SUPPORTING INFORMATION

Biomolecule-Compatible Dehydrogenative Chan-Lam Coupling of Free Sulfilimines

Tingting Meng,[†,‡] Lucille A. Wells,[&] Tianxin Wang,[‡] Jinyu Wang,[‡] Shishuo Zhang,[‡] Jie Wang,[‡] Marisa C. Kozlowski,[*,&] and Tiezheng Jia[*,‡,§]

[†]School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China

[‡]Shenzhen Grubbs Institute, Department of Chemistry and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, 1088 Xueyuan Blvd., Shenzhen, Guangdong, 518055, P. R. China

[&]Department of Chemistry, Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, University of Pennsylvania, 231 South 34th Street, Philadelphia, 19104, Pennsylvania, USA

[§]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, 94 Weijin Rd., Tianjin, 300071, P. R. China

*Correspondence: jiatz@sustech.edu.cn; marisa@sas.upenn.edu

Table of Contents

1 General Information

All reactions were carried out under dry argon. Anhydrous ethanol (EtOH), methanol (MeOH), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloroethane (DCE), acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF), cyclopentyl methyl ether (CPME), 1,2-dimethoxyethane (DME), *N*-methyl pyrrolidone (NMP), toluene, dichloromethane (DCM), 1,4-dioxane, methyl *tert*-butyl ether (MTBE), and isopropanol (*i*PrOH) were purchased from J&K Chemicals and used without further purification. Unless otherwise stated, reagents are commercially available and used as purchased without further purification. Chemicals were purchased from J&K Chemicals, Adamas-beta, Macklin Reagent, Energy Chemicals, Aladdin, JiuDing Chemicals, Bide Pharmatech Ltd., and Sangon-Peptide Biotech (Ningbo) Co., Ltd. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by the treatment with iodine. Flash chromatography was performed with silica gel (200–300 mesh). NMR spectra were obtained using a Bruker DPX 400 spectrometer at 400 M Hz for ^{1}H NMR. Infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum Vertex 80 spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Bruker Apex IV RTMS using electrospray ionization (ESI) in positive mode. Melting points were determined on a SGWX-4 melting point apparatus and are uncorrected. Gas chromatography (GC) used a Fuli GC 9790 plus. Mass spectrum of H_2 was obtained using a Hiden Analytical HPR-20 QIC mass spectrometer.

LC–MS method for analysis of peptide modification

Analytical LC-MS were performed on a Shimadzu LC-MS Prominence LC-20AT instrument equipped with Agilent Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 μm) using 0.1%

trifluoroacetic acid (TFA) in water (solvent A) and 0.1% trifluoroacetic acid (TFA) in acetonitrile (solvent B) as mobile phase at a flow rate of 0.5 mL·min^{-1}.

LC–MS method for analysis of protein modification

LC–MS was performed on using a Shimadzu LCMS-2020 instrument coupled to a Prominence UFLC system using an BioResolve RP mAb polyphenyl column (450Å, 2.7 μm, 2.1 mm × 50 mm). Solvents A (95% water, 5% acetonitrile and 0.1% formic acid) and solvents B (acetonitrile with 0.1% formic acid) were used as the mobile phase at a flow rate of 0.5 mL min^{-1}. The reaction was analyzed by reverse phase HPLC using a gradient of 10% to 60% buffer B over 5 minutes. Compounds were detected by UV detector at 280 nm.

Gel and blot analysis

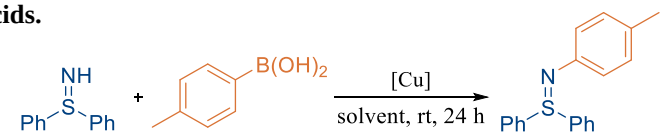
Gel and blot imaging was conducted on Tanon-6100s imager (Tanon). Sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) was carried out on a Mini-Protean apparatus (Tanon，VE-680), using a 12.5% precast linear gradient polyacrylamide gel (Epizyme Biotech). The sample and electrode buffers were prepared according to Laemmli.[1] Commercially available markers (Bio-Rad) were applied to at least one lane of each gel for assignment of apparent molecular masses. Gels were run for 50 minutes at 150 V to separate the bands. PVDF membranes (0.22 μm) were chosen as electrophoretic transfer membranes and towbin buffer (25 mM Tris; 192 mM glycine; 20% methanol; pH 8.3) was used as transfer buffer. The electrophoretic transfer process was conducted for 30 minutes at 300 mA. Upon the completion of the electrophoretic transfer, the blot membrane was subjected to a blocking process with 3% w/w aq BSA in TBST buffer (150 mM NaCl, 50 mM Tris, 0.1% Tween, pH 7.4) at room temperature for 60 minutes and washed with TBST buffer three times. And then, streptavidin–HRP antibody (20 μL, Solarbio #SE068) was added to the membrane in 4 mL of

secondary antibody dilution buffer, and the membrane in the buffer was shaken at room temperature for 120 minutes. After discarding the liquid, the membrane was washed with TBS buffer (150 mM NaCl, 50 mM Tris, pH 7.4) five times. Gel imaging was performed on Tanon-6100 chemiluminescent imaging system. Image J was used to determine the level of modification by optical densitometry.

2 Preparation of *NH*-Diaryl Sulfilimines: *NH*-Diary sulfilimines were prepared according to the literature procedures.[2, 3]

3 Optimization of the Copper-Catalyzed Chan-Lam Coupling of *NH*-Diaryl Sulfilimines

Table S1. Optimization of the Copper-Catalyzed C-N Cross-Coupling of *NH*-Diaryl Sulfilimines with Arylboronic Acids.



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

entry	[Cu] /mol %	**1a** /equiv	**2a** /equiv	solvent	conc. /M	assay yield[a]/%
1	$Cu(O_2CCF_3)_2{\cdot}H_2O$/10	1	2.3	EtOH	0.3	46
2	CuF_2/10	1	2.3	EtOH	0.3	42
3	$Cu(OTf)_2$/10	1	2.3	EtOH	0.3	15
4	$Cu(CH_3CN)_4BF_4$/10	1	2.3	EtOH	0.3	15
5	CuBr/10	1	2.3	EtOH	0.3	71
6	CuI/10	1	2.3	EtOH	0.3	61
7	Cu_2S/10	1	2.3	EtOH	0.3	49
8	$Cu(CH_3CN)_4PF_6$/10	1	2.3	EtOH	0.3	11
9	CuBr/10	1	2.3	THF	0.3	65
10	CuBr/10	1	2.3	DCE	0.3	0
11	CuBr/10	1	2.3	MeCN	0.3	80
12	CuBr/10	1	2.3	DMF	0.3	46
13	CuBr/10	1	2.3	CPME	0.3	0
14	CuBr/10	1	2.3	DME	0.3	65
15	CuBr/10	1	2.3	DMSO	0.3	43
16	CuBr/10	1	2.3	NMP	0.3	20
17	CuBr/10	1	2.3	toluene	0.3	0
18	CuBr/10	1	2.3	DCM	0.3	0
19	CuBr/10	1	2.3	dioxane	0.3	50
20	CuBr/10	1	2.3	MTBE	0.3	57
21	CuBr/10	1	2.3	*i*PrOH	0.5	79

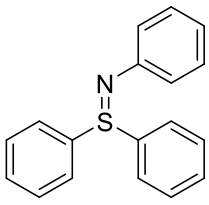
22	CuBr/10	1	2.3	*i*PrOH	1.0	70
23	CuBr/10	1	2.3	*i*PrOH	1.5	62
24	CuBr/10	1	2.3	*i*PrOH	2.0	30

[a]Assay yields determined by ^{1}H NMR spectroscopy of unpurified reaction mixtures using 0.1 mmol (7.0 μL) of CH_2Br_2 as internal standard.

4 Procedure and Characterization of Copper-Catalyzed Chan-Lam Coupling of *NH*-Diaryl Sulfilimines with Arylboronic Acids

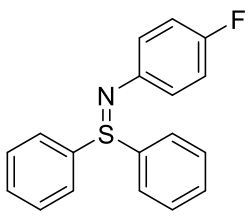
General Procedure for Catalysis: To an oven-dried microwave vial equipped with a stir bar was added free sulfilimine **1** (0.3 mmol, 1.0 equiv), boronic acid **2** (0.45 mmol, 1.5 equiv), CuBr (2.2 mg, 0.015 mmol, 5 mol %) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Upon completion of the reaction, the vial was opened to air, and the reaction mixture was passed through a short pad of silica gel. The pad was then rinsed with 20:1 dichloromethane:methanol (20.0 mL). The solvent was removed under reduced pressure. The residue was purified by flash chromatography to afford the purified product.

*** For all peptide substrates Tyr^s denotes 4-diphenylsulfiliminyl Tyrosine**

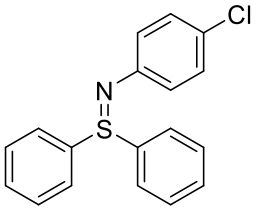


***N*,1,1-Triphenyl-γ^4-sulfanimine (3ab):** The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2b** (54.9 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ab** (81.9 mg, 99% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 4H), 7.52 – 7.40 (m, 6H), 7.24 – 7.14 (m, 2H), 7.05 (d, *J* = 7.9 Hz,

2H), 6.77 (t, J = 7.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 139.9, 131.2, 129.6, 129.0, 127.0, 119.3, 117.6 ppm. Other spectroscopic data were previously reported.[4]

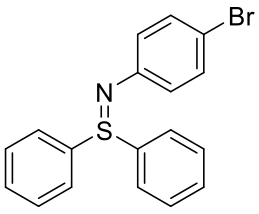


***N*-(4-Fluorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ac):** The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2c** (63.0 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ac** (78.0 mg, 87% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1); m.p. = 137-139 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.88 (m, 3H), 7.63 – 7.50 (m, 1H), 7.44 (d, J = 4.3 Hz, 4H), 7.17 – 6.97 (m, 4H), 6.87 – 6.74 (m, 1H), 6.70 (t, J = 8.5 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (d, $J_{C\text{-}F}$ = 235.3 Hz), 150.7, 139.8, 131.4, 129.7, 127.0, 119.9 (d, $J_{C\text{-}F}$ = 7.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.8 ppm; IR (thin film): 1590, 1505, 1347, 1209, 1152, 1092, 894, 831, 736, 676 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{15}FNS$ 296.0904, found 296.0903 $[M+H]^+$.

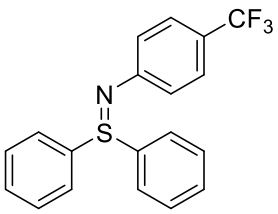


***N*-(4-Chlorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ad):** The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2d** (63.0 mg, 0.60 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ad** (66.0 mg, 72% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1); m.p. = 158-162 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 4H), 7.52 – 7.45 (m, 6H), 7.07 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 139.5, 131.5, 129.8,

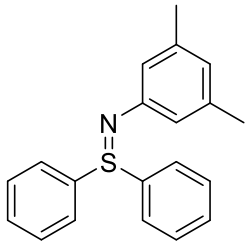
128.8, 127.0, 122.3, 120.3 ppm; IR (thin film): 1589, 1491, 1422, 1336, 1273, 1083, 991, 897, 764, 675 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{15}ClNS$ 312.0608, found 312.0606 $[M+H]^+$.



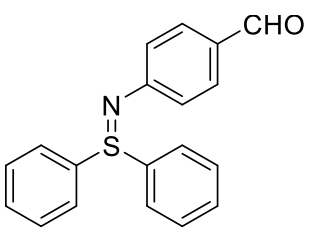
***N*-(4-Bromophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ae):** The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2e** (90.5 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ae** (120.0 mg, 95% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1); m.p. = 103-105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 4H), 7.54 – 7.41 (m, 6H), 7.25 – 7.14 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 139.3, 131.7, 131.6, 129.8, 127.1, 120.8, 109.6 ppm; IR (thin film): 1574, 1473, 1442, 1233, 1168, 1055, 910, 745, 687 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{15}BrNS$ 356.0103, found 356.0102 $[M+H]^+$.



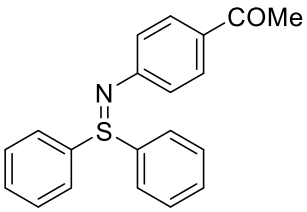
1,1-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3af): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2f** (85.5 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3af** (80.0 mg, 78% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 4H), 7.53 – 7.44 (m, 6H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 138.7, 131.7, 129.9, 127.1, 126.2 (q, J_{C-F} = 3.6 Hz), 125.3 (q, J_{C-F} = 270.3 Hz), 118.8 (q, J_{C-F} = 32.3 Hz), 118.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.8 ppm. Other spectroscopic data were previously reported.



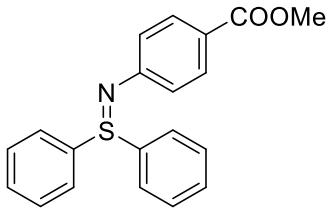
***N*-(3,5-Dimethylphenyl)-1,1-diphenyl-γ^4-sulfanimine (3ag):** The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2g** (67.5 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ag** (80.0 mg, 88% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 74-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.60 (m, 4H), 7.57 – 7.38 (m, 6H), 6.76 – 6.59 (m, 2H), 6.56 – 6.30 (m, 1H), 2.26 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 140.3, 138.6, 131.3, 129.7, 127.1, 119.9, 117.2, 21.6 ppm; IR (thin film): 2920, 2870, 1604, 1500, 1445, 1339, 1211, 1109, 725, 685 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{20}NS$ 306.1311, found 306.1308 $[M+H]^+$.



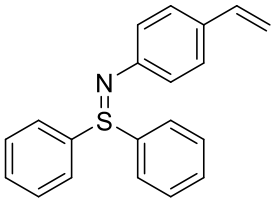
4-((Diphenyl-γ^4-sulfanylidene)amino)benzaldehyde (3ah): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2h** (67.6 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ah** (51.0 mg, 54% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 3:1); m.p. = 70-72 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.84 – 7.69 (m, 4H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.44 (m, 6H), 7.00 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 162.0, 137.9, 132.0, 131.9, 130.0, 127.2, 126.6, 118.6 ppm; IR (thin film): 2820, 2725, 1694, 1590, 1500, 1433, 1205, 903, 738 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{20}NOS$ 306.0947, found 306.0944 $[M+H]^+$.



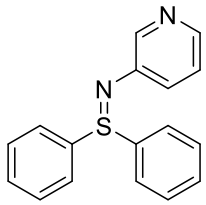
1-(4-((Diphenyl-γ^4-sulfanylidene)amino)phenyl)ethan-1-one (3ai): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2i** (74.0 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ai** (80.0 mg, 84% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 120-122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.76 – 7.68 (m, 4H), 7.58 – 7.41 (m, 6H), 6.95 (d, *J* = 8.8 Hz, 2H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 160.5, 138.2, 131.9, 130.4, 129.9, 127.1, 126.7, 118.1, 26.1 ppm; IR (thin film): 1658, 1573, 1493, 1350, 1250, 888, 782, 738, 678 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{18}NOS$ 320.1104, found 320.1103 $[M+H]^+$.



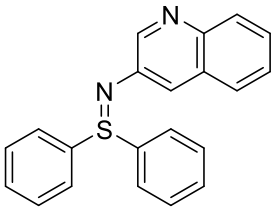
Methyl 4-((diphenyl-γ^4-sulfanylidene)amino)benzoate (3aj): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2j** (81.0 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3aj** (80.0 mg, 80% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 108-110 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.78 – 7.63 (m, 4H), 7.56 – 7.40 (m, 6H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 160.0, 138.4, 131.8, 131.1, 129.9, 127.1, 118.4, 118.2, 51.5 ppm; IR (thin film): 2920, 2850, 1714, 1595, 1495, 1241, 903, 732, 681 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{18}NO_2S$ 336.1053, found 336.1051 $[M+H]^+$.



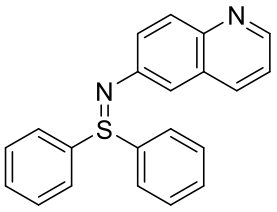
1,1-Diphenyl-*N*-(4-vinylphenyl)-γ^4-sulfanimine (3ak): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2k** (89.0 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3ak** (88.0 mg, 97% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 3:1); m.p. = 69-71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.60 (m, 4H), 7.59 – 7.36 (m, 6H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.61 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.50 (d, *J* = 17.5 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 139.5, 136.9, 131.4, 129.7, 129.2, 127.4, 127.1, 119.1, 109.2 ppm; IR (thin film): 1650, 1581, 1492, 1236, 1065, 997, 890, 743, 684 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{18}NS$ 304.1154, found 304.1150 $[M+H]^+$.



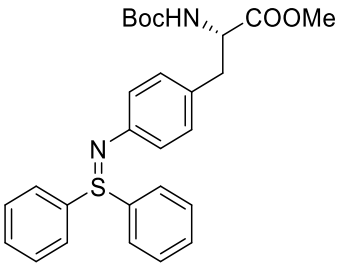
1,1-Diphenyl-*N*-(pyridin-3-yl)-γ^4-sulfanimine (3al): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2l** (74.0 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3al** (53.0 mg, 65% yield) as a light yellow solid. R_f = 0.2 (hexanes:EtOAc = 3:1); m.p. = 64-66 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.8 Hz, 1H), 7.94 (dd, *J* = 4.6, 1.0 Hz, 1H), 7.80 – 7.62 (m, 4H), 7.57 – 7.41 (m, 6H), 7.24 – 7.16 (m, 1H), 7.10 – 6.96 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 141.8, 139.2, 138.8, 131.7, 129.9, 127.0, 125.3, 123.5 ppm; IR (thin film): 3052, 1572, 1550, 1470, 1445, 1273, 912, 743, 686 cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{15}N_2S$ 279.0950, found 279.0950 $[M+H]^+$.



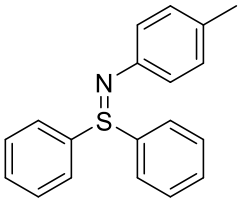
1,1-Diphenyl-*N*-(quinolin-3-yl)-γ^4-sulfanimine (3am): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2m** (103.0 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3am** (31.0 mg, 33% yield) as a light yellow solid. R_f = 0.1 (hexanes:EtOAc = 3:1); m.p. = 108-111 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 2.8 Hz, 1H), 8.05 – 7.90 (m, 1H), 7.84 – 7.69 (m, 4H), 7.61 – 7.48 (m, 7H), 7.42 – 7.30 (m, 2H), 7.18 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.7, 142.1, 138.6, 131.8, 129.9, 129.6, 128.9, 127.1, 126.4, 125.5, 124.6, 115.4 ppm; IR (thin film): 1570, 1342, 1274, 1208, 1183, 920, 863, 780, 690, 612 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{17}N_2S$ 329.1107, found 329.1104 $[M+H]^+$.



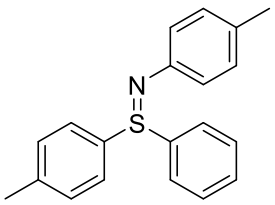
1,1-Diphenyl-*N*-(quinolin-6-yl)-γ^4-sulfanimine (3an): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2n** (103.0 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3an** (54.0 mg, 55% yield) as a light yellow solid. R_f = 0.2 (hexanes:EtOAc = 3:1); m.p. = 116-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.8 Hz, 1H), 7.98 – 7.90 (m, 1H), 7.83 – 7.72 (m, 4H), 7.60 – 7.47 (m, 7H), 7.41 – 7.31 (m, 2H), 7.16 (d, *J* = 2.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 146.0, 143.7, 139.0, 133.5, 131.7, 130.1, 129.9, 129.8, 127.9, 127.1, 121.0, 109.3 ppm; IR (thin film): 1600, 1580, 1482, 1372, 1224, 928, 831,740, 679 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{17}N_2S$ 329.1107, found 329.1106 $[M+H]^+$.



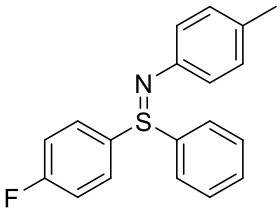
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((diphenyl-γ^4-sulfanylidene)amino)phenyl)propanoate (3ao): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **2o** (48.5 mg, 0.15 mmol), CuBr (0.8 mg, 5 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 1:1) to give the product **3ao** (40.0 mg, 87% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 1:1); m.p. = 131-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 4H), 7.59 – 7.39 (m, 6H), 7.00 – 6.82 (m, 4H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.50 (s, 1H), 3.70 (s, 3H), 2.97 (d, *J* = 5.3 Hz, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 155.3, 153.7, 139.7, 131.3, 129.9, 129.7, 127.1, 124.6, 119.3, 79.7, 54.6, 52.1, 37.4, 28.3 ppm; IR (thin film): 2980, 2927, 1749, 1686, 1607, 1500, 1441, 1250, 1161, 1060, 914, 736, 690 cm^{-1}; HRMS (ESI) calculated for $C_{27}H_{31}N_2O_4S$ 479.1999, found 479.1996 $[M+H]^+$.



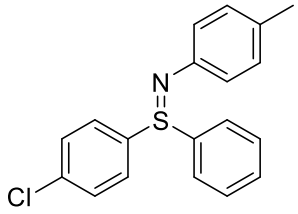
1,1-Diphenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3aa): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3aa** (87.0 mg, 99% yield) as a light yellow solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 101-103 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 4H), 7.51 – 7.41 (m, 6H), 7.07 – 6.82 (m, 4H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.4, 131.2, 129.7, 129.6, 129.3, 127.2, 127.1, 119.3, 20.6 ppm; IR (thin film): 2920, 2870, 1604, 1496, 1444, 1229, 913, 731, 685 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{17}NS$ 292.1154, found 292.1152 $[M+H]^+$.



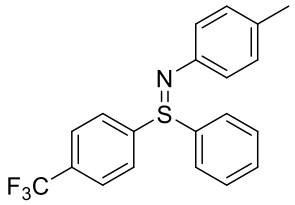
1-Phenyl-*N*,1-di-*p*-tolyl-γ^4-sulfanimine (3ba): The reaction was performed following the General Procedure with **1b** (65.0 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3ba** (80.0 mg, 88% yield) as a brown oil. R_f = 0.3 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.30 – 7.21 (m, 2H), 7.01 – 6.92 (m, 2H), 6.91 – 6.84 (m, 2H), 2.37 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 132.4, 131.4, 130.5, 130.2, 129.7, 129.6, 129.2, 128.2, 127.7, 127.3, 119.9, 21.5, 20.6 ppm; IR (thin film): 2920, 2870, 1609, 1510, 1257, 1177, 1020, 808, 734 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{20}NS$ 306.1311, found 306.1310 $[M+H]^+$.



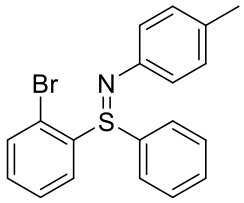
1-(4-Fluorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ca): The reaction was performed following the General Procedure with **1c** (66.0 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3ca** (74.2 mg, 79% yield) as a brown oil. R_f = 0.3 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.76 – 7.68 (m, 4H), 7.54 – 7.45 (m, 3H), 7.02 – 6.93 (m, 2H), 6.92 – 6.83 (m, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.8, 139.6, 133.0 (d, J_{C-F} = 32.6 Hz), 131.7, 129.9, 129.7, 127.6, 127.2, 127.1, 126.5 (d, J_{C-F} = 3.7 Hz), 119.4, 20.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3 ppm; IR (thin film): 2926, 2870, 1605, 1503, 1324, 1138, 929, 827, 683 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{17}FNS$ 310.1060, found 310.1057 $[M+H]^+$.



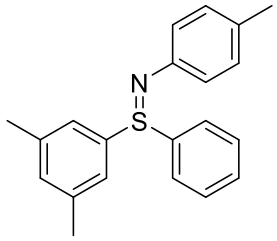
1-(4-Chlorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3da): The reaction was performed following the General Procedure with **1d** (70.7 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3da** (76.1 mg, 78% yield) as a brown oil. R_f = 0.4 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.67 – 7.61 (m, 2H), 7.53 – 7.38 (m, 5H), 7.00 – 6.93 (m, 2H), 6.91 – 6.84 (m, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 132.0, 131.5, 131.4, 129.9, 129.8, 129.6, 129.4, 129.3, 128.3, 127.1, 119.3, 20.5 ppm; IR (thin film): 2920, 2861, 1666, 1515, 1236, 1070, 742, 678 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{17}ClNS$ 326.0765, found 326.0765 $[M+H]^+$.



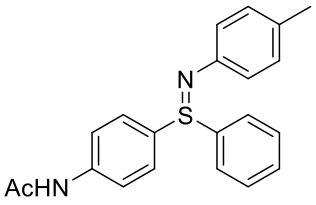
1-Phenyl-*N*-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3ea): The reaction was performed following the General Procedure with **1e** (81.0 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ea** (90.1 mg, 84% yield) as a brown oil. R_f = 0.4 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 4H), 7.53 – 7.43 (m, 3H), 7.16 (t, J = 8.6 Hz, 2H), 7.04 – 6.94 (m, 2H), 6.93 – 6.85 (m, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (q, J_{C-F} = 252.6 Hz), 151.9, 140.2, 135.8 (q, J_{C-F} = 2.9 Hz), 131.4, 129.7, 129.6, 129.4, 129.3, 127.2, 126.9, 119.3, 116.9 (q, J_{C-F} = 22.6 Hz), 20.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 ppm; IR (thin film): 2960, 2870, 1590, 1503, 1229, 926, 824, 738, 688 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{17}F_3NS$ 360.1028, found 360.1029 $[M+H]^+$.



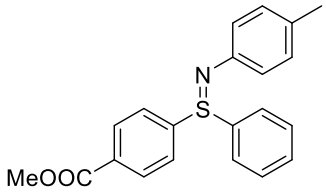
1-(2-Bromophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3fa): The reaction was performed following the General Procedure with **1f** (84.1 mg, 0.3 mmol), **2a** (81.6 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3fa** (83.3 mg, 75% yield) as a brown oil. R_f = 0.4 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.64 – 7.56 (m, 1H), 7.53 – 7.41 (m, 4H), 7.39 – 7.30 (m, 1H), 6.99 – 6.90 (m, 2H), 6.88 – 6.79 (m, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 140.1, 138.5, 133.6, 132.7, 131.5, 129.8, 129.7, 128.9, 128.6, 128.2, 127.5, 122.2, 119.5, 20.6 ppm; IR (thin film): 2925, 1570, 1500, 1444, 1318, 1120, 970, 824, 745 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{17}BrNS$ 370.0260, found 370.0260 $[M+H]^+$.



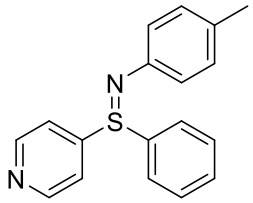
1-(3,5-Dimethylphenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ga): The reaction was performed following the General Procedure with **1g** (68.8 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ga** (80.2 mg, 84% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1); m.p. = 86-88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.49 – 7.39 (m, 3H), 7.30 (s, 2H), 7.07 (s, 1H), 7.03 – 6.92 (m, 2H), 6.92 – 6.85 (m, 2H), 2.31 (s, 6H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 133.2, 131.0, 130.5, 129.6, 129.5, 129.2, 129.1, 127.0, 126.9, 124.7, 119.2, 21.4, 20.5 ppm; IR (thin film): 3060, 2960, 1587, 1483, 1245, 993, 929, 744, 690 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{22}NS$ 320.1467, found 320.1468 $[M+H]^+$.



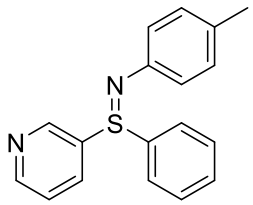
***N*-(4-(*S*-Phenyl-*N*-(*p*-tolyl)sulfinimidoyl)phenyl)acetamide (3ha):** The reaction was performed following the General Procedure with **1h** (77.6 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 2:1) to give the product **3ha** (83.2 mg, 80% yield) as a brown oil. R_f = 0.1 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.67 – 7.55 (m, 2H), 7.51 – 7.43 (m, 3H), 7.43 – 7.30 (m, 4H), 7.05 – 6.93 (m, 2H), 6.93 – 6.83 (m, 2H), 2.25 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 151.8, 141.7, 138.7, 132.5, 131.3, 130.0, 129.7, 129.1, 127.6, 126.7, 121.3, 118.7, 24.4, 20.6 ppm; IR (thin film): 2925, 1583, 1496, 1310, 1226, 898, 825, 688 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{21}N_2OS$ 349.1369, found 349.1368 $[M+H]^+$.



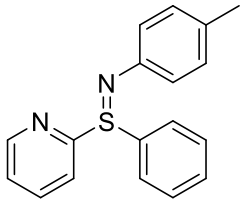
Methyl-4-(*S*-phenyl-*N*-(*p*-tolyl)sulfinimidoyl)benzoat (3ia): The reaction was performed following the General Procedure with **1i** (78.0 mg, 0.3 mmol), **2a** (81.6 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **3ia** (65.1 mg, 64% yield) as a light yellow solid. R_f = 0.4 (hexanes:EtOAc = 5:1); m.p. = 83-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.07 (m, 2H), 7.84 – 7.76 (m, 2H), 7.75 – 7.68 (m, 2H), 7.51 – 7.45 (m, 3H), 7.03 – 6.91 (m, 2H), 6.93 – 6.86 (m, 2H), 3.92 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 151.7, 145.4, 139.8, 132.6, 131.7, 130.7, 129.9, 129.7, 127.5, 127.3, 126.8, 119.5, 52.6, 20.6 ppm; IR (thin film): 2925, 1720, 1592, 1502, 1440, 1275, 1106, 920, 744, 690 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{20}NO_2S$ 350.1209, found 350.1208 $[M+H]^+$.



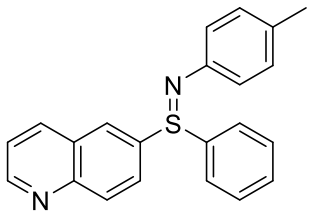
1-Phenyl-1-(pyridin-4-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ja): The reaction was performed following the General Procedure with **1j** (60.6 mg, 0.3 mmol), **2a** (81.6 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 2:1) to give the product **3ja** (55.2 mg, 64% yield) as a brown oil. R_f = 0.2 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.63 (m, 2H), 7.81 – 7.71 (m, 2H), 7.64 – 7.56 (m, 2H), 7.57 – 7.45 (m, 3H), 7.06 – 6.92 (m, 2H), 6.94 – 6.82 (m, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 151.0, 150.8, 139.1, 132.2, 130.1, 129.8, 128.0, 127.5, 120.6, 119.7, 20.6 ppm; IR (thin film): 2920, 2870, 1605, 1567, 1498, 1233, 926, 804, 749, 688 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{17}N_2S$ 293.1107, found 293.1104 $[M+H]^+$.



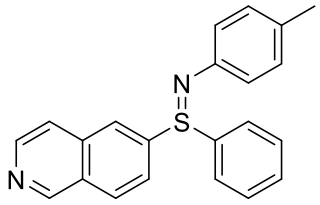
1-Phenyl-1-(pyridin-3-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ka): The reaction was performed following the General Procedure with **1k** (60.6 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 2:1) to give the product **3ka** (65.2 mg, 75% yield) as a brown oil. R_f = 0.2 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.0 Hz, 1H), 8.68 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.16 – 8.04 (m, 1H), 7.80 – 7.69 (m, 2H), 7.55 – 7.47 (m, 3H), 7.46 – 7.38 (m, 1H), 7.05 – 6.93 (m, 2H), 6.95 – 6.84 (m, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 151.4, 148.3, 139.4, 137.6, 134.6, 131.8, 130.0, 129.7, 127.7, 126.9, 124.6, 119.5, 20.6 ppm; IR (thin film): 2920, 2870, 1605, 1498, 1410, 1228, 1017, 920, 799, 688 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{17}N_2S$ 293.1107, found 293.1106 $[M+H]^+$.



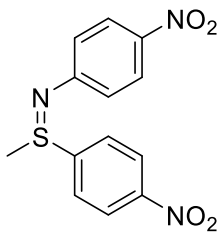
1-Phenyl-1-(pyridin-2-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3la): The reaction was performed following the General Procedure with **1l** (60.6 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3la** (61.3 mg, 69% yield) as a brown oil. R_f = 0.2 (hexanes:EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.9 Hz, 1H), 8.25 – 8.19 (m, 1H), 7.95 – 7.88 (m, 2H), 7.88 – 7.82 (m, 1H), 7.54 – 7.42 (m, 3H), 7.37 – 7.28 (m, 1H), 7.02 – 6.96 (m, 2H), 6.96 – 6.91 (m, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 151.7, 150.1, 139.2, 138.4, 131.3, 129.7, 129.5, 127.3, 127.2, 124.9, 120.9, 119.6, 20.6 ppm; IR (thin film): 3030, 2920, 2870, 1605, 1498, 1445, 1232, 927, 818, 688 cm^{-1}; HRMS (ESI) calculated for HRMS (ESI) calculated for $C_{18}H_{17}N_2S$ 293.1107, found 293.1105 $[M+H]^+$.



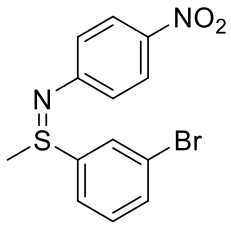
1-Phenyl-1-(quinolin-6-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ma): The reaction was performed following the General Procedure with **1m** (75.8 mg, 0.3 mmol), **2a** (81.6 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 1:1) to give the product **3ma** (78.3 mg, 77% yield) as a brown oil. R_f = 0.2 (hexanes:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.39 (d, *J* = 1.9 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.18 – 8.11 (m, 1H), 7.84 – 7.71 (m, 3H), 7.54 – 7.44 (m, 4H), 7.07 – 6.96 (m, 2H), 6.96 – 6.90 (m, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.8, 149.1, 139.8, 138.1, 136.8, 132.1, 131.6, 131.4, 129.8, 129.7, 128.1, 127.3, 127.1, 126.4, 122.3, 119.4, 20.5 ppm; IR (thin film): 2920, 2870, 1583, 1498, 1440, 1232, 922, 829, 745, 688 cm^{-1}; HRMS (ESI) calculated for $C_{22}H_{19}N_2S$ 343.1263, found 343.1261 $[M+H]^+$.



1-(Isoquinolin-6-yl)-1-phenyl-*N*-(*p* -tolyl)-γ^4-sulfanimine (3na): The reaction was performed following the General Procedure with **1n** (75.8 mg, 0.3 mmol), **2a** (81.6 mg, 0.6 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 1:1) to give the product **3na** (76.0 mg, 75% yield) as a brown oil. R_f = 0.2 (hexanes:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.62 (d, *J* = 5.8 Hz, 1H), 8.36 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.80 – 7.65 (m, 4H), 7.53 – 7.45 (m, 3H), 7.03 – 6.96 (m, 2H), 6.96 – 6.90 (m, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 151.6, 144.5, 142.7, 139.6, 135.5, 131.7, 129.9, 129.7, 129.5, 129.0, 127.5, 127.4, 125.5, 124.1, 120.9, 119.5, 20.5 ppm; IR (thin film): 2920, 1761, 1605, 1500, 1275, 1232, 922, 829, 688 cm^{-1}; HRMS (ESI) calculated for $C_{22}H_{19}N_2S$ 343.1263, found 343.1260 $[M+H]^+$.

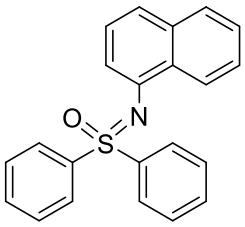


1-Methyl-*N*,1-bis(4-nitrophenyl)-λ^4-sulfanimine (3op): The reaction was performed following the General Procedure with **1o** (55.2 mg, 0.3 mmol), **2p** (76.5 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3op** (67.0 mg, 73% yield) as a brown solid. R_f = 0.2 (hexanes:EtOAc = 3:1); m.p. = 106-119 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.24 (m, 2H), 8.04 – 7.90 (m, 4H), 6.89 – 6.50 (m, 2H), 3.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 150.1, 145.2, 138.6, 126.6, 125.8, 125.2, 117.7, 38.3 ppm; IR (thin film): 1575, 1510, 1330, 1306, 1056, 1021, 740, 682 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{12}N_3O_4S$ 306.0543, found 306.0540 $[M+H]^+$.

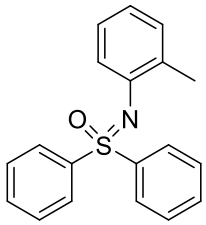


1-(3-Bromophenyl)-1-methyl-*N*-(4-nitrophenyl)-λ^4-sulfanimine (3pp): The reaction was performed following the General Procedure with **1p** (64.0 mg, 0.3 mmol), **2p** (76.5 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:1) to give the product **3pp** (65.0 mg, 64% yield) as a brown solid. R_f = 0.2 (hexanes:EtOAc = 3:1); m.p. = 96-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 2H), 7.84 (t, *J* = 1.8 Hz, 1H), 7.73 – 7.60 (m, 2H), 7.43 (t, *J* = 7.9 Hz, 1H), 6.81 – 6.65 (m, 2H), 2.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 139.9, 138.2, 135.5, 131.7, 128.1, 125.8, 124.3, 124.0, 117.5, 38.3 ppm; IR (thin film): 1653, 1520, 1347, 1244, 1100, 965, 737, 675 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{12}BrN_2O_2S$ 338.9797, found 338.9796 $[M+H]^+$.

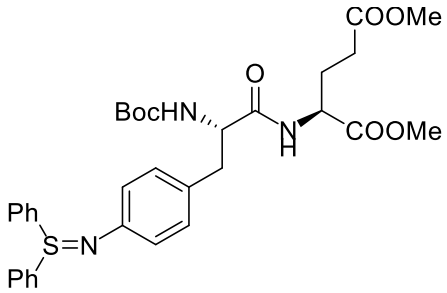
General Procedure for the Sequential Coupling/Oxidation to Prepare *N*-Aryl Sulfoximines: To an oven-dried microwave vial equipped with a stir bar was added free sulfilimine **1** (0.3 mmol), boronic acid **2** (0.45 mmol), CuBr (2.2 mg, 5 mol %) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Then, to the solution was added sodium hypochlorite (178.6 mg, 2.4 mmol) and tetrabutylammonium chloride (44.4 mg, 0.15 mmol) under the argon atmosphere and continued stirring for additional 24 h. Upon completion of the reaction, the vial was opened to air, and the reaction mixture was passed through a short pad of silica gel. The pad was then rinsed with EtOAc. The solvent was removed under reduced pressure. The residue was purified by flash chromatography as outlined below to afford the pure product.



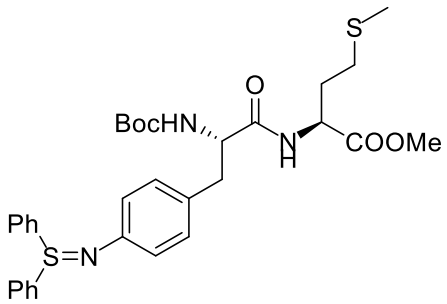
(Naphthalen-1-ylimino)diphenyl-γ^6-sulfanone (4aq): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2q** (77.4 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **4aq** (42.0 mg, 45% yield) as a colorless solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 168-170 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.6 Hz, 1H), 8.65 (d, *J* = 7.3 Hz, 1H), 8.12 (d, *J* = 6.8 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.21 – 7.13 (m, 2H), 7.12 – 7.04 (m, 2H), 6.83 (t, *J* = 7.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.1, 134.8, 134.5, 132.6, 131.7, 129.1, 129.0, 128.1, 126.7, 124.8, 124.5, 123.4, 121.7 ppm; IR (thin film): 3048, 1571, 1503, 1390, 1278, 1222, 1115, 972, 727, 681 cm^{-1}; HRMS (ESI) calculated for $C_{22}H_{18}NOS$ 344.1104, found 344.1099 $[M+H]^+$.



Diphenyl(*o*-tolylimino)-γ^6-sulfanone (4ar): The reaction was performed following the General Procedure with **1a** (60.3 mg, 0.3 mmol), **2r** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) and *i*PrOH (3.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to give the product **4ar** (45.2 mg, 49% yield) as a colorless solid. R_f = 0.3 (hexanes:EtOAc = 5:1); m.p. = 141-144 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.95 (m, 4H), 7.64 – 7.35 (m, 6H), 7.23 – 7.04 (m, 2H), 7.00 – 6.87 (m, 1H), 6.88 – 6.78 (m, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.3, 132.7, 132.5, 130.4, 129.3, 128.5, 126.4, 122.0, 121.7, 19.1 ppm; IR (thin film): 2920, 2870, 1596, 1485, 1446, 1282, 1086, 996, 719, 685 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{18}NOS$ 308.1104, found 308.1099 $[M+H]^+$.

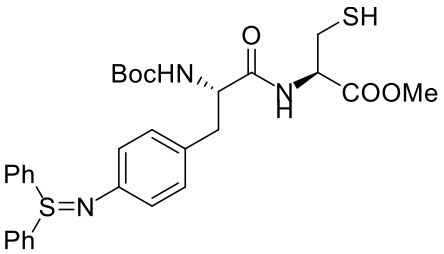


Boc-Tyr^{s}-Glu(OMe)-OMe (6aa): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5a** (69.9 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 1:1) to give the product **6aa** (53.0 mg, 85% yield) as a brown solid. R_f = 0.2 (hexanes:EtOAc = 1:1); m.p. = 79-81 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 4H), 7.53 – 7.45 (m, 6H), 7.01 – 6.90 (m, 4H), 6.61 (d, *J* = 8.3 Hz, 1H), 5.04 (br s, 1H), 4.56 (d, *J* = 3.2 Hz, 1H), 4.24 (q, *J* = 6.8 Hz, 1H), 3.96 – 3.81 (m, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.08 – 2.86 (m, 4H), 1.39 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 171.7, 171.6, 155.4, 131.6, 131.0, 130.0, 129.7, 129.2, 127.3, 127.1, 119.4, 80.3, 55.9, 52.5, 51.8, 51.6, 37.2, 29.8, 28.3, 27.4 ppm; IR (thin film): 1719, 1627, 1610, 1500, 1399, 1162, 1121, 980, 780, 691 cm^{-1}; HRMS (ESI) calculated for $C_{33}H_{40}N_3O_7S$ 622.2582, found 622.2587 $[M+H]^+$.

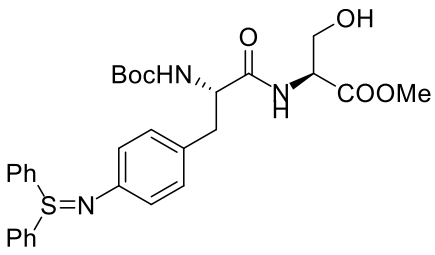


Boc-Tyr^{s}-Met-OMe (6ab): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5b** (68.1 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with dichloromethane:methanol = 20:1) to give the product **6ab** (56.0 mg, 92% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 90-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.64 (m, 4H), 7.53 – 7.40 (m, 6H), 7.08 – 6.80 (m, 4H), 6.57 (d, *J* = 7.7 Hz, 1H), 4.99 (br s, 1H), 4.63 (dd, *J* = 12.6, 7.2 Hz, 1H), 4.28 (d, *J* = 5.7 Hz, 1H), 3.68 (s, 3H), 3.14 – 2.79 (m, 2H), 2.49 – 2.27 (m, 2H), 2.15 – 1.82 (m, 2H), 2.02 (s, 3H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.5, 155.4,

153.7, 139.7, 131.3, 130.0, 129.6, 129.2, 127.0, 119.4, 80.2, 52.5, 51.6, 37.1, 31.7, 29.7, 28.3, 22.7, 15.4 ppm; IR (thin film): 1737, 1668, 1500, 1438, 1364, 1164, 977, 745, 696 cm^{-1}; HRMS (ESI) calculated for $C_{32}H_{40}N_3O_5S_2$ 610.2404, found 610.2405 $[M+H]^+$.

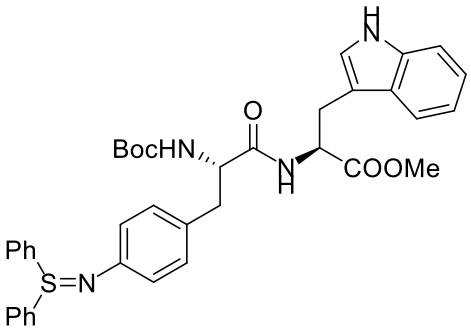


Boc-Tyr^s-Cys-OMe (6ac): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5c** (63.9 mg, 0.15 mmol), CuBr (0.8 mg, 5 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with dichloromethane:methanol = 20:1) to give the product **6ac** (44.0 mg, 75% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 71-74 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 4H), 7.55 – 7.41 (m, 6H), 7.04 – 6.87 (m, 4H), 6.61 (br s, 1H), 5.88 (br s, 1H), 4.99 – 4.66 (m, 1H), 4.34 (br s, 1H), 3.76 (s, 3H), 3.12 – 2.85 (m, 2H), 1.70 – 1.56 (m, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 164.0, 153.3, 131.9, 131.3, 129.8, 129.7, 128.0, 127.0, 119.5, 109.2, 80.3, 52.8, 29.3, 28.2, 24.6, 22.6, 14.1 ppm; IR (thin film): 1741, 1666, 1614, 1516, 1440, 1365, 1248, 1162, 1050, 1022, 952, 808, 746, 686 cm^{-1}; HRMS (ESI) calculated for $C_{30}H_{36}N_3O_5S_2$ 582.2091, found 582.2097 $[M+H]^+$.

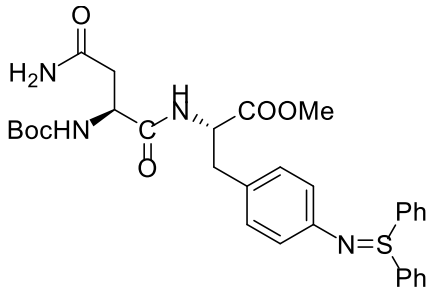


Boc-Tyr^s-Ser-OMe (6ad): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5d** (61.6 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with dichloromethane:methanol = 20:1) to give the product **6ad** (50.1 mg, 83% yield) as a brown solid. R_f = 0.4 (dichloromethane:methanol = 20:1); m.p. = 85-89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.70 (m, 4H), 7.71 – 7.47 (m, 6H), 7.41 – 7.09 (m, 4H), 6.93

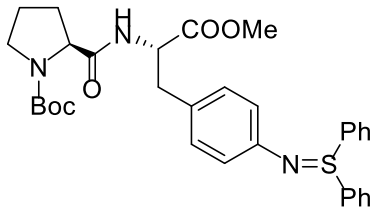
(br s, 1H), 5.25 (br s, 1H), 4.63 (br s, 1H), 4.35 (br s, 1H), 4.04 – 3.87 (m, 2H), 3.74 (s, 3H), 3.22 – 2.95 (m, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 170.6, 155.7, 139.4, 131.5, 131.0, 130.0, 129.7, 129.2, 127.2, 119.4, 80.3, 62.6, 56.1, 54.9, 52.6, 37.2, 28.3 ppm; IR (thin film): 1671, 1506, 1445, 1366, 1208, 1159, 1022, 836, 745, 686 cm^{-1}; HRMS (ESI) calculated for $C_{30}H_{36}N_3O_6S$ 566.2319, found 566.2325 $[M+H]^+$.



Boc-Tyr^s-Trp-OMe (6ae): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5e** (76.4 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with dichloromethane:methanol = 20:1) to give the product **6ae** (62.0 mg, 94% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 113-117 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.75 (dd, *J* = 26.0, 6.9 Hz, 4H), 7.57 – 7.36 (m, 7H), 7.35 – 7.30 (m, 1H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.08 (s, 1H), 7.04 – 6.95 (m, 5H), 6.51 (br s, 1H), 6.26 (br s, 1H), 4.83 – 4.77 (m, 1H), 4.31 (br s, 1H), 3.59 (s, 3H), 3.24 – 3.18 (m, 1H), 3.14 – 3.07 (m, 2H), 2.82 – 2.76 (m, 1H), 1.37 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 170.9, 155.3, 136.1, 132.2, 131.1, 130.4, 130.1, 130.0, 129.2, 127.6, 127.4, 123.2, 121.8, 119.9, 119.3, 118.2, 111.5, 108.9, 80.0, 52.8, 52.2, 37.6, 28.3, 27.4, 24.9 ppm; IR (thin film): 1713, 1674, 1604, 1500, 1391, 1366, 1240, 1162, 1121, 1020, 917, 728, 690 cm^{-1}; HRMS (ESI) calculated for $C_{38}H_{41}N_4O_5S$ 665.2792, found 665.2784 $[M+H]^+$.

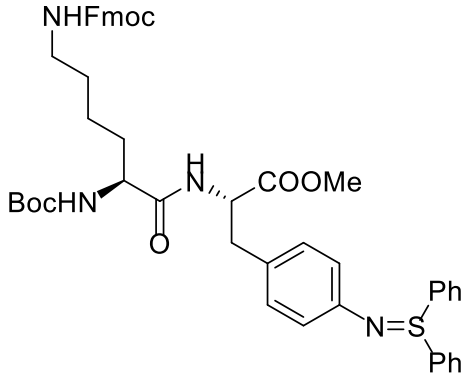


Boc-Asn-Tyr^{s}-OMe (6af): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5f** (65.6 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with dichloromethane:methanol = 20:1) to give the product **6af** (54.1 mg, 91% yield) as a light yellow solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 94-96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.55 (m, 4H), 7.50 – 7.41 (m, 6H), 7.33 – 7.31 (m, 1H), 7.11 – 6.81 (m, 4H), 6.37 (br s, 1H), 5.87 (br s, 1H), 4.69 (dd, *J* = 13.2, 6.1 Hz, 1H), 4.44 (br s, 1H), 3.65 (s, 3H), 3.03 – 2.90 (m, 2H), 2.83 – 2.41 (m, 2H), 1.39 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 171.9, 171.1, 155.7, 139.2, 131.5, 131.0, 130.0, 129.7, 129.2, 127.2, 119.4, 80.2, 53.8, 52.2, 51.1, 37.2, 36.9, 28.3 ppm; IR (thin film): 2918, 2848, 1645, 1469, 1344, 1246, 1166, 920, 740, 670 cm^{-1}; HRMS (ESI) calculated for $C_{31}H_{37}N_4O_6S$ 593.2428, found 593.2435 $[M+H]^+$.

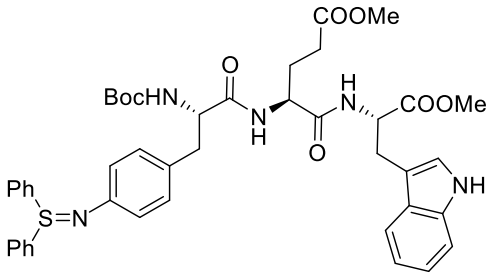


Boc-Pro-Tyr^{s}-OMe (6ag): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5g** (63.0 mg, 0.15 mmol), CuBr (0.8 mg, 5 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 3:7) to give the product **6ag** (55.0 mg, 97% yield) as a brown solid. R_f = 0.4 (hexanes:EtOAc = 3:7); m.p. = 76-78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 4H), 7.51 – 7.45 (m, 6H), 6.92 – 6.84 (m, 4H), 6.41 (br s, 1H), 4.77 (br s, 1H), 4.32 – 4.14 (m, 1H), 3.73 (s, 3H), 3.39 – 3.24 (m, 2H), 3.12 – 2.86 (m, 2H), 2.29 – 1.95 (m, 2H), 1.88 – 1.67 (m, 2H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.9, 154.6, 153.5, 139.4, 131.4, 131.0, 129.7, 129.2, 127.1, 119.3, 80.6, 61.0, 52.9, 52.2, 46.9, 37.3, 30.8, 28.2, 23.3 ppm; IR (thin film): 1745, 1682, 1539, 1393,

1366, 1285, 1162, 985, 729, 691 cm^{-1}; HRMS (ESI) calculated for $C_{32}H_{38}N_3O_5S$ 576.2527, found 576.2530 $[M+H]^+$.

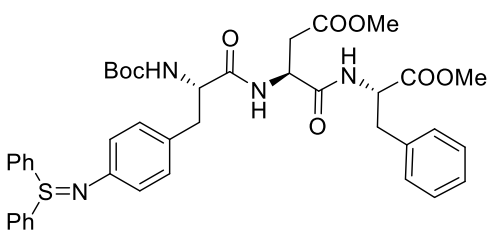


Boc-Lys(Fmoc)-Tyr^s-OMe (6ah): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5h** (101.0 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **6ah** (80.1 mg, 97% yield) as a light yellow solid. R_f = 0.4 (dichloromethane:methanol = 20:1); m.p. = 108-111 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.72 – 7.69 (m, 4H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.48 – 7.43 (m, 6H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 6.95 – 6.84 (m, 4H), 6.37 (d, *J* = 7.2 Hz, 1H), 5.11 (br s, 1H), 4.87 – 4.72 (m, 1H), 4.45 – 4.30 (m, 2H), 4.25 – 4.15 (m, 1H), 4.07 (br s, 1H), 3.68 (s, 3H), 3.22 – 2.96 (m, 4H), 1.83 – 1.70 (m, 2H), 1.62 – 1.54 (m, 2H), 1.41 (s, 9H), 1.34 – 1.24 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 171.6, 156.6, 155.6, 144.1, 141.4, 131.5, 131.1, 129.9, 129.7, 129.2, 127.7, 127.1, 127.0, 125.2, 120.0, 119.4, 115.4, 80.0, 66.6, 54.3, 53.3, 52.3, 47.4, 40.5, 37.0, 32.3, 29.4, 28.4, 22.3 ppm; IR (thin film): 1744, 1698, 1670, 1519, 1474, 1367, 1250, 1113, 1020, 995, 870, 757, 689 cm^{-1}; HRMS (ESI) calculated for $C_{48}H_{53}N_4O_7S$ 829.3629, found 829.3624 $[M+H]^+$.



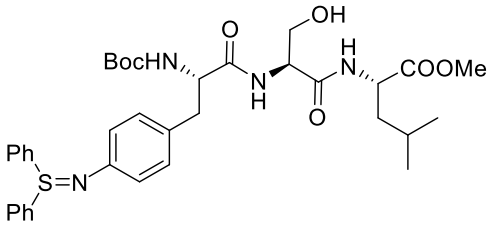
Boc-Tyr^s-Glu(OMe)-Trp-OMe (6ai): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5i** (97.9 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (hexanes:EtOAc = 3:7) to give the

product **6ai** (60.6 mg, 85% yield) as a brown solid. R_f = 0.3 (hexanes:EtOAc = 3:7); m.p. = 90-93 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.76 – 7.60 (m, 4H), 7.53 – 7.35 (m, 6H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.02 (m, 2H), 6.99 – 6.94 (m, 1H), 6.93 – 6.85 (m, 4H), 6.92 (br s, 1H), 6.85 – 6.73 (m, 1H), 5.01 (d, *J* = 7.5 Hz, 1H), 4.83 (dd, *J* = 12.4, 7.1 Hz, 1H), 4.41 (dd, *J* = 13.2, 7.5 Hz, 1H), 4.26 (d, *J* = 5.0 Hz, 1H), 3.66 (s, 3H), 3.57 (s, 3H), 3.36 – 3.12 (m, 2H), 3.00 – 2.78 (m, 2H), 2.44 – 2.22 (m, 2H), 2.12 – 1.82 (m, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.0, 171.9, 170.4, 153.5, 139.6, 136.2, 131.4, 129.9, 129.7, 127.4, 127.1, 127.0, 125.0, 123.4, 121.8, 119.4, 119.2, 118.3, 111.4, 109.3, 80.4, 56.1, 52.6, 52.4, 52.3, 51.8, 37.3, 29.9, 29.7, 28.3, 27.4 ppm; IR (thin film): 1734, 1605, 1540, 1441, 1400, 1281, 1234, 1021, 961, 741, 691 cm^{-1}; HRMS (ESI) calculated for $C_{44}H_{50}N_5O_8S$ 808.3375, found 808.3363 $[M+H]^+$.

