Supporting information

Heterogeneous copper-catalyzed synthesis of diaryl sulfones

Table of contents

1. General information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using 254nm UV light to visualize the course of the reactions. The ^{1}H(400MHz) and ^{13}C NMR (100MHz) data were recorded on Bruker AVANCEII400MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. Microstructure of NPs can be observed by Field Emission Scanning Electron Microscope JSM-6010PLUS/LA. X-ray diffraction data is obtained by XRD-6100 instrument, which is produced by Shimadzu Instruments Co., Ltd., Japan.

2. Preparation of NPs

(1) Preparation of Fe-Cu-NPs

1.5 g of sodium gluconate and 20 mL of deionized water were added to a 30mL reactor, then 160 mg $FeCl_3$, and 80 mg $CuCl_2$ were added. The resulted homogeneous solution was kept at 150°C for 24 hours. Then the reaction solution was centrifuged, and the left solid was washed three times with deionized water and ethanol to obtain a clean Fe-Cu-NPs.

(2) Preparation of $CuCl_2$-NP, CuO- NP and $Cu(OAc)_2$- NP

1.5 g of sodium gluconate and 20 mL of deionized water were added to a 30mL reactor, then 240mg $CuCl_2$/CuO/$Cu(OAc)_2$ was added. The resulted homogeneous solution was kept at 150°C for 24 hours. Then the reaction solution was centrifuged, and the left solid was washed three times with deionized water and ethanol to obtain a clean Cu-NP.

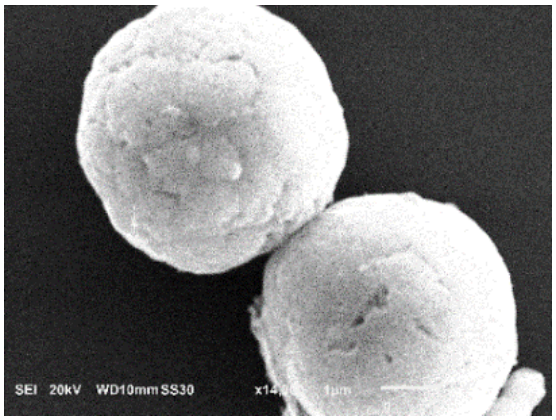
(3) Preparation of $Cu(OAc)_2$-NP with morphology

1.5 g of sodium gluconate and 20 mL of deionized water were added to a 30mL reactor, then 240mg $Cu(OAc)_2$ was added. The resulted homogeneous solution was kept at 90/120/150°C for 6/8/10/12/18/30 hours respectively. Then the reaction

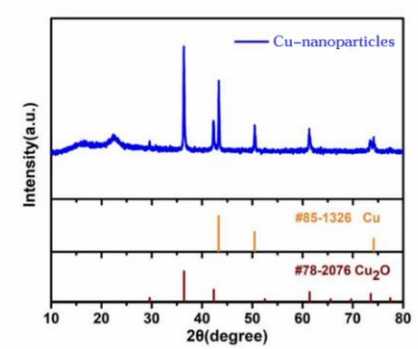
solution was centrifuged, and the left solid was washed three times with deionized water and ethanol to obtain a clean Cu-NP.

(4) **Charactrization of $Cu(OAc)_2$@sodium gluconate synthesized under 150℃**

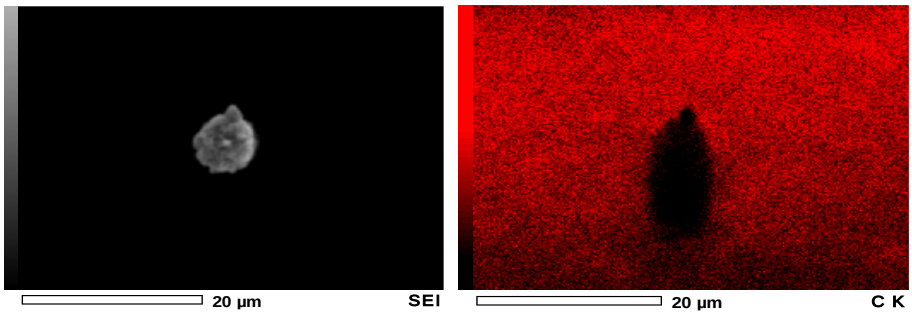
The SEM of Cu-NP:

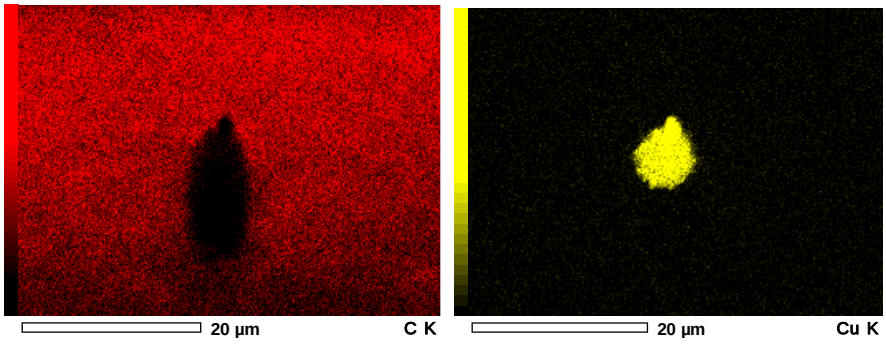


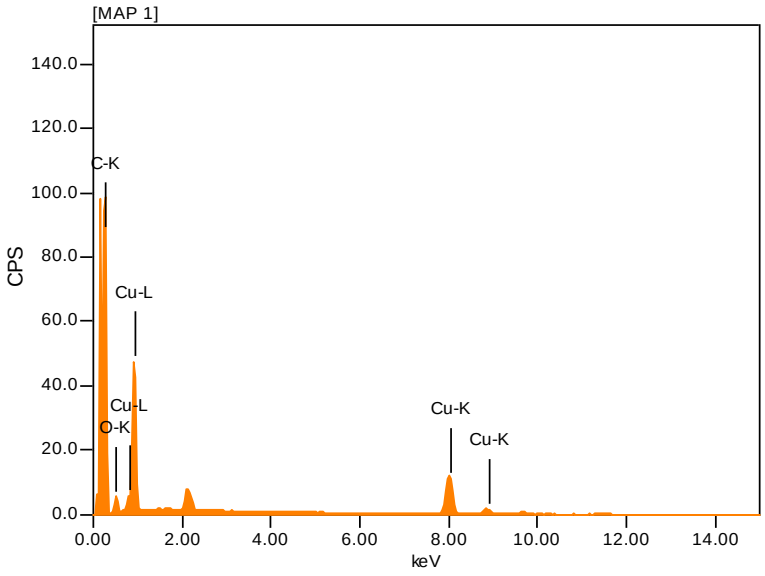
The XRD pattern of Cu-NP:



