Stereoselective *Z*-halosulfonylation of terminal alkynes using sulfonohydrazides and CuX (X = Cl, Br, I)

Jie-Ping Wan,*[,a] Deqing Hu,[a] Feicheng Bai,[a] Li Wei,[a] and Yunyun Liu*[,a]

[†]*College of Chemistry and Chemical Engineering, Jiangxi Normal University, 330022 China.*

Email: wanjieping@jxnu.edu.cn; chemliuyunyun@jxnu.edu.cn

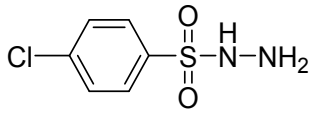
Contents

General experimental information

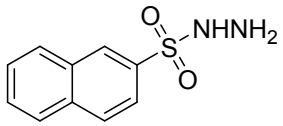
All experiments were carried out under air atmosphere. Except the sulfonohydrazides whose ^{1}H NMR data and spectra are shown below are synthesized following literature produre,[1] all other chemicals and solvents used in our experiments were obtained from commercial sources and directly used without further treatment. The ^{1}H and ^{13}C NMR were recorded in 400 MHz apparatus in $CDCl_3$ or DMSO-d_6, and the frequencies for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm with TMS as internal standard. Melting points were tested in an X-4A instrument without correcting temperature and the HRMS were obtained under ESI model with TOF analyzer.

Preparation and characterization of sulfonohydrazides

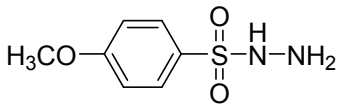
These sulfonohydrazides were prepared following literature process and their structures were confirmed by comparing the ^{1}H NMR with literature data.[1]



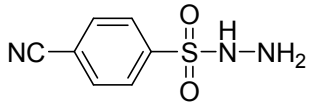
4-Chlorobenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 7.6 Hz, 2 H), 5.90 (brs, 1 H), 3.46 (brs, 2 H).



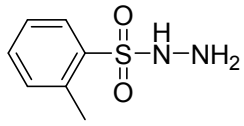
Naphthalene-2-sulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 8.51 (s, 1 H), 7.99 (t, J = 6.4 Hz, 2 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.70-7.62 (m, 2 H), 5.83 (brs, 1 H), 3.43 (brs, 2 H).



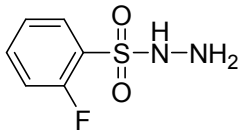
4-Methoxybenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, J = 8.8 Hz, 2 H), 7.02 (d, J = 8.8 Hz, 2 H), 5.90 (brs, 1H), 3.88 (s, 3 H), 3.52 (brs, 2 H).



4-Cyanobenzenesulfonohydrazide. ^{1}H NMR (400 MHz, DMSO-d_6): 8.68 (s, 1 H), 8.09 (d, J = 8.4 Hz, 2 H), 7.97 (d, J = 8.4 Hz, 2 H), 4.29 (brs, 2 H).

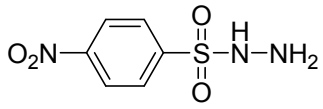


2-Methylbenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (d, J = 7.6 Hz, 1 H), 7.50 (t, J = 6.8 Hz, 1 H), 7.32 (t, J = 7.2 Hz, 2 H), 6.33 (brs, 1 H), 3.48 (brs, 2 H), 2.63 (s, 3 H).



2-Fluorobenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (t, J = 6.4 Hz, 1 H), 7.68-

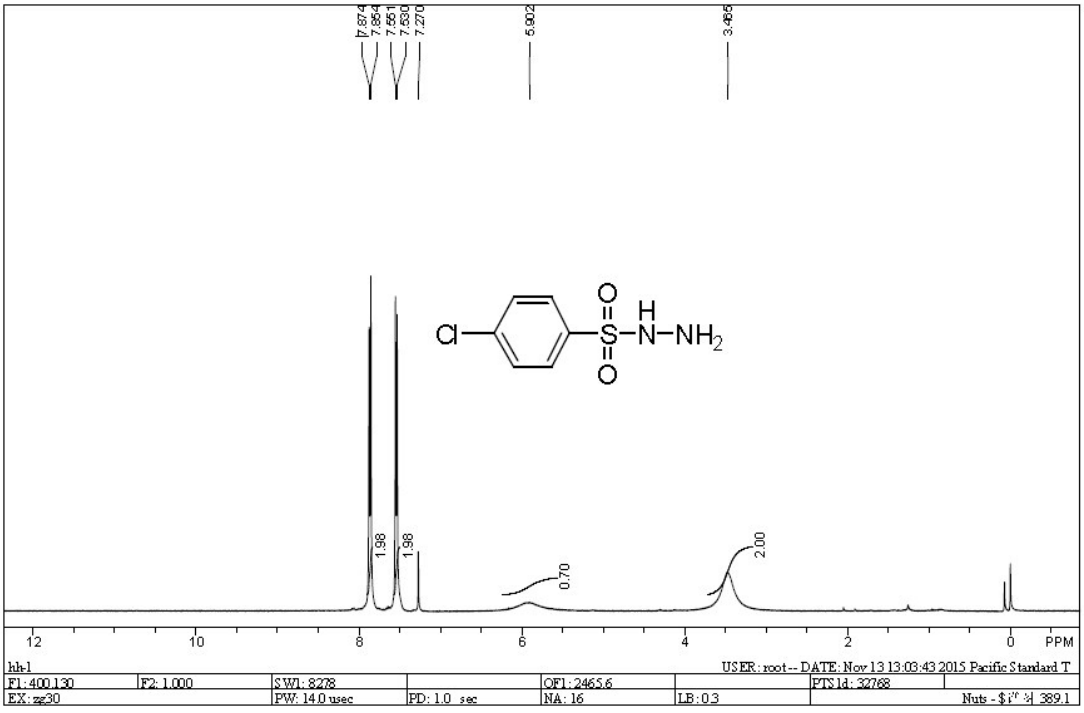
7.63 (m, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 9.2 Hz, 1 H), 6.34 (brs, 1 H), 3.73 (brs, 2 H).



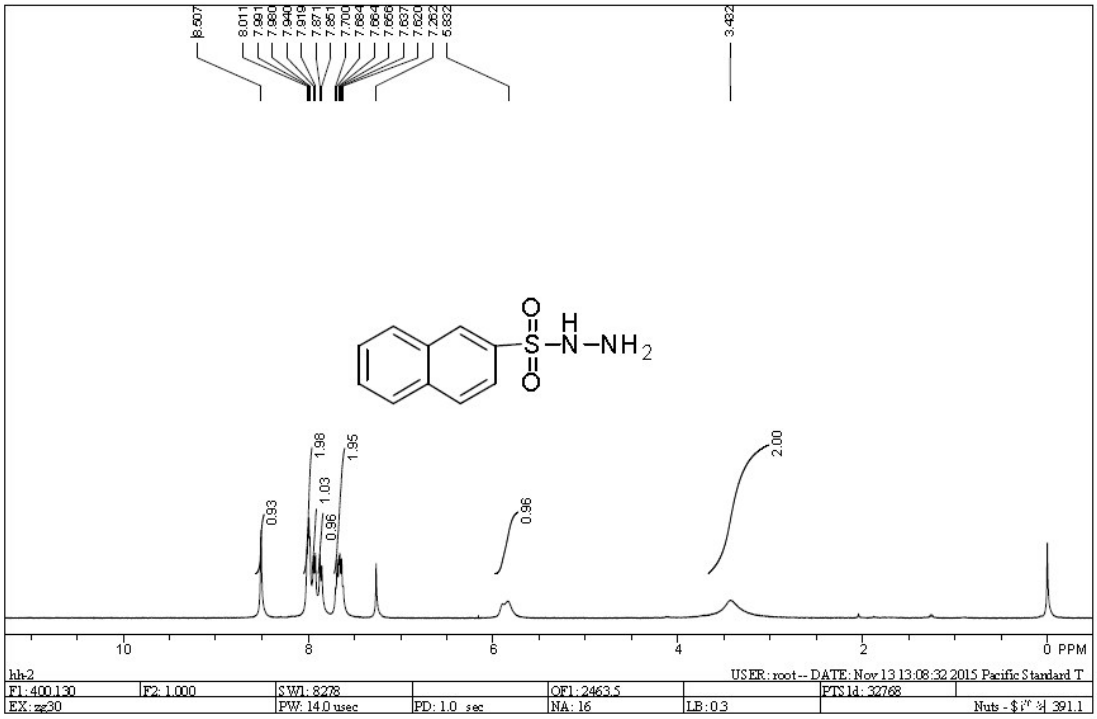
4-Nitrobenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$): 8.41 (d, *J* = 8.4 Hz, 2 H), 8.14 (d, *J* = 8.0 Hz, 2 H), 5.84 (brs, 1H), 2.86 (brs, 2 H).

^{1}H NMR spectra of sulfonohydrazides

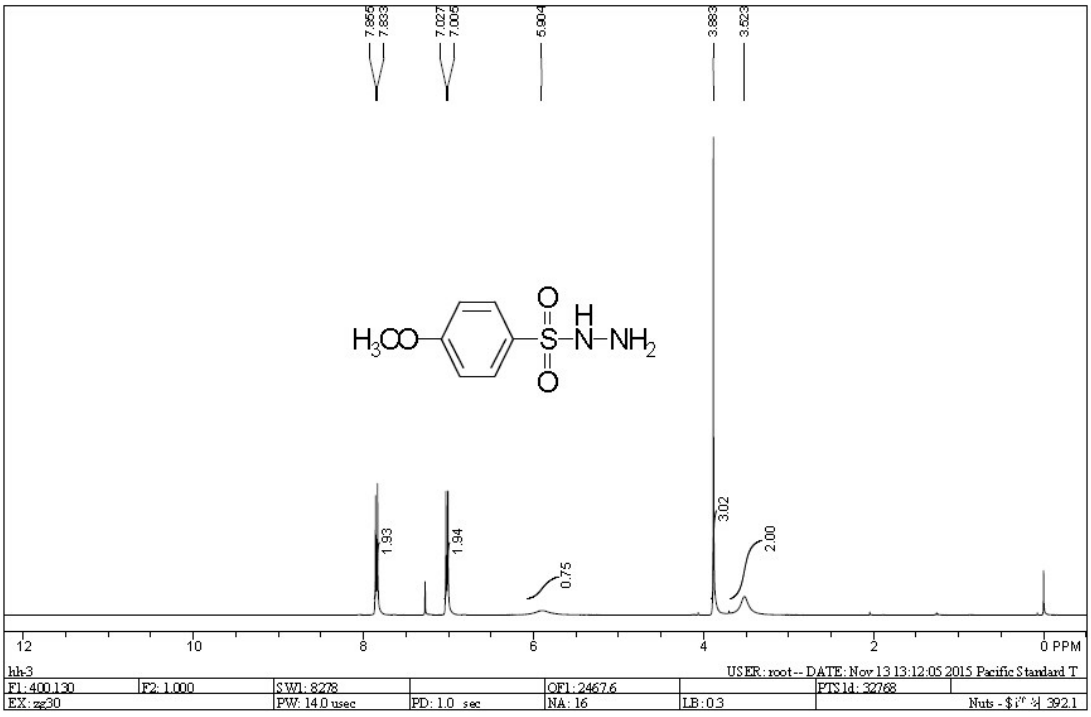
4-Chlorobenzenesulfonohydrazide



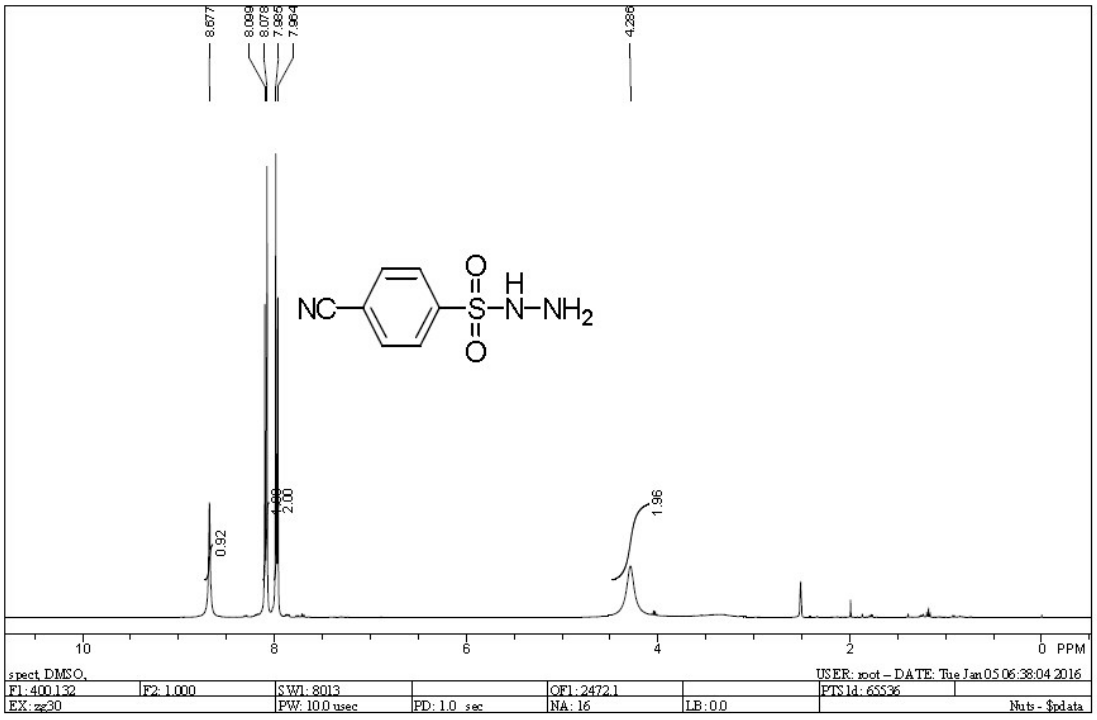
Naphthalene-2-sulfonohydrazide



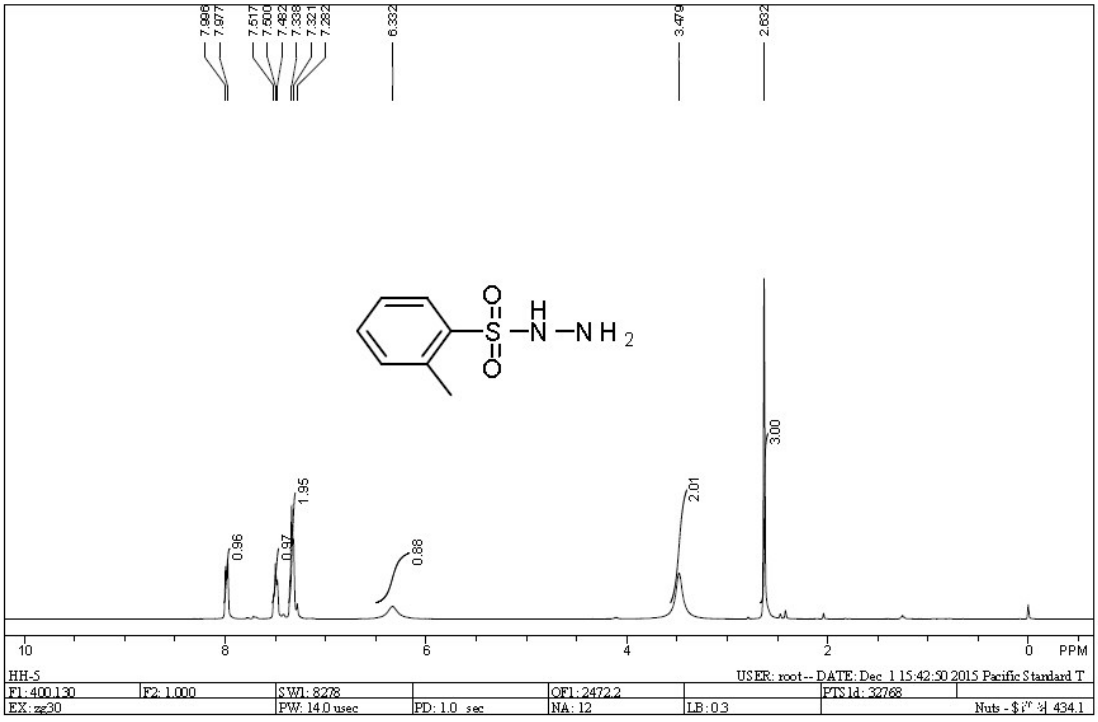
4-Methoxybenzenesulfonohydrazide



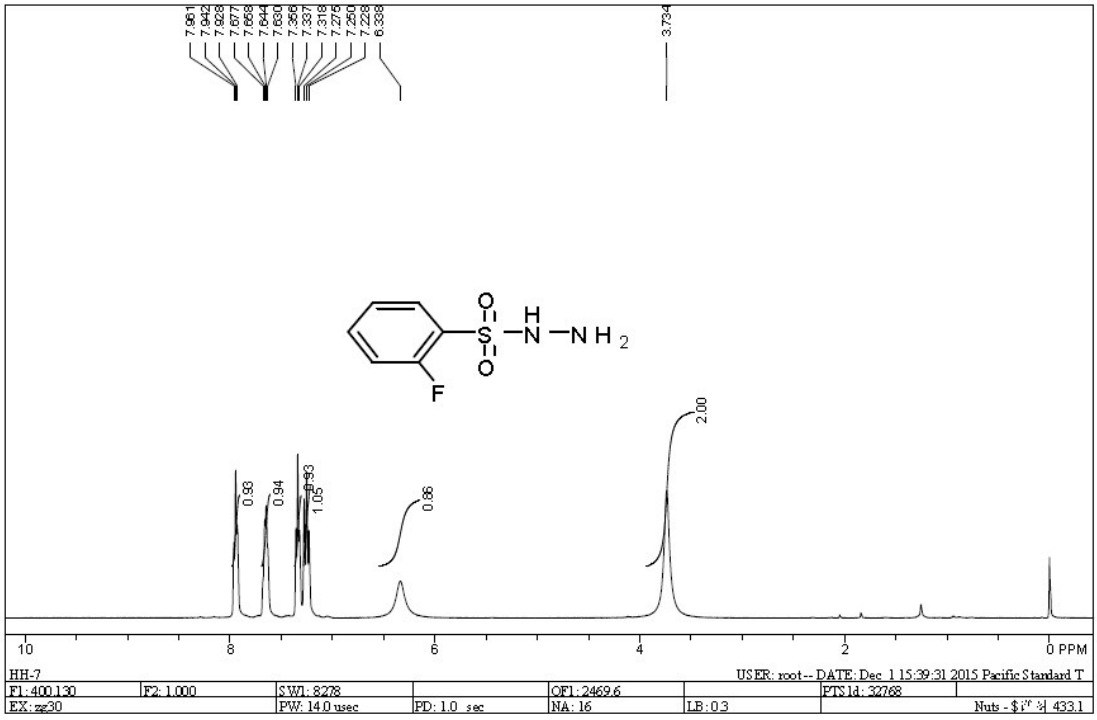
4-Cyanobenzenesulfonohydrazide



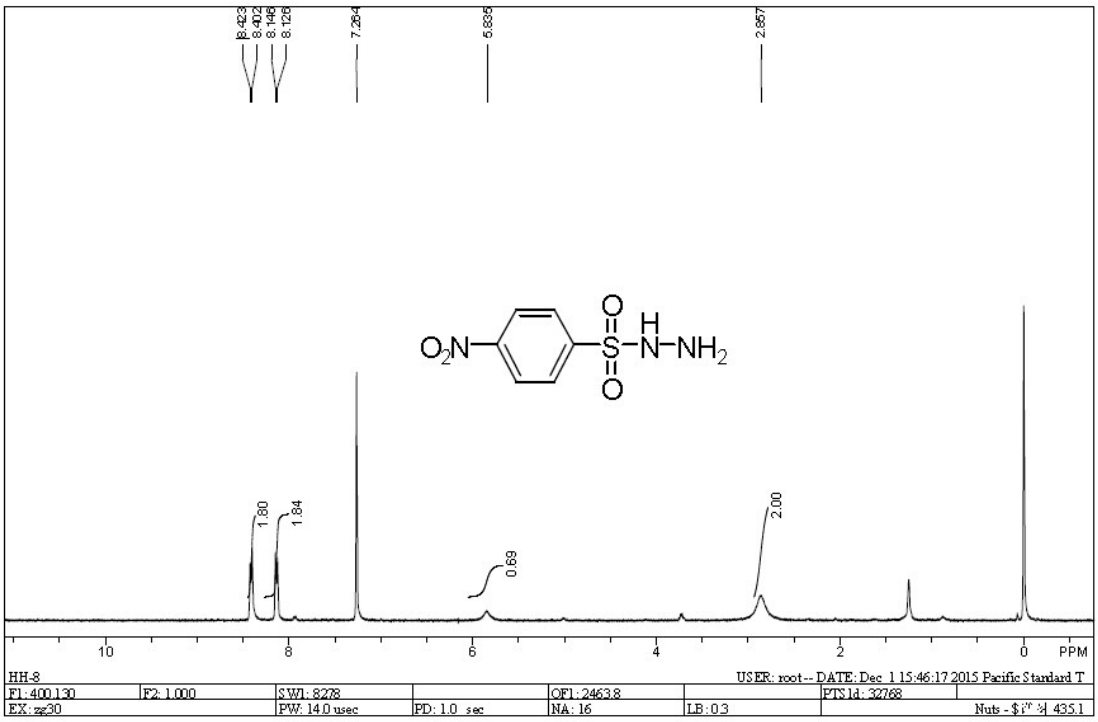
2-Methylbenzenesulfonohydrazide



2-Fluorobenzenesulfonohydrazide



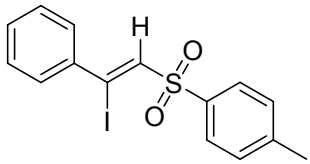
4-Nitrobenzenesulfonohydrazide



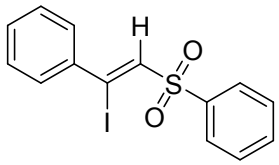
General procedure for the *Z*-selective alkyne halosulfonylation

To a 25 mL round-bottom flask was added alkyne **1** (0.2 mmol), sulfonohydrazide **2** (0.3 mmol), CuX (0.2 mmol, X = Cl, Br or I), BPO (0.2 mmol) and DMSO (2.0 mL). The resulting mixture was stirred at room temperature for 12h (TLC). Upon completion, water (10 mL) was added and the resulting suspension was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtrated. The solution was evaporated under reduced pressure to remove the solvent. Purification of the residue by flash column chromatography using mixed ethyl acetate (EA) and petroleum ether (PET) as eluent (V_{EA} : V_{PET} = 1:10) to provide analytically pure products.

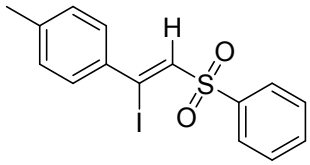
Characterization data of all products



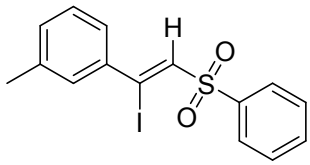
(*Z*)-1-(2-Iodo-2-phenylvinylsulfonyl)-4-methylbenzene (**3a**). Yellow solid; m.p. 88 ^oC; ^1H NMR (400 MHz, $CDCl_3$): 7.95 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 9.2 Hz, 5 H), 7.25 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 141.6, 137.7, 137.1, 130.8, 129.8, 128.64, 128.59, 128.5, 113.8, 21.7; ESI-HRMS: Calcd for $C_{15}H_{13}IO_2SNa$ $[M+Na]^+$ 406.9573, found 406.9576.



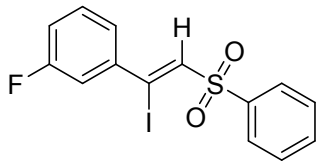
(*Z*)-(1-Iodo-2-(phenylsulfonyl)vinyl)benzene (**3b**). Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): 8.08 (d, *J* = 7.6 Hz, 2 H), 7.67 (d, *J* = 7.2 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 3 H), 7.27 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.6, 140.1, 137.4, 133.8, 130.9, 129.2, 128.7, 128.6, 128.4, 116.6; ESI-HRMS: Calcd for $C_{14}H_{11}IO_2SNa$ $[M+Na]^+$ 392.9417; found 392.9418.



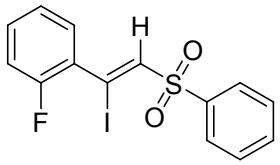
(*Z*)-1-(1-Iodo-2-(phenylsulfonyl)vinyl)-4-methylbenzene (**3c**). Yellow solid; m.p. 94 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (d, J = 8.0 Hz, 2 H), 7.55 (t, J = 6.8 Hz, 1 H), 7.46 (t, J = 7.2 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.16 (s, 1 H), 7.02 (d, J = 7.6 Hz, 2 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.6, 140.2, 138.6, 136.4, 133.8, 129.4, 129.2, 128.7, 128.4, 117.2, 21.3; ESI-HRMS: Calcd for $C_{15}H_{13}IO_2SNa$ $[M+Na]^+$ 406.9573; found 406.9576.



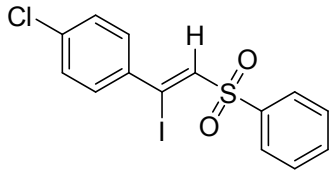
(*Z*)-1-(1-Iodo-2-(phenylsulfonyl)vinyl)-3-methylbenzene (**3d**). Brown solid; m.p. 86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, J = 7.2 Hz, 2 H), 7.66 (d, J = 6.4 Hz, 1 H), 7.58 (d, J = 6.8 Hz, 2 H), 7.25 (s, 4 H), 7.18 (s, 1 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.5, 140.1, 138.5, 137.1, 133.8, 131.7, 129.2, 129.1, 128.5, 128.4, 125.8, 116.9, 21.2; ESI-HRMS: Calcd for $C_{15}H_{13}IO_2SNa$ $[M+Na]^+$ 406.9573; found 406.9576.



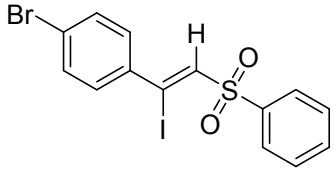
(*Z*)-1-Fluoro-3-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (**3e**). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, J = 7.2 Hz, 2 H), 7.67 (d, J = 7.2 Hz, 1 H), 7.58 (t, J = 7.2 Hz, 2 H), 7.32 (t, J = 6.8 Hz, 2 H), 7.29 (s, 1H), 7.15 (t, J = 7.2 Hz, 1 H), 7.03 (t, J = 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.3 (d, J = 245.9 Hz), 143.7, 139.9, 138.4, 134.0, 130.3, 130.2, 129.3, 128.4, 124.1 (d, J = 3.2 Hz), 117.7 (d, J = 19.9 Hz), 115.9 (d, J = 24.6 Hz); ESI-HRMS: Calcd for $C_{14}H_{10}FIO_2SNa$ $[M+Na]^+$ 410.9322, found 410.9327.



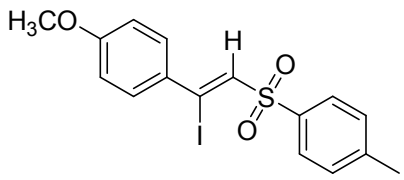
(Z)-1-Fluoro-2-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (**3f**). Yellow solid; m.p. 54 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, *J* = 7.2 Hz, 2 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.58 (t, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 6.8 Hz, 2 H), 7.29 (s, 1 H), 7.15 (t, *J* = 7.2 Hz, 1 H), 7.03 (t, *J* = 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.6 (d, *J* = 251.6 Hz), 140.9 (d, *J* = 3.4 Hz), 139.8, 134.0, 132.0, 131.9, 131.3, 129.3, 128.3, 124.3 (d, *J* = 3.6 Hz), 116.3 (d, *J* = 21.9 Hz), 105.5; ESI-HRMS: Calcd for $C_{14}H_{10}FIO_2SNa$ $[M+Na]^+$ 410.9322; found 410.9327.



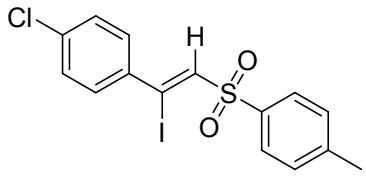
(*Z*)-1-Chloro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (**3g**). Brown solid; m.p. 123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, *J* = 7.2 Hz, 2 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.27 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.0, 139.9, 137.7, 137.1, 134.0, 129.9, 129.3, 128.8, 128.4, 114.7; ESI-HRMS: Calcd for $C_{14}H_{10}ClIO_2SNa$ $[M+Na]^+$ 426.9027; found 426.9021.



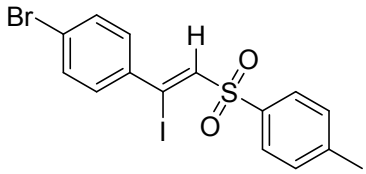
(*Z*)-1-Bromo-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (**3h**). White solid; m.p. 123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, *J* = 7.6 Hz, 2 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 7.58 (t, *J* = 7.2 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.8 Hz, 2 H), 7.27 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.5, 139.8, 137.8, 134.0, 131.8, 130.0, 129.3, 128.4, 125.4, 114.7; ESI-HRMS: Calcd for $C_{14}H_{10}BrIO_2SNa$ $[M+Na]^+$ 470.8522; found 470.8526.



