Cu-catalyzed Dehydrogenative Olefinsulfonation of Alkyl Arenes

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Supporting Information

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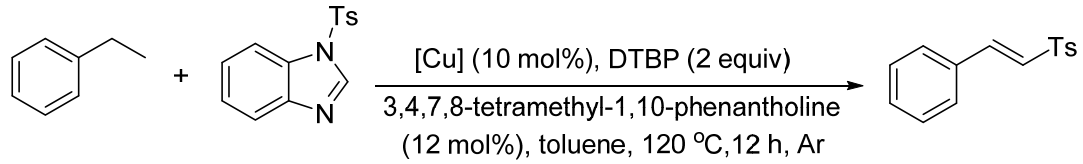
1. General Considerations

All manipulations were carried out in an oven-dried tube under the Ar atmosphere. Copper salts, bases, oxdiants, ligands and solvents were purchased from Energy chemical, Beta, 3A chemical and Aladdin Reagent. NMR spectra were recorded on AVIII-600 (600 MHz for ^{1}H; 565 MHz for ^{19}F; 150 MHz for ^{13}C). The chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H) or TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Compounds for HRMS were analyzed on a Waters Q-Tof Micro MS/MS System ESI spectrometer. X-ray diffraction data was collected on an Oxford Diffraction Xcalibur CCD (X-ray single-crystal diffractometer). The substrates **1a-1i,** were purchased from Aladdin, Energy chemical, Beta without further purification. The starting materials **1j-1n** [1-2], **2a-2v** [3]**,** were prepared according to previously reported procedures. All solvents were transferred by syringe to the reaction flask. Flash column chromatography was performed with silica gel (200-300 mesh). **All the reactions were carried out on an aluminum sand bath.**

2. Optimization for the Olefinsulfonation process

Table S1. Screening of Copper catalysis [a]

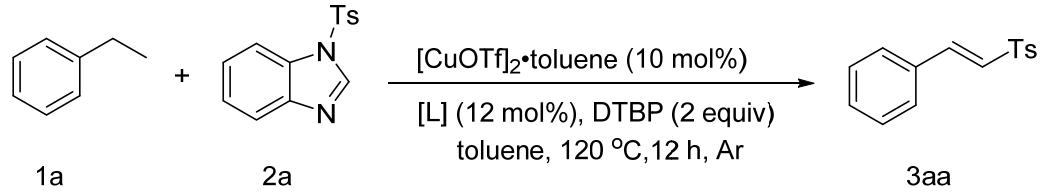


1a 2a 3aa

Entry	Catalyst	3aa[b] (%)
1	CuCl	trace
2	$CuCl_2$	trace
3	CuI	trace
4	$Cu(CH_3CN)_4PF_6$	trace
5	$[CuOTf]_2$•toluene	11
6[c]	$Cu(OAc)_2$	NR
7[c]	CuBr	NR
8[c]	$Cu(ClO_4)_2$•$6H_2O$	NR
9[c]	$Cu(OTf)_2$	NR
10[c]	$CuBr_2$	NR

[a]Reaction Conditions: 1a (2 mmol), 2a (0.2 mmol), Cu catalyst (0.02 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (12 mol%), DTBP (2 equiv), toluene (1.0 mL),120 °C,12 h, Argon. [b]Isolated yield, [c]NR=No Reaction.[d]DTBP=Di-tert-butyl peroxide.

Table S2. Screening of ligands[a]

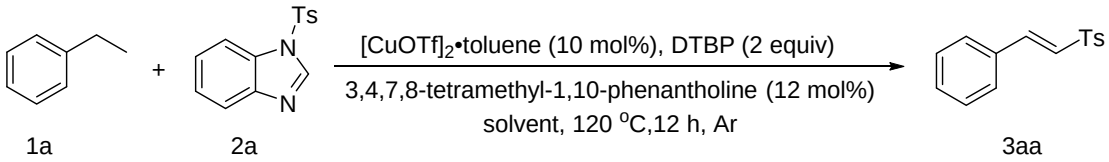


1a 2a 3aa

Entry	[L]	3aa[b] (%)
1	1,10-phenantroline	trace
2	4,7-diphenyl-1,10-phenantroline	trace
3	2,2-dipyridine	trace
4	1,10-phenantrolie-5,6-dione	trace
5	2,9-dimethyl-1,10-phenantroline hydrate	trace

[a]Reaction Conditions: 1a (2 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), [L] (12 mol%), DTBP (2 equiv), toluene (1.0 mL),120 °C,12 h, Argon. [b]Isolated yield.[d]DTBP=Di-tert-butyl peroxide.

Table S3. Screening of Solvents[a]

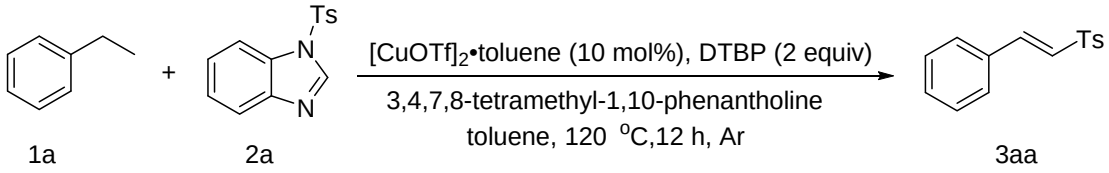


1a 2a 3aa

Entry	solvent	3aa[b] (%)
1	DMF	trace
2[c]	DMSO	NR
3[c]	THF	NR
4[c]	CH_3CN	NR
5[c]	CH_3OH	NR

[a]Reaction Conditions: 1a (2 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), 3,4,7,8-tetramethyl-1,10-phenantholine (12 mol%), DTBP (2 equiv), solvent (1.0 mL),120 °C,12 h, Argon. [b]Isolated yield, [c]NR=No Reaction.[d]DTBP=Di-tert-butyl peroxide.

Table S4. Screening of Ligand loading[a]

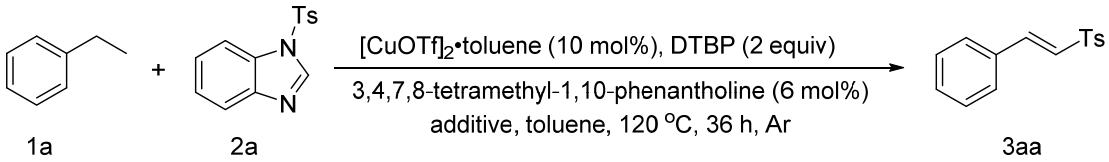


1a 2a 3aa

Entry	L(mmol%)	3aa[b] (%)
1	20	6
2	12	7
3	6	12

[a]Reaction Conditions:1a (1 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (2 equiv), [L]: 3,4,7,8-tetramethyl-1,10-phenantholine, toluene (1.0 mL), 120 °C,12 h. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide.

Table S5. Screening of Additives[a]

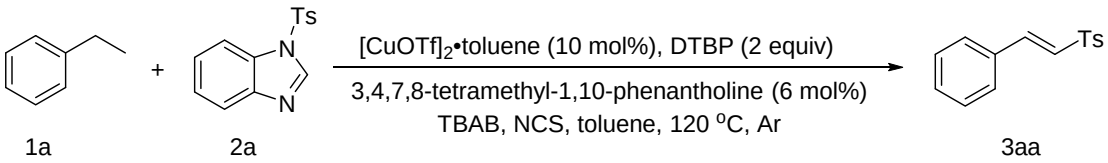


1a 2a 3aa

Entry	additive 1	additive 2	additive 3	3aa[b] (%)
1	TBAB	----	----	trace
2	----	NCS	----	6
3	----	----	3Å	trace
4	TBAB	NCS	----	20
5	TBAB	NCS	3Å	34

[a]Reaction Conditions:1a (1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), additive 1 (0.5 equiv), additive 2 NCS (1.2 equiv), additive 3 (25 mg), toluene (1.0 mL), 120 °C, 36 h, Argon. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, TBAB=Tetrabutylammonium bromide, NCS=N-Chlorosuccinimide.

Table S6. Optimization of Reaction Time[a]

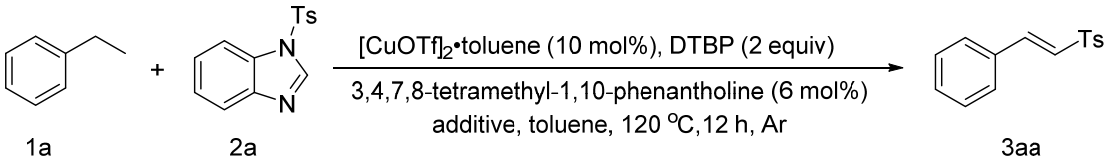


1a 2a 3aa

Entry	time/h	3aa[b] (%)
1	12	20
2	24	25
3	36	34

[a]Reaction Conditions:1a (1 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine(6 mol%), TBAB (0.5 equiv), NCS (1.2 equiv), toluene (1.0 mL),120 °C, Argon. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, TBAB=Tetrabutylammonium bromide, NCS=N-Chlorosuccinimide.

Table S7. Screening of Molecular Sieves [a]

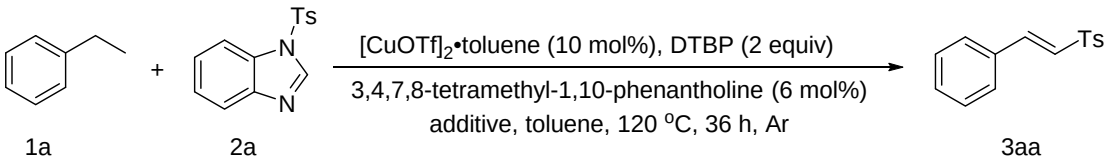


1a 2a 3aa

Entry	additive 3	3aa[b] (%)
1	3Å	26
2	4Å	22
3	5Å	20

[a]Reaction Conditions:1a (1 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), TBAB (0.5 equiv), NCS (1.2 equiv), additive 3 (50 mg), toluene (1.0 mL),120 °C, Argon,12 h. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, TBAB=Tetrabutylammonium bromide, NCS=N-Chlorosuccinimide.

Table S8. Screening of substrate loading[a]

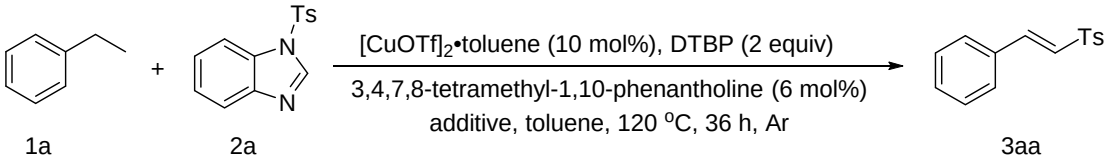


1a 2a 3aa

Entry	1a/mmol	3aa[b] (%)
1	1	29
2	1.4	38
3	2	33

[a]Reaction Conditions: 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), TBAB (0.5 equiv), NCS (1.2 equiv), toluene (1.0 mL),120 °C, 36 h, Argon. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, TBAB=Tetrabutylammonium bromide, NCS=N-Chlorosuccinimide.

Table S9. Screening of bromine source[a]

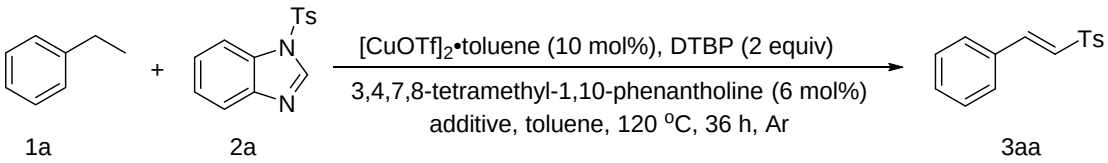


1a 2a 3aa

Entry	additive 1/mmol	3aa[b] (%)
1	KBr(0.4)	40
2	LiBr(0.4)	52
3	$ZnBr_2$(0.4)	33
4	$FeBr_3$(0.02)	37
5	LiBr(0.4)+$FeBr_3$(0.02)	70

[a]Reaction Conditions: 1a(1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), NCS (1.2 equiv), toluene (1.0 mL),120 °C, 36 h, Argon. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, NCS=N-Chlorosuccinimide.

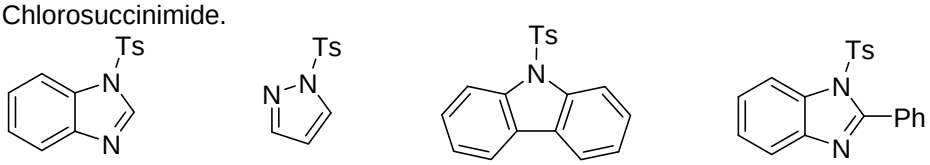
Table S10. Screening of Tosyl Radical Source[a]



1a 2a 3aa

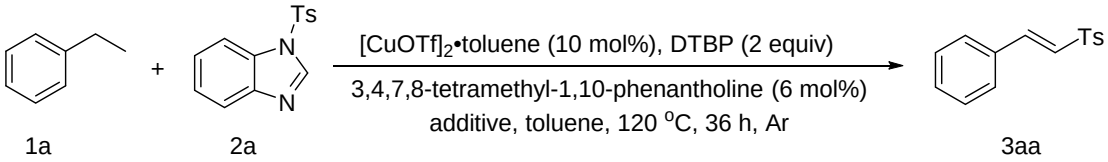
Entry	2a	3aa[b] (%)
1	$2a_1$	49
2	$2a_2$	NR
3	$2a_3$	NR
4	$2a_4$	trace

[a]Reaction Conditions: 1a(1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), NCS (1.2 equiv), LiBr (2 equiv), toluene (1.0 mL),120 °C, 36 h, Argon. [b]Isolated yield. [c]NR=No Reaction. [d]DTBP=Di-tert-butyl peroxide, NCS=N-Chlorosuccinimide.



$2a_1$ $2a_2$ $2a_3$ $2a_4$

Table S11. Screening of Iron Co-catalysis[a]

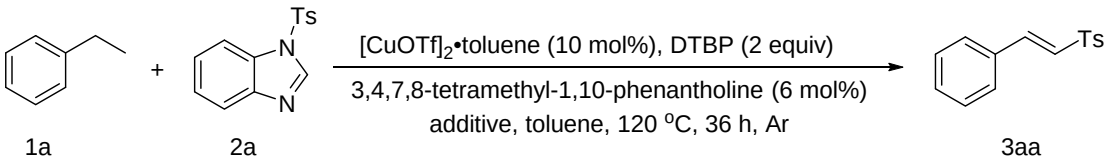


1a 2a 3aa

Entry	additive 4	3aa[b] (%)
1	$FeBr_3$	70
2	$FeCl_2$	60
3	$Fe(OTf)_2$	57
4	$Fe(BF_4)_2$•$6H_2O$	58
5	$FePO_4$	63
6	$Fe(OTf)_3$	61
7	$Fe(OAc)_2$	61
8	$Fe(acac)_3$	39
9	$Fe(ClO_4)_3$•xH_2O	70

[a]Reaction Conditions: 1a(1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), LiBr (2 equiv), NCS (1.2 equiv), additive 4 (0.02 mmol), toluene (1.0 mL),120 °C, 36 h, Argon.[b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, NCS=N-Chlorosuccinimide.

Table S12. Screening of Iron Co-catalysis Loading [a]

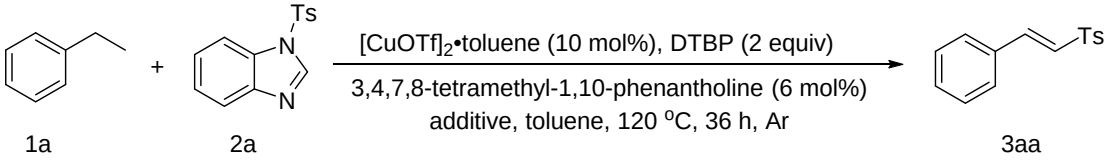


1a 2a 3aa

Entry	[Fe](mol%)	3aa[b] (%)
1	$Fe(ClO_4)_3•xH_2O$(5)	57
2	$Fe(ClO_4)_3•xH_2O$(10)	70
3	$Fe(ClO_4)_3•xH_2O$(20)	68

[a]Reaction Conditions: 1a(1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), LiBr (2 equiv), NCS (1.2 equiv), toluene (1.0 mL),120 °C, 36 h, Argon. [b]Isolated yield. [c]DTBP=Di-tert-butyl peroxide, NCS=N-Chlorosuccinimide.

Table S13. Screening of Base[a]

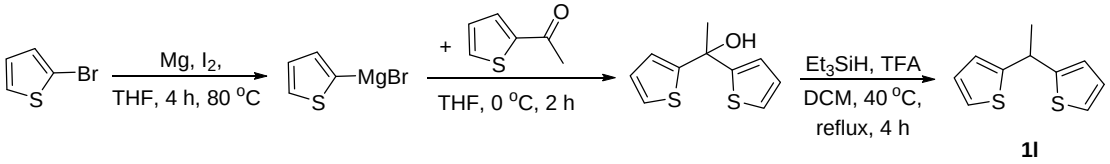


1a 2a 3aa

Entry	base/mmol	3aa[b] (%)
1	Cs_2CO_3(0.1)	67
2	Li_2CO_3(0.4)	75
3	NaOAc(0.4)	37
4	K_2CO_3(0.4)	NR
5	*t*-BuOLi(0.4)	50
6	DBU(0.4)	trace
7	DABCO(0.4)	trace

[a]Reaction Conditions: 1a(1.4 mmol), 2a (0.2 mmol), $[CuOTf]_2$•toluene (10 mol%), DTBP (0.4 mmol), 3,4,7,8-tetramethyl-1,10-phenantholine (6 mol%), 3Å(25 mg), LiBr (2 equiv), NCS (1.2 equiv), $Fe(ClO_4)_3•xH_2O$ (10 mol%), toluene (1.0 mL),120 °C, 36 h, Argon.[b]Isolated yield. [c]NR=No Reaction. [d]DTBP=Di-tert-butyl peroxide, NCS=N-Chlorosuccinimide, DABCO=triethylenediamine, DBU=1,8-diazabicyclo[5.4.0]undec-7-ene .

3. Procedures for the Preparation of Starting compounds [1-3]

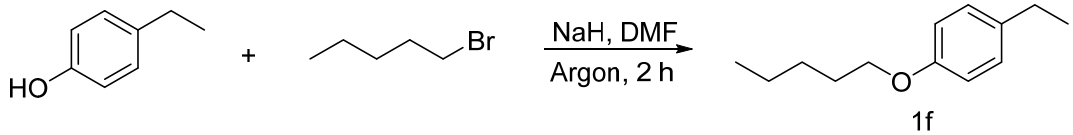


1l

2,2'-(ethane-1,1-diyl)dithiophene (1l): Under an argon atmosphere, to a 500 mL three-necked round-bottomed flask equipped with a stirrer bar charged with magnesium filings(3.65 g, 150 mmol, 1.5 equiv) and a piece of iodine, dry tetrahydrofuran (THF, 5mL) was added until the solution became colorless. Then 2- bromothiophene (1.63 g, 100 mmol, 1 equiv) in 100 mL THF was added dropwise slowly. After the dropwise addition finished, the resulting mixture was heated at 80 °C for 4 hours on an aluminum sand bath. After cooling to room temperature, thiophen-2-ylmagnesium bromide in THF solution (0.75 mol / L) was obtained by filtering under argon atmosphere.

Under an argon atmosphere, in a 250 mL three-necked flask, thiophen-2-ylmagnesium bromide (40 mL, 0.75 mol/L in THF, 30 mmol) was added dropwise slowly to a solution of 2-thiophene ethyl ketone (2.16 mL, 20 mmol, 1 equiv) in dry THF at 0 °C. After the dropwise addition finished, the resulting mixture was stirred at 0 °C for 2 h. The reaction was quenched with NH_4Cl solution and extracted with dichloromethane (30 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford 1,1-di(thiophen-2-yl)ethan-1-ol as yellow oil (0.9894 g, 24% yield).

Under argon atmosphere, trifluoroacetic acid (3.6 mL, 22.5 mmol, 4.5 equiv) was added to a 1,1-di(thiophen-2-yl)ethan-1-ol (1.05 g, 5 mmol, 1 equiv) solution in dry dichloromethane in a 250 mL three-necked round bottom flask at 0 °C. Then triethylsilane (2.4 mL, 15 mmol, 3 equiv) was added dropwise, the resulting mixture was refluxed at 40 °C for 4 h on an aluminum sand bath. After cooling to room temperature, the reaction was quenched with ammonium carbonate solution and extracted with dichloromethane (10 mL×3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether) to afford **1l** as colorless oil (0.9119 g, 54% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, J = 5.1 Hz, 2H), 6.94 - 6.92 (m, 2H), 6.88 (s, 2H), 4.63 (q, J = 7.1 Hz, 1H), 1.78 (d, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0 (overlap), 125.5 (overlap), 122.7 (overlap), 122.6 (overlap), 35.1, 23.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}S_2$ 195.0302; Found 195.0288.

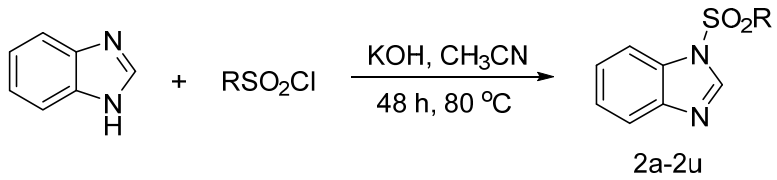


1f

1-ethyl-4-(pentyloxy)benzene (1f): Under an argon atmosphere, a 250 mL three-necked round-bottomed flask equipped with a stirrer bar was first charged with 4-ethylphenol (1.22 g, 0.01 mol) in 10 mL of DMF and sodium hydride (0.253 g, 0.011 mol, 60% in mineral oil, previously washed with hexane) at 0 °C, followed by the addition of 1-bromopentane (3.7 mL, 0.03 mol). The solution was stirred at room temperature for 2 h. The resulting mixture was quenched with water and extracted with EtOAc. The organic layer was dried over Na_2SO_4 and

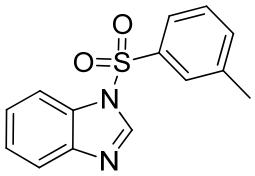
concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to afford **1f** as colorless oil (1.345 g, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.80 - 1.76 (m, 2H), 1.47 - 1.37 (m, 4H), 1.22 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 136.2, 128.7, 114.4, 68.0, 29.1, 28.3, 28.0, 22.5, 15.9, 14.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{21}O$ 193.1592; Found 193.1585.

N-sulfonyl benzo[d]imidazole (2a-2u) were synthesized according to a previously reported method.

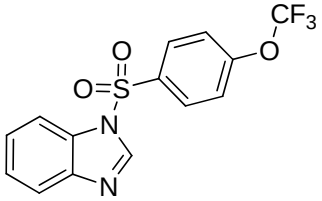


2a-2u

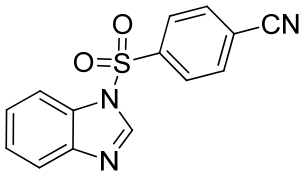
In a 25 mL Schlenk tube equipped with a stirrer bar was charged with benzimidazole (5 mmol, 1 equiv), potassium hydroxide (6 mmol, 1.2 equiv), and sulfonyl chloride (5 mmol, 1 equiv), followed by the addition of acetonitrile (10 mL). The solution was stirred at 80 °C for 48 h on an aluminum sand bath. After cooling to room temperature, the reaction was quenched with water (20 mL) and extracted with ethyl acetate (20 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the target product.



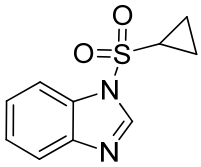
1-(m-tolylsulfonyl)-1H-benzo[d]imidazole (2l): White solid (775.4 mg, 57% yield, petroleum ether/ethyl acetate = 5/1)**;** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 - 7.77 (m, 3H), 7.42 - 7.35 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 141.3, 140.3, 137.5, 135.7, 130.8, 129.5, 127.4,125.6, 124.8, 124.4, 121.1, 112.5, 21.4; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0698; Found 273.0695.



1-((4-(trifluoromethoxy)phenyl)sulfonyl)-1H-benzo[d]imidazole (2h): White solid (208.6 mg, 12% yield, petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.44 - 7.38 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 144.1, 141.0, 135.6, 130.7, 129.5, 125.9, 125.2, 121.4, 121.3, 120.0 (q, *J* = 255 Hz), 112.4; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{14}H_{10}F_3N_2O_3S$ 343.0364; Found 343.0362.



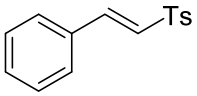
4-((1H-benzo[d]imidazol-1-yl)sulfonyl)benzonitrile (2j): White solid (1.1 g, 78% yield, petroleum ether/ethyl acetate = 5/1);. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.79 - 7.85 (m, 4H), 7.45 - 7.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 141.5, 140.9, 133.5, 130.5, 127.8, 126.2, 125.5, 121.5, 118.6, 116.5, 112.3; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{14}H_{10}N_3O_2S$ 284.0494; Found 284.0490.



1-(cyclopropylsulfonyl)-1H-benzo[d]imidazole (2t): White solid (621.7 mg, 56% yield, petroleum ether/ethyl acetate =3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.86 (t, *J* = 7.0 Hz, 2H), 7.46 - 7.41 (m, 2H), 2.75 - 2.71 (m, 1H), 1.51 - 1.48 (m, 2H), 1.17-1.14 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 141.3, 131.3, 125.6, 124.8, 121.2, 112.5, 32.3, 6.8; HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{10}H_{11}N_2O_2S$ 223.0541; Found 223.0538.

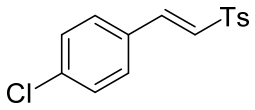
4. General Procedure for the Olefinsulfonation and Characterization Data of Products

In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with alkyl arenes compounds (1.4 mmol) and N-sulfonyl-benzo[d]imidazole (0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO_4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg), and LiBr (34.8 mg, 2 equiv), followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 ^{o}C for 36 h on an aluminum sand bath under an argon atmosphere. After the resulting mixture was detected to be complete by TLC, the reaction was cooled to room temperature, quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product.



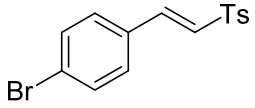
3aa

(E)-1-methyl-4-(styrylsulfonyl)benzene (3aa)[4]: White solid (38.5 mg, 75% yield, petroleum ether/ ethyl acetate= 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.47 - 7.46 (m, 2H), 7.40 - 7.37 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 141.9, 137.8, 132.5, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.6.



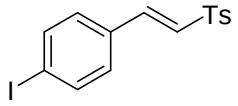
3ba

(E)-1-chloro-4-(2-tosylvinyl)benzene (3ba) [4]: White solid (37.4 mg, 64% yield, petroleum ether/ ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 15.4 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.37 - 7.34 (m, 4H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 140.4, 137.5, 137.2, 131.0, 130.0, 129.7, 129.4, 128.3, 127.8, 21.6.



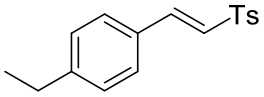
3ca

(E)-1-bromo-4-(2-tosylvinyl)benzene (3ca) [5]: White solid (39.4 mg, 60% yield, petroleum ether/ ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz 2H), 7.59 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.35 - 7.32 (m, 4H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 140.5, 137.5, 132.4, 131.4, 130.0, 129.9, 128.4, 127.8, 125.5, 21.6.



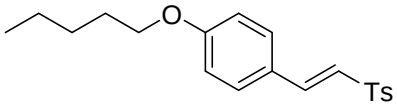
3da

(E)-1-iodo-4-(2-tosylvinyl)benzene (3da) [6]: White solid (41.8 mg, 54% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 15.4 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 15.4 Hz , 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 140.7, 138.3, 137.5, 131.9, 130.0, 129.9, 128.4, 127.8, 97.6, 21.6.



3ea

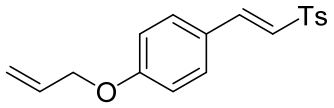
(E)-1-ethyl-4-(2-tosylvinyl)benzene (3ea) [7]: White solid (39.3 mg, 69% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 144.3, 142.1, 138.0, 130.0 (overlap), 128.7, 128.7, 127.7, 126.5, 28.9, 21.7, 15.3.



3fa

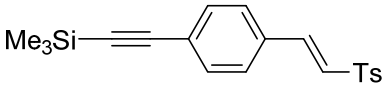
(E)-1-methyl-4-((4-(pentyloxy)styryl)sulfonyl)benzene (3fa) [8]: Colourless oil (38.5 mg, 5 6% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 15.4 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.1

Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 15.3 Hz, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 1.81-1.75 (m, 2H), 1.45-1.36 (m, 4H), 0.93 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6, 144.1, 141.8, 138.3, 130.3, 129.9, 127.6, 124.8, 124.6, 115.0, 68.2, 28.8,28.1, 22.4, 21.6,14.0.



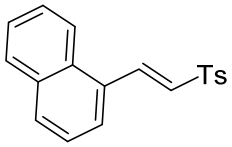
3ga

(E)-1-methyl-4-((4-(vinyloxy)styryl)sulfonyl)benzene (3ga) : White solid (13.3 mg, 21% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 - 7.81 (m, 2H), 7.59 (d, *J* = 15.3 Hz, 1H), 7.42 - 7.40 (m, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 6.91 - 6.90 (m, 2H), 6.70 - 6.68 (m, 1H), 6.06 - 5.99 (m, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.57 - 4.56 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 144.1, 141.7, 138.2, 132.6, 130.3, 129.9, 127.6, 125.2, 124.9, 118.1, 115.2, 68.9, 21.6. HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{18}H_{19}O_3S$ 315.1055; Found 315.1052.



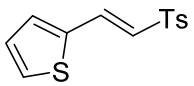
3ha

(E)-trimethyl((4-(2-tosylvinyl)phenyl)ethynyl)silane (3ha): White solid (14.3 mg, 20% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H), 0.25 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 141.0, 137.8, 132.7, 132.5, 130.2, 128.5, 128.4, 127.9, 126.0, 104.3, 97.6, 21.8. HRMS (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{20}H_{23}O_2SSi$ 355.1188; Found 355.1184.



3ia

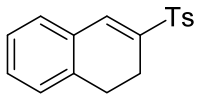
(E)-1-(2-tosylvinyl)naphthalene (3ia) [9]: White solid (41.8 mg, 68% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 15.1 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.91 - 7.87 (m, 4H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.62-7.60 (m, 1H), 7.56 - 7.54 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.5,139.0, 137.6, 133.7, 131.4, 131.3, 130.0, 129.9, 129.6, 128.9, 127.8, 127.3, 126.5, 125.7, 125.3,123.1, 21.7.



3ja

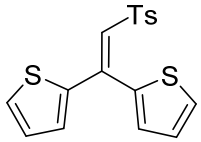
(E)-2-(2-tosylvinyl)thiophene (3ja) [5]: White solid (19.8 mg, 38% yield, petroleum ether/ethyl acetate = 10/1);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 15.1 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.07 - 7.06 (m, 1H),

6.63 (d, *J* = 15.1 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 137.9, 137.1, 134.6, 132.3, 130.0, 129.8, 128.3,127.7, 125.9, 21.6.



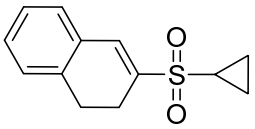
3ka

3-tosyl-1,2-dihydronaphthalene (3ka) [10]: White solid (34.1 mg, 60% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.26 - 7.22 (m, 3H), 7.12 (d, *J* = 7.1 Hz, 1H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.49 (t, *J* = 8.2 Hz, 2H), 2.42 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$)δ 144.3, 138.5, 136.6, 135.5, 134.7, 131.0, 130.4, 129.9, 129.0, 128.0,127.8, 127.1, 27.57, 21.7, 21.6.



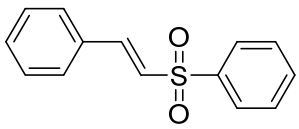
3la

2,2'-(2-tosylethene-1,1-diyl)dithiophene (3la): White solid (34.1 mg, 50% yield, petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 5.0 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 3.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.06 - 7.03 (m, 2H), 7.01 (s, 1H), 6.99 - 6.98 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 134.3, 132.2, 130.8, 129.7, 129.0, 128.2, 128.1, 127.8, 126.8, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}O_2S_3$ 347.0234; Found 347.0229.



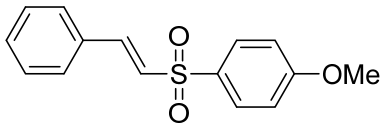
3kt

3-(cyclopropylsulfonyl)-1,2-dihydronaphthalene (3kt) [11]: White solid (33.9 mg, 60% yield, petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.4 (s, 1H), 7.31 - 7.29 (m, 1H), 7.25 (d, *J* = 4.1 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 3.02 - 2.99 (m, 2H), 2.76 - 2.74 (m, 2H), 2.43 - 2.39 (m, 1H), 1.30 - 1.29 (m, 2H), 1.06 - 1.03 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.8, 135.7, 135.1, 131.0, 130.4, 129.0, 127.8, 127.2, 30.0, 29.3, 27.7, 22.3, 5.1.



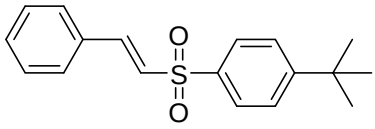
3ab

(E)-(2-(phenylsulfonyl)vinyl)benzene (3ab) [12]: White solid (36.1 mg, 74% yield, petroleum ether acetate / ethyl = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.42 - 7.38 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.5, 140.8, 133.4, 132.4, 131.2, 129.4, 129.1, 128.6, 127.7, 127.3.



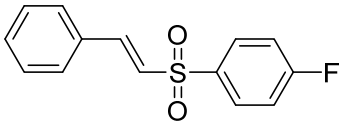
3ac

(E)-1-methoxy-4-(styrylsulfonyl)benzene (3ac) [12]: White solid (31.1 mg, 57% yield, petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 15.4 Hz, 1H), 7.47-7.46 (m, 2H), 7.39 - 7.38 (m, 3H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 141.4, 132.6, 132.3, 131.0, 129.9, 129.1, 128.5, 128.0, 114.6, 55.7.



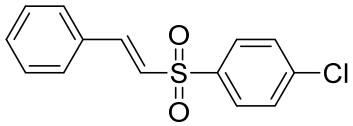
3ad

(E)-1-(tert-butyl)-4-(styrylsulfonyl)benzene (3ad) [12]: White solid (30.5 mg, 51% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.56 - 7.55 (m, 2H), 7.48 - 7.47 (m, 2H), 7.40 - 7.26 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 142.0, 137.7, 132.5, 131.1, 129.1, 128.5, 127.7, 127.6, 126.4, 35.2, 31.1.



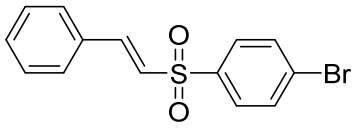
3ae

(E)-1-fluoro-4-(styrylsulfonyl)benzene (3ae) [4]: White solid (27.8 mg, 53% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.95 (m, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.49 - 7.48 (m, 2H), 7.43 - 7.40 (m, 3H), 7.23 (t, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ.165.6 (d, *J* = 256.1 Hz), 142.7, 136.8 (d, *J* = 3.0 Hz), 132.3, 131.4, 130.5 (d, *J* = 9.5 Hz), 129.1, 128.6, 127.1, 116.7 (d, *J* = 22.8 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -104.0.



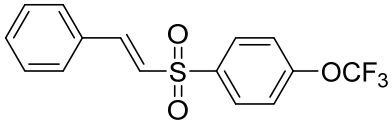
3af

(E)-1-chloro-4-(styrylsulfonyl)benzene (3af) [12]: White solid (29.4 mg, 53% yield, petroleu m ether/ethyl acetate = 10/1); ^{1}HNMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5Hz, 2H), 7.6 9 (d, *J* = 15.4 Hz, 1H), 7.52- 7.48 (m, 4H), 7.43- 7.38 (m, 3H), 6.84 (d, *J* = 15.4Hz, 1 H). ^{13}C NMR(150 MHz, $CDCl_3$) δ 142.0, 139.1, 138.3, 131.2, 130.4, 128.7, 128.1, 128.1, 127.6, 125.9.



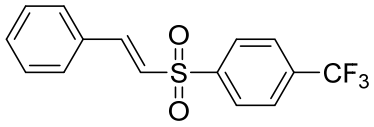
3ag

(E)-1-bromo-4-(styrylsulfonyl)benzene (3ag) [13]: White solid (29.0 mg, 45% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.70 - 7.67 (m, 3H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.41 - 7.39 (m, 3H), 6.84 (d, *J*= 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 139.8, 132.7, 132.2,131.4, 129.2,129.2, 128.7(overlap), 126.8.



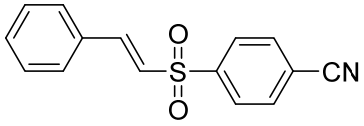
3ah

(E)-1-(styrylsulfonyl)-4-(trifluoromethoxy)benzene (3ah) [14]: White solid (35.6 mg, 54% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 - 8.00 (m, 2H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.50 - 7.49 (m, 2H), 7.43 - 7.36 (m, 5H), 6.85 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 143.3, 139.2, 132.2, 131.5, 129.9,129.2, 128.7, 126.8, 122.8, 121.2, 121.1, 119.4, 117.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -57.7.



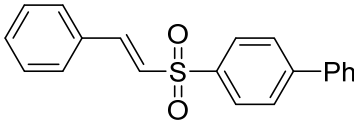
3ai

(E)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (3ai) [12]: White solid (26.7 mg, 43% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.46 - 7.40 (m, 3H), 6.86 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 144.1, 135.1 (dd, J_1 = 33.1 Hz, J_2 = 66.3 Hz), 132.0, 131.7, 129.2, 128.7, 128.3, 126.5 (q, *J* = 3.6 Hz), 126.3, 123.2 (d, *J* = 273.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.2.



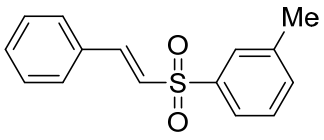
3aj

(E)-4-(styrylsulfonyl)benzonitrile (3aj) [14] : White solid (19.6 mg, 36% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.51 - 7.40 (m, 5H), 6.84 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.1, 144.7, 133.1, 131.9, 131.9, 129.3, 128.8, 128.3, 125.8, 117.2, 117.1.



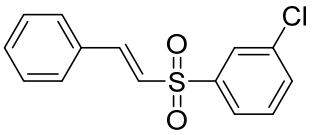
3ak

(E)-4-(styrylsulfonyl)-1,1'-biphenyl (3ak): White solid (36.7 mg, 57% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 15.4 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.51 - 7.48 (m, 4H), 7.44 - 7.38 (m, 4H), 6.91 (d, *J* =15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.6, 142.6, 139.4, 132.6, 131.4, 129.2, 129.2, 128.7 (overlap), 128.4, 128.1, 127.6, 127.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}O_2S$ 321.0949; Found 321.0947.



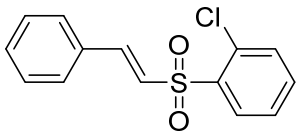
3al

(E)-1-methyl-3-(styrylsulfonyl)benzene (3al) [10]: White solid (35.5 mg, 69% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$)δ 7.75 (s, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.44 - 7.38 (m, 5H), 6.90 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 140.5, 139.7,134.2, 132.4,131.2, 129.2, 129.1, 128.6, 128.0, 127.4, 124.8, 21.4.



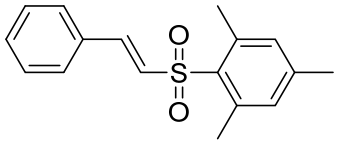
3am

(E)-1-chloro-3-(styrylsulfonyl)benzene (3am) [13]: White solid (25.0 mg, 45% yield, petrole um ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (t, *J* = 1.8 Hz, 1H), 7.84 - 7.83 (m, 1H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.58 - 7.26 (m, 7H), 6.85 (d, *J* = 15. 4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 142.6, 135.6, 133.5, 132.2, 131.5,130. 7, 129.2, 128.7, 127.8, 126.6, 125.8.



3an

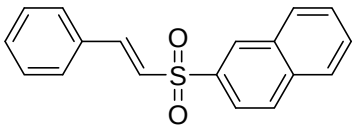
(E)-1-chloro-2-(styrylsulfonyl)benzene (3an) [13]: White solid (29.5 mg, 53% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 15.4 Hz, 1H), 7.56 - 7.40 (m, 8H), 7.08 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 138.3, 134.5, 132.9, 132.4, 131.9, 131.4, 130.7, 129.1, 128.7, 127.4, 125.3.



3ao

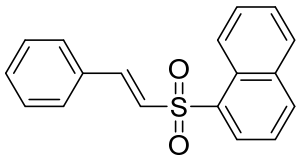
(E)-1,3,5-trimethyl-2-(styrylsulfonyl)benzene (3ao): White solid (19.5 mg, 34% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 15.4 Hz, 1H), 7.48 (d, *J* = 6.7 Hz, 2H), 7.39 (d, *J* = 6.7 Hz, 3H), 6.97 (s, 2H), 6.92 (d, *J* = 15.4 Hz, 1H), 2.68 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 140.7, 140.1, 133.9, 132.7, 132.4, 131.0,

129.2, 128.6, 128.2, 23.1, 21.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}O_2S$ 287.1106; Found 287.1104.



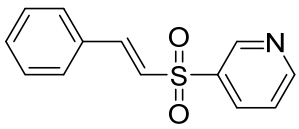
3ap

(E)-2-(styrylsulfonyl)naphthalene (3ap) [12]: White solid (42.2 mg, 72% yield, petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.00 (t, *J* = 7.7 Hz, 2H), 7.90 (dd, J_1 = 8.6 Hz, J_2 = 17.7 Hz, 2H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.67 - 7.61 (m, 2H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.41 - 7.37 (m, 3H), 6.92 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 137.5, 135.2, 132.4, 132.3, 131.2,129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.0, 127.7, 127.4, 122.6.



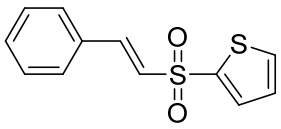
3aq

(E)-1-(styrylsulfonyl)naphthalene (3aq) [15]: White solid (36.0 mg, 61% yield, petroleum ether/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.6 Hz, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 15.2 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.63 - 7.59 (m, 2H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.39 - 7.35 (m, 3H), 7.01 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.8, 135.6, 135.3, 134.4, 132.5, 131.3, 130.0, 129.3, 129.2, 128.8, 128.7,128.7, 127.7, 127.1, 124.7, 124.4.



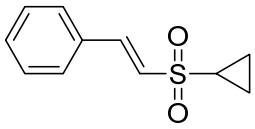
3ar

(E)-3-(styrylsulfonyl)pyridine (3ar) [13]: White solid (4.8 mg, 10% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.60 (d, *J* = 4.7 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.51 - 7.40 (m, 6H), 6.87 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 148.9, 144.1, 137.4,135.3, 132.0, 131.7, 129.2, 128.8, 126.6, 123.9.



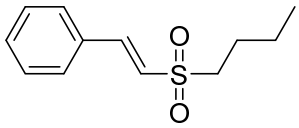
3as

(E)-2-(styrylsulfonyl)thiophene (3as) [16]: White solid (28.2 mg, 56% yield, petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 - 7.67 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.43 - 7.39 (m, 3H), 7.14 (t, *J* = 4.0 Hz, 1H), 6.96 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 142.2, 133.9, 133.5, 132.3, 131.3,129.1, 128.6, 128.0, 127.9.



3at

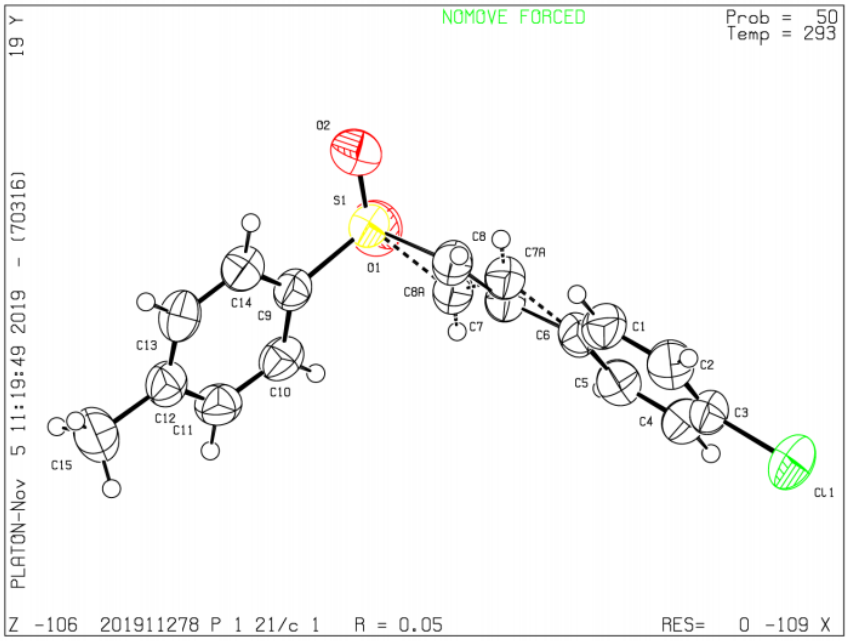
(E)-(2-(cyclopropylsulfonyl)vinyl)benzene (3at) [12]: White solid (29.0 mg, 70% yield, petroleum ether:/ethyl acetate = 7/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 15.4 Hz, 1H), 7.53 - 7.51 (m, 2H), 7.43 - 7.42 (m, 3H), 6.90 (dd, J_1 = 0.5 Hz , J_2 = 15.4 Hz, 1H), 2.46 - 2.42 (m, 1H)，1.32 - 1.29 (m, 2H), 1.08 - 1.05 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 132.6, 131.3, 129.3, 128.6, 125.8, 31.6, 5.5.



3au

(E)-(2-(butylsulfonyl)vinyl)benzene (3au) [17]**:** White solid (13.5 mg, 30% yield, petroleum ether/ ethyl acetate = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 15.4 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.46 - 7.42 (m, 3H), 6.83 (d, J = 15.4 Hz, 1H), 3.06 (t, J = 8.2 Hz, 2H), 1.84 - 1.79 (m, 2H), 1.50 - 1.44 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 132.3, 131.4, 129.2, 128.6, 124.8, 55.0,24.6, 21.7, 13.6.

5. X-Ray Structure of 3ba



Single-crystal X-ray Molecular Structure of 3ba in the solid state. Thermal ellipsoide at the 50% probability lever.

The structure of **3ba** (containing little solvent) was determined by the X-ray diffraction. Recrystallized from Chloroform-D. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **2033227.**

Table S14. Crystal data and structure refinement for **3ba**.

Identification code	3ba	
Empirical formula	$C_{15}H_{13}ClO_2S$	
Formula weight	292.76	
Temperature	293(2) K	
Crystal system, Space group	monoclinic, $P2_1/c$	
Unit cell dimensions	a =5.9131(4) Å b =7.2764(5) Å c =32.520(2) Å	α =90° β=94.268(5) ° γ=90°
Volume/Å^3	1395.32(16)	
Z, ρ_{calc}g/cm^3	4, 1.394	
μ/mm^{-1}	3.777	
F(000)	608	
Crystal size/mm^3	0.17 × 0.09 × 0.08	
Radiation	CuKα (λ = 1.54184)	
2Θ range for data collection/°	10.912 to 134.096	
Index ranges	$-7 \le h \le 4$, $-8 \le k \le 8$, $-38 \le l \le 38$	
Reflections collected	5017	
Independent reflections	2476 [R_{int} = 0.0274, R_{sigma} = 0.0413]	
Data/restraints/parameters	2476/0/180	
Goodness-of-fit on F^2	1.034	
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1316	
Final R indexes [all data]	R_1 = 0.0683, wR_2 = 0.1506	
Largest diff. peak/hole / e Å^{-3}	0.32/-0.28	

Table S15. Bond Lengths (Å) and bond angles (°) for **3ba**.