Elemental mapping of Cu-NP





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Acquisition Condition
Instrument: 6010LA
Volt:        20.00 kV
Current:      ---
Process Time: T3
Live time:    491.48 sec.
Real Time:    498.33 sec.
DeadTime:     1.00 %
Count Rate:   2036.00 CPS
```

Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	74.10	89.83	0.02	956414	0.0478668	K
O*	6.21	5.65	0.02	56845	0.0096619	K
Cu	19.68	4.51	0.04	416413	0.1480987	K
Total	100.00	100.00				

3. General procedure for synthesis 1b-1g [1]

A 100mL round bottom flask containing 22 mmol of hydrazine hydrate and 20mL of THF was placed in an ice bath, then a solution of arylsulfonyl chloride (10.0 mmol) in 10.0 mL THF was added. The reaction was kept stirring at 0°C for 30 minutes, monitered by TLC. After the starting material was consumed, 10 mL of ether was added to the reaction system to extract the product, and then the organic phase was washed 3 times with saturated brine, the organic phase was collected, and dried with anhydrous sodium sulfate, concentrated to obtain pure product arylsulfonyl hydrazide **1b-1g**.

4. General procedures for synthesis 3aa-3ai and 3ba-3ga

An oven-dried flask tube was charged with 5mg $Cu(OAc)_2$-NP, DABCO (1.5 mmol), arylboronic acid (1.0 mmol), arylsulfonyl hydrazide (1.5 mmol), and