Synthesis of (*E*)-β-iodo vinylsulfones via iodine-promoted iodosulfonylation of alkynes with sodium sulfinates in an aqueous medium at room temperature

Yadong Sun,* Ablimit Abdukader, Dong Lu, Haiyan Zhang and Chenjiang Liu*

The Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education & Xinjiang Uygur Autonomous Region, Urumqi Key Laboratory of Green Catalysis and Synthesis Technology, School of Chemistry and Chemical Engineering, Physics and Chemistry Detecting Center, Xinjiang University, Urumqi 830046, China.

E-mail: pxylcj@126.com

E-mail: syd19791016@163.com

Supporting Information

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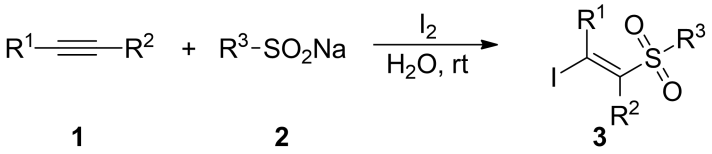
A. General method

Melting points were measured with a melting point instrument and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. GC-MS was obtained using electron ionization (EI). High-resolution mass spectra were obtained with a LCMS-IT-TOF mass spectrometer. Single-crystal X-ray analysis was obtained using Bruker APEX2 Smart CCD. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Alfa Aesar and Ark) and used without further purification.

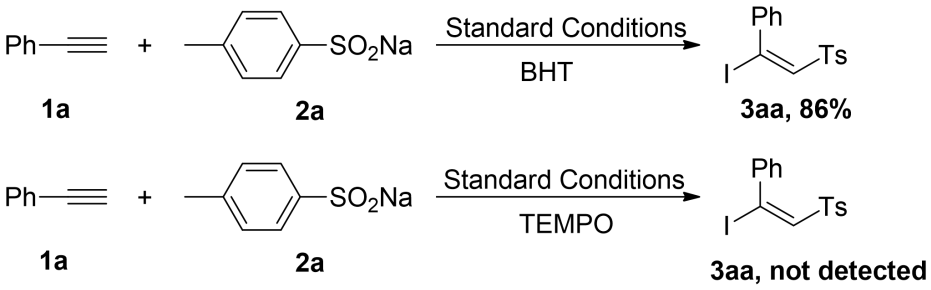
B. General procedure for the synthesis of products



1 **2** **3**

A mixture of sodium sulfinates (0.60 mmol), alkyne (0.30 mmol), and iodine (0.45 mmol) in water (2.0 mL) was placed in a test tube (25 mL) equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 2h. After the reaction was completed, the mixture was quenched by the addition of satd aq $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with ethyl acetate (2 × 15 mL). The organic layer was dried with anhydrous $MgSO_4$, concentrated in vacuo and purified by flash silica gel chromatography using petroleum ether/ethyl acetate 20:1 to give the desired products.

C. Control experiments for the study of mechanism



A mixture of **2a** (0.60 mmol), **1a** (0.30 mmol), iodine (0.45 mmol) and BHT (0.30 mmol) in water (2.0 mL) was placed in a test tube (25 mL) equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 2h. After the reaction was completed, the mixture was quenched by the addition of satd aq $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with ethyl acetate (2 × 15 mL). The organic layer was dried with anhydrous $MgSO_4$, concentrated in vacuo and purified by flash silica gel chromatography using petroleum ether/ethyl acetate 20:1 to give **3aa** in 86% yield.

A mixture of **2a** (0.60 mmol), **1a** (0.30 mmol), iodine (0.45 mmol) and TEMPO (0.30 mmol) in water (2.0 mL) was placed in a test tube (25 mL) equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 2h. After the reaction was completed, the mixture was quenched by the addition of satd aq $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with ethyl acetate (2 × 15 mL). The organic layer was dried with anhydrous $MgSO_4$, concentrated in vacuo and the crude product was detected by GC-MS.

D. Single-crystal X-ray analysis of 3aa

Datablock: 1

Bond precision: C-C = 0.0132 A Wavelength=0.71073

Cell: a=7.7369(8) b=10.2035(11) c=19.513(2)
alpha=102.425(4) beta=90.356(3) gamma=90.648(3)
Temperature: 296 K

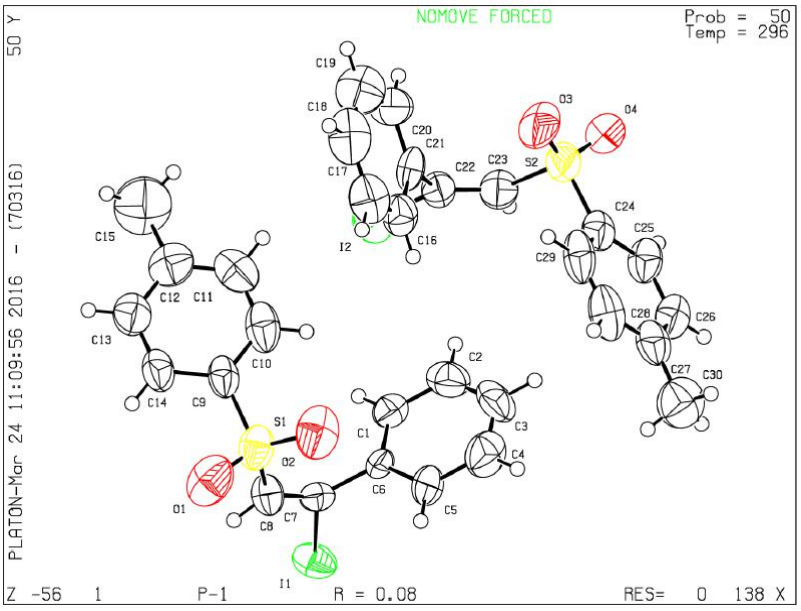
	Calculated	Reported
Volume	1504.2(3)	1504.2(3)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C15 H13 I O2 S	?
Sum formula	C15 H13 I O2 S	C15 H13 I O2 S
Mr	384.21	384.21
Dx,g cm-3	1.697	1.697
Z	4	4
Mu (mm-1)	2.262	2.262
F000	752.0	752.0
F000'	750.87	
h,k,lmax	9,12,23	9,12,23
Nref	5323	5220
Tmin,Tmax	0.614,0.666	0.636,0.686
Tmin'	0.602	

Correction method= # Reported T Limits: Tmin=0.636 Tmax=0.686
AbsCorr = MULTI-SCAN

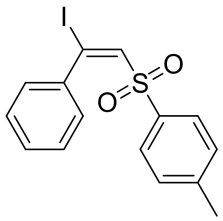
Data completeness= 0.981 Theta(max)= 25.050

R(reflections)= 0.0836(4279) wR2(reflections)= 0.2187(5220)

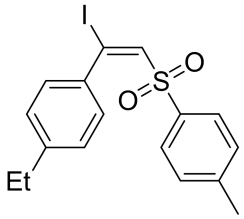
S = 1.075 Npar= 297



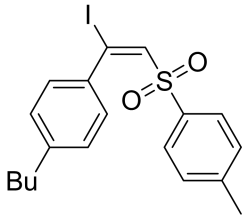
E. Analytical data for 3aa-3la, 4, 5 and 6.



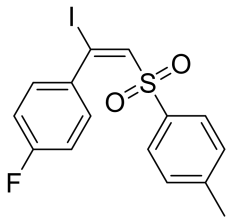
(*E*)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (**3aa**).[1] white solid (99.1 mg, 86%); mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.36 (s, 1H), 7.32 – 7.25 (m, 3H), 7.23 (dt, *J* = 3.7, 2.1 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.2, 139.6, 137.2, 129.7, 129.6, 127.8, 127.8, 127.6, 114.1, 21.5.



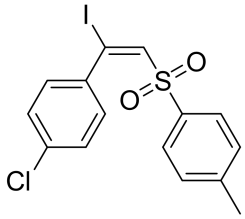
(*E*)-1-ethyl-4-(1-iodo-2-tosylvinyl)benzene (3ab). white solid (107.6 mg, 87%); mp 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 2H), 7.18 – 7.12 (m, 4H), 7.09 (d, *J* = 8.5 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.2, 140.6, 137.0, 136.7, 129.3, 127.7, 127.6, 127.1, 114.6, 28.5, 21.4, 15.1; ESI-HRMS calcd for $C_{17}H_{17}IO_2S$ $(M + H)^+$ 413.0067; found 413.0059.



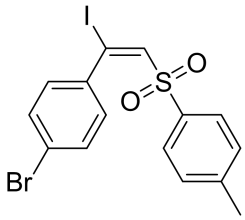
(*E*)-1-butyl-4-(1-iodo-2-tosylvinyl)benzene (3ac). Yellow liquid (116.2 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 10.4 Hz,2H), 7.34 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.60(t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 1.64 – 1.56 (m, 2H), 1.43 – 1.33 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.3, 140.8, 137.2, 136.7, 129.4, 127.7, 127.7, 127.7, 114.8, 35.4, 33.3, 22.2, 21.5, 13.9; ESI-HRMS calcd for $C_{19}H_{21}IO_2S$ $(M + H)^+$ 441.0380; found 441.0385.



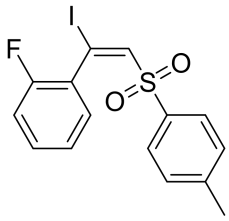
(*E*)-1-fluoro-4-(1-iodo-2-tosylvinyl)benzene (3ad).[1] white solid (90.5 mg, 75%); mp 91−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 1H), 7.28 – 7.20 (m, 4H), 6.98 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ163.1 (d, *J* = 251.4 Hz), 144.7, 141.6, 137.1, 135.6 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 8.7 Hz), 129.7, 127.7, 115.0 (d, *J* = 22.1 Hz), 112.5, 21.6.



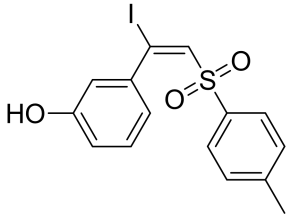
(*E*)-1-chloro-4-(1-iodo-2-tosylvinyl)benzene (3ae).[1] white solid (96.7 mg, 77%); mp 146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 1H), 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.7, 138.0, 137.1, 135.8, 129.7, 129.0, 128.1, 127.8, 112.0, 21.6.



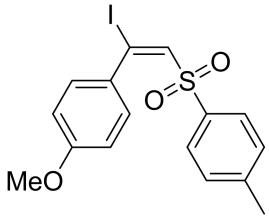
(*E*)-1-bromo-4-(1-iodo-2-tosylvinyl)benzene (3af).[2] white solid (109.8 mg, 79%); mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 7.34 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.09 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.7, 138.5, 137.0, 131.1, 129.7, 129.2, 127.8, 124.1, 111.9, 21.6.



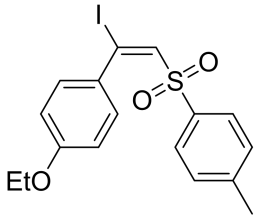
(*E*)-1-fluoro-2-(1-iodo-2-tosylvinyl)benzene (3ag). white solid (94.1 mg, 78%); mp 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.36 – 7.30 (m, 1H), 7.25 – 7.20 (m, 3H), 7.16 – 7.12(m, 1H), 6.99 – 6.94 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1 (d, *J* = 250.8 Hz), 144.8, 142.8, 136.6, 131.5 (d, *J* = 8.2 Hz), 129.7, 129.1 (d, *J* = 1.7 Hz), 127.8, 127.4 (d, *J* = 15.3 Hz), 123.7 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 20.7 Hz), 104.4, 21.5; ESI-HRMS calcd for $C_{15}H_{12}FIO_2S$ $(M + Na)^+$ 424.9479; found 424.9470.



(*E*)-3-(1-iodo-2-tosylvinyl)phenol (3ah). white solid (104.5 mg, 87%); mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.80 – 6.71 (m, 2H), 6.70 – 6.65 (m, 1H), 6.11 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 144.8, 140.8, 140.5, 136.7, 129.7, 129.2, 127.8, 119.7, 117.1, 114.5, 113.9, 21.6; ESI-HRMS calcd for $C_{15}H_{13}IO_3S$ $(M + Na)^+$ 422.9522; found 422.9516.

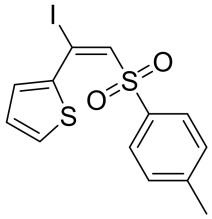


(*E*)-1-((2-iodo-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene (3ai).[2] Yellow liquid (113.1 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.29 (s, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.18 (m, 2H), 6.84 – 6.75 (m, 2H), 3.82 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 144.4, 140.1, 137.3, 131.7, 129.8, 129.5, 127.7, 114.8, 113.1, 55.3, 21.5;

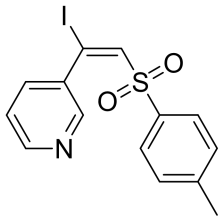


(*E*)-1-ethoxy-4-(1-iodo-2-tosylvinyl)benzene (3aj): Yellow liquid (119.5 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.28 (s, 1H), 7.25 – 7.21 (m, 2H), 7.18 (dd, *J* = 8.4, 0.5 Hz, 2H), 6.79 – 6.73 (m, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C

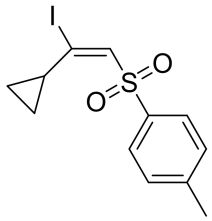
NMR (100 MHz, $CDCl_3$) δ 160.0, 144.3, 140.0, 137.2, 131.4, 129.8, 129.4, 127.6, 115.0, 113.4, 63.4, 21.4, 14.5; ESI-HRMS calcd for $C_{17}H_{17}IO_3S$ $(M + Na)^+$ 450.9835; found 450.9828.



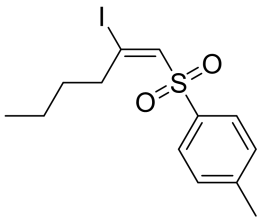
(*E*)-2-(1-iodo-2-tosylvinyl)thiophene (3ak).[3] Yellow solid (106.5 mg, 91%); mp 95−96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.53 (dd, J = 3.7, 1.2 Hz, 1H), 7.49 (dd, J = 5.1, 1.2 Hz, 1H), 7.31 (s, 1H), 7.24 – 7.22 (m, 1H), 7.21 (d, J = 0.7 Hz, 1H), 7.00 (dd, J = 5.1, 3.7 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.0, 140.8, 136.9, 131.3, 130.0, 129.6, 127.6, 127.3, 103.4, 21.5.



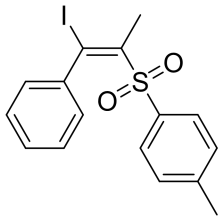
(*E*)-3-(1-iodo-2-tosylvinyl)pyridine (3al).[3] Yellow solid (94.8 mg, 82%); mp 140−141 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 4.9, 1.5 Hz, 1H), 8.46 (d, J = 2.2 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.44 (s, 1H), 7.31 – 7.26 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 147.3, 145.1, 142.8, 136.9, 136.1, 135.4, 130.0, 127.8, 122.7, 108.7, 21.6.



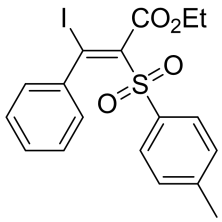
(*E*)-1-((2-cyclopropyl-2-iodovinyl)sulfonyl)-4-methylbenzene (3am). white solid (88.8 mg, 85%); mp 121−122 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.35– 7.33 (m, 2H), 7.03 (d, J = 2.3 Hz, 1H), 2.46 – 2.39 (m, 4H), 0.94 – 0.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.2, 137.7, 133.4, 129.9, 127.2, 21.6, 17.2, 12.0; ESI-HRMS calcd for $C_{12}H_{13}IO_2S$ $(M + Na)^+$ 370.9573; found 370.9577.



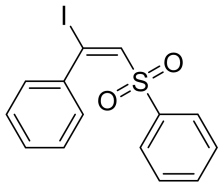
(*E*)-1-((2-iodohex-1-en-1-yl)sulfonyl)-4-methylbenzene (3an).[4] Yellow liquid (85.2 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 8.6, 0.6 Hz, 2H), 6.97 (s, 1H), 3.04 – 2.97 (m, 2H), 2.43 (s, 3H), 1.55 – 1.44 (m, 2H), 1.41 – 1.31 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 138.8, 138.0, 130.0, 127.4, 125.4, 39.7, 31.9, 21.6, 21.6, 13.82.



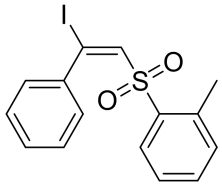
(*E*)-1-((1-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (3ao).[5] white solid (76.5 mg, 64%); mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.07 (m, 2H), 2.51 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.8, 142.9, 137.2, 129.4, 128.6, 127.7, 127.6, 127.5, 115.7, 27.0, 21.5.



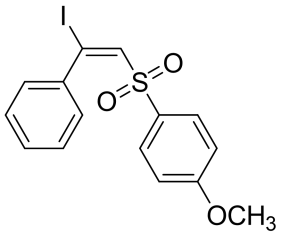
(*E*)-ethyl 3-iodo-3-phenyl-2-tosylacrylate (3ap): Yellow liquid (69.8 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (m, 1H), 7.24 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.08 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 146.4, 144.8, 139.5, 137.0, 129.5, 129.3, 128.2, 127.7, 127.3, 114.0, 63.2, 21.6, 13.9; ESI-HRMS calcd for $C_{18}H_{17}IO_4S$ $(M + Na)^+$ 478.9784; found 478.9775.



(*E*)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (3ba).[2] white solid (95.5 mg, 86%); mp 66−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 3H), 7.39 (s, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.23 (m, 3H), 7.22 – 7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.9, 139.3, 133.3, 129.6, 128.8, 127.7, 127.5, 127.4, 114.6.



(*E*)-1-((2-iodo-2-phenylvinyl)sulfonyl)-2-methylbenzene (3ca). white solid (100.3 mg, 87%); mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.37 – 7.33 (m, 1H), 7.25 – 7.12 (m, 2H), 7.06 – 7.00 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.1, 138.1, 137.4, 133.2, 132.0, 129.6, 129.2, 127.7, 127.4, 126.0, 114.2, 20.3; ESI-HRMS calcd for $C_{15}H_{13}IO_2S$ $(M + H)^+$ 384.9754; found 384.9751.



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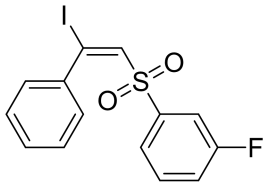
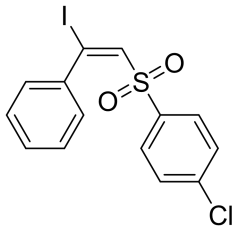
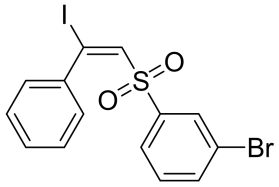
(*E*)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methoxybenzene (3da).[6] white solid (102.1 mg, 85%); mp 111−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 11.9 Hz, 2H), 7.37 (s, 1H), 7.32 – 7.20 (m, 5H), 6.85 – 6.79 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 141.4, 139.5, 131.4, 129.8, 129.5, 127.7, 127.5, 114.1, 113.5, 55.5.



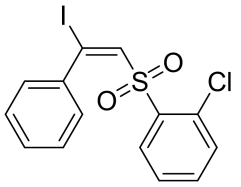
(*E*)-1-fluoro-3-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3ea): white solid (96.7 mg, 83%); mp 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.38 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.0 (d, J = 252.3 Hz), 142.0 (d, J = 6.6 Hz), 140.5, 139.2, 130.7 (d, J = 7.6 Hz), 129.9, 127.9, 127.4, 123.5 (d, J = 3.3 Hz), 120.6 (d, J = 21.2 Hz), 115.5, 115.1 (d, J = 24.5 Hz); ESI-HRMS calcd for $C_{14}H_{10}FIO_2S$ $(M + Na)^+$ 410.9322; found 410.9328.



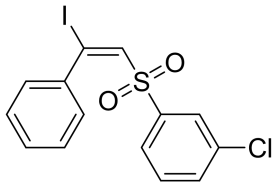
(*E*)-1-chloro-4-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3fa).[2] white solid (99.5 mg, 82%); mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.39 (s, 1H), 7.34 – 7.23 (m, 5H), 7.21 – 7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.9, 139.2, 138.3, 129.7, 129.0, 129.0, 127.8, 127.4, 115.1.



(*E*)-1-bromo-3-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3ga). white solid (114.5 mg, 85%); mp 59−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 1H), 7.55 (t, *J* = 1.7 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.40 (s, 1H), 7.36 – 7.31 (m, 1H), 7.31 – 7.24 (m, 3H), 7.19 – 7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.7, 139.1, 136.3, 130.7, 130.3, 130.0, 127.9, 127.4, 126.2, 122.7, 115.6; ESI-HRMS calcd for $C_{14}H_{10}BrIO_2S$ $(M + Na)^+$ 470.8522; found 470.8511.

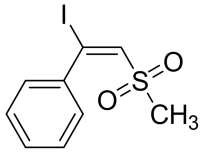


(*E*)-1-chloro-2-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3ha): white solid (102.0 mg, 84%); mp 100−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.48 – 7.44 (m, 1H), 7.42 – 7.37 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.2, 137.9, 134.2, 132.3, 131.3, 130.7, 129.7, 127.7, 127.3, 126.8, 114.8; ESI-HRMS calcd for $C_{14}H_{10}ClIO_2S$ $(M + Na)^+$ 426.9027; found 426.9021.

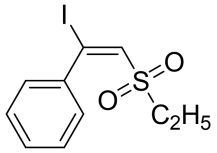


(*E*)-1-chloro-3-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3ia): white solid (98.3 mg, 81%); mp 63−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.41 – 7.40 (m, 2H), 7.35 – 7.25 (m,

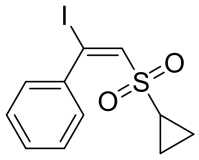
4H), 7.20 – 7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.7, 139.1, 134.9, 133.4, 130.1, 130.0, 127.9, 127.9, 127.3, 125.7, 115.6; ESI-HRMS calcd for $C_{14}H_{10}ClIO_2S$ $(M + Na)^+$ 426.9027; found 426.9030.