C(1)-C(2)	1.386(5)	C(8A)-S(1)	1.826(17)
C(1)-C(6)	1.389(5)	C(9)-C(10)	1.386(4)
C(2)-C(3)	1.375(5)	C(9)-C(14)	1.377(4)
C(3)-C(4)	1.366(5)	C(9)-S(1)	1.769(3)
C(3)-Cl1)	1.740(3)	C(10)-C(11)	1.376(4)
C(4)-C(5)	1.363(5)	C(11)-C(12)	1.380(4)
C(5)-C(6)	1.380(5)	C(12)-C(13)	1.377(4)
C(6)-C(7)	1.479(5)	C(12)-C(15)	1.518(4)
C(6)-C(7A)	1.580(19)	C(13)-C(14)	1.380(4)
C(7)-C(8)	1.316(6)	O(1)-S(1)	1.412(3)

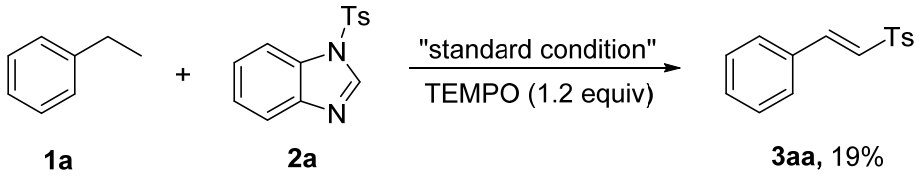
C(7A)-C(8A)	1.28(3)	O(2)-S(1)	1.436(3)
C(8)-S(1)	1.762(4)		
C(2)-C(1)-C(6)	121.3(3)	C(14)-C(9)-S(1)	119.7(2)
C(3)-C(2)-C(1)	118.2(4)	C(11)-C(10)-C(9)	118.7(3)
C(2)-C(3)-C(l1)	119.2(3)	C(10)-C(11)-C(12)	121.7(3)
C(4)-C(3)-C(2)	121.5(3)	C(11)-C(12)-C(15)	120.9(3)
C(4)-C(3)-C(l1)	119.4(3)	C(13)-C(12)-C(11)	118.3(3)
C(5)-C(4)-C(3)	119.7(3)	C(13)-C(12)-C(15)	120.8(3)
C(4)-C(5)-C(6)	121.3(3)	C(12)-C(13)-C(14)	121.3(3)
C(1)-C(6)-C(7)	126.3(3)	C(9)-C(14)-C(13)	119.2(3)
C(1)-C(6)-C(7A)	96.5(9)	C(8)-S(1)-C(9)	104.85(15)
C(5)-C(6)-C(1)	118.1(3)	C(9)-S(1)-C(8A)	102.4(5)
C(5)-C(6)-C(7)	115.6(4)	O(1)-S(1)-C(8)	112.88(18)
C(5)-C(6)-C(7A)	145.4(9)	O(1)-S(1)-C(8A)	83.1(6)
C(8)-C(7)-C(6)	124.4(4)	O(1)-S(1)-C(9)	107.88(16)
C(8A)-C(7A)-C(6)	111.9(18)	O(1)-S(1)-O(2)	118.93(19)
C(7)-C(8)-S(1)	119.0(3)	O(2)-S(1)-C(8)	103.48(18)
C(7A)-C(8A)-S(1)	114.0(16)	O(2)-S(1)-C(8A)	133.1(6)
C(10)-C(9)-S(1)	119.4(2)	O(2)-S(1)-C(9)	107.88(15)
C(14)-C(9)-C(10)	120.7(3)		

6. Mechanistic studies

6.1 Effect of radical scavengers and control experiments

To gain insight into the process of the present reaction, the radical scavengers TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and 1,1-diphenylethylene was added separately into the standard reaction system (**Scheme 6.1a, Scheme 6.1b**). To further clarify the reaction pathway of the dehydrogenative olefinsulfonation, experiments with styrene instead of ethylbenzene were carried out under the standard conditions (**Scheme 6.1c**).

a) addition of TEMPO

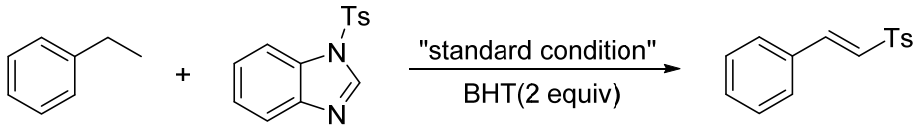


1a **2a** **3aa,** 19%

Under Standard Procedure for the Olefinsulfonation, In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with ethylbenzene (171µl, 1.4 mmol), N-sulfonyl-benzo[d]imidazole (54.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 µl, 2 equiv), 3Å (25 mg), LiBr (34.8 mg, 2.0 equiv), TEMPO (62.5 mg, 1.2 equiv) for **Scheme 6.1a,** followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction was quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and

concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (E)-1-methyl-4-(styrylsulfonyl)benzene as white solid (9.8 mg, 19% yield) .

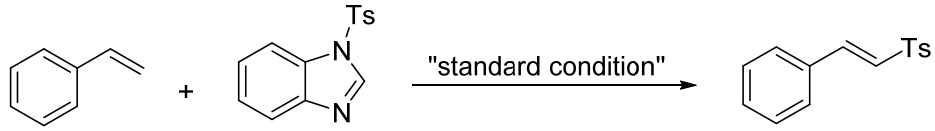
b) addition of BHT



1a **2a** **3aa,** ND

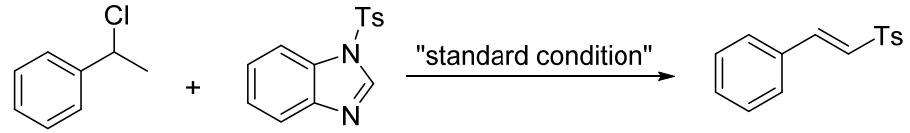
In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with alkyl arenes compounds (171μl, 1.4 mmol), N-sulfonyl-benzo[d]imidazole (54.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg), LiBr (34.8 mg, 2.0 equiv), BHT (88.1 mg, 2.0 equiv) for **Scheme 6.1b**, followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. The reaction did not occur and no desired product was detected by TLC.

c) control experiment



1a' **2a** **3aa**, 67%

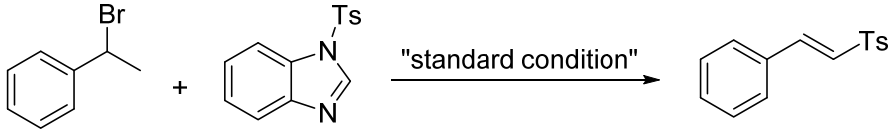
In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with styrene (161μl, 1.4 mmol), N-sulfonyl-benzo[d]imidazole (54.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg), LiBr (34.8 mg, 2.0 equiv), followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction was quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (E)-1-methyl-4-(styrylsulfonyl)benzene as white solid (35 mg, 67%).



1m **2a** **3aa,** 28%

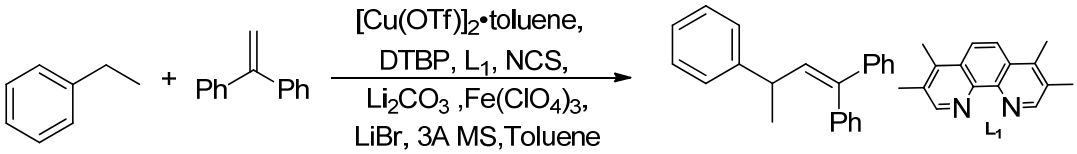
In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with (1-chloroethyl)benzene (1.4 mmol), N-sulfonyl-benzo[d]imidazole (54.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg,

6 mol%), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg), LiBr (34.8 mg, 2.0 equiv), followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction was quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (E)-1-methyl-4-(styrylsulfonyl)benzene as white solid (14 mg, 28%).



1n **2a** **3aa,** 91%

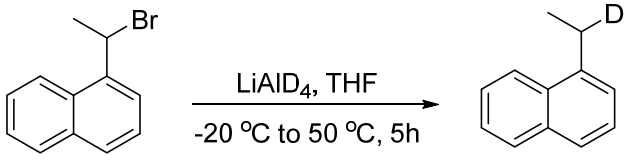
In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with (1-bromoethyl)benzene (1.4 mmol), N-sulfonyl-benzo[d]imidazole (54.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg),, followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction was quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (E)-1-methyl-4-(styrylsulfonyl)benzene as white solid (47 mg, 91%).



1a Trace analysized by GC-MS

In a 10 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with ethylbenzene (171μl, 1.4 mmol), diphenylethene (36 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg), followed by the addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C on an aluminum sand bath for 36 h under an argon atmosphere. The reaction afforded a trace desired product which was detected by GC-MS (MW：284.40).

6.2 kinetic isotope effect



1n **1o**

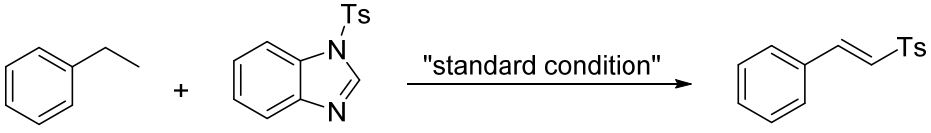
The synthetic procedure was similar to a previous report[18] 1-(1-bromoethyl)naphthalene (730 mg, 3 mmol) and anhydrous THF solvent (10 mL) was added to an oven-dried 100 mL-round bottom flask. The solution was cooling down to –20 °C, and then $LiAlD_4$ (252 mg, 6 mmol) was added to the solution. The reaction mixture was slowly warmed to room temperature and stirred for 5 h. Ice-water was added dropwise to the solution at –20 °C. The solution was slowly warmed to room temperature and extraction with *n*-pentane (3 x 30 mL). The combined organics were dried with $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using *n*-pentane as the eluent to yield the desired product of 1-(ethyl-1-d)naphthalene as colorless oil (236 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.34 Hz, 1H), 7.84 (d, *J* = 8.04 Hz, 1H), 7.70 (d, *J* = 8.16 Hz, 1H), 7.44 - 7.51 (m, 2H), 7.40 (t, $J_1 = J_2$ = 8.34 Hz, 1H), 7.33 (d, *J* = 6.96 Hz, 1H), 3.10 (q, *J* = 14.70 Hz,1H), 1.37 (d, *J* = 7.56 Hz, 3H).

3ia-H/D

k_H/k_D=1.5 (by ^{1}H NMR)

To a 10 mL oven-dried Schlenk tube with a stirrer bar was charged with 1-(ethyl-1-d)naphthalene (220 mg, 1.4 mmol), N-sulfonyl-benzo[d]imidazole (55.4 mg, 0.2 mmol), Copper(I) triflate toluene complex (10.34 mg, 10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (2.8 mg, 6 mol%), N-Chlorosuccinimide (31.9 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (7.08 mg, 10 mol%), Li_2CO_3 (29.6 mg, 2.0 equiv), Di-tert-butyl peroxide (74 μl, 2 equiv), 3Å (25 mg) and LiBr (34.8 mg, 2.0 equiv), followed by addition of anhydrous toluene (1.0 mL). The resulting solution was stirred at 120 °C for 36 hours on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction quenched with water and extracted with and dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **3ia-H/D** as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.60 Hz, 0.4 H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 3H), 7.66 - 7.67 (m, 1H), 7.61 - 7.65 (m, 1H), 7.55 - 7.60 (m, 1H), 7.44 - 7.47 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.94 - 6.96 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 133.9, 131.8, 128.8, 126.4, 125.7, 125.4, 124.9, 123.8, 25.7, 25.6, 25.5, 15.0.

7. Gram-scale reaction



1a **2a:** 1mmol **3aa:**154.9 mg, 60% yield

The procedure for 1 mmol-scale reaction was as follows. In a 25 mL oven-dried Schlenk tube equipped with a stirrer bar was charged with ethylbenzene (855 μl, 7 mmol), N-sulfonyl-benzo[d]imidazole (272.5 mg, 1 mmol), Copper(I) triflate toluene complex (51.7 mg,

10 mol%), 3,4,7,8-Tetramethyl-1,10-phenanthroline (14 mg, 6 mol%), N-Chlorosuccinimide (159.5 mg, 1.2 equiv), $Fe(ClO4)_3 \cdot xH_2O$ (35.4 mg, 10 mol%), Li_2CO_3 (148 mg, 2.0 equiv), Di-tert-butyl peroxide (370 μl, 2 equiv), 3Å (125 mg), LiBr (174 mg, 2.0 equiv), followed by the addition of anhydrous toluene (5.0 mL). The resulting solution was stirred at 120 °C for 36 h on an aluminum sand bath under an argon atmosphere. After cooling to room temperature, the reaction quenched with water (30 mL) and extracted with dichloromethane (30 mL × 3), the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford (E)-1-methyl-4-(styrylsulfonyl)benzene as white solid (154.9 mg, 60%).

8. References

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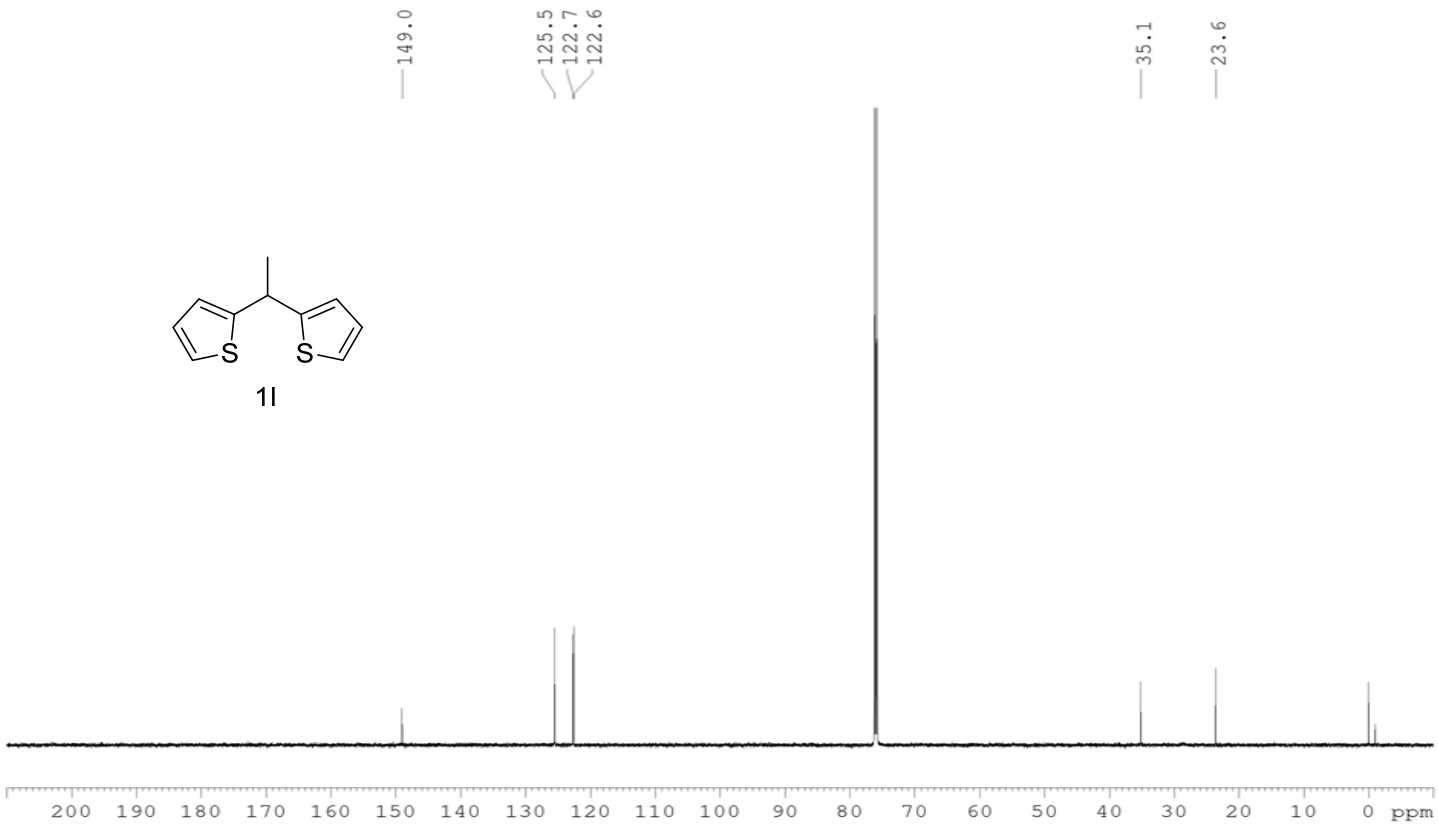
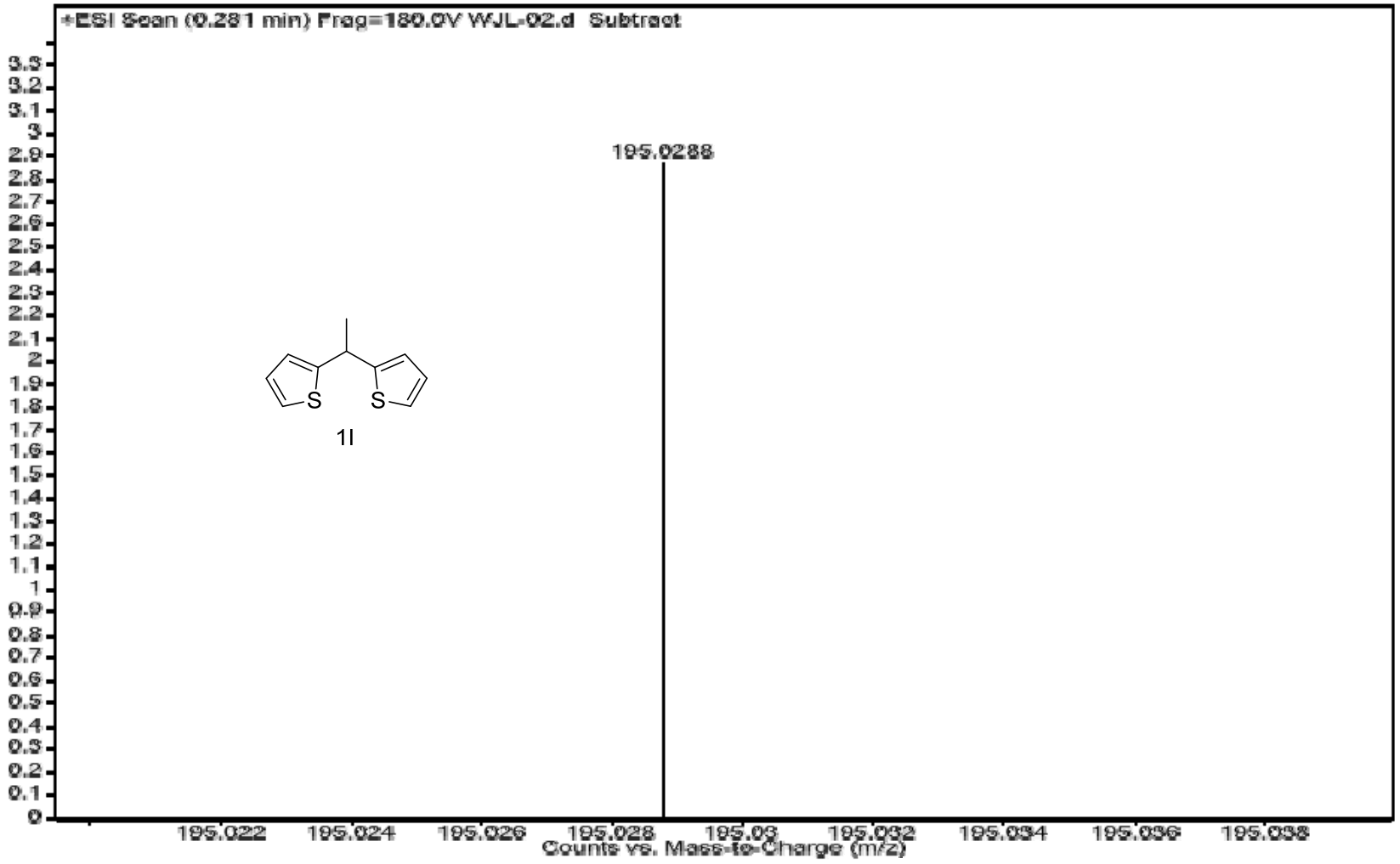
9. Images of ^{1}H, ^{13}C NMR, ^{19}F NMR, HRMS Spectra

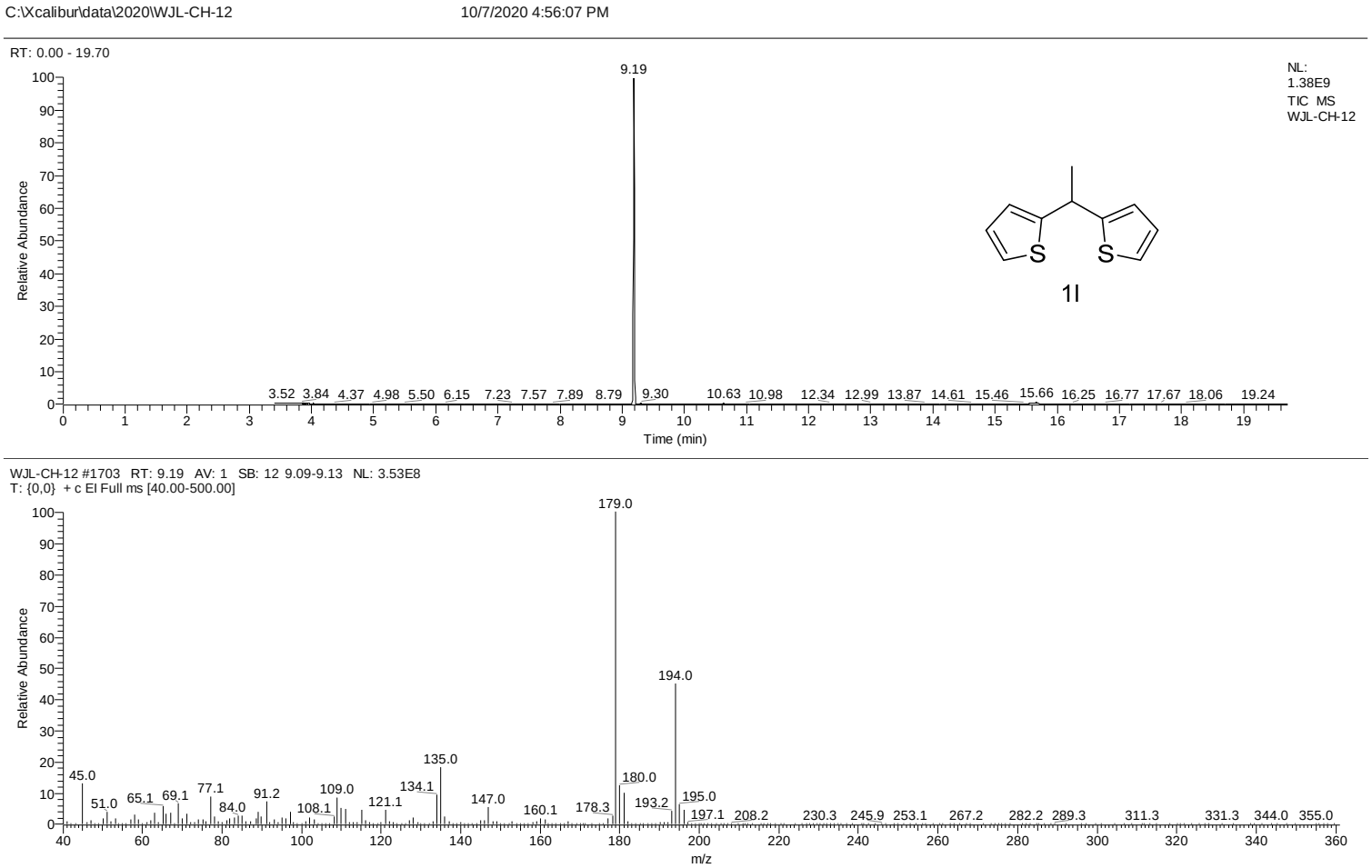
^{1}H NMR spectrum of compound 1l in $CDCl_3$ (600 MHz)



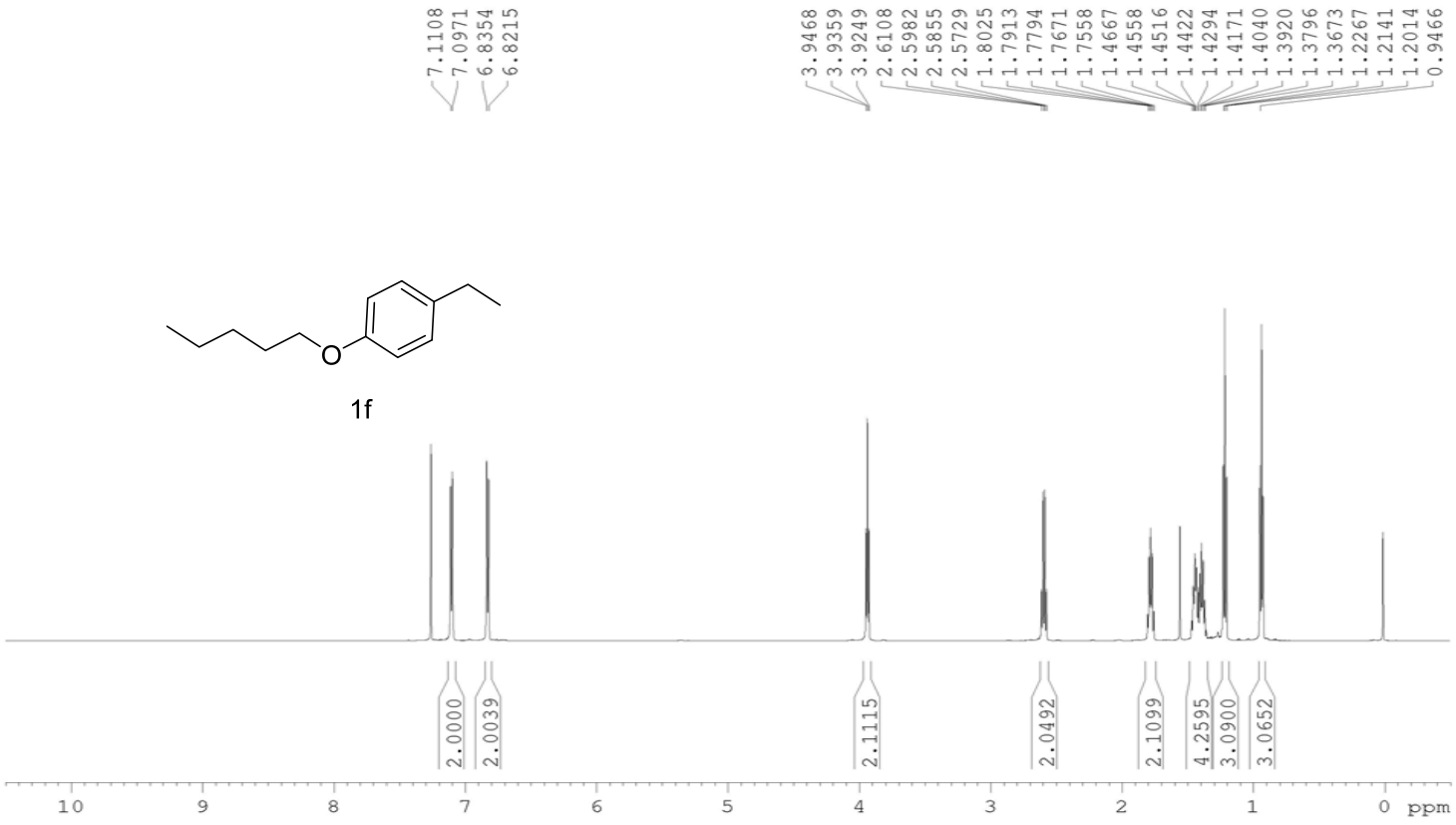
^{13}C NMR spectrum of compound 1l in $CDCl_3$ (150 MHz)



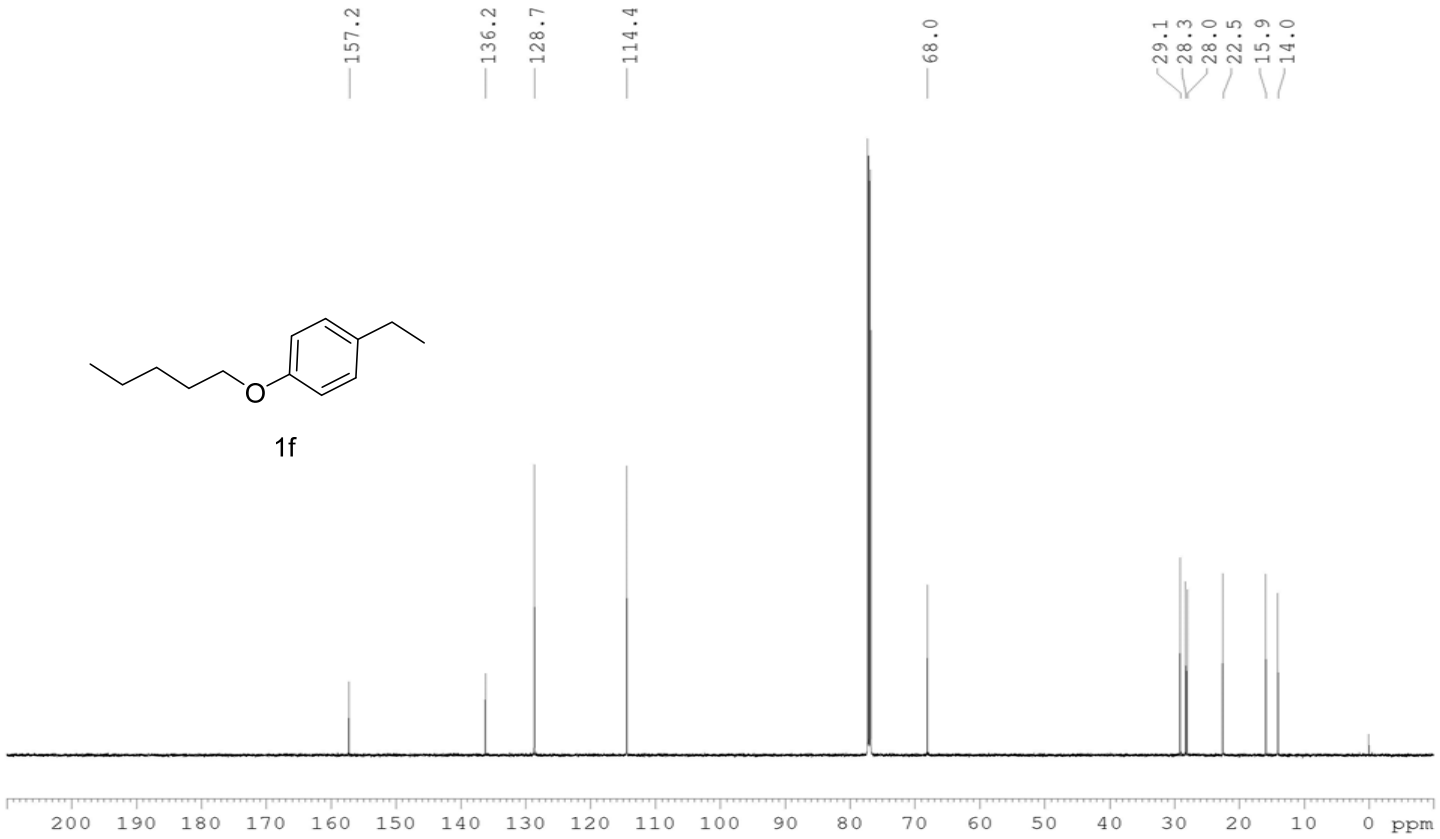
HRMS spectrum of compound 1l



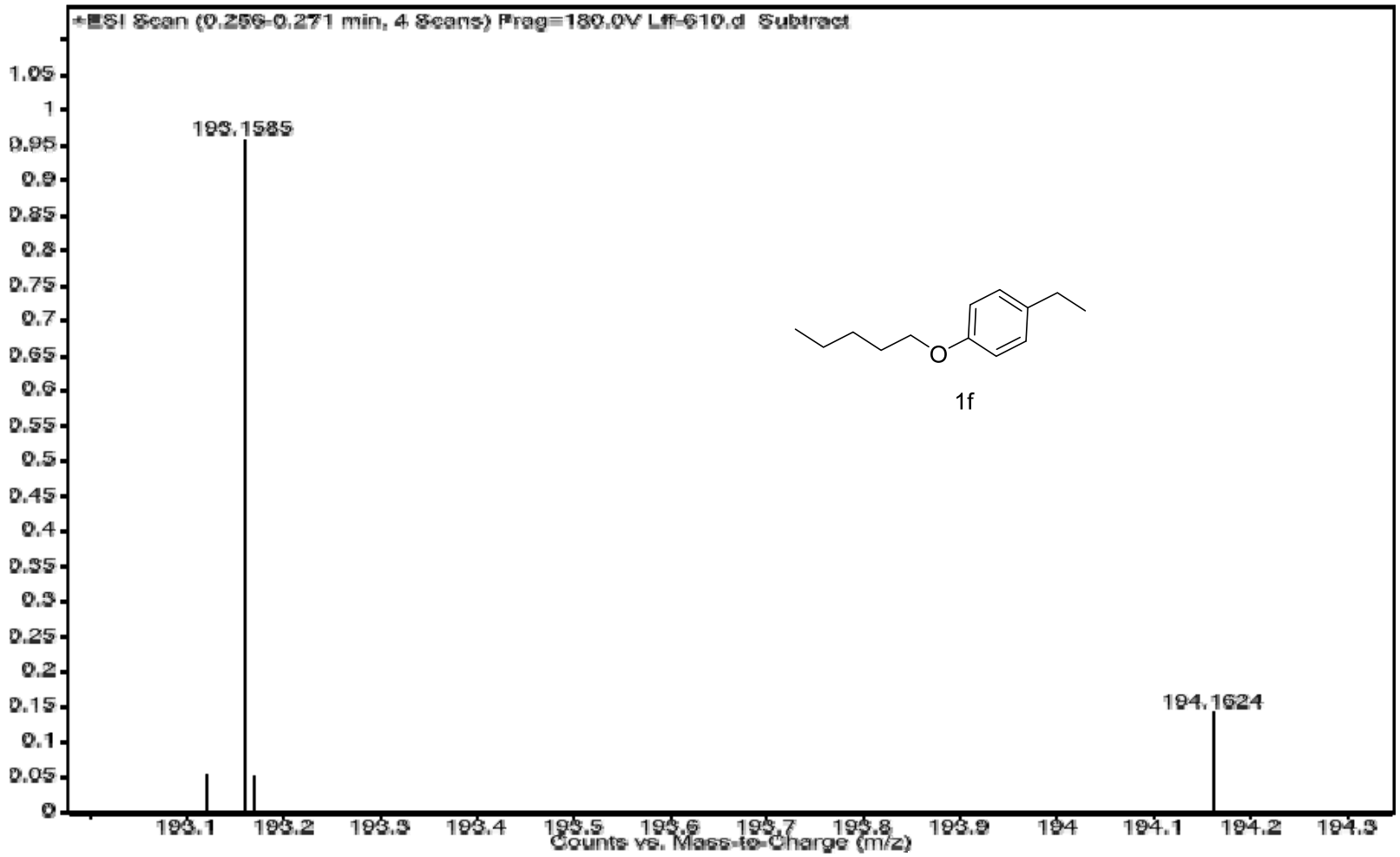
GC-MS spectrum of compound 1l



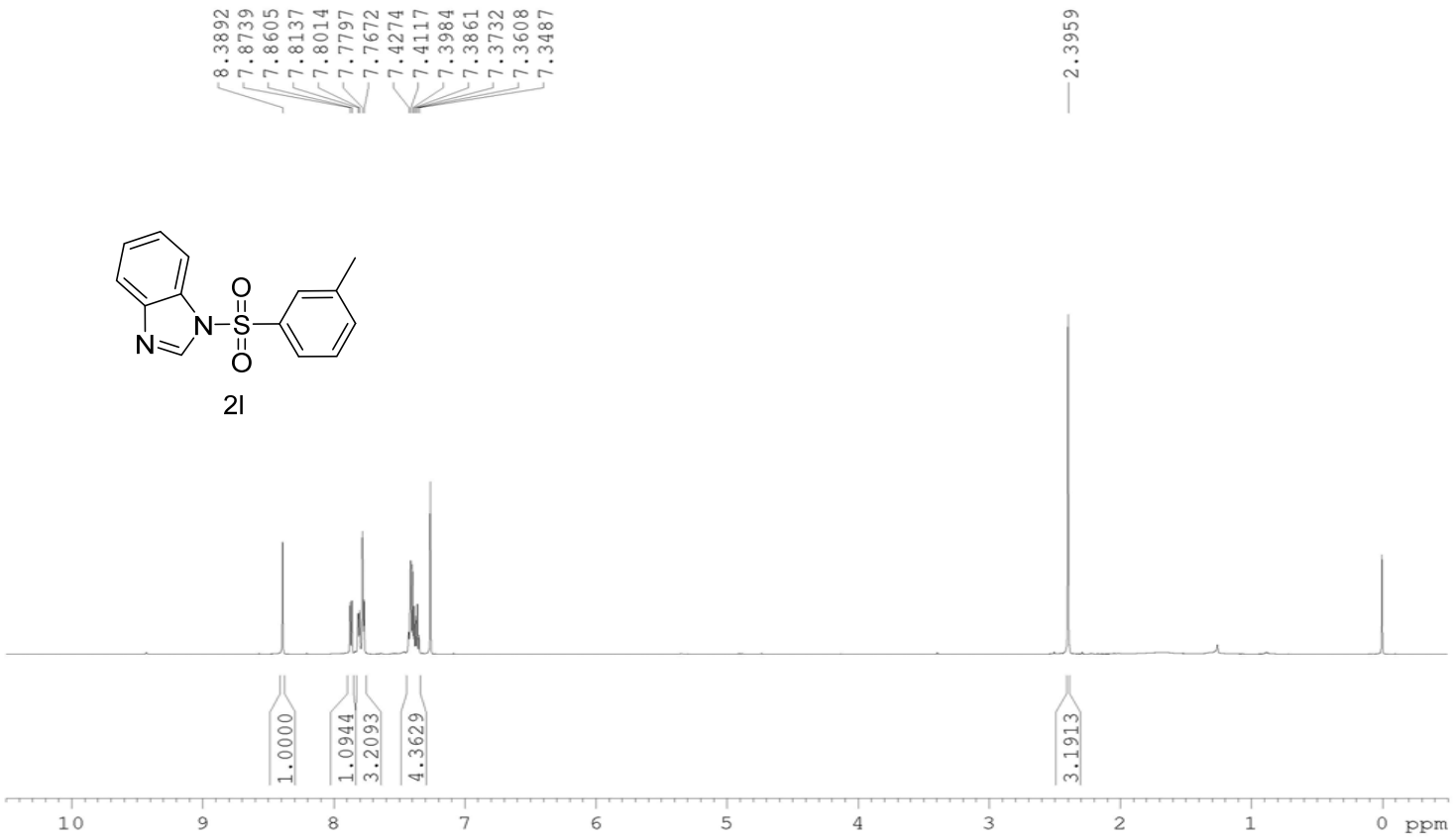
^{1}H NMR spectrum of compound 1f in $CDCl_3$ (600 MHz)



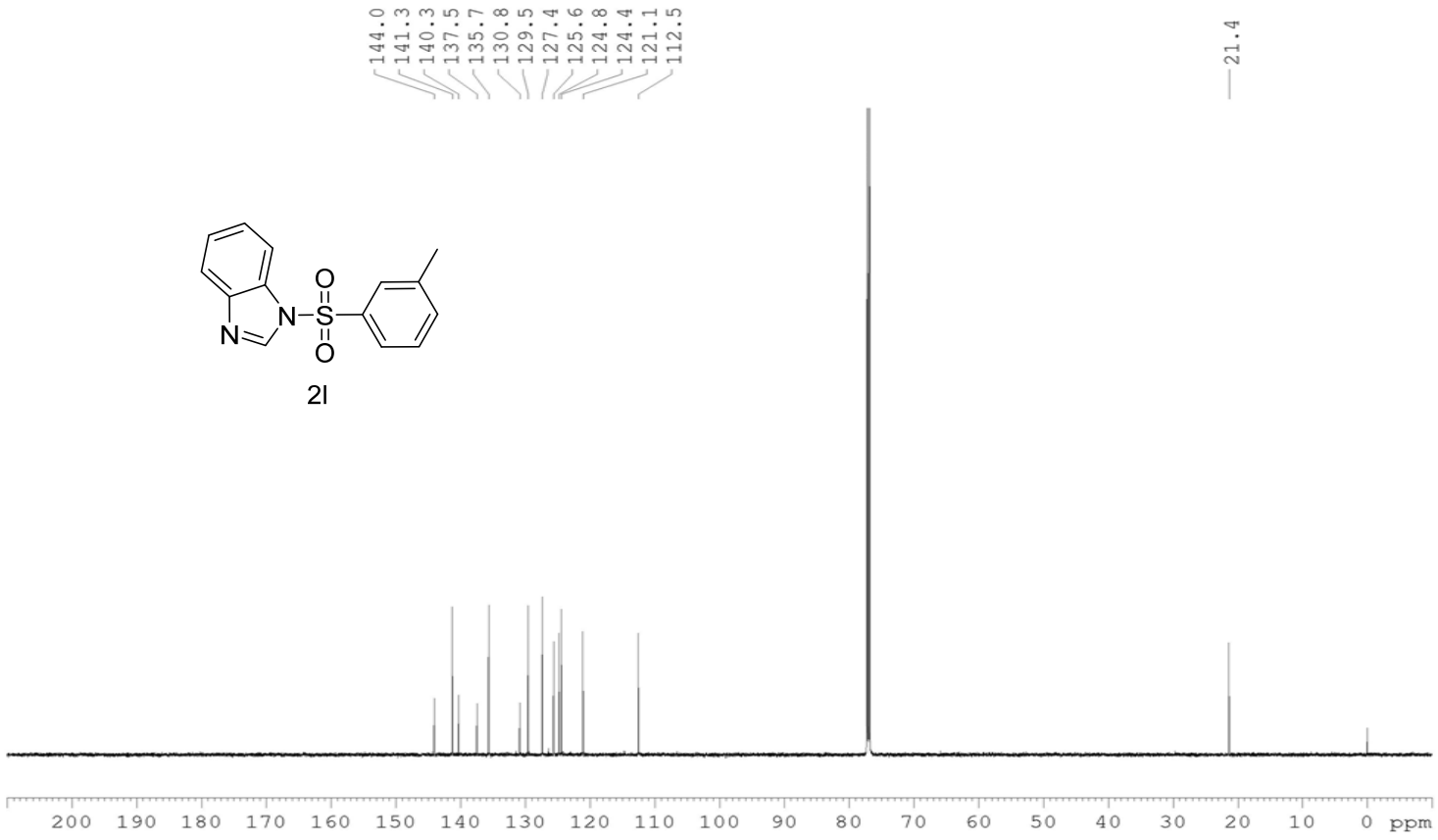
^{13}C NMR spectrum of compound 1f in $CDCl_3$ (150 MHz)



HRMS spectrum of compound 1f

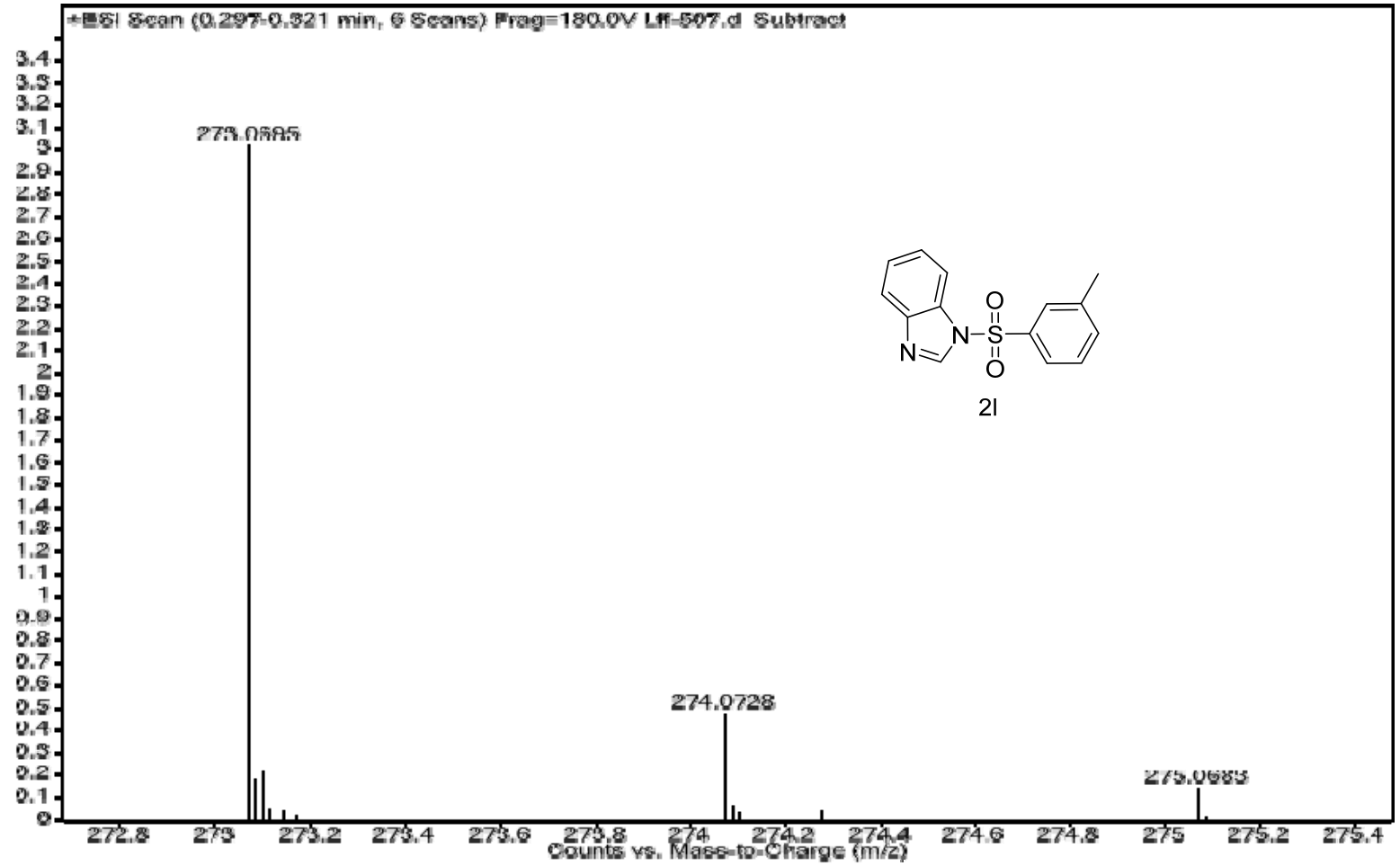


^{1}H NMR spectrum of compound 2l in $CDCl_3$ (600 MHz)

