Supporting Information

For

Visible-Light-Promoted C–S Cross-Coupling via Intermolecular Charge-Transfer

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General Information

DMSO was purchased from Sigma-Aldrich and sparged with nitrogen for 15 min at room temperature and stored under nitrogen atmosphere. 4′-Bromoacetophenone and *p*-Toluenethiol were purchased from TCI America. Cs_2CO_3 (*ReagentPlus®*, 99%) was purchased from Sigma-Aldrich and the suppliers for the other sources of base are specified in Table S2. Aryl halides and thiols were purchased from Sigma-Aldrich, TCI or Alfa Aesar. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. One, sixteen inch strip of double-density white LEDs, purchased from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH), was wrapped inside a 400 mL beaker and used as a visible light source. The emission spectrum of the white LEDs was measured with an Ocean Optics ADC1000 spectrometer.[1]

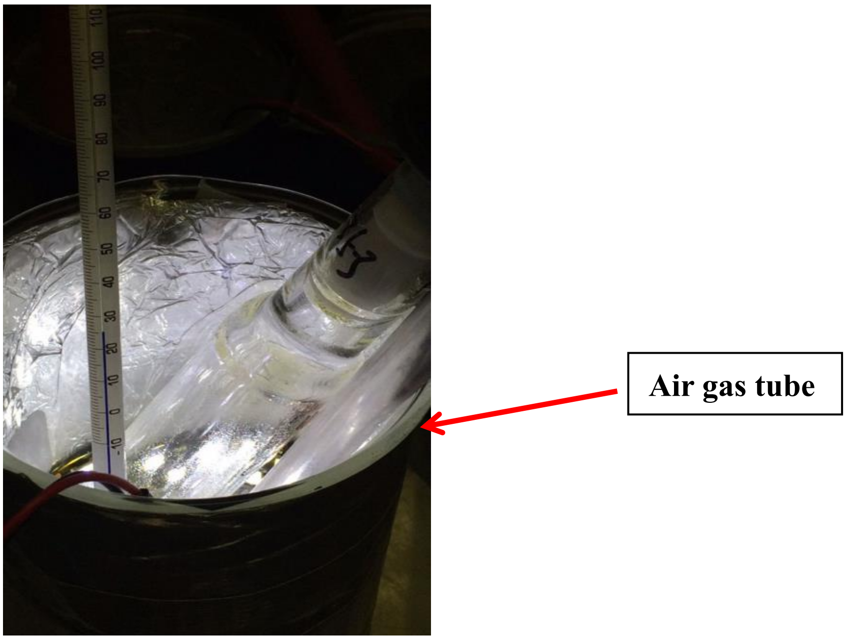
The ^1H and ^{13}C NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz for ^1H or at 75MHz, 100 MHz or 125 MHz for ^{13}C NMR, respectively. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received. All ^1H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvents. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets…etc, br = broad), coupling constant (Hz) and integration. All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.0 ppm). Trimethyoxybenzene was used as an internal standard for NMR yields from proton analysis for the C-S bond formation reaction.

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 40-63 μm from Aldrich. Fractions were analyzed by TLC using TLC silica gel F254 250 μm precoated-plates from Merck and permanganate stain was used for UV-inactive compounds.

ESI mass spectrometry analysis was performed at the University of Colorado Boulder mass spectrometry facility using a Synapt G2 HDMS instrument, or Agilent 6220 TOF LC/MS with Agilent 1200 HPLC with multi-mode (combined ESI and APCI) at Colorado State University.

General Experimental Procedure

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with a compressed air gas tube for cooling. After the time specified in the reaction schemes, the reaction mixture was washed with water and extracted with EtOAc. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

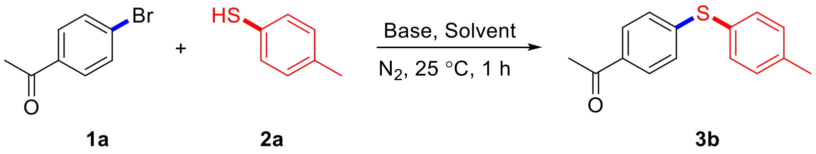


Air gas tube

Figure S1. Photograph of the reaction setup for C-S bond formation reaction using visible light LED beakers.

Optimization and Control Experiments

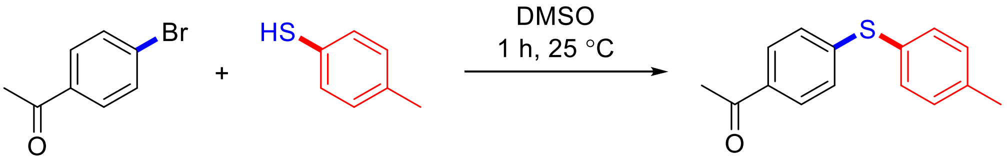
Table S1. Visible-Light Promoted C-S couplings, Effect of Reaction Parameters[a]



Entry	Base (eq)	Light	Solvent	Y (%)[b]
1	Cs_2CO_3 (1.5)	Yes	DMSO	97[c]
2	Cs_2CO_3 (1.5)	No	DMSO	Trace
3	Cs_2CO_3 (1.0)	Yes	DMSO	87
4	Cs_2CO_3 (0.5)	Yes	DMSO	12
5	Cs_2CO_3 (0.0)	Yes	DMSO	0
6	Cs_2CO_3 (1.5)	Yes[d]	DMSO	0
7	K_2CO_3 (1.5)	Yes	DMSO	91
8	Na_2CO_3 (1.5)	Yes	DMSO	24
9	Cs_2CO_3 (1.5)	Yes	DMF	35
10	Cs_2CO_3 (1.5)	Yes	CH_3CN	0
11	Cs_2CO_3 (1.5)	Yes	DMA	76

[a]The beaker with white light emitting diodes (LEDs) was cooled to room temperature with compressed air. [b]NMR yield using trimethoxybenzene as internal standard. [c]Isolated yield. [d]Reaction performed in the presence of air.

Table S2. Visible-Light Promoted C-S couplings, Effect of Base Purity



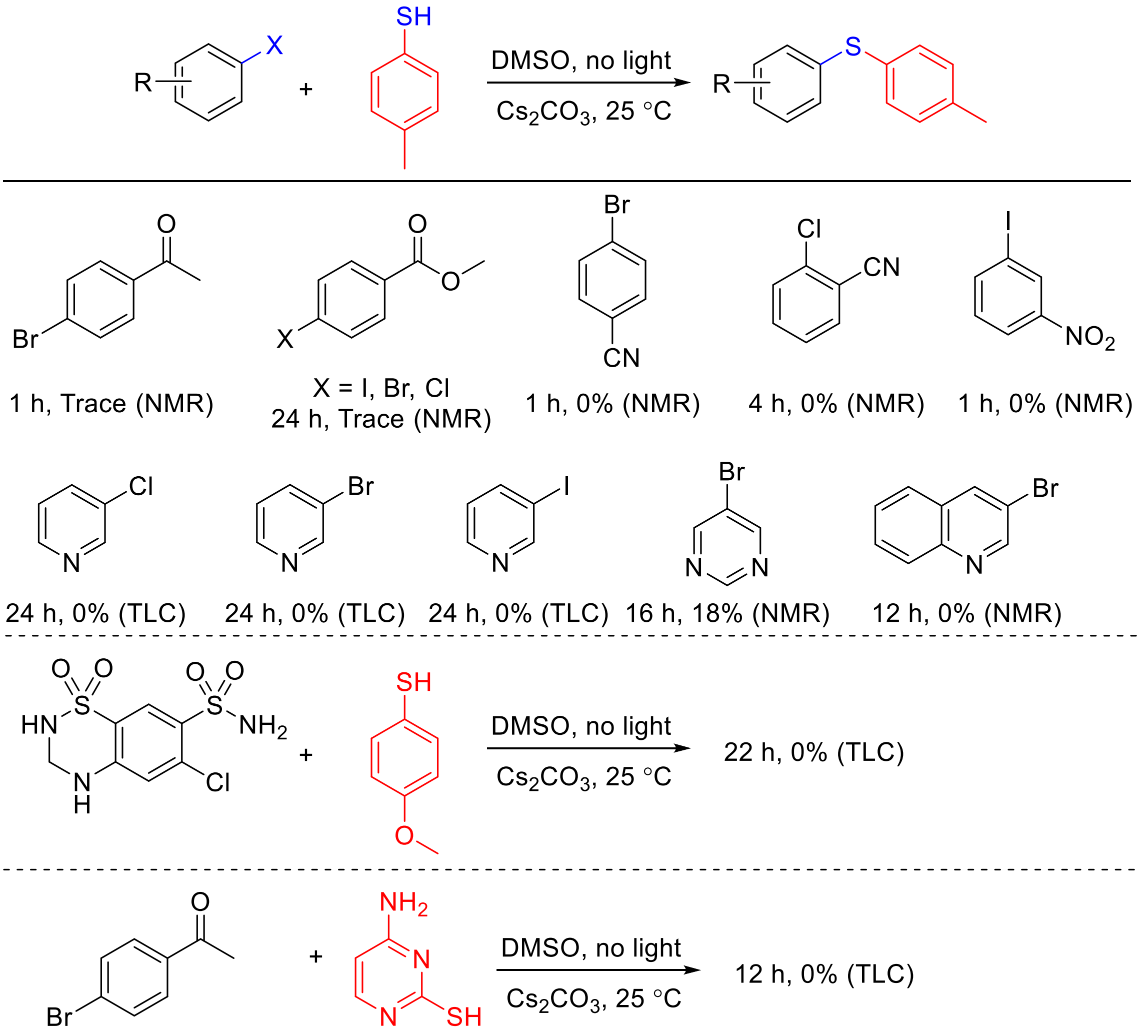
Entry	Base (1.5 eq)	Light	Atmosphere	Product (%)
1	Cs_2CO_3	No	N_2	trace
2	Cs_2CO_3	Yes	Air	0
3	No	Yes	N_2	0
4	Cs_2CO_3[a]	Yes	N_2	95
5	K_2CO_3[b]	Yes	N_2	92
6	Cs_2CO_3[c]	Yes	N_2	92
7	K_2CO_3[d]	Yes	N_2	96

[a]Sigma Aldrich 99.995% trace metals basis. [b]Sigma Aldrich 99.995% trace metals basis. [c]Alfa Aesar 99.994% trace metals basis. [d]Alfa Aesar 99.997% trace metals basis.

Control experiment with base of different grade purchased from different vendors.

Four reactions were performed in parallel (DMSO, 25 °C, *p*-Toluenethiol, 1.5 eq Base, 0.2 mmol scale): a) Cs_2CO_3 (Aldrich, 99.995% trace metal basis), b) K_2CO_3 (Aldrich, 99.995%), c) Cs_2CO_3 (Alfa-Aesar, 99.994%), and d) K_2CO_3 (Alfa-Aesar, 99.997%). The reactions were monitored by NMR and no appreciable differences in conversion and selectivity in these four reactions were observed.

Control experiments with substrates which could proceed through a S_NAr reaction.

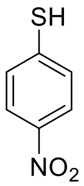


Determined using TLC: Thin Layer Chromatography or NMR: Nuclear Magnetic Resonance

Failed Substrates and S$_{n}$Ar Substrates

The substrates (**1-13**) did not yield products under standard reaction conditions. The substrates (**14-18**) yielded products even without light, which presumably reacted via S$_{n}$Ar (nucleophilic aromatic substitution) mechanism.

Failed Substrates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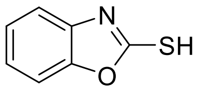
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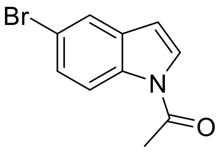
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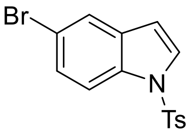
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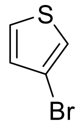
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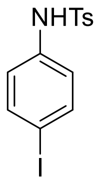
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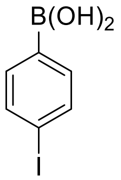
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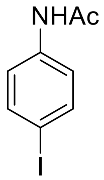
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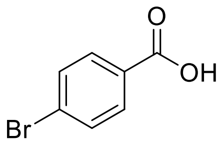
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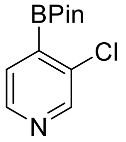
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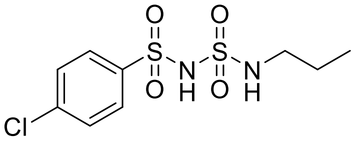
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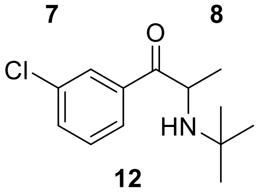
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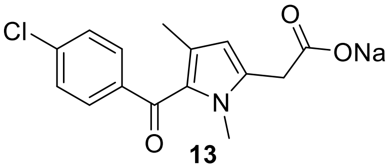
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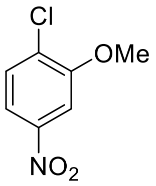
S$_{n}$Ar Substrates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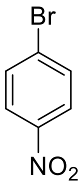
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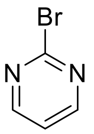
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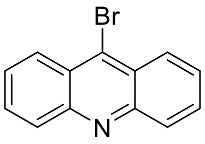
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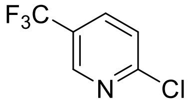
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Mechanistic Considerations

a. UV-vis Absorption Spectra

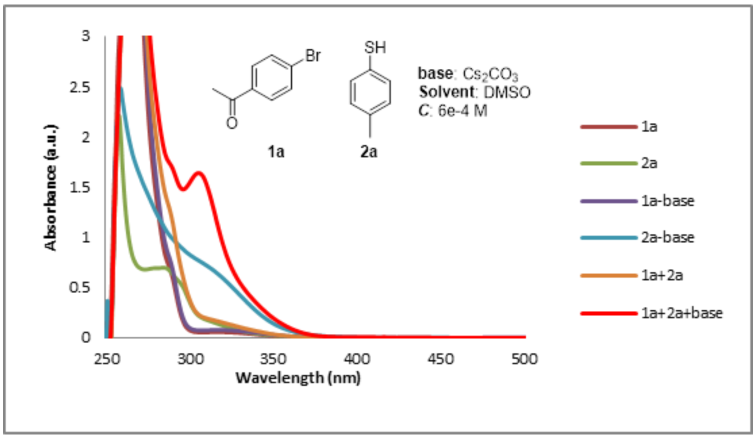


Figure S2. Control experiment with UV-visible absorption spectra (*c* = 6e-4 M)

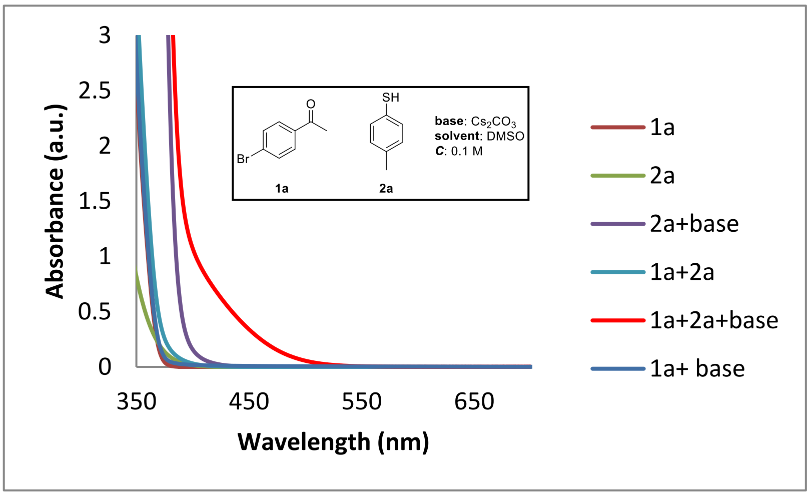


Figure S3. Control experiment with UV-visible absorption spectra (*c* = 0.1 M)

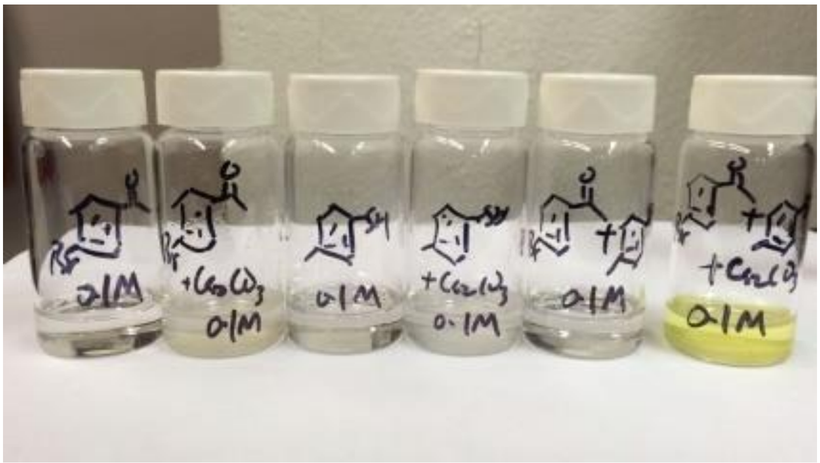


Figure S4. Photograph showing the control experiments with various mixtures of **1a**, **2a**, and Cs_2CO_3 (*c* = 0.1 M). The solution is visibly yellow in color when **1a**, **2a**, and Cs_2CO_3 were mixed together in DMSO.

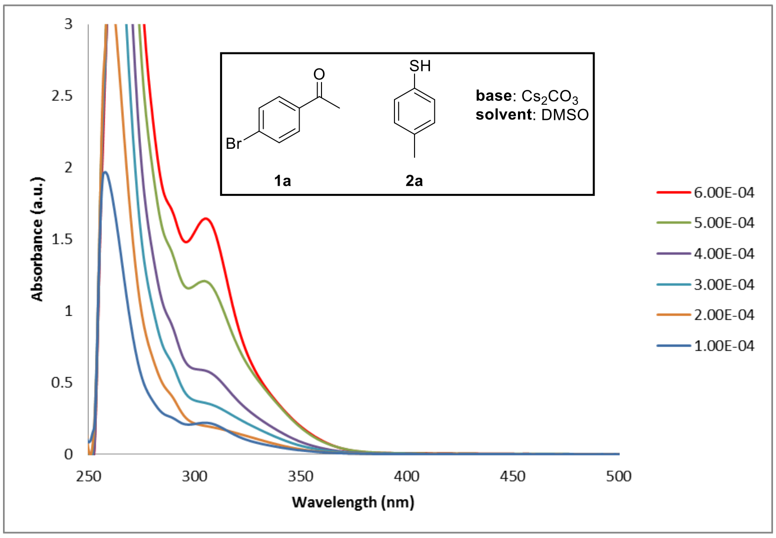


Figure S5. UV-vis absorption spectra at different concentrations (~10^{-4} M).

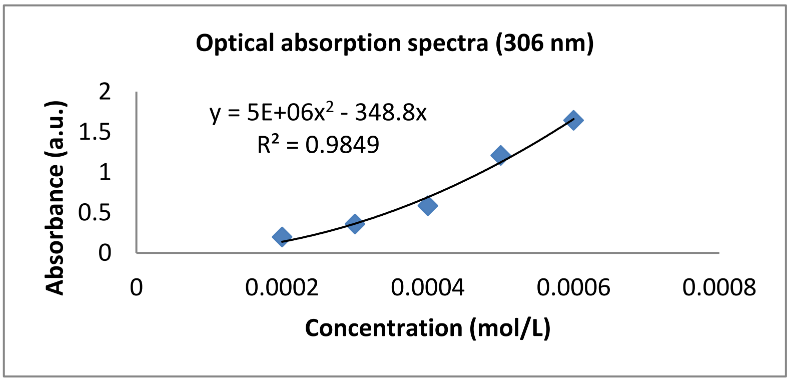


Figure S6. Plot of absorbance as a function of concentrations (~10^{-4} M). Path length = 1 cm.

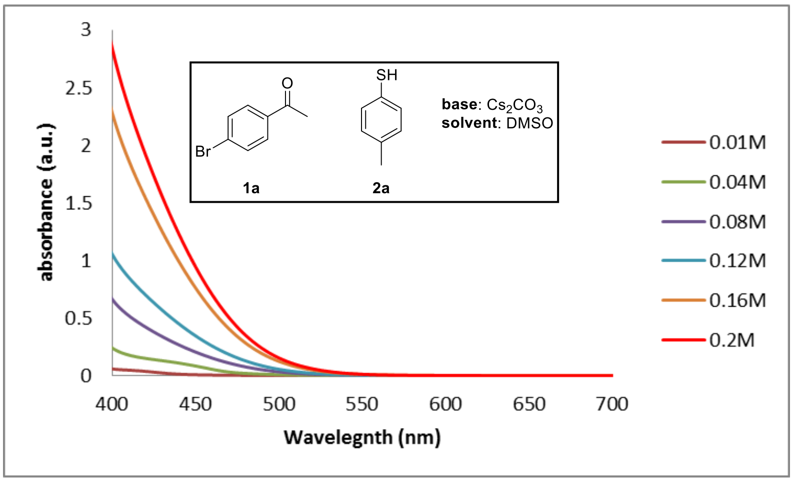


Figure S7. UV-vis absorption spectra at different concentrations (~10^{-1} M).

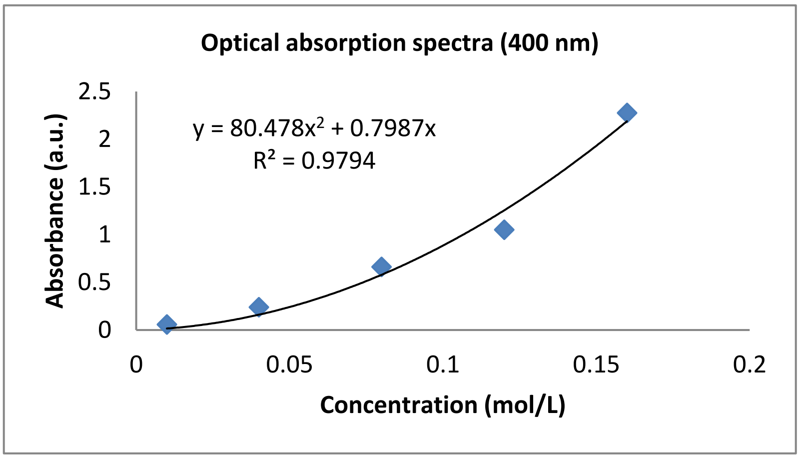


Figure S8. Plot of absorbance as a function of concentrations (~10^{-1} M). Path length = 1 cm.

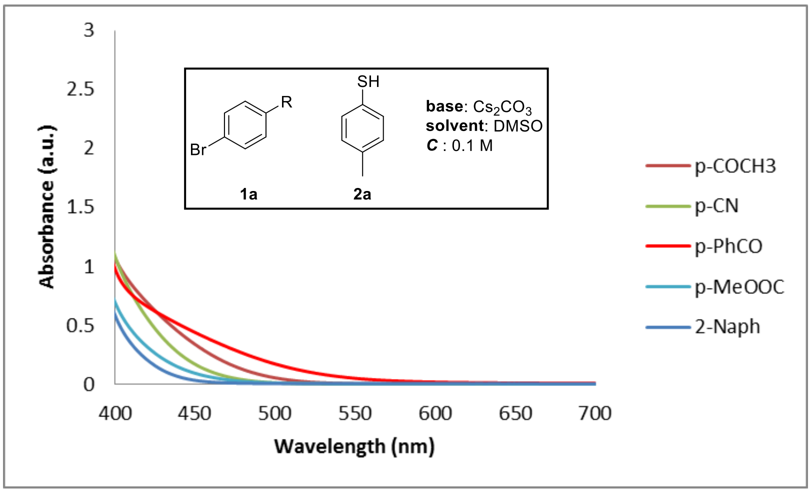


Figure S9. UV-vis absorption spectra with different functional groups substituted at the aryl bromides

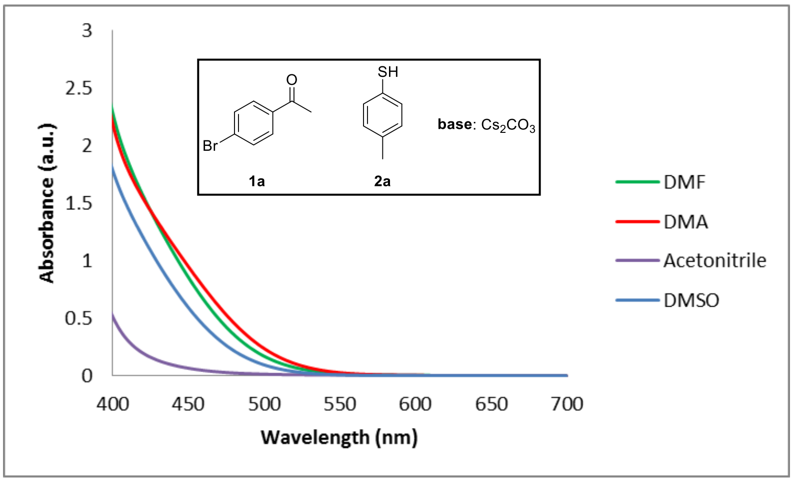
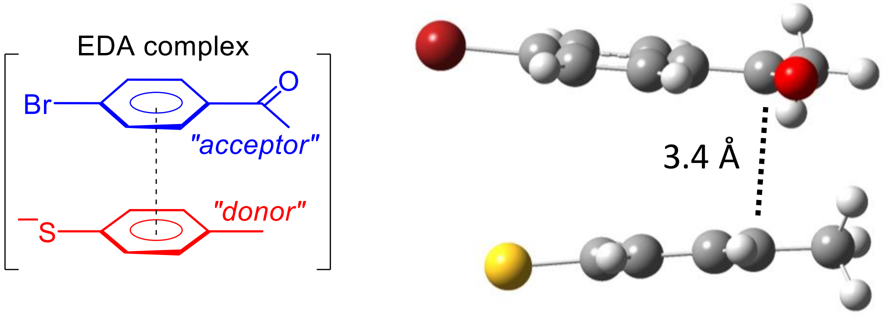


Figure S10. UV-vis absorption spectra with different Solvents (c = 0.15M).

b. Time-Dependent Density Functional Theory Calculations

All calculations were performed using computational chemistry software package Gaussian 09 ver. D01. We acknowledge the use of computational resources provided by XSEDE - Comet supercomputer.

Ground state geometry of the thiolate-aryl halide EDA complex was optimized at the rM06/6-31+G(d,p)/CPCM-DMSO level of theory. Using this geometry, single point time-dependent density functional theory (TD-DFT) calculation was then performed using the rCAM-B3LYP/6-31+G(d,p)/CPCM-DMSO level of theory. The first 10 excited states of the EDA complex (composed of species **1a** and the deprotonated **2a**) are reported below. Dominant UV-vis absorption peaks with significant and relevant oscillator strengths (f value) highlighted in red.



Excited State 1: Singlet-?Sym 3.2359 eV 383.15 nm f=0.0364 <S**2>=0.000
82 -> 83 0.70082 (π_{HOMO}-π_{LUMO}, 2*(0.70082)^2*100 = 98% contribution)

Excited state symmetry could not be determined.
Excited State 2: Singlet-?Sym 4.0543 eV 305.81 nm f=0.0001 <S**2>=0.000
81 -> 83 0.68847

Excited state symmetry could not be determined.
Excited State 3: Singlet-?Sym 4.0754 eV 304.23 nm f=0.0001 <S**2>=0.000
76 -> 83 0.65280
76 -> 91 0.11507

Excited state symmetry could not be determined.
Excited State 4: Singlet-?Sym 4.2165 eV 294.04 nm f=0.0216 <S**2>=0.000
82 -> 84 0.52518
82 -> 87 0.14545
82 -> 89 0.41827

