

Supporting Information For

Dual Ligand-promoted Palladium-catalyzed Nondirected C-H Alkenylation of Aryl Ethers

Author Full Name,^{*a} Author Full Name^b and Author Full Name^c

a. Address here.

b. Address here.

c. Address here.

Table of Contents

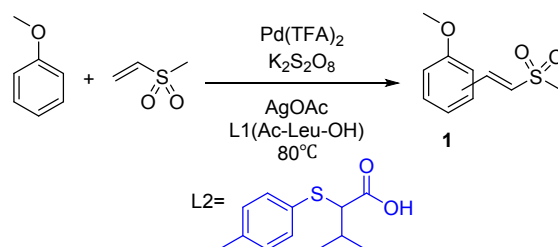
1. Experimental Sections.....	S2
2. Figures and Tables.....	S3
3. NMR Spectra	S11
4. Reference.....	S62

1. Experimental Sections

General information

All reactions were performed under ambient condition. All chemicals were obtained from commercial sources and used directly without further purification. Solvents used in the experiment have been previously treated following standard procedure. The reaction process was monitored by TLC. The NMR was recorded in 500 MHz apparatus using CDCl₃ or DMSO as solvent, and the frequency used for measuring ¹H, ¹³C NMR was 126 MHz. Chemical shifts were recorded in ppm by employing TMS (for ¹H NMR) or the solvent peak of CDCl₃ (77.0 ppm, for ¹³C NMR) as internal standard.

General procedure for the preparation of 1



25 ml schlenk flask was charged with K₂S₂O₈ (20 mmol), AgOAc (10 mmol), L1 (Ac-Leu-OH) (50 mol%), L2 (10 mol%). Then AcOH (2 ml), anisole (20 mmol), methyl vinyl sulfone (10 mmol), Pd (TFA)₂ (10 mmol%) was added. The reaction was maintained at 80 °C for 12 h. After the reaction was completed, it was extracted with ethyl acetate, filtered, and then applied to silica gel column chromatography (EtOAc: PE = 1: 20).

Cell culture and fluorescence imaging

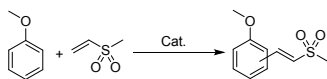
Human cervical carcinoma cells (HeLa cells) were cultured in DMEM and fetal bovine serum (DEME: FBS = 9: 1). The cells were grown at 37 °C incubator with 5 % CO₂. After the cells are over 60 % of the dish, drug was added for the corresponding time. After the incubation, it was washed 3 times with PBS for confocal imaging.

Cell viability assay

MTT assay was performed to assess the viability of Hela cells. The cells were seeded in 96 well plates at a density of 5000 cells per well and grown 24 h at 37 °C incubator with 5 % CO₂. The cells were then exposed to different concentrations of drug for 72 h. After the stipulated time of drug exposure, 10 μL of 3-(4, 5-dimethylthiazol-2-yl) - 2,5-diphenyltetrazolium bromide (5mg/ml) was added and incubate for 4h. Thereafter, 150 ul of DMSO was added to each well and shaken with a shaker. The readings were taken at 590 nm with a reference filter of 620 nm using Synergy HT Multi-Mode Microplate reader (Biotek). The same procedure was followed to assess the viability of the probe-treated Hela cells.

2. Figures and Tables

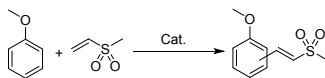
Table S1. Catalyst optimization of methyl vinyl sulfone reaction



Entry	Cata.	Oxidant	Additive	Solv.	Yield/% ^b
1	—	K ₂ S ₂ O ₈	—	AcOH	0
2	Pd(OAc) ₂	K ₂ S ₂ O ₈	—	AcOH	trace
3	NiCl ₂	K ₂ S ₂ O ₈	—	AcOH	0
4	FeCl ₃	K ₂ S ₂ O ₈	—	AcOH	0
5	Cu(OAc) ₂	K ₂ S ₂ O ₈	—	AcOH	0
6	PdCl ₂	K ₂ S ₂ O ₈	—	AcOH	0
7	Pd(TFA) ₂	K ₂ S ₂ O ₈	—	AcOH	5%

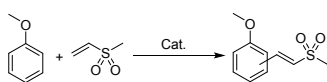
[a] Reaction conditions: Anisole (1 mmol), Methyl vinyl sulfone (2.0 mmol), AcOH (2 mL), cat. (10 mol %), 100 °C; [b] Isolated Yields.

Table S2. Substrate ratio optimization of methyl vinyl sulfone reaction



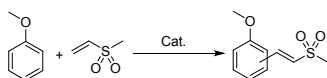
Entry	Cata.	Oxidant	Ether: olefin	Solv.	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	1:2	AcOH	3%
2	Pd(TFA) ₂	K ₂ S ₂ O ₈	1:1	AcOH	5%
3	Pd(TFA) ₂	K ₂ S ₂ O ₈	2:1	AcOH	10%
4	Pd(TFA) ₂	K ₂ S ₂ O ₈	3:1	AcOH	10%
5	Pd(TFA) ₂	K ₂ S ₂ O ₈	4:1	AcOH	11%

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), 80 °C; [b] Isolated Yields.

Table S3. Additive optimization of methyl vinyl sulfone reaction

Entry	Cata.	Oxidant	Additive	Solv.	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	—	AcOH	10%
2	Pd(TFA) ₂	TBHP	—	AcOH	5%
3	Pd(TFA) ₂	PhI(OAc) ₂	—	AcOH	7%
4	Pd(TFA) ₂	MnO ₂	—	AcOH	trace

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), 80 °C; [b] Isolated Yields .

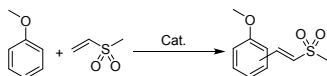
Table S4. Additive optimization of methyl vinyl sulfone reaction

Entry	Cata.	Oxidant	Additive	Solv.	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	Ag ₂ CO ₃	AcOH	17%
2	Pd(TFA) ₂	K ₂ S ₂ O ₈	Ag ₂ O	AcOH	7%
3	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgTFA	AcOH	18%
4	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	AcOH	20%
5	Pd(TFA) ₂	K ₂ S ₂ O ₈	TBAB	AcOH	12%
6	Pd(TFA) ₂	K ₂ S ₂ O ₈	BQ	AcOH	15%
7	Pd(TFA) ₂	K ₂ S ₂ O ₈	Cu(OAc) ₂	AcOH	17%
8	Pd(TFA) ₂	K ₂ S ₂ O ₈	KF	AcOH	16%
9	Pd(TFA) ₂	K ₂ S ₂ O ₈	DDQ	AcOH	12%

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), K₂S₂O₈ (1.0 equiv.), Additive (1.0 equiv.), 80 °C; [b]

Isolated Yields.

Table S5. Solvent optimization of methyl vinyl sulfone reaction

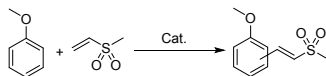


Entry	Cata.	Oxidant	Additive	Solv.	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	AcOH	20%
2	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	DMSO	trace
3	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	DMF	trace
4	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	DCE	7%
5	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Ac ₂ O	5%
6	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	H ₂ O	6%
7	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	t-amyl-OH	12%

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), K₂S₂O₈ (1.0 equiv.), AgOAc (1.0 equiv.), 80 °C; [b]

Isolated Yields.

Table S6. Temp. optimization of methyl vinyl sulfone reaction

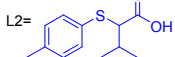
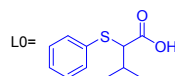
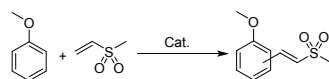


Entry	Cata.	Oxidant	Additive	Temp.	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	60	12%
2	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	80	20%
3	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	100	21%

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), K₂S₂O₈ (1.0 equiv.), AgOAc (1.0 equiv.), 80 °C; [b]

Isolated Yields.

Table S7. Ligand optimization of methyl vinyl sulfone reaction



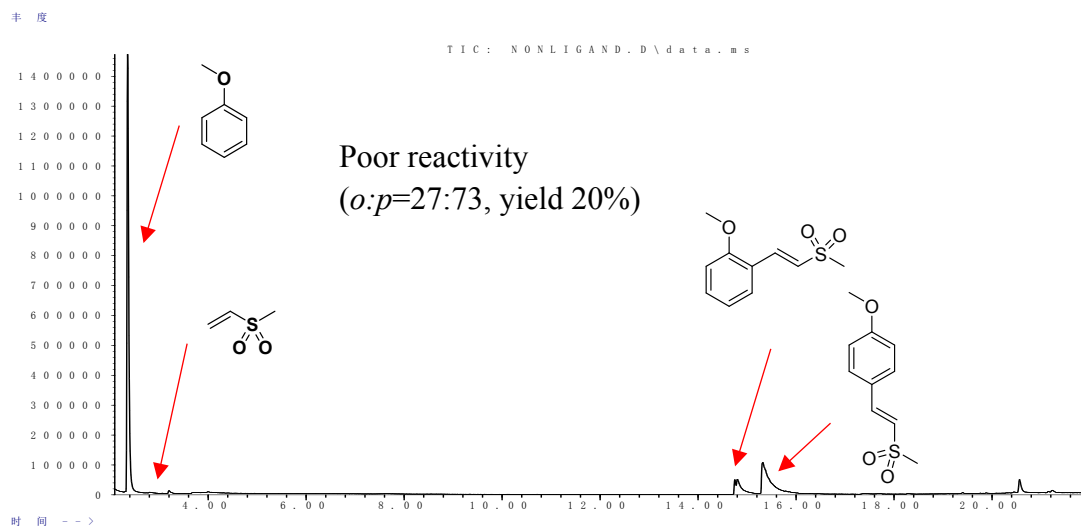
Entry	Cata.	Oxidant	Additive	Ligand	Yield/% ^b
1	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	-	20%
2	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	pyridine	10%
3	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	2-hydroxy-3-nitro-5-chloropyridine	5%
4	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	PPh ₃	trace
5	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	P(t-Bu) ₃	7%
6	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Leu	27%
7	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Ac-Gly-OH	16%
8	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Ac-Ile-OH	12%
9	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Ac-Leu-OH	52%
10	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Boc-Leu-OH	33%
11	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	Fmoc-Leu-OH	37%
12	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	L0	60%
13	Pd(TFA) ₂	K ₂ S ₂ O ₈	AgOAc	L2	70%

[a] Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd(TFA)₂ (10 mol %), MPAA Ligand (50 mmol%), L0, L2 (10 mmol%), K₂S₂O₈ (1.0 equiv.), AgOAc (1.0 equiv.), 80 °C; [b] Isolated Yields.

Figure S1 GC-MS results of reaction mixture

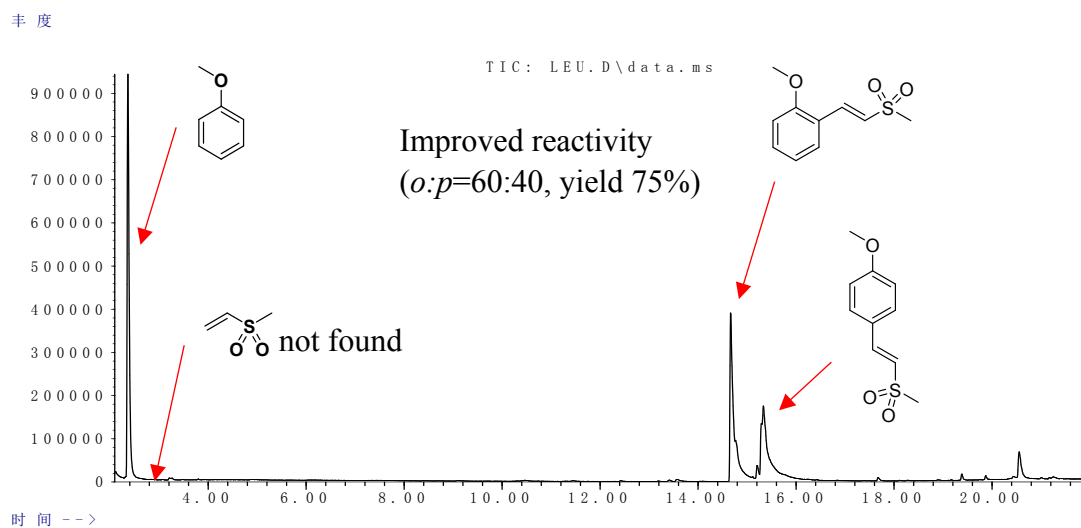
(1a) Non-ligand catalytic system

Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), $K_2S_2O_8$ (1 equiv.), AgOAc (1 equiv.), AcOH (2 mL), Pd (TFA)₂ (5 mol %), 80 °C.



(1b) L2 catalytic system

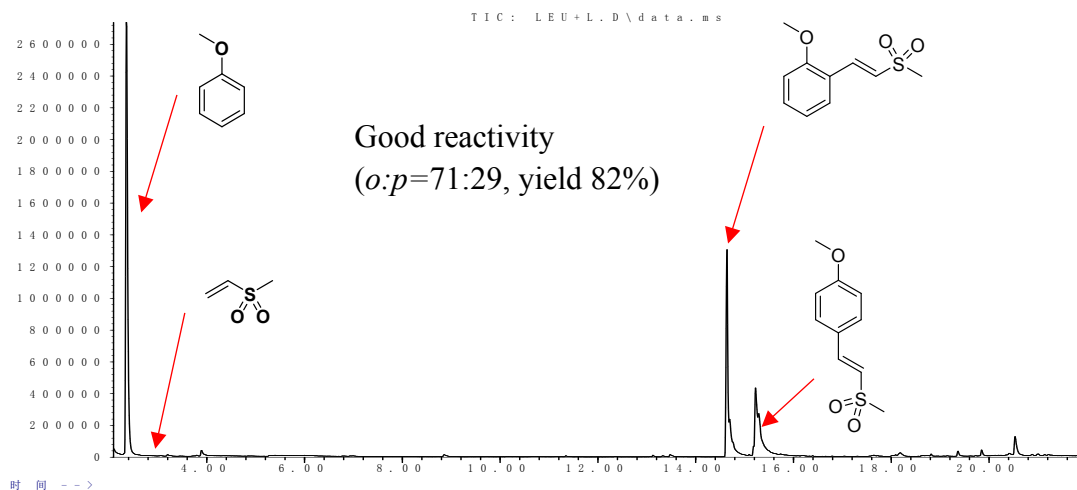
Reaction conditions: Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd (TFA)₂ (5 mol %), $K_2S_2O_8$ (1 equiv.), AgOAc (1 equiv.), L1 (10 mmol%), 80 °C.



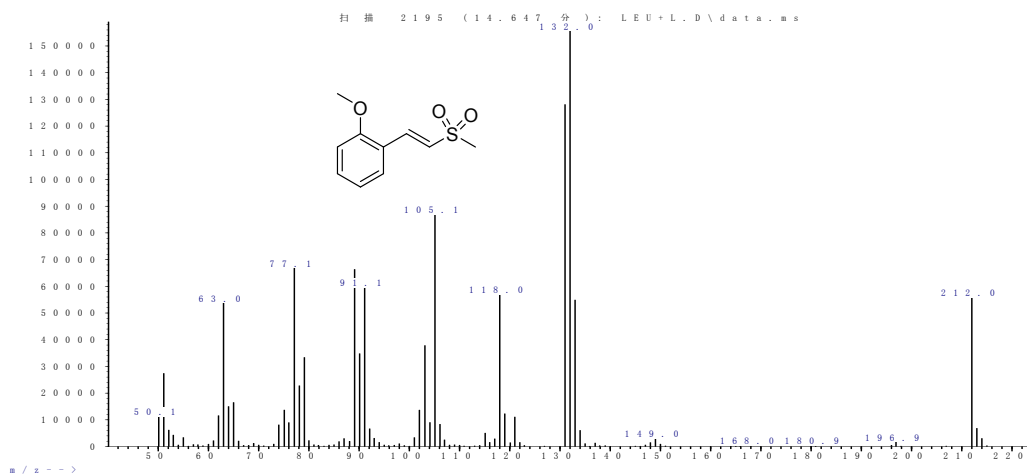
(1c) Dual-ligand catalytic system

Anisole (2.0 mmol), Methyl vinyl sulfone (1.0 mmol), AcOH (2 mL), Pd (TFA)₂ (5 mol %), K₂S₂O₈ (1 equiv.), AgOAc (1 equiv.), L1 (50 mmol%), L2 (10 mmol%), 80 °C.

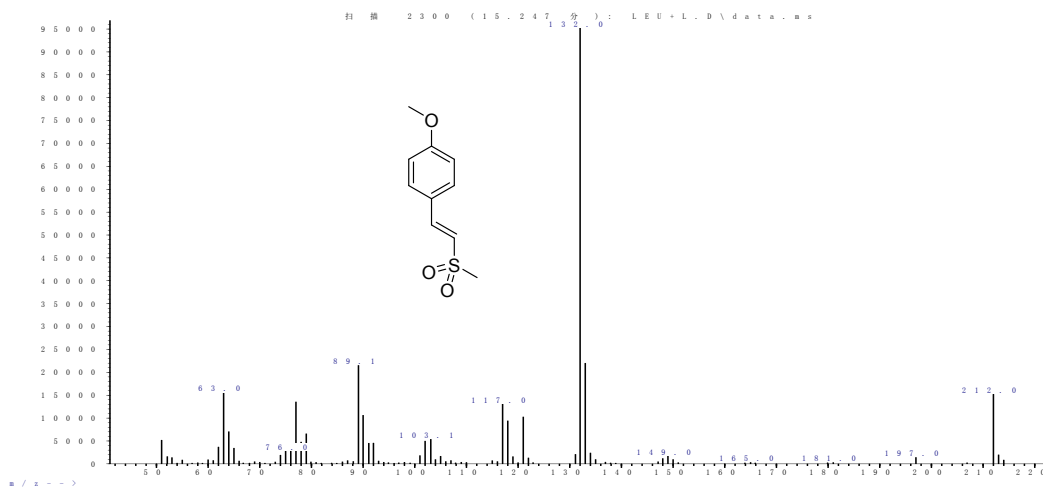
丰度



丰度



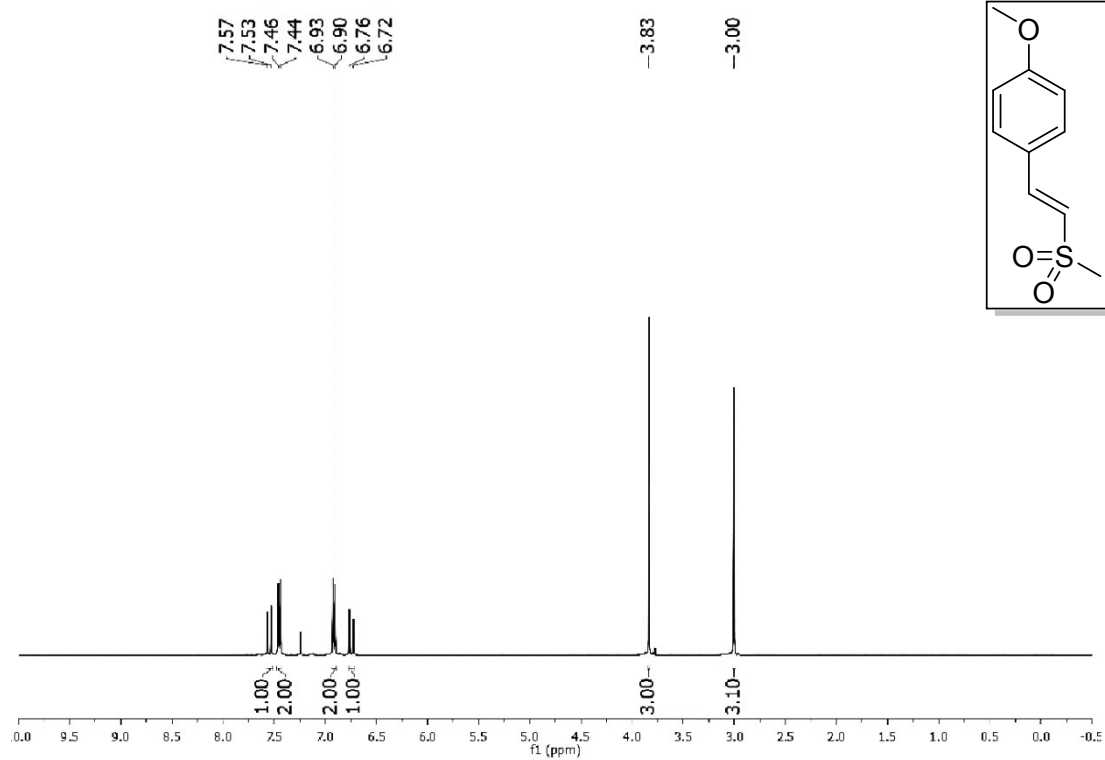
丰度

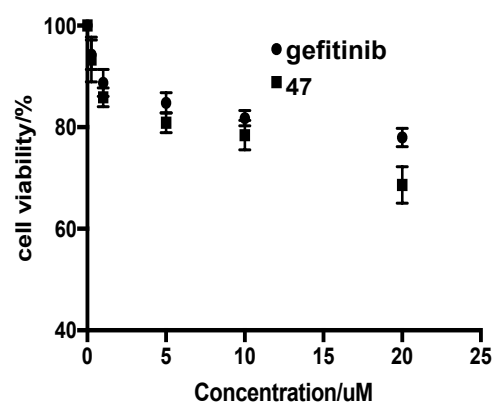


NMR {(E)-1-methoxy-2-(2-(methylsulfonyl)vinyl)benzene}



NMR {(E)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene}





FigureS2. Inhibition of proliferation of 47 and gefitinib.

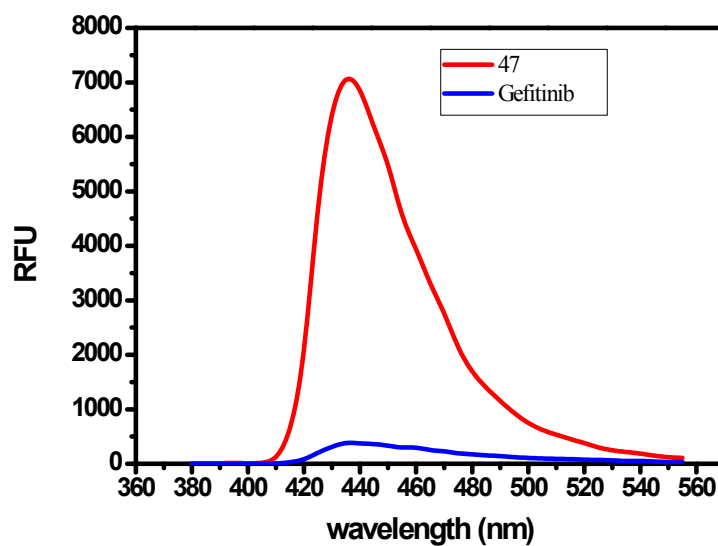


Figure S3 Fluorescence spectra of 47 (250um), gefitinib (250um).

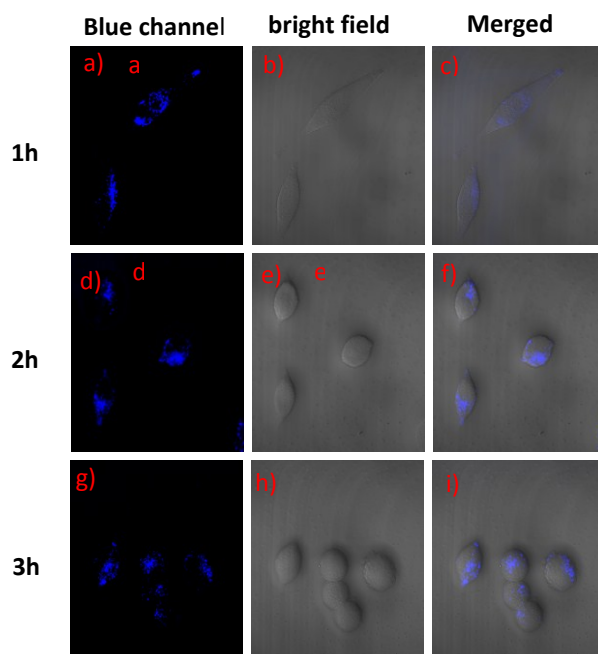
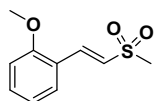


Figure S4. Fluorescence imaging of the olefination drugs in HeLa cell. Cells incubated with 47 (5 μ M), time from 1 h to 3.0 h; Ex =405 nm.

3. Characterization Data of the Compounds

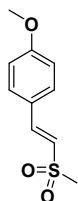
(E)-1-Methoxy-2-(2-(methylsulfonyl)vinyl)benzene (1a)¹

¹H NMR (500 MHz, CDCl₃): δ 7.79 (d, *J* = 15.1 Hz, 1H), 7.45-7.37 (m, 2H), 7.14 (d, *J* = 15.1 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 3.91 (s, 3H), 3.01 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.9, 139.9, 132.6, 131.0, 128.8, 127.0, 120.9, 111.3, 55.5, 43.4.



(E)-1-Methoxy-4-(2-(methylsulfonyl)vinyl)benzene (1b)²

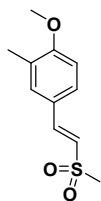
¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 15.4 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 15.4 Hz, 1H), 3.01 (s, 3H), 3.84 (s, 3H).



(E)-1-Methoxy-2-methyl-4-(2-(methylsulfonyl)vinyl)benzene (2)

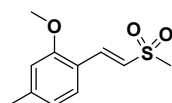
¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, *J* = 15.4 Hz, 1H), 7.34 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 15.4 Hz, 1H), 3.89 (s, 3H), 3.03 (s, 3H), 2.24 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 160.56,

144.07, 130.47, 128.70, 127.74, 124.24, 123.02, 110.13, 55.52, 43.54, 16.23; MS (EI) calculated $[M]^+$: 227.0664, found: 227.0669.



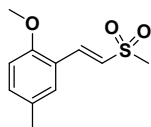
(E)-2-Methoxy-4-methyl-1-(2-(methylsulfonyl)vinyl)benzene (3)

^1H NMR (500 MHz, CDCl_3): δ 7.24 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.74 – 6.69 (m, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 158.26, 138.42, 131.12, 128.21, 121.30, 116.35, 111.92, 111.42, 55.14, 41.78, 19.94; MS (EI) calculated $[M]^+$: 227.0664, found: 227.0665.



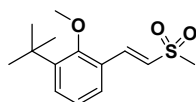
(E)-1-Methoxy-4-methyl-2-(2-(methylsulfonyl)vinyl)benzene (4)

^1H NMR (500 MHz, CDCl_3): δ 7.77 (d, J = 15.4 Hz, 1H), 7.26–7.19 (m, 2H), 7.14 (d, J = 15.4 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.03 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 157.00, 140.09, 133.18, 131.42, 130.12, 126.83, 120.63, 111.27, 55.60, 43.41, 20.28; MS (EI) calculated $[M]^+$: 227.0664, found: 227.0667.



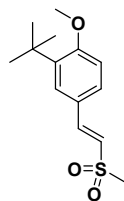
(E)-1-(Tert-butyl)-2-methoxy-3-(2-(methylsulfonyl)vinyl)benzene (5a)

^1H NMR (500 MHz, CDCl_3): δ 7.80 (d, J = 15.4 Hz, 1H), 7.45 (m, 2H), 7.20 (d, J = 15.4 Hz, 1H), 6.91 (d, J = 9.4 Hz, 1H), 3.92 (s, 3H), 3.05 (s, 3H), 1.33 (s, 9H); MS (EI) calculated $[M]^+$: 269.1133, found: 269.1138.



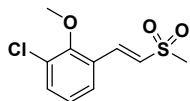
(E)-2-(Tert-butyl)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene (5b)

^1H NMR (500 MHz, CDCl_3): δ 7.59 (d, J = 15.4 Hz, 1H), 7.45 (d, J = 2.2 Hz, 1H), 7.38 (dd, J = 8.5, 2.2 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.77 (d, J = 15.4 Hz, 1H), 3.90 (s, 3H), 3.04 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3): δ 161.34, 144.57, 139.19, 128.43, 127.23, 124.13, 122.85, 111.77, 55.23, 43.61, 34.98, 29.50; MS (EI) calculated $[M]^+$: 269.1133, found: 269.1137.



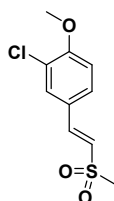
(E)-1-Chloro-2-methoxy-3-(2-(methylsulfonyl)vinyl)benzene (6a)

^1H NMR (500 MHz, CDCl_3): δ 7.84 (d, J = 15.6 Hz, 1H), 7.50 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 1.6 Hz, 1H), 7.17–7.10 (m, 2H), 3.92 (s, 3H), 3.06 (s, 3H); MS (EI) calculated $[\text{M}]^+$: 247.0117, found: 247.0117.



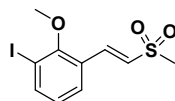
(E)-2-Chloro-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene (6b)

^1H NMR (500 MHz, CDCl_3): δ 7.58 (d, J = 2.3 Hz, 1H), 7.53 (d, J = 15.4 Hz, 1H), 7.40 (dd, J = 8.6, 2.3 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.80 (d, J = 15.4 Hz, 1H), 3.97 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 162.32, 139.75, 136.89, 129.42, 126.18, 122.76, 115.35, 114.07, 55.79, 43.41; MS (EI) calculated $[\text{M}]^+$: 247.0117, found: 247.0117.



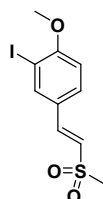
(E)-1-Iodo-2-methoxy-3-(2-(methylsulfonyl)vinyl)benzene (7a)

^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 15.5 Hz, 1H), 7.47–7.40 (m, 2H), 7.16 (d, J = 15.5 Hz, 1H), 6.97 (d, 1H), 3.93 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 158.98, 139.98, 138.97, 132.65, 131.07, 127.13, 120.97 (d, J = 12.8 Hz), 111.34, 55.55, 43.41; MS (EI) calculated $[\text{M}]^+$: 338.9474, found: 338.9477.



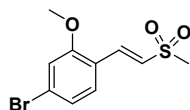
(E)-2-Iodo-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene (7b)

^1H NMR (500 MHz, CDCl_3): δ 7.74 (d, J = 2.2 Hz, 1H), 7.71 (d, J = 15.5 Hz, 1H), 7.68 (dd, J = 8.7, 2.2 Hz, 1H), 7.12 (d, J = 15.5 Hz, 1H), 6.74 (d, J = 8.7 Hz, 1H), 3.91 (s, 3H), 3.03 (s, 3H); MS (EI) calculated $[\text{M}]^+$: 338.9474, found: 338.9478.



(E)-4-Bromo-2-methoxy-1-(2-(methylsulfonyl)vinyl)benzene (8)

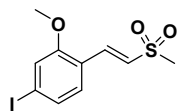
^1H NMR (500 MHz, CDCl_3): δ 7.73 (d, J = 15.5 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.18–7.12 (m, 2H), 7.12 (d, J = 1.6 Hz, 1H), 3.93 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 159.24, 138.87, 131.90, 127.63, 126.55, 124.26, 120.11, 115.14, 55.96, 43.33; MS (EI) calculated $[\text{M}]^+$: 290.9612, found: 290.9618.



(E)-4-Iodo-2-methoxy-1-(2-(methylsulfonyl)vinyl)benzene (9)

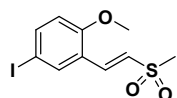
^1H NMR (500 MHz, CDCl_3): δ 7.60 (d, J = 15.5 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.00 (dd, J = 8.2, 2.1 Hz, 1H), 6.93 (d, J = 15.5 Hz, 1H), 3.84 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (126

MHz, CDCl₃): δ 160.04, 143.93, 133.40, 130.18, 126.50, 121.16, 117.22, 113.48, 55.37, 43.26; MS (EI) calculated [M]⁺: 338.9474, found: 338.9479.



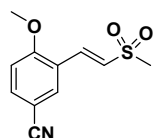
(E)-4-Iodo-1-methoxy-2-(2-(methylsulfonyl)vinyl)benzene (10)

¹H NMR (500 MHz, CDCl₃): δ 7.75 (d, *J* = 15.6 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.14 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 3.92 (s, 3H), 3.04 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.38, 138.41, 132.07, 130.07, 128.38, 125.98, 122.43, 112.68, 55.95, 43.30; MS (EI) calculated [M]⁺: 338.9474, found: 338.9475.



