Supporting Information for

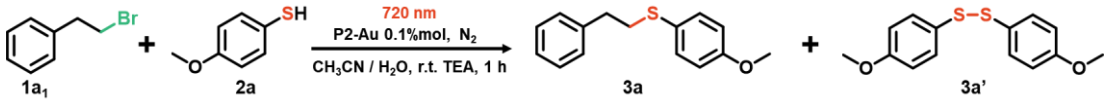
Near-infrared light-driven high-performance photocatalytic cross-coupling of non-active alkyl halides and thiols

1. Physical measurements

Powder X-ray diffraction (PXRD) was performed on a Rigaku Ultima IV diffractometer with experiment parameters of 40 kV, 30 mA using Cu-Kα radiation (λ = 1.5418 Å) with a scan speed of 0.5 °/min and a step size of 0.02°. The morphology and elemental distribution were studied by a transmission electron microscope (TEM, JEM-2100F) equipped with a focused ion beam electron beam microscope (FEI Helios Nanolab G3 CX). Gas Chromatography Mass Spectrometer (GC-MS, Agilent 7890B) was used to detect the mass-to-charge ratio information of the products. Liquid-phase ^{1}H and ^{13}C NMR spectra were collected on a Bruker Biospin Advance spectrometer (400 MHz). UV-vis diffuse reflection spectra were obtained on Agilent Cary 4000 with $BaSO_4$ as the reference. Ultraviolet photoelectron spectroscopy (UPS) spectra were collected on a Thermo ESCALAB 250XI system. The experiments of femtosecond transient absorption (fs-TA) were achieved on the Ti/sapphire laser system (Coherent, Astrella-Tunable-F-1k) and the fs-TA system (Ultrafast Systems, Helios Fire). The repetition rate of the amplifier is 1 KHz. The output power of 800 nm, which has a pulse wide of 84 fs, is about 7.04 W. Mott-Schottky curves were tested on an electrochemical workstation. Electron paramagnetic resonance (EPR) was performed using a Bruker A300 with DMPO as the capture agent at a concentration of 100 mM in a dosage of 500 μL, an excitation light of 808 nm, a nitrogen atmosphere, and an illumination time of 10 min. Finite-difference time domain (FDTD) was set to both the x, y, and z directions as perfectly matched layer conditions. In addition, all the simulation regions were divided into 0.5 nm meshes. Importantly, a total field scattered field plane wave with a wavelength of 780 nm is used as an excitation light source incident perpendicularly to the nanorods along the z-direction.

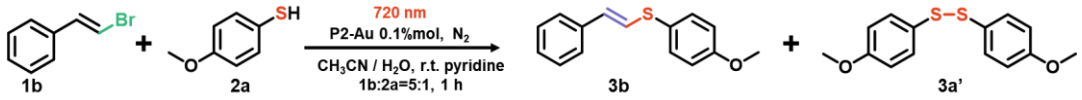
2. General catalytic procedure

2.1 Procedure A: Photocatalytic cross-coupling reaction of phenethyl bromide with *p*-methoxythiophenol



The as prepared **P2-Au** dispersion was introduced into a 15 mL photoreactor tube with a magnetic stirring bar. The tube was then charged with 0.1 mmol of *p*-methoxybenzenethiol (1 eq.), 0.5 mmol of phenylethyl bromide (5 eq.), and 0.5 mmol of triethylamine (TEA, 5 eq.). The tube was sealed and thoroughly degassed with N_2 for 15 min. The solution was then irradiated with a 6 W red-light reactor (720 nm) with a cooling cycle at 25 °C for 1 h. After the reaction, the remaining crude product was isolated by thin chromatography separation plate (n-hexane) to yield the desired product.

2.2 Procedure B: Photocatalytic cross-coupling reaction of styryl bromide with p-methoxythiophenol

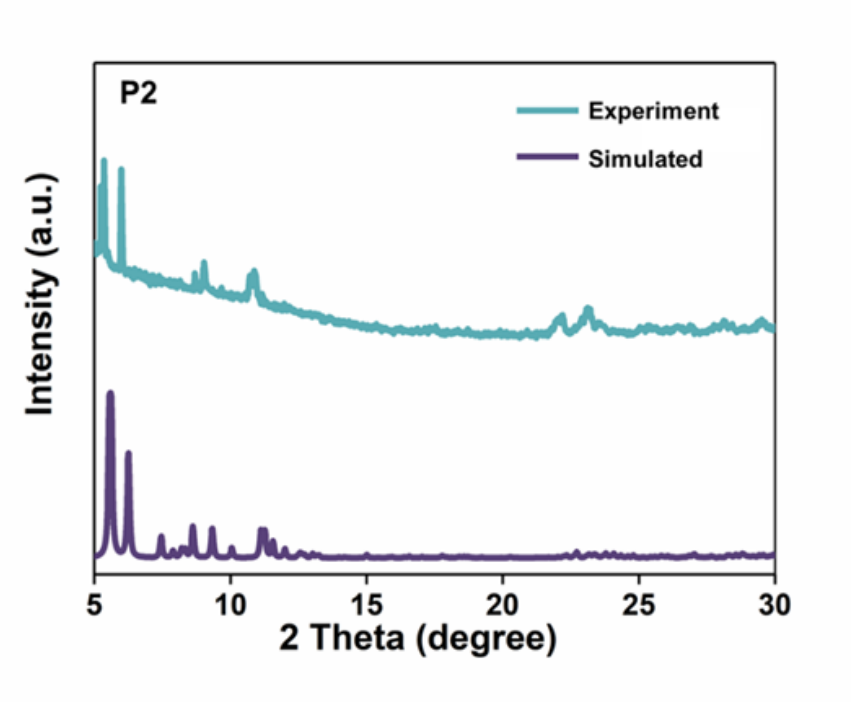


The as prepared **P2-Au** dispersion was transferred into a 15 mL photoreactor tube with a magnetic stirring bar. Deionized water was added until the total volume of the reaction solution reached 3 mL. The tube was then charged with 0.1 mmol of *p*-methoxybenzenethiol (1 eq.), 0.5 mmol of phenylethyl bromide (5 eq.), and 0.5 mmol of TEA (5 eq.). The tube was sealed and strictly degassed with N_2 for 15 min. The solution was then irradiated with a 6 W red-light reactor (720 nm) with a cooling cycle for 1 h at 25 °C. Following the reaction, the remaining crude product was separated via a thin chromatography separation plate (hexane) to obtain the desired product.

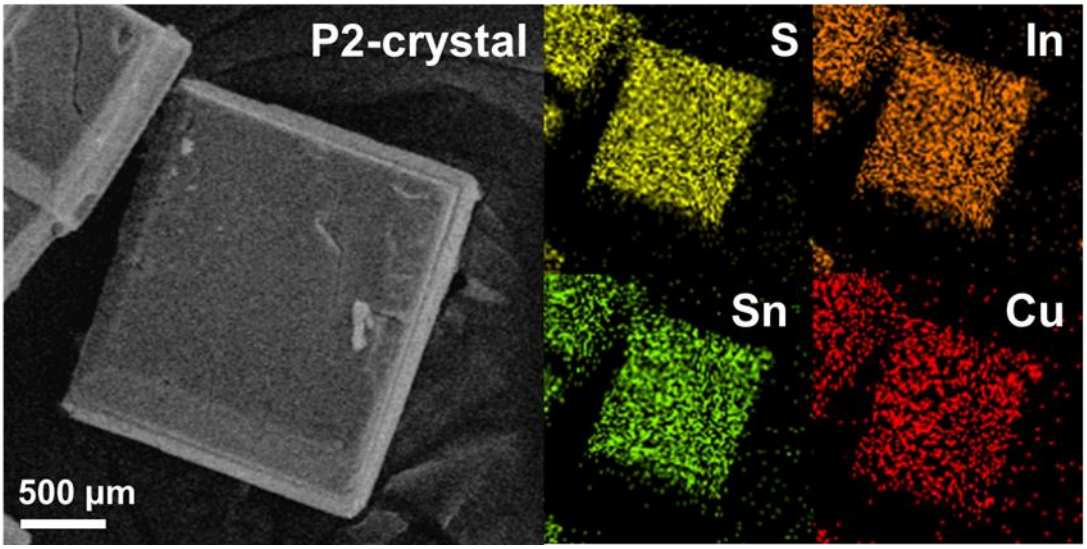
2.3 Procedure C: photocatalytic cross-coupling reaction of phenylethynyl bromide with p-methoxythiophenol

The prepared **P2-Au** dispersion was transferred to a 15 mL photoreactor tube equipped with a magnetic stirring bar. Deionized water was added until the total volume of the reaction solution reached 3 mL. Then 0.1 mmol of *p*-methoxybenzenethiol (1 eq.), 0.1 mmol of phenylnyl bromide (1 eq.), and 0.5 mmol of pyridine (5 eq.) were added to the tube. The tube was sealed and strictly degassed with N_2 for 15 min. The solution was then irradiated with 6 W red-light reactor (720 nm) with a cooling cycle at 25°C for 1 h. After the reaction, the remaining crude product was separated by thin chromatography separation plate (n-hexane) to give the desired product.

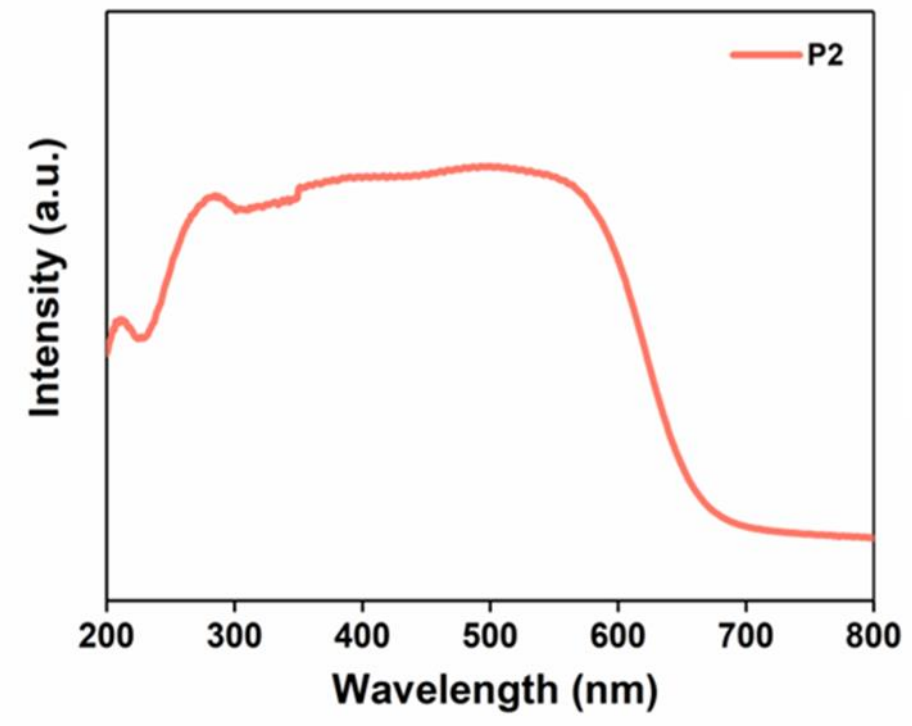
3. Complementary characterization



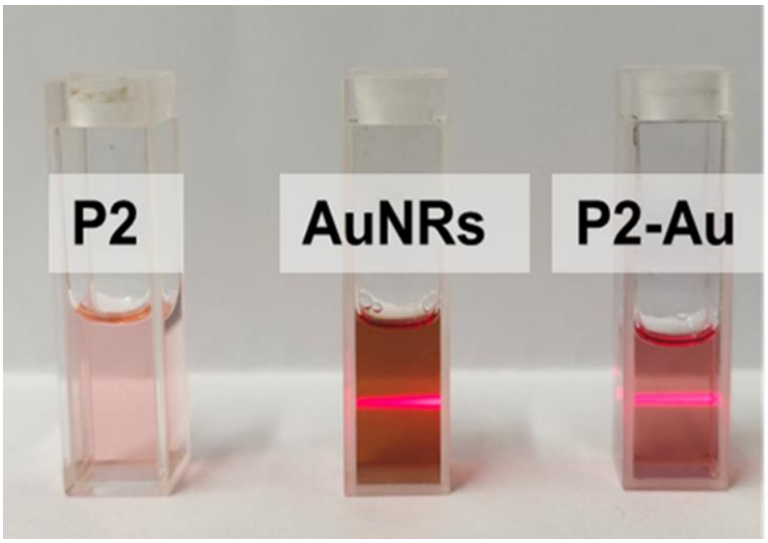
Supplementary Figure 1. Experimental and simulated PXRD patterns of **P2** crystals.



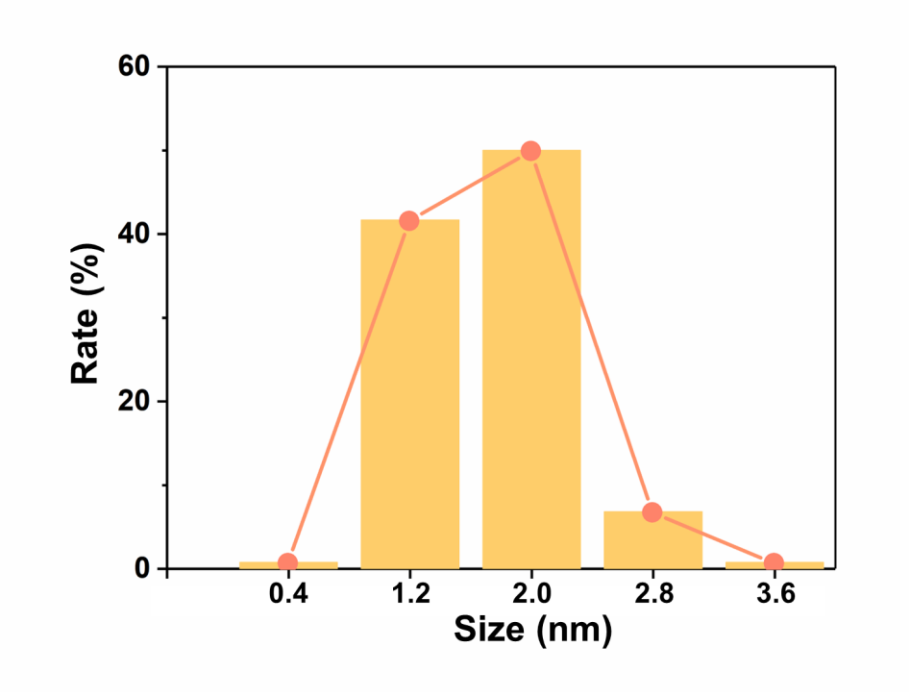
Supplementary Figure 2. Scanning electron microscope (SEM) images and mapping diagrams of **P2** crystals.



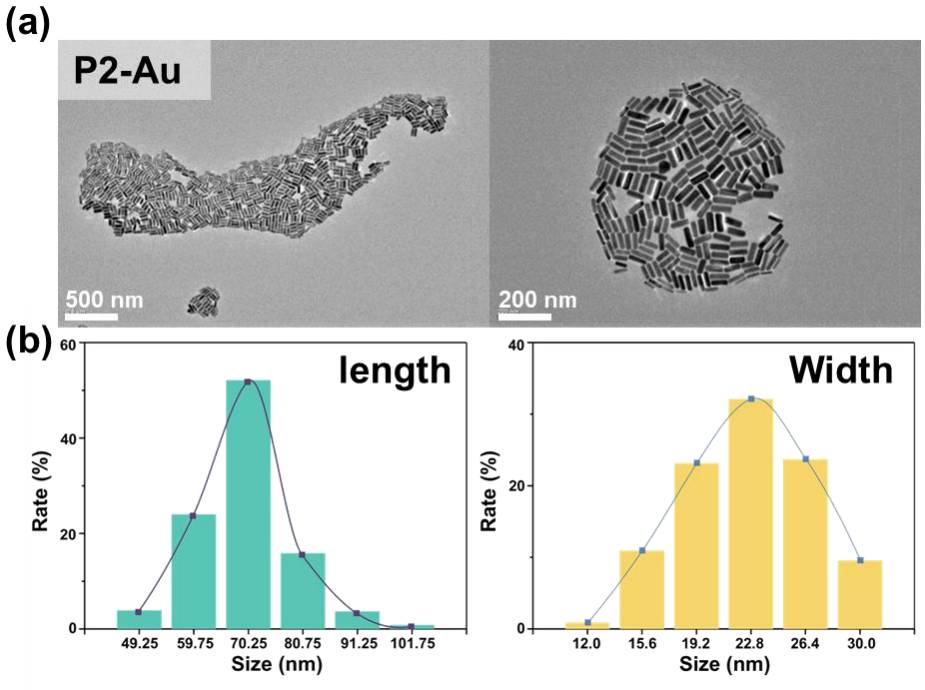
Supplementary Figure 3. Solid-state UV diffuse reflectance spectrum of **P2** crystals.



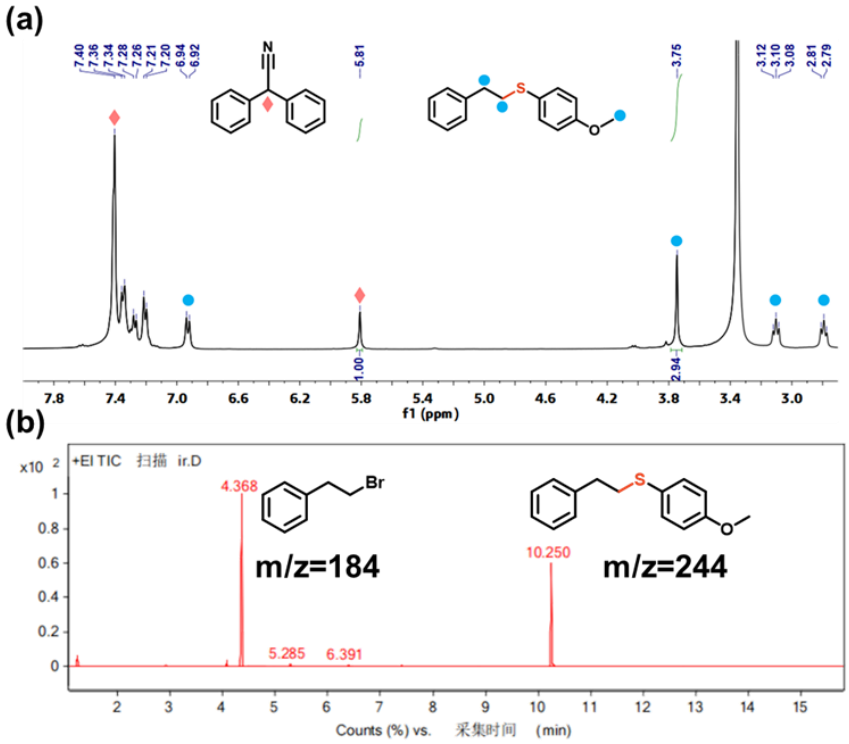
Supplementary Figure 4. Optical images of **P2**, **AuNRs**, and **P2-Au** dispersions.



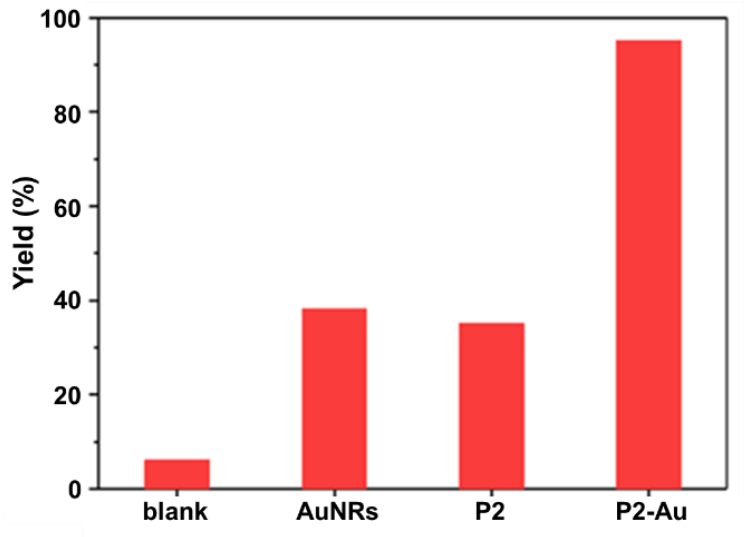
Supplementary Figure 5. Statistics of the size of dispersed **P2** clusters.



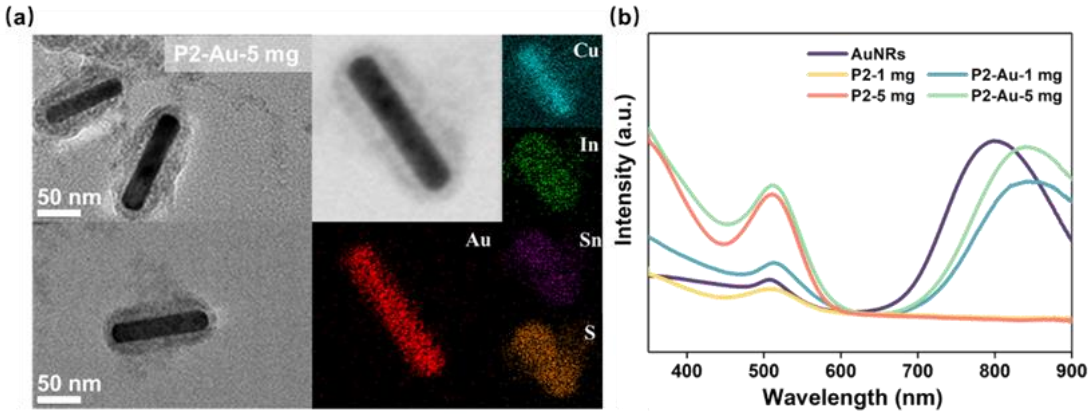
Supplementary Figure 6. (a) TEM images of **P2-Au**, (b) Statistics of the length of **P2-Au**, (c) Statistics of the width of **P2-Au**.



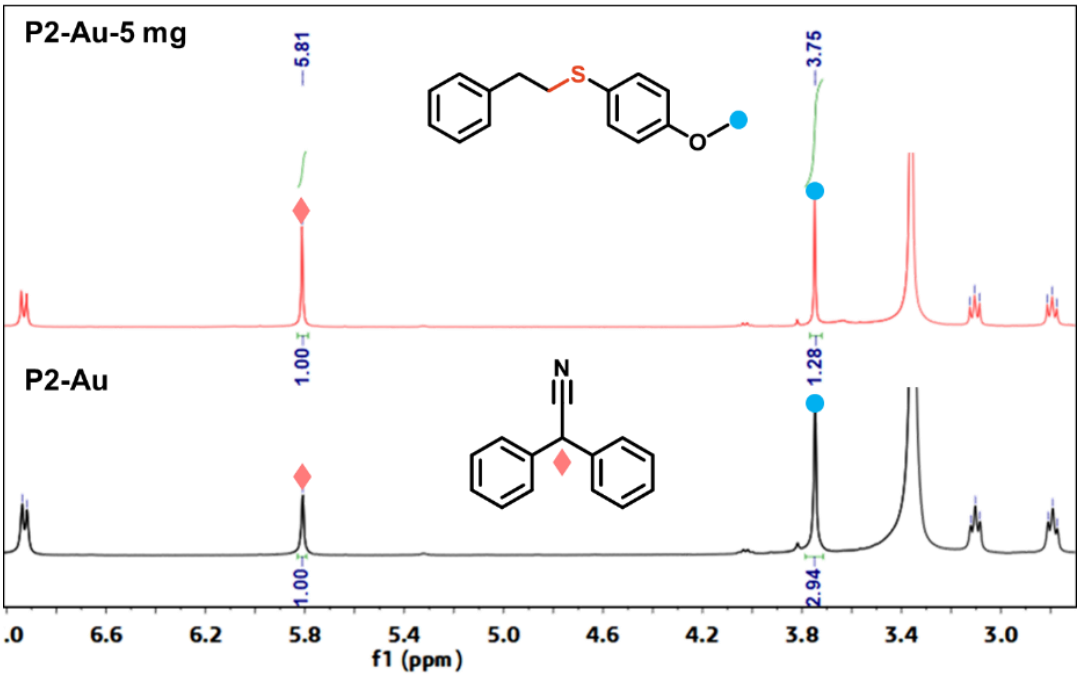
Supplementary Figure 7. (a) ^{1}H NMR calibration of product 3a using 0.1 mmol diphenylacetonitrile as internal standard[1], (b) GC-MS results for 3a.



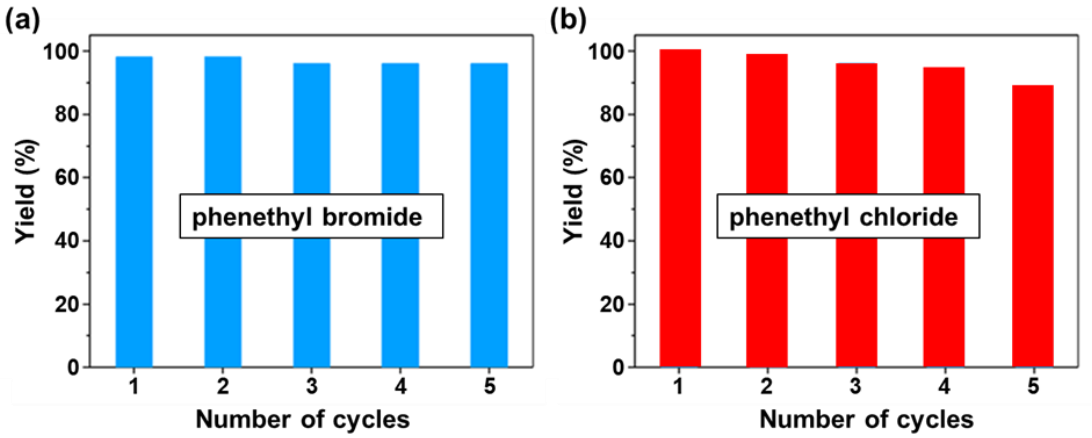
Supplementary Figure 8. Comparison of photocatalytic yields of blank (no catalyst), **AuNRs**, **P2**, and **P2-Au**.



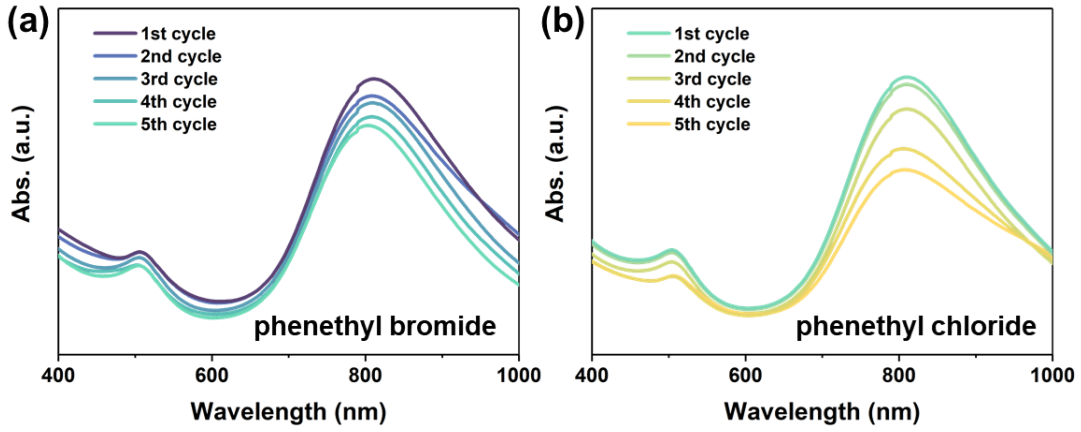
Supplementary Figure 9. (a) Transmission electron micrograph and elemental distribution of **P2-Au-5**, (b) UV-Vis-NIR absorption spectra of the related materials.



