

## *Supporting Information*

# Metal-free Alkynylsulfonylation of Vinylarenes

Fei Wang,<sup>a,c</sup> Huan Zhou,<sup>a</sup> Yajun Li,<sup>a,b</sup> Hongli Bao<sup>\*a,c</sup>

a Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, 155 Yangqiao Road West, Fuzhou, Fujian 350002, P. R. of China.

b Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences

c University of Chinese Academy of Sciences, Beijing, 100049, P. R. of China.

\*hlbao@fjirsm.ac.cn

## Table of contents

General information.....	3
Experimental procedure.....	4
The synthesis of aryl alkynylsulfones <b>2</b> .....	4
General procedure for the synthesis of <b>3</b> .....	5
Detailed reaction condition optimization .....	6
Characterization Data.....	7
Synthetic applications .....	20
Reaction of <b>3aa</b> to <b>4</b> .....	20
Reaction of <b>3ap</b> to <b>5</b> .....	20
Reaction of <b>3aa</b> to <b>6</b> .....	21
Reduction of <b>3ap</b> to <b>7</b> .....	22
A tentative mechanism.....	23
Single crystal data of <b>3ai</b> (CCDC 2046732).....	24
References.....	25
NMR spectra .....	27

## General information

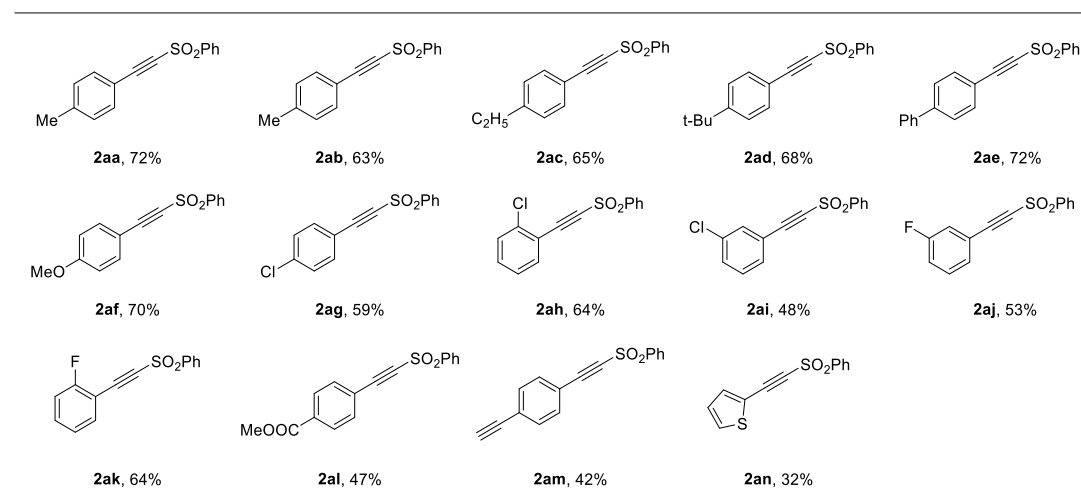
All reactions were carried out under an atmosphere of nitrogen in glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Inert PureSolv MD5. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker-BioSpin AVANCE III HD and JNM-ECZ600R/S1. Data for  $^1\text{H}$  NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for  $^{13}\text{C}$  NMR spectra are reported relative to chloroform as an internal standard (77.16 ppm) and are reported in terms of chemical shift (ppm). GC data were recorded on Thermo Trace 1300. GC-MS data were recorded on Thermo ISQ QD. HRMS data were recorded on Bruker Impact II Q-TOF from our institute.

## Experimental procedure

### The synthesis of aryl alkynylsulfones 2

Following a literature procedure.<sup>1</sup>

Arylacetylene (1 equiv, 5 mmol) and TBHP (3 equiv, 15 mmol) were added to a solution of sodium benzenesulfinate (2 equiv, 10 mmol) and iodine (0.5 equiv, 2.5 mmol) in THF (20 mL). The solution was stirred at room temperature for 8-12 h and monitored by TLC. H<sub>2</sub>O (10 mL) was added to quench the reaction, dropwise addition of sodium thiosulfate pentahydrate solution until the solution changed from brown to clear and transparent. The separated aqueous phase was extracted with EA (3×40 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography using EA/PE as eluent to afford the corresponding product. The aryl alkynylsulfones were shown below.<sup>1-2</sup>



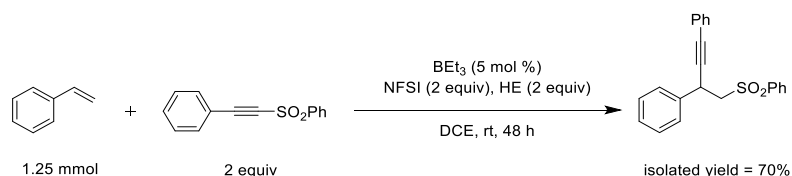
## General procedure for the synthesis of **3**

For repeatability, all reactions need to carry out in a glove box.

General procedure:

In a glove box, vinylarene (1 equiv, 0.25 mmol) and  $\text{BEt}_3$  (in hexane, 5 mol %, 14  $\mu\text{L}$ ) were added to a solution of alkynyl sulfone (2 equiv, 0.5 mmol), NFSI (2 equiv, 0.5 mmol, 158 mg), HE (2 equiv, 0.5 mmol, 127 mg) in DCE (1 mL). The solution was stirred at room temperature for 48 h and monitored by TLC. The solution was concentrated in vacuo and the remaining residue was purified by column chromatography using DCM/PE as eluent to afford the corresponding product **3**.

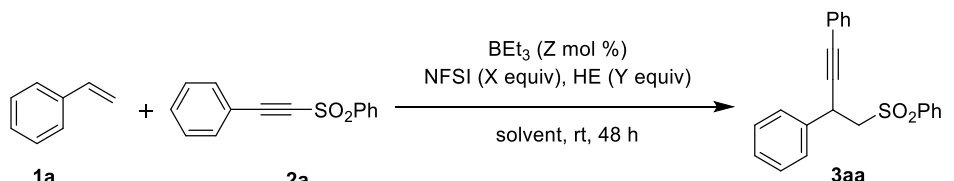
A scaled-up reaction:



In a glove box, **1a** (1 equiv, 1.25 mmol) and  $\text{BEt}_3$  (in hexane, 5 mol %, 70  $\mu\text{L}$ ) were added to a solution of alkynyl sulfone **2a** (2 equiv, 2.5 mmol), NFSI (2 equiv, 2.5 mmol, 790 mg), HE (2 equiv, 2.5 mmol, 635 mg) in DCE (5 mL). The solution was stirred at room temperature for 48 h and monitored by TLC. The solution was concentrated in vacuo and the remaining residue was purified by column chromatography using DCM/PE as eluent to afford the corresponding product **3aa** in 70% yield.

## Detailed reaction condition optimization

Table S1. Detailed reaction condition optimization<sup>a</sup>

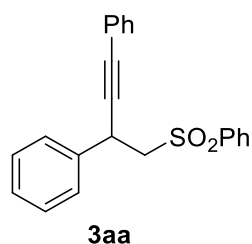


The reaction scheme shows styrene (1a) reacting with phenylacetylene (2a) in the presence of NFSI (X equiv), HE (Y equiv), and BEt<sub>3</sub> (Z mol %) in a solvent at room temperature for 48 hours to produce the propargyl ether product (3aa).

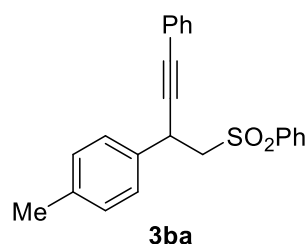
Entry	NFSI (X equiv)	HE (Y equiv)	BEt <sub>3</sub> (Z equiv)	Solvent	Yield (%) <sup>b</sup>
1	2	2	0.05	DCE	76 <sup>c</sup>
2	2	2	0	DCE	29
3	2	2	1	DCE	67
4	2	0	0.05	DCE	36
5	2	0.20	0.05	DCE	40
6	2	0.50	0.05	DCE	46
7	2	1.0	0.05	DCE	52
8	0.05	2	0.05	DCE	-
9	0.1	2	0.05	DCE	3
10	0.2	2	0.05	DCE	9
11	0.5	2	0.05	DCE	5
12	1	2	0.05	DCE	8
13	2	0	0	DCE	-
14	0	2	0	DCE	-
15	2	2	0.05	MeOH	-
16	2	2	0.05	THF	-
17	2	2	0.05	Toluene	40
18	2	2	0.05	DMF	-
19	2	2	0.05	DCM	62
20	2	2	0.05	DCE	51 <sup>d</sup>
21	2	2	0.05	DCE	59 <sup>e</sup>

<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2a** (2 equiv), NFSI (X equiv), HE (Y equiv), BEt<sub>3</sub> (in hexane, Z mol %), solvent (1 mL), glove box, rt, 48 h. <sup>b</sup> Yields were determined by <sup>1</sup>H NMR. <sup>c</sup> Isolated yield. <sup>d</sup> 50 °C instead of rt. <sup>e</sup> 90 °C instead of rt.

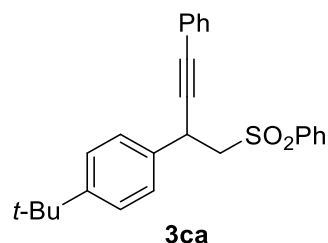
## Characterization Data



Following the general procedure, product **3aa** was obtained as a yellow solid (65.8 mg, 76% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1), mp = 93.4 – 94.8 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.2$  Hz, 2H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.4$  Hz, 2H), 7.37 (d,  $J = 7.1$  Hz, 2H), 7.31 (t,  $J = 7.3$  Hz, 2H), 7.28 – 7.20 (m, 6H), 4.48 (dd,  $J = 9.3, 4.5$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.52 (dd,  $J = 14.4, 4.5$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 139.0, 133.8, 131.8, 129.2, 129.1, 128.5, 128.4, 128.2, 127.9, 127.6, 122.7, 87.7, 85.4, 63.1, 33.8. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{18}\text{NaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 369.0920, found: 369.0917.

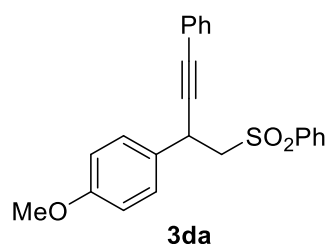


Following the general procedure, product **3ba** was obtained as a white solid (76.5 mg, 85% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 92.9 – 93.5 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J = 7.1$  Hz, 2H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.5$  Hz, 2H), 7.36 (d,  $J = 7.0$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 2H), 7.27 – 7.22 (m, 1H), 7.11 (d,  $J = 8.2$  Hz, 2H), 7.04 (d,  $J = 8.0$  Hz, 2H), 4.47 (dd,  $J = 9.2, 4.5$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.2$  Hz, 1H), 3.51 (dd,  $J = 14.4, 4.5$  Hz, 1H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 139.1, 138.5, 133.8, 131.6, 129.2, 129.1, 128.9, 128.5, 127.8, 127.6, 119.6, 86.9, 85.4, 63.2, 33.8, 21.6. HRMS (ESI) calculated for  $[\text{C}_{23}\text{H}_{20}\text{NaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 383.1076, found: 383.1076.

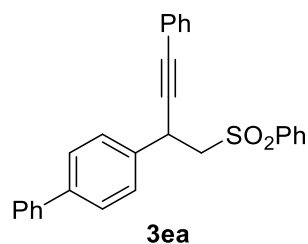


Following the general procedure, product **3ca** was obtained as a yellow solid (86.5 mg, 86% yield,  $R_f = 0.5$  (petroleum ether/dichloromethane = 1:1), mp = 93.2 – 94.5 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.91 (d,  $J = 7.2$  Hz, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.44 (t,  $J = 7.4$  Hz, 2H), 7.33 – 7.20 (m, 9H), 4.46 (dd,  $J = 9.2, 4.6$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.53 (dd,  $J = 14.4, 4.6$

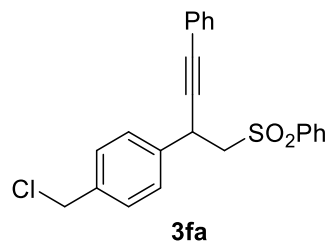
Hz, 1H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  150.8, 139.7, 135.8, 133.7, 131.8, 129.2, 128.5, 128.3, 128.2, 127.2, 126.0, 122.8, 87.9, 85.1, 63.1, 34.6, 33.3, 31.4. HRMS (ESI) calculated for  $[\text{C}_{26}\text{H}_{26}\text{NaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 425.1546, found: 425.1548.



Following the general procedure, product **3da** was obtained as a colorless oil (67.8 mg, 72% yield,  $R_f$  = 0.3 (petroleum ether/dichloromethane = 2:3)).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J$  = 7.2 Hz, 2H), 7.53 (t,  $J$  = 7.4 Hz, 1H), 7.46 (t,  $J$  = 7.4 Hz, 2H), 7.30 – 7.20 (m, 7H), 6.83 (d,  $J$  = 8.7 Hz, 2H), 4.43 (dd,  $J$  = 9.1, 4.7 Hz, 1H), 3.78 (s, 3H), 3.71 (dd,  $J$  = 14.4, 9.1 Hz, 1H), 3.50 (dd,  $J$  = 14.4, 4.8 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  159.2, 139.7, 133.7, 131.8, 130.9, 129.2, 128.7, 128.4, 128.3, 128.2, 122.8, 114.5, 88.0, 85.1, 63.2, 55.4, 33.0. HRMS (ESI) calculated for  $[\text{C}_{23}\text{H}_{20}\text{NaO}_3\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 399.1025, found: 399.1024.



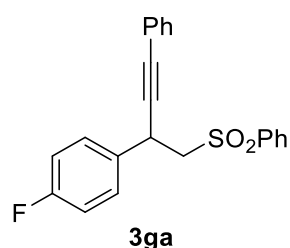
Following the general procedure, product **3ea** was obtained as a yellow solid (78.2 mg, 74% yield,  $R_f$  = 0.5 (petroleum ether/dichloromethane = 1:1), mp = 46.2 – 46.5 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J$  = 7.0 Hz, 2H), 7.57 – 7.50 (m, 5H), 7.49 – 7.39 (m, 6H), 7.35 (t,  $J$  = 7.3 Hz, 1H), 7.30 – 7.22 (m, 5H), 4.53 (dd,  $J$  = 9.0, 4.8 Hz, 1H), 3.78 (dd,  $J$  = 14.4, 9.0 Hz, 1H), 3.58 (dd,  $J$  = 14.4, 4.9 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  140.9, 140.6, 139.6, 137.9, 133.8, 131.8, 129.2, 129.0, 128.5, 128.4, 128.2, 128.1, 127.8, 127.6, 127.2, 122.7, 87.6, 85.4, 63.1, 33.6. HRMS (ESI) calculated for  $[\text{C}_{28}\text{H}_{22}\text{NaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 445.1233, found: 445.1235.



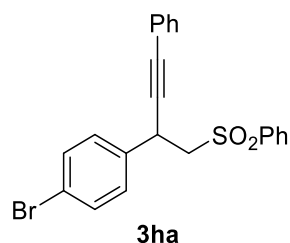
Following the general procedure, product **3fa** was obtained as a yellow solid (71.1 mg, 72% yield,  $R_f$  = 0.3 (petroleum ether/dichloromethane = 1:1), mp = 116.5 – 116.7 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.90 (d,  $J$  = 7.3 Hz, 2H), 7.53 (t,  $J$  = 7.4 Hz, 1H), 7.45 (t,  $J$  = 7.5 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.29 – 7.19 (m, 5H), 4.54 (s, 2H), 4.49 (dd,  $J$  = 8.8, 4.9 Hz, 1H), 3.73 (dd,  $J$  = 14.4, 8.8 Hz, 1H), 3.52 (dd,  $J$  = 14.4, 4.9 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.5, 139.1, 137.2, 133.9, 131.8, 129.3, 129.3, 128.5, 128.4, 128.2, 128.0, 122.6, 87.4, 85.4, 62.9, 45.8, 33.5.



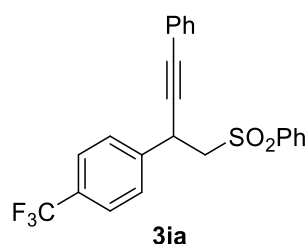
HRMS (ESI) calculated for  $[C_{23}H_{19}ClNaO_2S]^+$   $[M+Na^+]$ : 417.0686, found: 417.0684.



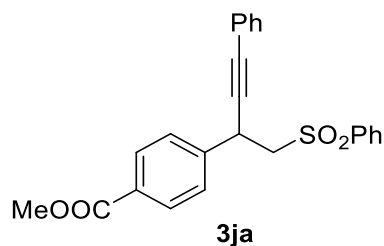
Following the general procedure, product **3ga** was obtained as a yellow oil (67.4 mg, 74% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1)).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.90 (d,  $J = 7.2$  Hz, 2H), 7.54 (t,  $J = 7.5$  Hz, 1H), 7.46 (d,  $J = 15.0$  Hz, 2H), 7.34 (dd,  $J = 8.7, 5.2$  Hz, 2H), 7.29 – 7.21 (m, 5H), 6.99 (t,  $J = 8.6$  Hz, 2H), 4.48 (dd,  $J = 8.7, 5.0$  Hz, 1H), 3.72 (dd,  $J = 14.4, 8.8$  Hz, 1H), 3.50 (dd,  $J = 14.4, 5.0$  Hz, 1H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  162.3 (d,  $J = 246.8$  Hz), 139.5, 134.7 (d,  $J = 3.2$  Hz), 133.8, 131.7, 129.3, 129.2, 128.5, 128.3 (d,  $J = 14.8$  Hz), 122.5, 115.9 (d,  $J = 21.7$  Hz), 87.5, 85.4, 63.0, 33.1.  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -114.4. HRMS (ESI) calculated for  $[C_{22}H_{17}FNaO_2S]^+$   $[M+Na^+]$ : 387.0825, found: 387.0826.



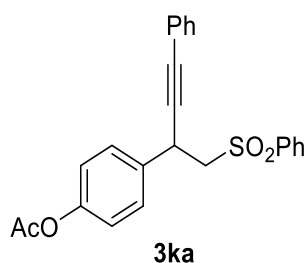
Following the general procedure, product **3ha** was obtained as a colorless oil (60.6 mg, 57% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1)).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.89 (d,  $J = 7.3$  Hz, 2H), 7.61 – 7.51 (m, 2H), 7.55 – 7.40 (m, 4H), 7.28 – 7.21 (m, 6H), 4.46 (dd,  $J = 8.6, 5.1$  Hz, 1H), 3.72 (dd,  $J = 14.4, 8.6$  Hz, 1H), 3.50 (dd,  $J = 14.4, 5.2$  Hz, 1H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.5, 137.9, 133.8, 132.2, 131.7, 129.4, 129.3, 128.6, 128.4, 128.3, 122.4, 121.9, 87.1, 85.6, 62.7, 33.3. HRMS (ESI) calculated for  $[C_{22}H_{17}BrNaO_2S]^+$   $[M+Na^+]$ : 447.0025, found: 447.0027.



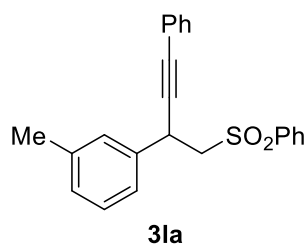
Following the general procedure, product **3ia** was obtained as a colorless oil (73.6 mg, 72% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1)).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.91 – 7.86 (m, 2H), 7.58 – 7.43 (m, 7H), 7.31 – 7.22 (m, 5H), 4.57 (dd,  $J = 8.3, 5.4$  Hz, 1H), 3.76 (dd,  $J = 14.4, 8.4$  Hz, 1H), 3.55 (dd,  $J = 14.4, 5.4$  Hz, 1H).  $^{13}C$  NMR (150 MHz, Chloroform-*d*)  $\delta$  142.8, 139.4, 134.0, 131.8, 130.2 (q,  $J = 32.8$  Hz), 129.3, 128.7, 128.4, 128.3, 128.2, 126.1 (d,  $J = 3.8$  Hz), 124.0 (q,  $J = 272.0$  Hz), 122.3, 86.7, 85.8, 62.6, 33.7.  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.6. HRMS (ESI) calculated for  $[C_{23}H_{17}F_3NaO_2S]^+$   $[M+Na^+]$ : 437.0794, found: 437.0794.



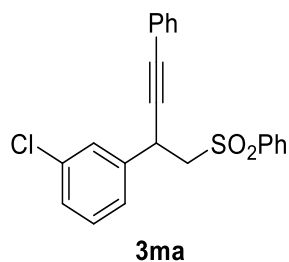
Following the general procedure, product **3ja** was obtained as a colorless oil (52.6 mg, 52% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 3:1)).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.90 (d,  $J = 8.3$  Hz, 2H), 7.84 (d,  $J = 7.3$  Hz, 2H), 7.46 (t,  $J = 7.3$  Hz, 1H), 7.38 (t,  $J = 7.2$  Hz, 4H), 7.16 (q,  $J = 7.7$  Hz, 5H), 4.47 (dd,  $J = 8.9, 4.8$  Hz, 1H), 3.82 (s, 3H), 3.67 (dd,  $J = 14.4, 8.9$  Hz, 1H), 3.44 (dd,  $J = 14.4, 4.8$  Hz, 1H).  $^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  166.6, 143.9, 139.4, 133.9, 131.7, 130.4, 129.8, 129.3, 128.6, 128.4, 128.2, 127.7, 122.4, 86.8, 85.8, 62.6, 52.3, 33.7. HRMS (ESI) calculated for  $[\text{C}_{24}\text{H}_{20}\text{NaO}_4\text{S}]^+ [\text{M}+\text{Na}^+]$ : 427.0975, found: 427.0975.



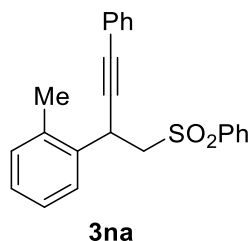
Following the general procedure, product **3ka** was obtained as a yellow oil (68.8 mg, 68% yield,  $R_f = 0.2$  (petroleum ether/dichloromethane = 2:3)).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.84 (d,  $J = 7.4$  Hz, 2H), 7.46 (t,  $J = 7.4$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 2H), 7.30 (d,  $J = 8.5$  Hz, 2H), 7.21 – 7.13 (m, 5H), 6.95 (d,  $J = 8.6$  Hz, 2H), 4.42 (dd,  $J = 9.1, 4.6$  Hz, 1H), 3.65 (dd,  $J = 14.4, 9.2$  Hz, 1H), 3.43 (dd,  $J = 14.4, 4.6$  Hz, 1H), 2.20 (s, 3H).  $^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  169.5, 150.2, 139.5, 136.4, 133.9, 131.7, 129.3, 128.7, 128.4, 128.2, 122.2, 87.3, 85.5, 63.0, 33.2, 21.2. HRMS (ESI) calculated for  $[\text{C}_{24}\text{H}_{20}\text{NaO}_4\text{S}]^+ [\text{M}+\text{Na}^+]$ : 427.0975, found: 427.0975.



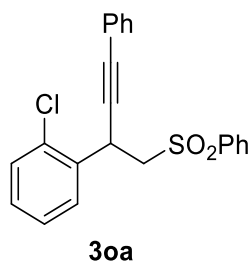
Following the general procedure, product **3la** was obtained as a colorless oil (63.9 mg, 71% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J = 7.1$  Hz, 2H), 7.52 (t,  $J = 7.4$  Hz, 1H), 7.45 (t,  $J = 7.4$  Hz, 2H), 7.28 – 7.20 (m, 5H), 7.18 – 7.14 (m, 2H), 7.06 (d,  $J = 6.9$  Hz, 1H), 4.43 (dd,  $J = 9.3, 4.5$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.51 (dd,  $J = 14.4, 4.5$  Hz, 1H), 2.31 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.9, 138.9, 133.7, 131.8, 129.2, 129.0, 128.6, 128.5, 128.3, 128.2, 128.2, 124.6, 122.8, 87.8, 85.2, 63.1, 33.7, 21.5. HRMS (ESI) calculated for  $[\text{C}_{23}\text{H}_{20}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 383.1076, found: 383.1077.



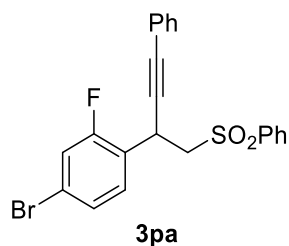
Following the general procedure, product **3ma** was obtained as a yellow oil (60.0 mg, 63% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.91 (d,  $J = 7.2$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.34 (s, 1H), 7.31 – 7.20 (m, 8H), 4.47 (dd,  $J = 8.8, 4.9$  Hz, 1H), 3.73 (dd,  $J = 14.4, 8.8$  Hz, 1H), 3.51 (dd,  $J = 14.4, 5.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  140.8, 139.5, 134.9, 133.9, 131.8, 130.4, 129.3, 128.6, 128.4, 128.3, 128.2, 127.9, 125.9, 122.4, 86.9, 85.7, 62.7, 33.5. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 403.0530, found: 403.0530.



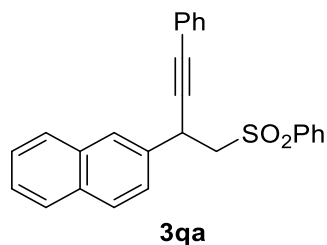
Following the general procedure, product **3na** was obtained as a white solid (63.9 mg, 71% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 107.3 – 108.0 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 (d,  $J = 7.1$  Hz, 2H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.50 – 7.42 (m, 3H), 7.28 – 7.19 (m, 5H), 7.18 – 7.13 (m, 3H), 4.65 (dd,  $J = 9.8, 3.7$  Hz, 1H), 3.70 (dd,  $J = 14.5, 9.8$  Hz, 1H), 3.41 (dd,  $J = 14.5, 3.7$  Hz, 1H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.5, 137.2, 135.0, 133.8, 131.8, 131.1, 129.2, 128.5, 128.3, 128.2, 127.9, 127.7, 126.8, 122.8, 88.0, 84.7, 61.8, 30.4, 19.3. HRMS (ESI) calculated for  $[\text{C}_{23}\text{H}_{20}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 383.1076, found: 383.1076.



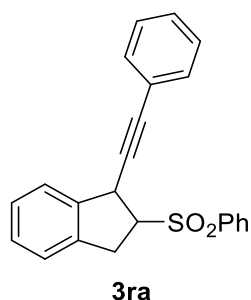
Following the general procedure, product **3oa** was obtained as a white solid (63.8 mg, 67% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 104.5 – 105.8 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.98 (d,  $J = 7.1$  Hz, 2H), 7.64 (dd,  $J = 7.5, 1.9$  Hz, 1H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.4$  Hz, 2H), 7.34 – 7.25 (m, 7H), 7.24 – 7.19 (m, 1H), 4.82 (t,  $J = 6.9$  Hz, 1H), 3.61 – 3.57 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.4, 136.0, 133.9, 132.7, 131.9, 130.1, 129.8, 129.4, 129.3, 128.6, 128.5, 128.3, 127.6, 122.6, 86.5, 85.9, 60.7, 31.4. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 403.0530, found: 403.0531.



Following the general procedure, product **3pa** was obtained as a yellow solid (66.3 mg, 60% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 78.2 – 78.6 °C).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.88 (d,  $J = 7.3$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.36 (t,  $J = 8.1$  Hz, 1H), 7.30 – 7.22 (m, 6H), 7.14 (dd,  $J = 9.7$ , 1.8 Hz, 1H), 4.63 (dd,  $J = 8.1$ , 5.7 Hz, 1H), 3.69 (dd,  $J = 14.4$ , 8.2 Hz, 1H), 3.60 (dd,  $J = 14.4$ , 5.6 Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  159.78 (d,  $J = 252.5$  Hz), 139.3, 133.8, 131.8, 130.9 (d,  $J = 4.2$  Hz), 129.3, 128.7, 128.4, 128.3, 128.0 (d,  $J = 3.7$  Hz), 124.8 (d,  $J = 13.6$  Hz), 122.3 (d,  $J = 9.6$  Hz), 119.6 (d,  $J = 24.7$  Hz), 85.7, 85.4, 60.4, 28.1 (d,  $J = 2.7$  Hz).  $^{19}\text{F NMR}$  (376 MHz, Chloroform-*d*)  $\delta$  -114.28. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{19}\text{BrFNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 464.9931, found: 464.9929.

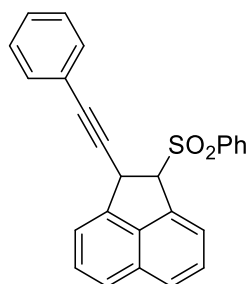


Following the general procedure, product **3qa** was obtained as a colorless oil (69.3 mg, 70% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.91 (d,  $J = 7.4$  Hz, 2H), 7.85 – 7.75 (m, 4H), 7.52 – 7.36 (m, 6H), 7.32 – 7.22 (m, 5H), 4.65 (dd,  $J = 9.0$ , 4.8 Hz, 1H), 3.83 (dd,  $J = 14.4$ , 9.0 Hz, 1H), 3.63 (dd,  $J = 14.4$ , 4.8 Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  139.5, 136.1, 133.7, 133.5, 132.9, 131.8, 129.2, 129.1, 128.5, 128.4, 128.2, 128.0, 127.8, 126.7, 126.6, 126.4, 125.2, 122.7, 87.7, 85.5, 62.9, 34.0. HRMS (ESI) calculated for  $[\text{C}_{26}\text{H}_{20}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : 419.1076, found: 419.1074.



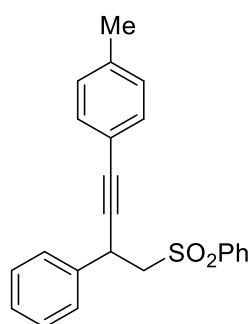
Following the general procedure, product **3ra** was obtained as a brown solid (53.8 mg, 60% yield, dr > 20:1,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1), mp = 102.0 – 102.3 °C).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.04 (dd,  $J = 8.1$ , 1.6 Hz, 2H), 7.66 – 7.50 (m, 3H), 7.40 – 7.32 (m, 1H), 7.31 – 7.18 (m, 6H), 7.17 – 7.08 (m, 2H), 4.68 (d,  $J = 8.9$  Hz, 1H), 4.20 – 4.11 (m, 1H), 3.65 (dd,  $J = 16.3$ , 9.4 Hz, 1H), 3.39 (dd,  $J = 16.3$ , 8.9 Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  140.5,

138.6, 138.2, 134.1, 131.8, 129.4, 129.1, 128.3, 128.3, 128.1, 127.9, 124.7, 124.6, 122.7, 87.8, 83.2, 70.3, 39.3, 32.0. HRMS (ESI) calculated for  $[C_{23}H_{18}NaO_2S]^+$   $[M+Na^+]$ : 381.0920, found: 381.0917.



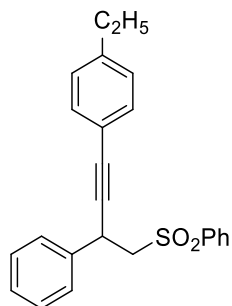
**3sa**

Following the general procedure, product **3sa** was obtained as a yellow oil (62.1 mg, 63% yield, dr = 6:1,  $R_f$  = 0.3 (petroleum ether/dichloromethane = 1:1), contains some impurity).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.88 (d,  $J$  = 7.0 Hz, 2H), 7.80 (d,  $J$  = 8.2 Hz, 1H), 7.70 (dd,  $J$  = 7.3, 5.4 Hz, 2H), 7.63 – 7.41 (m, 7H), 7.30 – 7.24 (m, 2H), 7.25 – 7.20 (m, 2H), 5.37 (d,  $J$  = 4.0 Hz, 1H), 5.08 (d,  $J$  = 4.0 Hz, 1H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  140.8, 137.8, 137.4, 134.2, 133.7, 131.8, 131.6, 129.3, 129.2, 128.6, 128.4, 128.3, 128.3, 126.0, 124.4, 123.3, 122.7, 120.4, 87.4, 83.0, 75.9, 39.2. HRMS (ESI) calculated for  $[C_{26}H_{18}NaO_2S]^+$   $[M+Na^+]$ : 417.0920, found: 417.0922.



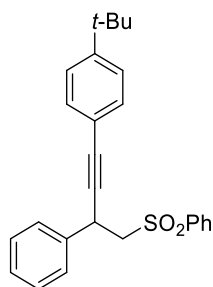
**3ab**

Following the general procedure, product **3ab** was obtained as a colorless oil (66.6 mg, 74% yield,  $R_f$  = 0.4 (petroleum ether/dichloromethane = 1:1)).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J$  = 7.3 Hz, 2H), 7.54 (t,  $J$  = 7.4 Hz, 1H), 7.46 (dd,  $J$  = 8.3, 6.7 Hz, 2H), 7.37 (d,  $J$  = 7.1 Hz, 2H), 7.31 (t,  $J$  = 7.3 Hz, 2H), 7.26 (d,  $J$  = 7.0 Hz, 1H), 7.19 – 6.98 (m, 4H), 4.47 (dd,  $J$  = 9.2, 4.5 Hz, 1H), 3.73 (dd,  $J$  = 14.4, 9.3 Hz, 1H), 3.51 (dd,  $J$  = 14.4, 4.5 Hz, 1H), 2.32 (s, 3H).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 139.1, 138.5, 133.8, 131.7, 129.2, 129.1, 128.9, 128.5, 127.8, 127.6, 119.6, 86.9, 85.5, 63.2, 33.8, 21.6. HRMS (ESI) calculated for  $[C_{23}H_{20}NaO_3S]^+$   $[M+Na^+]$ : 383.1076, found: 383.1076.