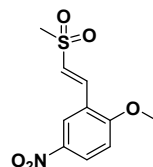
(E)-4-Methoxy-3-(2-(methylsulfonyl)vinyl)benzonitrile (11)

¹H NMR (500 MHz, CDCl₃): δ 8.80 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.61 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 173.71, 165.07, 163.69, 129.88, 124.77, 114.26, 55.57, 25.48; MS (EI) calculated [M]⁺: 238.0460, found: 238.0462.



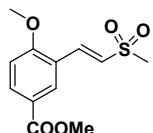
(E)-1-methoxy-2-(2-(methylsulfonyl)vinyl)-4-nitrobenzene (12)

¹H NMR (500 MHz, CDCl₃): δ 8.41 (d, *J* = 2.8 Hz, 1H), 8.34 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.86 (d, *J* = 15.6 Hz, 1H), 7.23 (d, *J* = 15.6 Hz, 1H), 7.08 (d, *J* = 9.1 Hz, 1H), 4.07 (s, 3H), 3.08 (s, 3H); MS (EI) calculated [M]⁺: 258.0358, found: 258.0358.



Methyl (E)-4-methoxy-3-(2-(methylsulfonyl)vinyl)benzoate (13)

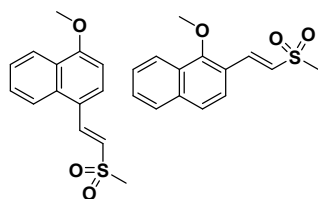
¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.18 (d, *J* = 15.6 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.03 (s, 3H); MS (EI) calculated [M]⁺: 271.0562, found: 271.0569.



(E)-1-Methoxy-2-(2-(methylsulfonyl)vinyl)naphthalene/(E)-1-methoxy-8-(2-(methylsulfonyl)vinyl)naphthalene= 1:1 (14)

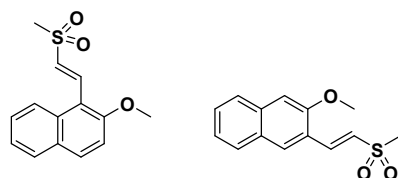
¹H NMR (500 MHz, CDCl₃): δ 8.34 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.30 – 7.25 (m, 1H), 6.77–6.69 (m, 3H), 6.47 (d, *J* = 16.6 Hz, 2H), 6.15 (d, *J* = 10.0 Hz, 2H), 3.98 (s, 3H), 2.96 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 155.18, 137.54, 129.48, 128.39, 127.66, 126.36,

125.43, 122.93, 122.83, 102.85, 59.35, 55.48, 42.28; MS (EI) calculated $[M]^+$: 263.0664, found: 263.0664.



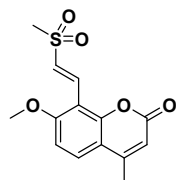
(E)-2-Methoxy-1-(2-(methylsulfonyl)vinyl)naphthalene/(E)-2-methoxy-3-(2-(methylsulfonyl)vinyl)naphthalene=1:1 (15)

^1H NMR (500 MHz, CDCl_3): δ 8.35 (d, $J = 15.4$ Hz, 1H), 8.18 (d, $J = 8.7$ Hz, 1H), 7.94 (d, $J = 9.1$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.58 (m, 1H), 7.48 – 7.40 (m, 2H), 7.33 (d, $J = 9.1$ Hz, 1H), 6.74 (dd, $J = 16.6, 9.9$ Hz, 1H), 6.48 (d, $J = 16.6$ Hz, 1H), 6.15 (d, $J = 9.9$ Hz, 1H), 4.07 (s, 3H), 3.09 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 157.79, 137.54, 135.78, 133.19, 132.96, 129.97, 129.49, 128.85 (d, $J = 4.3$ Hz), 128.08, 124.23, 122.40, 113.43, 112.44, 56.22, 43.47, 42.29; MS (EI) calculated $[M]^+$: 263.0664, found: 263.0664.



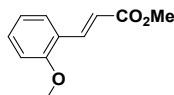
(E)-7-Methoxy-4-methyl-6-(2-(methylsulfonyl)vinyl)-2H-chromen-2-one (16)

^1H NMR (500 MHz, CDCl_3): δ 8.14 (d, $J = 15.9$ Hz, 1H), 7.71 (d, $J = 15.9$ Hz, 1H), 7.66 (d, $J = 8.9$ Hz, 1H), 6.95 (d, $J = 8.9$ Hz, 1H), 6.21 (d, $J = 1.2$ Hz, 1H), 4.03 (s, 3H), 3.07 (s, 3H), 2.44 (d, $J = 1.2$ Hz, 3H); MS (EI) calculated $[M]^+$: 295.0562, found: 295.0569.



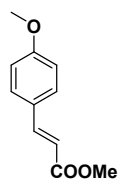
Methyl (E)-3-(2-methoxyphenyl)acrylate (17a)³

^1H NMR (500 MHz, CDCl_3): δ 7.98-8.02 (d, $J = 16.0$ Hz, 1H), 7.48-7.50 (d, $J = 8.0$ Hz, 1H), 7.32-7.36 (t, $J = 7.6$ Hz, 1H), 6.93-6.97 (t, $J = 7.6$ Hz, 1H), 6.89-6.91 (d, $J = 8.0$ Hz, 1H), 6.51-6.55 (d, $J = 16.0$ Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 167.8, 158.2, 140.2, 131.4, 128.8, 123.2, 120.6, 118.2, 111.0, 55.4, 51.5.



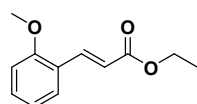
Methyl (E)-3-(4-methoxyphenyl)acrylate (17b)⁴

^1H NMR (500 MHz, CDCl_3): δ 7.65 (d, $J = 16.0$ Hz, 1H), 7.58-7.40 (m, 2H), 6.98-6.82 (m, 2H), 6.31 (d, $J = 16.0$ Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 167.8, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3, 55.38, 51.6.



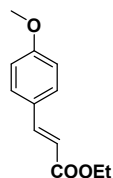
Ethyl (*E*)-3-(2-methoxyphenyl)acrylate (18a)

¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, *J* = 16.2 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38-7.34 (m, 1H), 7.00-6.91 (m, 2H), 6.54 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.35 (d, *J* = 14.3 Hz, 4H); ¹³C NMR (126 MHz, CDCl₃): 167.57, 158.39, 140.05, 131.41, 128.97, 123.54, 120.73, 118.88, 111.18, 60.36, 55.50, 14.39.



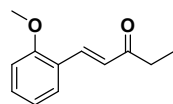
Ethyl (*E*)-3-(4-methoxyphenyl)acrylate (18b)⁵

¹H NMR (500 MHz, CDCl₃): δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.46 (m, 2H), 6.88 (m, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H).



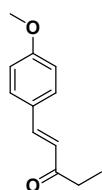
(*E*)-1-(2-Methoxyphenyl)pent-1-en-3-one (19a)⁶

¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 15.5 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.39 (dd, *J* = 19.4, 7.9 Hz, 2H), 7.08 (d, *J* = 15.5 Hz, 1H), 6.98-6.90 (m, 2H), 3.88 (s, 3H).



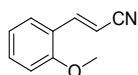
(*E*)-1-(4-Methoxyphenyl)pent-1-en-3-one (19b)⁷

¹H NMR (500 MHz, CDCl₃): δ 7.44–7.60 (m, 3H), 6.85–6.95 (m, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.68 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 200.7, 161.3, 141.8, 129.7, 127.0, 123.7, 114.2, 55.3, 33.9, 8.4.



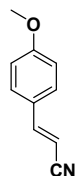
(*E*)-3-(2-Methoxyphenyl)acrylonitrile (20a)

¹H NMR (500 MHz, CDCl₃): δ 7.53 (d, *J* = 16.8 Hz, 1H), 7.32-7.28 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 5.96 (d, *J* = 16.8 Hz, 1H), 3.80 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.3, 146.5, 132.4, 129.0, 122.6, 120.9, 119.1, 111.4, 97.0, 55.6.



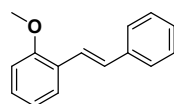
(E)-3-(4-Methoxyphenyl)acrylonitrile (20b)⁸

¹H NMR (500 MHz, CDCl₃): δ 7.35-7.40 (m, 2H), 7.26-7.32 (d, J = 16.6 Hz, 1H), 3.83 (s, 3H), 6.88-6.94 (m, 2H), 5.66-5.72 (d, J = 16.6 Hz, 1H).



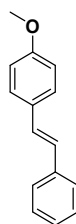
(E)-1-Methoxy-2-styrylbenzene (21a)

¹H NMR (500 MHz, CDCl₃): δ 7.62 (dd, J = 7.7, 1.3 Hz, 1H), 7.56 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 16.5 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.26 (s, 1H), 7.13 (d, J = 16.5 Hz, 1H), 6.99 (s, 1H), 6.93 (d, J = 8.2 Hz, 1H), 3.91 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 156.99, 138.03, 129.16, 128.69, 128.62, 127.38, 126.60, 126.52, 126.47, 123.57, 120.79, 111.01, 55.57.



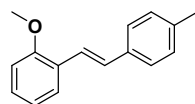
(E)-1-Methoxy-4-styrylbenzene (21b)⁸

¹H NMR (500 MHz, CDCl₃): δ 3.86 (s, 3H), 6.92-6.98 (m, 2H), 7.04-7.09 (d, J = 14.3 Hz, 2H), 7.25-7.30 (m, 1H), 7.36-7.41 (m, 2H), 7.47-7.55 (m, 4H); ¹³C NMR (126 MHz, CDCl₃): δ 56.20, 115.02, 127.14, 127.50, 128.10, 128.61, 129.10, 129.53, 131.03, 138.54, 160.19.



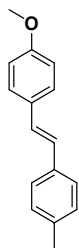
(E)-1-Methoxy-2-(4-methylstyryl)benzene (22a)⁹

¹H NMR (500 MHz, CDCl₃): δ = 7.53-7.46 (m, 1H), 7.39-7.31 (m, 3H), 7.17-7.10 (m, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 16.5 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 3.78 (s, 3H), 2.26 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.0, 137.3, 135.3, 129.4, 129.2, 128.6, 126.8, 126.6, 126.4, 122.6, 120.9, 111.1, 55.6, 21.4.



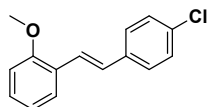
(E)-1-Methoxy-4-(4-methylstyryl)benzene (22b)¹⁰

¹H NMR (500 MHz, CDCl₃): δ 7.39-7.46 (m, 4H), 7.06-7.24 (m, 2H), 7.00 (d, 2H, J = 9.0 Hz), 6.90 (d, 2H, J = 6.0 Hz), 2.36 (s, 3H), 3.82 (s, 3H).



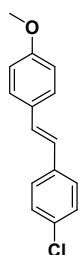
(E)-1-(4-Chlorostyryl)-2-methoxybenzene (23a)¹¹

¹H NMR (500 MHz, CDCl₃): δ 7.57 (d, J = 7.2 Hz, 1H), 7.48-7.42 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 1.2 Hz, 1H), 7.06 (d, J = 16.2 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.0, 136.5, 132.8, 131.0, 128.9, 128.7, 127.7, 127.7, 126.5, 124.1, 120.8, 110.9, 55.5.



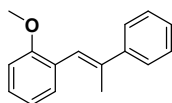
(E)-1-(4-Chlorostyryl)-4-methoxybenzene (23b)¹²

¹H NMR (500 MHz, CDCl₃): δ 7.32-7.47 (m, 4H), 7.27-7.30 (d, J = 14.0 Hz, 2H), 7.0 (s, 1H), 6.88-6.96 (m, 3H), 3.85 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 160.2, 136.9, 133.4, 130.5, 129.5, 128.5, 128.0, 126.0, 114.9, 56.0.



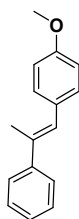
(E)-1-Methoxy-2-(2-phenylprop-1-en-1-yl)benzene (24a)¹³

¹H NMR (500 MHz, CDCl₃): δ 7.55-7.58 (m, 2H), 7.23-7.39 (m, 5H), 6.89-7.00 (m, 3H), 2.33 (s, 3H), 3.84 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.62, 143.89, 137.11, 17.55, 130.50, 128.40, 128.22, 127.39, 127.23, 126.22, 55.60, 123.45, 120.21, 110.55.



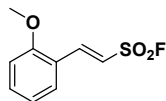
(E)-1-Methoxy-4-(2-phenylprop-1-en-1-yl)benzene (24b)¹⁴

¹H NMR (500 MHz, CDCl₃): δ 7.63-7.51 (m, 2H), 7.47-7.29 (m, 5H), 7.03-6.92 (m, 2H), 6.86 (s, 1H), 3.88 (s, 3H), 2.35 (d, J = 1.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.3, 144.3, 136.0, 131.1, 130.5, 128.4, 127.4, 127.1, 126.0, 113.7, 55.3, 17.6.



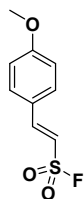
(E)-2-(2-Methoxyphenyl)ethene-1-sulfonyl fluoride (25a)¹⁵

¹H NMR (500 MHz, CDCl₃): δ 7.92 (d, J = 15.5 Hz, 1H), 7.48 (td, J = 8.2 Hz, J = 1.6 Hz, 1H), 7.43 (dd, J = 7.6 Hz, J = 1.3 Hz, 1H), 7.16 (dd, J = 15.5 Hz, J = 2.3 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H).



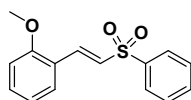
(E)-2-[4-Methoxyphenyl]ethenesulfonyl fluoride (25b)¹⁶

¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, J = 15.5 Hz, 1H), 7.50 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.69 (dd, J = 15.6, 2.5 Hz, 1H), 3.87 (3H, s).



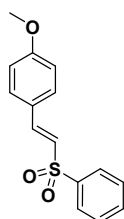
(E)-1-Methoxy-2-(2-(phenylsulfonyl)vinyl)benzene (26a)¹⁷

¹H NMR (500 MHz, CDCl₃): δ 7.95 (d, J = 7.8 Hz, 2H), 7.89 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 7.0 Hz, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.39 (dd, J = 19.4, 7.9 Hz, 2H), 7.08 (d, J = 15.5 Hz, 1H), 6.98-6.90 (m, 2H), 3.88 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.8, 141.2, 138.6, 133.1, 132.5, 130.8, 129.2, 127.9, 127.6, 121.2, 120.8, 111.2, 55.5.



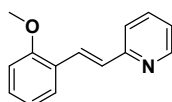
(E)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (26b)¹⁸

¹H NMR (500 MHz, CDCl₃): 7.96–7.94 (m, 2H), 7.67–7.59 (m, 2H), 7.56–7.52 (m, 2H), 7.38–7.37 (m, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 15.4 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): 142.7, 142.0, 141.1, 133.4, 129.9, 129.7, 129.4, 128.7, 127.7, 126.2, 21.7.



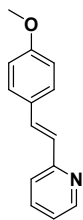
(E)-2-(2-Methoxystyryl)pyridine (27a)¹⁹

¹H NMR (500 MHz, CDCl₃): δ 8.59 (1H, d, J = 4.5 Hz), 7.93 (d, J = 16.1 Hz, 1H), 7.62 (m, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.26 (m, 1H), 7.23 (d, J = 16.1 Hz, 1H), 7.10 (dd, J = 8, 4.5 Hz, 1H), 6.96 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 3.87 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.5, 156.4, 125.6, 149.5, 136.3, 129.3, 128.7, 127.8, 127.3, 121.7, 121.6, 120.7, 110.9, 55.4.



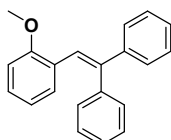
(E)-2-(4-Methoxystyryl)pyridine (27b)²⁰

¹H NMR (500 MHz, CDCl₃): δ 8.58-8.56 (m, 1H), 7.64-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.33 (d, J = 7.9 Hz, 1H), 7.09 (m, 1H), 7.03 (d, J = 16.1 Hz, 1H), 6.91-6.88 (m, 2H), 3.81 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 159.9, 156.0, 149.7, 136.6, 132.4, 129.5, 128.5, 125.9, 121.9, 121.8, 114.3, 55.4.



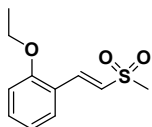
(2-(2-Methoxyphenyl)ethene-1,1-diyl)dibenzene (28)

^1H NMR (500 MHz, CDCl_3): δ 7.37 (s, 1H), 7.35 (q, J = 1.6 Hz, 2H), 7.33-7.31 (m, 4H), 7.28 (s, 1H), 7.25-7.23 (m, 2H), 7.00-6.95 (m, 2H), 6.94 (s, 1H), 6.71-6.67 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 158.43, 140.66, 130.83, 130.46, 130.13, 128.74, 128.27, 128.20, 127.70, 127.57, 127.43, 127.30, 127.22, 113.46, 55.18.



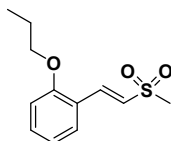
(E)-1-Ethoxy-2-(2-(methylsulfonyl vinyl)benzene (29)

^1H NMR (500 MHz, CDCl_3): δ 7.57 (d, J = 15.4 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 6.80-6.68 (m, 2H), 6.48 (d, J = 15.4 Hz, 1H), 4.09 (q, J = 7.0 Hz, 2H), 2.97 (s, 3H), 1.48 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 161.69, 143.83, 137.56, 130.42, 124.53, 123.25, 115.09, 76.79, 63.78, 43.53, 14.68; MS (EI) calculated $[\text{M}]^+$: 227.0664 found: 227.0669.



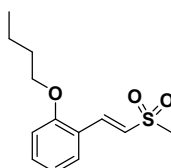
(E)-1-(2-(Methylsulfonyl)vinyl)-2-propoxybenzene (30)

^1H NMR (500 MHz, CDCl_3): δ 7.82 (d, J = 15.5 Hz, 1H), 7.45 (dd, J = 7.6, 1.5 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.18 (d, J = 15.5 Hz, 1H), 6.99-6.69 (m, 2H), 4.05 (t, J = 6.5 Hz, 2H), 3.03 (s, 3H), 1.91 (q, J = 7.0 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 158.50, 140.16, 132.61, 131.17, 127.01, 120.73, 115.02, 112.21, 70.19, 43.39, 22.49, 10.68; MS (EI) calculated $[\text{M}]^+$: 241.0820 found: 241.0823.



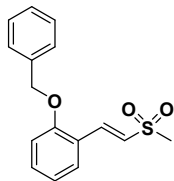
(E)-1-butoxy-2-(2-(Methylsulfonyl)vinyl)benzene (31)

^1H NMR (500 MHz, CDCl_3): δ 7.81 (d, J = 15.5 Hz, 1H), 7.45 (dd, J = 7.5, 1.5 Hz, 1H), 7.42-7.38 (m, 1H), 7.16 (d, J = 15.5 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.09 (t, J = 6.6 Hz, 2H), 3.03 (s, 3H), 1.87 (m, 2H), 1.54 (dd, J = 15.0, 7.5 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 140.15, 132.61, 131.67, 131.15, 127.02, 122.61, 120.73, 112.21, 68.40, 43.40, 31.16, 19.37, 13.85; m/z (EI) calculated $[\text{M}]^+$: 255.0977 found: 255.0979.



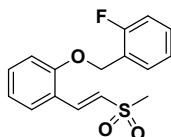
(E)-1-(Benzyloxy)-2-(2-(methylsulfonyl)vinyl)benzene (32)

¹H NMR (500 MHz, CDCl₃): δ 7.85 (d, *J* = 15.5 Hz, 1H), 7.49 – 7.36 (m, 7H), 7.15 (d, *J* = 15.5 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 5.21 (s, 2H), 2.98 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.05, 139.78, 136.15, 132.56, 131.19, 128.84, 128.37, 127.45, 127.38, 121.41, 121.25, 112.91, 70.70, 43.28; MS (EI) calculated [M]⁺: 289.0820 found: 289.0821.



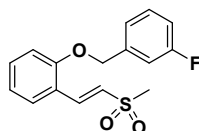
(E)-1-Fluoro-2-((2-(2-(methylsulfonyl)vinyl)phenoxy)methyl)benzene (33)

¹H NMR (500 MHz, CDCl₃): δ 7.85 (d, *J* = 15.5 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.12 (d, *J* = 15.5 Hz, 2H), 7.05 (dd, *J* = 7.9, 2.5 Hz, 2H), 5.27 (s, 2H), 2.99 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.73, 139.65, 133.55, 132.61, 131.00, 129.76, 129.73, 127.42, 124.57, 124.54, 121.48, 115.69, 115.52, 112.83, 64.47, 43.28; MS (EI) calculated [M]⁺: 307.0726 found: 307.0728.



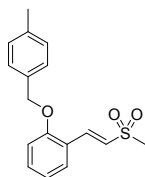
(E)-1-((3-Fluorobenzyl)oxy)-2-(2-(methylsulfonyl)vinyl)benzene (34)

¹H NMR (500 MHz, CDCl₃): δ 7.87 (d, *J* = 15.5 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.39 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 15.5 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.20 (s, 2H), 3.01 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 157.67, 139.59, 132.60, 131.02, 130.55, 130.48, 127.50, 122.72, 122.69, 121.51, 115.37, 115.19, 114.25, 114.07, 69.87, 43.28; MS (EI) calculated [M]⁺: 307.0726 found: 307.0728.



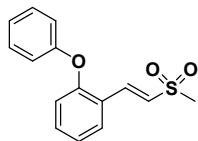
(E)-1-((4-Methylbenzyl)oxy)-2-(2-(methylsulfonyl)vinyl)benzene (35)

¹H NMR (500 MHz, CDCl₃): δ 7.83 (d, *J* = 15.5 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 15.5 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 2H), 2.98 (s, 3H), 2.38 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 158.15, 139.89, 138.19, 133.08, 132.54, 131.27, 129.49, 127.49, 127.41, 121.38, 121.15, 115.06, 114.89, 112.91, 70.65, 43.29, 21.22; MS (EI) calculated [M]⁺: 303.0977 found: 303.0979.



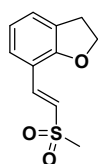
(E)-1-(2-(Methylsulfonyl)vinyl)-2-phenoxybenzene (36)

^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, J = 15.6 Hz, 1H), 7.56 (dd, J = 7.8, 1.7 Hz, 1H), 7.41-7.37 (m, 3H), 7.36 (d, J = 1.5 Hz, 1H), 7.21 - 7.14 (m, 2H), 7.05 - 7.03 (m, 2H), 6.87 (d, J = 8.3 Hz, 1H), 3.01 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 157.03, 155.88, 139.20, 132.48, 130.50, 130.09, 128.02, 124.38, 123.39, 123.10, 119.60, 118.27, 43.28; MS (EI) calculated $[\text{M}]^+$: 275.0664 found: 275.0668.



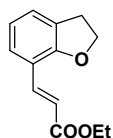
(E)-7-(2-(Methylsulfonyl) vinyl)-2,3-dihydrobenzofuran (37)

^1H NMR (500 MHz, CDCl_3): δ 7.54 (d, J = 15.4 Hz, 1H), 7.32 (d, J = 15.4 Hz, 1H), 7.29-7.24 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 4.71 (t, J = 8.8 Hz, 2H), 3.26 (t, J = 8.8 Hz, 2H), 3.02 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 159.69, 139.88, 130.26, 128.35, 127.76, 127.52, 120.89, 115.38, 72.12, 43.39, 29.11; MS (EI) calculated $[\text{M}]^+$: 225.0507 found: 225.0507.



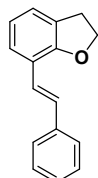
Ethyl(E)-3-(2,3-dihydrobenzofuran-7-yl)acrylate (38)

^1H NMR (500 MHz, CDCl_3): δ 7.69 (d, J = 16.0 Hz, 1H), 7.24-7.18 (m, 2H), 6.86 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 4.68 (t, J = 8.8 Hz, 2H), 4.27 (q, J = 7.2 Hz, 2H), 3.24 (t, J = 8.7 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 167.72, 159.47, 140.40, 128.94, 128.06, 126.34, 120.65, 119.81, 117.73, 71.71, 60.30, 29.33, 14.38; MS (EI) calculated $[\text{M}]^+$: 219.0943 found: 219.0948.



(E)-7-Styryl-2,3-dihydrobenzofuran (39)

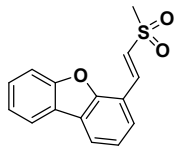
^1H NMR (500 MHz, CDCl_3): δ 7.54 (d, J = 7.4 Hz, 2H), 7.38-7.29 (m, 4H), 7.25 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 16.4 Hz, 1H), 7.12-7.09 (m, 1H), 6.87 (t, J = 7.5 Hz, 1H), 4.68 (t, J = 8.7 Hz, 2H), 3.25 (t, J = 8.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3): δ 158.79, 139.38, 138.04, 130.07, 129.96, 128.61, 127.37, 126.50, 126.25, 124.04, 123.76, 120.66, 71.27, 29.72; MS (EI) calculated $[\text{M}]^+$: 223.1045 found: 223.1047.



(E)-4-(2-(Methylsulfonyl)vinyl)dibenzo[b,d]furan (40)

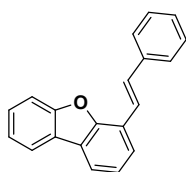
^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 15.4 Hz, 1H), 7.73 (d, J = 15.4 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.58-7.53 (m, 2H), 7.43 (m, 2H), 3.14 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 156.19, 154.36, 139.04, 129.67, 129.58, 127.99, 125.39, 123.60 (d, J =

3.3 Hz), 123.32, 120.92, 117.45, 115.75, 112.02, 43.45; MS (EI) calculated $[M]^+$: 273.0507 found: 273.0509.



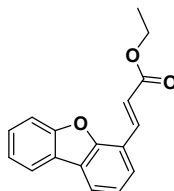
(E)-4-Styryldibenzo[b,d]furan (41)

^1H NMR (500 MHz, CDCl_3): δ 8.11 (d, $J = 1.6$ Hz, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 7.97 – 7.92 (m, 1H), 7.66 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.59 – 7.57 (m, 4H), 7.40 (t, $J = 7.6$ Hz, 3H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 6.6$ Hz, 1H), 7.19 (d, $J = 16.3$ Hz, 1H); MS (EI) calculated $[M]^+$: 271.1045 found: 271.1047.



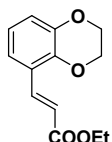
Ethyl(E)-3-(dibenzo[b,d]furan-4-yl)acrylate (42)

^1H NMR (500 MHz, CDCl_3): δ 8.56 (d, $J = 15.8$ Hz, 1H), 8.17 (d, $J = 7.8$ Hz, 1H), 7.63 – 7.57 (m, 3H), 7.52 (m, 1H), 7.47 (d, $J = 15.8$ Hz, 1H), 7.43 – 7.39 (m, 1H), 6.63 (d, $J = 15.8$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 166.85, 156.50, 156.38, 140.94, 130.59, 127.62, 127.12, 123.63, 123.22, 123.07, 120.94, 120.62, 112.86, 111.87, 60.76, 14.39; MS (EI) calculated $[M]^+$: 267.0943 found: 267.0943.



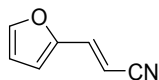
Ethyl(E)-3-(2,3-dihydrobenzo[b][1,4]dioxin-5-yl)acrylate (43)

^1H NMR (500 MHz, CDCl_3): δ 7.91 (d, $J = 16.1$ Hz, 1H), 7.09 (dd, $J = 7.7, 1.7$ Hz, 1H), 6.90 (dd, $J = 8.0, 1.7$ Hz, 1H), 6.84 (t, $J = 7.7$ Hz, 1H), 6.54 (d, $J = 16.1$ Hz, 1H), 4.37 – 4.34 (q, $J = 7.1$ Hz, 2H), 4.30 – 4.26 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 167.42, 143.92, 139.21, 134.47, 131.54, 121.13, 120.96, 119.43, 119.00, 64.50, 64.03, 60.41, 14.34; MS (EI) calculated $[M]^+$: 235.0892 found: 235.0899.



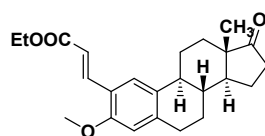
(E)-3-(Furan-2-yl)acrylonitrile (44)

^1H NMR (500 MHz, CDCl_3): δ 7.49 (d, $J = 1.8$ Hz, 1H), 7.10 (d, $J = 16.2$ Hz, 1H), 6.62 (d, $J = 3.0$ Hz, 1H), 6.50–6.49 (m, 1H), 5.75 (d, $J = 16.2$, 1H); ^{13}C NMR (126 MHz, CDCl_3): δ 149.9, 145.6, 136.2, 118.4, 115.6, 112.8, 93.5; MS (EI) calculated $[M]^+$: 120.0371 found: 120.0373.



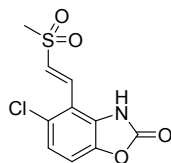
(E)-3-((8R,9S,13S,14S)-3-Methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl) ethyl acrylate(45)¹⁰

¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 16.1 Hz, 1H), 7.42 (s, 1H), 6.63 (s, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 2.93 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.51 (m, 1H), 2.46–2.41 (m, 1H), 2.25 (td, *J* = 10.9, 4.3 Hz, 1H), 2.15 (dt, *J* = 19.0, 9.0 Hz, 1H), 2.10–2.00 (m, 2H), 2.00–1.95 (m, 1H), 1.69–1.39 (m, 7H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30–1.19 (m, 1H), 0.91 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 220.65, 167.67, 156.44, 140.53, 140.32, 132.01, 126.18, 121.02, 117.80, 111.39, 60.22, 50.34, 47.93, 43.71, 38.23, 35.82, 31.48, 29.88, 26.39, 25.86, 21.55, 14.36, 13.81.