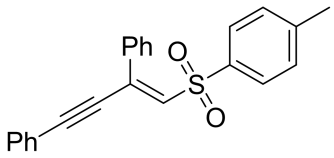
(*E*)-(1-iodo-2-(methylsulfonyl)vinyl)benzene (3ga).[7] white solid (75.8 mg, 82%); mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.41 – 7.36 (m, 3H), 7.30 (s, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.3, 130.2, 128.2, 127.7, 114.8, 42.9.



(*E*)-(2-(ethylsulfonyl)-1-iodovinyl)benzene (3ka): white solid (82.2 mg, 85%); mp 76−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.41 – 7.34 (m, 3H), 7.20 (s, 1H), 2.71 (q, J = 7.4 Hz, 2H), 1.26 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.9, 130.1, 128.0, 127.6, 115.4, 49.0, 6.6; ESI-HRMS calcd for $C_{10}H_{11}IO_2S$ $(M + H)^+$ 322.9597; found 322.9593.

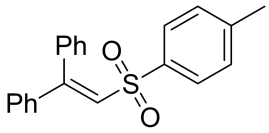


(*E*)-(2-(cyclopropylsulfonyl)-1-iodovinyl)benzene (3la). white solid (84.2 mg, 84%); mp 73−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.46 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 7.30 (s, 1H), 2.17 – 2.10 (m, 1H), 1.13 – 1.06 (m, 2H), 0.93 – 0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 139.3, 129.9, 127.9, 127.7, 113.9, 31.6, 5.2; ESI-HRMS calcd for $C_{11}H_{11}IO_2S$ $(M + H)^+$ 334.9597; found 334.9599.

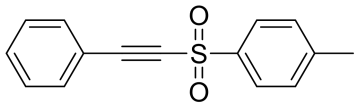


(*E*)-(4-(phenylsulfonyl)but-3-en-1-yne-1,3-diyl)dibenzene (4).[1] white solid (155.9 mg, 87%); mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.44 – 7.30 (m, 8H), 7.20 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

144.1, 137.9, 136.7, 135.3, 134.1, 131.8, 129.5, 129.4, 129.4, 128.9, 128.3, 127.8, 127.6, 121.4, 97.2, 88.3, 21.5.



(2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (5).[1] Yellow solid (37.1 mg, 82%); mp 98−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.28 (m, 4H), 7.23 – 7.18 (m, 2H), 7.18 – 7.07 (m, 4H), 7.01 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.6, 139.0, 138.4, 135.4, 130.1, 129.6, 129.2, 128.8, 128.7, 128.4, 128.0, 127.6, 127.5, 21.4.



1-methyl-4-((phenylethynyl)sulfonyl)benzene (6).[8] white solid (108.9 mg, 85%); mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.49 – 7.44 (m, 1H), 7.41 – 7.34 (m, 4H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.9, 132.6, 131.4, 129.9, 128.6, 127.4, 117.9, 92.9, 85.5, 21.7.

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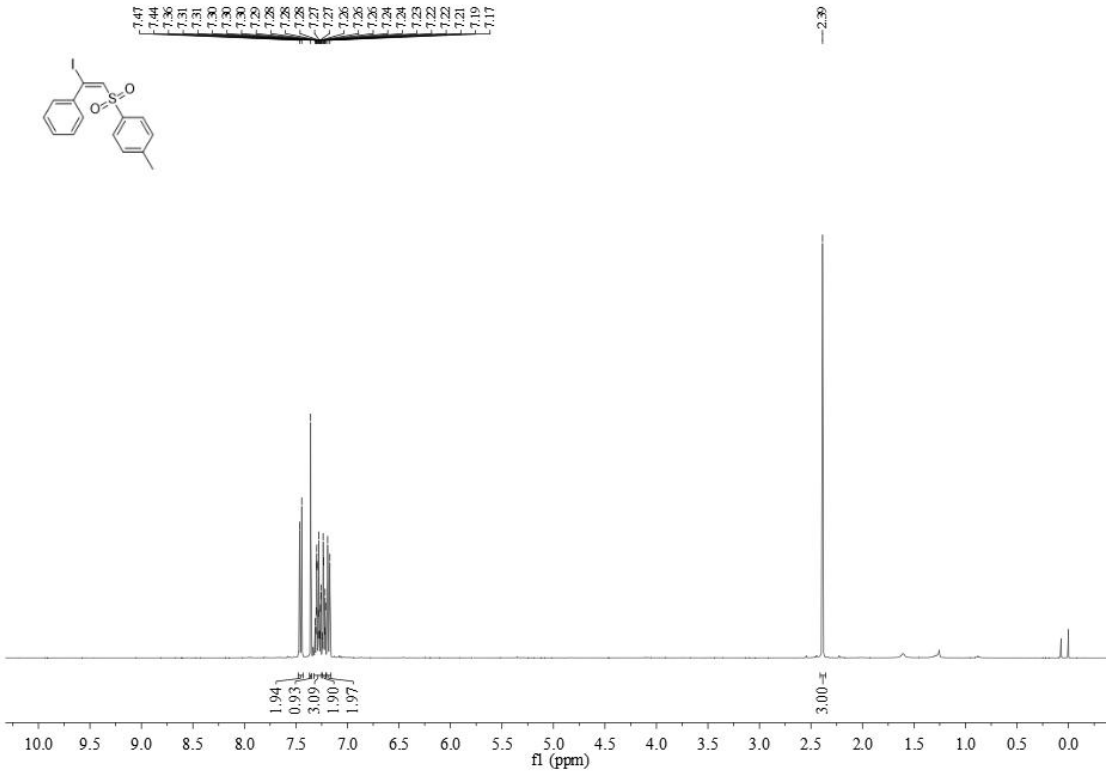
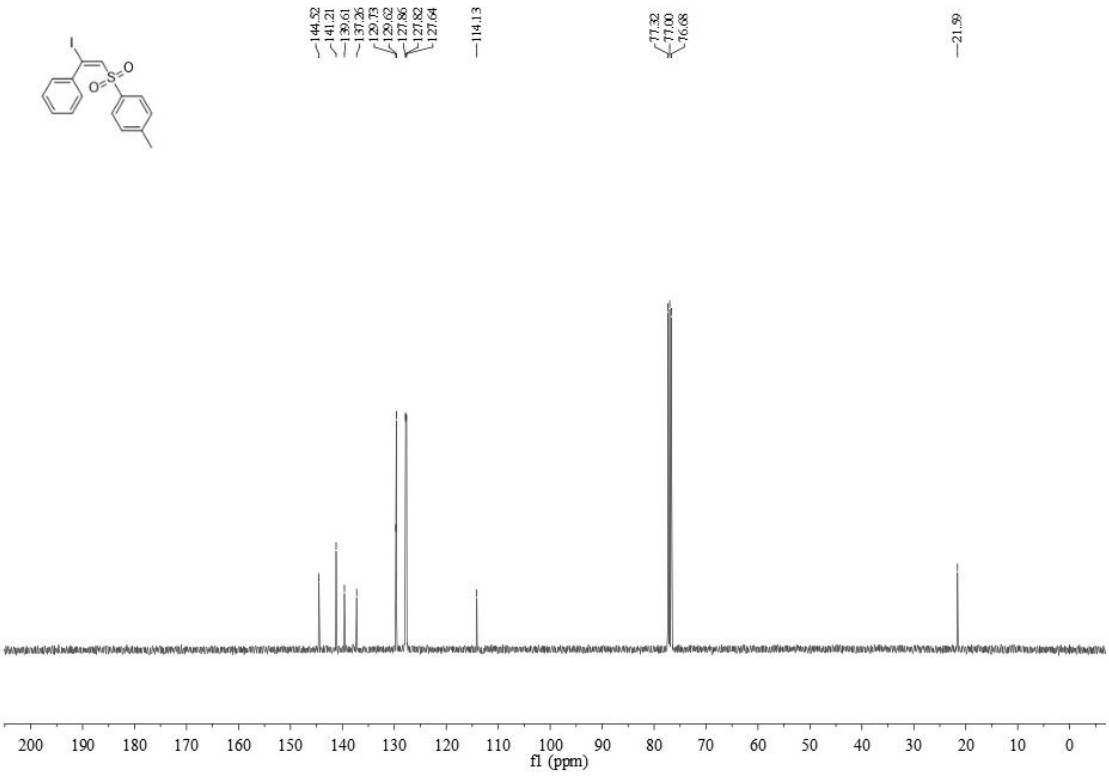
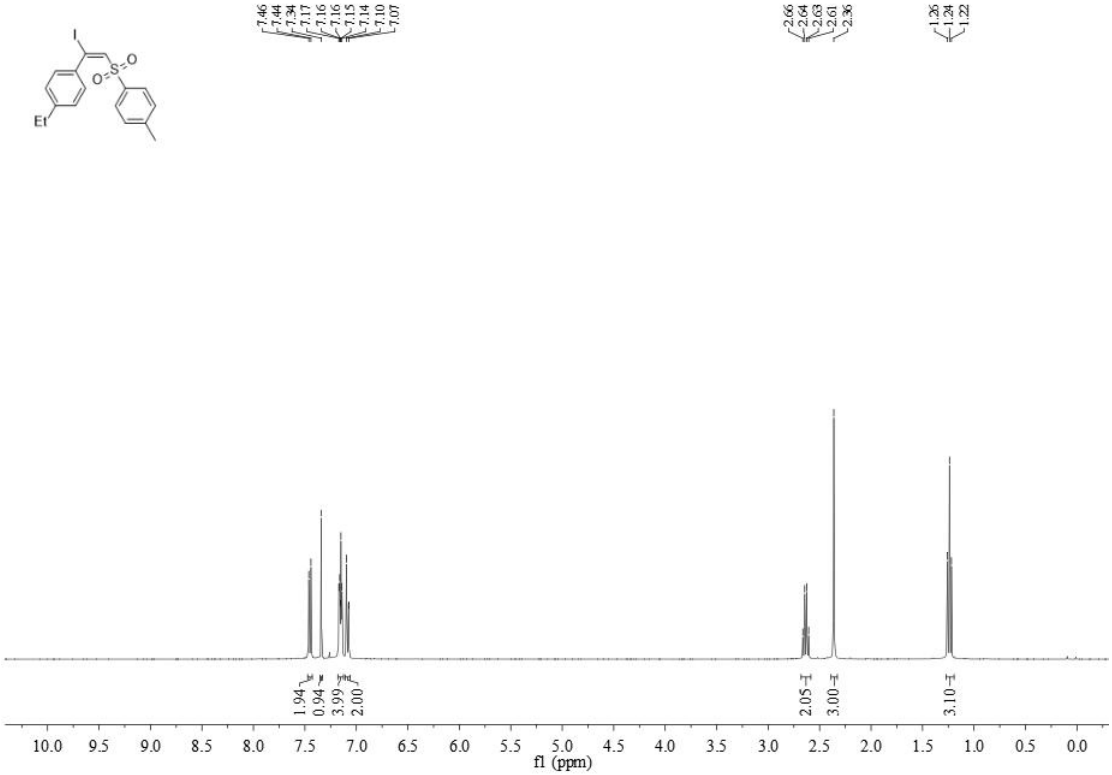
F. NMR Spectra

