Supporting Information

Photo-induced intramolecular alkyl/aryl group transfer and SO2 Insertion: A new strategy for the synthesis of 3-(alkyl/arylsulfonyl)benzothiophenes

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1. General considerations

All materials were obtained from commercial suppliers or prepared according to standard procedure unless otherwise noted. Solvents were purified and dried

according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (b.p. 60-90 ℃) are used. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz, 150 MHz or 564 MHz, respectively). For ^{1}H NMR, tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; For ^{13}C NMR, Chloroform-d (δ = 77.16 ppm) serves as the internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), tt (triplet of triplet), qd (quartet of doublet). The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on a Thermo Scientific Q Exactive and Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). All the visible-light-induced cyclization reactions were carried out under a Kessil (PR160L-427 nm, 40 W) lamp irradiation (Figure S1) in a plastic box, the distance from the LEDs to reaction tubes was 2.0 cm, and no filter was used during irradiation, and the reaction temperature between 40 to 45 ℃, and which was detected by an uncorrected thermometer.

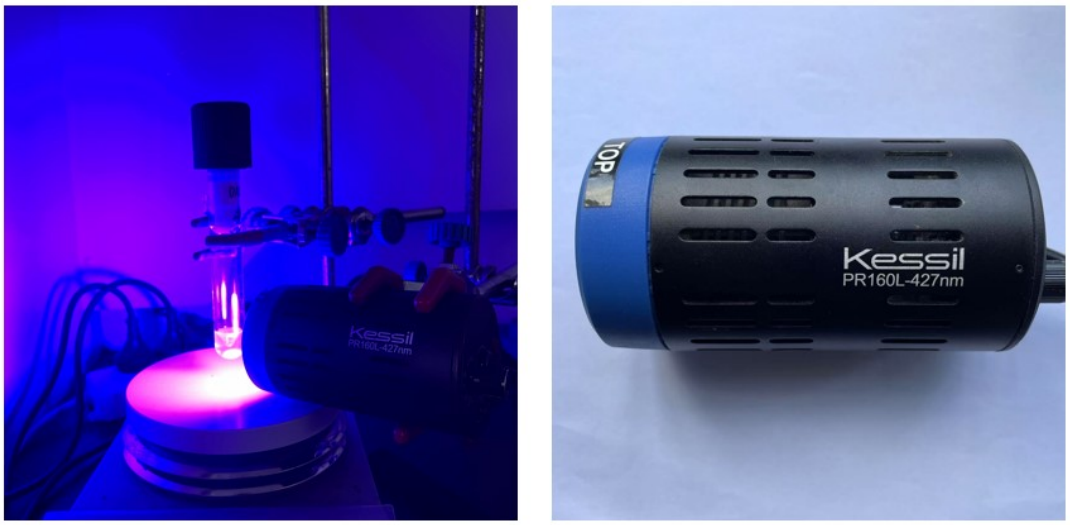
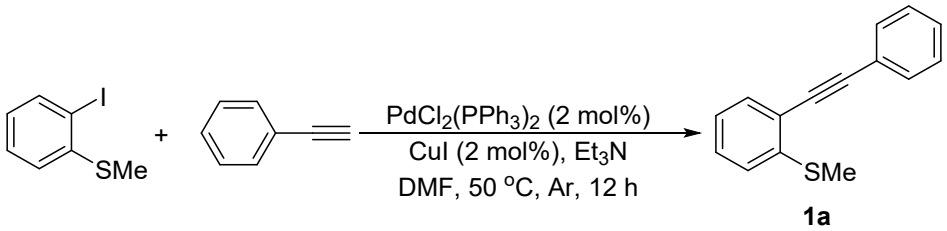


Figure S1. Reaction setup

2. Experimental Section

2.1 General procedure for the preparation of substrates

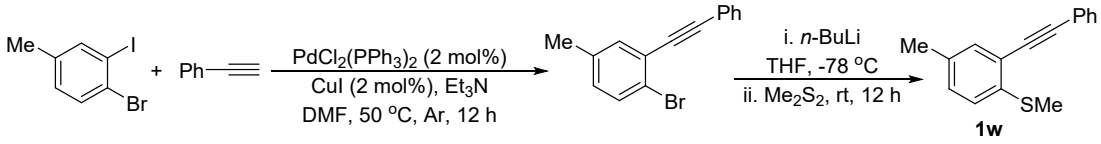
2.1.1 Typical procedure for the preparation of methyl(2-(phenylethynyl) phenyl)sulfane (1a)[1]



1a

To a solution of (2-iodophenyl)(methyl)sulfane (2.50 g, 10.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (140.40 mg, 2 mol%), CuI (38.10 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 ℃ for 12 h under an argon atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:200, V/V) as the eluent to afford the corresponding product **1a** as a yellow oil (2.02 g, 90% yield).

2.1.2 Typical procedure for the preparation of methyl(4-methyl-2-(phenylethynyl)phenyl)sulfane (1w)[1]



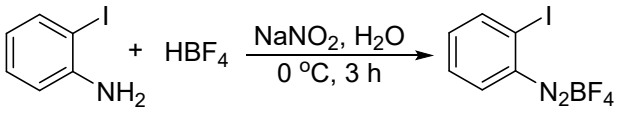
1w

To a solution of 1-bromo-2-iodo-4-methylbenzene (2.97 g, 10.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (140.40 mg, 2 mol%), CuI (38.10 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 ℃ for 12 h under an argon atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:200, V/V) as the eluent to afford the corresponding product 1-bromo-4-methyl- 2-(phenylethynyl)benzene as a yellow oil (2.39 g, 88% yield).

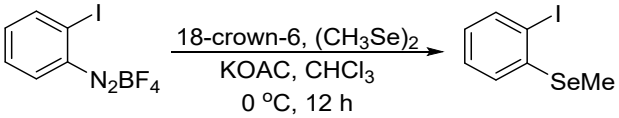
The 1-bromo-4-methyl-2-(phenylethynyl)benzene (2.17 g, 8.0 mmol) was dissolved in dry THF (80 mL) under an argon atmosphere and cooled to -78 °C for 0.5 h. Then, 2.0 equiv. of *n*-BuLi (2.0 M solution in cyclohexane, 16.0 mmol) was

added dropwise to the stirred solution. After the addition was complete, the reaction was stirred at -78 °C for 1 h. Dimethyl disulfide (0.90 g, 9.6 mmol, 1.2 equiv.) was then added and the reaction mixture was stirred at this temperature under an argon atmosphere for 18 h before being allowed to warm to room temperature. After completion, the solvent was evaporated under reduced pressure, then the mixture was diluted with ethyl acetate (50 mL) and water (50 mL), and then extracted with ethyl acetate (2*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:200, V/V) as the eluent to afford the corresponding product methyl(4-methyl-2-(phenylethynyl)phenyl)sulfane (**1w)** as a yellow oil (1.43 g, 75% yield).

2.1.3 Typical procedure for the preparation of methyl(2-(phenylethynyl)phenyl)selane (1q)[1, 2, 3]

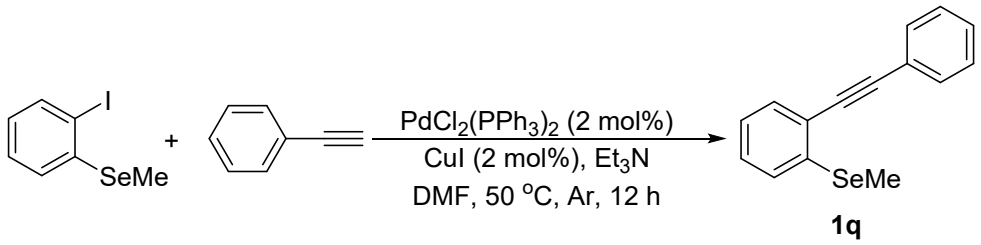


In a 100 mL round-bottom flask, 2-iodoaniline (2.19 g, 10 mmol) was dissolved in an aqueous solution of HBF_4 (48%, 4.0 mL), followed by dropwise addition of aqueous solution of $NaNO_2$ (1.38 g, 20 mmol, 2 equiv. in 3.0 mL H_2O). The reaction mixture was stirred at 0 ℃ for 3 h. Then the reaction mixture was worked up by filtration, washing successively with a small amount of ice water, alcohol and diethyl ether, the diazonium salt was dried under vacuum and used for the next step without purification. The product was obtained as a white solid (2.77 g, 87% yield).



To a flame-dried round-bottom flask, crude diazonium salt (3.18 g, 10.0 mmol), 18-crown-6 (1.30 g, 5 mmol, 0.5 equiv.), dimethyl diselenide (2.07 g, 11 mmol, 1.1 equiv.) and $CHCl_3$ (40 mL) were added, the mixture was stirred at 0 ℃. Then, KOAc (1.96 g, 20 mmol, 2 equiv.) was added in small portions over a period of 20 min and the resulting solution was allowed to stir for 12 h and then filtered. The solid residue was washed with chloroform and the resulting filtrate was washed with water, and the organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The

obtained crude product was then purified by flash chromatography on silica gel using petroleum ether as the eluent, and the product was obtained as a yellow oil (2.14 g, 72% yield).

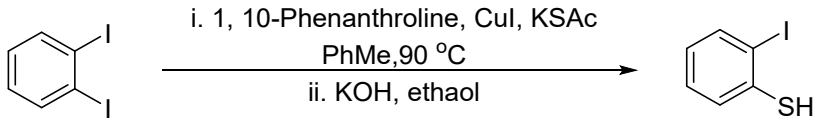


1q

To a solution of (2-iodophenyl)(methyl)selane (2.97 g, 10.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol, 1.2 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (140.40 mg, 2 mol%), CuI (38.10 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction mixture was stirred vigorous in an oil bath at 50 ℃ for 12 h under an argon atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:200, V/V) as the eluent to afford the corresponding product methyl(2-(phenylethynyl)phenyl)selane (**1q)** as a yellow oil (2.30 g, 86% yield).

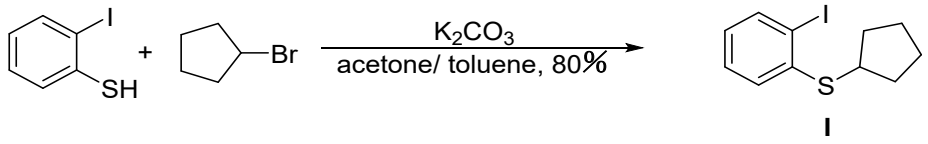
2.1.4 Typical procedure for the preparation of cyclopentyl(2-(phenylethynyl)phenyl)sulfane (1ak)[1, 3, 4, 5]

Method A:



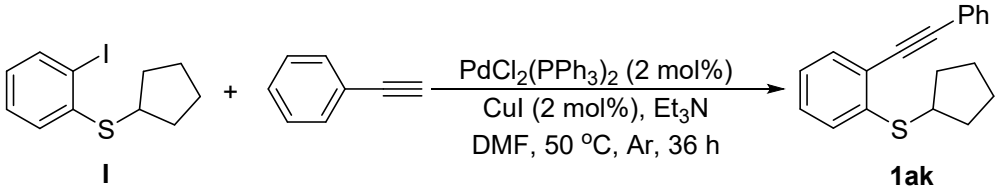
A mixture of 1,10-Phenanthroline (827 mg, 4.59 mmol), CuI (437 mg, 2.29 mmol) and KSAc (2.73 g, 23.9 mmol) in dry toluene (225 mL) was degassed and refilled with N_2 for three time at -78 °C, to which 1,2-diiodo-benzene (3.0 mL, 23.0 mmol) was added under N_2 atmosphere. Then the mixture was heated to 90 °C and the stirring was continued for 24 h at the same temperature. Upon cooling to room temperature, the mixture was filtered in vacuo, which was followed by addition of ethyl acetate to dilute the mixture. The resulting mixture was washed successively with water and brine, and was then dried over anhydrous Na_2SO_4. Filtration was

followed by concentration under reduced pressure afforded the crude product, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to provide acetylated 2-iodothiophenol intermediate, which was directly used as the starting material for the next step. The above obtained acetylated 2-iodothiophenol in ethaol (10 mL) was added KOH (1.70 g, 30.3 mmol) at 0 °C under N_2 atmosphere. After stirring for 2 h at room temperature, HCl (5 M) was added to quench the reaction and the pH of the resulting mixture was adjusted to about 3-4, which was followed by addition of ethyl acetate to dilute the mixture. The resulting mixture was washed successively with water and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure afforded the crude product, which was further purified by silica gel column chromatography (petroleum ether) to provide 2-iodothiophenol as a colorless liquid (2.77 g, 51% for 2 steps).



I

To a solution of 2-iodothiophenol (5.90 g, 25.0 mmol) in dry acetone (40 mL) was added K_2CO_3 (3.46 g, 25.0 mmol), after being stirred at 40 °C for 30 min, to which a solution of bromocyclopentane (4.44 g, 21.2 mmol) in dry toluene (40 mL) was added, and the resulting mixture was stirred at room temperature for another 10 h, After completion of the reaction (TLC). Filtration was followed by CH_2Cl_2. addition to dilute the reaction mixture, and the resulting mixture was successively washed with water and brine. After being dried over anhydrous Na_2SO_4, the volatile solvent was removed in vacuo to give the crude product, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 200:1) to furnish **I** as a white foam (6.08 g, 80%).

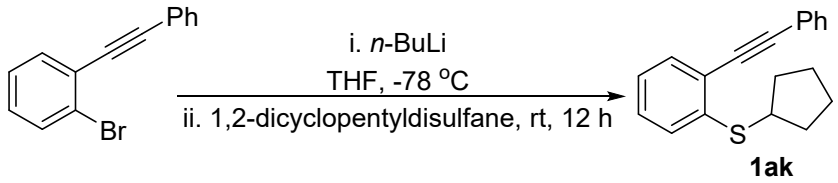


I 1ak

To a solution of cyclopentyl(2-iodophenyl)sulfane (**I**, 1.52 g, 5.0 mmol) and phenylacetylene (0.76 g, 7.5 mmol, 1.5 equiv.) in DMF (5 mL), $PdCl_2(PPh_3)_2$ (70.20 mg, 2 mol%), CuI (19.10 mg, 2 mol%) and Et_3N (20 mL) were added. The reaction

mixture was stirred vigorous in an oil bath at 50 ℃ for 36 h under an argon atmosphere. After completion, the mixture was diluted with water (50 mL), and then extracted with ethyl acetate (3*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether as the eluent to afford the corresponding product cyclopentyl(2-(phenylethynyl)phenyl)sulfane (**1ak)** as a pale yellow solid (0.93 g, 67% yield).

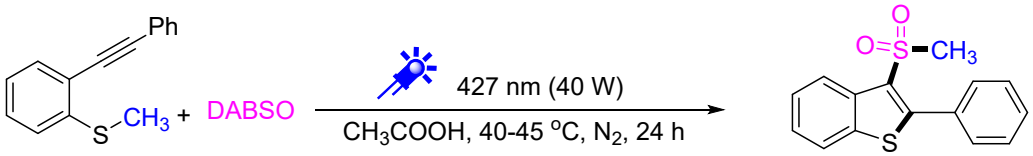
Method B:



1ak

The 1-bromo-2-(phenylethynyl)benzene (2.06 g, 8.0 mmol) was dissolved in dry THF (80 mL) under an argon atmosphere and cooled to -78 °C for 0.5 h. Then, 2.0 equiv. of *n*-BuLi (2.0 M solution in cyclohexane, 16.0 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction was stirred at -78 °C for 1 h. 1,2-dicyclopentyldisulfane (1.94 g, 9.6 mmol, 1.2 equiv.) was then added and the reaction mixture was stirred at this temperature under an argon atmosphere for 18 h before being allowed to warm to room temperature. After completion, the solvent was evaporated under reduced pressure, then the mixture was diluted with ethyl acetate (50 mL) and water (50 mL), and then extracted with ethyl acetate (2*50 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (1:200, V/V) as the eluent to afford the corresponding product cyclopentyl(2-(phenylethynyl)phenyl)sulfane (**1ak)** as a White solid (1.67 g, 75% yield).

2.2 Typical procedure for the cyclization reactions of 1a

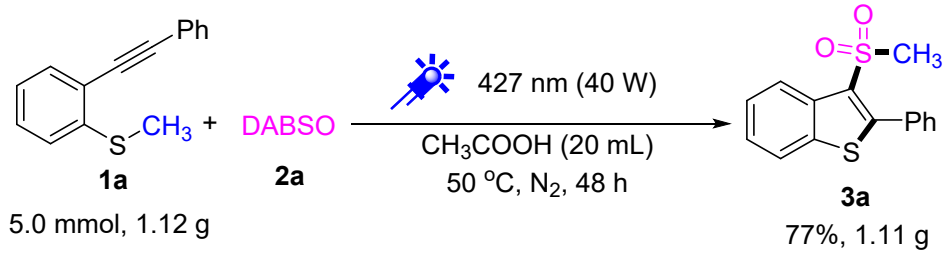


1a **2a** **3a**

A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was

charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 44.8 mg, 0.20 mmol), 1,4-Diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate (**2a**, DABSO, 57.7 mg, 1.2 equiv.) and CH_3COOH (2.0 mL). The reaction mixture was exposed to blue LED (427 nm, 40 W) irradiation (the reaction temperature is about 40-45 °C) in N_2 atmosphere with stirring for 24 h. After completion of the reaction, the solvent was removed directly by rotary evaporation and purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3a** as a white solid (52.4 mg, 91% yield).

2.3 Typical procedure for gram-scale synthesis



A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 1.12 g, 5 mmol), 1,4-diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate (**2a**, DABSO, 1.44 g, 6.0 mmol), and CH_3COOH (20.0 mL). The reaction mixture was exposed to blue LED (427 nm, 40 W) irradiation (the reaction temperature is about 50 °C) in N_2 atmosphere with stirring for 48 h. After completion of the reaction, the solvent was removed directly by rotary evaporation and the crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired product **3a** as a white solid (1.11 g, 77% yield).

3. Preliminary mechanistic study

3.1 UV-visible absorption spectra

The ultraviolet/visible absorption spectra of **1a** ($1*10^{-2}$M), DABSO ($1.2*10^{-2}$M) and **1a** ($1*10^{-2}$M) + DABSO ($1.2*10^{-2}$M) in CH_3COOH were recorded on a UV-Visible U-4100 spectrophotometer. As shown in **Figure S2**, When DABSO was added to **1a**, the UV absorption curve (blue line) of the mixed solution is red shifted. Subsequently, we irradiated a mixture of solvent **1a** and DABSO at 427 nm (40 W) for 20 min, its absorption spectrum clearly depicted a bathochromic displacement in the visible region.

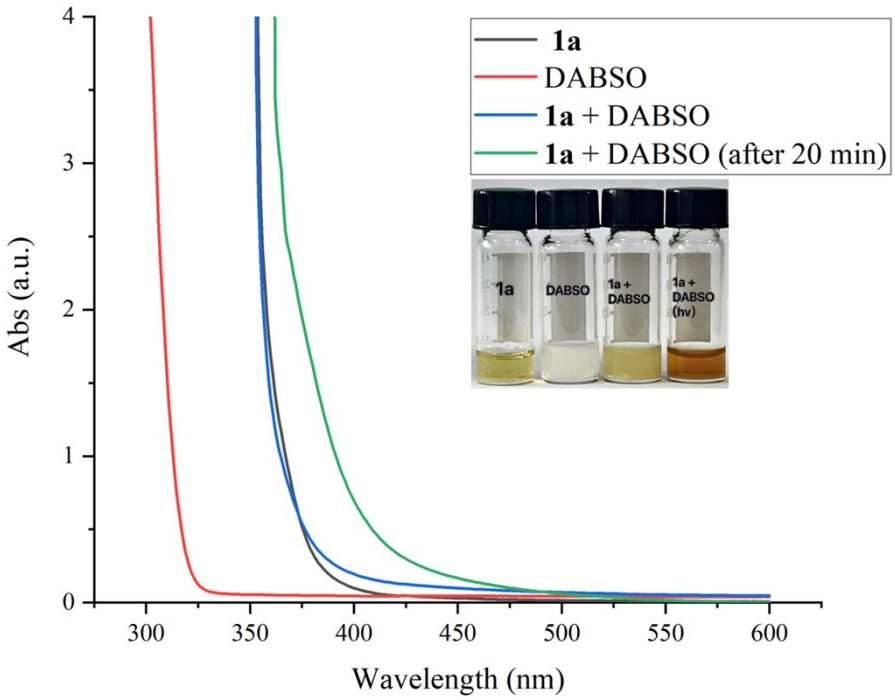


Figure S2. Absorption spectra of **1a** and DABSO in CH_3COOH solution

3.2 Fluorescence quenching experiment

To further elucidate the possible reaction pathway, the related fluorescence quenching experiments were performed and the results were shown in Figure S3. In each experiment, fluorescence quenching of methyl(2-(phenylethynyl)phenyl)sulfane (**1a)** ($1.0*10^{-3}$ mol/L) by increasing concentrations of DABSO and irradiated at 352 nm. Emission spectrum were recorded after each addition. The results in Figure S3 (left) shows an obvious change in the emission intensity of **1a** with a calculated Ksv of 46.67 mM^{-1} [Figure S3 (right)], and which also confirms the formation of an EDA complex.

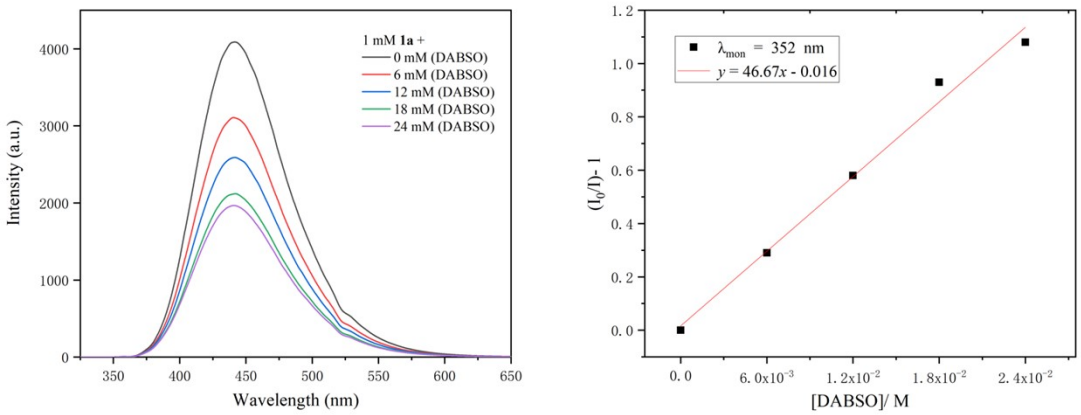


Figure S3. (a) Fluorescence quenching of **1a** by DABSO in CH_3COOH (left); (b) Stern-Volmer plots of **1a** quenching with DABSO (right).

3.3 Switched light on/off experiment

In order to illustrate the alkylation/cyclization reaction by self-sustaining in an autocatalytic manner, the light/dark experiments were conducted, as shown in Figure S4. A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 44.9 mg, 0.20 mmol), 1,4-diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate (DABSO, 57.7 mg, 1.2 equiv.) and CH_3COOH (2.0 mL). The reaction mixture was exposed to a 427 nm LED (40 W) irradiation at room temperature in air with stirring for 2 h, then stirring for 2 h without irradiation. The following product yields based on the irradiation with LED (427 nm, 40 W) for a certain time, and without irradiation for a certain time were also presented in the Figure S4.

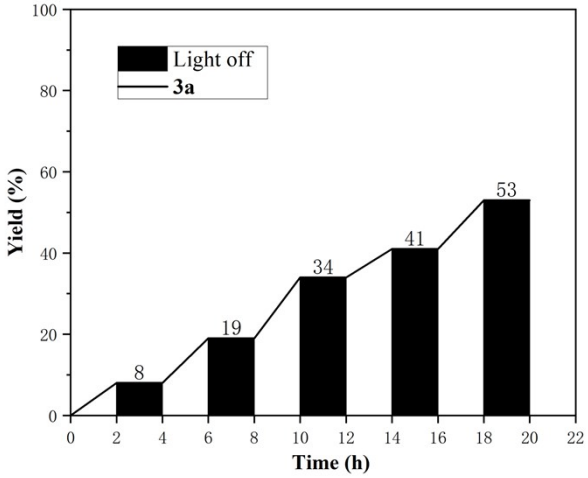
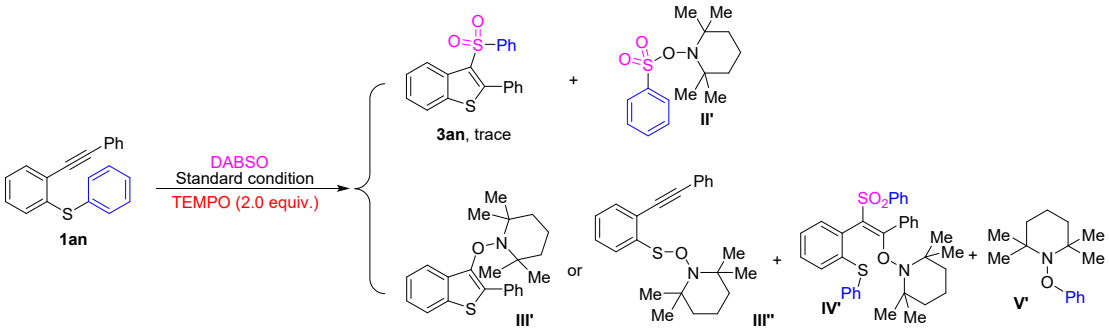


Figure S4. Light/dark experiments

3.4 The Radical Inhibiting experiments

Methyl(2-(phenylethynyl)phenyl)sulfane (**1a**, 44.9 mg, 0.2 mmol), 1,4-diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate (DABSO, 57.7 mg, 1.2 equiv.), TEMPO (62.5 mg, 0.4 mmol), and CH_3COOH (2.0 mL) were added to an oven-dried reaction vessel. The reaction mixture was exposed to blue LED (427 nm, 40 W) irradiation (the reaction temperature is about 40-45 °C) in N_2 atmosphere with stirring for 24 h. After completion, only trace amount of **3an** was detected in the reaction mixture, and the corresponding adducts (**II'**, **III'**, **III''**, **IV'** and **V'**) of free radical and TEMPO were detected by HRMS analysis of the reaction mixture, and the related results were shown in Figure S5, Figure S6, Figure S7 and Figure S8.



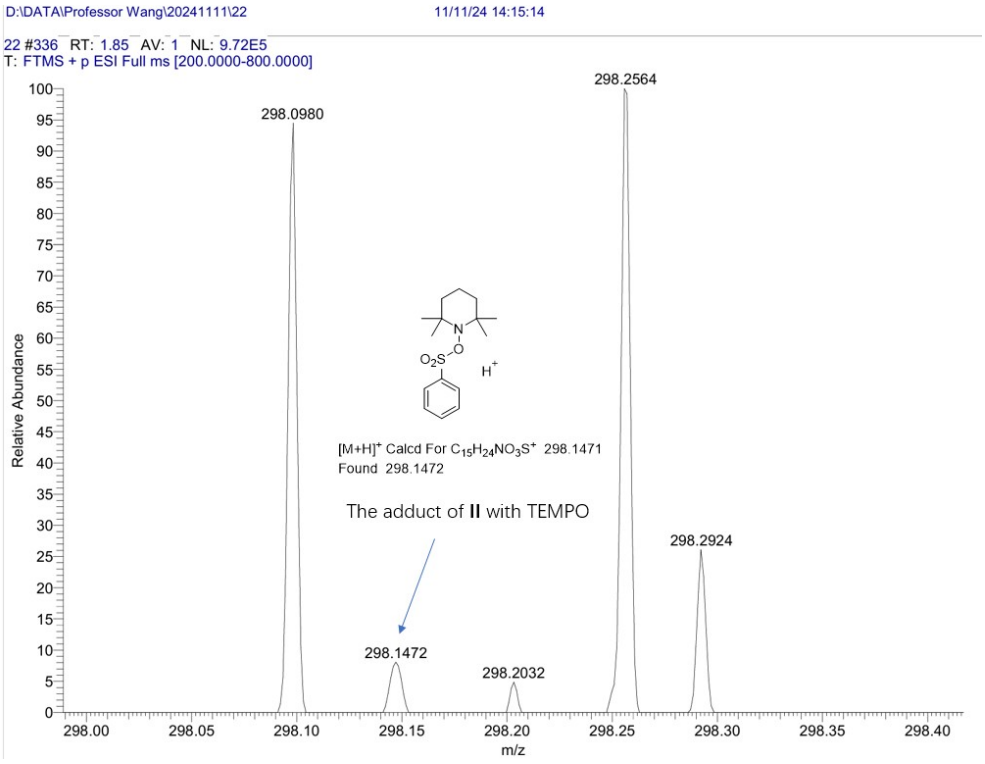


Figure S5. Analysis of reaction mixture by HRMS for the adduct of **II'**

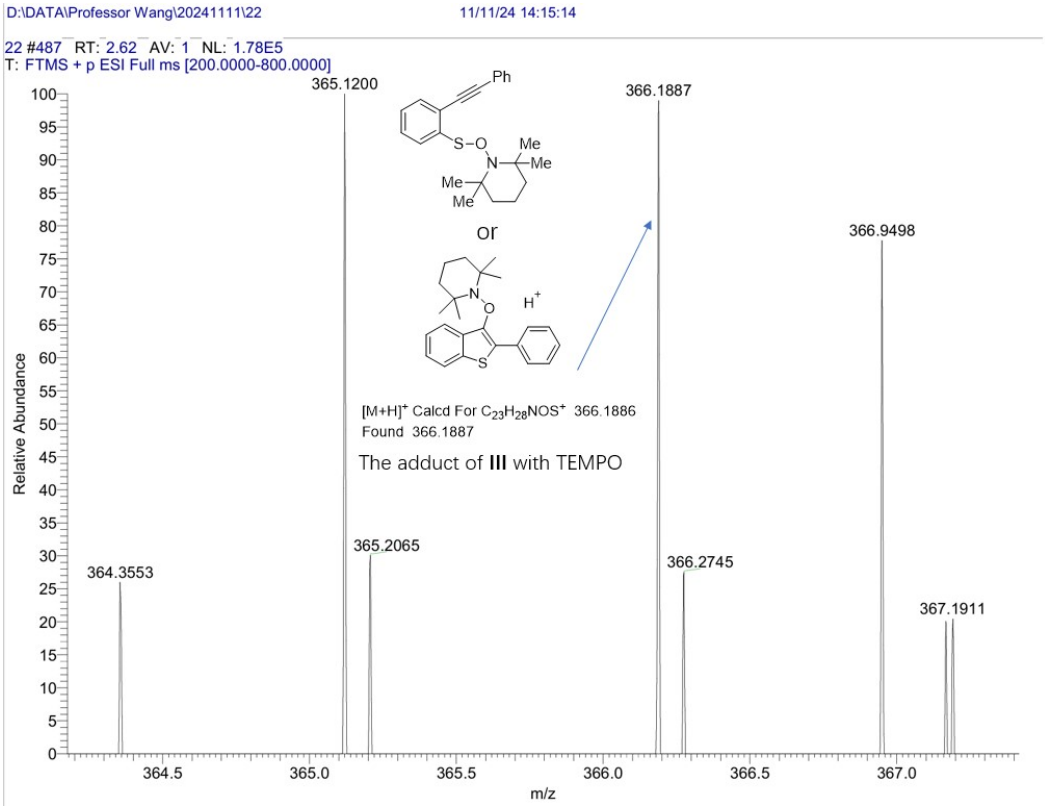


Figure S6. Analysis of reaction mixture by HRMS for the adduct of **III'**

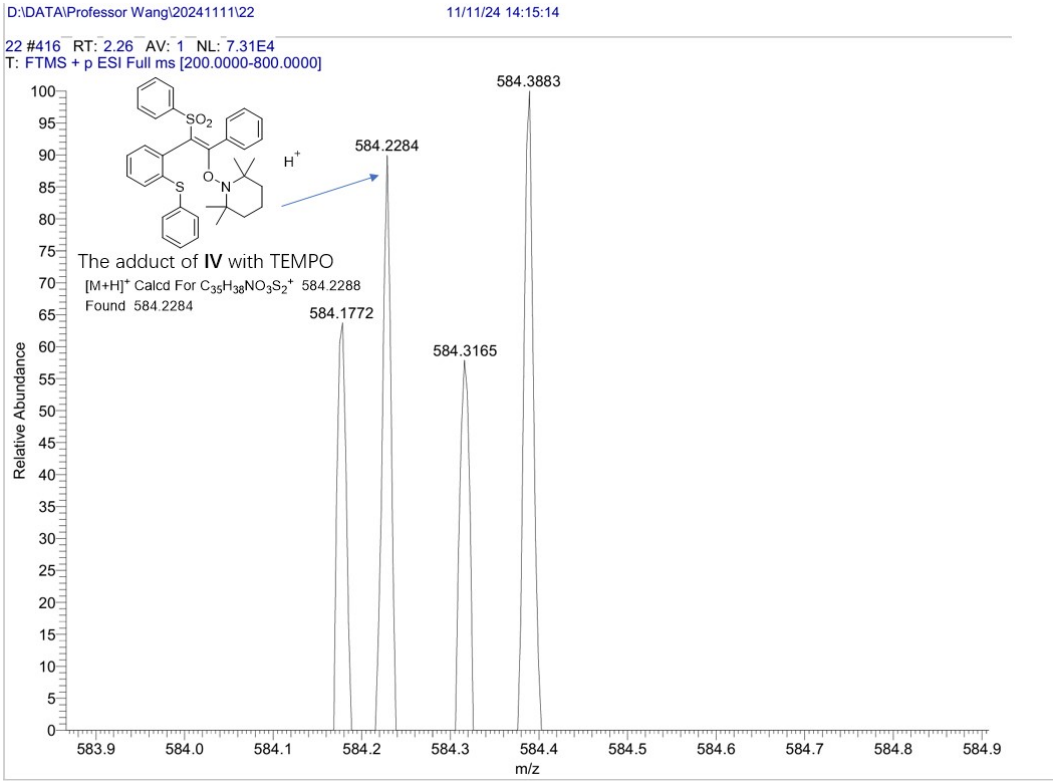


Figure S7. Analysis of reaction mixture by HRMS for the adduct of **IV'**

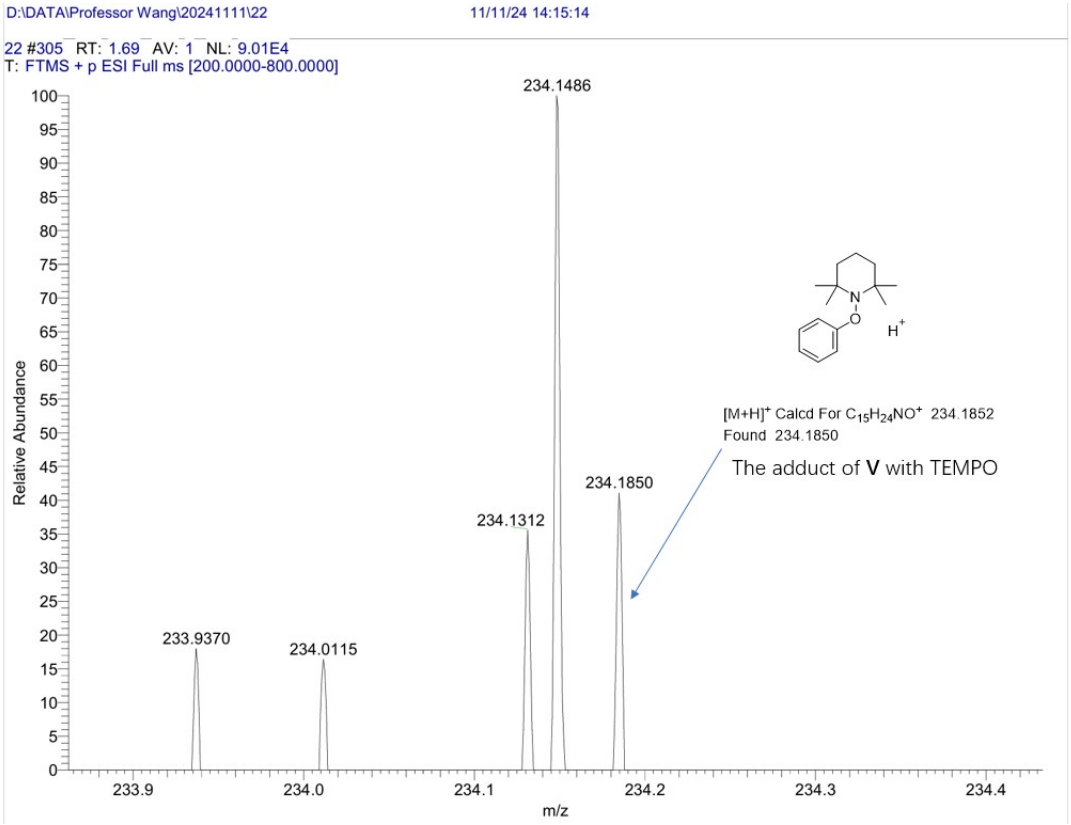


Figure S8. Analysis of reaction mixture by HRMS for the adduct of **V'**

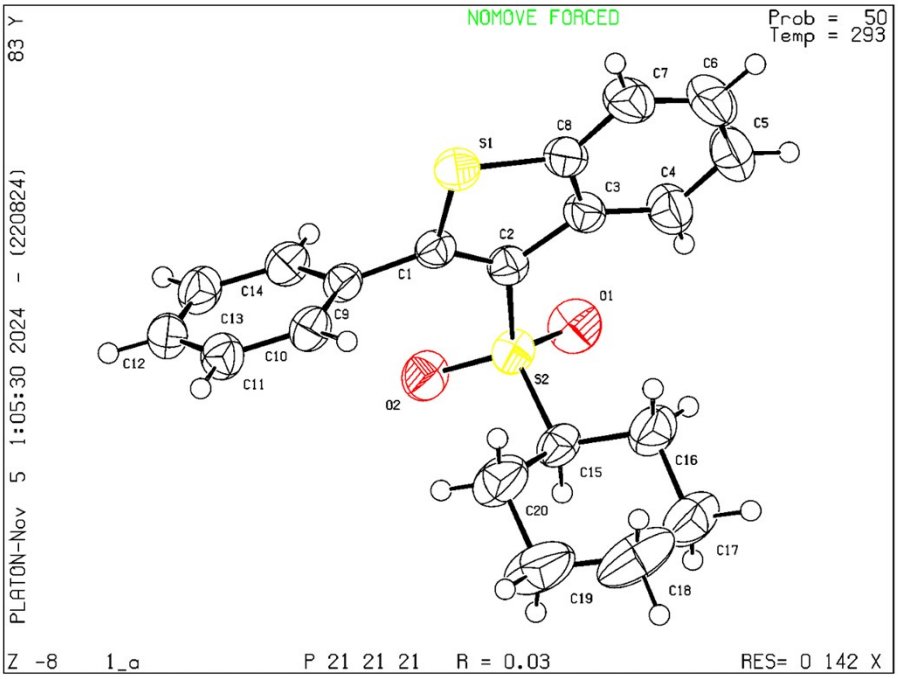
4. X-Ray Cystallographic Data of products

4.1 X-Ray crystallographic data for **2al**

Diffraction was performed on a Bruker D8 VENTURE area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for all complexes at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvents were squeezed by using PLATON. All crystal structural pictures drawn by *OLEX* 2 program.

Single crystals of **2al** were grown from slow evaporation of dichloromethane

solution at room temperature. The data of the crystal structure **2al** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2400530.