Excited state symmetry could not be determined.
Excited State 5: Singlet-?Sym 4.3896 eV 282.45 nm f=0.1373 <S**2>=0.000
82 -> 85 0.20104
82 -> 86 0.20812
82 -> 87 0.41952 (π_{HOMO}-π_{LUMO+4}, 2*(0.41952)^2*100 = 35% contribution)
82 -> 88 0.39804 (π_{HOMO}-π_{LUMO+5}, 2*(0.39804)^2*100 = 32% contribution)

```
      82 -> 89         -0.12413
      82 -> 92          0.13025

Excited state symmetry could not be determined.
Excited State   6:      Singlet-?Sym     4.5069 eV   275.10 nm   f=0.0162   <S**2>=0.000
      82 -> 84          0.46663
      82 -> 87         -0.17226
      82 -> 89         -0.46169
Excited state symmetry could not be determined.
Excited State   7:      Singlet-?Sym     4.5838 eV   270.49 nm   f=0.1135   <S**2>=0.000
      82 -> 85          0.37118
      82 -> 86          0.24615
      82 -> 87         -0.26832
      82 -> 89          0.10525
      82 -> 90          0.11234
      82 -> 91          0.24975
      82 -> 92         -0.15793
      82 -> 93         -0.21253
      82 -> 95          0.10313
Excited state symmetry could not be determined.
Excited State   8:      Singlet-?Sym     4.7694 eV   259.96 nm   f=0.0407   <S**2>=0.000
      77 -> 83         -0.29954
      79 -> 84         -0.18071
      80 -> 83          0.54640
      82 -> 86         -0.12367
Excited state symmetry could not be determined.
Excited State   9:      Singlet-?Sym     4.7730 eV   259.76 nm   f=0.0094   <S**2>=0.000
      80 -> 83         -0.16233
      82 -> 85          0.38498
      82 -> 86         -0.33730
      82 -> 87          0.11451
      82 -> 92         -0.27487
      82 -> 93          0.11525
      82 -> 97         -0.19303
Excited state symmetry could not be determined.
Excited State  10:      Singlet-?Sym     4.8448 eV   255.91 nm   f=0.0646   <S**2>=0.000
      81 -> 84          0.16037
      81 -> 85          0.10830
      81 -> 86          0.21540
      81 -> 87          0.40282
      81 -> 88          0.37849
      81 -> 90          0.13087
      81 -> 92          0.20198
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NMR Shifts upon Base Addition to Thiols and Aryl Halides

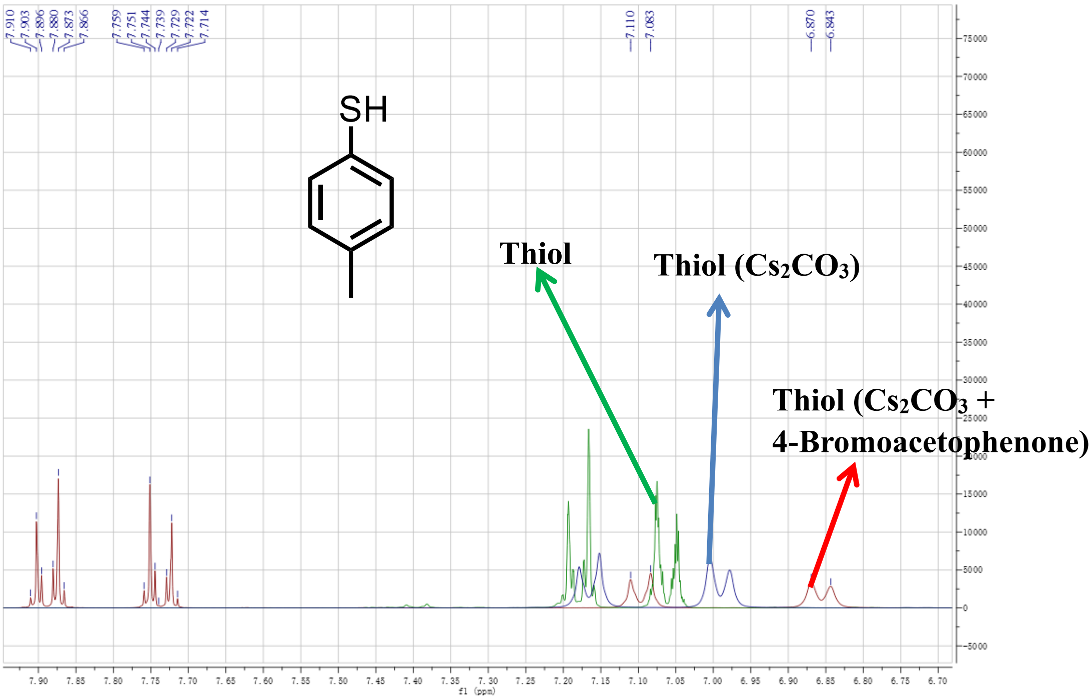


Figure S11. NMR shift of thiol. Thiol: thiol+d_6-DMSO. Thiol (Cs_2CO_3): thiol+Cs_2CO_3+d_6-DMSO. Thiol (Cs_2CO_3+4-Bromoacetophenone): thiol+Cs_2CO_3 +4-Bromoacetophenone +d_6-DMSO.

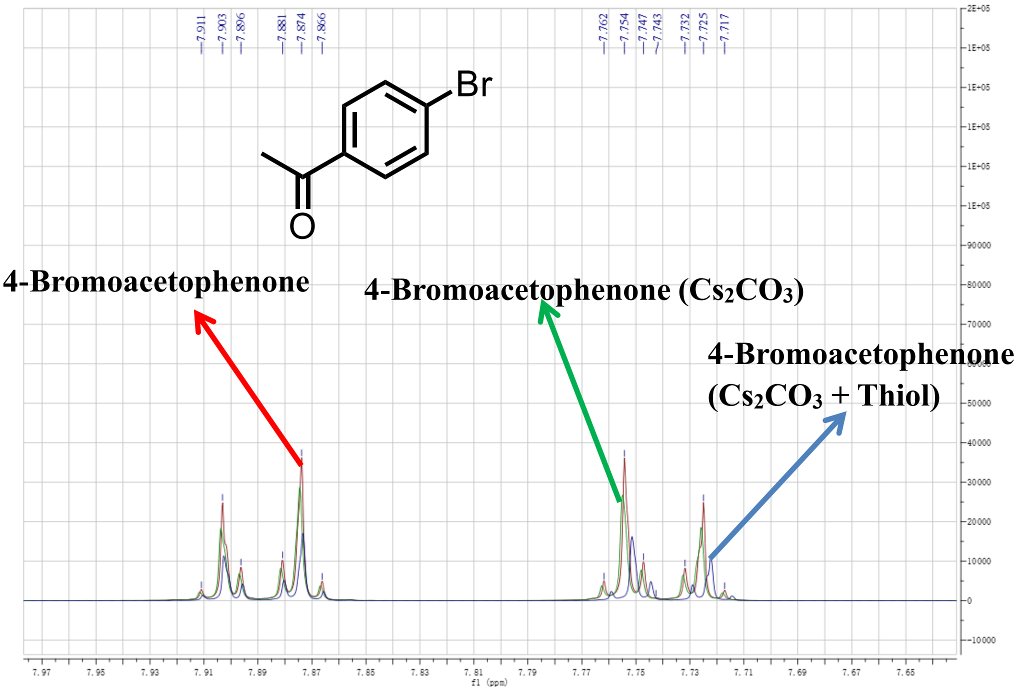
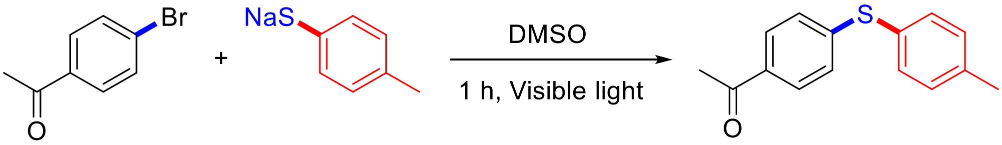


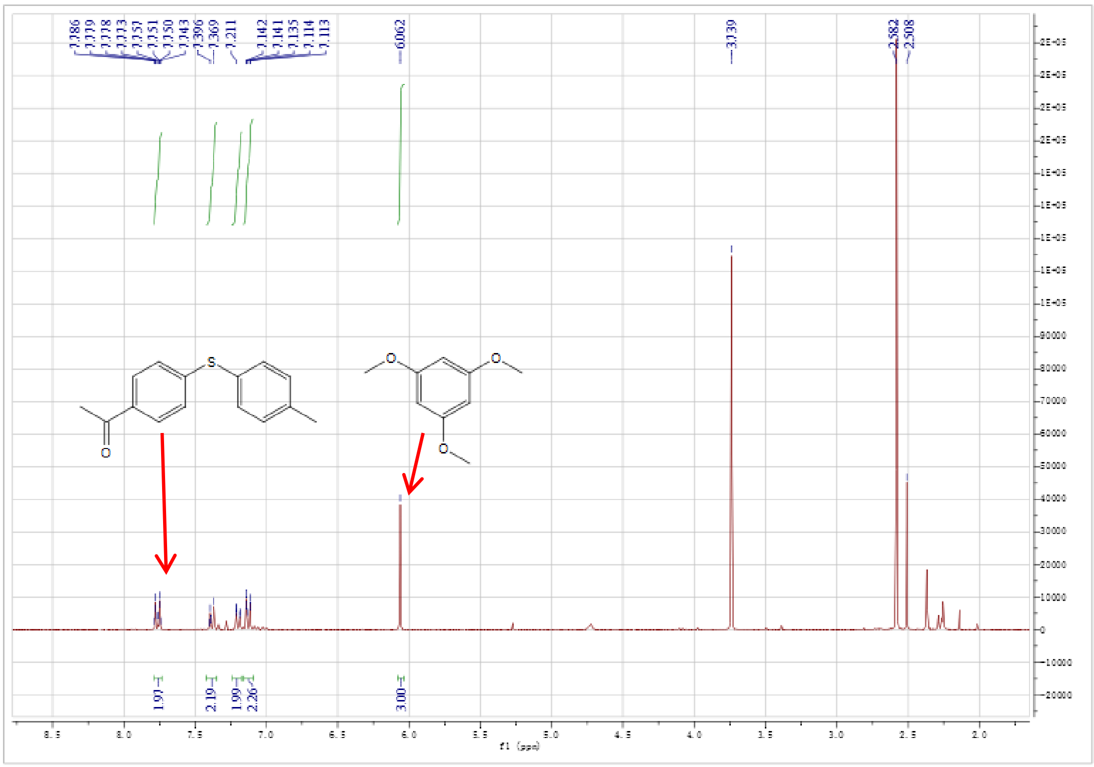
Figure S12. NMR shift of 4-Bromoacetophenone. 4-Bromoacetophenone: 4-Bromoacetophenone+d_6-DMSO. 4-Bromoacetophenone (Cs_2CO_3): 4-Bromoacetophenone+Cs_2CO_3+d_6-DMSO. 4-Bromoacetophenone (Cs_2CO_3+thiol): thiol+Cs_2CO_3 +4-Bromoacetophenone +d_6-DMSO.

4-Methylbenzenethiol Sodium Salt as Cross-Coupling Partner

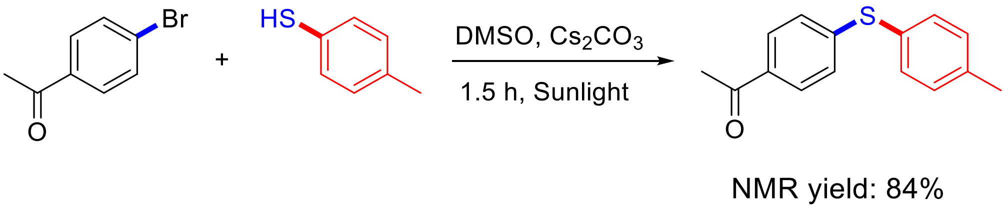
To investigate if the varying metal carbonate bases affecting reactivity is due to the deprotonation step or due to a secondary effect in the charge transfer event, we subjected 4-methylbenzenethiol sodium salt to our C-S bond formation conditions without external base. The reactions proceeded smoothly and yielded the desired compound in high yield. This result revealed that varying metal carbonate bases affecting reactivity is due to the deprotonation step.



NMR yield: 95%



Chemistry on the Roof: Sunlight-Driven Reaction



The reaction was set up in the laboratory according to the general procedure, using the Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), p-toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. Then, the storage flask was exposed to natural sunlight irradiation beside the window of room 363 in the Department of Chemistry and Biochemistry at the University of Colorado, Boulder from 2:20 PM to 3:50 PM on April 10th, 2017, on a partially cloudy day. The ^{1}H NMR yield is 84% by using trimethoxybenzene as internal standard.

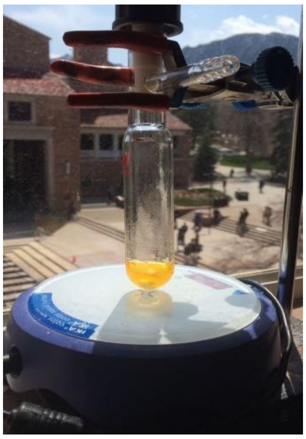
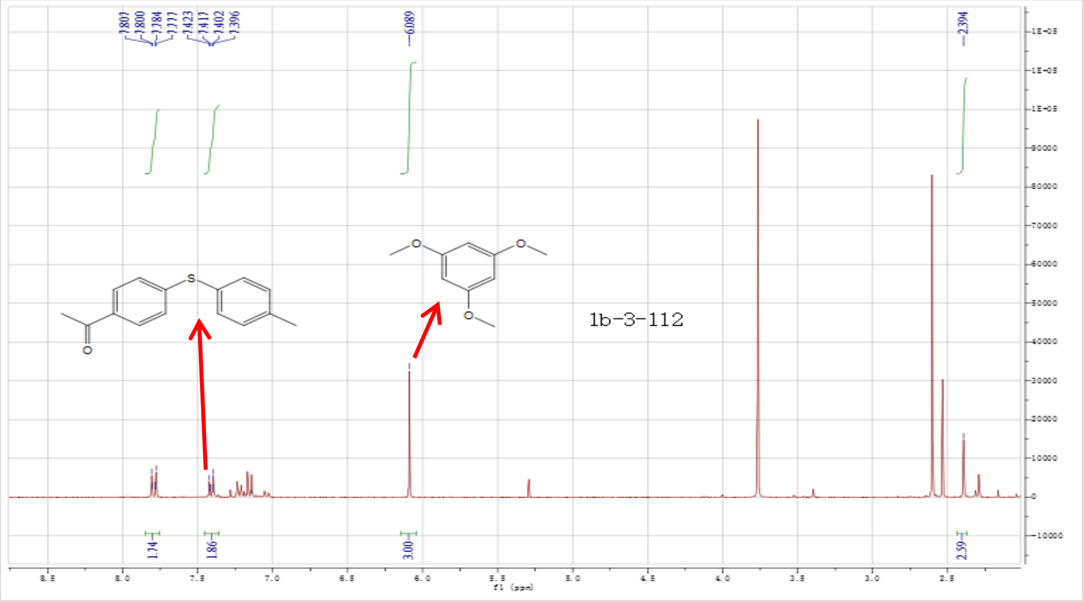


Figure S13. Picture of set-up for the sunlight-driven reaction



Multi-Gram Scale Experiment

A 100 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (19.54 g, 60 mmol, 1.2 eq.), 4′-Bromoacetophenone (9.95 g, 50 mmol, 1.00 eq.), *p*-Toluenethiol (7.45 g, 60 mmol, 1.2 eq.) and 60 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After 14 hours, the reaction mixture was washed with water and extracted with EtOAc three times. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product (9.710 g, 80%).

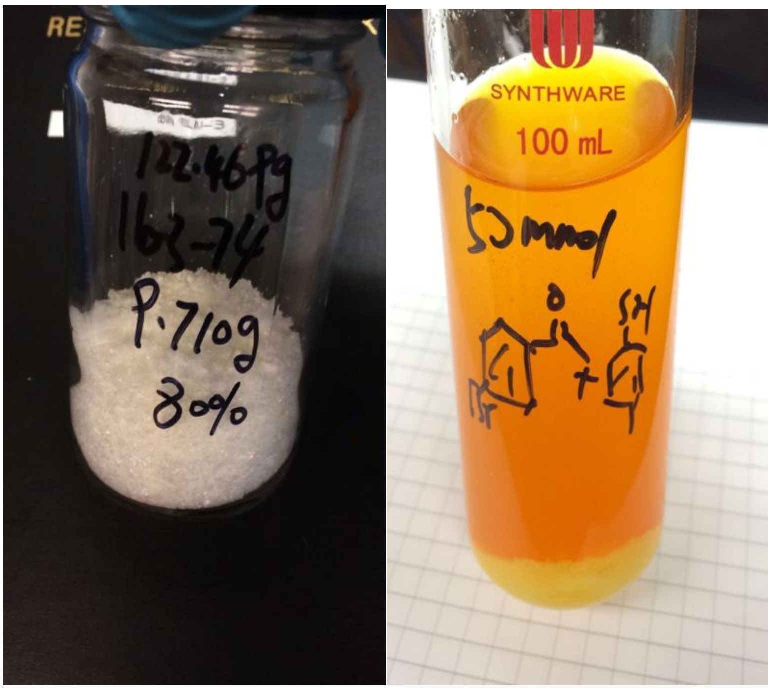
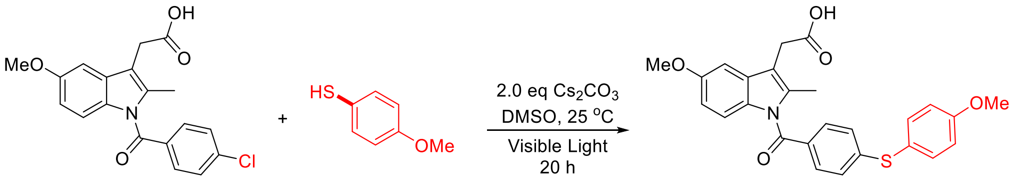


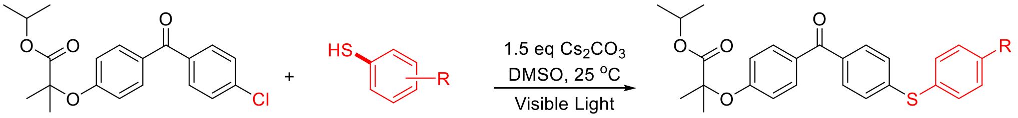
Figure S14. Photographs of multi-gram scale experiment. Left: Isolated C-S coupled product; Right: Reaction mixture after irradiation.

Late-Stage Modifications of Drug Molecules



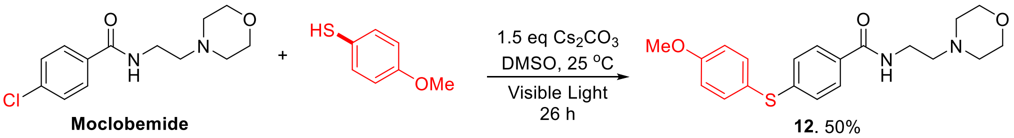
Indometacin

8. 76% Yield



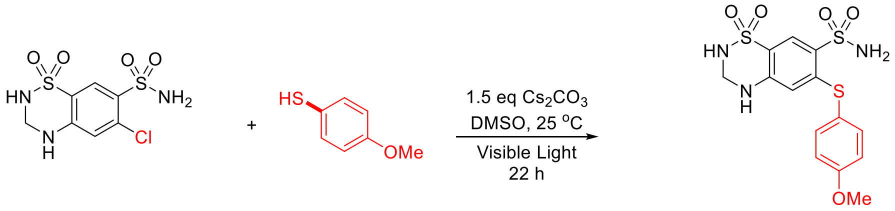
Fenofibrate

9. R = OMe, 22 h, 79%
10. R = NH_2, 22 h, 77%
11. R = CH_3, 22 h, 60%



Moclobemide

12. 50%

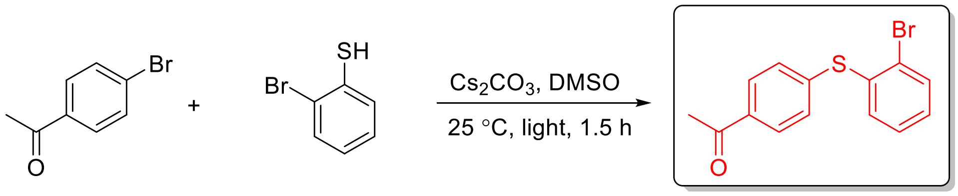


Hydrochlorothiazide

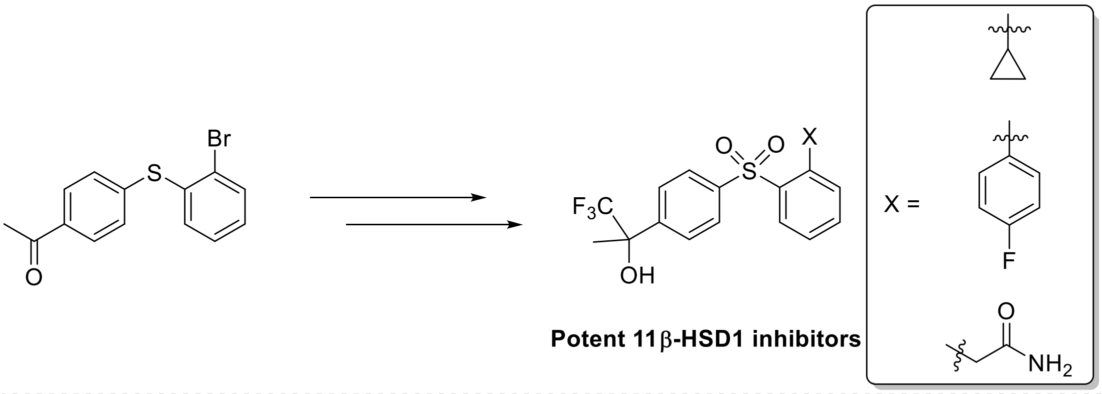
13. 65%

Synthesis of Key Structures of 11β-HSD1 Inhibitors

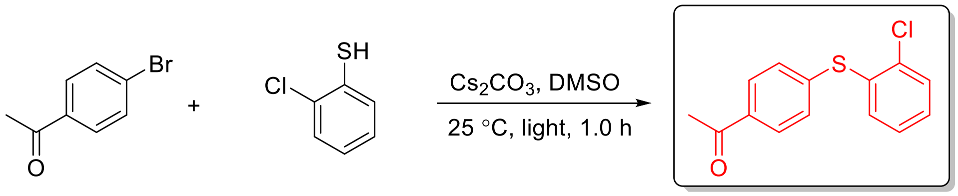
To evaluate our method for making bioactivities molecules, we subjected 2-chlorobenzenethiol and 2-bromobenzenethiol to our C-S bond formation conditions. The reactions proceeded smoothly and yielded the C-S bond containing target compounds in high yield.



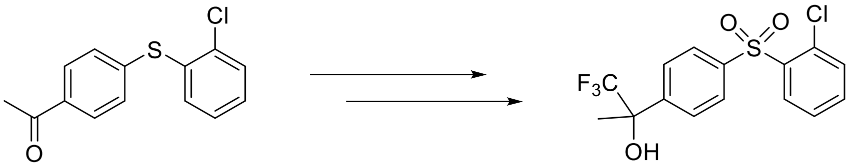
Yield: 84%



Potent 11β-HSD1 inhibitors



Yield: 93%

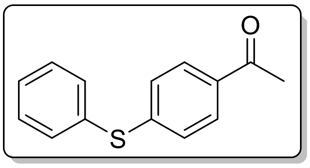


Potent 11β-HSD1 inhibitors

Characterizations

General Procedure

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), aryl halides (0.2 mmol, 1.00 eq.), thiols (0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After the time specified in the reaction schemes, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.



1-(4-(Phenylthio)phenyl)ethan-1-one (3a)[2]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), benzenethiol (33.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 4 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 43mg, 92%).

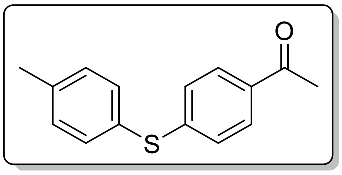
Physical State: white solid;

R_f = 0.5 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.44 –7.41 (m, 3H), 7.23 (dt, *J* = 8.7, 2.1 Hz, 2H), 2.57 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 144.9, 134.5, 133.8, 132.1, 129.7, 128.9, 128.8, 127.5, 26.44

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{12}OS$ ($[M+H]^+$) 229.0687, found 229.0685.



1-(4-(*p*-Tolylthio)phenyl)ethan-1-one (3b)[3]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Cl, 95%; X = Br, 47 mg, 97%; X = I, 89%).

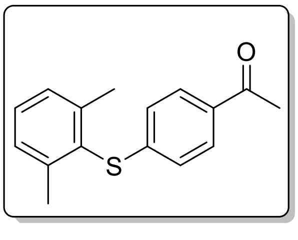
Physical State: white solid;

R_f = 0.5 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, $CDCl_3$) δ7.82 – 7.78 (m, 2H), 7.41 (dt, *J* = 8.1 2.1 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.18 – 7.14 (m, 2H), 2.54 (s, 3H), 2.40 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 145.9, 139.3, 134.4, 134.1, 130.5, 128.8, 127.9, 126.6, 26.4, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{14}OS$ ([M+H]+) 243.0844, found 243.0848.



1-(4-((2,6-Dimethylphenyl)thio)phenyl)ethan-1-one (3c)[4]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 2,6-dimethylbenzenethiol (41.4 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 44 mg, 85%).

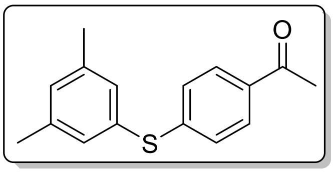
Physical State: white solid;

R R_f = 0.5 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 8.7 Hz, 2.1 Hz, 2H), 7.31 – 7.22 (m, 3H), 6.97 (dt, *J* = 8.7 Hz, 2.1 Hz, 2H), 2.54 (s, 3H), 2.43 (s, 6H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 145.3, 143.9, 133.6, 129.9, 128.9, 128.7, 124.8, 26.4, 21.7

HRMS (ESI-TOF): m/z calcd. for $C_{16}H_{16}OS$ ($[M+H]^+$) 257.1000, found 257.0998.



1-(4-((3,5-Dimethylphenyl)thio)phenyl)ethan-1-one (3d)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 3,5-dimethylbenzenethiol (41.4 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 36 mg, 70%).

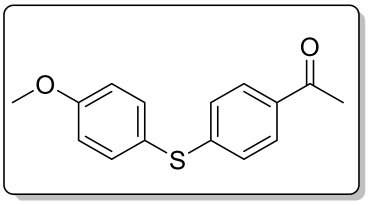
Physical State: white solid;

R_f = 0.5 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.22 – 7.19 (m, 2H), 7.14 – 7.13 (m, 2H), 7.02 (dt, *J* = 3.0, 1.1 Hz, 1H), 2.55 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 145.5, 139.4, 134.3, 131.6, 131.2, 130.7, 128.8, 127.2, 26.4, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{16}H_{16}OS$ ($[M+H]^+$) 257.1000, found 257.1000.



1-(4-((4-Methoxyphenyl)thio)phenyl)ethan-1-one (3e)[5]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 44 mg, 85%).

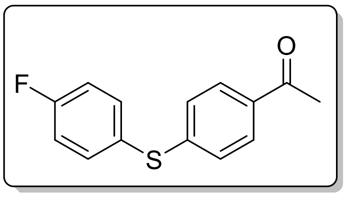
Physical State: white solid;

***R**_f* = 0.4 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 8.7 Hz, 2.1 Hz, 2H), 7.49 (dt, *J* = 8.7 Hz, 2.1 Hz, 2H), 7.11 (dt, *J* = 8.7 Hz, 2.1 Hz, 2H), 6.98 (dt, *J* = 8.7 Hz, 2.7 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 160.7, 146.8, 136.8, 133.9, 128.8, 125.8, 121.4, 115.4, 55.4, 26.4

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{14}O_2S$ ($[M+H]^+$) 259.0793, found 259.0794.



