Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition Metal-free and Regioselective Alkenyl C−S Cross-Coupling Reaction of Alkenyl Sulfonium Salts

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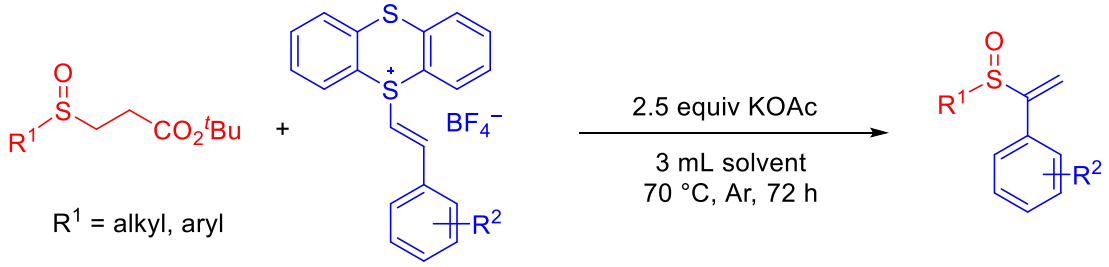
1. General Information:

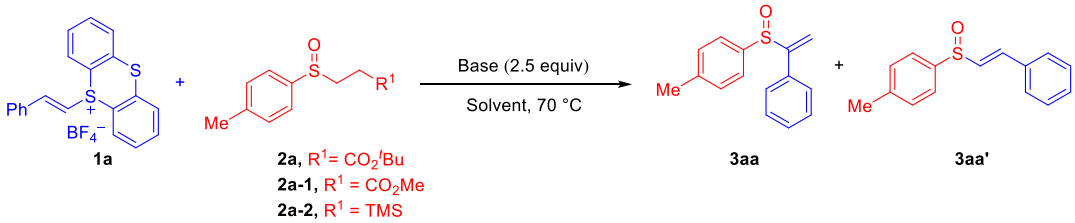
Unless otherwise noted, all reactions were carried out under a argon atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on an Agilent 400 or on a Bruker 400 MHz spectrometer in $CDCl_3$. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (*d* 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Copies of NMR were processed with MestReNova Software.

2. General procedure:



A sealed tube was charged with β-sulfinyl ester (0.5 mmol, 1.0 equiv), alkenylsulfonium salts (1.0 mmol, 2.0 equiv), KOAc (122.67 mg, 1.25 mmol, 2.5 equiv), and 3.0 mL solvent were added sequentially. Degassed solvent and backfilled with argon for 3 times (3 ×1 min) at -78 ºC. The reaction mixture was stirred at 70 °C for 72 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to give the desired product.

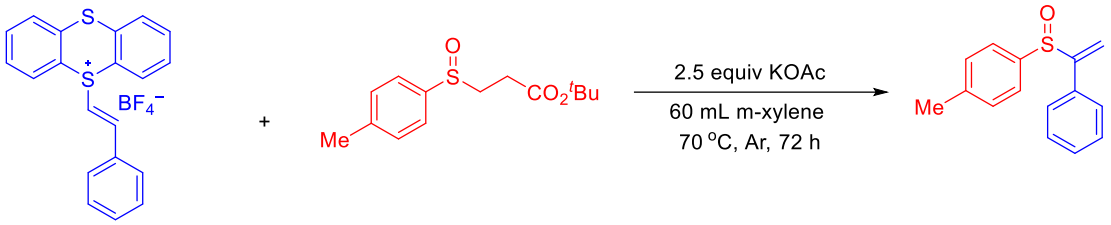
3. Table S1. Optimization of reaction conditions: [a]



Entry	Base	Solvent	Yield of **3aa**(%)[b]	Yield of **3aa'**(%)[b]
1	Na_2CO_3	*m*-Xylene	11	0
2	NaH_2PO_4	*m*-Xylene	trace	0
3	Cs_2CO_3	*m*-Xylene	trace	0
4	CsOAc	*m*-Xylene	28	0
5	KOAc	*m*-Xylene	47	0
6	KO^{t}Bu	*m*-Xylene	0	26
7	NaO^{t}Bu	*m*-Xylene	0	22
8	LiO^{t}Bu	*m*-Xylene	8	11
9	K_3PO_4	*m*-Xylene	7	11
10	Na_3PO_4	*m*-Xylene	11	7
11	KOAc	Toluene	46	0
12	KOAc	MeCN	17	0
13	KOAc	Cyclohexane	51	0
14	KOAc	THF	31	0
15[c]	KOAc	*m*-Xylene	61	0
16[d]	KOAc	*m*-Xylene	65	0
17	-	*m*-Xylene	0	0
18	KOAc	*o*-xylene	41	0
19	KOAc	Mesitylene	45	0
20	KHMDS	*m*-Xylene	0	3
21	Potassium trimethylacetate	*m*-Xylene	16	0
22[e]	KOAc	*m*-Xylene	31	0
23[d,f]	KOAc	*m*-Xylene	59	0
24[d,g]	KOAc	*m*-Xylene	35	0

[a]Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol), and base (0.5 mmol, 2.5 equiv) in solvent (2.0 mL) at 70 °C under argon for 24 h. [b]Isolated yield. [c]In dry *m*-xylene (2.0 mL). [d]**1a** (1 mmol, 2.0 equiv), **2a** (0.5 mmol) and KOAc (1.25 mmol, 2.5 equiv) in dry *m*-xylene (3.0 mL) at 70 °C under argon for 72 h. [e]Under air for 72 h. [f]**2a-1** instead of **2a**. [g]**2a-2** instestd of **2a**.

4. Gram-scale synthesis of 3aa:

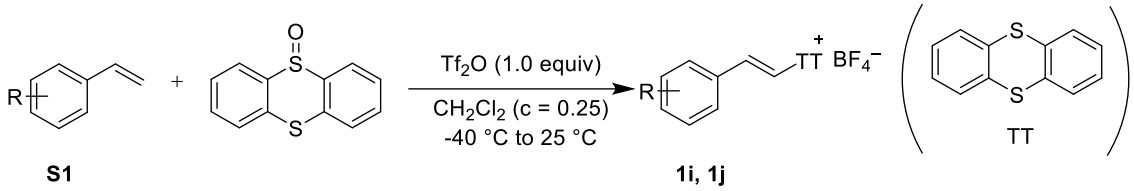


1a **2a** **3aa**

An oven-dried 100 mL Schlenk tube was charged with KOAc (2.4535 g, 25 mmol, 2.5 equiv), **2a** (2.6800 g, 10 mmol), **1a** (8.1250 g, 20 mmol) and dry m-xylene (60.0 mL) were added sequentially. Degassed m-xylene and backfilled with argon for 3 times (3 × 1 min) at -78 °C. The reaction mixture was stirred at 70 °C for 72 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3aa** (1.5500 g, 64% yield).

5. General procedure for preparation of substrates.

The alkenylsulfonium salts **1** were known compounds and synthesized according to the reported literature[1], except for the **1i**, **1j**, which were synthesized as shown below[2].



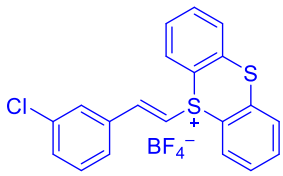
S1 **1i, 1j**

Under ambient atmosphere, a 100 mL Shrek bottle equipped with a magnetic stir bar charged with styrene (1.00 equiv.), CH_2Cl_2 (30 mL), and thianthrene S-oxide (1.1 equiv.). After cooling to -40 ºC, triflic anhydride (1.0 equiv.) was added dropwise. After stirring the lilac mixture at -40 ºC for 30 min following the resulting dark blue mixture was stirred at 25 ºC for another 10 h. After then, the solution was poured into a saturated aqueous $NaHCO_3$ solution. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with aqueous $NaBF_4$ solution (5% w/w). The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2 / MeOH (1:0 gradient to 20:1 (v/v). The product-containing fractions were collected and concentrated under reduced pressure. The residue was further dried in vacuo to afford the corresponding product **1**.

6. Characterization data

6.1 Characterization data for the substrates alkenylsulfonium salts

(E)-5-(3-chlorostyryl)-5H-thianthren-5-ium tetrafluoroborate (1i)



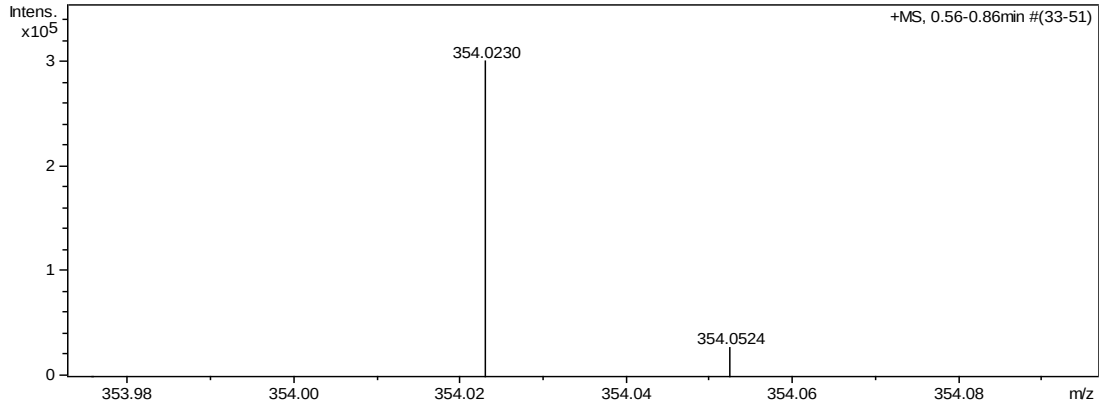
1i

Flash column chromatography on a silica gel (CH_2Cl_2/MeOH = 40/1) give the product (980 mg, 57% yield) as a gray solid.

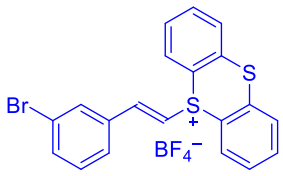
^{1}H NMR ($CDCl_3$, 400MHz) δ 8.34 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 15.2 Hz, 1H), 7.87-7.85 (m, 2H), 7.77-7.74 (m, 2H), 7.66-7.62 (m, 2H), 7.38-7.36 (m, 2H), 7.28-7.20 (m, 2H), 7.10 (d, *J* = 15.2 Hz, 1H):

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 135.7, 134.8, 134.6, 133.6(2C), 131.8, 130.4, 130.2(2C), 128.2, 127.2, 119.9, 108.4.

HRMS Calcd (ESI) m/z for $C_{20}H_{15}ClS_2$ $[M + H]^+$: 354.0293, found:354.0230.



(E)-5-(3-bromostyryl)-5H-thianthren-5-ium tetrafluoroborate (1j)



1j

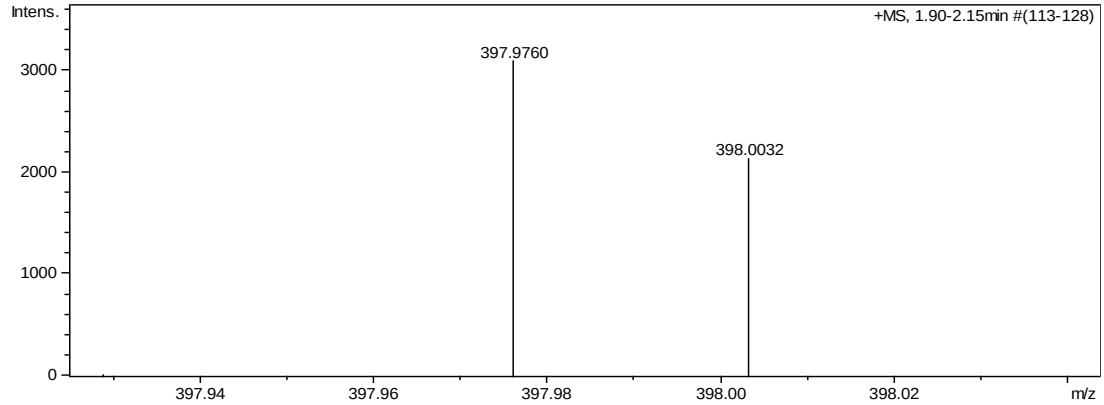
Flash column chromatography on a silica gel (CH_2Cl_2/MeOH = 40/1) give the product (2.8 g, 54% yield) as a gray solid.

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.37-8.35 (m, 2H), 7.93 (d, *J* = 15.2 Hz, 1H), 7.87-7.85 (m, 2H), 7.77-7.74 (m, 2H), 7.67-7.63 (m, 2H), 7.52 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 2H),

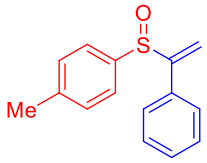
7.19-7.15 (m, 1H), 7.13-7.08 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 135.8, 134.8, 134.6, 133.9, 133.7, 131.1, 130.6, 130.3, 130.2, 127.7, 122.9, 119.9, 108.4.

HRMS Calcd (ESI) m/z for $C_{20}H_{15}BrS_2$ $[M + H]^+$: 397.9788, found: 397.9760.



6.2 Characterization data for the product 1-methyl-4-((1-phenylvinyl)sulfinyl)benzene (3aa)[3]



3aa

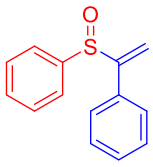
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3aa** (81.1 mg, 65% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.27-7.14 (m, 7H), 7.05 (d, J = 7.2 Hz, 2H), 6.17 (s, 1H), 5.85 (s, 1H), 2.23 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 141.7, 139.4, 133.7, 129.6, 128.9, 128.5, 127.4, 125.4, 116.1, 21.4.

The NMR data are consistent with the reported literature.[3]

(1-(phenylsulfinyl)vinyl)benzene (3ab)[3]



3ab

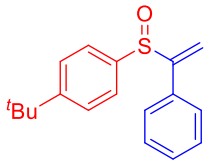
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ab** (66.2 mg, 58% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.41 (m, 2H), 7.34-7.23 (m, 6H), 7.20-7.17 (m, 2H), 6.24 (s, 1H), 5.90 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 142.6, 133.5, 131.0, 129.0, 128.8, 128.4, 127.4, 125.1, 116.2.

The NMR data are consistent with the reported literature.[3]

1-(tert-butyl)-4-((1-phenylvinyl)sulfinyl)benzene (3ac)



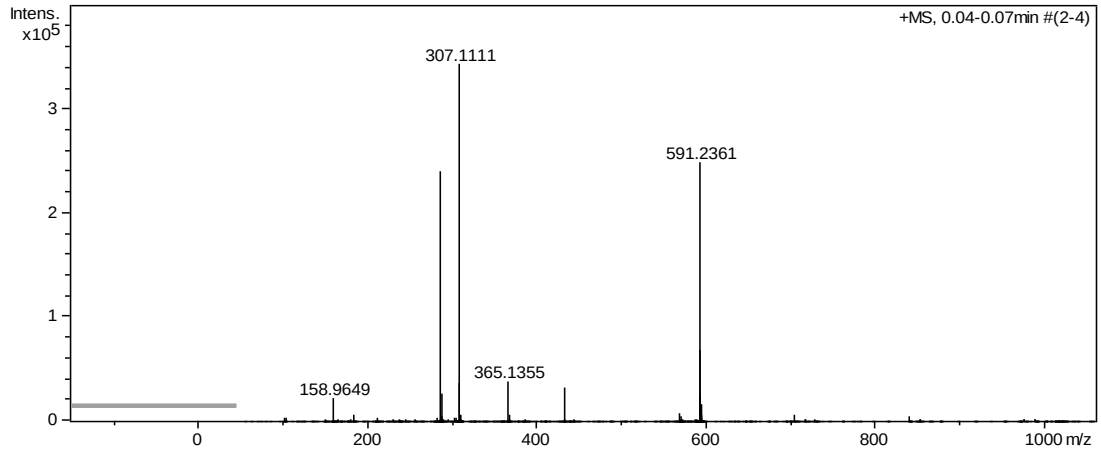
3ac

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **3ac** (90.3 mg, 63% yield) as a brown oil.

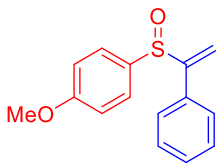
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.32 (m, 4H), 7.28-7.23 (m, 5H), 6.25 (s, 1H), 5.93 (s, 1H), 1.25 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 154.1, 139.3, 133.7, 128.9, 128.5, 127.4, 125.9, 125.1, 116.0, 34.8, 31.0;

HRMS Calcd (ESI) m/z for $C_{18}H_{20}NaOS$ $[M + Na]^+$: 307.1127, found: 307.1111.



1-methoxy-4-((1-phenylvinyl)sulfinyl)benzene (3ad)[3]



3ad

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give

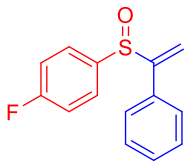
the product **3ad** (62.7 mg, 49% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.27-7.24 (m, 3H), 7.20-7.18 (m, 2H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.25 (s, 1H), 5.93 (s, 1H), 3.75 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 154.1, 133.7, 133.4, 128.8, 128.4, 127.5, 127.2, 115.9, 114.3, 55.3.

The NMR data are consistent with the reported literature.[3]

1-fluoro-4-((1-phenylvinyl)sulfinyl)benzene (3ae)[3]



3ae

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ae** (70.9 mg, 58% yield) as a brown oil.

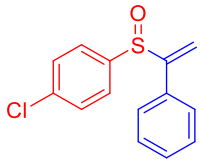
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.40 (m, 2H), 7.30-7.25 (m, 3H), 7.19-7.17 (m, 2H), 6.99 (t, *J* = 8.8 Hz, 2H), 6.24 (s, 1H), 5.91 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.2 (d, *J* = 250.7 Hz), 154.3, 138.2 (d, *J* = 3.1 Hz), 133.4, 129.1, 128.6, 127.5, 127.4, 116.3 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 22.4 Hz);

^{19}F NMR ($CDCl_3$, 376 MHz) δ -108.0.

The NMR data are consistent with the reported literature.[3]

1-chloro-4-((1-phenylvinyl)sulfinyl)benzene(3af)



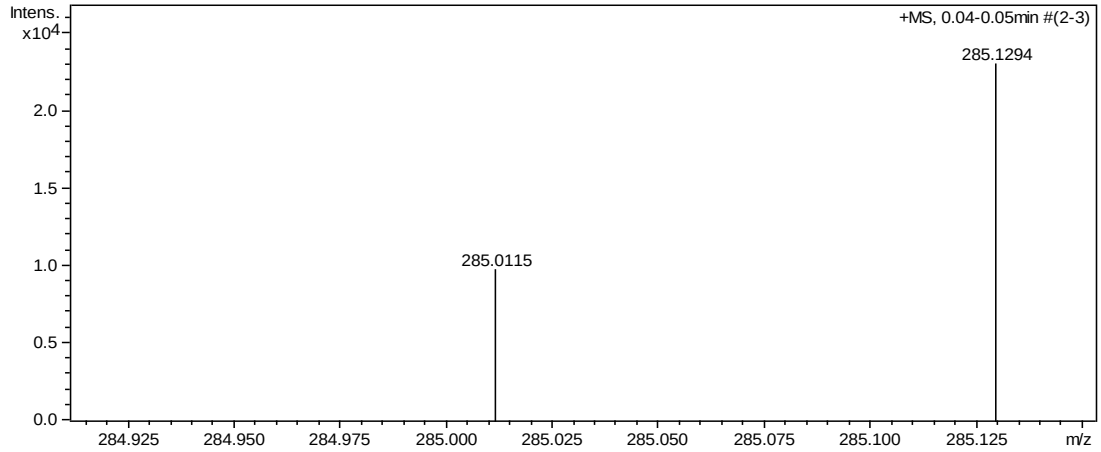
3af

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3af** (48.5 mg, 37% yield) as a brown solid. Mp: 47-50 ℃.

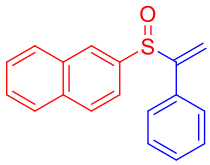
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.27 (m, 7H), 7.20-7.18 (m, 2H), 6.23 (s, 1H), 5.91 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 141.3, 137.2, 133.3, 129.2, 129.1, 128.6, 127.5, 126.4, 116.5;

HRMS Calcd (ESI) m/z for $C_{14}H_{11}ClNaOS$ $[M + Na]^+$: 285.0111, found:285.0115.



2-((1-phenylvinyl)sulfinyl)naphthalene (3ag)[3]



3ag

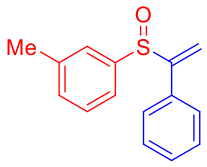
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ag** (69.4 mg, 50% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (s, 1H), 7.78-7.75 (m, 3H), 7.52-7.41 (m, 3H), 7.24-7.20 (m, 5H), 6.32 (s, 1H), 5.95 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 139.6, 134.3, 133.5, 132.4, 129.2, 129.0, 128.5, 128.4, 127.8, 127.7, 127.4, 126.9, 126.3, 120.5, 116.6;

The NMR data are consistent with the reported literature.[3]

1-methyl-3-((1-phenylvinyl)sulfinyl)benzene(3ah)



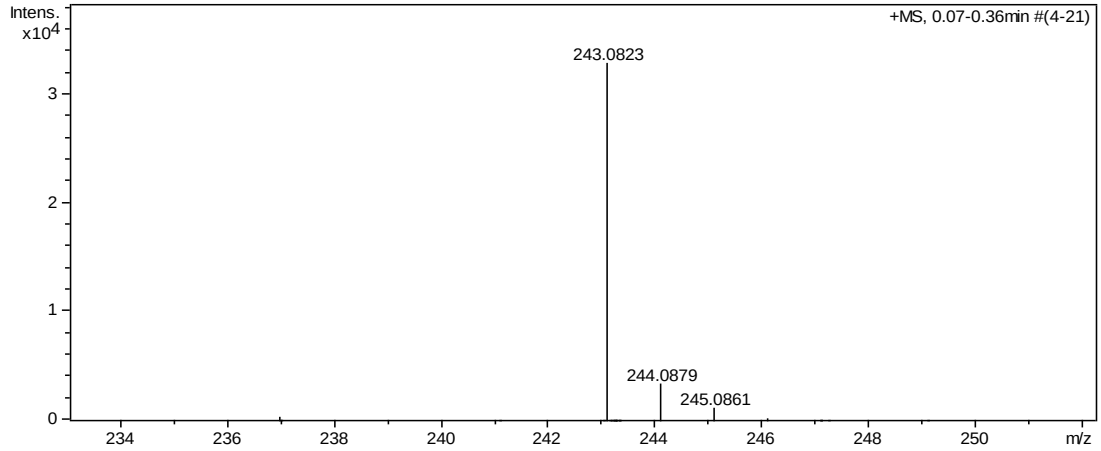
3ah

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 2:13) give the product **3ah** (67.4 mg, 56% yield) as a brown oil.

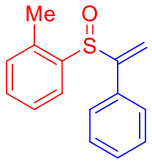
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.24 (m, 4H), 7.20-7.14 (m, 5H), 6.24 (s, 1H), 5.90 (s, 1H), 2.27 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 142.3, 139.0, 133.6, 131.9, 128.9, 128.5, 128.4, 127.5, 125.3, 122.4, 116.2, 21.2;

HRMS Calcd (ESI) m/z for $C_{15}H_{15}OS$ $[M + H]^+$: 243.0838, found: 243.0823.



1-methyl-2-((1-phenylvinyl)sulfinyl)benzene (3ai)[3]



3ai

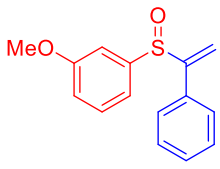
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ai** (35.6 mg, 29% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.66-7.64 (m, 1H), 7.26-7.20 (m, 5H), 7.11-7.09 (m, 2H), 7.02-7.00 (m, 1H), 6.27 (s, 1H), 5.91 (s, 1H), 2.20 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.0, 140.9, 137.2, 133.6, 131.1, 130.4, 128.9, 128.3, 127.7, 127.0, 125.2, 117.3, 18.6;

The NMR data are consistent with the reported literature.[3]

1-methoxy-3-((1-phenylvinyl)sulfinyl)benzene(3aj)



3aj

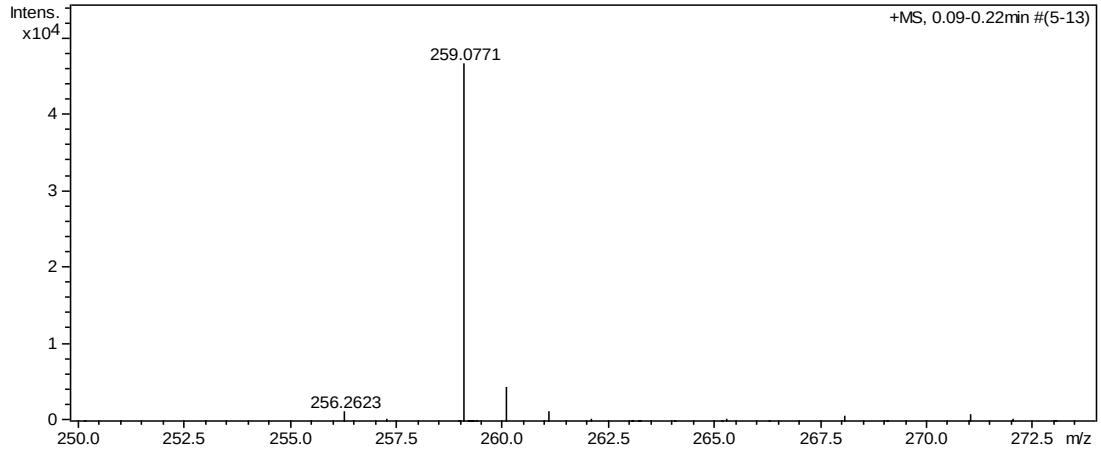
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product **3aj** (75.3 mg, 58% yield) as a brown solid. Mp: 39-41 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.25 (m, 3H), 7.22-7.17 (m, 3H), 6.96-6.93 (m, 2H), 6.88-6.86 (m, 1H), 6.22 (s, 1H), 5.89 (s, 1H), 3.69 (s, 3H);

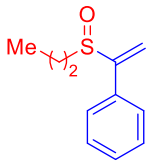
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 154.3, 143.9, 133.6, 129.7, 129.0, 128.5, 127.6,

117.7, 117.3, 116.3, 109.0, 55.3;

HRMS Calcd (ESI) m/z for $C_{15}H_{15}O_2S$ $[M + H]^+$: 259.0787, found: 259.0771.



(1-(propylsulfinyl)vinyl)benzene(3ak)



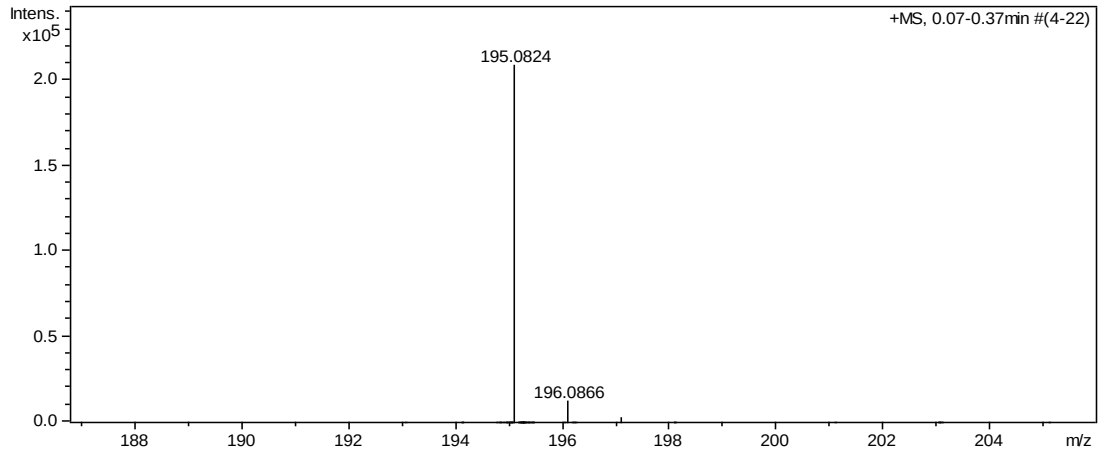
3ak

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ak** (64.6 mg, 66% yield) as a brown oil.

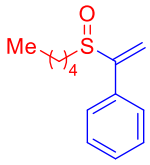
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.33 (m, 5H), 6.01 (s, 1H), 5.97 (s, 1H), 2.60-2.53 (m, 1H), 2.39-2.32 (m, 1H), 1.81-1.72 (m, 1H), 1.68-1.58 (m, 1H), 0.94 (t, J = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 134.0, 129.2, 129.0, 126.5, 116.9, 53.6, 15.2, 13.0;

HRMS Calcd (ESI) m/z for $C_{11}H_{15}OS$ $[M + H]^+$:195.0838 , found: 195.0824.



(1-(pentylsulfinyl)vinyl)benzene(3al)



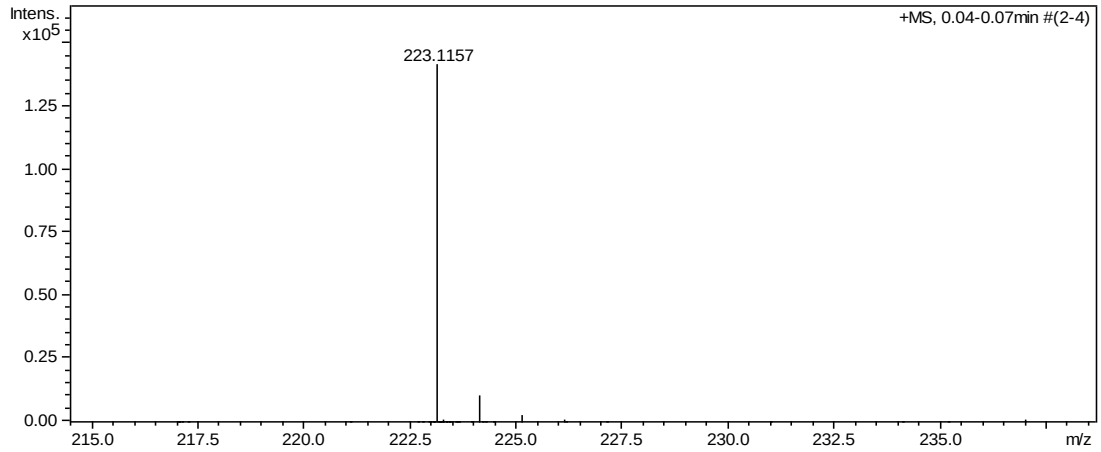
3al

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3al** (63.0 mg, 57% yield) as a brown oil.

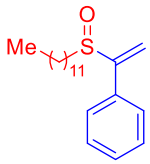
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.35 (m, 5H), 6.00 (s, 1H), 5.97 (s, 1H), 2.63-2.56 (m, 1H), 2.38-2.31 (m, 1H), 1.74-1.69 (m, 1H), 1.60-1.56 (m, 1H), 1.33-1.22 (m, 4H), 0.84-0.80 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.3, 134.0, 129.2, 129.0, 126.5, 117.0, 51.5, 30.5, 22.1, 21.0, 13.7;

HRMS Calcd (ESI) m/z for $C_{13}H_{19}OS$ $[M + H]^+$:223.1151 , found: 223.1157.



(1-(dodecylsulfinyl)vinyl)benzene (3am)[4]



3am

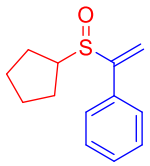
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3am** (100.8 mg, 63% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.34 (m, 5H), 6.01 (s, 1H), 5.97 (s, 1H), 2.64-2.57 (m, 1H), 2.39-2.32 (m, 1H), 1.77-1.68 (m, 1H), 1.61-1.52 (m, 1H), 1.34-1.20 (m, 18H), 0.86 (t, J = 6.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 134.1, 129.2, 129.0, 126.5, 117.0, 51.6, 31.8, 29.5, 29.5, 29.4, 29.2, 29.2, 29.0, 28.4, 22.6, 21.4, 14.0;

The NMR data are consistent with the reported literature.[4]

(1-(cyclopentylsulfinyl)vinyl)benzene (3an)



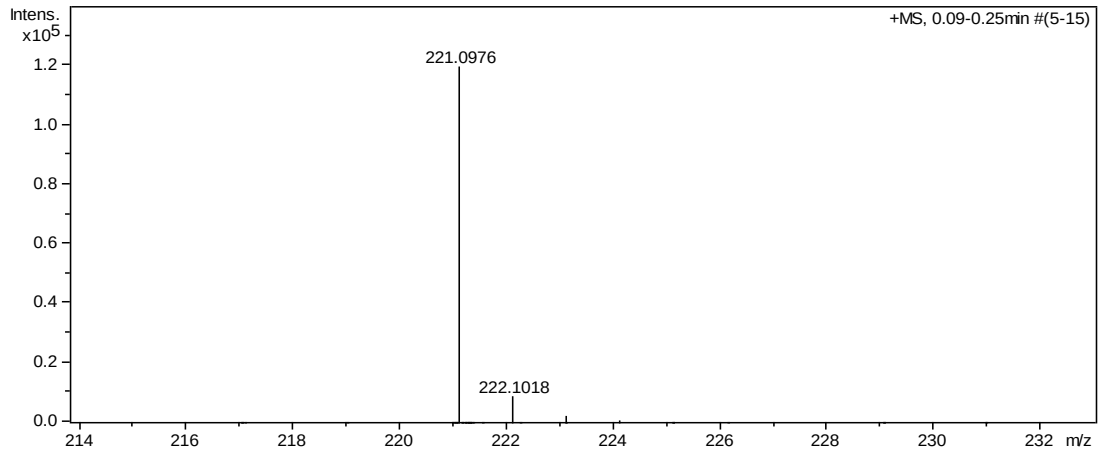
3an

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3an** (45.1 mg, 41% yield) as a brown solid. Mp: 38-42 ℃.

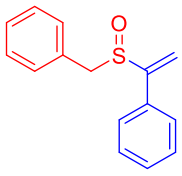
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.34 (m, 5H), 5.95 (s, 1H), 5.93 (s, 1H), 2.75-2.67 (m, 1H), 1.96-1.81 (m, 3H), 1.70-1.62 (m, 2H), 1.54-1.44 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 134.6, 129.0, 128.9, 126.6, 117.5, 57.0, 28.5, 26.6, 25.7, 21.9;

HRMS Calcd (ESI) m/z for $C_{13}H_{17}OS$ $[M + H]^+$: 221.0995, found: 221.0976.



(1-(benzylsulfinyl)vinyl)benzene (3ao)[3]



3ao

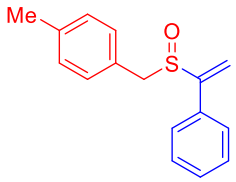
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ao** (75.8 mg, 63% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.39 (m, 5H), 7.31-7.29 (m, 3H), 7.12-7.10 (m, 2H), 5.92 (s, 1H), 5.76 (s, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.58 (d, *J* = 13.2 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 133.9, 130.3, 129.5, 129.3, 129.1, 128.2, 128.1, 126.5, 118.0, 57.7;

The NMR data are consistent with the reported literature.[3]

1-methyl-4-(((1-phenylvinyl)sulfinyl)methyl)benzene (3ap)



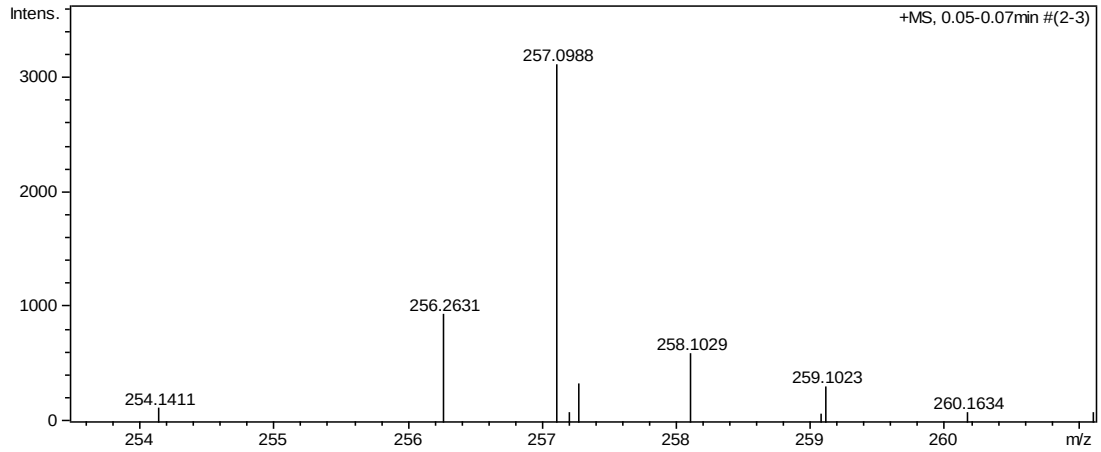
3ap

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ap** (84.1 mg, 66% yield) as a brown oil.

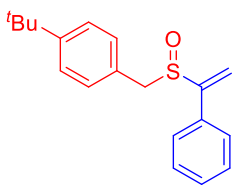
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.39 (s, 5H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 1H), 5.77 (s, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 2.33 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 137.9, 134.0, 130.1, 129.3, 129.1, 128.9, 126.5, 126.3, 117.9, 57.3, 21.1;

HRMS Calcd (ESI) m/z for $C_{16}H_{17}OS$ $[M + H]^+$: 257.0995, found: 257.0988.



1-(tert-butyl)-4-(((1-phenylvinyl)sulfinyl)methyl)benzene (3aq)



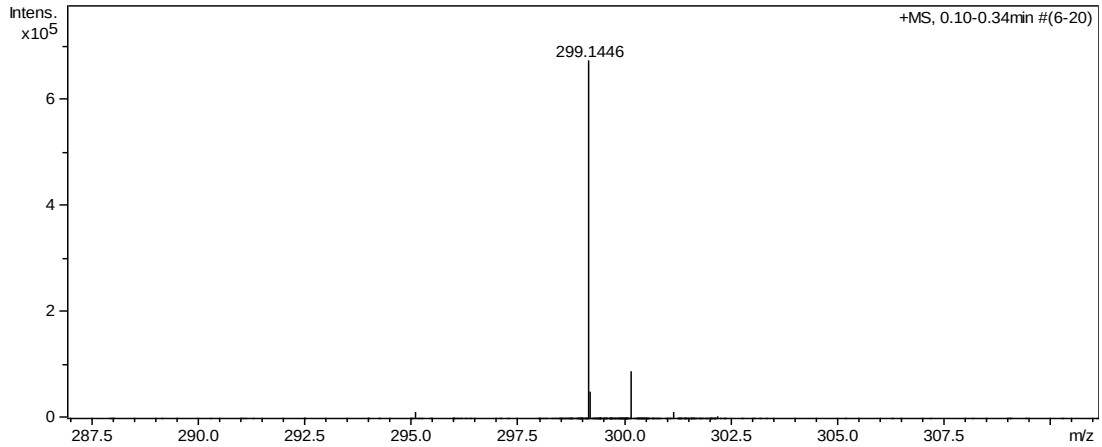
3aq

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3aq** (78.3 mg, 53% yield) as a yellow oil.

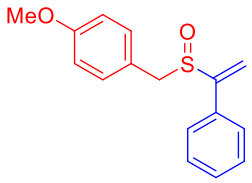
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.40 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 5.83 (s, 1H), 3.93 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 12.8 Hz, 1H), 1.30 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.7, 151.0, 134.1, 129.9, 129.3, 129.1, 126.6, 126.5, 125.3, 117.7, 57.9, 34.5, 31.2;

HRMS Calcd (ESI) m/z for $C_{19}H_{23}OS$ $[M + H]^+$: 299.1464, found: 299.1446.