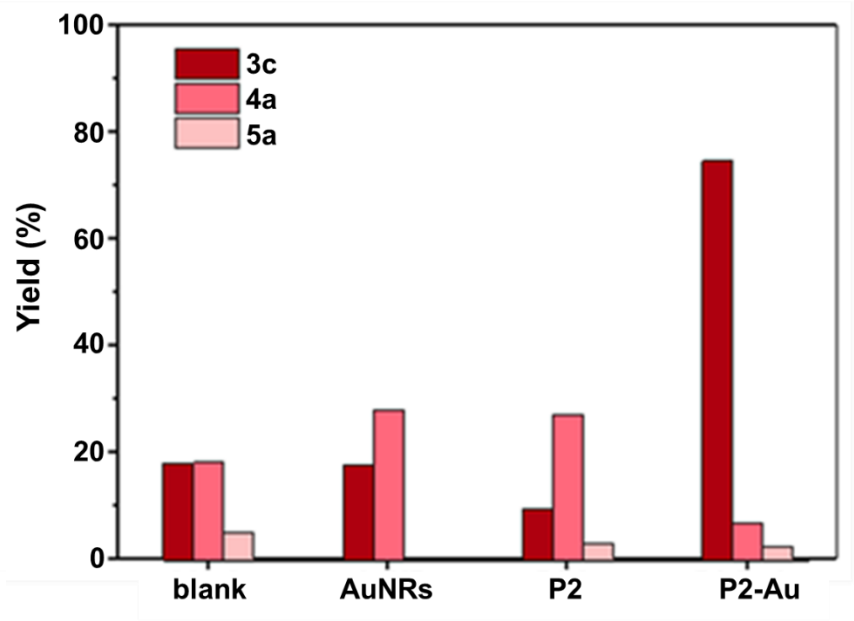
Supplementary Figure 10. ^{1}H NMR quantitative analysis of coupling products under catalyzation by **P2-Au** and **P2-Au-5**, respectively (diphenylacetonitrile as internal standard).



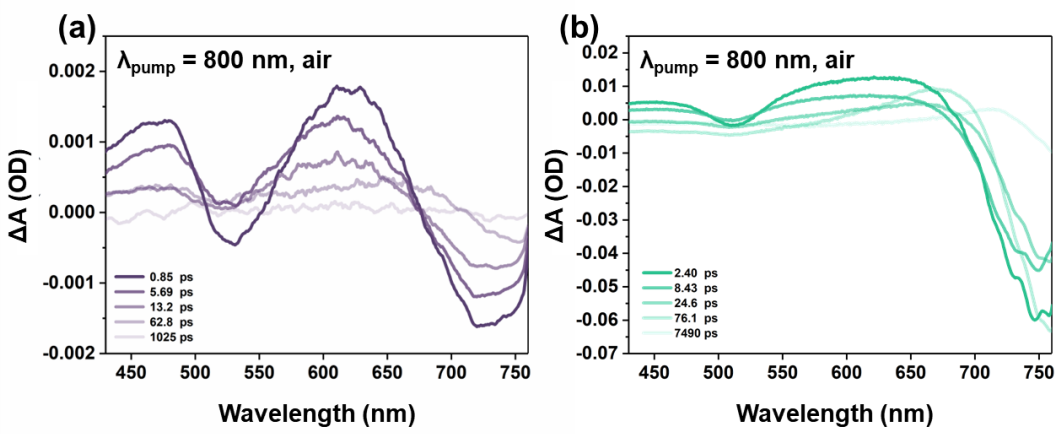
Supplementary Figure 11. Cyclic stability of the **P2-Au** photocatalyzed cross-coupling reaction of *p*-methoxythiophenol with phenethyl bromide (a) and phenylethyl chloride (b), respectively.



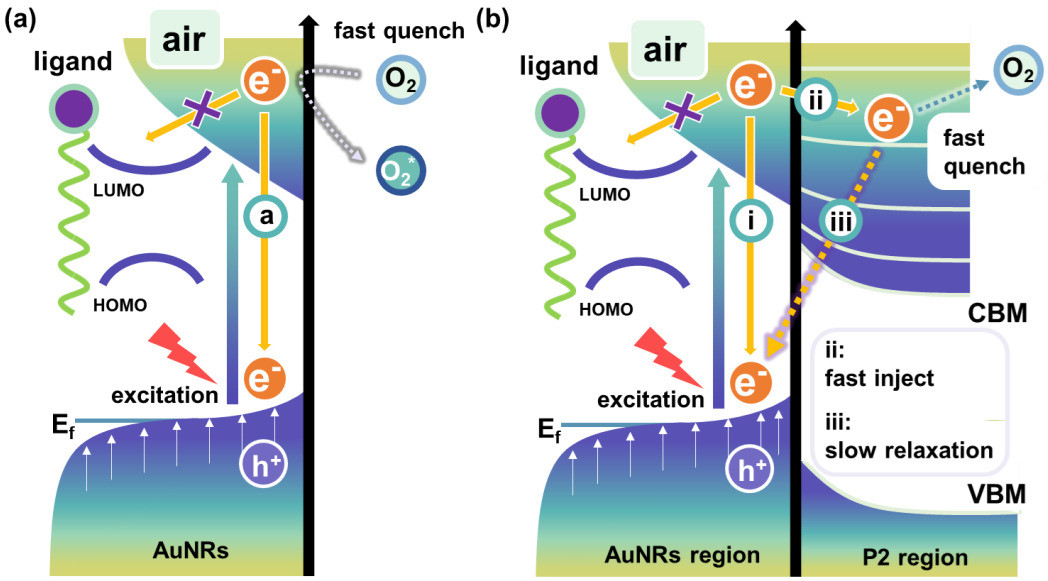
Supplementary Figure 12. UV-Vis-NIR absorption spectra of **P2-Au** corresponding to different number of cycles when the substrate is phenylethyl bromide (a) or phenylethyl chloride (b).



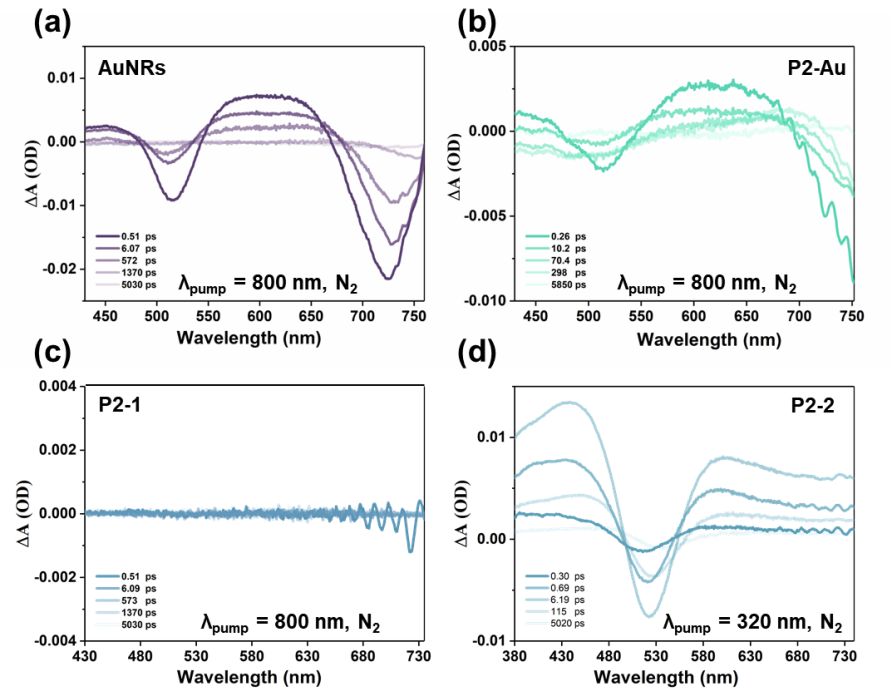
Supplementary Figure 13. Comparison of blank (no catalyst), **AuNRs**, **P2**, and **P2-Au** photocatalyzed cross-coupling reactions of phenylethynyl bromide with *p*-methoxythiophenol.



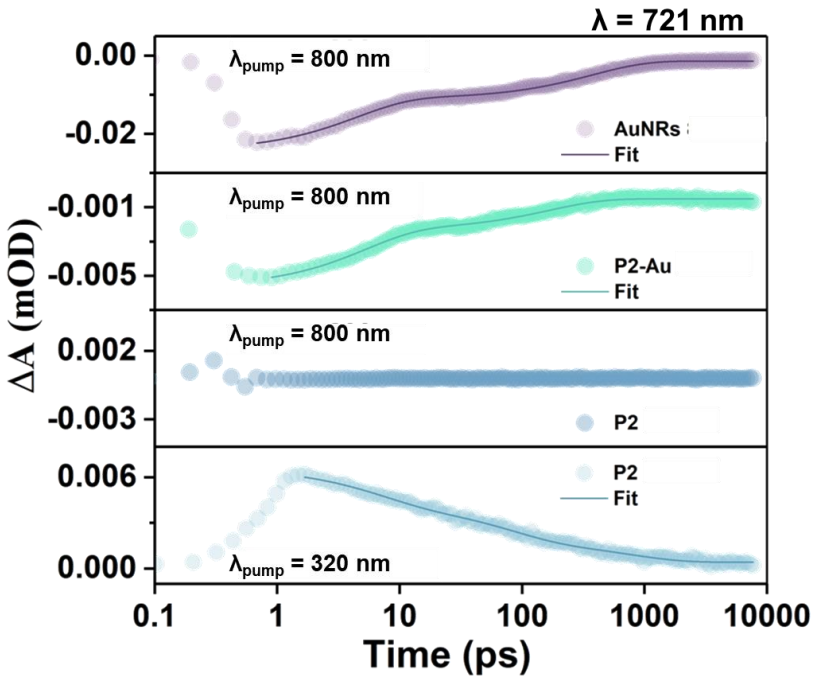
Supplementary Figure 14. Time-dependent transient spectra of **AuNRs** (a), **P2-Au** (b) pumped at 800 nm in air atmosphere.



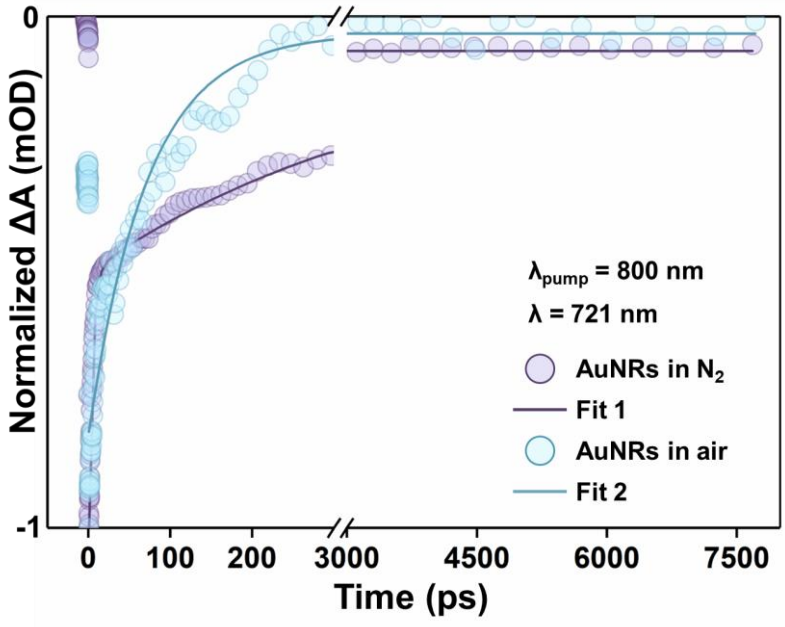
Supplementary Figure 15. Proposed electron transfer paths of (a) **AuNRs** and (b) **P2-Au** in air atmosphere.



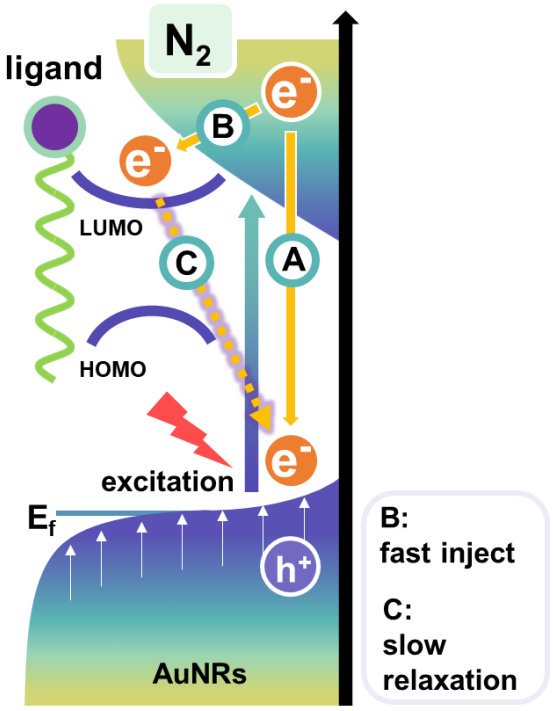
Supplementary Figure 16. Time-dependent transient spectra of **AuNRs** (a), **P2-Au** (b), and **P2** (c) pumped at 800 nm, and (d) **P2** pumped at 320 nm in nitrogen atmosphere.



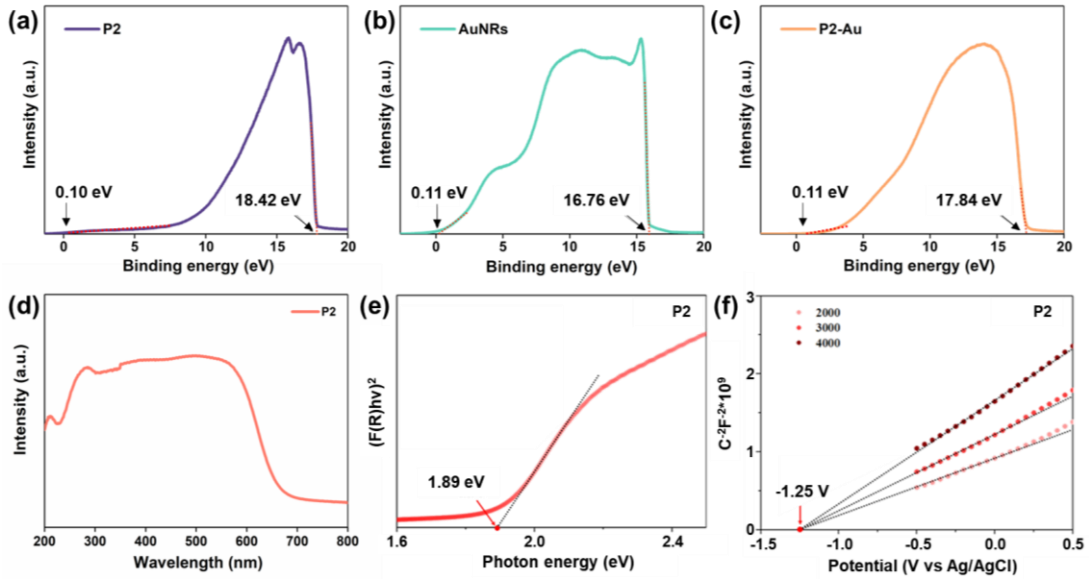
Supplementary Figure 17. Kinetic decay curves at λ = 721 nm for **AuNRs**, **P2-Au**, **P2** (λ_{pump} = 800 nm), and **P2** (λ_{pump} = 320 nm) in nitrogen atmosphere.



Supplementary Figure 18. Kinetic decay curves at λ = 721 nm for **AuNRs** in nitrogen and air atmosphere (λ_{pump} = 800 nm).



Supplementary Figure 19. Proposed electron transfer paths of **AuNRs** in nitrogen atmosphere.



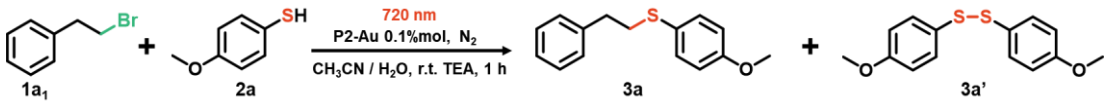
Supplementary Figure 20. UPS results of **P2** (a), **AuNRs** (b), and **P2-Au** (c). Solid UV-vis diffuse reflectance of **P2** (d) and that in energy mode (e), and Mott-Schottky curve of **P2** (f).

The relevant data were calculated from Figure S10 and equation (1)

$$\Phi = hv - (E_{cut\,off} - E_F) \quad (1)$$

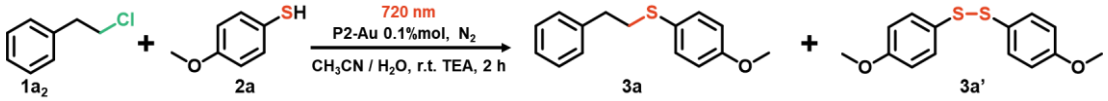
where Φ is work function, $E_{cut\,off}$ is energy of electron cut-off edge, and E_F is energy of Fermi edge. The test conditions are: vacuum is 3×10^{-8} Pa, the light source used is the He resonance source (21.22 eV), bias voltage: -5 eV. The secondary electron cutoffs of **P2**, **AuNRs**, and **P2-Au** were determined to be 18.42, 16.76, and 17.84 eV, respectively. Φ were calculated to be 2.80 eV (**P2**), 4.57 eV (**AuNRs**), and 3.38 eV (**P2-Au**), respectively. From the Mott Schottky curve, the flat band potential of **P2** is calculated to be -1.25 V vs Ag/AgCl. The positive slope observed in the Mott-Schottky curve for **P2** indicates that **P2** is an n-type semiconductor. For n-type semiconductors, the flat-band potential is deemed to be more positive about 0.1 V that its conduction band potentials. Consequently, the conduction band bottom potential of **P2** is estimated to be -1.35 V vs Ag/AgCl (-1.15 V vs NHE). Upon combining **P2** with **AuNRs**, the Fermi level aligns, causing a downward shift in the **P2** energy band and resulting in the formation of a Mott-Schottky barrier. The band gap of **P2**, determined using the Tauc plot formula, is found to be 1.89 eV. Considering the conduction band potential, it can be inferred that the valence band top potential of **P2** is 0.74 V.

Supplementary Table 1. Detailed results of photocatalytic cross-coupling of phenethyl bromide with *p*-methoxythiophenol.



Entry	Deviation	Con.	Sel. (3a)	Sel. (3a')
1	none	99%	99%	n.d.
2	**AuNRs** as PC	40%	95%	trace
3	**P2** as PC	39%	90%	trace
4	without PC	trace	trace	trace
5	without base	trace	trace	trace
6	r.t. without light	trace	trace	trace
7	50°C, without light	32%	n.d.	99%
8	1a:2a = 1:1	99%	trace	99%
9	pyridine instead of TEA	8%	99%	n.d.
10	piperidine instead of TEA	99%	99%	n.d.
11	DBU instead of TEA	99%	99%	n.d.
12	CH_3CN:H_2O (2:3)	99%	8%	91%
13	visible light (510 nm)	99%	86%	14%
14	2.0 eq. DDQ	n.d.	n.d.	n.d.
15	2.0 eq. TEMPO	n.d.	n.d.	n.d.

Supplementary Table 2. Detailed results of photocatalytic cross-coupling of phenylethyl chloride with *p*-methoxythiophenol.



Entry	Deviation	Con.	Sel. (3a)	Sel. (3a')
1	none	99%	99%	n.d.
2	**AuNRs** as PC	14%	99%	n.d.
3	**P2** as PC	8%	99%	n.d.
4	without PC	trace	n.d.	trace
5	without base	trace	n.d.	trace
6	r.t., without light	trace	n.d.	trace
7	50°C, without light	n.d.	n.d.	n.d.
8	1a:2a = 1:1	67%	48%	52%
9	pyridine instead of TEA	99%	99%	trace
10	piperidine instead of TEA	19%	99%	trace
11	DBU instead of TEA	21%	trace	95%
12	CH_3CN:H_2O (2:3)	99%	trace	99%
13	visible light (510 nm)	99%	90%	10%
14	2.0 eq. DDQ	n.d.	n.d.	n.d.
15	2.0 eq. TEMPO	n.d.	n.d.	n.d.

Supplementary Table 3. Lifetime (τ_i) and amplitudes (A_i) of the transient absorption decays at 721 nm for **AuNRs**, **P2**, and **P2-Au** (λ_{pump} = 800 nm, air).

λ = 721 nm	A_1 **(%)**	τ_1 **(ps)**	A_2 **(%)**	τ_2 **(ps)**	A_3 **(%)**	τ_3 **(ps)**
AuNRs	100.00	71.29±3.58	——	——	——	——
P2-Au	62.52	5.33±0.54	37.48	>2244.49±243.16	——	——

Supplementary Table 4. Lifetime (τ_i) and amplitudes (A_i) of the transient absorption decays at 721 nm for **AuNRs**, **P2**, and **P2-Au** (λ_{pump} = 800 nm, N_2).

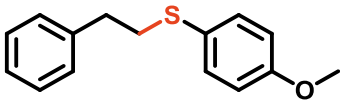
λ = 721 nm	A_1 **(%)**	τ_1 **(ps)**	A_2 **(%)**	τ_2 **(ps)**	A_3 **(%)**	τ_3 **(ps)**
AuNRs	57.93	4.43±0.09	42.07	>377.24±6.84	——	——
P2	——	——	——	——	——	——
P2-Au	62.36	4.35±0.10	17.12	175.46±27.75	20.52	>883.66±113.53

Supplementary Table 5. Lifetime (τ_i) and amplitudes (A_i) of the transient absorption decays at 721 nm for **P2** (λ_{pump} = 320 nm, N_2).

λ = 721 nm	A_1 **(%)**	τ_1 **(ps)**	A_2 **(%)**	τ_2 **(ps)**	A_3 **(%)**	τ_3 **(ps)**
P2	64.41	6.56±0.76	8.46	77.10±9.42	27.13	>754.22±107.29

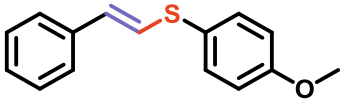
4. Characterization data for all organic compounds

(4-methoxyphenyl)(phenethyl)sulfane 3a or 4a



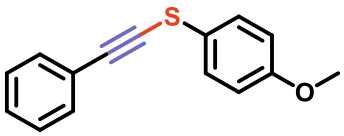
The compound was prepared according to the General procedure A. Yellow oil; R_f= 0.3 (hexane); yield 99% (3a or 4a). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 3H), 6.93 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.10 (t, J = 8.0 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.74, 140.55, 132.49, 128.98, 128.77, 126.67, 126.28, 115.47, 115.24, 55.63, 36.04，35.37. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}OS$: 244.09; Found: 244.35.

(4-methoxyphenyl)(styryl)sulfane 3b



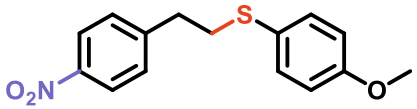
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 3H), 6.93 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.10 (t, J = 8.0 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d6) δ 133.16, 132.68, 132.56, 129.34, 129.10, 128.91, 128.82, 128.11, 127.49, 127.32, 126.35, 125.97, 115.561, 115.49, 55.79, 29.48. HRMS (ESI) m/z: Calcd for $C_{15}H_{14}OS$: 242.08; Found: 242.34.

(4-methoxyphenyl)(phenylethynyl)sulfane 3c



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53-7.40 (m, 7H), 7.04 (d, J = 8.0 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 159.36, 132.57, 131.90, 129.54, 129.27, 129.19, 122.39, 121.86, 115.98, 115.49, 96.84, 55.83, 29.49, 29.18, 22.57, 14.44. HRMS (ESI) m/z: Calcd for $C_{15}H_{12}OS$: 240.06 Found: 240.32.

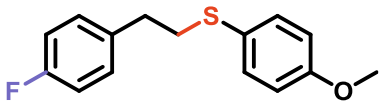
(4-methoxyphenyl)(4-nitrophenethyl)sulfane 3d



The compound was prepared according to the General procedure A. Orange oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 12.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 1.51 (s, 3H), 3.18 (t, J = 4.0 Hz, 2H), 2.93 (d, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6)

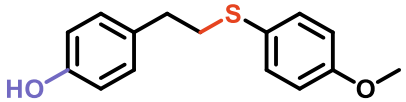
δ 158.87, 148.81, 146.53, 132.74, 130.41, 125.82, 123.81, 115.25, 55.63, 35.33, 34.98. HRMS (ESI) m/z: Calcd for $C_{15}H_{15}NO_3S$: 289.08 Found: 289.35.

(4-fluorophenethyl)(4-methoxyphenyl)sulfane 3e or 4e



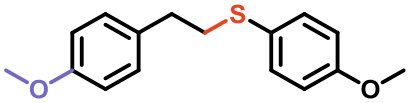
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane/ethyl acetate 9:1); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 12.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 1.58 (s, 3H), 3.10 (t, J = 4.0 Hz, 2H), 2.78 (d, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 139.33, 129.17, 128.82, 127.09, 47.41, 38.75, 35.71, 35.06, 29.90. HRMS (ESI) m/z: Calcd for $C_{15}H_{15}FOS$: 262.08 Found: 262.34.

4-(2-((4-methoxyphenyl)thio)ethyl)phenol 3f



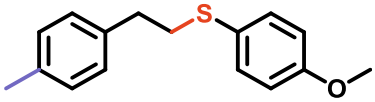
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.05 (d, J = 12.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.68 (t, J = 8.0 Hz, 3H), 3.74 (s, 3H), 3.01 (m, 2H), 2.67 (d, J = 8.0 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.67, 156.53, 156.17, 132.38, 130.67, 130.15, 129.84, 126.46, 115.56, 115.51, 115.21, 55.62, 38.27, 36.44, 35.45, 34.63. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}O_2S$: 260.09 Found: 260.35.

(4-methoxyphenethyl)(4-methoxyphenyl)sulfane 3g or 4g



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 (t, J = 8.0 Hz, 2H), 7.11 (t, J = 12.0 Hz, 2H), 6.93 (t, J = 8.0 Hz, 2H), 6.84 (t, J = 8.0 Hz, 2H), 3.745 (d, J = 4.0 Hz, 3H), 3.715 (d, J = 8.0 Hz, 3H), 3.05 (t, J = 8.0 Hz, 2H), 2.72 (d, J = 8.0 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.69, 158.18, 132.42, 129.95, 126.38, 115.22, 114.16, 55.62, 55.43, 36.33, 34.51. HRMS (ESI) m/z: Calcd for $C_{16}H_{18}O_2S$: 274.10 Found: 274.38.

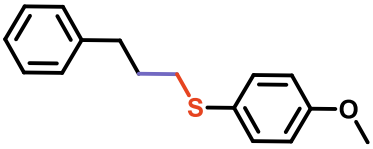
(4-methoxyphenyl)(4-methylphenethyl)sulfane 3h



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, J = 8.0 Hz, 2H),

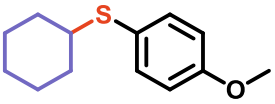
7.08 (s, 4H), 6.925 (d, J = 12.0 Hz, 2H), 3.75 (s, 3H), 3.07 (t, J = 8.0 Hz, 2H), 2.74 (t, J = 8.0 Hz, 3H), 2.26 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.71, 137.45, 135.60, 132.47, 129.34, 128.84, 126.32, 115.23, 55.63, 36.16, 34.95, 21.11. HRMS (ESI) m/z: Calcd for $C_{16}H_{18}OS$: 258.11 Found: 258.38.

(4-methoxyphenyl)(3-phenylpropyl)sulfane 3i or 4i



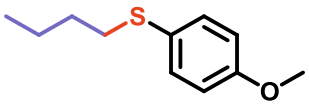
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); 3i yield 99%, 4i yield 62%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32-7.26 (m, 4H), 7.16 (d, J = 8.0 Hz, 3H), 6.90 (d, J = 8.0 Hz, 2H), 3.73 (s, 3H), 2.82 (t, J = 8.0 Hz, 2H), 2.867 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.76, 141.77, 132.70, 128.78, 128.76, 126.29, 126.21, 115.19, 55.61, 34.20, 30.98. HRMS (ESI) m/z: Calcd for $C_{16}H_{18}OS$: 258.11 Found: 258.36.

Cyclohexyl(4-methoxyphenyl)sulfane 3j or 4j



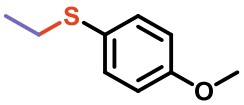
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); 3j yield 99%, 4j yield 70%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.355 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 2.98 (s, 1H), 1.83 (d, J = 8.0 Hz, 2H), 1.68 (d, J = 8.0 Hz, 2H), 1.55 (s, 1H), 1.27-1.17 (m, 5H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.72, 132.51, 126.32, 115.16, 55.63, 28.72, 14.87. HRMS (ESI) m/z: Calcd for $C_{13}H_{18}OS$: 222.11 Found: 222.35.

