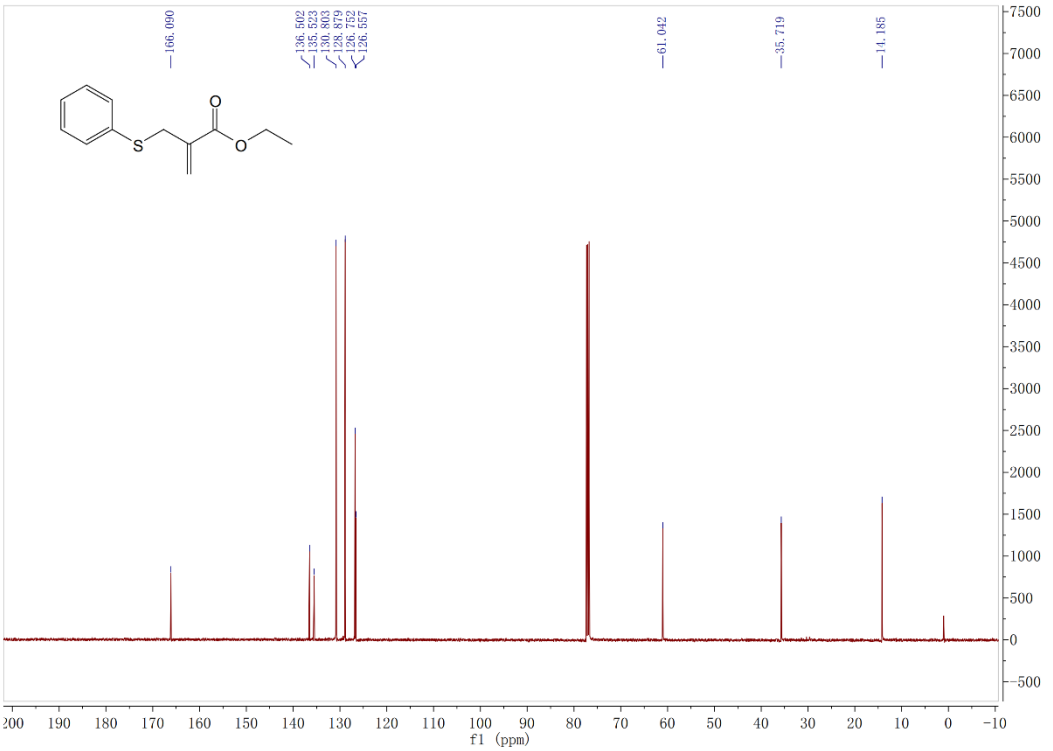
1aa; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



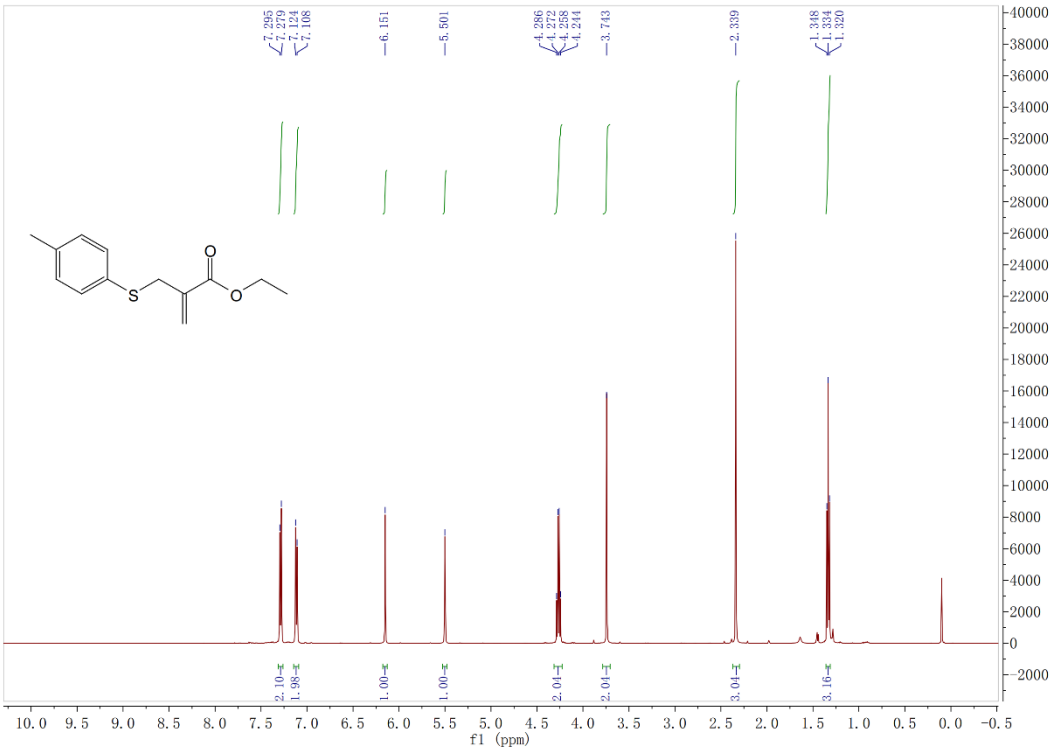


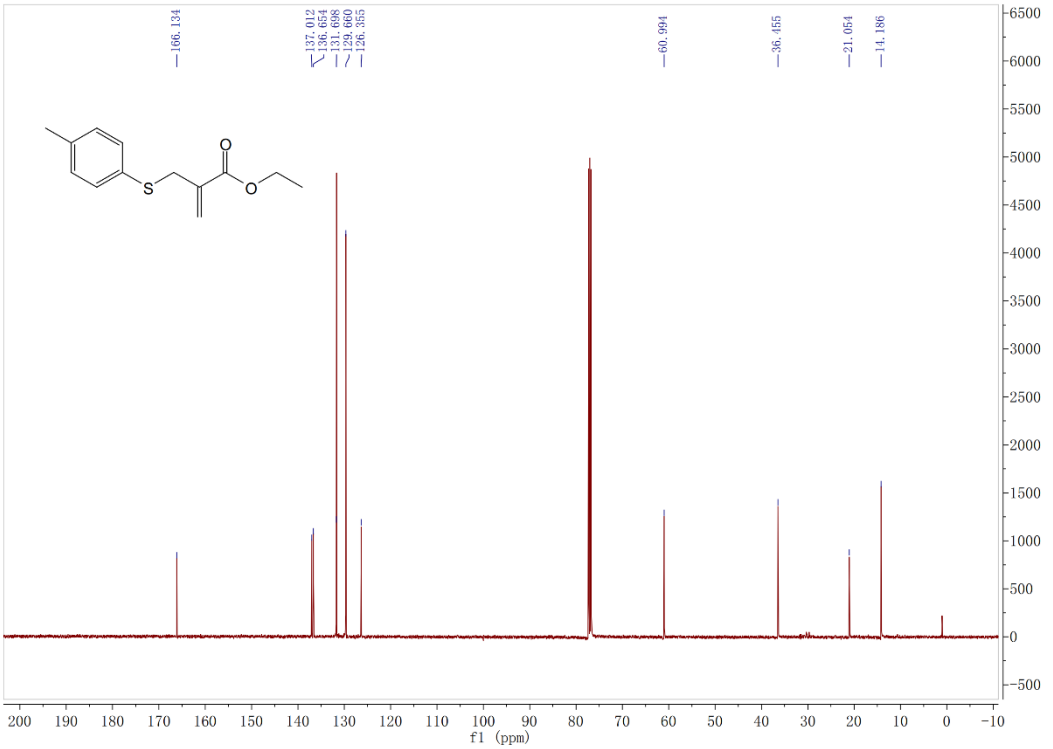
2a; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



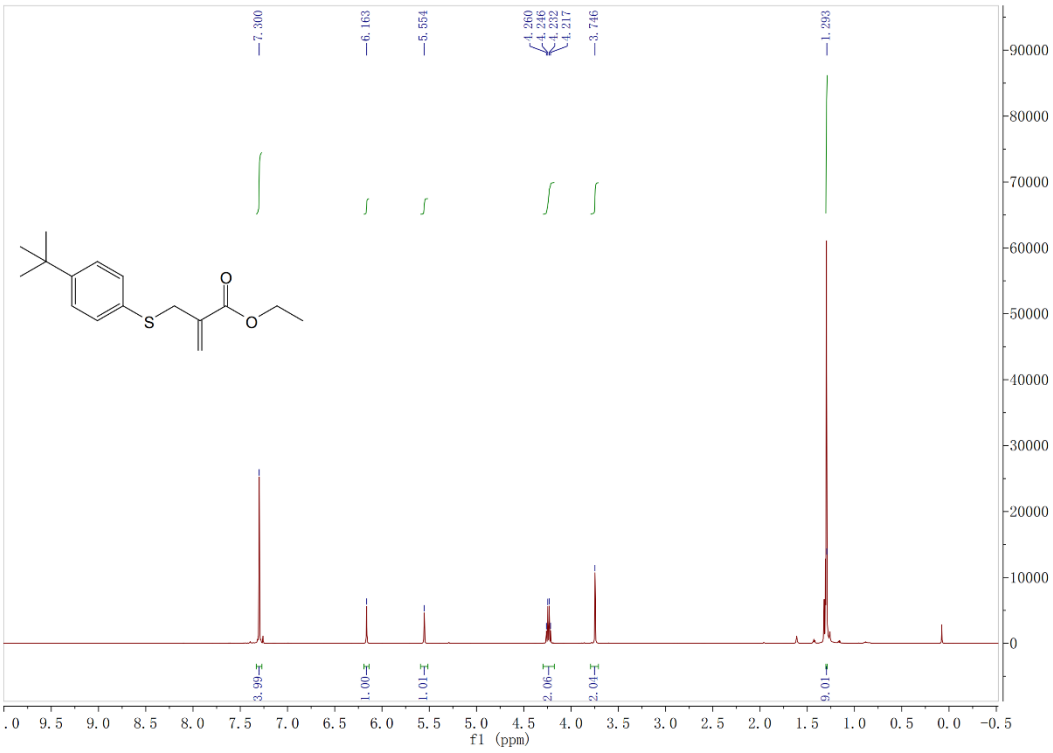


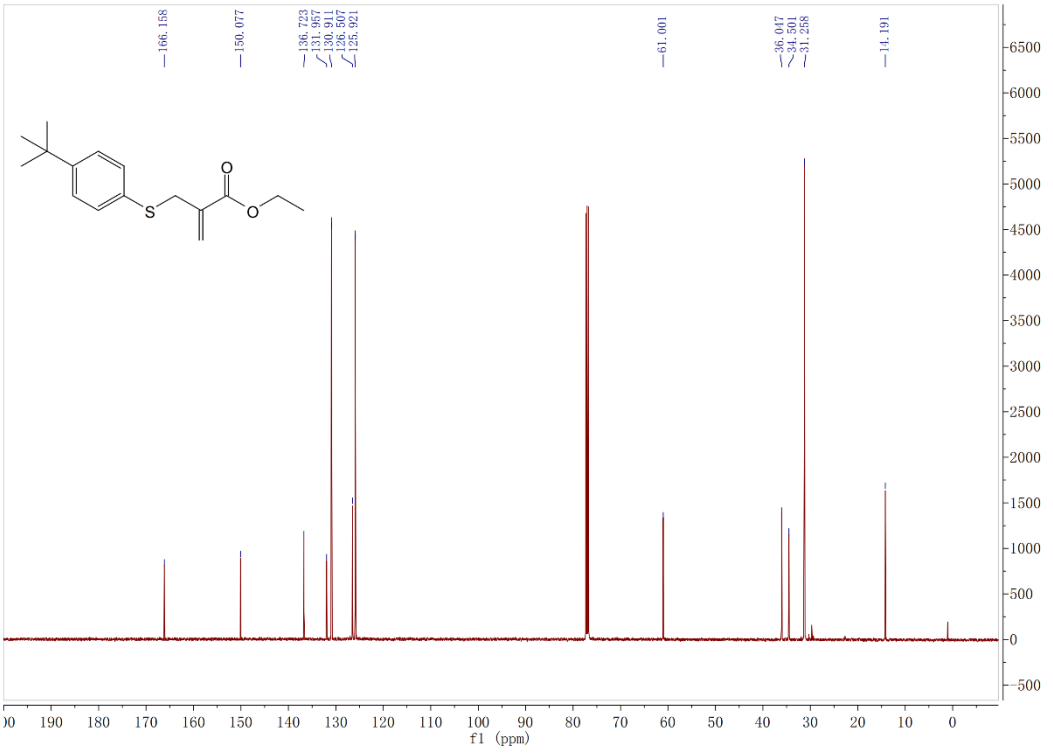
2b; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



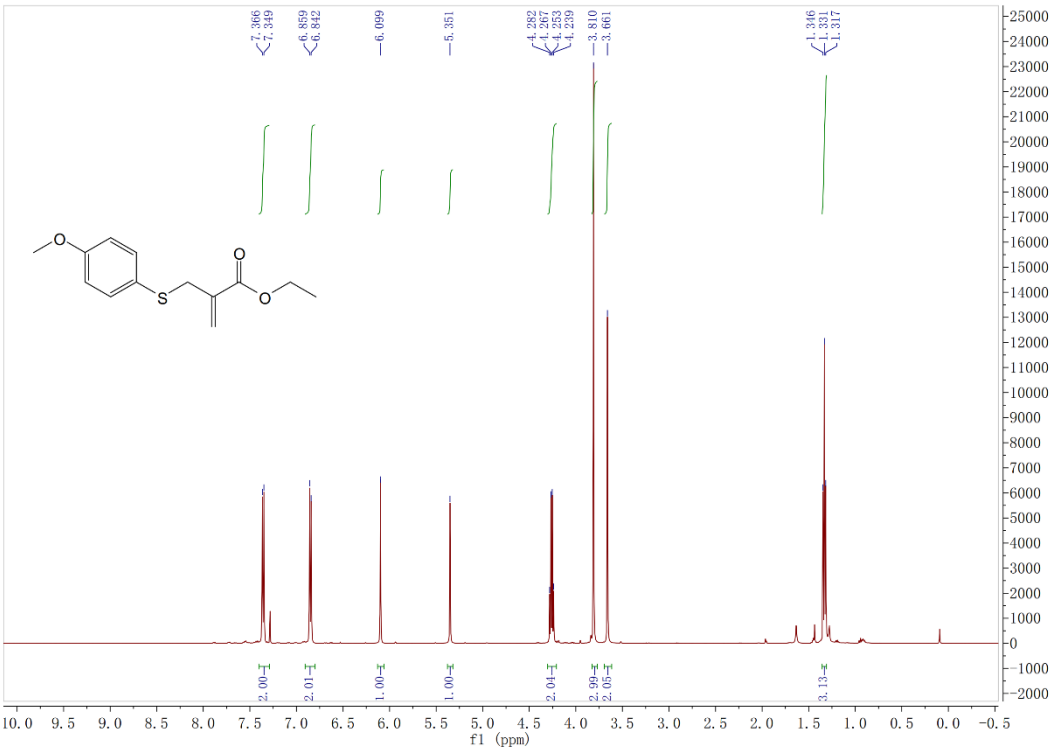


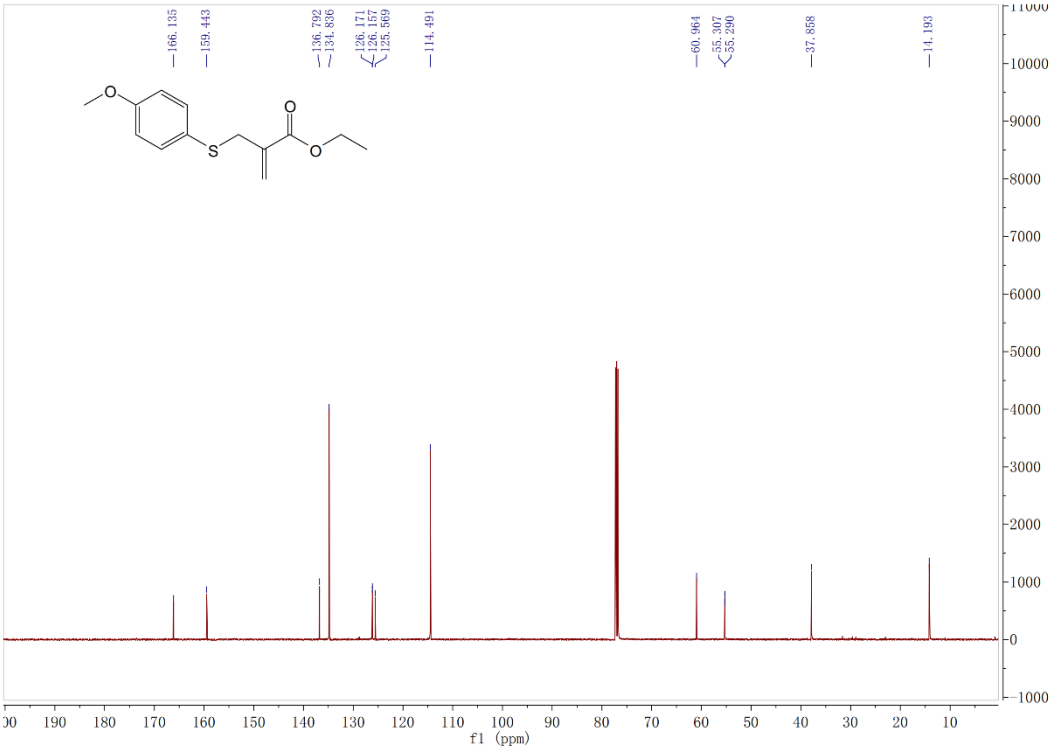
2c; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



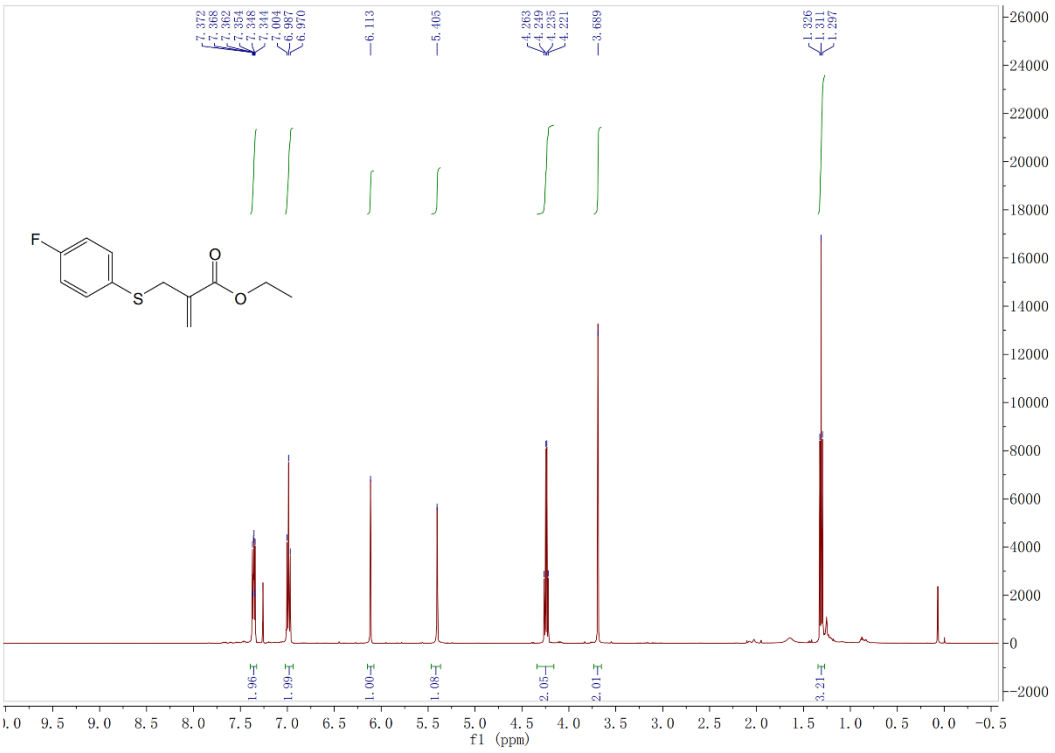


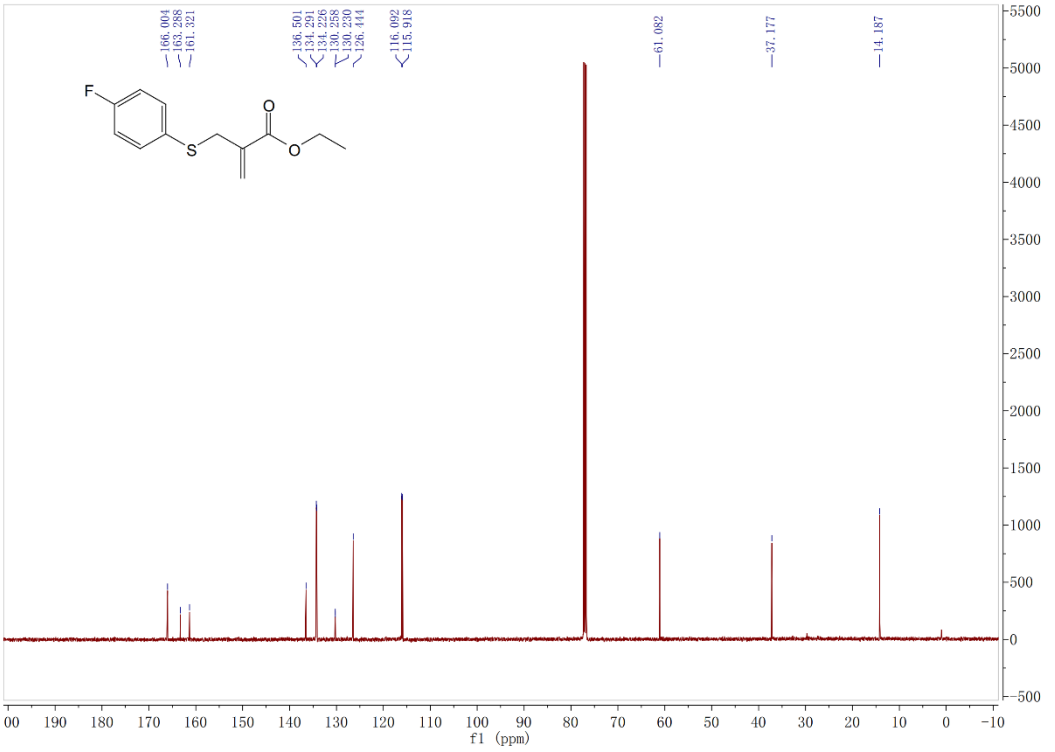
2d; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