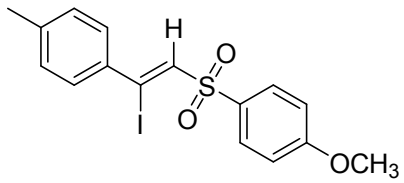
(*Z*)-1-(2-Iodo-2-(4-methoxyphenyl)vinylsulfonyl)-4-methylbenzene (**3i**). White solid; m.p. 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.20 (s, 1 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 144.7, 137.4, 135.5, 133.6, 130.4, 129.8, 128.4, 116.5, 113.9, 55.6, 21.7; ESI-HRMS: Calcd for $C_{16}H_{15}IO_3SNa$ $[M+Na]^+$ 436.9679; found 436.9682.



(*Z*)-1-Chloro-4-(1-iodo-2-tosylvinyl)benzene (**3j**). Yellow solid; m.p. 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 8.0 Hz, 2 H), 7.38 (t, *J* = 8.0 Hz, 4 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.23 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 140.1, 138.1, 137.0, 136.9, 129.9, 129.8, 128.8, 128.5, 114.0, 21.7; ESI-HRMS: Calcd for $C_{15}H_{12}ClIO_2SNa$ $[M+Na]^+$ 440.9183; found 440.9180.

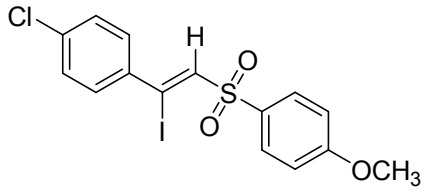


(*Z*)-1-Bromo-4-(1-iodo-2-tosylvinyl)benzene (**3k**). Yellow solid; m.p. 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.24 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 140.6, 138.1, 136.9, 131.7, 130.0, 129.9, 128.5, 125.3, 114.2, 21.8; ESI-HRMS: Calcd for $C_{15}H_{12}BrIO_2SNa$ $[M+Na]^+$ 484.8678; found 484.8678.

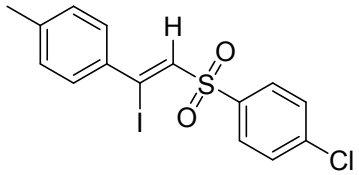


(*Z*)-1-(1-Iodo-2-(4-methoxyphenylsulfonyl)vinyl)-4-methylbenzene (**3l**). White solid; m.p. 107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (d, *J* = 8.8 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.23 (s, 1 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 3.89

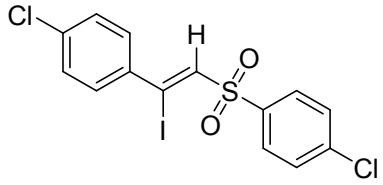
(s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 141.4, 138.7, 137.0, 131.7, 130.7, 129.3, 128.6, 116.1, 114.3, 55.7, 21.2; ESI-HRMS: Calcd for $C_{16}H_{15}IO_3SNa$ $[M+Na]^+$ 436.9679; found 436.9681.



(*Z*)-1-Chloro-4-(1-iodo-2-(4-methoxyphenylsulfonyl)vinyl)benzene (**3m**). Yellow solid; m.p. 87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (d, J = 8.8 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.23 (s, 1 H), 7.03 (d, J = 9.2 Hz, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 140.1, 138.4, 136.9, 131.3, 130.8, 129.8, 128.8, 114.5, 113.6, 55.8; ESI-HRMS: Calcd for $C_{15}H_{12}ClIO_3SNa$ $[M+Na]^+$ 456.9133; found 456.9137.

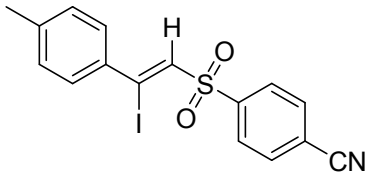


(*Z*)-1-Chloro-4-(2-iodo-2-p-tolylvinylsulfonyl)benzene (**3n**). Yellow solid; m.p. 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.25 (s, 1 H), 7.15 (d, J = 8.0 Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.8, 140.5, 138.6, 138.5, 136.0, 129.9, 129.5, 129.4, 128.7, 118.2, 21.3; ESI-HRMS: Calcd for $C_{15}H_{12}ClIO_2SNa$ $[M+Na]^+$ 440.9183; found 440.9179.

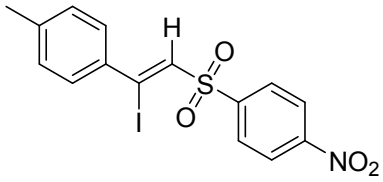


(*Z*)-1-Chloro-4-(2-(4-chlorophenyl)-2-iodovinylsulfonyl)benzene (**3o**). Brown solid; m.p. 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.24 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 139.8, 138.2, 137.4, 137.3, 129.9, 129.8, 129.6, 128.9,

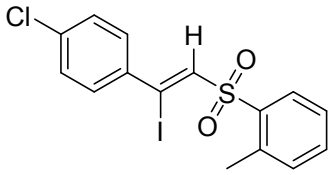
115.6; ESI-HRMS: Calcd for $C_{14}H_9Cl_2IO_2SNa$ $[M+Na]^+$ 460.8637; found 460.8630.



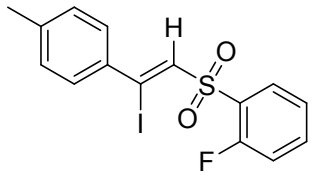
(*Z*)-4-(2-Iodo-2-p-tolylvinylsulfonyl)benzonitrile (**3p**). Yellow solid; m.p. 123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (d, J = 8.0 Hz, 2 H), 7.88 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.29 (s, 1 H), 7.16 (d, J = 8.0 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.2, 142.2, 138.2, 135.0, 132.9, 129.5, 129.1, 128.7, 120.3, 117.4, 117.3, 21.3; ESI-HRMS: Calcd for $C_{16}H_{12}INO_2SNa$ $[M+Na]^+$ 431.9526; found 431.9529.



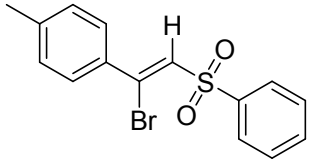
(*Z*)-1-(1-Iodo-2-(4-nitrophenylsulfonyl)vinyl)-4-methylbenzene (**3q**). Yellow solid; m.p. 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.42 (d, J = 8.8 Hz, 2 H), 8.27 (d, J = 8.8 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.31 (s, 1 H), 7.17 (d, J = 7.6 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 150.7, 145.7, 142.3, 138.1, 134.9, 129.8, 129.5, 128.7, 124.3, 120.7, 21.3; ESI-HRMS: Calcd for $C_{15}H_{12}INO_4SNa$ $[M+Na]^+$ 451.9424; found 451.9374.



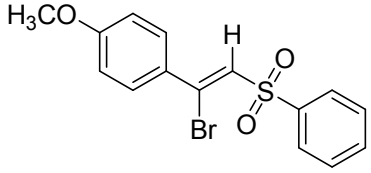
(*Z*)-1-(2-(4-Chlorophenyl)-2-iodovinylsulfonyl)-2-methylbenzene (**3r**). Yellow solid; m.p. 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (d, J = 7.6 Hz, 1 H), 7.54 (d, J = 7.6 Hz, 1 H), 7.42 (d, J = 8.4 Hz, 3 H), 7.34 (d, J = 7.6 Hz, 3 H), 7.30 (s, 1 H), 2.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.0, 137.9, 137.8, 137.6, 137.1, 133.9, 132.5, 131.0, 129.7, 128.9, 128.4, 126.2, 20.7; ESI-HRMS: Calcd for $C_{15}H_{12}ClIO_2SNa$ $[M+Na]^+$ 440.9183; found 440.9179.



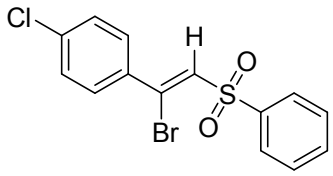
(*Z*)-1-Fluoro-2-(2-iodo-2-*p*-tolylvinylsulfonyl)benzene (**3s**). Yellow solid; m.p. 98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (t, *J* = 6.8 Hz, 1 H), 7.65 (t, *J* = 5.6 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 3 H), 7.35 (d, *J* = 7.2 Hz, 1 H), 7.22 (t, *J* = 8.8 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 2 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.4 (d, *J* = 254.9 Hz), 141.8, 138.3, 136.2, 136.1, 131.5, 129.4, 128.8, 127.8 (d, *J* = 13.7 Hz), 124.3 (d, *J* = 2.9 Hz), 118.4, 117.1 (d, *J* = 20.9 Hz), 21.3; ESI-HRMS: Calcd for $C_{15}H_{12}FIO_2SNa$ [M+Na] 424.9479; found 424.9475.



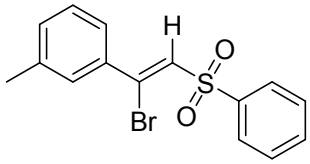
(*Z*)-1-(1-Bromo-2-(phenylsulfonyl)vinyl)-4-methylbenzene (**3t**). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, *J* = 7.6 Hz, 2 H), 7.64 (d, *J* = 7.2 Hz, 1 H), 7.56 (t, *J* = 7.2 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.32 (s, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.2, 140.7, 138.7, 134.3, 133.7, 130.2, 129.5, 129.1, 128.3, 128.0, 21.3; ESI-HRMS: Calcd for $C_{15}H_{13}BrO_2SNa$ $[M+Na]^+$: 358.9712; found 358.9714.



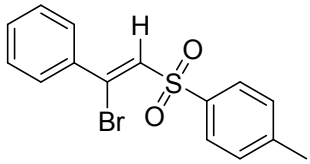
(*Z*)-1-(1-Bromo-2-(phenylsulfonyl)vinyl)-4-methoxybenzene (**3u**). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 7.2 Hz, 1 H), 7.58-7.53 (m, 4 H), 7.27 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.3, 140.8, 138.4, 133.6, 129.8, 129.2, 129.1, 128.8, 128.3, 114.1, 55.6; ESI-HRMS: Calcd for $C_{15}H_{13}BrO_3SNa$ $[M+Na]^+$ 374.9661; found 374.9665.



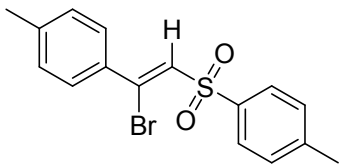
(*Z*)-1-(1-Bromo-2-(phenylsulfonyl)vinyl)-4-chlorobenzene (**3v**). White solid; m.p. 131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 9.2 Hz, 2 H), 7.36 (d, *J* = 8.8 Hz, 2 H), 7.31 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.3, 137.8, 136.8, 135.7, 133.9, 131.6, 129.3, 129.2, 129.0, 128.3; ESI-HRMS: Calcd for $C_{14}H_{10}BrClO_2SNa$ $[M+Na]^+$ 378.9166; found 378.9161.



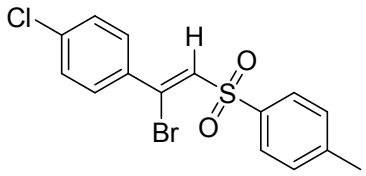
(*Z*)-1-(1-Bromo-2-(phenylsulfonyl)vinyl)-3-methylbenzene (**3w**). White solid; m.p. 61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, *J* = 7.6 Hz, 2 H), 7.66 (t, *J* = 6.8 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 2 H), 7.36 (s, 2 H), 7.32 (s, 1 H), 7.25 (d, *J* = 4.8 Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.6, 138.7, 137.2, 133.8, 132.3, 131.0, 129.1, 128.7, 128.6, 128.3, 125.3, 21.3; ESI-HRMS: Calcd for $C_{15}H_{13}BrO_2SNa$ $[M+Na]^+$ 358.9712; found 358.9715.



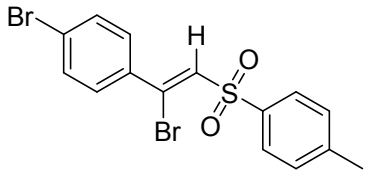
(*Z*)-1-(2-Bromo-2-phenylvinylsulfonyl)-4-methylbenzene (**3x**). White solid; m.p. 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.95 (d, *J* = 7.6 Hz, 2 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.42 (d, *J* = 6.8 Hz, 1 H), 7.37 (t, *J* = 6.8 Hz, 4 H), 7.32 (s, 1 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 137.9, 137.6, 137.3, 131.6, 131.4, 129.8, 128.8, 128.4, 128.0, 21.7; ESI-HRMS: Calcd for $C_{15}H_{13}BrO_2SNa$ $[M+Na]^+$ 358.9712; found 358.9714.



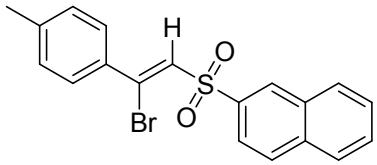
(*Z*)-1-(2-Bromo-2-p-tolylvinylsulfonyl)-4-methylbenzene (**3y**). White solid; m.p. 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.29 (s, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 2.45 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.7, 142.1, 138.2, 137.7, 134.5, 130.5, 129.7, 129.4, 128.4, 128.0, 21.7, 21.3; ESI-HRMS: Calcd for $C_{16}H_{15}BrO_2SNa$ $[M+Na]^+$ 372.9868; found 372.9862.



(*Z*)-1-(2-Bromo-2-(4-chlorophenyl)vinylsulfonyl)-4-methylbenzene (**3z**). White solid; m.p. 93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.36 (t, *J* = 7.6 Hz, 4 H), 7.30 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 137.7, 137.4, 136.3, 135.8, 132.0, 129.8, 129.3, 129.0, 128.4, 21.7; ESI-HRMS: Calcd for $C_{15}H_{12}BrClO_2SNa$ $[M+Na]^+$ 392.9322; found 392.9325.

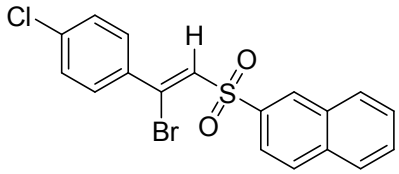


(*Z*)-1-Bromo-4-(1-bromo-2-tosylvinyl)benzene (**3aa**). White solid; m.p. 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.31 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 137.3, 136.34, 136.29, 132.0, 131.98, 129.8, 129.5, 128.4, 126.0, 21.7; ESI-HRMS: Calcd for $C_{15}H_{12}Br_2O_2SNa$ $[M+Na]^+$ 436.8817; found 436.8820.

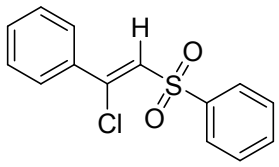


(*Z*)-2-(2-Bromo-2-*p*-tolylvinylsulfonyl)naphthalene (**3ab**). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.66 (s, 1 H), 8.00 (d, *J* = 10.8 Hz, 3 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.67-7.59 (m, 2 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.39 (s, 1 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.2, 138.8, 137.4, 135.3, 134.3, 132.0,

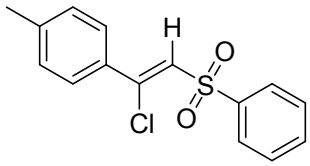
130.22, 130.17, 129.6, 129.5, 129.44, 129.36, 128.5, 128.0, 127.7, 122.9, 21.4; ESI-HRMS: Calcd for $C_{19}H_{15}BrO_2SNa$ $[M+Na]^+$ 408.9868; found 408.9865.



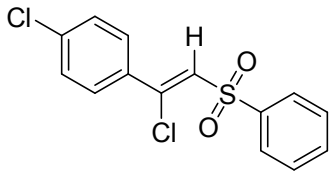
(*Z*)-2-(2-Bromo-2-(4-chlorophenyl)vinylsulfonyl)naphthalene (**3ac**). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.67 (s, 1 H), 8.04-7.98 (m, 3 H), 7.94 (d, *J* = 7.6 Hz, 1 H), 7.71-7.63 (m, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.38 (s, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.8, 137.1, 136.9, 135.7, 135.4, 132.1, 131.7, 130.4, 129.58, 129.55, 129.5, 129.3, 129.0, 128.0, 127.8, 122.9; ESI-HRMS: Calcd for $C_{18}H_{12}BrClO_2SNa$ $[M+Na]^+$ 428.9322; found 428.9327.



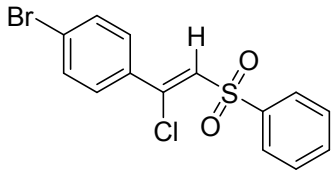
(*Z*)-(1-Chloro-2-(phenylsulfonyl)vinyl)benzene (**3ad**). White solid; m.p. 78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, *J* = 7.6 Hz, 2 H), 7.66 (t, *J* = 6.8 Hz, 1 H), 7.62-7.56 (m, 4 H), 7.46 (t, *J* = 6.8 Hz, 1 H), 7.40 (t, *J* = 7.2 Hz, 2 H), 7.14 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.4, 140.8, 135.1, 133.8, 131.7, 129.1, 128.9, 128.2, 127.6, 127.2; ESI-HRMS: Calcd for $C_{14}H_{11}ClO_2SNa$ $[M+Na]^+$ 301.0060; found 301.0065.



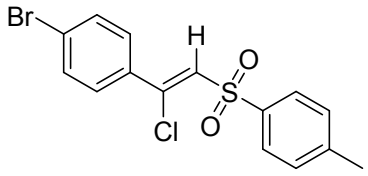
(*Z*)-1-(1-Chloro-2-(phenylsulfonyl)vinyl)-4-methylbenzene (**3ae**). White solid; m.p. 71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, *J* = 7.6 Hz, 2 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 7.11 (s, 1 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.6, 142.5, 141.0, 133.7, 132.3, 129.5, 129.1, 128.2, 127.2, 126.5, 21.4; ESI-HRMS: Calcd for $C_{15}H_{13}ClO_2SNa$ $[M+Na]^+$ 315.0217; found: 315.0211.



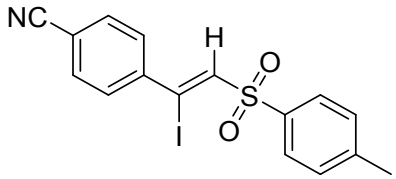
(*Z*)-1-Chloro-4-(1-chloro-2-(phenylsulfonyl)vinyl)benzene (**3af**). Brown solid; m.p. 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, J = 7.2 Hz, 2 H), 7.67 (t, J = 7.2 Hz, 1 H), 7.60-7.54 (m, 4 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.12 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 140.7, 138.1, 133.9, 133.6, 129.2, 129.1, 128.5, 128.1, 128.0; ESI-HRMS: Calcd for $C_{14}H_{10}ClO_2SNa$ $[M+Na]^+$ 334.9671; found 334.9673.



(*Z*)-1-Bromo-4-(1-chloro-2-(phenylsulfonyl)vinyl)benzene (**3ag**). White solid; m.p. 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 7.6 Hz, 2 H), 7.67 (t, J = 7.2 Hz, 1 H), 7.60-7.53 (m, 4 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 140.6, 134.1, 133.9, 132.1, 129.2, 128.7, 128.2, 128.0, 126.5; ESI-HRMS: Calcd for $C_{14}H_{10}BrClO_2SNa$ $[M+Na]^+$ 378.9166; found 378.9161.

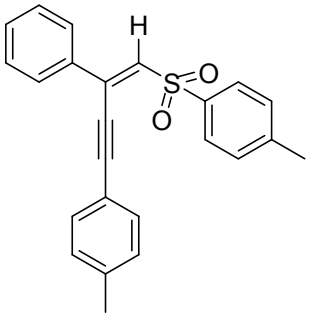


(*Z*)-1-Bromo-4-(1-chloro-2-tosylvinyl)benzene (**3ah**). White solid; m.p. 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 7.6 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 7.6 Hz, 2 H), 7.12 (s, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 144.6, 137.7, 134.2, 132.1, 129.8, 128.6, 128.4, 128.3, 126.3, 21.7; ESI-HRMS: Calcd for $C_{15}H_{12}BrClO_2SNa$ $[M+Na]^+$ 392.9322; found 392.9326.

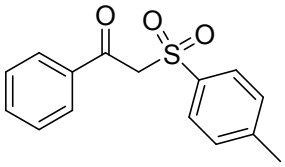


(*Z*)-4-(1-Iodo-2-tosylvinyl)benzonitrile (**3ai**). Light yellow solid, m.p. 120 °C; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H) 7.39 (d, *J* = 8.0 Hz, 2 H), 7.29 (s, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.9, 145.4, 140.0, 136.6, 132.3, 130.0, 129.2, 128.5, 117.7, 114.2, 111.9, 21.8; ESI-HRMS: Calcd for $C_{16}H_{16}IN_2O_2S$ $[M+NH_4]^+$ 426.9972, found 426.9953.



(*Z*)-1-Methyl-4-(2-phenyl-4-p-tolylbut-1-en-3-ynylsulfonyl)benzene (**4**). Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): 7.95 (d, *J* = 8.4 Hz, 2 H), 7.70-7.67 (m, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 6.0 Hz, 3 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 7.08 (s, 1 H), 2.41 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 140.3, 138.7, 135.8, 135.6, 132.5, 132.1, 130.6, 129.6, 129.4, 128.8, 128.0, 127.2, 118.9, 106.2, 83.7, 21.7, 21.6; ESI-HRMS: calcd for $C_{24}H_{20}O_2SNa$ $[M+Na]^+$: 395.1076; found 395.1115.



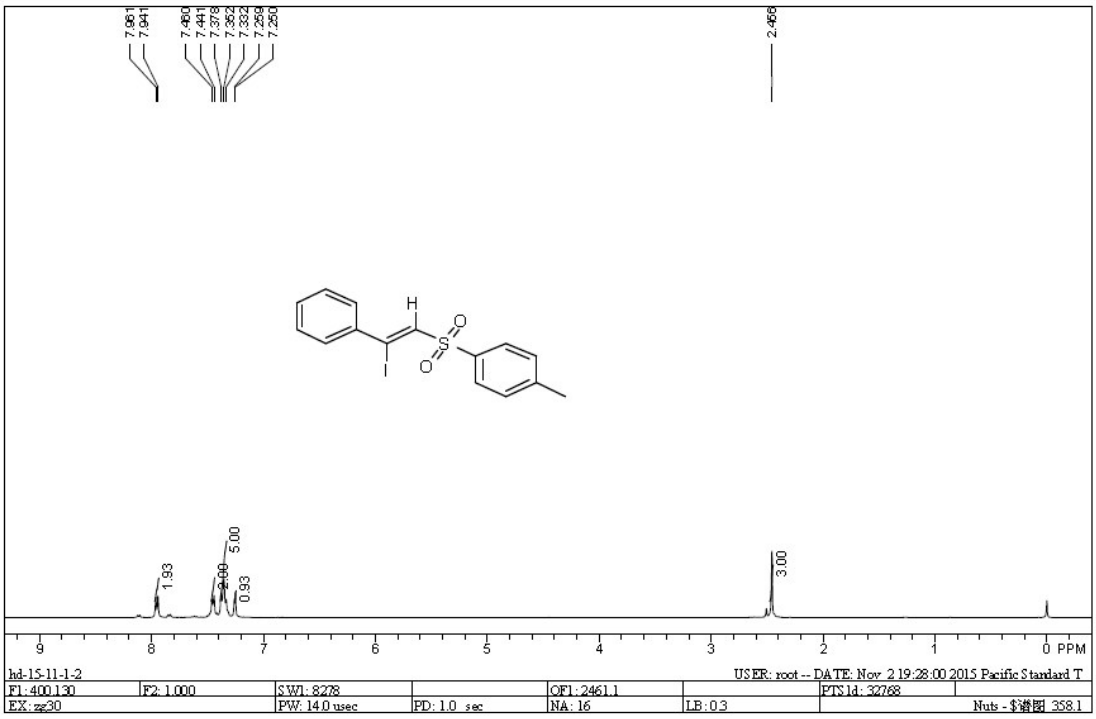
1-Phenyl-2-tosylethanone (**5**). White solid; m.p. 100 ^oC; ^1H NMR (400 MHz, $CDCl_3$): 7.95 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 4.72 (s, 2 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.2, 145.4, 135.7, 134.4, 129.9, 129.4, 128.9, 128.6, 63.5, 21.7; ESI-HRMS: calcd for $C_{15}H_{14}O_3SNa$ $[M+Na]^+$ 297.0556 found 297.0581.

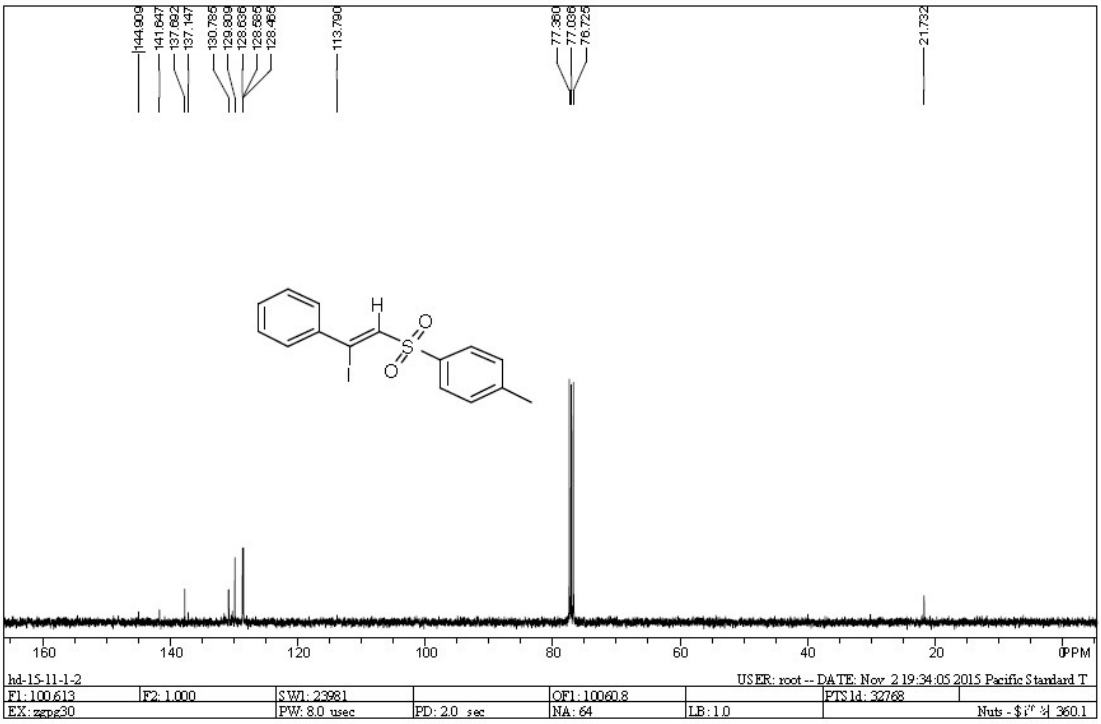
References :

(1) Yu, X.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2012**, *10*, 7479.