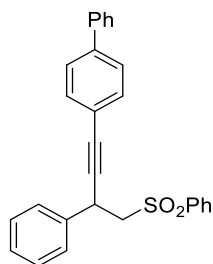
**3ac**

Following the general procedure, product **3ac** was obtained as a white solid (72.0 mg, 77% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1), mp = 84.5 – 85.2 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.2$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.5$  Hz, 2H), 7.37 (d,  $J = 7.1$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 2H), 7.27 – 7.24 (m, 1H), 7.14 (d,  $J = 8.2$  Hz, 2H), 7.07 (d,  $J = 8.2$  Hz, 2H), 4.47 (dd,  $J = 9.2, 4.5$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.2$  Hz, 1H), 3.52 (dd,  $J = 14.4, 4.6$  Hz, 1H), 2.62 (q,  $J = 7.6$  Hz, 2H), 1.21 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  144.8, 139.6, 139.1, 133.8, 131.8, 129.2, 129.1, 128.5, 127.8, 127.8, 127.6, 119.9, 86.9, 85.5, 63.2, 33.8, 28.9, 15.5. HRMS (ESI) calculated for  $[\text{C}_{24}\text{H}_{22}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .397.1233, found: 397.1232.



**3ad**

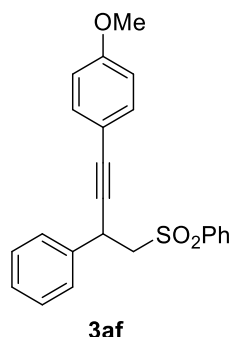
Following the general procedure, product **3ad** was obtained as a yellow solid (97.6 mg, 97% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 76.0 – 77.0 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.1$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.37 (d,  $J = 6.7$  Hz, 2H), 7.34 – 7.22 (m, 5H), 7.16 (d,  $J = 8.4$  Hz, 2H), 4.47 (dd,  $J = 9.1, 4.6$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.2$  Hz, 1H), 3.52 (dd,  $J = 14.4, 4.6$  Hz, 1H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  151.7, 139.6, 139.1, 133.8, 131.5, 129.2, 129.1, 128.5, 127.8, 127.6, 125.2, 119.7, 87.0, 85.4, 63.3, 34.9, 33.9, 31.3. HRMS (ESI) calculated for  $[\text{C}_{26}\text{H}_{26}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .425.1546, found: 425.1542.



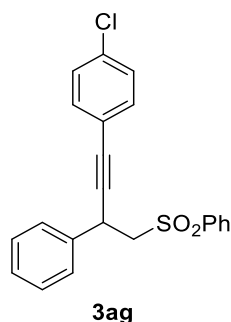
**3ae**

Following the general procedure, product **3ae** was obtained as a white solid (96.0 mg, 91% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1), mp = 105.2 – 106.4 °C).  $^1\text{H}$  NMR (400 MHz,

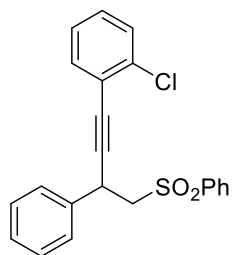
Chloroform-*d*)  $\delta$  7.95 (d,  $J = 7.0$  Hz, 2H), 7.60 – 7.52 (m, 3H), 7.52 – 7.31 (m, 11H), 7.30 – 7.22 (m, 3H), 4.51 (dd,  $J = 9.3, 4.5$  Hz, 1H), 3.75 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.53 (dd,  $J = 14.4, 4.5$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  141.1, 140.4, 139.6, 139.0, 133.8, 132.2, 129.3, 129.2, 129.0, 128.5, 127.9, 127.8, 127.6, 127.1, 126.9, 121.6, 88.4, 85.2, 63.2, 33.9. HRMS (ESI) calculated for  $[\text{C}_{28}\text{H}_{22}\text{NaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 445.1233, found: 445.1234.



Following the general procedure, product **3af** was obtained as a yellow oil (78.0 mg, 83% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.86 (d,  $J = 7.2$  Hz, 2H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 2H), 7.30 (d,  $J = 7.1$  Hz, 2H), 7.24 (t,  $J = 7.3$  Hz, 2H), 7.20 – 7.18 (m, 1H), 7.08 (d,  $J = 8.9$  Hz, 2H), 6.70 (d,  $J = 8.9$  Hz, 2H), 4.39 (dd,  $J = 9.3, 4.5$  Hz, 1H), 3.73 (s, 3H), 3.65 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.44 (dd,  $J = 14.4, 4.5$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  159.7, 139.7, 139.2, 133.7, 133.2, 129.2, 129.1, 128.5, 127.8, 127.6, 114.9, 113.8, 86.2, 85.2, 63.2, 55.4, 33.8. HRMS (ESI) calculated for  $[\text{C}_{23}\text{H}_{20}\text{NaO}_3\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 399.1025, found: 399.1028.

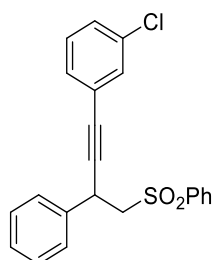


Following the general procedure, product **3ag** was obtained as a colorless oil (58.3 mg, 83% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.1$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.38 – 7.20 (m, 8H), 7.16 (d,  $J = 8.5$  Hz, 2H), 4.47 (dd,  $J = 9.5, 4.3$  Hz, 1H), 3.72 (dd,  $J = 14.4, 9.5$  Hz, 1H), 3.50 (dd,  $J = 14.4, 4.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.7, 134.4, 133.9, 133.0, 129.3, 129.2, 128.6, 128.5, 128.0, 127.5, 121.2, 88.7, 84.3, 63.0, 33.8. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : 403.0530, found: 403.0529.



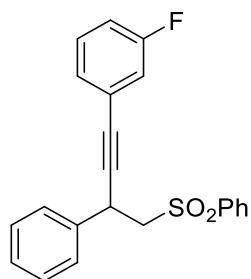
**3ah**

Following the general procedure, product **3ah** was obtained as a white solid (79.8 mg, 84% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 55.1 – 56.4 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J = 6.6$  Hz, 2H), 7.49 – 7.37 (m, 5H), 7.37 – 7.28 (m, 3H), 7.25 (d,  $J = 2.3$  Hz, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.09 (m, 1H), 4.52 (dd,  $J = 9.1, 4.6$  Hz, 1H), 3.77 (dd,  $J = 14.4, 9.1$  Hz, 1H), 3.54 (dd,  $J = 14.4, 4.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.5, 138.6, 136.1, 133.7, 133.5, 129.4, 129.2, 129.1, 128.5, 128.0, 127.7, 126.4, 122.7, 93.0, 82.2, 63.1, 34.0. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .403.0530, found: 403.0529.



**3ai**

Following the general procedure, product **3ai** was obtained as a white solid (73.1 mg, 77% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 107.0 – 108.0 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.94 (d,  $J = 7.1$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.38 – 7.29 (m, 4H), 7.28 – 7.20 (m, 2H), 7.22 – 7.06 (m, 3H), 4.48 (dd,  $J = 9.6, 4.2$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.6$  Hz, 1H), 3.50 (dd,  $J = 14.4, 4.3$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.6, 134.0, 133.9, 131.7, 129.9, 129.5, 129.3, 129.2, 128.7, 128.5, 128.0, 127.5, 124.4, 89.0, 84.0, 63.0, 33.7. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .403.0530, found: 403.0528.

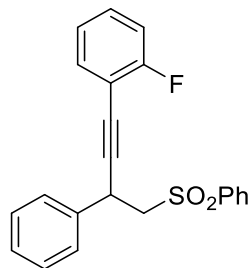


**3aj**

Following the general procedure, product **3aj** was obtained as a white solid (62.8 mg, 69% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 108.8 – 109.7 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.2$  Hz, 2H), 7.56 (t,  $J = 7.3$  Hz, 1H), 7.48 (t,  $J = 7.5$  Hz, 2H), 7.38 – 7.29 (m, 4H), 7.29 – 7.25 (m, 1H), 7.24 – 7.17 (m, 1H), 7.05 – 6.94 (m, 2H), 6.90 (d,  $J = 9.6$  Hz, 1H), 4.48 (dd,  $J = 9.5, 4.3$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.5$  Hz, 1H), 3.51 (dd,  $J = 14.4, 4.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.7, 133.9, 129.8 (d,  $J = 8.5$  Hz), 129.3, 129.2,

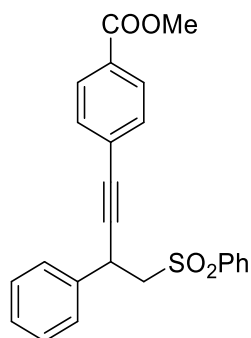


128.5, 128.0, 127.7 (d,  $J = 3.2$  Hz), 127.5, 124.5 (d,  $J = 9.4$  Hz), 118.7, 117.2 (d,  $J = 265.3$  Hz), 115.7, 88.7, 84.2 (d,  $J = 3.4$  Hz), 63.0, 33.7.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -113.15. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{FNaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : .387.0825, found: 387.0824.



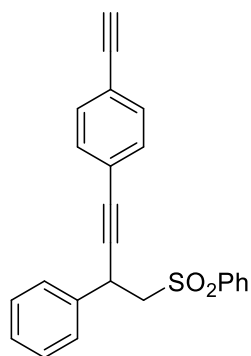
**3ak**

Following the general procedure, product **3ak** was obtained as a white solid (64.6 mg, 71% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 66.4 – 66.7 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.94 (d,  $J = 7.1$  Hz, 2H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 2H), 7.39 – 7.26 (m, 5H), 7.25 – 7.18 (m, 1H), 7.07 – 6.94 (m, 2H), 6.90 (d,  $J = 9.5$  Hz, 1H), 4.48 (dd,  $J = 9.4$ , 4.4 Hz, 1H), 3.73 (dd,  $J = 14.4$ , 9.5 Hz, 1H), 3.51 (dd,  $J = 14.4$ , 4.4 Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )  $\delta$  162.3 (d,  $J = 246.8$  Hz), 139.6, 138.6, 133.9, 129.8 (d,  $J = 8.5$  Hz), 129.2 (d,  $J = 14.8$  Hz), 128.5, 128.0, 127.7 (d,  $J = 2.2$  Hz), 127.5, 124.5 (d,  $J = 9.7$  Hz), 124.2, 121.9, 118.6 (d,  $J = 22.5$  Hz), 88.7, 84.1, 62.9, 33.7.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  -113.16. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{FNaO}_2\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : .387.0827, found: 387.0825.



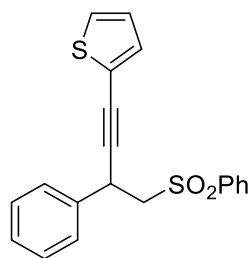
**3al**

Following the general procedure, product **3al** was obtained as a white solid (76.8 mg, 76% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 100.4 – 101.4 °C).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.96 – 7.90 (m, 4H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.41 – 7.22 (m, 7H), 4.51 (dd,  $J = 9.5$ , 4.3 Hz, 1H), 3.91 (s, 3H), 3.74 (dd,  $J = 14.7$ , 9.8 Hz, 1H), 3.52 (dd,  $J = 14.4$ , 4.3 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  166.6, 139.6, 138.6, 133.9, 131.7, 129.7, 129.4, 129.3, 129.2, 128.5, 128.1, 127.5, 127.4, 90.8, 84.7, 62.9, 52.4, 33.8. HRMS (ESI) calculated for  $[\text{C}_{24}\text{H}_{20}\text{NaO}_4\text{S}]^+$   $[\text{M}+\text{Na}^+]$ : .427.0975, found: 427.0973.



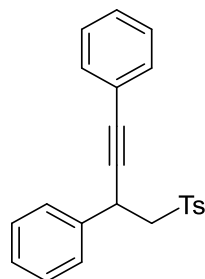
**3am**

Following the general procedure, product **3am** was obtained as a colorless oil (29.6 mg, 32% yield,  $R_f = 0.3$  (petroleum ether/dichloromethane = 1:1)).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.3$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.40 – 7.27 (m, 7H), 7.17 (d,  $J = 8.2$  Hz, 2H), 4.49 (dd,  $J = 9.5, 4.3$  Hz, 1H), 3.73 (dd,  $J = 14.4, 9.5$  Hz, 1H), 3.51 (dd,  $J = 14.4, 4.4$  Hz, 1H), 3.16 (s, 1H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.7, 133.9, 131.9, 131.7, 129.3, 129.2, 128.5, 128.0, 127.6, 123.2, 122.1, 89.8, 84.8, 83.3, 63.0, 33.8. HRMS (ESI) calculated for  $[\text{C}_{24}\text{H}_{18}\text{NaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .393.0920, found: 393.0919.



**3an**

Following the general procedure, product **3an** was obtained as brown solid (28.2 mg, 32% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 100.5 – 100.8 °C).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.1$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.38 – 7.15 (m, 7H), 6.90 (dd,  $J = 4.9, 1.2$  Hz, 1H), 4.46 (dd,  $J = 9.3, 4.5$  Hz, 1H), 3.72 (dd,  $J = 14.4, 9.3$  Hz, 1H), 3.51 (dd,  $J = 14.4, 4.5$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  139.6, 138.9, 133.8, 130.0, 129.2, 129.1, 128.9, 128.5, 127.9, 127.6, 125.2, 121.7, 87.2, 63.1, 33.8. HRMS (ESI) calculated for  $[\text{C}_{22}\text{H}_{17}\text{ClNaO}_2\text{S}]^+ [\text{M}+\text{Na}^+]$ : .375.0484, found: 375.0487.



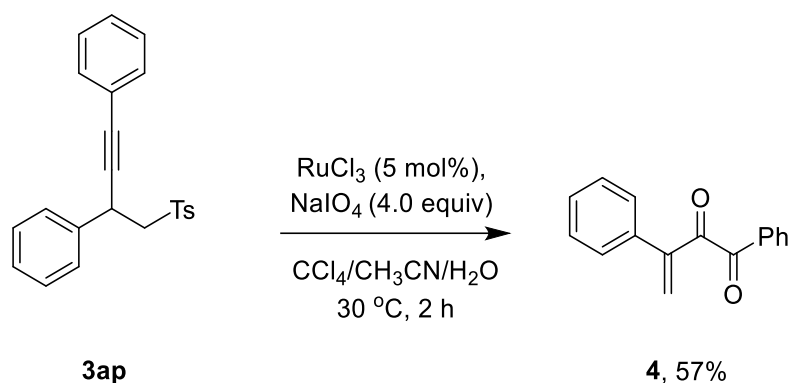
**3ap**

Following the general procedure, product **3ap** was obtained as yellow solid (629 mg, 70% yield,  $R_f = 0.4$  (petroleum ether/dichloromethane = 1:1), mp = 104.5 – 105.3 °C).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J = 8.1$  Hz, 2H), 7.38 (d,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.29 – 7.22 (m, 6H), 7.18 (d,  $J = 6.5$  Hz, 2H), 4.45 (dd,  $J = 9.6, 4.0$  Hz, 1H), 3.70 (dd,  $J = 14.4, 9.7$  Hz,

1H), 3.48 (dd,  $J = 14.4, 4.0$  Hz, 1H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  144.9, 139.1, 136.5, 131.7, 129.9, 129.1, 128.6, 128.3, 127.9, 127.6, 122.8, 87.7, 85.3, 63.3, 33.9, 21.7. These data matches with the reported value.<sup>3</sup>

## Synthetic applications

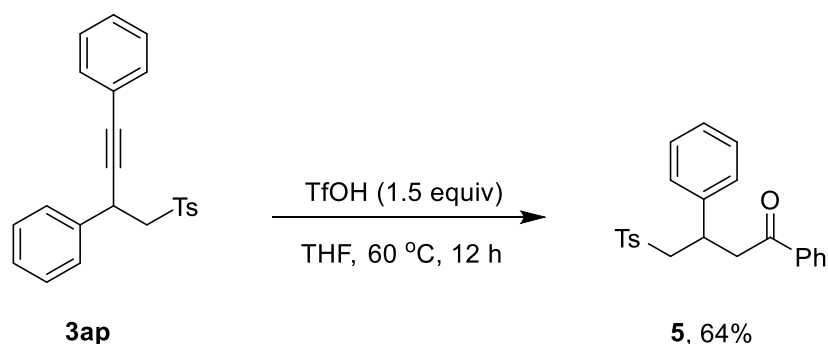
### Reaction of 3aa to 4



Product **4** was prepared according literature method.<sup>4</sup> A solution of **3ap** (0.1 mmol, 36 mg), RuCl<sub>3</sub> (5mol%, 1 mg) and NaIO<sub>4</sub> (0.4 mmol, 86 mg) in CCl<sub>4</sub>/CH<sub>3</sub>CN/H<sub>2</sub>O (0.7 mL, (2:2:3)). The solution was stirred at room temperature for 2 h and monitor by TLC. The solution was extracted with DCM (3×10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (PE/EA, 5:1) to yield **4**.

Product **4** was obtained as a yellow oil (13.5 mg, 57% yield, R<sub>f</sub> = 0.5 (petroleum ether/ethyl acetate = 5:1)). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.40 (m, 5H), 6.45 (s, 1H), 6.19 (s, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 195.8, 194.6, 145.3, 135.0, 134.9, 133.7, 133.1, 129.9, 129.2, 129.0, 128.7, 128.6. HRMS (ESI) calculated for dimer of **4** [C<sub>32</sub>H<sub>25</sub>O<sub>4</sub>]<sup>+</sup> [2M+H<sup>+</sup>]: .401.1182, found: 401.1183.

### Reaction of 3ap to 5

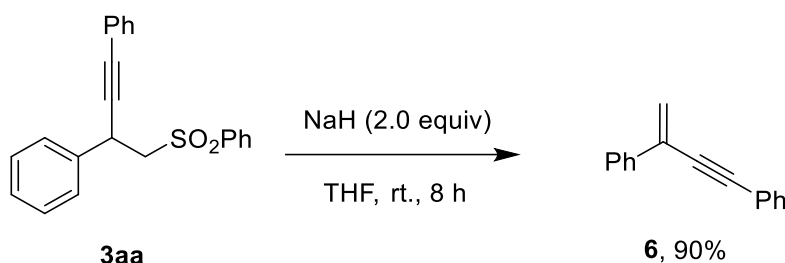


Product **5** was prepared according literature method.<sup>5</sup> TfOH (0.15 mmol, 14 μL) was added to a solution of **3ap** (0.1 mmol, 35 mg) in THF (1 mL). The solution was stirred at 60 °C for 12 h and

monitor by TLC. NaHCO<sub>3</sub> (3 mL) was added to quench the reaction. The separated aqueous phase was extracted with DCM (3×10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (PE/EA, 5:1) to yield **5**.

Product **5** was obtained as a white solid (24.3 mg, 64% yield, R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 5:1). mp = 100.5 – 101.3 °C) <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.08 (m, 5H), 3.95 – 3.88 (m 1H), 3.75 – 3.62 (m, 2H), 3.51 – 3.41 (m, 2H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 197.4, 144.7, 141.8, 136.7, 133.3, 129.9, 128.8, 128.7, 128.1, 127.5, 127.2, 61.0, 44.2, 36.2, 21.7. HRMS (ESI) calculated for [C<sub>23</sub>H<sub>22</sub>NaO<sub>3</sub>S]<sup>+</sup> [M+Na<sup>+</sup>]: .401.1182, found: 401.1183.

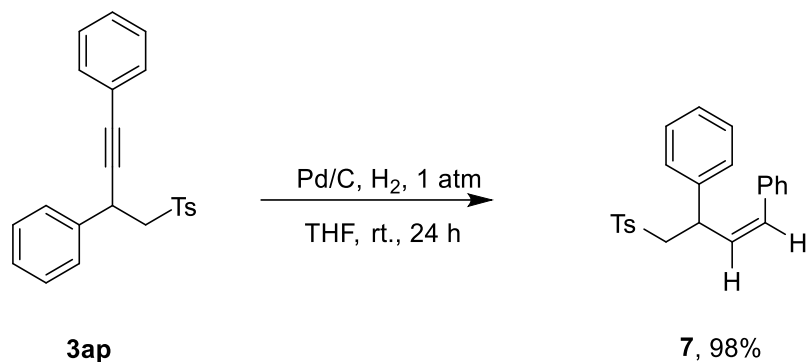
## Reaction of **3aa** to **6**



Product **6** was prepared according literature method.<sup>6</sup> NaH (0.2 mmol, 8 mg) was added to a solution of **3aa** (0.1 mmol, 35.5 mg) in THF (1 mL). The solution was stirred at room temperature for 8 h and monitor by TLC. NaHCO<sub>3</sub> (3 mL) was added to quench the reaction. The separated aqueous phase was extracted with DCM (3×10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel to get product **6** in 90% yield.

Product **6** was obtained as a yellow oil (R<sub>f</sub> = 0.3 (petroleum ether/ethyl acetate = 10:1)). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.47 – 7.30 (m, 6H), 6.00 (s, 1H), 5.78 (s, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 137.4, 131.8, 130.7, 128.6, 128.5, 126.2, 123.2, 120.8, 90.9, 88.7. These data matches with the reported value.<sup>7</sup>

## Reduction of **3ap** to **7**



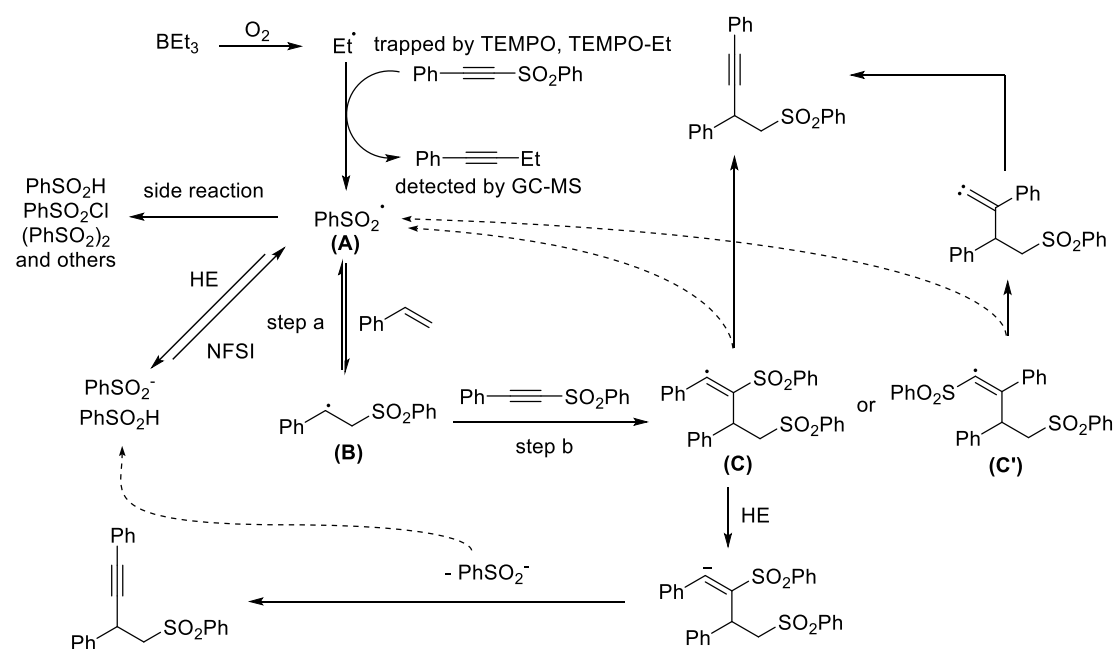
Product **7** was prepared according literature method.<sup>8</sup> To a solution of **3ap** (0.1 mmol, 36 mg) and 10 wt% Pd/C (10mol%, 10 mg) in THF (1 mL), the hydrogenation was performed at room temperature for 24 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA, 10:1) to yield **7**.

Product **7** was obtained as a colorless oil (35.5 mg, 98% yield,  $R_f$  = 0.4 (petroleum ether/ethyl acetate = 5:1)). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.52 (d,  $J$  = 8.1 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.20 (d,  $J$  = 7.0 Hz, 1H), 7.18 – 7.09 (m, 6H), 6.52 (d,  $J$  = 11.5 Hz, 1H), 5.79 (t,  $J$  = 10.8 Hz, 1H), 4.41 – 4.20 (m, 1H), 3.48 (d,  $J$  = 6.9 Hz, 2H), 2.38 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*)  $\delta$  144.5, 142.0, 136.6, 136.2, 131.6, 130.7, 129.7, 129.2, 128.7, 128.4, 128.2, 127.3, 127.2, 63.1, 39.4, 21.7. These data matches with the reported value.<sup>9</sup>

## A tentative mechanism

On the basis of these results and previous reports,<sup>10</sup> a tentative mechanism for this radical alkynylsulfonylation process is depicted in Scheme S1. During the reaction condition optimization, but-1-yn-1-ylbenzene, presumably generated from the interaction between ethyl radical and alkynylsulfone (**2a**), was observed by GC-MS analysis (Table 1, entry 3). Therefore, catalytic amount of  $\text{BEt}_3$  can successfully initiate the reaction to generate a phenyl sulfonyl radical (**A**),<sup>11</sup> which can add to a styrene (step a) to form a benzylic radical (**B**). Then, the radical **B** reacts with **2a** (step b) to produce the final alkynylsulfonylation product and to regenerate the sulfonyl radical (**A**) species. However, without the assistance of HE and NFSI, only a trace amount of the alkynylsulfonylation product was observed, presumably because of the reversible addition of the sulfonyl radical to the styrene (step a) and the steric hindrance for step b.<sup>12</sup> As a result, random side reactions of the sulfonyl radical **A** terminate the reaction. On the basis of the previous studies, HE can reduce the aryl sulfonyl radical to an arylsulfonic acid,<sup>13</sup> while NFSI has the power to oxidize an arylsulfonic acid back to the corresponding aryl sulfonyl radical.<sup>14</sup> Therefore, the overall effect of HE and NFSI presumably is that they can maintain exist of the sulfonyl radical in this study and consequently promote the reaction. However, other possibilities should also be considered.

Scheme S1. Mechanism hypothesis



## Single crystal data of 3ai (CCDC 2046732)

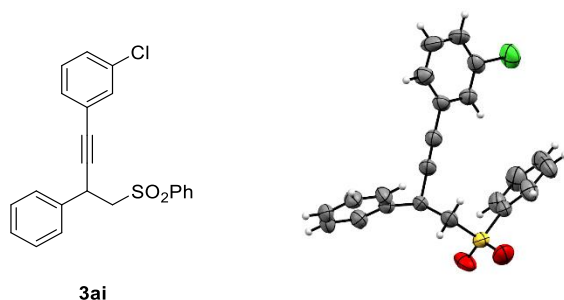


Table 1. Crystal data and structure refinement for **3ai**.

Identification code	<b>3ai</b>	
Empirical formula	C <sub>22</sub> H <sub>16</sub> Cl N <sub>0</sub> O <sub>2</sub> S	
Formula weight	379.86	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub>	
Unit cell dimensions	a = 5.556(5) Å	α = 90°.
	b = 16.760(16) Å	β = 90.089(17)°.
	c = 10.120(9) Å	γ = 90°.
Volume	942.4(15) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.339 Mg/m <sup>3</sup>	
Absorption coefficient	0.326 mm <sup>-1</sup>	
F(000)	394	
Crystal size	0.2 x 0.1 x 0.1 mm <sup>3</sup>	
Theta range for data collection	3.156 to 27.514°.	
Index ranges	-7 ≤ h ≤ 7, -21 ≤ k ≤ 21, -13 ≤ l ≤ 13	
Reflections collected	7376	
Independent reflections	4045 [R(int) = 0.0456]	
Completeness to theta = 25.242°	97.9 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4045 / 1 / 237	
Goodness-of-fit on F <sup>2</sup>	0.867	
Final R indices [I > 2σ(I)]	R1 = 0.0441, wR2 = 0.0960	
R indices (all data)	R1 = 0.0531, wR2 = 0.0994	
Absolute structure parameter	-0.03(6)	
Extinction coefficient	0.015(3)	
Largest diff. peak and hole	0.304 and -0.192 e.Å <sup>-3</sup>	

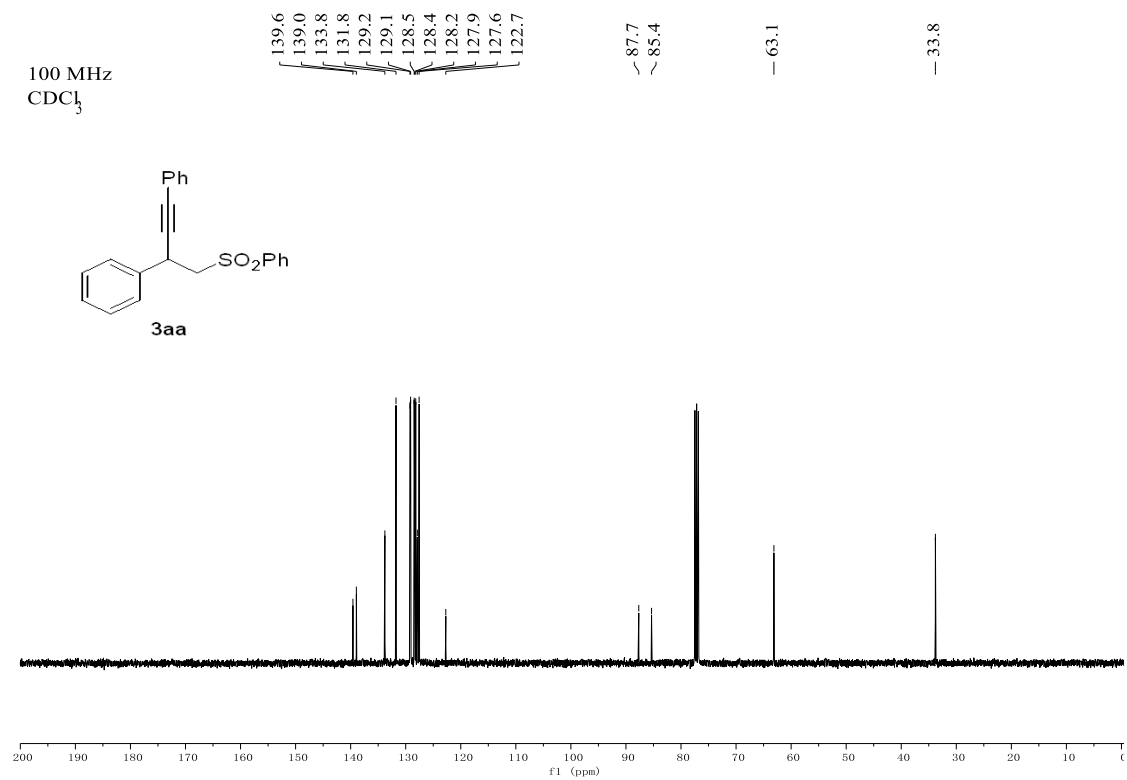
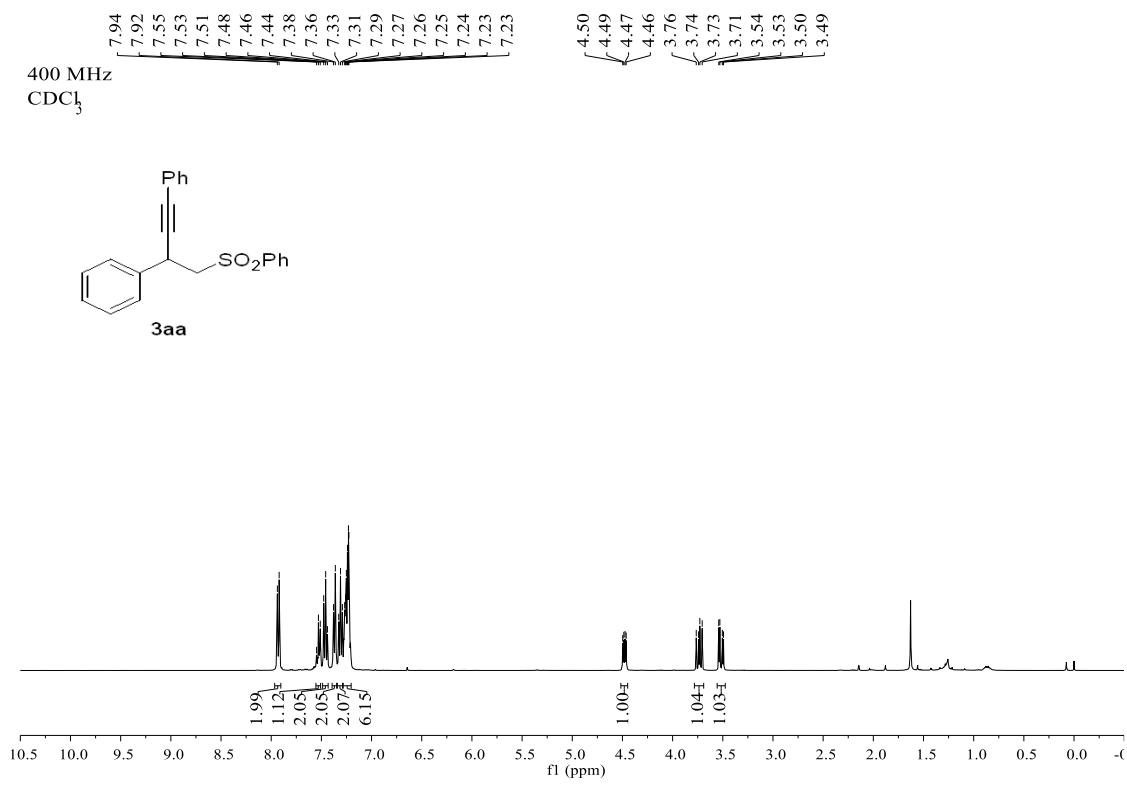