Bond precision:	C-C = 0.0041 A		Wavelength=1.54178
Cell:	a=5.8241(3)	b=10.0409(6)	c=29.8544(18)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	1745.86(17)	1745.86(17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H20 O2 S2	C20 H20 O2 S2
Sum formula	C20 H20 O2 S2	C20 H20 O2 S2
Mr	356.48	356.48
Dx,g cm-3	1.356	1.356
Z	4	4
Mu (mm-1)	2.832	2.832
F000	752.0	752.0
F000'	756.45	
h,k,lmax	7,12,36	7,12,36
Nref	3461[2036]	3434
Tmin,Tmax	0.747,0.753	0.477,0.754
Tmin'	0.541	

Correction method= # Reported T Limits: Tmin=0.477 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.69/0.99 Theta(max)= 72.501

R(reflections)= 0.0303(3383) wR2(reflections)= 0.0800(3434)

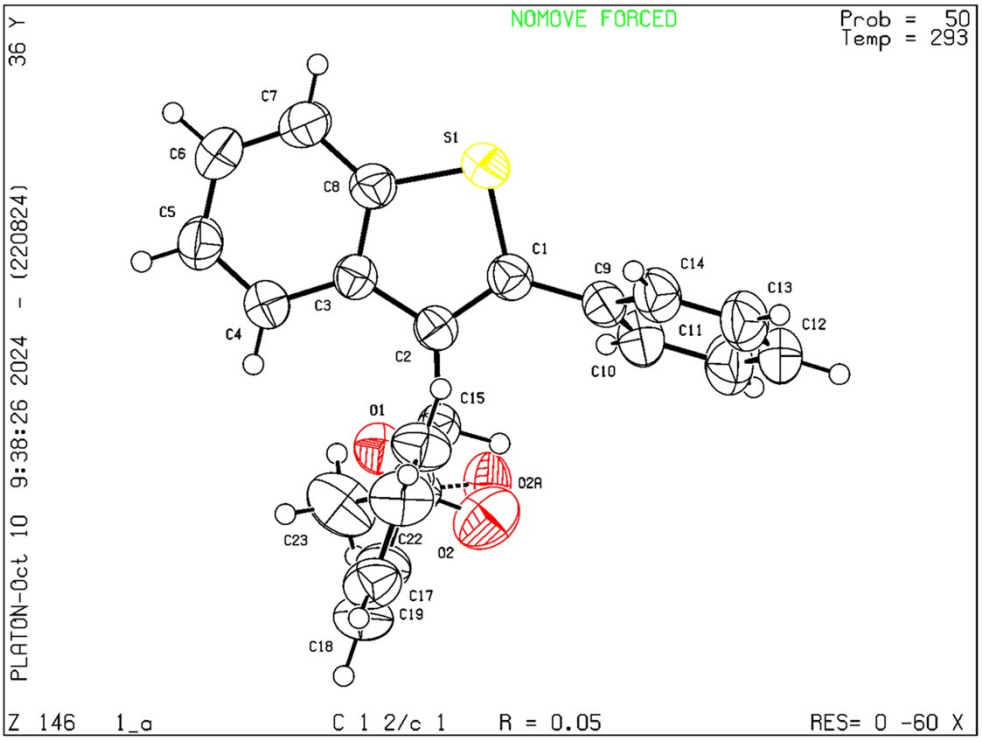
S = 1.059 Npar= 218

4.2 X-Ray crystallographic data for **4**

Diffraction was performed on a Bruker D8 VENTURE area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for

all complexes at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvents were squeezed by using PLATON. All crystal structural pictures drawn by *OLEX* 2 program.

Single crystals of **5** were grown from slow evaporation of dichloromethane solution at room temperature. The data of the crystal structure **5** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2400641.



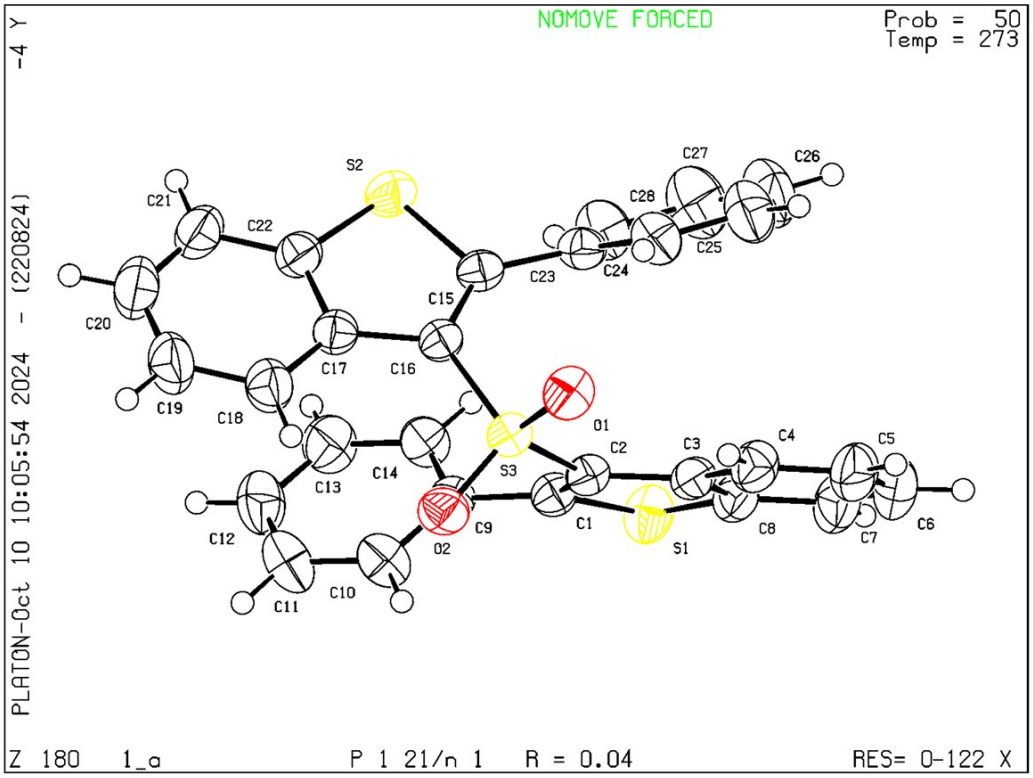
```
Bond precision:   C-C = 0.0036 A          Wavelength=0.71073

Cell:              a=28.64(2)     b=6.895(5)          c=18.824(15)
                   alpha=90       beta=95.56(3)       gamma=90
Temperature:       293 K

                  Calculated                Reported
Volume            3700(5)                   3700(5)
Space group       C 2/c                     C 1 2/c 1
Hall group        -C 2yc                    -C 2yc
Moiety formula    C23 H18 O2 S              C23 H18 O2 S
Sum formula       C23 H18 O2 S              C23 H18 O2 S
Mr                358.43                    358.43
Dx,g cm-3         1.287                     1.287
Z                 8                         8
Mu (mm-1)         0.189                     0.189
F000              1504.0                    1504.0
F000'             1505.61
h,k,lmax          37,8,24                   37,8,24
Nref              4268                      4250
Tmin,Tmax         0.978,0.981               0.636,0.746
Tmin'             0.965

Correction method= # Reported T Limits: Tmin=0.636 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996           Theta(max)= 27.560

R(reflections)= 0.0545( 2653)                  wR2(reflections)=
                                               0.1435( 4250)
S = 1.050                 Npar= 246
```

4.3 X-Ray crystallographic data for **6**

Diffraction was performed on a Bruker D8 VENTURE area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for all complexes at 273(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvents were squeezed by using PLATON. All crystal structural pictures drawn by *OLEX* 2 program.

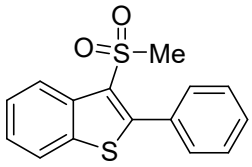
Single crystals of **6** were grown from slow evaporation of dichloromethane solution at room temperature. The data of the crystal structure **6** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number:

CCDC 2400604.

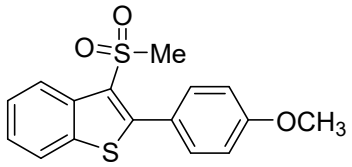



```
Bond precision:   C-C = 0.0025 A          Wavelength=0.71073

Cell:             a=12.6015(4)     b=14.4095(5)         c=13.0640(4)
                  alpha=90         beta=105.544(1)      gamma=90
Temperature:      273 K

                 Calculated                Reported
Volume           2285.42(13)               2285.42(13)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C28 H18 O2 S3             C28 H18 O2 S3
Sum formula      C28 H18 O2 S3             C28 H18 O2 S3
Mr               482.60                    482.60
Dx,g cm-3        1.403                     1.403
Z                4                         4
Mu (mm-1)        0.349                     0.349
F000             1000.0                    1000.0
F000'            1001.85
h,k,lmax         19,21,19                  17,21,19
Nref             8419                      7293
Tmin,Tmax        0.946,0.956               0.689,0.747
Tmin'            0.946

Correction method= # Reported T Limits: Tmin=0.689 Tmax=0.747
AbsCorr = MULTI-SCAN

Data completeness= 0.866          Theta(max)= 32.733

R(reflections)= 0.0435( 5127)                wR2(reflections)=
                                             0.1140( 7293)
S = 1.039                 Npar= 298
```

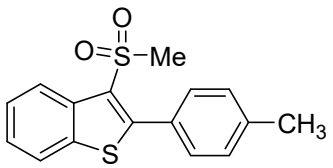
5. Characterization data for the products



3-(Methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3a). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 91% yield (52.5 mg), mp: 134.1–135.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.59–7.57 (m, 2H), 7.56–7.53 (m, 1H), 7.50–7.45 (m, 4H), 3.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 138.4, 136.3, 131.6, 130.5, 129.9, 129.3, 128.1, 126.2, 125.9, 124.4, 122.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}O_2S_2^+$ 289.0351; Found 289.0353.

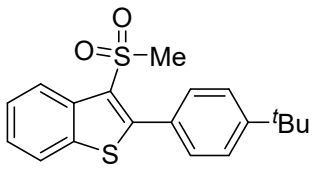


2-(4-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3b). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid. 93% yield (59.2 mg), mp: 133.1–133.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54–7.51 (m, 3H), 7.47–7.44 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0, 152.8, 138.2, 136.5, 132.0, 128.8, 126.1, 125.7, 124.3, 123.5, 122.0, 113.7, 55.5, 45.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0457.

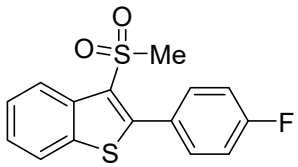


3-(Methylsulfonyl)-2-(*p*-tolyl)benzo[*b*]thiophene (3c). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid, 87% yield (52.6 mg), mp: 156.7–158.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 1H), 7.49–7.45 (m, 3H), 7.28 (d, *J* = 7.8 Hz,

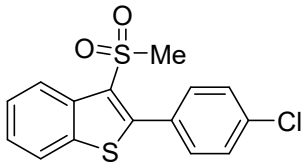
2H), 3.00 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.0, 140.2, 138.3, 136.4, 130.4, 129.1, 128.9, 128.6, 126.2, 125.8, 124.4, 122.0, 45.1, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0507.



2-(4-(*tert*-Butyl)phenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3d)[6]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 88% yield (60.6 mg), mp: 190.2–191.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H), 7.54–7.52 (m, 3H), 7.49–7.45 (m, 3H), 2.99 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.2, 153.0, 138.3, 136.5, 130.3, 128.9, 128.6, 126.1, 125.7, 125.2, 124.4, 122.0, 45.0, 35.0, 31.4.

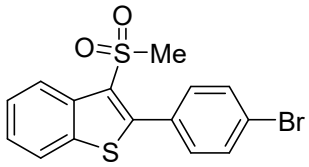


2-(4-Fluorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3e). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 85% yield (52.1 mg), mp: 140.2–140.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.58–7.54 (m, 3H), 7.50–7.48 (m, 1H), 7.16 (t, *J* = 8.4 Hz, 2H), 3.02 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –110.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.8 (d, *J* = 249.2 Hz), 151.6, 138.3, 136.2, 132.5 (d, *J* = 8.9 Hz), 129.5, 127.4 (d, *J* = 3.8 Hz), 126.2 (d, *J* = 43.4 Hz), 124.3, 122.1, 115.4, 115.3, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}FO_2S_2^+$ 307.0257; Found 307.0258.

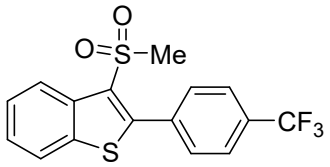


2-(4-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3f). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 89% yield (57.5 mg), mp: 175.1–177.2 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz,

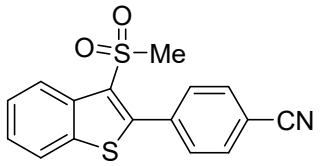
1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 1H), 7.52–7.48 (m, 3H), 7.45–7.43 (m, 2H), 3.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.4, 136.3, 136.2, 131.9, 129.9, 129.5, 128.5, 126.4, 126.2, 124.4, 122.1, 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9965.



2-(4-Bromophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3g)[6]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 81% yield (59.5 mg), mp: 169.1–169.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.60–7.59 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.50–7.48 (m, 1H), 7.45–7.44 (m, 2H), 3.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.4, 136.2, 132.1, 131.4, 130.4, 129.5, 126.4, 126.1, 124.6, 124.3, 122.1, 45.2.

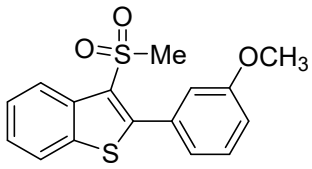


3-(Methylsulfonyl)-2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene (3h). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 79% yield (56.3 mg), mp: 183.7–184.9 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.73–7.68 (m, 4H), 7.59–7.57 (m, 1H), 7.53–7.50 (m, 1H), 3.06 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.8; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.7, 138.6, 136.0, 135.3, 131.8 (q, *J* = 32.5 Hz), 131.0, 129.9, 126.6, 126.4, 125.0 (q, *J* = 270.8 Hz), 124.3, 122.2, 45.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{12}F_3O_2S_2^+$ 357.0225; Found 357.0225.

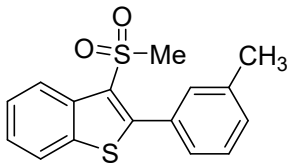


4-(3-(Methylsulfonyl)benzo[*b*]thiophen-2-yl)benzonitrile (3i)[6]. Purified by flash column chromatography (petroleum ether/AcOEt = 9:1, v/v). Pale yellow solid; 75%

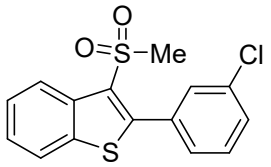
yield (47.0 mg), mp: 218.4–220.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.76–7.75 (m, 2H), 7.68–7.67 (m, 2H), 7.61–7.58 (m, 1H), 7.550–7.52 (m, 1H), 3.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.2, 138.6, 136.4, 135.9, 131.7, 131.4, 130.7, 126.7, 126.6, 124.3, 122.3, 118.3, 113.7, 45.3.



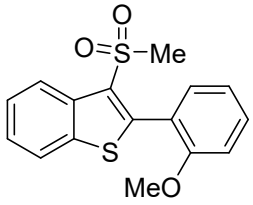
2-(3-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3j). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 84% yield (53.5 mg), mp: 105.7–106.5°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.55–7.52 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.16–7.15 (m, 2H), 7.03–7.01 (m, 1H), 3.85 (s, 3H), 2.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.1, 152.2, 138.3, 136.3, 132.7, 129.4, 129.2, 126.2, 125.9, 124.4, 122.8, 122.0, 116.2, 116.0, 55.5, 45.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0456.



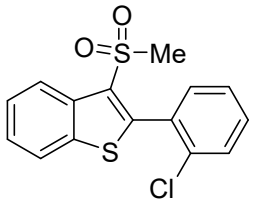
3-(Methylsulfonyl)-2-(*m*-tolyl)benzo[*b*]thiophene (3k)[6]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 87% yield (52.6 mg), mp: 135.4–136.7 °C. δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54–7.52 (m, 1H), 7.47–7.44 (m, 1H), 7.38–7.37 (m, 2H), 7.35–7.33 (m, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 2.99 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.8, 138.3, 137.9, 136.3, 131.4, 131.0, 130.7, 129.1, 128.0, 127.6, 126.1, 125.8, 124.3, 122.0, 45.1, 21.5.



2-(3-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3l). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 92% yield (59.4 mg), mp: 144.2–145.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 2H), 7.50–7.48 (m, 1H), 7.47–7.45 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.7, 138.4, 136.0, 134.0, 133.2, 130.3, 130.0, 129.7, 129.3, 128.9, 126.4, 126.2, 124.3, 122.1, 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9960.

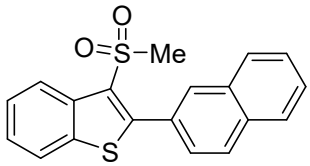


2-(2-Methoxyphenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3m). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 95% yield (58.6 mg), mp: 161.7–162.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.54–7.52 (m, 1H), 7.47–7.43 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.0, 149.1, 138.9, 136.0, 131.6, 131.3, 129.9, 126.0, 125.6, 123.8, 122.2, 120.7, 120.4, 110.9, 55.6, 43.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0455.

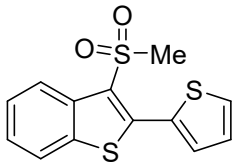


2-(2-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]thiophene (3n). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 95% yield (61.3 mg), mp: 132.4–133.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.52–7.49 (m, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43–7.41 (m, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.1, 139.0, 135.4, 133.6, 132.2, 131.0, 130.9, 130.7, 129.4,

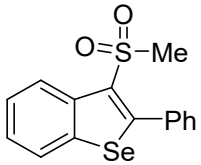
126.4, 126.3, 126.2, 124.0, 122.3, 44.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9960.



3-(Methylsulfonyl)-2-(naphthalen-2-yl)benzo[*b*]thiophene (3o). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 57% yield (38.5 mg), mp: 169.5–170.7 ℃: mp 169.5–170.7 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.93–7.88 (m, 4H), 7.69 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.58–7.54 (m, 3H), 7.51–7.49 (m, 1H), 3.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.7, 138.5, 136.4, 133.7, 132.6, 130.1, 129.4, 129.0, 128.6, 128.0, 127.9, 127.7, 127.5, 127.0, 126.3, 126.0, 124.4, 122.1, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{15}O_2S_2^+$ 339.0508; Found 339.0508.

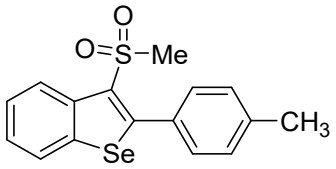


3-(Methylsulfonyl)-2-(thiophen-2-yl)benzo[*b*]thiophene (3p)[6]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 74% yield (43.5 mg), mp: 119.0–119.6 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.47–7.45 (m, 1H), 7.17–7.16 (m, 1H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.5, 138.3, 136.7, 132.1, 131.2, 129.8, 129.5, 128.1, 126.3, 126.1, 124.7, 121.8, 44.4.

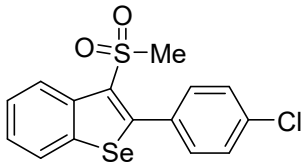


3-(Methylsulfonyl)-2-phenylbenzo[*b*]selenophene (3q). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 71% yield (47.6 mg), mp: 138.7–140.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1H),

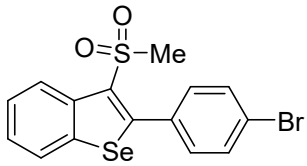
7.90 (d, J = 7.8 Hz, 1H), 7.55–7.52 (m, 3H), 7.44–7.41 (m, 4H), 3.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.6, 140.8, 138.0, 133.8, 131.9, 129.7, 129.5, 128.0, 126.4, 126.2, 126.1, 125.1, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{13}O_2SSe^+$ 336.9796; Found 336.9796.



3-(Methylsulfonyl)-2-(*p*-tolyl)benzo[*b*]selenophene (3r). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 75% yield (52.4 mg), mp: 156.7–158.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.53–7.51 (m, 1H), 7.42–7.39 (m, 3H), 7.24–7.23 (m, 2H), 3.00 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 140.7, 139.6, 138.1, 131.7, 130.8, 129.6, 128.7, 126.3, 126.1, 125.9, 125.1, 45.0, 21.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2SSe^+$ 350.9952; Found 350.9951.

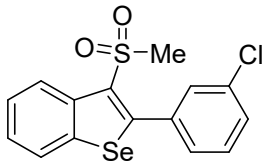


2-(4-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (3s). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 70% yield (51.8 mg), mp: 179.6–180.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.56–7.54 (m, 1H), 7.46–7.43 (m, 3H), 7.41–7.40 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 140.8, 137.9, 135.8, 132.21, 132.17, 131.0, 128.2, 126.4, 126.3, 125.2, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2SSe^+$ 370.9406; Found 370.9404.

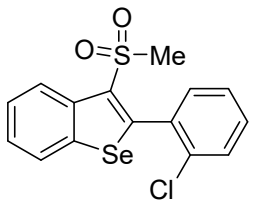


2-(4-Bromophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (3t). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Pale **y**ellow solid; 61%

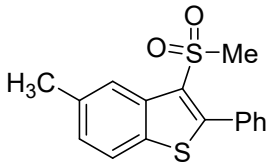
yield (50.5 mg), mp: 163.7–164.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.40–7.38 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.2, 140.8, 137.9, 132.7, 132.2, 131.23, 131.21, 126.4, 126.3, 125.2, 124.1, 45.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{11}BrO_2SSe^+$ 414.8901; Found 414.8889



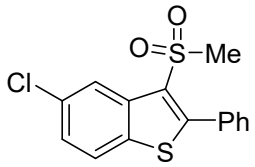
2-(3-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (3u). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 68% yield (50.3 mg), mp: 158.6–159.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.57–7.54 (m, 1H), 7.49 (s, 1H), 7.46–7.40 (m, 3H), 7.38–7.35 (m, 1H), 3.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.6, 140.9, 137.7, 135.5, 133.9, 132.4, 129.5, 129.4, 129.1, 128.1, 126.39, 126.35, 125.2, 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2SSe^+$ 370.9406; Found 370.9408.



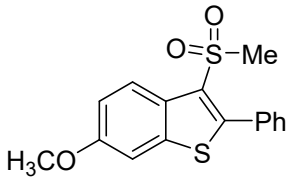
2-(2-Chlorophenyl)-3-(methylsulfonyl)benzo[*b*]selenophene (3v). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow solid; 67% yield (49.5 mg), mp: 161.4–161.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.57–7.55 (m, 1H), 7.48–7.44 (m, 3H), 7.40–7.37 (m, 1H), 7.35–7.33 (m, 1H), 3.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.8, 141.4, 137.2, 133.3, 133.2, 132.7, 131.3, 130.6, 129.4, 126.4, 126.34, 126.28, 126.1, 125.4, 43.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2SSe^+$ 370.9406; Found 370.9406.



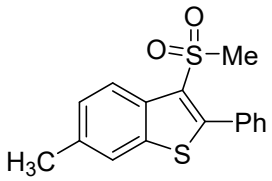
5-Methyl-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3w). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 89% yield (53.8 mg), mp: 158.7–159.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.56–7.55 (m, 2H), 7.47–7.43 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 2.99 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.7, 136.5, 136.3, 135.6, 131.7, 130.4, 129.8, 128.8, 128.1, 127.6, 124.0, 121.6, 45.1, 21.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0507.



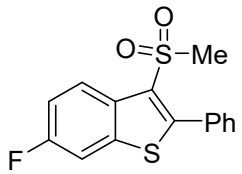
5-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3x). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 81% yield (52.2 mg), mp: 162.2–163.1 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.58–7.56 (m, 2H), 7.52–7.46 (m, 3H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.3, 137.4, 136.4, 132.8, 131.1, 130.4, 130.2, 128.9, 128.3, 126.5, 124.1, 123.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9961.



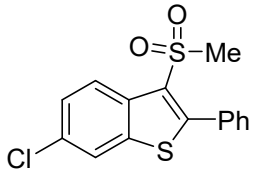
6-Methoxy-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3y). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 80% yield (50.9 mg), mp: 149.6–150.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 9.0 Hz, 1H), 7.57–7.56 (m, 2H), 7.49–7.44 (m, 3H), 7.30 (d, *J* = 1.8 Hz, 1H), 7.14 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.90 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.3, 149.6, 140.0, 131.7, 130.6, 130.1, 129.8, 129.0, 128.1, 125.1, 116.1, 104.3, 55.8, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_3S_2^+$ 319.0457; Found 319.0457.



6-Methyl-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3z). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 91% yield (55.0 mg), mp: 149.6–150.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.57–7.56 (m, 2H), 7.47–7.44 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 1H), 2.98 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.3, 138.7, 136.2, 134.0, 131.7, 130.5, 129.8, 129.1, 128.1, 127.9, 123.9, 121.7, 45.1, 21.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{15}O_2S_2^+$ 303.0508; Found 303.0506.

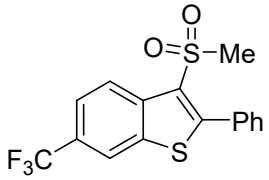


6-Fluoro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3aa). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 94% yield (57.6 mg), mp: 177.1–180.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.55 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.50–7.46 (m, 3H), 7.27 (td, *J* = 9.0, 2.4 Hz, 1H), 2.97 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –114.4; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.0 (d, *J* = 246.6 Hz), 152.1 (d, *J* = 3.3 Hz), 139.4 (d, *J* = 10.0 Hz), 132.8, 131.3, 130.5, 130.1, 129.1, 128.3, 126.0 (d, *J* = 8.9 Hz), 115.3 (d, *J* = 23.7 Hz), 108.2 (d, *J* = 25.5 Hz), 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}FO_2S_2^+$ 307.0257; Found 307.0256.

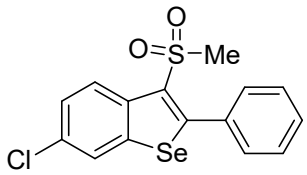


6-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]thiophene (3ab). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Pale yellow solid; 85% yield (54.9 mg), mp: 167.9–168.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.58–7.57 (m, 2H), 7.51–7.46 (m, 3H), 7.44–7.43 (m, 2H),

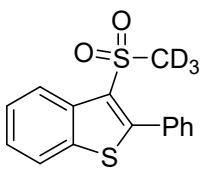
2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.4, 137.4, 136.4, 132.8, 131.1, 130.4, 130.2, 128.9, 128.3, 126.5, 124.1, 123.0, 45.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{12}ClO_2S_2^+$ 322.9962; Found 322.9964.



3-(Methylsulfonyl)-2-phenyl-6-(trifluoromethyl)benzo[*b*]thiophene (3ac). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 83% yield (59.2 mg), mp: 156.4–158.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.85 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.61–7.59 (m, 2H), 7.53–7.49 (m, 3H), 2.98 (s, 3H); ^{19}F NMR (564 MHz, $CDCl_3$): δ = –61.7; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.5, 141.3, 136.1, 130.9, 130.44, 130.40, 130.0, 128.8 (q, *J* = 32.4 Hz), 128.4, 124.3 (q, *J* = 270.9 Hz), 122.7, 122.3 (q, *J* = 3.1 Hz), 122.0 (q, *J* = 4.9 Hz), 45.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{16}H_{12}F_3O_2S_2^+$ 357.0225; Found 357.0223.

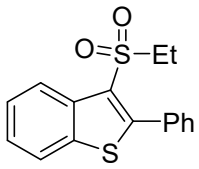


6-Chloro-3-(methylsulfonyl)-2-phenylbenzo[*b*]selenophene (3ad). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Pale yellow solid; 72% yield (53.2 mg), mp: 184.7–185.4 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.53–7.51 (m, 3H), 7.48–7.43 (m, 3H), 2.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 139.6, 139.2, 133.4, 131.4, 129.8, 129.6, 129.2, 129.1, 128.1, 126.3, 120.6, 45.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}D_3O_2S_2^+$ 370.9406; Found 370.9406.

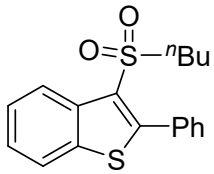


3-((Methyl-*d*$_3$)sulfonyl)-2-phenylbenzo[*b*]thiophene (3ae). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 80% yield (46.6

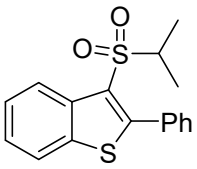
mg), mp: 132.6–133.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.86 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.58–7.57 (m, 2H), 7.56–7.53 (m, 1H), 7.49–7.46 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 138.4, 136.3, 131.6, 130.5, 129.9, 129.2, 128.1, 126.2, 125.9, 124.4, 122.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}D_3O_2S_2^+$ 292.0540; Found 292.0538.



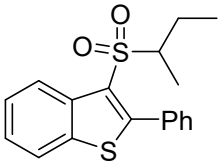
3-(Ethylsulfonyl)-2-phenylbenzo[*b*]thiophene (3af). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Brown solid; 76% yield (46.0 mg), mp: 103.5–104.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.58–7.57 (m, 2H), 7.55–7.52 (m, 1H), 7.50–7.43 (m, 4H), 3.05 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.5, 138.4, 136.7, 131.6, 130.6, 129.8, 128.0, 127.3, 126.2, 125.9, 124.5, 122.0, 51.0, 7.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{15}H_{10}D_3O_2S_2^+$ 292.0540; Found 292.0538.



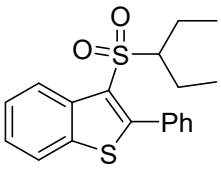
3-(butylsulfonyl)-2-phenylbenzo[b]thiophene (3ag). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 88% yield (58.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.49–7.43 (m, 4H), 3.00 (t, *J* = 7.7 Hz, 2H), 1.63–1.59 (m, 2H), 1.30–1.23 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.0, 138.3, 136.6, 131.6, 130.6, 129.8, 127.9, 126.1, 125.8, 124.4, 121.9, 56.4, 24.3, 21.5, 13.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{19}O_2S_2^+$ 331.0821; Found 331.0820.



3-(Isopropylsulfonyl)-2-phenylbenzo[b]thiophene (3ah). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 67% yield (42.4 mg), mp: 124.2–124.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.42 (m, 4H), 3.18–3.11 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.9, 138.4, 136.9, 131.7, 130.7, 129.7, 127.8, 126.3, 126.1, 125.8, 124.7, 121.9, 55.7, 15.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{17}O_2S_2^+$ 317.0664; Found 317.0663.

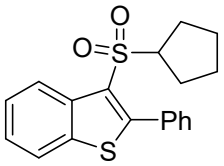


3-(Sec-butylsulfonyl)-2-phenylbenzo[*b*]thiophene (3ai). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 65% yield (43.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 1H), 7.48–7.42 (m, 4H), 2.92–2.86 (m, 1H), 1.90–1.84 (m, 1H), 1.45–1.37 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.7, 138.3, 136.9, 131.7, 130.7, 129.7, 127.8, 126.7, 126.1, 125.8, 124.7, 121.9, 61.6, 22.0, 12.1, 11.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{18}H_{19}O_2S_2^+$ 331.0821; Found 331.0820.

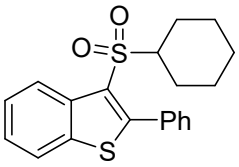


3-(Pentan-3-ylsulfonyl)-2-phenylbenzo[*b*]thiophene (3aj). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Colourless oil; 61% yield (42.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.49–7.43 (m, 4H), 2.75–2.71 (m, 1H), 1.82–1.75 (m, 2H), 1.66–1.59 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (150 MHz,

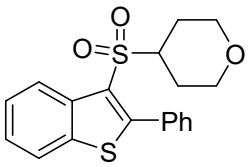
$CDCl_3$): δ = 153.2, 138.4, 137.0, 131.7, 130.8, 129.8, 127.8, 127.6, 126.1, 125.8, 124.7, 122.0, 67.0, 20.0, 11.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{21}O_2S_2^+$ 345.0977; Found 345.0973.



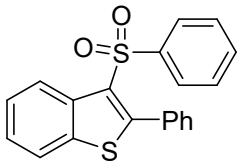
3-(cyclopentylsulfonyl)-2-phenylbenzo[b]thiophene (3ak). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 54% yield (36.9 mg), mp: 124.2–125.9 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.49–7.43 (m, 4H), 3.45–3.40 (m, 1H), 1.99–1.93 (m, 2H), 1.74–1.67 (m, 4H), 1.53–1.49 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.1, 138.4, 136.9, 131.8, 130.8, 129.8, 128.1, 127.9, 126.1, 125.8, 124.7, 121.9, 64.4, 26.8, 25.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}O_2S_2^+$ 343.0821; Found 343.0819.



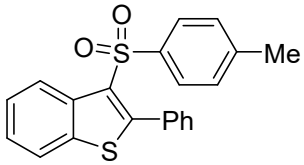
3-(cyclohexylsulfonyl)-2-phenylbenzo[b]thiophene (3al). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 62% yield (44.2 mg), mp: 128.0–129.9 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.58–7.57 (m, 2H), 7.54–7.51 (m, 1H), 7.49–7.43 (m, 4H), 2.87 (tt, *J*1 = 12.1 Hz, *J*2 = 6.7 Hz, 1H), 1.92–1.90 (m, 2H), 1.80–1.77 (m, 2H), 1.60–1.59 (m, 1H), 1.48–1.41 (m, 2H), 1.10–1.08 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.7, 138.3, 136.8, 131.7, 130.6, 129.6, 127.7, 126.3, 125.9, 125.7, 124.6, 121.9, 63.6, 25.04, 25.02, 24.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{20}H_{21}O_2S_2^+$ 357.0977; Found 357.0976.



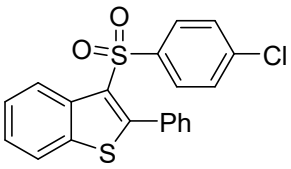
4-((2-phenylbenzo[b]thiophen-3-yl)sulfonyl)tetrahydro-2H-pyran (3am). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Colourless oil; 53% yield (38.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57–7.52 (m, 3H), 7.50–7.44 (m, 4H), 3.98–3.96 (m, 2H), 3.19 (t, *J* = 11.6 Hz, 2H), 3.09–3.05 (m, 1H), 1.83–1.76 (m, 2H), 1.71 (d, *J* = 12.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.5, 138.3, 136.8, 131.5, 130.7, 129.9, 127.8, 126.2, 125.9, 125.6, 124.6, 122.0, 66.5, 61.0, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd For $C_{19}H_{19}O_3S_2^+$ 359.0770; Found 359.0768.



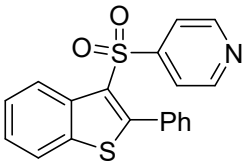
2-phenyl-3-(phenylsulfonyl)benzo[b]thiophene (3an)[7]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 68% yield (47.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45–7.38 (m, 7H), 7.31 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.0, 142.4, 138.2, 136.3, 133.1, 131.7, 130.6, 130.0, 129.6, 128.9, 127.8, 127.0, 126.1, 125.7, 124.7, 121.9.



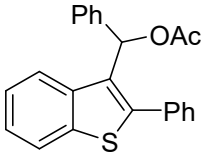
2-phenyl-3-tosylbenzo[b]thiophene (3ao)[7]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). White solid; 70% yield (51.0 mg). mp: 134.5–139.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46–7.38 (m, 6H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 144.0, 139.5, 138.2, 136.2, 131.8, 130.6, 130.4, 129.52, 129.49, 127.7, 127.1, 126.0, 125.7, 124.7, 121.8, 21.6.



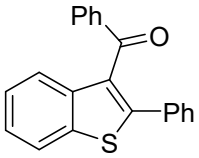
3-((4-chlorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3ap)[7]. Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 65% yield (49.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.55–7.52 (m, 3H), 7.48–7.43 (m, 2H), 7.42–7.39 (m, 4H), 7.27 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 153.2, 140.8, 139.7, 138.2, 136.1, 131.5, 130.6, 129.78, 129.76, 129.1, 128.5, 127.9, 126.2, 125.9, 124.6, 122.0.



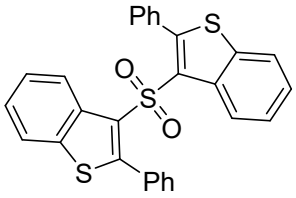
4-((2-phenylbenzo[b]thiophen-3-yl)sulfonyl)pyridine (3aq). Purified by flash column chromatography (petroleum ether/AcOEt = 7:1, v/v). Colourless oil; 51% yield (35.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.66 (s, 2H), 8.62 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.49 (q, *J* = 8.2 Hz, 2H), 7.44–7.39 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.8, 150.8, 150.5, 138.3, 136.1, 131.2, 130.7, 130.1, 128.3, 128.1, 126.5, 126.1, 124.5, 122.1, 120.2.



phenyl(2-phenylbenzo[b]thiophen-3-yl)methyl acetate (4). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 35% yield (25.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.43–7.41 (m, 3H), 7.30–7.28 (m, 4H), 7.26–7.25 (m, 5H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.2, 143.4, 139.6, 139.2, 138.6, 133.7, 130.0, 129.9, 128.84, 128.81, 128.6, 126.6, 124.6, 124.40, 124.39, 122.3, 72.0, 21.2.



phenyl(2-phenylbenzo[b]thiophen-3-yl)methanone (5). Purified by flash column chromatography (petroleum ether/AcOEt = 100:1, v/v). Yellow solid; 41% yield (25.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.6 Hz, 1H), 7.77–7.74 (m, 3H), 7.42–7.37 (m, 5H), 7.27–7.25 (m, 2H), 7.22–7.21 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.4, 146.6, 139.8, 139.1, 137.6, 133.40, 133.36, 131.7, 130.0, 129.5, 128.9, 128.7, 128.4, 125.3, 125.2, 123.8, 122.1.



3,3'-sulfonylbis(2-phenylbenzo[b]thiophene) (6). Purified by flash column chromatography (petroleum ether/AcOEt = 10:1, v/v). Yellow oil; 45% yield (43.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20–8.19 (m, 1H), 7.65–7.63 (m, 1H), 7.31–7.30 (m, 2H), 7.25–7.24 (m, 2H), 7.14–7.11 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.7, 137.5, 137.0, 131.1, 131.0, 130.2, 129.2, 127.7, 125.5, 125.2, 124.8, 121.3.