1-(4-((4-Fluorophenyl)thio)phenyl)ethan-1-one (3f)[6]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-fluorobenzenethiol (38.4 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 38 mg, 77%).

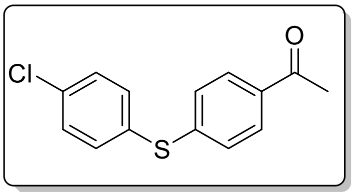
Physical State: white solid;

R$_f$ = 0.5 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.84 – 7.79 (m, 2H), 7.54 – 7.44 (m, 2H), 7.17 – 7.09 (m, 4H), 2.55 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.0, 163.3 (d, *J* = 248.5 Hz), 145.1, 136.5 (d, *J* = 8.4 Hz), 134.5, 128.9, 126.8, 117.0 (d, *J* = 21.9 Hz), 26.4

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}FOS$ ([M+H]+) 247.0593, found 247.0594.



1-(4-((4-Chlorophenyl)thio)phenyl)ethan-1-one (3g)[7]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-chlorobenzenethiol (43.2 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 50 mg, 95%).

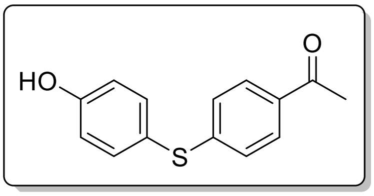
Physical State: white solid;

R$_f$ = 0.5 (silica gel, 1:6 EtOAc : hexanes);

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85 – 7.81 (m, 2H), 7.43 – 7.35 (m, 4H), 7.23 – 7.20 (m, 2H), 2.56 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.0, 143.9, 134.9, 134.8, 130.94, 129.9, 129.0, 127.8, 26.5

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}ClOS$ ($[M+H]^+$) 263.0297, found 263.0294.



1-(4-((4-Hydroxyphenyl)thio)phenyl)ethan-1-one (3h)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-mercaptophenol (37.8 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:2 EtOAc:hexanes) as white solid (X = Br, 25mg, 50%).

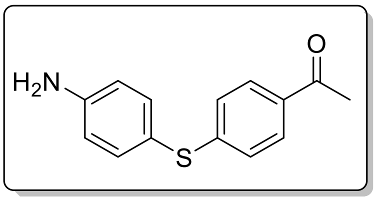
Physical State: white solid;

R_f = 0.1 (silica gel, 1:6 EtOAc:hexanes);

^{1}H NMR (300 MHz, *d_6*-DMSO) δ 10.03 (s, 1H), 7.82 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.39 (dt, *J* = 8.7, 2.6 Hz, 2H), 7.09 (dt, *J* = 8.7, 2.1 Hz, 2H), 6.90 (dt, *J* = 8.7, 2.7 Hz, 2H), 2.50 (s, 3H)

^{13}C NMR (75 MHz, *d_6*-DMSO) δ 197.3, 159.5, 146.7, 137.4, 134.1, 129.4, 125.7, 118.4, 117.6, 26.9

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{12}O_2S$ ($[M-H]^-$) 243.0480, found 243.0478.



1-(4-((4-Aminophenyl)thio)phenyl)ethan-1-one (3i)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-aminobenzenethiol (37.5 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 14 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as yellow solid (X = Br, 30 mg, 60%).

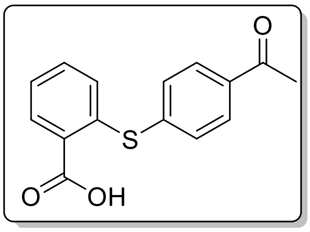
Physical State: yellow solid;

R_f = 0.4 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.33 (dt, *J* = 8.7, 2.4 Hz, 2H), 7.08 (dt, *J* = 8.7, 2.1 Hz, 2H), 6.72 (dt, *J* = 8.7, 2.4 Hz, 2H), 3.91 (s, 2H), 2.53 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 147.9, 147.8, 137.0, 133.6, 128.7, 125.3, 117.7, 116.0, 26.4

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{13}NOS$ ($[M+H]^+$) 244.0796, found 244.0805.



2-((4-Acetylphenyl)thio)benzoic acid (3j)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 2-mercaptobenzoic acid (46.2 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (8:1 DCM:MeOH) as white solid (X = Br, 35 mg, 64%).

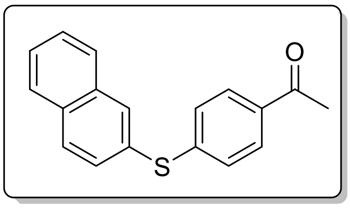
Physical State: white solid;

R_f = 0.3 (silica gel, 8:1 DCM:MeOH)

^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 7.99 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.56 (dt, *J* = 8.4, 2.1 Hz, 2H, 2H), 7.46 – 7.40 (m, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.0, 0.9 Hz, 1H), 2.60 (s, 3H).

^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 197.7, 167.9, 140.3, 138.6, 136.7, 133.4, 132.9, 131.2, 130.6, 129.9, 129.6, 126.5, 27.2

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{12}O_3S$ ([M-H]$^+$) 271.0429, found 271.0433.



1-(4-(Naphthalen-2-ylthio)phenyl)ethan-1-one (3k)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), naphthalene-2-thiol (48.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1.5 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 40 mg, 71%).

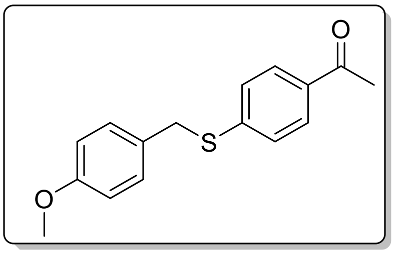
Physical State: white solid;

R$_f$ = 0.5 (silica gel, 1:6 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (t, *J* = 1.2 Hz, 1H), 7.84 – 7.78 (m, 5H), 7.57 – 7.48 (m, 3H), 7.28 – 7.24 (m, 2H), 2.55 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.1, 144.8, 134.6, 133.8, 133.3, 133.0, 130.4, 129.4, 129.3, 128.9, 127.8, 127.7, 127.6, 127.0, 126.9, 26.5

HRMS (ESI-TOF): m/z calcd. for $C_{18}H_{14}OS$ ([M+H]$^+$) 279.0844, found 279.0844.



1-(4-((4-Methoxybenzyl)thio)phenyl)ethan-1-one (3l)[8]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7

mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), (4-methoxyphenyl)methanethiol (46.2 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as white solid (X = Br, 40 mg, 74%).

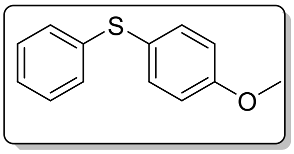
Physical State: white solid;

R_f = 0.5 (silica gel, 1:5 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.35 – 7.28 (m, 4H), 6.86 (dt, *J* = 8.7, 2.1 Hz, 2H), 4.19 (s, 2H), 3.81 (s, 3H), 2.57 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 159.0, 144.4, 134.1, 129.9, 128.7, 128.0, 126.9, 114.1, 55.3, 36.6, 26.4

HRMS (ESI-TOF): m/z calcd. for $C_{16}H_{16}O_2S$ ($[M+H]^+$) 273.0949, found 273.0947.



(4-Methoxyphenyl)(phenyl)sulfane (4a)[9]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), iodobenzene (40.8 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 24 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow oil (X = I, 37 mg, 85%).

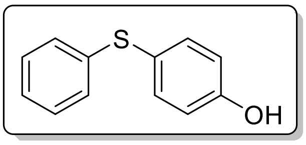
Physical State: pale yellow oil;

R_f = 0.4 (silica gel, hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.32 – 7.11 (m, 5H), 6.93 (dt, *J* = 8.7, 2.7 Hz, 2H), 3.85 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 159.8, 138.6, 135.4, 128.9, 128.2, 125.8, 124.3, 115.0, 55.4

HRMS (ESI-TOF): m/z calcd. for $C_{13}H_{12}OS$ ([M+H]$^+$) 216.0609, found 216.0612.



4-(Phenylthio)phenol (4b)[10]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), iodobenzene (40.8 mg, 0.2 mmol, 1.00 eq.), 4-mercaptophenol (37.8 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 24 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as white solid (X = I, 10 mg, 25%).

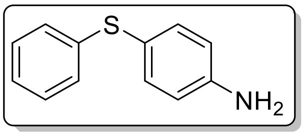
Physical State: white solid;

R$_f$ = 0.4 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 – 7.35 (m, 2H), 7.27 – 7.12 (m, 5H), 6.86 – 6.82 (m, 2H), 4.98 (s, 1H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 155.8, 138.4, 135.5, 128.9, 128.4, 125.9, 124.7, 116.5

HRMS (ESI-TOF): m/z calcd. for $C_{12}H_{10}OS$ ([M]$^+$) 202.0452, found 202.0457.



4-(Phenylthio)aniline (4c)[10]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), iodobenzene (40.8 mg, 0.2 mmol, 1.00 eq.), 4-aminobenzenethiol (37.5 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 24 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as yellow solid (X = I, 15 mg, 37%).

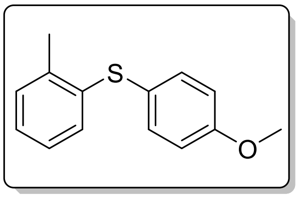
Physical State: yellow solid;

R_f = 0.4 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.07 (m, 3H), 6.70 – 6.66 (m, 2H), 3.78 (s, 2H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 139.7, 136.1, 128.8, 127.3, 125.2, 120.5, 115.9

HRMS (ESI-TOF): m/z calcd. for $C_{12}H_{11}NS$ ($[M]^+$) 202.0690, found 202.0691.



(4-Methoxyphenyl)(o-tolyl)sulfane (4d)[11]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-iodo-2-methylbenzene (43.6 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 20 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (X = I, 25 mg, 54%).

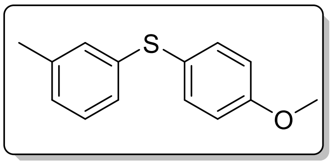
Physical State: colorless oil;

R_f = 0.4 (silica gel, hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.19 – 7.17 (m, 1H), 7.13 – 7.03 (m, 2H), 6.99 (dd, *J* = 6.6, 1.8 Hz, 1H), 6.91 – 6.87 (m, 2H), 3.82 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 137.1, 134.5, 130.2, 129.1, 126.5, 126.1, 124.5, 115.0, 55.4, 20.3

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{14}OS$ ($[M]^+$) 230.0765, found 230.0772.



(4-Methoxyphenyl)(m-tolyl)sulfane (e)[12]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-iodo-3-methylbenzene (43.6 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 20 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (X = I, 33 mg, 72%).

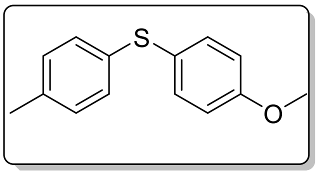
Physical State: colorless oil;

R_f = 0.4 (silica gel, hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 7.01 –6.97 (m, 2H), 6.94 – 6.91 (m, 2H), 3.85 (s, 3H), 2.31 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 138.8, 138.2, 135.1, 129.0, 128.7, 126.8, 125.5, 124.6, 114.9, 55.4, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{14}OS$ ($[M]^+$) 230.0765, found 230.0769.



(4-Methoxyphenyl)(p-tolyl)sulfane (4f)[13]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-iodo-4-methylbenzene (43.6 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 20 hours, the reaction mixture was washed with water, extracted with EtOA and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (X = I, 35 mg, 76%).

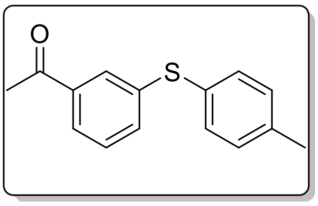