Butyl(4-methoxyphenyl)sulfane 3k or 4k



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); 3k yield 99%, 4k yield 70%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.30 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 3.73 (s, 3H), 2.83 (t, J = 8.0 Hz, 2H), 1.51-1.44 (m, 2H), 1.40-1.33 (m, 2H), 0.85 (t, J = 8.0 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.63, 132.39, 126.60, 115.14, 55.60, 34.32, 31.29, 21.60, 13.96. HRMS (ESI) m/z: Calcd for $C_{11}H_{16}OS$: 196.09 Found: 196.31.

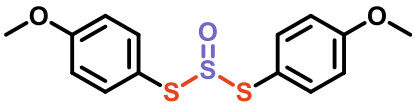
Ethyl(4-methoxyphenyl)sulfane 3l



The compound was prepared according to the General procedure A. White solid; R_f =

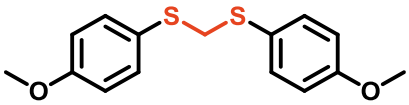
0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.74 (s, 3H), 2.845 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 1.16 (t, J = 8.0 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 158.71, 132.51, 126.32, 115.16, 55.63, 28.72, 14.87. HRMS (ESI) m/z: Calcd for $C_9H_{12}OS$: 168.06 Found: 168.25.

Bis(4-methoxyphenyl)sulfurodithioite 4m



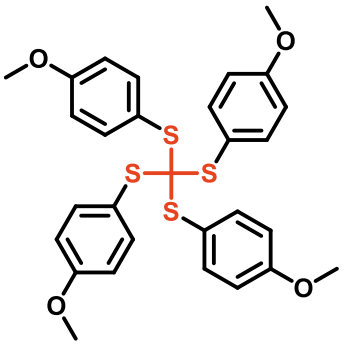
The compound was prepared according to the General procedure A. Yellow solid; R_f = 0.3 (hexane/ethyl acetate 4:1); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.00-6.93 (m, 4H), 3.77 (d, J = 8.0 Hz, 6H), 2.845 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 1.16 (t, J = 8.0 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 134.33, 132.55, 115.51, 115.47, 55.84, 55.78. HRMS (ESI) m/z: Calcd for $C_{14}H_{14}O_3S_3$: 326.01 Found: 326.44.

Bis((4-methoxyphenyl)thio)methane 3n or 4n



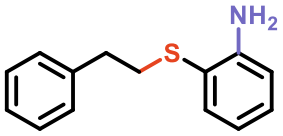
The compound was prepared according to the General procedure A. White solid; R_f = 0.3 (hexane/ethyl acetate 4:1); 3n yield 99%, 4n yield 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, J = 8.0 Hz, 4H), 6.925 (d, J = 8.0 Hz, 4H), 4.365 (d, J = 8.0 Hz, 2H), 3.755 (d, J = 8.0 Hz, 6H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 159.33, 133.69, 125.06, 115.15, 55.68. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}O_2S_2$: 292.06 Found: 292.41.

Tetrakis((4-methoxyphenyl)thio)methane 3o



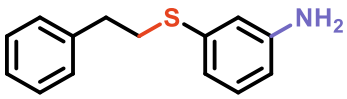
The compound was prepared according to the General procedure A. White solid; R_f = 0.3 (hexane/ethyl acetate 1:1); yield 81%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, J = 8.0 Hz, 8H), 6.96 (d, J = 8.0 Hz, 8H), 3.76 (s, 12H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 160.17, 132.55, 127.39, 115.48, 55.79. HRMS (ESI) m/z: Calcd for $C_{29}H_{28}O_4S_4$: 568.09 Found: 568.78.

2-(phenethylthio)aniline 3p or 4p



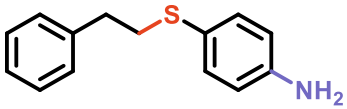
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); 3p yield 99%, 4p yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.30-7.18 (m, 6H), 7.04 (t, J = 8.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.54 (t, J = 8.0 Hz, 1H), 5.25 (s, 2H), 2.97 (t, J = 8.0 Hz, 2H), 2.76 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d^6) δ 149.69, 140.69, 135.07, 129.57, 128.92, 128.78, 126.63, 116.94, 116.14, 114.81, 60.22, 35.58, 35.04, 29.49, 21.23, 14.56. HRMS (ESI) m/z: Calcd for $C_{14}H_{15}NS$: 229.09 Found: 229.34.

3-(phenethylthio)aniline 3q or 4q



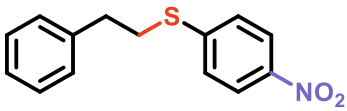
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.30-7.21 (m, 5H), 6.96 (t, J = 8.0 Hz, 1H), 6.56 (s, 2H), 6.47 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 5.16 (s, 2H), 3.12 (t, J = 8.0 Hz, 2H), 2.85 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 149.73, 140.65, 136.57, 129.90, 128.99, 128.80, 126.71, 115.67, 113.37, 111.97, 35.29, 33.82. HRMS (ESI) m/z: Calcd for $C_{14}H_{15}NS$: 229.09 Found: 229.33.

4-(phenethylthio)aniline 3r or 4r



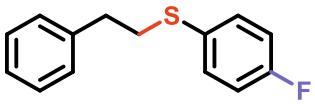
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29-7.20 (m, 2H), 7.18 (d, J = 8.0 Hz, 3H), 7.12 (d, J = 8.0 Hz, 2H), 6.47 (d, J = 8.0 Hz, 2H), 5.26 (s, 2H), 2.95 (t, J = 8.0 Hz, 2H), 2.74 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 148.88, 140.81, 134.11, 128.95, 128.75, 126.56, 119.15, 114.94, 37.54, 35.57. HRMS (ESI) m/z: Calcd for $C_{14}H_{15}NS$: 229.09 Found: 229.34.

(4-nitrophenyl)(phenethyl)sulfane 3s or 4s



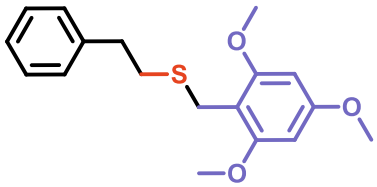
The compound was prepared according to the General procedure A. Orange oil; R_f = 0.3 (hexane); 3s yield 99%, 4s yield 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 4H), 7.23 (s, 1H), 3.40 (t, J = 8.0 Hz, 2H), 2.95 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 147.89, 144.79, 140.00, 129.09, 128.85, 126.93, 126.72, 124.41, 34.45, 32.46. HRMS (EI) m/z: Calcd for $C_{14}H_{13}NO_2S$: 259.07; Found: 259.32.

(4-fluorophenyl)(phenethyl)sulfane 3t or 4t



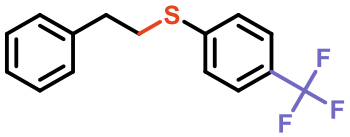
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane/ethyl acetate 3:2); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44-7.16 (m, 9H), 3.20 (t, J = 8.0 Hz, 2H), 2.83 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 162.42, 160.01, 140.37, 131.85, 131.51, 131.43, 129.01, 128.78, 126.74, 116.67, 116.46, 34.89. HRMS (ESI) m/z: Calcd for $C_{14}H_{13}FS$: 232.07; Found: 232.34.

Phenethyl(2,4,6-trimethoxybenzyl)sulfane 3u or 4u



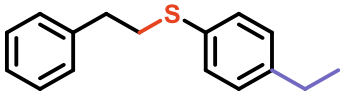
The compound was prepared according to the General procedure A. White solid; R_f = 0.3 (hexane); 3u yield 99%, 4u yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29-7.18 (m, 5H), 6.245 (d, J = 8.0 Hz, 2H), 3.76 (s, 9H), 3.64 (s, 2H), 2.80 (t, J = 8.0 Hz, 2H), 2.64 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 160.40, 159.48, 158.77, 141.26, 128.97, 128.91, 128.71, 126.48, 107.54, 91.40, 91.16, 56.36, 56.16, 55.78, 55.66, 36.36, 33.24, 29.50, 29.18, 27.81, 23.46, 22.58. HRMS (ESI) m/z: Calcd for $C_{18}H_{22}O_3S$: 318.13; Found: 318.43.

Phenethyl(4-(trifluoromethyl)phenyl)sulfane 3v or 4v



The compound was prepared according to the General procedure A. White solid; R_f = 0.3 (hexane/ethyl acetate 3:2); 3v yield 99%, 4v yield 83%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45-7.39 (m, 2H), 7.31-7.17 (m, 7H), 3.20 (t, J = 8.0 Hz, 2H), 2.83 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 162.42, 160.01, 157.90, 140.37, 131.52, 131.44, 129.01, 128.79, 126.74, 116.68, 116.46. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}F_3S$: 282.07; Found: 282.32.

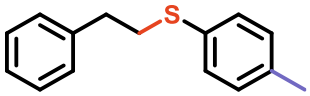
(4-ethylphenyl)(phenethyl)sulfane 3w or 4w



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31-7.17 (m, 9H), 3.18 (t, J = 8.0 Hz, 2H), 2.89-2.82 (m, 2H), 2.57 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 1.20-1.12

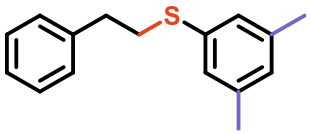
(m, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 142.03, 140.51, 129.23, 129.01, 128.99, 128.78, 126.71, 35.25, 34.46, 28.11, 15.98. HRMS (ESI) m/z: Calcd for $C_{16}H_{18}S$: 242.11; Found: 242.38.

(4-methylphenyl)(phenethyl)sulfane 3x or 4x



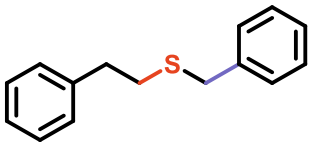
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31-7.14 (m, 9H), 3.17 (t, J = 8.0 Hz, 2H), 2.82 (t, J = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 140.52, 135.73, 130.20, 129.30, 128.99, 128.78, 126.70, 35.22, 34.62, 21.00. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}S$: 228.10; Found: 228.35.

(3,5-dimethylphenyl)(phenethyl)sulfane 3y or 4y



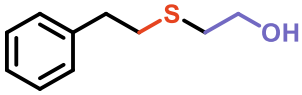
The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32-7.21 (m, 5H), 6.94 (s, 2H), 6.80 (s, 1H), 3.19 (t, J = 8.0 Hz, 2H), 2.85 (t, J = 8.0 Hz, 2H), 2.24 (s, 6H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 140.54, 138.61, 136.18, 129.00, 128.78, 127.74, 126.71, 126.01, 35.18, 33.82, 21.27. HRMS (ESI) m/z: Calcd for $C_{16}H_{18}S$: 242.11; Found: 242.35.

Benzyl(phenethyl)sulfane 3z or 4z



The compound was prepared according to the General procedure A. Yellow oil; R_f= 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33-7.17 (m, 10H), 3.75 (s, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.61 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 140.95, 139.14, 129.35, 128.94, 128.81, 128.74, 127.23, 126.58, 35.65, 35.44, 32.58. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}S$: 228.10; Found: 228.34.

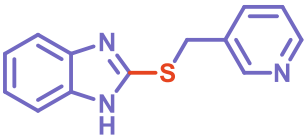
2-(phenethylthio)ethan-1-ol 3α or 4α



The compound was prepared according to the General procedure A. Yellow oil; R_f = 0.3 (hexane); yield 99%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.30-7.18 (m, 5H), 4.79 (t, J = 8.0 Hz, 1H), 3.535 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 2.79 (dd, J_1 = 8.0 Hz, J_2 =

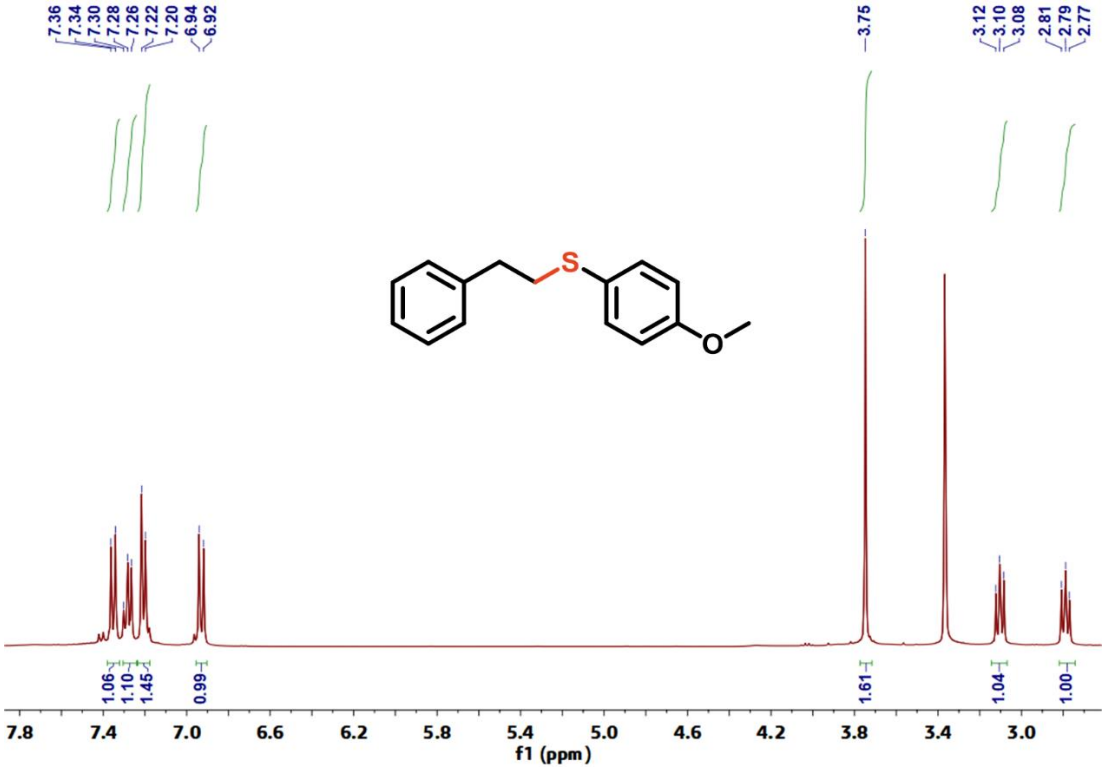
12.0 Hz, 4H), 2.59 (t, J = 8.0 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 141.00, 128.96, 128.72, 126.56, 61.41, 36.18,34.38,33.40. HRMS (ESI) m/z: Calcd for $C_{15}H_{16}S$: 182.08; Found: 182.28.

2-((pyridin-3-ylmethyl)thio)-1H-benzoimidazole 3β

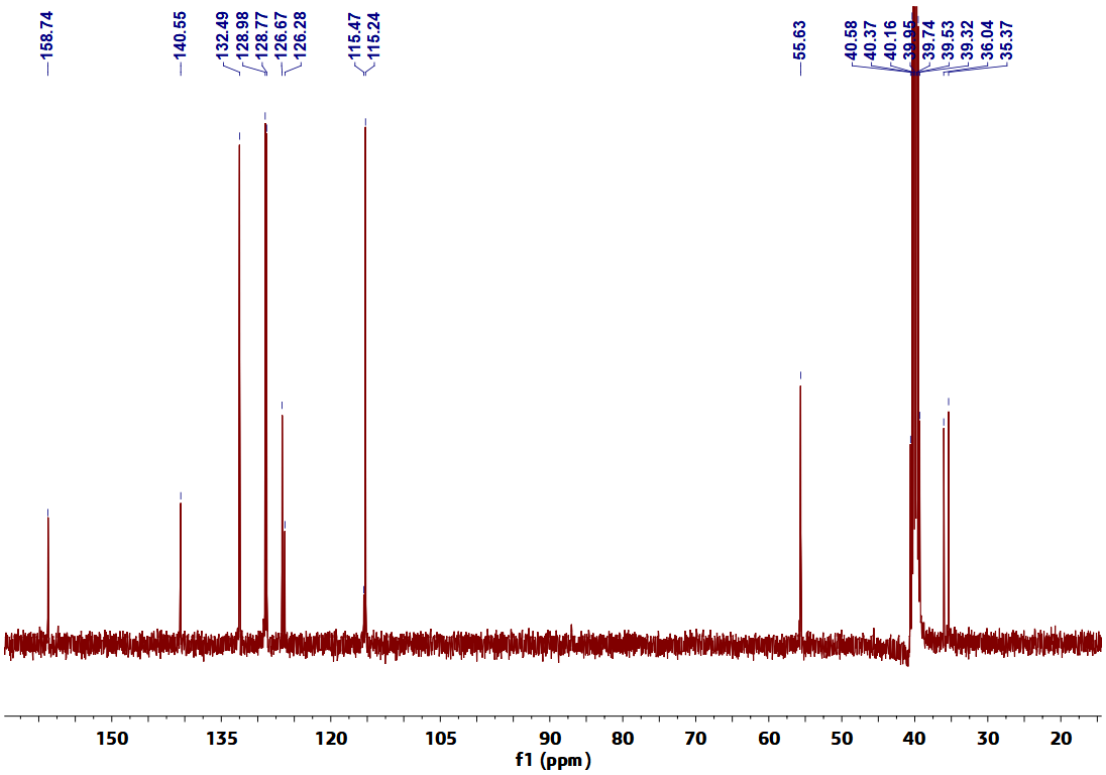


The compound was prepared according to the General procedure A. Orange oil; R_f = 0.3 (hexane/ethyl acetate 1:1); yield 62%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.525 (d, J=4.0 Hz, 1H), 7.78 (t, J = 8.0 Hz, 2H), 7.55 (s, 1H), 7.34-7.28 (m, 4H), 7.20 (m, 1H), 3.92 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 162.75, 127.19, 122.74, 60.21, 36.24, 31.23, 21.22, 14.55. HRMS (ESI) m/z: Calcd for $C_{13}H_{11}N_3S$: 241.07; Found: 241.31.

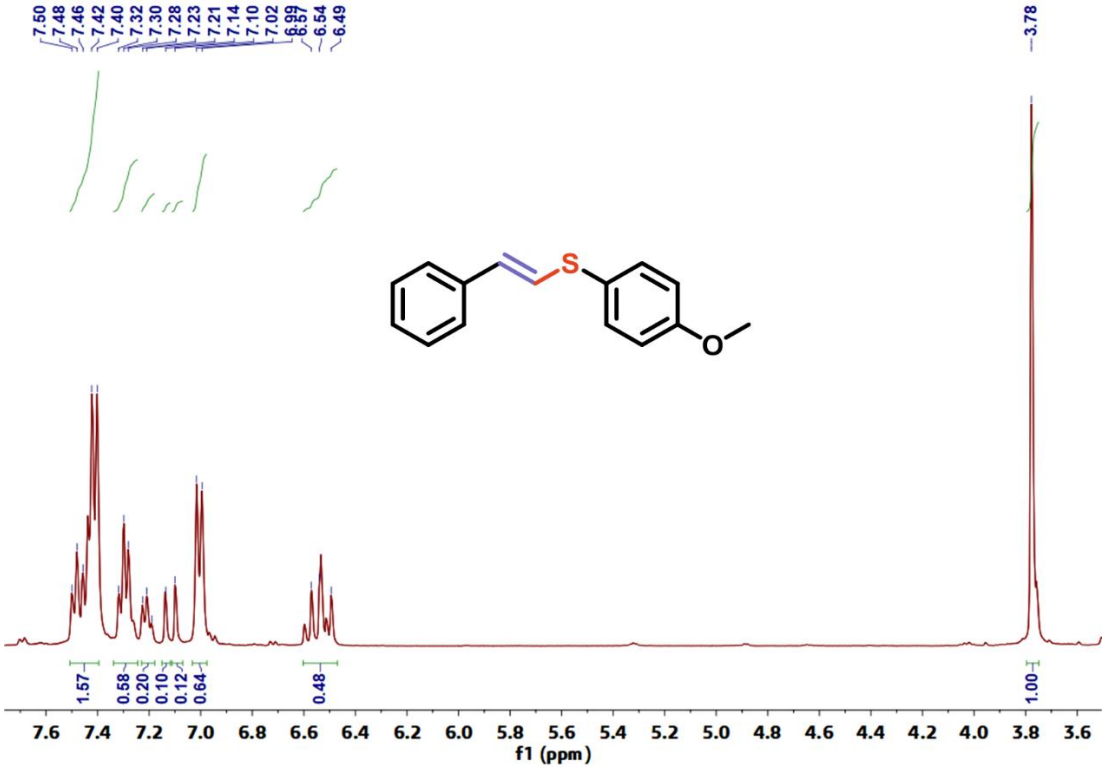
5. Copies of ^{1}H NMR and ^{13}C NMR



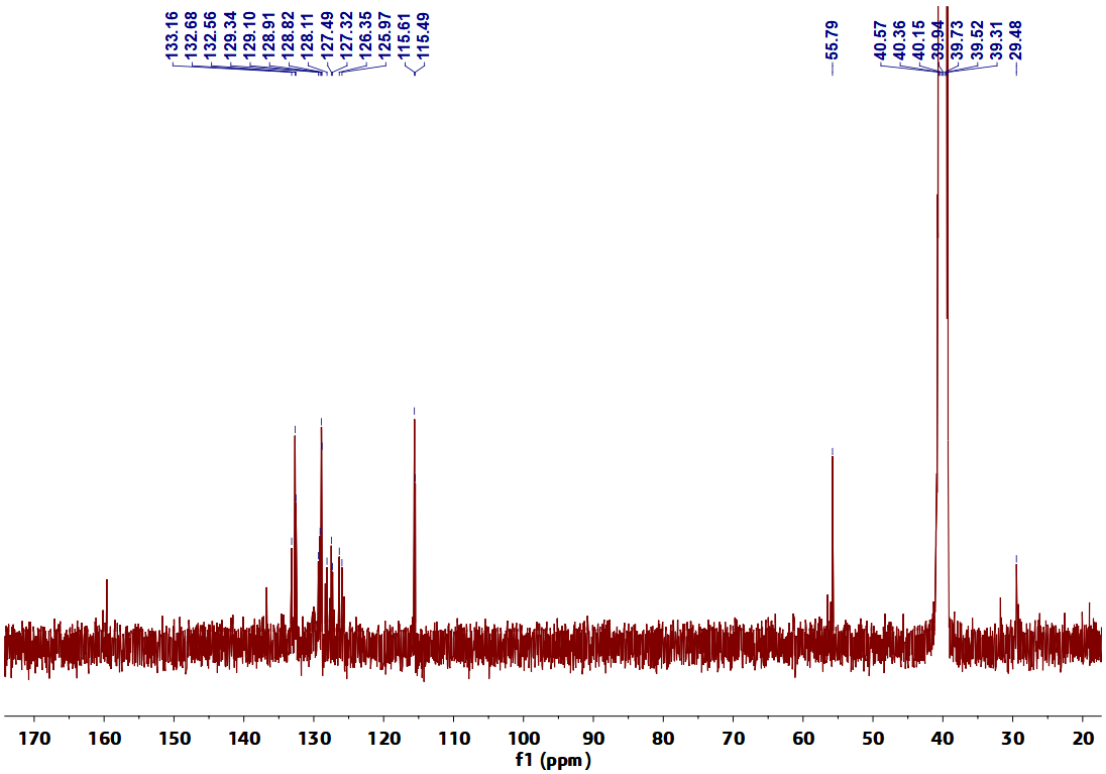
^{1}H NMR (400 MHz, DMSO-d6) of **3a** or **4a**



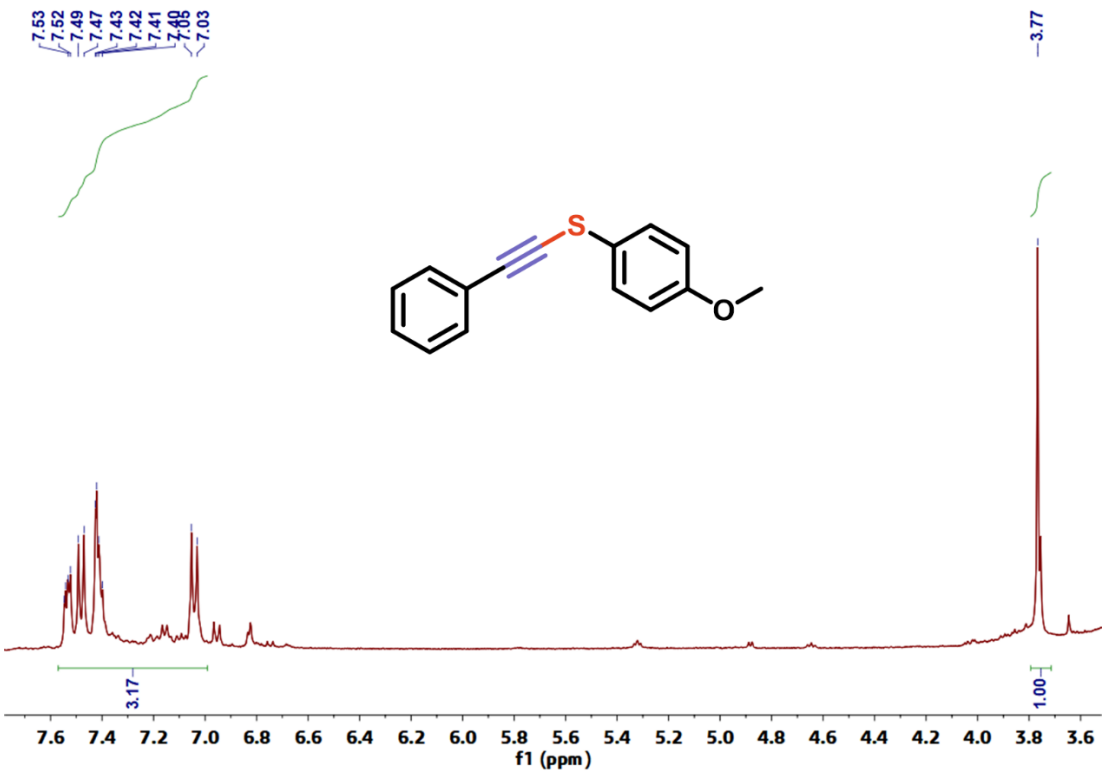
^{13}C NMR (400 MHz, DMSO-d6) of **3a** or **4a**