6. References

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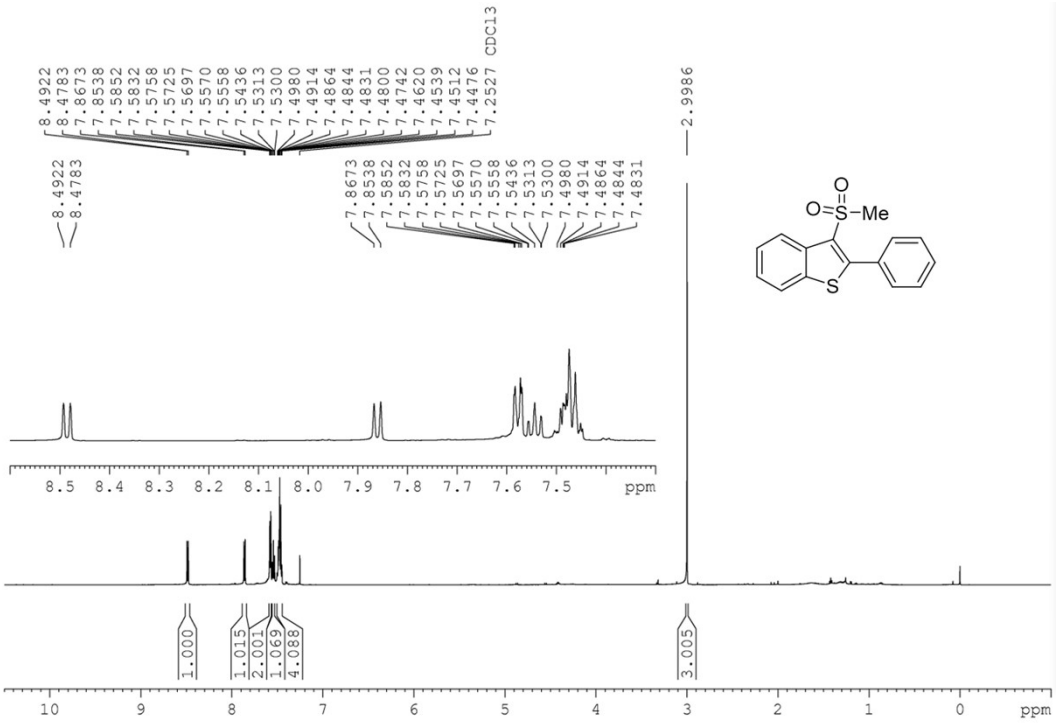
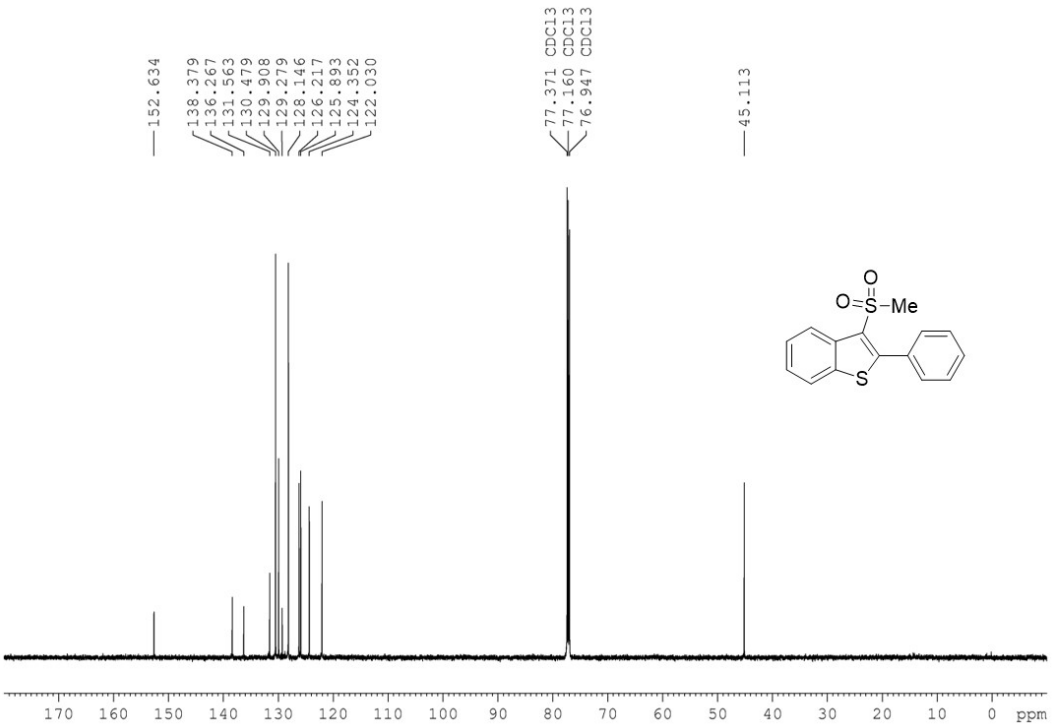
7. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products

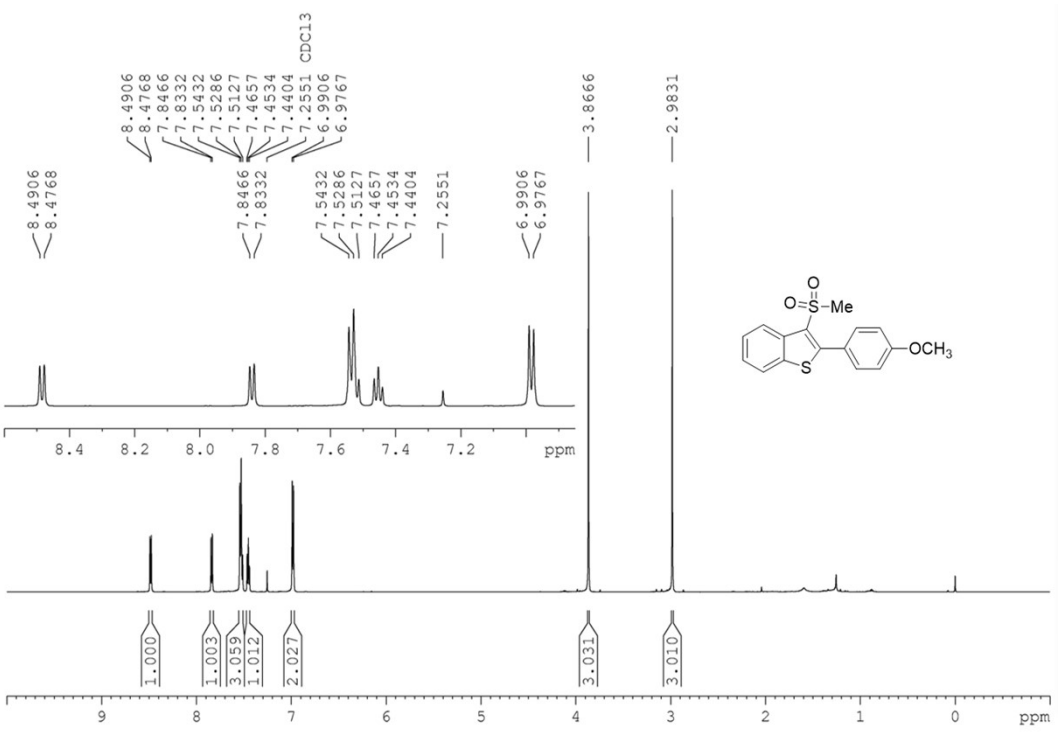
^{1}H NMR (600 MHz, $CDCl_3$) of **3a**



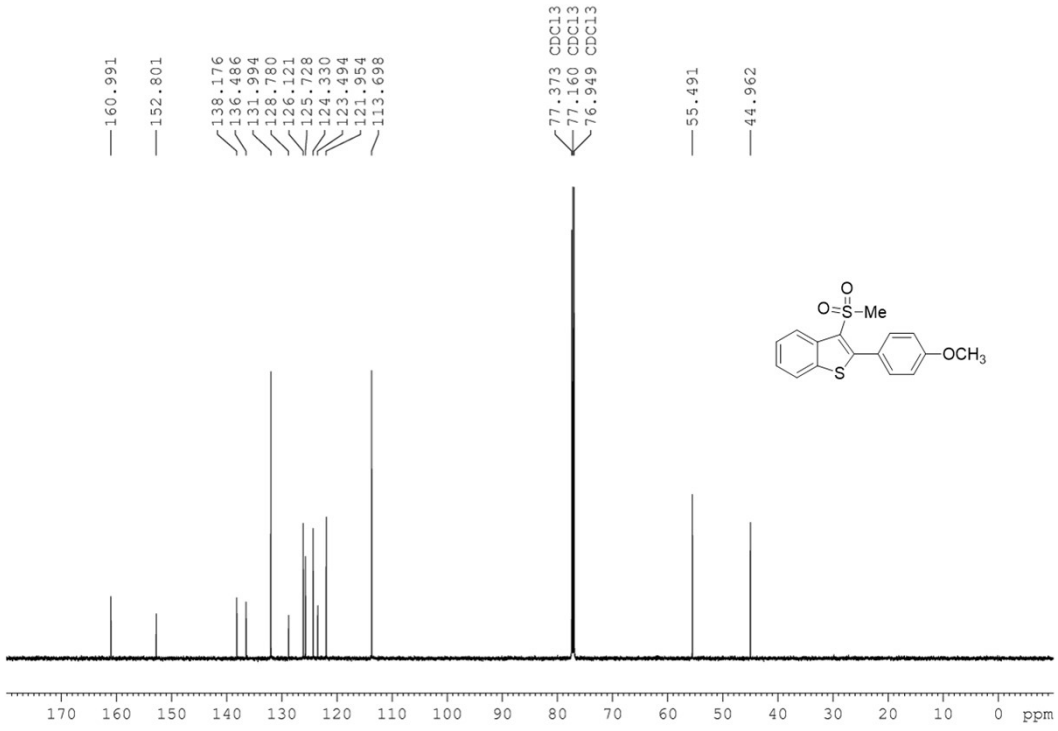
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3a**



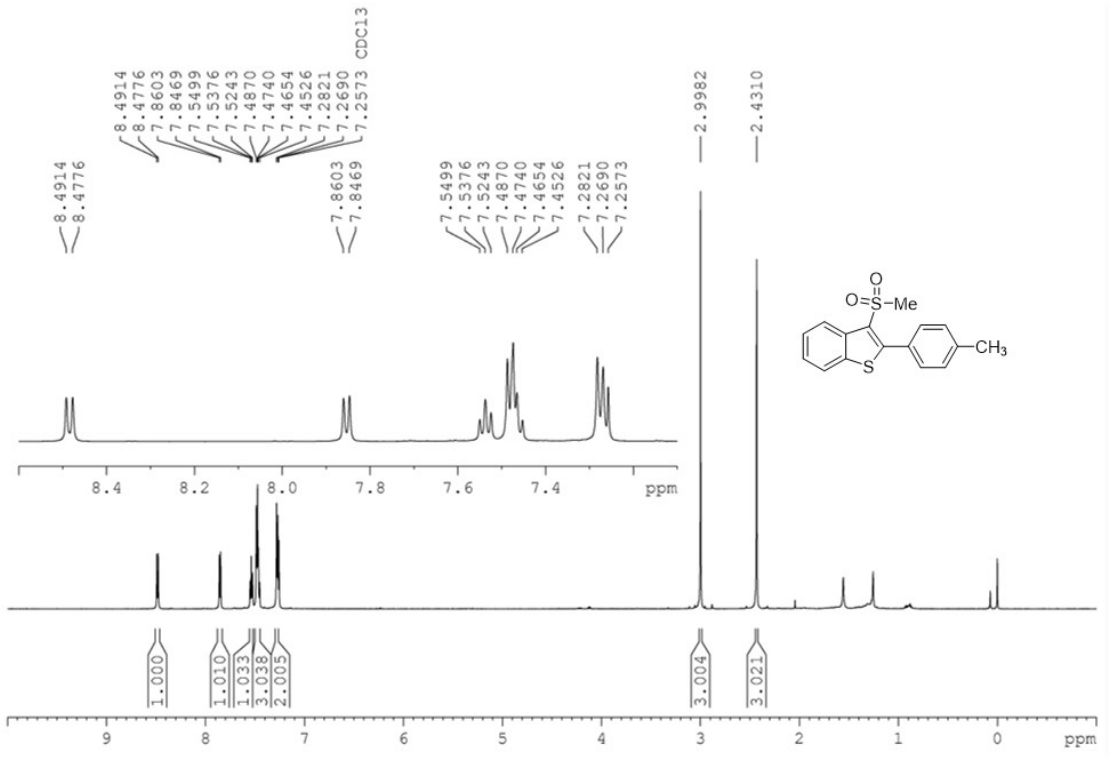
^{1}H NMR (600 MHz, $CDCl_3$) of **3b**



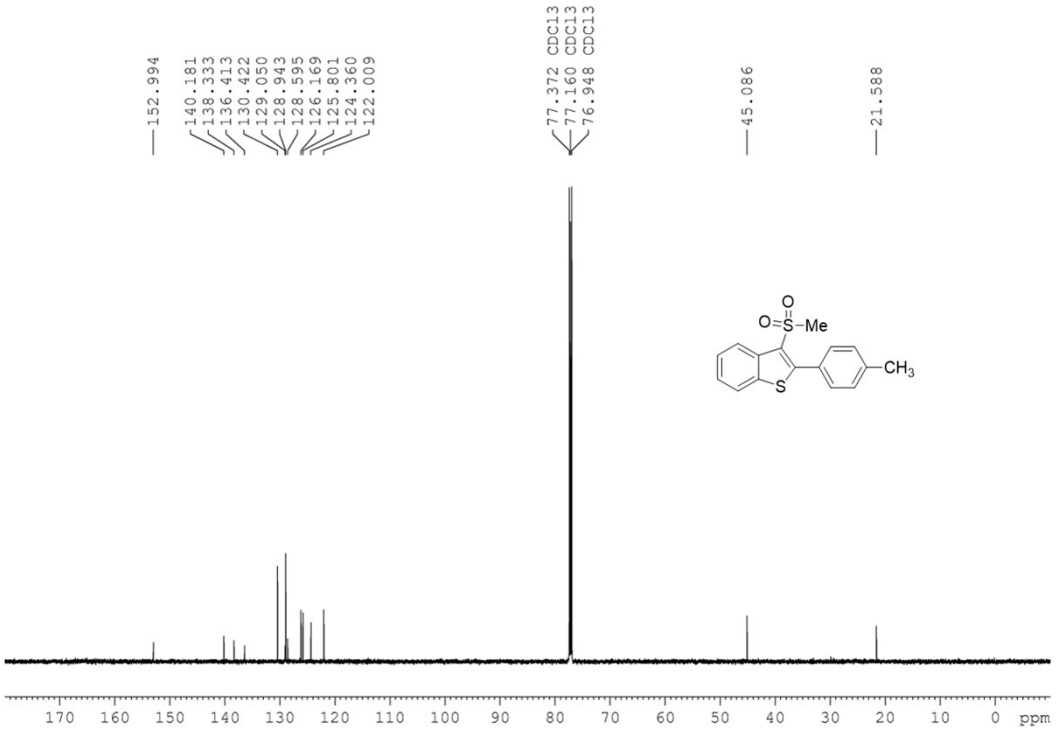
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3b**



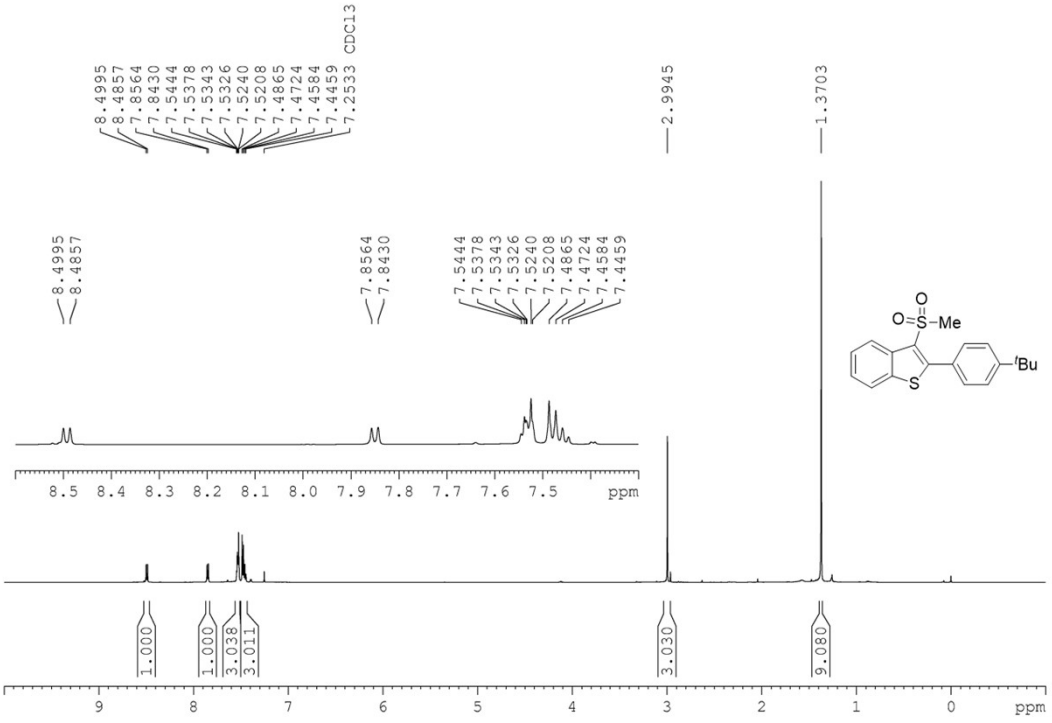
^{1}H NMR (600 MHz, $CDCl_3$) of **3c**



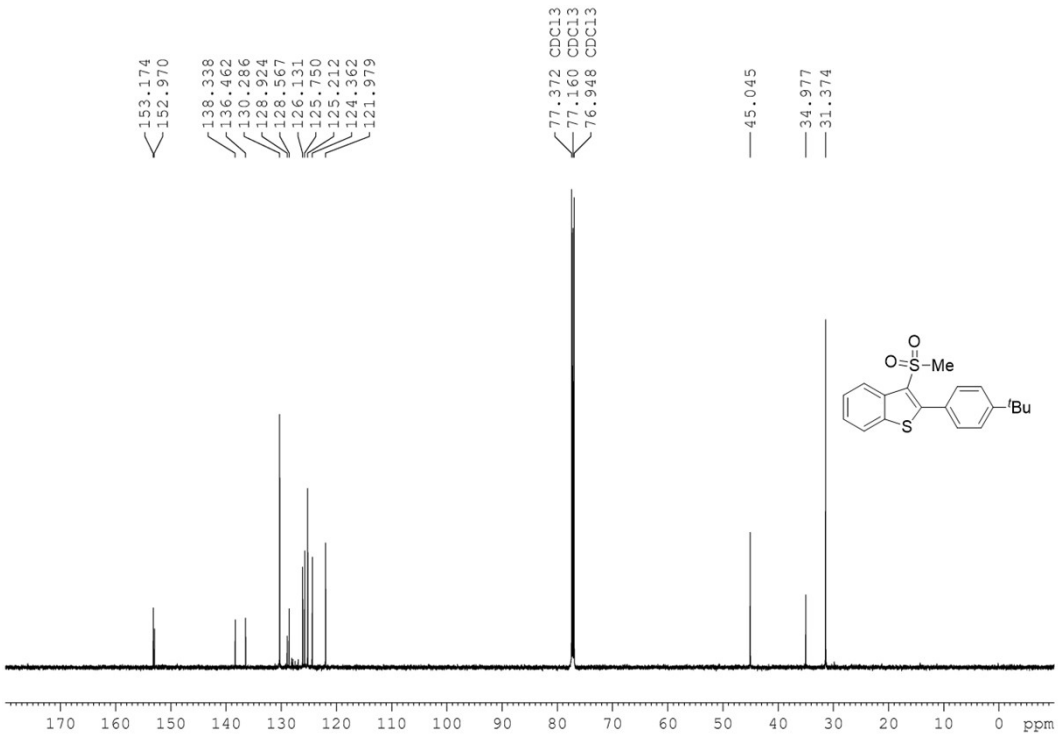
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3c**



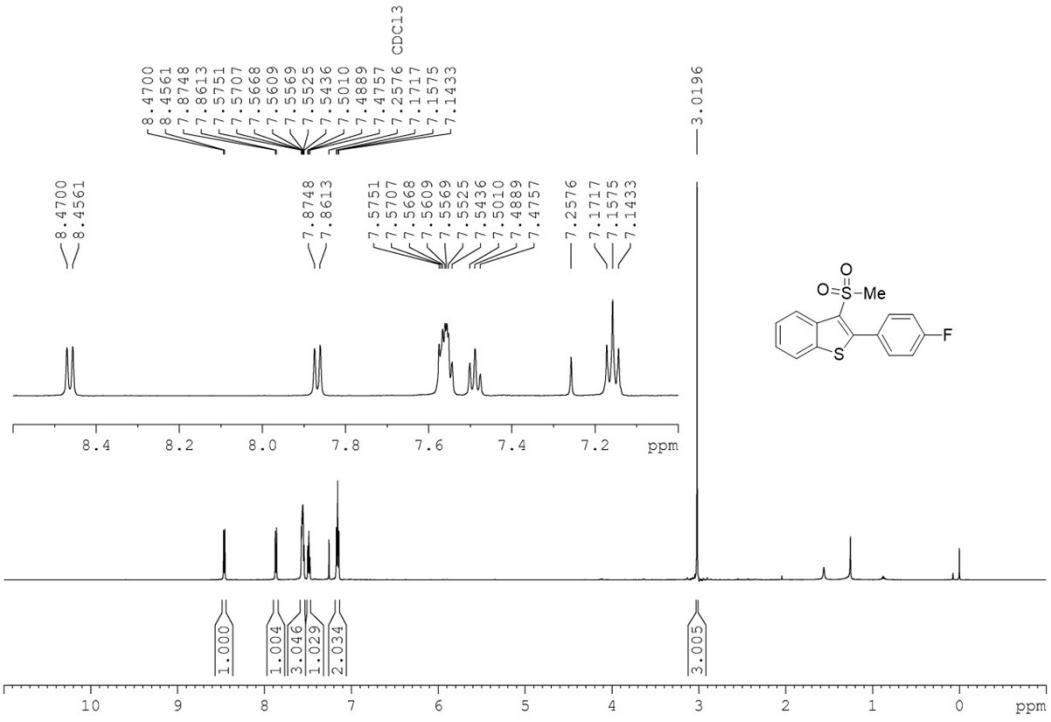
^{1}H NMR (600 MHz, $CDCl_3$) of **3d**



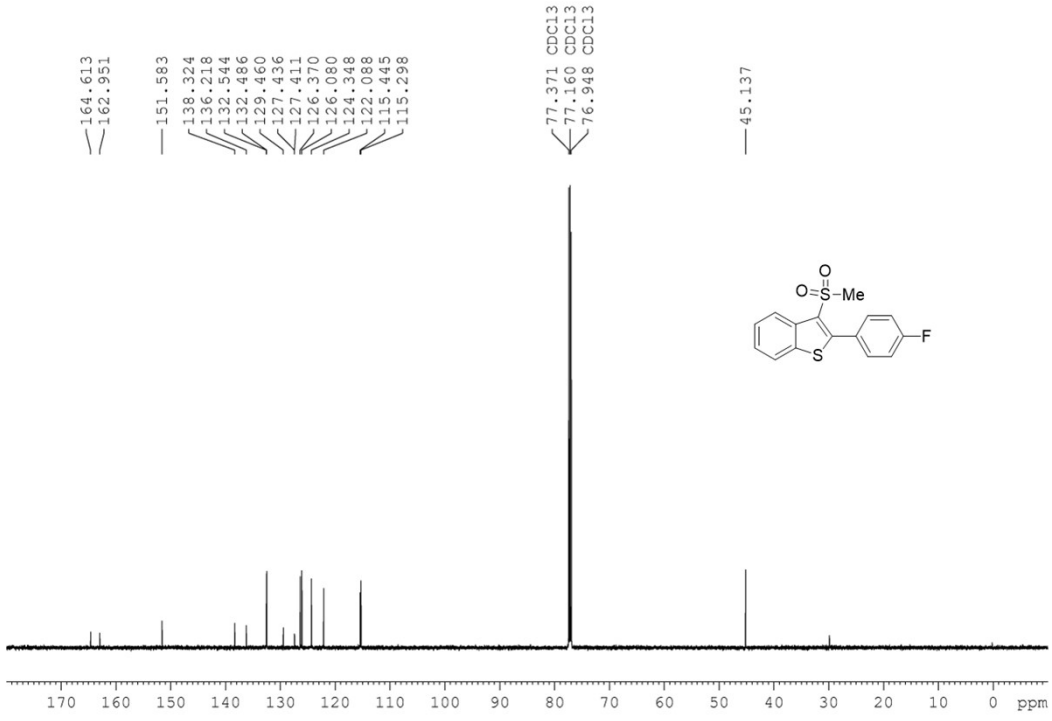
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3d**



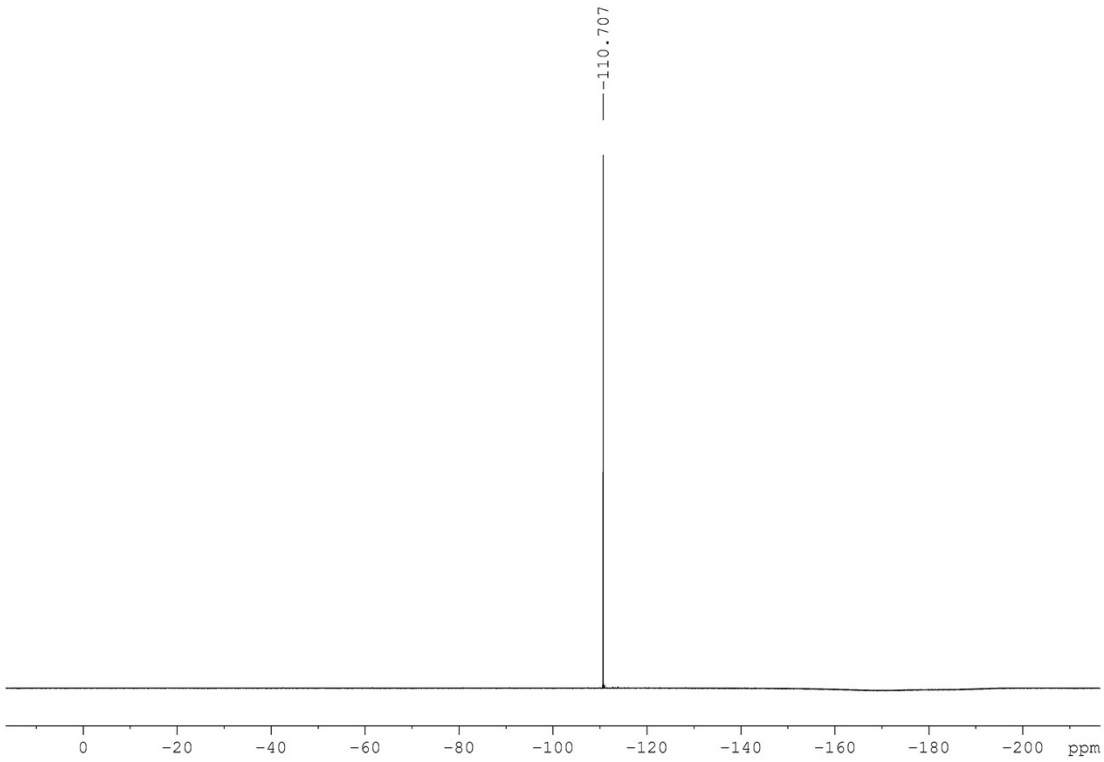
^{1}H NMR (600 MHz, $CDCl_3$) of **3e**



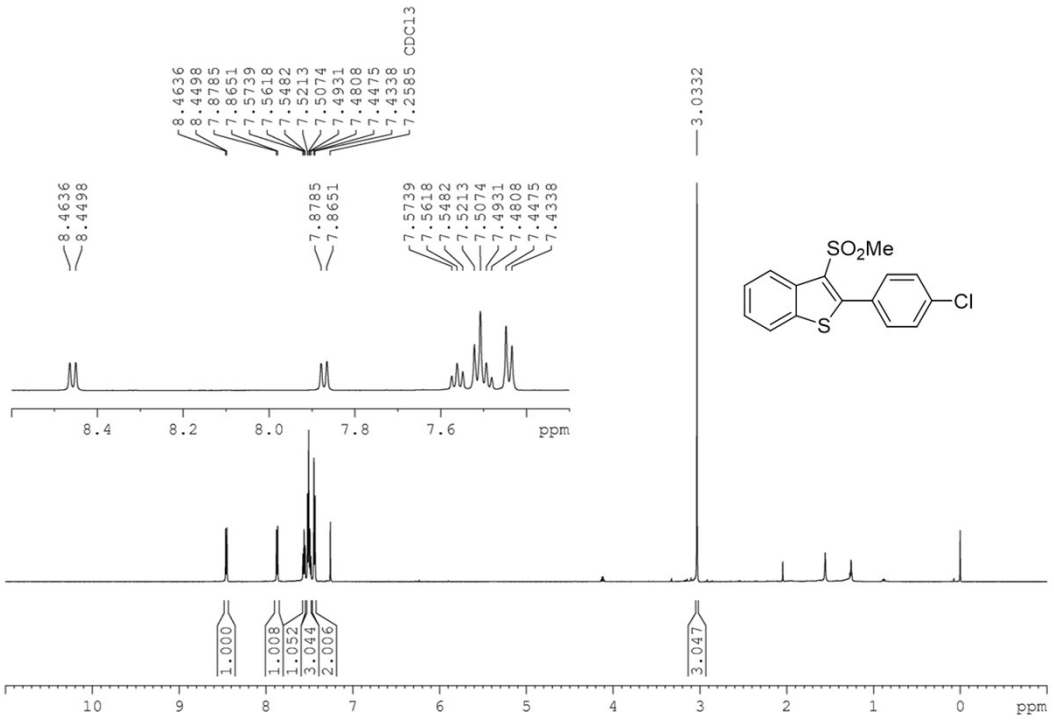
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3e**



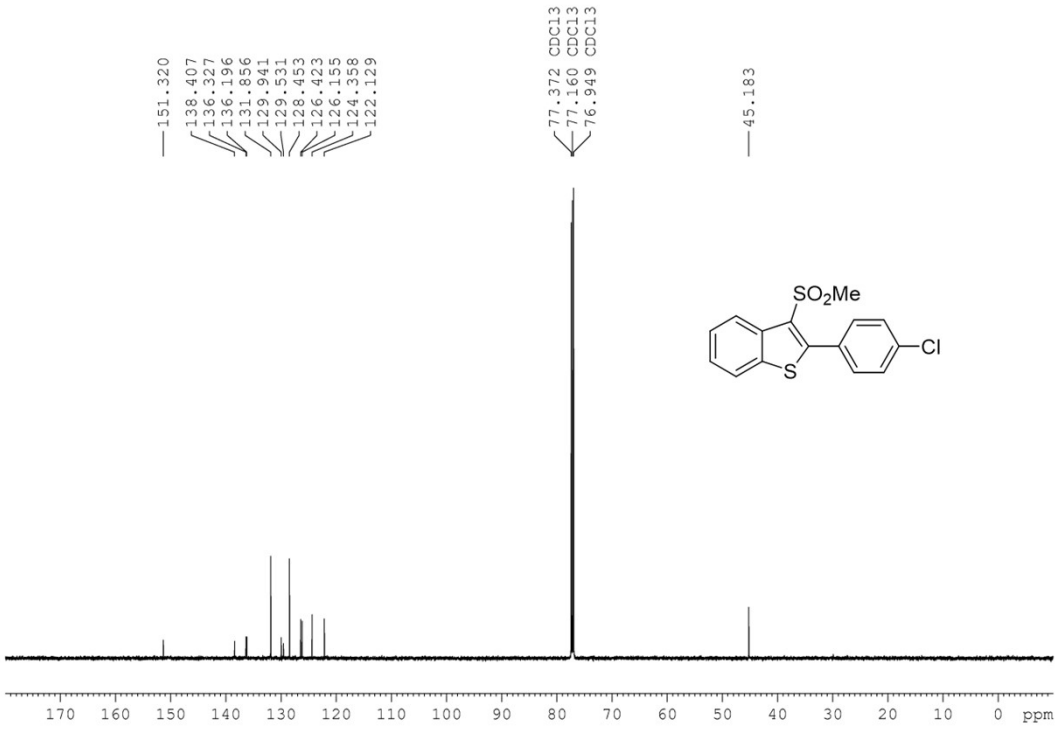
^{19}F NMR (564 MHz, $CDCl_3$) of **3e**



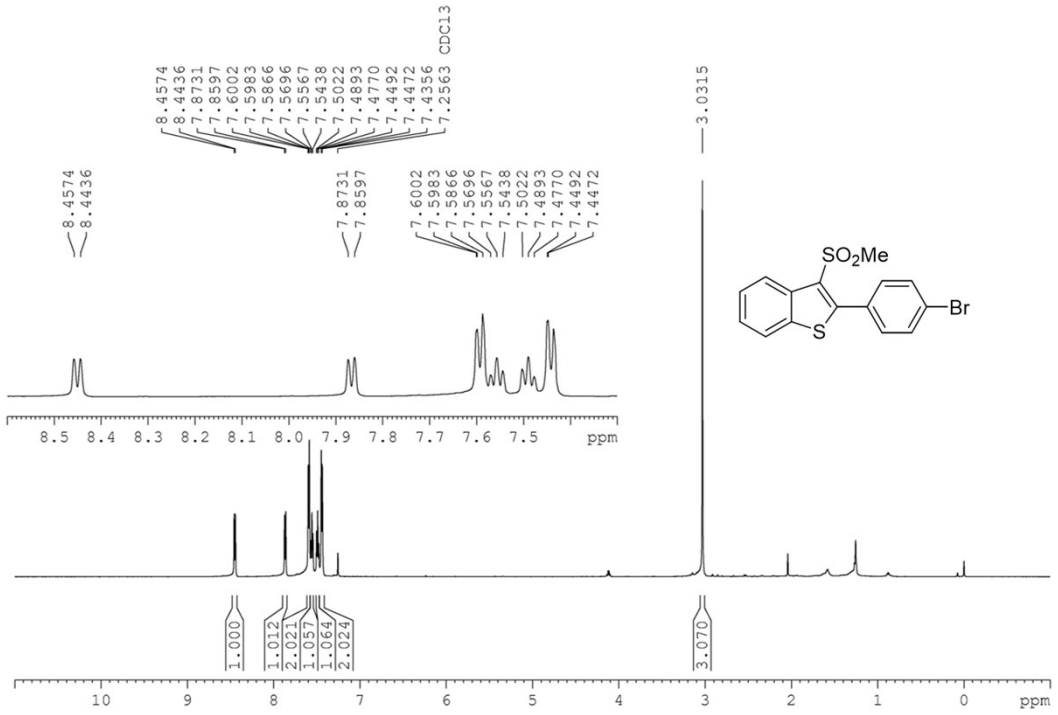
^{1}H NMR (600 MHz, $CDCl_3$) of **3f**



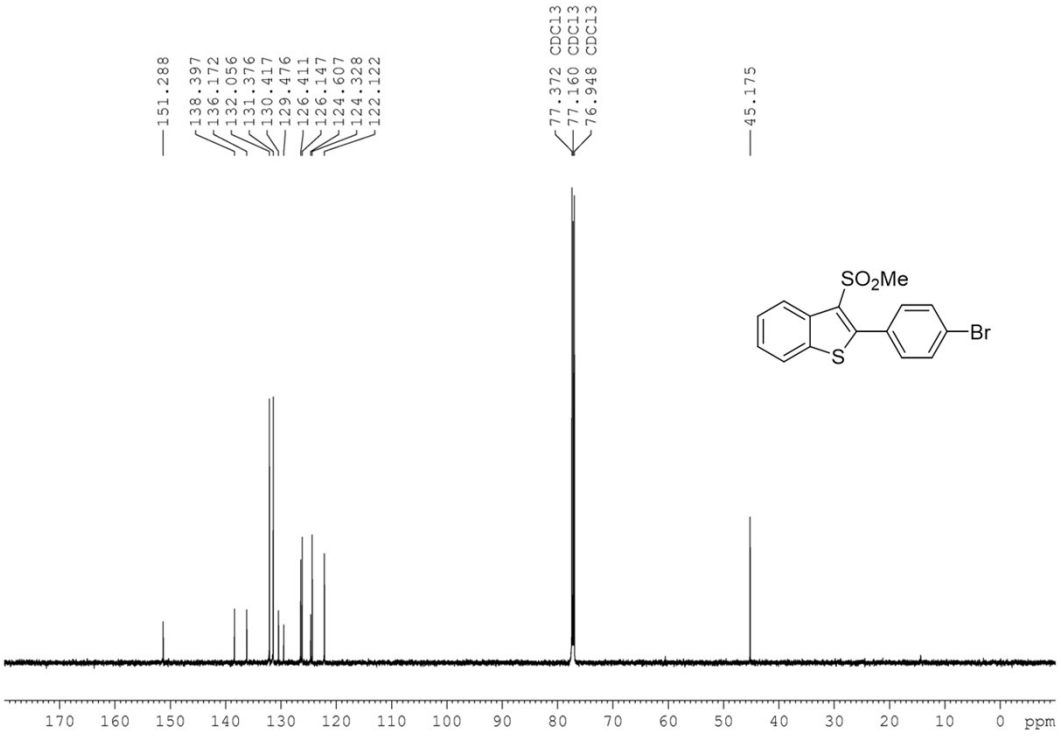
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3f**



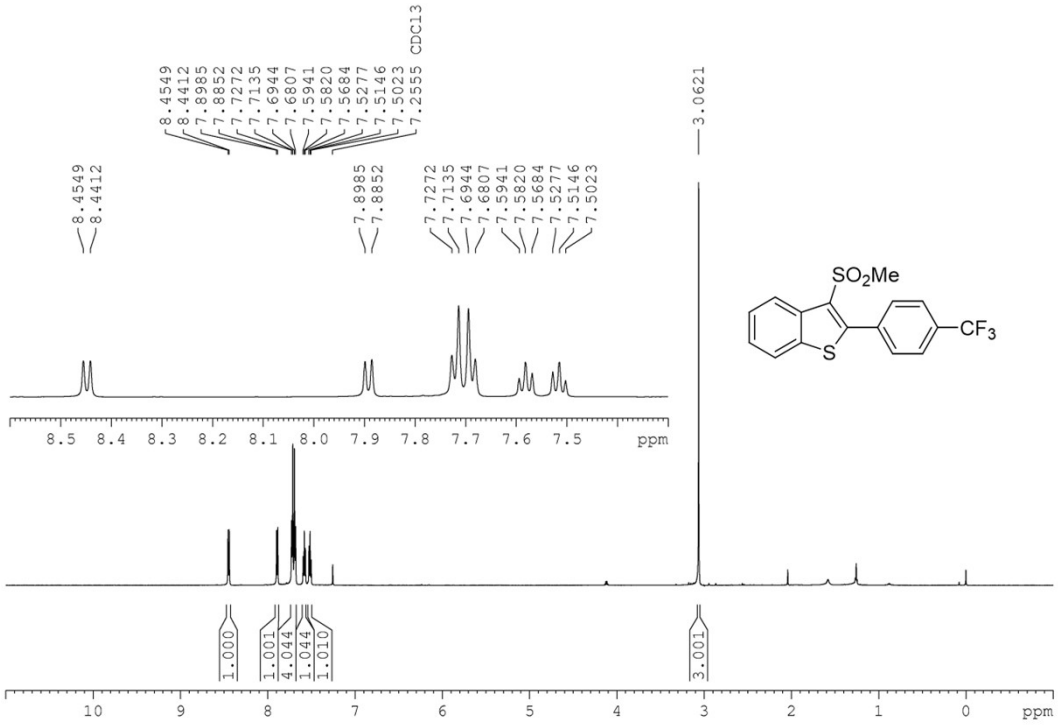
^{1}H NMR (600 MHz, $CDCl_3$) of **3g**



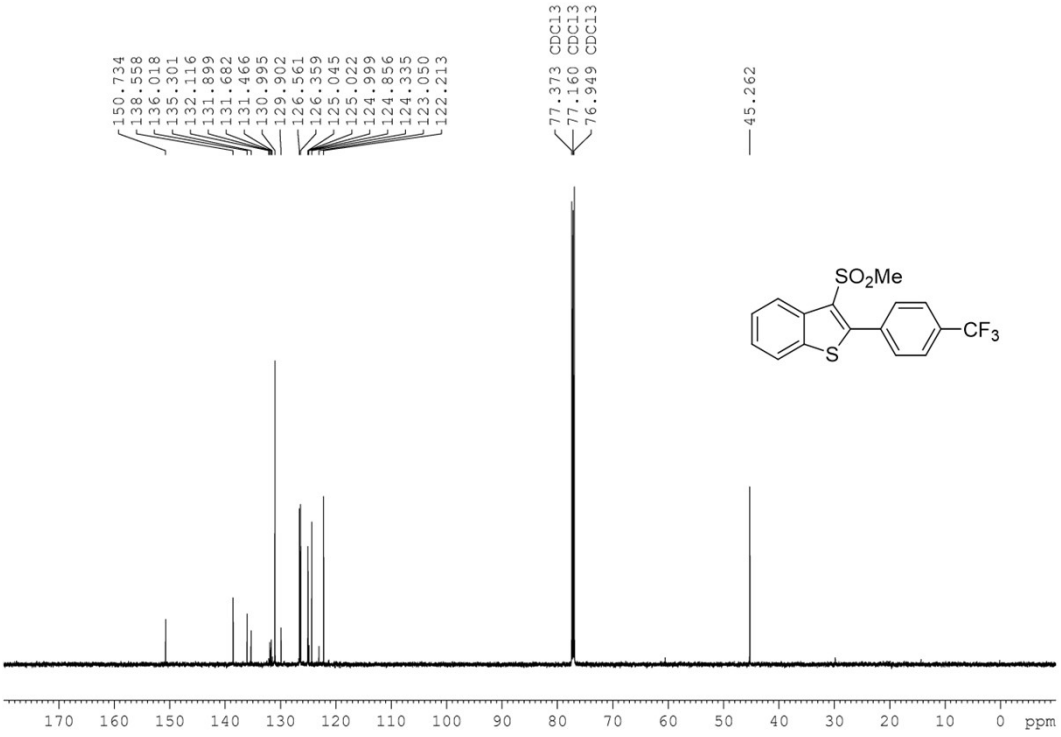
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3g**