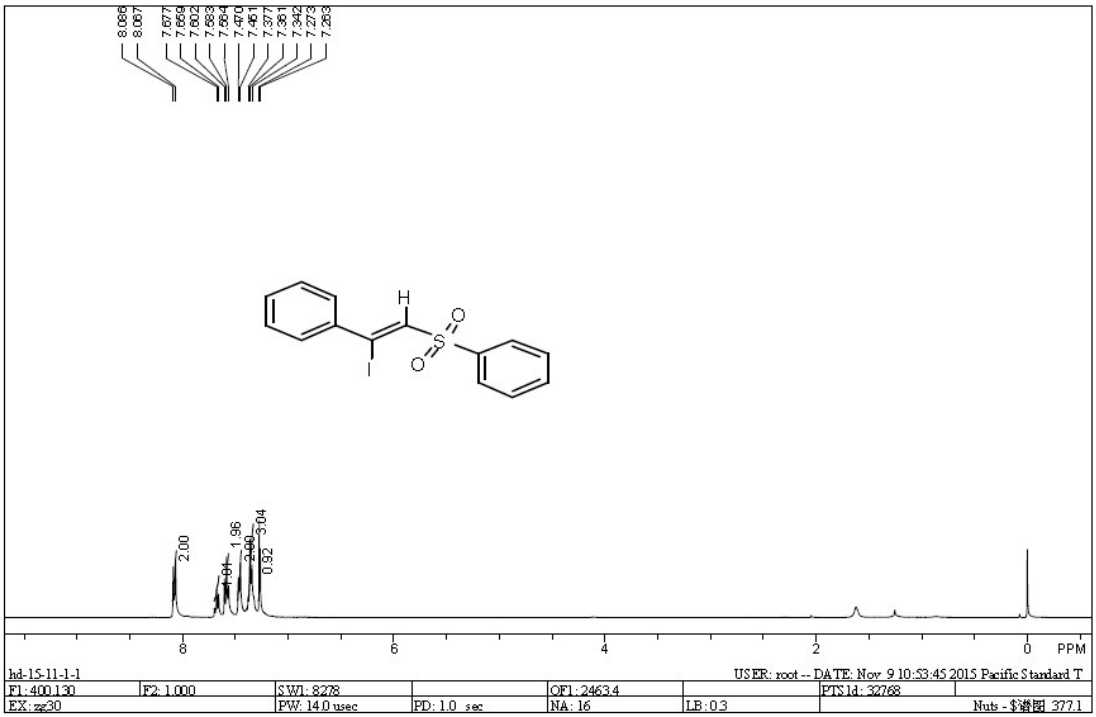
^{1}H and ^{13}C NMR spectra of all products