1-methoxy-4-(((1-phenylvinyl)sulfinyl)methyl)benzene (3ar)[5]



3ar

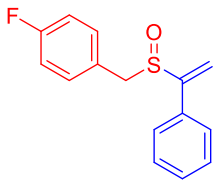
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product **3ar** (67.9 mg, 50% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.40 (m, 5H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.91 (s, 1H), 5.73 (s, 1H), 3.92 (d, *J* = 13.6 Hz, 1H), 3.78 (s, 3H), 3.52 (d, *J* = 13.2 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.4, 151.1, 134.0, 131.4, 129.3, 129.1, 126.4, 121.2, 118.0, 113.6, 56.8, 55.1;

The NMR data are consistent with the reported literature.[5]

1-fluoro-4-(((1-phenylvinyl)sulfinyl)methyl)benzene (3as)



3as

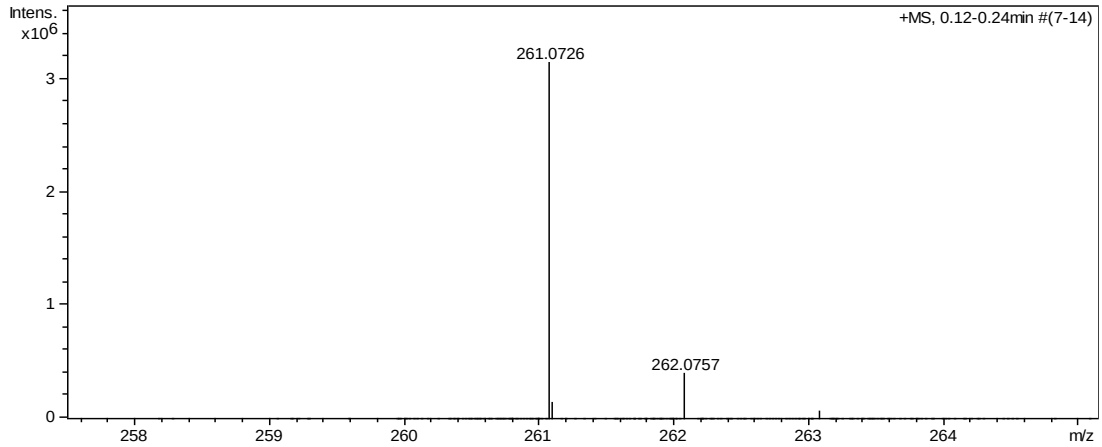
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3as** (74.3 mg, 57% yield) as a yellow solid. Mp: 82-85 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45-7.38 (m, 5H), 7.07-7.03 (m, 2H), 7.01-6.96 (m, 2H), 5.91 (s, 1H), 5.70 (s, 1H), 3.94 (d, *J* = 13.6 Hz, 1H), 3.53 (d, *J* = 13.2 Hz, 1H);

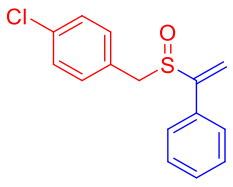
^{13}C NMR (CDCl3, 100 MHz) δ 162.7 (d, *J* = 246.0 Hz), 150.9, 133.8, 132.0 (d, *J* = 8.2 Hz), 129.4, 129.2, 126.4, 125.0 (d, *J* = 3.1 Hz), 118.2 (d, *J* = 2.4 Hz), 115.2 (d, *J* = 21.5 Hz), 56.3;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -113.6;

HRMS Calcd (ESI) m/z for $C_{15}H_{14}FOS$ $[M + H]^+$: 261.0744, found: 261.0726.



1-chloro-4-(((1-phenylvinyl)sulfinyl)methyl)benzene (3at)



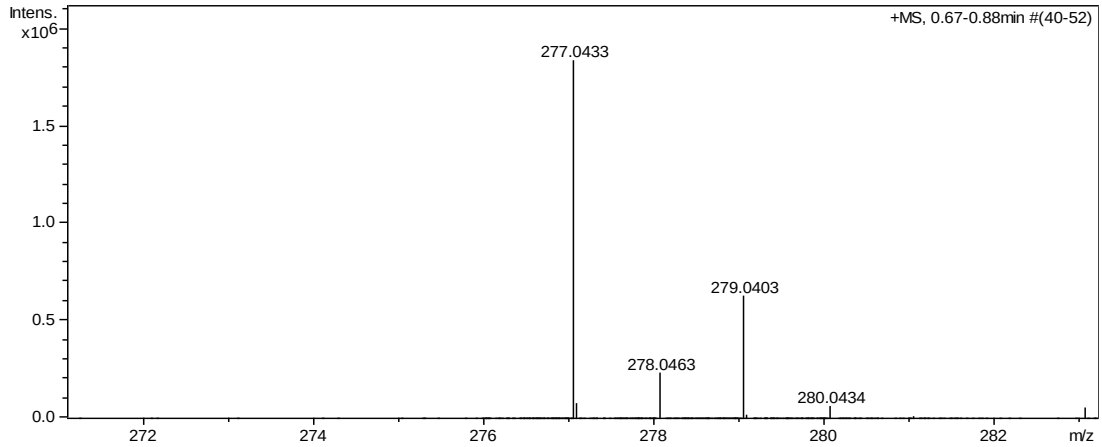
3at

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product **3at** (70.7 mg, 51% yield) as a yellow solid. Mp: 91-95 ℃.

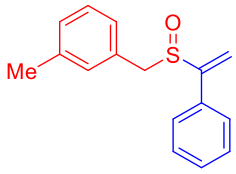
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.30 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.84 (s, 1H), 5.63 (s, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 13.2 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8, 134.2, 133.7, 131.6, 129.5, 129.2, 128.4, 127.7, 126.4, 118.3, 56.3;

HRMS Calcd (ESI) m/z for $C_{15}H_{14}ClOS$ $[M + H]^+$: 277.0448, found: 277.0433.



1-methyl-3-(((1-phenylvinyl)sulfinyl)methyl)benzene (3au)



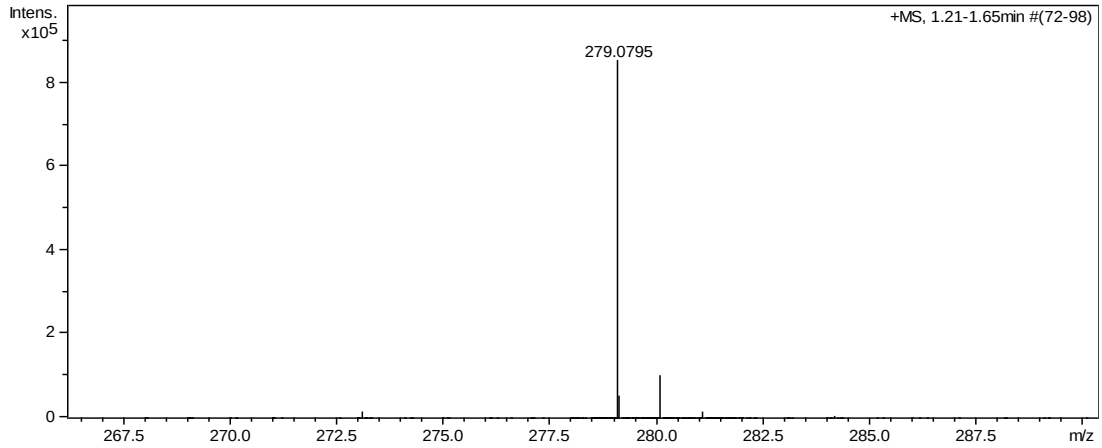
3au

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 2: 11) give the product **3au** (61.7 mg, 48% yield) as a yellow oil.

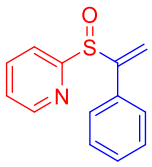
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.39 (s, 5H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 6.4 Hz, 2H), 5.94 (s, 1H), 5.83 (s, 1H), 3.93 (d, *J* = 13.2 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 2.32 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.6, 137.8, 134.0, 130.9, 129.5, 129.3, 129.0, 128.8, 128.1, 127.2, 126.5, 117.8, 58.1, 21.2;

HRMS Calcd (ESI) m/z for $C_{16}H_{16}NaOS$ $[M + Na]^+$: 279.0814, found: 279.0795.



2-((1-phenylvinyl)sulfinyl)pyridine(3av)



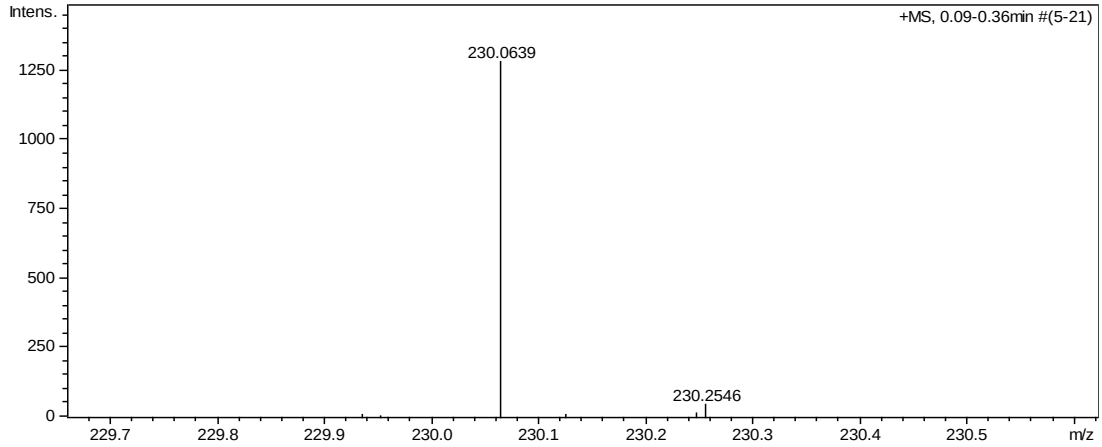
3av

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 2: 11) give the product **3av** (37.6 mg, 33% yield) as a brown solid. Mp: 44-47 ℃.

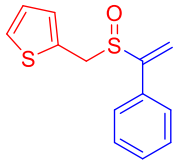
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65-8.64 (m, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.79-7.75 (m, 1H), 7.42-7.38 (m, 1H), 7.35-7.33 (m, 2H), 7.28-7.19 (m, 3H), 6.78 (s, 1H), 6.16 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6, 150.2, 148.3, 137.8, 132.1, 129.2, 128.9, 128.4, 128.2, 127.0, 123.3;

HRMS Calcd (ESI) m/z for $C_{13}H_{12}NOS$ $[M + H]^+$: 230.0634, found: 230.0639.



2-(((1-phenylvinyl)sulfinyl)methyl)thiophene (3aw)



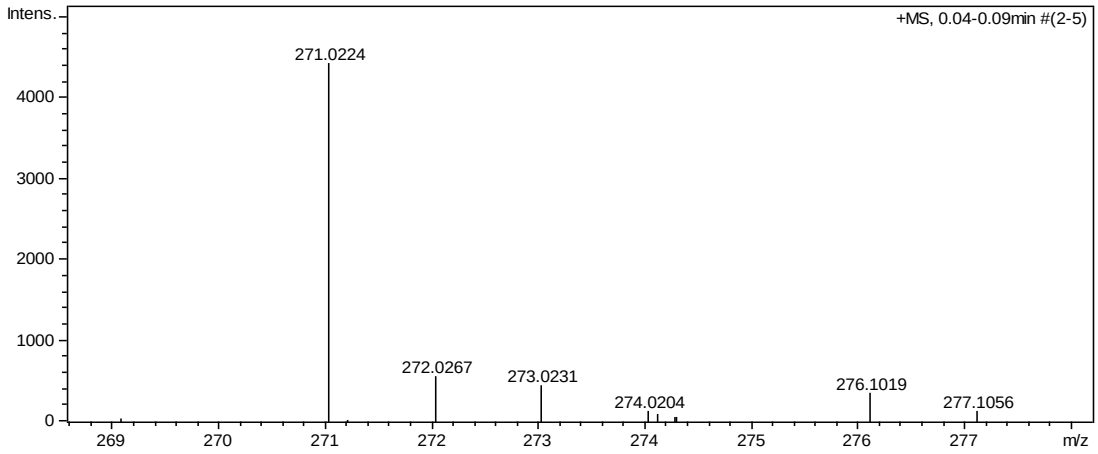
3aw

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product 3aw (75.0 mg, 60% yield) as a brown oil.

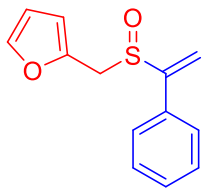
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.37 (m, 5H), 7.25 (d, *J* = 4.8 Hz, 1H), 6.98 (t, *J* = 3.6 Hz, 1H), 6.86 (d, *J* = 2.8 Hz, 1H), 5.93 (s, 1H), 5.79 (s, 1H), 4.16 (d, *J* = 14.0 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8, 133.6, 129.5, 129.4, 129.1, 129.0, 126.9, 126.6, 126.4, 118.5, 51.8;

HRMS Calcd (ESI) m/z for $C_{13}H_{12}NaOS_2$ $[M + Na]^+$: 271.0222, found: 271.0224.



2-(((1-phenylvinyl)sulfinyl)methyl)furan (3ax)



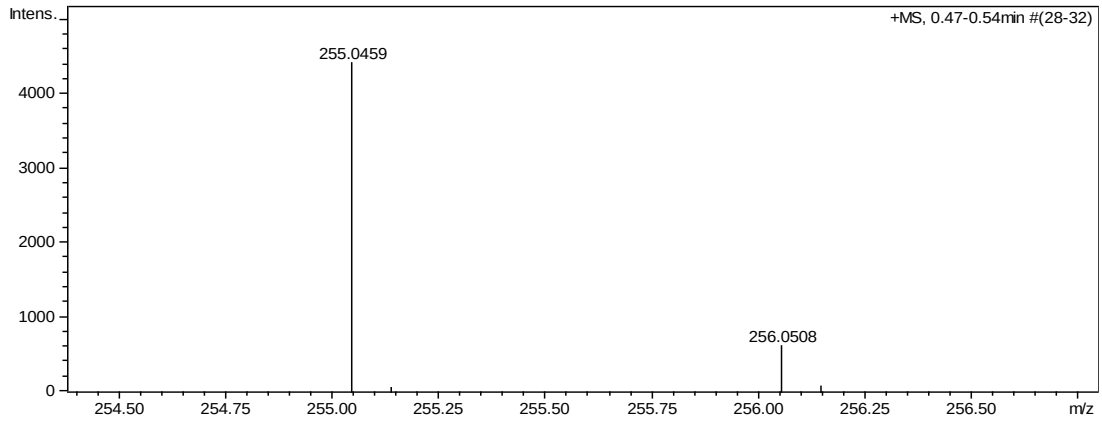
3ax

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ax** (59.4 mg, 51% yield) as a brown oil.

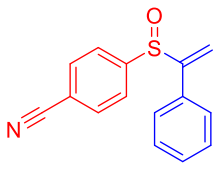
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.39 (s, 5H), 7.36 (s, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 5.95 (s, 1H), 5.89 (s, 1H), 4.00 (d, *J* = 14.0 Hz, 1H), 3.71 (d, *J* = 14.0 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 143,8, 143.4, 133.7, 129.4, 129.1, 126.7, 118.0, 111.5, 110.9, 51.2;

HRMS Calcd (ESI) m/z for $C_{13}H_{12}NaO_2S$ $[M + Na]^+$: 255.0450, found: 255.0459.



4-((1-phenylvinyl)sulfinyl)benzonitrile (3ay)



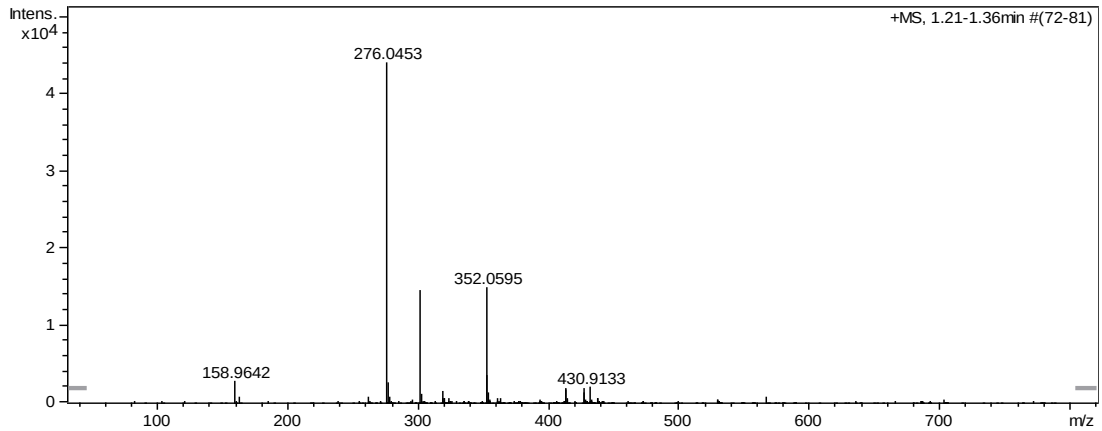
3ay

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:5) give the product **3ay** (38.3 mg, 30% yield) as a yellow oil.

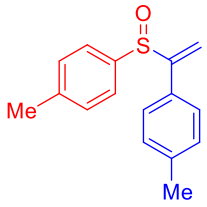
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.56 (m, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.36-7.31 (m, 3H), 7.19-7.17 (m, 2H), 6.21 (s, 1H), 5.91 (s, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 148.5, 132.8, 132.4, 129.6, 128.8, 127.6, 125.1, 117.7, 117.2, 114.6;

HRMS Calcd (ESI) m/z for $C_{15}H_{11}NNaOS$ $[M + Na]^+$: 276.0454, found: 276.0453.



1-methyl-4-((1-(p-tolyl)vinyl)sulfinyl)benzene (3ba)



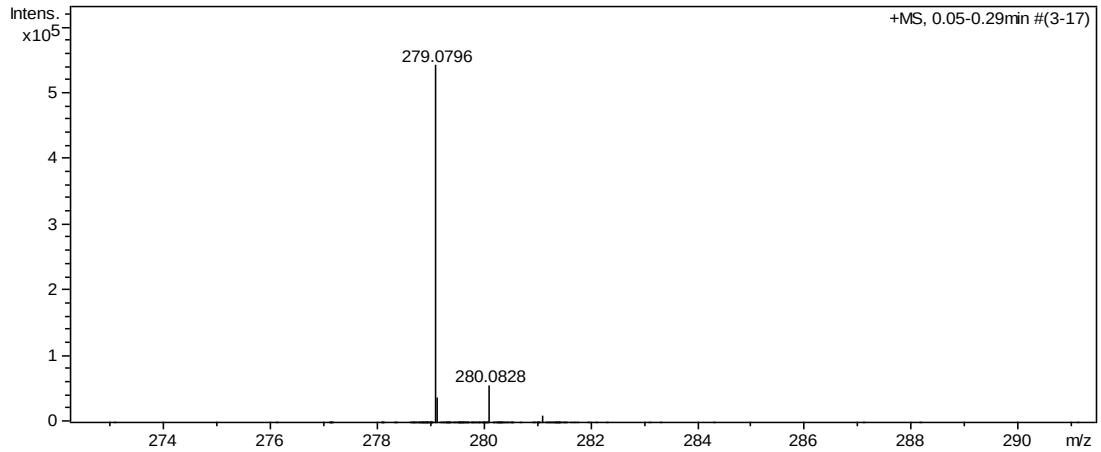
3ba

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ba** (74.9 mg, 58% yield) as a brown solid. Mp: 76-79 ℃.

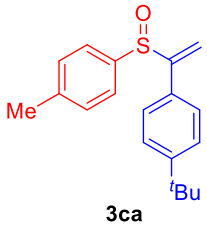
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.33 (m, 2H), 7.12-7.05 (m, 6H), 6.20 (s, 1H), 5.88 (s, 1H), 2.92 (s, 3H*2);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.1, 141.5, 139.6, 138.9, 130.8, 129.6, 129.2, 127.2, 125.4, 115.4, 21.3, 21.2;

HRMS Calcd (ESI) m/z for $C_{16}H_{16}NaOS$ $[M + Na]^+$: 279.0814, found: 279.0796.



1-(tert-butyl)-4-(1-(p-tolylsulfinyl)vinyl)benzene (3ca)



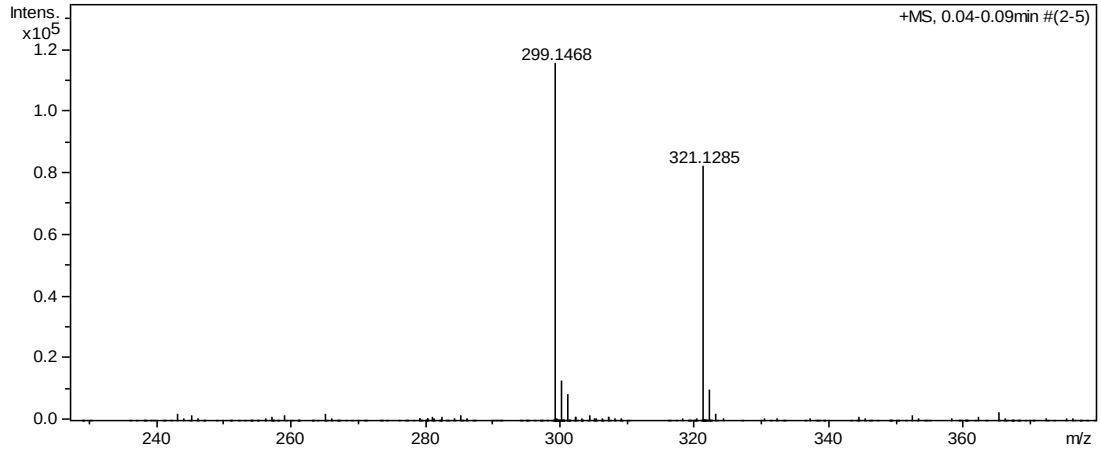
3ca

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ca** (71.8 mg, 48% yield) as a yellow oil.

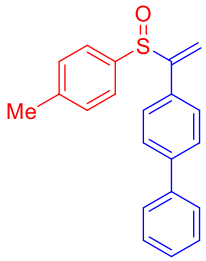
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.16-7.11 (m, 4H), 6.21 (s, 1H), 5.90 (s, 1H), 2.30 (s, 3H), 1.27 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.9, 152.1, 141.5, 139.6, 130.6, 129.6, 127.0, 125.4, 125.4, 115.5, 34.5, 31.1, 21.3;

HRMS Calcd (ESI) m/z for $C_{19}H_{22}NaOS$ $[M + Na]^+$: 321.1284, found: 321.1285.



4-(1-(p-tolylsulfinyl)vinyl)-1,1'-biphenyl (3da)[3]



3da

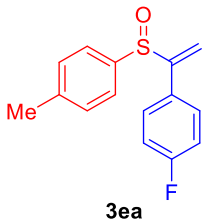
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3da** (92.5 mg, 58% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.50 (m, 4H), 7.43-7.39 (m, 4H), 7.35-7.29 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.30 (s, 1H), 5.98 (s, 1H), 2.29 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.9, 141.7, 141.7, 140.0, 139.4, 132.6, 129.7, 128.8, 127.8, 127.7, 127.1, 126.9, 125.5, 116.1, 21.4;

The NMR data are consistent with the reported literature.[3]

1-fluoro-4-(1-(p-tolylsulfinyl)vinyl)benzene (3ea)



3ea

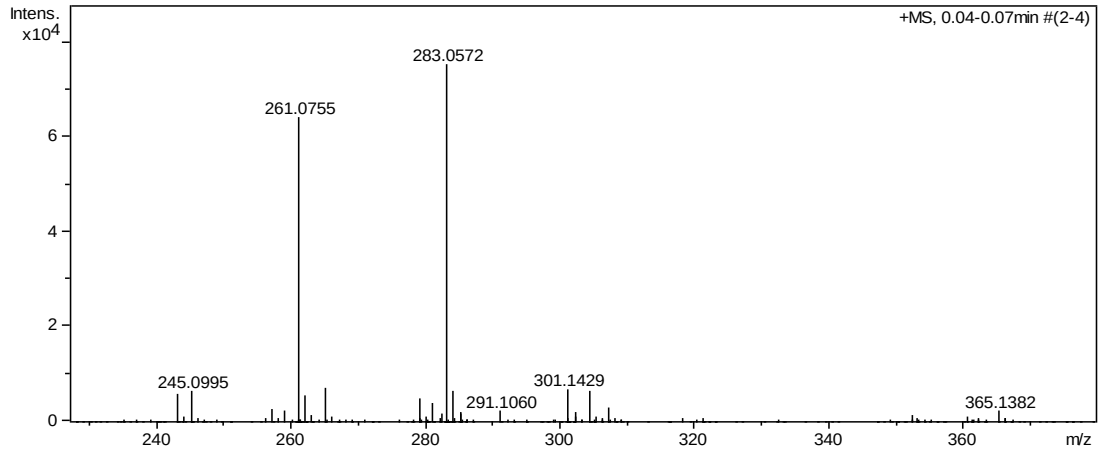
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 2: 11) give the product **3ea** (60.1 mg, 46% yield) as a yellow solid. Mp: 37-41 ℃.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.17-7.11 (m, 4H), 6.97-6.92 (m, 2H), 6.23 (s, 1H), 5.87 (s, 1H), 2.30 (s, 3H);

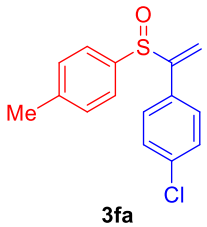
^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0 (d, *J* = 248.0 Hz), 153.4, 141.8, 139.1, 129.7 (d, *J* = 23.4 Hz), 129.7, 129.3 (d, *J* = 8.2 Hz), 125.3, 116.6, 115.6 (d, *J* = 21.6 Hz), 21.3;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.8;

HRMS Calcd (ESI) m/z for $C_{15}H_{13}FNaOS$ $[M + Na]^+$: 283.0563, found: 283.0572.



1-chloro-4-(1-(p-tolylsulfinyl)vinyl)benzene (3fa)



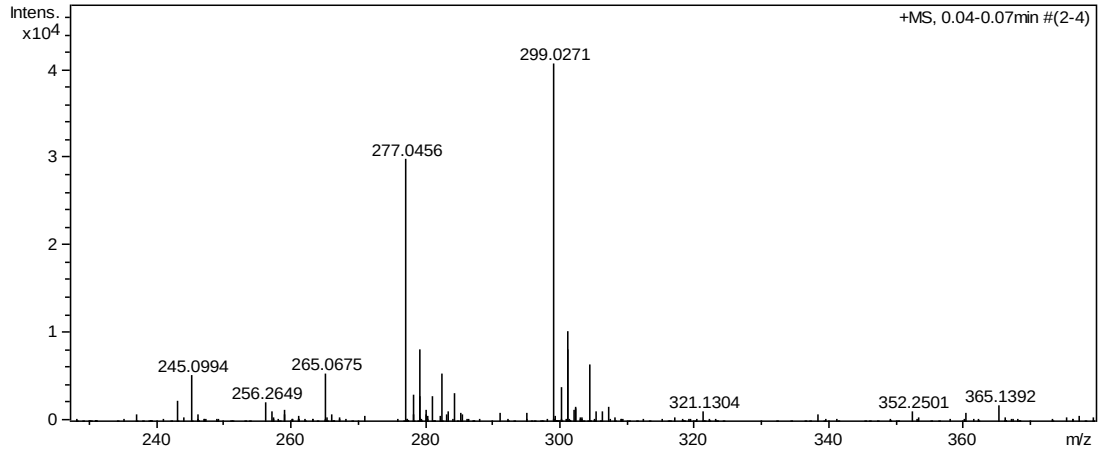
3fa

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3fa** (78.8 mg, 57% yield) as a yellow solid. Mp: 53-57 ℃.

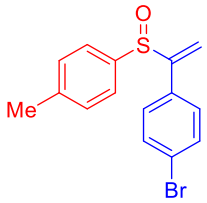
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.23-7.20 (m, 2H), 7.13-7.11 (m, 4H), 6.25 (s, 1H), 5.90 (s, 1H), 2.30 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 141.9, 139.0, 135.0, 132.1, 129,7, 128.7, 128.7, 125.3, 117.0, 21.3;

HRMS Calcd (ESI) m/z for $C_{15}H_{13}ClNaOS$ $[M + Na]^+$: 299.0268, found: 299.0271.



1-bromo-4-(1-(p-tolylsulfinyl)vinyl)benzene (3ga)[3]



3ga

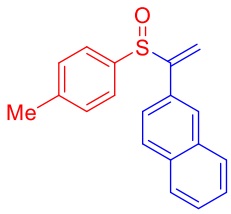
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ga** (77.7 mg, 48% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.25 (s, 1H), 5.91 (s, 1H), 2.30 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 141.9, 139.0, 132.6, 131.7, 129.7, 128.9, 125.3, 123.2, 117.0, 21.3;

The NMR data are consistent with the reported literature.[3]

2-(1-(p-tolylsulfinyl)vinyl)naphthalene (3ha)



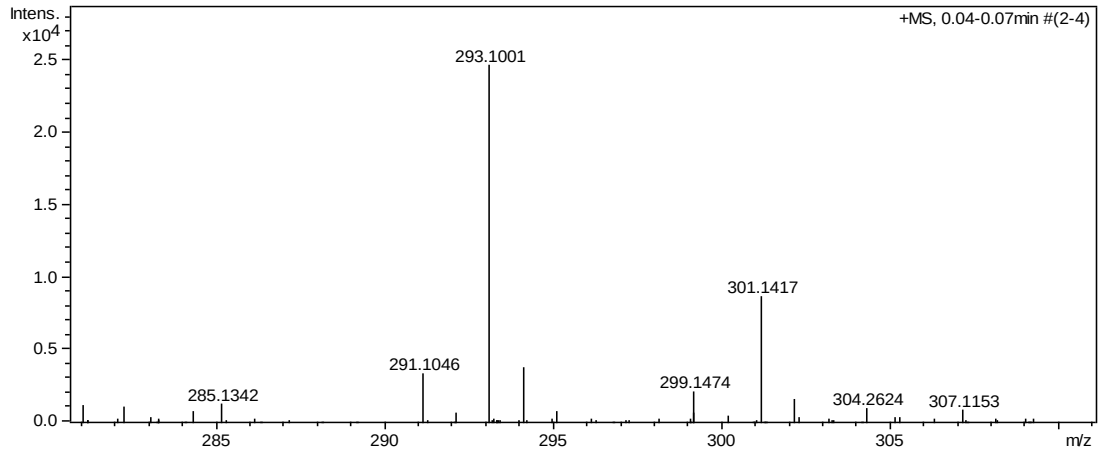
3ha

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3ha** (32.8 mg, 22% yield) as a brown oil.

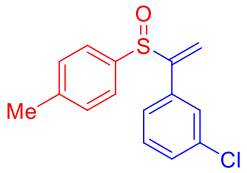
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80-7.73 (m, 4H), 7.50-7.47 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 6.05 (s, 1H), 2.26 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.1, 141.7, 139.4, 133.2, 132.8, 131.2, 129.7, 128.4, 128.2, 127.6, 126.7, 126.6 (2C), 125.4, 124.9, 116.5, 21.3;

HRMS Calcd (ESI) m/z for $C_{19}H_{17}OS$ $[M + H]^+$: 293.0995, found: 293.1001.



1-chloro-3-(1-(p-tolylsulfinyl)vinyl)benzene (3ia)



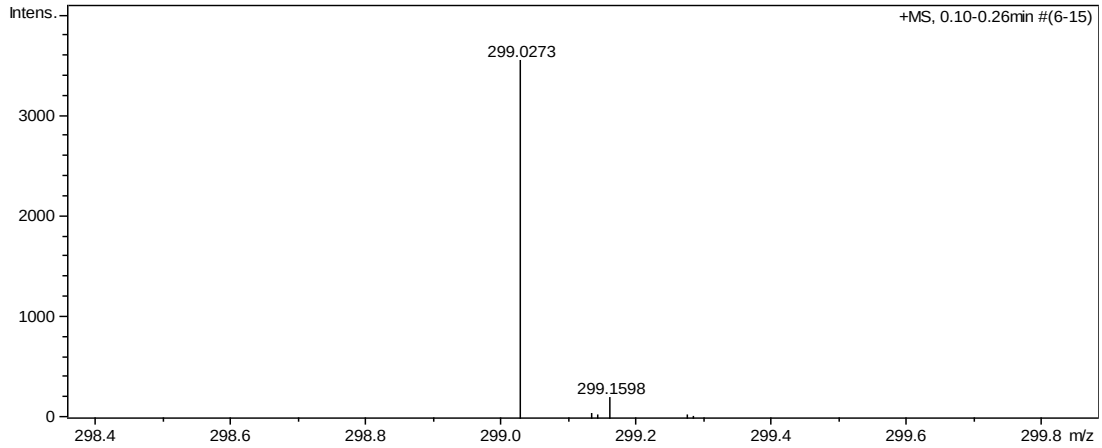
3ia

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ia** (80.6 mg, 58% yield) as a yellow solid. Mp: 47-50 ℃.

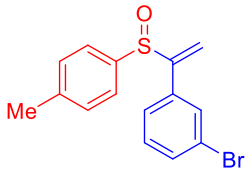
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.25-7.22 (m, 1H), 7.20-7.16 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09-7.07 (m, 1H), 6.26 (s, 1H), 5.92 (s, 1H), 2.30 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 141.9, 138.9, 135.4, 134.4, 129.7, 129.0, 127.4, 125.5, 125.3(2C), 117.3, 21.3;

HRMS Calcd (ESI) m/z for $C_{15}H_{13}ClNaOS$ $[M + Na]^+$: 299.0268, found: 299.0273.



1-bromo-3-(1-(p-tolylsulfinyl)vinyl)benzene (3ja)



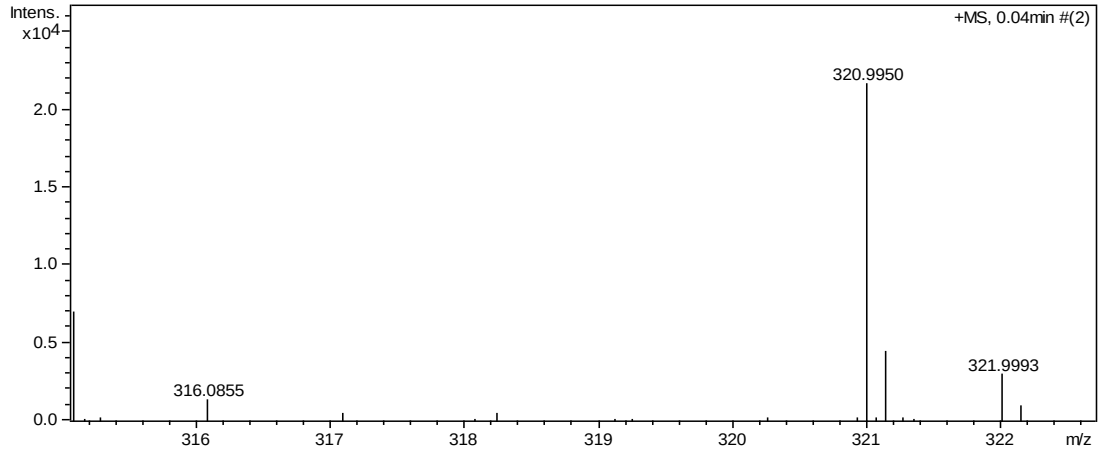
3ja

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ja** (97.1 mg, 60% yield) as a yellow oil.

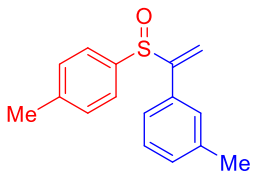
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.35 (m, 1H), 7.32-7.30 (m, 3H), 7.12-7.11 (m, 4H), 6.25 (s, 1H), 5.90 (s, 1H), 2.28 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 141.9, 138.8, 135.6, 131.9, 130.2, 129.9, 129.7, 125.9, 125.3, 122.4, 117.3, 21.3;

HRMS Calcd (ESI) m/z for $C_{15}H_{14}BrOS$ $[M + H]^+$: 320.9943, found: 320.9950.



1-methyl-3-(1-(p-tolylsulfinyl)vinyl)benzene(3ka)



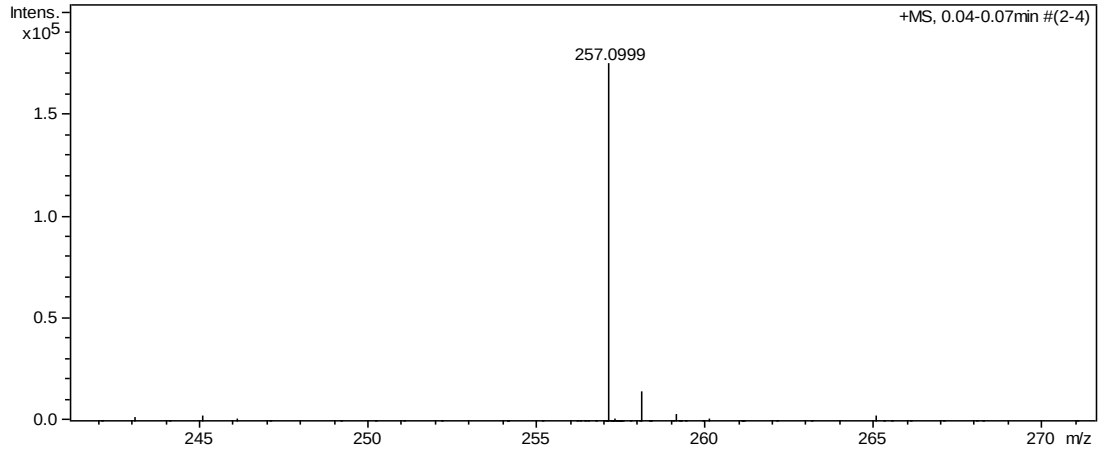
3ka

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3ka** (49.3 mg, 39% yield) as a brown oil.

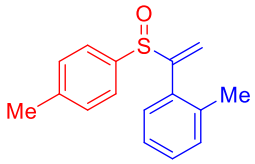
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.16-7.07 (m, 4H), 7.02-6.98 (m, 2H), 6.21 (s, 1H), 5.89 (s, 1H), 2.29 (s, 3H), 2.27 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 141.5, 139.4, 138.2, 133.6, 129.7, 129.5, 128.3, 127.9, 125.3, 124.4, 115.7, 21.3, 21.2;

HRMS Calcd (ESI) m/z for $C_{16}H_{17}OS$ $[M + H]^+$: 257.0995, found: 257.0999.



1-methyl-2-(1-(p-tolylsulfinyl)vinyl)benzene (3la)



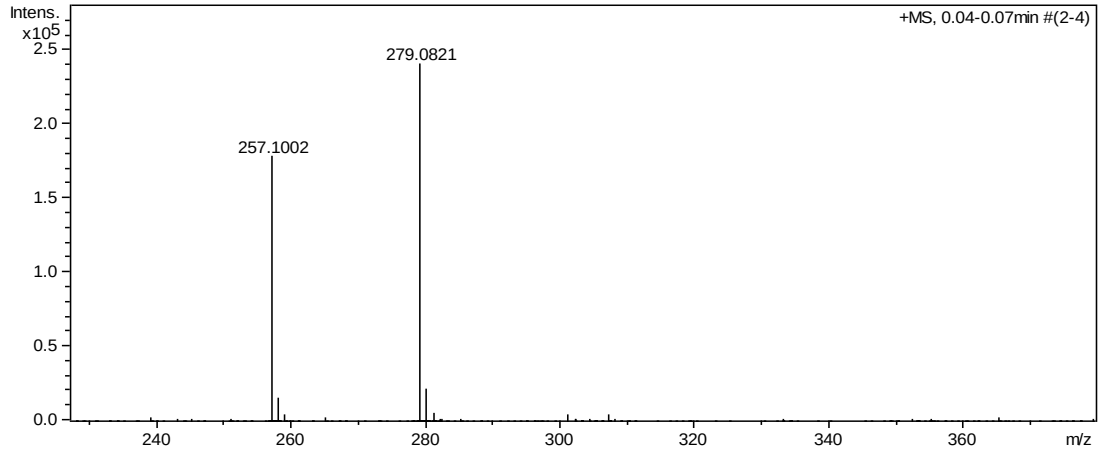
3la

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product **3la** (37.9 mg, 30% yield) as a yellow oil.

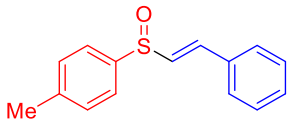
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21-7.15 (m, 3H), 7.10-7.04 (m, 4H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 5.68 (s, 1H), 2.33 (s, 3H), 1.94 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 141.5, 138.7, 137.0, 132.4, 130.1, 129.9, 129.3, 128.8, 125.3, 124.9, 116.7, 21.4, 19.2;

HRMS Calcd (ESI) m/z for $C_{16}H_{16}NaOS$ $[M + Na]^+$: 279.0814, found: 279.0821.