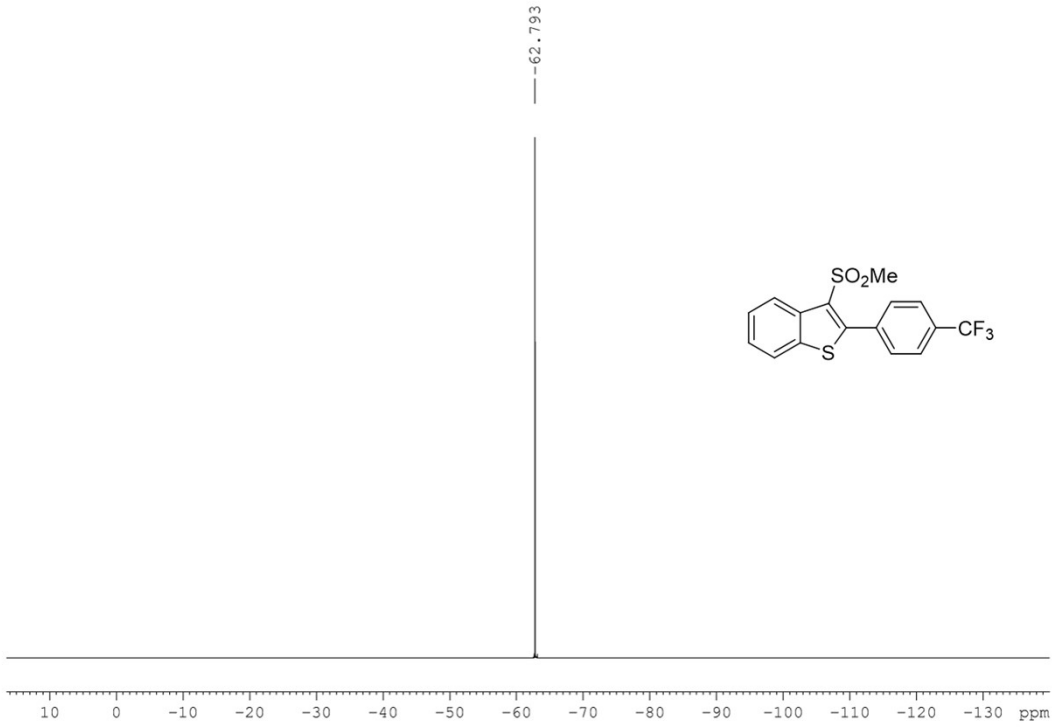
^{1}H NMR (600 MHz, $CDCl_3$) of **3h**



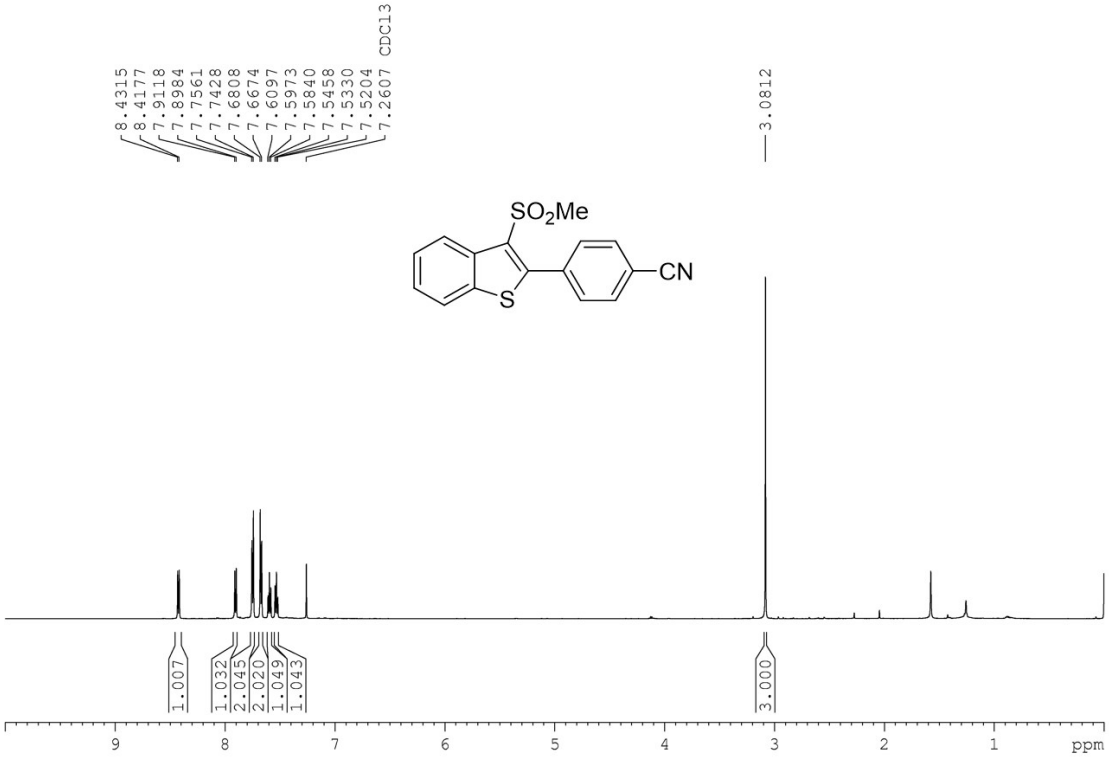
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3h**



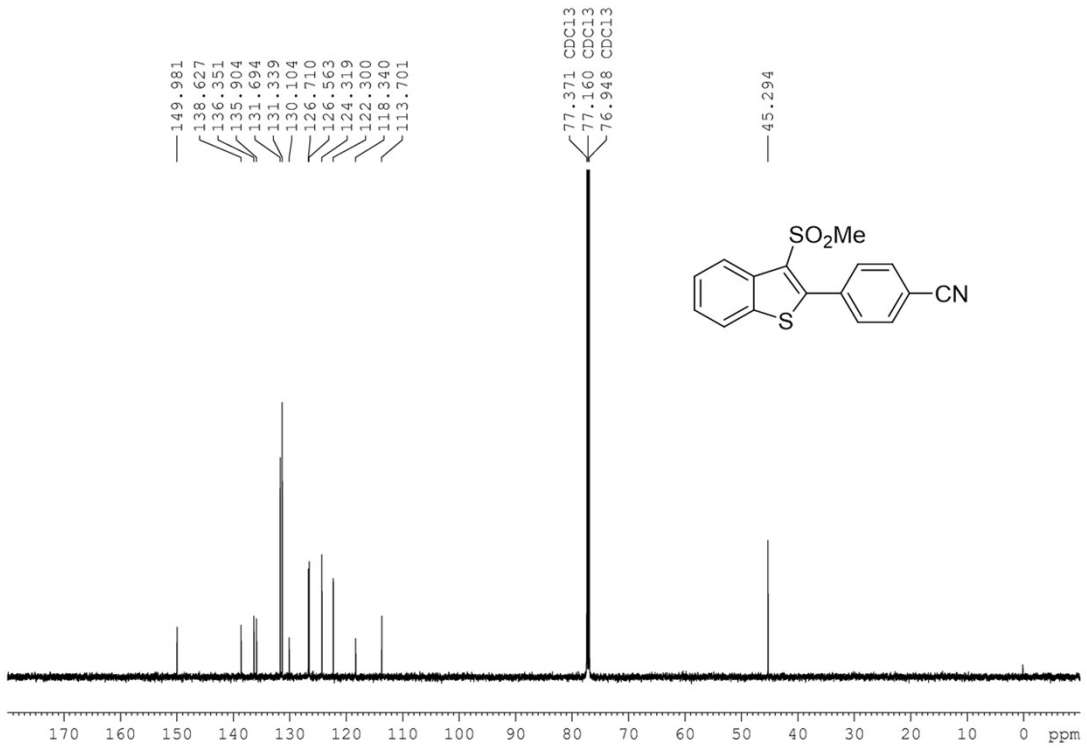
^{19}F NMR (564 MHz, $CDCl_3$) of **3h**



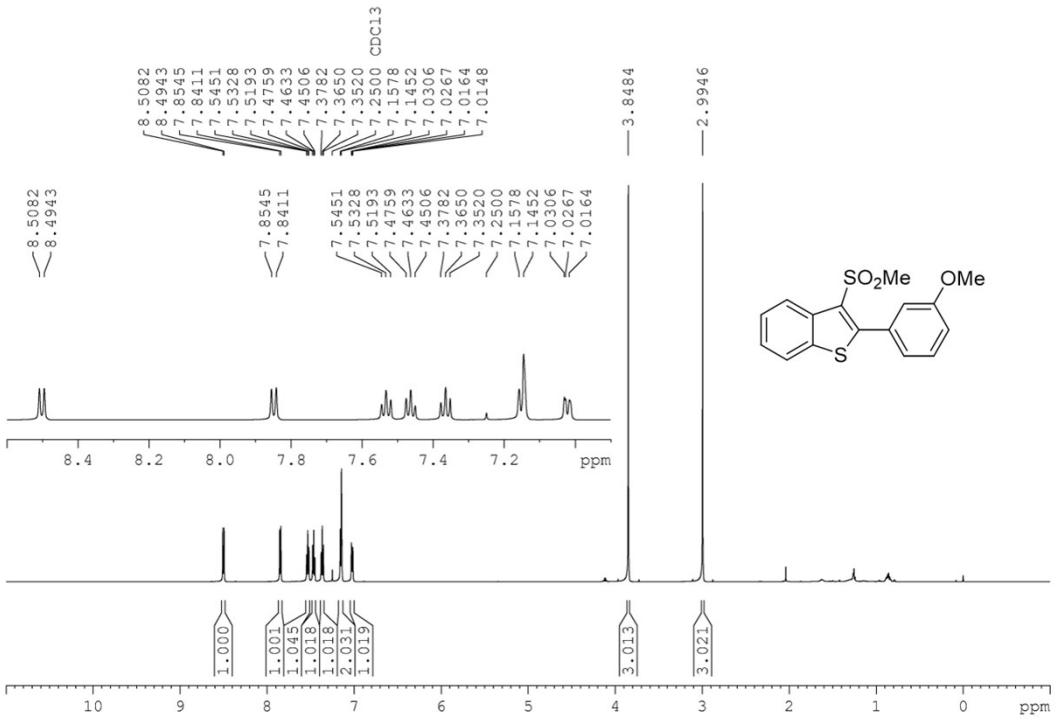
^{1}H NMR (600 MHz, $CDCl_3$) of **3i**



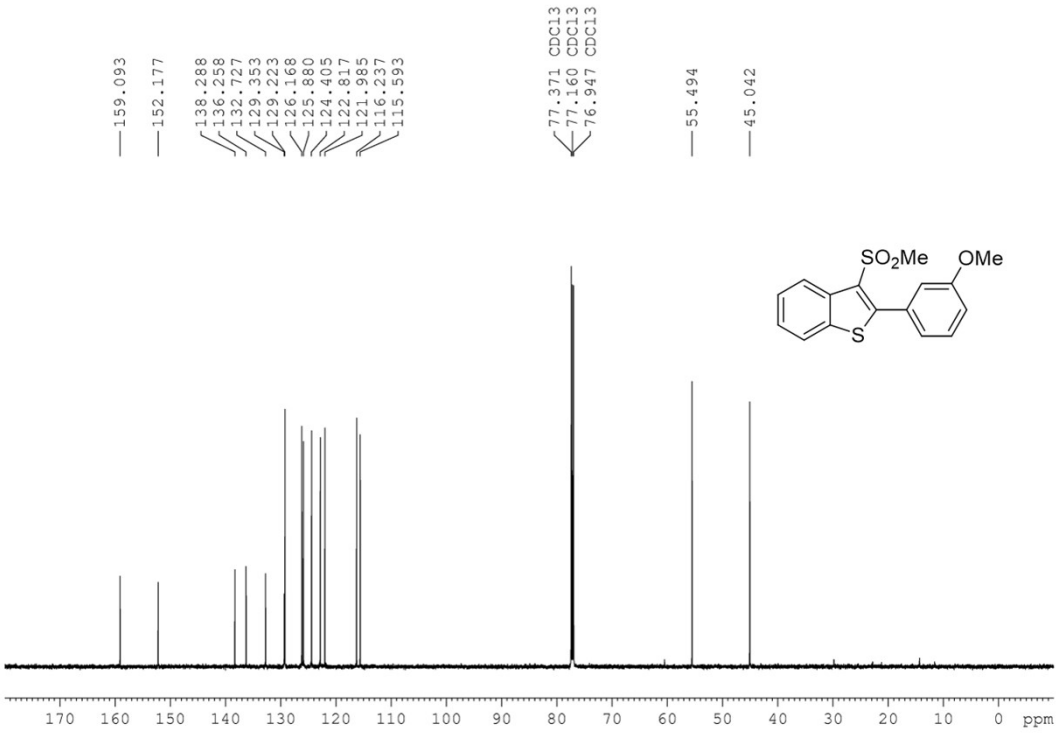
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3i**



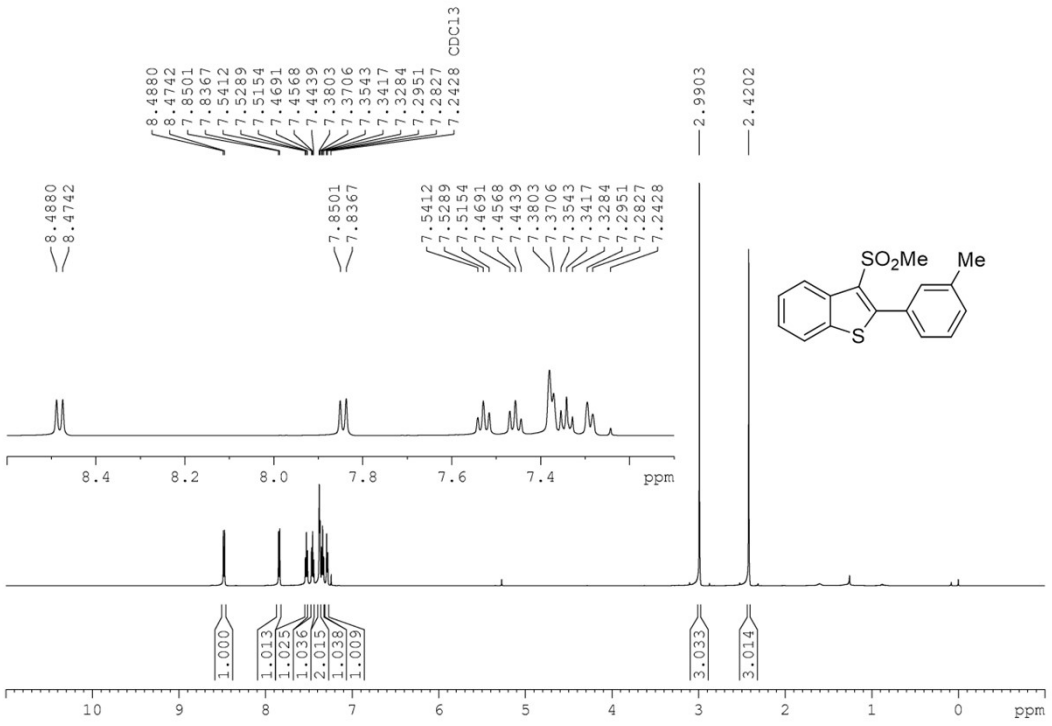
^{1}H NMR (600 MHz, $CDCl_3$) of **3j**



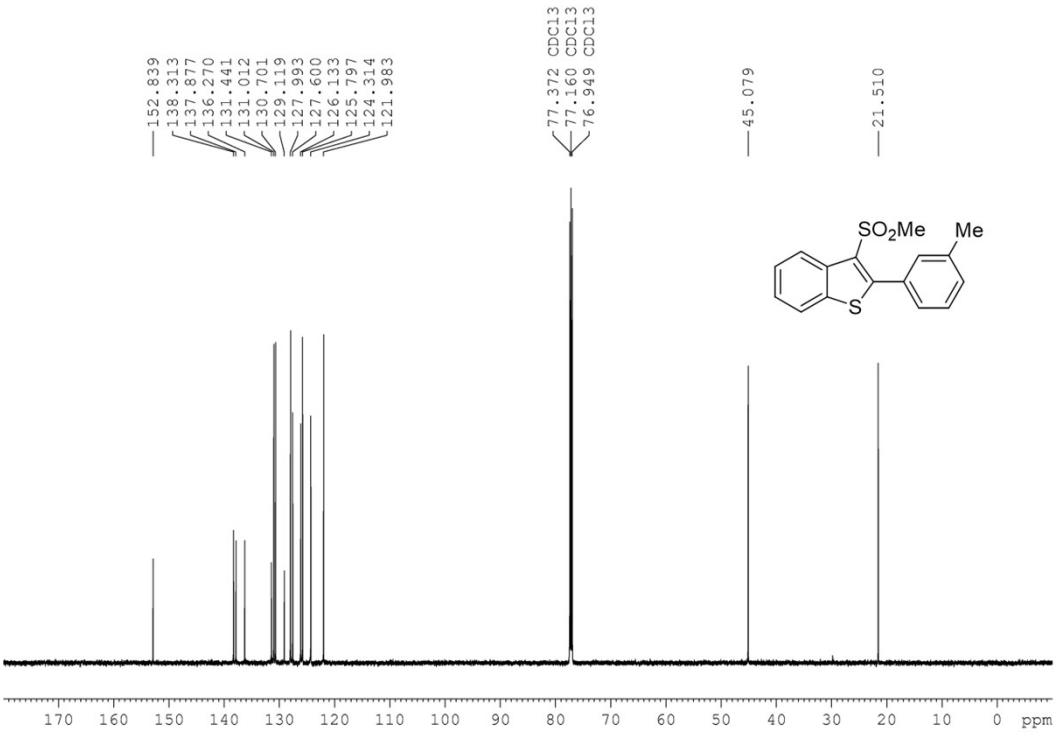
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3j**



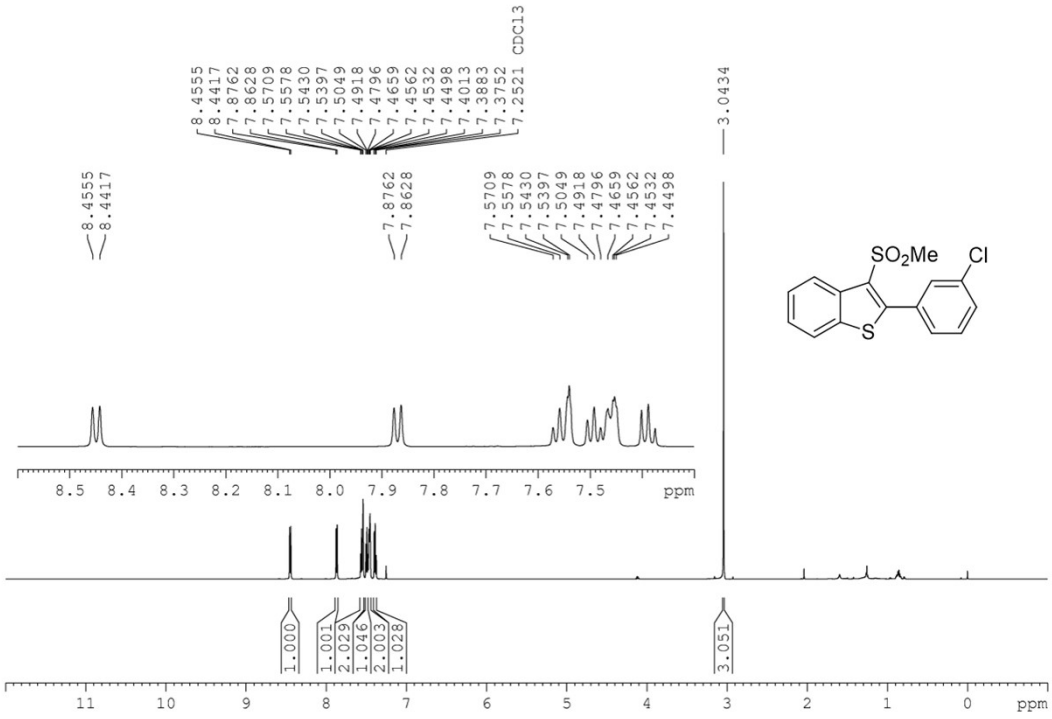
^{1}H NMR (600 MHz, $CDCl_3$) of **3k**



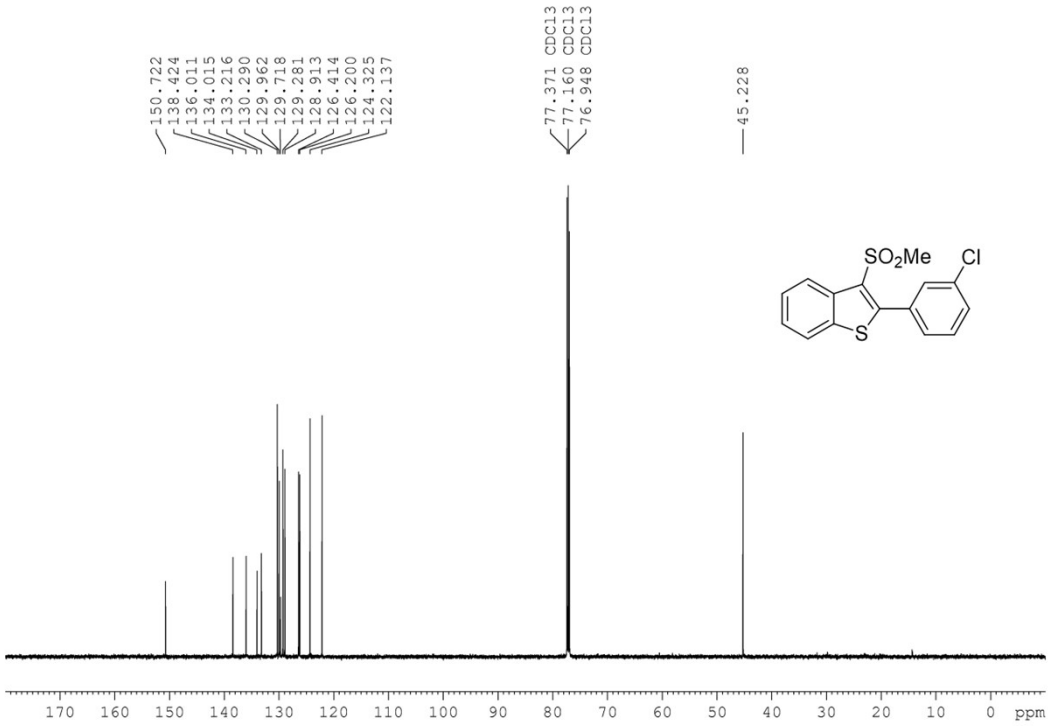
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3k**



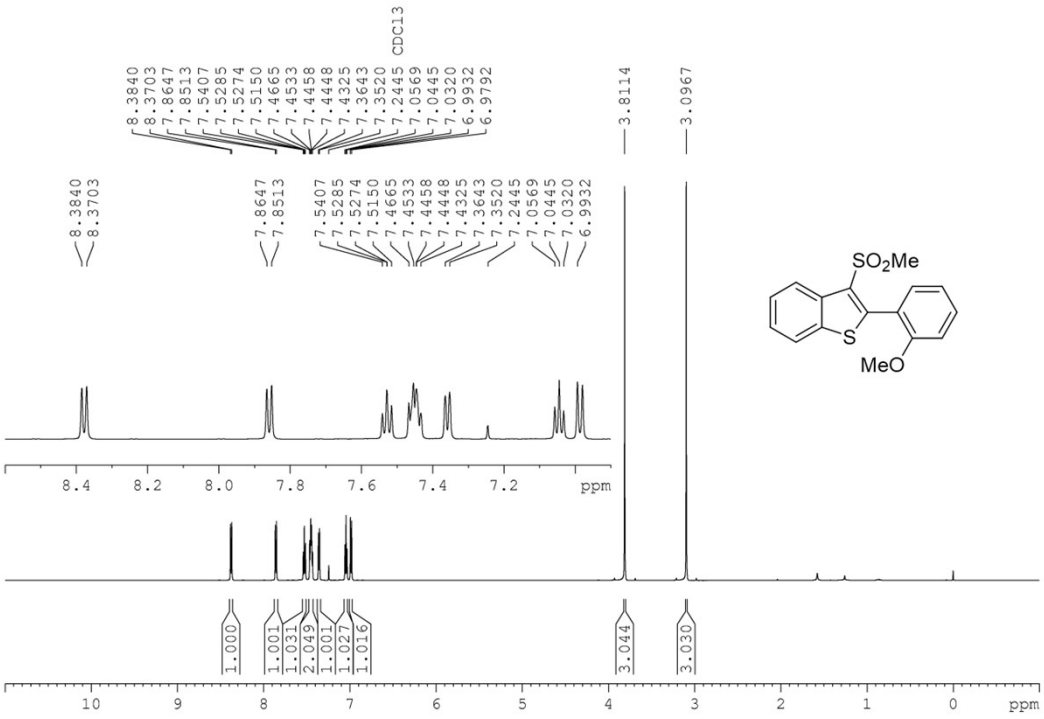
^{1}H NMR (600 MHz, $CDCl_3$) of **3l**



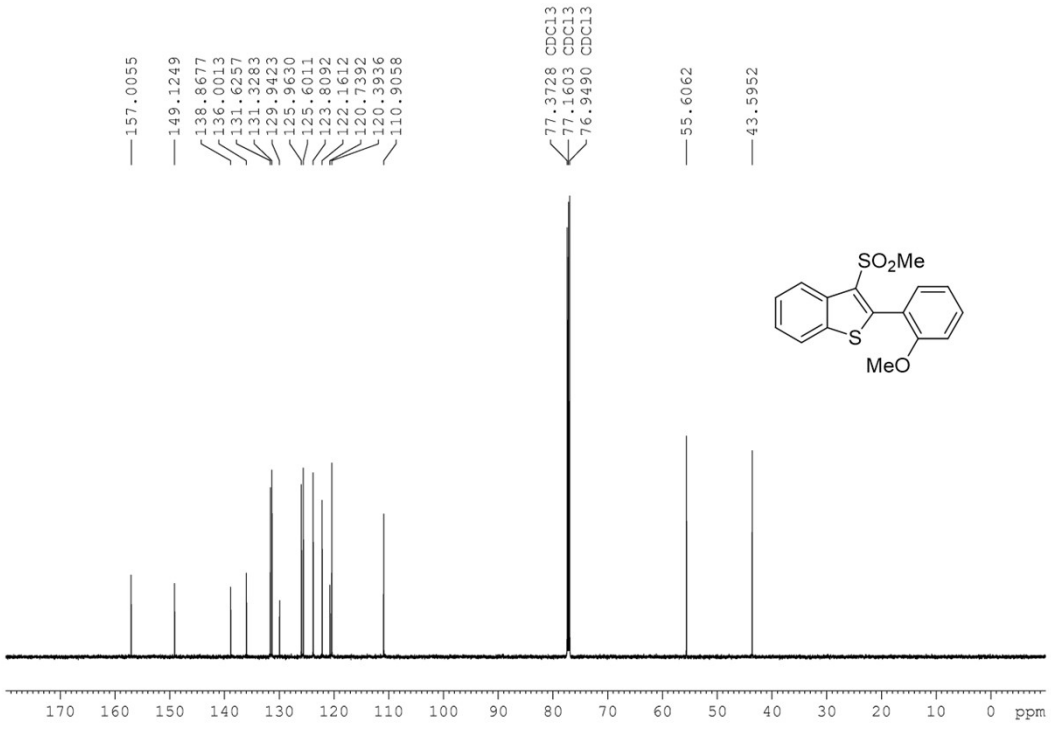
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3l**



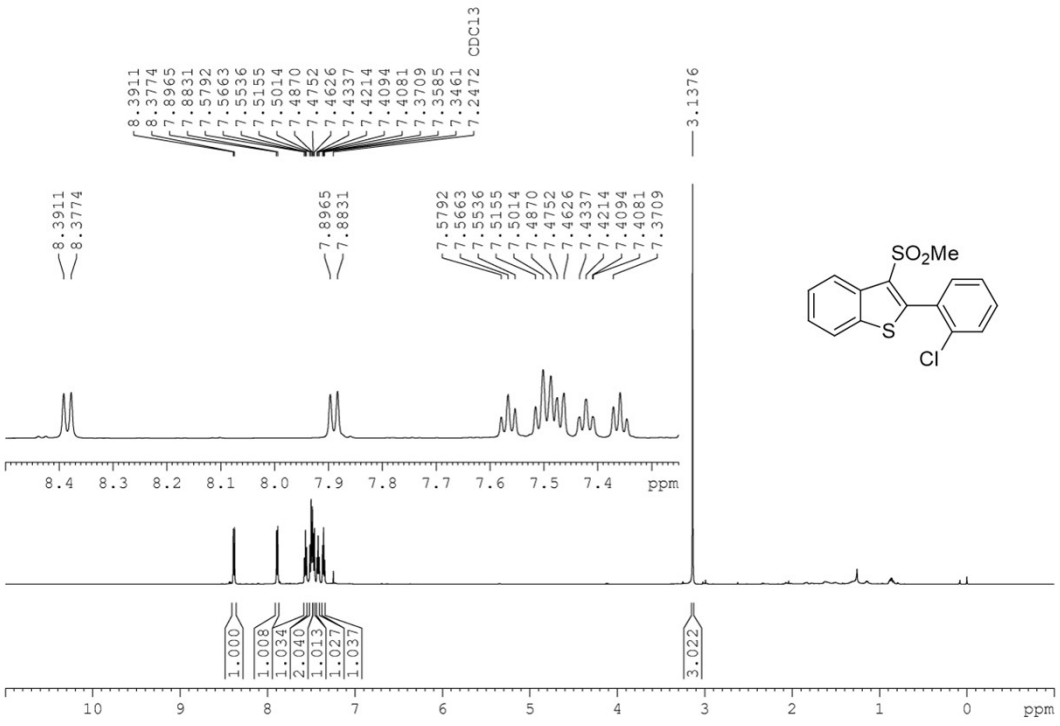
^{1}H NMR (600 MHz, $CDCl_3$) of **3m**



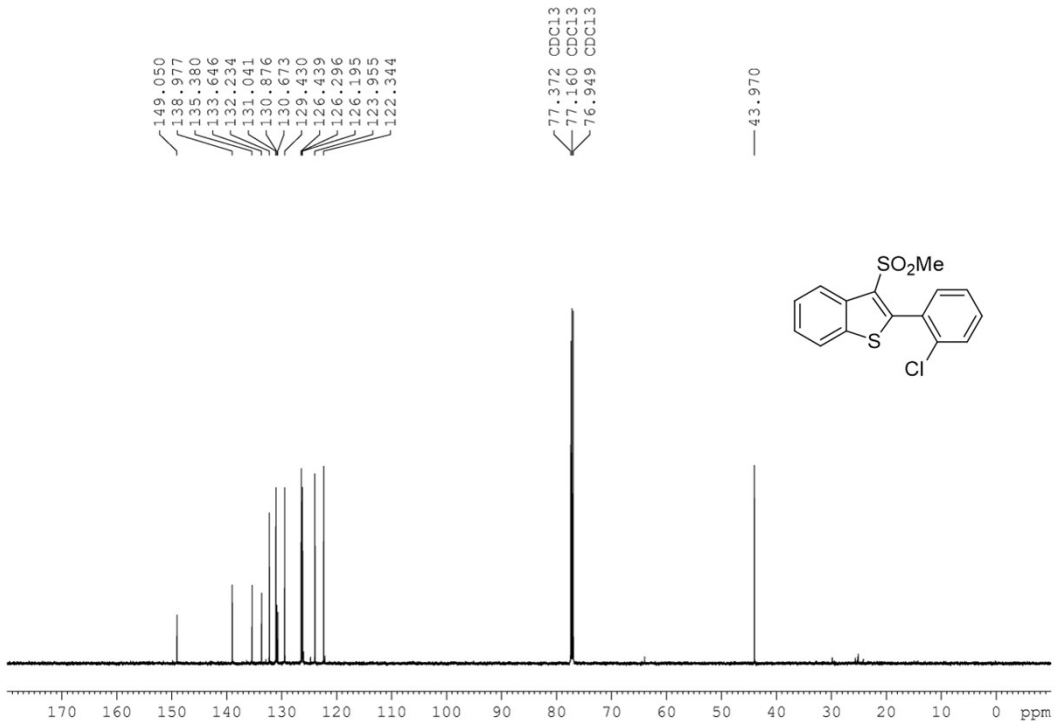
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3m**



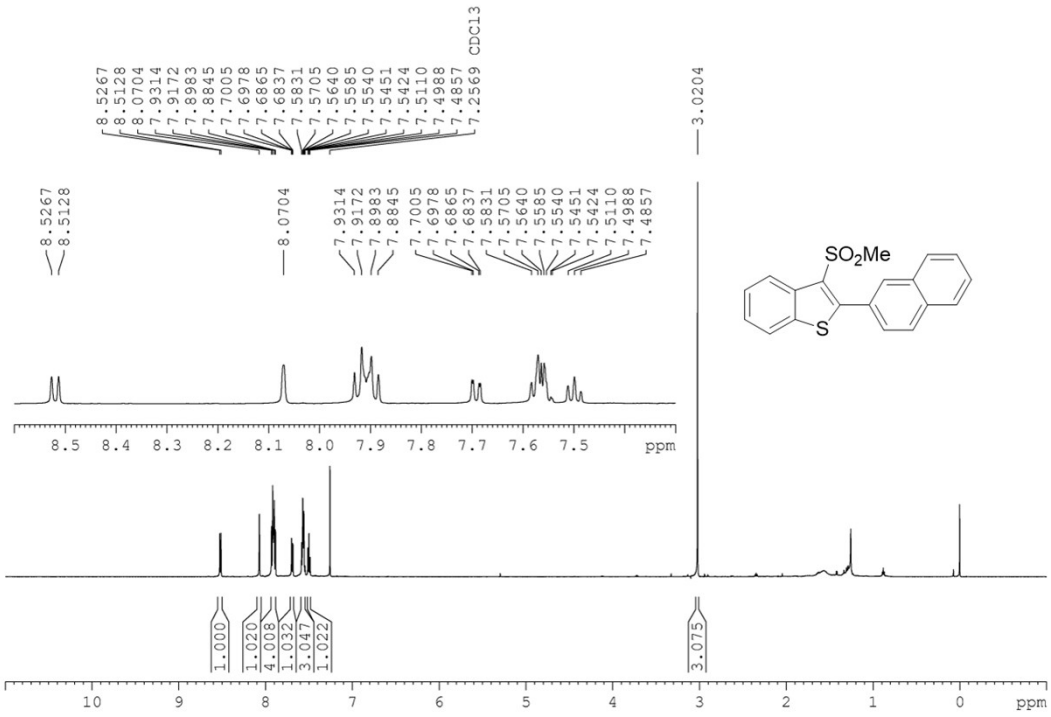
^{1}H NMR (600 MHz, $CDCl_3$) of **3n**



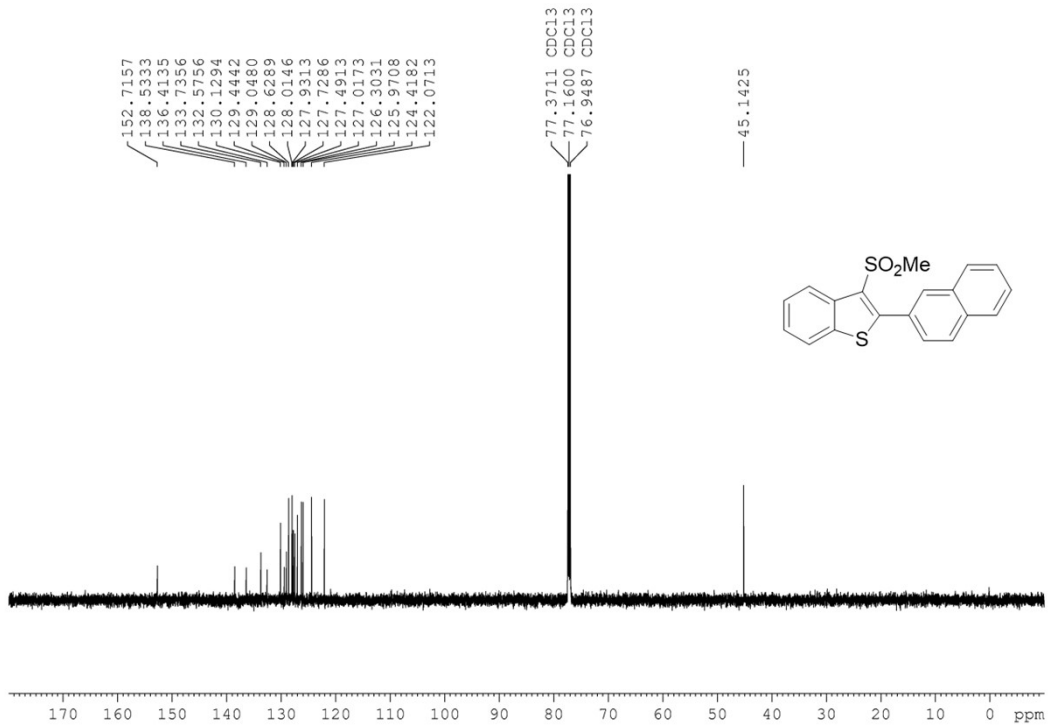
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3n**