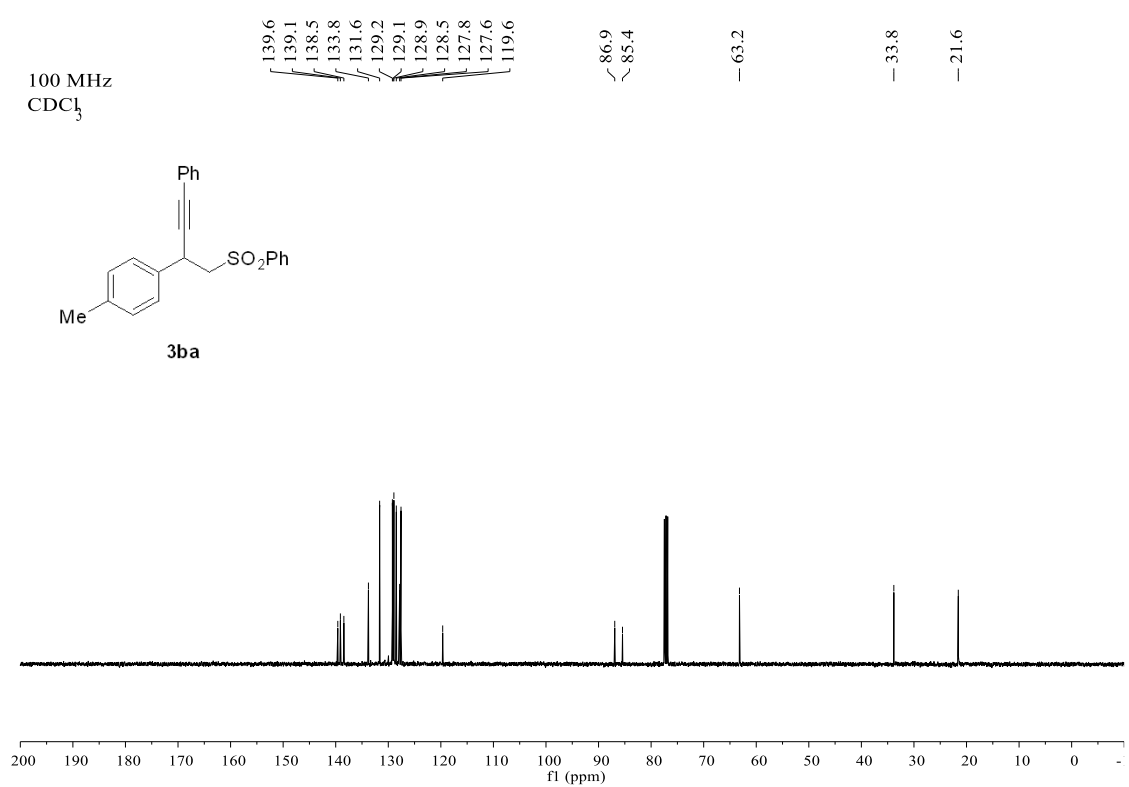
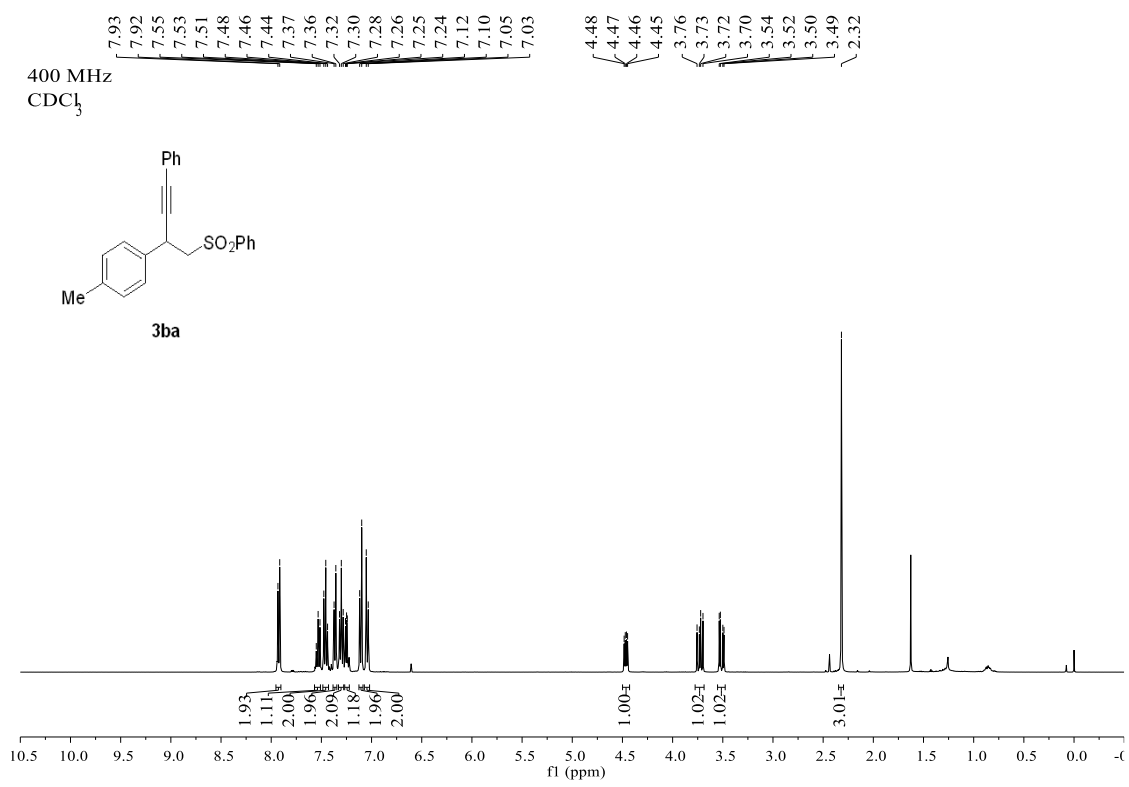
## References

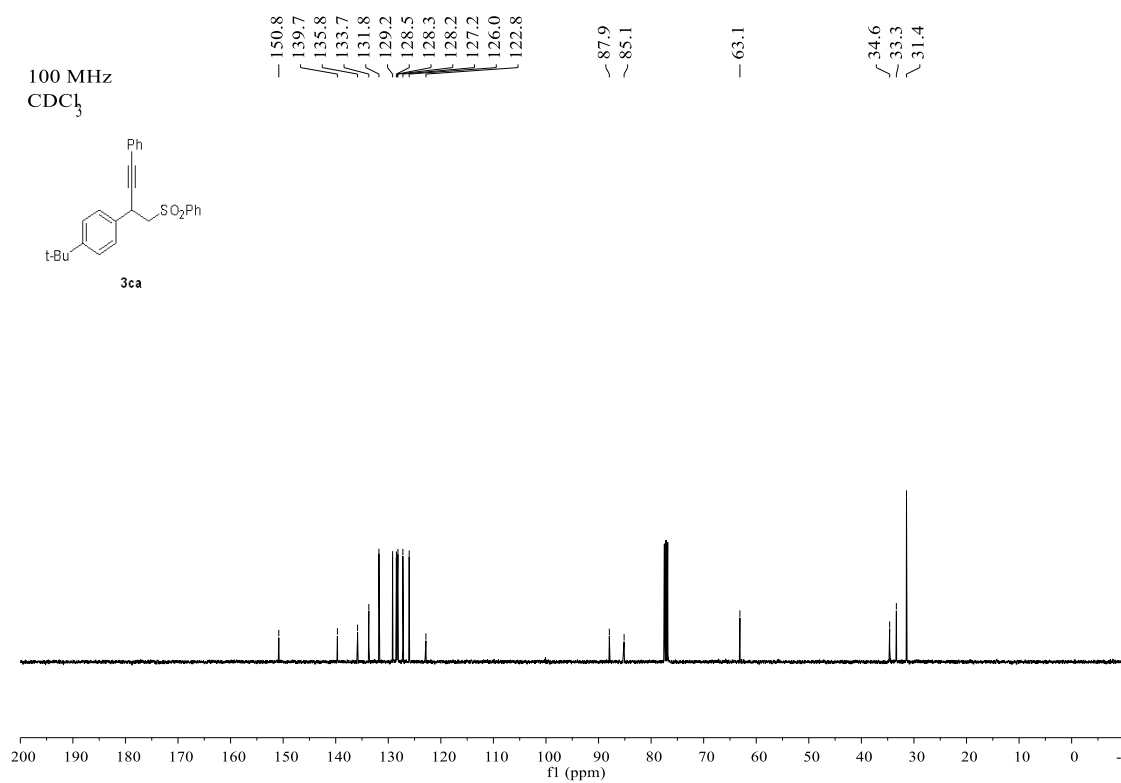
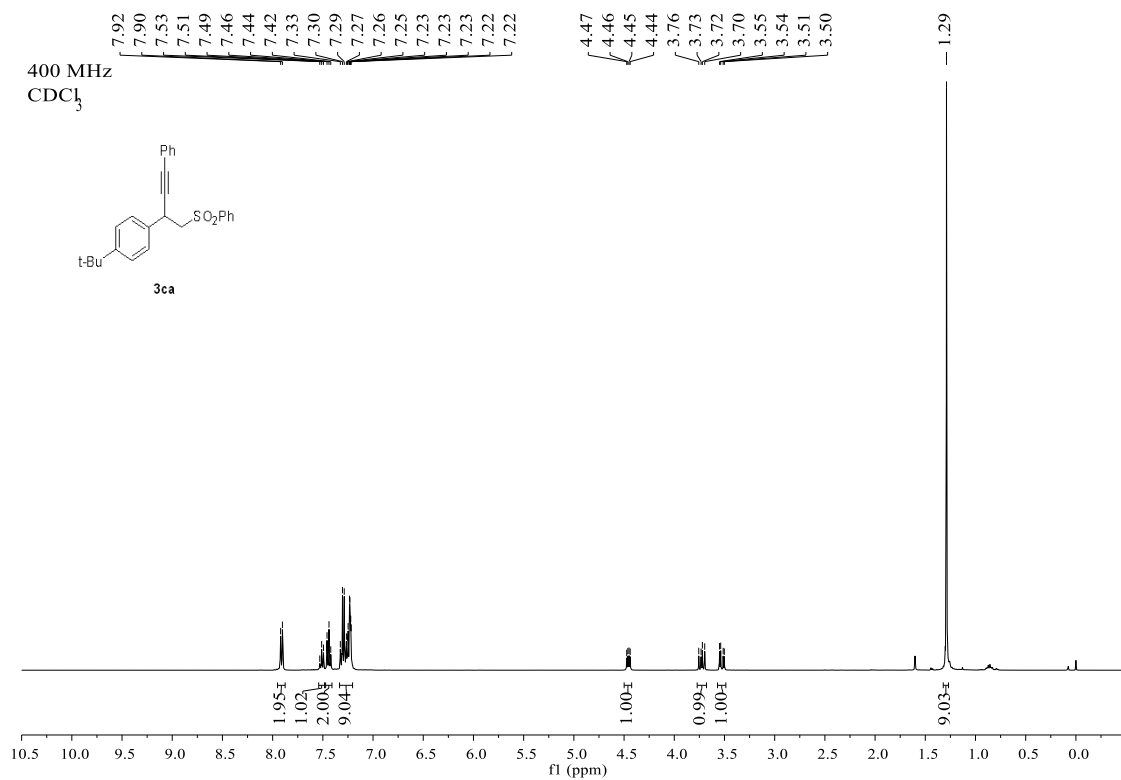
1. J. Meesin, P. Katrun, C. Pareseecharoen, M. Pohmakotr, V. Reutrakul, D. Soorukram and C. Kuhakarn, Iodine-catalyzed Sulfonylation of Arylacetylenic Acids and Arylacetylenes with Sodium Sulfinates: Synthesis of Arylacetylenic Sulfones, *J. Org. Chem.*, 2016, **81**, 2744.
2. (a) J. Li, H. Tian, M. Jiang, H. Yang, Y. Zhao and H. Fu, Consecutive visible-light photoredox decarboxylative couplings of adipic acid active esters with alkynyl sulfones leading to cyclic compounds, *Chem. Commun.*, 2016, **52**, 8862; (b) R. Roman, P. Barrio, N. Mateu, D. M. Sedgwick and S. Fustero, Copper-Catalyzed Regioselective Synthesis of (E)- $\beta$ -Fluorovinyl Sulfones, *Molecules*, 2019, **24**, 1569; (c) Q. Zhong, Y. Zhao, S. Sheng and J. Chen, Electrochemical decarboxylative sulfonylation of arylacetylenic acids with sodium arylsulfonates: Access to arylacetylenic sulfones, *Synthetic Commun.*, 2020, **50**, 161.
3. Q. Q. Zhao, J. Chen, X. S. Zhou, X. Y. Yu, J. R. Chen and W. J. Xiao, Photogenerated Neutral Nitrogen Radical Catalyzed Bifunctionalization of Alkenes, *Chem. Eur. J.*, 2019, **25**, 8024.
4. X. Y. Dong, J. T. Cheng, Y. F. Zhang, Z. L. Li, T. Y. Zhan, J. J. Chen, F. L. Wang, N. Y. Yang, L. Ye, Q. S. Gu and X. Y. Liu, Copper-Catalyzed Asymmetric Radical 1,2-Carboalkynylation of Alkenes with Alkyl Halides and Terminal Alkynes, *J. Am. Chem. Soc.*, 2020, **142**, 9501.
5. X. Mo, B. Chen and G. Zhang, Copper-Catalyzed Enantioselective Sonogashira Type Coupling of Alkynes with  $\alpha$ -Bromoamides, *Angew. Chem. Int. Ed.*, 2020, **59**, 13998.
6. A. A. Fesenko and A. D. Shutalev, Different modes of acid-catalyzed cyclization of 4-( $\gamma$ -oxoalkyl) semicarbazide hydrazones: 7-membered versus 14-membered cyclic semicarbazones formation, *Tetrahedron*, 2015, **71**, 9528.
7. X. Zhu, W. Deng, M. F. Chiou, C. Ye, W. Jian, Y. Zeng, Y. Jiao, L. Ge, Y. Li, X. Zhang and H. Bao, Copper-Catalyzed Radical 1,4-Difunctionalization of 1,3-Enynes with Alkyl Diacyl Peroxides and N-Fluorobenzenesulfonimide, *J. Am. Chem. Soc.*, 2019, **141**, 548.
8. H. L. Zhang, Z. F. Sun, L. N. Zhou, L. Liu, T. Zhang and Z. T. Du, Synthesis of the Sex Pheromone of the Tea Tussock Moth Based on a Resource Chemistry Strategy, *Molecules*, 2018, **23**, 1347.
9. F. Han, L. Yang, Z. Li, Y. Zhao and C. Xia, Metal-Free and Recyclable Route to Synthesize Polysubstituted Olefins via C-C Bond Construction from Direct Dehydrative Coupling of Alcohols or Alkenes with Alcohols Catalyzed by Sulfonic Acid-Functionalized Ionic Liquids, *Adv. Synth. Catal.*, 2014, **356**, 2506.
10. (a) V. Liautard, F. Robert and Y. Landais, Free-Radical Carboalkynylation and Carboalkenylation of Olefins, *Org. Lett.*, 2011, **13**, 2658; (b) H. Jiang, Y. He, Y. Cheng and S. Yu, Radical Alkynyltrifluoromethylation of Alkenes Initiated by an Electron Donor-Acceptor Complex, *Org. Lett.*, 2017, **19**, 1240; (c) S. Zhou, T. Song, H. Chen, Z. Liu, H. Shen and C. Li, Catalytic Radical Trifluoromethylalkynylation of Unactivated Alkenes, *Org. Lett.*, 2017, **19**, 698; (d) S. B. Nagode, R. Kant and N. Rastogi, Hantzsch Ester-Mediated Benzannulation of Diazo Compounds under Visible Light Irradiation, *Org. Lett.*, 2019, **21**,

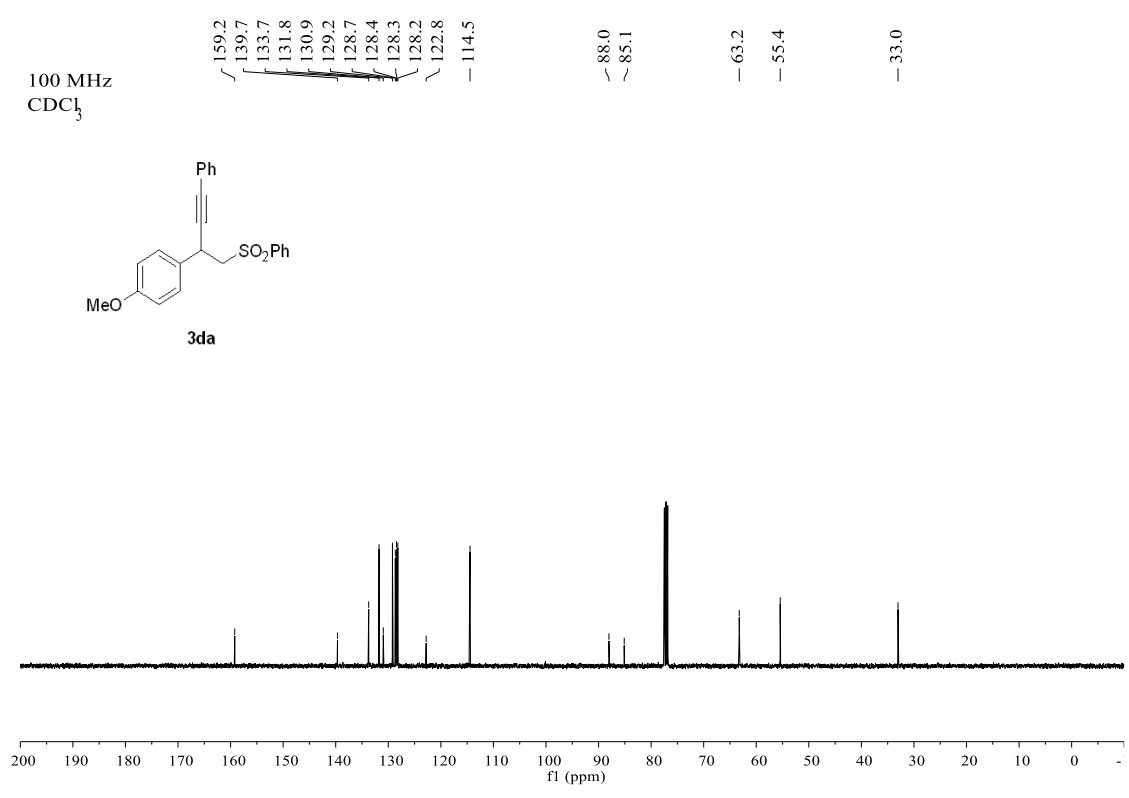
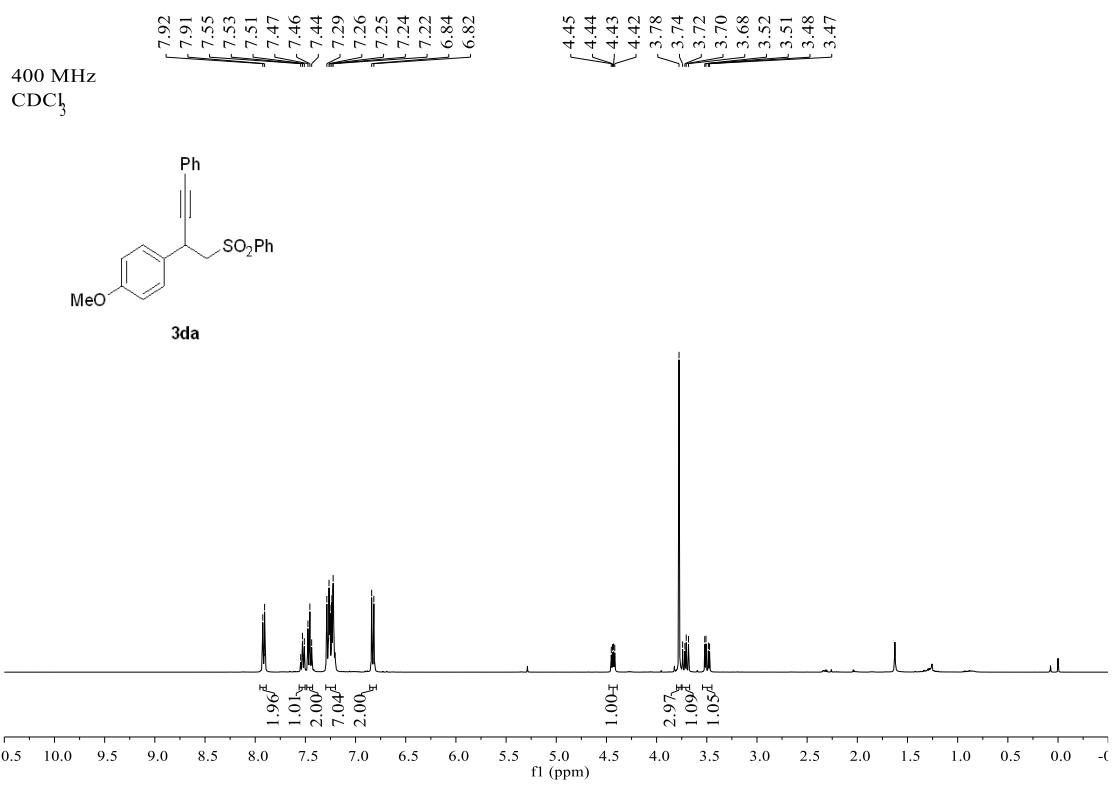
- 6249; (e) D. L. Zhu, Q. Wu, H. Y. Li, H. X. Li and J. P. Lang, Hantzsch Ester as a Visible - Light Photoredox Catalyst for Transition-Metal-Free Coupling of Arylhalides and Arylsulfonates, *Chem. Eur. J.*, 2020, **26**, 3484; (f) H. Zhang, Y. Song, J. Zhao, J. Zhang and Q. Zhang, Regioselective radical aminofluorination of styrenes, *Angew. Chem. Int. Ed.*, 2014, **53**, 11079; (g) D. P. Curran and T. R. McFadden, Understanding Initiation with Triethylboron and Oxygen: The Differences between Low-Oxygen and High-Oxygen Regimes, *J. Am. Chem. Soc.*, 2016, **138**, 7741.
11. (a) N. Miyamoto, D. Fukuoka, K. Utimoto and H. Nozaki, The Reaction of Styryl Sulfoxides or Sulfones with Boranes, *B. Chem. Soc. Jpn.*, 1974, **47**, 503; (b) D. Markovic, A. Varela-Alvarez, J. A. Sordo and P. Vogel, Mechanism of the diphenyldisulfone - catalyzed isomerization of alkenes. Origin of the chemoselectivity: experimental and quantum chemistry studies, *J. Am. Chem. Soc.*, 2006, **128**, 7782; (c) N. P. Ramirez, B. Konig and J. C. Gonzalez-Gomez, Decarboxylative Cyanation of Aliphatic Carboxylic Acids via Visible-Light Flavin Photocatalysis, *Org. Lett.*, 2019, **21**, 1368.
12. (a) V. I. Timokhin, S. Gastaldi, M. P. Bertrand and C. Chatgililoglu, Rate constants for the beta-elimination of tosyl radical from a variety of substituted carbon-centered radicals, *J. Org. Chem.*, 2003, **68**, 3532; (b) C. Chatgililoglu, O. Mozziconacci, M. Tamba, K. Bobrowski, G. Kciuk, M. P. Bertrand, S. Gastaldi and V. I. Timokhin, Kinetic Studies on the Formation of Sulfonyl Radicals and Their Addition to Carbon-Carbon Multiple Bonds, *J. Phys. Chem. A*, 2012, **116**, 7623.
13. J. Li, H. Tian, M. Jiang, H. Yang, Y. Zhao and H. Fu, Consecutive visible-light photoredox decarboxylative couplings of adipic acid active esters with alkynyl sulfones leading to cyclic compounds, *Chem. Commun.*, 2016, **52**, 8862.
14. Y. L. Zhu, C. F. Zhu, P. Zhou, W. J. Hao, D. C. Wang, S. J. Tu and B. Jiang, Pd(II)-Catalyzed Carbonyl-Directing Activation of Alkenes: Selective Fluorosulfonylation and Aminosulfonylation of 1,7-Enynes, *J. Org. Chem.*, 2018, **83**, 9641.

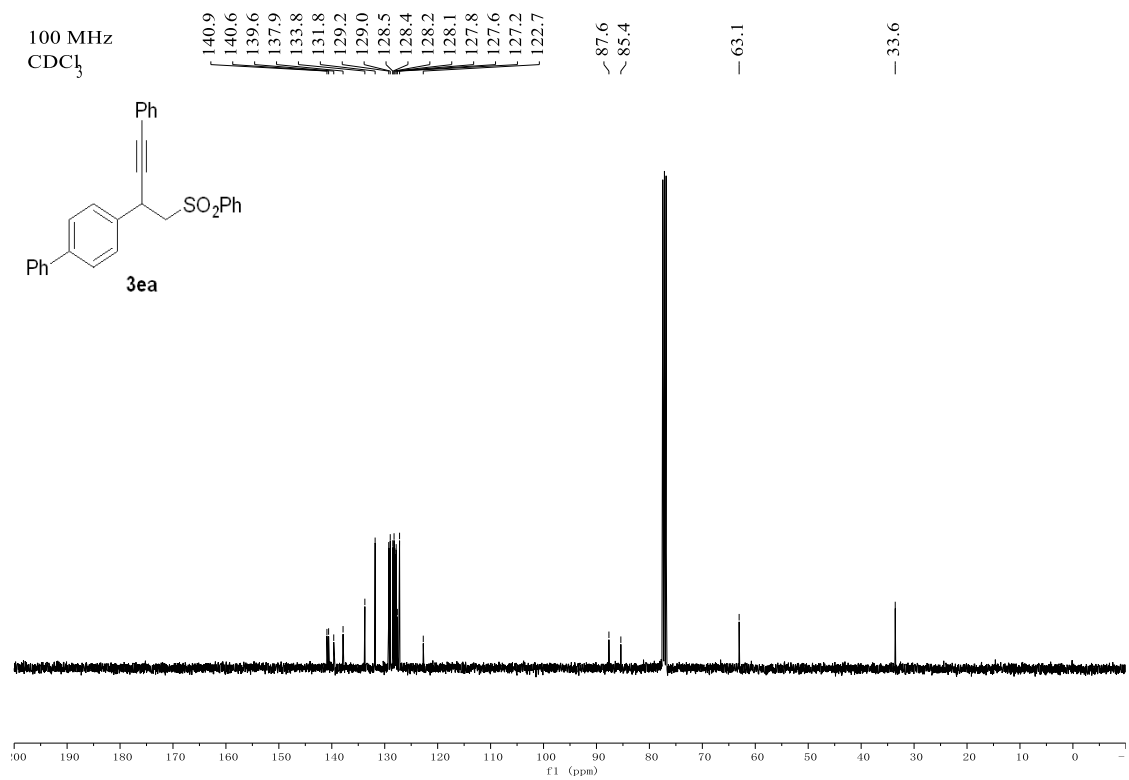
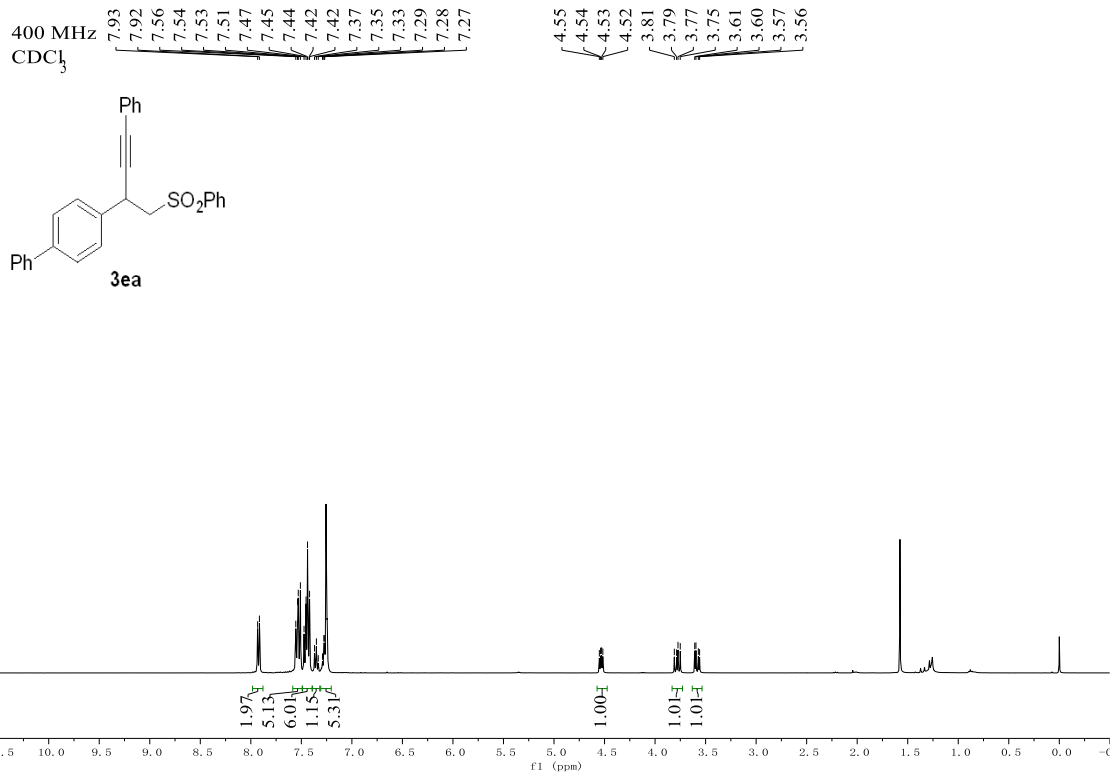
# NMR spectra





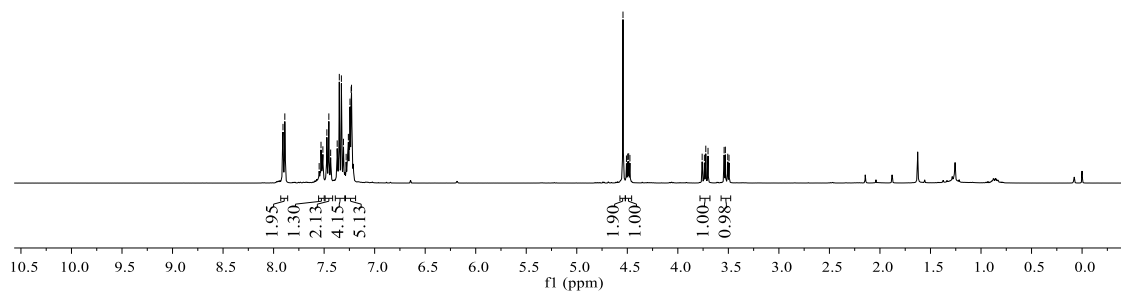
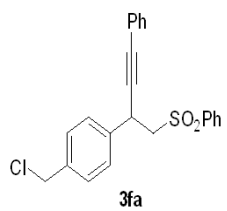






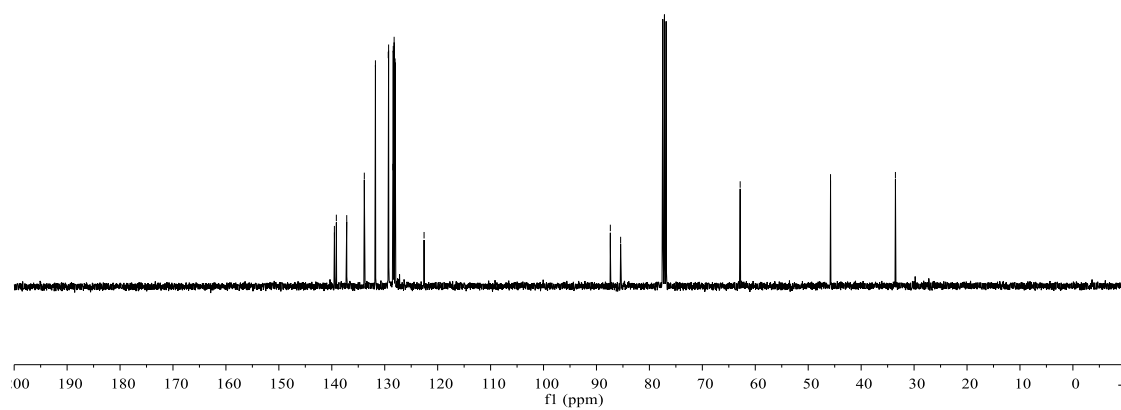
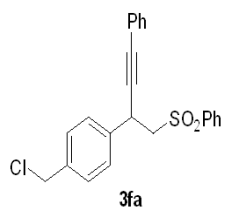
400 MHz  
CDCl<sub>3</sub>

7.91, 7.89, 7.55, 7.53, 7.51, 7.47, 7.45, 7.44, 7.37, 7.35, 7.33, 7.31, 7.28, 7.26, 7.25, 7.24, 7.23, 7.23, 4.54, 4.51, 4.50, 4.49, 4.47, 3.76, 3.74, 3.72, 3.70, 3.54, 3.53, 3.51, 3.49



100 MHz  
CDCl<sub>3</sub>

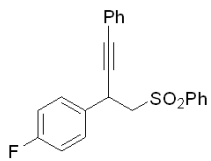
139.5, 139.1, 137.2, 133.9, 131.8, 129.3, 129.3, 128.5, 128.4, 128.2, 128.0, 122.6, 87.4, 85.4, 62.9, 45.8, 33.5