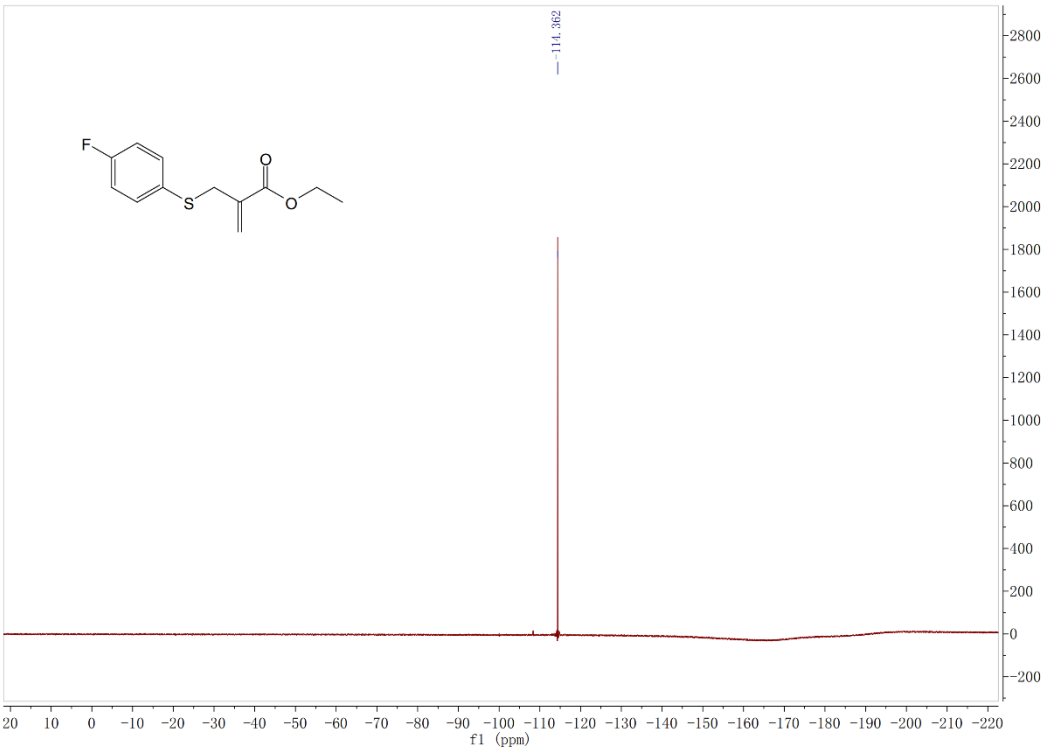


2e; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

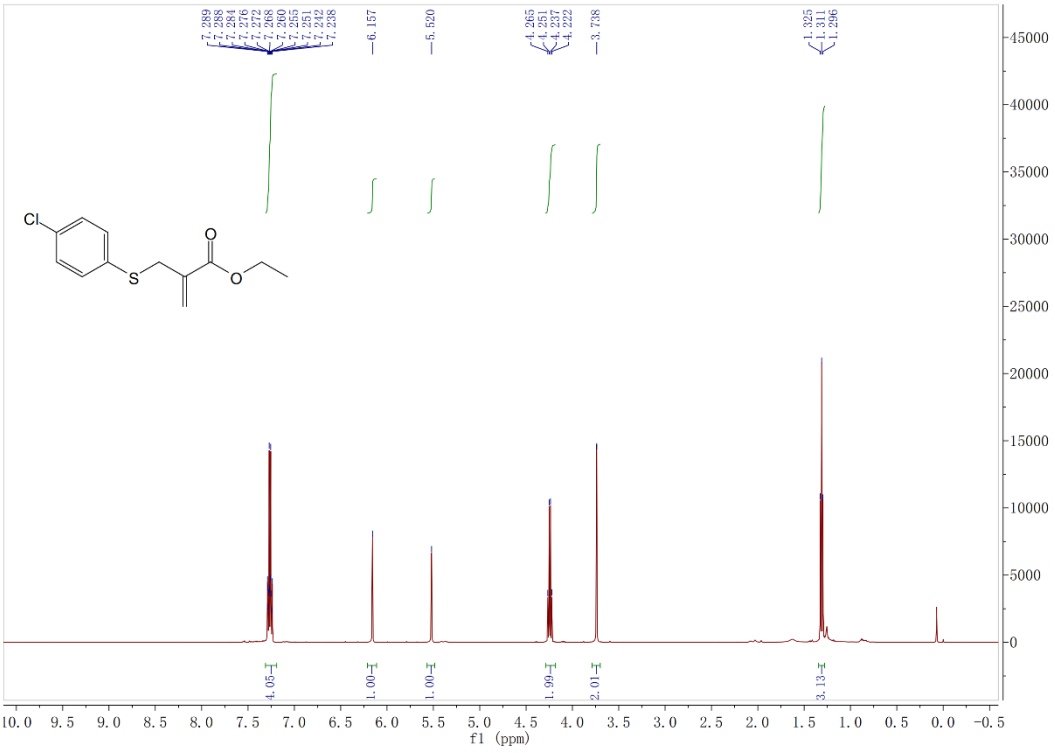


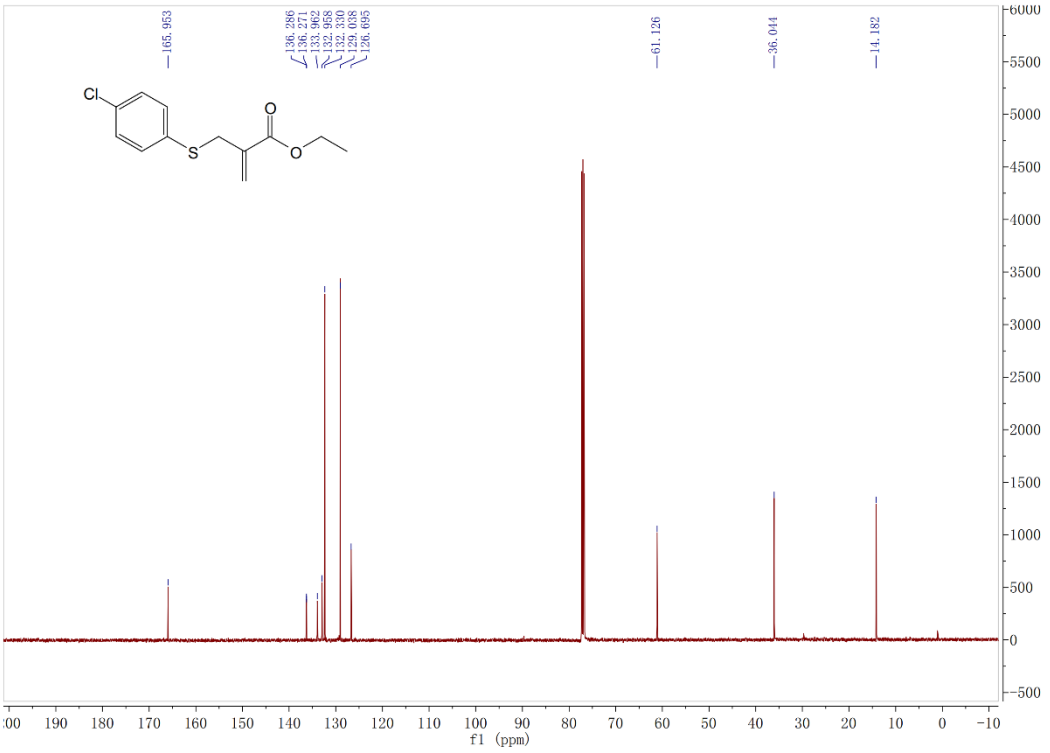


2e; ^{19}**F NMR (471 MHz, CDCl$_3$)**

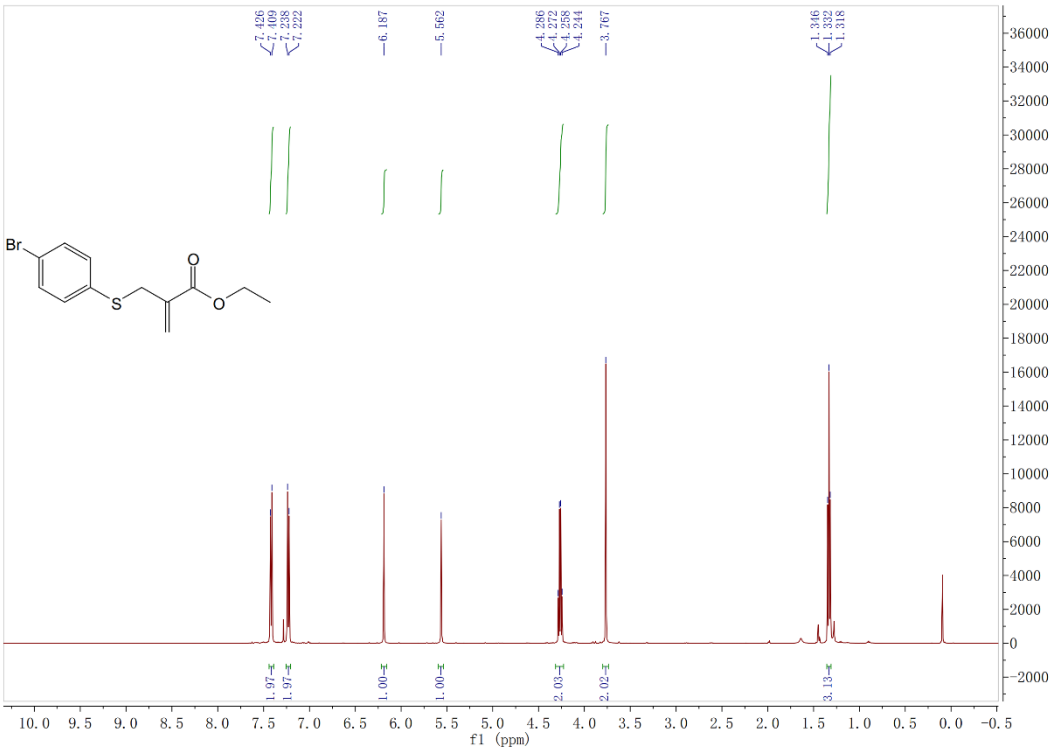


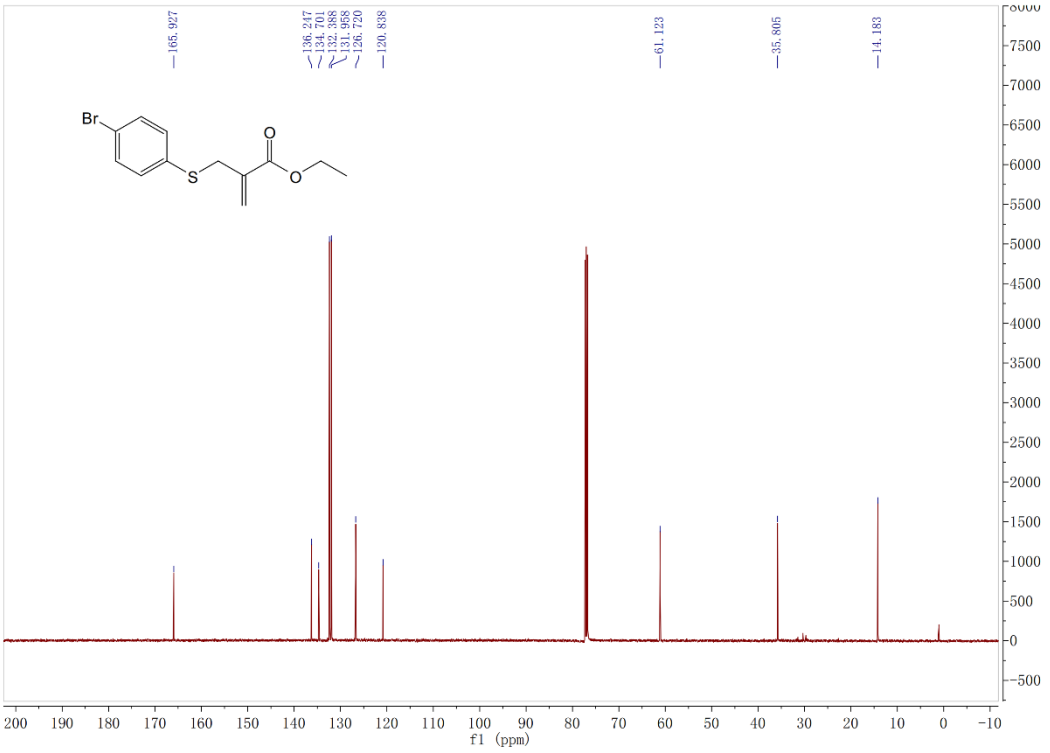
2f; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



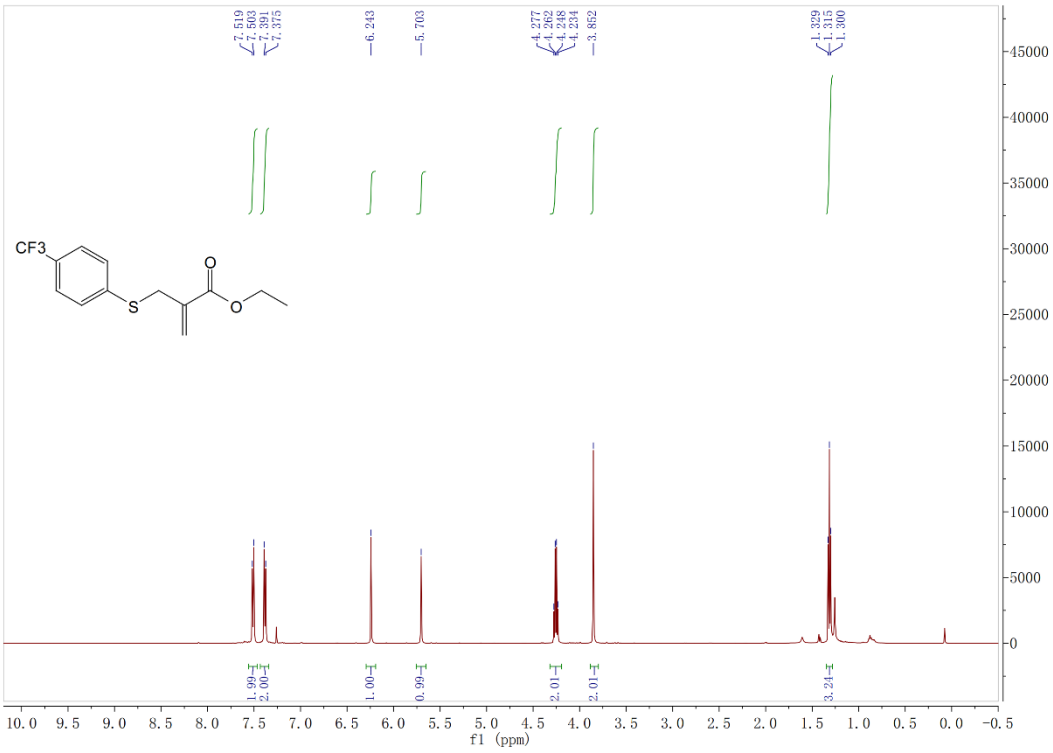


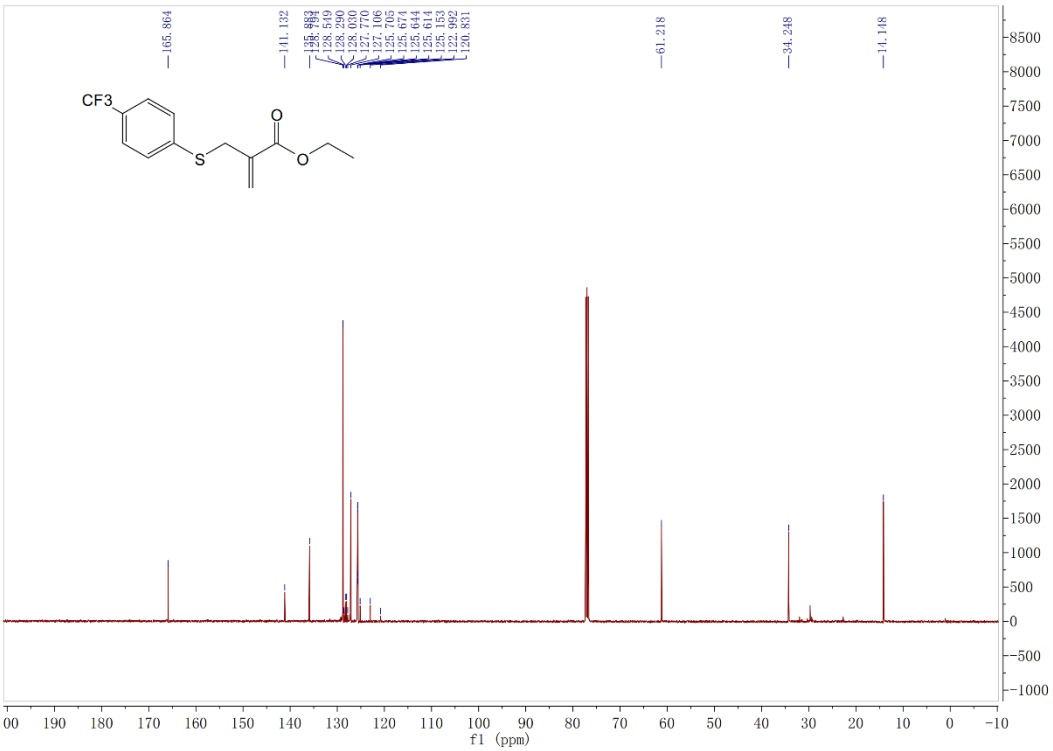
2g; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