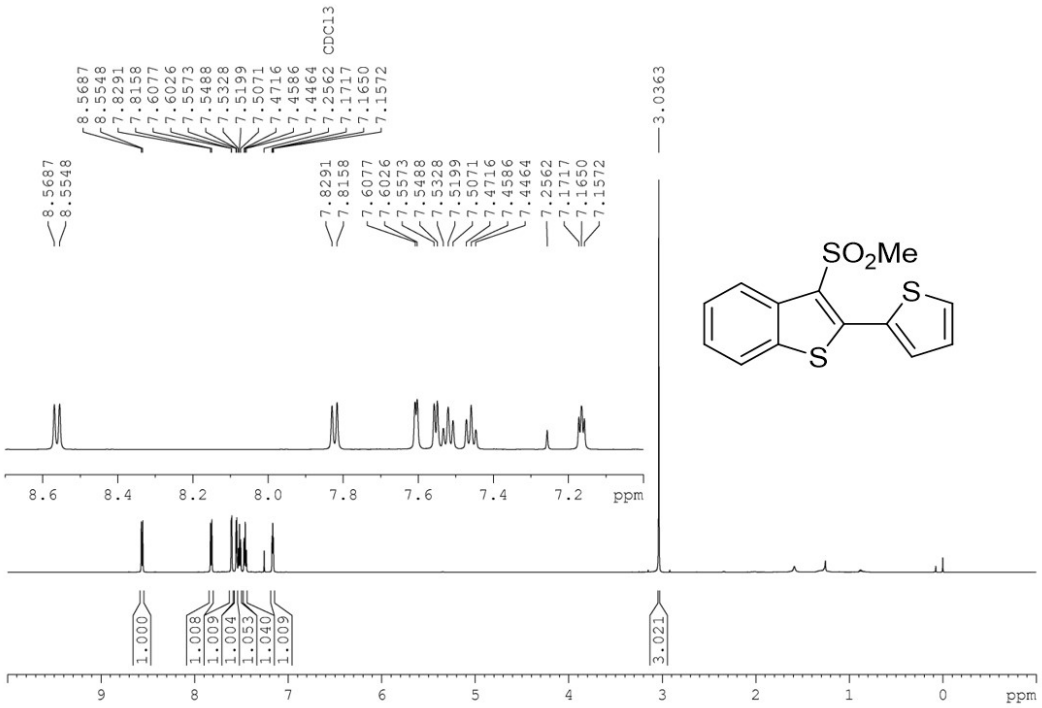
^{1}H NMR (600 MHz, $CDCl_3$) of **3o**



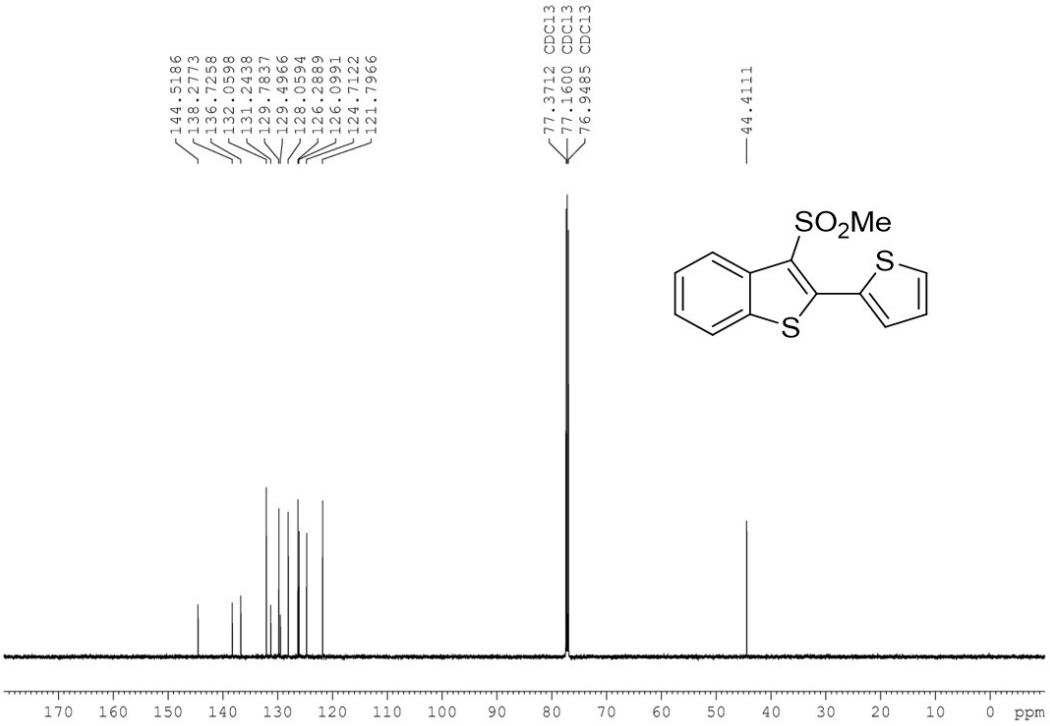
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3o**



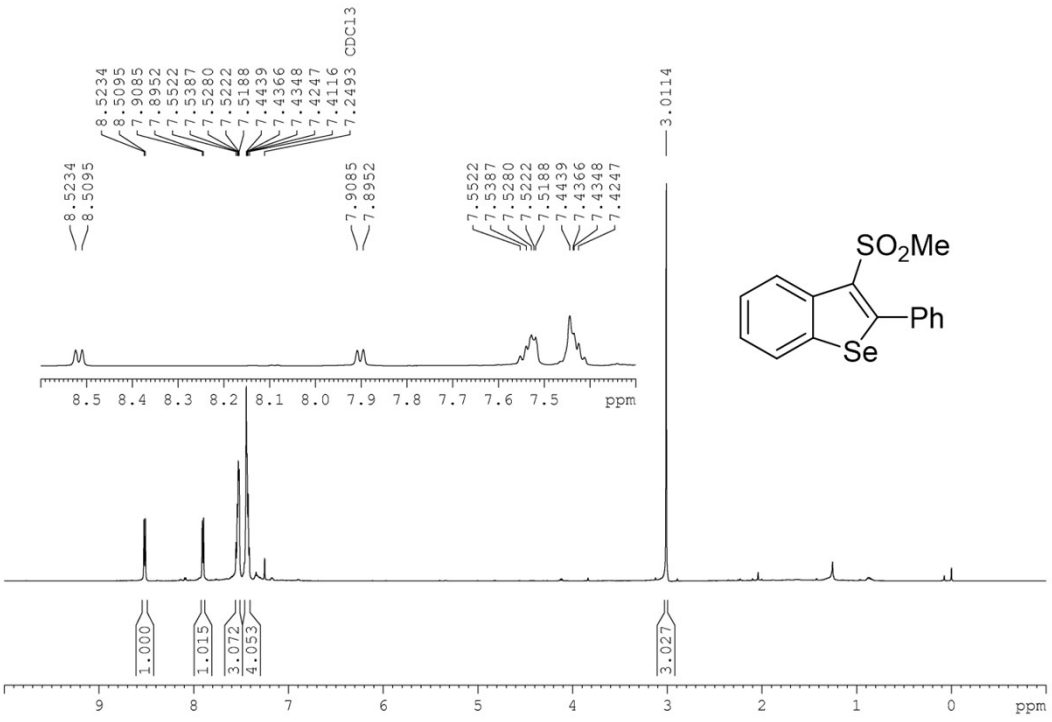
^{1}H NMR (600 MHz, $CDCl_3$) of **3p**



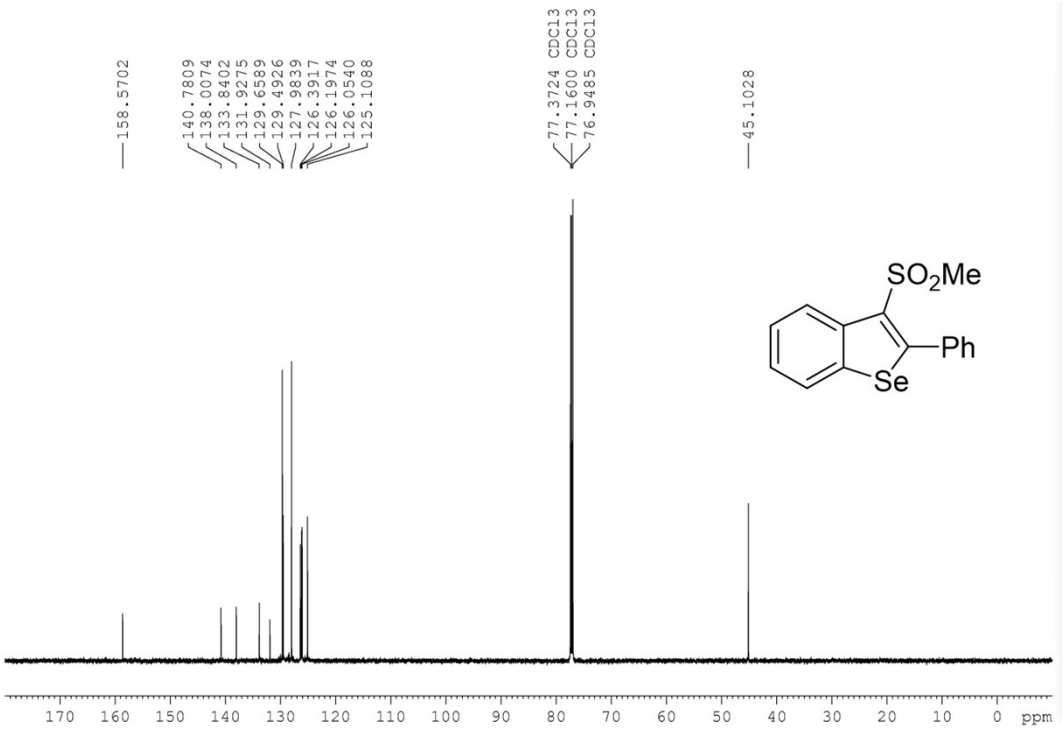
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3p**



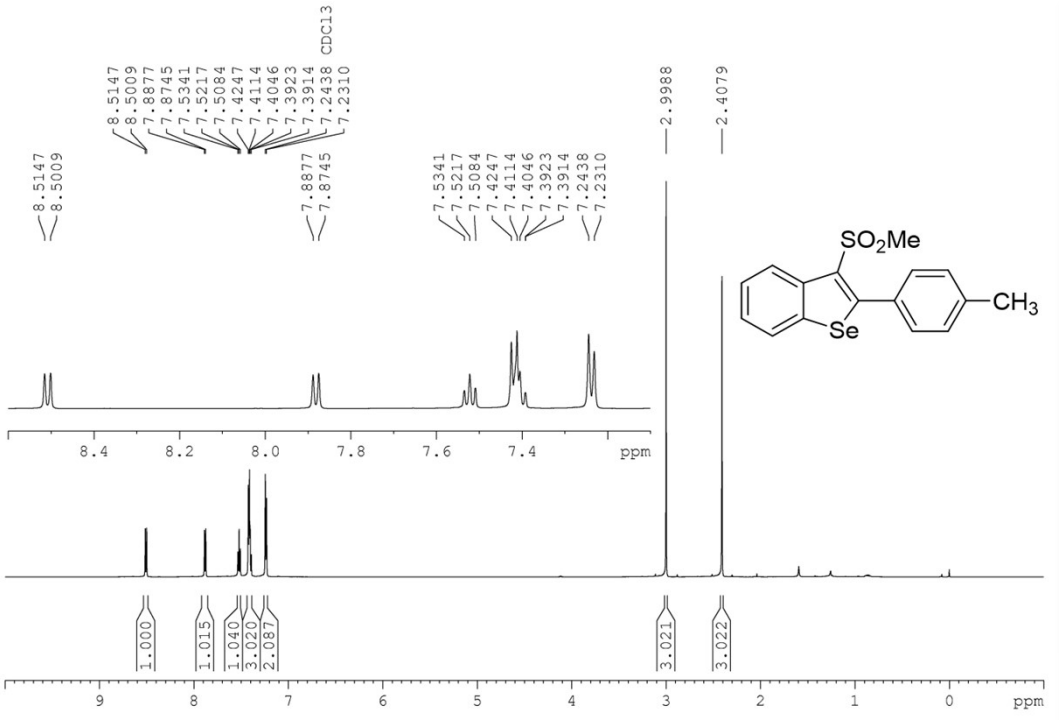
^{1}H NMR (600 MHz, $CDCl_3$) of **3q**



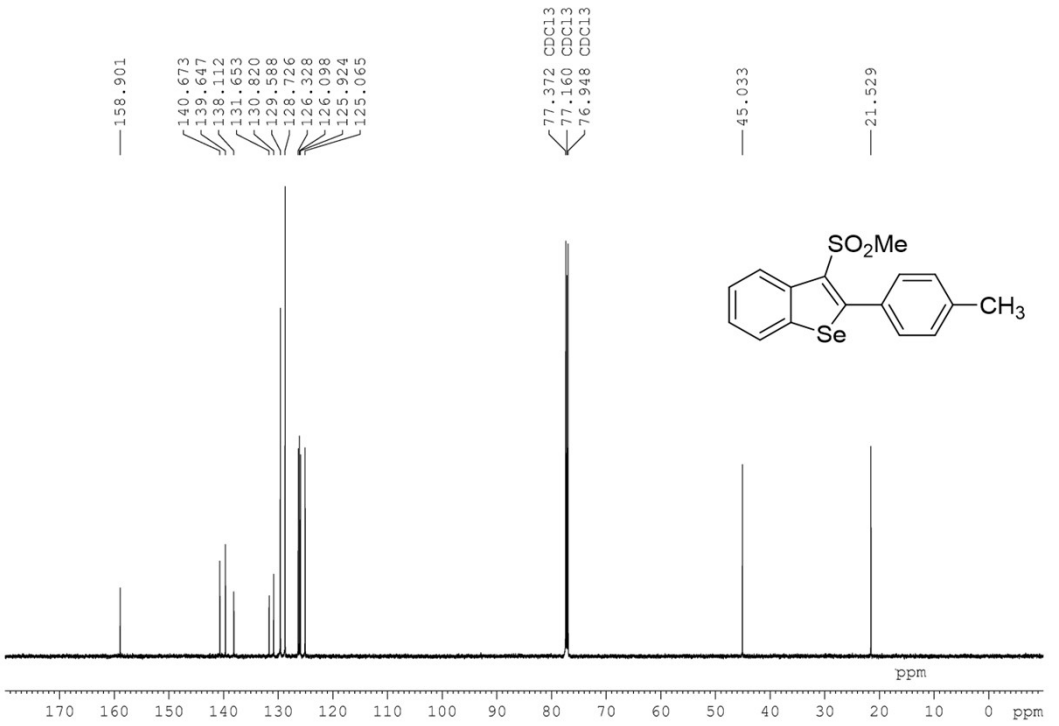
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3q**



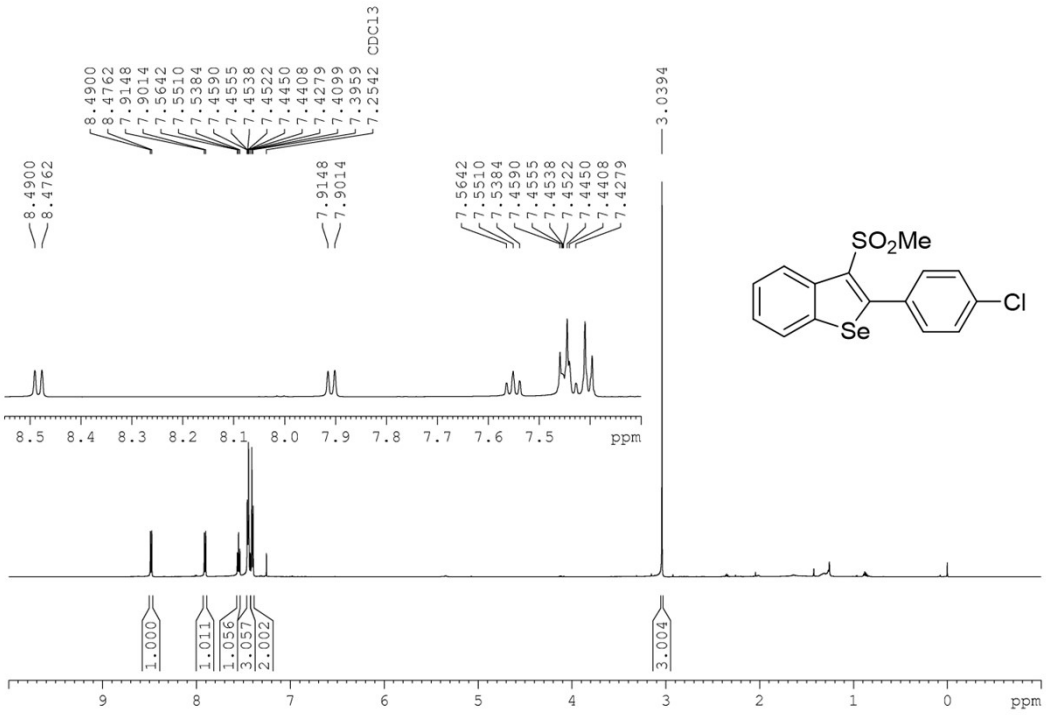
^{1}H NMR (600 MHz, $CDCl_3$) of **3r**



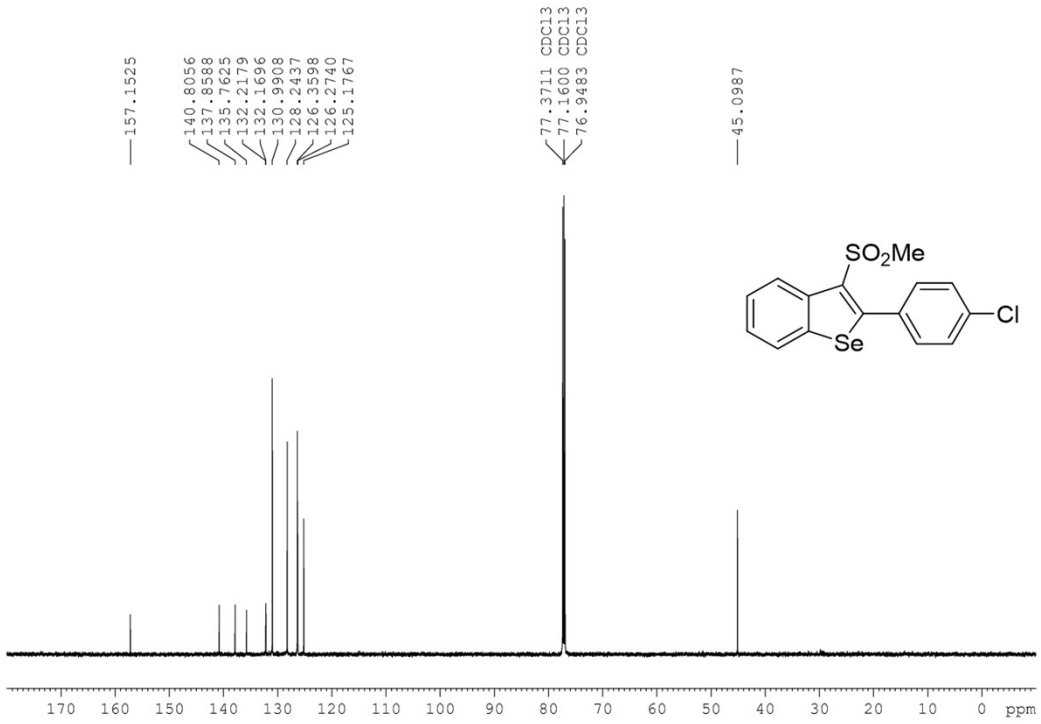
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3r**



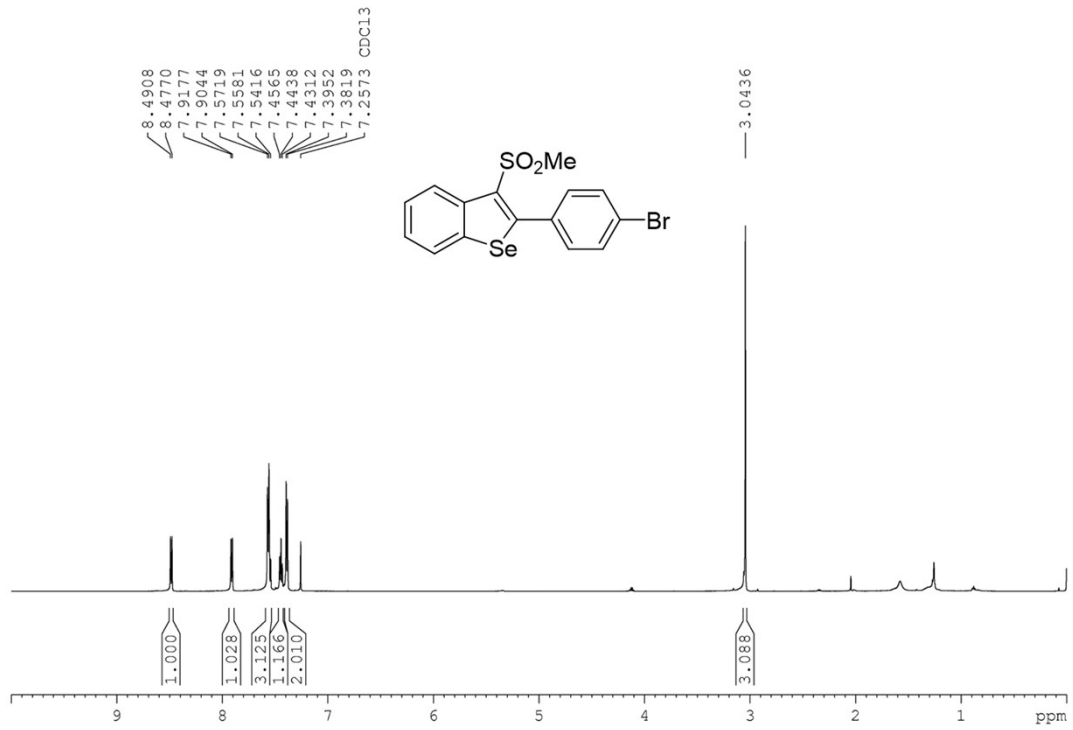
^{1}H NMR (600 MHz, $CDCl_3$) of **3s**



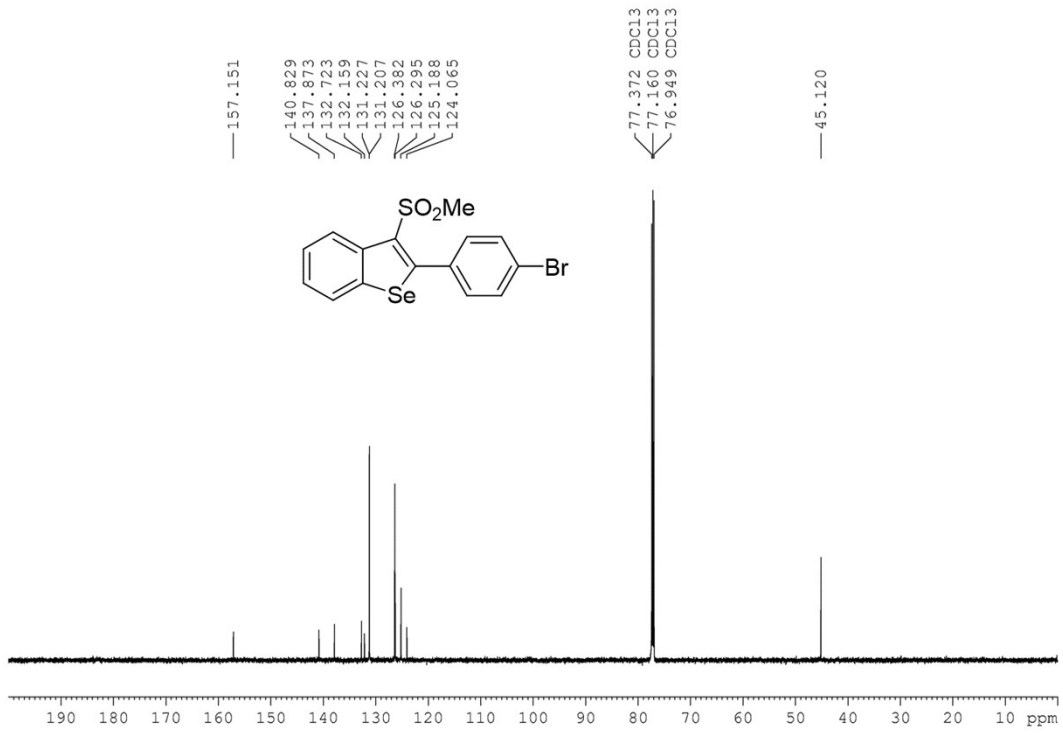
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3s**



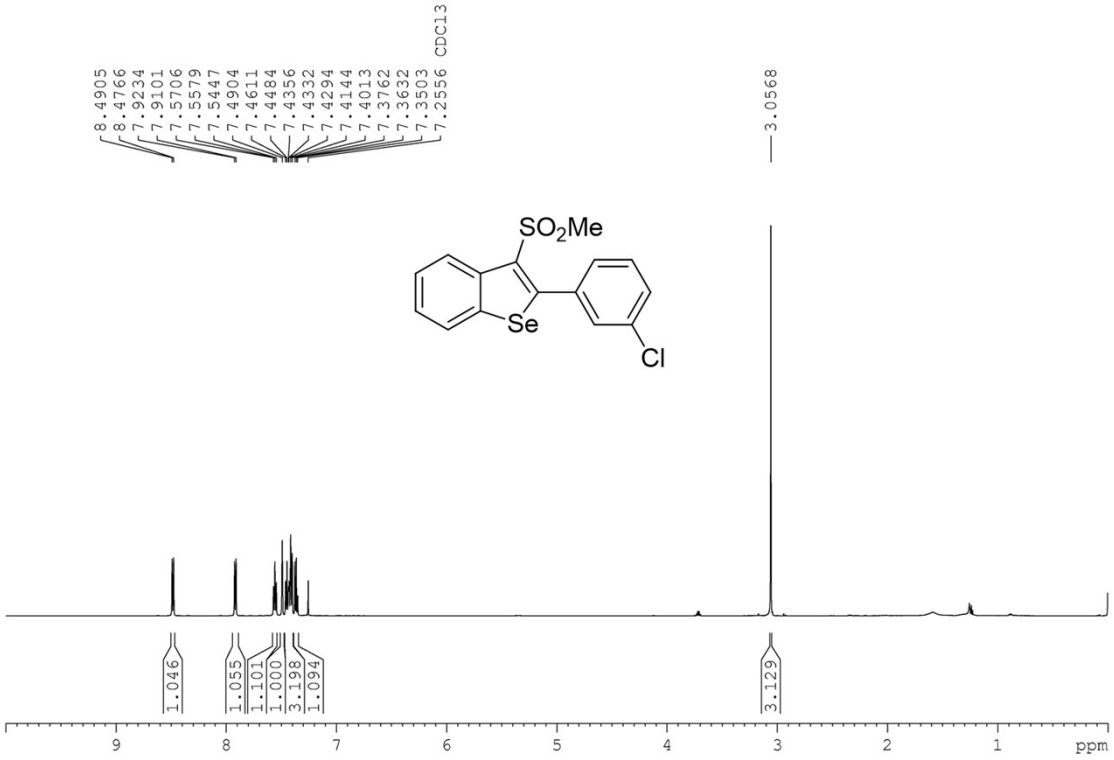
^{1}H NMR (600 MHz, $CDCl_3$) of **3t**



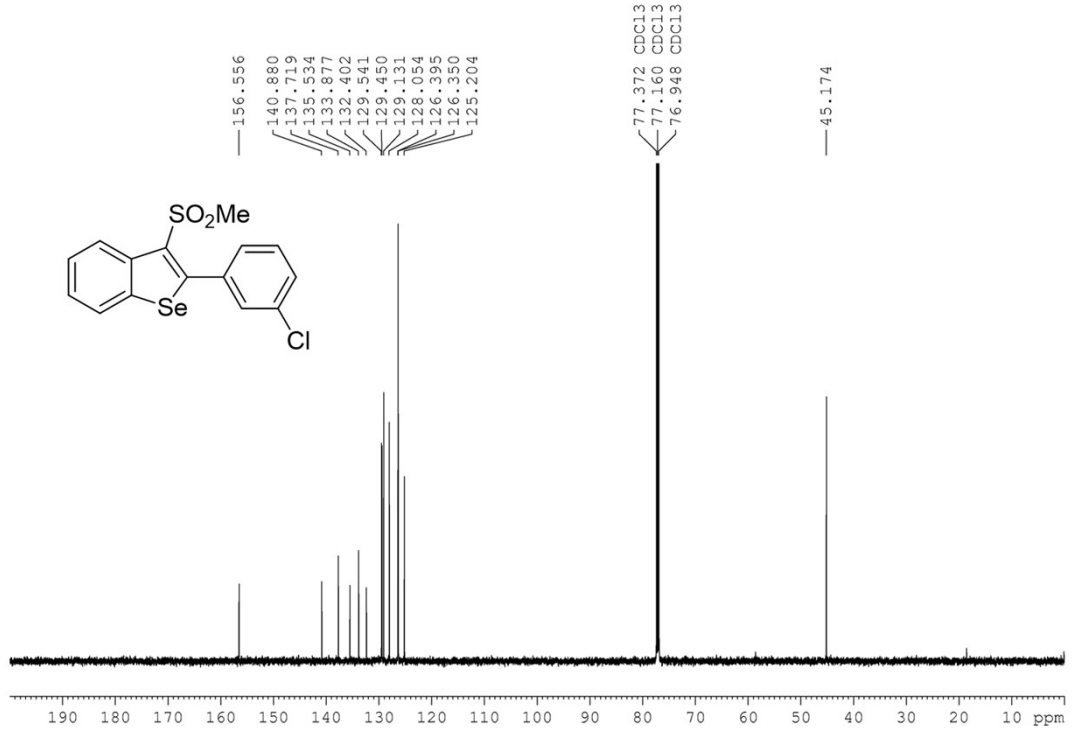
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3t**



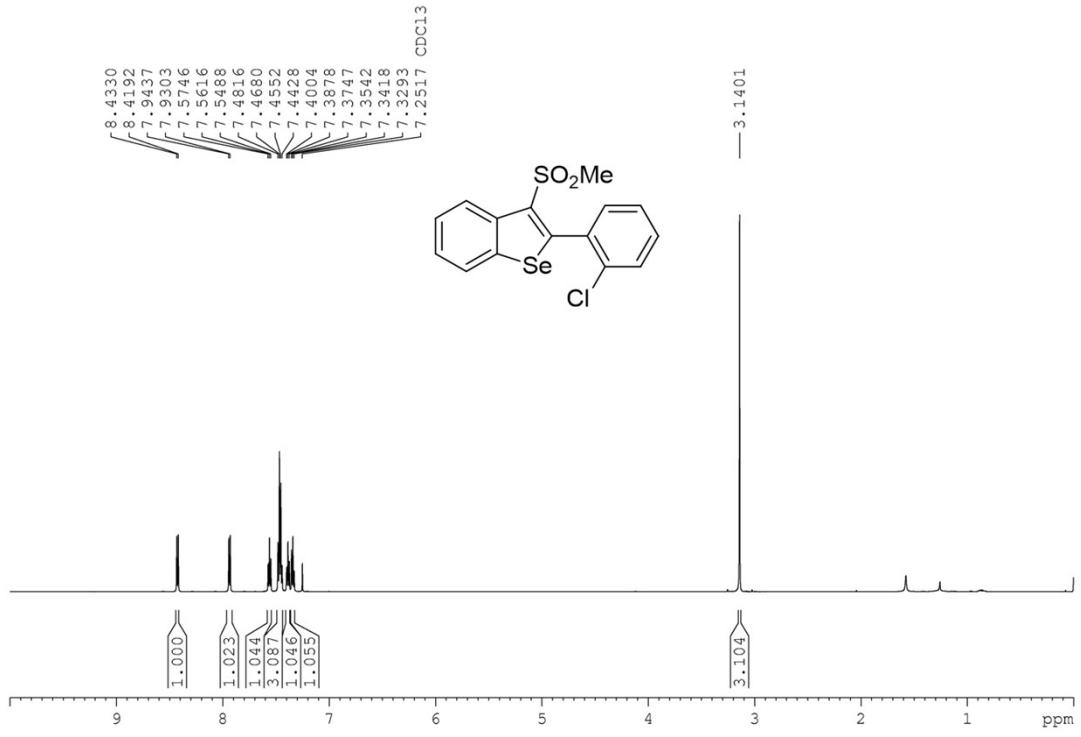
^{1}H NMR (600 MHz, $CDCl_3$) of **3u**



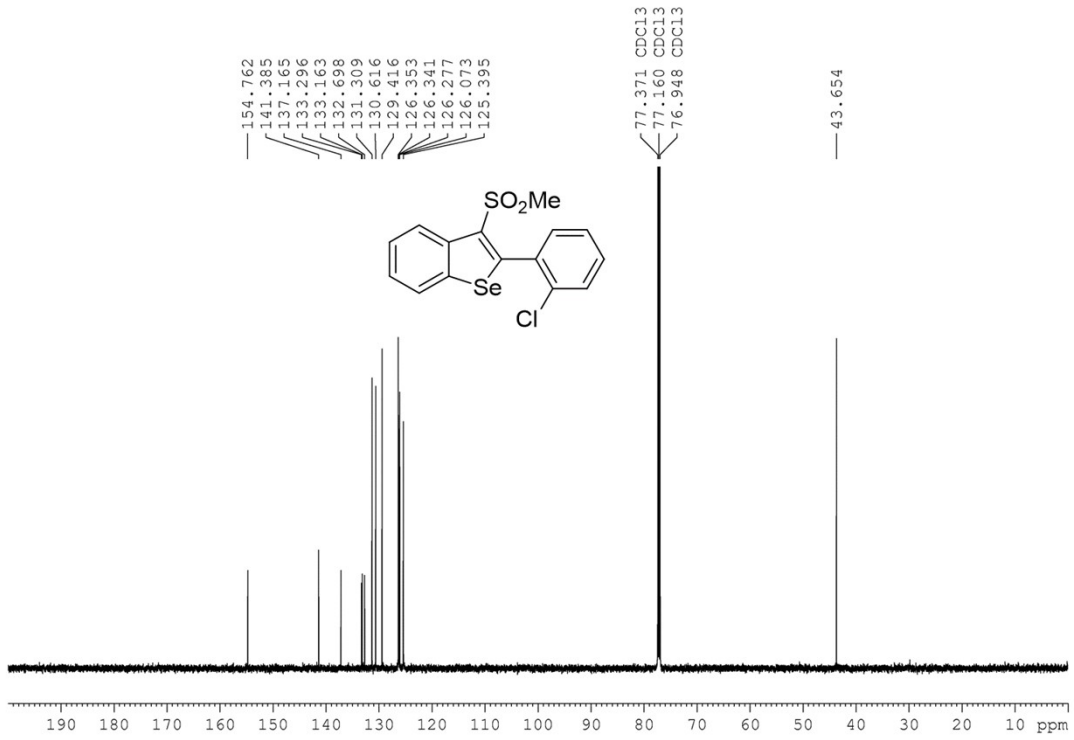
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3u**



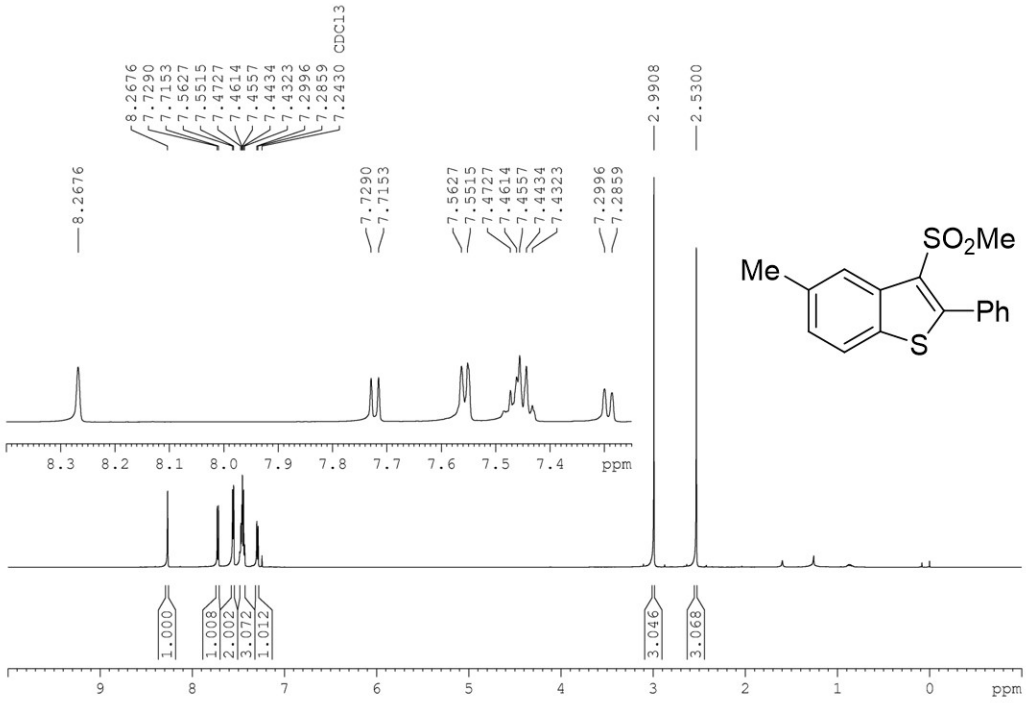
^{1}H NMR (600 MHz, $CDCl_3$) of **3v**



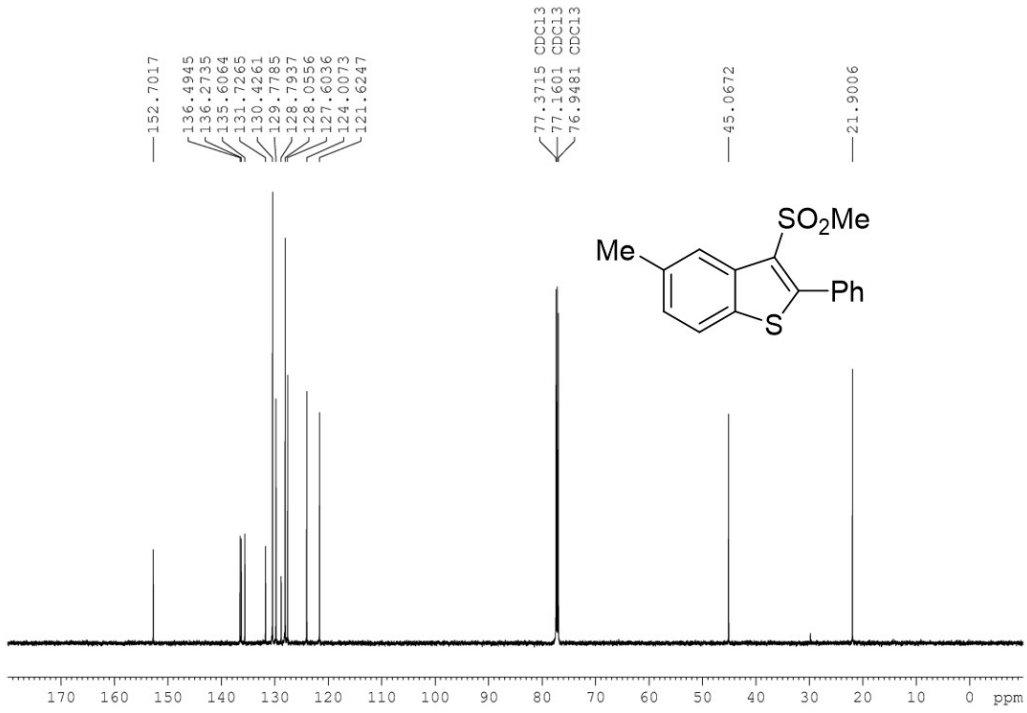
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3v**