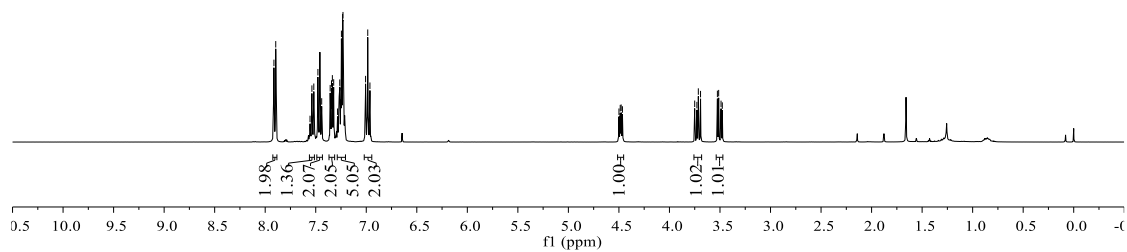


400 MHz  
CDCl<sub>3</sub>

7.91, 7.90, 7.56, 7.54, 7.52, 7.48, 7.44, 7.36, 7.34, 7.34, 7.32, 7.28, 7.26, 7.26, 7.25, 7.23, 7.23, 7.01, 6.99, 6.96, 4.50, 4.49, 4.48, 4.47, 3.75, 3.73, 3.71, 3.69, 3.53, 3.51, 3.49, 3.48

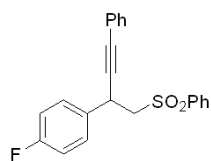


3ga

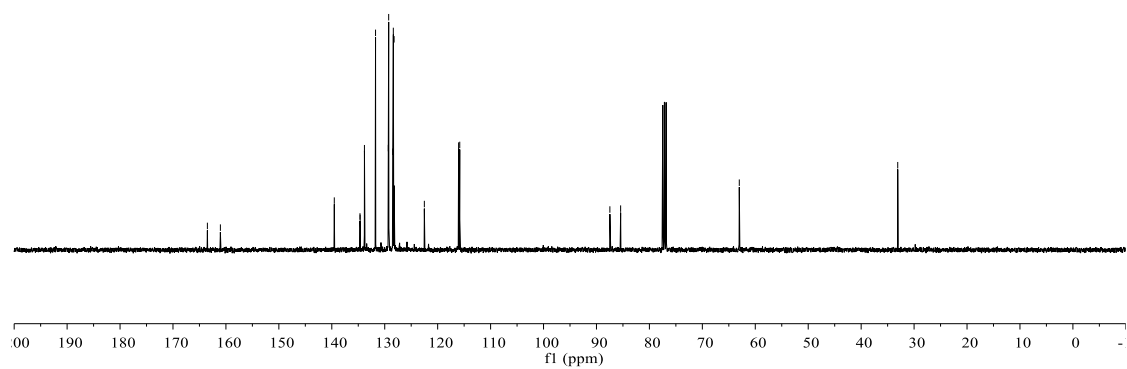


100 MHz  
CDCl<sub>3</sub>

163.5, 161.0, 139.5, 134.7, 134.6, 133.8, 131.7, 129.3, 128.5, 128.4, 128.2, 122.5, 116.0, 115.8, 87.5, 85.4, 63.0, 33.1

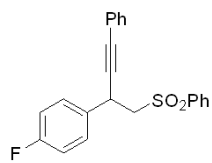


3ga

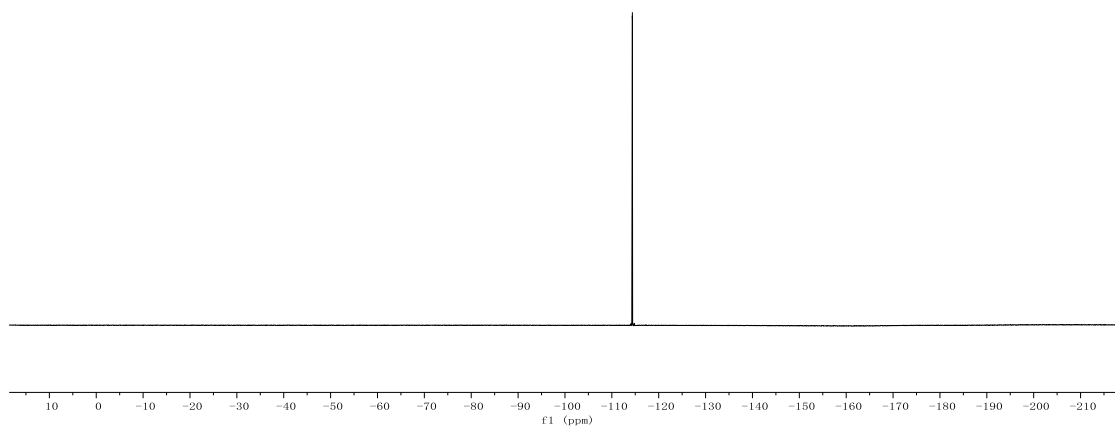


376 MHz  
CDCl<sub>3</sub>

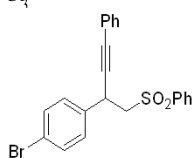
-114.4



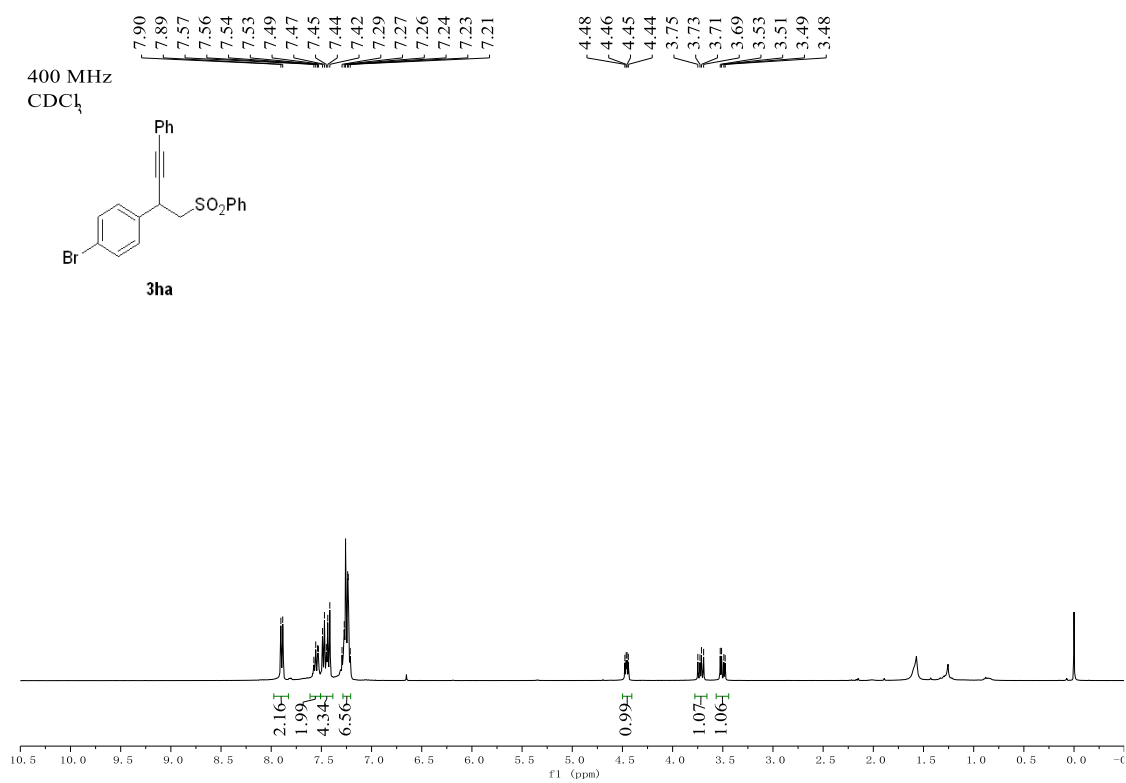
**3ga**

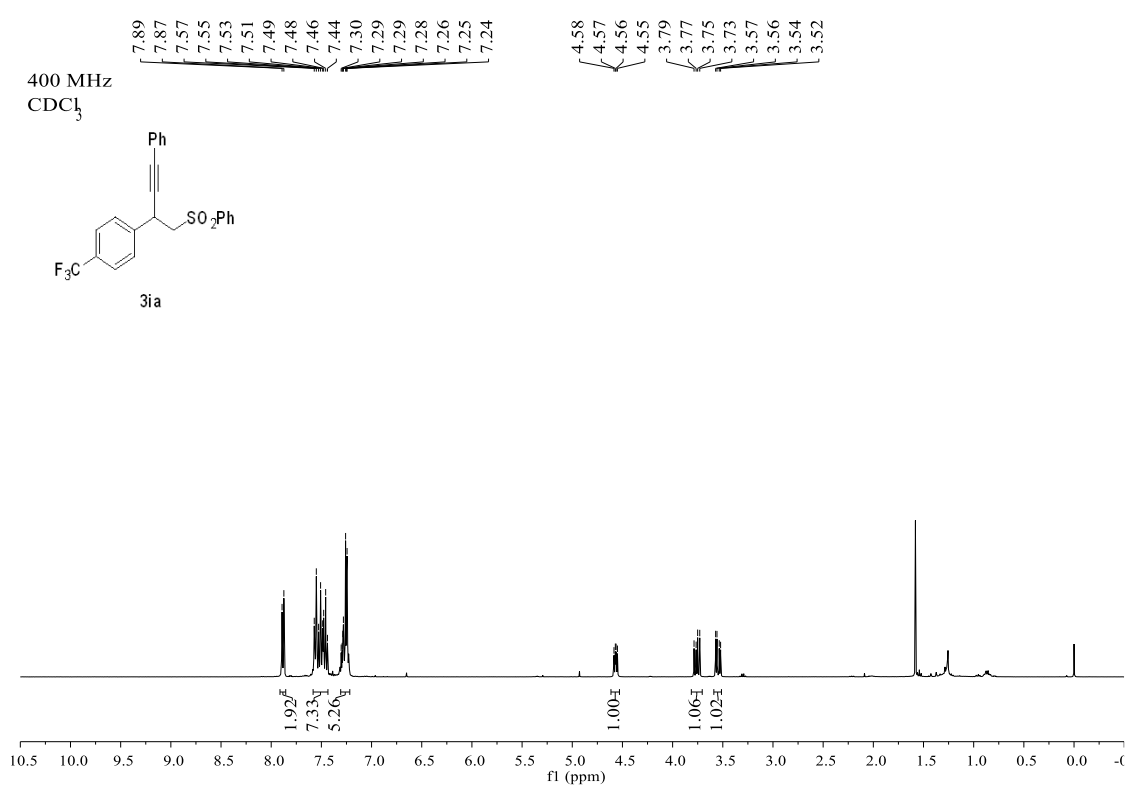
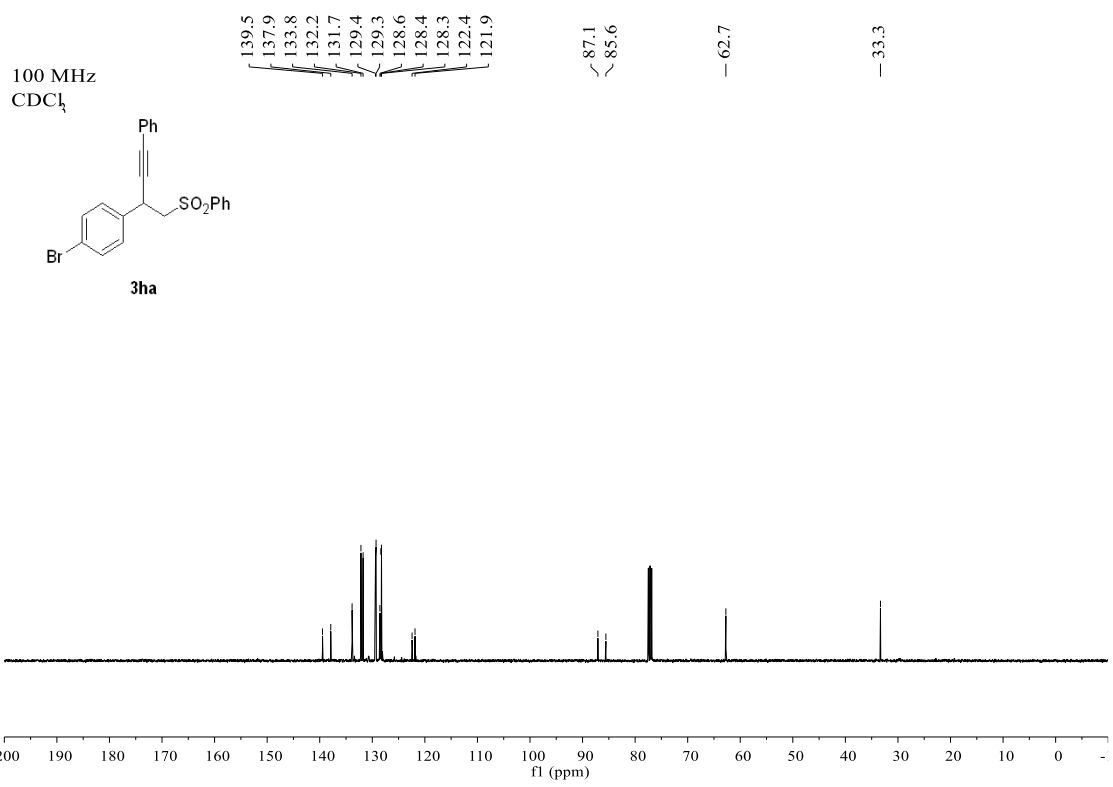


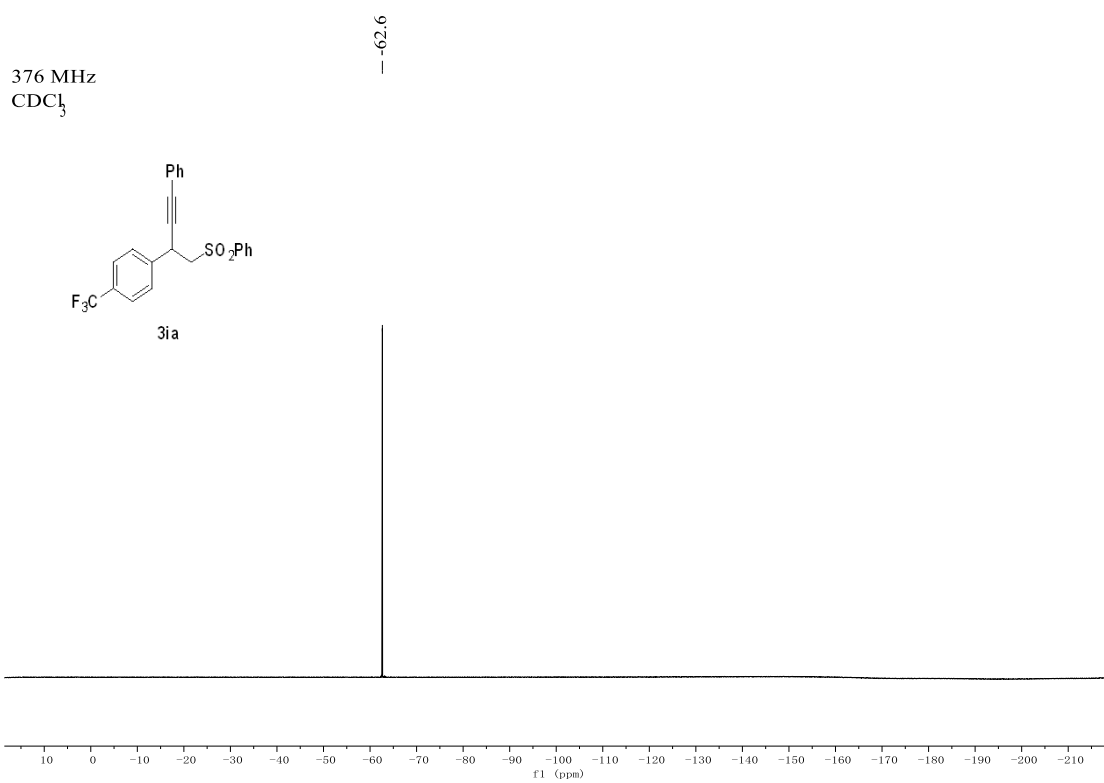
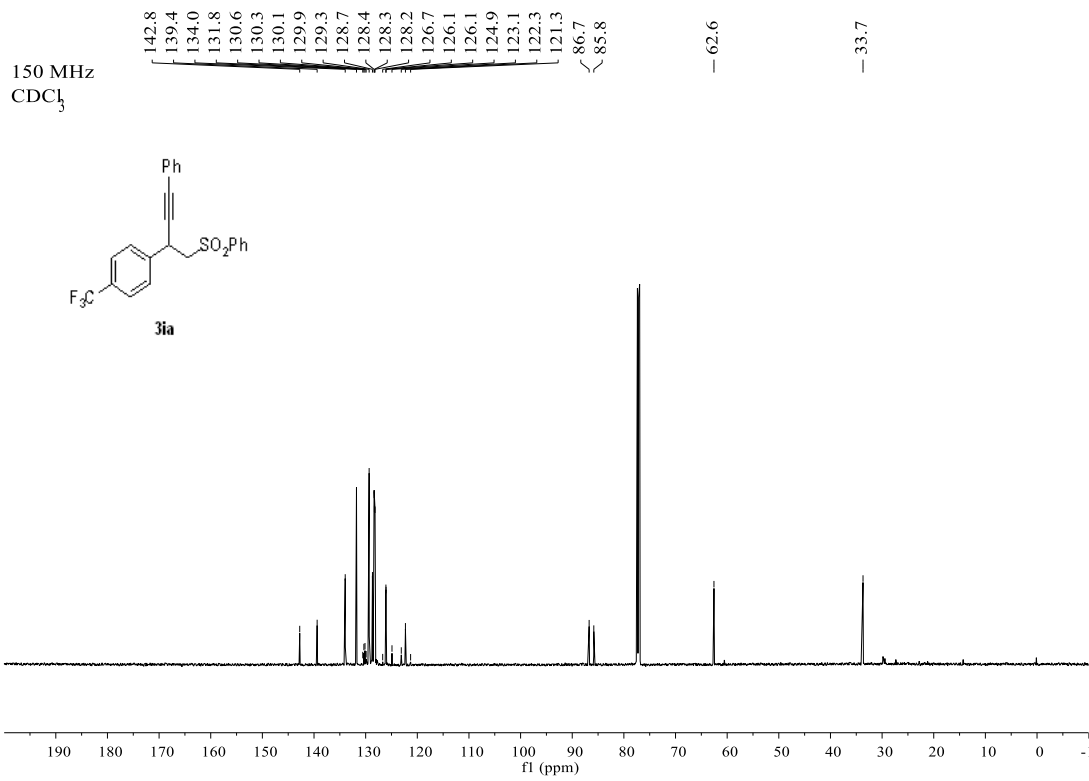
400 MHz  
CDCl<sub>3</sub>



**3ha**



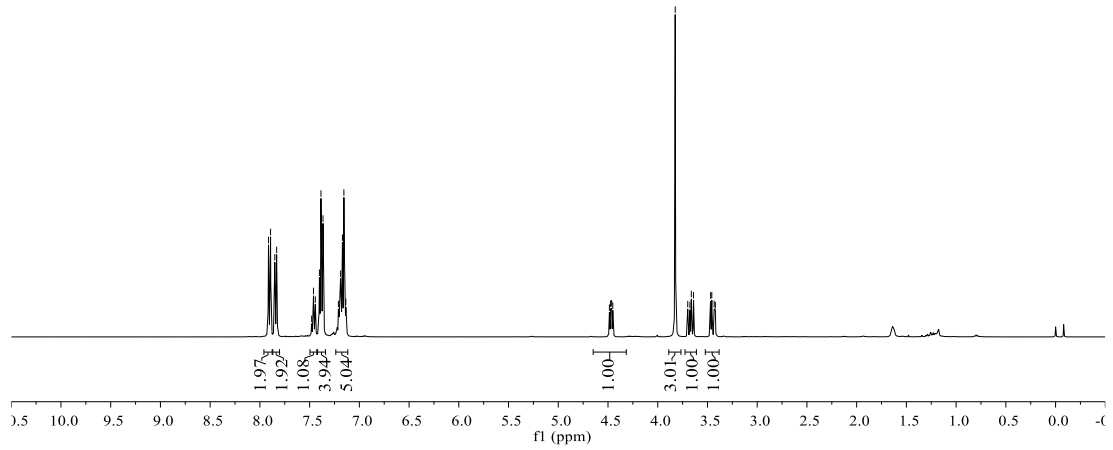
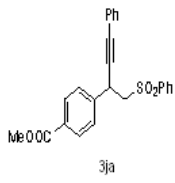




400 MHz  
CDCl<sub>3</sub>

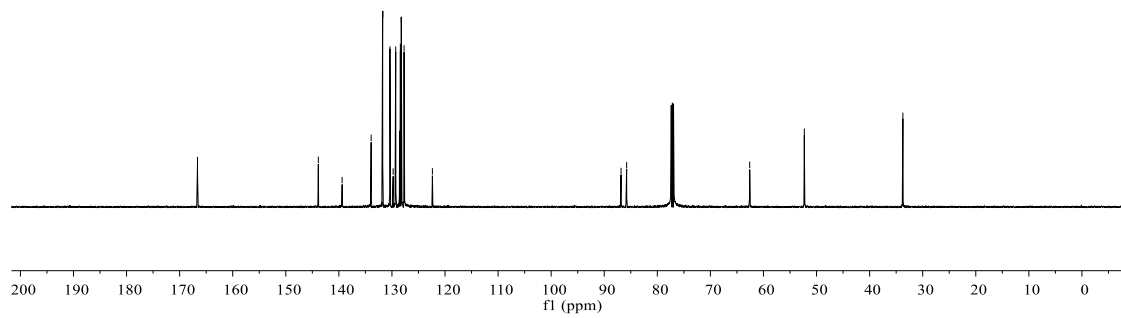
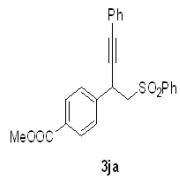
7.91  
7.89  
7.85  
7.83  
7.48  
7.46  
7.44  
7.40  
7.39  
7.37  
7.21  
7.19  
7.17  
7.16  
7.14

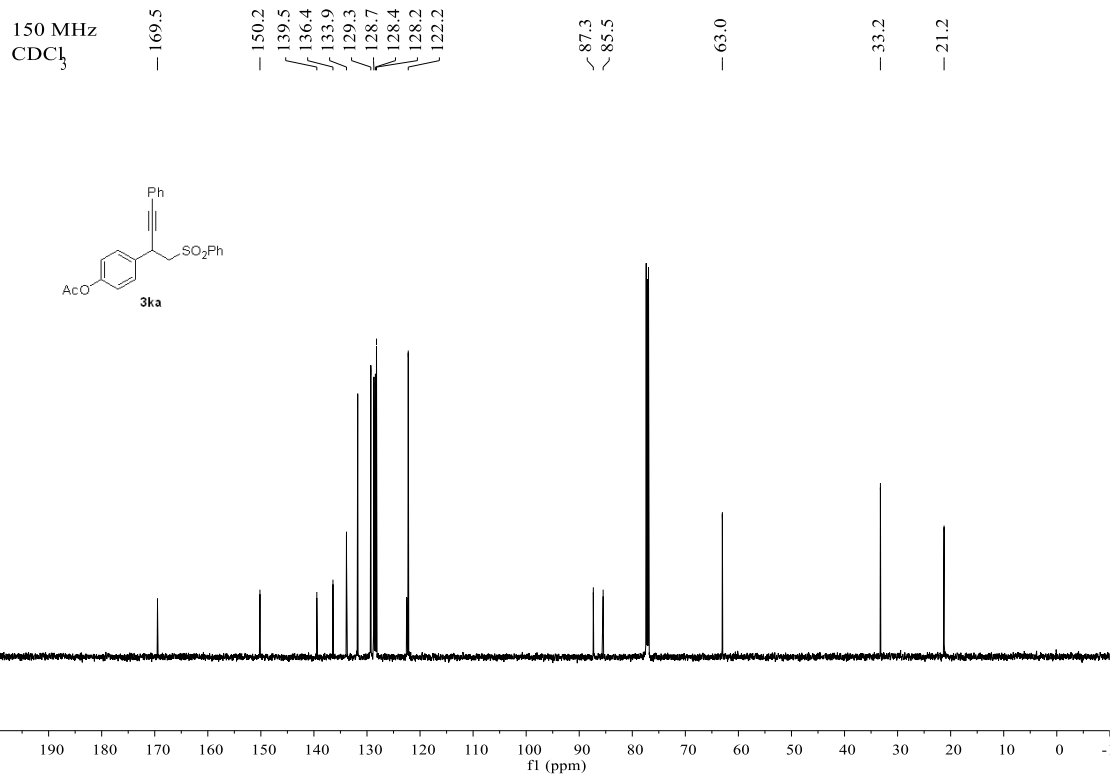
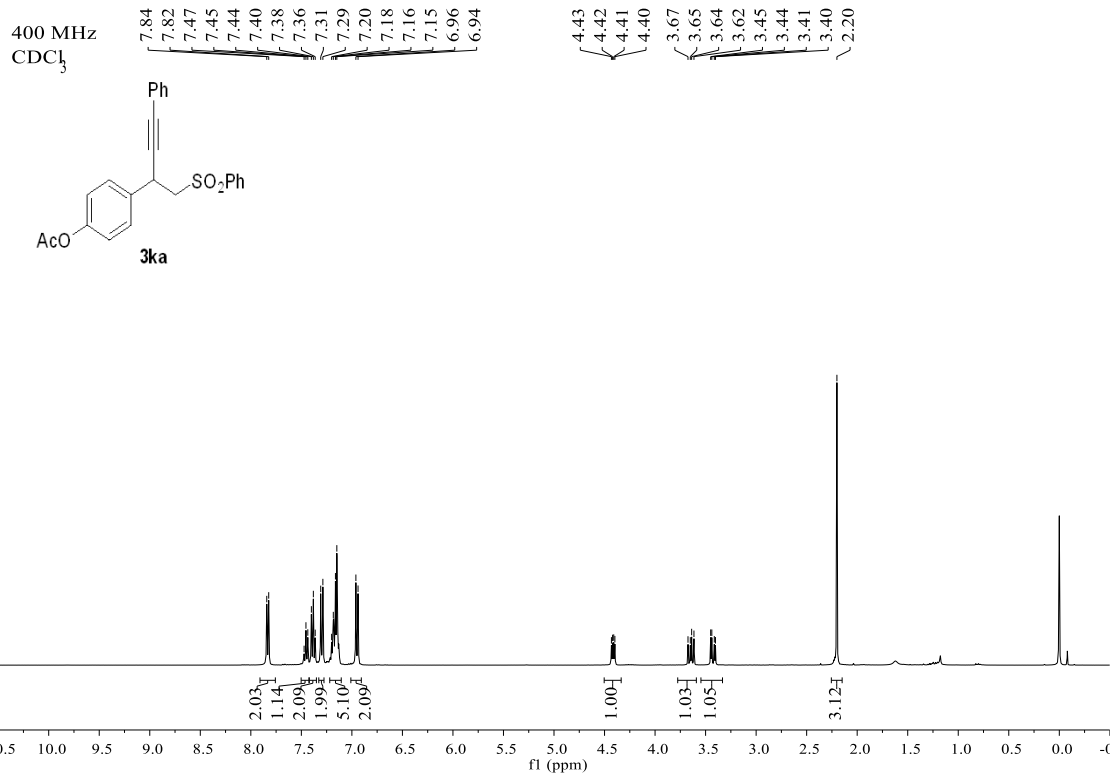
4.49  
4.47  
4.46  
4.45  
3.82  
3.70  
3.68  
3.66  
3.64  
3.47  
3.46  
3.43  
3.42



150 MHz  
CDCl<sub>3</sub>

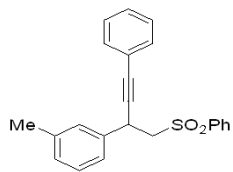
166.6  
143.9  
139.4  
133.9  
131.7  
131.7  
130.4  
129.8  
129.3  
128.6  
128.4  
128.2  
127.7  
122.4  
86.8  
85.8  
62.6  
52.3  
33.7



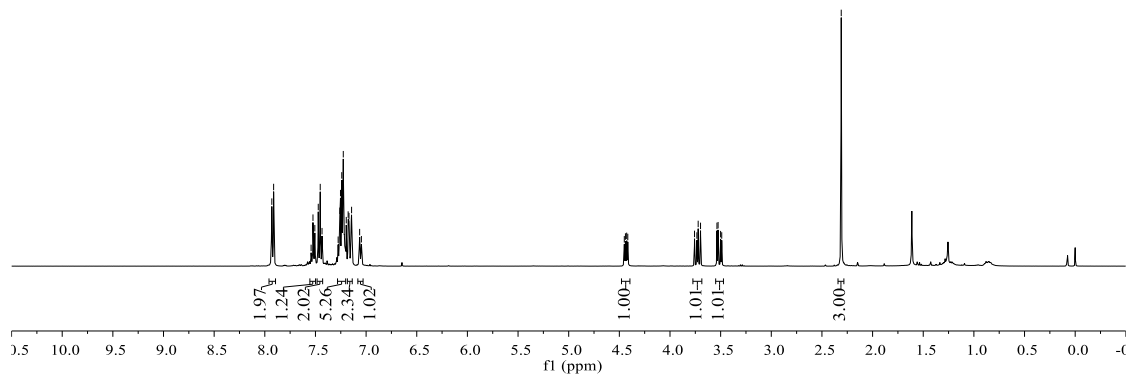


400 MHz  
 CDCl<sub>3</sub>

7.93, 7.91, 7.54, 7.52, 7.51, 7.47, 7.45, 7.44, 7.28, 7.26, 7.25, 7.24, 7.23, 7.20, 7.18, 7.17, 7.14, 7.06, 7.05, 4.45, 4.44, 4.43, 4.42, 3.76, 3.73, 3.72, 3.70, 3.54, 3.53, 3.50, 3.49, 2.31

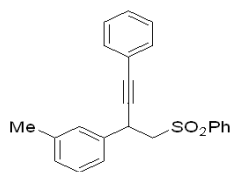


31a

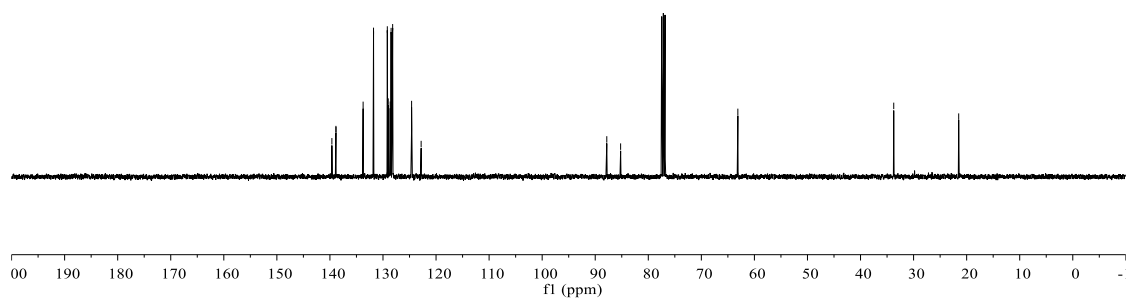


100 MHz  
 CDCl<sub>3</sub>

139.6, 138.9, 138.9, 133.7, 131.8, 129.2, 129.0, 128.6, 128.5, 128.3, 128.2, 128.2, 124.6, 122.8, 87.8, 85.2, 63.1, 33.7, 21.5



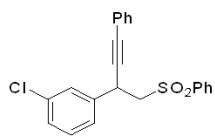
31a



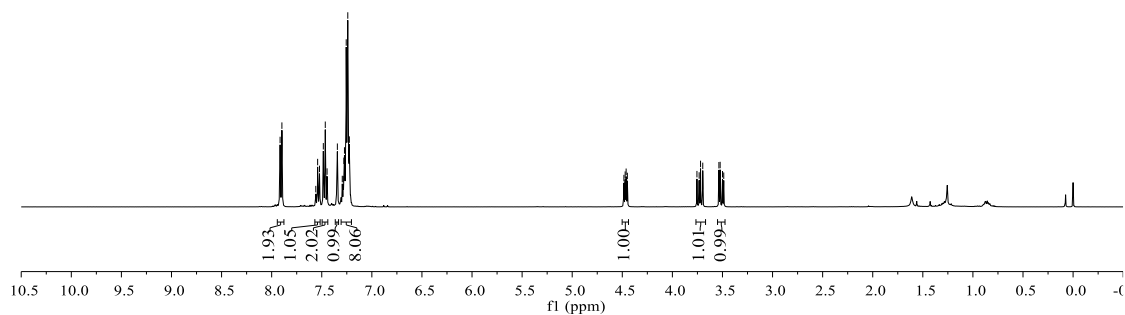
400 MHz  
CDCl<sub>3</sub>

7.92  
7.90  
7.56  
7.54  
7.52  
7.48  
7.46  
7.45  
7.34  
7.30  
7.29  
7.28  
7.27  
7.26  
7.24  
7.22

4.48  
4.47  
4.46  
4.45  
3.75  
3.73  
3.72  
3.70  
3.54  
3.52  
3.50  
3.49



**3ma**



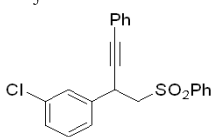
100 MHz  
CDCl<sub>3</sub>

140.8  
139.5  
134.9  
133.9  
131.8  
130.4  
129.3  
128.6  
128.4  
128.3  
128.2  
127.9  
125.9  
122.4