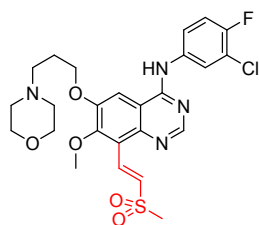
(E)-5-Chloro-4-(2-(methylsulfonyl)vinyl)benzo[d]oxazol-2(3H)-one (46)

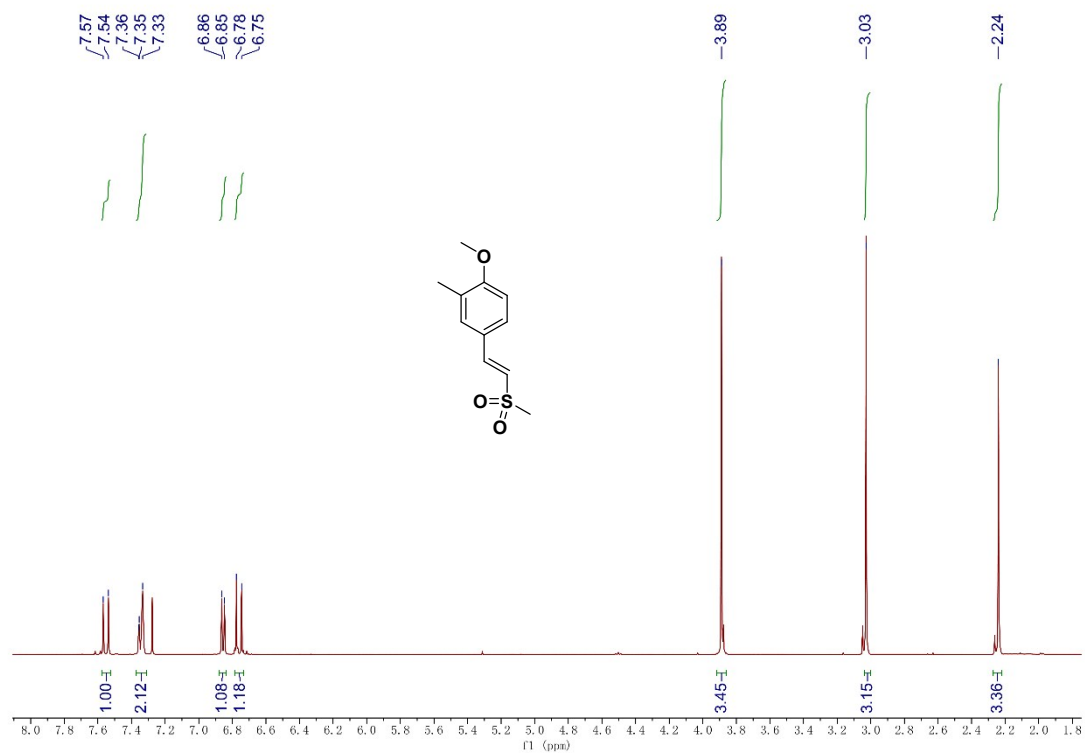
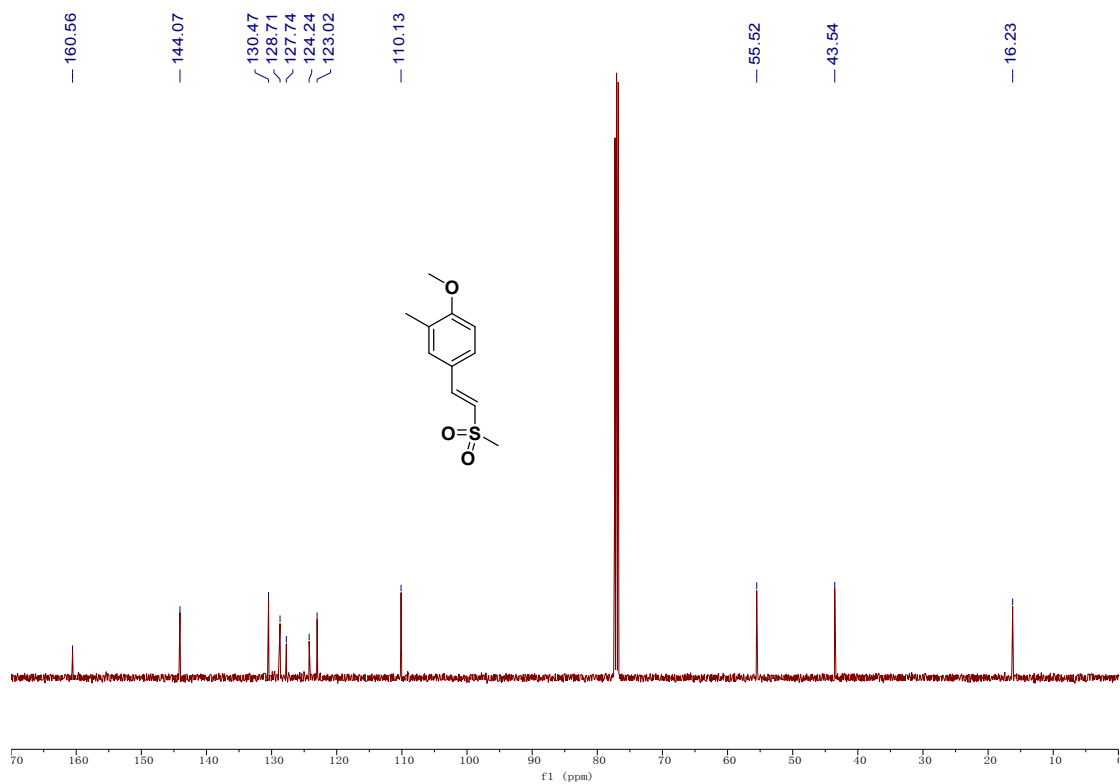
¹H NMR (500 MHz, CDCl₃): δ 7.76 (d, *J* = 13.8 Hz, 1H), 7.37 (d, *J* = 13.8 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H), 3.12 (s, 3H); MS (EI) calculated [M]⁺: 272.9863 found: 272.9866.

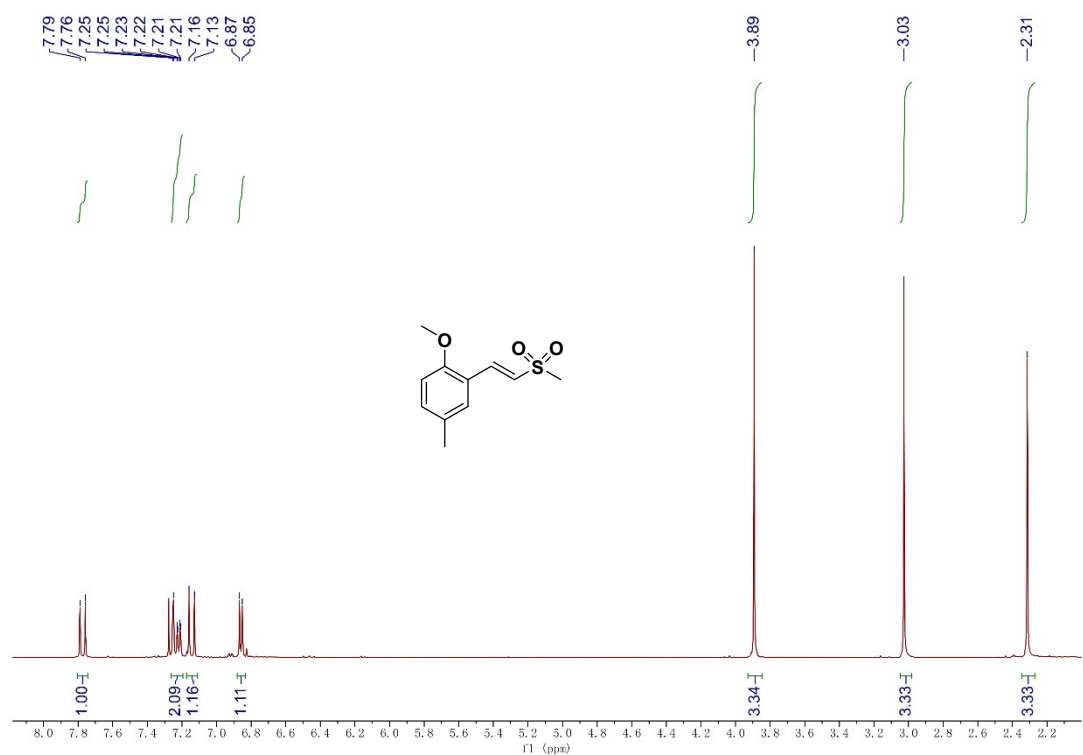
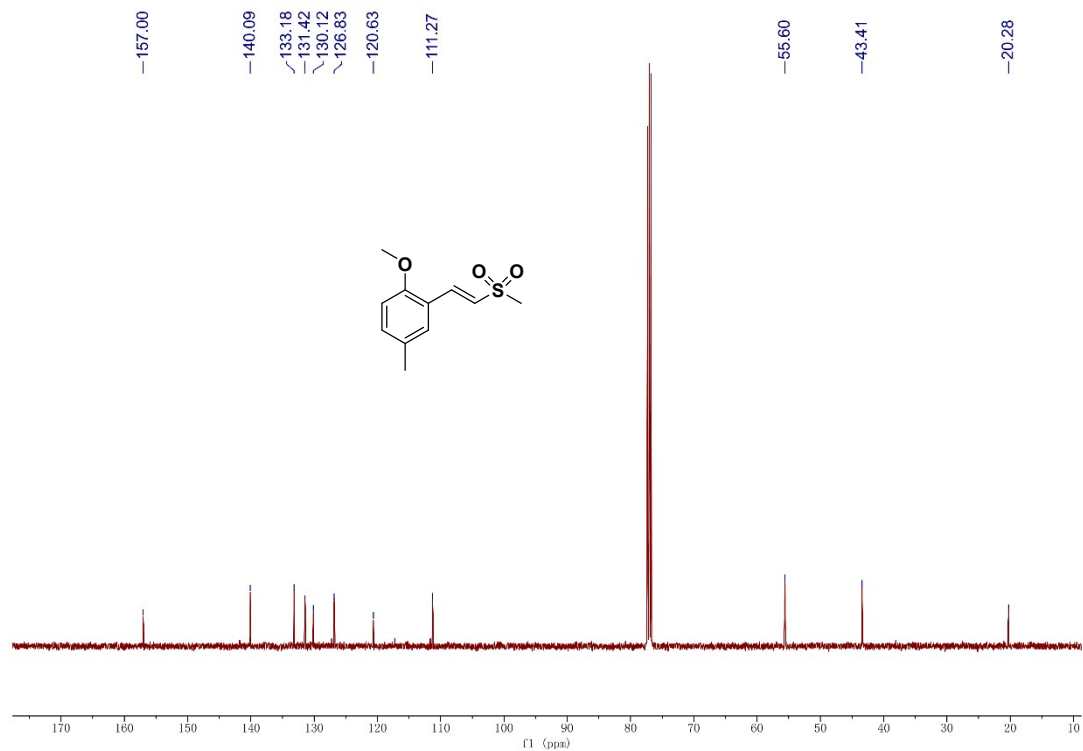


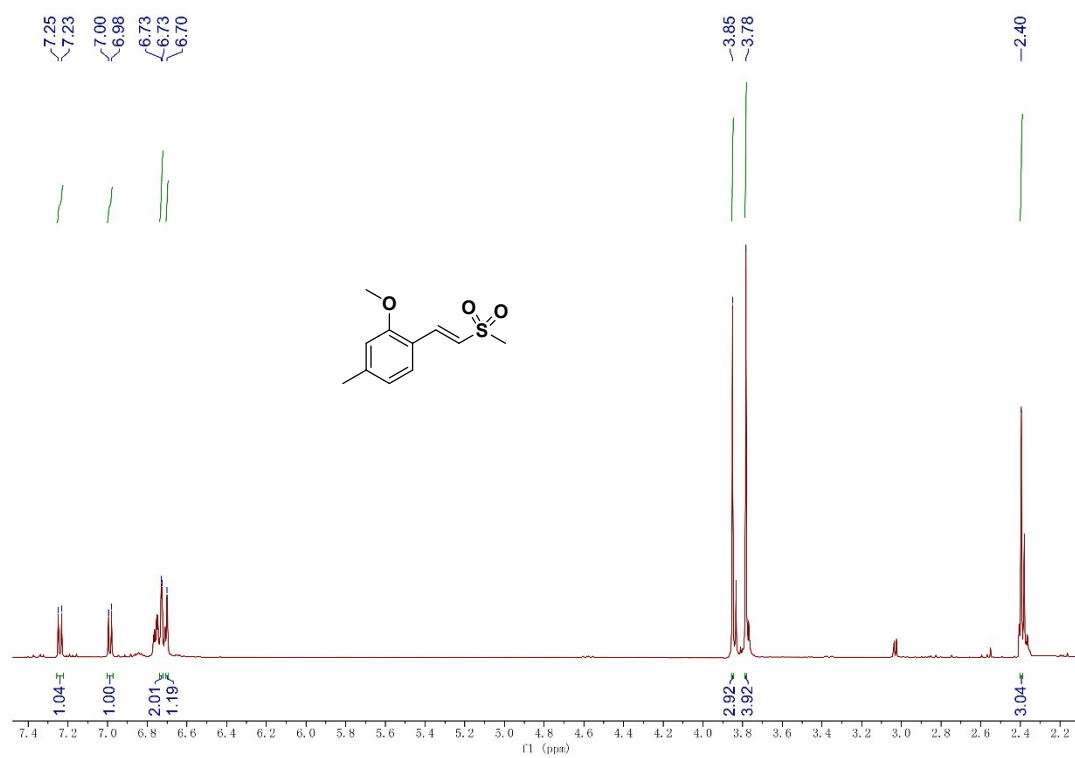
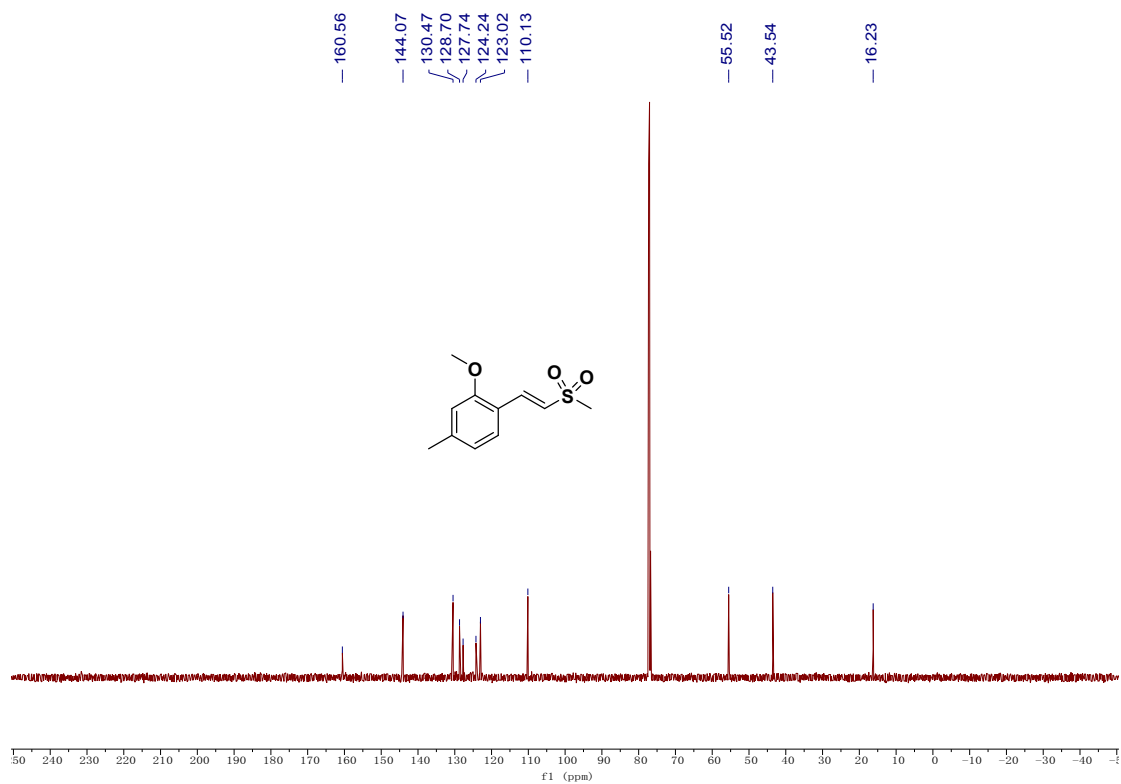
(E)-N-(3-Chloro-4-fluorophenyl)-7-methoxy-8-(2-(methylsulfonyl)vinyl)-6-(3-morpholinopropoxy)quinazolin-4-amine (47)

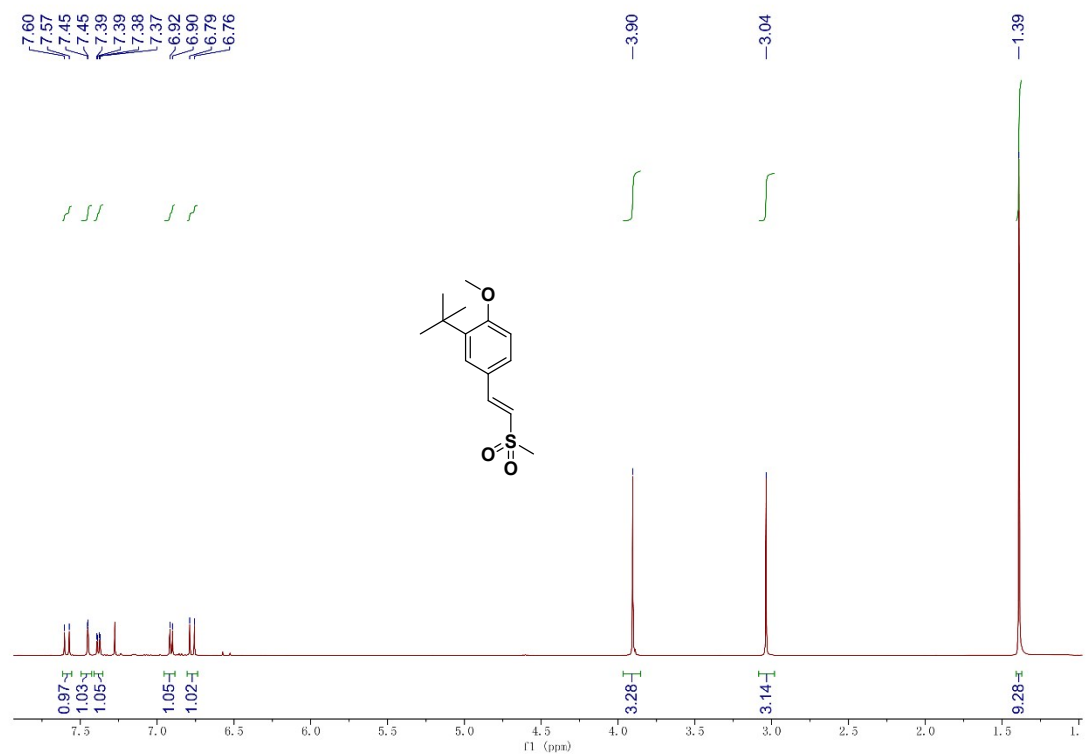
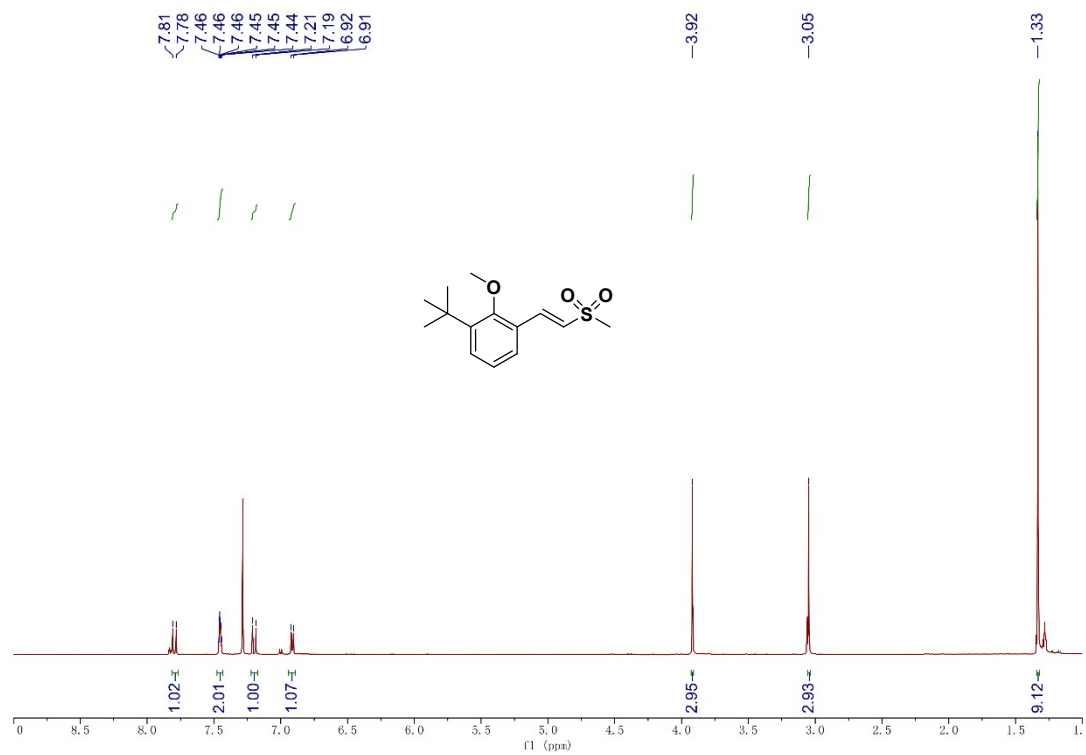
¹H NMR (500 MHz, CDCl₃): δ 8.65 (s, 1H), 8.00 (s, 1H), 7.92 (s, 1H), 7.81 (d, *J* = 6.5 Hz, 1H), 7.46 (d, *J* = 6.7 Hz, 1H), 7.22–7.18 (m, 1H), 7.09 (m, 2H), 4.31–4.27 (m, 2H), 3.98 (s, 3H), 3.79 (m, 4H), 2.77 (s, 3H), 2.65–2.55 (m, 6H), 2.26–2.20 (m, 2H). HRMS (ESI) Calculated for C₂₅H₂₉ClF₄N₄O₅S: [M+H]⁺: 551.1531, found 551.1533.

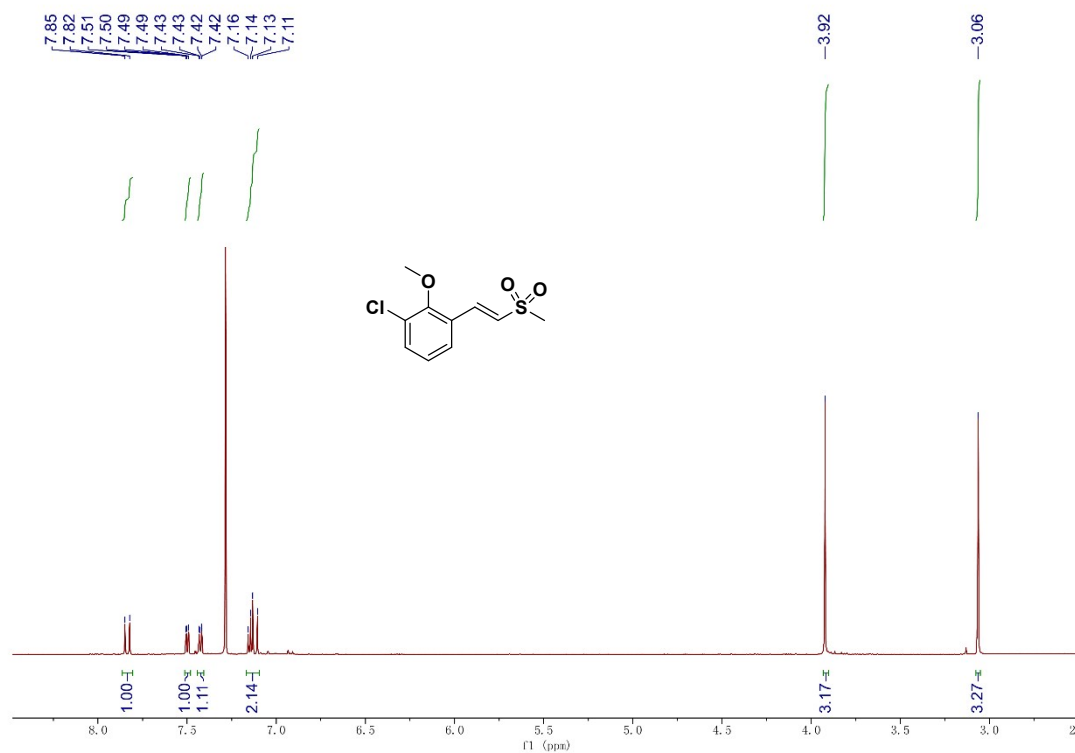
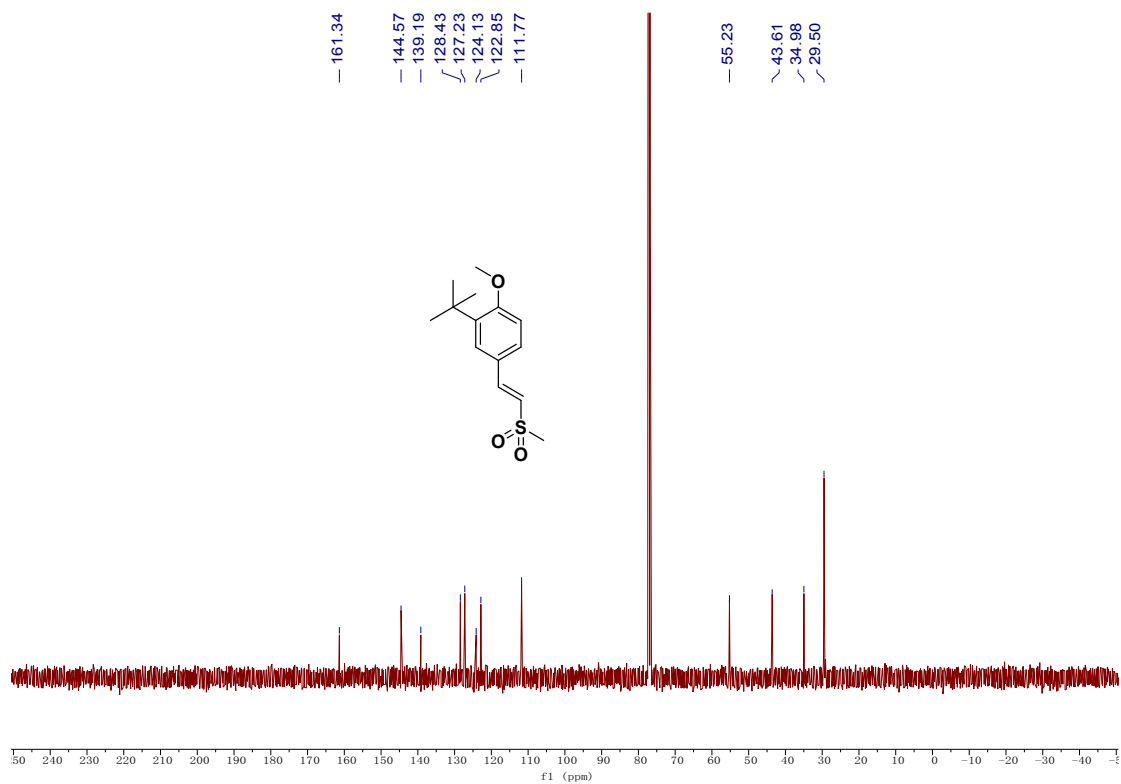


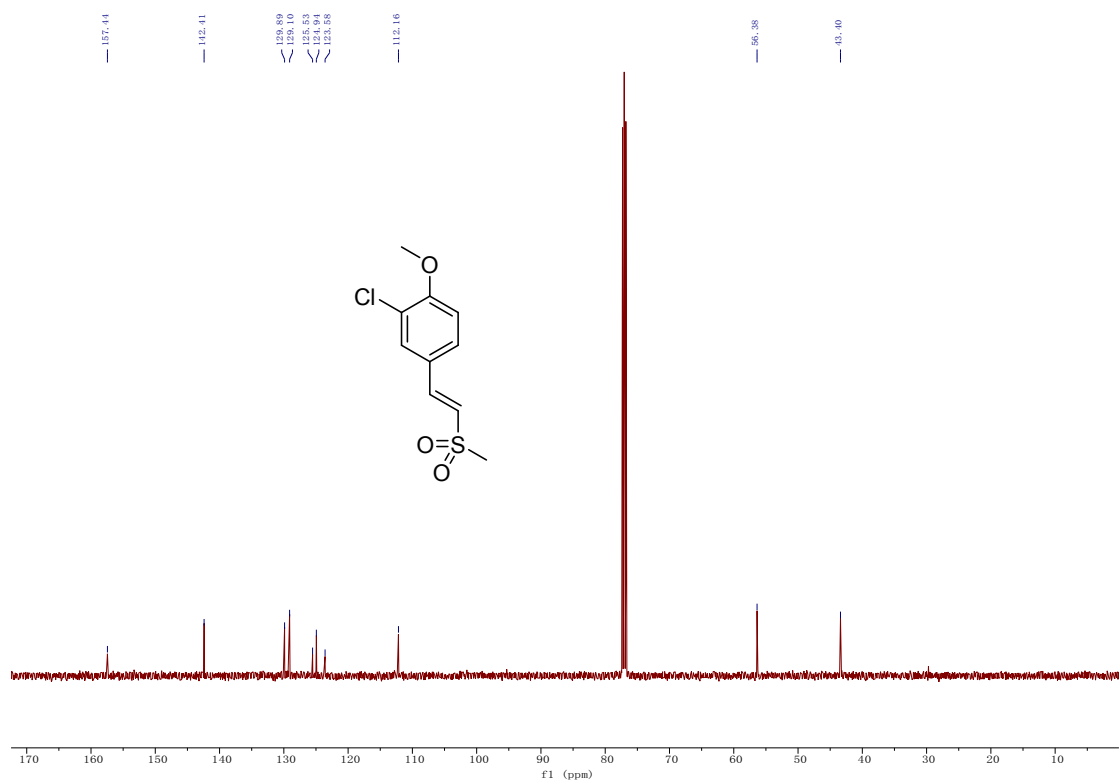
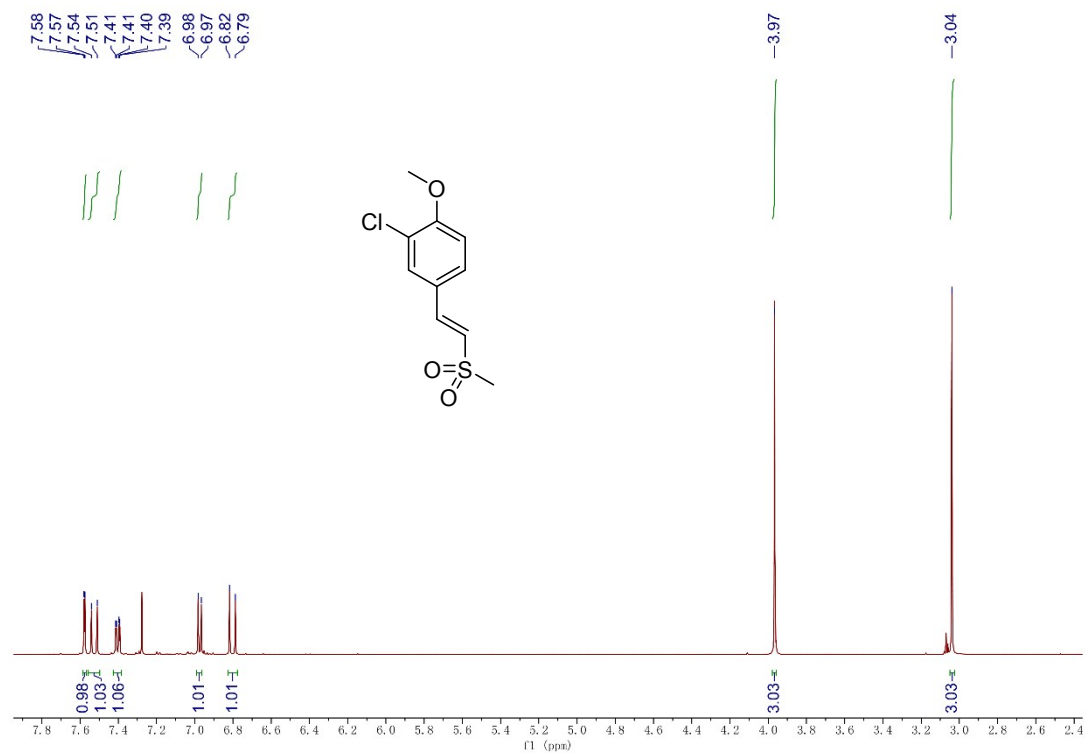