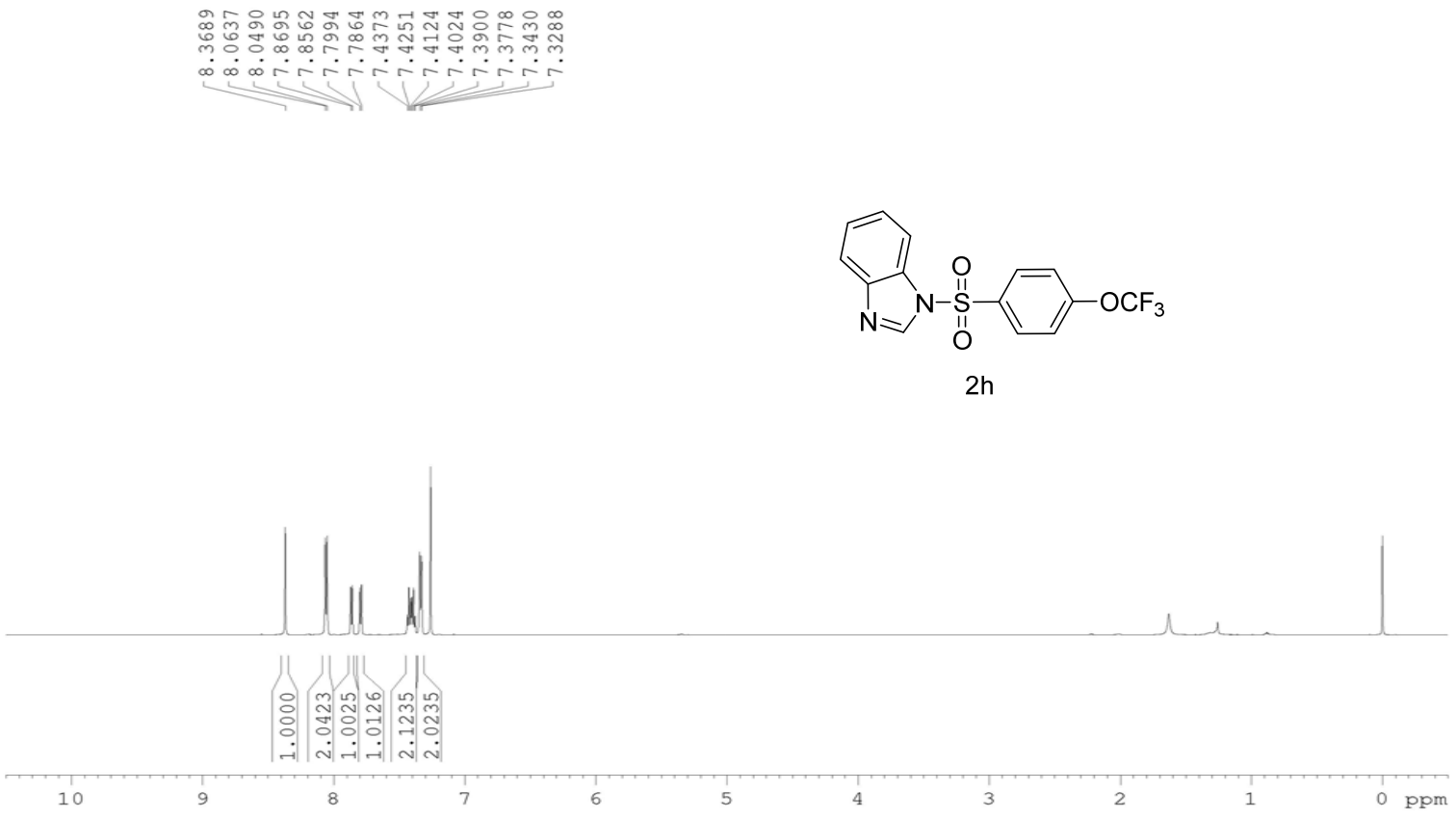


2l

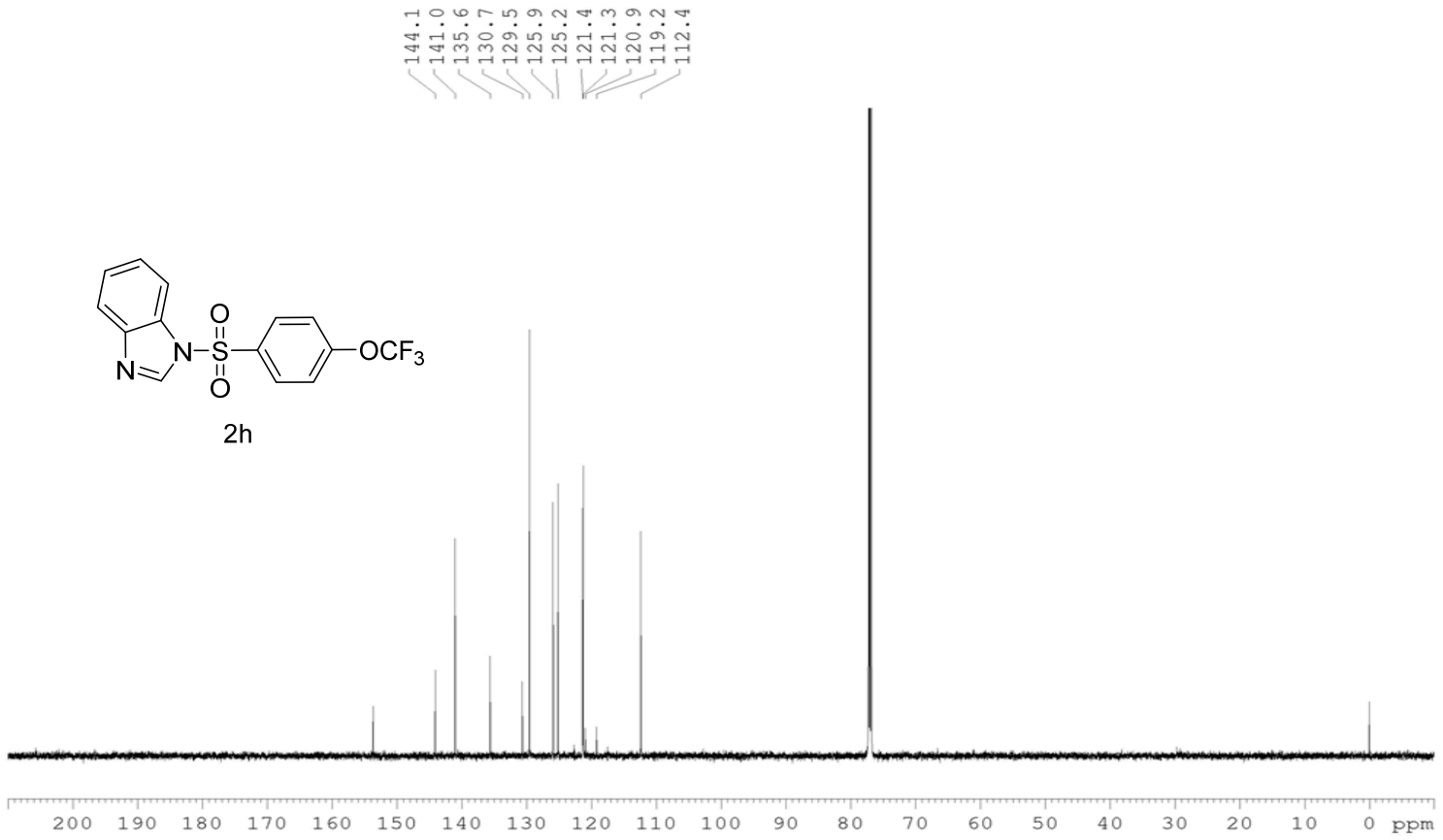
^{13}C NMR spectrum of compound 2l in $CDCl_3$ (150 MHz)



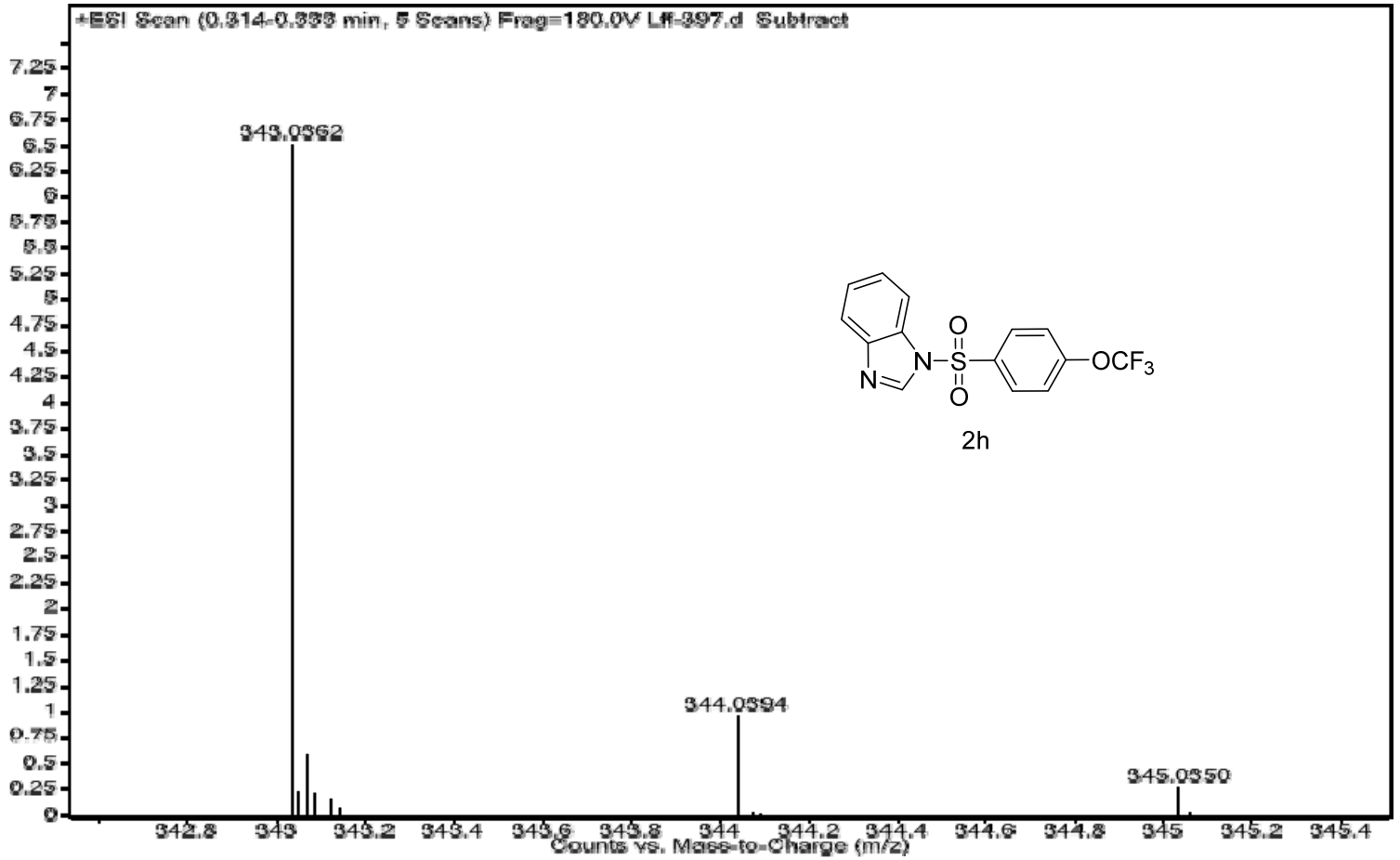
HRMS spectrum of compound 2l



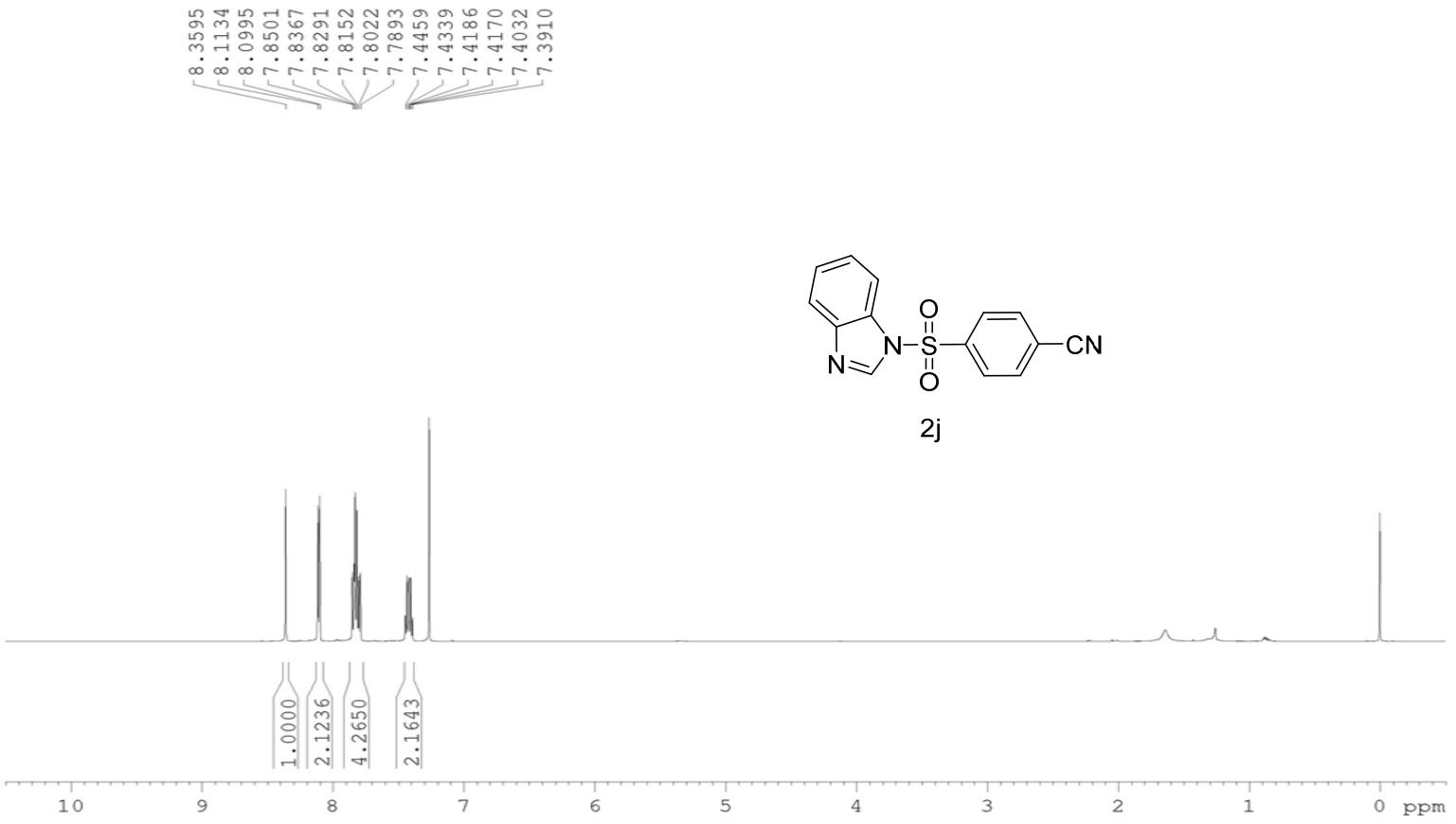
^{1}H NMR spectrum of compound 2h in $CDCl_3$ (600 MHz)



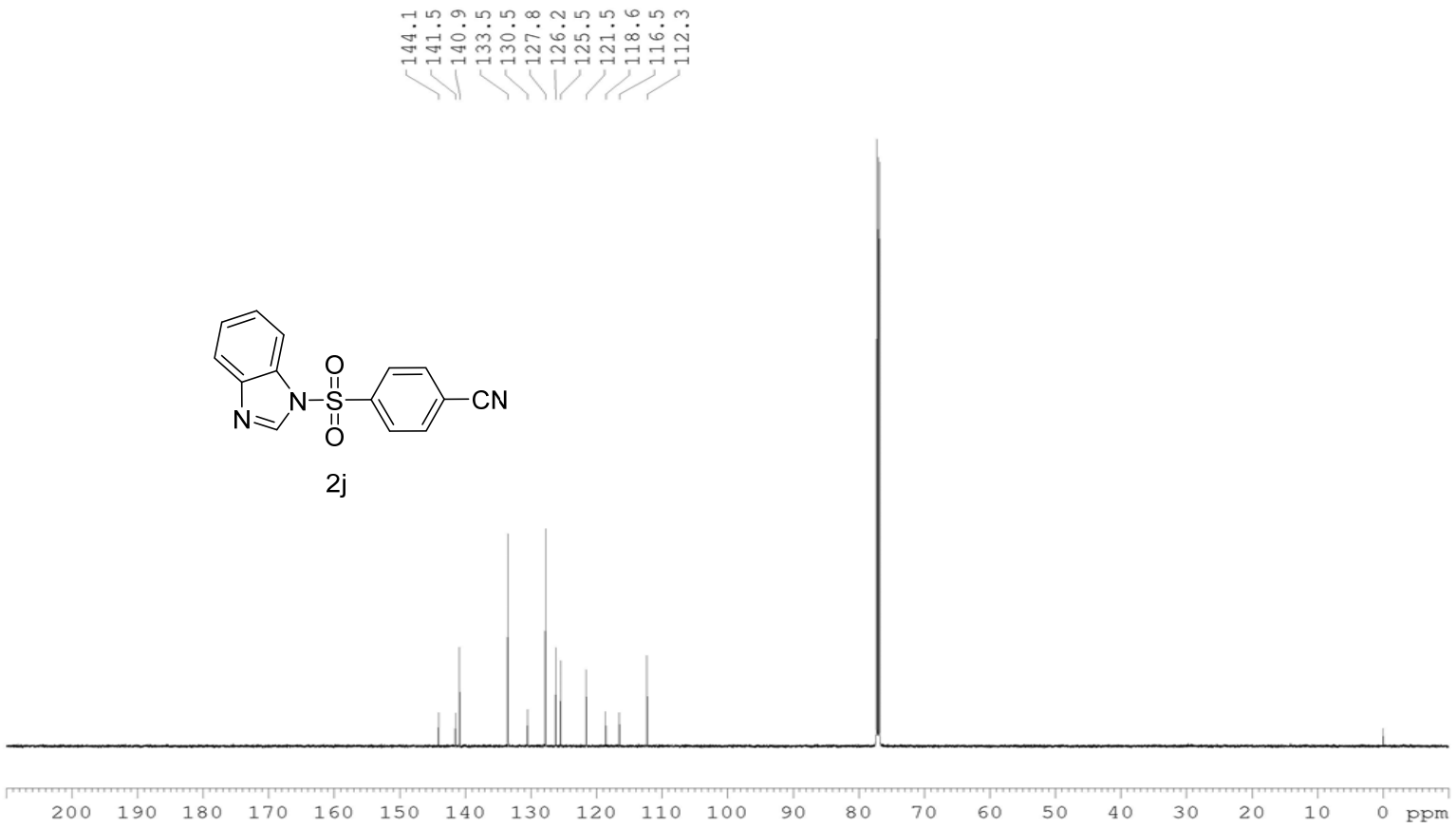
^{13}C NMR spectrum of compound 2h in $CDCl_3$ (150 MHz)



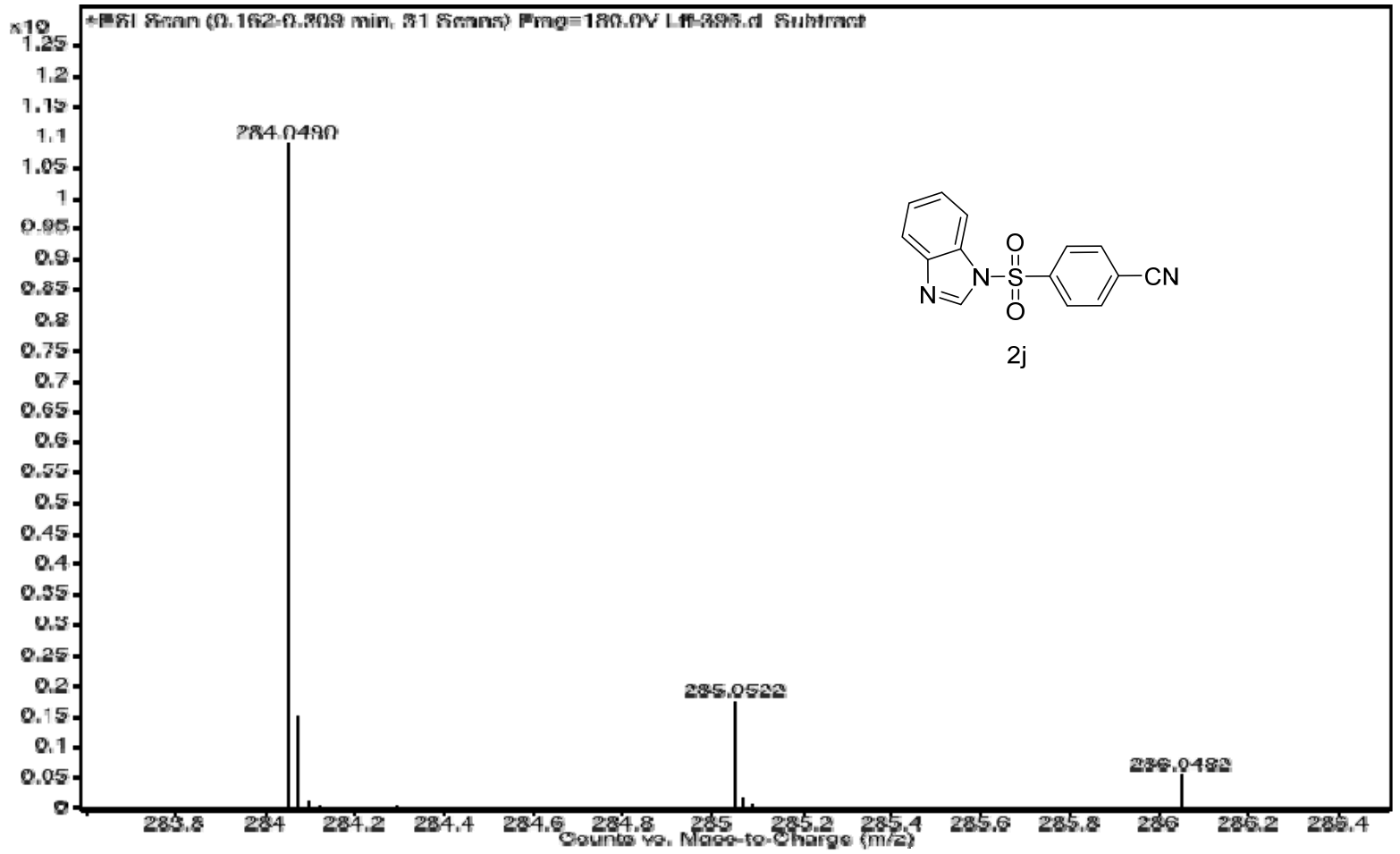
HRMS spectrum of compound 2h



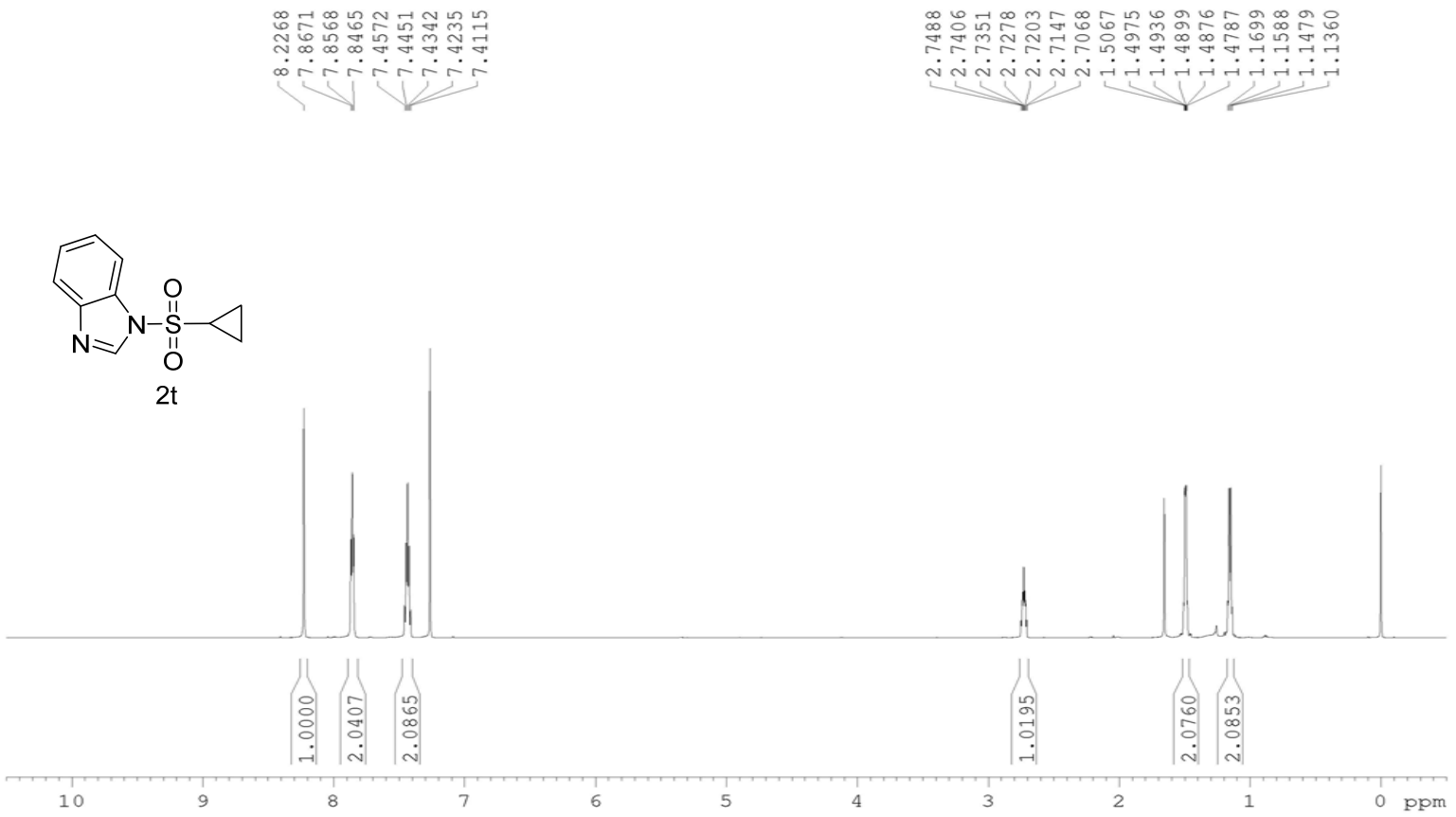
^{1}H NMR spectrum of compound 2j in $CDCl_3$ (600 MHz)



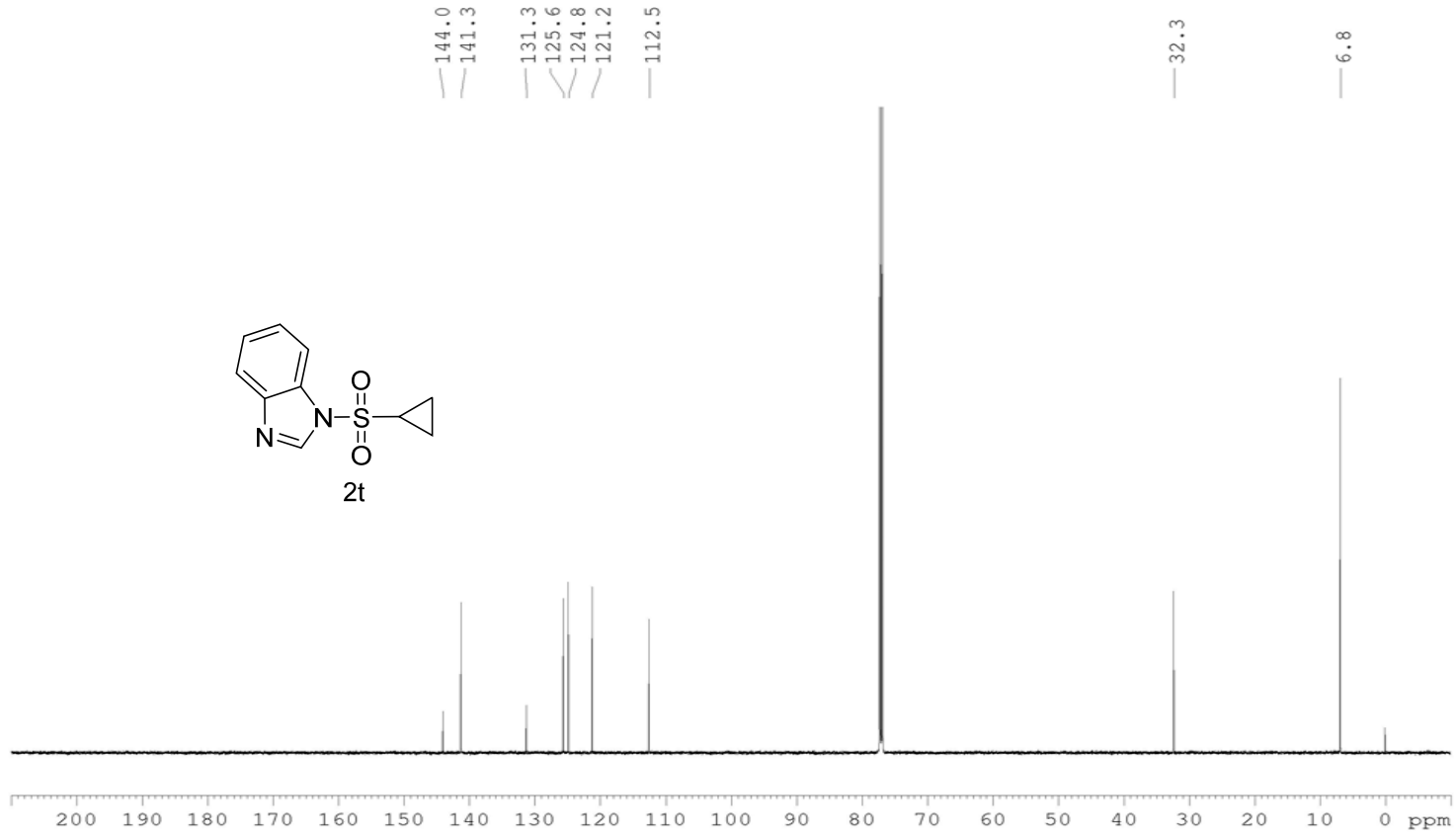
^{13}C NMR spectrum of compound 2j in $CDCl_3$ (150 MHz)



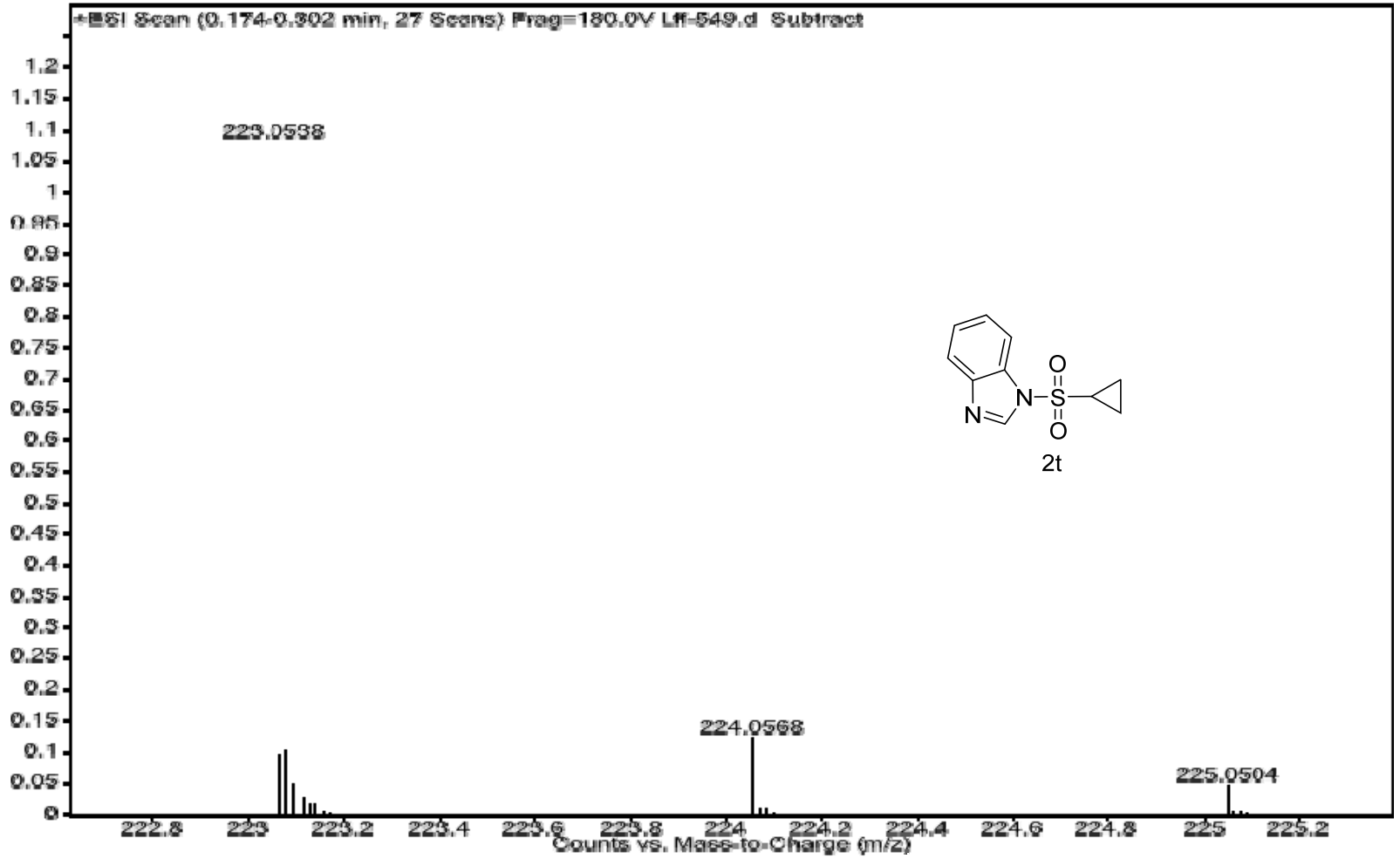
HRMS spectrum of compound 2j



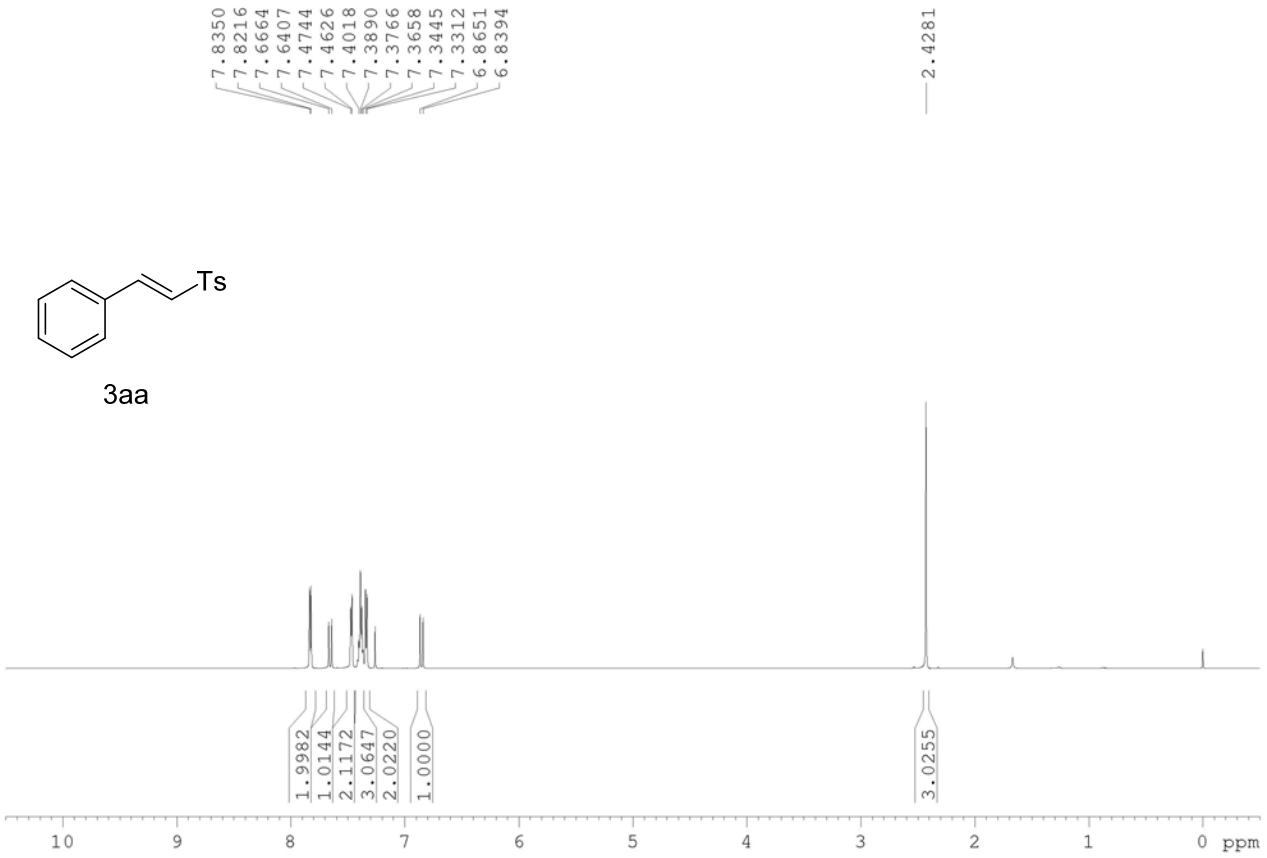
^{1}H NMR spectrum of compound 2t in $CDCl_3$ (600 MHz)



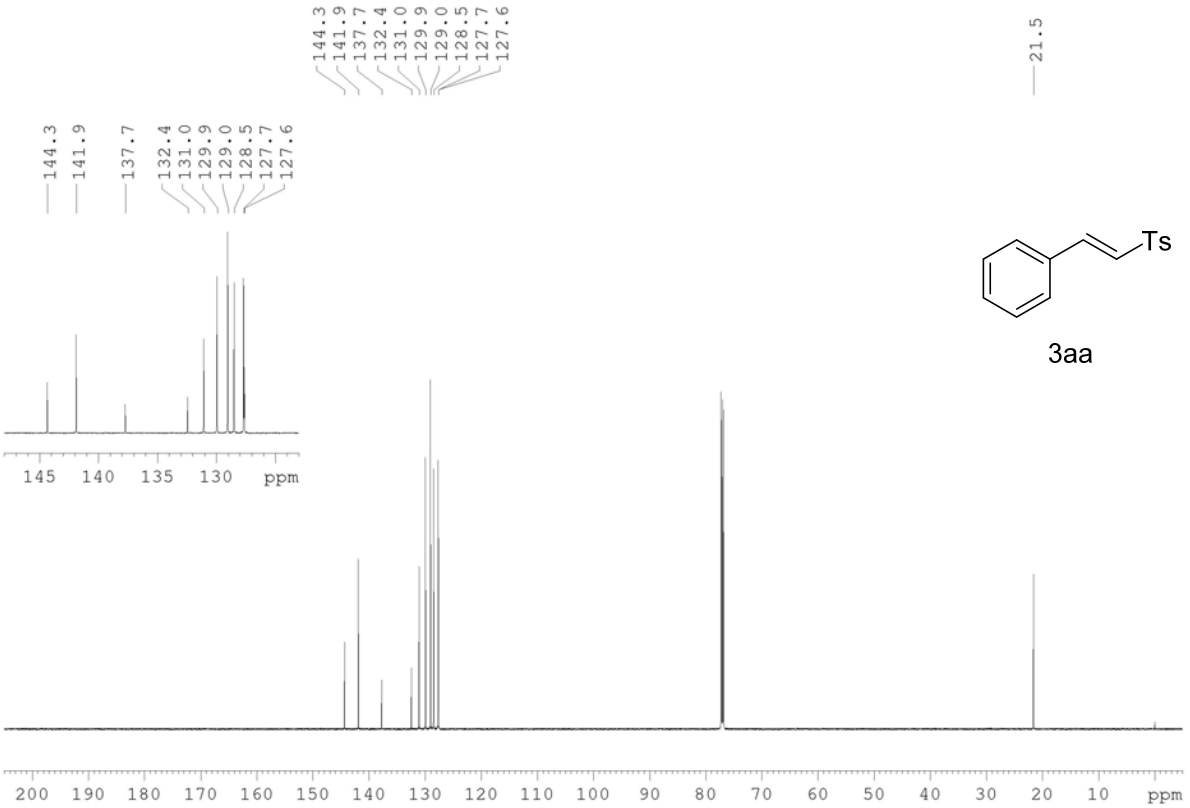
^{13}C NMR spectrum of compound 2t in $CDCl_3$ (150 MHz)



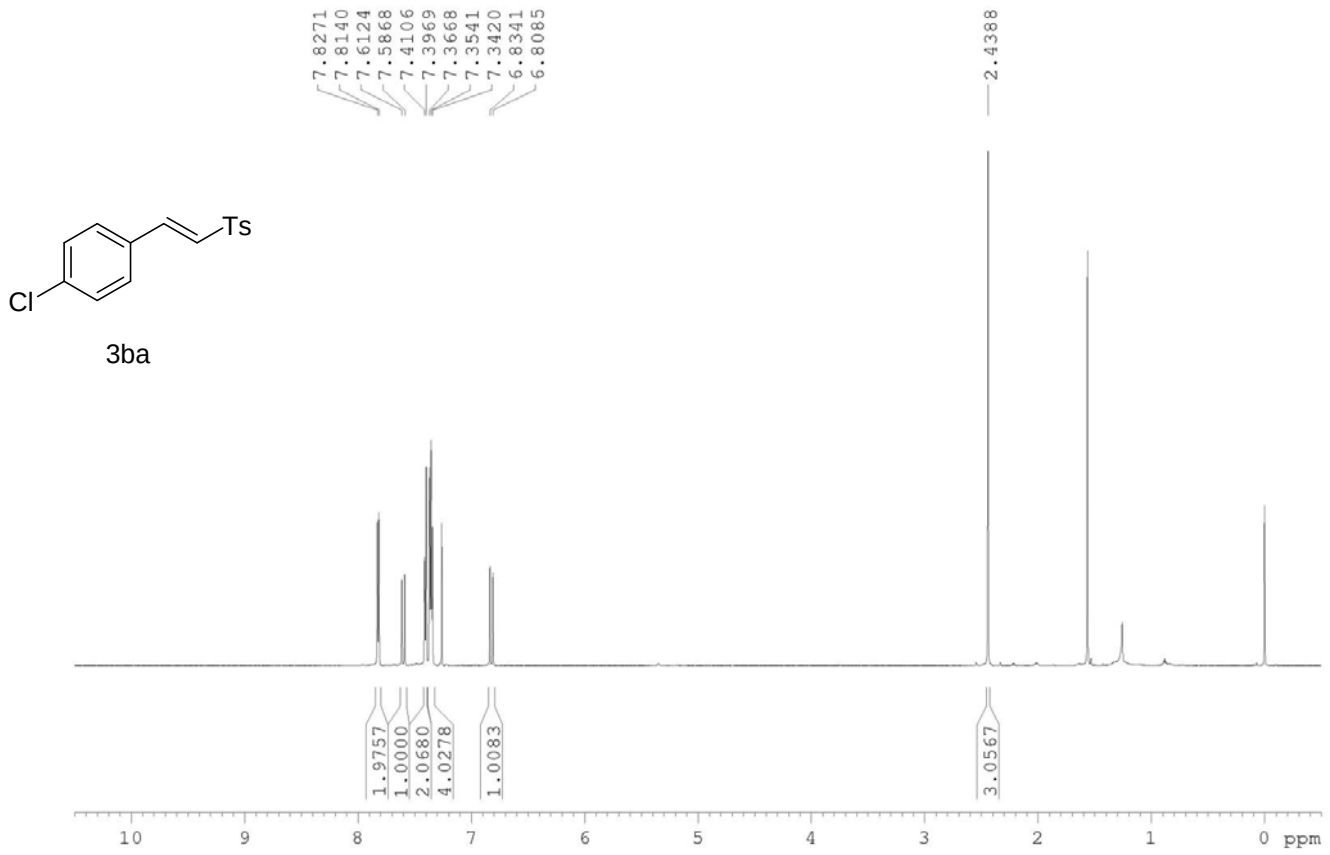
HRMS spectrum of compound 2t



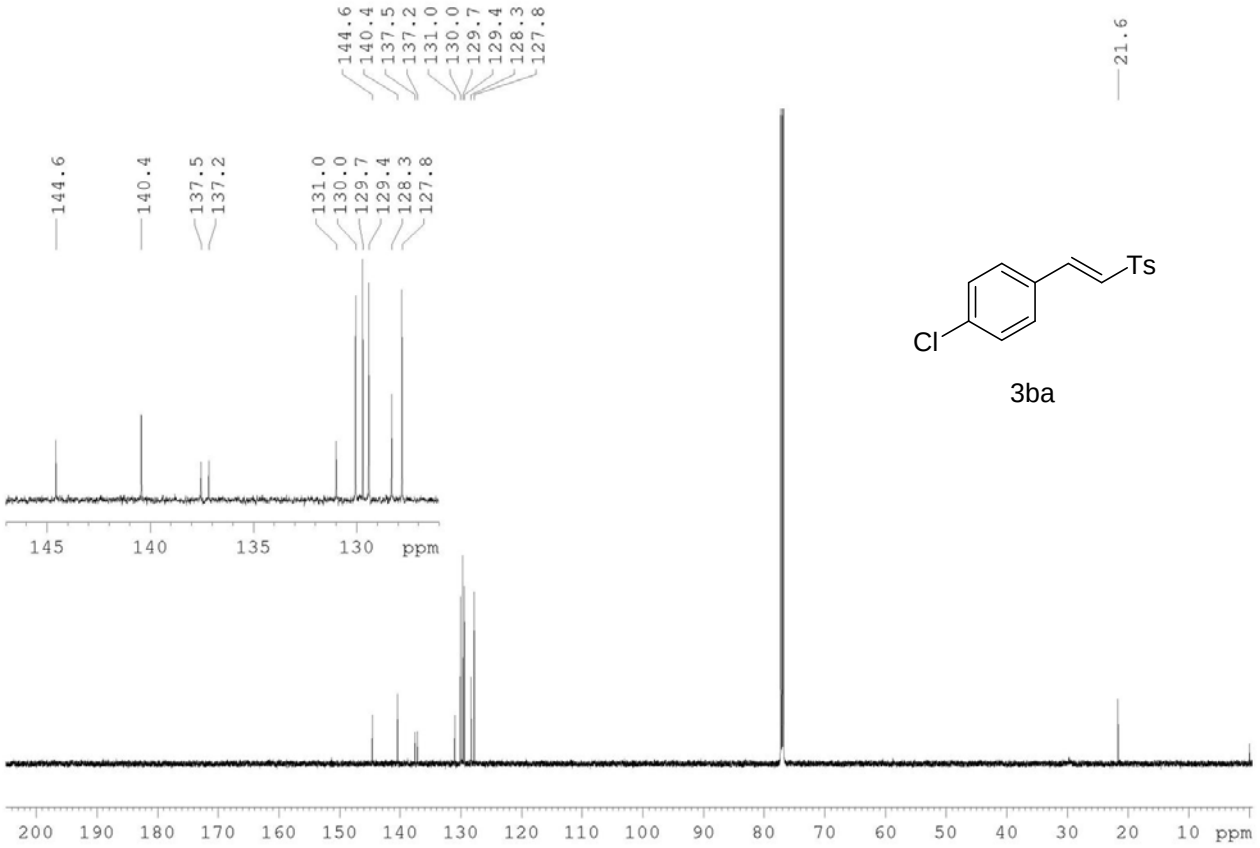
^{1}H NMR spectrum of compound 3aa in $CDCl_3$ (600 MHz)



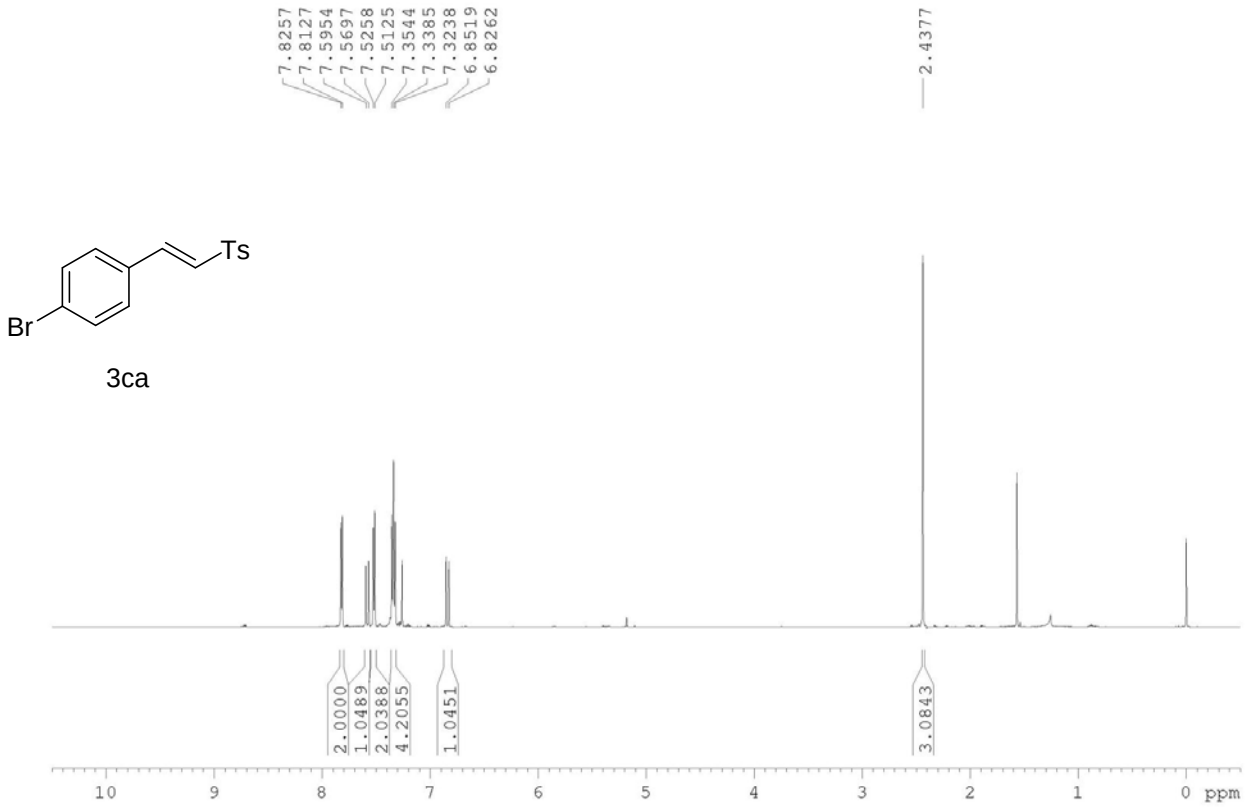
^{13}C NMR spectrum of compound 3aa in $CDCl_3$ (150 MHz)