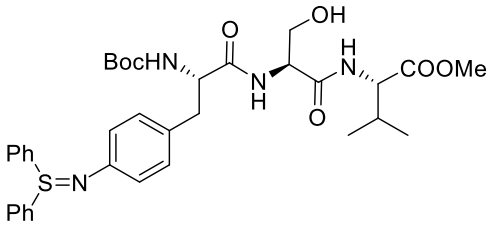


Boc-Tyr^s-Asp(OMe)-Phe-OMe (6aj): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5j** (89.9 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **6aj** (68.1 mg, 90% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 84-87 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.65 (m, 4H), 7.52 – 7.42 (m, 6H), 7.34 – 7.19 (m, 3H), 7.18 – 7.08 (m, 2H), 6.97 – 6.88 (m, 4H), 4.97 (dd, *J* = 10.8, 5.5 Hz, 1H), 4.89 (d, *J* = 4.7 Hz, 1H), 4.81 – 4.72 (m, 1H), 4.68 (dd, *J* = 14.0, 6.7 Hz, 1H), 4.23 (d, *J* = 5.8 Hz, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 3.16 – 2.82 (m, 6H), 1.40 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.9, 171.5, 169.9, 153.9, 139.6, 136.1, 131.4, 131.1, 129.9, 129.7, 129.3, 129.2, 129.1, 128.6, 127.1, 119.5, 80.5,

53.9, 52.1, 49.1, 37.7, 31.6, 28.3, 22.7, 14.2 ppm; IR (thin film): 1735, 1671, 1498, 1400, 1333, 1207, 1113, 854, 692 cm^{-1}; HRMS (ESI) calculated for $C_{41}H_{47}N_4O_8S$ 755.3109, found 755.3106 $[M+H]^+$.

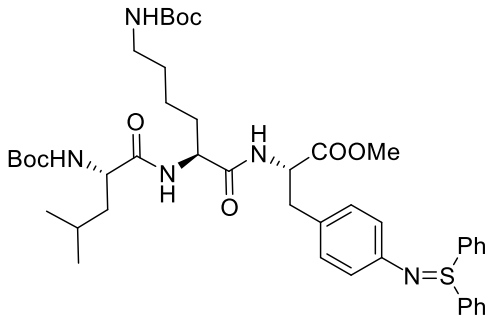


Boc-Tyr^s-Ser-Leu-OMe (6ak): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5k** (78.5 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (hexanes:EtOAc = 1:1) to give the product **6ak** (65.2 mg, 96% yield) as a brown solid. R_f = 0.3 (hexanes:EtOAc = 1:1); m.p. = 80-83 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.61 (m, 4H), 7.56 – 7.38 (m, 6H), 7.06 – 6.83 (m, 4H), 6.32 (d, *J* = 8.1 Hz, 2H), 5.01 (br s, 1H), 4.65 – 4.45 (m, 1H), 4.27 (br s, 1H), 3.67 (br s, 1H), 3.66 (s, 3H), 3.10 – 2.83 (m, 4H), 1.63 – 1.51 (m, 2H), 1.41 (s, 9H), 1.31 – 1.23 (m, 1H), 0.96 – 0.78 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 171.4, 155.5, 153.5, 139.7, 131.3, 131.0, 130.0, 129.7, 129.2, 127.1, 119.4, 80.1, 52.2, 50.8, 41.6, 37.2, 31.6, 28.3, 24.6, 22.8, 21.9, 14.0 ppm; IR (thin film): 1742, 1700, 1605, 1498, 1442, 1239, 1167, 1055, 1021, 920, 826, 743, 690 cm^{-1}; HRMS (ESI) calculated for $C_{36}H_{47}N_4O_7S$ 679.3160, found 679.3169 $[M+H]^+$.

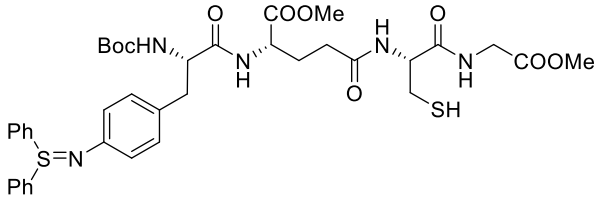


Boc-Tyr^s-Ser-Val-OMe (6al): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5l** (76.4 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and *i*PrOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (hexanes:EtOAc = 1:1) to give the product **6al** (65.0 mg, 93% yield) as a brown solid. R_f = 0.3 (hexanes:EtOAc = 1:1); m.p. = 88-91 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.61 (m, 4H), 7.53 – 7.39 (m, 6H), 7.00 – 6.89 (m, 4H), 6.48 – 6.26 (m,

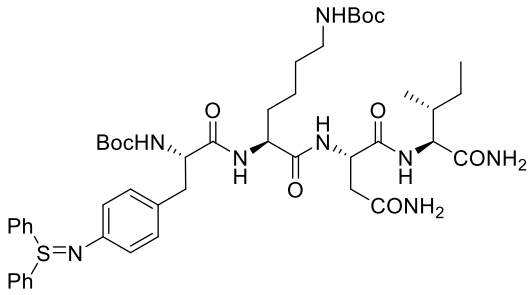
2H), 5.01 (br s, 1H), 4.45 (dd, *J* = 8.5, 5.1 Hz, 2H), 4.27 (d, *J* = 6.3 Hz, 1H), 3.68 (br s, 1H), 3.65 (s, 3H), 3.02 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.9 Hz, 2H), 2.14 – 2.02 (m, 1H), 1.42 (s, 9H), 0.90 – 0.80 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 155.5, 153.6, 139.8, 131.3, 131.0, 129.9, 129.6, 129.2, 127.0, 119.4, 80.1, 57.3, 57.1, 56.0, 52.0, 37.2, 31.3, 28.3, 18.8, 17.9 ppm; IR (thin film): 1740, 1732, 1661, 1556, 1491, 1366, 1238, 1169, 1020, 920, 743, 690 cm^{-1}; HRMS (ESI) calculated for $C_{35}H_{45}N_4O_7S$ 665.3003, found 665.3013 $[M+H]^+$.



Boc-Leu-Lys(Boc)-Tyr^s-OMe (6am): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5m** (99.7 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **6am** (56.1 mg, 68% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 115-117 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 4H), 7.74 – 7.60 (m, 6H), 7.38 – 7.28 (m, 2H), 7.10 – 7.02 (m, 2H), 6.84 (br s, 1H), 6.67 (br s, 1H), 5.22 (br s, 1H), 4.83 (br s, 1H), 4.81 – 4.72 (m, 1H), 4.36 (dd, *J* = 12.7, 7.6 Hz, 1H), 4.10 (br s, 1H), 3.71 (s, 3H), 3.21 – 2.92 (m, 4H), 1.84 – 1.61 (m, 6H), 1.58 – 1.50 (m, 1H), 1.42 (s, 18H), 1.37 – 1.19 (m, 2H), 1.03 – 0.83 (m, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 171.8, 171.7, 171.1, 156.1, 135.7, 132.2, 131.0, 130.0, 129.1, 127.7, 127.0, 119.4, 79.9, 78.9, 53.4, 53.2, 52.7, 52.3, 39.8, 37.0, 36.8, 32.1, 29.5, 28.4, 28.3, 24.7, 23.0, 22.3, 21.8 ppm; IR (thin film): 2933, 2865, 1697, 1604, 1516, 1476, 1443, 1419, 1365, 1240, 1170, 916, 781, 737, 690 cm^{-1}; HRMS (ESI) calculated for $C_{44}H_{62}N_5O_8S$ 820.4314, found 820.4317 $[M+H]^+$.

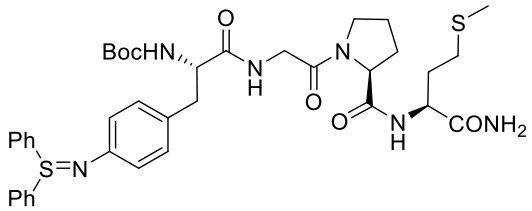


Boc-Tyr^{s}-Glu(OMe)-Cys-Gly-OMe (6an): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5n** (94.0 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **6an** (32.1 mg, 41% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 140-143 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 4H), 7.55 – 7.40 (m, 6H), 7.24 – 7.18 (m, 1H), 7.17 – 7.10 (m, 2H), 6.92 (d, *J* = 2.9 Hz, 4H), 4.91 (d, *J* = 6.1 Hz, 1H), 4.83 – 4.73 (m, 2H), 4.66 (dd, *J* = 14.1, 6.9 Hz, 1H), 4.25 (d, *J* = 6.1 Hz, 1H), 3.64 (s, 3H), 3.60 (s, 3H), 3.13 – 3.01 (m, 2H), 2.97 – 2.83 (m, 4H), 2.59 – 2.47 (m, 1H), 1.40 (s, 9H), 1.31 – 1.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 172.0, 171.9, 171.8, 169.0, 155.4, 131.0, 130.6, 130.1, 129.2, 127.9, 127.8, 127.0, 119.6, 79.9, 61.5, 61.0, 55.9, 53.5, 52.0, 50.4, 47.2, 38.4, 29.3, 28.4, 24.9 ppm; IR (thin film): 1598, 1488, 1464, 1444, 1383, 1231, 1041, 959, 926, 840, 759, 695 cm^{-1}; HRMS (ESI) calculated for $C_{38}H_{48}N_5O_9S_2$ 782.2888, found 782.2880 $[M+H]^+$.

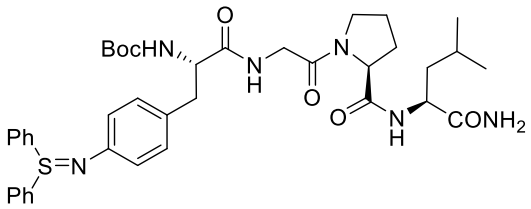


Boc-Tyr^{s}-Lys(Boc)-Gly-Ile-CONH$_2$ (6ao): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5o** (114.0 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 15:1) to give the product **6ao** (41.0 mg, 45% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 15:1); m.p. = 130-133 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 4H), 7.58 – 7.43 (m, 6H), 7.38 – 7.24 (m, 4H), 7.11 (br s, 1H), 7.04 – 6.92 (m, 4H), 6.92 – 6.86 (m,

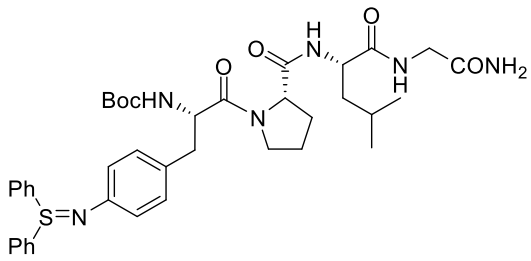
1H), 6.71 (br s, 1H), 5.88 – 5.47 (m, 1H), 5.42 – 5.14 (m, 1H), 4.60 – 4.32 (m, 2H), 4.27 – 4.09 (m, 1H), 3.94 (d, *J* = 12.3 Hz, 1H), 3.72 – 3.34 (m, 2H), 3.17 (br s, 1H), 3.02 – 2.82 (m, 1H), 2.46 – 2.13 (m, 2H), 1.91 – 1.53 (m, 7H), 1.40 (s, 9H), 1.39 (s, 9H), 1.35 – 1.22 (m, 2H), 1.07 – 0.72 (m, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 172.6, 172.5, 172.4, 172.3, 172.2, 155.9, 131.6, 129.9, 129.8, 129.7, 129.6, 127.1, 126.9, 119.5, 80.9, 80.7, 62.3, 60.9, 54.5, 52.5, 47.8, 43.0, 39.5, 28.6, 28.3, 25.7, 25.1, 23.0, 22.9, 21.9, 21.3, 21.2 ppm; IR (thin film): 2980, 2927, 1730, 1698, 1607, 1500, 1441, 1389, 1250, 1161, 1025, 920, 856, 736, 695 cm^{-1}; HRMS (ESI) calculated for $C_{47}H_{67}N_8O_9S$ 919.4746, found 919.4750 $[M+H]^+$.



Boc-Tyr^s-Gly-Pro-Met-CONH$_2$ (6ap): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5p** (89.1 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 15:1) to give the product **6ap** (51.1 mg, 67% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 15:1); m.p. = 135-138 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (br s, 1H), 7.99 – 7.78 (m, 4H), 7.65 – 7.46 (m, 6H), 7.17 – 6.79 (m, 6H), 6.64 – 6.45 (m, 1H), 5.69 (br s, 1H), 4.40 (br s, 1H), 4.35 – 4.19 (m, 2H), 3.89 – 3.71 (m, 2H), 3.58 (br s, 1H), 3.16 – 3.00 (m, 1H), 2.92 – 2.74 (m, 2H), 2.65 – 2.44 (m, 2H), 2.34 – 2.18 (m, 4H), 2.07 (s, 3H), 2.07 – 1.93 (m, 2H), 1.36 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 172.9, 171.9, 169.4, 155.6, 131.0, 130.2, 130.1, 129.2, 128.3, 127.0, 119.6, 115.2, 79.7, 61.2, 56.1, 52.9, 47.7, 45.9, 37.8, 31.2, 29.7, 28.4, 24.9, 15.4, 8.7 ppm; IR (thin film): 1667, 1644, 1530, 1514, 1443, 1400, 1243, 1165, 1012, 919, 774, 745, 729, 690 cm^{-1}; HRMS (ESI) calculated for $C_{38}H_{49}N_6O_6S_2$ 749.3150, found 749.3151 $[M+H]^+$.

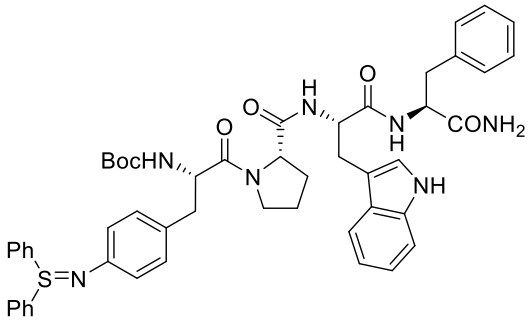


Boc-Tyr^{s}-Gly-Pro-Leu-CONH$_2$ (6aq): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5q** (86.3 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **6aq** (61.0 mg, 84% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 119-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 4H), 7.58 – 7.40 (m, 6H), 7.38 – 7.31 (m, 1H), 6.98 – 6.83 (m, 4H), 6.80 (br s, 1H), 6.17 (br s, 1H), 5.55 (br s, 1H), 4.46 – 4.32 (m, 2H), 4.28 (br s, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.85 – 3.70 (m, 2H), 3.60 – 3.37 (m, 1H), 3.03 – 2.72 (m, 2H), 2.24 – 1.90 (m, 4H), 1.84 – 1.72 (m, 2H), 1.62 (d, *J* = 6.2 Hz, 1H), 1.36 (s, 9H), 1.06 – 0.80 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 173.6, 171.8, 169.3, 155.8, 139.6, 131.5, 131.3, 130.3, 129.9, 129.7, 127.2, 119.2, 80.0, 61.2, 52.2, 47.4, 42.4, 39.2, 37.7, 29.3, 28.4, 25.3, 24.9, 23.3, 21.4 ppm; IR (thin film): 1764, 1573, 1510, 1465, 1400, 1378, 1312, 1276, 1200, 1121, 1083, 880, 789, 715, 680 cm^{-1}; HRMS (ESI) calculated for $C_{39}H_{51}N_6O_6S$ 731.3585, found 731.3587 $[M+H]^+$.

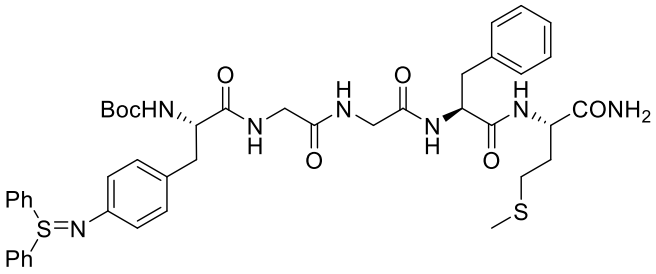


Boc-Tyr^{s}-Pro-Leu-Gly-CONH$_2$ (6ar): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5r** (86.3 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (EtOAc:methanol = 20:1) to give the product **6ar** (39.1 mg, 54% yield) as a brown solid. R_f = 0.4 (EtOAc:methanol = 20:1); m.p. = 124-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 4H), 7.55 – 7.40 (m, 6H), 7.38 – 7.27 (m, 1H), 7.10 (br s, 1H), 7.02 – 6.85 (m, 4H), 6.78 (br s, 1H), 5.36 (br s,

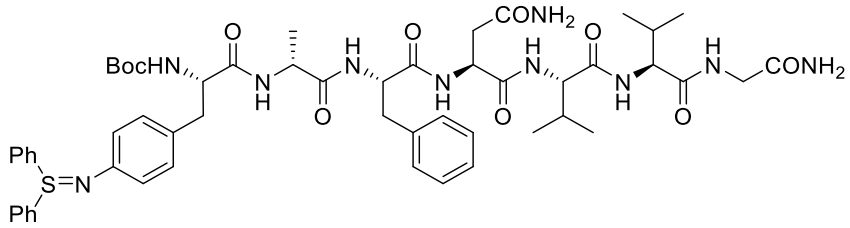
1H), 4.55 – 4.40 (m, 1H), 4.40 – 4.21 (m, 1H), 3.93 (br s, 1H), 3.64 – 3.33 (m, 2H), 3.06 – 2.71 (m, 4H), 2.16 (br s, 1H), 1.94 – 1.51 (m, 6H), 1.38 (s, 9H), 0.97 – 0.75 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 173.0, 172.8, 172.6, 155.9, 131.6, 131.0, 130.0, 129.8, 129.2, 127.2, 127.0, 119.5, 80.4, 64.4, 61.9, 60.4, 55.7, 42.6, 39.4, 30.6, 28.2, 24.9, 22.9, 21.3, 21.1, 14.2 ppm; IR (thin film): 1684, 1615, 1558, 1540, 1498, 1474, 1327, 1219, 1161, 1072, 922, 826, 747, 685, 608 cm^{-1}; HRMS (ESI) calculated for $C_{39}H_{51}N_6O_6S$ 731.3585, found 731.3580 $[M+H]^+$.



Boc-Tyr^s-Pro-Trp-Phe-CONH$_2$ (6as): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5s** (110.7 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (EtOAc:methanol = 20:1) to give the product **6as** (54.0 mg, 61% yield) as a brown solid. R_f = 0.4 (EtOAc:methanol = 20:1); m.p. = 130-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.11 (m, 1H), 7.72 – 7.61 (m, 4H), 7.51 – 7.39 (m, 7H), 7.24 – 7.17 (m, 3H), 7.14 – 7.07 (m, 5H), 6.96 – 6.84 (m, 3H), 6.79 – 6.69 (m, 2H), 6.63 (br s, 1H), 6.59 (br s, 1H), 5.51 (d, *J* = 10.4 Hz, 1H), 4.94 (d, *J* = 14.4 Hz, 2H), 4.53 (q, *J* = 5.8 Hz, 1H), 4.31 (d, *J* = 6.8 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.71 – 3.40 (m, 2H), 3.28 – 2.93 (m, 4H), 2.38 – 1.90 (m, 2H), 1.77 (d, *J* = 11.2 Hz, 2H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 173.0, 172.4, 171.2, 155.2, 137.7, 136.0, 131.5, 131.1, 129.8, 129.7, 129.2, 128.9, 128.5, 127.5, 127.2, 127.1, 126.5, 123.4, 122.4, 119.8, 119.2, 118.0, 111.9, 109.4, 80.0, 61.4, 55.1, 53.7, 53.1, 47.4, 37.0, 36.4, 28.6, 28.3, 25.8, 25.1 ppm; IR (thin film): 1682, 1672, 1590, 1530, 1457, 1390, 1366, 1290, 1245, 1208, 1158, 1033, 910, 882, 838, 751, 679 cm^{-1}; HRMS (ESI) calculated for $C_{51}H_{56}N_7O_6S$ 894.4007, found 894.3992 $[M+H]^+$.



Boc-Tyr^{s}-Gly-Gly-Phe-Met-CONH$_2$ (6at): The reaction was performed following the General Procedure with **1a** (20.1 mg, 0.1 mmol), **5t** (105.1 mg, 0.15 mmol), CuBr (1.4 mg, 10 mol %) and MeOH (1.0 mL). The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 15:1) to give the product **6at** (50.0 mg, 58% yield) as a brown solid. R_f = 0.3 (dichloromethane:methanol = 15:1); m.p. = 149-151 ℃; ^{1}H NMR (400 MHz, CD_3OD) δ 7.70 (dd, *J* = 7.7, 1.8 Hz, 4H), 7.61 – 7.52 (m, 5H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 1H), 7.29 – 7.26 (m, 6H), 7.24 – 7.16 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.64 – 4.57 (m, 1H), 4.53 – 4.43 (m, 1H), 4.34 – 4.21 (m, 1H), 3.87 – 3.76 (m, 4H), 3.34 – 3.29 (m, 1H), 3.20 (dd, *J* = 14.0, 5.8 Hz, 2H), 3.06 – 2.98 (m, 2H), 2.89 – 2.75 (m, 1H), 2.58 – 2.32 (m, 2H), 2.06 (s, 3H), 2.20 – 1.88 (m, 2H), 1.37 (s, 9H) ppm; ^{13}C NMR (100 MHz, CD_3OD) δ 178.8, 176.1, 174.5, 174.4, 160.6, 155.9, 142.2, 140.9, 135.6, 135.1, 133.7, 133.6, 132.9, 132.2, 131.1, 131.0, 130.5, 122.7, 83.5, 60.6, 59.3, 56.3, 46.5, 46.4, 40.8, 34.9, 33.8, 31.3, 31.2, 17.8 ppm; IR (thin film): 1684, 1613, 1590, 1509, 1481, 1429, 1377, 1347, 1320, 1275, 1268, 1197, 1124, 1093, 968, 893, 854, 721, 668 cm^{-1}; HRMS (ESI) calculated for $C_{44}H_{54}N_7O_7S_2$ 856.3521, found 856.3527 $[M+H]^+$.



Boc-Tyr^{s}-D-Ala-Phe-Asn-Val-Val-Gly-CONH$_2$ (6au): The reaction was performed following the General Procedure with **1a** (10.1 mg, 0.05 mmol), **5u** (67.2 mg, 0.075 mmol), CuBr (0.8 mg, 10 mol %), MeOH (1.0 mL), H_2O (1.0 mL) and DMF (0.15 mL). After reaction completion, the solutions were centrifuged at 600 rad/min for 3.0 min. And then the supernatant (100 μL) was transferred to a clean centrifuge tube and added 200 μL of distilled water and 800 μL of acetonitrile. After workup, the reaction was analyzed by reverse phase HPLC using a gradient of 30% to 50% buffer B over 20 minutes. Yield was determined by taking the ratio of A_{prod}/A_{total} where A_{prod} = area in mAU of the product peak (**6au**, with retention time of 16.10 min) and A_{total} = area in mAU of the combined peptide containing species (product **6au**, starting material **5u**, and byproducts).

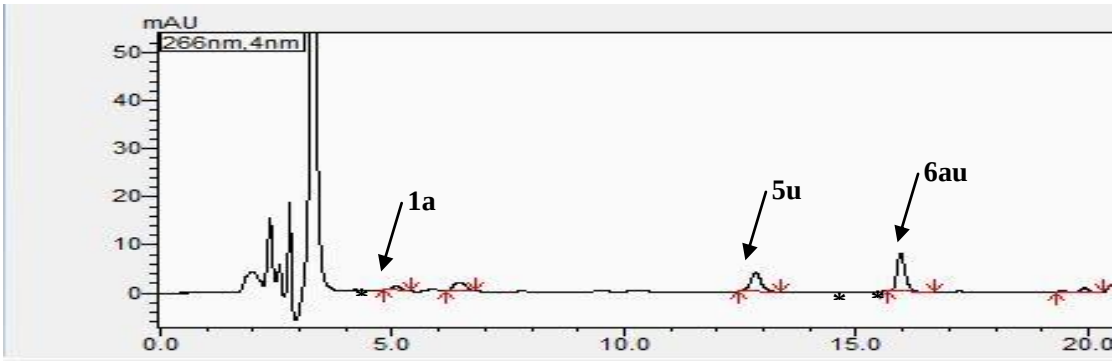


Figure S1. LC trace of the reaction mixture (30-50% **B** over 20 min, 0.1% TFA, λ = 266 nm, Agilent Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 μm)).

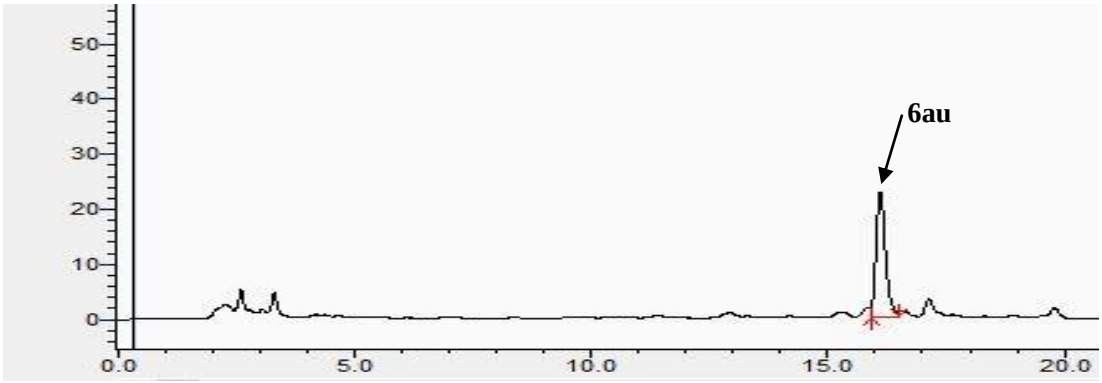


Figure S2. LC trace of purified 6au (30-50% **B** over 20 min, 0.1% TFA, λ = 266 nm, Agilent Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 μm)).

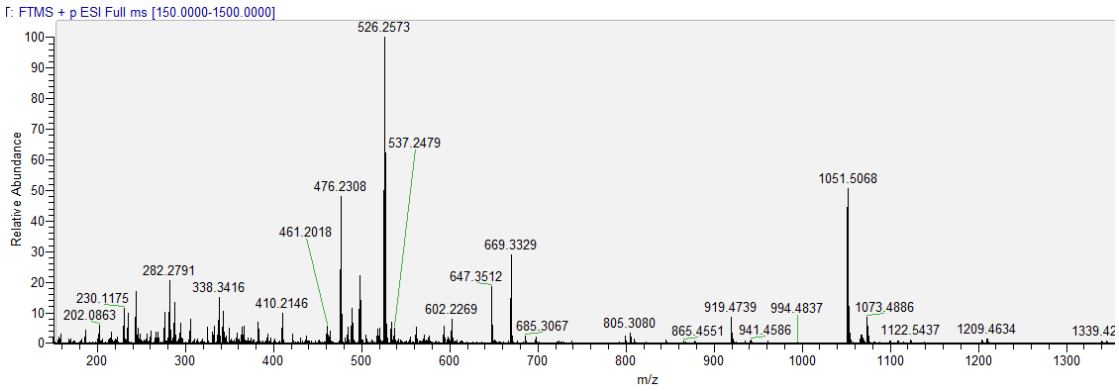


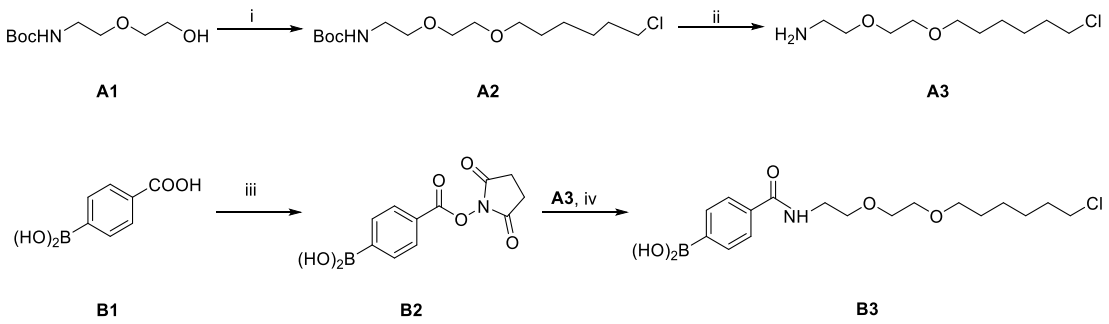
Figure S3. ESI Mass spectrum of purified 6au. Calculated for $C_{54}H_{71}N_{10}O_{10}S$ 1051.5070, found 1051.5068 $[M+H]^+$, 526.2573 $[M+2H]^{2+}$.

5 Chan-Lam Coupling-Based Bioconjugation in Halotag 7

General reaction condition

To an eppendorf tube with **1q** (40 mM, 10.0 equiv) and MeOH (8% of total volume), a solution of **halotag 7'** (final concentration 330 μM) in PBS (pH 7.4) was added. And then, a solution of CuBr (1.0 equiv) in PBS (pH 7.4) was added and the resulting mixture was vortexed. The mixture was incubated for 56 h at 25 ℃. Then, the reaction was quenched with ethylenediaminetetraacetic acid (EDTA, 5 equiv to copper) and purified by spin desalting columns (Bio-spin 6 Tris columns). An aliquot of the purified reaction solution (2.0 μL) was diluted with deionized water (48.0 μL) and analyzed by LC–MS and conversion to the expected product **7** was observed.

Synthesis of halolinker boronic acid B3

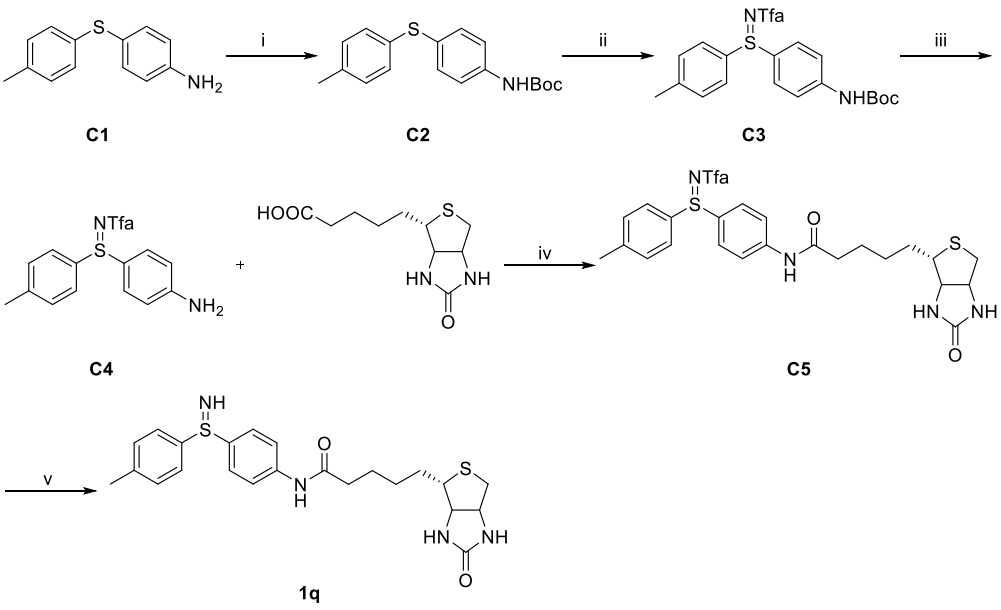


[a]Reagents and conditions: (i) NaH, 6-chloro-1-iodohexane, THF/DMF, 0 ℃ to rt, overnight, 69%. (ii) TFA, DCM, 0 ℃ to rt, 2 h, 81%. (iii) N-Hydroxysuccinimide, DCC, DCM, 0 ℃ to rt, 95%. (iv) DIPEA, DCM, rt, 82%.

The halolinker boronic acid **B3** was prepared by coupling of precursors **A3** and **B2** following a procedure reported in the literature.[5] The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **B3** as a brown oil. R_f = 0.3 (dichloromethane:methanol = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.62 (m, 4H), 7.06 (s, 1H), 3.85 – 3.58 (m, 8H), 3.51 – 3.41 (m, 4H), 1.85 – 1.69 (m, 2H), 1.65 – 1.52 (m, 2H), 1.43 – 1.37 (m, 2H), 1.35 – 1.30 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 134.5, 133.8, 126.4, 126.2, 71.3, 70.1, 69.9, 45.0, 39.8, 32.5, 29.3, 29.2, 26.6, 25.3 ppm; IR (thin film): 1673, 1476, 1400, 1361, 1294, 1200, 1180, 1129, 833, 800, 720 cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{28}BClNO_5$ 372.1744, found 372.1735 $[M+H]^+$.

Synthesis of the biotinylated *NH*-sulfilimine 1q

1q was prepared as shown below:



[a]Reagents and conditions: (i) Boc_2O, Et_3N, DCM, 0 ℃ to rt, 3 h, 99%. (ii) NaH, DBDMH, THF, 0 ℃ to rt, 3 h, 75%. (iii) TFA, DCM, 0 ℃ to rt, 3 h, 92%. (iv) DCC, DMAP, DCM, rt, 24 h, 73%. (v) KOH, MeOH, rt, 3 h, 93%.

***tert*-Butyl (4-(*p*-tolylthio)phenyl)carbamate (C2)**

To a solution of 4-(*p*-tolylthio)aniline **C1** (0.98 g, 4.5 mmol) in DCM (15.0 mL) was added Boc_2O (11.97 g, 9.0 mmol), Et_3N (0.91 g, 9.0 mmol) at 0 ℃. After stirring at room temperature for 3 h, the solvent was removed under vacuum. The product was then extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum to obtain the product **C2** as brown solid (0.96 g, 99%), which was used for the next step without further purification.

***tert*-Butyl (*E*)-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl)sulfinimidoyl)phenyl)carbamate (C3)**

Under an argon atmosphere, a mixture of **C2** (0.96 g, 4.5 mmol) directly obtained from the precious step and trifluoroacetamide (0.77 g, 6.8 mmol) in THF (11.3 mL) was added under ice cooling within 45 min to a suspension of NaH (60% in mineral oil; 0.20 g, 5.0 mmol) in THF (5.0 mL). Then, a freshly prepared solution of 1,3-dibromo-5,5-dimethylhydantoin (1.43 g, 5.0 mmol) in THF (5.0 mL)

was added within 60 min at 20 ℃. The mixture was stirred for 3 h. Then, the reaction was quenched with 10% aq citric acid solution (35 mL), and EtOAc (40 mL) was added. The organic layer was washed with 25% aq sodium sulfite solution (35 mL) and water (3 × 40 mL). The solvent was removed by distillation and the residue was purified by silica gel chromatography (hexanes:EtOAc = 3:1) to give the product **C3** as yellow solid (1.45 g, 75%). R_f = 0.2 (hexanes:EtOAc = 5:1); m.p. = 97-101 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 1.49 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6 (q, J_{C-F} = 35.0 Hz), 152.3, 143.6, 143.2, 130.8, 130.6, 129.2, 127.7, 126.0, 119.2, 117.2 (q, J_{C-F} = 288.0 Hz), 81.4, 28.2, 21.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.3 ppm; IR (thin film): 2920, 2870, 1604, 1496, 1444, 1229, 1110, 913, 731, 685 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{22}F_3N_2O_3S$ 427.1298, found 427.1795 $[M+H]^+$.

(*Z*)-*N*-((4-Aminophenyl)(*p*-tolyl)- γ^4-sulfanylidene)-2,2,2-trifluoroacetamide (C4)

To a solution of **C3** (1.28 g, 3.0 mmol) in DCM (10.0 mL) at 0 ℃ was added TFA (3.42 g, 30.0 mmol) in a small portion. The reaction mixture was warmed to room temperature and stirred for 3 h. Upon completion of the reaction as monitored by TLC analysis, the solvent was removed and the residue was treated with excess K_2CO_3 solution in MeOH. The mixture was filtered and the filtrate was concentrated to obtain crude product, which was then purified by silica gel chromatography (hexanes:EtOAc = 3:1) to give the product **C4** as yellow solid (0.90 g, 92%). R_f = 0.2 (hexanes:EtOAc = 3:1); m.p. = 178-181 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 4.19 (br s, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4 (q, J_{C-F} = 34.7 Hz), 151.3, 143.0, 131.3, 130.6, 130.5, 127.4, 119.7, 117.3 (q, J_{C-F} = 288.4 Hz), 115.3, 21.4 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -73.30 ppm; IR (thin film): 2920,

2870, 1600, 1500, 1440, 1250, 1100, 900, 850, 720, 691 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{14}F_3N_2OS$ 327.0773, found 327.0776 $[M+H]^+$.

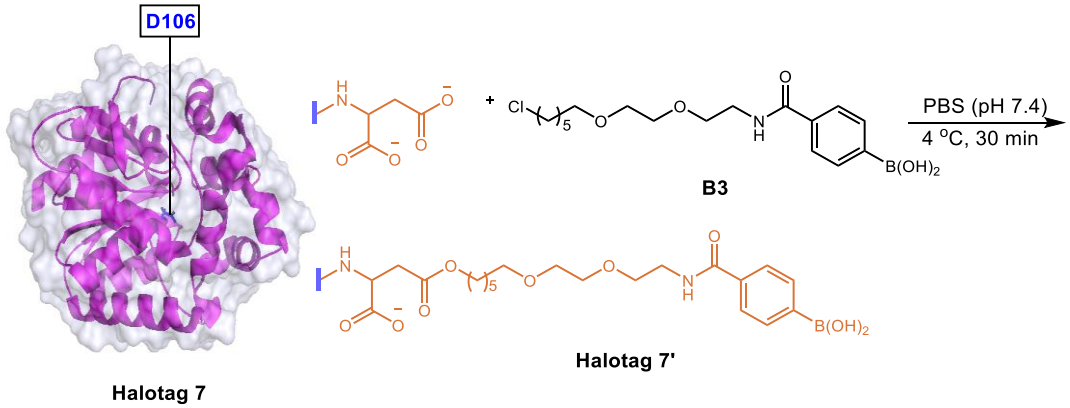
(*E*)-5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl) sulfinimidoyl)phenyl)pentanamide (C5)

To a solution of **C4** (97.8 mg, 0.3 mmol) in DCM (0.6 mL) was added biotin (88.0 mg, 0.36 mmol), DCC (80.3 mg, 0.39 mmol) and DMAP (7.3 mg, 20 mol %) at 0 ℃. After stirring at room temperature for 24 h, the solvent was removed under vacuum. The product was then extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel (dichloromethane:methanol = 20:1) to give the product **C5** as a brown solid (120.9 mg, 73%). R_f = 0.3 (dichloromethane:methanol = 20:1); m.p. = 214-217 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (d, *J* = 20.7 Hz, 1H), 7.76 (br s, 2H), 7.59 (dd, *J* = 19.9, 7.2 Hz, 4H), 7.37 – 7.10 (m, 2H), 6.89 (d, *J* = 13.5 Hz, 1H), 6.02 (br s, 1H), 4.47 (s, 1H), 4.27 (s, 1H), 3.10 (s, 1H), 2.93 – 2.62 (m, 2H), 2.38 (s, 3H), 2.31 – 2.23 (m, 2H), 1.72 – 1.57 (m, 4H), 1.38 (d, *J* = 9.6 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 166.5 (q, J_{C-F} = 34.8 Hz), 164.6, 143.7, 143.3, 130.9, 130.0, 129.0, 127.8, 127.1, 120.8, 117.2 (q, J_{C-F} = 287.8 Hz), 61.7, 60.4, 55.7, 40.6, 36.6, 28.0, 27.9, 25.5, 21.5 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -73.2 ppm; IR (thin film): 2930, 2850, 1700, 1665, 1600, 1540, 1495, 1450, 1400, 1285, 1125, 940, 830, 785 cm^{-1}; HRMS (ESI) calculated for $C_{25}H_{28}F_3N_4O_3S_2$ 553.1549, found 553.1541 $[M+H]^+$.

5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)sulfinimidoyl)phenyl) pentanamide (1q)

To a solution of KOH (65.9 mg, 1.0 mmol) in MeOH (0.8 mL) at 0 ℃ was added **C5** in solid form. The reaction mixture was warmed to room temperature and stirred for 3h. Upon completion of reaction as monitored by TLC analysis, the solvent was removed and the crude product was purified with flash chromatography on silica gel (dichloromethane:methanol = 10:1) to give the product **1q** (87.0 mg, 93% yield) as a white solid. R_f = 0.2 (dichloromethane:methanol = 10:1); m.p. = 146-148 ℃; ^{1}H NMR (600 MHz, CD_3OD) δ 7.89 (br s, 2H), 7.77 – 7.57 (m, 4H), 7.48 (br s, 2H), 4.53 (s, 1H), 4.35 (s, 1H), 3.39 (br s, 2H), 3.25 (s, 1H), 3.03 – 2.68 (m, 2H), 2.63 – 2.22 (m, 5H), 1.90 – 1.39 (m, 6H) ppm; ^{13}C NMR (150 MHz, CD_3OD) δ 173.5, 164.7, 143.5, 142.9, 134.6, 131.5, 130.5, 128.1, 126.8, 120.3, 62.0, 60.3, 55.6, 39.7, 36.3, 28.4, 28.1, 25.1, 20.0 ppm; IR (thin film): 2926, 2852, 2349, 2318, 1691, 1673, 1587, 1532, 1494, 1450, 1399, 1257, 1151, 918, 835, 809 cm^{-1}; HRMS (ESI) calculated for $C_{23}H_{29}N_4O_2S_2$ 457.1726, found 457.1719 $[M+H]^+$.

Preparation and characterization of HaloTag Ligand halotag 7'



To an Eppendorf tube with protein **halotag 7** (PDB ID 5VNP) solution (0.4 mM in PBS, pH 7.4, 100 μL, 40 nmol), a solution of halolinker boronic acid **B3** (400 mM in MeOH, 1 μL, 400 nmol) was added. The resulting mixture was vortexed and incubated for 30 min at 4 ℃. Afterwards, the reaction solution was purified by spin desalting columns (Bio-spin 6 Tris columns), split into aliquots, and stored in -20 ℃ before use.

Procedure: The total ion chromatogram, combined ion series and deconvoluted spectra are shown for the product **halotag 7'**.

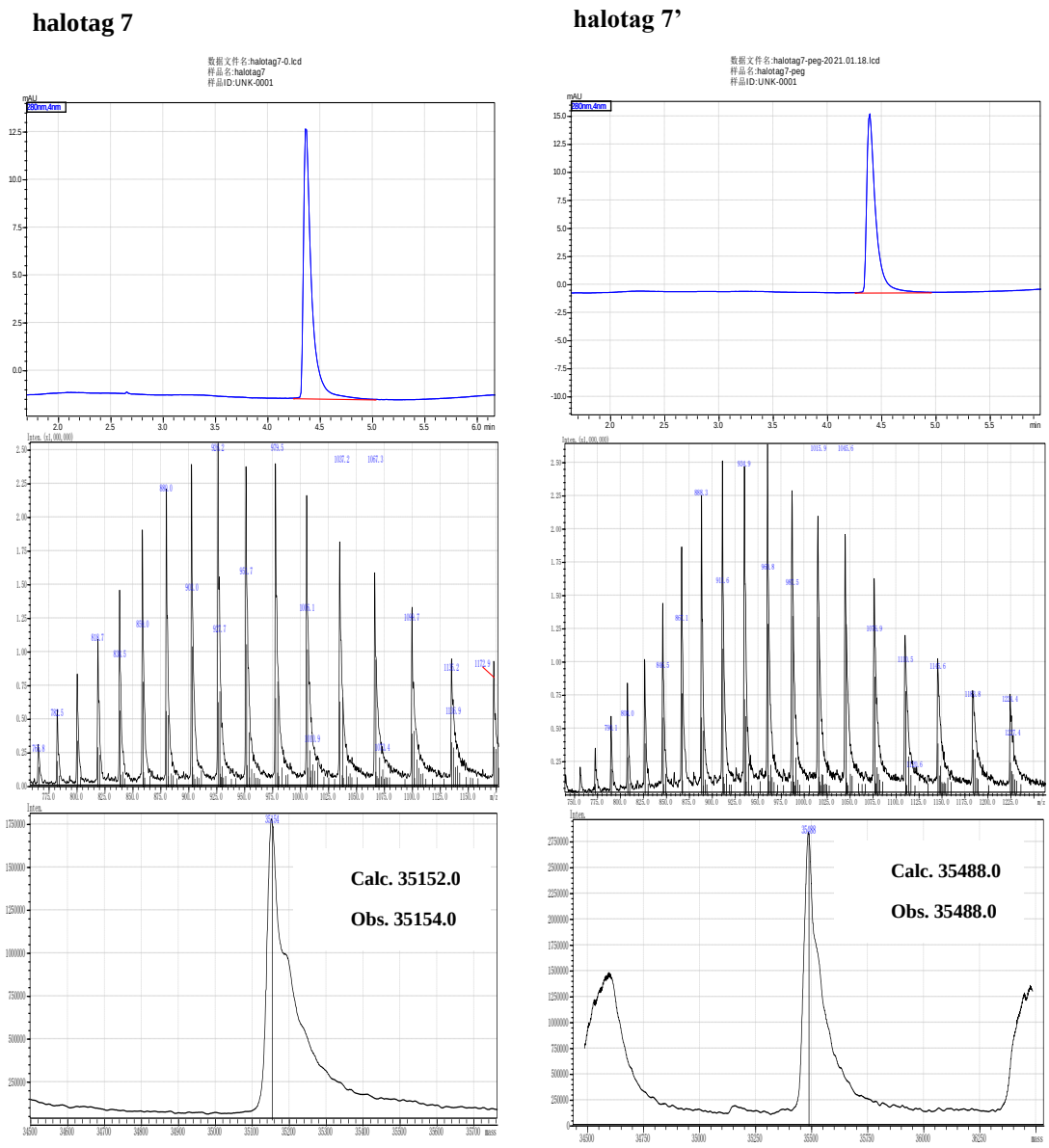
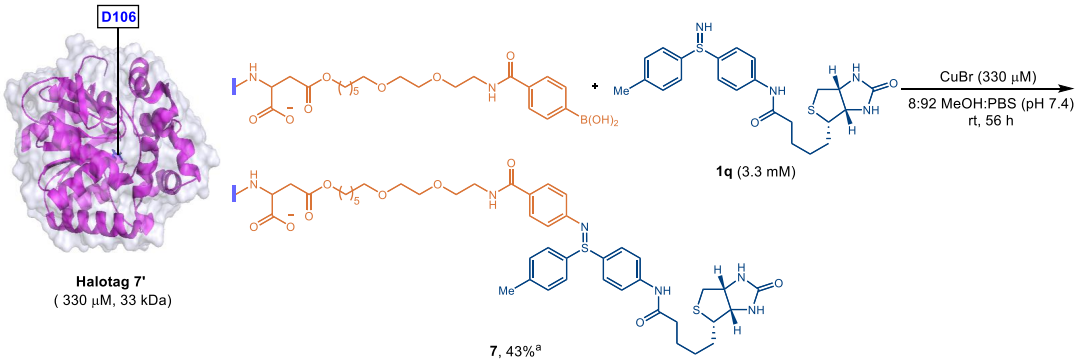


Figure S4. A typical analysis of the halolinker labelling reaction by LC–MS. The total ion chromatogram, combined ion series and deconvoluted spectra are shown for the starting protein **halotag 7** and the halolinker labelling product **halotag 7'**.

Cross coupling reaction of halotag 7' with biotin group containing *NH*-sulfilimine 1q



Procedure: To a microreactor equipped with a stir bar was added **1q** (40 mM in MeOH, 3.5 μL, 140 nmol), **halotag 7'** (0.4 mM in PBS, pH 7.4, 35 μL, 14 nmol) and CuBr (4.0 mM in PBS, pH 7.4, 3.5 μL, 14 nmol). The reaction mixture was kept stirring for 56 h at 25 ℃. Upon completion of the reaction, an aliquot of the reaction solution (2.0 μL) was diluted with deionized water (48 μL), and purified by spin desalting columns (Bio-spin 6 Tris columns). Purified solution was subjected to LC-MS for intact mass analysis. Conversion (43%) was determined based on intact protein mass analysis.

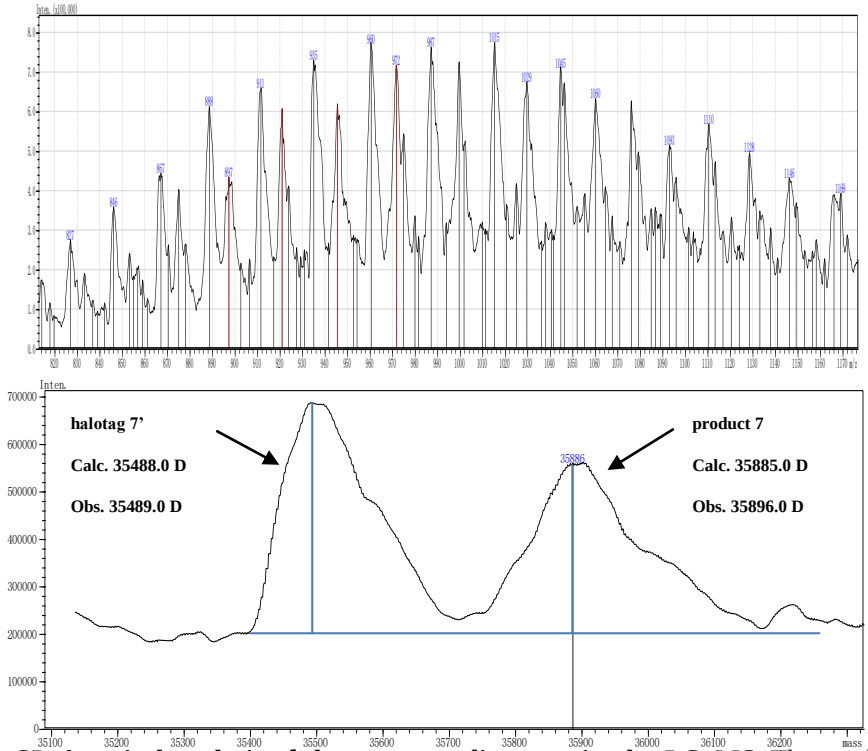


Figure S5. A typical analysis of the cross-coupling reaction by LC–MS. The combined ion series and deconvoluted spectra are shown for the reaction.

Procedure for stability experiments

Purified protein **7** (5.0 μL, 50 μM) was incubated in a buffer containing a given reagent (50.0 μL) at room temperature overnight. Subsequently, the sample was mixed with 0.1% v/v SDS loading buffer (Epizyme Biotech) to prepare a final volume of 10 μL in an Eppendorf tube and was loaded to a pre-cassette 12% bis-tris gel (Epizyme Biotech) without heat denaturation process if no any other special instructions. The sample was directly analyzed by western blotting as described in Gel and blot analysis (page S3). Quantification of the bands was conducted using Image J software. The purified protein **7** (5.0 μL, 50 μM) in PBS buffer (5 mM, pH 7.4) was used as a standard (chemiluminescence intensity = 1.0). Average of two standard bands was used for one experiment.

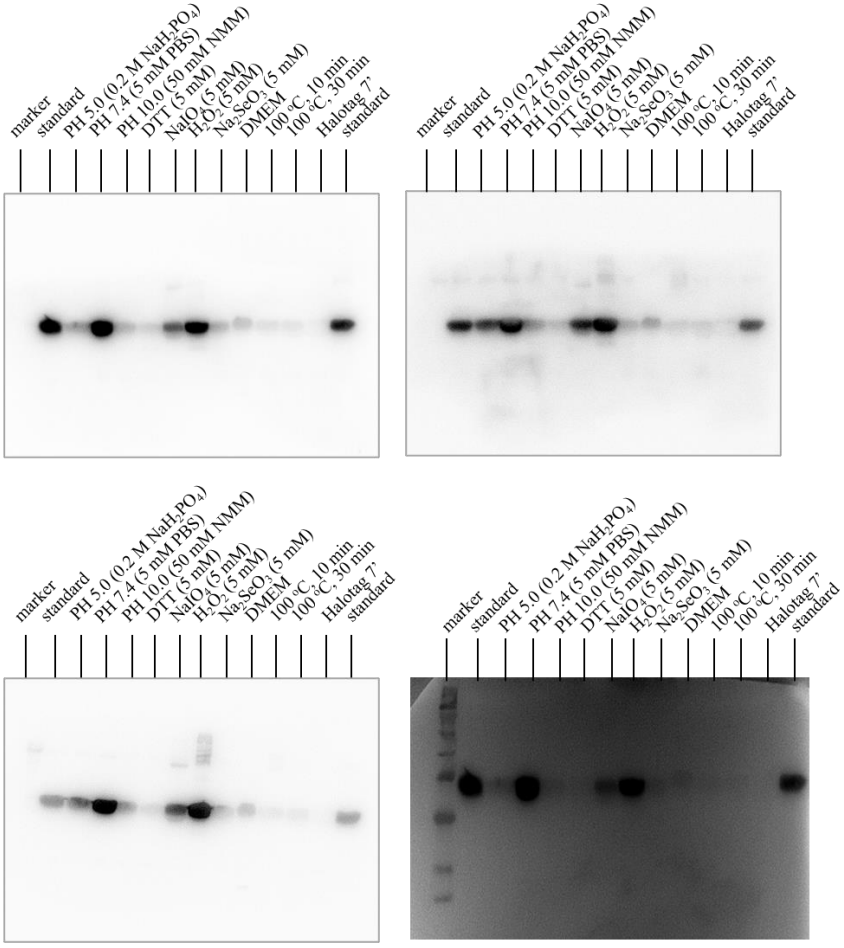


Figure S6. Blot images of the stability experiments of compound 7 under different reagents

6 Mechanistic Studies

6.1 Control Experiments

6.1.1 Cross-coupling reaction in dark

Procedure: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.3 mg, 0.3 mmol), boronic acid **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %) under an argon atmosphere in a dry box. The vial was capped with a septum, wrapped by tin foil completely and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe under the argon atmosphere, and the reaction solution was stirred at room temperature in dark for 24 h. Upon completion of the reaction, The reaction solution was concentrated and then purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 5:1) to afford product **3aa** as a light yellow solid (82.1 mg, 94% yield).

6.1.2 Cross-coupling reaction in the presence of tetramethylpiperidine *N*-oxide (TEMPO)

Procedure: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.3 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %), TEMPO (93.8 mg, 0.6 mmol, 2.0 equiv) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Upon completion of the reaction, the vial was opened to air, and the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with hexane:EtOAc = 5:1) to afford product **3aa** (78.1 mg, 89% yield).

6.1.3 Cross-coupling reaction in the presence of 1,4-Dinitrobenzene (*p*-DNB)

Procedure: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.3 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %), *p*-DNB (100.9 mg, 0.6 mmol, 2.0 equiv) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Upon completion of the reaction, the vial was opened to air, and the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with hexane:EtOAc = 5:1) to afford product **3aa** (65.7 mg, 74% yield).

6.1.4 Cross-coupling reaction in the presence of 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy)

Procedure: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.3 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %), dtbpy (8.4 mg, 10 mol %) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Product **3aa** was obtained in 18% yield determined by analysis of ^{1}H NMR of crude reaction mixture using CH_2Br_2 (7.0 μL) as internal standard.

6.1.5 Cross-coupling reaction in the presence of neocuproine

Procedure: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.3 mg, 0.3 mmol), **2a** (61.2 mg, 0.45 mmol), CuBr (2.2 mg, 5 mol %), neocuproine (6.3 mg, 10 mol %) under an argon atmosphere in a dry box. The vial was capped with a septum and removed from the dry box. *i*PrOH (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred

at room temperature under the argon atmosphere for 24 h. The desired product **3aa** was not detected by TLC.