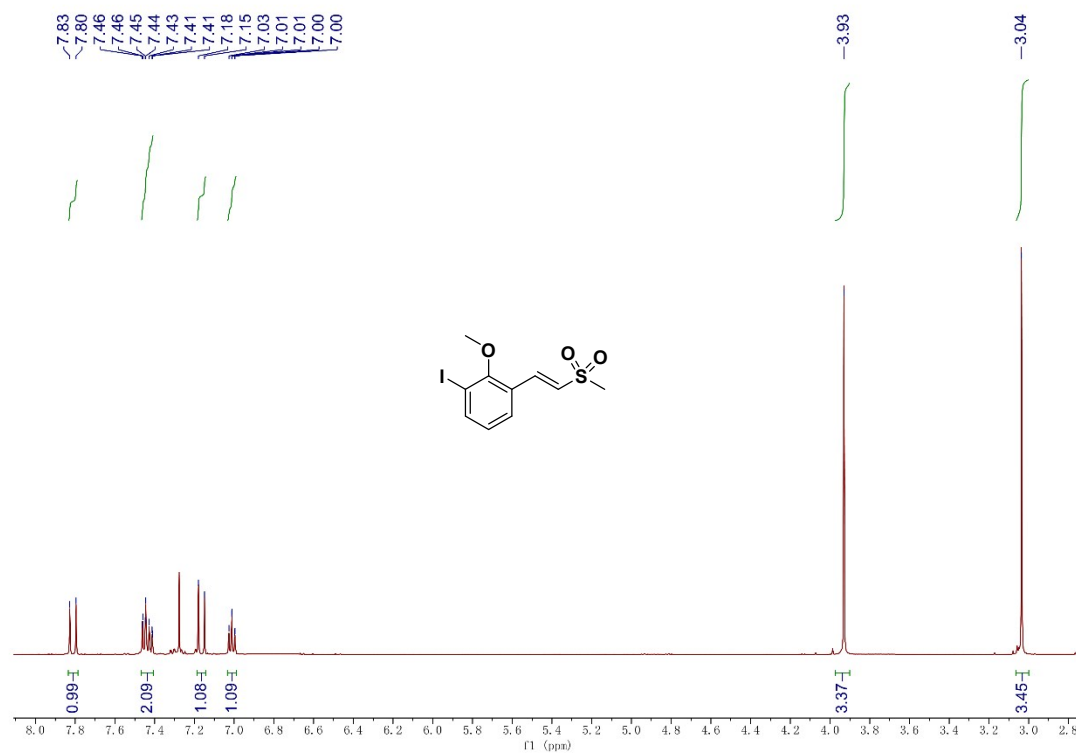
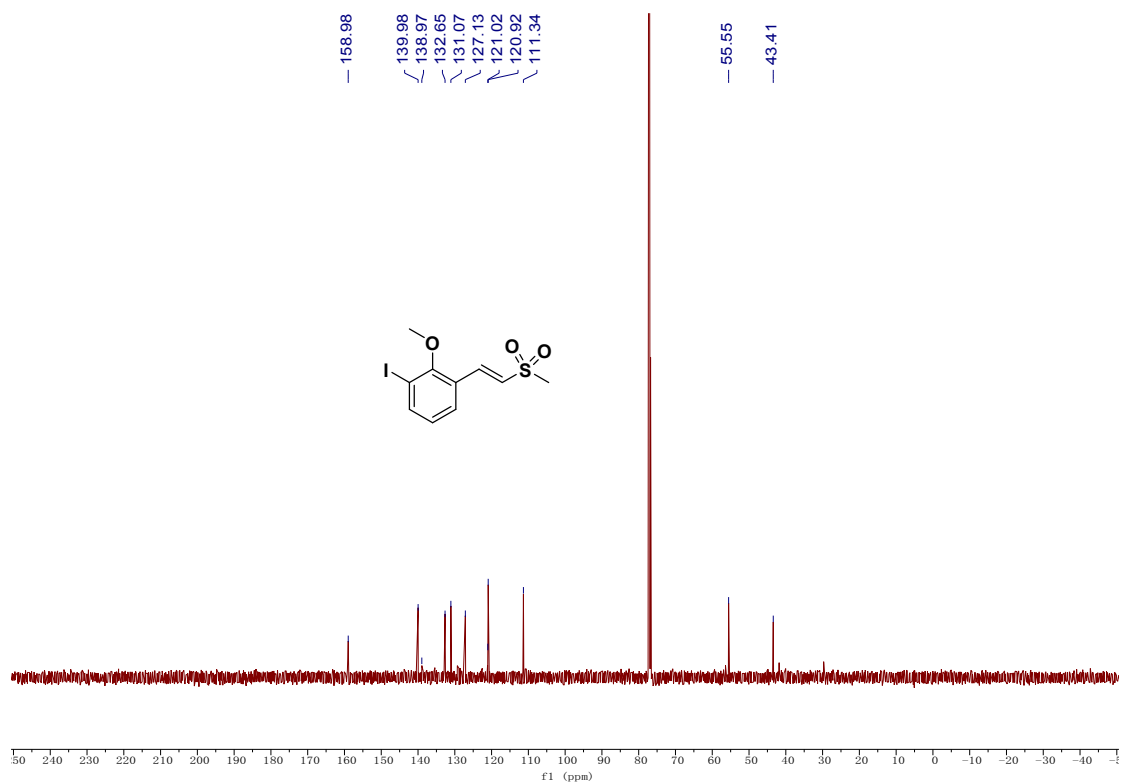


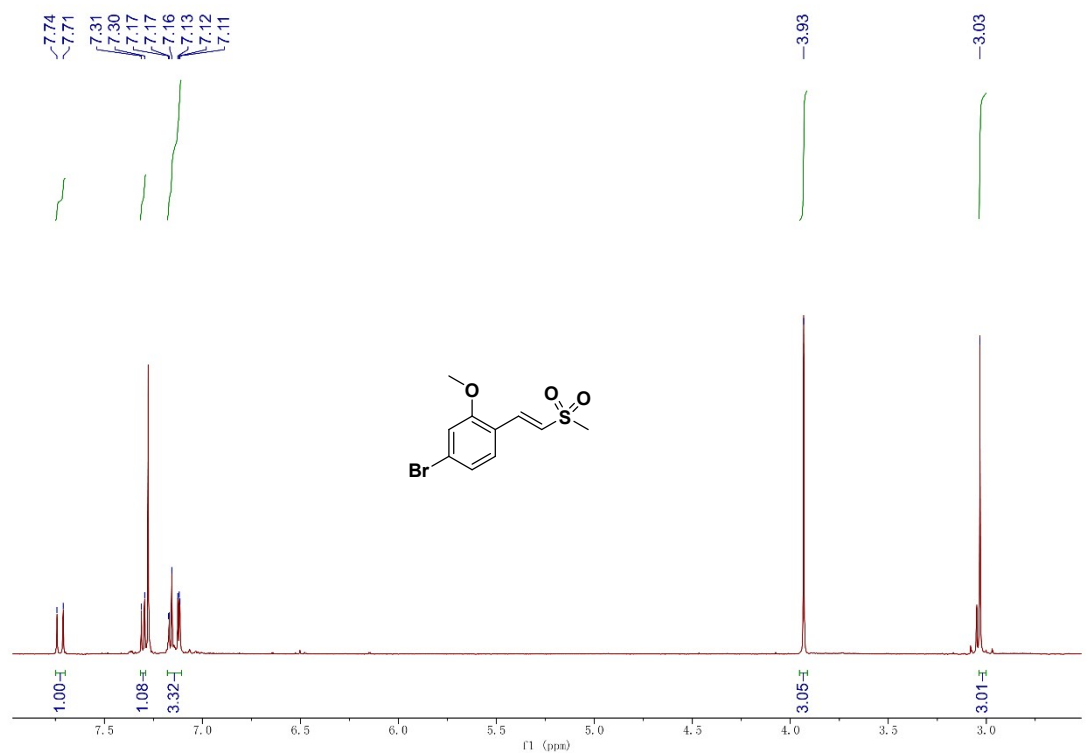
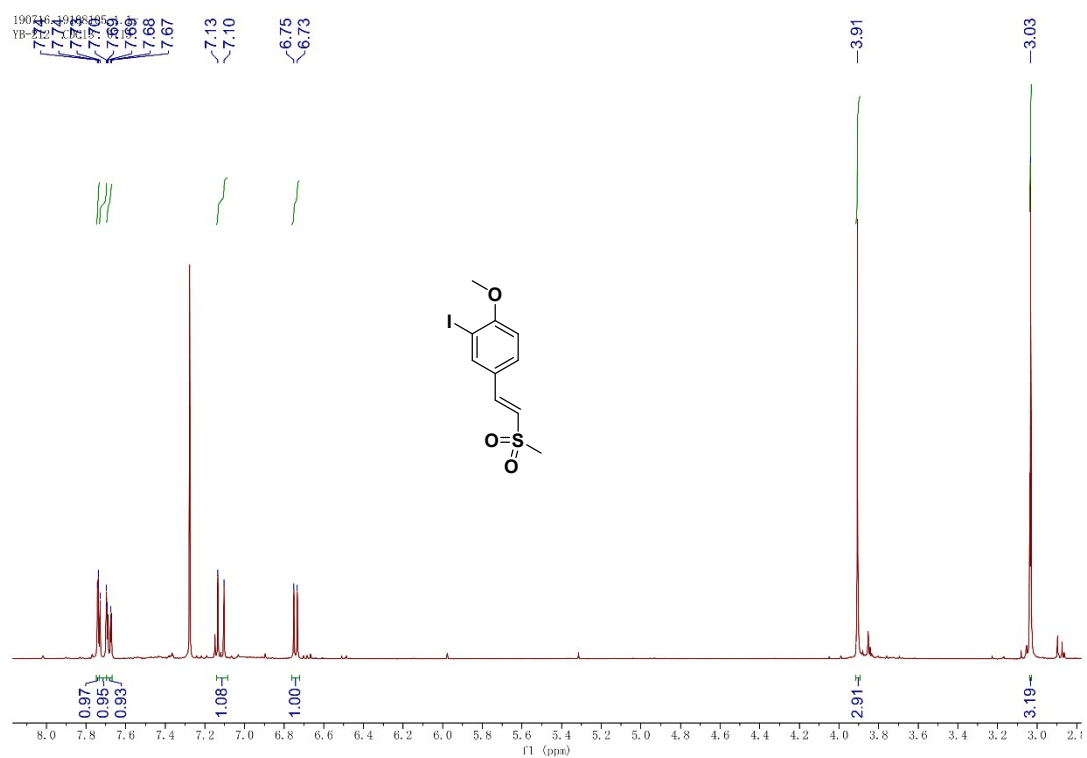


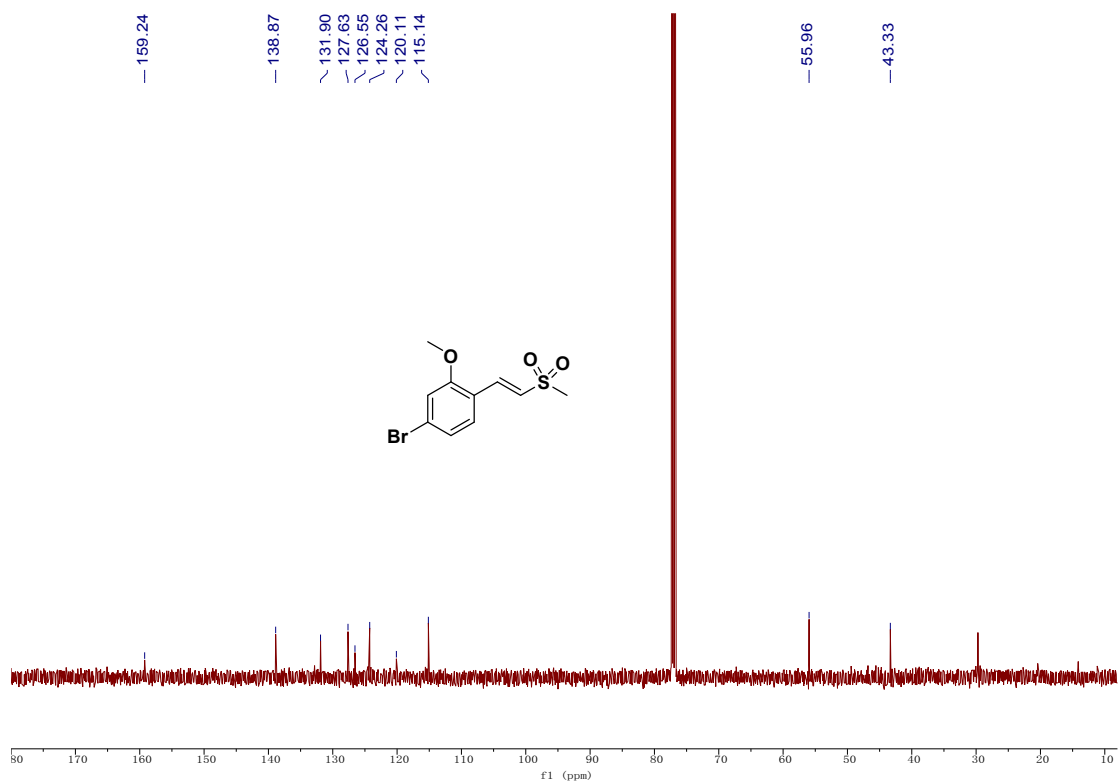


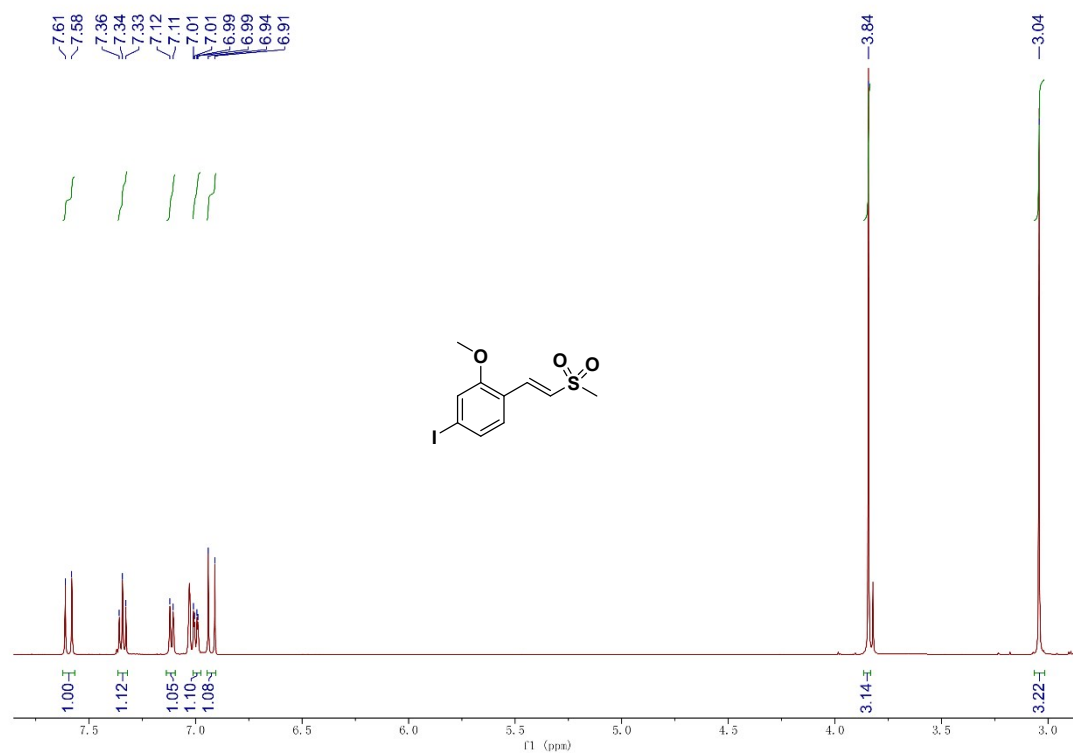
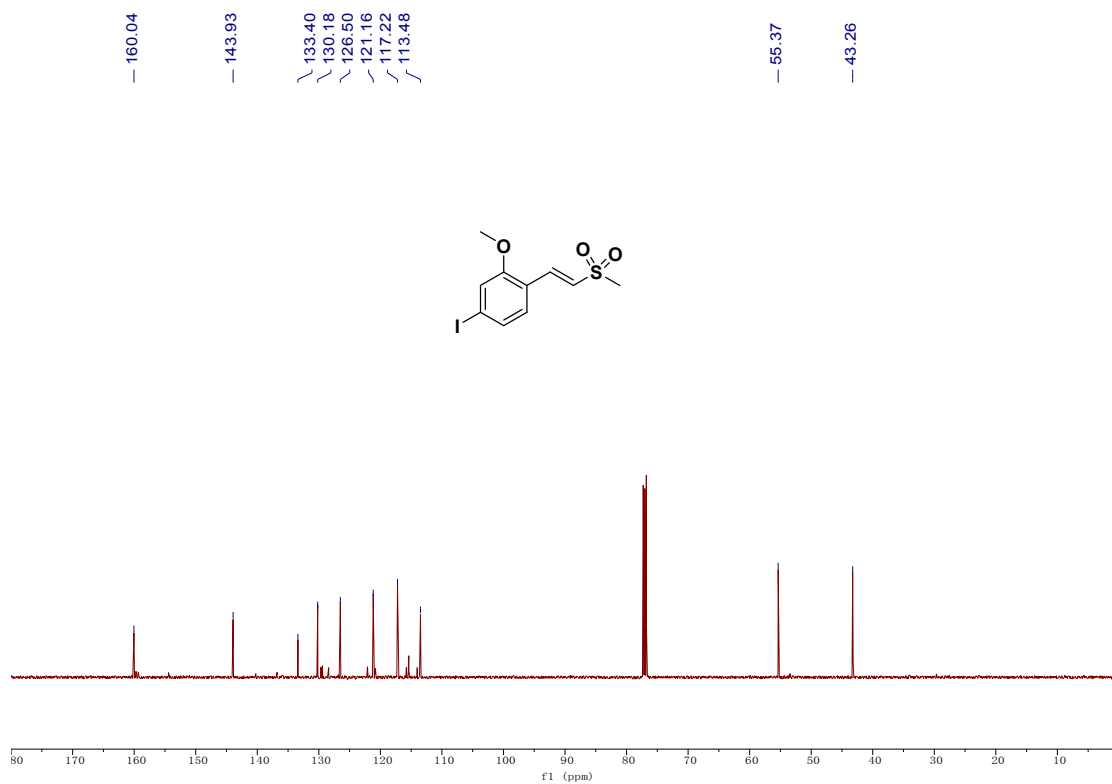


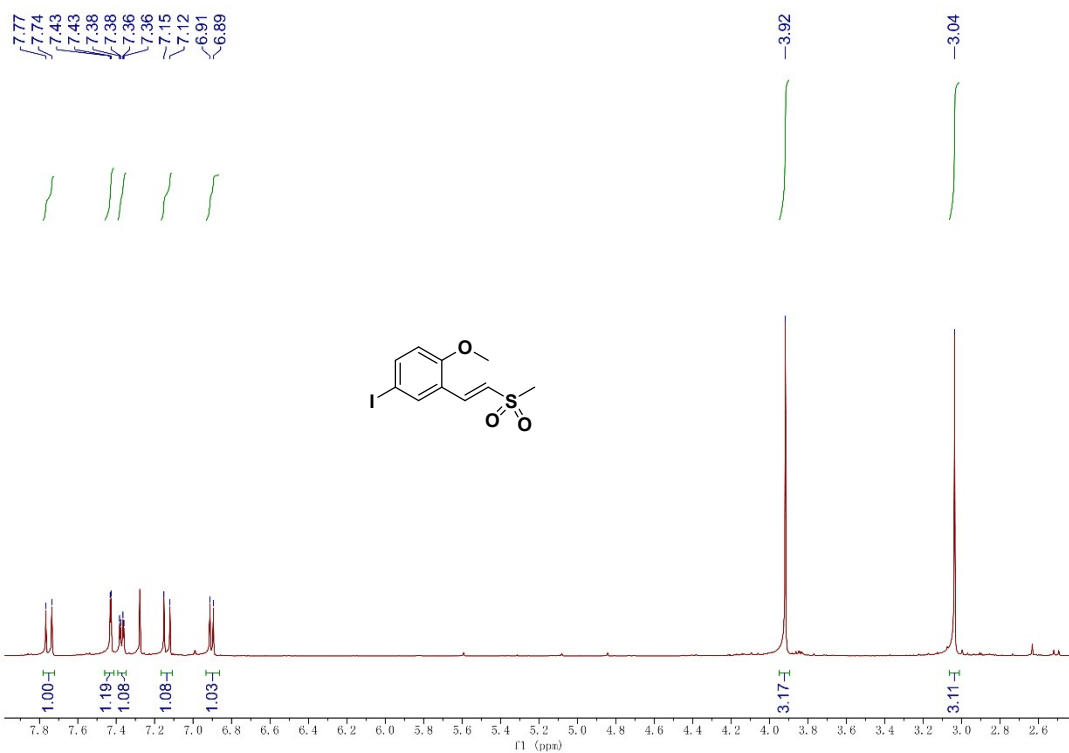
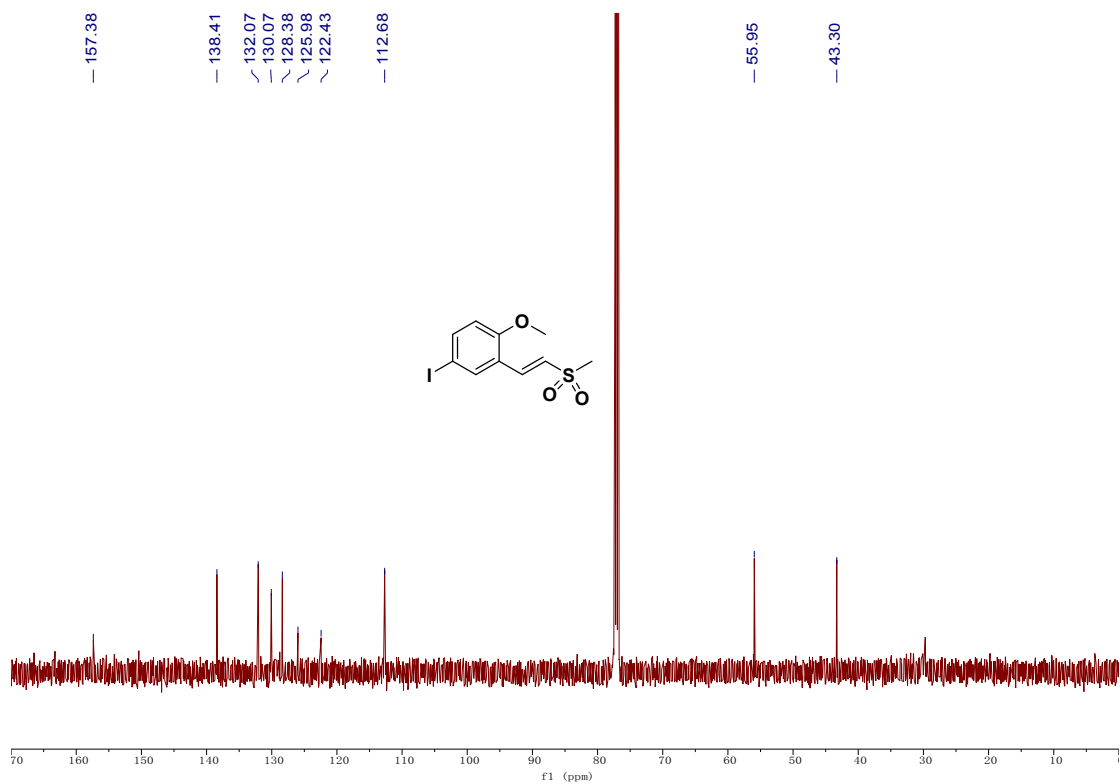


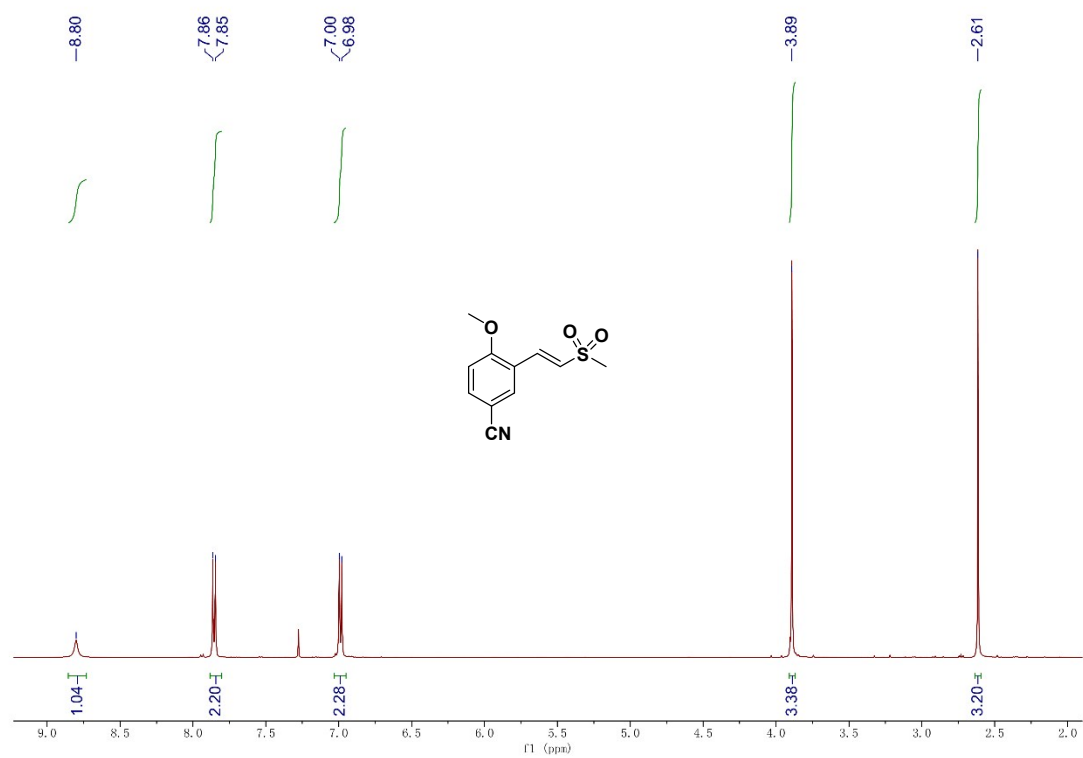
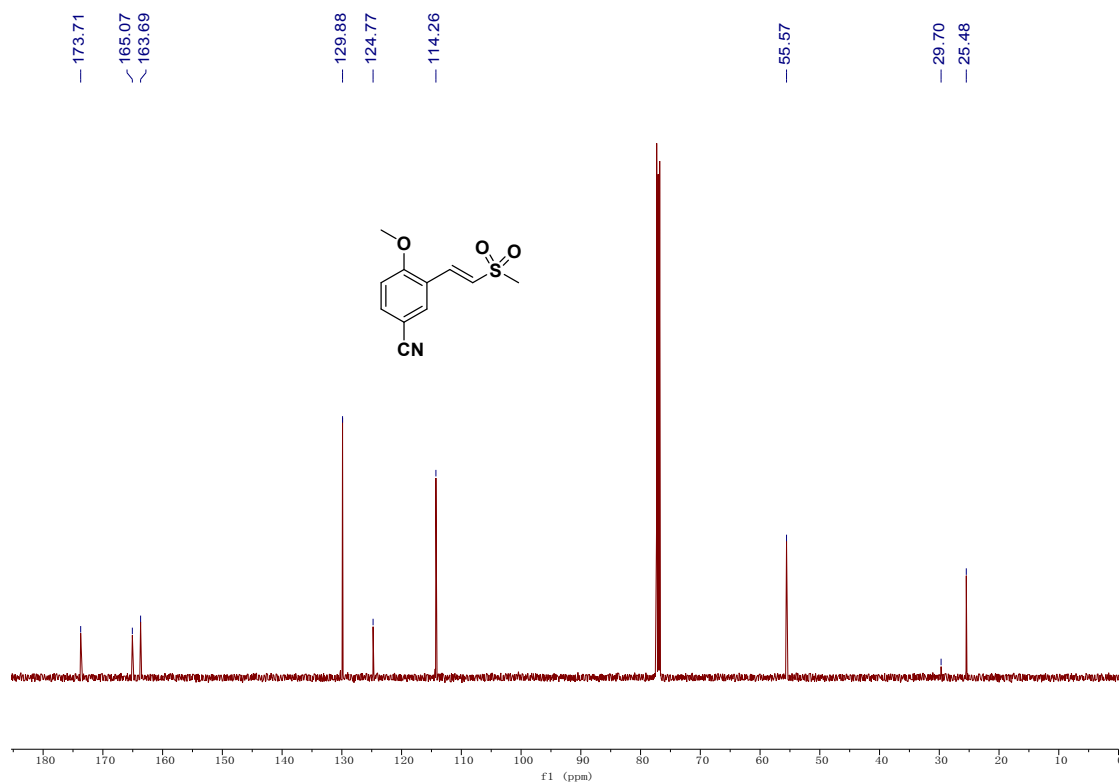


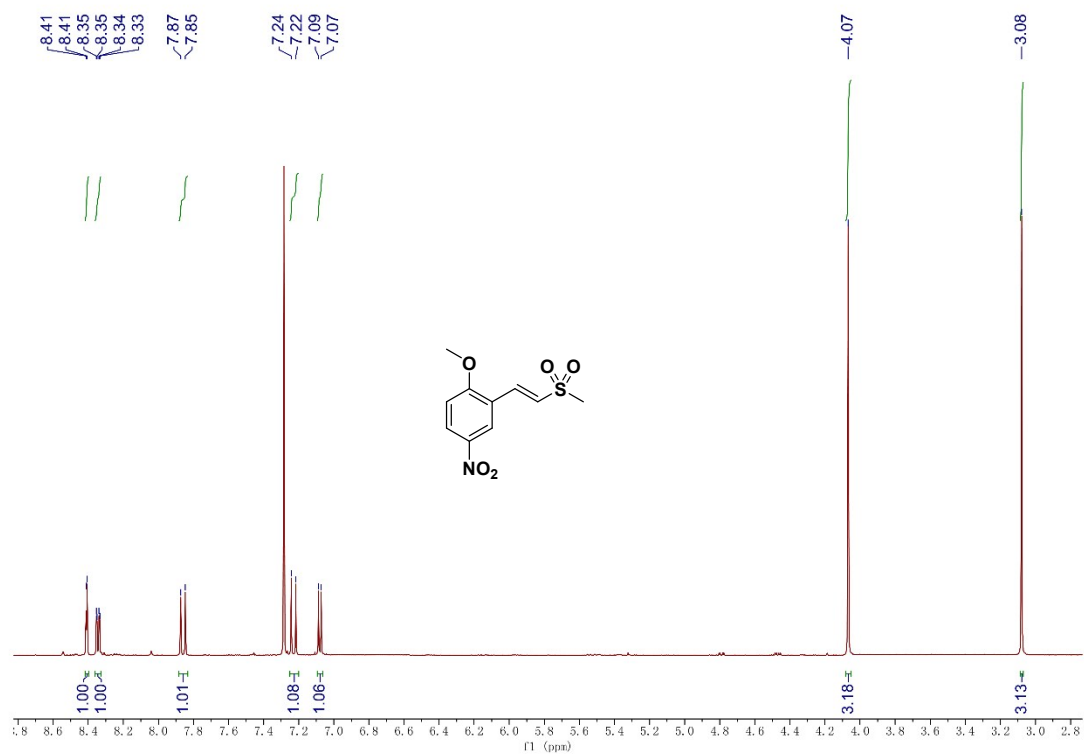
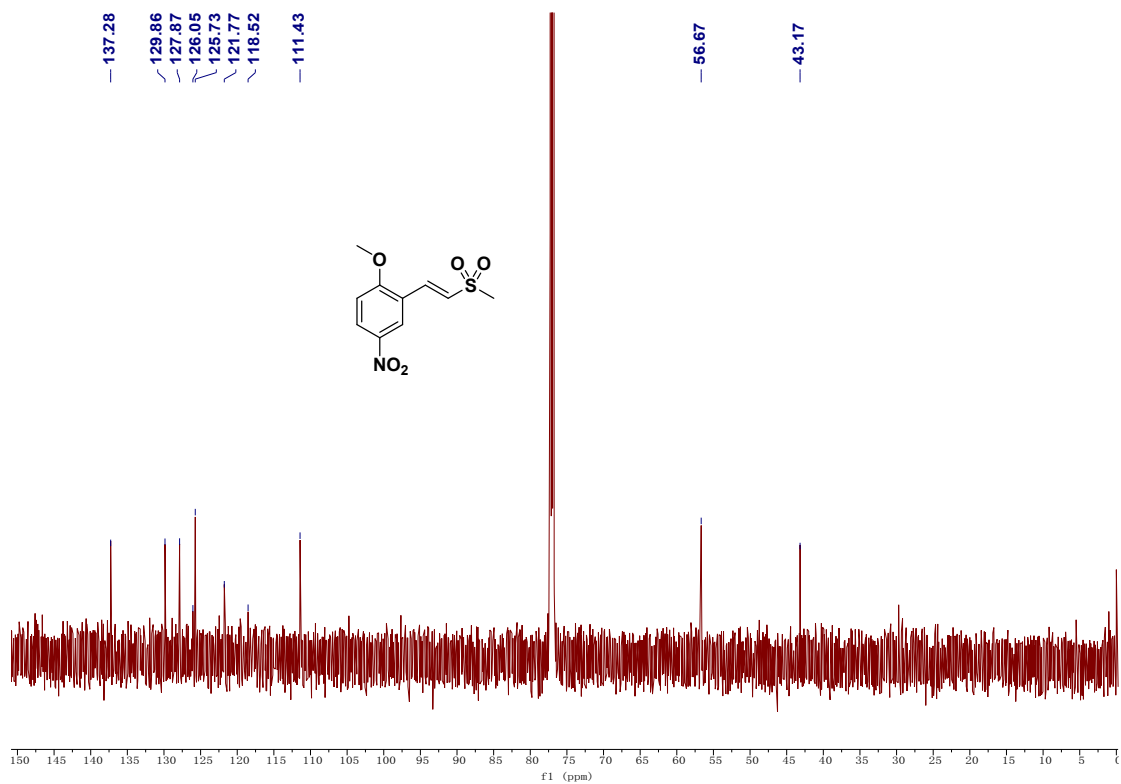