EtOH (2 mL). The reaction mixture was stirred at room temperature under air atmosphere for 16h. The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, the solid was removed by filtration and washed with DCM. The organic phase was collected and concentrated, followed by column

chromatography to afford desired products **3aa-3a**i and **3ba-3ga**.

5. Copies of spectra

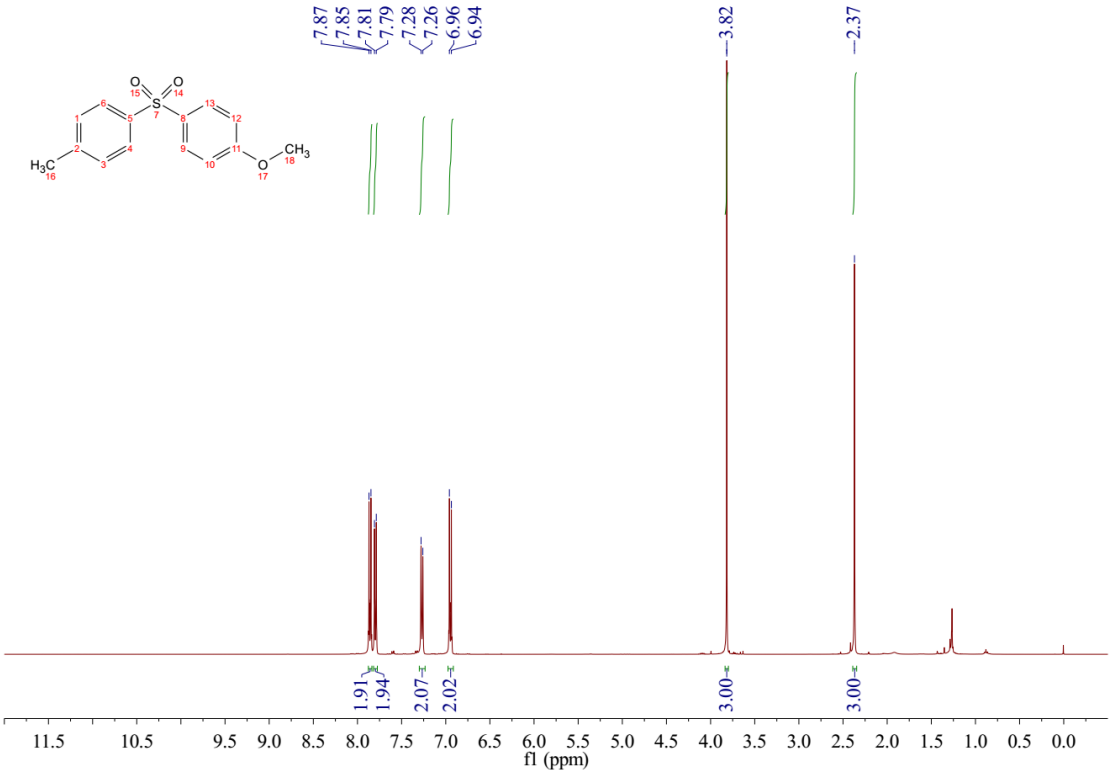

Figure **S1**. The ^{1}H-NMR spectrum of 3aa.

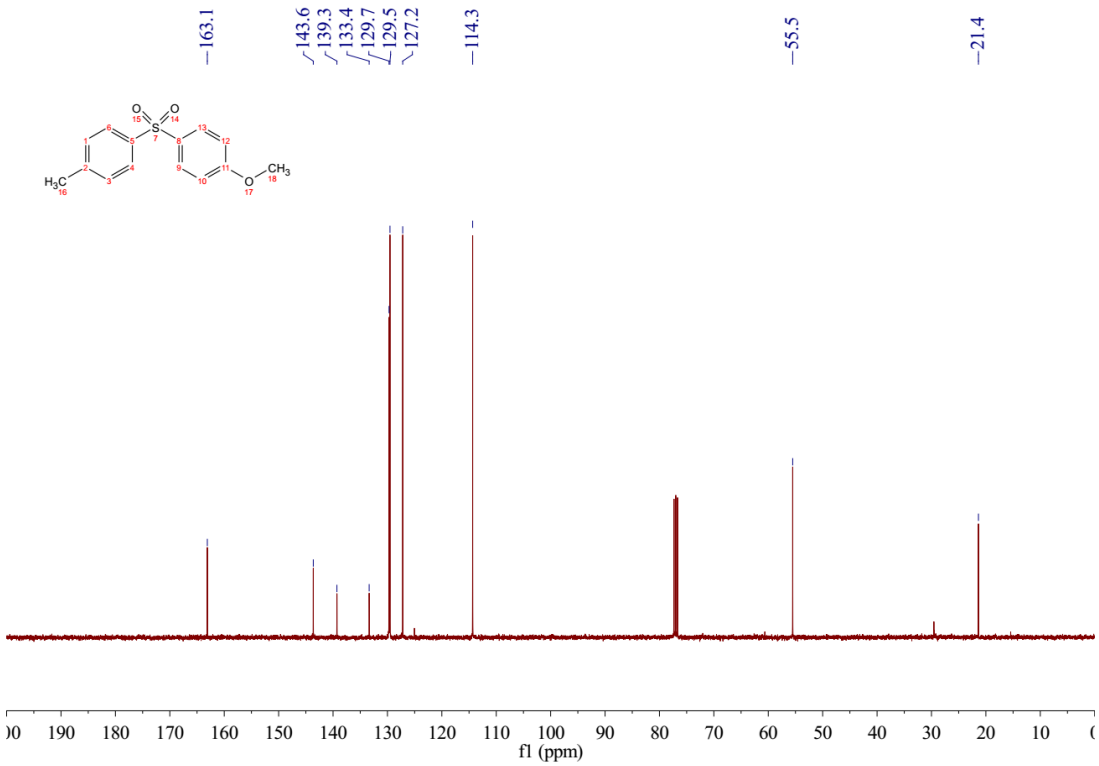

Figure **S2**. The ^{13}C-NMR spectrum of 3aa.

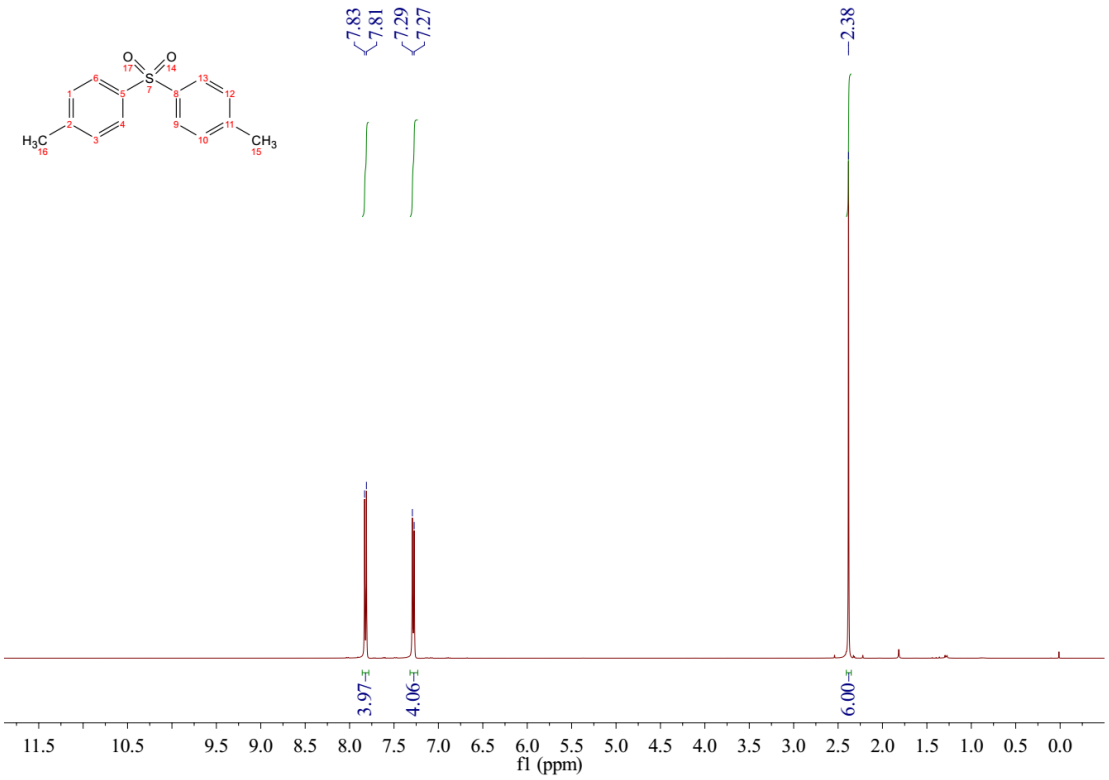

Figure **S3**. The ^{1}H-NMR spectrum of 3ab.