Physical State: colorless oil;

R_f = 0.4 (silica gel, hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 (dt, *J* = 9.0, 2.7 Hz, 2H), 7.16 – 7.13 (m, 2H), 7.09 – 7.05 (m, 2H), 6.91 – 6.83 (dt, *J* = 9.0, 2.7 Hz, 2H), 3.81 (s, 3H), 2.31 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 159.5, 136.1, 134.3, 129.8, 129.4, 125.7, 114.9, 55.4, 21.0

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{14}OS$ ($[M+H]^+$) 230.0765, found 230.0767.



1-(3-(*p*-Tolylthio)phenyl)ethan-1-one (4g)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 3′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = I, 43 mg, 89%).

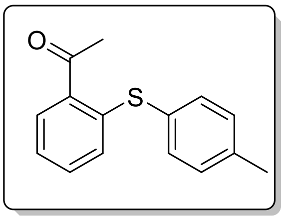
Physical State: white solid;

R_f = 0.4 (silica gel, 1:6 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 (td, *J* = 1.8, 0.6 Hz, 1H), 7.75 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.54 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.5, 138.8, 138.4, 137.8, 133.5, 132.9, 130.3, 130.0, 129.2, 128.8, 126.0, 26.6, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{14}OS$ ($[M+H]^+$) 243.0844, found 243.0844.



1-(2-(*p*-Tolylthio)phenyl)ethan-1-one (4h)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 3′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour (X = I) or 12 hours (X = Cl), the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Cl, 40 mg, 82%; X = I, 37 mg, 76%).

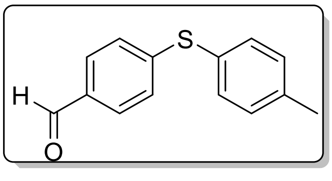
Physical State: white solid;

$\boldsymbol{R_f}$ = 0.4 (silica gel, 1:6 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 (td, *J* = 7.8, 1.5 Hz, 1H), 6.87 (dd, *J* = 8.1, 0.9 Hz, 1H), 2.66 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 142.9, 139.2, 135.4, 134.2, 132.0, 130.6, 130.5, 129.4, 127.8, 124.1, 28.2, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{14}OS$ ($[M+H]^+$) 243.0844, found 243.0847.



4-(*p*-Tolylthio)benzaldehyde (4i)[14]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4-iodobenzaldehyde (46.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Cl, 36 mg, 78%; X = I, 40 mg, 87%).

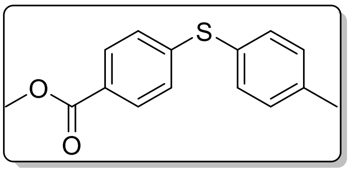
Physical State: white solid;

R_f = 0.4 (silica gel, 1:6 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.74 – 7.70 (m, 2H), 7.45 (dt, *J* = 8.1, 2.1 Hz, 2H), 7.29 – 7.19 (m, 4H), 2.43 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 148.2, 139.7, 134.8, 133.5, 130.7, 130.1, 127.3, 126.6, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{12}OS$ ($[M+H]^+$) 229.0687, found 229.0687.



Methyl 4-(*p*-Tolylthio)benzoate (4j)[15]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), methyl 4-iodobenzoate (52.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 4 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:20 EtOAc:hexanes) as white solid (X = I, 47 mg, 90%, X = Br, 45 mg, 87%, X = Cl, 48 mg, 92%).

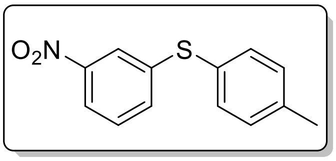
Physical State: white solid;

R_f = 0.4 (silica gel, 1:20 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 9.0, 1.8 Hz, 2H), 7.40 (dt, *J* = 8.1, 1.8 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.17 – 7.13 (m, 2H), 3.88 (s, 3H), 2.39 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 145.4, 139.2, 134.3, 130.5, 130.0, 128.2, 127.1, 126.7, 52.0, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{14}O_2S$ ($[M+H]^+$) 259.0793, found 259.0796.



(3-Nitrophenyl)(p-tolyl)sulfane (4k)[16]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-iodo-3-nitrobenzene (49.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 4 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:10 EtOAc:hexanes) as yellow solid (X = I, 41 mg, 83%).

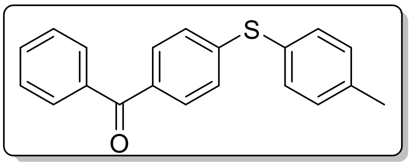
Physical State: yellow solid;

R$_f$ = 0.4 (silica gel, 1:20 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.46 – 7.35 (m, 4H), 7.25 – 7.22 (m, 2H), 2.40 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 141.6, 139.6, 134.2, 133.3, 130.7, 129.5, 127.9, 122.2, 120.4, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{13}H_{11}NO_2S$ ($[M+H]^+$) 246.0589, found 246.0588.



Phenyl-(4-(*p*-tolylthio)phenyl)methanone (4l)[2]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), (4-bromophenyl)(phenyl)methanone (52.2 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6 EtOAc:hexanes) as white solid (X = Br, 55 mg, 90%).

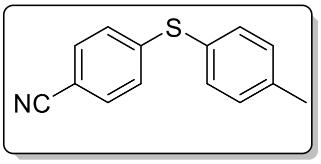
Physical State: white solid;

R$_f$ = 0.4 (silica gel, 1:5 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.77 – 7.74 (m, 2H), 7.70 – 7.66 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.42 (m, 4H), 7.25 – 7.17 (m, 4H), 2.40 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 195.7, 145.3, 139.3, 137.7, 134.5, 134.4, 132.2, 130.7, 130.5, 129.8, 128.2, 128.0, 126.5, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{20}H_{16}OS$ ($[M+H]^+$) 305.1000, found 305.0998.



4-(*p*-Tolylthio)benzonitrile (4m)[2]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4-bromobenzonitrile (36.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hour, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:10 EtOAc:hexanes) as white solid (X = Br, 32 mg, 71%).

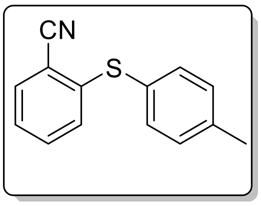
Physical State: white solid;

R_f = 0.5 (silica gel, 1:10 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.47 – 7.39 (m, 4H), 7.28 – 7.23 (m, 2H), 7.14 – 7.10 (m, 2H), 2.41 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 146.6, 139.9, 134.9, 132.3, 130.7, 126.8 126.7, 118.9, 108.3, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}NS$ ($[M+H]^+$) 226.0690, found 226.0692.



2-(*p*-Tolylthio)benzonitrile (4n)[17]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 2-chlorobenzonitrile (27.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 4 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:7 EtOAc:hexanes) as colorless oil (X = Cl, 40 mg, 88%).

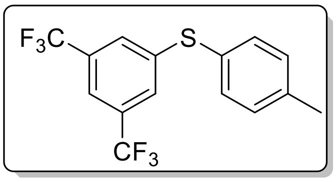
Physical State: white solid;

R_f = 0.5 (silica gel, 1:7 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.23 – 7.18 (m, 2H), 7.04 (ddd, *J* = 8.1, 1.1, 0.5 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 139.5, 134.3, 133.5, 132.8, 130.6, 128.9, 127.6, 125.9, 117.0, 111.9, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}NS$ ($[M+H]^+$) 226.0690, found 226.0694.



(3,5-Bis(trifluoromethyl)phenyl)(*p*-tolyl)sulfane (4o)[18]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-bromo-3,5-bis(trifluoromethyl)benzene (58.6 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 16 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (X = Br, 34 mg, 50%)..

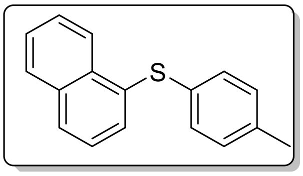
Physical State: colorless oil;

R R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.5, 0.9 Hz, 1H), 7.52 – 7.51 (m, 2H), 7.43 – 7.39 (m, 2H), 7.27 – 7.24 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 140.0, 134.3, 132.3 (q, *J* = 33.1 Hz), 130.9, 128.9, 127.0 (m), 123.0 (q *J* = 270.0 Hz), 119.1(m), 21.3.

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{10}F_6S$ ($[M]^+$) 336.0407, found 336.0403.



Naphthalen-1-yl(*p*-tolyl)sulfane (4p)[19]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-bromonaphthalene (41.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 16 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (X = Br, 42 mg, 84%).

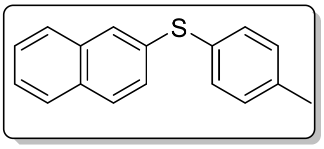
Physical State: white solid;

R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 – 8.39 (m, 1H), 7.90 – 7.80 (m, 2H), 7.58 – 7.50 (m, 3H), 7.43 – 7.38(m, 1H), 7.22 – 7.17 (m, 2H), 7.11 – 7.07 (m, 2H), 2.32 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 134.1, 133.1, 132.7, 132.5, 131.0, 130.3, 130.0, 128.5, 128.4, 126.7, 126.4, 125.8, 125.4, 21.1

HRMS (ESI-TOF): m/z calcd. for $C_{17}H_{14}S$ ($[M]^+$) 250.0816, found 250.0818.



Naphthalen-2-yl(*p*-tolyl)sulfane (4q)[20]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 2-bromonaphthalene (41.4 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (X = Br, 28 mg, 56%).

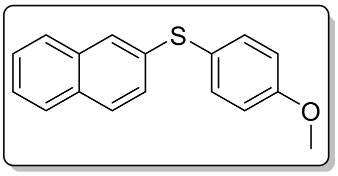
Physical State: white solid;

R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 4H), 7.50 – 7.43 (m, 2H), 7.40 – 7.34 (m, 3H), 7.19 – 7.15 (m, 2H), 2.38 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 134.4, 133.8, 132.1, 132.0, 131.4, 130.1, 128.7, 128.4, 127.9, 127.7, 127.3, 126.5, 125.9, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{17}H_{14}S$ ($[M]^+$) 250.0816, found 250.0817.



(4-Methoxyphenyl)(naphthalen-2-yl)sulfane (4r)[21]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-bromonaphthalene (41.4 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (X = Br, 44 mg, 81%).

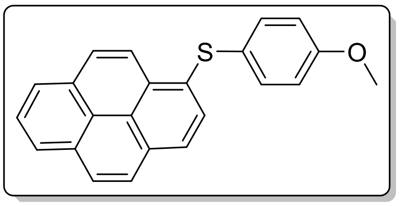
Physical State: white solid;

R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 4H), 7.49 – 7.39 (m, 4H), 7.31 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.95 – 6.90 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 135.9, 135.2, 133.8, 131.7, 128.5, 127.7, 127.2, 126.7, 126.5, 126.4, 125.6, 124.4, 115.1, 55.4

HRMS (ESI-TOF): m/z calcd. for $C_{17}H_{14}OS$ ($[M]^+$) 266.0765, found 266.0769.