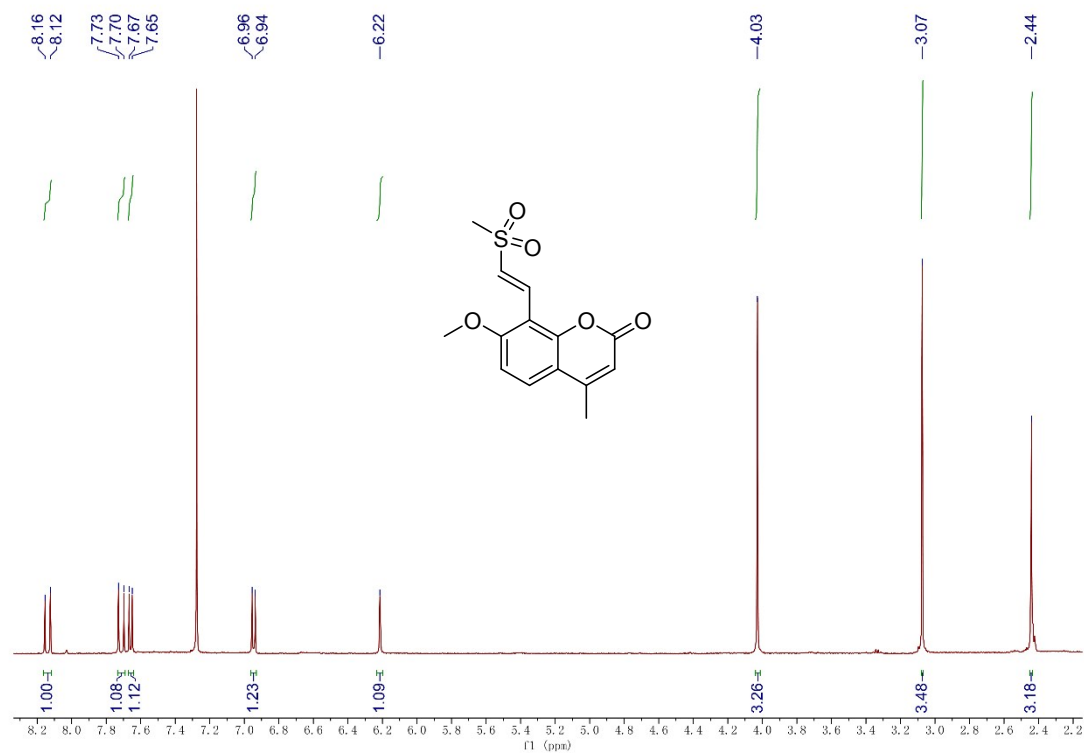
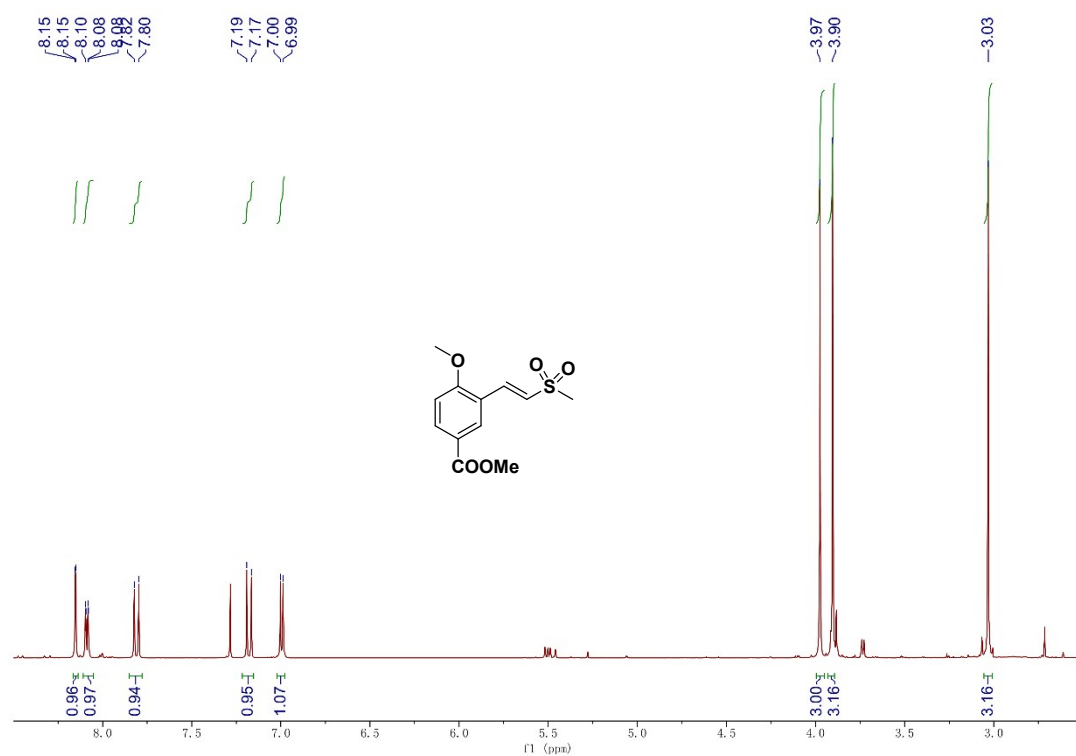


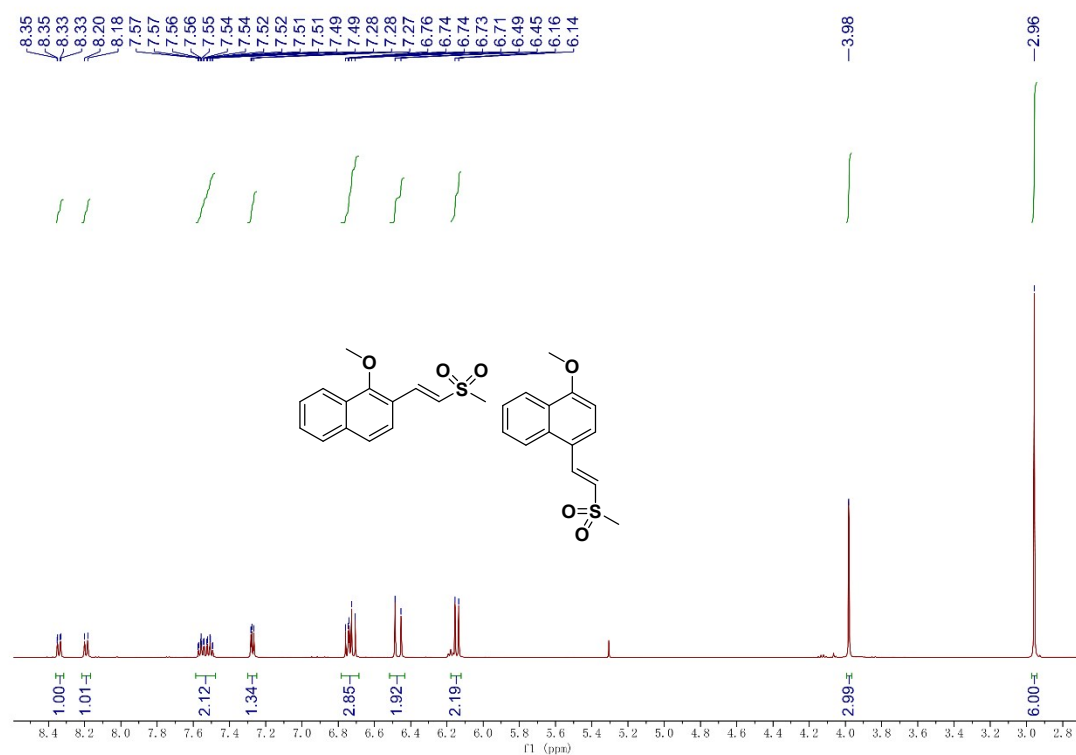
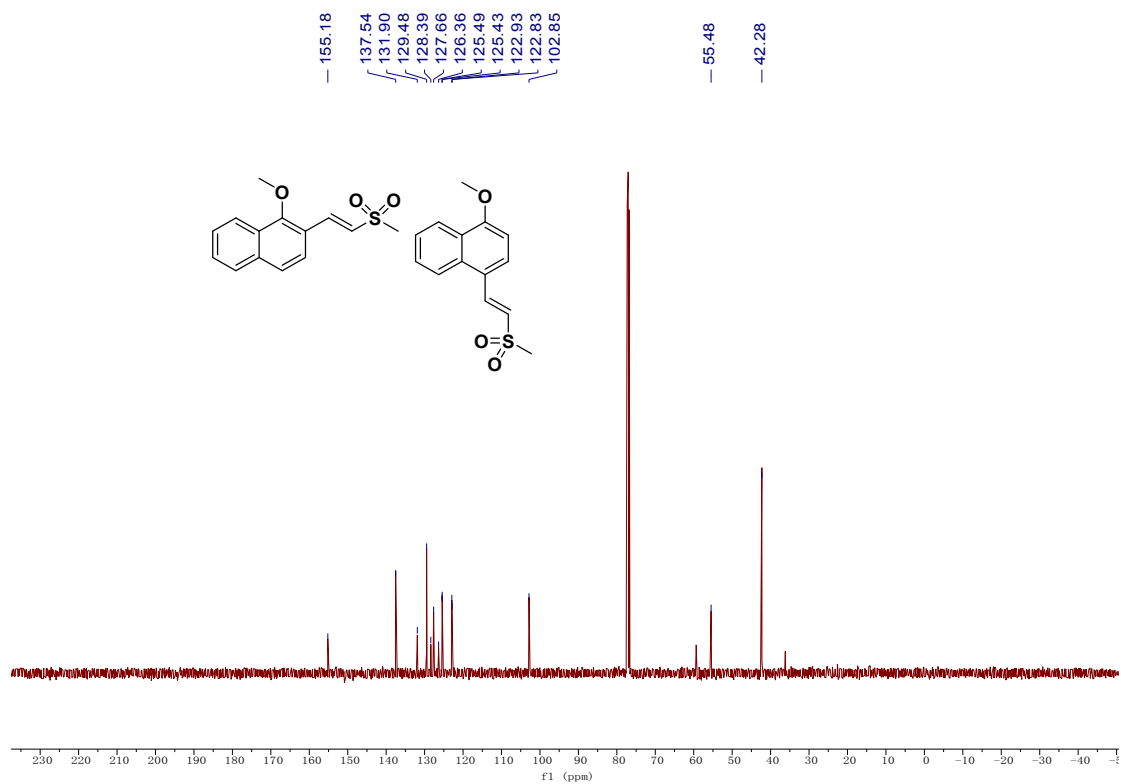


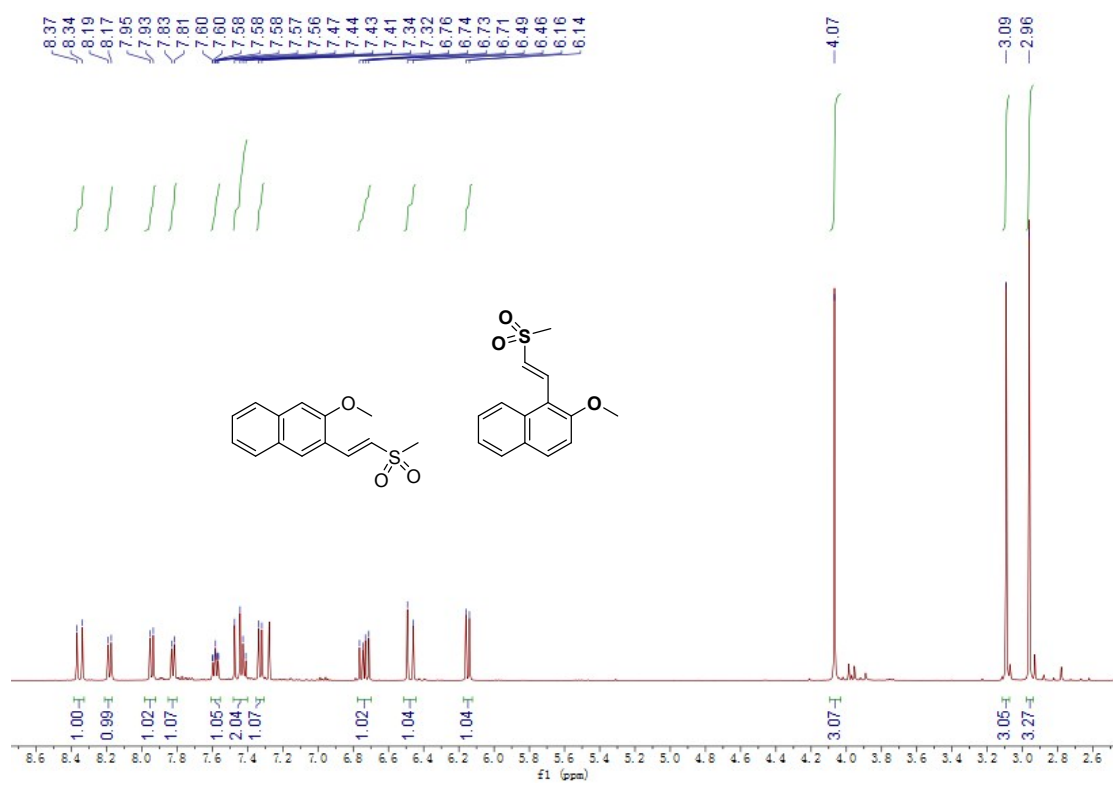
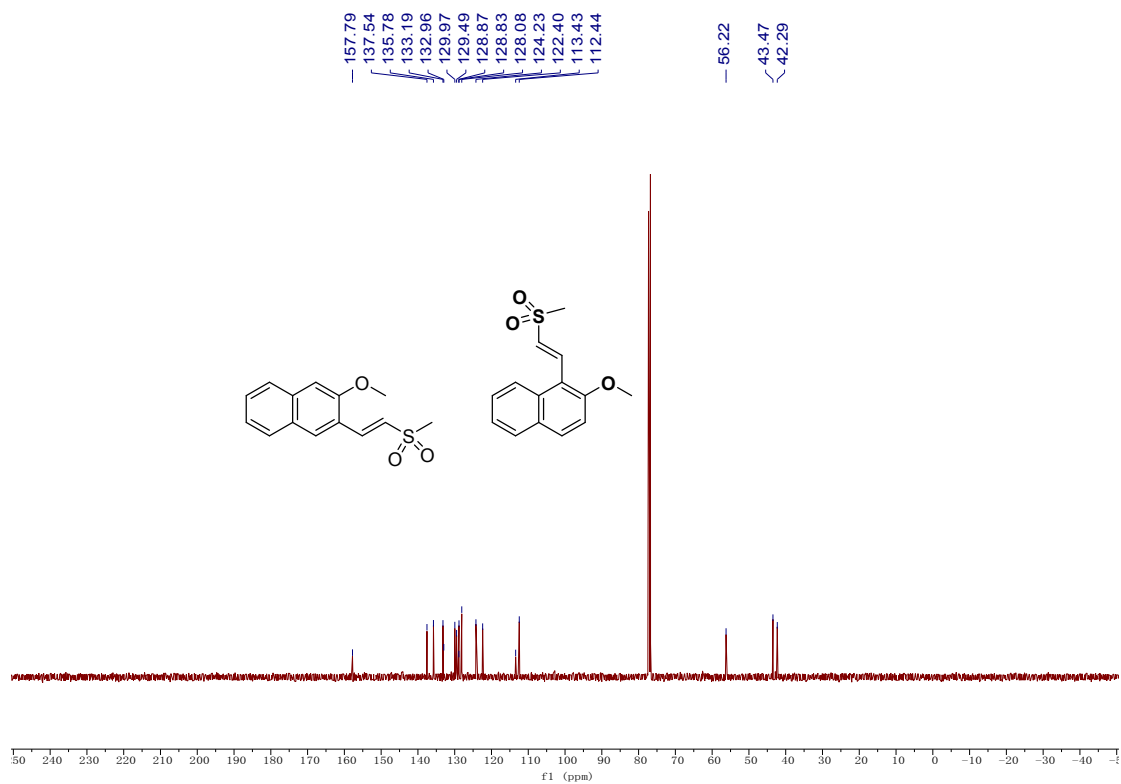


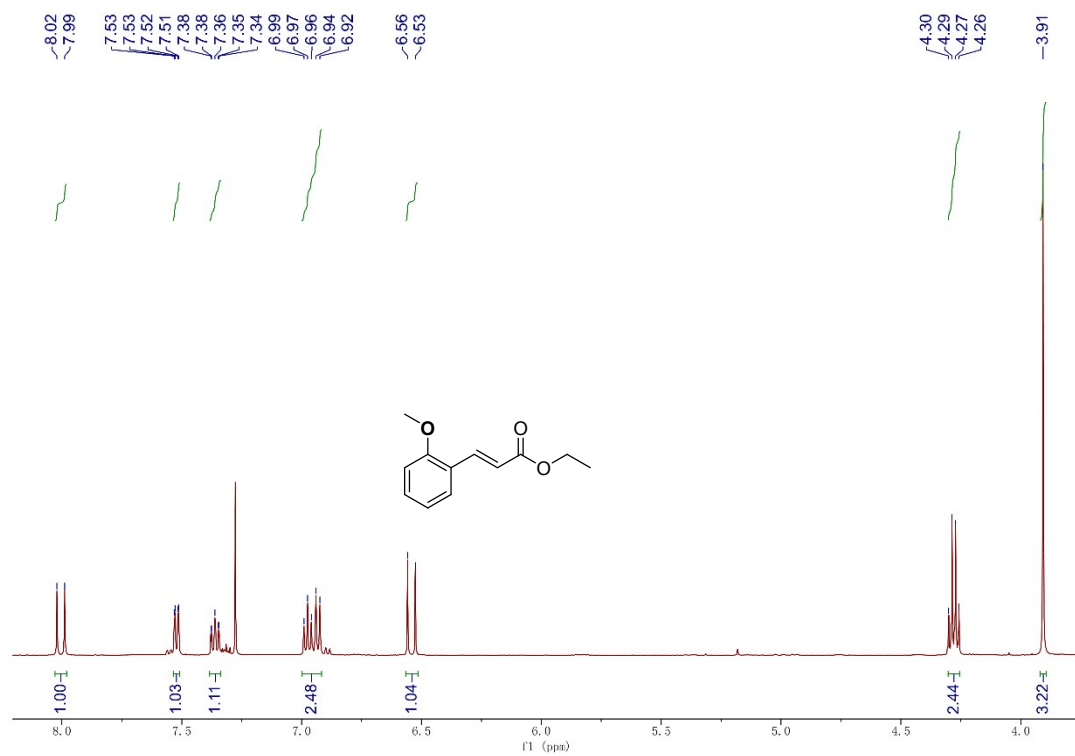
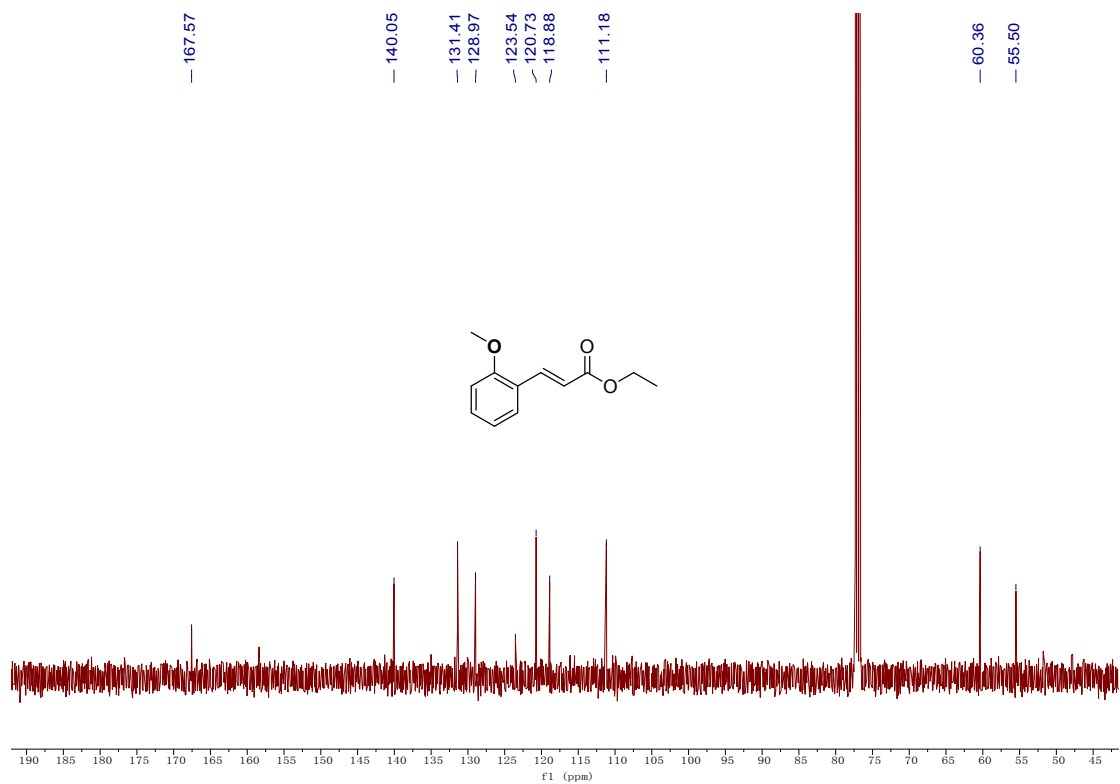


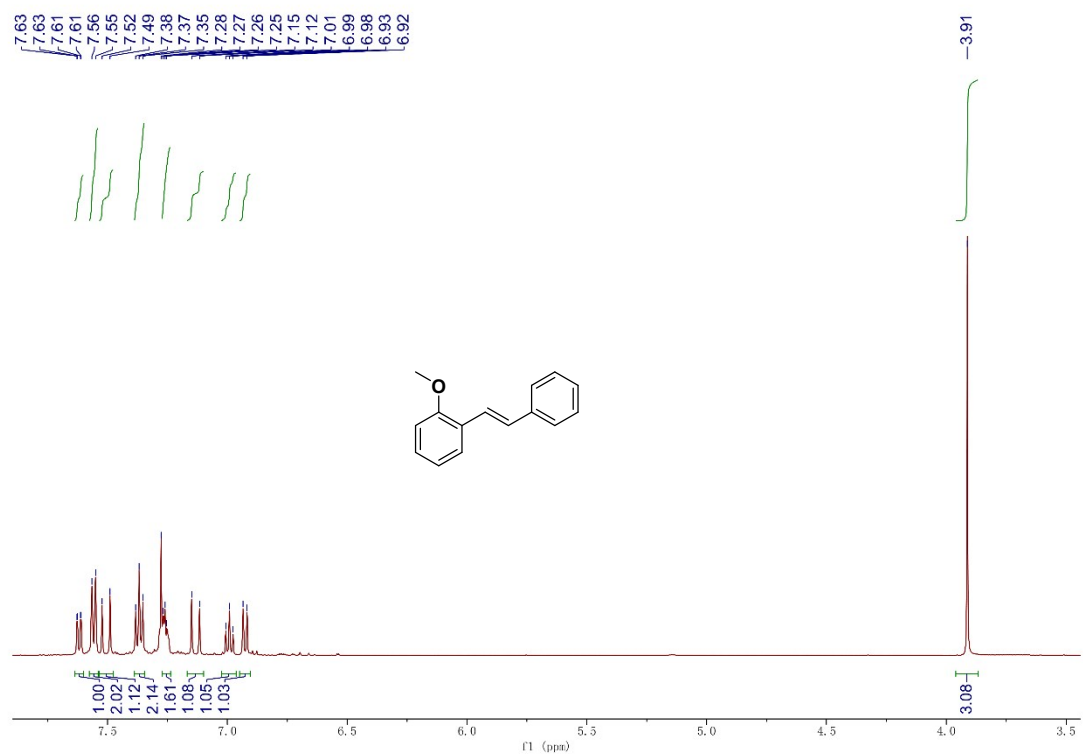
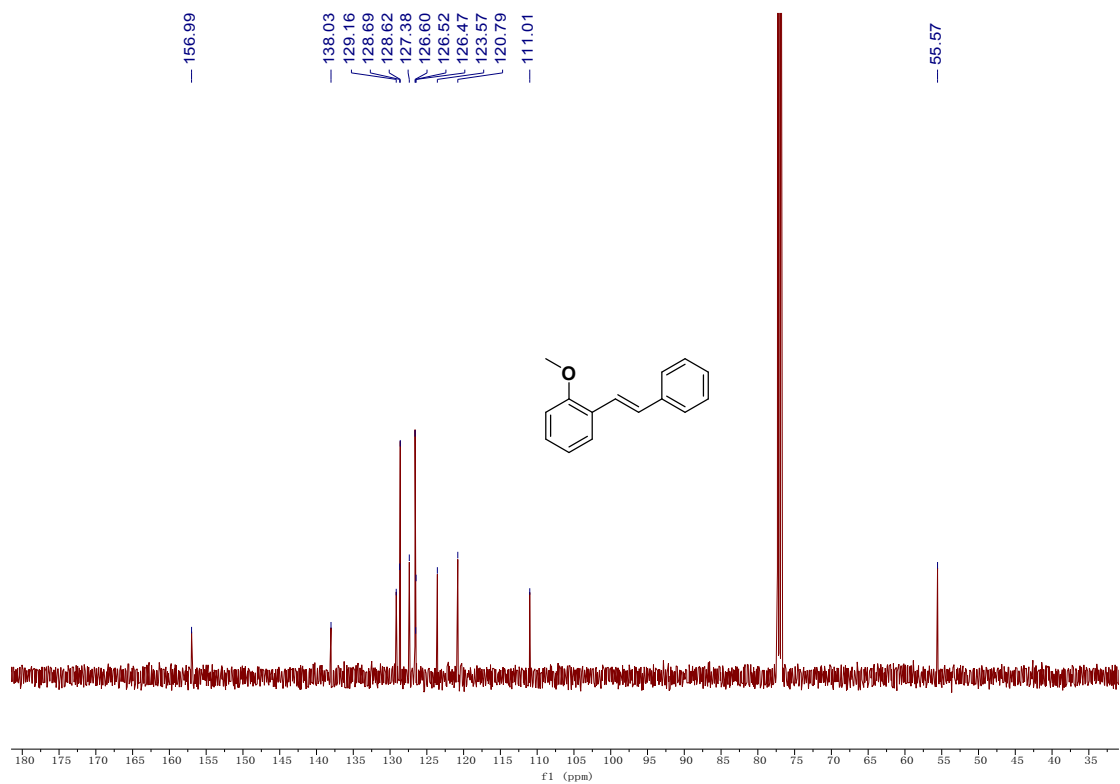


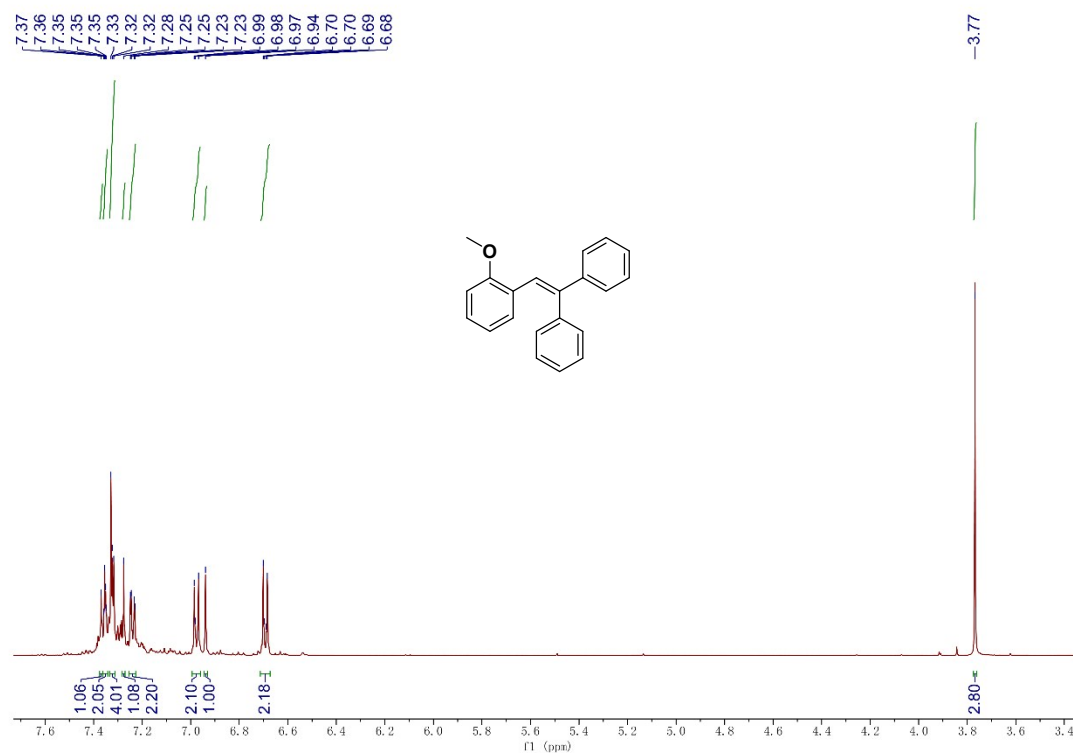
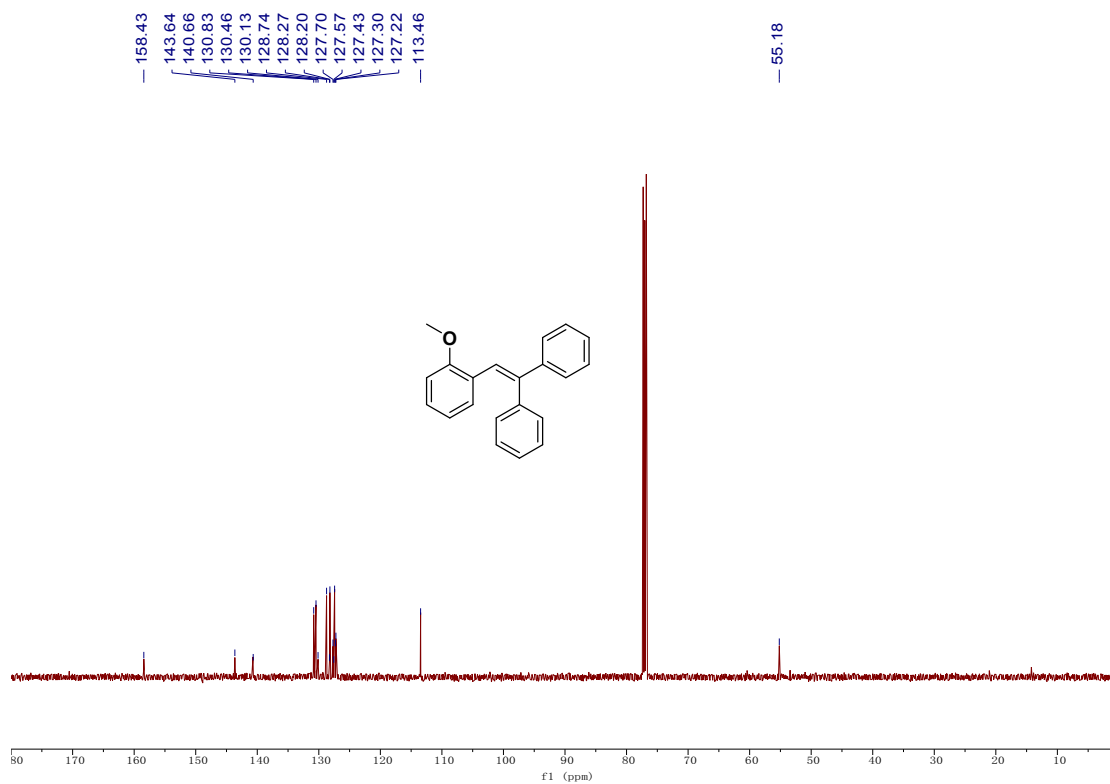