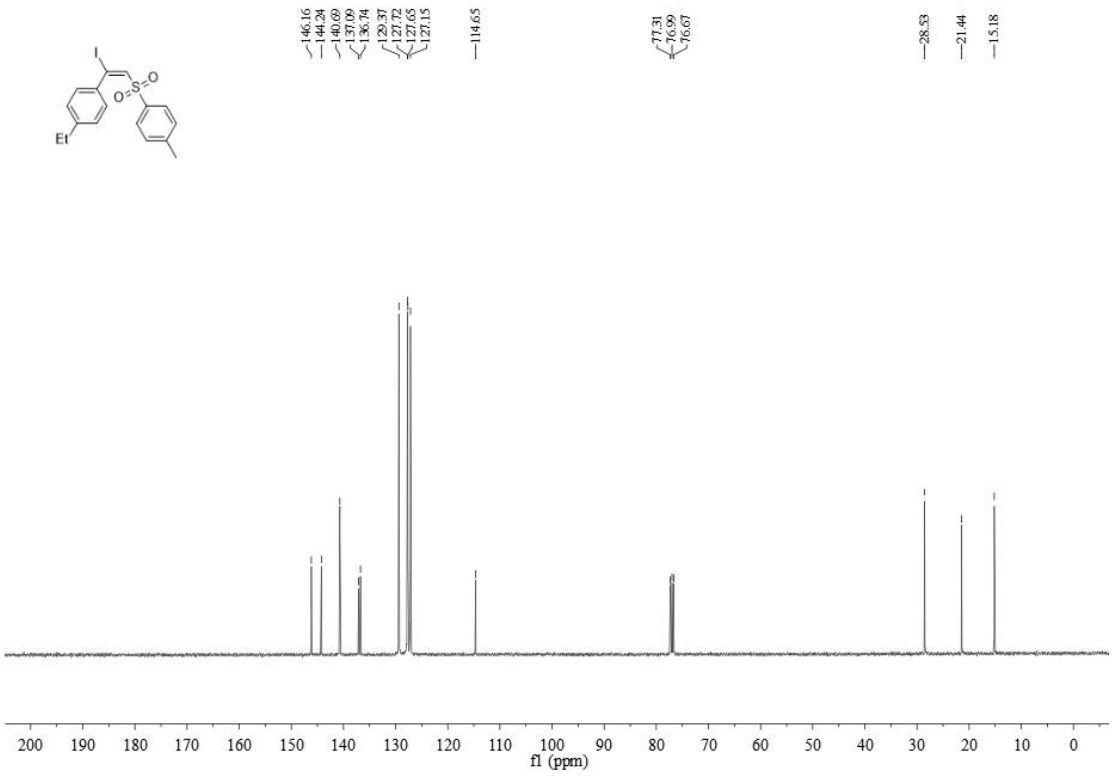
^{1}H-NMR and ^{13}C-NMR of 3aa



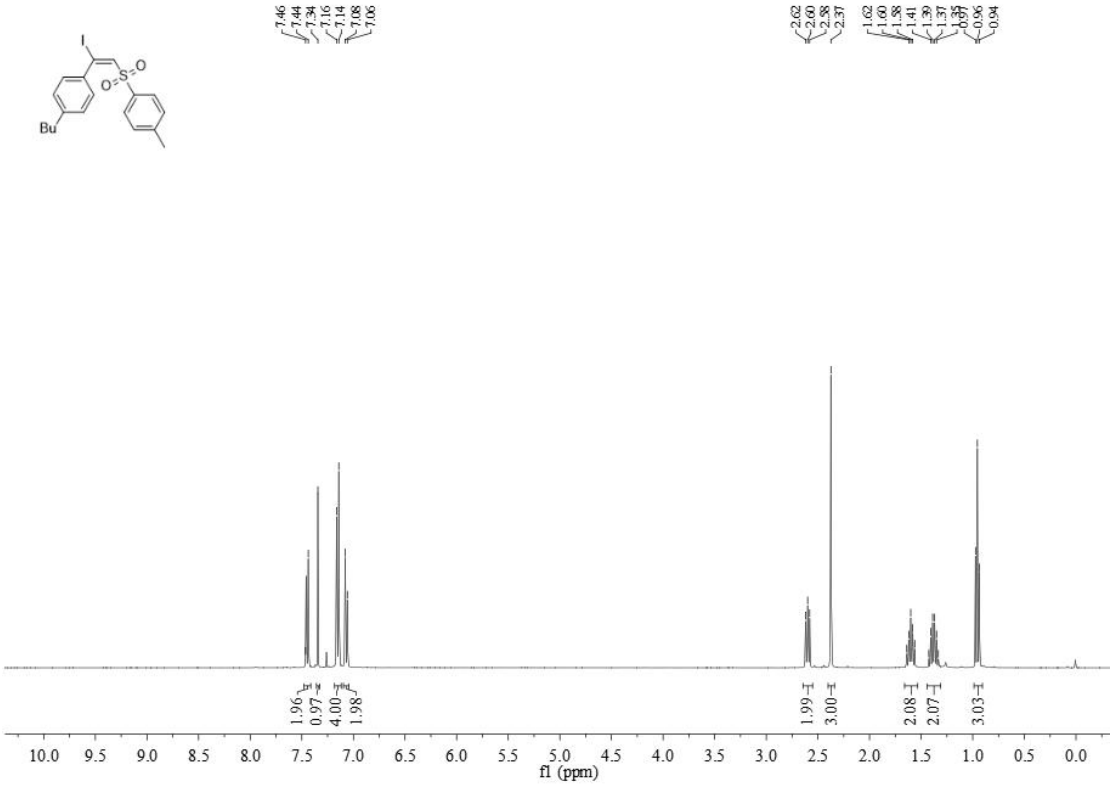


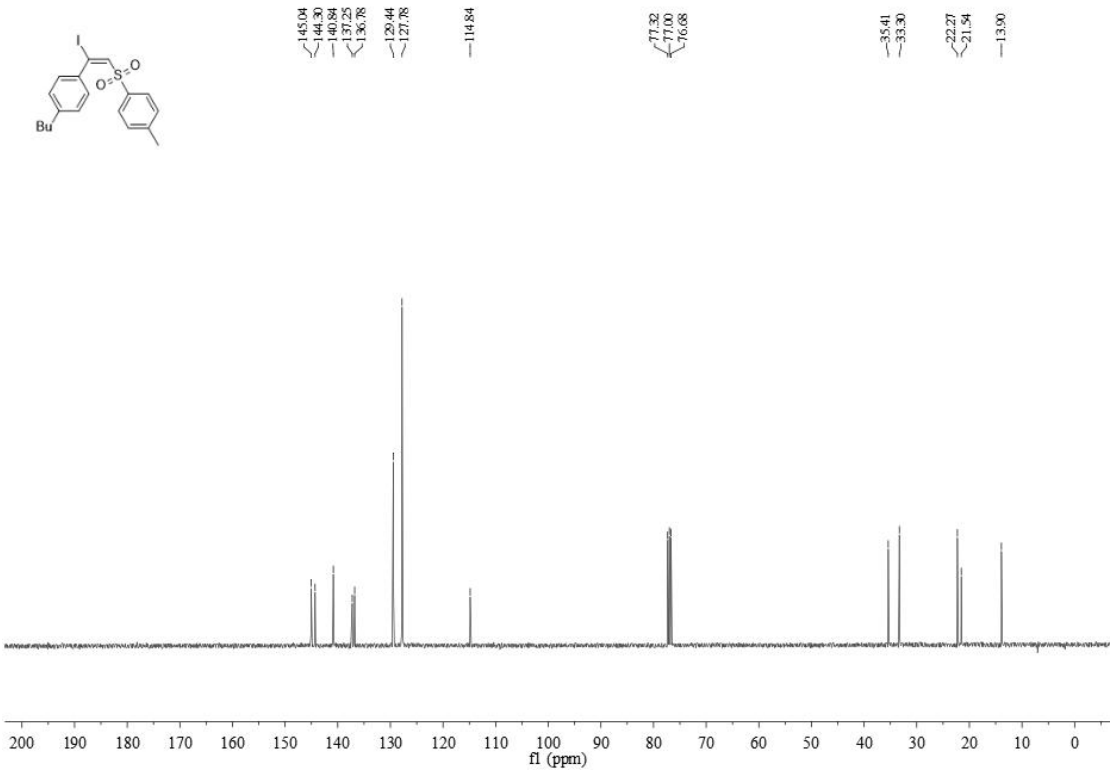
^{1}H-NMR and ^{13}C-NMR of 3ab



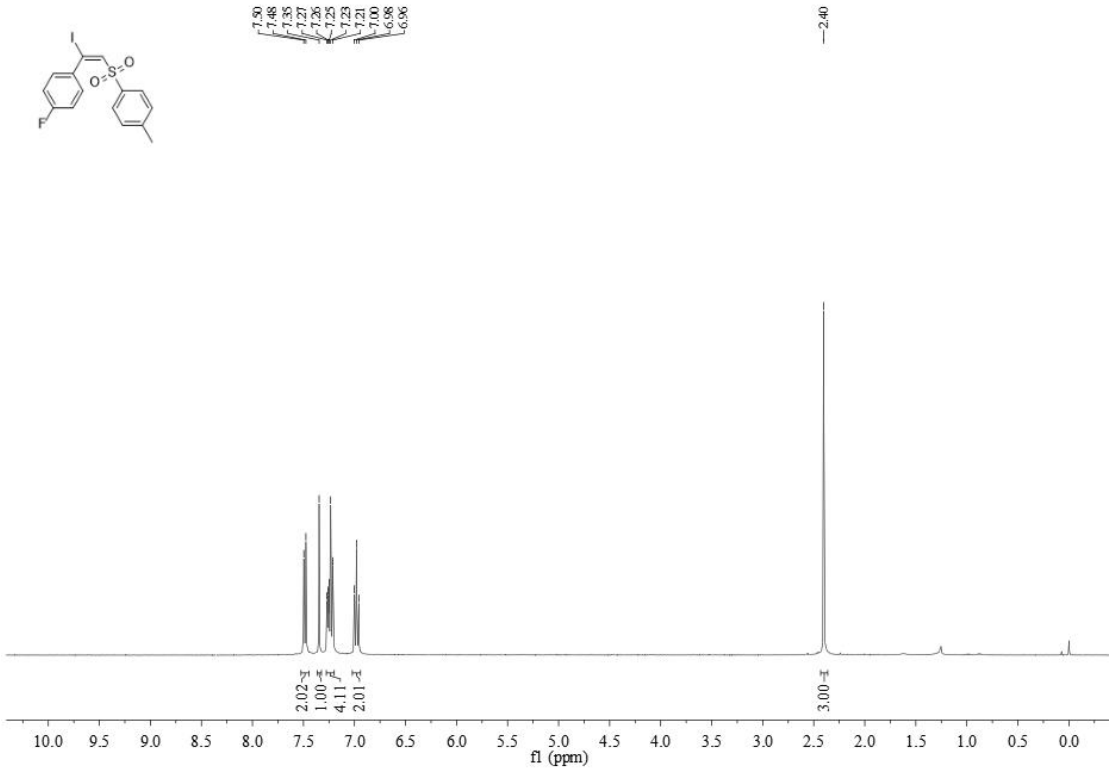


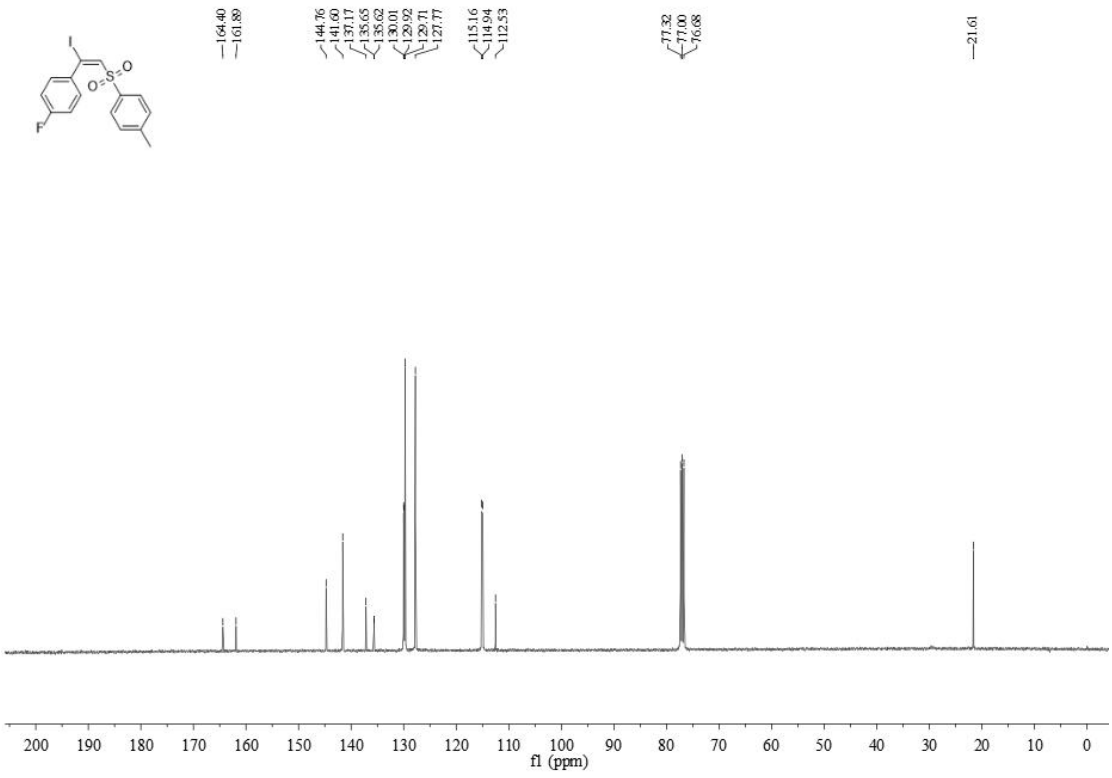
^{1}H-NMR and ^{13}C-NMR of 3ac



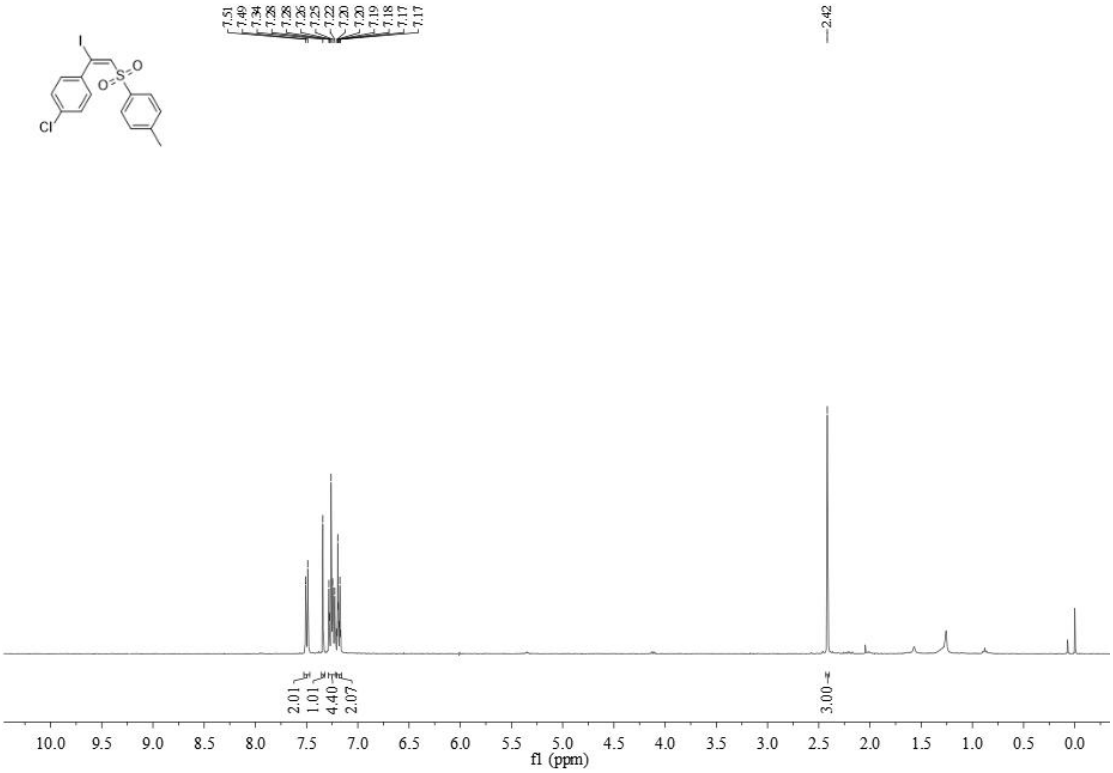


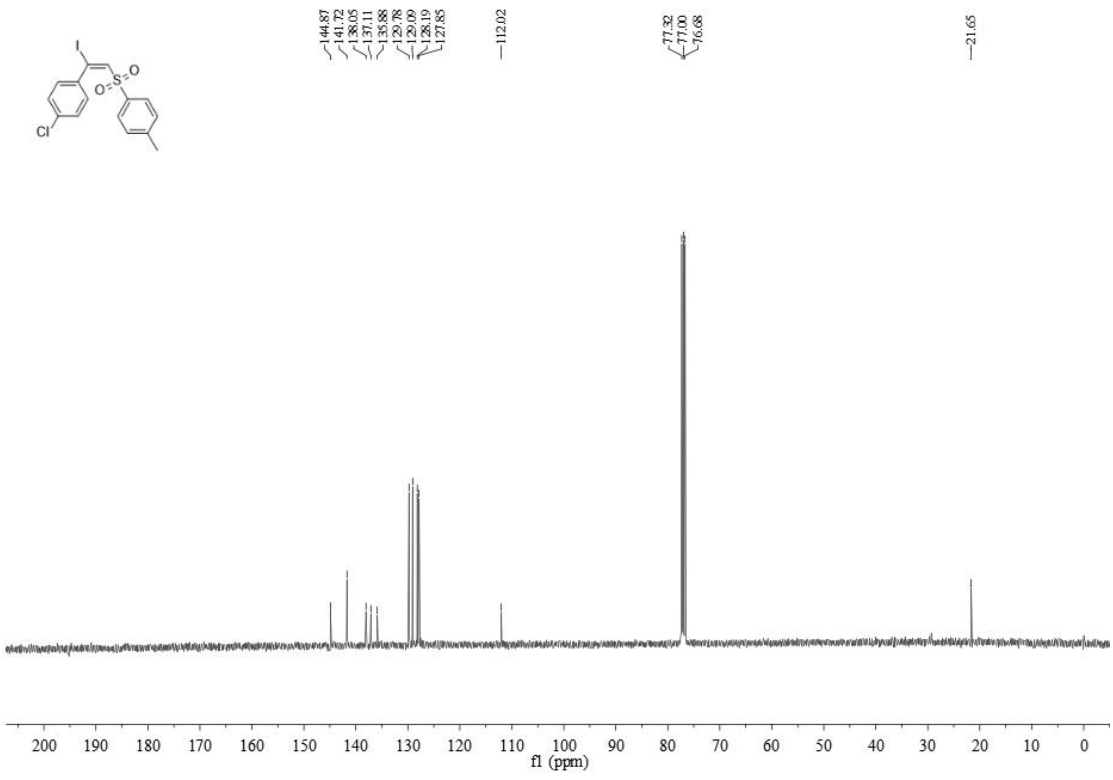
^{1}H-NMR and ^{13}C-NMR of 3ad



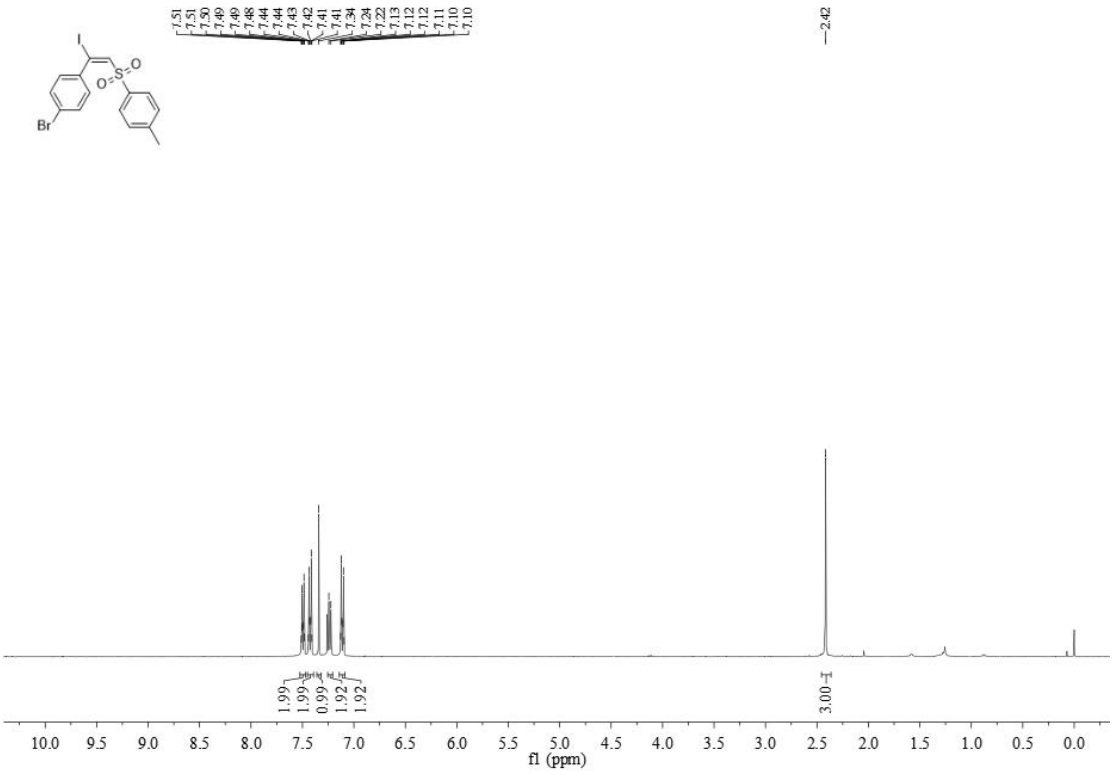


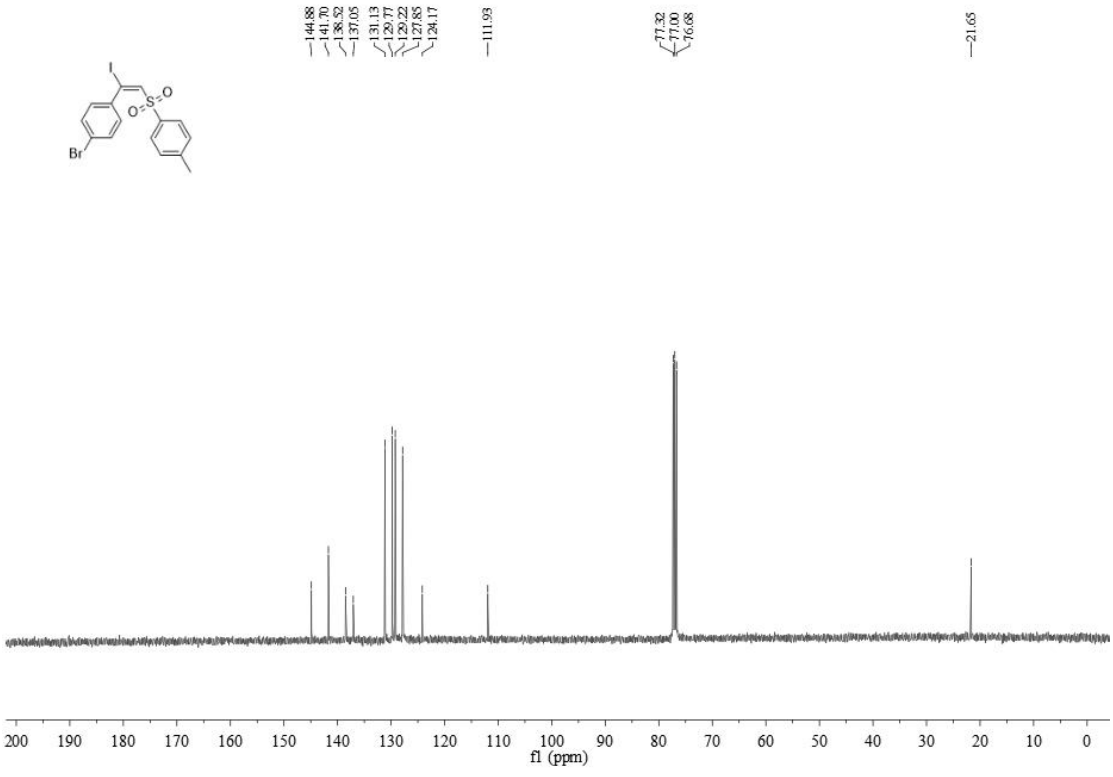
^{1}H-NMR and ^{13}C-NMR of 3ae



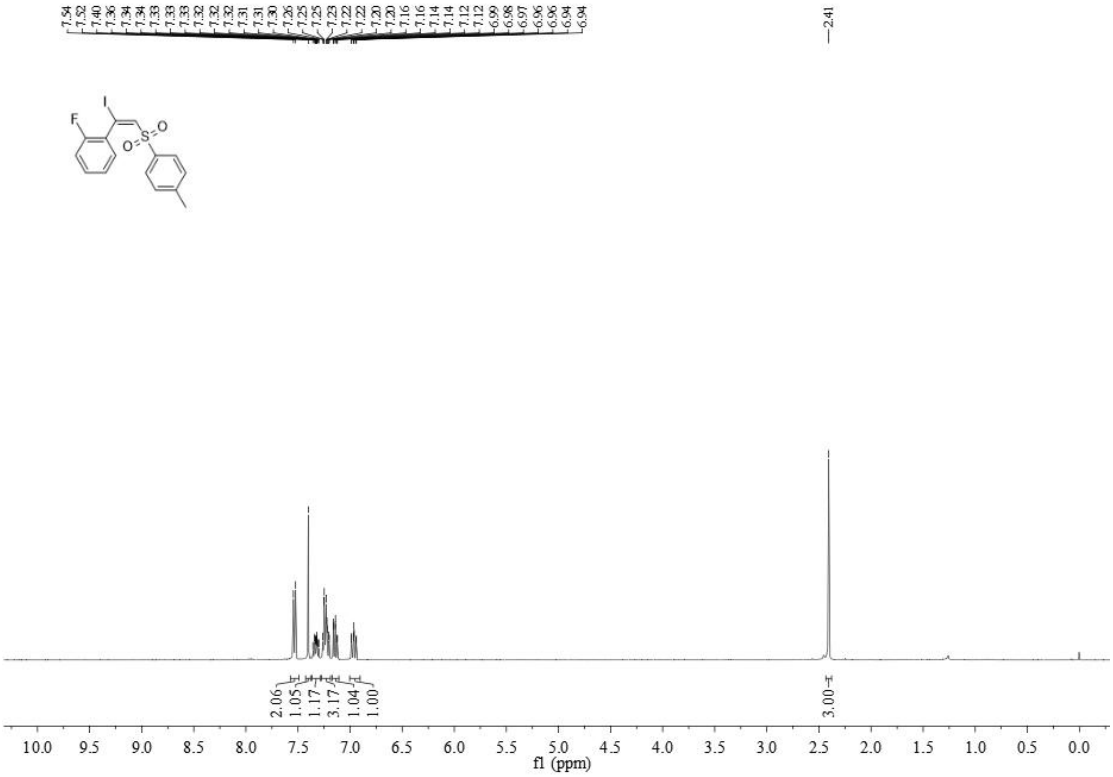