(4-Methoxyphenyl)(pyren-1-yl)sulfane (4s)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1-bromopyrene (56.2 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as yellow solid (X = Br, 57 mg, 83%).

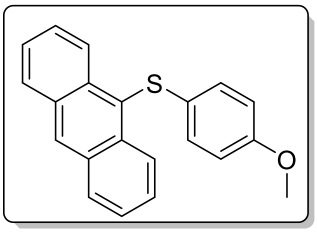
Physical State: yellow solid;

R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 9.3 Hz, 1H), 8.23 – 8.20 (m, 2H), 8.16 (d, *J* = 9.3 Hz, 1H), 8.10 – 8.01 (m, 4H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.36 (m, 2H), 6.90 – 6.87 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 159.2, 133.3, 132.7, 131.5, 131.4, 131.0, 130.5, 130.4, 129.4, 128.1, 127.5, 127.3, 126.4, 126.2, 125.3, 125.1, 124.5, 124.3, 115.0, 114.6, 55.4

HRMS (ESI-TOF): m/z calcd. for $C_{23}H_{16}OS$ ($[M]^{\cdot+}$) 340.0922, found 340.0926.



Anthracen-9-yl(4-methoxyphenyl)sulfane (4t)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 9-bromoanthracene (51.4 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as yellow solid (X = Br, 53 mg, 84%).

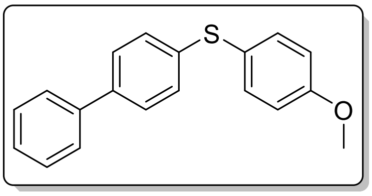
Physical State: yellow solid;

R$_f$ = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.91– 8.87 (m, 1H), 8.57 (s, 1H), 8.06 – 8.03 (m, 2H), 7.59 – 7.48 (m, 4H), 6.99 – 6.96 (m, 2H), 6.68 – 6.65 (m, 2H), 3.68 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 157.7, 134.8, 132.0, 130.0, 129.4, 128.9, 128.5, 127.1, 127.0, 126.9, 125.5, 114.6, 55.2

HRMS (ESI-TOF): m/z calcd. for $C_{21}H_{16}OS$ ($[M]^{\cdot+}$) 316.0922, found 316.0926.



[1,1'-Biphenyl]-4-yl(4-methoxyphenyl)sulfane (4u)[22]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4-bromo-1,1'-biphenyl (46.6 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOA and concentrated in vacuum. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (X = Br, 42 mg, 70%).

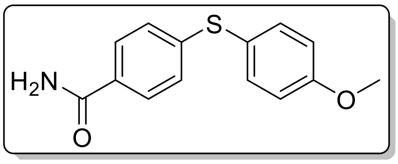
Physical State: white solid;

R_f = 0.4 (silica gel, hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.50 – 7.40 (m, 6H), 7.36 – 7.31 (m, 1H), 7.27 – 7.23 (m, 2H), 6.96 – 6.92 (m, 2H), 3.84 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 140.5, 138.8, 137.8, 135.4, 128.8, 128.5, 127.6, 127.3, 126.9, 124.2, 115.1, 55.4

HRMS (ESI-TOF): m/z calcd. for $C_{19}H_{16}OS$ ([M+H]+) 293.1000, found. 293.0995



4-((4-Methoxyphenyl)thio)benzamide (4v)[23]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (195.4 mg, 0.6 mmol, 1.5 eq.), 4-bromobenzamide (80.4.2 mg, 0.4 mmol, 1.00 eq.), 4-methoxybenzenethiol (84.0 mg, 0.6 mmol, 1.5 eq.) and 3.0 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 16 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (4:1 EtOAc:hexanes) as white solid (X = Br, 83 mg, 80%).

Physical State: white solid;

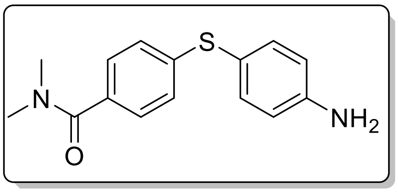
R_f = 0.5 (silica gel, 4:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, d_6-DMSO) δ 7.91 (s, 1H), 7.77 (d, J = 8.7 Hz, 2H), 7.48 (d, J =

8.9 Hz, 2H), 7.33 (s, 1H), 7.12 – 7.01 (m, 4H), 3.81 (s, 3H).

^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 167.7, 160.6, 143.0, 136.7, 131.8, 128.7, 126.4, 121.8, 116.1, 55.8

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{13}NO_2S$ ($[M+H]^+$) 260.0745, found 260.0748.



4-((4-Aminophenyl)thio)-*N*,*N*-dimethylbenzamide (4w)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 4-Iodo-*N*,*N*-dimethylbenzamide (55.0 mg, 0.2 mmol, 1.00 eq.), 4-aminobenzenethiol (37.5 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 16 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (6:1 EtOAc:hexanes) as white solid (X = I, 27 mg, 49%).

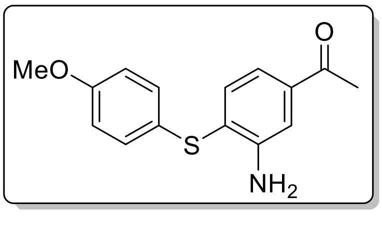
Physical State: white solid;

R$_f$ = 0.4 (silica gel, 6:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.33 – 7.26 (m, 4H), 7.10 – 7.07 (m, 2H), 6.69 – 6.66 (m, 2H), 3.94 (s, 2H), 3.07 (s, 3H), 2.99 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 171.3, 147.7, 142.5, 136.6, 132.7, 127.7, 126.1, 118.7, 115.9, 39.6, 35.4

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{16}N_2OS$ ($[M+H]^+$) 273.1062, found 273.1054.



1-(3-Amino-4-((4-methoxyphenyl)thio)phenyl)ethan-1-one (4x)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 3′-Amino-4′-bromoacetophenone (42.8 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 2 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:2 EtOAc:hexanes) as pale yellow oil (X = Br, 36 mg, 66%).

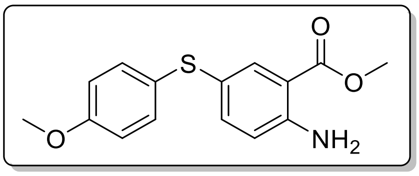
Physical State: pale yellow oil;

R_f = 0.3 (silica gel, 1:2 EtOAc:hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.6 Hz, 1H), 7.26 – 7.19 (m, 4H), 6.88 – 6.77 (m, 2H), 4.27 (s, 2H), 3.77 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 159.3, 146.4, 137.6, 133.5, 132.2, 124.9, 124.2, 118.7, 115.1, 114.3, 55.4), 26.6

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{15}NO_2S$ ($[M+H]^+$) 274.0902, found 274.0904.



Methyl 2-amino-5-((4-methoxyphenyl)thio)benzoate (4y)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), methyl 2-amino-5-iodobenzoate (55.4 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 4 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:2 EtOAc:hexanes) as pale yellow oil (X = I, 34 mg, 52%).

Physical State: pale yellow oil;

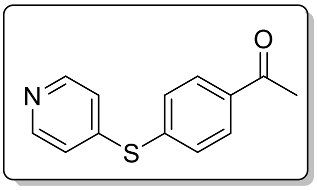
R_f = 0.3 (silica gel, 1:2 EtOAc:hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 0.3, 2.1 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.3

Hz, 1H), 7.25 – 7.20 (m, 2H), 6.86 – 6.81 (m, 2H), 6.69 – 6.61 (dd, *J* = 0.3, 8.4 Hz, 1H), 5.86 (s, 2H), 3.87 (s, 3H), 3.79 (s, 3H)..

^{13}C NMR (75 MHz, CDCl$_3$) δ 168.0, 158.6, 150.1, 139.0, 136.2, 131.2), 128.7, 121.1, 117.8, 114.7, 111.2, 55.4, 51.7

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{15}NO_2S$ ([M]$^+$) 289.0773, found 289.0772.



1-(4-(Pyridin-4-ylthio)phenyl)ethan-1-one (5a)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), pyridine-4-thiol (33.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 14 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (3:1 EtOAc:hexanes) as yellow solid (X = Br, 38 mg, 82%).

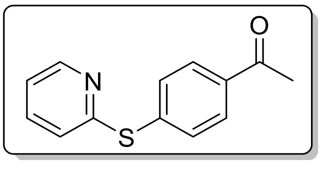
Physical State: yellow solid;

R$_f$ = 0.4 (silica gel, 3:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.42 (dd, *J* = 4.5, 1.6 Hz, 2H), 8.00 – 7.95 (m, 2H), 7.59 – 7.55 (m, 2H), 7.06 (dd, *J* = 4.5, 1.5 Hz, 2H), 2.62 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.0, 149.9, 147.7, 137.1, 137.0, 133.4, 129.4, 122.4, 26.6

HRMS (ESI-TOF): m/z calcd. for $C_{13}H_{11}NOS$ ([M+H]$^+$) 230.0640, found 230.0645.



1-(4-(Pyridin-2-ylthio)phenyl)ethan-1-one (5b)[24]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), pyridine-2-thiol (33.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (3:1 EtOAc:hexanes) as yellow solid (X = Br, 32 mg, 70%).

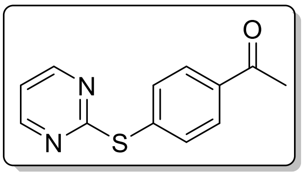
Physical State: yellow solid;

R_f = 0.4 (silica gel, 3:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.61 – 7.57 (m, 2H), 7.56 – 7.52 (m, 1H), 7.15 – 7.07 (m, 2H), 2.60 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 158.7, 150.1, 138.7, 137.0, 136.5, 132.8, 129.1, 123.5, 121.1, 26.6

HRMS (ESI-TOF): m/z calcd. for $C_{13}H_{11}NOS$ ($[M+H]^+$) 230.0640, found 230.0645.



1-(4-(Pyrimidin-2-ylthio)phenyl)ethan-1-one (5c)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), pyrimidine-2-thiol (33.6 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 14 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as white solid (X = Br, 35 mg, 76%).

Physical State: white solid;

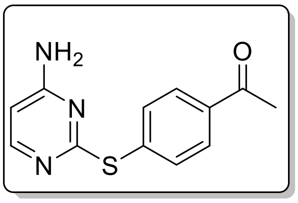
R_f = 0.1 (silica gel, 1:4 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.8 Hz, 2H), 8.02 – 7.97 (m, 2H), 7.75 –

7.71 (m, 2H), 7.02 (t, *J* = 4.8 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 171.7, 157.7, 137.1, 135.7, 134.6, 128.8, 117.5, 26.7

HRMS (ESI-TOF): m/z calcd. for $C_{12}H_{10}N_2OS$ ($[M+H]^+$) 231.0592, found 231.0594.



1-(4-((4-Aminopyrimidin-2-yl)thio)phenyl)ethan-1-one (5d)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-aminopyrimidine-2-thiol (38.1 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (3:1 EtOAc:hexanes) as white solid (X = Br, 41 mg, 83%).

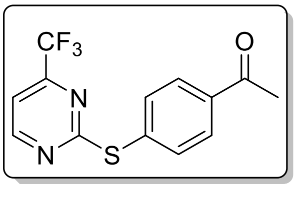
Physical State: white solid;

R$_f$ = 0.1 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 7.98 – 7.94 (m, 2H), 7.86 (d, *J* = 6.0 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.03 (s, 2H), 6.20 (d, *J* = 6.7 Hz, 1H), 2.60 (s, 3H)

^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 197.8, 169.1, 163.8, 155.5, 137.1, 136.6, 134.3, 128.9, 102.8, 27.2

HRMS (ESI-TOF): m/z calcd. for $C_{12}H_{11}N_3OS$ ($[M+H]^+$) 246.0701, found 246.0709.



1-(4-((4-(Trifluoromethyl)pyrimidin-2-yl)thio)phenyl)ethan-1-one (5e)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 4-(trifluoromethyl)pyrimidine-2-thiol (54.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 22 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:2 EtOAc:hexanes) as yellow solid (X = Br, 45 mg, 79%).

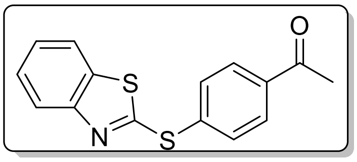
Physical State: yellow solid;