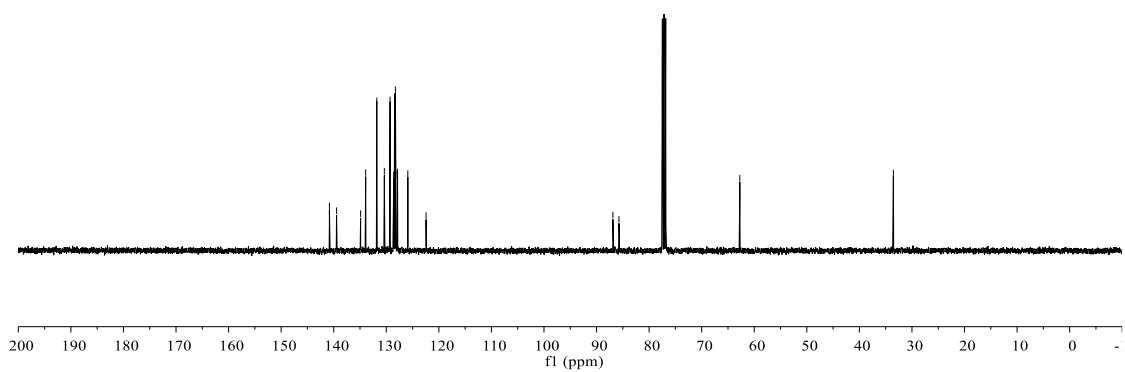
86.9  
85.7

62.7

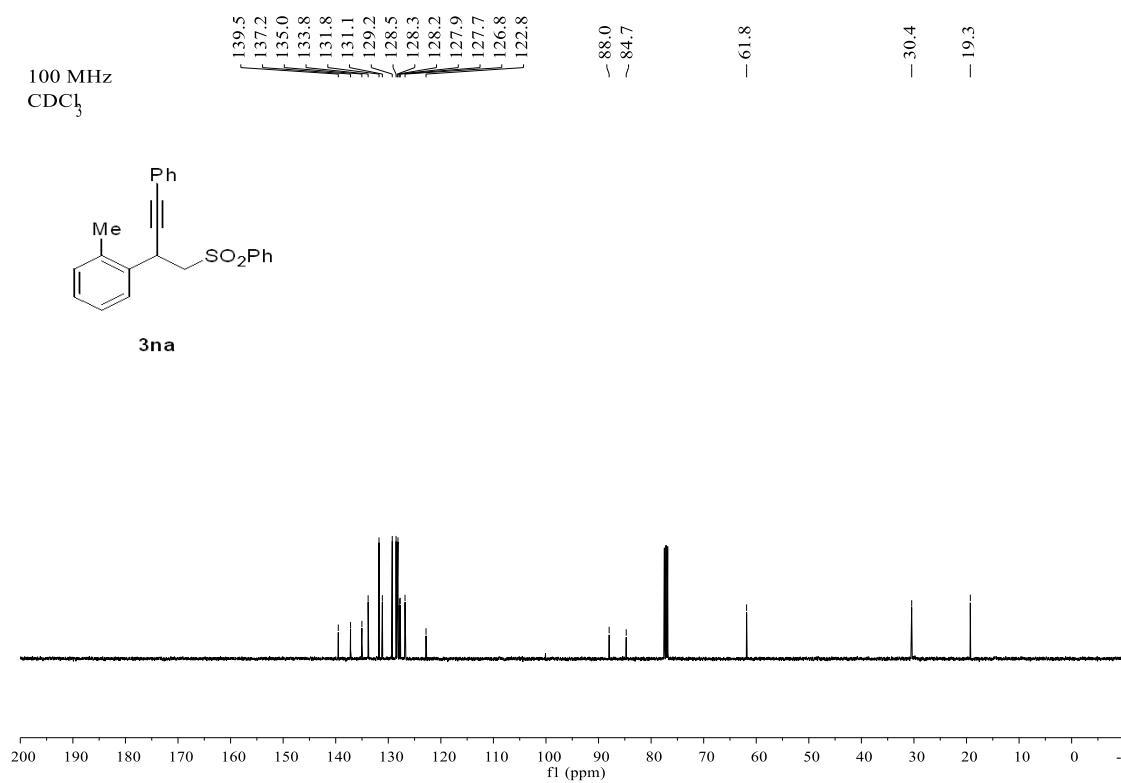
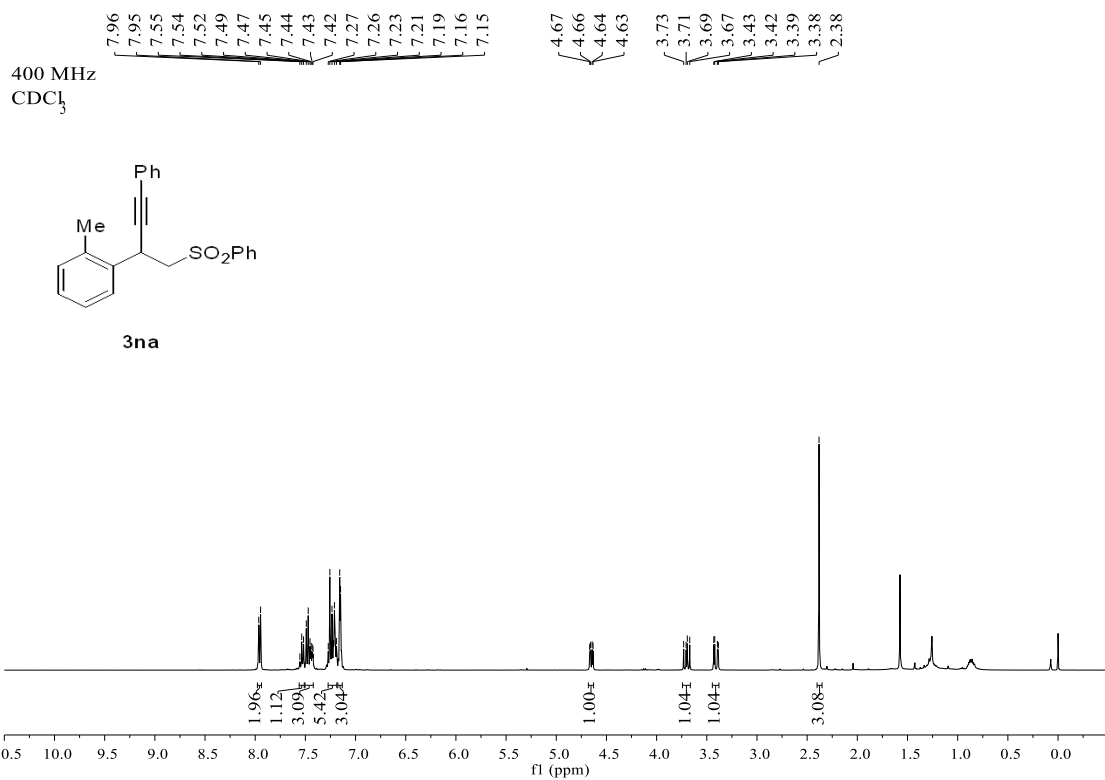
33.5



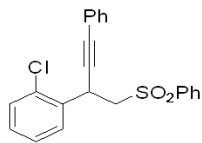
**3ma**



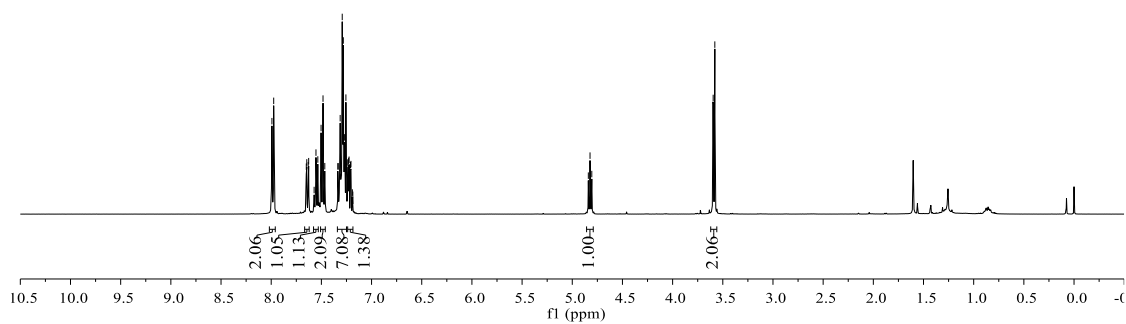




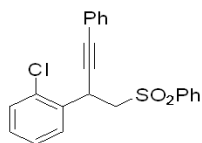
400 MHz  
 CDCl<sub>3</sub>



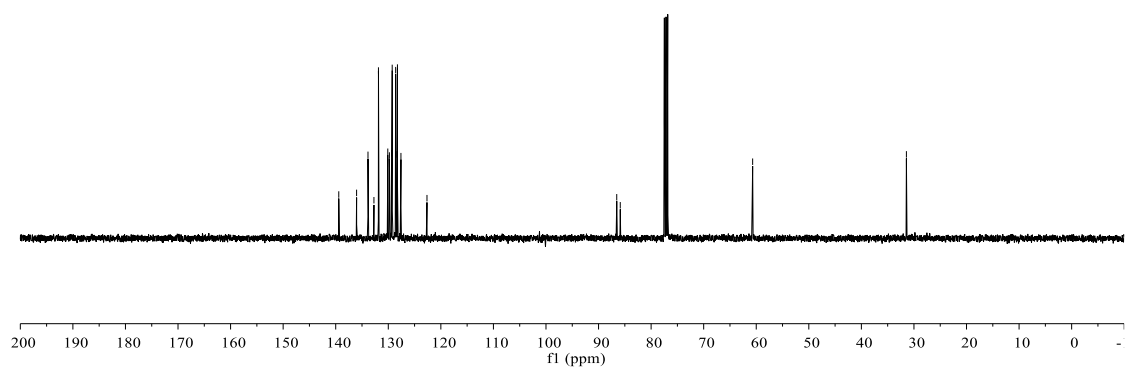
3oa

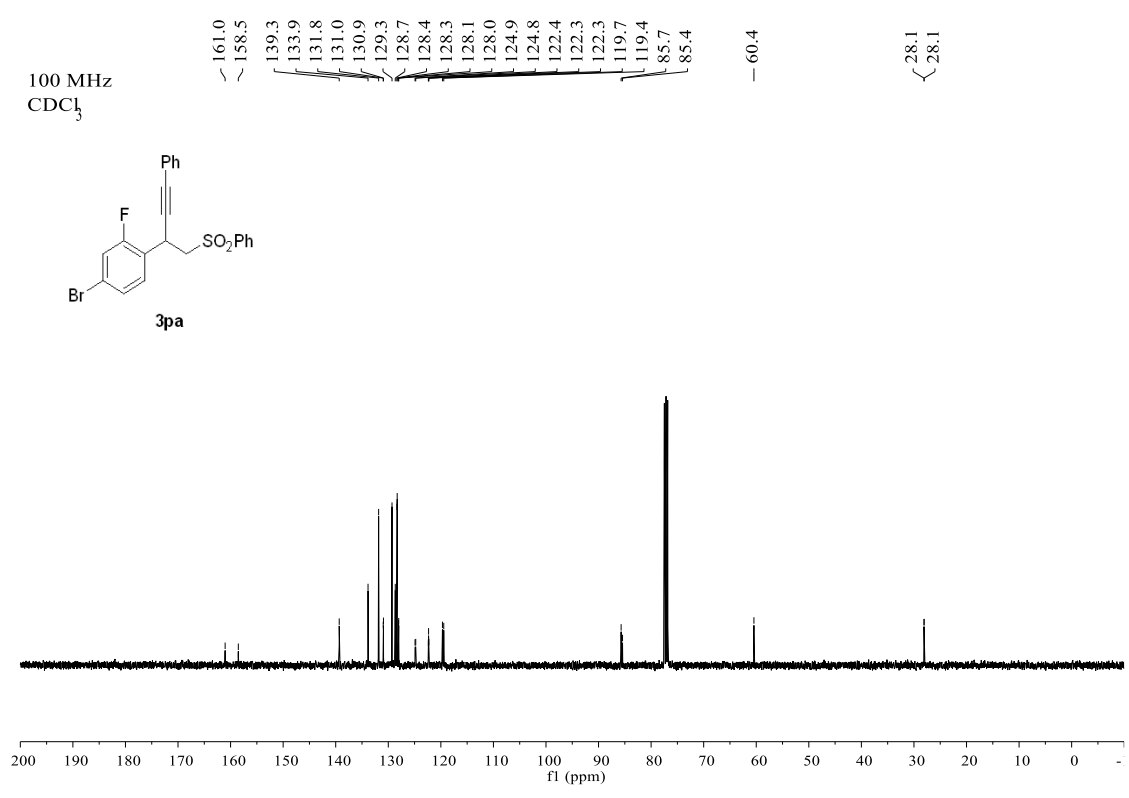
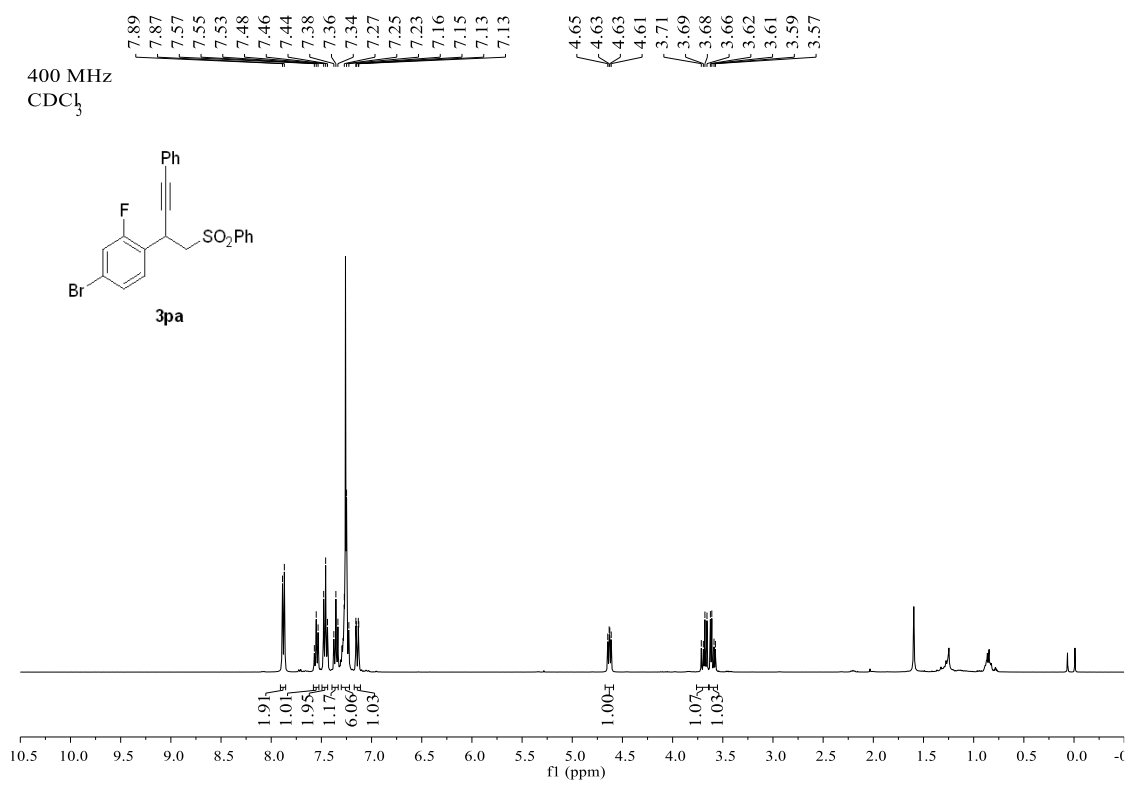


100 MHz  
 CDCl<sub>3</sub>



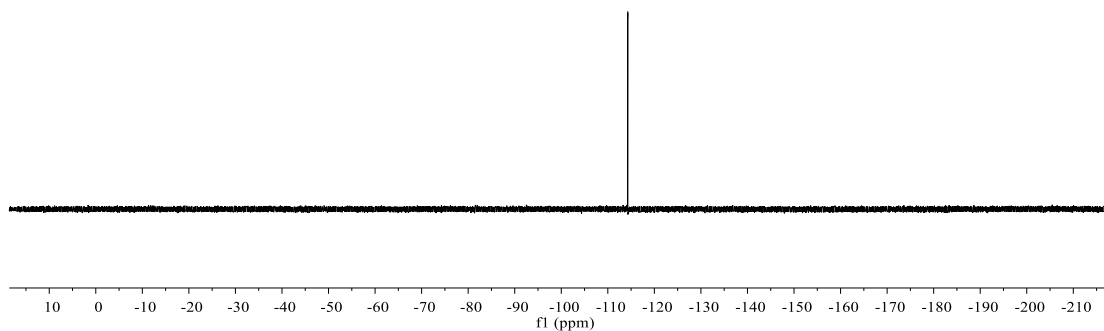
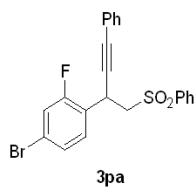
3oa



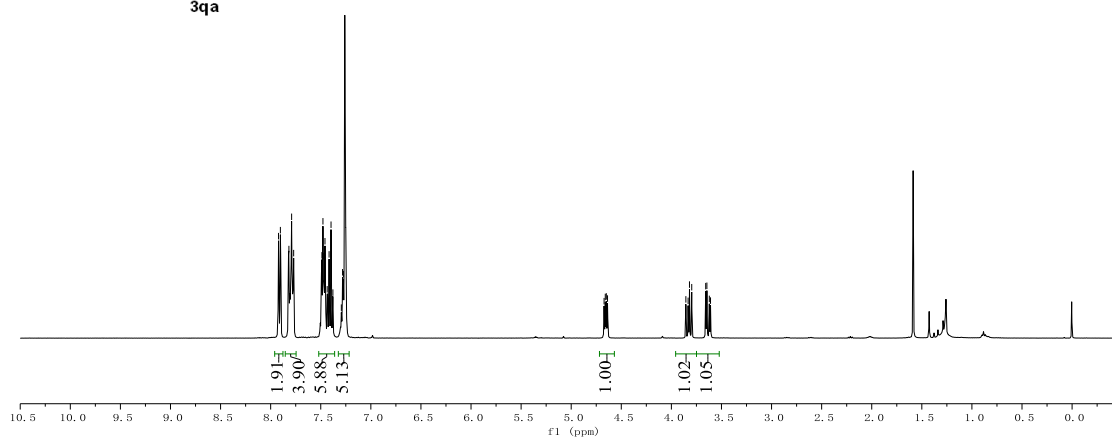
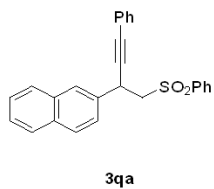


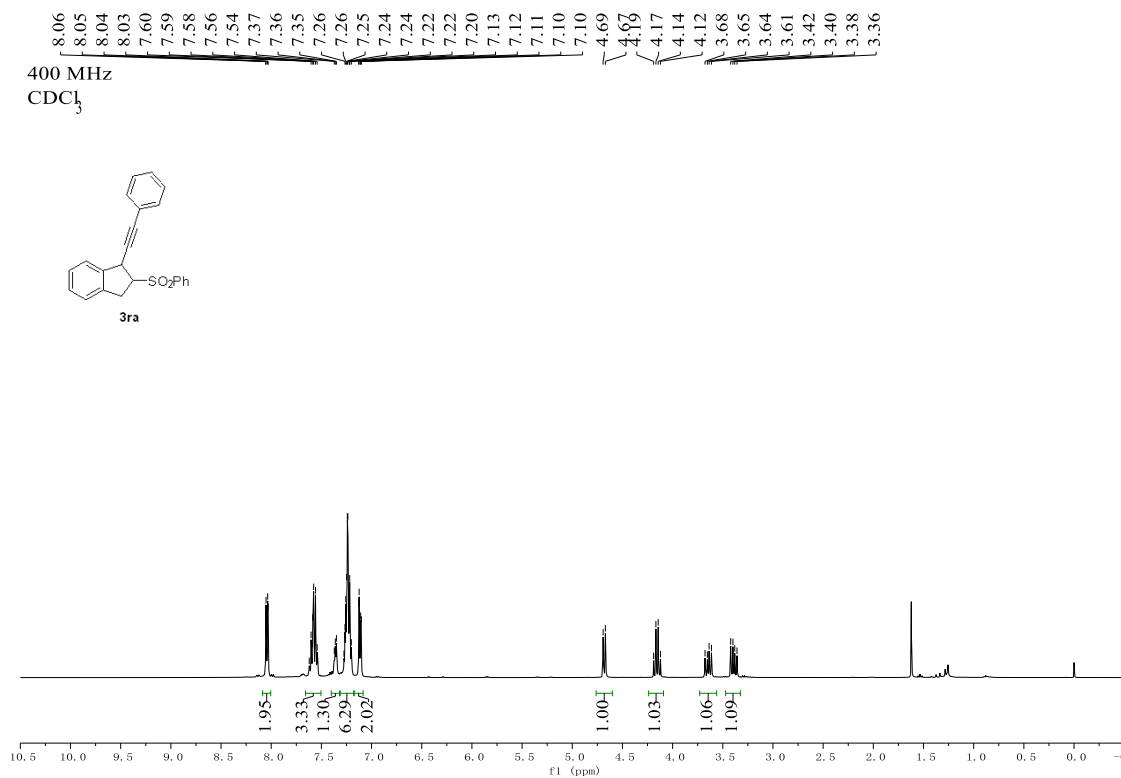
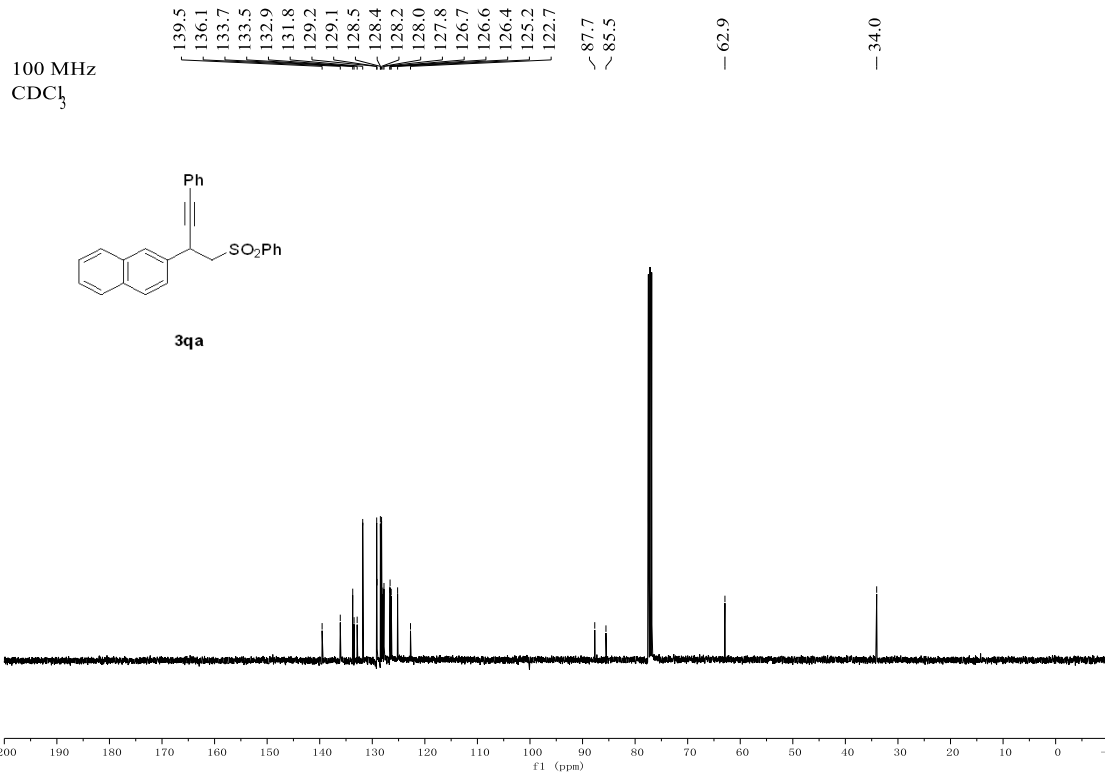
376 MHz  
CDCl<sub>3</sub>

-114.28



400 MHz  
CDCl<sub>3</sub>





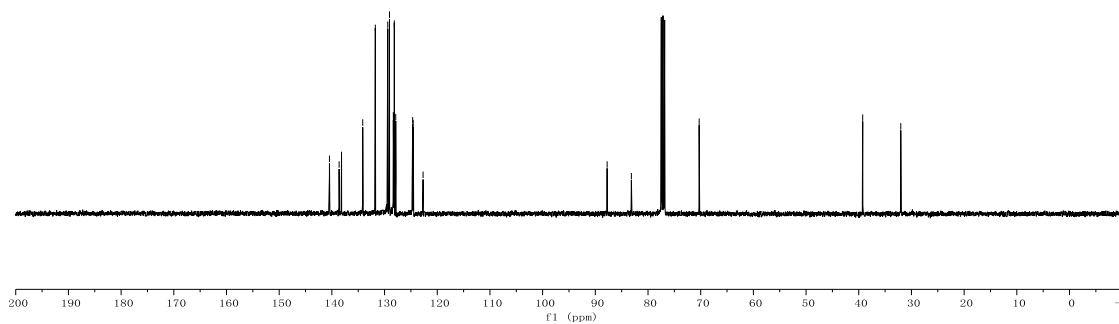
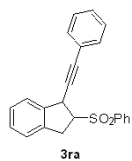
100 MHz  
CDCl<sub>3</sub>

140.5  
138.6  
138.2  
134.1  
131.8  
129.4  
129.1  
128.3  
128.3  
128.2  
128.1  
127.9  
124.7  
124.6  
122.7

- 87.8  
- 83.2

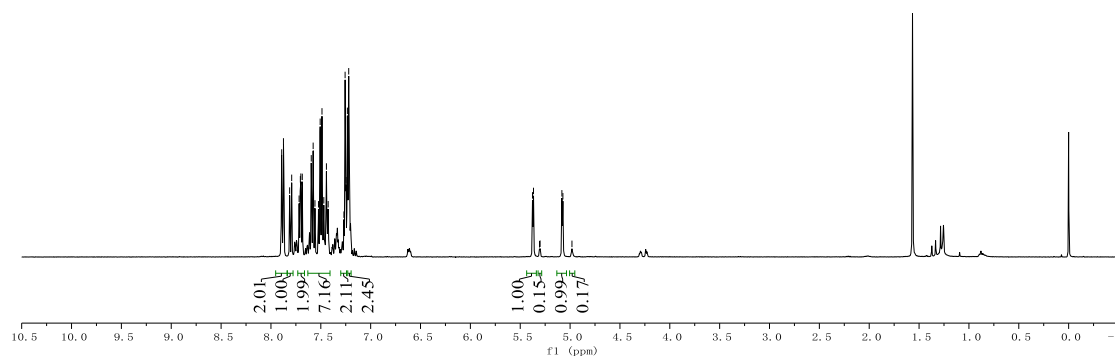
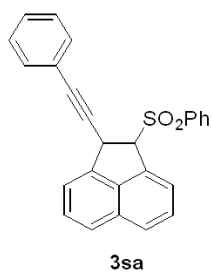
- 70.3

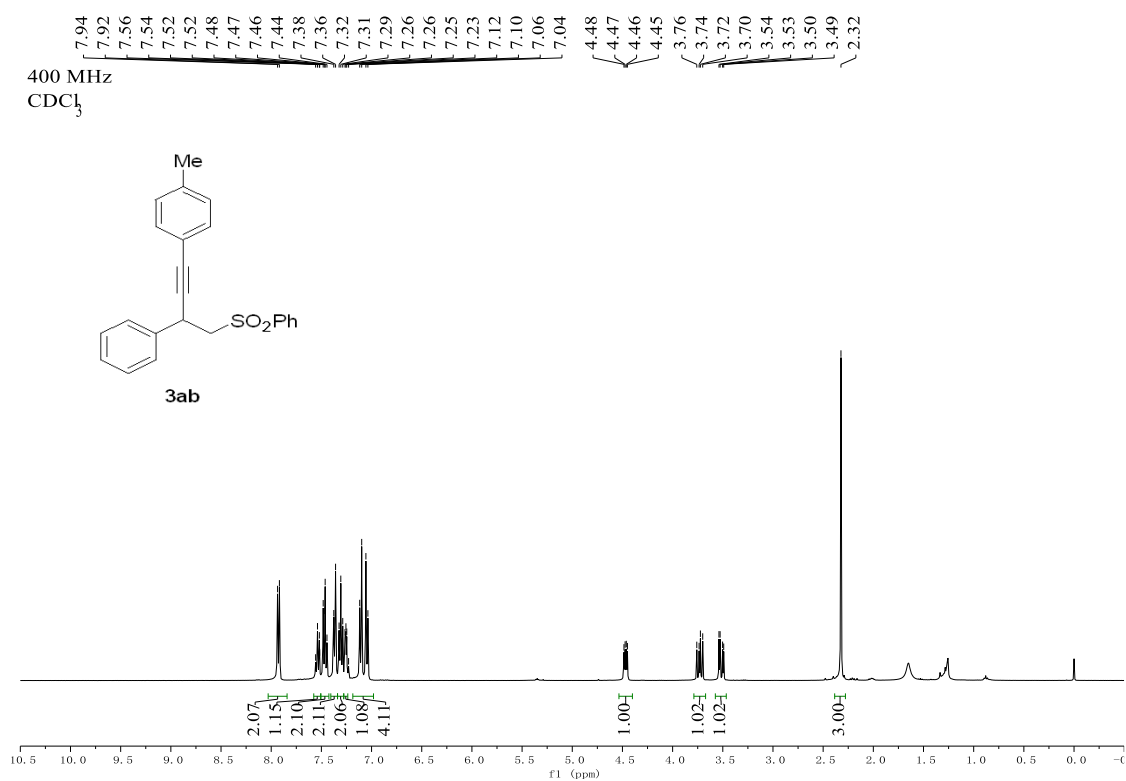
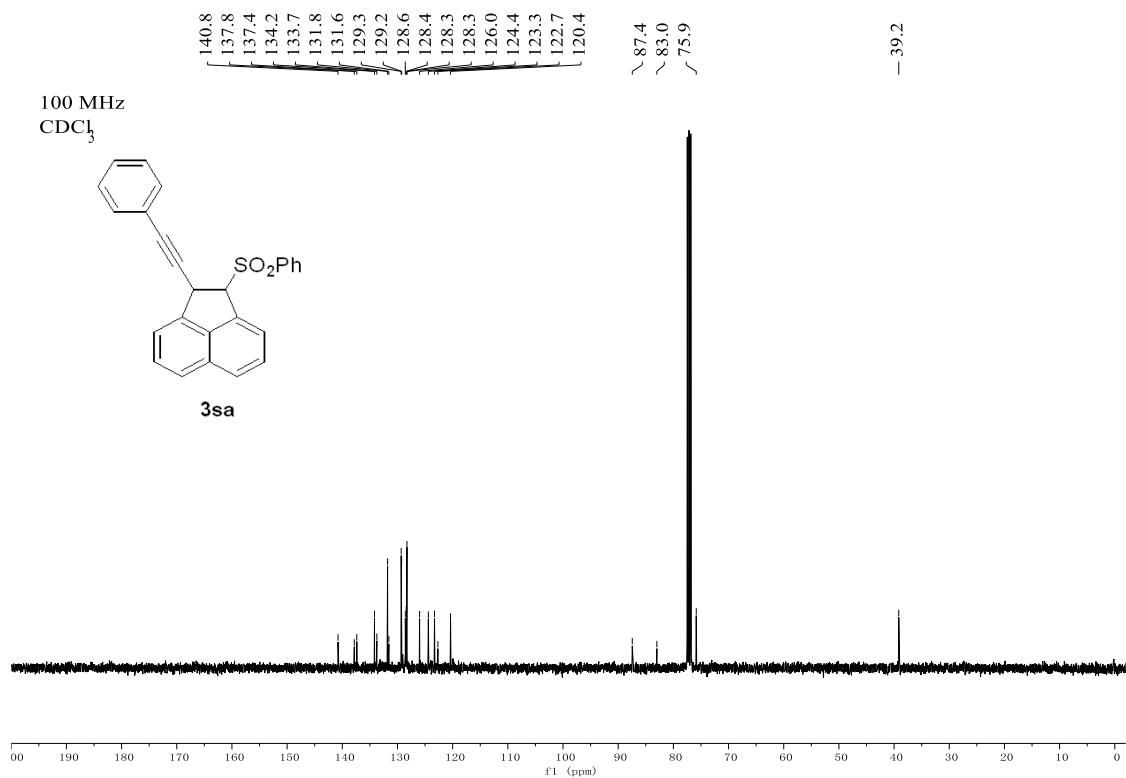
- 39.3  
- 32.0