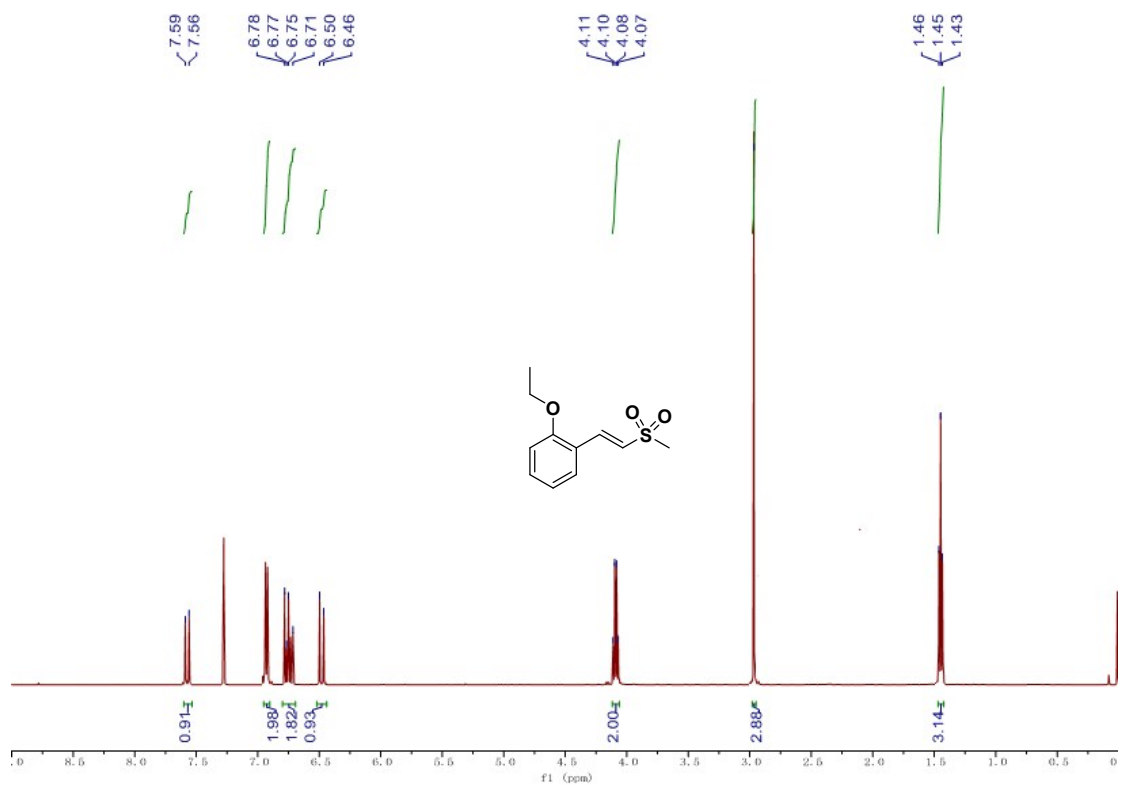
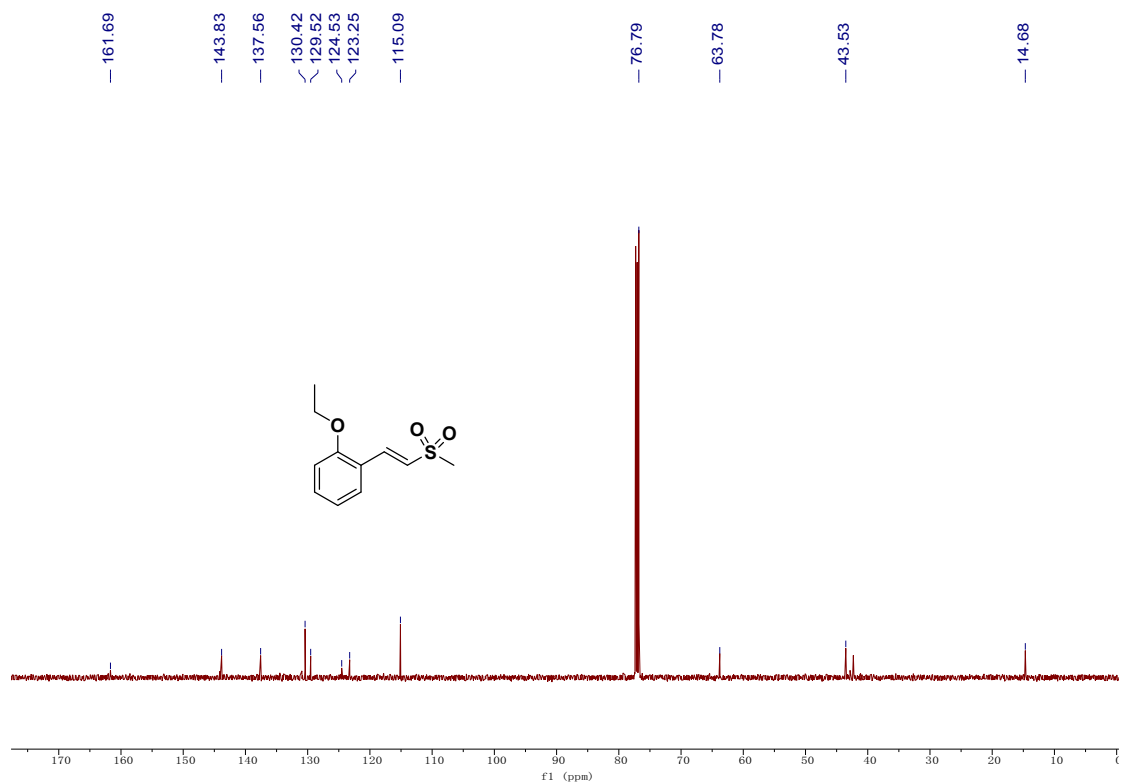


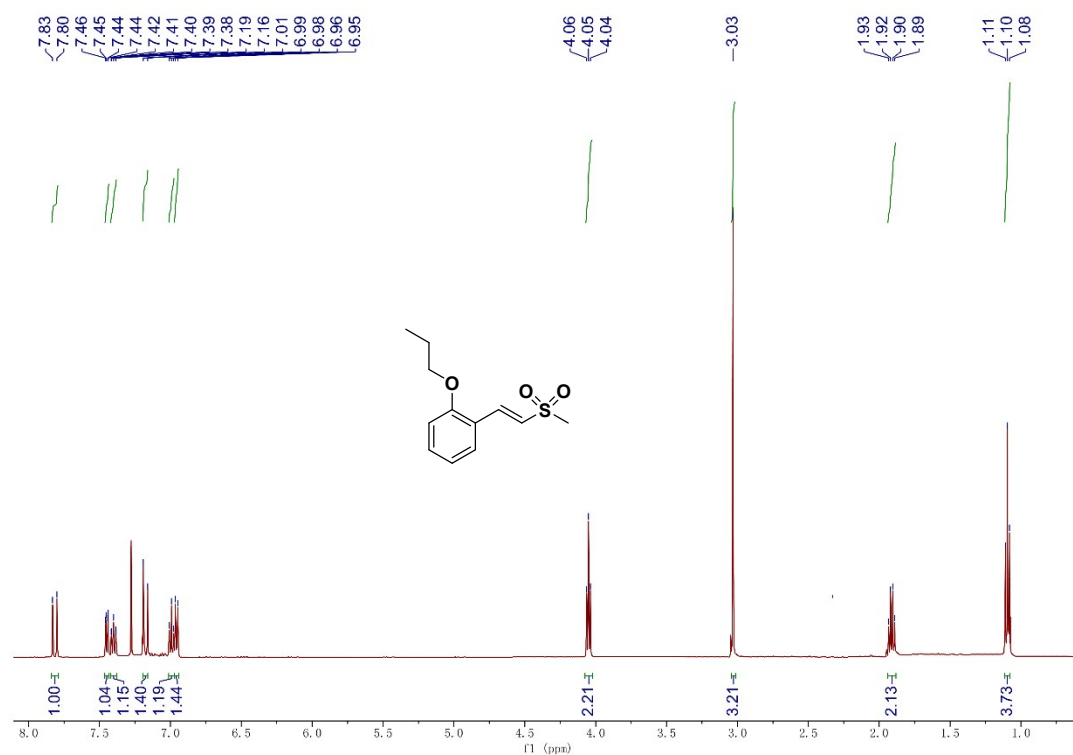
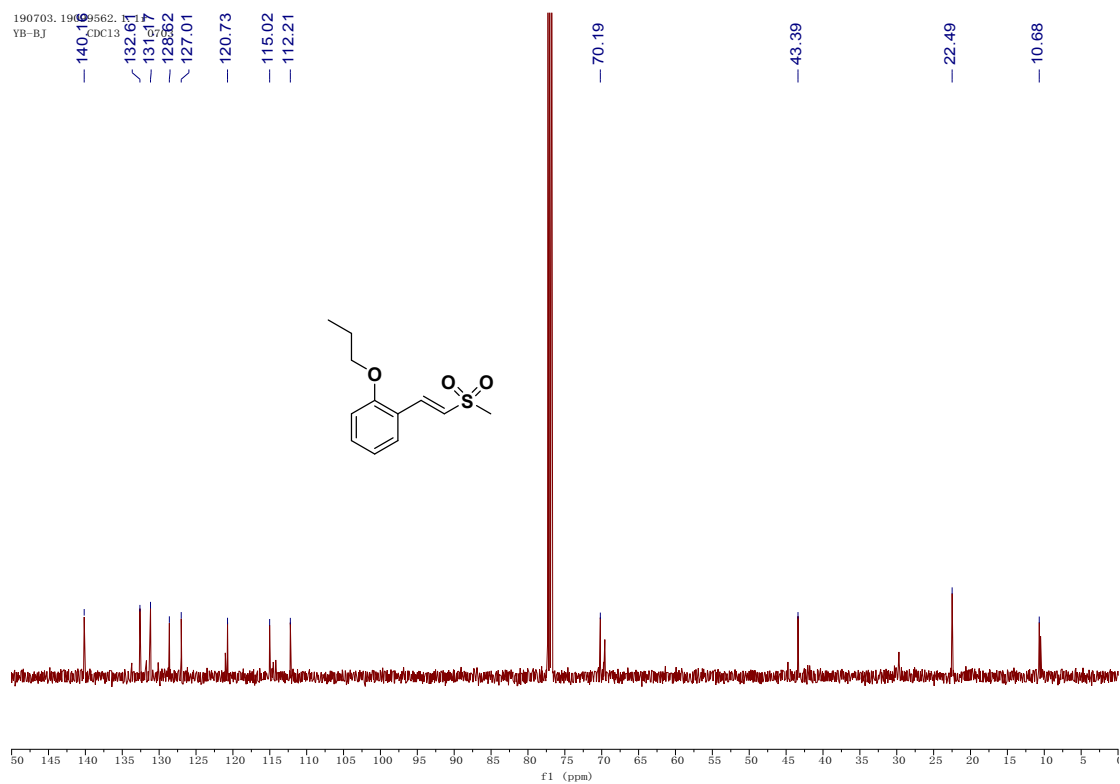


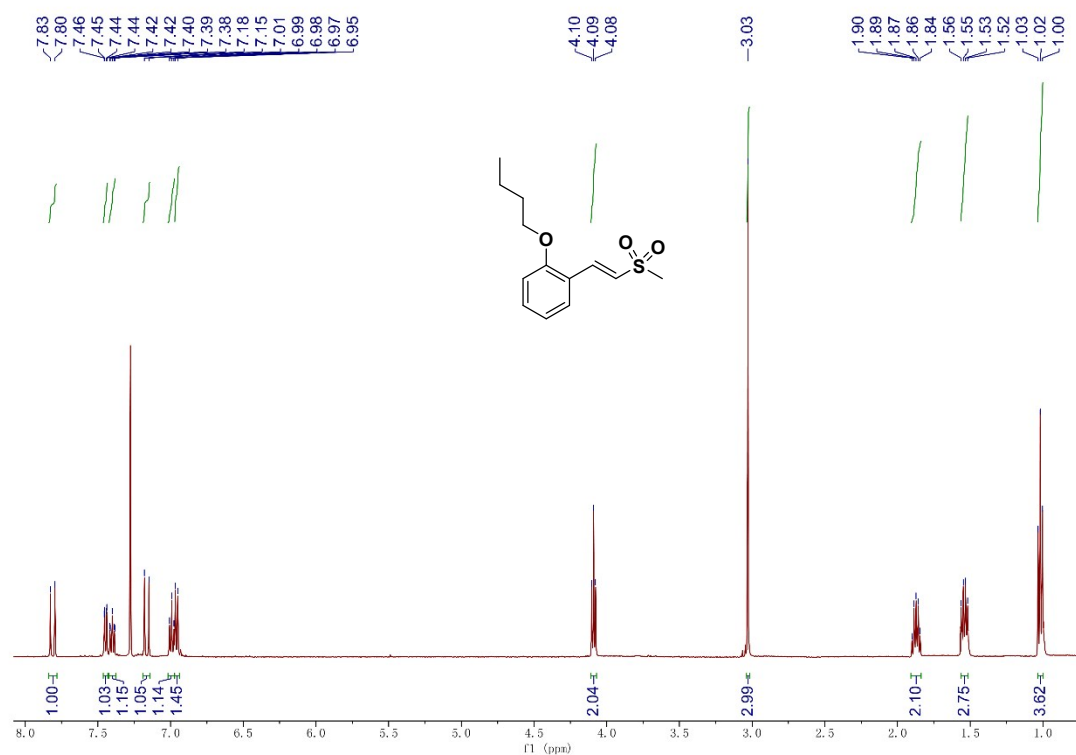
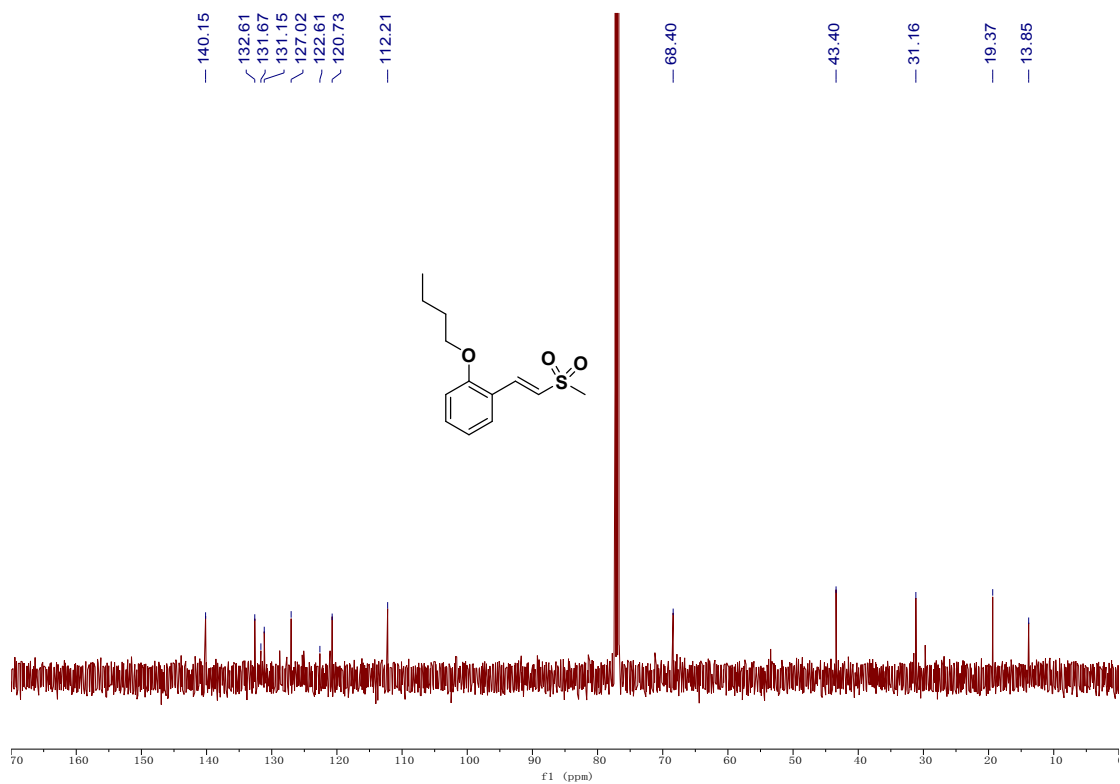


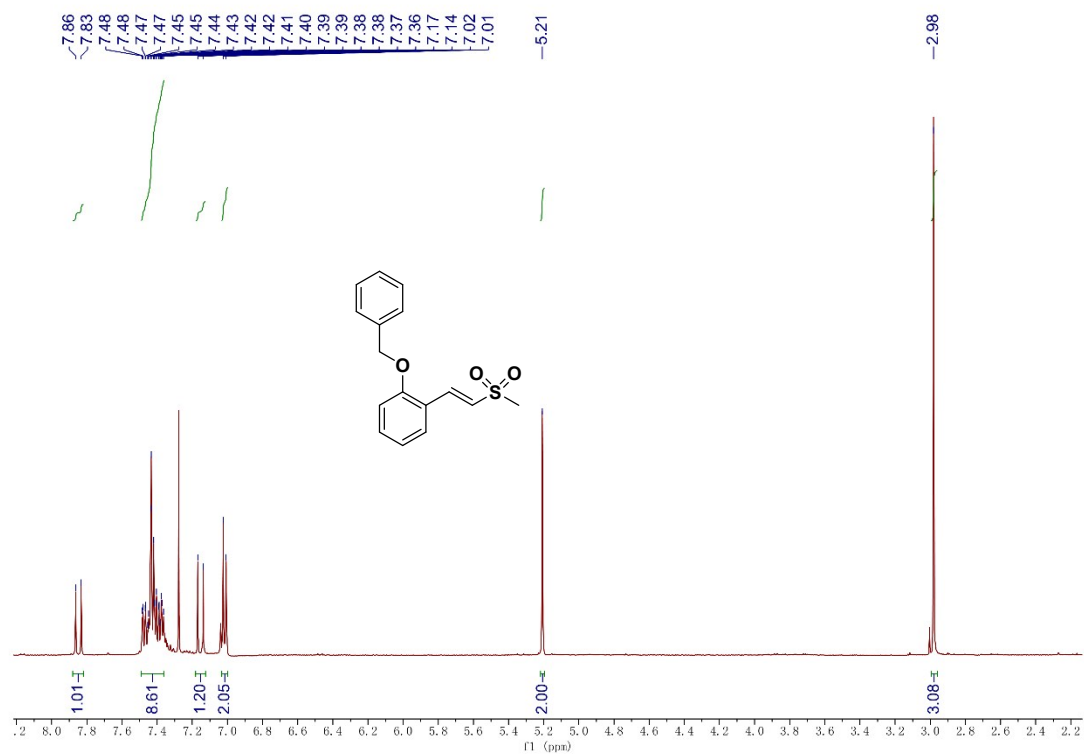
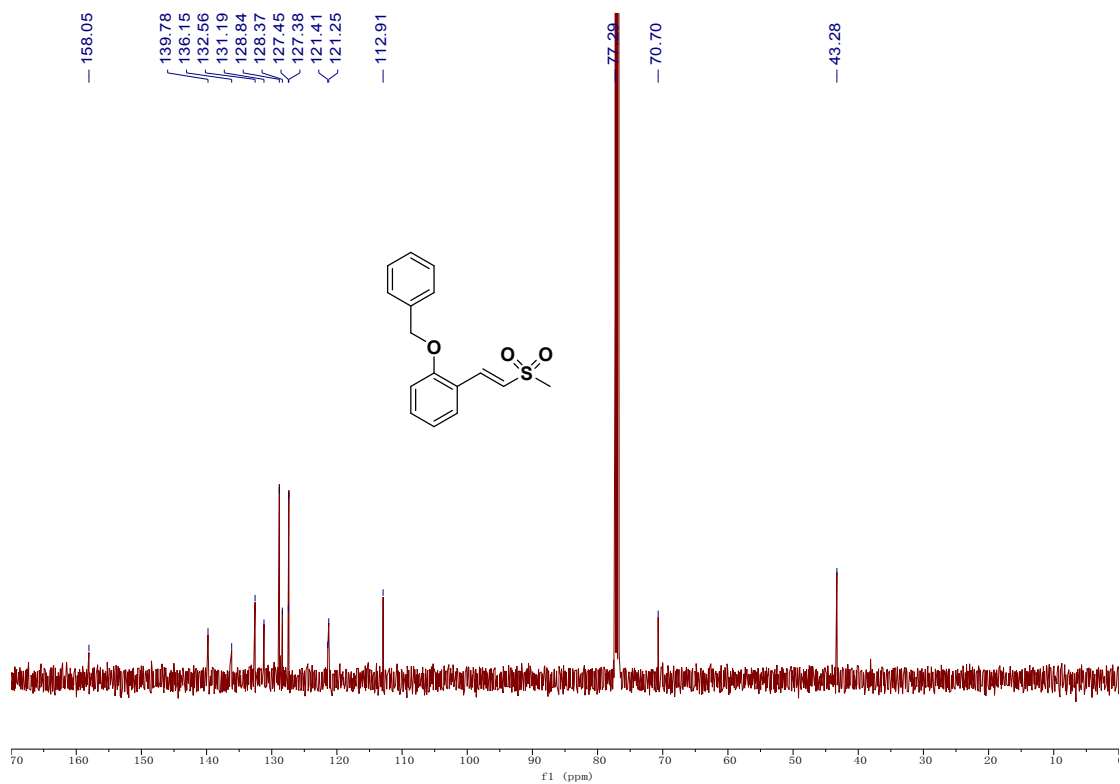


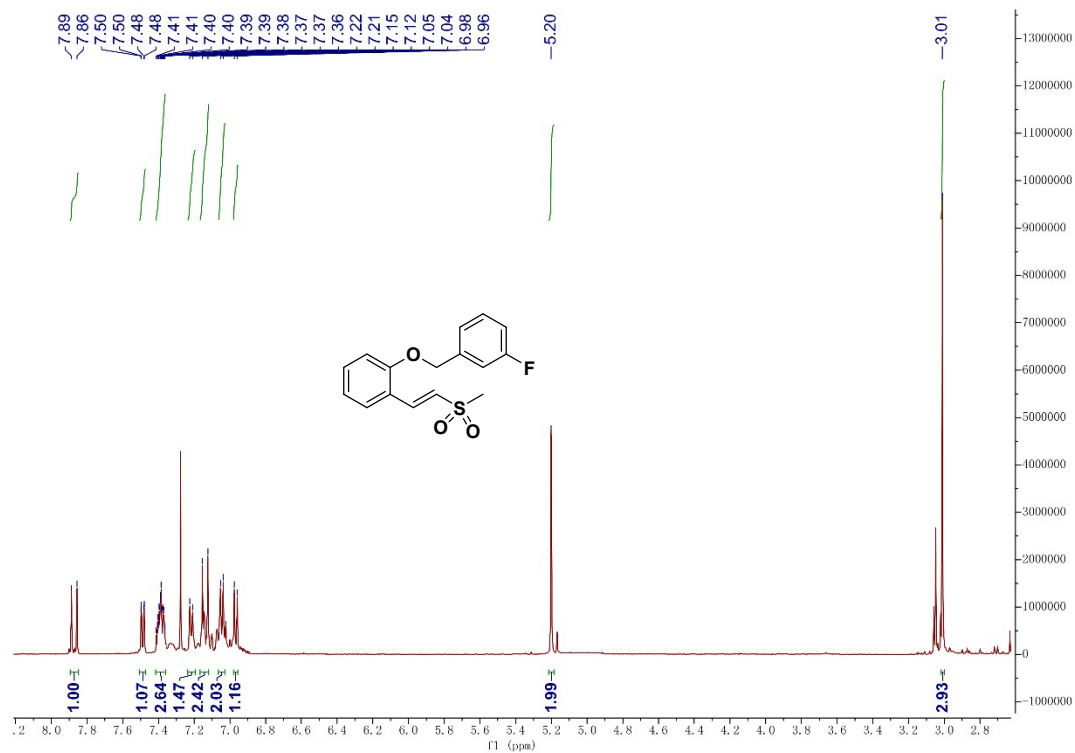
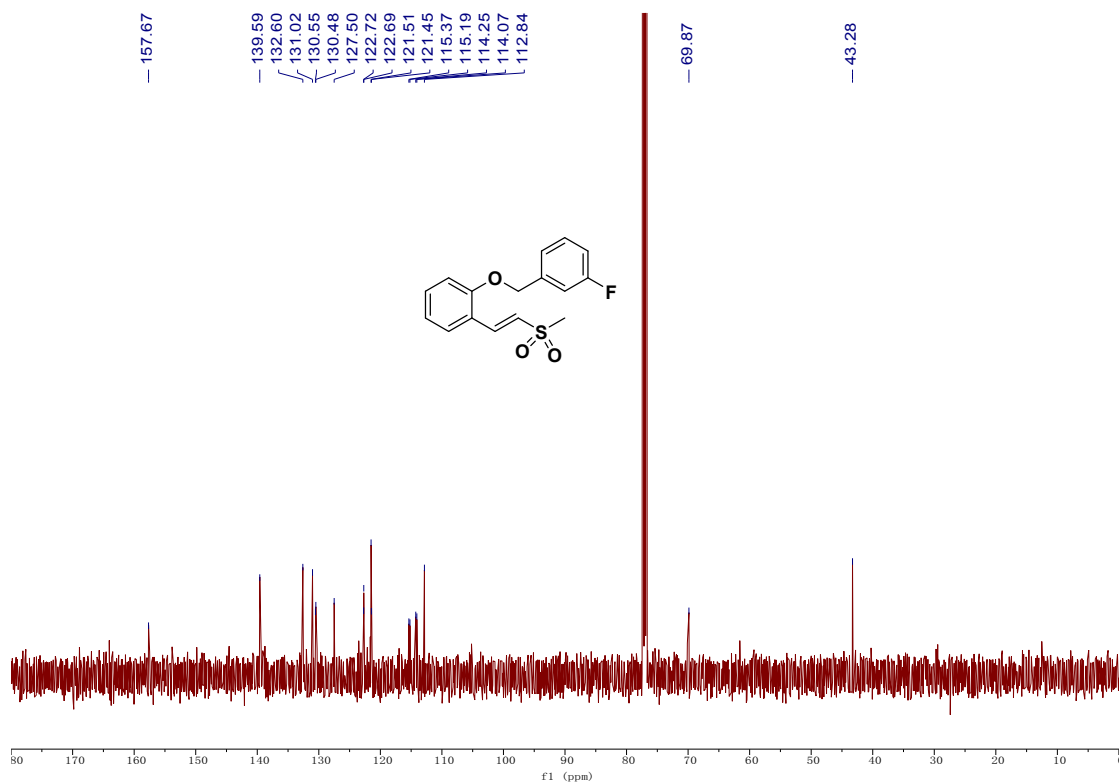


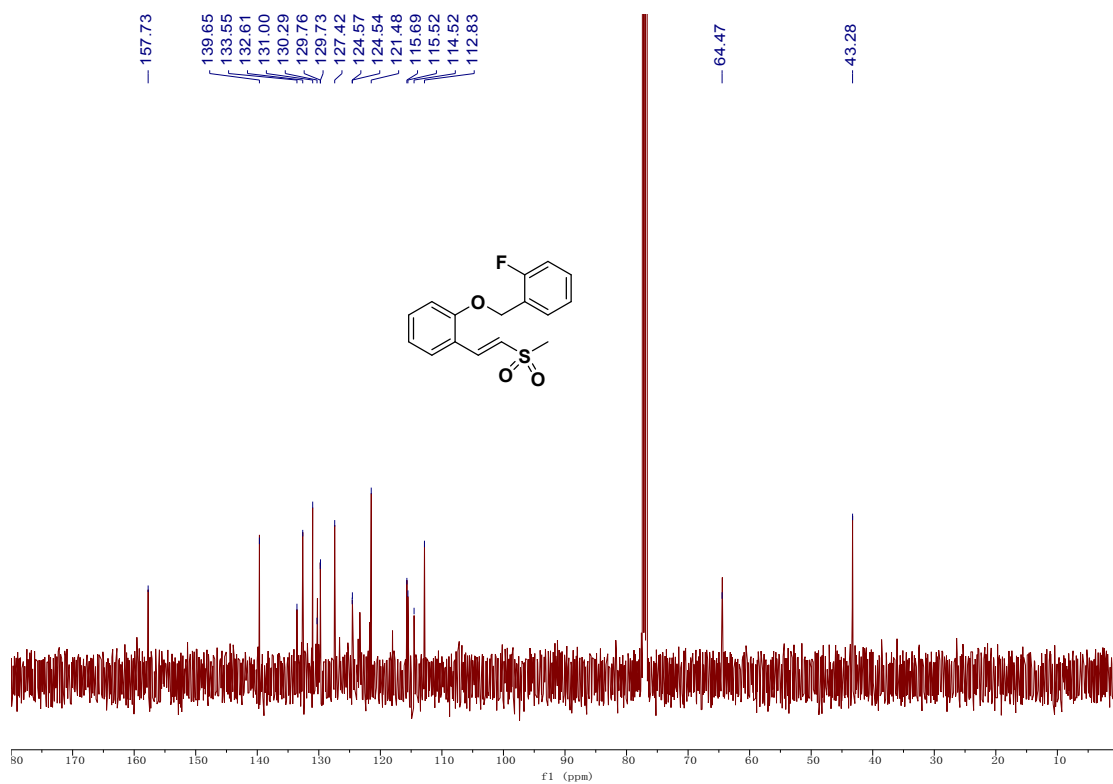
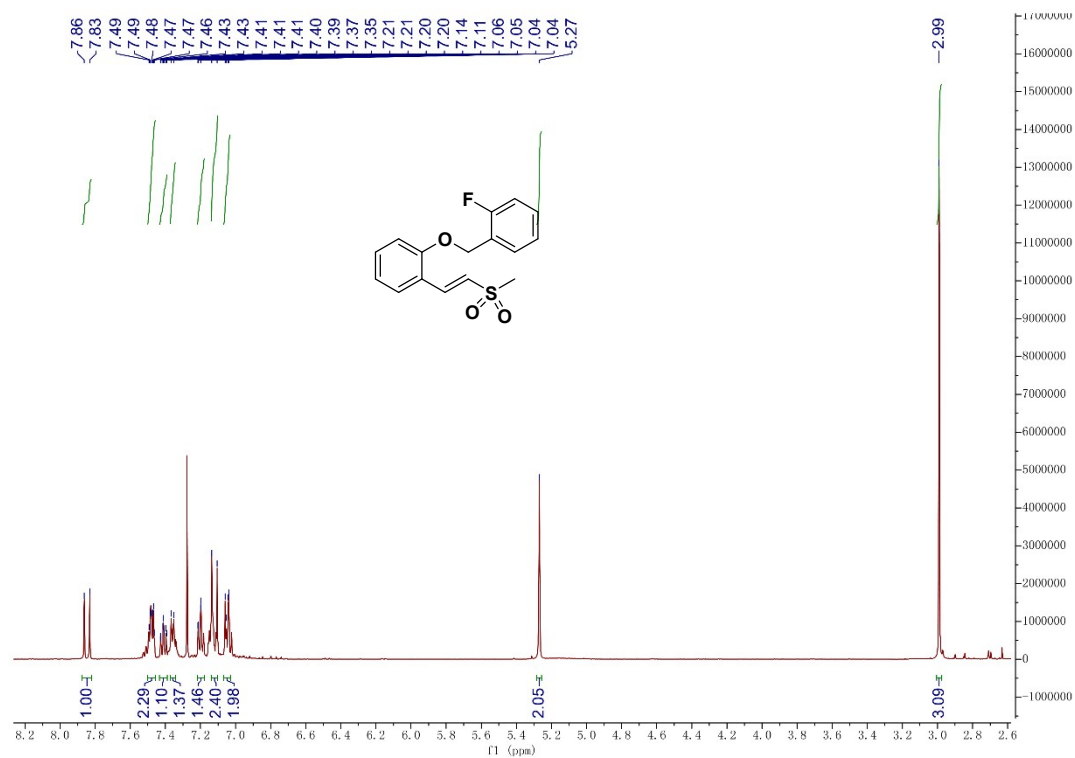