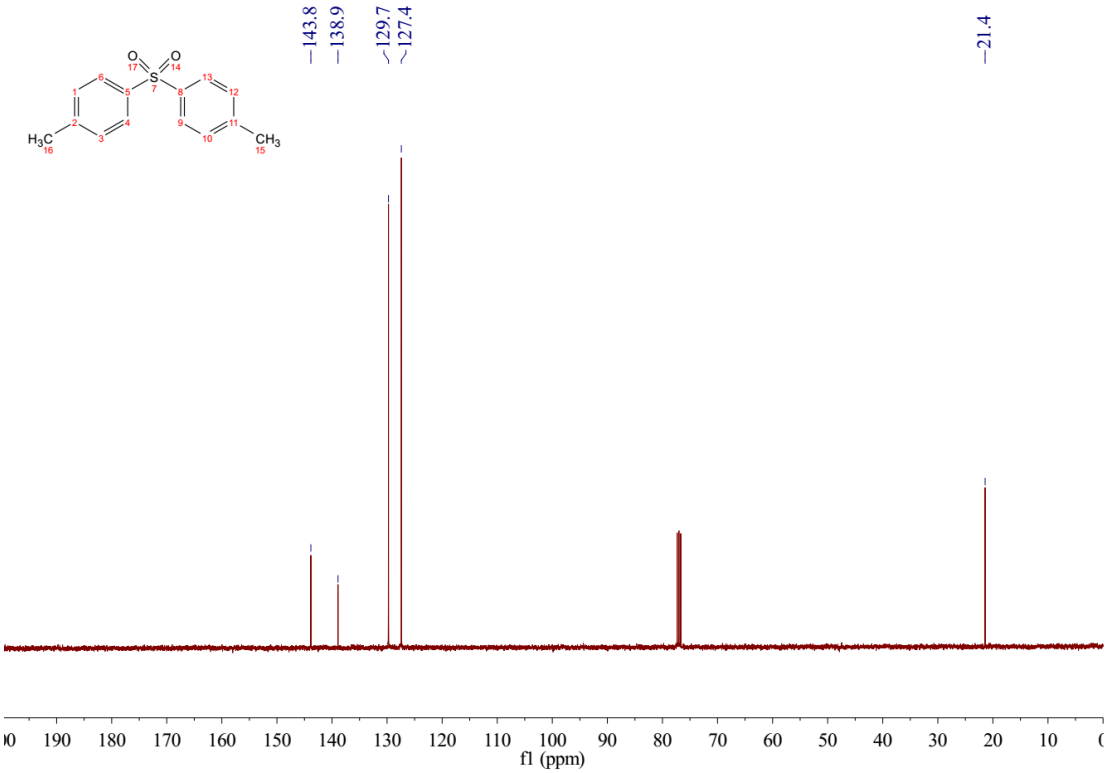

Figure **S4**. The ^{13}C-NMR spectrum of 3ab.

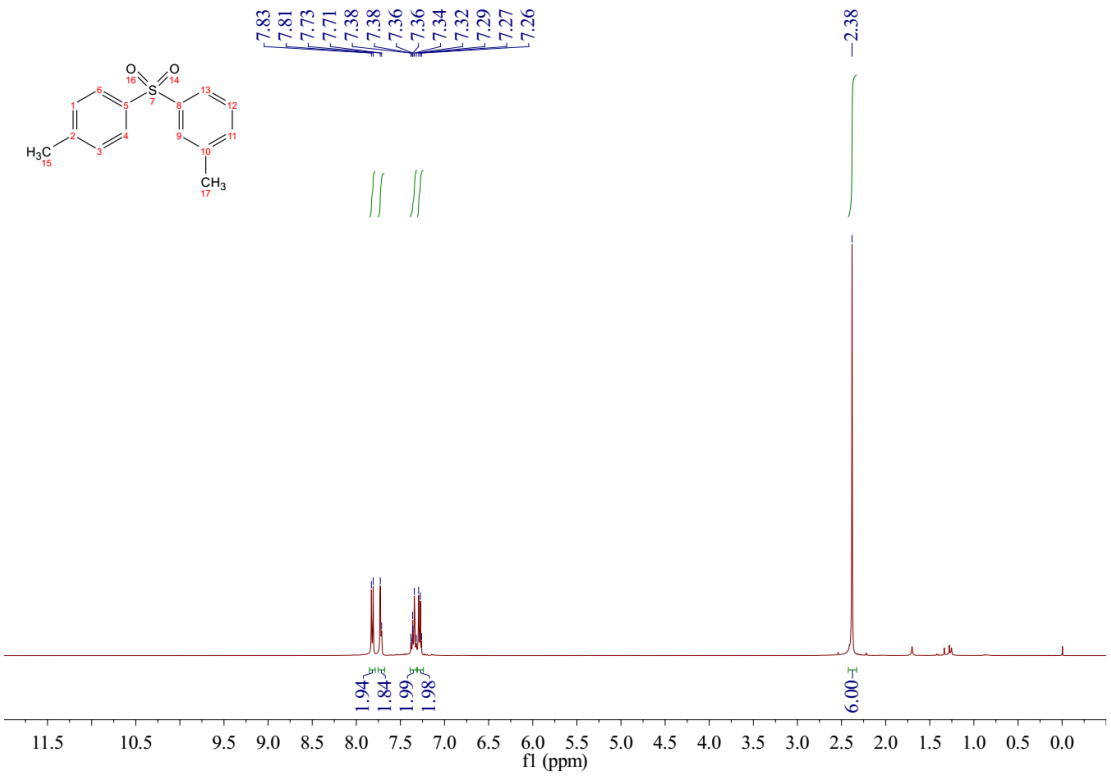

Figure **S5**. The ^{1}H-NMR spectrum of 3ac.

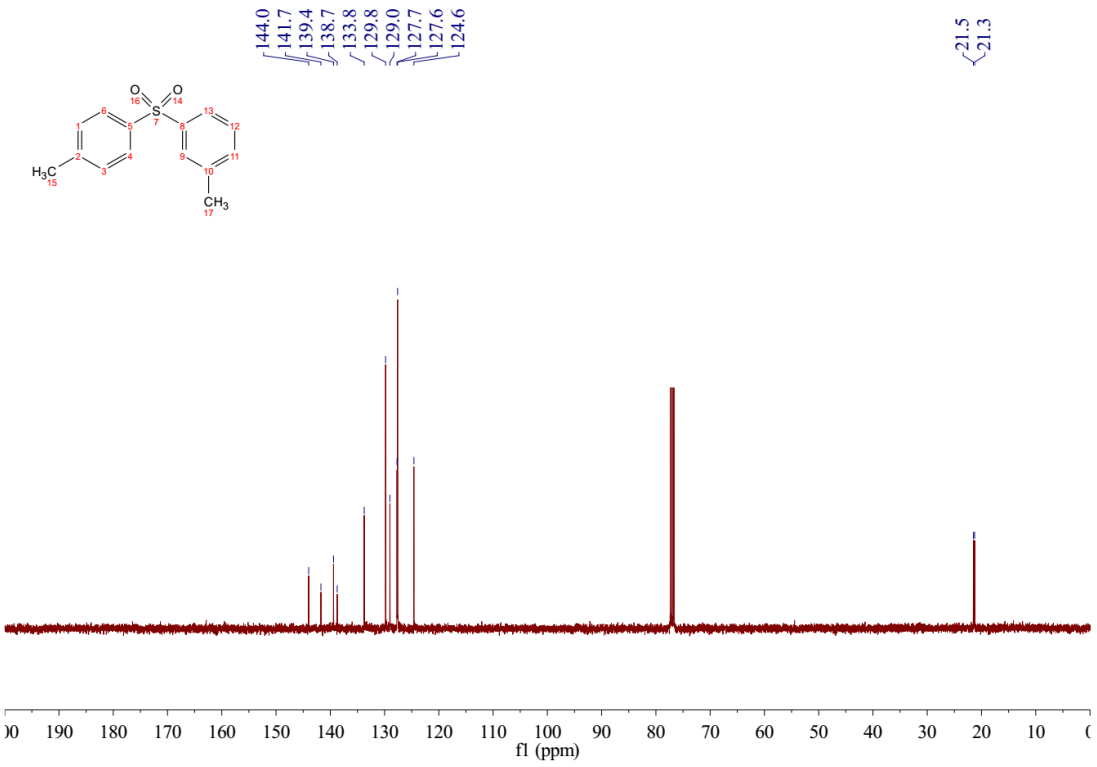

Figure **S6**. The ^{13}C-NMR spectrum of 3ac.

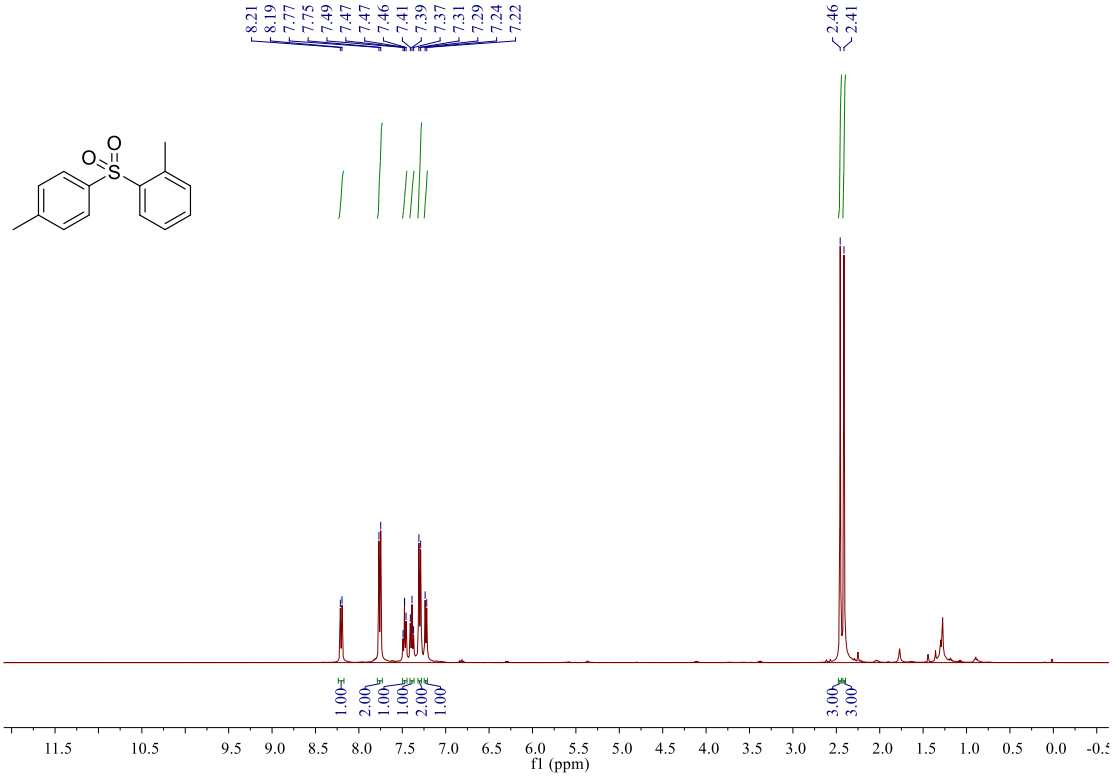

Figure **S7**. The ^{1}H-NMR spectrum of 3ad.

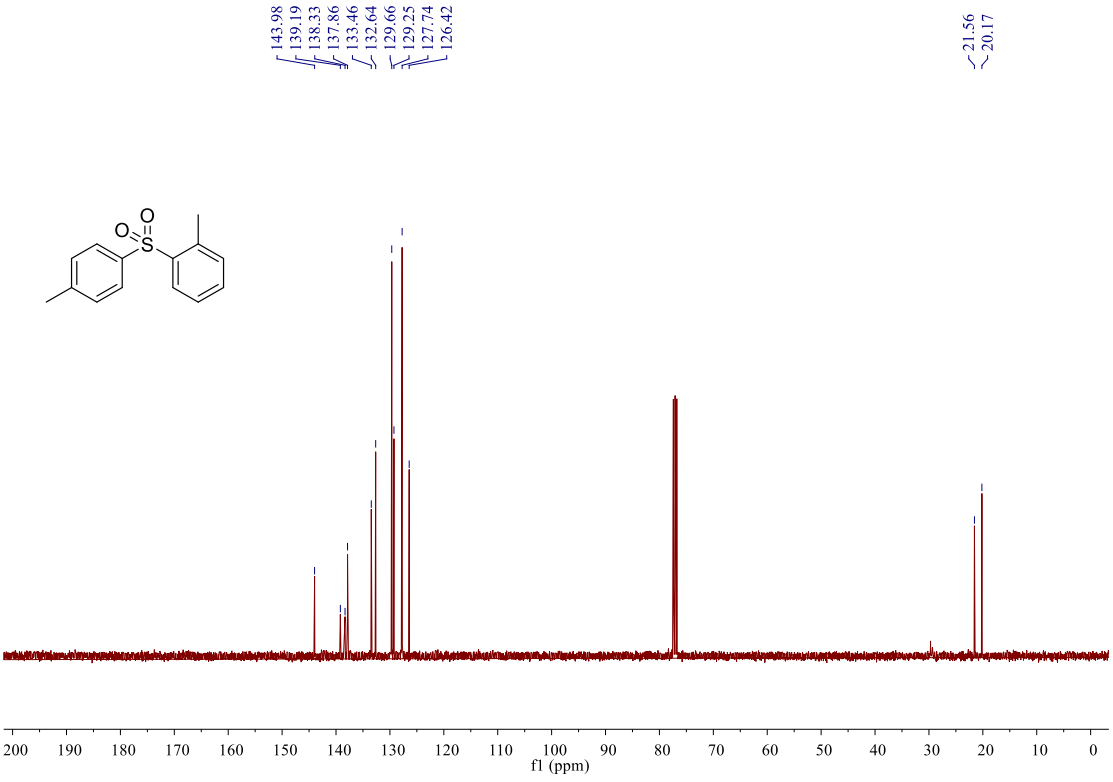

Figure **S8**. The ^{13}C-NMR spectrum of 3ad.

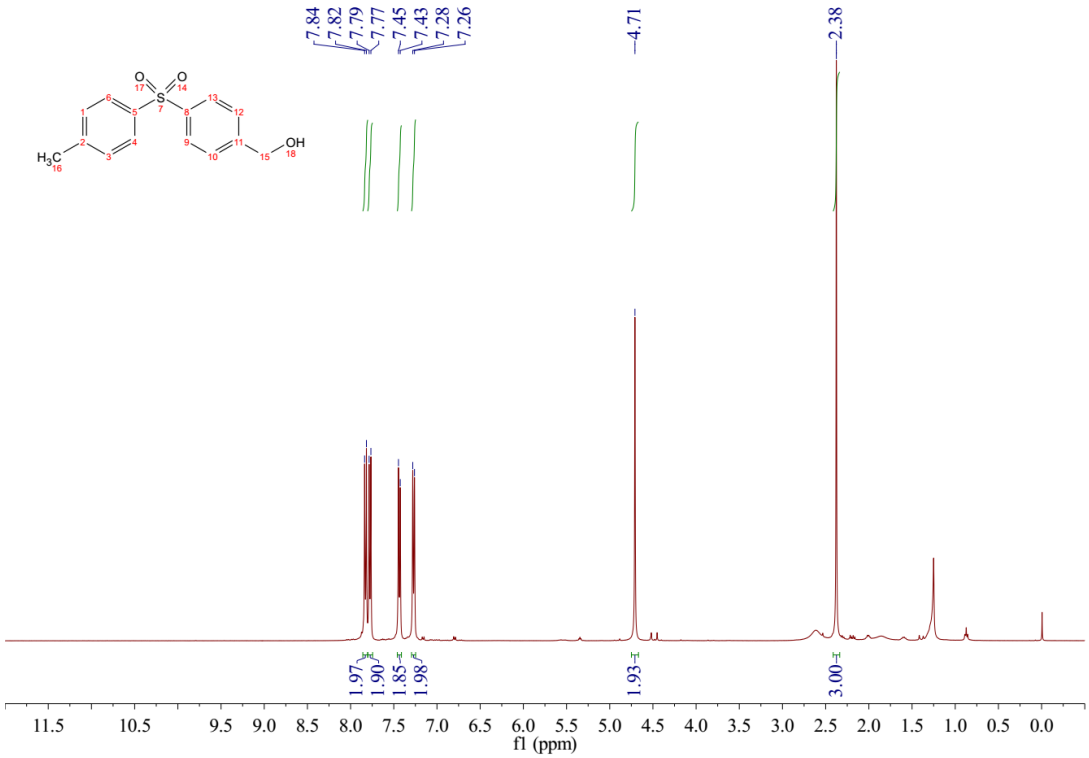

Figure **S9**. The ^{1}H-NMR spectrum of 3ae.

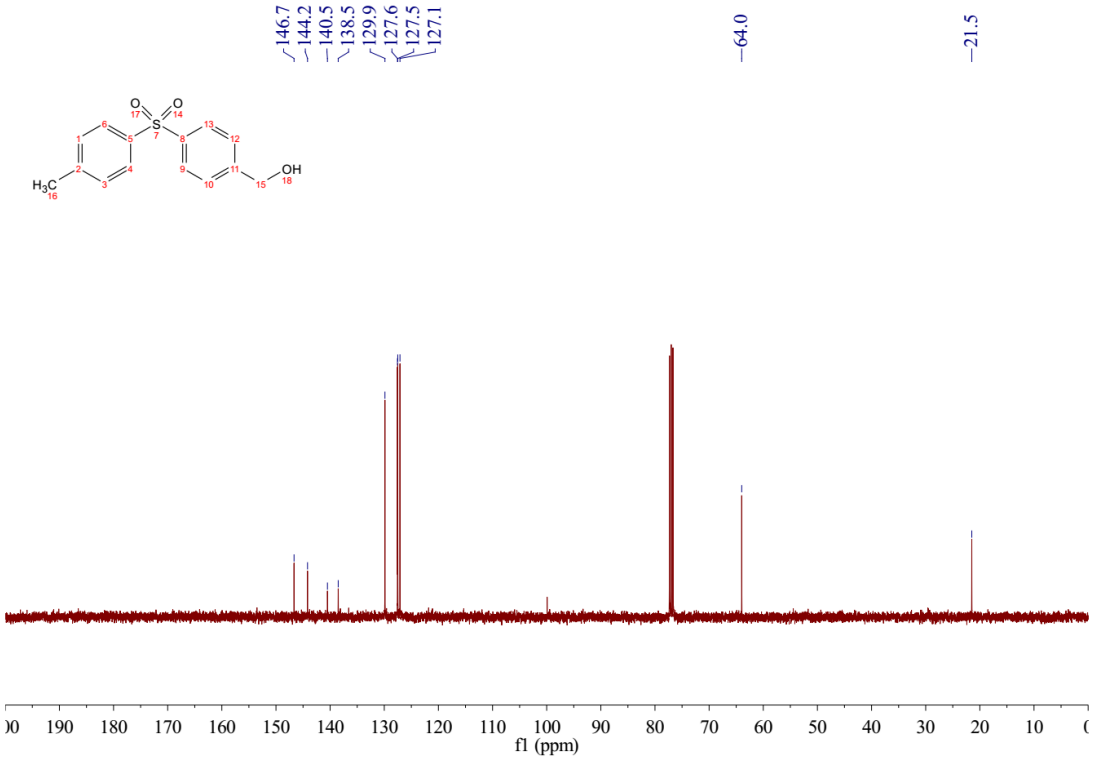

Figure **S10**. The ^{13}C-NMR spectrum of 3ae.

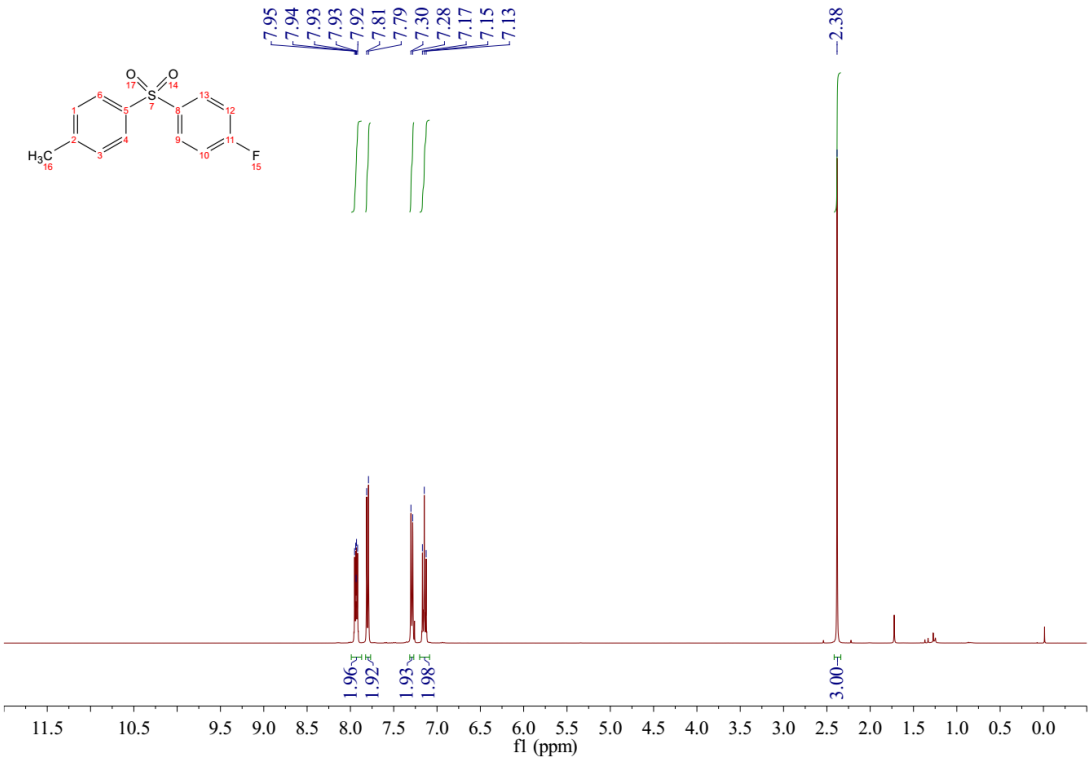