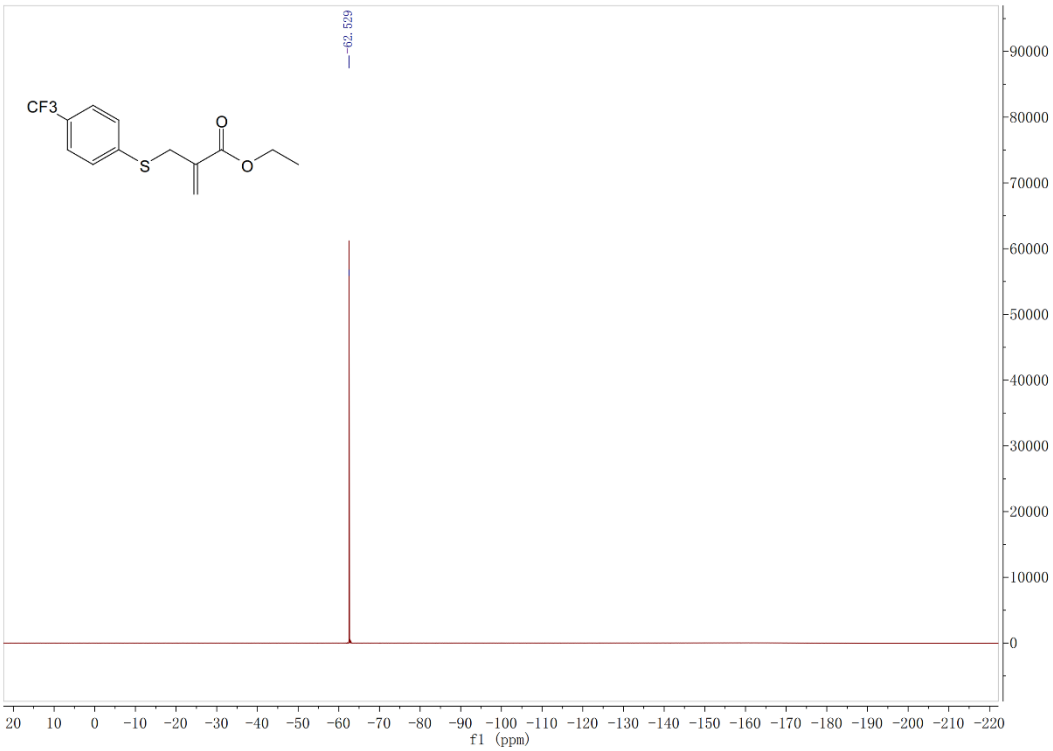


2h; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**

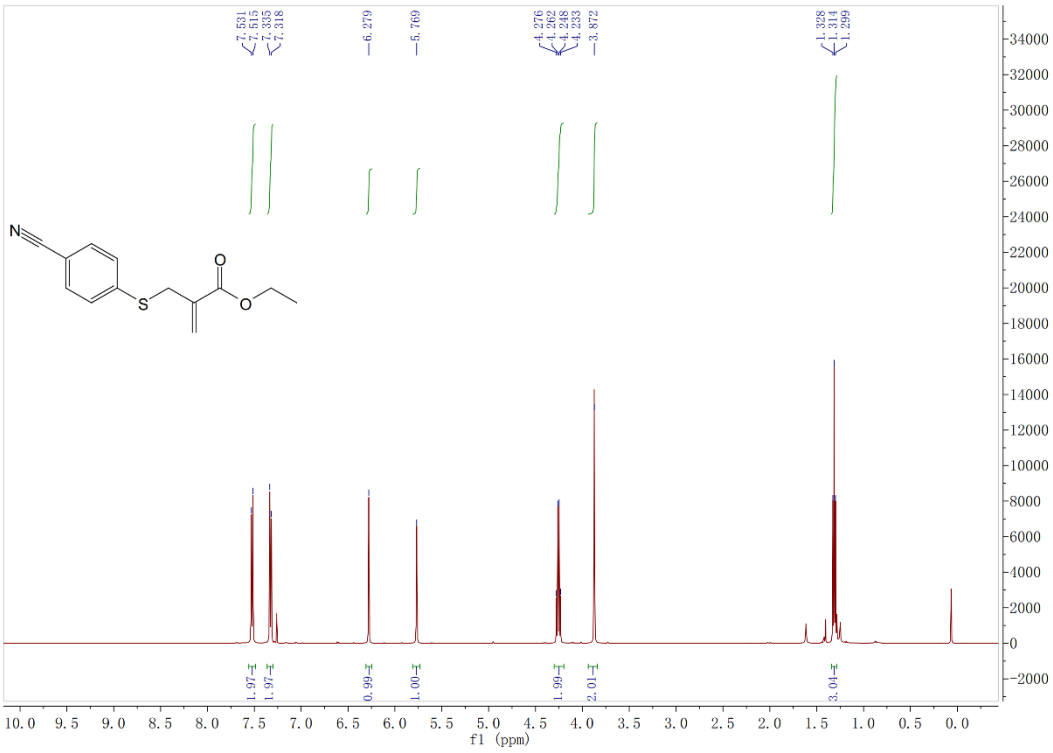


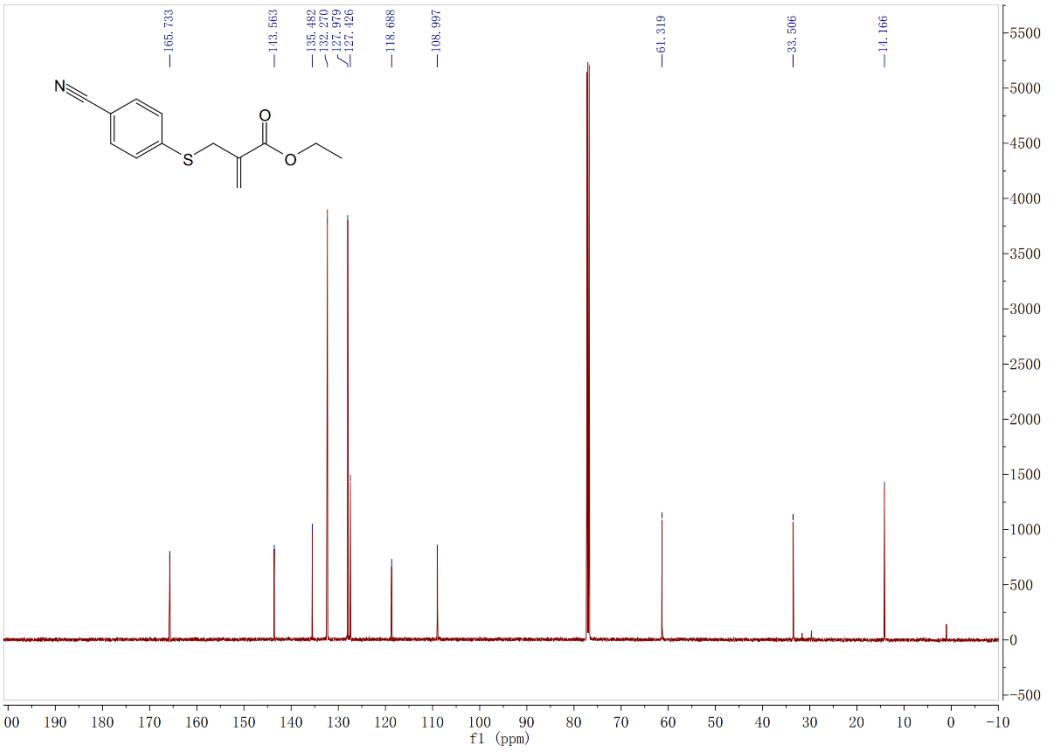


2h; **^{19}F NMR (471 MHz, $CDCl_3$)**

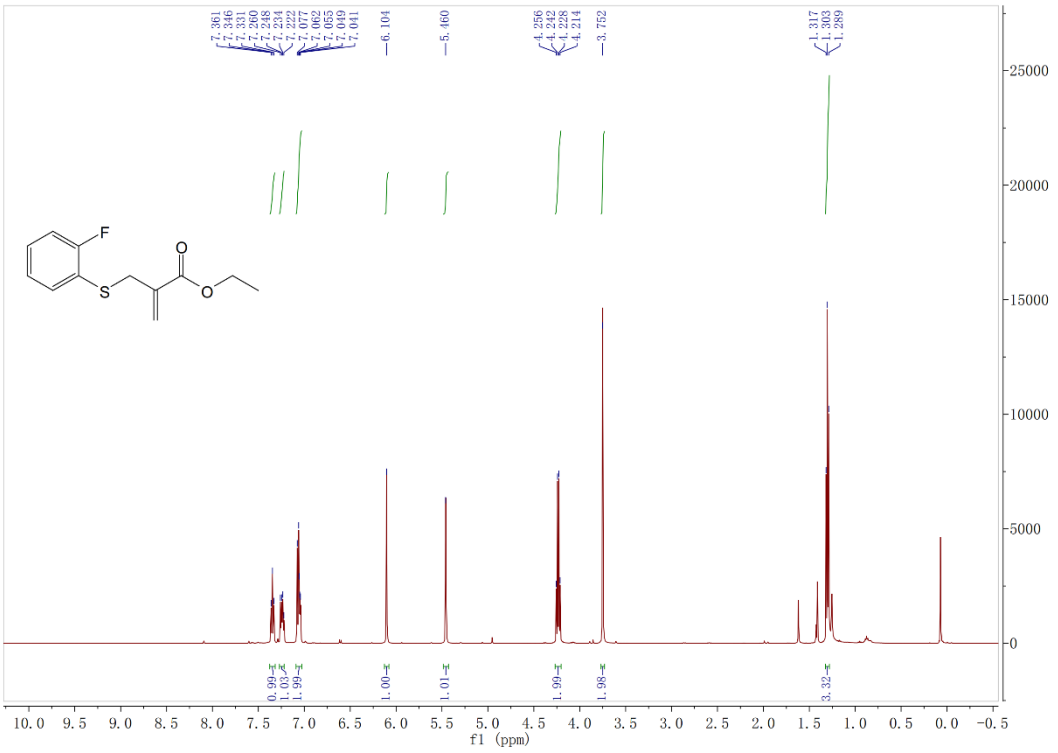


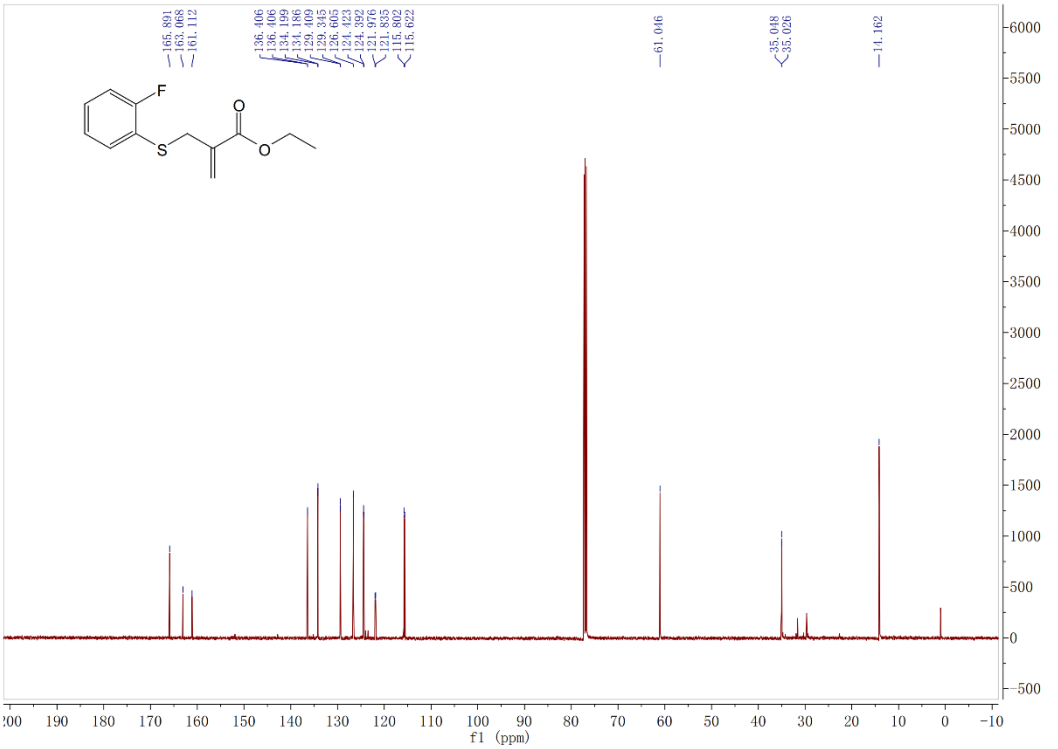
2i; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



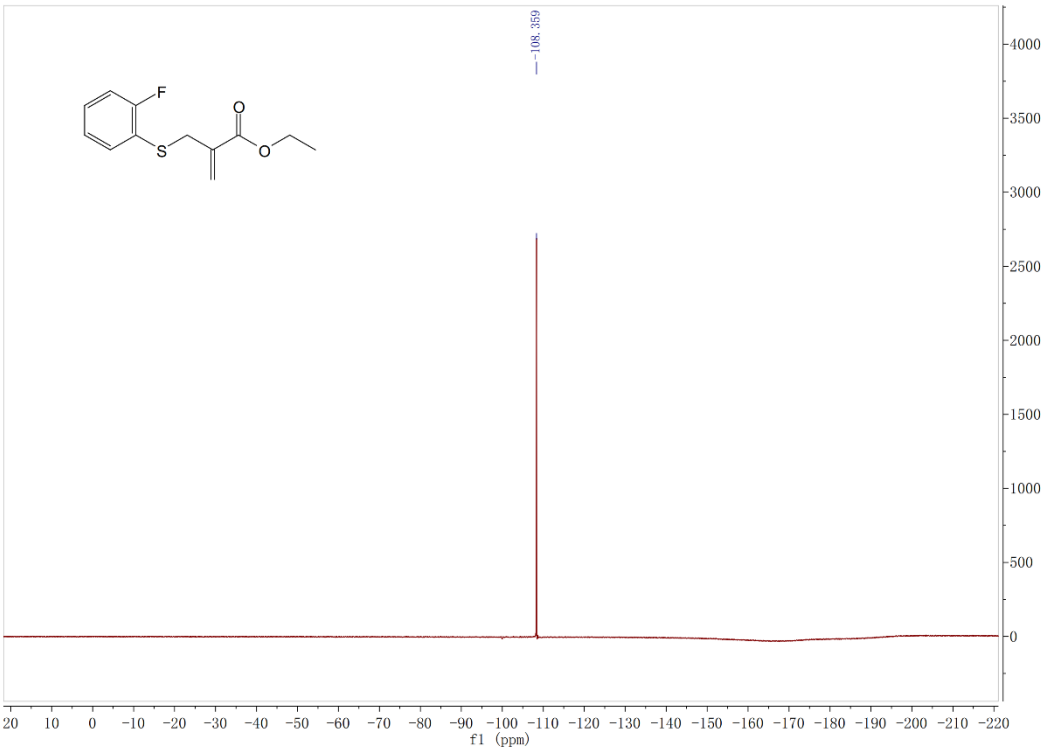


2j; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**

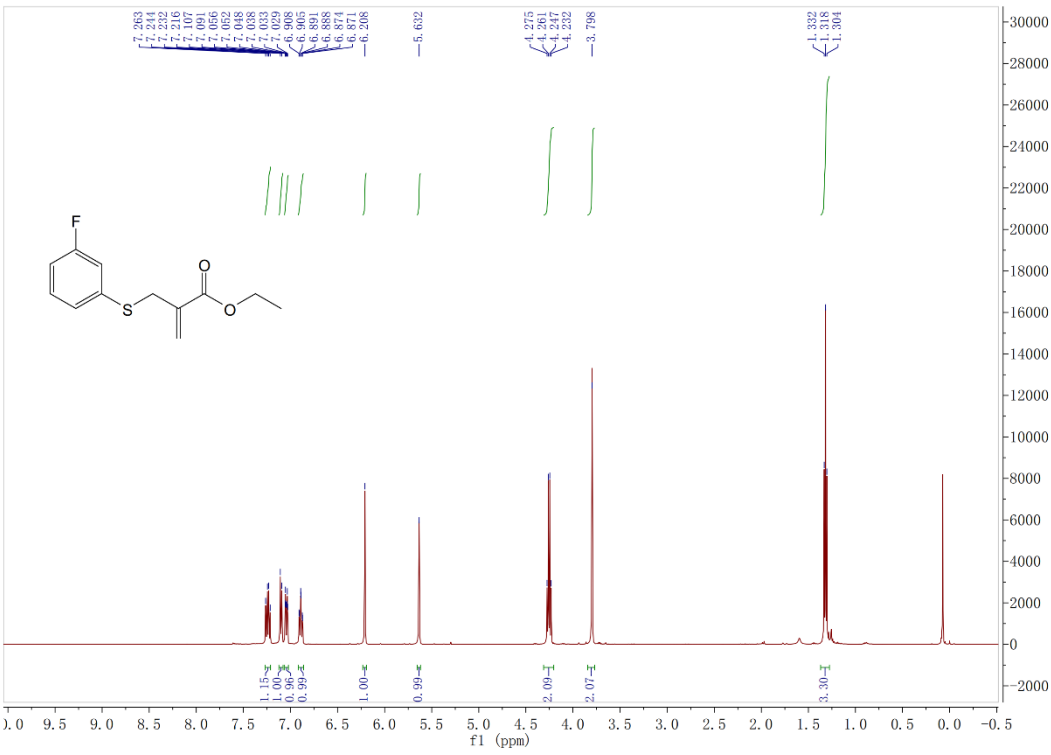


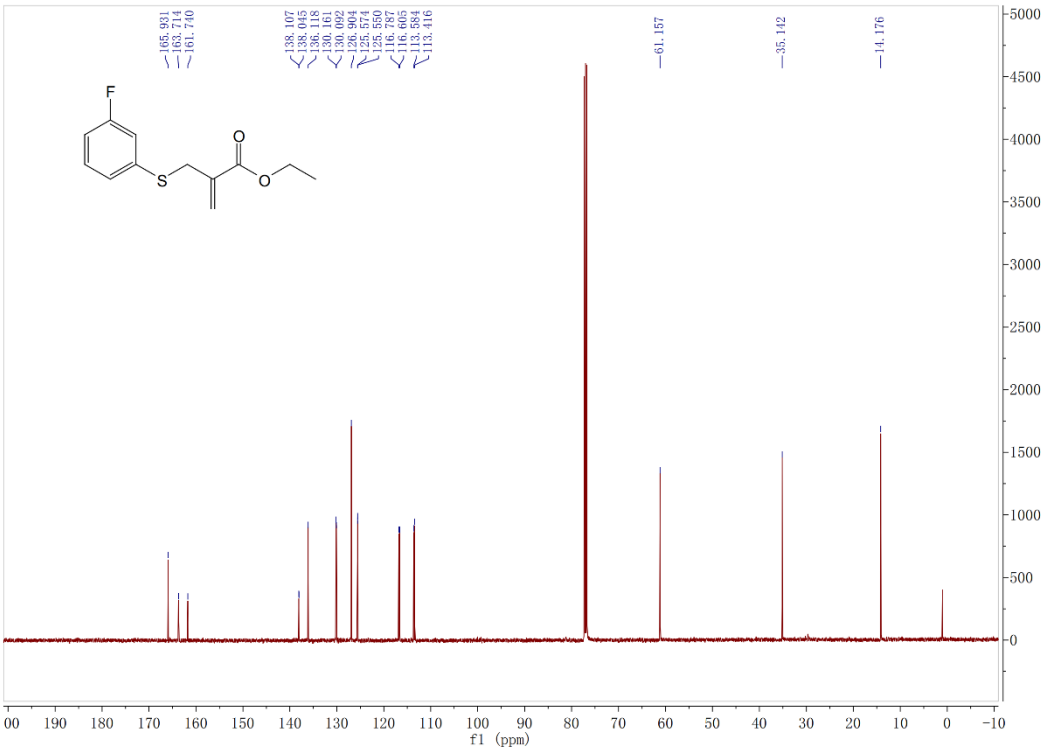


2j; ^{19}F NMR (471 MHz, $CDCl_3$)