(E)-1-methyl-4-(styrylsulfinyl)benzene (3aa')[5]



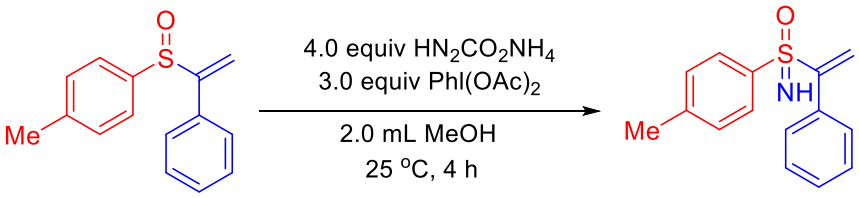
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3aa'** as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.46-7.44 (m, 2H), 7.38-7.31 (m, 6H), 6.81 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.7, 140.7, 136.0, 133.8, 133.0, 130.1, 129.7, 128.9, 127.7, 124.9, 21.4;

The NMR data are consistent with the reported literature.[5]

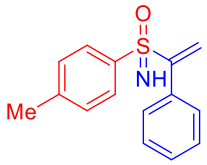
7. Experimental procedure for synthesis of 4



3aa **4**

A sealed tube was charged with product **3aa** (0.3 mmol, 1.0 equiv), methanol (2.0 mL), $PhI(OAc)_2$ (0.9 mmol, 3.0 equiv) and ammonium carbamate (1.2 mmol, 4.0 equiv). The reaction mixture was stirred at 25 °C for 4 h. Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **4** (53.2 mg, 69% yield) as a yellow oil.

imino(1-phenylvinyl)(p-tolyl)-l6-sulfanone(4) [6]



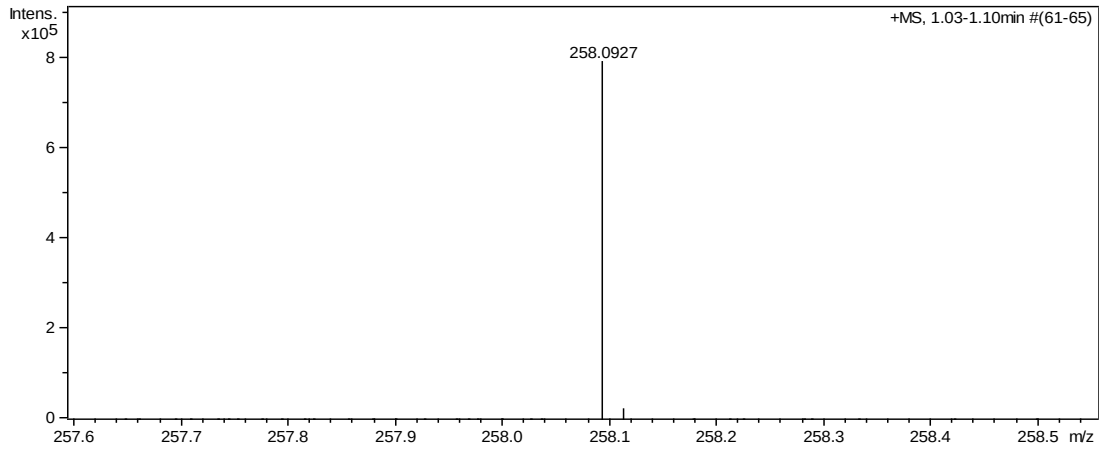
4

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **4** (53.2 mg, 69% yield) as a yellow oil.

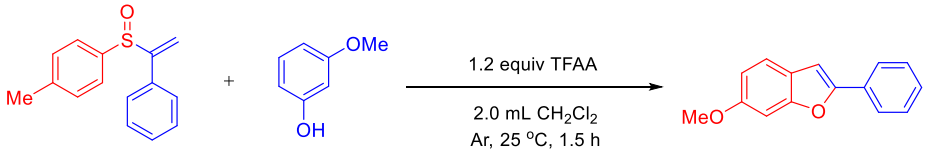
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.25-7.12 (m, 7H), 6.46 (s, 1H), 5.76 (s, 1H), 2.85 (s, 1H), 2.31 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 143.6, 136.8, 133.4, 129.3 (2C), 128.9, 128.7, 128.0, 124.2, 21.5;

HRMS Calcd (ESI) m/z for $C_{15}H_{15}NOS$ $[M + H]^+$: 258.0947, found: 258.0927.



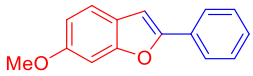
8. Experimental procedure for synthesis of 5.



3aa **5**

A sealed tube was charged with product **3aa** (0.3 mmol, 1.0 equiv), 3-methoxyphenol (0.36 mmol, 1.2 equiv), dry DCM (2.0 mL), and TFAA (0.36 mmol, 1.2 equiv). The reaction mixture was stirred at 25 °C for 1.5 h. Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **5** (38.6 mg, 57% yield) as a yellow solid.

6-methoxy-2-phenylbenzofuran (5)[7]



5

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 0:1) give the product **5** (38.6 mg 57% yield) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85-7.83 (m, 2H), 7.47-7.43 (m, 3H), 7.34 (t, *J*= 7.2 Hz, 1H), 7.10 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 0.8 Hz, 1H), 6.90 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 3.89 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 155.9, 155.1, 130.7, 128.7, 128.0, 124.4, 122.5, 121.0, 111.9, 101.1, 95.8, 55.7;

The NMR data are consistent with the reported literature.[7]

9. References:

[1] J. Zhu, Y. Ye and Y. Huang, Palladacycle-Catalyzed Olefinic C–P Cross-Coupling of Alkenylsulfonium Salts with Diarylphosphines to Access Alkenylphosphines. *Organometallics*, 2022, **41**, 2342–2348.

[2] R. Xie, J. Zhu and Y. Huang, Cu-Catalyzed highly selective silylation and borylation of alkenylsulfonium salts†. *Org. Chem. Front.*, 2021, **8**, 5699-5704.

[3] A. V. Kalyanakrishnan, A. Joshy, A. K. Arya and A. Kaliyamoorthy, Synthesis of Various α-Substituted Alkenyl Sulfoxides from Alkynes and β-Sulfinyl Esters. *ChemistrySelect*, 2021, **6**, 14054-14059.

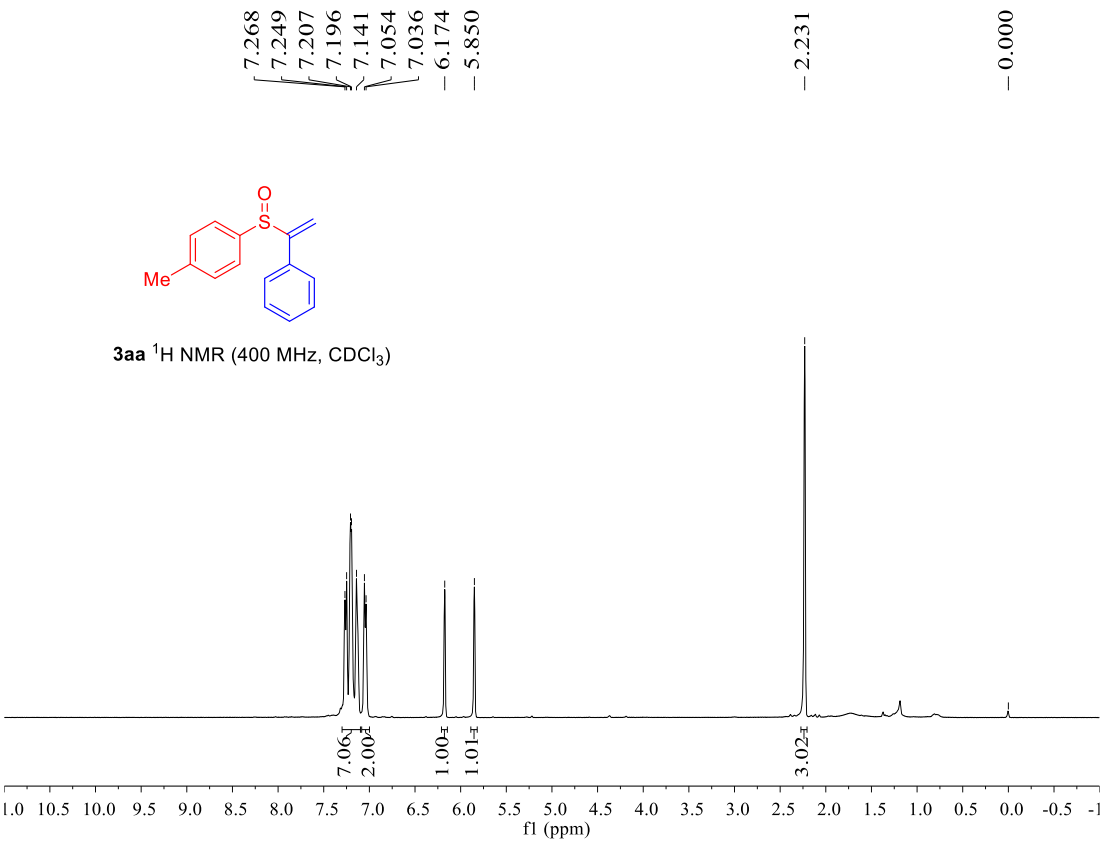
[4] M. Hori, T. Yanagi, K. Murakami, K. Nogi and H. Yorimistu, Annulative Synthesis of Benzofurans from General Alkenyl Sulfoxides and Phenols via Pummerer/Sigmatropic Cascade. *Bull. Chem. Soc. Jpn.*, 2019, **92**, 302-311.

[5] Y. Zhao, X. Guo, S. Li, Y. Fan, X. Sun and L. Tian, $PhB(OH)_2$-Promoted Electrochemical Sulfuration–Formyloxylation of Styrenes and Selectfluor-Mediated Oxidation–Olefination. *Org. Lett*., 2021, **23**, 9140-9145.

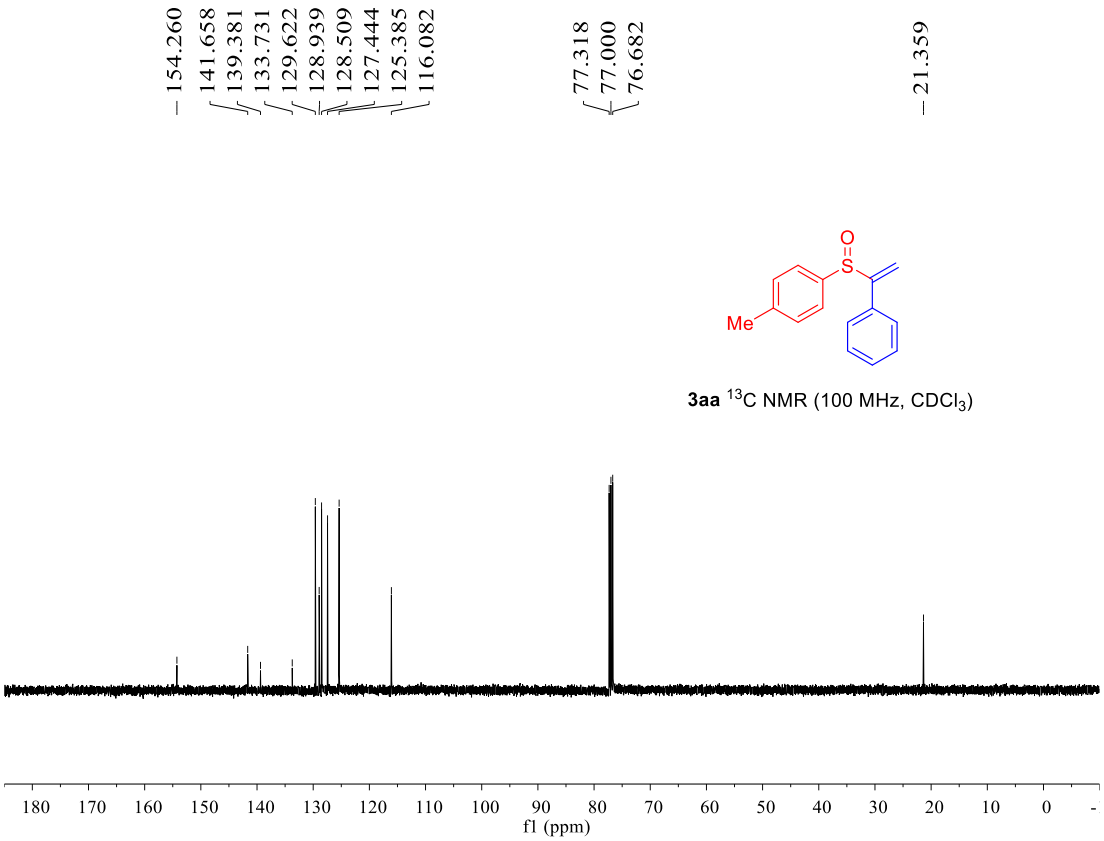
[6] L. Wang, M. Chen, P. Zhang, W. Li and J. Zhang, Palladium/PC-Phos-Catalyzed Enantioselective Arylation of General Sulfenate Anions: Scope and Synthetic Applications. *J. Am. Chem. Soc.*, 2018, **140**, 3467-3473.

[7] S. R. Polimera, M. A. M. Subbaiah and A. Ilangovan, The Ligand Free Palladium(II)-Catalyzed Regioselective 1,2-Addition of Enol Silanes to Quinones to Access 4-Hydroxy-4-(2-oxo-2-arylethyl)cyclohexadien-1-ones and Synthetic Applications. *J. Org. Chem.*, 2021, **86**, 14356-14370.

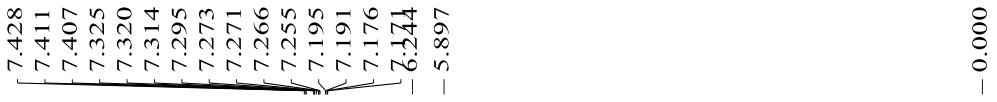
10. Copies of NMR spectra

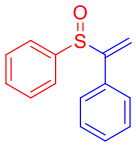


3aa ^{1}H NMR (400 MHz, $CDCl_3$)

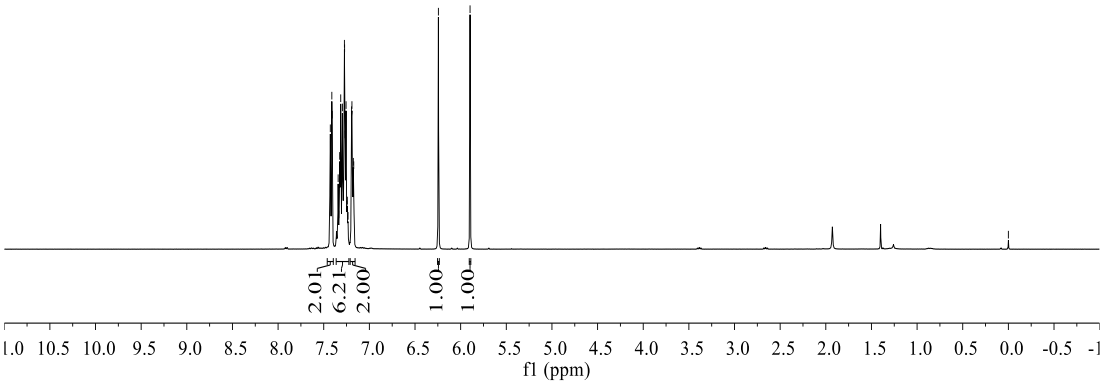


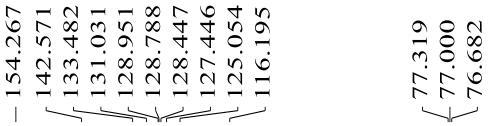
3aa ^{13}C NMR (100 MHz, $CDCl_3$)

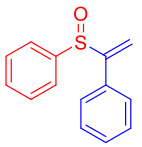




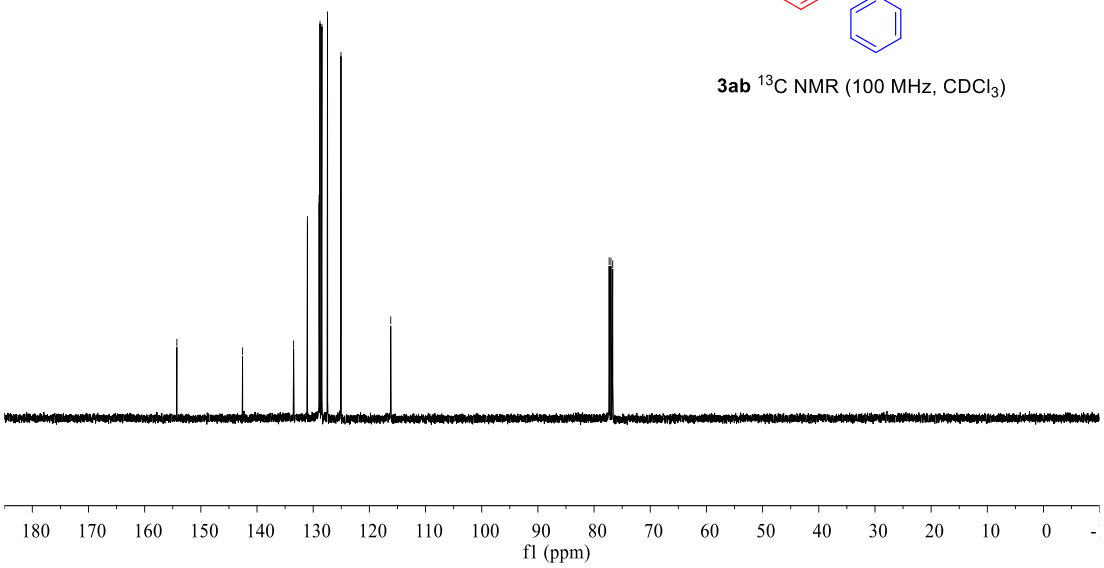
3ab ^{1}H NMR (400 MHz, $CDCl_3$)

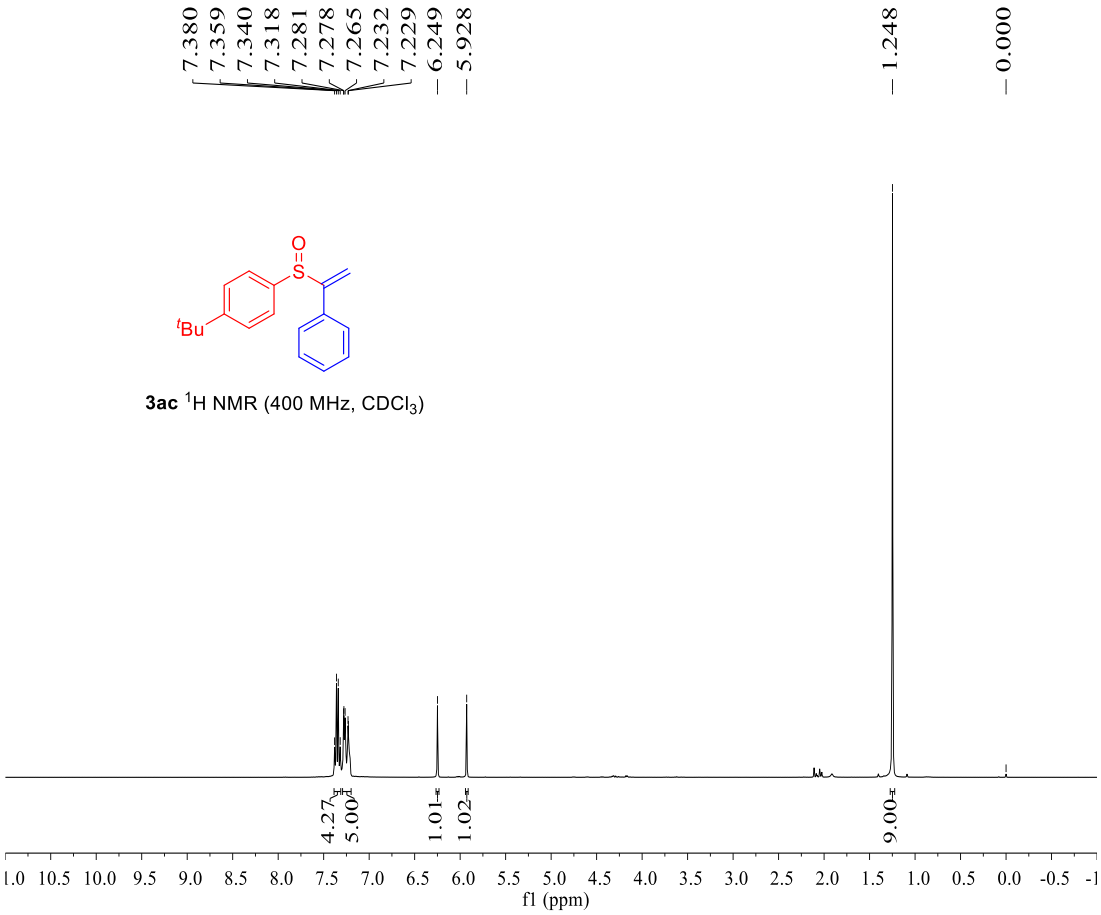




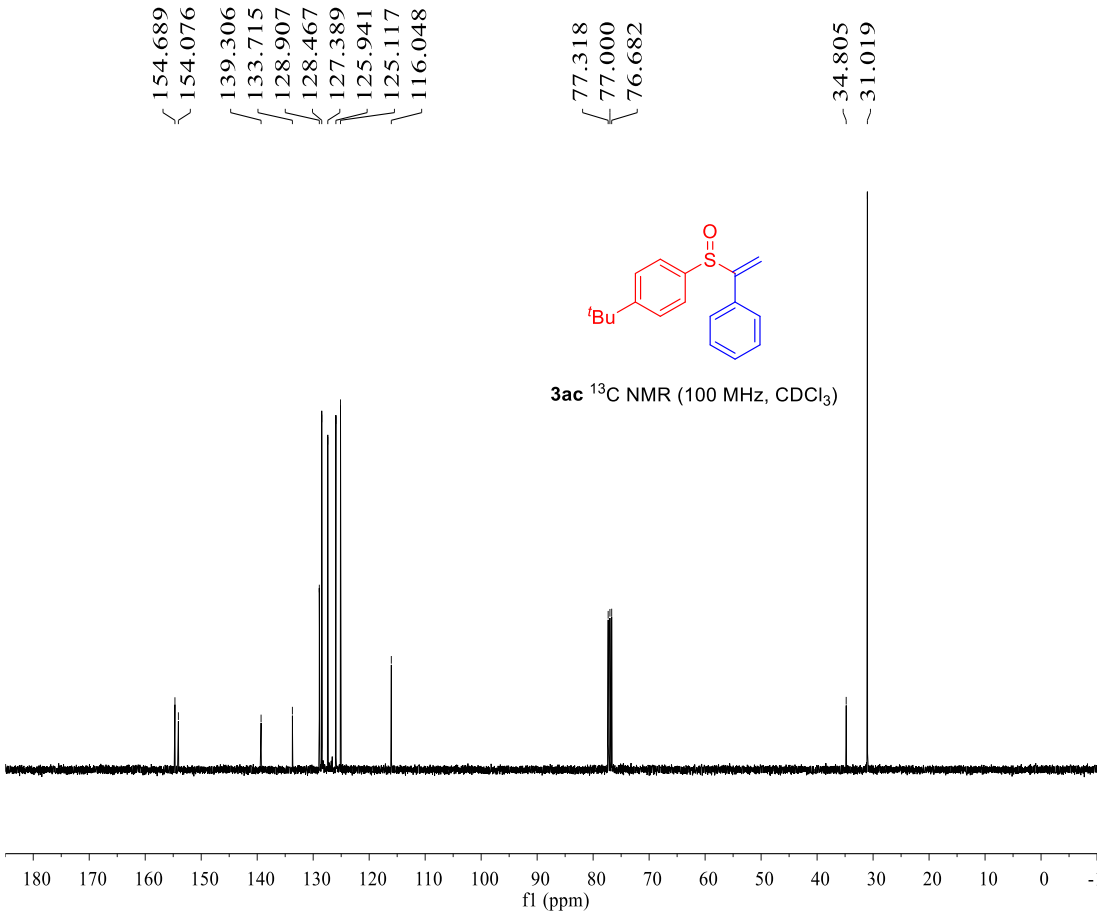


3ab ^{13}C NMR (100 MHz, $CDCl_3$)

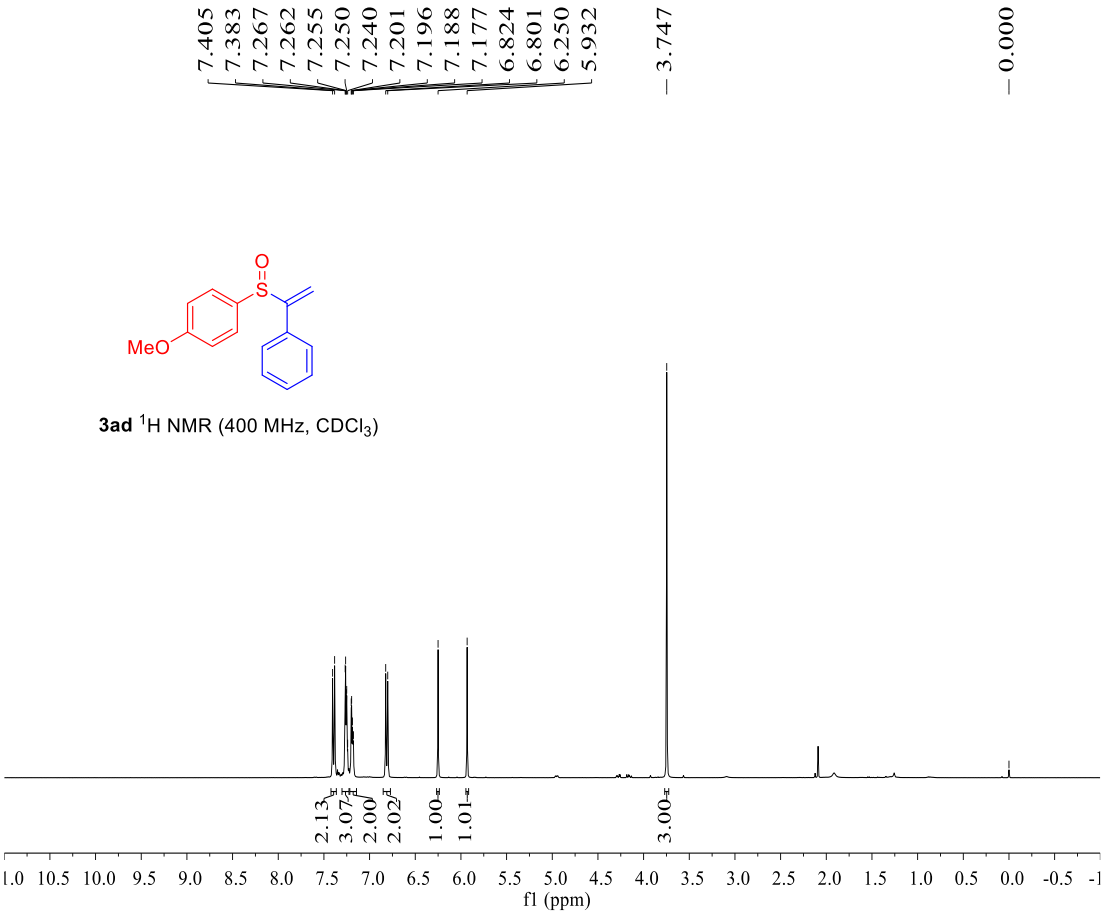




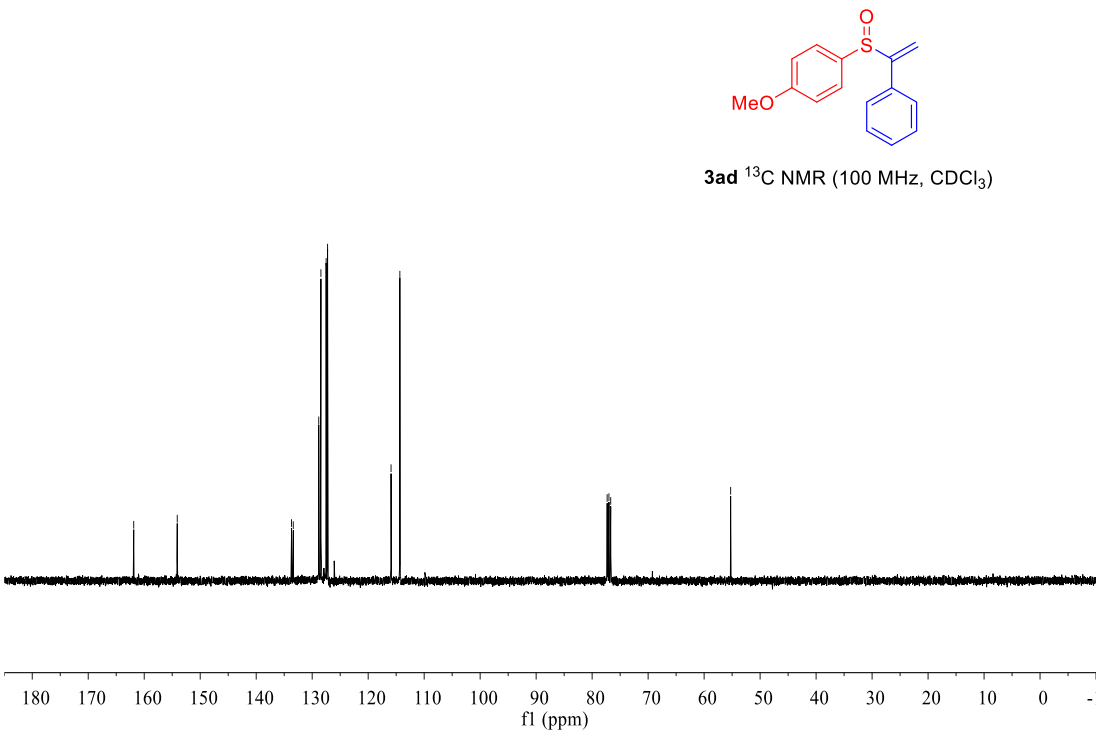
3ac ^{1}H NMR (400 MHz, $CDCl_3$)



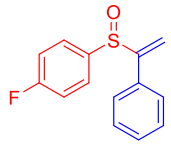
3ac ^{13}C NMR (100 MHz, $CDCl_3$)



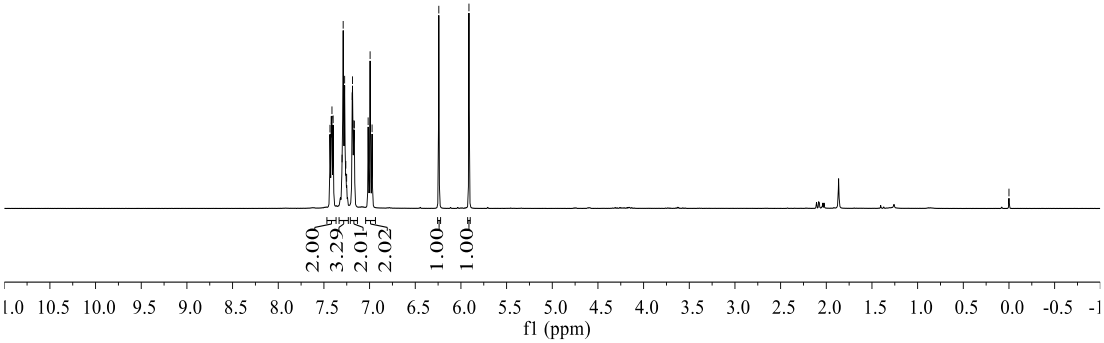
3ad ^{1}H NMR (400 MHz, $CDCl_3$)

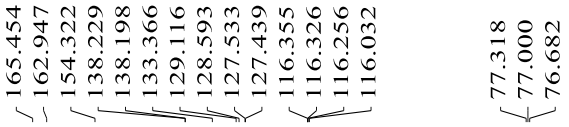


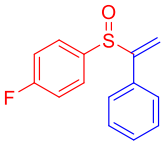
3ad ^{13}C NMR (100 MHz, $CDCl_3$)



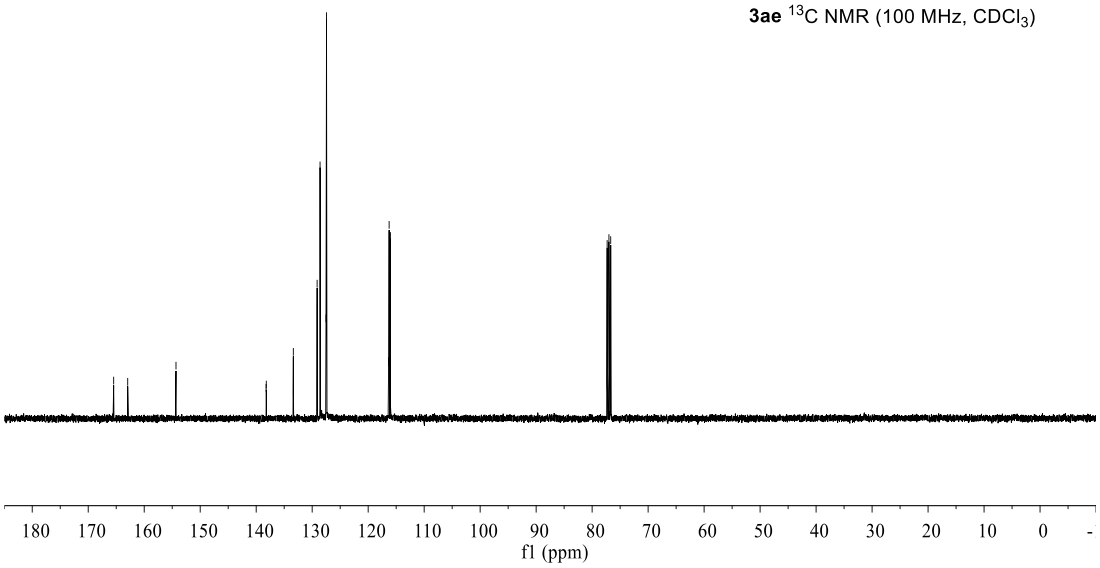
3ae ^{1}H NMR (400 MHz, $CDCl_3$)

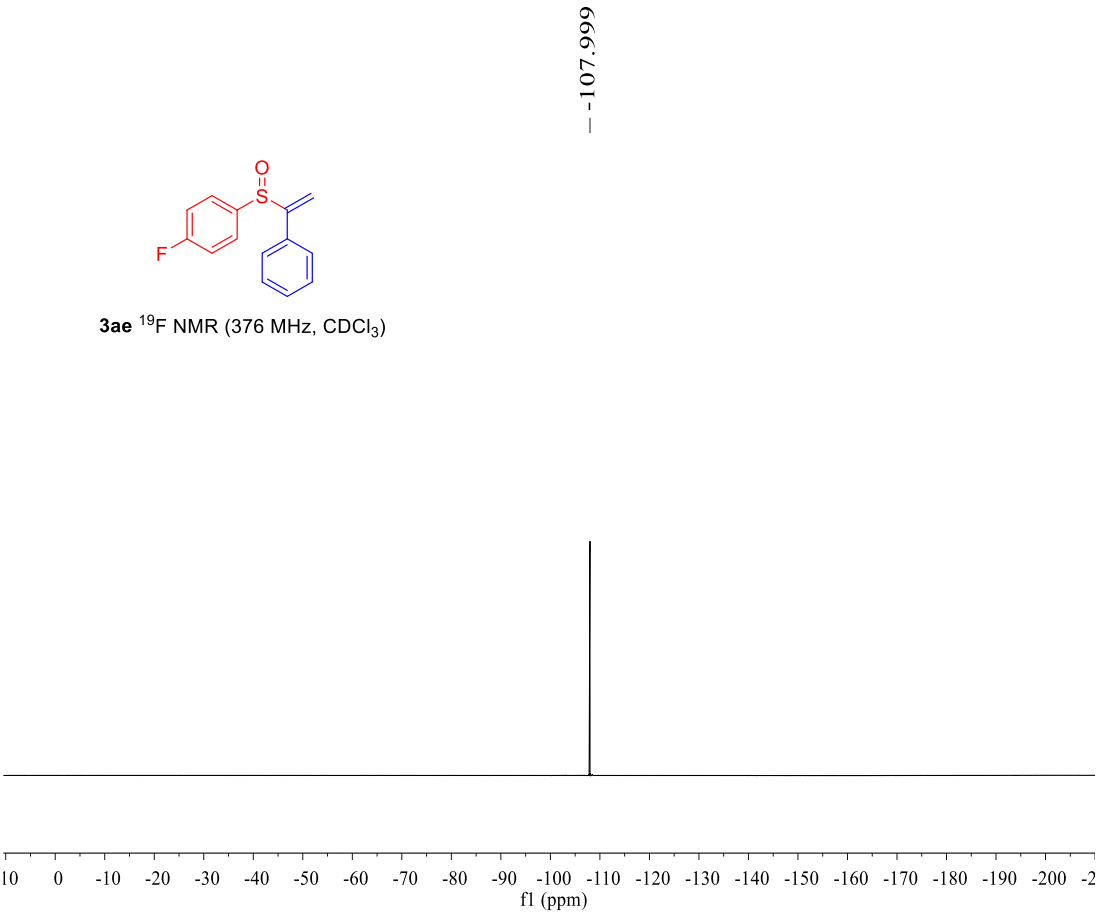




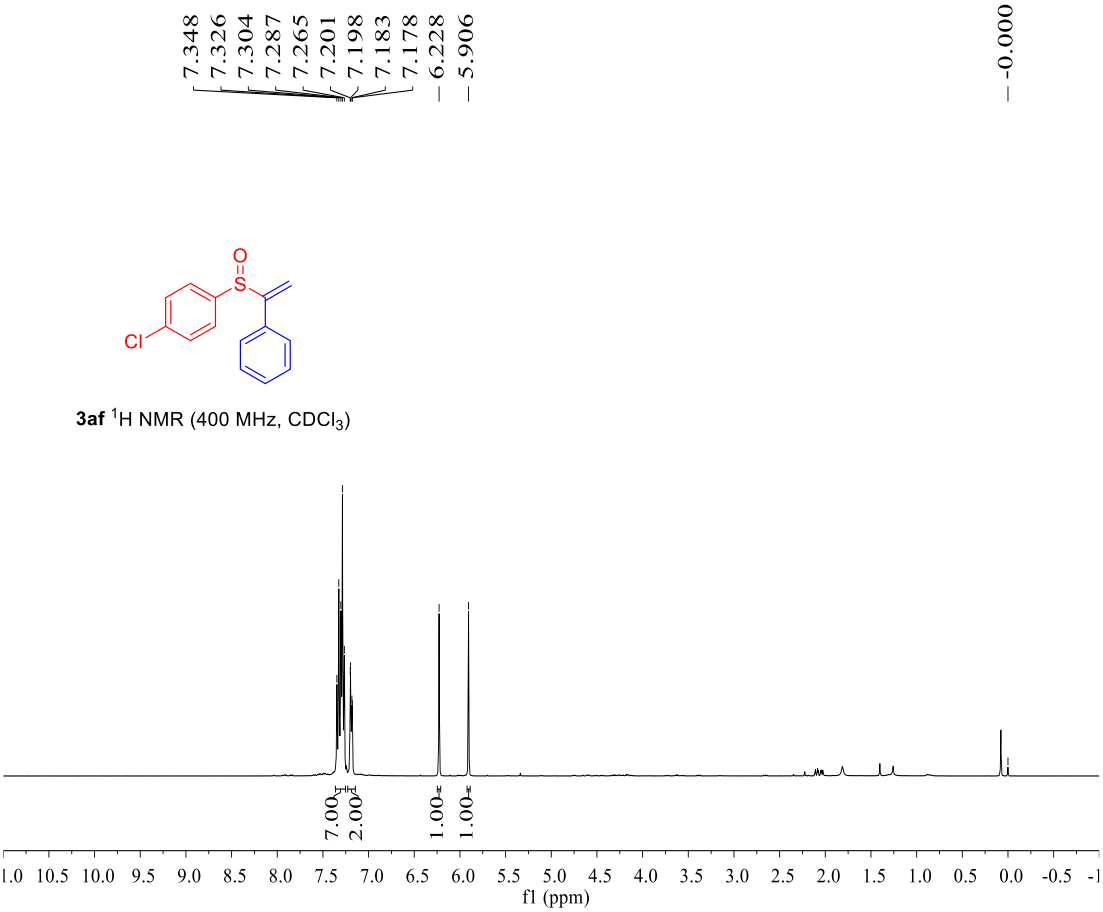


3ae ^{13}C NMR (100 MHz, $CDCl_3$)

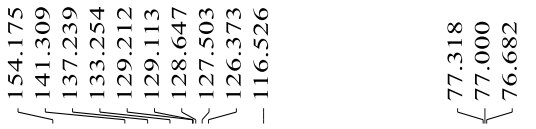


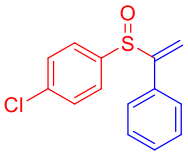


3ae ^{19}F NMR (376 MHz, $CDCl_3$)

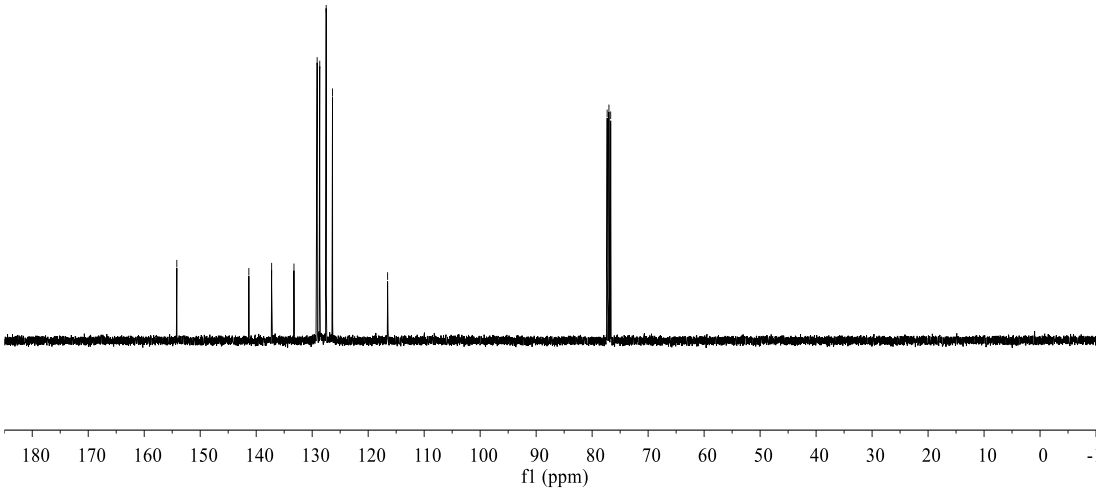


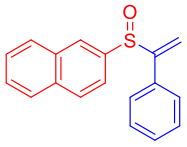
3af ^{1}H NMR (400 MHz, $CDCl_3$)