6.2 Electron Paramagnetic Resonance (EPR) Studies of Cu(II)

All the EPR spectrums were recorded at -173 ℃. EPR spectrometer operated at 9.3044 GHz. Typical spectrometer parameters are shown as follows, scan range: 200 G; center field set: 3200.00 G; scan time: 60 s; modulation amplitude: 4.0 G; modulation frequency: 100 kHz; receiver gain: 30 db; microwave power: 2.00 mW.

CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added CuBr (7.2 mg, 0.05 mmol) and *i*PrOH (2.0 mL) under an argon atmosphere in a dry box. The vial was capped with a septum and stirred at room temperature for 12 h. The mixture was analyzed by electron paramagnetic resonance (EPR) immediately.

1a and CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (20.1 mg, 0.1 mmol), CuBr (7.2 mg, 0.05 mmol) and *i*PrOH (2.0 mL) under an argon atmosphere in a dry box. The vial was capped with a septum and stirred at room temperature for 12 h. The mixture was analyzed by electron paramagnetic resonance (EPR) immediately.

2a and CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added boronic acid **2a** (13.6 mg, 0.1 mmol), CuBr (7.2 mg, 0.05 mmol) and *i*PrOH (2.0 mL) under an argon atmosphere in a dry box. The vial was capped with a septum and stirred at room temperature for 12 h. The mixture was analyzed by electron paramagnetic resonance (EPR) immediately.

Reaction mixture: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (20.1 mg, 0.1 mmol), boronic acid **2a** (21.2 mg, 0.15 mmol), CuBr (0.7 mg, 5 mol % mmol) and

*i*PrOH (1.0 mL) under an argon atmosphere in a dry box. The vial was capped with a septum and stirred at room temperature for 12 h. The mixture was analyzed by electron paramagnetic resonance (EPR) immediately.

6.3 UV/Vis-Absorption Spectra of the Reaction Components.

CuBr in DMF (0.05 M): In a dry box, CuBr (18.0 mg, 0.125 mmol) was dissolved in dry DMF (2.5 mL). The solution was kept stirring at room temperature for 0.5 h. After the solution was transferred into a cuvette with a PTFE plug, the cuvette was then moved out from the dry box and the UV-Vis spectrum was measured immediately.

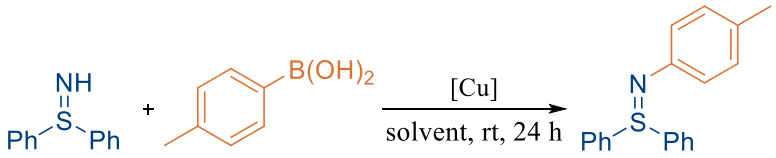
CuBr and 1a in DMF (0.05 M): In a dry box, CuBr (18.0 mg, 0.125 mmol) and *NH*-sulfilimine **1a** (50.5 mg, 0.25 mmol) were mixed in dry DMF (2.5 mL). The mixture was kept stirring at room temperature for 0.5 h. After the solution was transferred into a cuvette with a PTFE plug, the cuvette was then moved out from the dry box and the UV-Vis spectrum was measured immediately.

$CuBr_2$ in DMF (0.004 M): In a dry box, $CuBr_2$ (2.2 mg, 0.01 mmol) was dissolved in dry DMF (2.5 mL). The solution was kept stirring at room temperature for 0.5 h. After the solution was transferred into a cuvette with a PTFE plug, the cuvette was then moved out from the dry box and the UV-Vis spectrum was measured immediately.

$CuBr_2$ and 1a in DMF (0.004 M): In a dry box, $CuBr_2$ (2.2 mg, 0.01 mmol) and *NH*-sulfilimine **1a** (4.1 mg, 0.02 mmol) were mixed in dry DMF (2.5 mL). The solution was kept stirring at room temperature for 0.5 h. After the solution was transferred into a cuvette with a PTFE plug, the cuvette was then moved out from the dry box and the UV-Vis spectrum was measured immediately.

6.4 Headspace-Gas Chromatography (GC)

Table S2. Dihydrogen detection via Headspace GC.



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

entry	**1a**	**2a**	CuBr	solvent	H_2
1	✔	✔	✔	*i*PrOH	detected
2	✔	-	✔	*i*PrOH	detected
3	-	-	✔	*i*PrOH	N.D.
4	-	-	-	-	N.D.

General information of the GC headspace analysis: 0.5 mL of the gas above the liquid surface was extracted by the GC sampling needle and then was injected into a Fuli GC 9790 plus gas chromatograph equipped with an Msieve 5A packed column (Restek, 60/80 mesh, 3 m × 4 mm × 3 mm) and thermal conductivity detector. The column temperature was 50 ℃, and the temperature of inlet port and thermal conductivity detector was 120 and 150 ℃, respectively. Argon was used as carrier gas at a flow rate of 25 mL min^{-1}.

1a, 2a and CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (202.0 mg, 1.0 mmol), **2a** (204.0 mg, 1.5 mmol), CuBr (7.2 mg, 0.05 mmol, 5 mol %) under an argon atmosphere in a dry box. The vial was sealed with a cap and removed from the dry box. *i*PrOH (2.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 12 h. Then, the gas (0.5 mL) above the liquid surface was extracted by the GC sampling needle for GC analysis. Of note, to exclude the air residue in the needle head before injection, the needle was refilled with argon and injected to empty for three times. GC spectrum was recorded at room temperature on a Fuli GC 9790 plus gas chromatograph. The GC spectrum clearly showed the existence of H_2 in the sealed reaction vial (Figure S7).

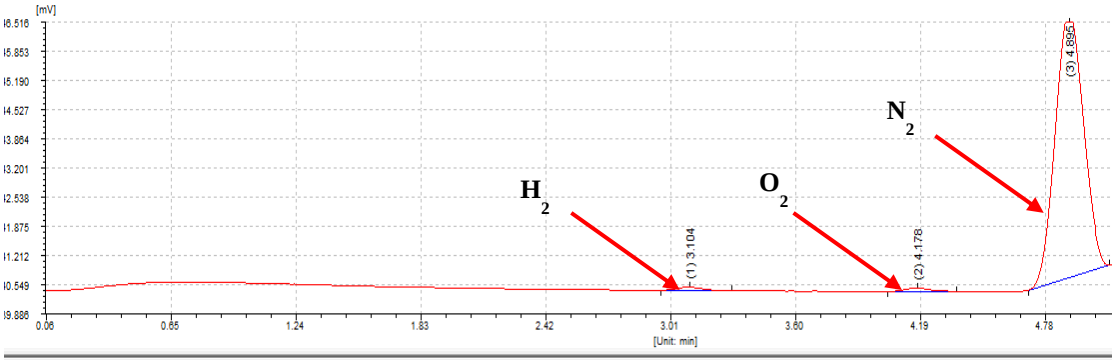


Figure S7. Headspace GC spectrum of model reaction between 1a and 2a in the sealed reaction vial.

1a and CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (202.0 mg, 1.0 mmol), CuBr (7.2 mg, 0.05 mmol, 5 mol %) under an argon atmosphere in a dry box. The vial was sealed with a cap and removed from the dry box. *i*PrOH (2.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 12 h. Then the gas above the liquid surface was extracted by the GC sampling needle for GC analysis. Of note, to exclude the air residue in the needle head before injection, the needle was refilled with argon and injected to be empty for three times. GC spectrum was recorded at room temperature on a Fuli GC 9790 plus gas chromatograph. The GC spectrum clearly showed the existence of H_2 in the sealed reaction vial with the *i*PrOH solution of **1a** and CuBr (Figure S8).

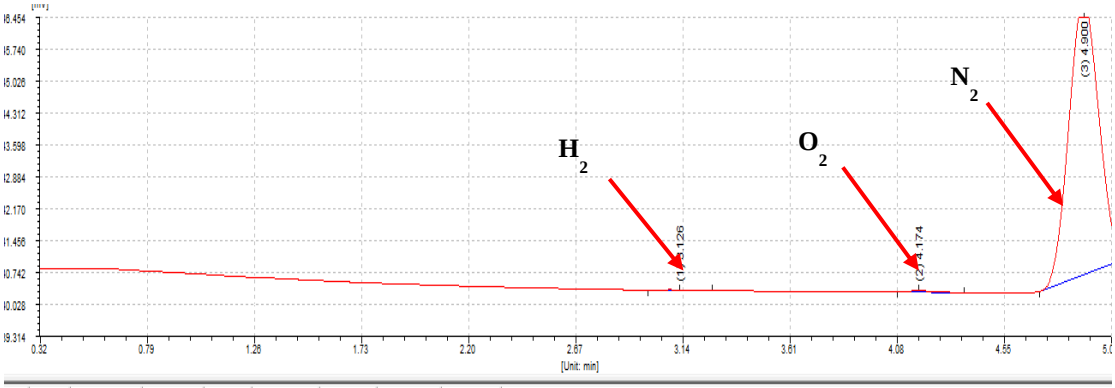


Figure S8. Headspace GC spectrum of 1a and CuBr in *i*PrOH in the sealed reaction vial.

CuBr in *i*PrOH: To an oven-dried microwave vial equipped with a stir bar was added CuBr (7.2 mg, 0.05 mmol, 5 mol %) under an argon atmosphere in a dry box. The vial was sealed with a cap and removed from the dry box. *i*PrOH (2.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 12 h. Then the gas above the liquid surface was extracted by the GC sampling needle for GC analysis. Of note, to exclude the air residue in the needle head before injection, the needle was refilled with argon and injected to be empty for three times. GC spectrum was recorded at room temperature on a Fuli GC 9790 plus gas chromatograph. No H_2 signal was observed in the sealed vial with the *i*PrOH solution of CuBr (Figure S9).

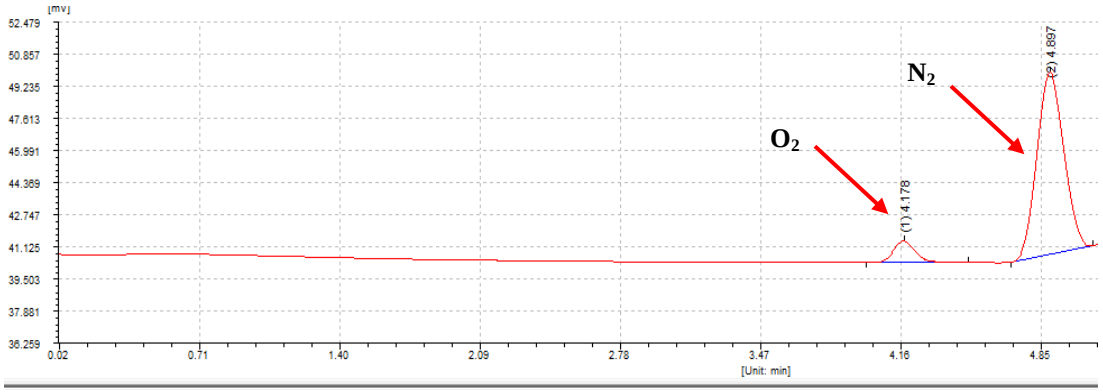


Figure S9. Headspace GC spectrum of CuBr in *i*PrOH in the sealed reaction vial.

A control experiment with no solvent under other identical conditions was carried out and analyzed by headspace GC (Figure S10). There was no H_2 detected, ruling out the possibility that dihydrogen might be incorporated by analysis process. Furthermore, signals of O_2 and N_2 were still observed, indicating that both of them should be attributed to the residue of air in the needle.

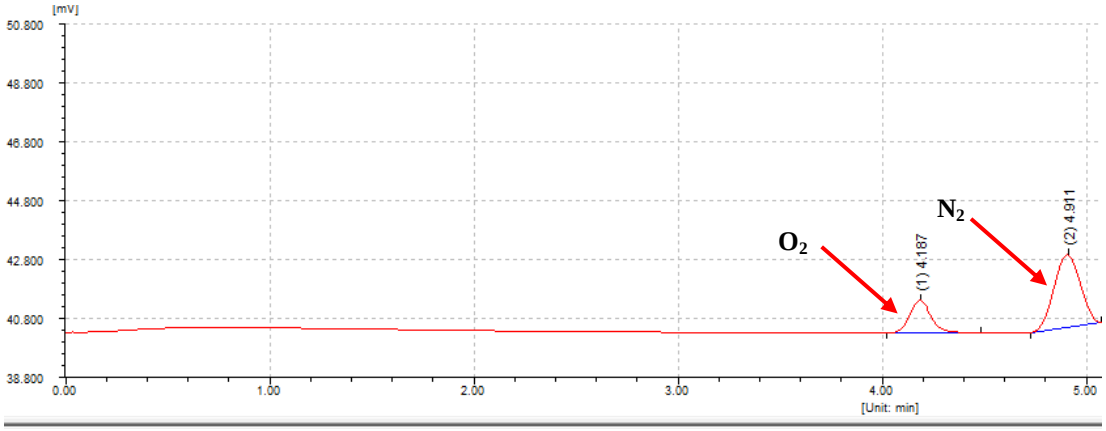


Figure S10. Headspace GC spectrum of model reaction between 1a and 2a in the sealed reaction vial with no solvent.

6.5 Mass spectrum of the H_2 and HD.

Procedure of Catalysis in CD_3OD: To an oven-dried microwave vial equipped with a stir bar was added sulfilimine **1a** (60.6 mg, 0.3 mmol), **2a** (61.2 mg, 1.5 mmol), CuBr (2.2 mg, 0.015 mmol, 5 mol %) under an argon atmosphere in a dry box. The vial was sealed and removed from the dry box. CD_3OD (3.0 mL) was added into the reaction vial via syringe, and the reaction solution was stirred at room temperature under the argon atmosphere for 24 h. Upon completion of the reaction, the gas above the liquid surface was transferred to a gas sampling bag (5 mL, single valve) via syringe. The collected gaseous content was analyzed using a Hiden Analytical HPR-20 QIC mass spectrometer. A typical mass spectrum was shown in Figure S11, and indeed signals at *m/z* = 2 (H_2 or D^+) and *m/z* = 3 (HD) were observed, which confirmed the generation of H_2 and HD. Proton on free sulfilimines (NH) could undergo H-D exchange with CD_3OD, leading to the formation of H_2. The presence of HD strongly revealed that one H of H_2 is from NH-sulfilimine and the other H atom is from alcoholic solvent.

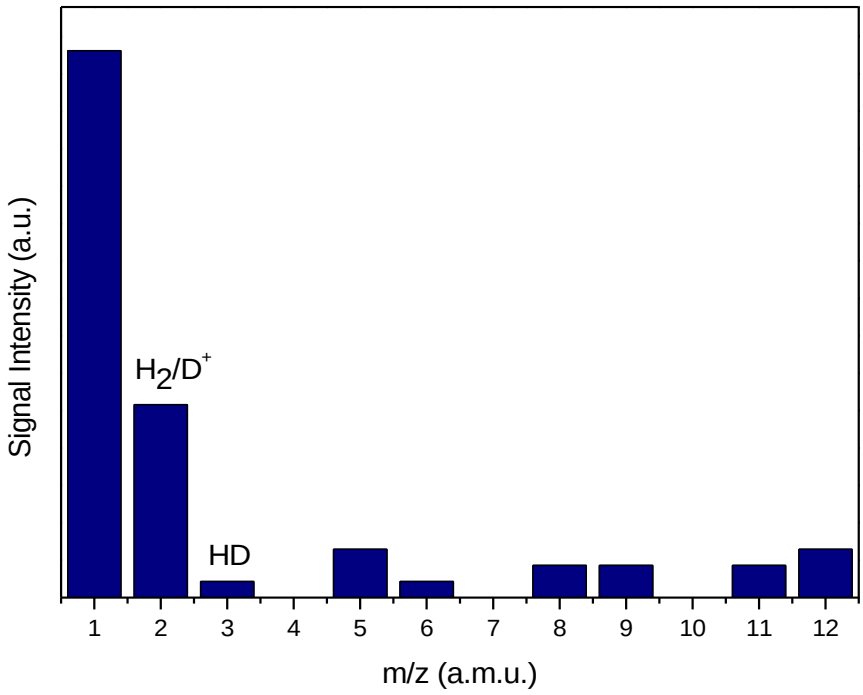


Figure S11. Mass spectrum of H_2 and HD generated from the model reaction between 1a and 2a in CD_3OD.

To further verify the generation of HD, we monitored the fluctuation of mass signal intensity at *m/z* = 2 and *m/z* = 3 when mass spectrometer was intermittently connected to the gas sampling bag (Figure S12). When the valve of sampling bag was opened to mass spectrometer for 5 seconds, both of the signals of *m/z* = 2 and *m/z* = 3 were enhanced. After 9 min, the process was repeated, and the same phenomenon was observed, which indicates the existence of H_2 and HD in the valved air bag.

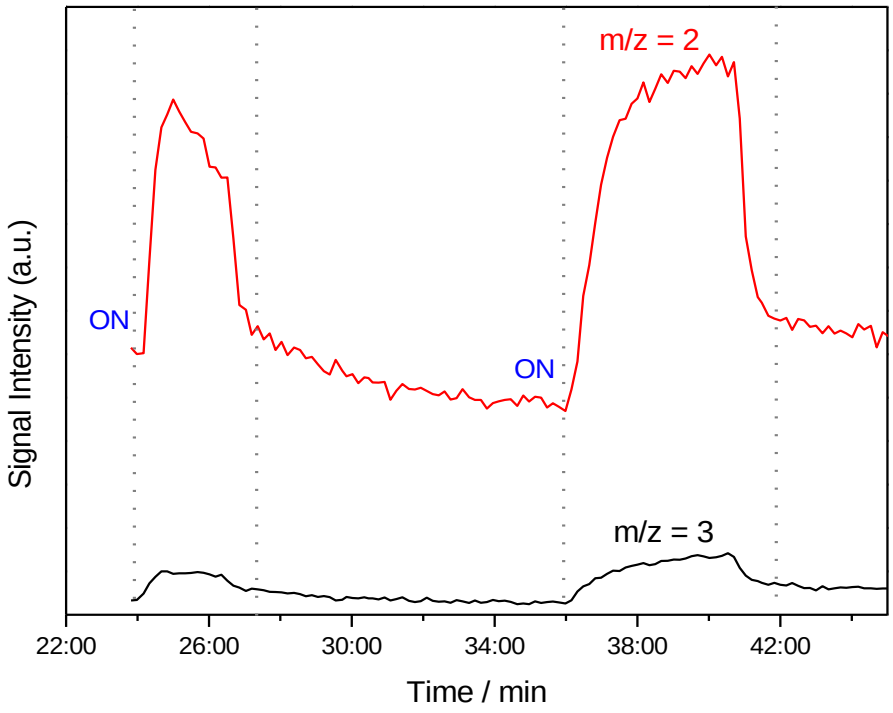


Figure S12. Monitoring H_2 and HD when the air bag was open/closed to mass spectrometer intermittently.

7 Computational Studies

Optimizations and calculations of vibrational frequencies of the transition states, starting materials, products, and intermediates were done with unrestricted DFT in Gaussian 16[6] using a UBP86[7] functional with a GD3 empirical dispersion and split basis set [6-311G(d,p) for C, S, O, H, N and SDD for Cu] in the gas phase. Single points energies were calculated with SMD-solvation model.[8] The default grid spacing from Gaussian 16 was employed (99,590 grid). Optimizations and calculations vibrational frequencies of the species in the Born-Haber cycle were performed with UB3LYP[9] and split basis set (6-31G(d) for C, S, H, N and SDD for Cu). For all species, the correct multiplicities from the unrestricted calculations were confirmed. Vibrational frequencies were computed to obtain thermal Gibbs free energy corrections (at 298 K) and to characterize the stationary points as transition states (one and only one imaginary frequency) or minima (zero imaginary frequencies). For each frequency

job, it was confirmed that convergence fully occurred. Transition states were confirmed by intrinsic reaction coordinate analysis. Conformational analysis was performed manually. Graphics were made in Cylview.[10]

A Born-Haber cycle (Figure S13) was used to determine the redox potential of Cu^{+} and **1a** following a literature procedure.[11] The redox potential indicates that Cu^{+} to Cu^{2+} is spontaneous in the presence of *NH*-sulfilimines.

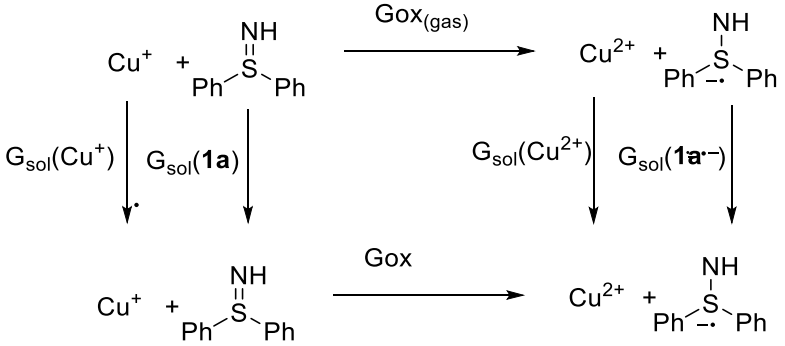


Figure S13. Born-Haber Cycle. Energies were computed using B3LYP/6-31G(d), Cu:SDD.

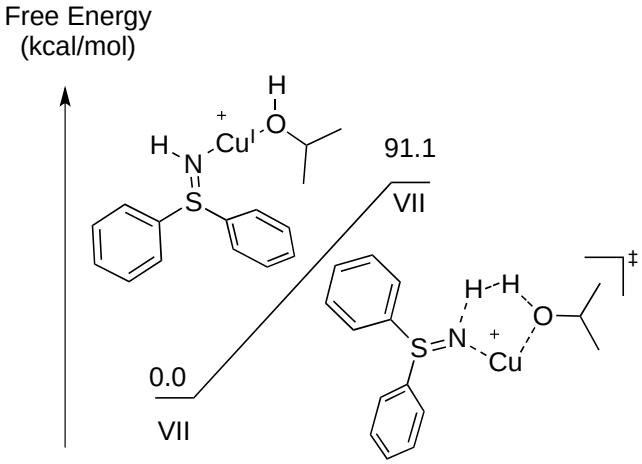
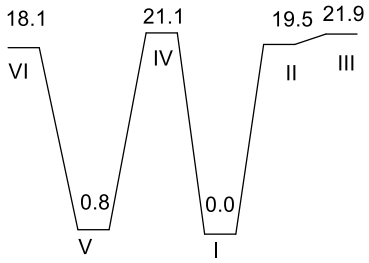


Figure S14. Five-membered transition state computed pathways. Free energies were computed using SMD-2-propanol-BP86-d3/6-311G(d,p), Cu:SDD//BP86-d3/6-311G(d,p), Cu:SDD.

A five-membered transition state (Figure S14) was calculated. This transition state has a barrier of 91.1 kcal/mol excluding it from being a possible mechanism for the formation of hydrogen.

Coordinates and thermochemical data computed starting materials, intermediates, and transition states

Pathways



I

Zero-point correction = 0.297610 (Hartree/Particle)

Thermal correction to Energy = 0.319288

Thermal correction to Enthalpy = 0.320232

Thermal correction to Gibbs Free Energy = 0.241265

Sum of electronic and zero-point Energies = -1308.310810

Sum of electronic and thermal Energies = -1308.289132

Sum of electronic and thermal Enthalpies = -1308.288187

Sum of electronic and thermal Free Energies = -1308.367154

Electronic energy -1308.705064

1 3

S	0.48355100	0.43220100	0.37045200
N	-0.10160900	1.24091500	-1.03165900
C	-3.11673300	0.73653600	1.30788900

H	-2.46319800	1.61016800	1.46262000
Cu	-2.00090300	1.29866100	-1.50182600
H	0.50519900	0.96743000	-1.82856800
O	-2.47378300	0.06869600	0.13622500
H	-3.02493700	-0.69594200	-0.12832900
C	2.25155800	0.75886000	0.31341800
C	2.70665000	1.85204400	1.07225000
C	3.11196200	0.01134800	-0.51052500
C	4.06216700	2.18960000	1.01080900
H	2.01779200	2.42213100	1.69988300
C	4.46269500	0.36480900	-0.55460500
H	2.73761200	-0.84053400	-1.08251300
C	4.93648200	1.45052000	0.20035200
H	4.43543600	3.02972500	1.59984600
H	5.14940000	-0.21038200	-1.17917100
H	5.99387400	1.71988200	0.15688900
C	0.42113600	-1.36258000	0.05455300
C	0.91821900	-2.21002500	1.05418800
C	-0.15925600	-1.85427200	-1.11831400
C	0.84216000	-3.59352100	0.85429100

H	1.37129900	-1.80535100	1.96275400
C	-0.22919300	-3.24268300	-1.30081000
H	-0.55251700	-1.17105400	-1.87674700
C	0.27020500	-4.10811500	-0.31882500
H	1.23173400	-4.26922800	1.61862500
H	-0.67254500	-3.64379400	-2.21481700
H	0.21418500	-5.18858300	-0.46686400
C	-3.02586600	-0.21581400	2.49257100
H	-3.39681600	0.28292400	3.40159300
H	-3.64612000	-1.11222100	2.32608500
H	-1.98641400	-0.53091500	2.66481500
C	-4.52817500	1.18022800	0.95052400
H	-4.97209000	1.74202500	1.78684700
H	-4.51947500	1.82908600	0.06034400
H	-5.17557000	0.31065600	0.74763900

II

Zero-point correction = 0.288817 (Hartree/Particle)

Thermal correction to Energy = 0.311376

Thermal correction to Enthalpy = 0.312320

Thermal correction to Gibbs Free Energy = 0.232607

Sum of electronic and zero-point Energies = -1308.281839

Sum of electronic and thermal Energies = -1308.259280

Sum of electronic and thermal Enthalpies = -1308.258336

Sum of electronic and thermal Free Energies = -1308.338049

Electronic energy -1308.665374

1 3

Cu	-1.46327600	-1.64971800	0.02914100
H	-4.63589100	-3.34627400	-0.82337200
H	-3.87546100	-2.31758500	0.14849200
O	-3.30375300	-1.61134900	0.54400800
N	0.28239200	-1.72794200	-0.36404700
S	1.01374000	-0.44279900	-1.02459600
C	-4.03211900	-0.29971500	0.49382200
H	-5.01007300	-0.50229100	0.96011500
C	-4.18382700	0.13938300	-0.95516200
H	-4.73511100	-0.60473000	-1.55109200
H	-4.73567000	1.09060500	-1.00744700
H	-3.18774400	0.29000800	-1.40551300
C	-3.21787300	0.65534200	1.34982400
H	-3.73718100	1.62222500	1.42535500

H	-3.07466800	0.25212200	2.36205700
H	-2.23087200	0.84278700	0.89228500
C	2.70896700	-0.41825200	-0.35209800
C	3.14249900	-1.49032700	0.43164500
C	3.53783100	0.65703000	-0.69820600
C	4.46160500	-1.46660800	0.90525900
H	2.46312600	-2.31471000	0.65794600
C	4.85075000	0.65975500	-0.21340000
H	3.17093900	1.47892300	-1.31792900
C	5.31032800	-0.39845600	0.58468800
H	4.82267400	-2.28852900	1.52718400
H	5.51545000	1.48844400	-0.46611500
H	6.33748300	-0.39074900	0.95553100
C	0.34475100	1.14756600	-0.42081000
C	-0.49579700	1.85624000	-1.29032700
C	0.58439400	1.56589000	0.89597900
C	-1.10759300	3.02797500	-0.82372900
H	-0.65789900	1.51048500	-2.31447100
C	-0.03581800	2.73753200	1.34436100
H	1.25180400	0.99606200	1.54645600

C	-0.87712900	3.46551300	0.48780200
H	-1.75225900	3.60390300	-1.49117600
H	0.14320900	3.08549600	2.36411600
H	-1.34924200	4.38360600	0.84439400

III

Zero-point correction = 0.285268 (Hartree/Particle)

Thermal correction to Energy = 0.306886

Thermal correction to Enthalpy = 0.307830

Thermal correction to Gibbs Free Energy = 0.230148

Sum of electronic and zero-point Energies = -1308.281905

Sum of electronic and thermal Energies = -1308.260287

Sum of electronic and thermal Enthalpies = -1308.259343

Sum of electronic and thermal Free Energies = -1308.337025

Electronic energy -1308.659041

1 3

S	1.12554500	-0.33141100	-1.07135000
N	0.33585900	-1.64130700	-0.54119200
C	0.43685800	1.20575000	-0.37689300
C	-0.07494100	2.15393200	-1.27052400
C	-0.69370900	3.29769700	-0.74531100

C	-0.79854400	3.46502400	0.64180100
C	-0.28275300	2.49678500	1.51996000
C	0.34199200	1.35243500	1.01528400
C	2.77720600	-0.40237300	-0.28925300
C	3.20914200	-1.61340300	0.25705100
C	4.49792100	-1.66132700	0.80627900
C	5.31980800	-0.52629400	0.78681000
C	4.86220900	0.67225800	0.22055200
C	3.57837500	0.74543400	-0.33326200
H	0.01070300	2.01006100	-2.35034200
H	-1.08964800	4.05703700	-1.42297000
H	-1.28032200	4.35859100	1.04477700
H	-0.36046100	2.63806000	2.60027300
H	0.75921700	0.59418600	1.68222400
H	2.55157600	-2.48487900	0.25876200
H	4.85557300	-2.59231500	1.25123400
H	6.32359500	-0.57524200	1.21405400
H	5.50430100	1.55536400	0.20476100
H	3.21291200	1.67758600	-0.77045800
H	-4.33715300	-3.26593600	0.78046400

H	-3.75294700	-2.38882500	0.63824000
O	-3.17929600	-1.46487200	0.38484100
C	-4.13970800	-0.43536700	-0.09799300
H	-4.63832100	-0.85888400	-0.98605500
C	-5.13688800	-0.15704400	1.01524600
H	-4.62259900	0.23338300	1.90643900
H	-5.87591000	0.58615000	0.67826300
H	-5.68642100	-1.06963200	1.29589200
C	-3.29692800	0.77309100	-0.49354000
H	-2.62764600	0.53777700	-1.33651200
H	-3.95923100	1.59511300	-0.80541400
H	-2.68801000	1.11937000	0.35640500
Cu	-1.40775300	-1.63502900	-0.14917400

IV

Zero-point correction = 0.290859 (Hartree/Particle)

Thermal correction to Energy = 0.312629

Thermal correction to Enthalpy = 0.313573

Thermal correction to Gibbs Free Energy = 0.233565

Sum of electronic and zero-point Energies = -1308.277119

Sum of electronic and thermal Energies = -1308.255349

Sum of electronic and thermal Enthalpies = -1308.254405

Sum of electronic and thermal Free Energies = -1308.334413

Electronic energy -1308.663761

1 3

S	-0.63164100	-0.22031300	0.51886200
N	0.54561700	-0.35474200	-0.66853300
C	-1.51673800	1.37688900	0.41394200
C	-0.92637400	2.48341700	-0.20474300
C	-1.60893600	3.70755600	-0.18085900
C	-2.84852900	3.81377200	0.46292400
C	-3.41666300	2.69529600	1.08929100
C	-2.75081500	1.46483800	1.07827000
C	-1.92070900	-1.40901400	0.09837800
C	-2.68730700	-1.22467600	-1.06401800
C	-3.63582900	-2.19764600	-1.38931300
C	-3.79833800	-3.32916600	-0.57398700
C	-3.01379600	-3.49772900	0.57574400
C	-2.05617700	-2.53661400	0.92141900
H	0.03563700	2.39660100	-0.71763800
H	-1.16781200	4.57590500	-0.67460200

H	-3.37463200	4.77055100	0.47613900
H	-4.38366600	2.77610600	1.59011200
H	-3.19610200	0.59049400	1.55798900
H	-2.55382300	-0.33675800	-1.68529200
H	-4.24756500	-2.07357200	-2.28548500
H	-4.54142700	-4.08450600	-0.83827900
H	-3.14717300	-4.37708400	1.20920500
H	-1.44011300	-2.65645100	1.81532100
H	0.71966100	0.65765000	-1.63844900
Cu	2.20991700	0.63244200	-1.05887900
O	3.93618500	0.45589700	-0.13011600
C	4.39020300	-0.90684600	0.31124900
H	4.13598900	1.09731300	0.58026700
H	4.26806400	-1.49790600	-0.60949000
C	5.85667900	-0.81127000	0.70101000
C	3.46708400	-1.42087000	1.40673300
H	6.24349300	-1.81473900	0.93604400
H	6.45691800	-0.39079000	-0.11810200
H	5.98730200	-0.18735800	1.60199600
H	2.42418300	-1.43623900	1.05331000

H	3.75297900	-2.44617000	1.68823400
H	3.53543000	-0.79046900	2.30884900

V

Zero-point correction = 0.292573 (Hartree/Particle)

Thermal correction to Energy = 0.314637

Thermal correction to Enthalpy = 0.315581

Thermal correction to Gibbs Free Energy = 0.234537

Sum of electronic and zero-point Energies = -1308.313475

Sum of electronic and thermal Energies = -1308.291410

Sum of electronic and thermal Enthalpies = -1308.290466

Sum of electronic and thermal Free Energies = -1308.371511

Electronic energy -1308.697009

1 3

S	0.99935800	-0.09879400	-1.07775300
N	-0.44648200	-0.70445800	-0.67949900
C	1.33701300	1.47958600	-0.23461700
C	1.20765500	2.64602900	-0.99734100
C	1.37041300	3.87901400	-0.35258700
C	1.64553400	3.92257600	1.02085800
C	1.76431800	2.73781300	1.76408300

C	1.60666300	1.49580900	1.14017200
C	2.25144500	-1.21335300	-0.36185300
C	1.84484400	-2.41885600	0.21557900
C	2.83552200	-3.27358400	0.71756400
C	4.18893300	-2.92116700	0.62410600
C	4.56831300	-1.70918600	0.02870300
C	3.59676500	-0.83958100	-0.47995800
H	0.98871200	2.59817400	-2.06637700
H	1.28572900	4.80348600	-0.92744400
H	1.77238800	4.88715300	1.51720800
H	1.98018400	2.77917000	2.83393800
H	1.70550500	0.56475600	1.70231700
H	0.78473100	-2.67381700	0.26953900
H	2.54403800	-4.21723500	1.18364500
H	4.95377000	-3.59549700	1.01505000
H	5.62340400	-1.43810800	-0.04608500
H	3.88347600	0.10904100	-0.94007100
H	-1.76061300	1.77655600	-0.48795600
H	-4.40991400	1.05945100	-0.23707500
O	-3.99526300	0.19604400	-0.42400000

C	-4.70219100	-0.88576000	0.32819200
H	-5.73438100	-0.88338300	-0.06027700
C	-3.99725700	-2.17598300	-0.05583800
H	-2.95979200	-2.18574600	0.32521800
H	-4.52047600	-3.03644100	0.38625100
H	-3.97842400	-2.30408600	-1.14792900
C	-4.66936700	-0.57494600	1.81793500
H	-5.16437000	0.38237800	2.04587400
H	-5.19250700	-1.36293600	2.38135900
H	-3.62678600	-0.52736700	2.17367400
Cu	-2.00581200	0.25232900	-0.53718200

VI

Zero-point correction = 0.287155 (Hartree/Particle)

Thermal correction to Energy = 0.308516

Thermal correction to Enthalpy = 0.309461

Thermal correction to Gibbs Free Energy = 0.230371

Sum of electronic and zero-point Energies = -1308.282807

Sum of electronic and thermal Energies = -1308.261445

Sum of electronic and thermal Enthalpies = -1308.260501

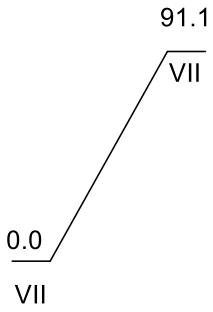
Sum of electronic and thermal Free Energies = -1308.339591

Electronic energy -1308.665335

1 3

S	1.12742200	-0.14150400	-1.14739400
N	-0.14732400	-1.06653700	-0.75389600
C	0.98839000	1.47702300	-0.33094100
C	0.50661900	2.53565200	-1.11204400
C	0.21295100	3.74802000	-0.47481100
C	0.39508100	3.87558500	0.90944700
C	0.88310900	2.80021300	1.66945900
C	1.18286500	1.58084600	1.05356200
C	2.58312500	-0.89601100	-0.35710800
C	2.44911800	-2.12126000	0.30142900
C	3.59870200	-2.68655300	0.86954900
C	4.83566700	-2.03564500	0.76269800
C	4.94011300	-0.81122400	0.08621500
C	3.80736000	-0.22791200	-0.49298900
H	0.36361900	2.42107300	-2.18927900
H	-0.15282900	4.59227700	-1.06279200
H	0.16201200	4.82276600	1.40073000
H	1.03014900	2.91038800	2.74608200

H	1.56418500	0.73450400	1.62910700
H	1.47605700	-2.61224000	0.36347200
H	3.52205700	-3.63901000	1.39823900
H	5.72582700	-2.48641300	1.20644200
H	5.90576600	-0.30886600	0.00057200
H	3.87952800	0.72569400	-1.02158300
H	-1.98428700	1.25035000	0.35079100
H	-2.89175700	0.98101200	0.17487800
O	-3.67406500	0.04376900	-0.38691000
C	-4.56498400	-0.70630700	0.48892000
H	-5.46473500	-0.07794300	0.60272000
C	-4.90479200	-2.01227900	-0.22970300
H	-3.99616500	-2.62801400	-0.34468200
H	-5.64210200	-2.58372600	0.35554200
H	-5.32560200	-1.81164000	-1.22485200
C	-3.91576600	-0.93586100	1.85876000
H	-3.66096100	0.01951300	2.34186100
H	-4.60382500	-1.48699000	2.51701300
H	-2.99463400	-1.53888000	1.75243400
Cu	-1.81078000	-0.39344500	-0.49243100



VII

Zero-point correction = 0.300550 (Hartree/Particle)

Thermal correction to Energy = 0.321217

Thermal correction to Enthalpy = 0.322161

Thermal correction to Gibbs Free Energy = 0.249829

Sum of electronic and zero-point Energies = -1308.425232

Sum of electronic and thermal Energies = -1308.404565

Sum of electronic and thermal Enthalpies = -1308.403621

Sum of electronic and thermal Free Energies = -1308.475953

Electronic energy -1308.814976

1 1

Cu	0.99819600	-1.51774900	-0.83352700
H	-0.46720100	-1.08122300	-2.90131400
H	2.78463000	-2.98286400	0.13044800
O	2.20635600	-2.26679300	0.45507900
N	-0.15637000	-0.68348100	-2.01034600

S	-1.21090800	0.51461200	-1.57978400
C	3.02290200	-1.32742100	1.29776700
H	3.52242900	-1.97556400	2.03673000
C	2.02674800	-0.40941200	1.98609200
H	1.27956100	-0.99161100	2.54423900
H	2.55460000	0.24782700	2.69278700
H	1.51521100	0.23439000	1.25007700
C	4.03222600	-0.60292100	0.41963900
H	4.64537700	0.07755400	1.03057400
H	4.71161300	-1.30587000	-0.08713000
H	3.50261700	-0.00542700	-0.34071100
C	-0.11445700	1.60387300	-0.61185400
C	1.18497600	1.80088600	-1.10266900
C	-0.57990700	2.26358500	0.53280400
C	2.04534300	2.65727900	-0.40450700
H	1.51457500	1.27731900	-2.00217900
C	0.29663400	3.11498400	1.21870600
H	-1.59698500	2.10851100	0.89662100
C	1.60492500	3.30929800	0.75551500
H	3.05962100	2.81910000	-0.77596600

H	-0.05014300	3.62723600	2.11863600
H	2.27928900	3.97811400	1.29472000
C	-2.36303400	-0.05254000	-0.28843200
C	-3.72431100	0.18062300	-0.52290200
C	-1.91309900	-0.74211600	0.84596100
C	-4.65733600	-0.28037700	0.41733100
H	-4.05262000	0.71323900	-1.41916400
C	-2.85374200	-1.20332000	1.76981500
H	-0.84346800	-0.91139300	1.00441900
C	-4.22287300	-0.97043500	1.55564600
H	-5.72245100	-0.10479000	0.25302100
H	-2.52249000	-1.74312600	2.65970100
H	-4.95356000	-1.33369700	2.28162600

VIII

Zero-point correction = 0.287650 (Hartree/Particle)

Thermal correction to Energy = 0.308942

Thermal correction to Enthalpy = 0.309886

Thermal correction to Gibbs Free Energy = 0.232538

Sum of electronic and zero-point Energies = -1308.260799

Sum of electronic and thermal Energies = -1308.239506

Sum of electronic and thermal Enthalpies = -1308.238562

Sum of electronic and thermal Free Energies = -1308.315910

Electronic energy -1308.652422

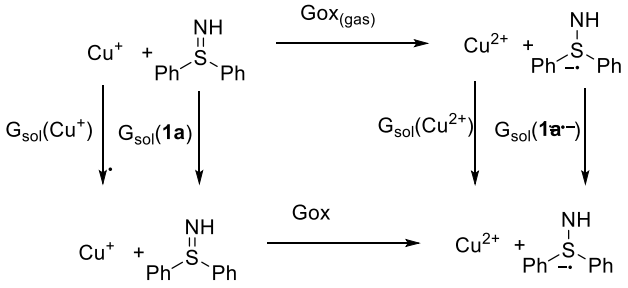
1 1

Cu	1.93190700	-0.05307100	-0.45527200
H	1.24897800	-2.10123000	0.80979200
H	2.07684100	-1.97167300	1.04911100
O	3.18242400	-0.79767900	0.73497800
N	0.33098800	-0.90392900	-0.28644300
S	-0.79146700	-0.27107700	0.75028300
C	4.59470600	-0.82780500	0.54130600
H	5.07718500	-0.83435100	1.53601800
C	4.94341700	0.49159800	-0.17561000
H	4.63278500	1.36025400	0.42283700
H	6.02812400	0.55379700	-0.35979600
H	4.44925800	0.52803200	-1.17026600
C	5.00253900	-2.05719100	-0.27354500
H	6.09418400	-2.09344100	-0.41280500
H	4.68610300	-2.97572400	0.24245400
H	4.51937300	-2.02964800	-1.26472300

C	-2.35073900	-1.11296500	0.32194000
C	-2.33384000	-2.15685000	-0.60607600
C	-3.50967300	-0.70175000	0.99335000
C	-3.54666900	-2.80217000	-0.88566400
H	-1.40021700	-2.45005700	-1.09014500
C	-4.70842100	-1.35955100	0.69416200
H	-3.48758400	0.11361000	1.72039400
C	-4.72573100	-2.40568500	-0.24020200
H	-3.56443400	-3.61610300	-1.61351000
H	-5.62723200	-1.05686700	1.20060200
H	-5.66462000	-2.91689100	-0.46303200
C	-1.08861300	1.44949200	0.26305000
C	-0.52196400	2.44525900	1.07210500
C	-1.78174200	1.73679600	-0.92209200
C	-0.66695400	3.78094300	0.67608800
H	0.00749100	2.18742700	1.99266800
C	-1.91609800	3.07798600	-1.29599600
H	-2.21857600	0.93555900	-1.52192800
C	-1.35962200	4.09346300	-0.50244600
H	-0.24825200	4.57606800	1.29646300

H	-2.45808600	3.32965500	-2.21012400
H	-1.47305200	5.13740100	-0.80259600

Born-Haber cycle



1a

Zero-point correction = 0.197307 (Hartree/Particle)

Thermal correction to Energy = 0.209458

Thermal correction to Enthalpy = 0.210402

Thermal correction to Gibbs Free Energy = 0.156931

Sum of electronic and zero-point Energies = -916.558124

Sum of electronic and thermal Energies = -916.545973

Sum of electronic and thermal Enthalpies = -916.545028

Sum of electronic and thermal Free Energies = -916.598499

0 1

N	0.09487100	2.59831400	-0.13802500
S	0.01632900	1.22558700	-0.97452200
C	-1.38826300	0.26218300	-0.29121600
C	-1.95904400	0.69017200	0.90494100

C	-3.05040500	-0.00703800	1.42404900
C	-3.56914600	-1.11063000	0.74100200
C	-3.00252800	-1.51532400	-0.46939300
C	-1.90841200	-0.82415400	-0.99532100
H	-1.48032400	-1.12272700	-1.94906500
H	-3.41758500	-2.36117200	-1.01096400
H	-4.42325100	-1.64731300	1.14519700
H	-3.50057600	0.31368400	2.35991200
H	-1.54710000	1.57136000	1.39017800
C	1.38300900	0.19939100	-0.31460000
C	2.22778300	0.77769700	0.62787600
C	3.30735900	0.03843000	1.11685400
C	3.53912300	-1.25802700	0.65425100
C	2.68950700	-1.82173500	-0.30155700
C	1.60586000	-1.09311500	-0.79284200
H	0.94717100	-1.53269300	-1.53649700
H	2.87217400	-2.82807900	-0.66875800
H	4.38349200	-1.82828600	1.03204800
H	3.96928800	0.47846800	1.85816500
H	2.01746100	1.79323500	0.95242100

H 0.00484000 3.33884600 -0.83836500

1a solvated

Zero-point correction = 0.197158 (Hartree/Particle)

Thermal correction to Energy = 0.209423

Thermal correction to Enthalpy = 0.210367

Thermal correction to Gibbs Free Energy = 0.156642

Sum of electronic and zero-point Energies = -916.574621

Sum of electronic and thermal Energies = -916.562355

Sum of electronic and thermal Enthalpies = -916.561411

Sum of electronic and thermal Free Energies = -916.615136

0 1

N 0.13513100 2.63712700 0.04512800

S 0.02190800 1.30363000 -0.85942400

C -1.38497100 0.32030300 -0.23398300

C -1.78287100 0.45142600 1.09748100

C -2.87973100 -0.27969400 1.55339000

C -3.57285900 -1.12554100 0.68034000

C -3.17499200 -1.23617600 -0.65326800

C -2.07759600 -0.50584400 -1.12030500

H -1.77530900 -0.57722800 -2.16199500

H	-3.72156500	-1.88154700	-1.33565800
H	-4.42906700	-1.69043500	1.03925600
H	-3.19593500	-0.18841600	2.58922900
H	-1.24740200	1.12904100	1.75655100
C	1.37820800	0.20853000	-0.29911100
C	2.34242900	0.73627800	0.55514200
C	3.41638900	-0.06676100	0.95047300
C	3.52253500	-1.37762400	0.48211300
C	2.55229800	-1.89148000	-0.38448600
C	1.47394100	-1.09984900	-0.78182600
H	0.72122500	-1.50444500	-1.45290500
H	2.63462200	-2.91009700	-0.75418600
H	4.36080400	-1.99846600	0.78689700
H	4.16952500	0.33571700	1.62299400
H	2.23759000	1.76127900	0.89893400
H	0.07238200	3.40521600	-0.62998500

Radical anion of **1a**

Zero-point correction = 0.191260 (Hartree/Particle)

Thermal correction to Energy = 0.204240

Thermal correction to Enthalpy = 0.205185

Thermal correction to Gibbs Free Energy = 0.149974

Sum of electronic and zero-point Energies = -916.541147

Sum of electronic and thermal Energies = -916.528166

Sum of electronic and thermal Enthalpies = -916.527222

Sum of electronic and thermal Free Energies = -916.582433

-1 2

N	-0.10436500	2.67463200	0.45051500
S	-0.00608800	1.47675900	-0.66942900
C	-1.45121300	0.47880500	-0.25896800
C	-1.85183600	0.28753400	1.08997100
C	-2.77091900	-0.70274900	1.40702100
C	-3.33269100	-1.52397600	0.41181500
C	-2.93955200	-1.32858800	-0.92812900
C	-2.00258700	-0.35886900	-1.25678400
H	-1.69483000	-0.22406000	-2.29345400
H	-3.38273500	-1.93628300	-1.71725300
H	-4.05464500	-2.29531300	0.67071000
H	-3.08145100	-0.82983100	2.44488300
H	-1.45679700	0.95928600	1.84583700
C	1.42111300	0.45070400	-0.25828600

C	1.83425500	0.28302700	1.08897600
C	2.79197000	-0.66729700	1.41122100
C	3.38236000	-1.47238700	0.41773100
C	2.97863700	-1.29924500	-0.92282700
C	2.00678900	-0.36651800	-1.25585400
H	1.69415900	-0.24732800	-2.29340200
H	3.44068500	-1.89791900	-1.70832700
H	4.13619300	-2.21215300	0.67795900
H	3.10845800	-0.77876700	2.44919200
H	1.41028600	0.94762800	1.83777100
H	0.31068400	3.48152500	-0.03197800

Solvated radical anion of **1a**

Zero-point correction = 0.191820 (Hartree/Particle)

Thermal correction to Energy = 0.204764

Thermal correction to Enthalpy = 0.205708

Thermal correction to Gibbs Free Energy = 0.150755

Sum of electronic and zero-point Energies = -916.623702

Sum of electronic and thermal Energies = -916.610759

Sum of electronic and thermal Enthalpies = -916.609815

Sum of electronic and thermal Free Energies = -916.664767

-1 2

N	-0.08076200	2.67831600	0.69959800
S	-0.00781800	1.55531100	-0.50439600
C	-1.43775600	0.51901900	-0.16631000
C	-1.74510500	0.06873100	1.14996600
C	-2.65184600	-0.96955700	1.33605600
C	-3.28835800	-1.58551500	0.24543300
C	-2.99205800	-1.13410700	-1.05982400
C	-2.07049800	-0.11673000	-1.26457400
H	-1.83853100	0.21040500	-2.27734500
H	-3.49586600	-1.58053500	-1.91552700
H	-4.00001200	-2.39158400	0.40309600
H	-2.88597800	-1.29538400	2.34897400
H	-1.30146600	0.56884900	2.00590600
C	1.40938700	0.49096800	-0.19696000
C	1.79715400	0.12207700	1.12014500
C	2.73659400	-0.88558100	1.31400500
C	3.32941000	-1.54421900	0.22377300
C	2.95764400	-1.16777200	-1.08581800
C	2.00474300	-0.18021200	-1.29452500

H	1.71552500	0.09082600	-2.30941200
H	3.42608000	-1.65085500	-1.94175000
H	4.06778500	-2.32531300	0.38465600
H	3.02956300	-1.15428500	2.32838200
H	1.38638400	0.66727700	1.96597200
H	0.29108200	3.52479200	0.25200500

8 References

(1) Laemmli, U. K. Cleavage of structural proteins during the assembly of the head of bacteriophage T4. *Nature* **1970**, *227*, 680.

(2) Marzinzik, A. L.; Sharpless, K. B. A simple method for the preparation of *N*-sulfonylsulfilimines from sulfides. *J. Org. Chem.* **2001**, *66*, 594.

(3) Yoshimura, T.; Omata, T.; Furukawa, N.; Oae, S. Free sulfilimines. 5. Preparation and physical and chemical properties of "free" sulfilimines. *J. Org. Chem.* **1976**, *41*, 1728.

(4) Tian, X.; Song, L.; Rudolph, M.; Rominger, F.; Oeser, T.; Hashmi, A. S. K. Sulfilimines as versatile nitrene transfer reagents: Facile access to diverse aza-heterocycles. *Angew. Chem., Int. Ed.* **2019**, *58*, 3589.

(5) Singh, V.; Wang, S.; Chan, K. M.; Clark, S. A.; Kool, E. T. Genetically encoded multispectral labeling of proteins with polyfluorophores on a DNA backbone. *J. Am. Chem. Soc.* **2013**, *135*, 6184.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision B.01. **2016**.

(7) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, *33*, 8822.

(8) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378.

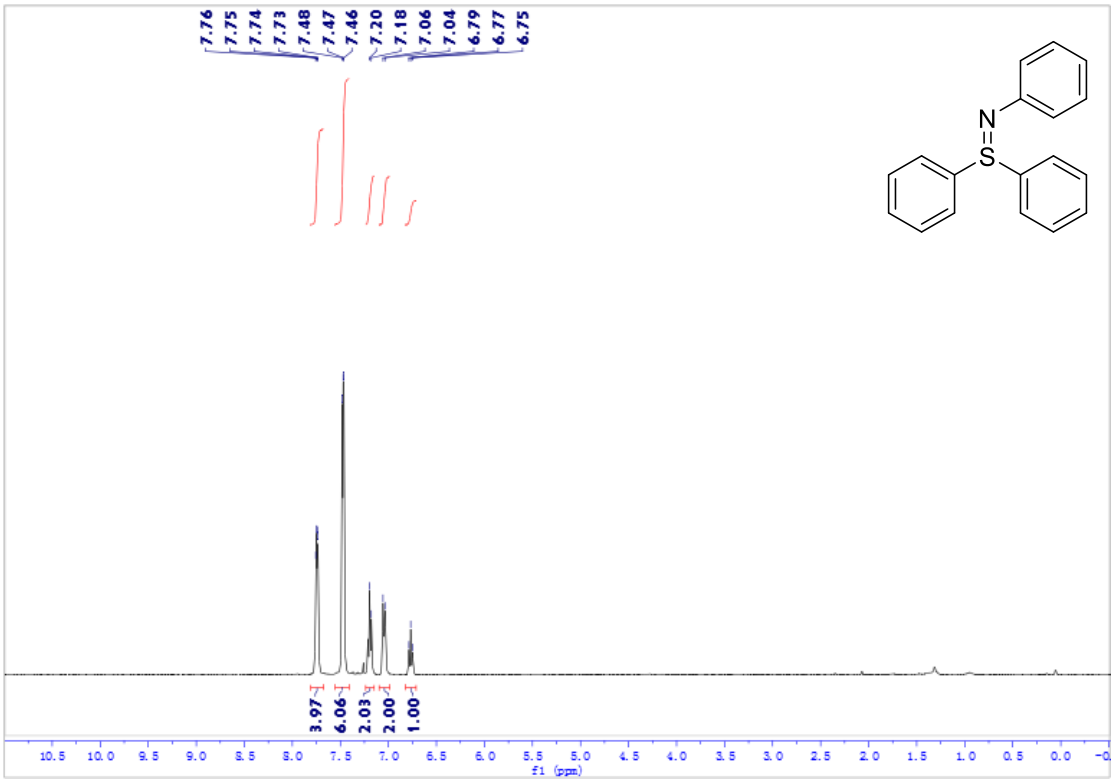
(9) (a) Becke, A. D. A new mixing of hartree-fock and local density‐functional theories. *J. Chem. Phys.* **1993**, *98*, 1372; (b) Becke, A. D. Density‐functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648; (c) Lee, C.; Yang, W.; Parr, R. G. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.

(10) CYLview, 1.0b. Legault, C. Y. Universit éde sherbrooke. (http://www.cylview.org). **2009**.

