Supporting Information

A neutral nickel-catalyzed dehydrosulfonylation of unactivated allylic alcohols under mild conditions

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1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Unless otherwise specified, all reactions were carried out in sealed Schlenk tubes under N_2 and then monitored by TLC. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. Dimethyl sulfoxide (DMSO) was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N_2. DMSO-d_6 and $CDCl_3$ were purchased from Shanghai aladdin Biochemical Technology Co., Ltd. All Schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet.

2. Experimental sections

2.1 General procedures for Ni(II)-catalysed synthesis of sulfones.

To a 50 mL Schlenk tube containing cinnamyl alcohol **(1a)** (0.2 mmol), 4-methylbenzenesulfonyl hydrazide (**2a**) (2.0 equiv.), $Ni(acac)_2$ (20 mol%), DPPF (20 mol%), and the tube was purged with N_2 for 3 times, followed by 2 mL of DMSO. The resulting mixture was stirred at 70 °C for 6 h. After cooling to room temperature, the mixture was partitioned between water (15 mL) and ethyl acetate (15 mL). The phases were separated and the aqueous phase extracted with further ethyl acetate (3×15 mL). The organic phases were dried over sodium sulfate. Filtration of the drying agent, and removal of all volatiles in vacuo gave a residue. Directly purified by flash chromatography to give the desired product **3a**.

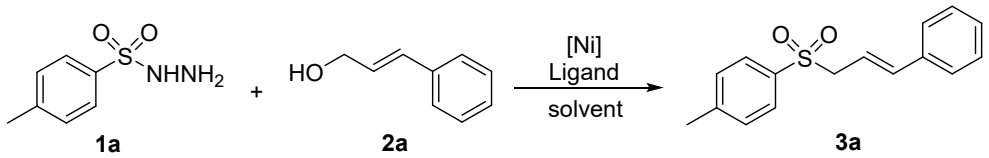
2.2 The synthesis of sulfonyl hydrazides

Hydrazine monohydrochloride (6.0 mmol) and NaOH (6.6 mmol) was added to water (30 mL) and was cooled to 0 °C. A solution of arylsulfonyl chloride (3.0 mmol) in THF (10 mL) was added by dropwise at 0 °C. The mixture was further stirred at 0

°C for 30 min, followed by addition of EtOAc (20 mL). The mixture was extracted with water (3×10 mL). The combined organic extract was concentrated and concentrated by silica gel column chromatography to provide the desired product.[1]

2.2 Optimization of reaction conditions

Table S1. Nickel catalysts and additive screening[a]



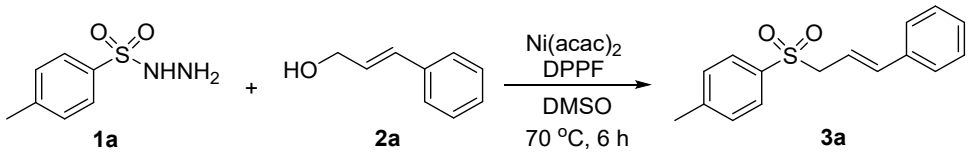
1a **2a** **3a**

Entry	Catalyst	Ligand	Solvent	Yield(%)[b]
1	$NiCl_2$	DPPF	DMF	11
2	$NiBr_2$	DPPF	DMF	13
3	$Ni(OTf)_2$	DPPF	DMF	0
4	$Ni(acac)_2$	DPPF	DMF	60
5	$Ni(OAc)_2$	DPPF	DMF	29
6	$Ni(PPh_3)Cl_2$	DPPF	DMF	0
7	$Ni(acac)_2$	-	DMF	0
8	-	DPPF	DMF	0
9	$Ni(acac)_2$	DPPB	DMF	48
10	$Ni(acac)_2$	DPEphos	DMF	16
11	$Ni(acac)_2$	BINAP	DMF	43
12	$Ni(acac)_2$	Pcy_3	DMF	0
13	$Ni(acac)_2$	PPh_3	DMF	0
14	$Ni(acac)_2$	Xantphos	DMF	trace
15	$Ni(acac)_2$	1,10-Phenanthroline monohydrate	DMF	0
16	$Ni(acac)_2$	1,10-Phenanthroline-5,6-dione	DMF	0
17	$Ni(acac)_2$	4,7-Dimethoxy-1,10-phenanthroline	DMF	0
18	$Ni(acac)_2$	DPPF	DMSO	71
19	$Ni(acac)_2$	DPPF	Dioxane	55
20	$Ni(acac)_2$	DPPF	DCE	trace
21	$Ni(acac)_2$	DPPF	MeCN	59

22	$Ni(acac)_2$	DPPF	EtOH	trace
23	$Ni(acac)_2$	DPPF	H_2O	0
24	$Ni(acac)_2$	DPPF	PhCl	trace
25	$Ni(acac)_2$	DPPF	toluene	59
26 [c]	$Ni(acac)_2$	DPPF	DMSO	66
27 [d]	$Ni(acac)_2$	DPPF	DMSO	74
28 [e]	$Ni(acac)_2$	DPPF	DMSO	71
29 [f]	$Ni(acac)_2$	DPPF	DMSO	75
30 [g]	$Ni(acac)_2$	DPPF	DMSO	77

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ni] (10 mol%), Ligand (20 mol%), solvent (2 mL), 24 h, 80 °C, N_2. [b] Isolated yields. [c] Reaction temperature: 60 °C. [d] Reaction temperature: 70 °C. [e] Reaction time and temperature:2 h, 70 °C. [f] Reaction time and temperature: 6 h, 70 °C. [g] Reaction time and temperature: 12 h, 70 °C.

Table S2. Variation of time and molar ratio in optimization of reaction conditions[a]

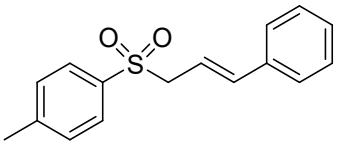


1a **2a** **3a**

Entry	**1a** (mmol)	**2a** (mmol)	**$Ni(acac)_2$** (mol%)	**DPPF** (mol%)	**Yield** (%)[b]
1	0.3	0.2	10	20	72
2	0.2	0.2	10	20	73
3	0.2	0.3	10	20	84
4	0.2	0.4	10	20	91
5	0.2	0.5	10	20	90
6	0.2	0.4	5	20	70
7	0.2	0.4	20	20	87
8	0.2	0.4	10	30	85
9	0.2	0.4	10	20	0 [c]

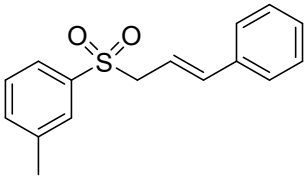
[a] Reaction conditions: cinnamyl alcohol **1a**, 4-methylbenzenesulfonyl hydrazide **2a**, $Ni(acac)_2$ and DPPF in DMSO (2 mL), 6 h, 70 °C, under N_2. [b] Isolated yield. [c] Under air.

3. Data for the sulfone products



1-(cinnamylsulfonyl)-4-methylbenzene[2]

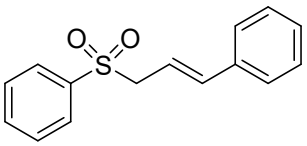
(**3a**): white solid, mp: 118.6-120.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.26 (m, 7H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.16 – 6.03 (m, 1H), 3.93 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.76, 139.02, 135.86, 135.59, 129.73, 128.66, 128.53, 128.49, 126.63, 115.37, 60.58, 21.64.



1-(cinnamylsulfonyl)-3-methylbenzene[2]

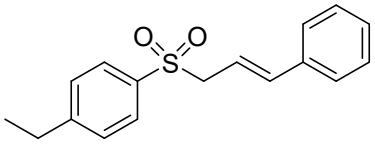
(**3b**) white solid, mp: 95.5-96.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.45 – 7.39 (m, 2H), 7.33 – 7.27 (m, 5H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.10 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.94 (d, *J* = 8.3 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.41, 139.22, 138.20, 135.81, 134.62, 129.00, 128.88, 128.69, 128.54, 126.64, 125.67, 115.20, 60.50, 21.31.

HRMS (ESI) calcd for $C_{12}H_{11}NO_3S$ $(M + Na)^+$ 295.07632, found 295.07669.



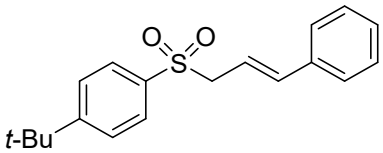
(cinnamylsulfonyl)benzene[2]

(**3c**) white solid, mp: 108.0-108.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.27 (m, 5H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.96 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.26, 138.32, 135.74, 133.85, 129.15, 128.71, 128.58, 128.56, 126.65, 115.10, 60.51.



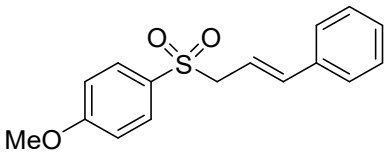
1-(cinnamylsulfonyl)-4-ethylbenzene[2]

(**3d**) white solid, mp: 118.0-109.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 5H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.14-6.07 (m, 1H), 3.94 (d, *J* = 7.5 Hz, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H).



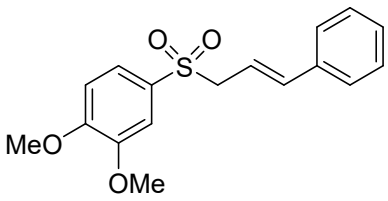
1-(*tert*-butyl)-4-(cinnamylsulfonyl)benzene[3]

(**3e**) white solid, mp: 120.3-122.1 ℃. ^{1}H NMR (500 MHz, $CDCl_3$ δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.26 (m, 5H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.12 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.94 (d, *J* = 7.6 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.73, 139.16, 135.86, 135.44, 128.68, 128.50, 128.39, 126.65, 126.15, 115.27, 60.56, 35.30, 31.09.



1-(cinnamylsulfonyl)-4-methoxybenzene[2]

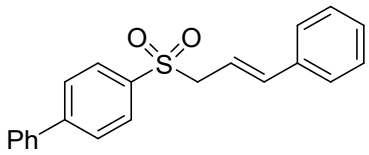
(**3f**) white solid, mp: 119.2-120.6 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.26 (m, 5H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.11 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.93 (d, *J* = 7.6 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 163.78, 138.97, 135.84, 130.72, 129.94, 128.70, 128.51, 126.65, 115.53, 114.29, 60.76, 55.72.



4-(cinnamylsulfonyl)-1,2-dimethoxybenzene

(**3g**) white solid, mp: 123.3-125.3 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.30 (s, 4H), 7.27 (d, *J* = 3.2 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.13 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.94 (d, *J* = 5.7 Hz, 5H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.37, 148.92, 139.01, 135.76, 129.91, 128.73, 128.57, 126.59, 122.63, 115.55, 110.82, 110.59, 60.76, 56.27, 56.16.

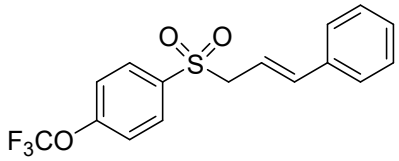
HRMS (ESI) calcd for $C_{12}H_{11}NO_3S$ $(M + Na)^+$ 341.08180, found 341.08254.



4-(cinnamylsulfonyl)-1,1'-biphenyl[3]

(**3h**) white solid, mp: 123.2-125.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.27 (m, 5H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.99 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.71, 139.31, 139.10, 136.92, 135.77, 129.14, 129.11, 128.74, 128.73, 128.60, 127.72, 127.44, 126.68, 115.15, 60.63.

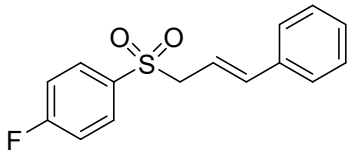
HRMS (ESI) calcd for $C_{12}H_{11}NO_3S$ $(M + Na)^+$ 357.09197, found 357.09271.



1-(cinnamylsulfonyl)-4-(trifluoromethoxy)benzene[3]

(**3i**) white solid, mp: 112.3-113.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32-7.26 (m, 5H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.14-6.08 (m, 1H), 3.97 (d, *J* = 7.5 Hz, 2H).

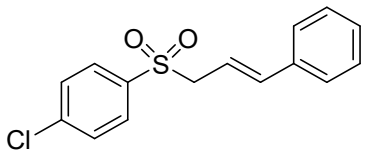
^{19}F NMR (471 MHz, $CDCl_3$) δ -57.65.



1-(cinnamylsulfonyl)-4-fluorobenzene[2]

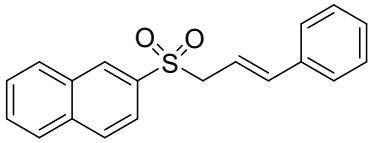
(**3j**) white solid, mp: 98.6-98.9 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.30 (q, *J* = 7.2, 6.6 Hz, 5H), 7.21 (t, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.11 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.96 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.66 (d, J_{C-F} = 257.55 Hz), 139.42, 135.61, 134.41(d, J_{C-F} = 3.03 Hz), 131.46 (d, J_{C-F} = 10.1 Hz), 128.75, 128.69, 126.63, 116.44 (d, J_{C-F} = 22.22 Hz), 114.98, 60.63.

^{19}F NMR (471 MHz, DMSO) δ -101.88.



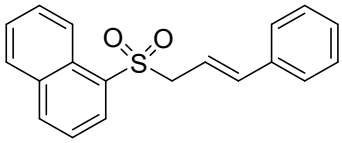
1-chloro-4-(cinnamylsulfonyl)benzene[2]

(**3k**) white solid, mp: 88.5-89.3 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.34-7.29 (m, 5H), 6.39 (d, *J* = 15.5 Hz, 1H), 6.13-6.07 (m, 1H), 3.95 (d, *J* = 7.5 Hz, 2H).



2-(cinnamylsulfonyl)naphthalene[2]

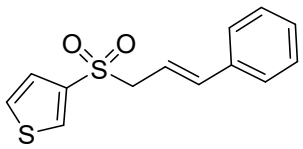
(**3l**) white solid, mp: 141.8-143.7 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.99 – 7.90 (m, 3H), 7.85 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.63 – 7.59 (m, 1H), 7.29 – 7.24 (m, 5H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.5, 7.6 Hz, 1H), 4.03 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.32, 135.74, 135.39, 135.36, 132.12, 130.41, 129.49, 129.36, 128.68, 128.55, 128.02, 127.73, 126.66, 123.20, 115.12, 60.61.



1-(cinnamylsulfonyl)naphthalene[3]

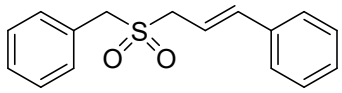
(**3m**) white solid, mp: 97.5-98.6 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.74-7.71 (m, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.26-7.24 (m, 3H), 7.19-

7.17 (m, 2H), 6.27 (d, *J* = 16 Hz, 1H), 6.08-6.02 (m, 1H), 4.16 (d, *J* = 7.5 Hz, 2H).



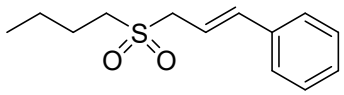
3-(cinnamylsulfonyl)thiophene[2]

(**3n**) white solid, mp: 91.3-92.6 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 1H), 7.43 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.33 – 7.27 (m, 5H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.14 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.97 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.32, 138.82, 135.72, 133.26, 128.75, 128.65, 128.12, 126.68, 126.42, 115.11, 60.72.



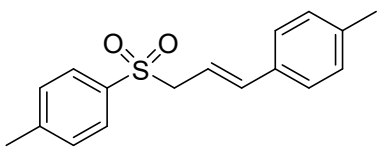
(3-(benzylsulfonyl)prop-1-en-1-yl)benzene[2]

(**3o**) white solid, mp: 115.8-117.1 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.0 Hz, 7H), 7.34 (dt, *J* = 23.4, 7.1 Hz, 3H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.6, 7.5 Hz, 1H), 4.25 (s, 2H), 3.75 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.27, 135.53, 130.82, 129.14, 129.11, 128.82, 127.75, 126.77, 115.20, 58.15, 55.82.



(3-(butylsulfonyl)prop-1-en-1-yl)benzene

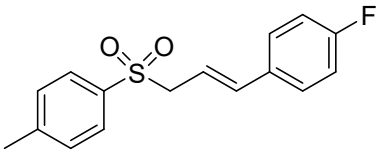
(**3p**) white solid, mp: 78.5-79.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.86 (d, *J* = 7.6 Hz, 2H), 3.03 – 2.94 (m, 2H), 1.83 (p, *J* = 7.7 Hz, 2H), 1.45 (dt, *J* = 14.9, 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).



1-methyl-4-((3-(*p*-tolyl)allyl)sulfonyl)benzene

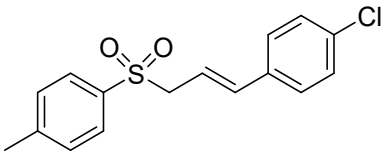
(**3p**) white solid, mp: 98.7-99.1 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.92 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.74, 138.94, 138.52, 135.48, 133.09, 129.73, 129.38, 128.56, 126.57, 114.20, 60.64, 21.69, 21.30.

HRMS (ESI) calcd for $C_{12}H_{11}NO_3S$ $(M + Na)^+$ 309.09197, found 309.09265.



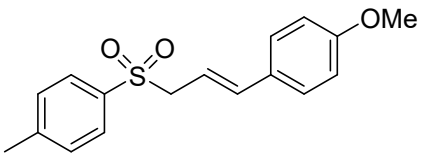
1-fluoro-4-(3-tosylprop-1-en-1-yl)benzene[2]

(**3q**) white solid, mp: 143.2-144.6 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.02 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.92 (d, *J* = 7.6 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 13C NMR (101 MHz, CDCl3) δ δ 162.81 (d, J_{C-F} = 249.47 Hz), 144.83, 137.83, 135.59, 132.05(d, J_{C-F} = 3.03 Hz), 129.77, 128.49, 128.27(d, J_{C-F} = 8.08 Hz), 115.66(d, J_{C-F} = 21.21 Hz), 115.04(d, J_{C-F} = 1.01 Hz), 60.48, 21.66. ^{19}F NMR (471 MHz, DMSO) δ -112.77.



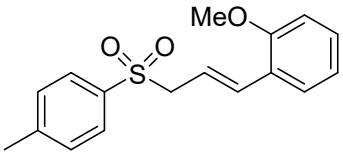
1-chloro-4-(3-tosylprop-1-en-1-yl)benzene[2]

(**3r**) white solid, mp: 141.1-142.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.1 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.08 (ddt, *J* = 15.6, 7.5, 3.8 Hz, 1H), 3.92 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.89, 137.76, 135.54, 134.31, 134.24, 129.79, 128.88, 128.48, 127.83, 116.03, 60.45, 21.67.



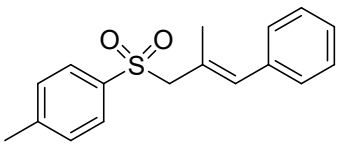
1-methoxy-4-(3-tosylprop-1-en-1-yl)benzene[2]

(**3s**) white solid, mp: 118.4-118.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.94 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.90 (d, *J* = 7.6 Hz, 2H), 3.79 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.88, 144.69, 138.51, 135.62, 129.70, 128.66, 128.53, 127.93, 114.06, 112.82, 60.66, 55.30, 21.64.



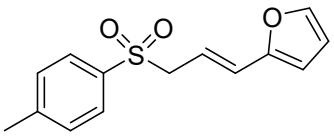
1-methoxy-2-(3-tosylprop-1-en-1-yl)benzene[2]

(**3t**) white solid, mp: 109.3-110.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 3H), 7.27 – 7.22 (m, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.12 (dt, *J* = 15.8, 7.6 Hz, 1H), 3.95 (d, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.85, 144.62, 135.59, 134.18, 129.69, 129.58, 128.57, 127.29, 124.92, 120.68, 115.90, 110.90, 61.12, 55.41, 21.68.



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

(**3u**) colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 15.4, 7.9 Hz, 4H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.07 (s, 1H), 3.88 (s, 2H), 2.44 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.74, 136.64, 135.34, 134.74, 129.70, 128.74, 128.66, 128.22, 127.17, 126.28, 67.12, 21.71, 18.64.

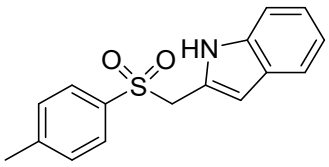


2-(3-tosylprop-1-en-1-yl)furan[2]

(**3v**) white solid, mp: 85.7-87.1 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz,

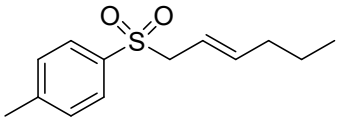
2H), 7.37 – 7.30 (m, 3H), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.24 (dd, *J* = 9.5, 6.2 Hz, 2H), 6.00 (dt, *J* = 15.6, 7.8 Hz, 1H), 3.90 (d, *J* = 7.7 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.47, 144.77, 142.82, 135.64, 129.76, 128.52, 126.70, 113.49, 111.43, 109.65, 60.41, 21.66.

HRMS (ESI) calcd for $C_{12}H_{11}NO_3S$ $(M + Na)^+$ 285.05559, found 285.05515.



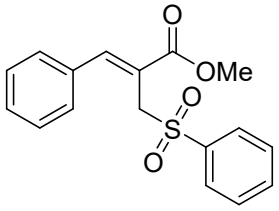
2-(tosylmethyl)-1*H*-indole

(**3w**) White solid, mp: 157.4-159.4 ℃. ^{1}H NMR (400 MHz, DMSO) δ 11.15 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 8.0, 4.2 Hz, 3H), 7.12 – 7.05 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 4.73 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 144.35, 136.49, 136.32, 129.92, 128.50, 127.59, 127.42, 121.73, 119.42, 119.35, 111.94, 101.97, 53.72, 21.50.