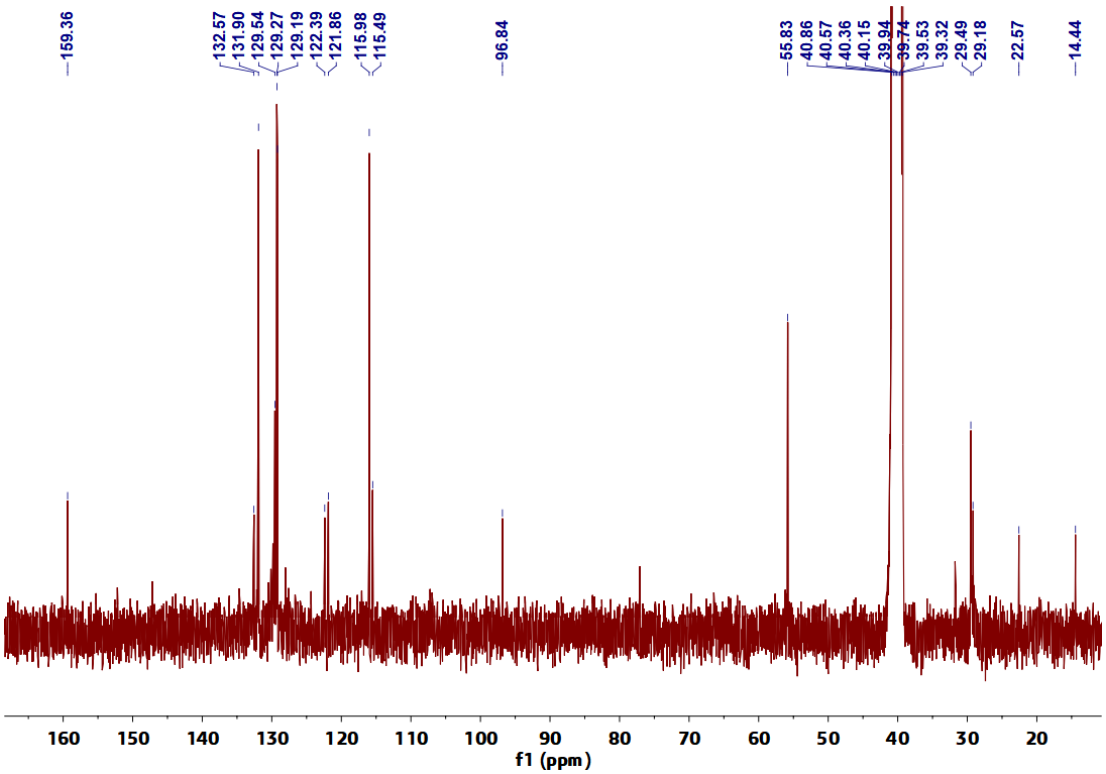
^{1}H NMR (400 MHz, DMSO-d6) of **3b**



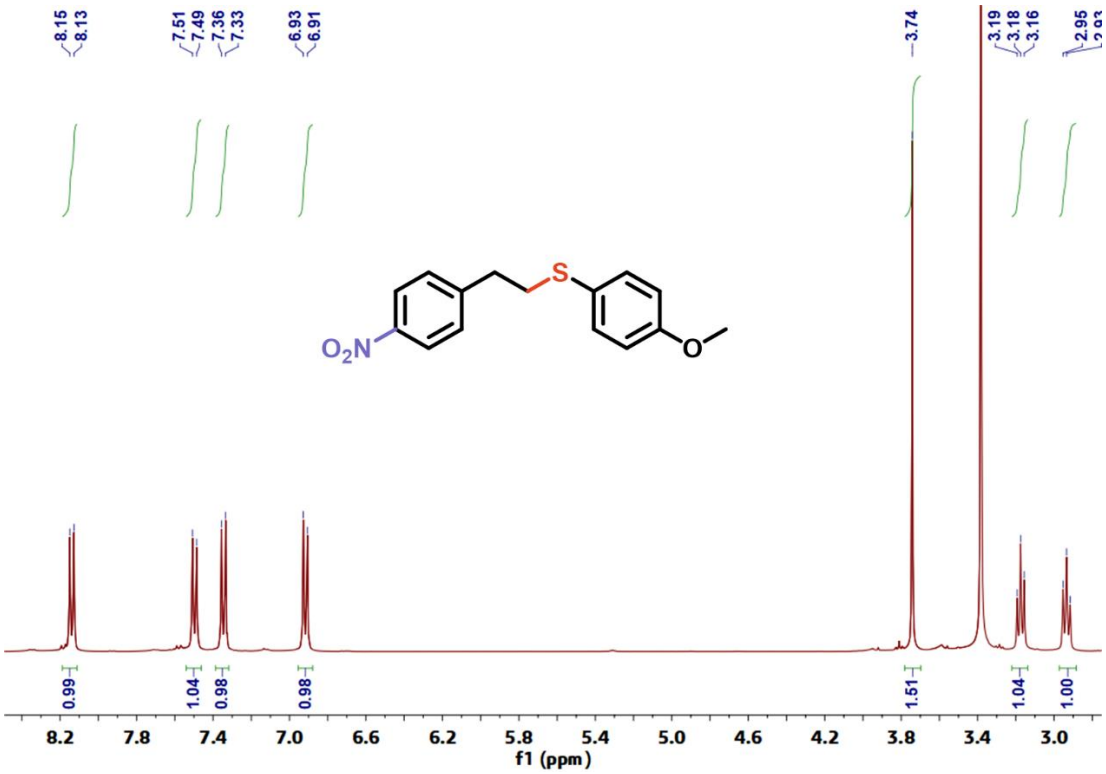
^{13}C NMR (400 MHz, DMSO-d6) of **3b**



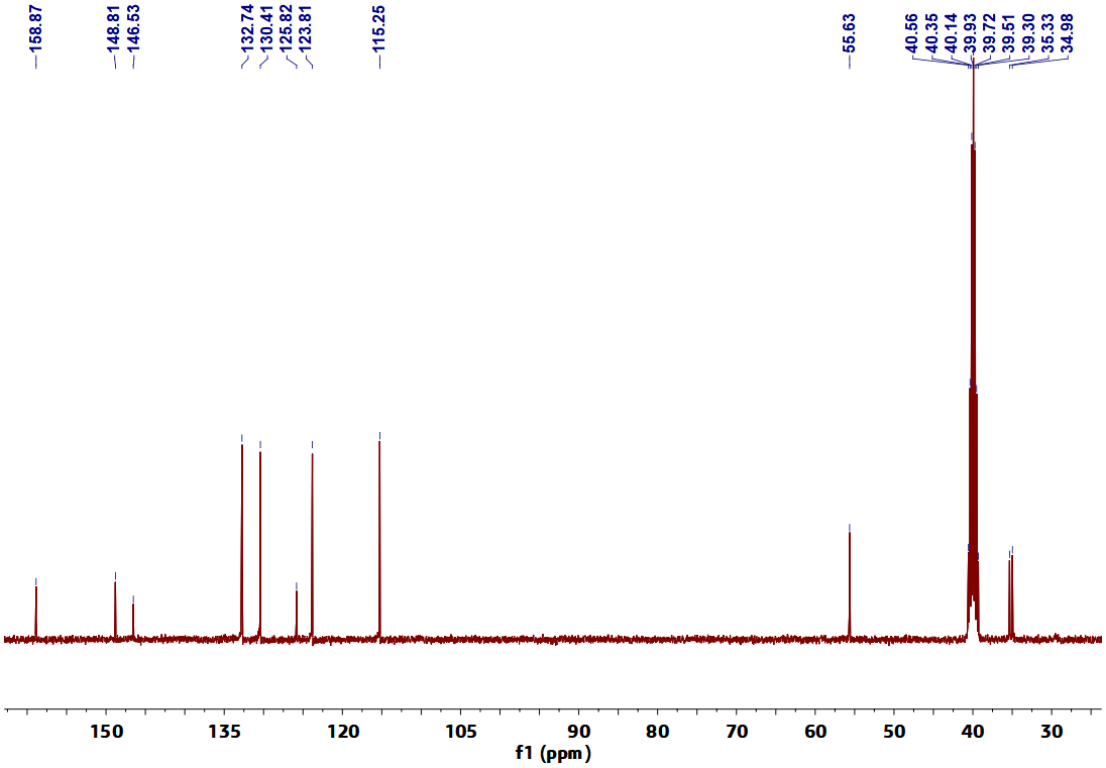
^{1}H NMR (400 MHz, DMSO-d6) of **3c**



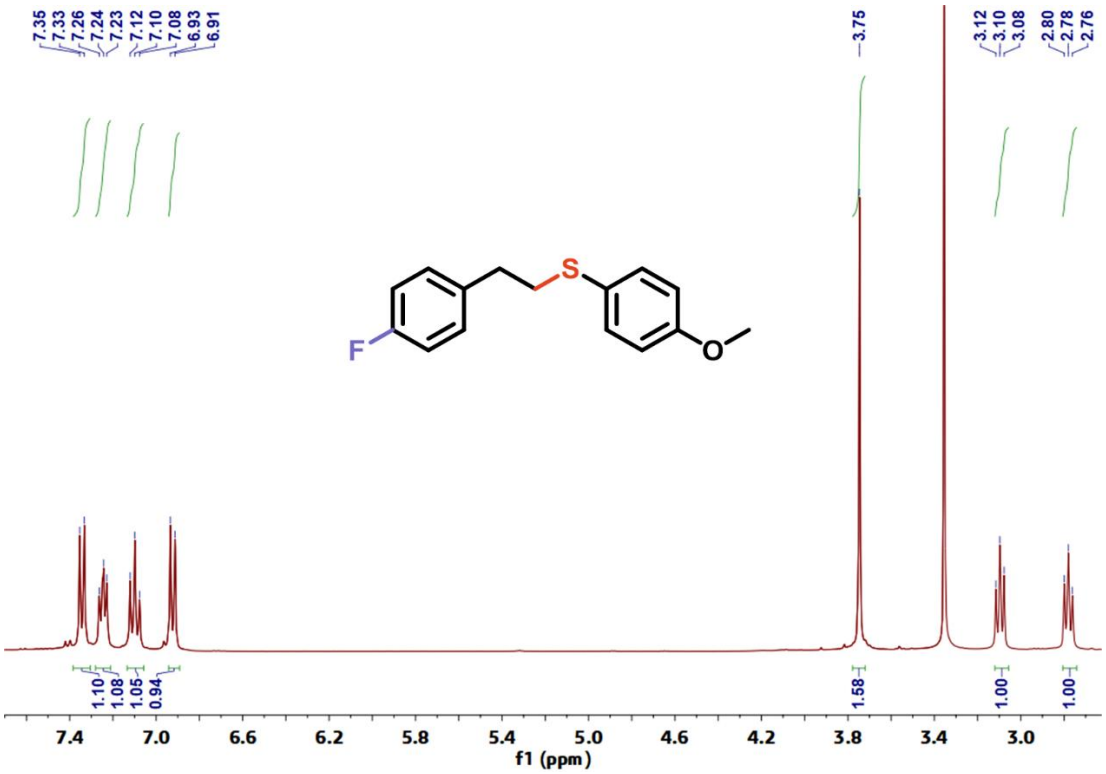
^{13}C NMR (400 MHz, DMSO-d6) of **3c**



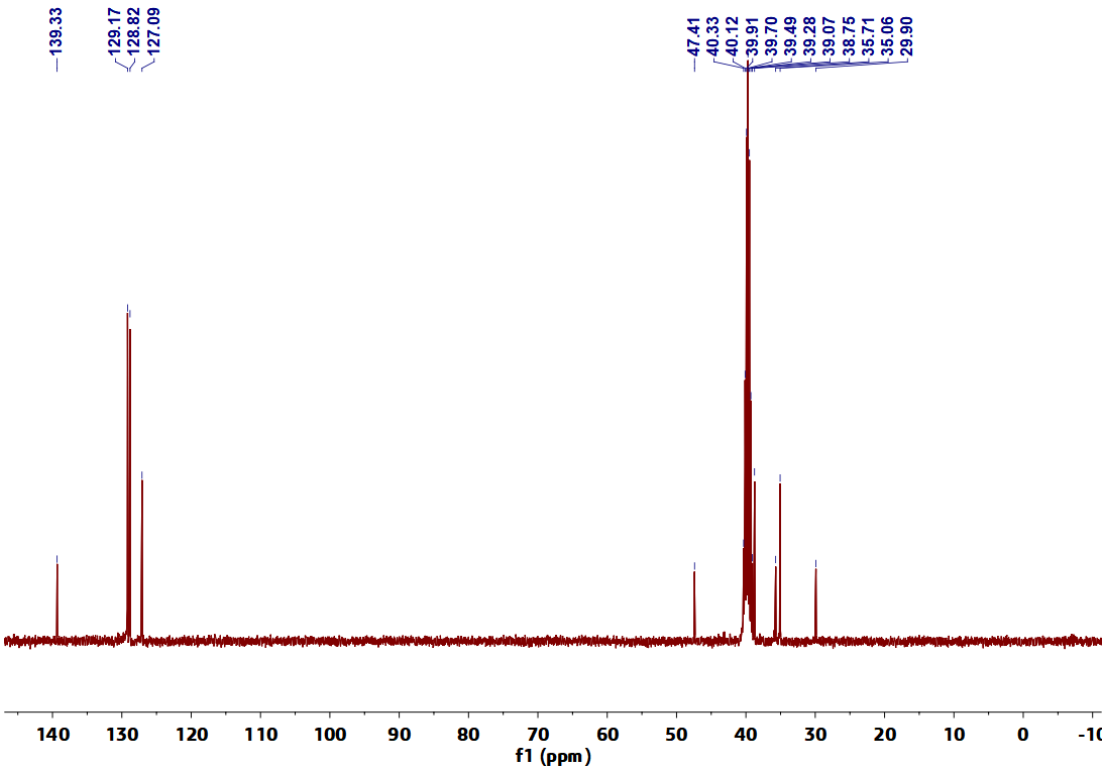
^{1}H NMR (400 MHz, DMSO-d6) of **3d**



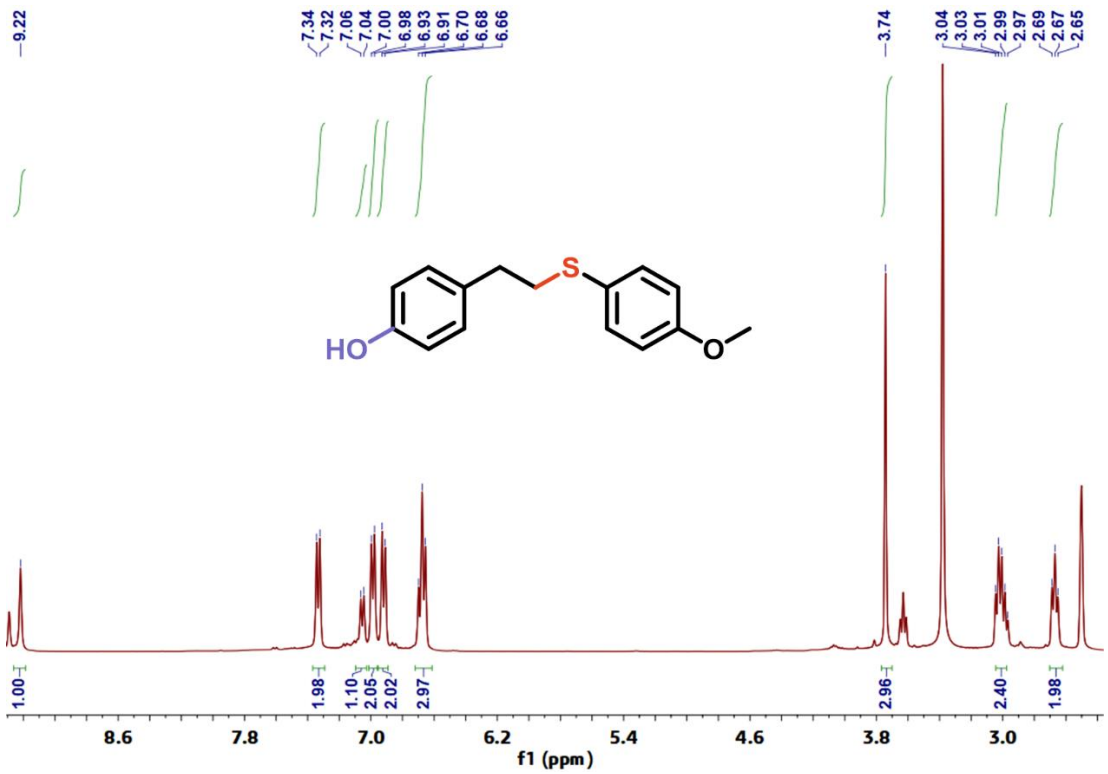
^{13}C NMR (400 MHz, DMSO-d6) of **3d**



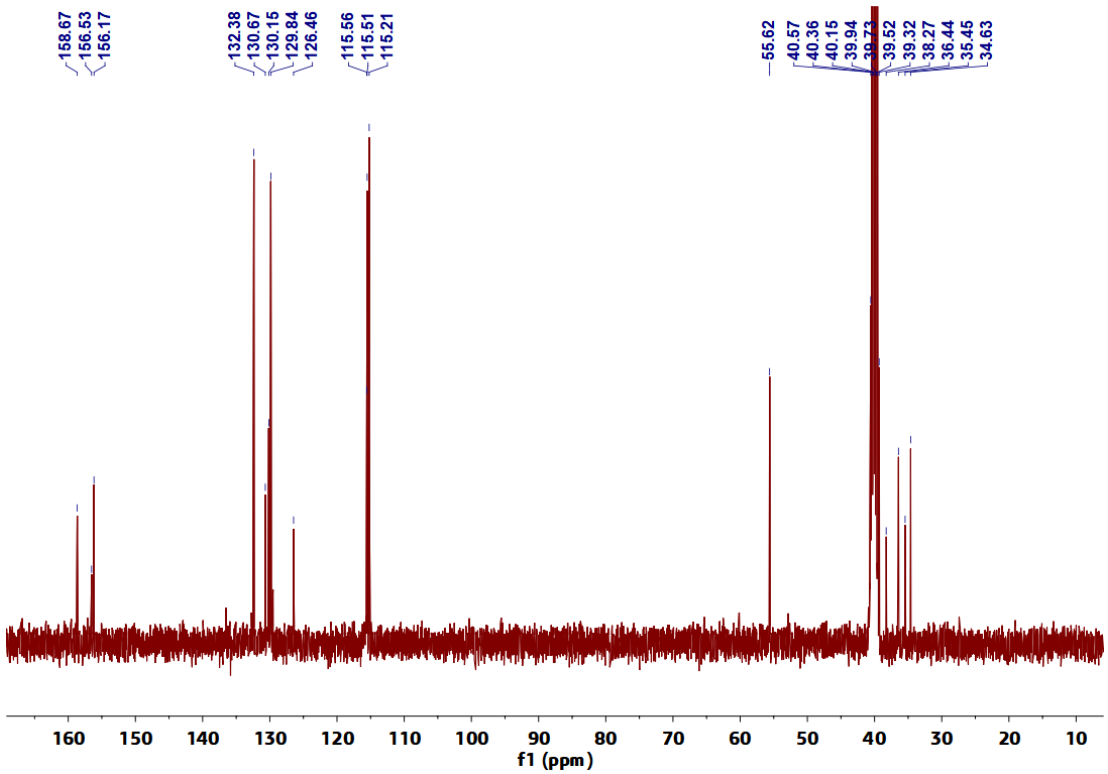
^{1}H NMR (400 MHz, DMSO-d6) of **3e** or **4e**



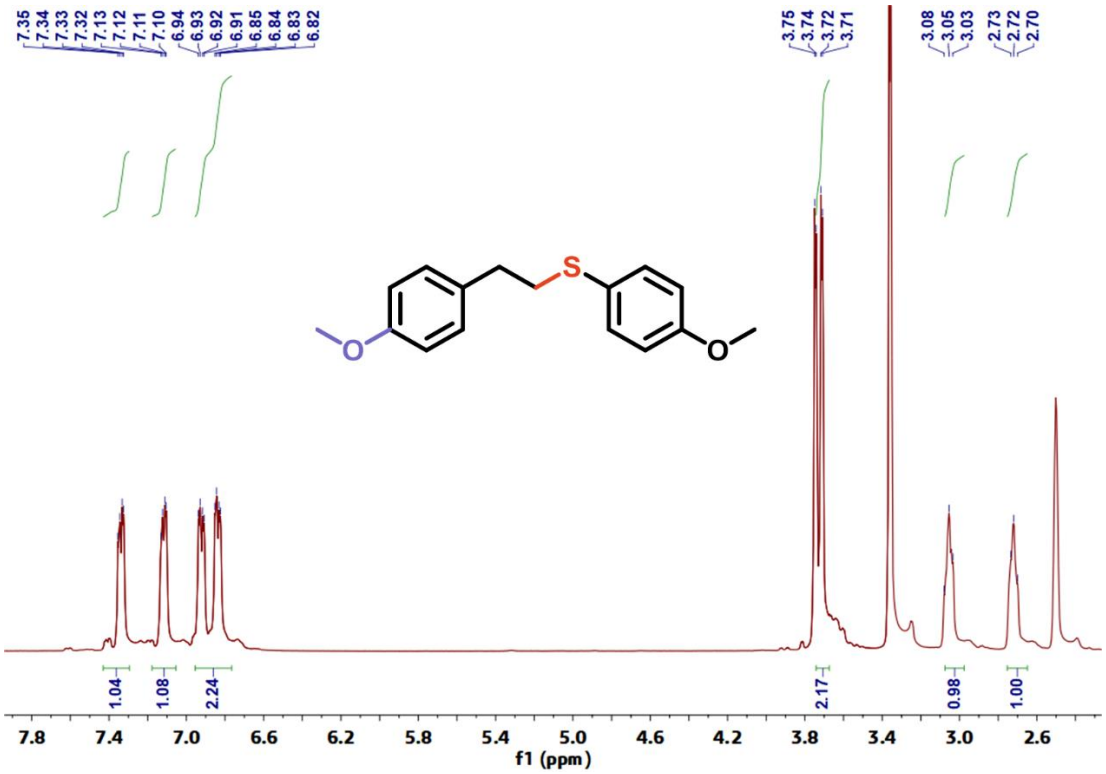
^{13}C NMR (400 MHz, DMSO-d6) of **3e** or **4e**



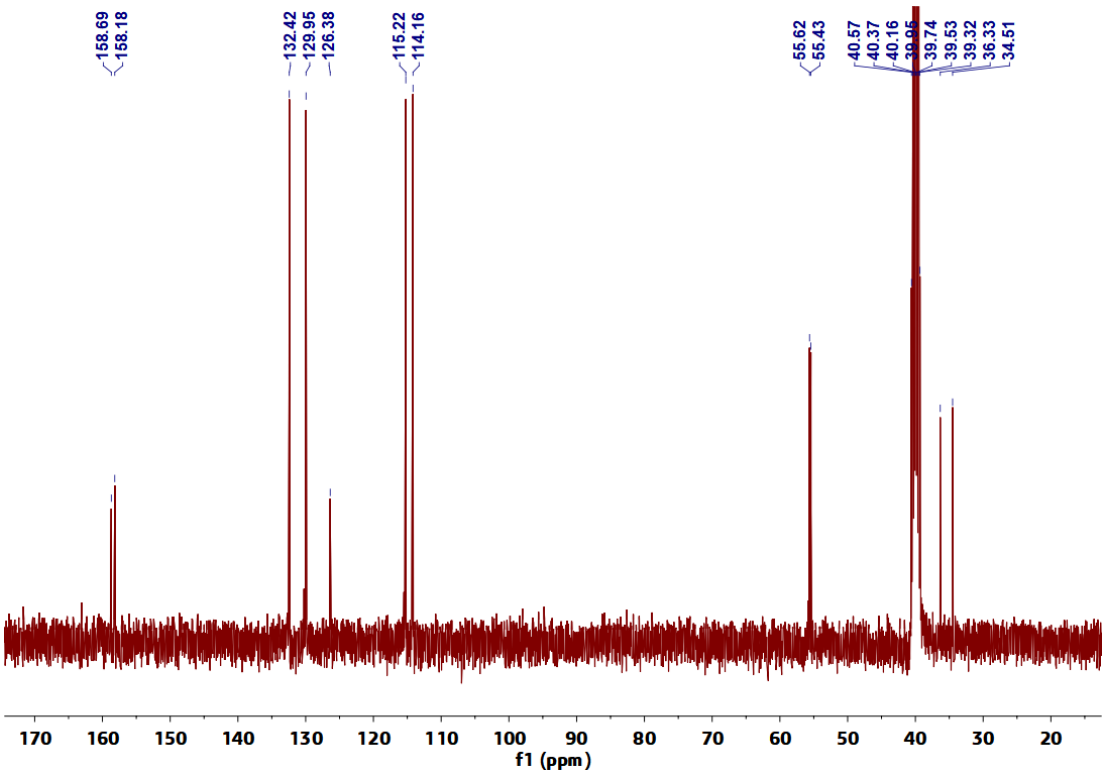
^{1}H NMR (400 MHz, DMSO-d6) of **3f**



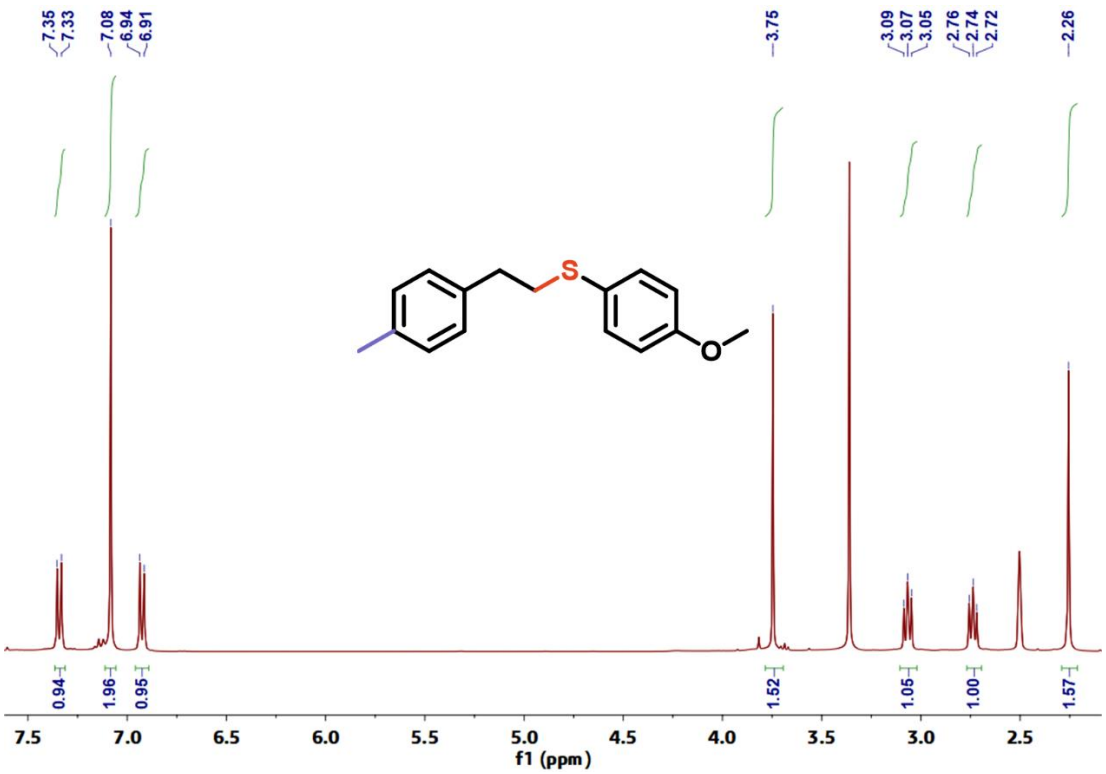
^{13}C NMR (400 MHz, DMSO-d6) of **3f**



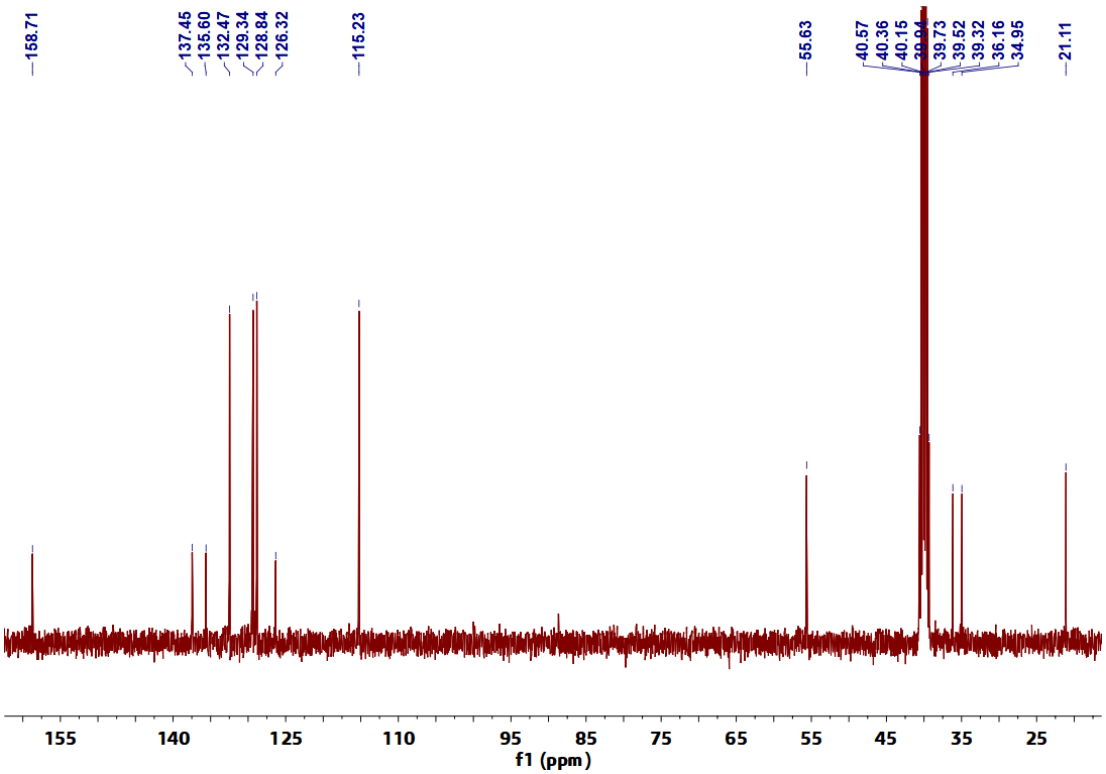
^{1}H NMR (400 MHz, DMSO-d6) of **3g** or **4g**