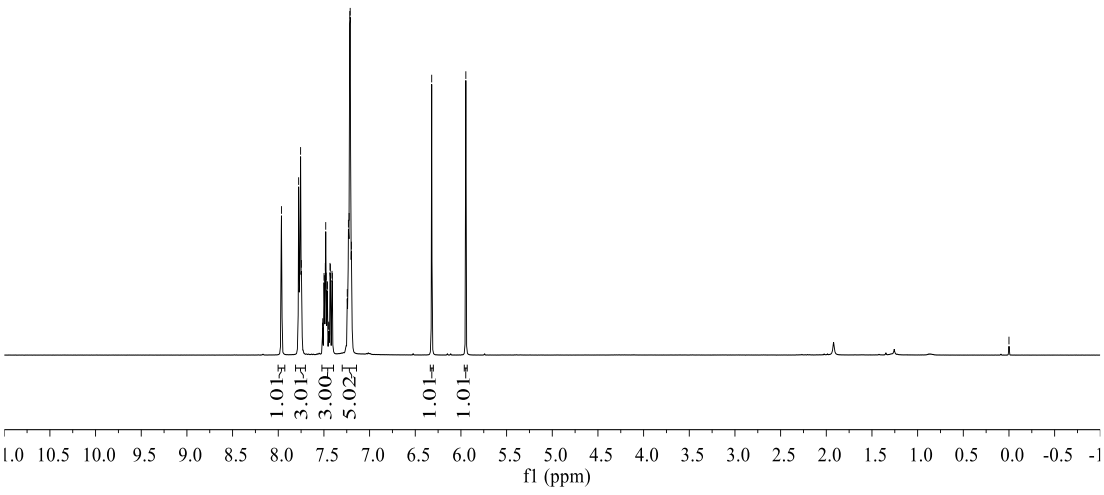


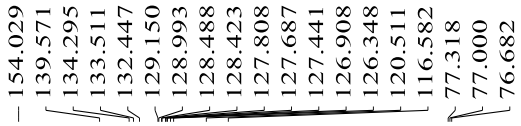
3af ^{13}C NMR (100 MHz, $CDCl_3$)

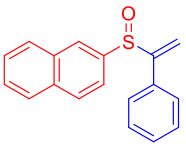




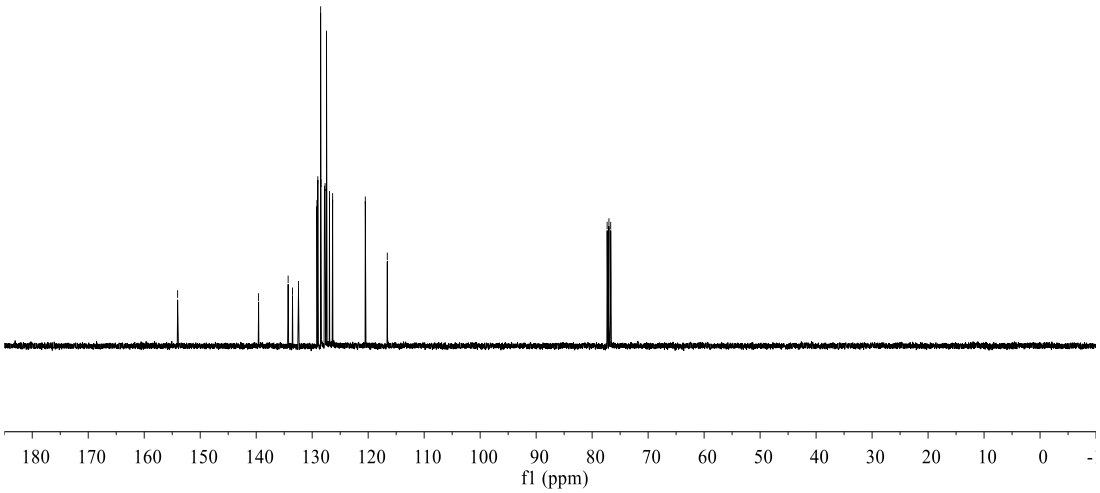
3ag ^{1}H NMR (400 MHz, $CDCl_3$)

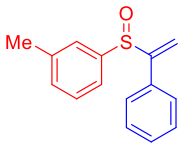




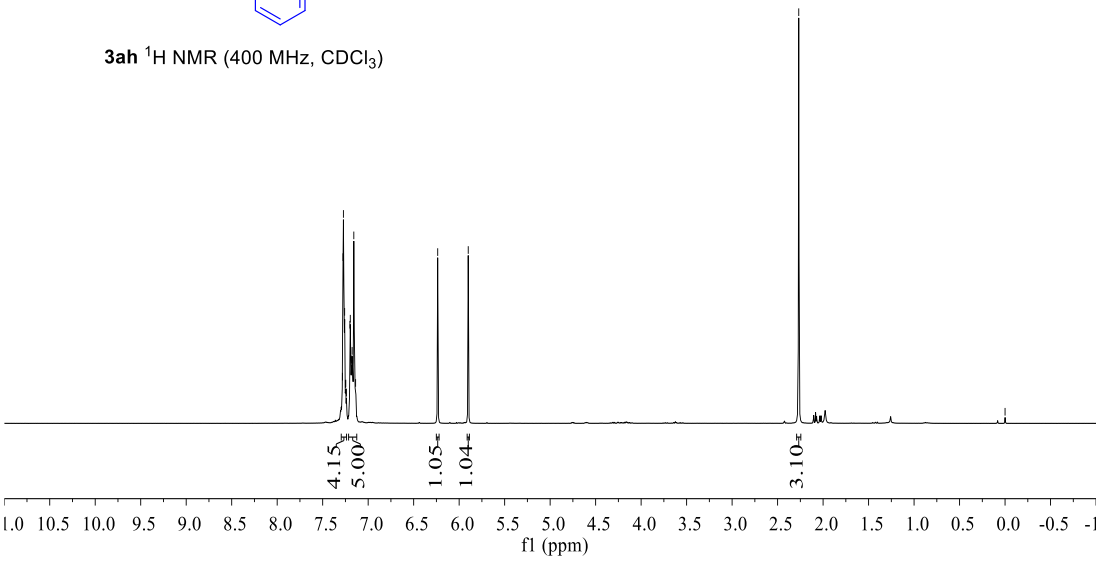


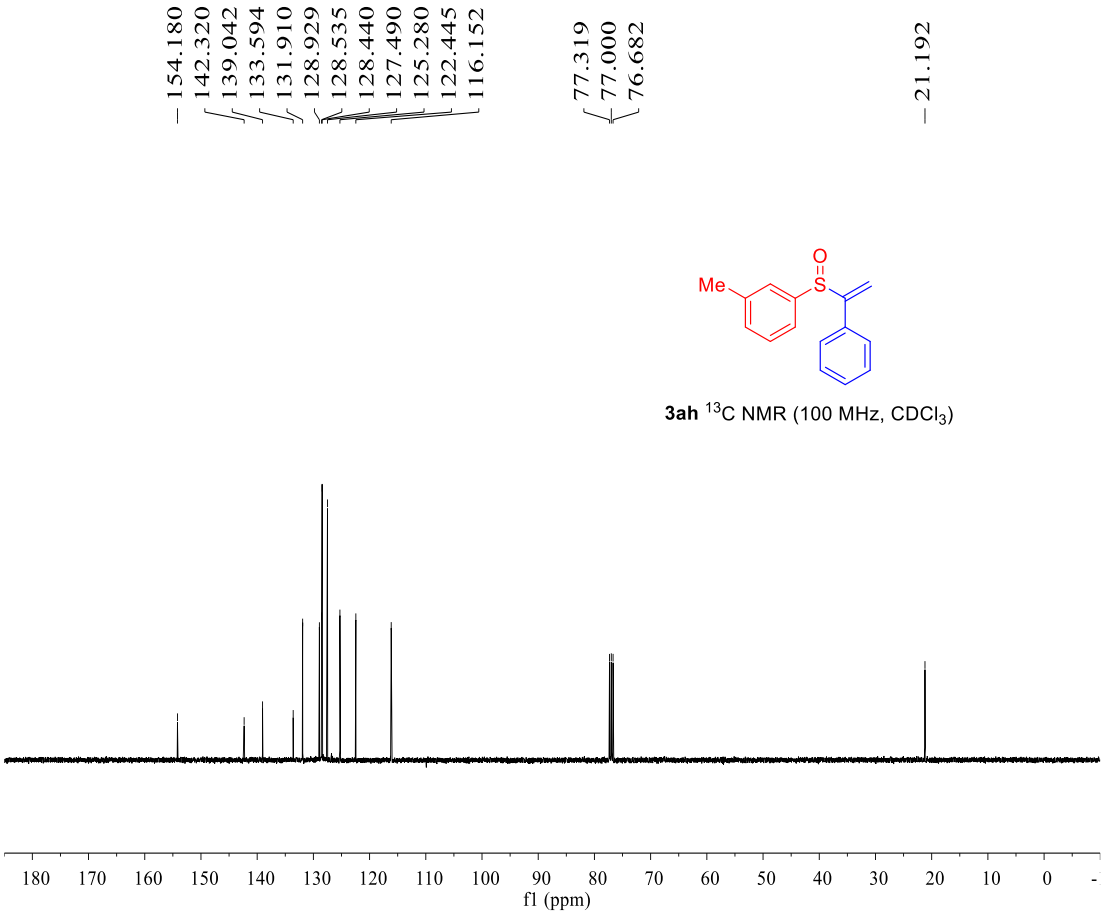
3ag ^{13}C NMR (100 MHz, $CDCl_3$)



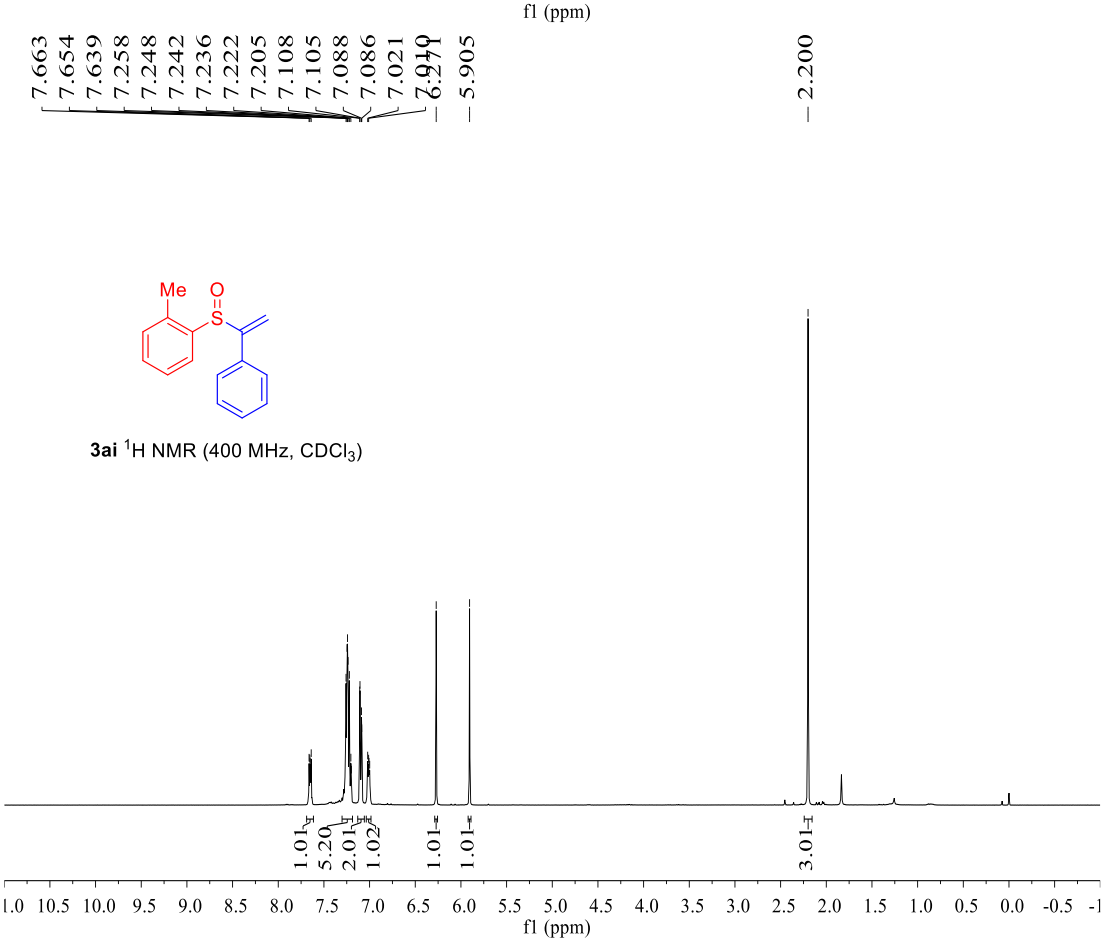


3ah ^{1}H NMR (400 MHz, $CDCl_3$)

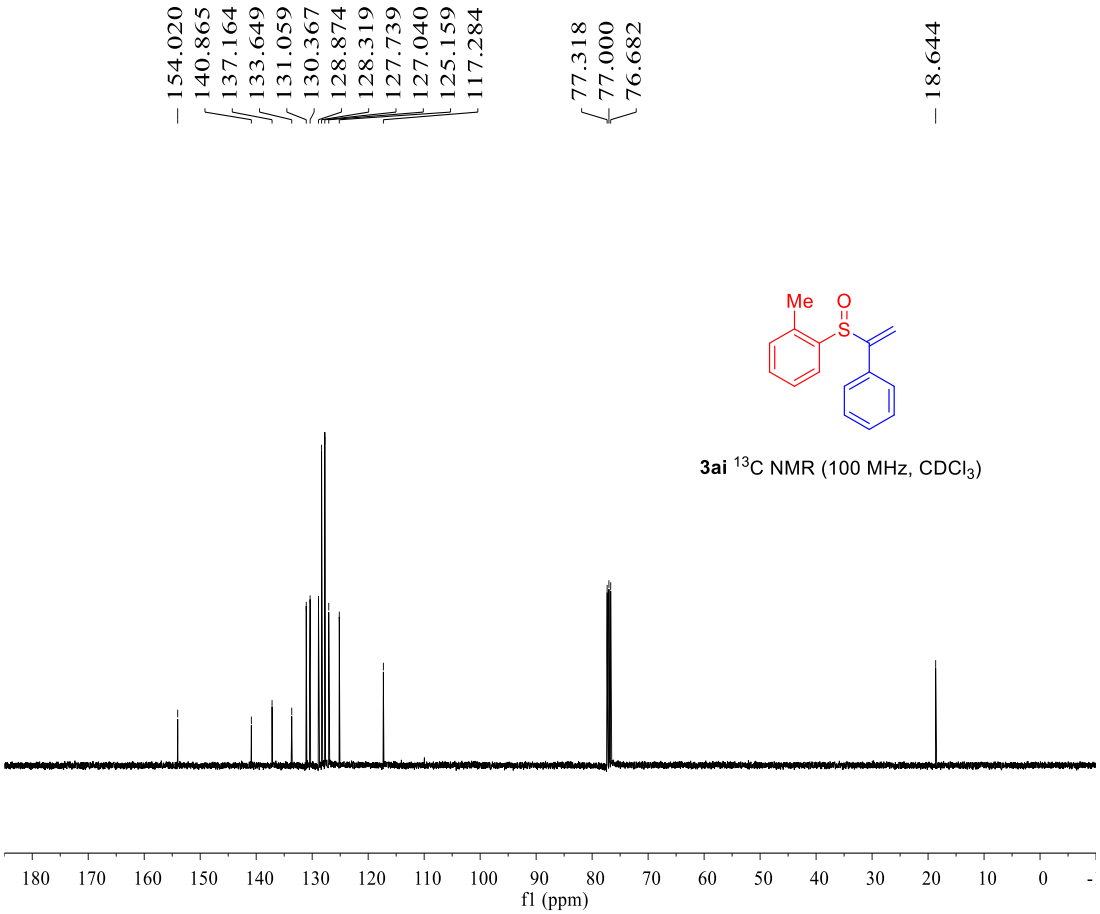




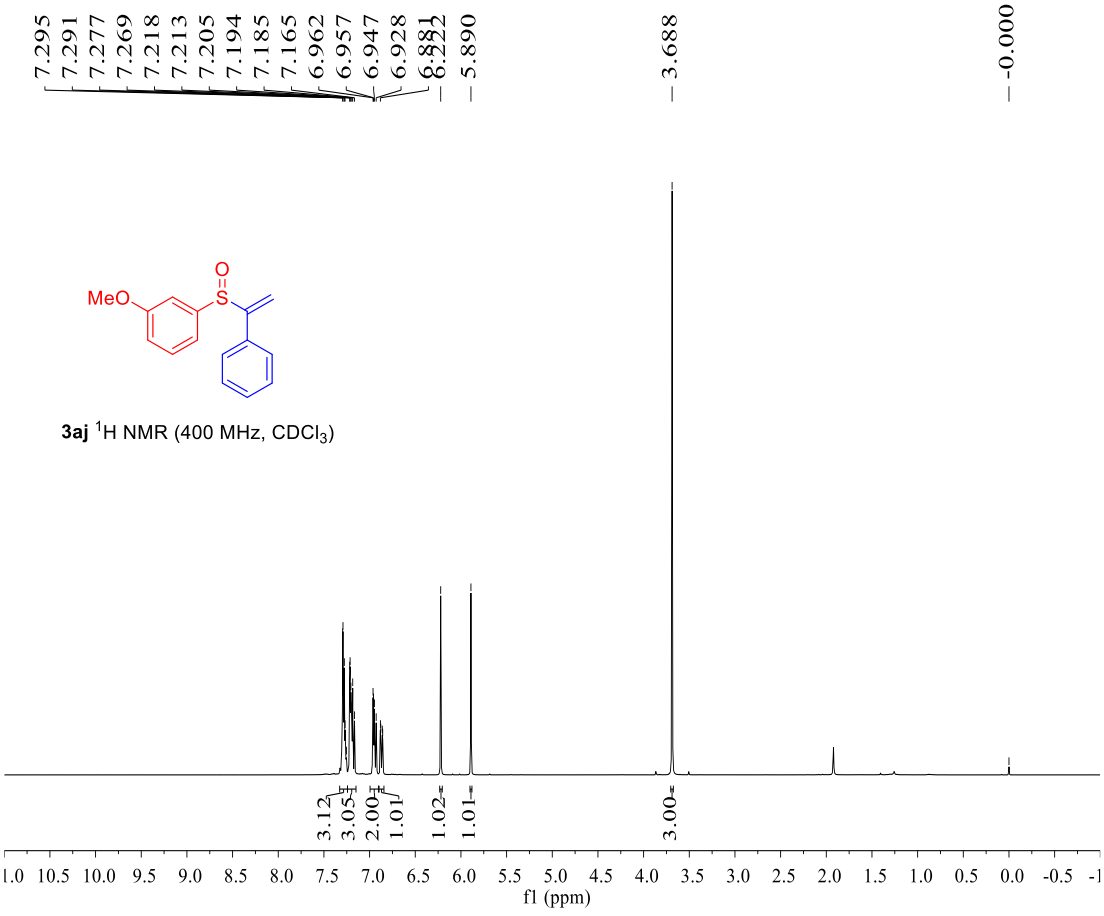
3ah ^{13}C NMR (100 MHz, $CDCl_3$)



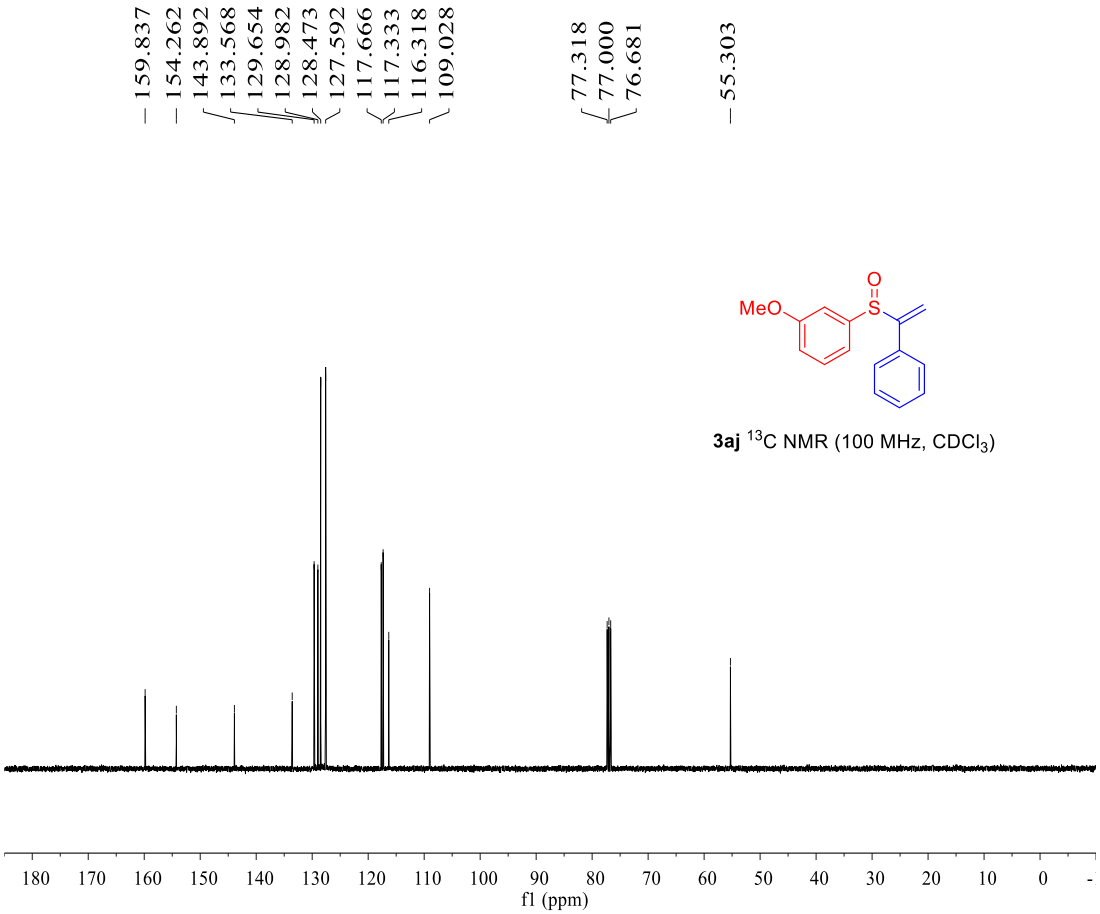
3ai ^{1}H NMR (400 MHz, $CDCl_3$)



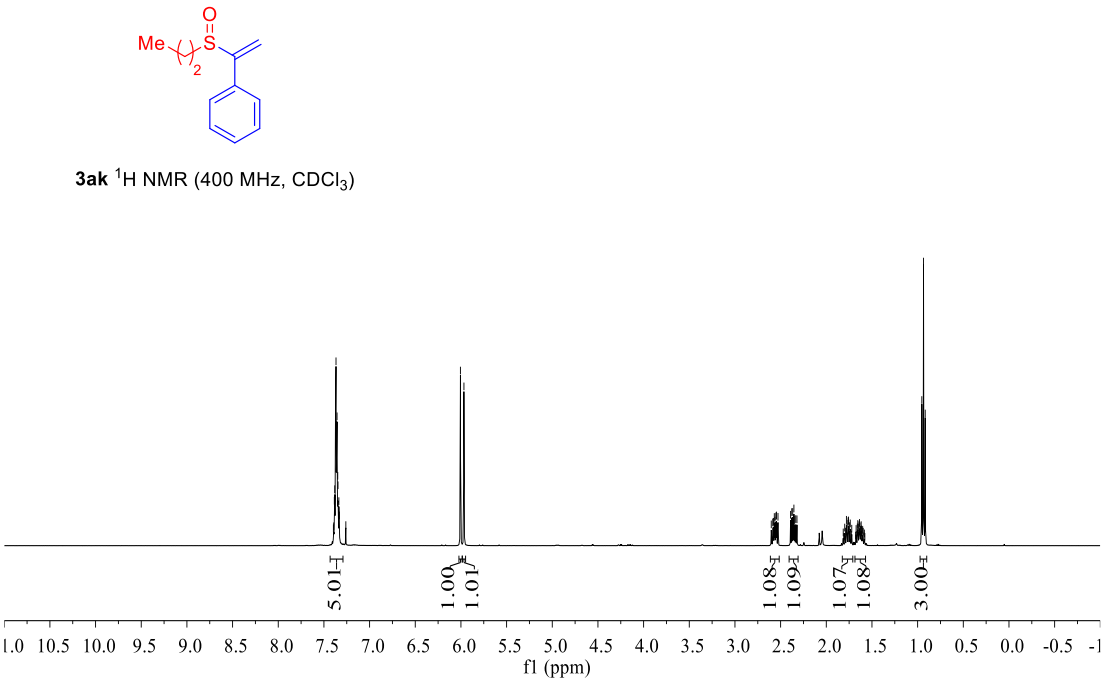
3ai ^{13}C NMR (100 MHz, $CDCl_3$)



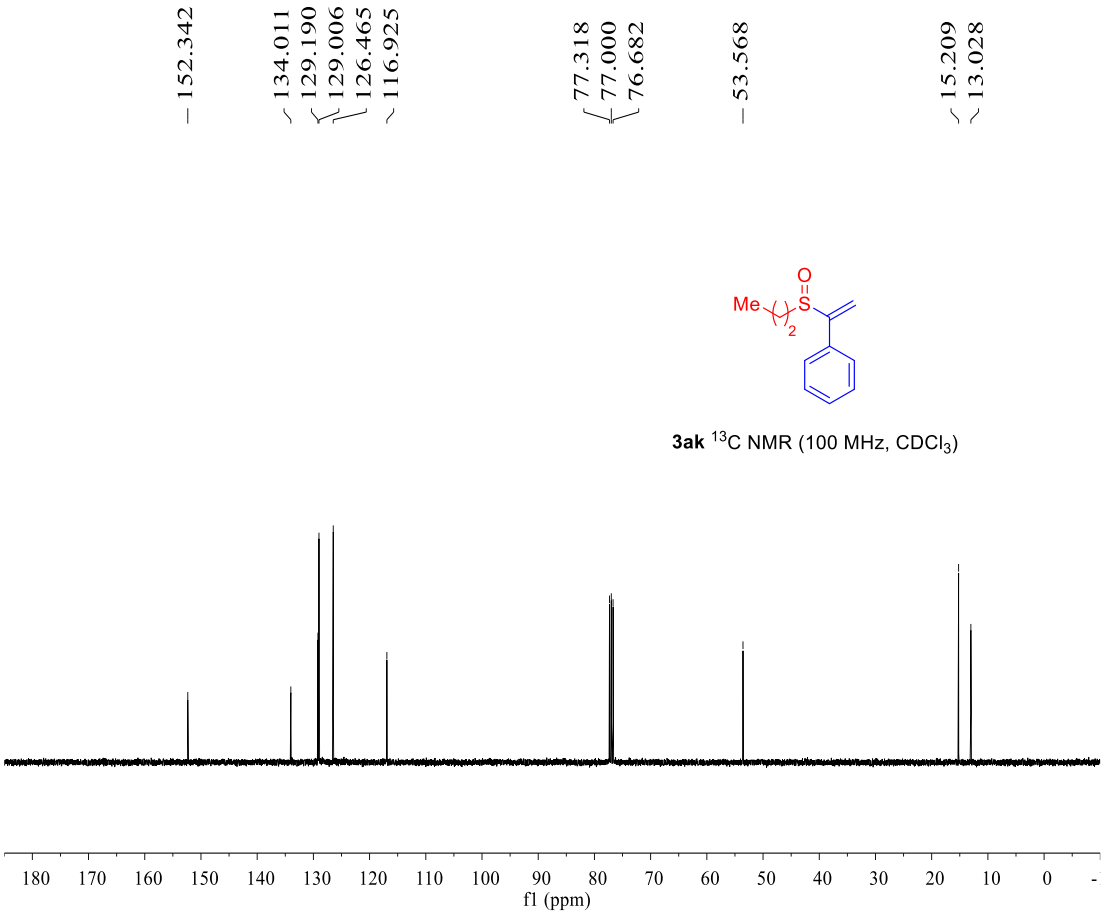
3aj ^{1}H NMR (400 MHz, $CDCl_3$)

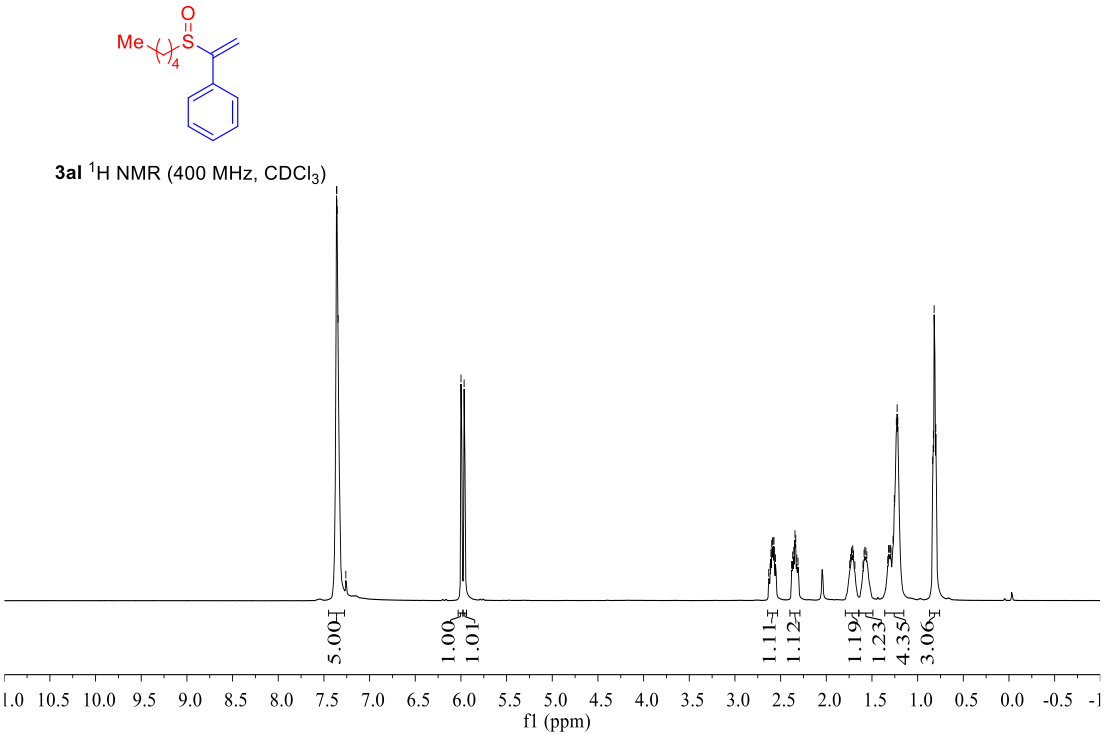


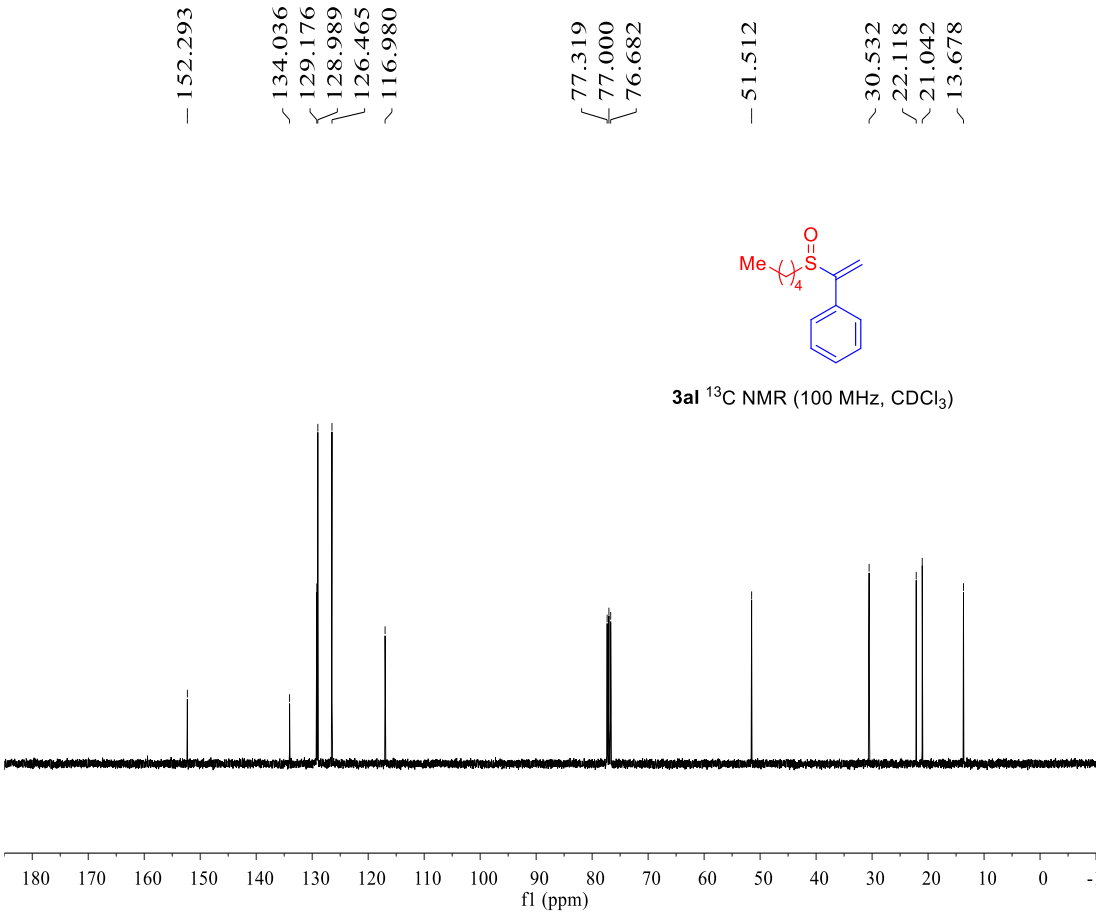
3aj ^{13}C NMR (100 MHz, $CDCl_3$)

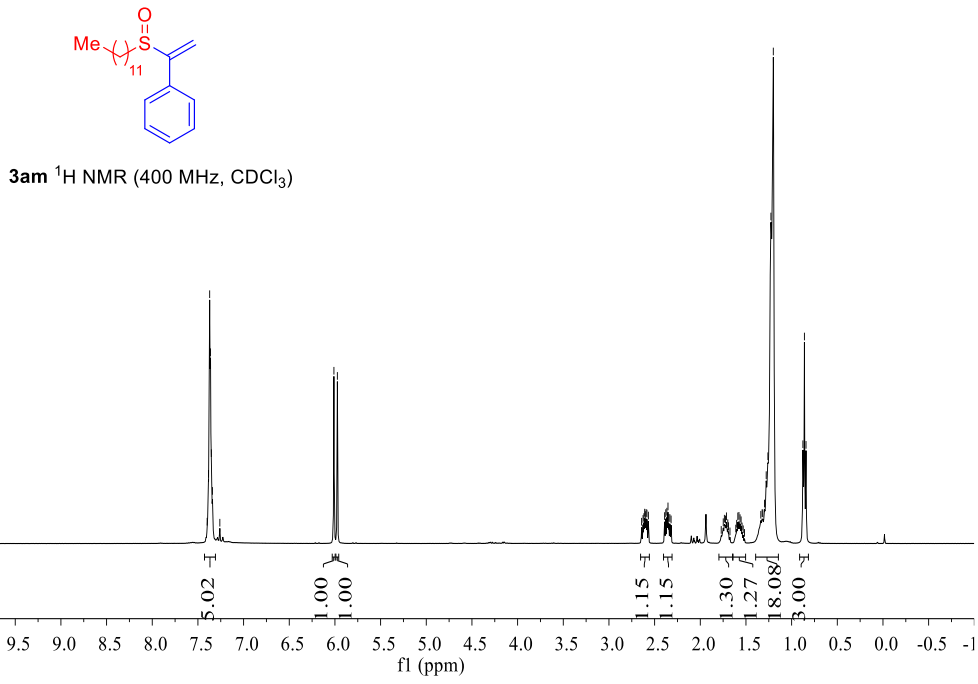


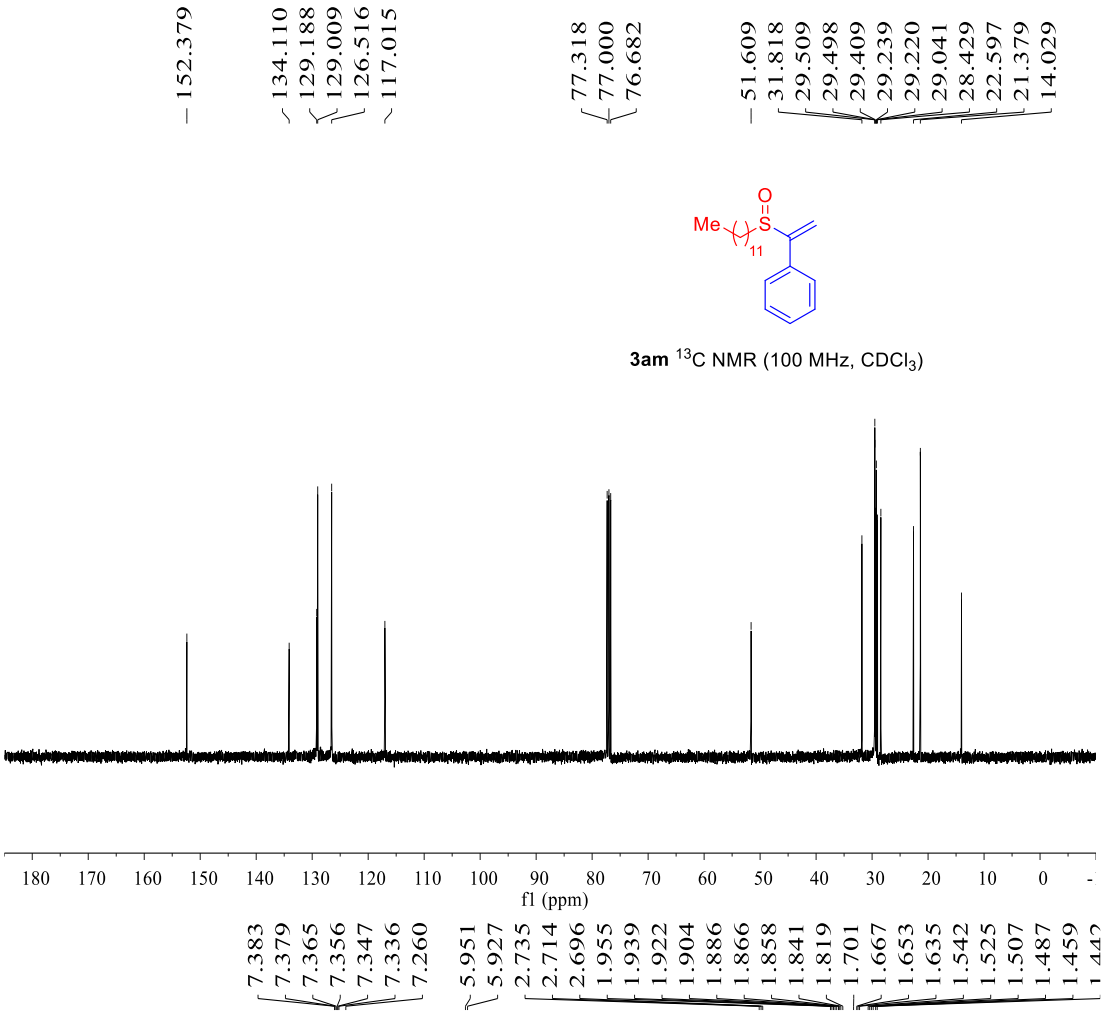
3ak ^{1}H NMR (400 MHz, $CDCl_3$)


152.342
134.011
129.190
129.006
126.465
116.925
77.318
77.000
76.682
53.568
15.209
13.028
Me
O
S
2
3ak 13C NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.362
7.359
7.355
7.345
5.999
5.965
2.606
2.597
2.590
2.582
2.573
2.557
2.368
2.356
2.343
2.334
2.322
1.735
1.725
1.720
1.710
1.701
1.587
1.578
1.566
1.556
1.327
1.318
1.310
1.296
1.291
1.269
1.255
1.233
1.224
1.217
0.836
0.827
0.819
0.801