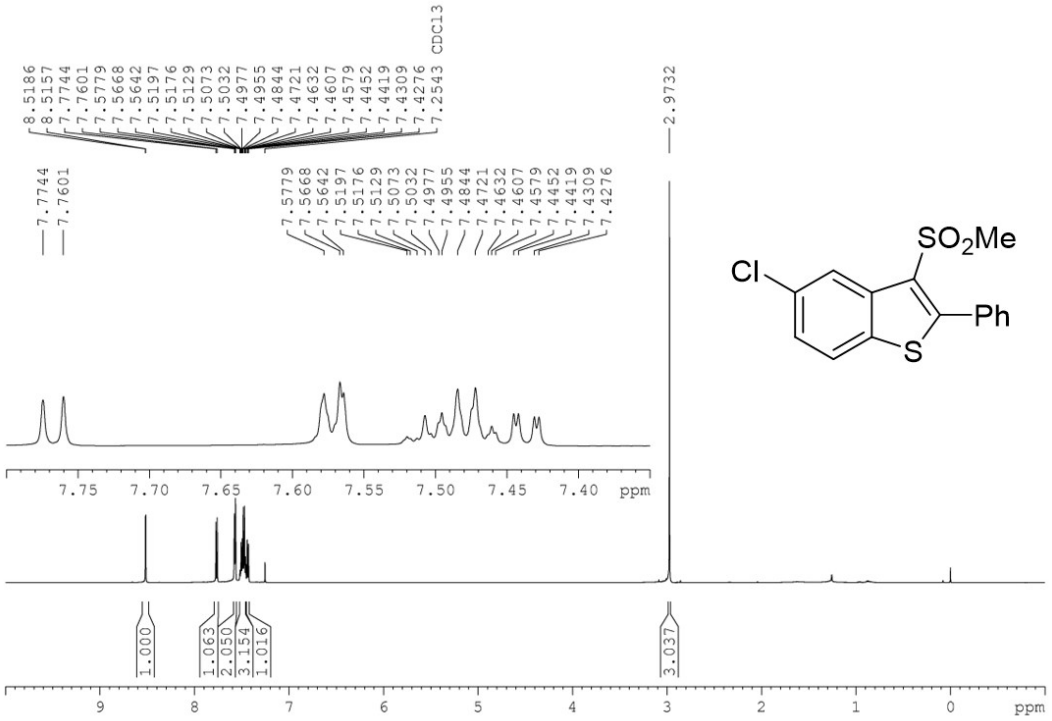
^{1}H NMR (600 MHz, $CDCl_3$) of **3w**



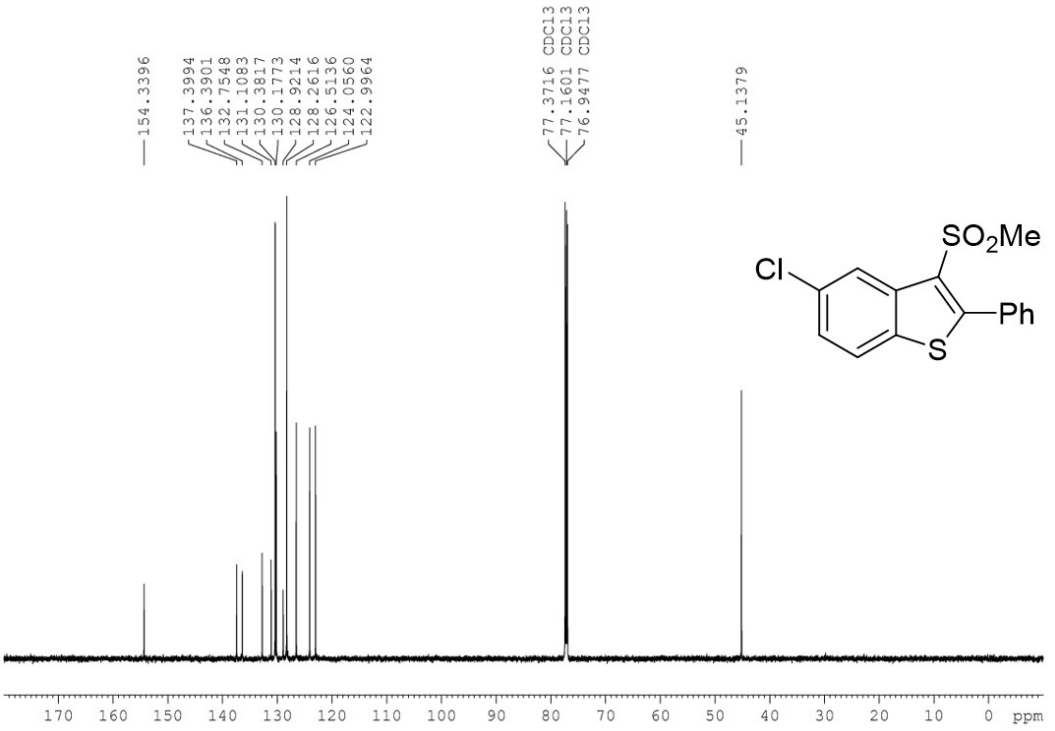
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3w**



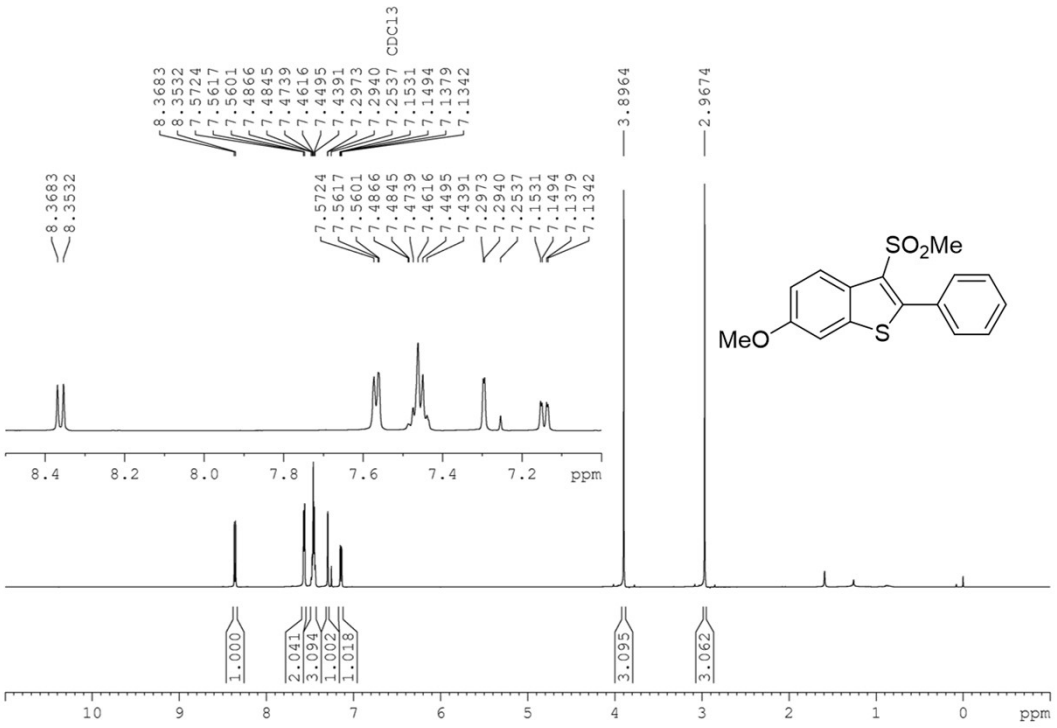
^{1}H NMR (600 MHz, $CDCl_3$) of **3x**



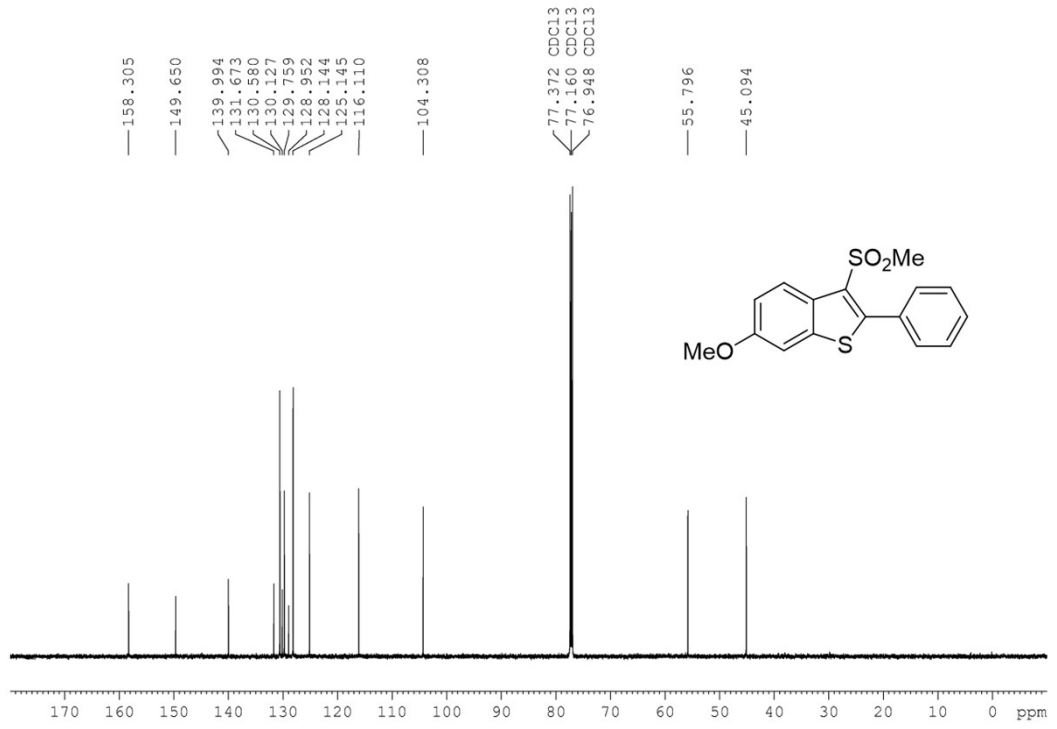
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3x**



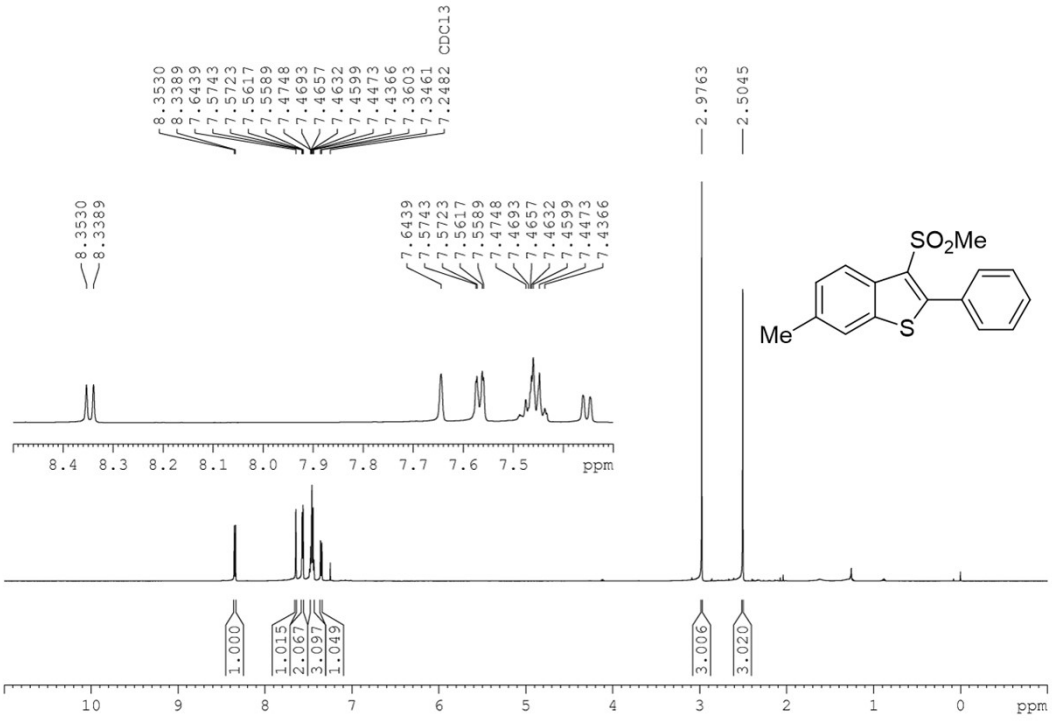
^{1}H NMR (600 MHz, $CDCl_3$) of **3y**



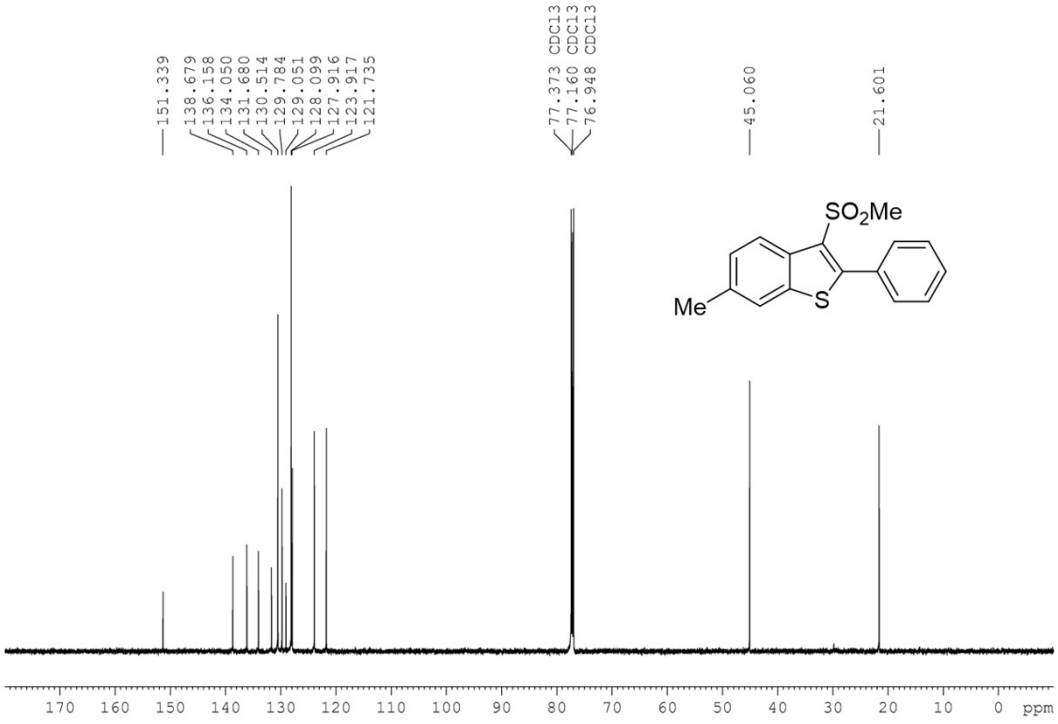
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3y**



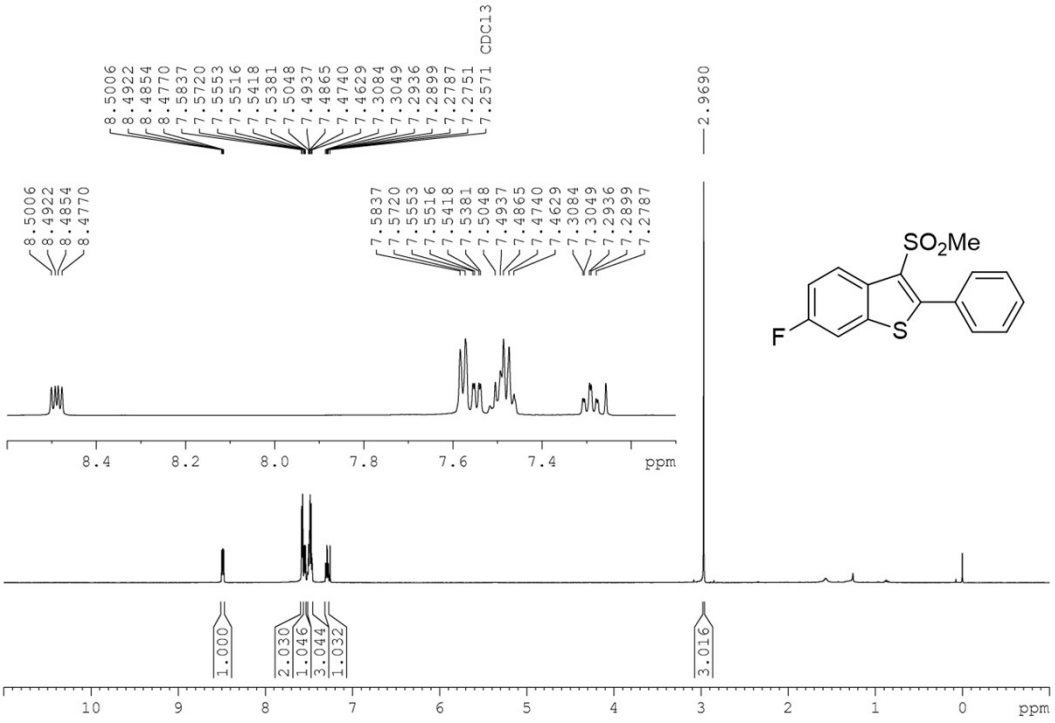
^{1}H NMR (600 MHz, $CDCl_3$) of **3z**



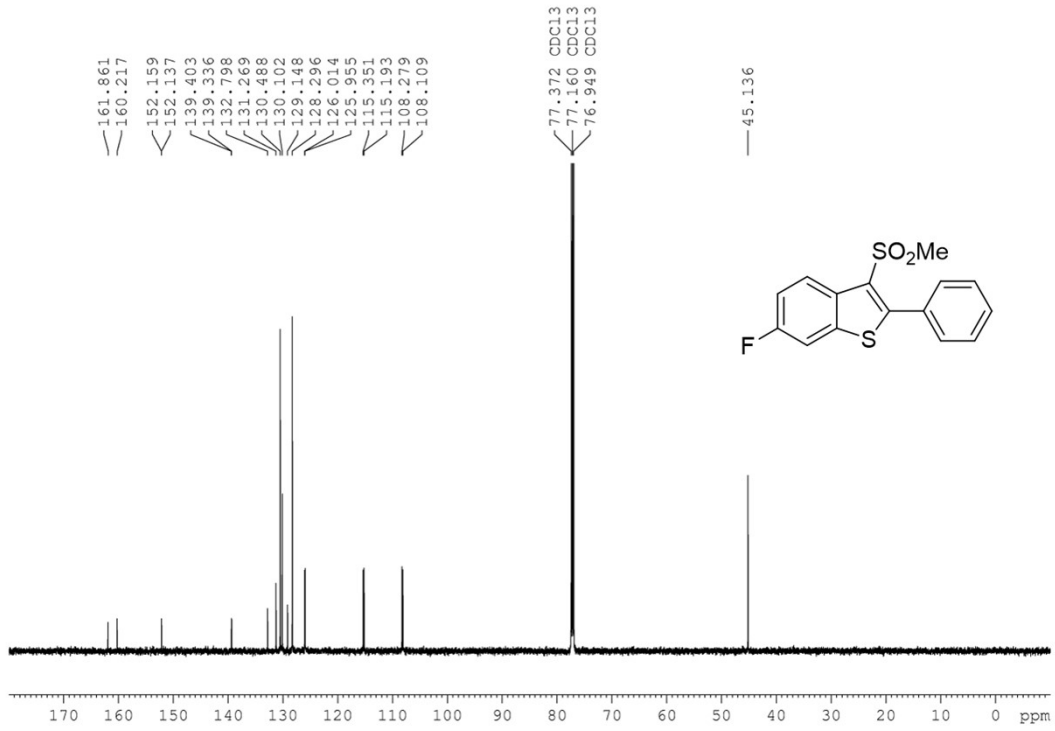
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3z**



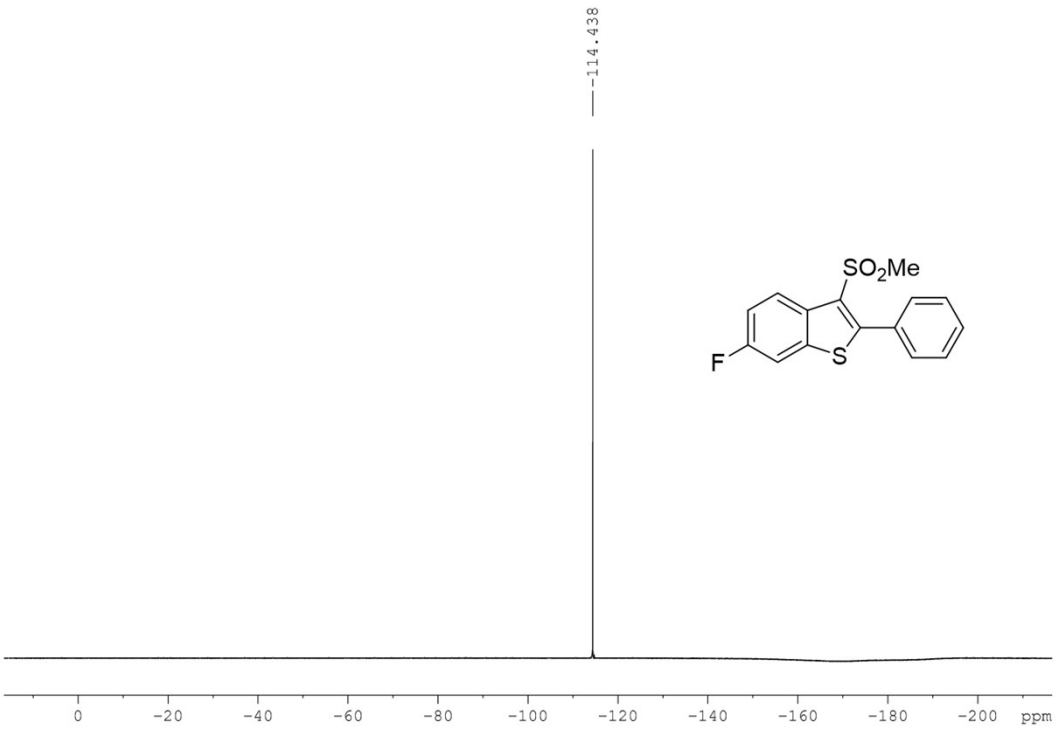
^{1}H NMR (600 MHz, $CDCl_3$) of **3aa**



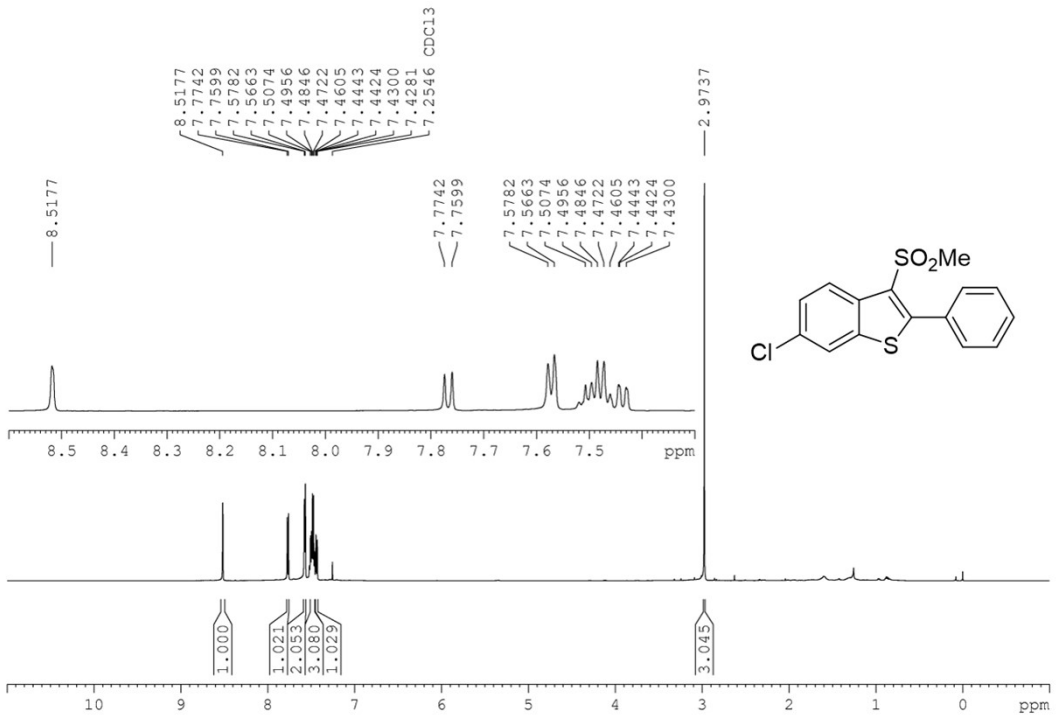
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3aa**



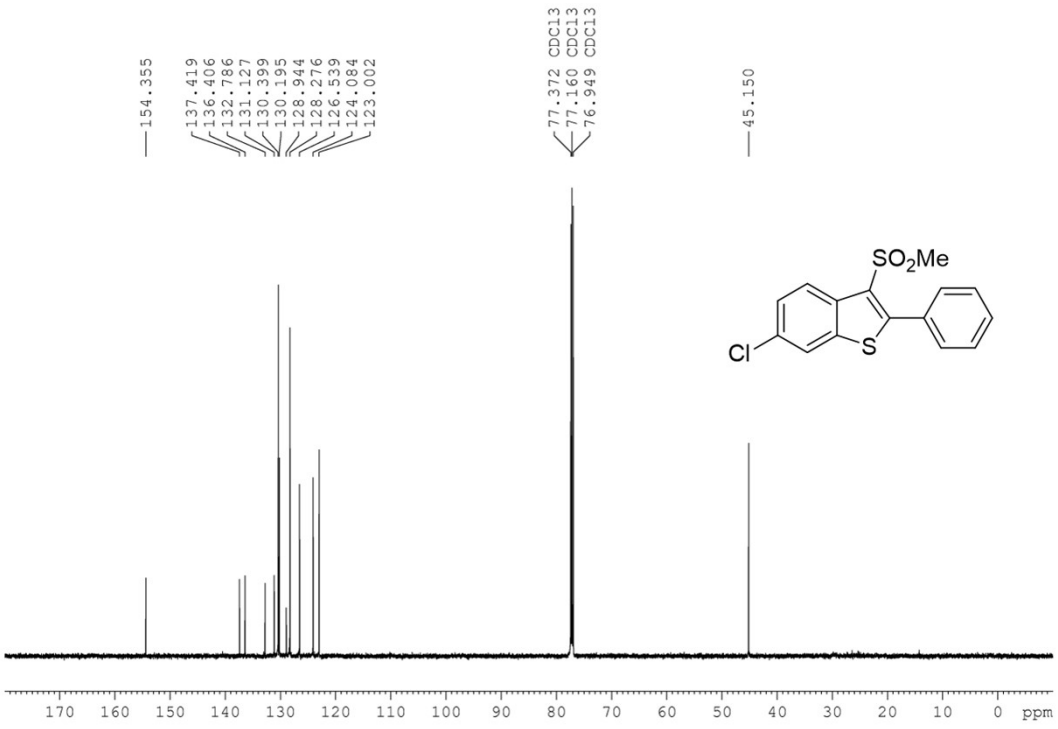
^{19}F NMR (564 MHz, $CDCl_3$) of **3aa**



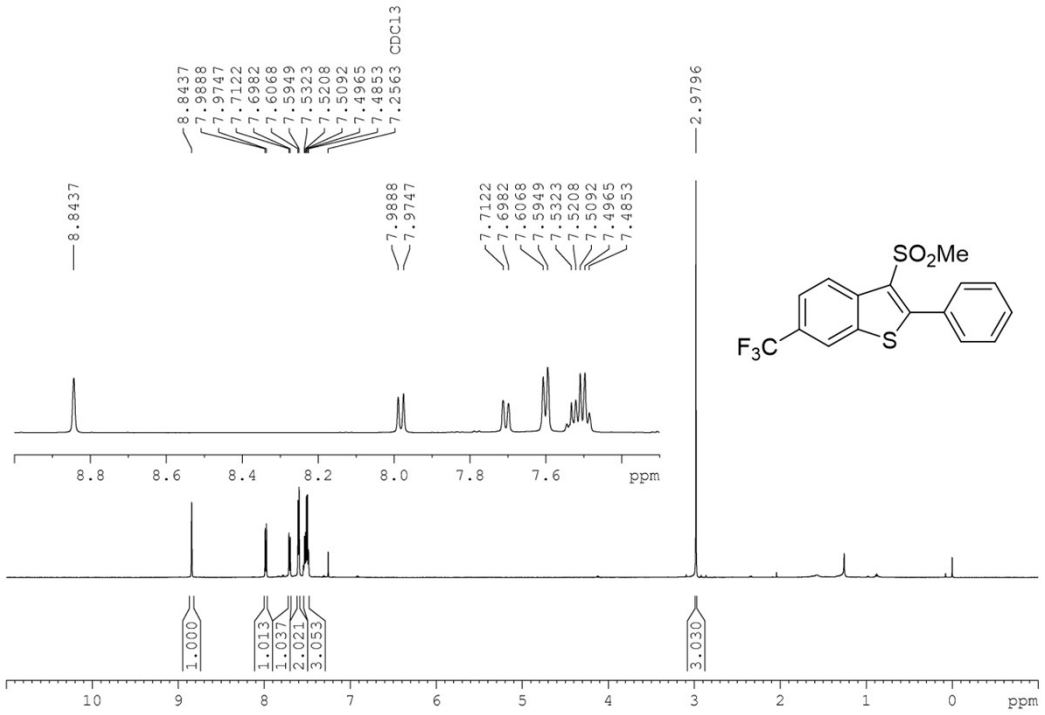
^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**



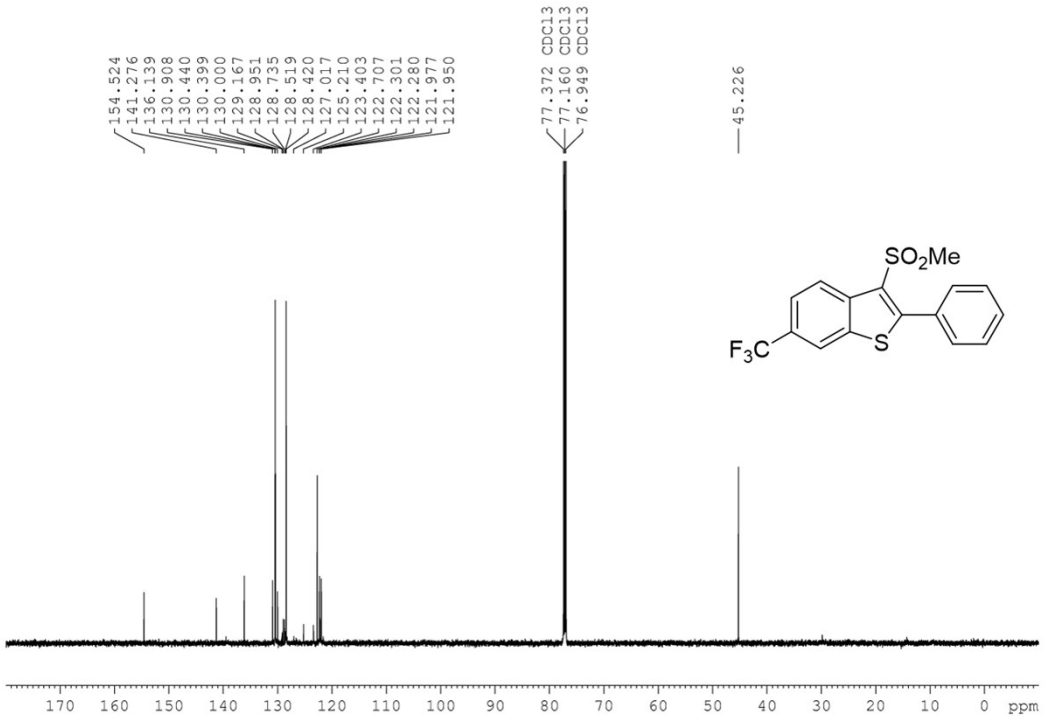
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ab**



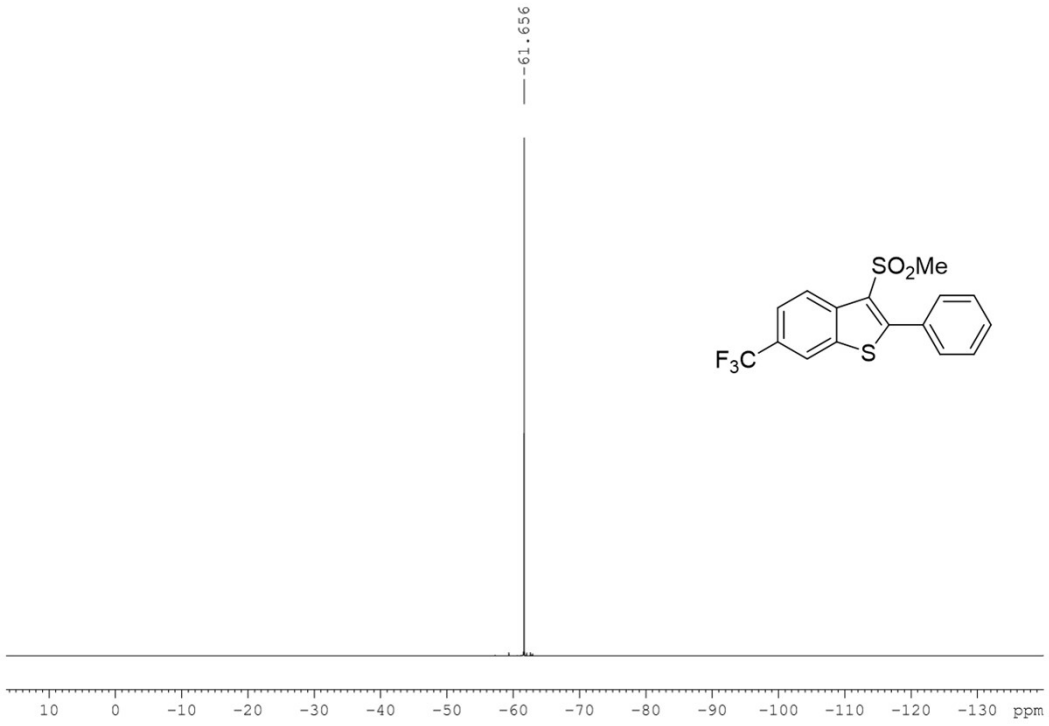
^{1}H NMR (600 MHz, $CDCl_3$) of **3ac**



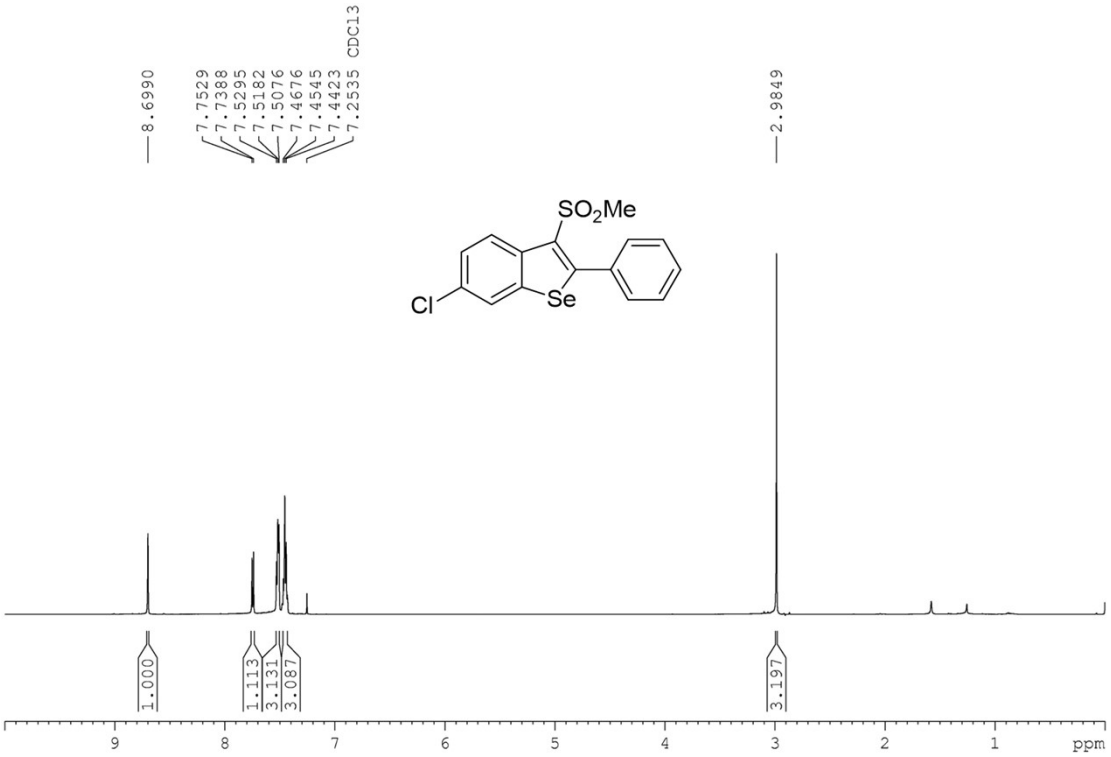
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ac**



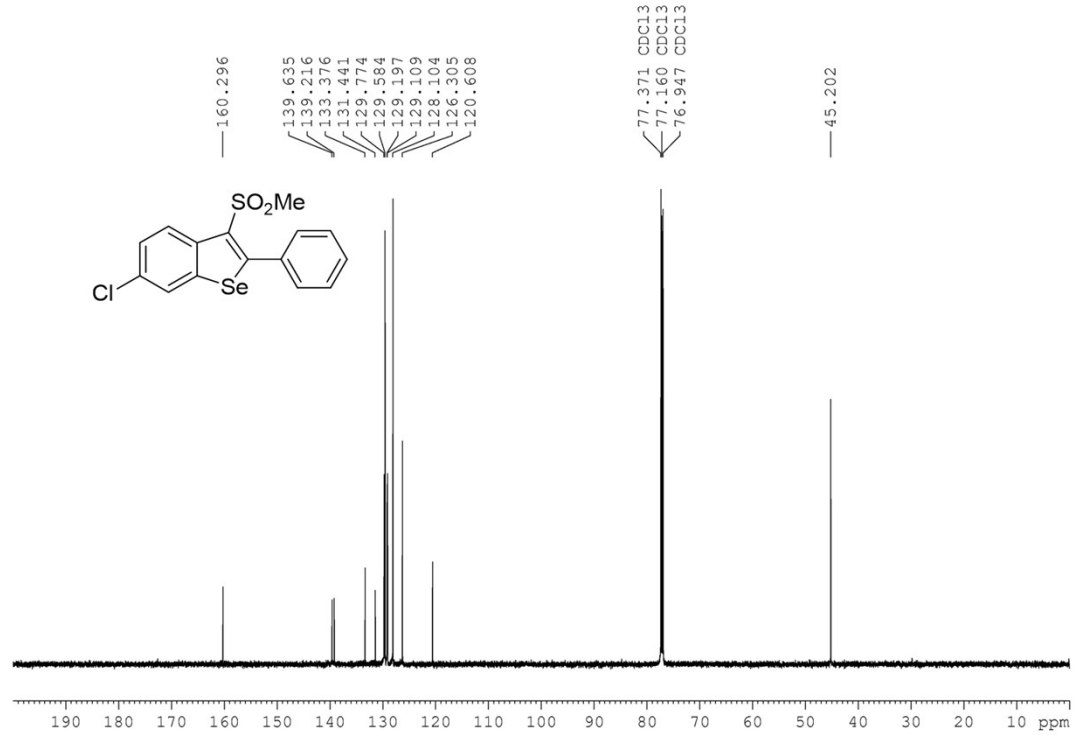
^{19}F NMR (564 MHz, $CDCl_3$) of **3ac**



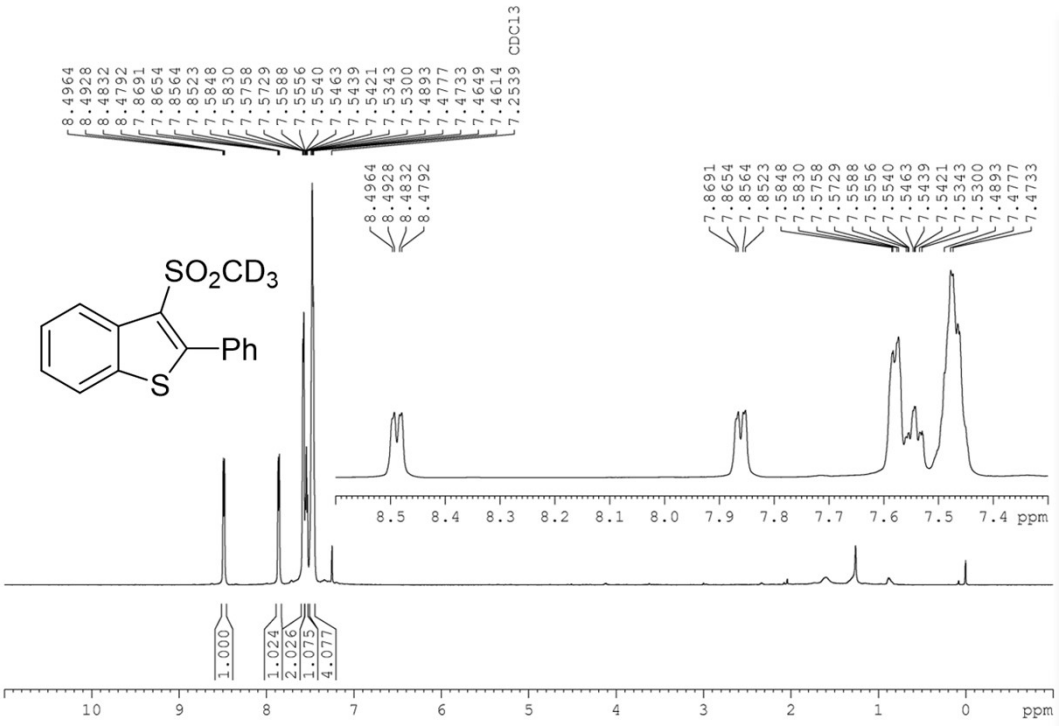
^{1}H NMR (600 MHz, $CDCl_3$) of **3ad**