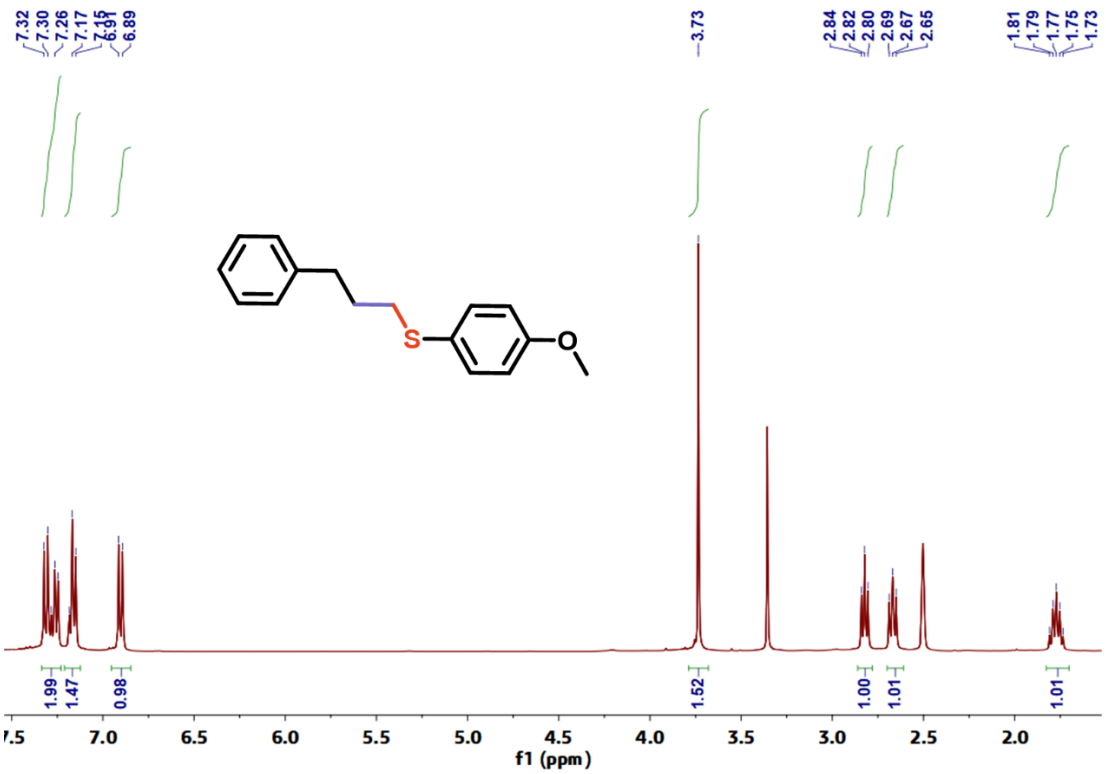
^{13}C NMR (400 MHz, DMSO-d6) of **3g** or **4g**



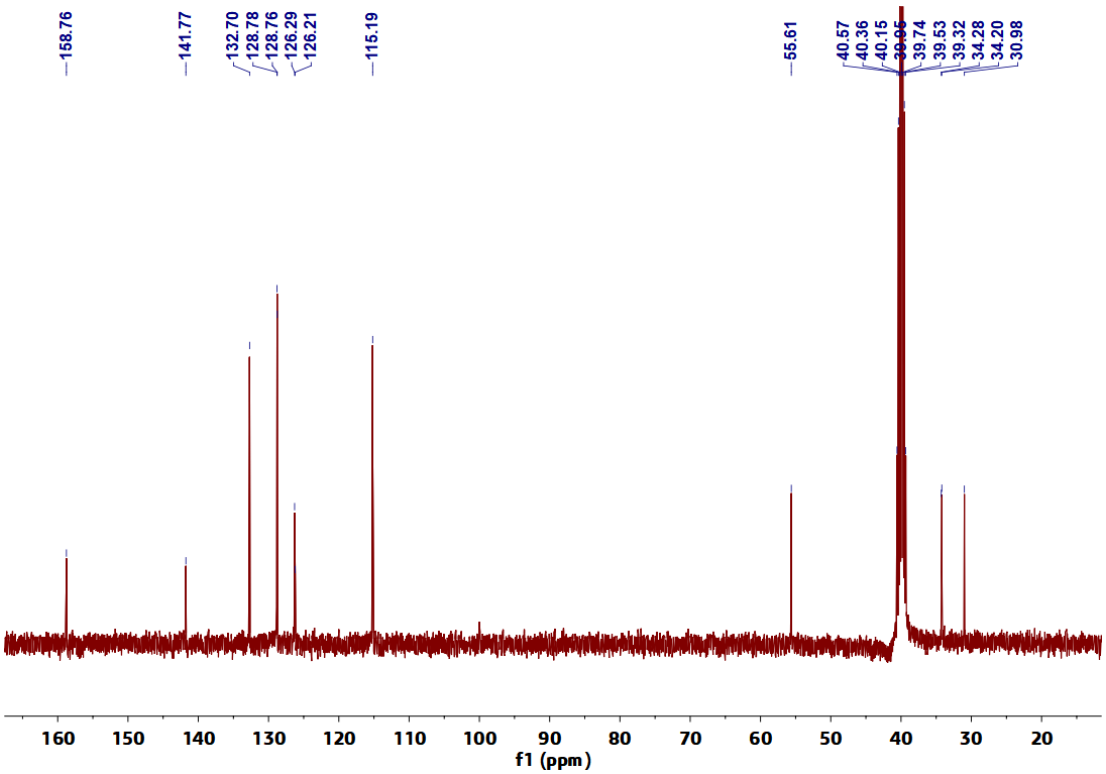
^{1}H NMR (400 MHz, DMSO-d6) of **3h**



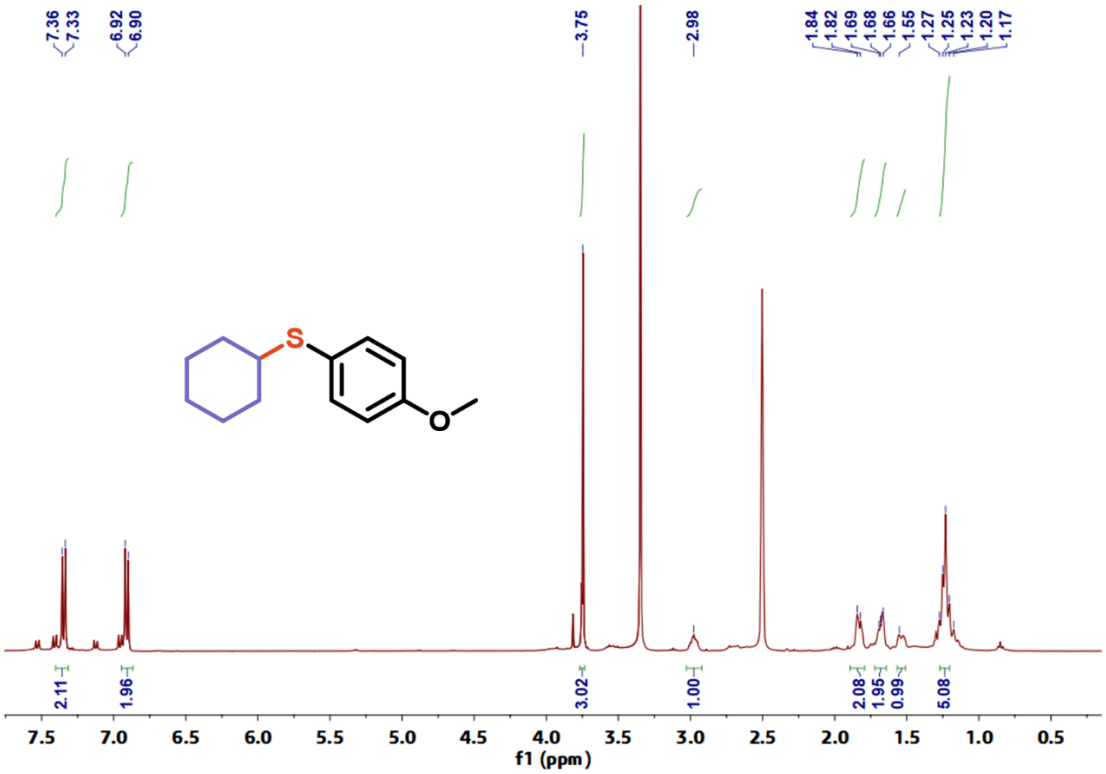
^{13}C NMR (400 MHz, DMSO-d6) of **3h**



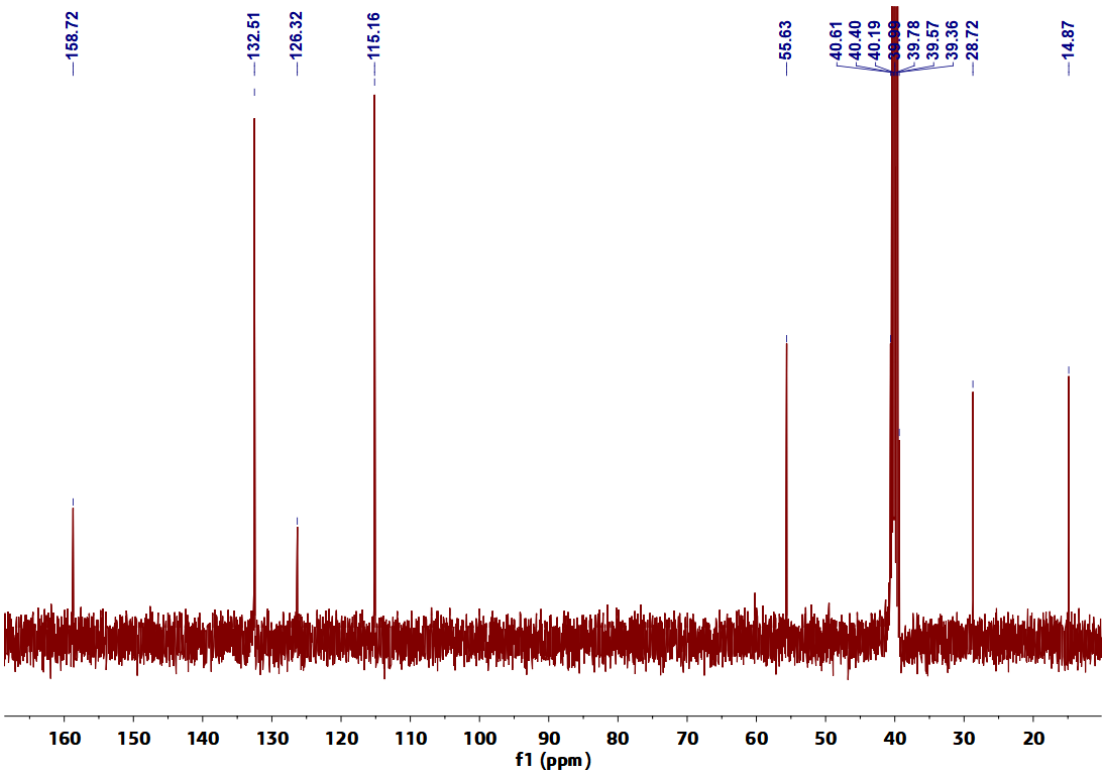
^{1}H NMR (400 MHz, DMSO-d6) of **3i** or **4i**



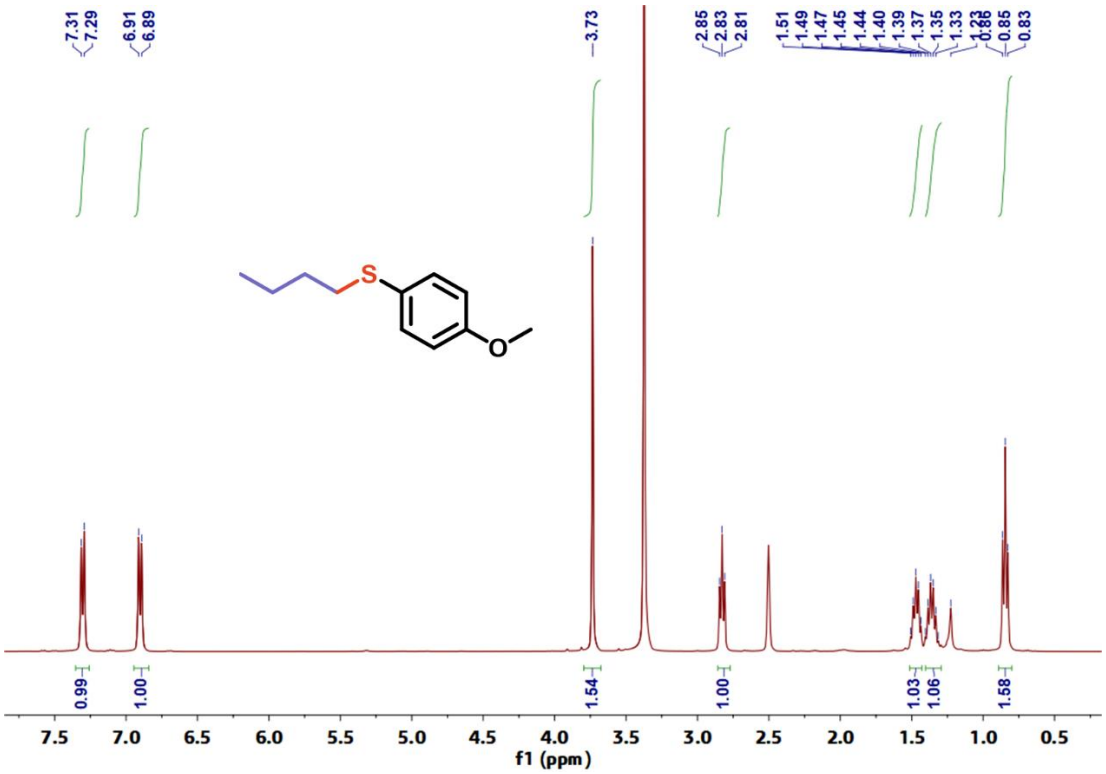
^{13}C NMR (400 MHz, DMSO-d6) of **3i** or **4i**



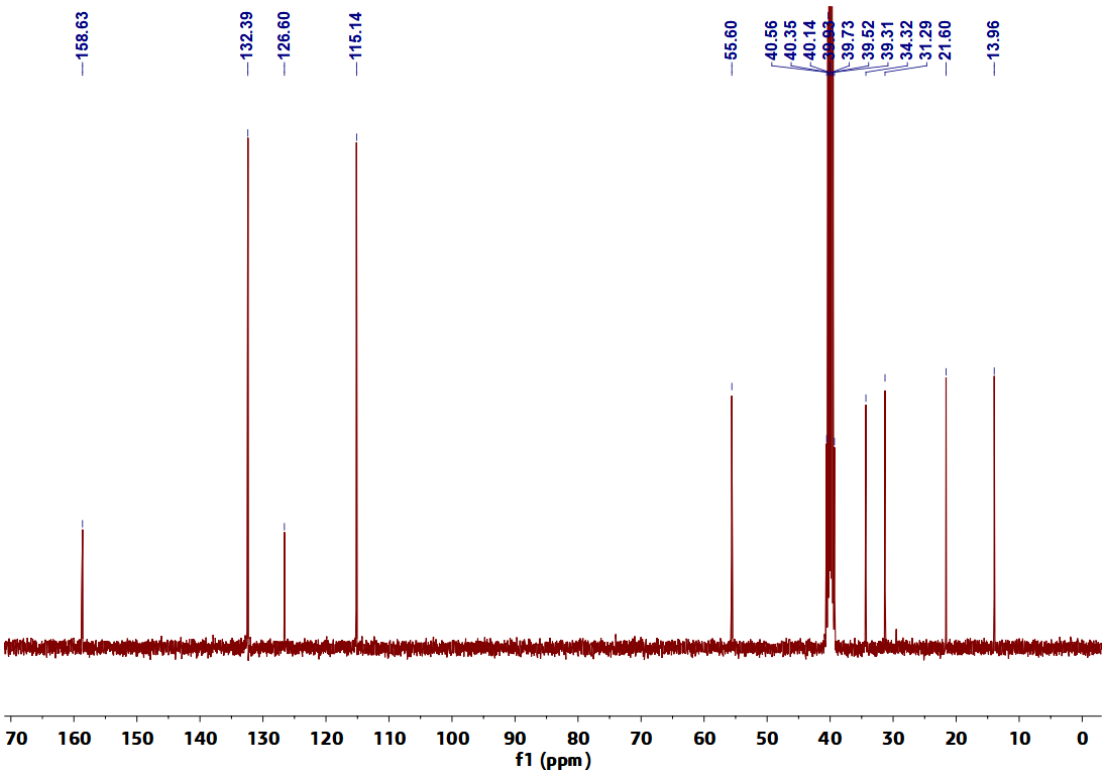
^{1}H NMR (400 MHz, DMSO-d6) of **3j** or **4j**



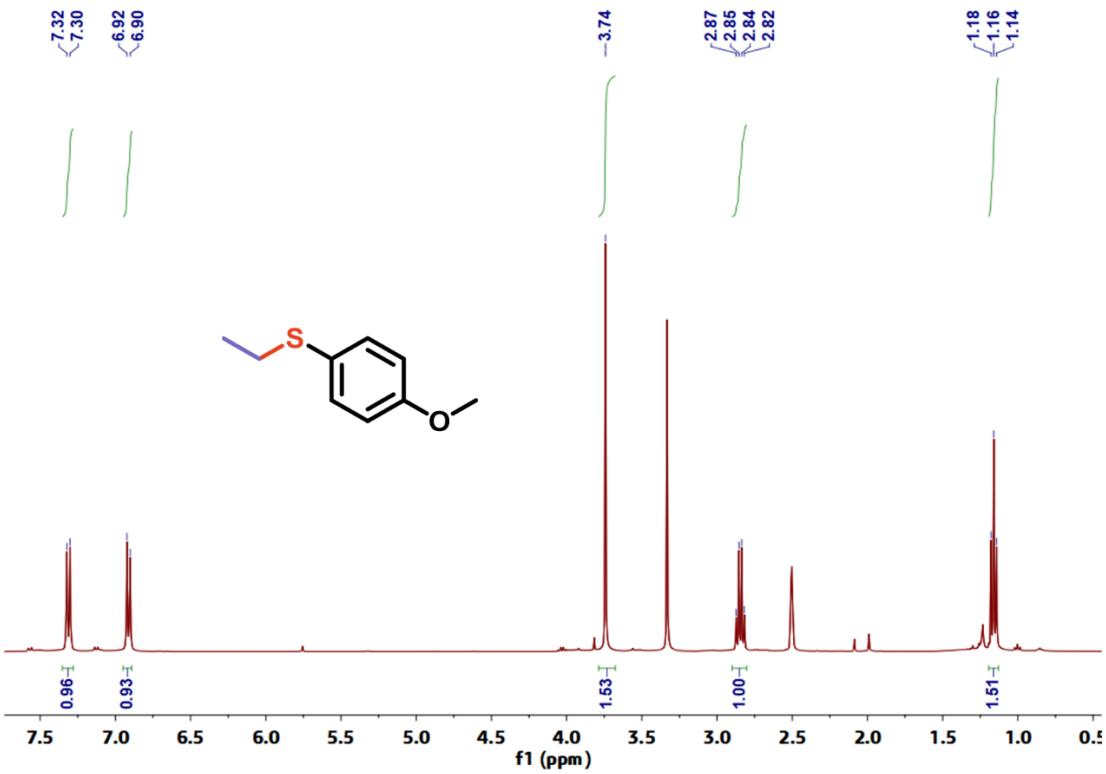
^{13}C NMR (400 MHz, DMSO-d6) of **3j** or **4j**



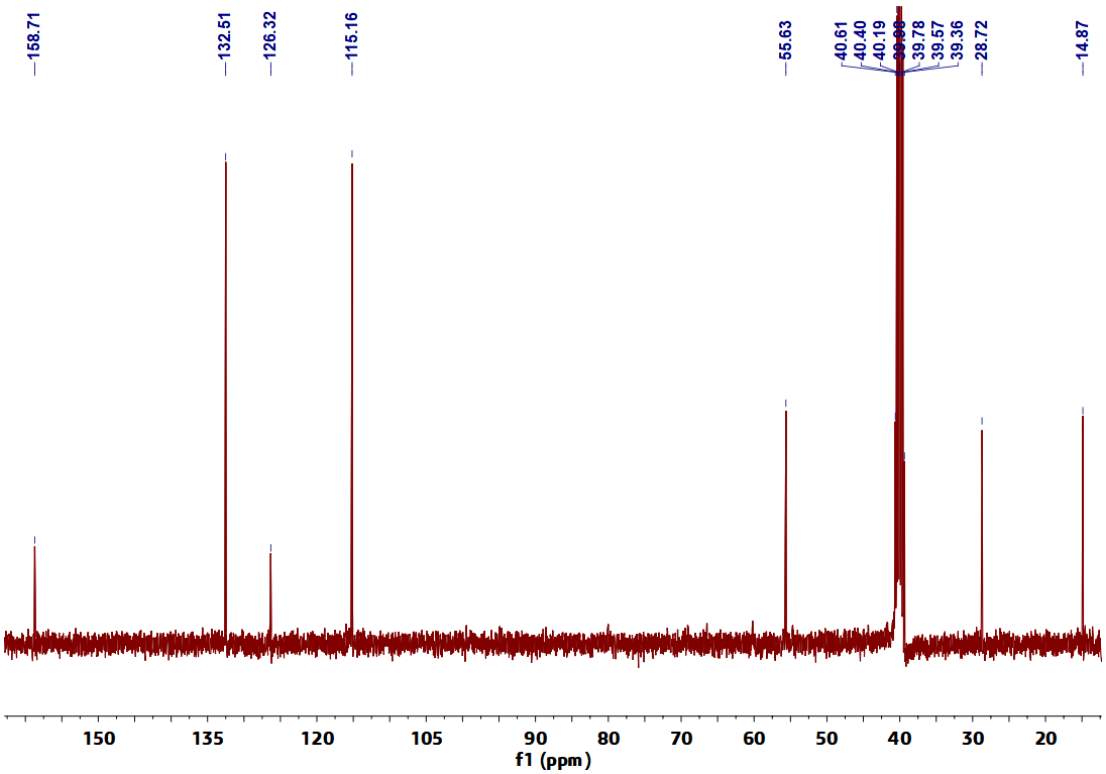
^{1}H NMR (400 MHz, DMSO-d6) of **3k** or **4k**



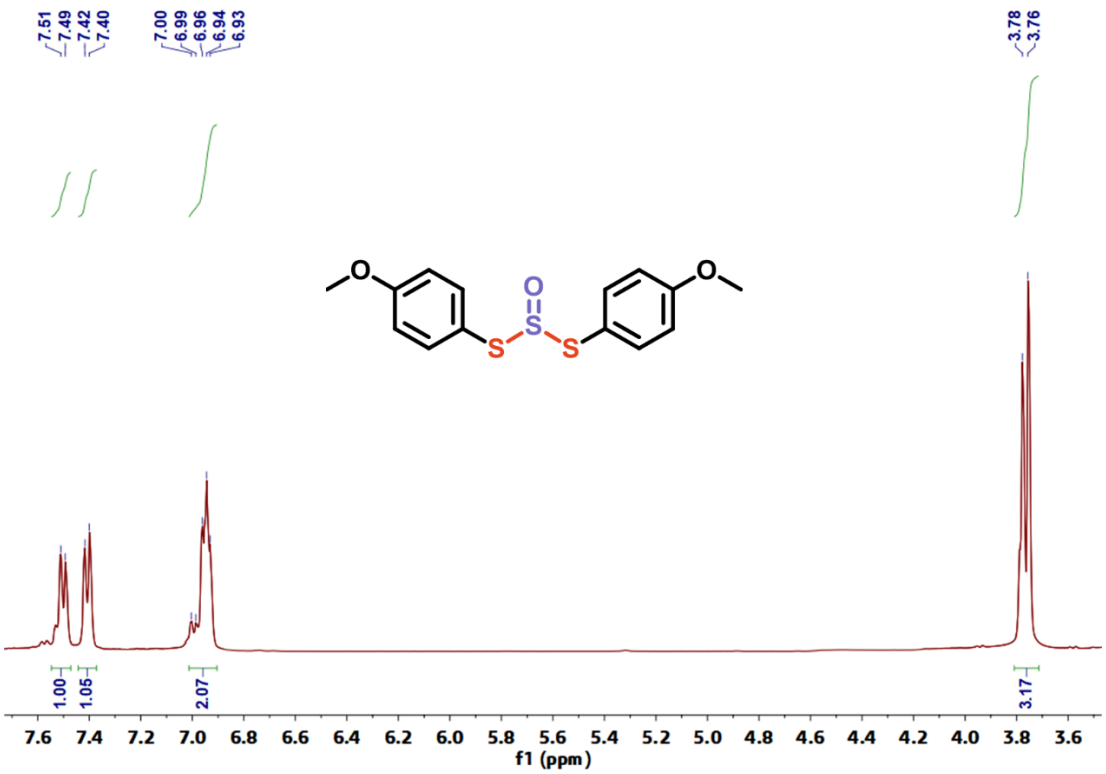
^{13}C NMR (400 MHz, DMSO-d6) of **3k** or **4k**