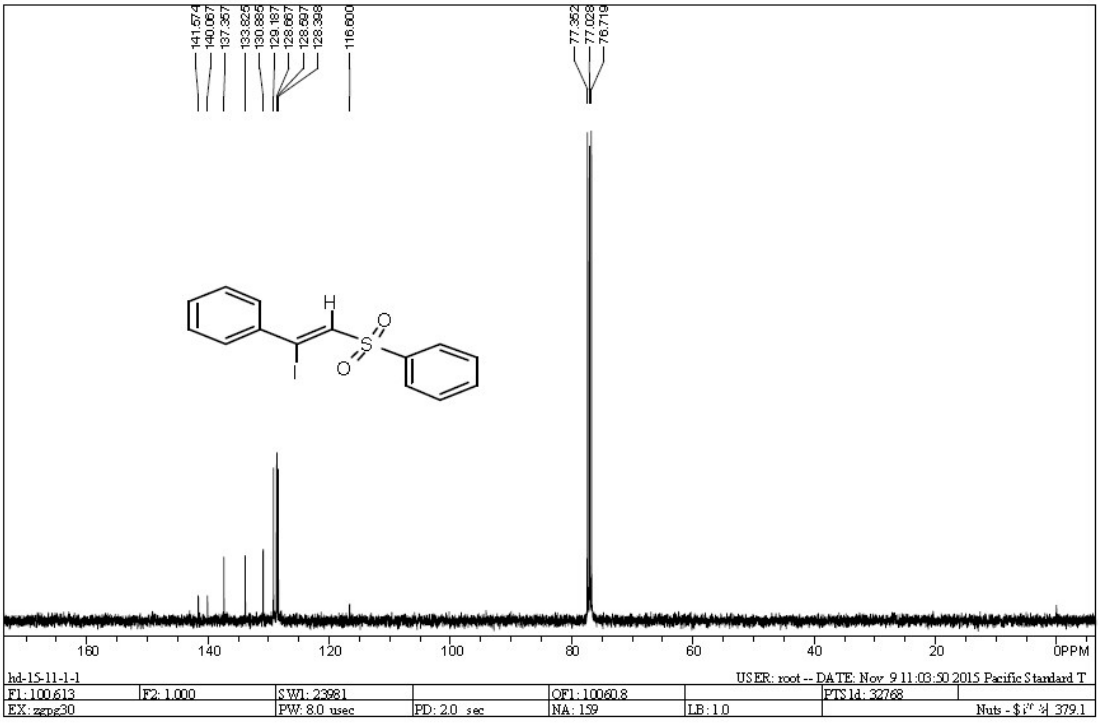
^{1}H and ^{13}C NMR spectra of **3a**



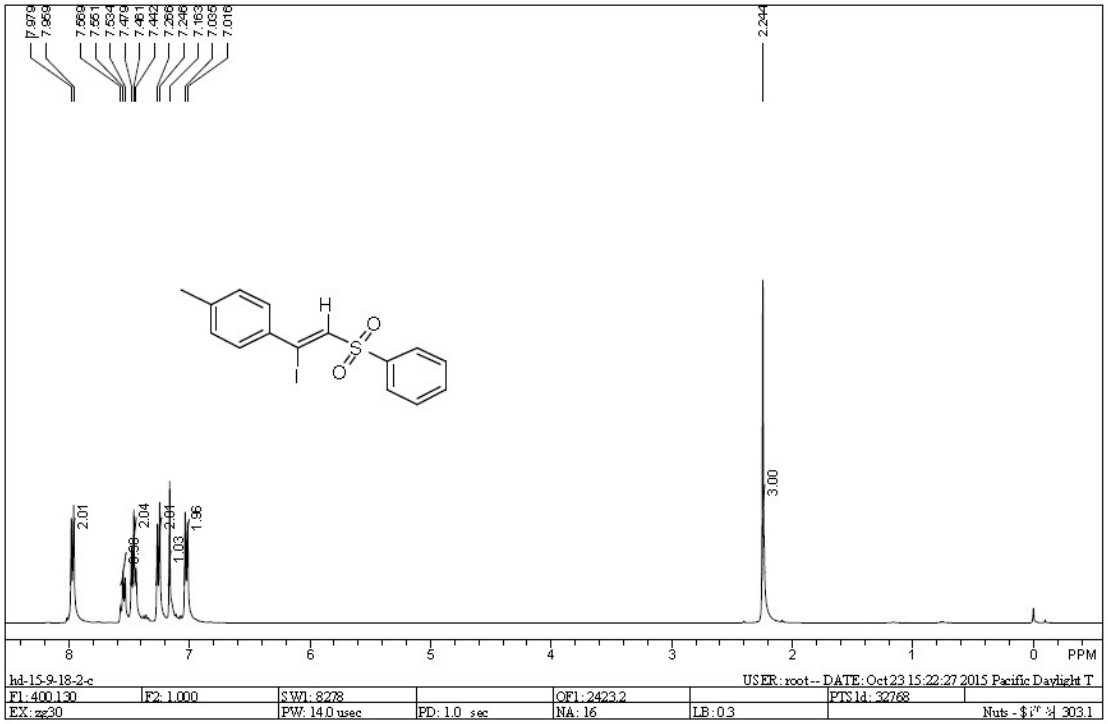


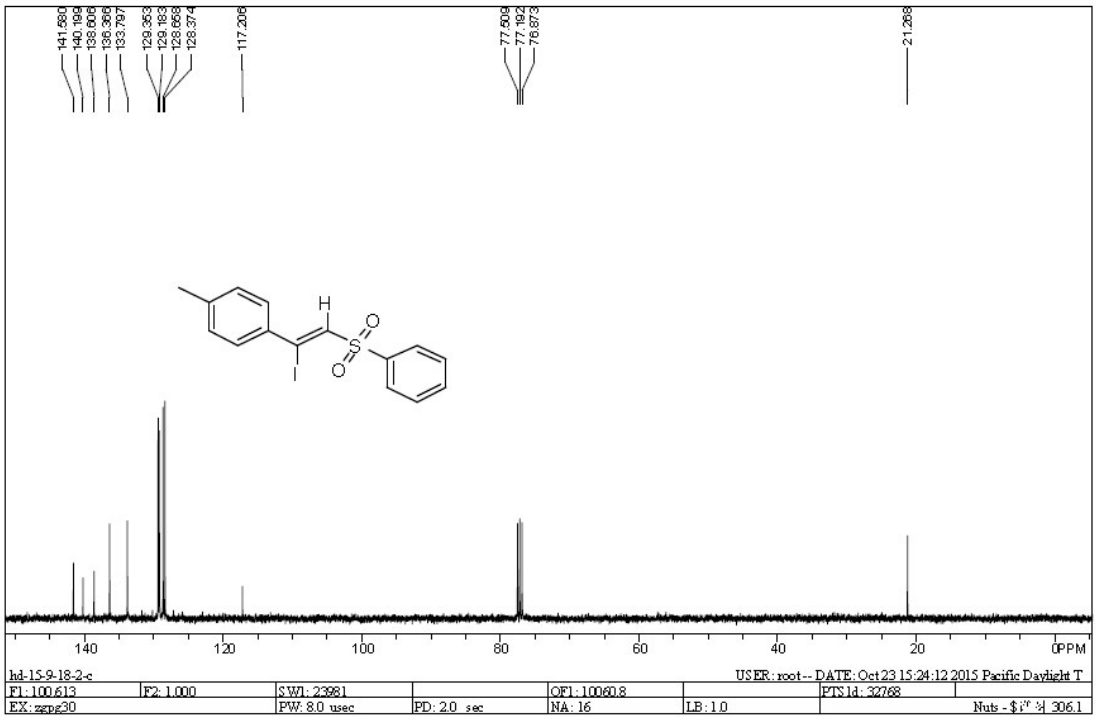
^{1}H and ^{13}C NMR spectra of **3b**



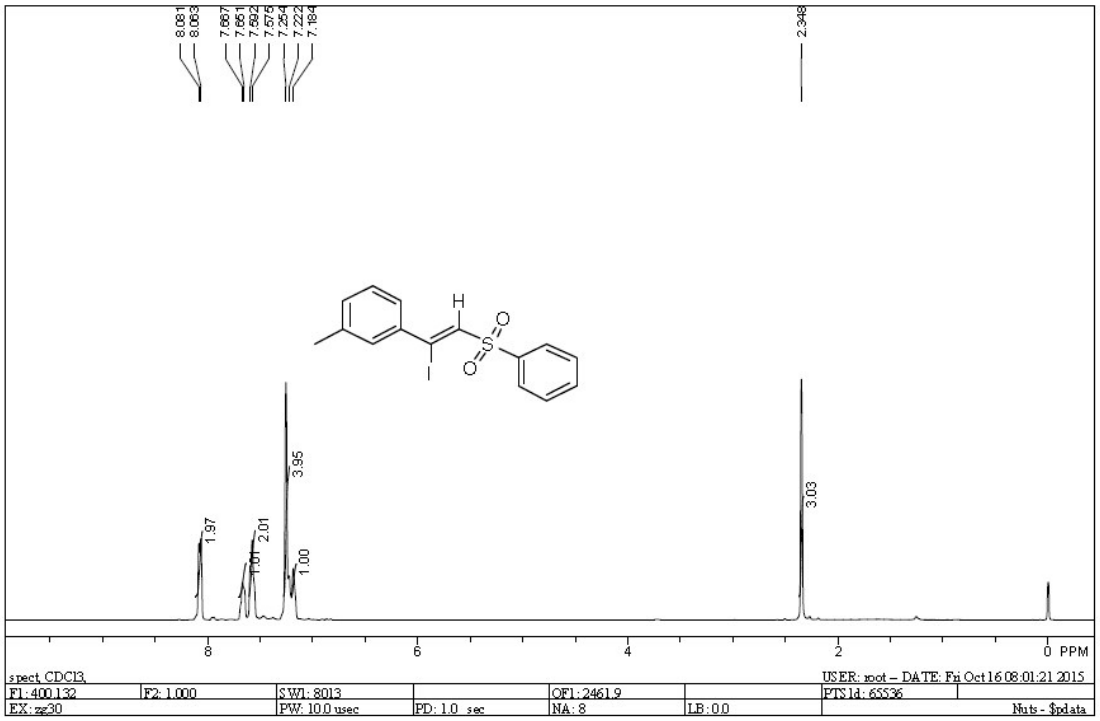


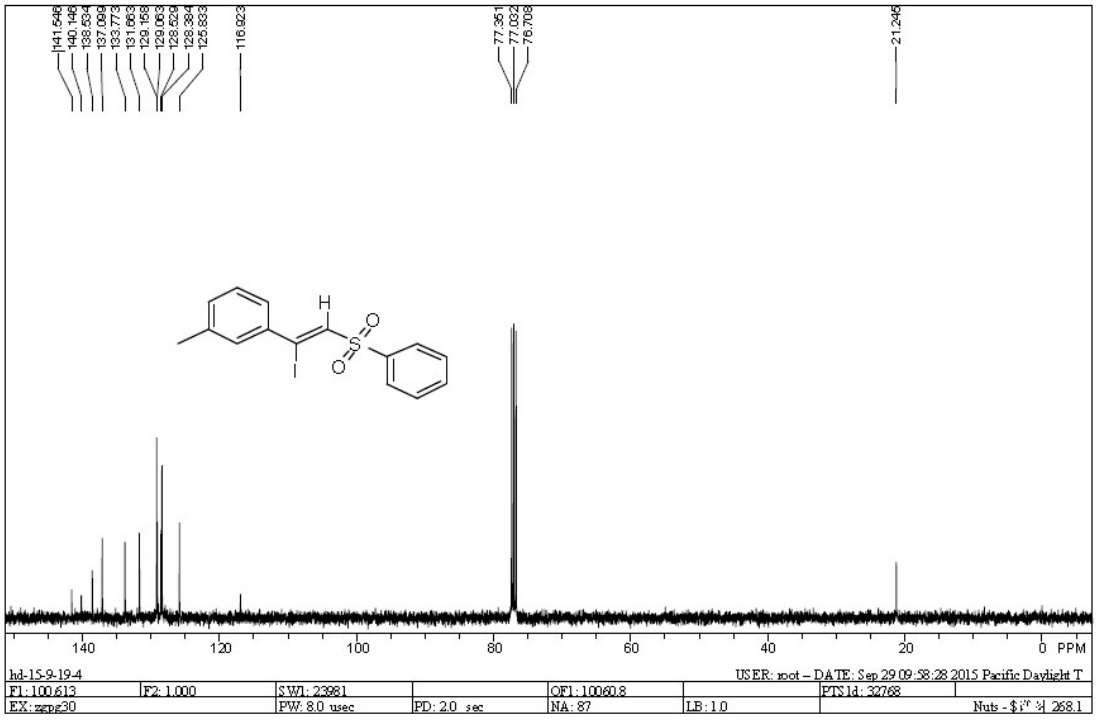
^{1}H and ^{13}C NMR spectra of **3c**



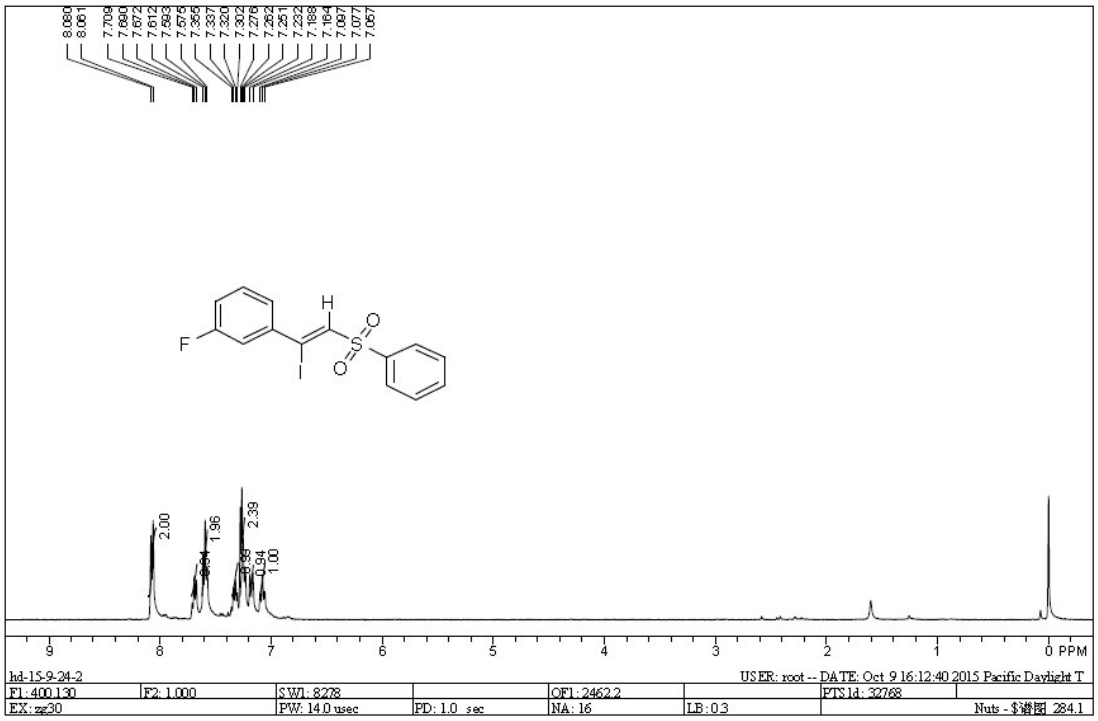


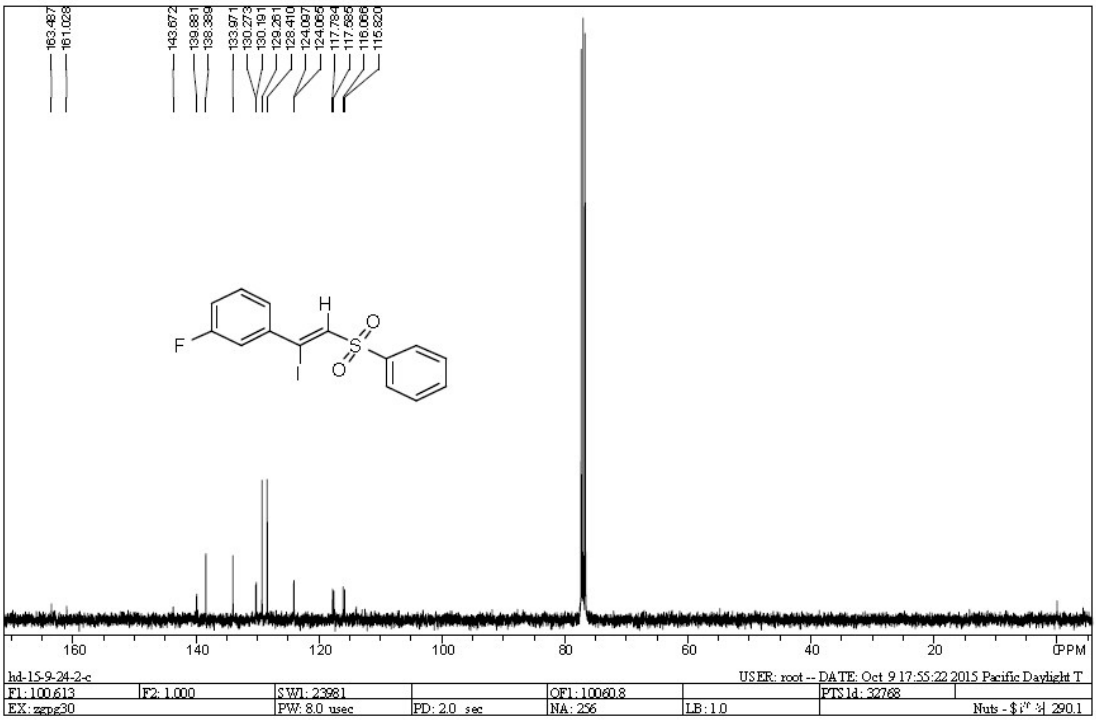
^{1}H and ^{13}C NMR spectra of **3d**



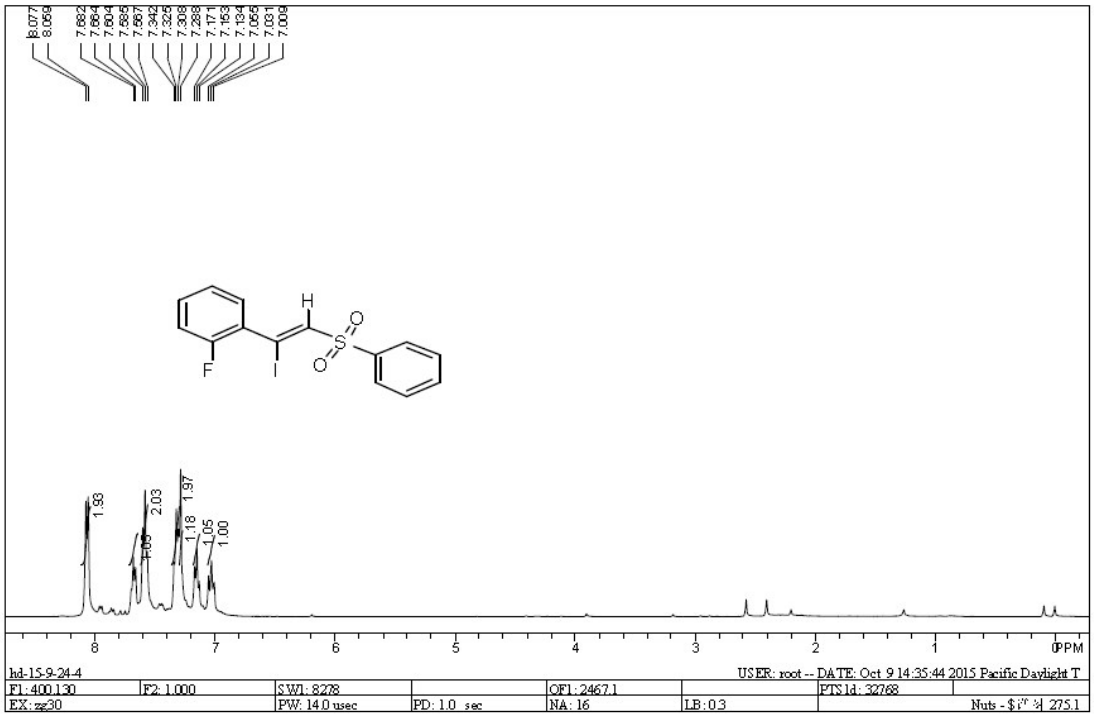


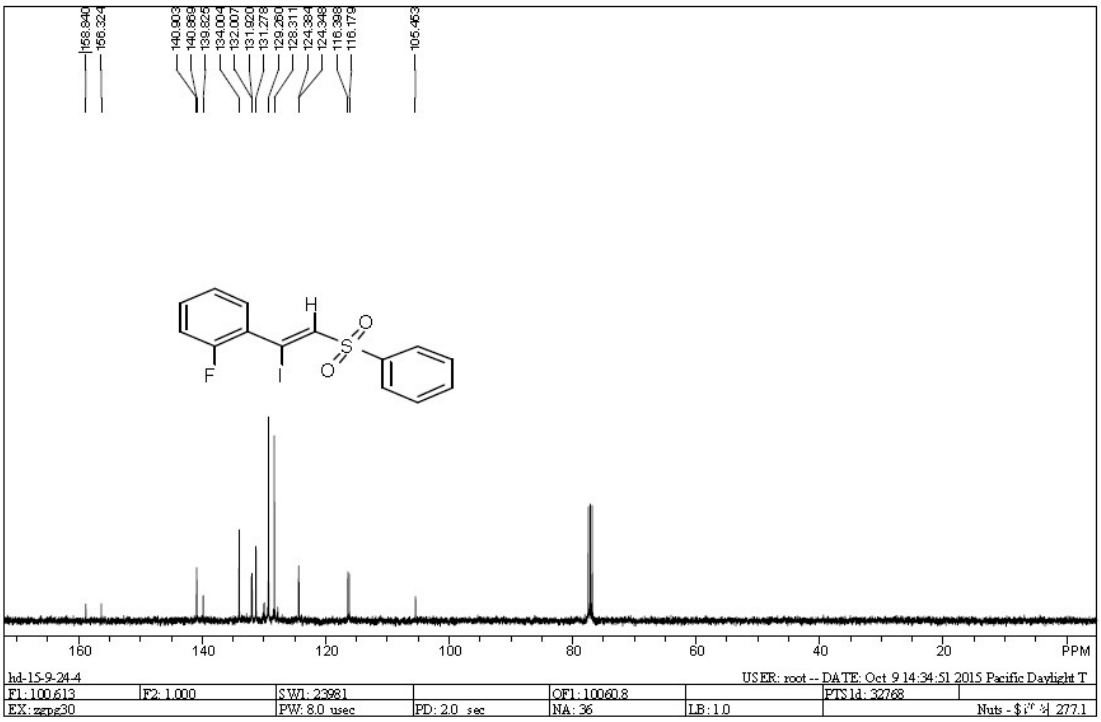
^{1}H and ^{13}C NMR spectra of **3e**



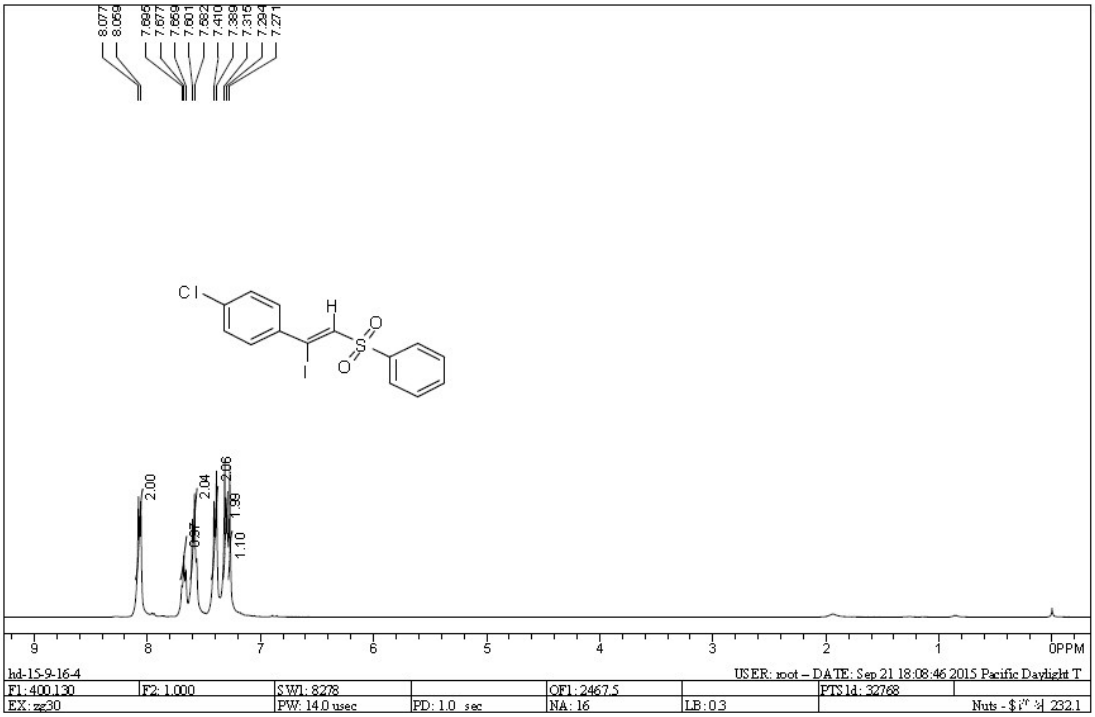


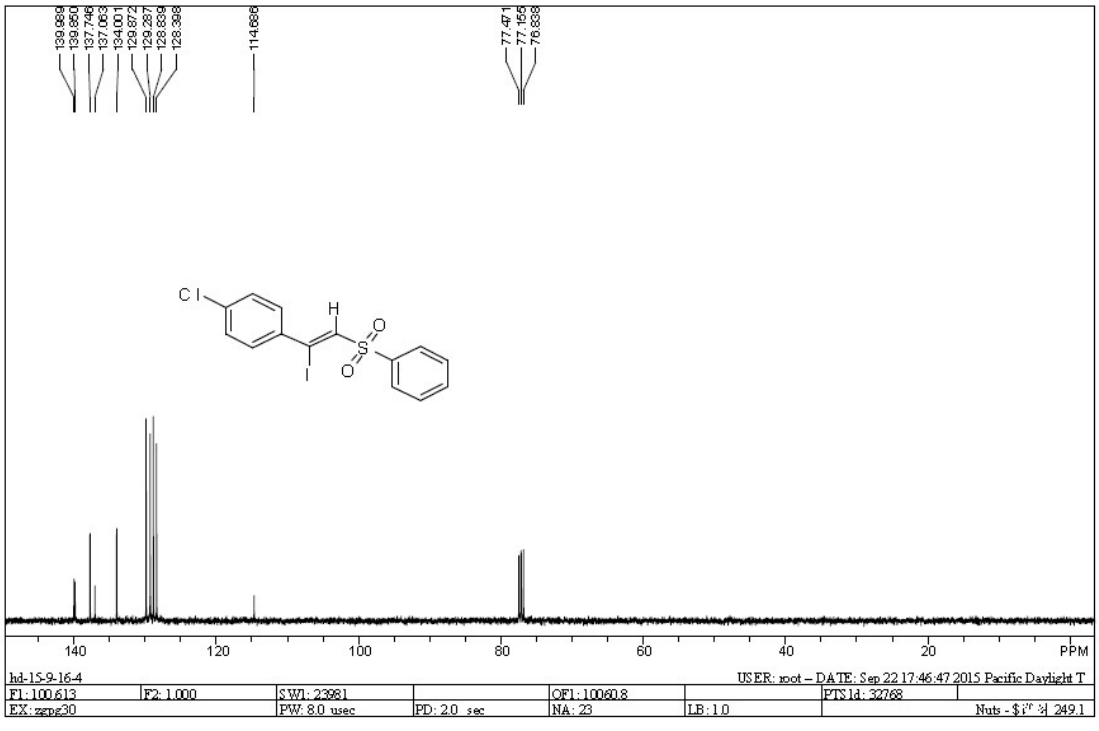
^{1}H and ^{13}C NMR spectra of **3f**



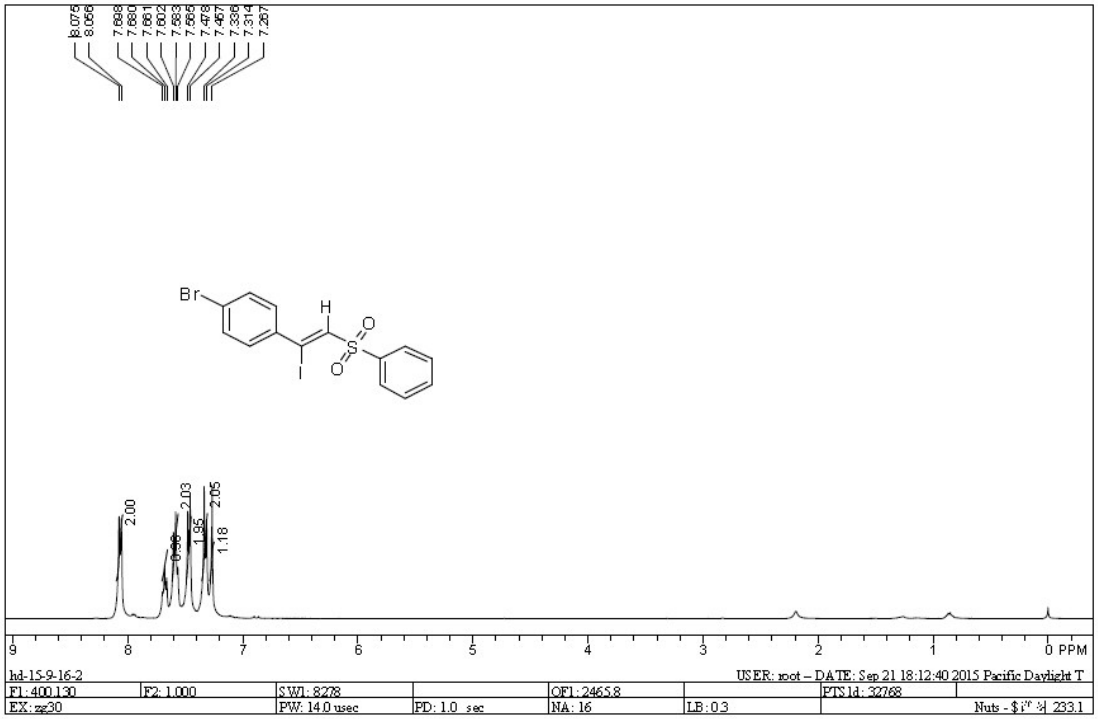


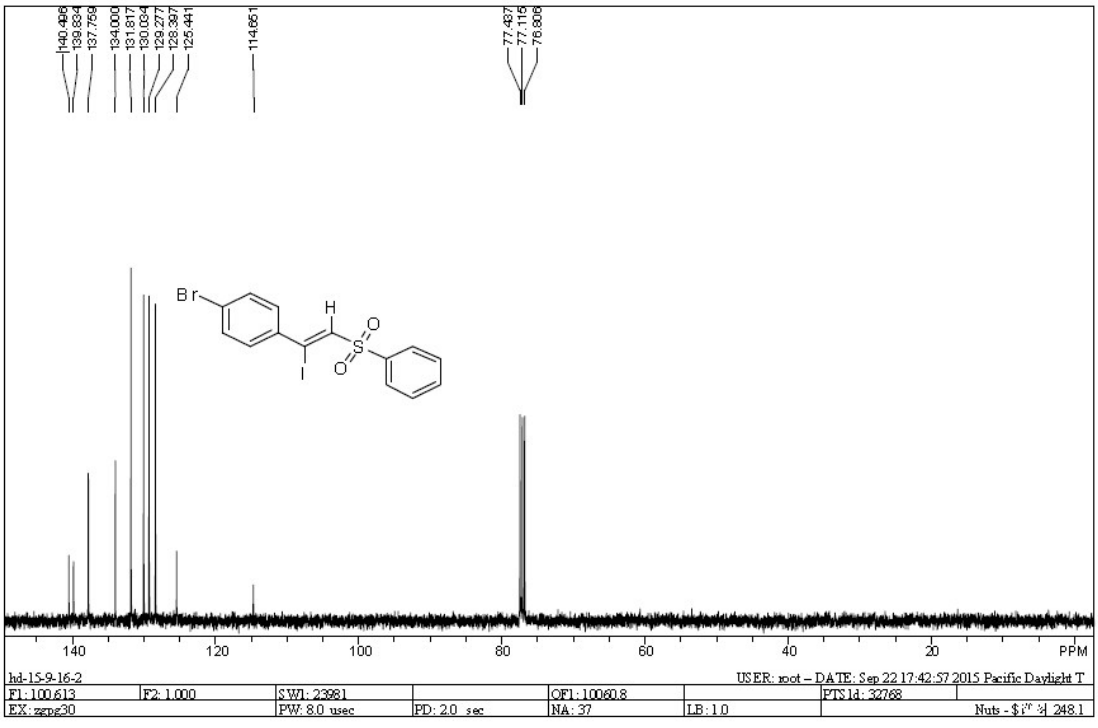
^{1}H and ^{13}C NMR spectra of **3g**



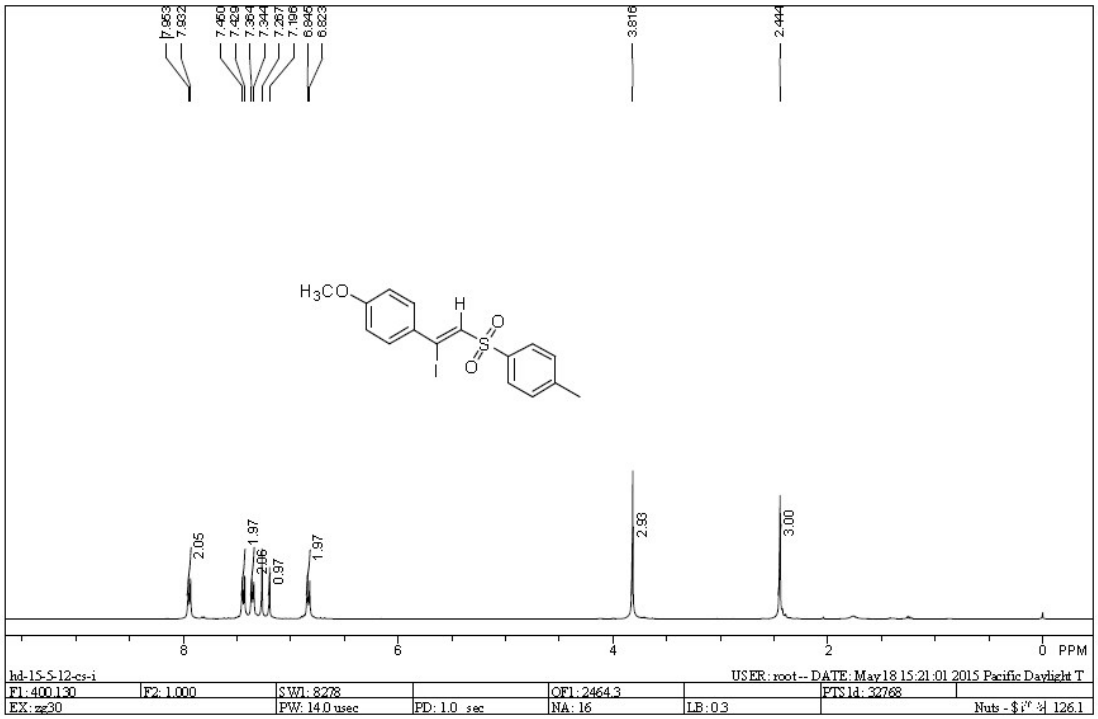