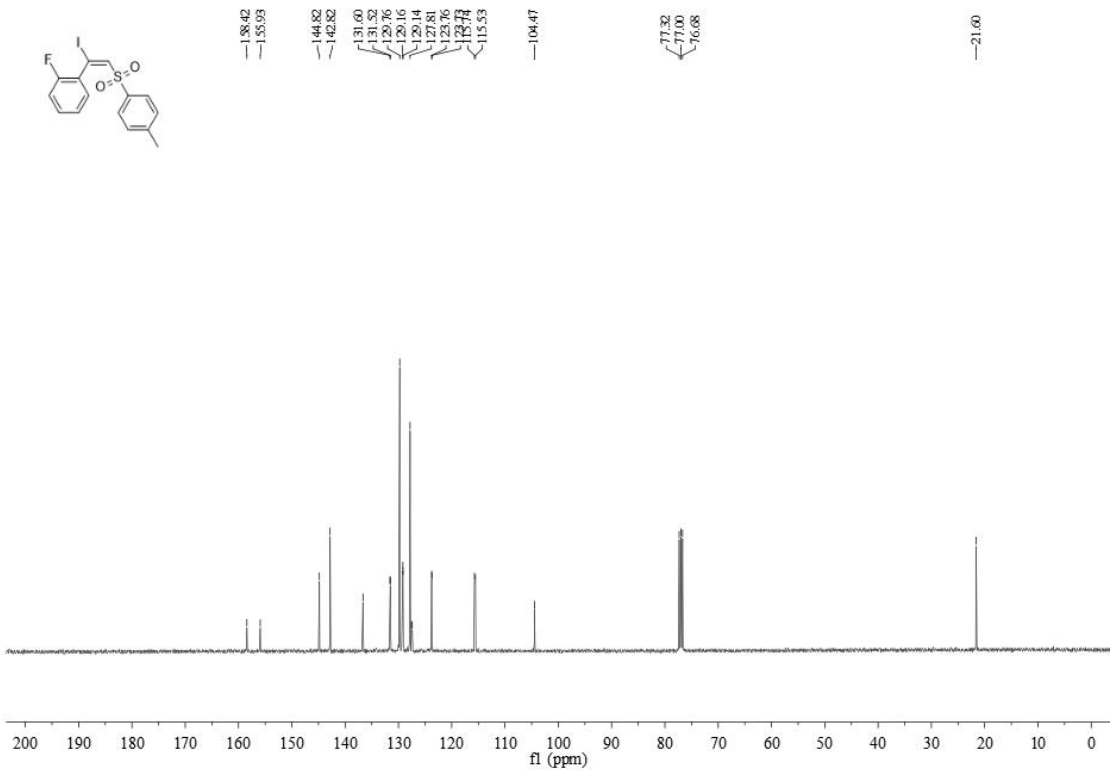
^{1}H-NMR and ^{13}C-NMR of 3af



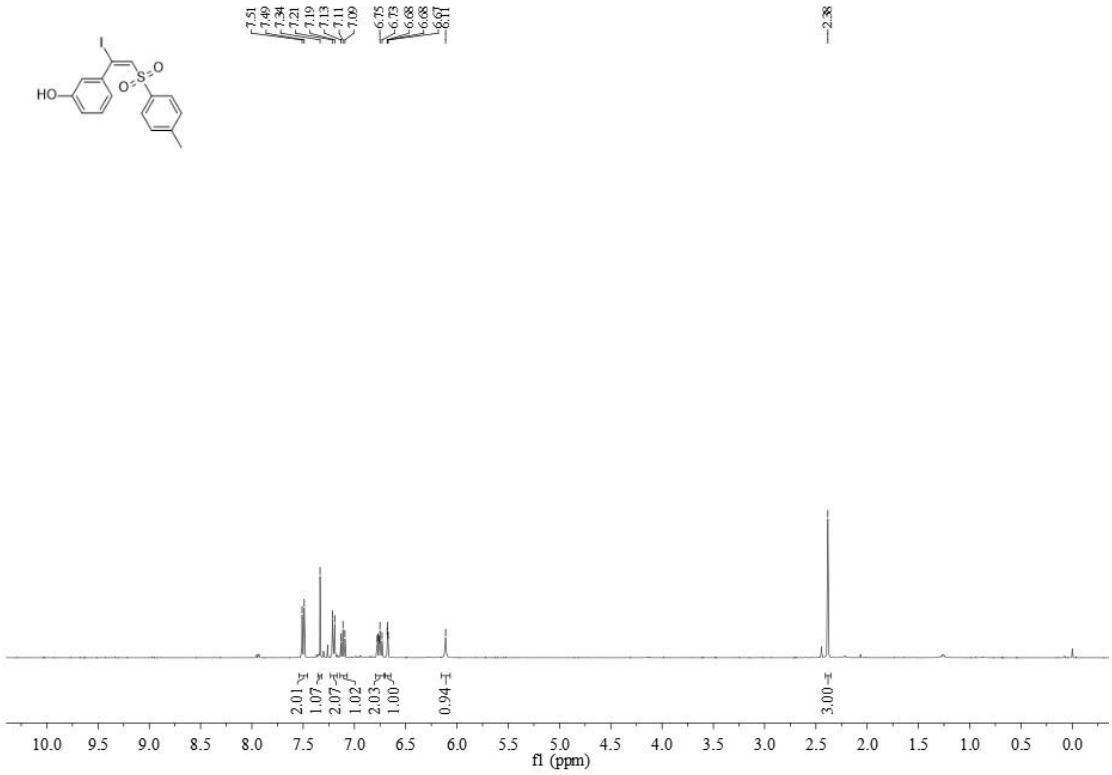


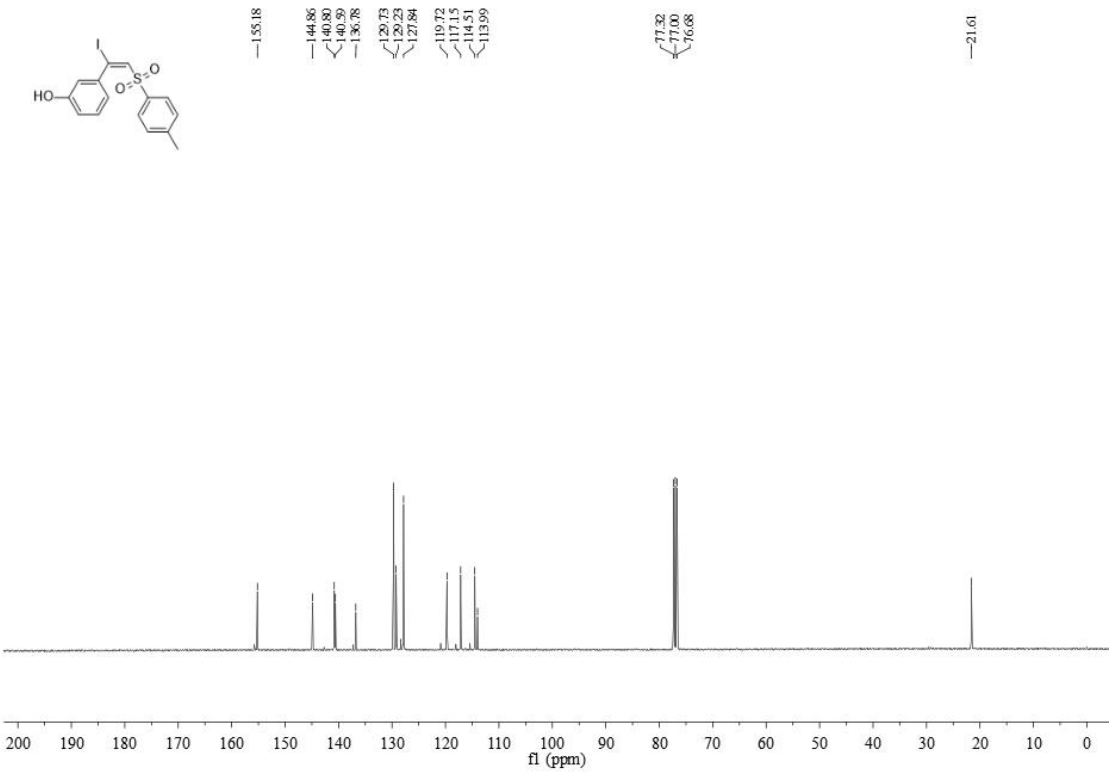
^{1}H-NMR and ^{13}C-NMR of 3ag



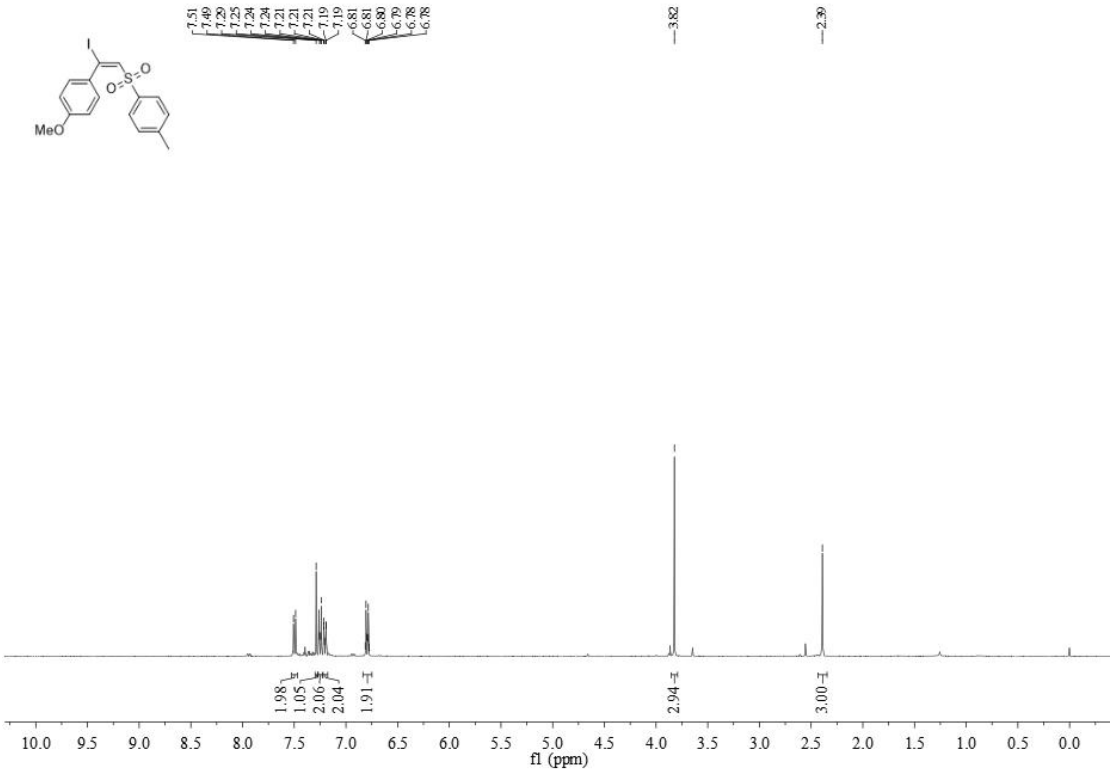


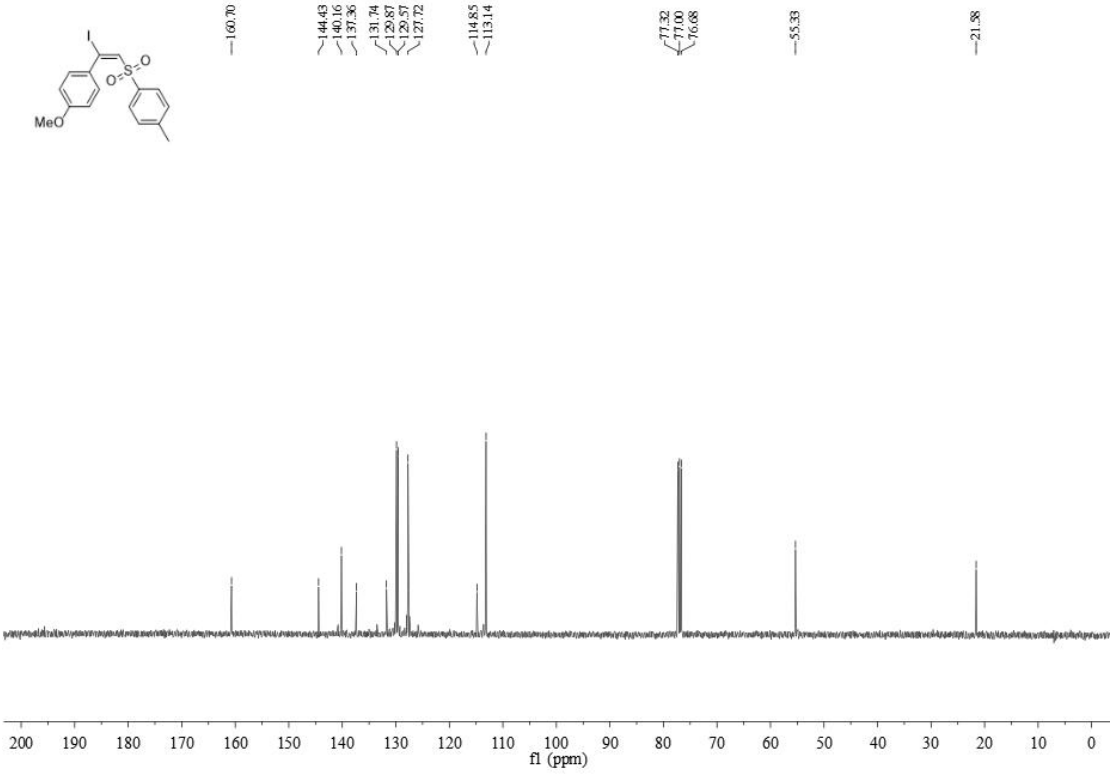
^{1}H-NMR and ^{13}C-NMR of 3ah



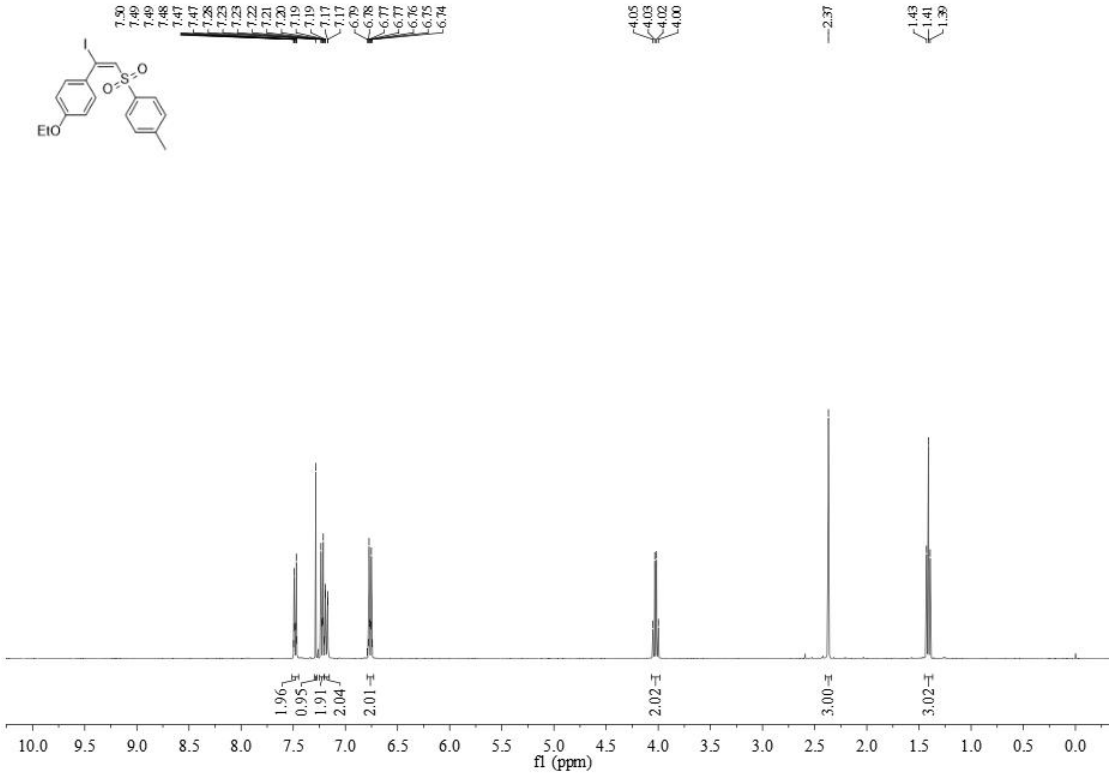


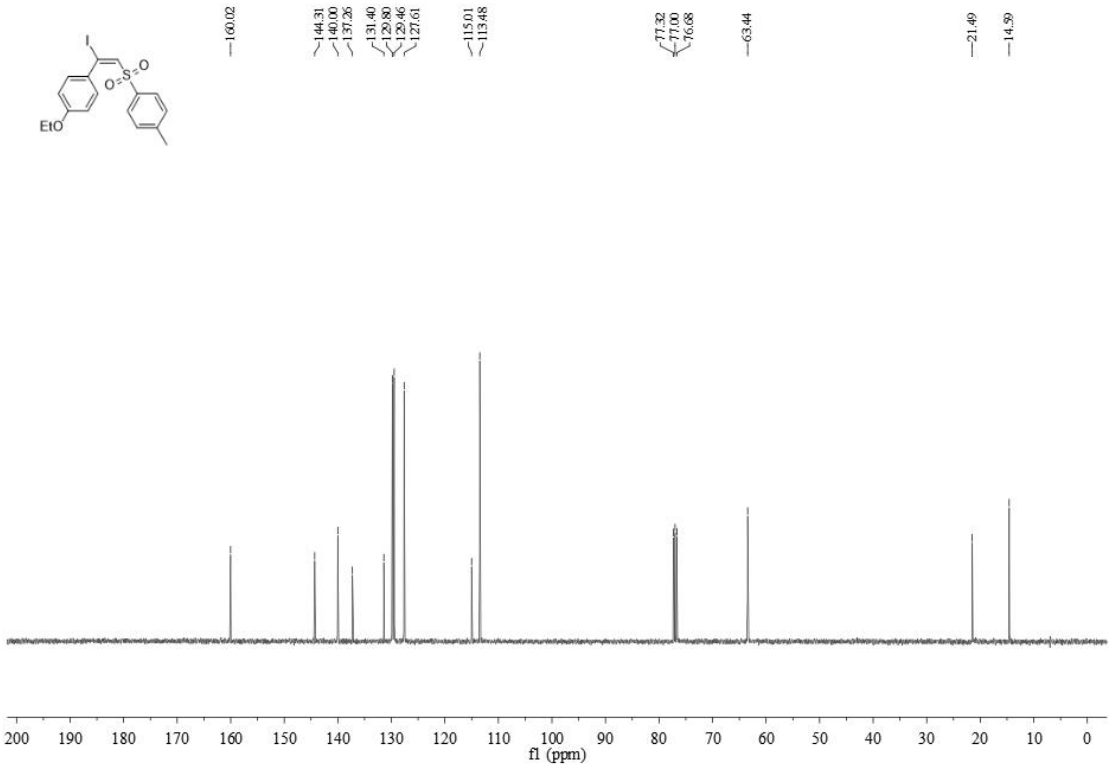
^{1}H-NMR and ^{13}C-NMR of 3ai



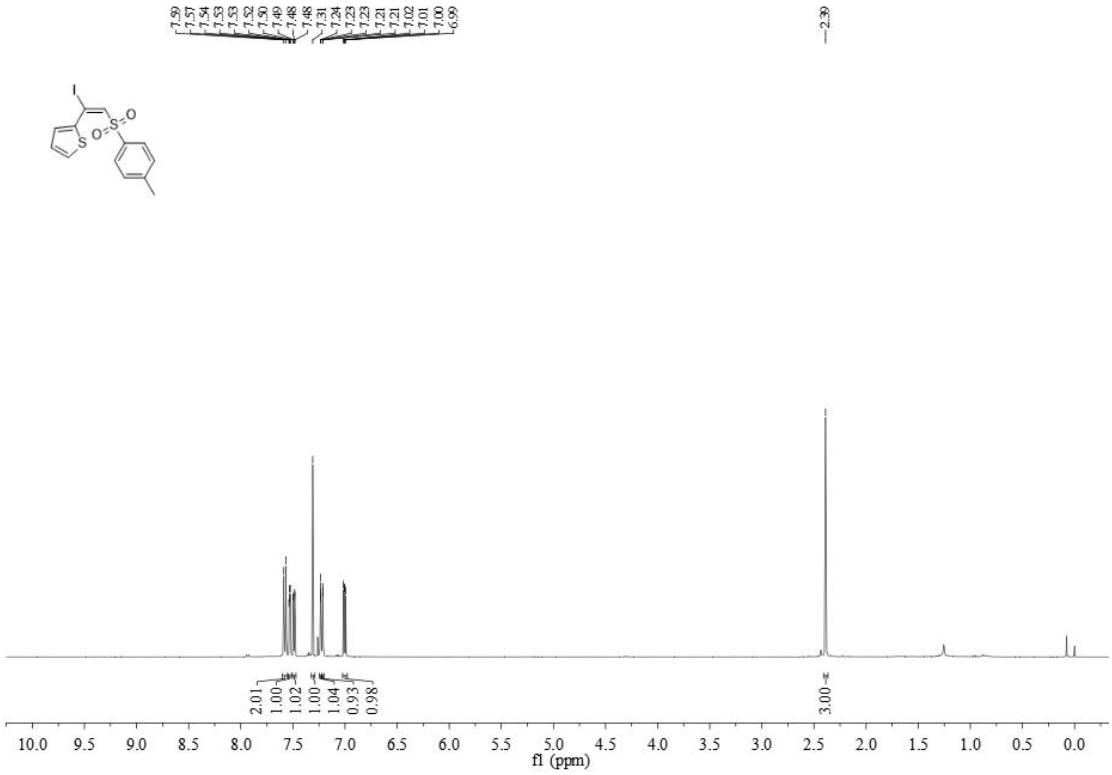


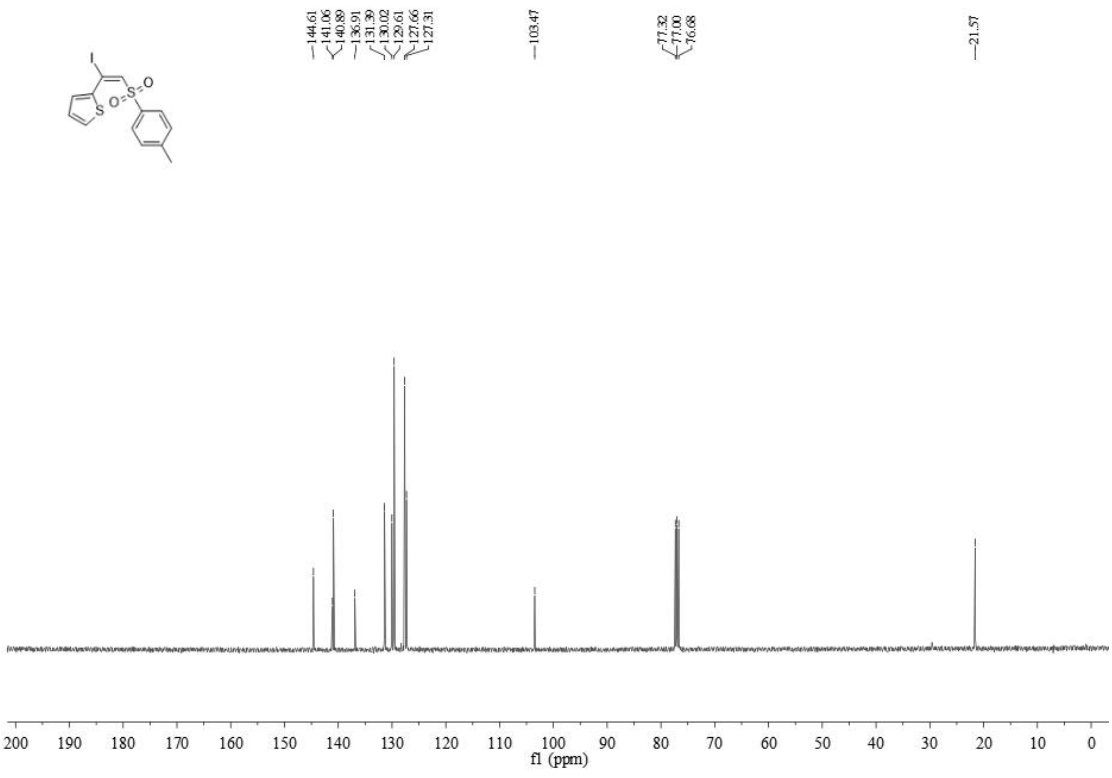
^{1}H-NMR and ^{13}C-NMR of 3aj



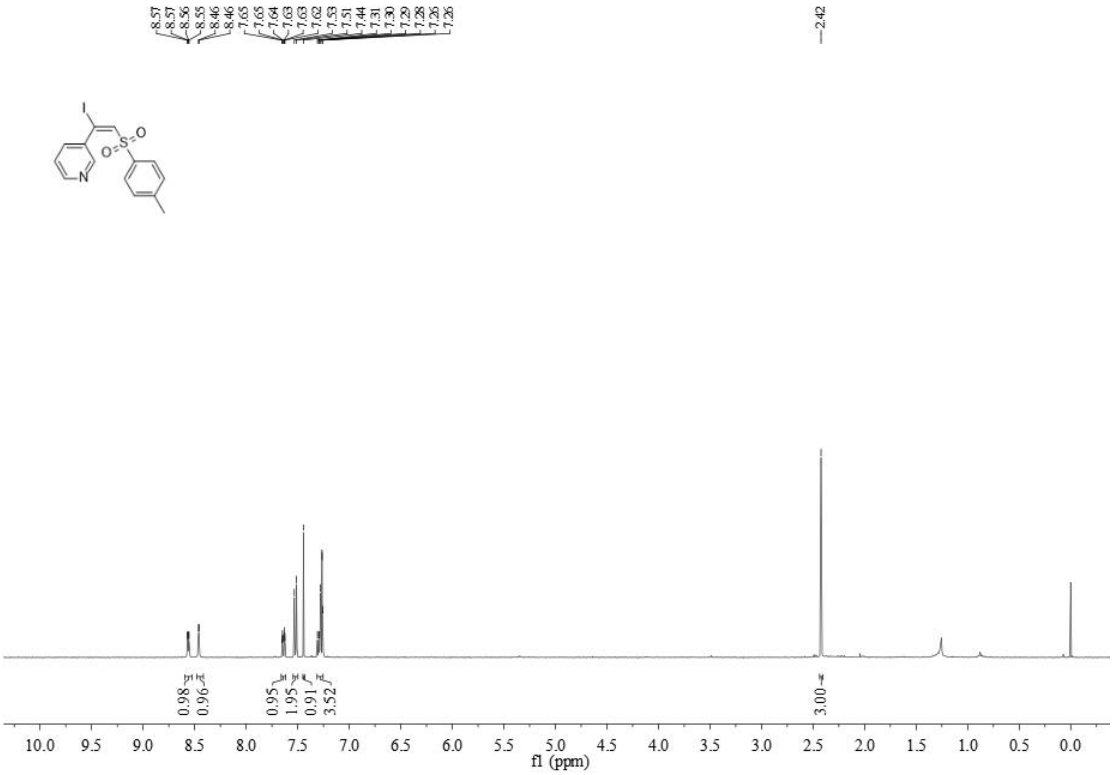