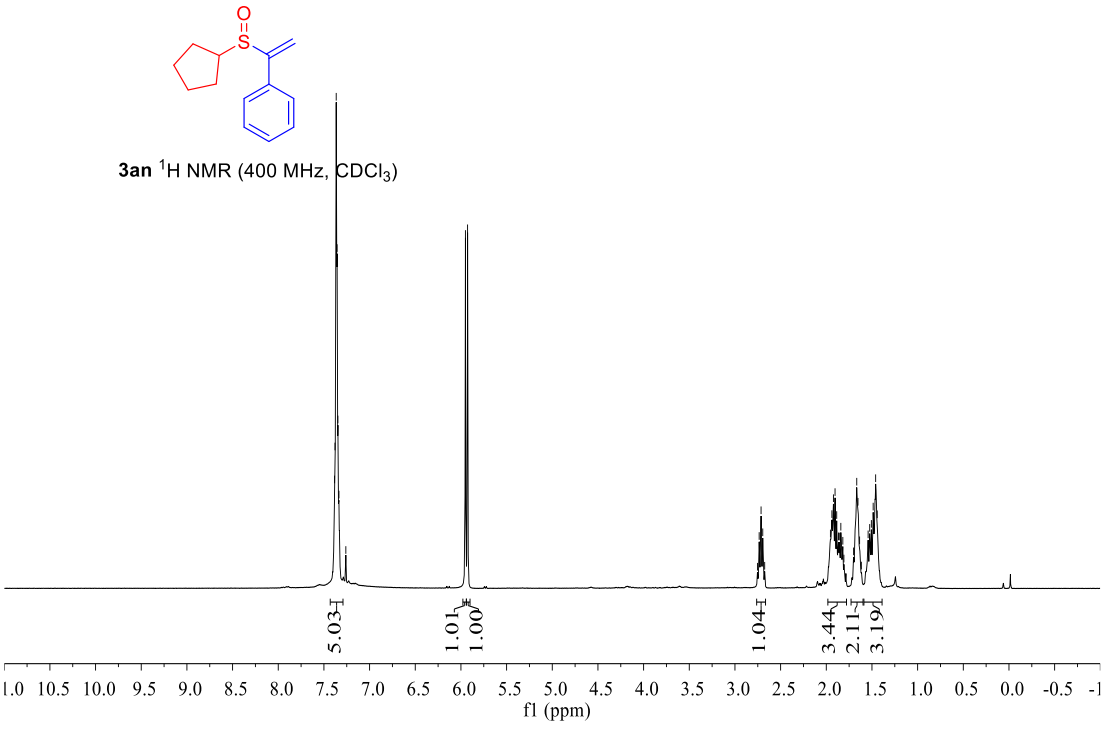

Me
O
S
4
3al 1H NMR (400 MHz, CDCl3)
5.00
1.00
1.01
1.11
1.12
1.19
1.23
4.35
3.06
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


152.293
134.036
129.176
128.989
126.465
116.980
77.319
77.000
76.682
51.512
30.532
22.118
21.042
13.678
Me
4
O
S
3al 13C NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.399
7.384
7.371
7.362
7.353
7.341
6.011
5.973
2.627
2.617
2.609
2.602
2.593
2.584
2.568
2.390
2.378
2.366
2.354
2.344
2.332
2.320
1.736
1.724
1.714
1.589
1.577
1.565
1.553
1.337
1.323
1.315
1.297
1.278
1.260
1.227
1.201
0.877
0.860
0.843

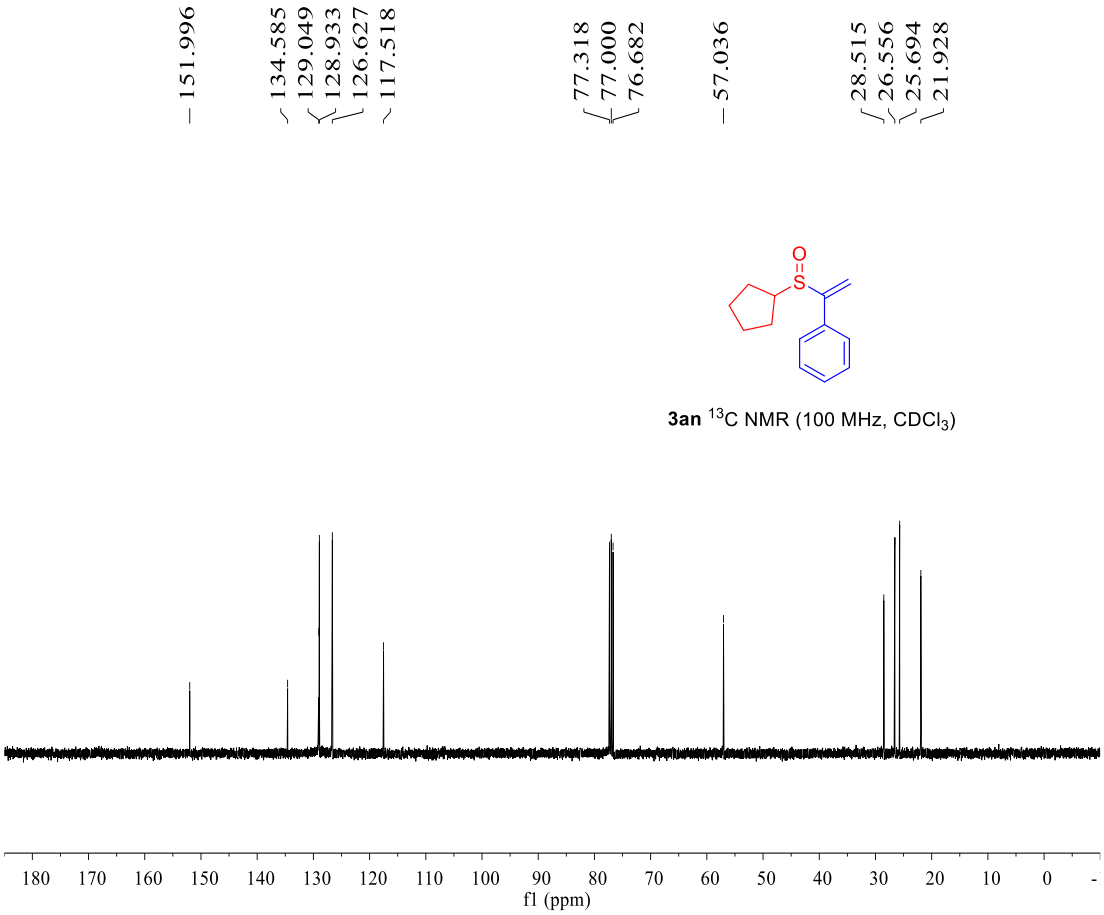

Me
11
O
S
3am 1H NMR (400 MHz, CDCl3)
5.02
1.00
1.00
1.15
1.15
1.30
1.27
18.08
3.00
f1 (ppm)



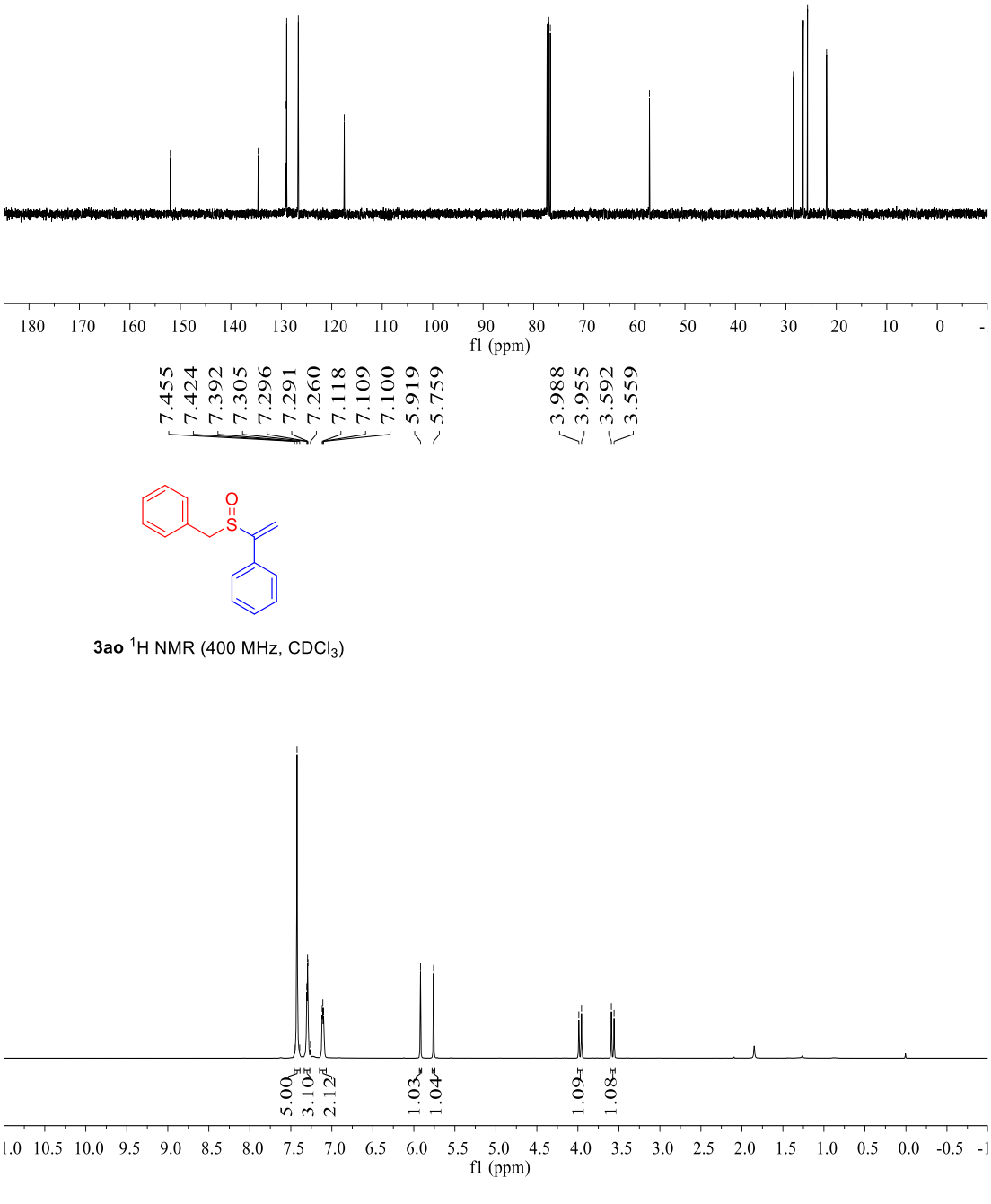
3am ^{13}C NMR (100 MHz, $CDCl_3$)



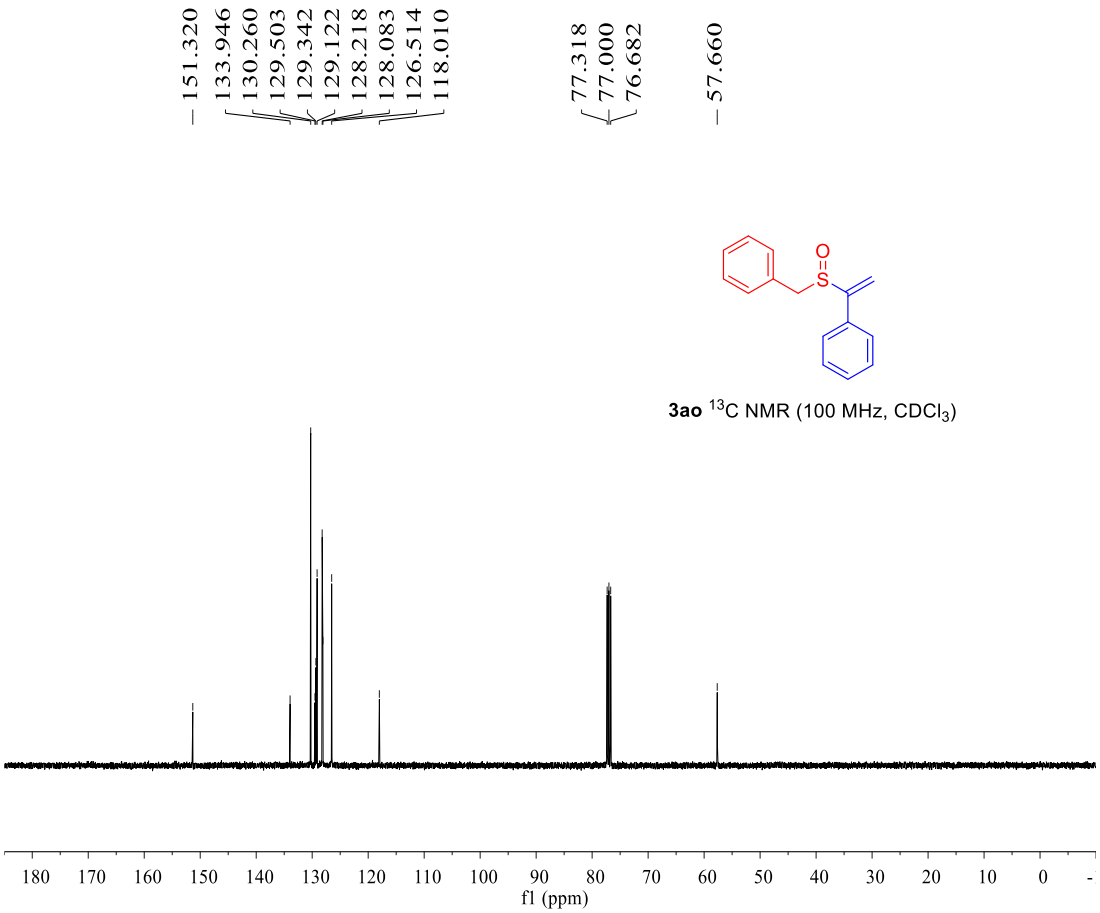
3an ^{1}H NMR (400 MHz, $CDCl_3$)



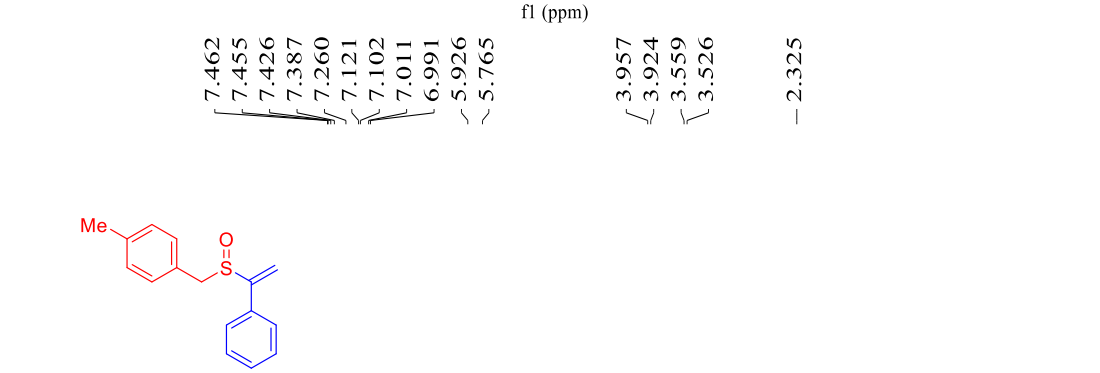
3an ^{13}C NMR (100 MHz, $CDCl_3$)



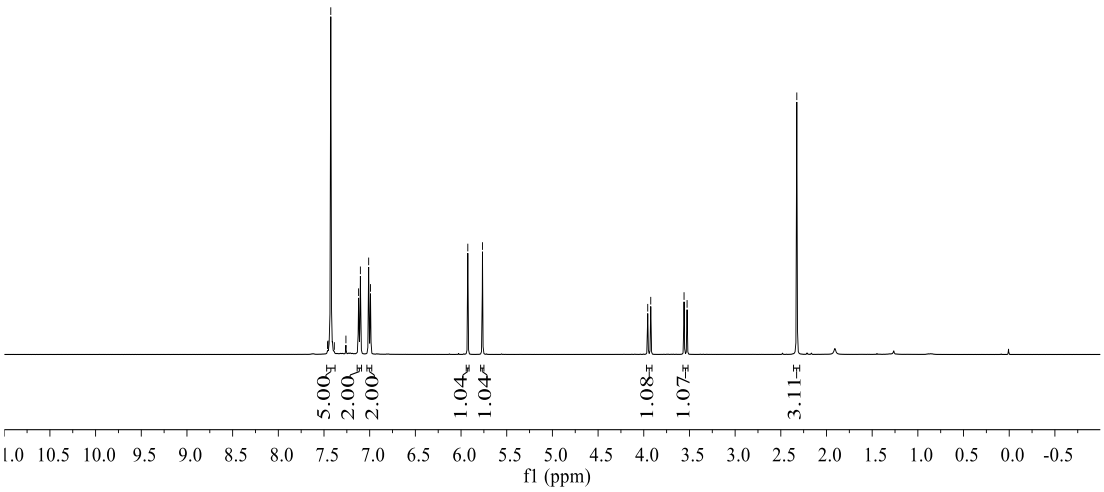
3ao ^{1}H NMR (400 MHz, $CDCl_3$)

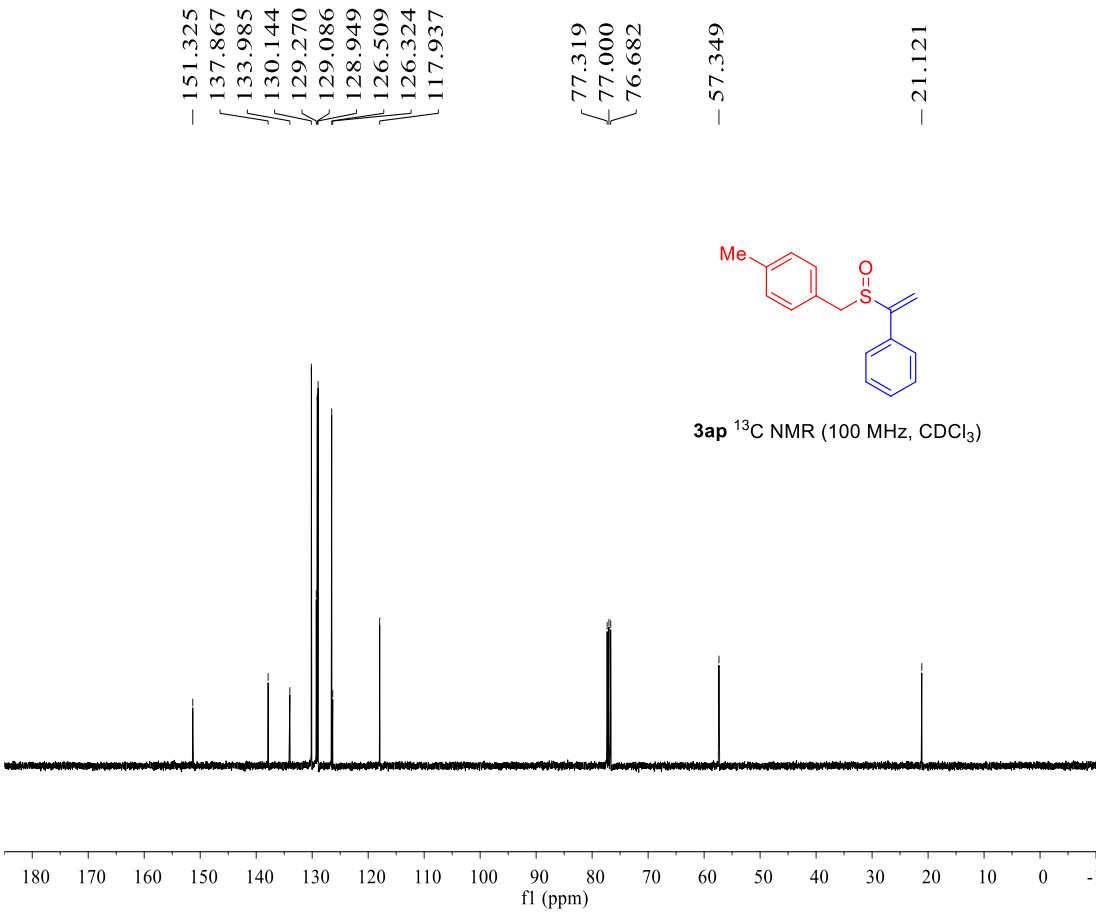


3ao ^{13}C NMR (100 MHz, $CDCl_3$)

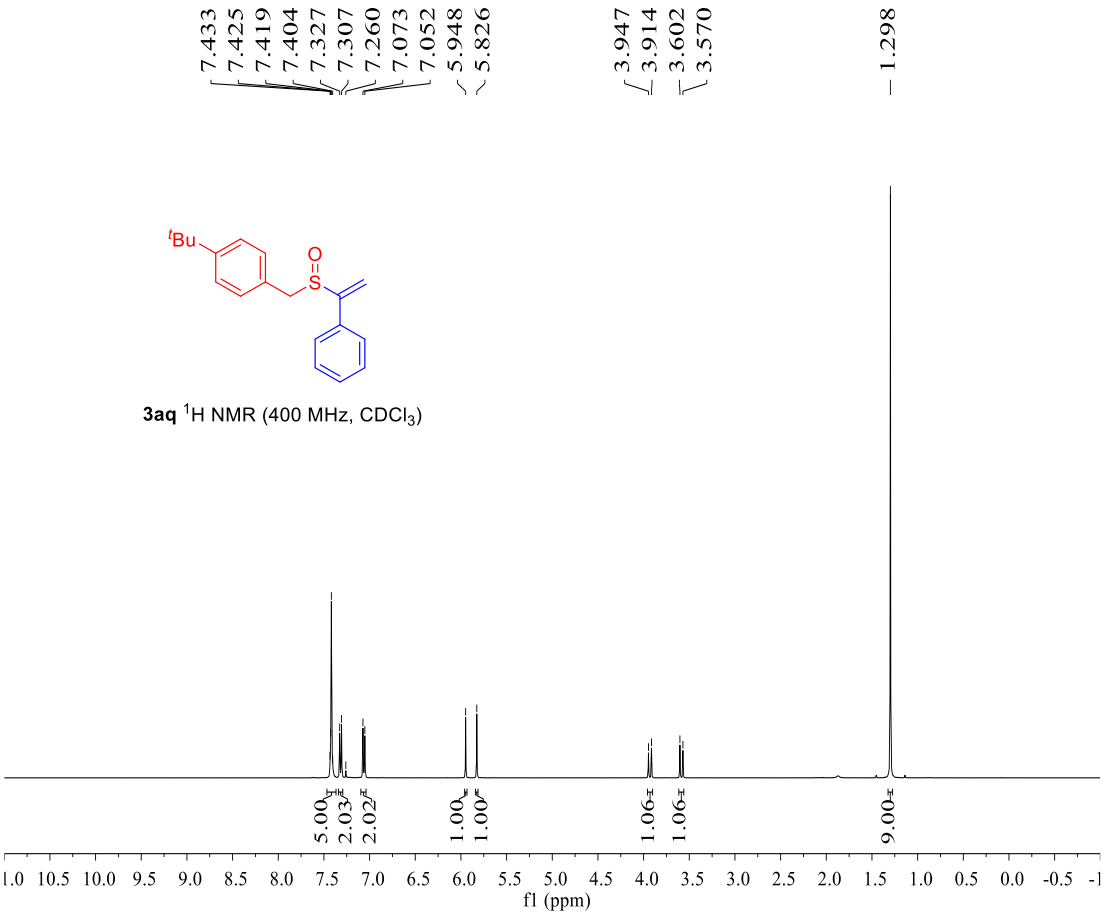


3ap ^{1}H NMR (400 MHz, $CDCl_3$)

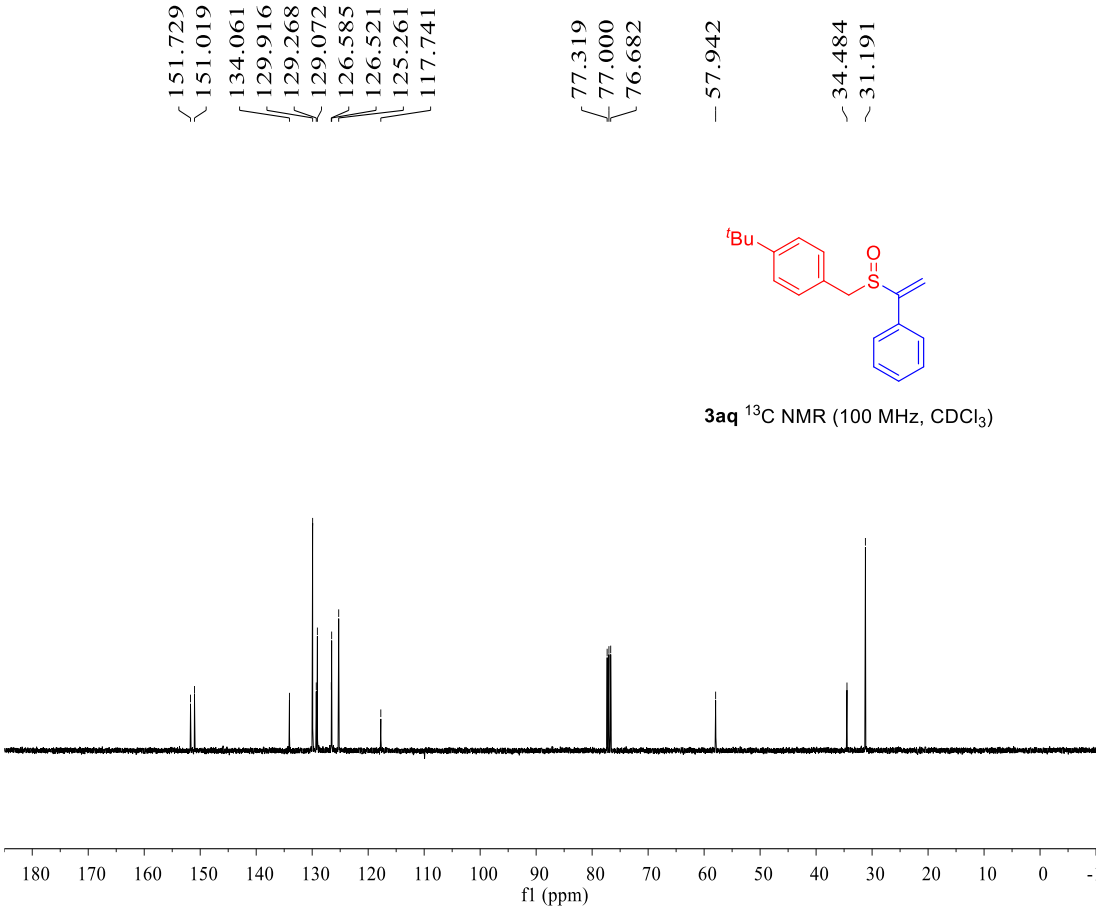




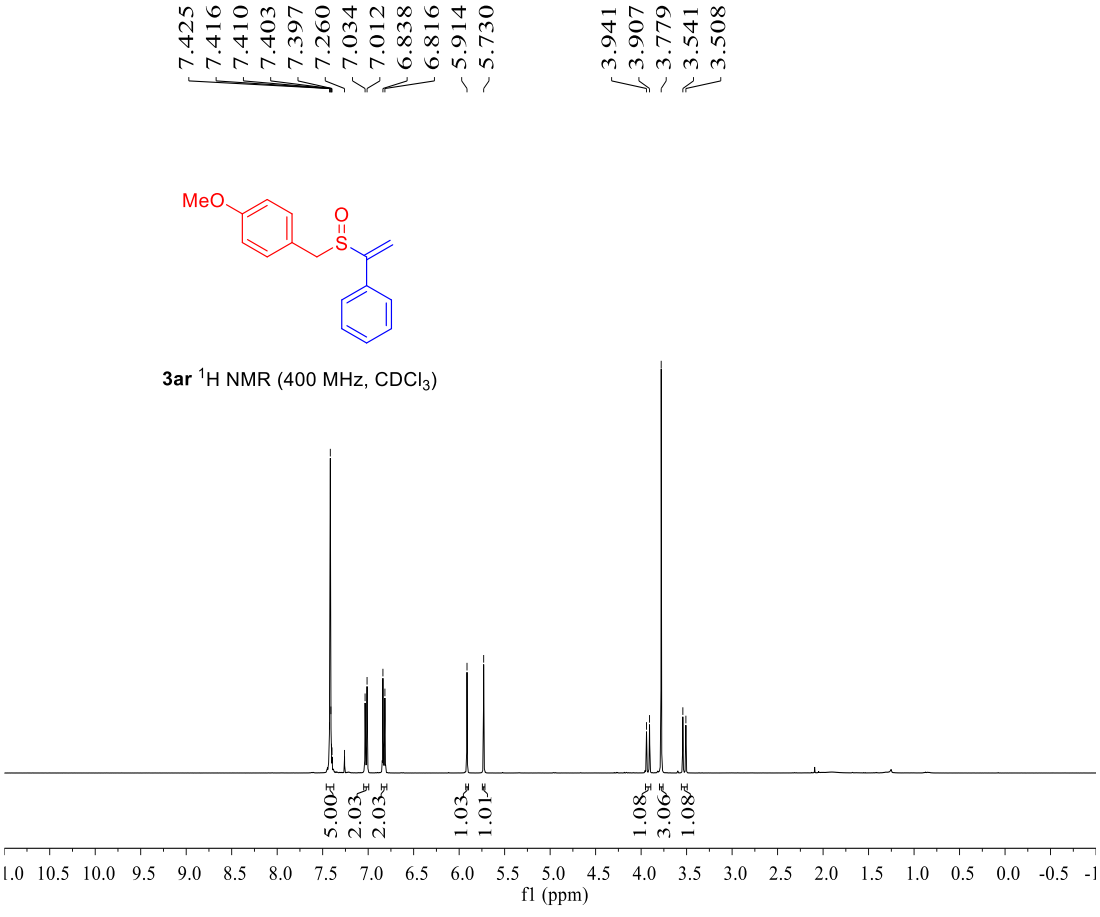
3ap ^{13}C NMR (100 MHz, $CDCl_3$)



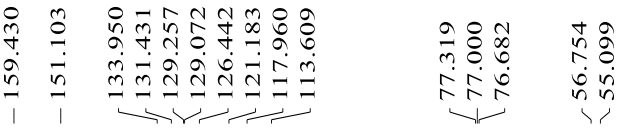
3aq ^{1}H NMR (400 MHz, $CDCl_3$)

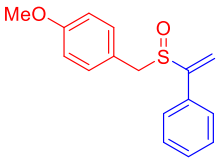


3aq ^{13}C NMR (100 MHz, $CDCl_3$)

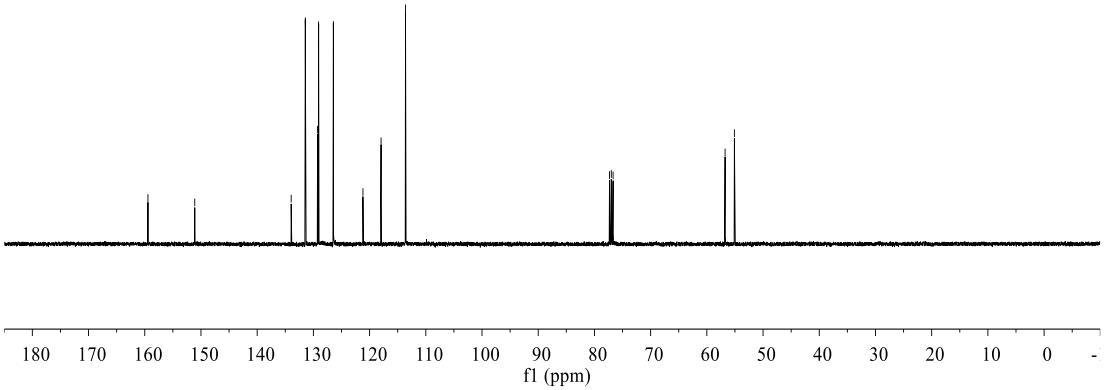


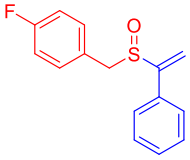
3ar ^{1}H NMR (400 MHz, $CDCl_3$)



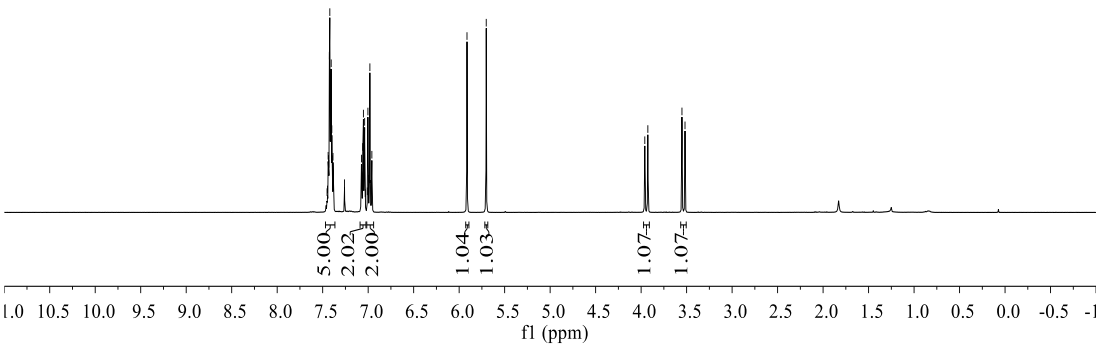


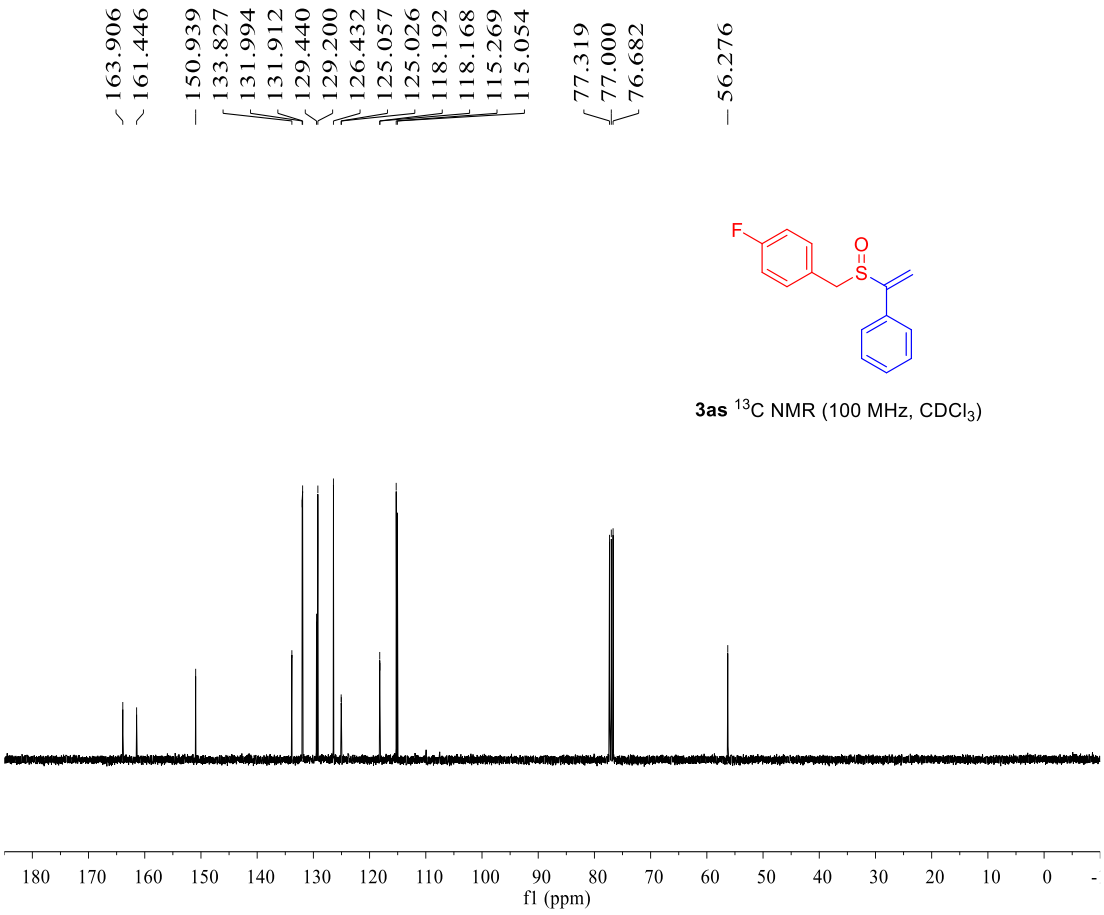
3ar ^{13}C NMR (100 MHz, $CDCl_3$)



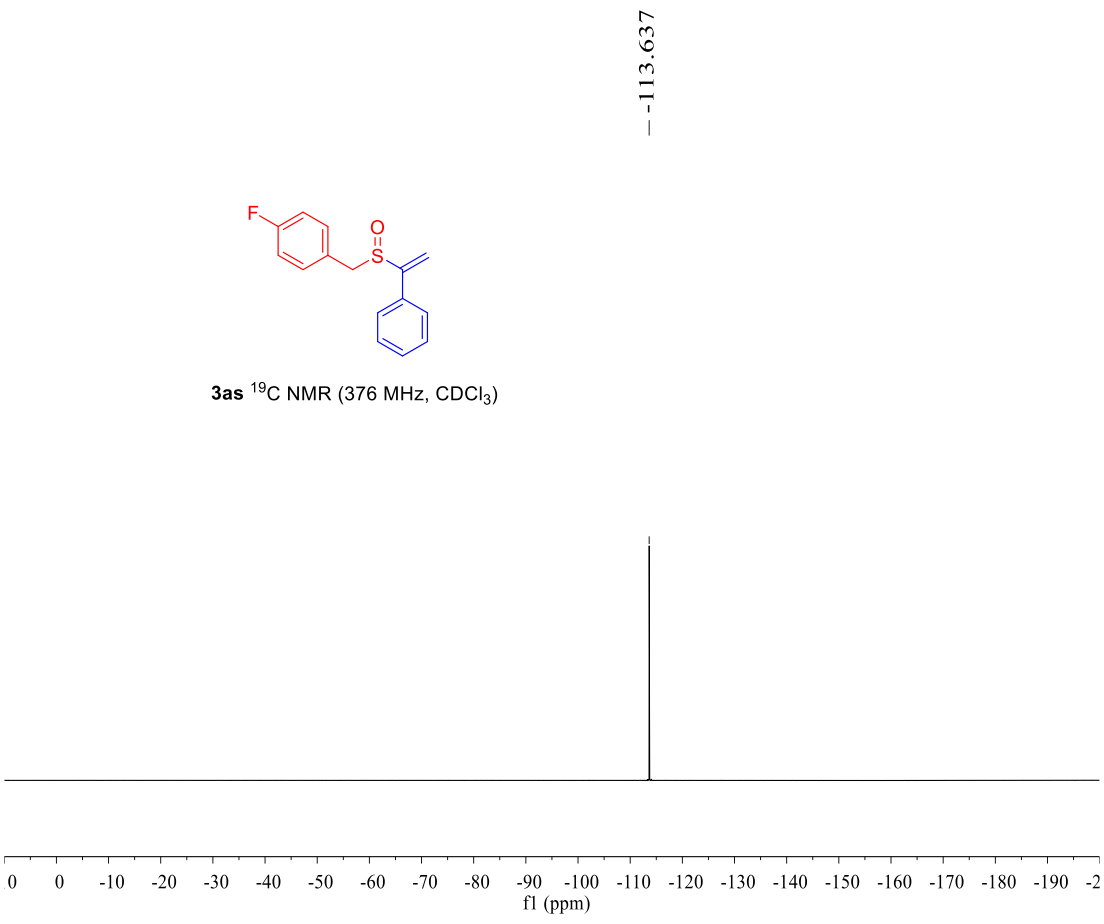


3as ^{1}H NMR (400 MHz, $CDCl_3$)

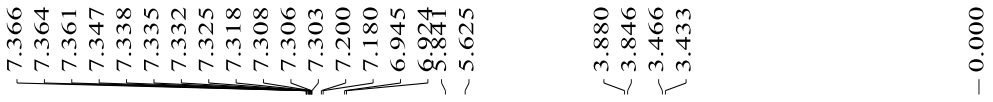


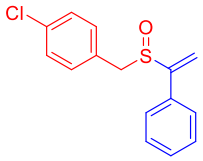


3as ^{13}C NMR (100 MHz, $CDCl_3$)