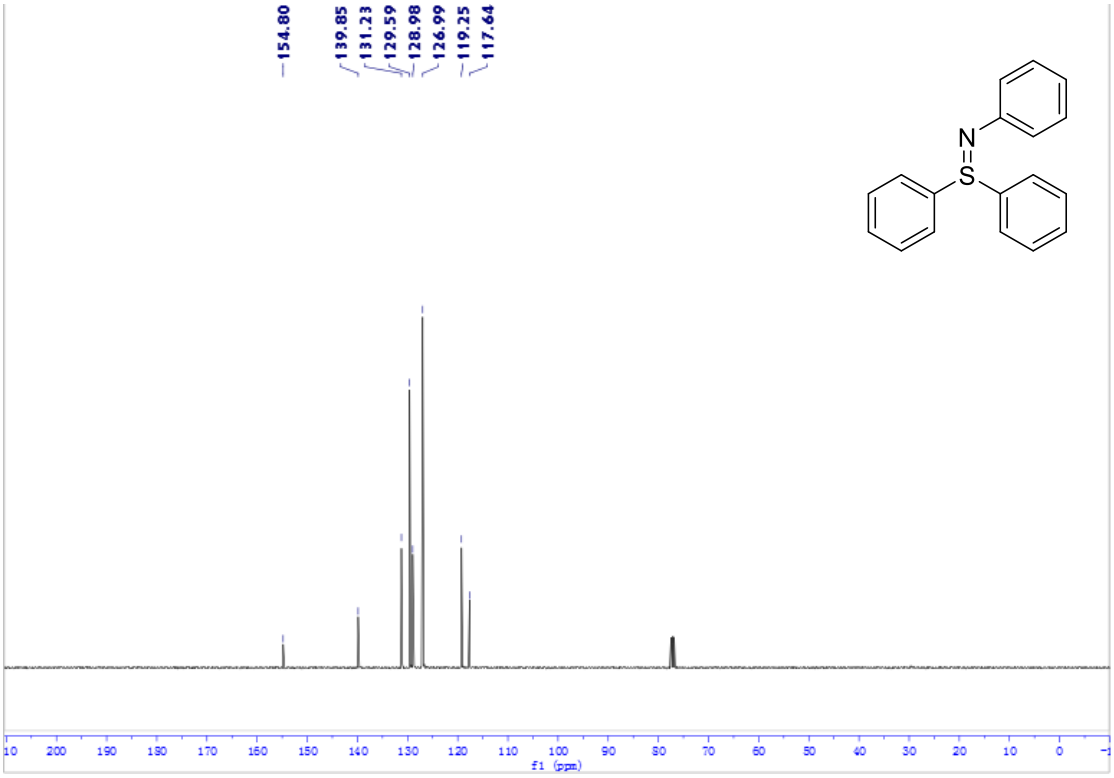
(11) Yan, L.; Lu, Y.; Li, X. A density functional theory protocol for the calculation of redox potentials of copper complexes. *Phys. Chem. Chem. Phys.* **2016**, *18*, 5529.

9 NMR Spectra

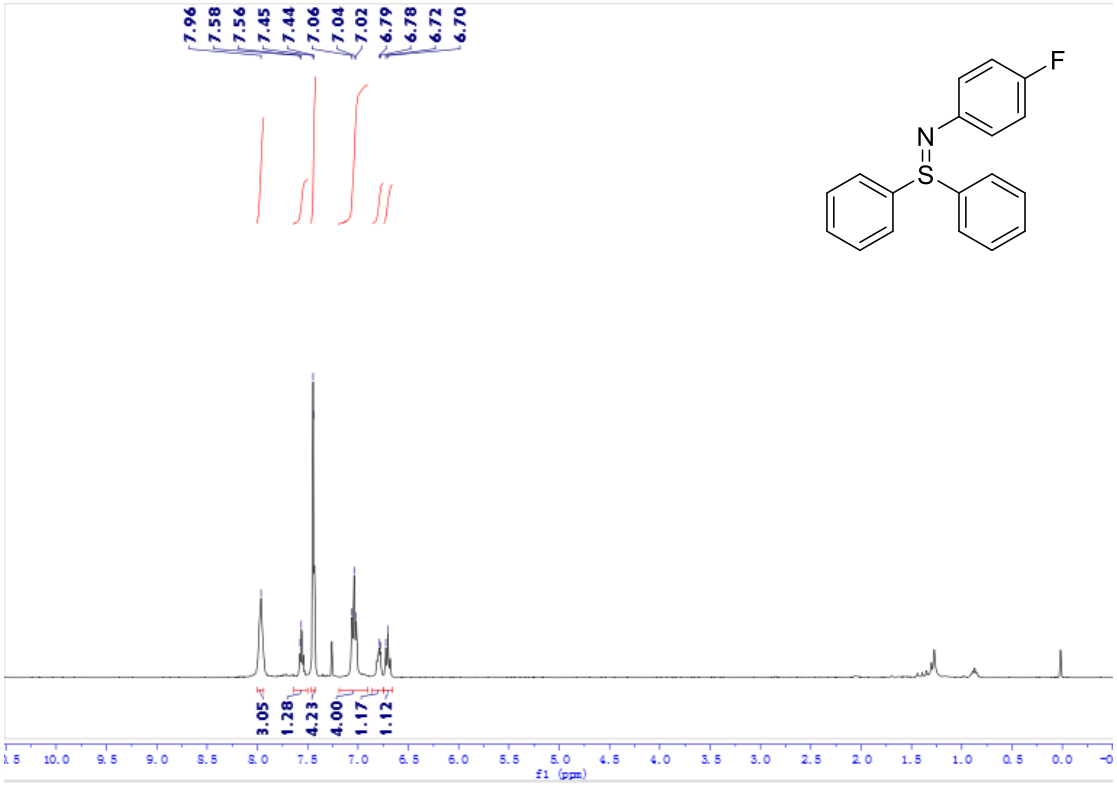
^{1}H NMR (400 MHz, $CDCl_3$) of *N*,1,1-Triphenyl-γ^4-sulfanimine (3ab)



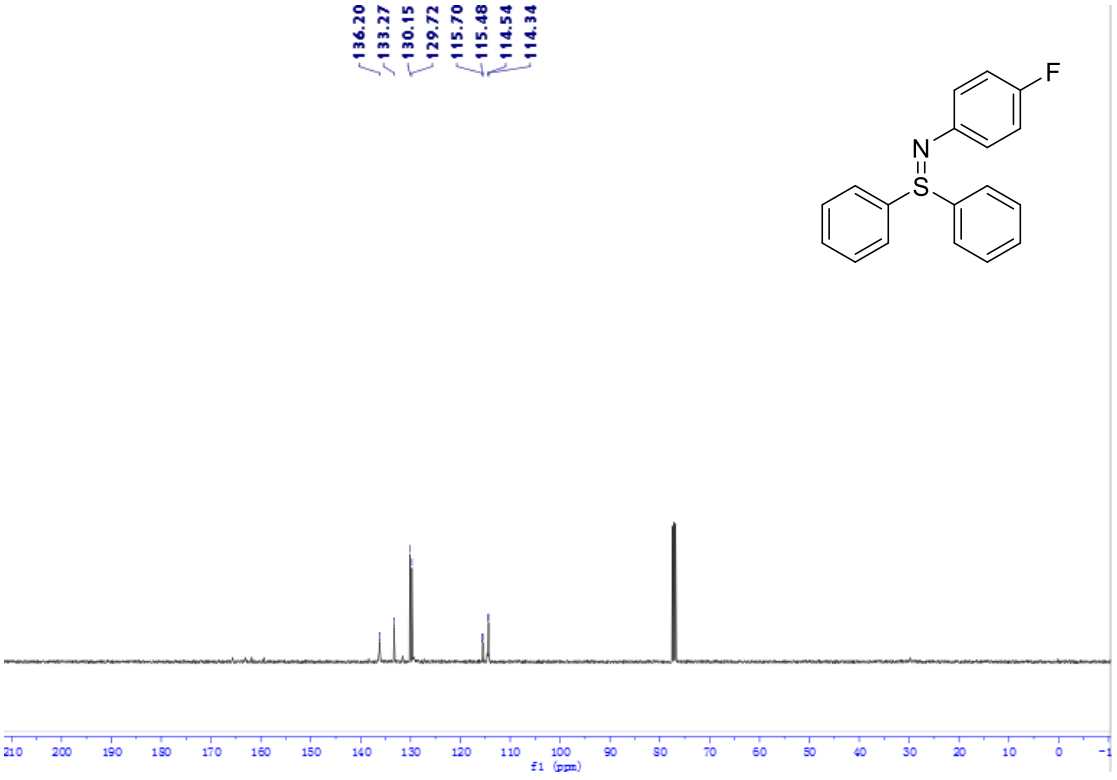
^{13}C NMR (100 MHz, $CDCl_3$) of *N*,1,1-Triphenyl-γ^4-sulfanimine (3ab)



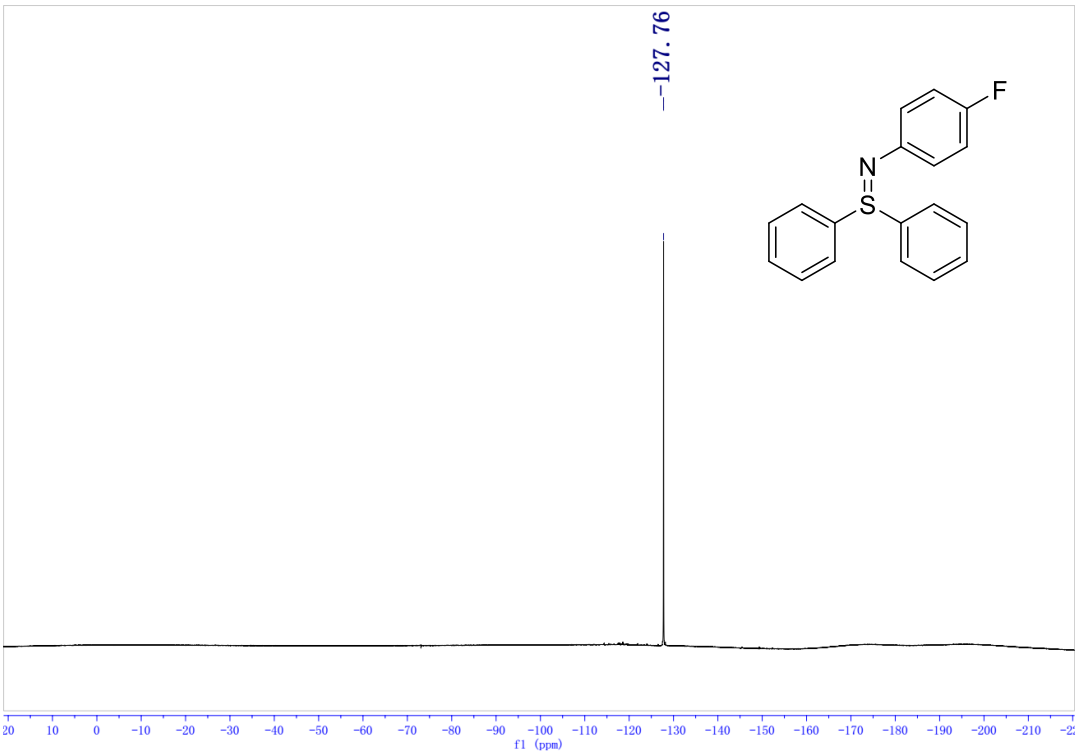
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-Fluorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ac)



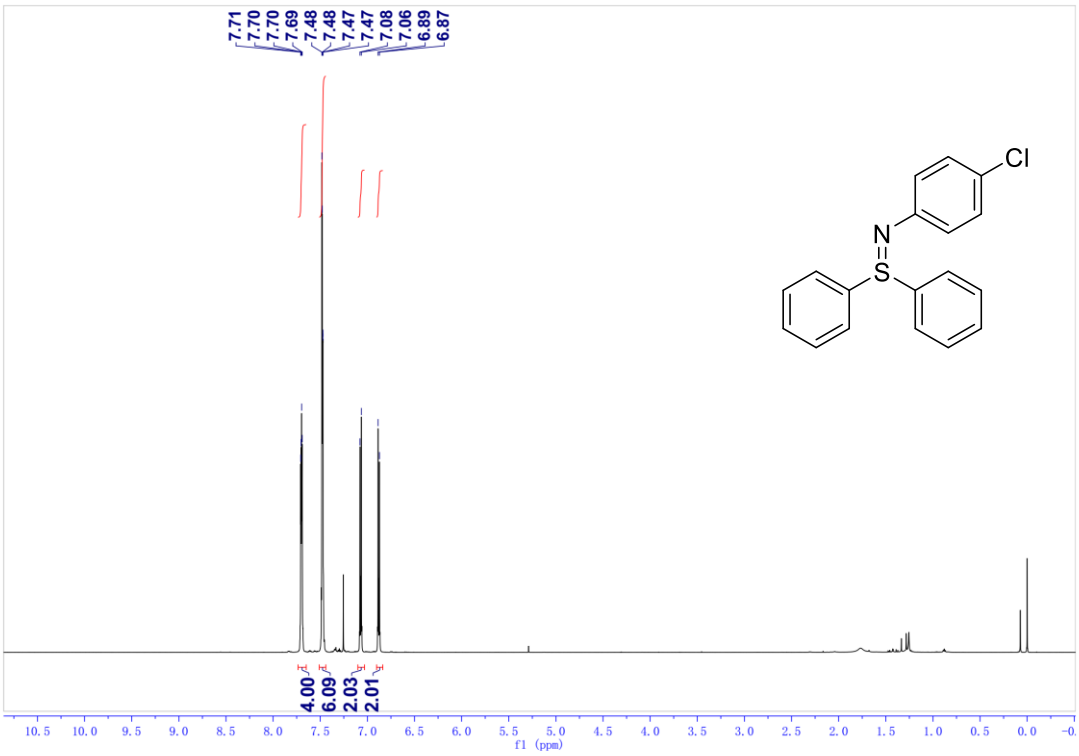
^{13}C NMR (100 MHz, $CDCl_3$) of *N*-(4-Fluorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ac)



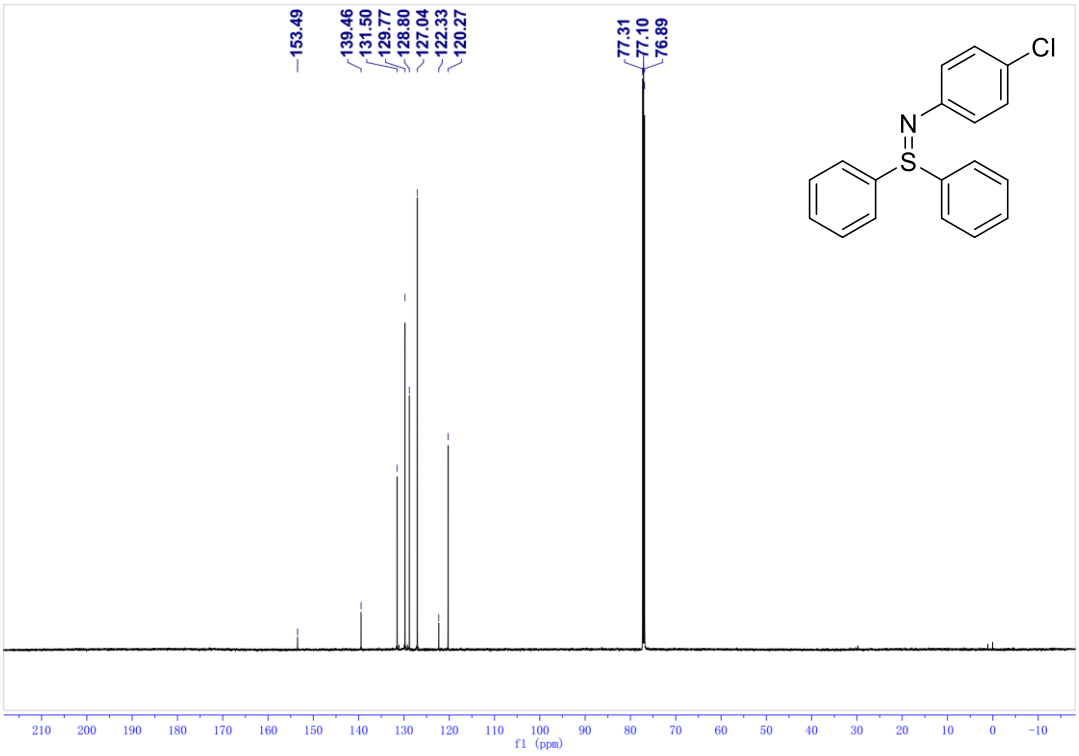
^{19}F NMR (376 MHz, $CDCl_3$) of *N*-(4-Fluorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ac)



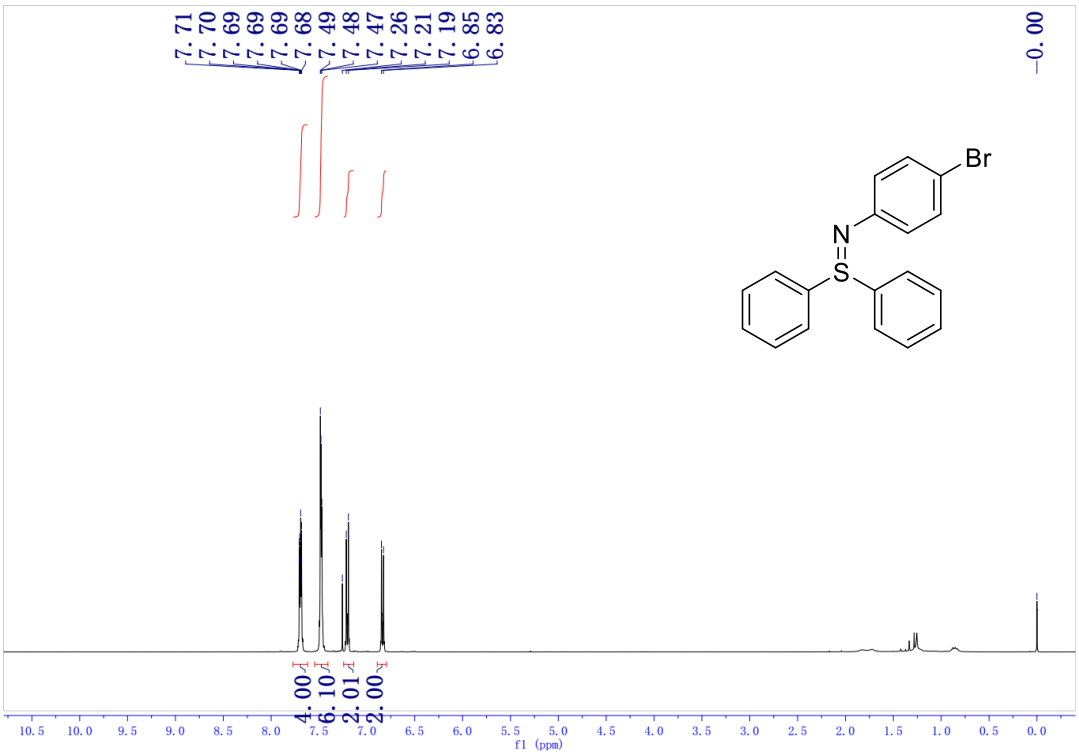
^{1}H NMR (600 MHz, $CDCl_3$) of *N*-(4-Chlorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ad)



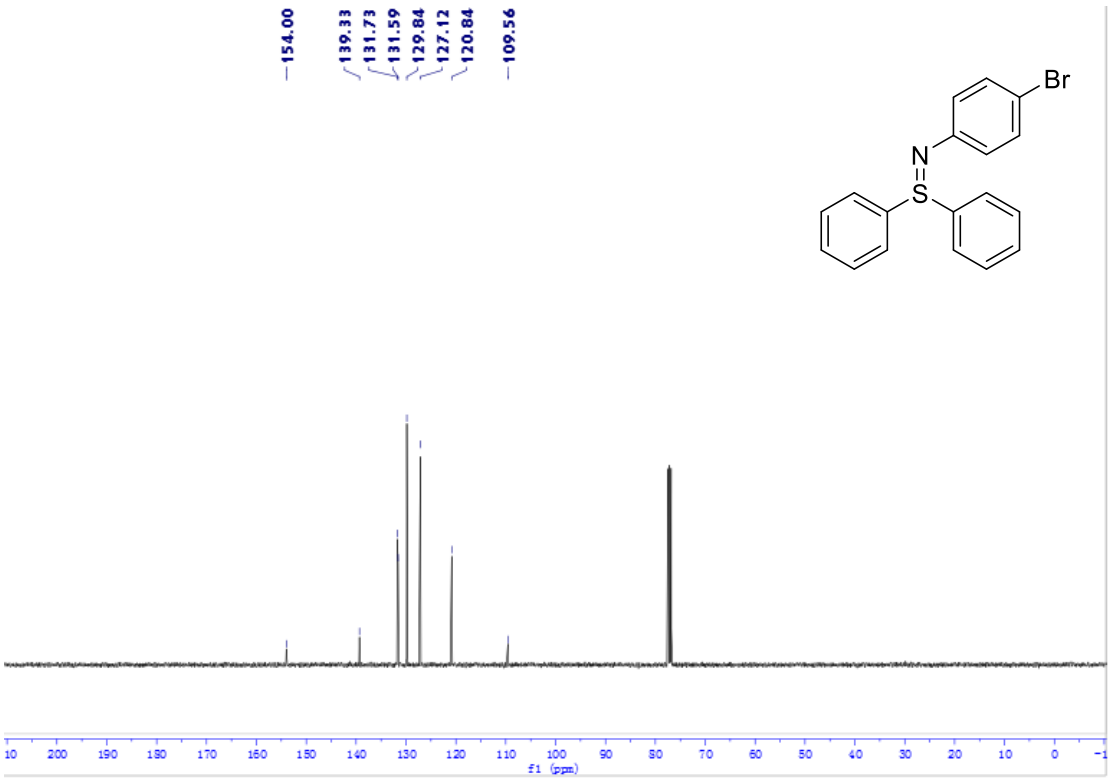
^{13}C NMR (150 MHz, $CDCl_3$) of *N*-(4-Chlorophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ad)



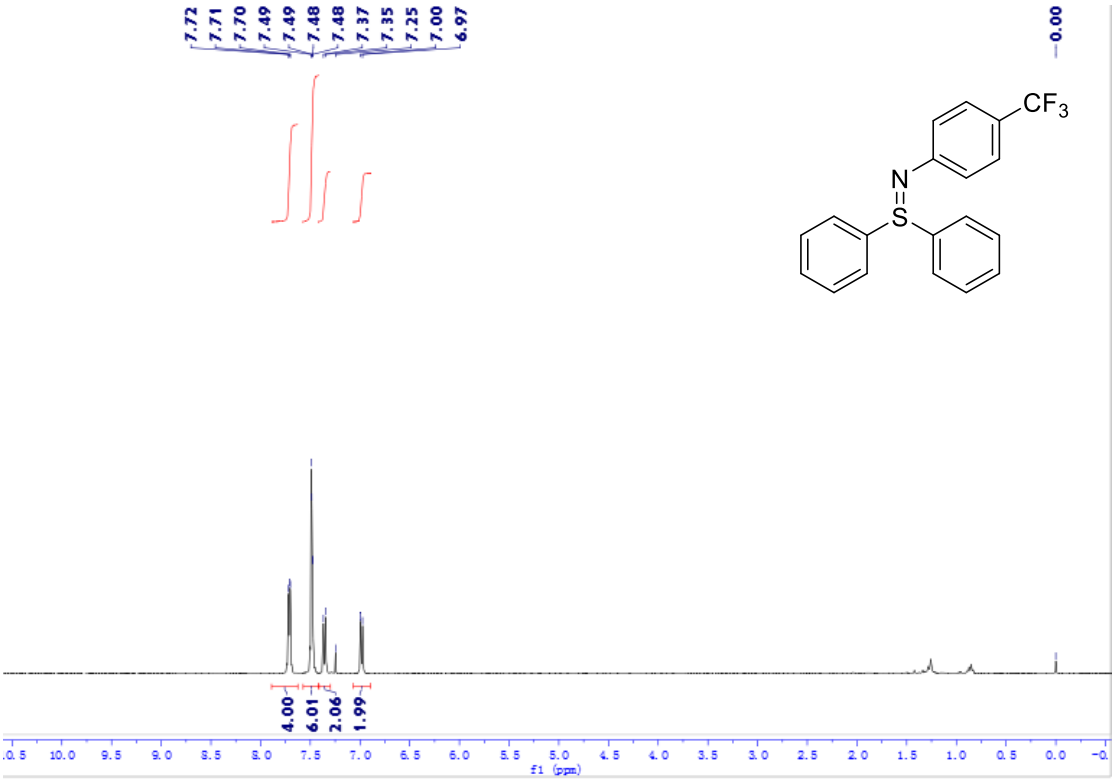
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-Bromophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ae))



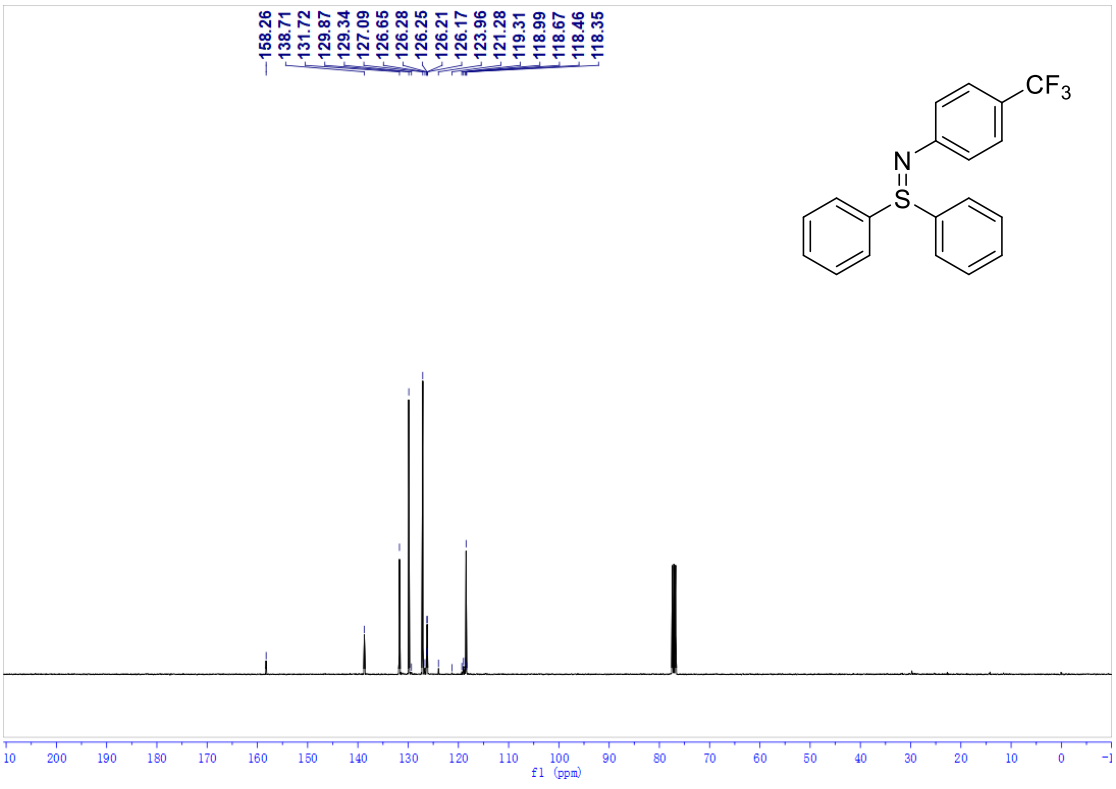
^{13}C NMR (100 MHz, $CDCl_3$) of *N*-(4-Bromophenyl)-1,1-diphenyl-γ^4-sulfanimine (3ae)



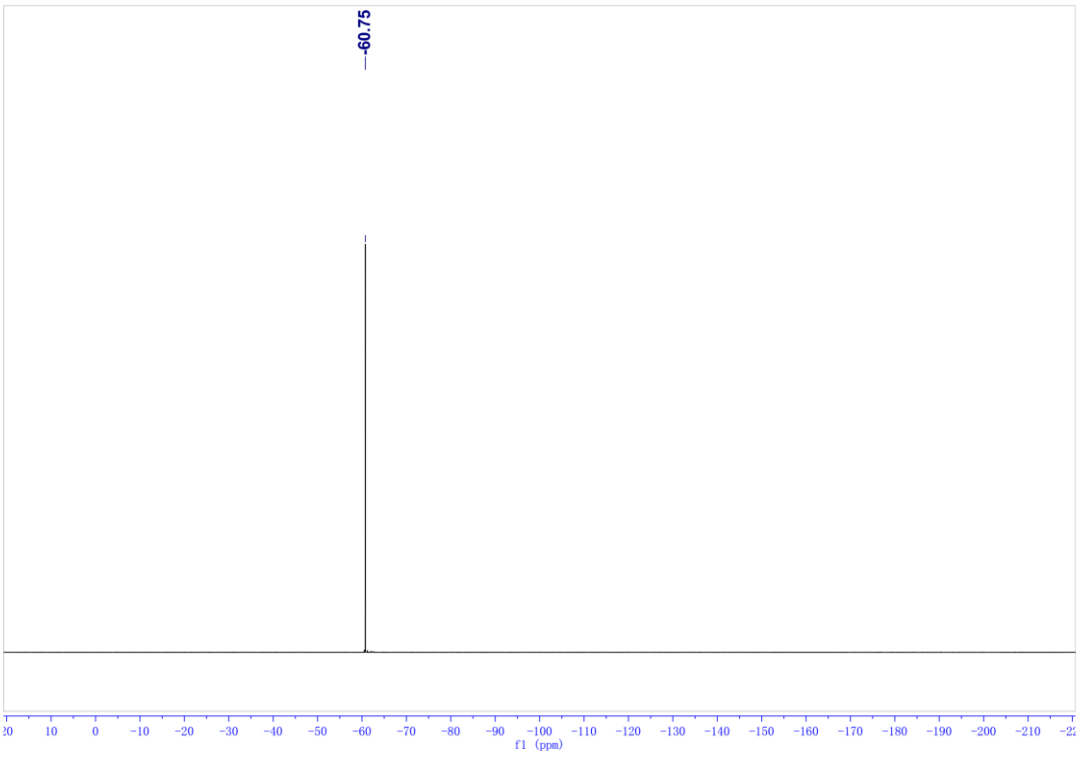
^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3af)



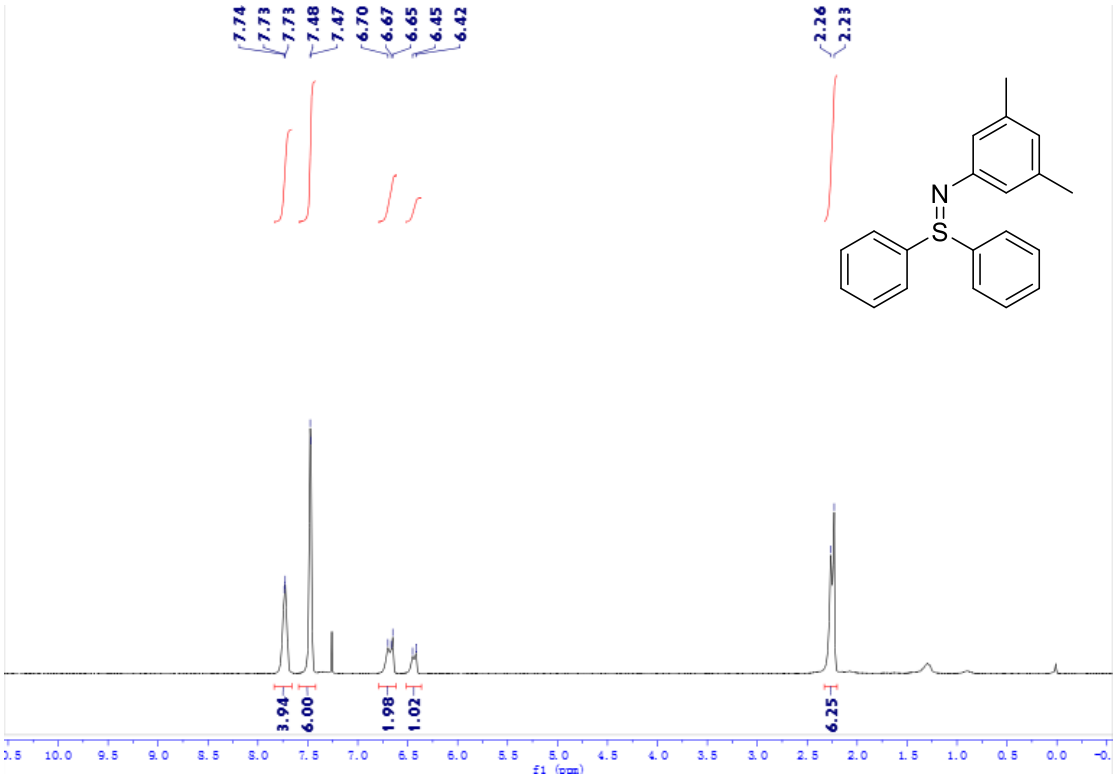
^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3af)



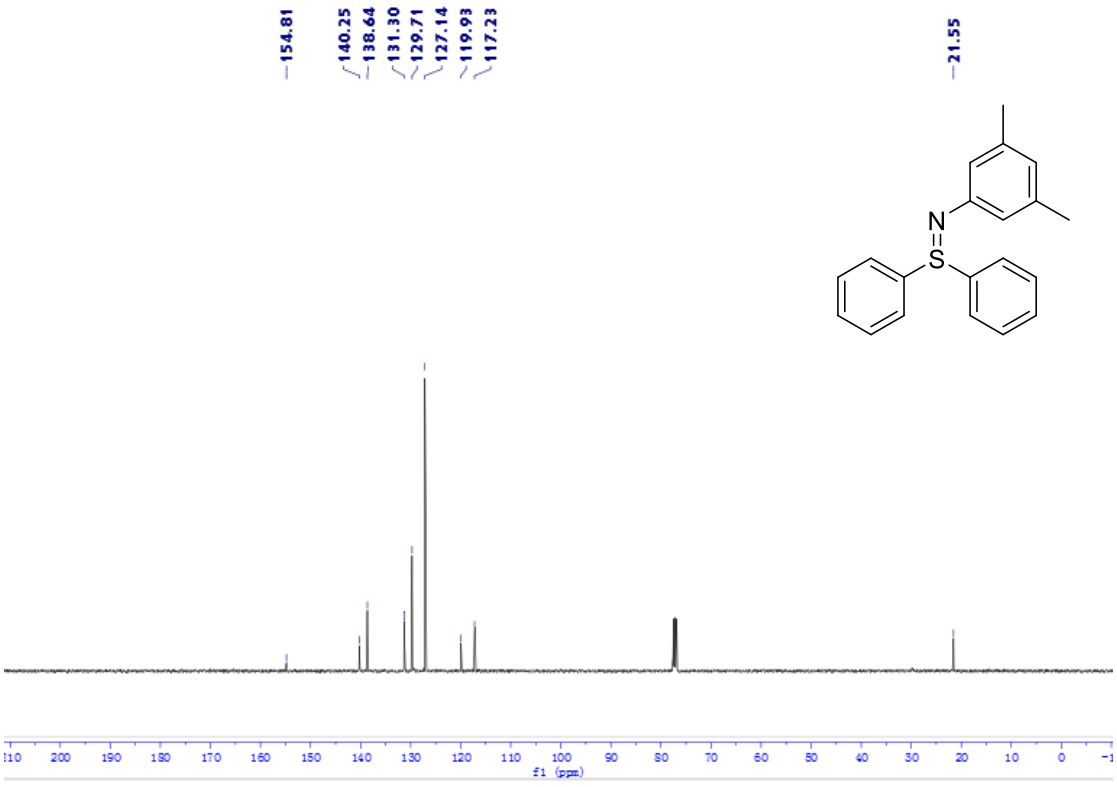
^{19}F NMR (376 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3af)



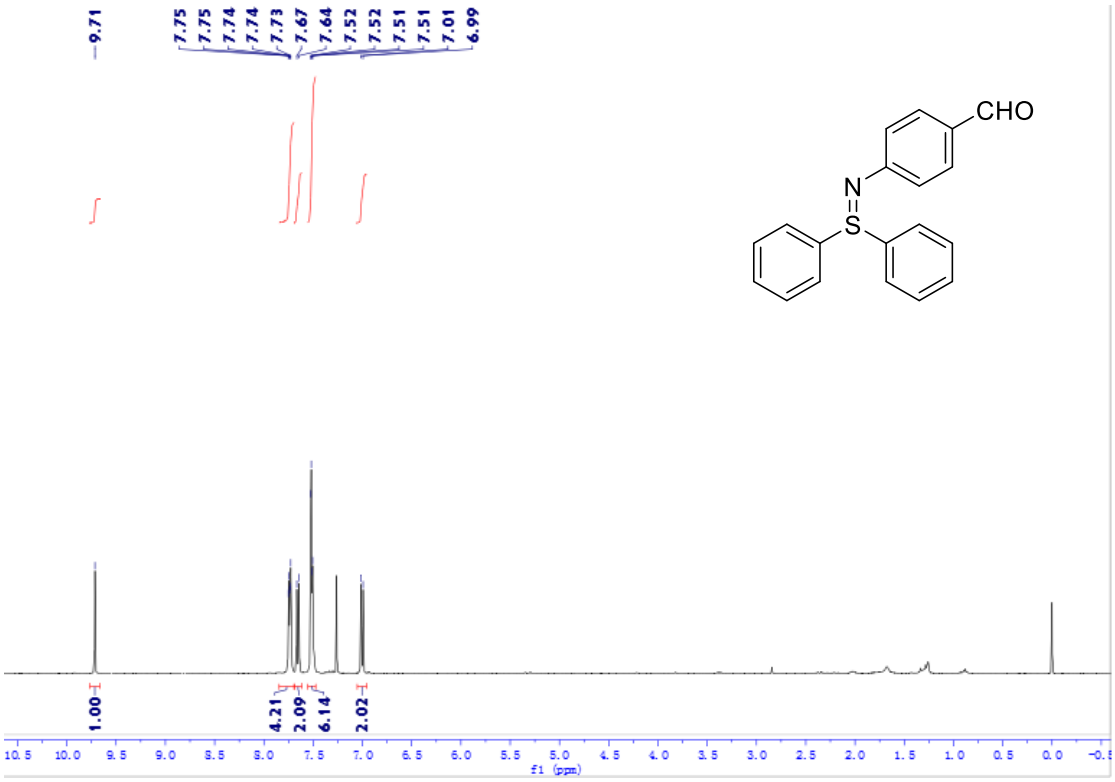
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(3,5-Dimethylphenyl)-1,1-diphenyl-γ^4-sulfanimine (3ag)



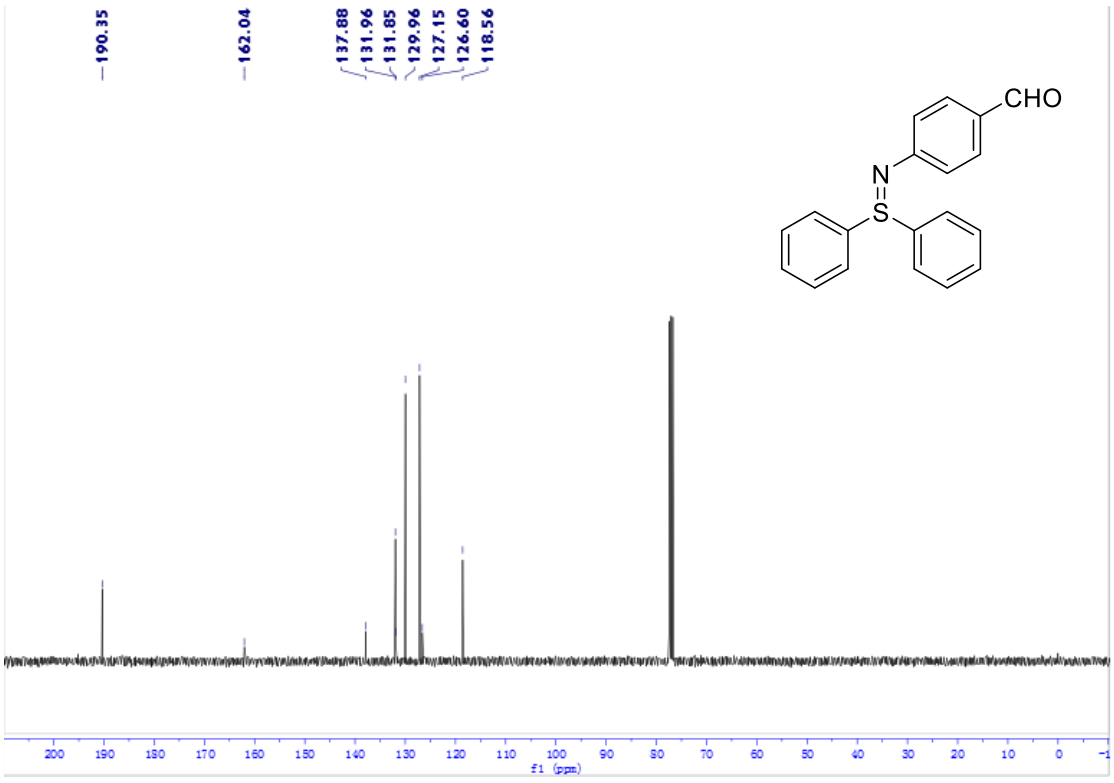
^{13}C NMR (100 MHz, $CDCl_3$) of *N*-(3,5-Dimethylphenyl)-1,1-diphenyl-γ^4-sulfanimine (3ag)



^{1}H NMR (400 MHz, $CDCl_3$) of 4-((Diphenyl-γ^4-sulfanylidene)amino)benzaldehyde (3ah)

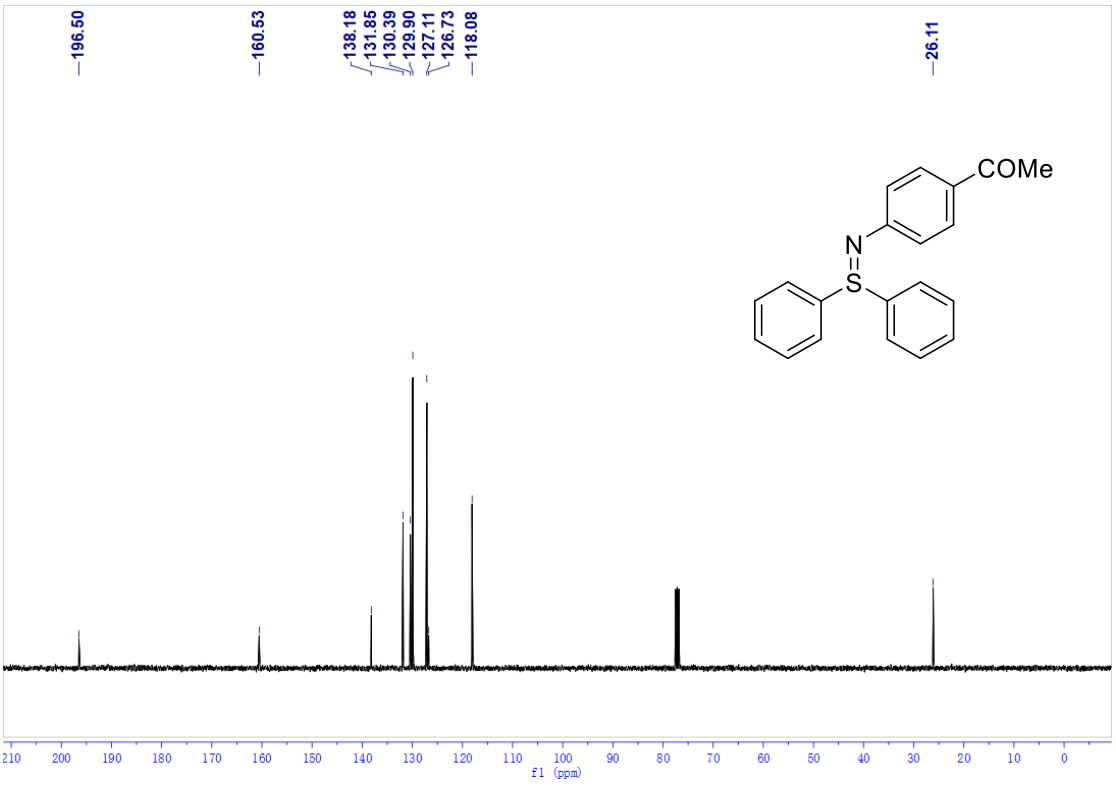


^{13}C NMR (100 MHz, $CDCl_3$) of 4-((Diphenyl-γ^4-sulfanylidene)amino)benzaldehyde (3ah)



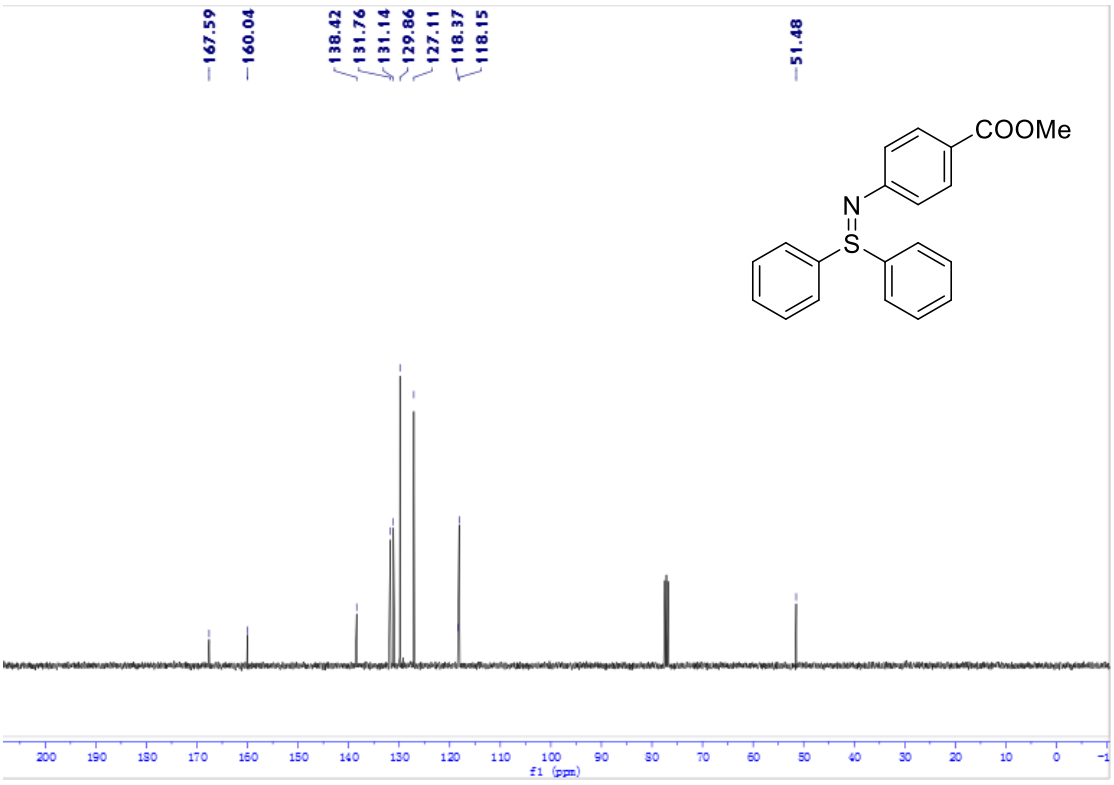
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(4-((Diphenyl-γ^4-sulfanylidene)amino)phenyl)ethan-1-one (3ai)

^{13}C NMR (100 MHz, $CDCl_3$) of 1-(4-((Diphenyl-γ^4-sulfanylidene)amino)phenyl)ethan-1-one (3ai)

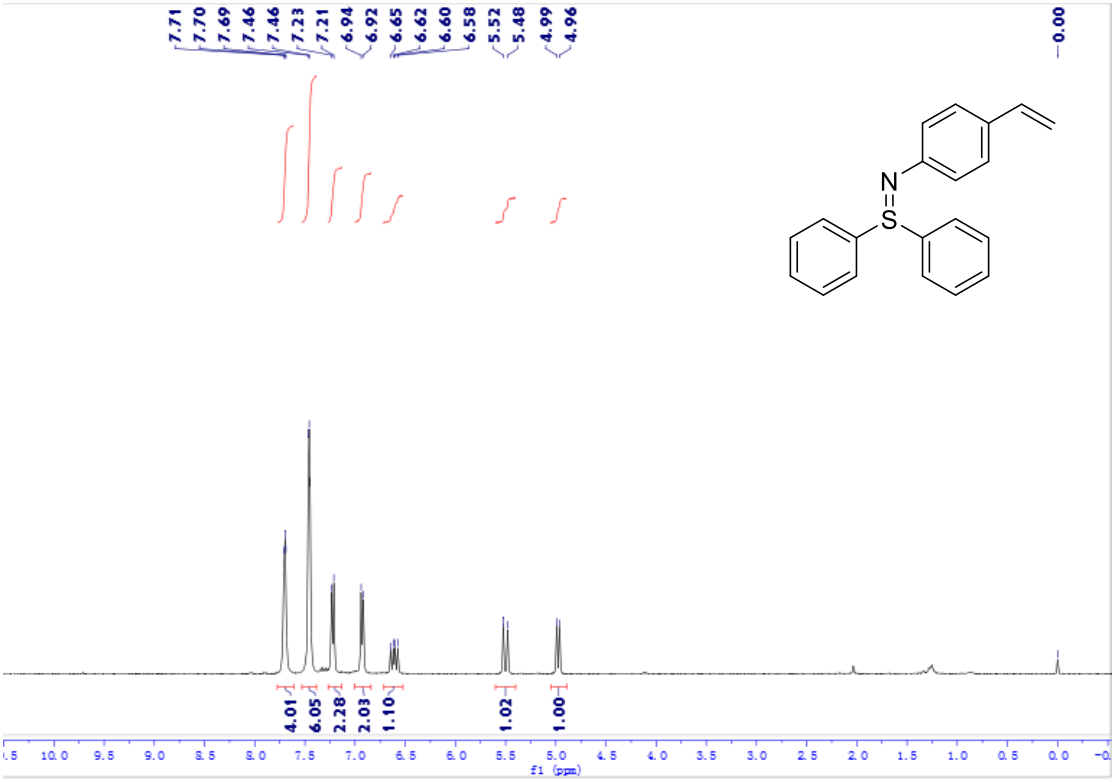


^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4-((diphenyl-γ^4-sulfanylidene)amino)benzoate (3aj)

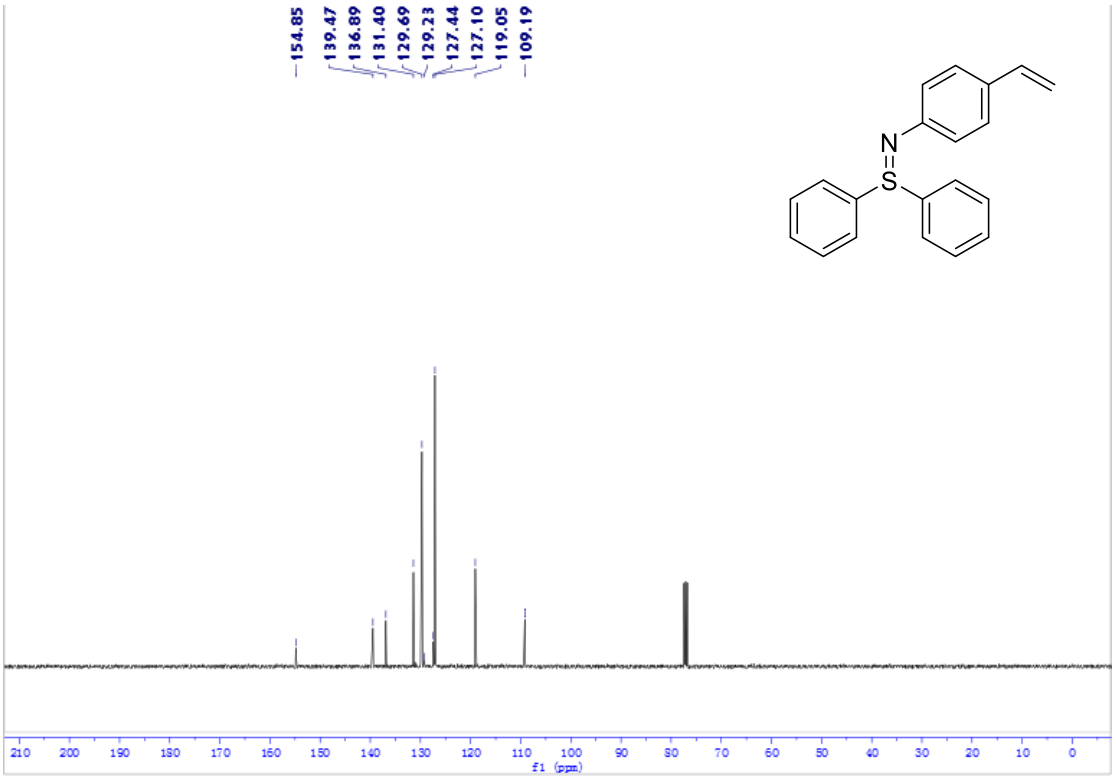
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4-((diphenyl-γ^4-sulfanylidene)amino)benzoate (3aj)



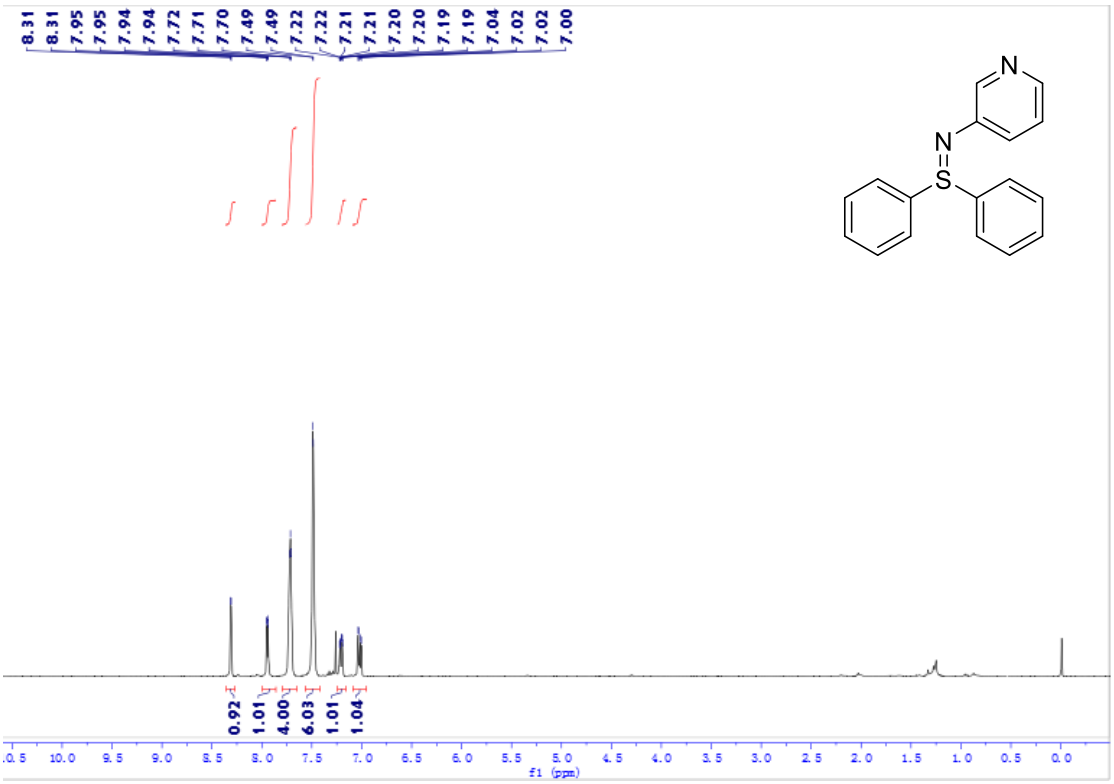
^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(4-vinylphenyl)-γ^4-sulfanimine (3ak)