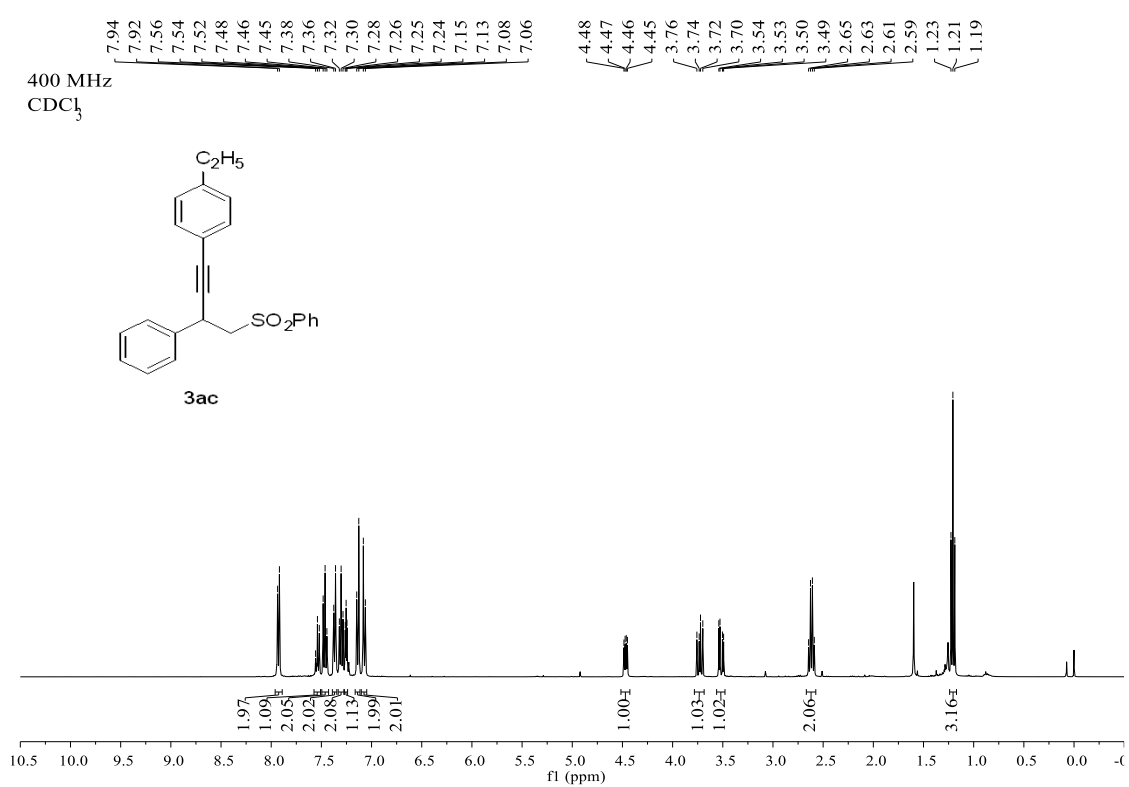
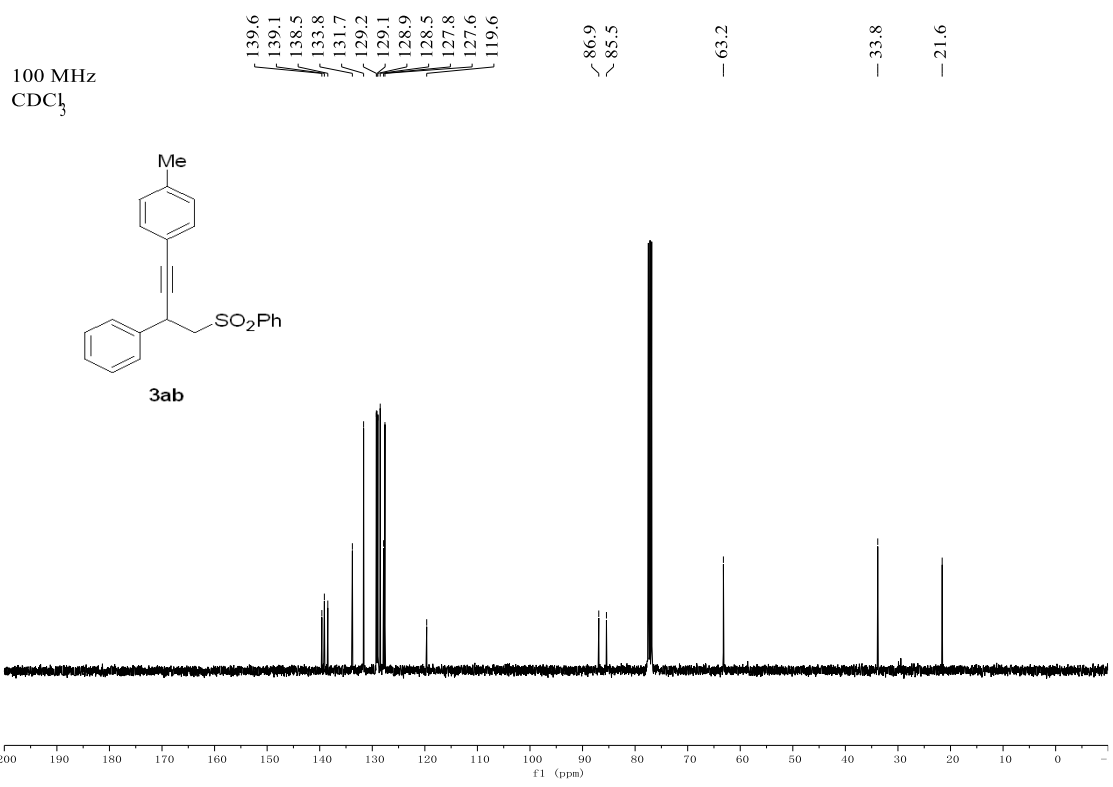


7.89  
7.87  
7.81  
7.79  
7.72  
7.71  
7.70  
7.69  
7.60  
7.58  
7.56  
7.52  
7.51  
7.49  
7.47  
7.44  
7.43  
7.26  
7.25  
7.23  
7.22  
5.38  
5.37  
5.31  
5.30  
5.08  
5.07  
4.98

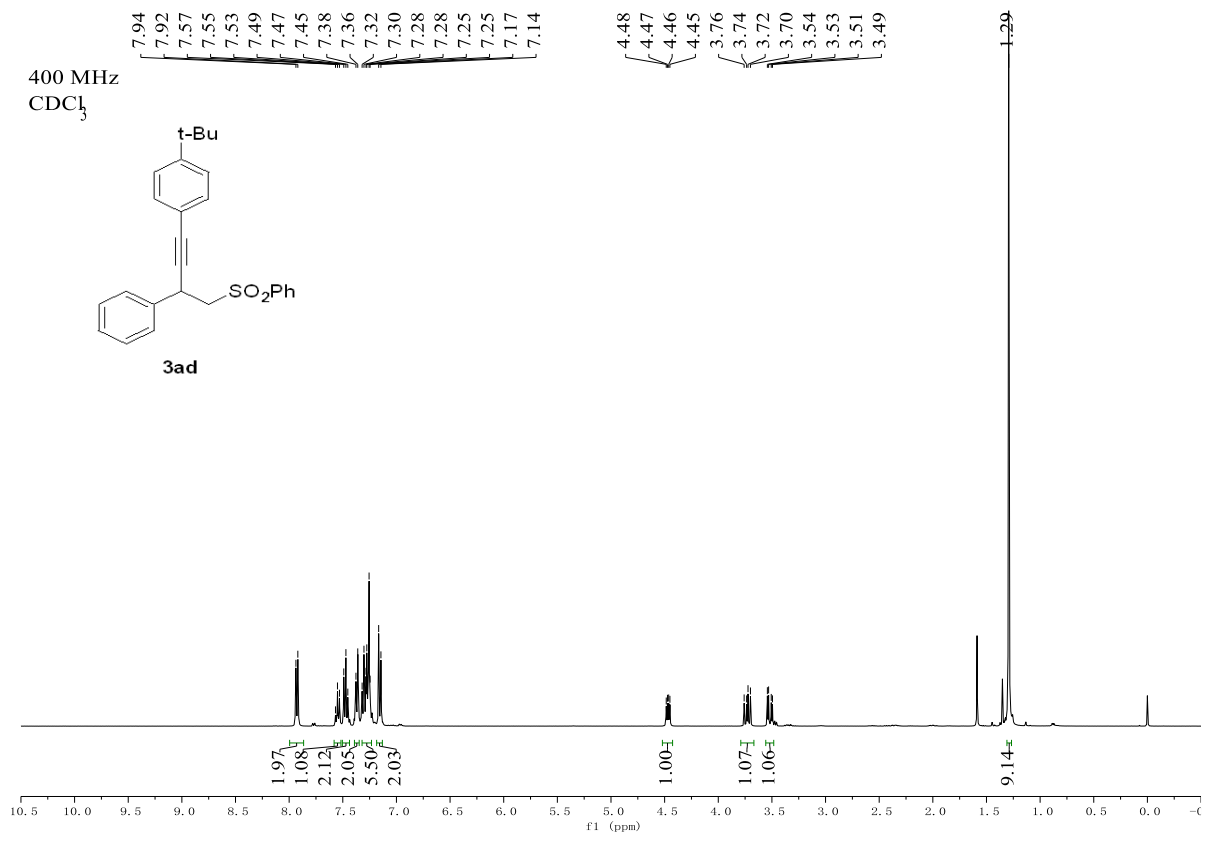
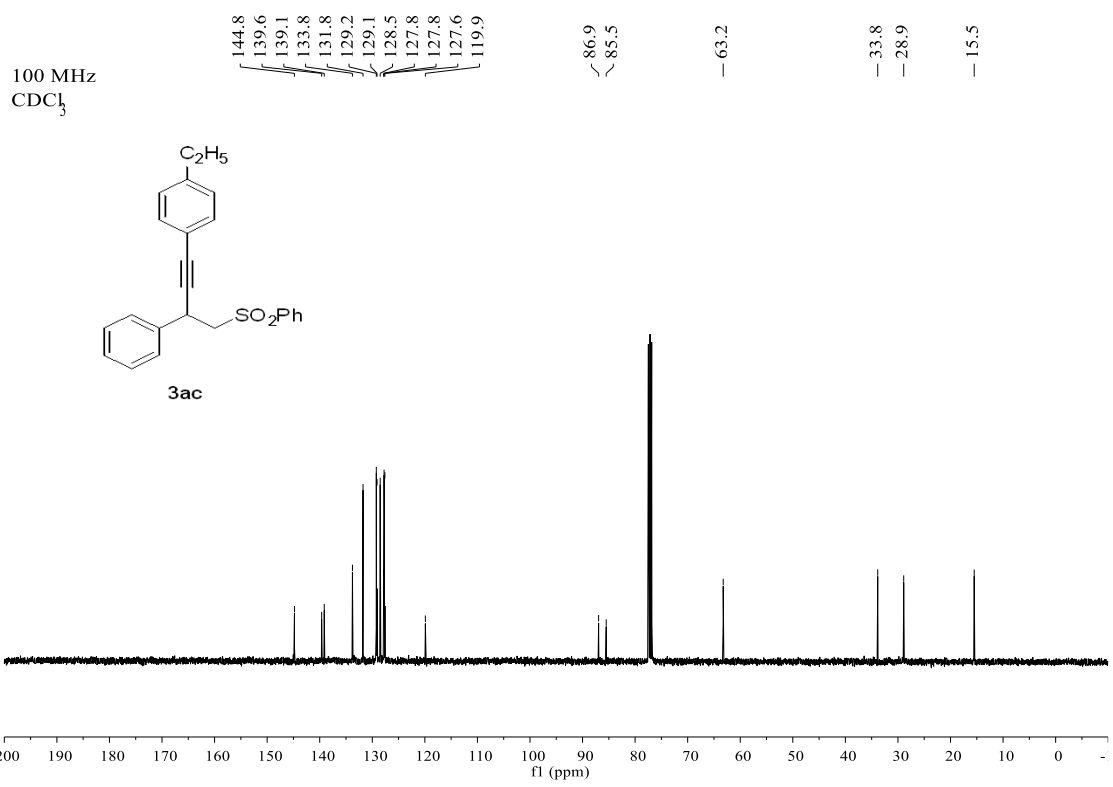
400 MHz  
CDCl<sub>3</sub>

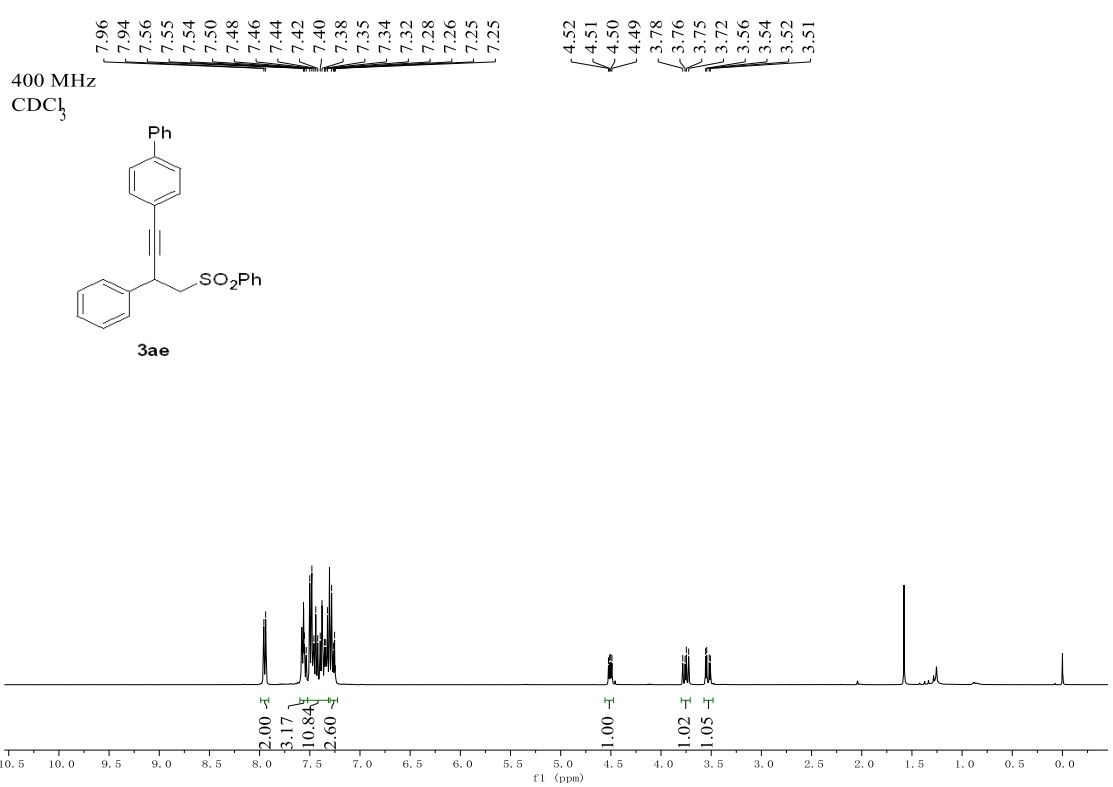
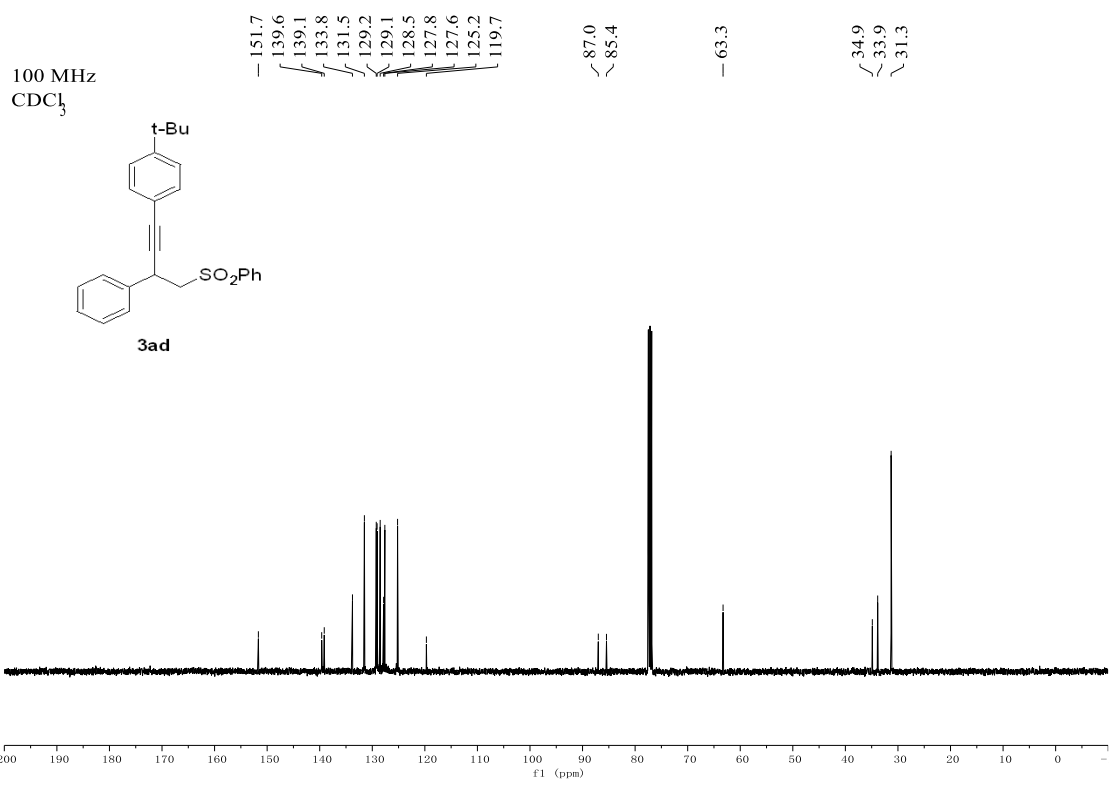


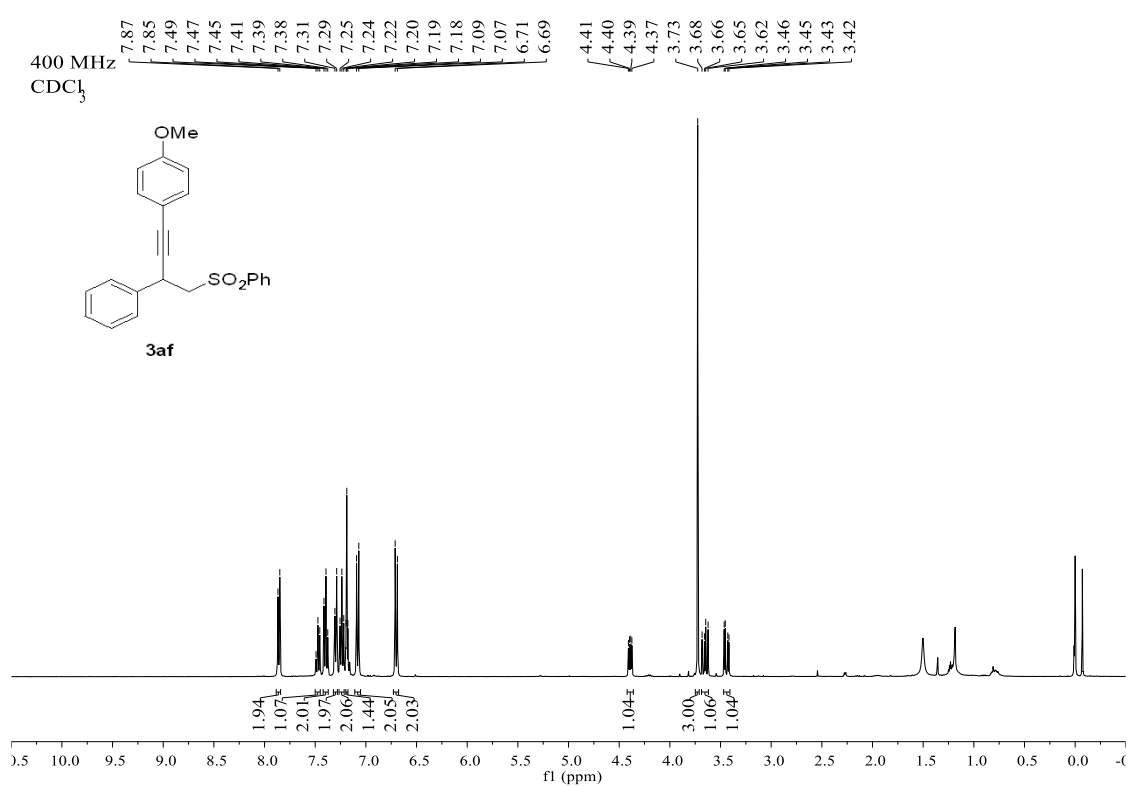
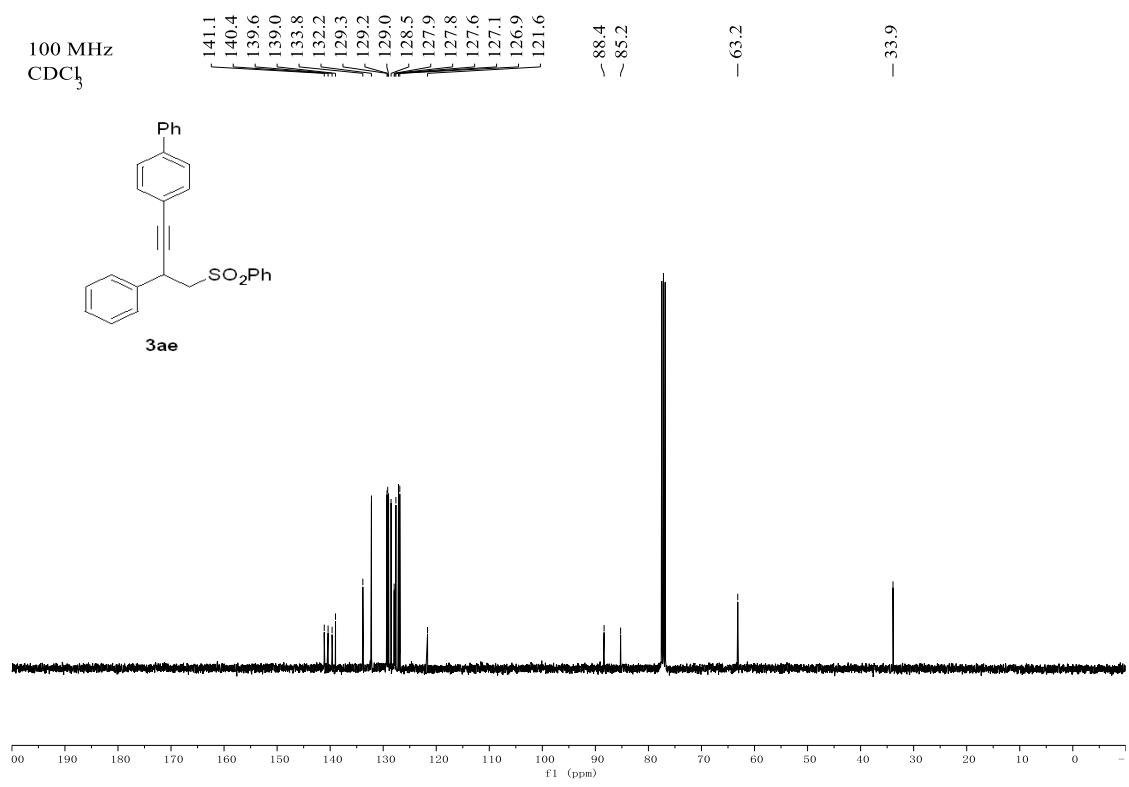


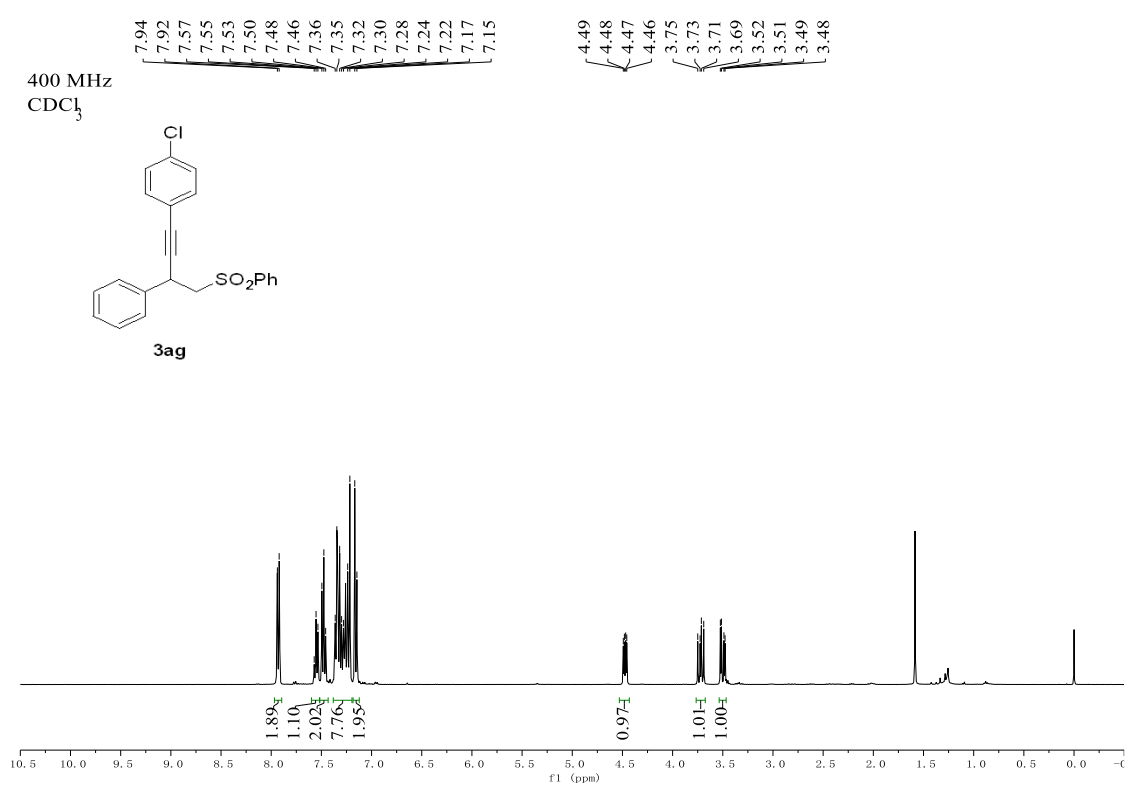
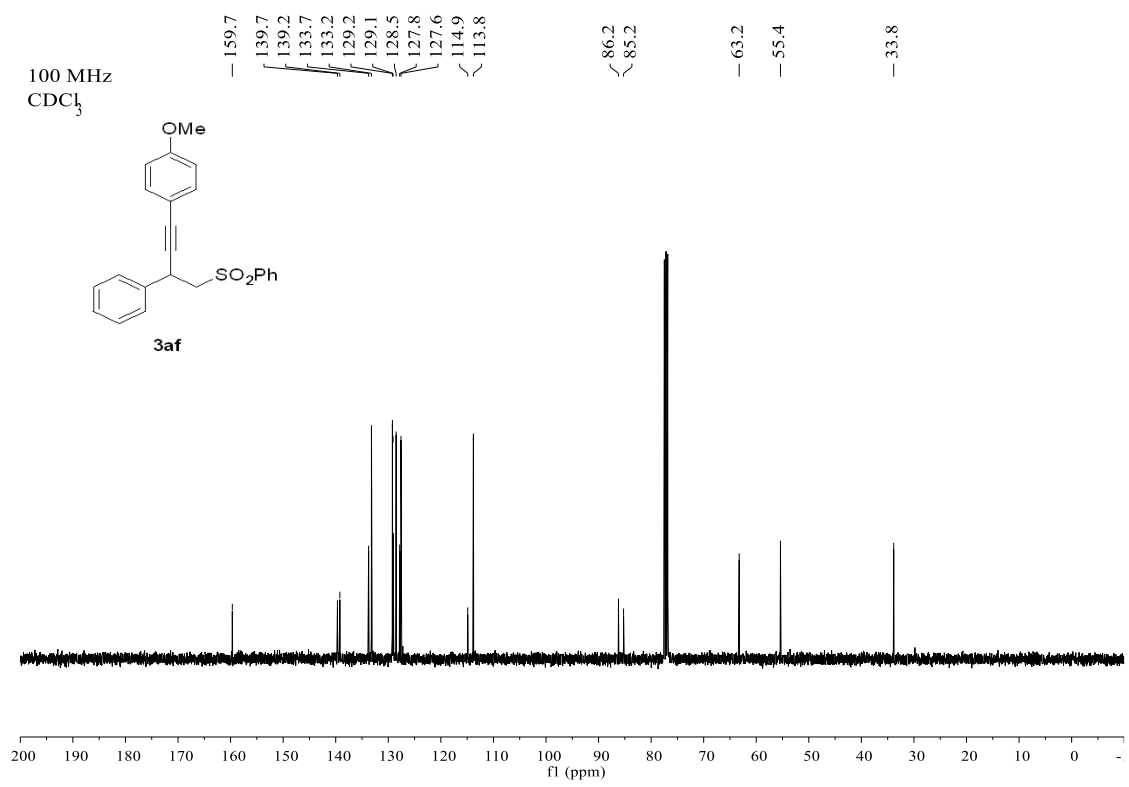


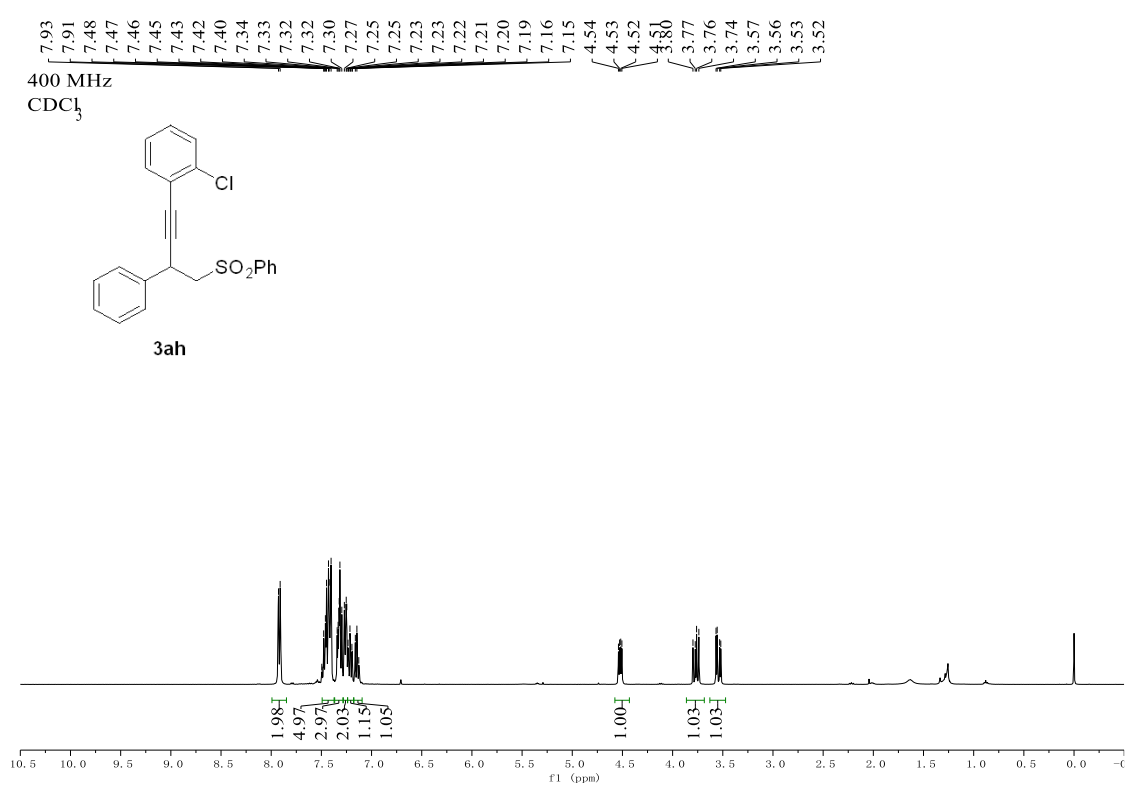
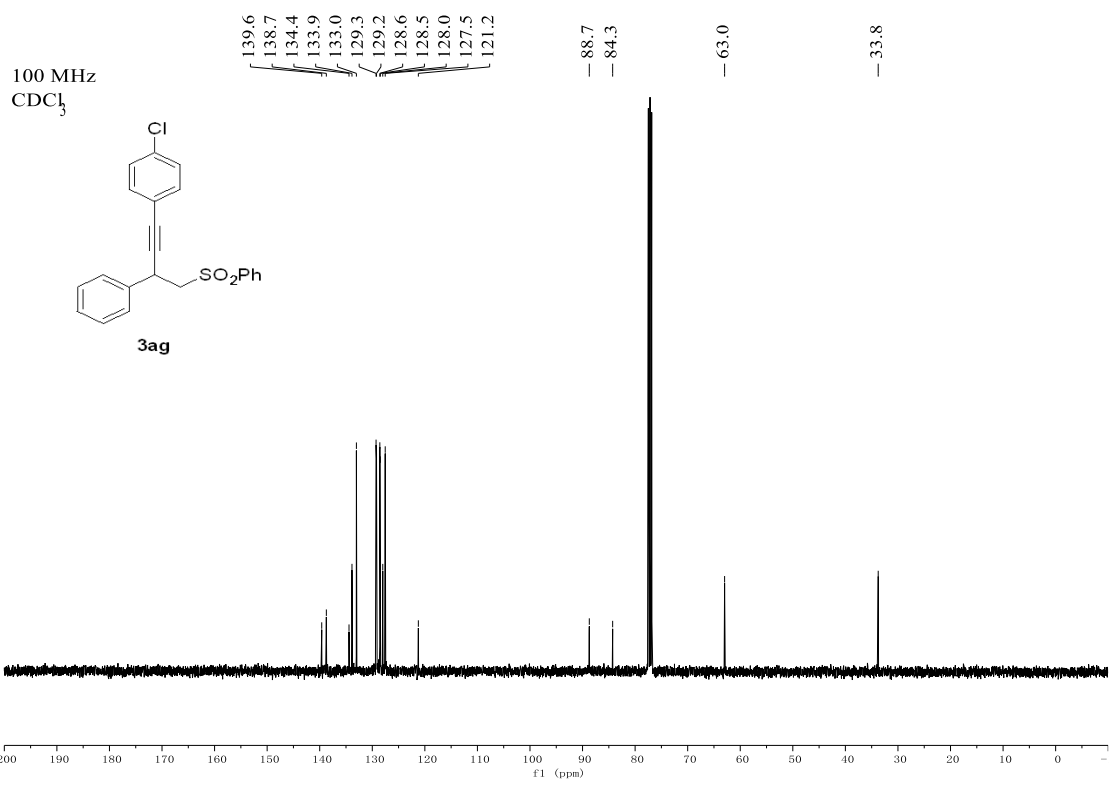