1-(hex-2-en-1-ylsulfonyl)-4-methylbenzene[3]

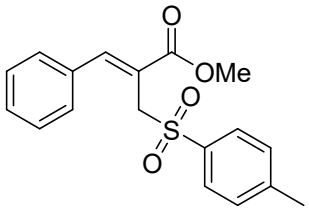
(**3x**) White solid, mp: 87.5-88.9 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 14.9, 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.51 (dt, *J* = 13.8, 6.7 Hz, 1H), 5.39 (dt, *J* = 15.1, 7.3 Hz, 1H), 3.73 (d, *J* = 7.3 Hz, 2H), 2.44 (s, 3H), 1.97 (q, *J* = 7.1 Hz, 2H), 1.34-1.25 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.55, 141.48, 135.43, 129.59, 128.53, 116.18, 60.24, 34.56, 21.88, 21.65, 13.53.



methyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate[4]

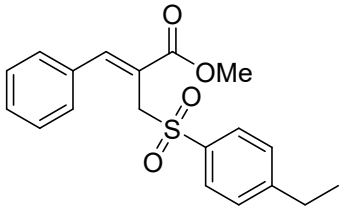
(**5a**) White solid, mp: 59.4-60.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.86

(d, *J* = 8.0 Hz, 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 4H), 7.39-7.37 (m, 3H), 4.50 (s, 2H), 3.59 (s, 3H).



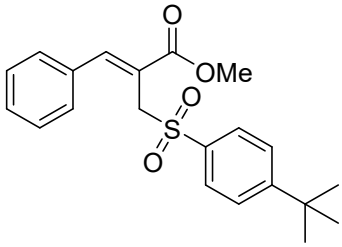
methyl (*Z*)-3-phenyl-2-(tosylmethyl)acrylate[4]

(**5b**) White solid, mp: 120.4-121.6 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.47 (s, 2H), 7.37-7.36 (m, 3H), 7.27-7.26 (d, *J* = 5 Hz, 2H), 4.48 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.90, 146.14, 144.70, 136.14, 133.57, 129.57, 129.12, 128.64, 128.48, 120.93, 55.03, 52.34, 21.57.



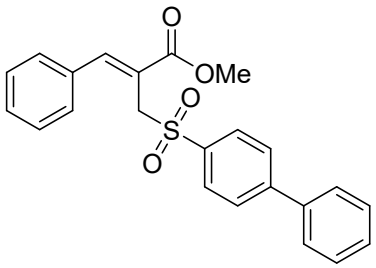
methyl (*Z*)-2-(((4-ethylphenyl)sulfonyl)methyl)-3-phenylacrylate[4]

(**5c**) White solid, mp: 112.1-113.4 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.48-7.46 (m, 2H), 7.37-7.36 (m, 3H), 7.31-7.30 (m, 2H), 4.48 (s, 2H), 3.59 (s, 3H), 2.74-2.69 (m, 2H), 1.26 (t, *J* = 5.0 Hz, 3H).



methyl (*Z*)-2-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)-3-phenylacrylate[4]

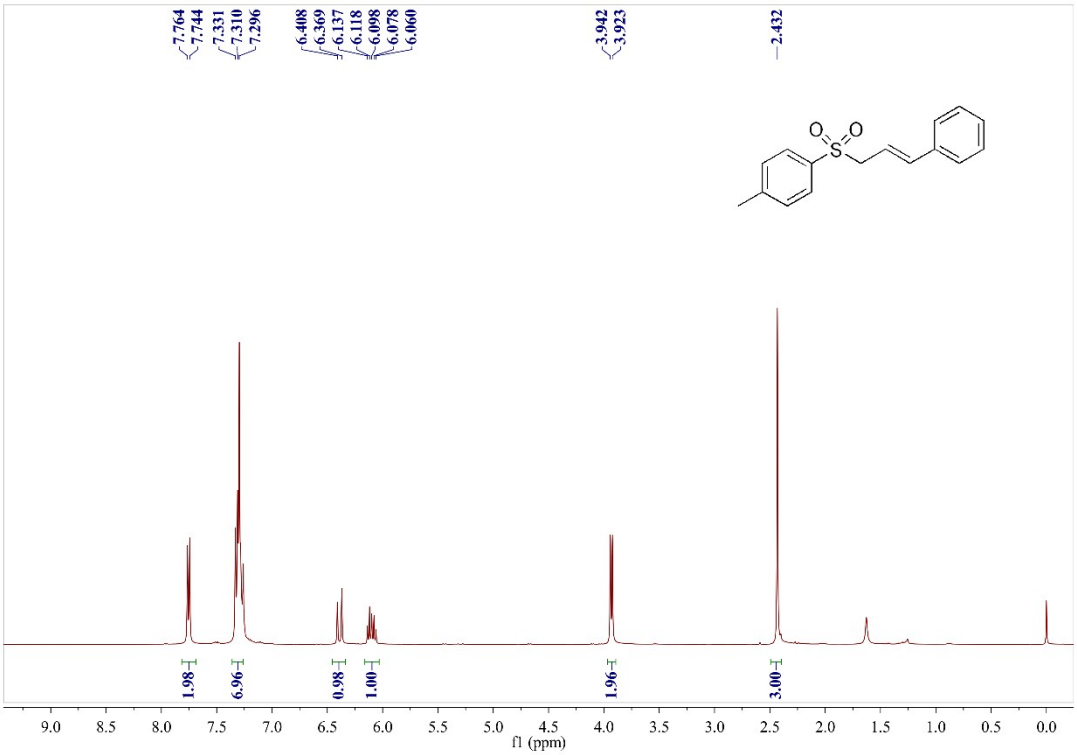
(**5d**) White solid, mp: 99.5-100.2 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.51-7.46 (m, 4H), 7.37-7.36 (m, 3H), 4.48 (s, 2H), 3.58 (s, 3H), 1.34 (s, 9H).

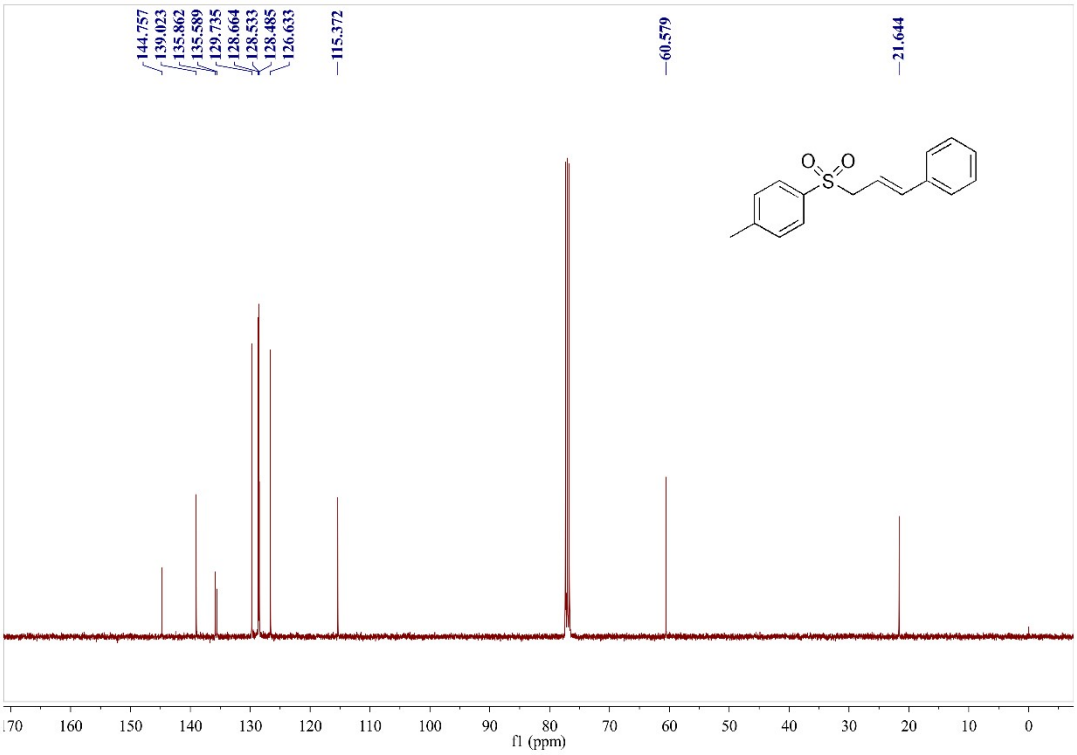


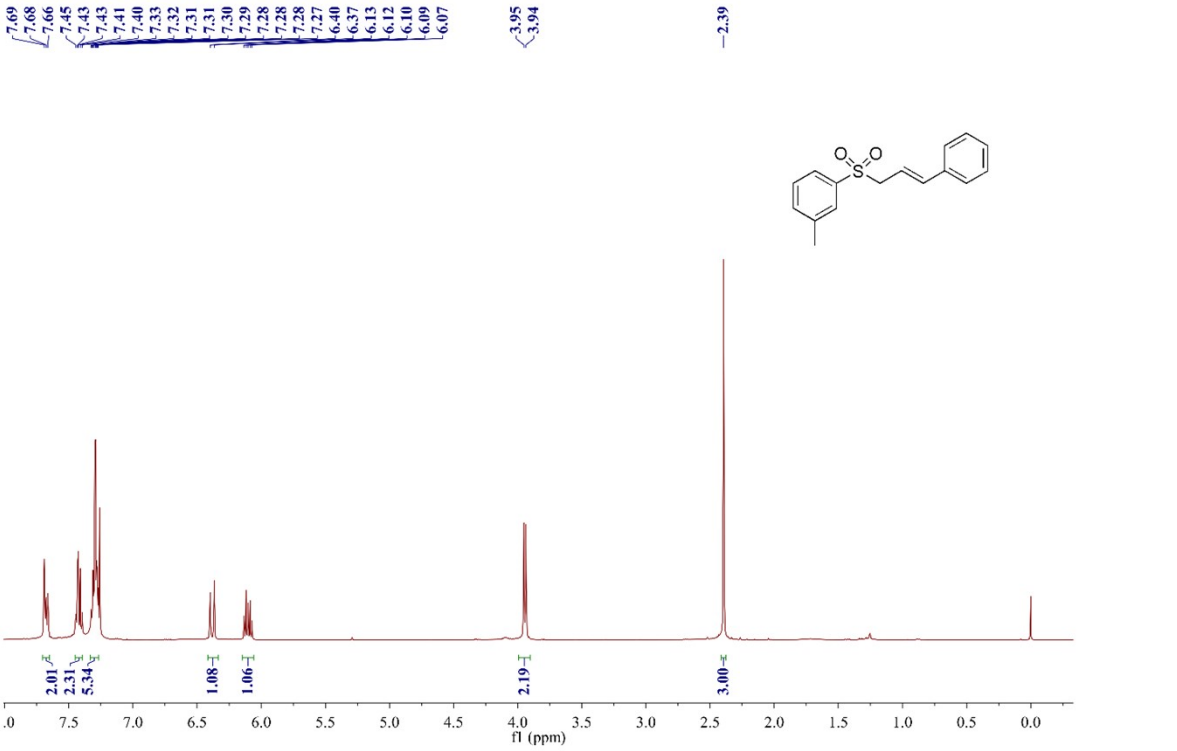
methyl (*Z*)-2-(([1,1'-biphenyl]-4-ylsulfonyl)methyl)-3-phenylacrylate[4]

(**5e**) Light yellow solid, mp: 135.2-136.7 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.50 (t, *J* = 7.0 Hz, 2H), 7.45-7.43 (m, 3H), 7.35-7.34 (m, 3H), 4.55 (s, 2H), 3.62 (s, 3H).