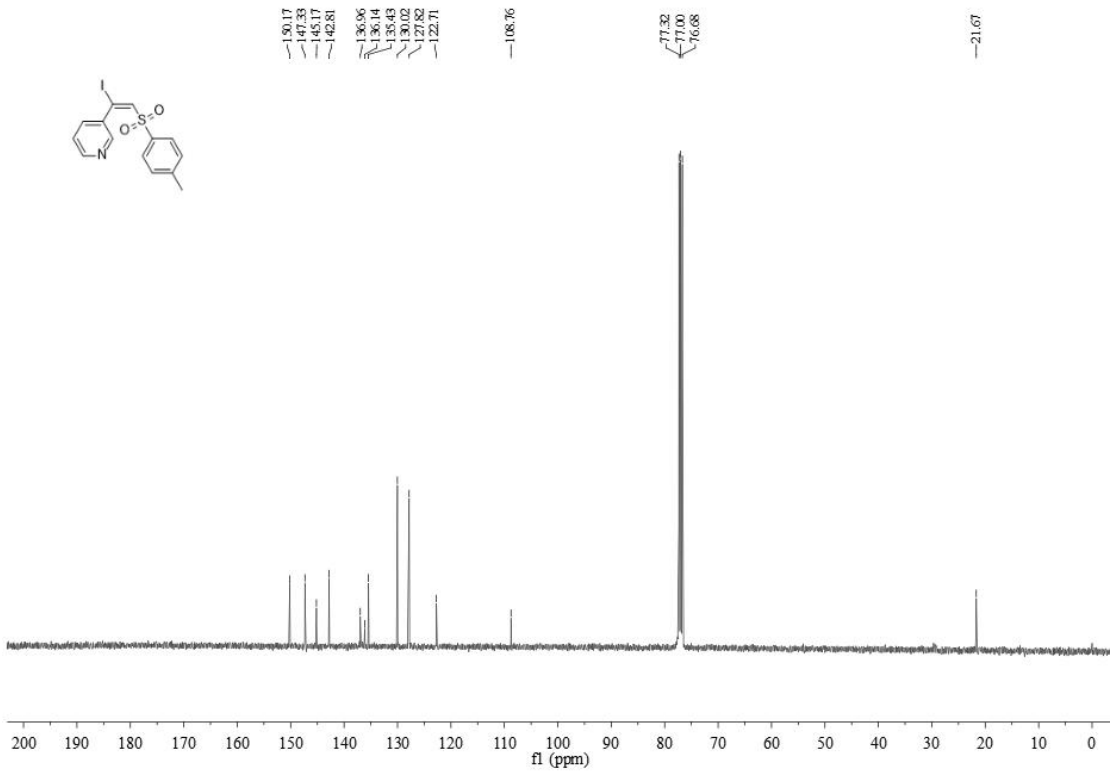
^{1}H-NMR and ^{13}C-NMR of 3ak



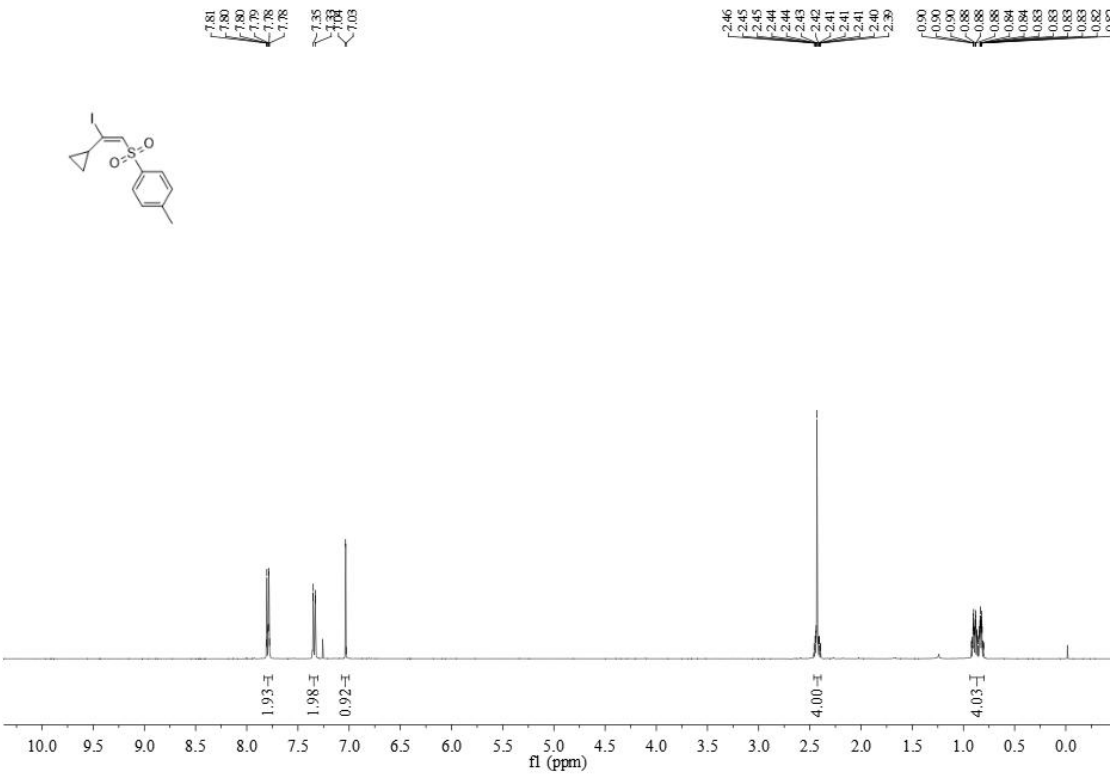


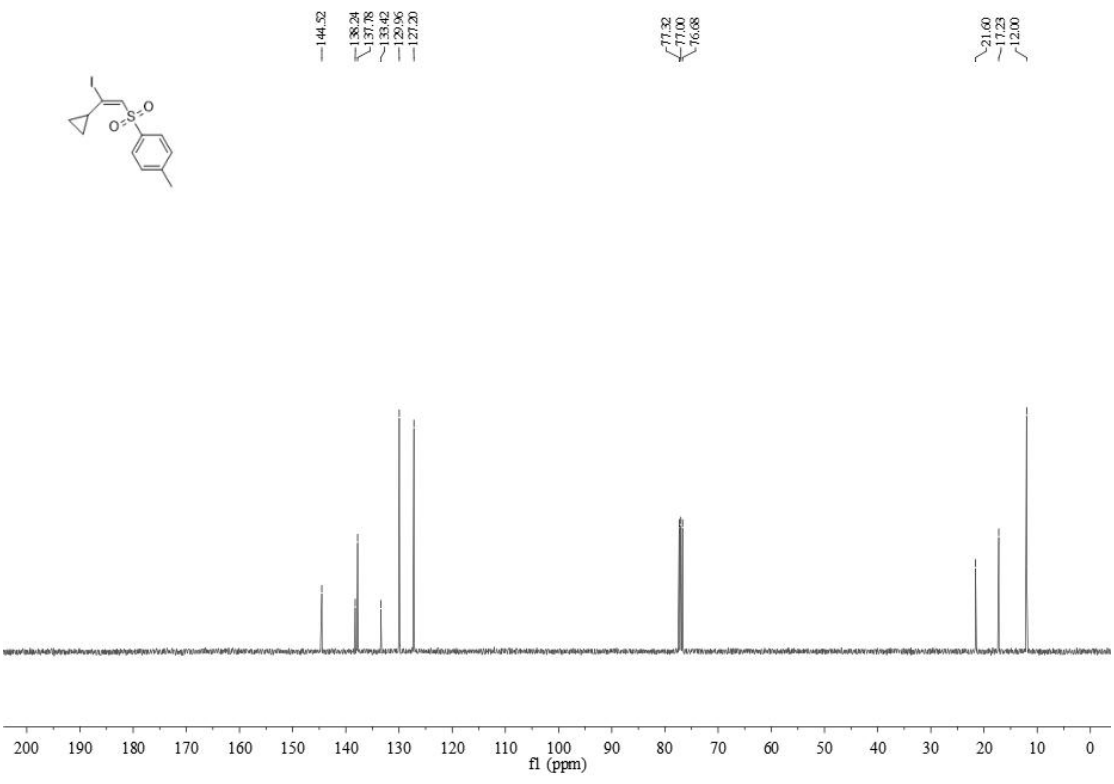
^{1}H-NMR and ^{13}C-NMR of 3al



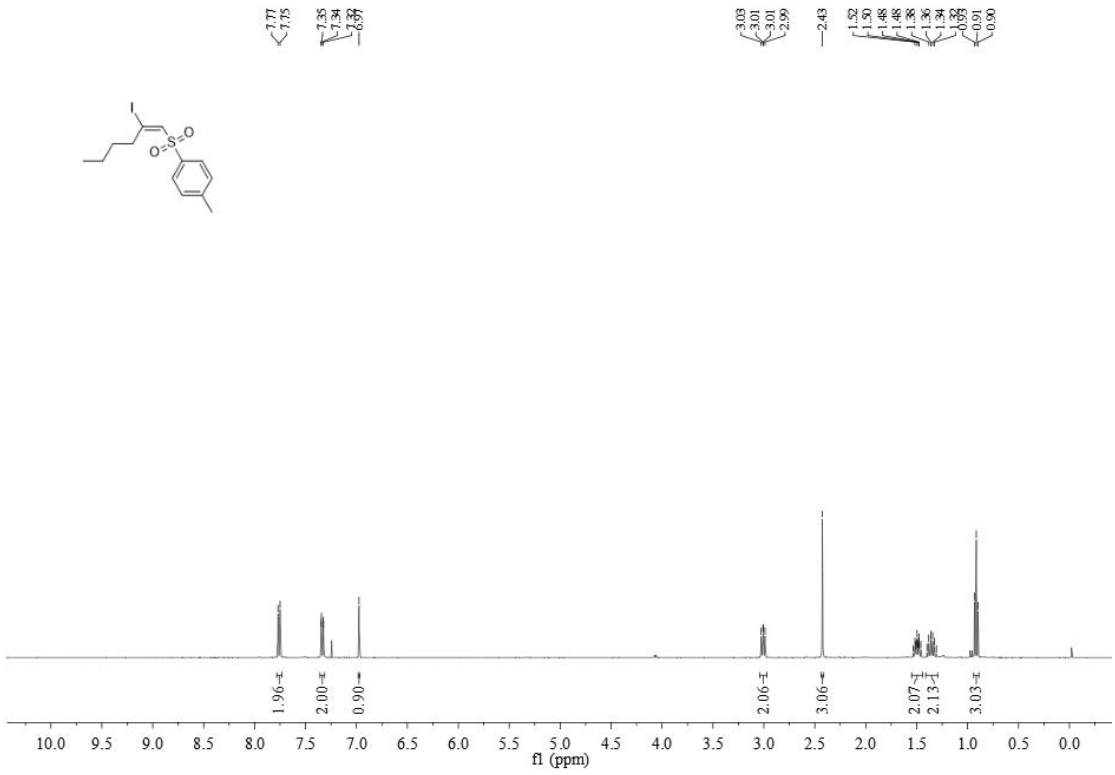


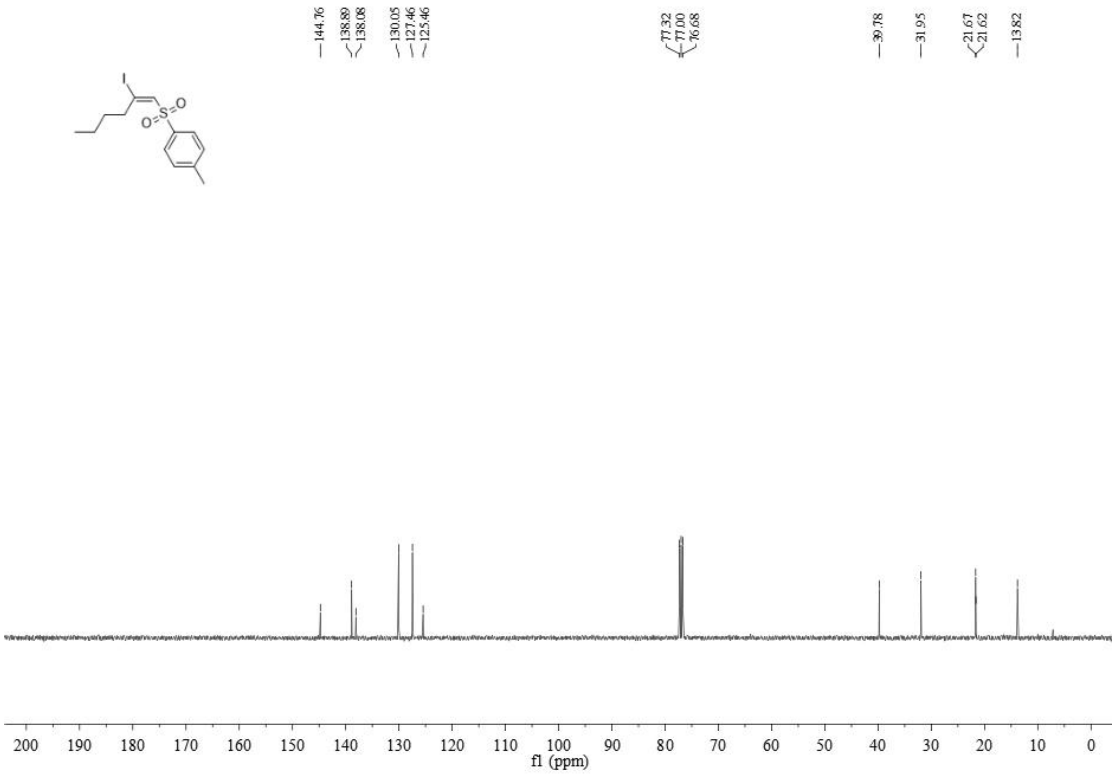
^{1}H-NMR and ^{13}C-NMR of 3am



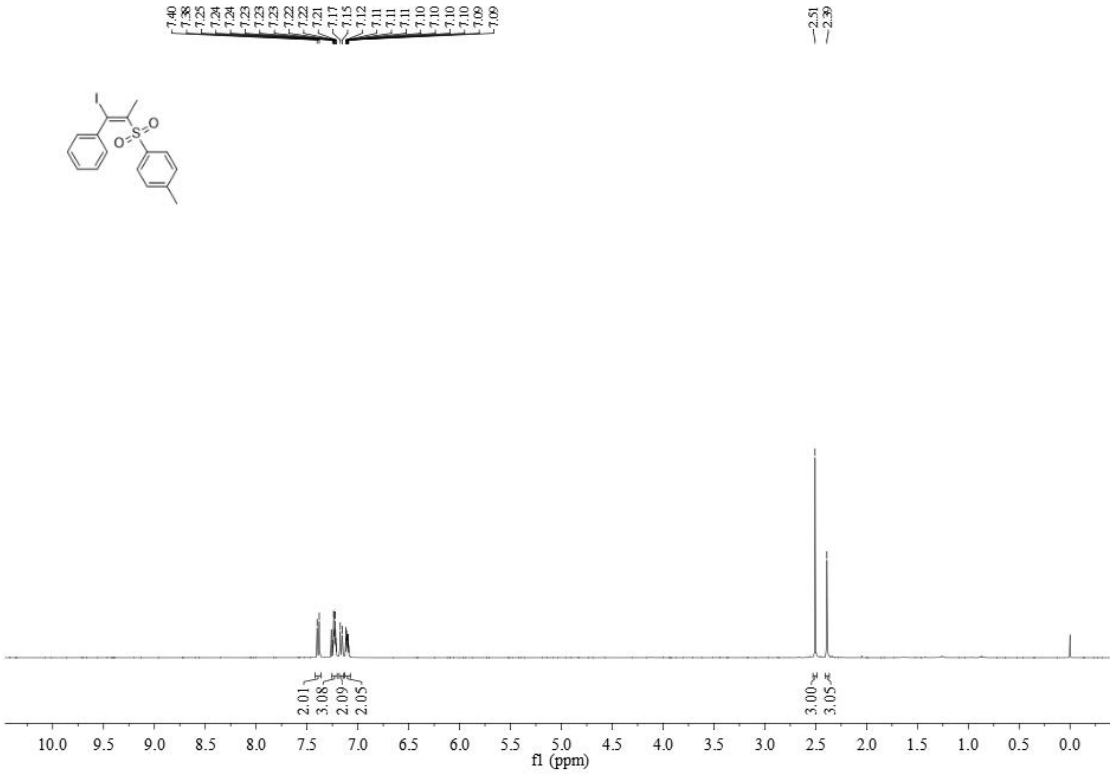


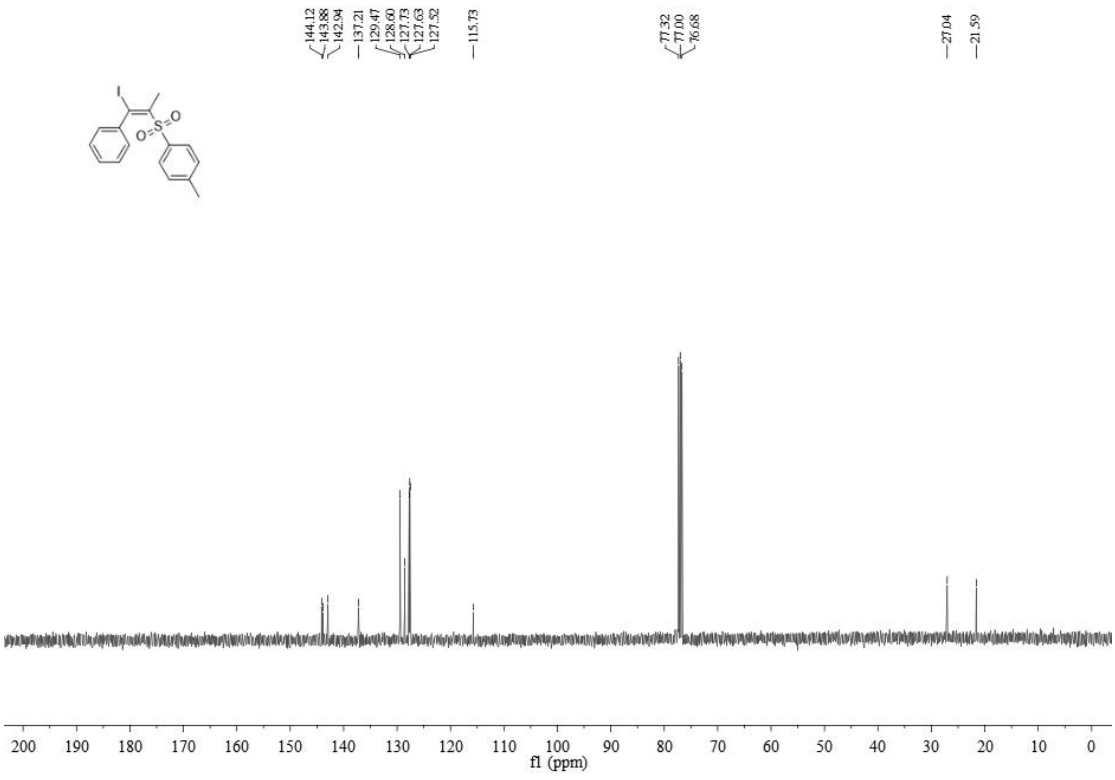
^{1}H-NMR and ^{13}C-NMR of 3an



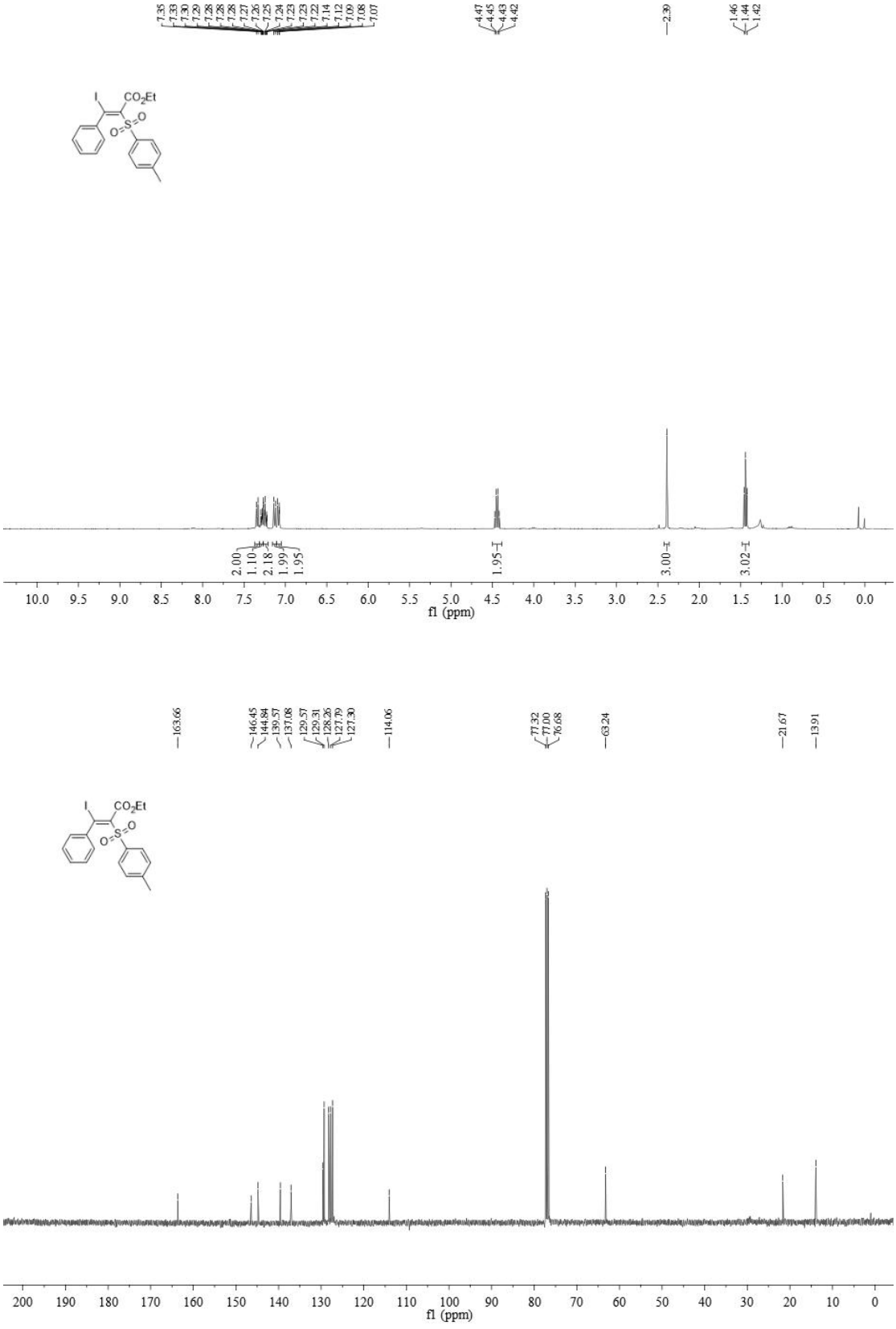


^{1}H-NMR and ^{13}C-NMR of 3ao

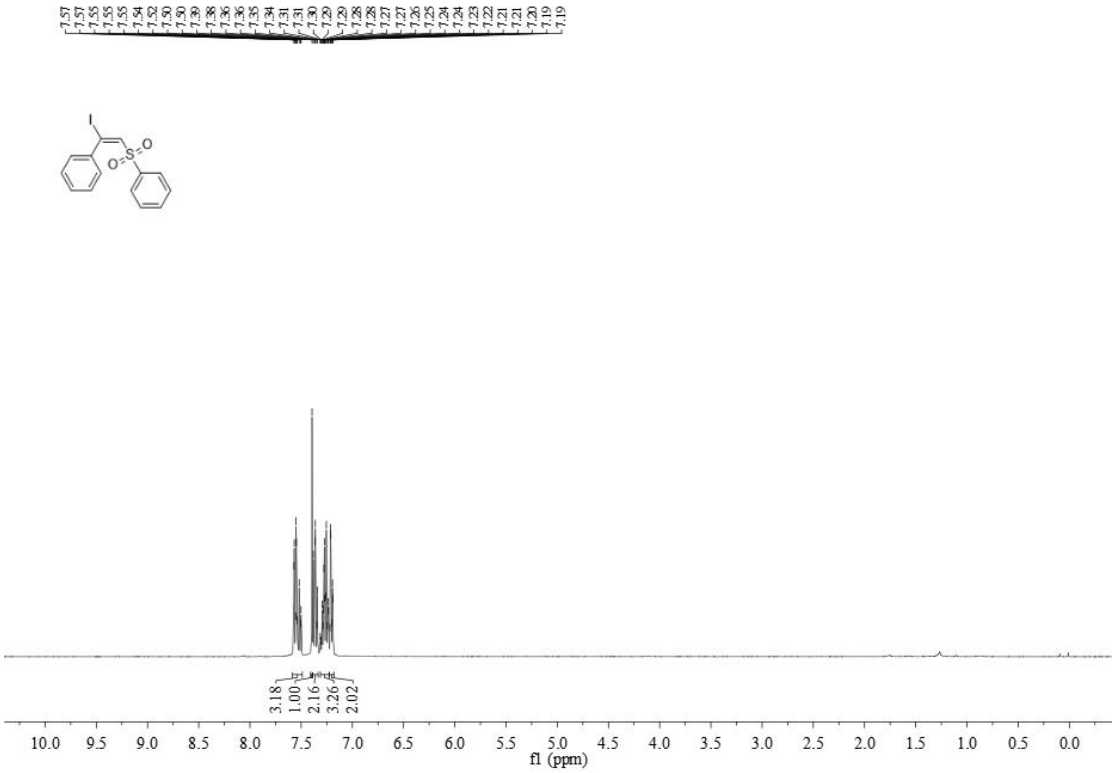