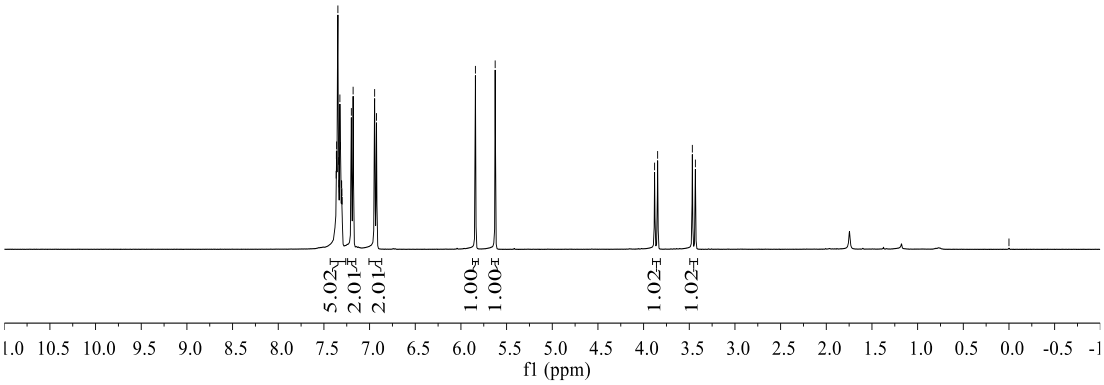


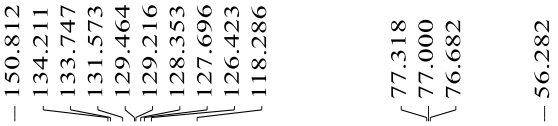
3as ^{19}C NMR (376 MHz, $CDCl_3$)

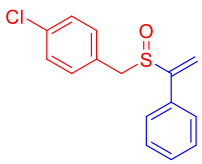




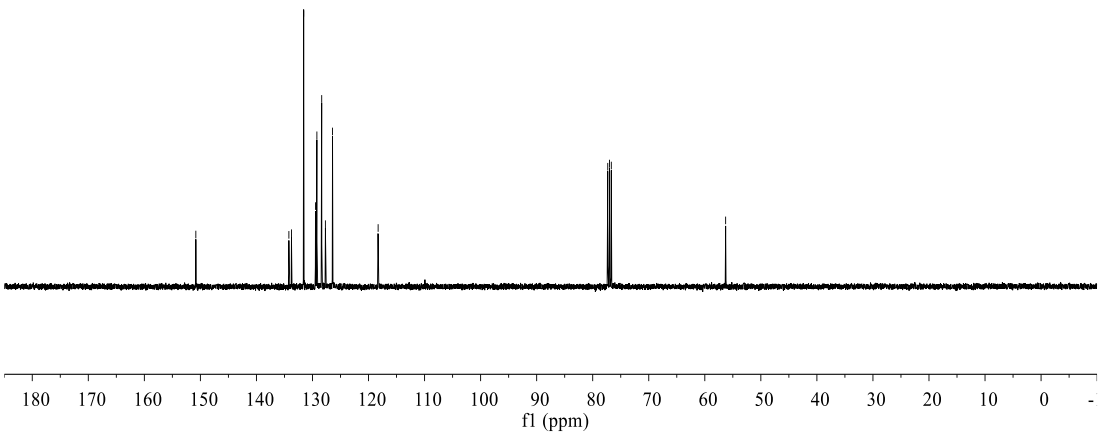
3at ^{1}H NMR (400 MHz, $CDCl_3$)

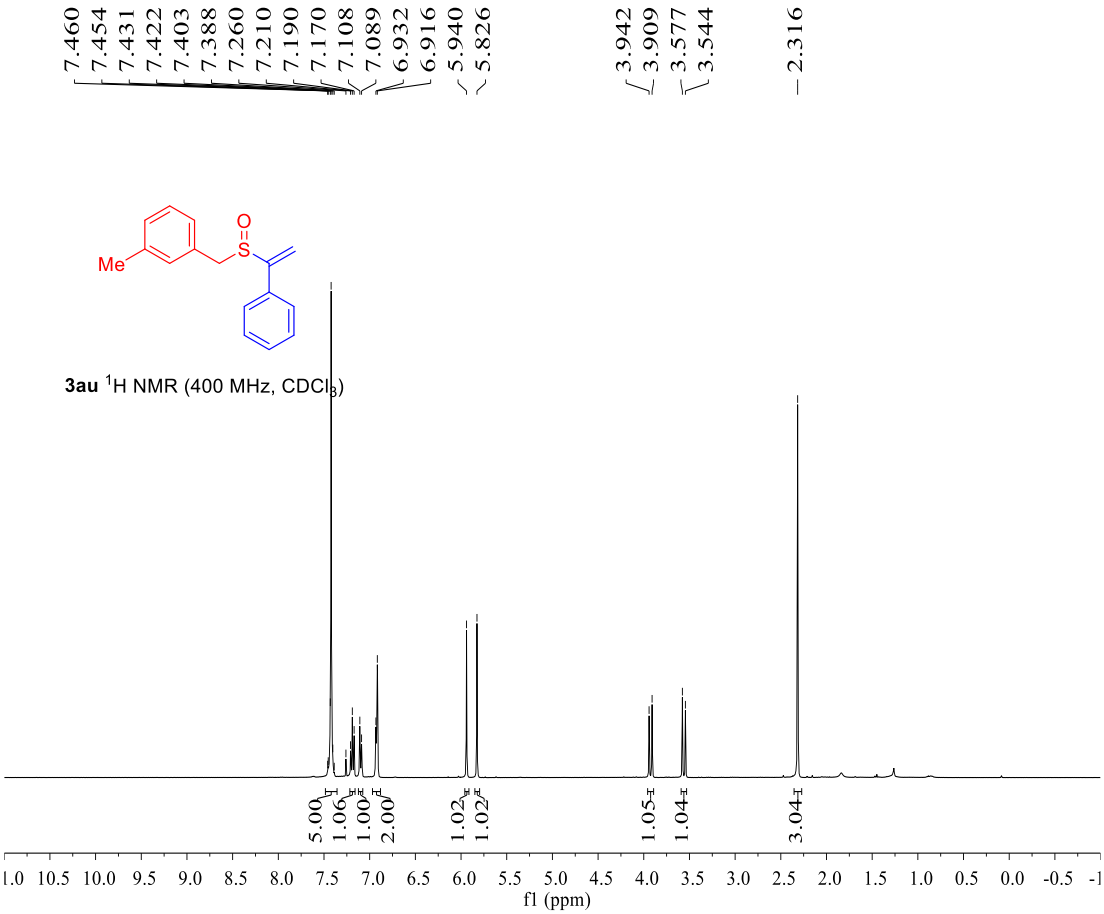




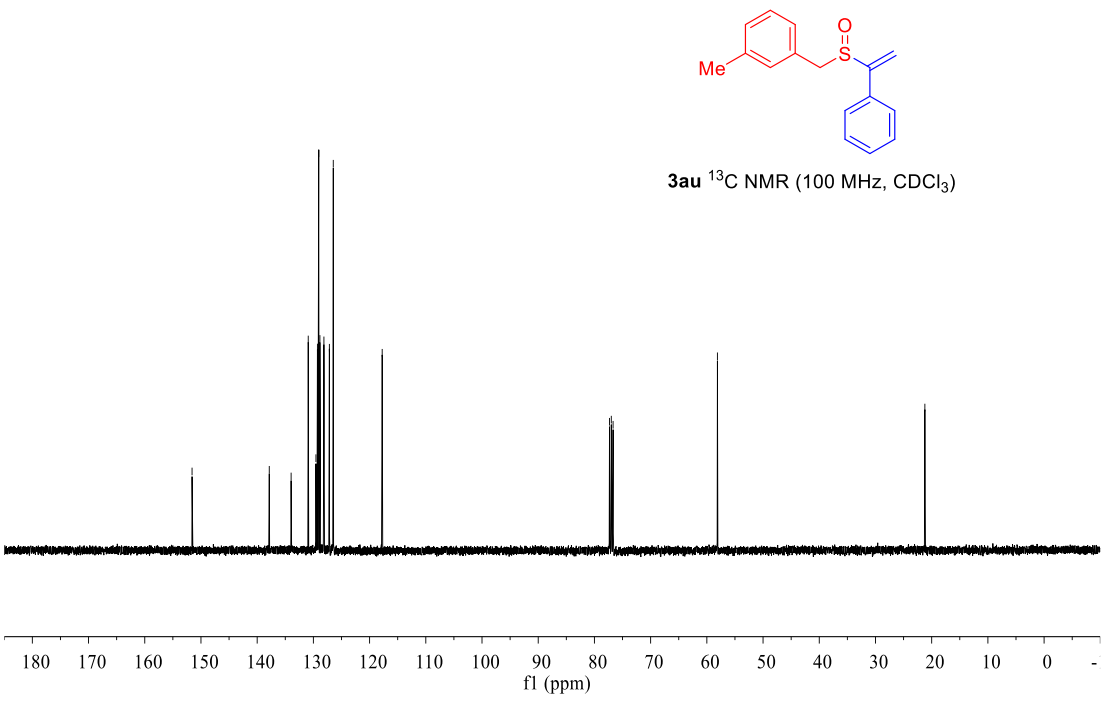


3at ^{13}C NMR (100 MHz, $CDCl_3$)

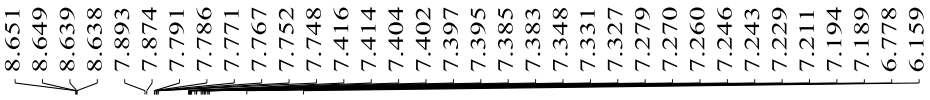


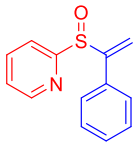


3au ^{1}H NMR (400 MHz, $CDCl_3$)

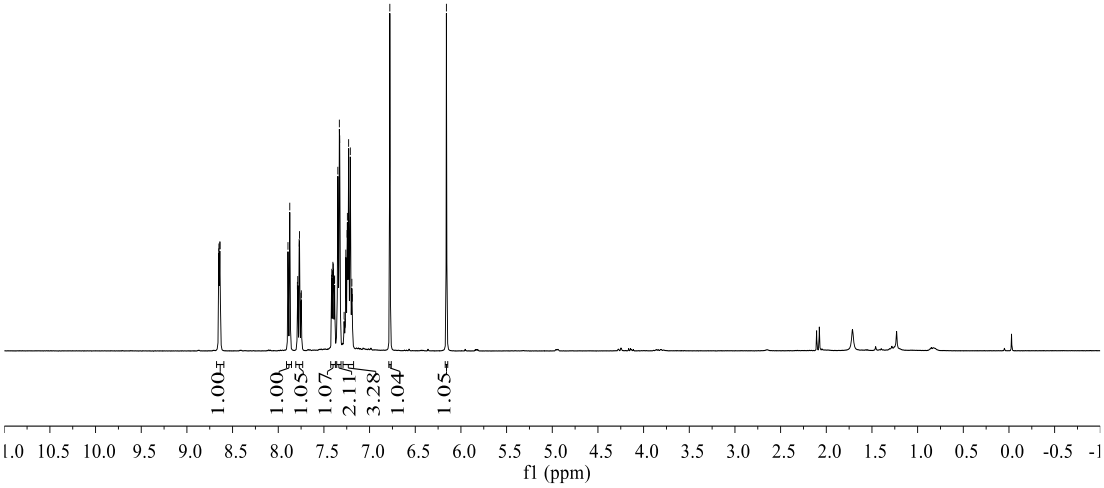


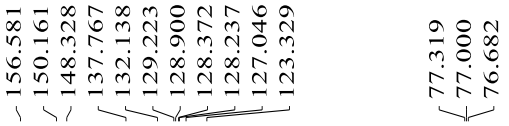
3au ^{13}C NMR (100 MHz, $CDCl_3$)

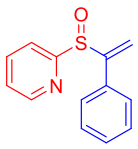




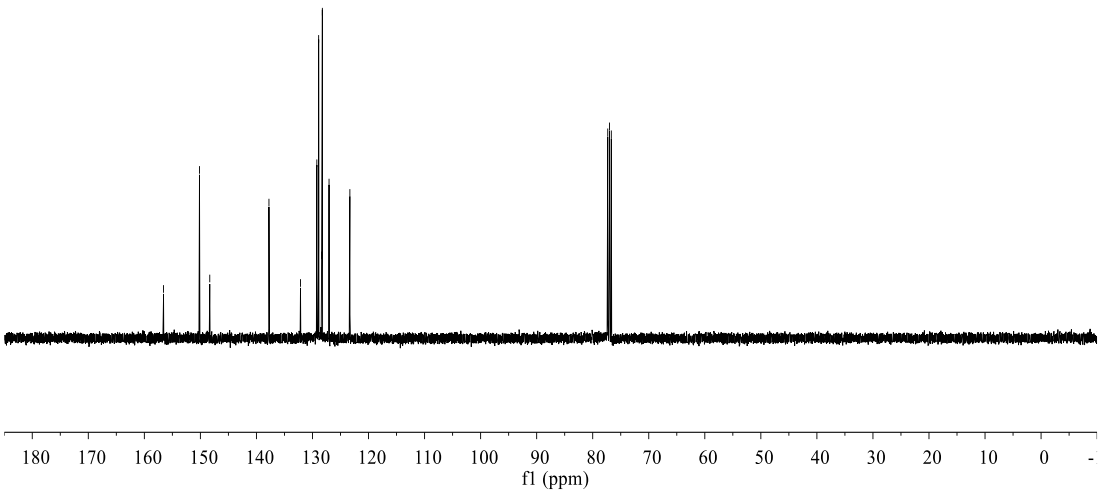
3av ^{1}H NMR (400 MHz, $CDCl_3$)

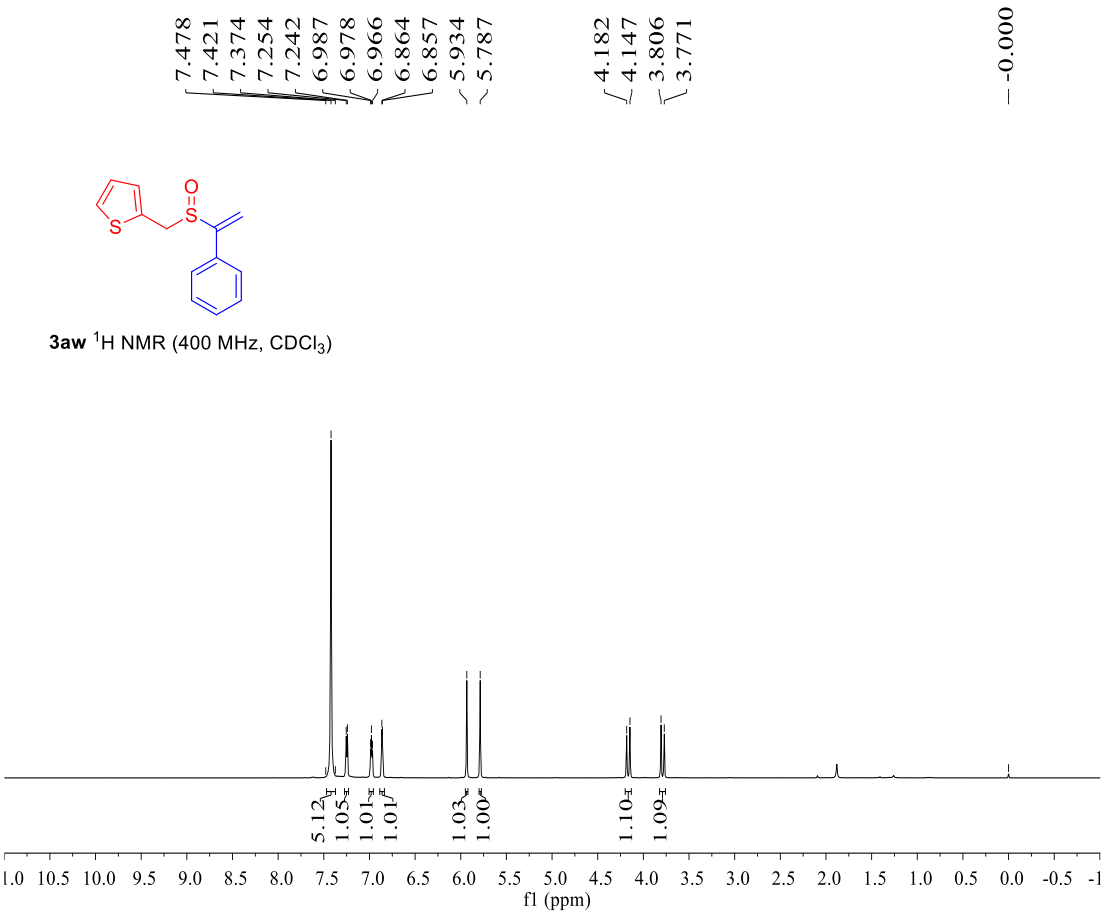




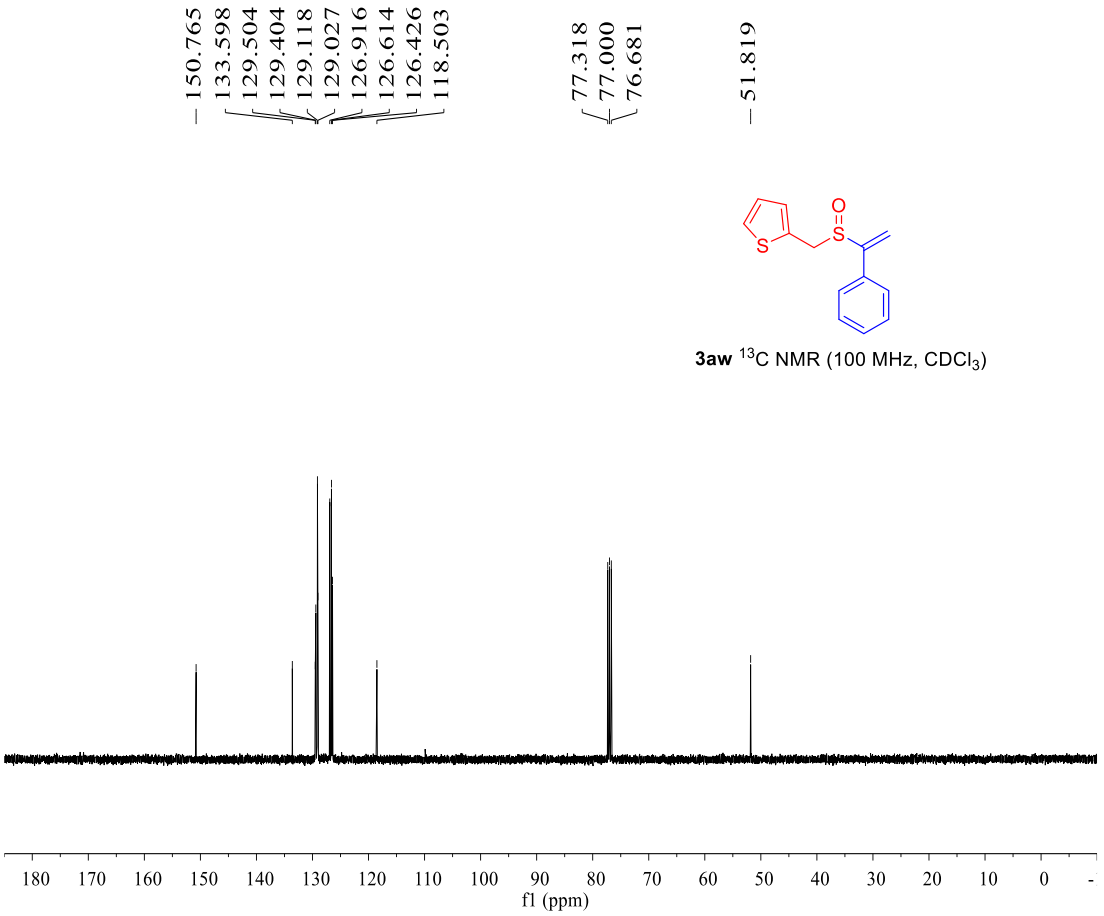


3av ^{13}C NMR (100 MHz, $CDCl_3$)

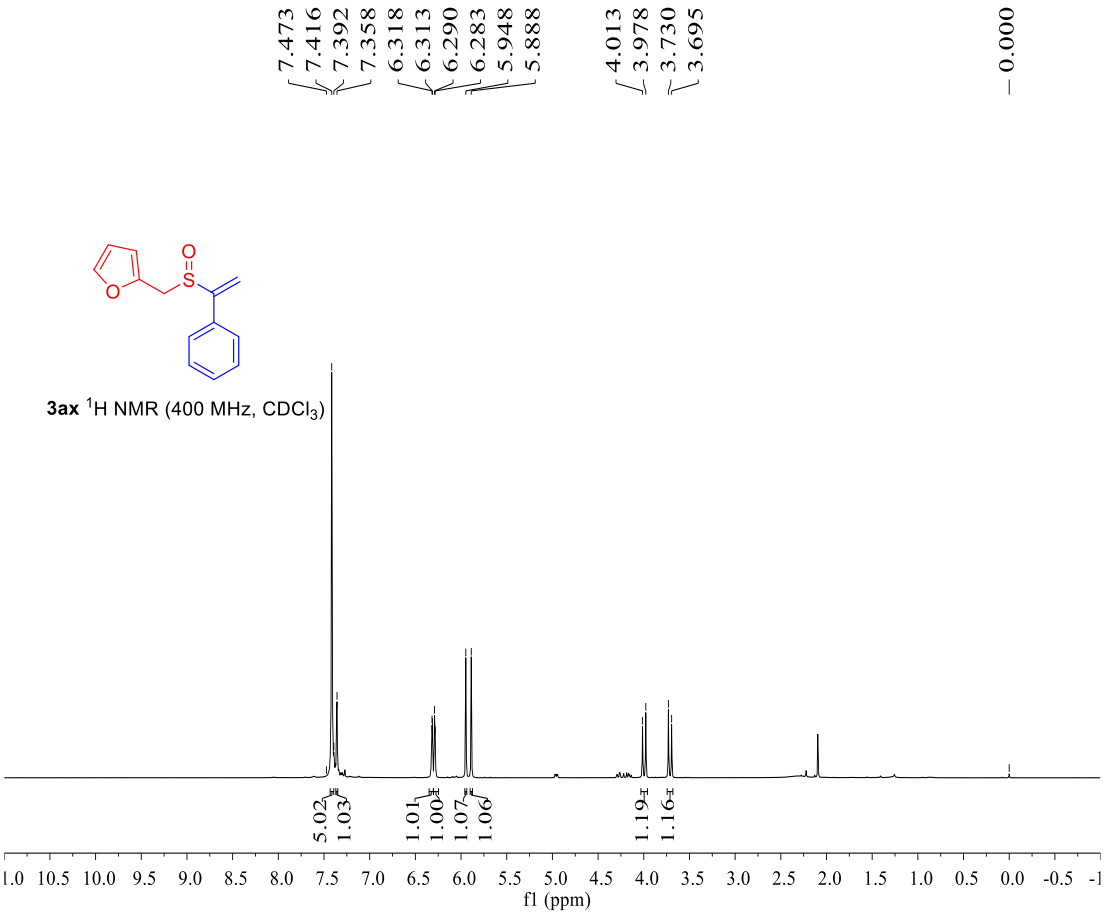




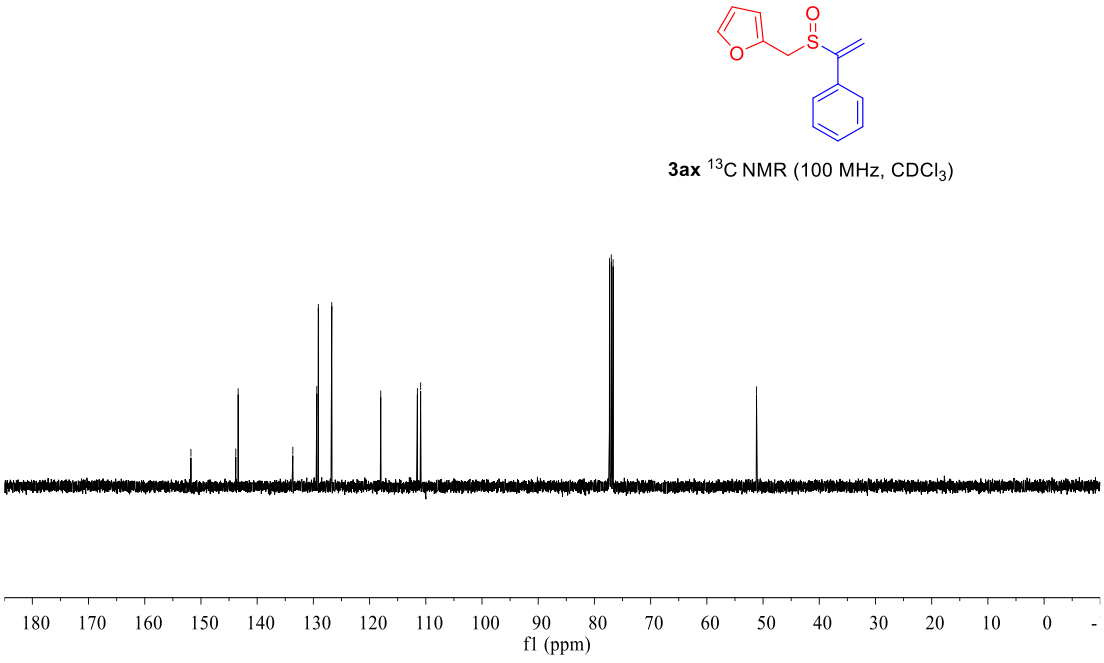
3aw ^{1}H NMR (400 MHz, $CDCl_3$)



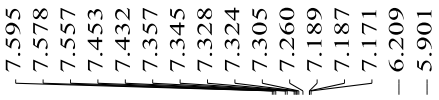
3aw ^{13}C NMR (100 MHz, $CDCl_3$)

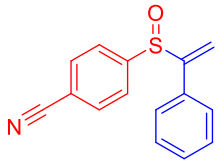


3ax ^{1}H NMR (400 MHz, $CDCl_3$)

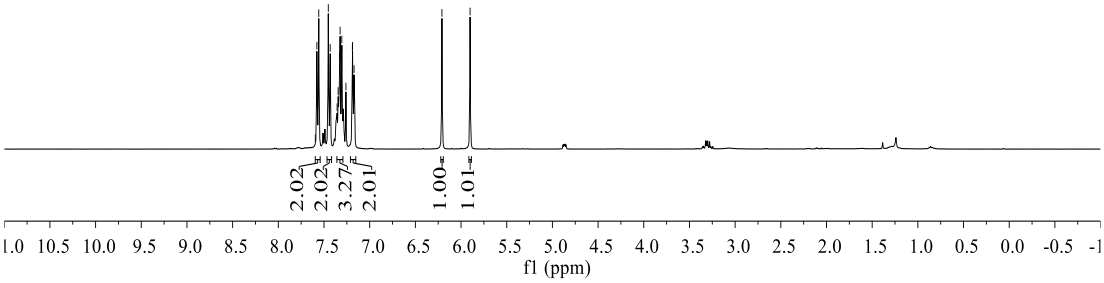


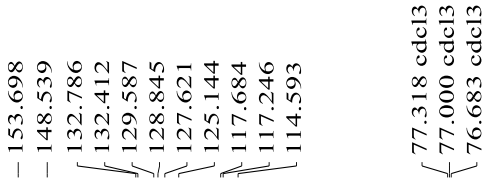
3ax ^{13}C NMR (100 MHz, $CDCl_3$)

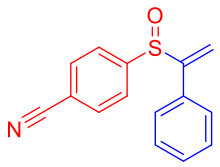




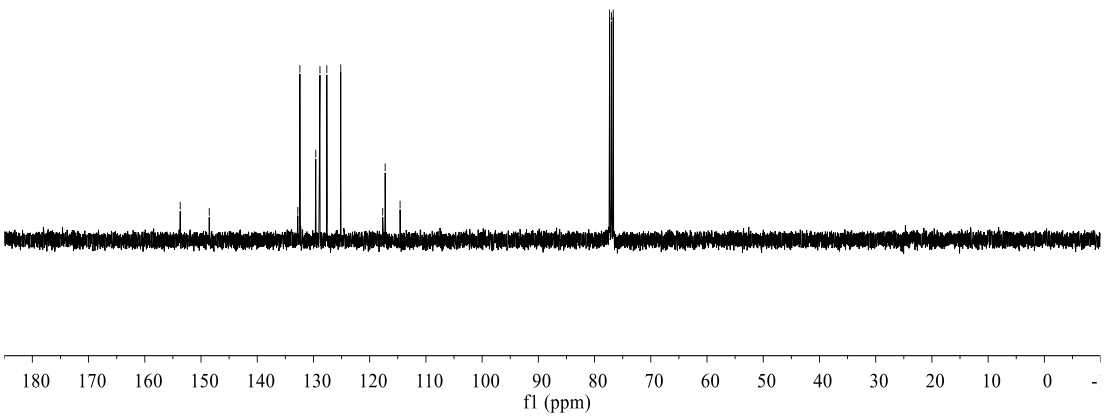
3ay ^{1}H NMR (400 MHZ, $CDCl_3$)

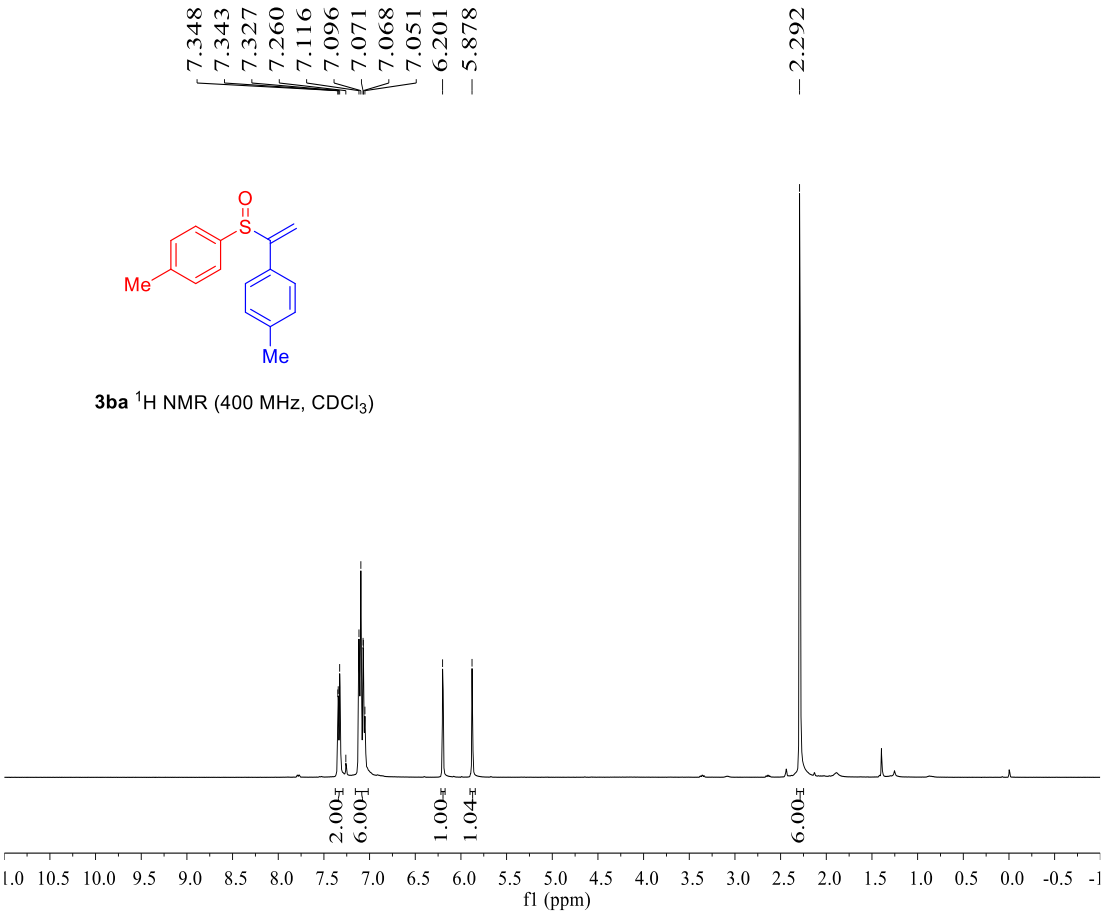




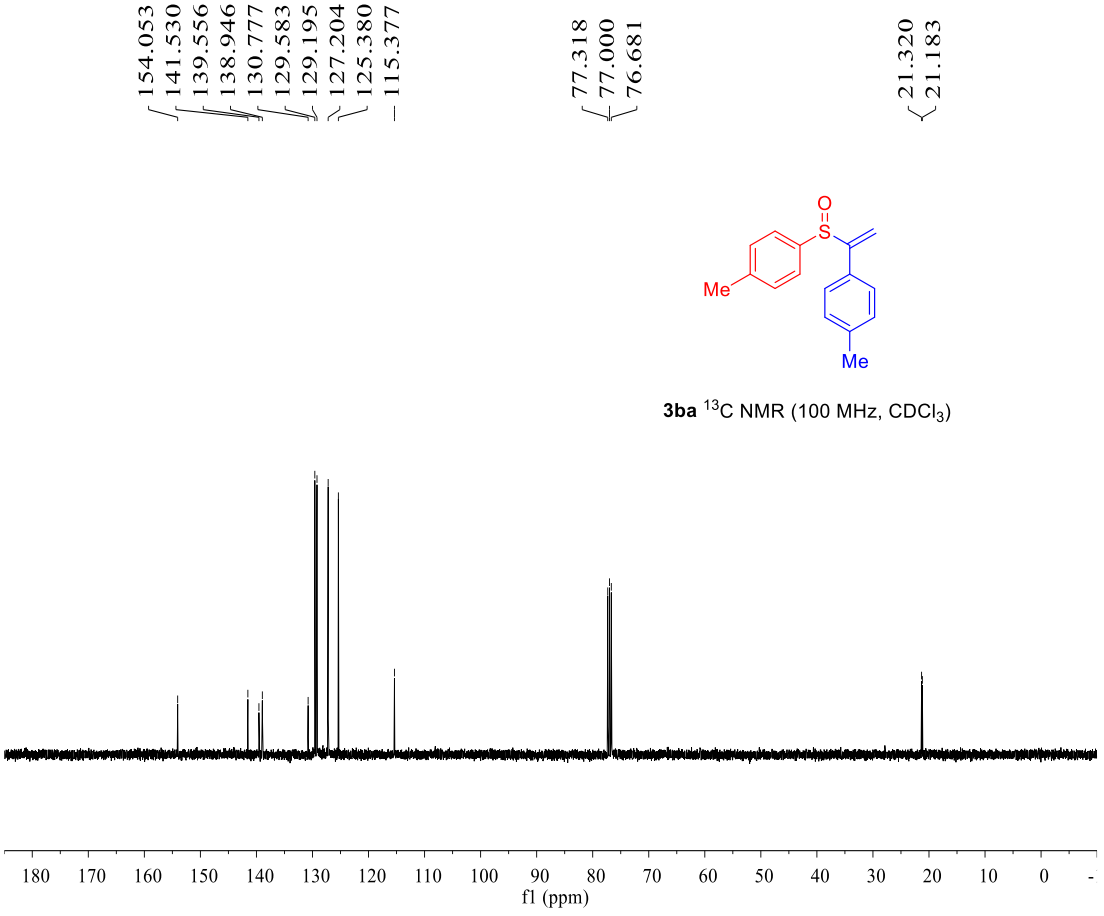


3ay ^{13}C NMR (100 MHZ, $CDCl_3$)

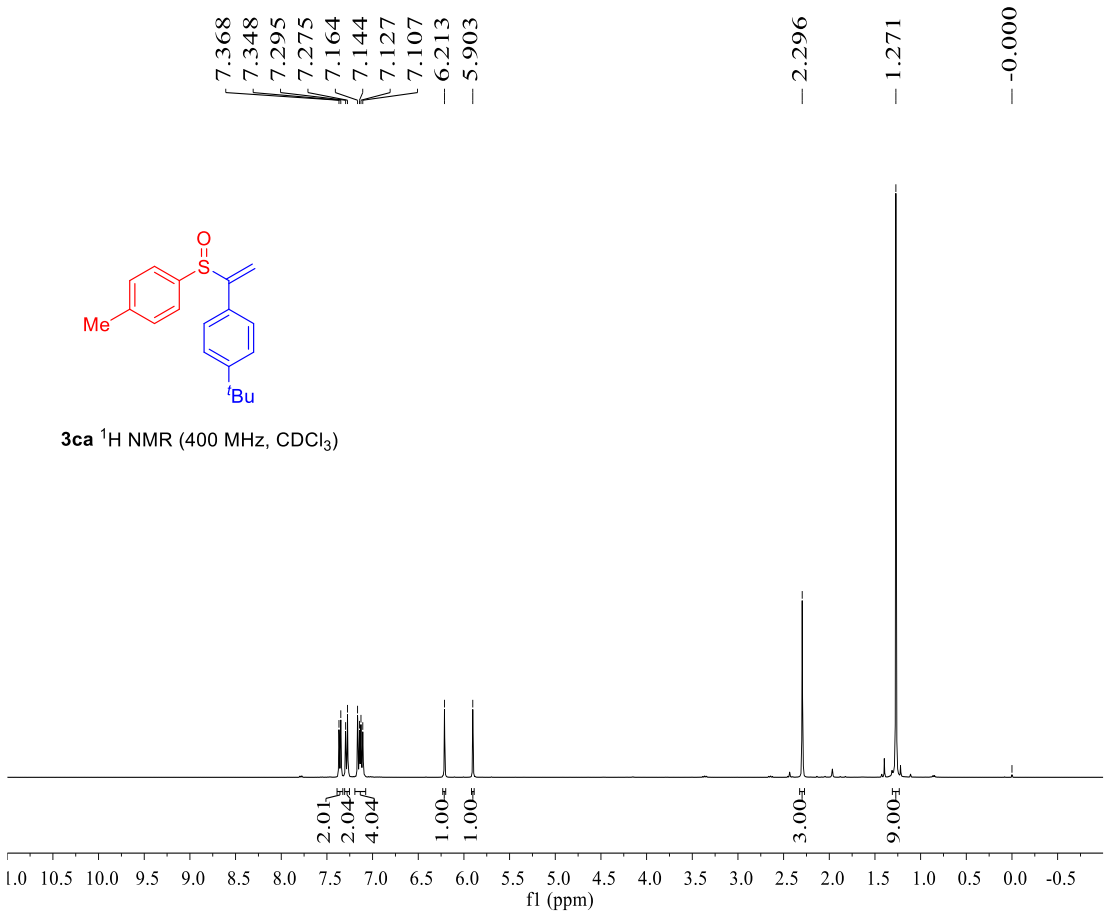




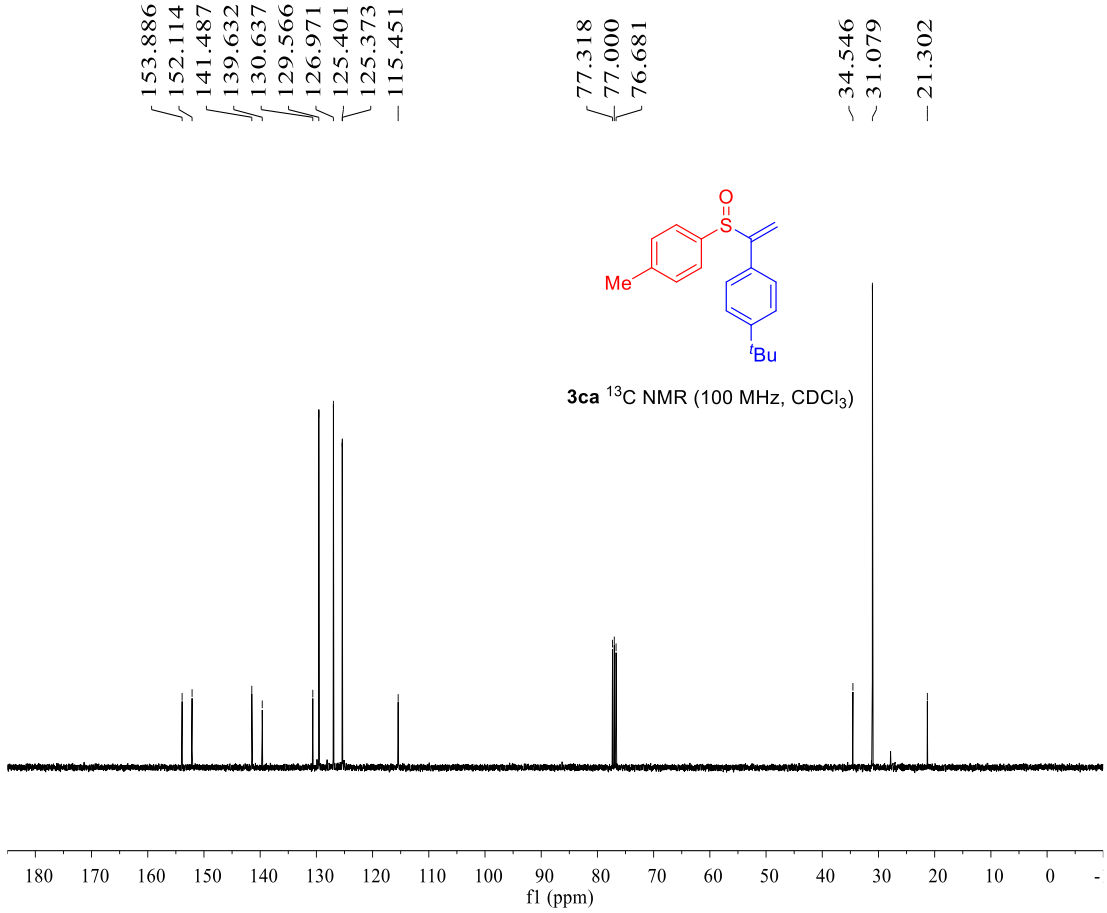
3ba ^{1}H NMR (400 MHz, $CDCl_3$)