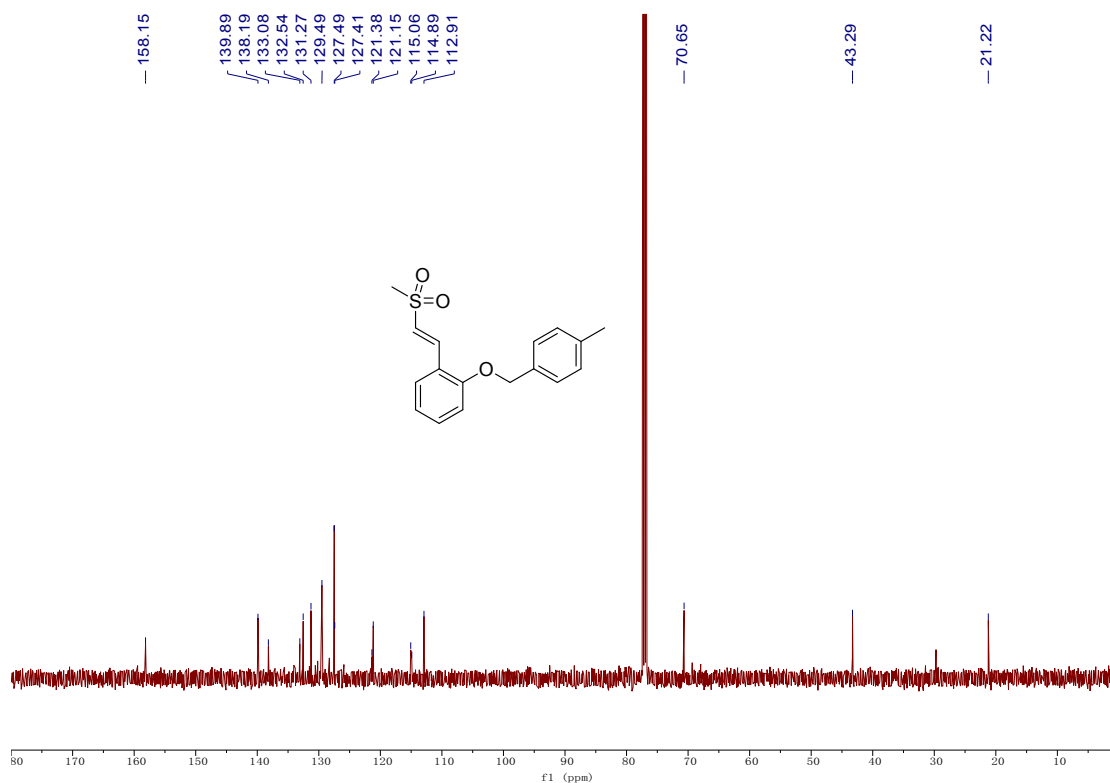
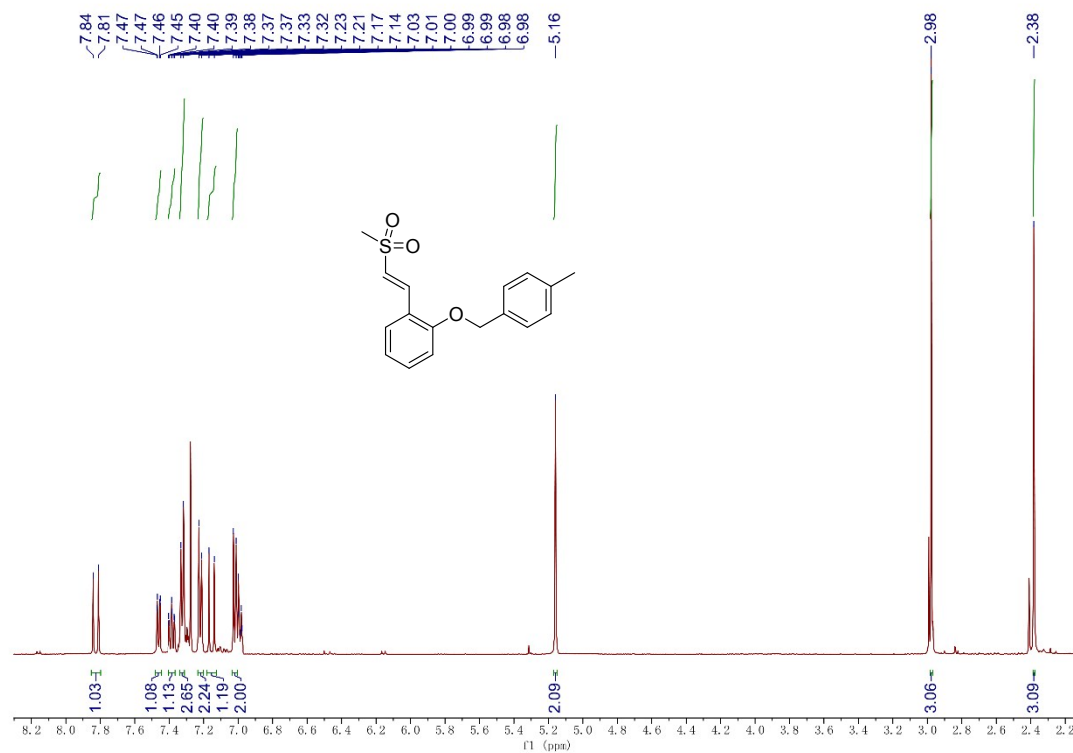


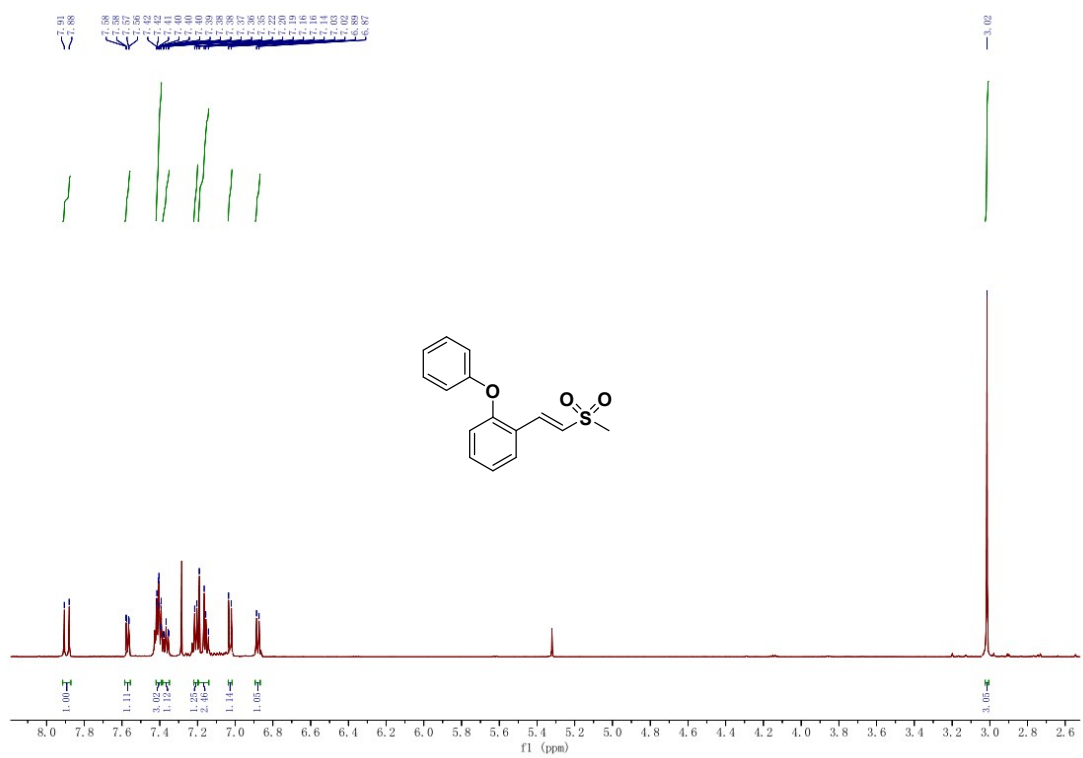
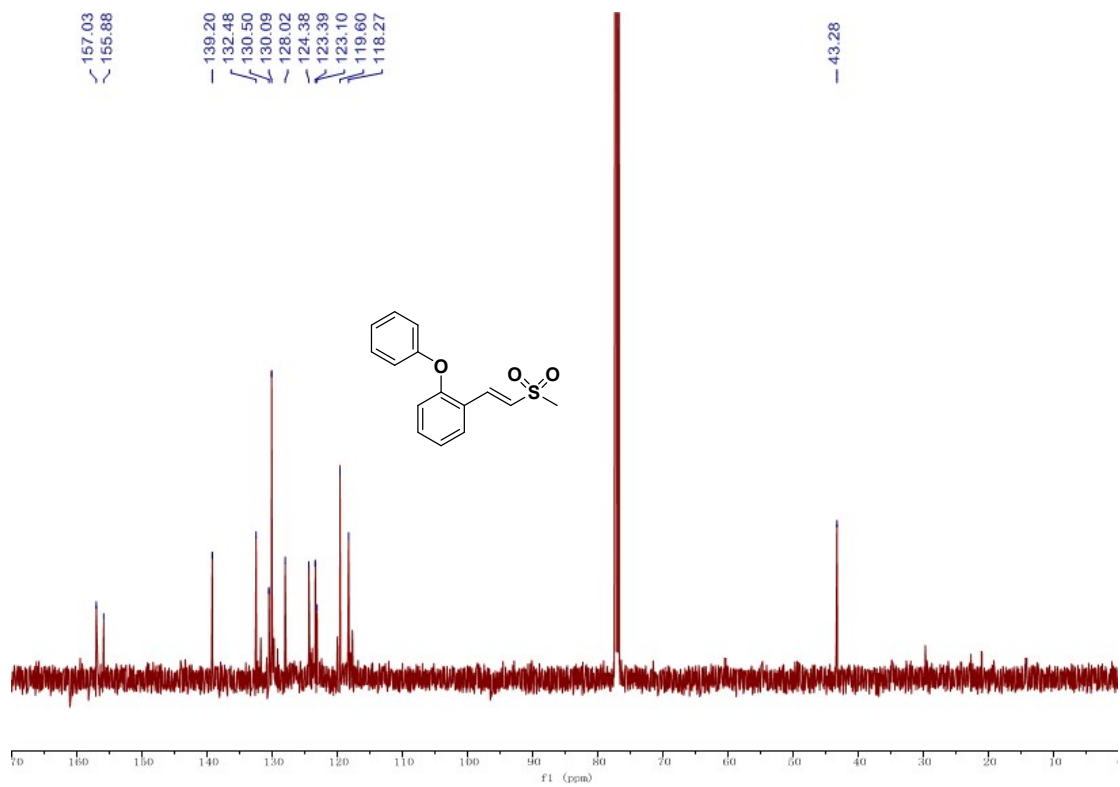


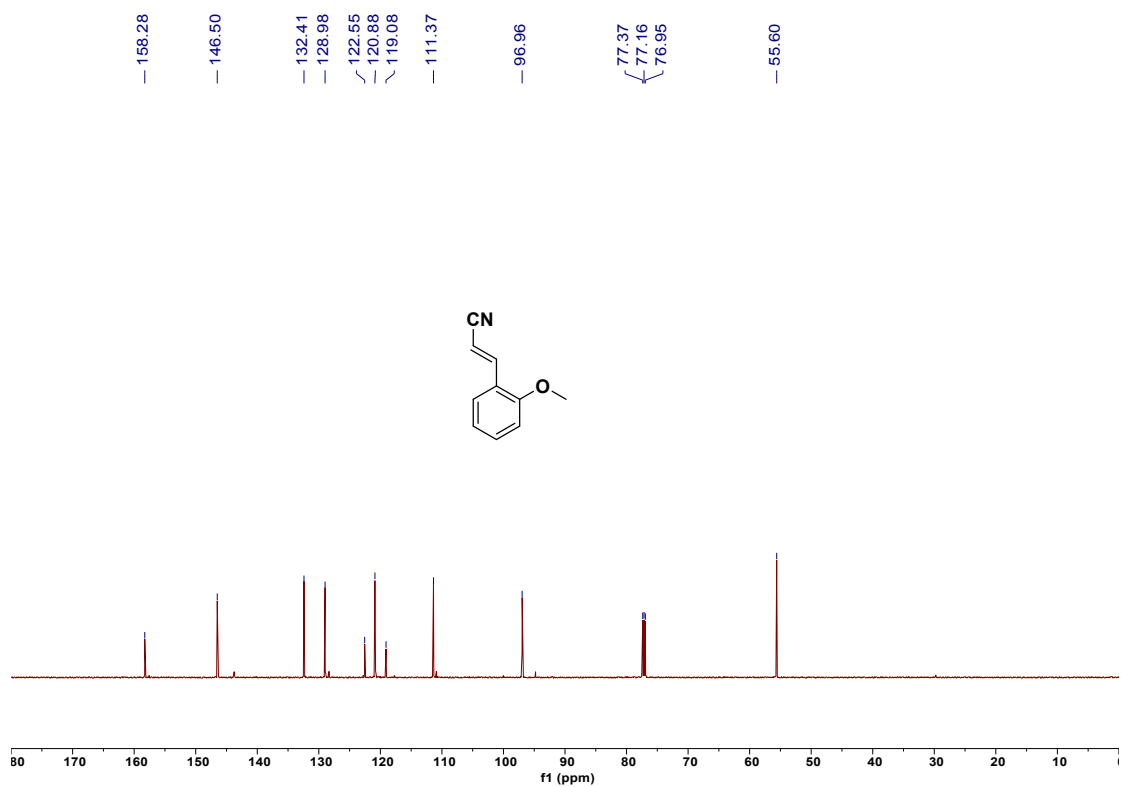
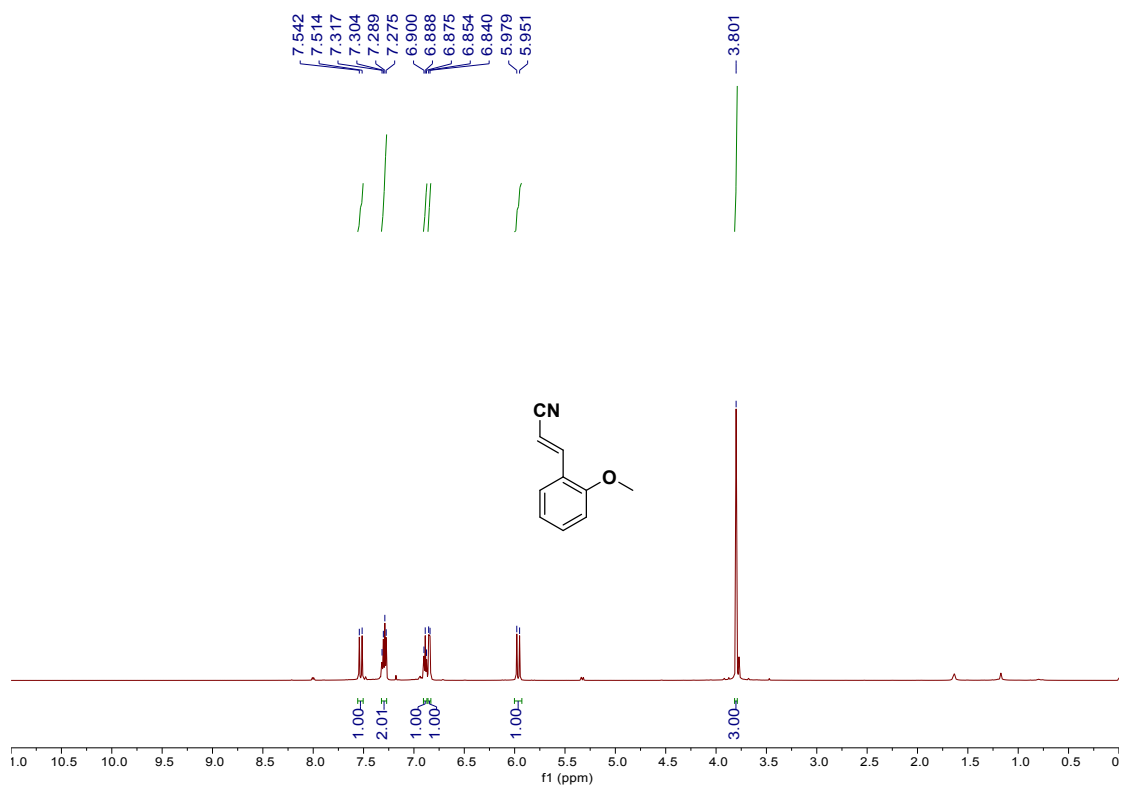


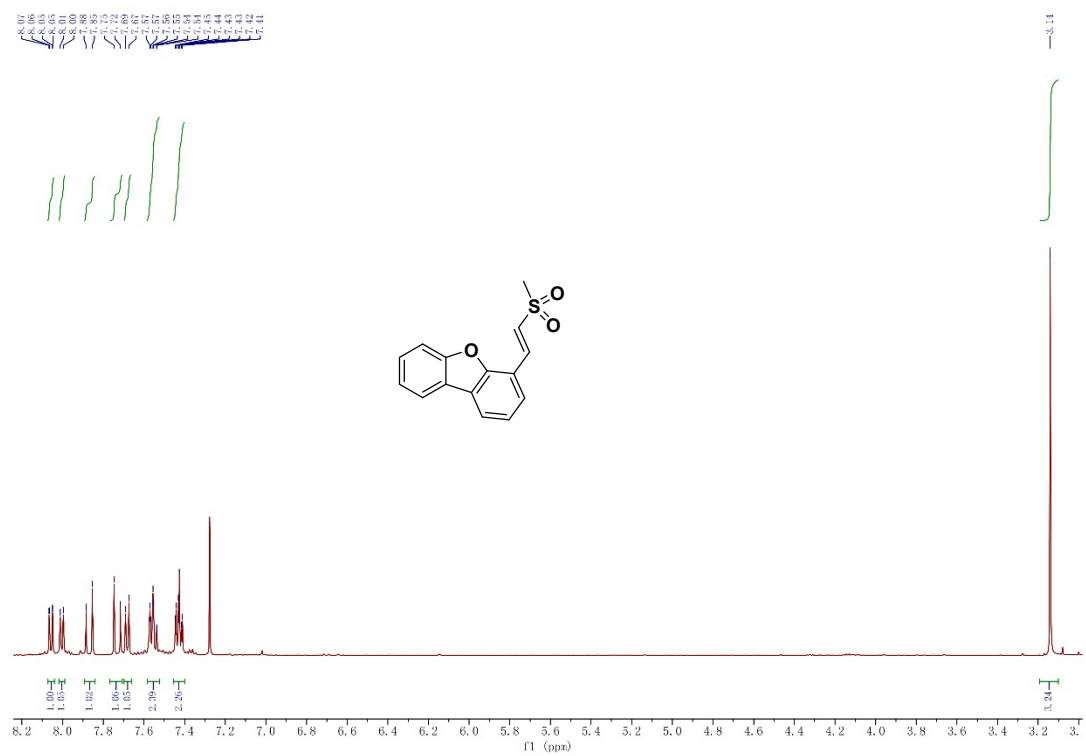
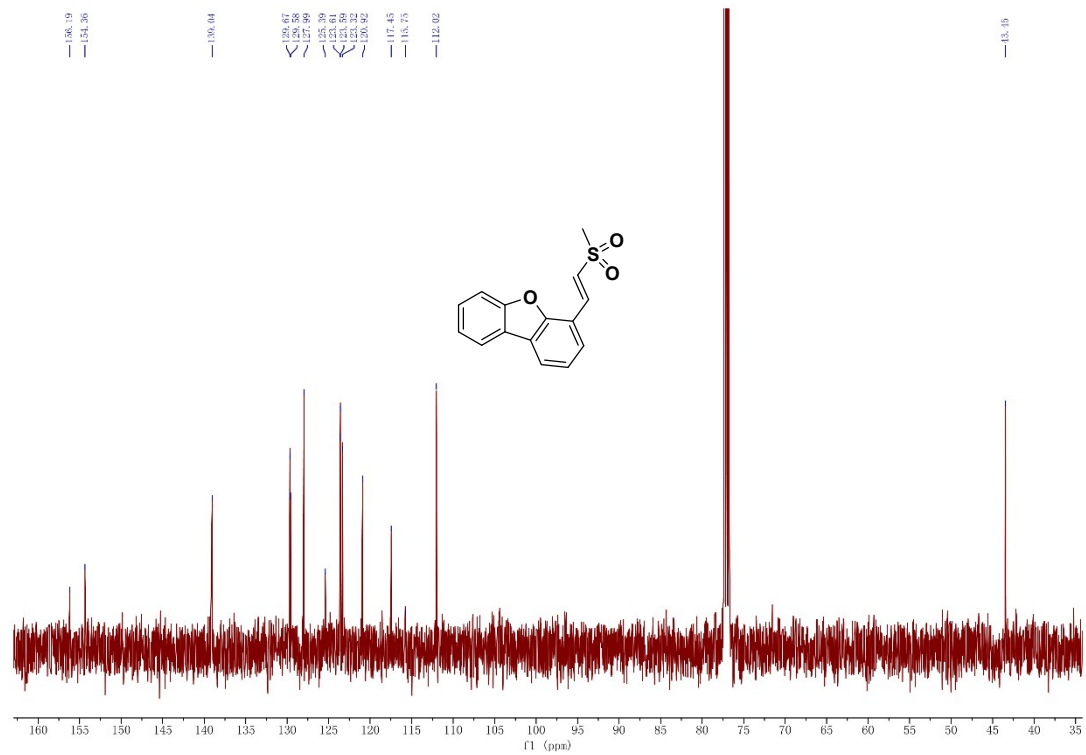


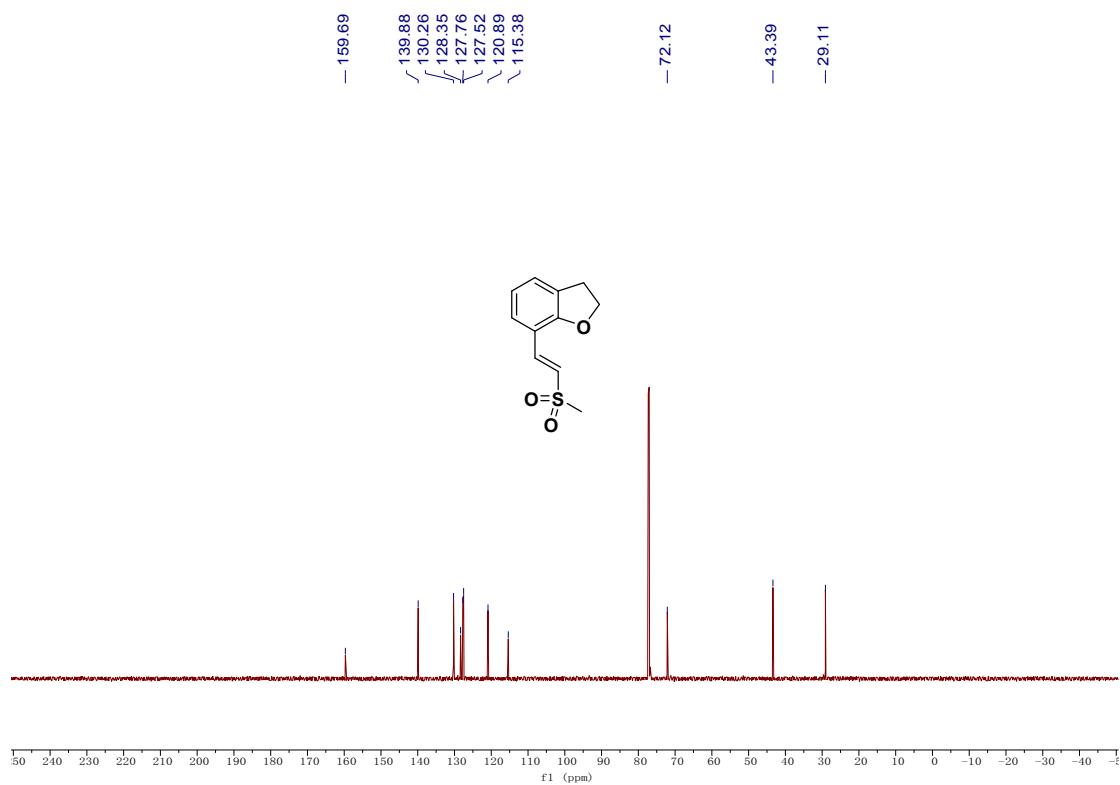
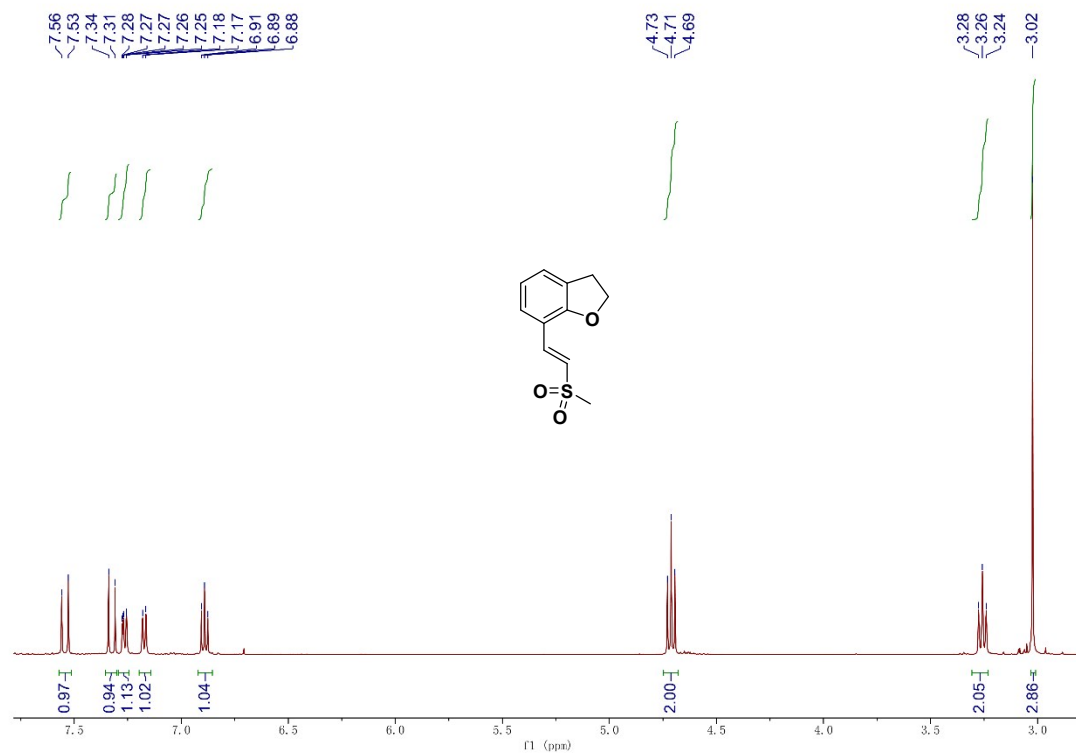


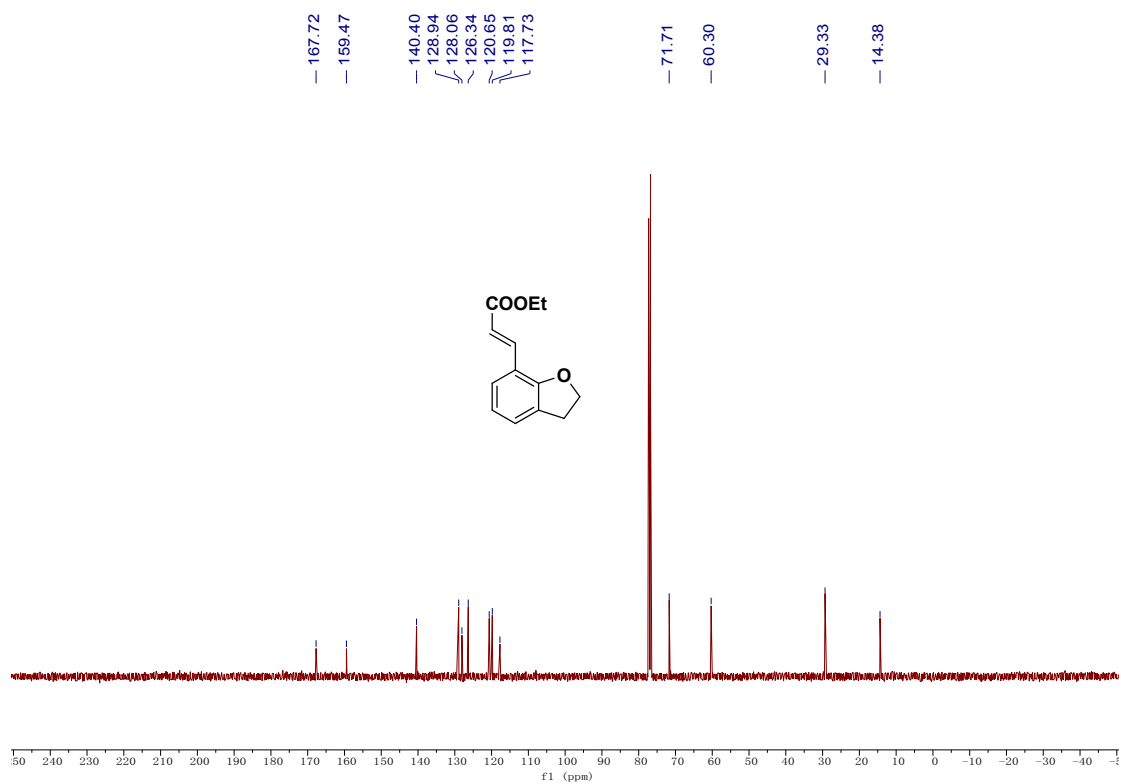
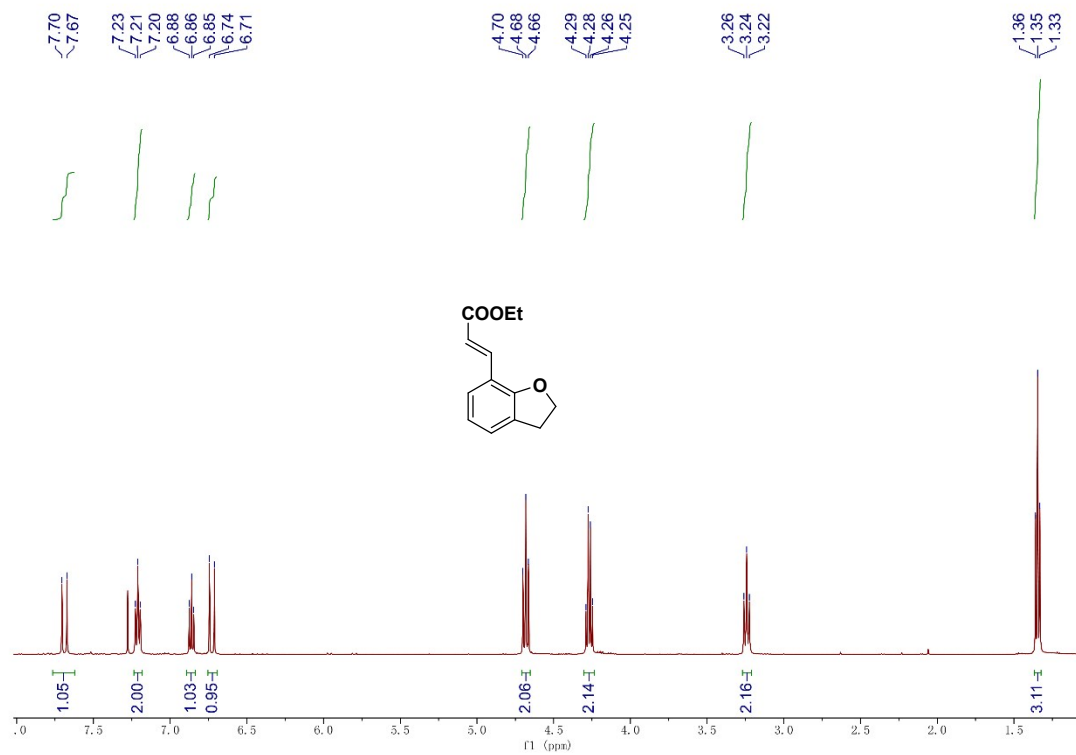