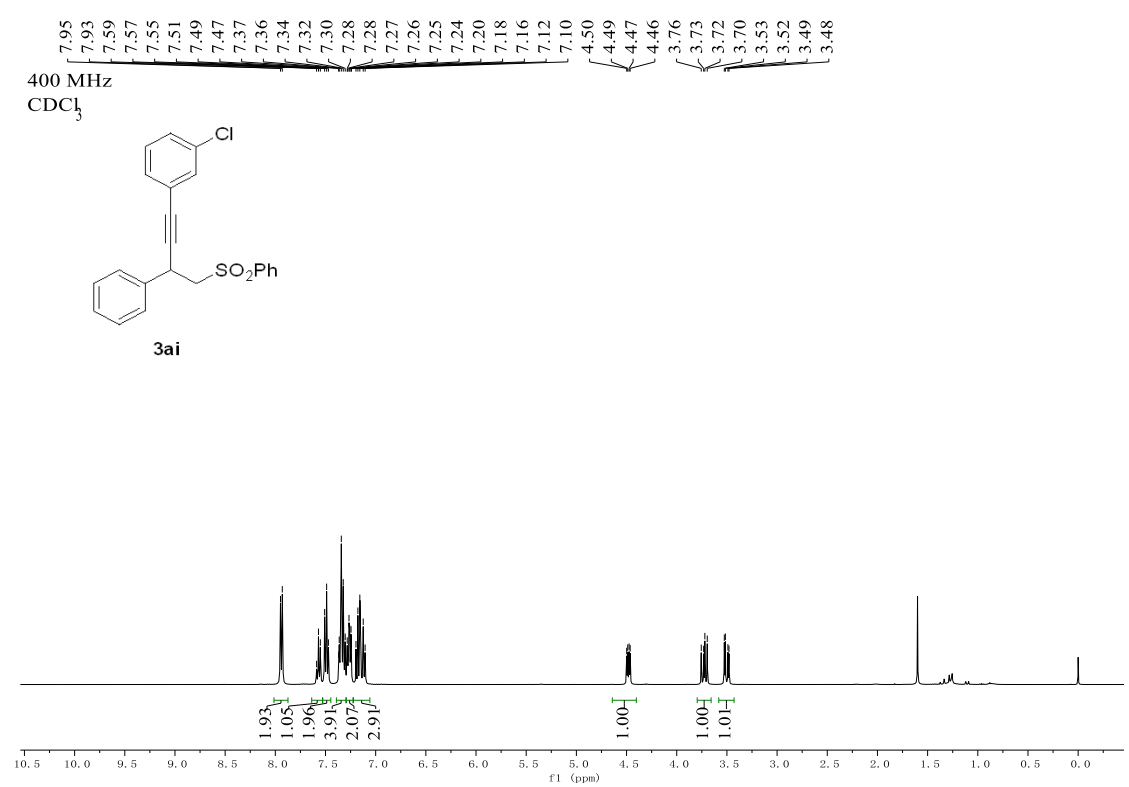
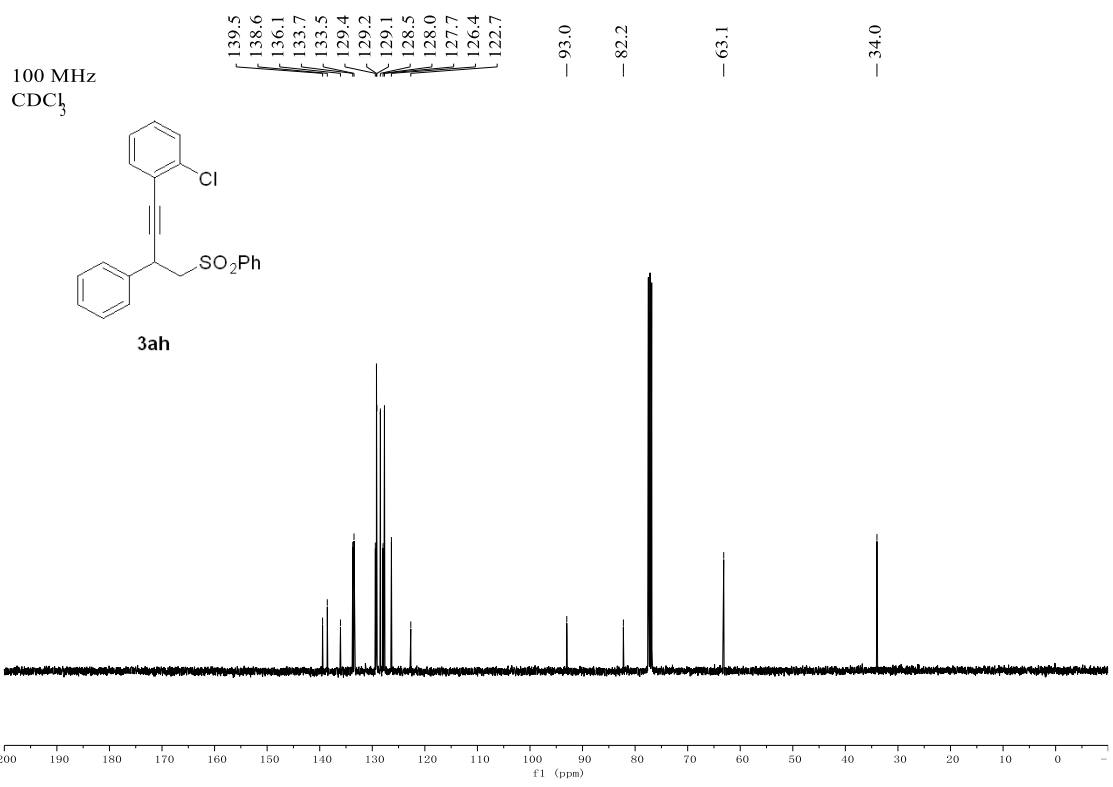


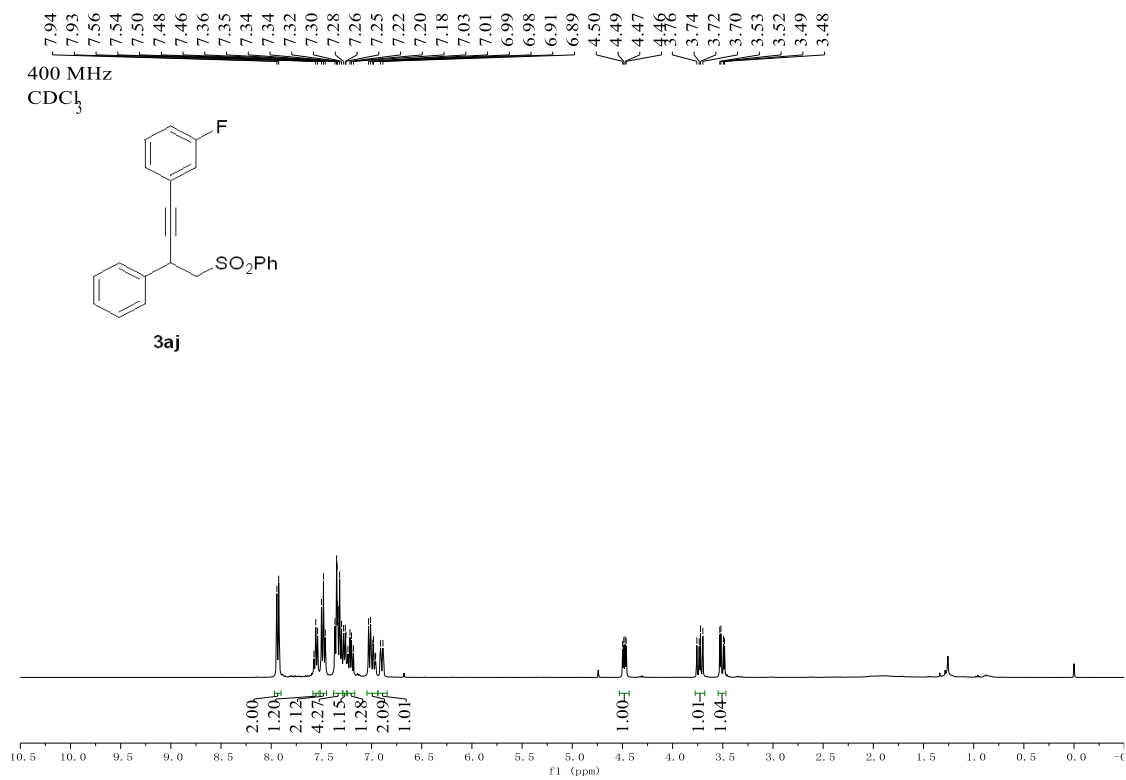
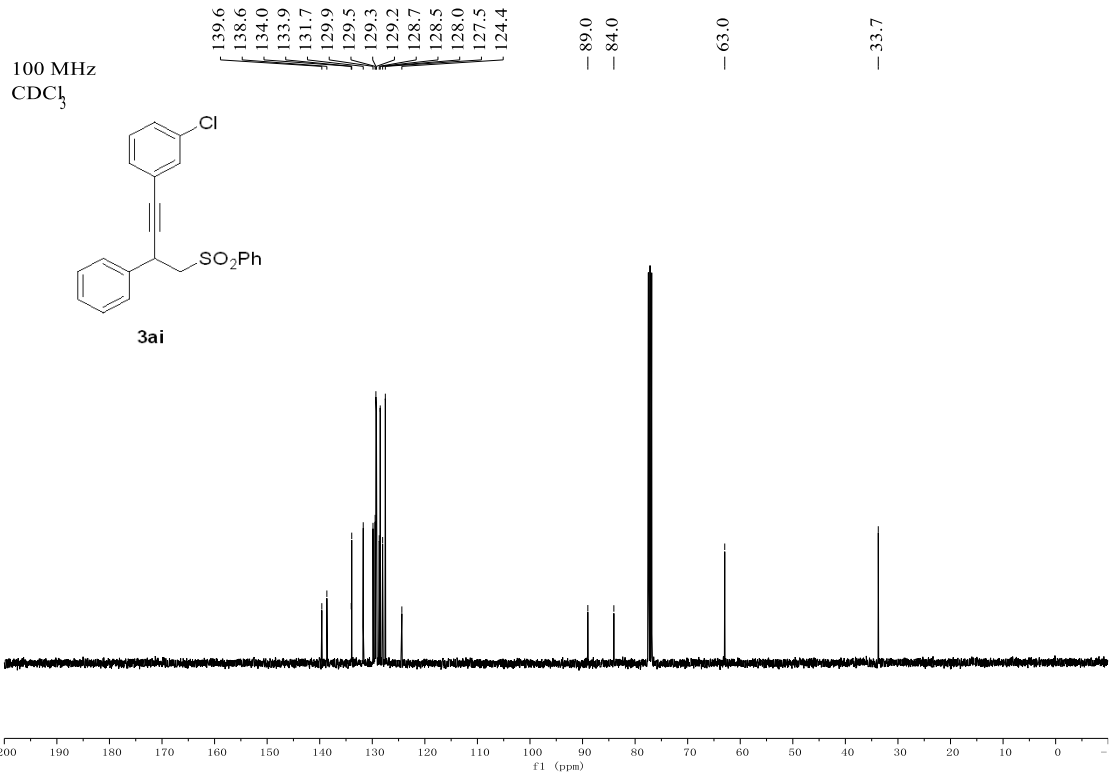


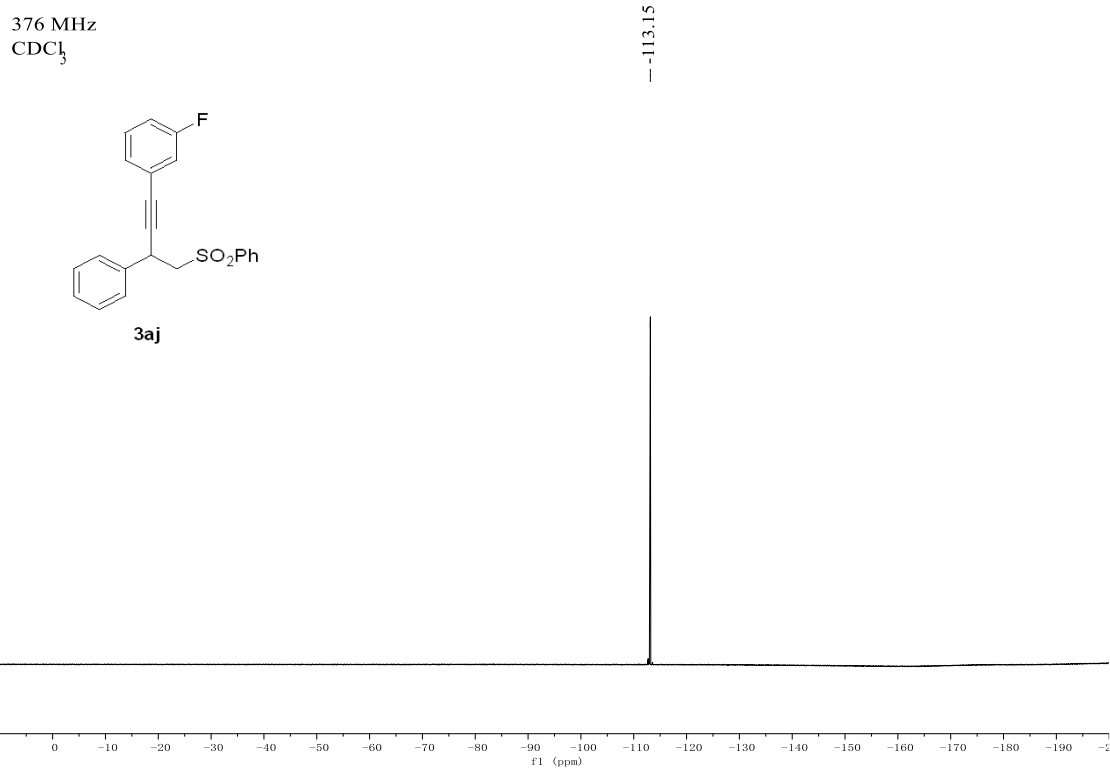
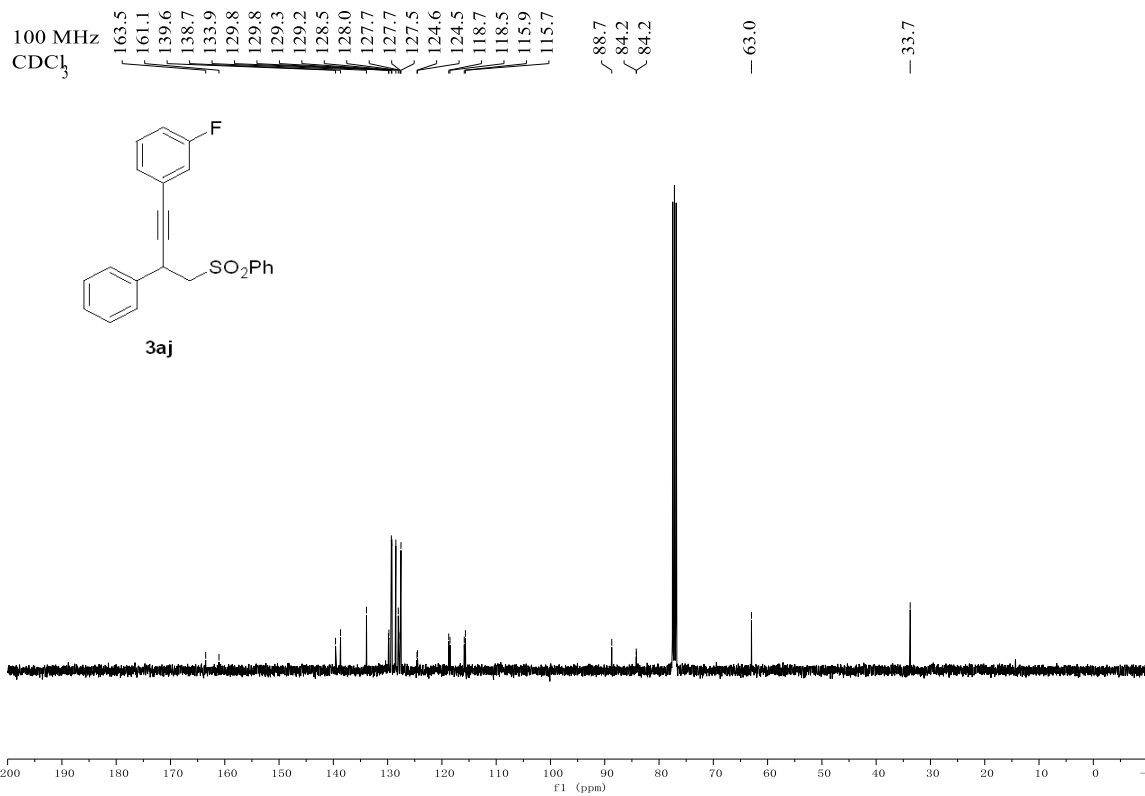




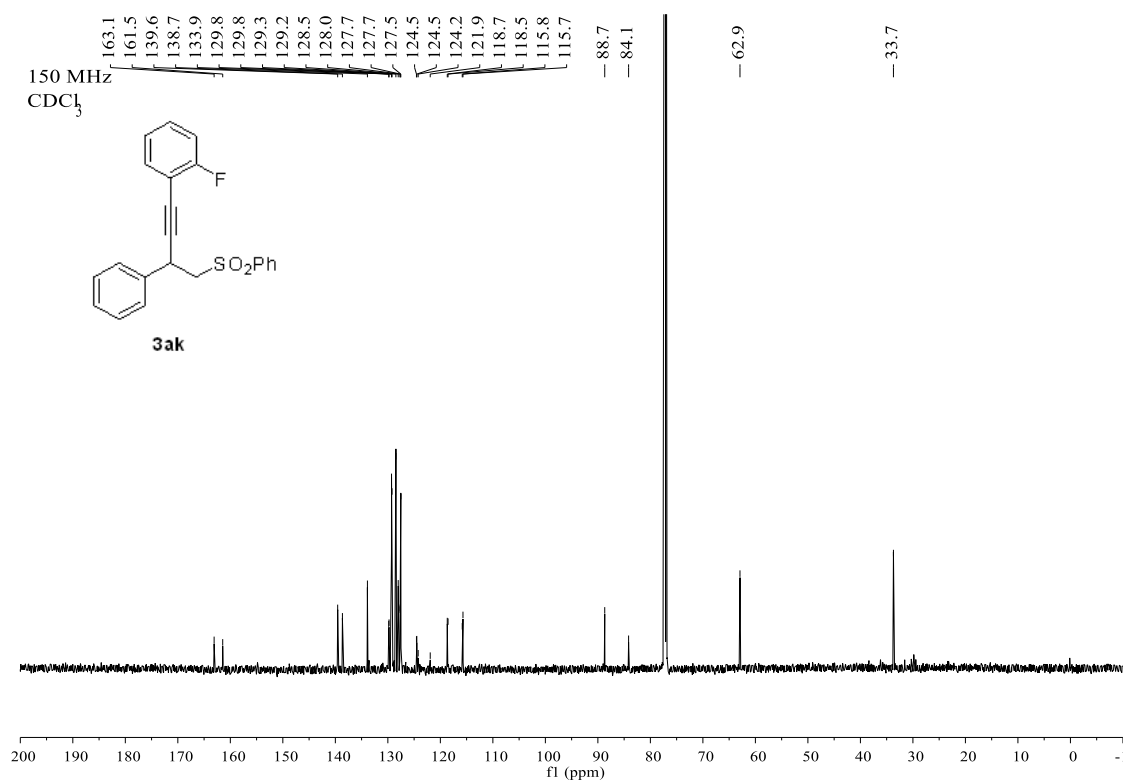
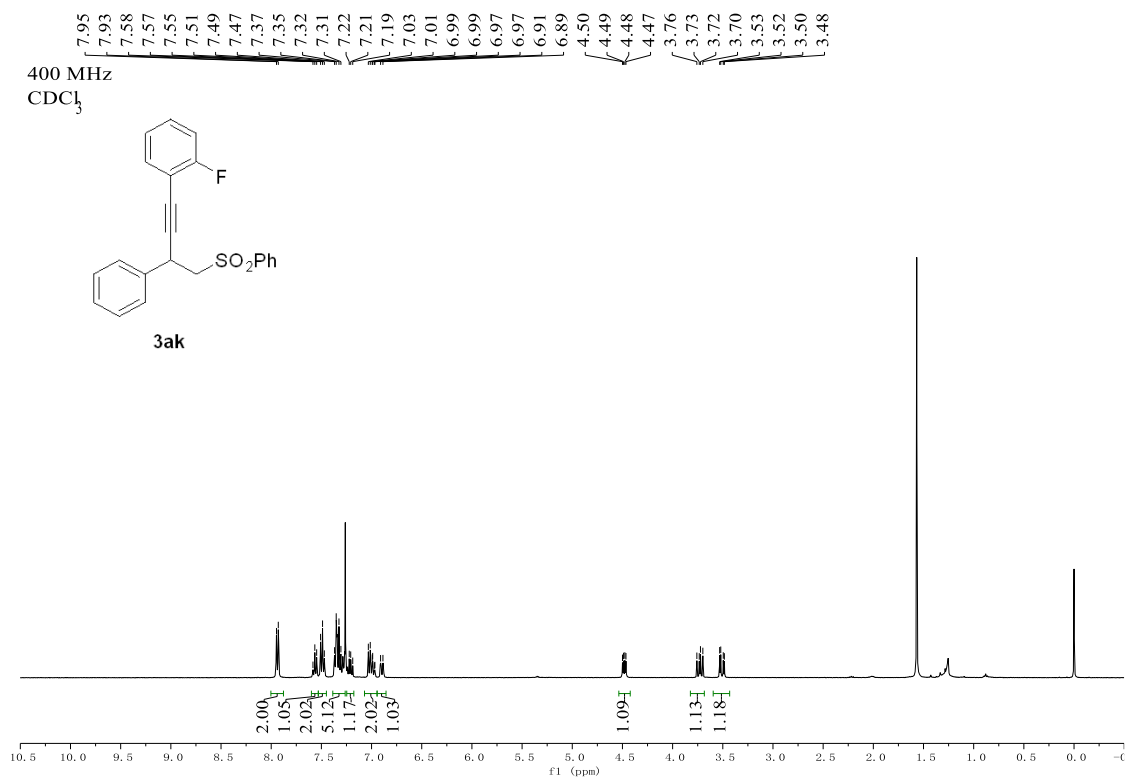




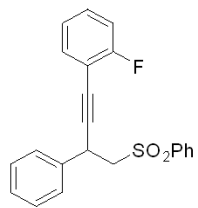






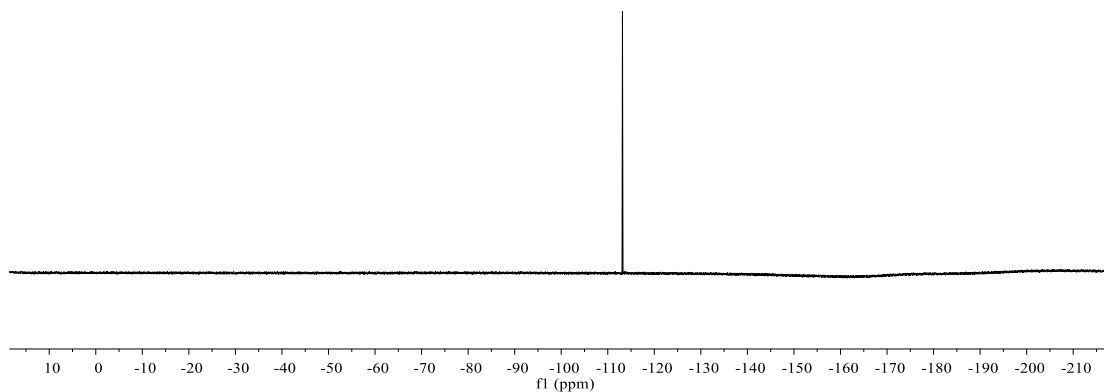


376 MHz  
CDCl<sub>3</sub>

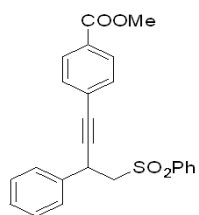


**3ak**

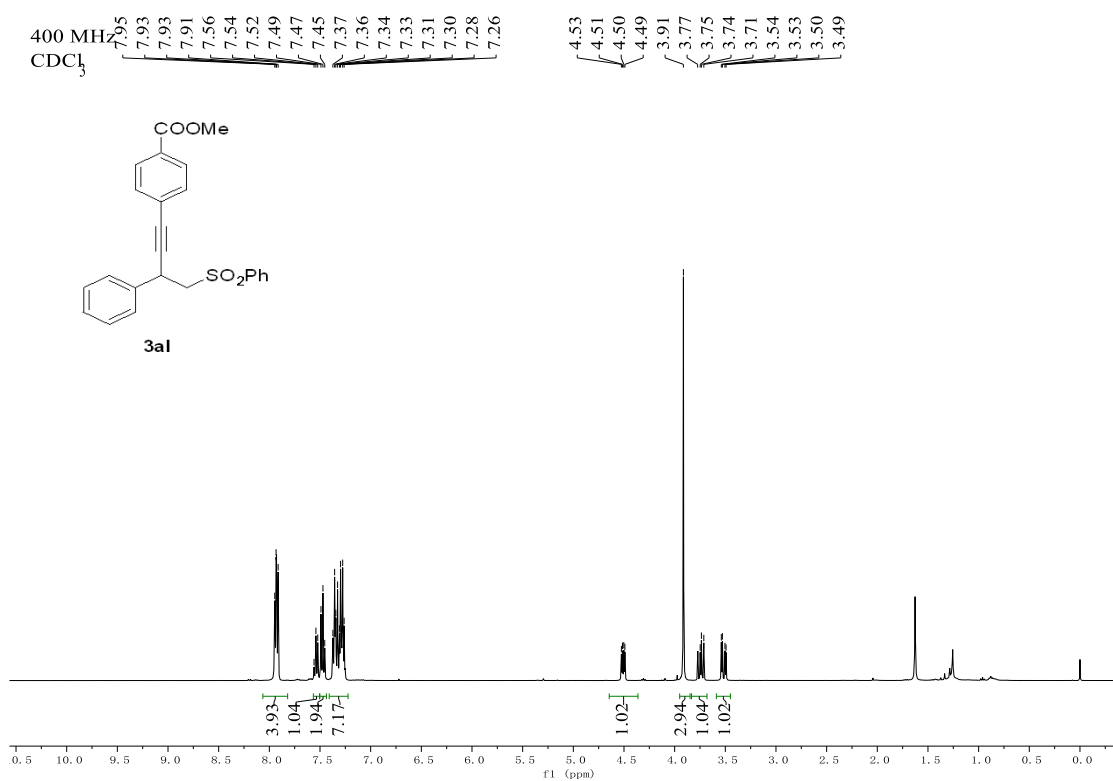
-113.16

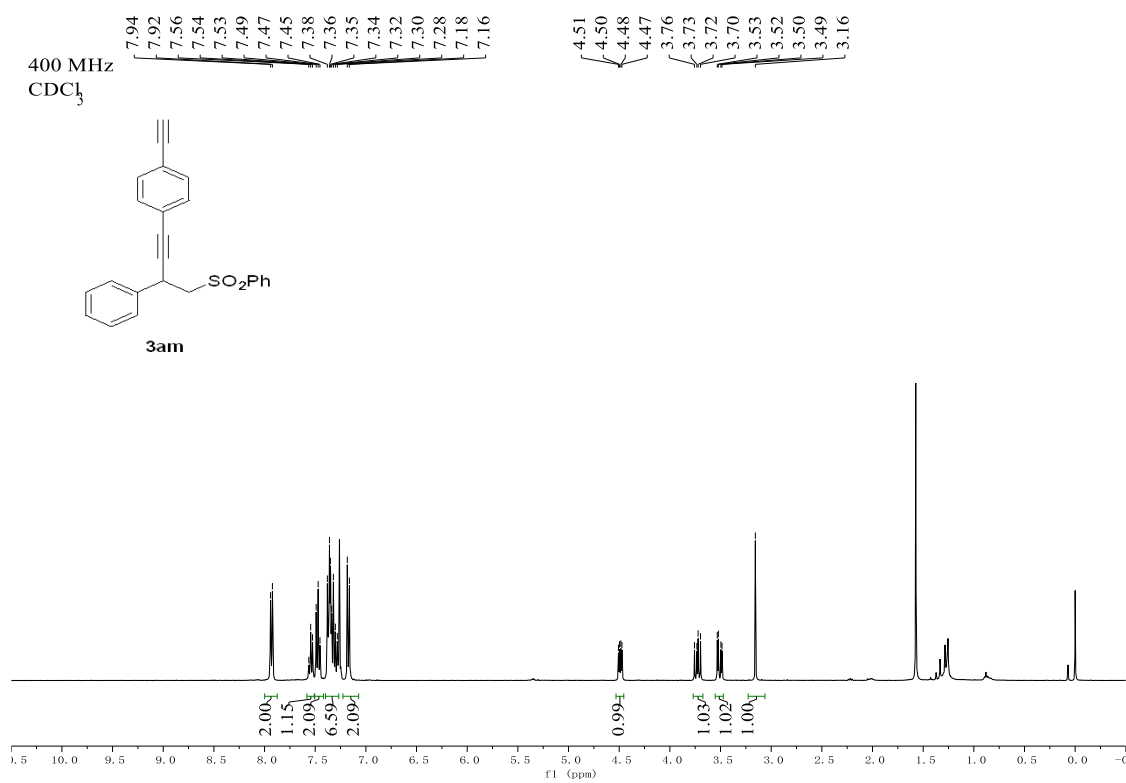
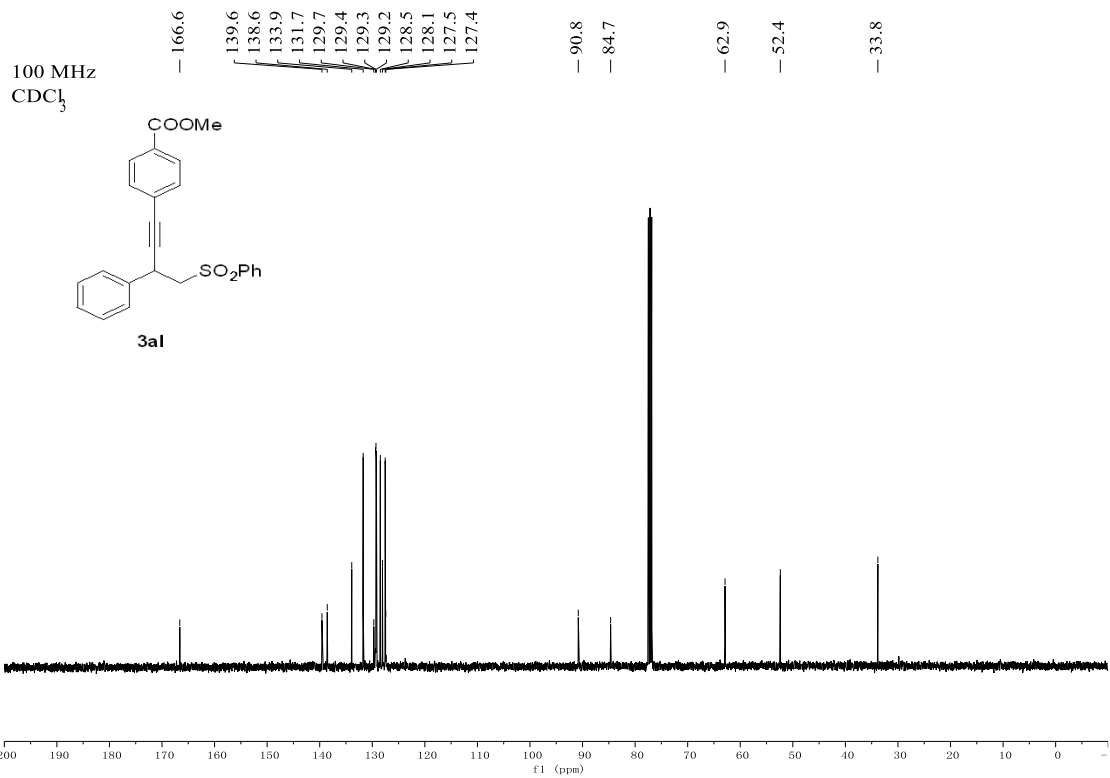