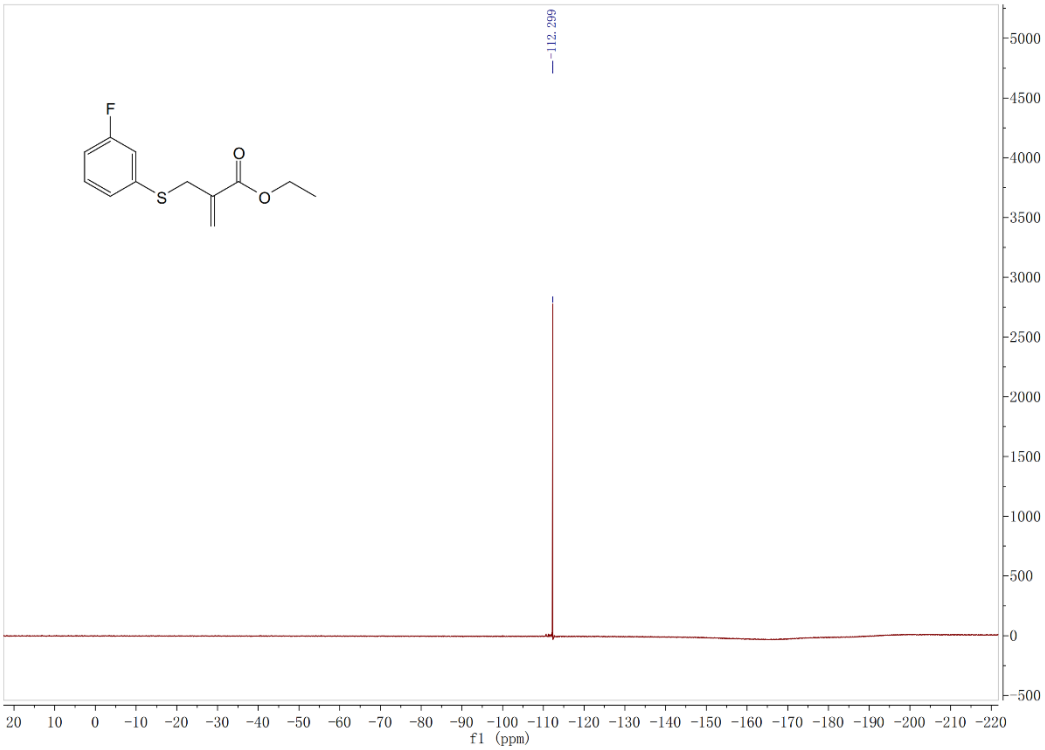


2k; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

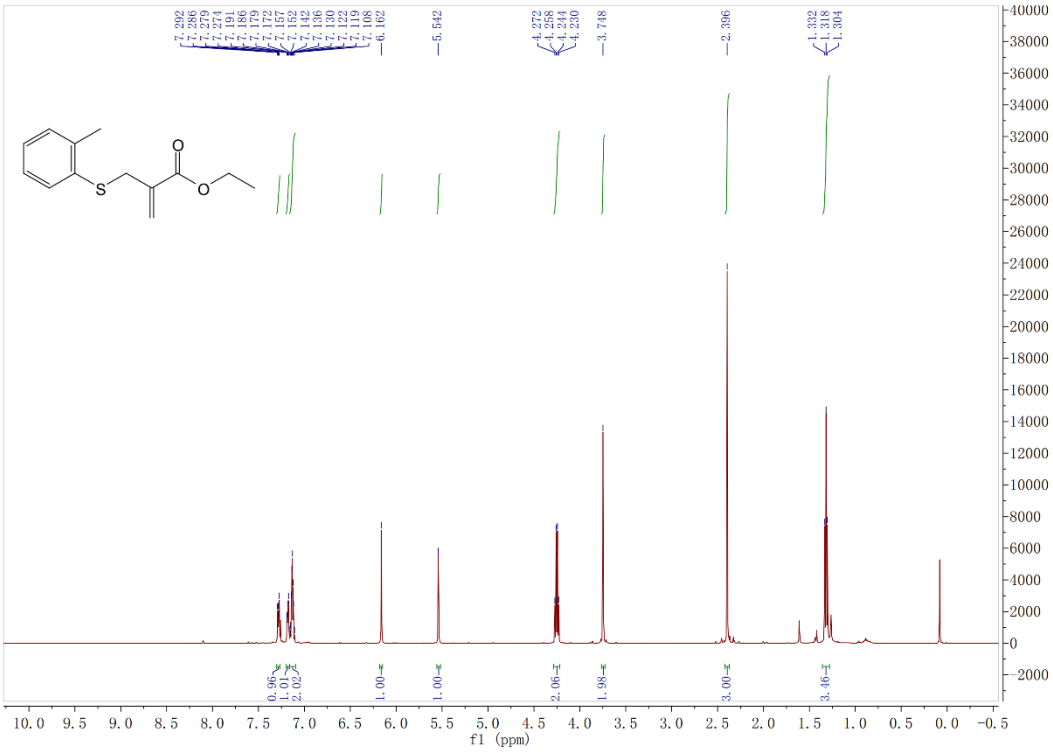


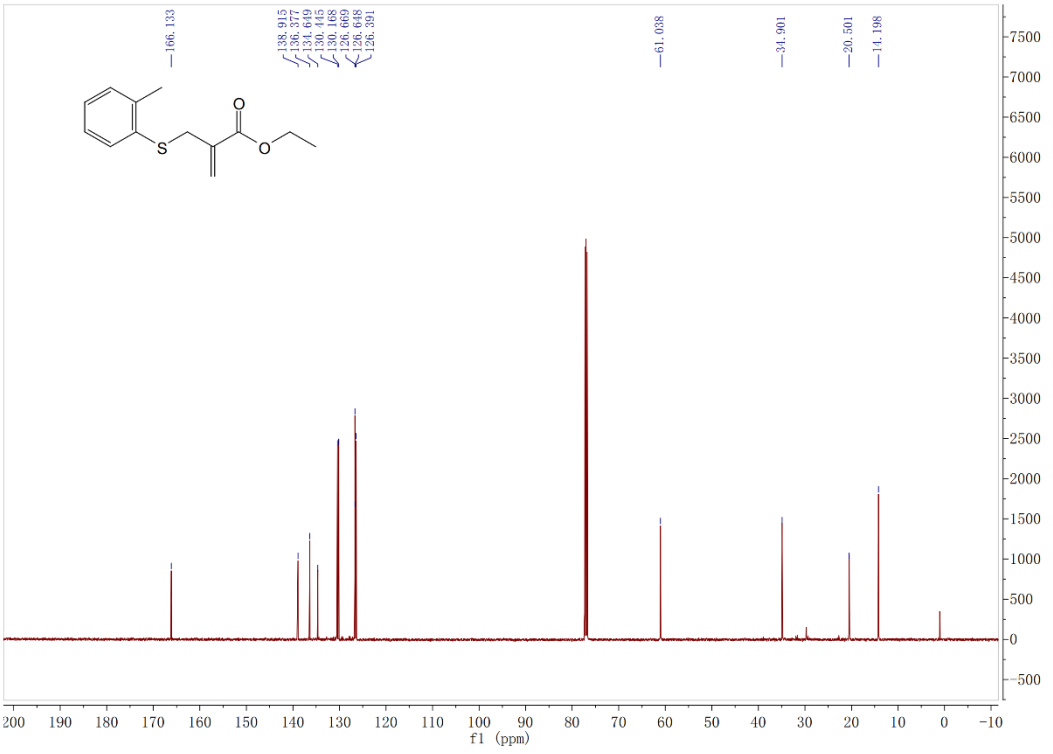


2k; **^{19}F NMR (471 MHz, $CDCl_3$)**

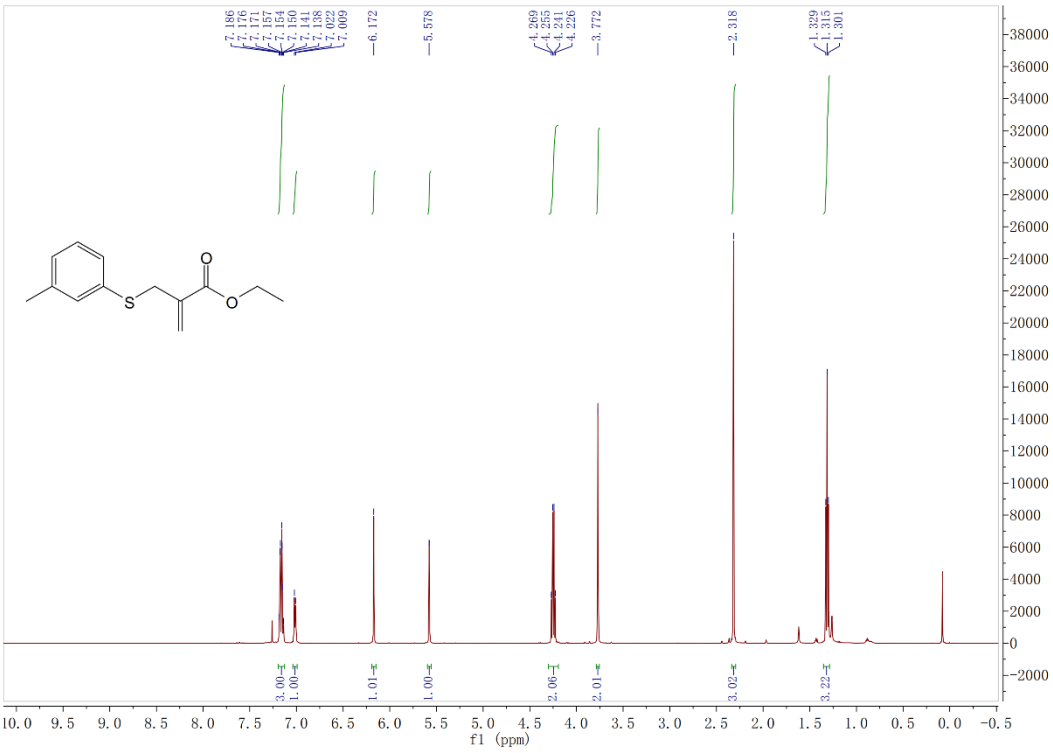


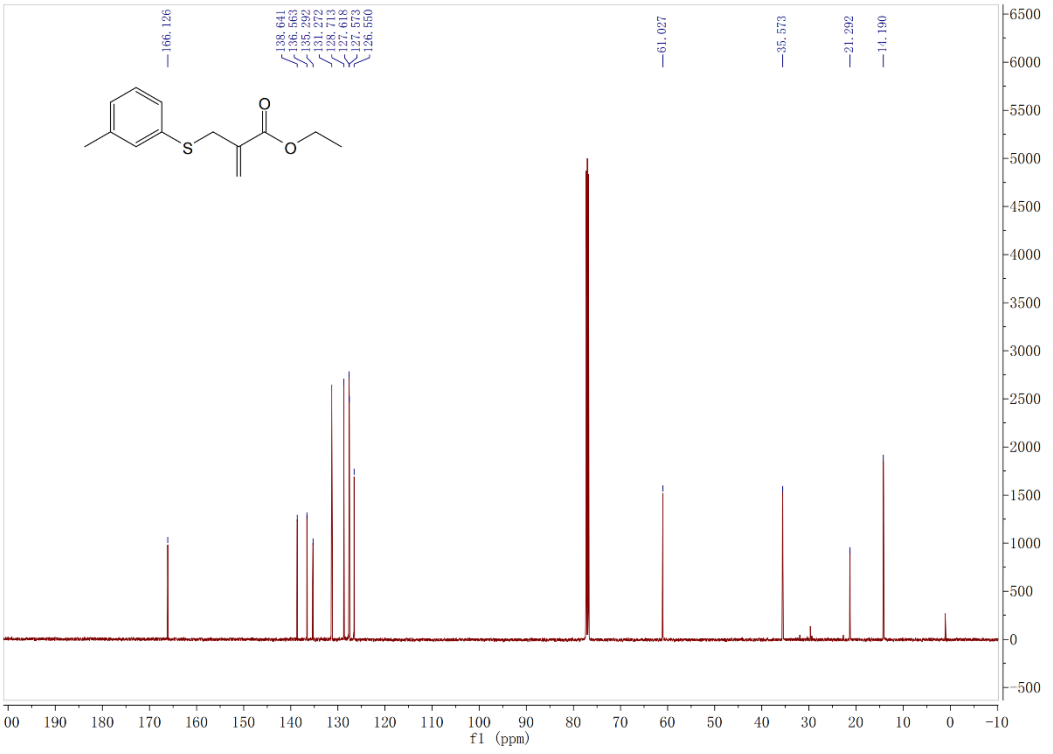
2l; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



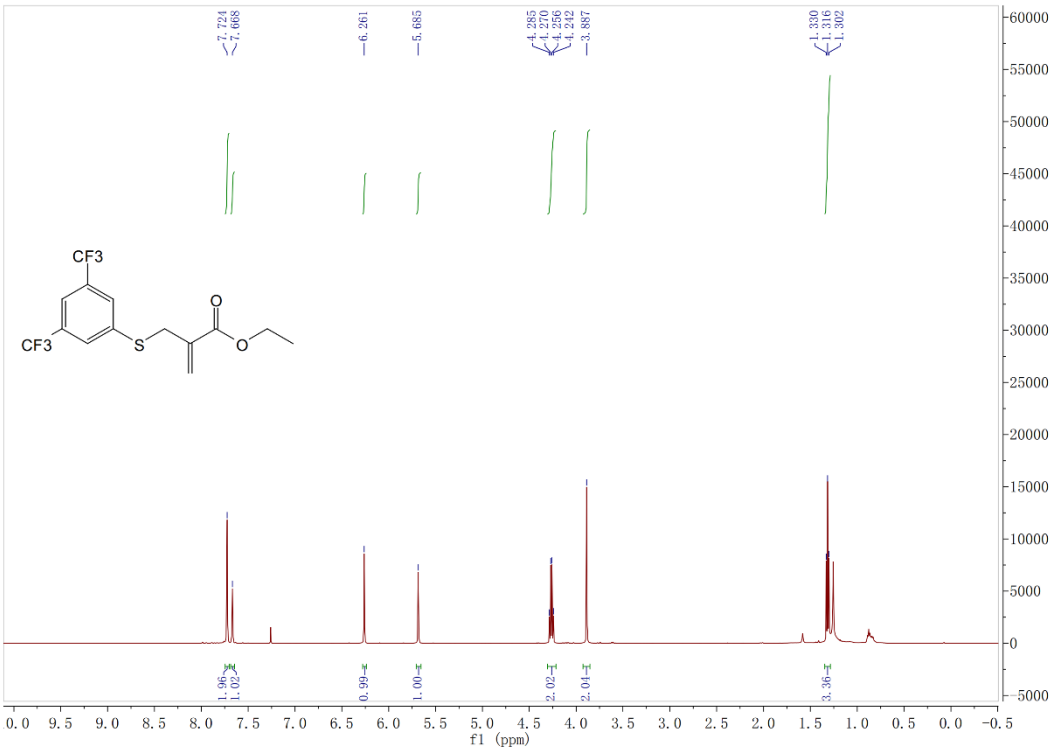


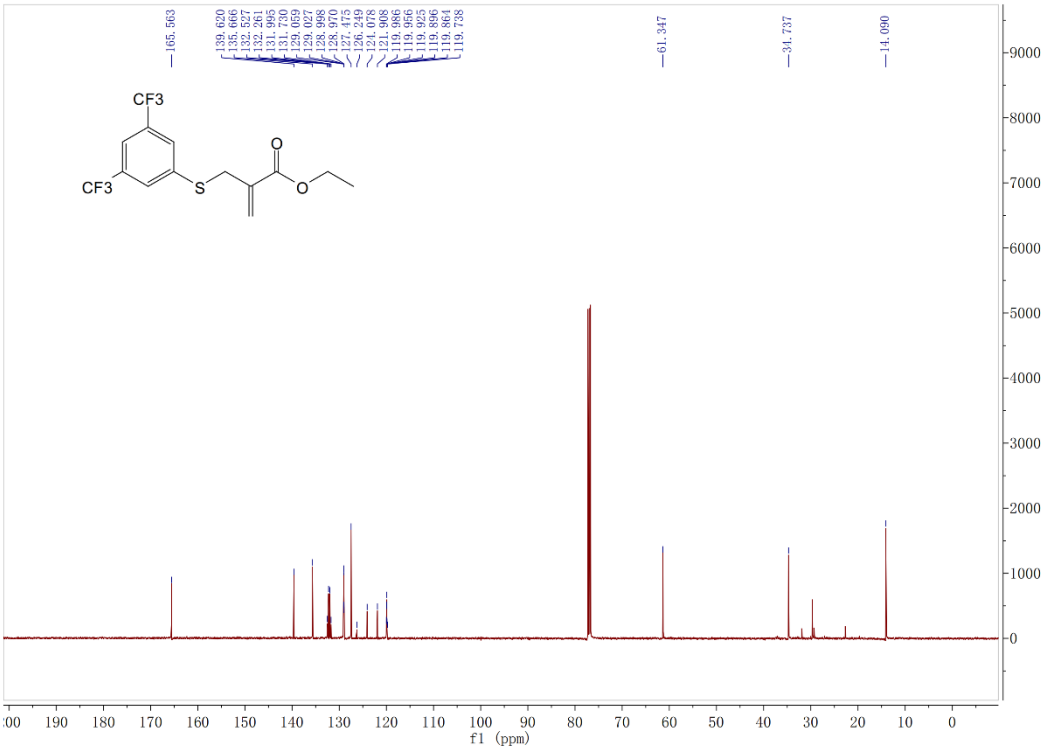
2m; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