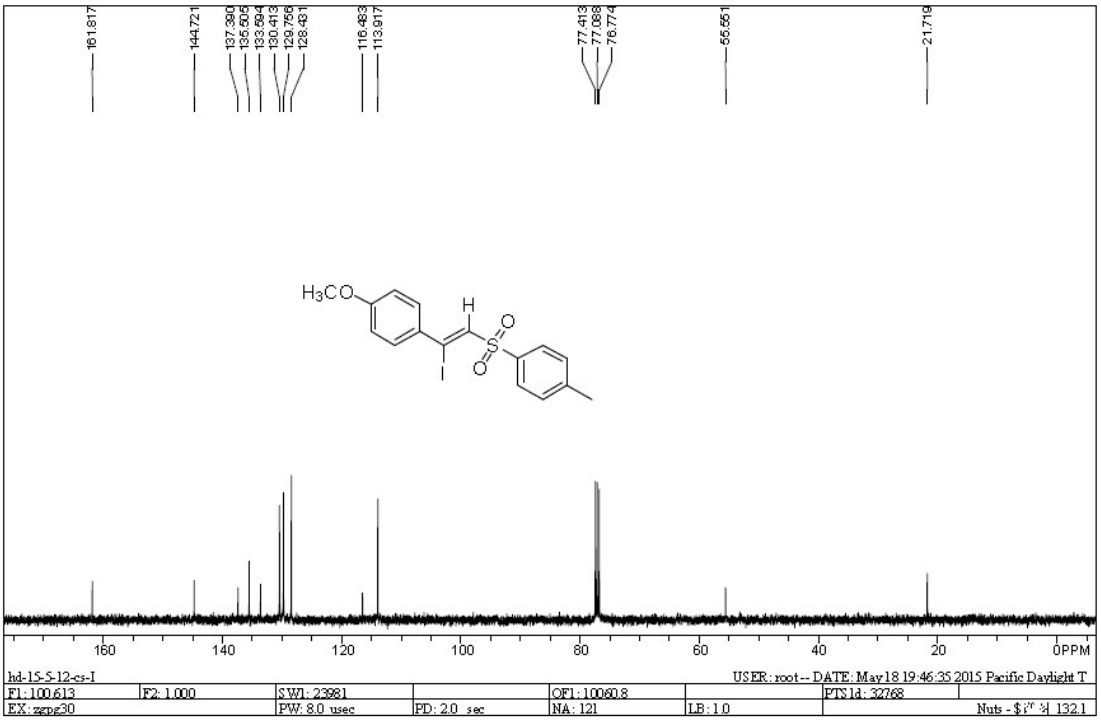
^{1}H and ^{13}C NMR spectra of **3h**



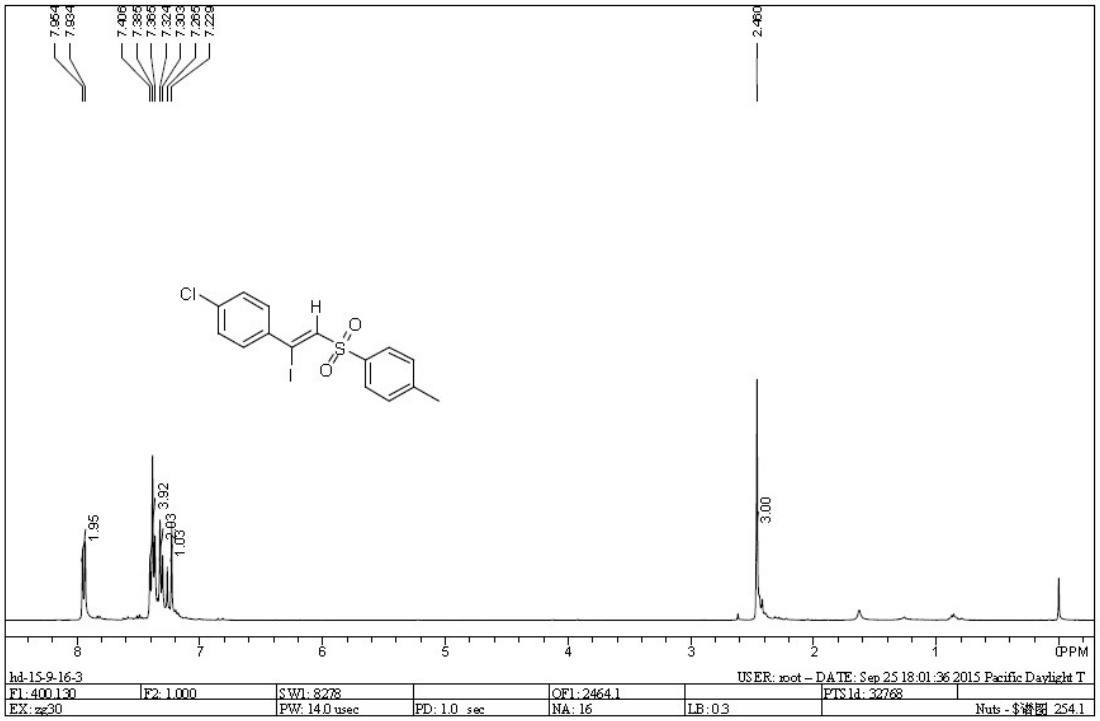


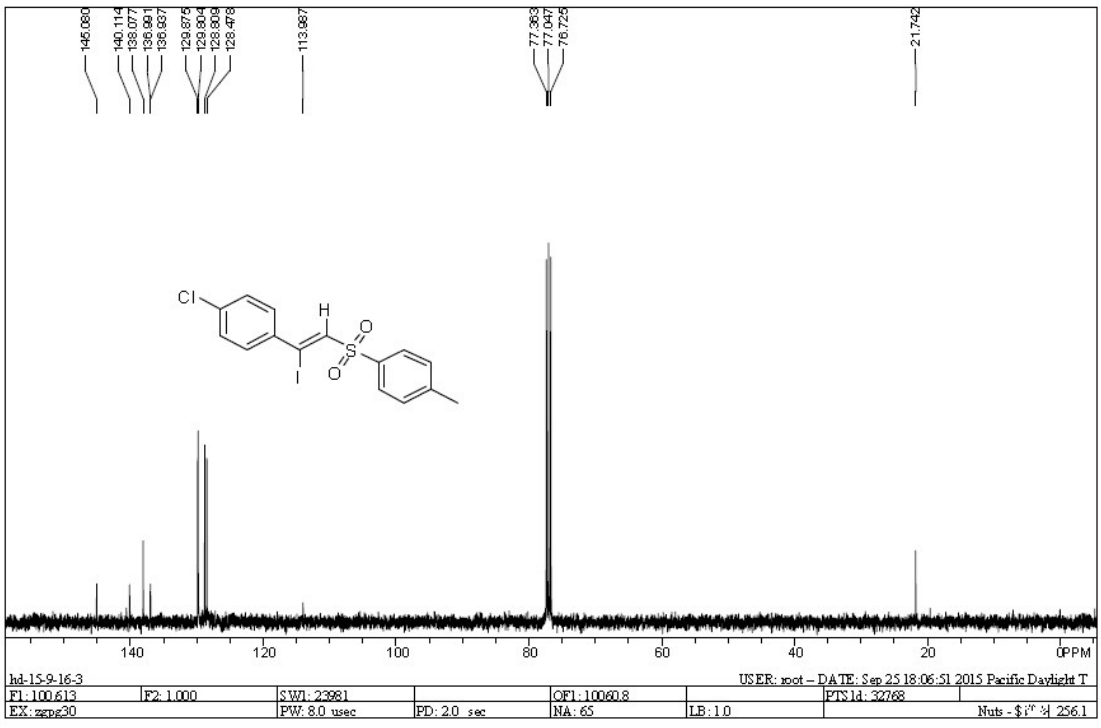
^{1}H and ^{13}C NMR spectra of **3i**



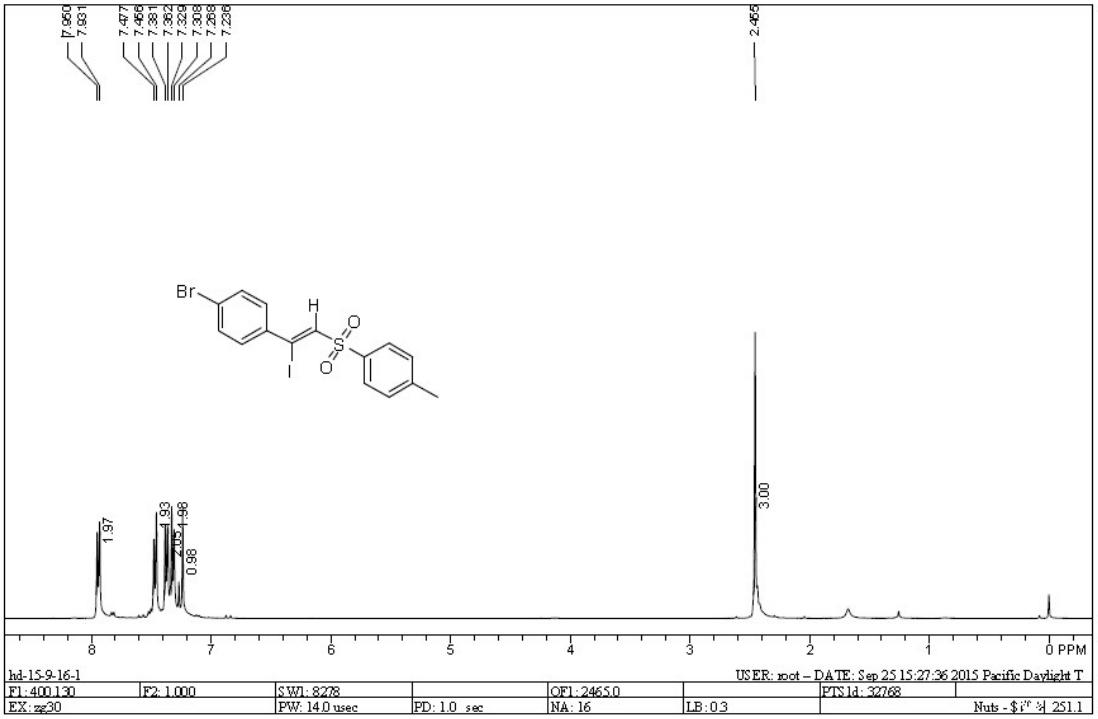


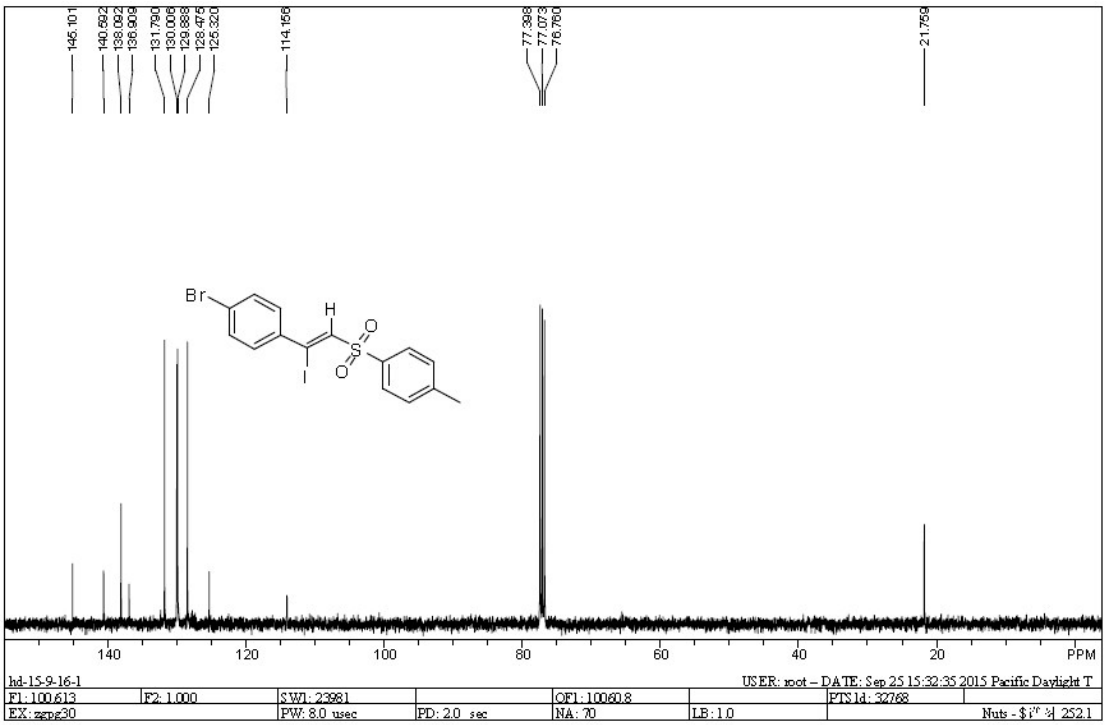
^{1}H and ^{13}C NMR spectra of **3j**



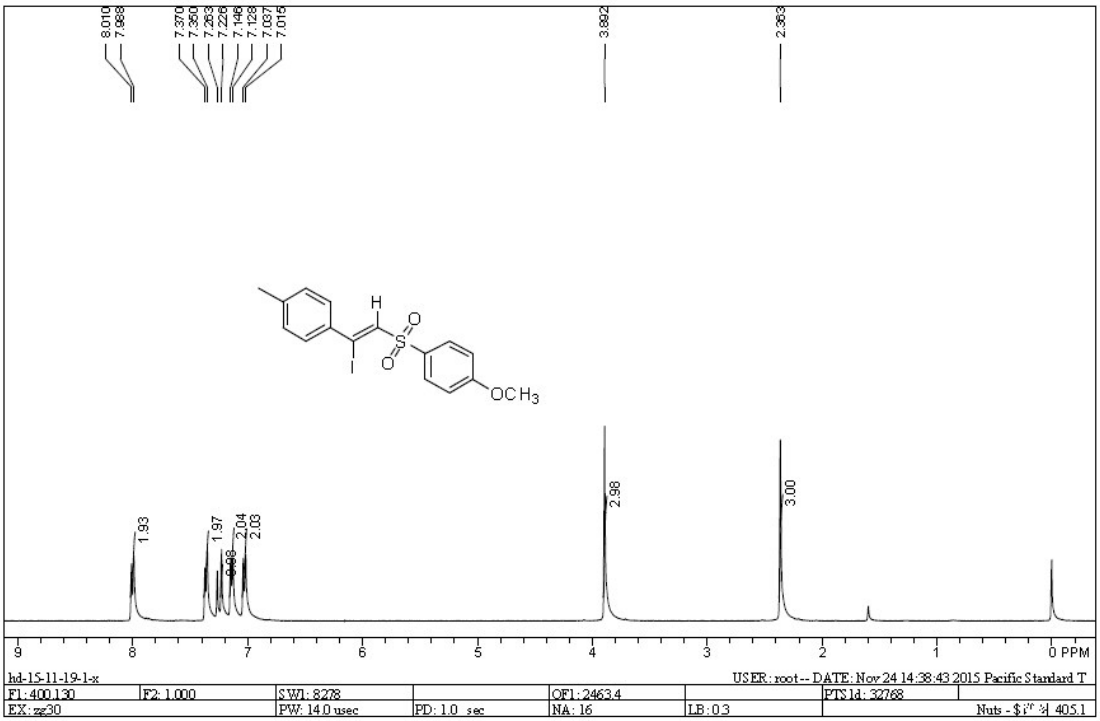


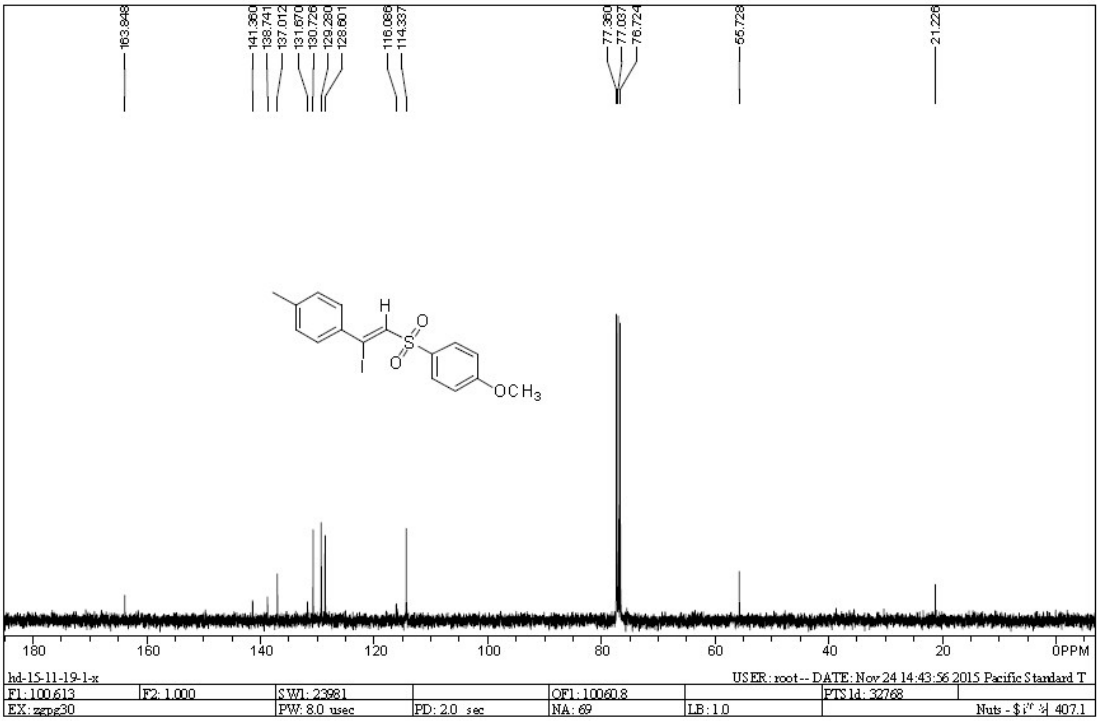
^{1}H and ^{13}C NMR spectra of **3k**



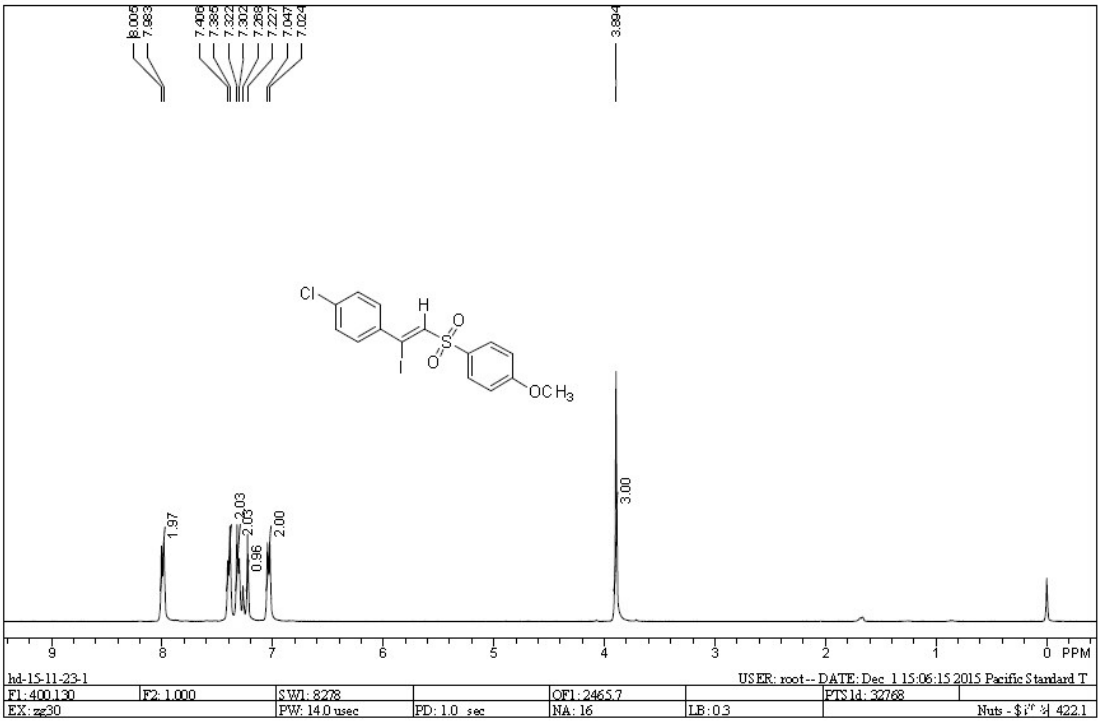


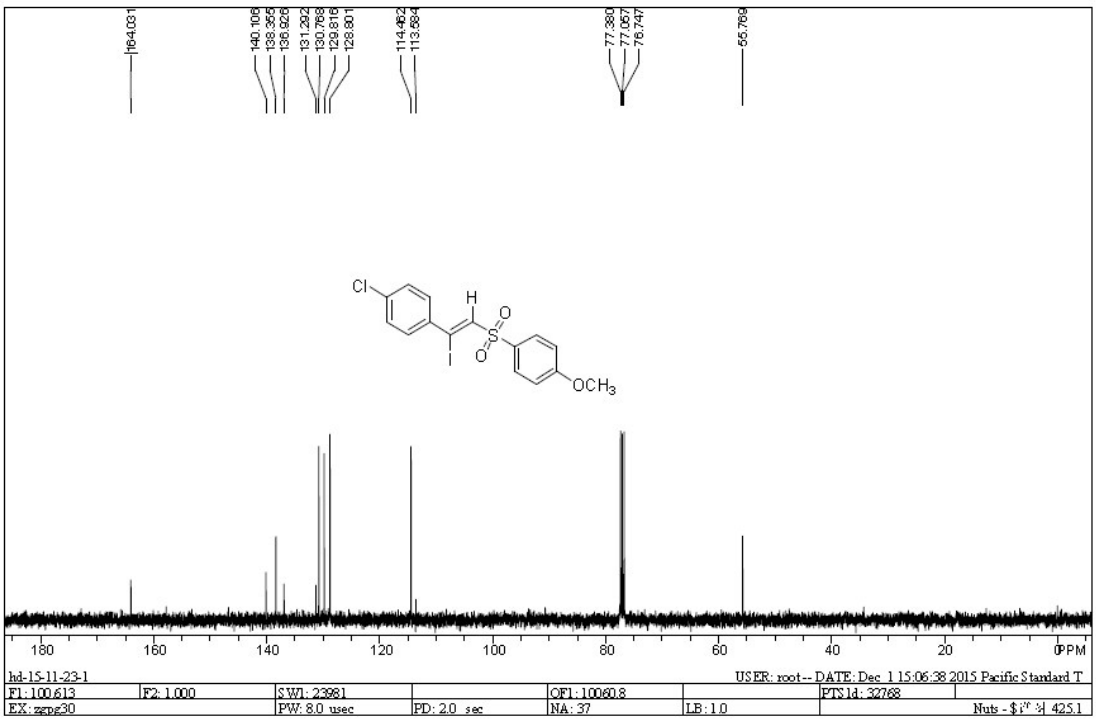
^{1}H and ^{13}C NMR spectra of **3l**



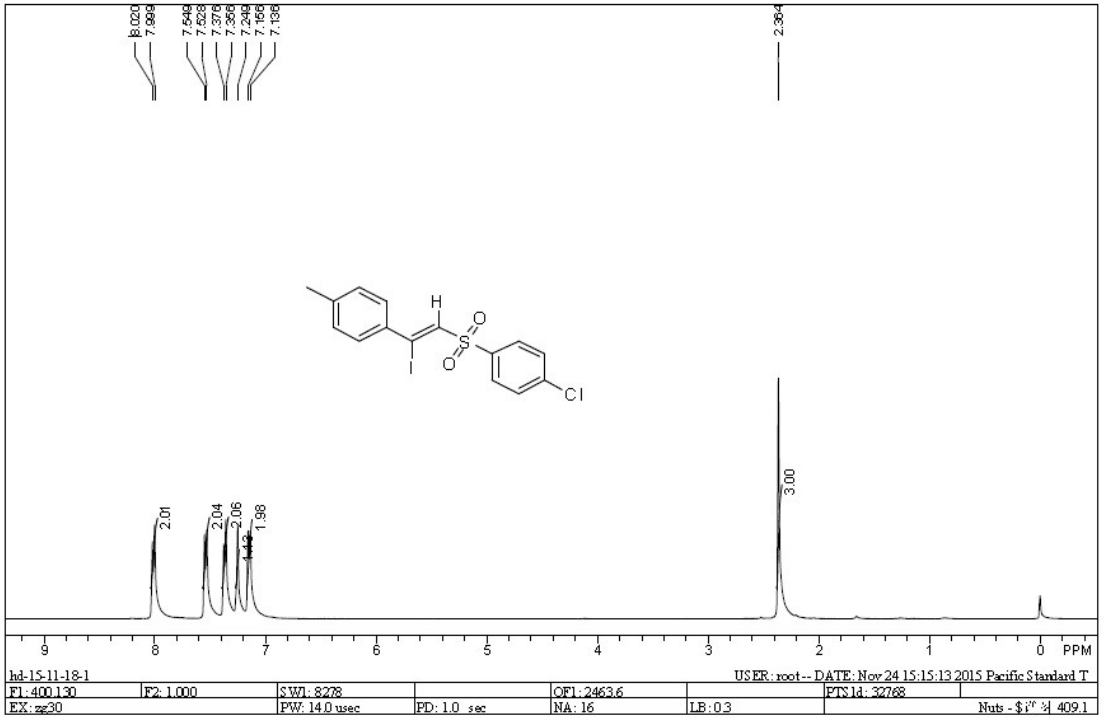


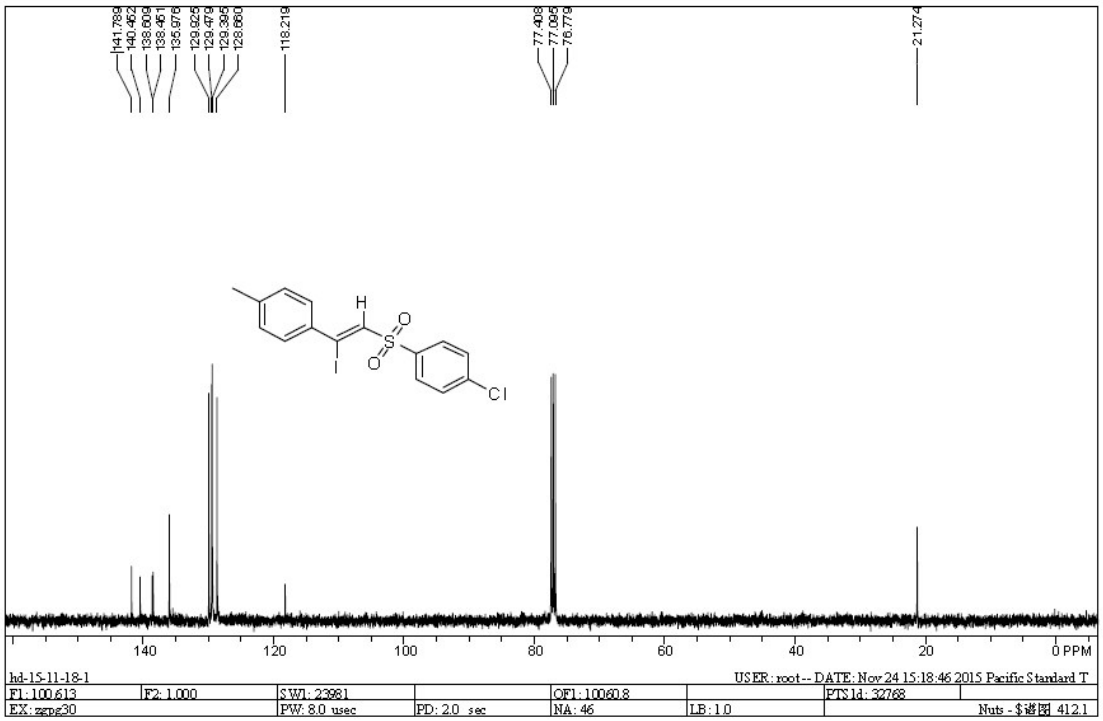
^{1}H and ^{13}C NMR spectra of **3m**



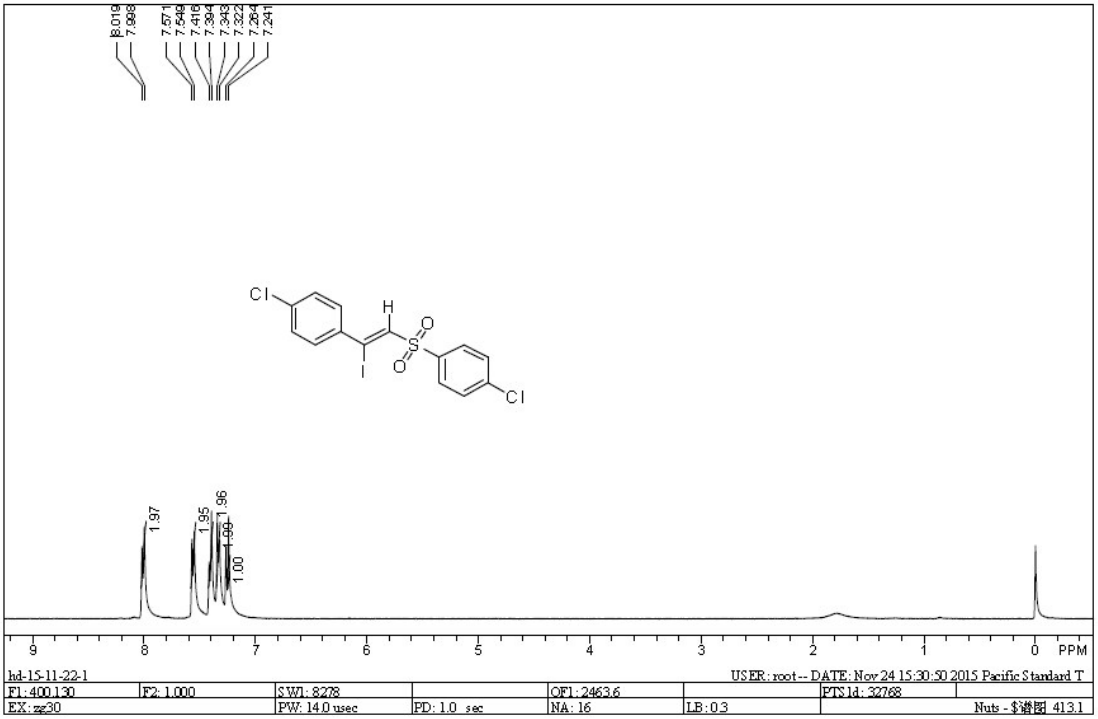


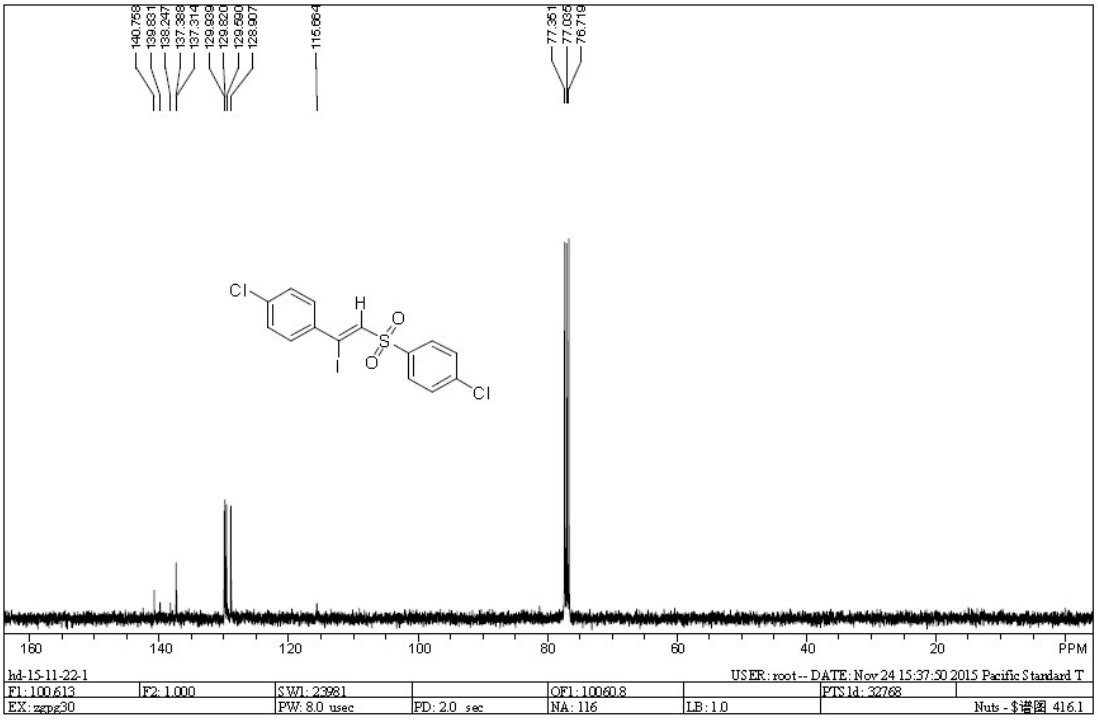
^{1}H and ^{13}C NMR spectra of **3n**



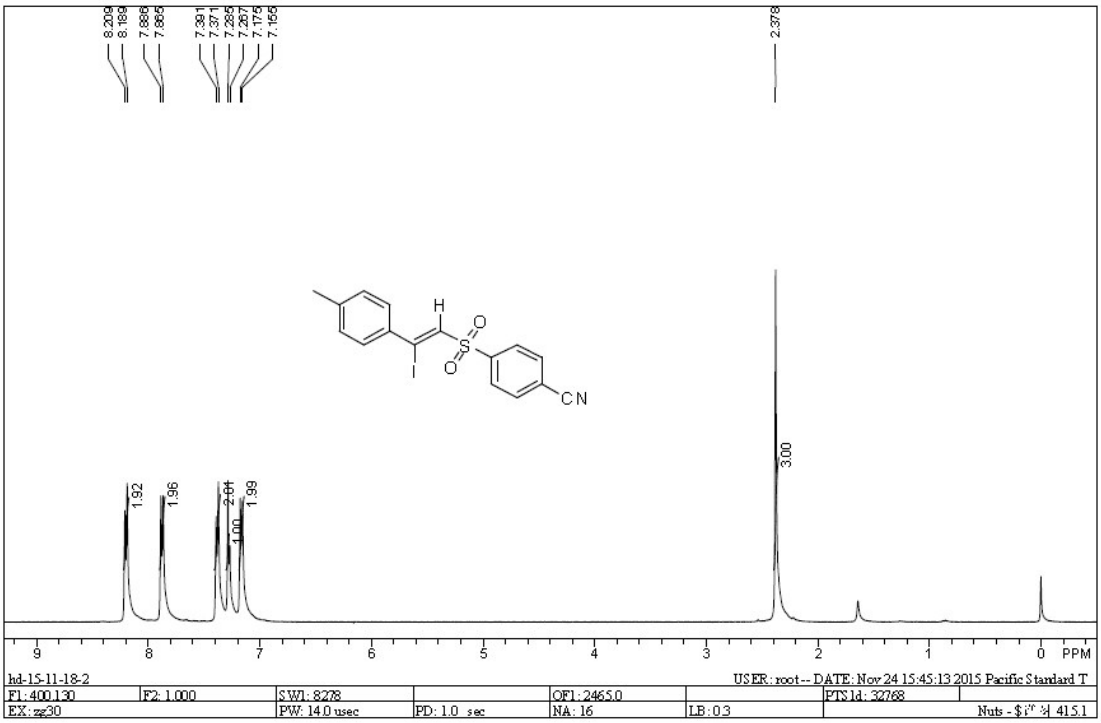