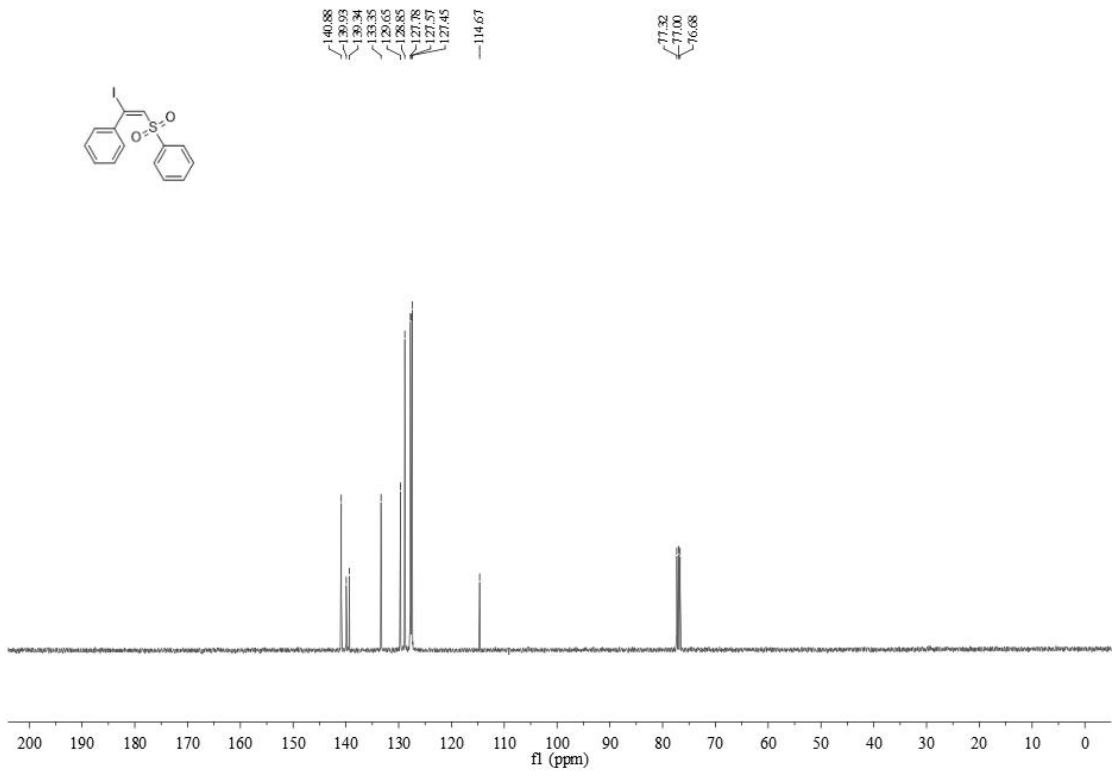


^{1}H-NMR and ^{13}C-NMR of 3ap

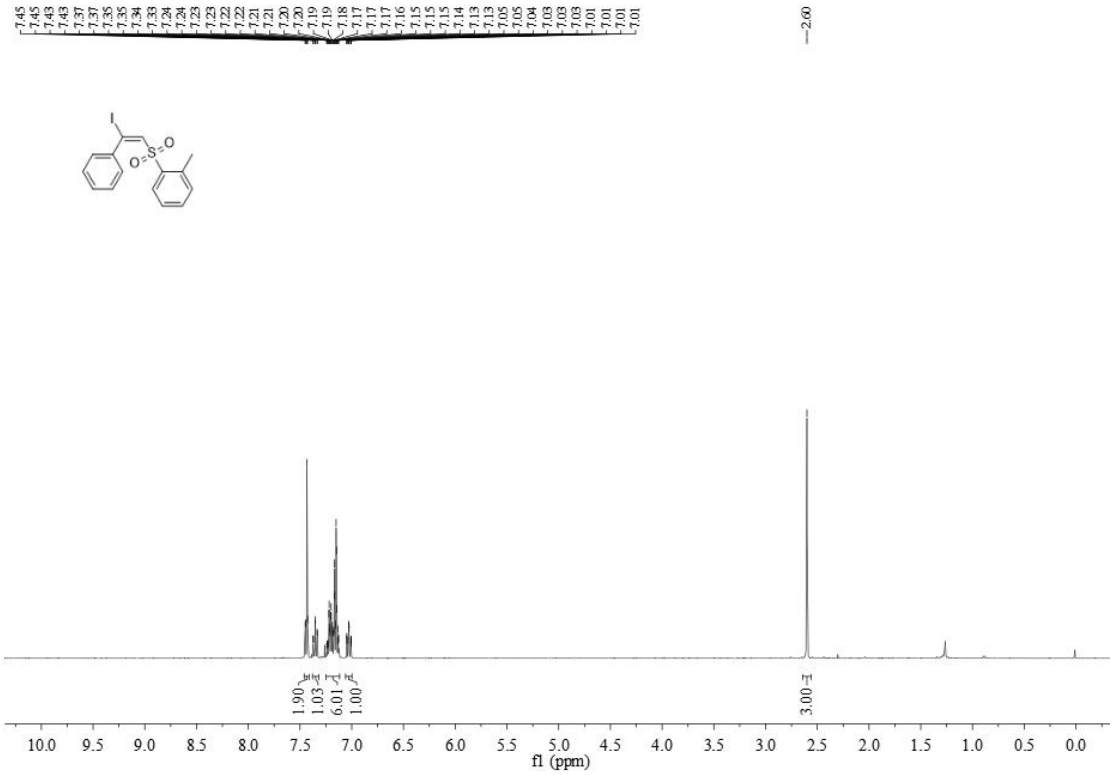


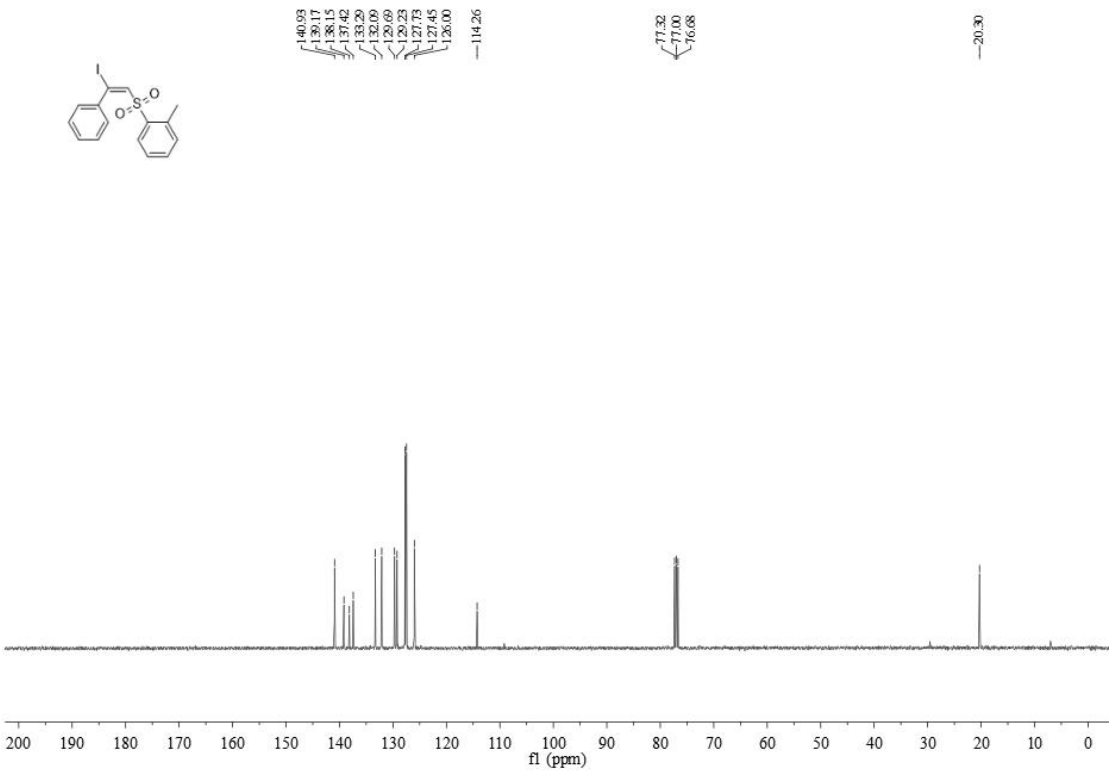
^{1}H-NMR and ^{13}C-NMR of 3ba



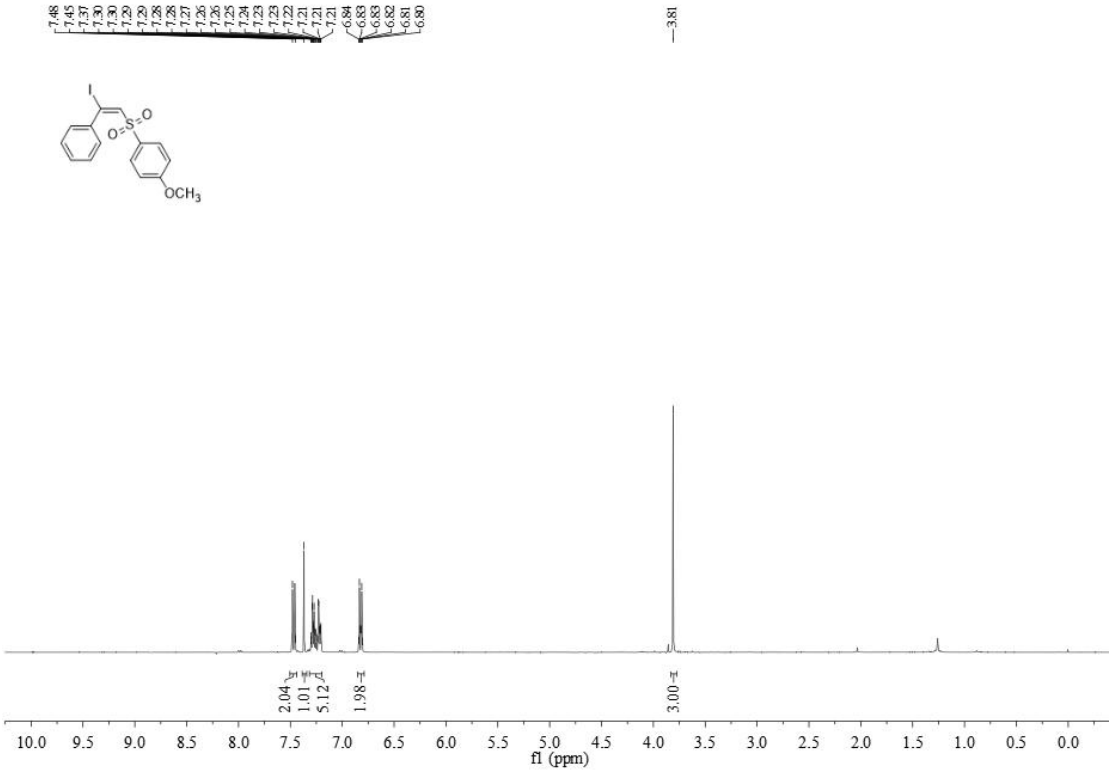


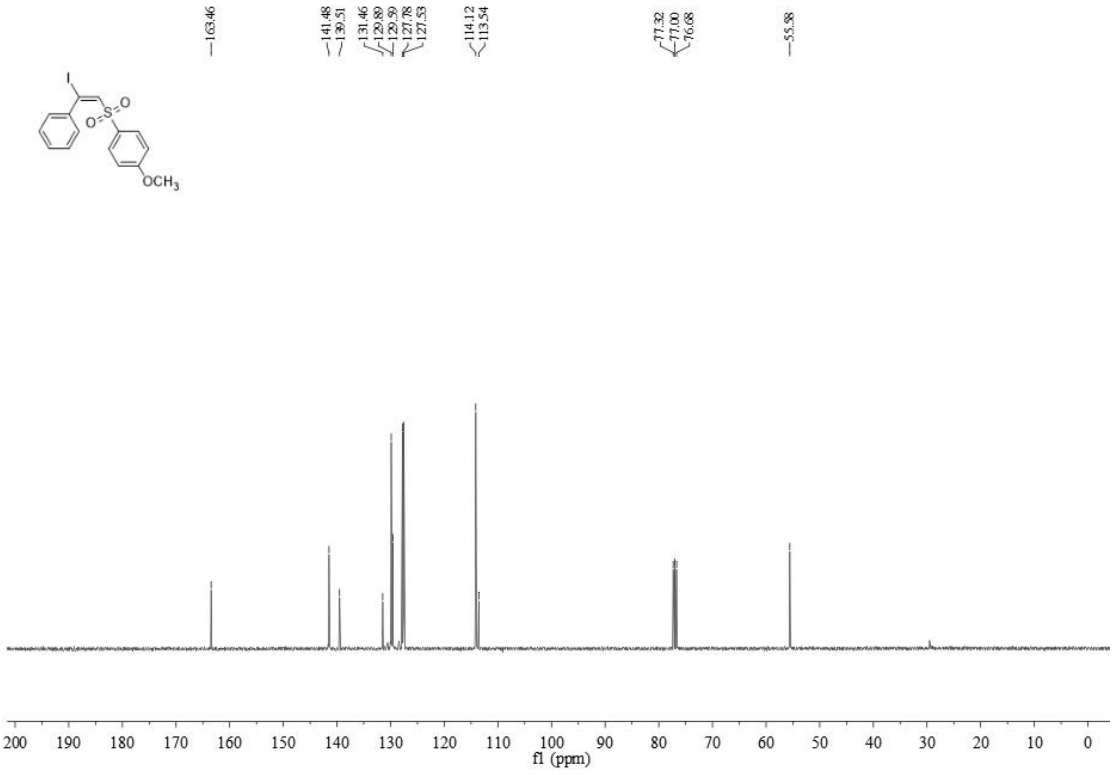
^{1}H-NMR and ^{13}C-NMR of 3ca



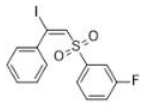


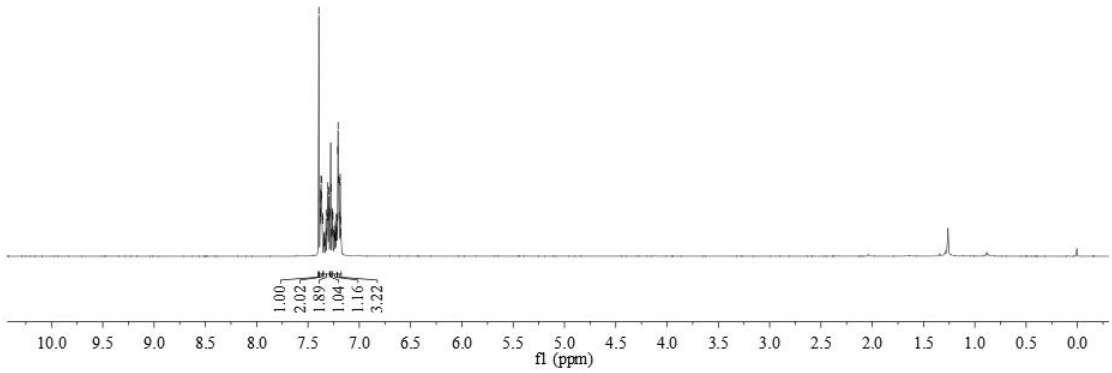
^{1}H-NMR and ^{13}C-NMR of 3da

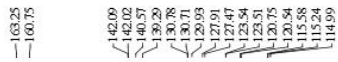


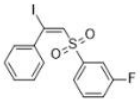


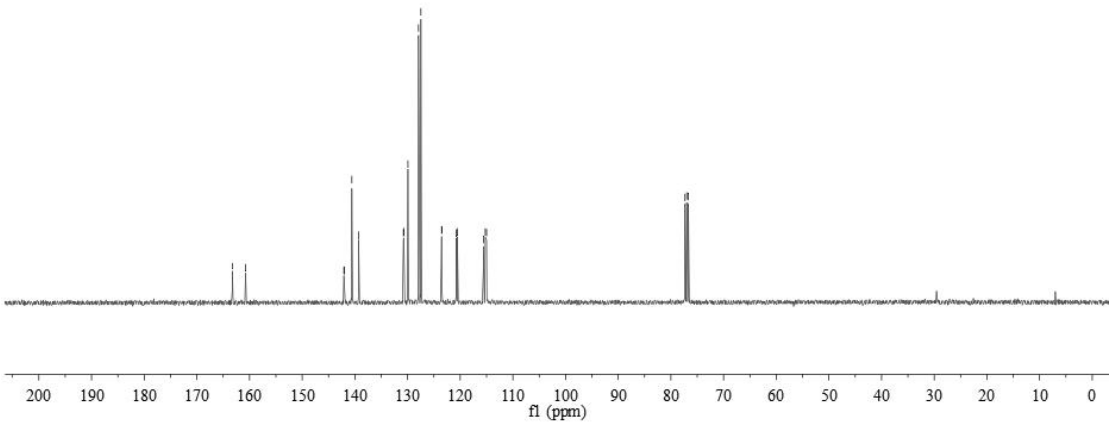
^{1}H-NMR and ^{13}C-NMR of 3ea