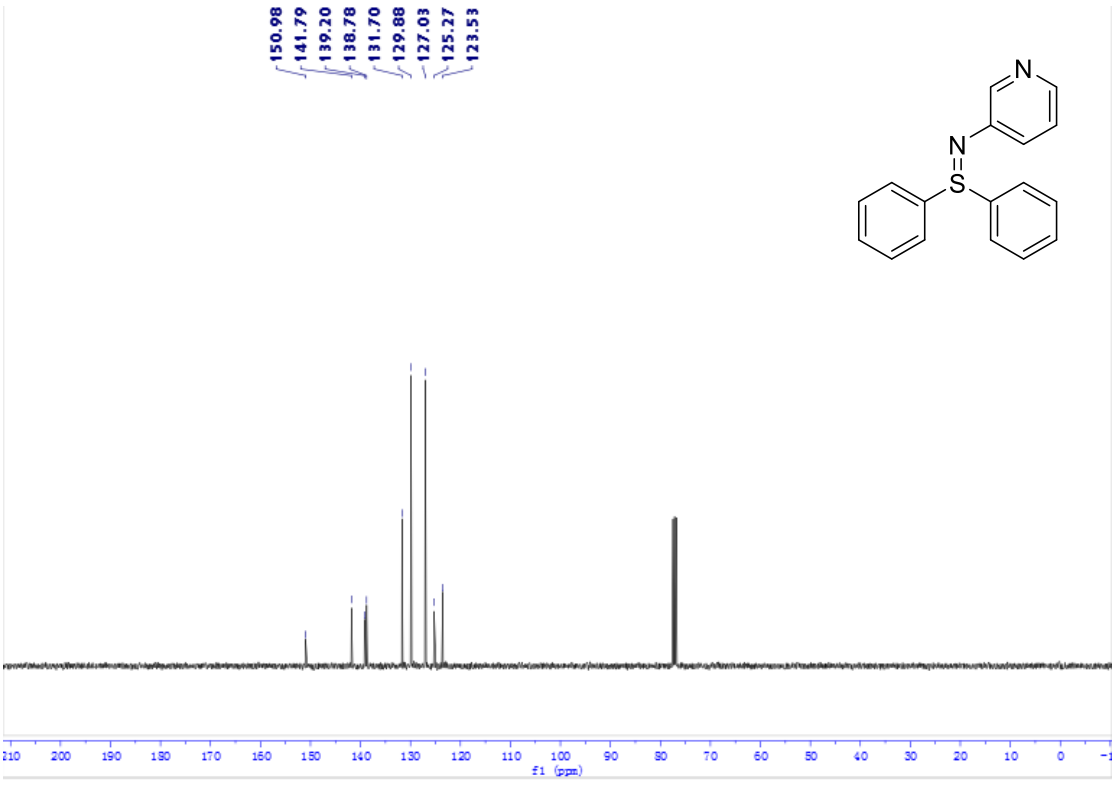
^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(4-vinylphenyl)-γ^4-sulfanimine (3ak)



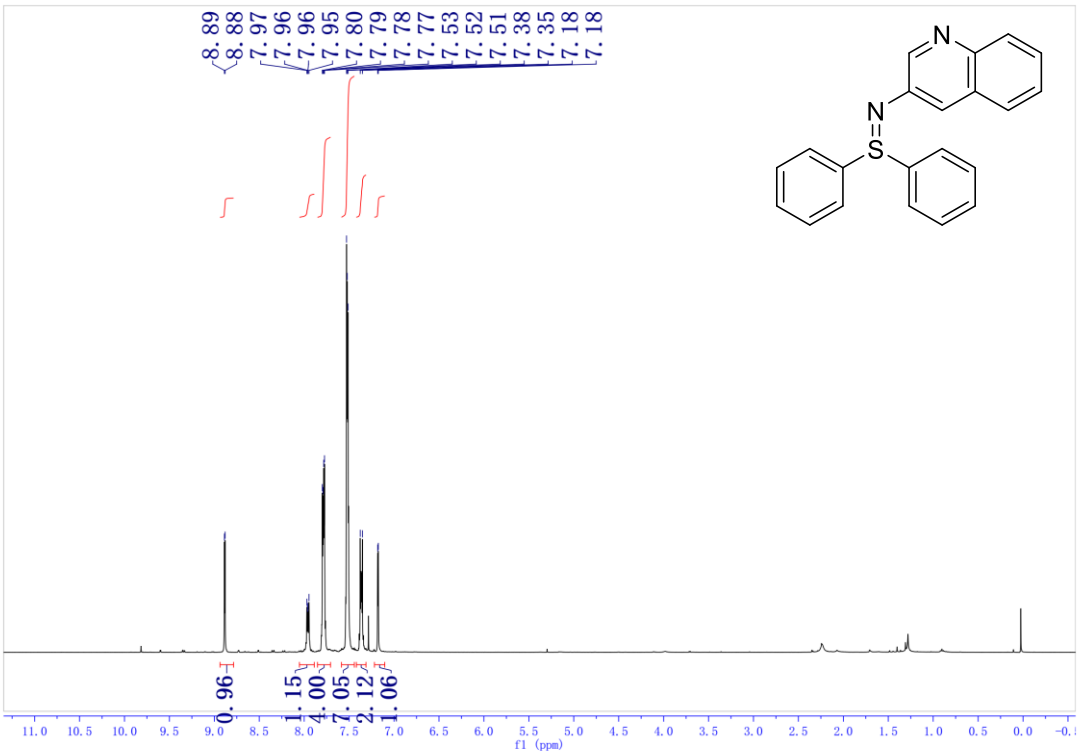
^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(pyridin-3-yl)-γ^4-sulfanimine (3al)



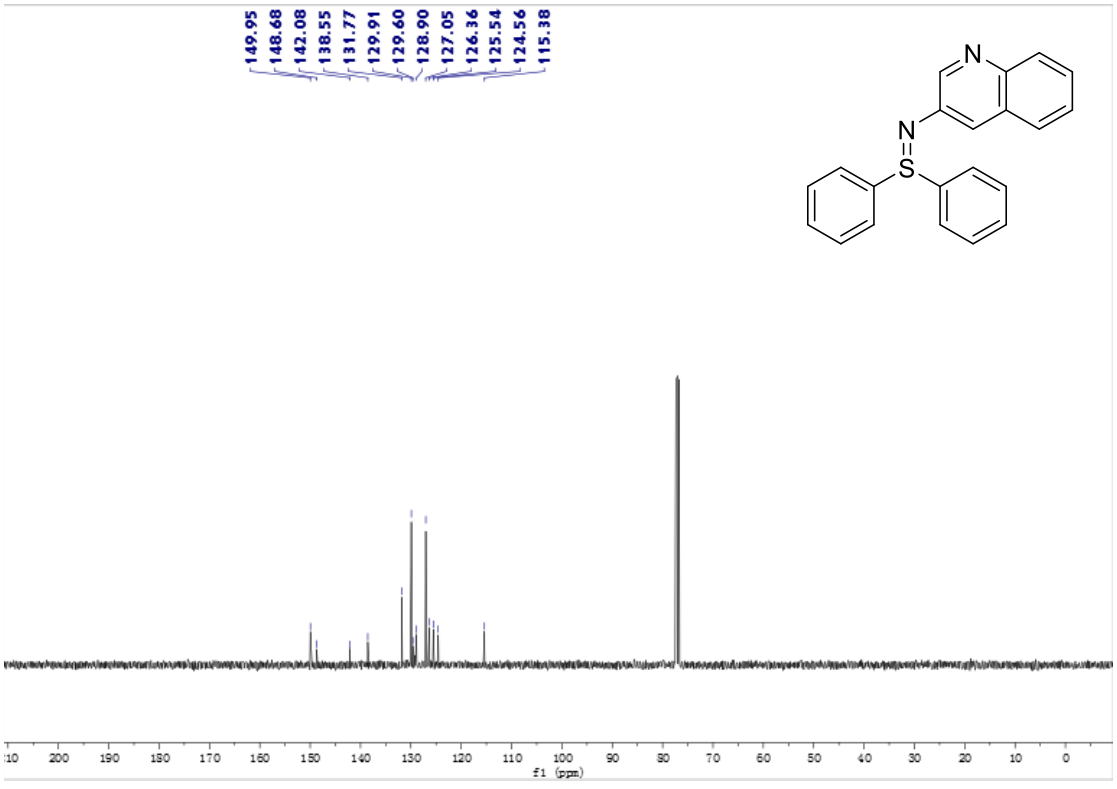
^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(pyridin-3-yl)-γ^4-sulfanimine (3al)



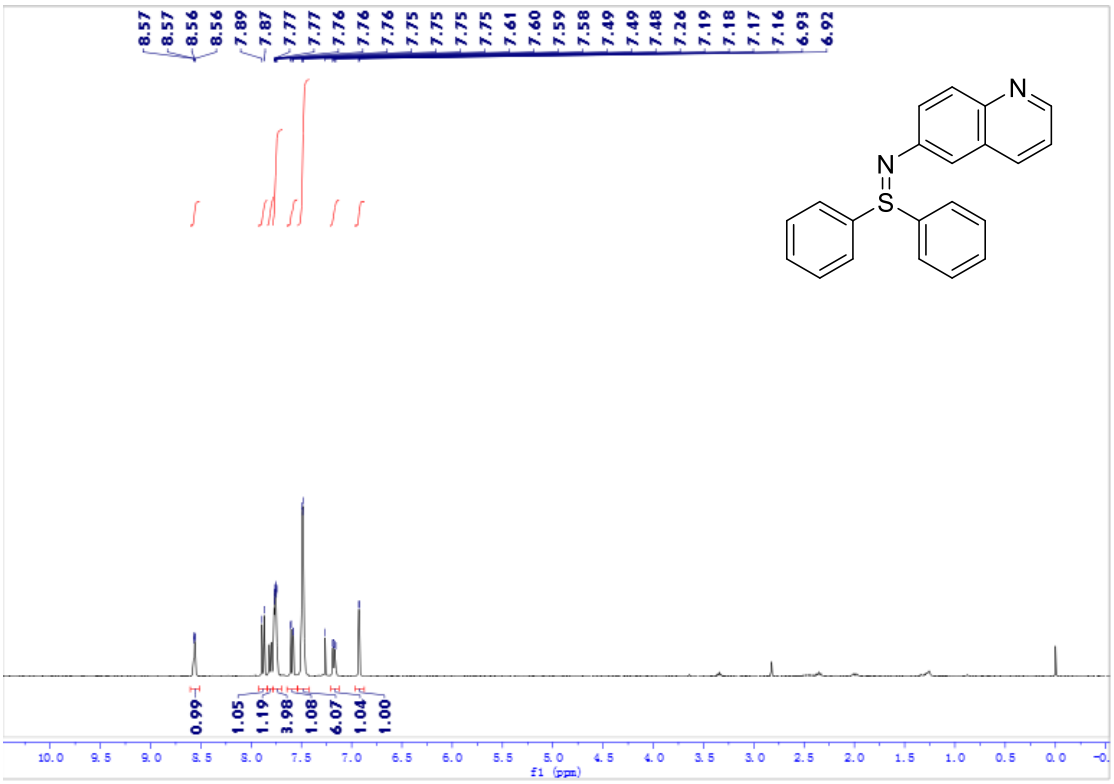
^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(quinolin-3-yl)-γ^4-sulfanimine (3am)



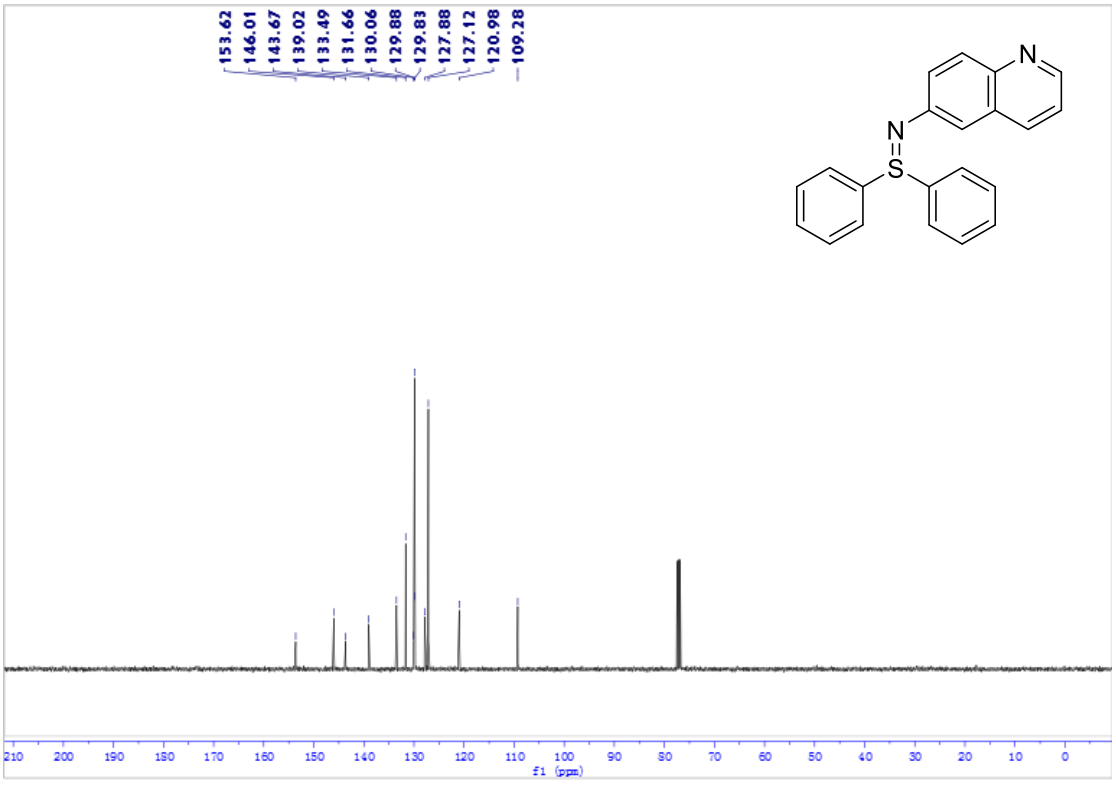
^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(quinolin-3-yl)-γ^4-sulfanimine (3am)



^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(quinolin-6-yl)-γ^4-sulfanimine (3an)

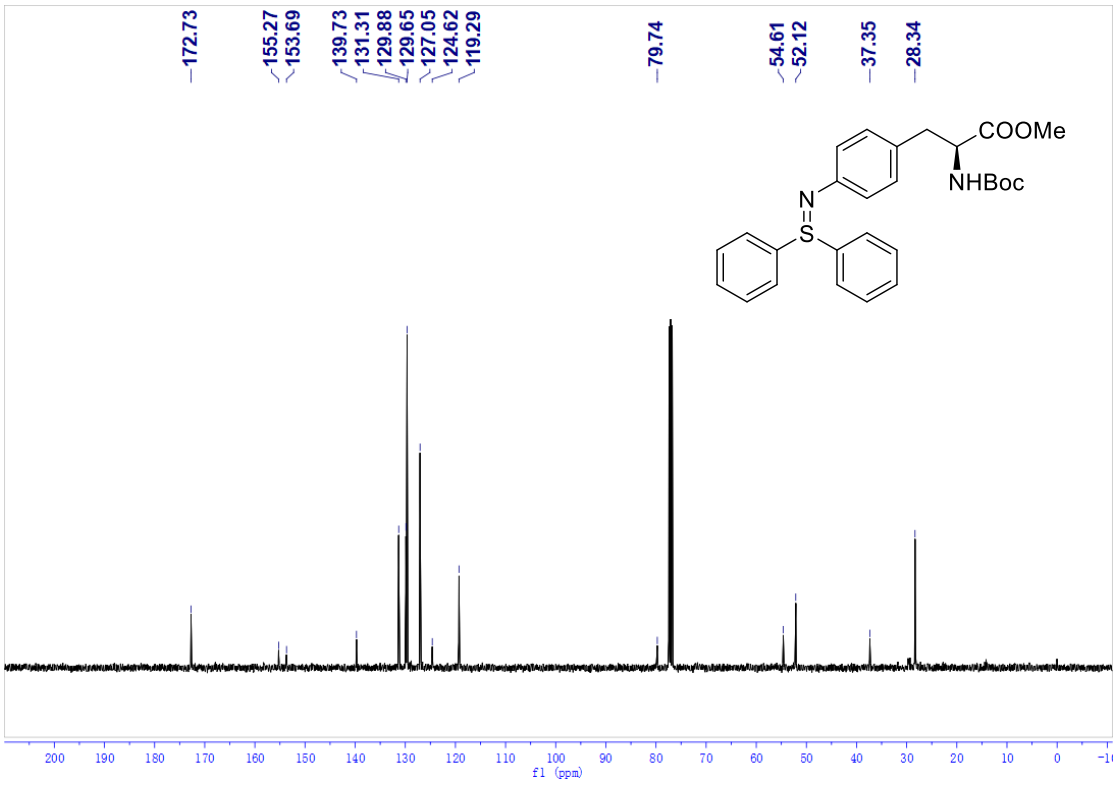


^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(quinolin-6-yl)-γ^4-sulfanimine (3an)

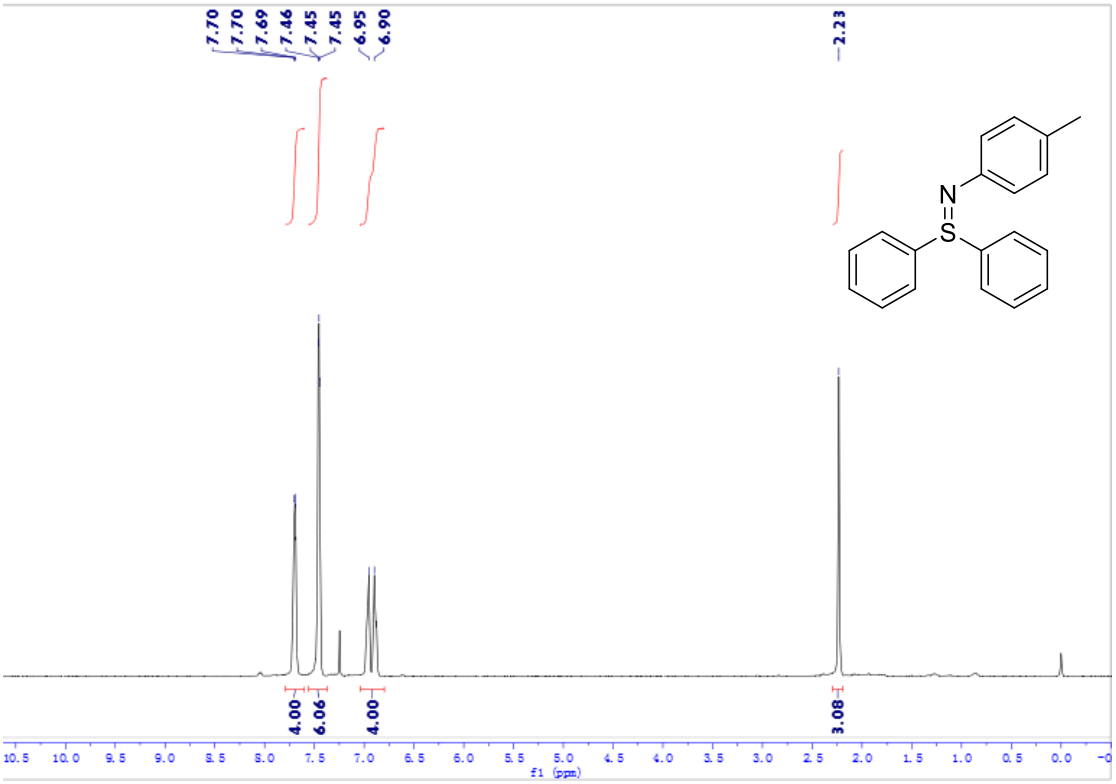


^{1}H NMR (400 MHz, $CDCl_3$) of Methyl (S)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((diphenyl-γ^4-sulfanylidene)amino)phenyl)propanoate (3ao)

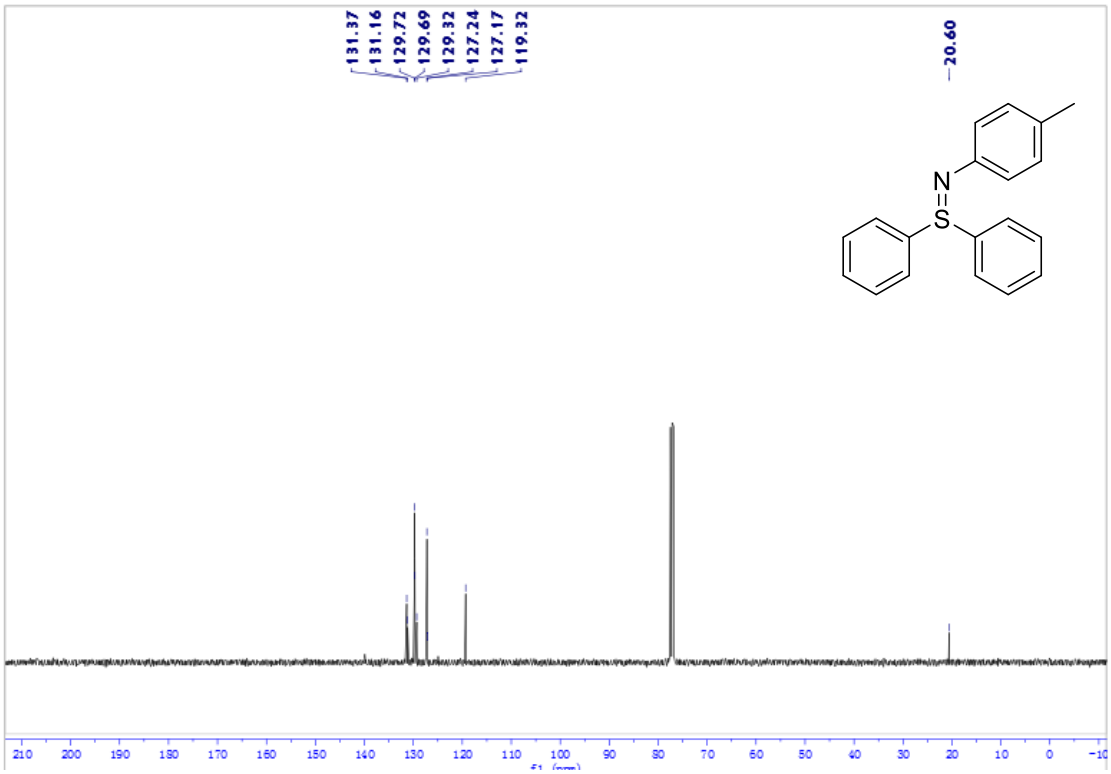
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl (S)-2-((*tert*-butoxycarbonyl) amino)-3-(4-((diphenyl-γ^4-sulfanylidene)amino)phenyl)propanoate (3ao)



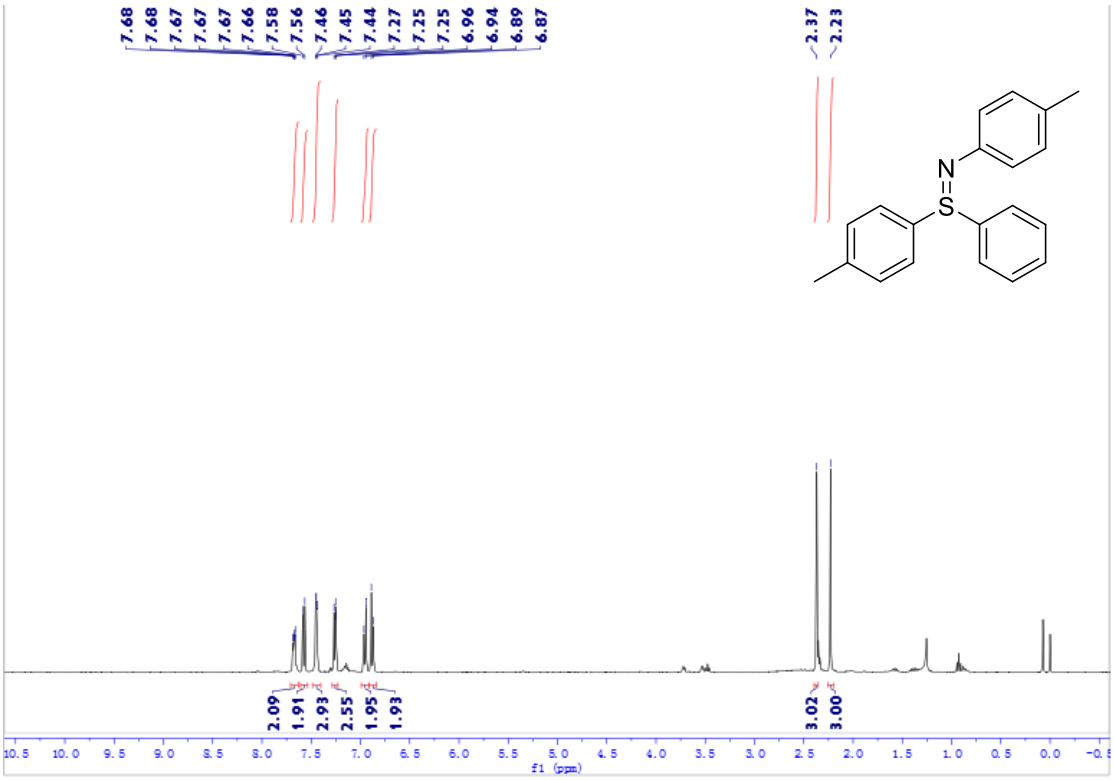
^{1}H NMR (400 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3aa)



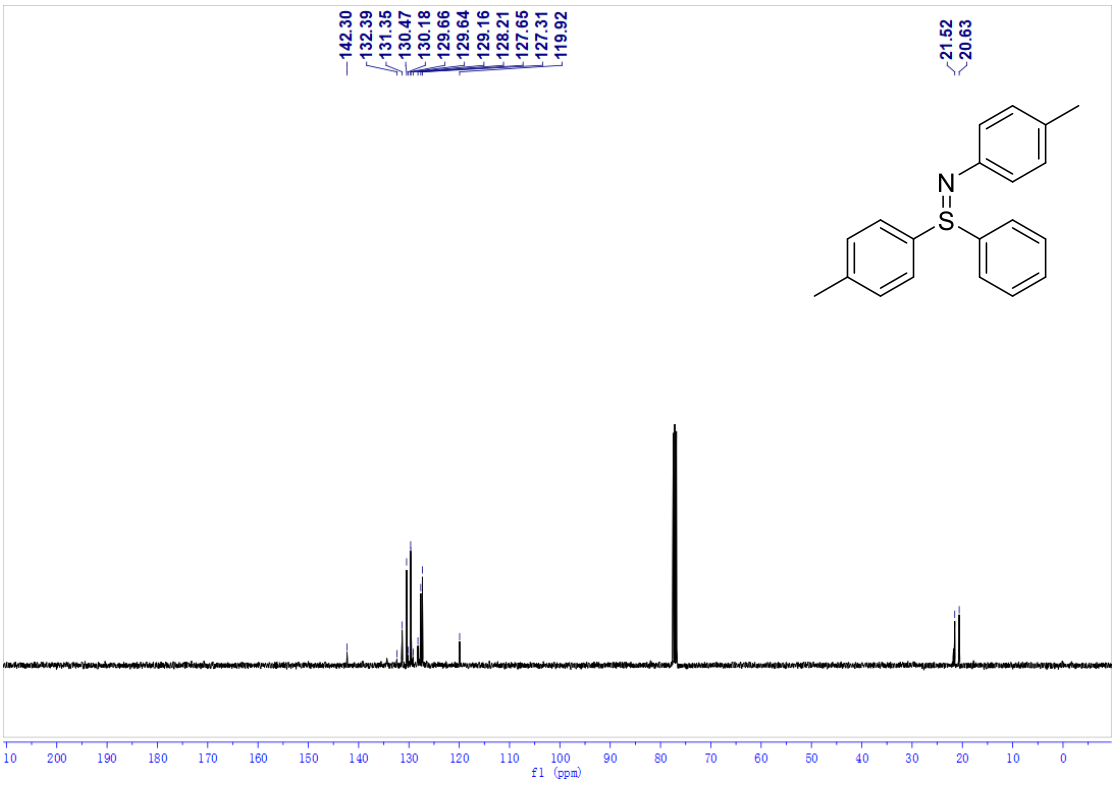
^{13}C NMR (100 MHz, $CDCl_3$) of 1,1-Diphenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3aa)



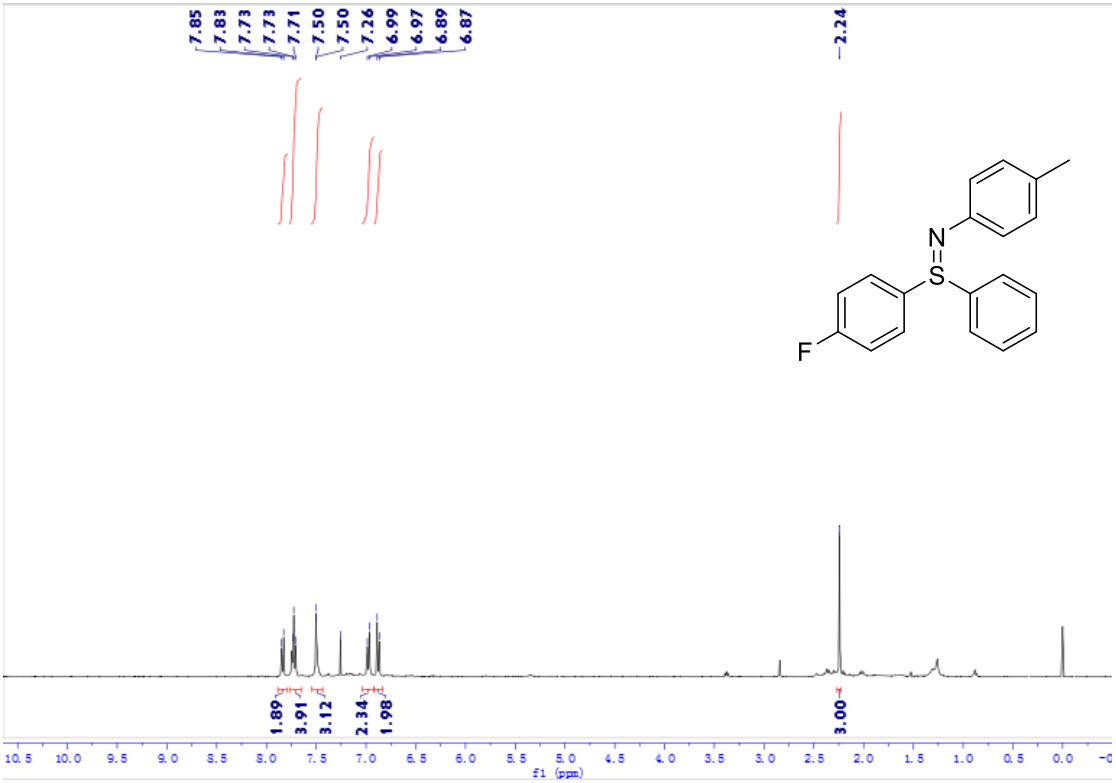
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-*N*,1-di-*p*-tolyl-γ^4-sulfanimine (3ba)



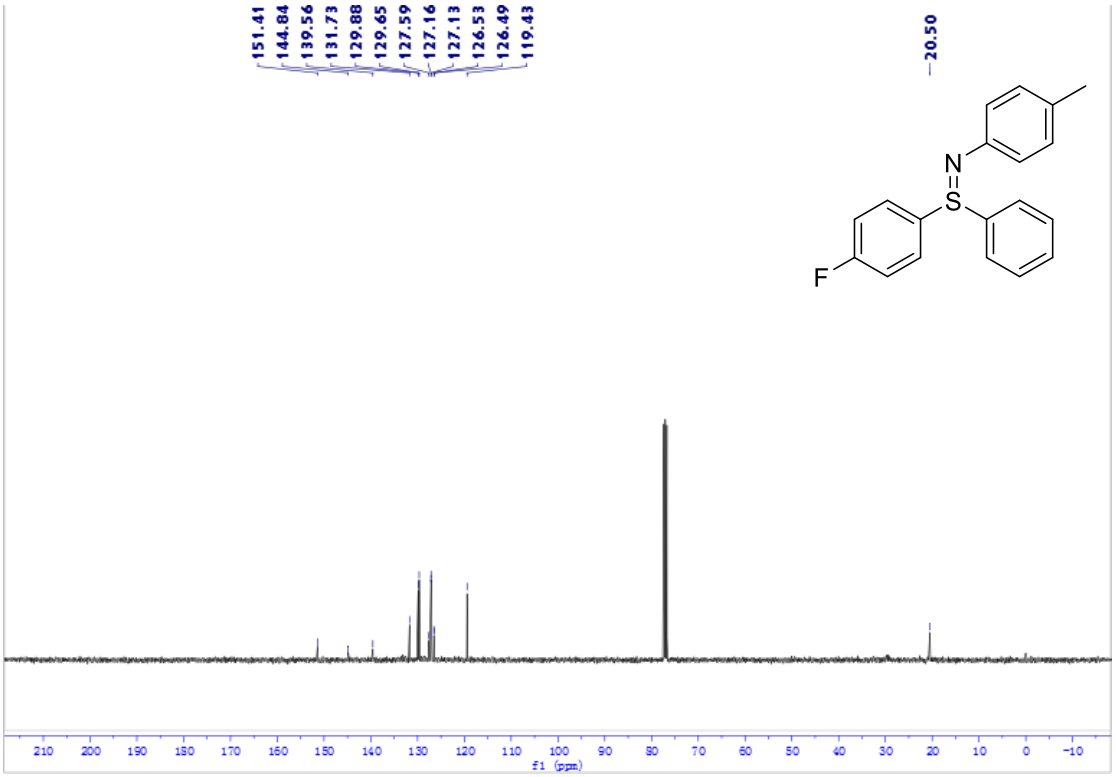
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-*N*,1-di-*p*-tolyl-γ^4-sulfanimine (3ba)



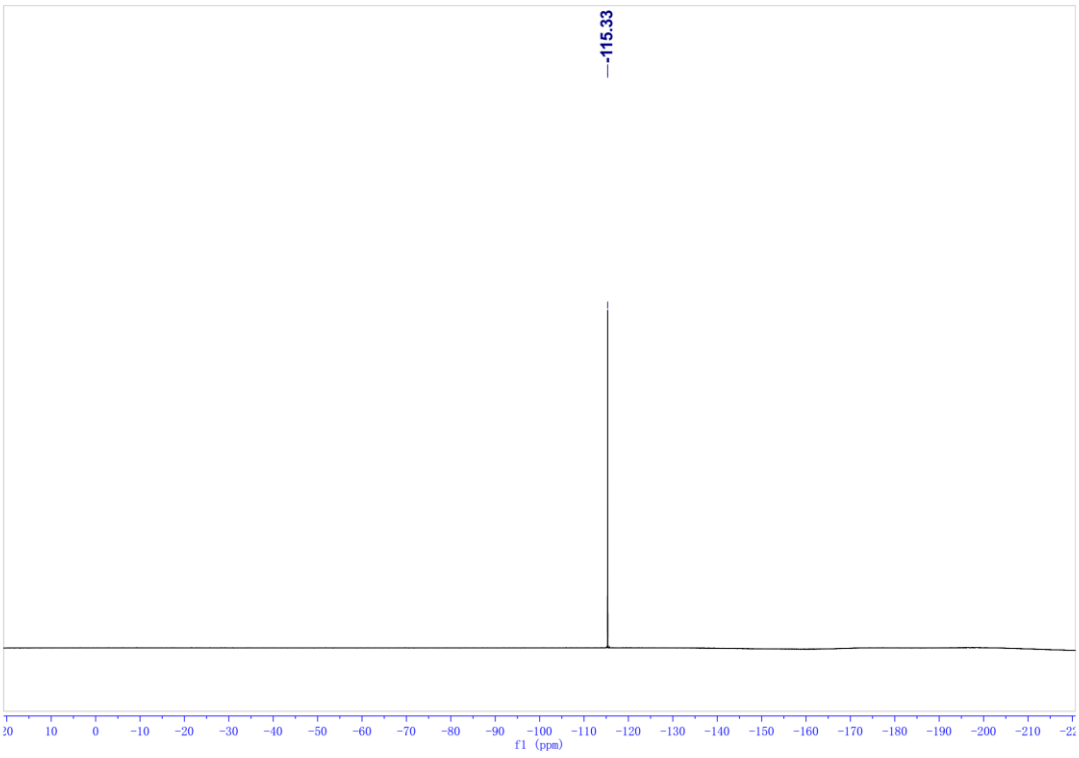
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(4-Fluorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ca)



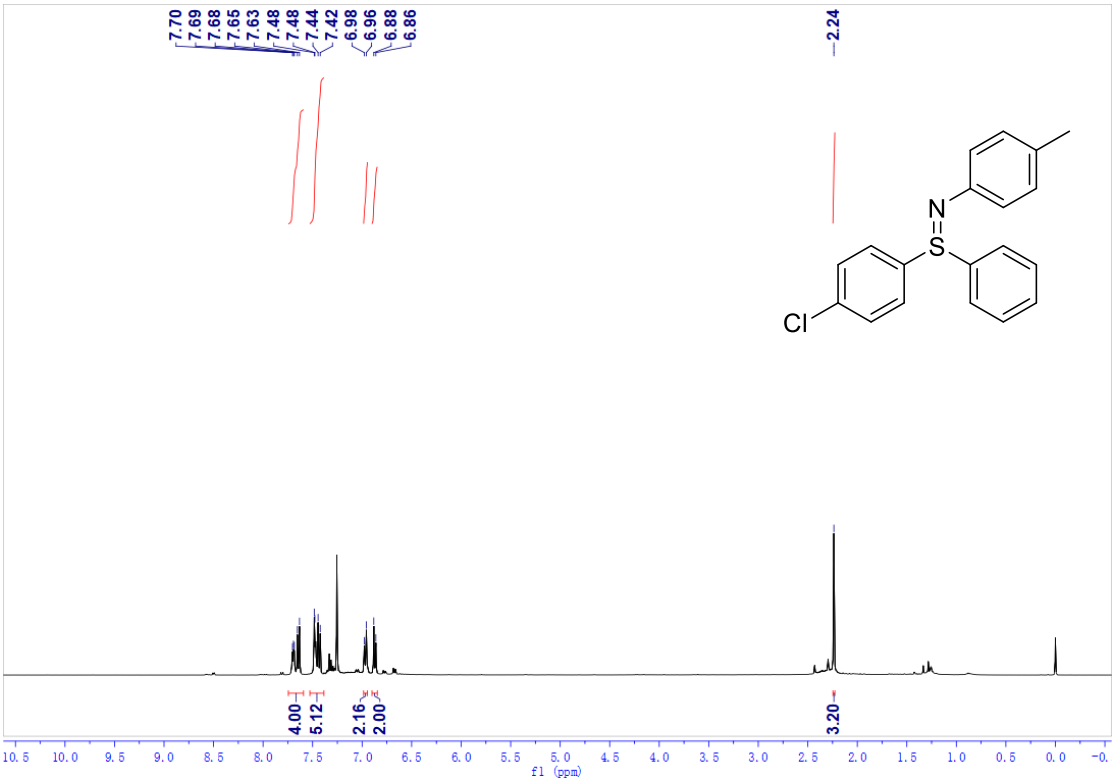
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(4-Fluorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ca)



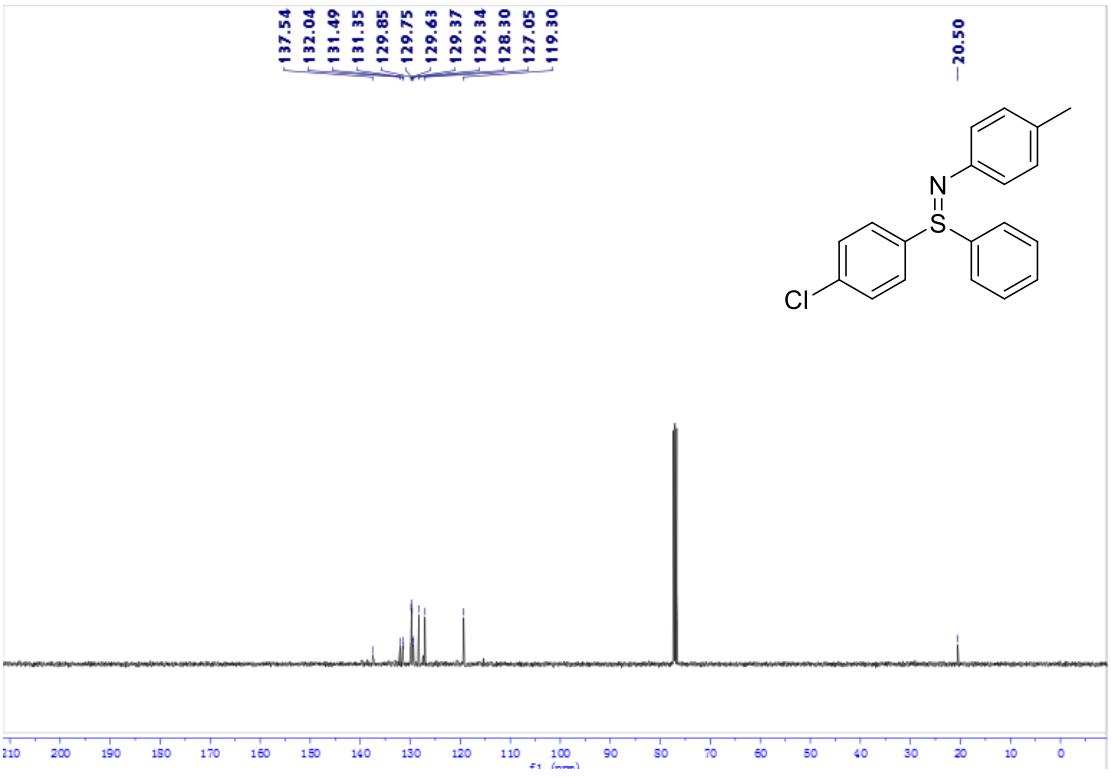
^{19}F NMR (376 MHz, $CDCl_3$) of 1-(4-Fluorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ca)



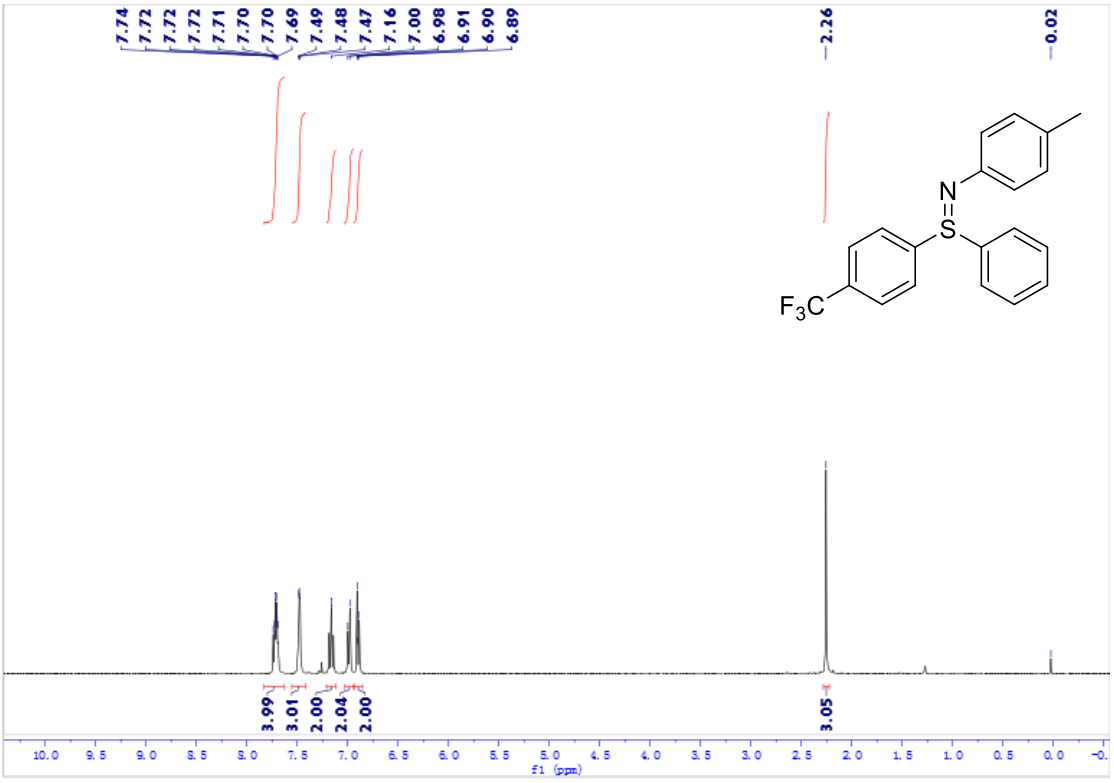
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(4-Chlorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3da)



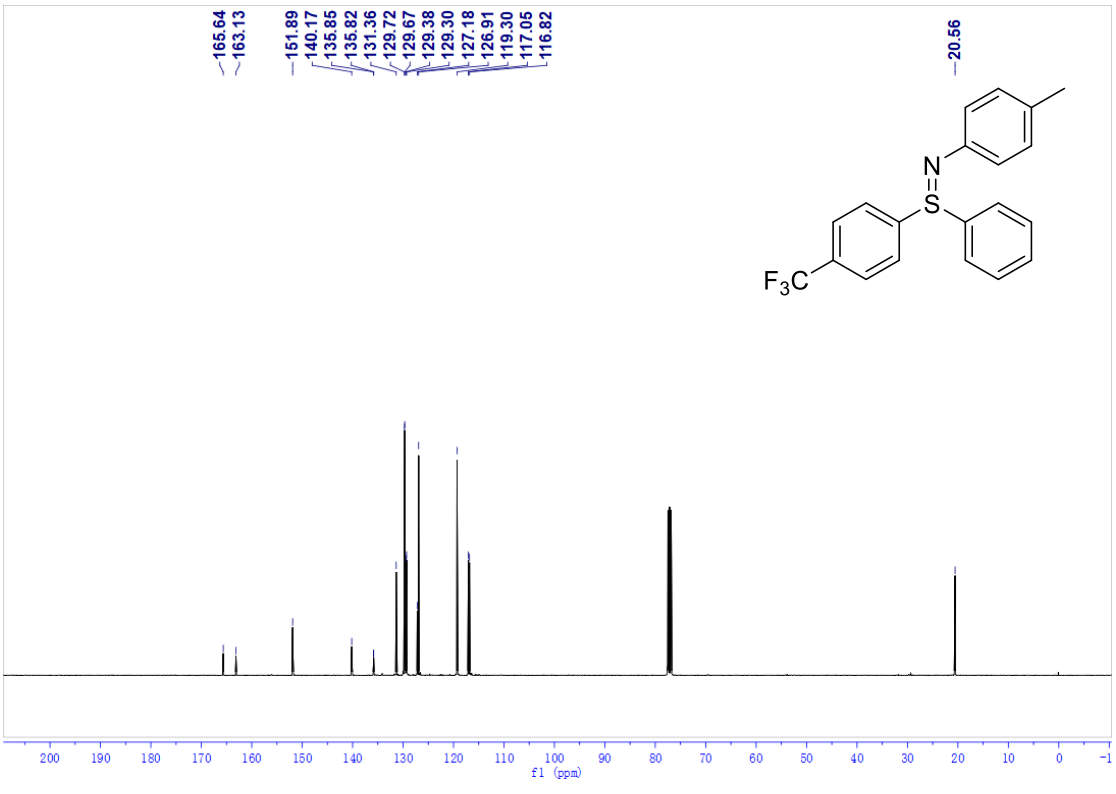
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(4-Chlorophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3da)



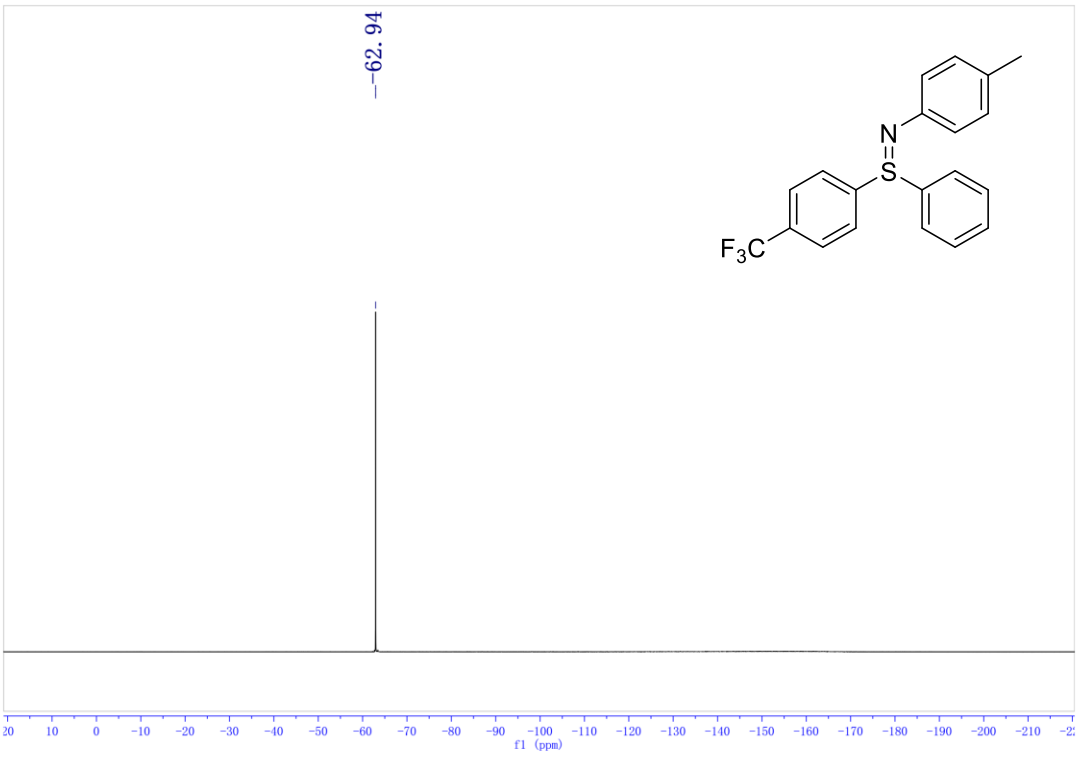
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-*N*-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3ea)



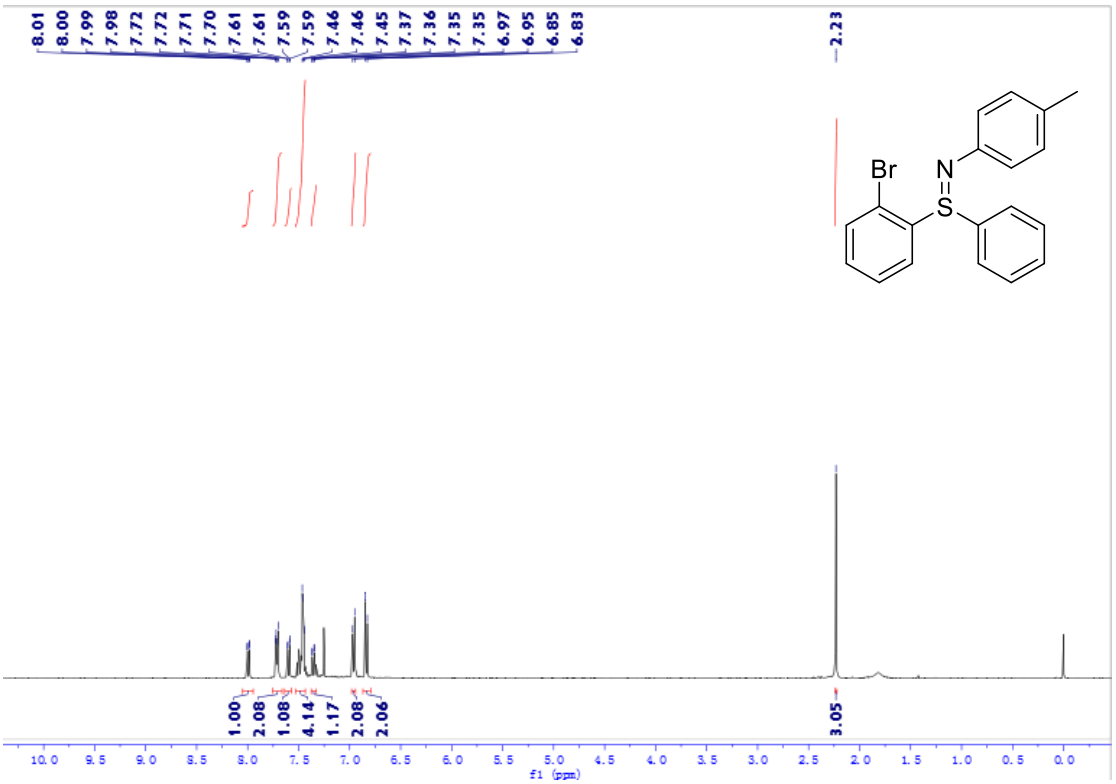
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-*N*-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3ea)



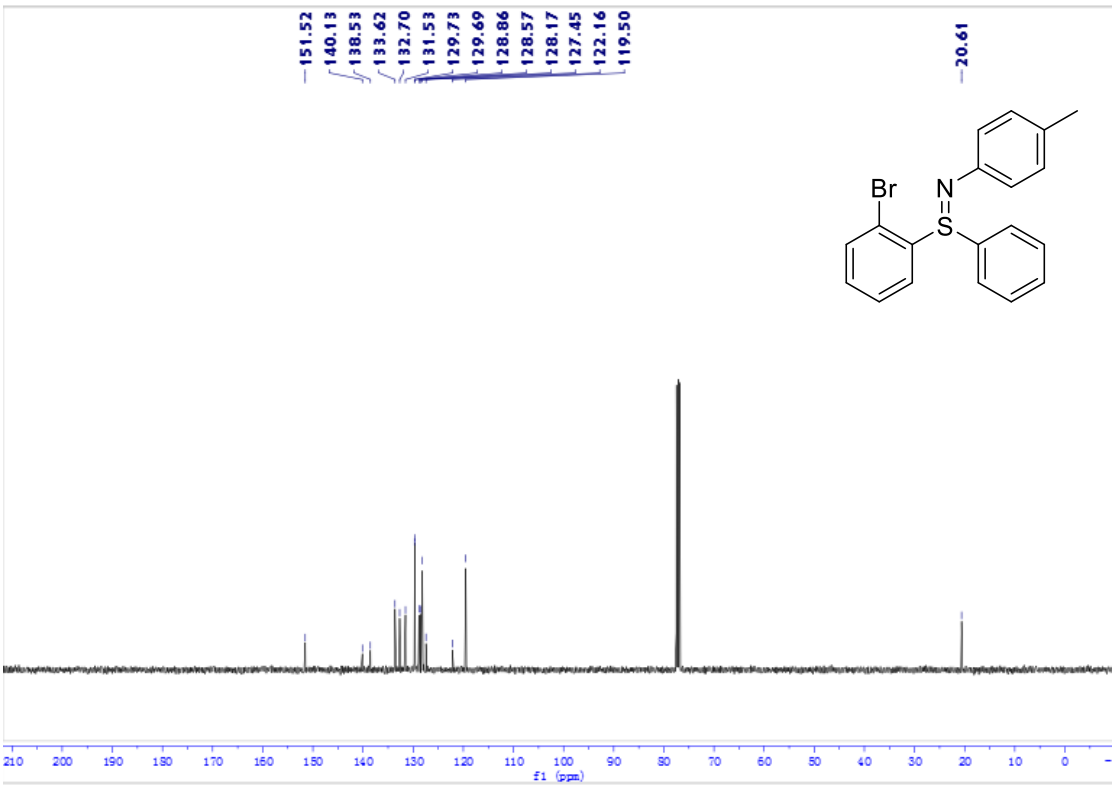
^{19}F NMR (376 MHz, $CDCl_3$) of 1-Phenyl-*N*-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)-γ^4-sulfanimine (3ea)