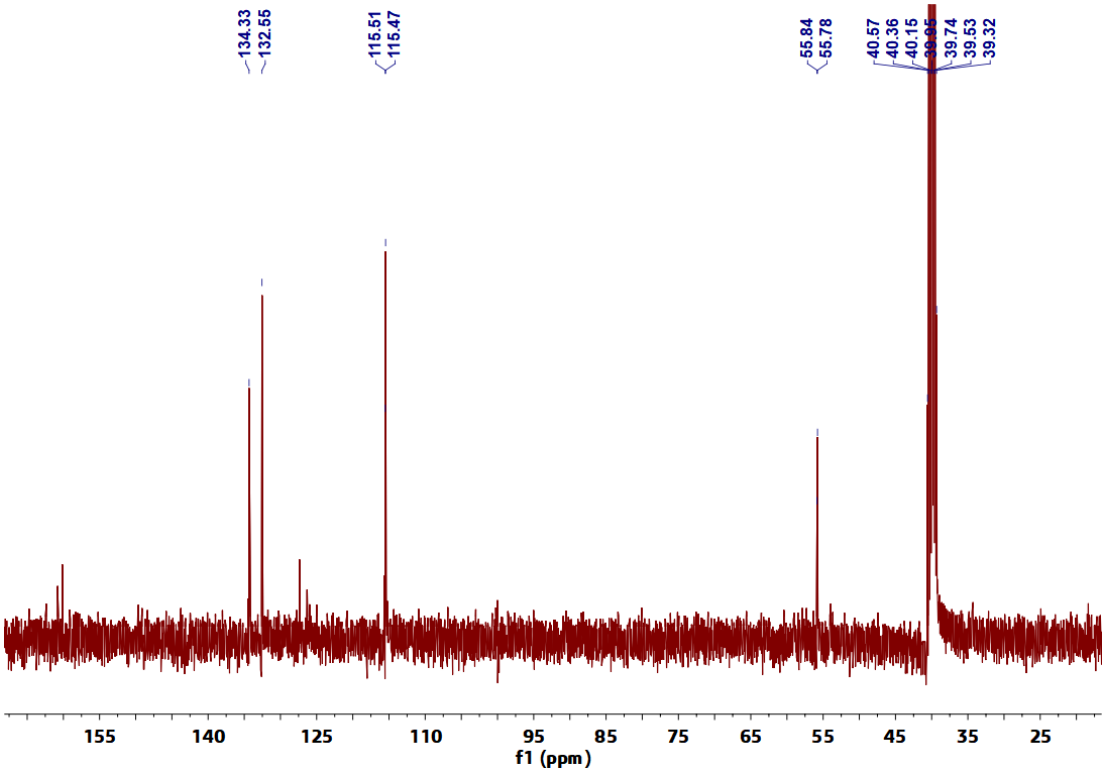
^{1}H NMR (400 MHz, DMSO-d6) of **3l**



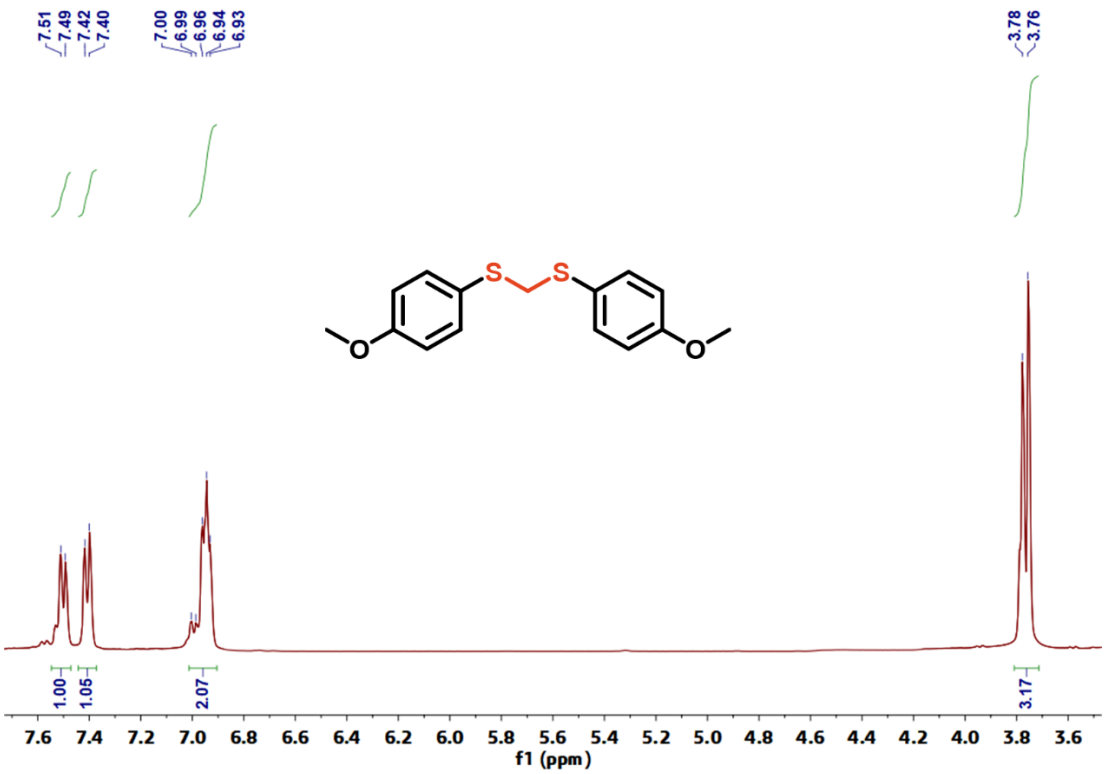
^{13}C NMR (400 MHz, DMSO-d6) of **3l**



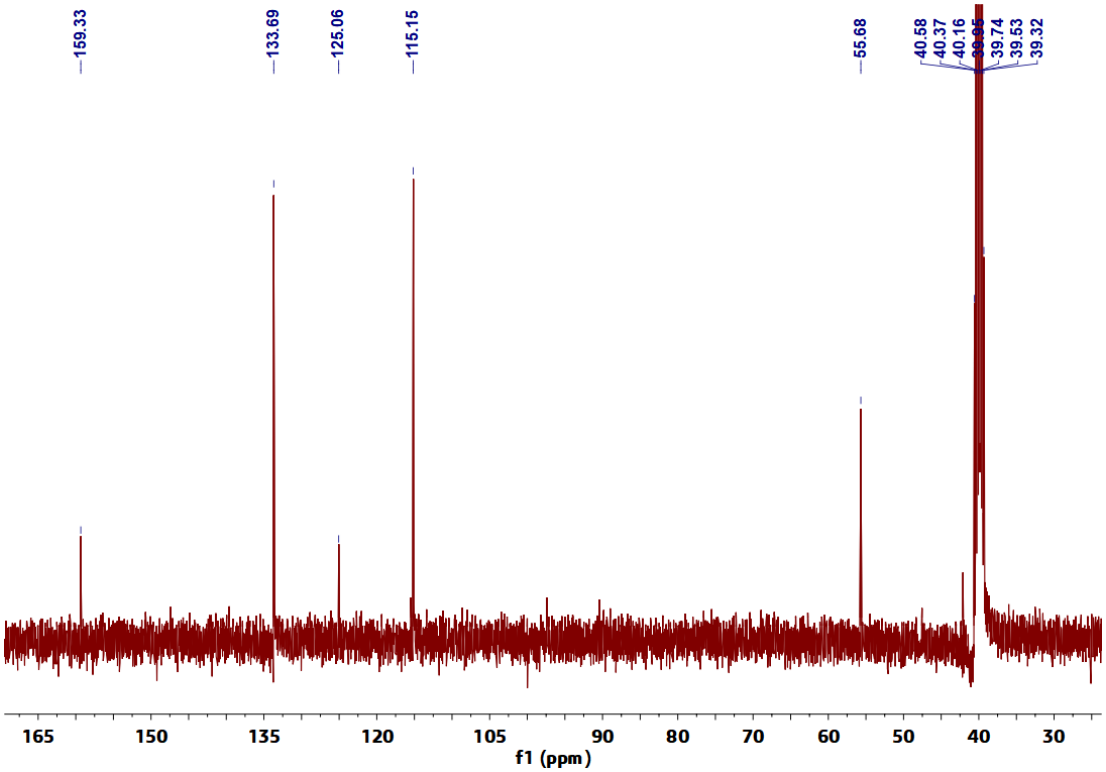
^{1}H NMR (400 MHz, DMSO-d6) of **4m**



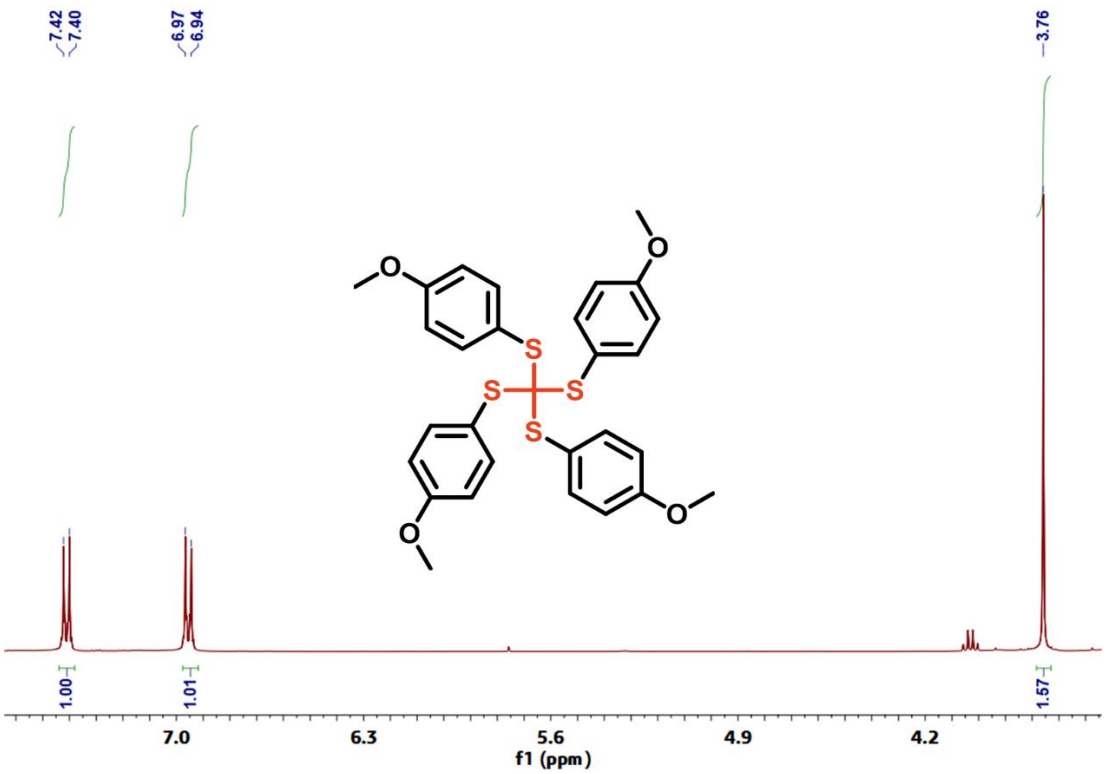
^{13}C NMR (400 MHz, DMSO-d6) of **4m**



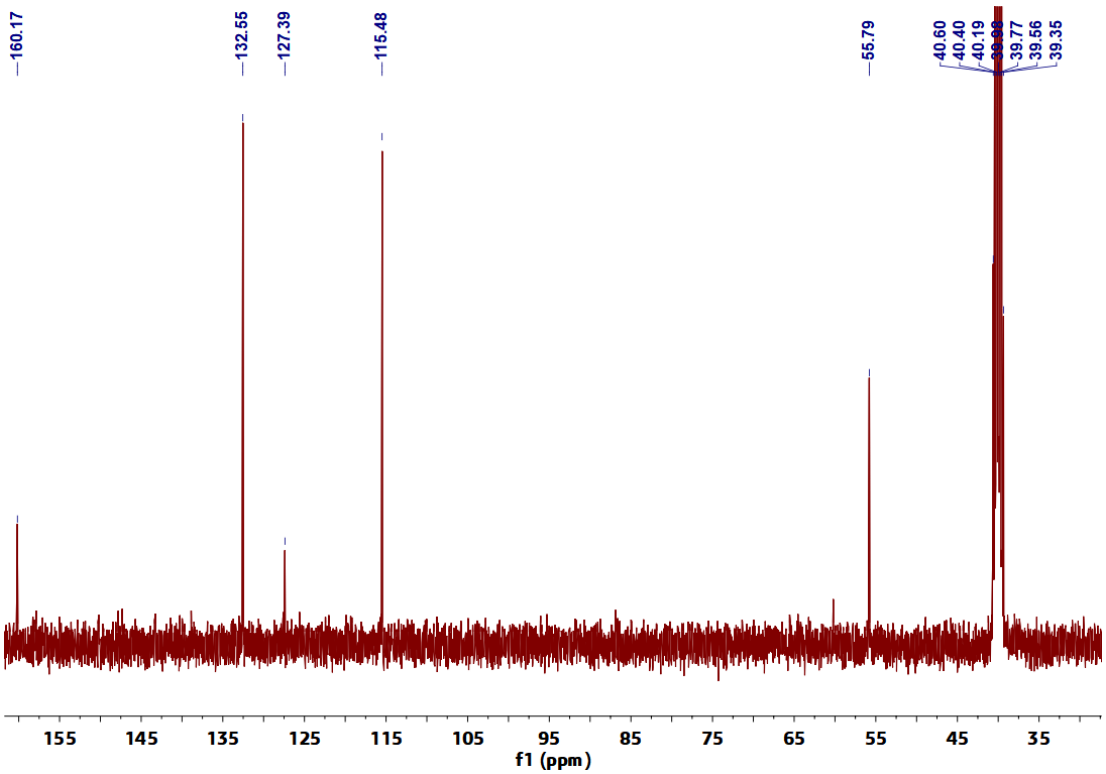
^{1}H NMR (400 MHz, DMSO-d6) of **3n** or **4n**



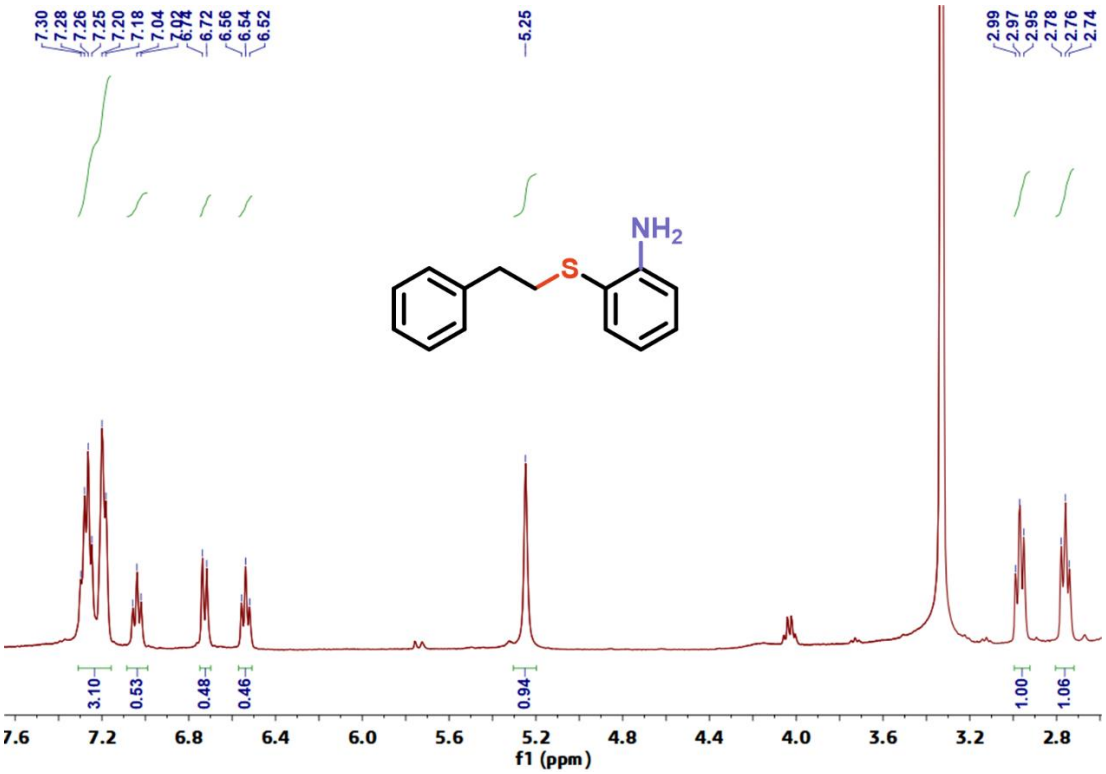
^{13}C NMR (400 MHz, DMSO-d6) of **3n** or **4n**



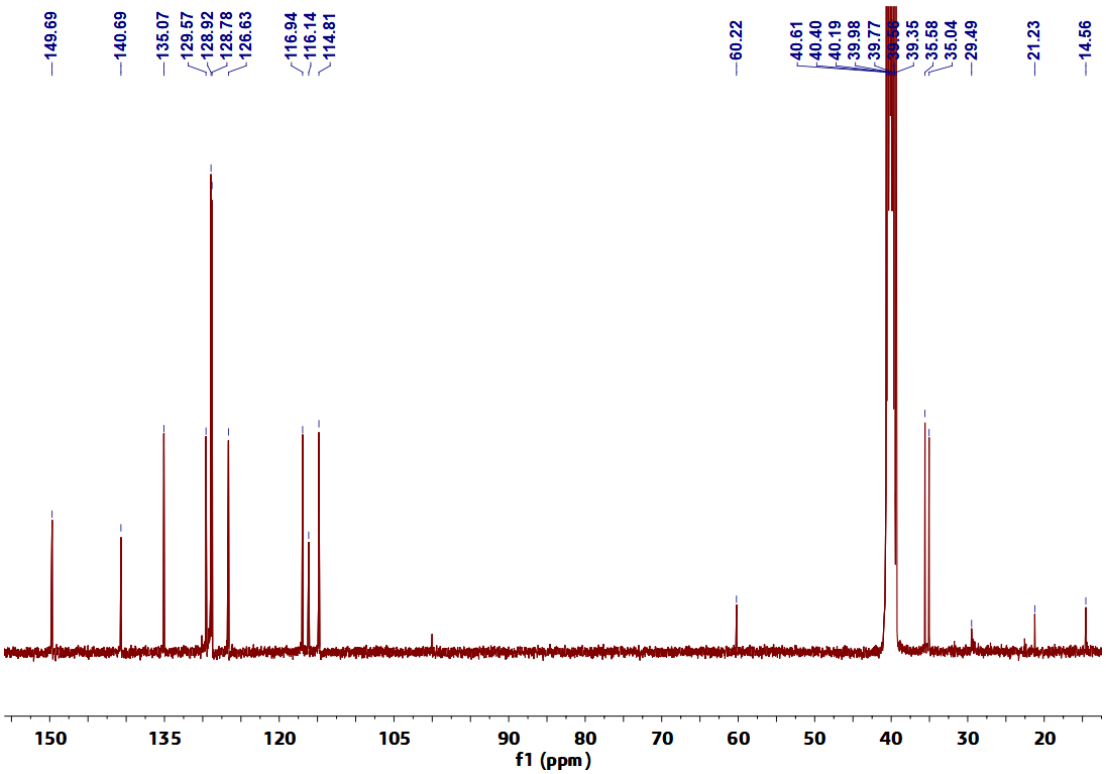
^{1}H NMR (400 MHz, DMSO-d6) of **3o**



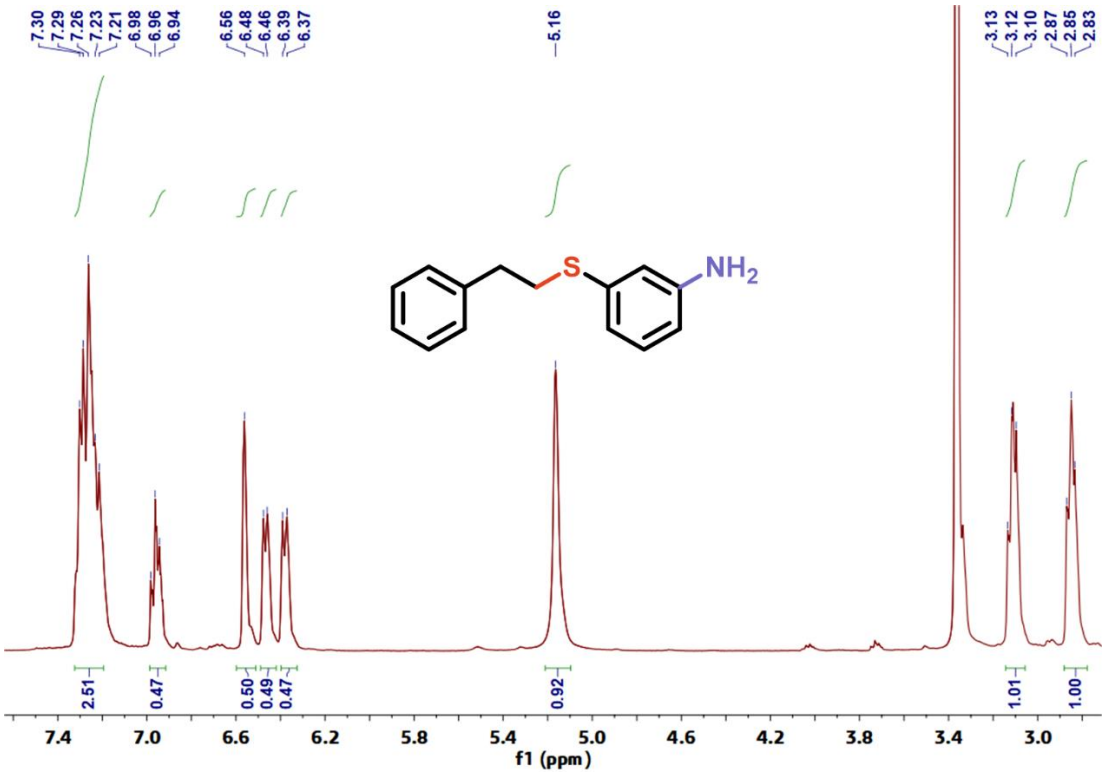
^{13}C NMR (400 MHz, DMSO-d6) of **3o**



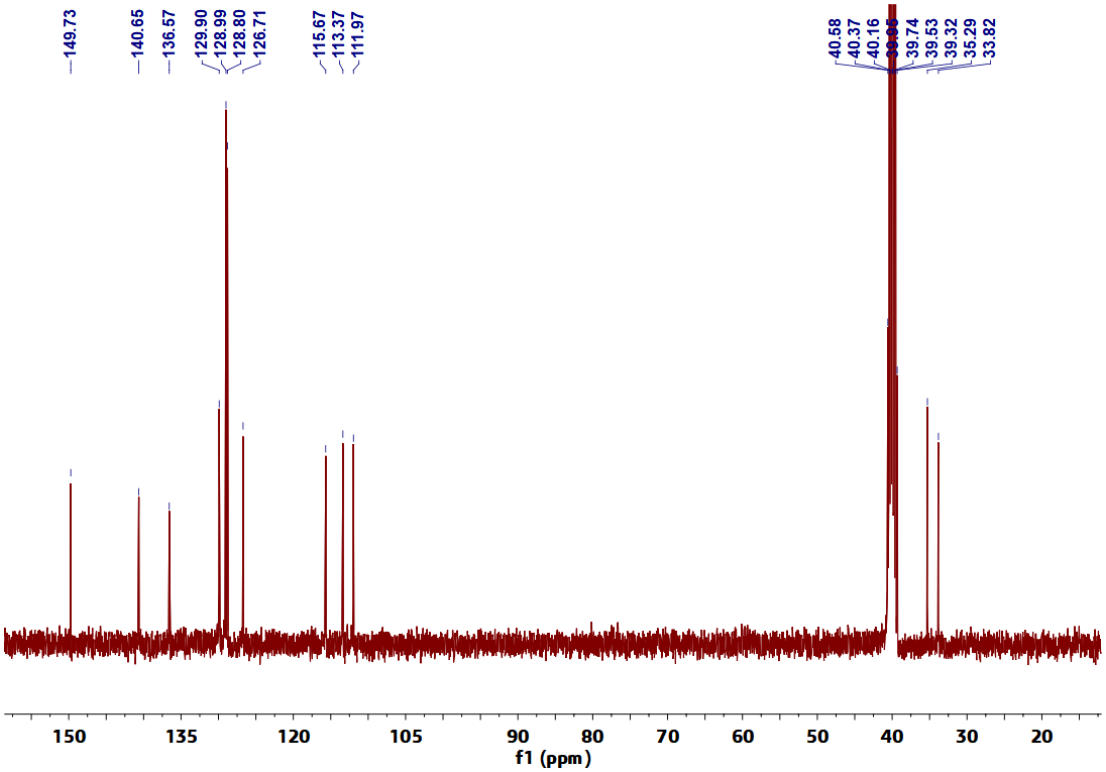
^{1}H NMR (400 MHz, DMSO-d6) of **3p** or **4p**



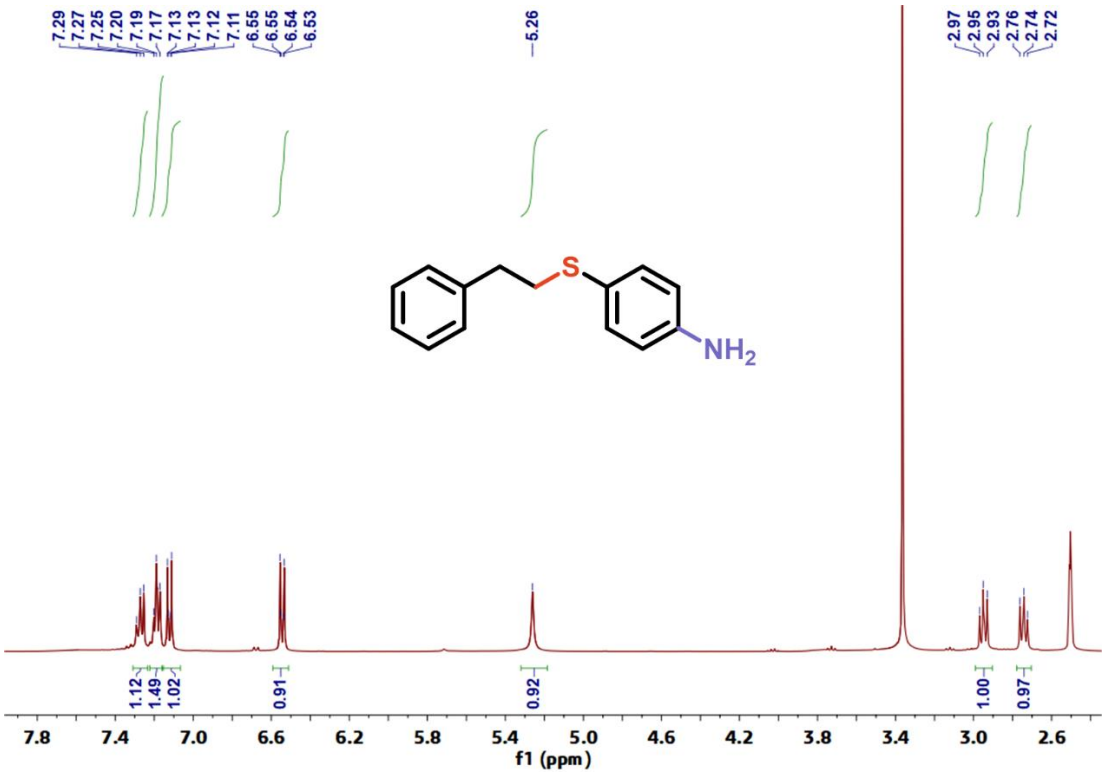
^{13}C NMR (400 MHz, DMSO-d6) of **3p** or **4p**



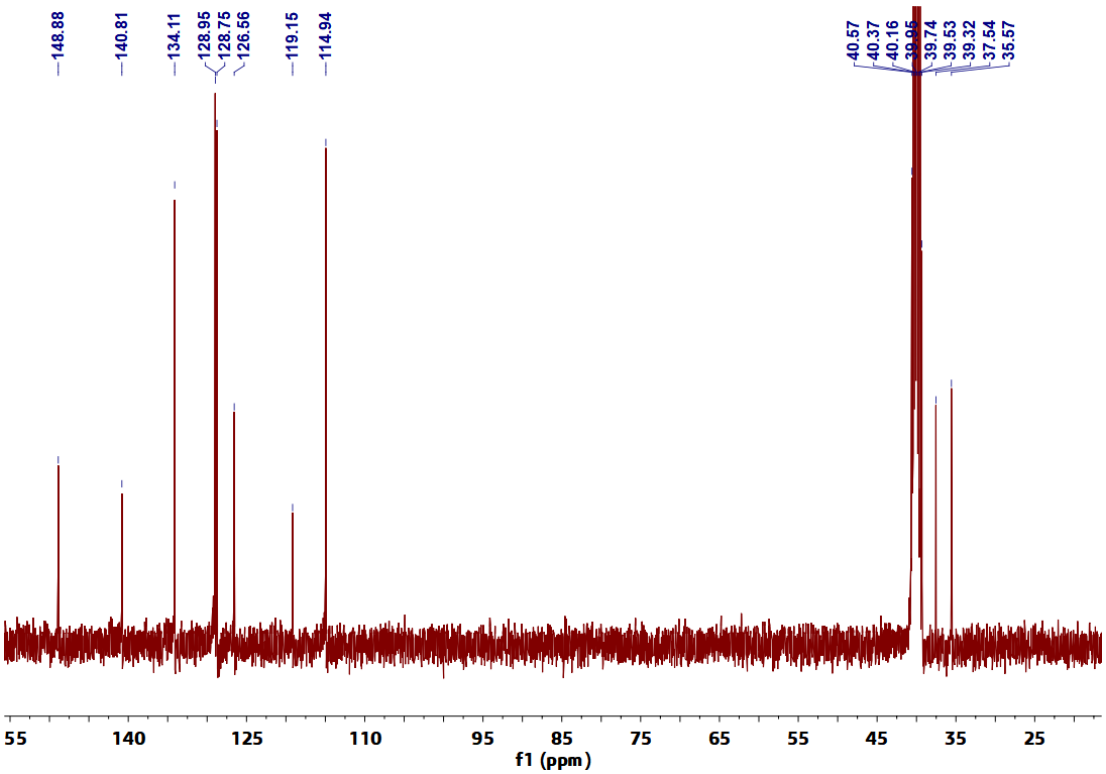
^{1}H NMR (400 MHz, DMSO-d6) of **3q** or **4q**