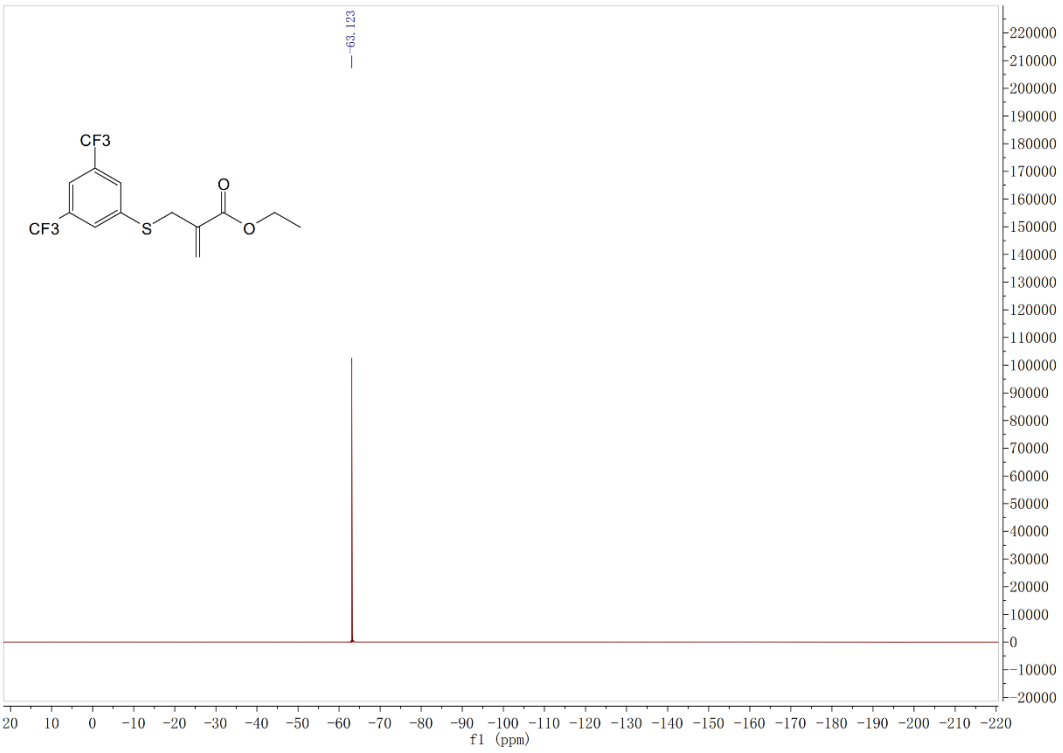


2n; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**

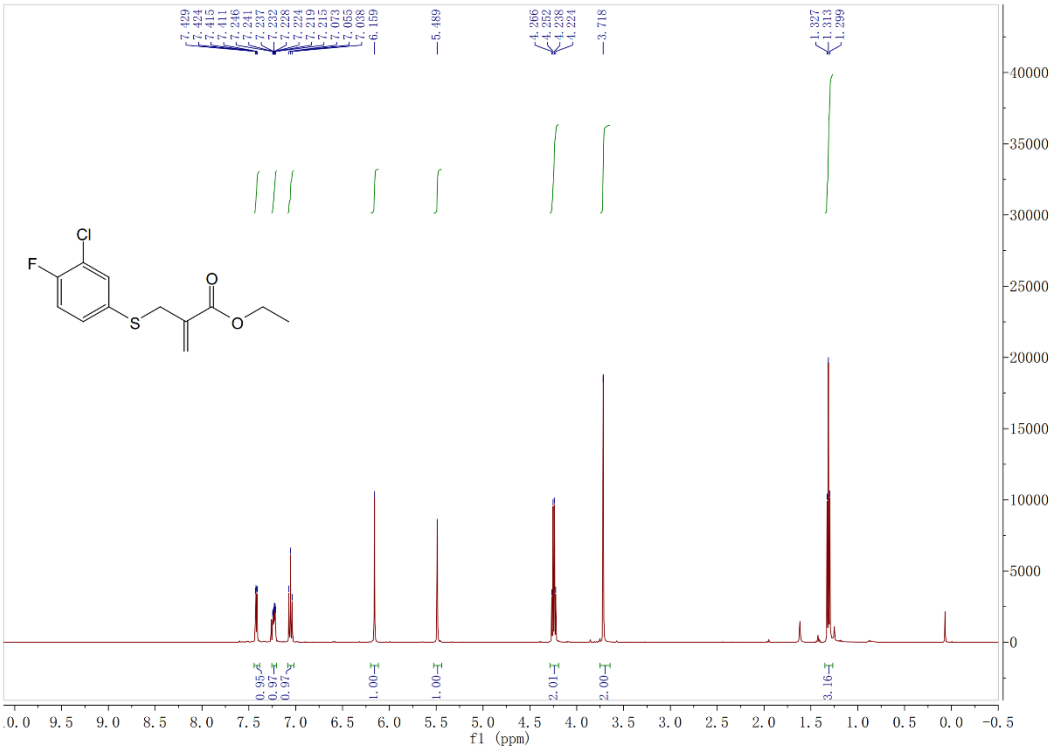


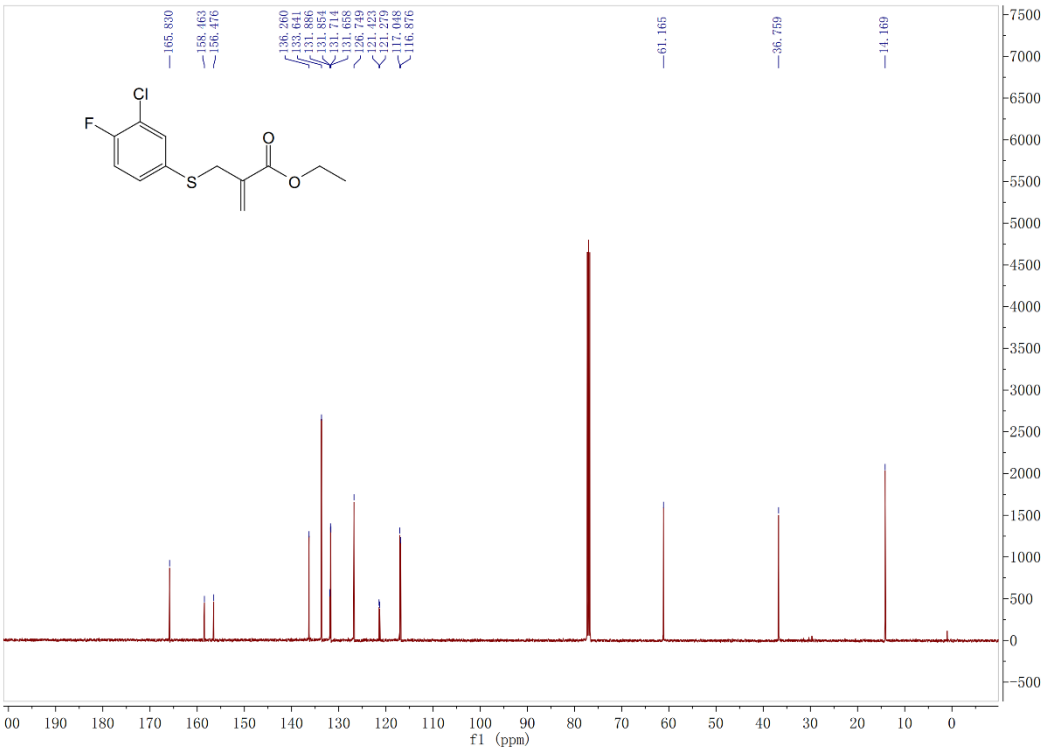


2n; ^{19}F NMR (471 MHz, $CDCl_3$)

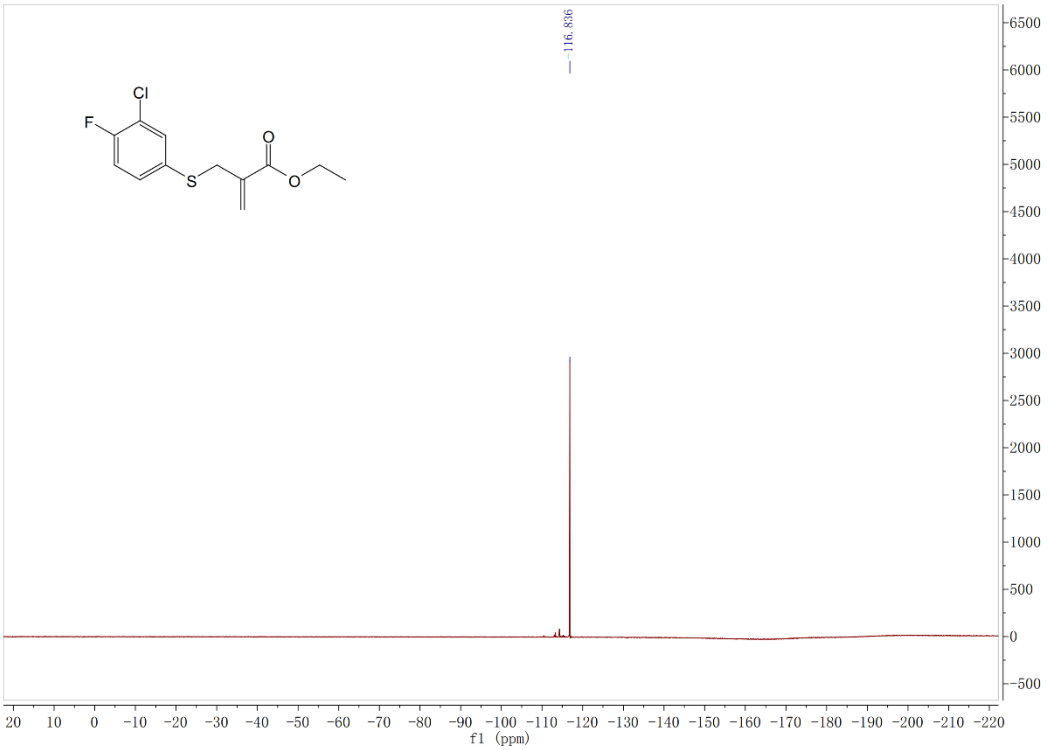


2o; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)

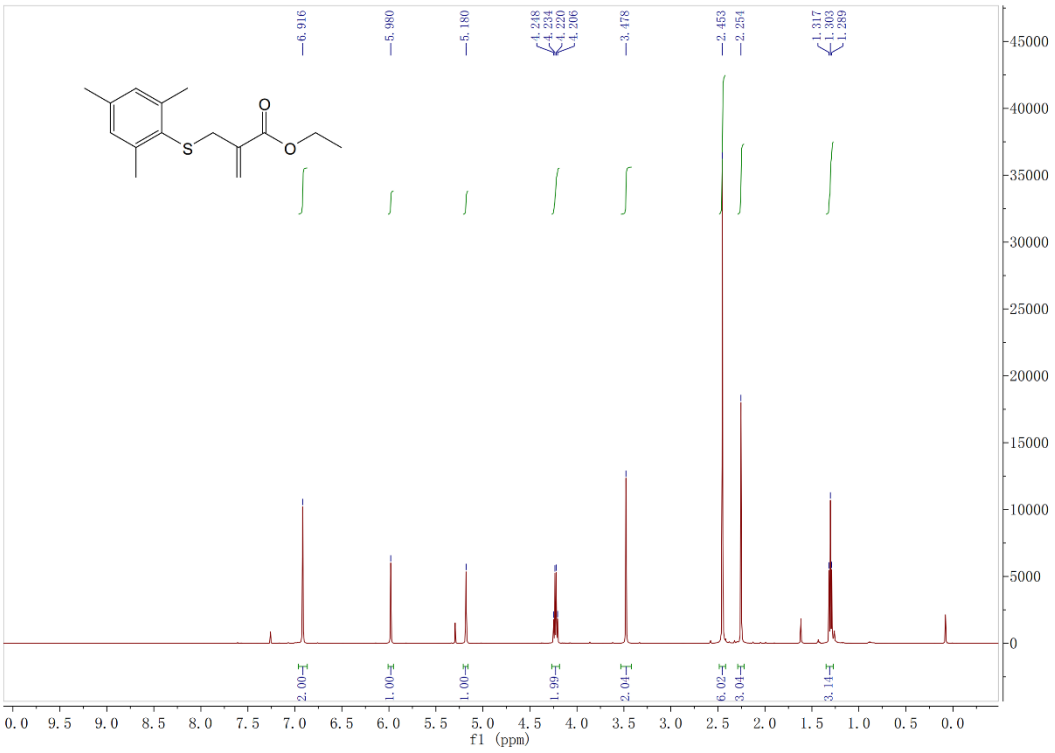


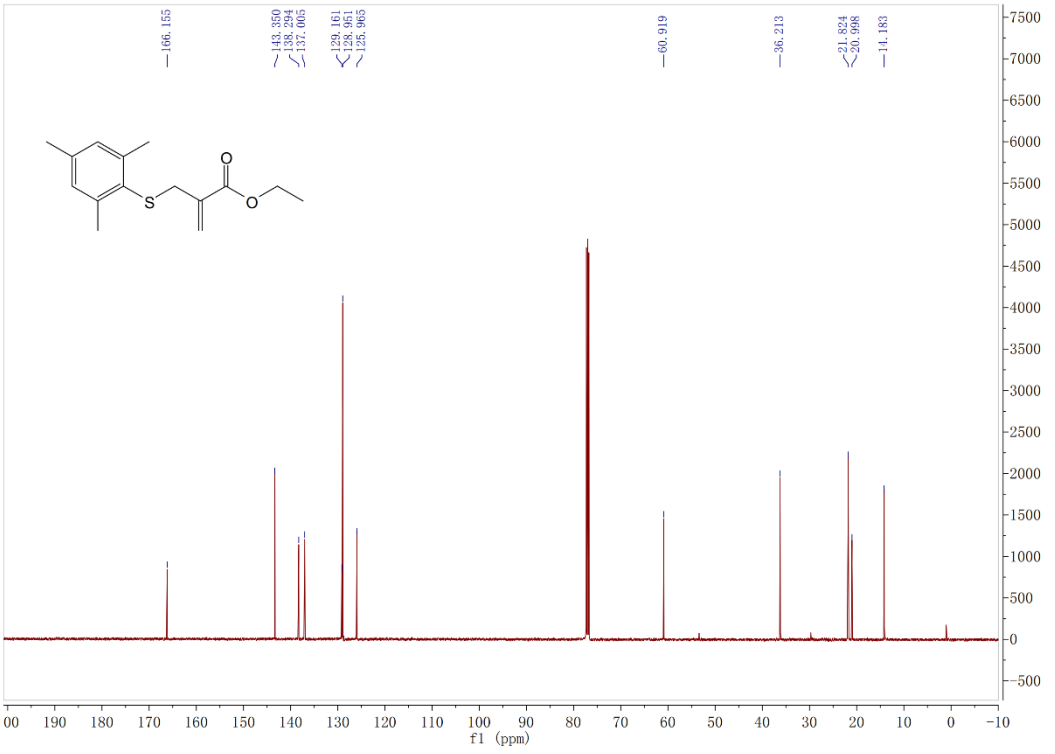


2o; **^{19}F NMR (471 MHz, $CDCl_3$)**

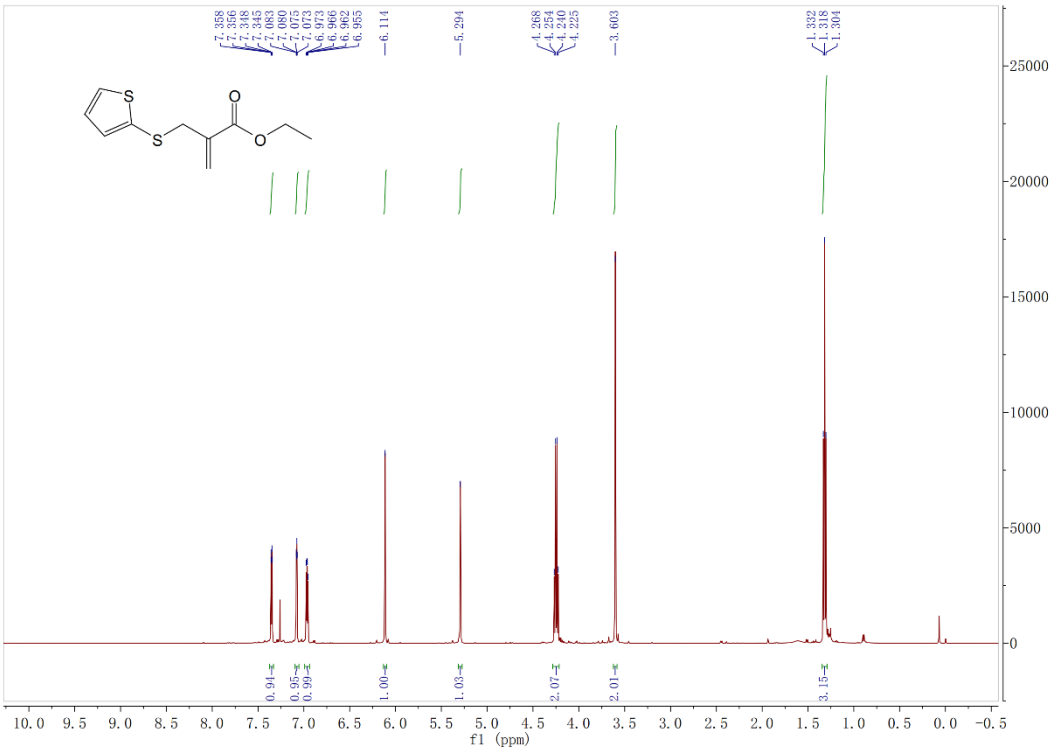


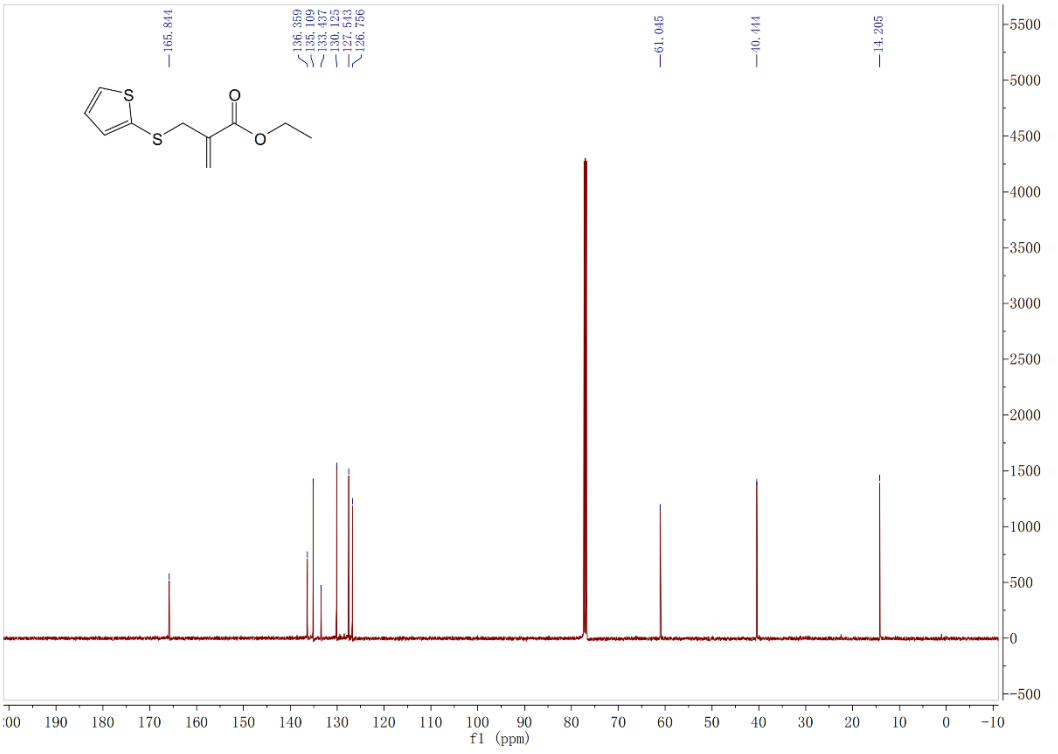
2p; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



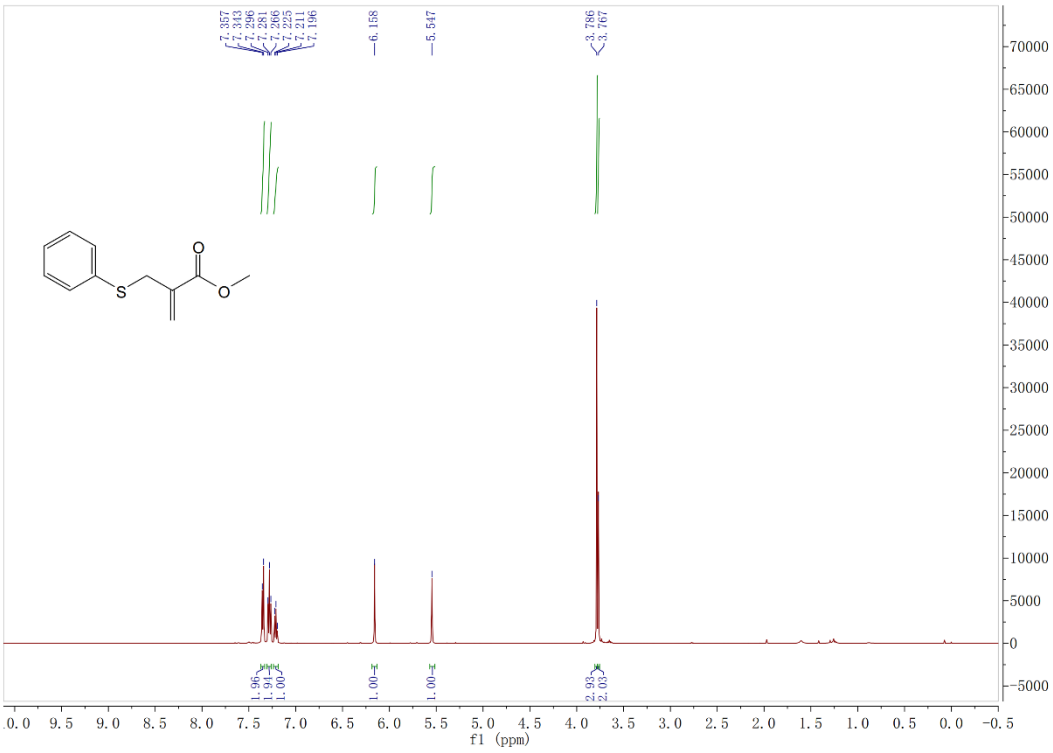


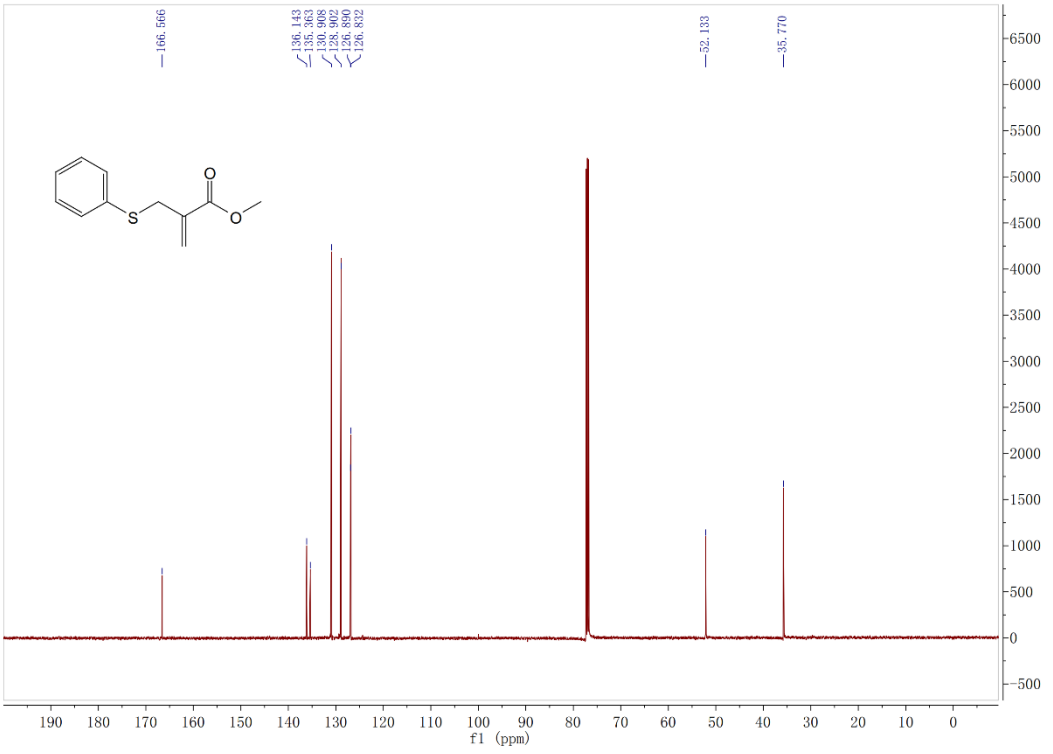
2q; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