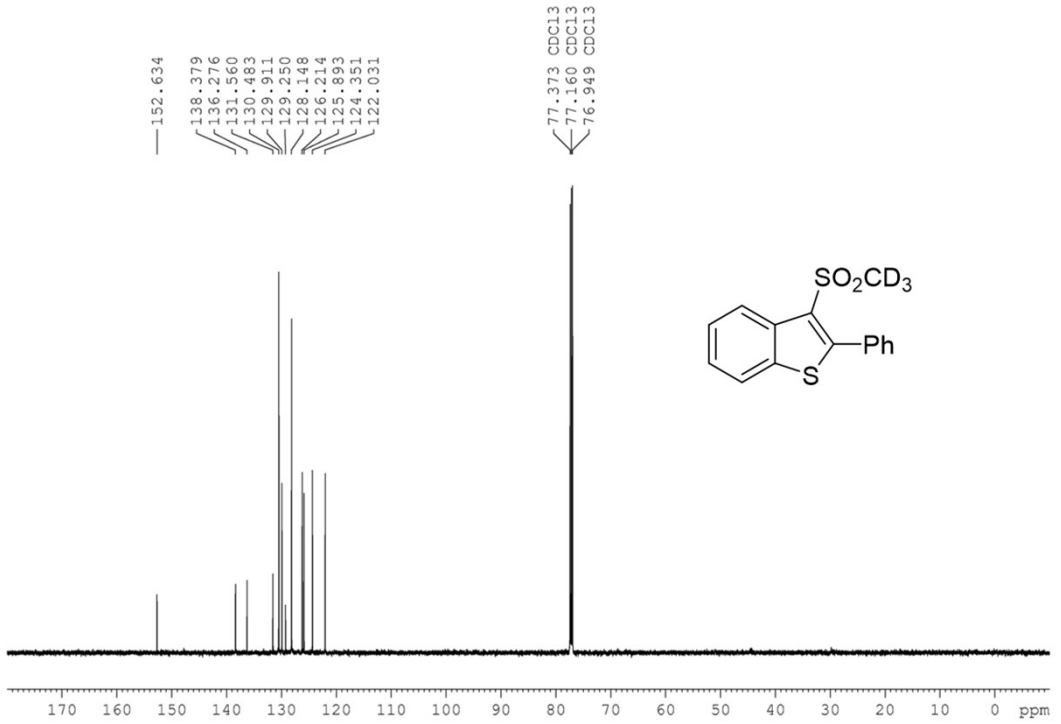
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ad**



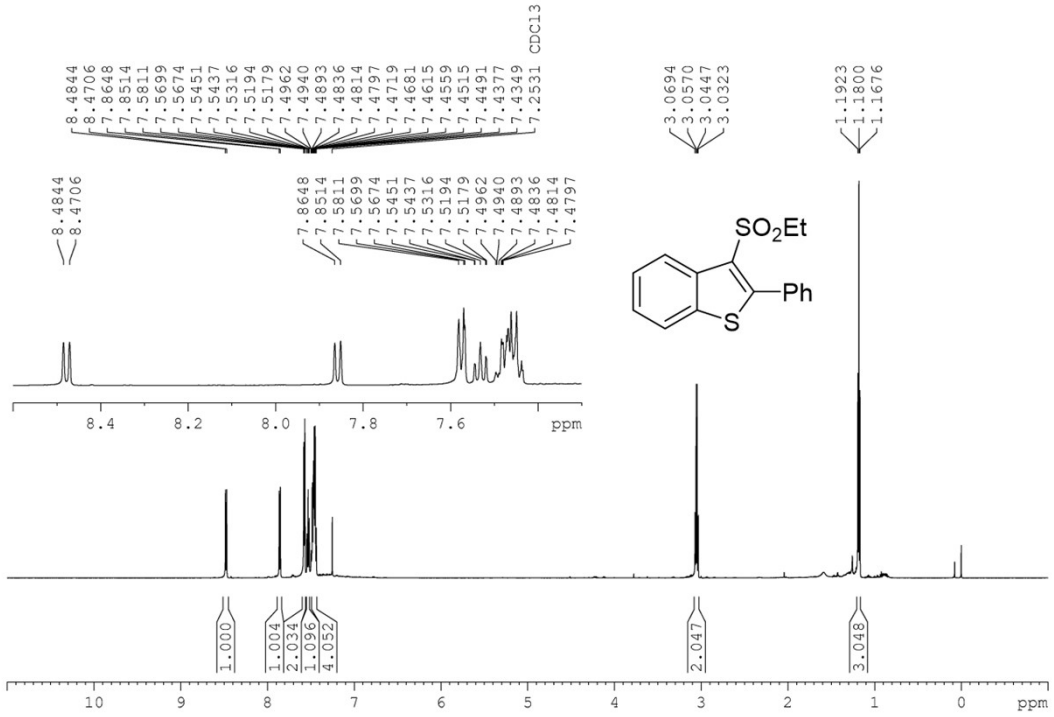
^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**



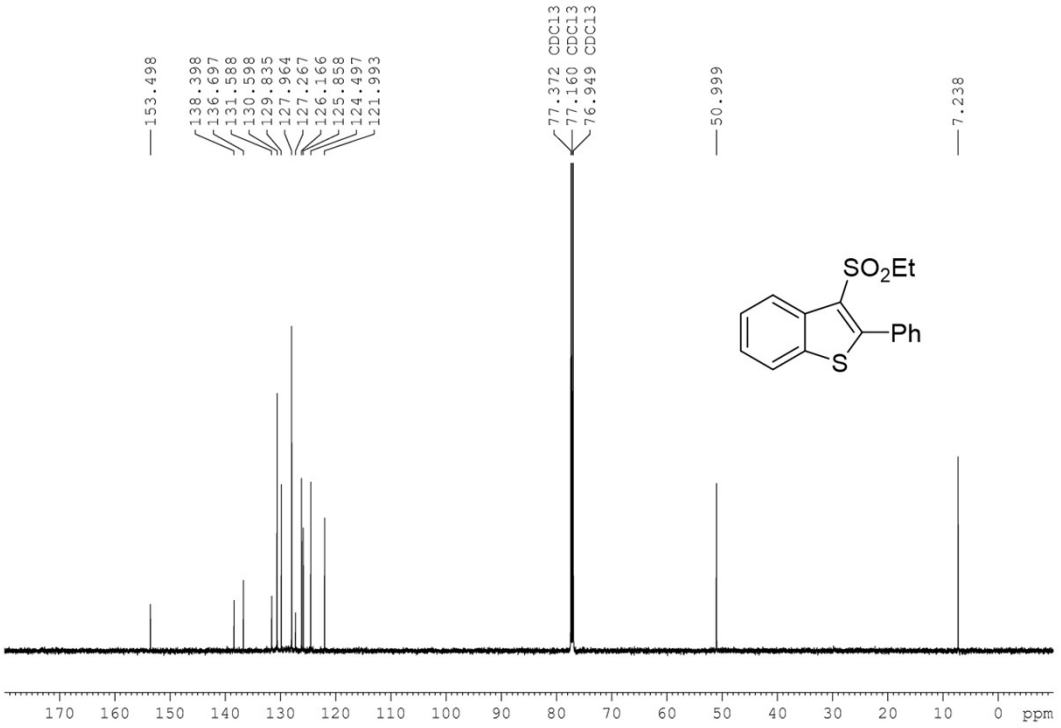
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ae**



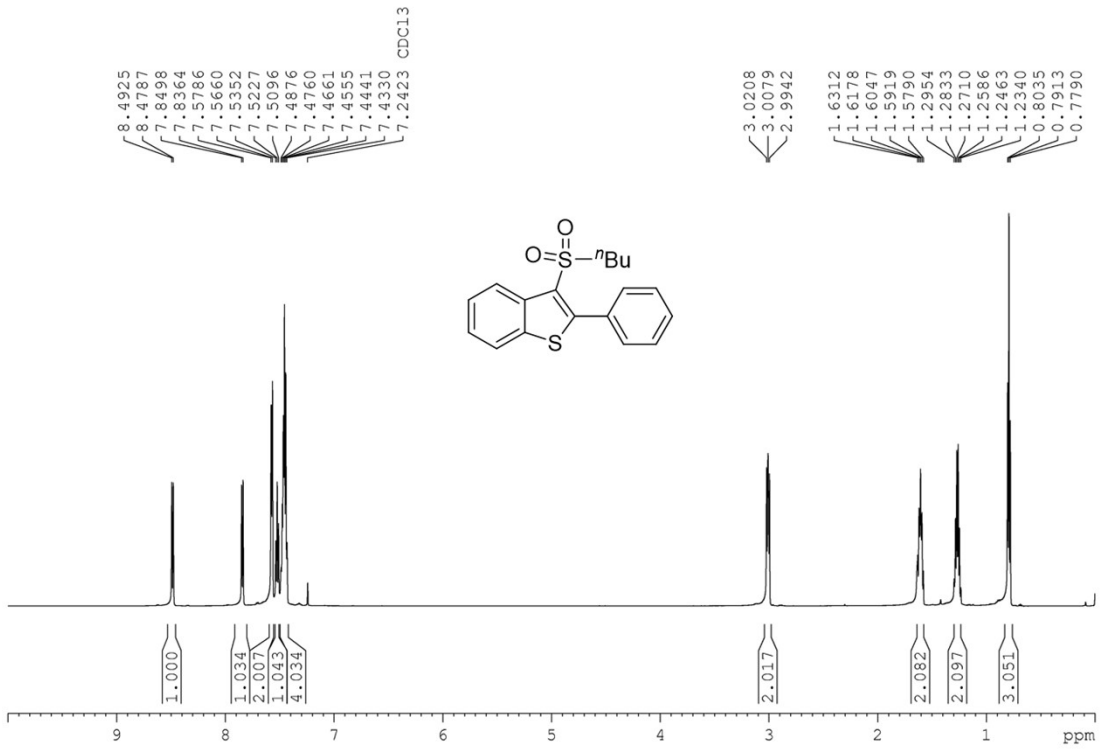
^{1}H NMR (600 MHz, $CDCl_3$) of **3af**



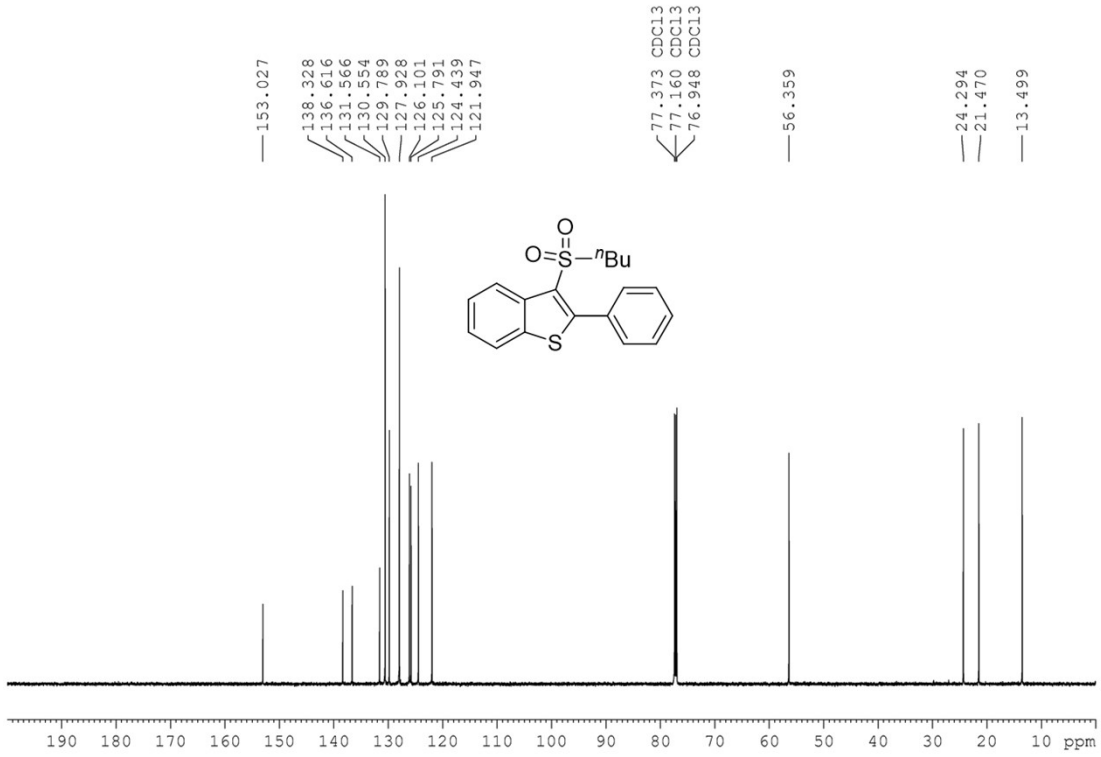
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3af**



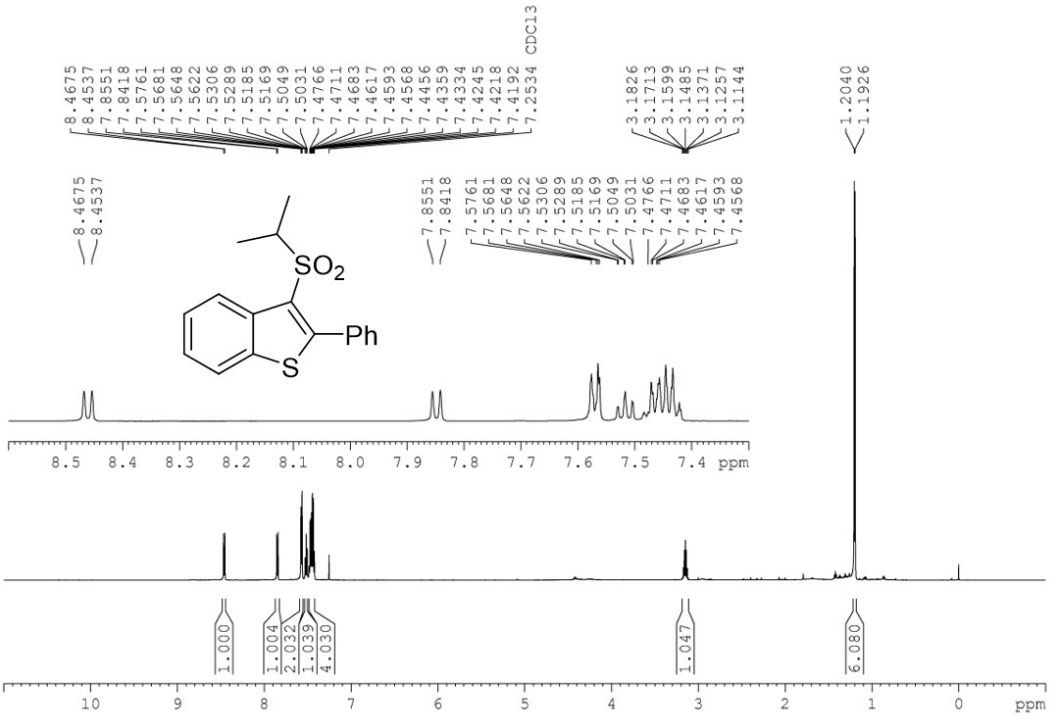
^{1}H NMR (600 MHz, $CDCl_3$) of **3ag**



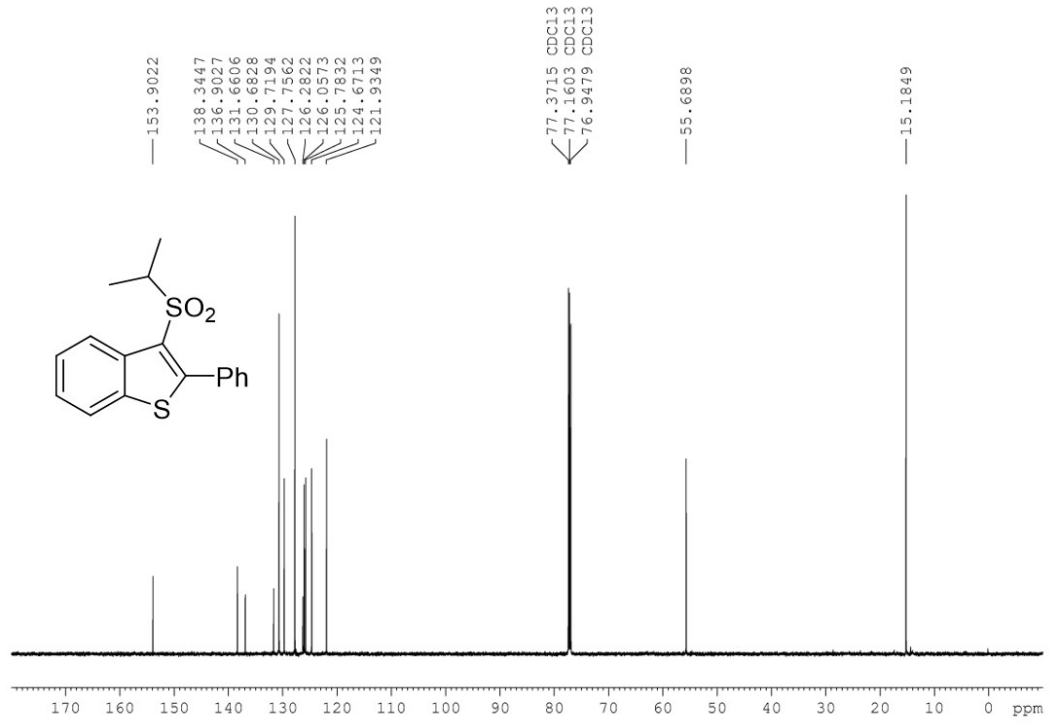
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ag**



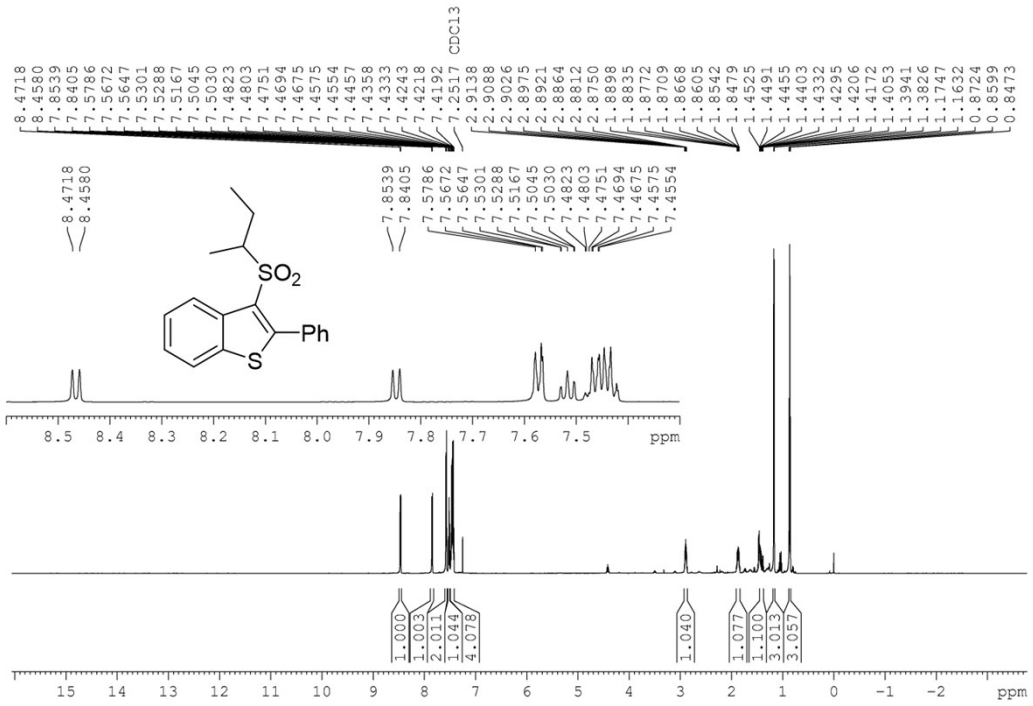
^{1}H NMR (600 MHz, $CDCl_3$) of **3ah**



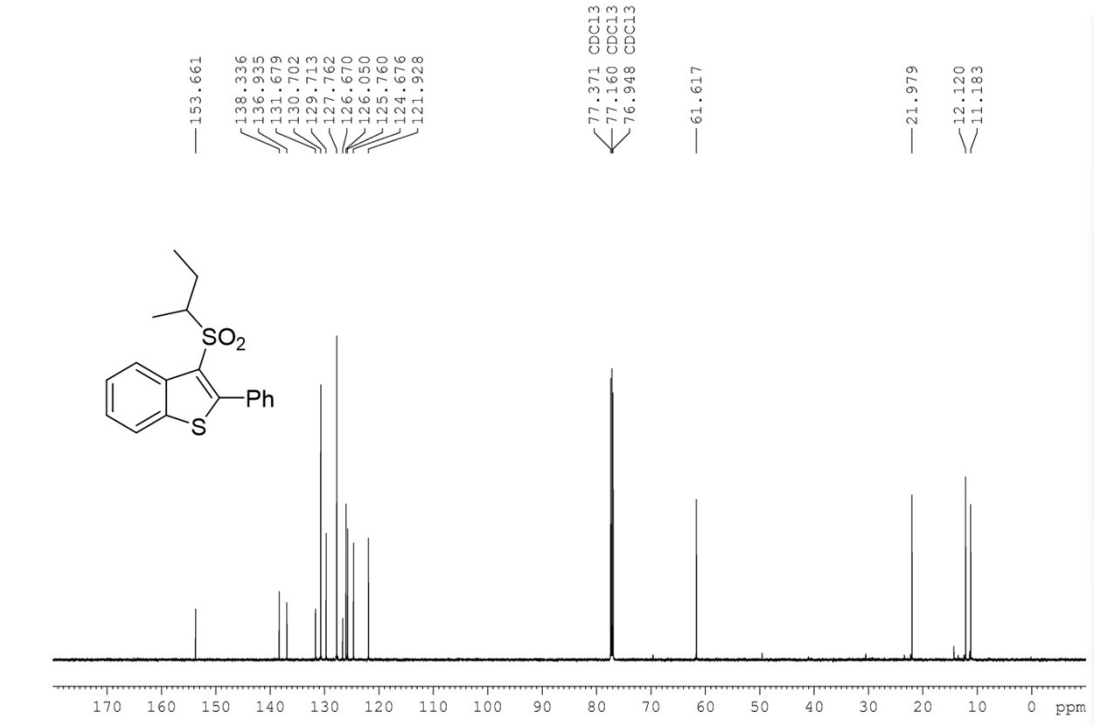
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ah**



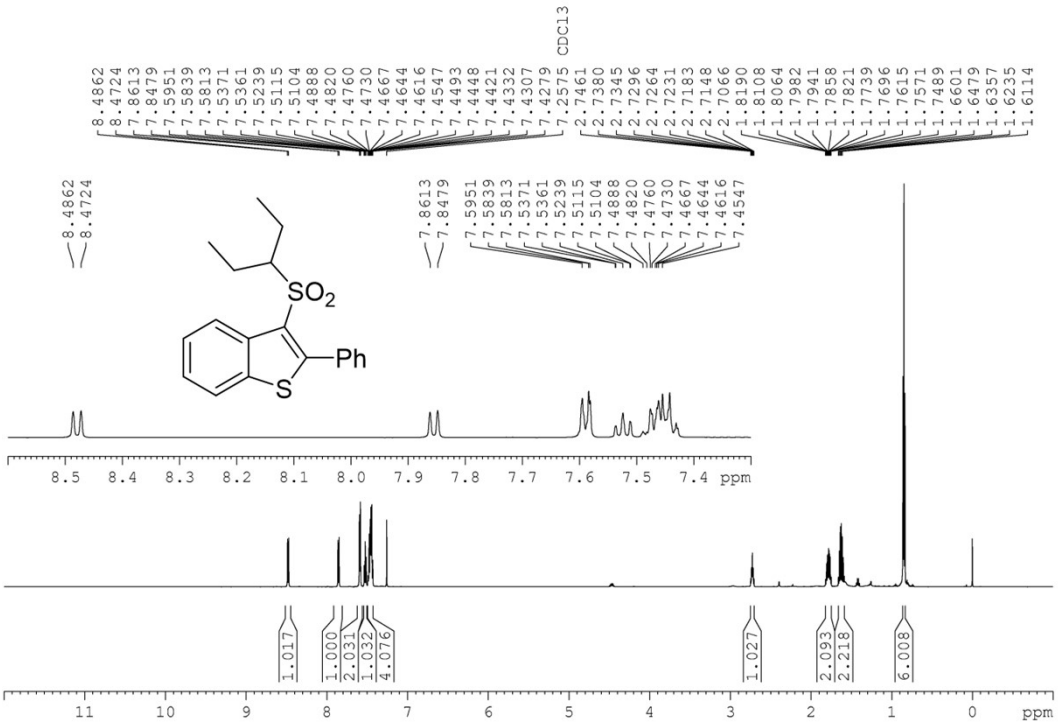
^{1}H NMR (600 MHz, $CDCl_3$) of **3ai**



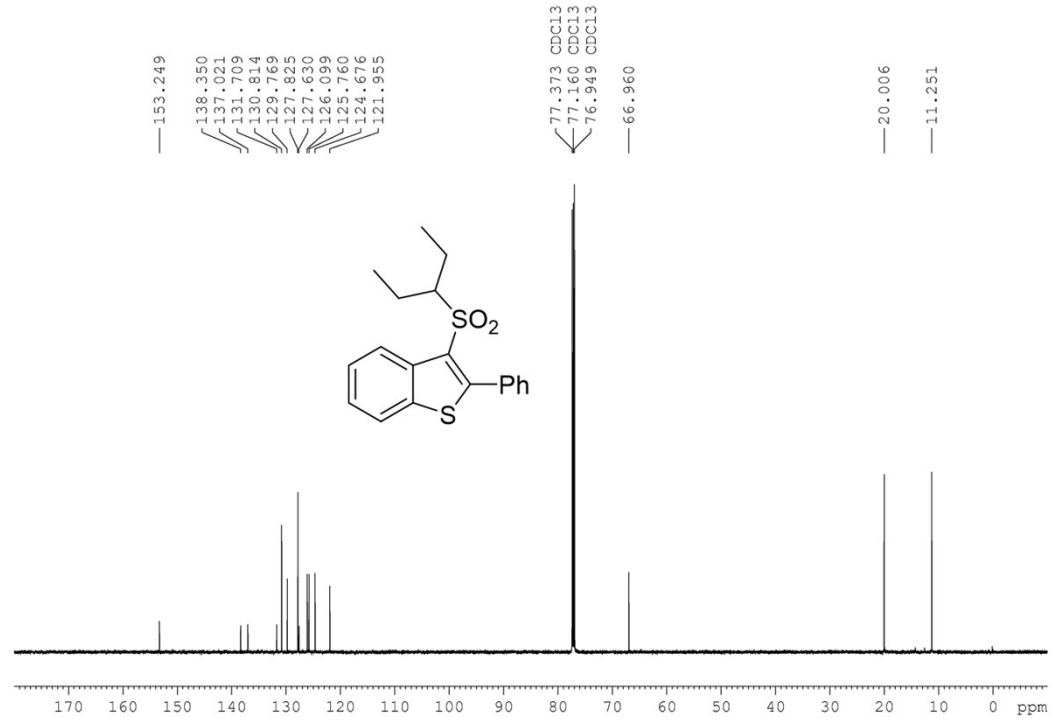
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ai**



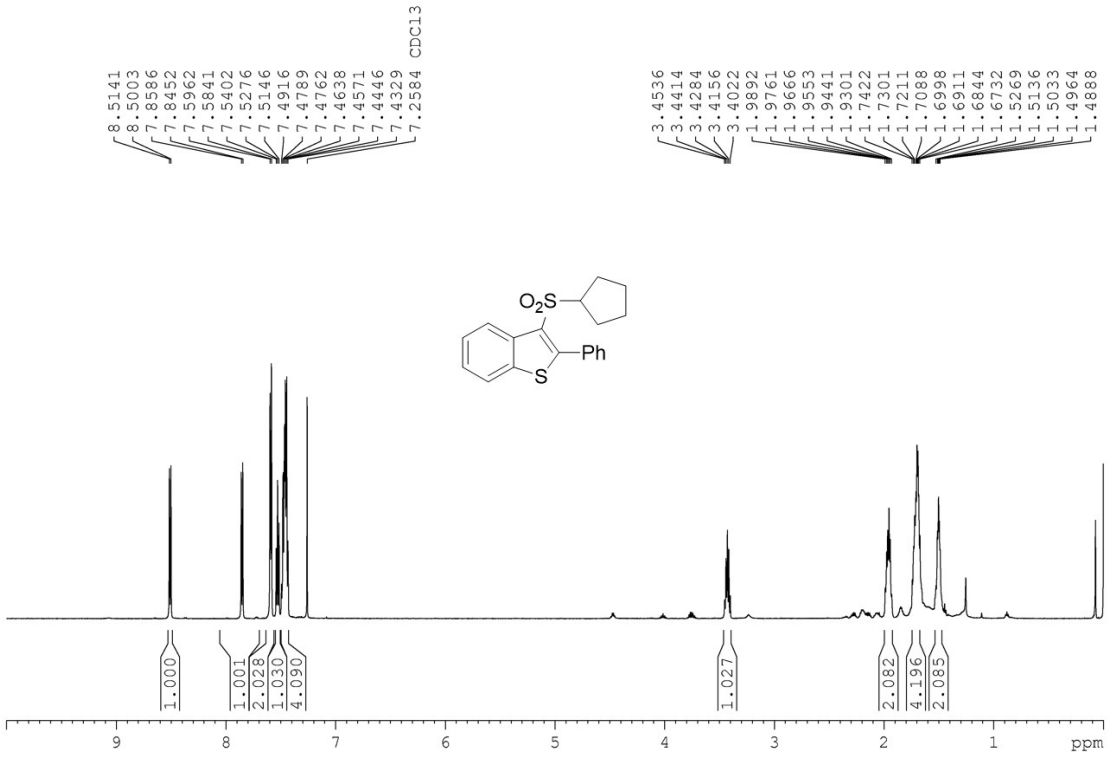
^{1}H NMR (600 MHz, $CDCl_3$) of **3aj**



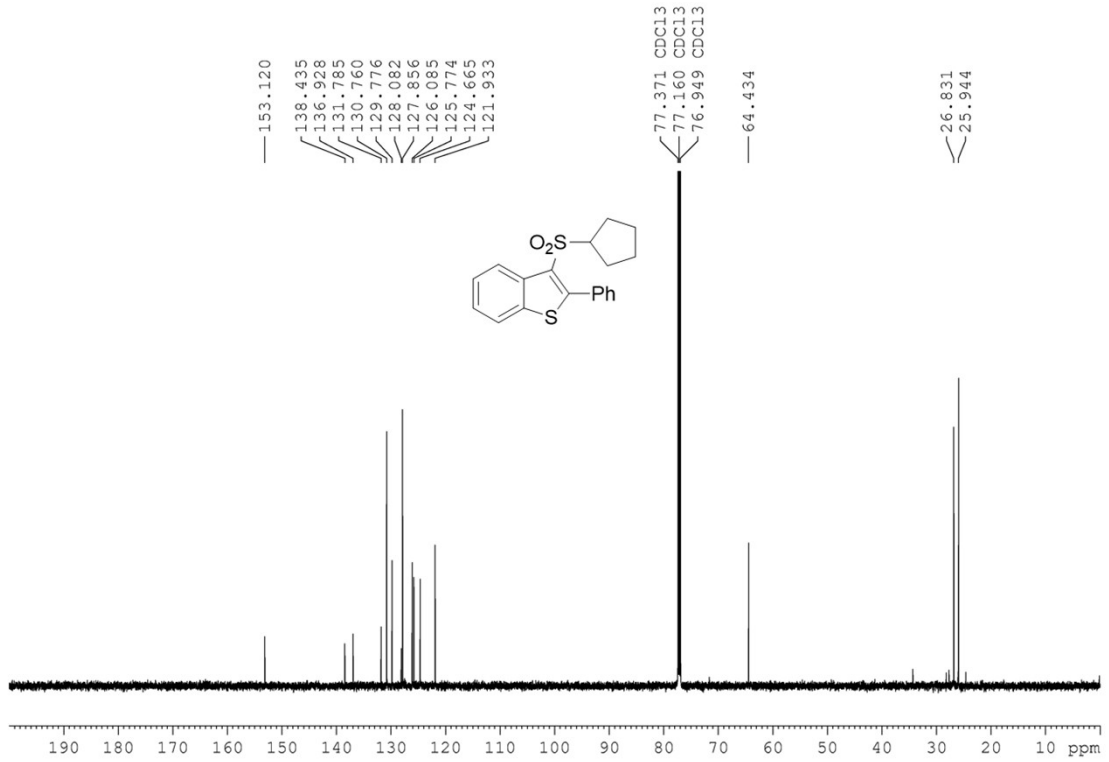
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3aj**



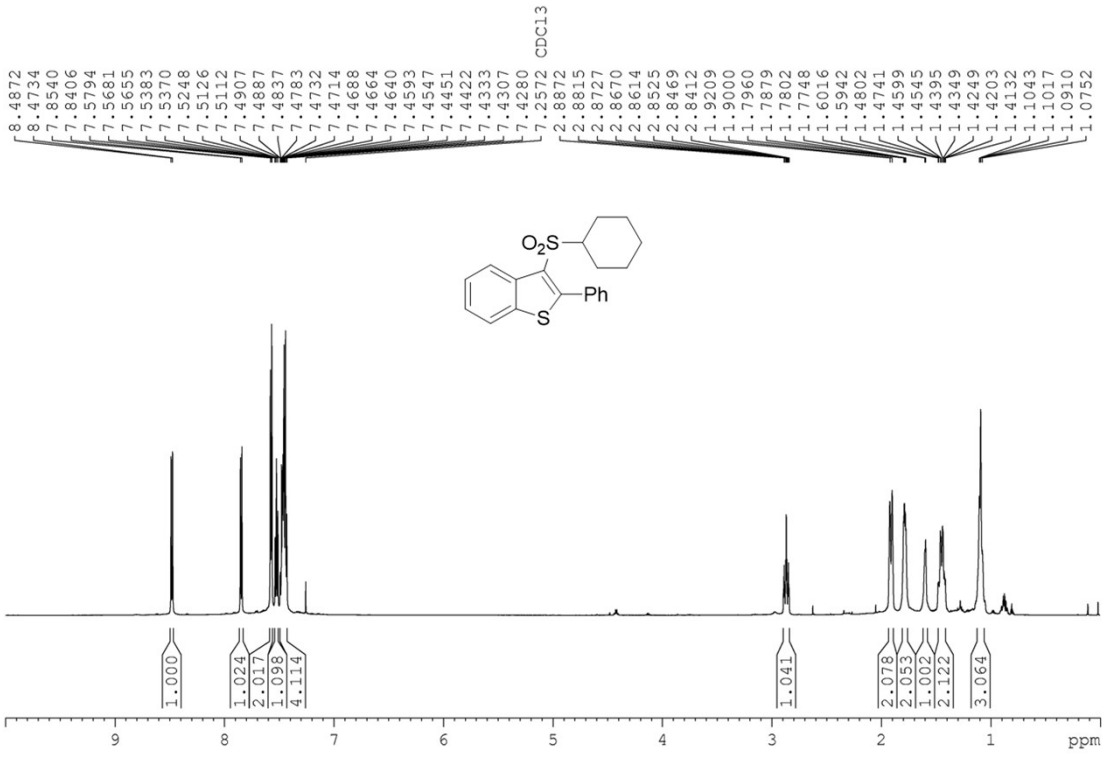
^{1}H NMR (600 MHz, $CDCl_3$) of **3ak**



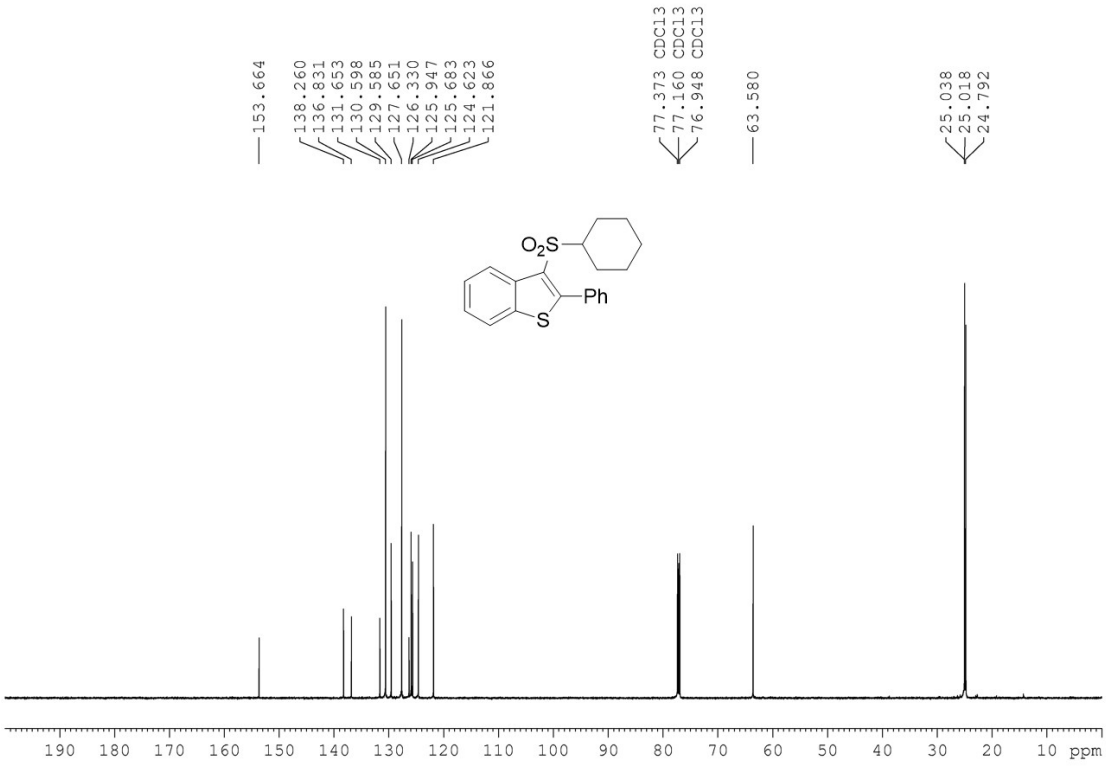
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ak**