4. NMR spectra for compounds



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7.27
6.40
6.37
6.13
6.12
6.10
6.09
6.07
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2.01
2.31
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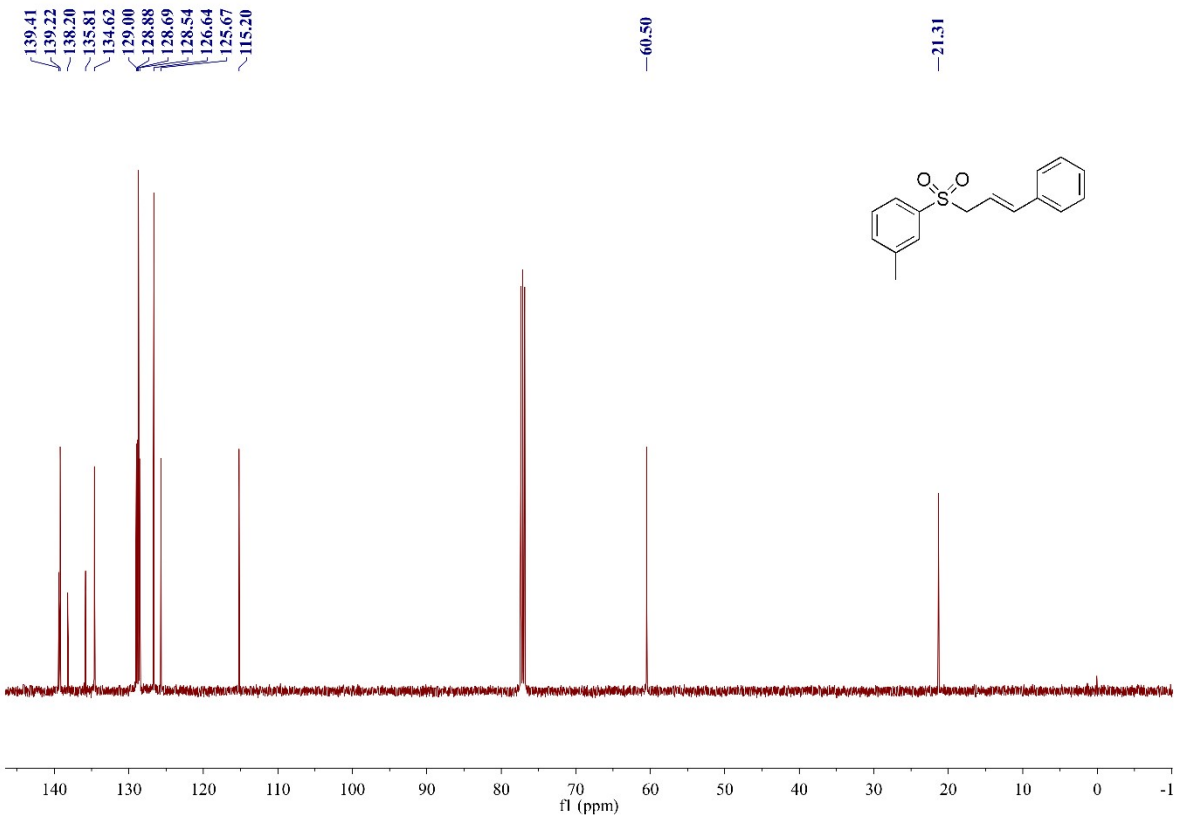
1.06
2.19
3.00
f1 (ppm)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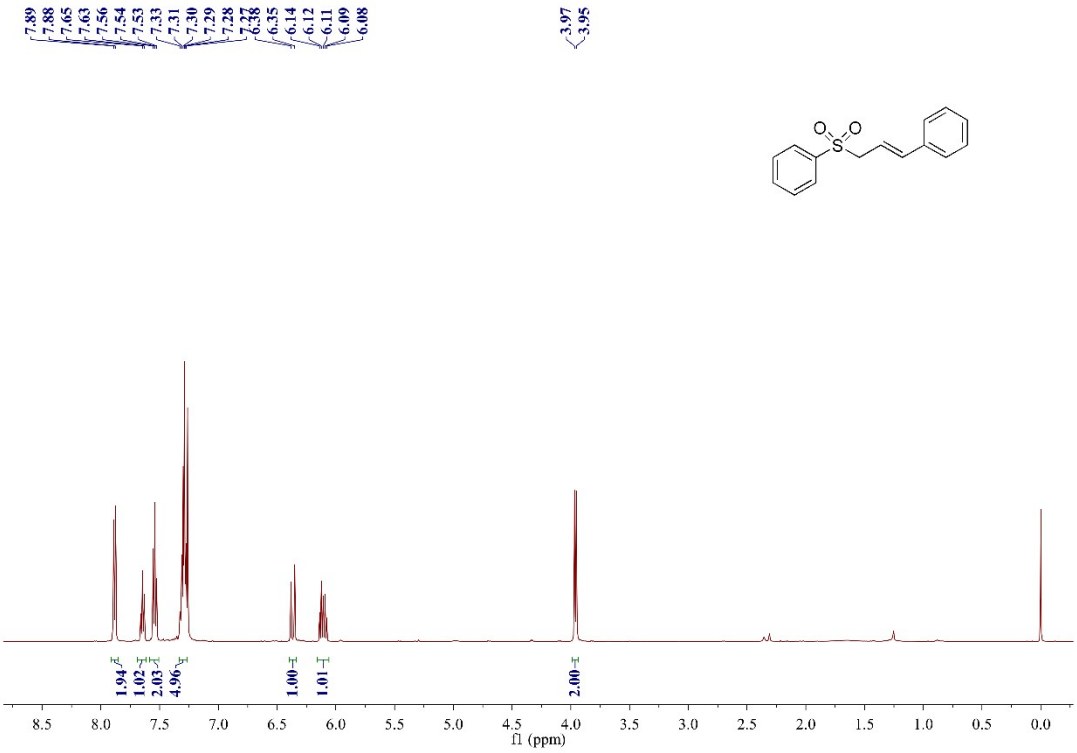
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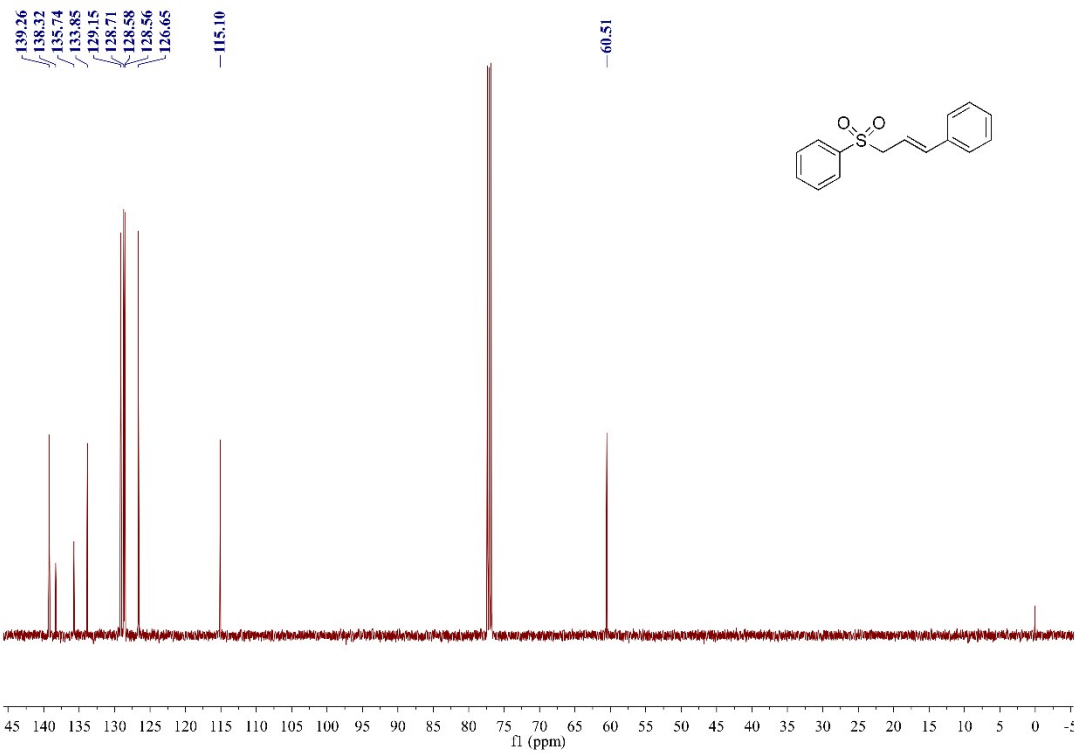
f1 (ppm)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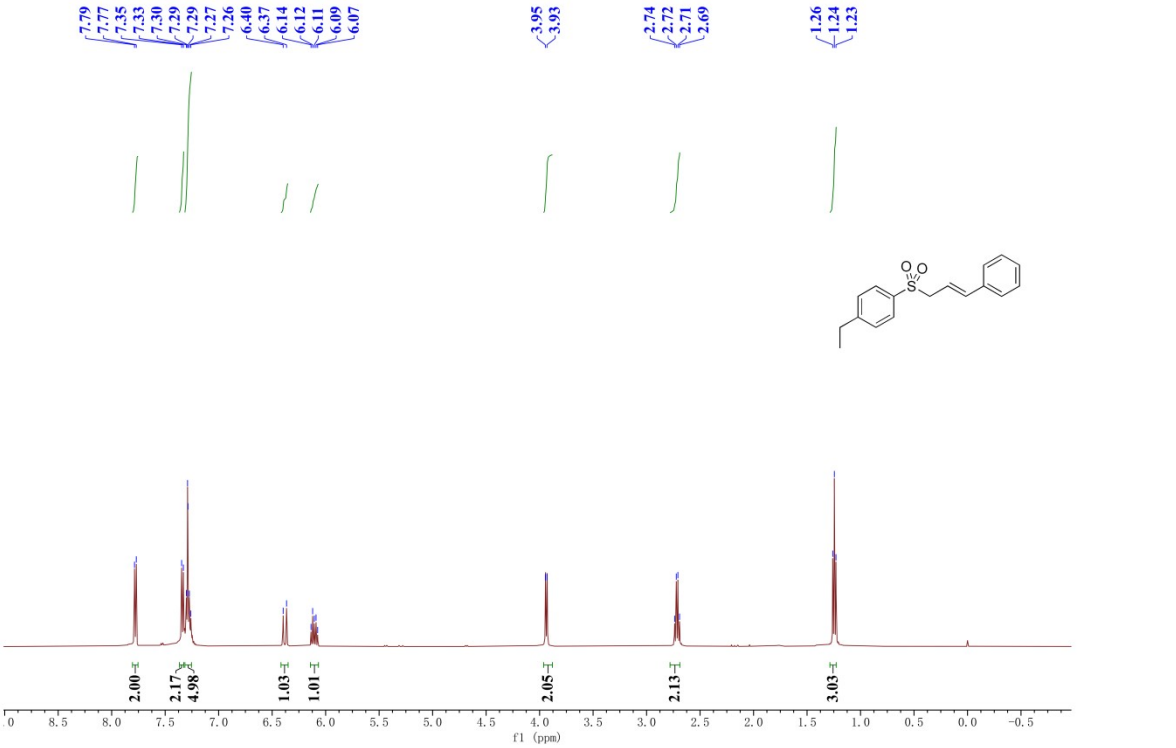
f1 (ppm)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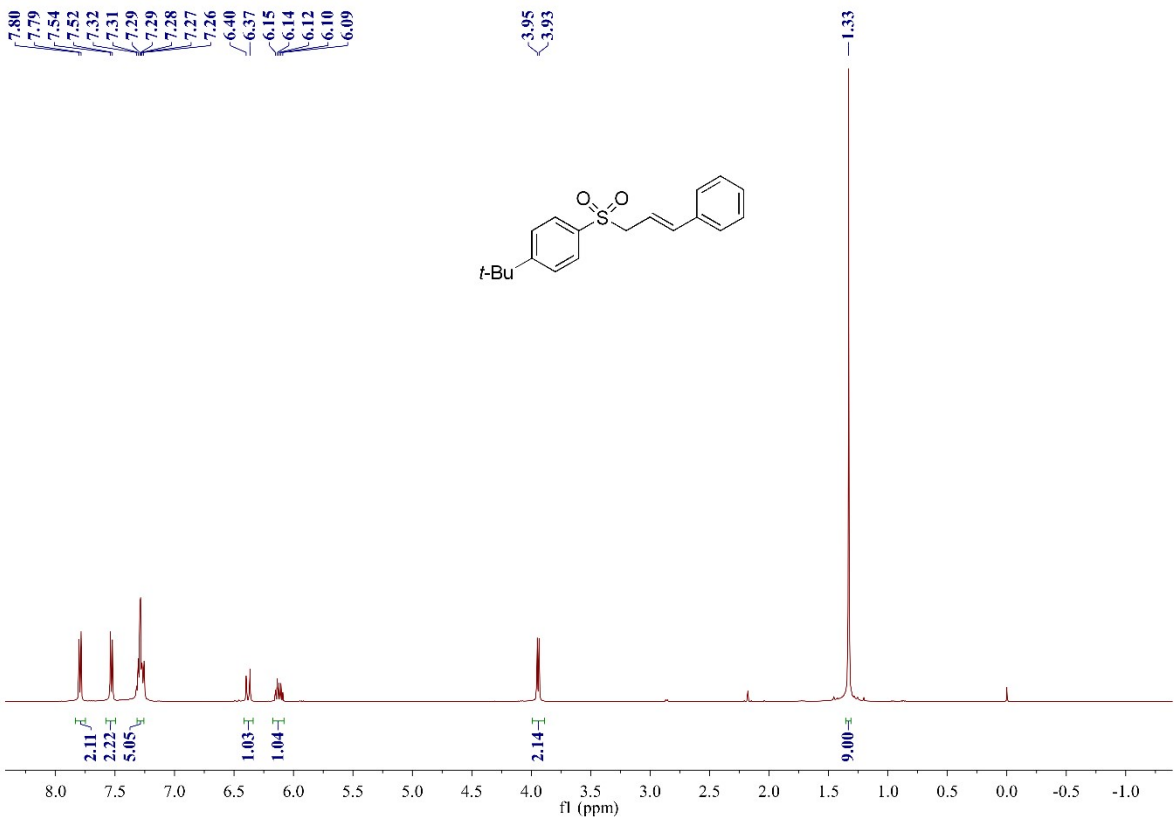
3.03
f1 (ppm)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6.12
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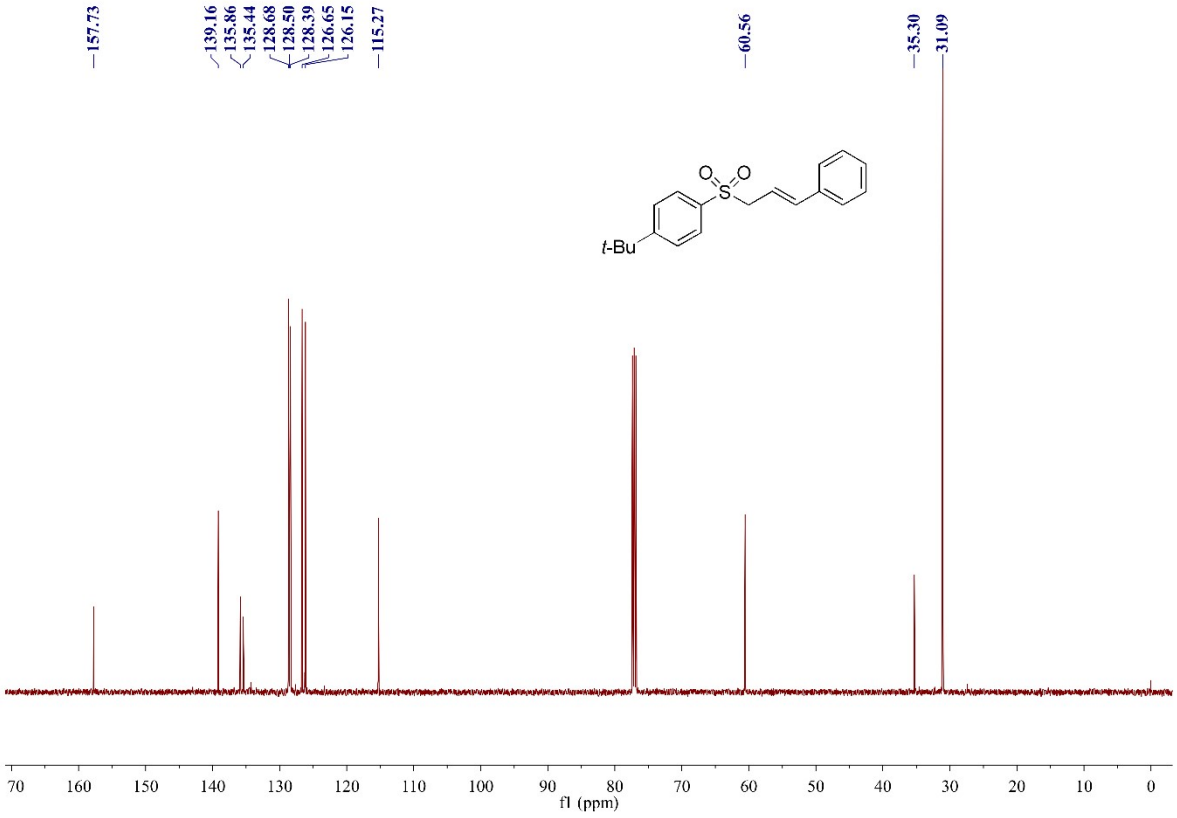
f1 (ppm)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O
O
S
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120
110
100
90
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50
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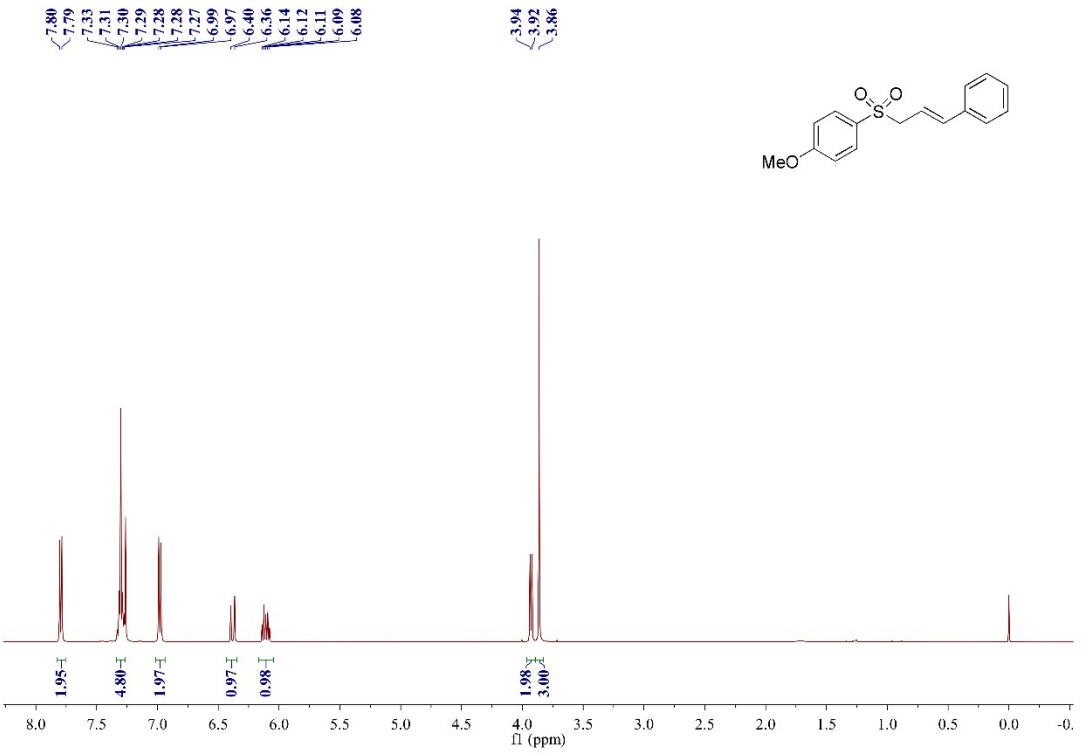
10
0
f1 (ppm)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6.11
6.09
6.08
3.94
3.92
3.86
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O
O
S
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4.80
1.97
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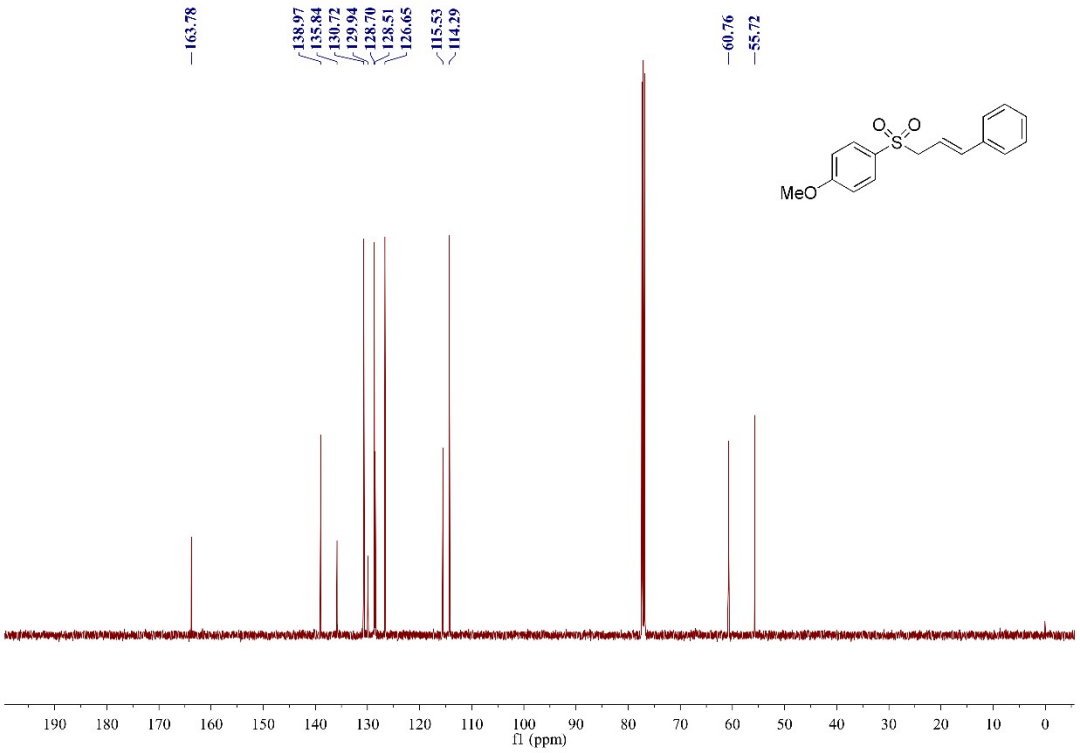
f1 (ppm)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MeO
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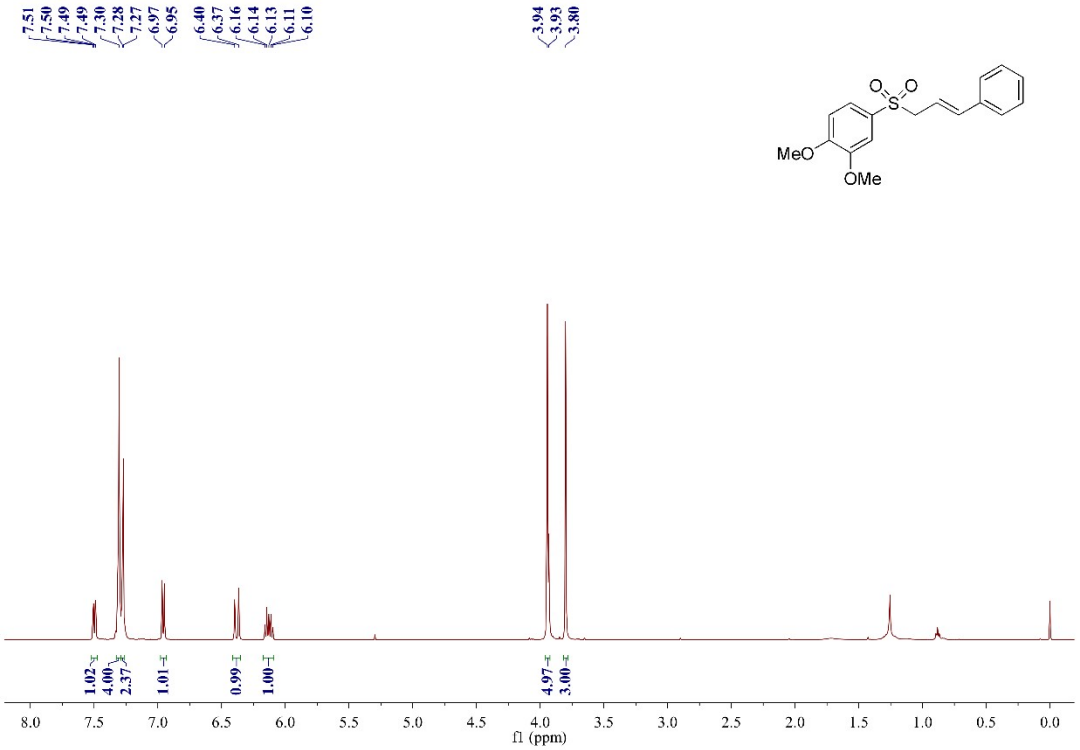
f1 (ppm)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6.40
6.37
6.16
6.14
6.13
6.11
6.10
3.94
3.93
3.80
MeO
OMe
1.02
4.00
2.37
1.01
0.99
1.00
4.97
3.00