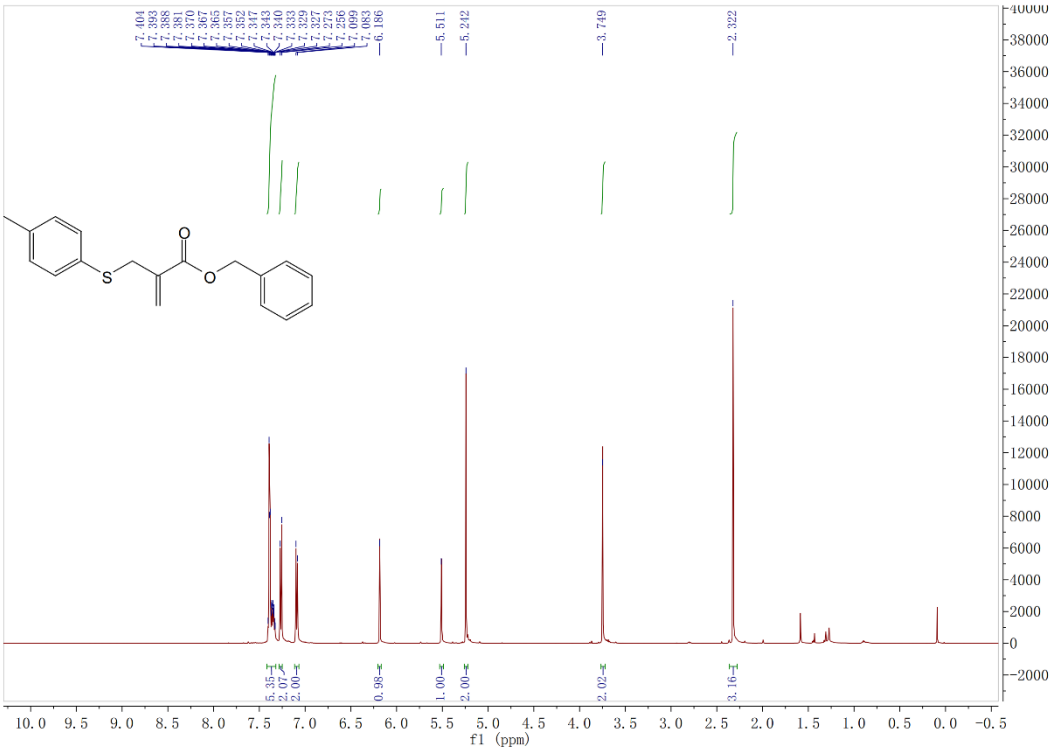


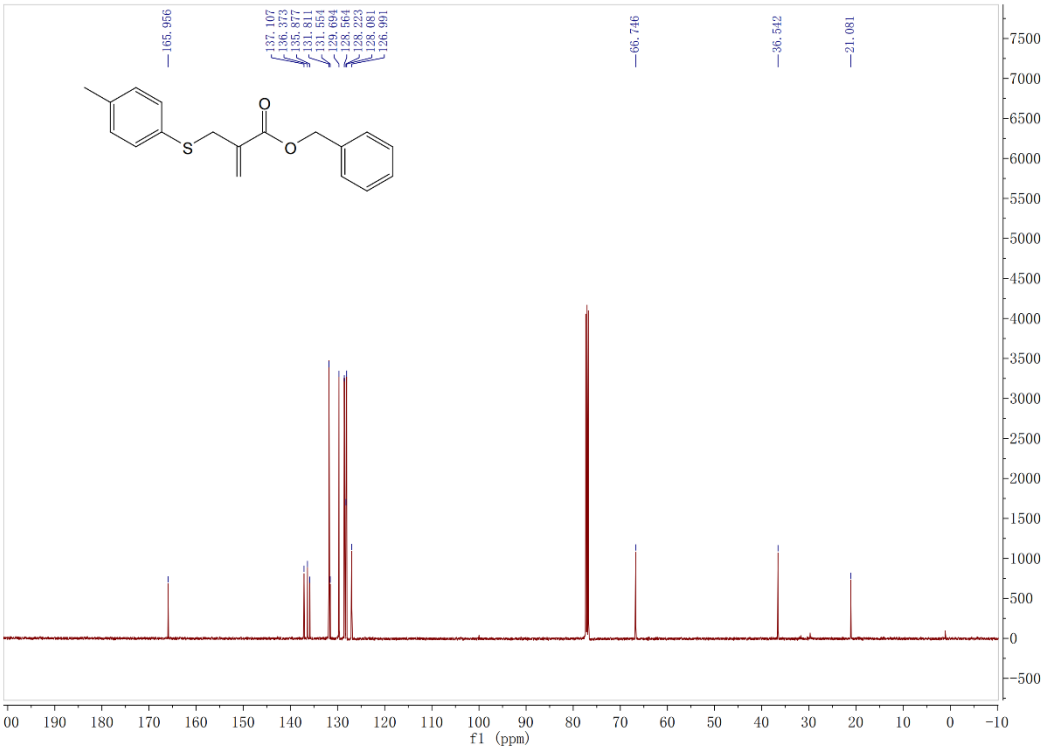
2r; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



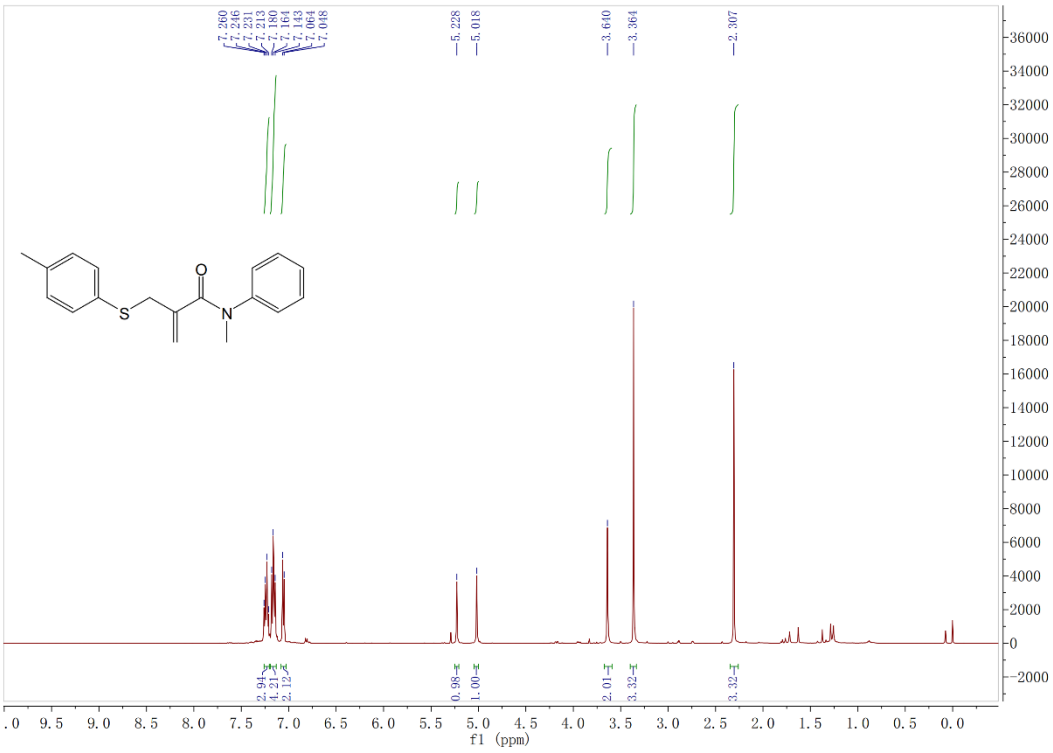


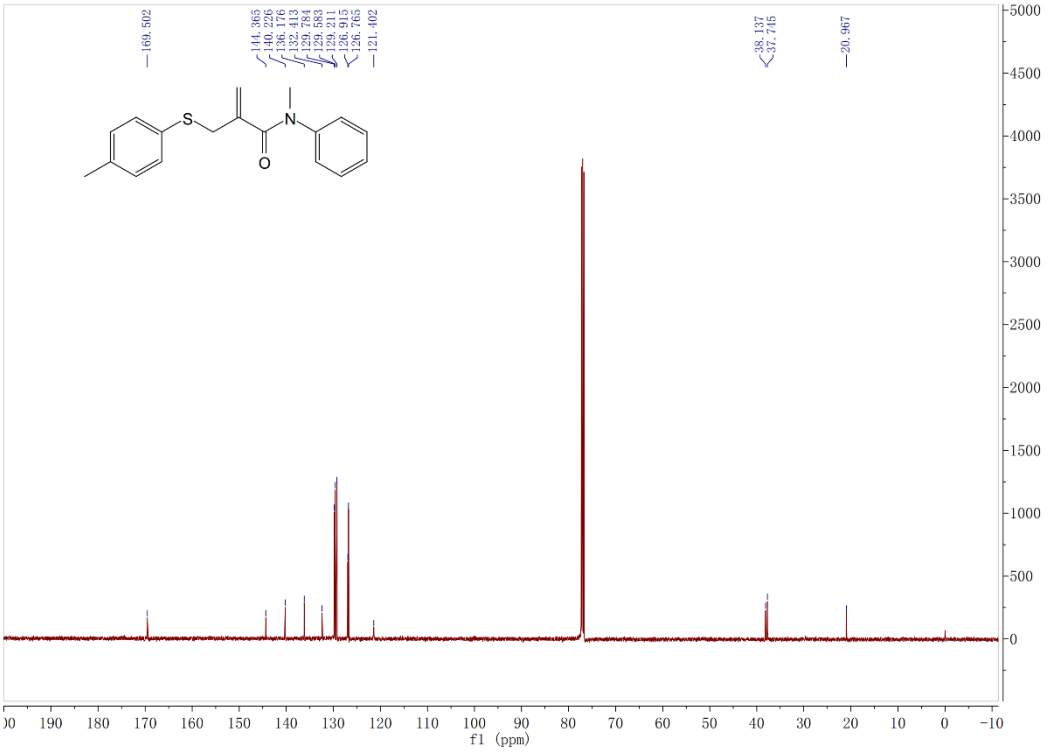
2s; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



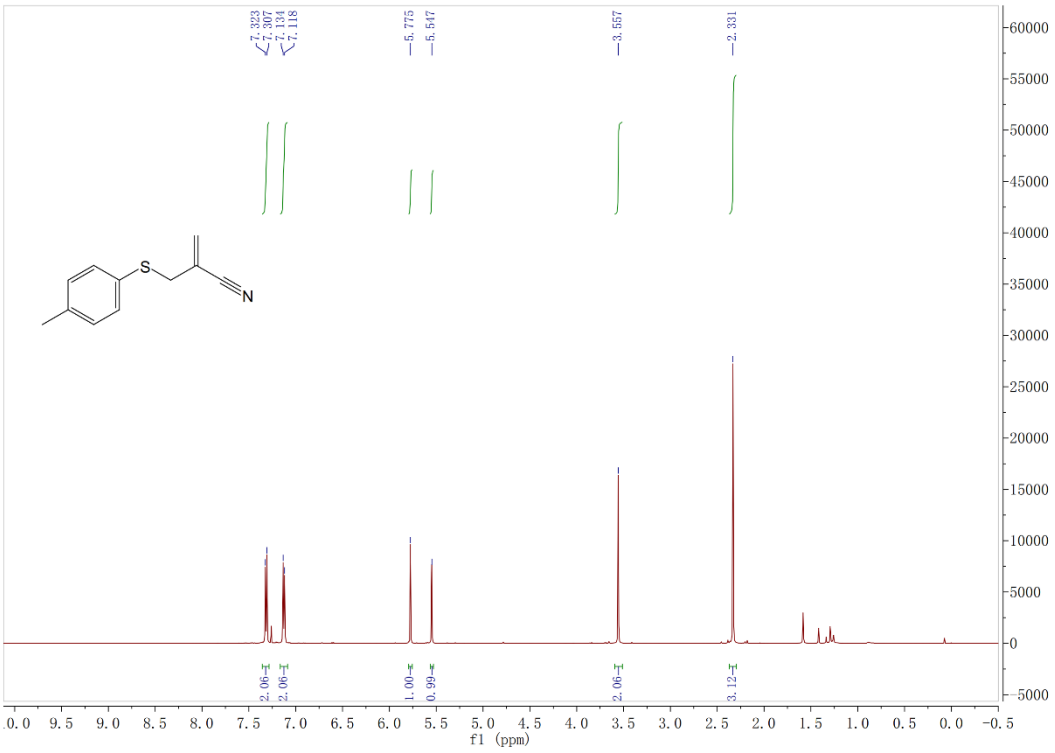


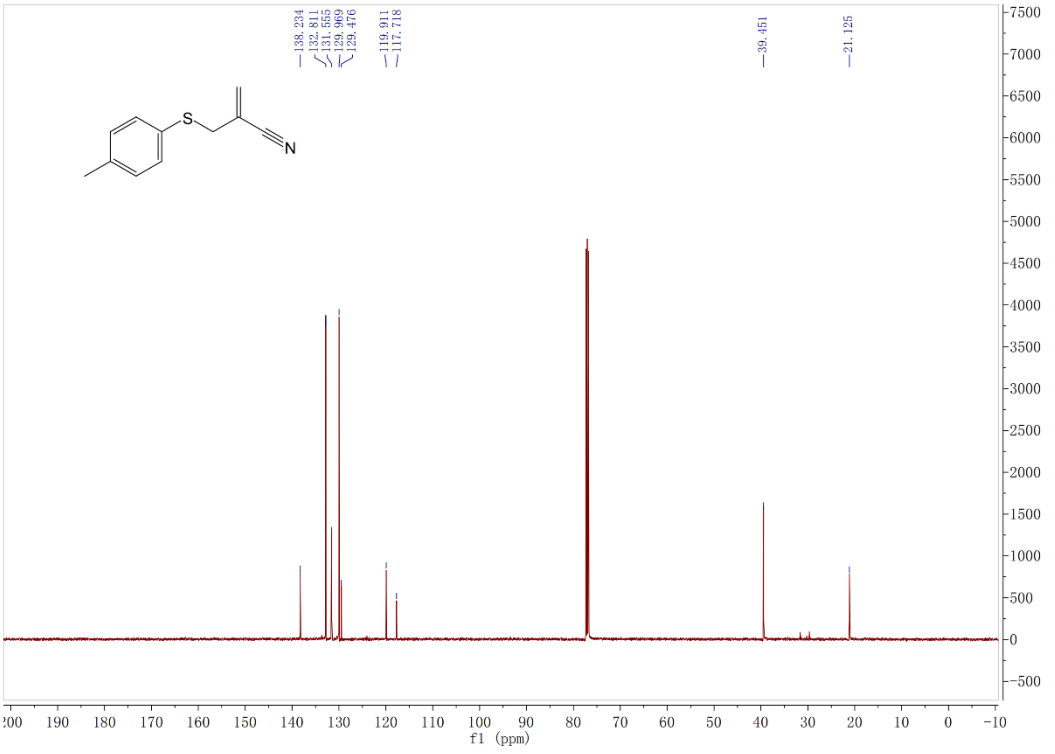
2t; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**



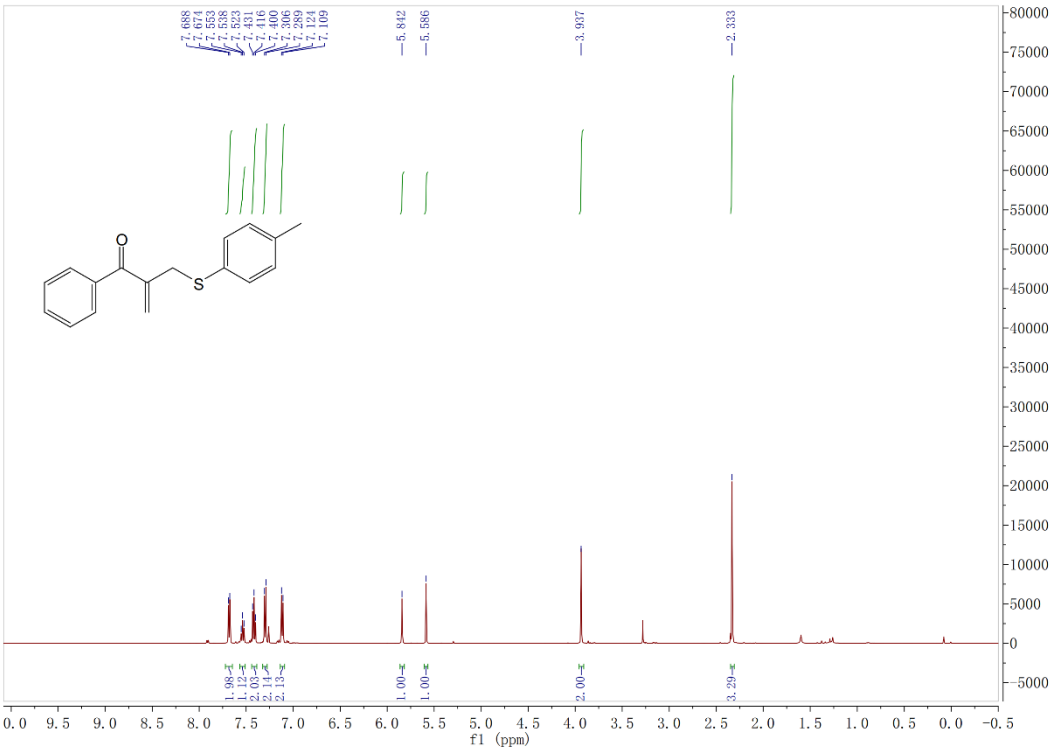


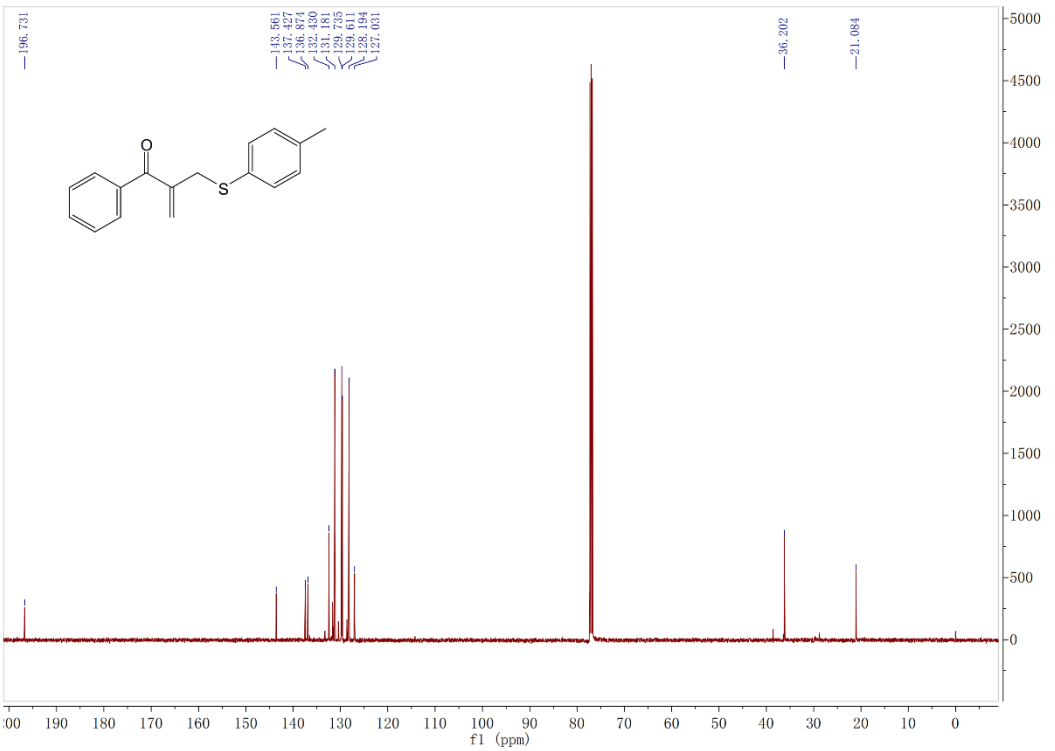
2u; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