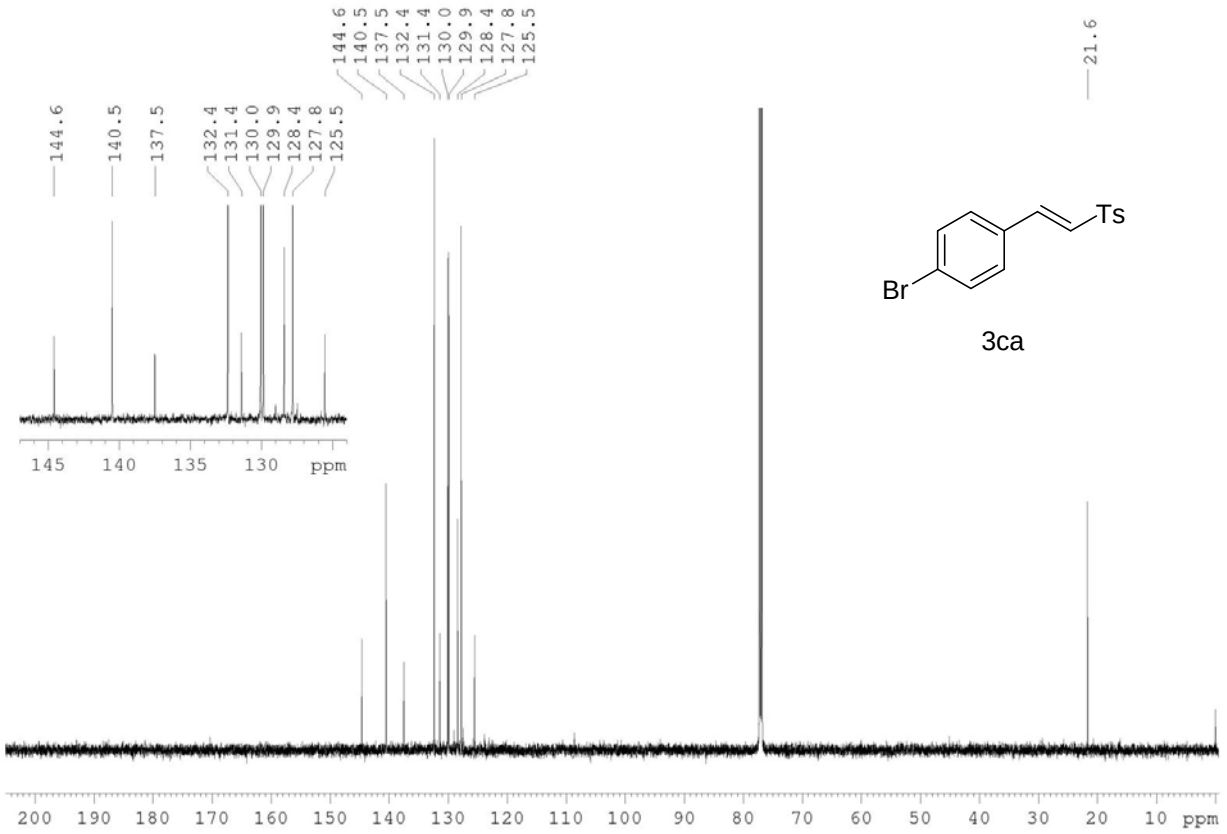
^{1}H NMR spectrum of compound 3ba in $CDCl_3$ (600 MHz)



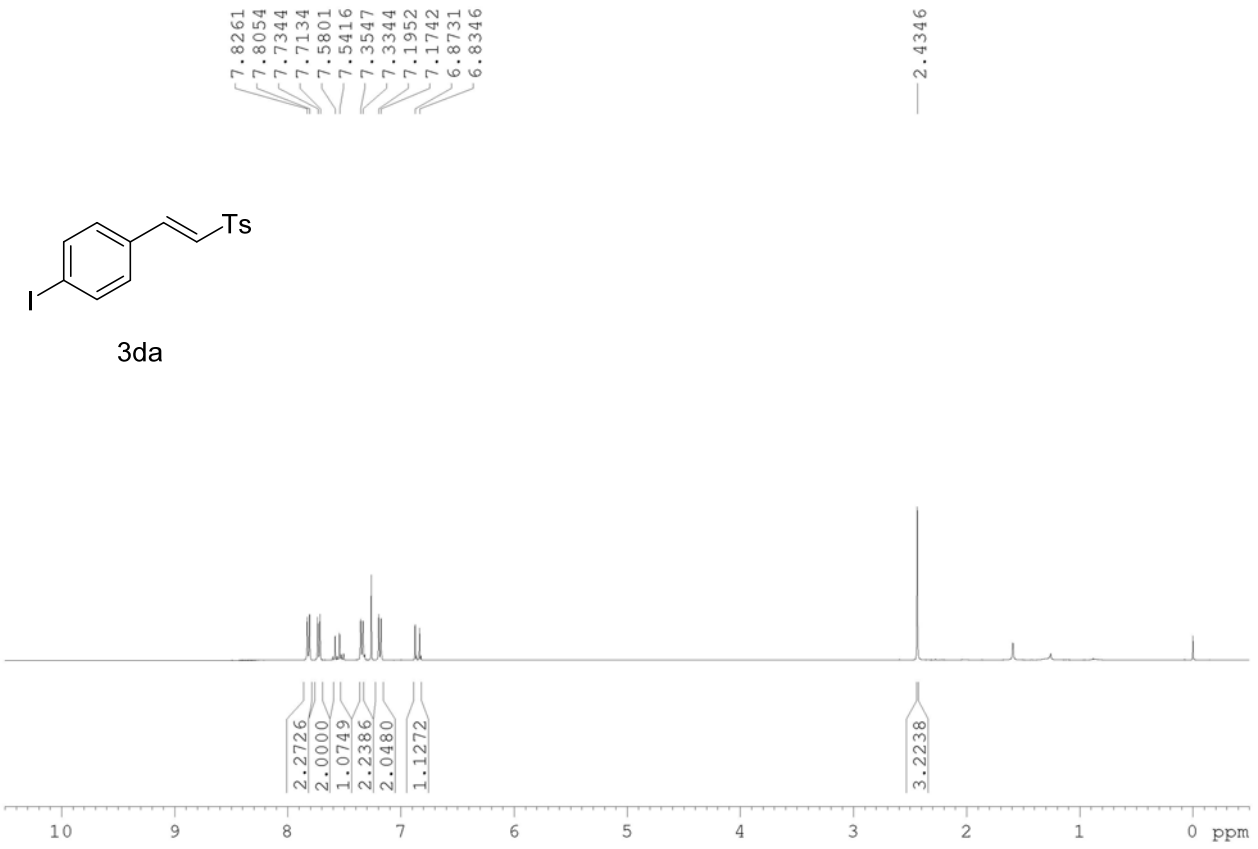
^{13}C NMR spectrum of compound 3ba in $CDCl_3$ (150 MHz)



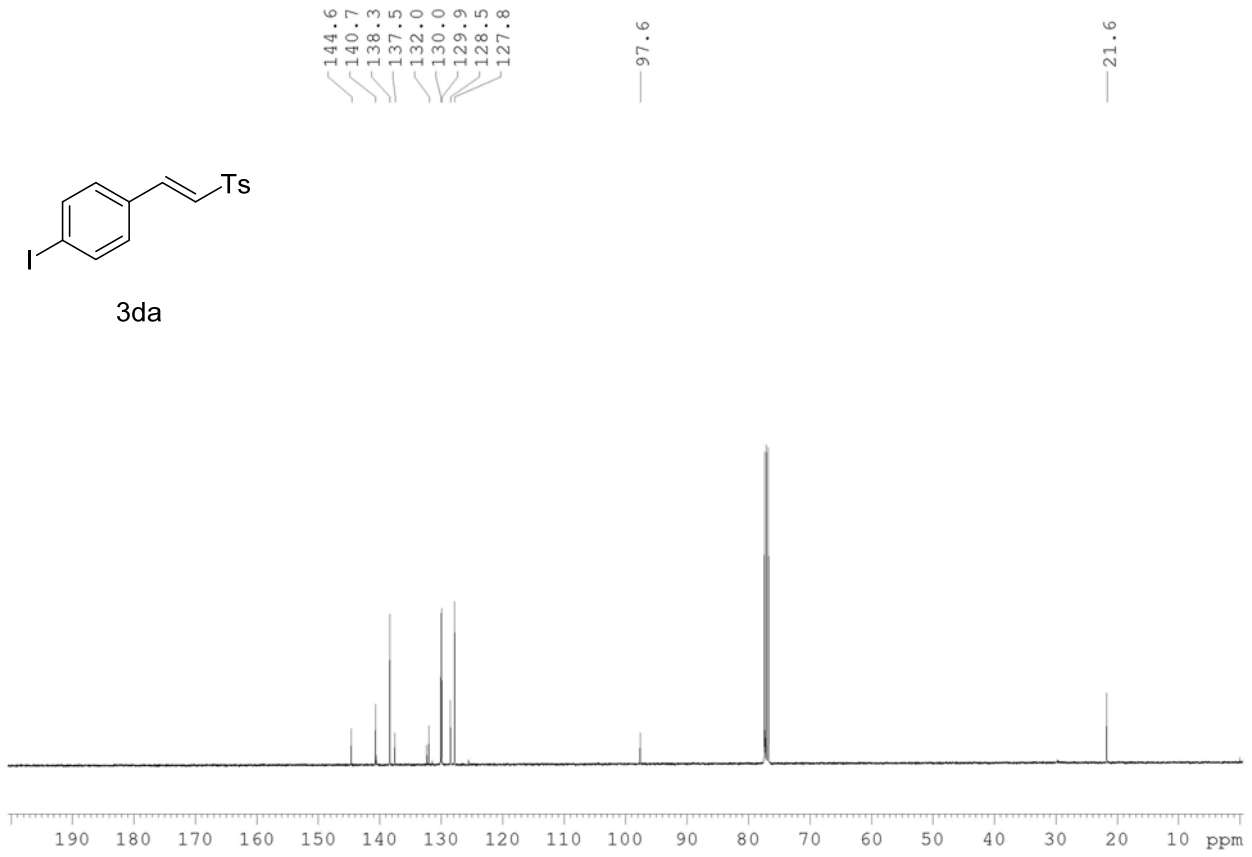
^{1}H NMR spectrum of compound 3ca in $CDCl_3$ (600 MHz)



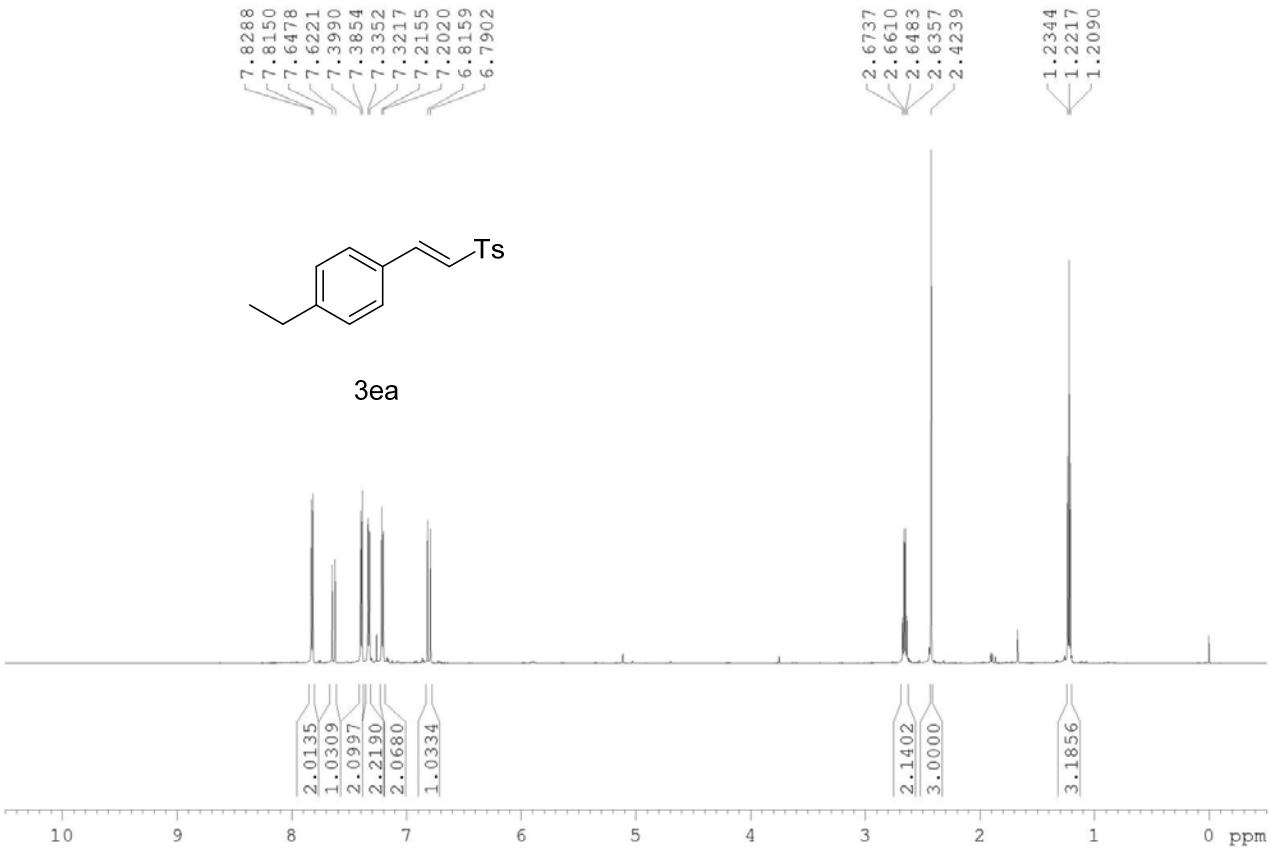
^{13}C NMR spectrum of compound 3ca in $CDCl_3$ (150 MHz)



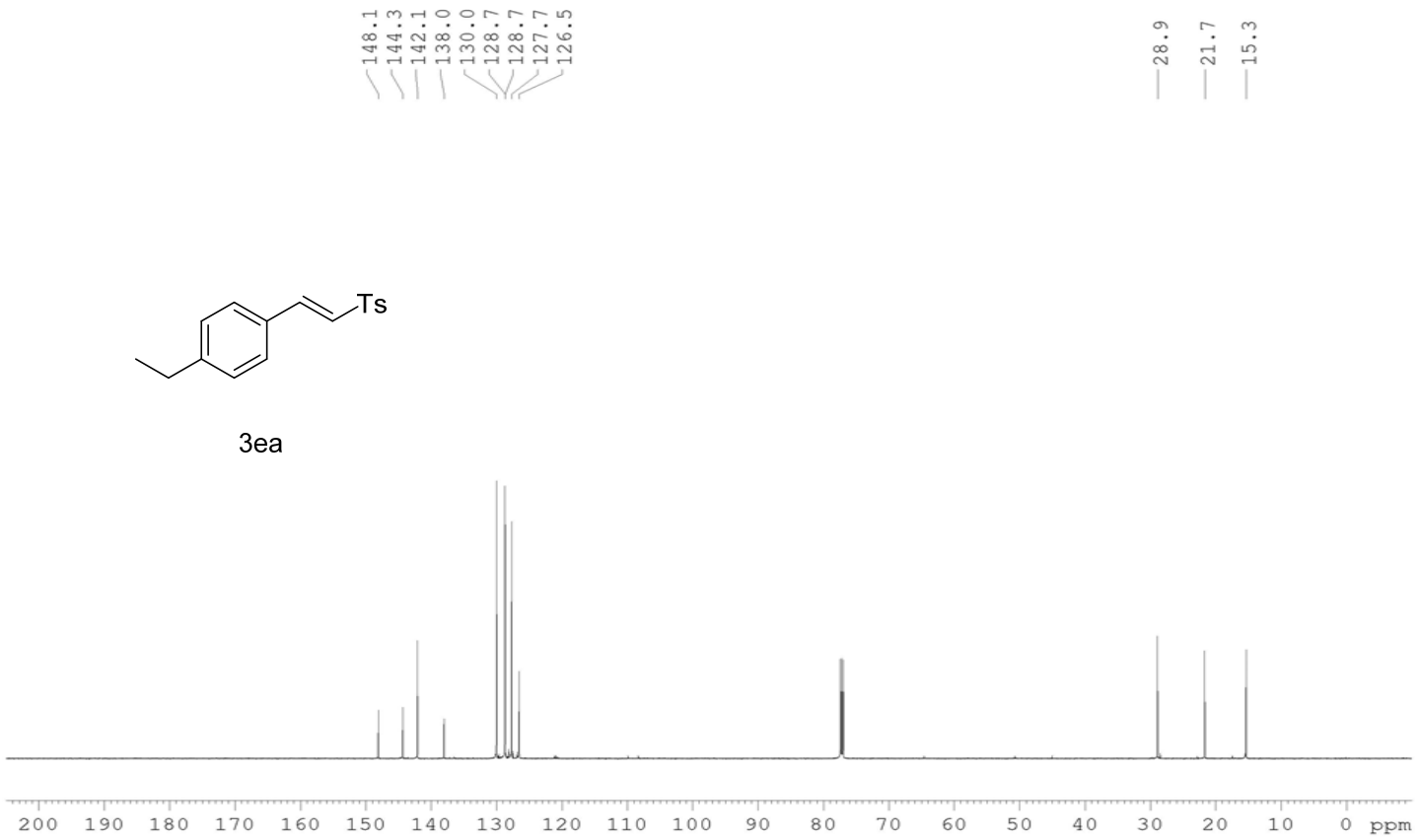
^{1}H NMR spectrum of compound 3da in $CDCl_3$ (600 MHz)



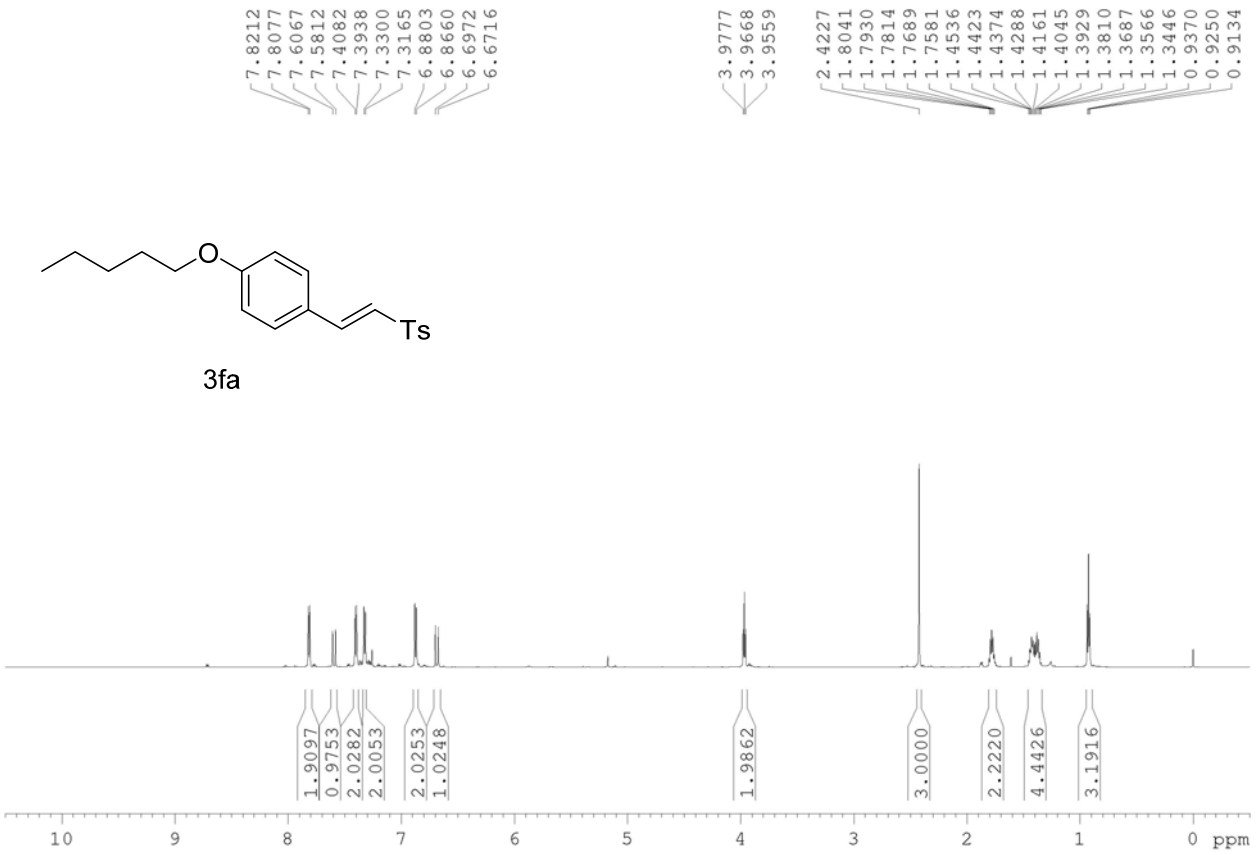
^{13}C NMR spectrum of compound 3da in $CDCl_3$ (150 MHz)



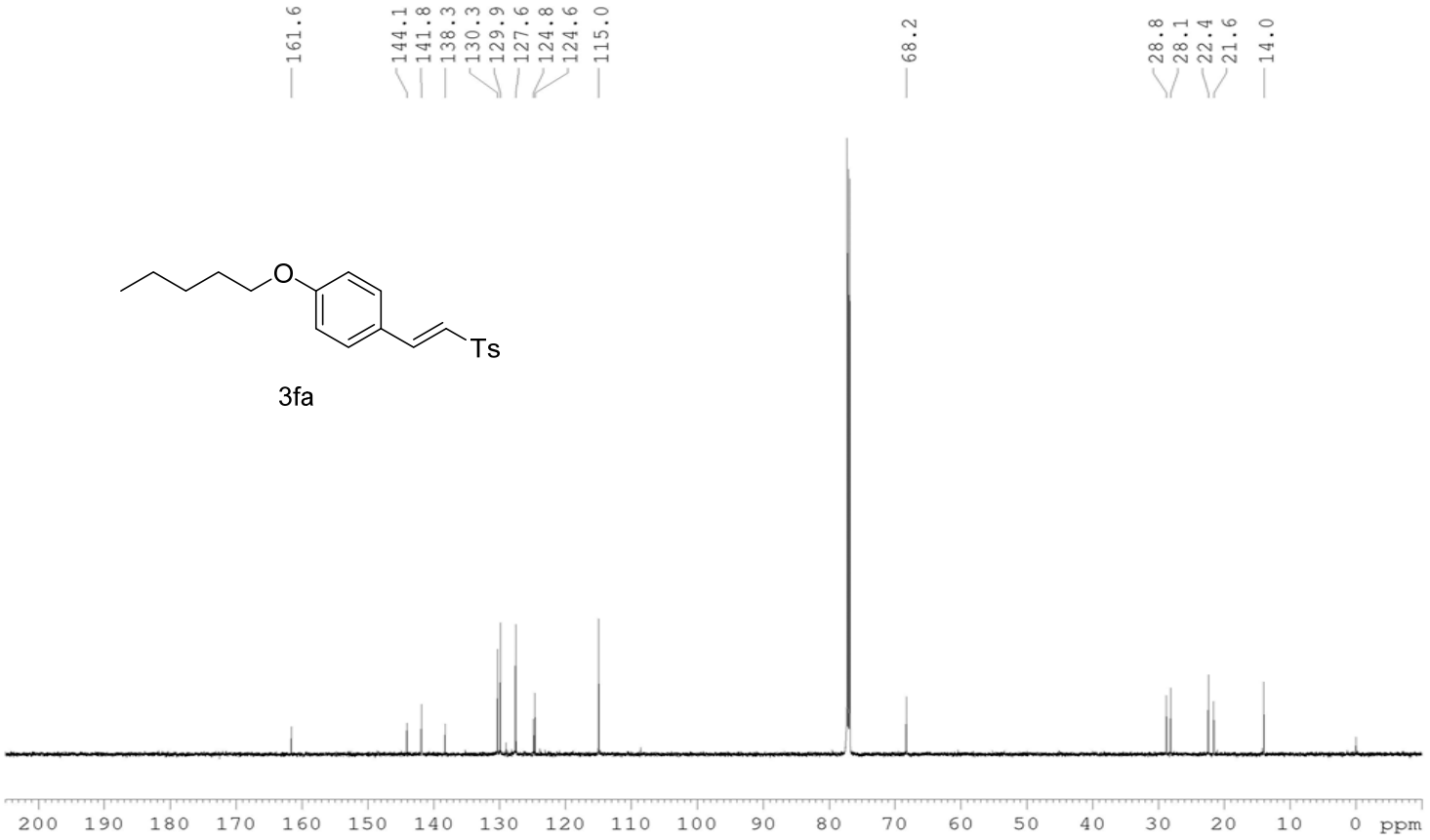
^{1}H NMR spectrum of compound 3ea in $CDCl_3$ (600 MHz)



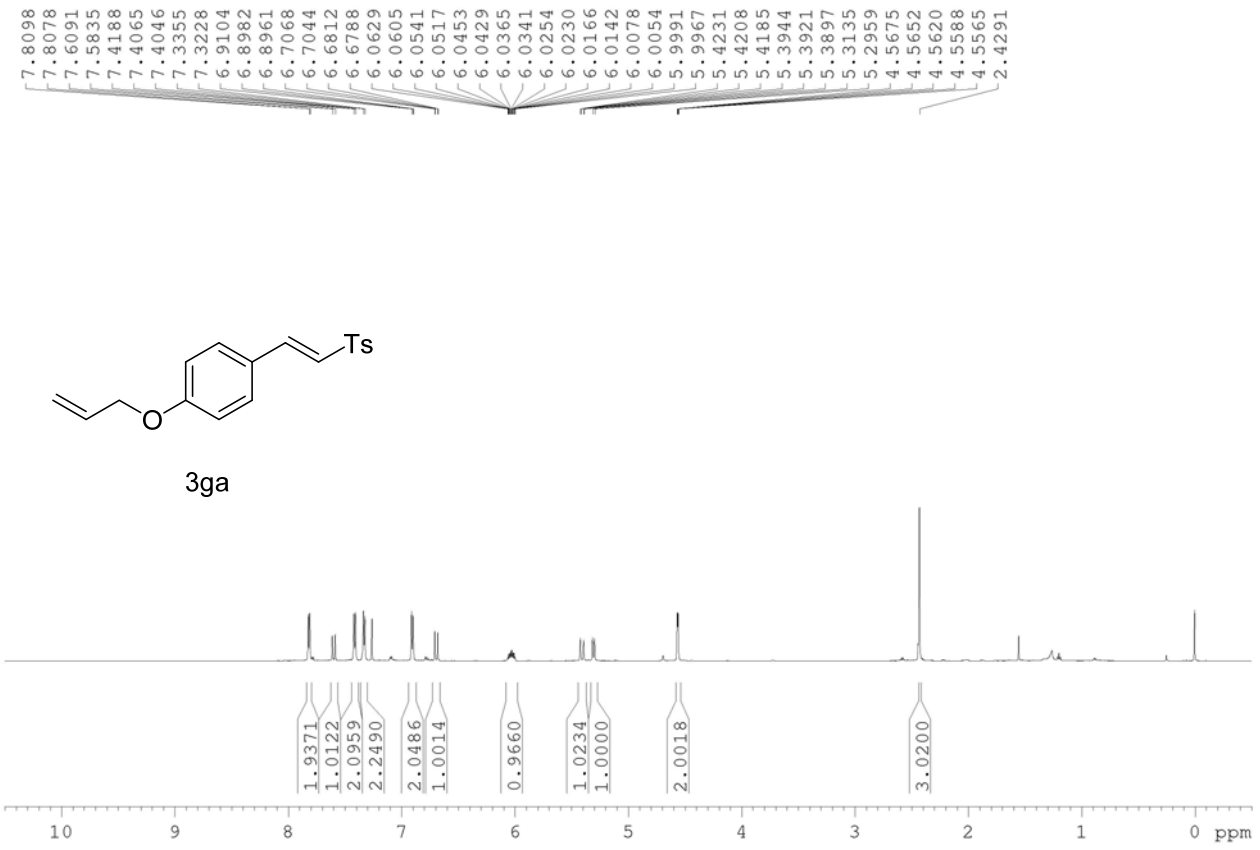
^{13}C NMR spectrum of compound 3ea in $CDCl_3$ (150 MHz)



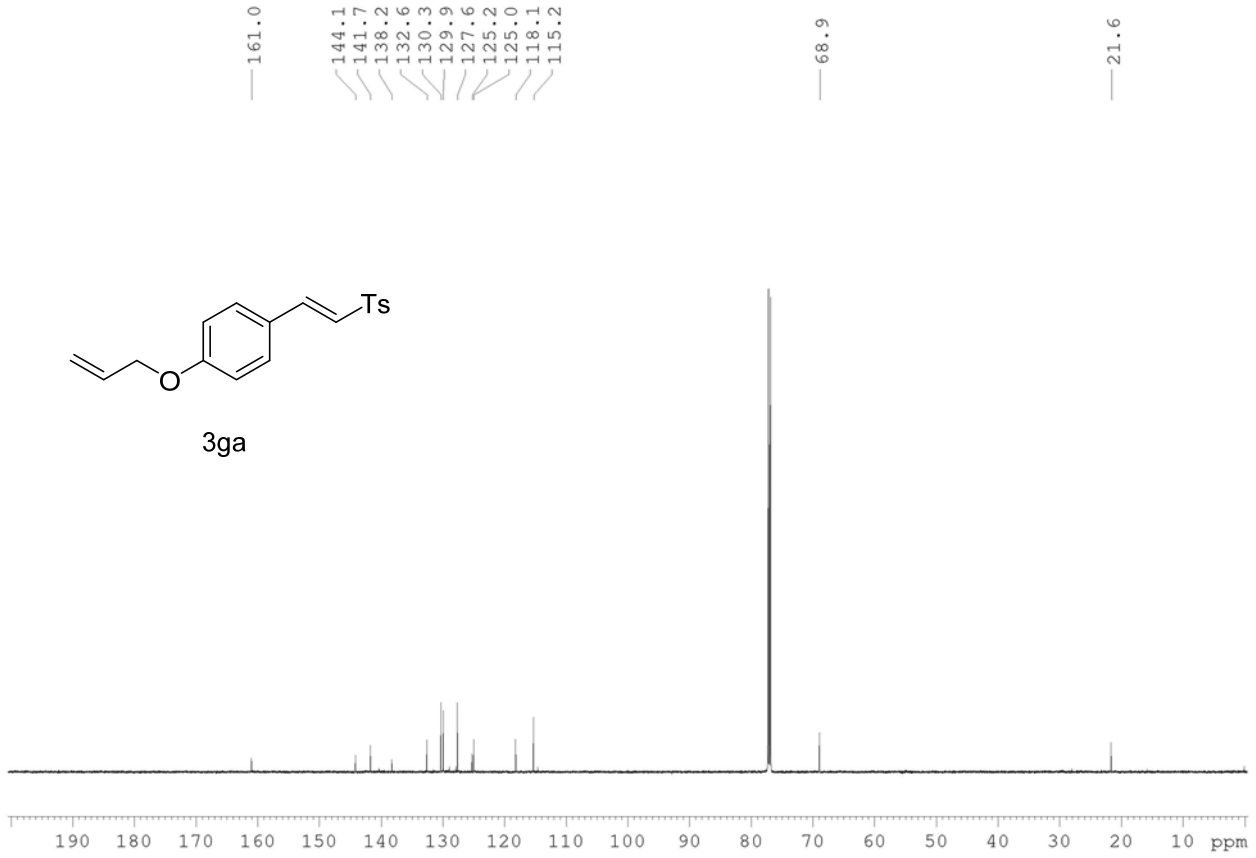
^{1}H NMR spectrum of compound 3fa in $CDCl_3$ (600 MHz)



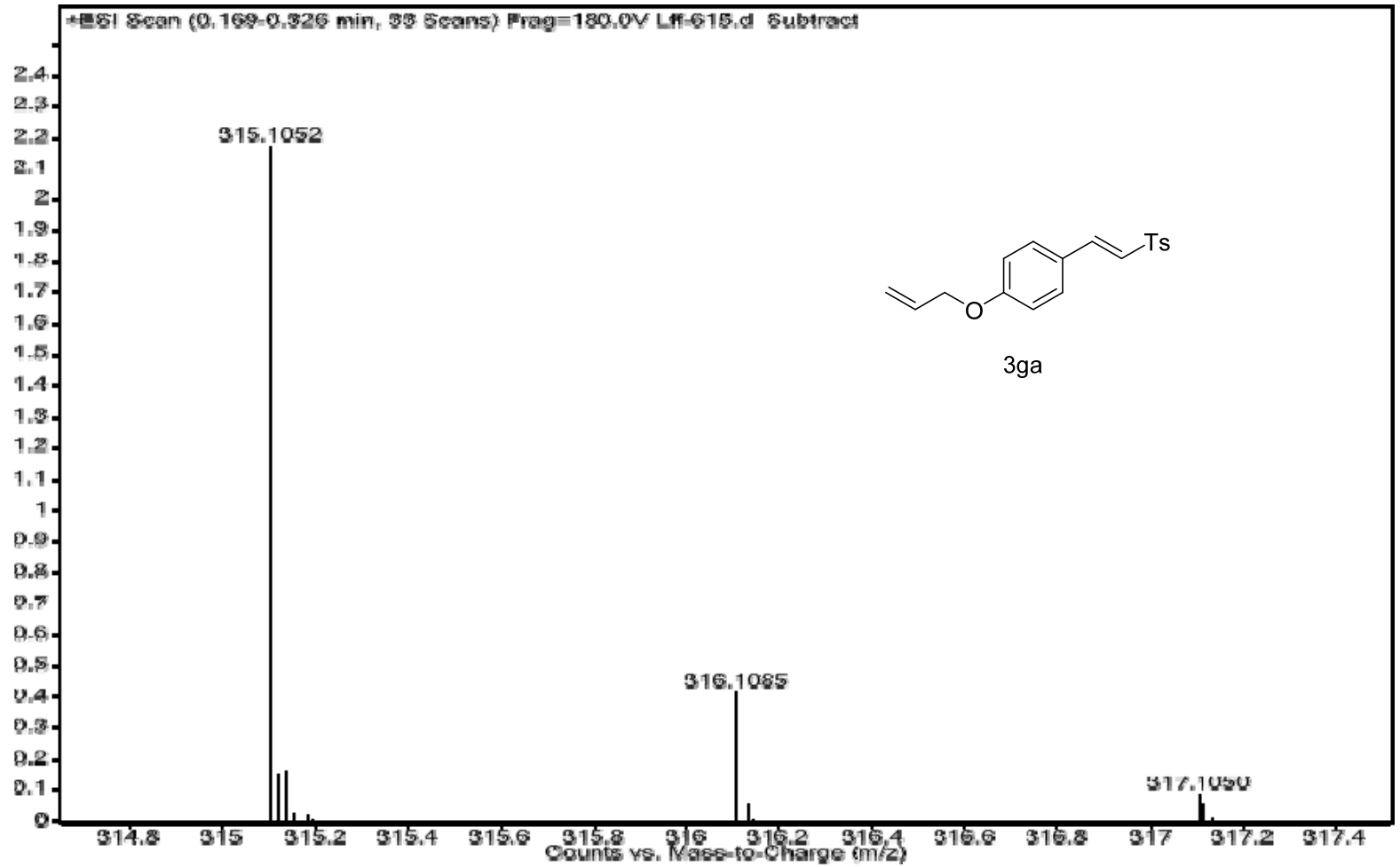
^{13}C NMR spectrum of compound 3fa in $CDCl_3$ (150 MHz)



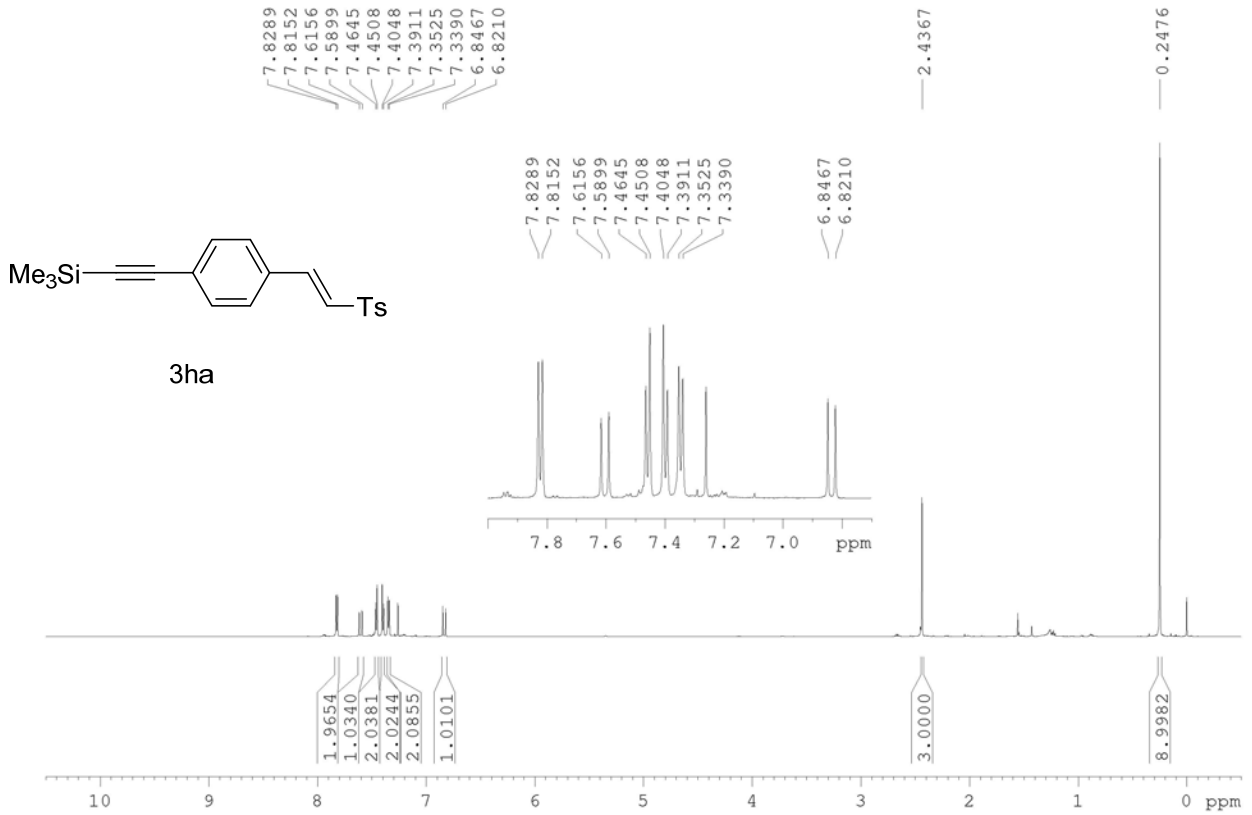
^{1}H NMR spectrum of compound 3ga in $CDCl_3$ (600 MHz)



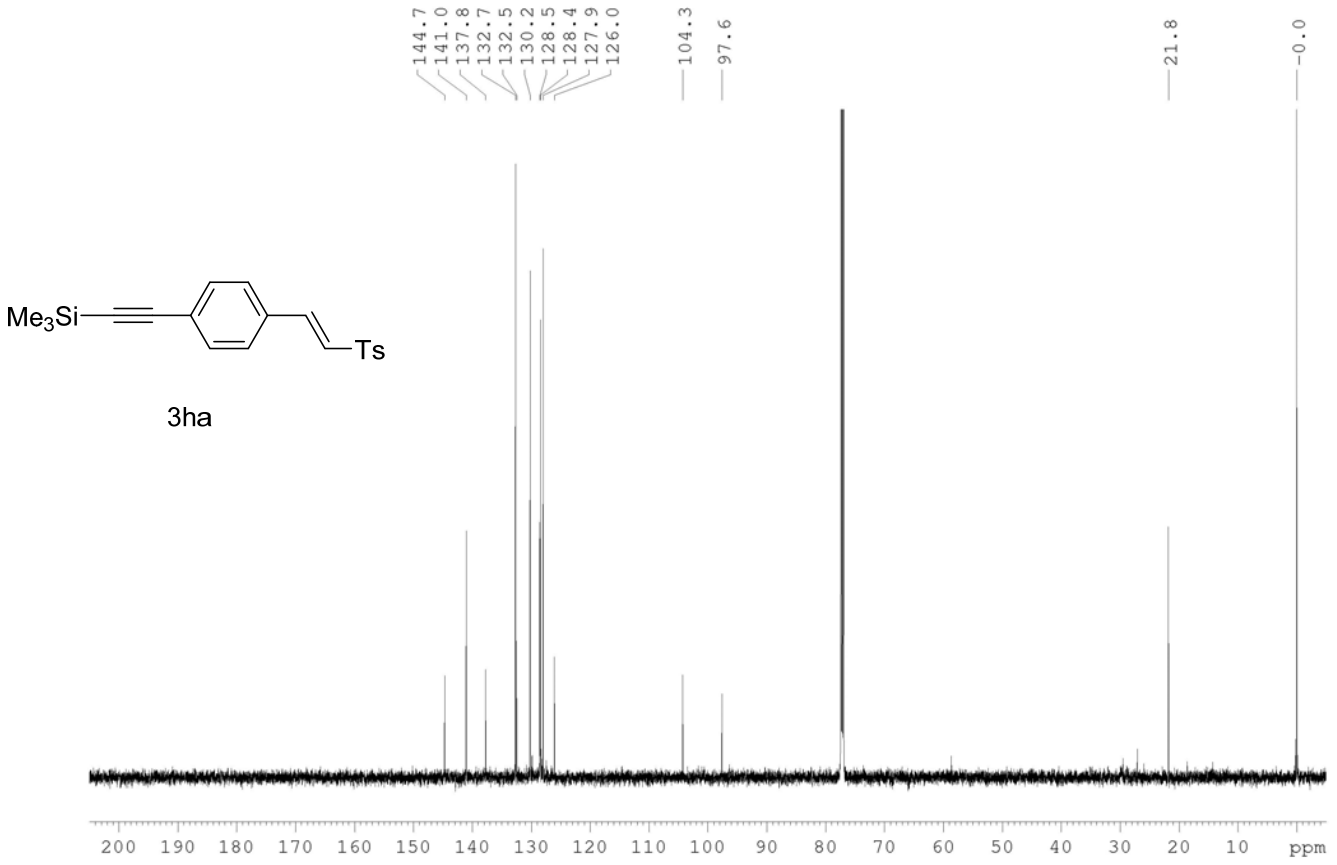
^{13}C NMR spectrum of compound 3ga in $CDCl_3$ (150 MHz)



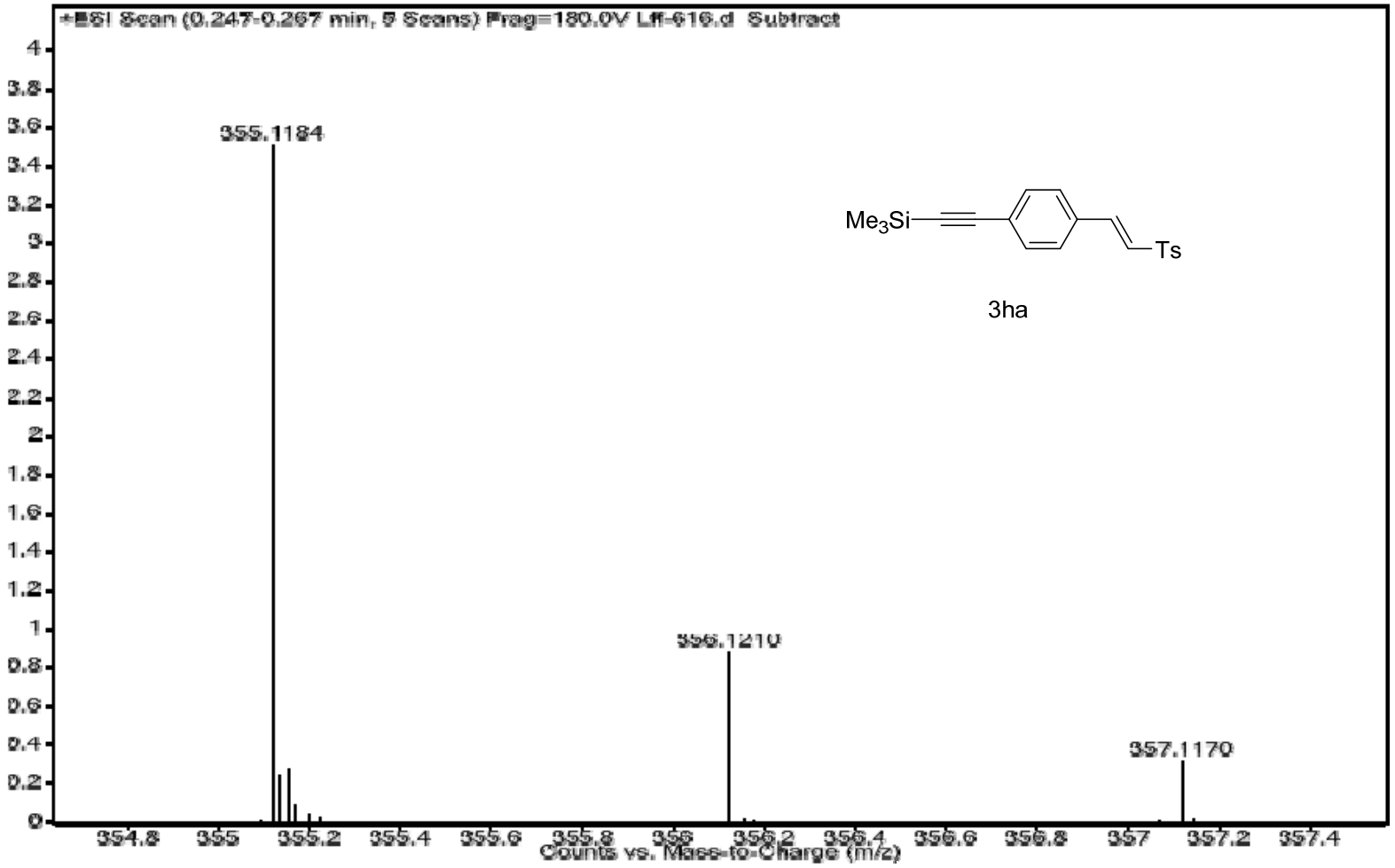
HRMS spectrum of compound 3ga



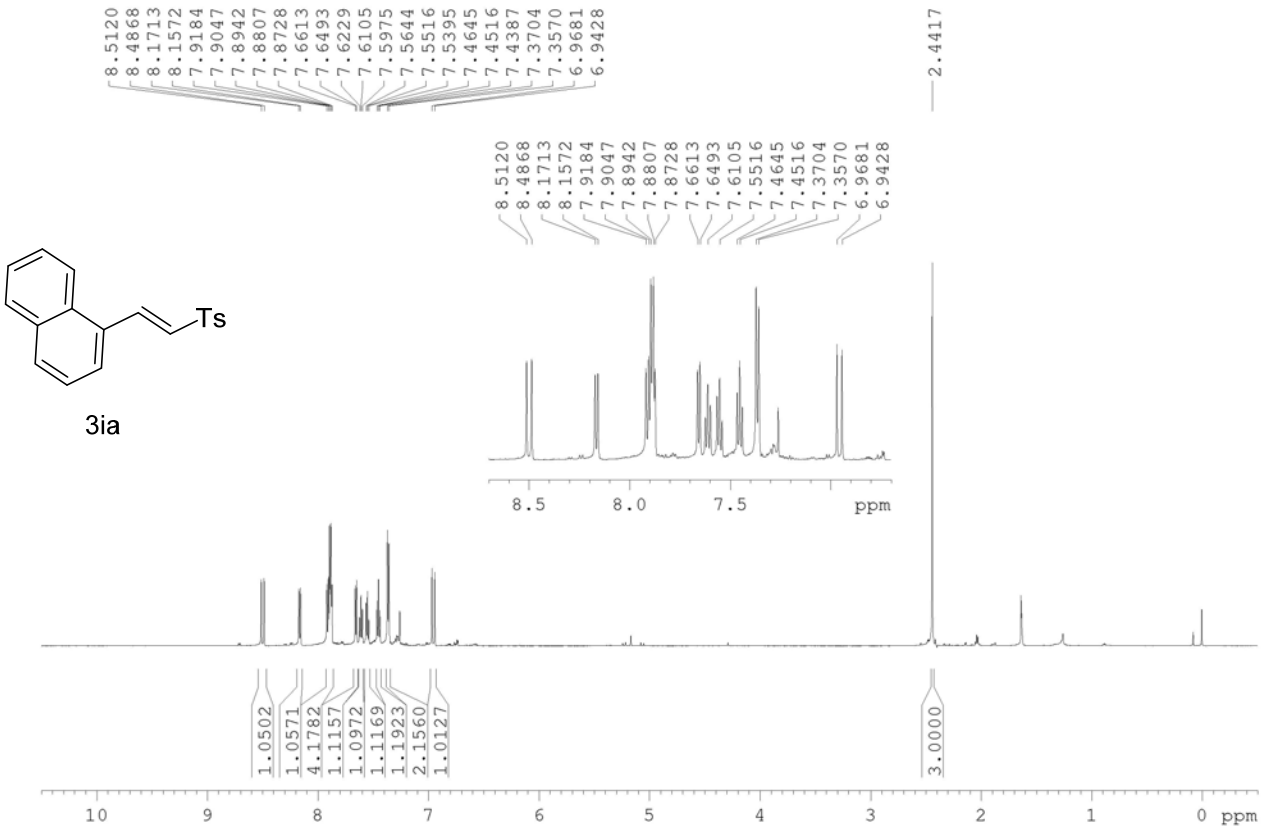
^{1}H NMR spectrum of compound 3ha in $CDCl_3$ (600 MHz)