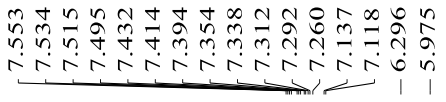
3ba ^{13}C NMR (100 MHz, $CDCl_3$)

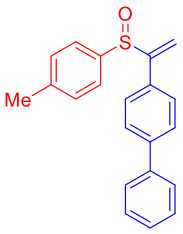


3ca ^{1}H NMR (400 MHz, $CDCl_3$)

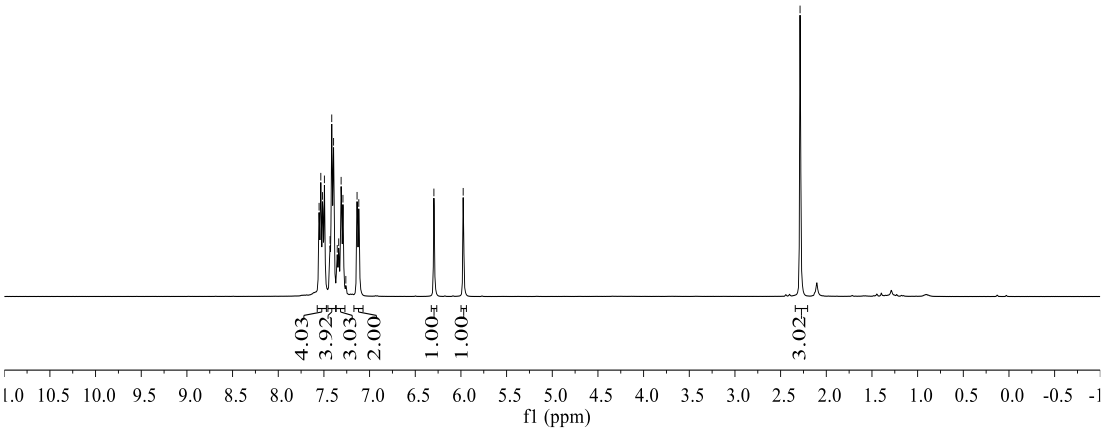


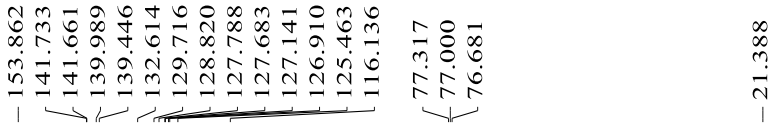
3ca ^{13}C NMR (100 MHz, $CDCl_3$)

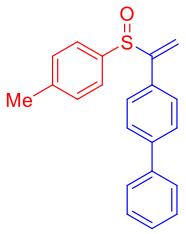




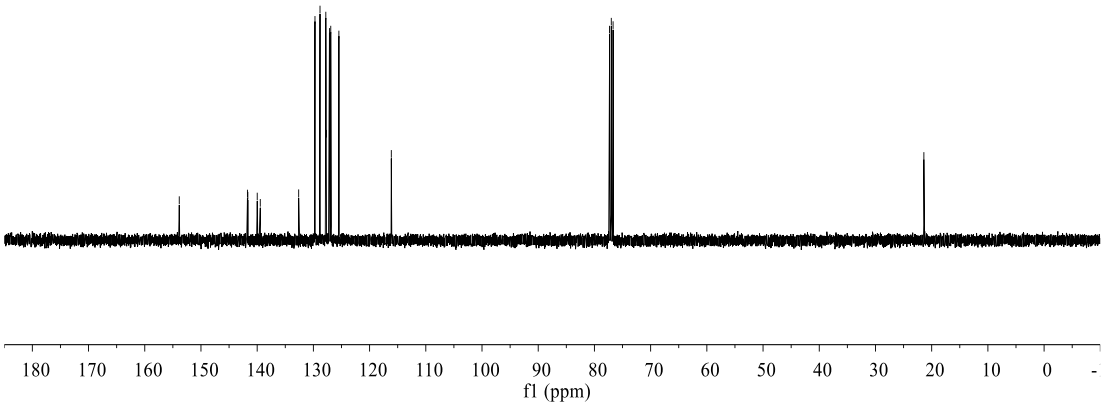
3da ^{1}H NMR (400 MHz, $CDCl_3$)

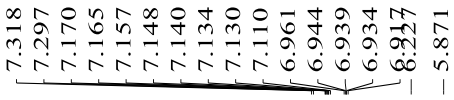


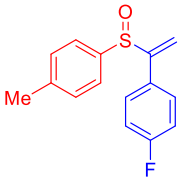




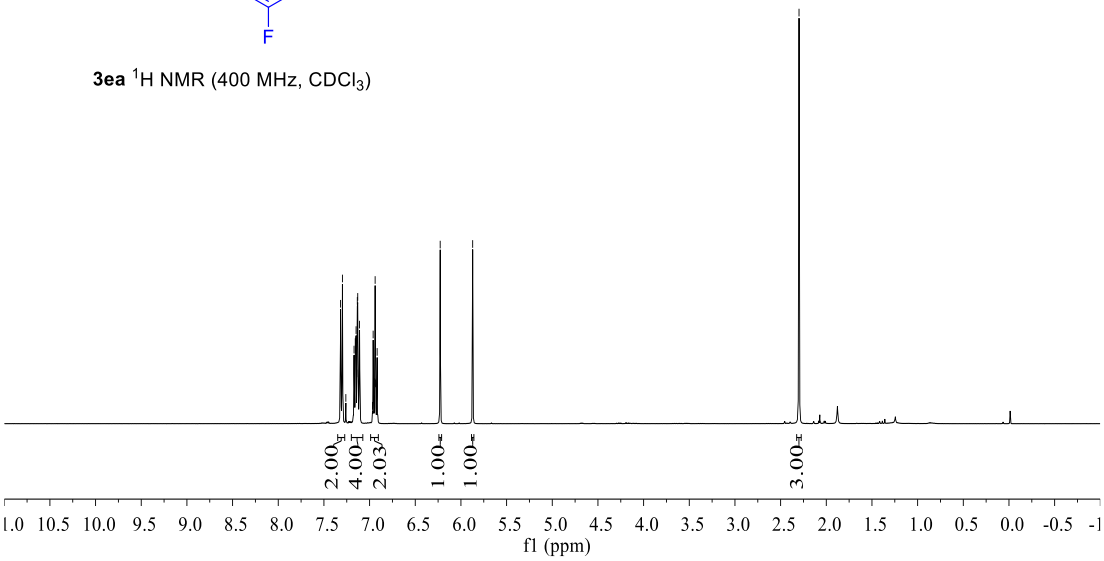
3da ^{13}C NMR (100 MHz, $CDCl_3$)

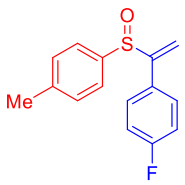




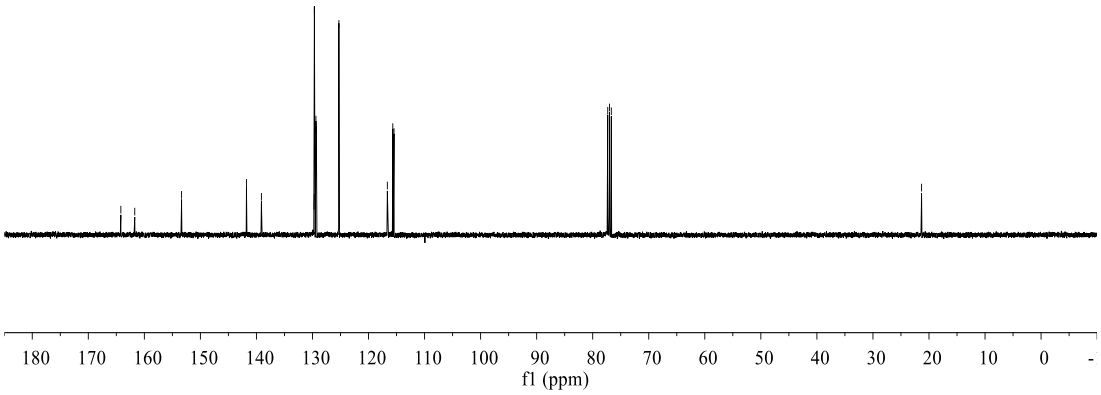


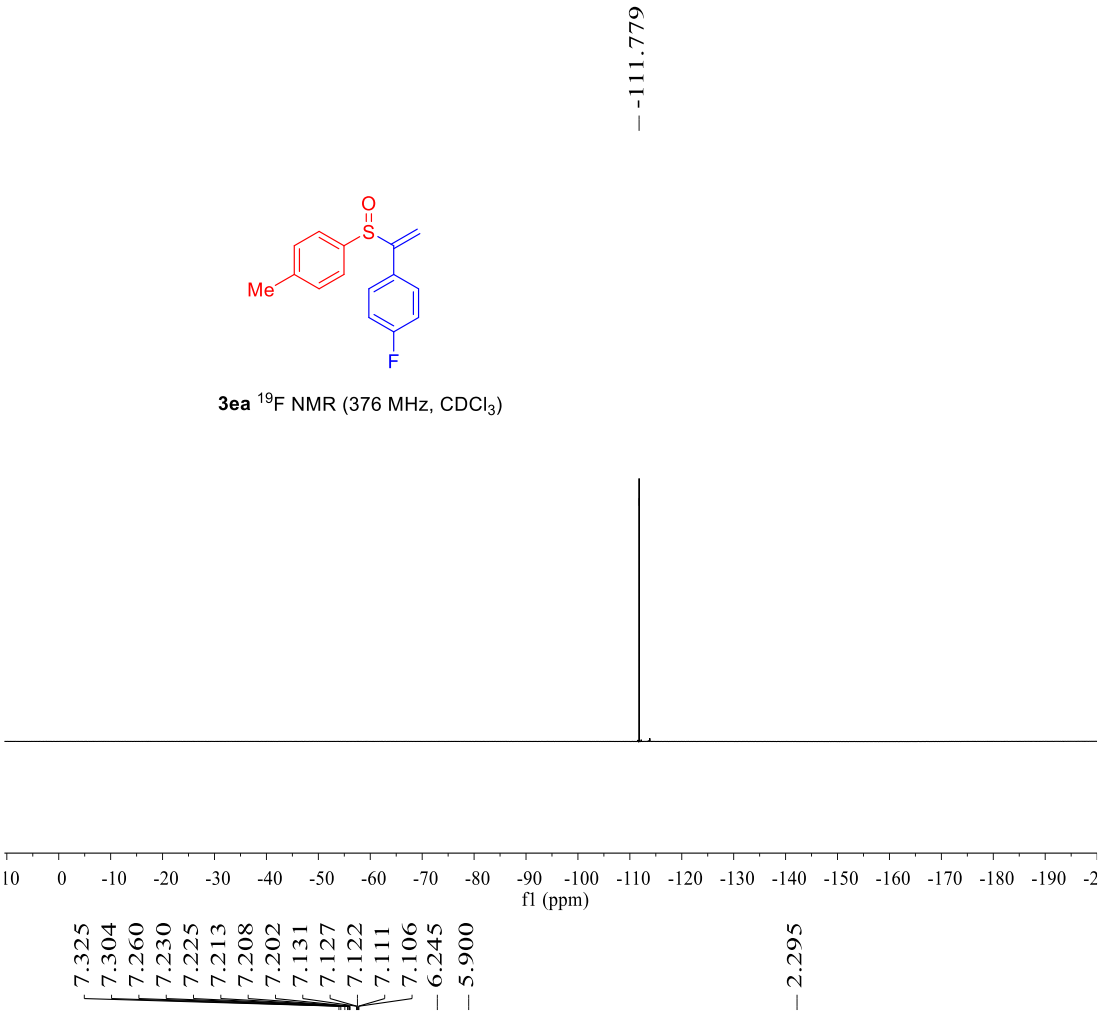
3ea ^{1}H NMR (400 MHz, $CDCl_3$)



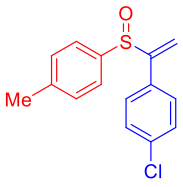


3ea ^{13}C NMR (100 MHz, $CDCl_3$)

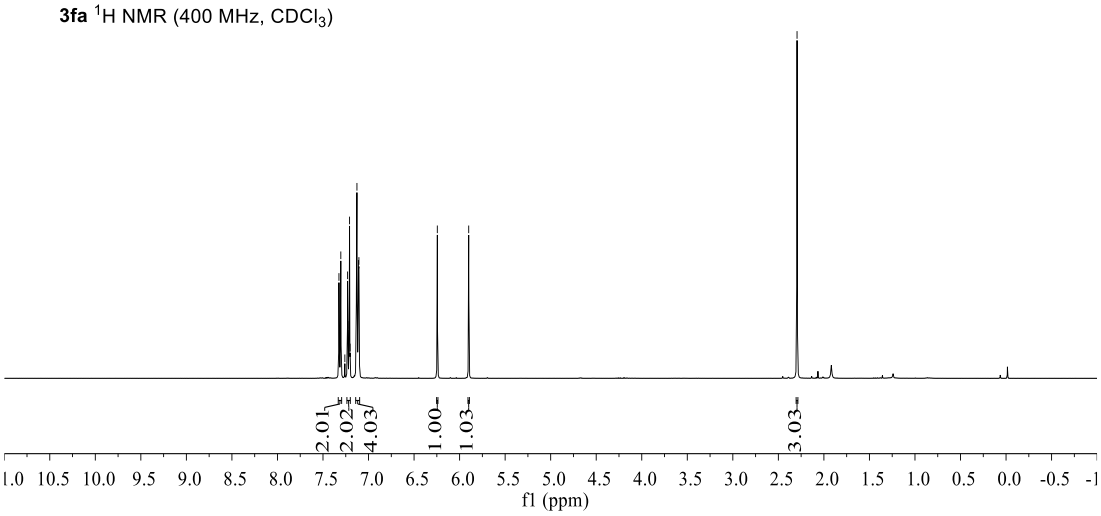


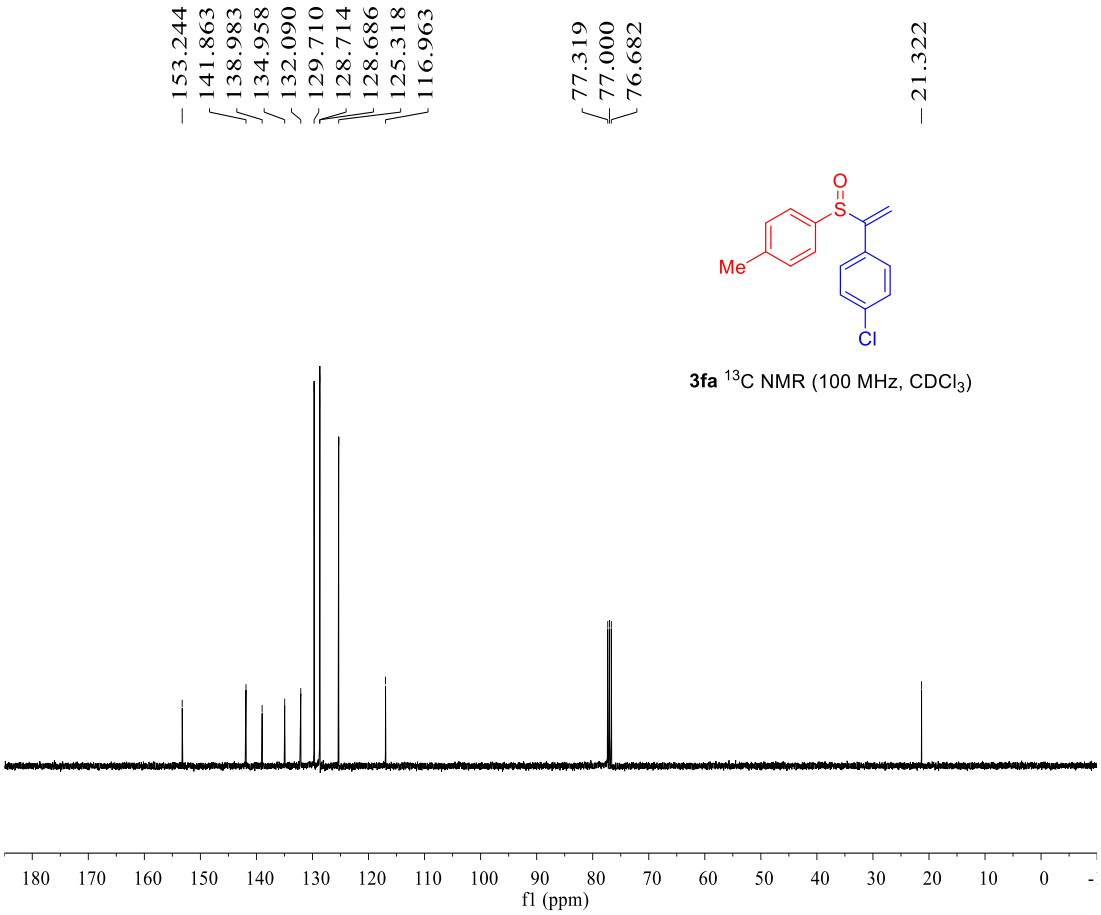


3ea ^{19}F NMR (376 MHz, $CDCl_3$)

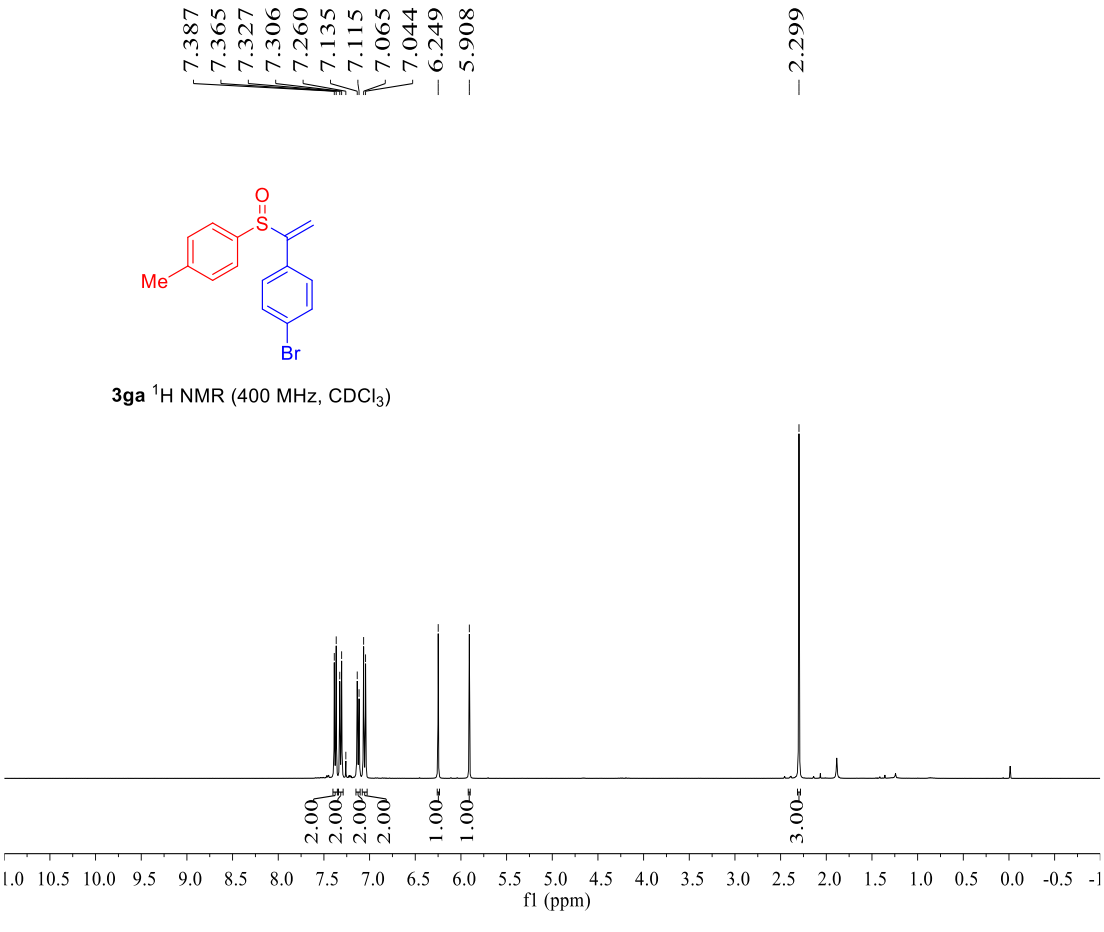


3fa ^{1}H NMR (400 MHz, $CDCl_3$)

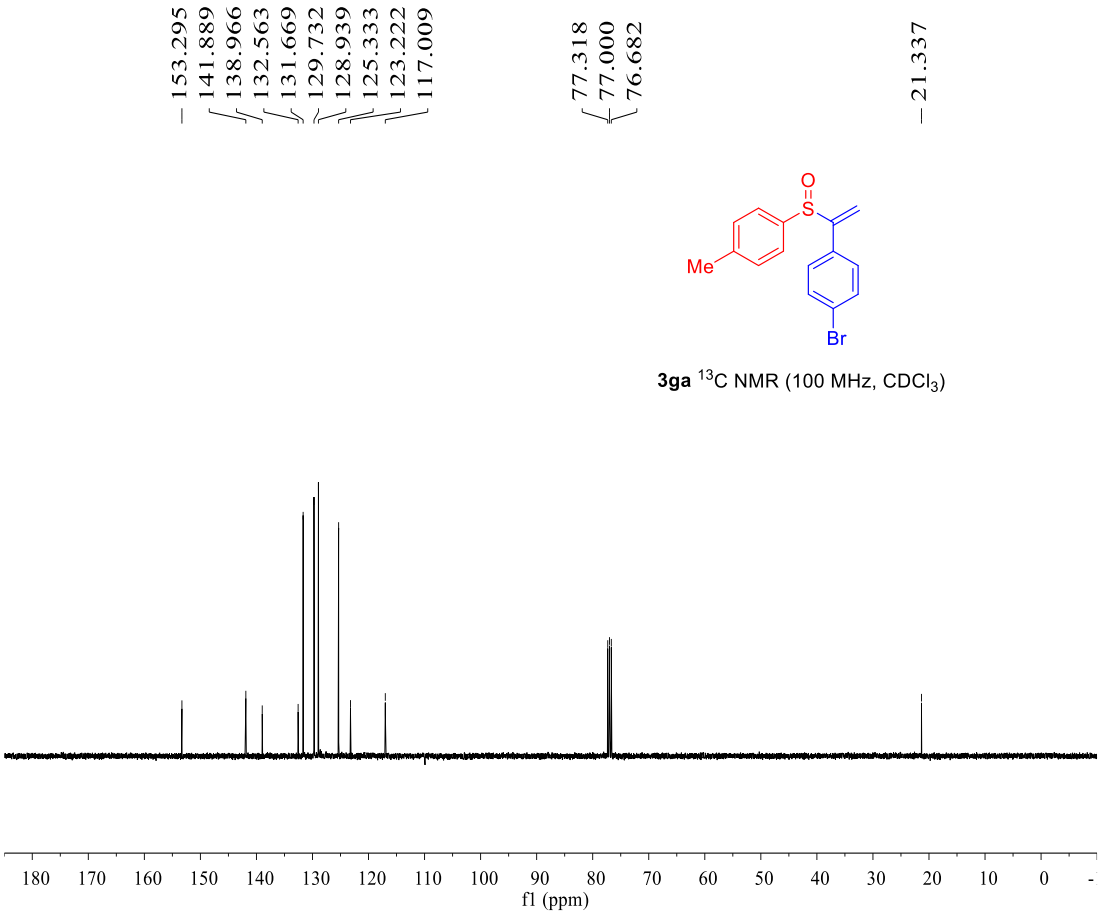




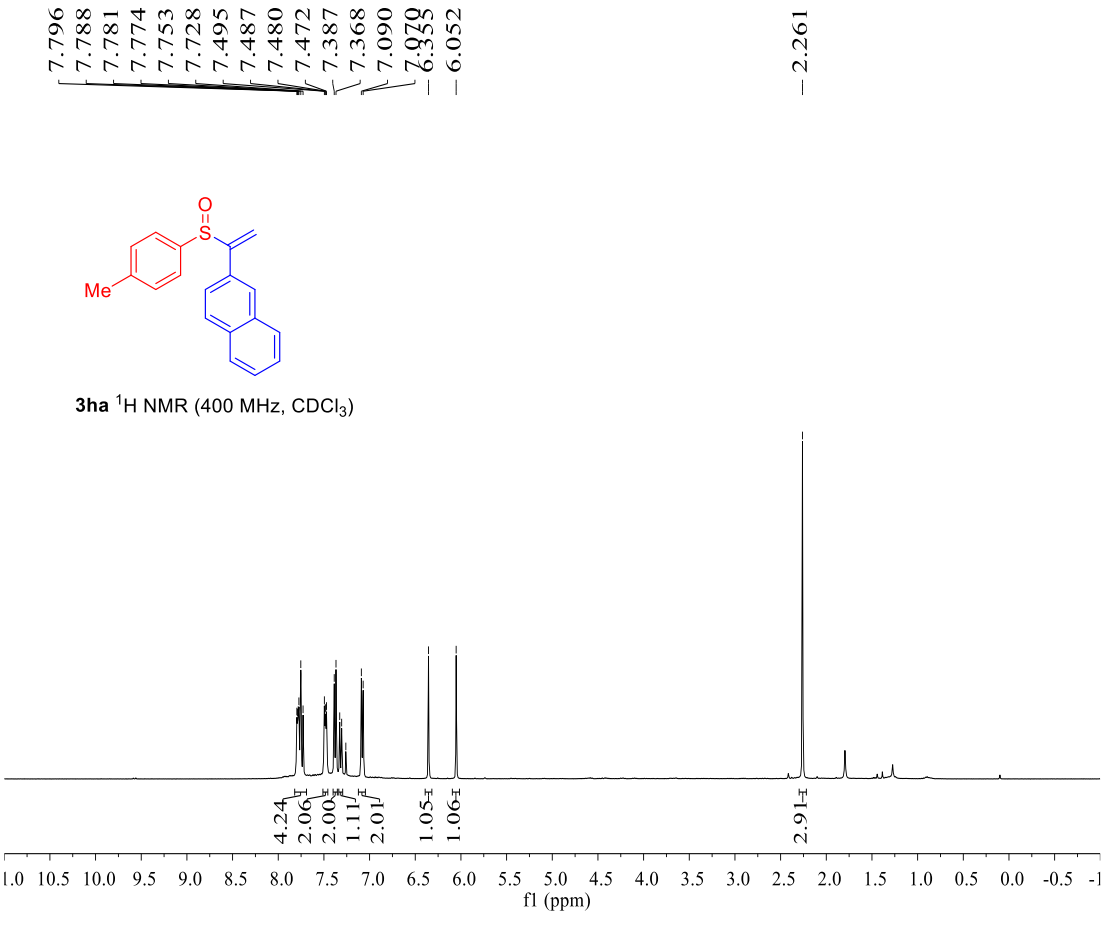
3fa ^{13}C NMR (100 MHz, $CDCl_3$)



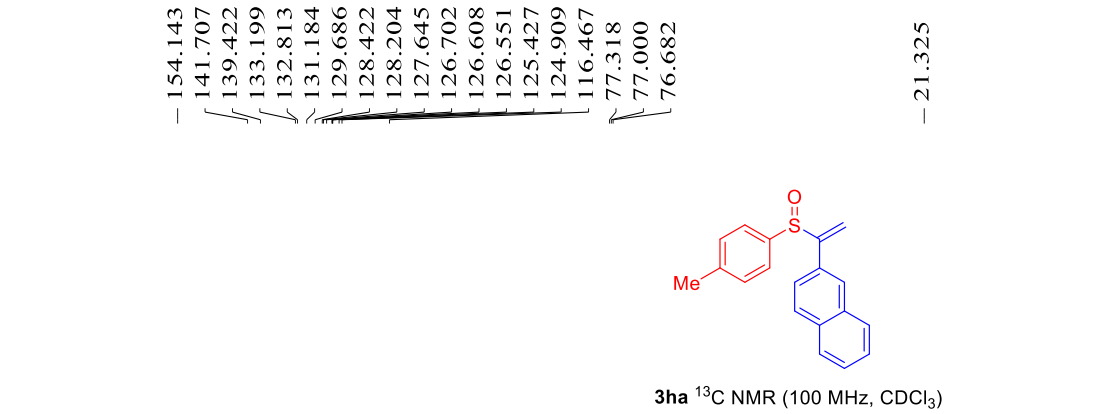
3ga ^{1}H NMR (400 MHz, $CDCl_3$)



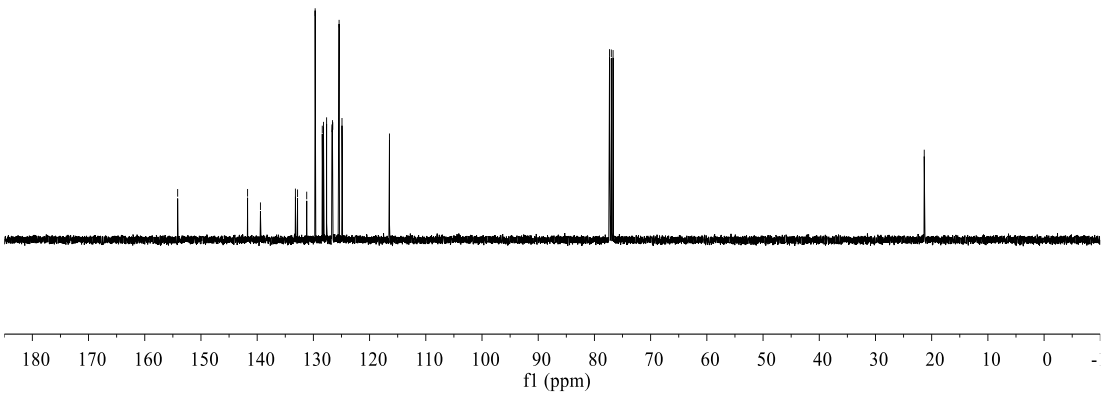
3ga ^{13}C NMR (100 MHz, $CDCl_3$)

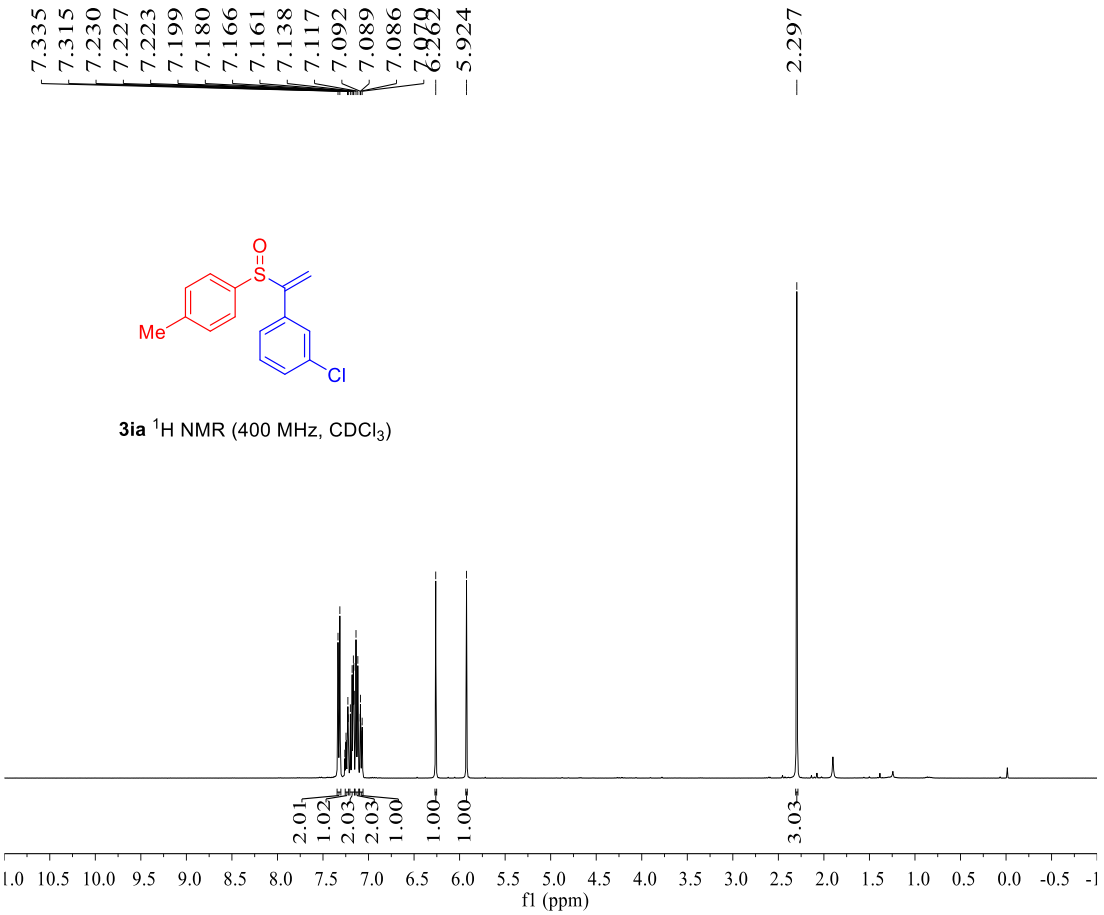


3ha ^{1}H NMR (400 MHz, $CDCl_3$)

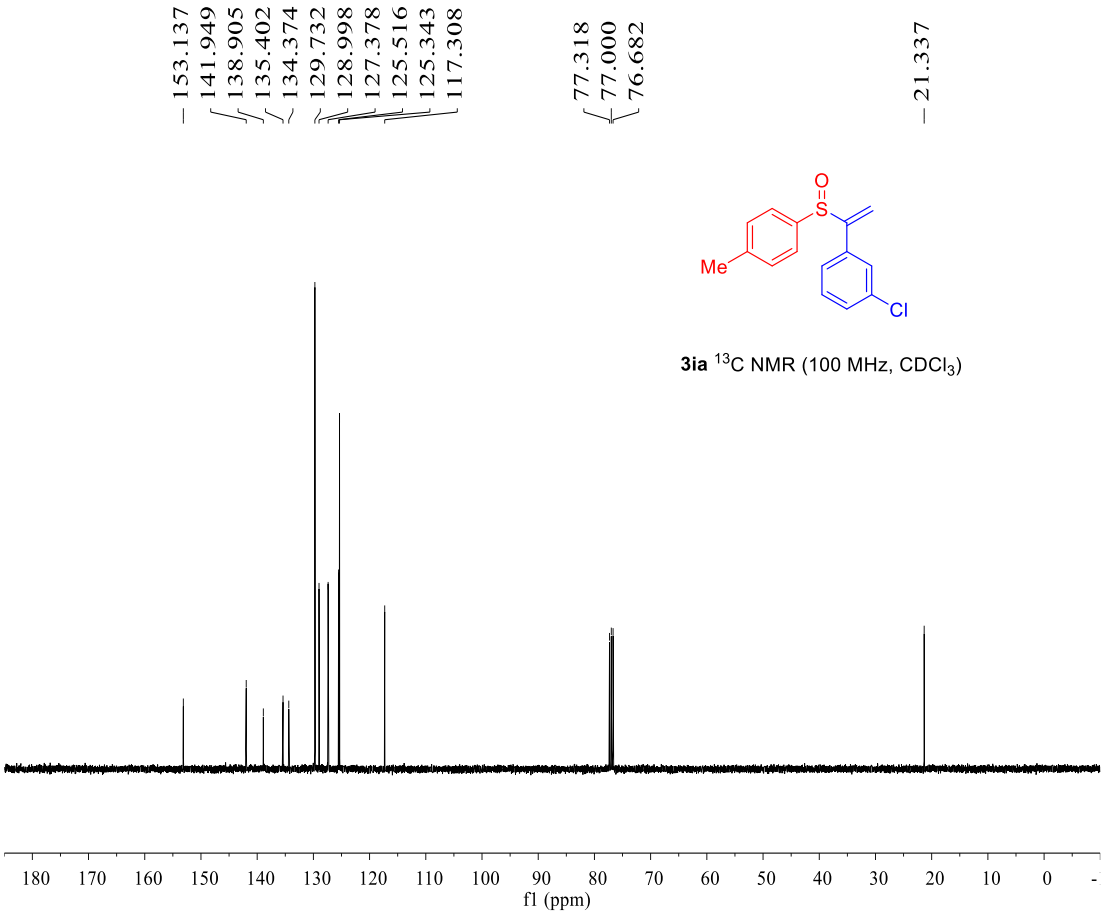


3ha ^{13}C NMR (100 MHz, $CDCl_3$)

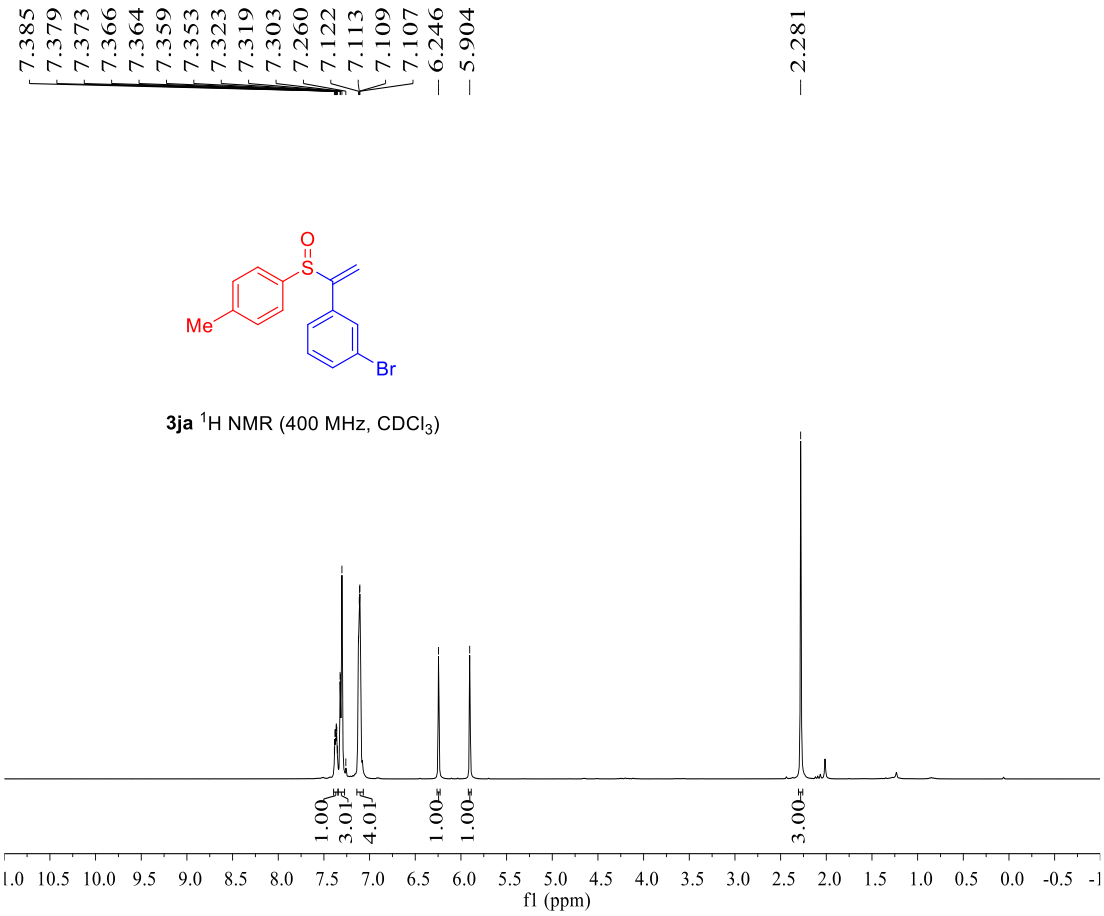




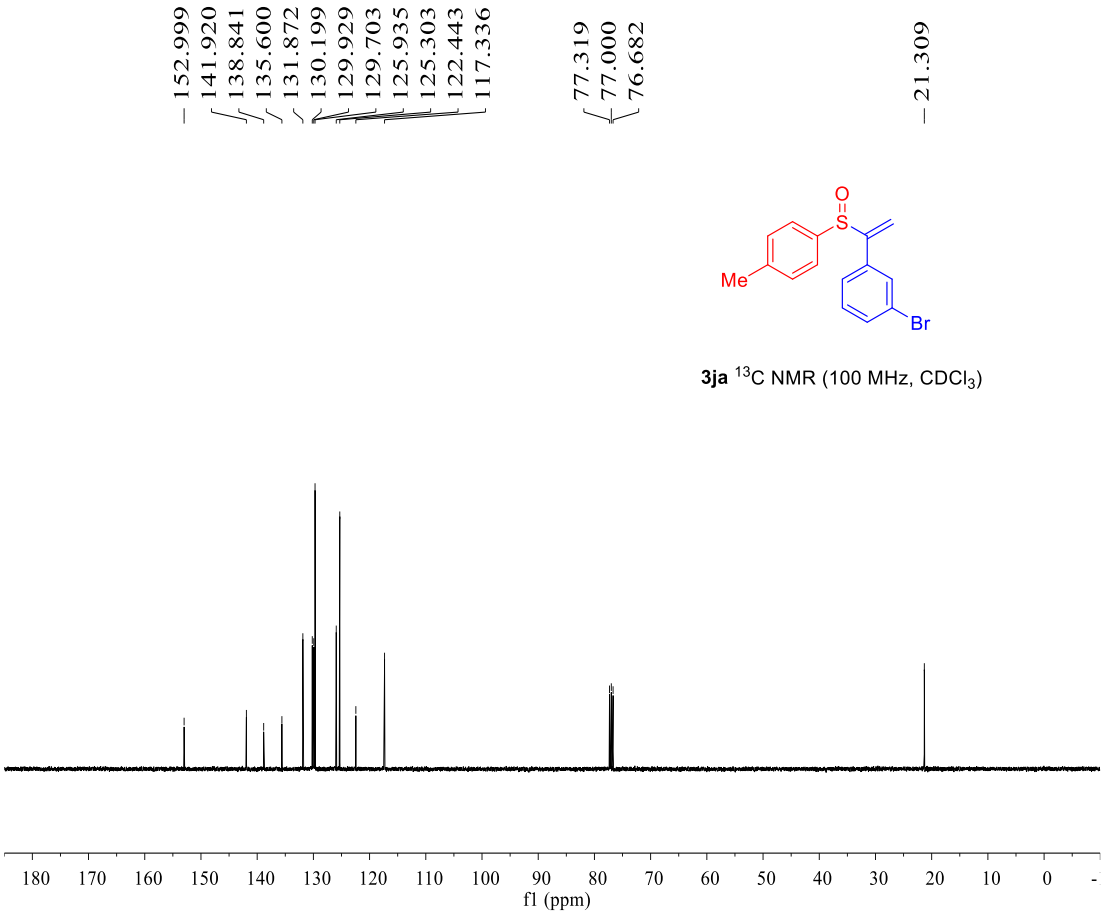
3ia ^{1}H NMR (400 MHz, $CDCl_3$)