Figure **S11**. The ^{1}H-NMR spectrum of 3af.

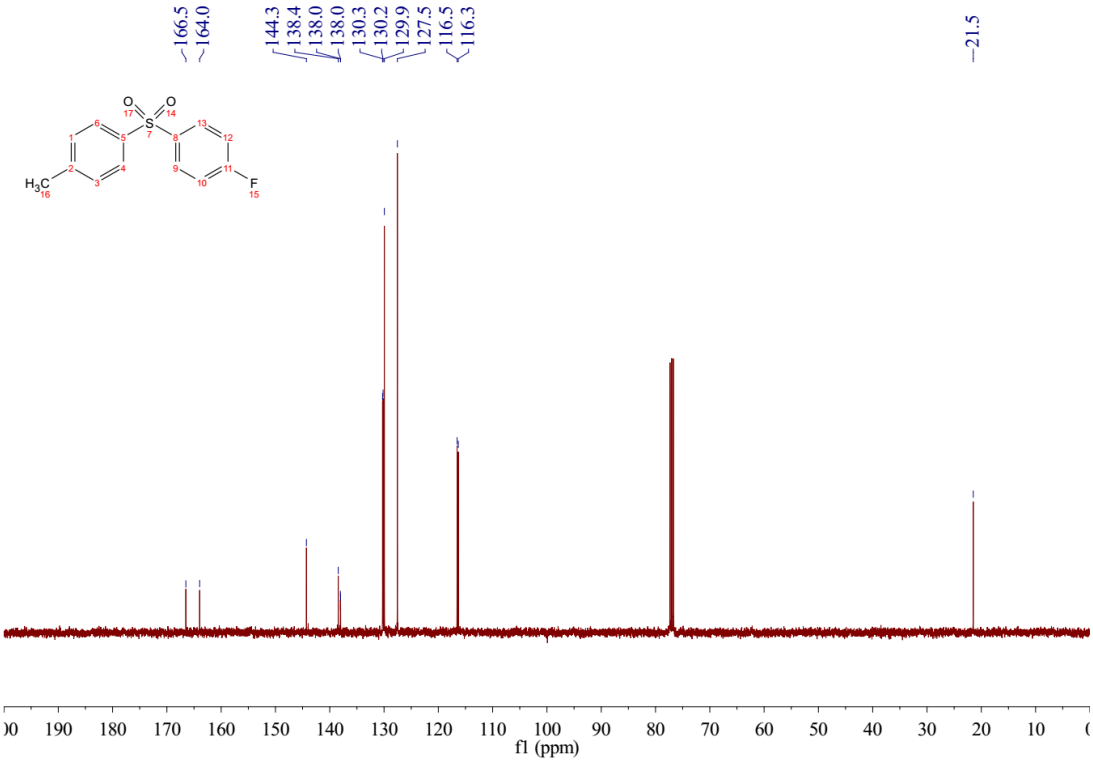

Figure **S12**. The ^{13}C-NMR spectrum of 3af.

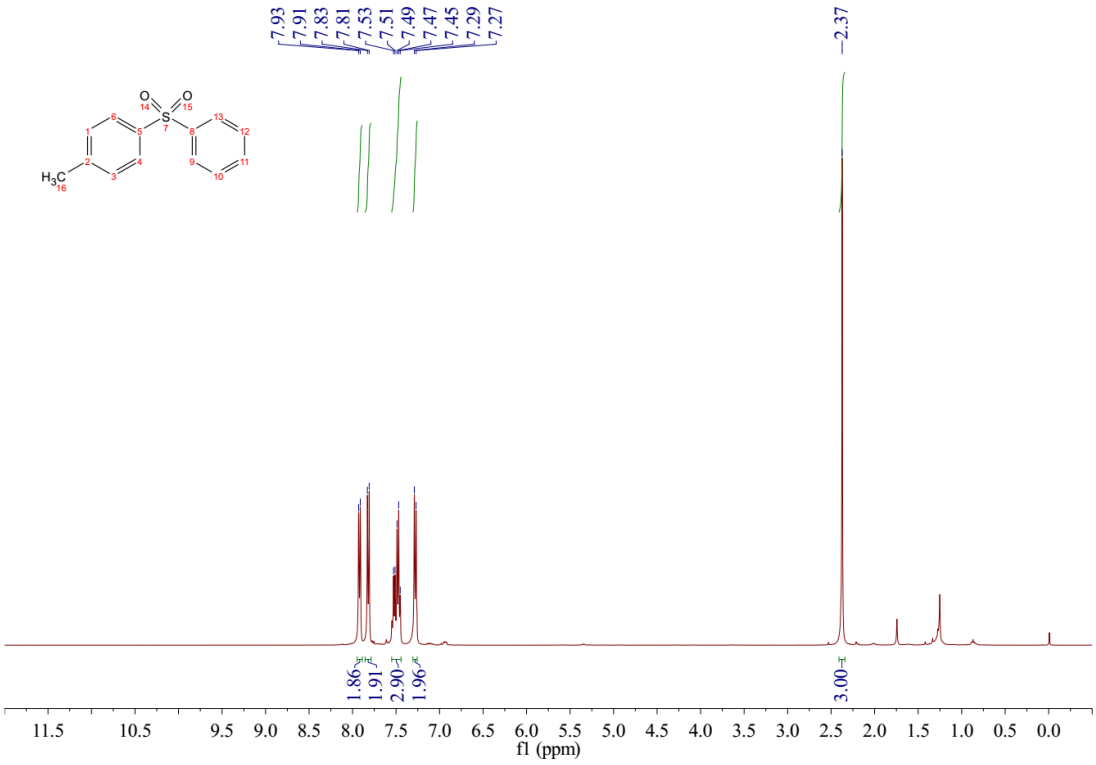

Figure **S13**. The ^{1}H-NMR spectrum of 3ag.

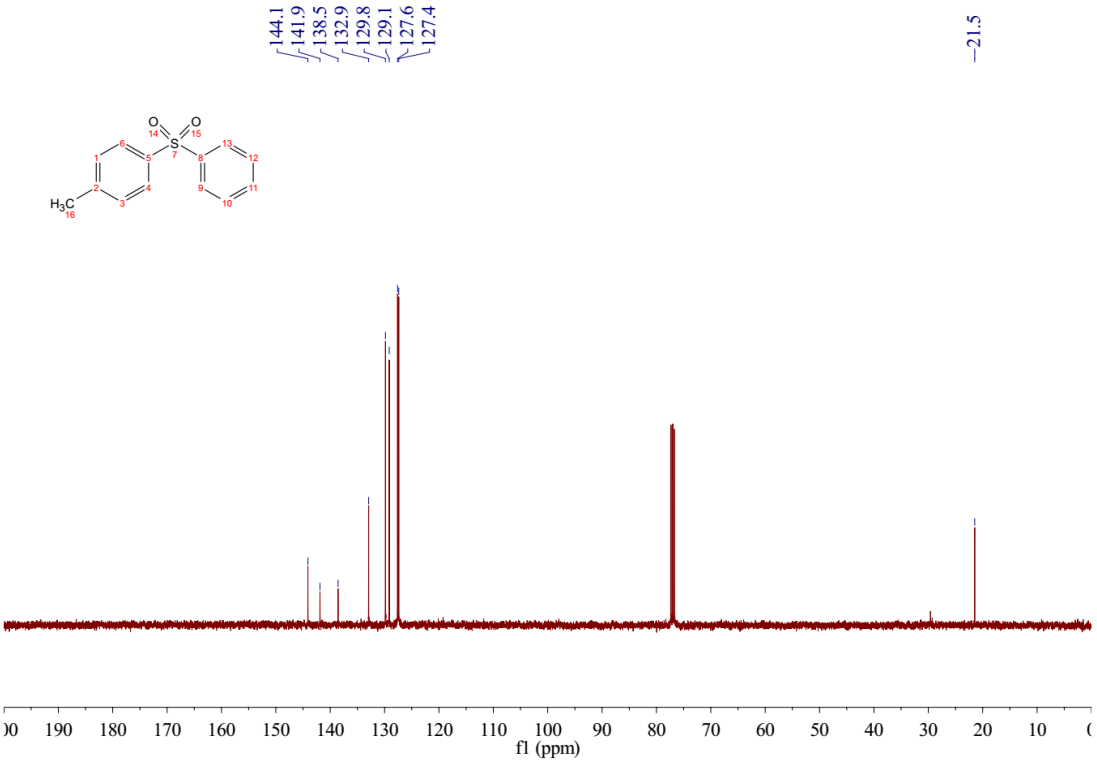

Figure **S14**. The ^{13}C-NMR spectrum of 3ag.

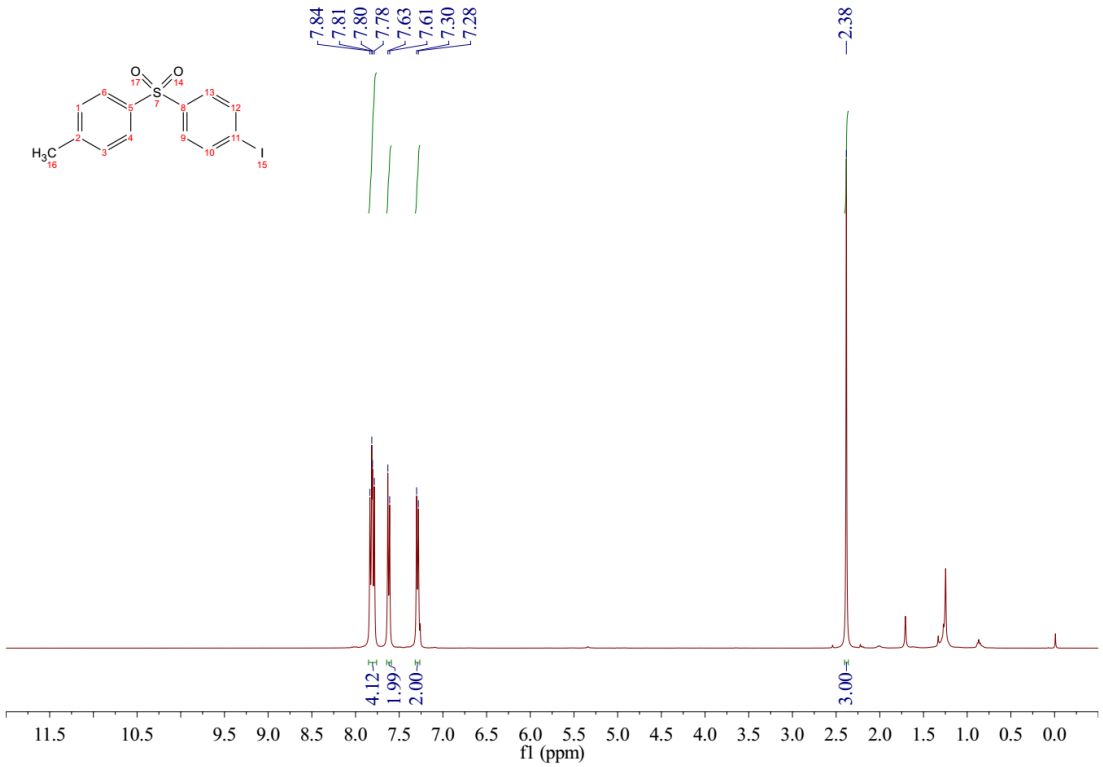

Figure **S15**. The ^{1}H-NMR spectrum of 3ah.

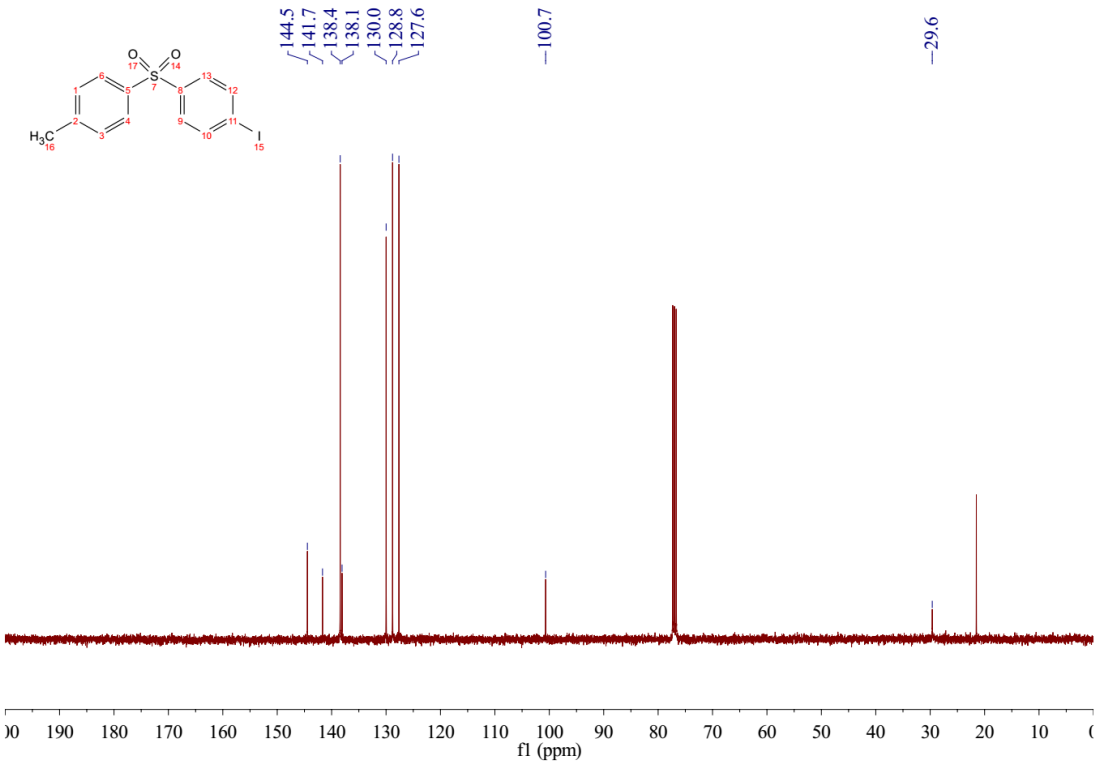

Figure **S16**. The ^{13}C-NMR spectrum of 3ah.

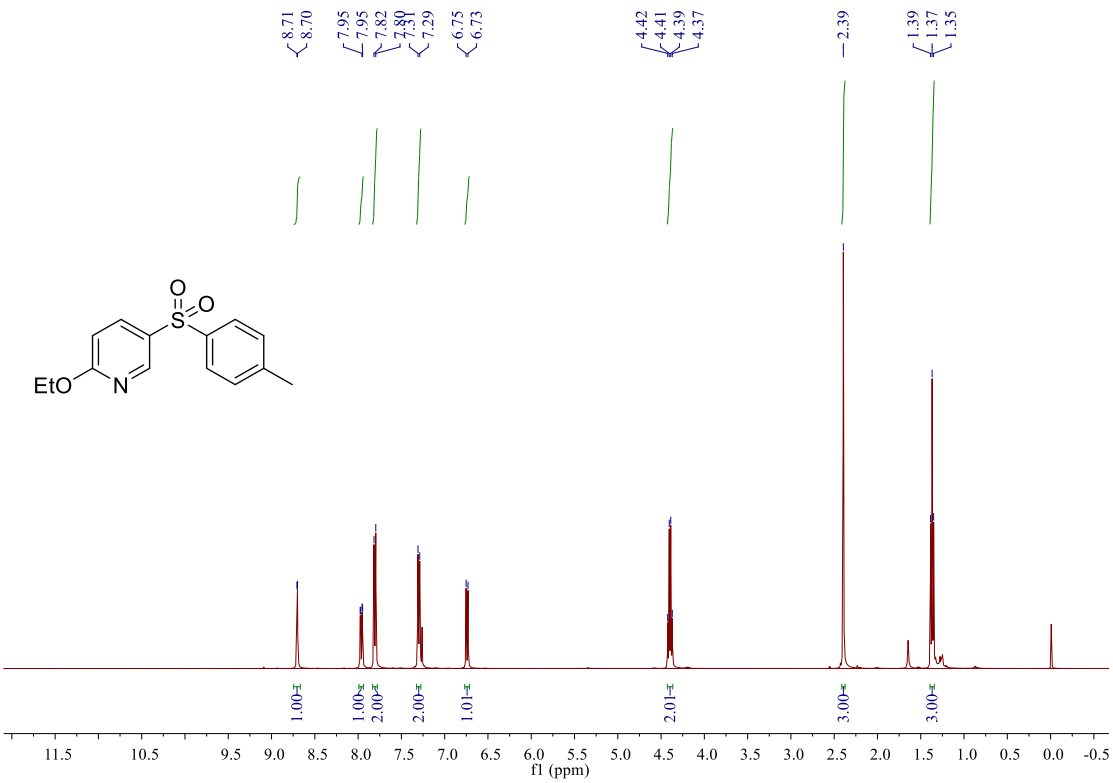

Figure **S17**. The ^{1}H-NMR spectrum of 3aj.

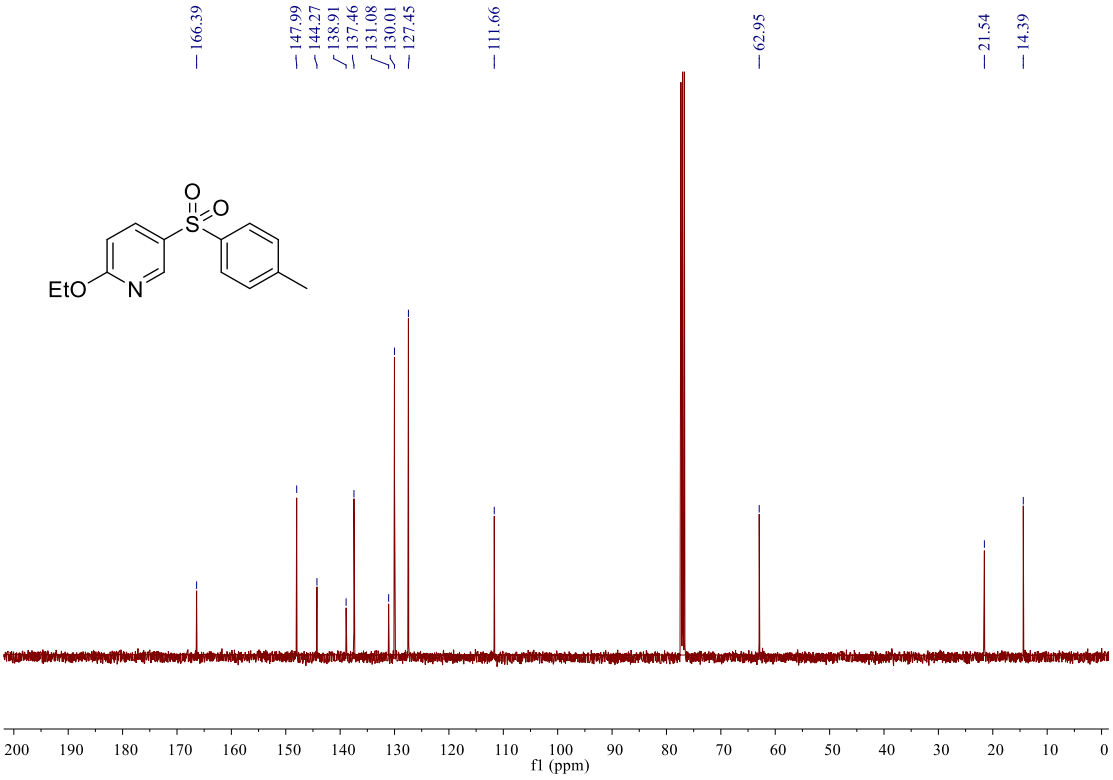