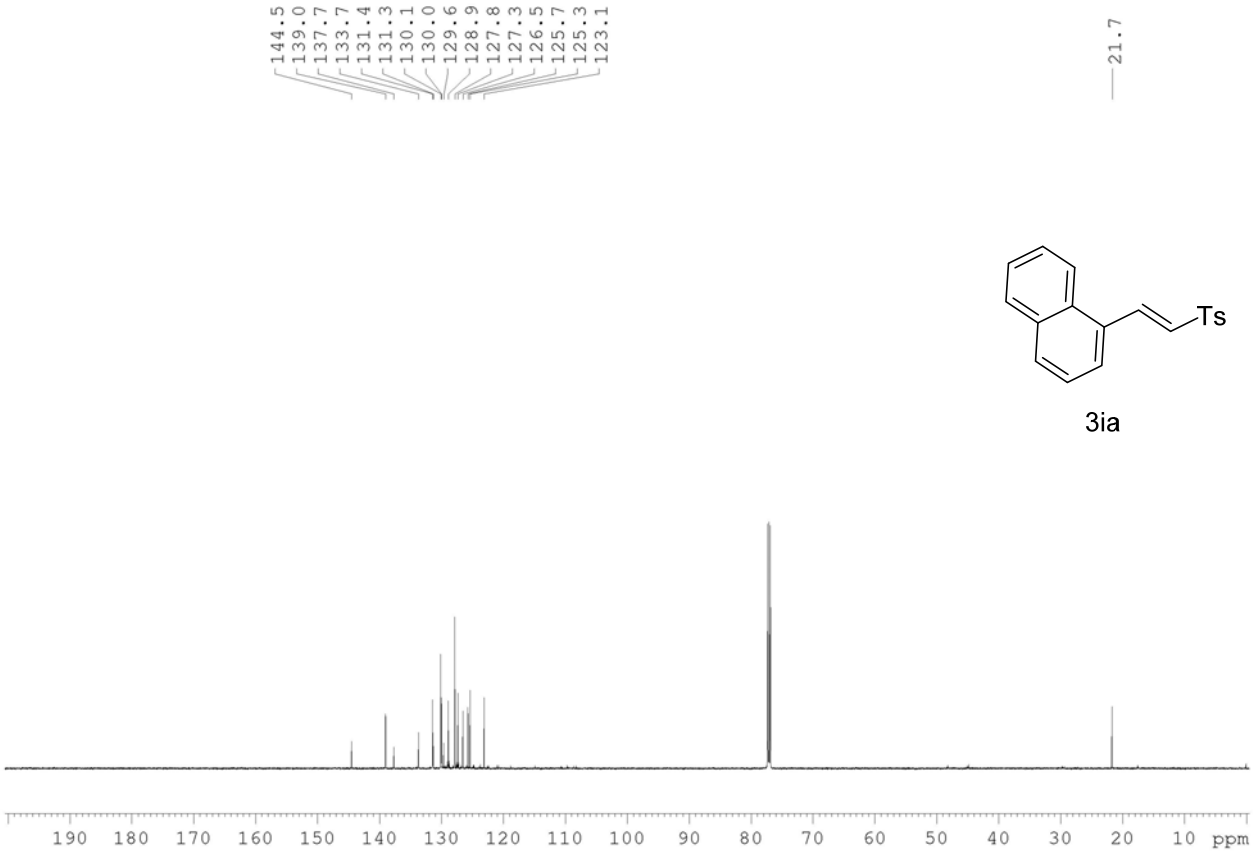
^{13}C NMR spectrum of compound 3ha in $CDCl_3$ (150 MHz)



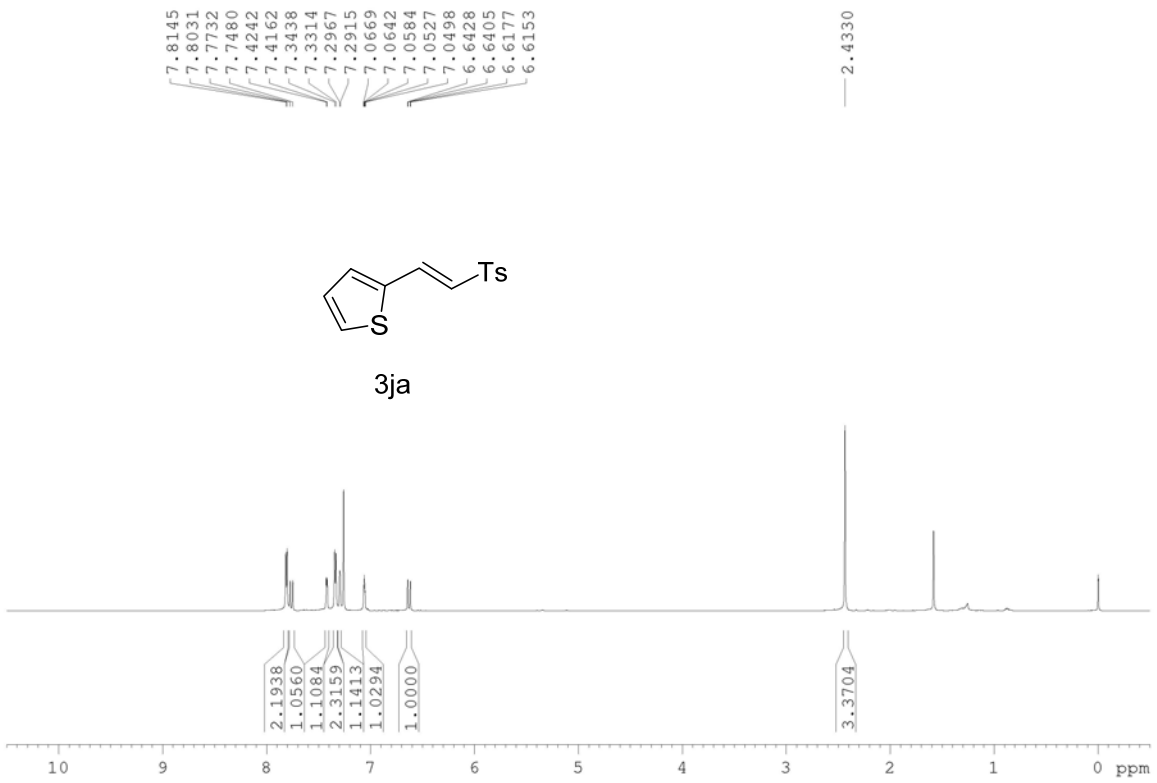
HRMS spectrum of compound 3ha



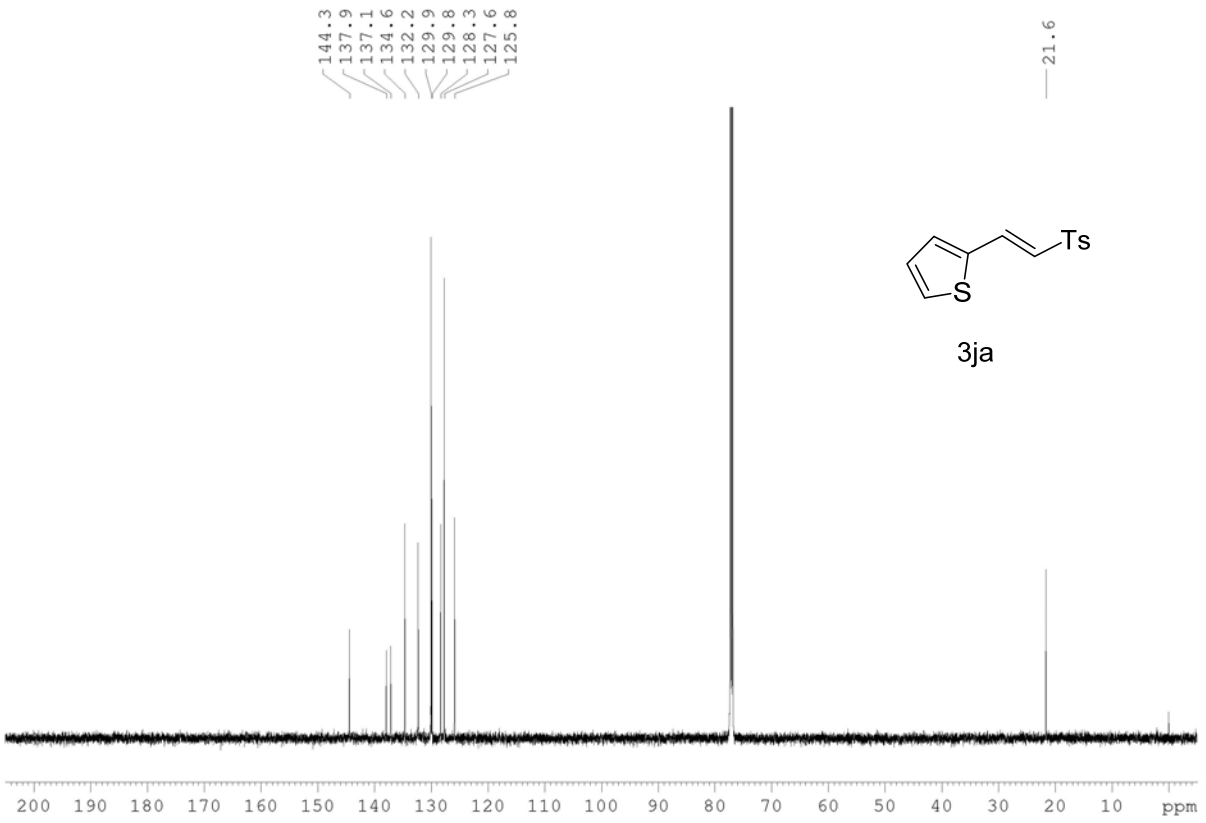
^{1}H NMR spectrum of compound 3ia in $CDCl_3$ (600 MHz)



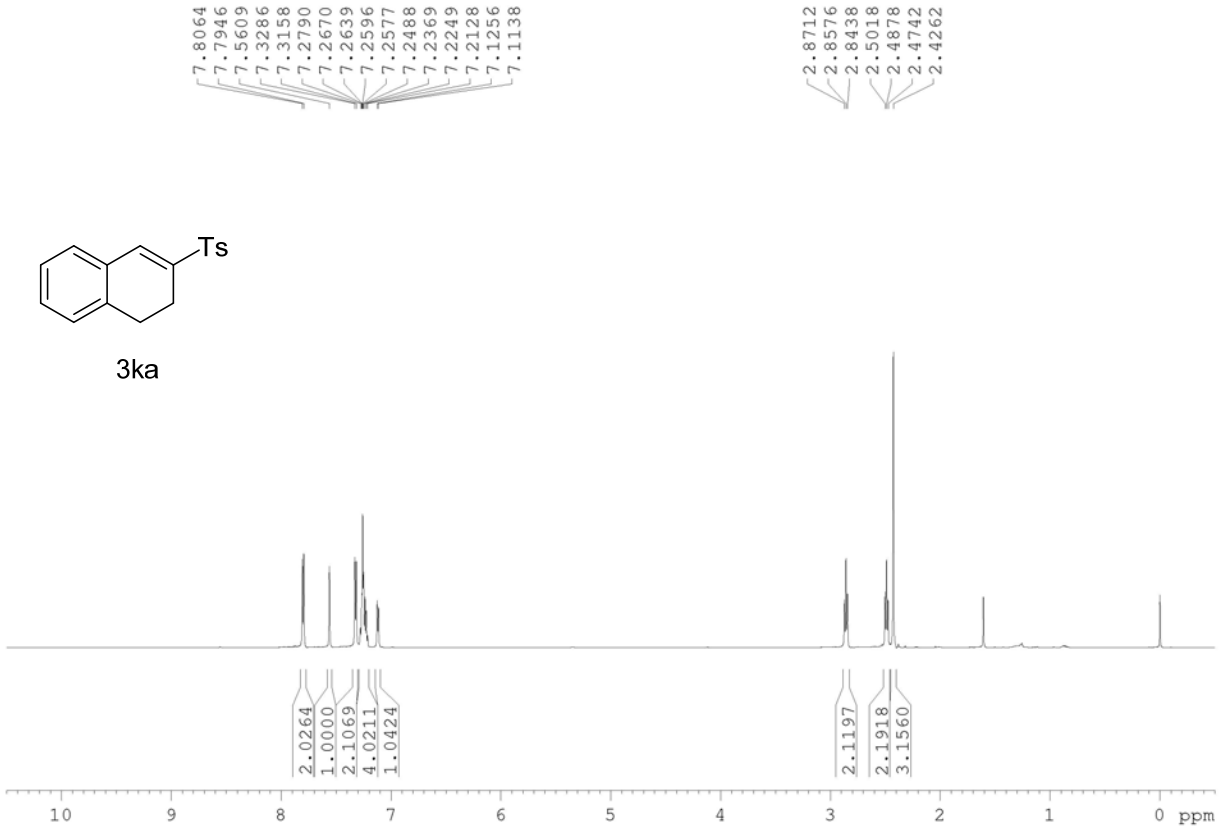
^{13}C NMR spectrum of compound 3ia in $CDCl_3$ (150 MHz)



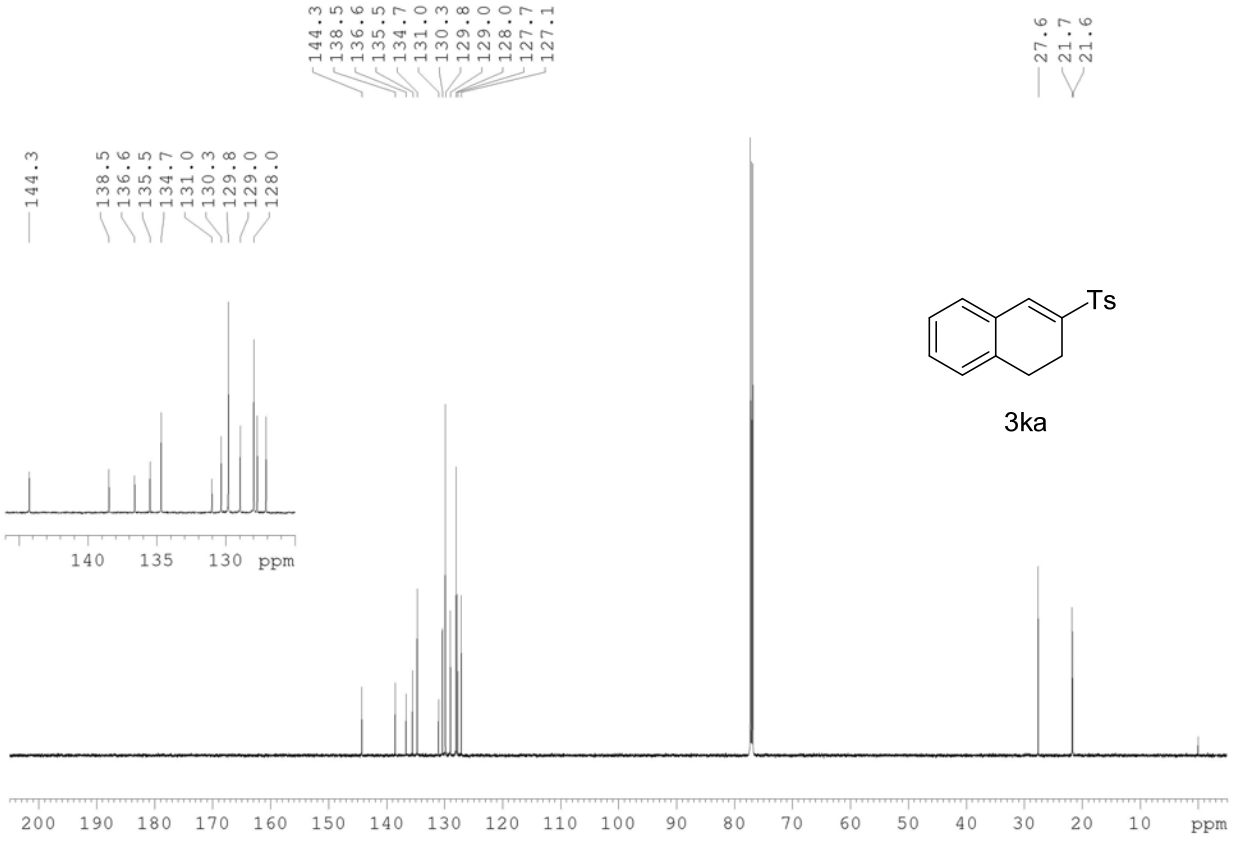
^{1}H NMR spectrum of compound 3ja in $CDCl_3$ (600 MHz)



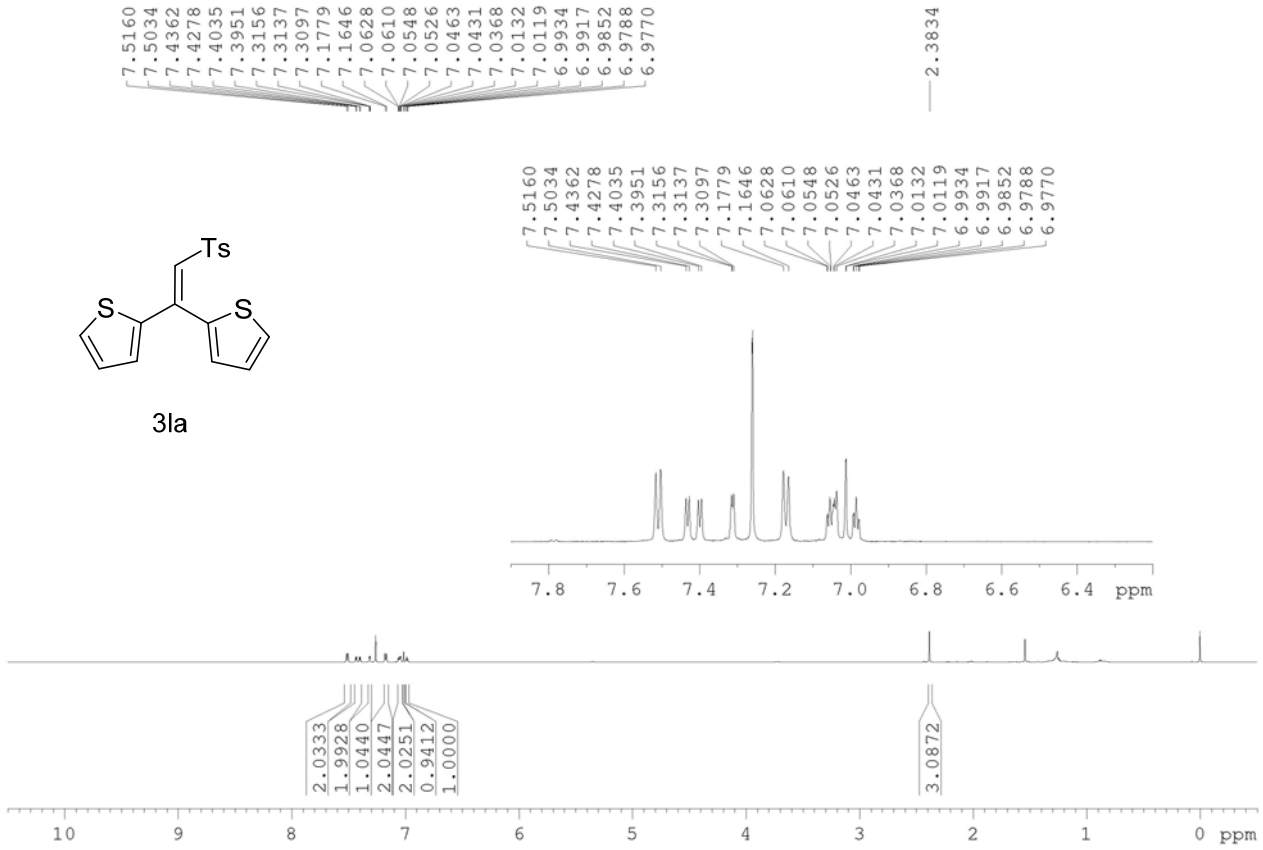
^{13}C NMR spectrum of compound 3ja in $CDCl_3$ (150 MHz)



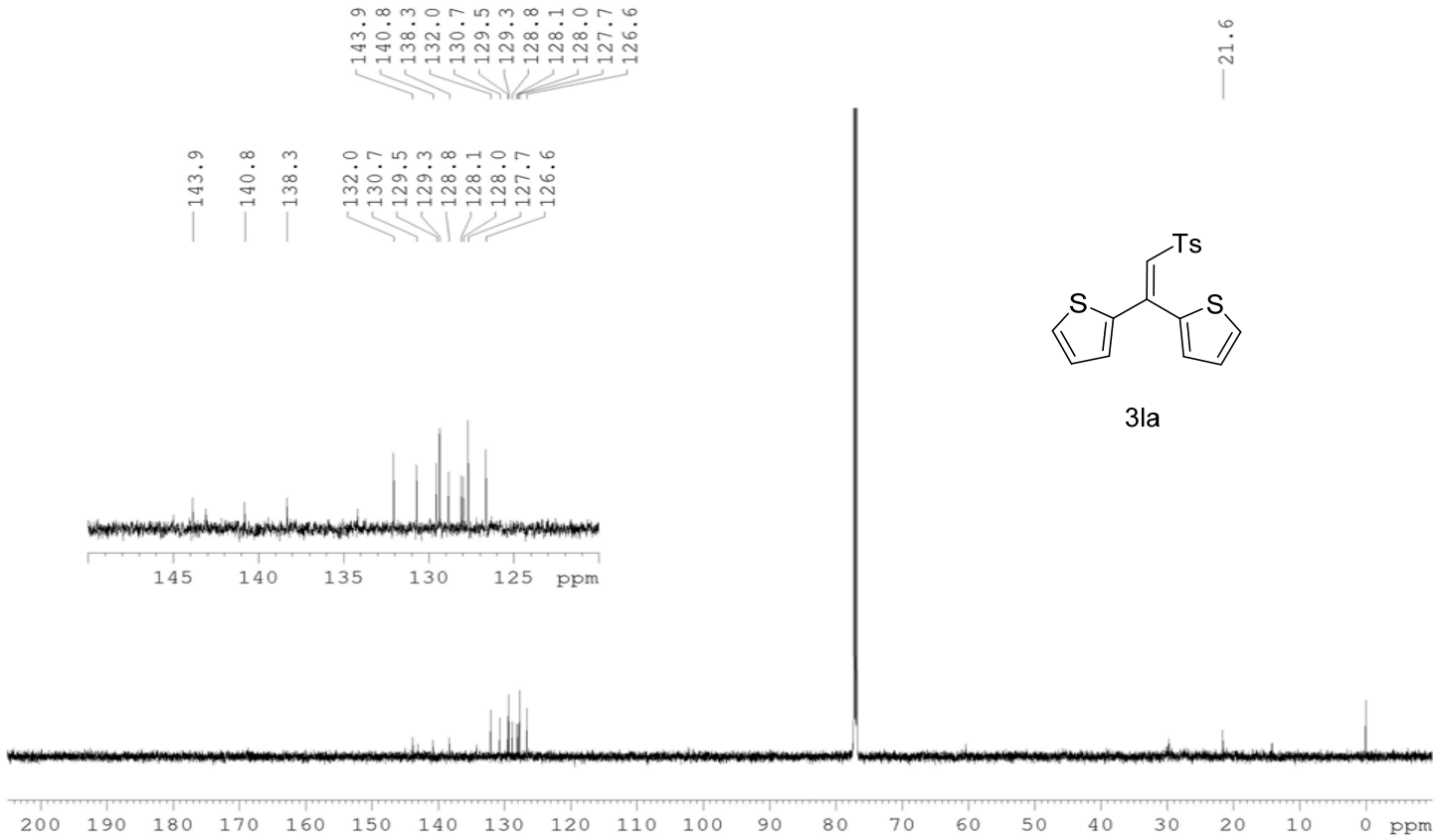
^{1}H NMR spectrum of compound 3ka in $CDCl_3$ (600 MHz)



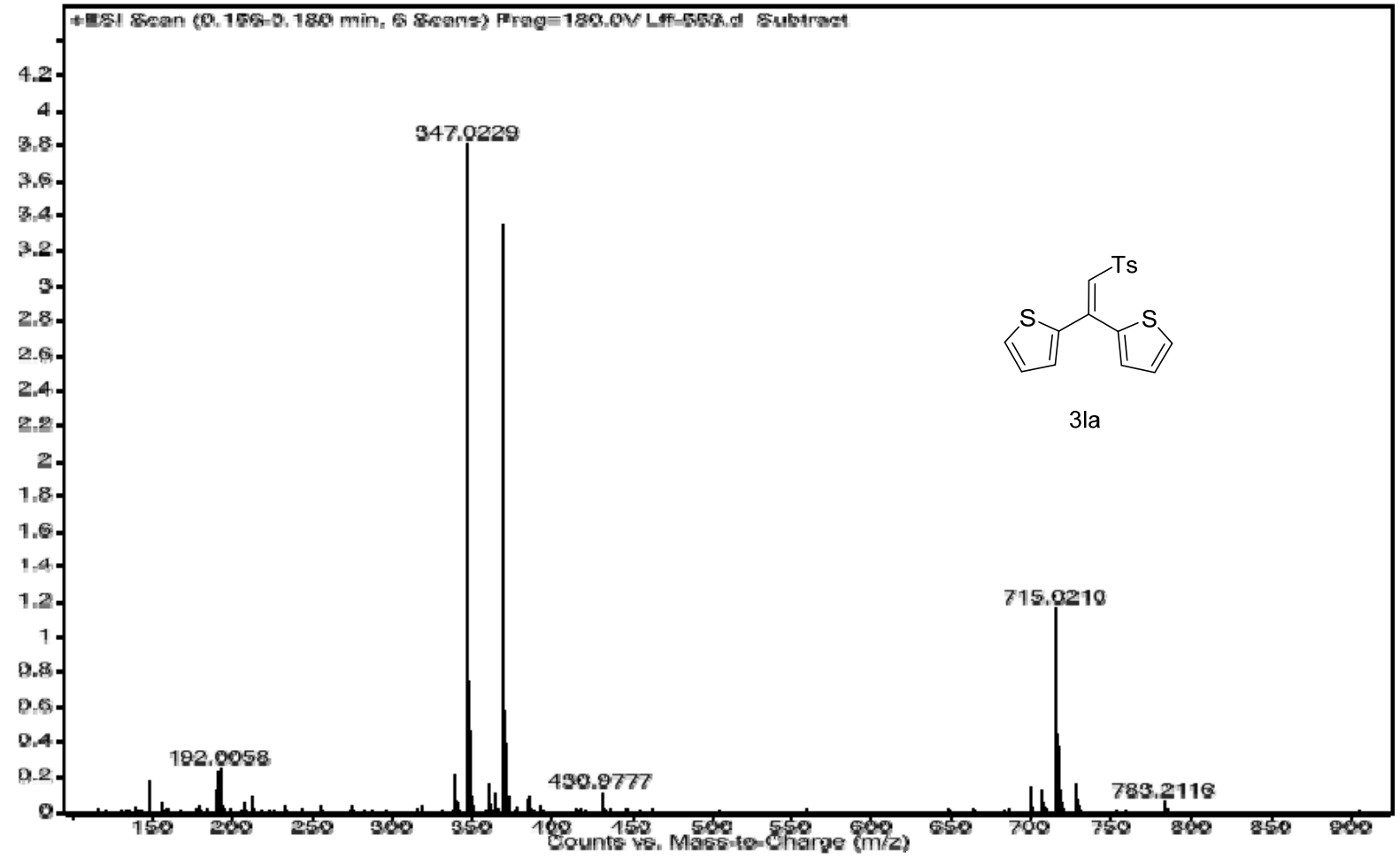
^{13}C NMR spectrum of compound 3ka in $CDCl_3$ (150 MHz)



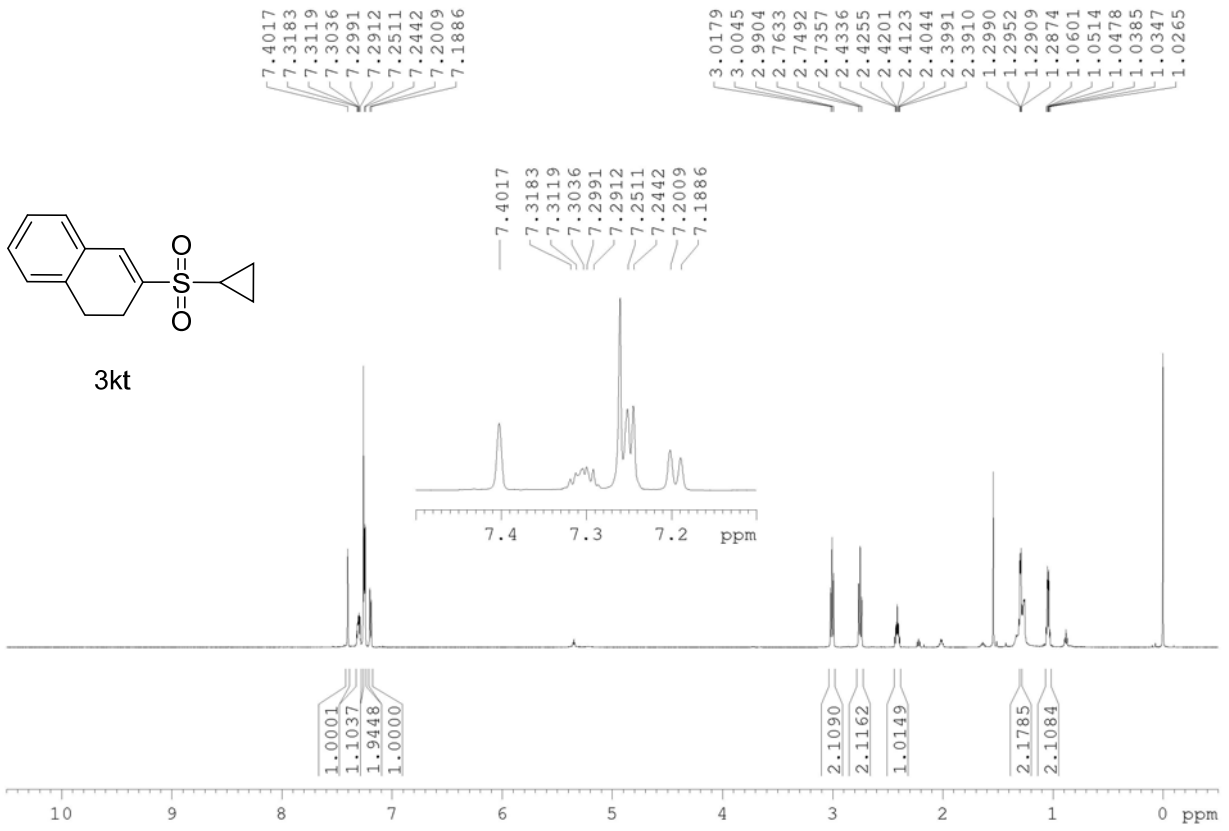
^{1}H NMR spectrum of compound 3la in $CDCl_3$ (600 MHz)



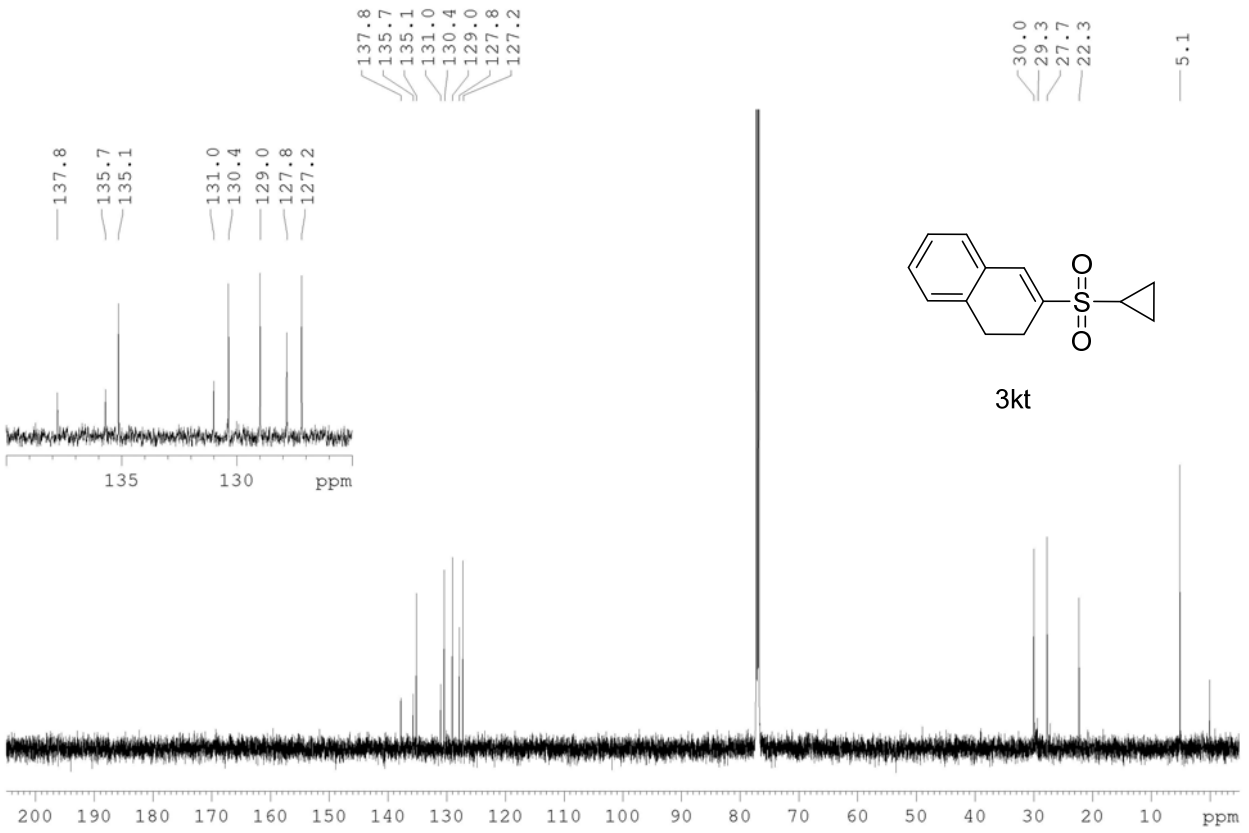
^{13}C NMR spectrum of compound 3la in $CDCl_3$ (150 MHz)



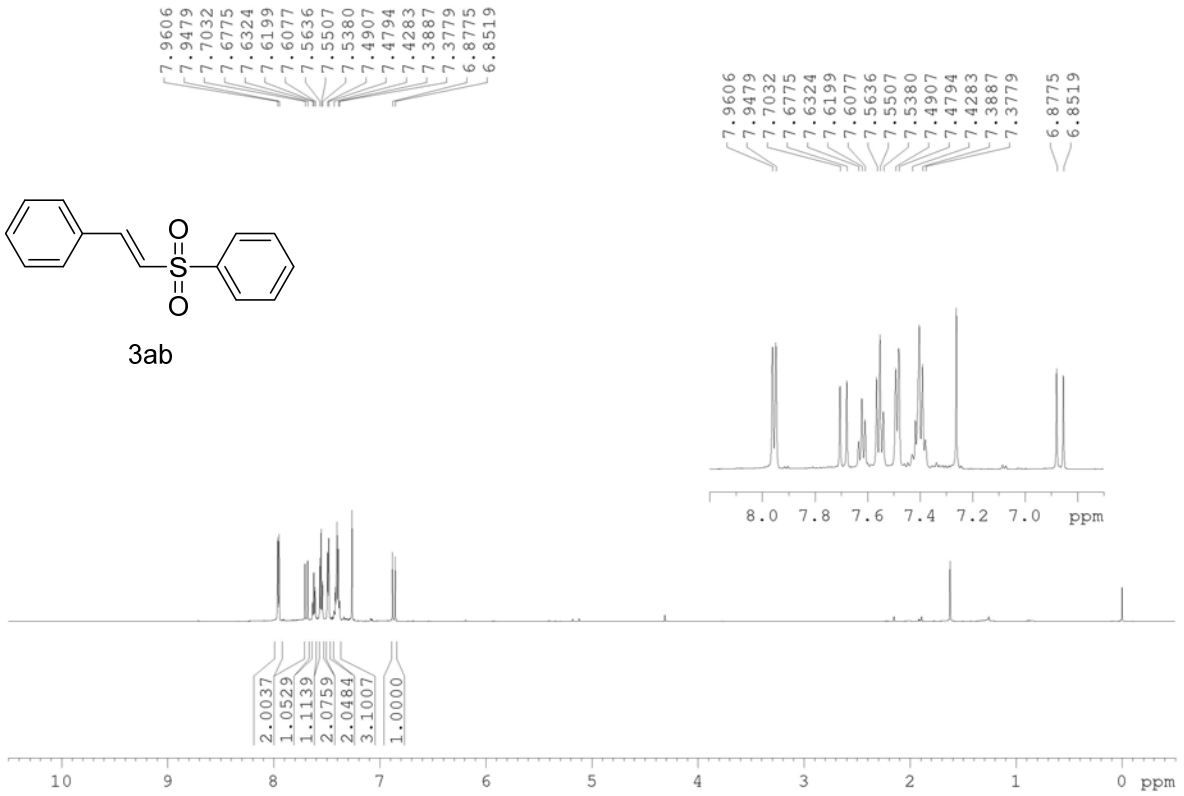
HRMS spectrum of compound 3la



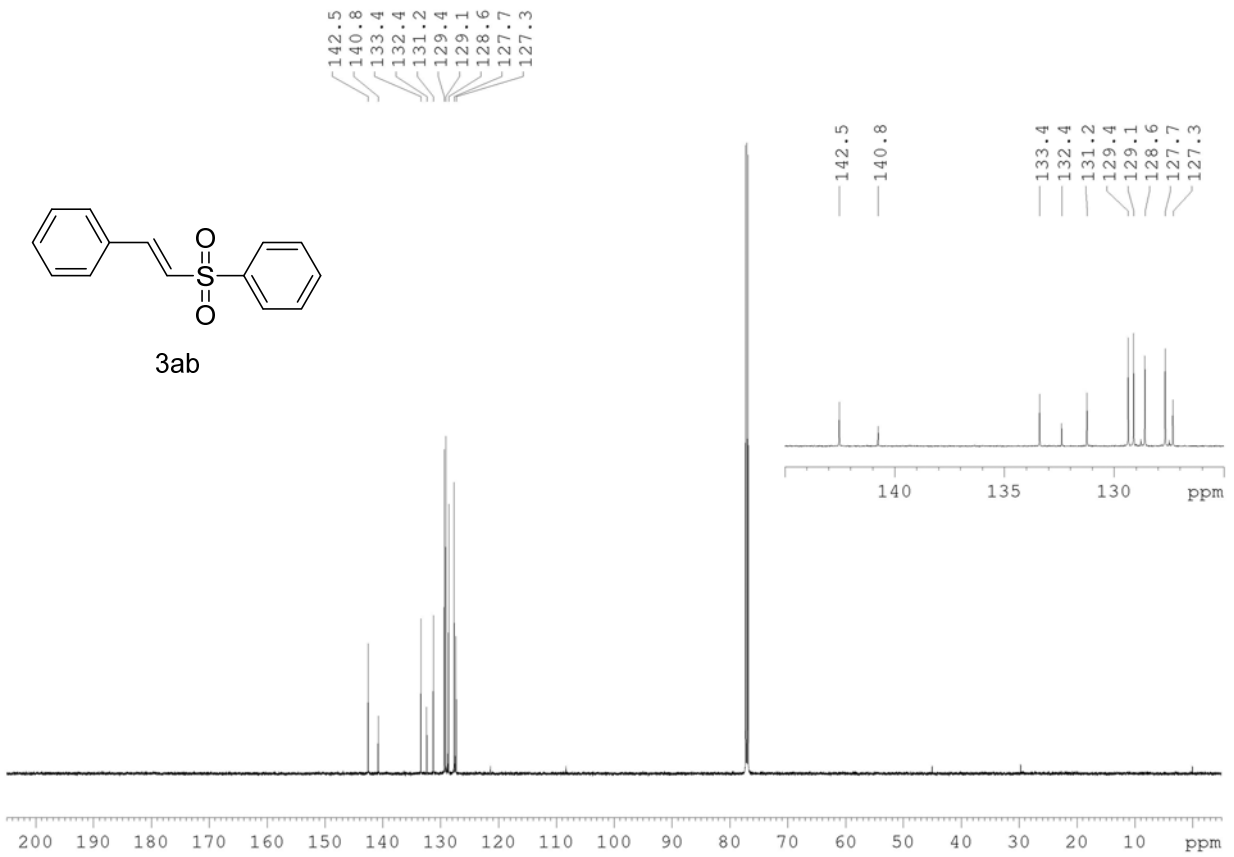
^{1}H NMR spectrum of compound 3kt in $CDCl_3$ (600 MHz)



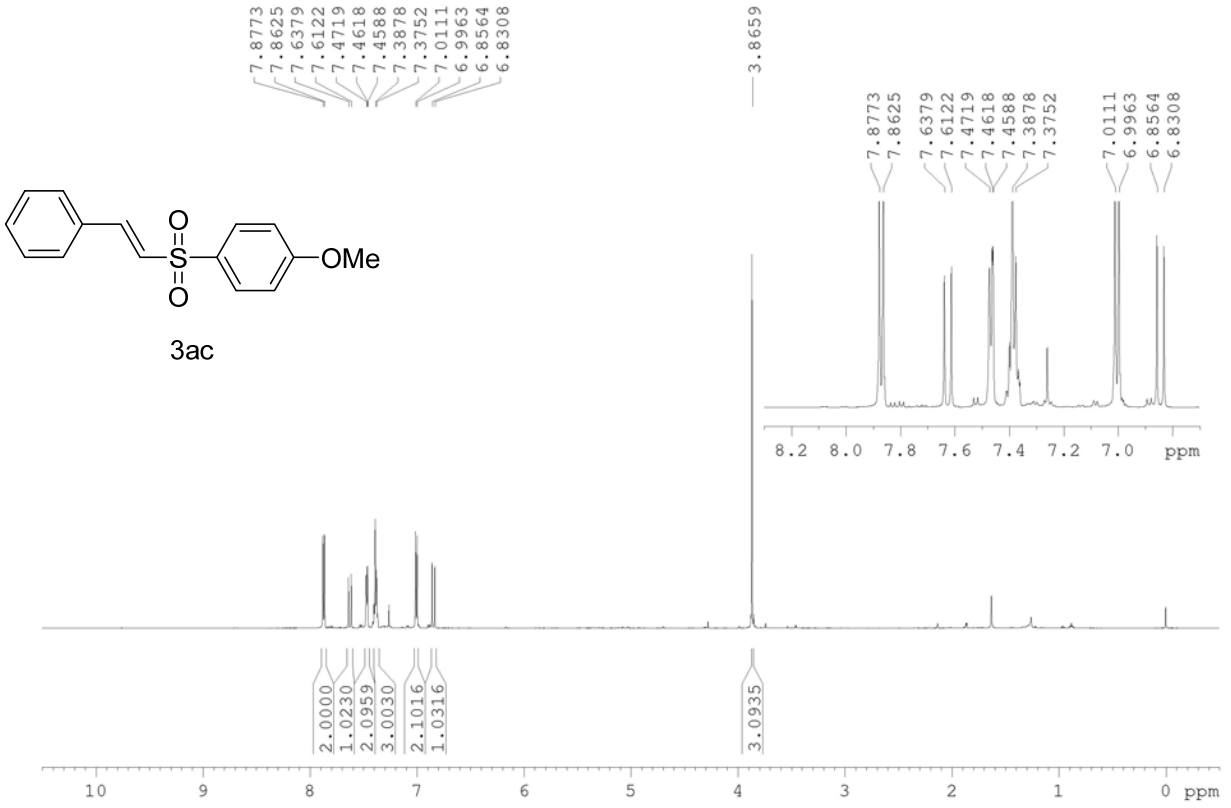
^{13}C NMR spectrum of compound 3kt in $CDCl_3$ (150 MHz)



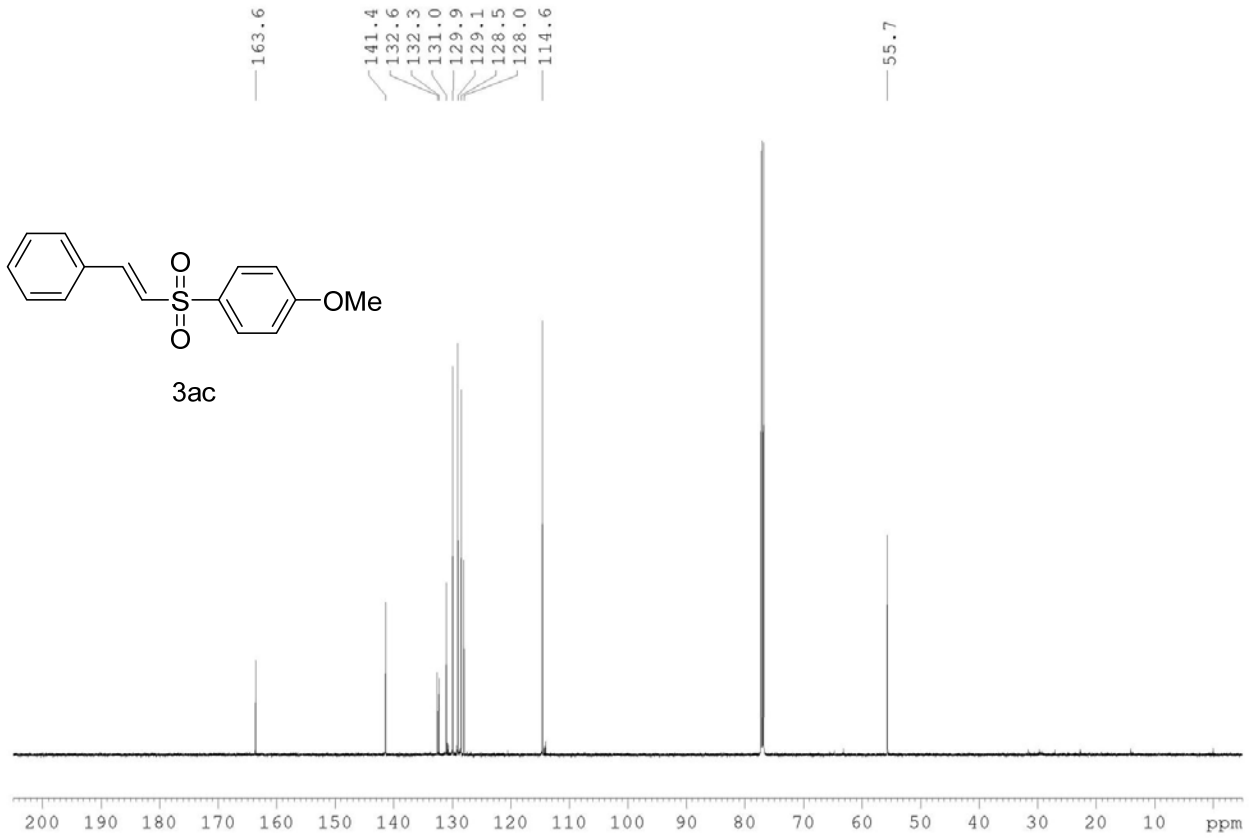
^{1}H NMR spectrum of compound 3ab in $CDCl_3$ (600 MHz)



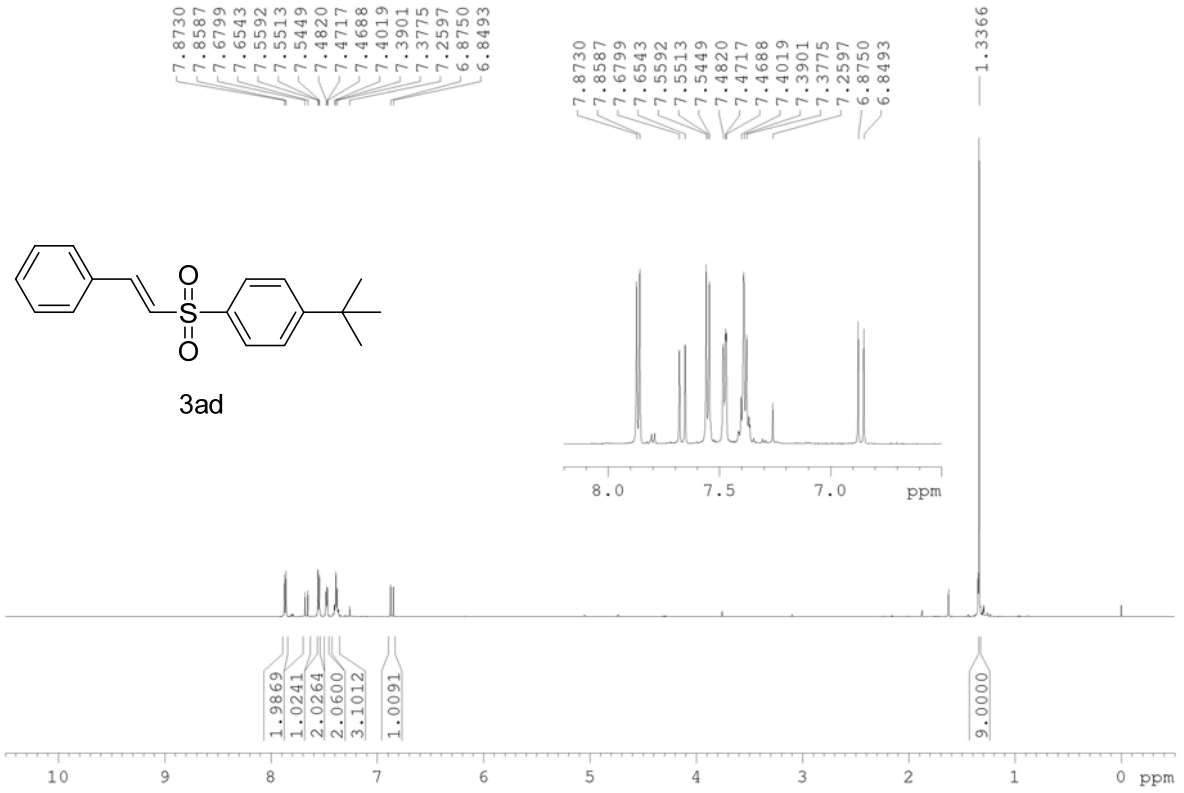
^{13}C NMR spectrum of compound 3ab in $CDCl_3$ (150 MHz)