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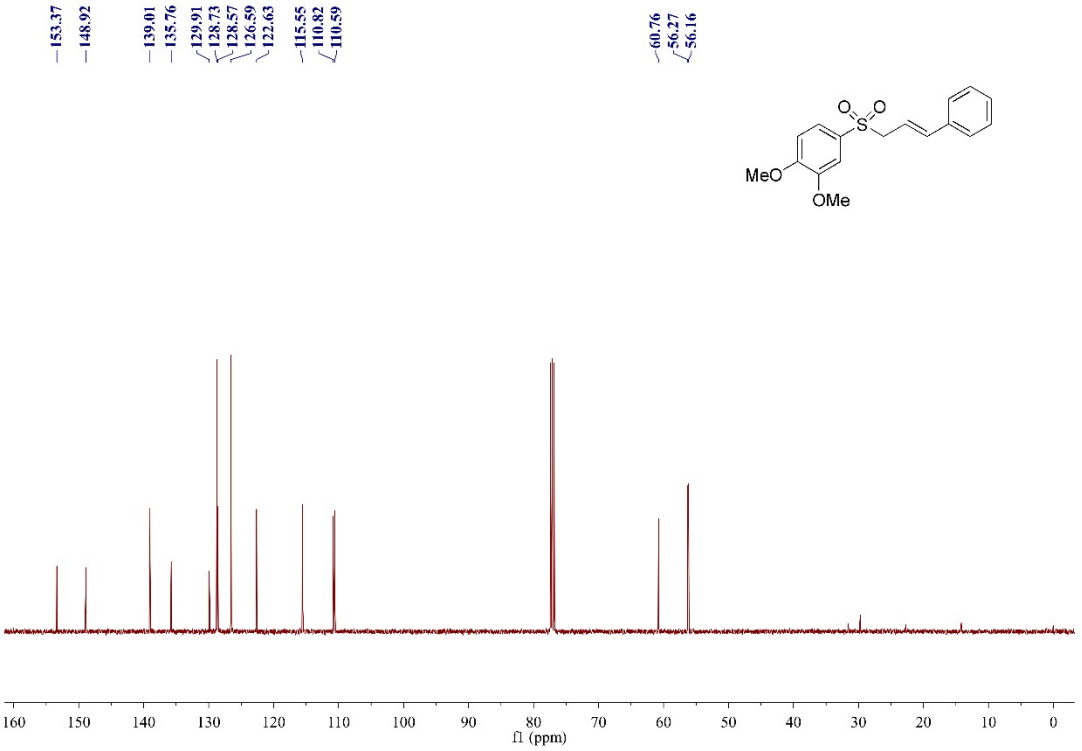
f1 (ppm)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128.57
126.59
122.63
115.55
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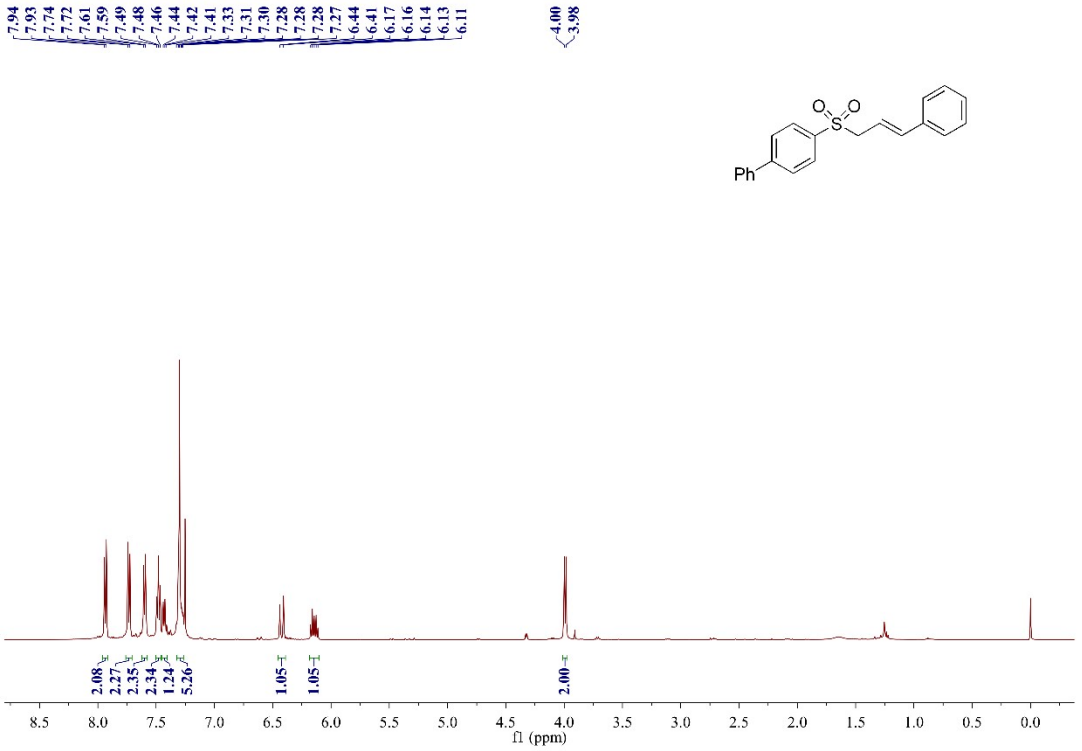
110.59
60.76
56.27
56.16
MeO
OMe
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.33
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7.28
7.28
7.28
7.27
6.44
6.41
6.17
6.16
6.14
6.13
6.11
4.00
3.98
Ph
2.08
2.27
2.35
2.34
1.24
5.26
1.05
1.05
2.00
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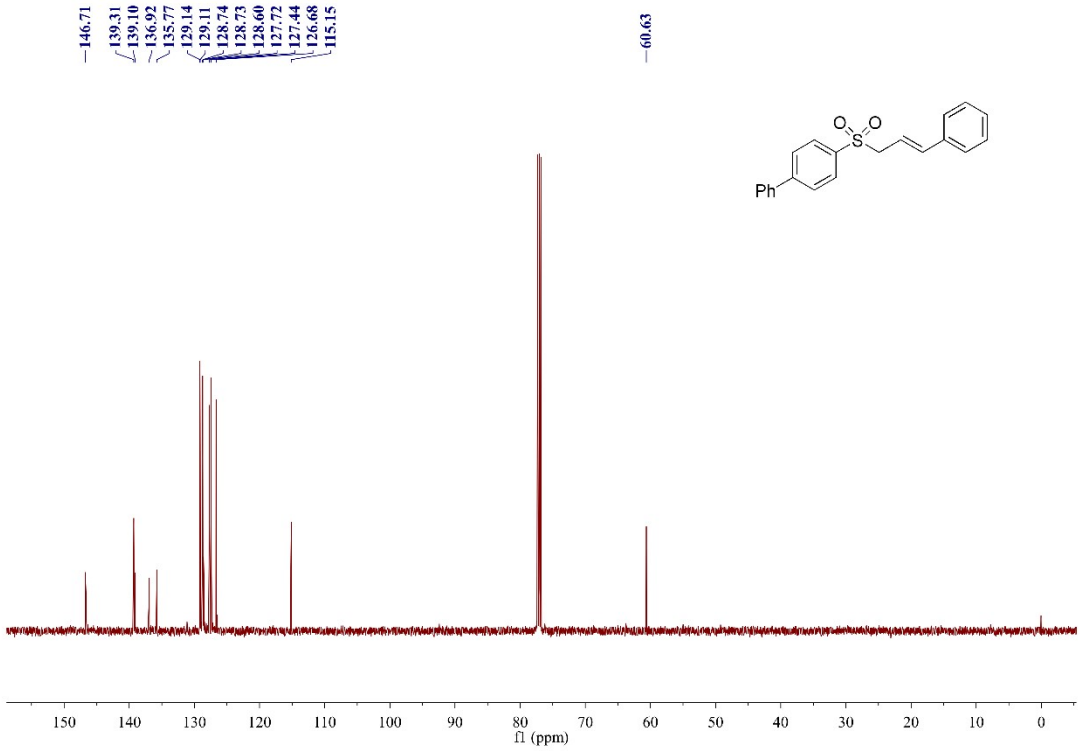
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128.74
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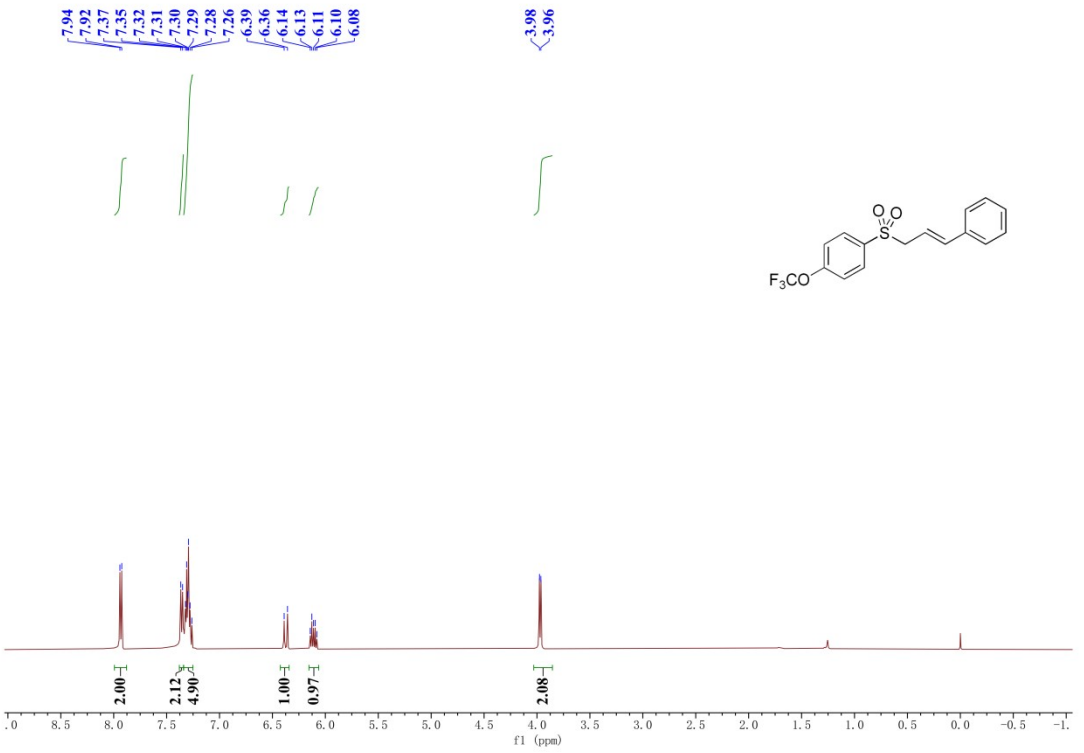
115.15
60.63
Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.29
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7.26
6.39
6.36
6.14
6.13
6.11
6.10
6.08
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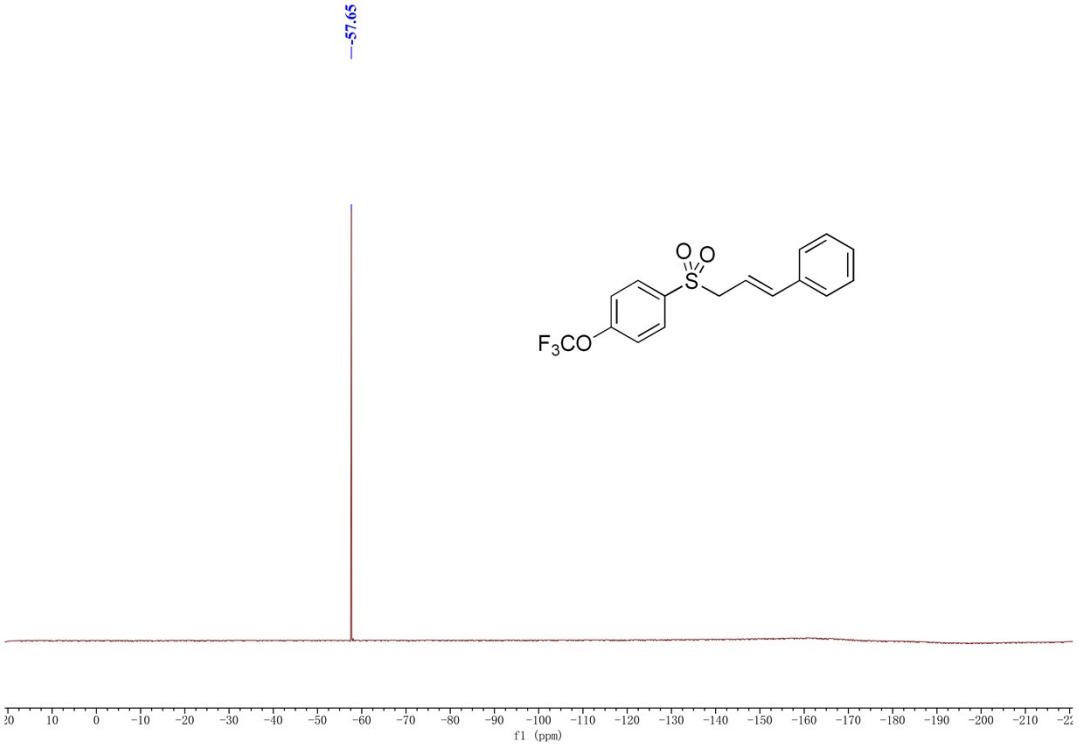
3.96
F3CO
2.00
2.12
4.90
1.00
0.97
2.08
f1 (ppm)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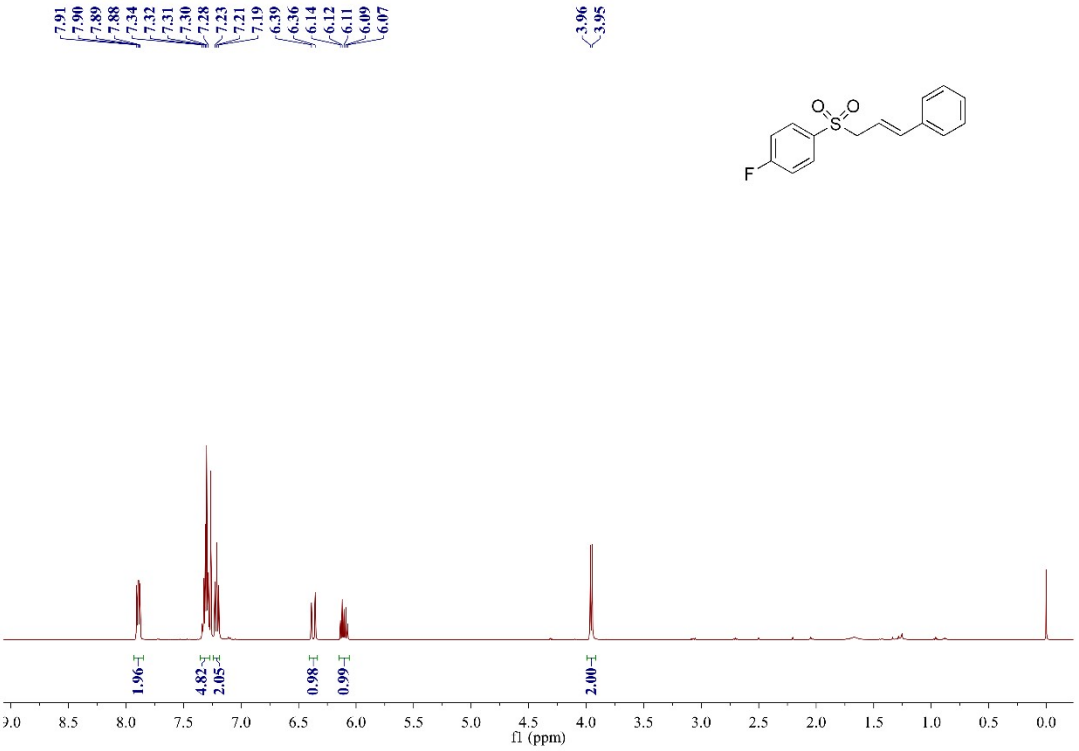
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6.36
6.14
6.12
6.11
6.09
6.07
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O
O
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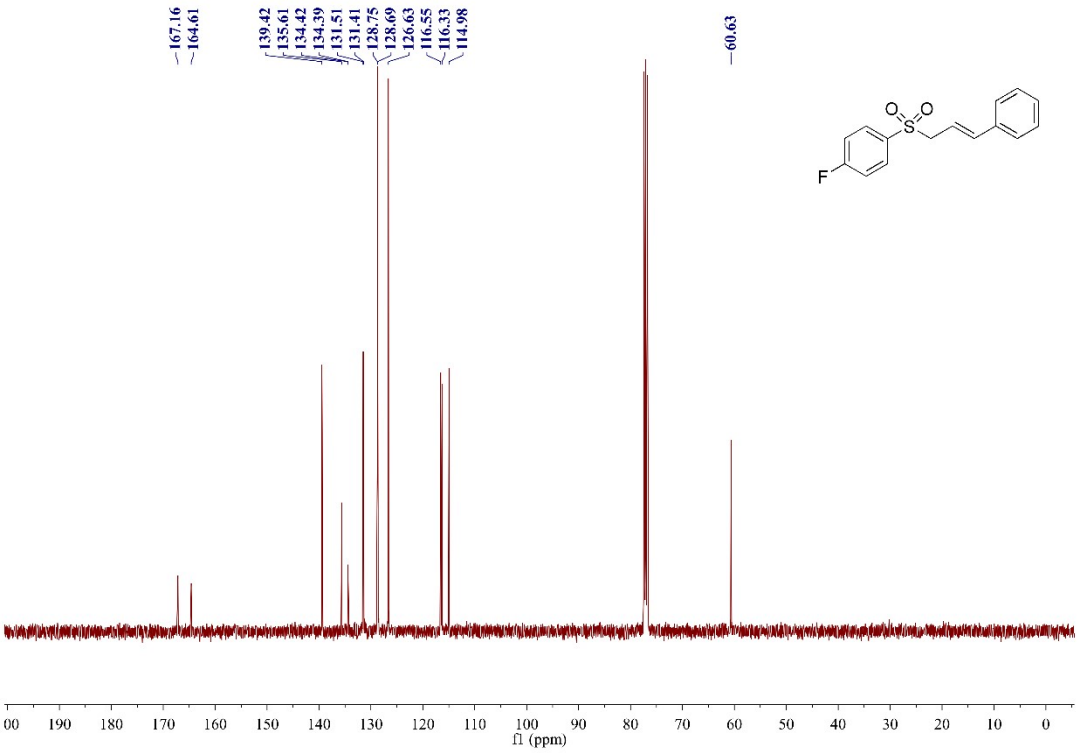
F
1.96
4.82
2.05
0.98
0.99
2.00
f1 (ppm)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131.51
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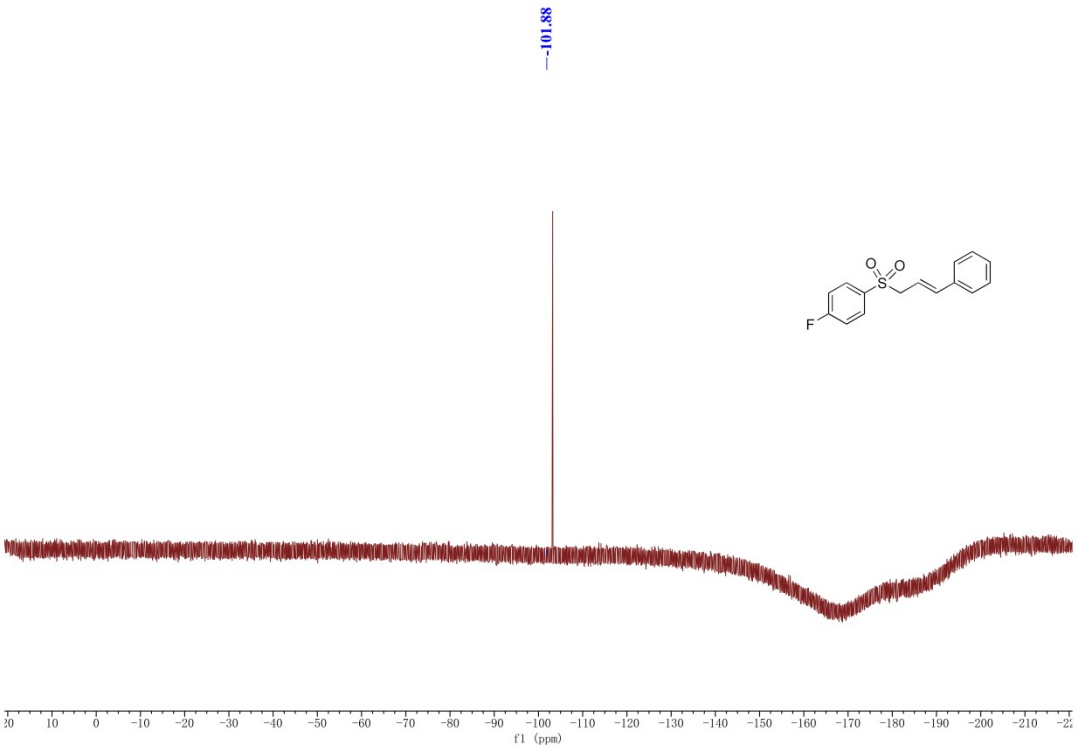
128.69
126.63
116.55
116.33
114.98
60.63
O
O
S
F
f1 (ppm)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O
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F
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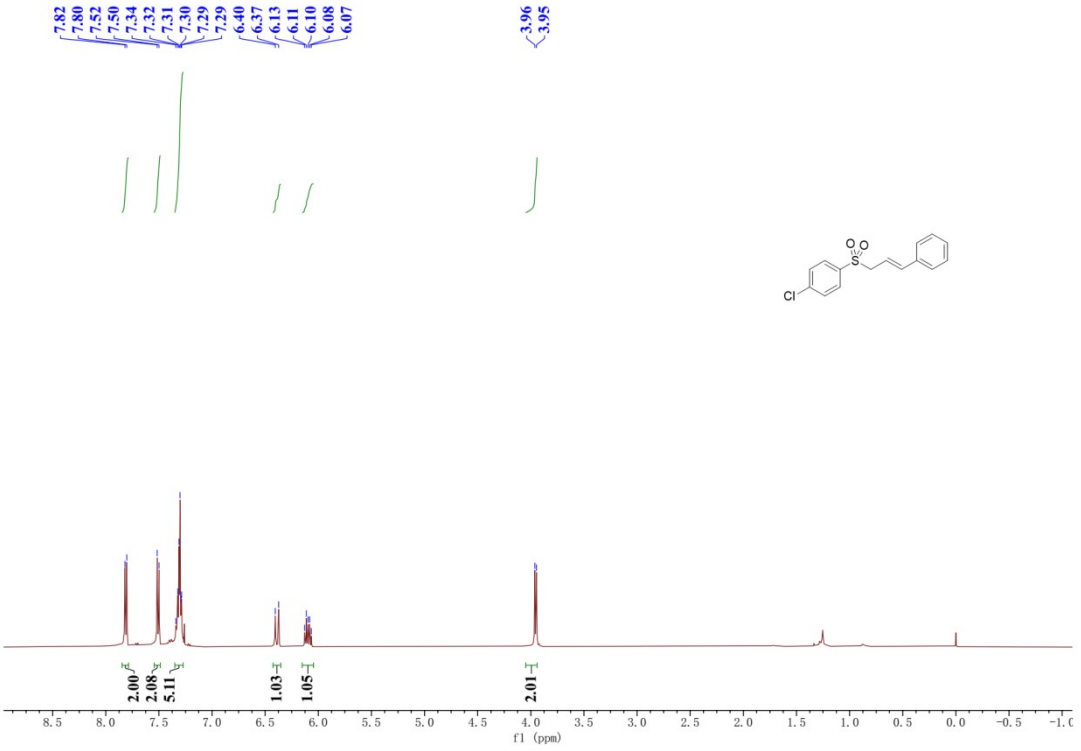