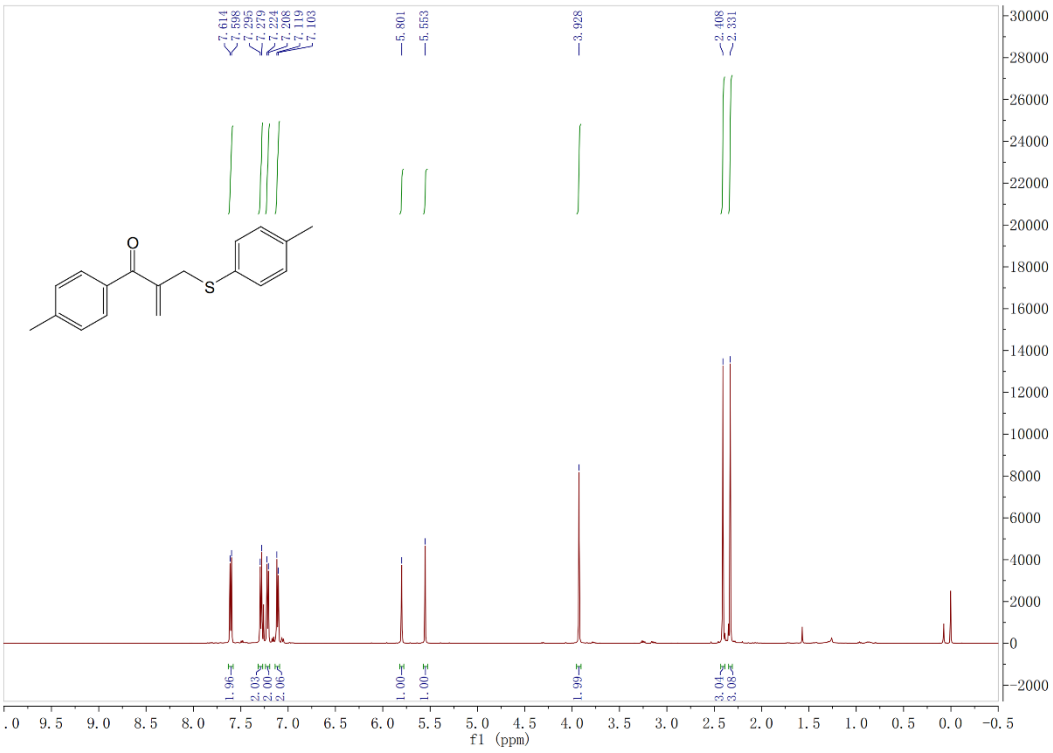


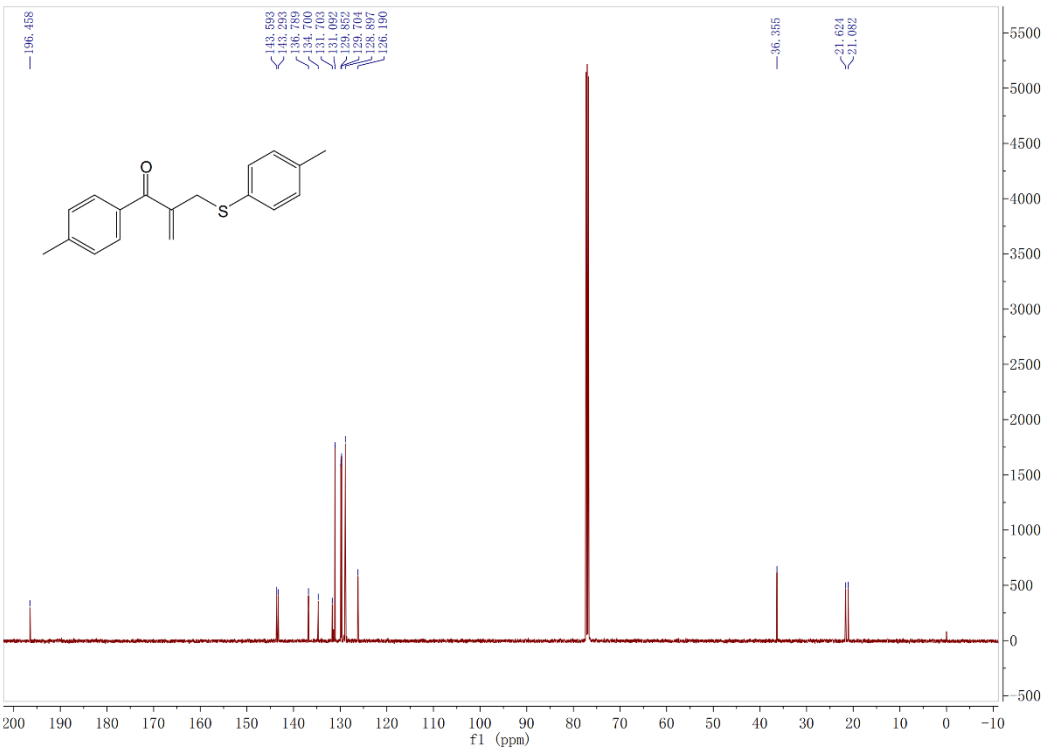
2v; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



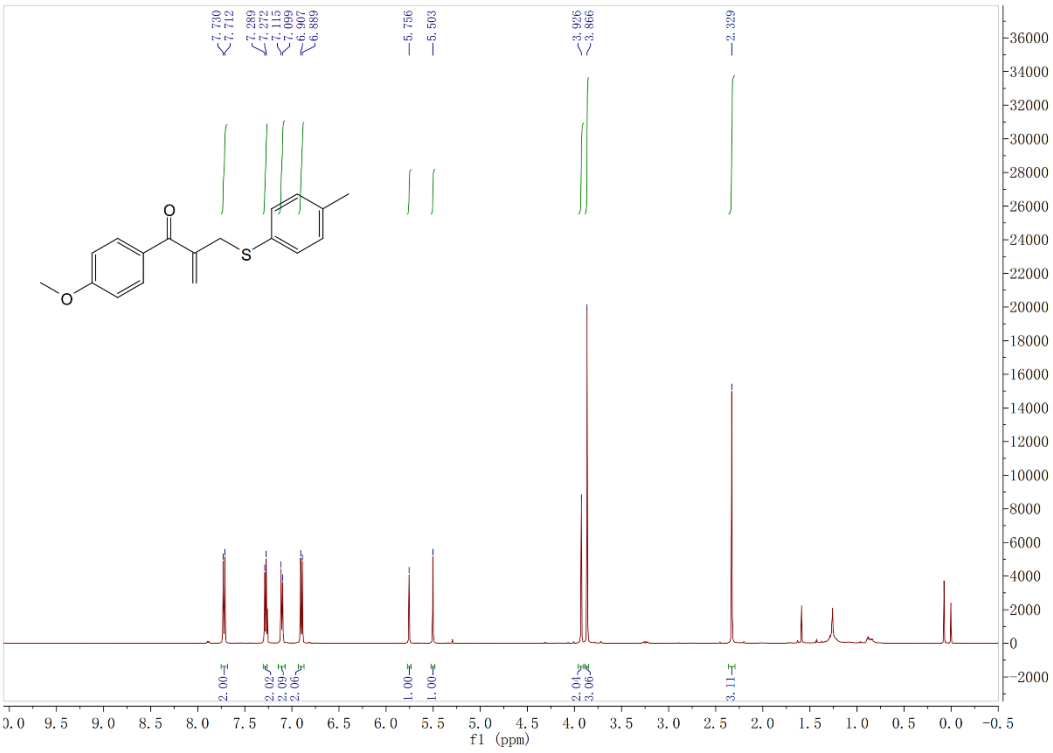


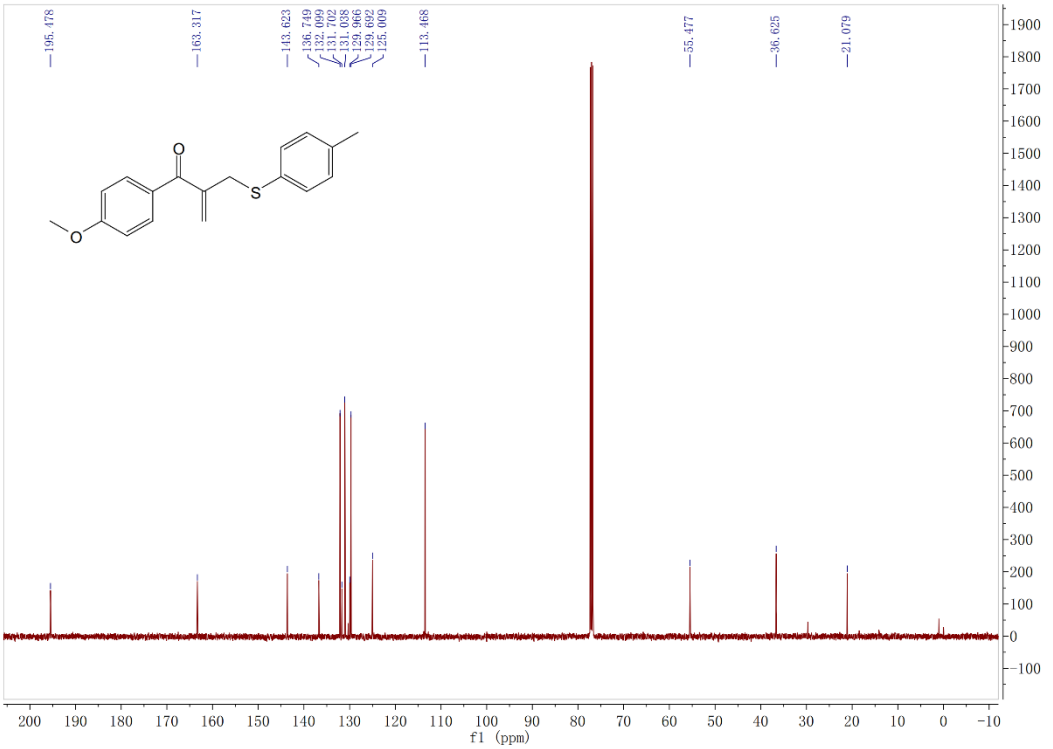
2w; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



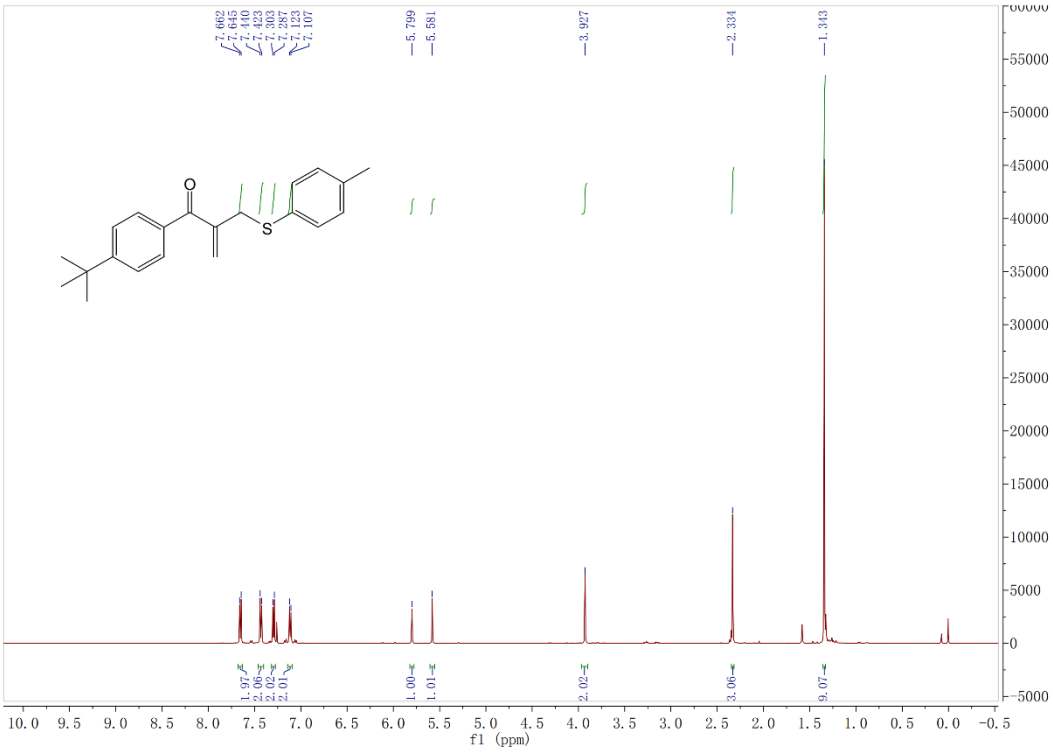


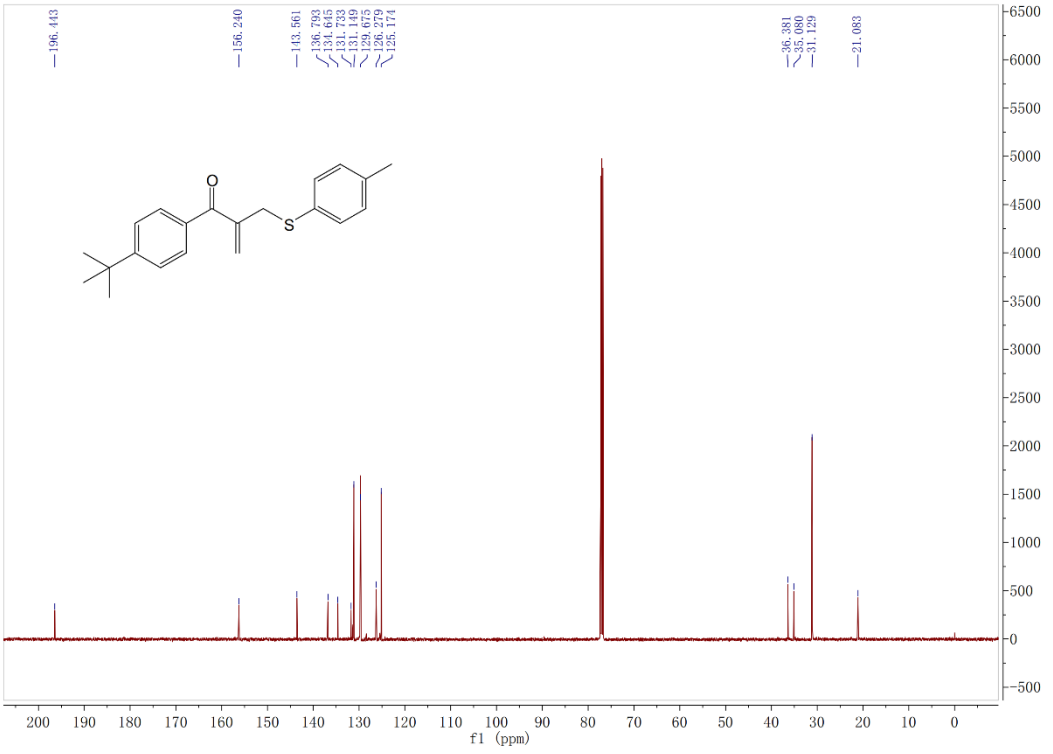
2x; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



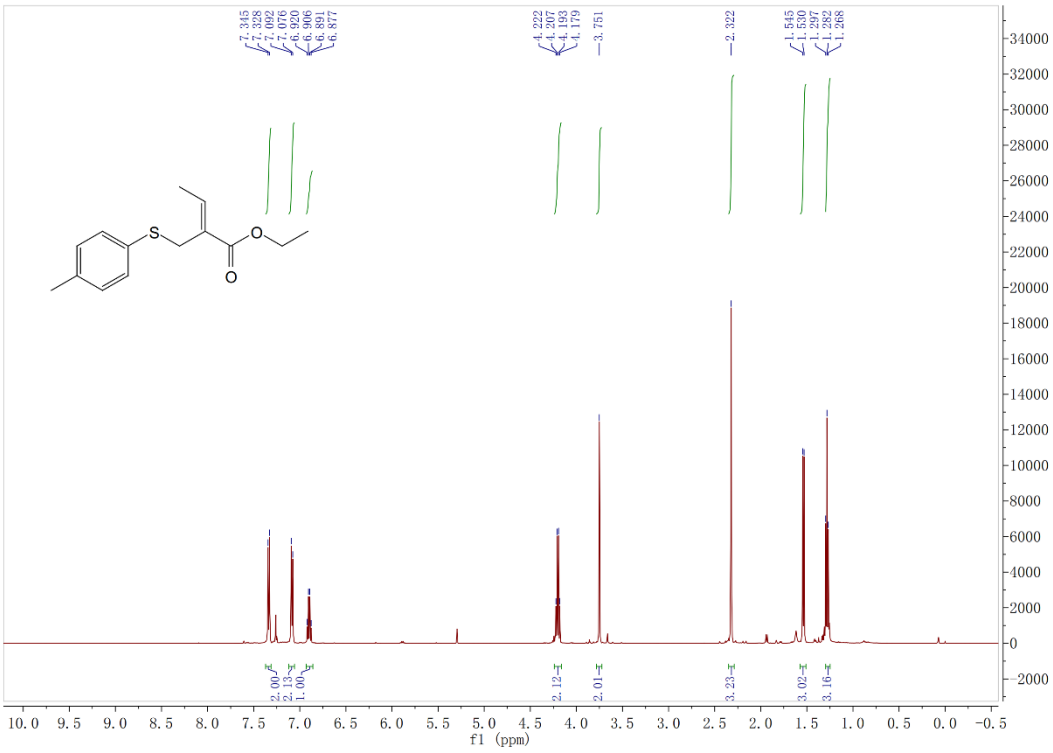


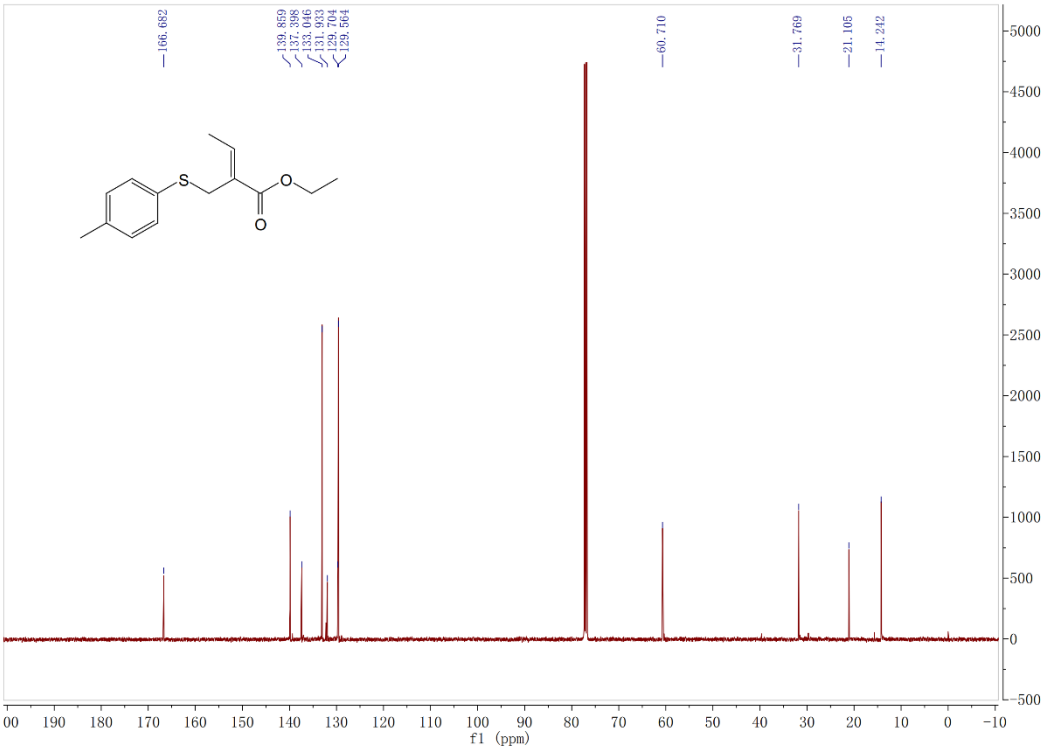
2y; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