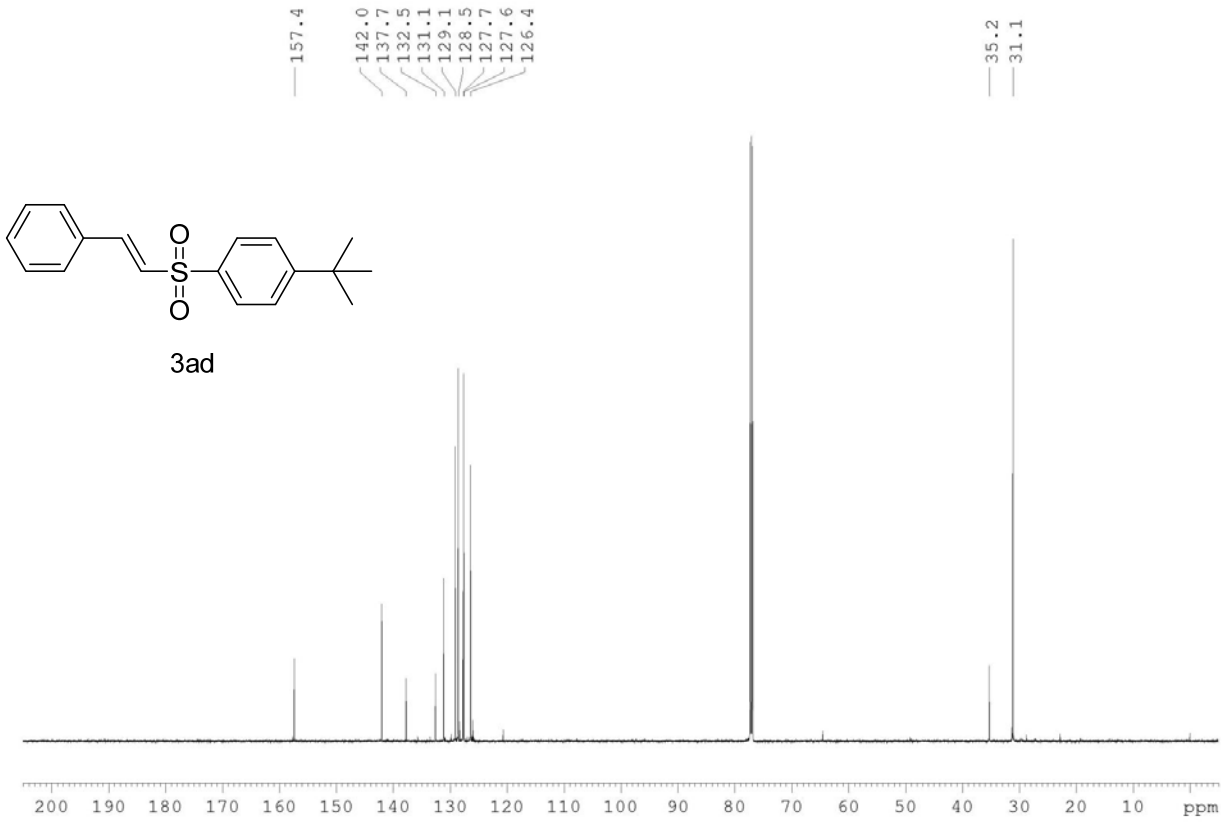
^{1}H NMR spectrum of compound 3ac in $CDCl_3$ (600 MHz)



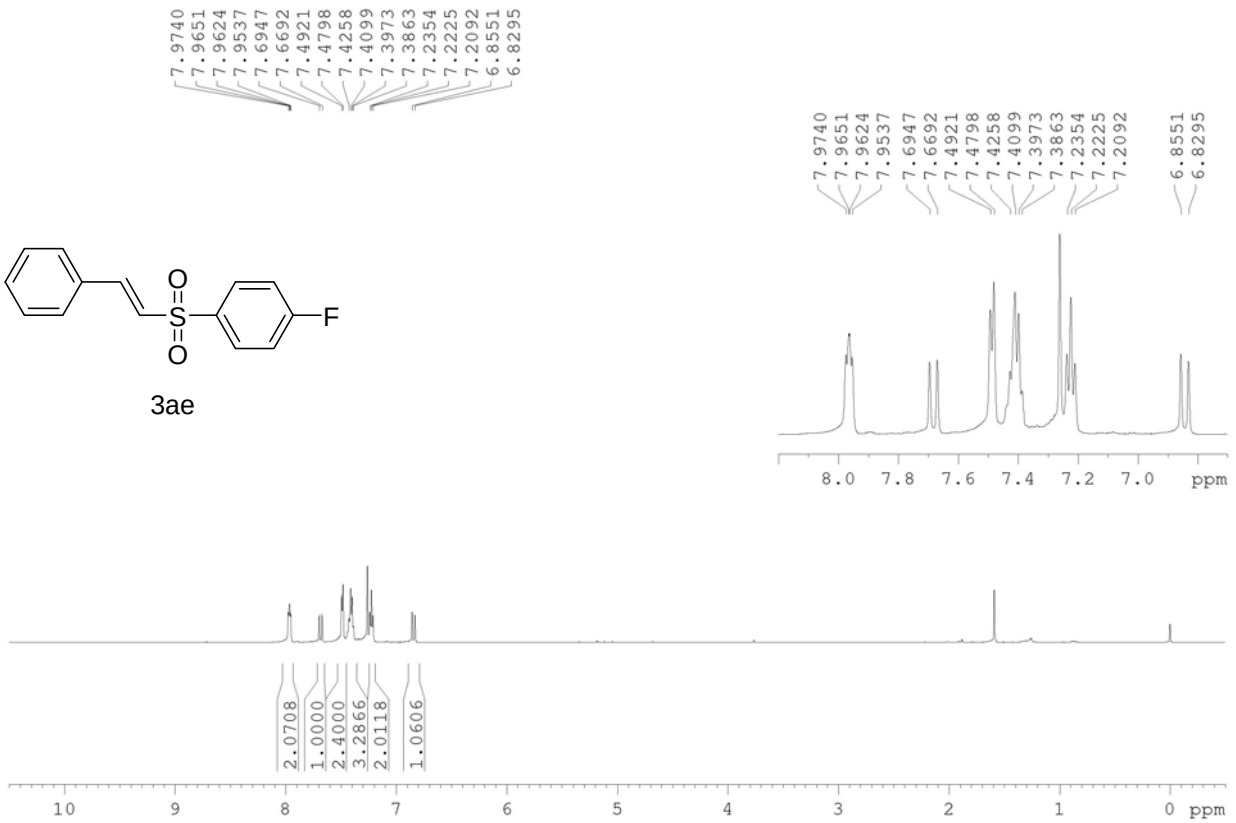
^{13}C NMR spectrum of compound 3ac in $CDCl_3$ (150 MHz)



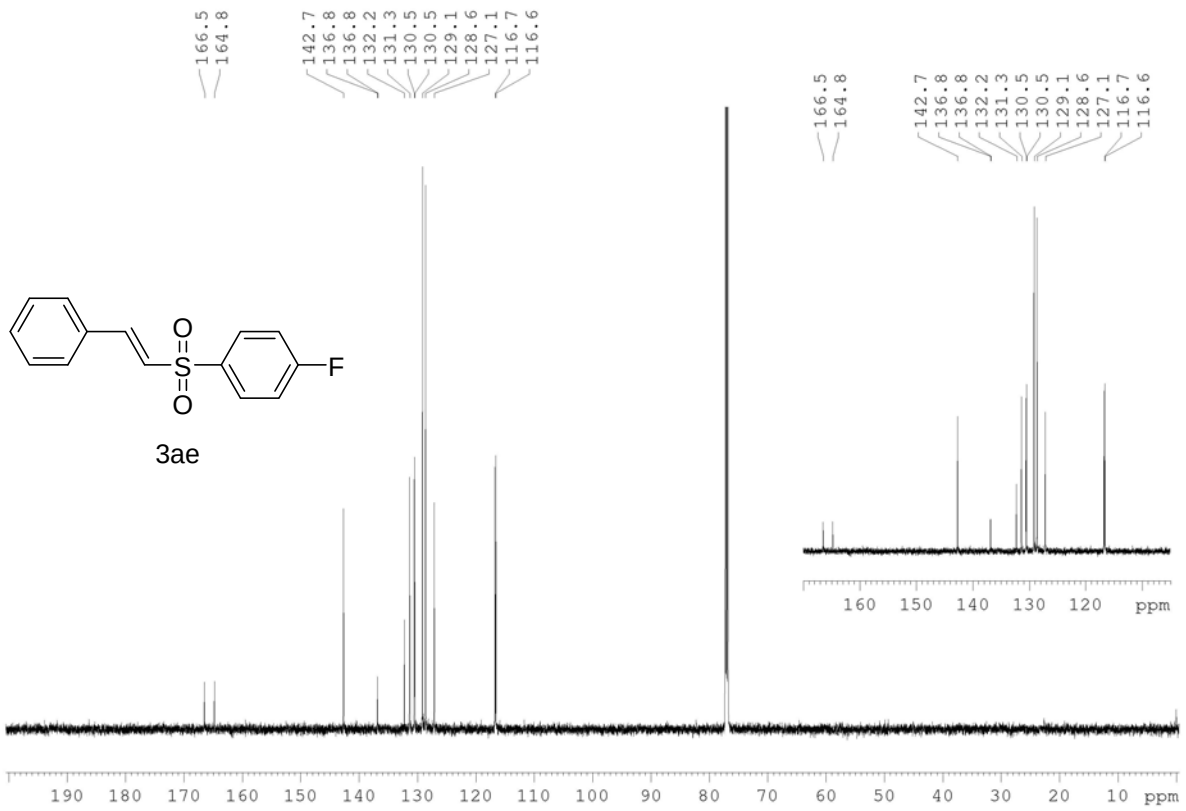
^{1}H NMR spectrum of compound 3ad in $CDCl_3$ (600 MHz)



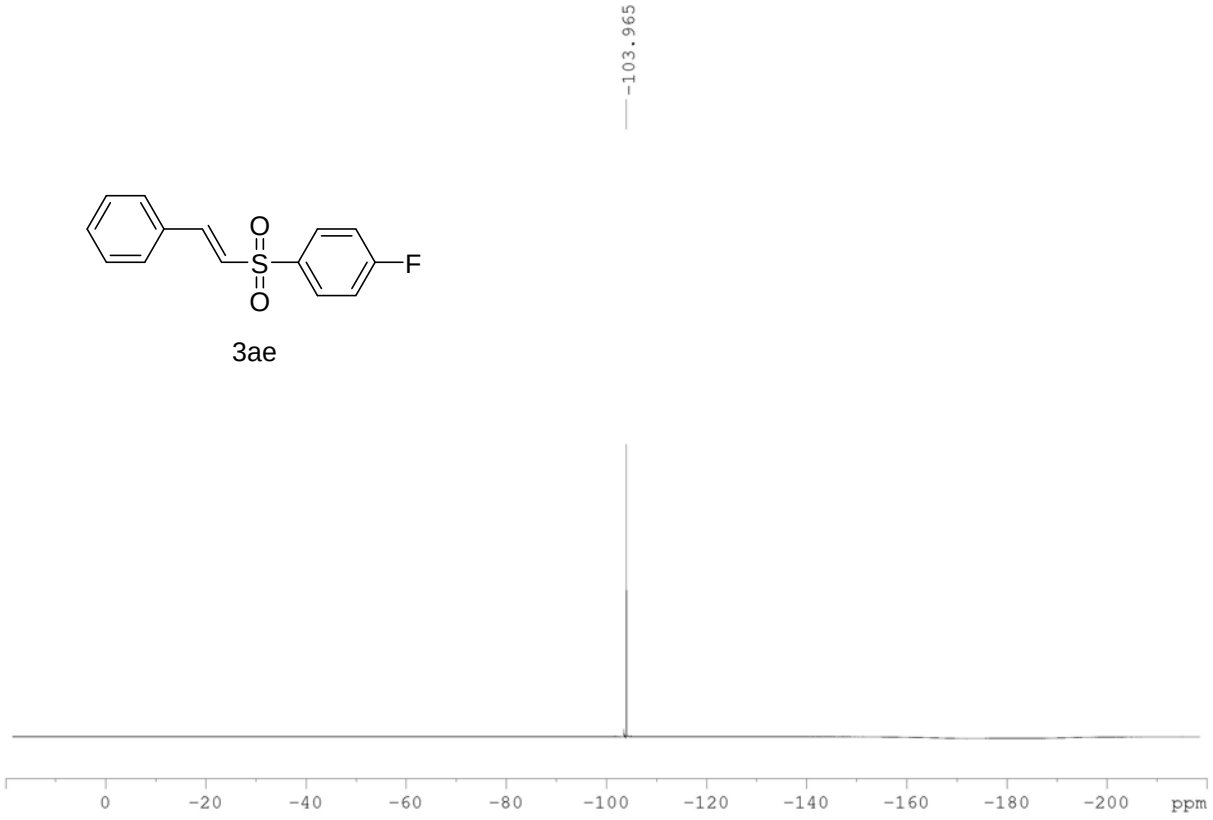
^{13}C NMR spectrum of compound 3ad in $CDCl_3$ (150 MHz)



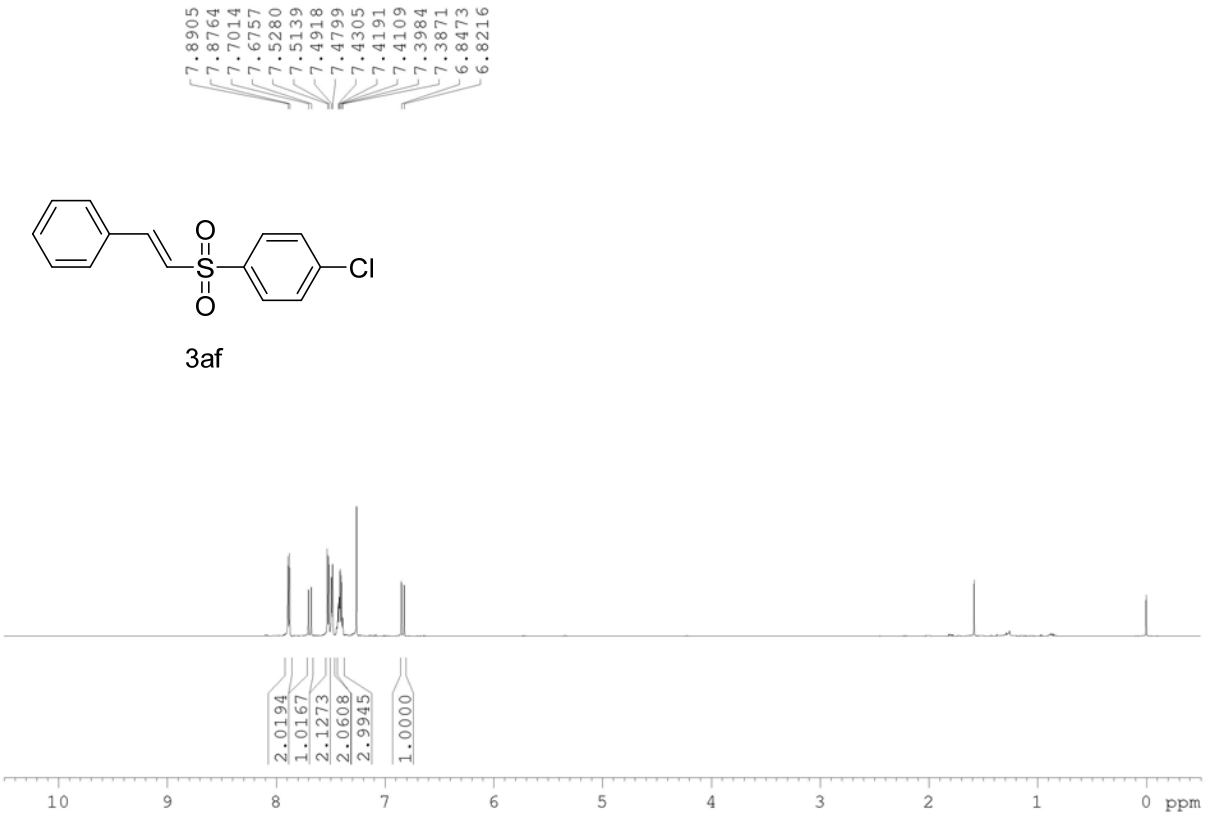
^{1}H NMR spectrum of compound 3ae in $CDCl_3$ (600 MHz)



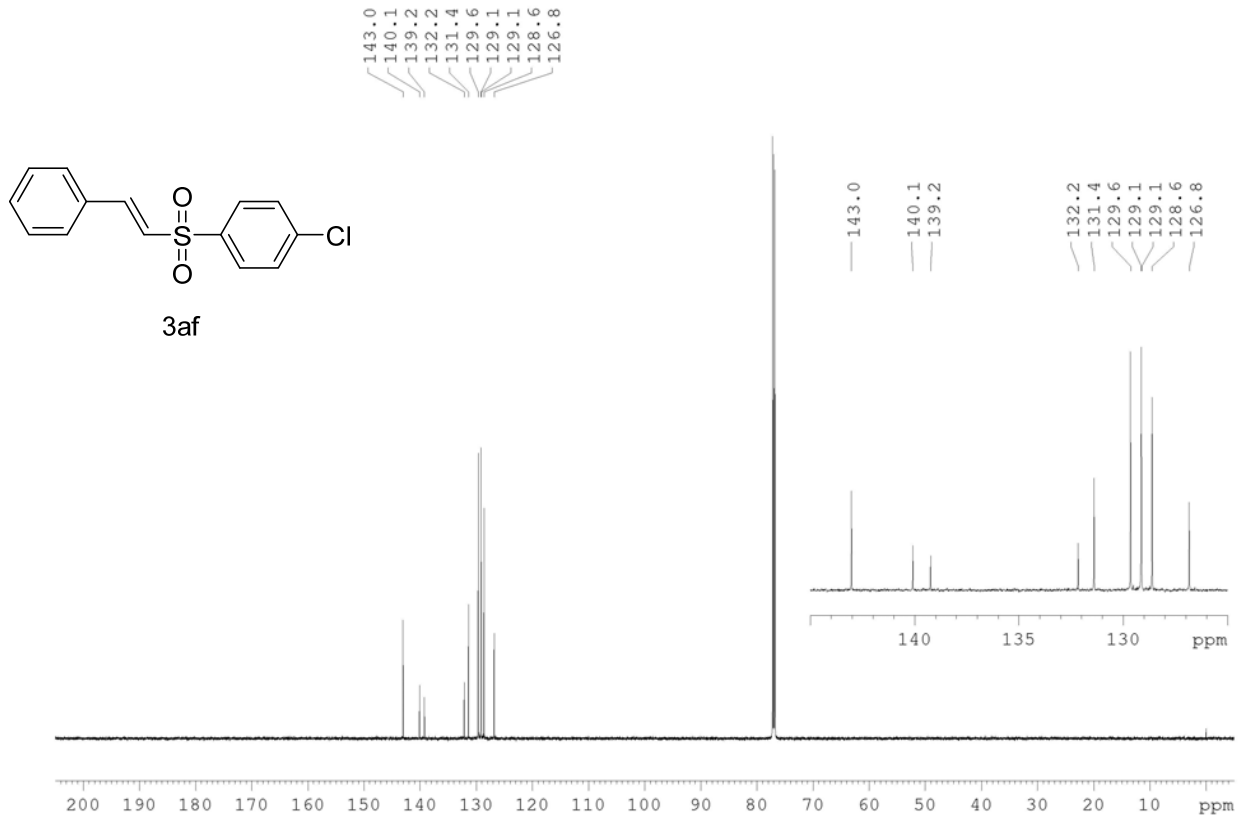
^{13}C NMR spectrum of compound 3ae in $CDCl_3$ (150 MHz)



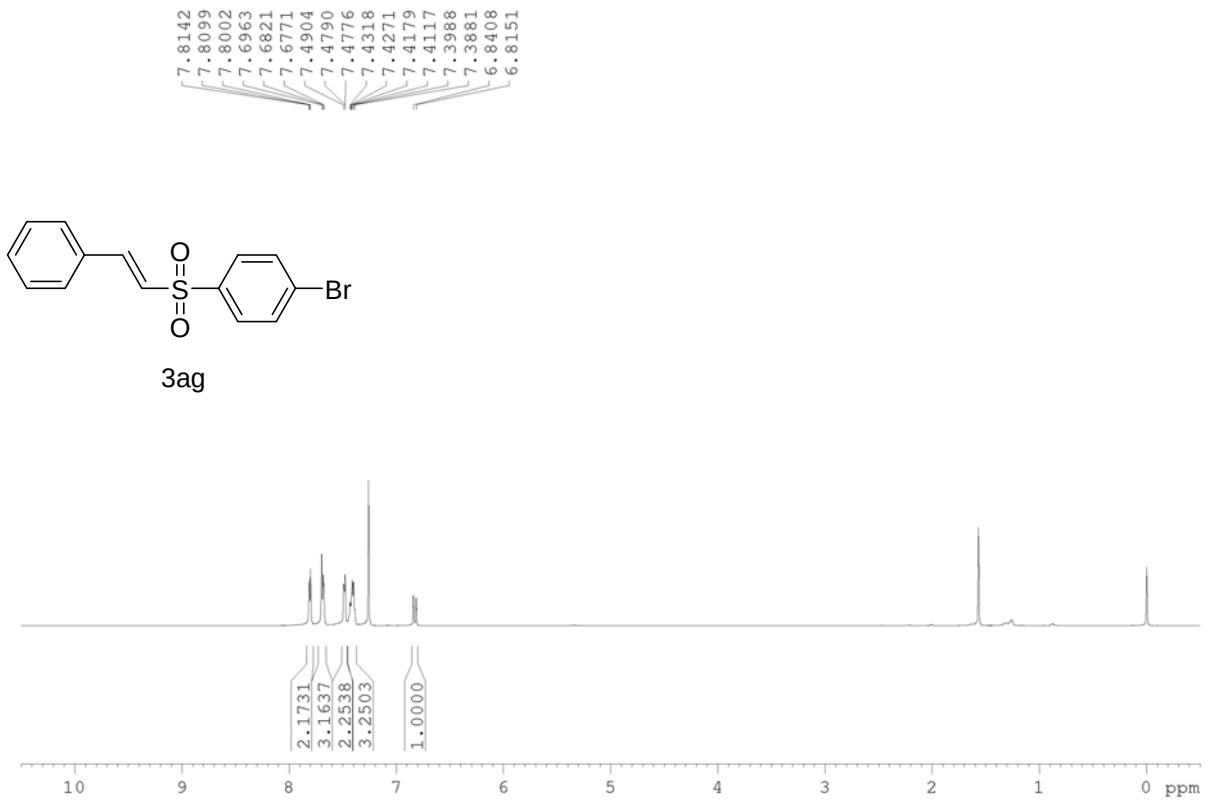
^{19}F NMR spectrum of compound 3ae in $CDCl_3$ (565 MHz)



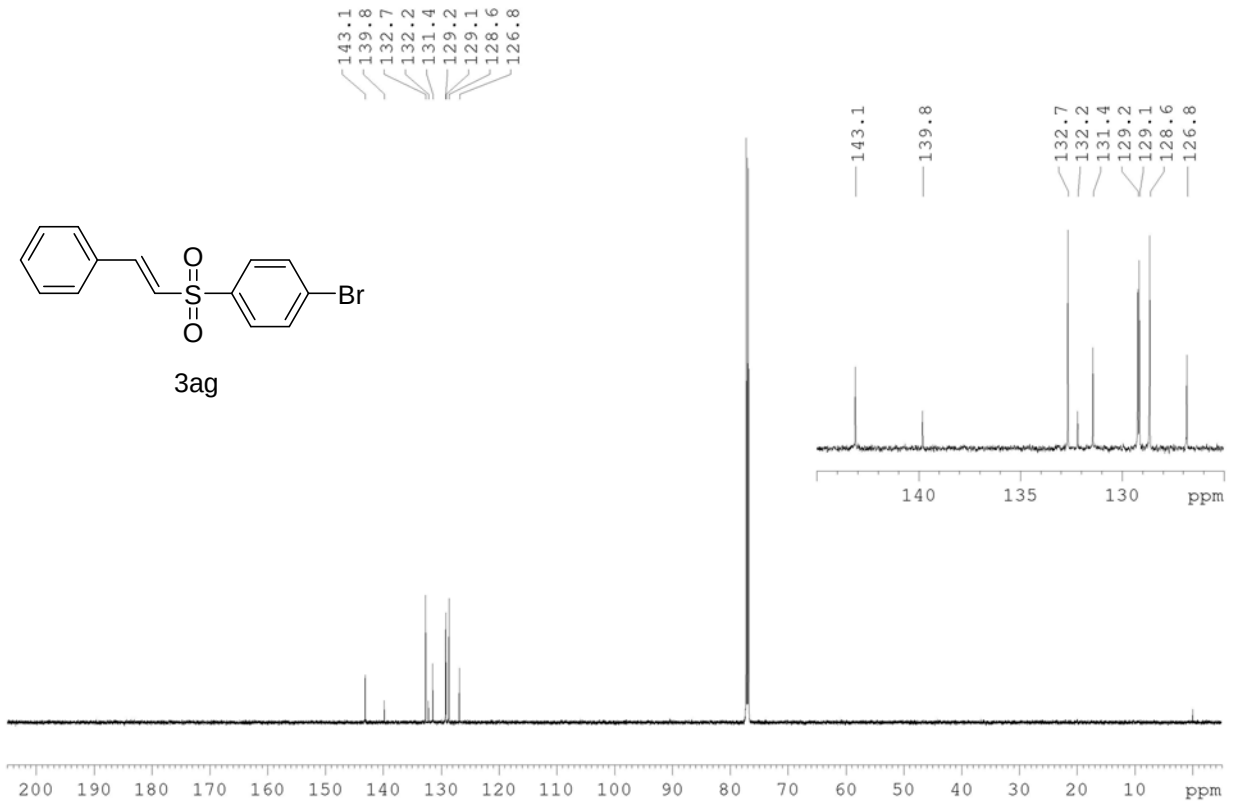
^{1}H NMR spectrum of compound 3af in $CDCl_3$ (600 MHz)



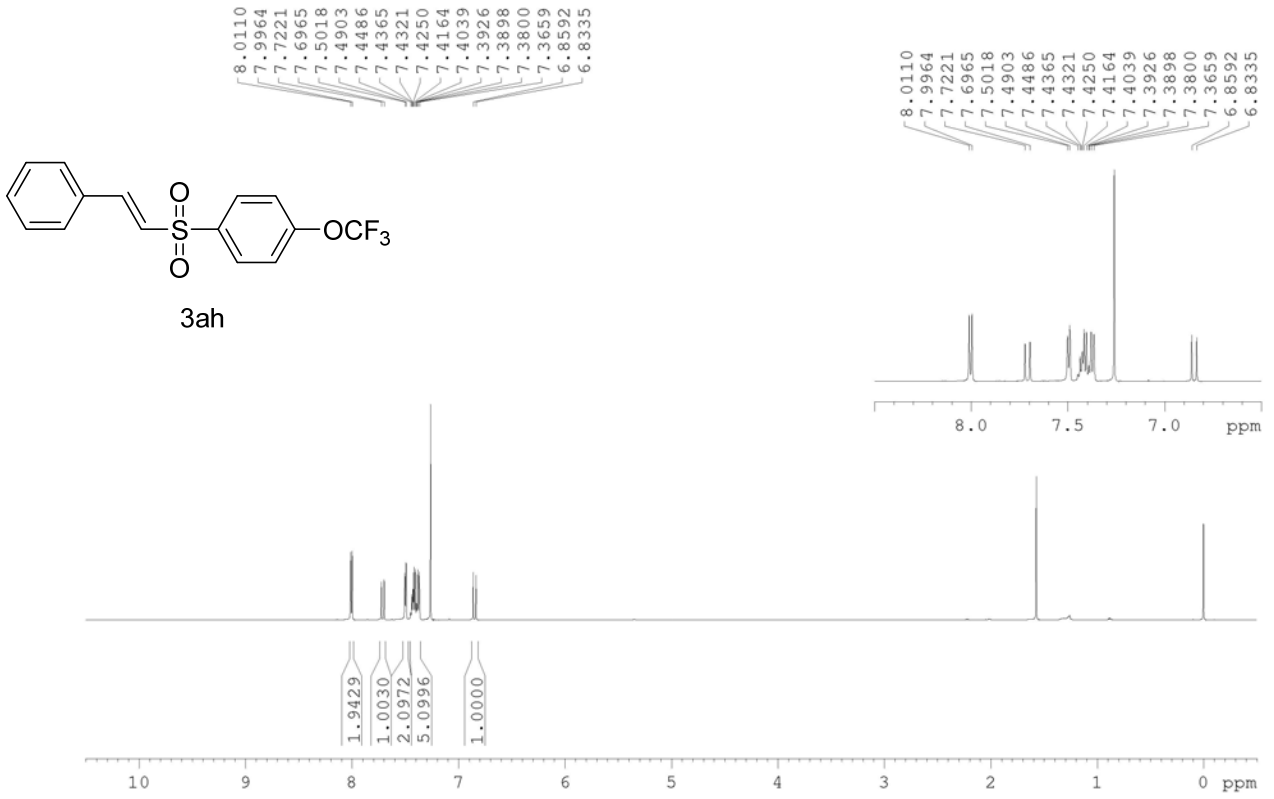
^{13}C NMR spectrum of compound 3af in $CDCl_3$ (150 MHz)



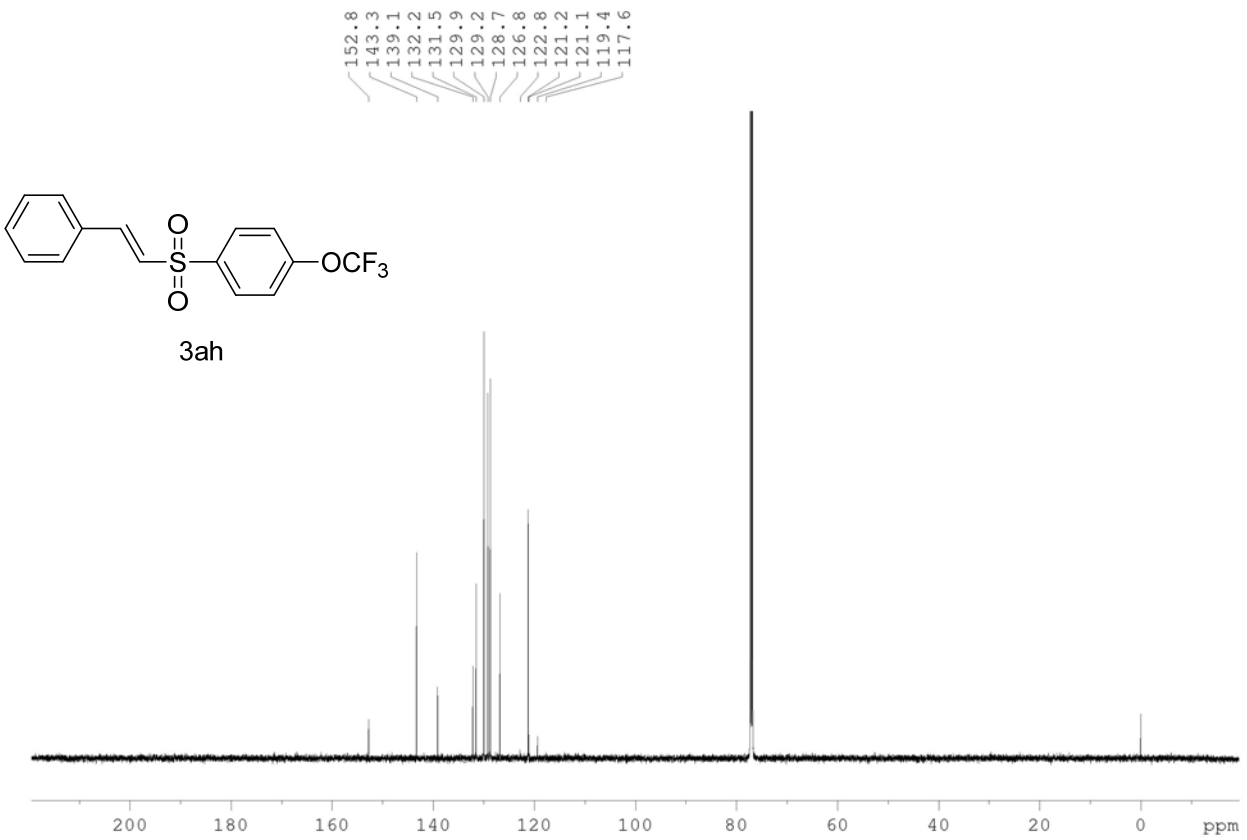
^{1}H NMR spectrum of compound 3ag in $CDCl_3$ (600 MHz)



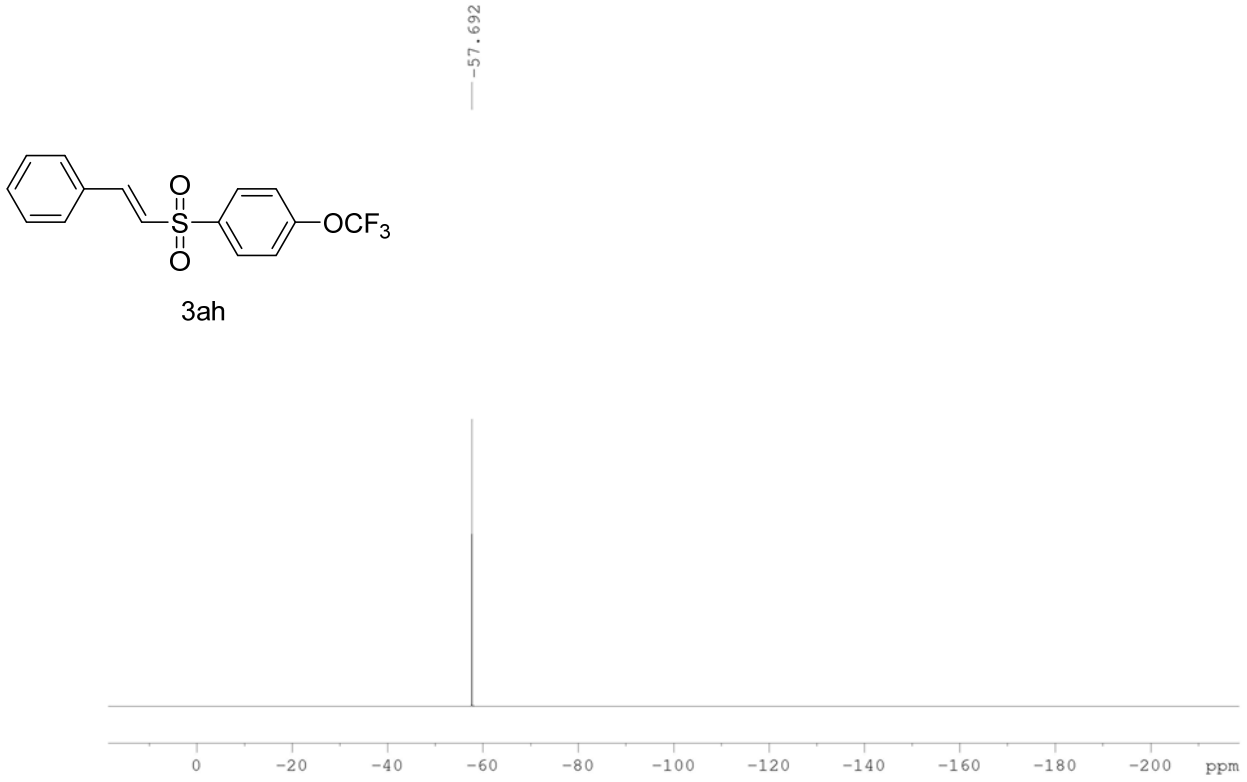
^{13}C NMR spectrum of compound 3ag in $CDCl_3$ (150 MHz)



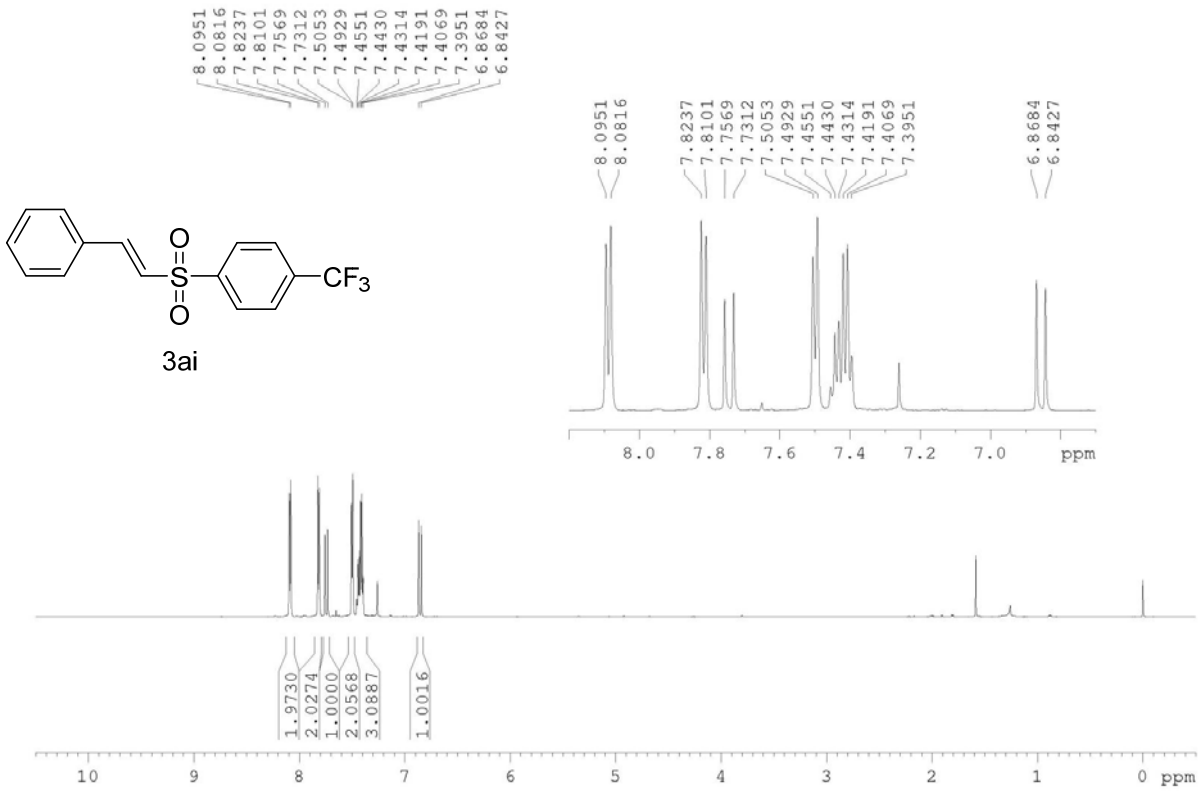
^{1}H NMR spectrum of compound 3ah in $CDCl_3$ (600 MHz)



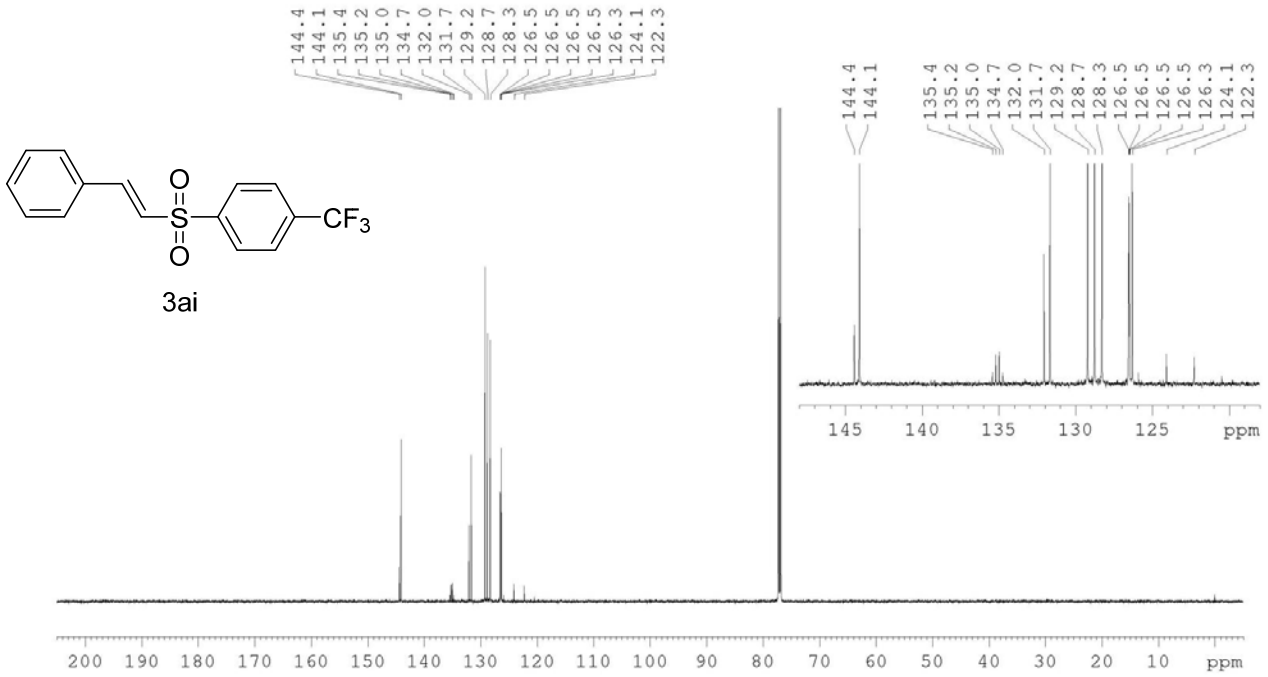
^{13}C NMR spectrum of compound 3ah in $CDCl_3$ (150 MHz)



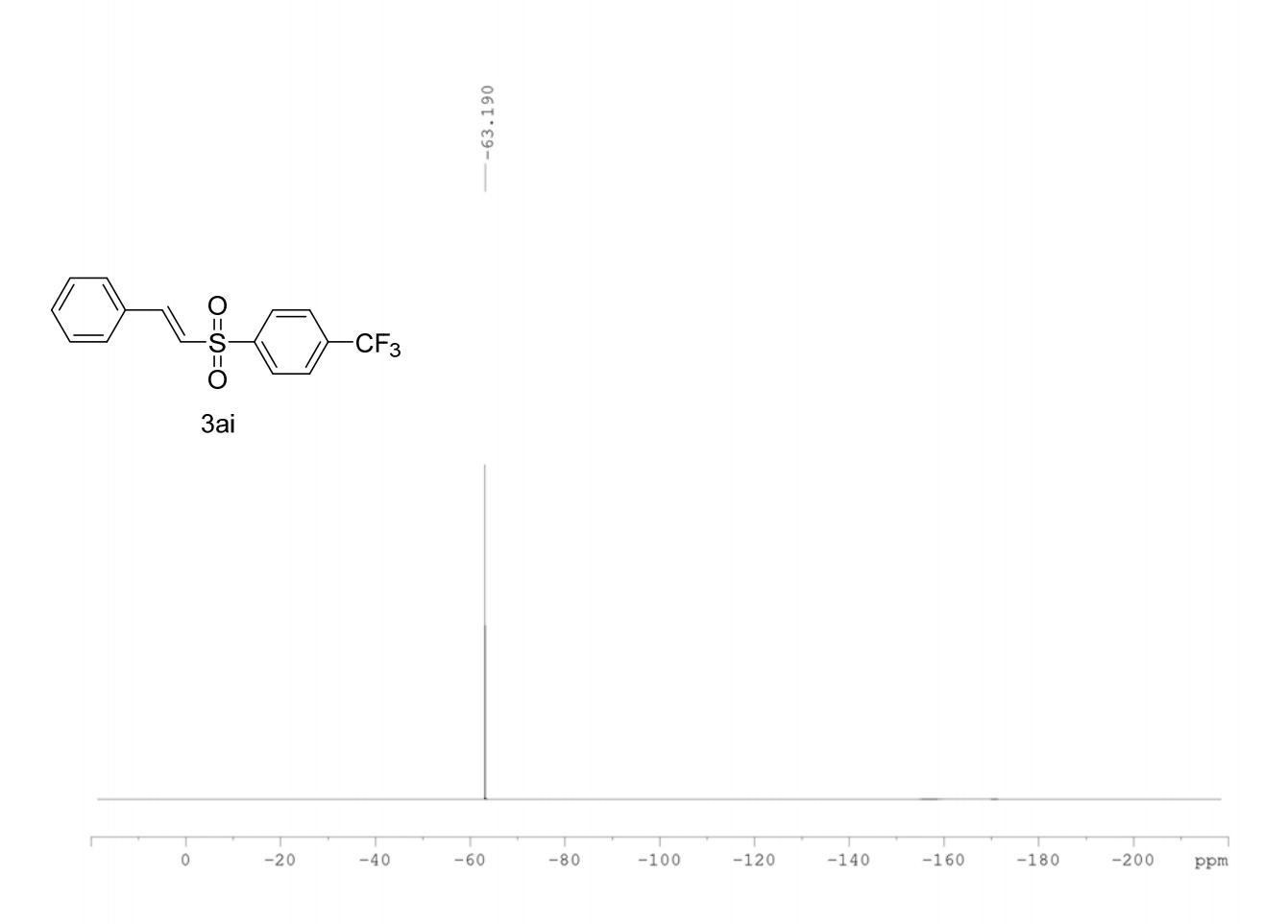
^{19}F NMR spectrum of compound 3ah in $CDCl_3$ (565 MHz)



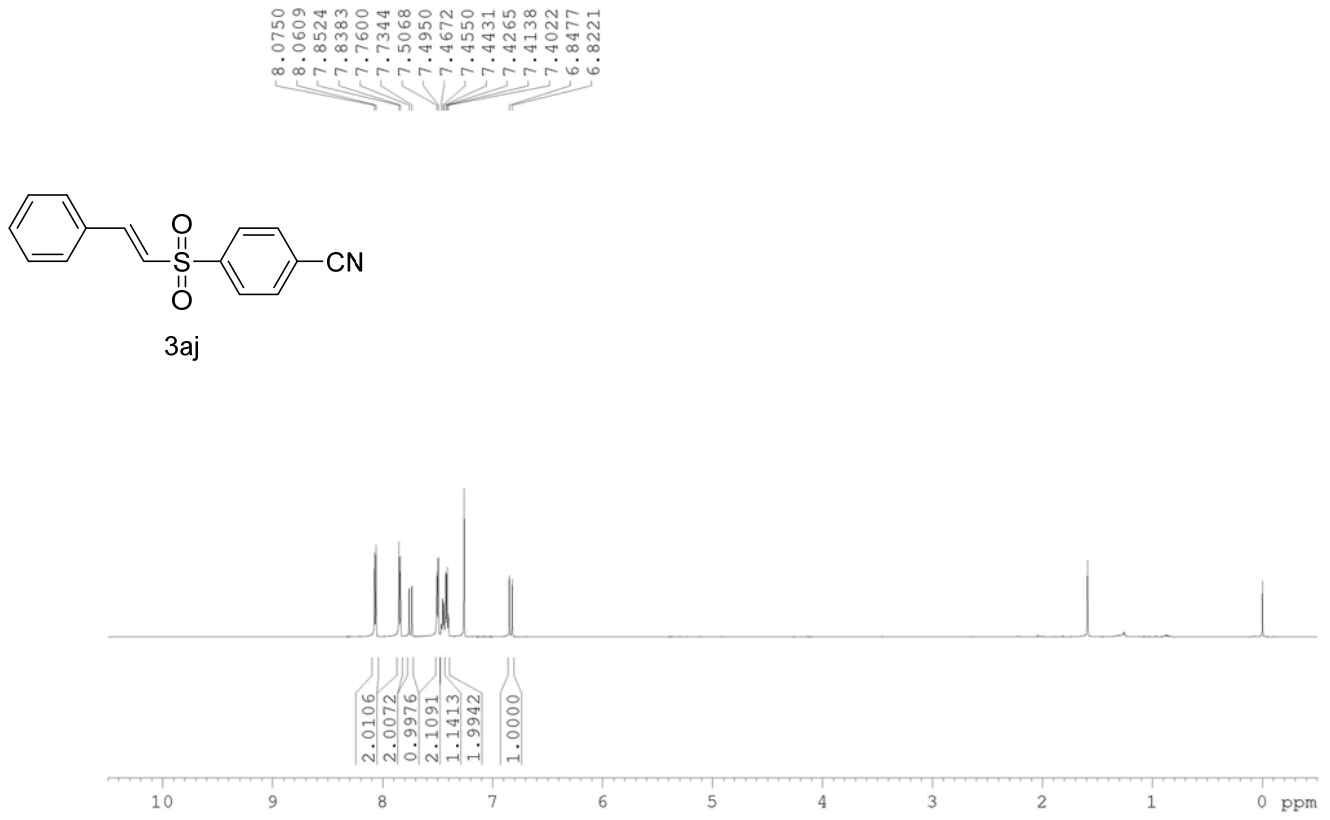
^{1}H NMR spectrum of compound 3ai in $CDCl_3$ (600 MHz)