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6.37
6.13
6.11
6.10
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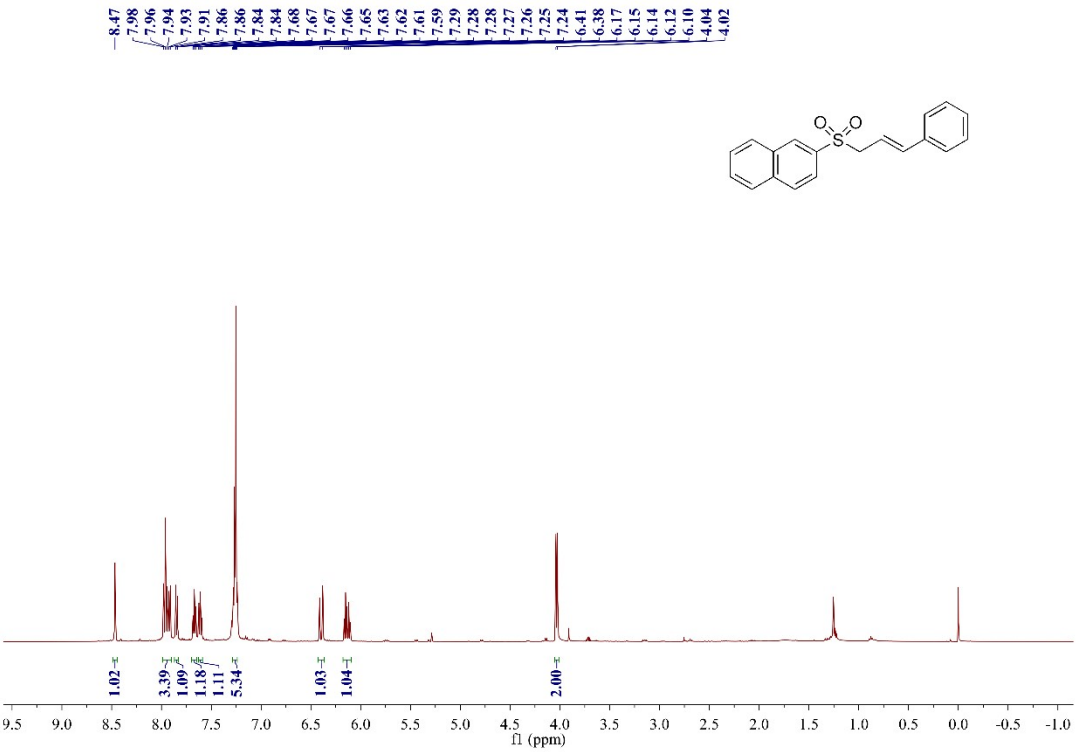
6.07
3.96
3.95
Cl
2.00
2.08
5.11
1.03
1.05
2.01
f1 (ppm)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7.67
7.67
7.66
7.65
7.63
7.62
7.61
7.59
7.29
7.28
7.28
7.27
7.26
7.25
7.24
6.41
6.38
6.17
6.15
6.14
6.12
6.10
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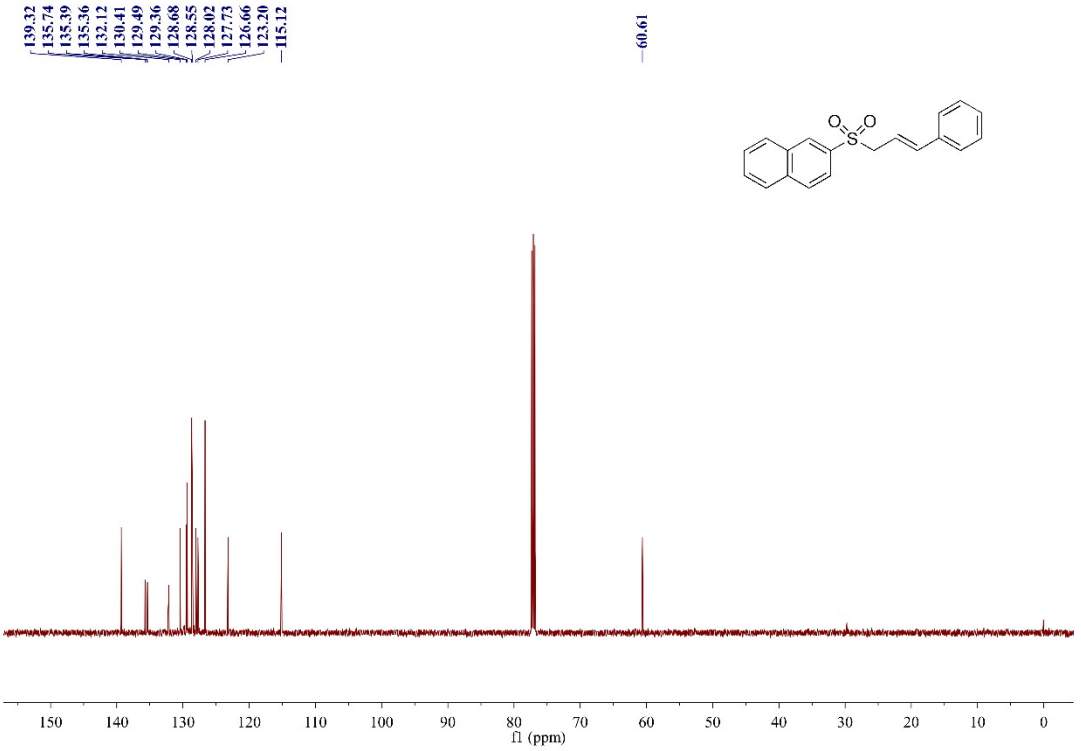
1.18
1.11
5.34
1.03
1.04
2.00
f1 (ppm)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130.41
129.49
129.36
128.68
128.55
128.02
127.73
126.66
123.20
115.12
60.61
O
O
S
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130
120
110
100
90
80
70
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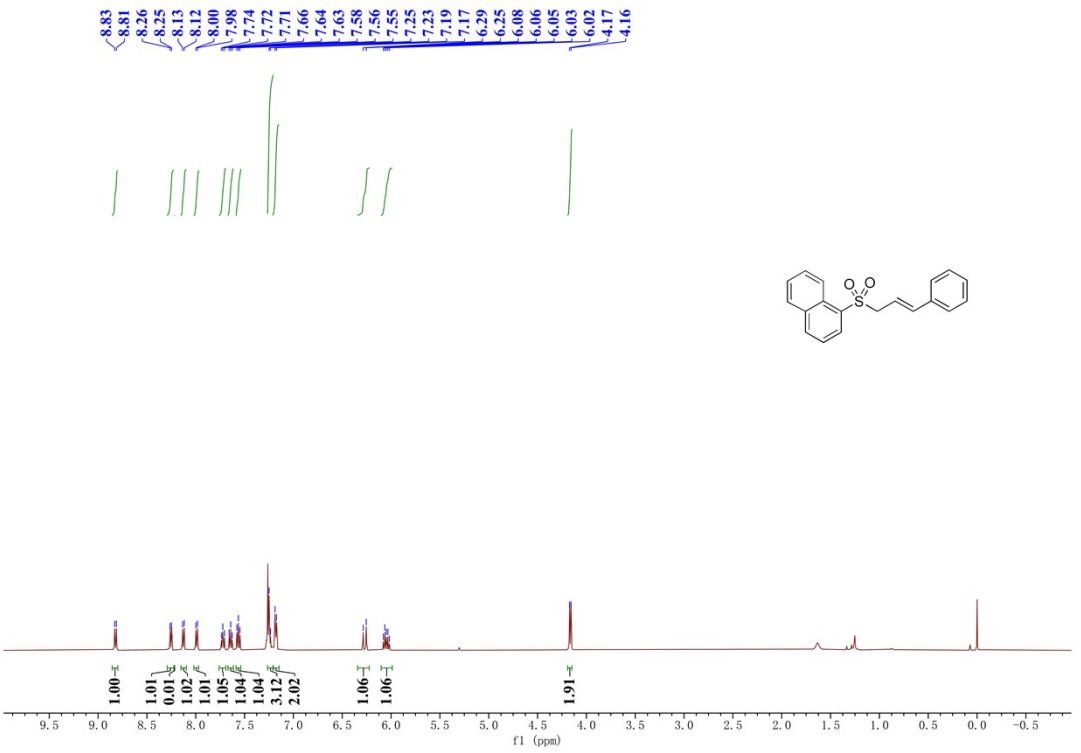
50
40
30
20
10
0
f1 (ppm)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7.64
7.63
7.58
7.56
7.55
7.25
7.23
7.19
7.17
6.29
6.25
6.08
6.06
6.05
6.03
6.02
4.17
4.16
O
O
S
1.00
1.01
0.01
1.02
1.01
1.05
1.04
1.04
3.12
2.02
1.06
1.06
1.91
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
1.5
1.0
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0.0
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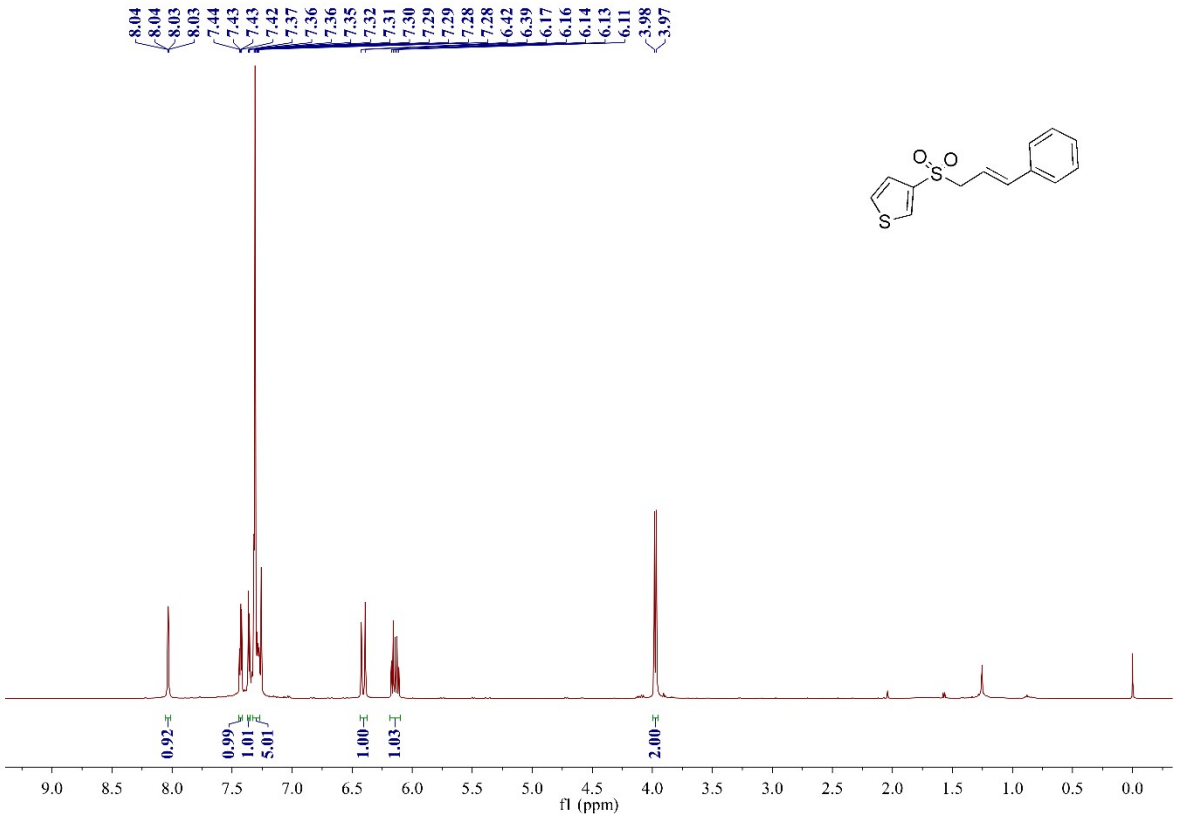
f1 (ppm)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7.31
7.30
7.29
7.29
7.28
7.28
6.42
6.39
6.17
6.16
6.14
6.13
6.11
3.98
3.97
O
O
S
S
0.92
0.99
1.01
5.01
1.00
1.03
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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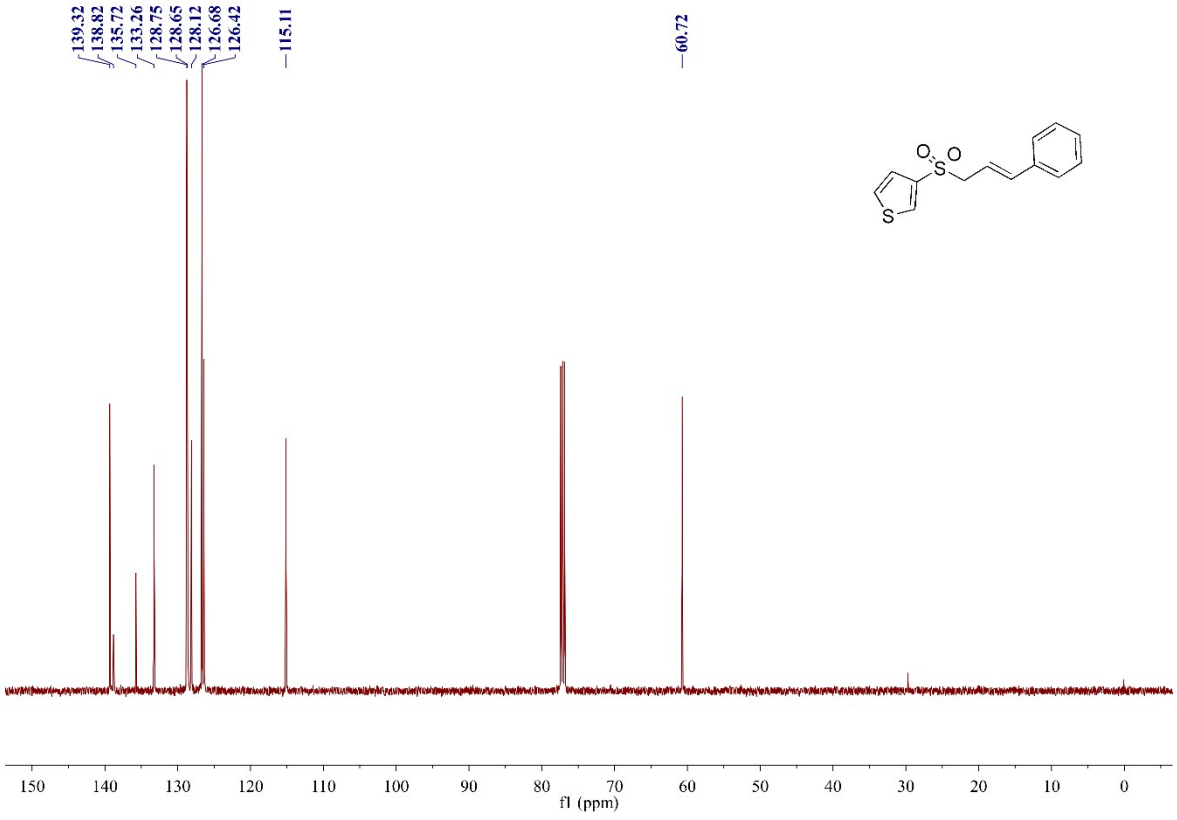
0.0
f1 (ppm)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115.11
60.72
O
O
S
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110
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70