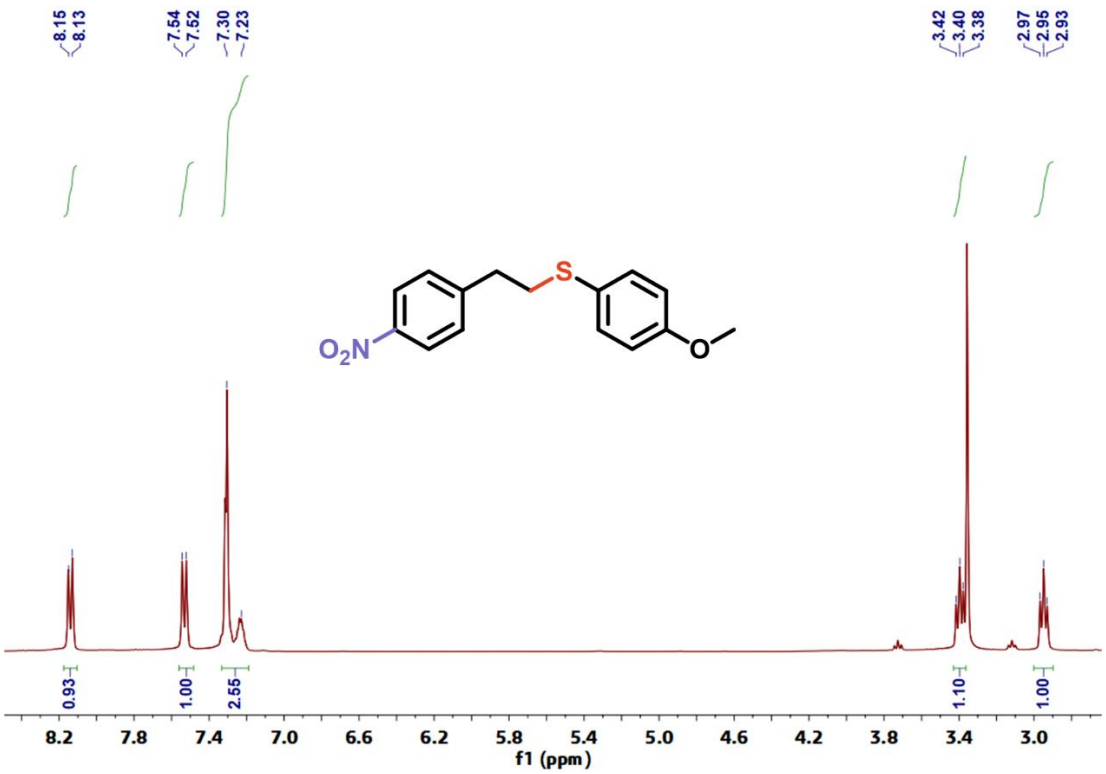
^{13}C NMR (400 MHz, DMSO-d6) of **3q** or **4q**



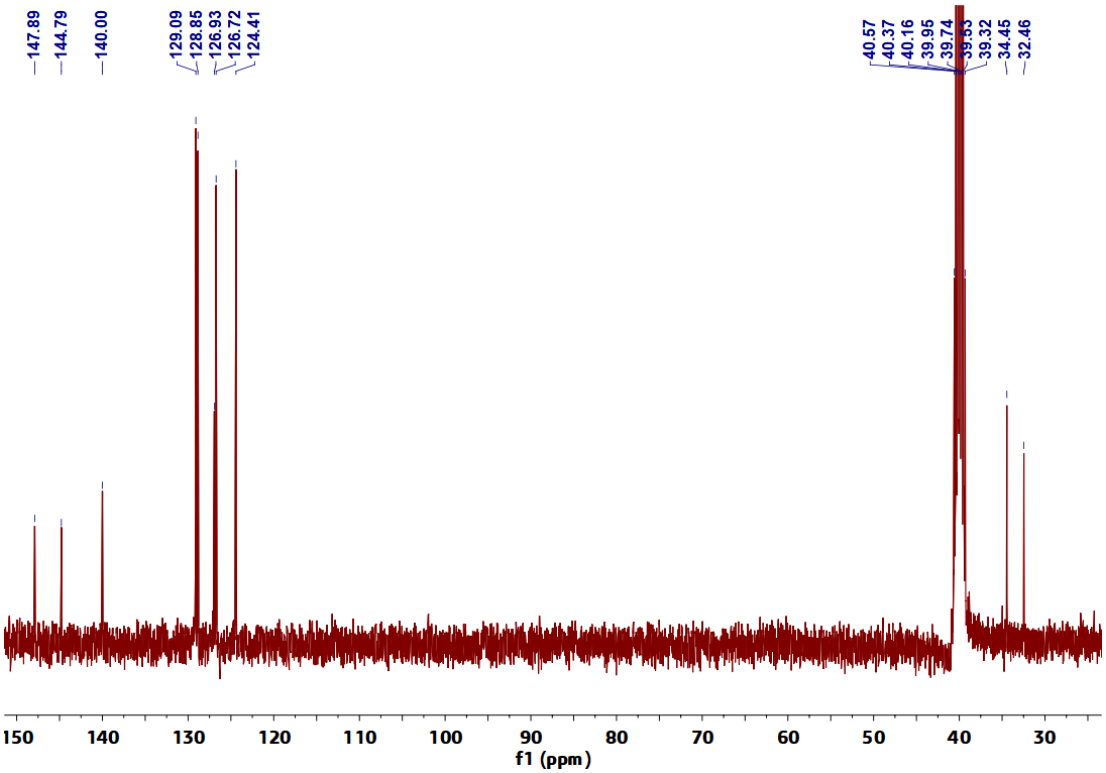
^{1}H NMR (400 MHz, DMSO-d6) of **3r** or **4r**



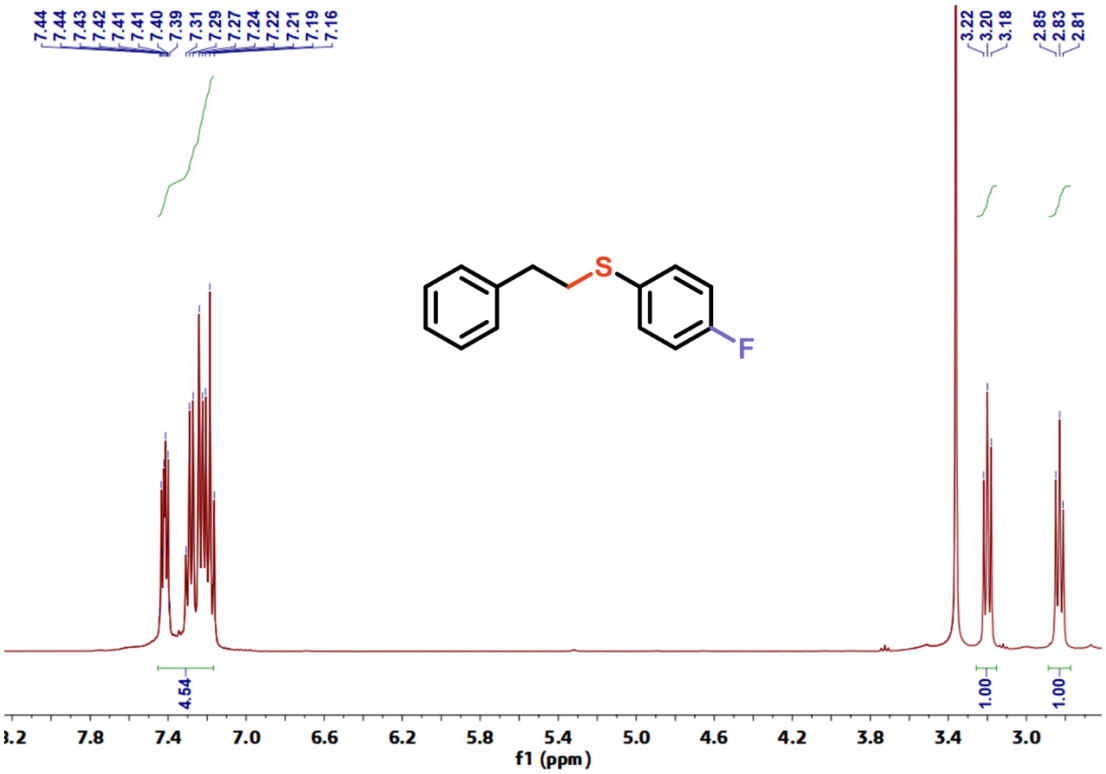
^{13}C NMR (400 MHz, DMSO-d6) of **3r** or **4r**



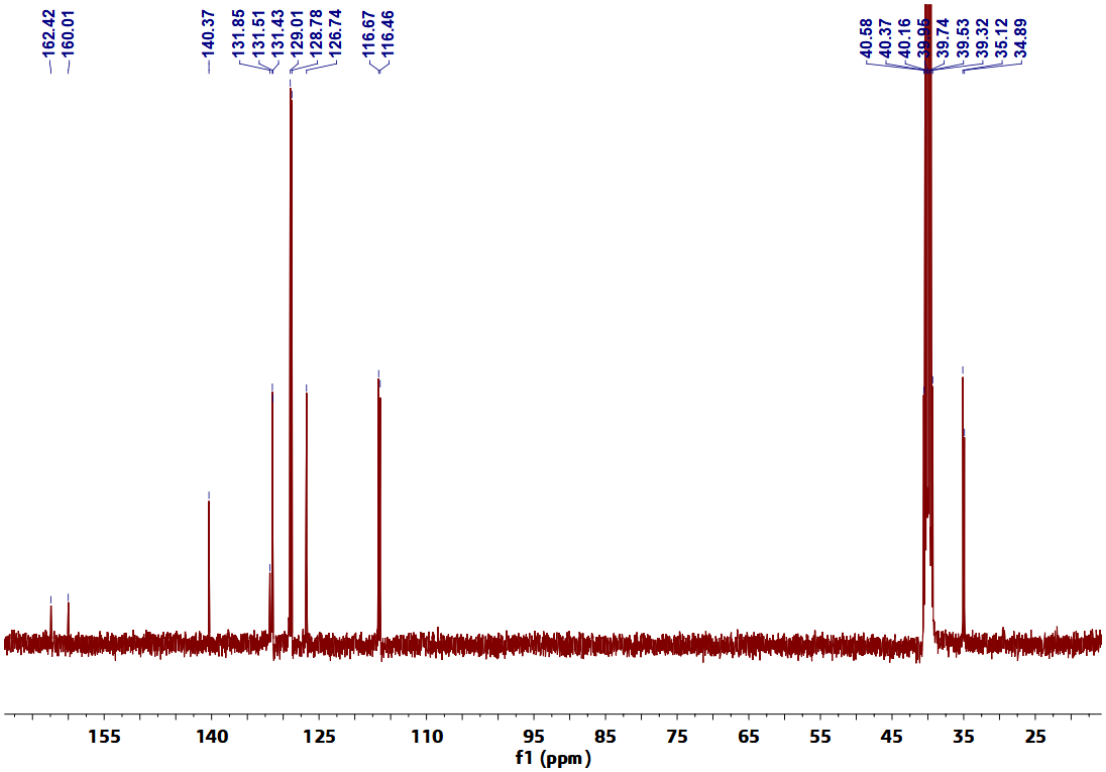
^{1}H NMR (400 MHz, DMSO-d6) of **3s** or **4s**



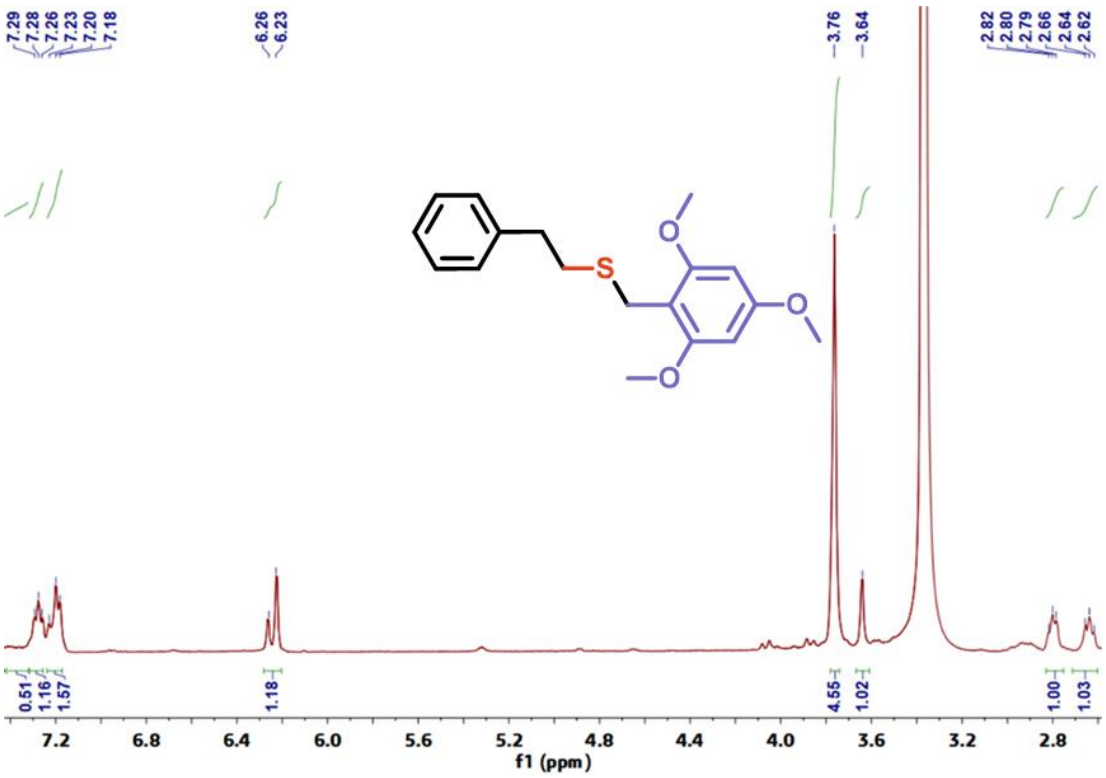
^{13}C NMR (400 MHz, DMSO-d6) of **3s** or **4s**



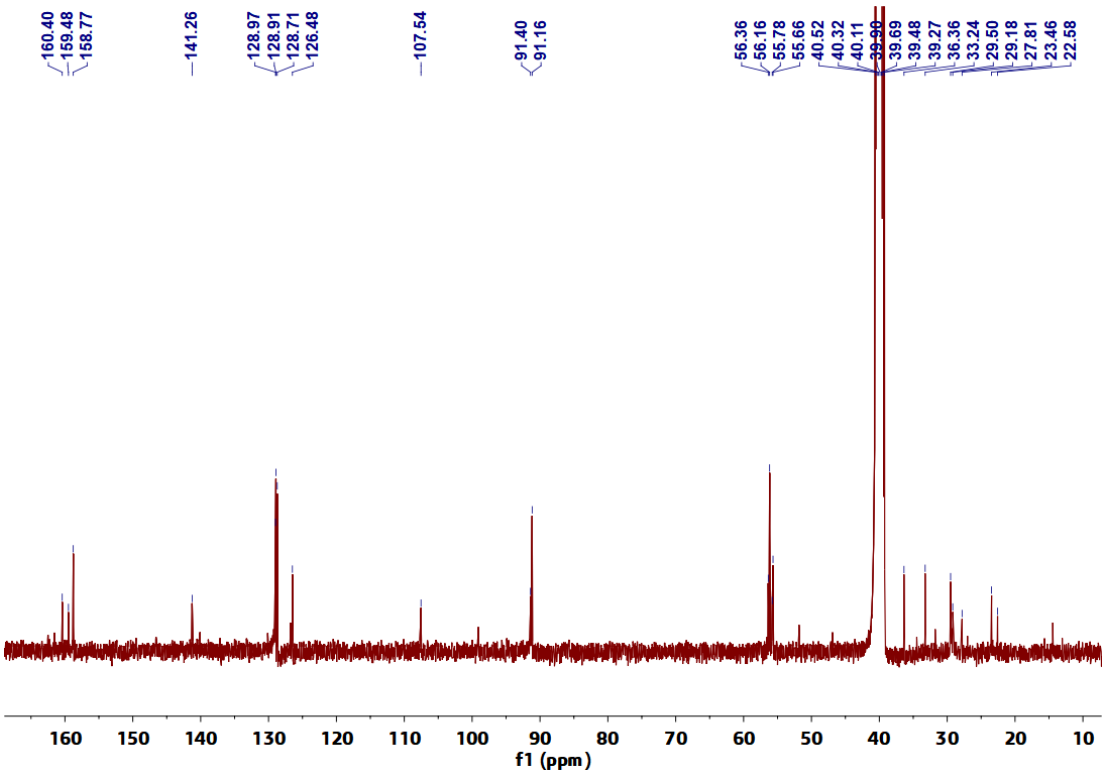
^{1}H NMR (400 MHz, DMSO-d6) of **3t** or **4t**



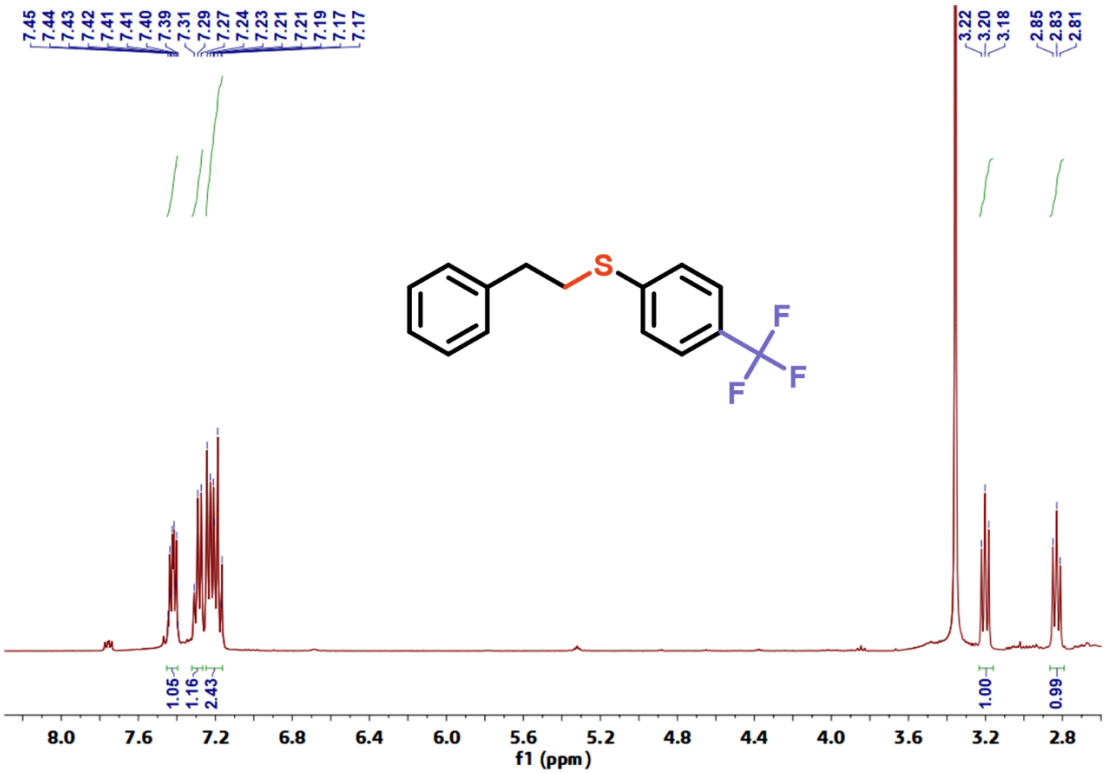
^{13}C NMR (400 MHz, DMSO-d6) of **3t** or **4t**



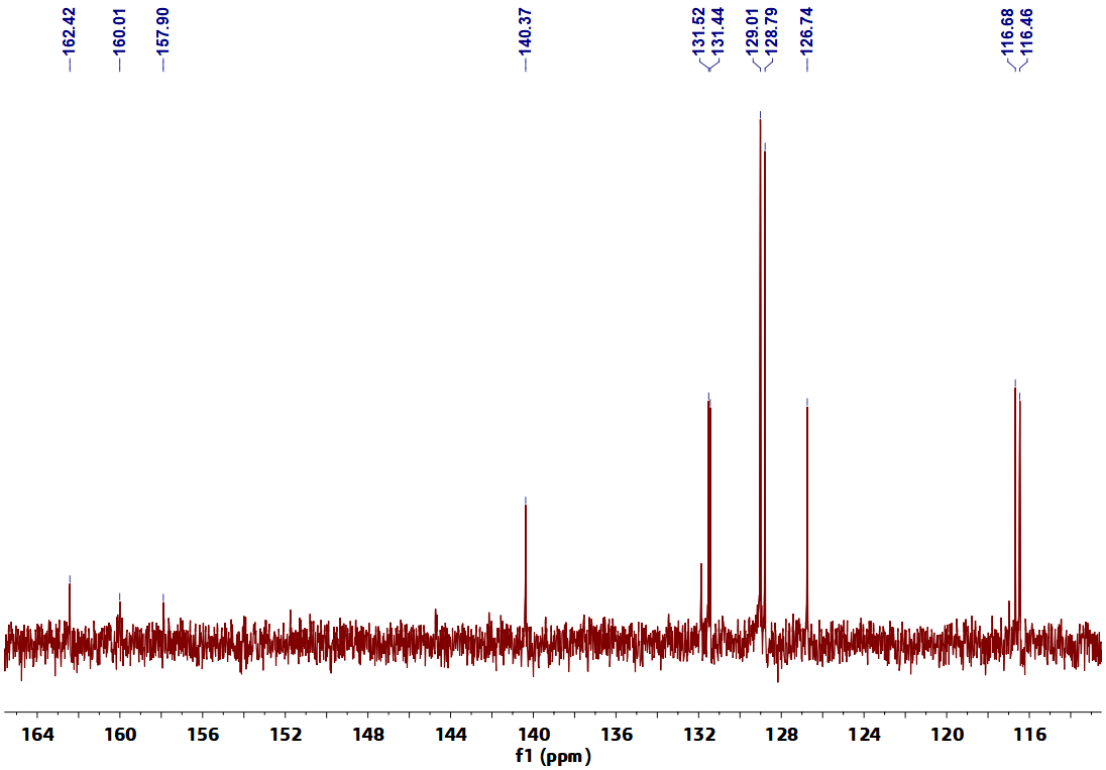
^{1}H NMR (400 MHz, DMSO-d6) of **3u** or **4u**



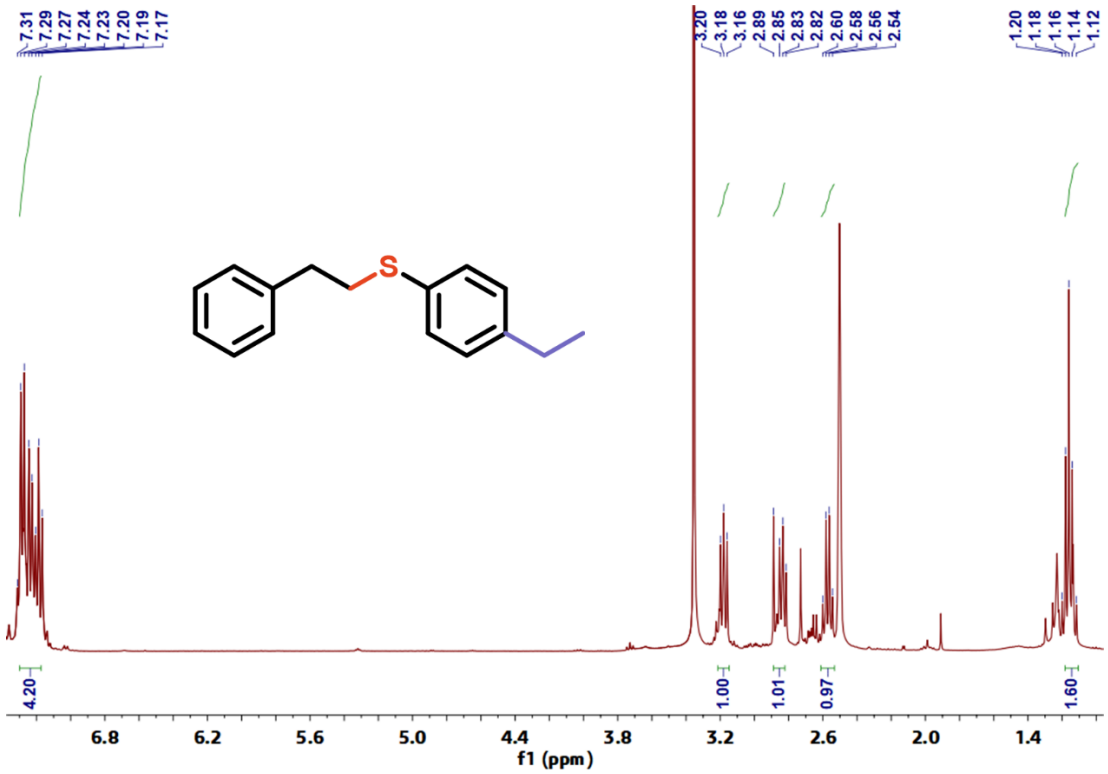
^{13}C NMR (400 MHz, DMSO-d6) of **3u** or **4u**



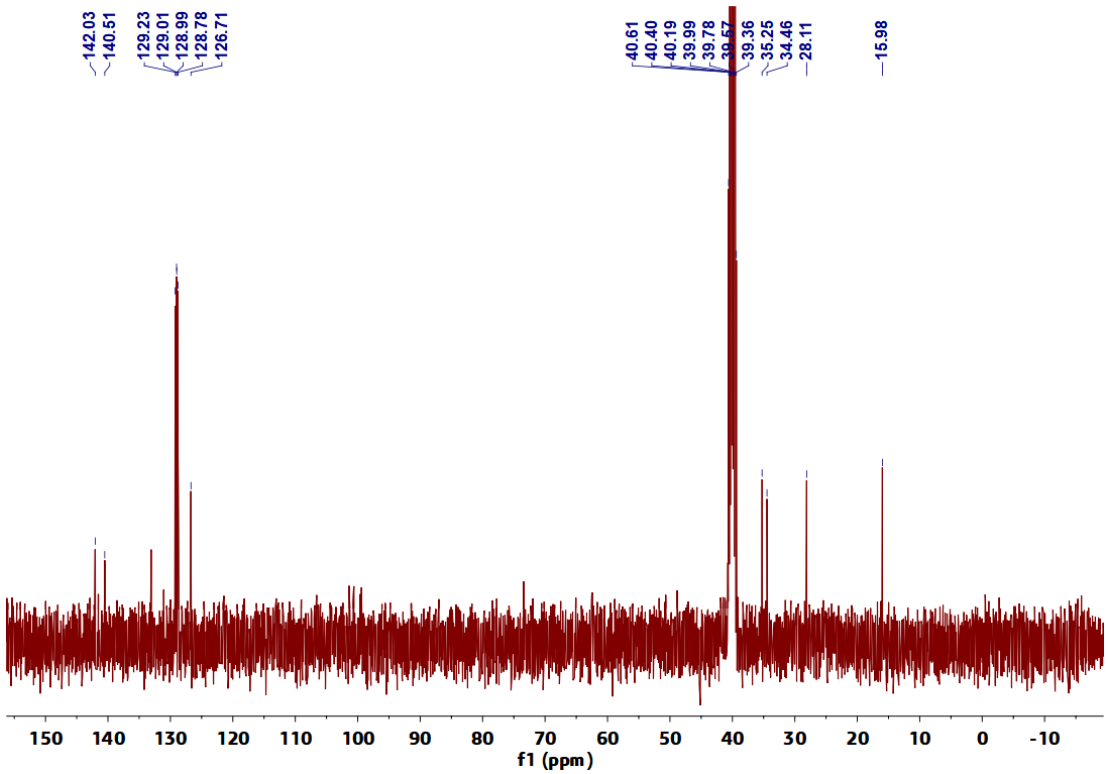
^{1}H NMR (400 MHz, DMSO-d6) of **3v** or **4v**