R_f = 0.2 (silica gel, 1:4 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.8, 0.5 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.76 – 7.71 (m, 2H), 7.32 (d, *J* = 5.1 Hz, 1H), 2.64 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 173.2, 159.8, 156.1 (q, *J* = 36.7 Hz), 137.5, 134.7, 134.4, 128.9, 120.0 (q, *J* = 273.7 Hz), 112.8 (q, *J* = 2.6 Hz), 26.7.

HRMS (ESI-TOF): m/z calcd. for $C_{13}H_9F_3N_2OS$ ($[M+H]^+$) 299.0466, found 299.0458.



1-(4-(Benzo[d]thiazol-2-ylthio)phenyl)ethan-1-one (5f)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), benzo[*d*]thiazole-2-thiol (40.1 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 21 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:3 EtOAc:hexanes) as white solid (X = Br, 50 mg, 87%).

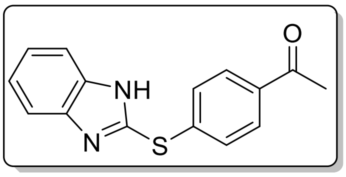
Physical State: white solid;

R_f = 0.3 (silica gel, 1:4 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.96 – 7.93 (m, 1H), 7.79 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.75 – 7.72 (m, 1H), 7.49 – 7.43 (m, 1H), 7.37 – 7.28 (m, 1H), 2.65 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.0, 165.7, 153.6, 137.6, 136.6, 135.9, 133.6, 129.4, 126.4, 124.9, 122.4, 120.9, 26.7

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{11}NOS_2$ ($[M+H]^+$) 286.0360, found 286.0363.



1-(4-((1*H*-benzo[*d*]imidazol-2-yl)thio)phenyl)ethan-1-one (5g)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 1*H*-benzo[*d*]imidazole-2-thiol (45.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as white solid (X = Br, 42 mg, 78%).

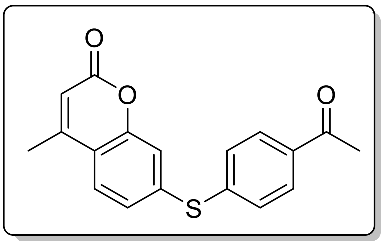
Physical State: white solid;

R$_f$ = 0.3 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.69 – 7.65 (m, 2H), 7.50 (dd, *J* = 6.0, 3.0 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.24 (dd, *J* = 6.0, 3.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.1, 145.7, 138.2, 136.0, 130.3, 130.1, 129.1, 128.8, 123.2, 26.5

HRMS (ESI-TOF): m/z calcd. for $C_{15}H_{12}N_2OS$ ($[M+H]^+$) 269.0749, found 269.0746.



7-((4-Acetylphenyl)thio)-4-methyl-2H-chromen-2-one (5h)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 7-mercapto-4-methylcoumarin (57.6 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as white solid (X = Br, 46 mg, 74%).

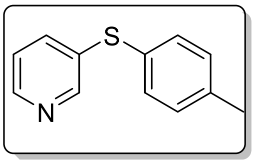
Physical State: white solid;

R_f = 0.5 (silica gel, 1:1 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.44 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.23 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.20 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.25 (q, *J* = 1.2 Hz, 1H), 2.60 (s, 3H), 2.41 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 160.2, 153.9, 151.8, 140.2, 140.1, 136.3, 131.2, 129.3, 125.9, 125.2, 118.9, 118.1, 115.0, 26.6, 18.6

HRMS (ESI-TOF): m/z calcd. for $C_{18}H_{14}O_3S$ ($[M+H]^+$) 311.0742, found 311.0735.



3-(*p*-Tolylthio)pyridine (5i)[25]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 3-iodopyridine (40.8 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 23 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:2 EtOAc:hexanes) as yellow oil (X = Br, 28 mg, 70%, X = I, 38 mg, 92%, X = Cl, 36 mg, 90%).

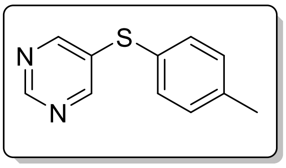
Physical State: yellow oil;

R_f = 0.4 (silica gel, 1:2=EtOAc:hexanes).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.50 (d, *J* = 1.8 Hz, 1H), 8.41 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 7.19 – 7.14 (m, 3H), 2.35 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 150.1, 147.3, 138.4, 136.8, 132.8, 130.3, 129.6, 123.8, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{12}H_{11}NS$ ($[M+H]^+$) 202.0690, found 202.0696.



5-(*p*-Tolylthio)pyrimidine (5j)[26]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 5-bromopyrimidine (31.6 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:1 EtOAc:hexanes) as yellow solid (X = Br, 33 mg, 81%).

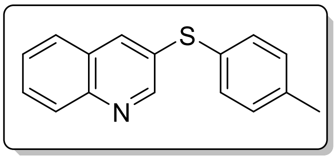
Physical State: yellow solid;

R_f = 0.7 (silica gel, 2:1 EtOAc:hexanes).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.98 (s, 1H), 8.52 (s, 2H), 7.39 – 7.35 (m, 2H), 7.22 – 7.19 (m, 2H), 2.37 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 156.1, 155.8, 139.4, 133.5, 130.7, 127.4, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{11}H_{10}N_2S$ ($[M+H]^+$) 203.0643, found 203.0646.



3-(p-Tolylthio)quinolone (5k)[27]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 6-bromoquinoline (41.6 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 13 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as colorless oil (X = Br, 52 mg, 92%).

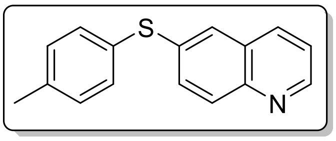
Physical State: yellow oil;

R_f = 0.3 (silica gel, 1:5 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.4 Hz, 1H), 8.10 – 8.06 (m, 1H), 7.99 (dd, *J* = 2.1, 0.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.57 – 7.51 (m, 1H), 7.39 – 7.35 (m, 2H), 7.21 – 7.17 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 146.5, 138.3, 135.6, 132.4, 131.3, 130.4, 129.9, 129.3, 129.2, 128.2, 127.2, 127.1, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{16}H_{13}NS$ ($[M+H]^+$) 252.0847, found 252.0849.



6-(*p*-Tolylthio)quinolone (5l)[28]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 3-bromoquinoline (41.6 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 12 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as yellow oil (X = Br, 46 mg, 91%).

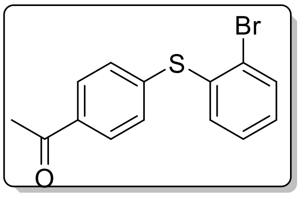
Physical State: yellow oil;

R_f = 0.3 (silica gel, 1:5 EtOAc:hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.54 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.37 – 7.32 (m, 1H), 7.21 – 7.17 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 150.1, 147.0, 138.4, 136.5, 135.1, 133.1, 130.6, 130.3, 130.1, 130.0, 128.7, 126.5, 121.6, 21.2

HRMS (ESI-TOF): m/z calcd. for $C_{16}H_{13}NS$ ([M+H]$^+$) 252.0847, found 252.0851.



1-(4-((2-Bromophenyl)thio)phenyl)ethan-1-one (6)[29]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 2-bromobenzenethiol (37.8 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1.5 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as white solid (X = Br, 52 mg, 84%).

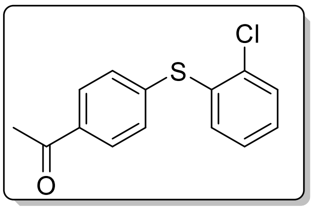
Physical State: white solid;

R$_f$ = 0.5 (silica gel, 1:4 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.92 – 7.87 (m, 2H), 7.71 – 7.68 (m, 1H), 7.42 – 7.38 (m, 1H), 7.34 – 7.28 (m, 3H), 7.26 – 7.12 (m, 1H), 2.59 (s, 3H)

^{13}C NMR (75 MHz, CDCl$_3$) δ 197.1, 142.0 135.3, 134.5, 134.3, 133.7, 129.7, 129.1 129.0, 128.3, 127.4, 26.5

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}BrOS$ ([M+H]$^+$) 308.9772, found 308.9766.



1-(4-((2-Chlorophenyl)thio)phenyl)ethan-1-one (7)[29]

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 4′-Bromoacetophenone (39.8 mg, 0.2 mmol, 1.00 eq.), 2-bromobenzenethiol (37.8 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 1.5 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as white solid (X = Br, 49 mg, 93%).

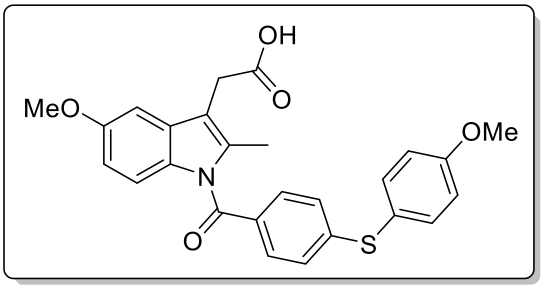
Physical State: white solid;

R_f = 0.5 (silica gel, 1:4 EtOAc:hexanes)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.51 – 7.48 (m, 1H), 7.42 – 7.39 (m, 1H), 7.34 – 7.29(m, 1H), 7.29 – 7.22 (m, 3H), 2.57 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 142.0, 137.0, 135.2, 134.6, 132.2, 130.4, 129.7, 129.1, 128.8, 127.6, 26.5

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{11}ClOS$ ($[M+H]^+$) 263.0297, found 263.0299.



2-(5-Methoxy-1-(4-((4-methoxyphenyl)thio)benzoyl)-2-methyl-1H-indol-3-yl)acetic acid (8)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), Indometacin (71.6 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 20 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (10:1 DCM:MeOH) as yellow solid (X = Cl, 70 mg, 76%).

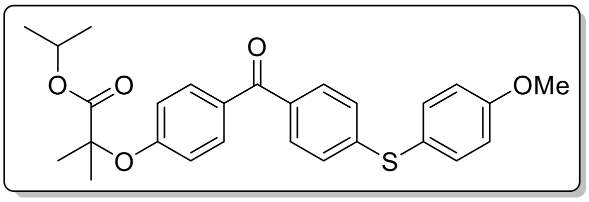
Physical State: yellow solid;

R$_f$ = 0.5 (silica gel, 10:1 DCM:MeOH)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 – 7.48 (m, 4H), 7.11 (dd, *J* = 6.6 Hz, 1.8 Hz, 2H), 6.98 – 6.90 (m, 4H), 6.67 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.68 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 177.0, 168.8, 160.8, 155.9, 147.1, 136.9, 136.3 131.6, 131.0, 130.5, 130.3, 125.8, 121.0, 115.5, 115.0, 111.6, 111.2, 101.0, 55.7, 55.4, 30.1, 13.2

HRMS (ESI-TOF): m/z calcd. for $C_{26}H_{23}NO_5S$ ($[M+H]^+$) 462.1375, found 462.1365.



Isopropyl 2-(4-(4-((4-methoxyphenyl)thio)benzoyl)phenoxy)-2-methylpropanoate (9)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), Fenofibrate (72.0 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 22 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:5 EtOAc:hexanes) as white solid (X = Cl, 74 mg, 79%).

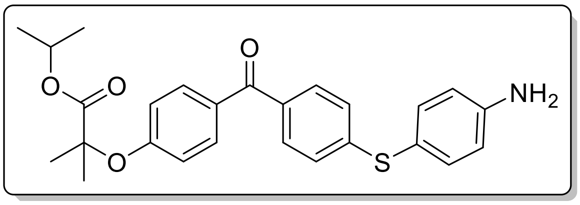
Physical State: white solid;

R$_f$ = 0.5 (silica gel, 1:5 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 (dt, *J* = 9.0, 2.4 Hz, 2H), 7.62 (dt, *J* = 8.7, 1.8 Hz, 2H), 7.49 (dt, *J* = 9.0, 2.4 Hz, 2H), 7.16 – 7.06 (m, 2H), 7.00 – 6.92 (m, 2H), 6.91 – 6.78 (m, 2H), 5.12 – 5.04 (m, 1H), 3.85 (s, 3H), 1.65 (s, 6H), 1.20 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 194.5, 173.1, 160.6, 159.4, 145.4, 136.7, 134.7, 131.8, 130.8, 130.4, 125.8, 121.7, 117.2, 115.3, 79.4, 69.3, 55.4, 25.4, 21.5