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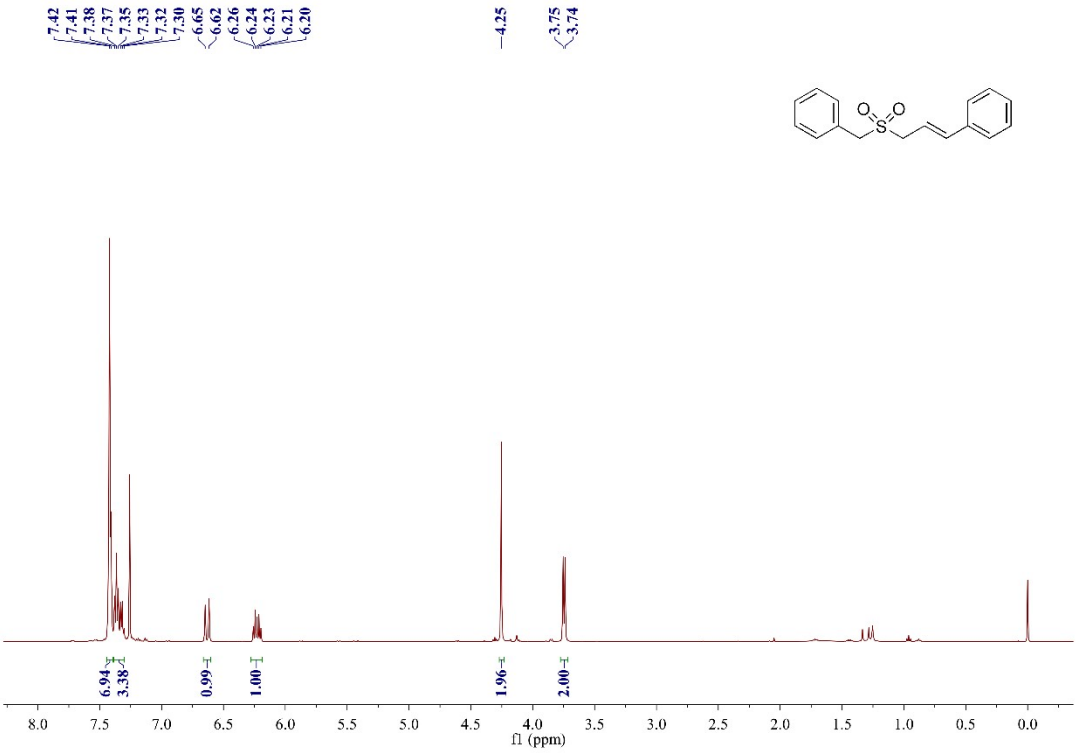
50
40
30
20
10
0
f1 (ppm)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6.24
6.23
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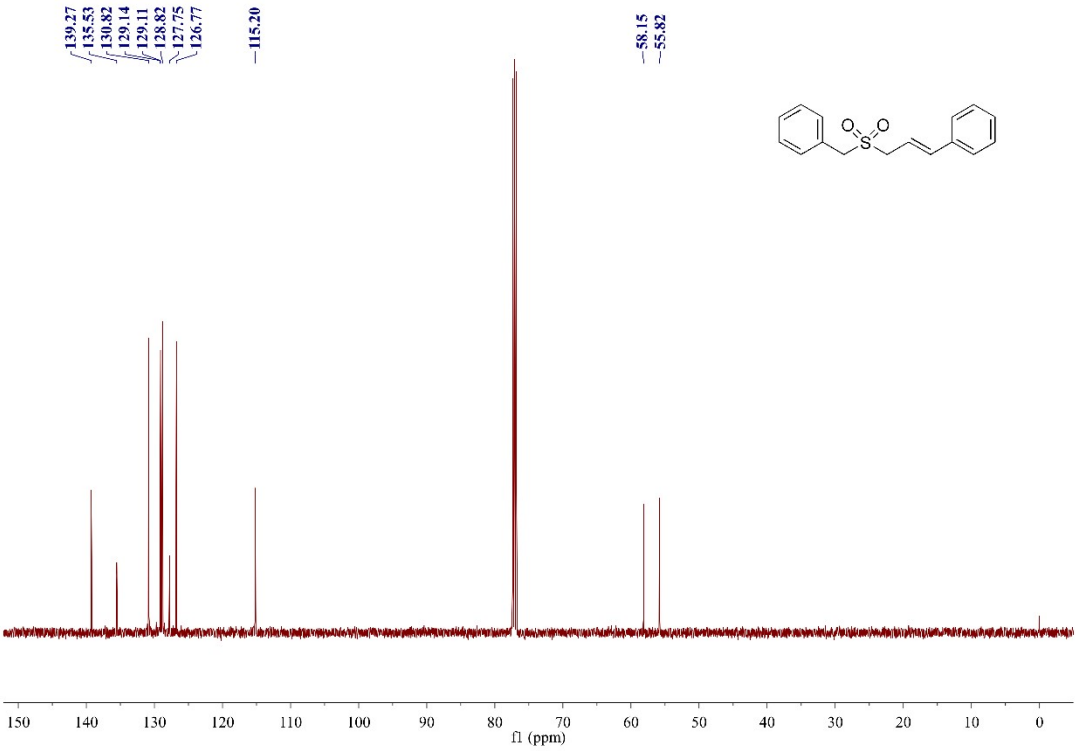
3.75
3.74
6.94
3.38
0.99
1.00
1.96
2.00
f1 (ppm)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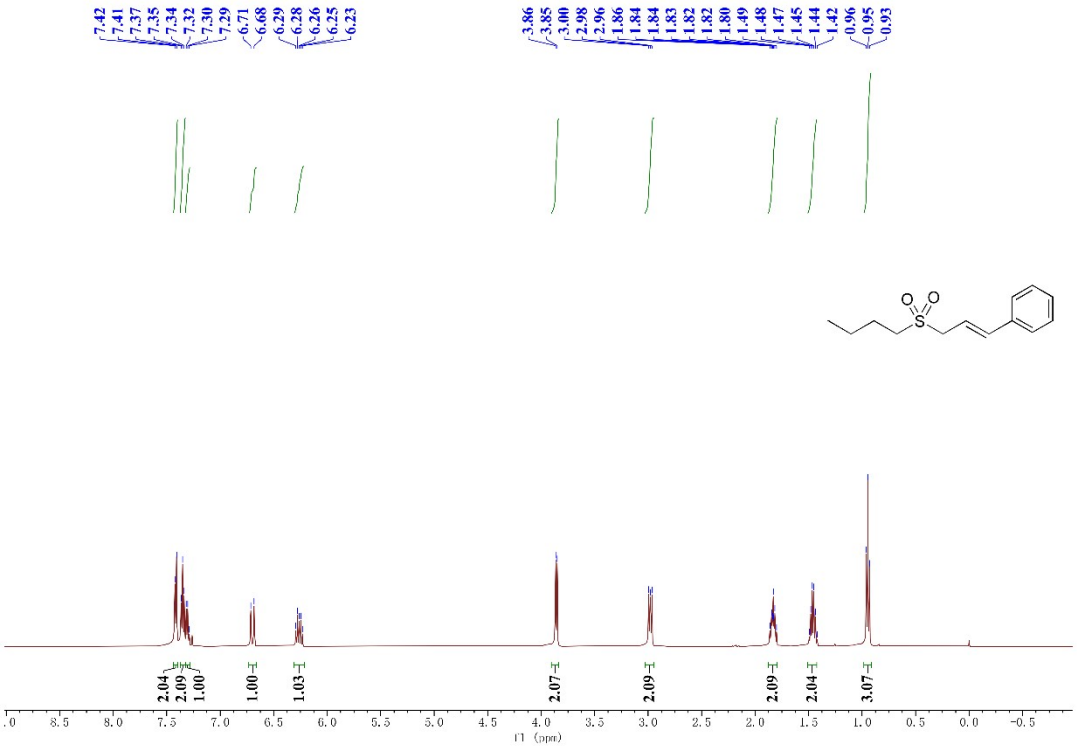
f1 (ppm)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6.26
6.25
6.23
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3.85
3.00
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2.96
1.86
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1.84
1.83
1.82
1.82
1.80
1.49
1.48
1.47
1.45
1.44
1.42
0.96
0.95
0.93
O
O
S
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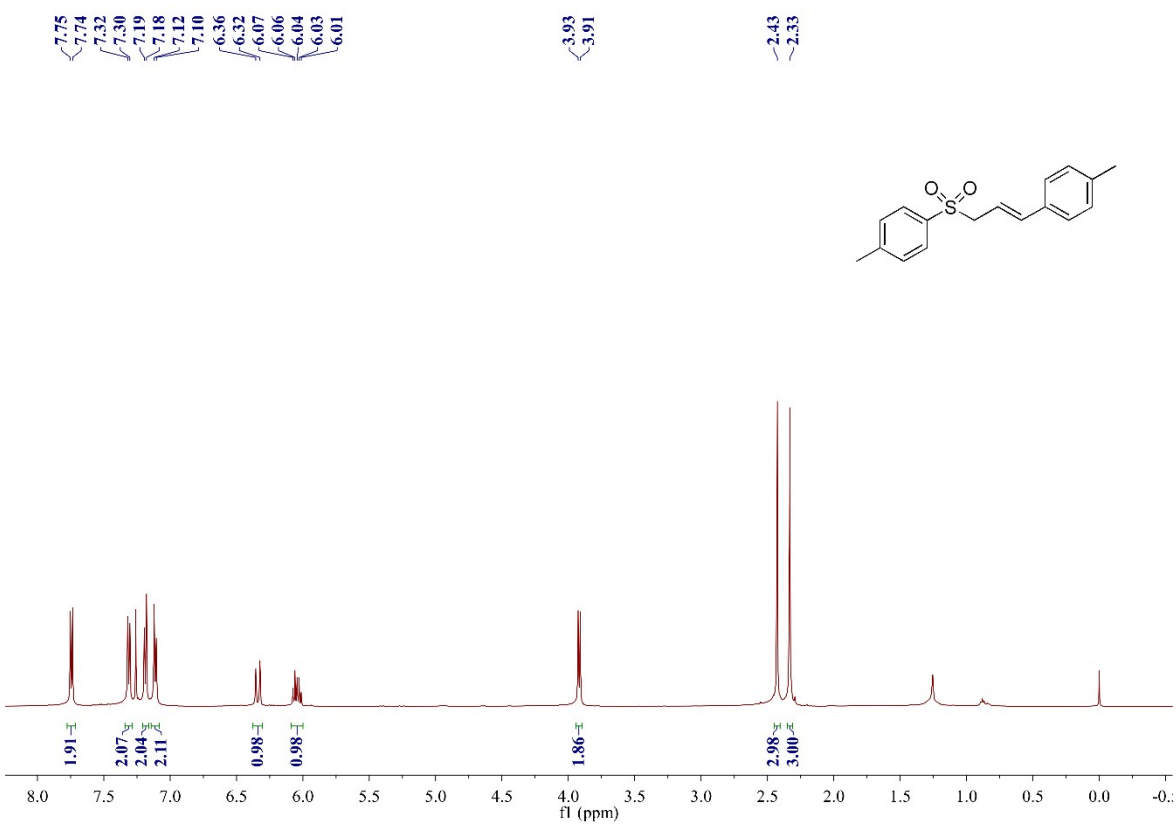
1.00
1.00
1.03
2.07
2.09
2.09
2.04
3.07
f1 (ppm)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6.06
6.04
6.03
6.01
3.93
3.91
2.43
2.33
O
O
S
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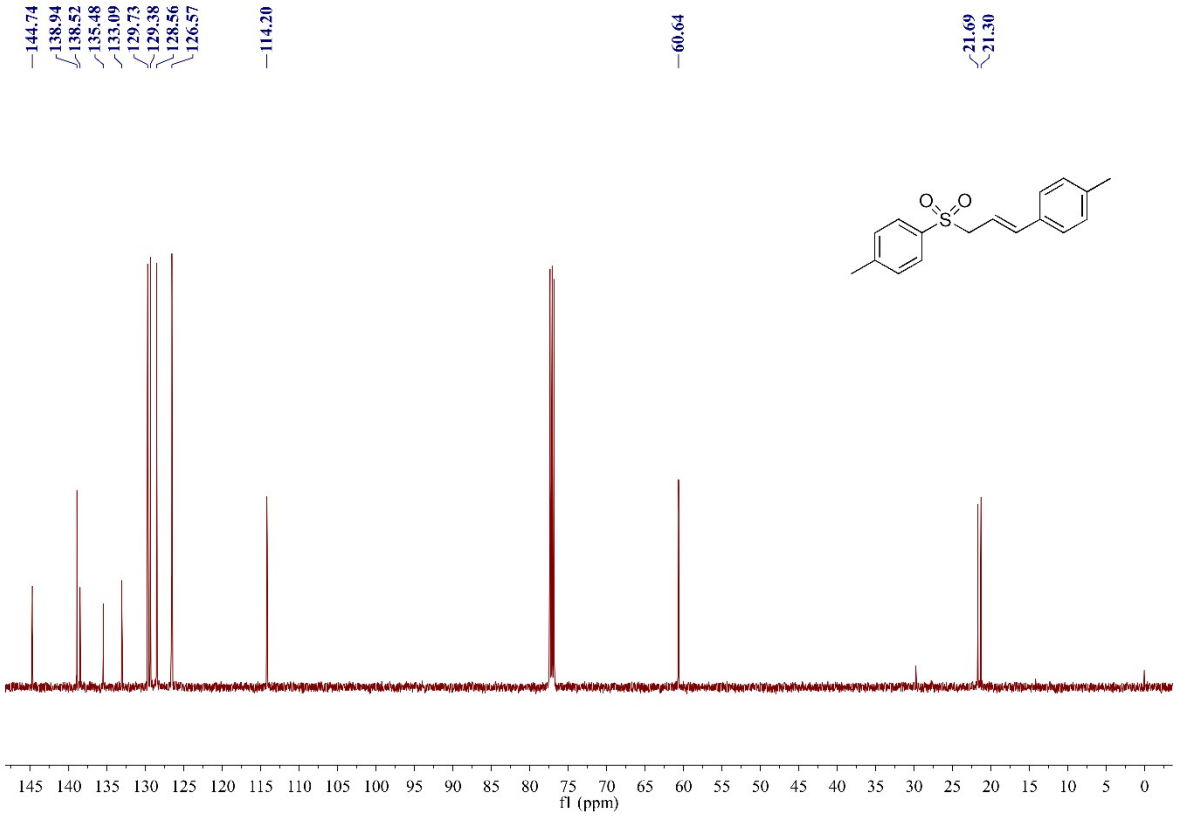
2.07
2.04
2.11
0.98
0.98
1.86
2.98
3.00
f1 (ppm)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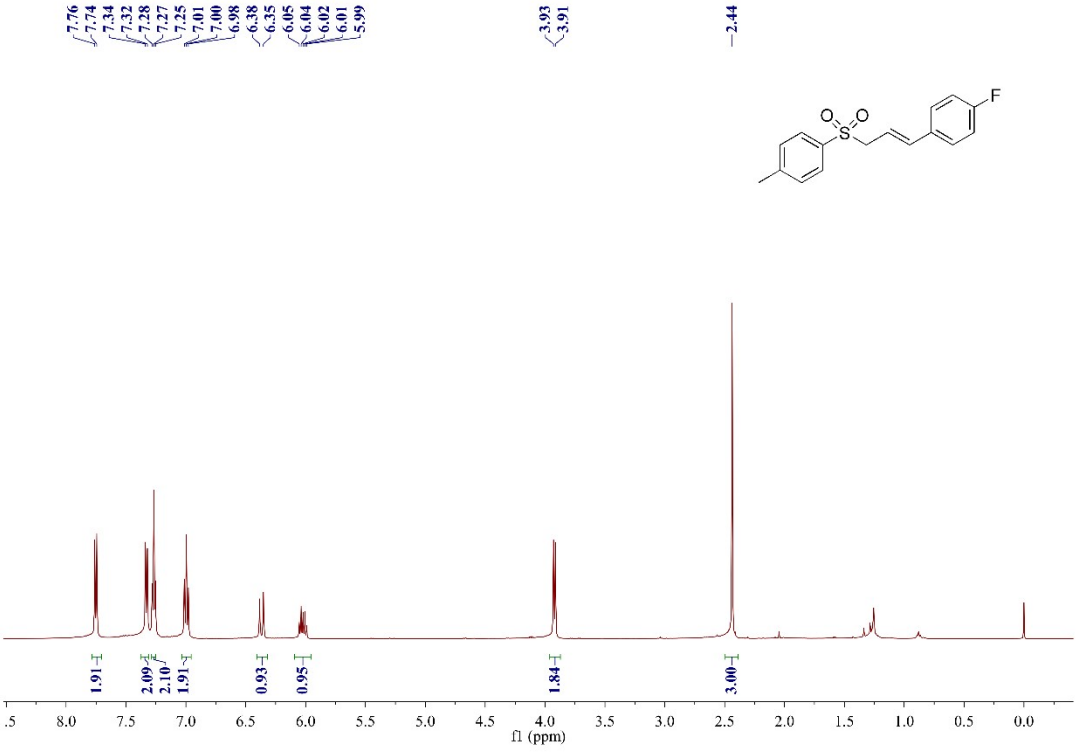
O
S
O
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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6.38
6.35
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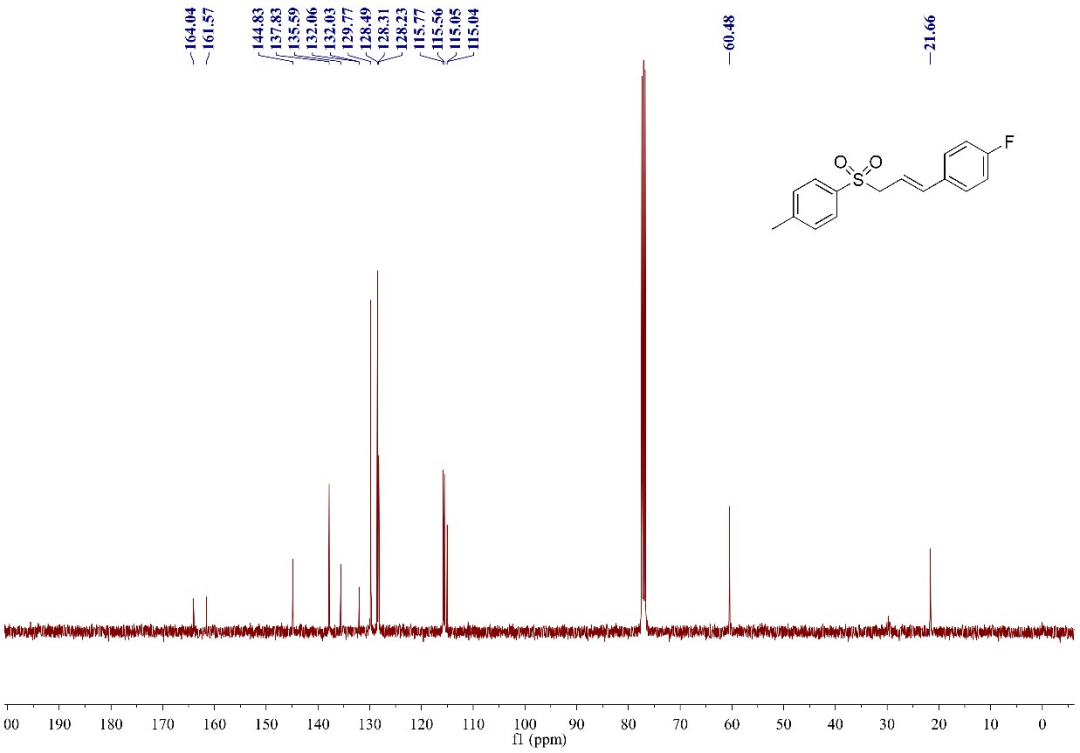
6.04
6.02
6.01
5.99
3.93
3.91
2.44
O
S
O
F
1.91
2.09
2.10
1.91
0.93
0.95
1.84
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.49
128.31
128.23
115.77
115.56
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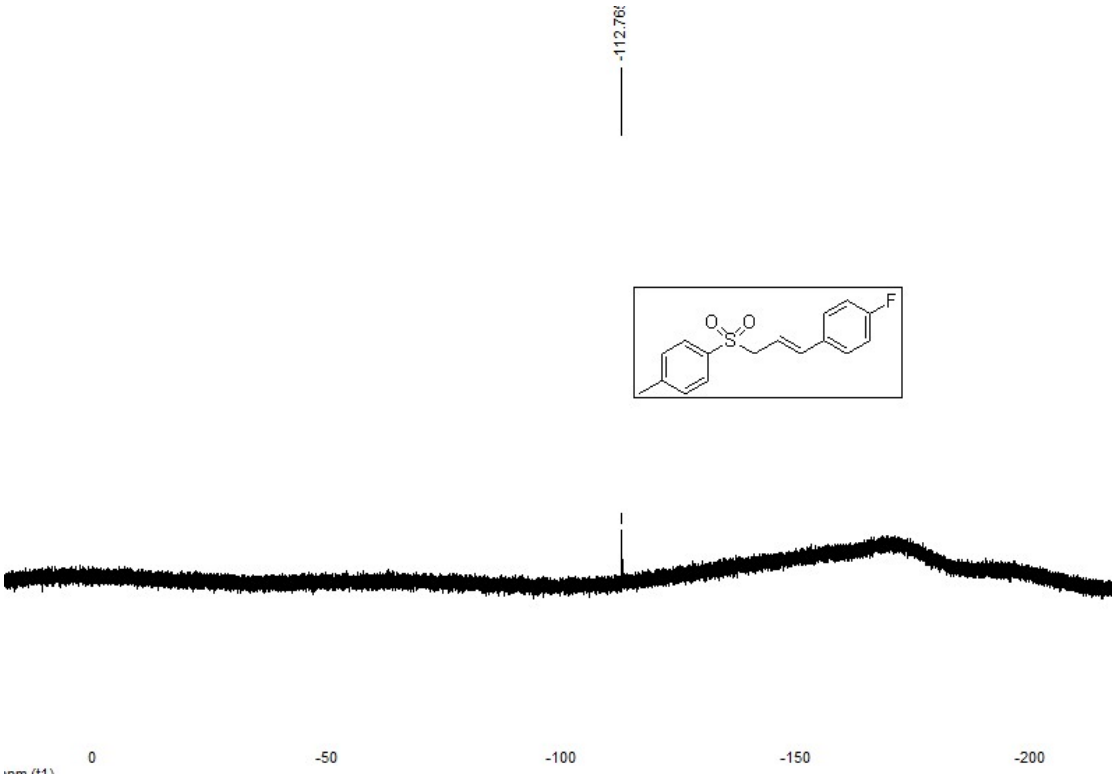
115.04
60.48
21.66
O
S
O
F
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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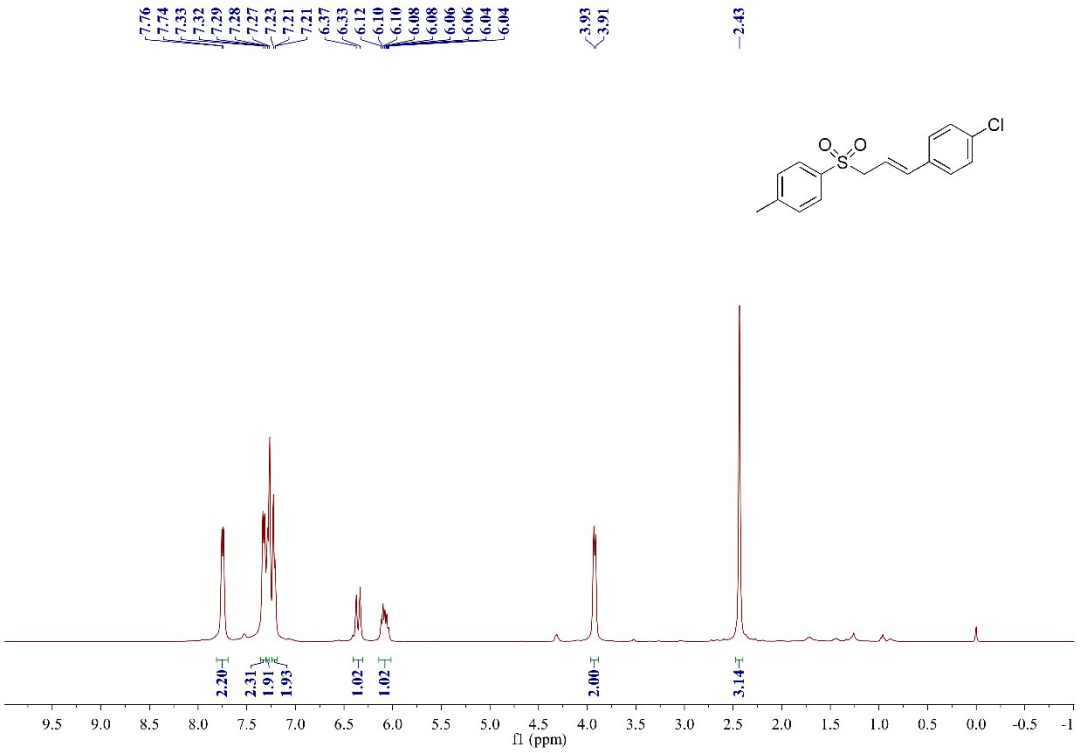