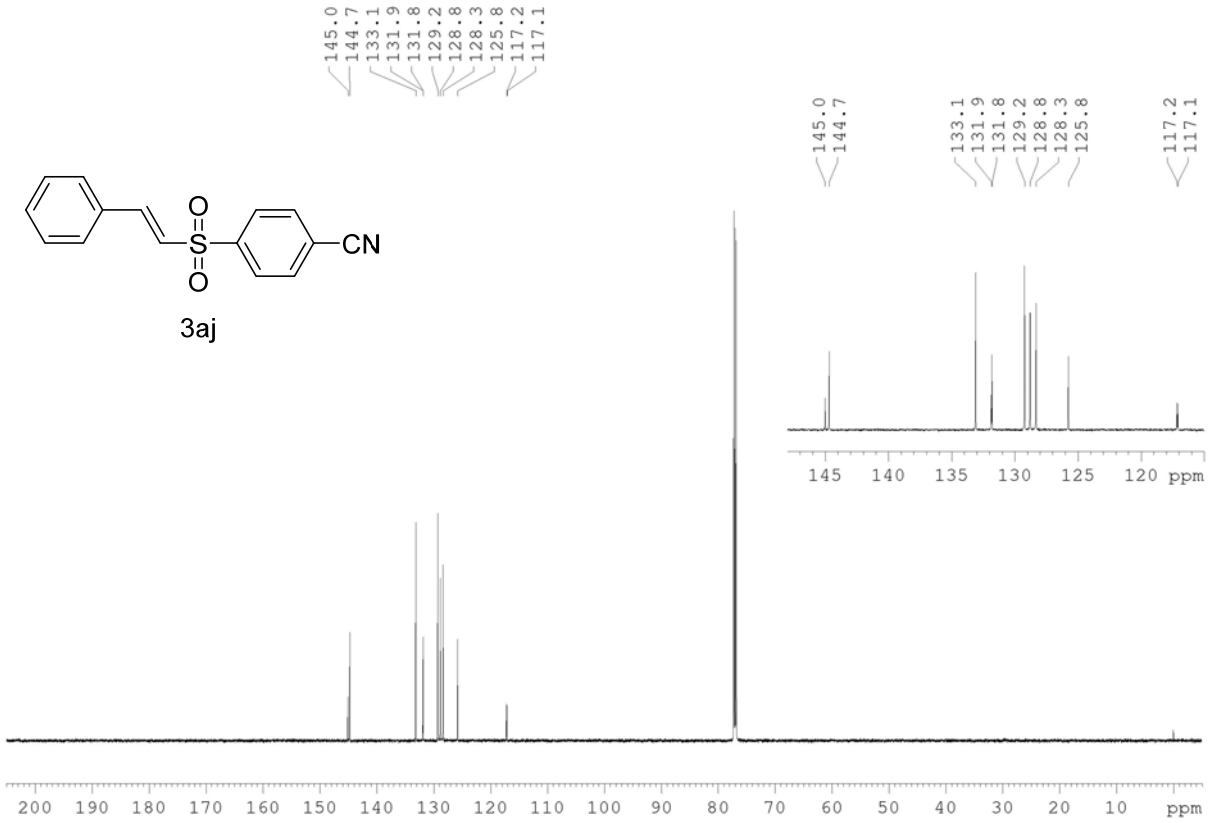
^{13}C NMR spectrum of compound 3ai in $CDCl_3$ (150 MHz)



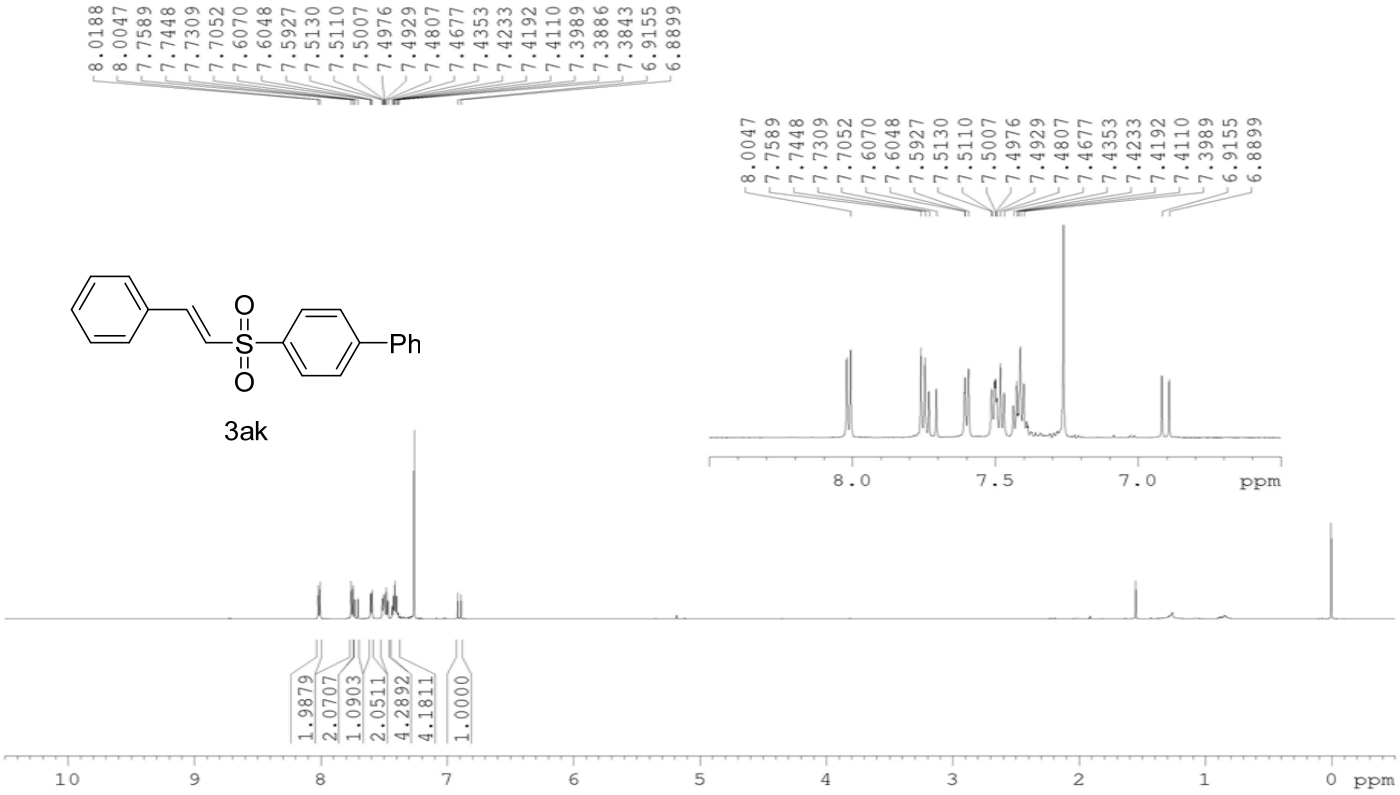
^{19}F NMR spectrum of compound 3ai in $CDCl_3$ (565 MHz)



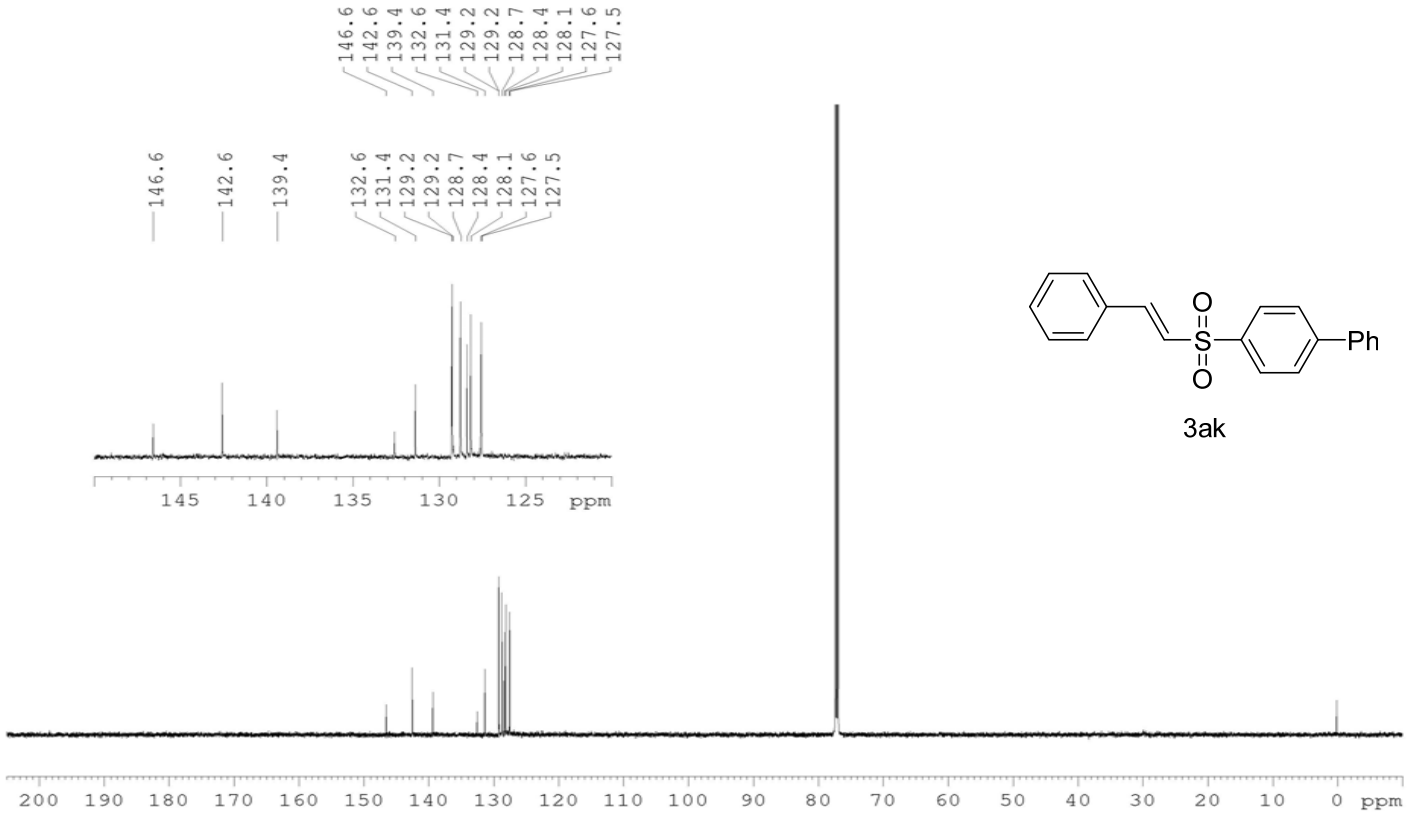
^{1}H NMR spectrum of compound 3aj in $CDCl_3$ (600 MHz)



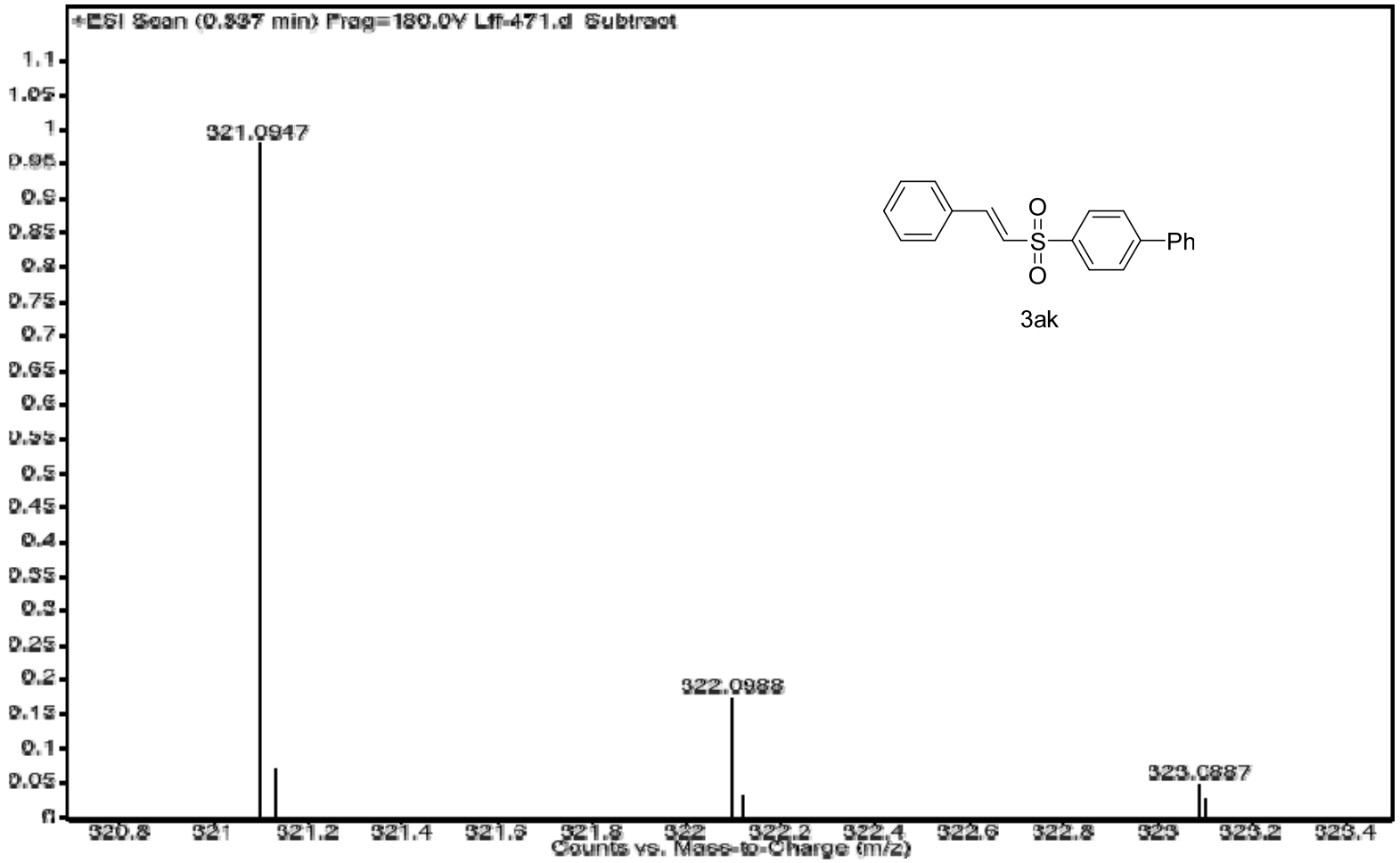
^{13}C NMR spectrum of compound 3aj in $CDCl_3$ (150 MHz)



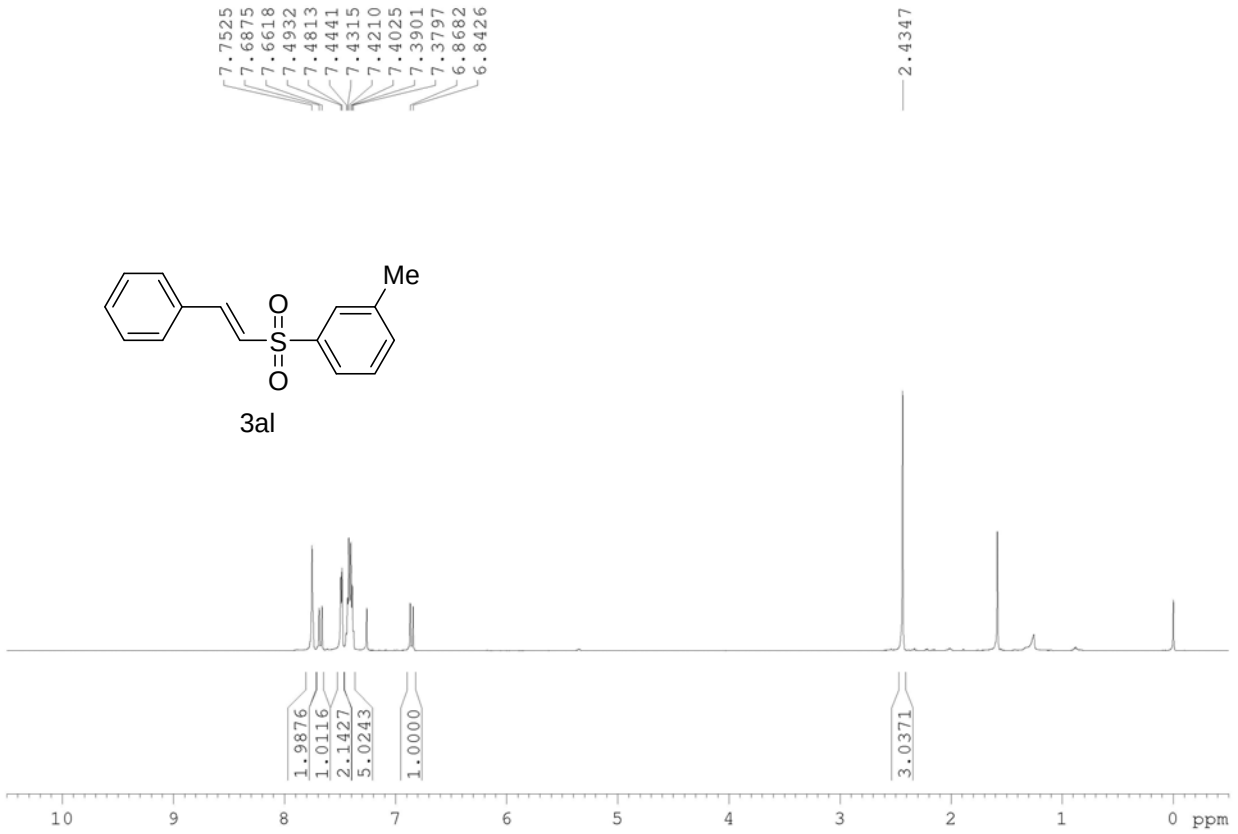
^{1}H NMR spectrum of compound 3ak in $CDCl_3$ (600 MHz)



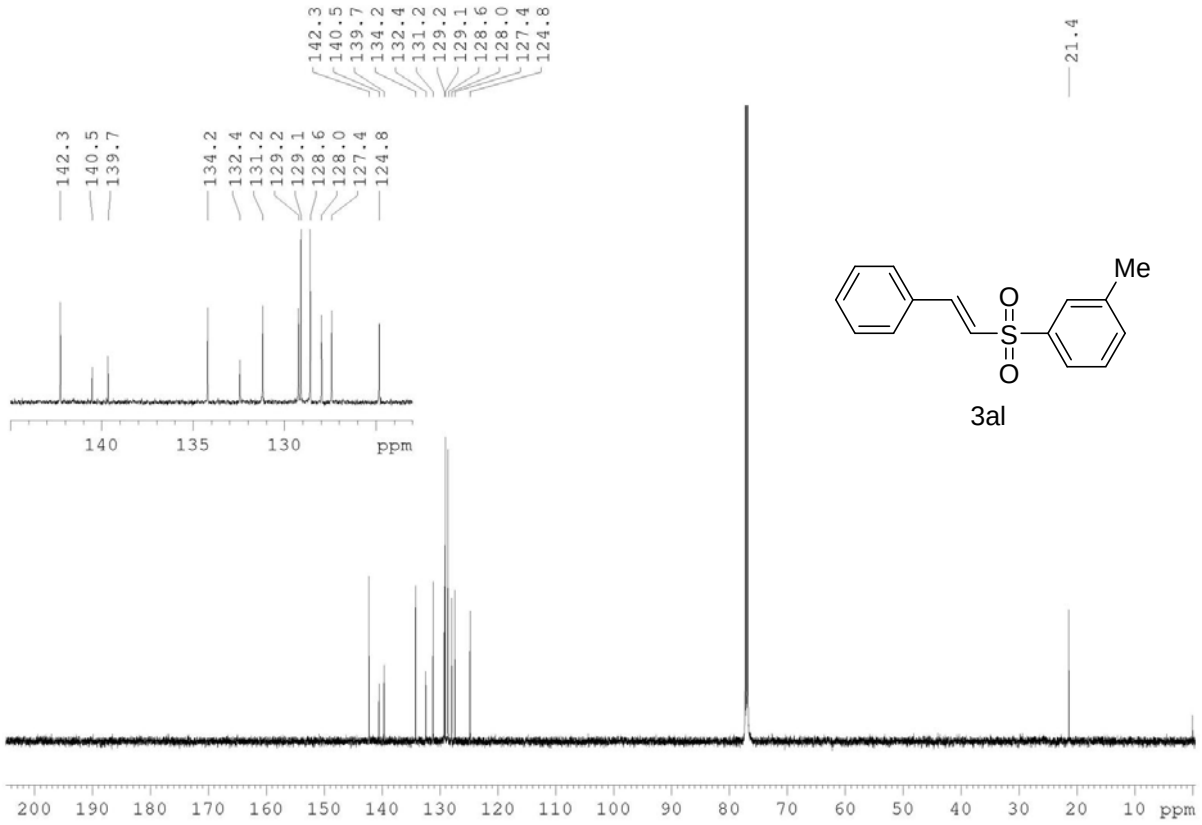
^{13}C NMR spectrum of compound 3ak in $CDCl_3$ (150 MHz)



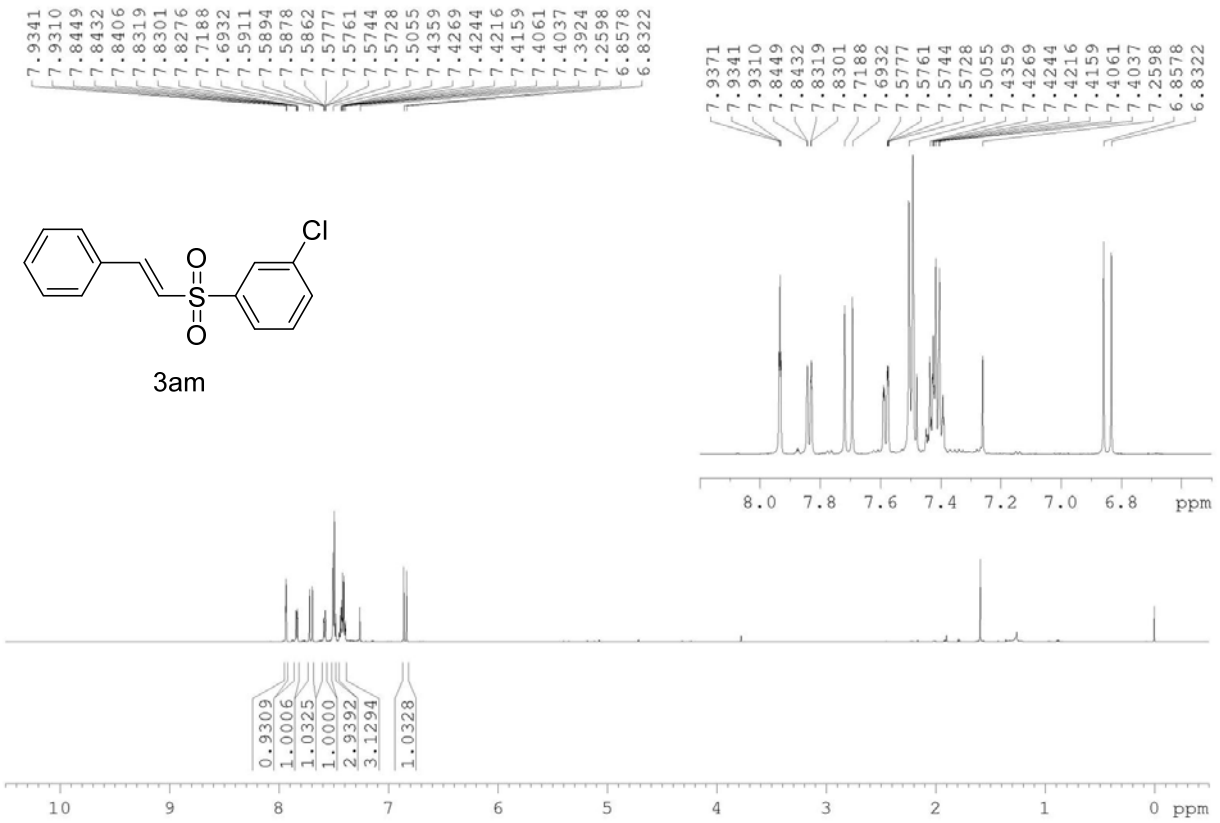
HRMS spectrum of compound 3ak



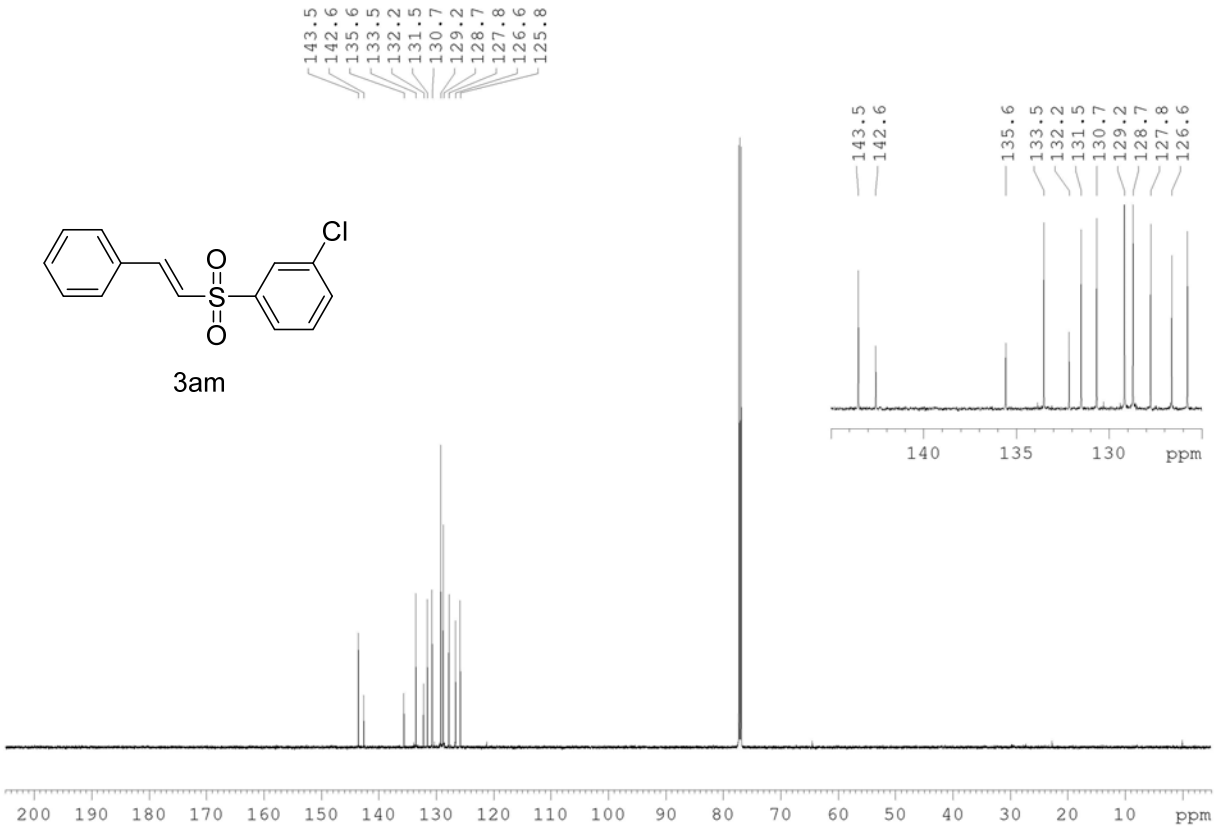
^{1}H NMR spectrum of compound 3al in $CDCl_3$ (600 MHz)



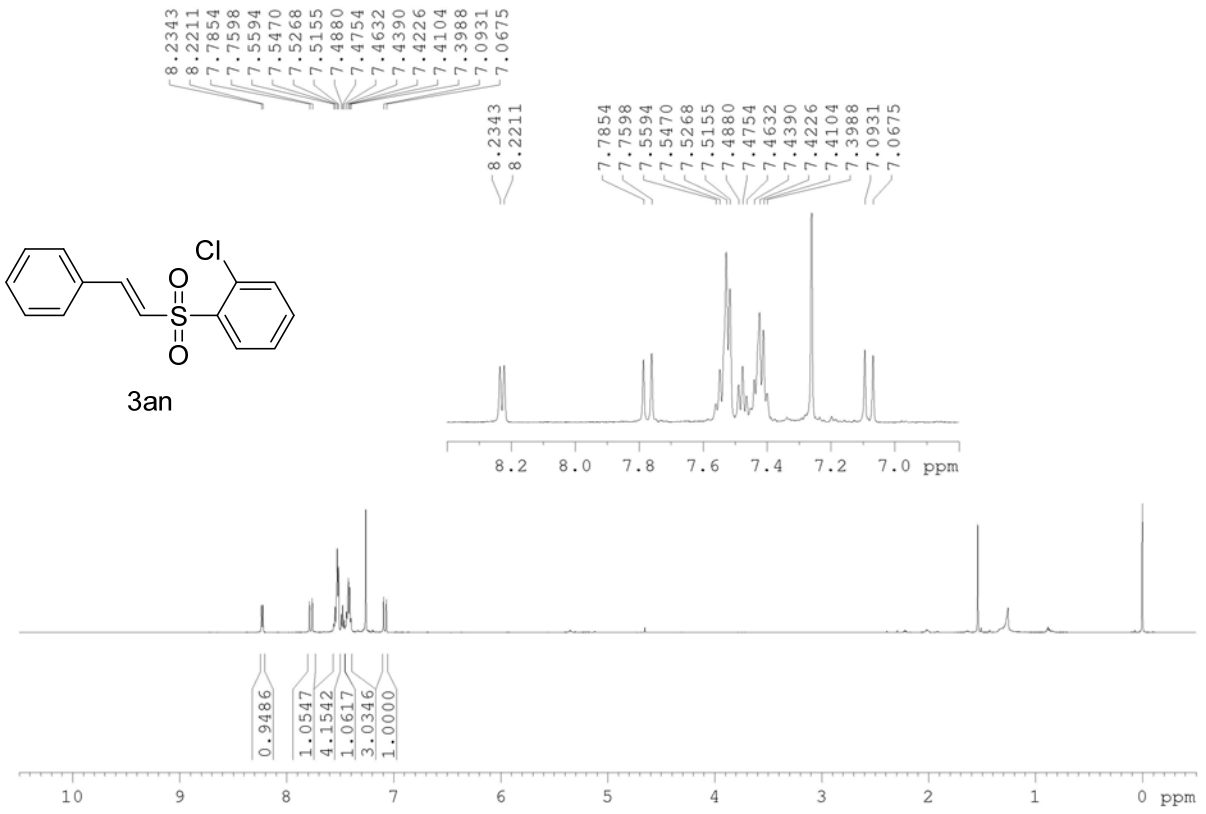
^{13}C NMR spectrum of compound 3al in $CDCl_3$ (150 MHz)



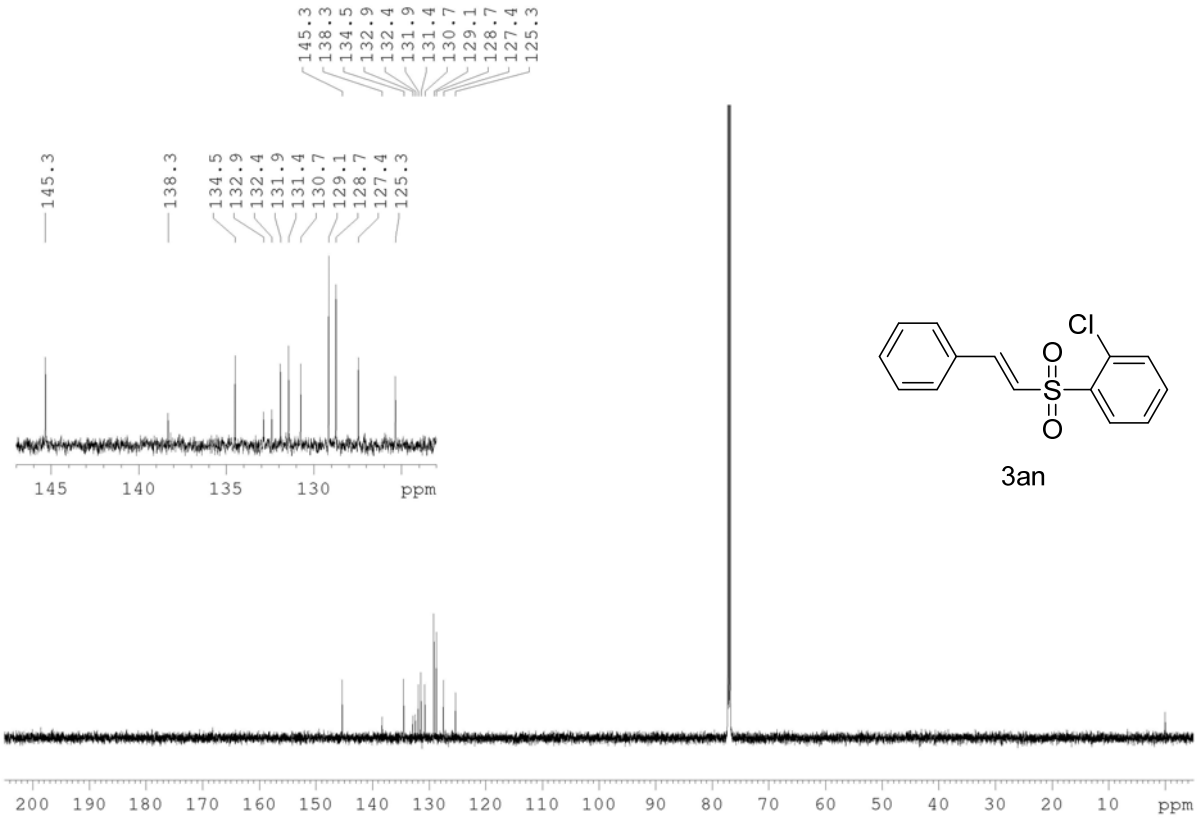
^{1}H NMR spectrum of compound 3am in $CDCl_3$ (600 MHz)



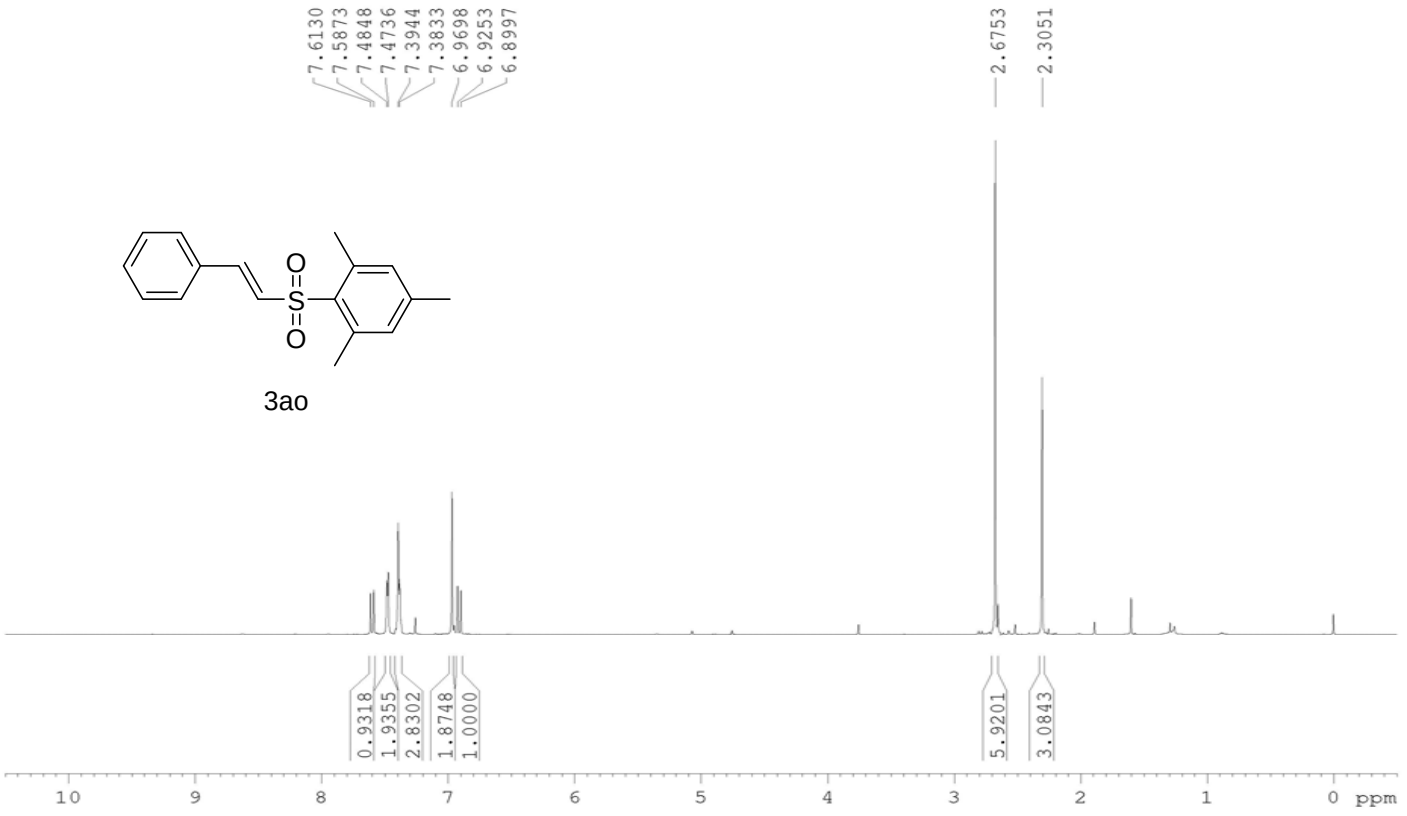
^{13}C NMR spectrum of compound 3am in $CDCl_3$ (150 MHz)



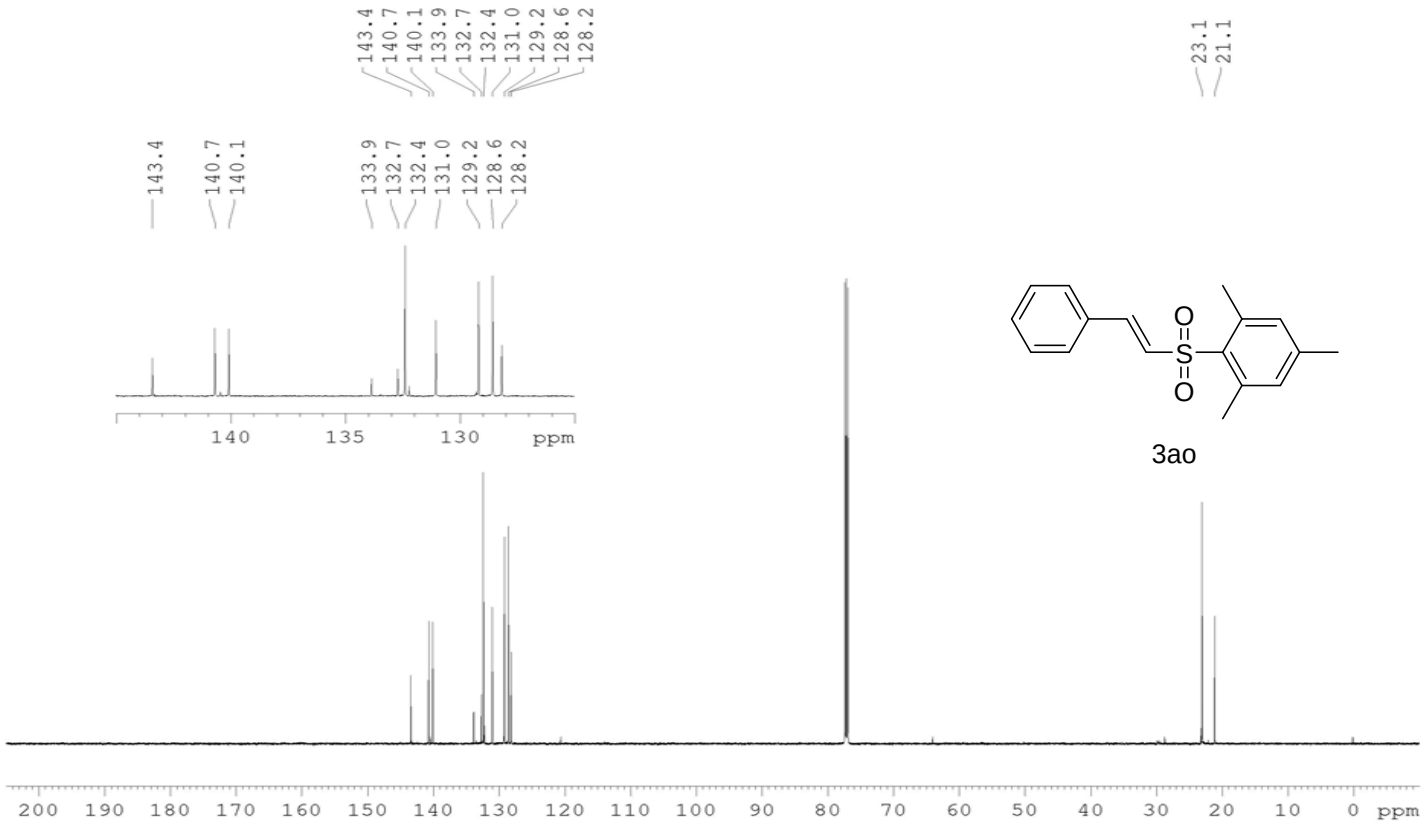
^{1}H NMR spectrum of compound 3an in $CDCl_3$ (600 MHz)



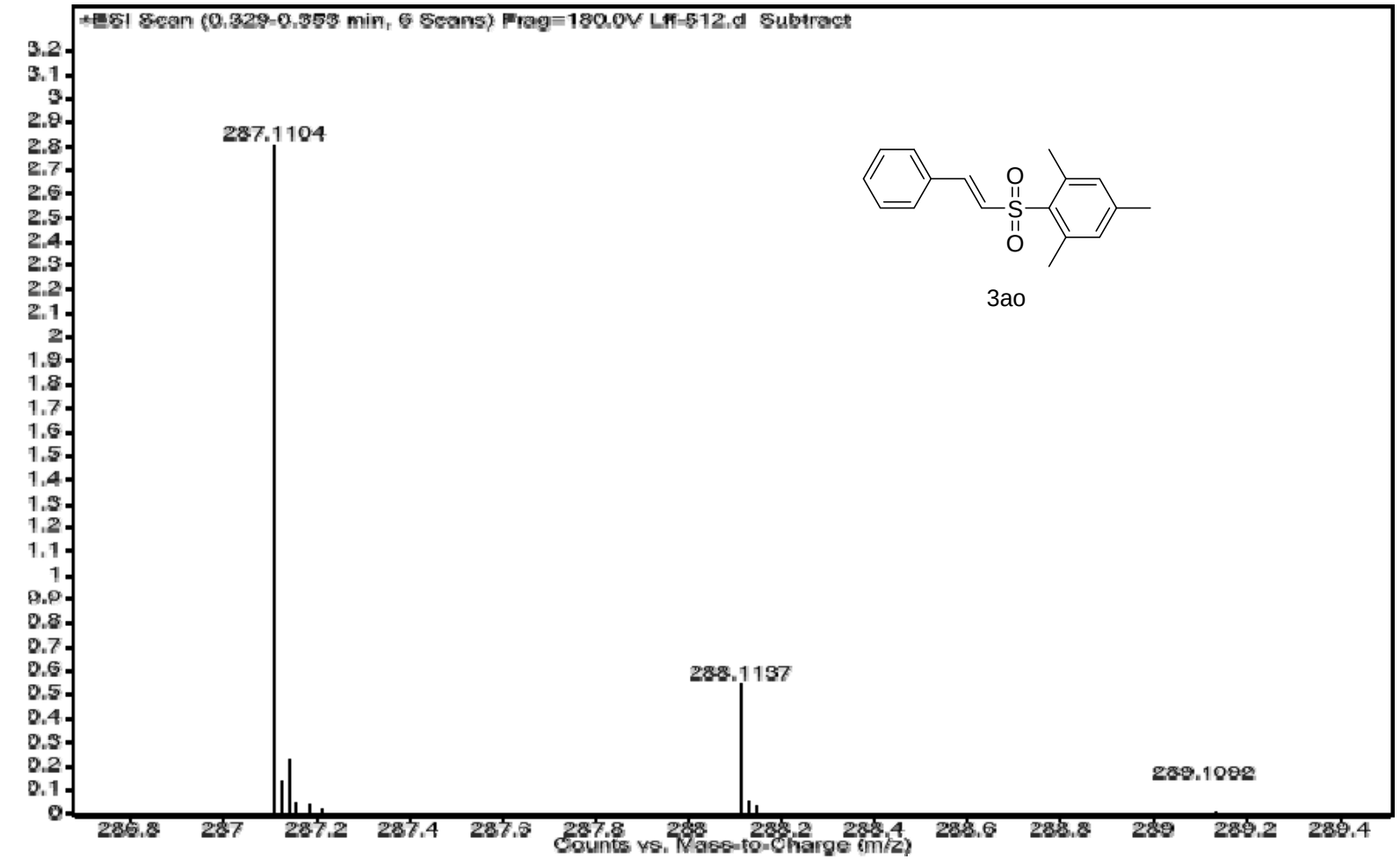
^{13}C NMR spectrum of compound 3an in $CDCl_3$ (150 MHz)



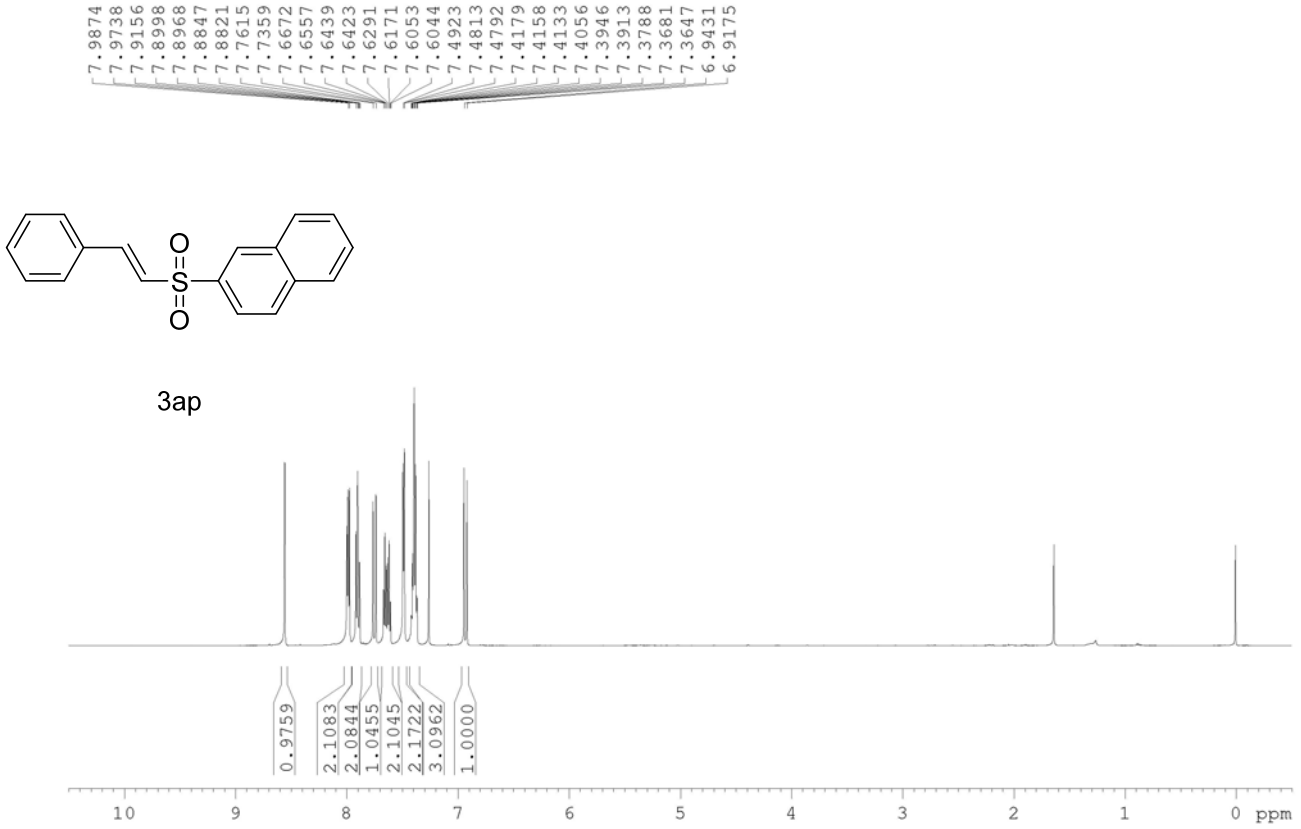
^{1}H NMR spectrum of compound 3ao in $CDCl_3$ (600 MHz)