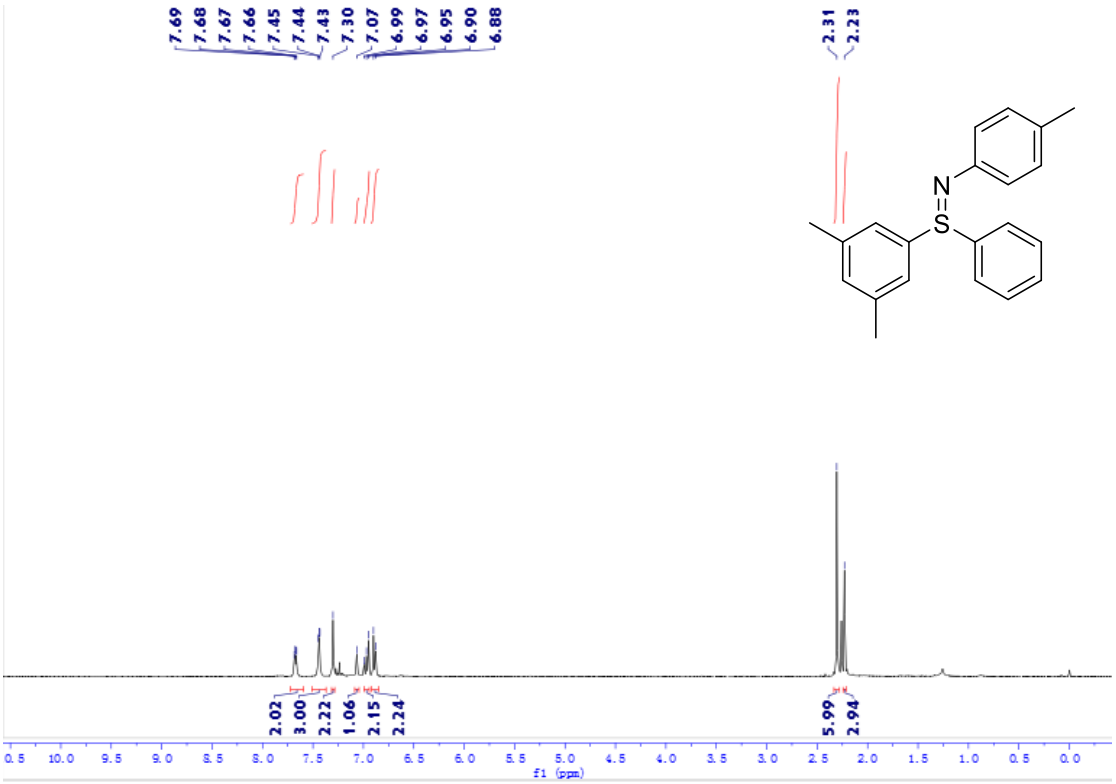
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-Bromophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3fa)



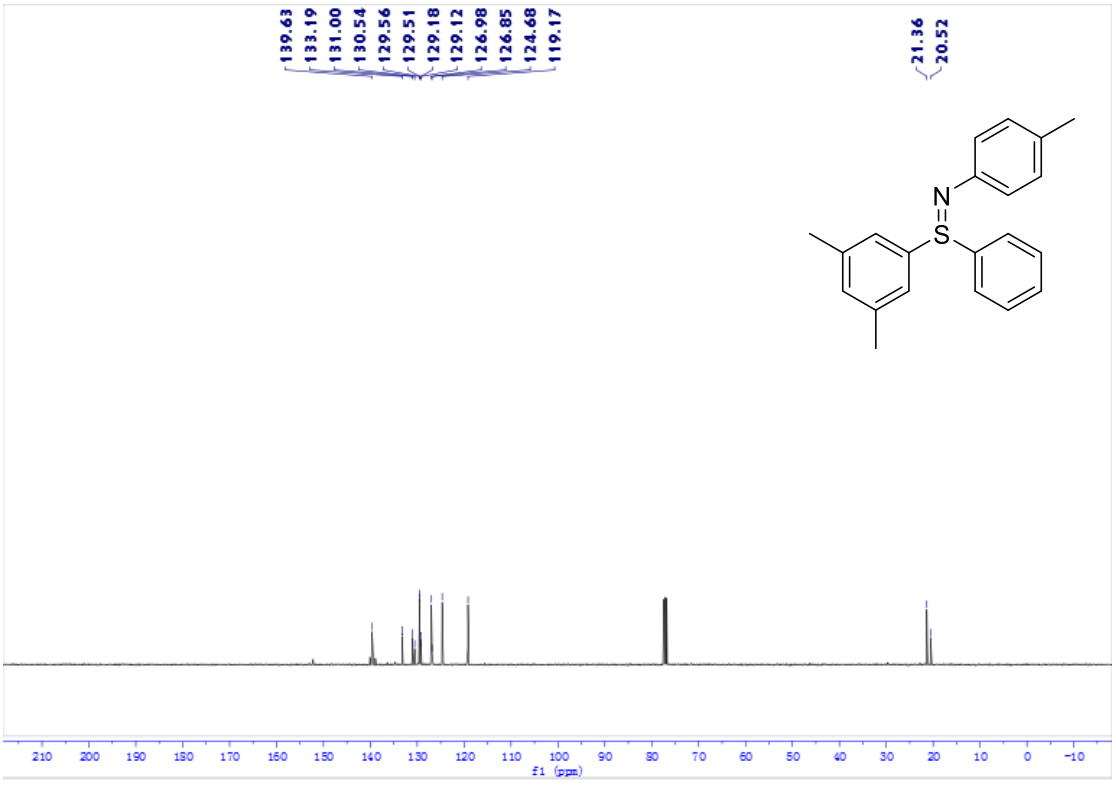
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(2-Bromophenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3fa)



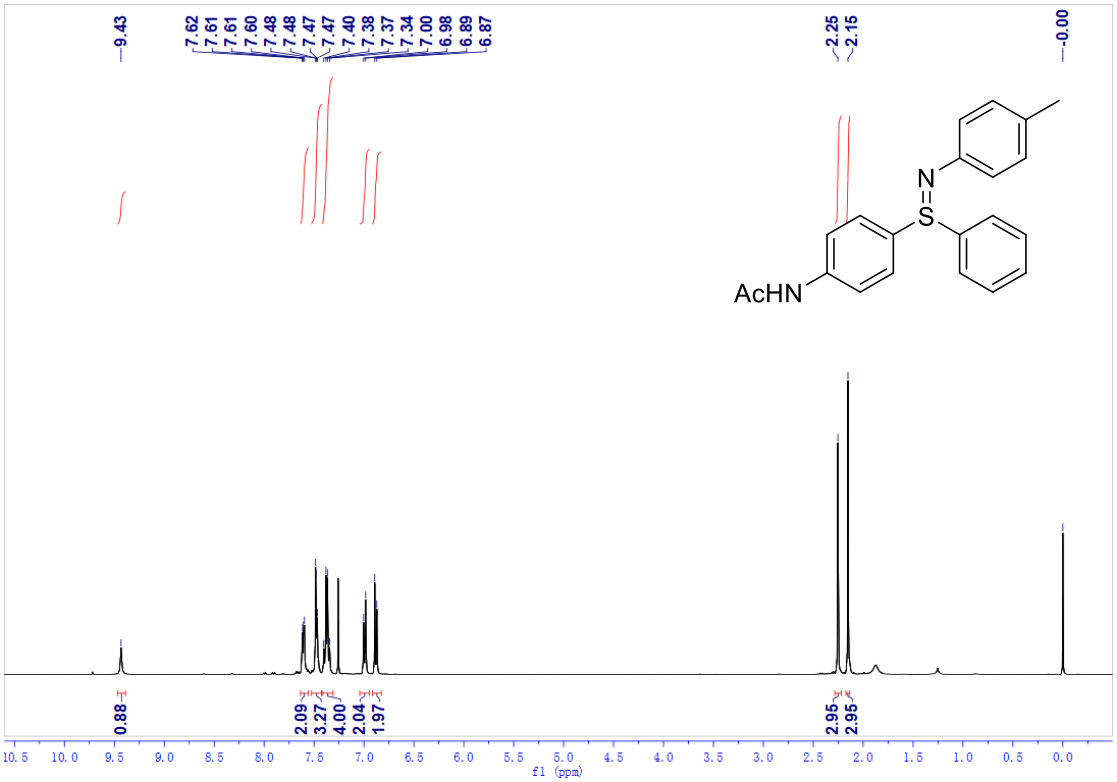
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(3,5-Dimethylphenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ga)



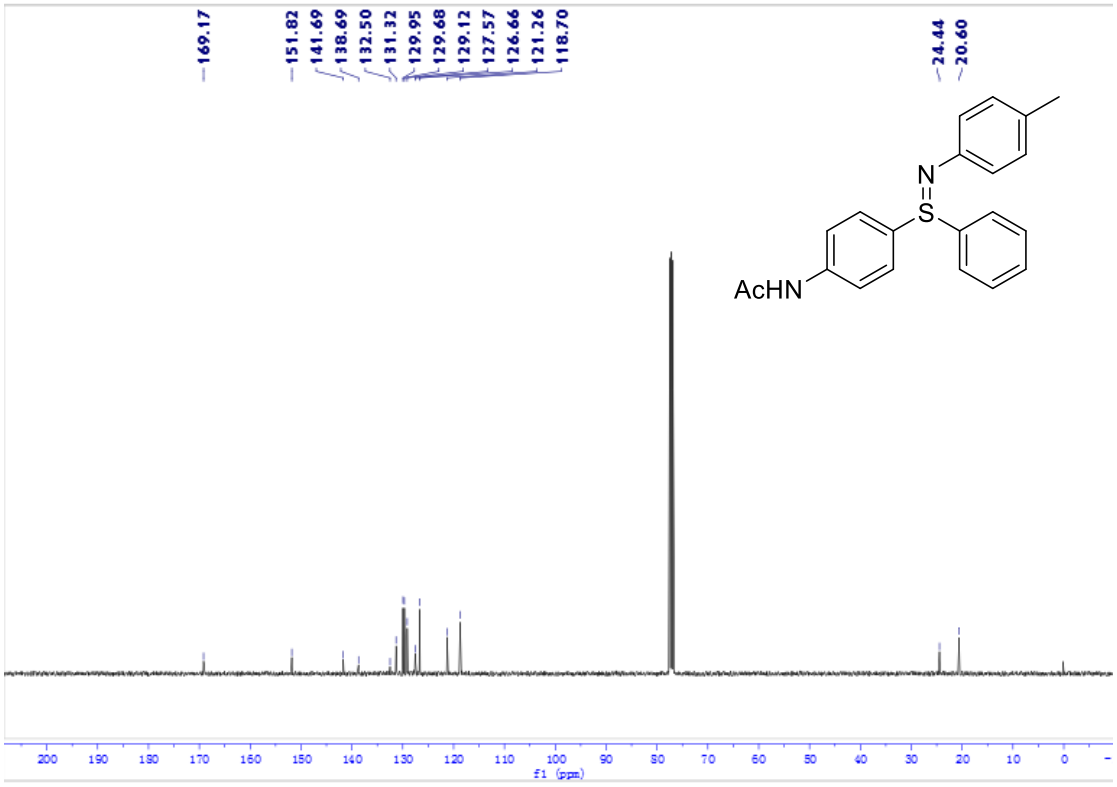
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(3,5-Dimethylphenyl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ga)



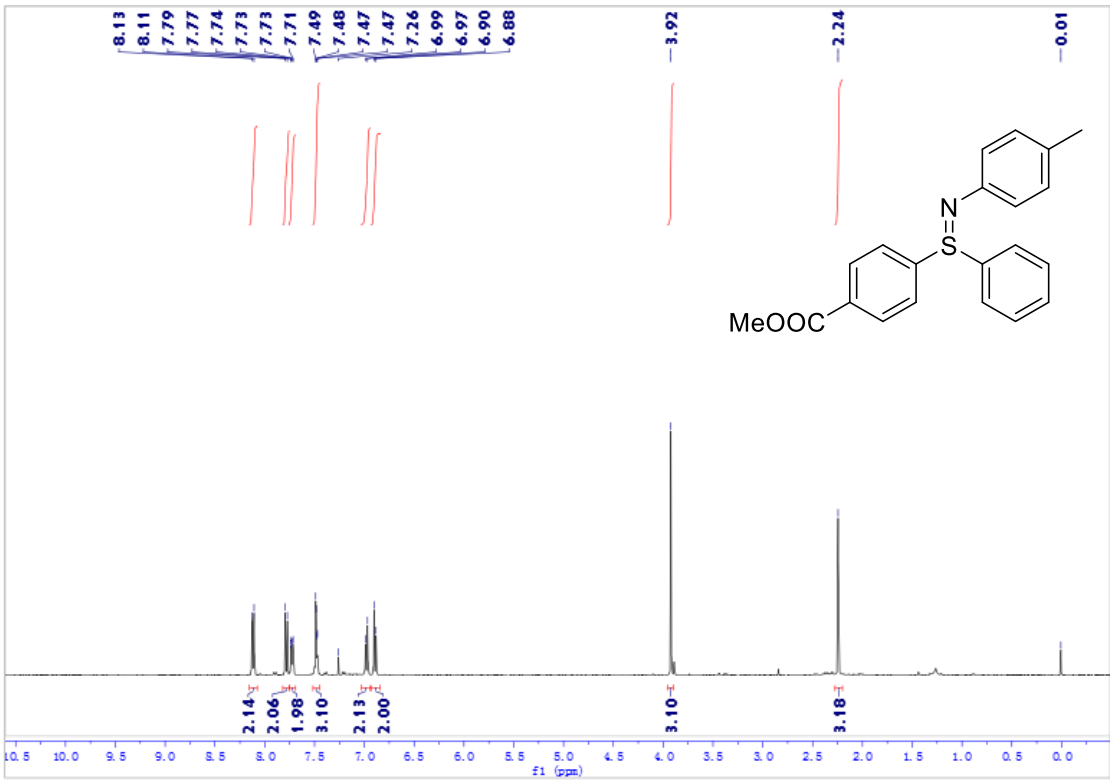
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(4-(*S*-Phenyl-*N*-(*p*-tolyl)sulfinimidoyl)phenyl)acetamide (3ha)



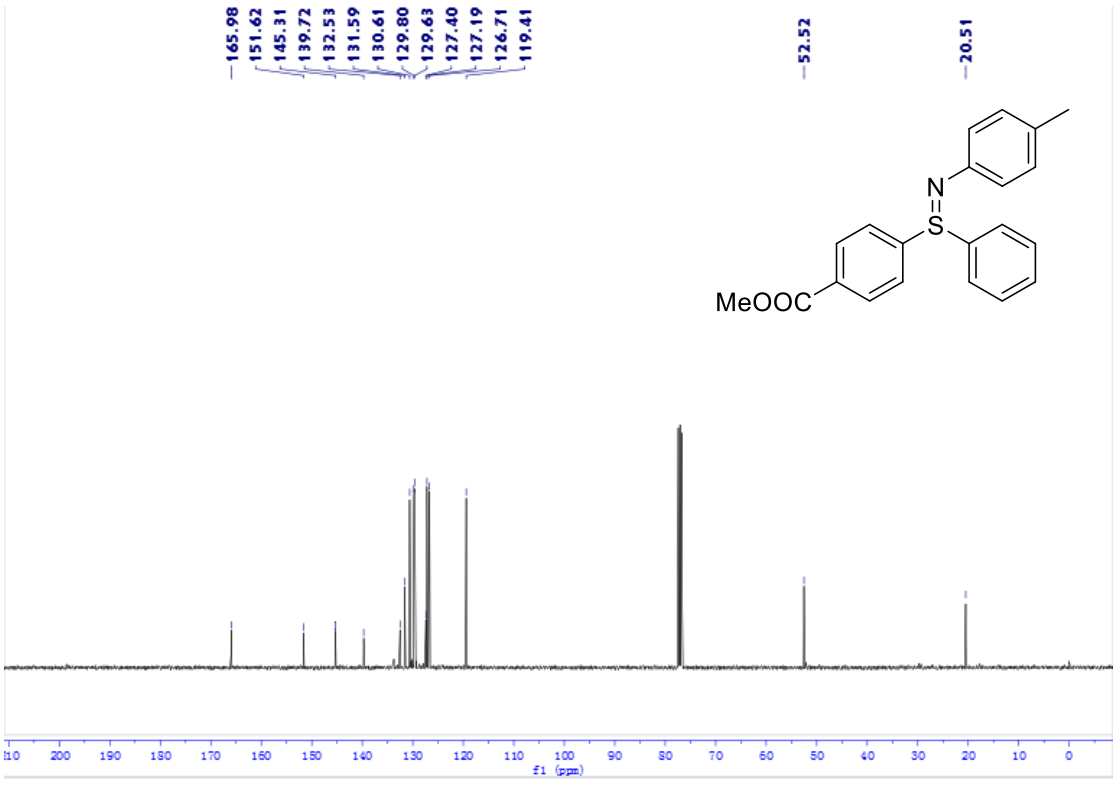
^{13}C NMR (100 MHz, $CDCl_3$) of *N*-(4-(*S*-Phenyl-*N*-(*p*-tolyl)sulfinimidoyl)phenyl)acetamide (3ha)



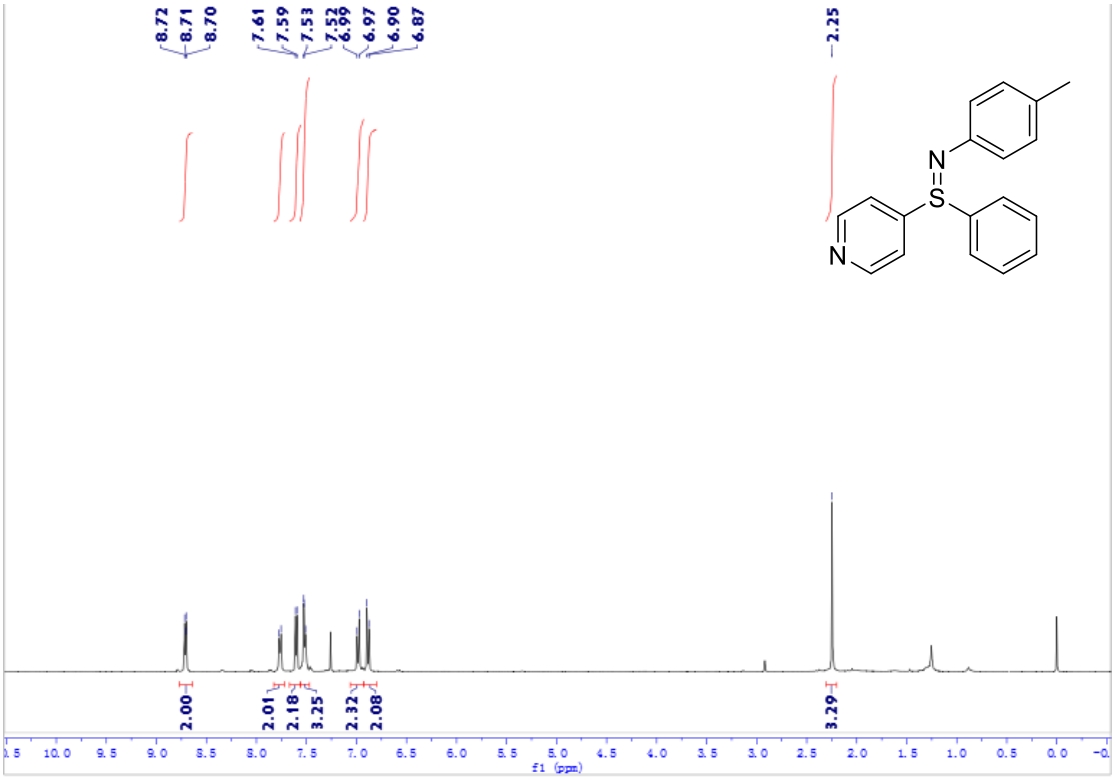
^{1}H NMR (400 MHz, $CDCl_3$) of Methyl 4-(*S*-phenyl-*N*-(*p*-tolyl)sulfinimidoyl)benzoate (3ia)



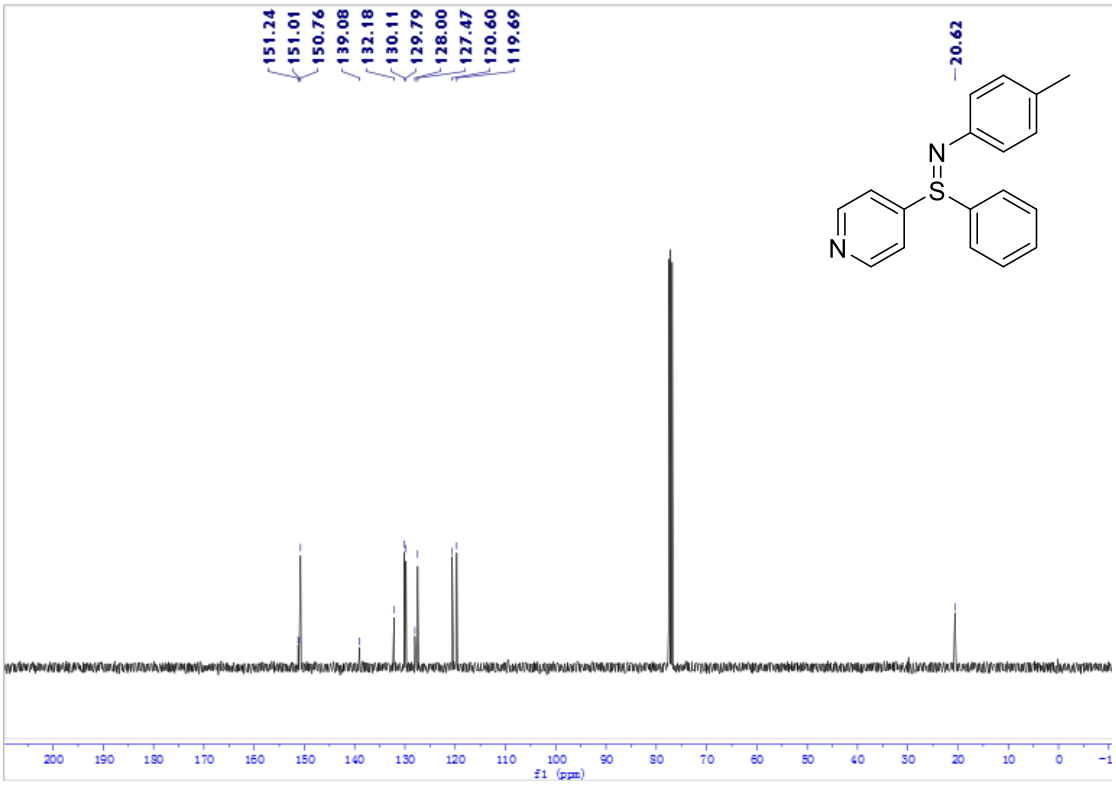
^{13}C NMR (100 MHz, $CDCl_3$) of Methyl 4-(*S*-phenyl-*N*-(*p*-tolyl)sulfinimidoyl)benzoat (3ia)



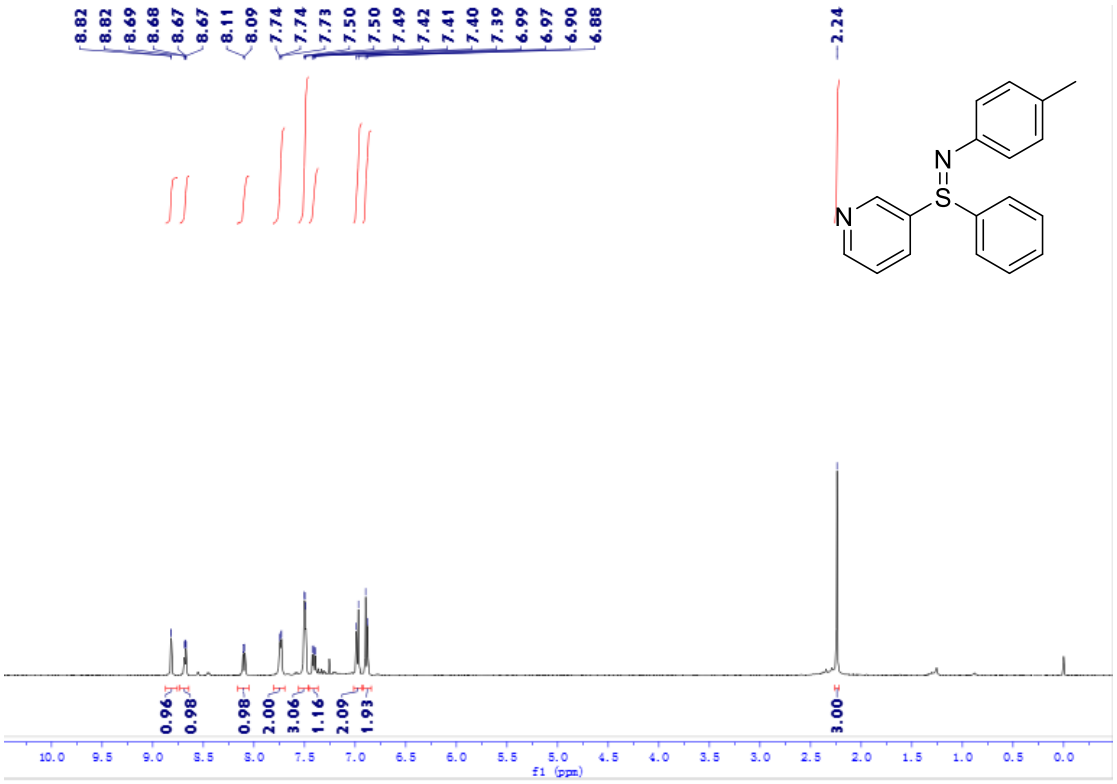
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-4-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ja)



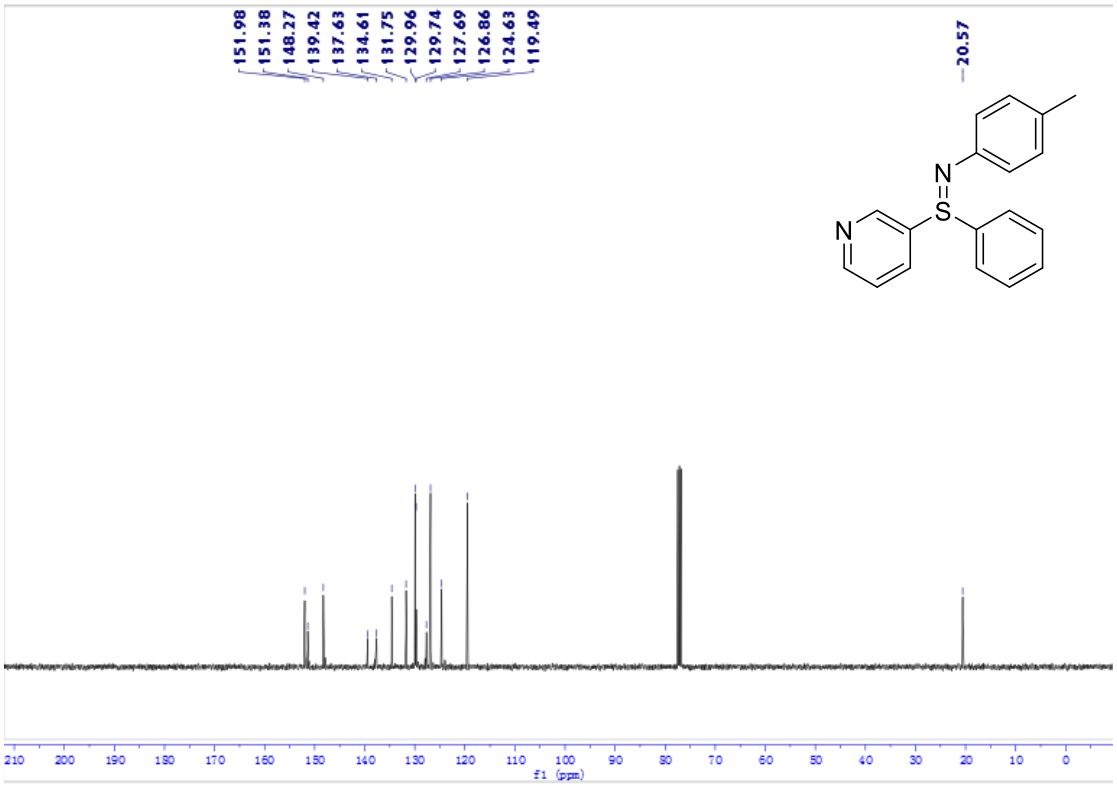
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-4-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ja)



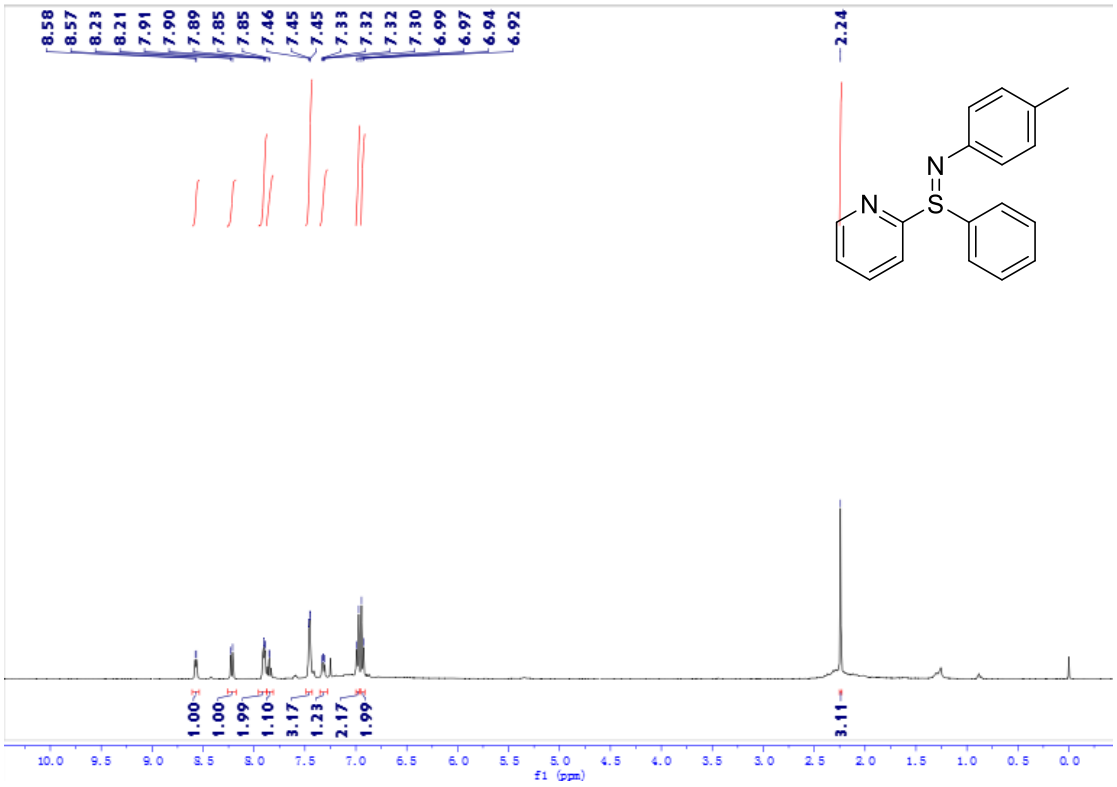
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-3-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ka)



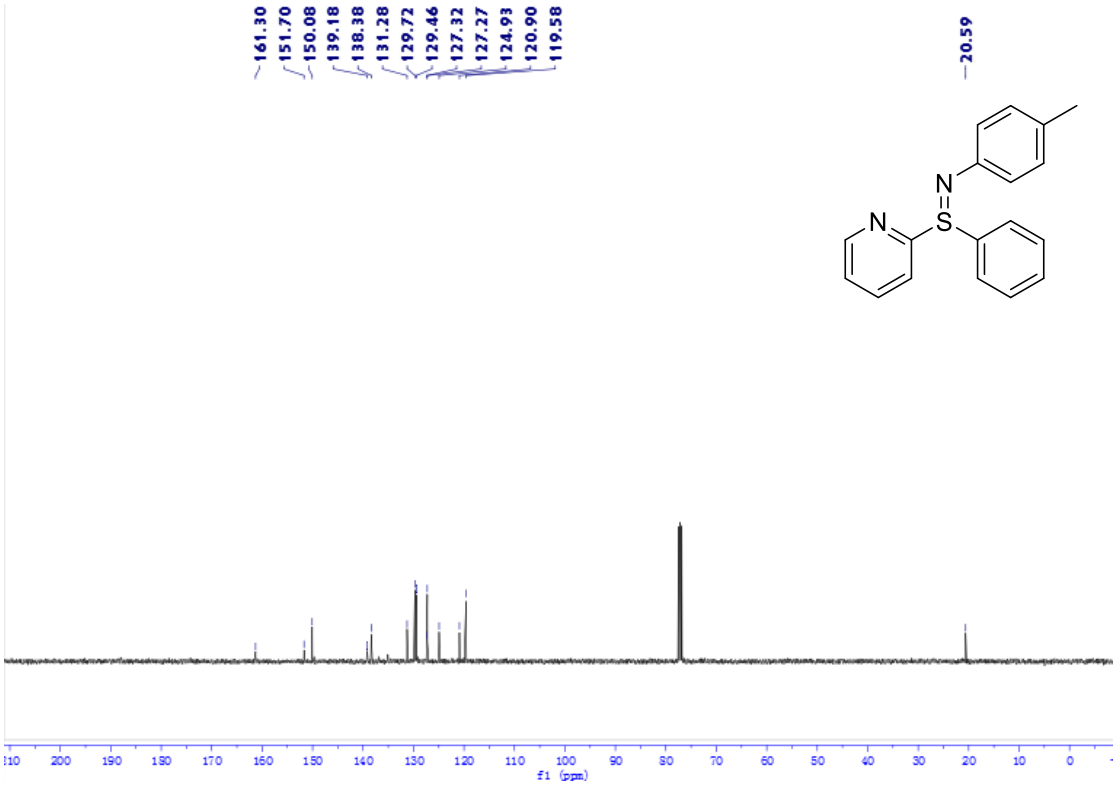
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-3-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ka)



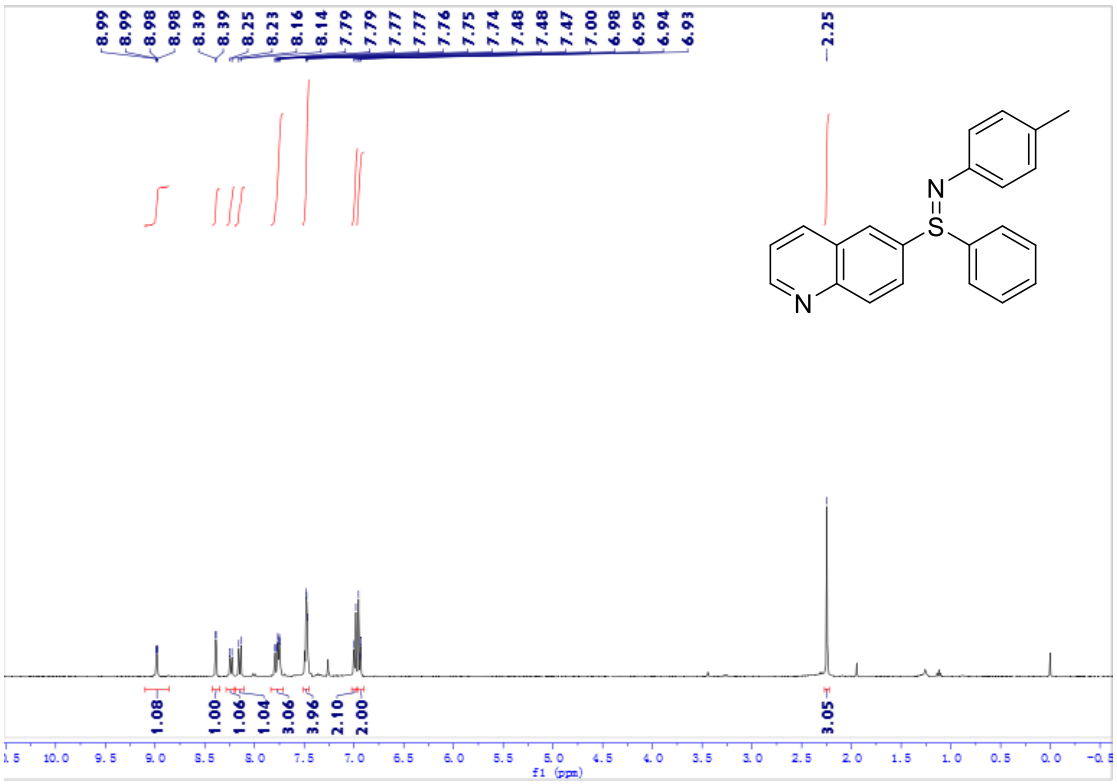
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-2-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3la)



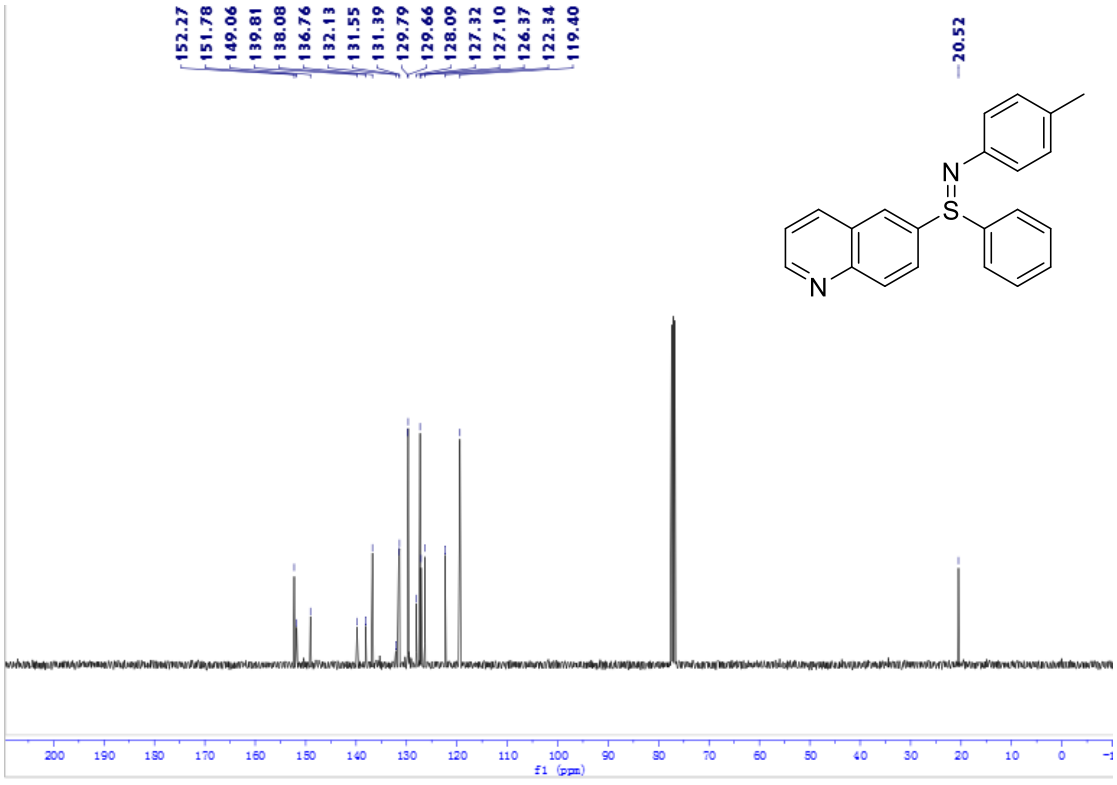
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-1-(pyridin-2-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3la)



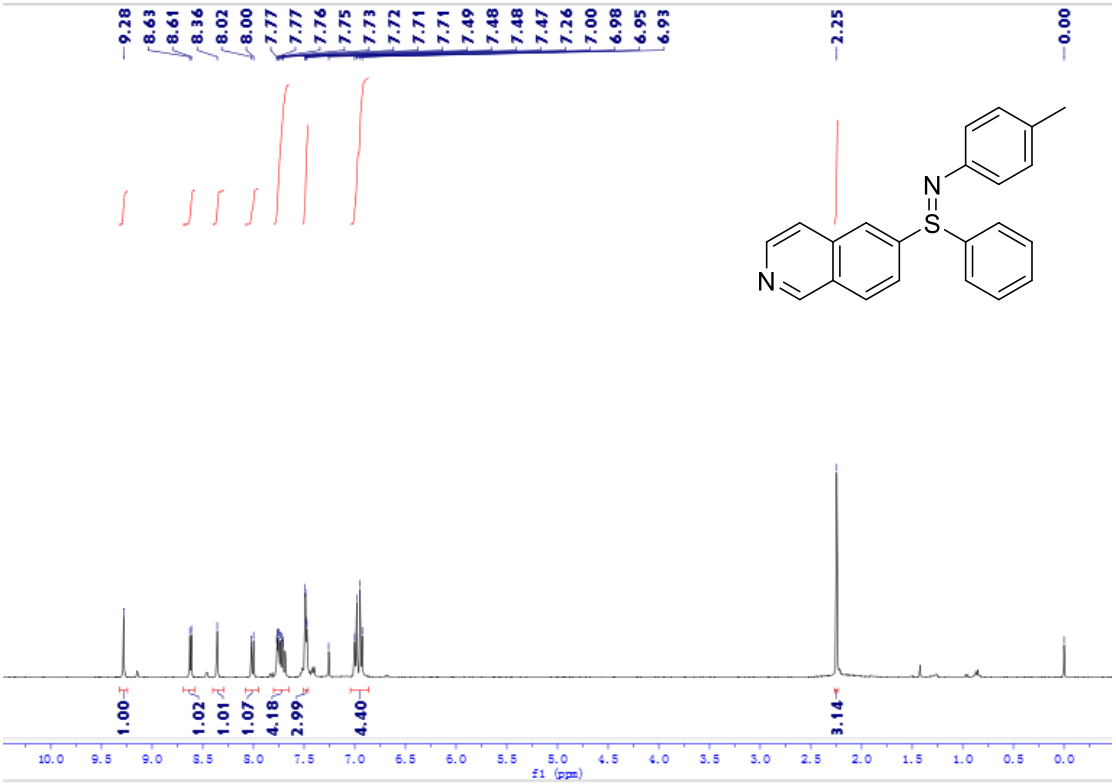
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Phenyl-1-(quinolin-6-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ma)



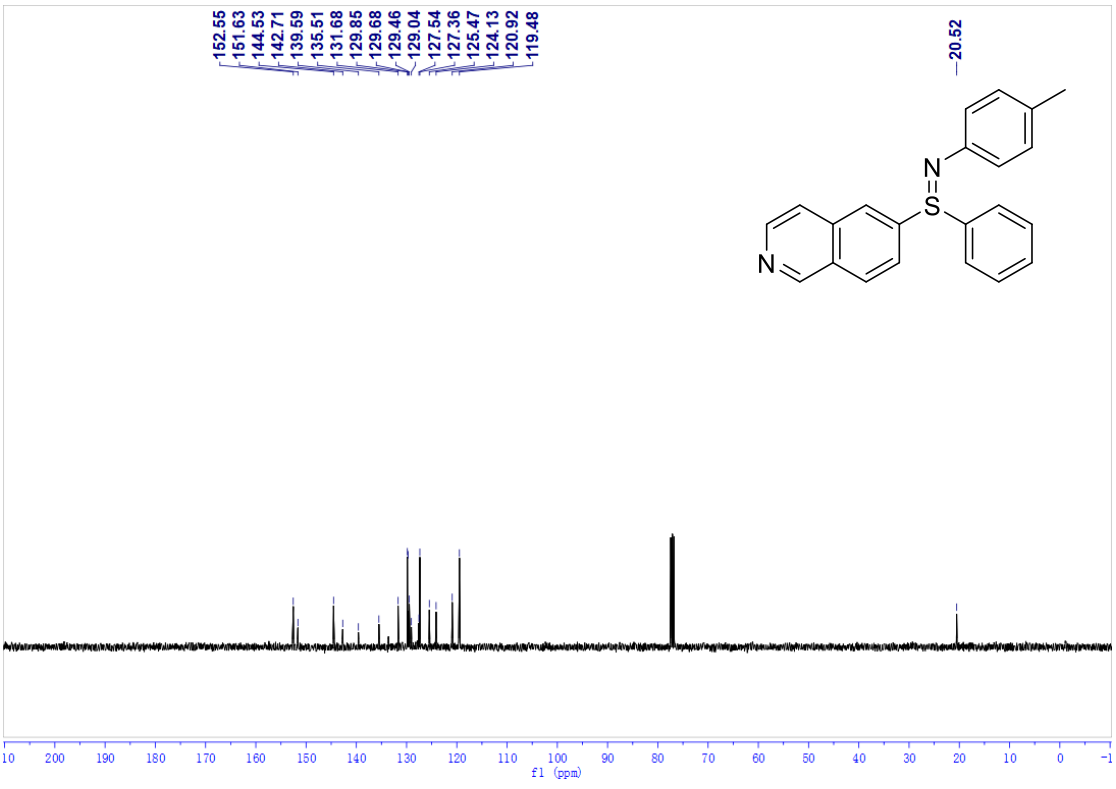
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Phenyl-1-(quinolin-6-yl)-*N*-(*p*-tolyl)-γ^4-sulfanimine (3ma)



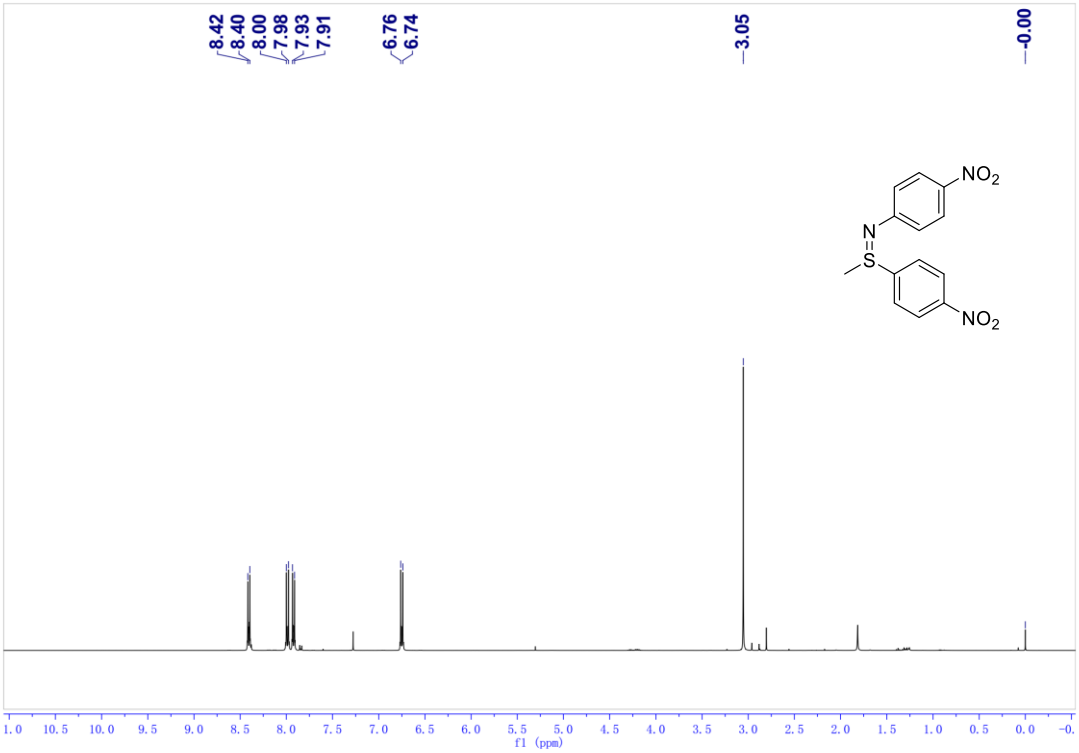
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(Isoquinolin-6-yl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3na)



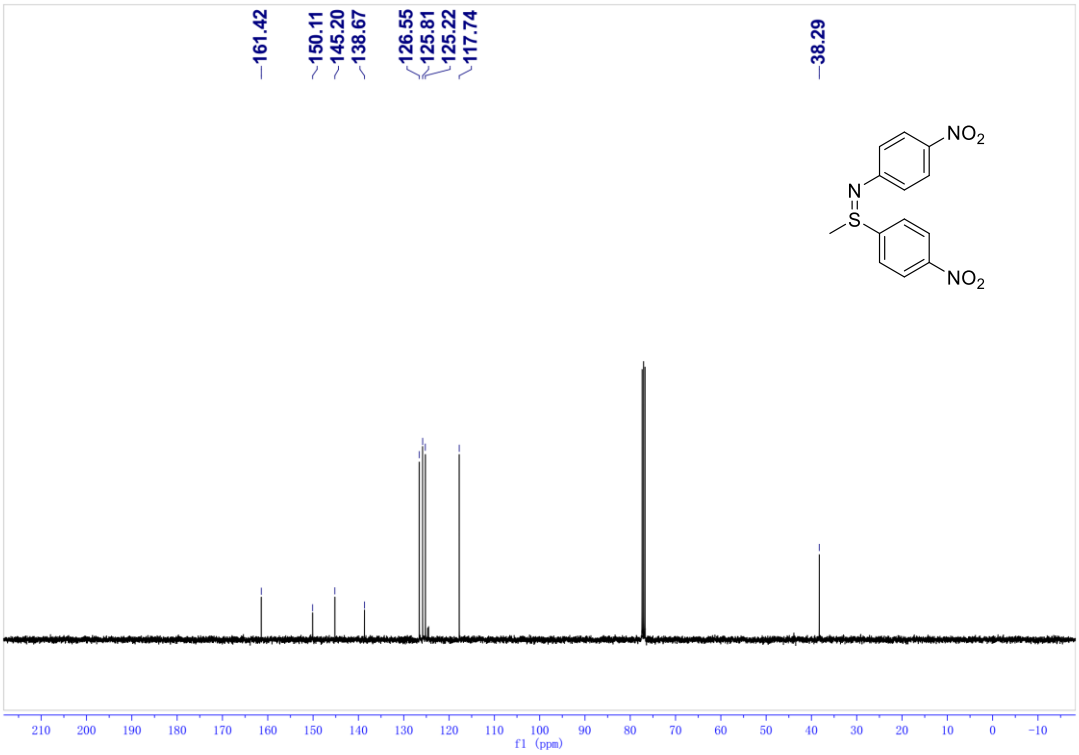
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(Isoquinolin-6-yl)-1-phenyl-*N*-(*p*-tolyl)-γ^4-sulfanimine (3na)



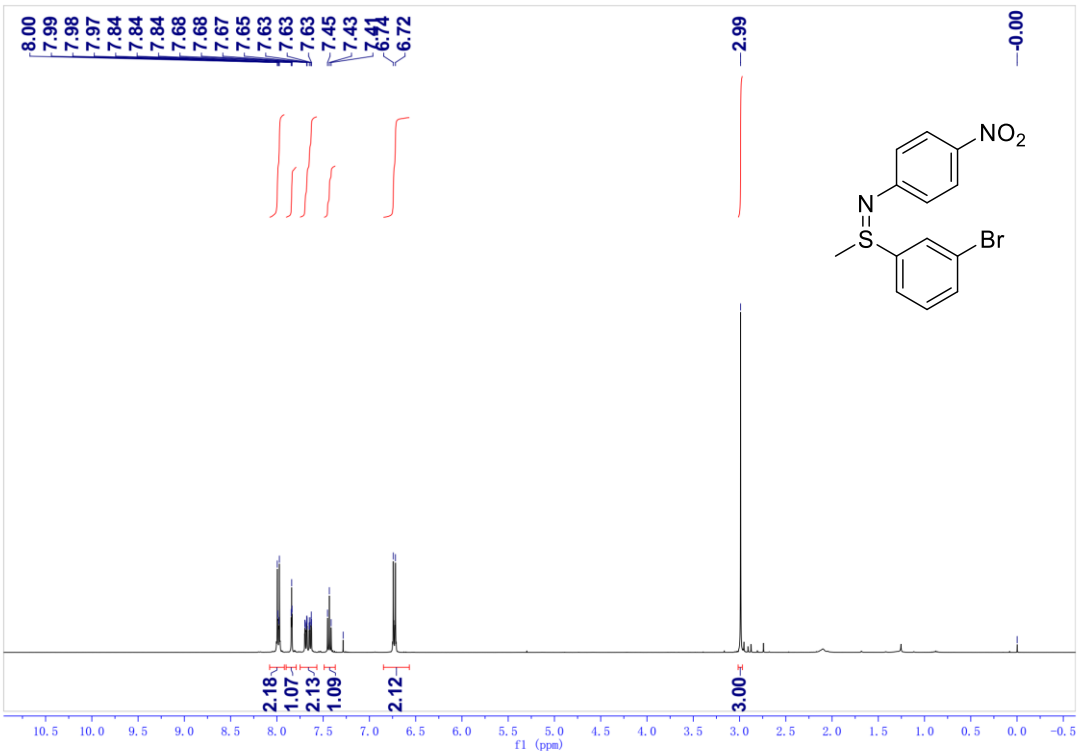
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Methyl-*N*,1-bis(4-nitrophenyl)-λ^4-sulfanimine (3op)



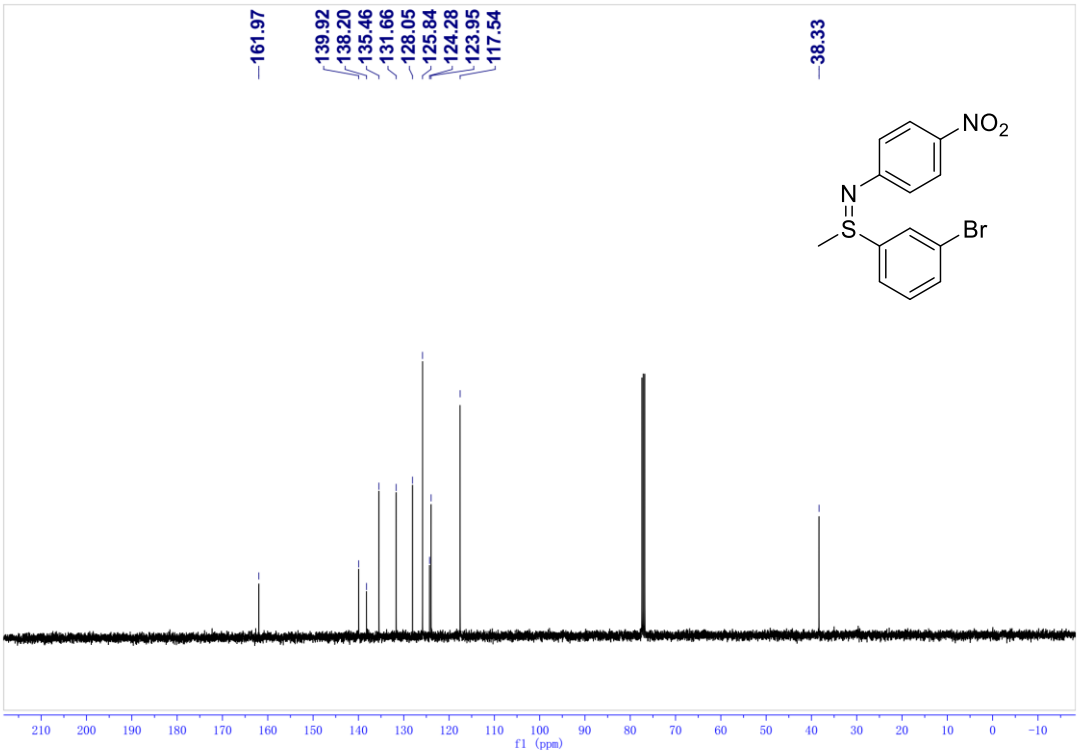
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Methyl-*N*,1-bis(4-nitrophenyl)-λ^4-sulfanimine (3op)