HRMS (ESI-TOF): m/z calcd. for $C_{27}H_{28}O_5S$ ($[M+H]^+$) 465.1736, found 465.1722.



Isopropyl 2-(4-(4-((4-aminophenyl)thio)benzoyl)phenoxy)-2-methylpropanoate (10)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), Fenofibrate (72.0 mg, 0.2 mmol, 1.00 eq.), 4-aminobenzenethiol (37.5 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 22 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:3 EtOAc:hexanes) as yellow solid (X = Cl, 70 mg, 79%).

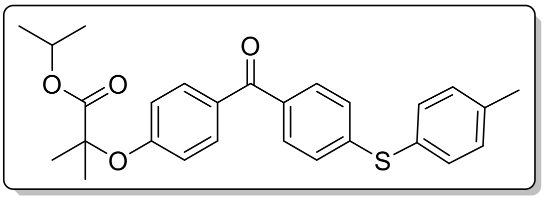
Physical State: yellow solid;

R$_f$ = 0.5 (silica gel, 1:2 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.73 – 7.68 (m, 2H), 7.62 – 7.58 (m, 2H), 7.37 – 7.32 (m, 2H), 7.12 – 7.08 (m, 2H), 6.85 – 6.82 (m, 2H), 6.73 – 6.69 (m, 2H), 5.12 – 5.03 (m, 1H), 3.92 (s, 2H), 1.64 (s, 6H), 1.20 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 194.6, 173.2, 159.3, 147.9, 146.5, 137.0, 134.3, 131.8, 130.9, 130.4, 125.2, 117.9, 117.2, 116.0, 79.4, 69.3, 25.4, 21.5

HRMS (ESI-TOF): m/z calcd. for $C_{26}H_{27}NO_4S$ ($[M+H]^+$) 450.1739, found 450.1750.



Isopropyl 2-methyl-2-(4-(4-(p-tolylthio)benzoyl)phenoxy)propanoate (11)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), Fenofibrate (72.0 mg, 0.2 mmol, 1.00 eq.), *p*-Toluenethiol (37.3 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 22 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (1:6

EtOAc:hexanes) as white solid (X = Cl, 57 mg, 60%).

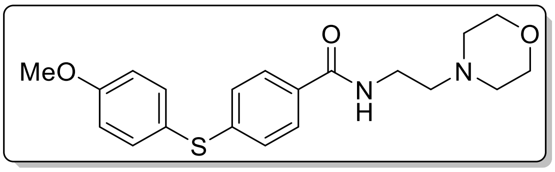
Physical State: white solid;

R_f = 0.5 (silica gel, 1:6 EtOAc:hexanes)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 – 7.69 (m, 2H), 7.64 – 7.60 (m, 2H), 7.44 – 7.40 (m, 2H), 7.24 – 7.16 (m, 4H), 6.86 – 6.83 (m, 2H), 5.12 – 5.04 (m, 1H), 2.39 (s, 3H), 1.65 (s, 6H), 1.21 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 194.6, 173.1, 159.4, 144.4, 139.2, 135.0, 134.3, 131.8, 130.7, 130.5, 130.4, 128.3, 126.7, 117.2, 79.4, 69.3, 25.4, 21.5, 21.3

HRMS (ESI-TOF): m/z calcd. for $C_{27}H_{28}O_4S$ ([M+H]$^+$) 449.1786, found 449.1775.



4-((4-Methoxyphenyl)thio)-N-(2-morpholinoethyl)benzamide (12)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), Moclobemide (53.7 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 26 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (10:1 DCM:MeOH) as white solid (X = Cl, 41 mg, 50%).

Physical State: white solid;

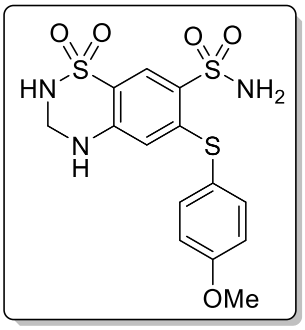
R_f = 0.5 (silica gel, 10:1 DCM:MeOH)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.63 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.48 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.14 (dd, *J* = 6.9, 2.1 Hz, 2H), 6.96 (dd, *J* = 6.9, 2.1 Hz, 2H), 6.73 (s, 1H), 3.87 (s, 3H), 3.73 (t, *J* = 4.5 Hz, 4H), 3.55 (dd, *J* = 11.4, 5.4 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 4.5 Hz, 4H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 166.8, 160.5, 144.1, 136.5, 131.3, 127.4, 126.5, 122.2, 115.3, 66.9, 56.9, 55.4, 53.3, 35.9

HRMS (ESI-TOF): m/z calcd. for $C_{20}H_{24}N_2O_3S$ ([M+H]$^+$) 373.1586, found

373.1578.



6-((4-Methoxyphenyl)thio)-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (13)

A 25 mL storage flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with Cs_2CO_3 (130.3 mg, 0.4 mmol, 2.0 eq.), Hydrochlorothiazide (59.5 mg, 0.2 mmol, 1.00 eq.), 4-methoxybenzenethiol (42.0 mg, 0.3 mmol, 1.5 eq.) and 1.5 mL DMSO. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The reaction mixture was then placed into an LED-lined beaker and stirred with an air gas tube for cooling. After stirred for 22 hours, the reaction mixture was washed with water, extracted with EtOAc and concentrated in vacuum. The product was isolated by flash chromatography (10:1 EtOAc:hexane) as white solid (X = Cl, 48 mg, 65%).

Physical State: white solid;

***R**f* = 0.5 (silica gel, EtOAc)

^{1}H NMR (300 MHz, *d*$_6$-DMSO) δ 7.92 (s, 1H), 7.72 (t, *J* = 7.8 Hz, 2H), 7.50 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.36 (s, 2H), 7.10 (dd, *J* = 6.6, 2.1 Hz, 2H), 6.12 (s, 1H), 4.56 (dd, *J* = 8.1, 2.4 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (75 MHz, *d*$_6$-DMSO) δ 161.1, 146.1, 144.6, 137.8, 127.7, 125.2, 121.1, 117.3, 116.33, 113.5, 55.9, 54.6

HRMS (ESI-TOF): m/z calcd. for $C_{14}H_{15}N_3O_5S_3$ ($[M]^-$) 400.0096, found 400.0099.

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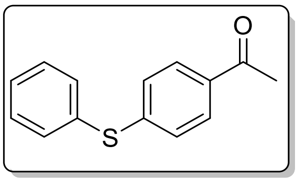
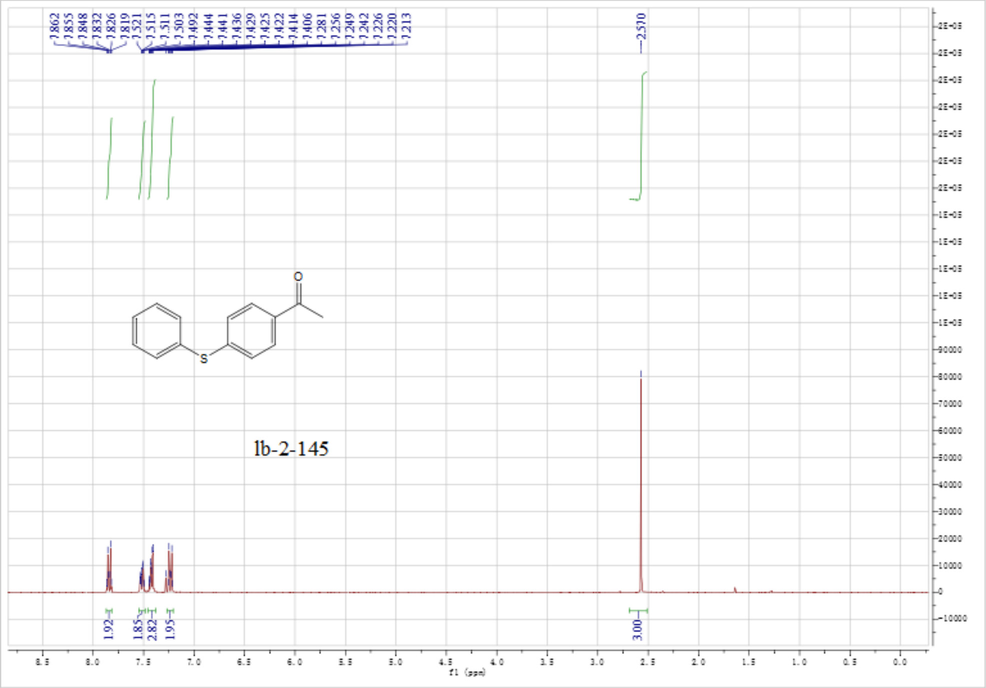
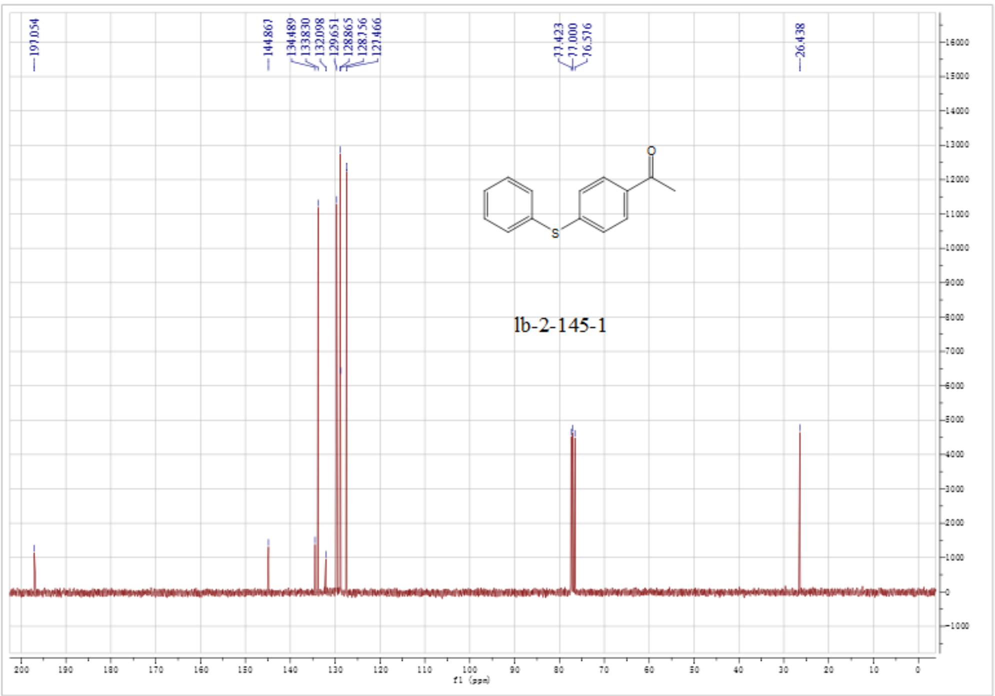
^{1}H NMR and ^{13}C NMR Spectra of New Compounds

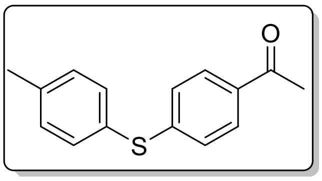


1-(4-(Phenylthio)phenyl)ethan-1-one (3a), ^{1}H NMR (300 MHz, CDCl$_3$)



^{13}C NMR (75 MHz, CDCl$_3$)





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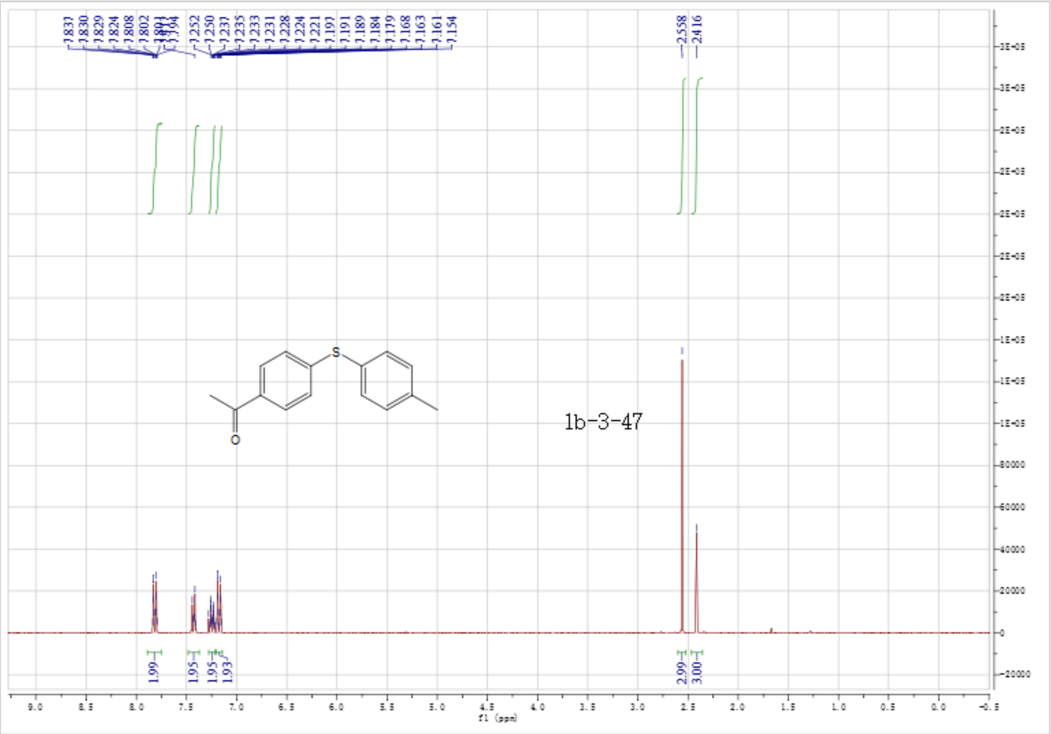

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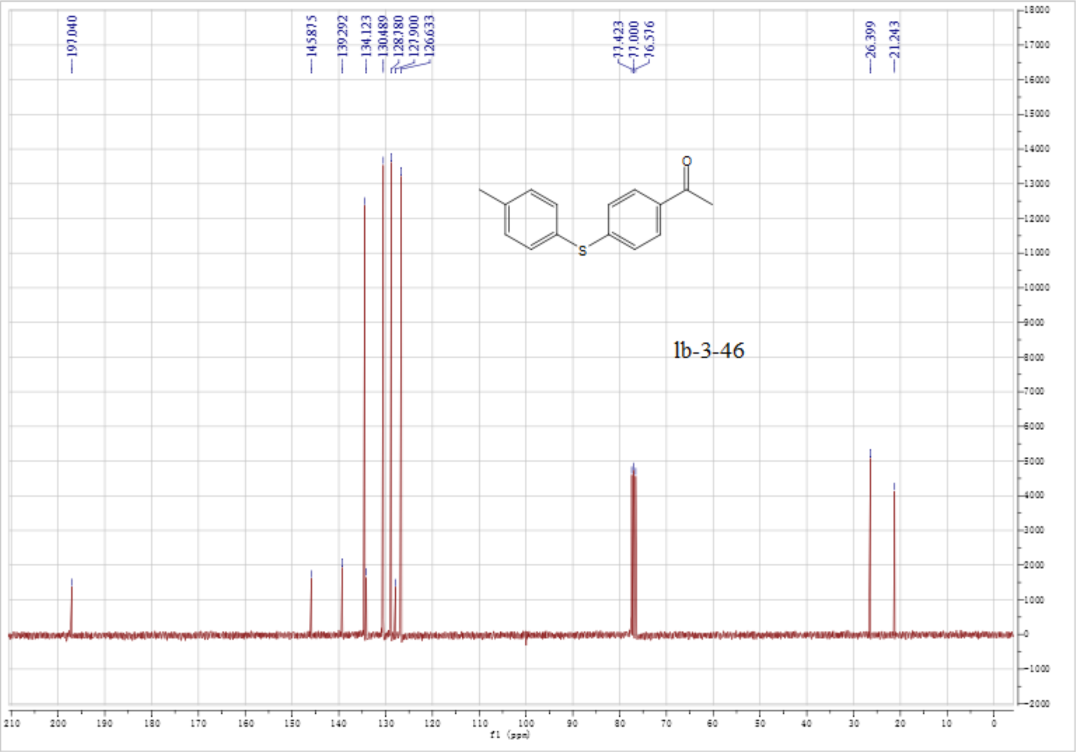
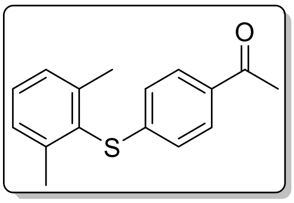
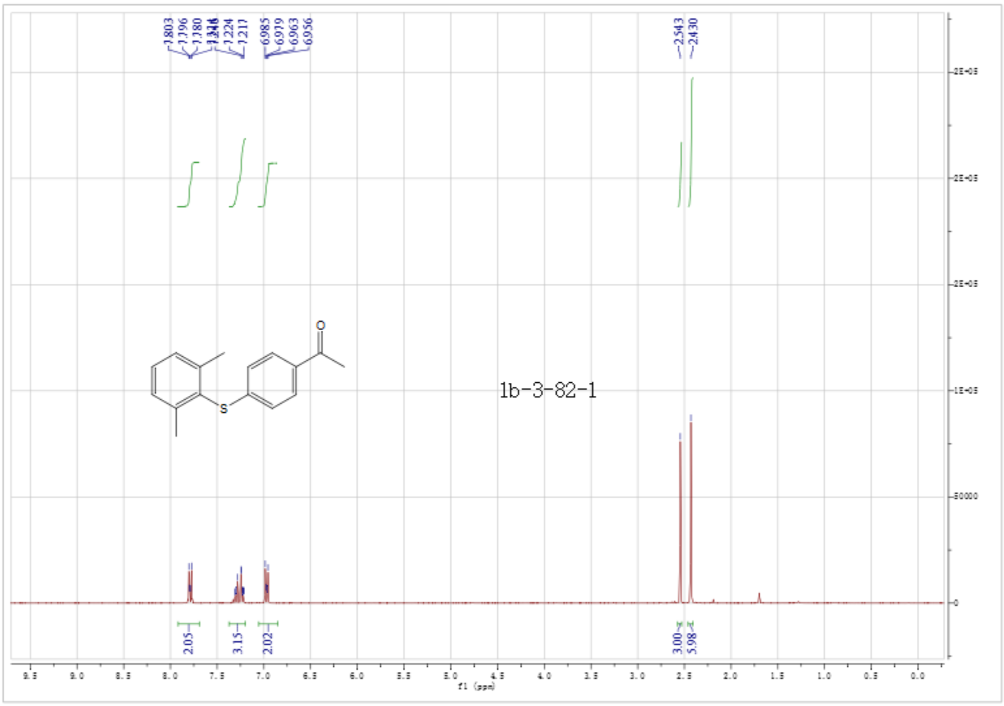
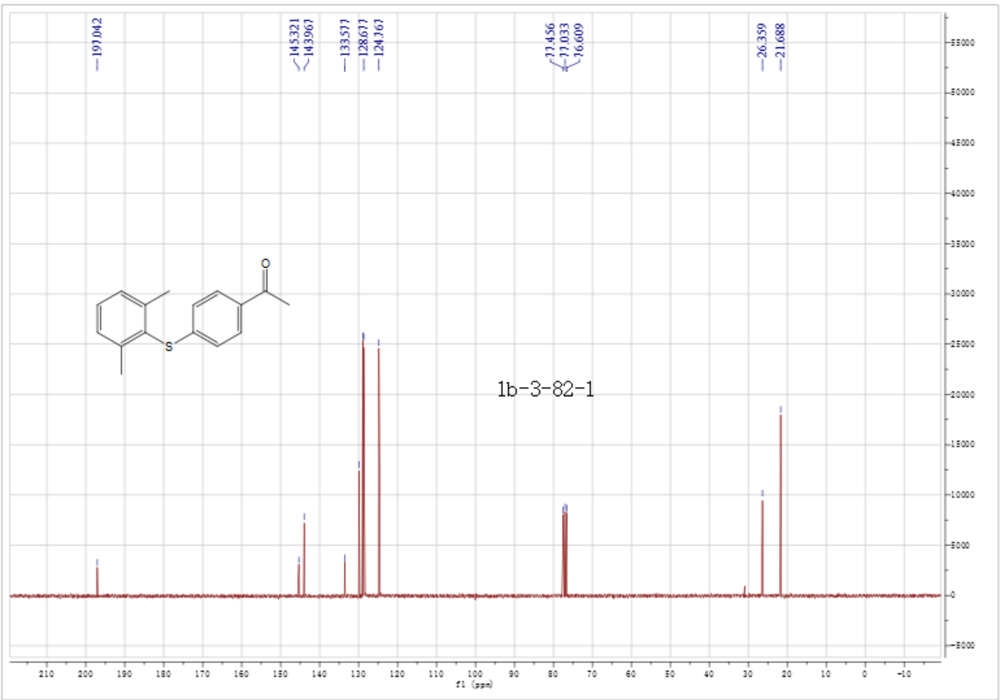


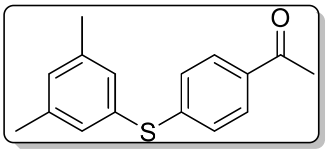


1-(4-((2,6-Dimethylphenyl)thio)phenyl)ethan-1-one (3c), ^{1}H NMR (300 MHz, CDCl$_3$)

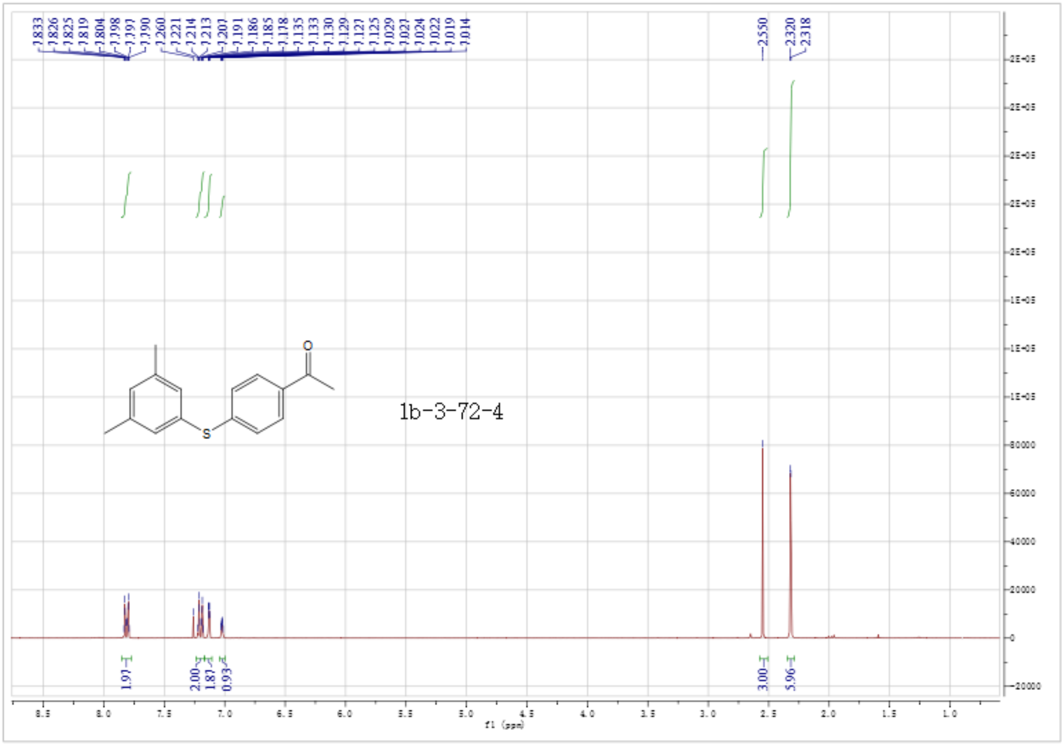


^{13}C NMR (75 MHz, CDCl$_3$)

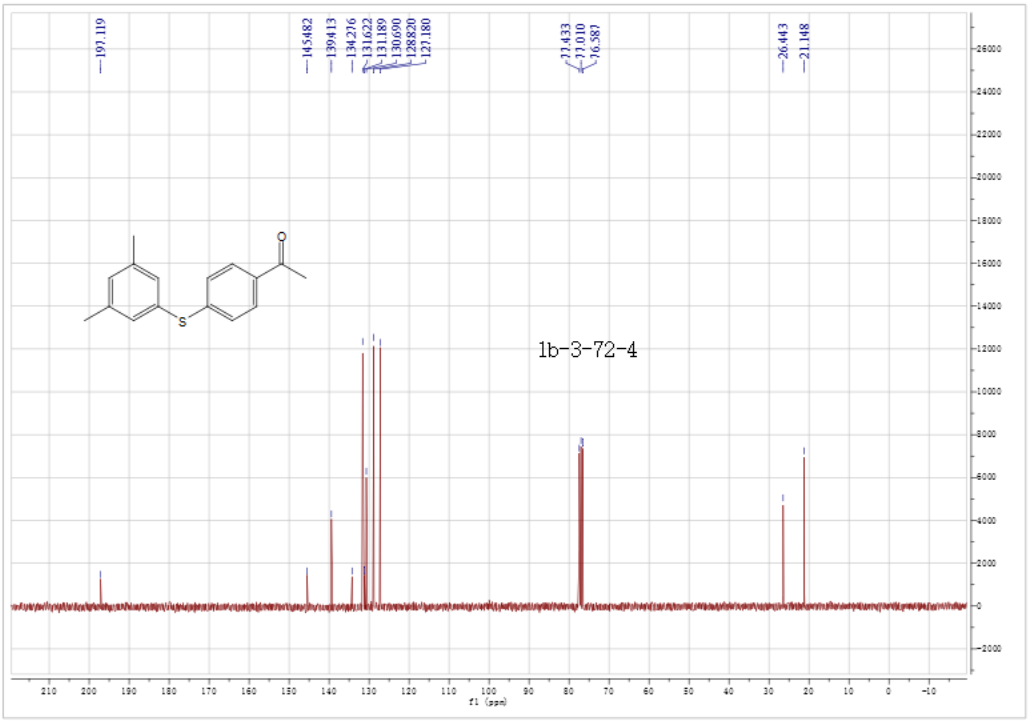


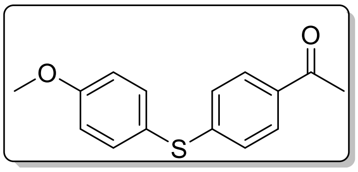


1-(4-((3,5-Dimethylphenyl)thio)phenyl)ethan-1-one (3d), ^{1}H NMR (300 MHz, CDCl$_3$)

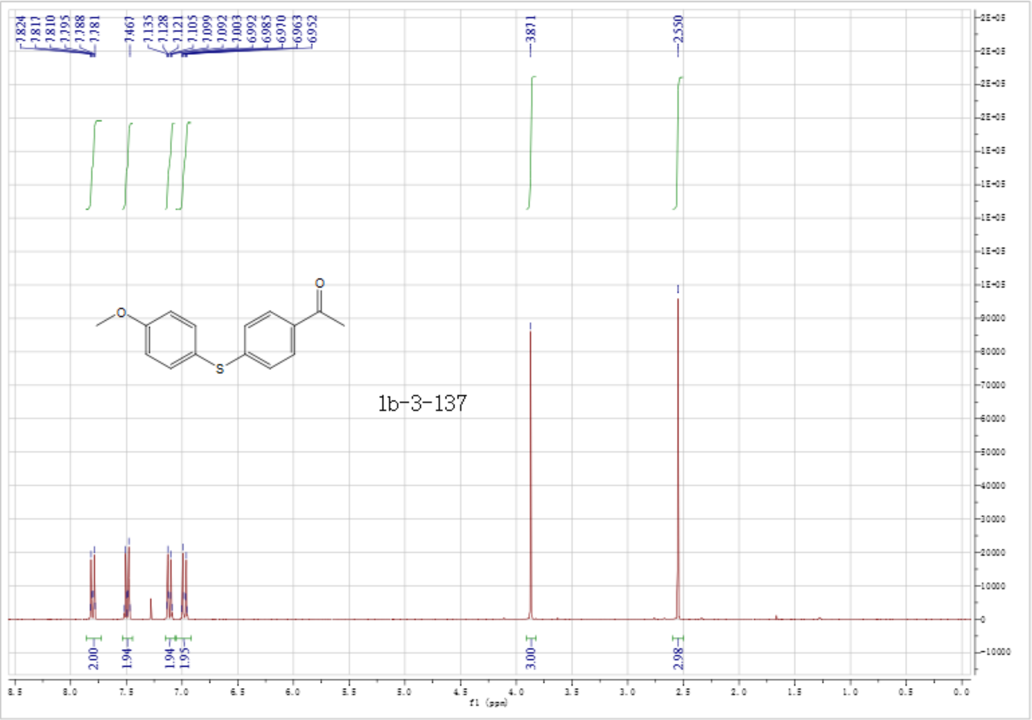


^{13}C NMR (75 MHz, CDCl$_3$)

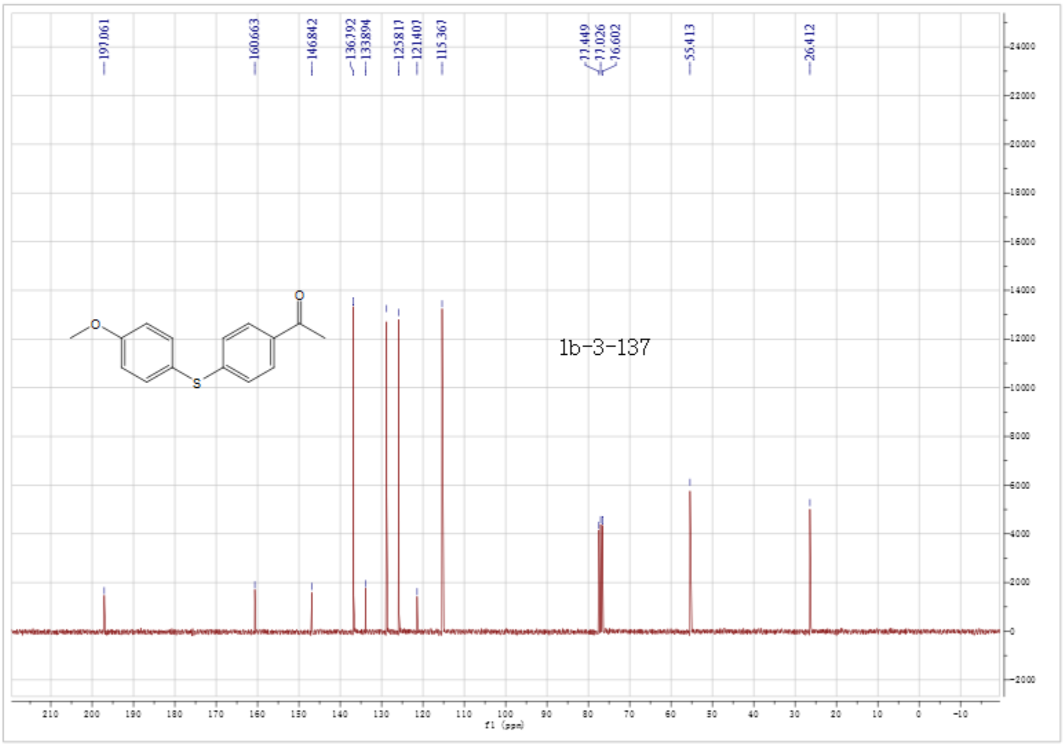


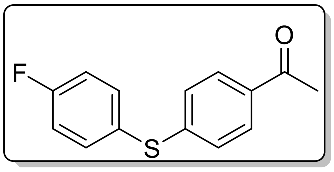


1-(4-((4-Methoxyphenyl)thio)phenyl)ethan-1-one (3e), ^{1}H NMR (300 MHz, CDCl$_3$)



^{13}C NMR (75 MHz, CDCl$_3$)





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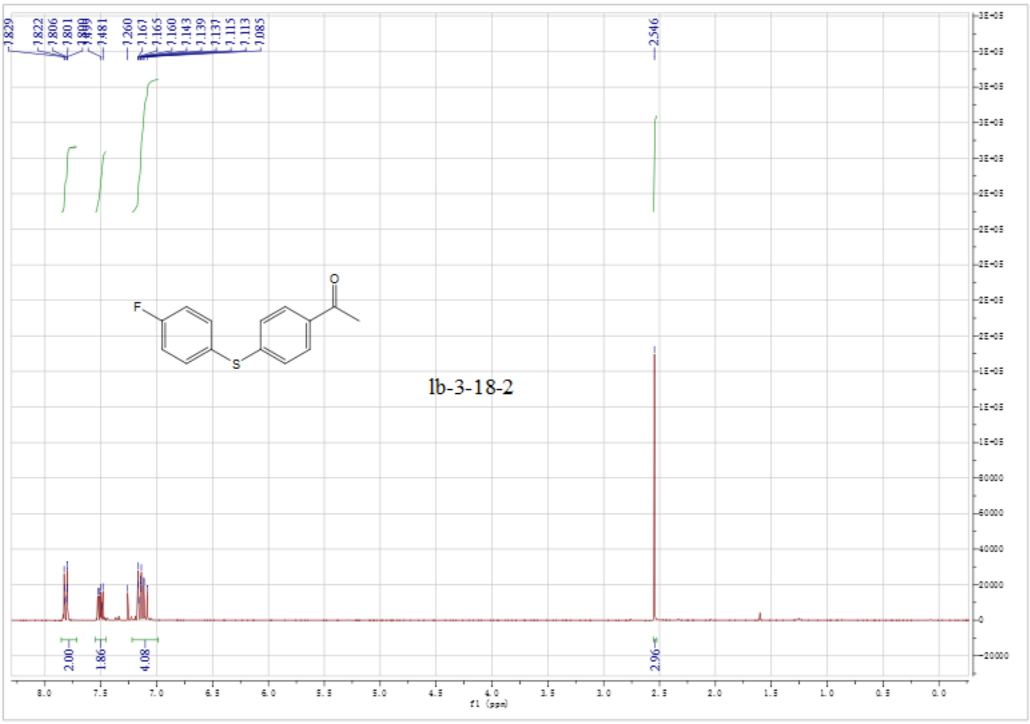

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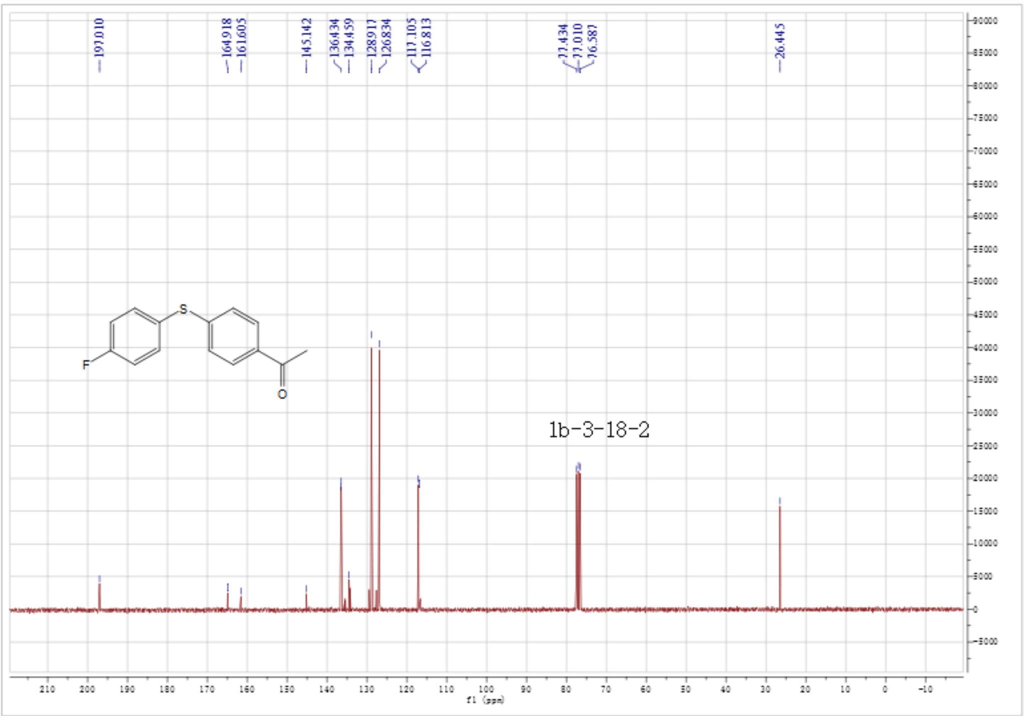
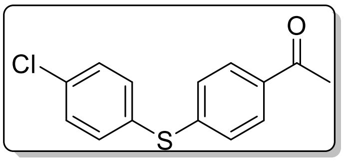
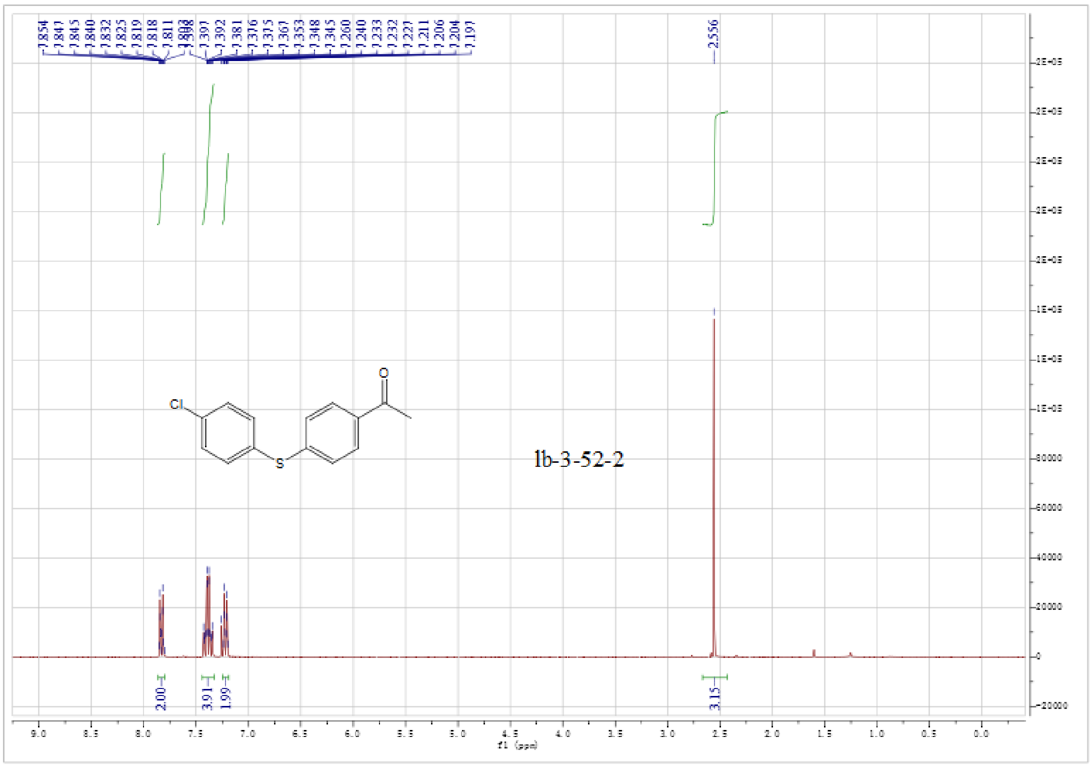
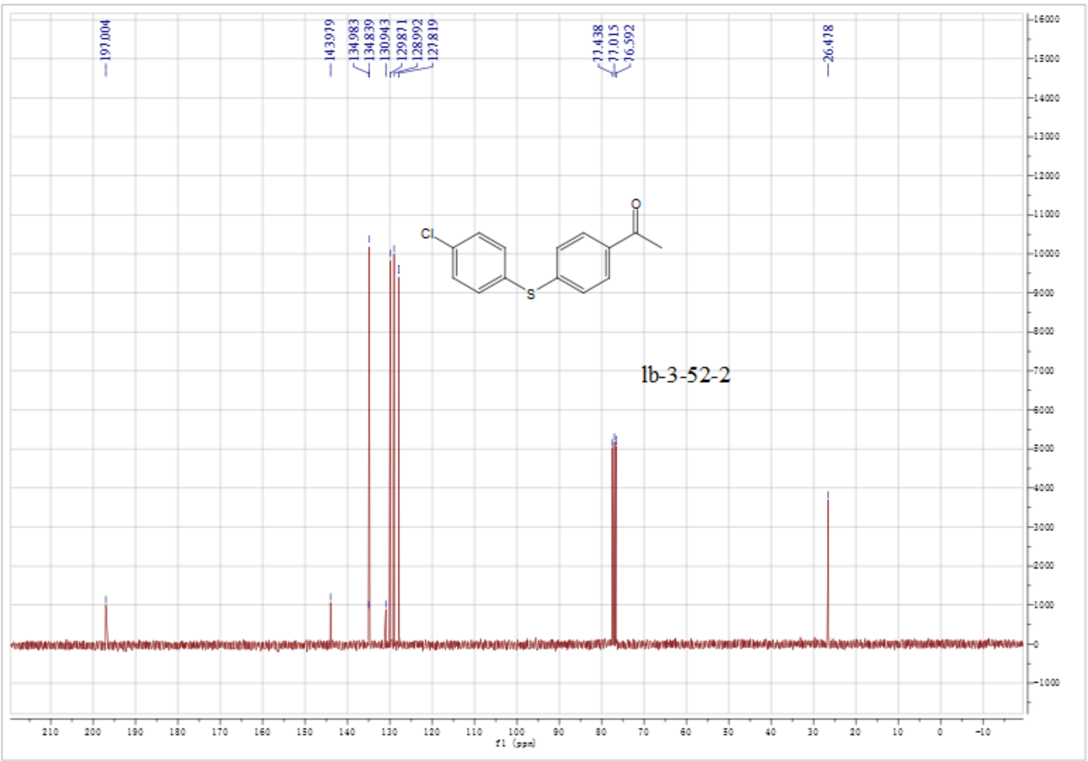


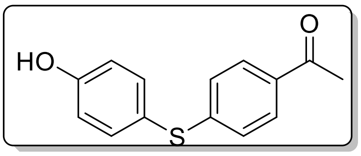


1-(4-((4-Chlorophenyl)thio)phenyl)ethan-1-one (3g), ^{1}H NMR (300 MHz, CDCl$_3$)

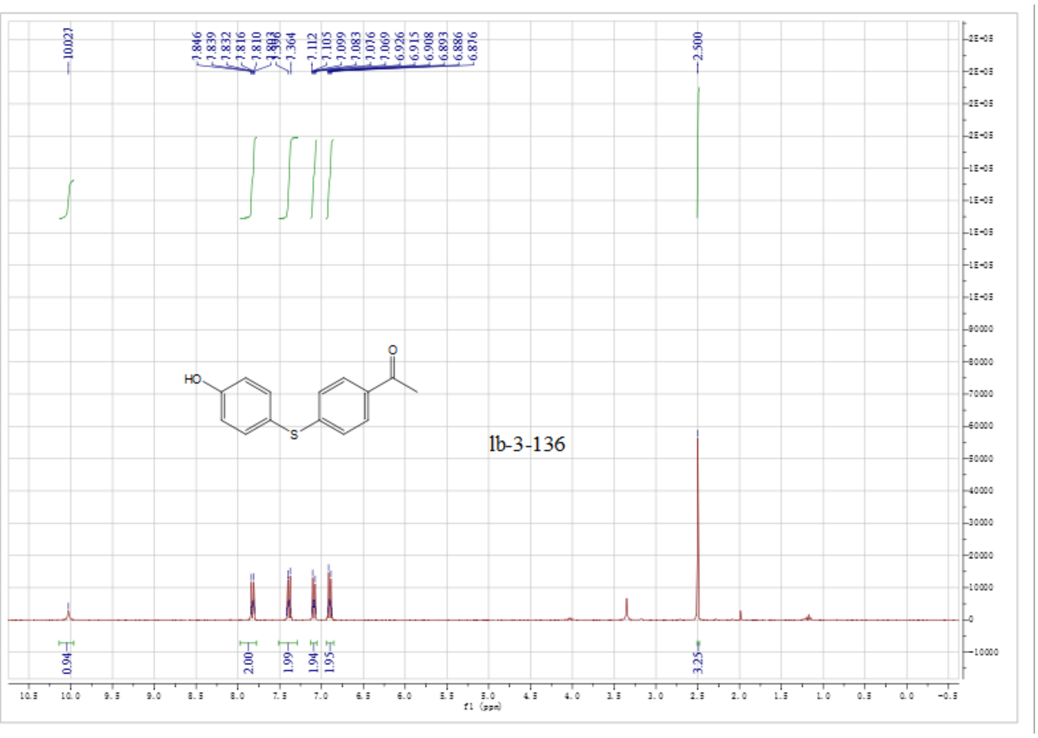


^{13}C NMR (75 MHz, CDCl$_3$)

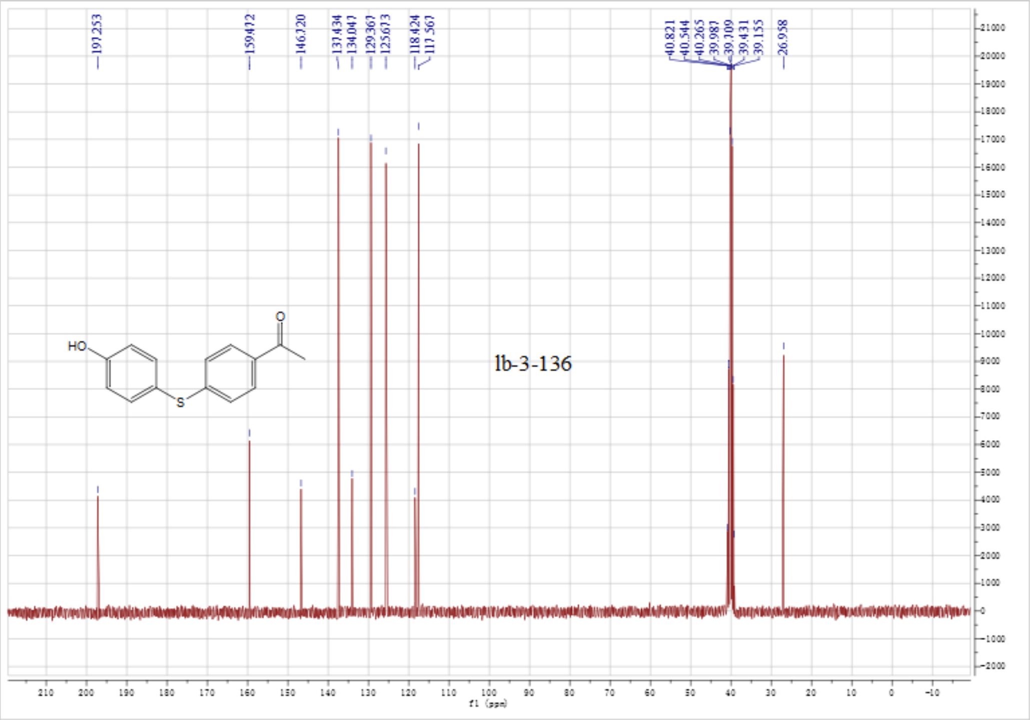


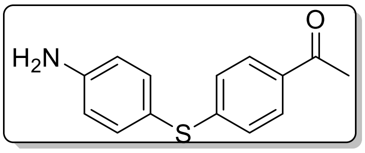


1-(4-((4-Hydroxyphenyl)thio)phenyl)ethan-1-one (3h), ^{1}H NMR (300 MHz, d_6-DMSO)

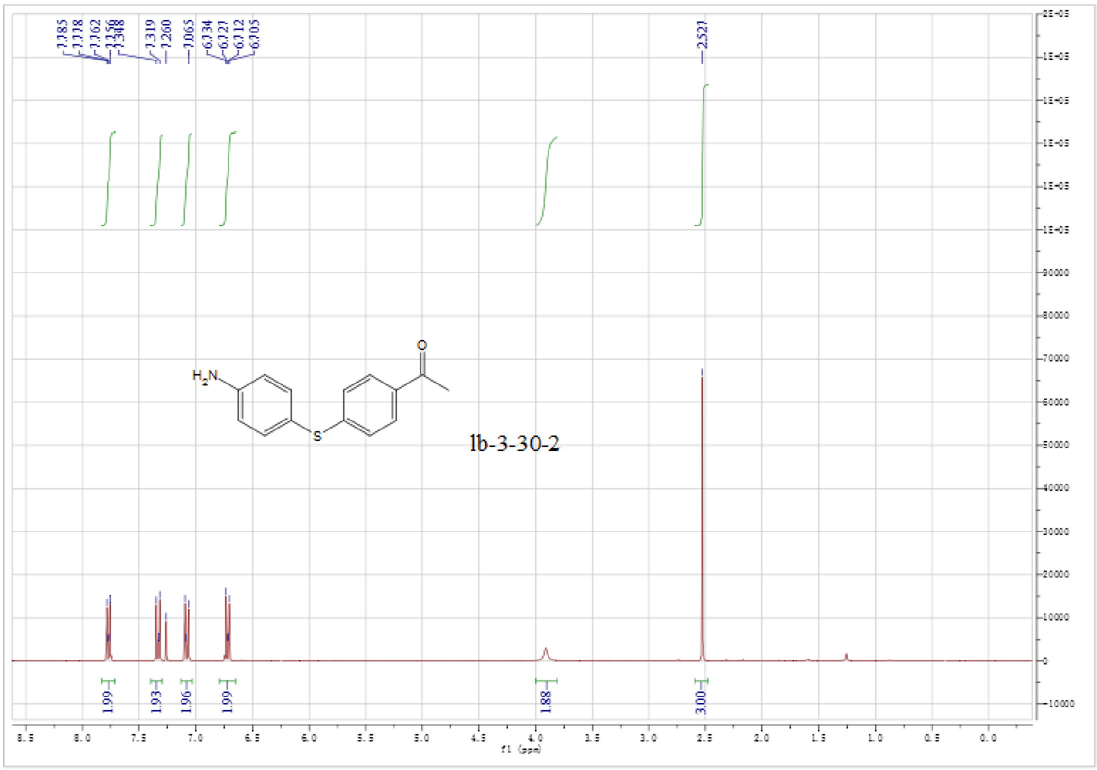


^{13}C NMR (75 MHz, d_6-DMSO)

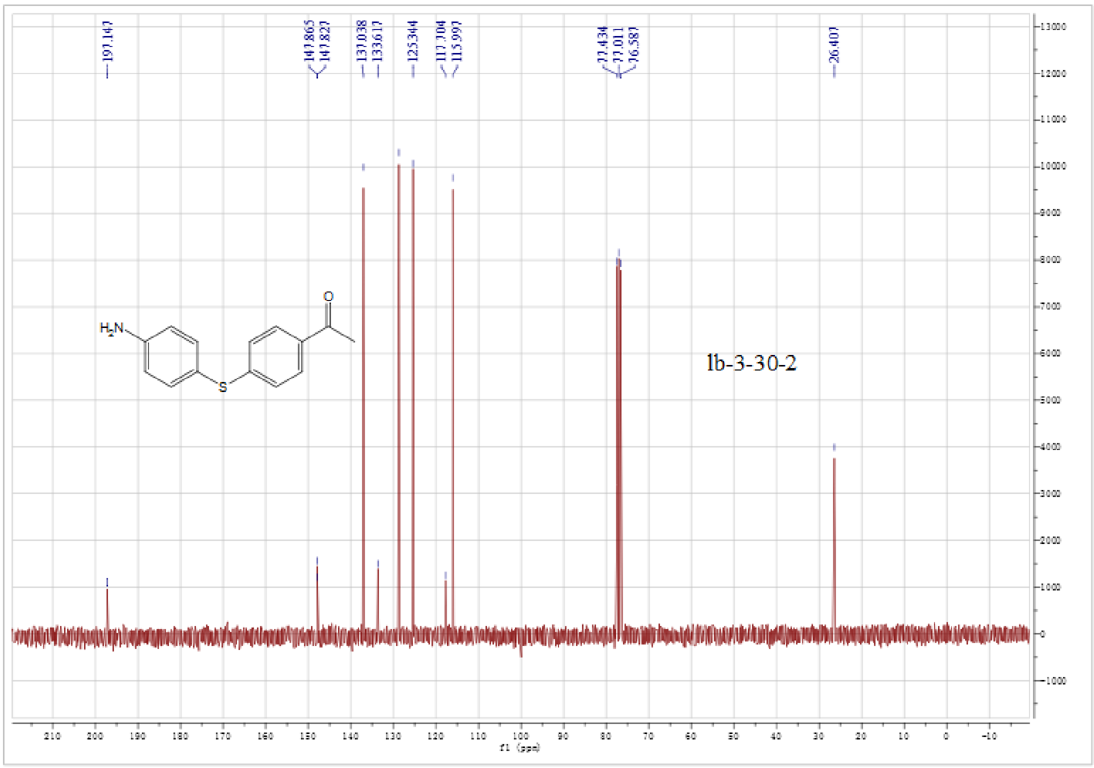


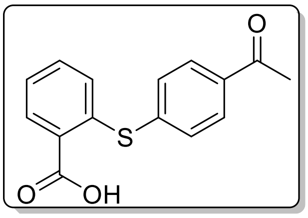


1-(4-((4-Aminophenyl)thio)phenyl)ethan-1-one (3i), ^{1}H NMR (300 MHz, $CDCl_3$)

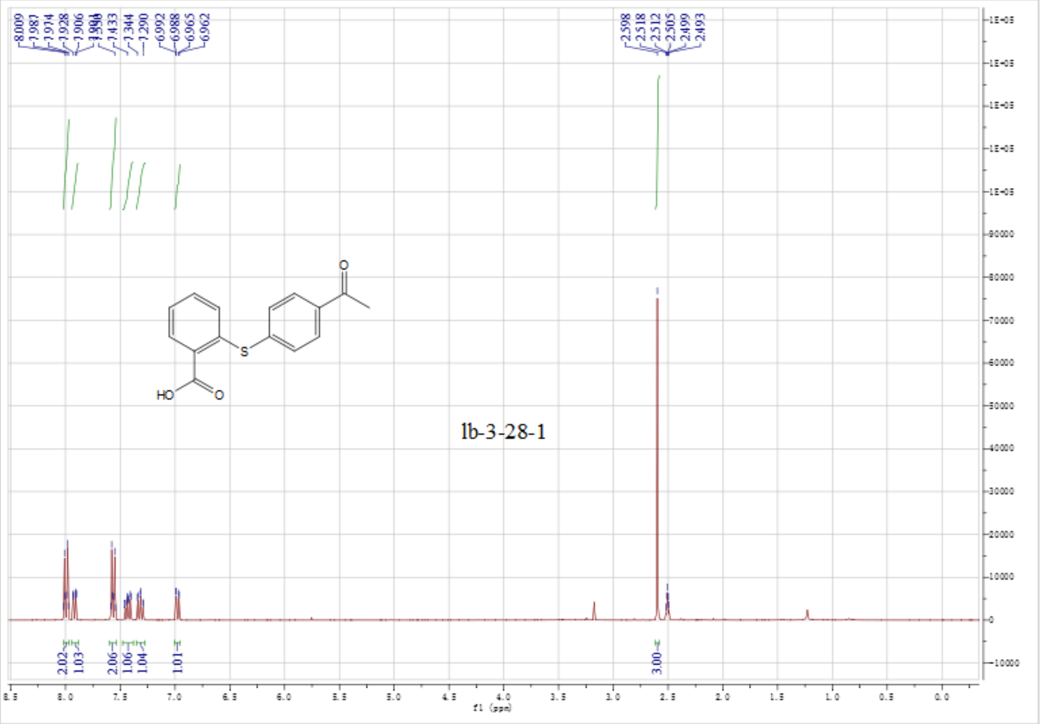


^{13}C NMR (75 MHz, $CDCl_3$)

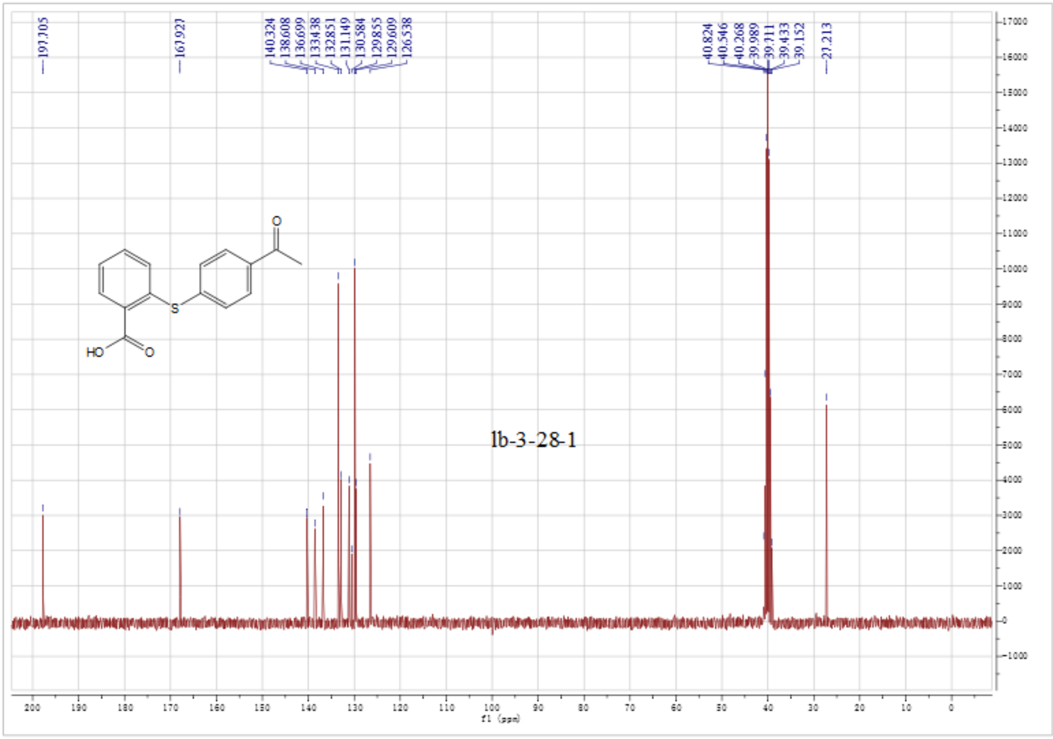


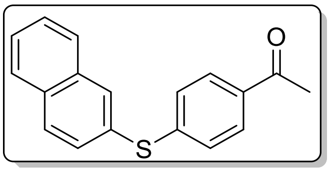


2-((4-Acetylphenyl)thio)benzoic acid (3j), ^{1}H NMR (300 MHz, d_6-DMSO)

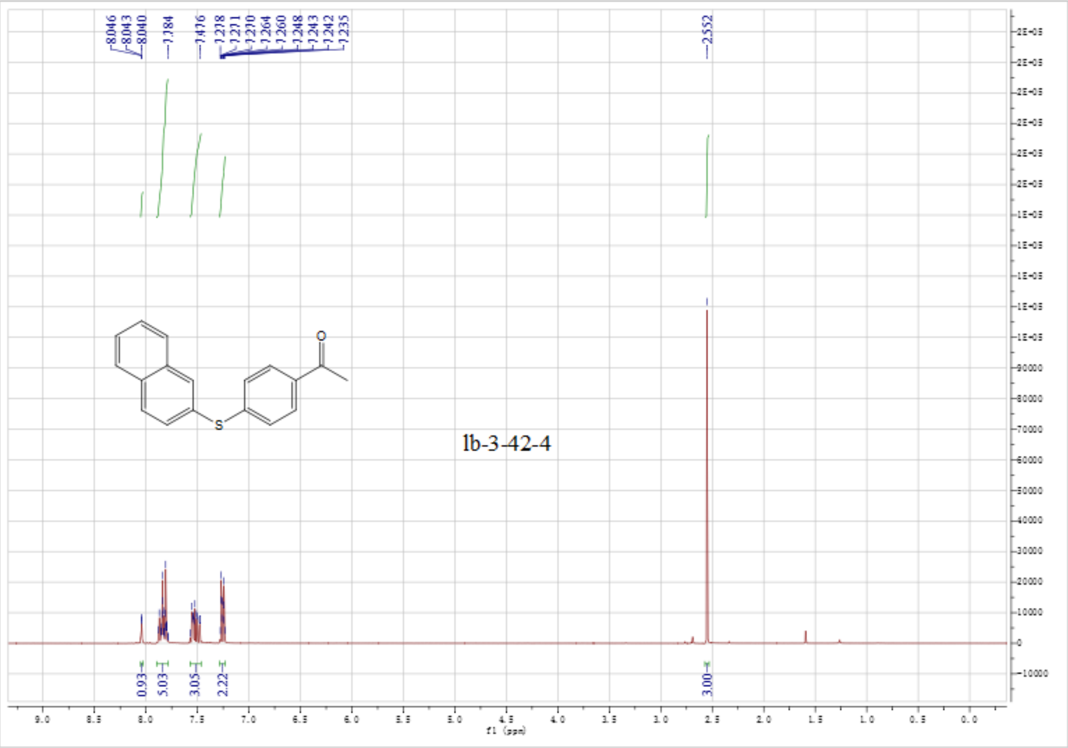


^{13}C NMR (75 MHz, d_6-DMSO)

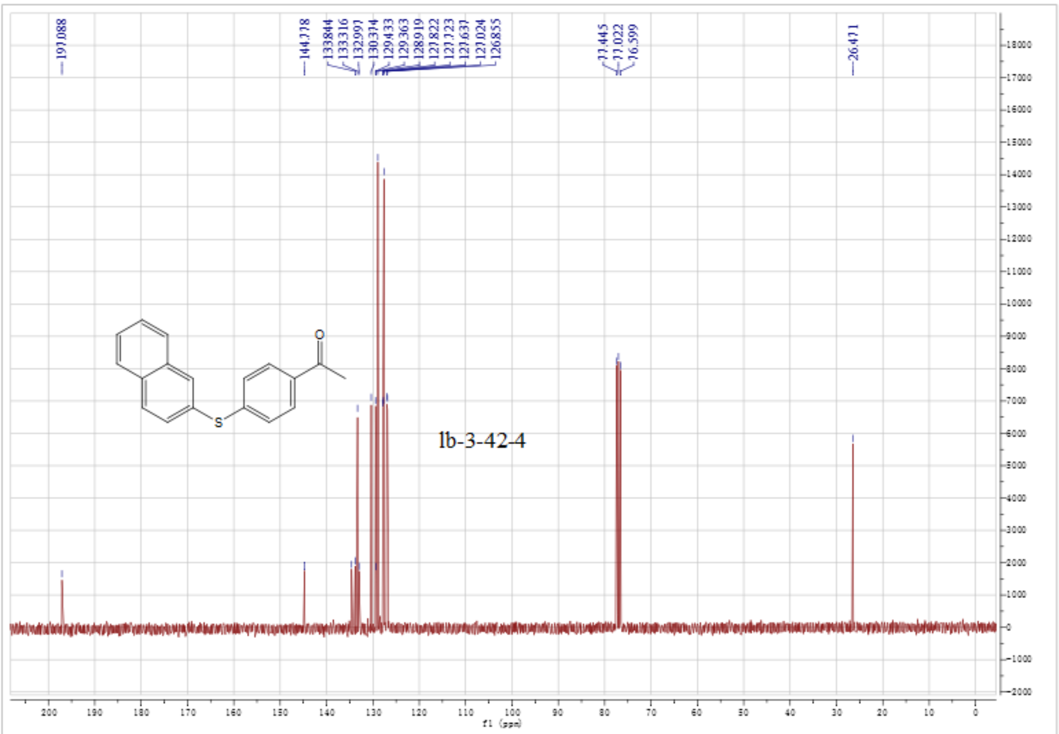


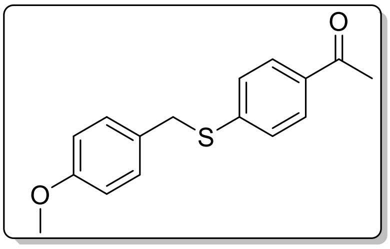


1-(4-(Naphthalen-2-ylthio)phenyl)ethan-1-one (3k), ^{1}H NMR (300 MHz, CDCl$_3$)

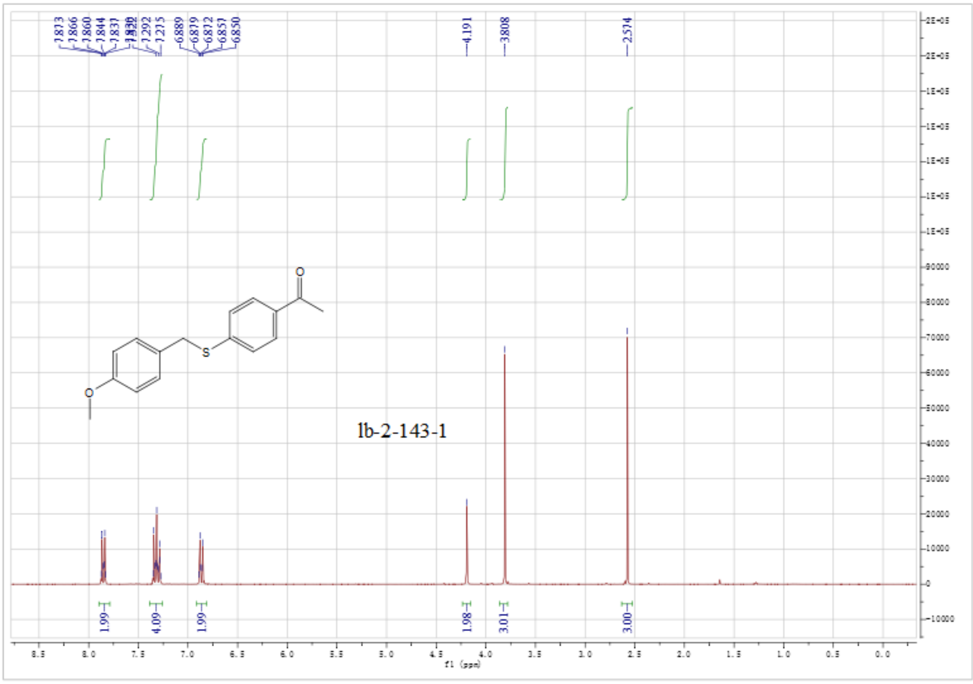


^{13}C NMR (75 MHz, CDCl$_3$)

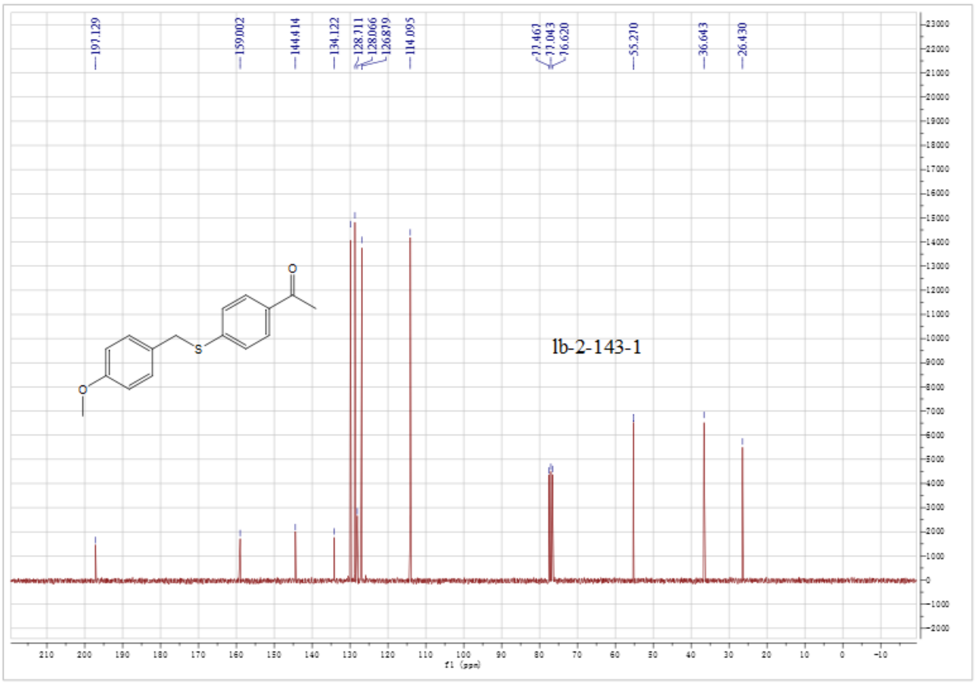


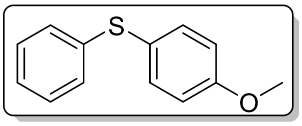


1-(4-((4-Methoxybenzyl)thio)phenyl)ethan-1-one (3l), ^{1}H NMR (300 MHz, CDCl$_3$)

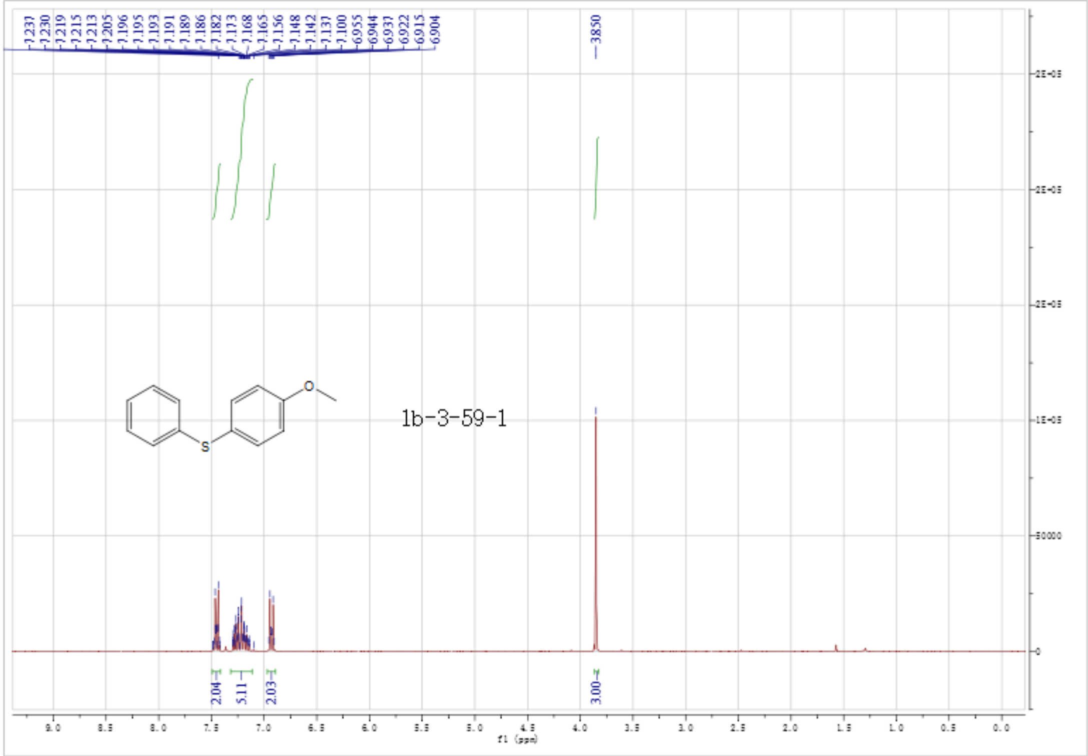


^{13}C NMR (75 MHz, CDCl$_3$)

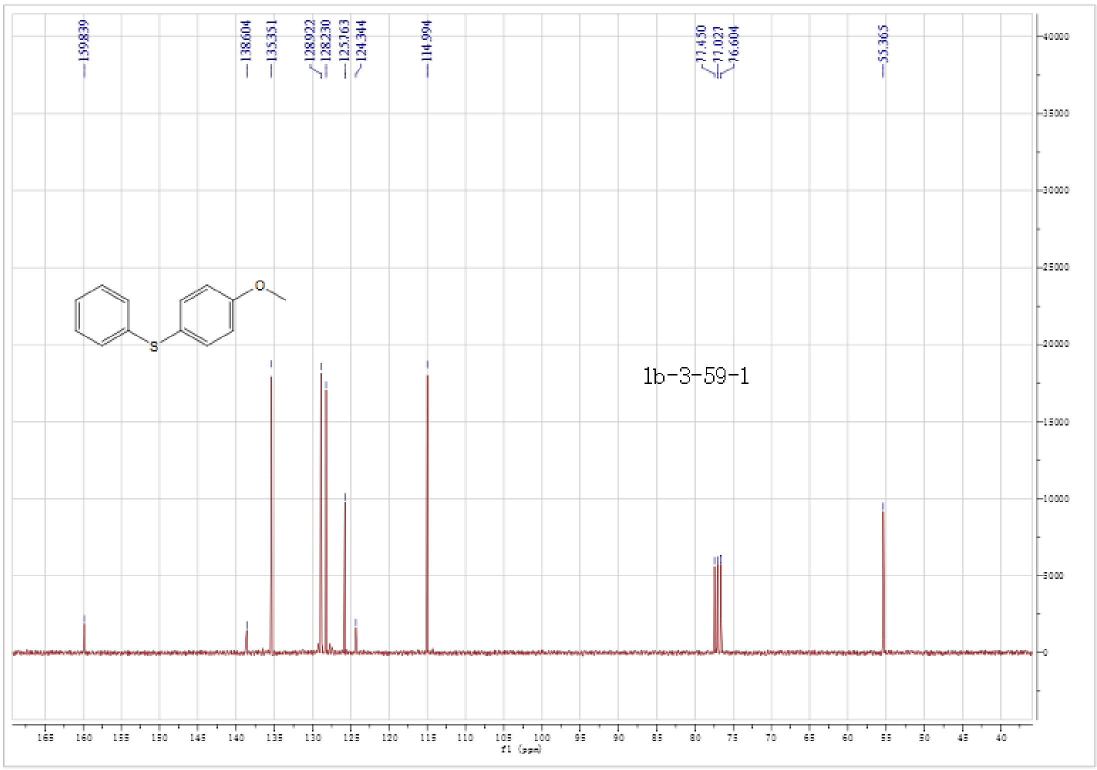


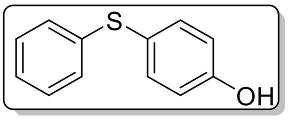


(4-Methoxyphenyl)(phenyl)sulfane (4a), ^{1}H NMR (300 MHz, CDCl$_3$)

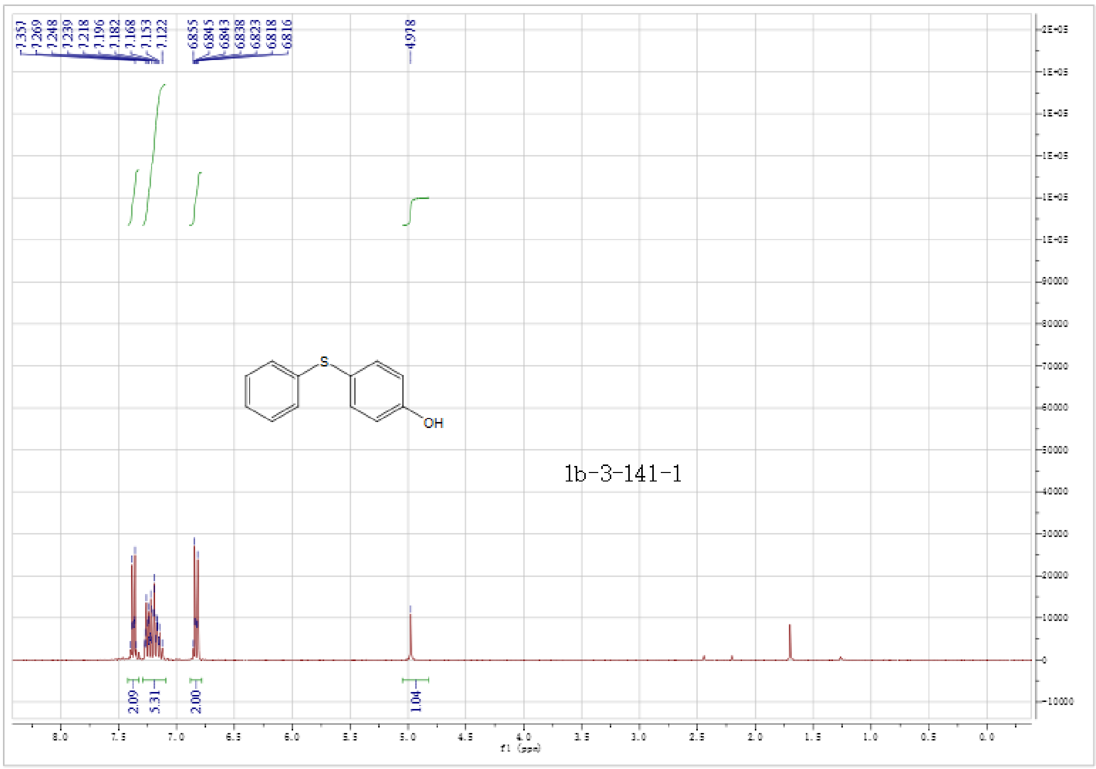


^{13}C NMR (75 MHz, CDCl$_3$)

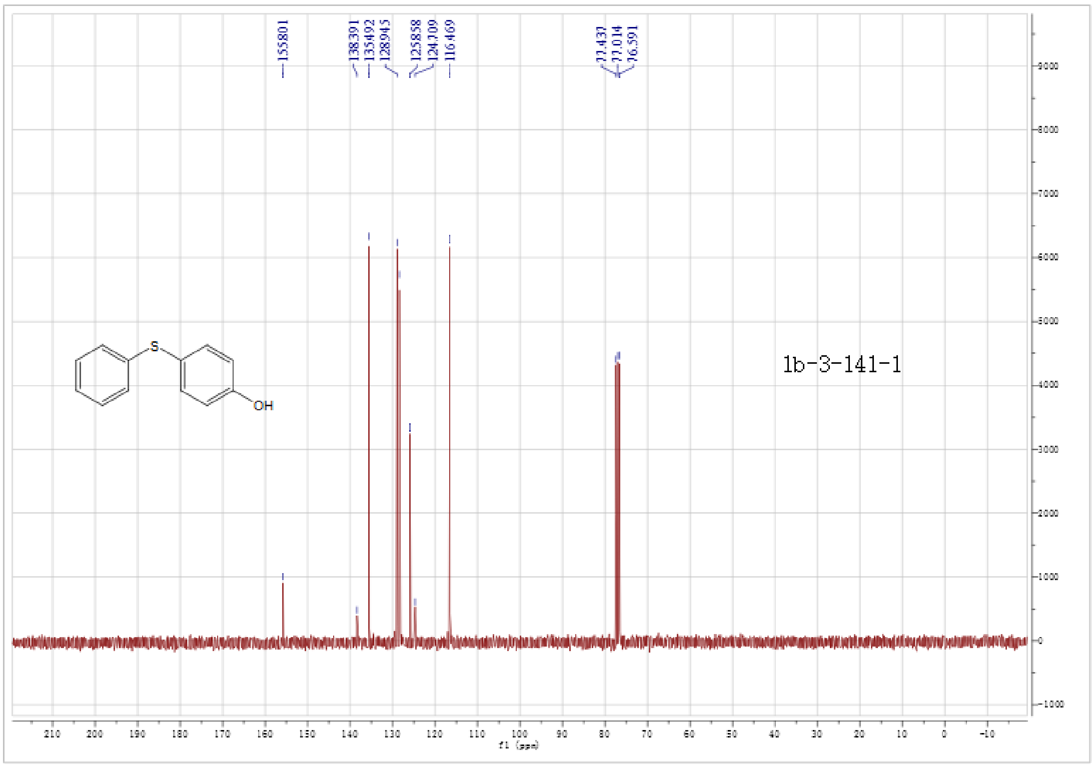


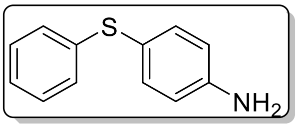


4-(Phenylthio)phenol (4b), ^{1}H NMR (300 MHz, $CDCl_3$)

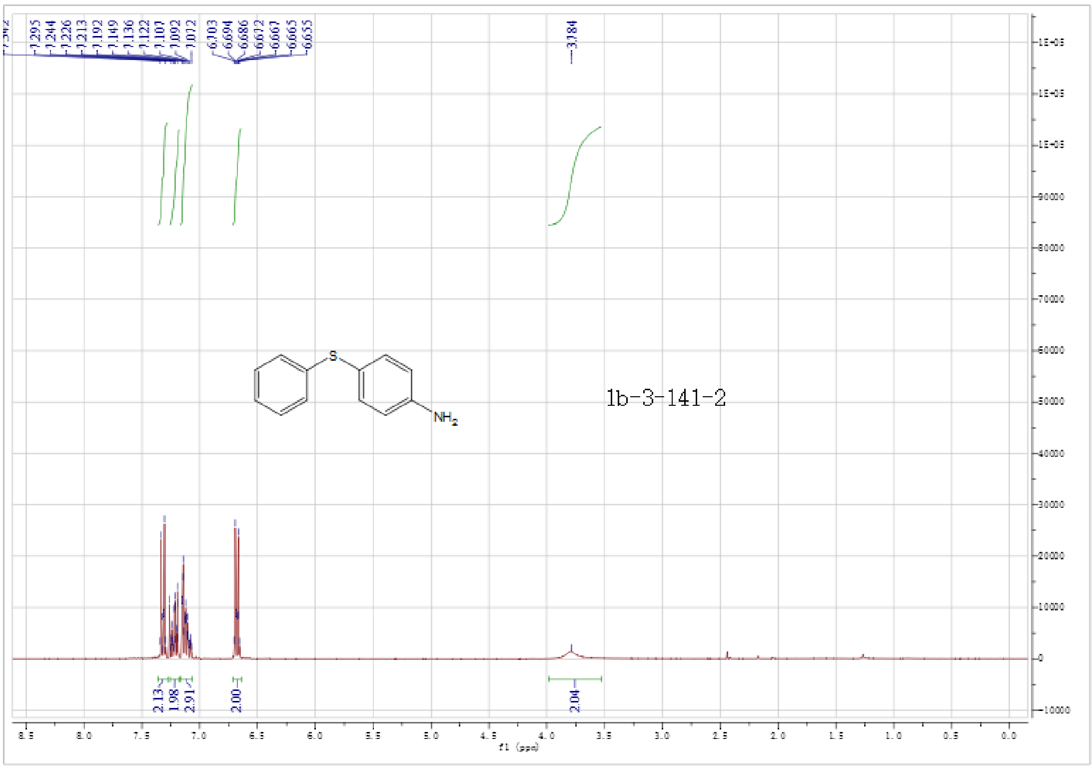


^{13}C NMR (75 MHz, $CDCl_3$)

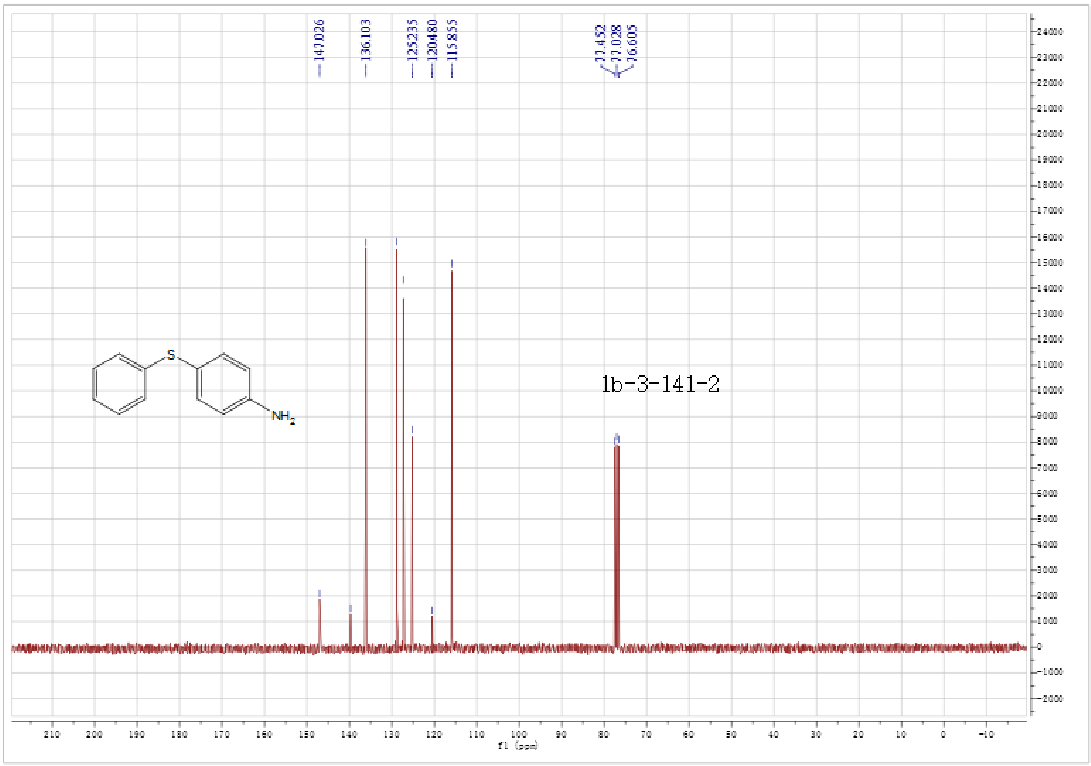


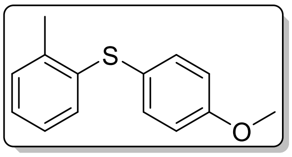


4-(Phenylthio)aniline (4c), ^{1}H NMR (300 MHz, CDCl$_3$)

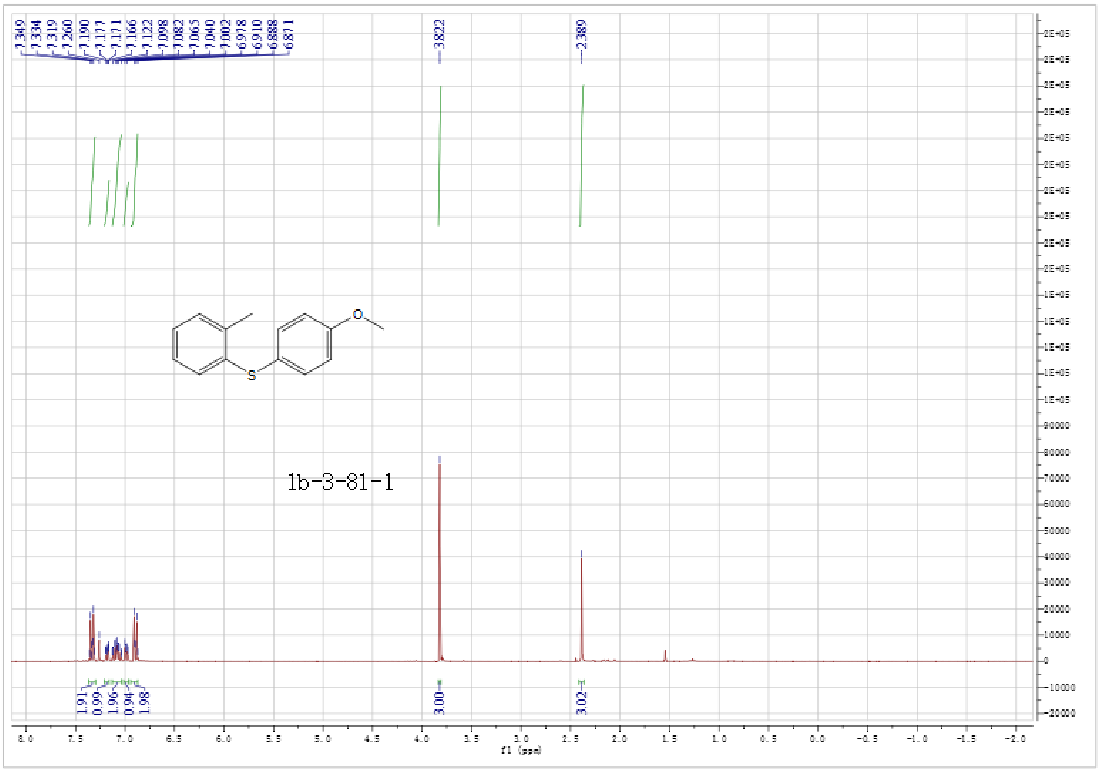


^{13}C NMR (75 MHz, CDCl$_3$)

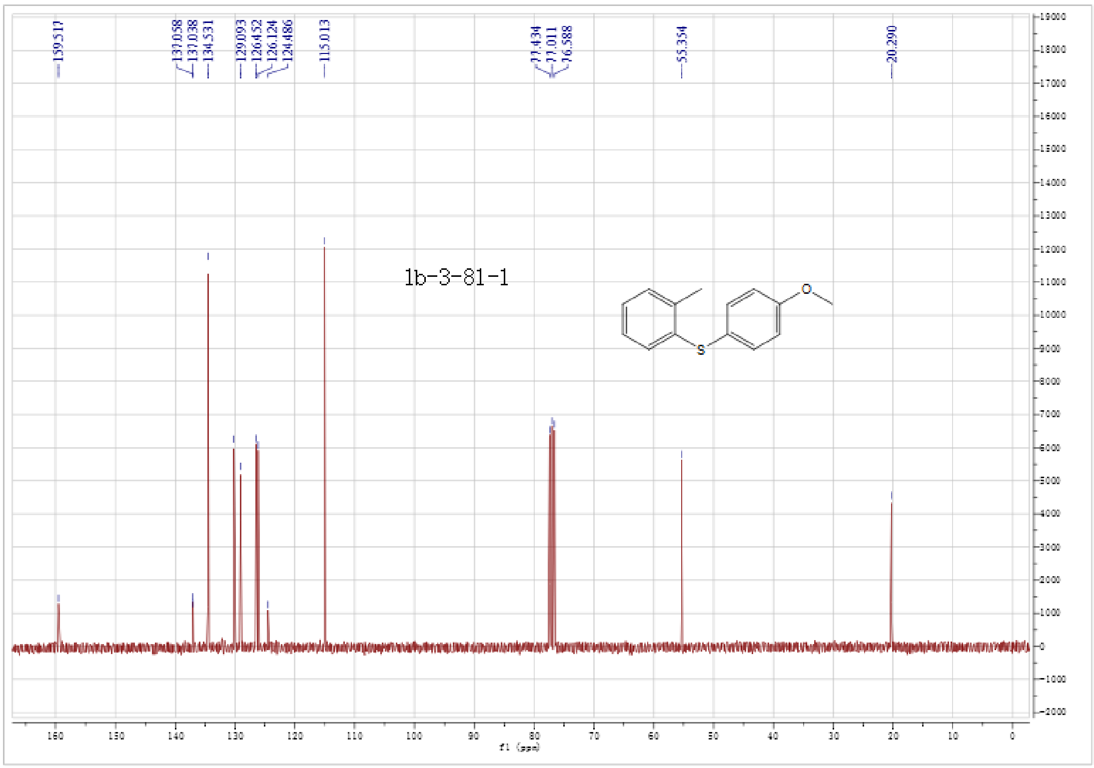


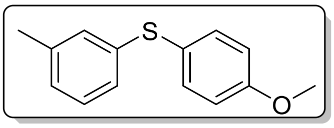


(4-Methoxyphenyl)(*o*-tolyl)sulfane (4d), ^{1}H NMR (300 MHz, CDCl$_3$)

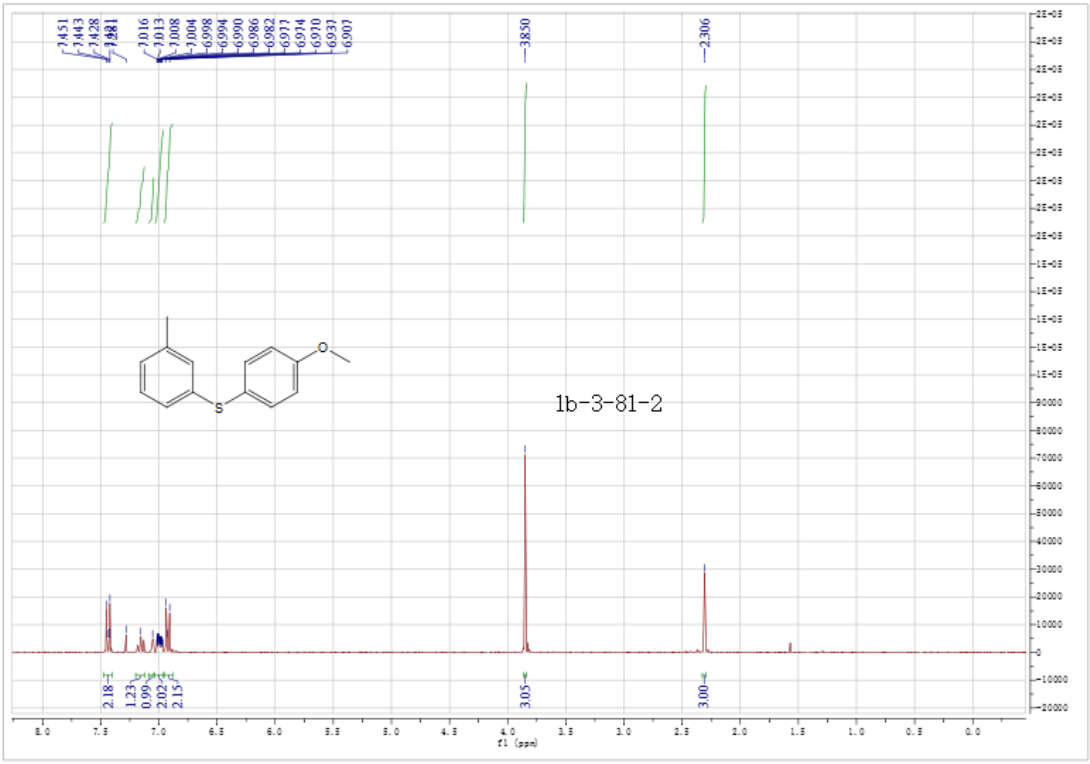


^{13}C NMR (75 MHz, CDCl$_3$)

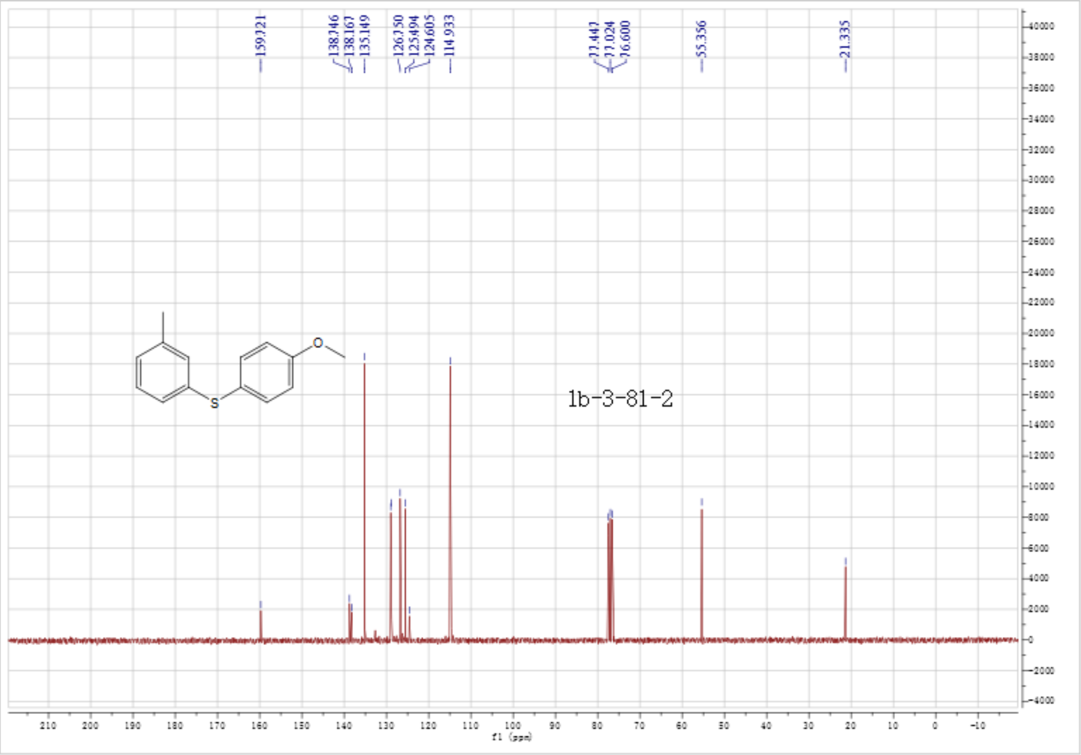


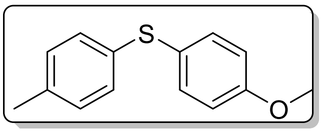


(4-Methoxyphenyl)(*m*-tolyl)sulfane (4e), ^{1}H NMR (300 MHz, CDCl$_3$)

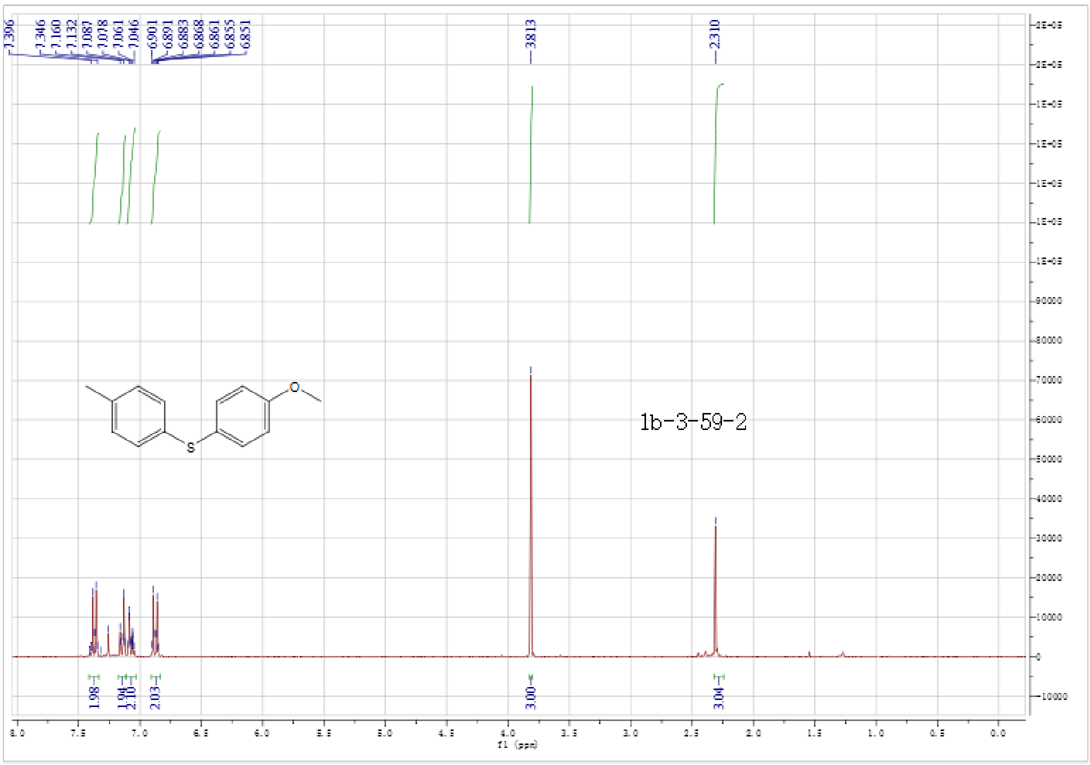


^{13}C NMR (75 MHz, CDCl$_3$)

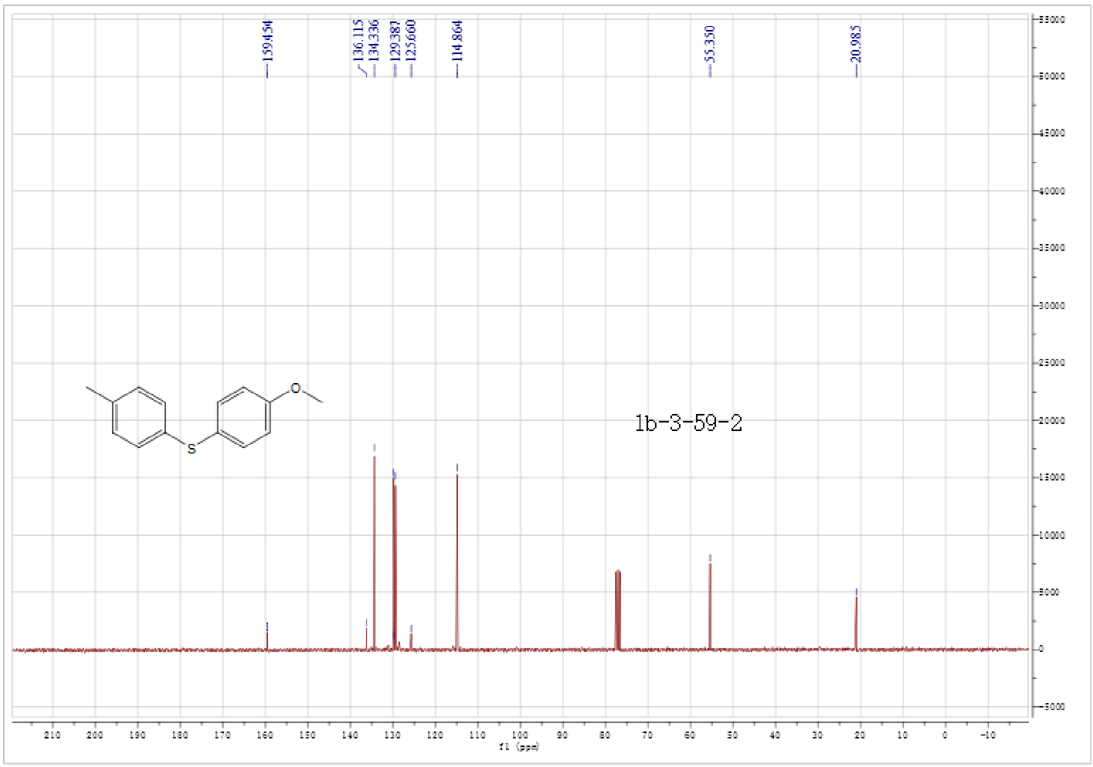


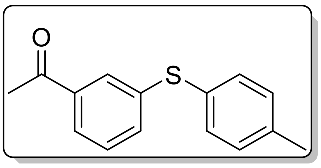


(4-Methoxyphenyl)(p-tolyl)sulfane (4f), ^{1}H NMR (300 MHz, CDCl$_3$)

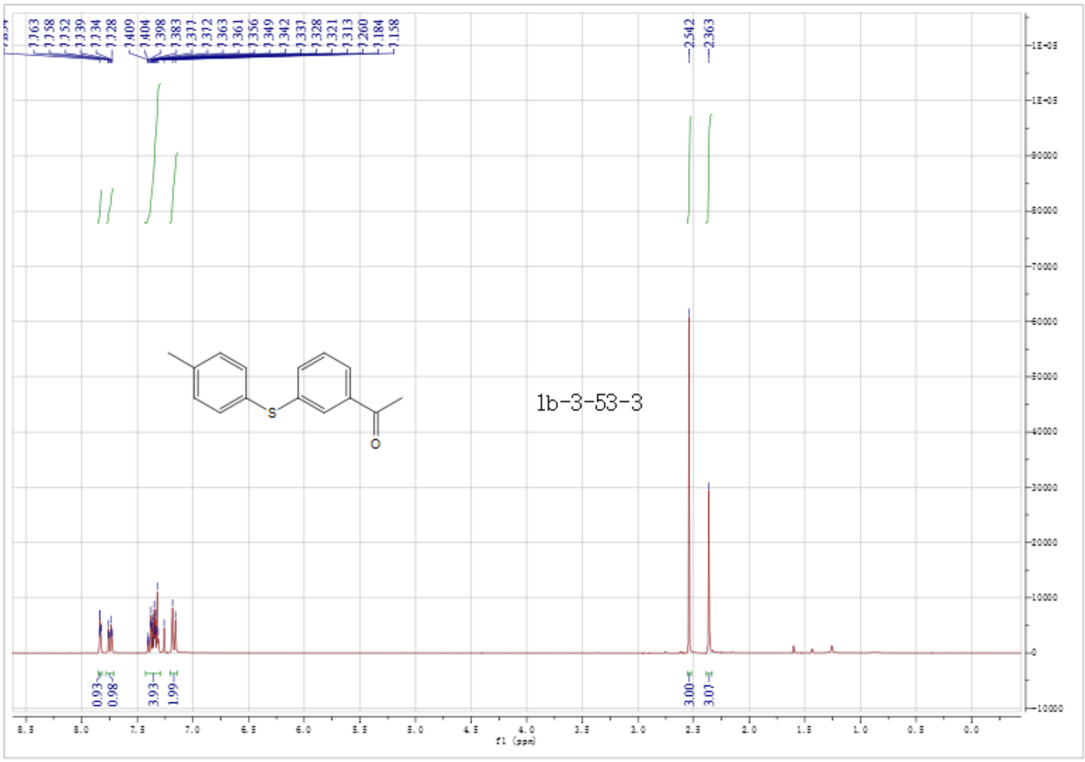


^{13}C NMR (75 MHz, CDCl$_3$)

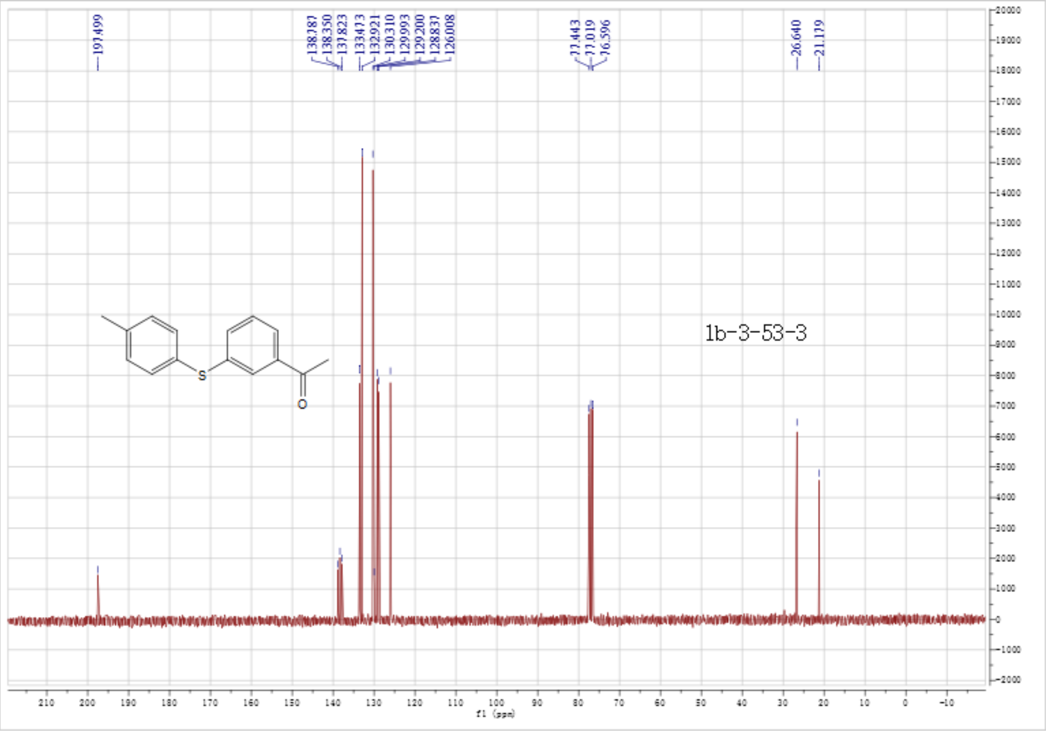


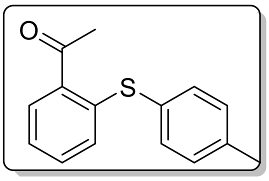


1-(3-(*p*-Tolylthio)phenyl)ethan-1-one (4g), ^{1}H NMR (300 MHz, $CDCl_3$)

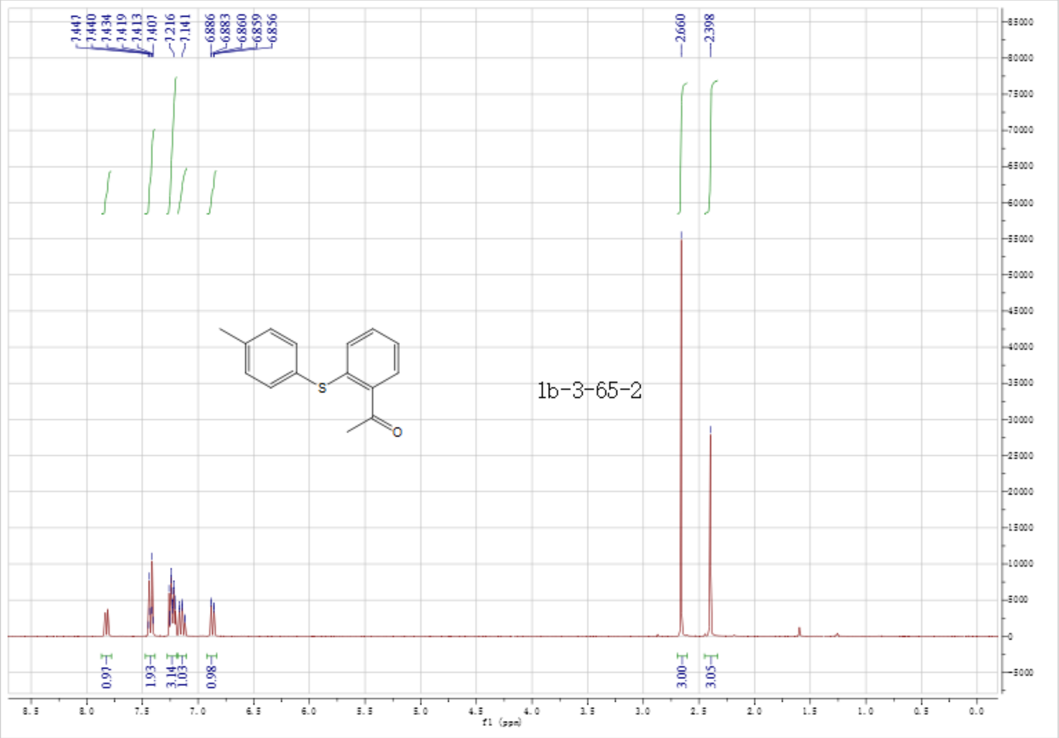


^{13}C NMR (75 MHz, $CDCl_3$)

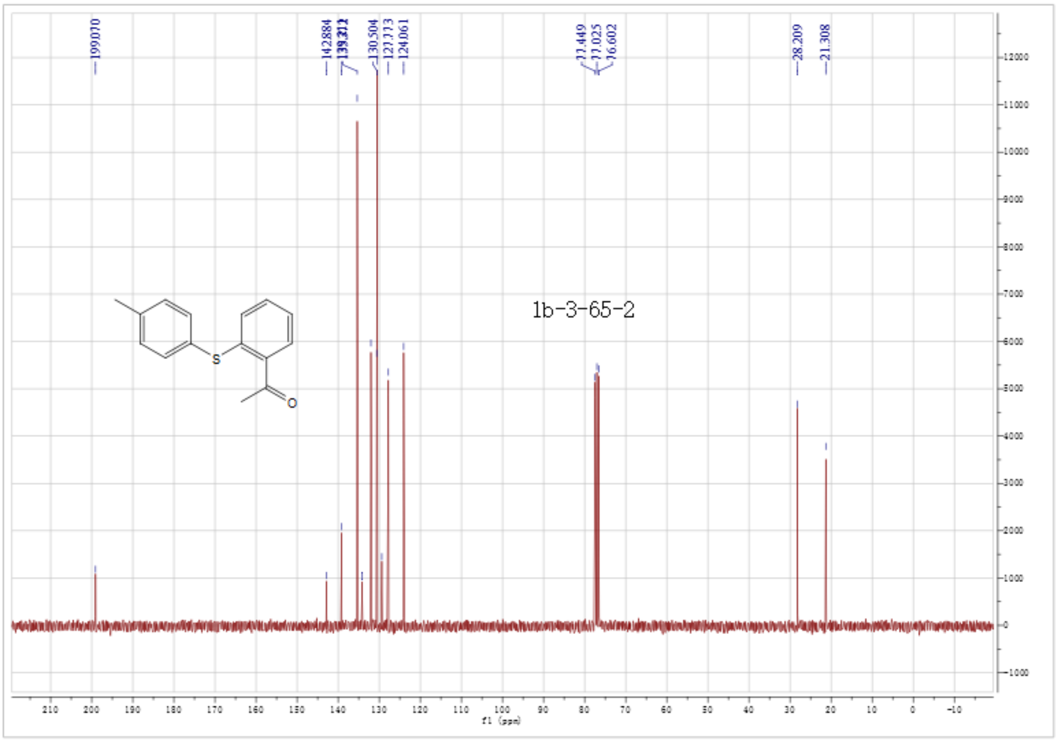