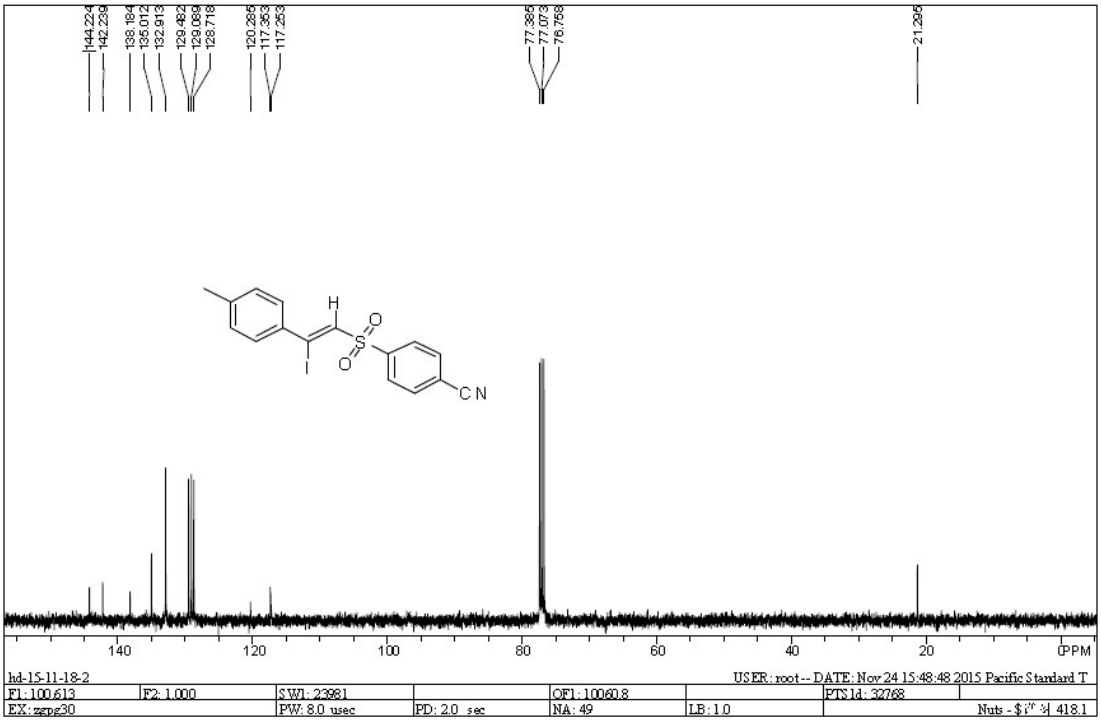
^{1}H and ^{13}C NMR spectra of **3o**



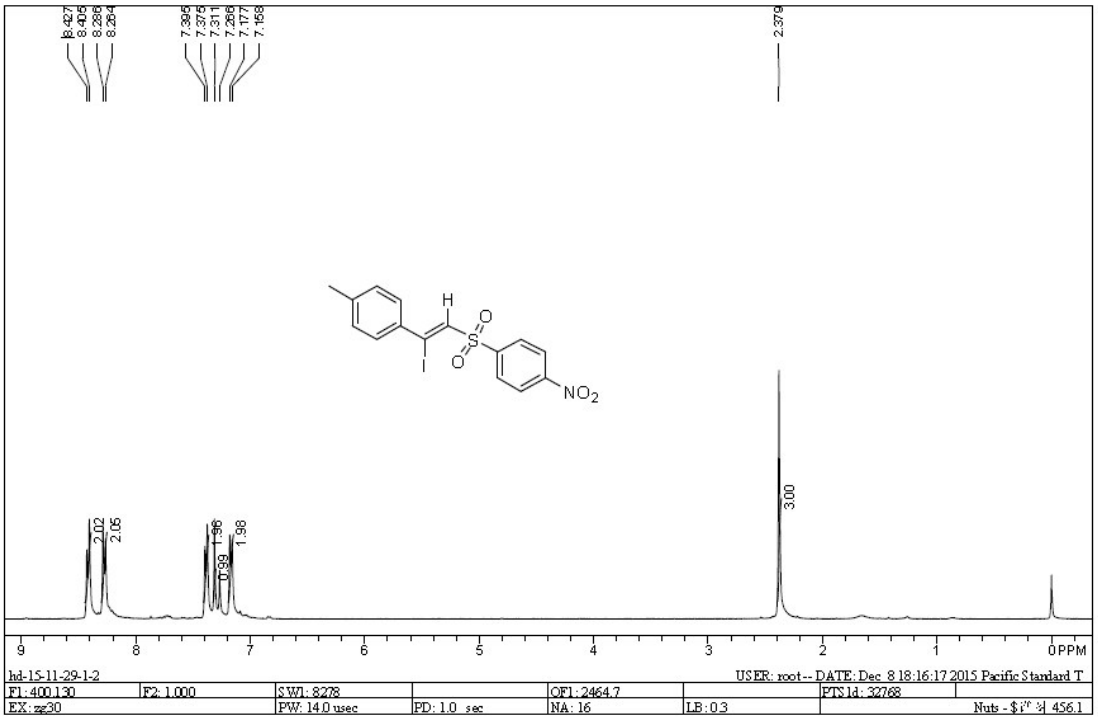


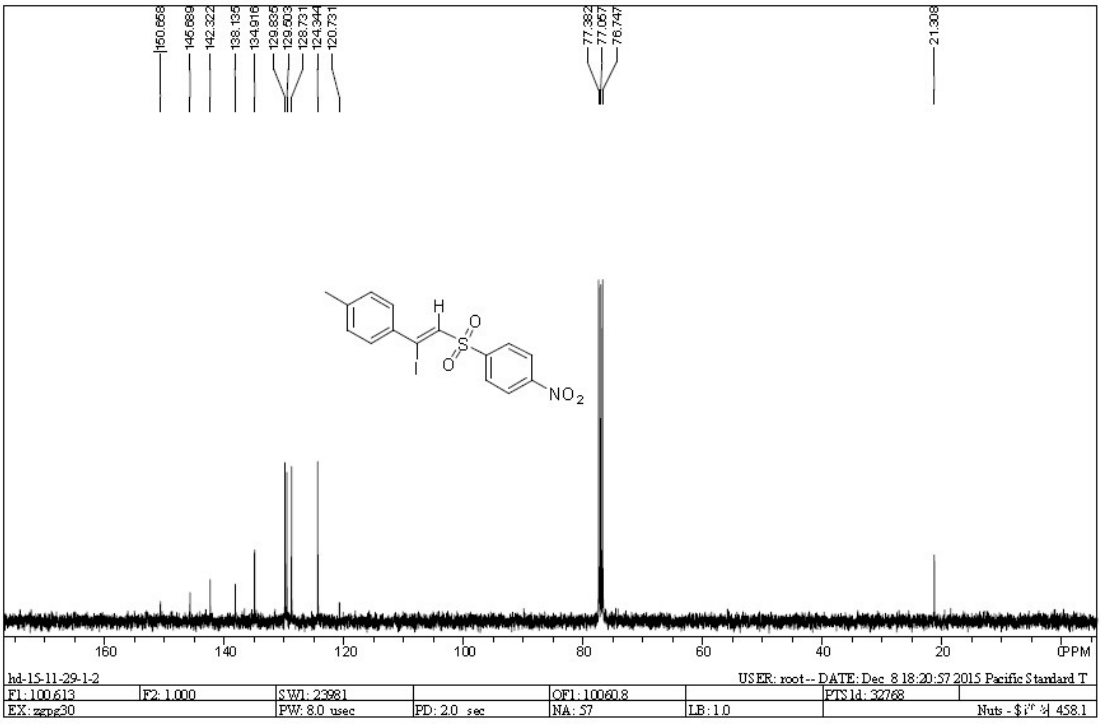
^{1}H and ^{13}C NMR spectra of **3p**



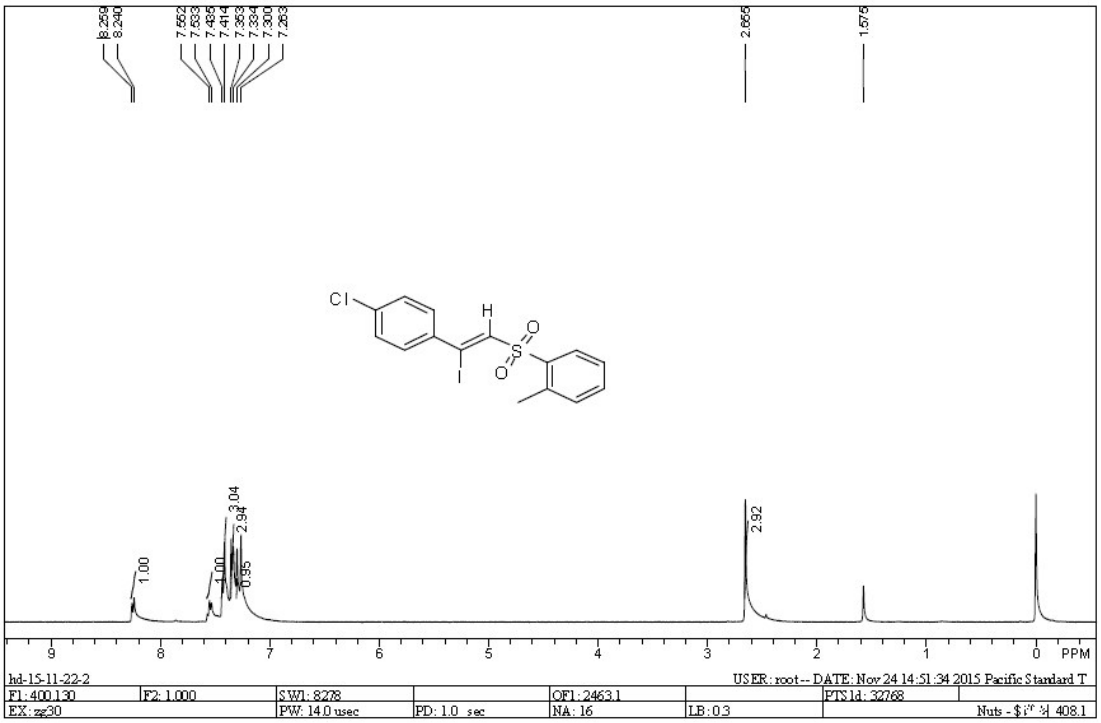


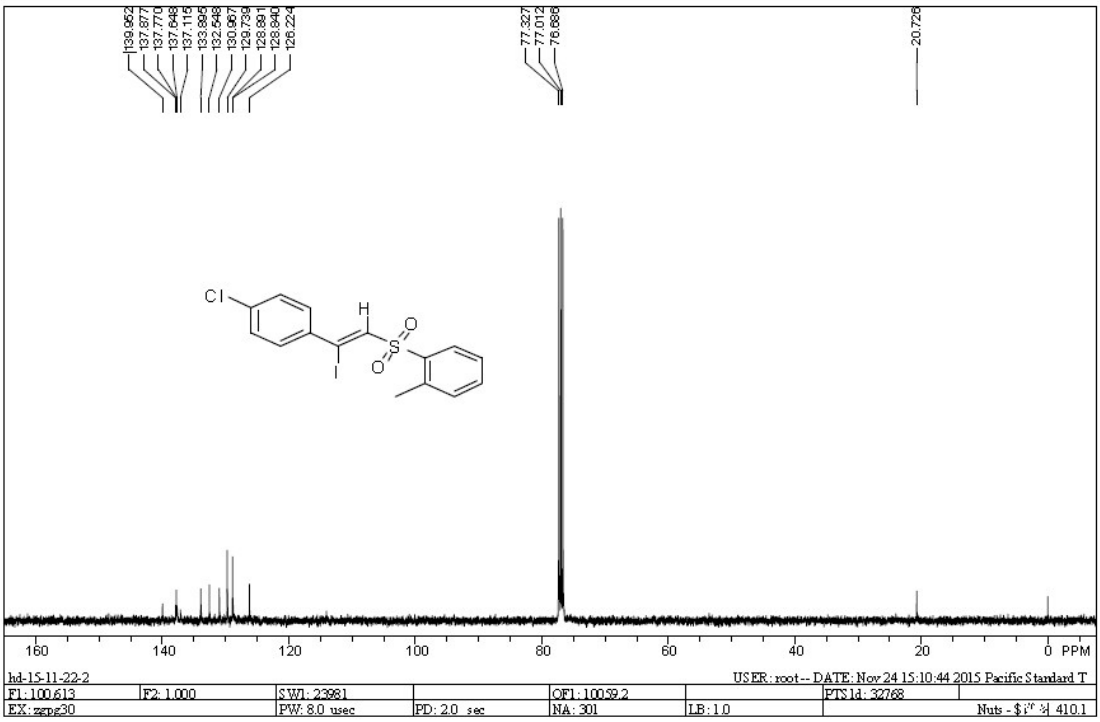
^{1}H and ^{13}C NMR spectra of **3q**



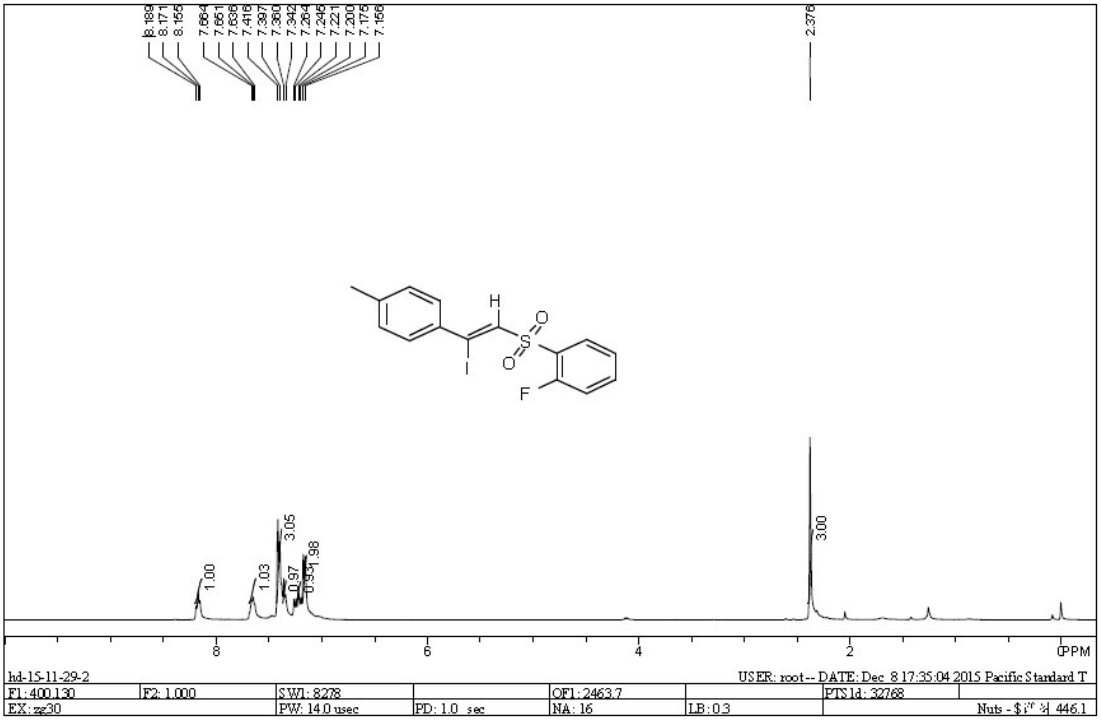


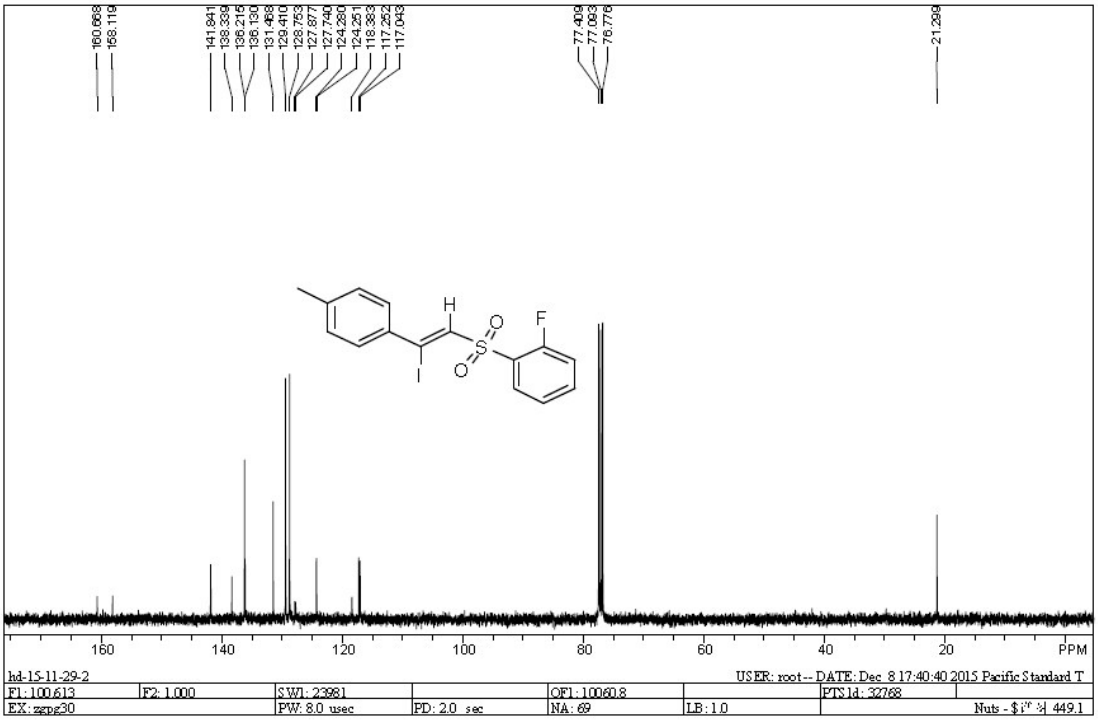
^{1}H and ^{13}C NMR spectra of **3r**



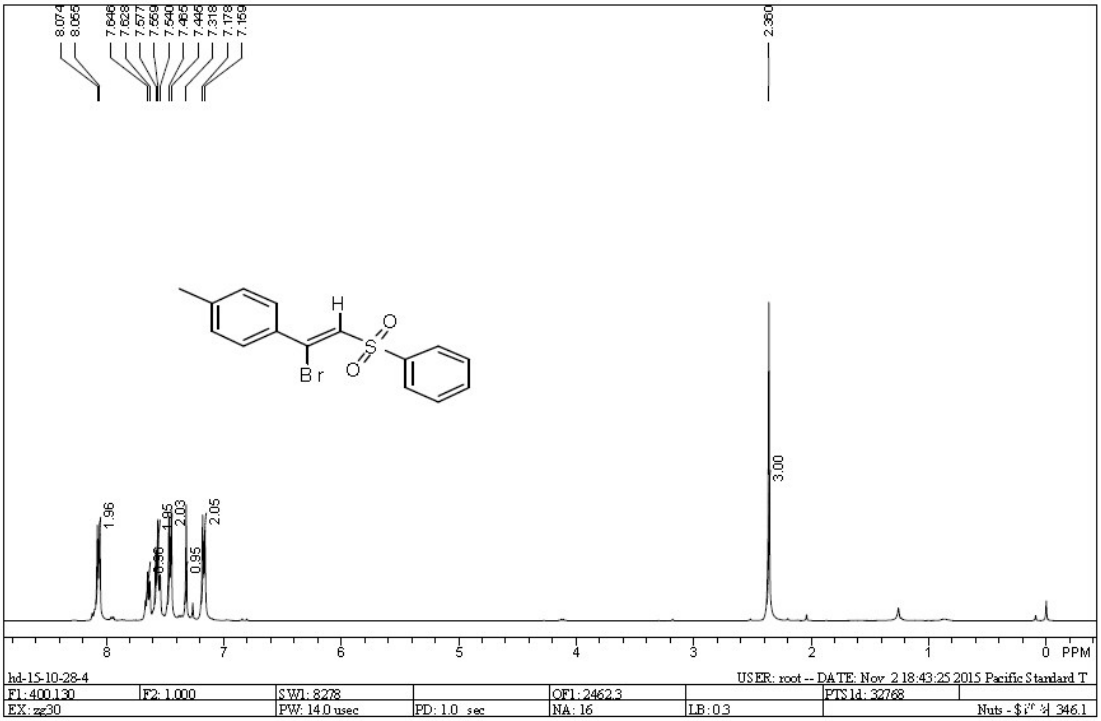


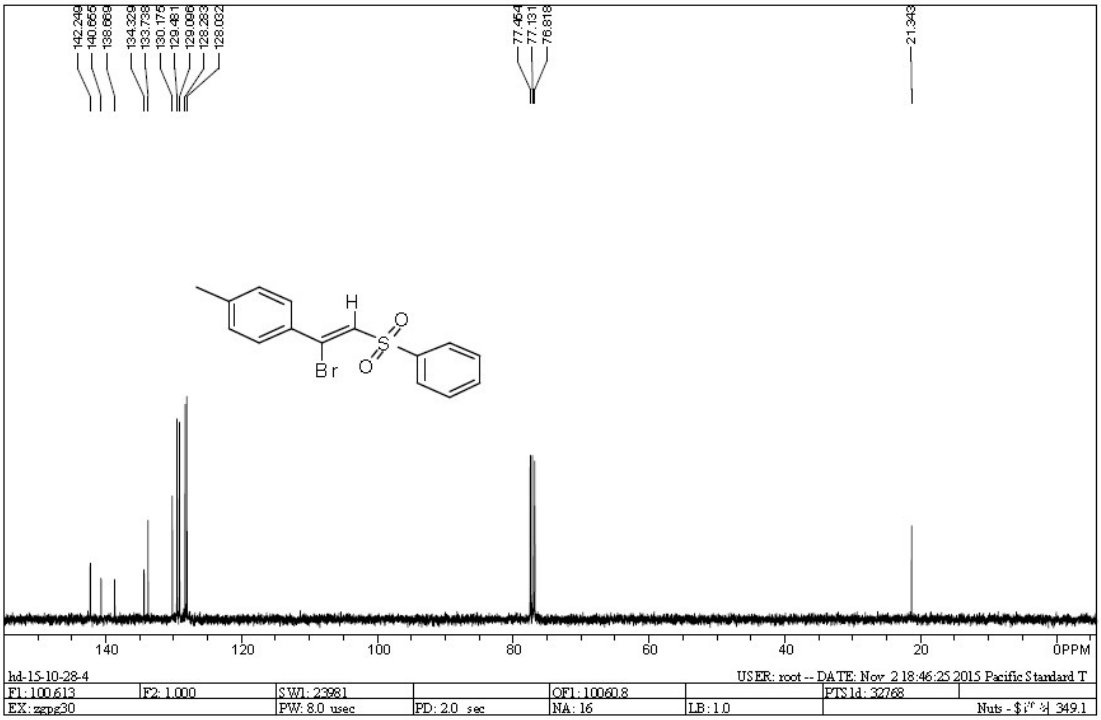
^{1}H and ^{13}C NMR spectra of **3s**



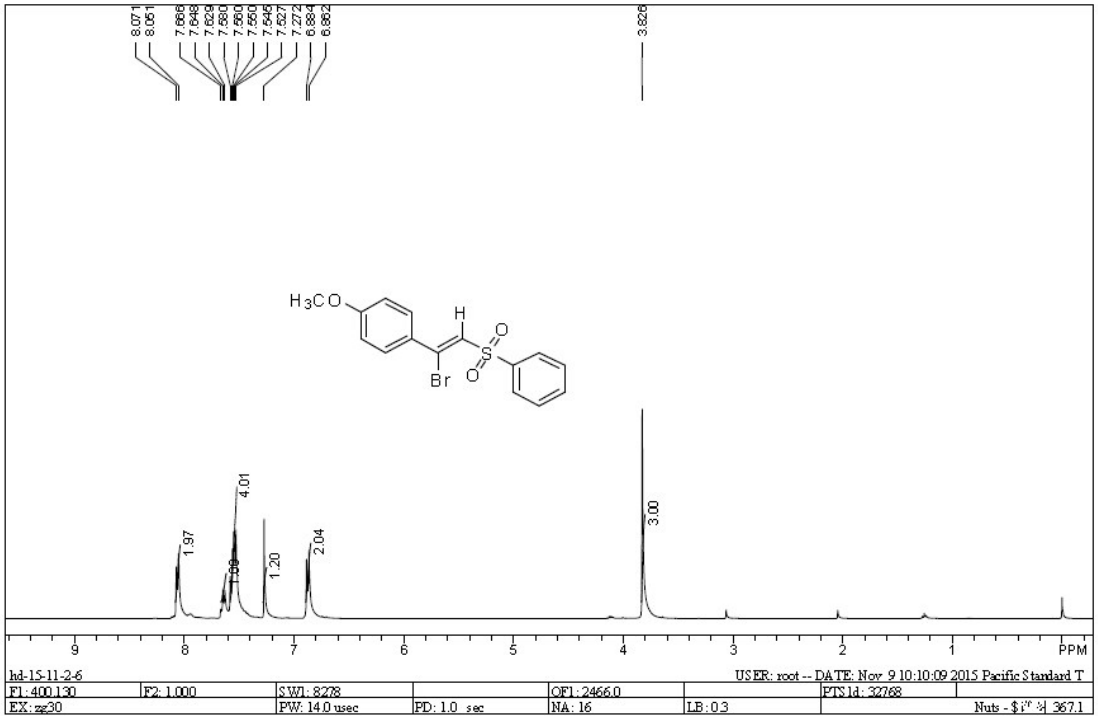


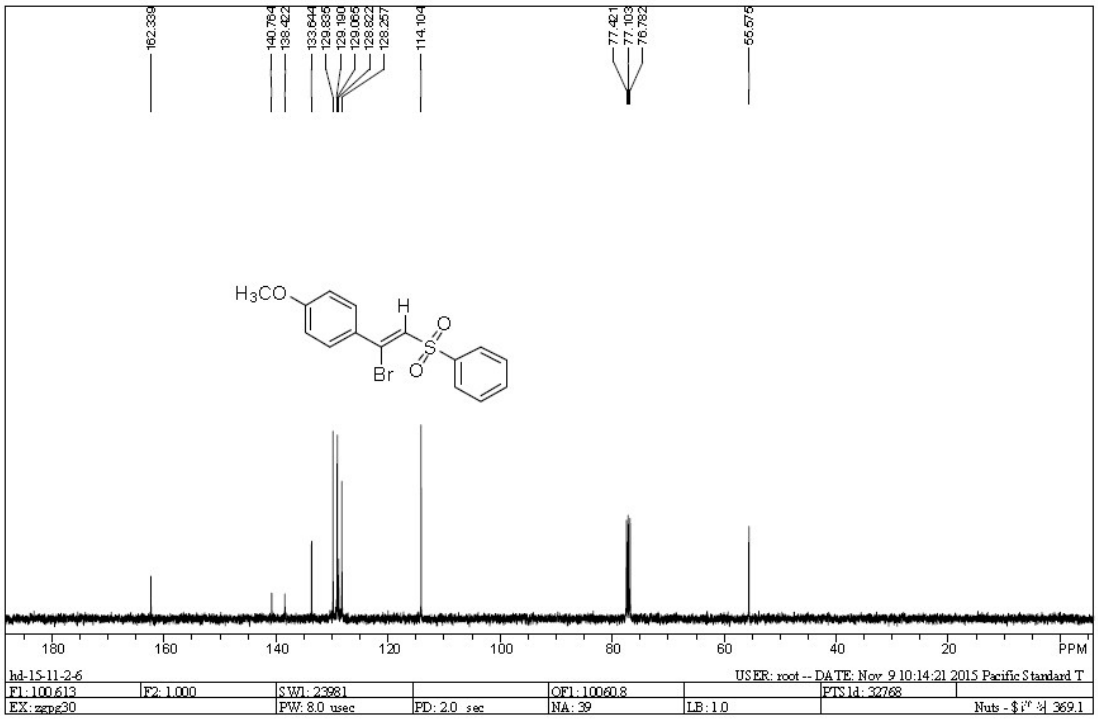
^{1}H and ^{13}C NMR spectra of **3t**



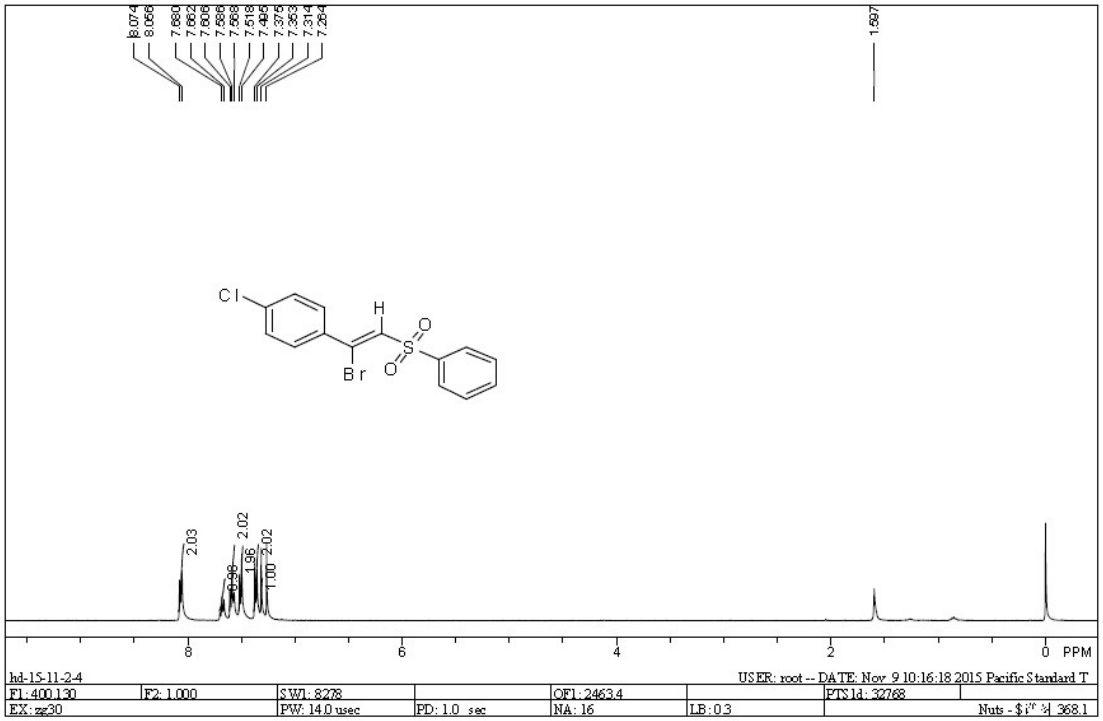


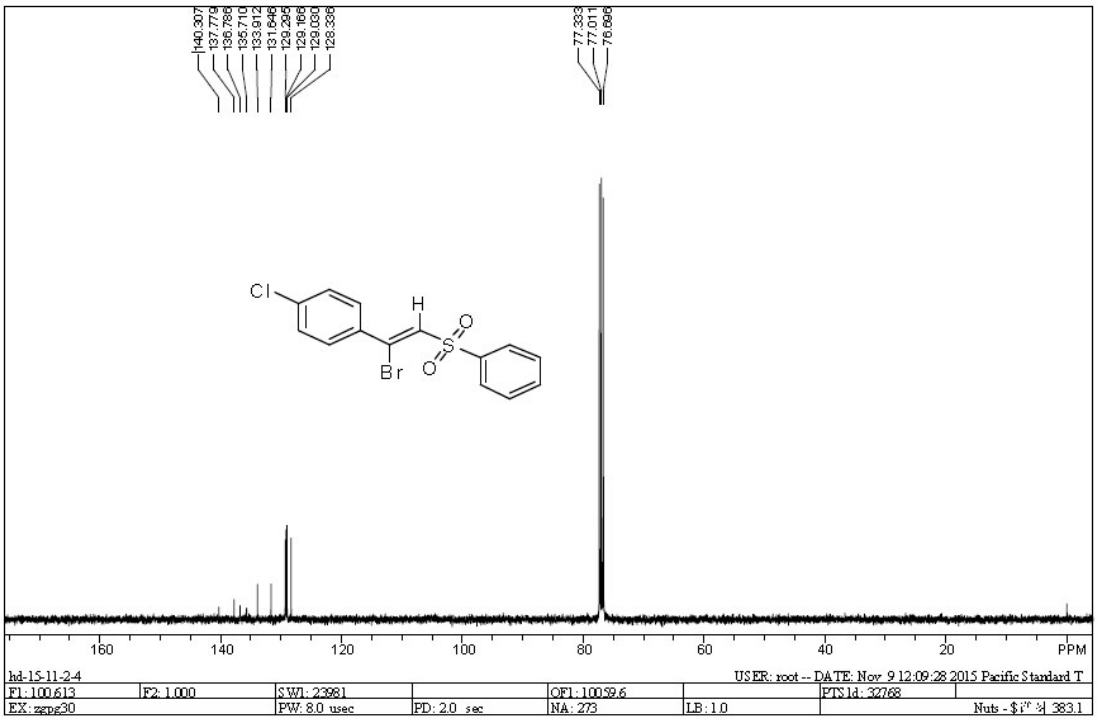
^{1}H and ^{13}C NMR spectra of **3u**



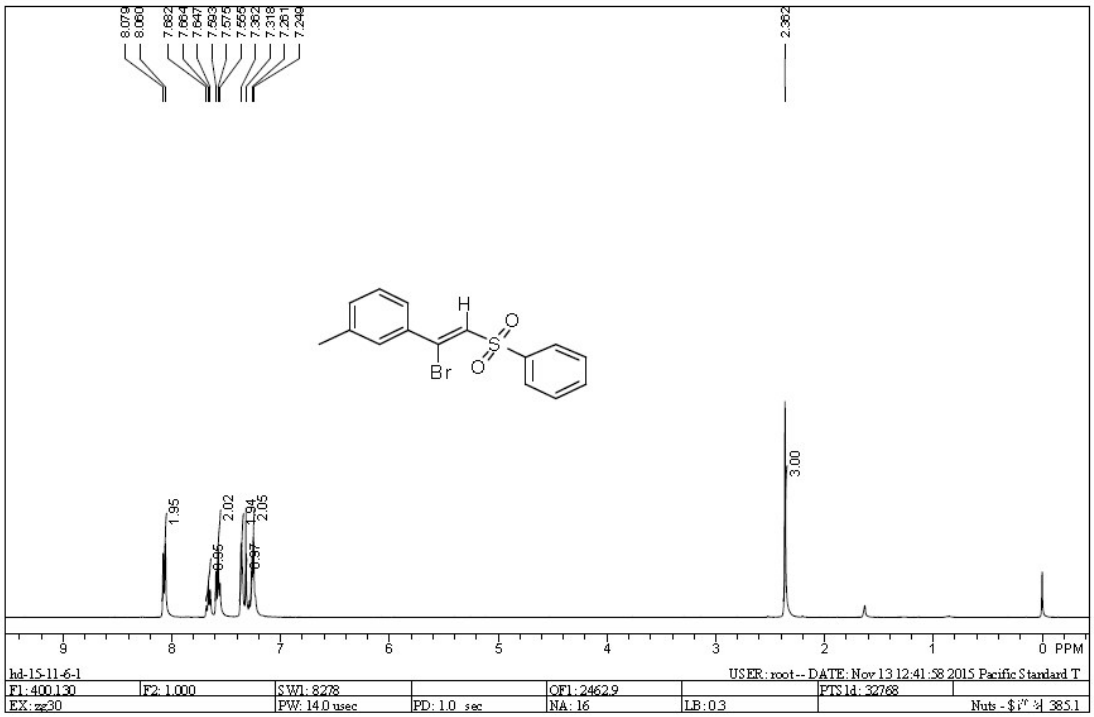


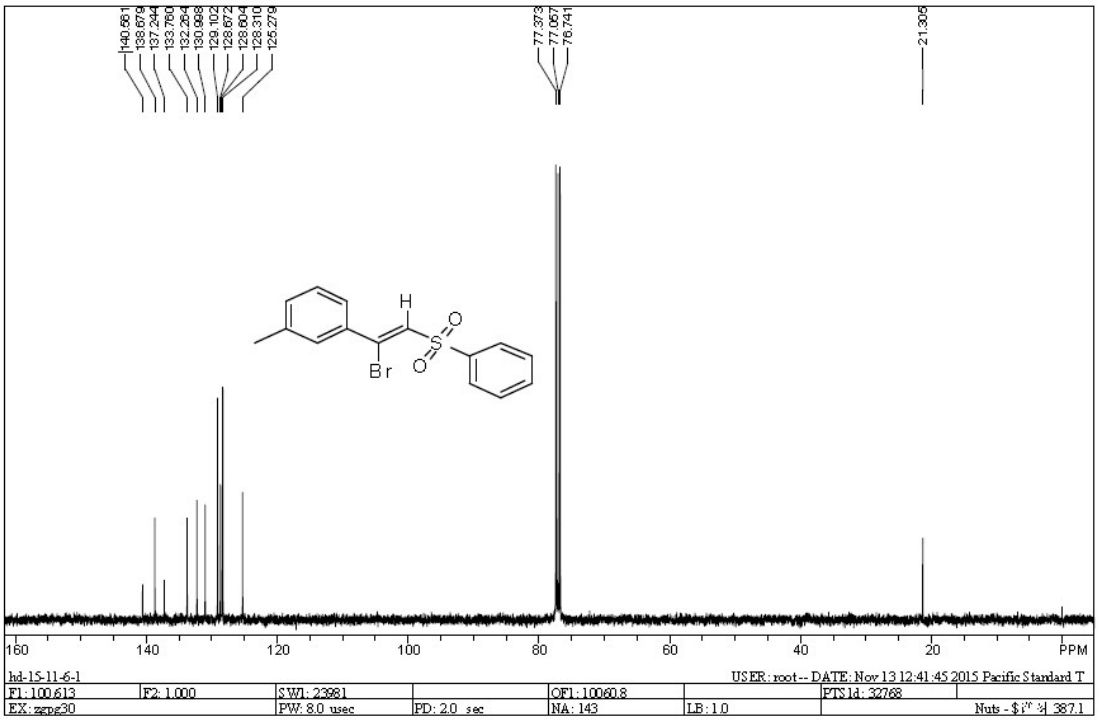