Figure **S18**. The ^{13}C-NMR spectrum of 3aj.

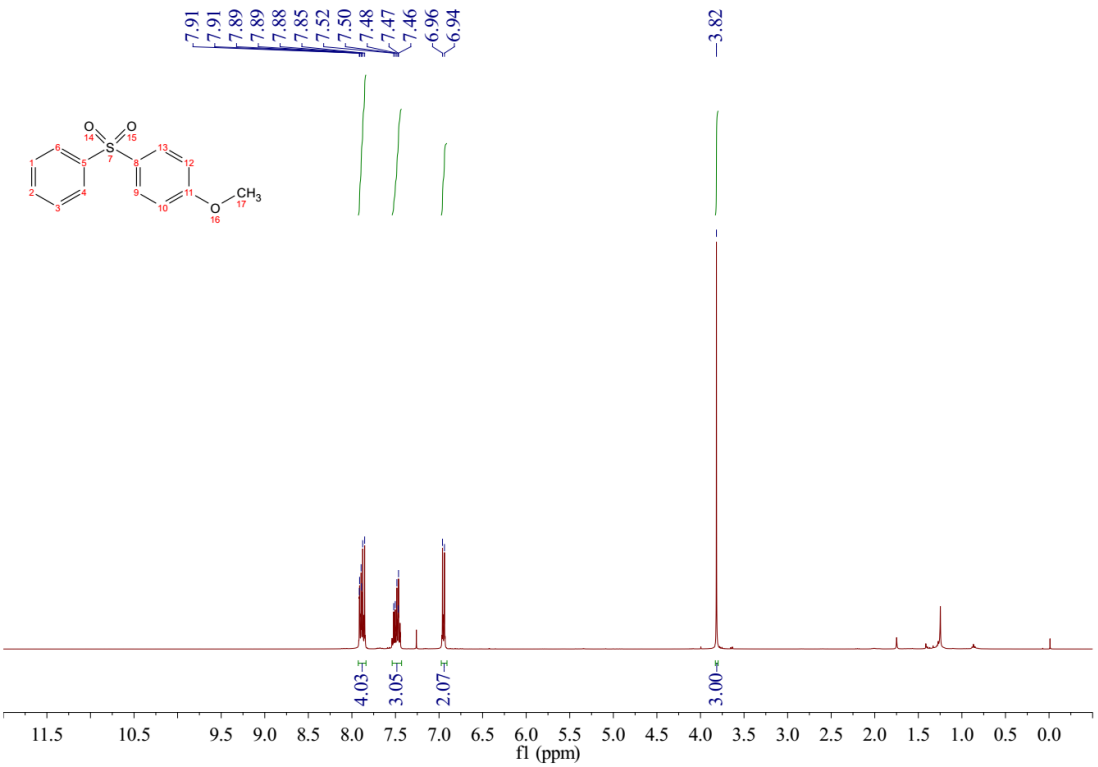

Figure **S19**. The ^{1}H-NMR spectrum of 3ba.

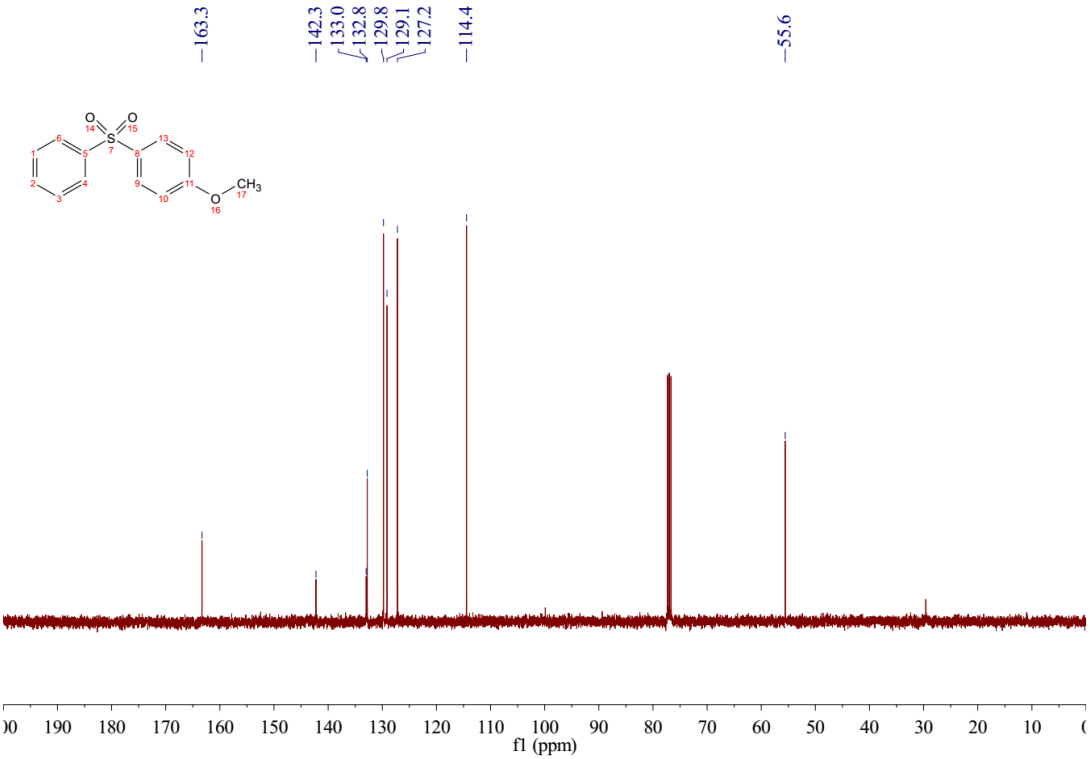

Figure **S20**. The ^{13}C-NMR spectrum of 3ba.

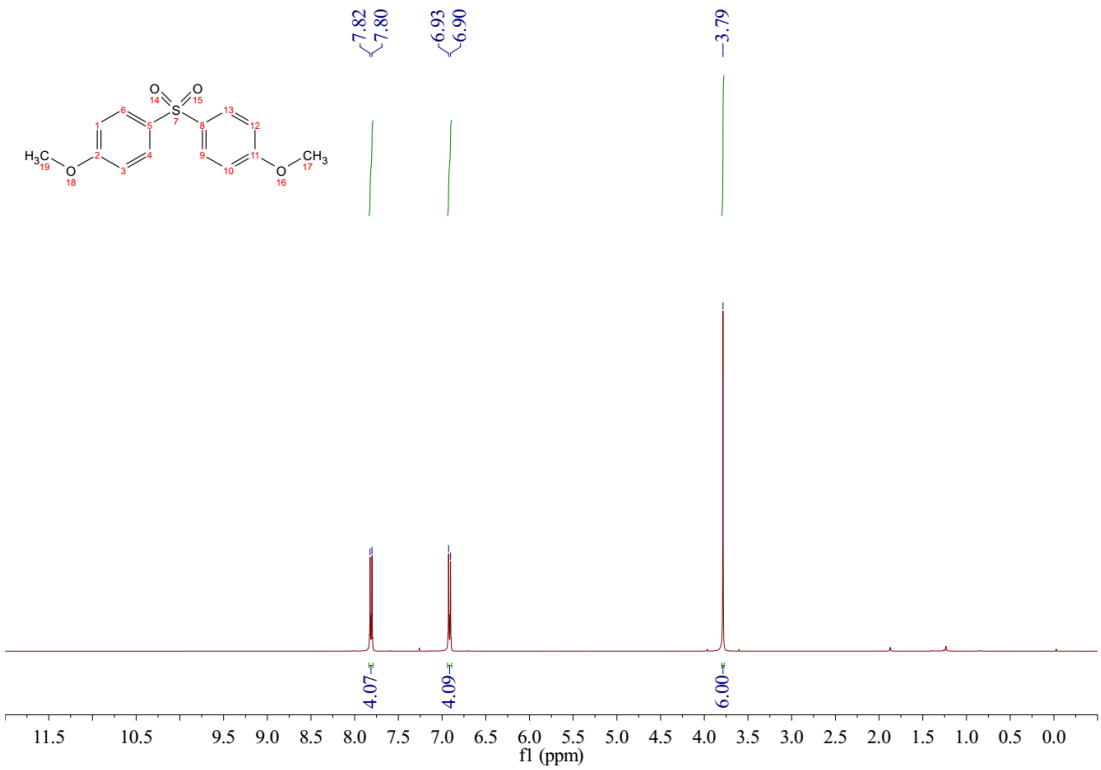

Figure **S21**. The ^{1}H-NMR spectrum of 3ca.

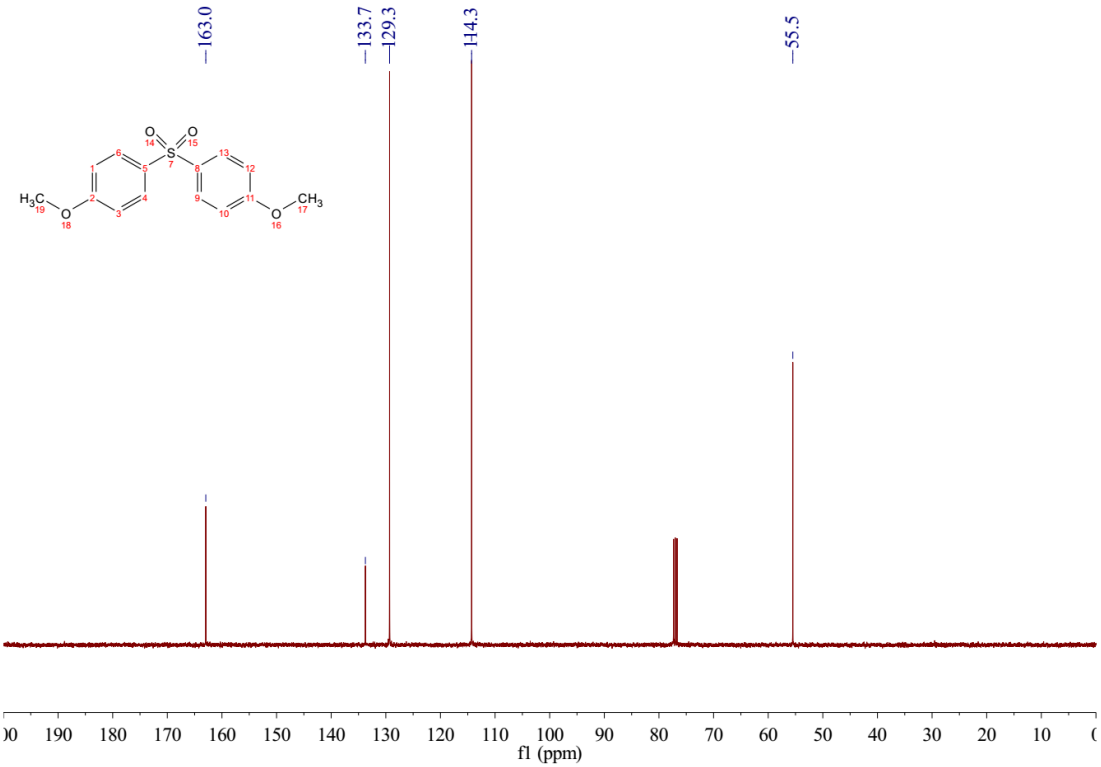

Figure **S22**. The ^{13}C-NMR spectrum of 3ca.

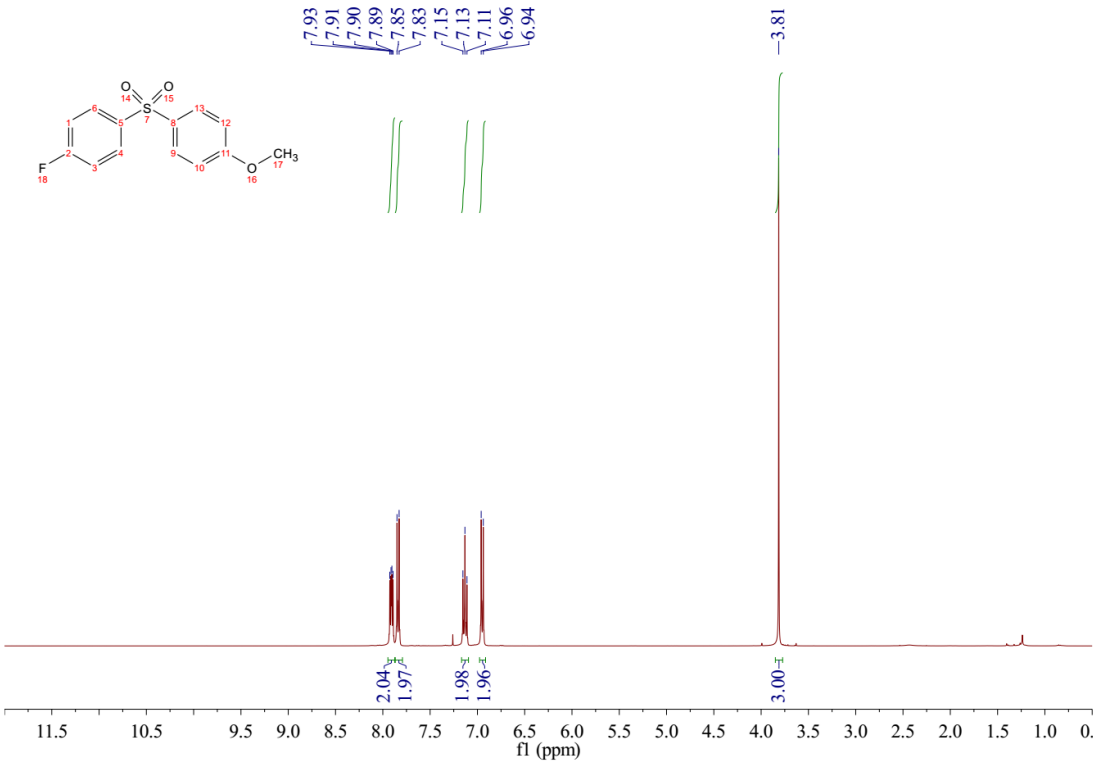

Figure **S23**. The ^{1}H-NMR spectrum of 3da.

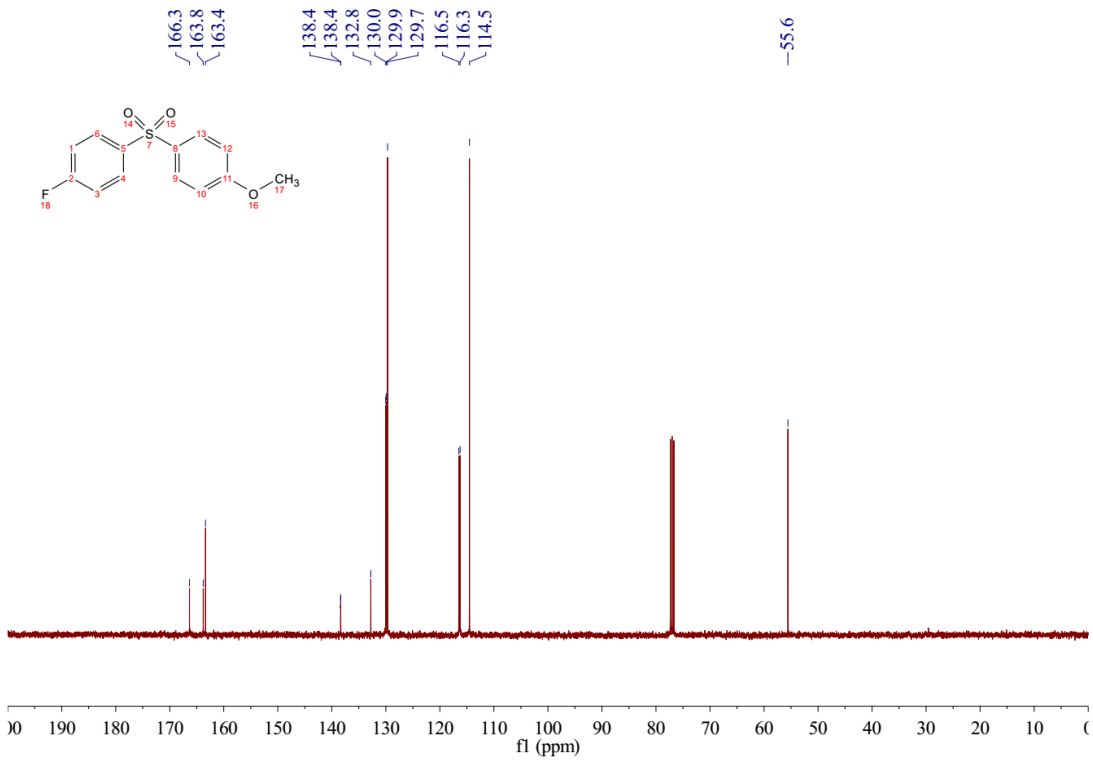

Figure **S24**. The ^{13}C-NMR spectrum of 3da.

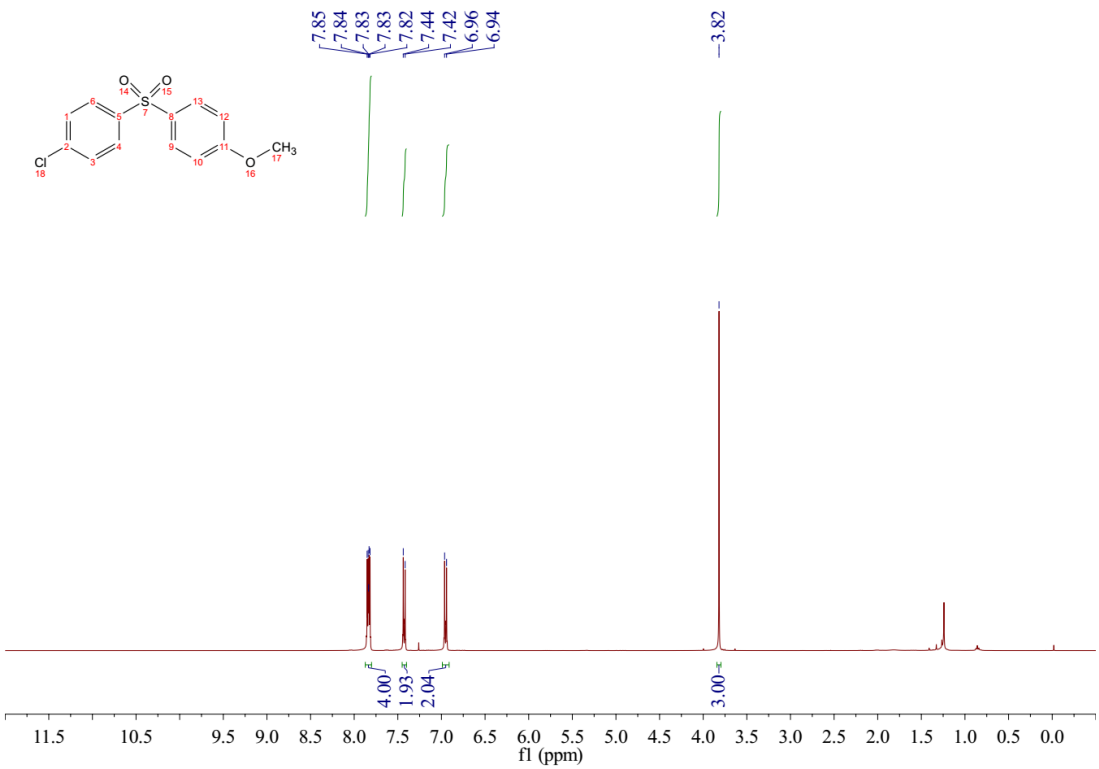

Figure **S25**. The ^{1}H-NMR spectrum of 3ea.