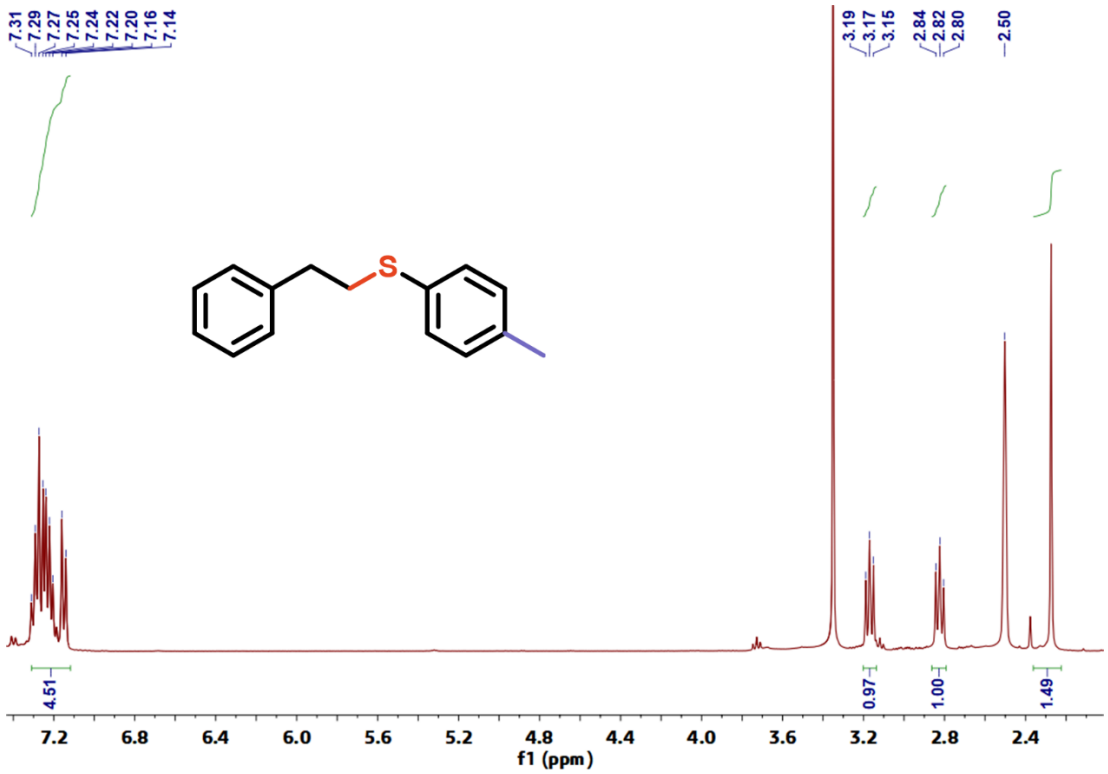
^{13}C NMR (400 MHz, DMSO-d6) of **3v** or **4v**



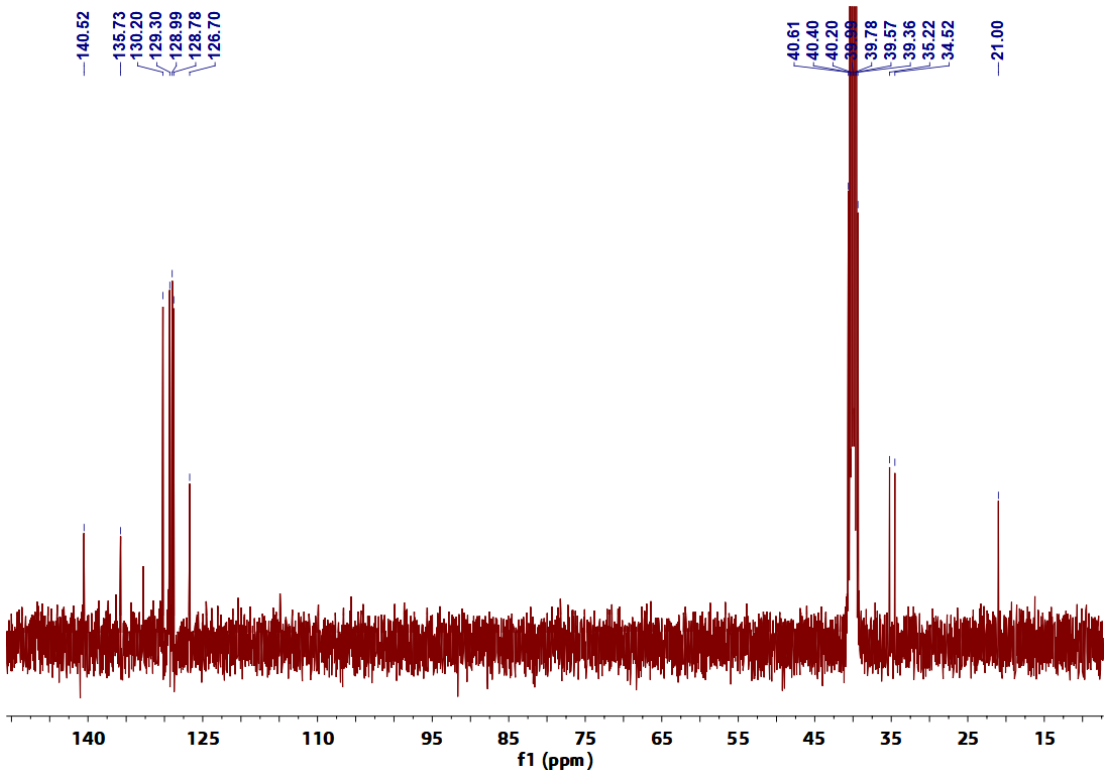
^{1}H NMR (400 MHz, DMSO-d6) of **3w** or **4w**



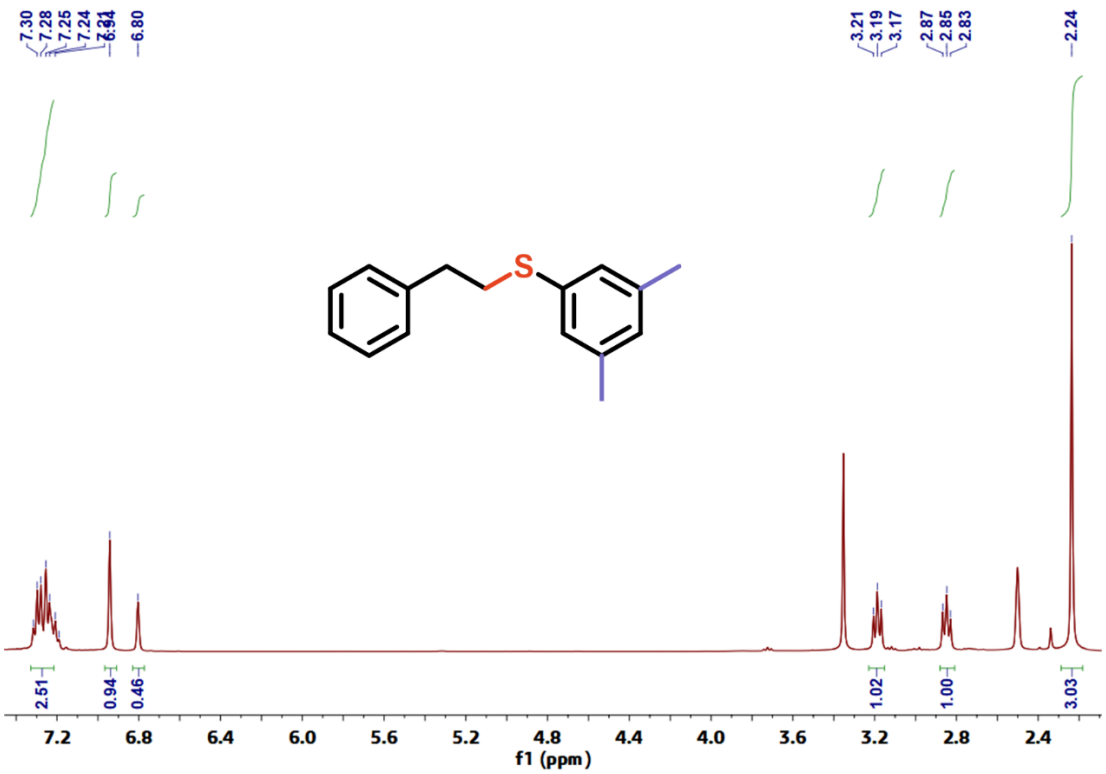
^{13}C NMR (400 MHz, DMSO-d6) of **3w** or **4w**



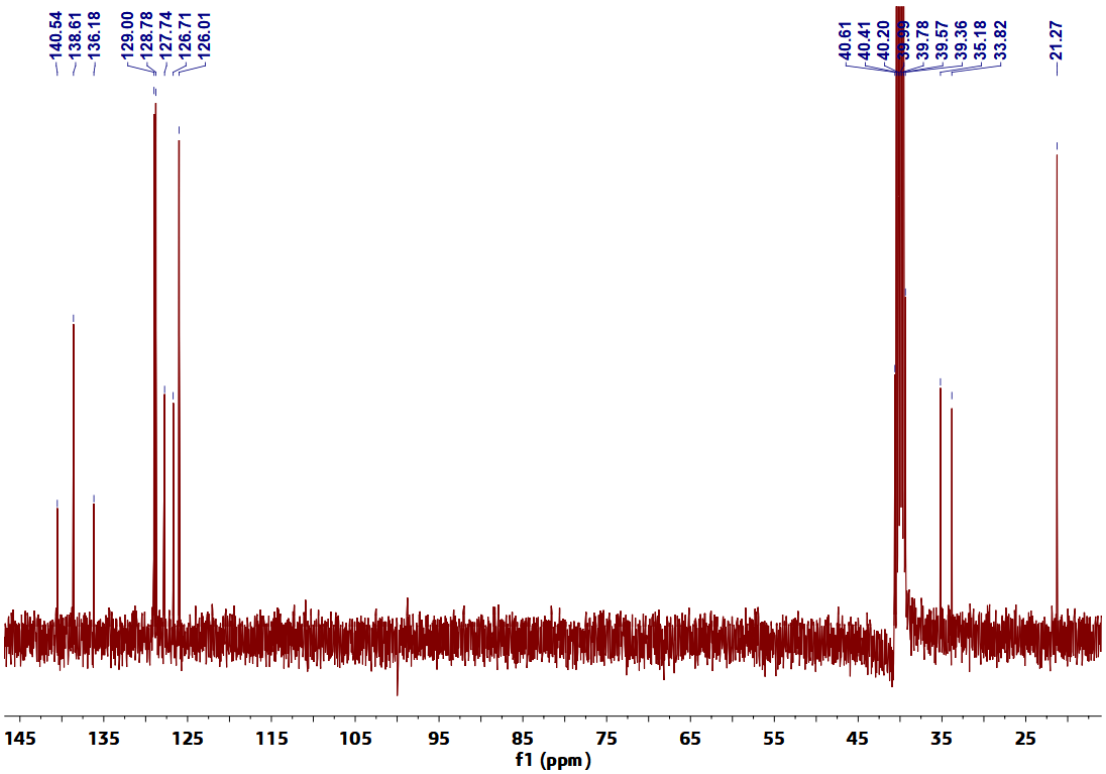
^{1}H NMR (400 MHz, DMSO-d6) of **3x** or **4x**



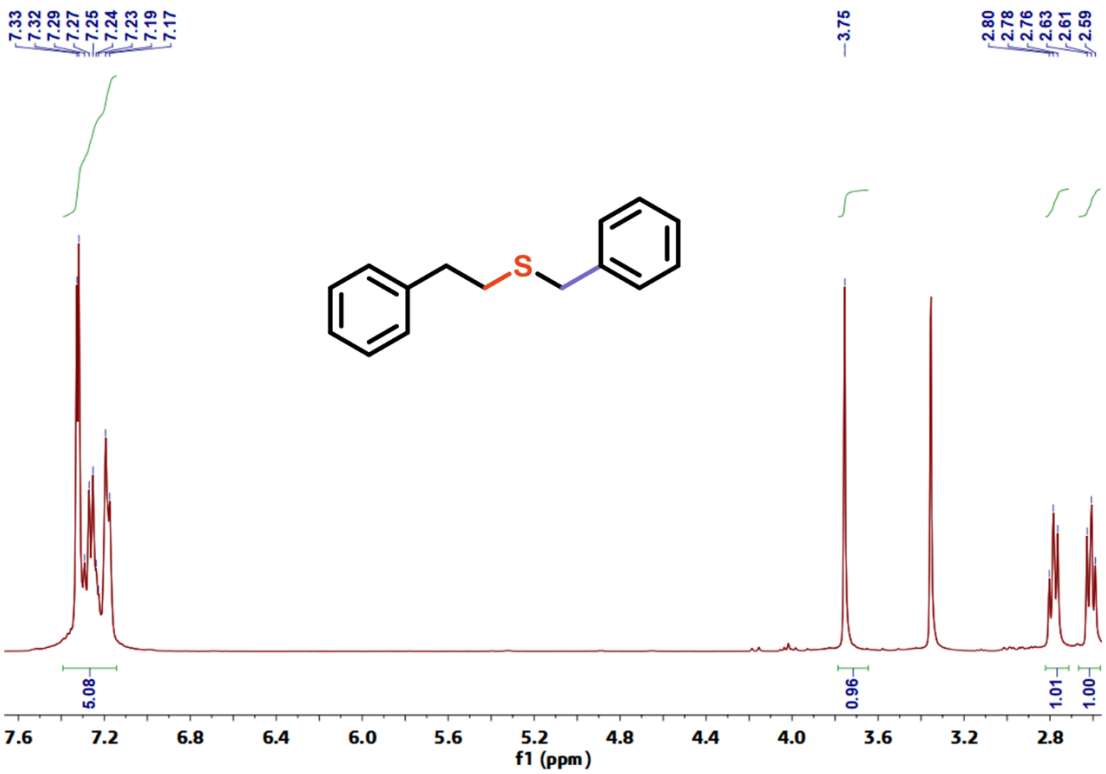
^{13}C NMR (400 MHz, DMSO-d6) of **3x** or **4x**



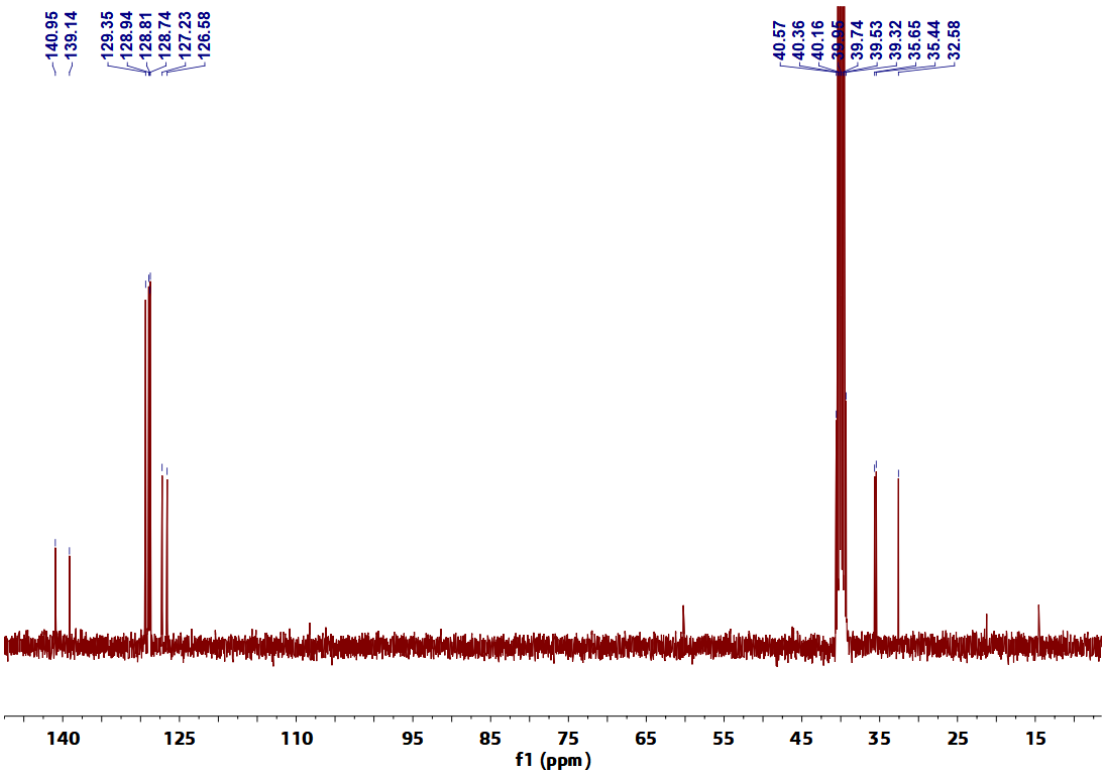
^{1}H NMR (400 MHz, DMSO-d6) of **3y** or **4y**



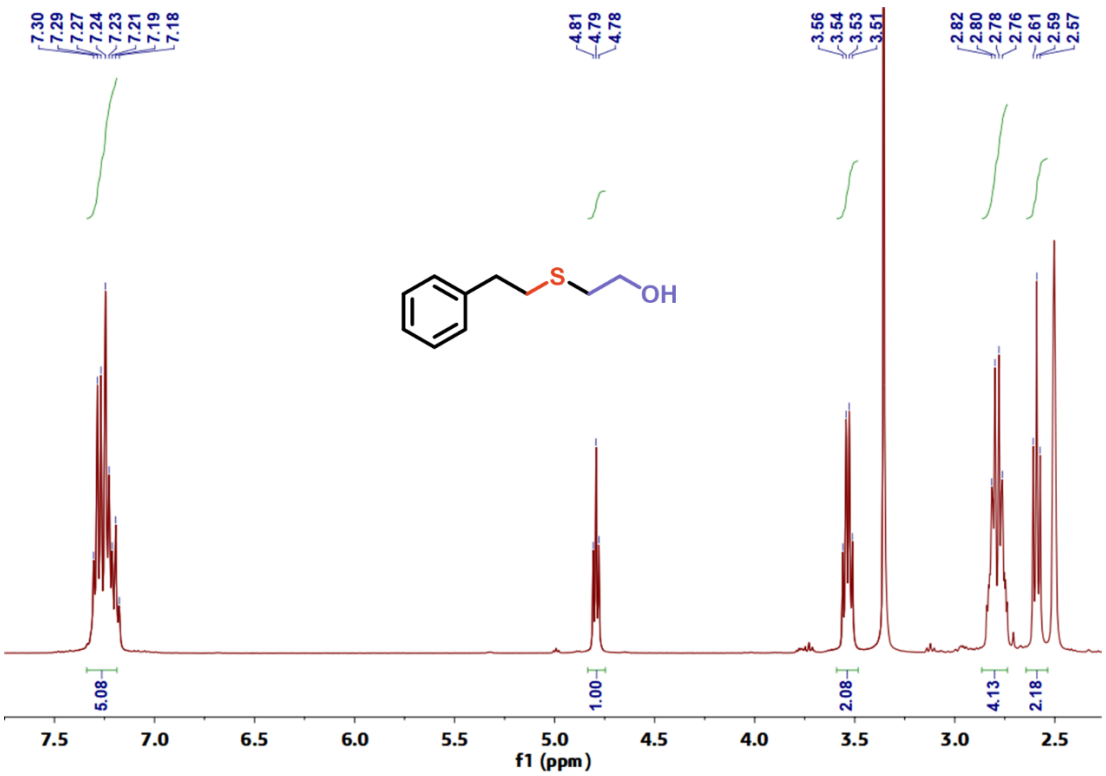
^{13}C NMR (400 MHz, DMSO-d6) of **3y** or **4y**



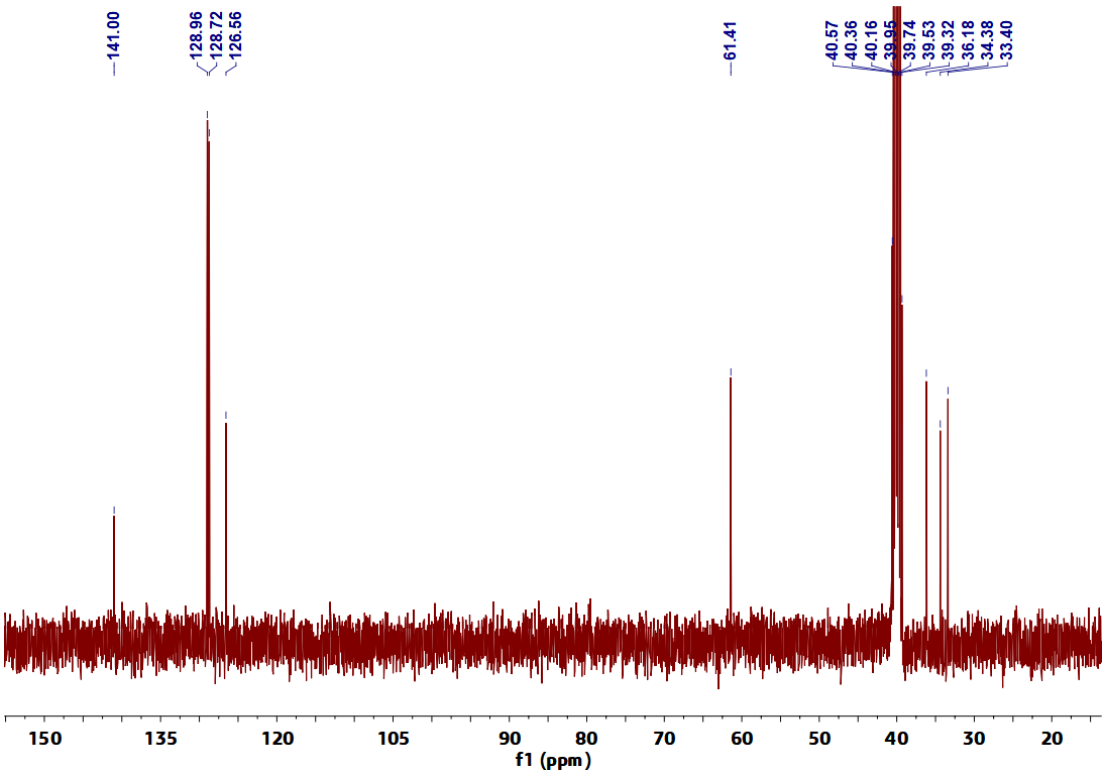
^{1}H NMR (400 MHz, DMSO-d6) of **3z** or **4z**



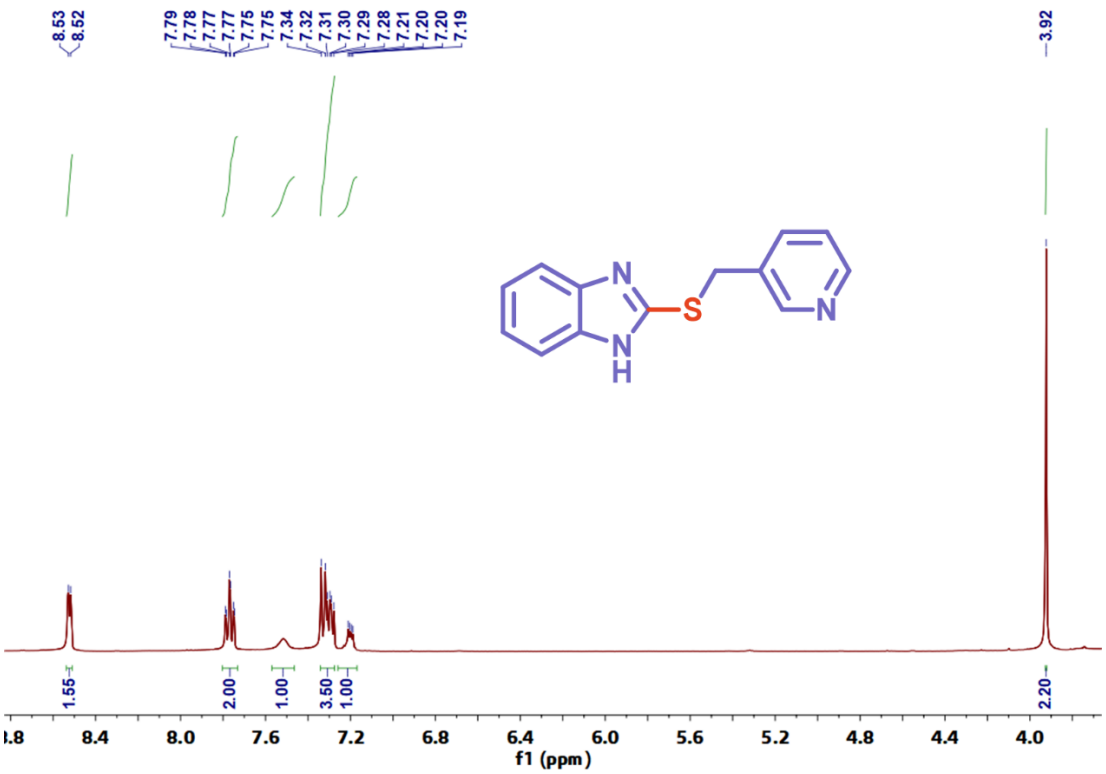
^{13}C NMR (400 MHz, DMSO-d6) of **3z** or **4z**



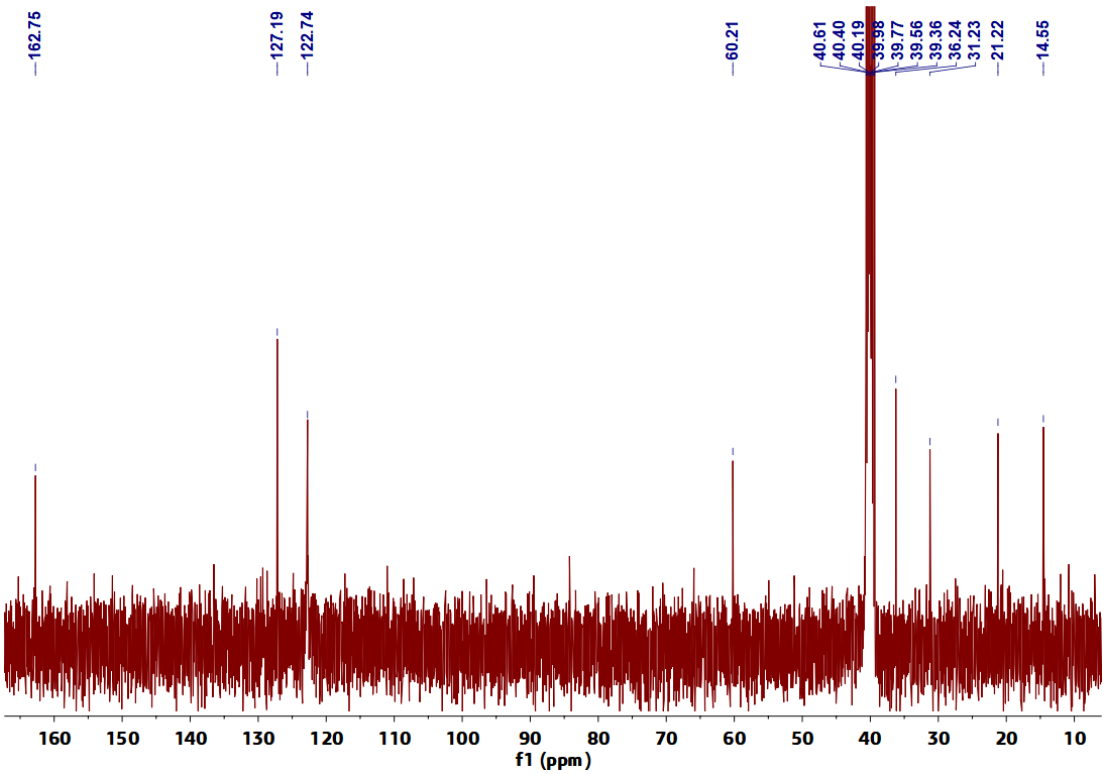
^{1}H NMR (400 MHz, DMSO-d6) of **3α** or **4α**



^{13}C NMR (400 MHz, DMSO-d6) of **3α** or **4α**



^{1}H NMR (400 MHz, DMSO-d6) of **3β** or **4β**



^{13}C NMR (400 MHz, DMSO-d6) of **3β** or **4β**

6. References

(1) Huang, C.; Ci, R.; Qiao, J.; Wang, X.; Feng, K.; Chen, B.; Tung, C.; Wu, L.; Direct Allylic C(sp^3)−H and Vinylic C(sp^2)−H Thiolation with Hydrogen Evolution by Quantum Dots and Visible Light. *Angew. Chem. Int. Ed.* **2021**, *60*, 11779–11783.