^{1}H and ^{13}C NMR spectra of **3v**



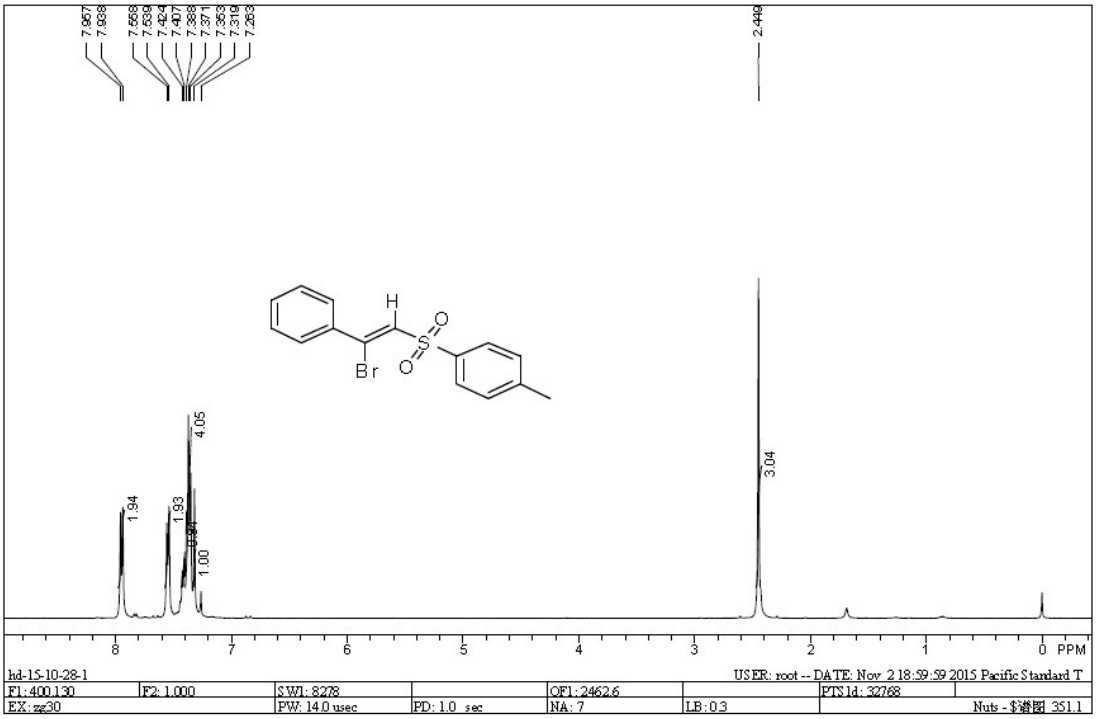


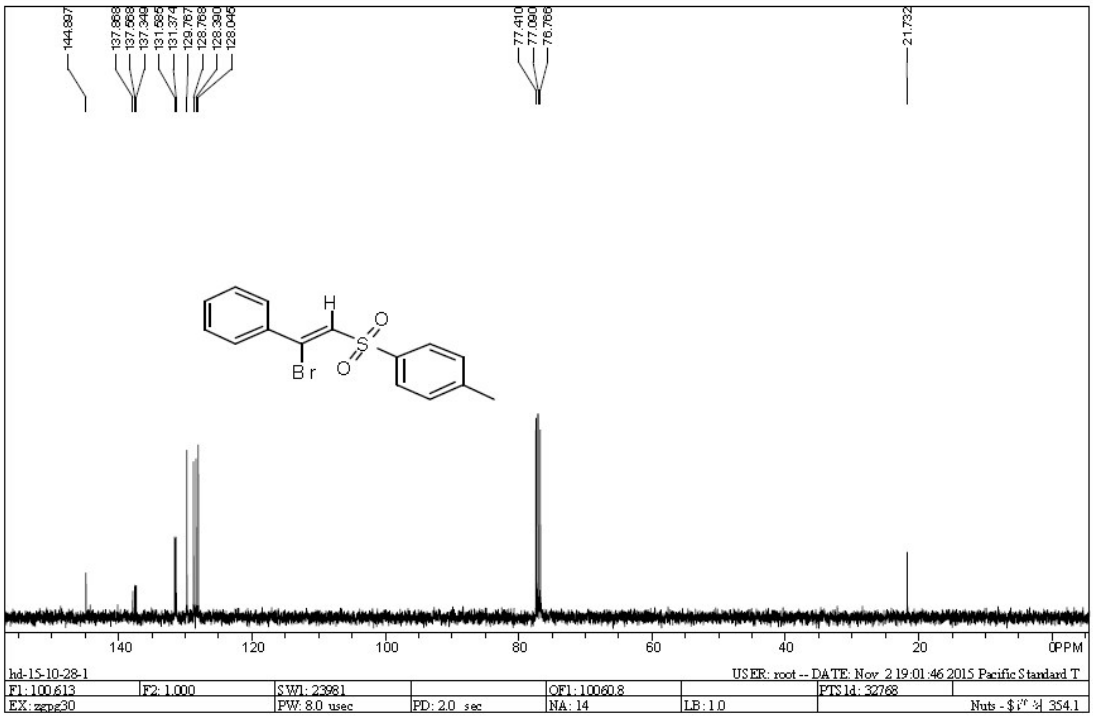
^{1}H and ^{13}C NMR spectra of **3w**



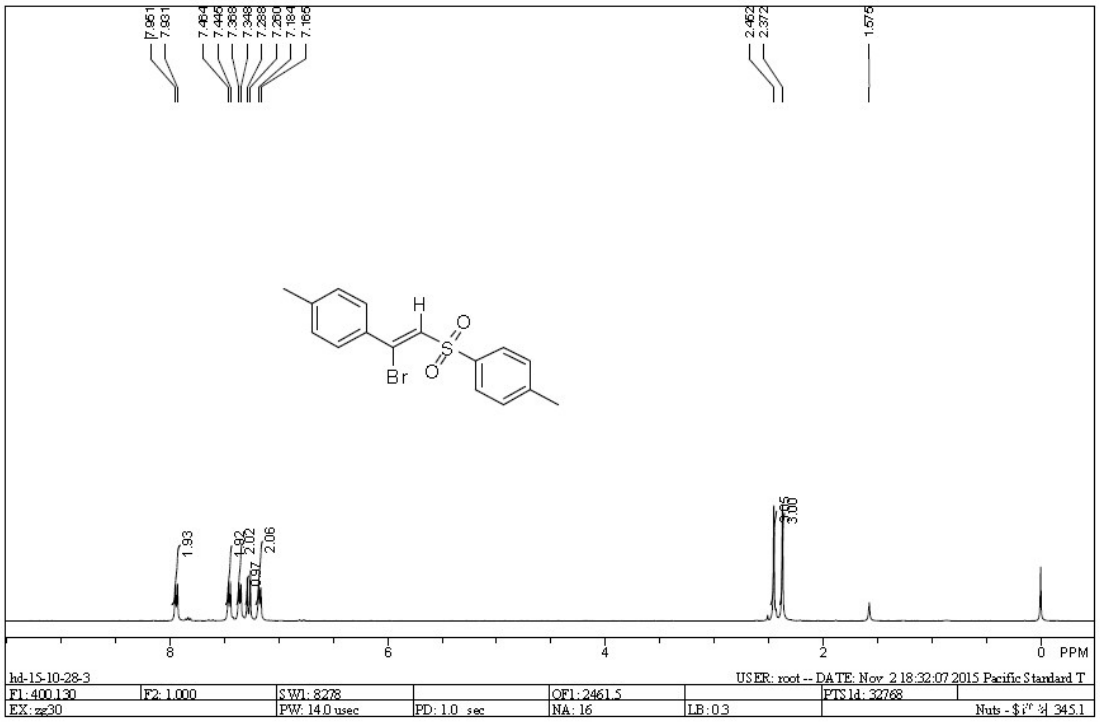


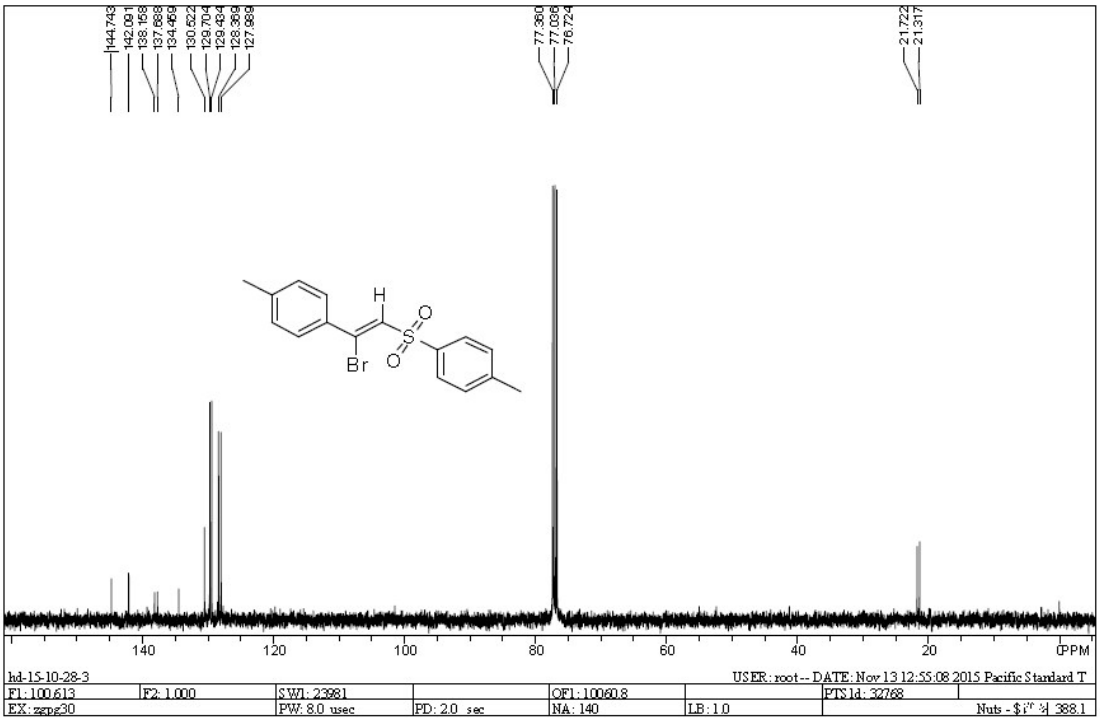
^{1}H and ^{13}C NMR spectra of **3x**



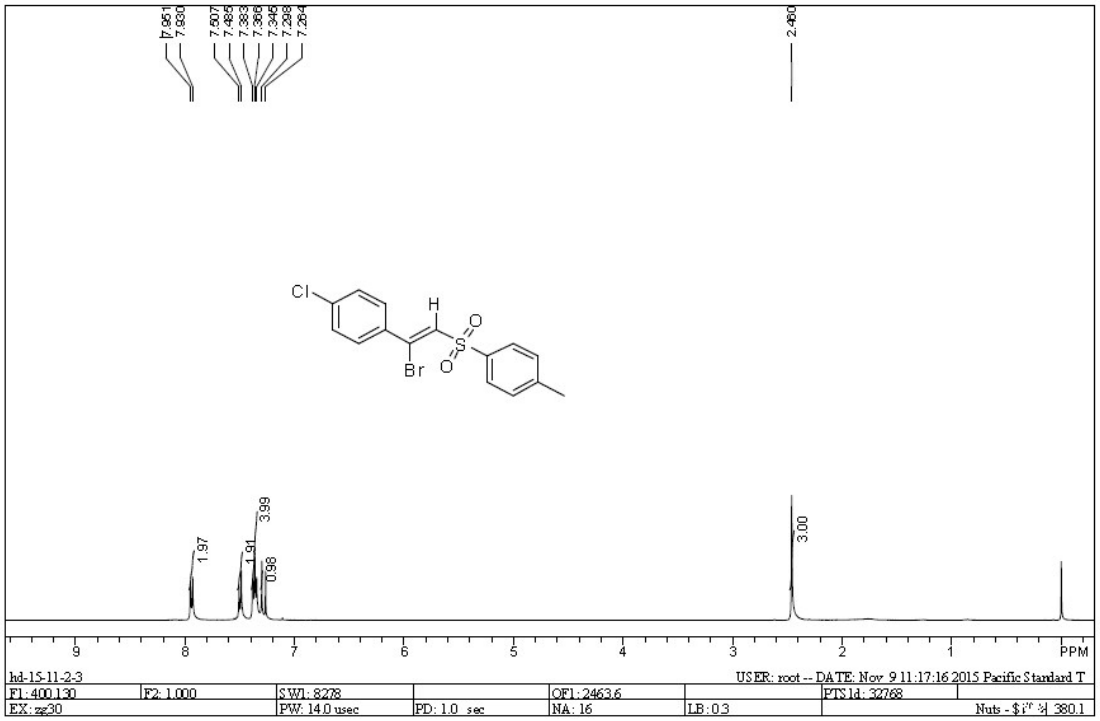


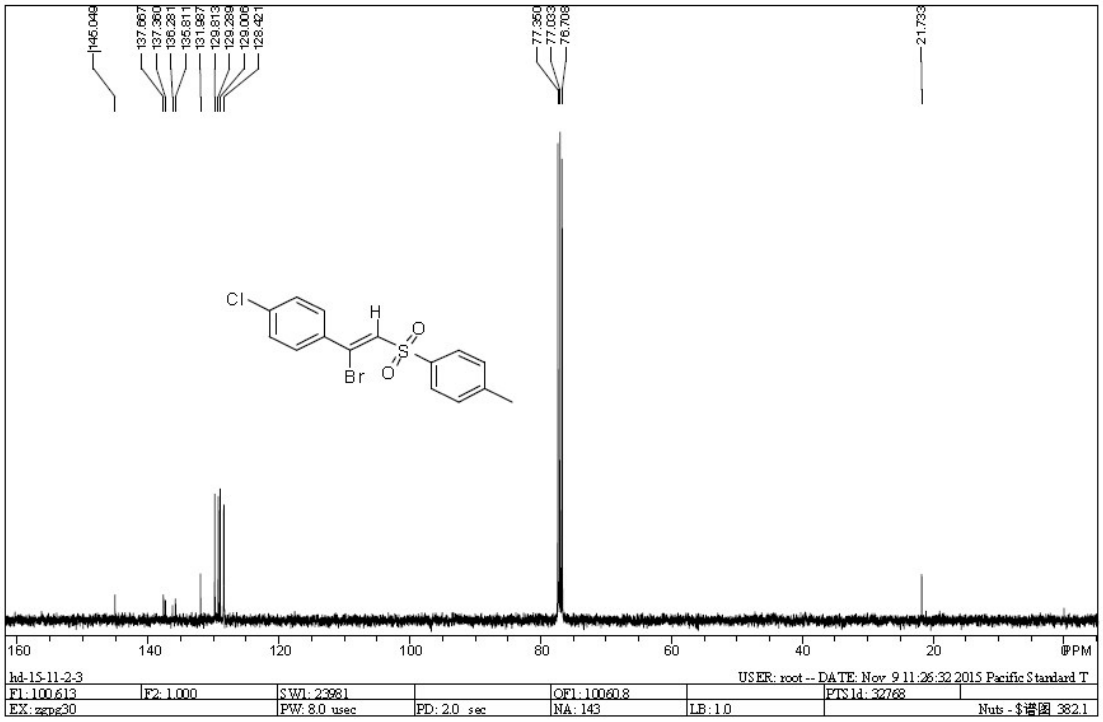
^{1}H and ^{13}C NMR spectra of **3y**



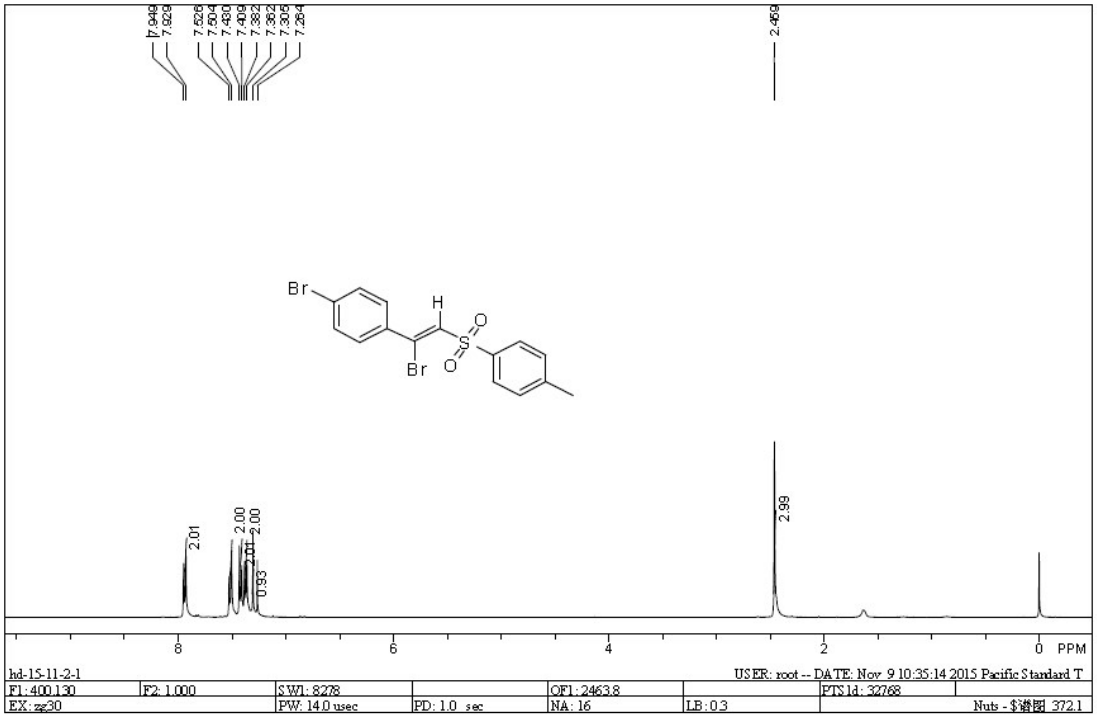


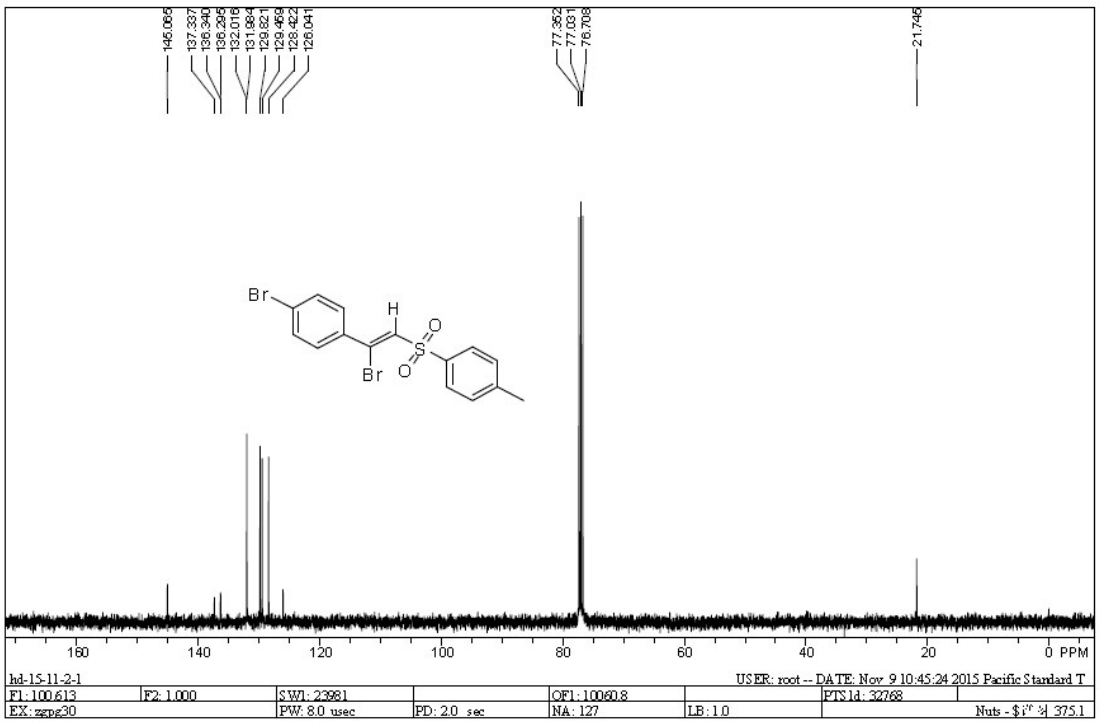
^{1}H and ^{13}C NMR spectra of **3z**



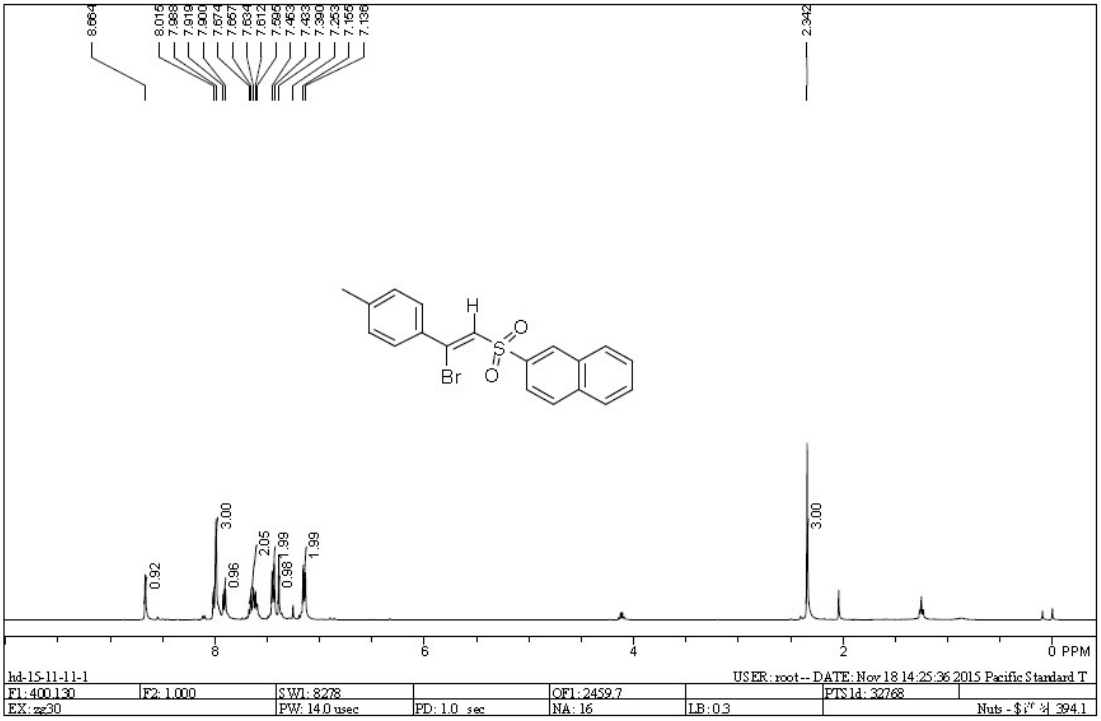


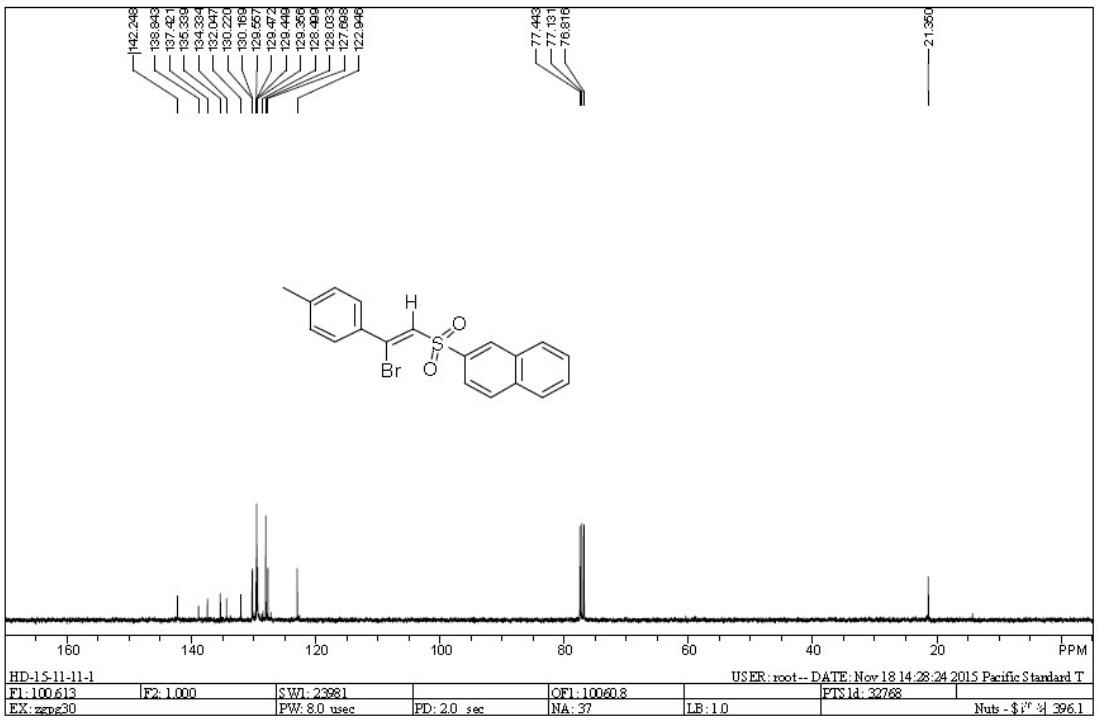
^{1}H and ^{13}C NMR spectra of **3aa**



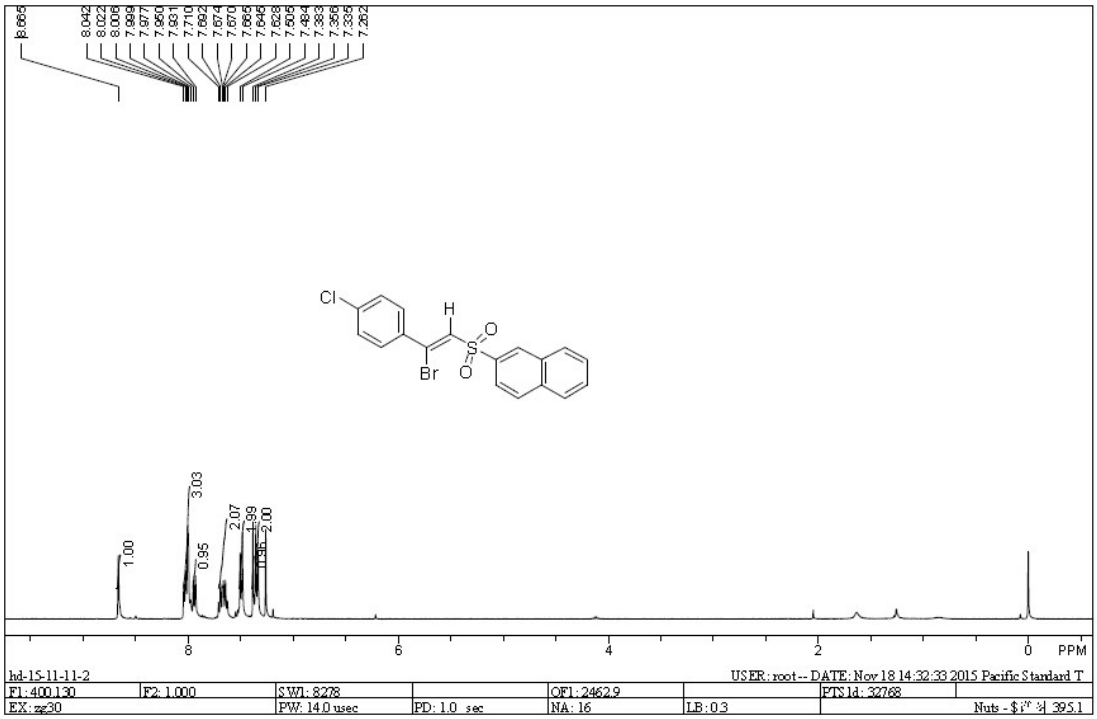


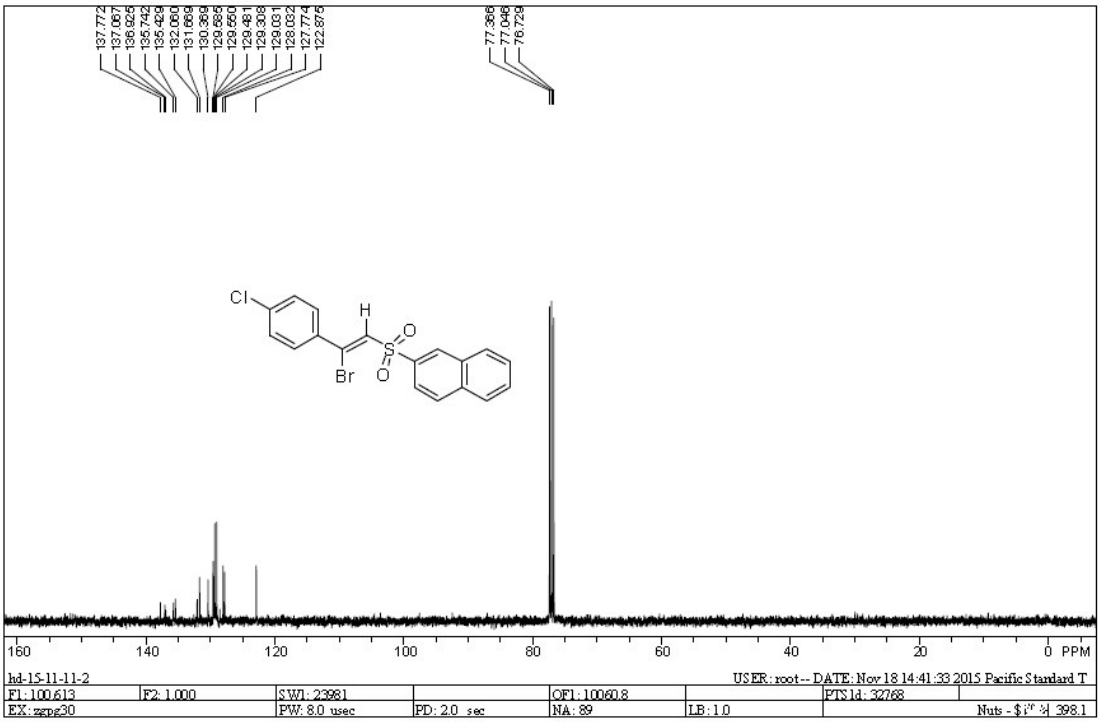
^{1}H and ^{13}C NMR spectra of **3ab**



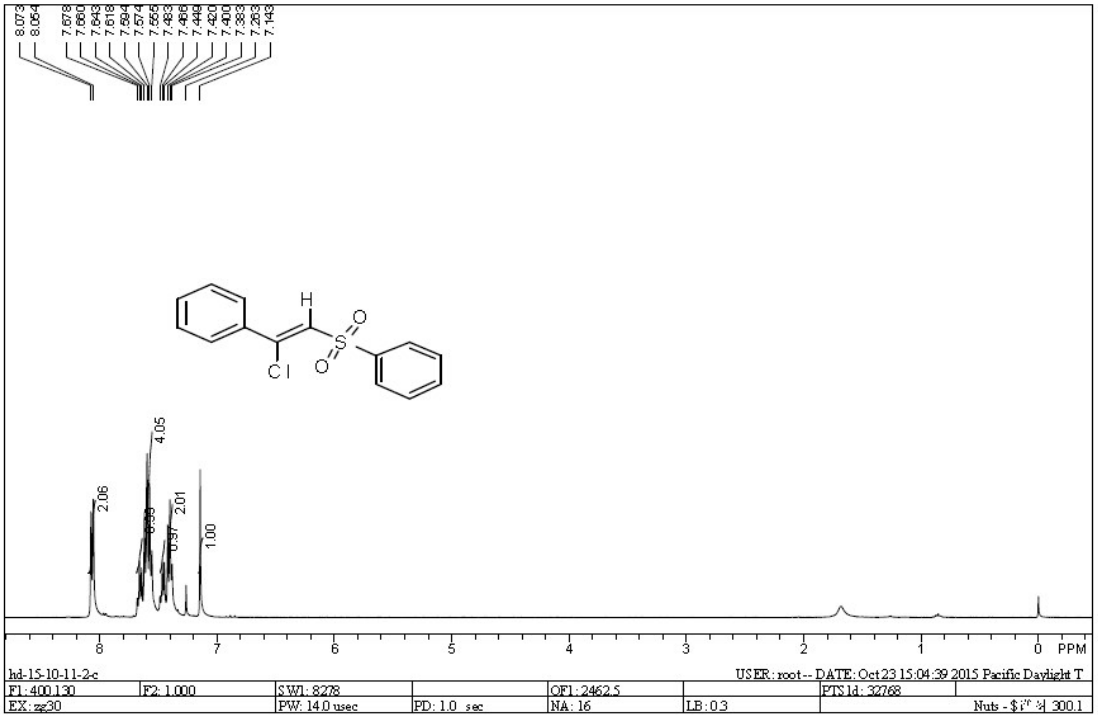


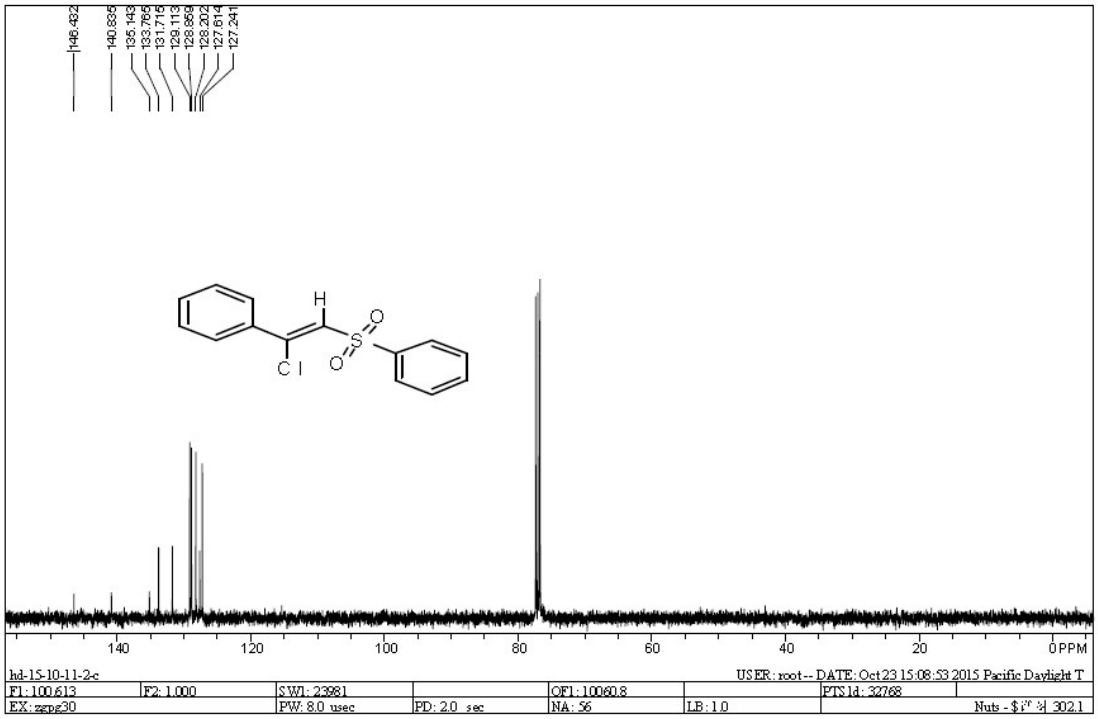