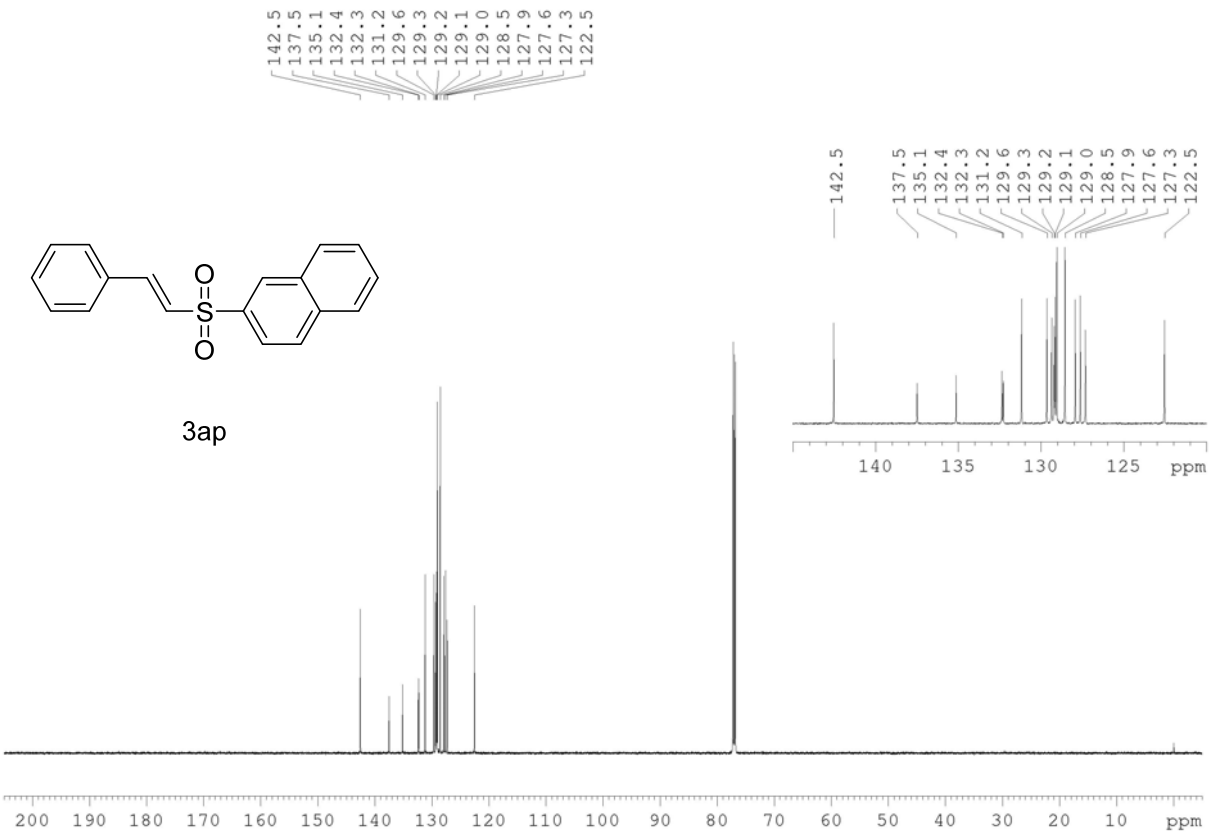
^{13}C NMR spectrum of compound 3ao in $CDCl_3$ (150 MHz)



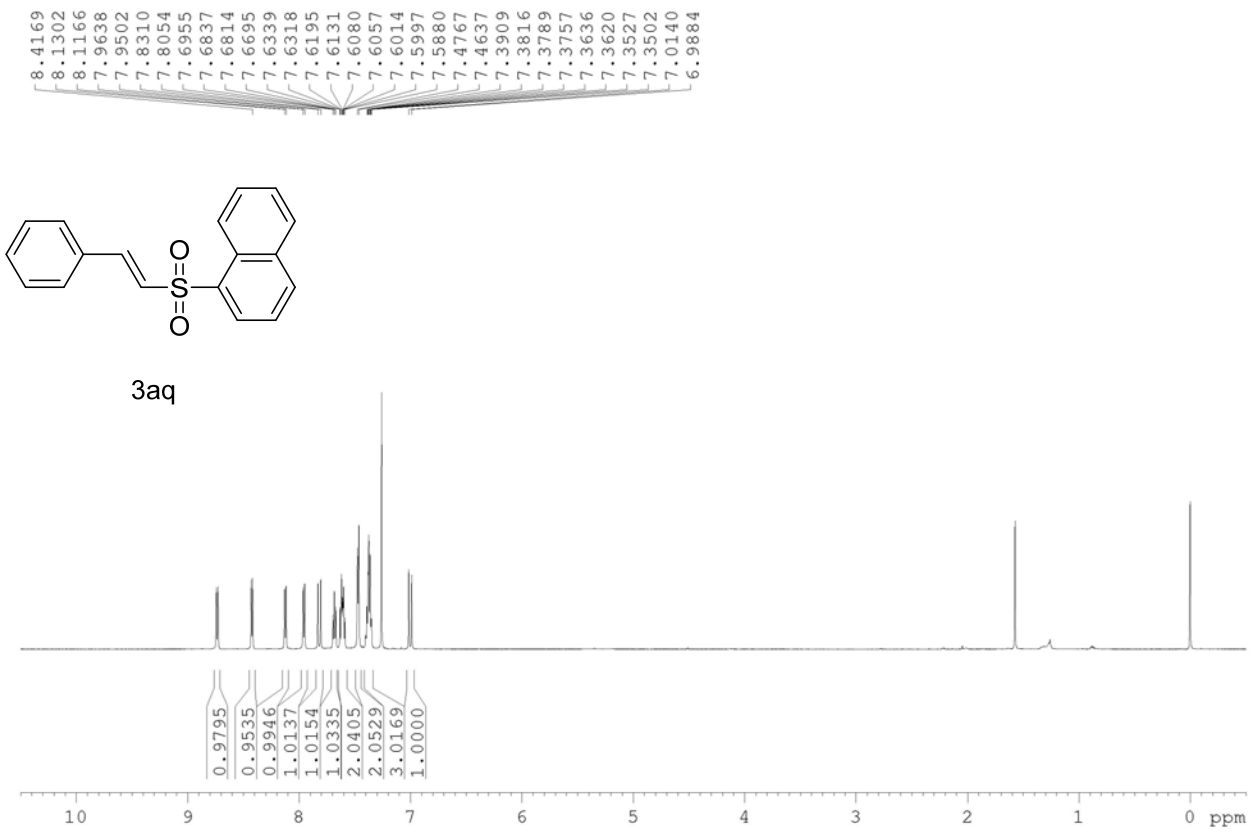
HRMS spectrum of compound 3ao



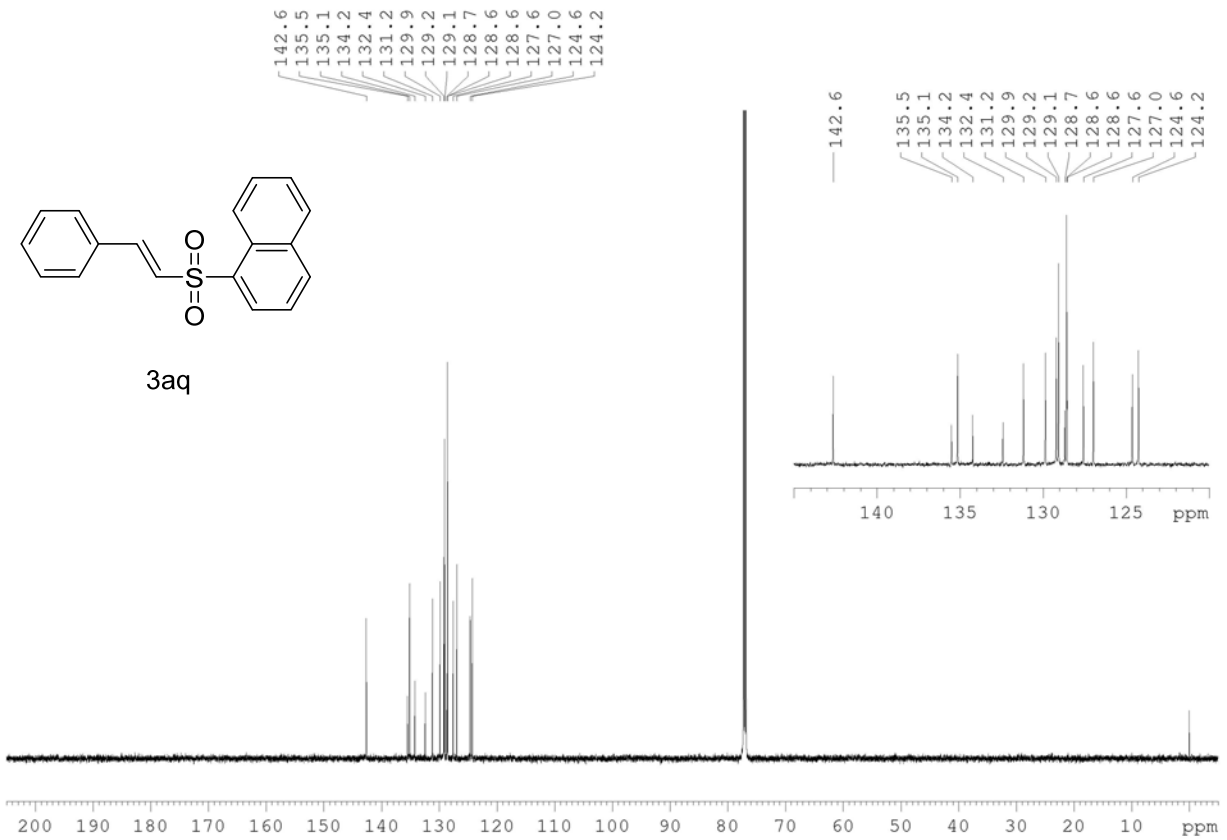
^{1}H NMR spectrum of compound 3ap in $CDCl_3$ (600 MHz)



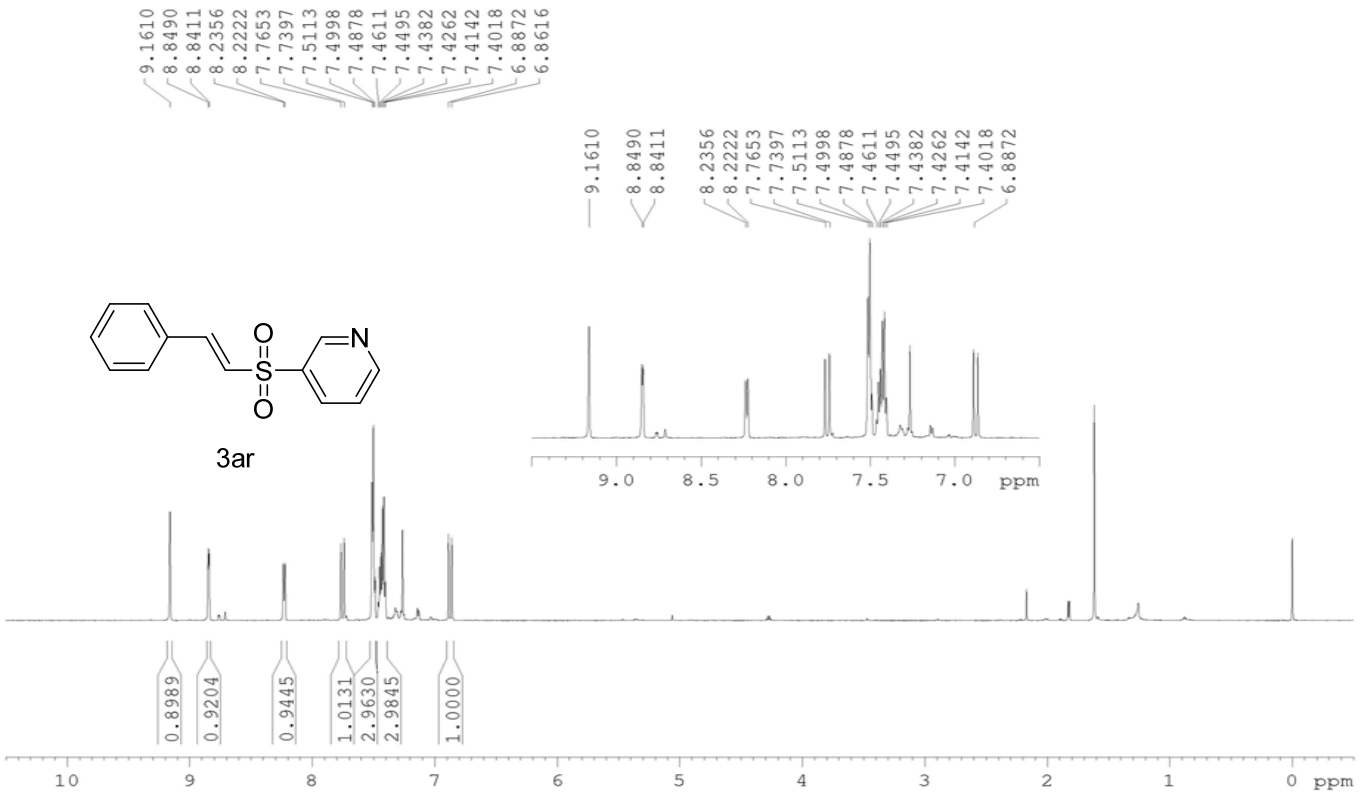
^{13}C NMR spectrum of compound 3ap in $CDCl_3$ (150 MHz)



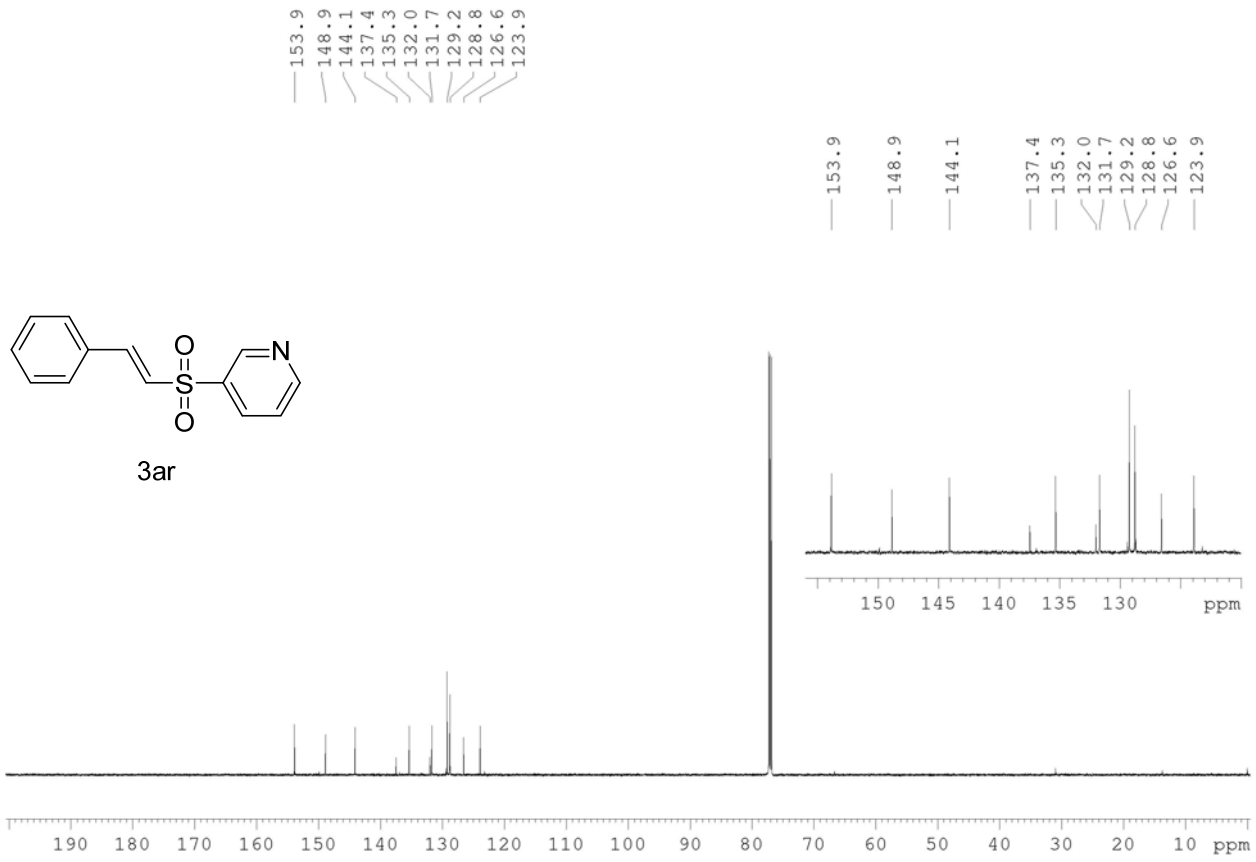
^{1}H NMR spectrum of compound 3aq in $CDCl_3$ (600 MHz)



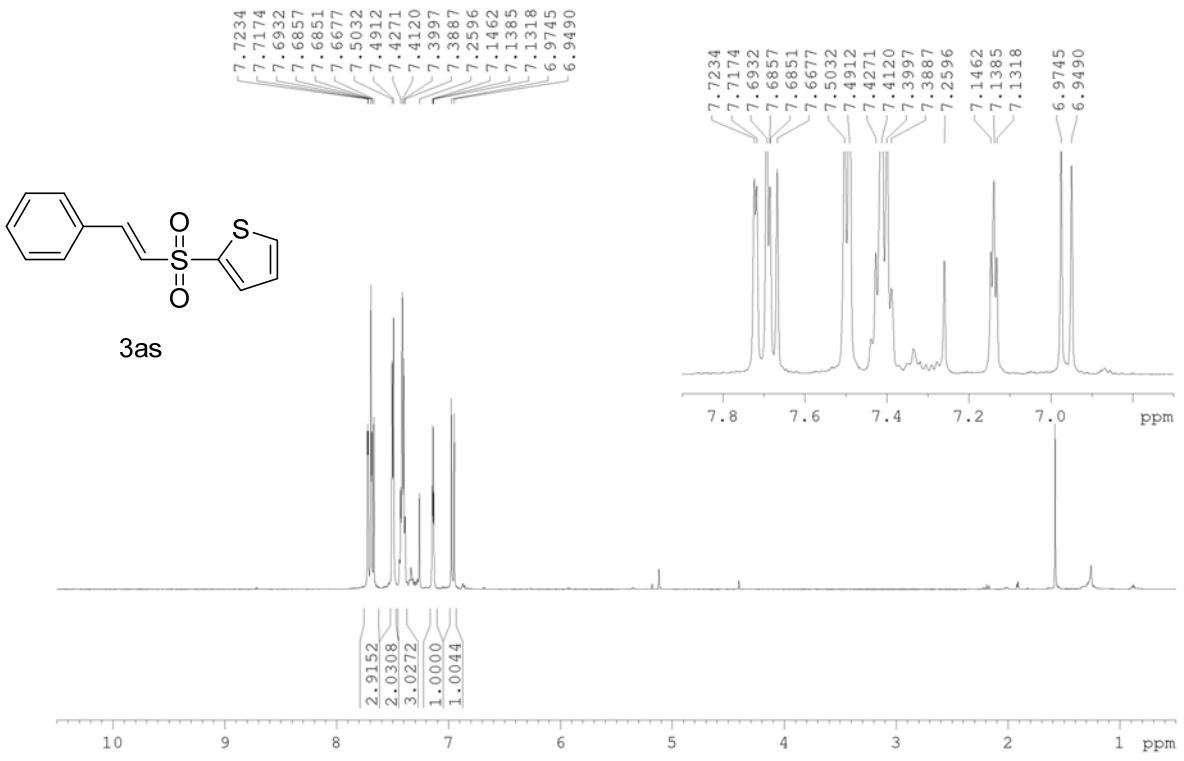
^{13}C NMR spectrum of compound 3aq in $CDCl_3$ (150 MHz)



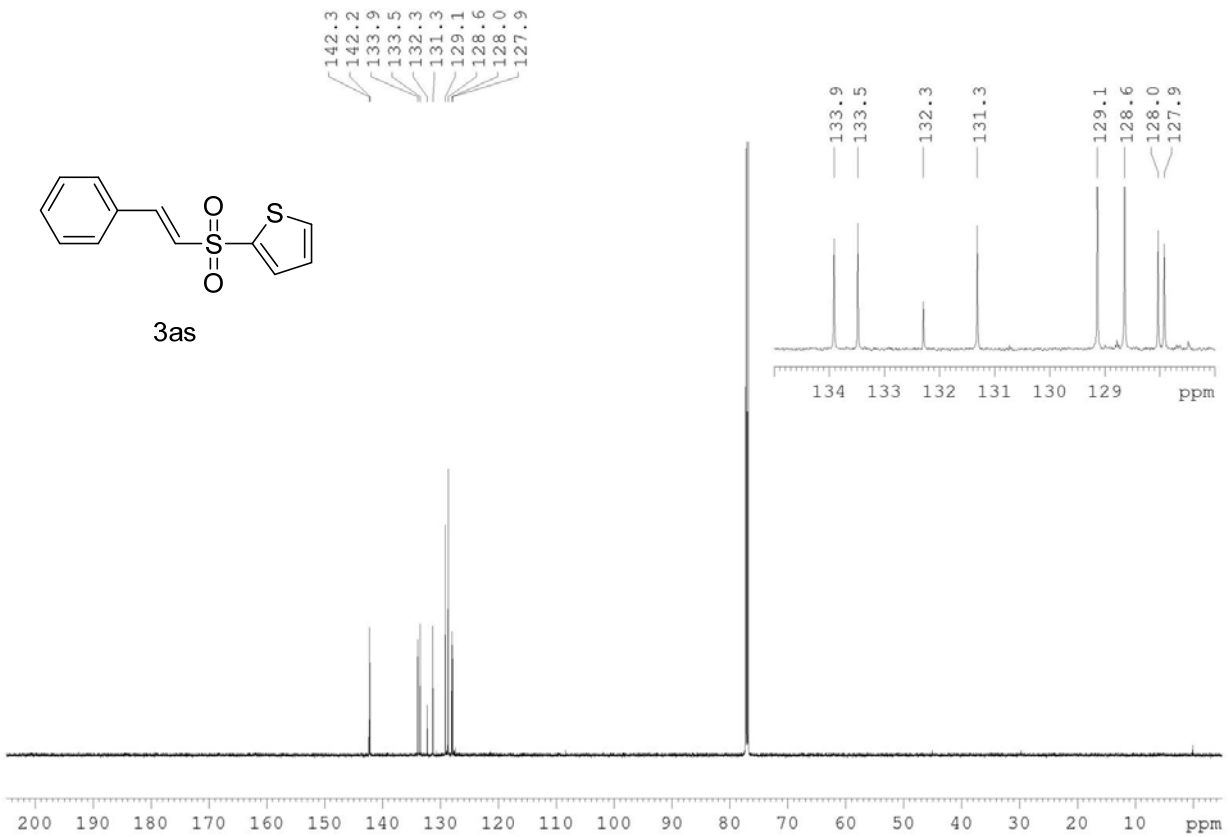
^{1}H NMR spectrum of compound 3ar in $CDCl_3$ (600 MHz)



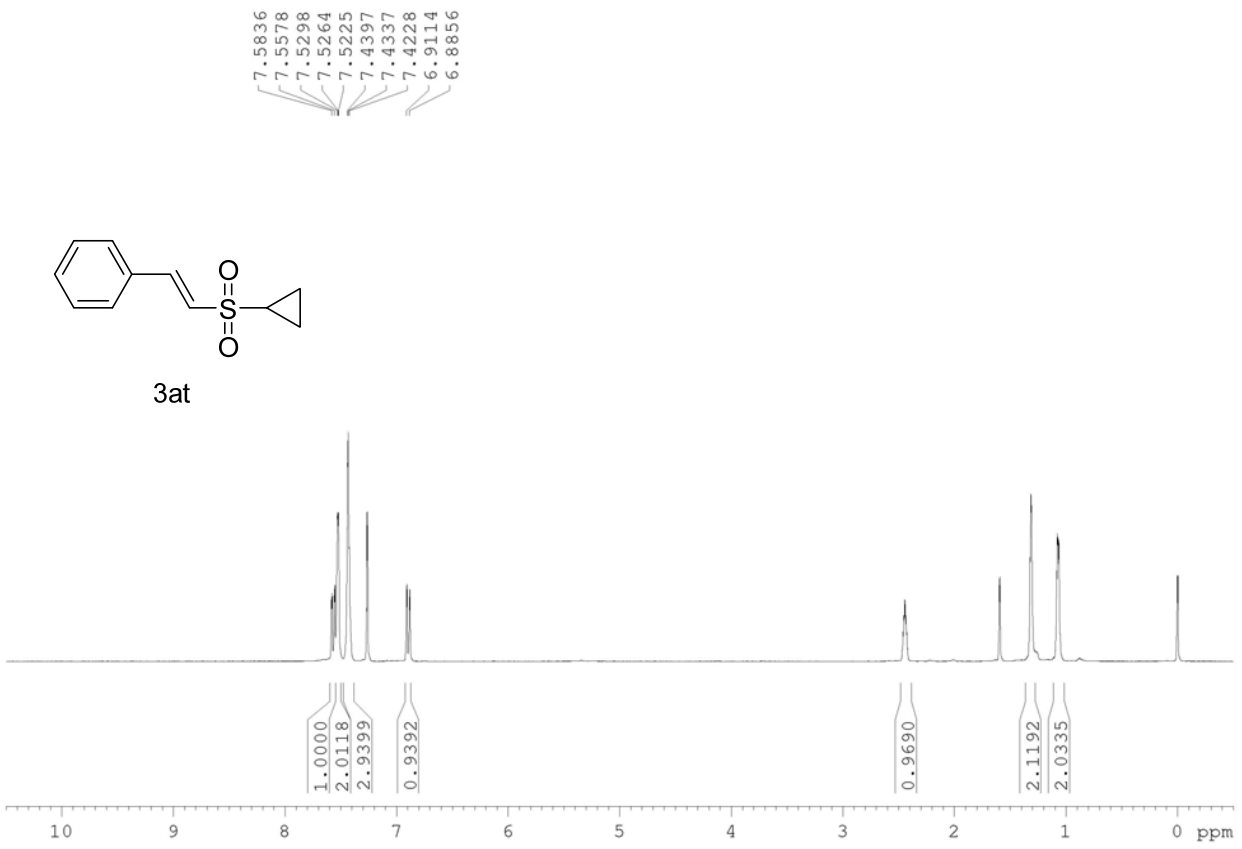
^{13}C NMR spectrum of compound 3ar in $CDCl_3$ (150 MHz)



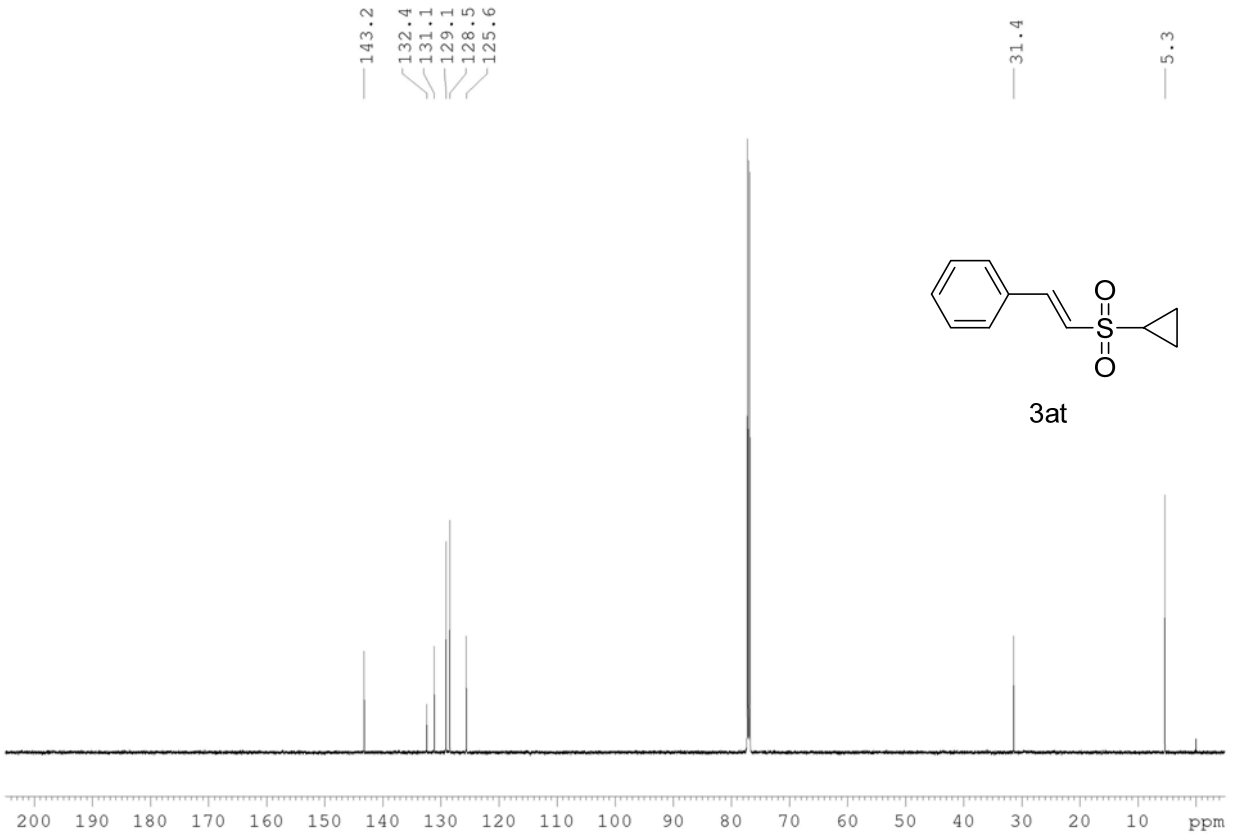
^{1}H NMR spectrum of compound 3as in $CDCl_3$ (600 MHz)



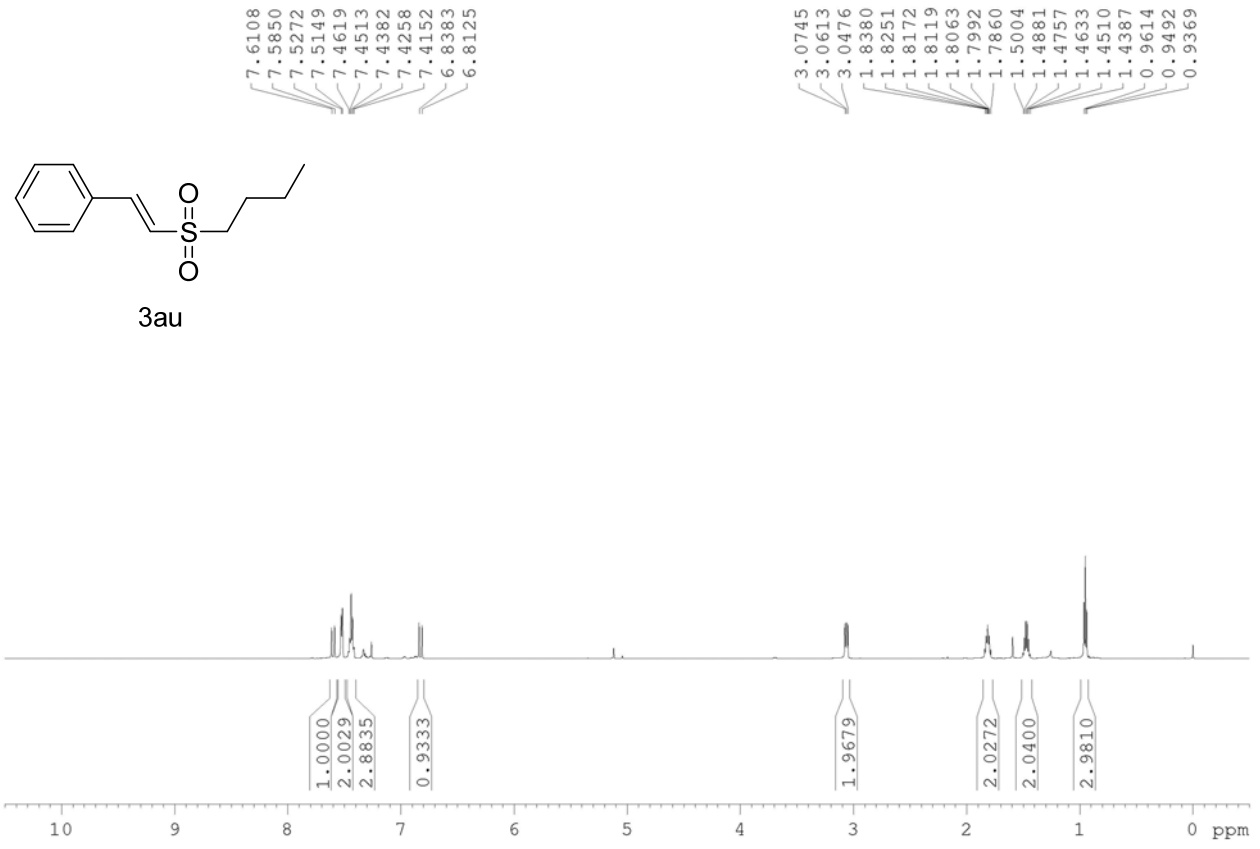
^{13}C NMR spectrum of compound 3as in $CDCl_3$ (150 MHz)



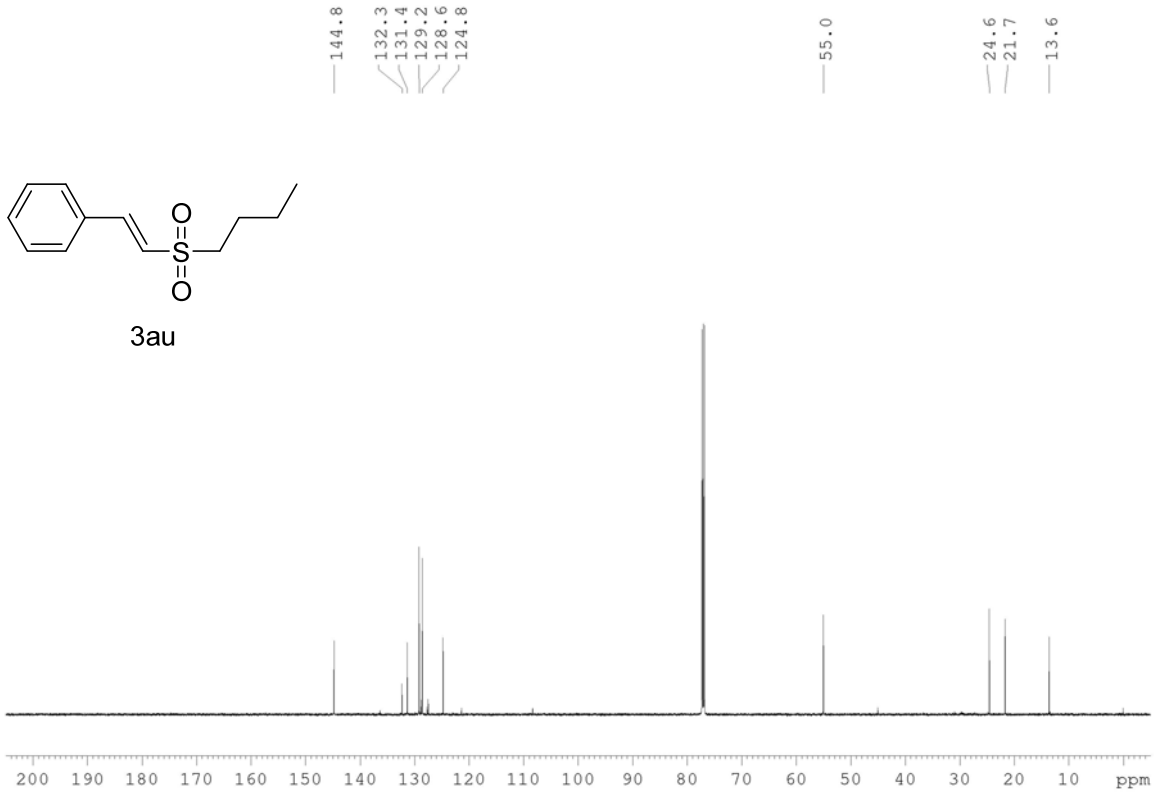
^{1}H NMR spectrum of compound 3at in $CDCl_3$ (600 MHz)



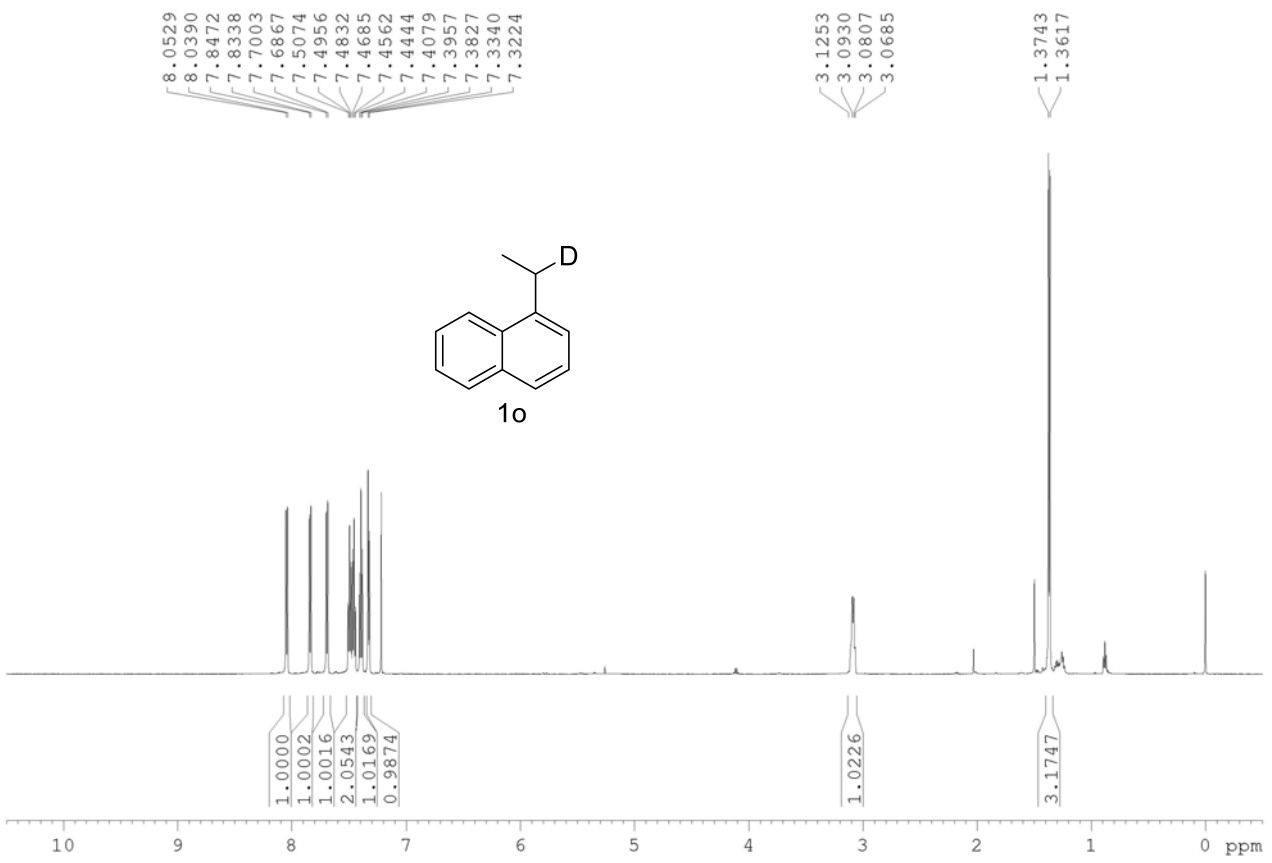
^{13}C NMR spectrum of compound 3at in $CDCl_3$ (150 MHz)



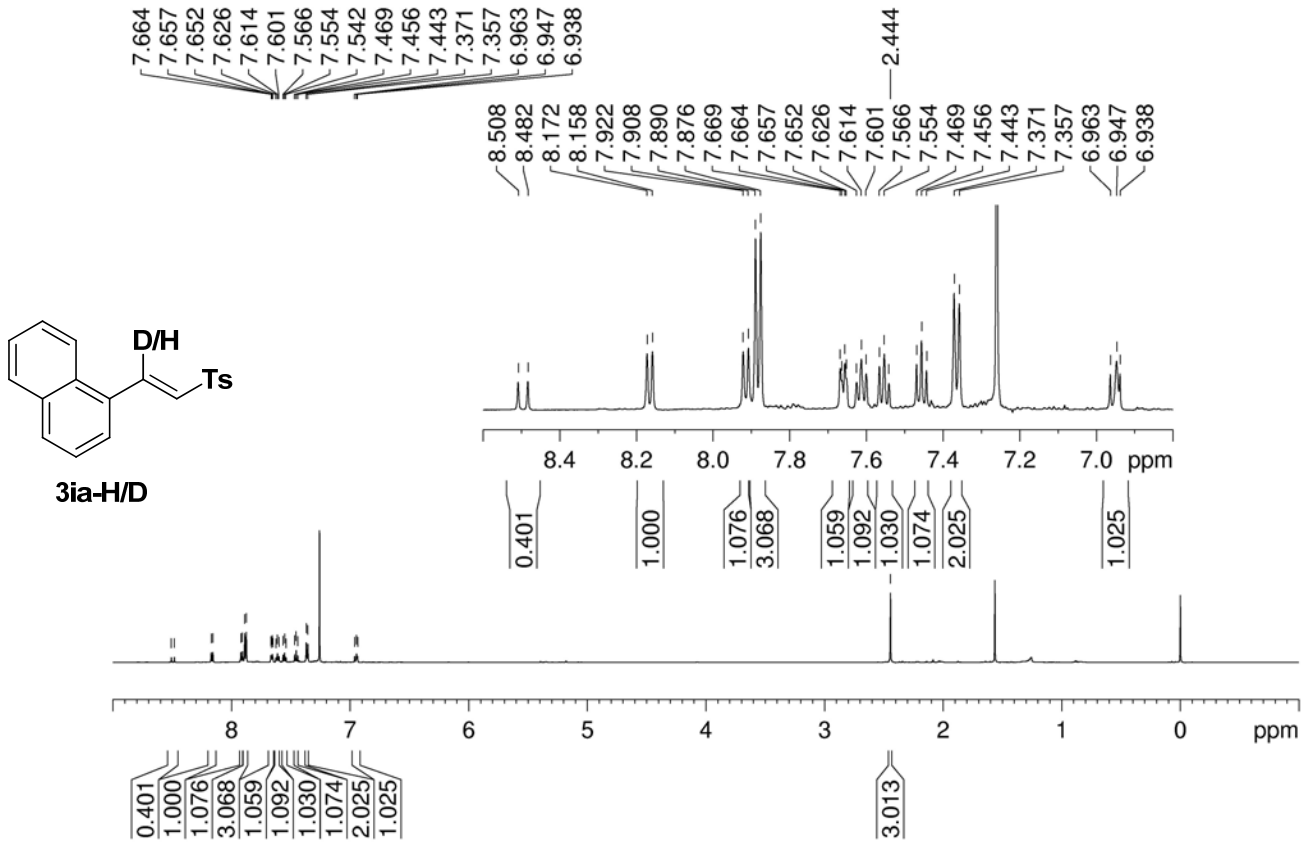
^{1}H NMR spectrum of compound 3au in $CDCl_3$ (600 MHz)



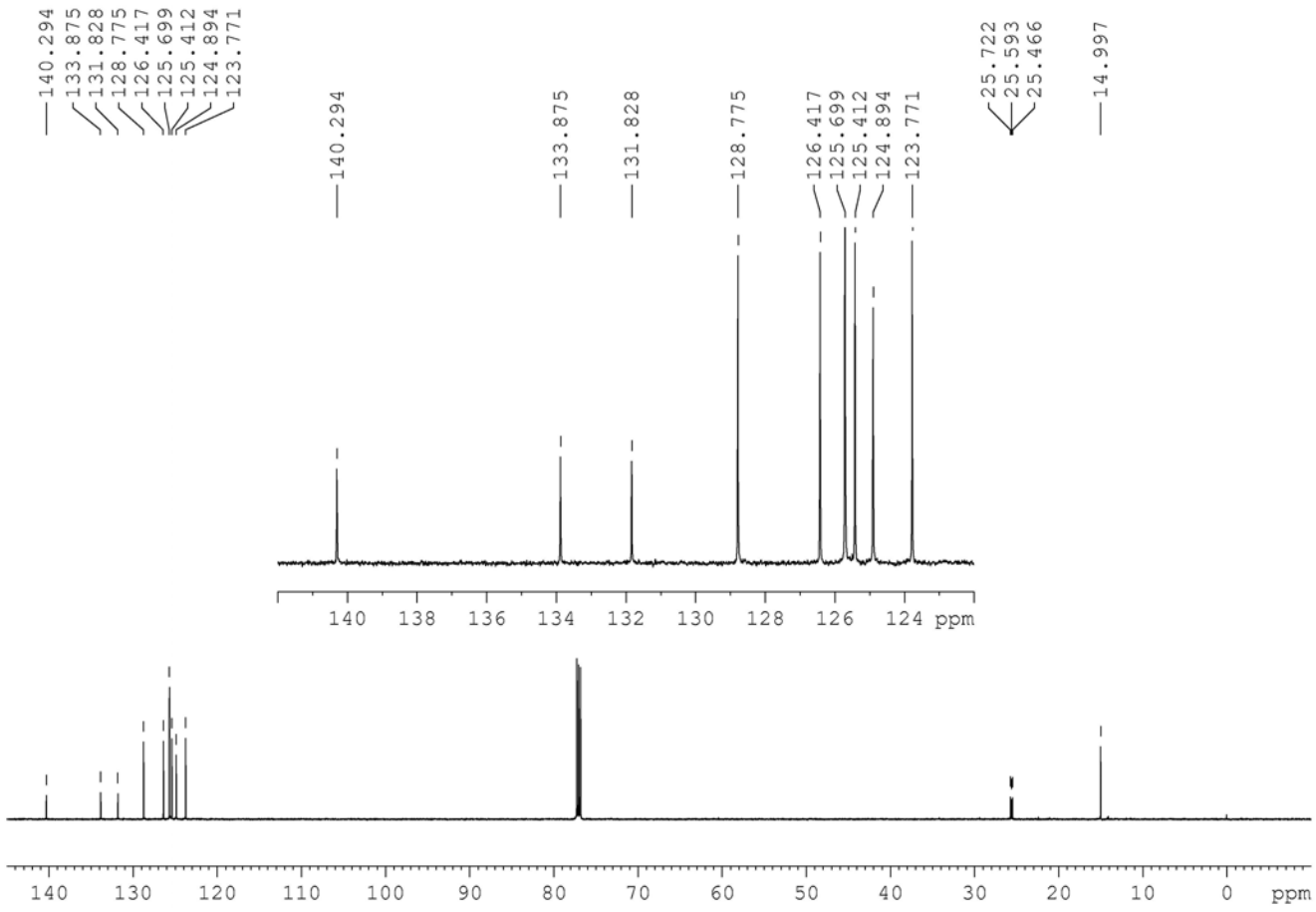
^{13}C NMR spectrum of compound 3au in $CDCl_3$ (150 MHz)



^{1}H NMR spectrum of compound 1o in $CDCl_3$ (600 MHz)



^{1}H NMR spectrum of compound 3ia-H/D in $CDCl_3$ (600 MHz)



^{13}C NMR spectrum of compound 3ia-H/D in $CDCl_3$ (150 MHz)