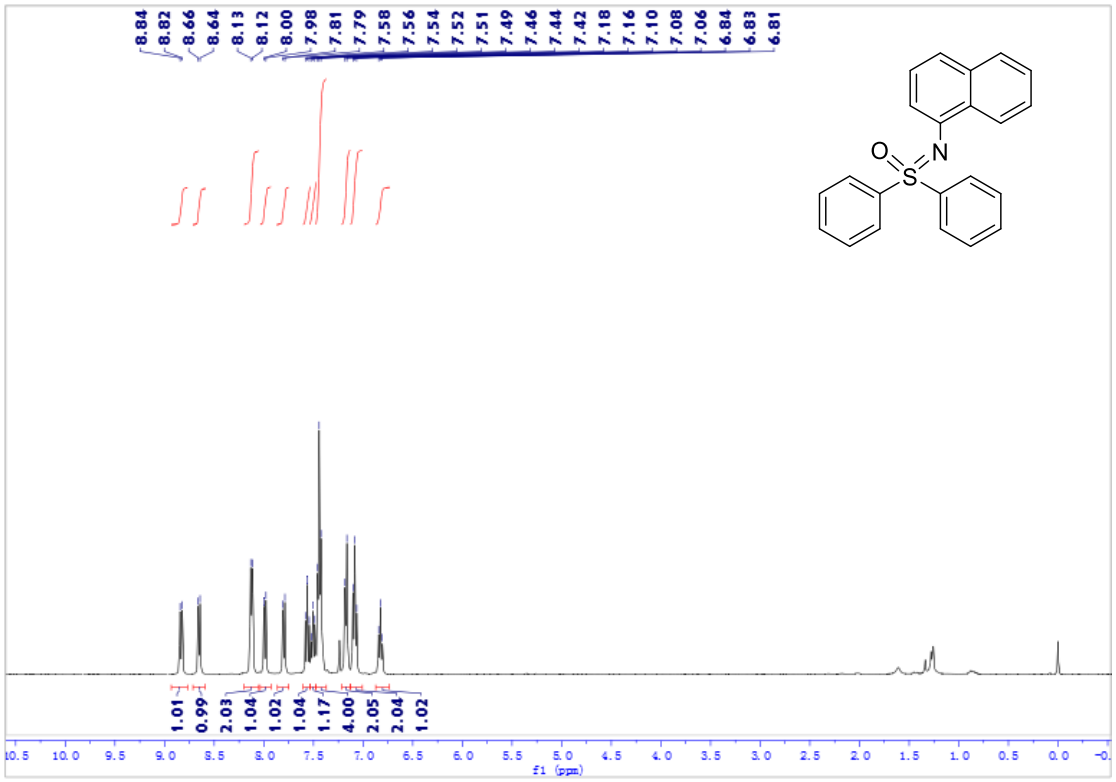
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(3-Bromophenyl)-1-methyl-*N*-(4-nitrophenyl)-λ^{4}-sulfanimine (3pp)



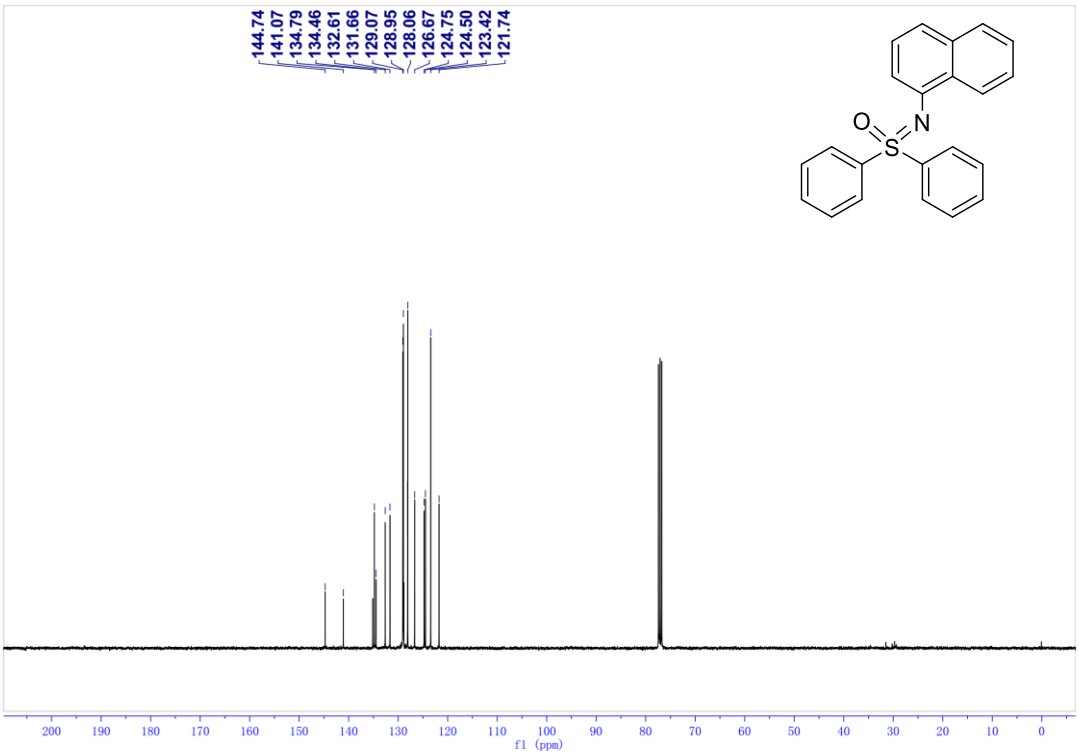
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(3-Bromophenyl)-1-methyl-*N*-(4-nitrophenyl)-λ^{4}-sulfanimine (3pp)



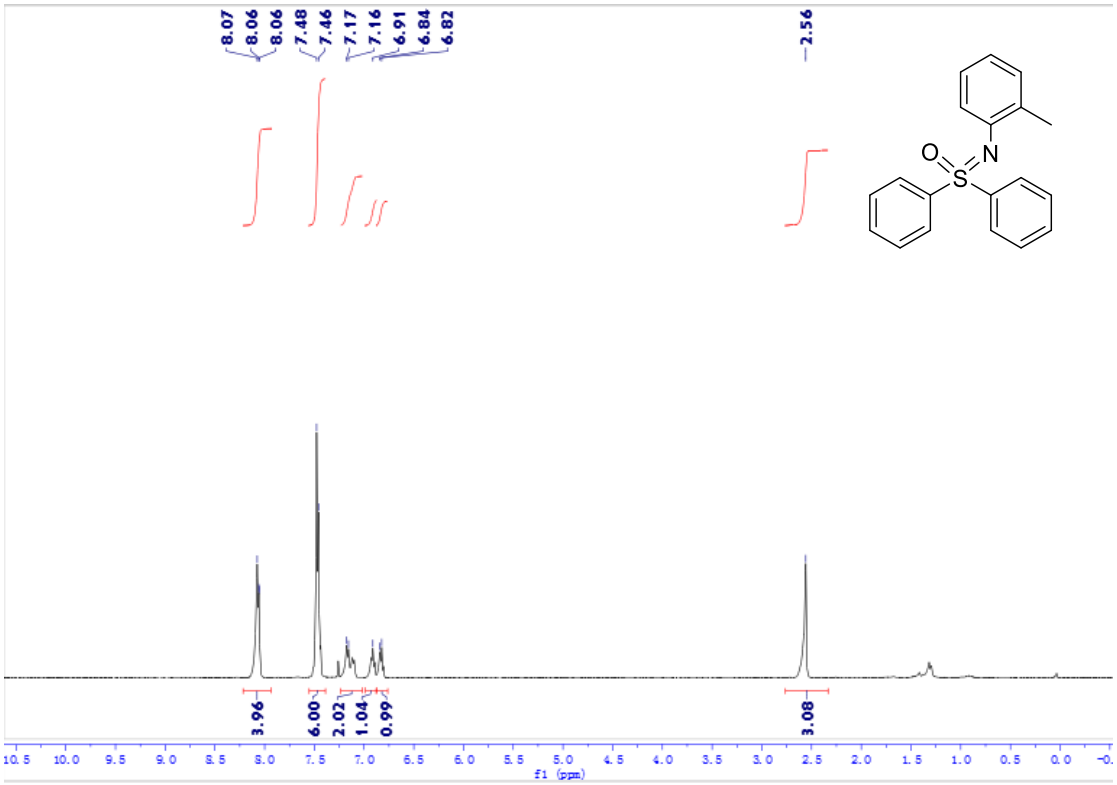
^{1}H NMR (400 MHz, $CDCl_3$) of (Naphthalen-1-ylimino)diphenyl-γ^6-sulfanone (4aq)



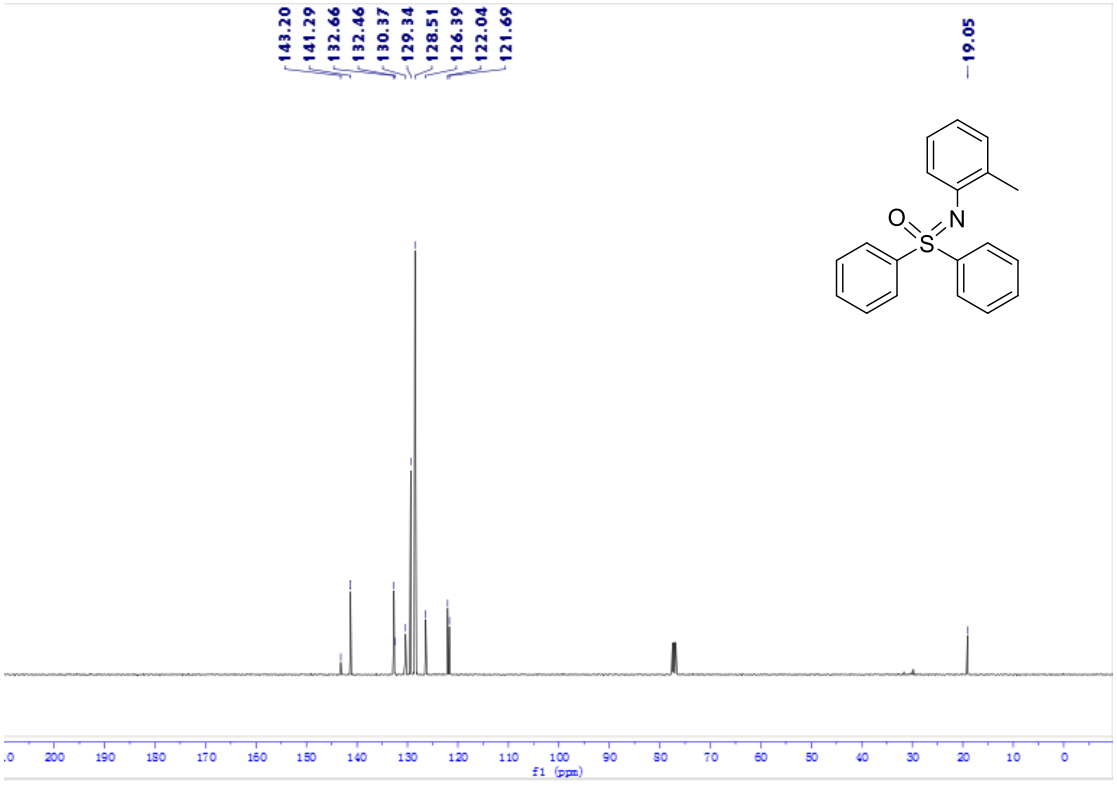
^{13}C NMR (100 MHz, $CDCl_3$) of (Naphthalen-1-ylimino)diphenyl-γ^6-sulfanone (4aq)



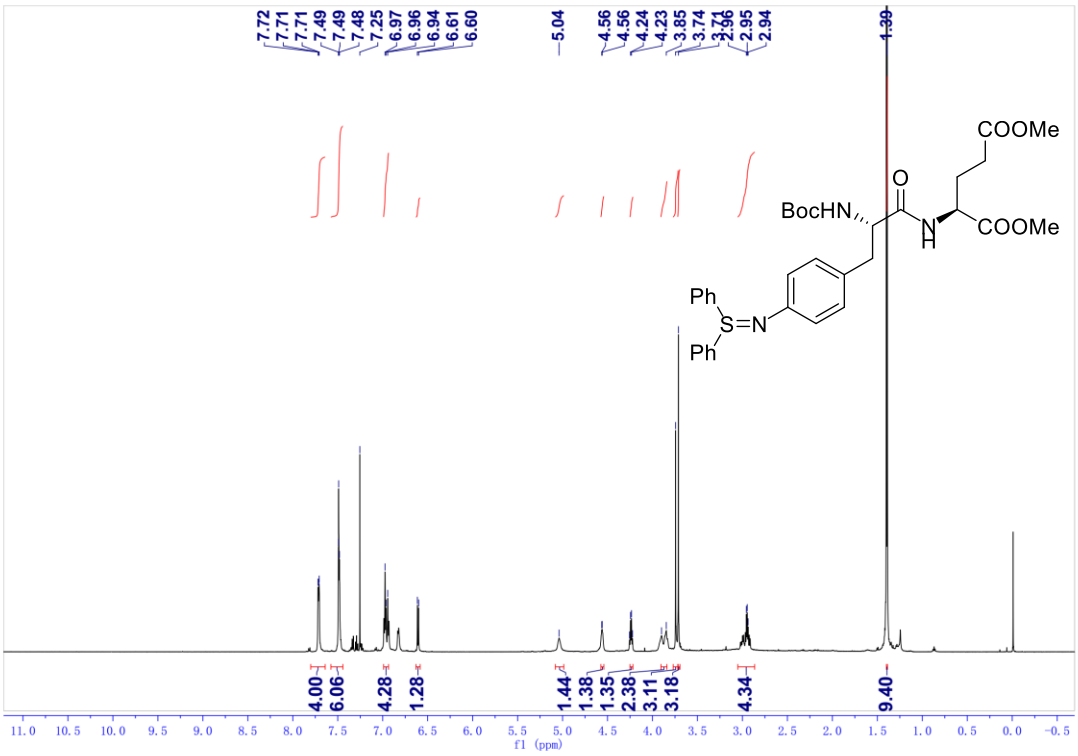
^{1}H NMR (400 MHz, $CDCl_3$) of Diphenyl(*o*-tolylimino)-γ^6-sulfanone (4ar)



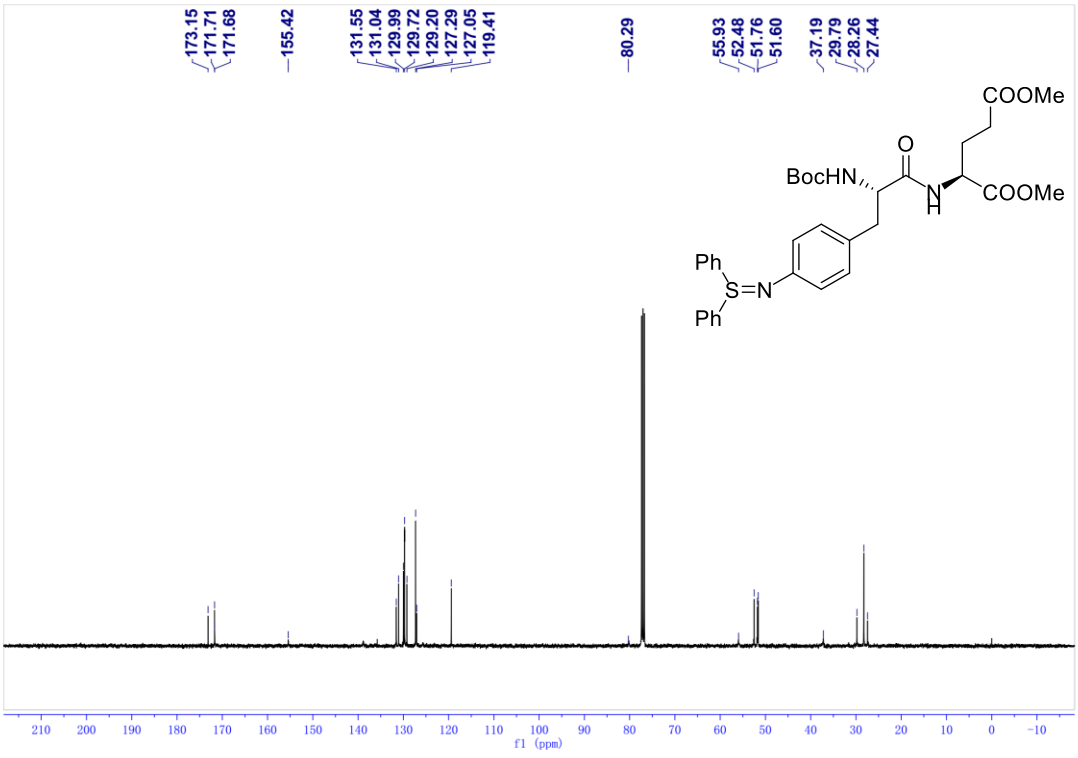
^{13}C NMR (100 MHz, $CDCl_3$) of Diphenyl(*o*-tolylimino)-γ^6-sulfanone (4ar)



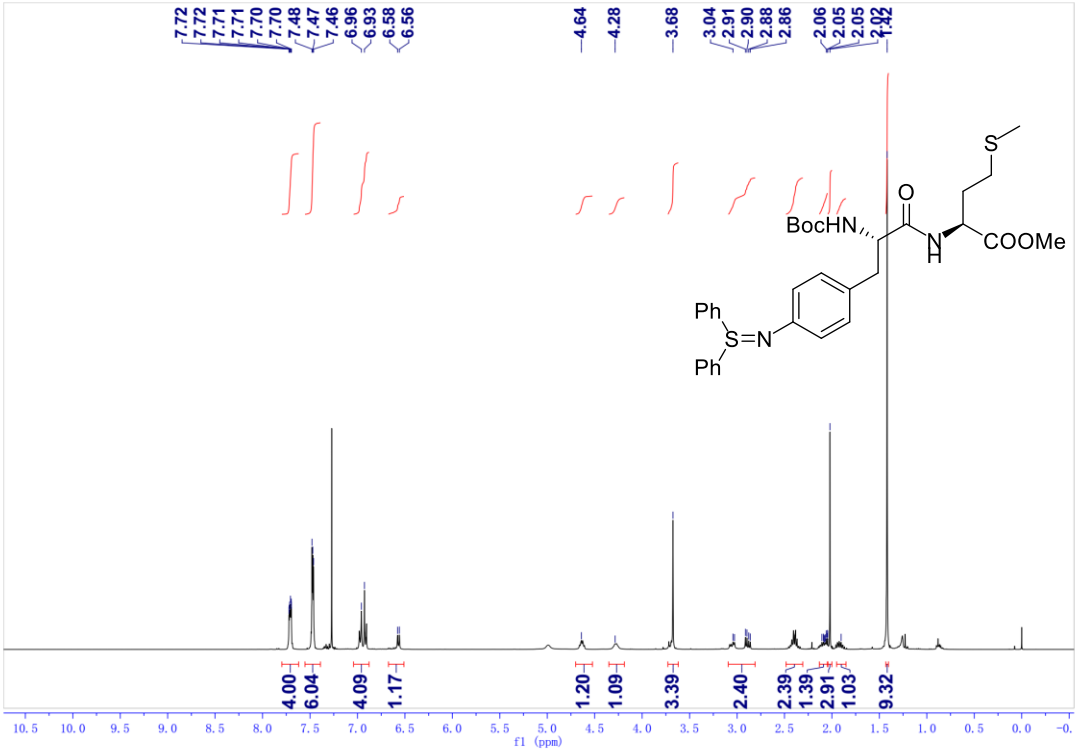
^{1}H NMR (600 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-OMe (6aa)



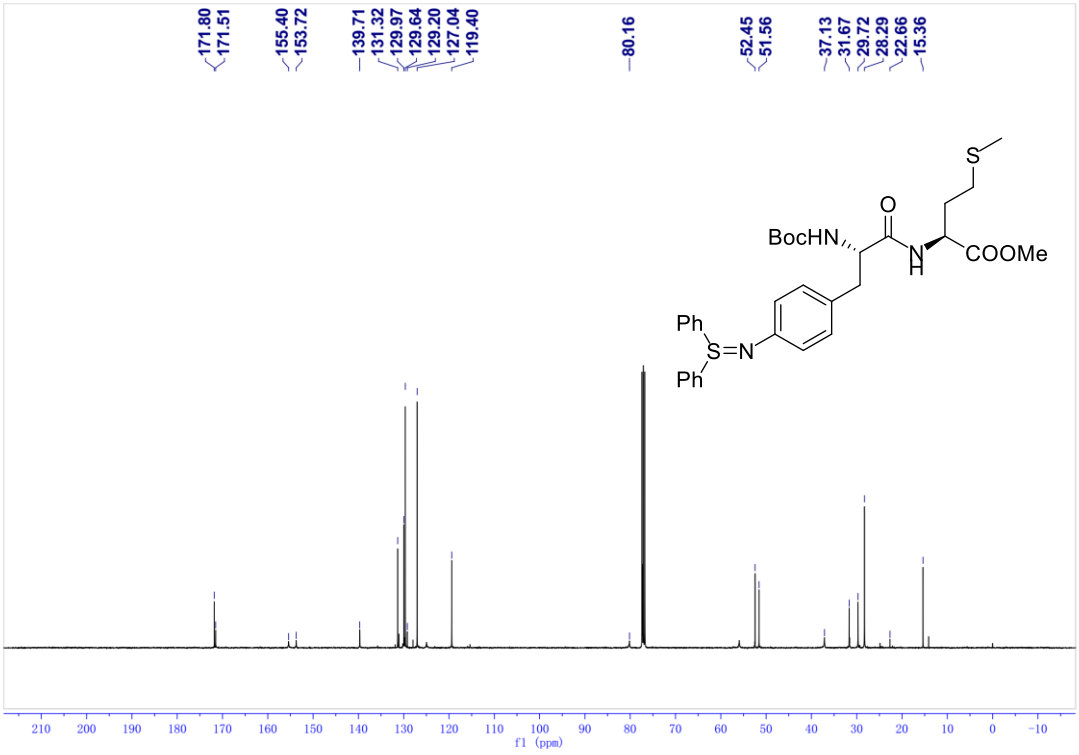
^{13}C NMR (150 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-OMe (6aa)



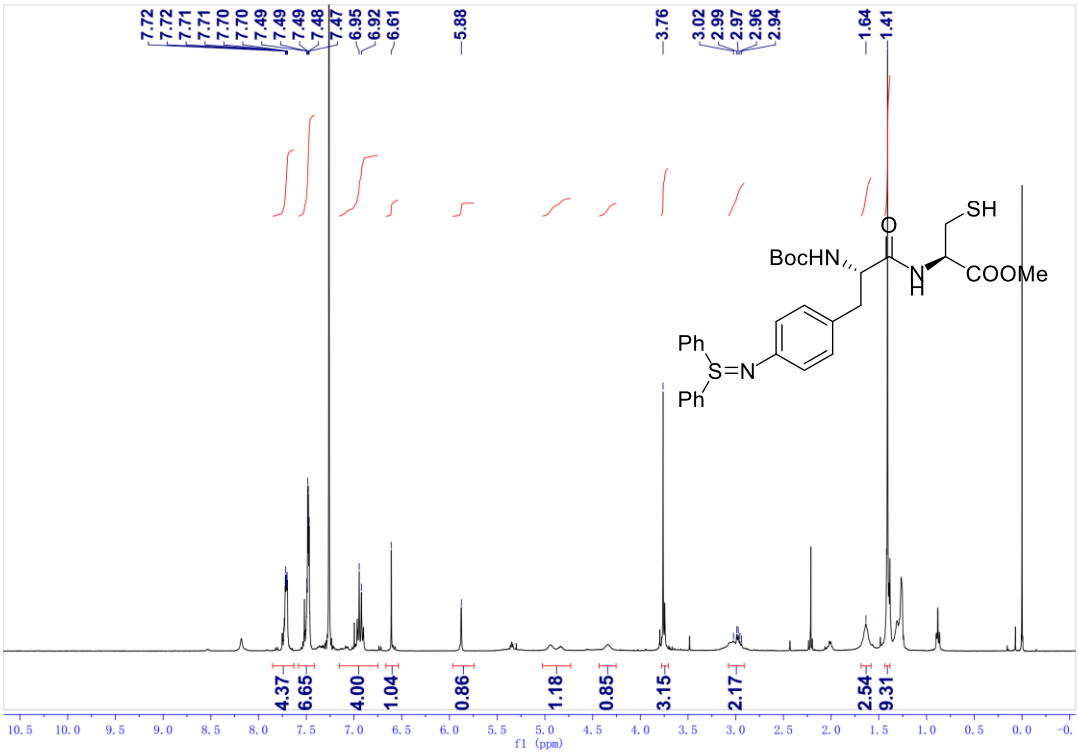
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Met-OMe (6ab)



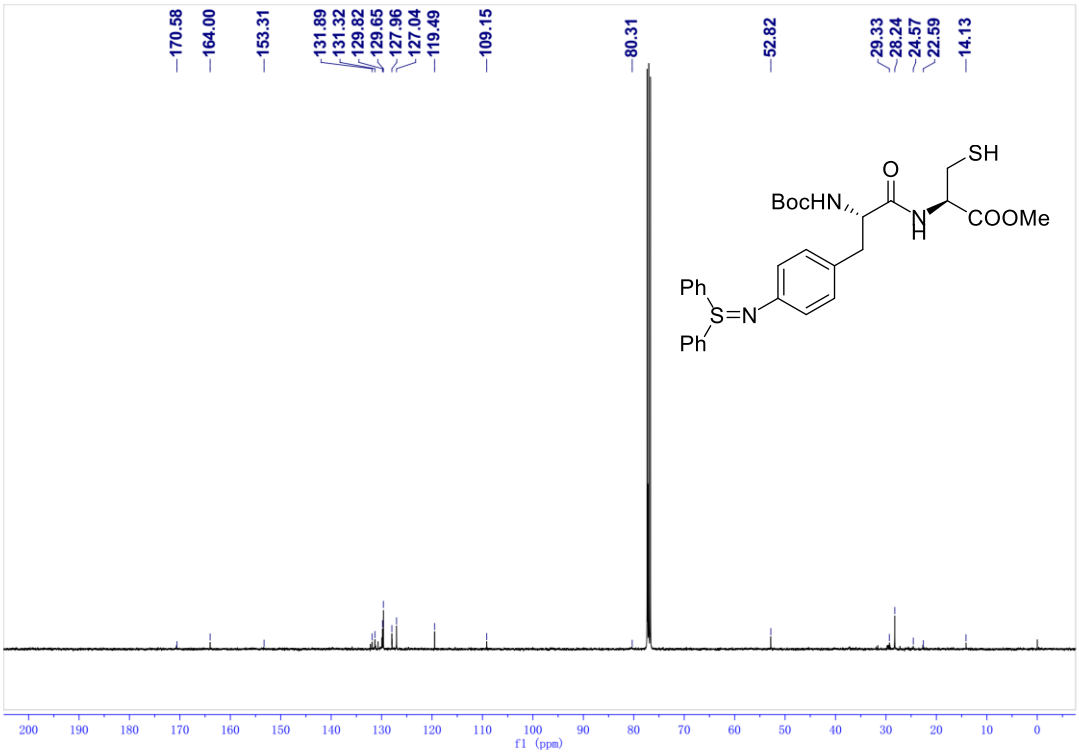
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Met-OMe (6ab)



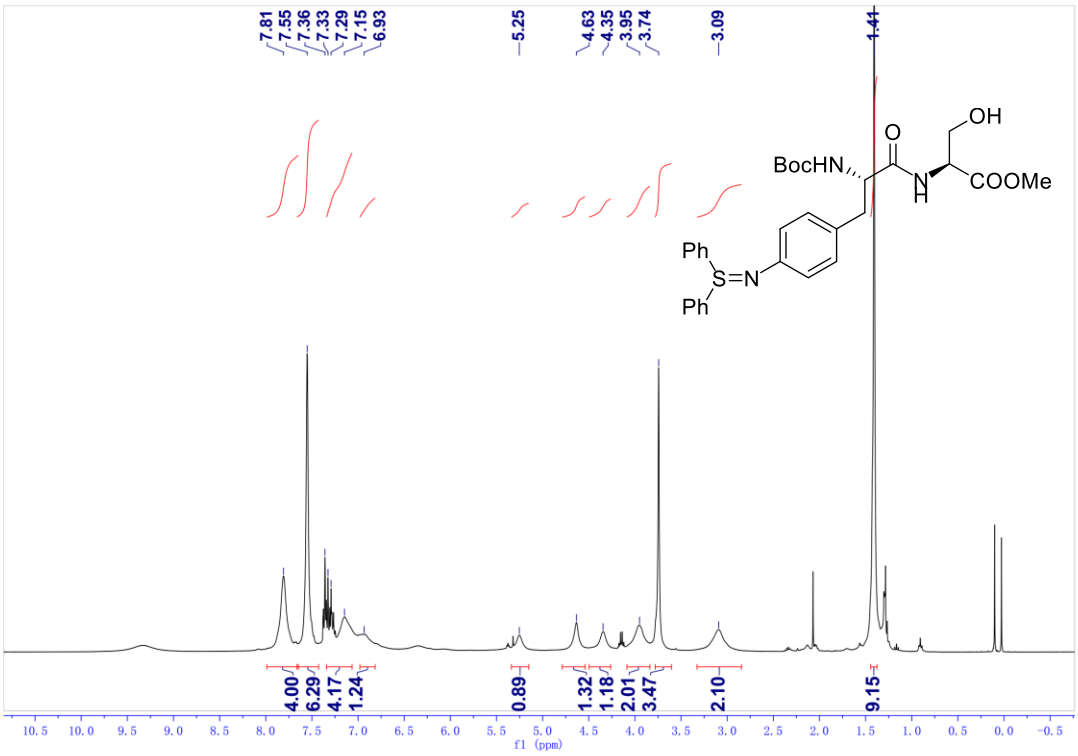
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Cys-OMe (6ac)



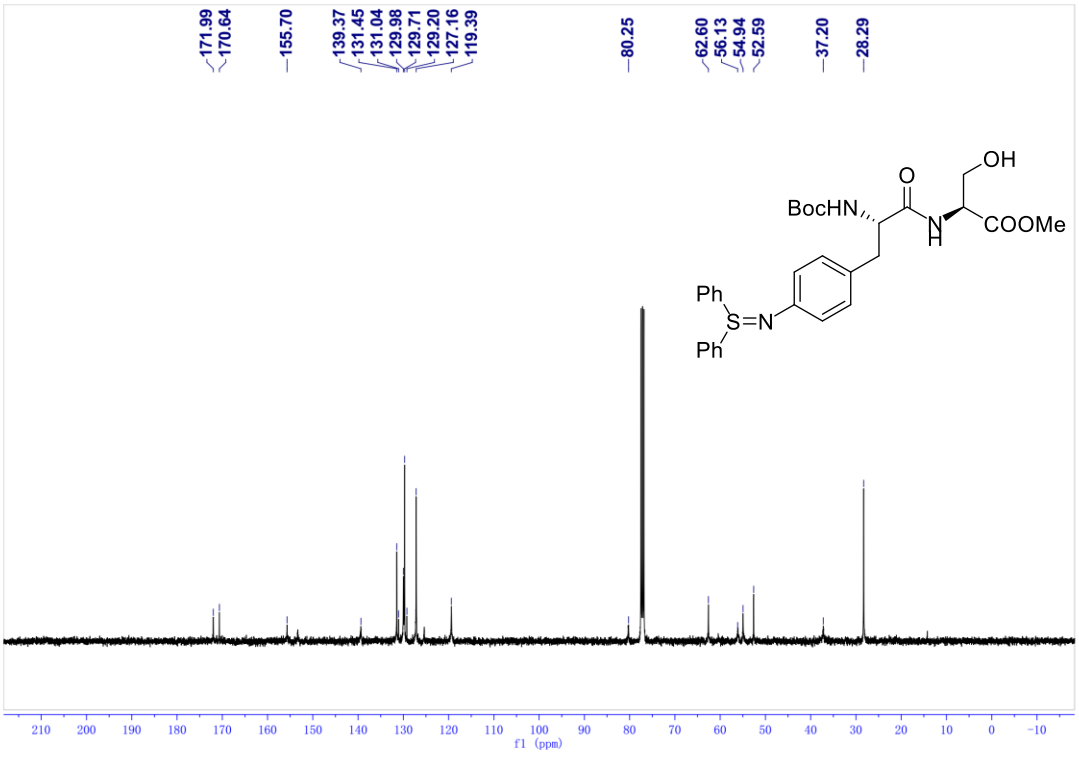
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Cys-OMe (6ac)



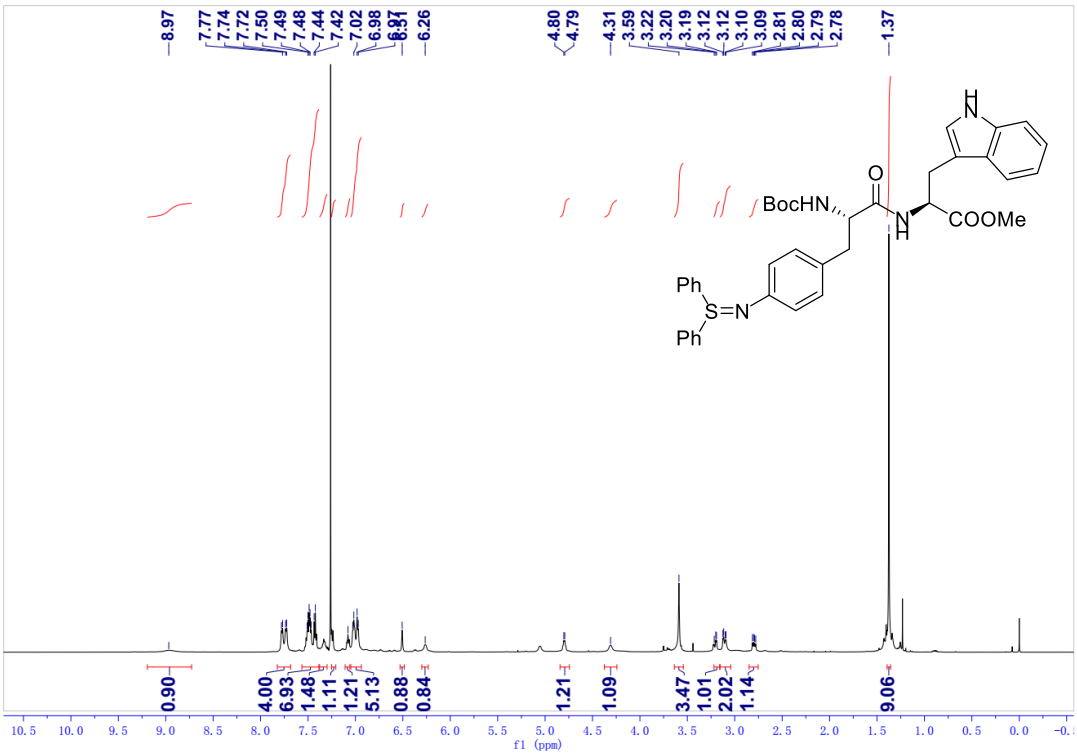
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-OMe (6ad)



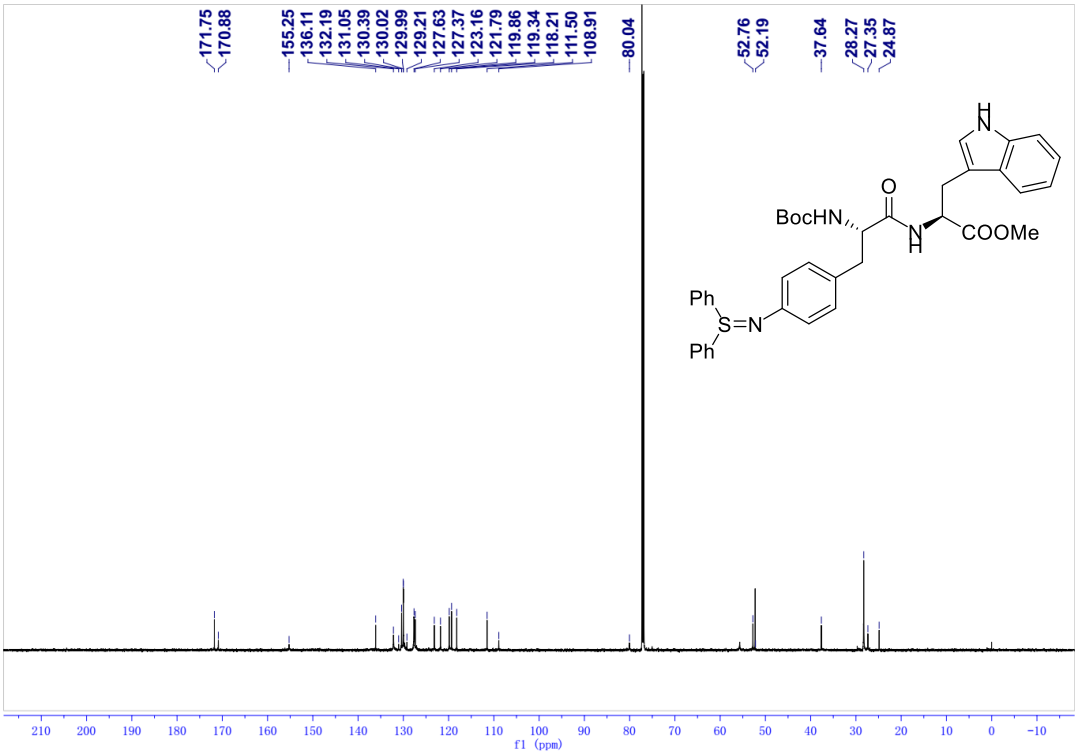
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-OMe (6ad)



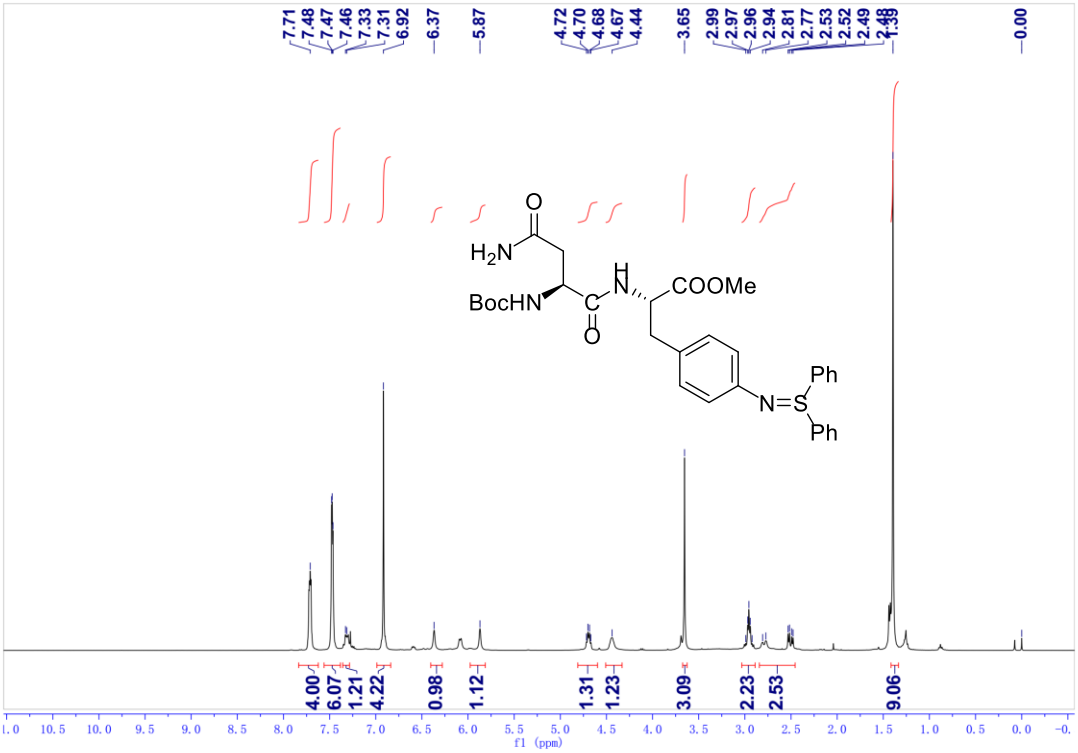
^{1}H NMR (600 MHz, $CDCl_3$) of Boc-Tyr^{s}-Trp-OMe (6ae)



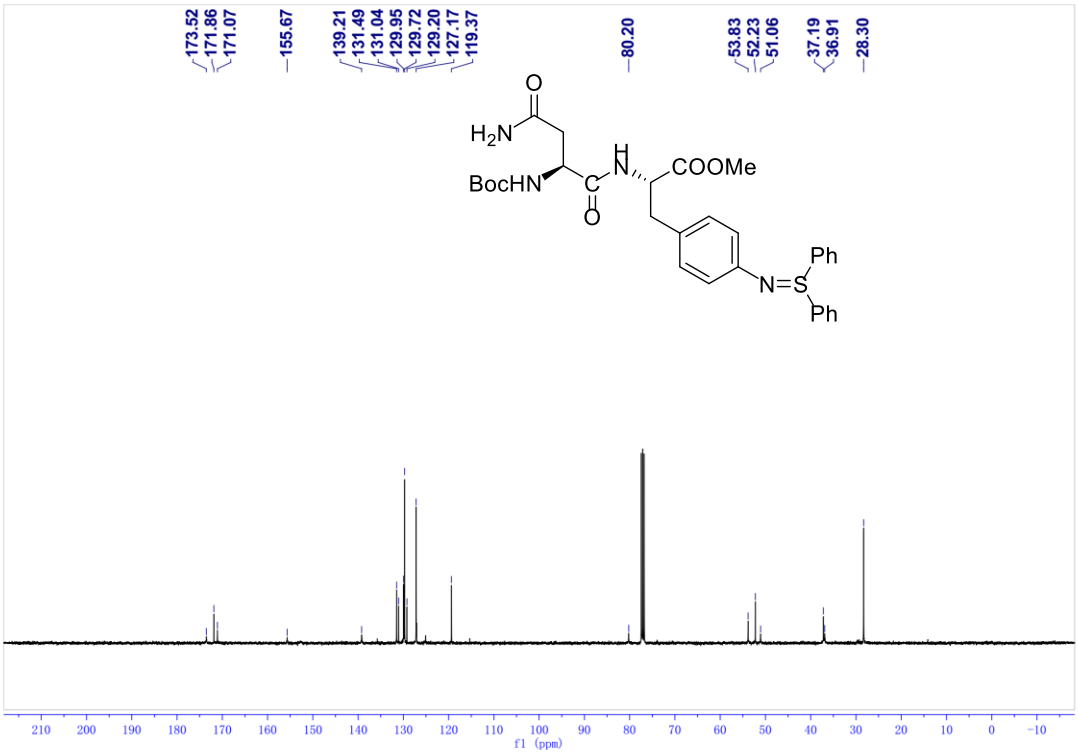
^{13}C NMR (150 MHz, $CDCl_3$) of Boc-Tyr^{s}-Trp-OMe (6ae)



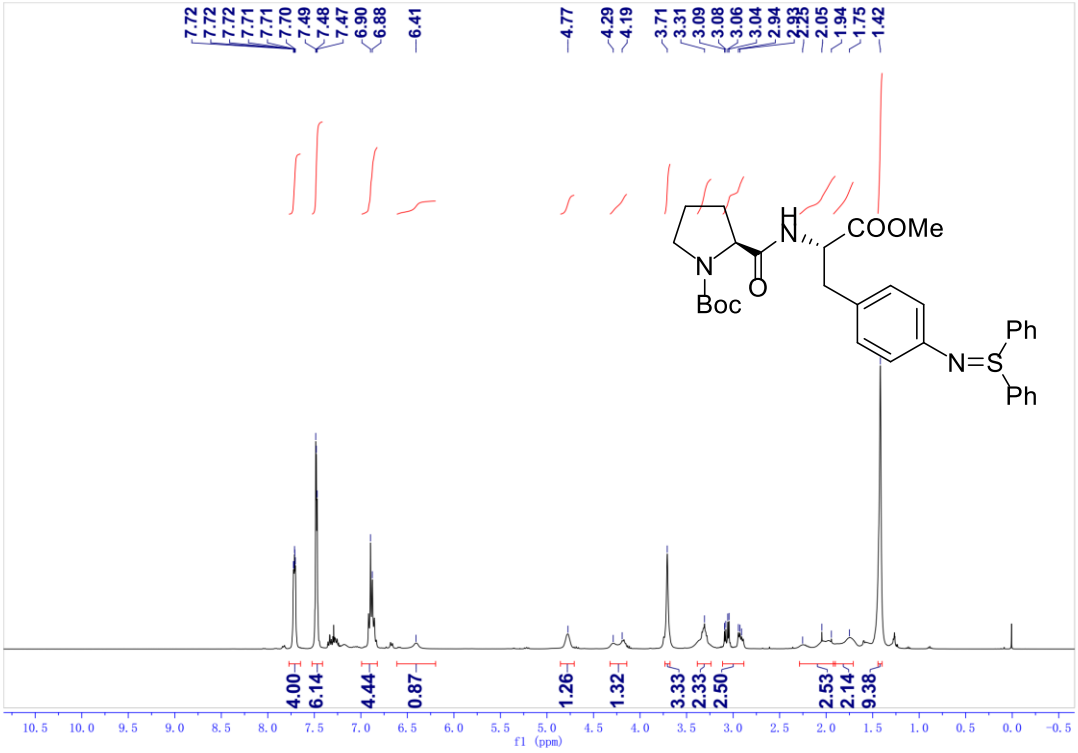
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Asn-Tyr^{s}-OMe (6af)



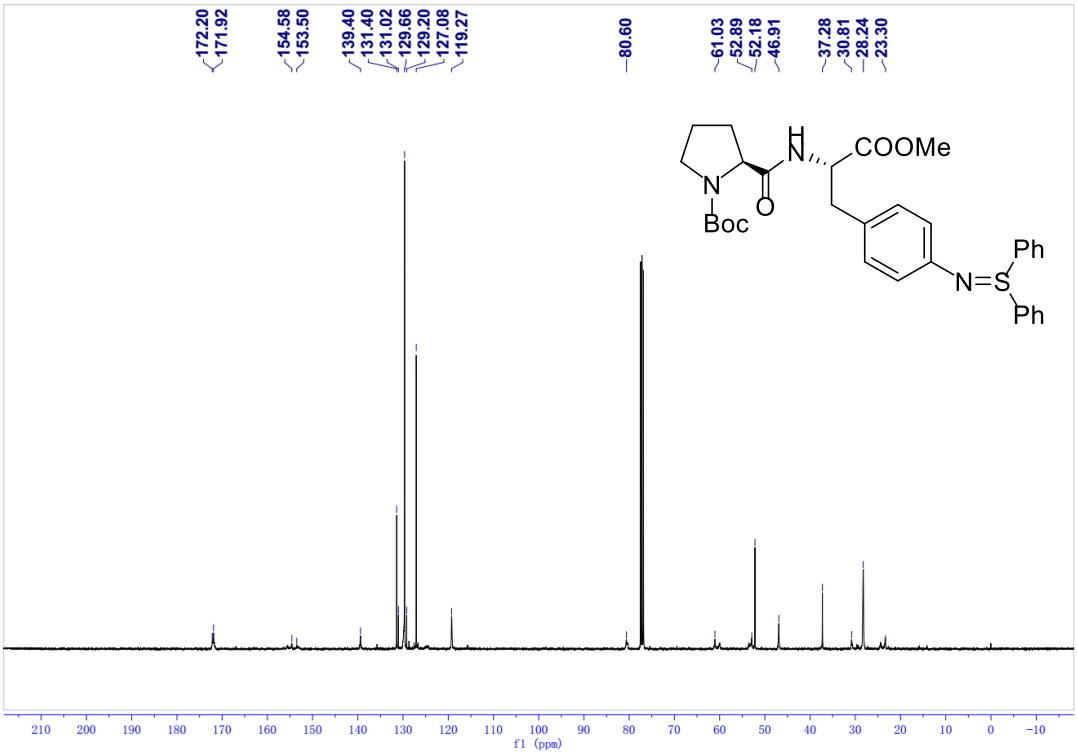
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Asn-Tyr^{s}-OMe (6af)



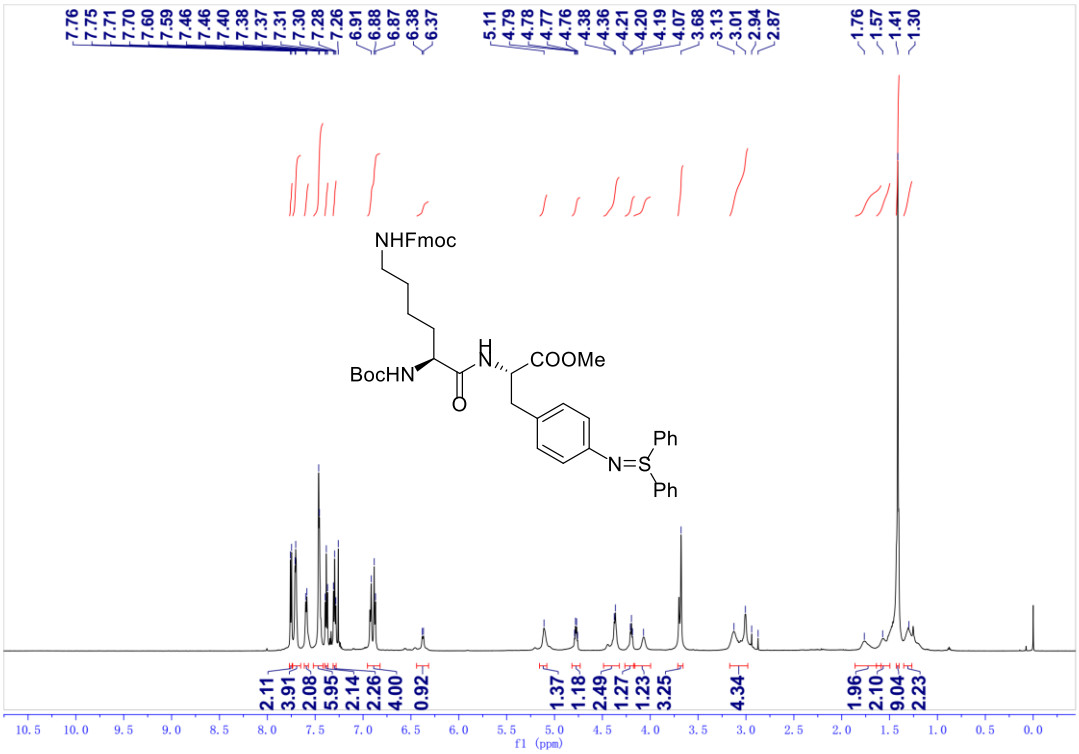
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Pro-Tyr^{s}-OMe (6ag)



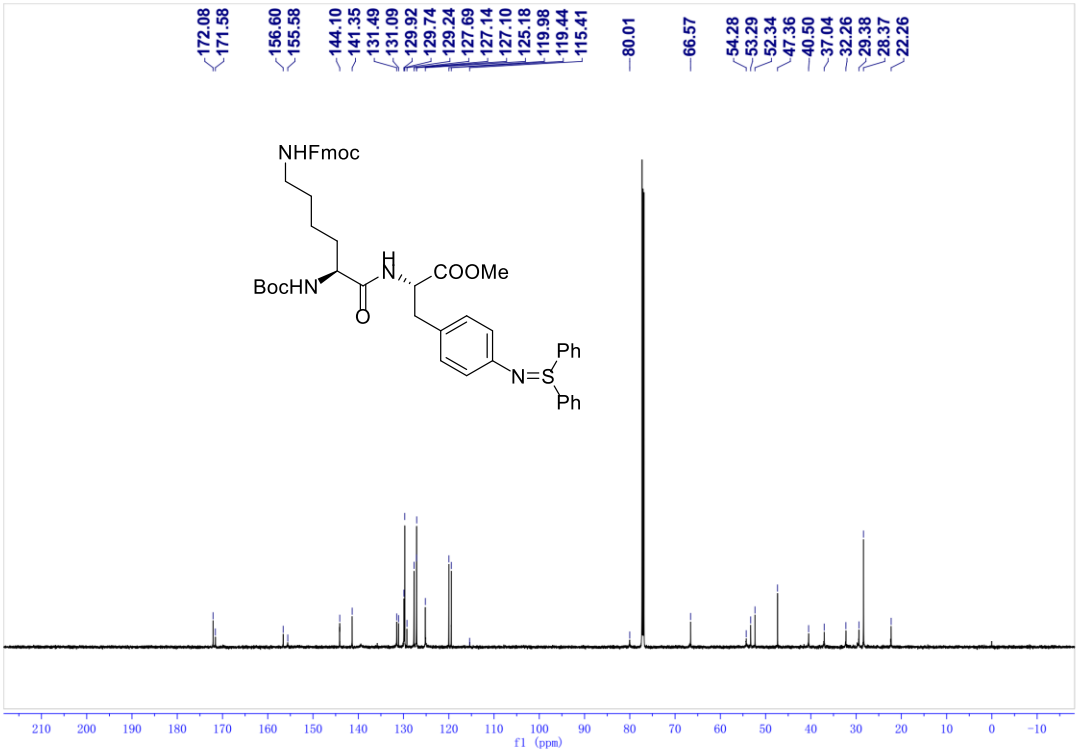
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Pro-Tyr^{s}-OMe (6ag)



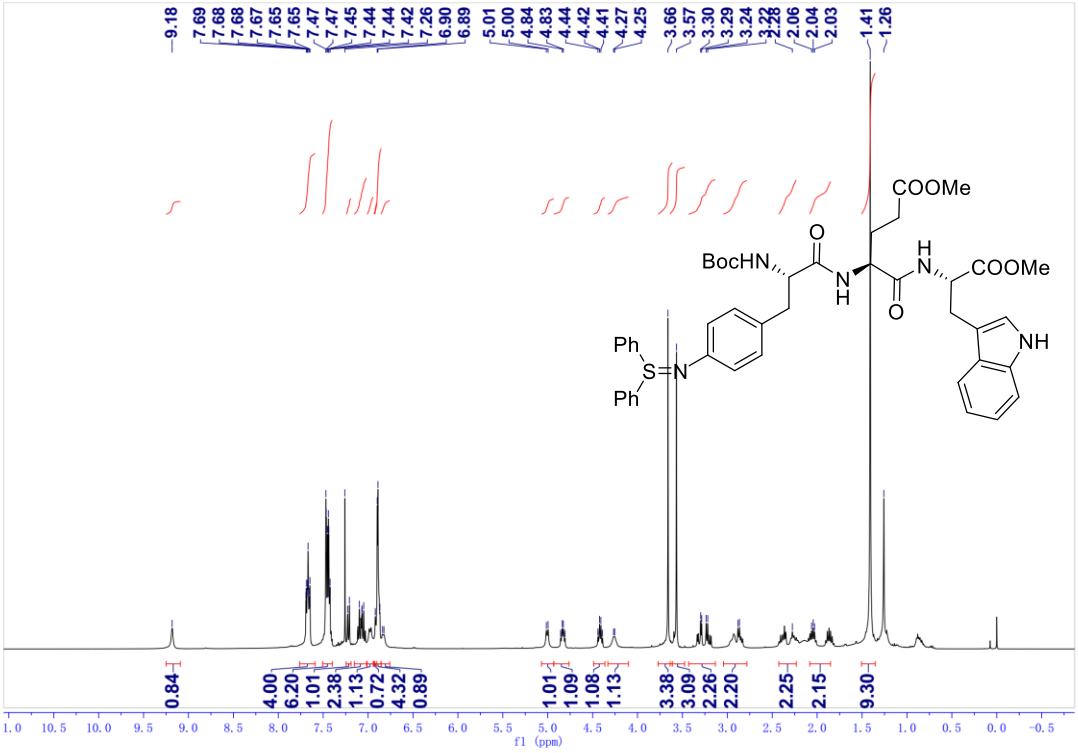
^{1}H NMR (600 MHz, $CDCl_3$) of Boc-Lys(Fmoc)-Tyr^{s}-OMe (6ah)