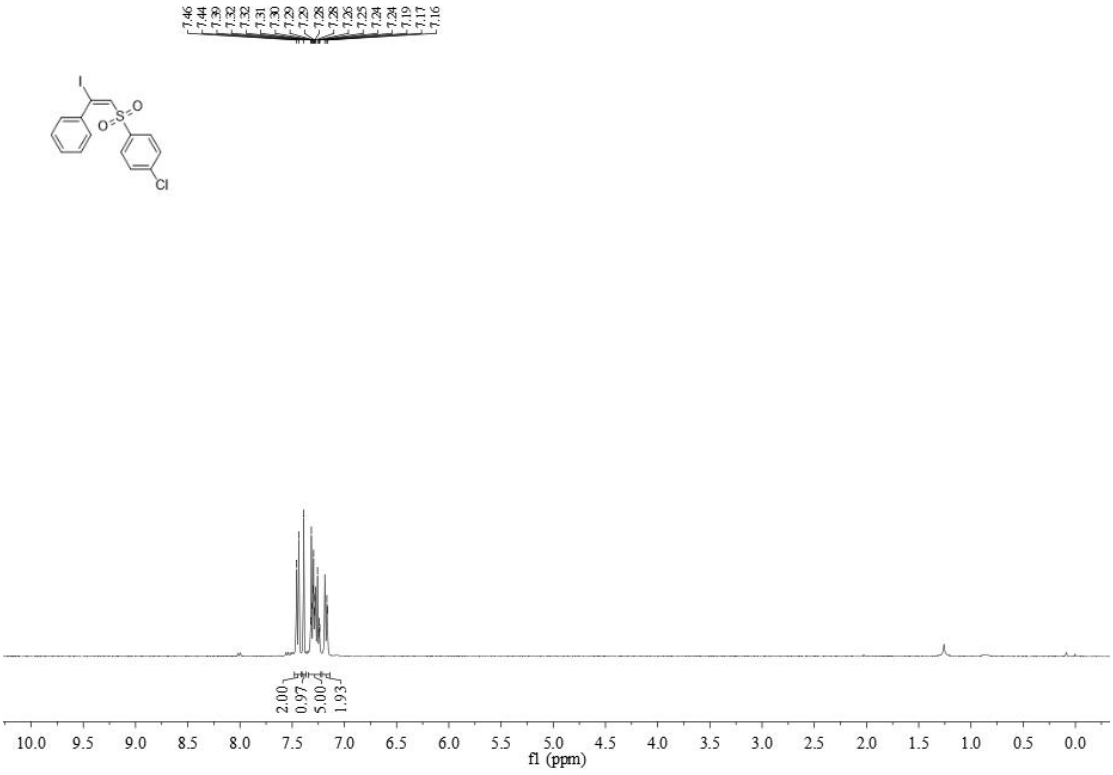


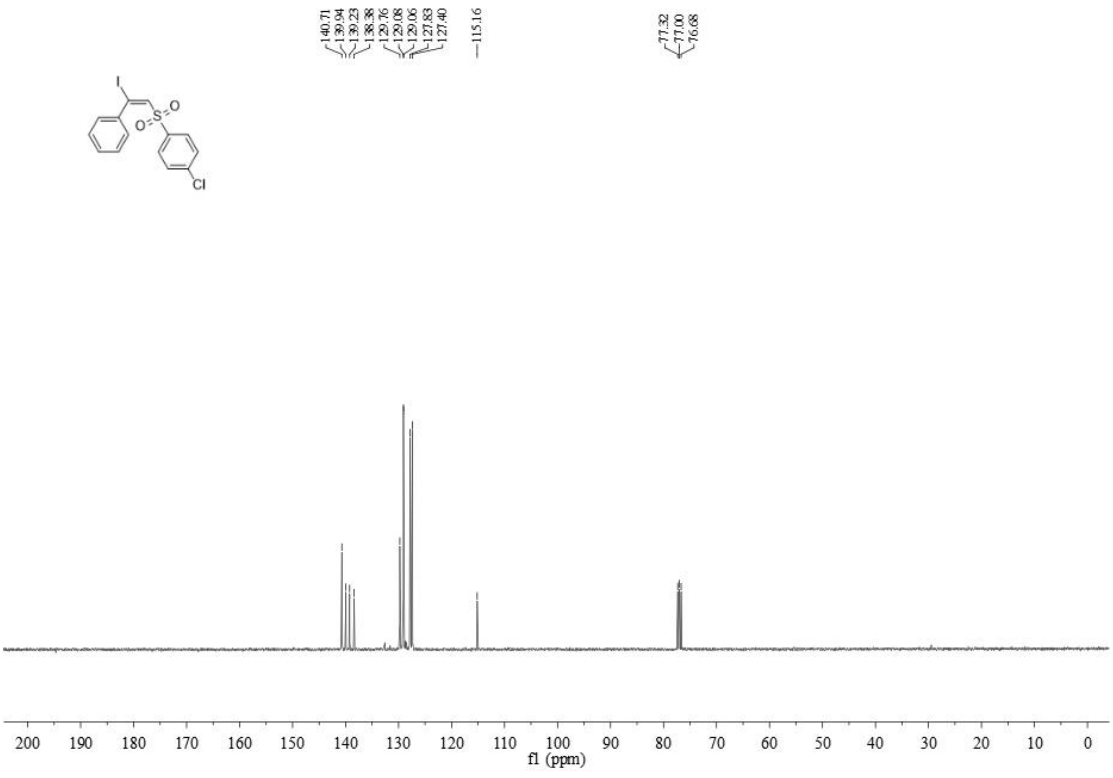




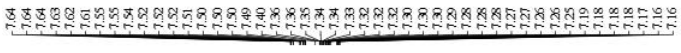


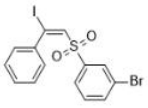
^{1}H-NMR and ^{13}C-NMR of 3fa

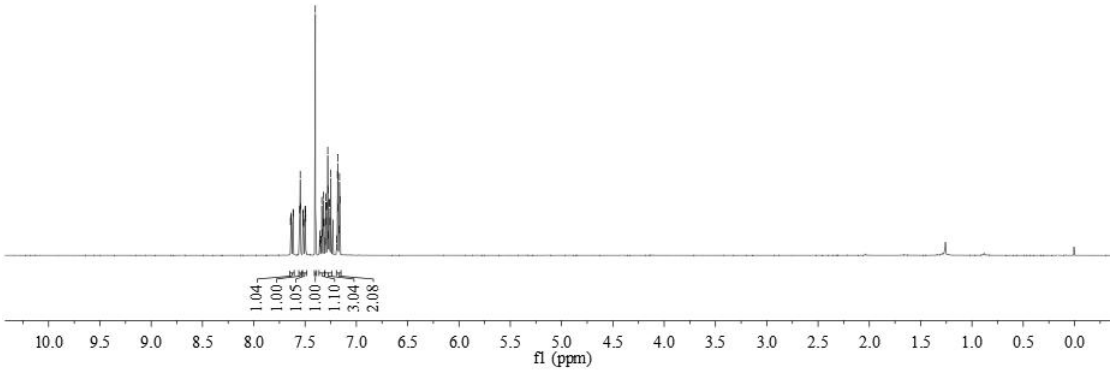


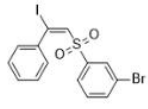


^{1}H-NMR and ^{13}C-NMR of 3ga

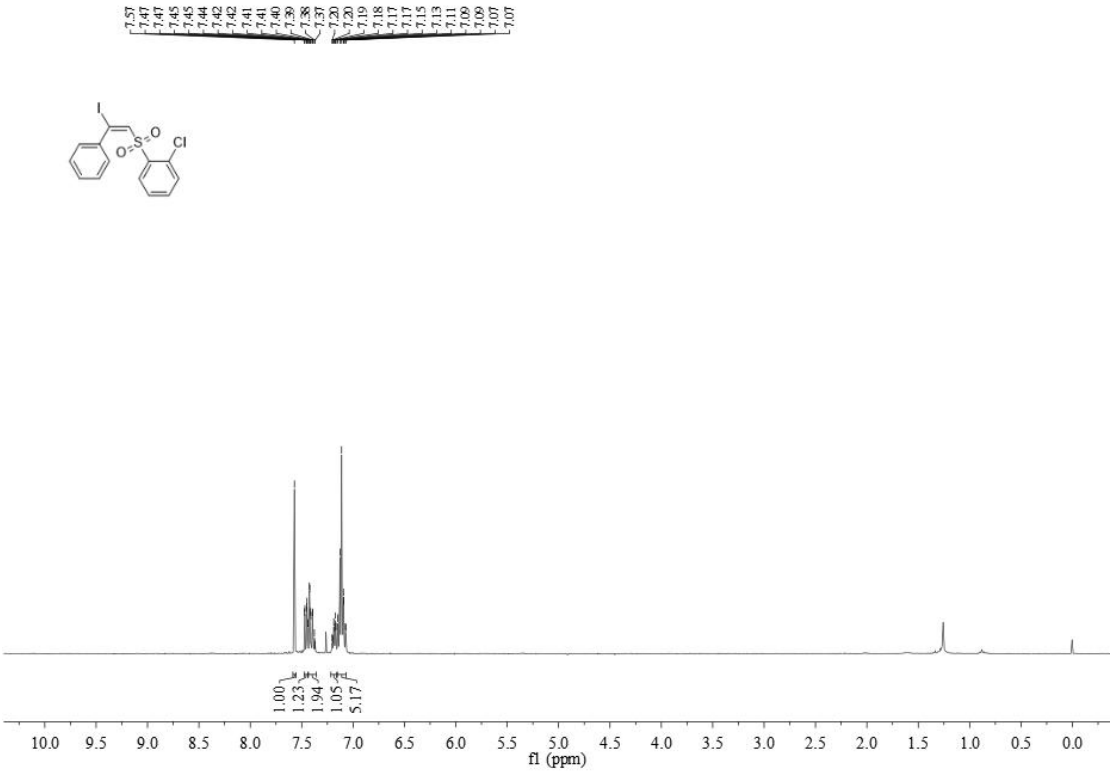


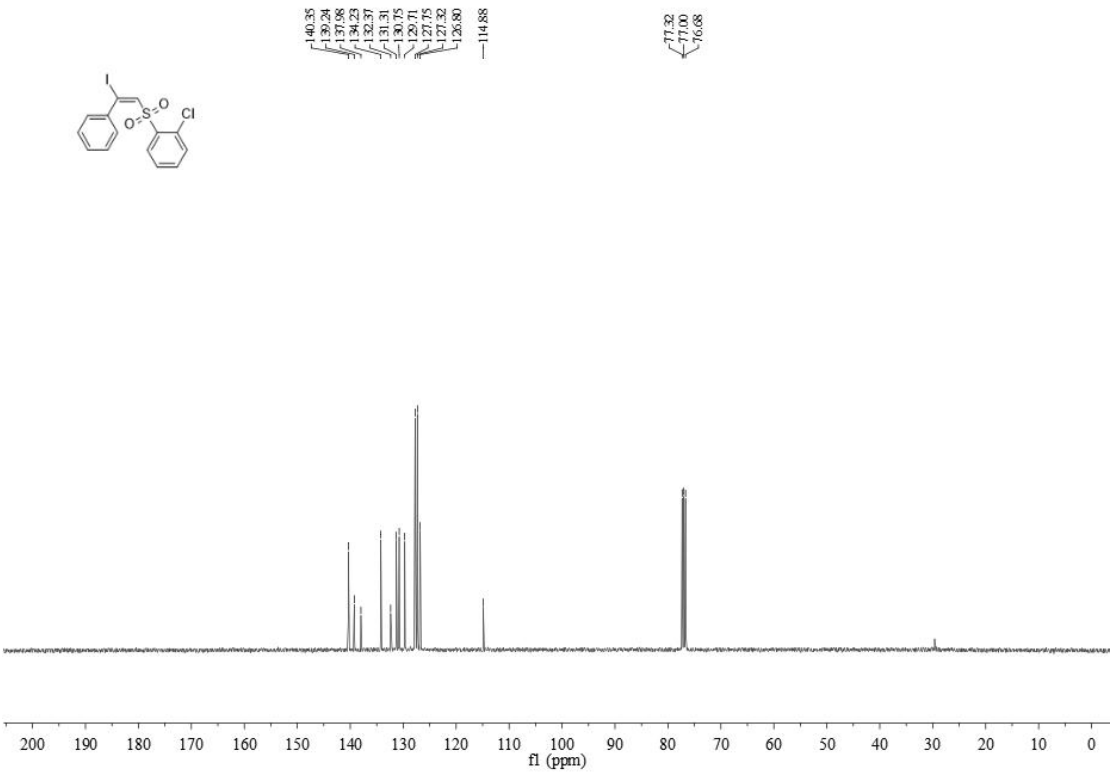




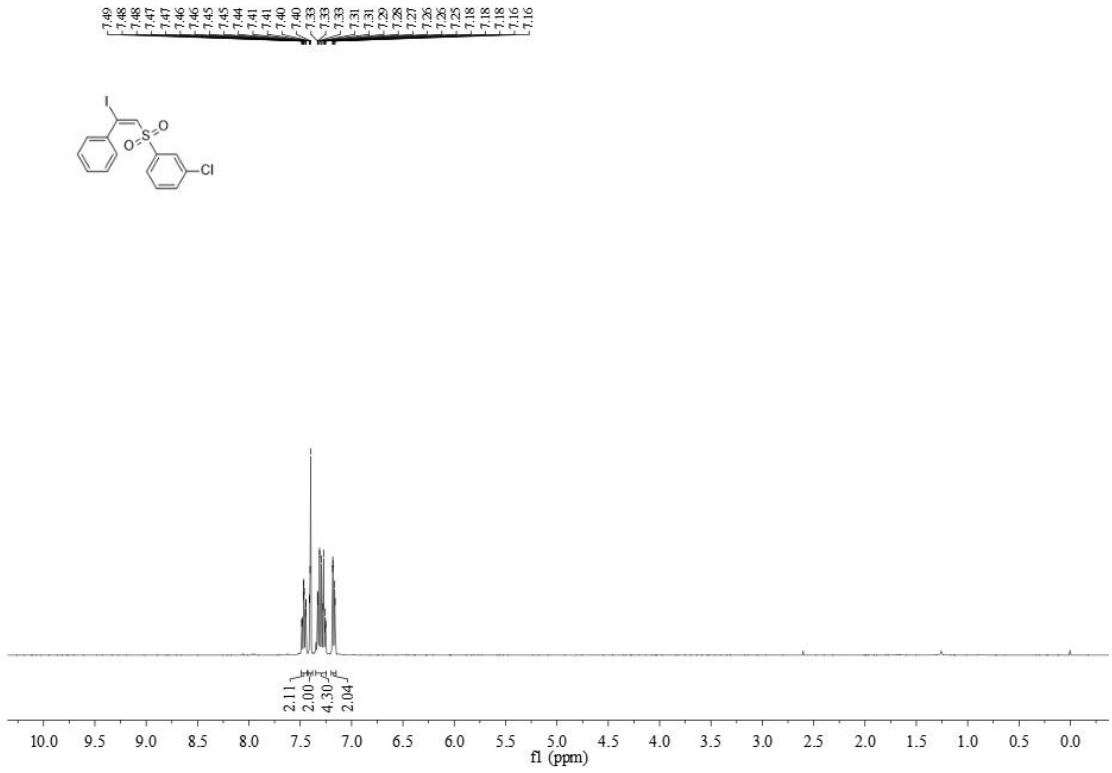


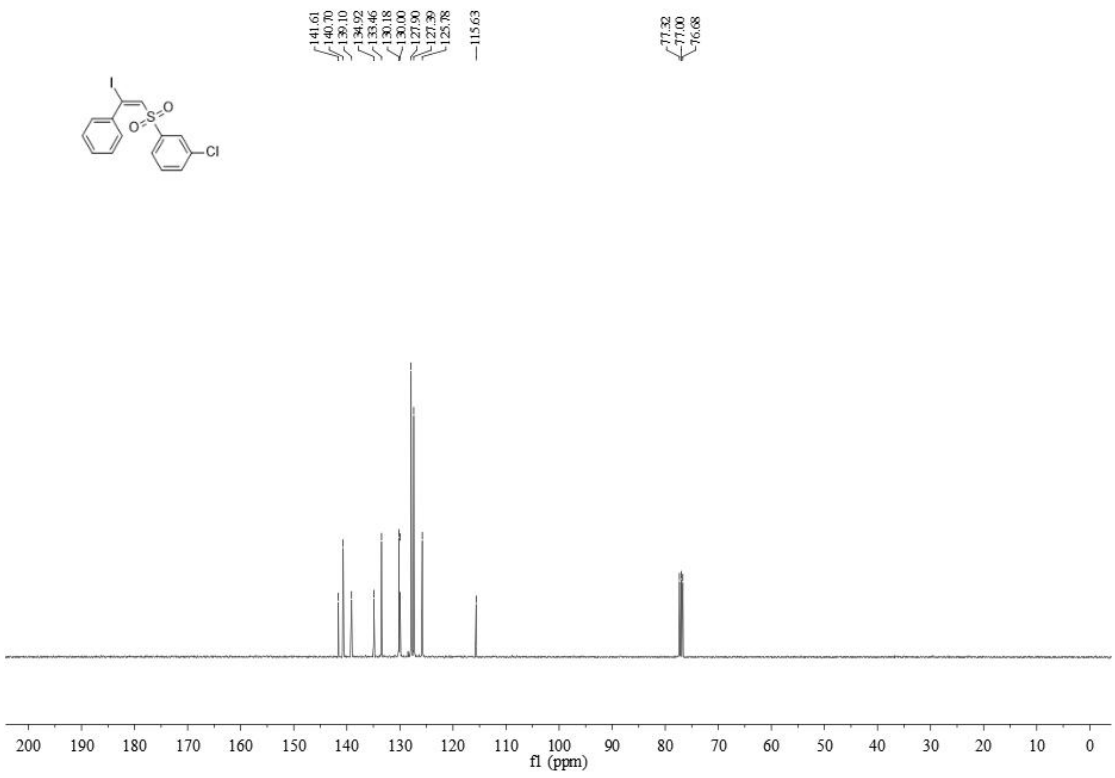
^{1}H-NMR and ^{13}C-NMR of 3ha



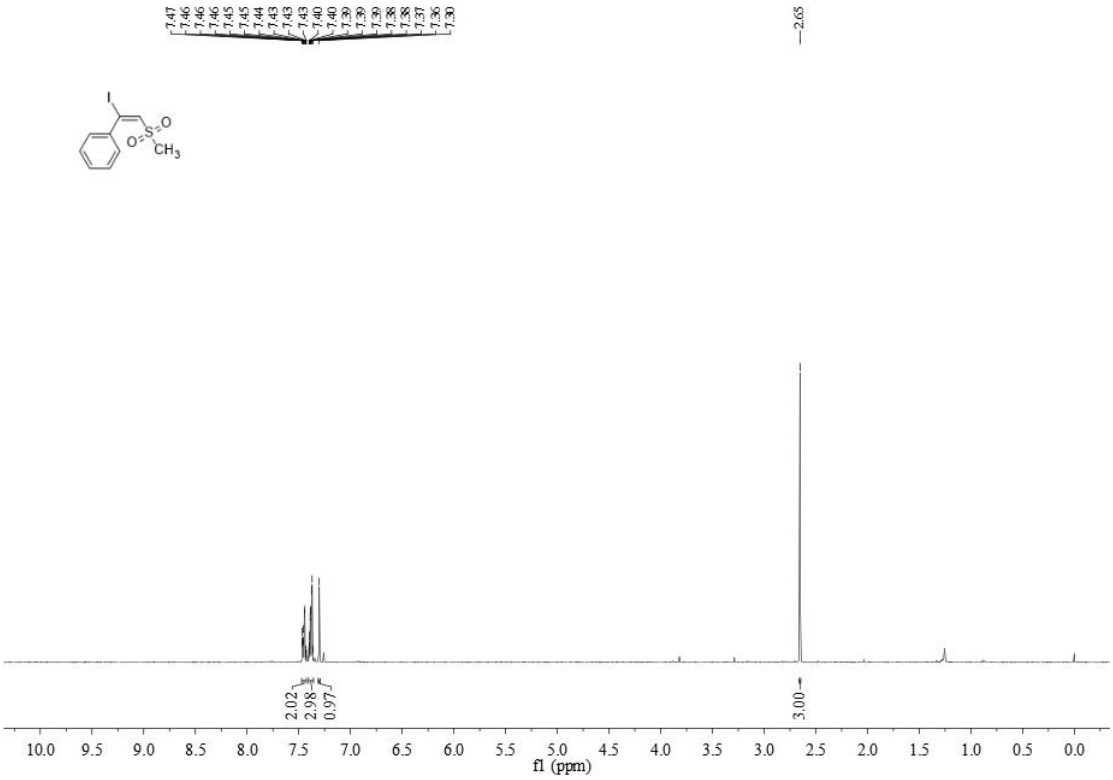


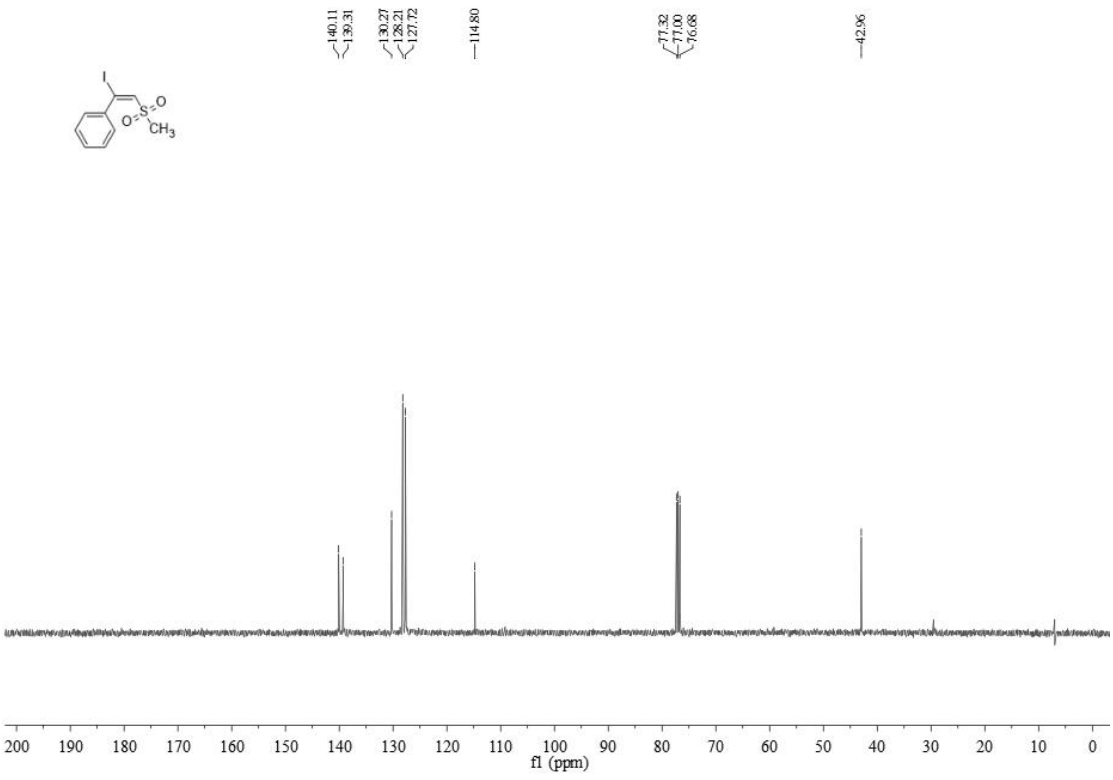