O
S
O
F
0 -50 -100 -150 -200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6.12
6.10
6.10
6.08
6.08
6.06
6.06
6.04
6.04
3.93
3.91
2.43
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1.93
1.02
1.02
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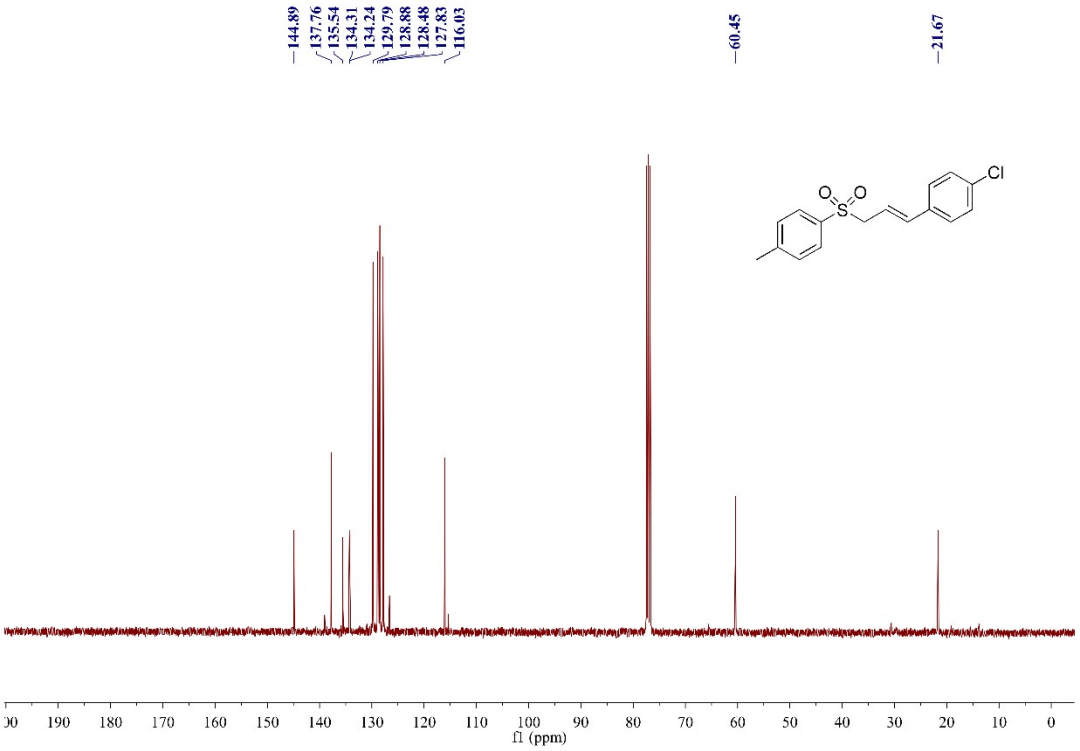
3.14
f1 (ppm)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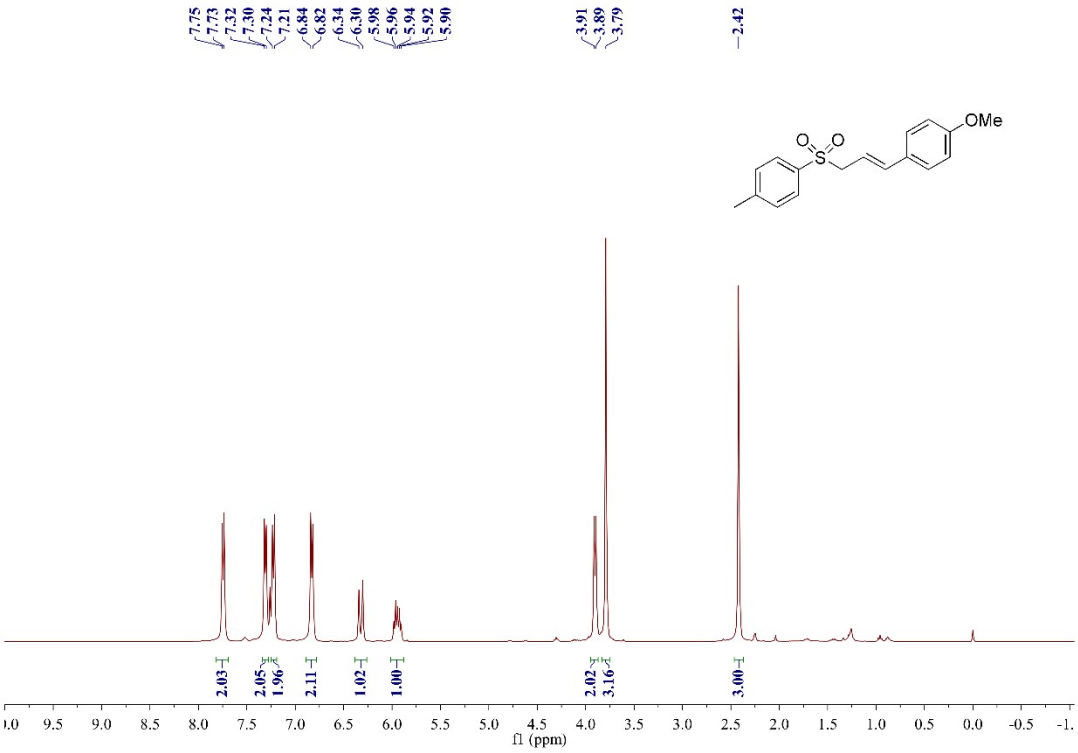
116.03
60.45
21.67
Cl
O
O
S
f1 (ppm)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5.94
5.92
5.90
3.91
3.89
3.79
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OMe
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2.02
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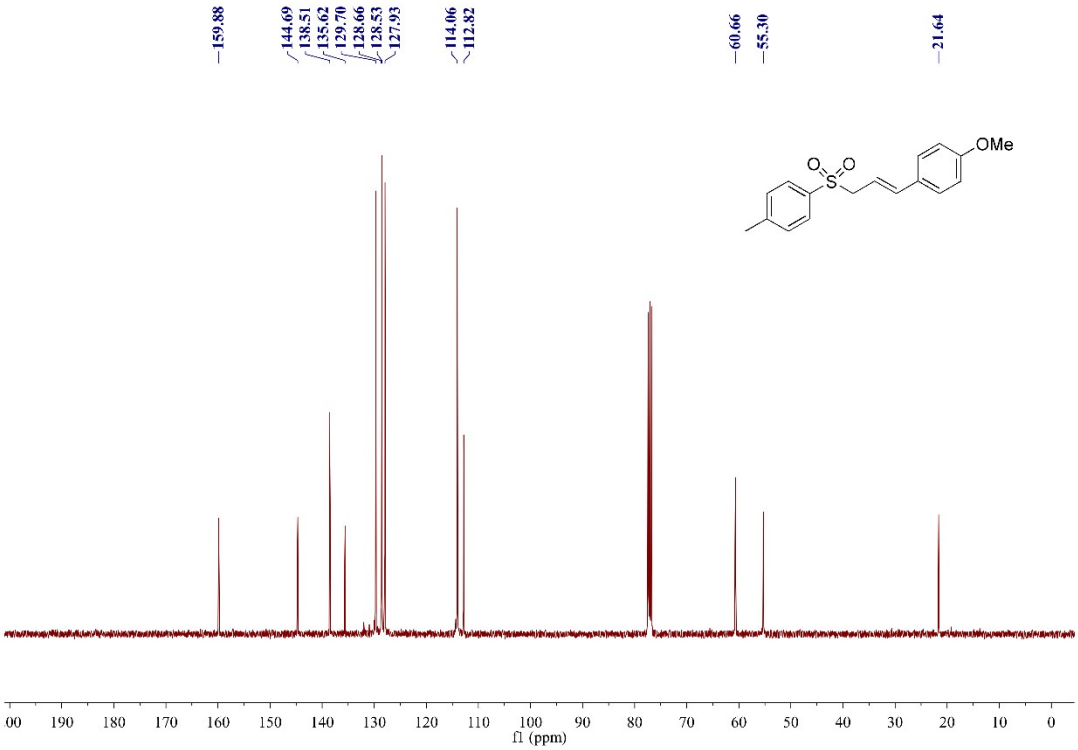
3.00
f1 (ppm)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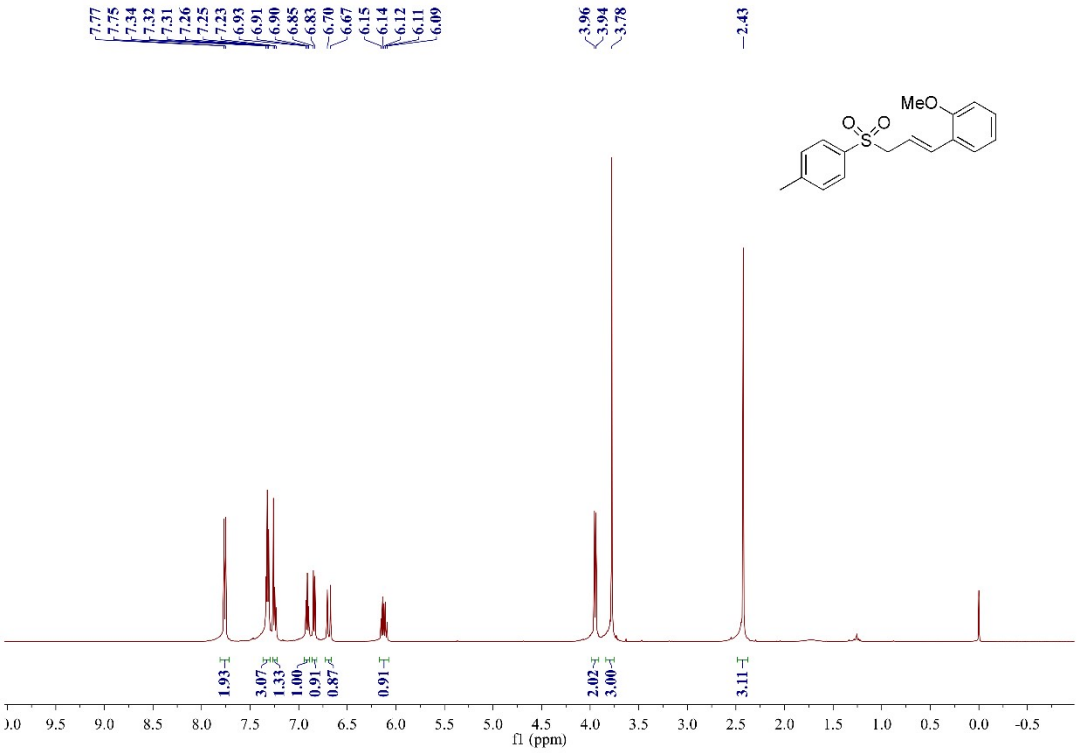
114.06
112.82
60.66
55.30
21.64
OMe
f1 (ppm)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6.70
6.67
6.15
6.14
6.12
6.11
6.09
3.96
3.94
3.78
2.43
MeO
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0.91
0.87
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2.02
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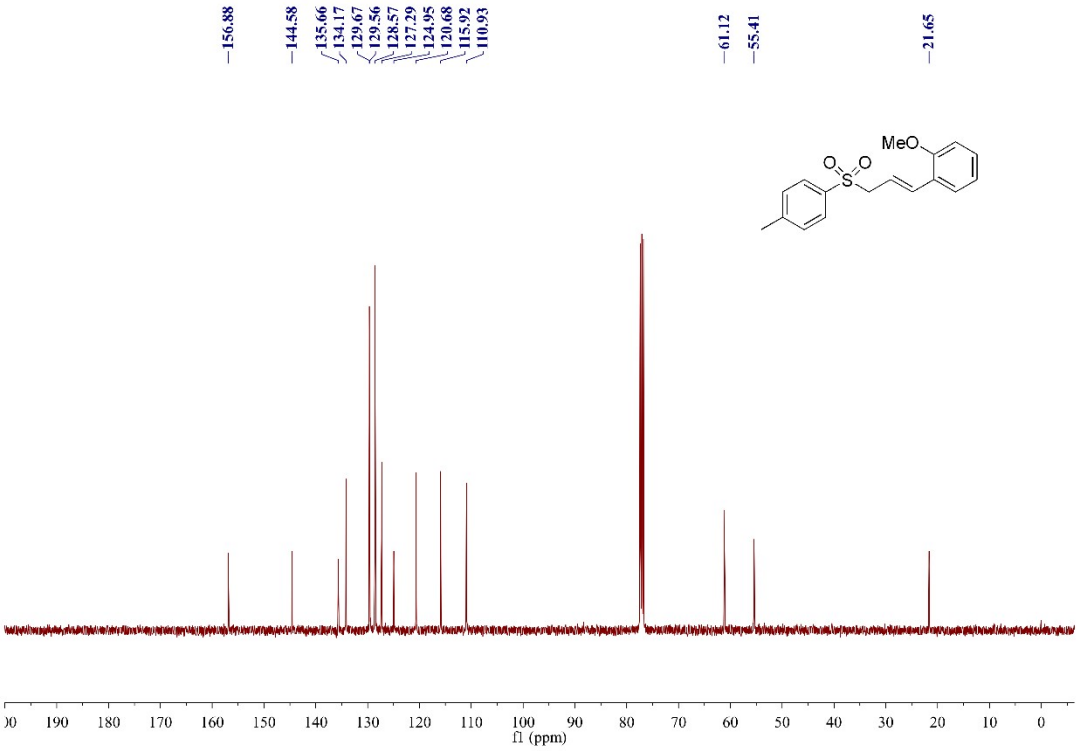
3.11
f1 (ppm)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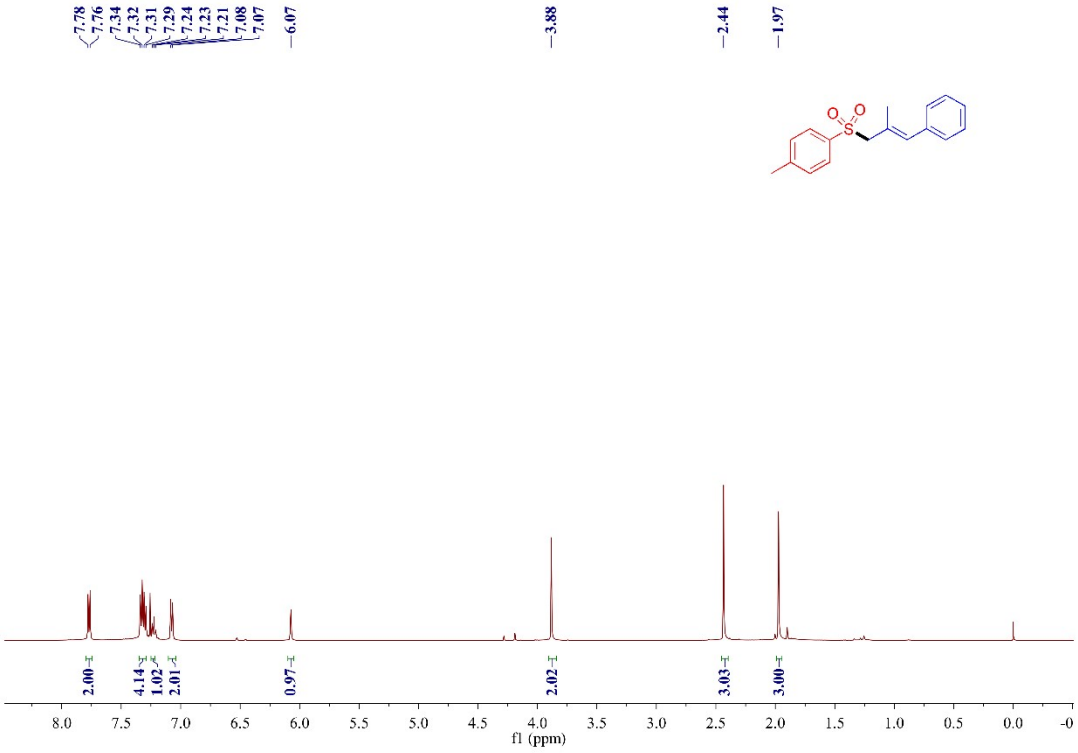
55.41
21.65
MeO
f1 (ppm)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6.07
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2.00
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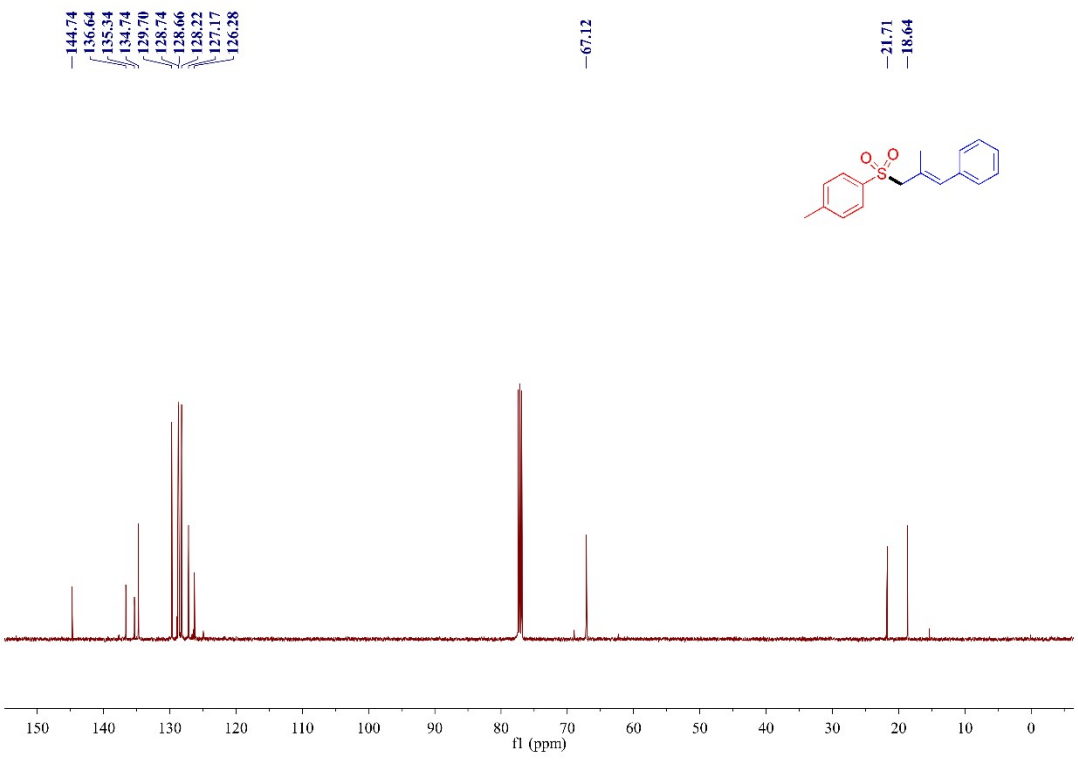
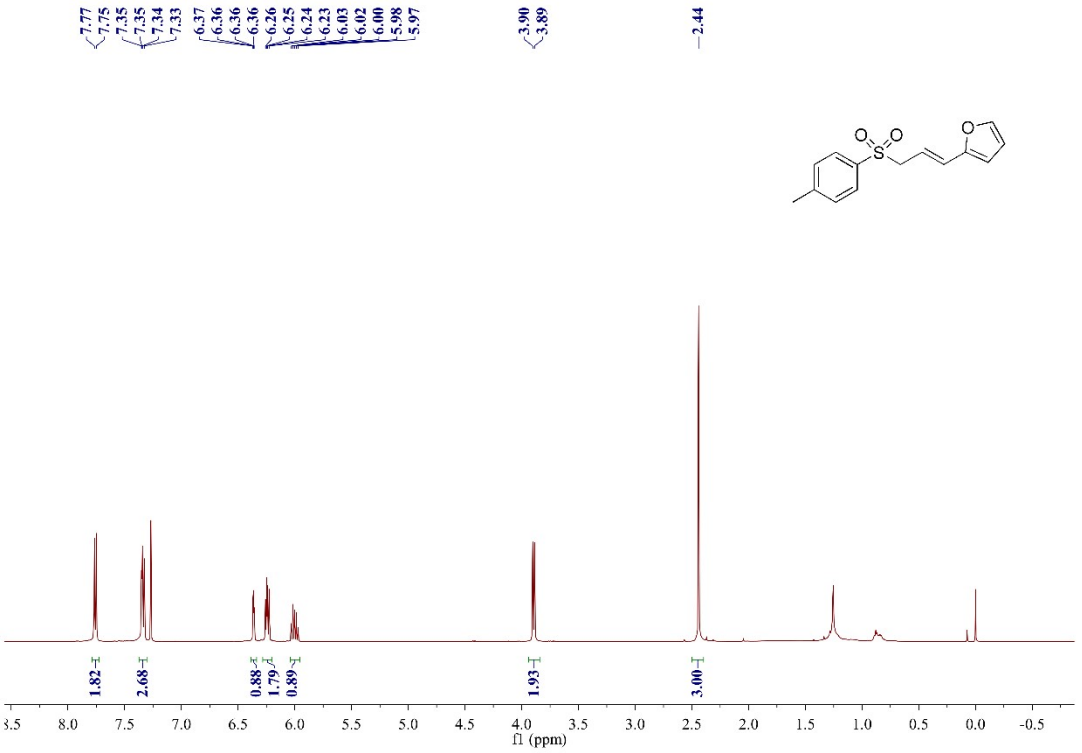
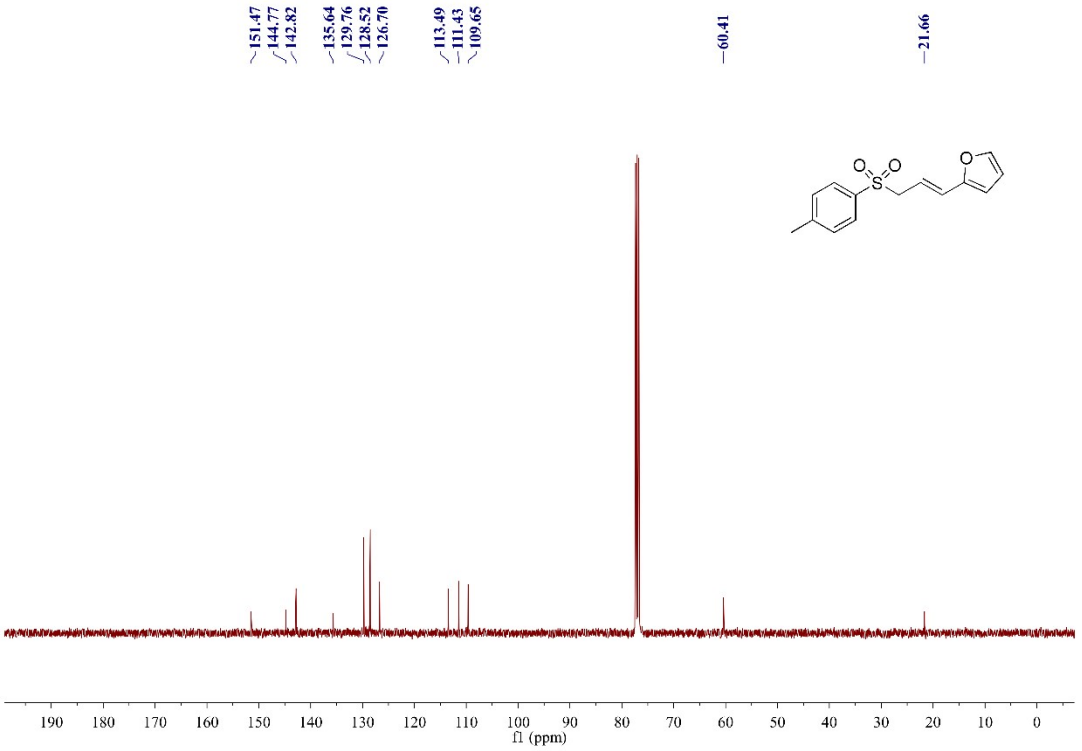
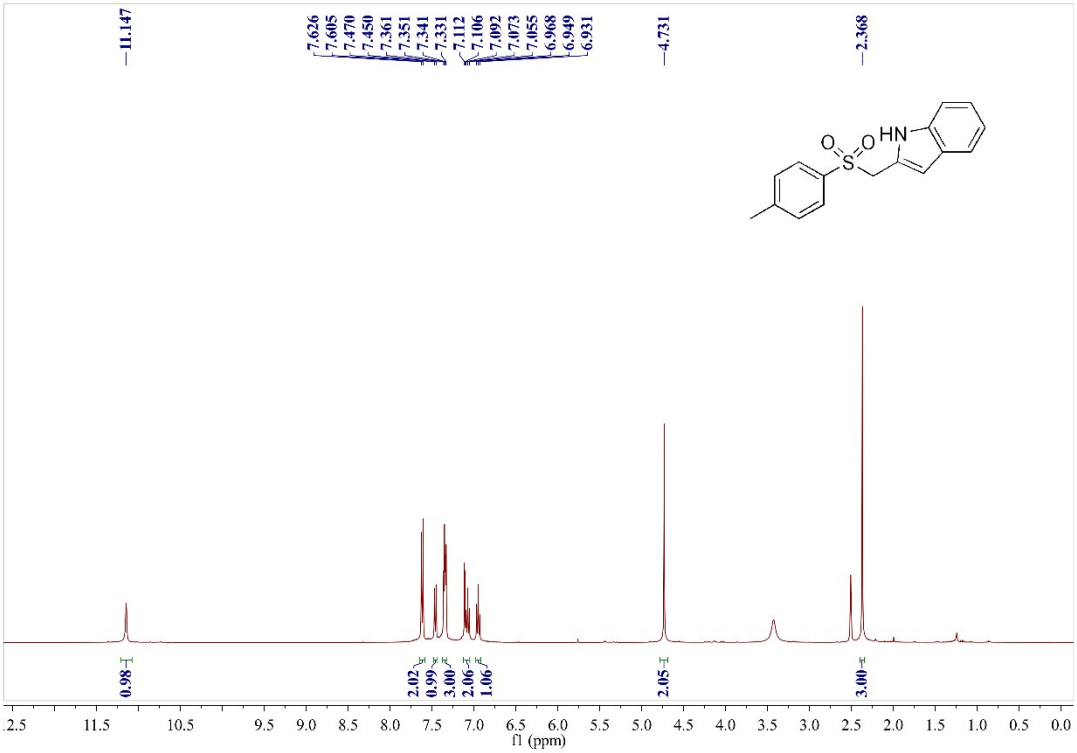
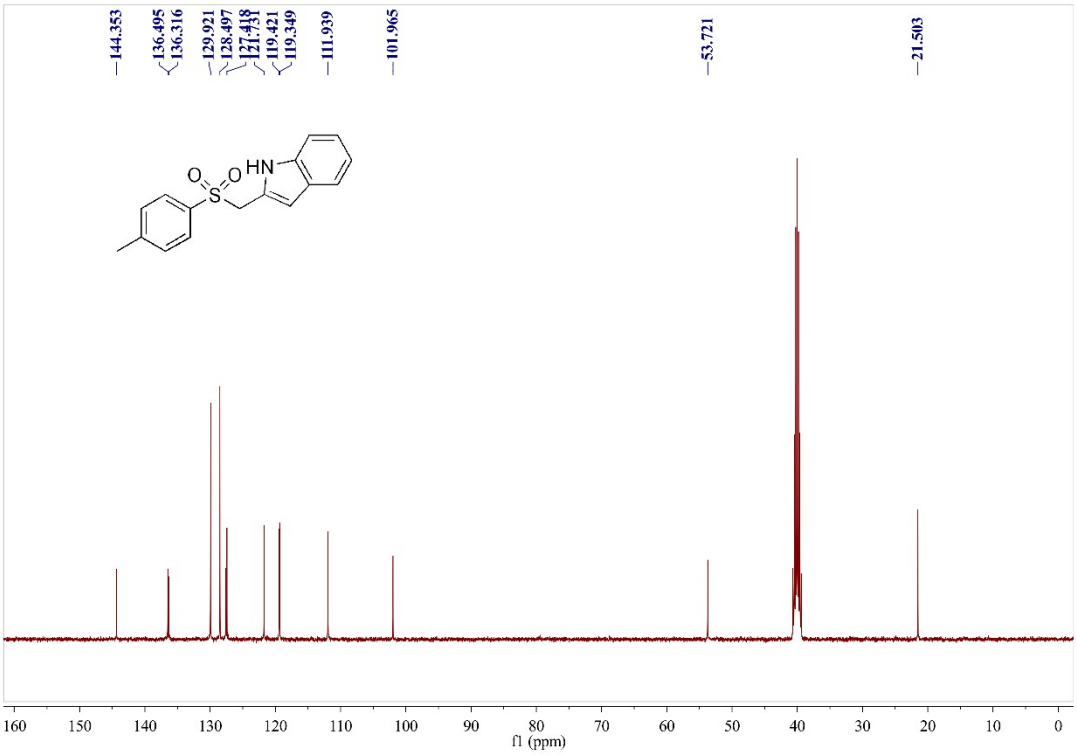
1.02
2.01
0.97
2.02
3.03
3.00
fl (ppm)