400 MHz  
CDCl<sub>3</sub>

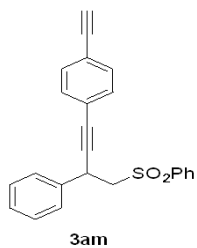


**3al**



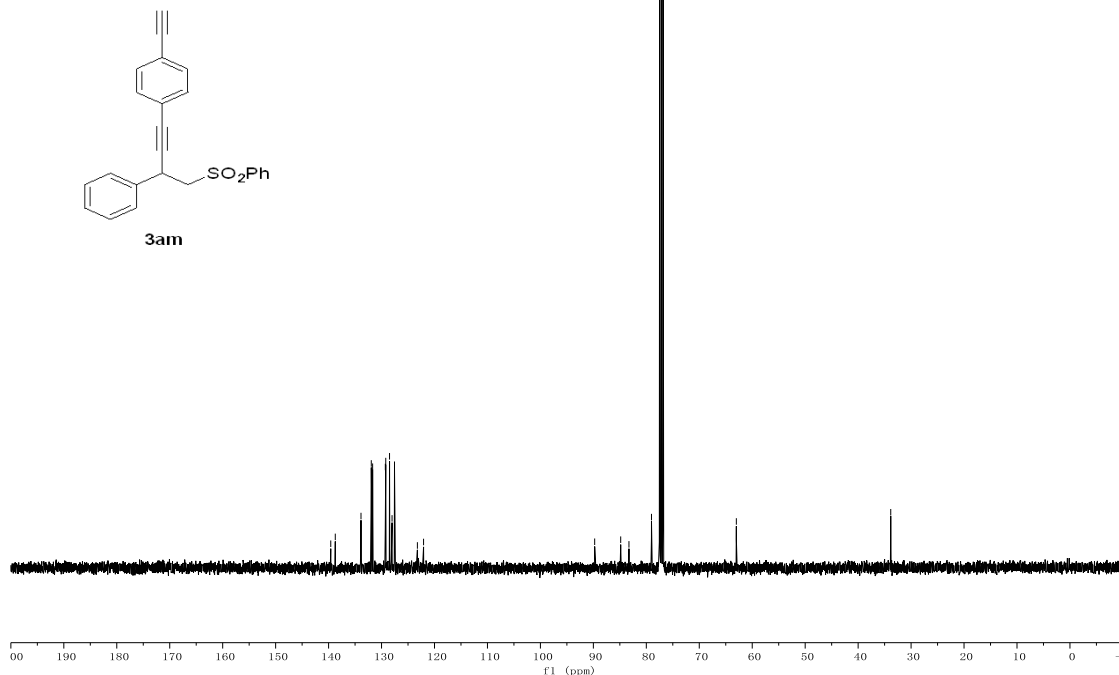


100 MHz  
CDCl<sub>3</sub>

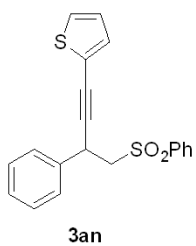


139.6  
138.7  
133.9  
131.9  
131.7  
129.3  
129.2  
128.5  
128.0  
127.6  
123.2  
122.1

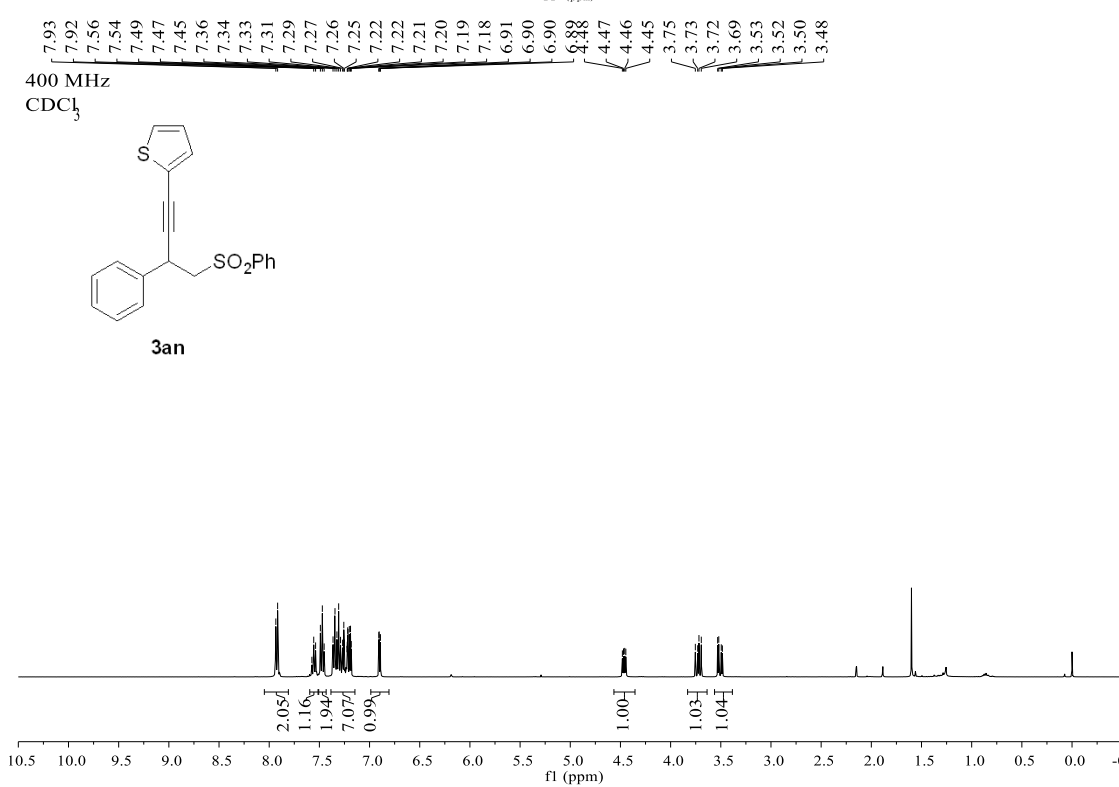
~ 89.8  
~ 84.8  
~ 83.3  
~ 79.0  
— 63.0  
— 33.8

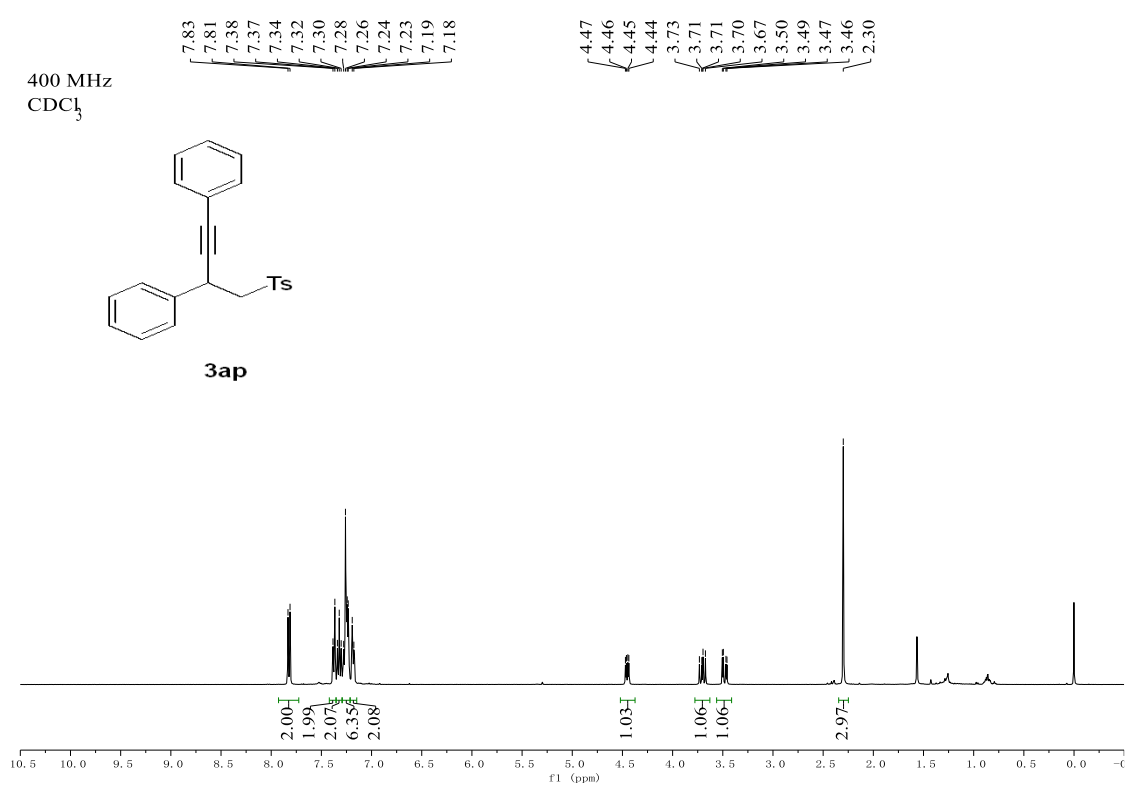
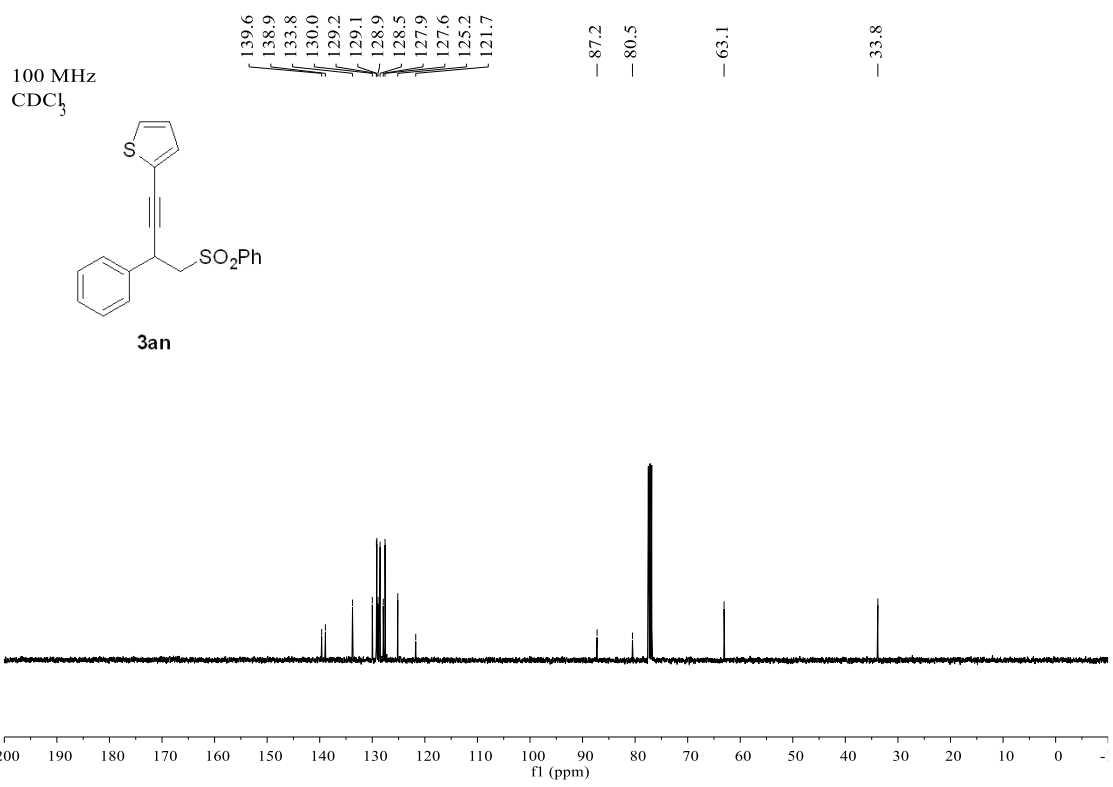


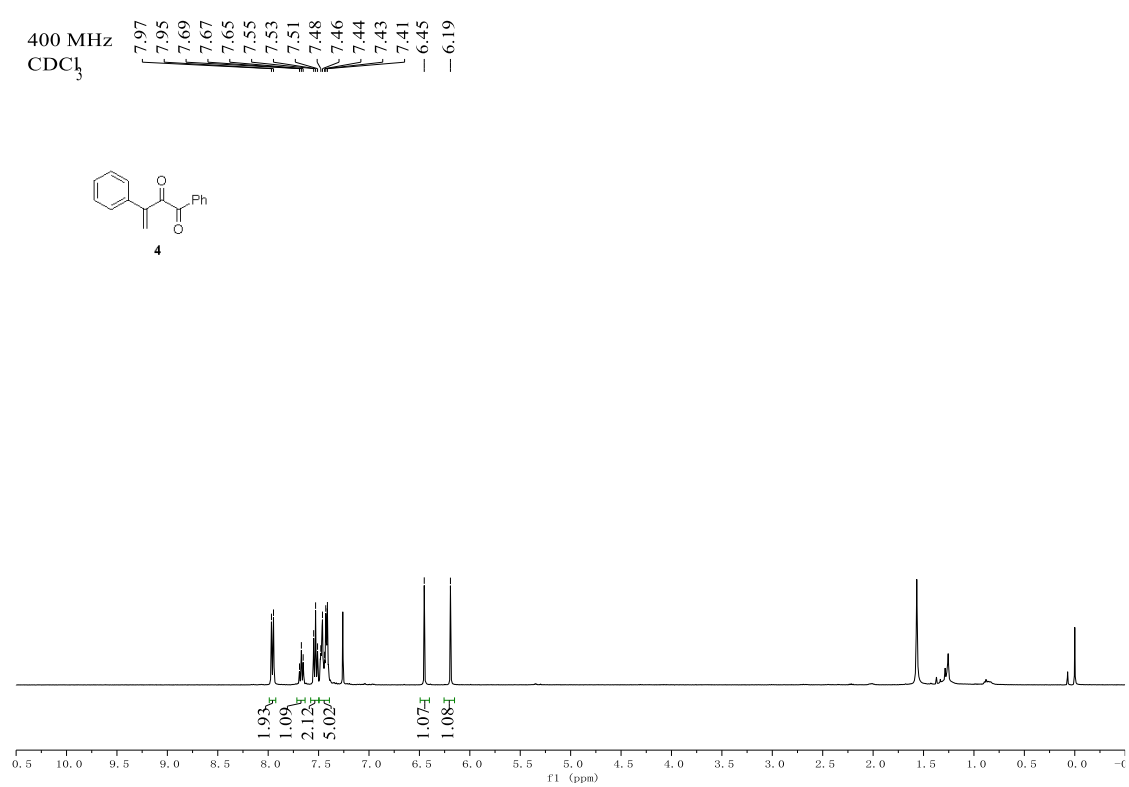
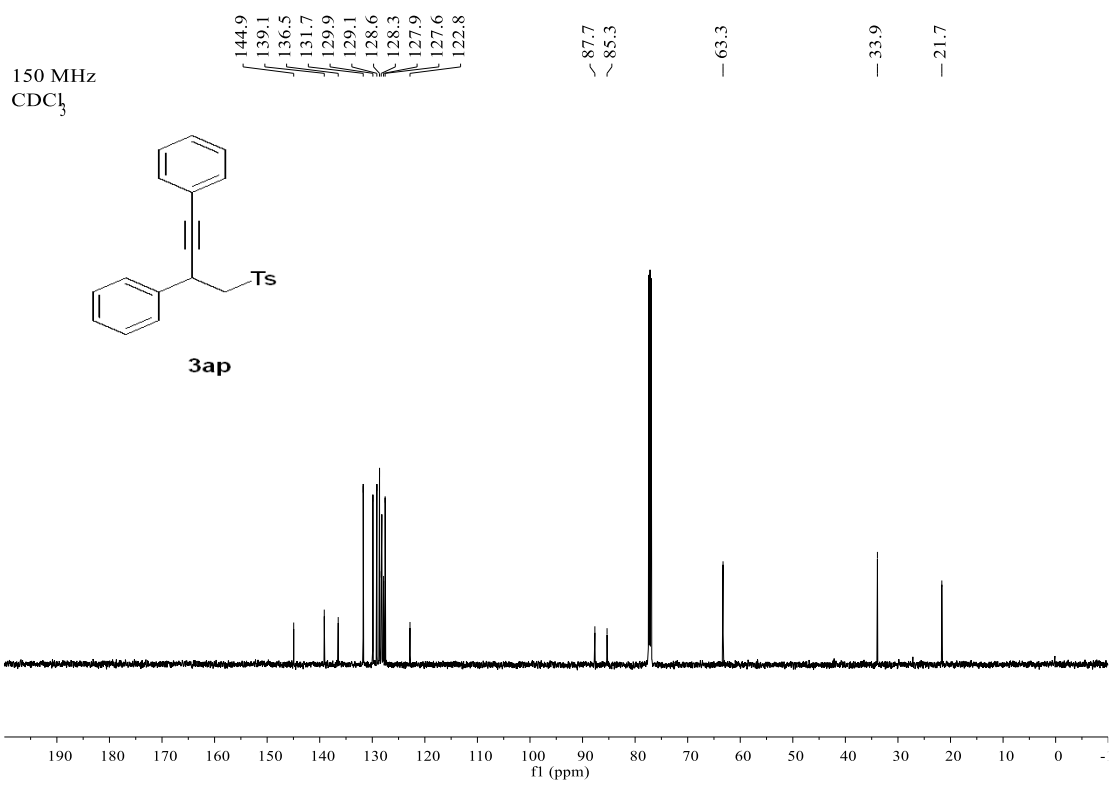
400 MHz  
CDCl<sub>3</sub>

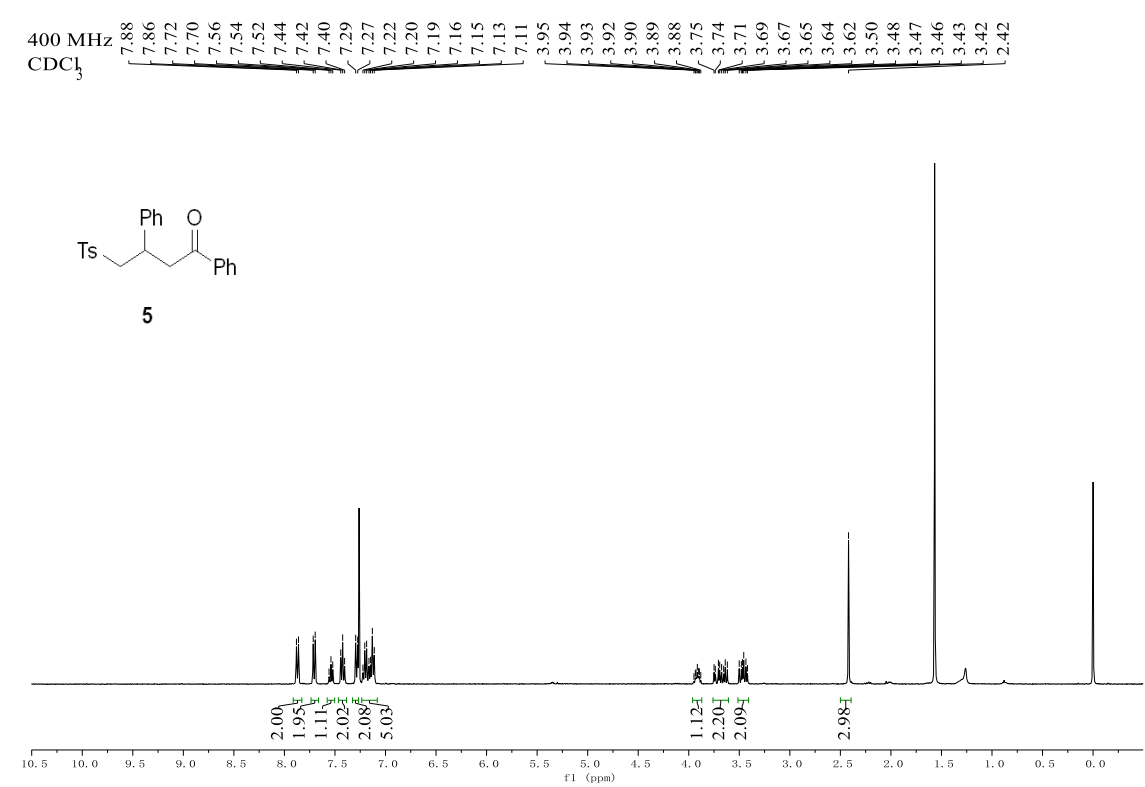
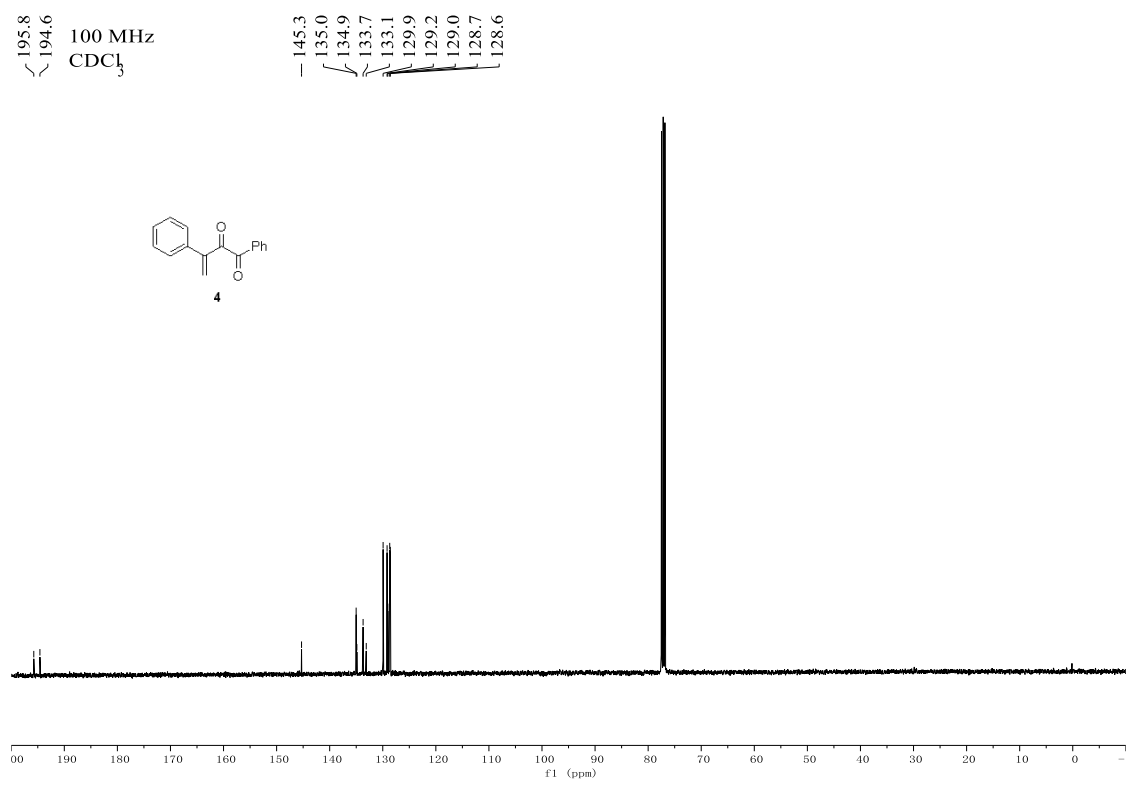


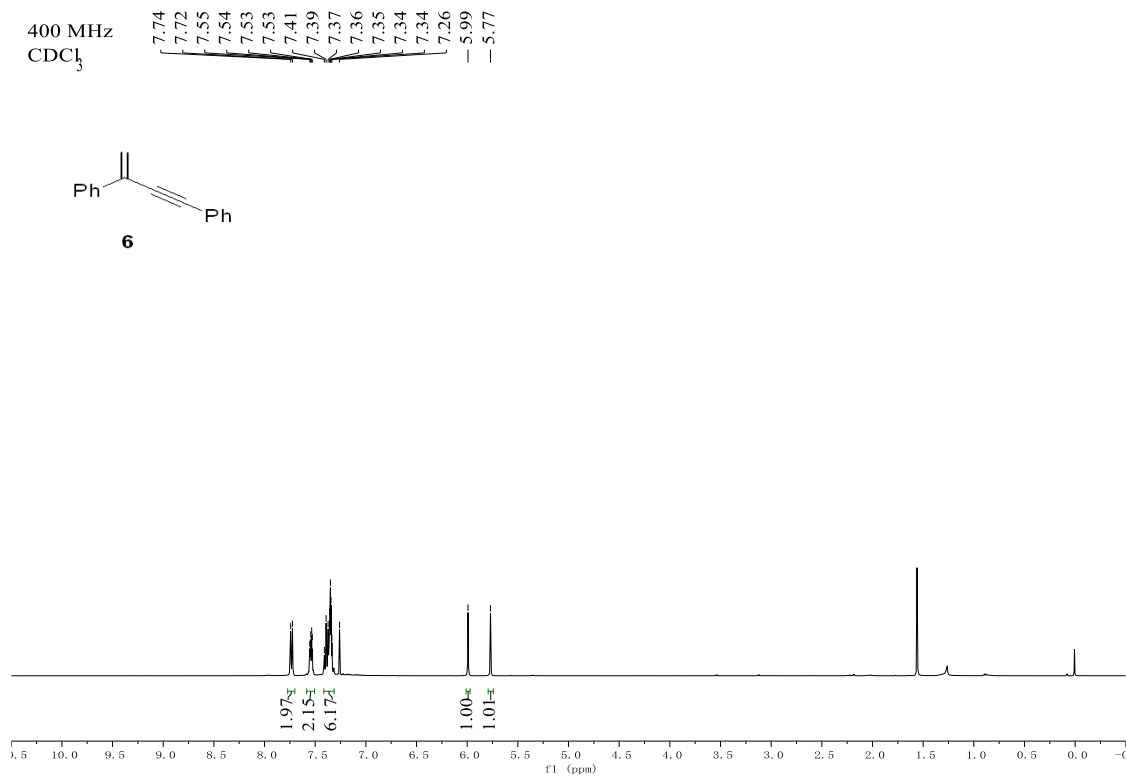
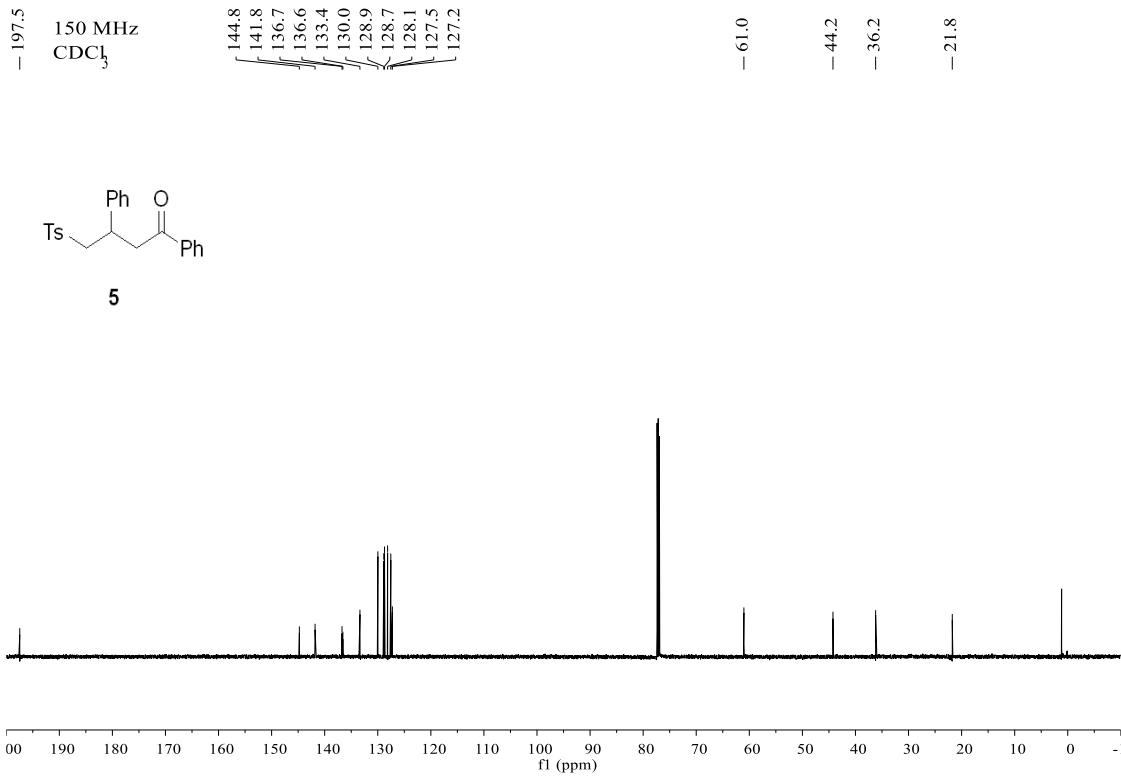
7.93  
7.92  
7.56  
7.54  
7.49  
7.47  
7.45  
7.36  
7.34  
7.33  
7.31  
7.29  
7.27  
7.26  
7.25  
7.22  
7.22  
7.21  
7.20  
7.19  
7.18  
7.18  
6.91  
6.90  
6.89  
6.88  
4.47  
4.46  
4.45  
3.75  
3.73  
3.72  
3.69  
3.53  
3.52  
3.50  
3.48









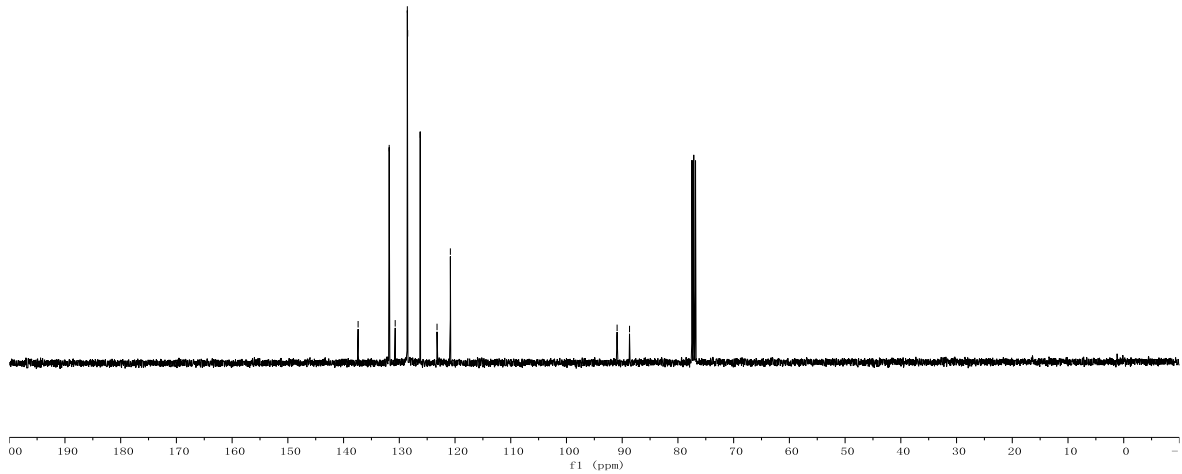
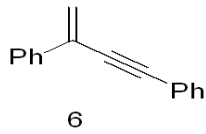




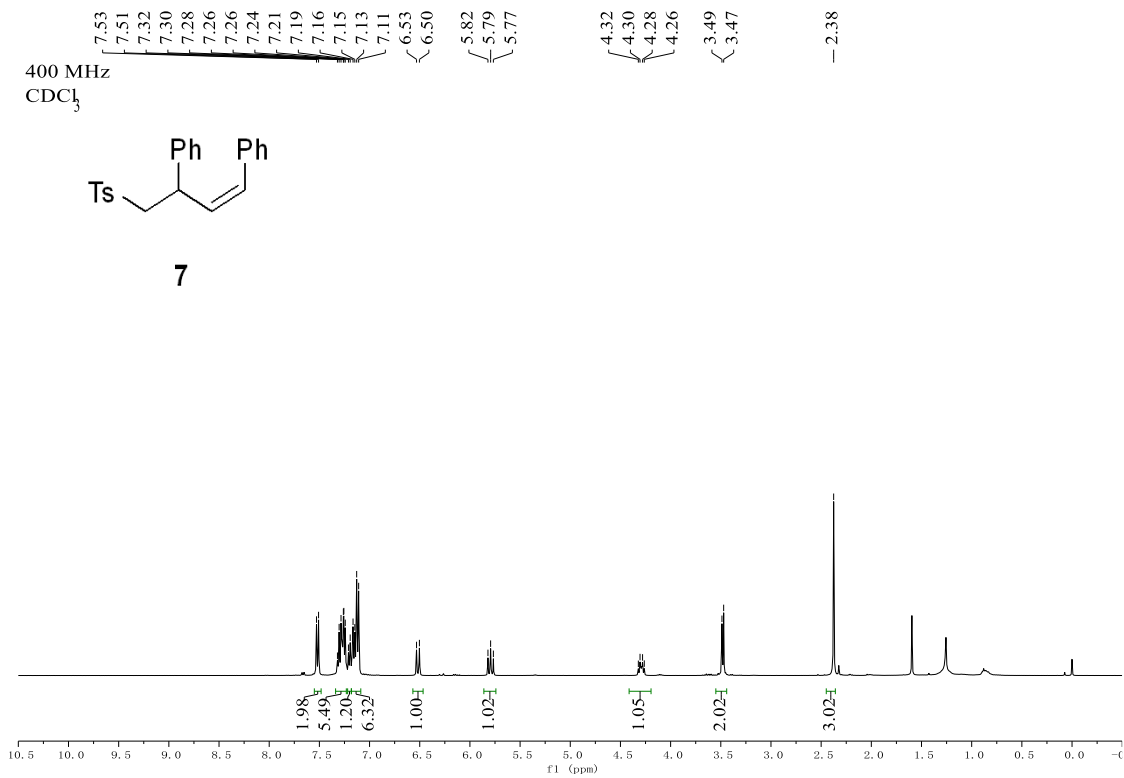
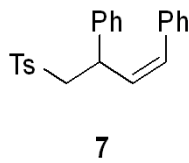
100 MHz  
CDCl<sub>3</sub>

137.4  
131.8  
130.7  
128.6  
128.5  
126.2  
123.2  
120.8

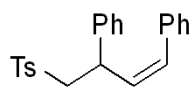
90.9  
88.7



400 MHz  
CDCl<sub>3</sub>



100 MHz  
CDCl<sub>3</sub>



7