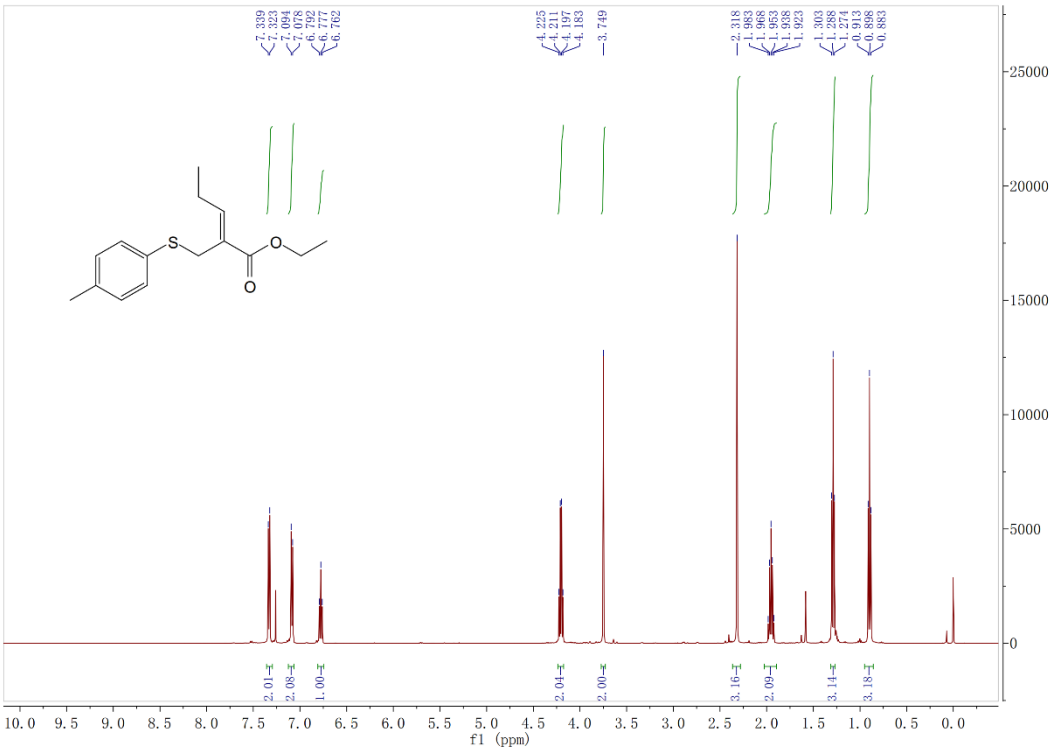


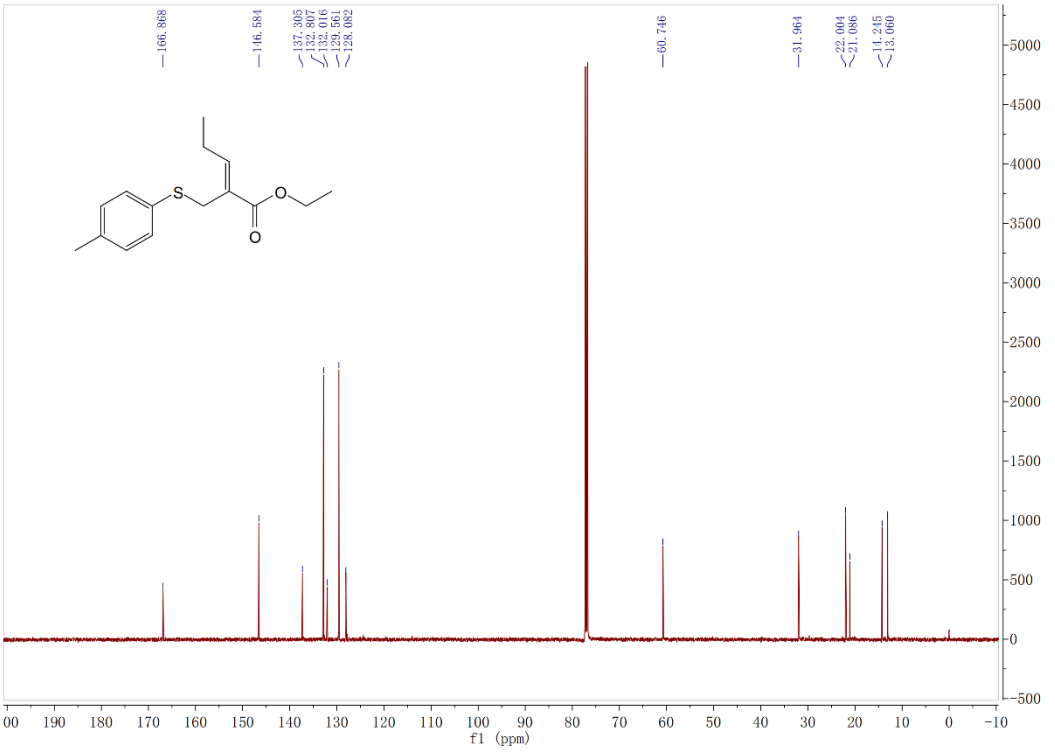
2z; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



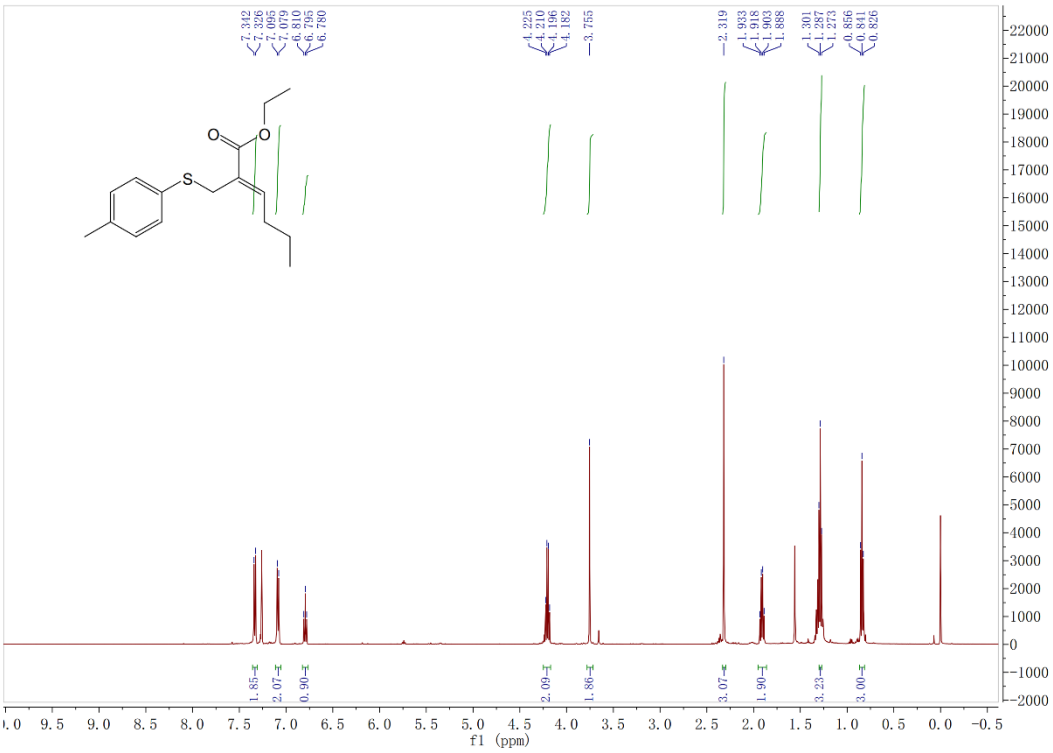


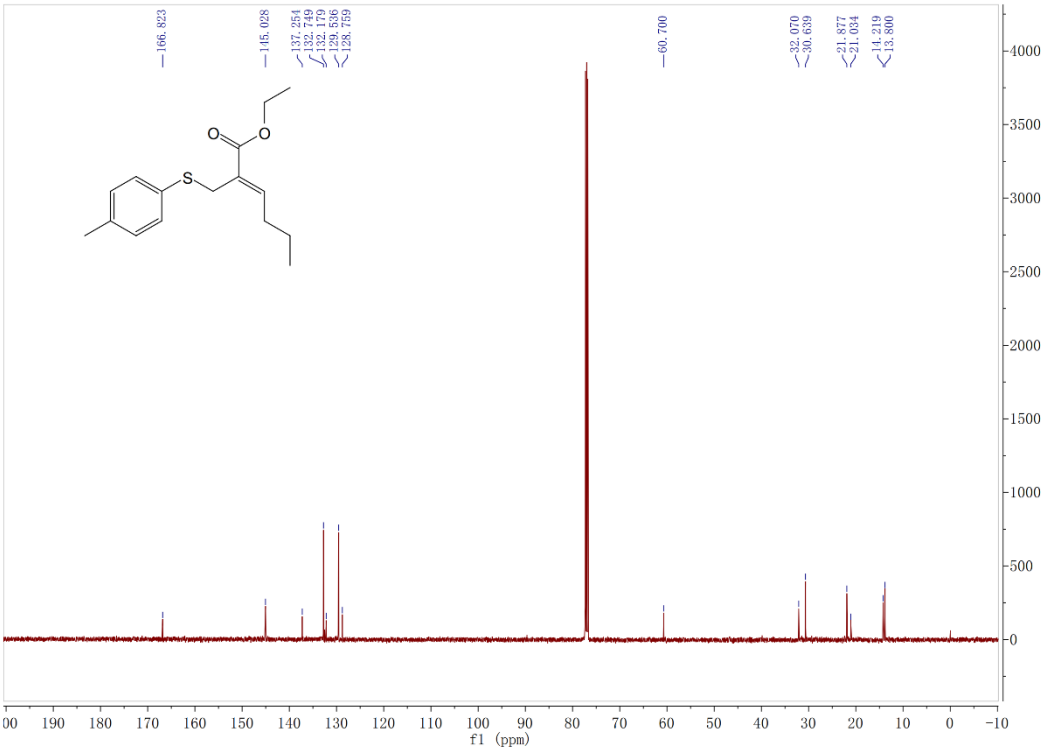
2aa; ^{1}**H NMR (500 MHz, CDCl$_3$)**; ^{13}**C NMR (126 MHz, CDCl$_3$)**



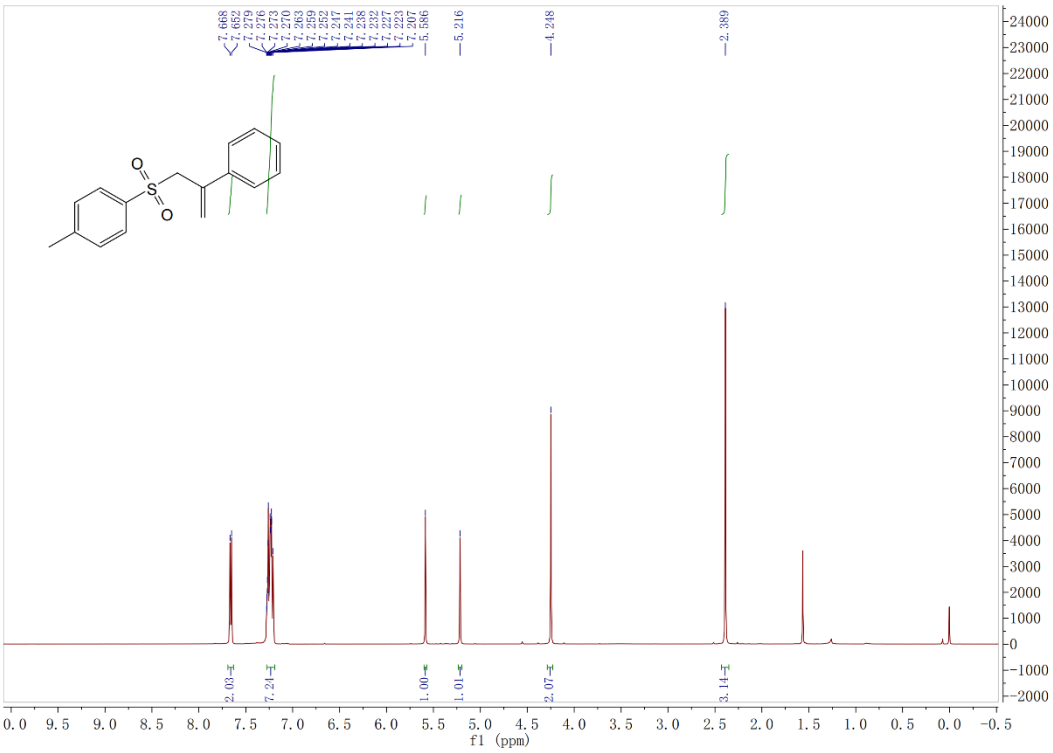


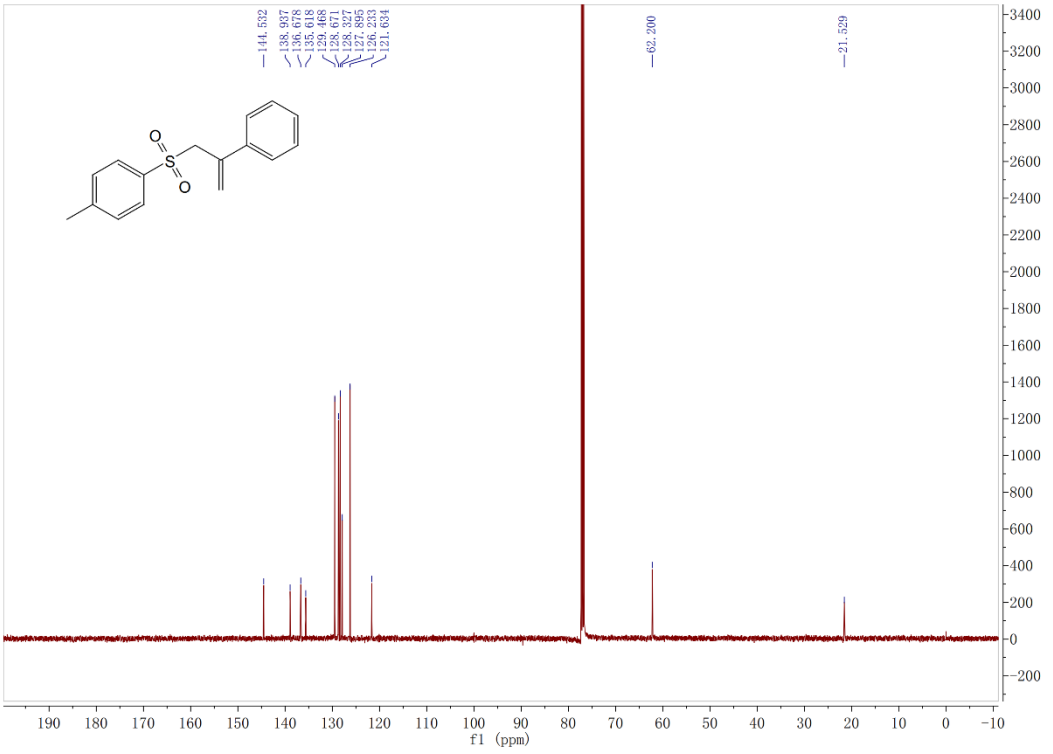
2ab; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)



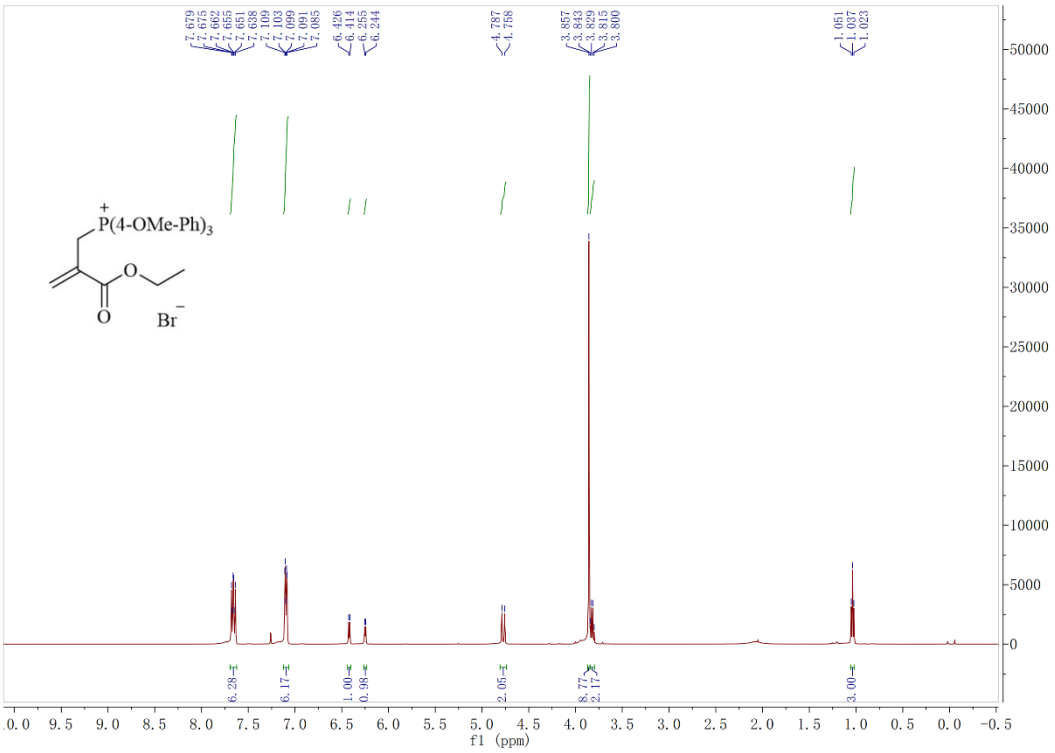


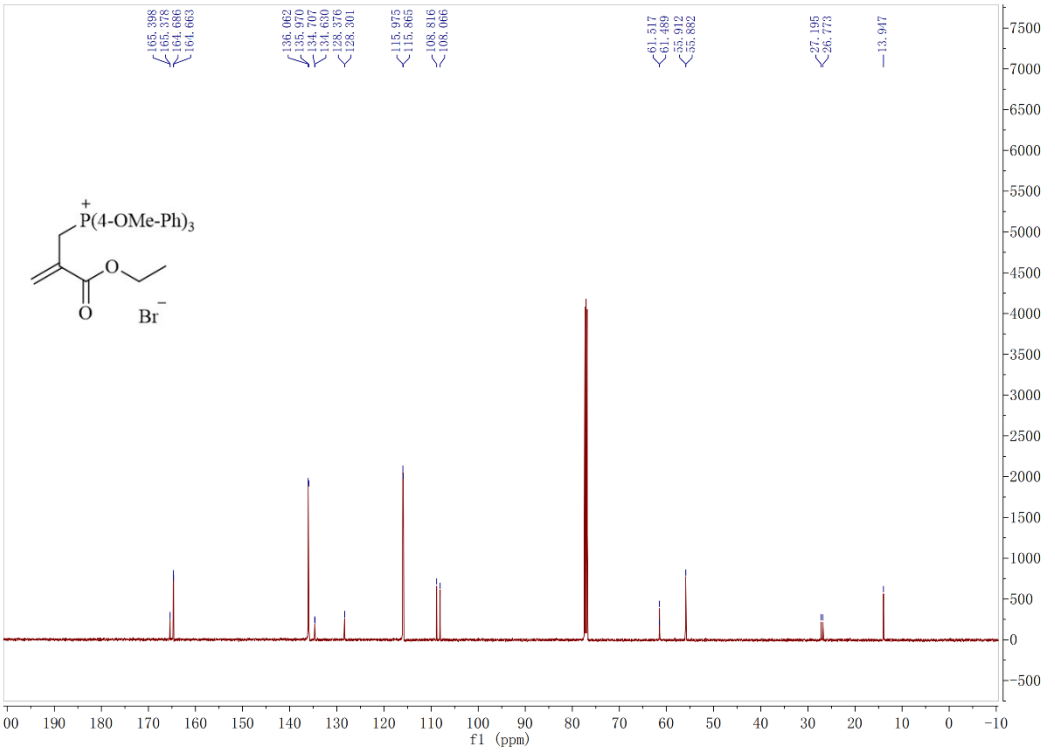
3; **^{1}H NMR (500 MHz, $CDCl_3$)**; **^{13}C NMR (126 MHz, $CDCl_3$)**





4; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)





6; ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$)