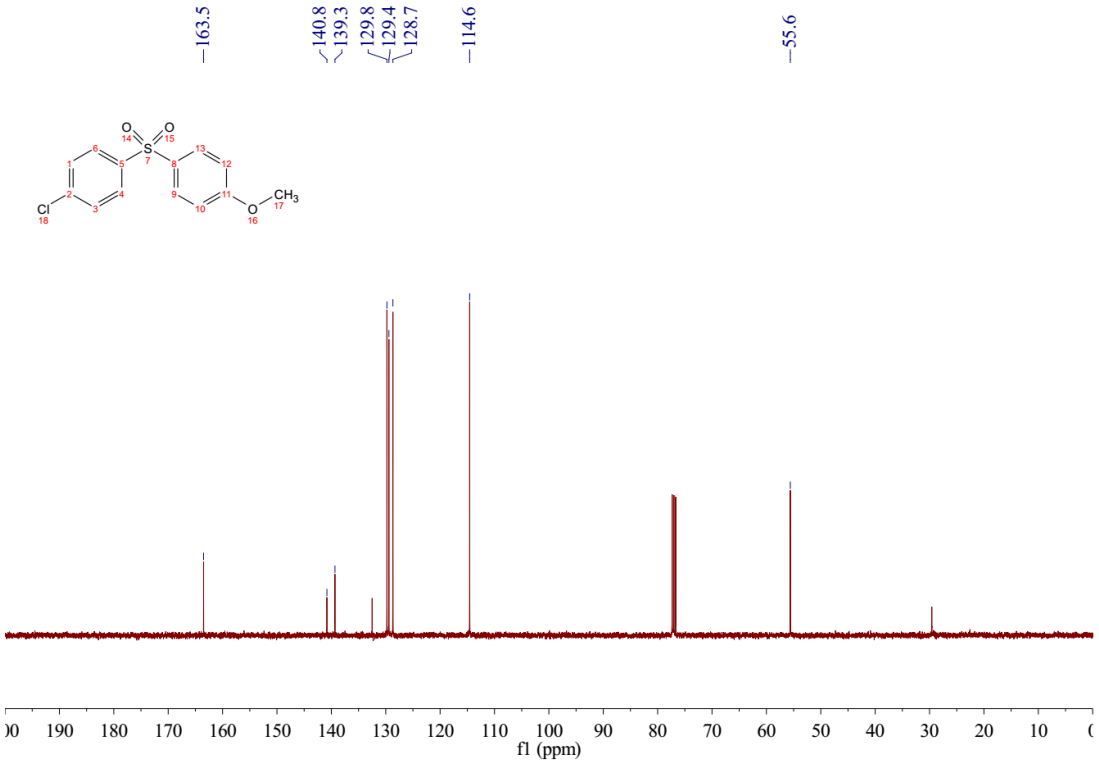

Figure **S26**. The ^{13}C-NMR spectrum of 3ea.

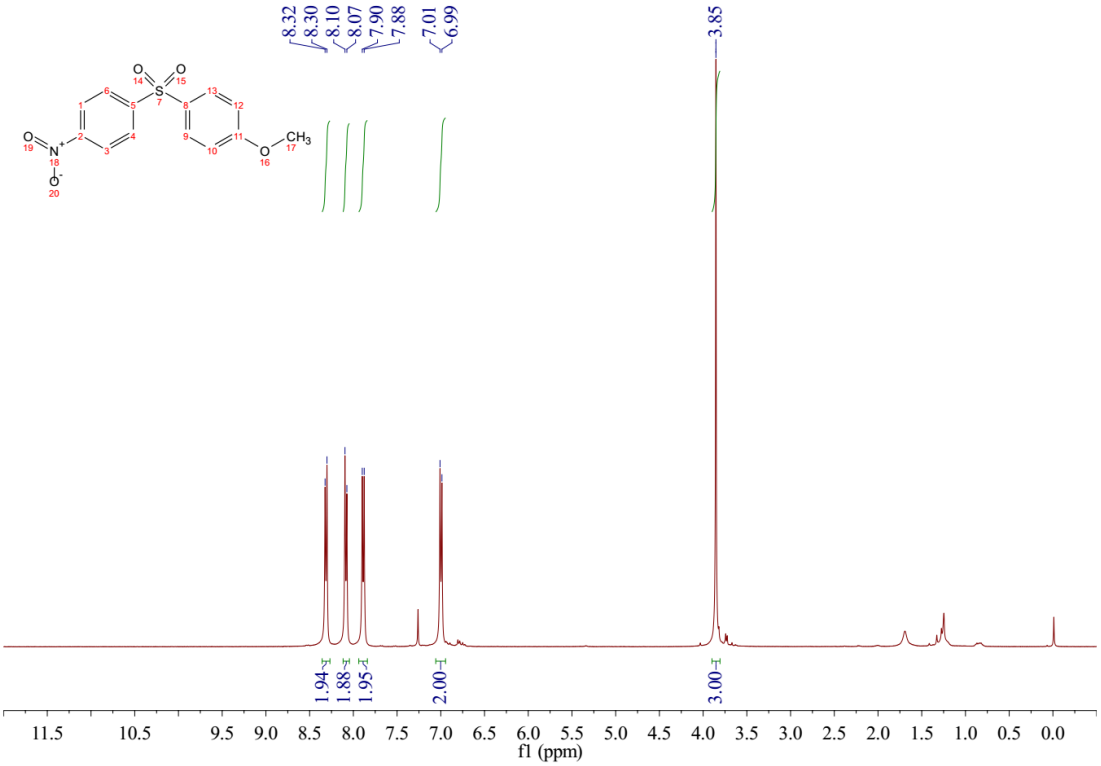

Figure **S27**. The ^{1}H-NMR spectrum of 3fa.

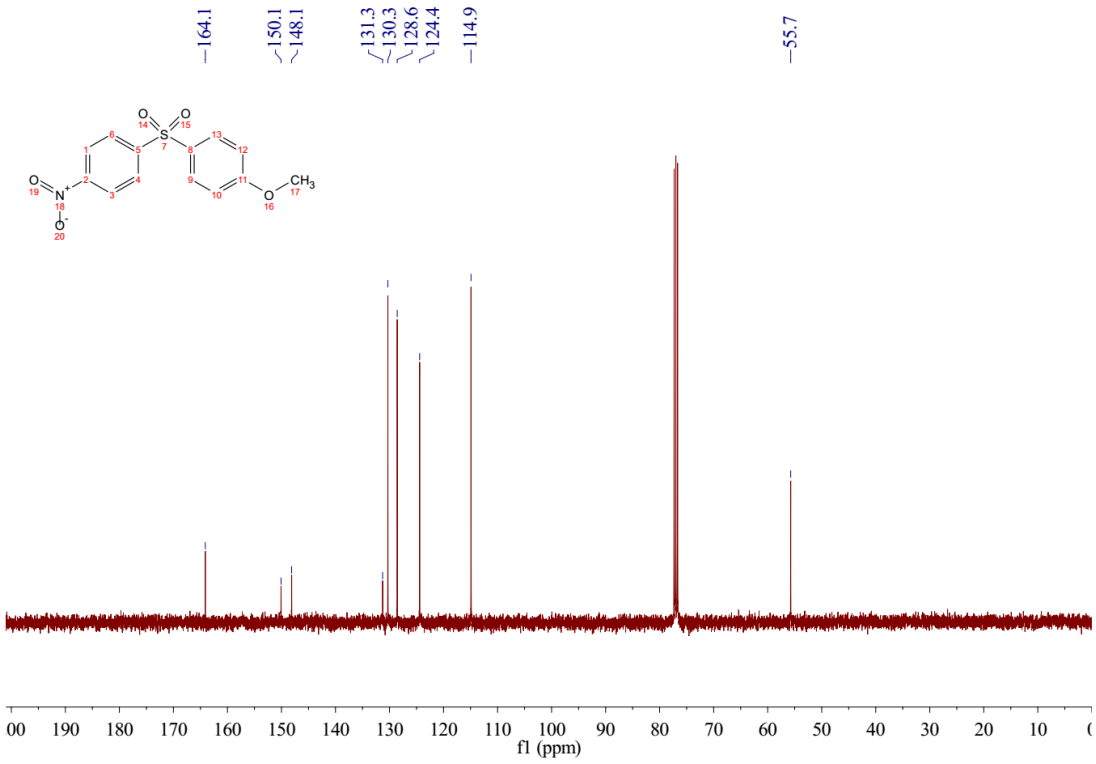

Figure **S28**. The ^{13}C-NMR spectrum of 3fa.

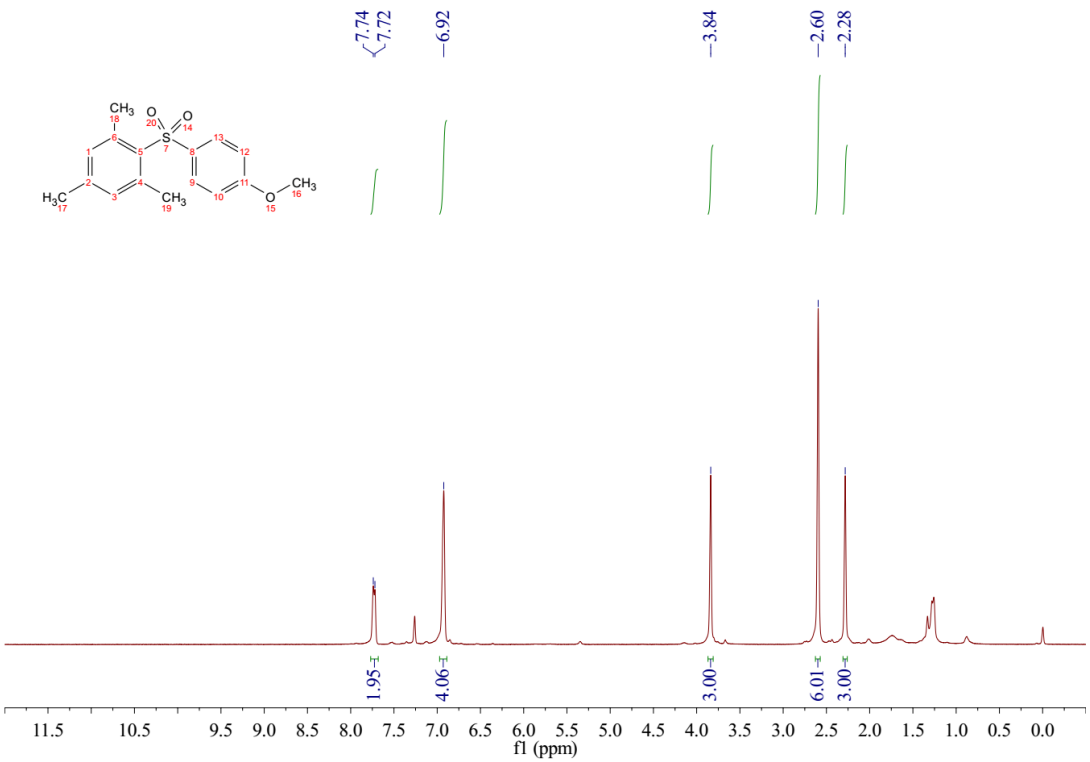

Figure **S29**. The ^{1}H-NMR spectrum of 3ga.

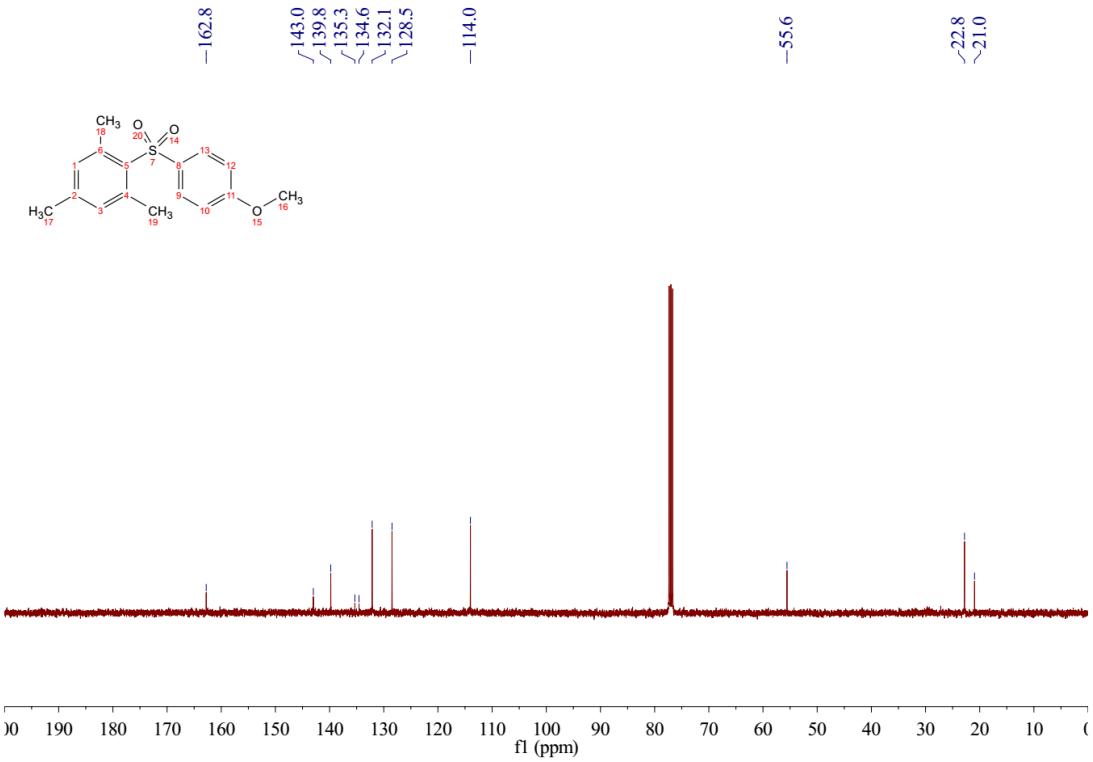

Figure **S30**. The ^{13}C-NMR spectrum of 3ga.

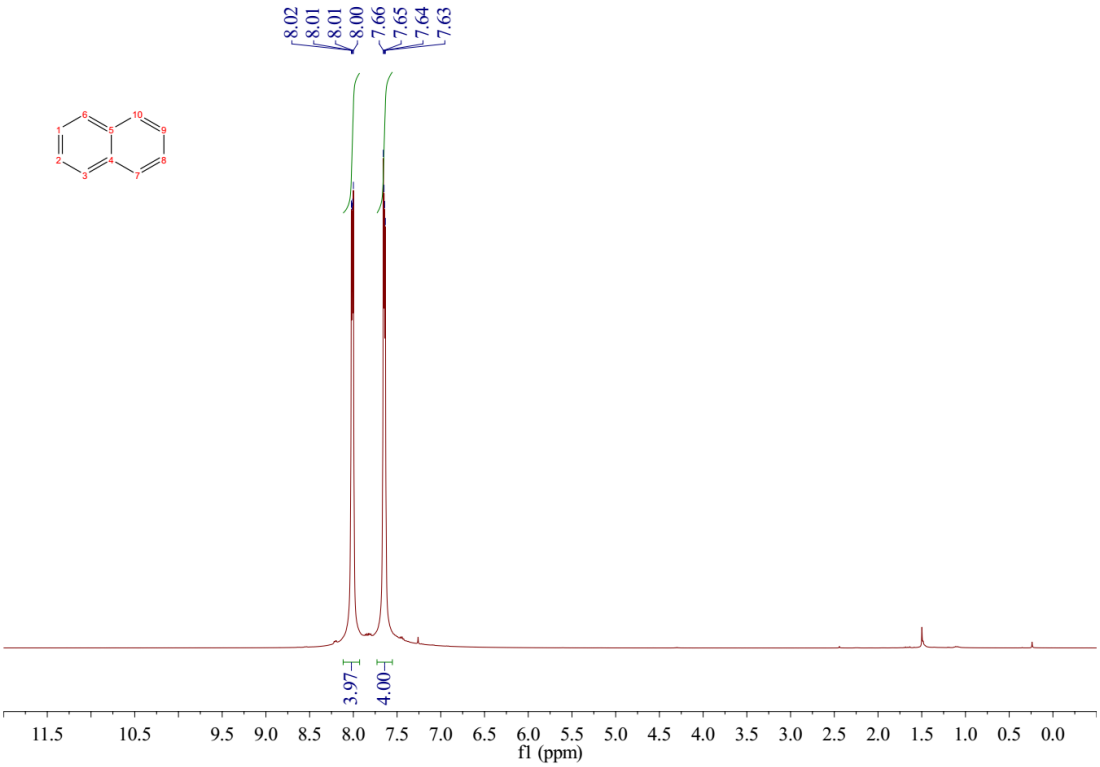

Figure **S31**. The ^{1}H-NMR spectrum of naphthalene.

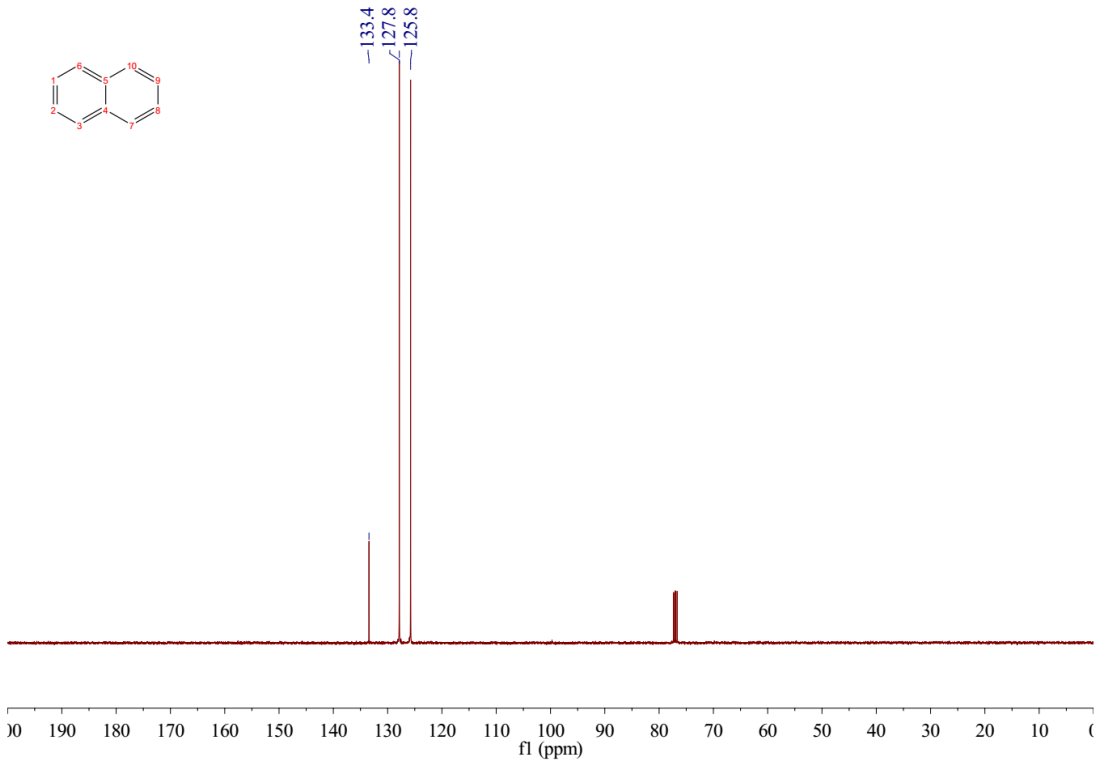

Figure **S32**. The ^{13}C-NMR spectrum of naphthalene.