^{1}H and ^{13}C NMR spectra of **3ac**



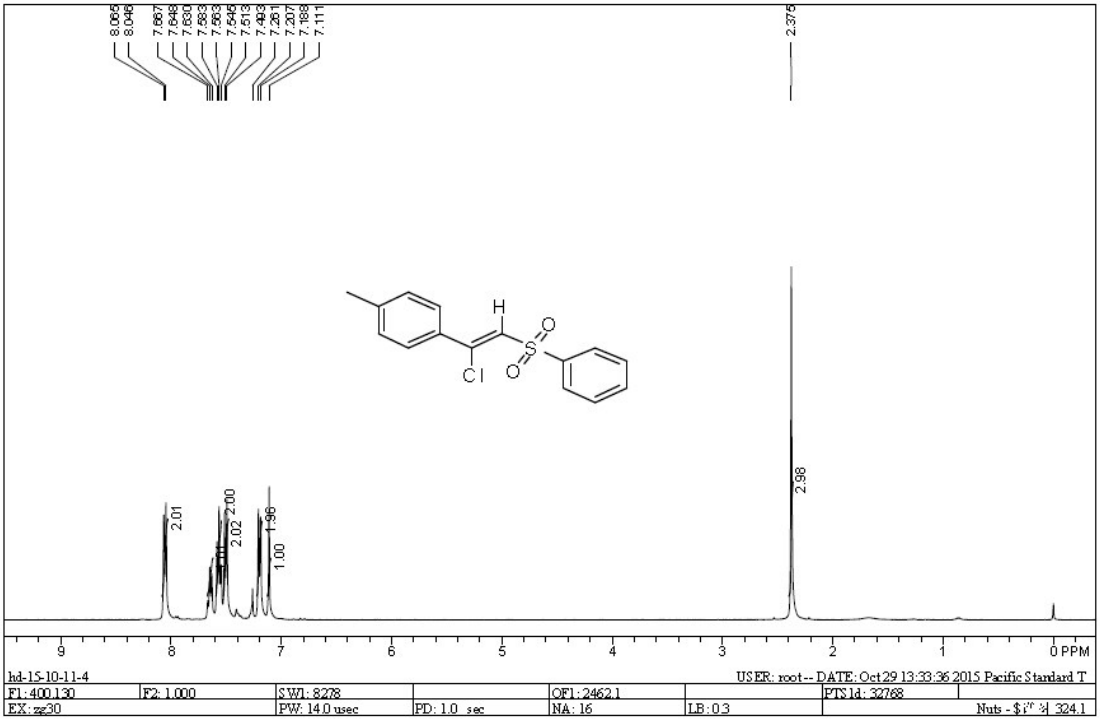


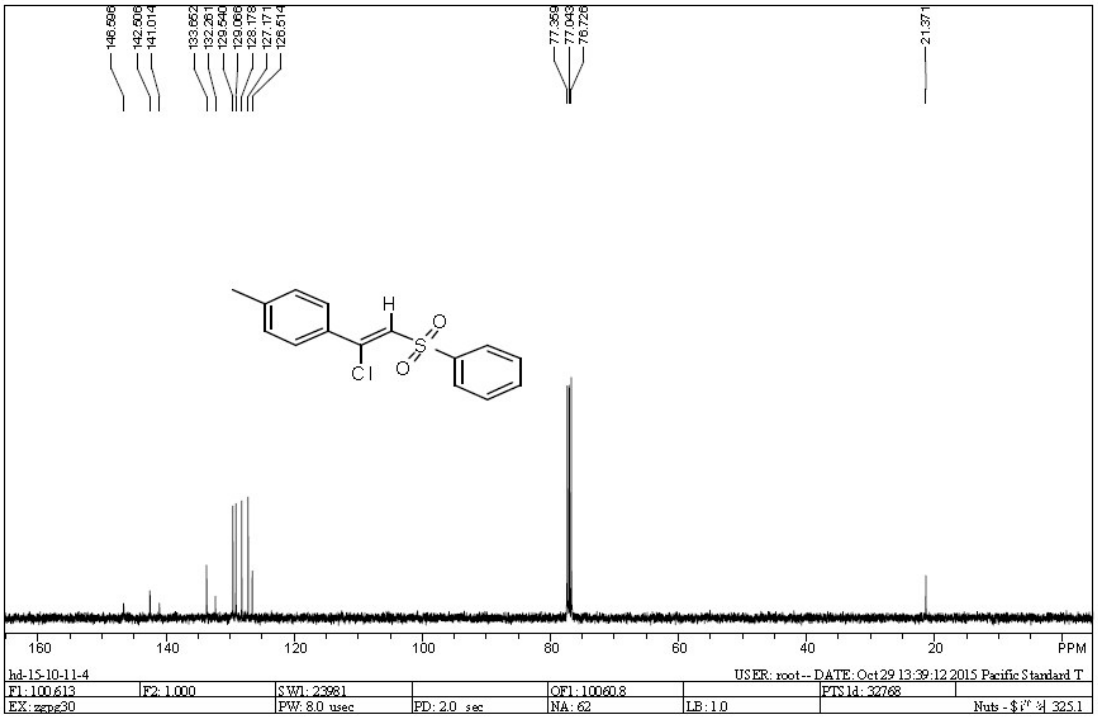
^{1}H and ^{13}C NMR spectra of **3ad**



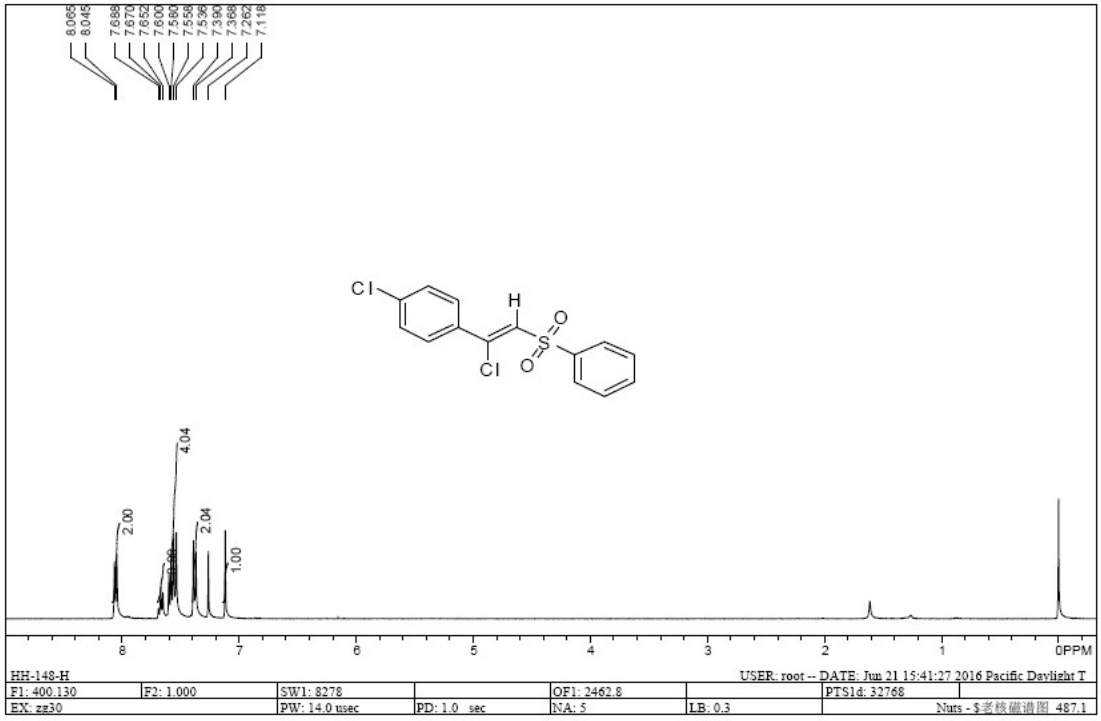


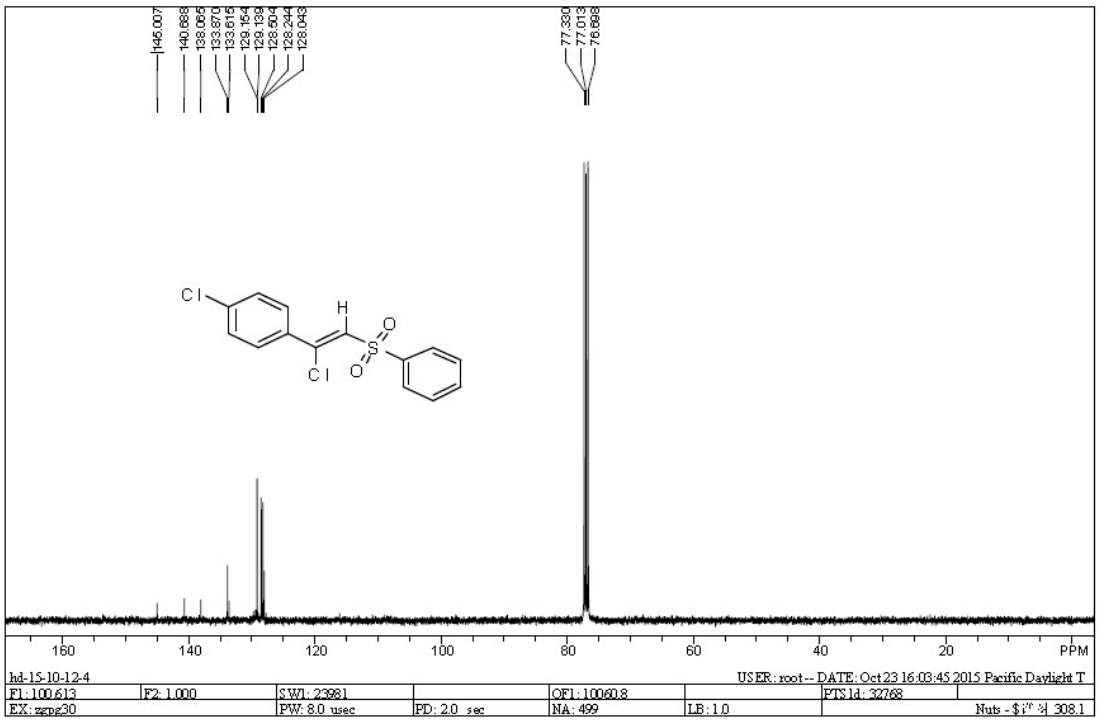
^{1}H and ^{13}C NMR spectra of **3ae**



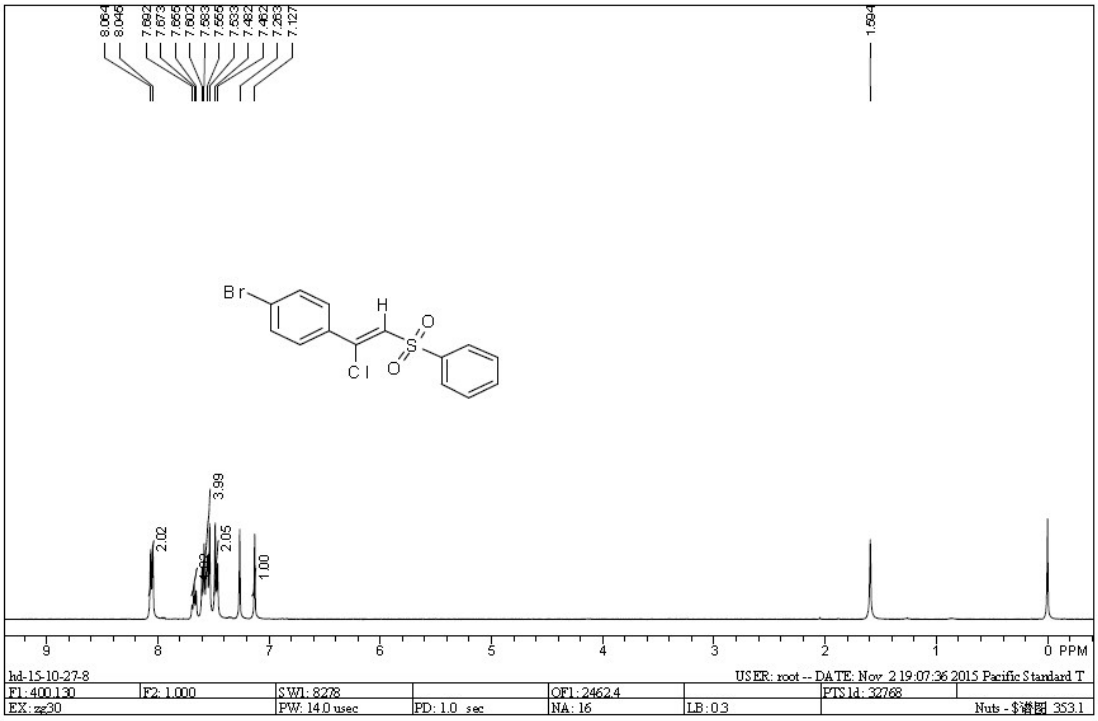


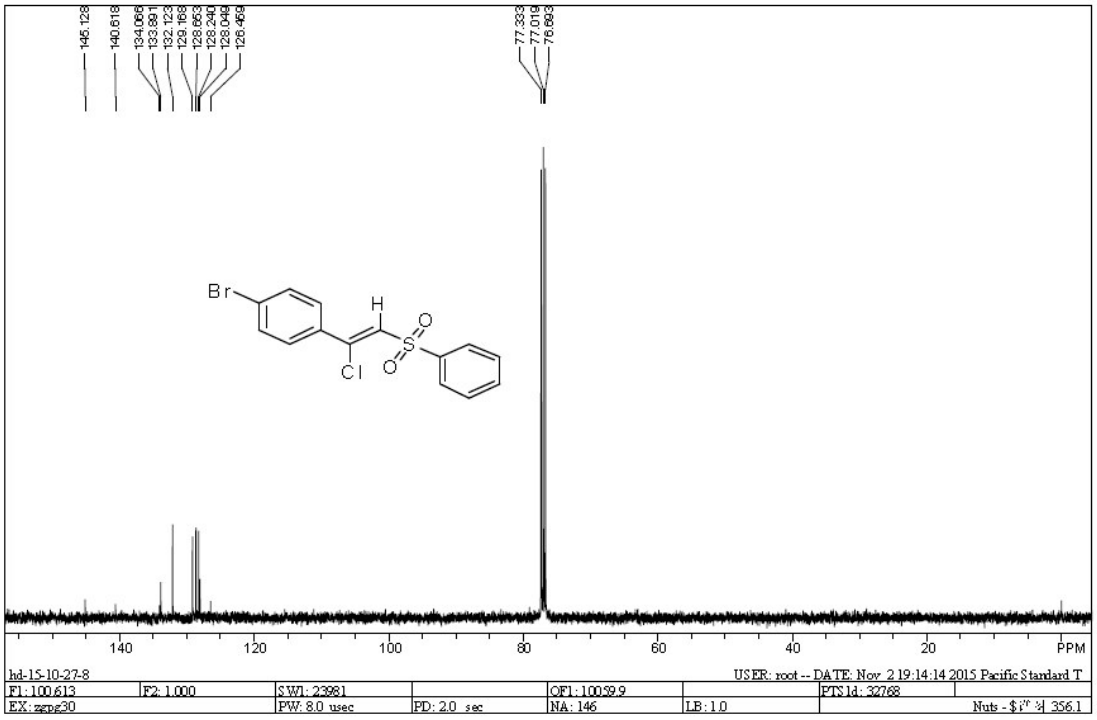
^{1}H and ^{13}C NMR spectra of **3af**



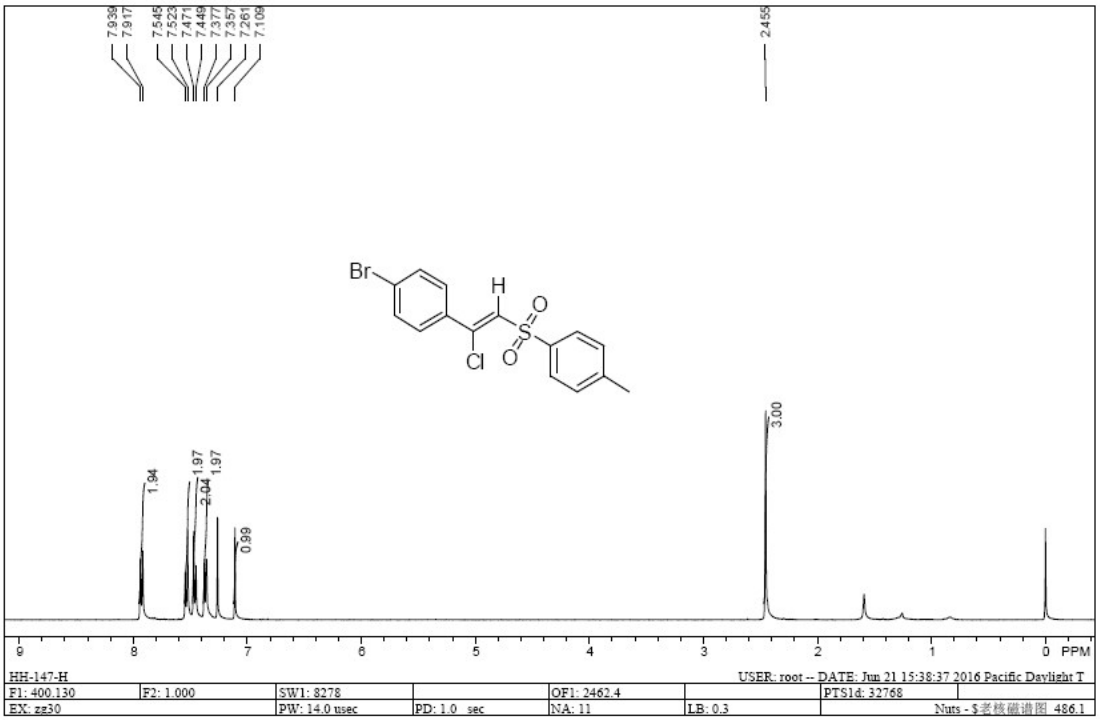


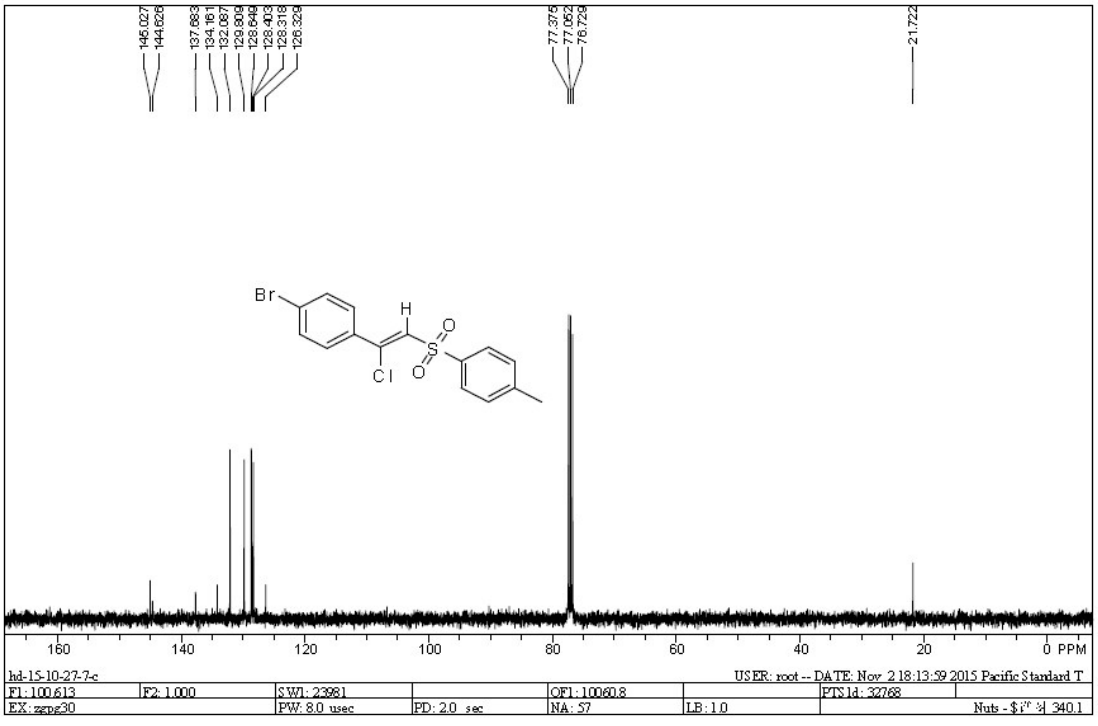
^{1}H and ^{13}C NMR spectra of **3ag**



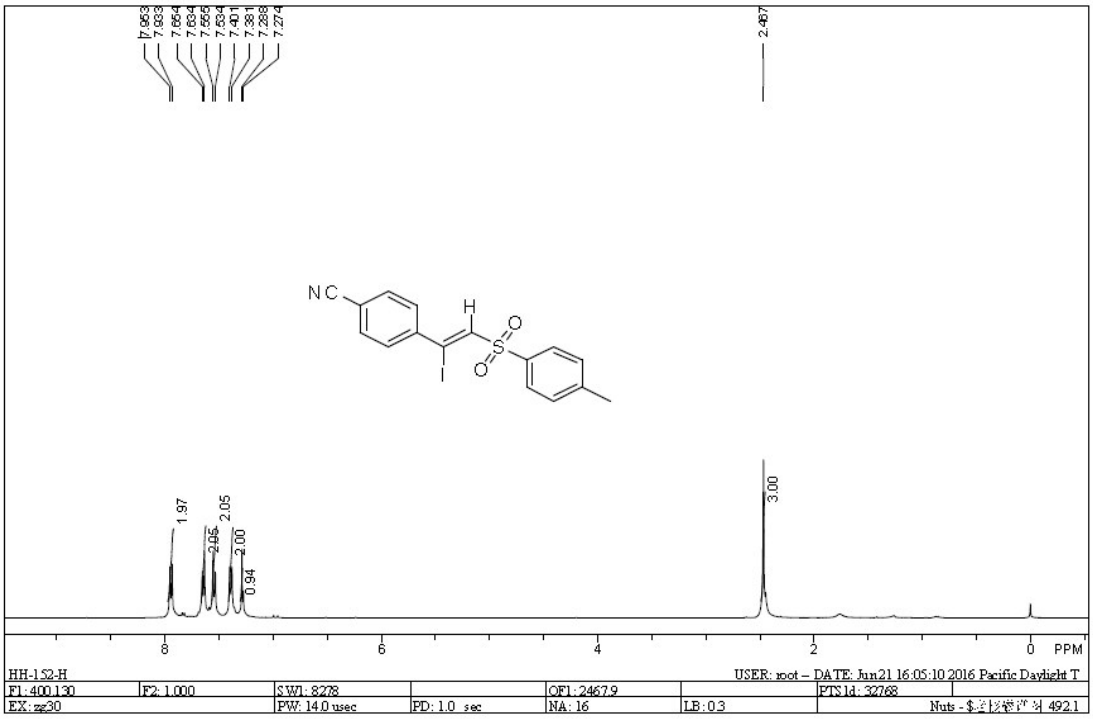


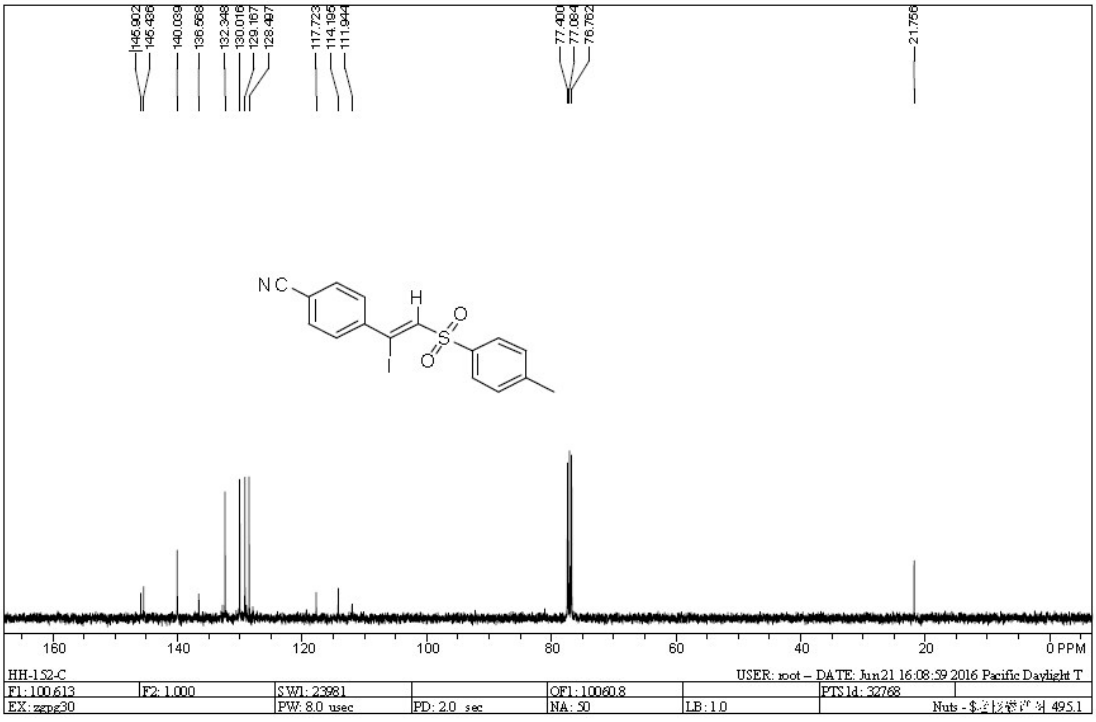
^{1}H and ^{13}C NMR spectra of **3ah**



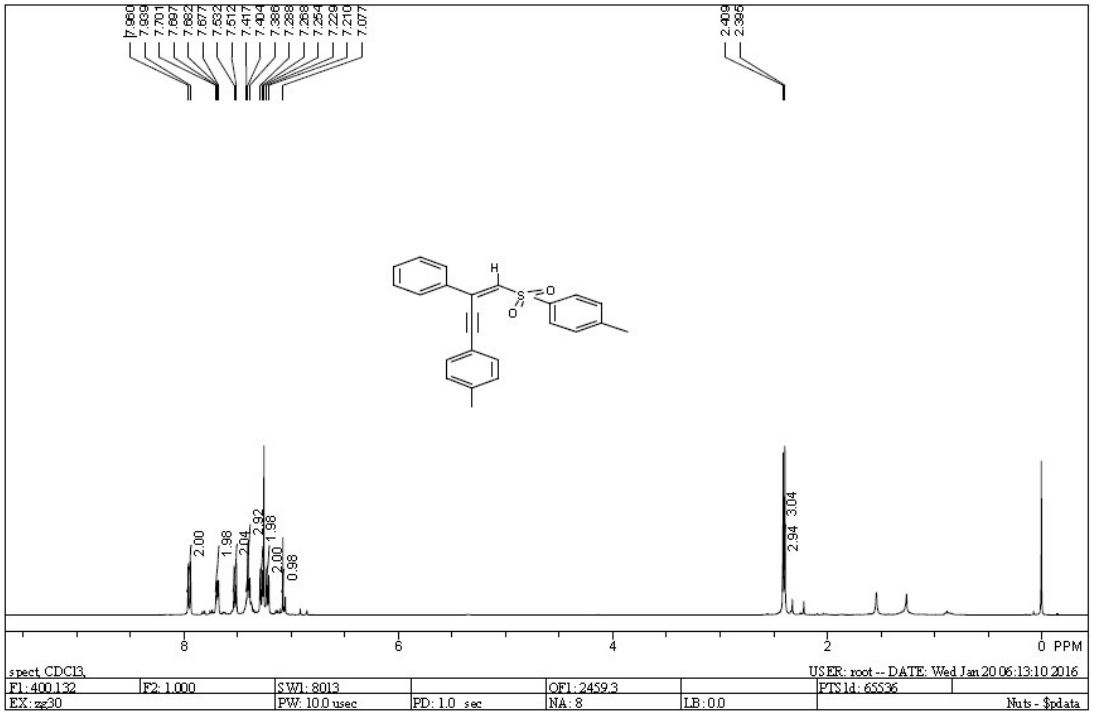


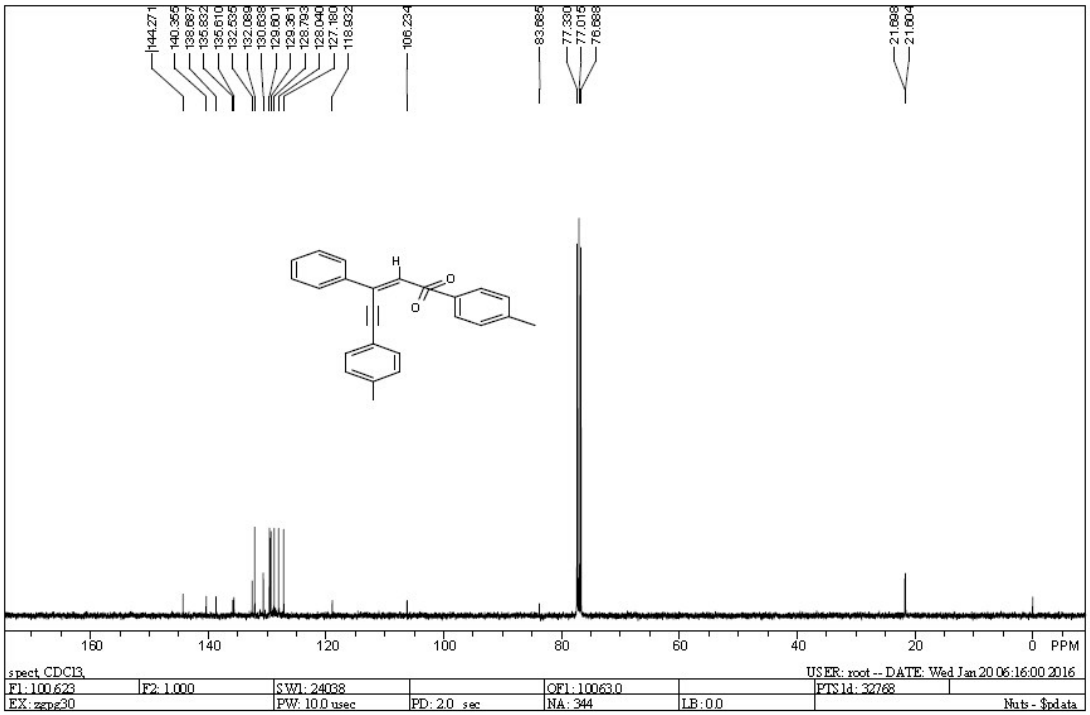
^{1}H and ^{13}C NMR spectra of **3ai**





^{1}H and ^{13}C NMR spectra of **4**





^{1}H and ^{13}C NMR spectra of **5**