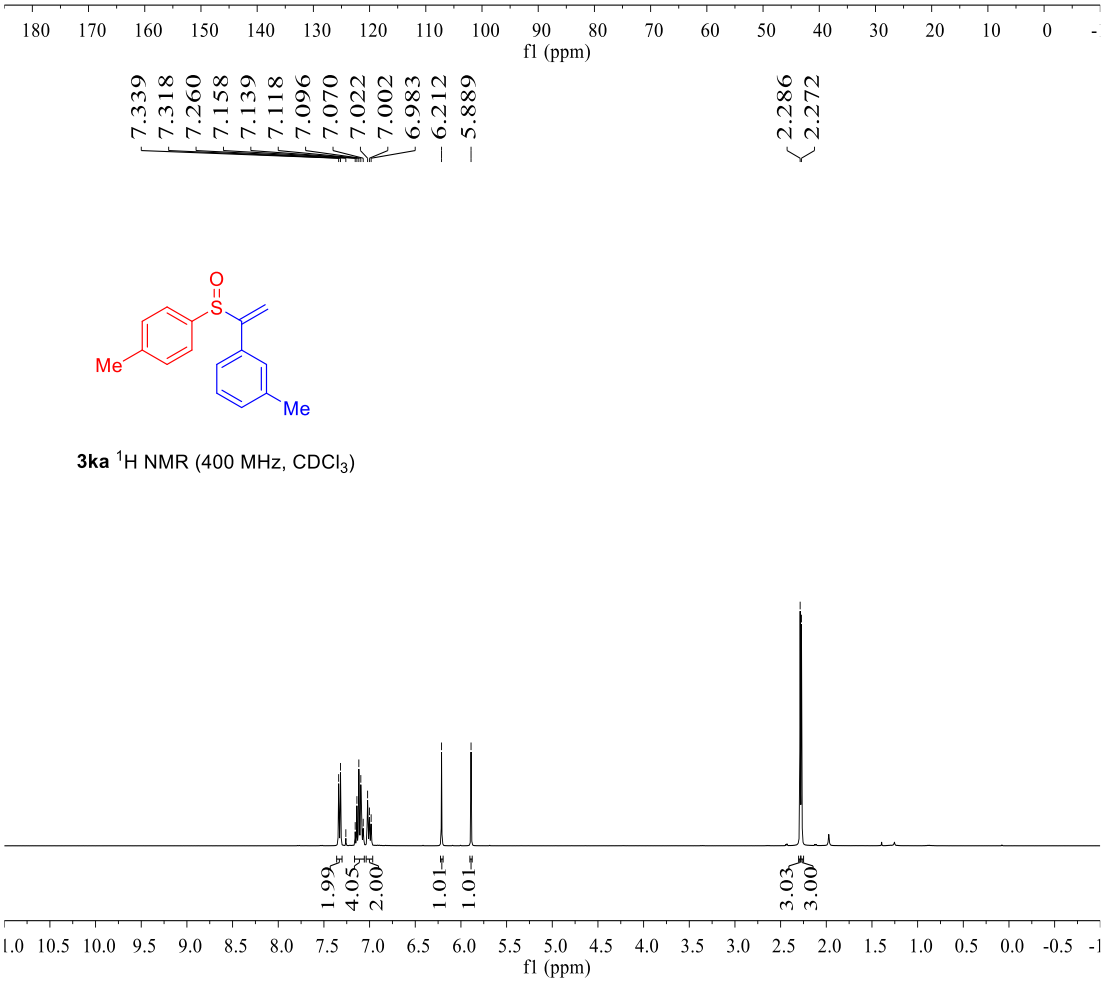
3ia ^{13}C NMR (100 MHz, $CDCl_3$)



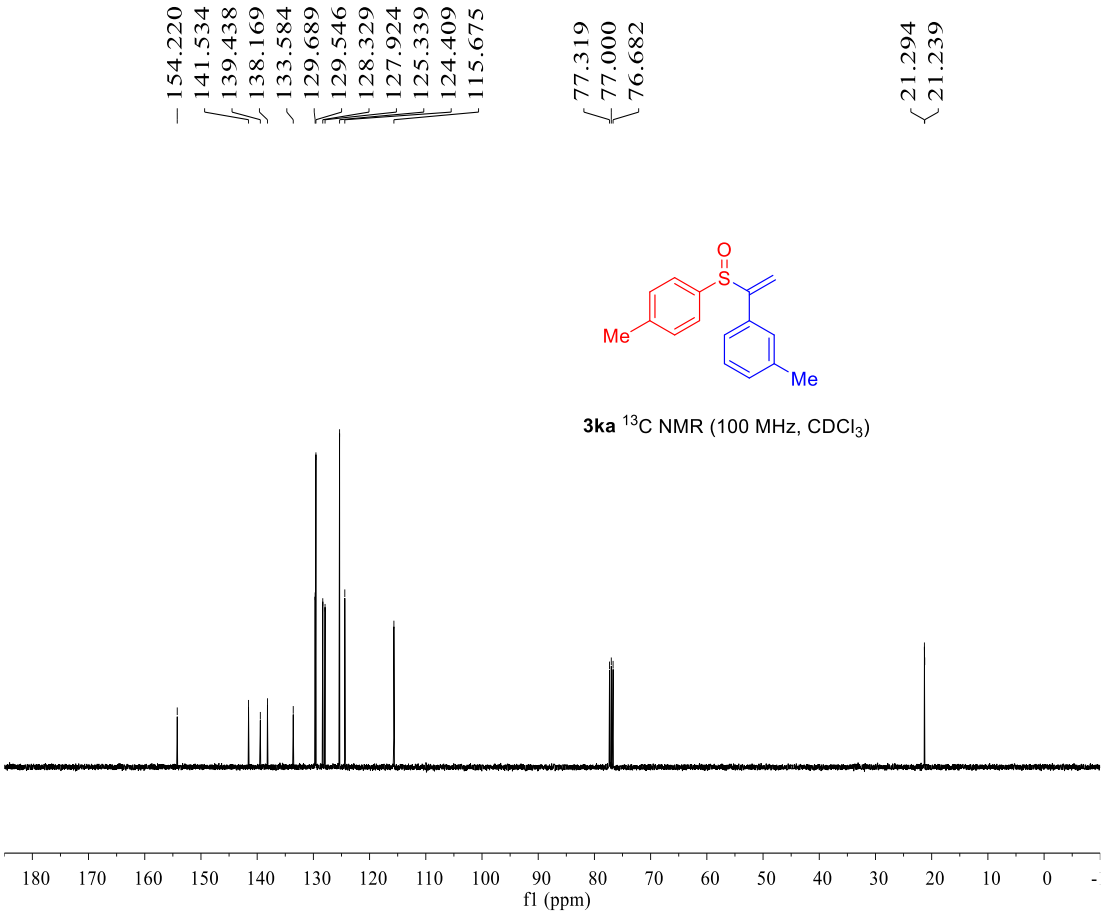
3ja ^{1}H NMR (400 MHz, $CDCl_3$)



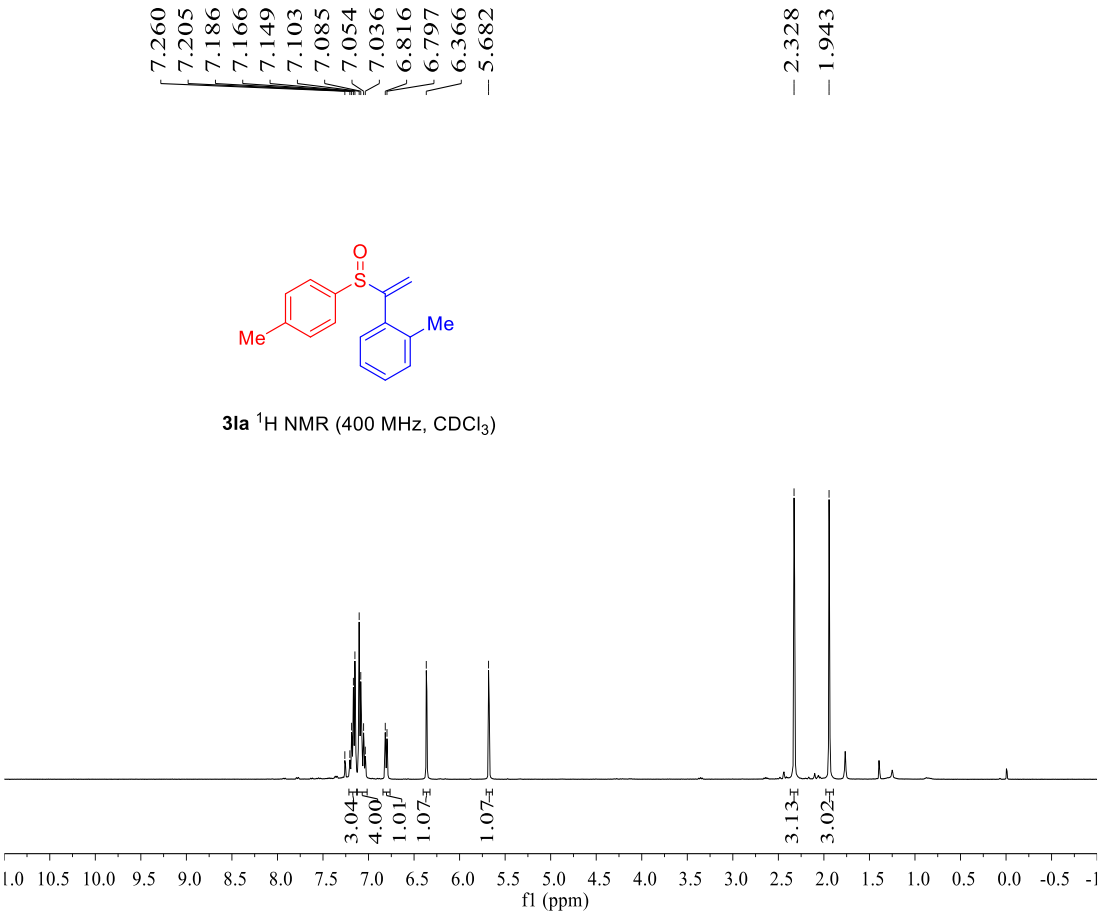
3ja ^{13}C NMR (100 MHz, $CDCl_3$)



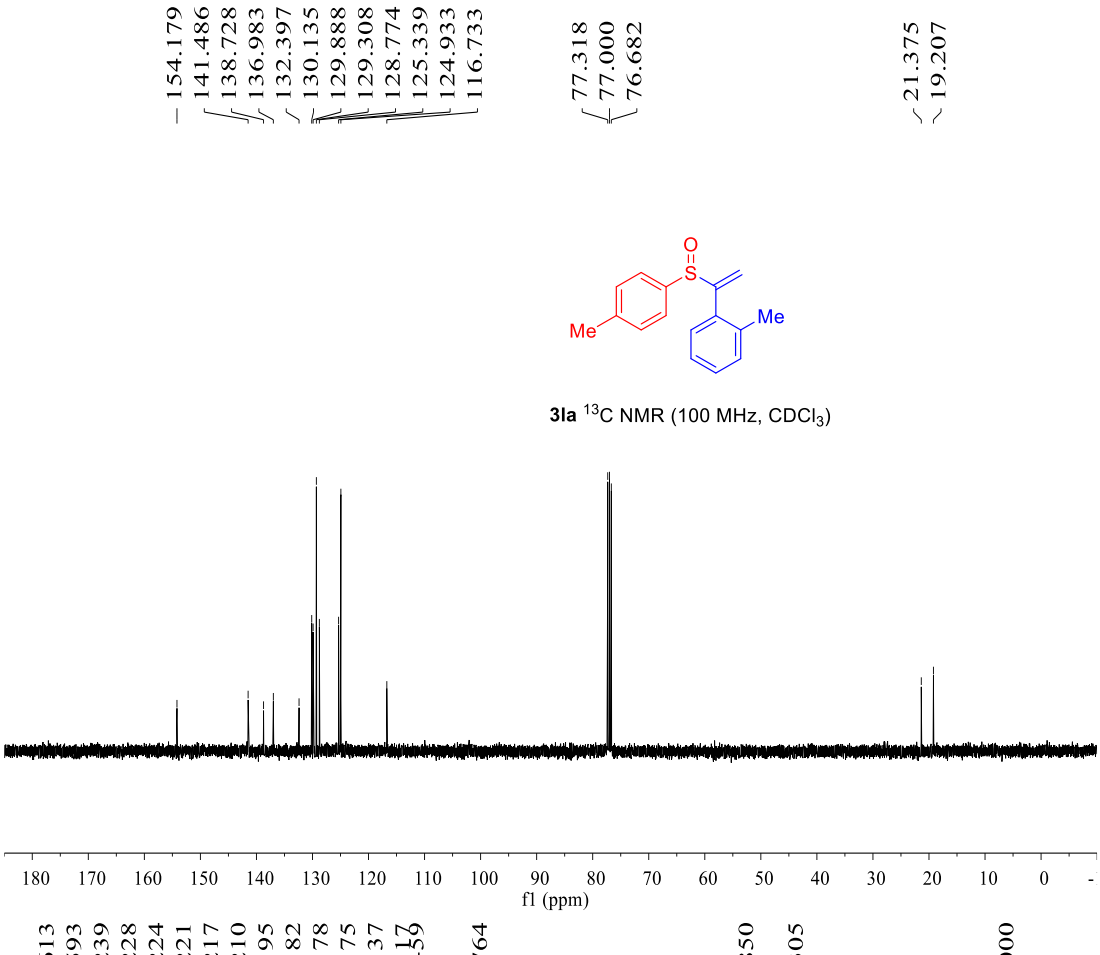
3ka ^{1}H NMR (400 MHz, $CDCl_3$)



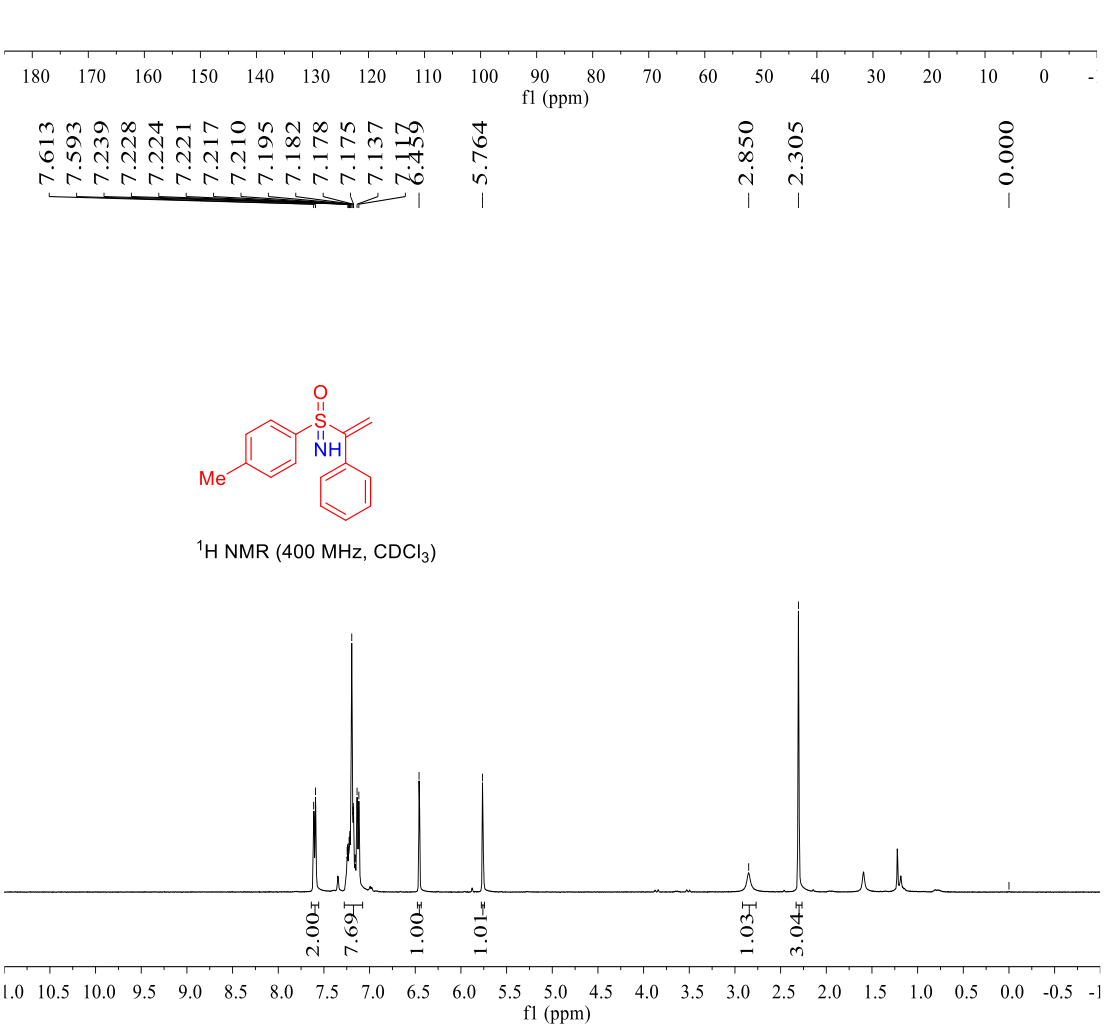
3ka ^{13}C NMR (100 MHz, $CDCl_3$)



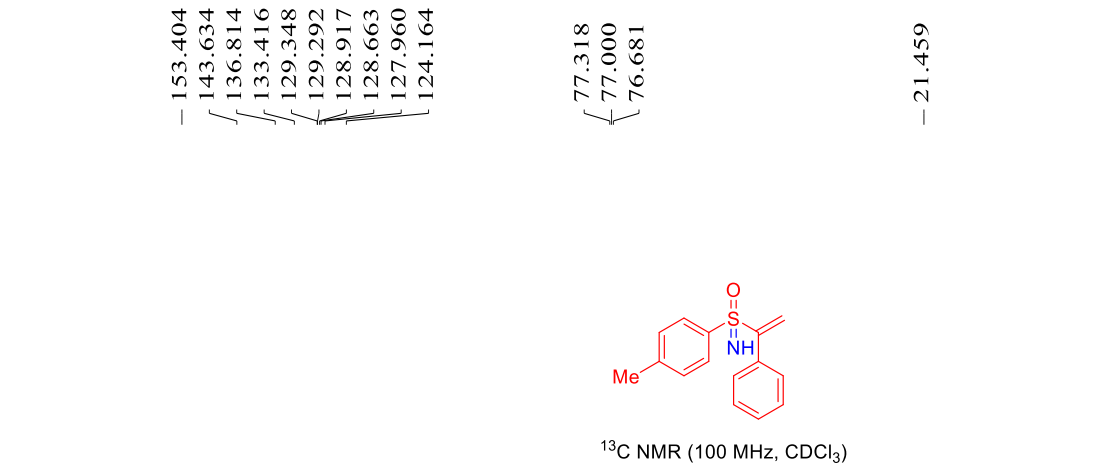
3la ^{1}H NMR (400 MHz, $CDCl_3$)

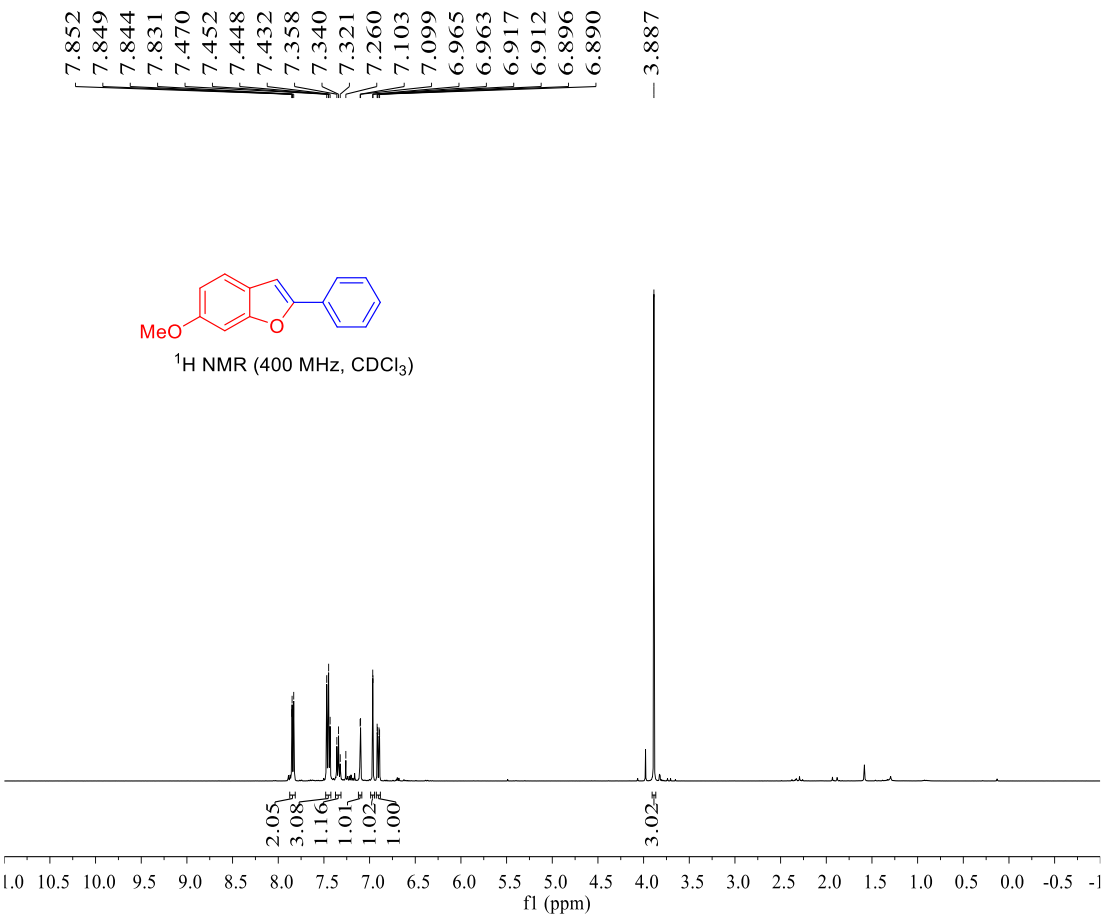


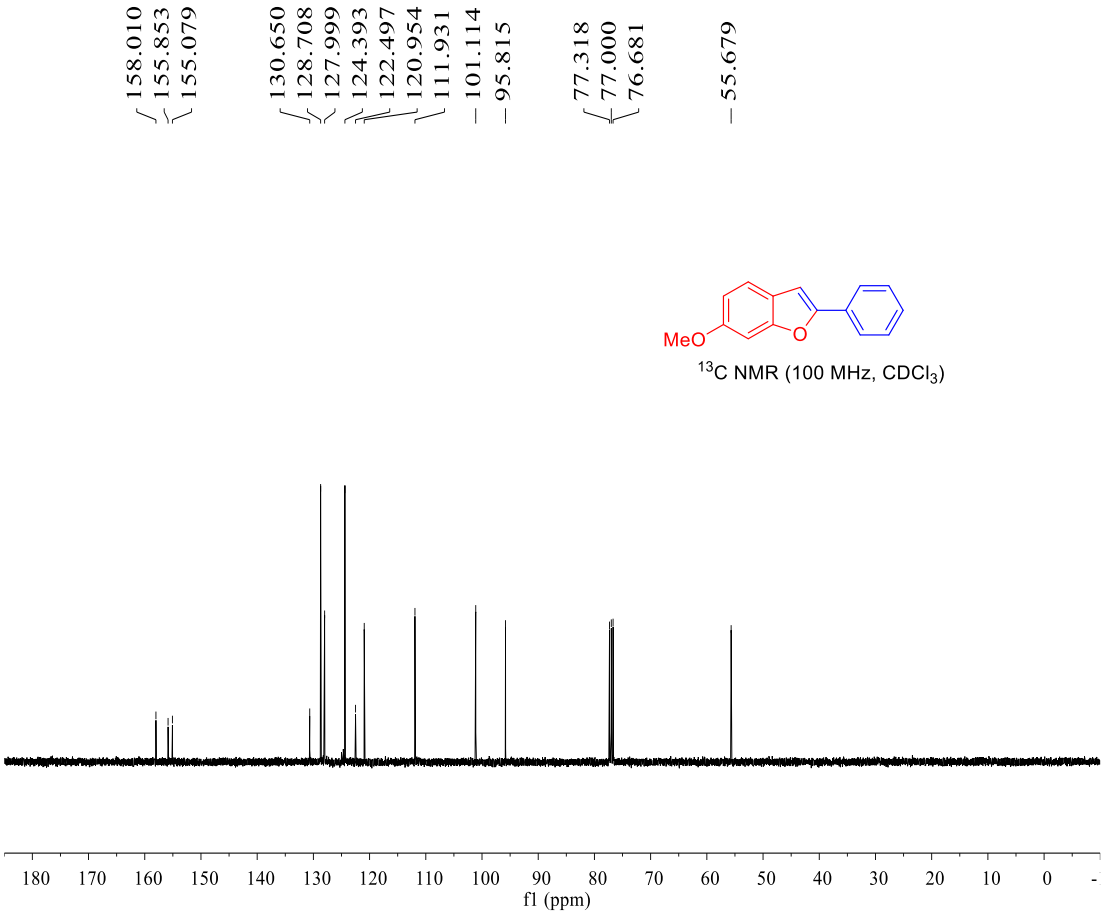
3la ^{13}C NMR (100 MHz, $CDCl_3$)

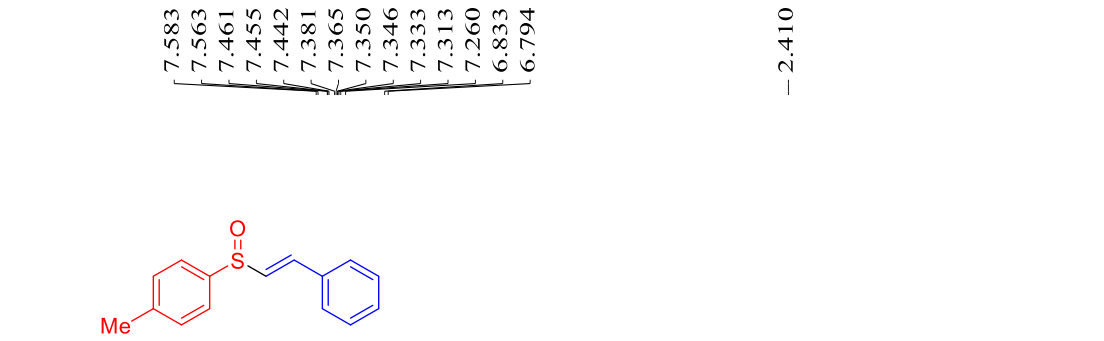


^{1}H NMR (400 MHz, $CDCl_3$)

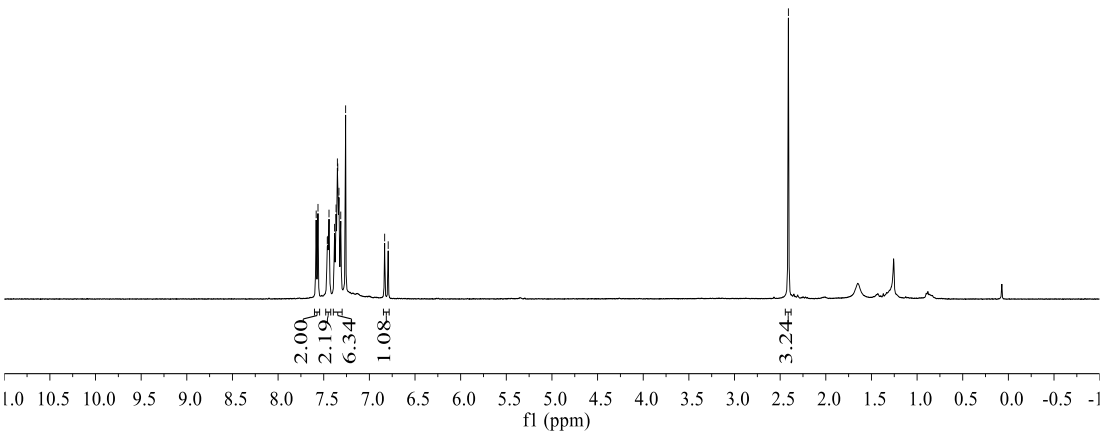

153.404
143.634
136.814
133.416
129.348
129.292
128.917
128.663
127.960
124.164
77.318
77.000
76.681
21.459
O
S
NH
Me
13C NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

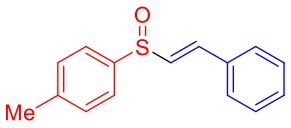

7.852
7.849
7.844
7.831
7.470
7.452
7.448
7.432
7.358
7.340
7.321
7.260
7.103
7.099
6.965
6.963
6.917
6.912
6.896
6.890
3.887
MeO
O
1H NMR (400 MHz, CDCl3)
2.05
3.08
1.16
1.01
1.02
1.00
3.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



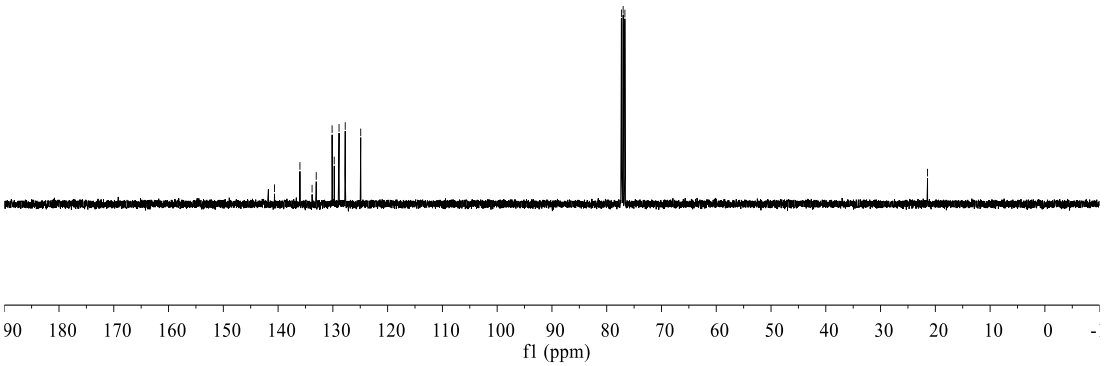


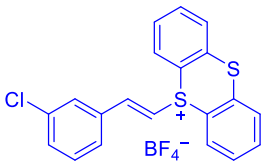
3aa' ^{1}H NMR (400 MHz, $CDCl_3$)



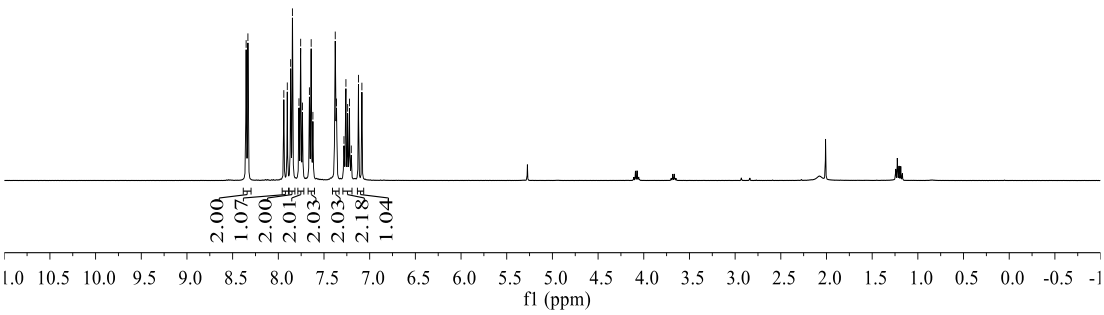


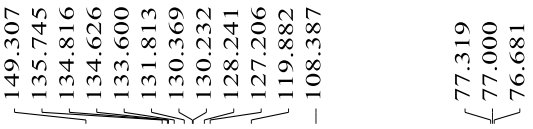
3aa' ^{13}C NMR (100 MHz, $CDCl_3$)

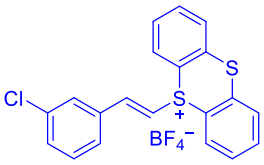




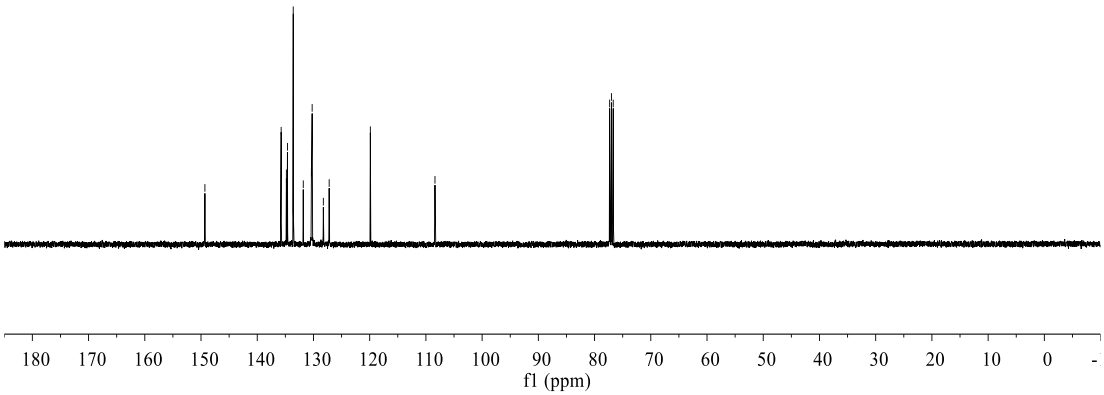
1i ^{1}H NMR (400 MHz, $CDCl_3$)

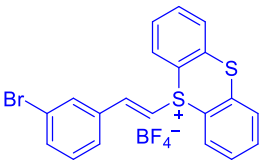




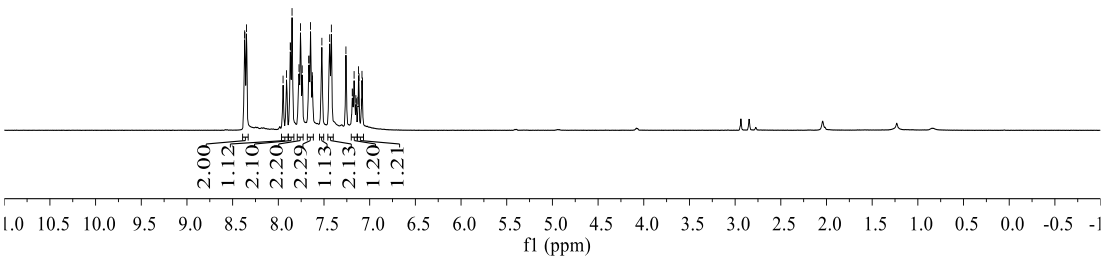


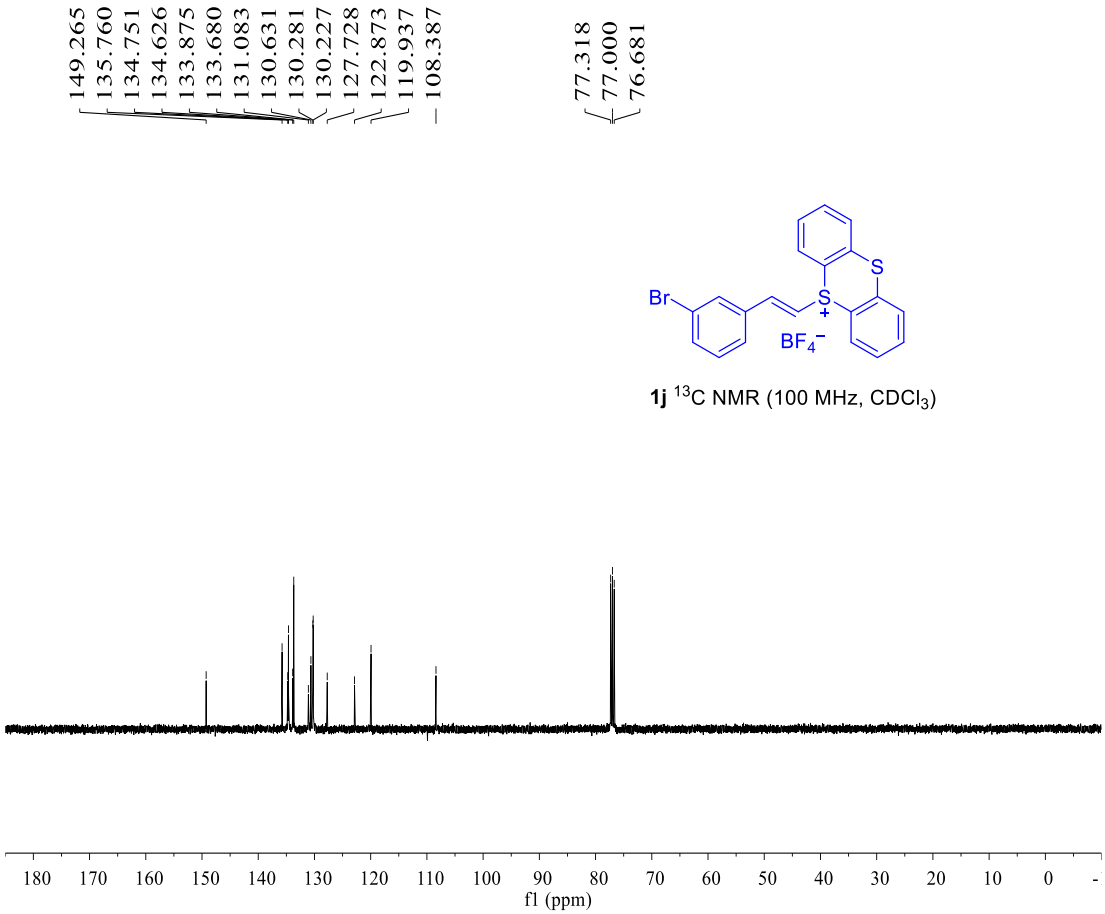
1i ^{13}C NMR (100 MHz, $CDCl_3$)





1j ^{1}H NMR (400 MHz, $CDCl_3$)





1j ^{13}C NMR (100 MHz, $CDCl_3$)