144.74
136.64
135.34
134.74
129.70
128.74
128.66
128.22
127.17
126.28
67.12
21.71
18.64
fl (ppm)

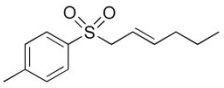

7.77
7.75
7.35
7.35
7.34
7.33
6.37
6.36
6.36
6.36
6.26
6.25
6.24
6.23
6.03
6.02
6.00
5.98
5.97
3.90
3.89
2.44
1.82
2.68
0.88
1.79
0.89
1.93
3.00
f1 (ppm)

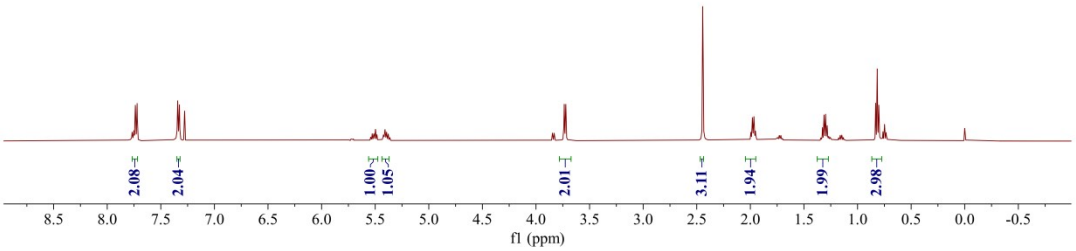

151.47
144.77
142.82
135.64
129.76
128.52
126.70
113.49
111.43
109.65
60.41
21.66
f1 (ppm)


11.147
7.626
7.605
7.470
7.450
7.361
7.351
7.341
7.331
7.112
7.106
7.092
7.073
7.055
6.968
6.949
6.931
4.731
2.368
O
S
O
HN
0.98
2.02
0.99
3.00
2.06
1.06
2.05
3.00
f1 (ppm)

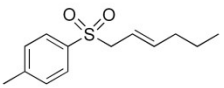

144.353
136.495
136.316
129.921
128.497
127.418
127.131
119.421
119.349
111.939
101.965
53.721
21.503
O
S
O
HN
f1 (ppm)

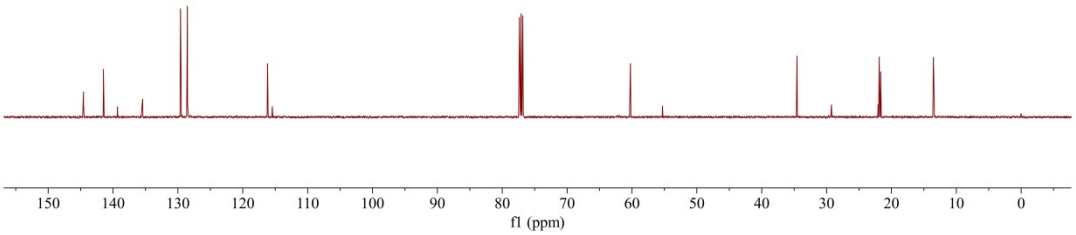

7.77
7.75
7.74
7.72
7.34
7.33
5.54
5.53
5.51
5.50
5.48
5.42
5.41
5.39
5.38
5.36
3.74
3.72
2.44
2.00
1.98
1.97
1.95
1.34
1.33
1.31
1.30
1.28
1.27
1.25
0.83
0.82
0.80

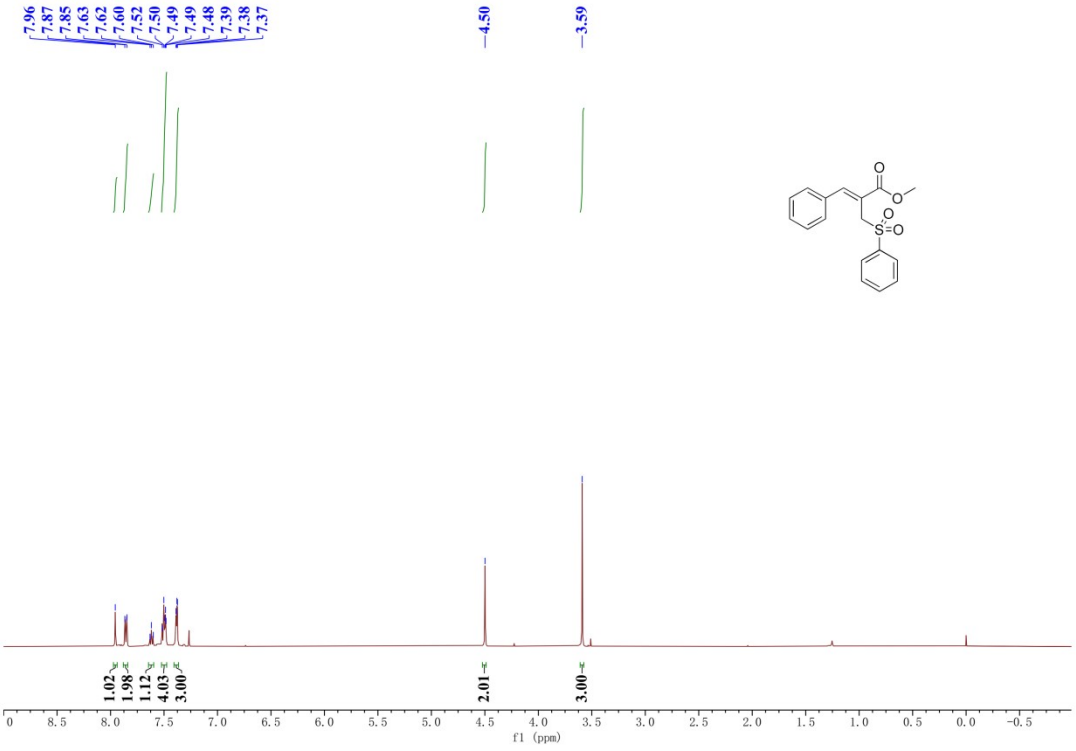


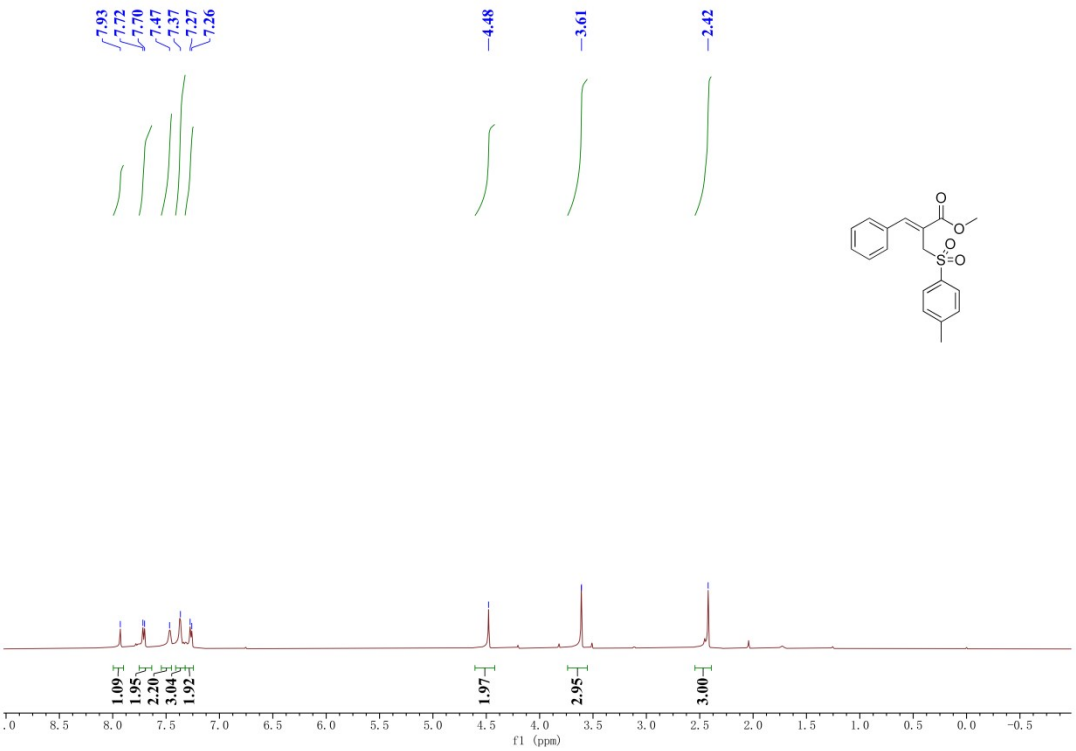

2.08
2.04
1.00
1.05
2.01
3.11
1.94
1.99
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

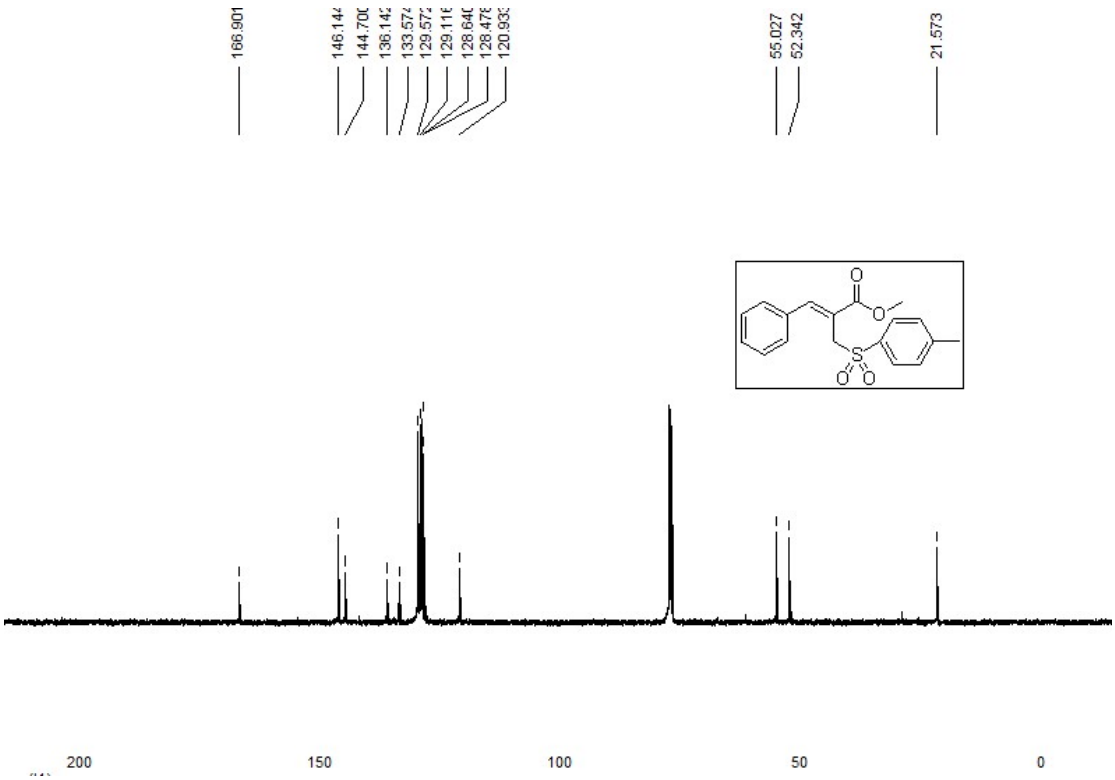

144.55
141.48
135.43
129.59
128.53
116.18
60.24
34.56
21.88
21.65
13.53

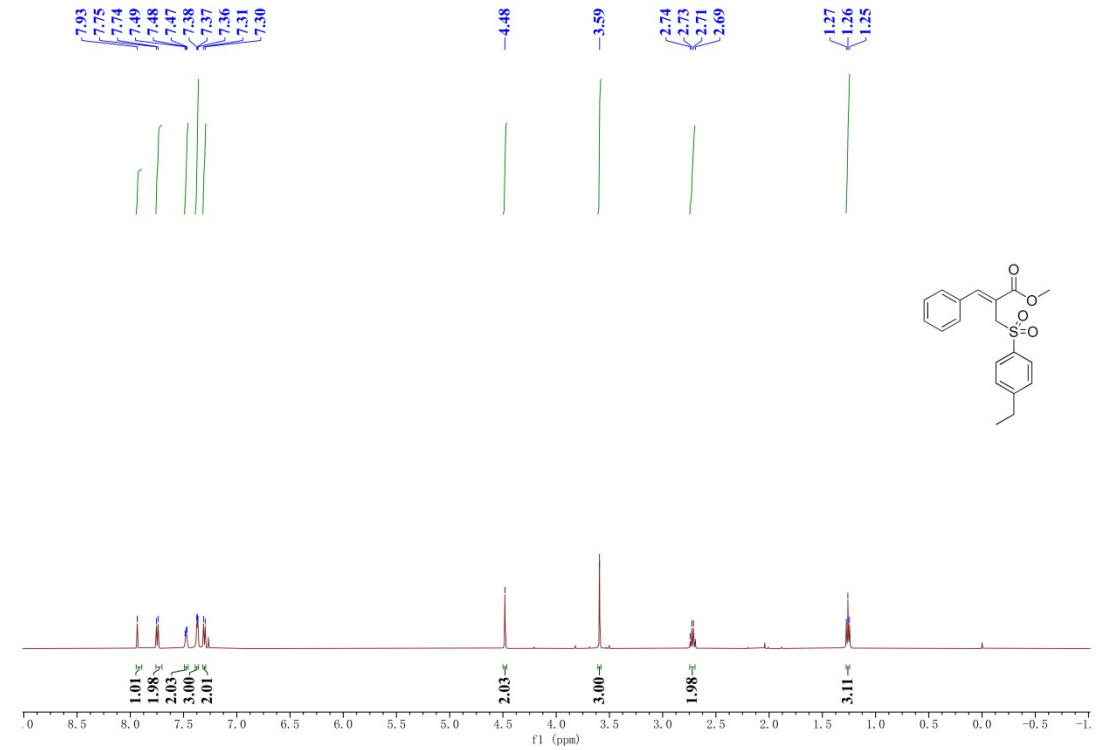


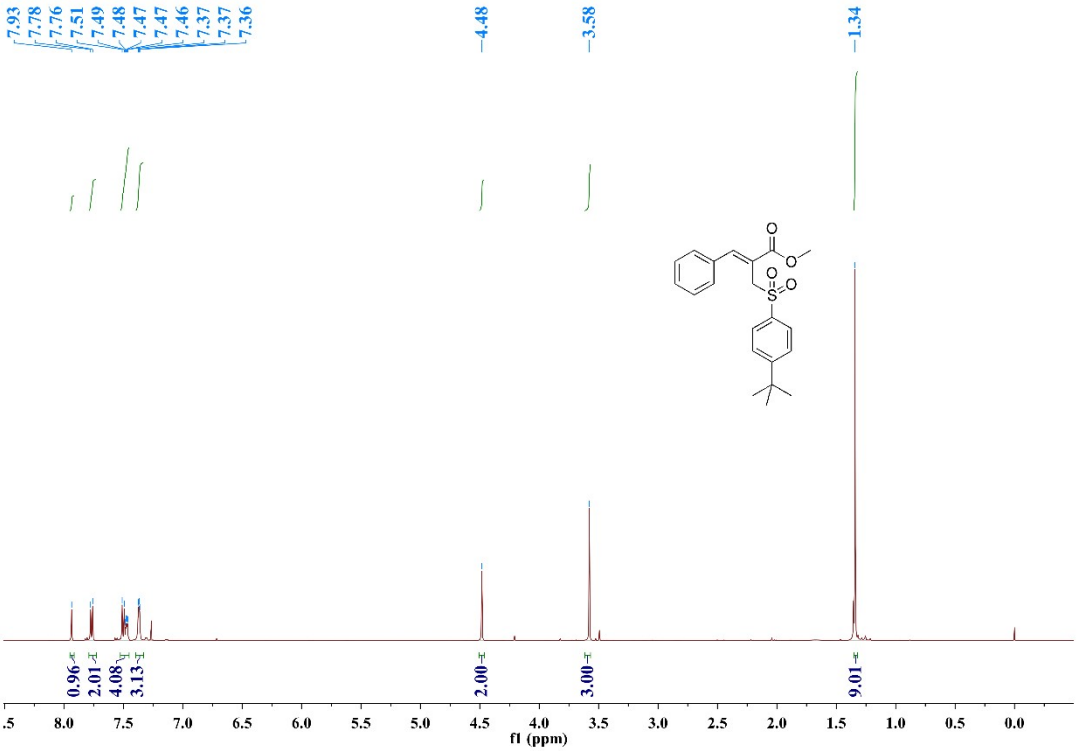

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

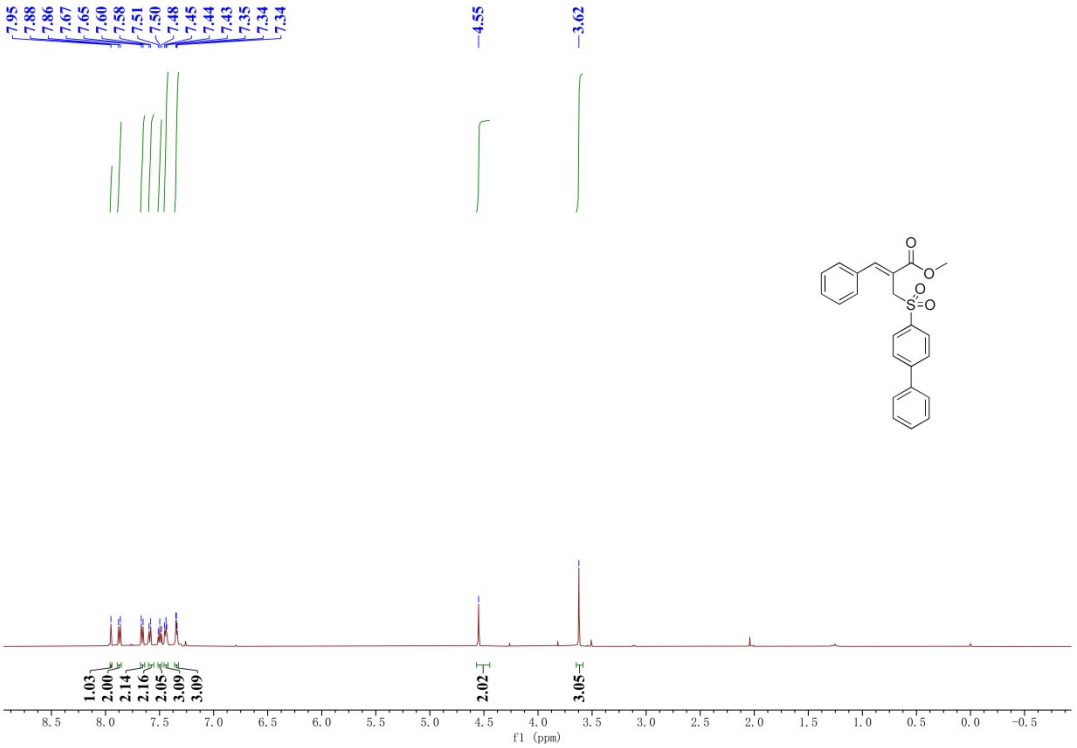

7.96
7.87
7.85
7.63
7.62
7.60
7.52
7.50
7.49
7.49
7.48
7.39
7.38
7.37
4.50
3.59
1.02
1.98
1.12
4.03
3.00
2.01
3.00
f1 (ppm)


7.93
7.72
7.70
7.47
7.37
7.27
7.26
4.48
3.61
2.42
1.09
1.95
2.20
3.04
1.92
1.97
2.95
3.00
f1 (ppm)


166.901
146.144
144.700
136.142
133.574
129.572
129.116
128.640
128.478
120.933
55.027
52.342
21.573
200
150
100
50
0


7.93
7.75
7.74
7.49
7.48
7.47
7.38
7.37
7.36
7.31
7.30
4.48
3.59
2.74
2.73
2.71
2.69
1.27
1.26
1.25
1.01
1.98
2.03
3.00
2.01
2.03
3.00
1.98
3.11
f1 (ppm)


7.93
7.78
7.76
7.51
7.49
7.48
7.47
7.47
7.46
7.37
7.37
7.36
4.48
3.58
1.34
0.96
2.01
4.08
3.13
2.00
3.00
9.01
f1 (ppm)


7.95
7.88
7.86
7.67
7.65
7.60
7.58
7.51
7.50
7.48
7.45
7.44
7.43
7.35
7.34
7.34
4.55
3.62
1.03
2.00
2.14
2.16
2.05
3.09
3.09
2.02
3.05
f1 (ppm)

5. References

1. X. Yu, X. Li, and B. Wan, *Org.Biomol. Chem.,* 2012, **10**, 7479-7482.
2. J. Yu, X. Chang, R. Ma, Q. Zhou, M. Wei, X. Cao and X. Ma, *Eur. J. Org. Chem.*, 2020, **2020**, 7238-7242.
3. T. Chen, J. Lahbi, G. Broggini, A.Pradal and G. Poli, *Eur. J. Org. Chem.*, 2023, **26**, e202201493.
4. P. Xie, J. Wang, Y. Liu, J. Fan, X. Wo, W. Fu, Z. Sun and T.-P. Loh, *Nature Commun.*, 2018, **9**, 1321.