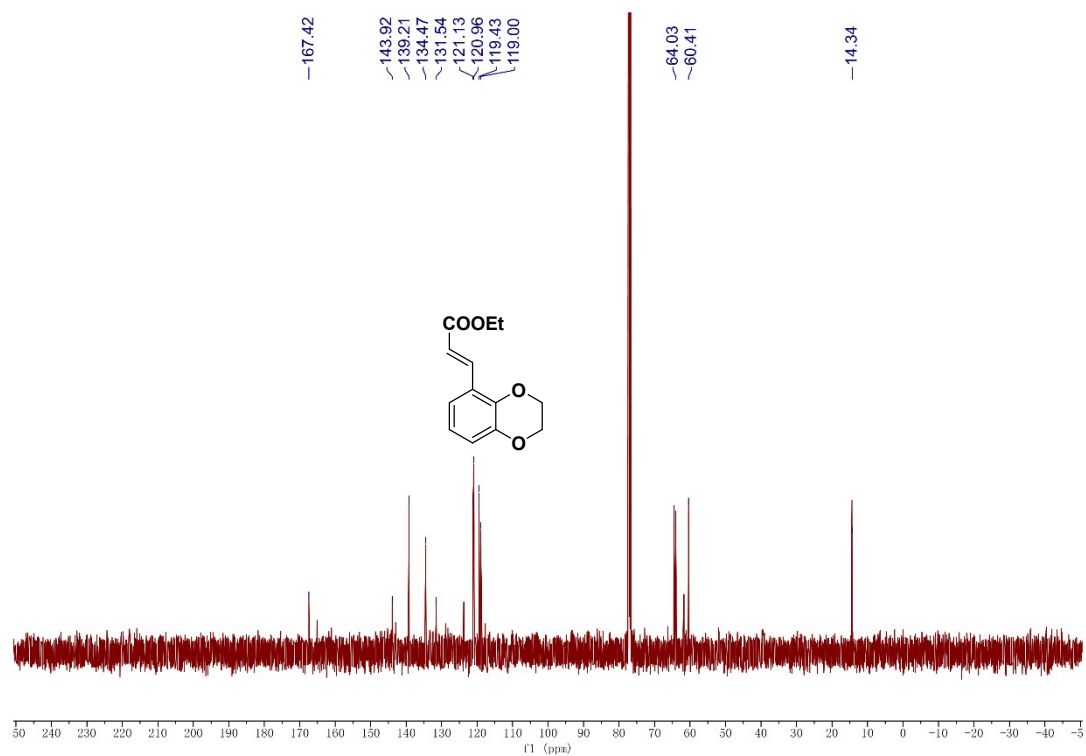
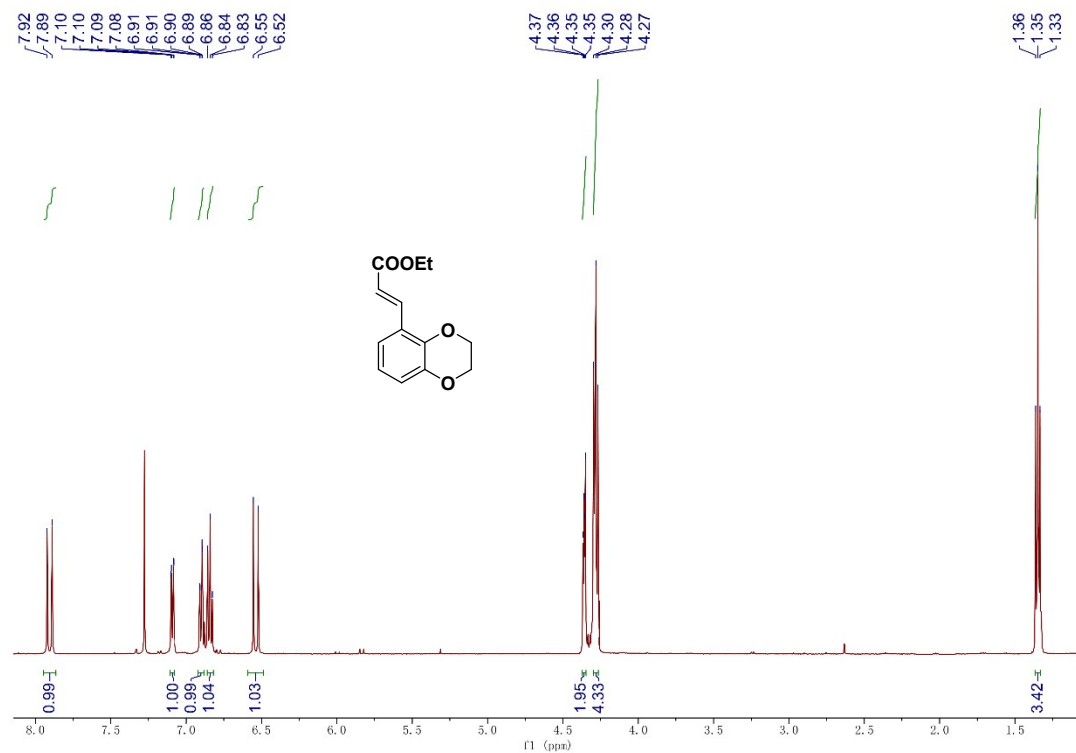


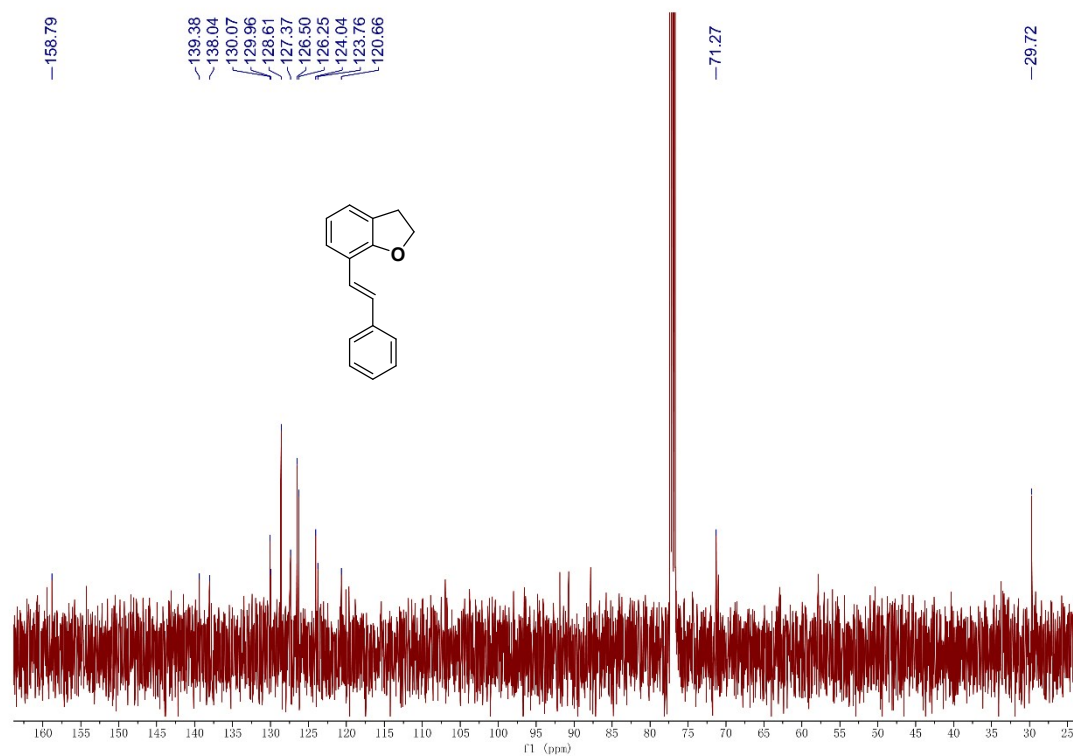
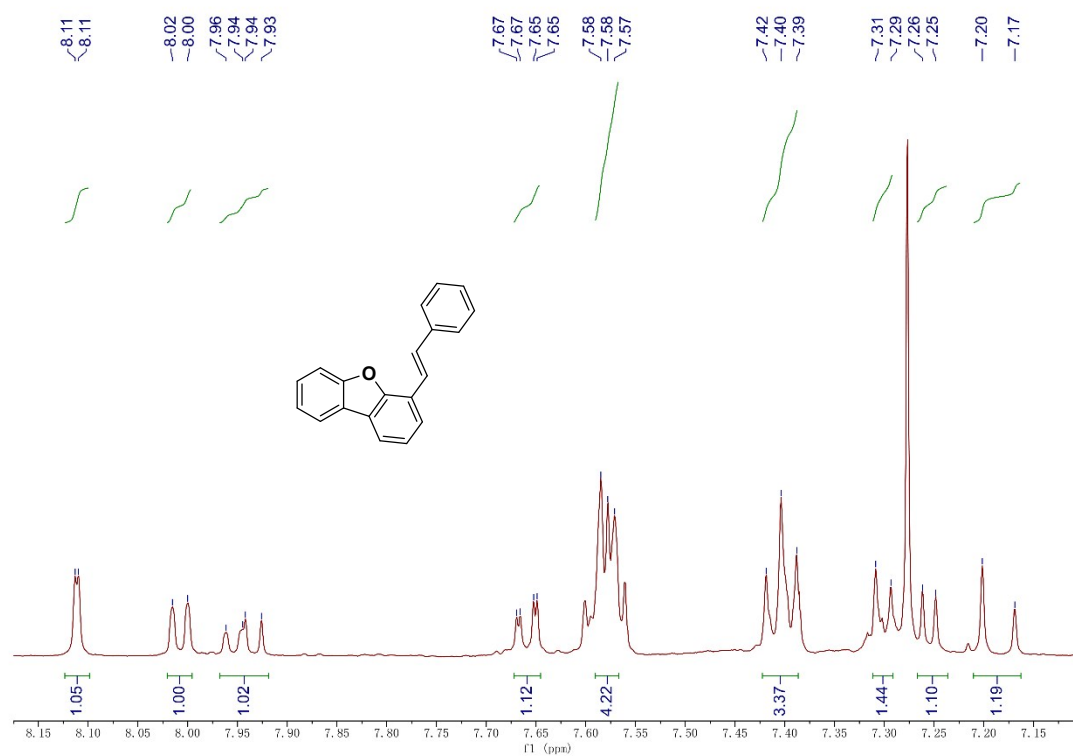


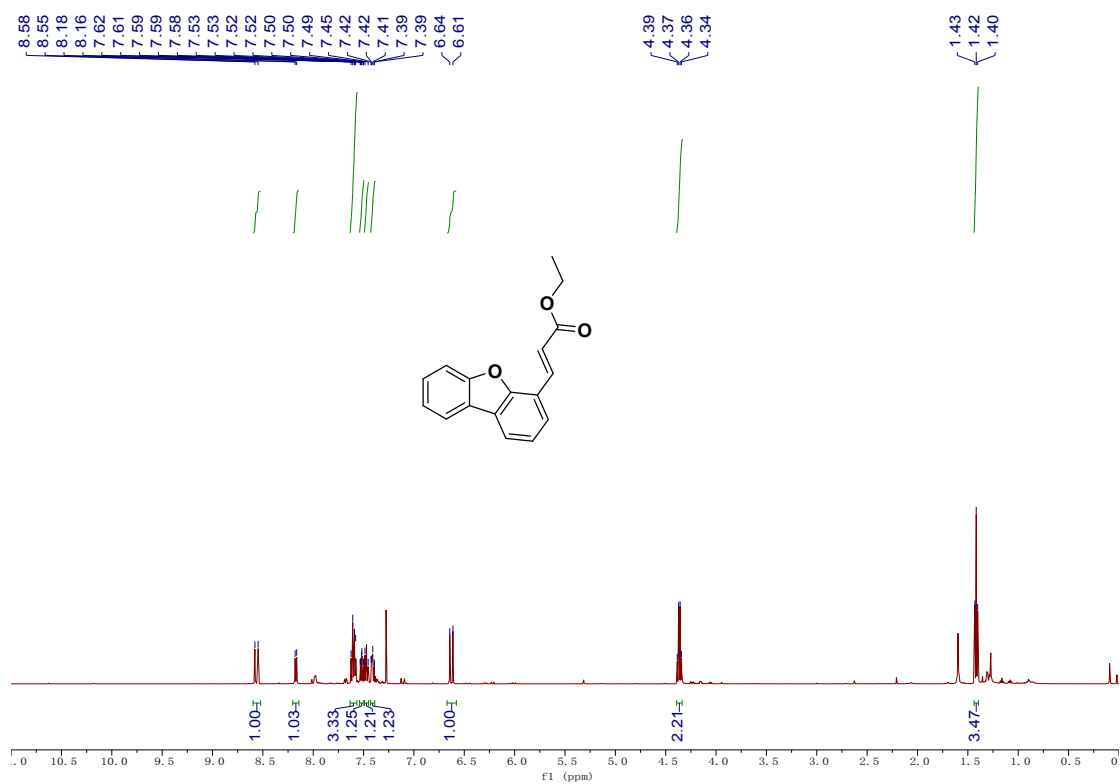
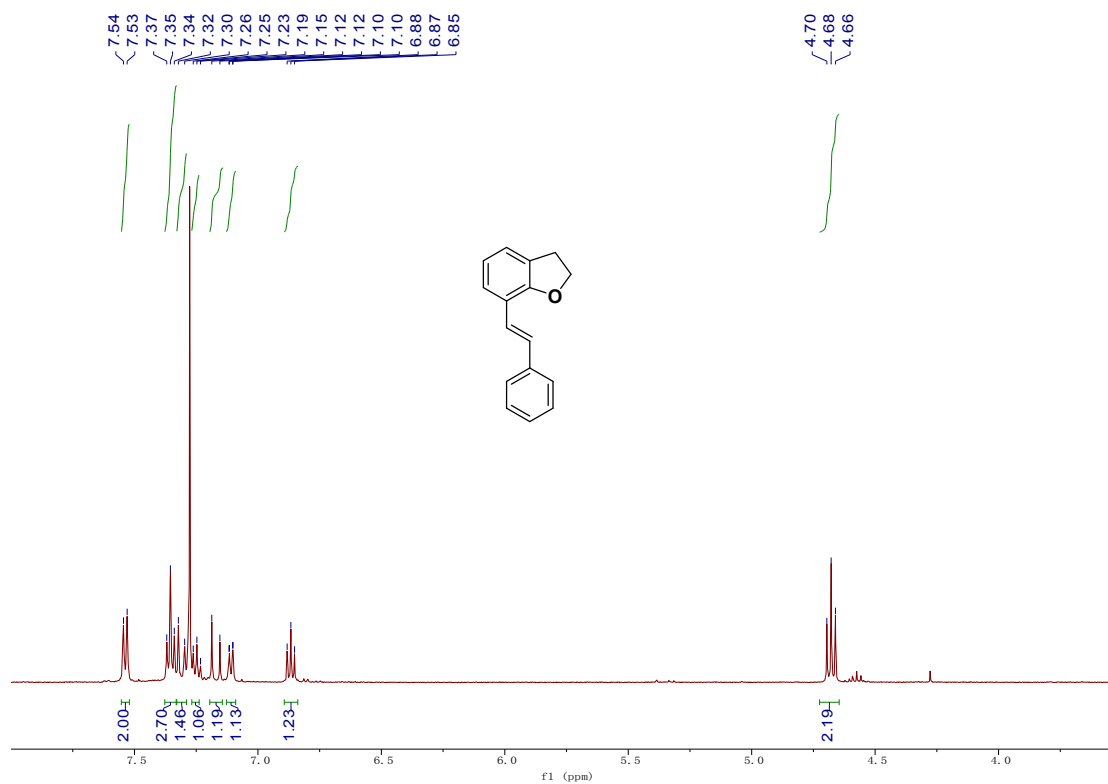


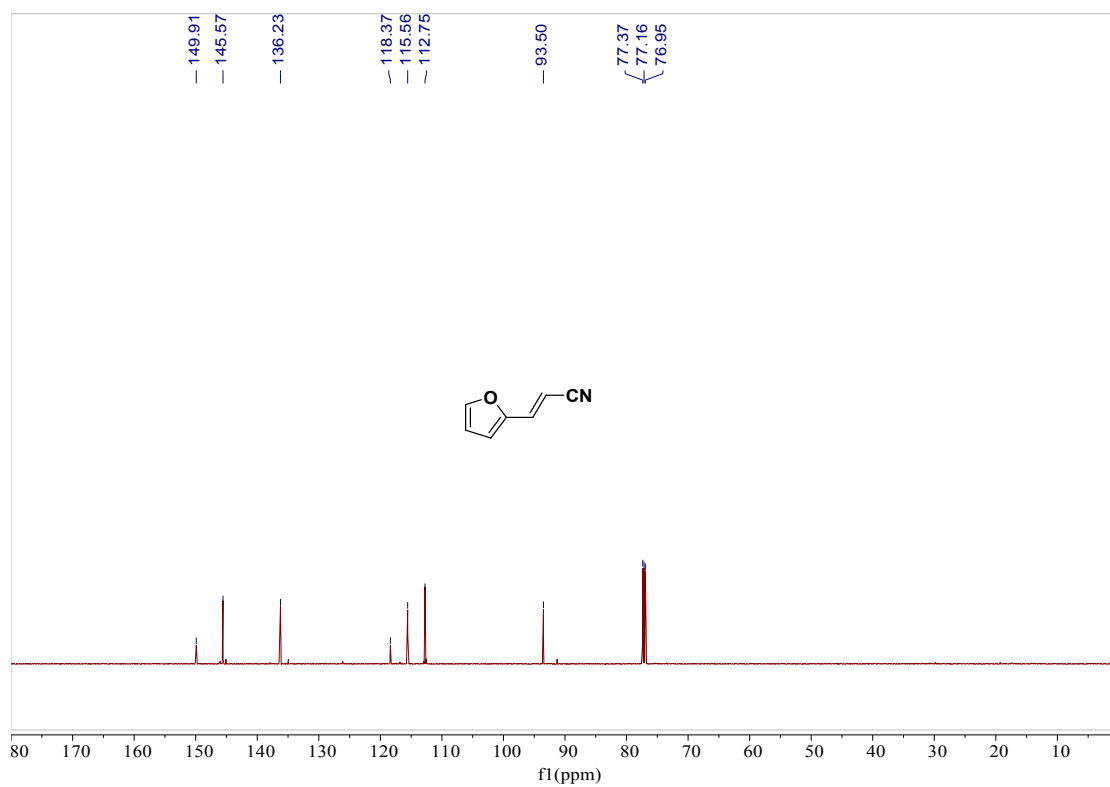
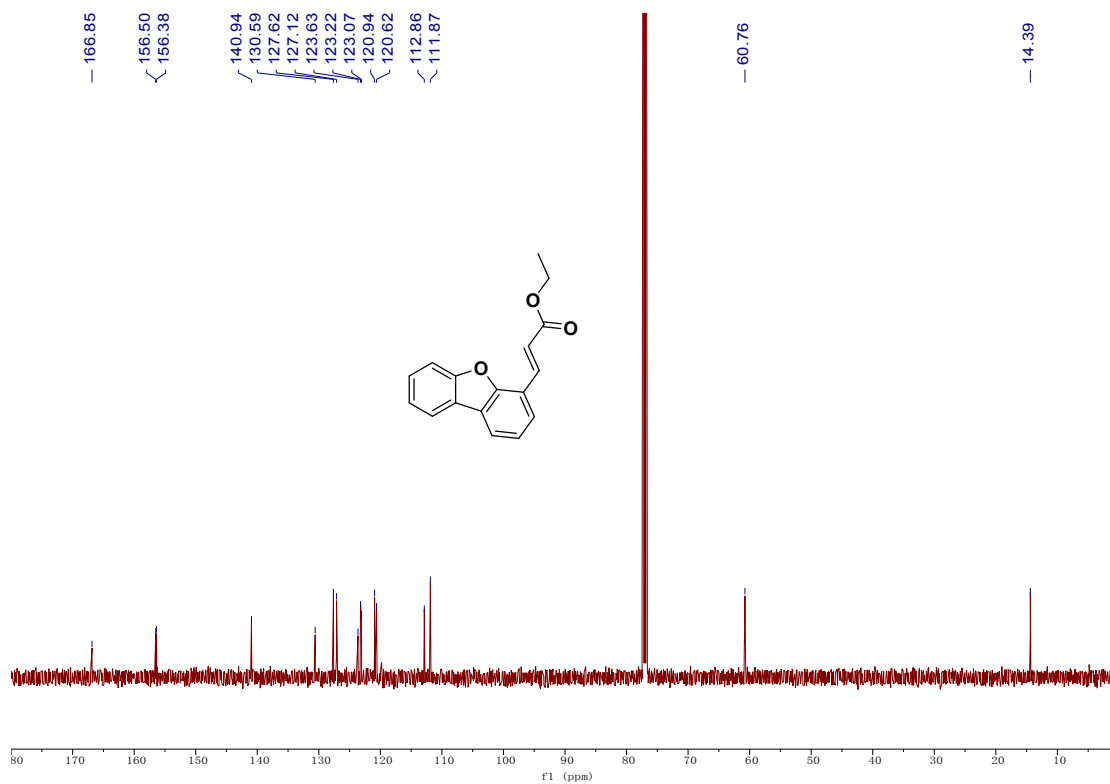


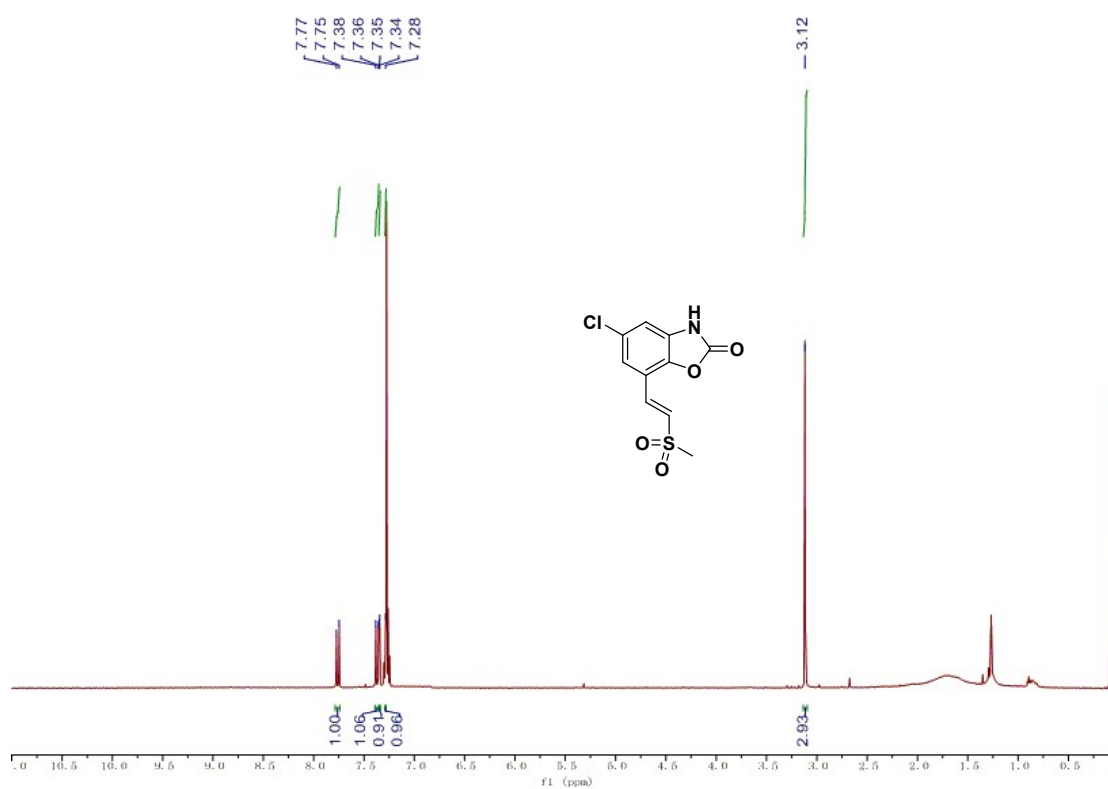
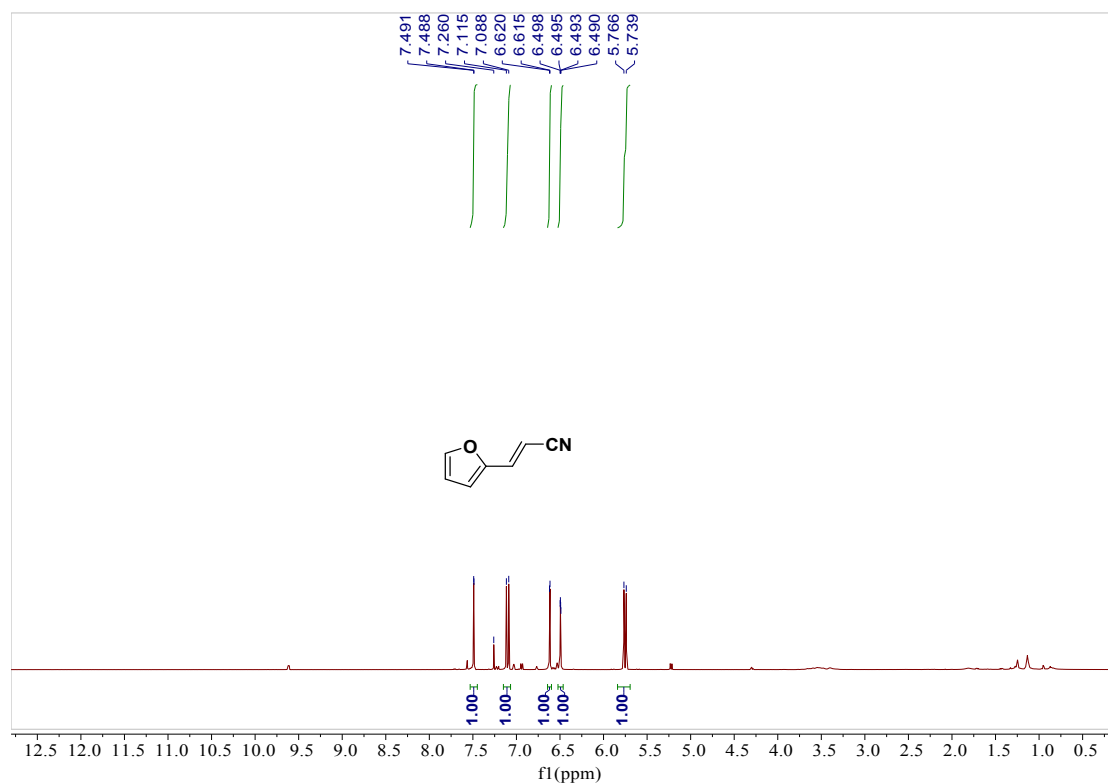


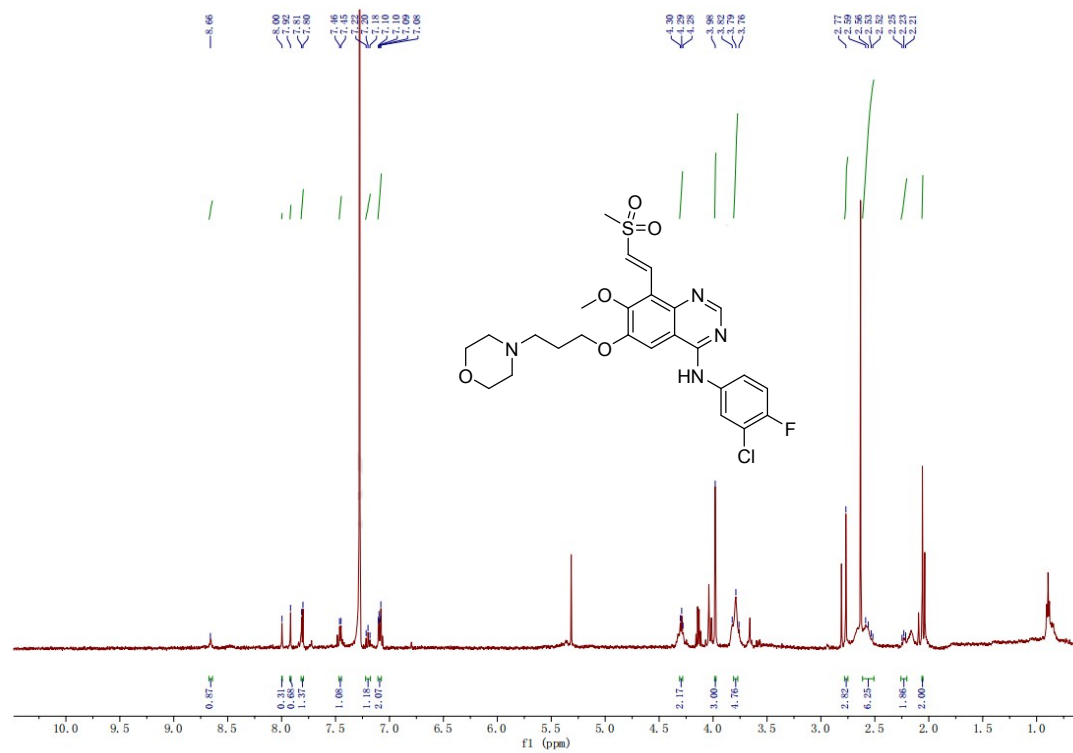












3. References

- [1] Battacea, A.; Zairb, T.; Doucet, H.; Santelli, M. *Synthesis*, **2006**, 20, 3495-3505.
- [2] Meyer, A. Y.; Straková, K.; Slanina, T.; König, B. *Chem. Eur. J.* **2016**, 22, 8694-8699.
- [3] Yuan, N.; Pascanu, V.; Huang, Z. H.; Valiente, A.; Stock, N.; Zou, X. D. *J. Am. Chem. Soc.* **2018**, 140, 8206-8217.
- [4] Yoshioka, E.; Inoue, M.; Nagoshi, Y.; Kobayashi, A.; Mizobuchi, R.; Kawashima, A.; Kohtani, S.; Miyabe, H. *J. Org. Chem.* **2018**, 83, 8962-8970.
- [5] Cho, H.; Shin, J. E.; Lee, S.; Jeon, H.; Park, S.; Kim, S. *Org. Lett.* **2018**, 20, 6121-6125.
- [6] Xu, Y. L.; Tang, X. D.; Hu, W. G.; Wua, W. Q.; Jiang, H. F.; *Green Chem.* **2014**, 16, 3720-3723.
- [7] Tanaka, K.; Shoji, T. *Org. Lett.* **2005**, 7, 16, 3561-3563.
- [8] Sharma, D.; Kumar, S.; Shil, A. K.; Guha, N. R.; Das, P. *Tetrahedron Letters*. **2012**, 53, 7044-7051.
- [9] Schmidt, B.; Elizarov, N.; Berger, R.; Hölter, F. *Org. Biomol. Chem.* **2013**, 11, 3674-3691.
- [10] Lee, J-Y.; Su, Y-S.; Wang, Y-S.; Lee, H. M. *Adv. Synth. Catal.* **2019**, 361, 4714-4726.
- [11] Zhang, N.; Quan, Z. J.; Zhang, Z.; Da, Y. X.; Wang, X. C. *Chem. Commun.* **2016**, 52, 14234-14237.
- [12] Liu, X.; Zhao, X. H.; Liu, Ming. *Catalysis Letters*, **2015**, 145, 1549-1556.
- [13] MurakamiHideki, K.; Oshima, Y. K. *Org. Lett.* **2009**, 11, 2373-2375.
- [14] Wang, C.; Wu, C.; Ge, S. Z. *ACS Catal.* **2016**, 6, 11, 7585-7589.
- [15] Zha, G. F.; Zheng, Q. H.; Leng, J.; Wu, P.; Qin, H. L.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2017**, 56, 4849-4852.
- [16] Chinthakind, P. K.; Govender, K. B.; Kumar, S.; Kruger, H. G.; Govender, T.; Naicker, T.; Arvidsson, P. I. *Org. Lett.* **2017**, 19, 3, 480-483.
- [17] Xu, Y. L.; Tang, X. D.; Hu, W. G.; Wu, W. Q.; Jiang, H. F. *Green Chem.* **2014**, 16, 3720-3723.
- [18] Zhang, J. Z.; Li, Y.; Xu, R.; Chen, Y. *Angew. Chem. Int. Ed.* **2017**, 56, 12619-12623.
- [19] Marti-Centelles, R.; Falomir, E.; Murga, J.; Carda, M.; Marco, J. A. *Eur. J. Med. Chem.* **2015**, 103, 488-496.
- [20] Das, J.; Vellakkaran, M.; Sk, M.; Banerjee, D. *Org. Lett.* **2019**, 21, 18, 7514-7518.
- [21] Wang, P.; Verma, P.; Xia, G. Q.; Shi, J.; Qiao, J. X.; Tao, S. W.; Yu, J. Q.; *Nature*, **551**, 489-493.