^{1}H-NMR and ^{13}C-NMR of 3ia



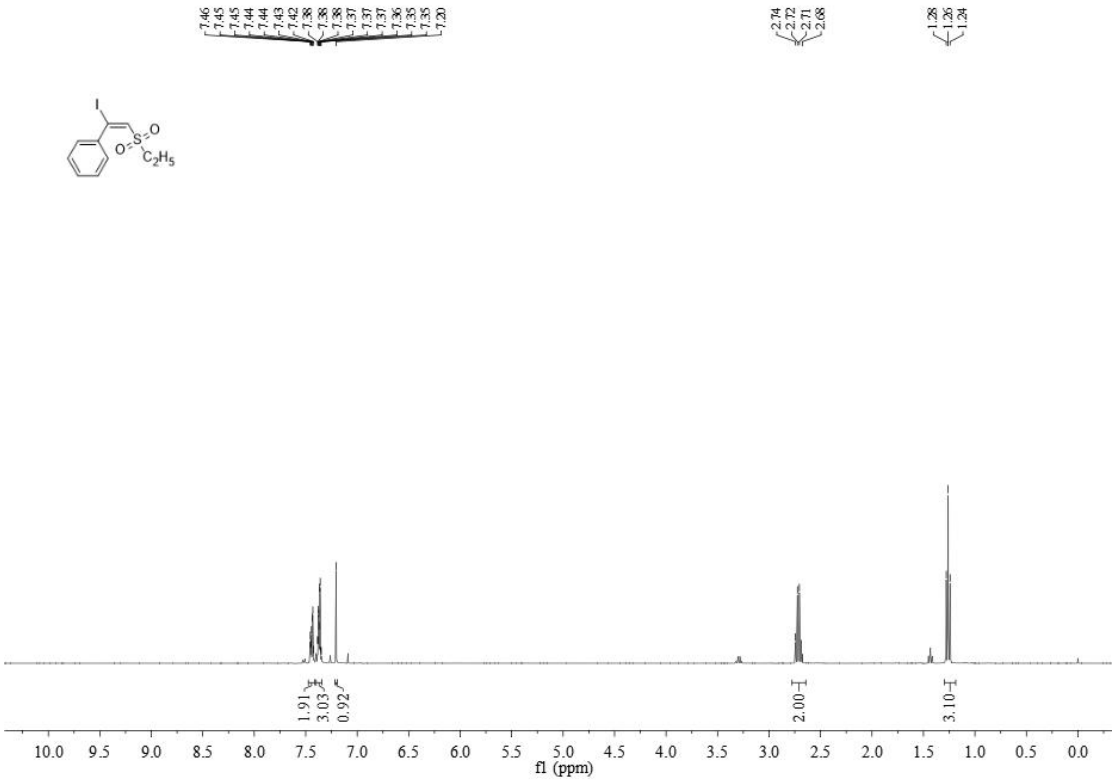


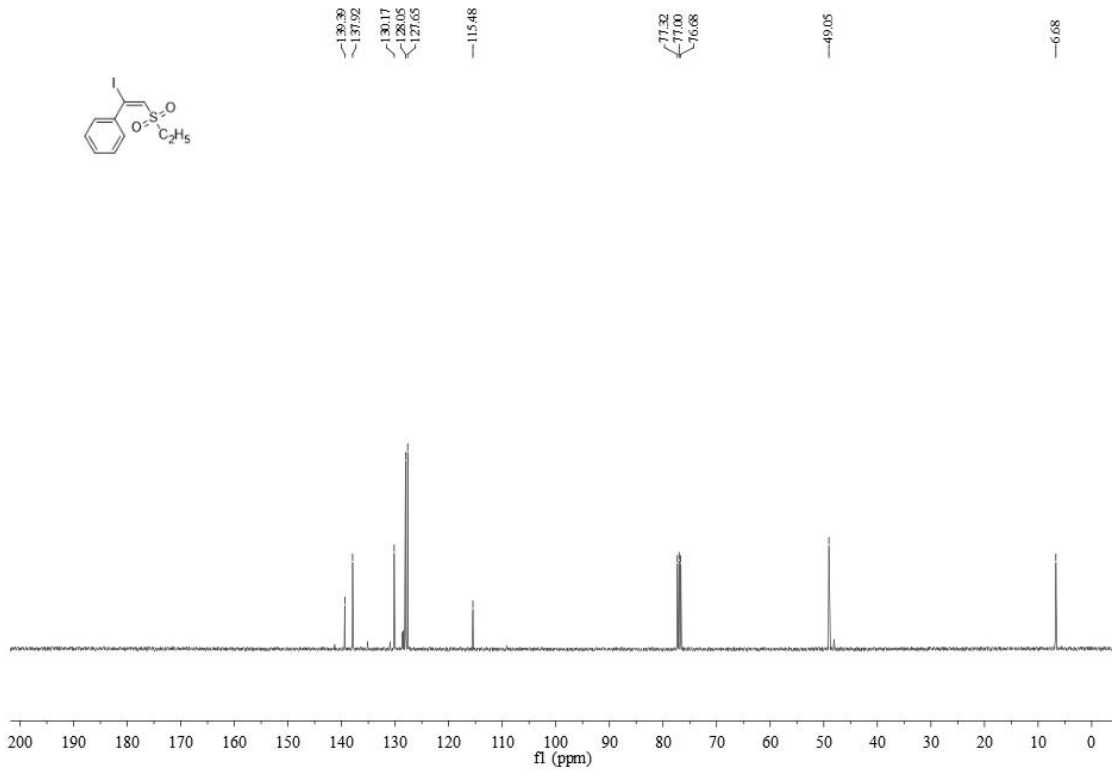
^{1}H-NMR and ^{13}C-NMR of 3ja



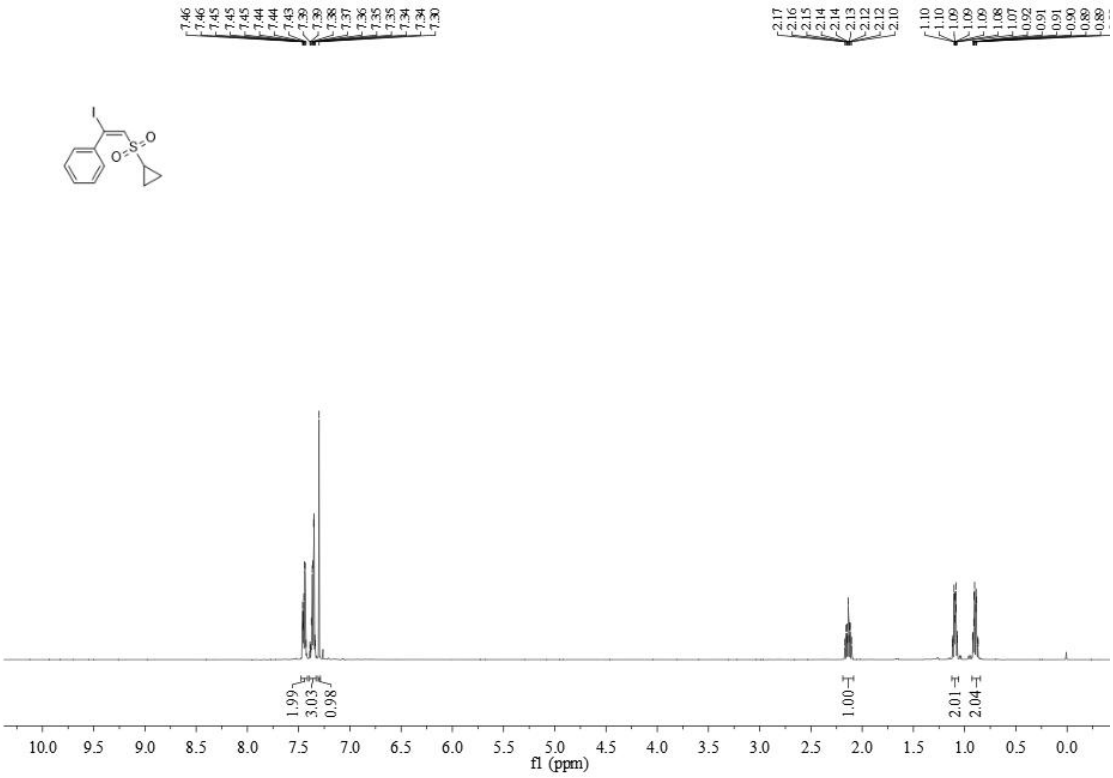


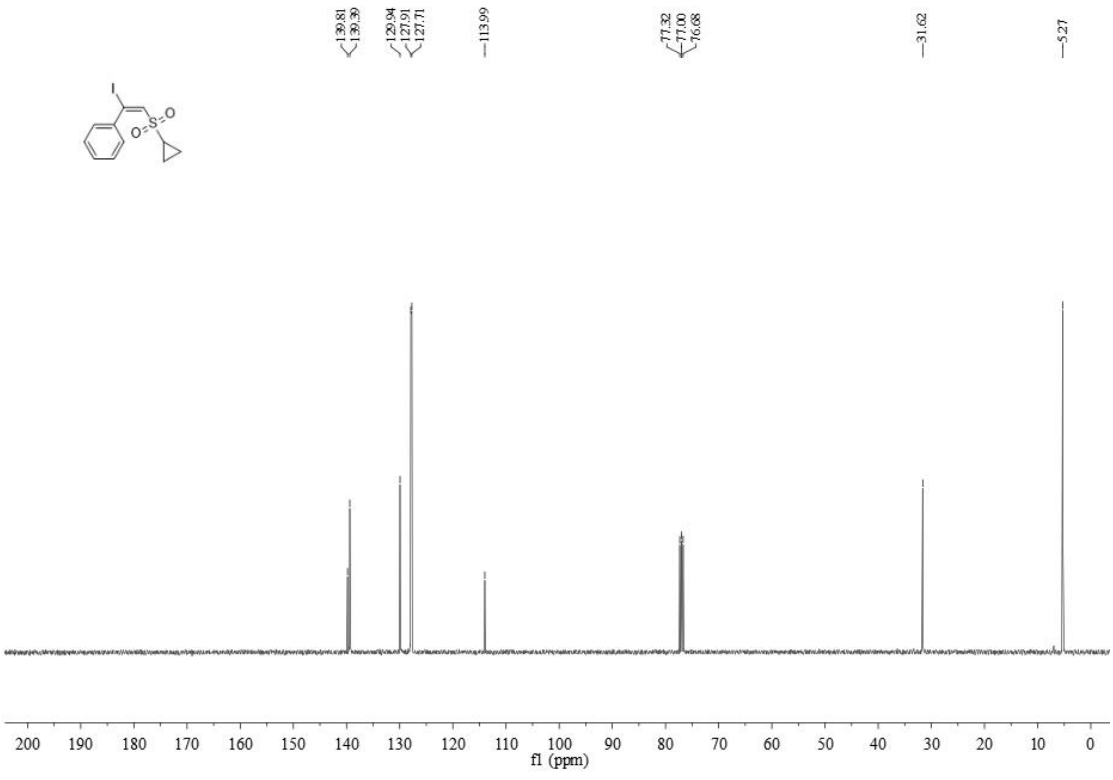
^{1}H-NMR and ^{13}C-NMR of 3ka



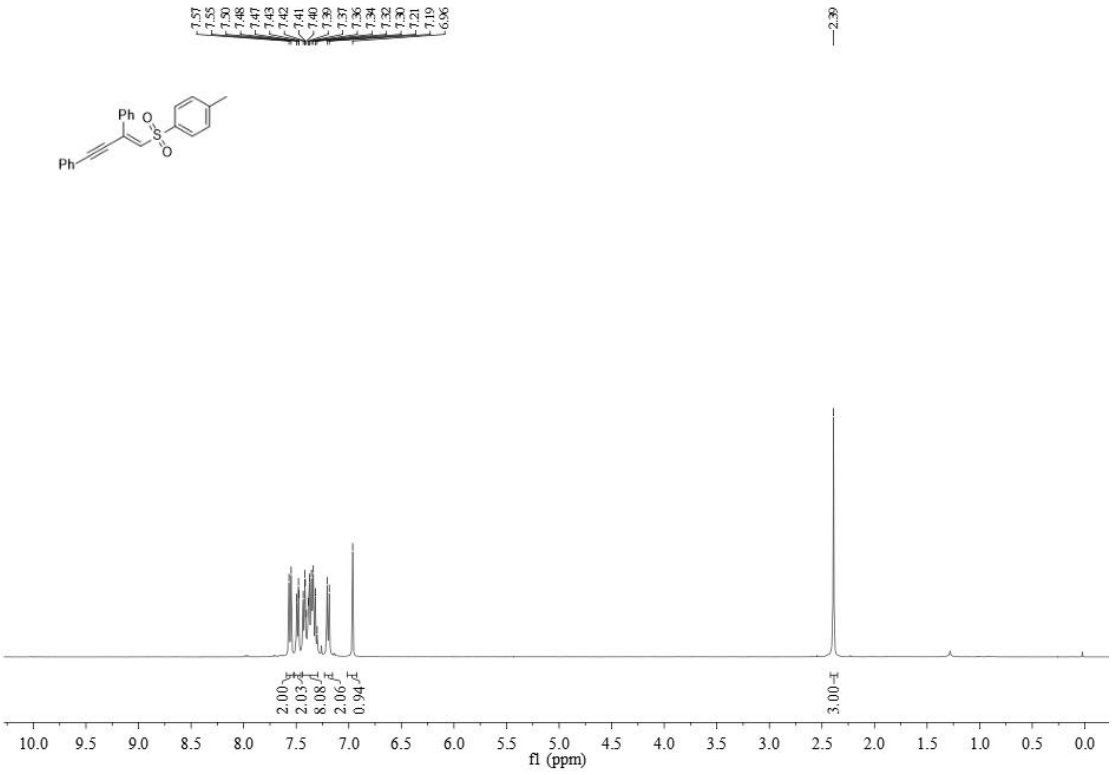


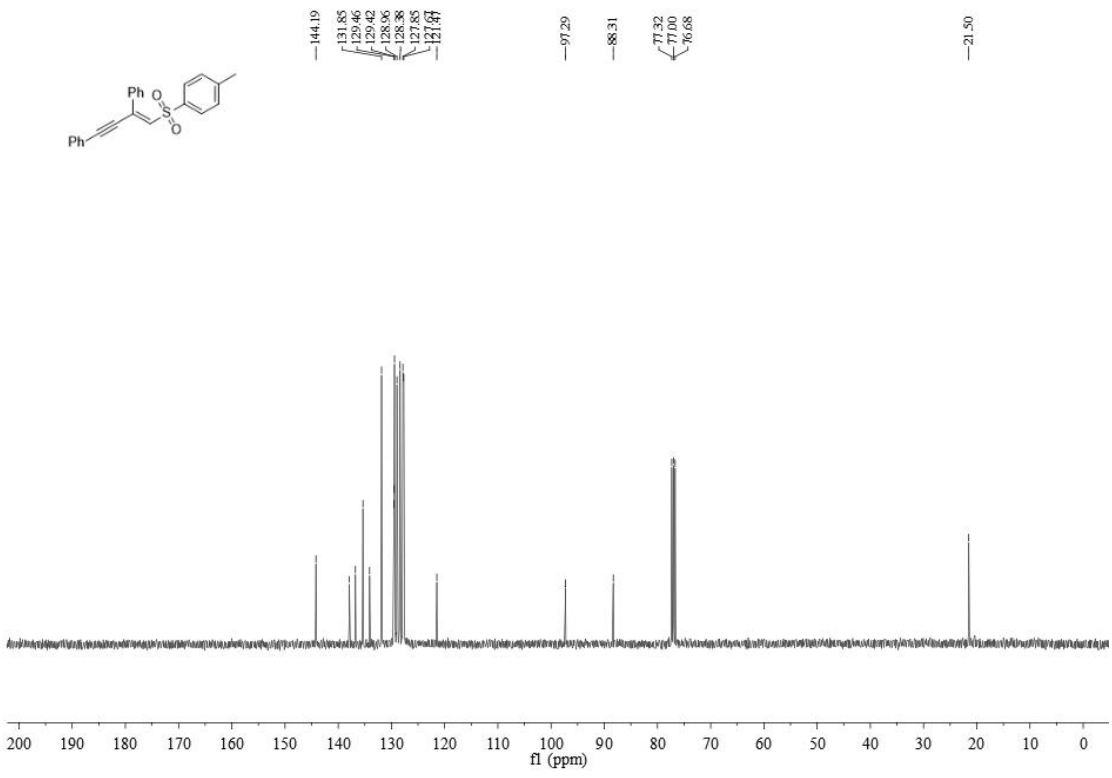
^{1}H-NMR and ^{13}C-NMR of 3la



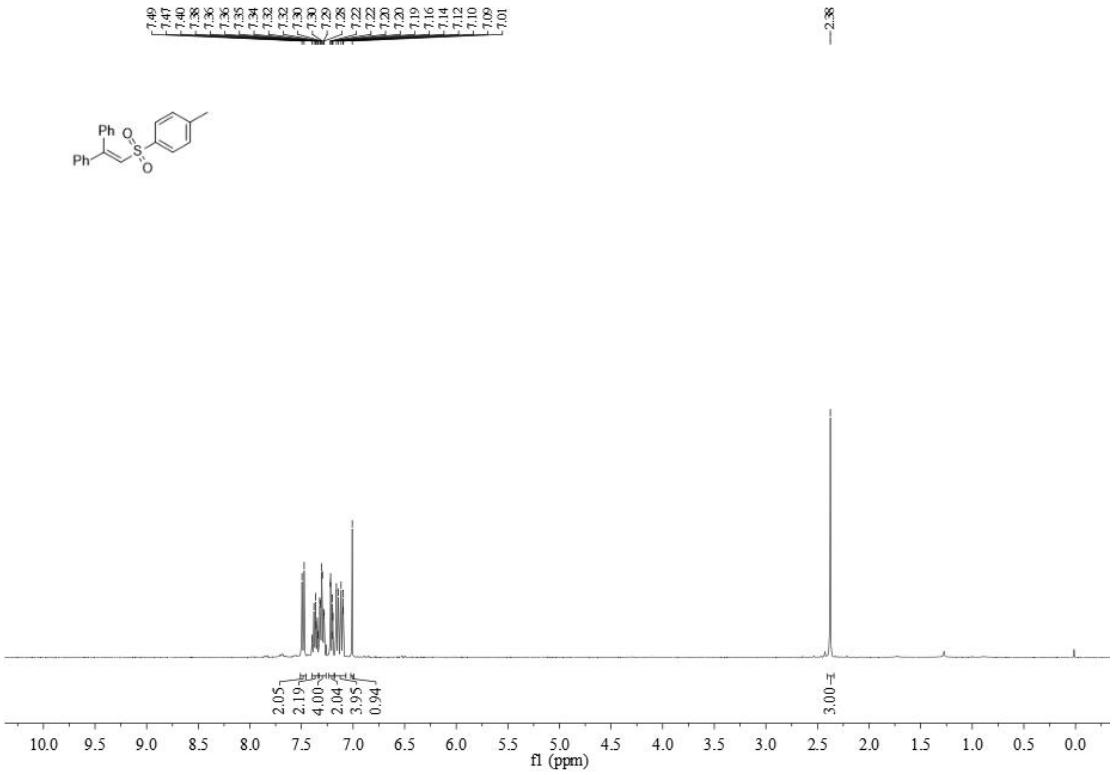


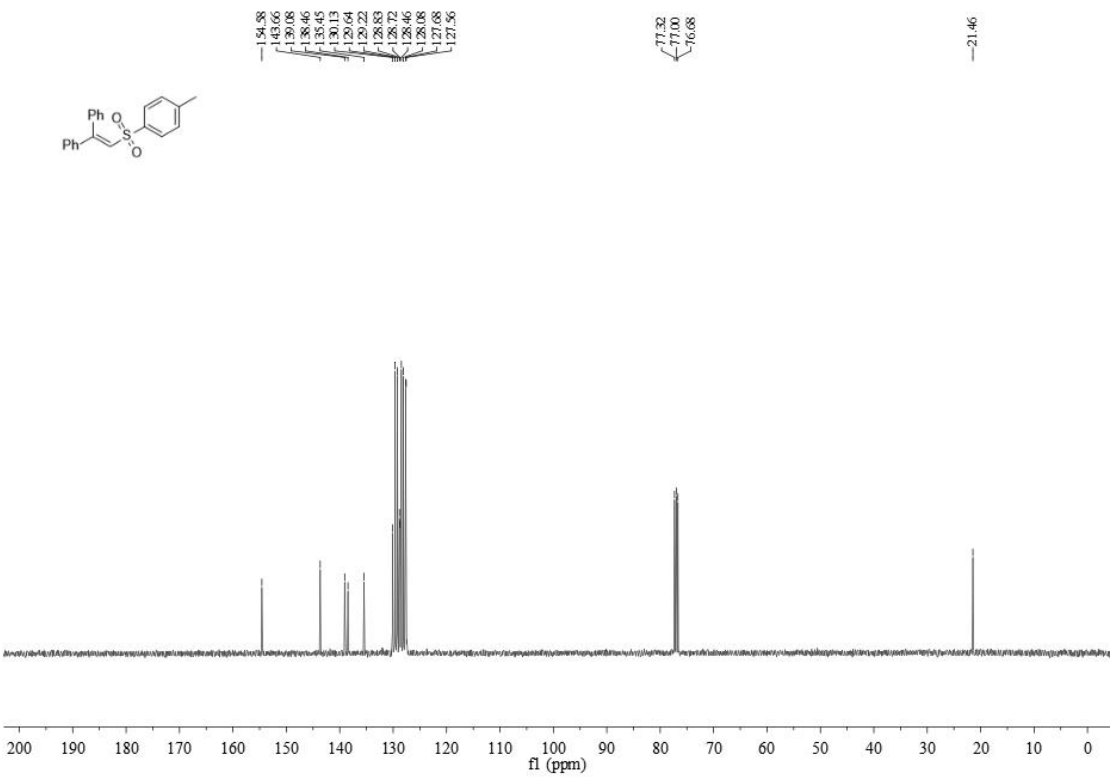
^{1}H-NMR and ^{13}C-NMR of 4





^{1}H-NMR and ^{13}C-NMR of 5





^{1}H-NMR and ^{13}C-NMR of 6