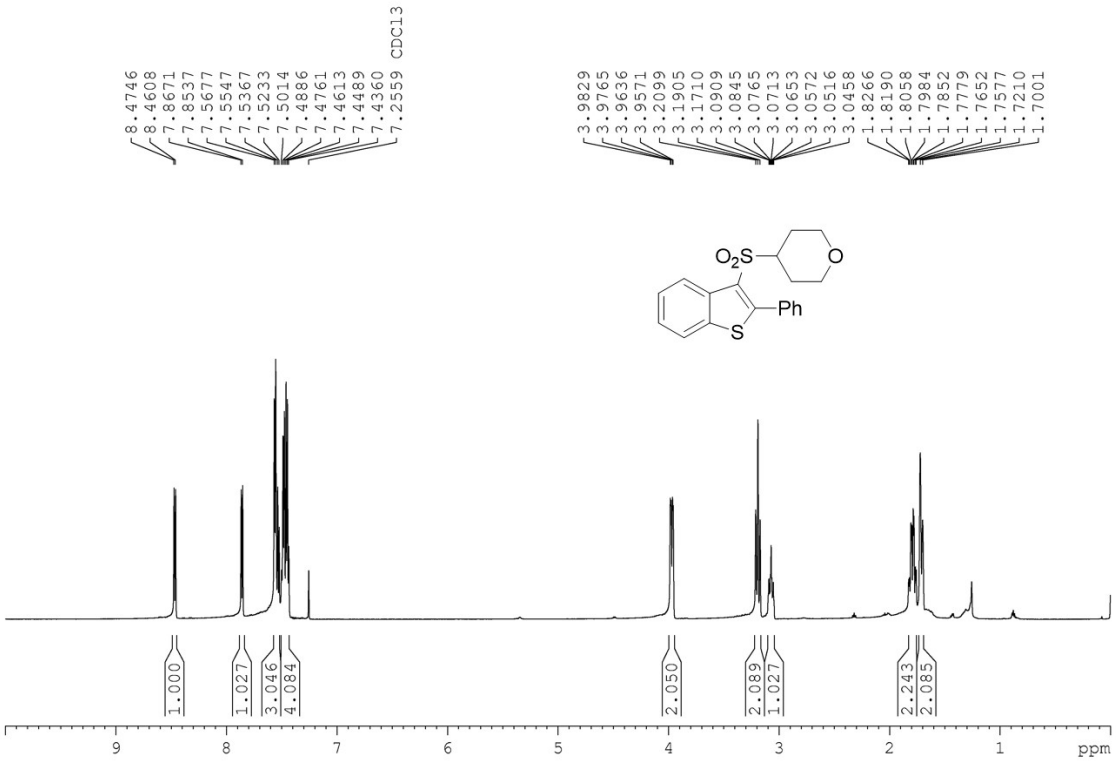
^{1}H NMR (600 MHz, $CDCl_3$) of **3al**



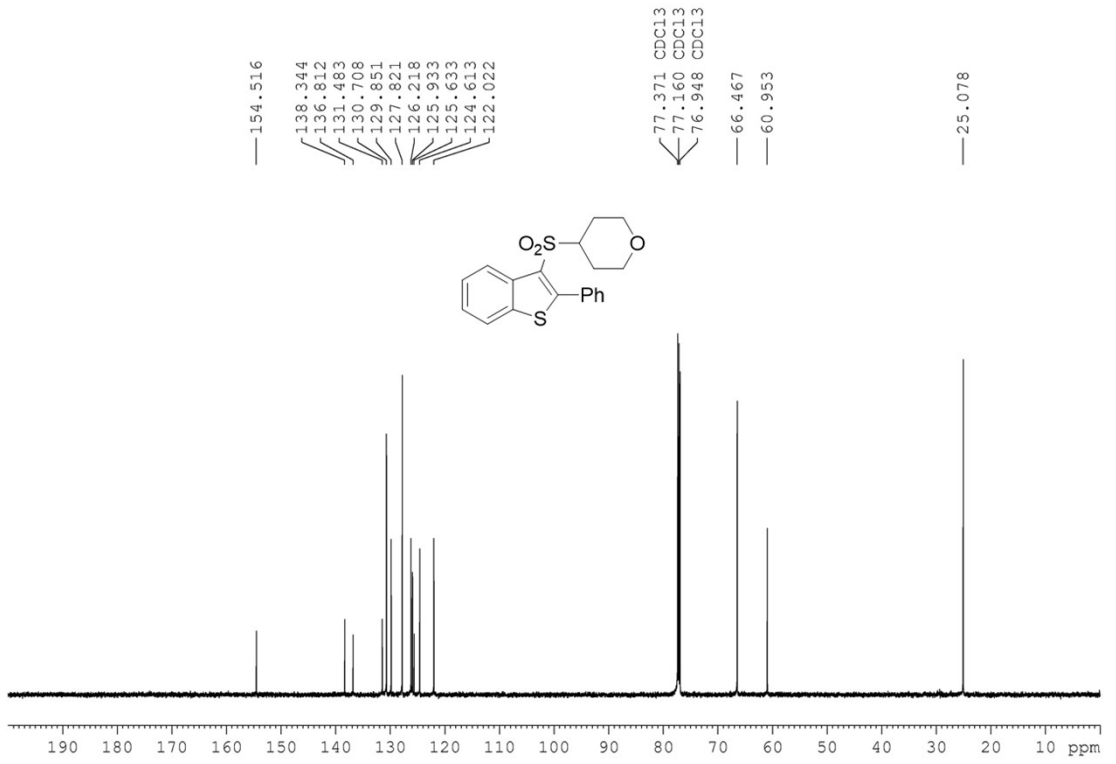
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3al**



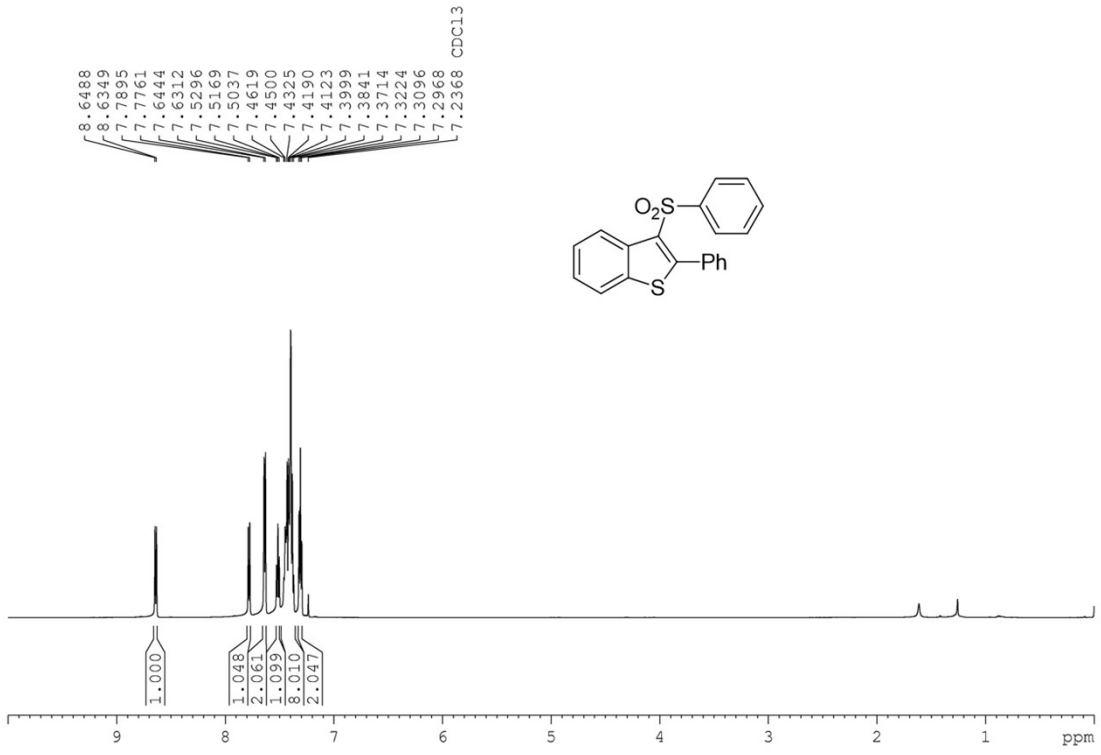
^{1}H NMR (600 MHz, $CDCl_3$) of **3am**



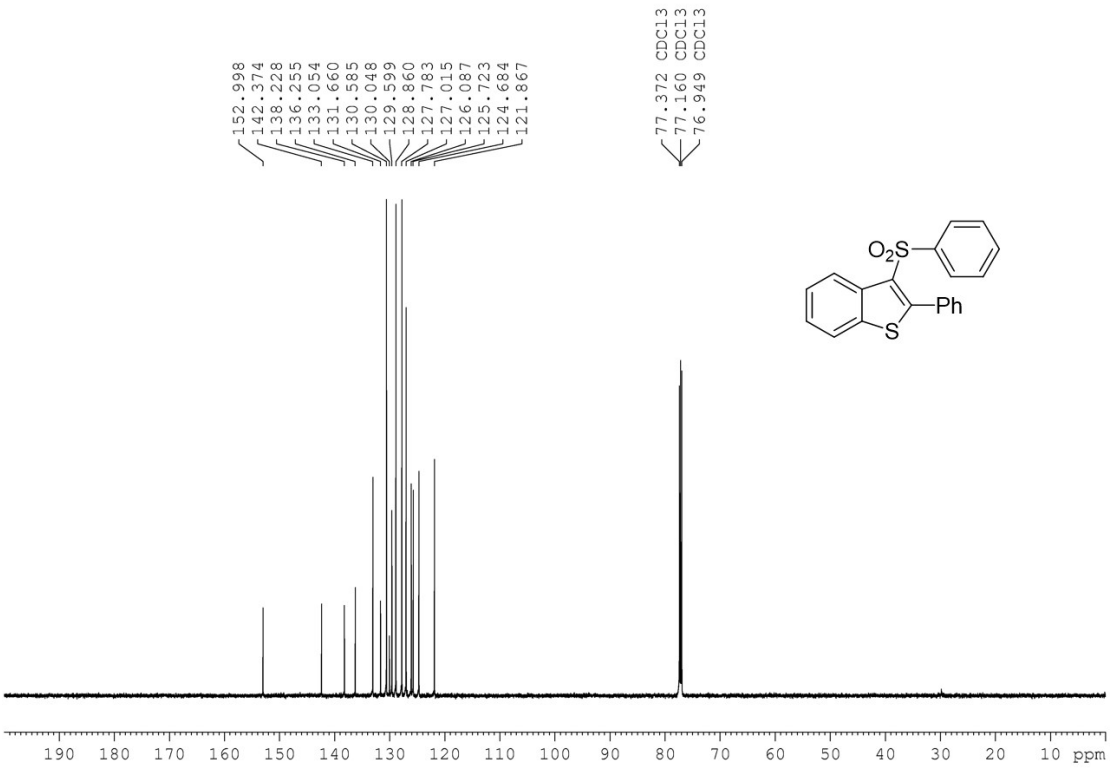
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3am**



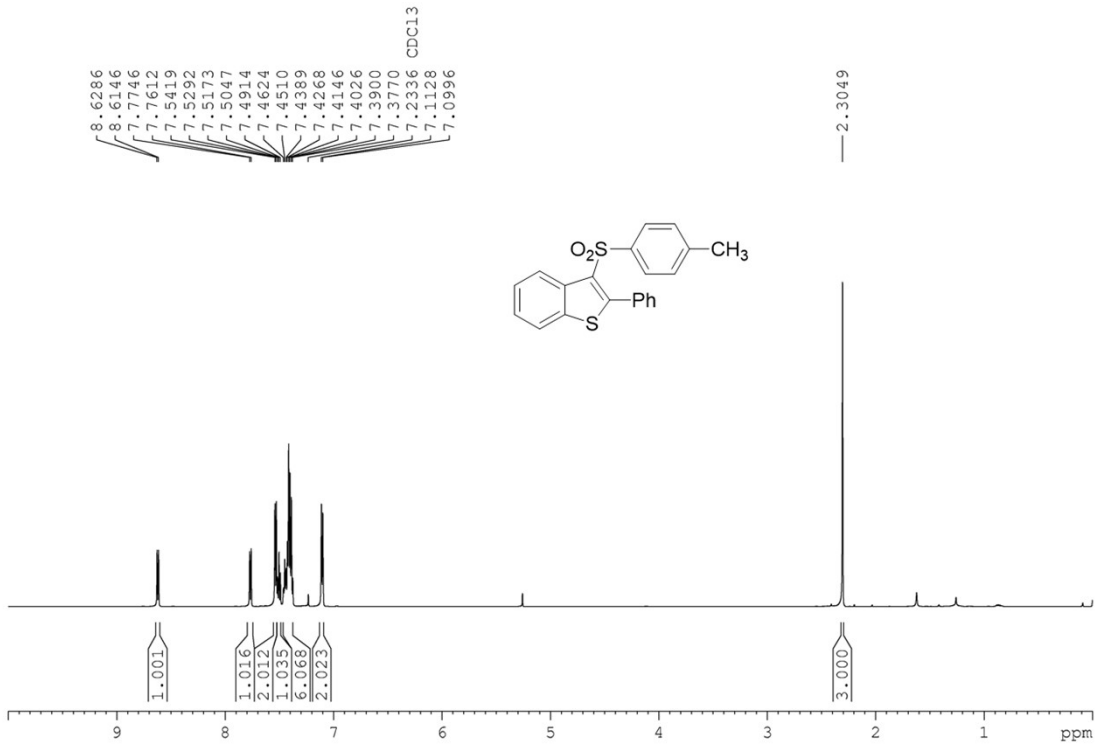
^{1}H NMR (600 MHz, $CDCl_3$) of **3an**



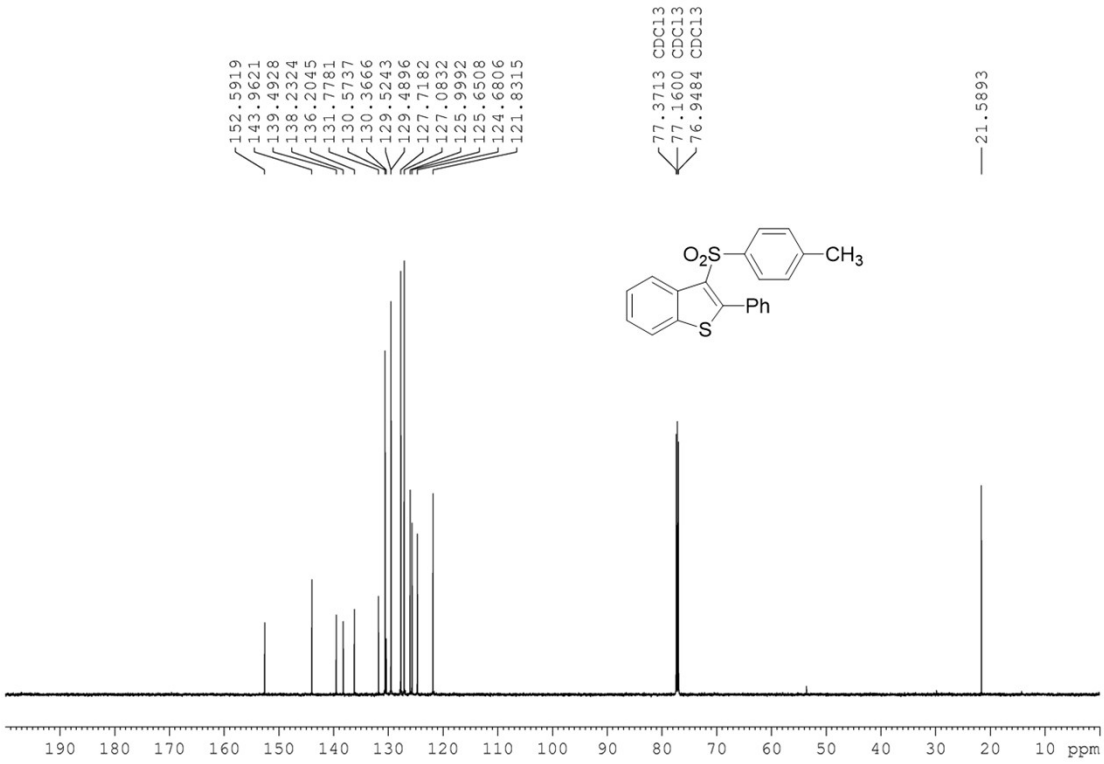
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3an**



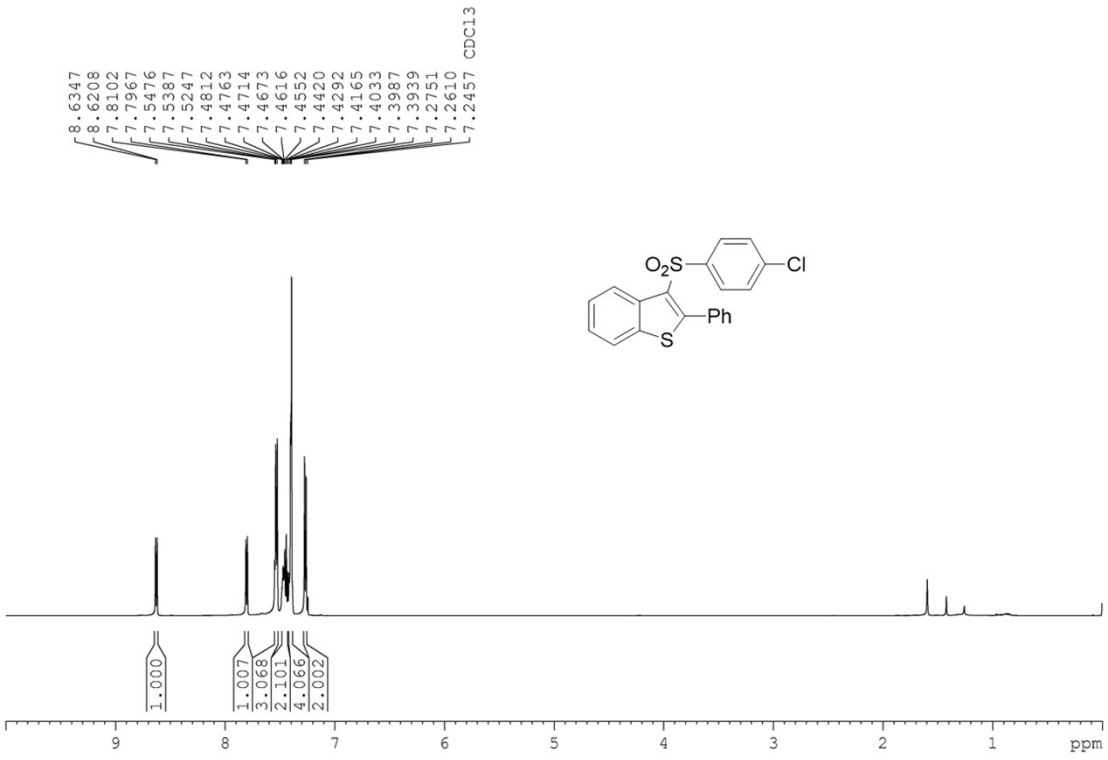
^{1}H NMR (600 MHz, $CDCl_3$) of **3ao**



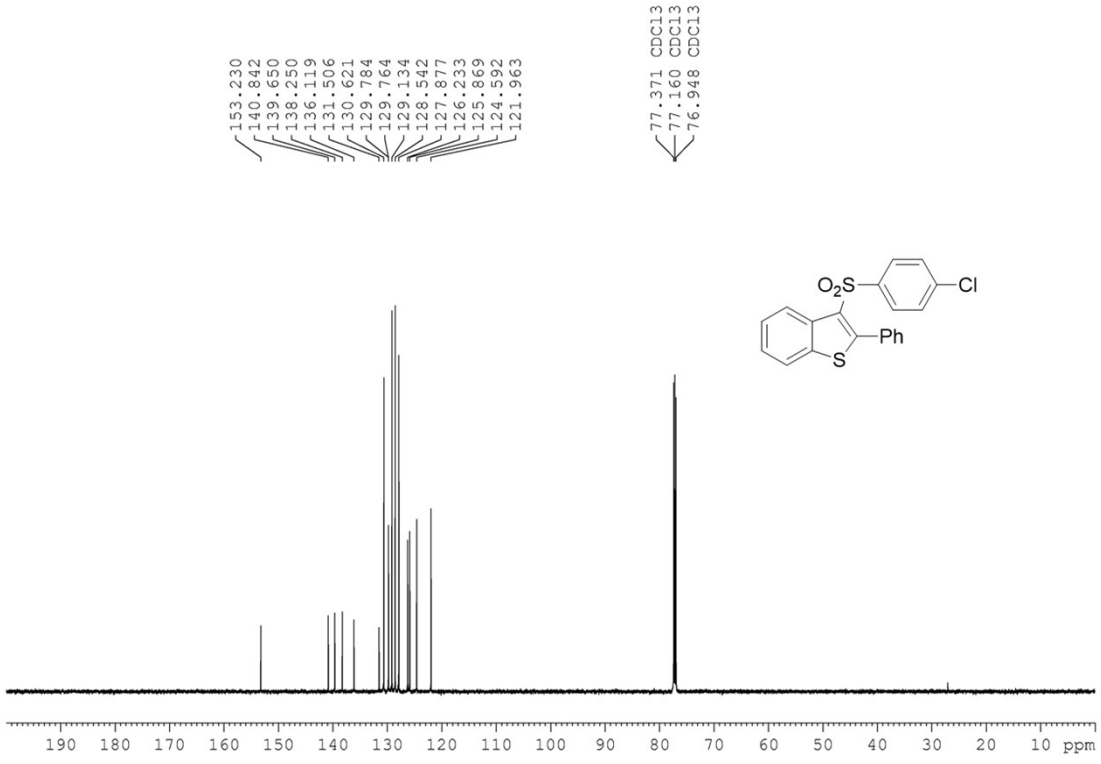
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ao**



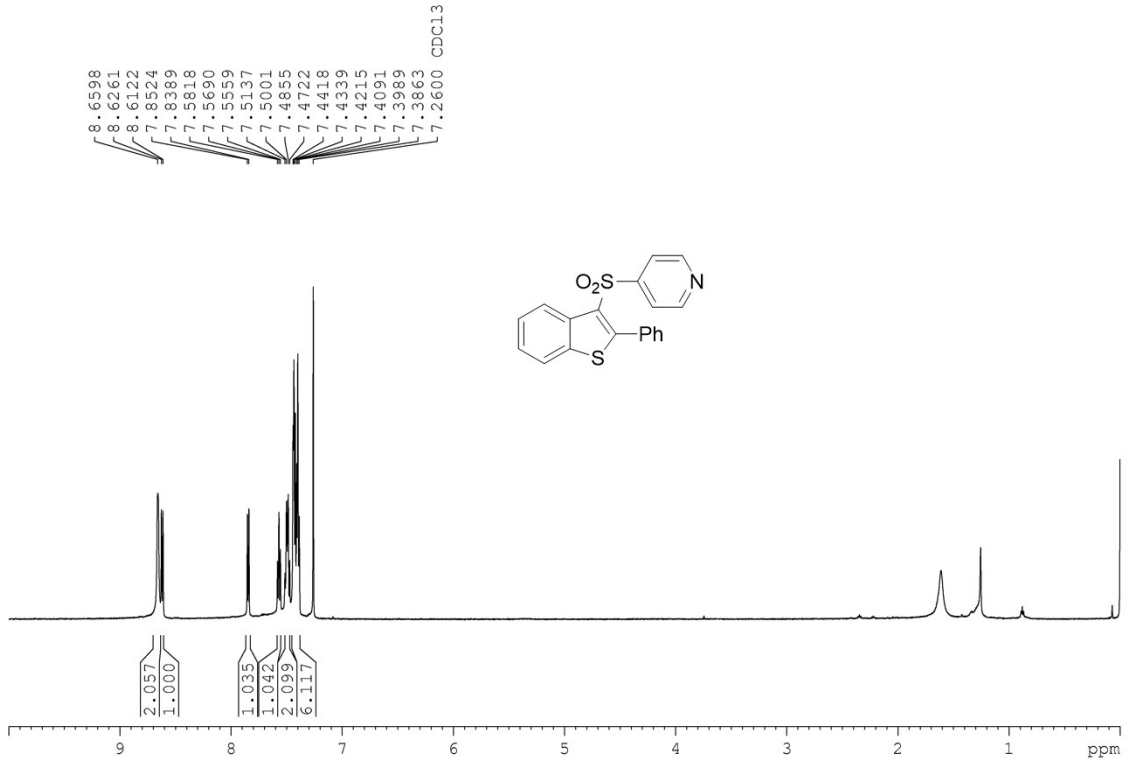
^{1}H NMR (600 MHz, $CDCl_3$) of **3ap**



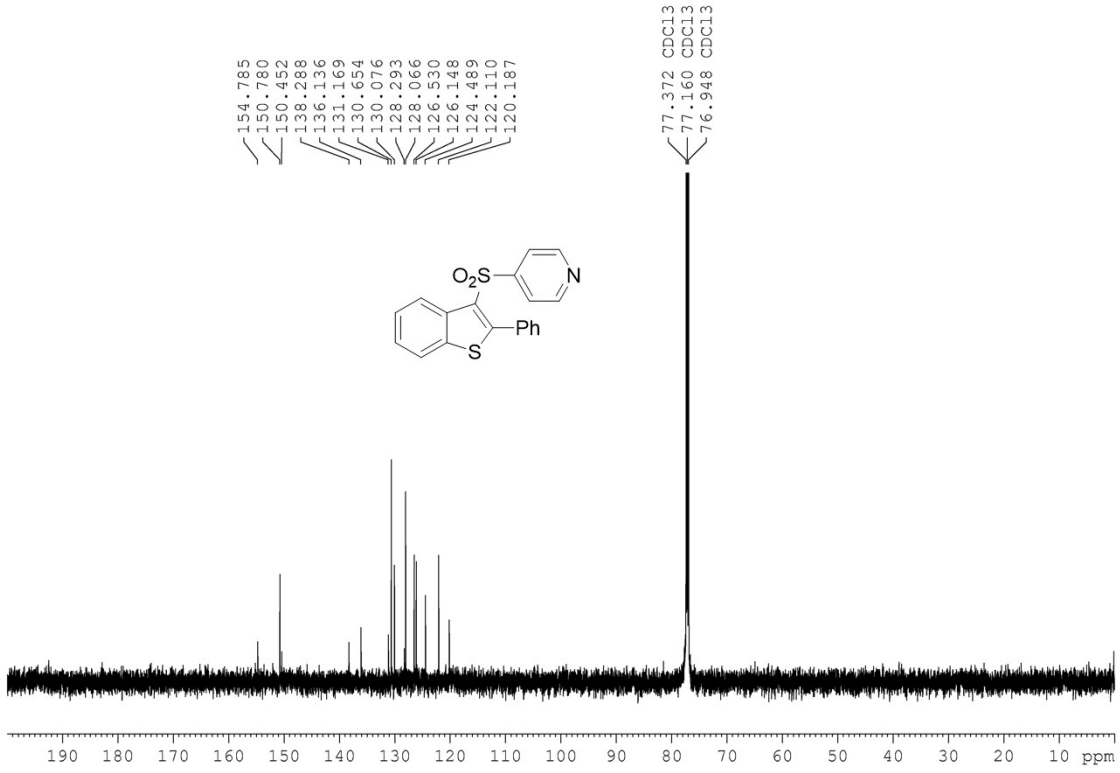
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3ap**



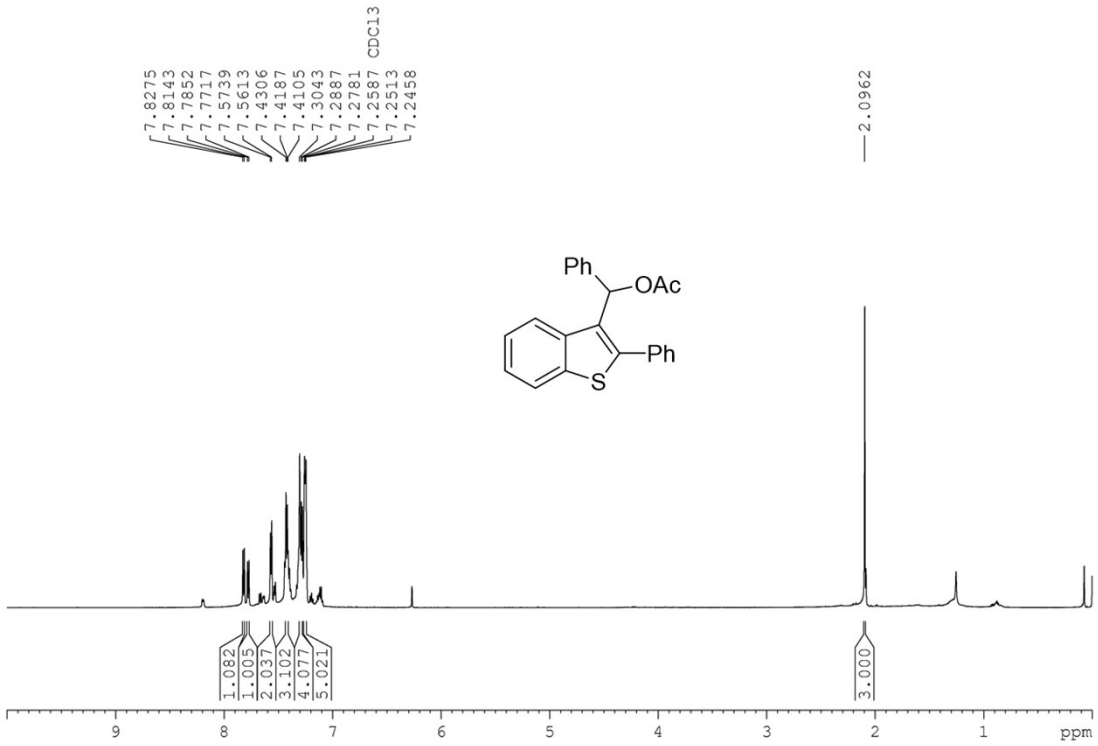
^{1}H NMR (600 MHz, $CDCl_3$) of **3aq**



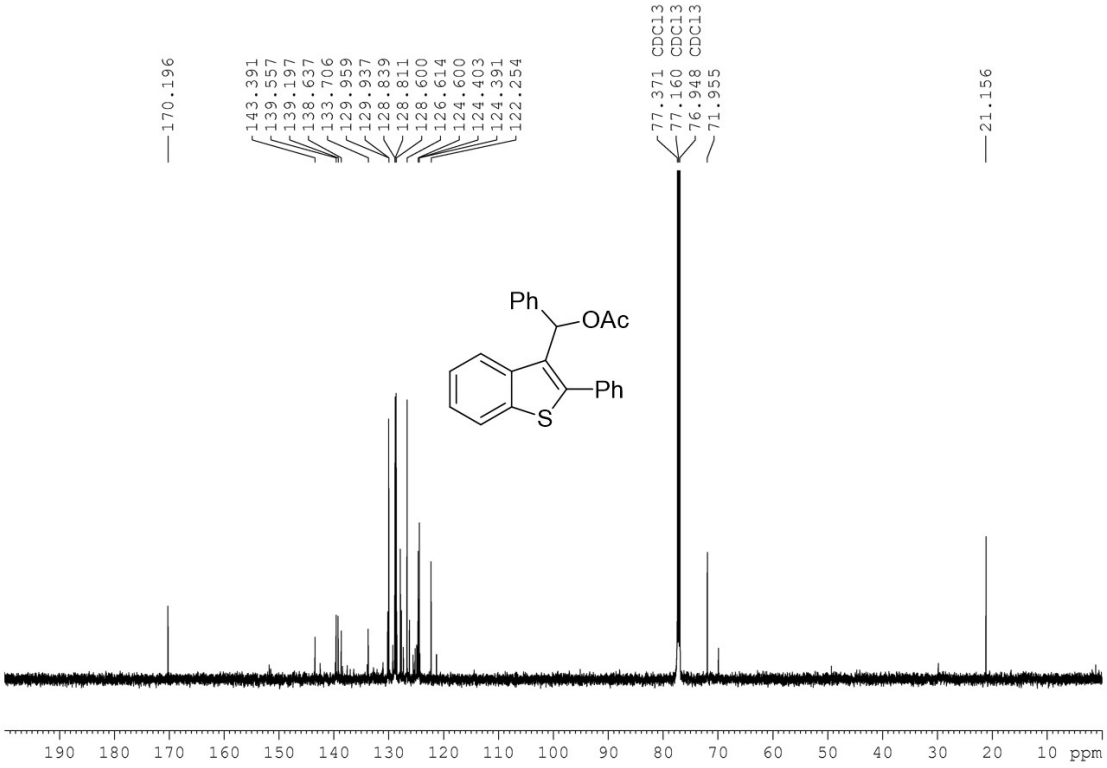
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **3aq**



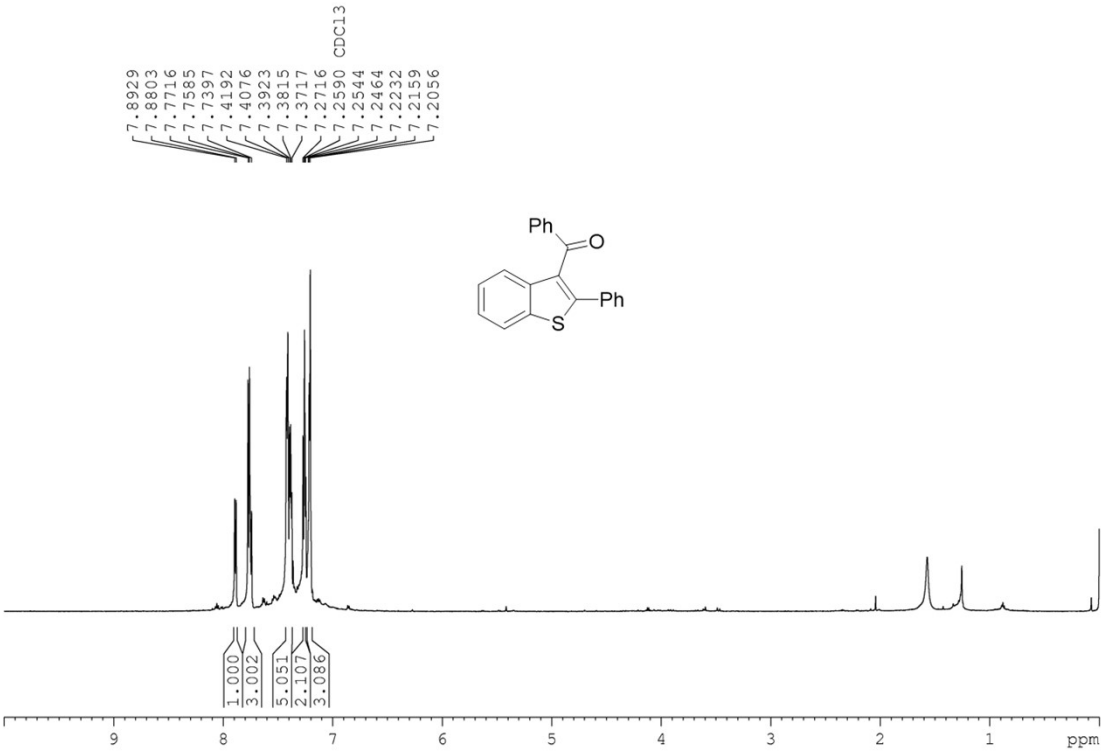
^{1}H NMR (600 MHz, $CDCl_3$) of **4**



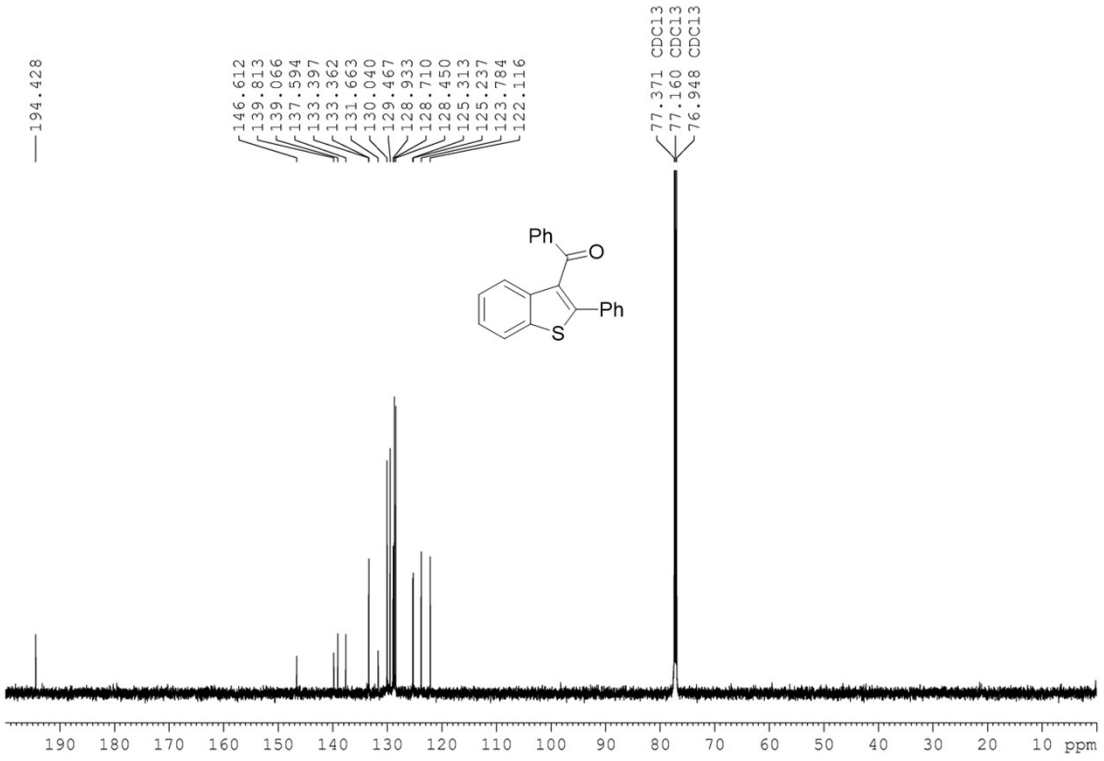
^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **4**



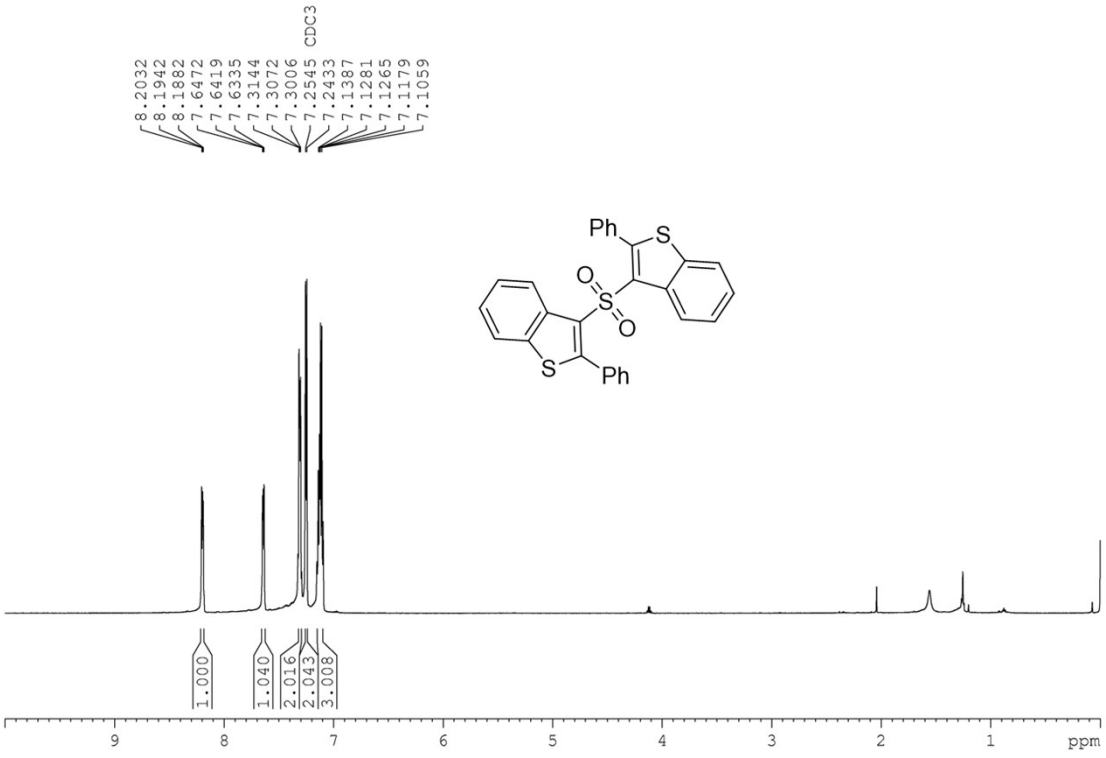
^{1}H NMR (600 MHz, $CDCl_3$) of **5**



^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **5**



^{1}H NMR (600 MHz, $CDCl_3$) of **6**



^{13}C NMR {1H} (150 MHz, $CDCl_3$) of **6**