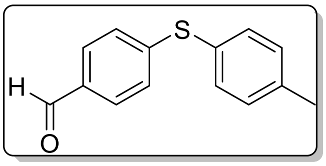


1-(2-(*p*-Tolylthio)phenyl)ethan-1-one (4h), ^{1}H NMR (300 MHz, CDCl$_3$)

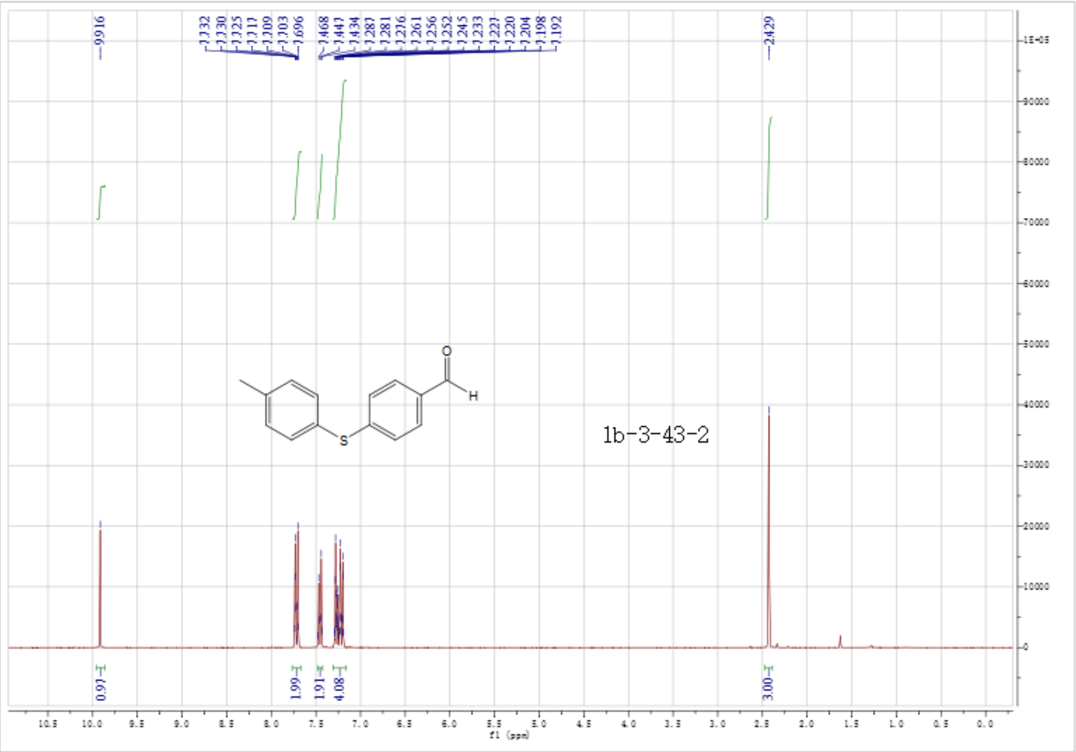


^{13}C NMR (75 MHz, CDCl$_3$)

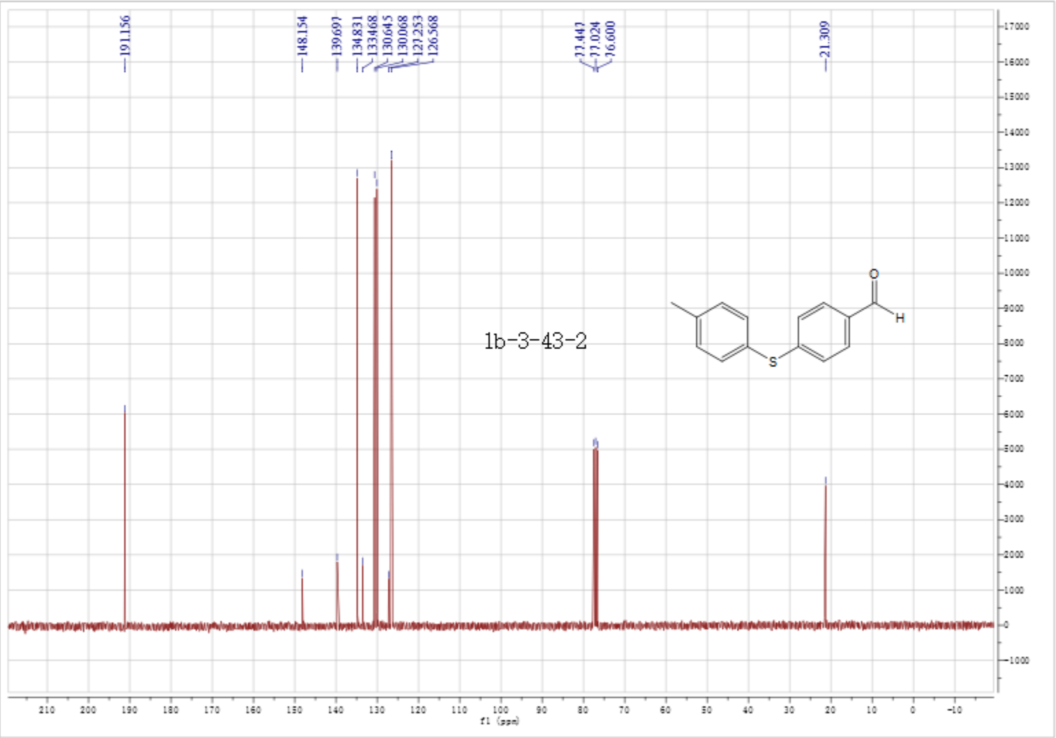


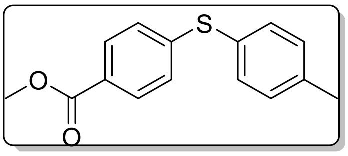


4-(*p*-Tolylthio)benzaldehyde (4i), ^{1}H NMR (300 MHz, CDCl$_3$)

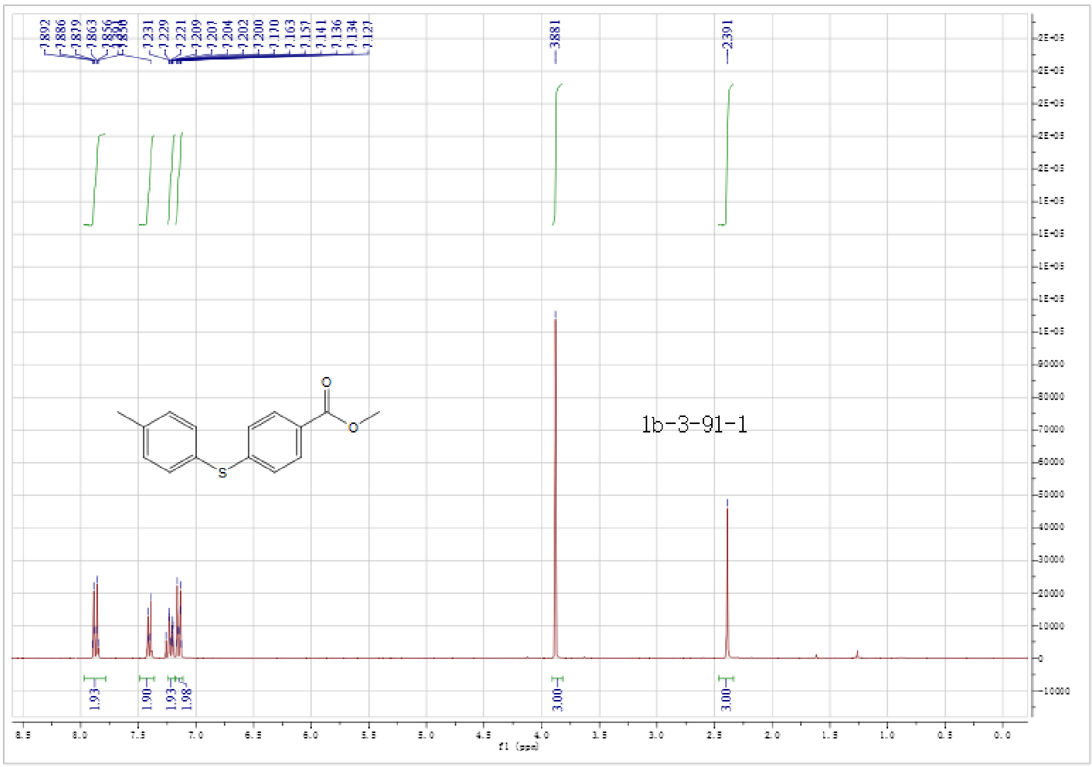


^{13}C NMR (75 MHz, CDCl$_3$)

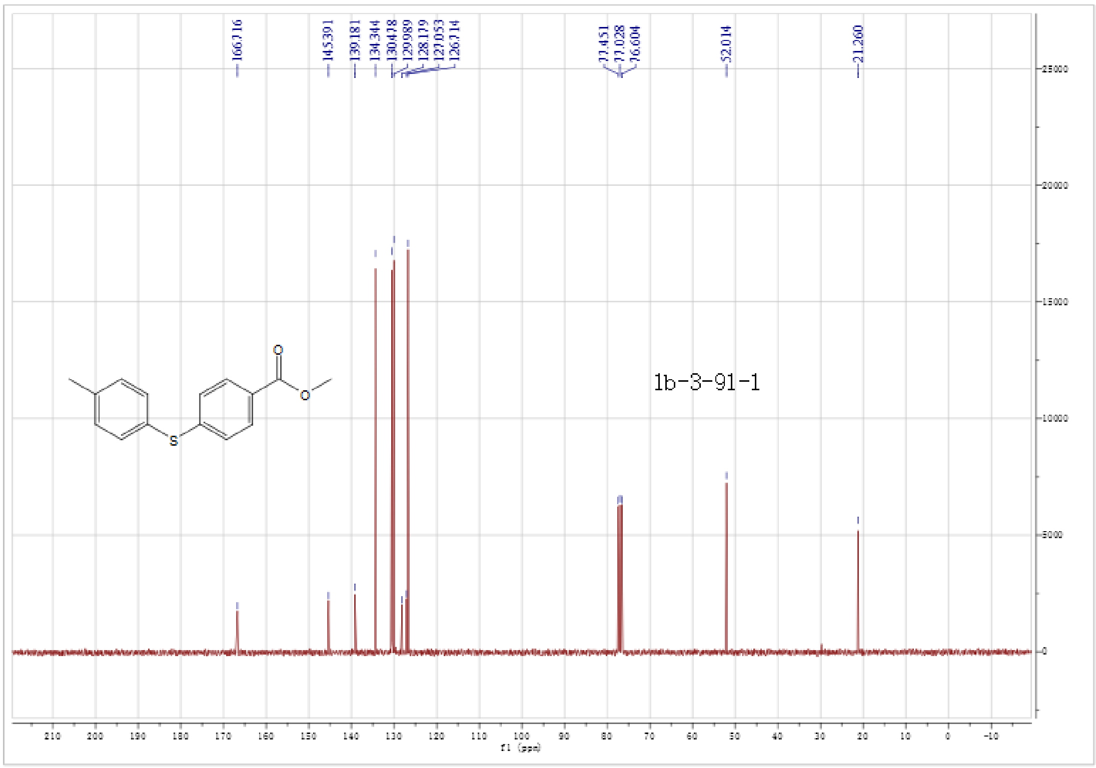


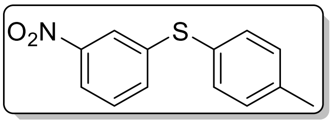


Methyl 4-(*p*-Tolylthio)benzoate (4j), ^{1}H NMR (300 MHz, CDCl$_3$)

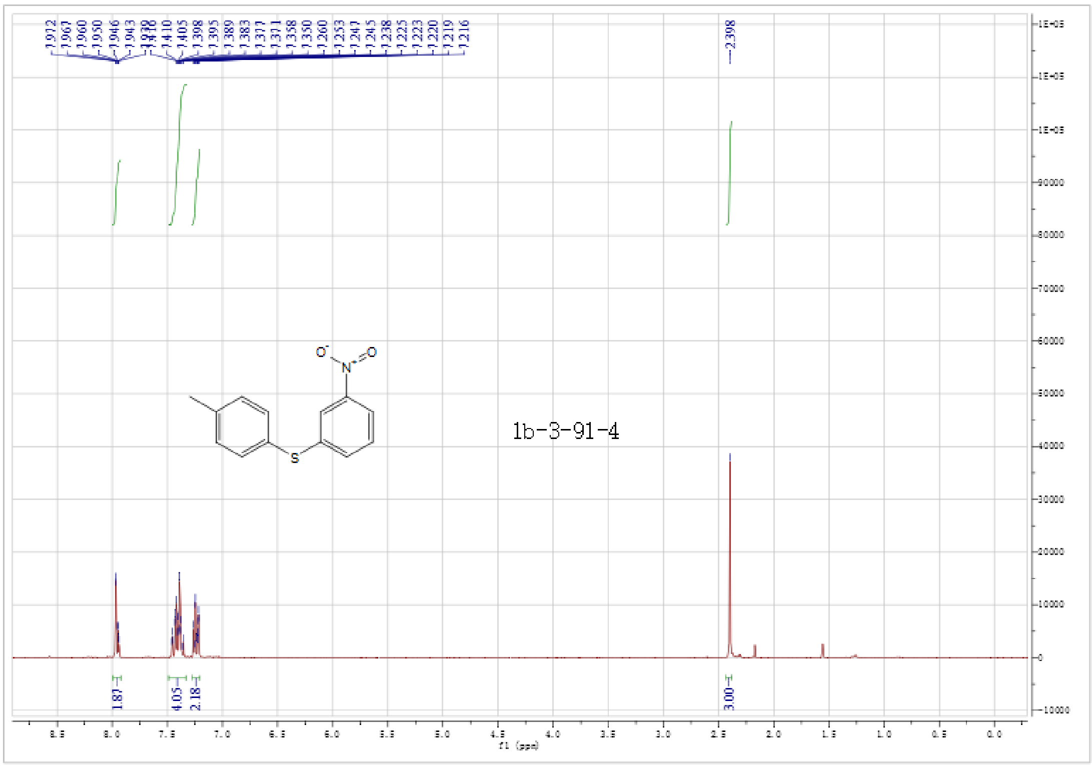


^{13}C NMR (75 MHz, CDCl$_3$)

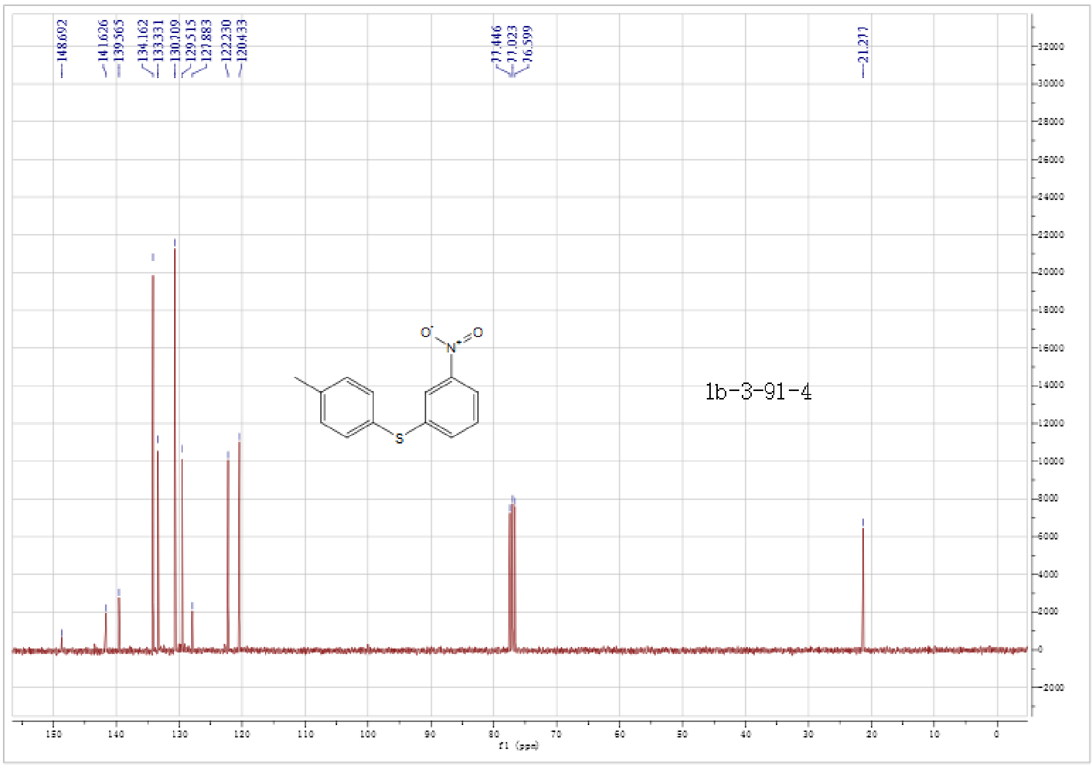


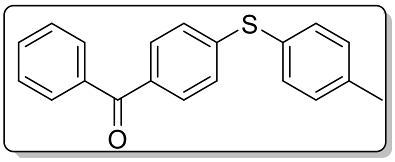


(3-Nitrophenyl)(p-tolyl)sulfane (4k), ^{1}H NMR (300 MHz, $CDCl_3$)

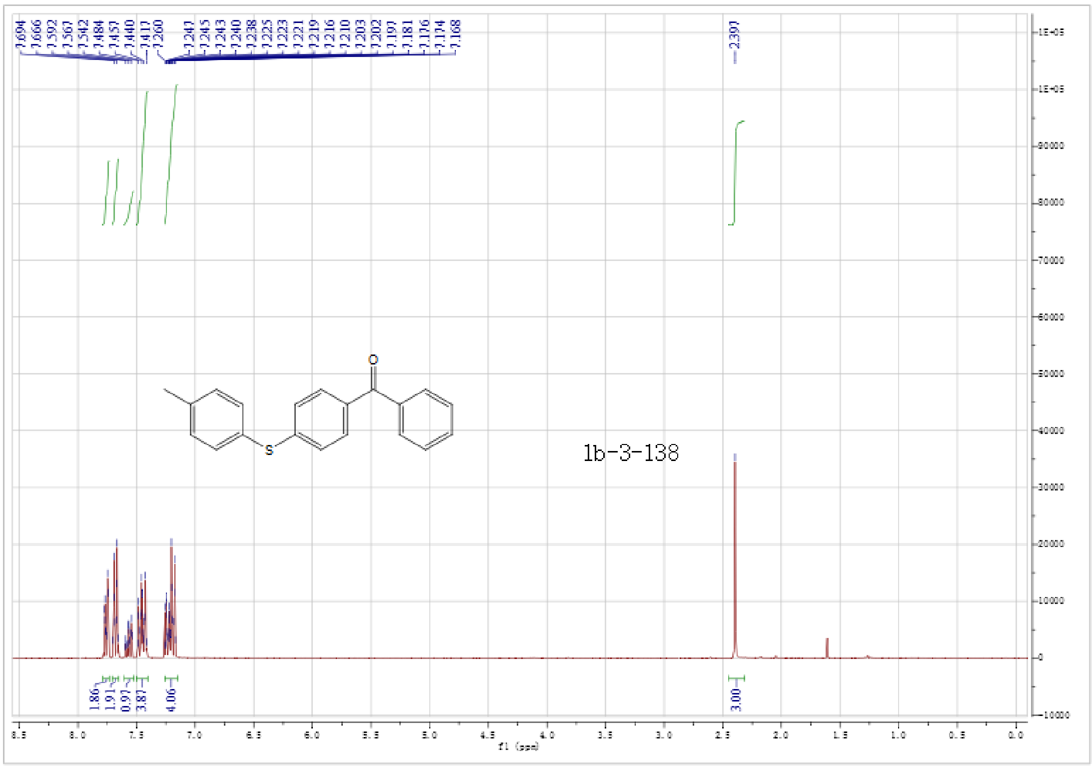


^{13}C NMR (75 MHz, $CDCl_3$)

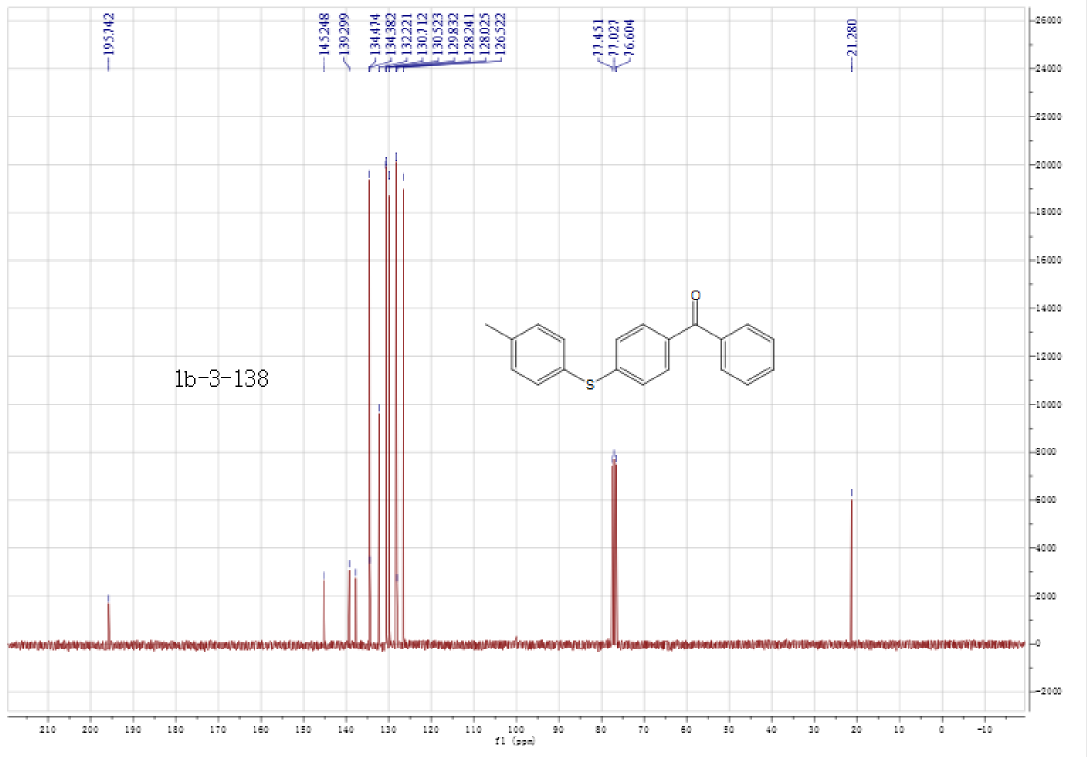


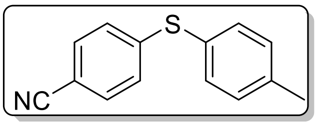


Phenyl-(4-(*p*-tolylthio)phenyl)methanone (4l), ^{1}H NMR (300 MHz, CDCl$_3$)

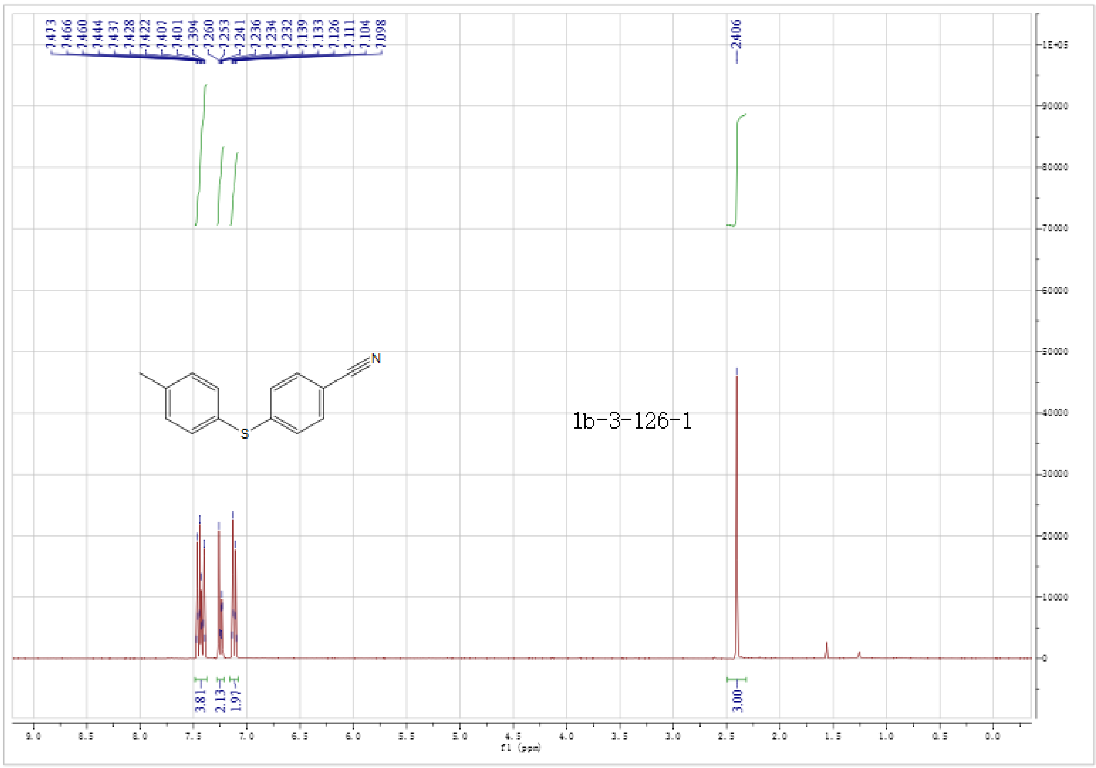


^{13}C NMR (75 MHz, CDCl$_3$)

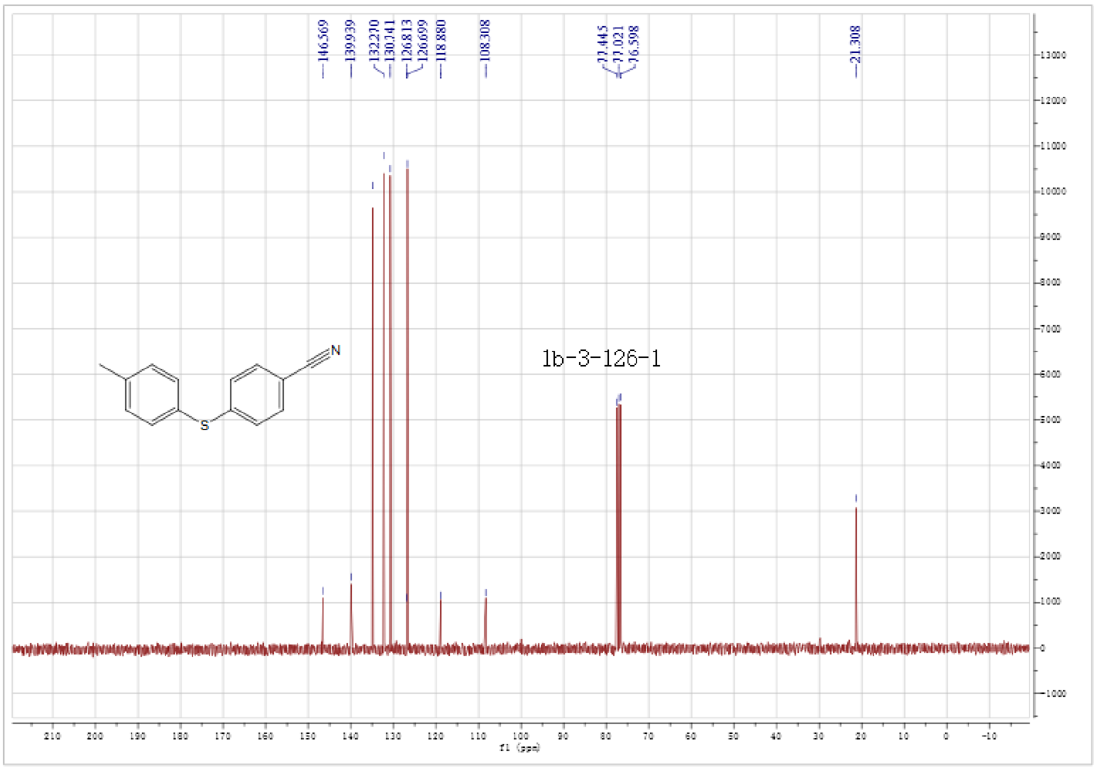


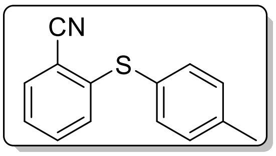


4-(*p*-Tolylthio)benzonitrile (4m), ^{1}H NMR (300 MHz, $CDCl_3$)

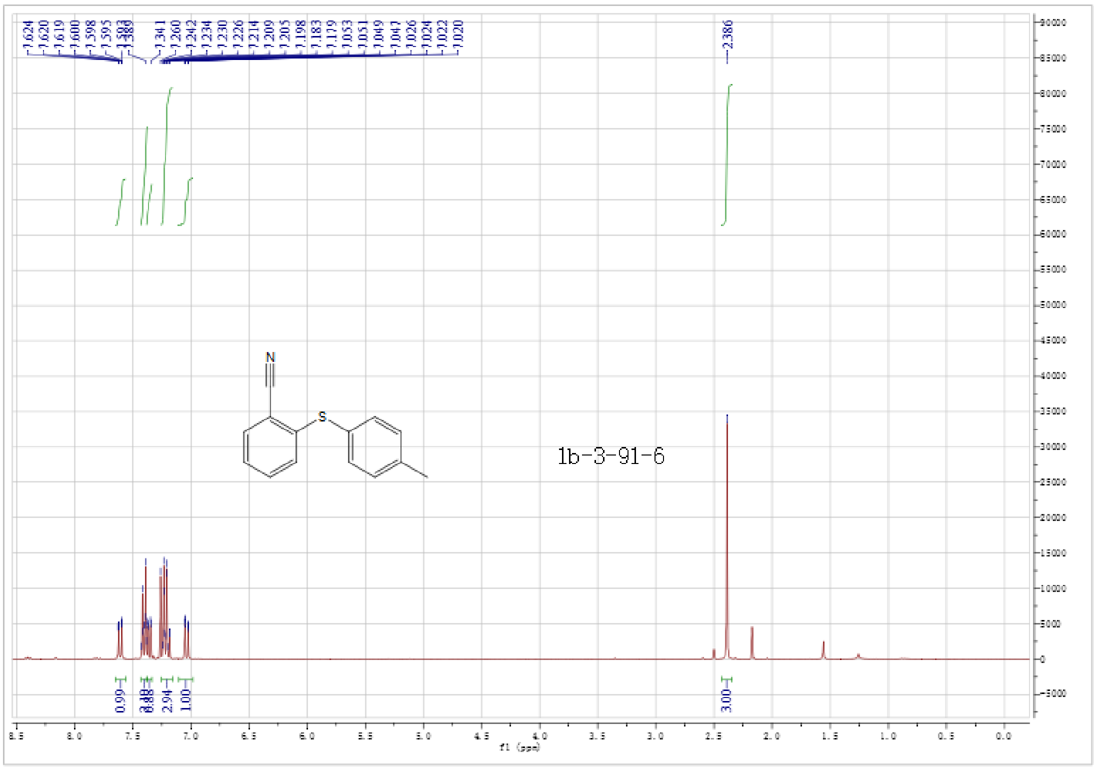


^{13}C NMR (75 MHz, $CDCl_3$)

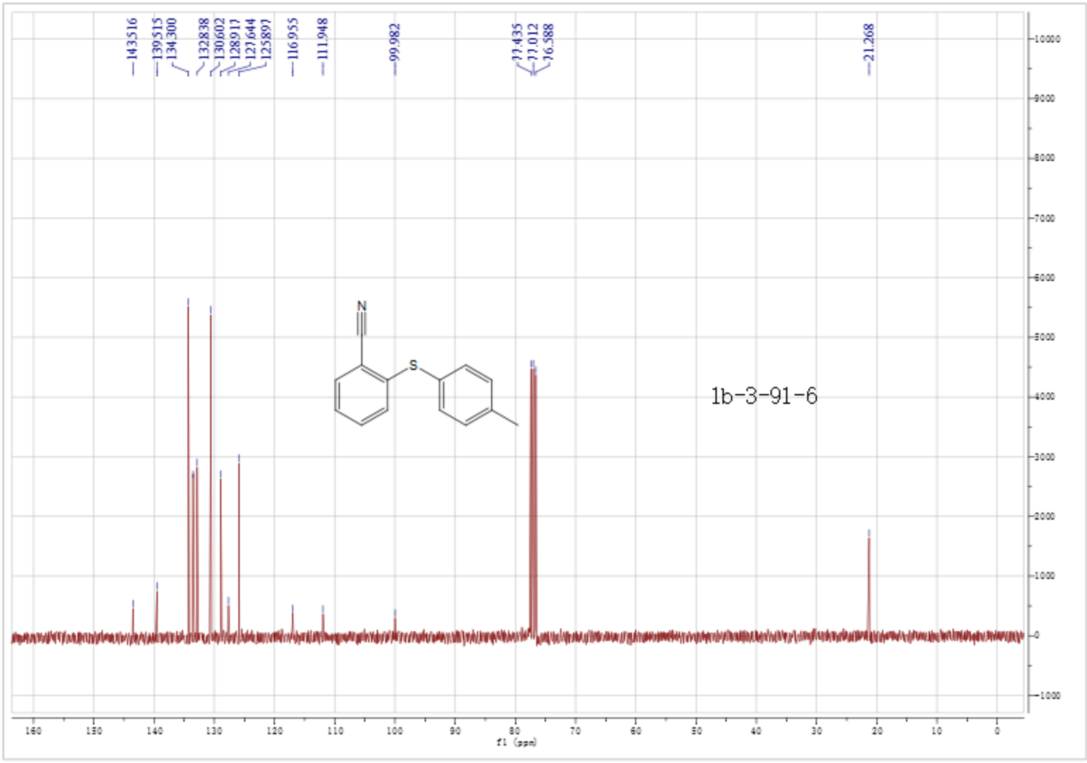


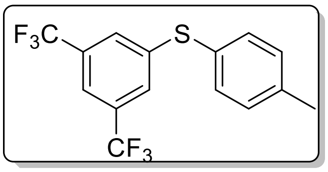


2-(*p*-Tolylthio)benzonitrile (4n), ^{1}H NMR (300 MHz, $CDCl_3$)

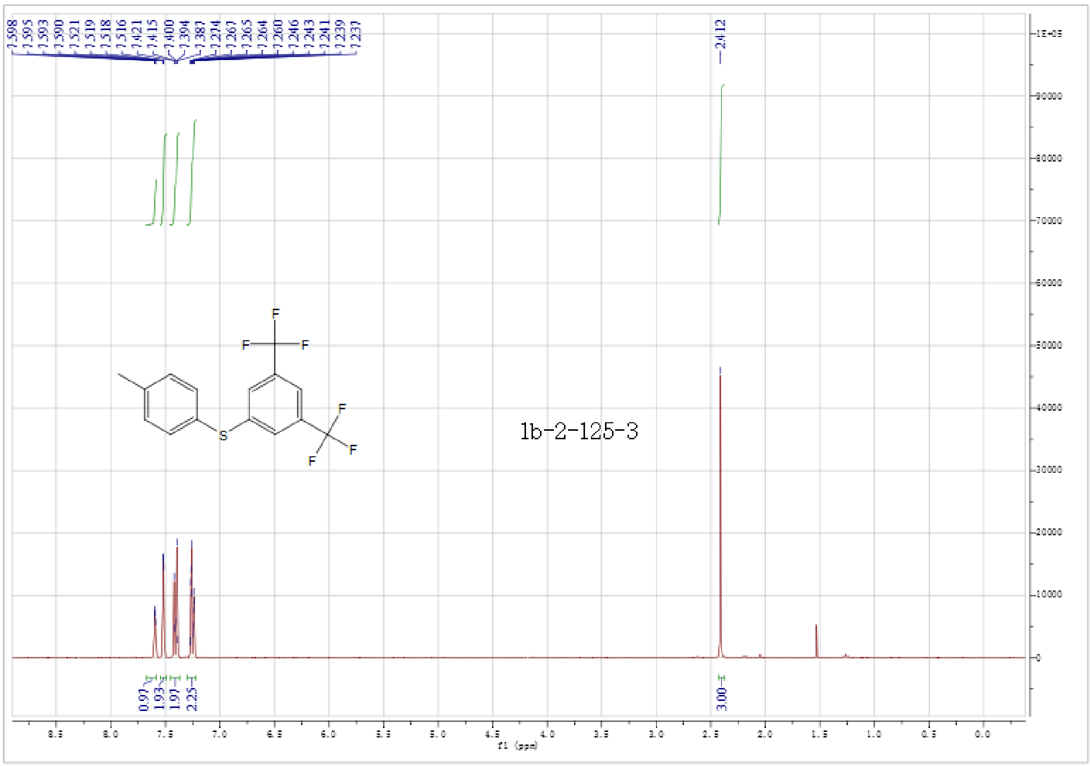


^{13}C NMR (75 MHz, $CDCl_3$)

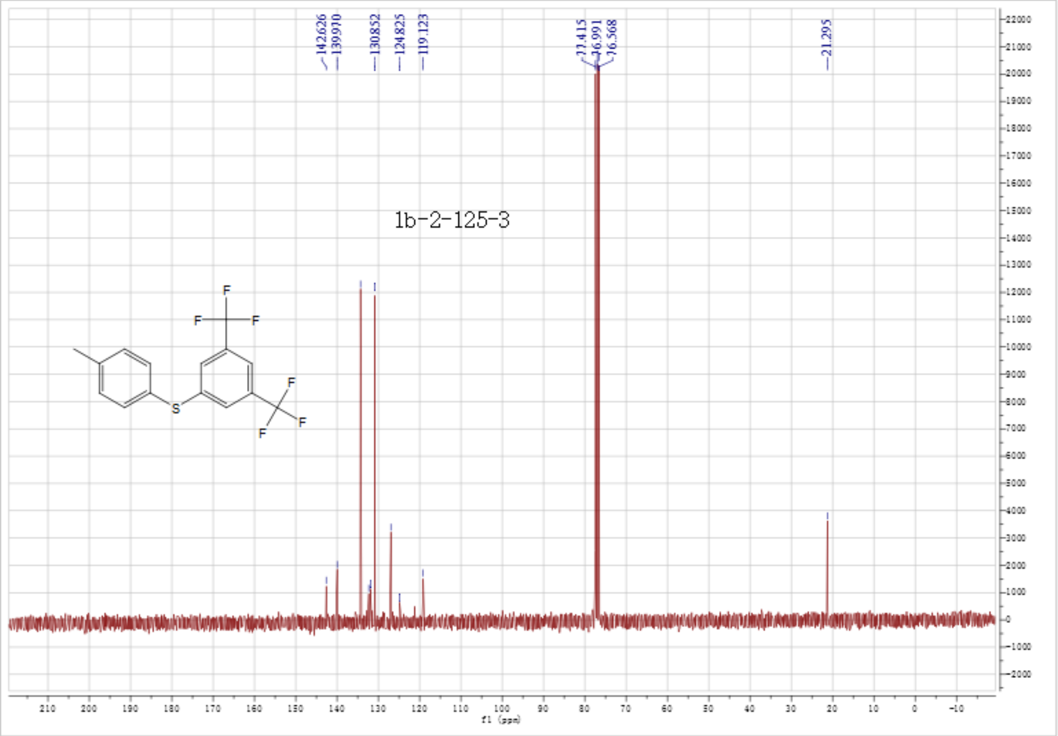


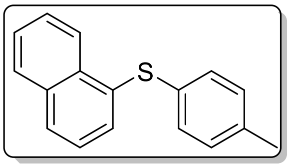


(3,5-Bis(trifluoromethyl)phenyl)(*p*-tolyl)sulfane (4o), ^{1}H NMR (300 MHz, CDCl$_3$)

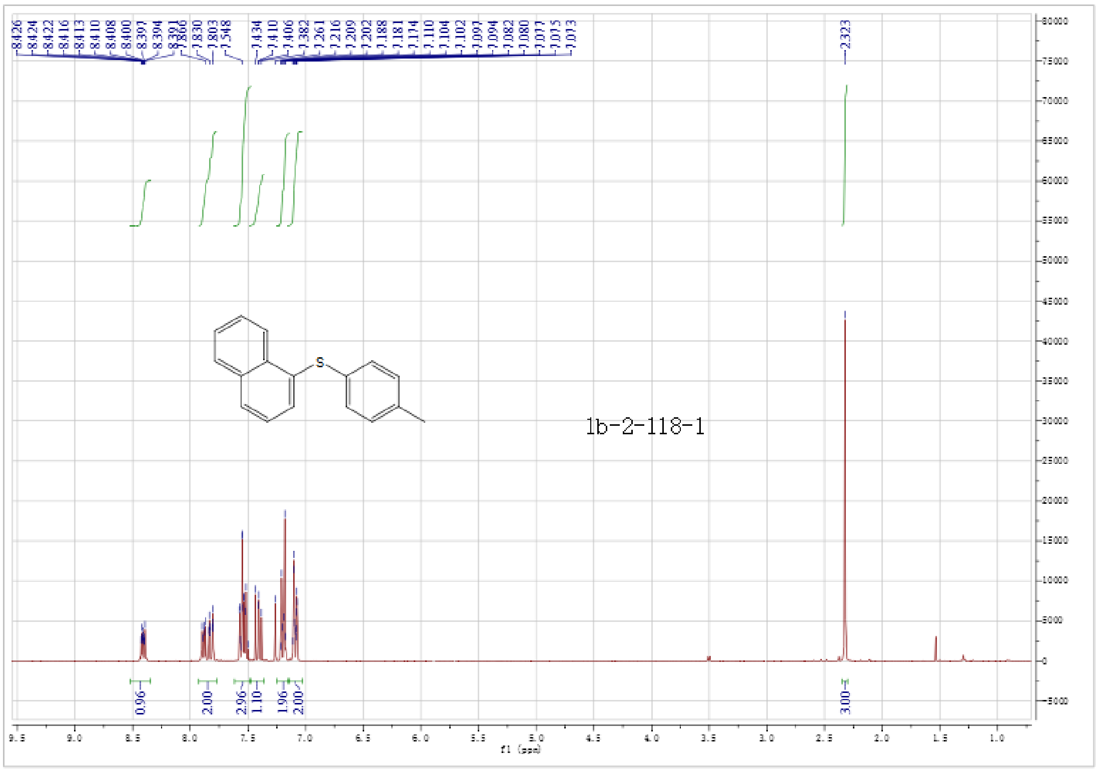


^{13}C NMR (75 MHz, CDCl$_3$)

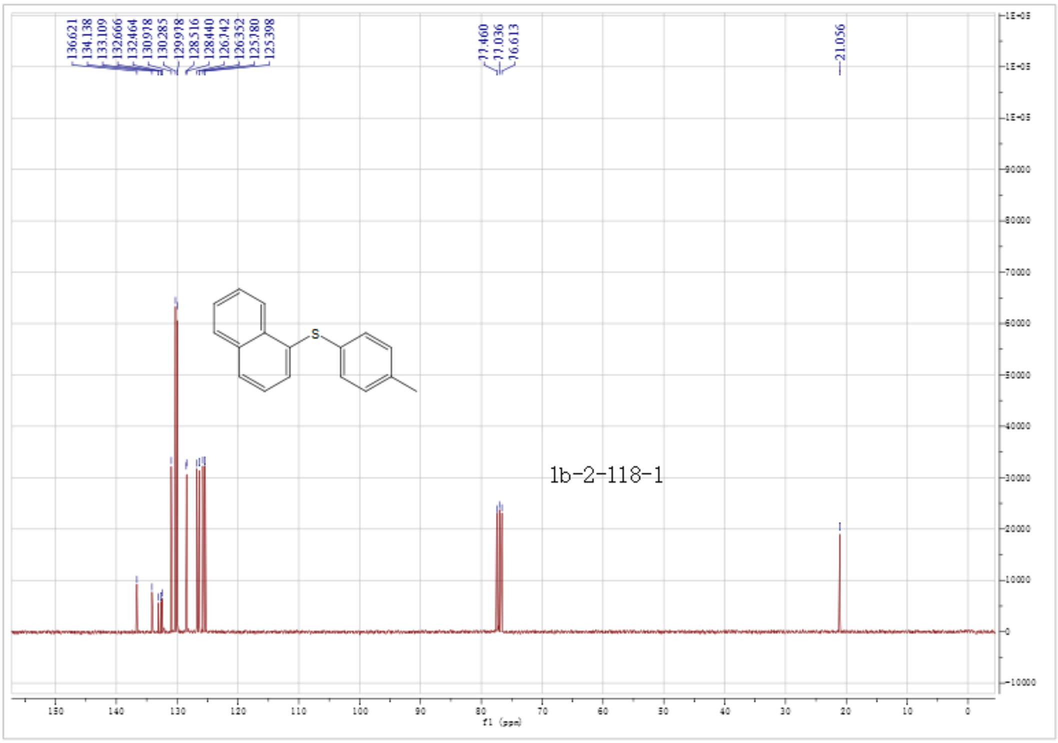


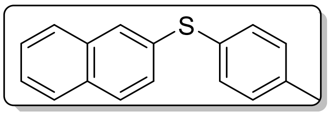


Naphthalen-1-yl(*p*-tolyl)sulfane (4p), ^{1}H NMR (300 MHz, $CDCl_3$)

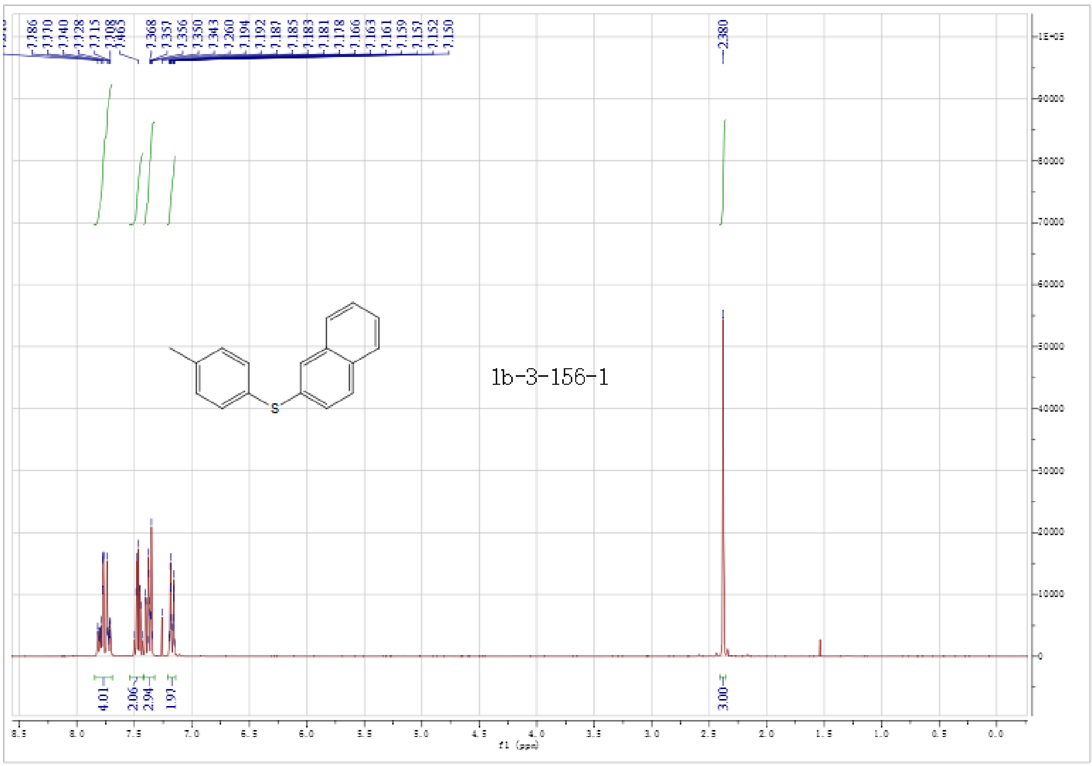


^{13}C NMR (75 MHz, $CDCl_3$)

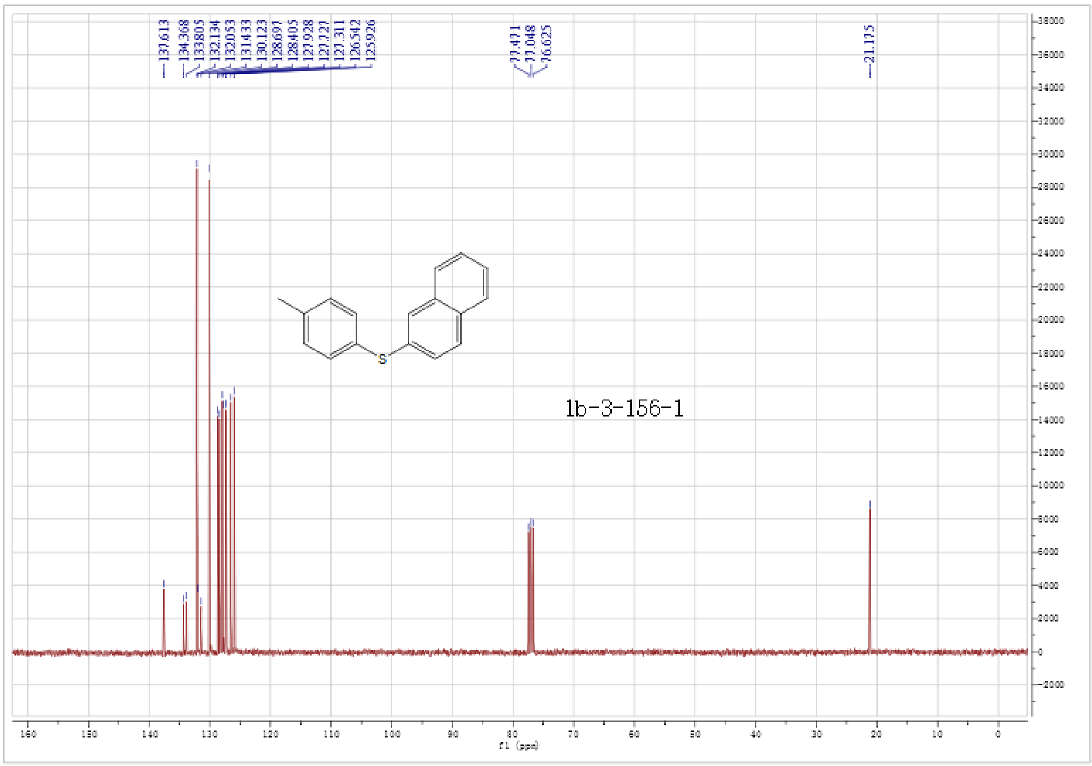


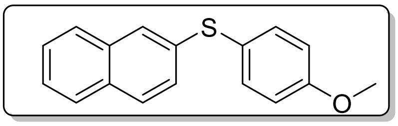


Naphthalen-2-yl(*p*-tolyl)sulfane (4q), ^{1}H NMR (300 MHz, CDCl$_3$)

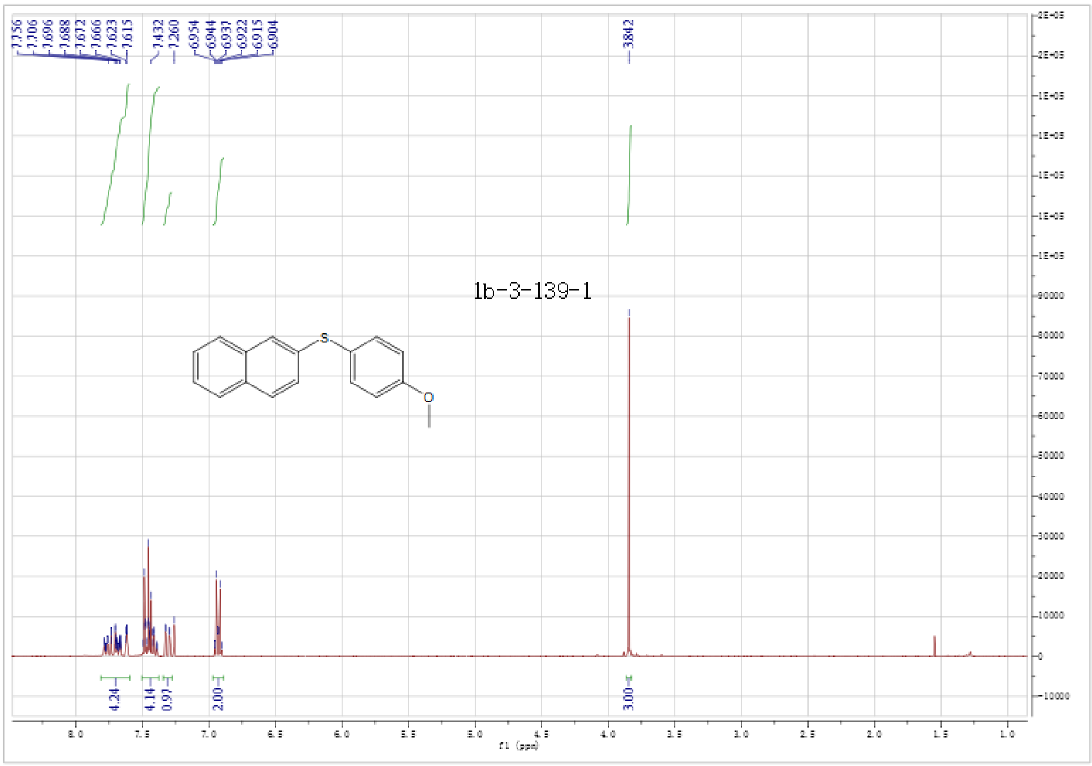


^{13}C NMR (75 MHz, CDCl$_3$)

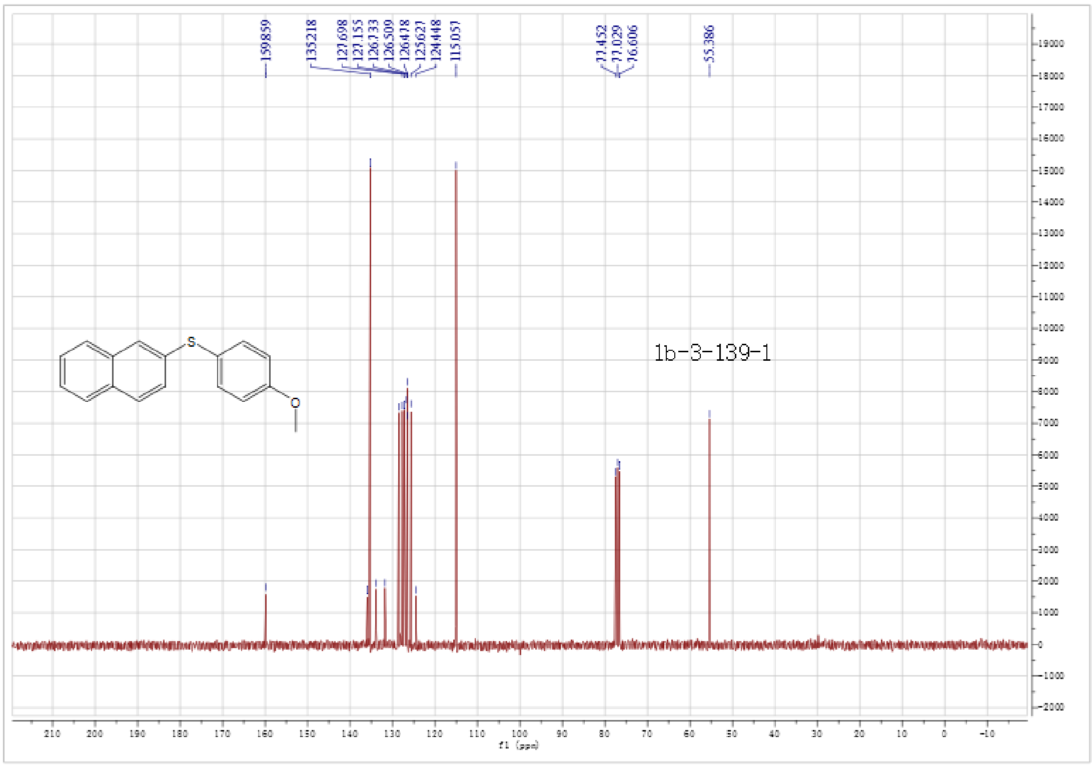


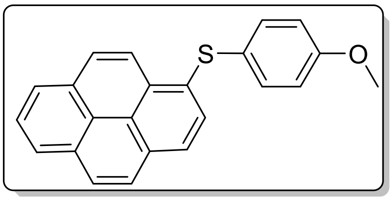


(4-Methoxyphenyl)(naphthalen-2-yl)sulfane (4r), ^{1}H NMR (300 MHz, CDCl$_3$)

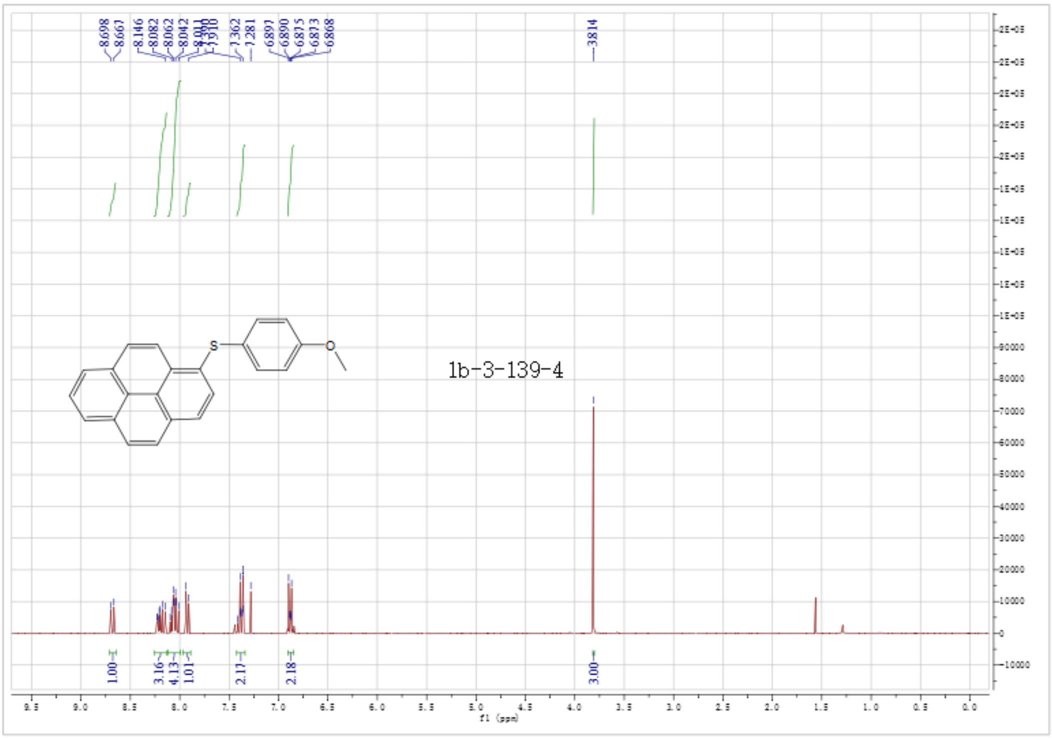


^{13}C NMR (75 MHz, CDCl$_3$)

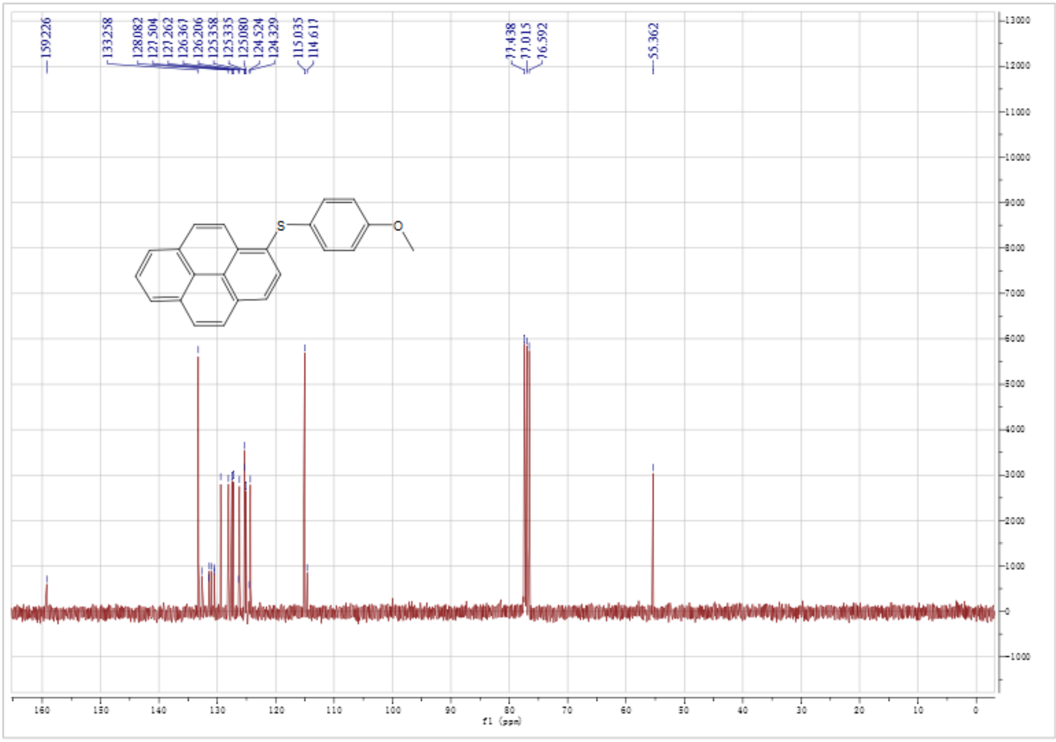


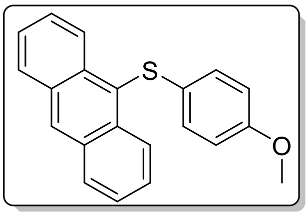


(4-Methoxyphenyl)(pyren-1-yl)sulfane (4s), ^{1}H NMR (300 MHz, $CDCl_3$)

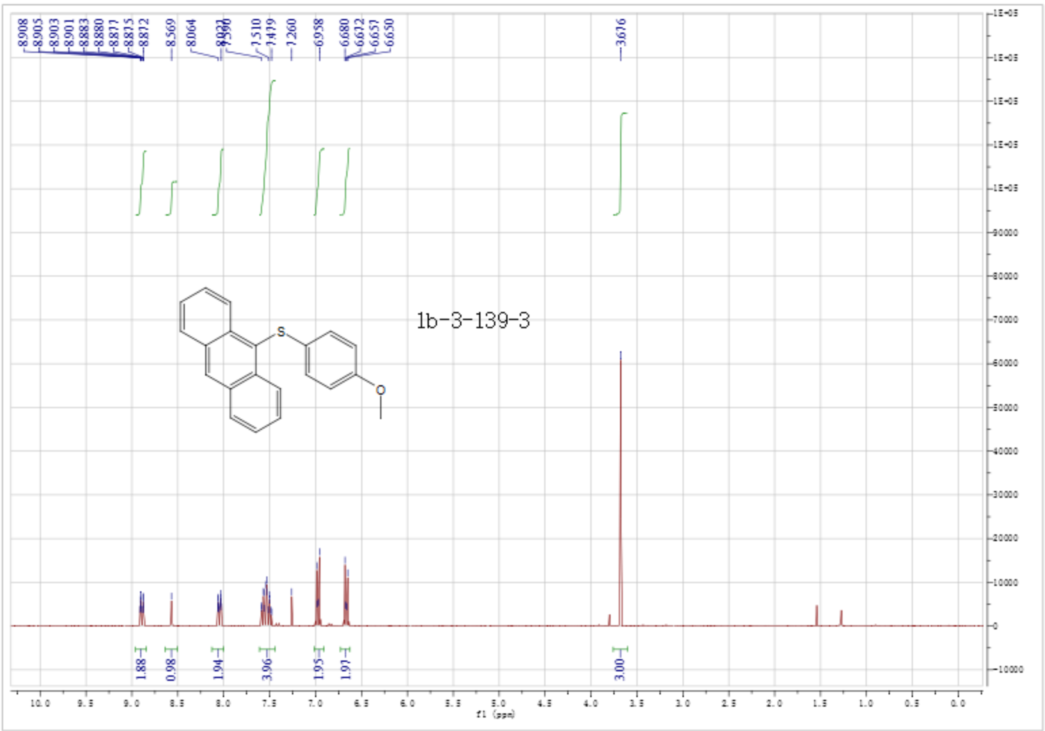


^{13}C NMR (75 MHz, $CDCl_3$)

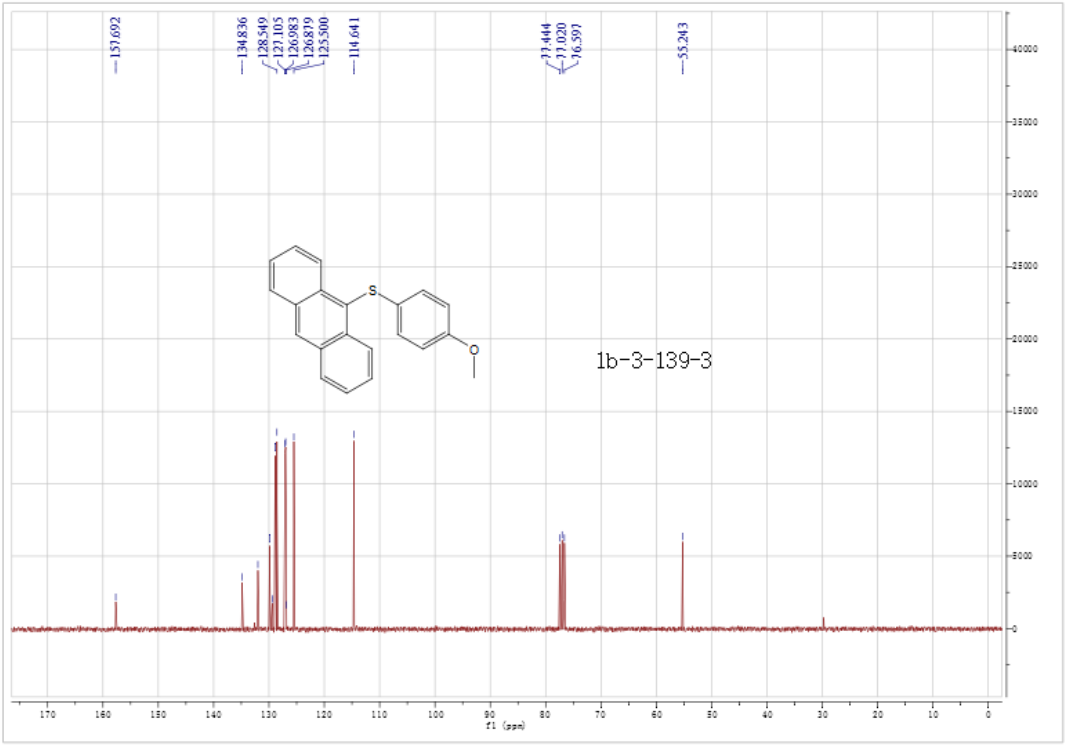


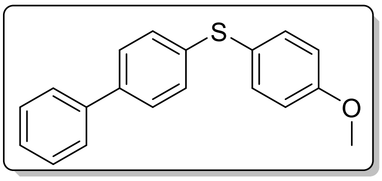


Anthracen-9-yl(4-methoxyphenyl)sulfane (4t), ^{1}H NMR (300 MHz, CDCl$_3$)

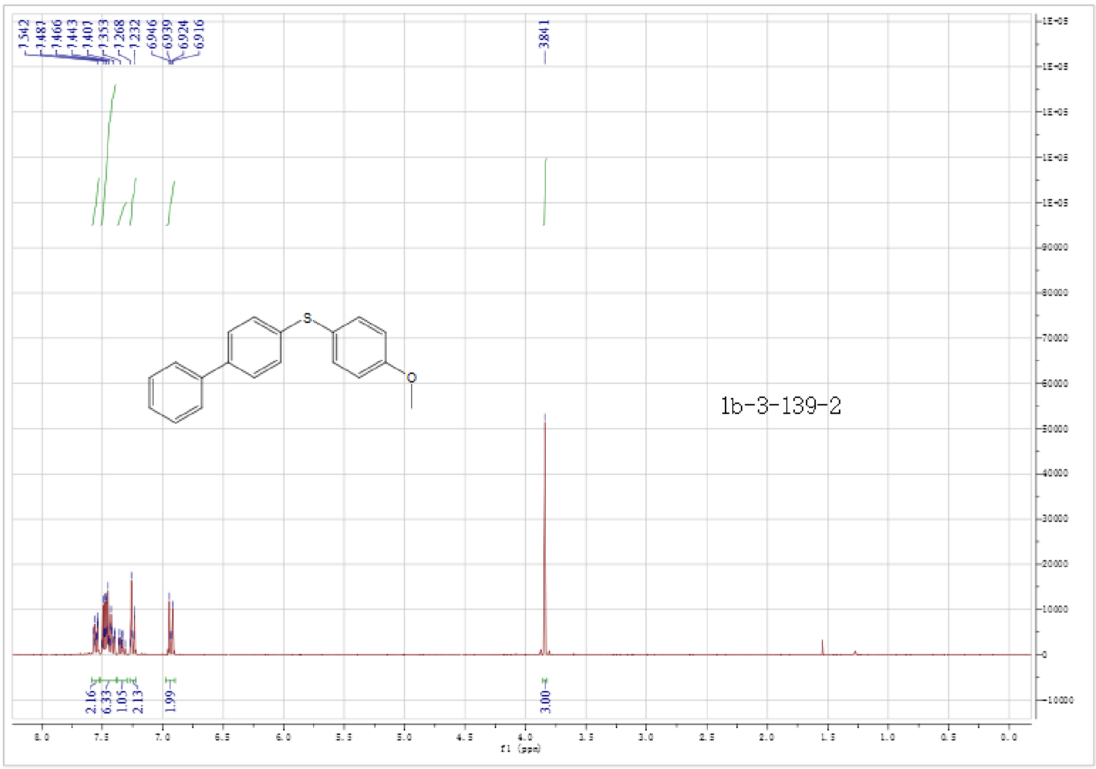


^{13}C NMR (75 MHz, CDCl$_3$)

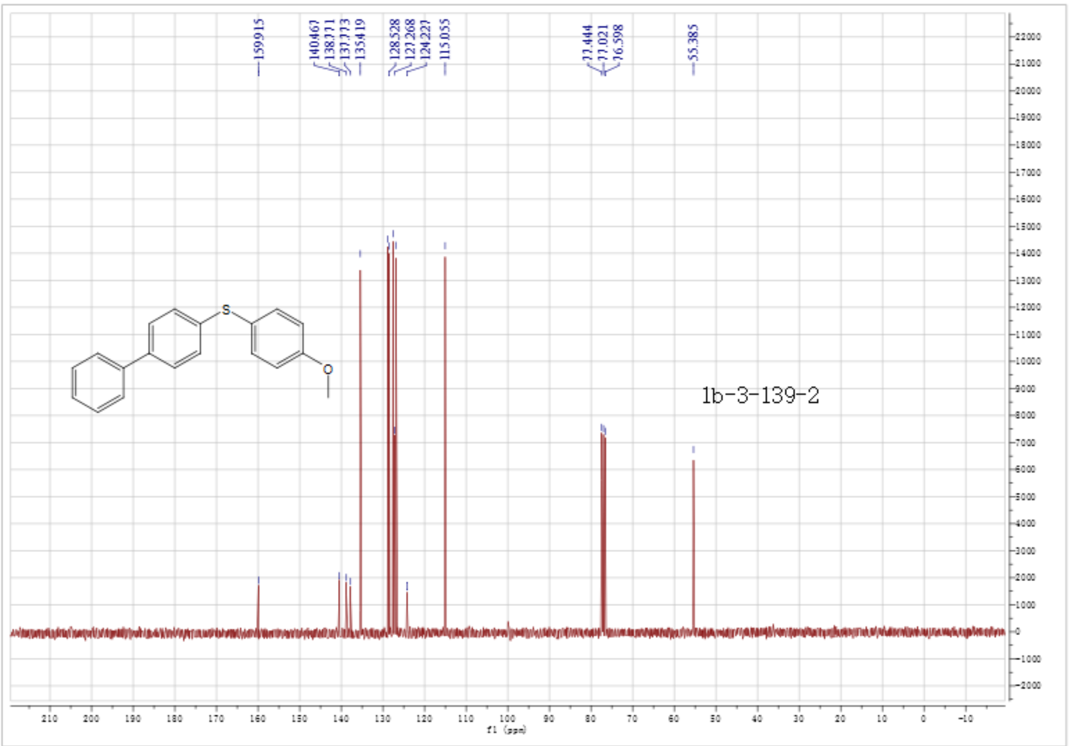


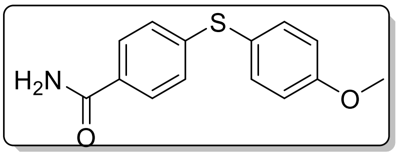


[1,1'-Biphenyl]-4-yl(4-methoxyphenyl)sulfane (4u), ^{1}H NMR (300 MHz, CDCl$_3$)

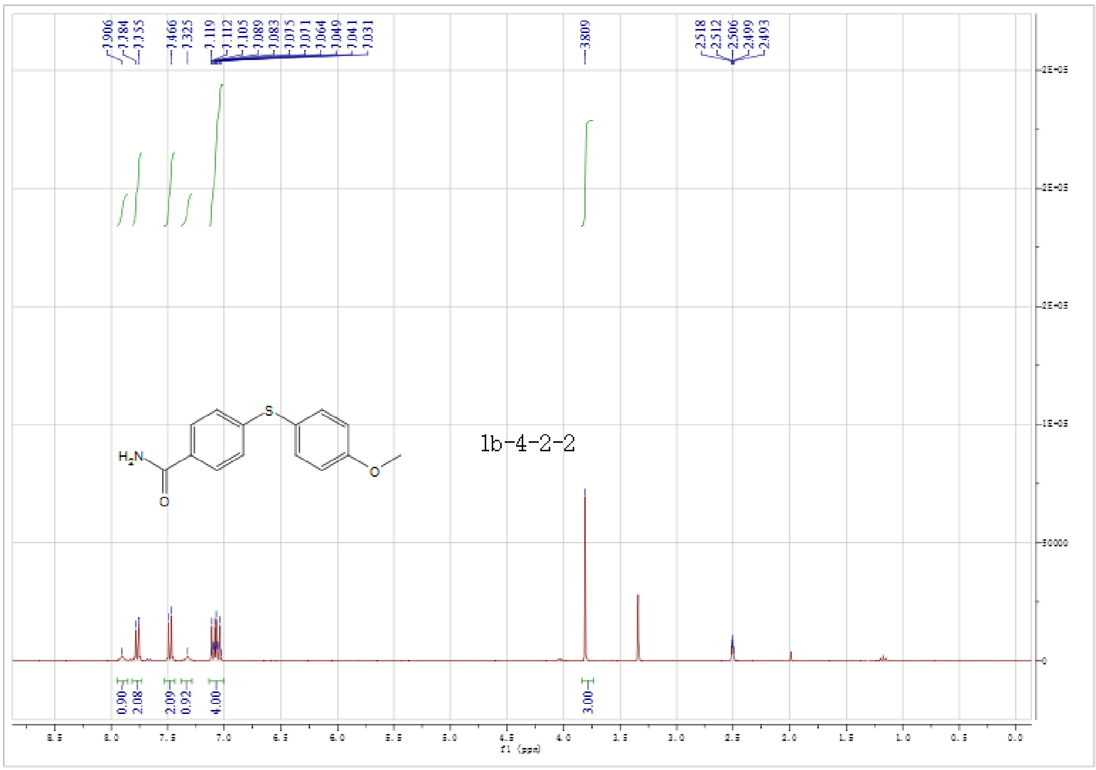


^{13}C NMR (75 MHz, CDCl$_3$)

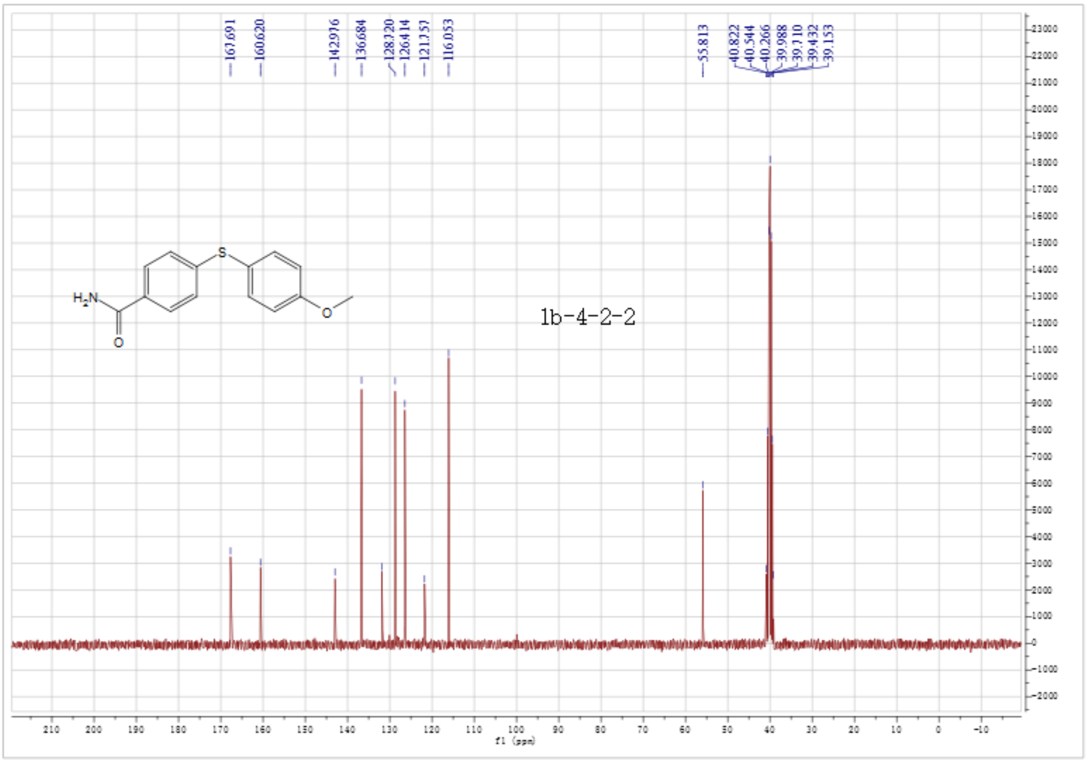


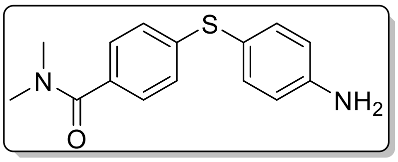


4-((4-Methoxyphenyl)thio)benzamide (4v), ^{1}H NMR (300 MHz, d_6-DMSO)

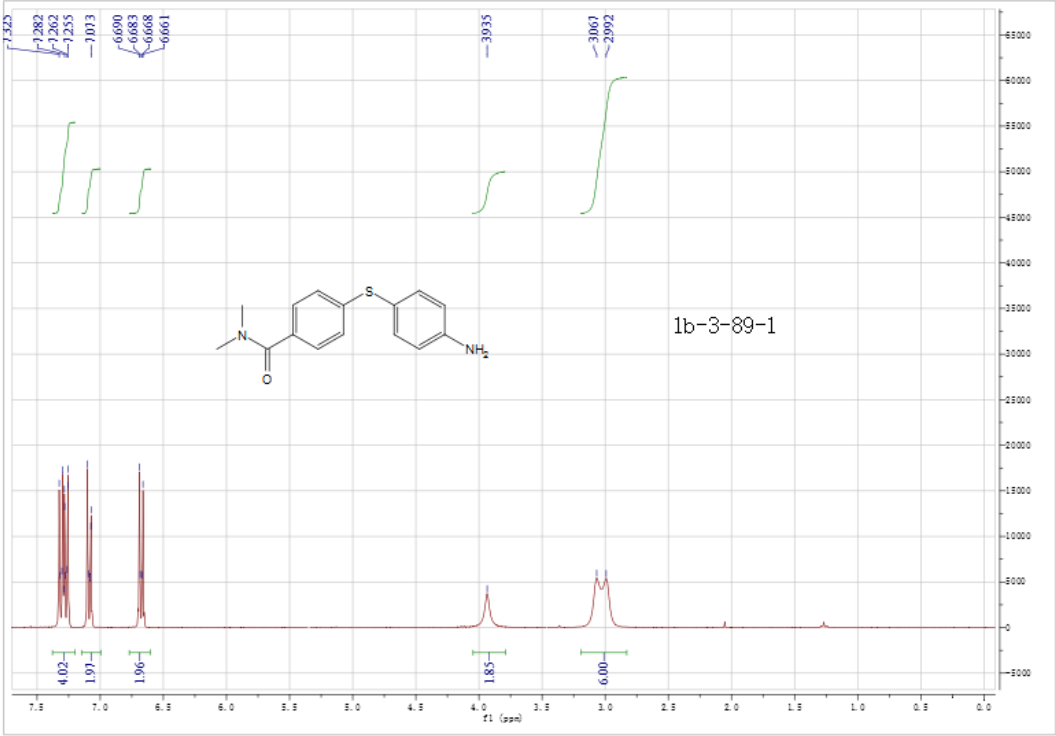


^{13}C NMR (75 MHz, d_6-DMSO)

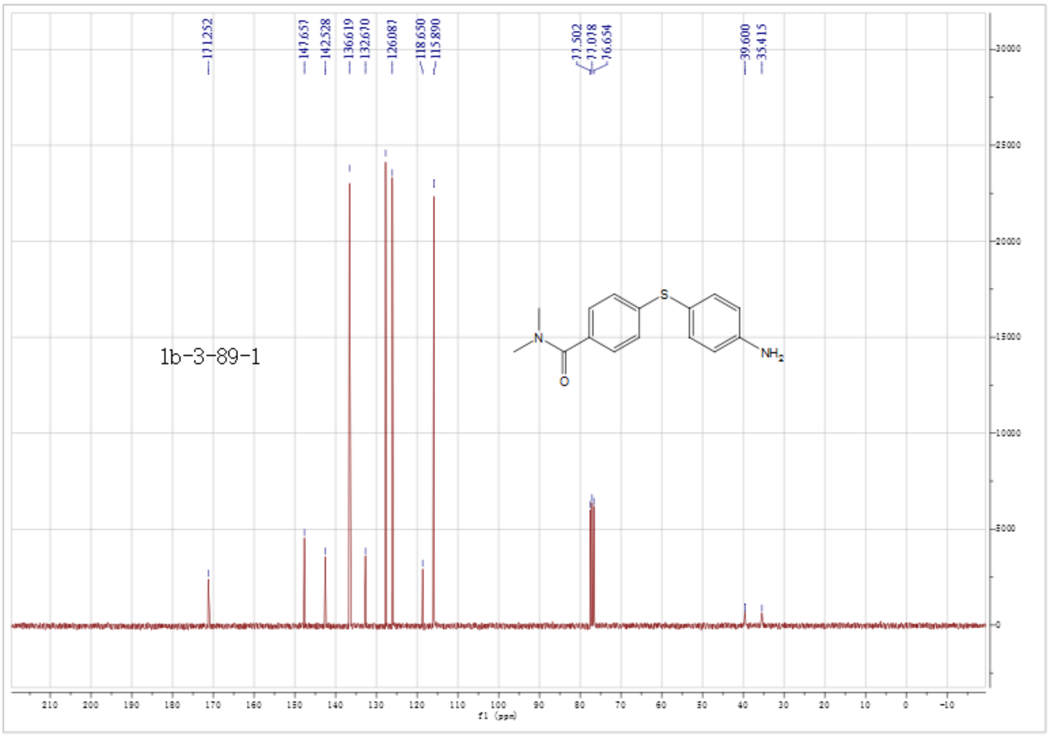


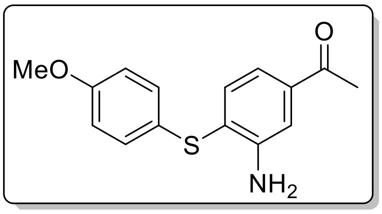


4-((4-Aminophenyl)thio)-*N*,*N*-dimethylbenzamide (4w), ^{1}H NMR (300 MHz, CDCl$_3$)

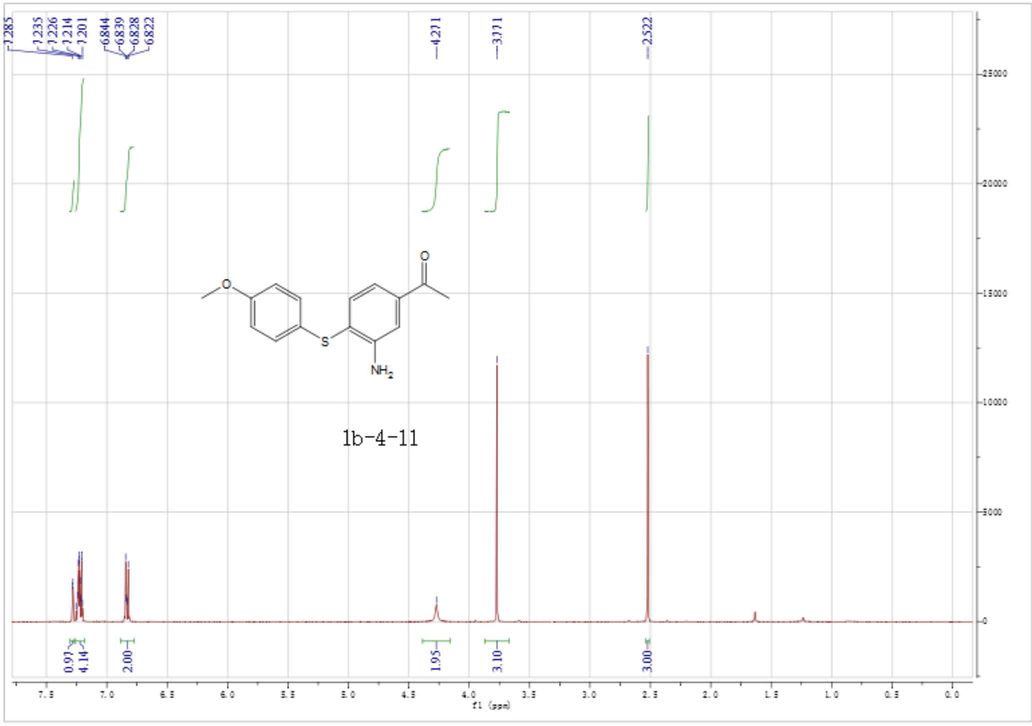


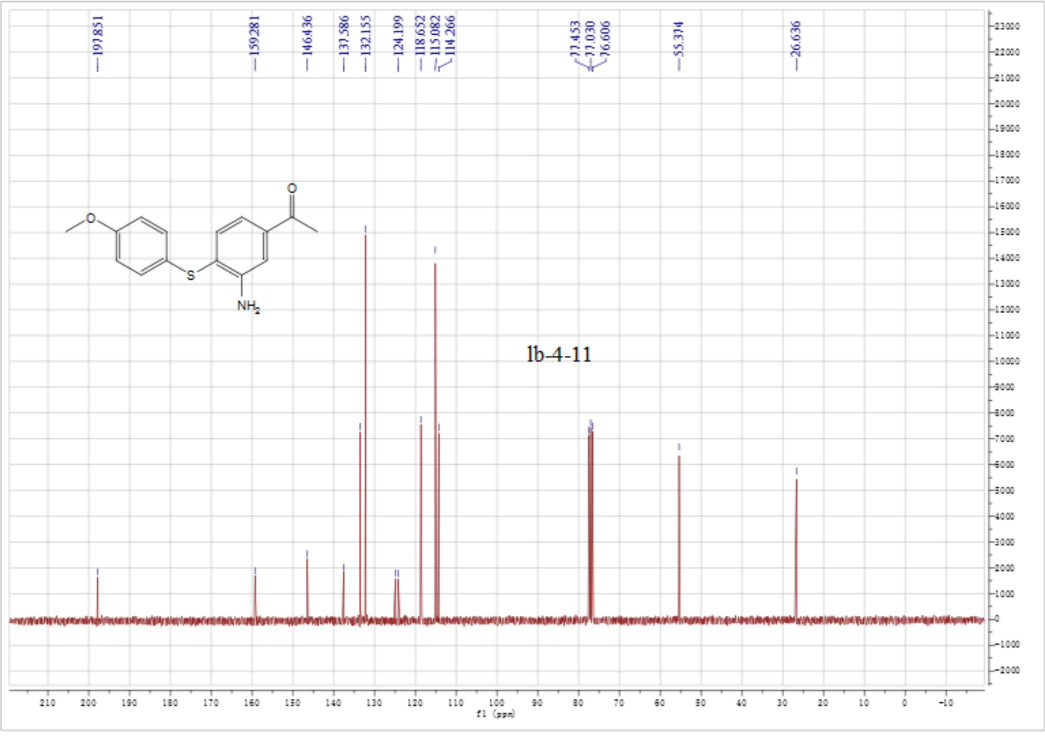
^{13}C NMR (75 MHz, CDCl$_3$)

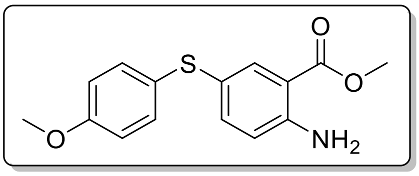




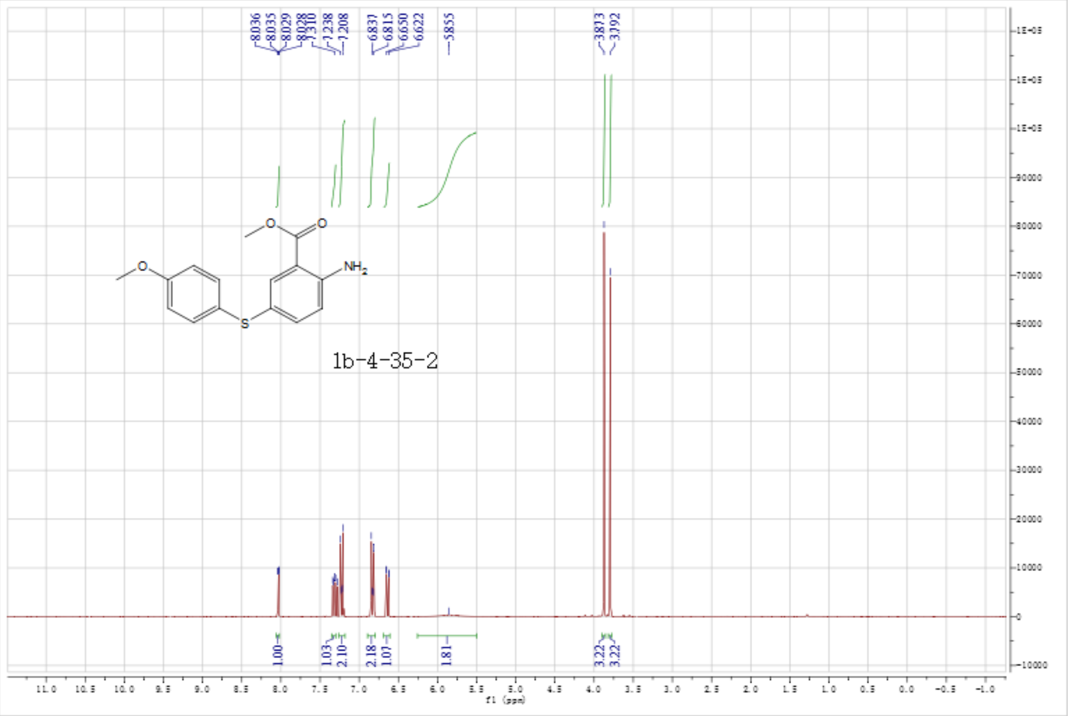
1-(3-Amino-4-((4-methoxyphenyl)thio)phenyl)ethan-1-one (4x), ^{1}H NMR (400 MHz, CDCl$_3$)



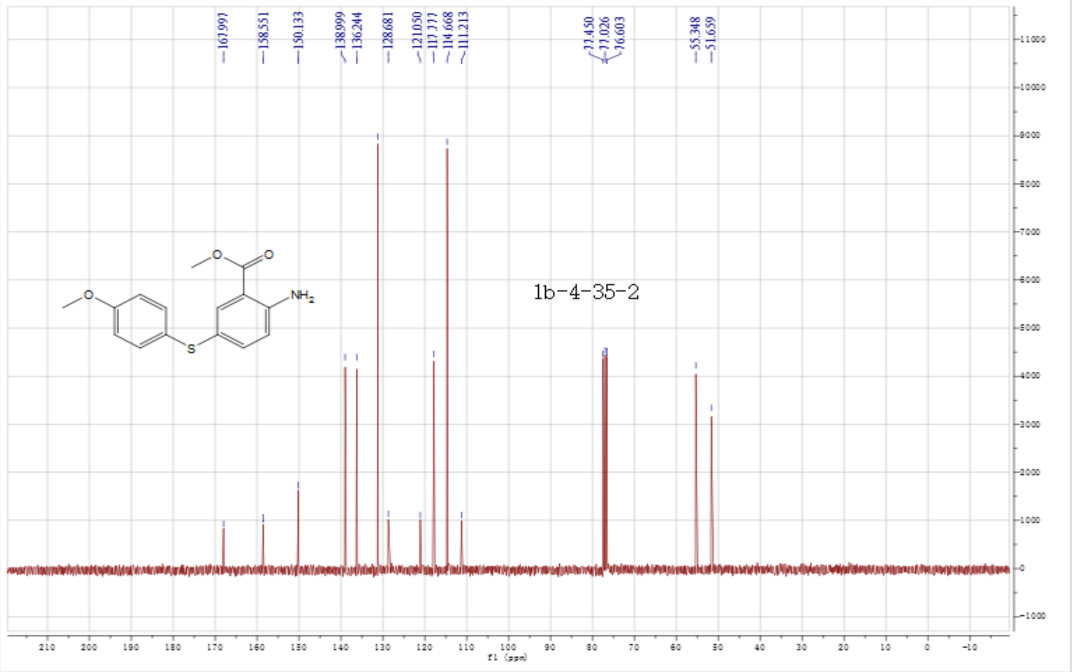


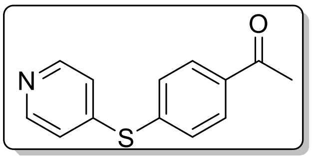


Methyl 2-amino-5-((4-methoxyphenyl)thio)benzoate (4y) , ^{1}H NMR (300 MHz, CDCl$_3$)

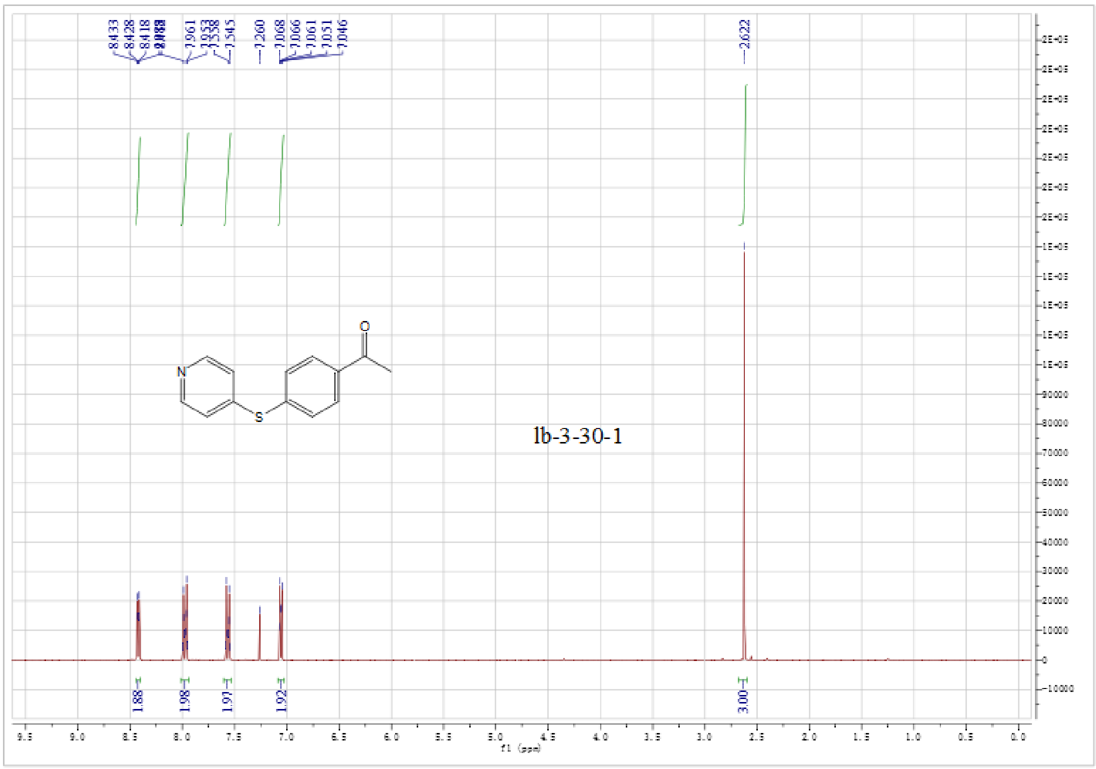


^{13}C NMR (75 MHz, CDCl$_3$)

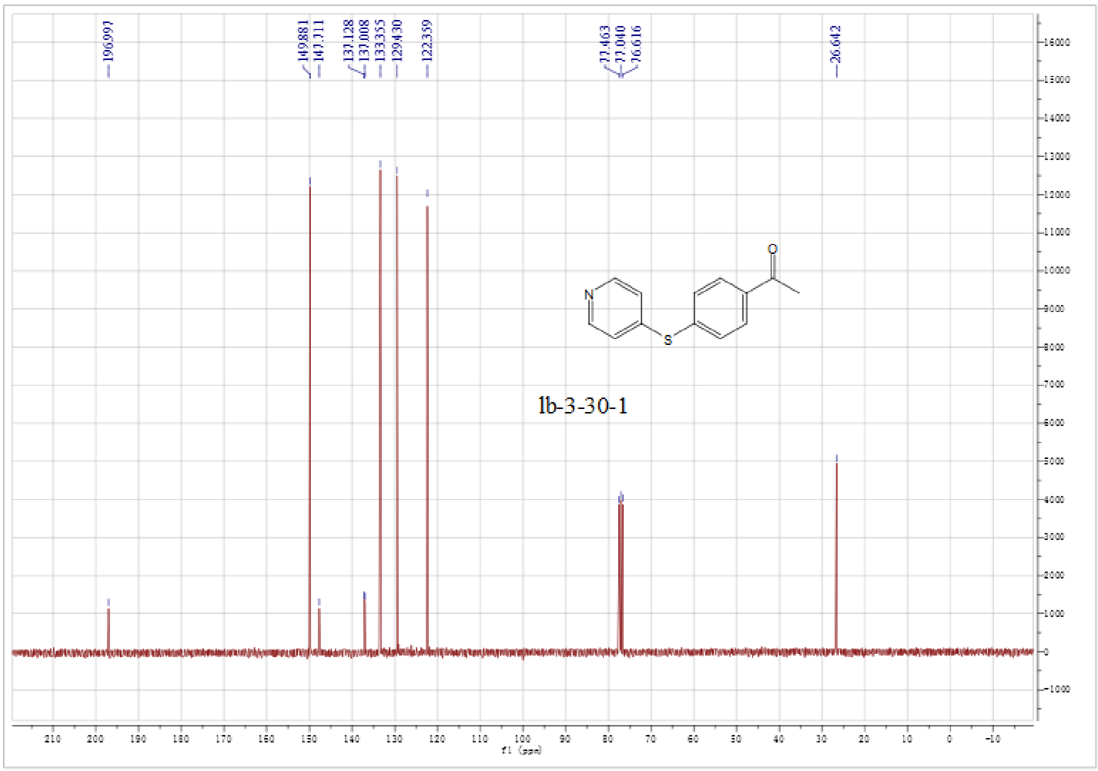


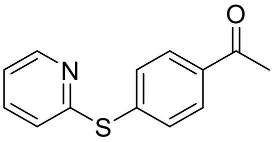


1-(4-(Pyridin-4-ylthio)phenyl)ethan-1-one (5a), ^{1}H NMR (300 MHz, CDCl$_3$)

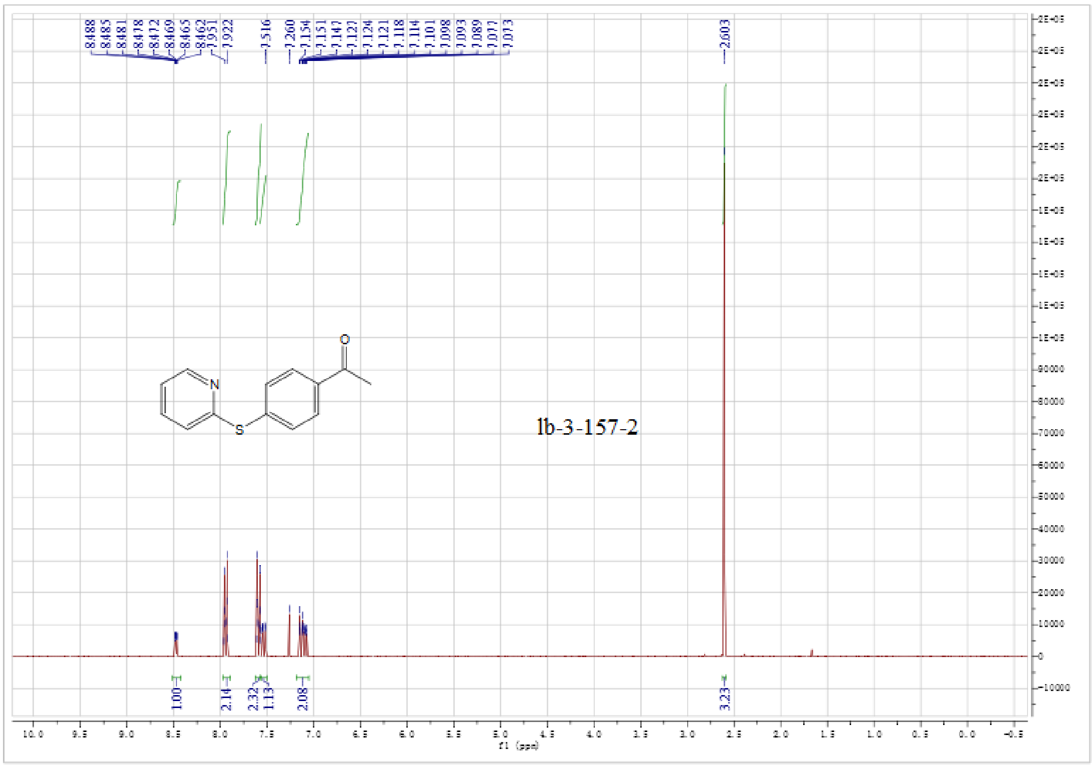


^{13}C NMR (75 MHz, CDCl$_3$)

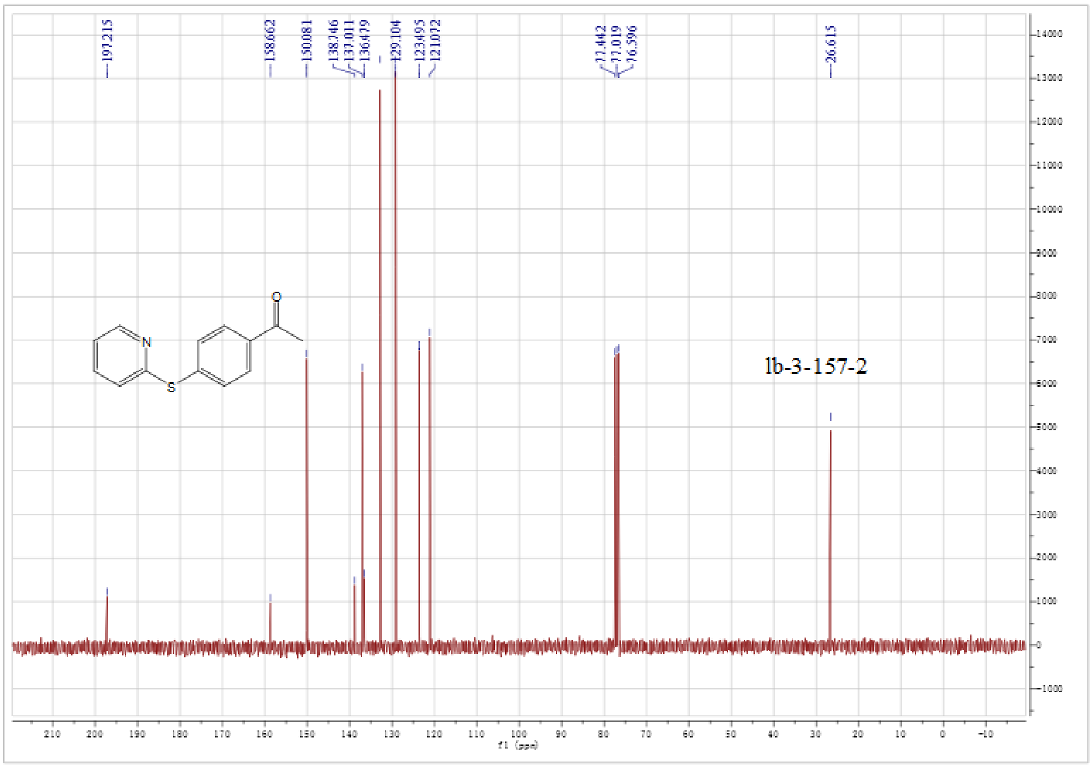


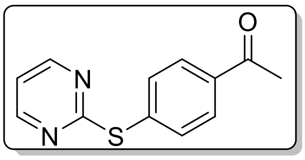


1-(4-(Pyridin-2-ylthio)phenyl)ethan-1-one (5b), ^{1}H NMR (300 MHz, CDCl$_3$)

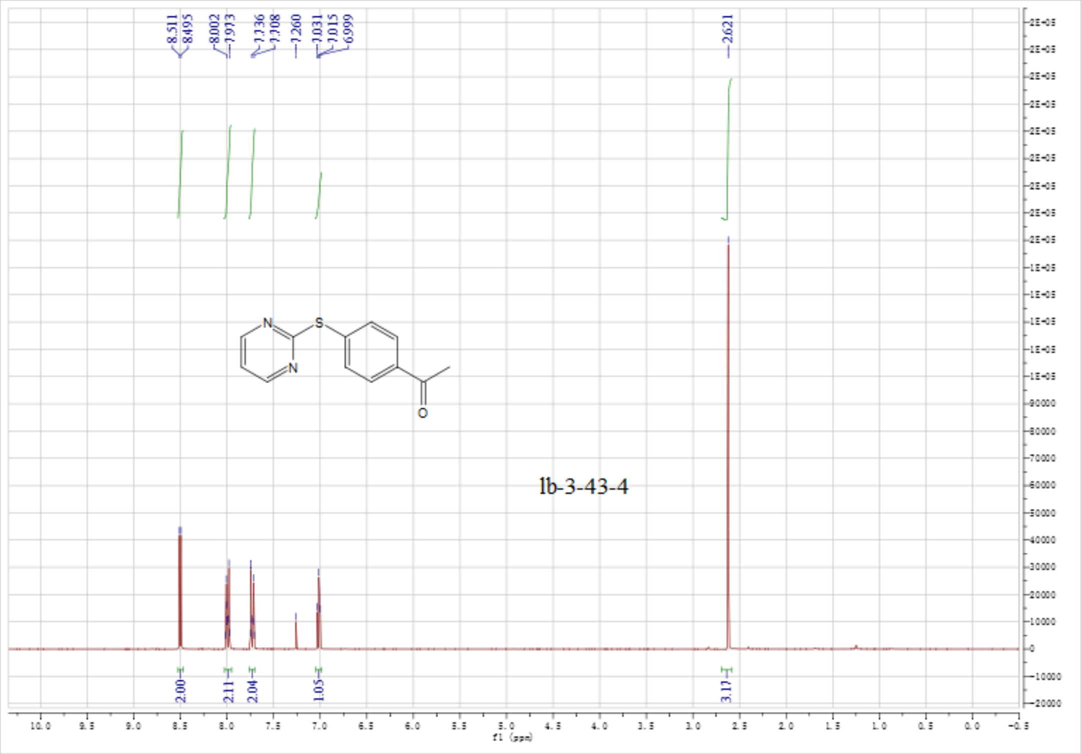


^{13}C NMR (75 MHz, CDCl$_3$)

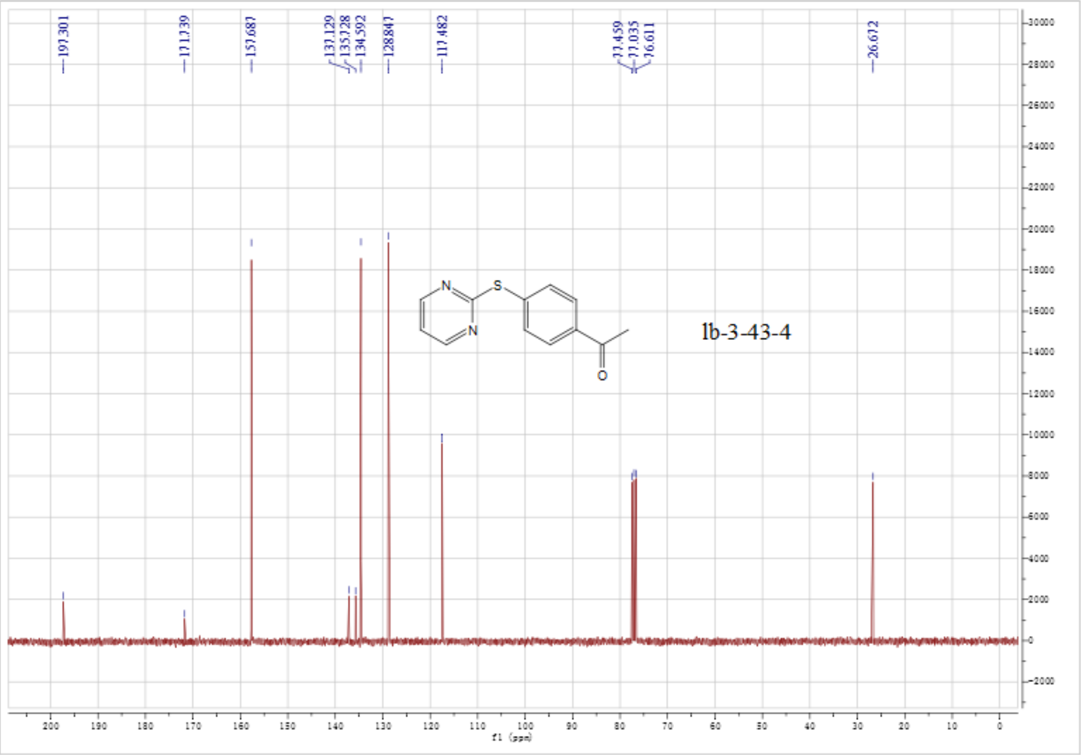


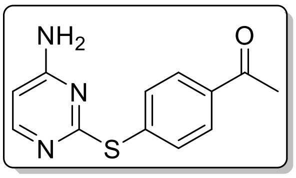


1-(4-(Pyrimidin-2-ylthio)phenyl)ethan-1-one (5c), ^{1}H NMR (300 MHz, CDCl$_3$)

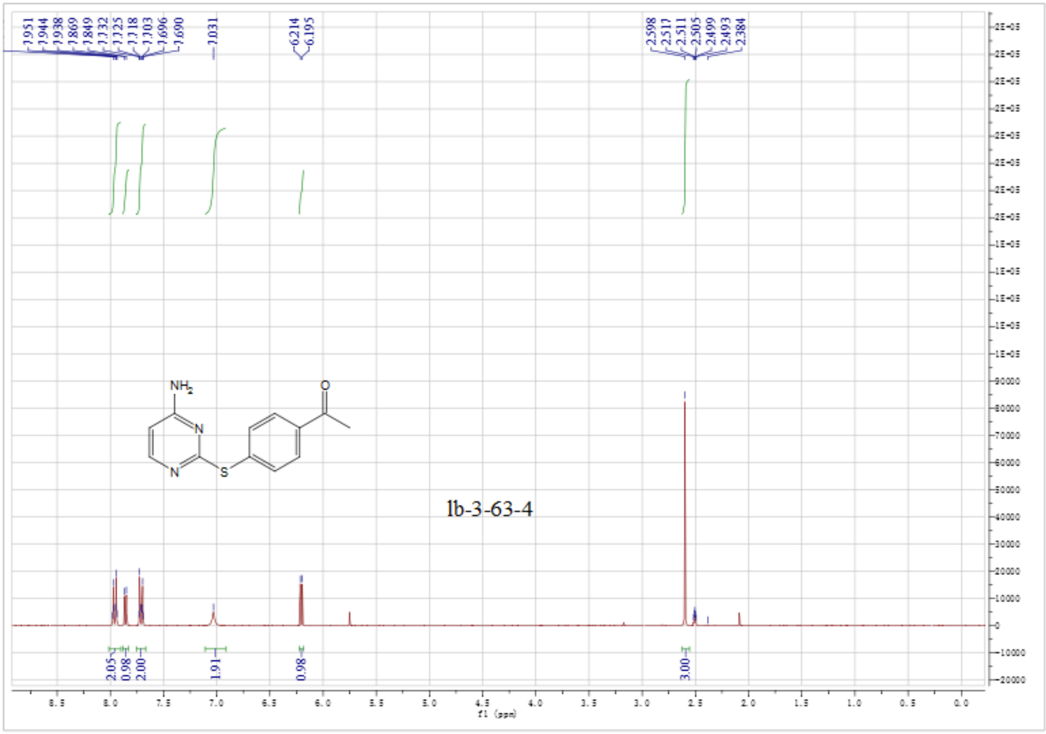


^{13}C NMR (75 MHz, CDCl$_3$)

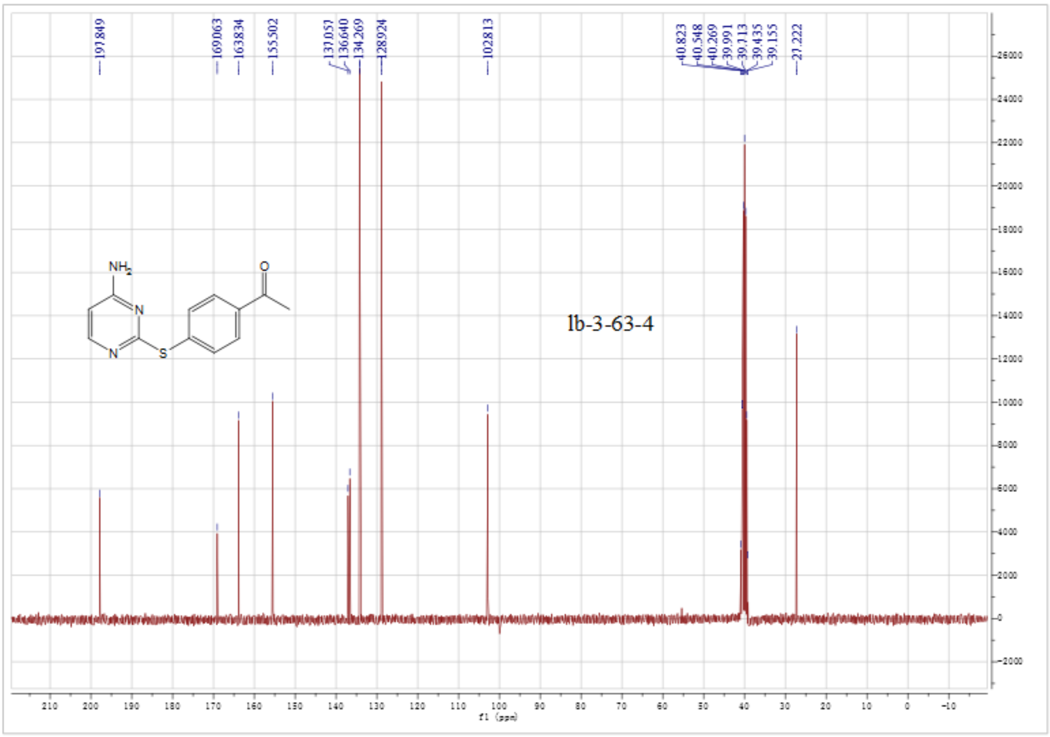


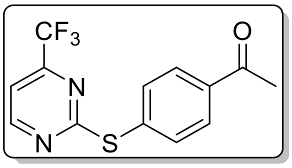


1-(4-((4-Aminopyrimidin-2-yl)thio)phenyl)ethan-1-one (5d), ^{1}H NMR (300 MHz, *d*$_6$-DMSO)

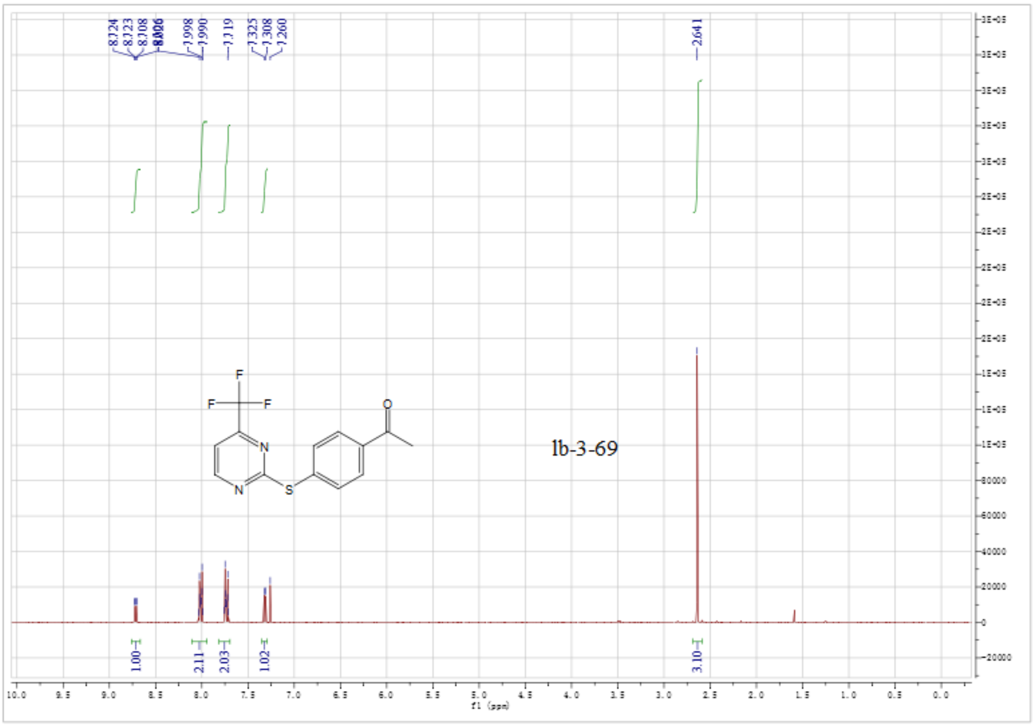


^{13}C NMR (75 MHz, *d*$_6$-DMSO)

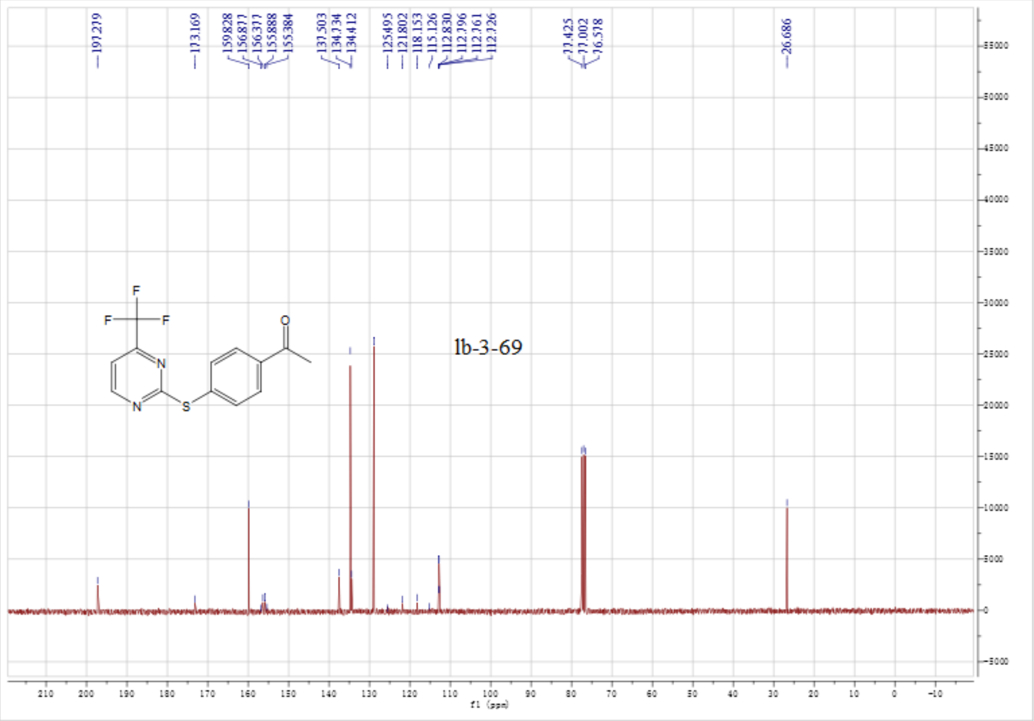


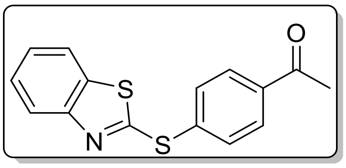


1-(4-((4-(Trifluoromethyl)pyrimidin-2-yl)thio)phenyl)ethan-1-one (5e), ^{1}H NMR (300 MHz, CDCl$_3$)

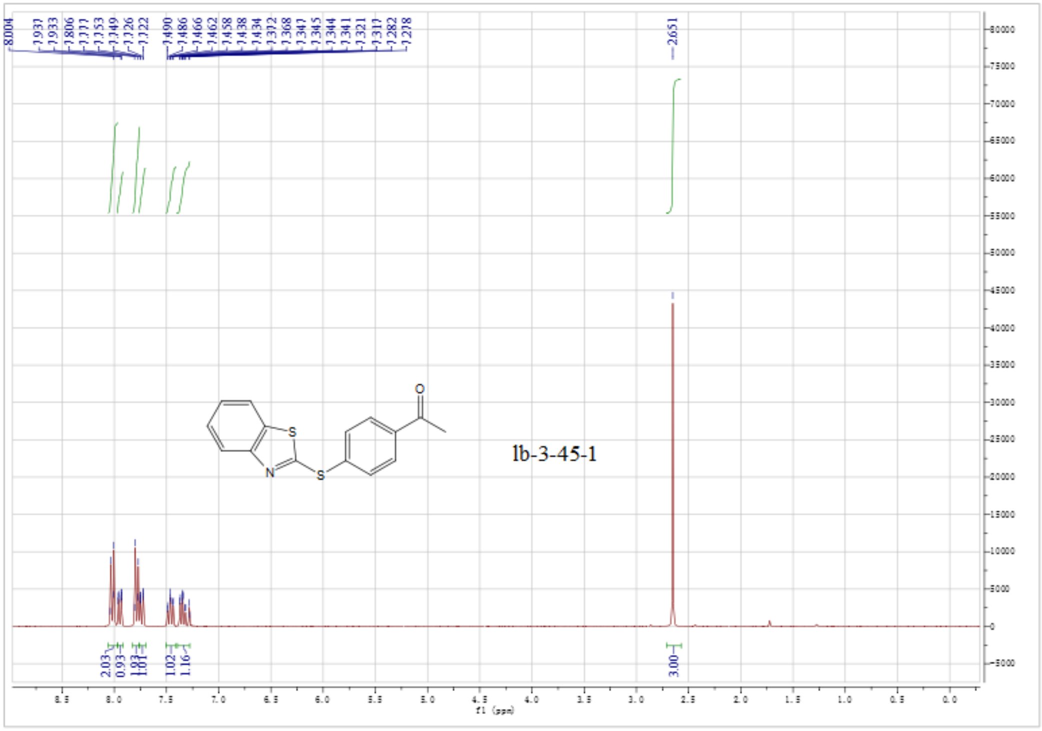


^{13}C NMR (75 MHz, CDCl$_3$)

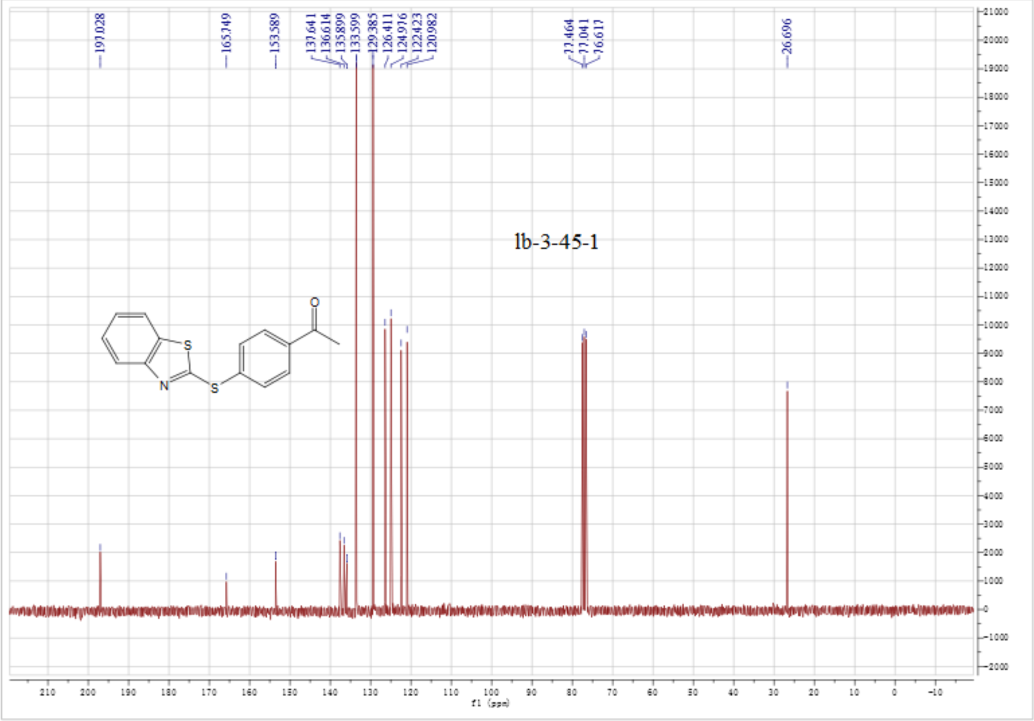


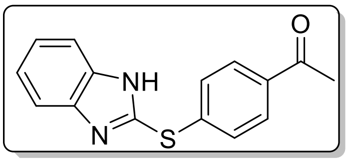


1-(4-(Benzo[d]thiazol-2-ylthio)phenyl)ethan-1-one (5f), ^{1}H NMR (300 MHz, CDCl$_3$)

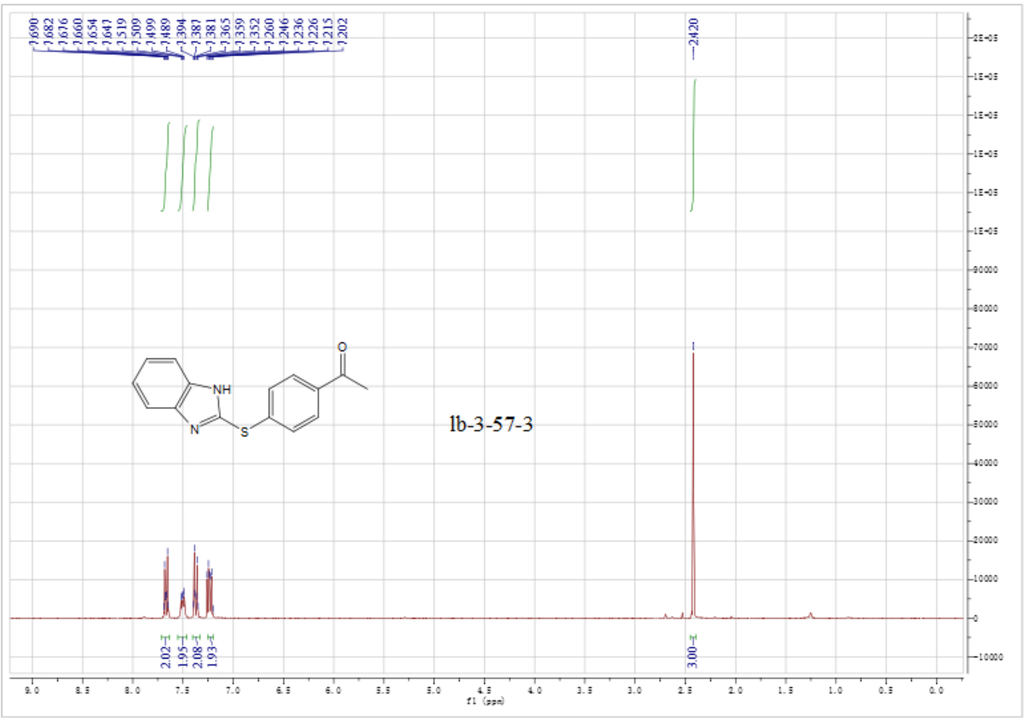


^{13}C NMR (75 MHz, CDCl$_3$)

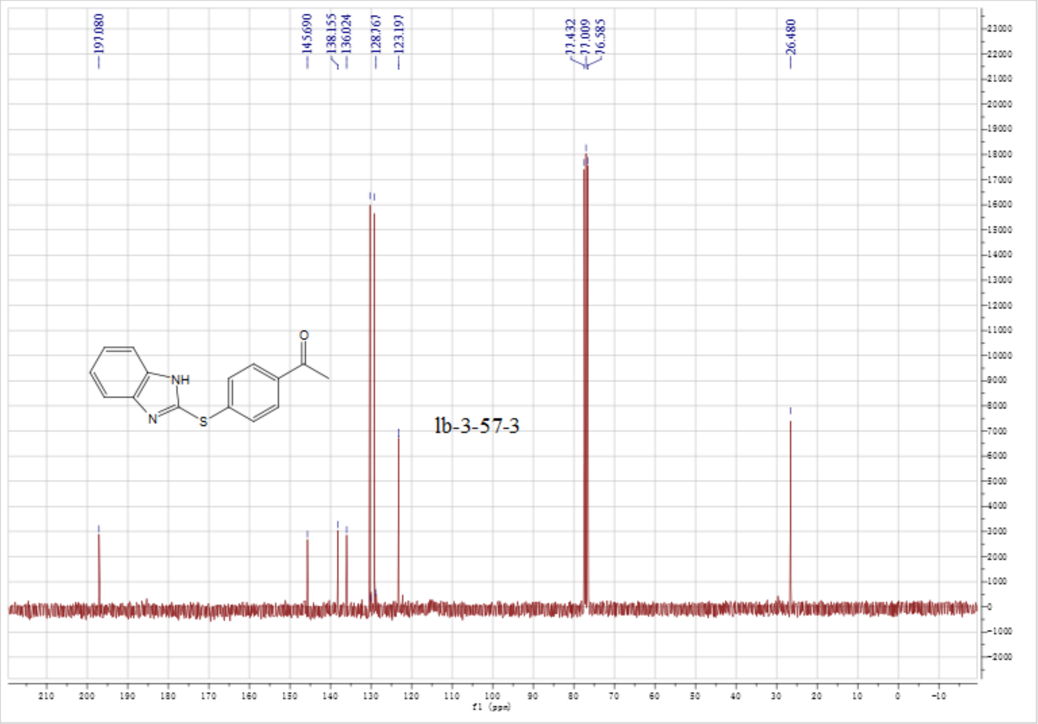


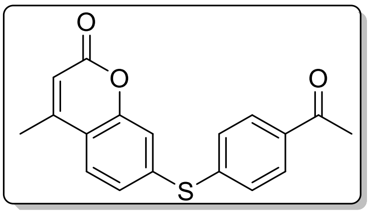


1-(4-((1*H*-benzo[*d*]imidazol-2-yl)thio)phenyl)ethan-1-one (5g), ^{1}H NMR (300 MHz, CDCl$_3$)

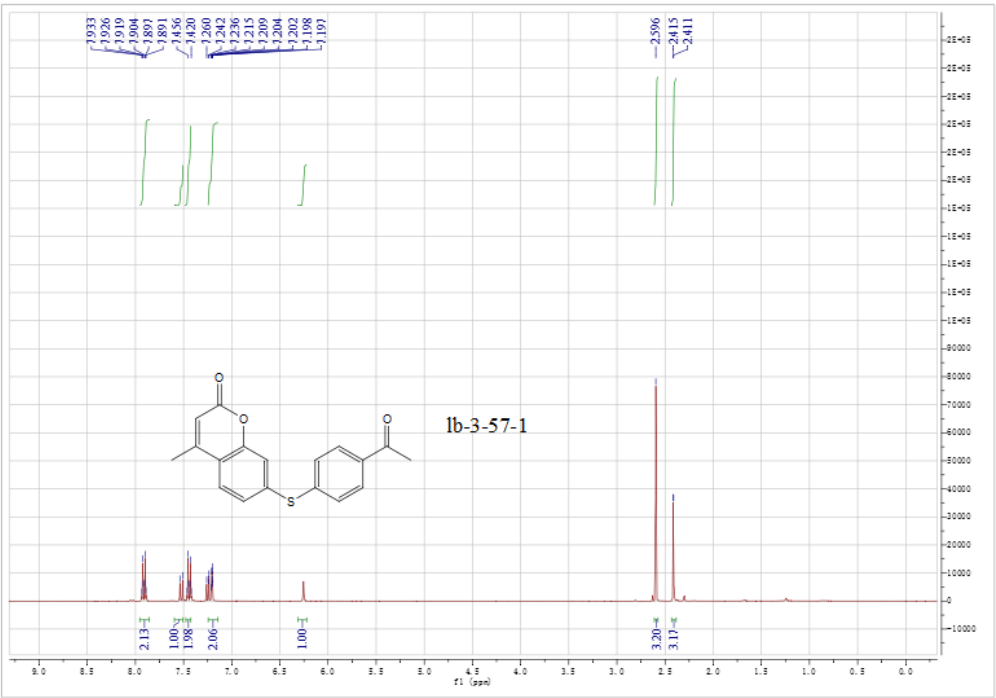


^{13}C NMR (75 MHz, CDCl$_3$)

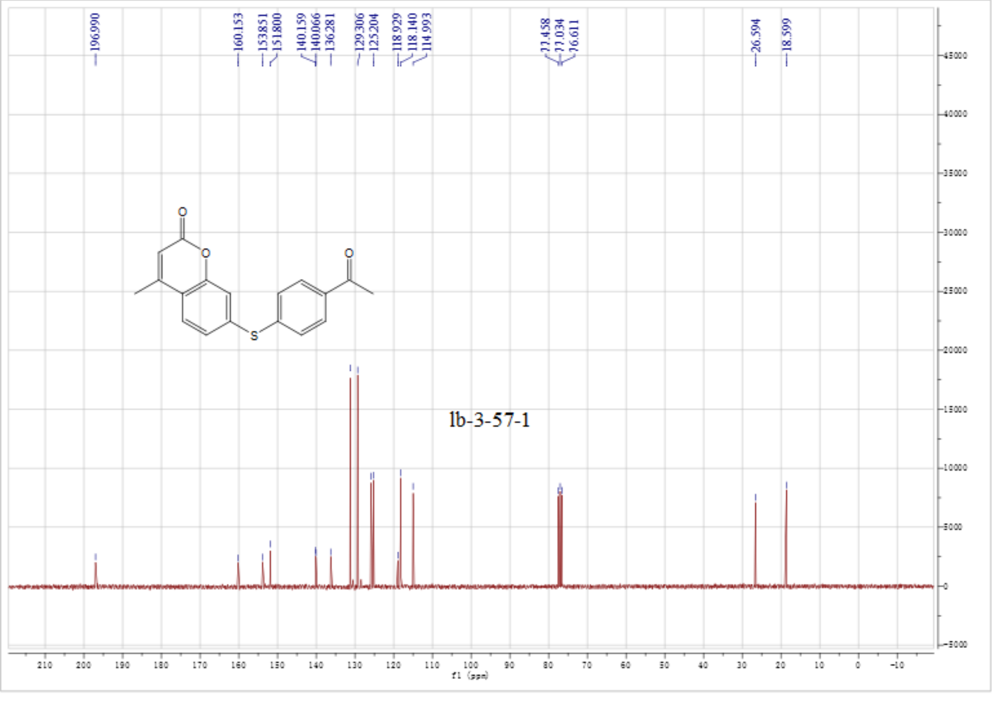


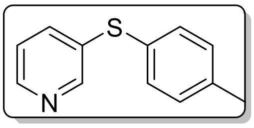


7-((4-Acetylphenyl)thio)-4-methyl-2H-chromen-2-one (5h), ^{1}H NMR (300 MHz, $CDCl_3$)

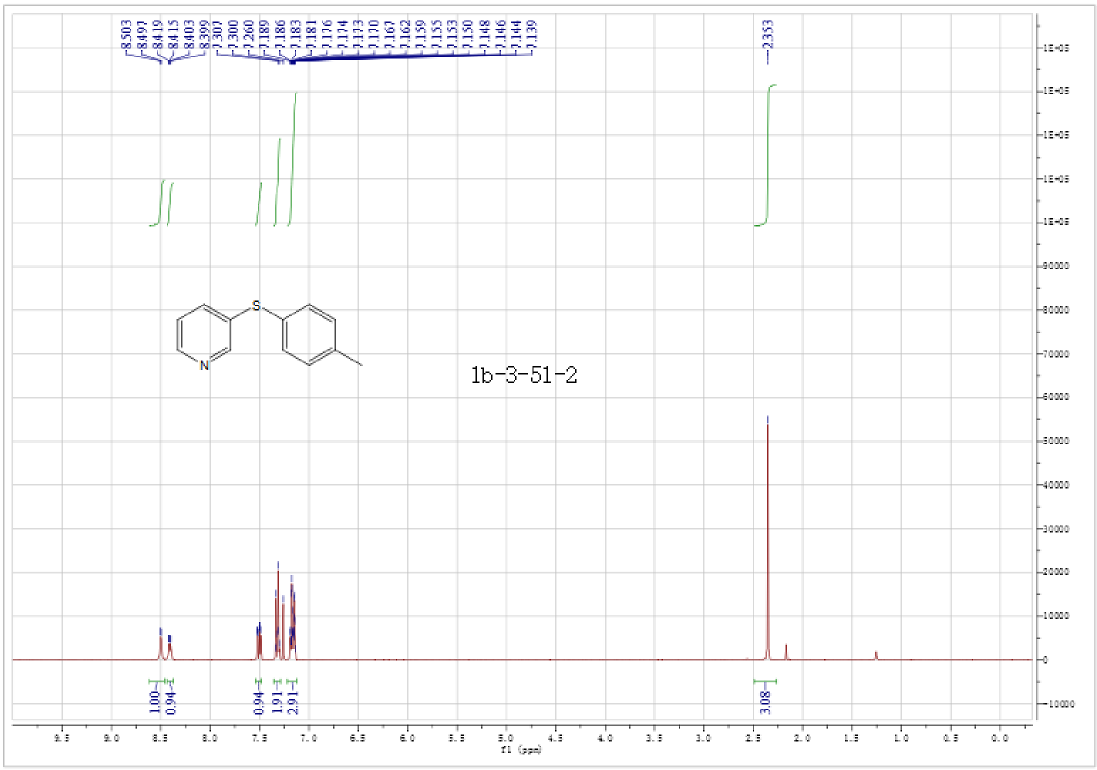


^{13}C NMR (75 MHz, $CDCl_3$)

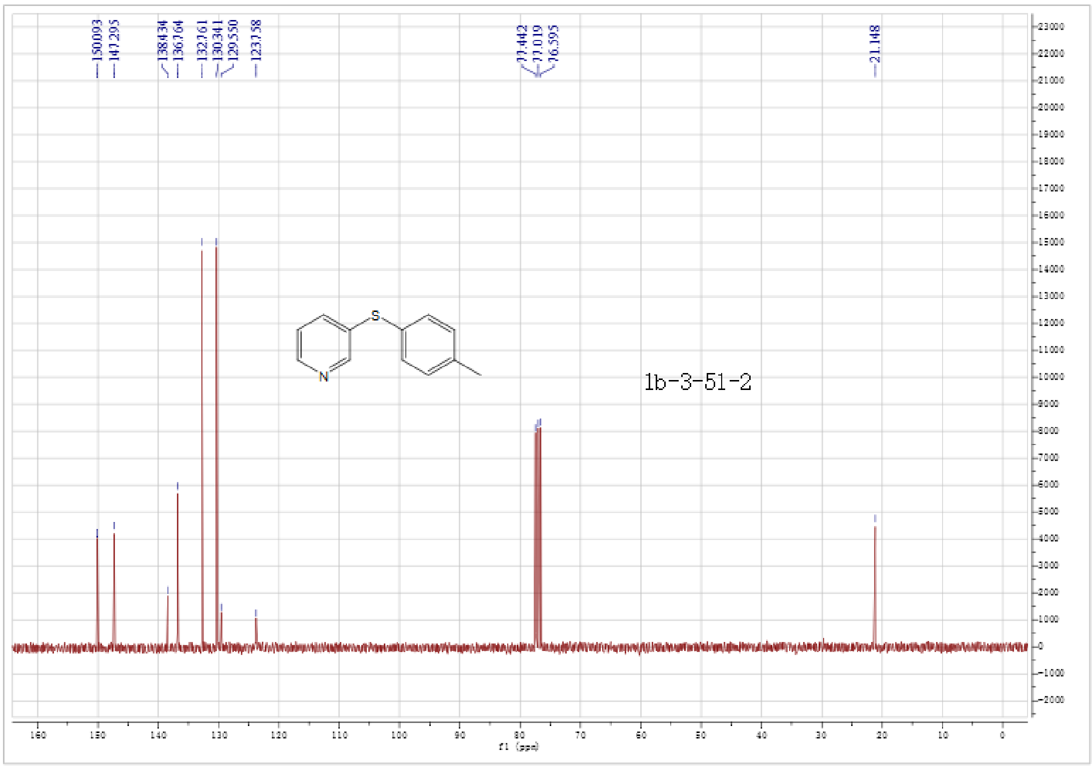


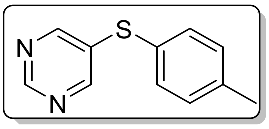


3-(*p*-Tolylthio)pyridine (5i), ^{1}H NMR (300 MHz, CDCl$_3$)

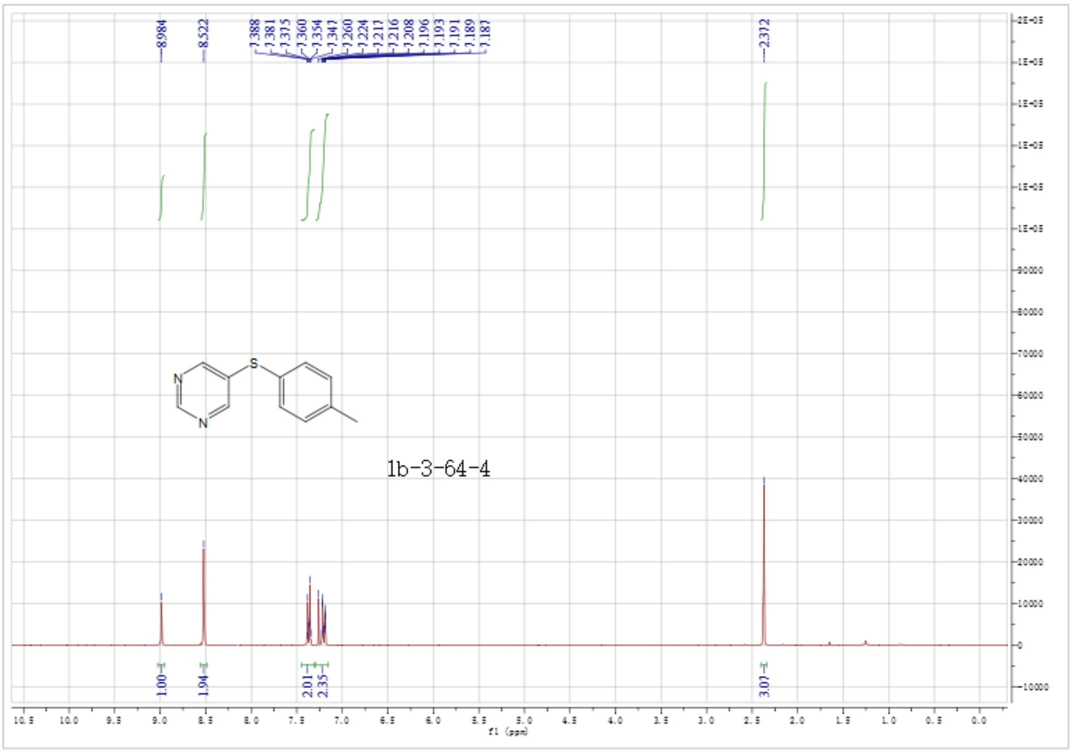


^{13}C NMR (75 MHz, CDCl$_3$)

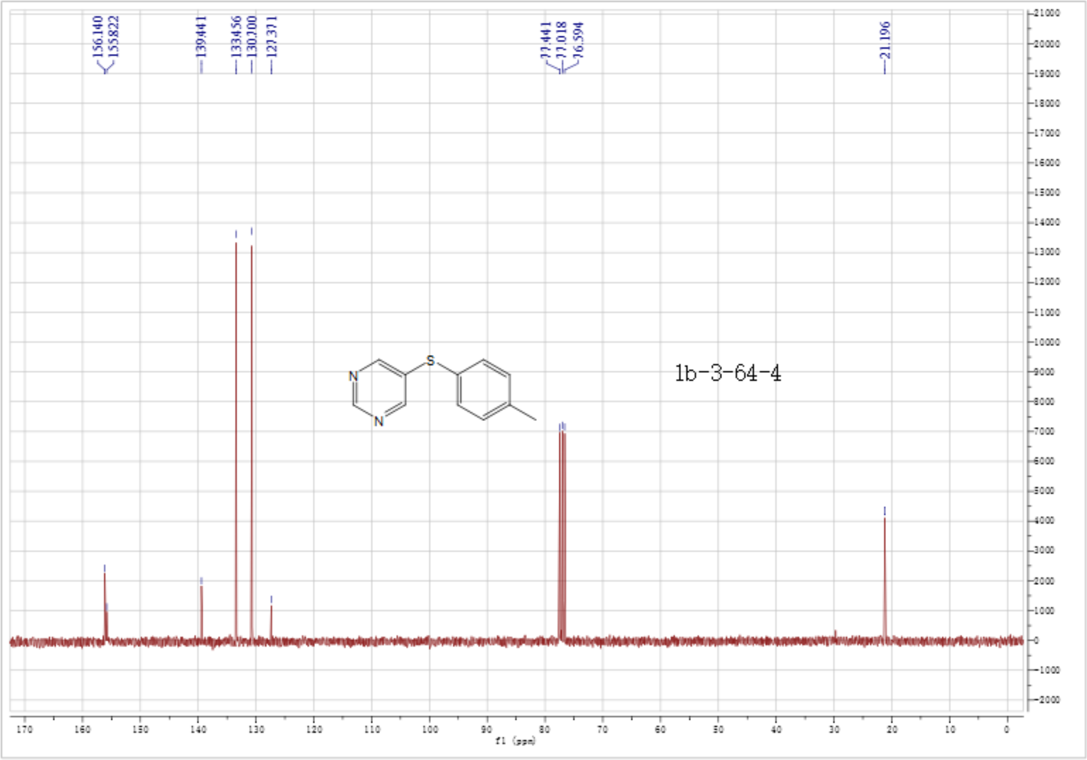


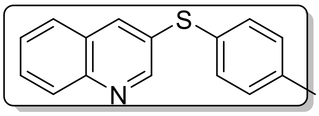


5-(*p*-Tolylthio)pyrimidine (5j), ^{1}H NMR (300 MHz, $CDCl_3$)

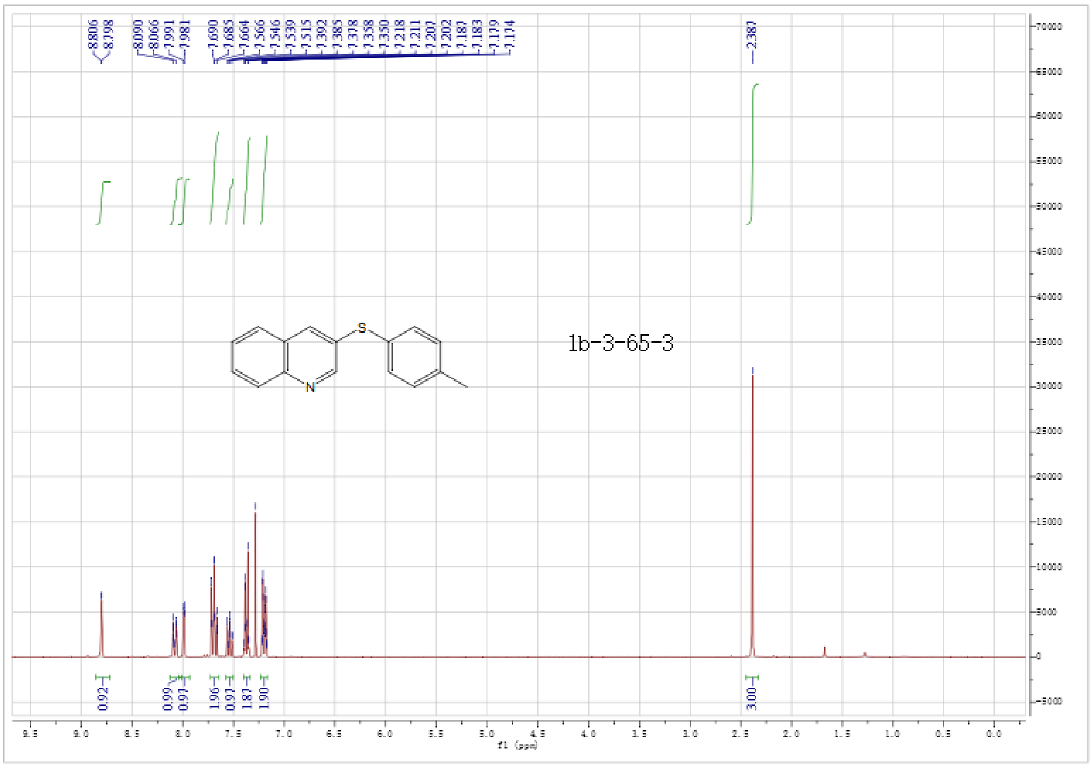


^{13}C NMR (75 MHz, $CDCl_3$)

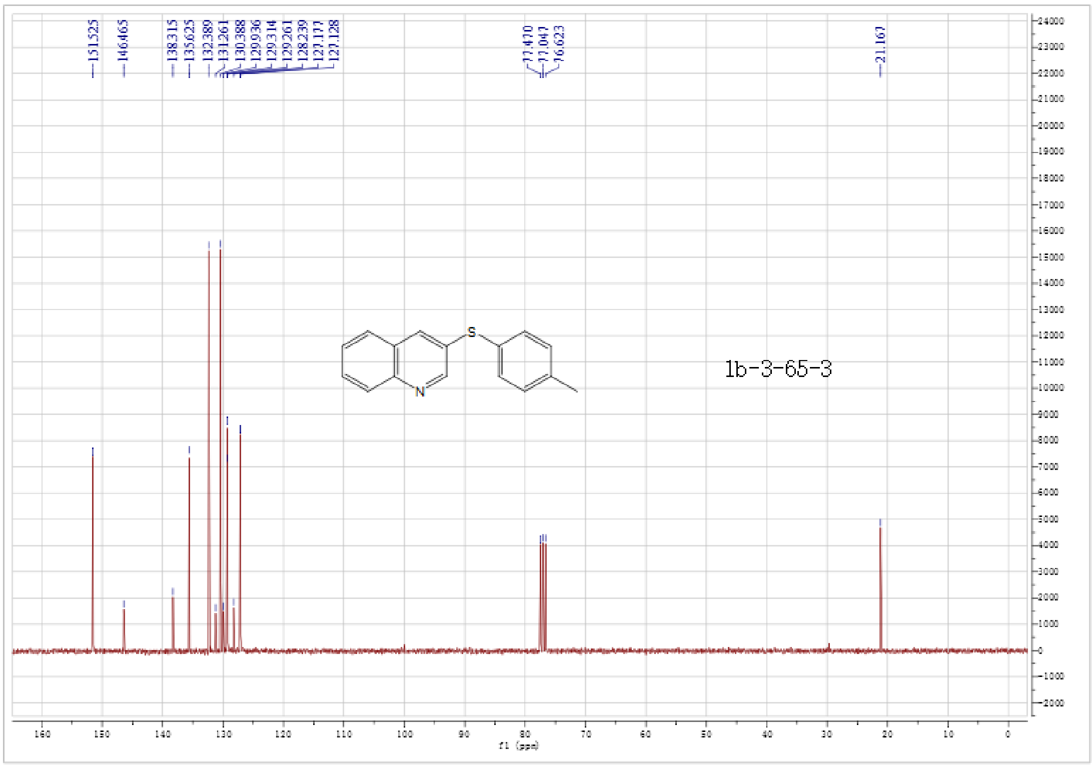


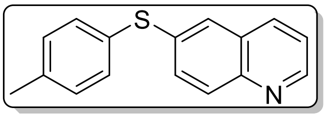


3-(p-Tolylthio)quinolone (5k), ^{1}H NMR (300 MHz, CDCl$_3$)

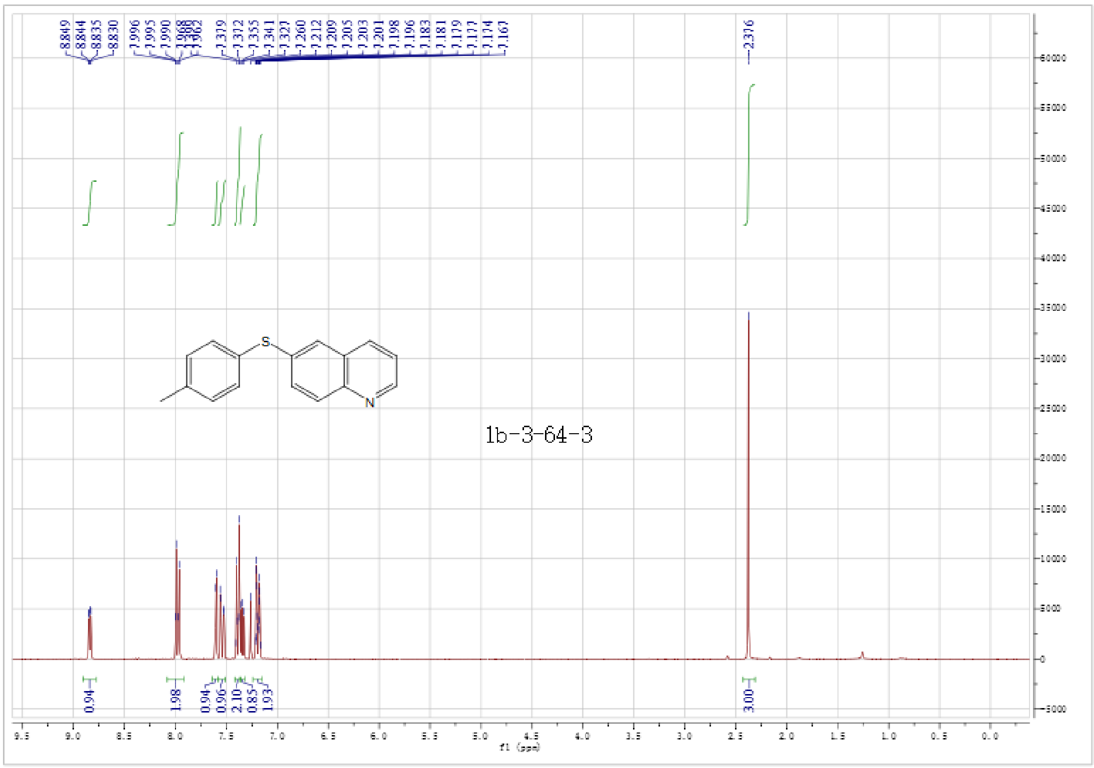


^{13}C NMR (75 MHz, CDCl$_3$)

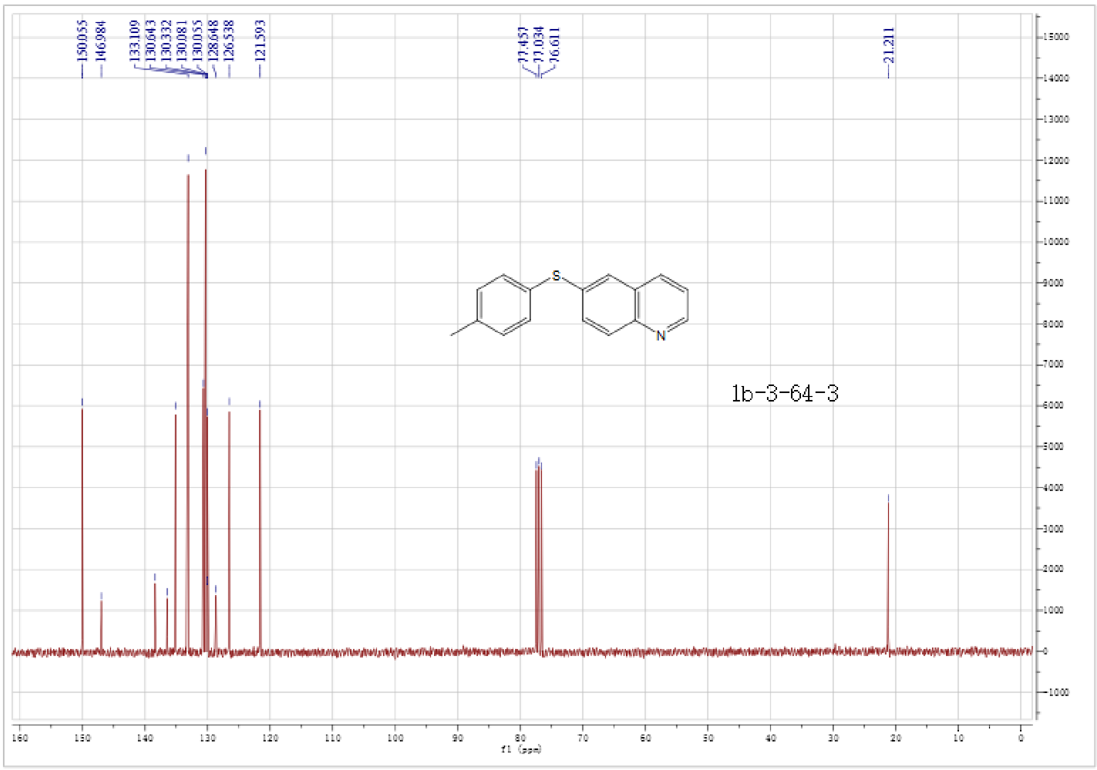


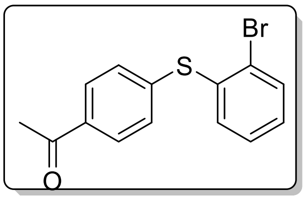


6-(*p*-Tolylthio)quinolone (5l), ^{1}H NMR (300 MHz, CDCl$_3$)

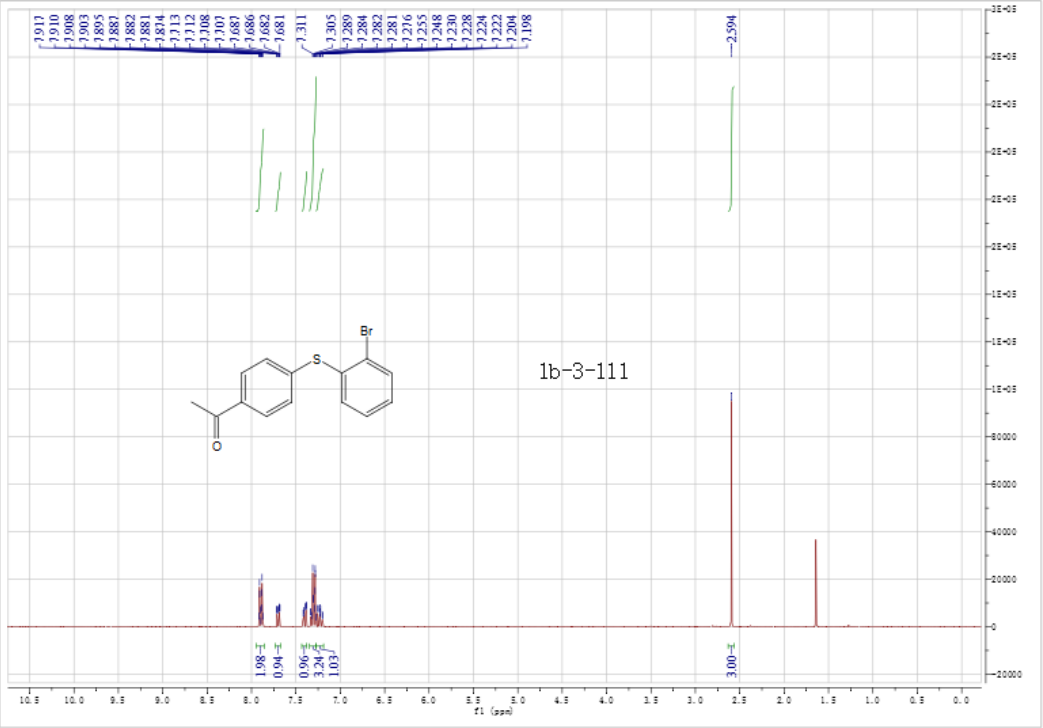


^{13}C NMR (75 MHz, CDCl$_3$)

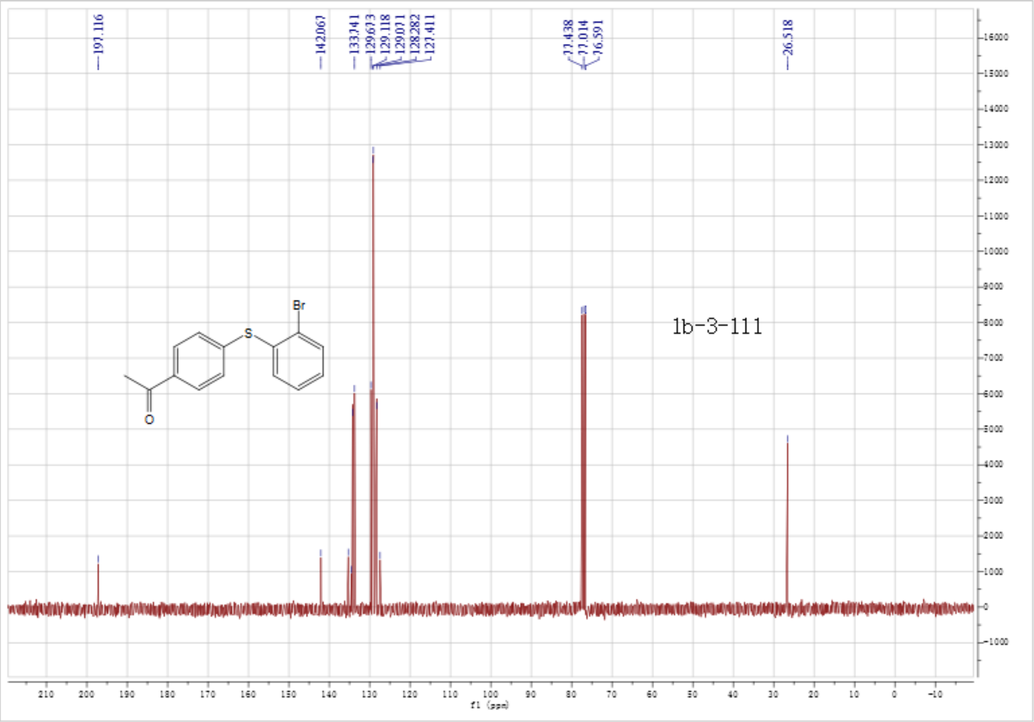


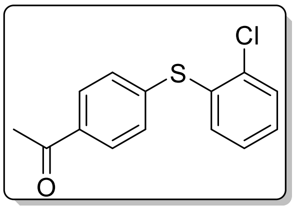


1-(4-((2-Bromophenyl)thio)phenyl)ethan-1-one (6), ^{1}H NMR (300 MHz, CDCl$_3$)

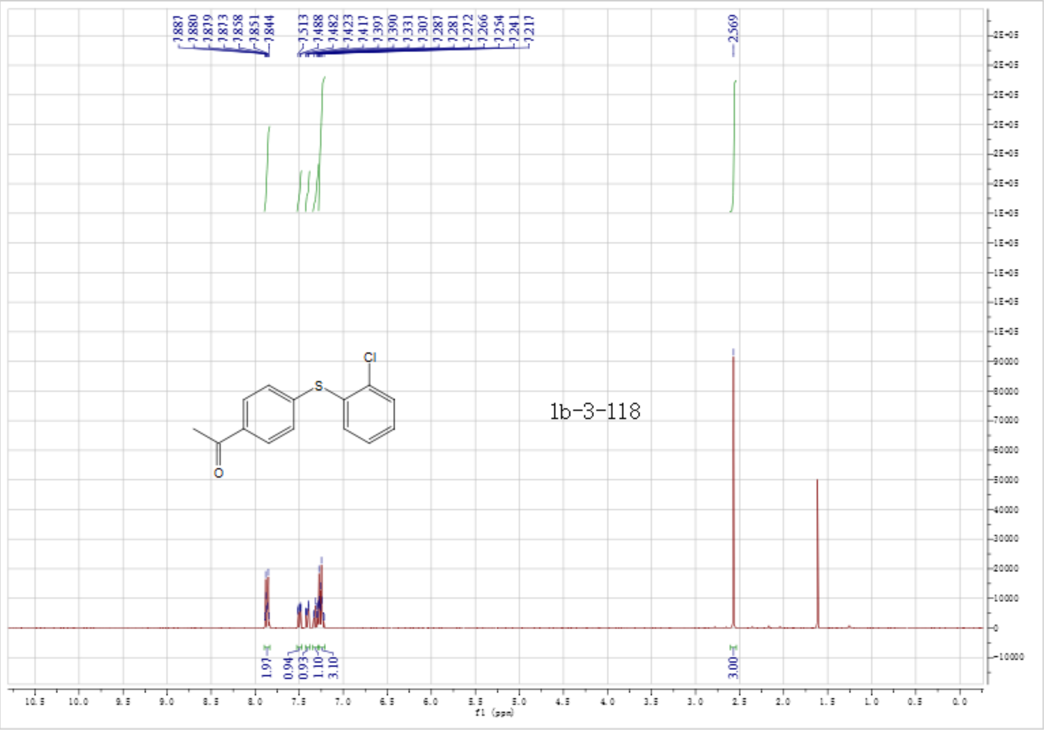


^{13}C NMR (75 MHz, CDCl$_3$)

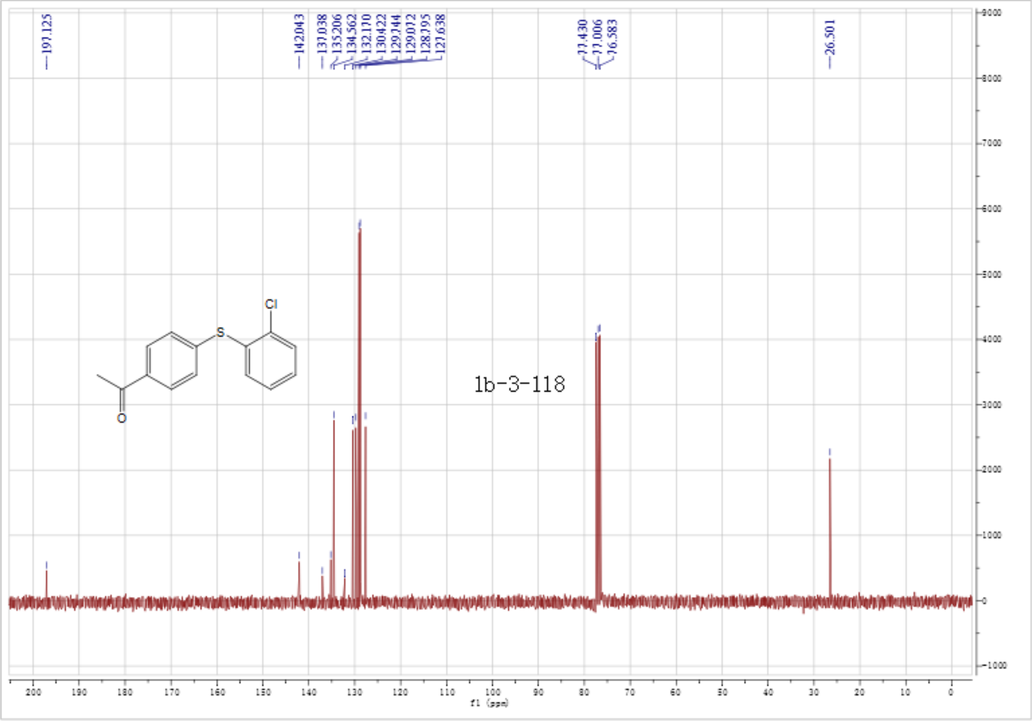


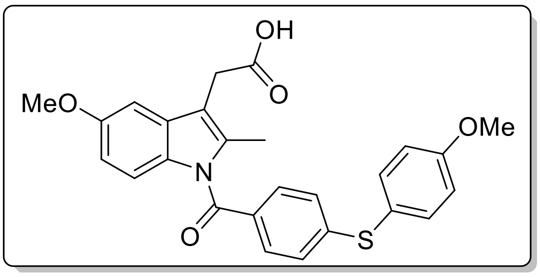


1-(4-((2-Chlorophenyl)thio)phenyl)ethan-1-one (7), ^{1}H NMR (300 MHz, CDCl$_3$)

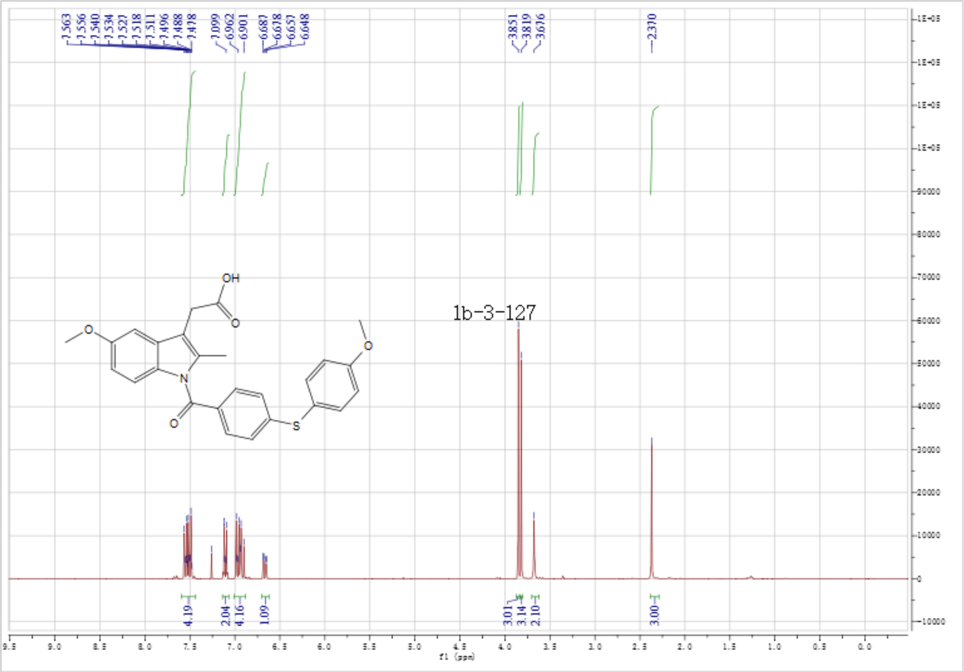


^{13}C NMR (75 MHz, CDCl$_3$)

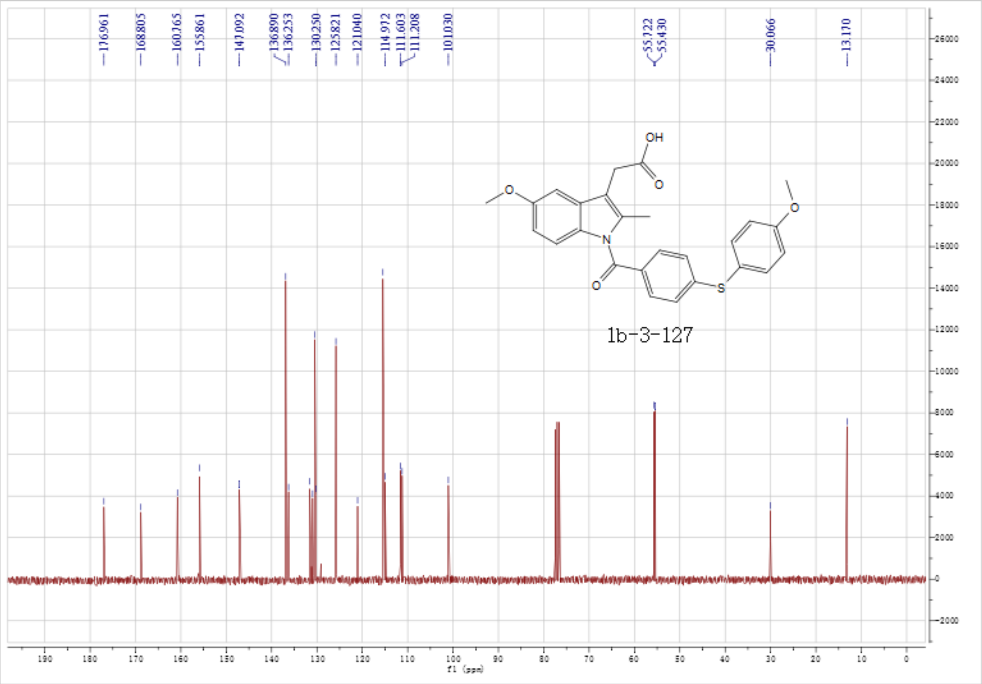


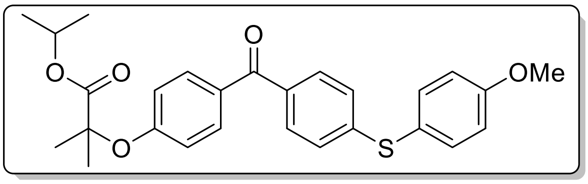


2-(5-Methoxy-1-(4-((4-methoxyphenyl)thio)benzoyl)-2-methyl-1H-indol-3-yl)acetic acid (8), ^{1}H NMR (300 MHz, CDCl$_3$)

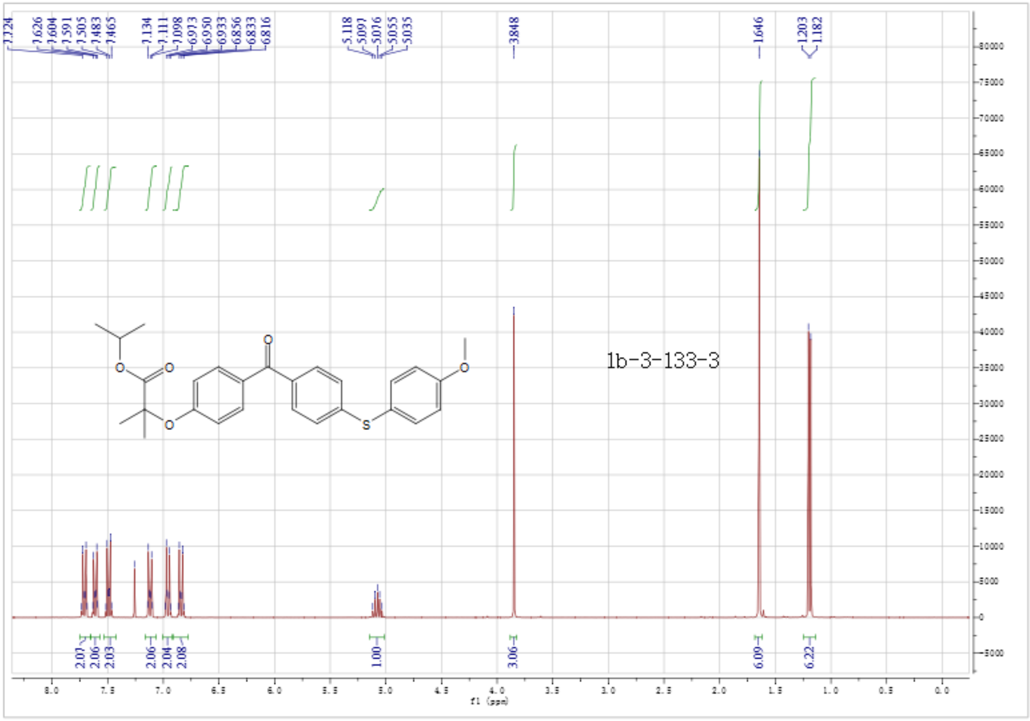


^{13}C NMR (75 MHz, CDCl$_3$)

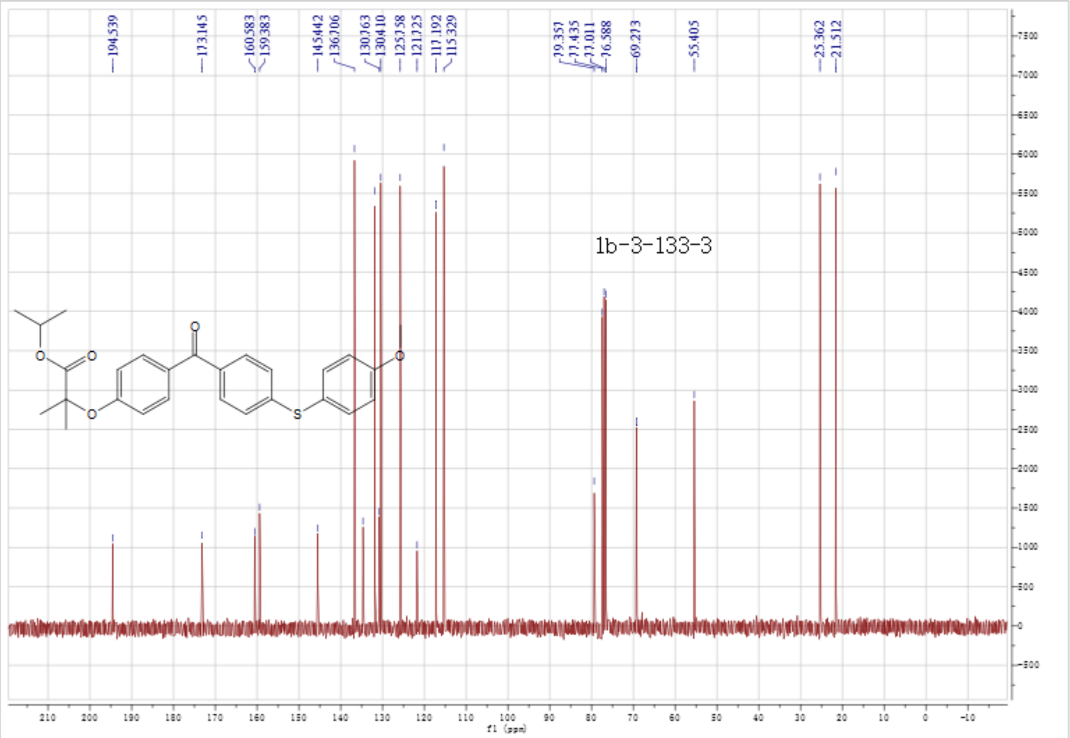


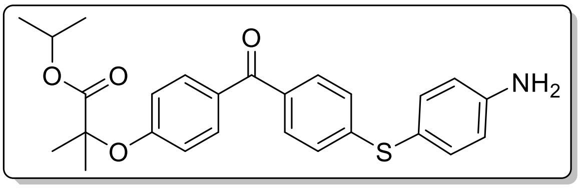


Isopropyl 2-(4-(4-((4-methoxyphenyl)thio)benzoyl)phenoxy)-2-methylpropanoate (9), ^{1}H NMR (300 MHz, CDCl$_3$)

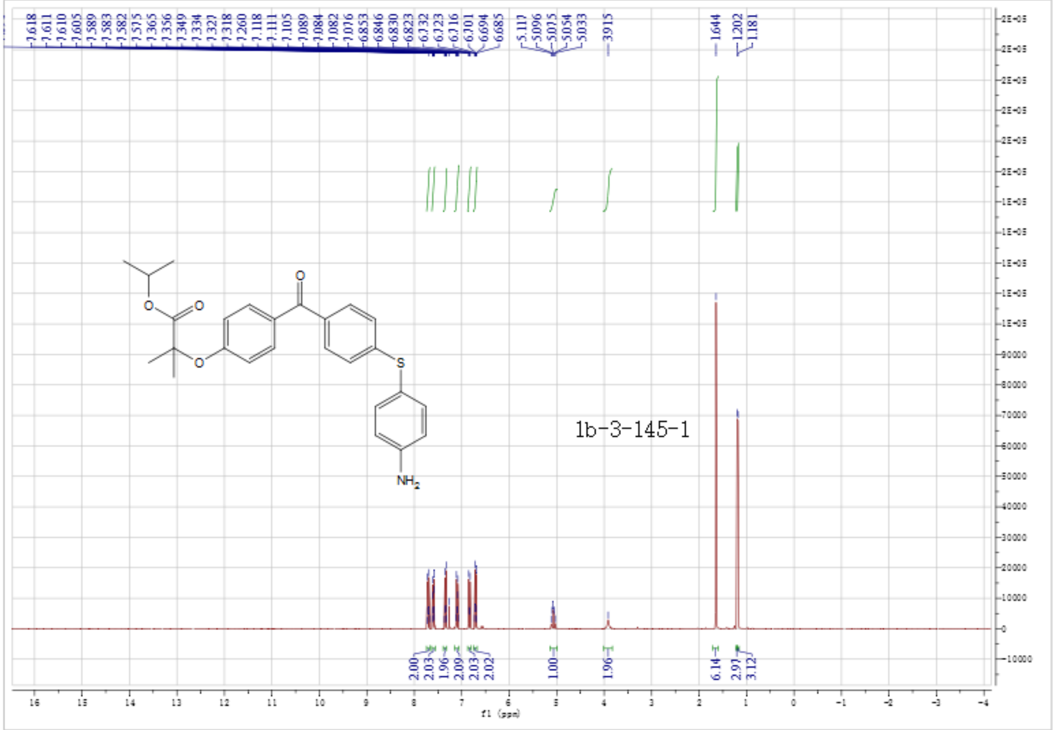


^{13}C NMR (75 MHz, CDCl$_3$)

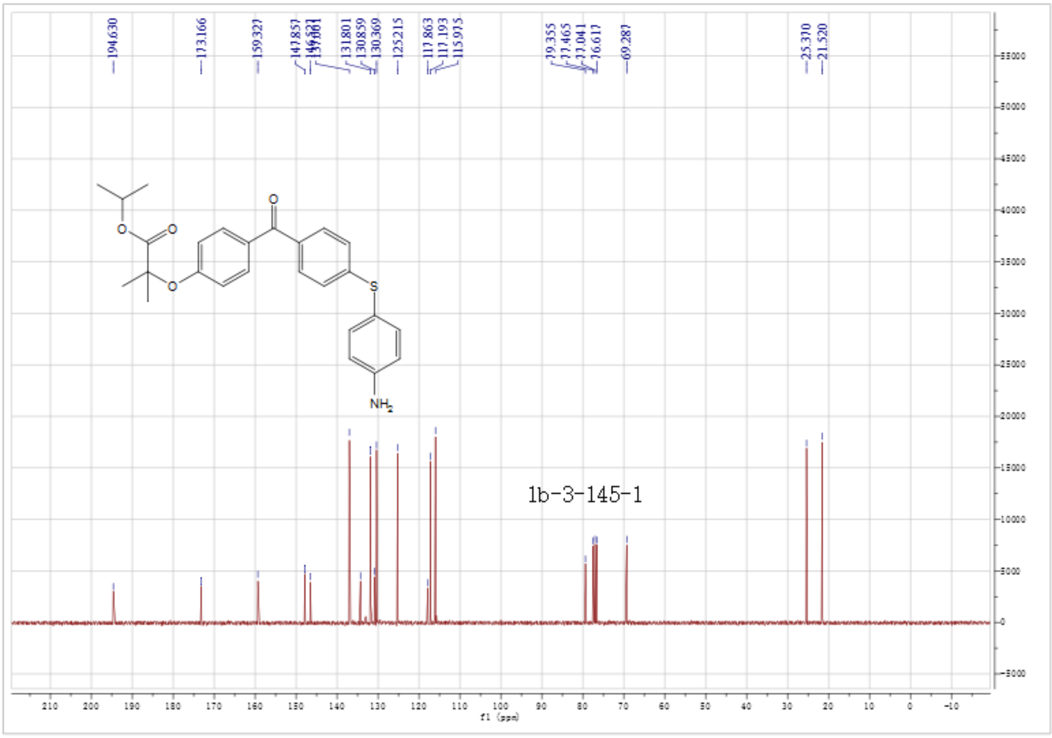


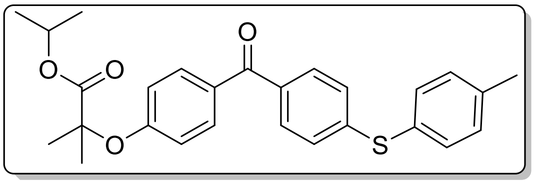


Isopropyl 2-(4-(4-((4-aminophenyl)thio)benzoyl)phenoxy)-2-methylpropanoate (10), ^{1}H NMR (300 MHz, CDCl$_3$)

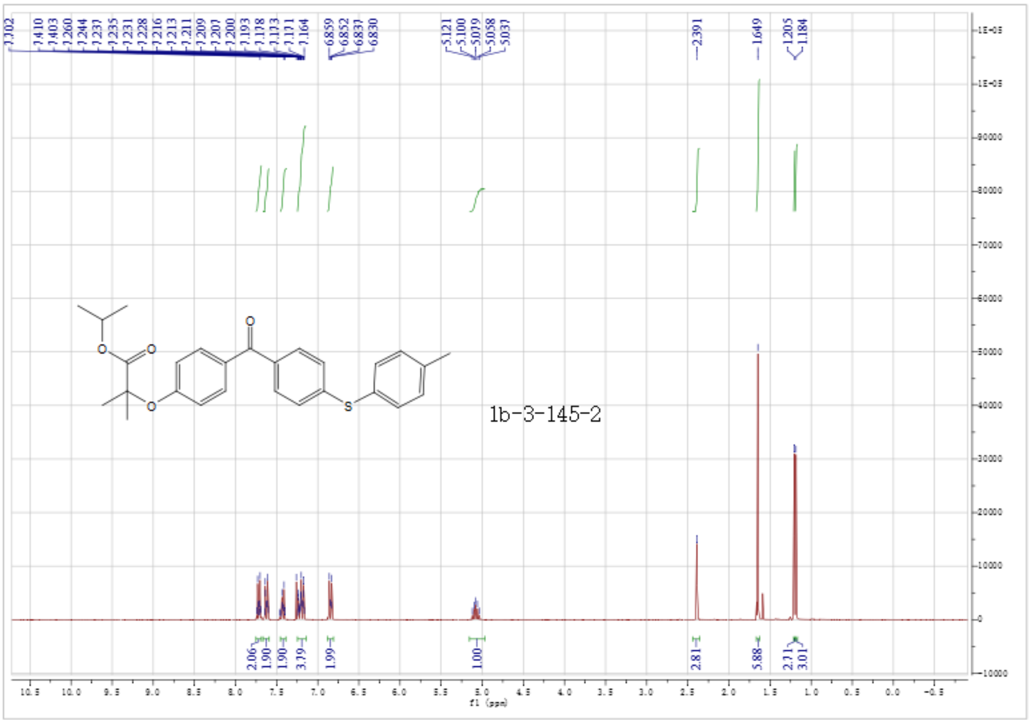


^{13}C NMR (75 MHz, CDCl$_3$)

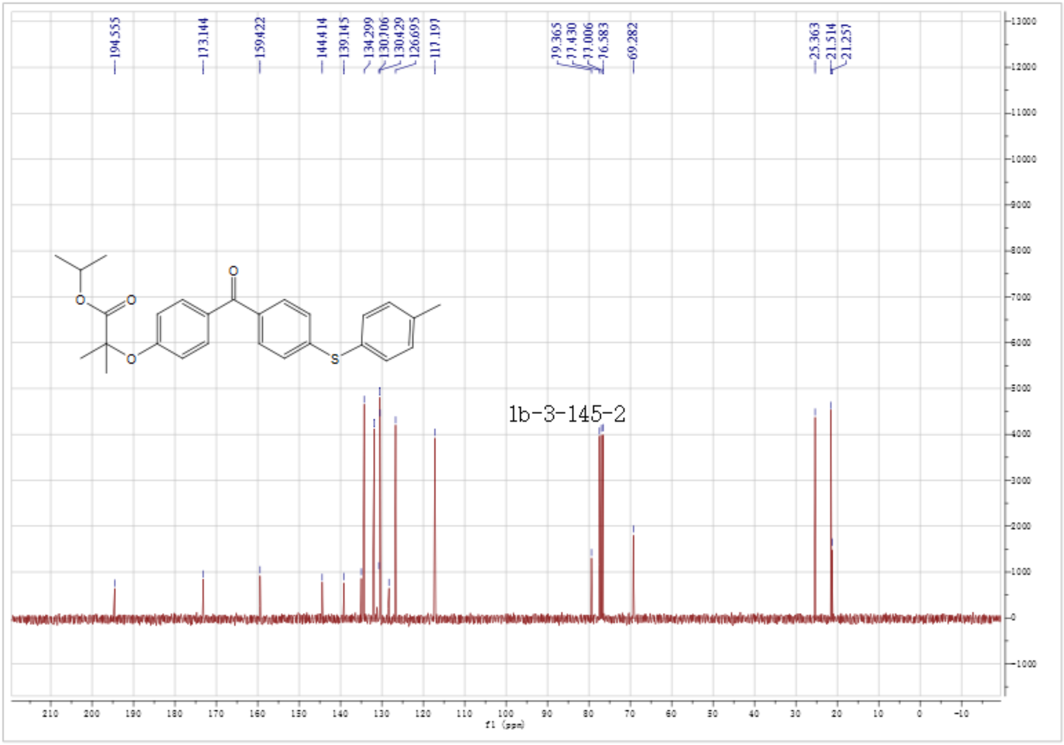


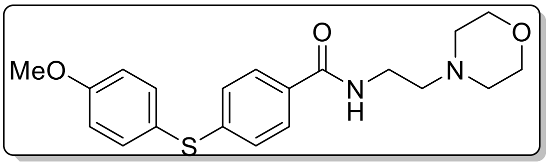


Isopropyl 2-methyl-2-(4-(4-(p-tolylthio)benzoyl)phenoxy)propanoate (11), ^{1}H NMR (300 MHz, CDCl$_3$)

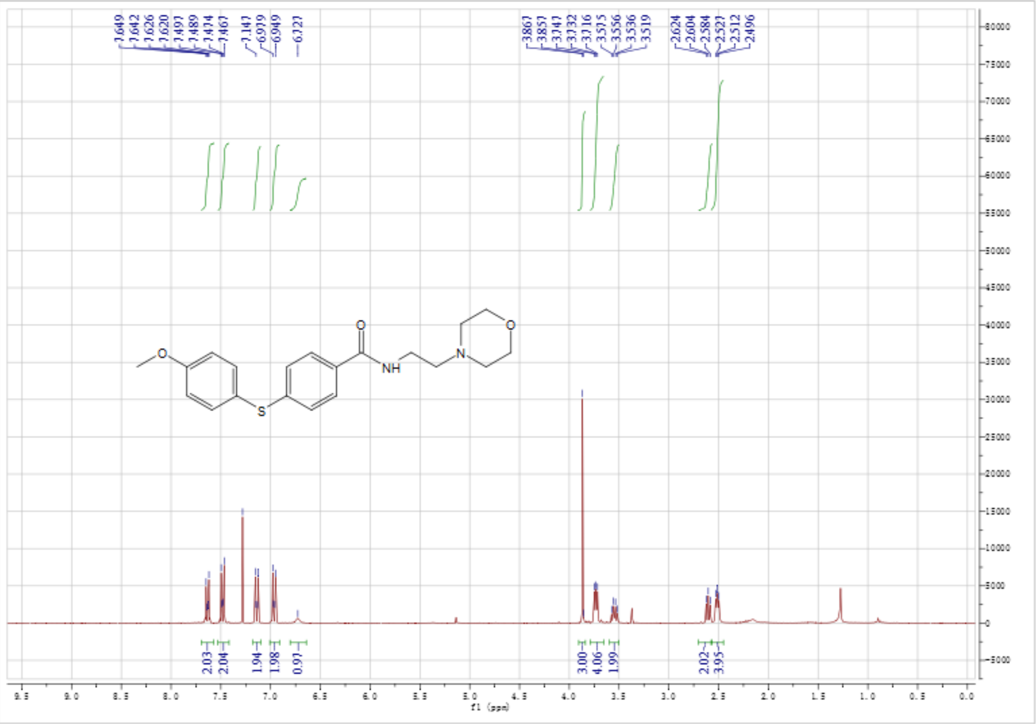


^{13}C NMR (75 MHz, CDCl$_3$)

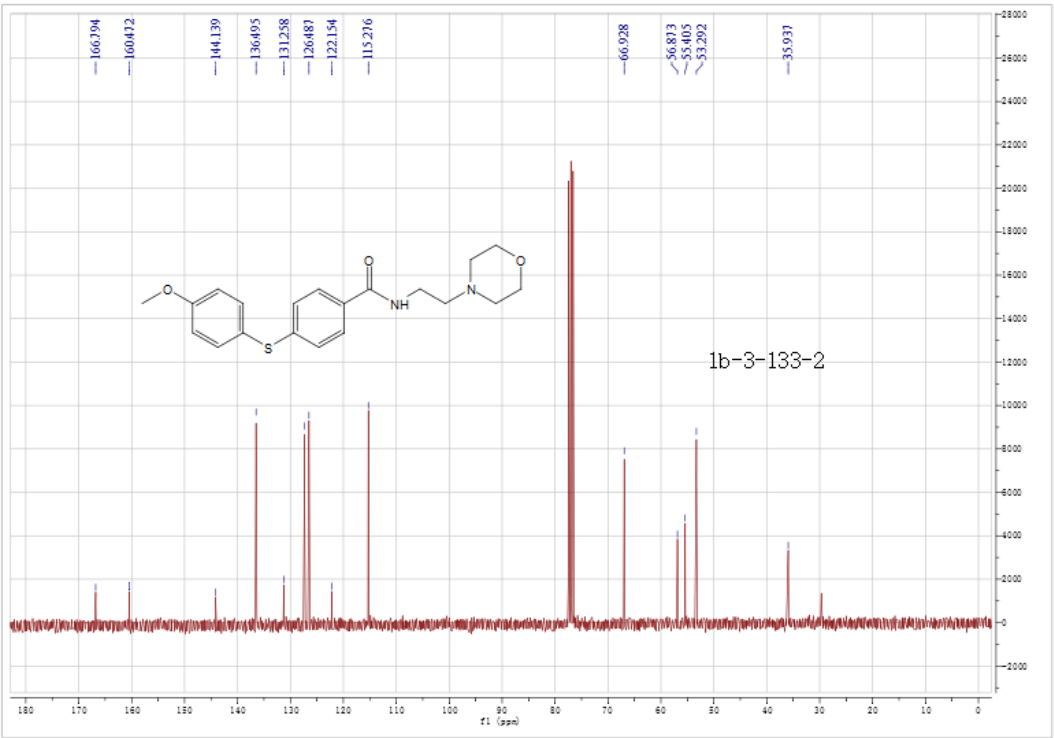


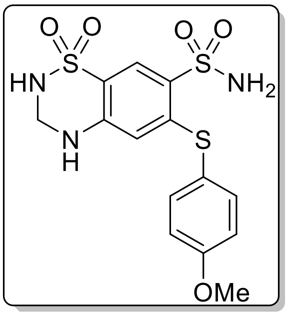


4-((4-Methoxyphenyl)thio)-N-(2-morpholinoethyl)benzamide (12), ^{1}H NMR (300 MHz, CDCl$_3$)

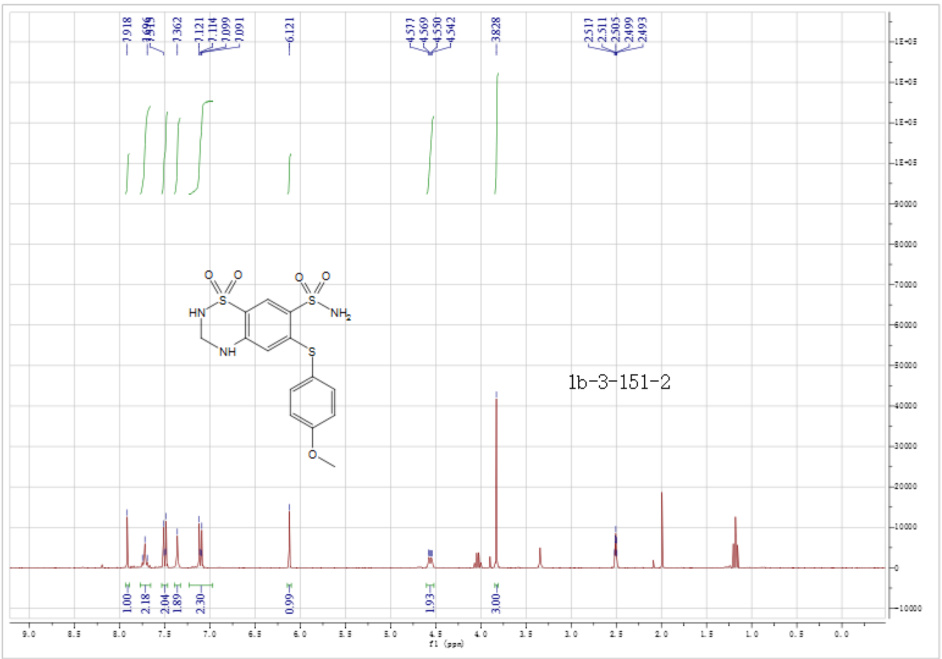


^{13}C NMR (75 MHz, CDCl$_3$)





6-((4-Methoxyphenyl)thio)-3,4-dihydro-2H-benzo[e][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (13) ^{1}H NMR (300 MHz, *d*$_6$-DMSO)



^{13}C NMR (75 MHz, *d*$_6$-DMSO)