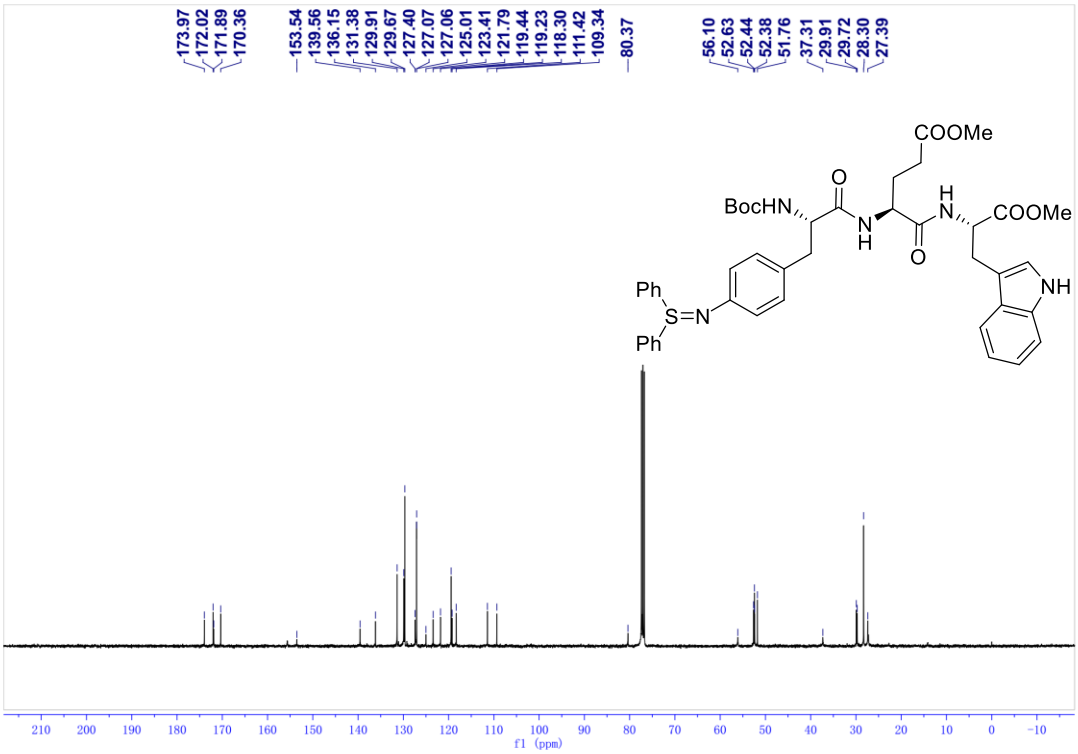
^{13}C NMR (150 MHz, $CDCl_3$) of Boc-Lys(Fmoc)-Tyr^{s}-OMe (6ah)



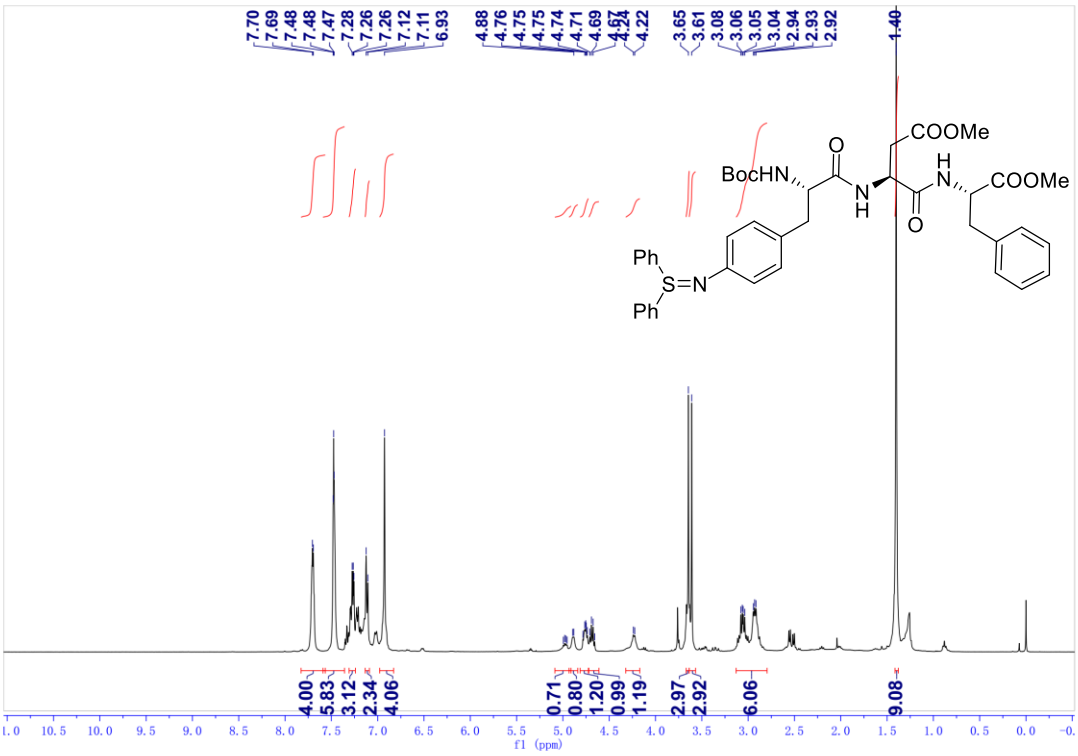
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-Trp-OMe (6ai)



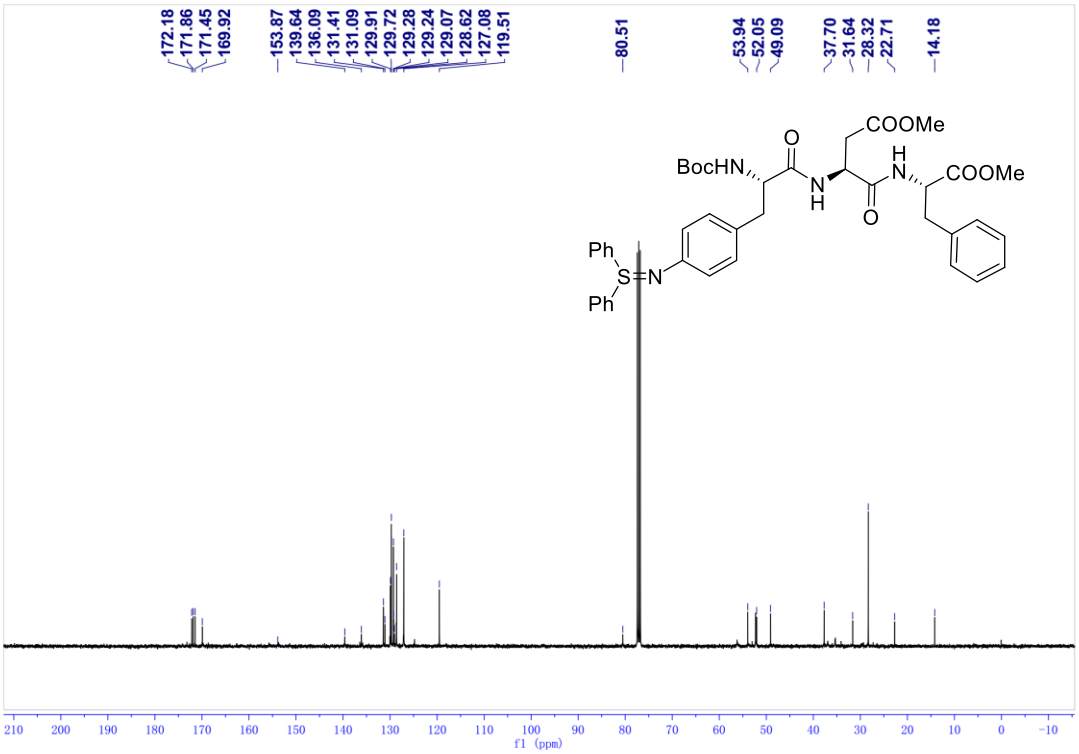
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-Trp-OMe (6ai)



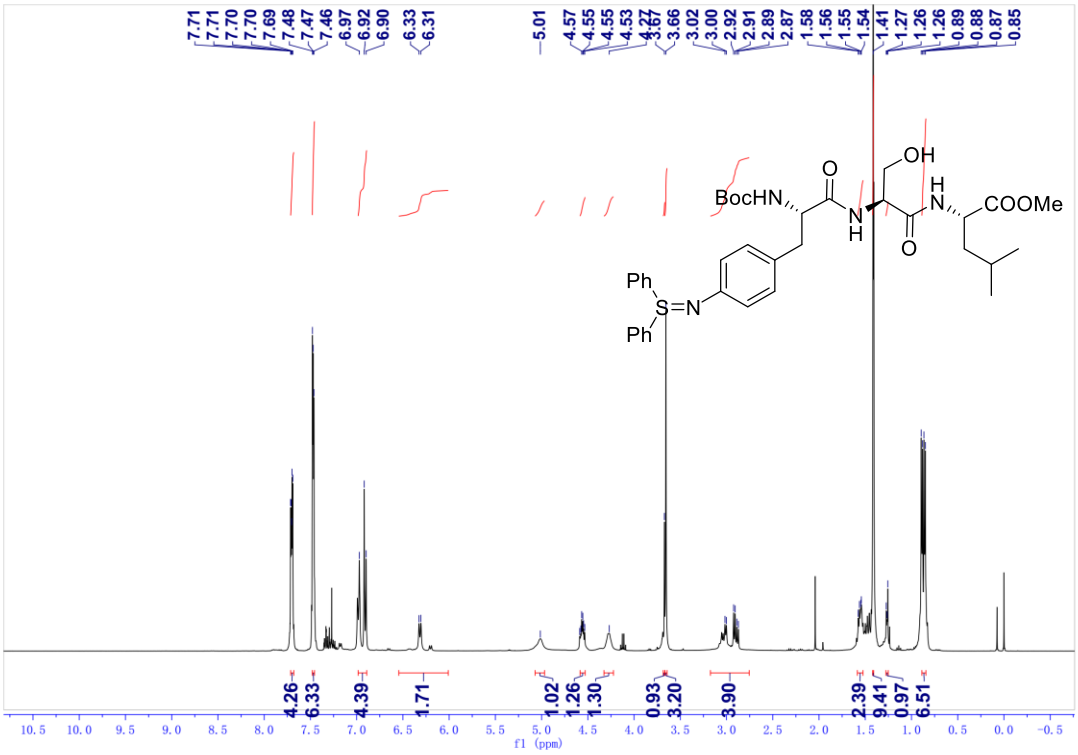
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Asp(OMe)-Phe-OMe (6aj)



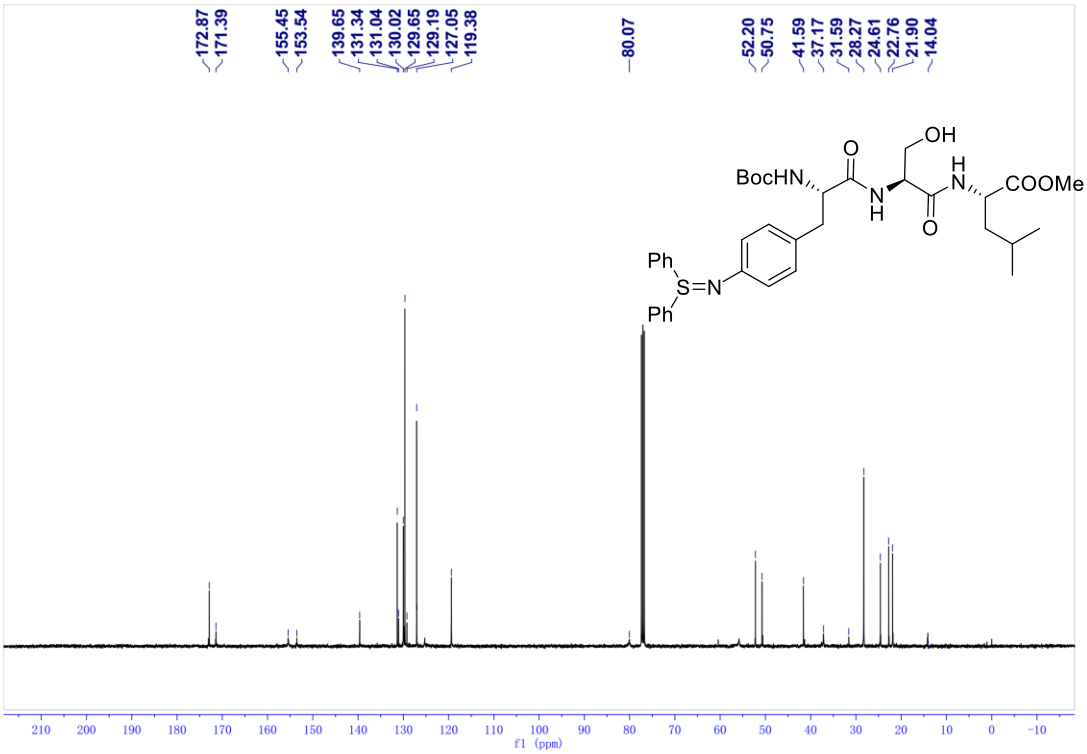
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Asp(OMe)-Phe-OMe (6aj)



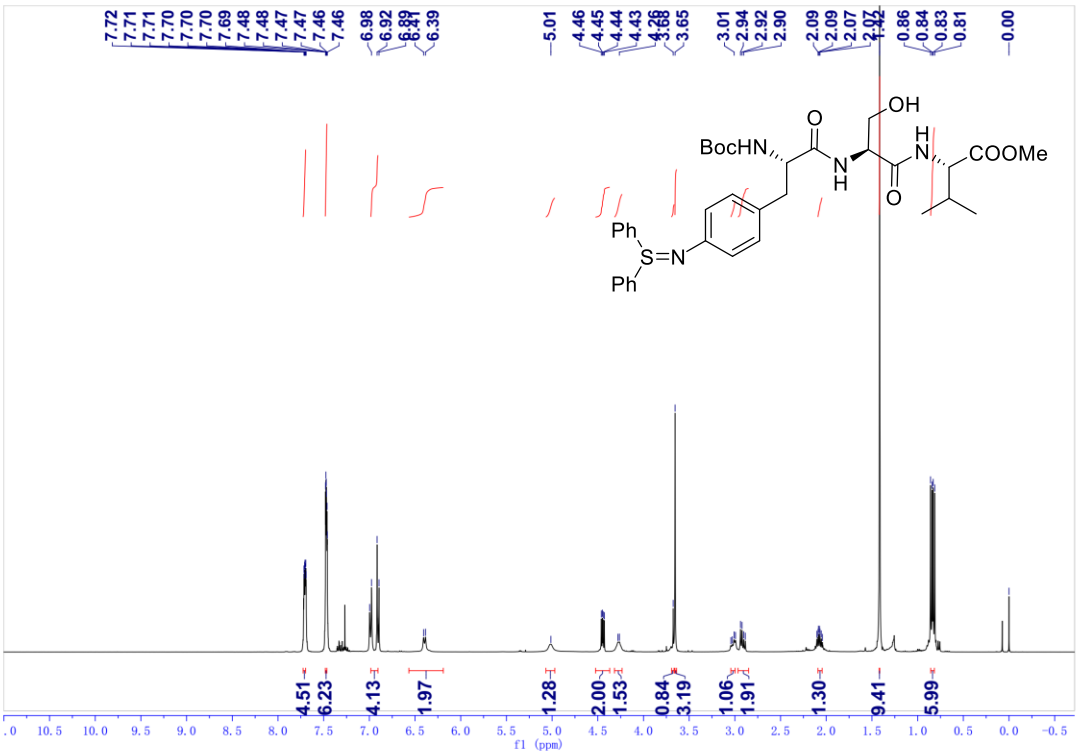
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-Leu-OMe (6ak)



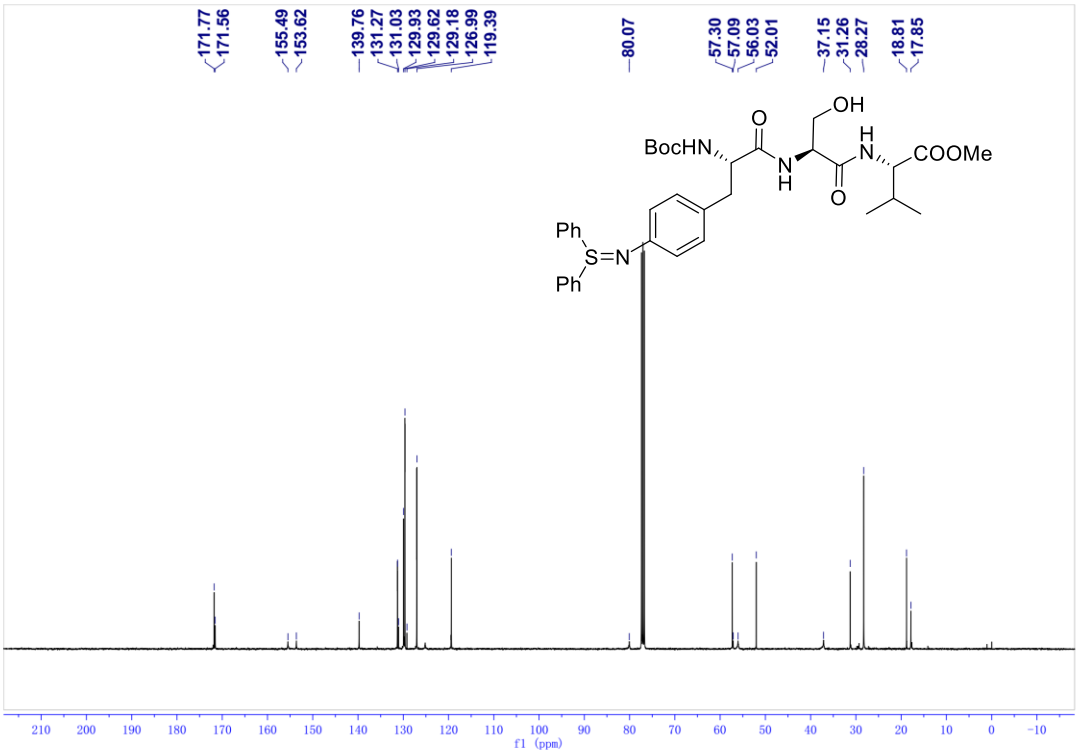
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-Leu-OMe (6ak)



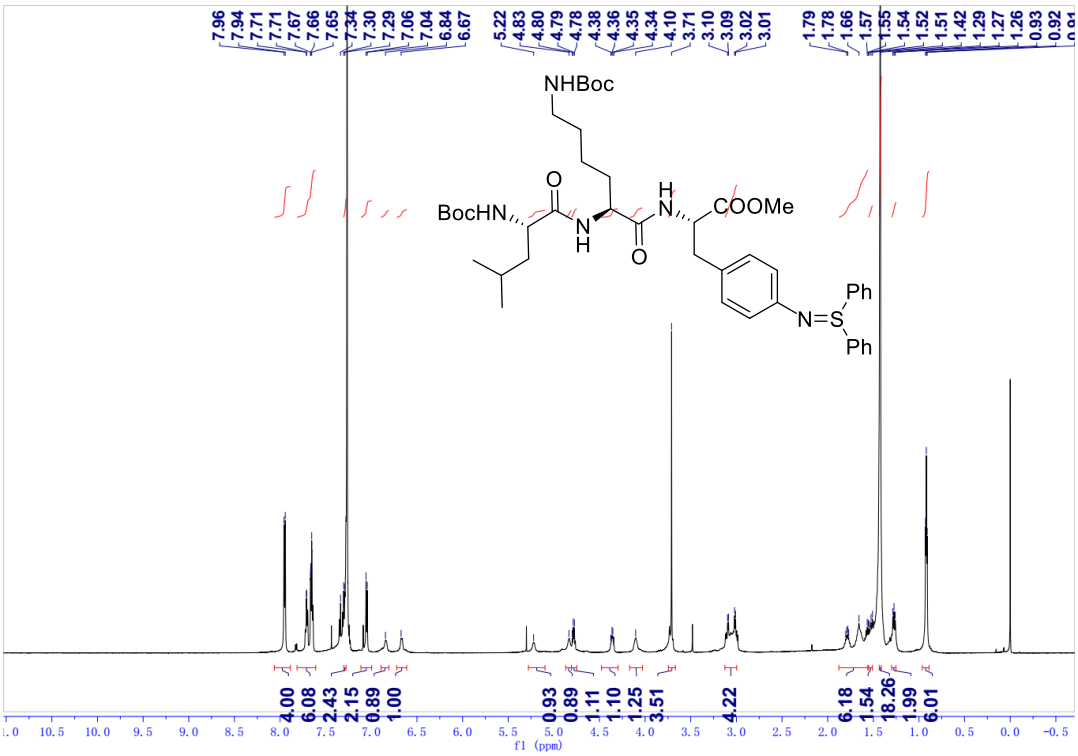
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-Val-OMe (6al)



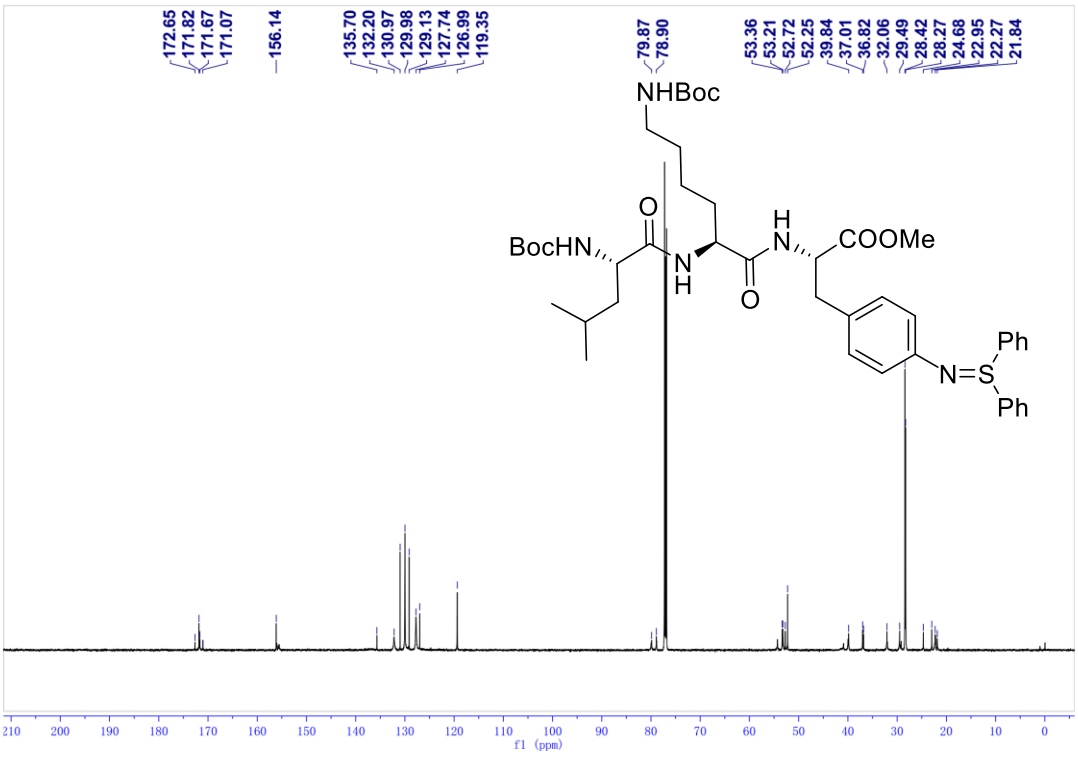
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Ser-Val-OMe (6al)



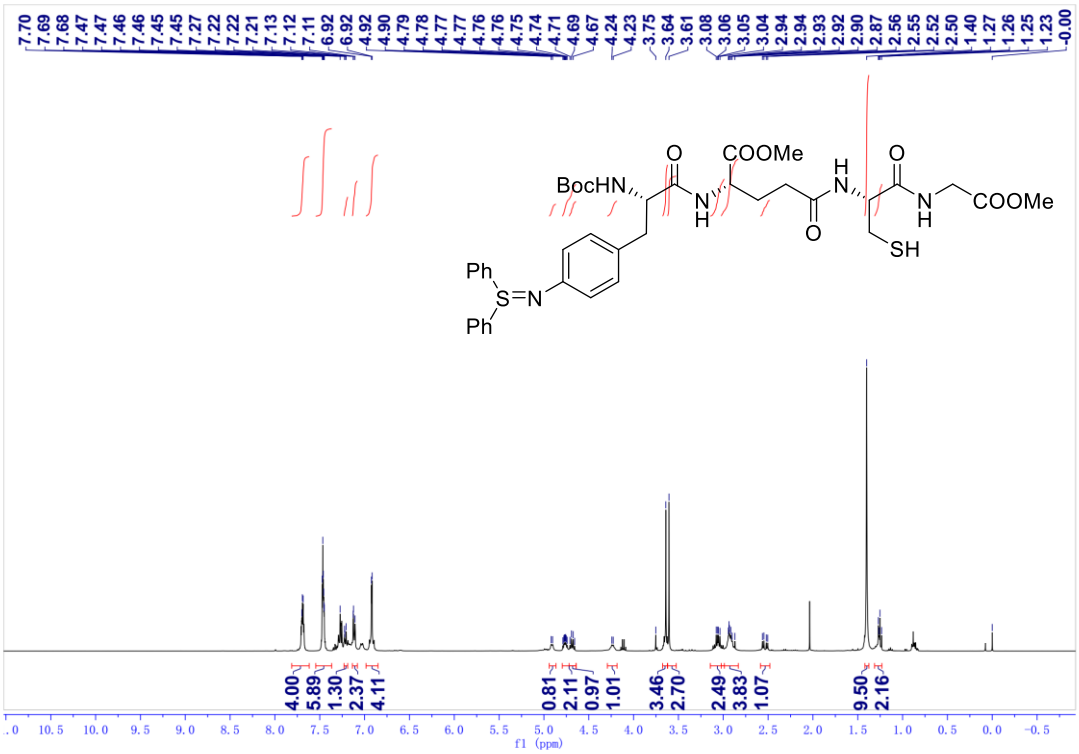
^{1}H NMR (600 MHz, $CDCl_3$) of Boc-Leu-Lys(Boc)-Tyr^{s}-OMe (6am)



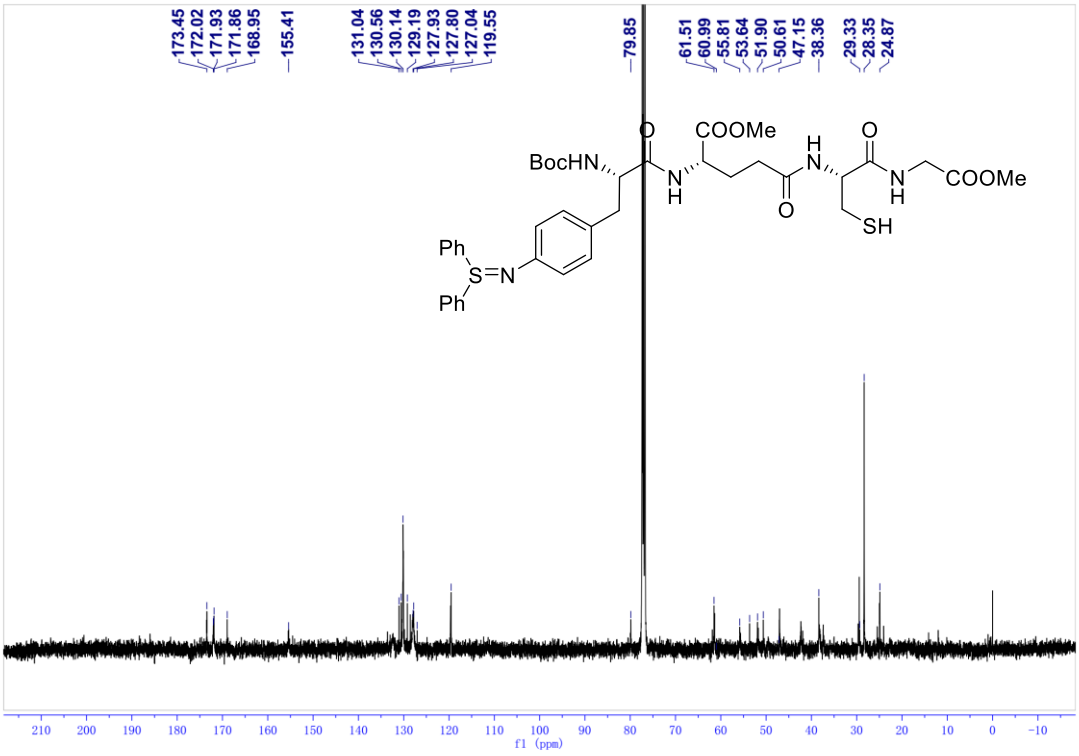
^{13}C NMR (150 MHz, $CDCl_3$) of Boc-Leu-Lys(Boc)-Tyr^{s}-OMe (6am)



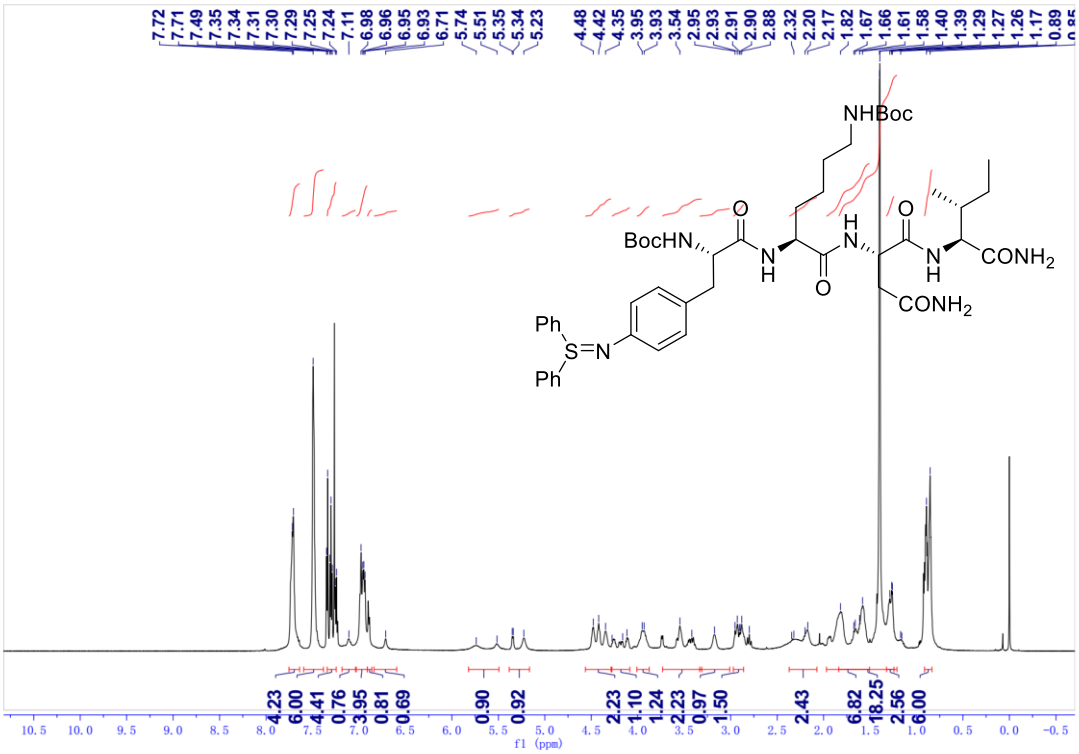
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-Cys-Gly-OMe (6an)



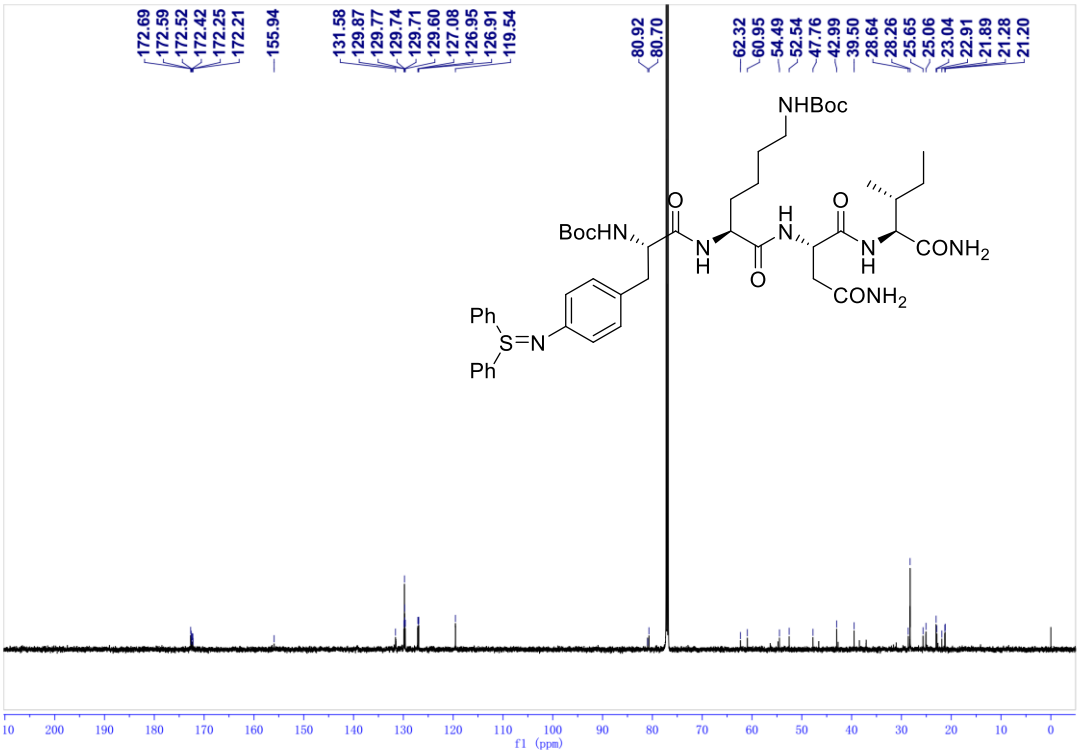
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Glu(OMe)-Cys-Gly-OMe (6an)



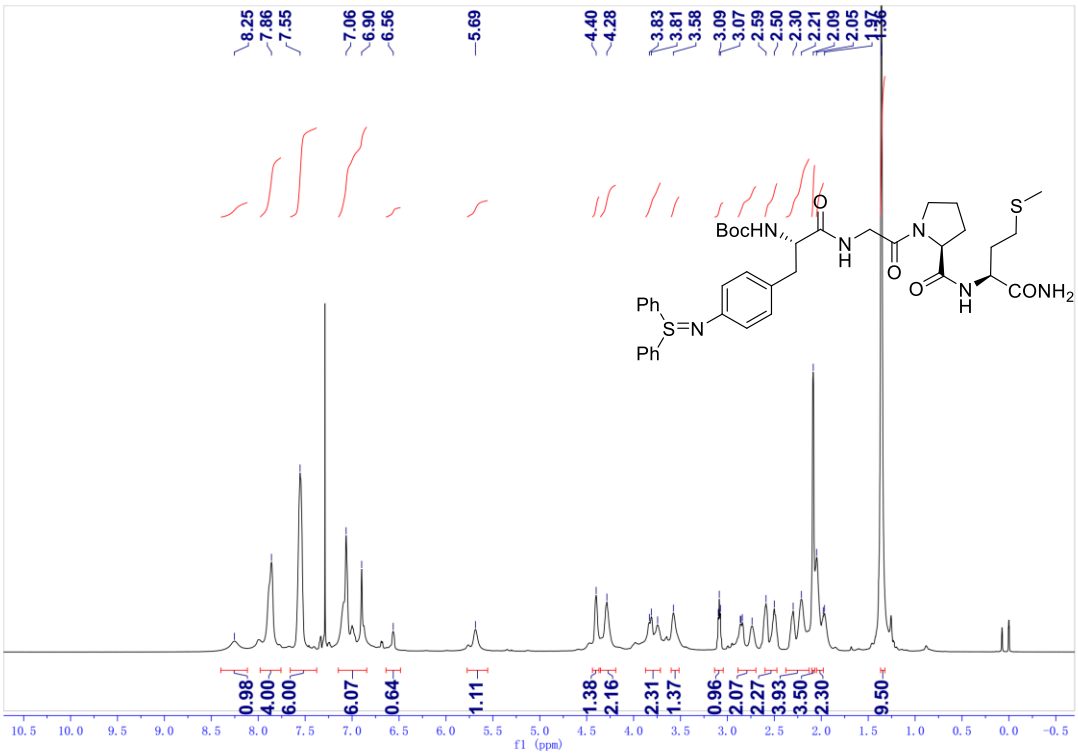
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Lys(Boc)-Gly-Ile-$CONH_2$ (6ao)



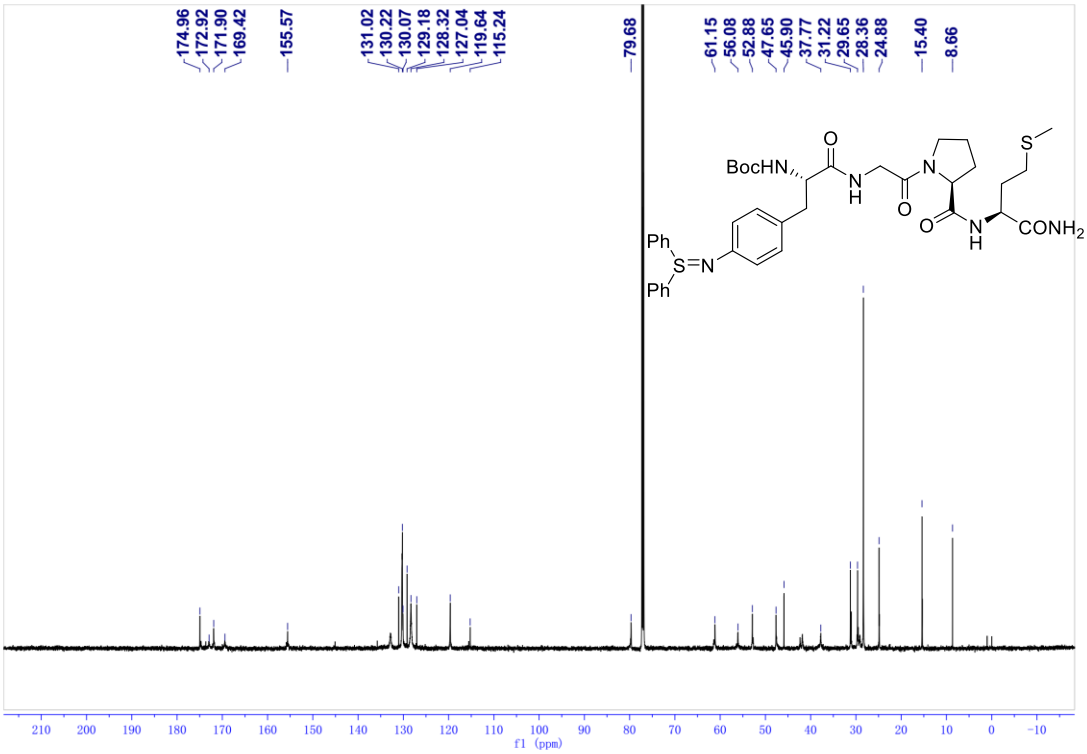
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Lys(Boc)-Gly-Ile-$CONH_2$ (6ao)



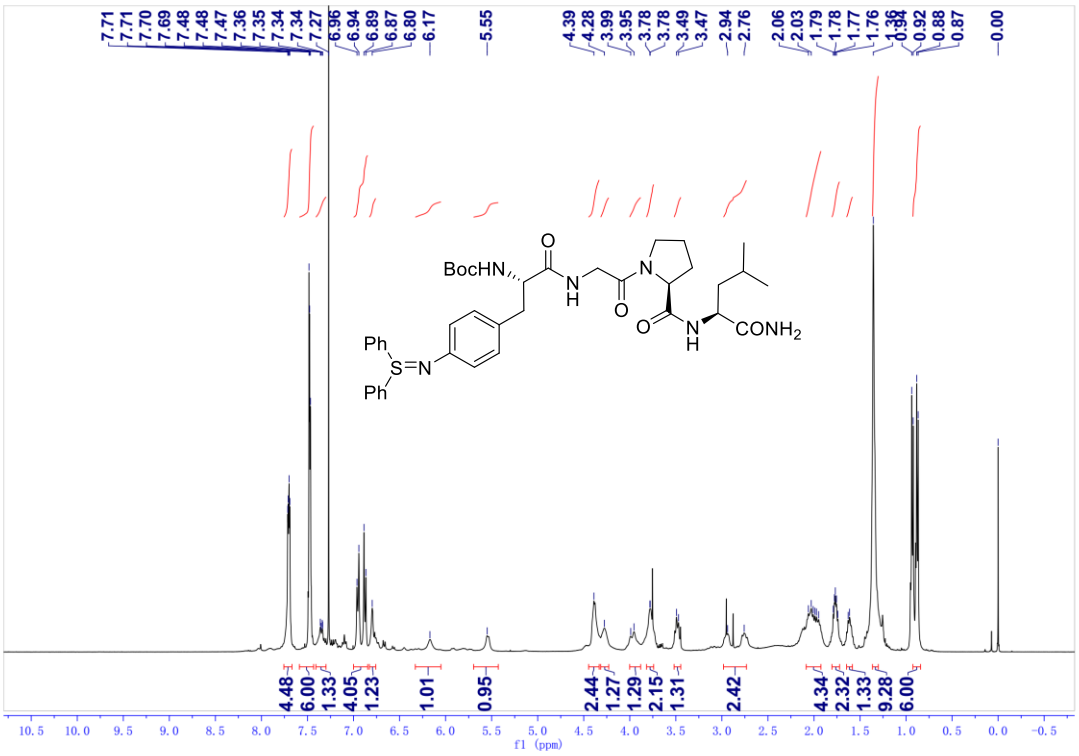
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Gly-Pro-Met-$CONH_2$ (6ap)



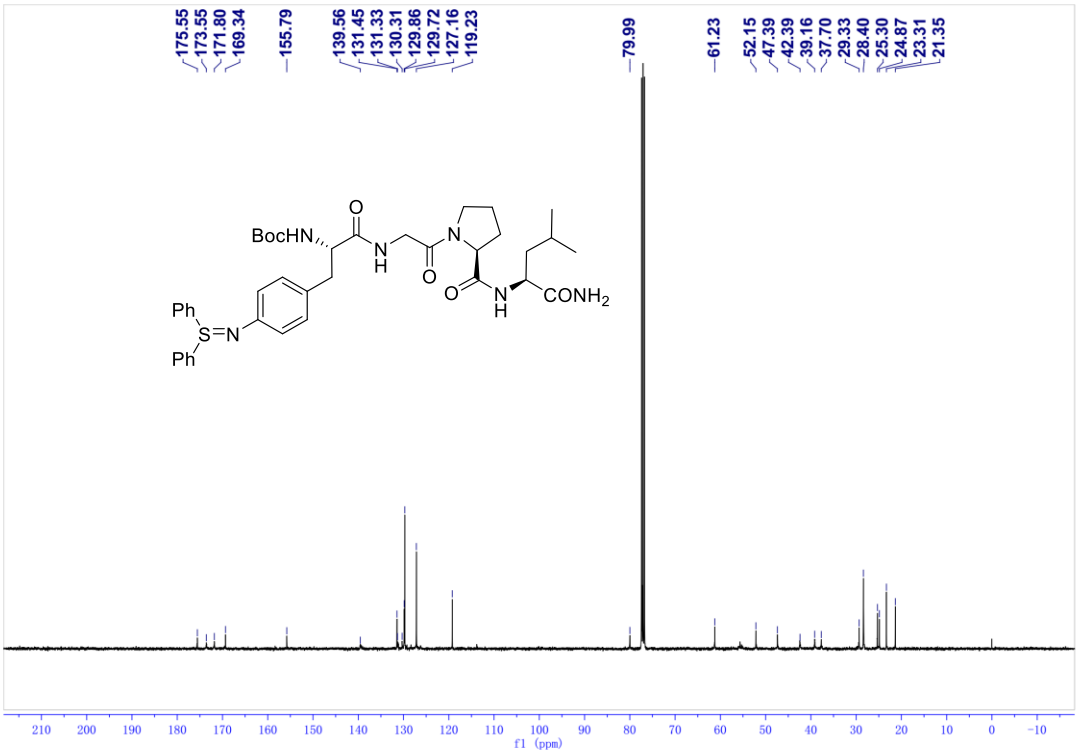
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Gly-Pro-Met-$CONH_2$ (6ap)



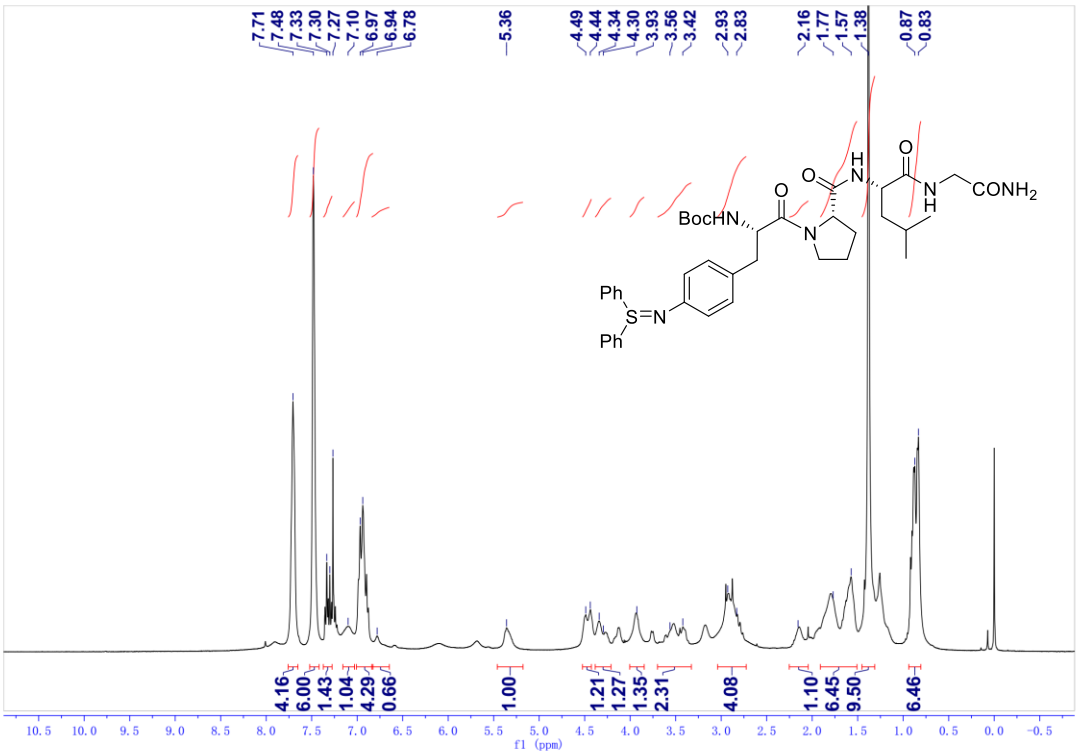
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Gly-Pro-Leu-$CONH_2$ (6aq)



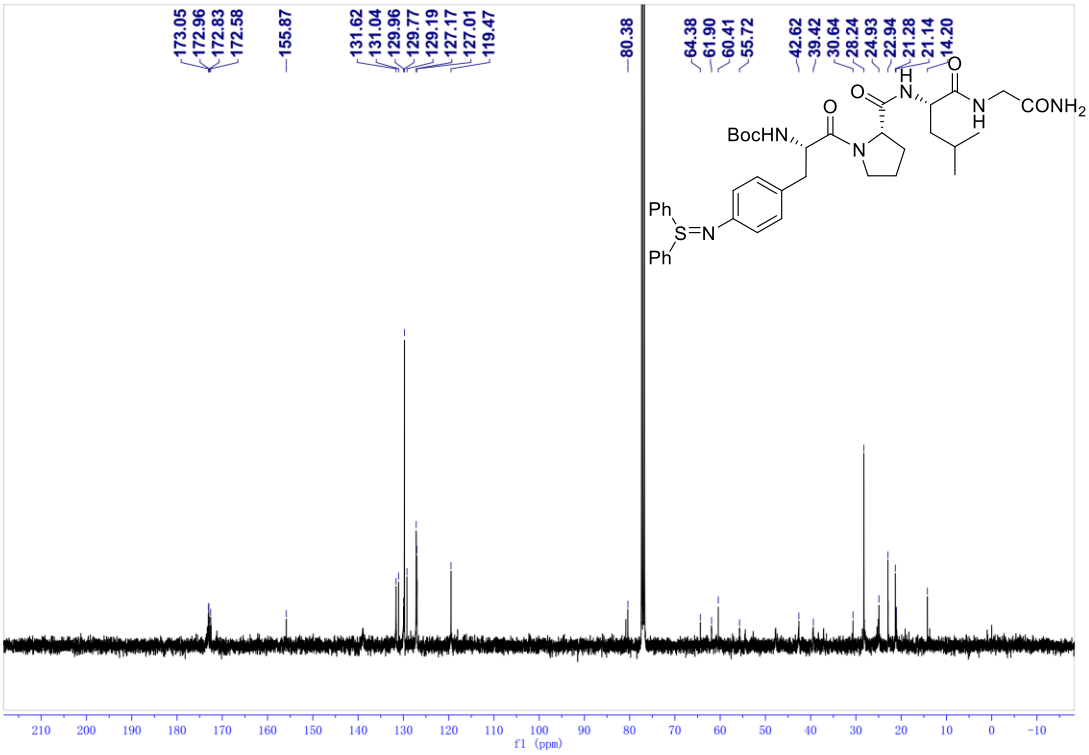
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Gly-Pro-Leu-$CONH_2$ (6aq)



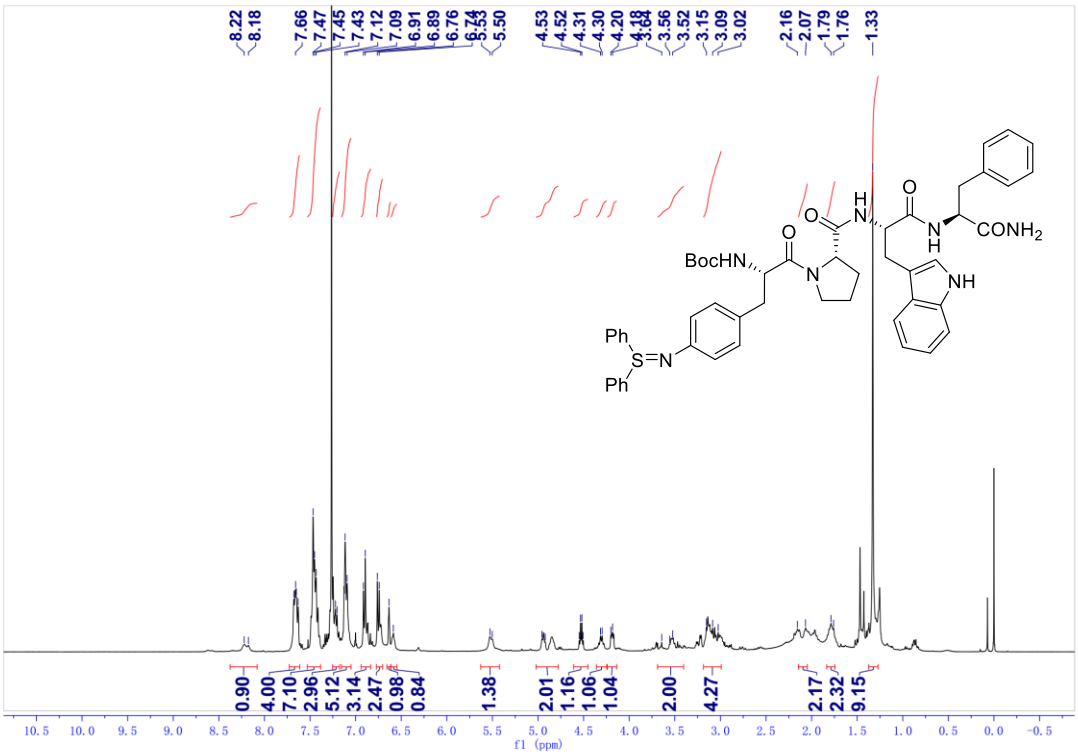
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Pro-Leu-Gly-$CONH_2$ (6ar)



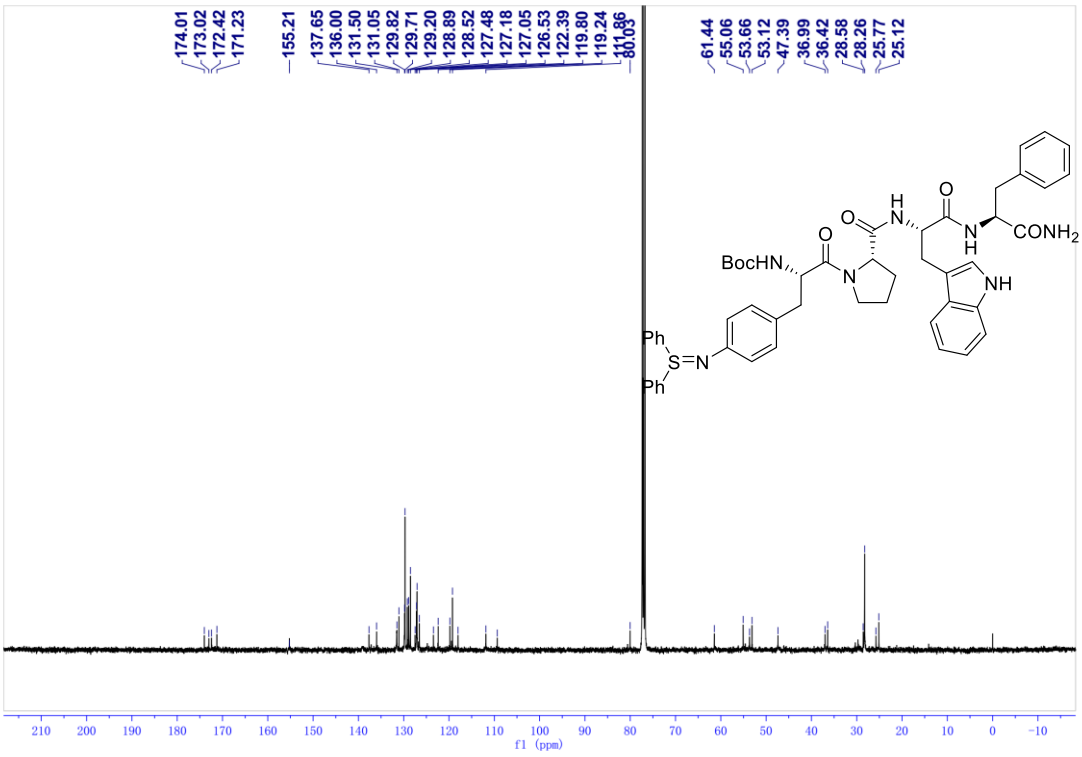
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Pro-Leu-Gly-$CONH_2$ (6ar)



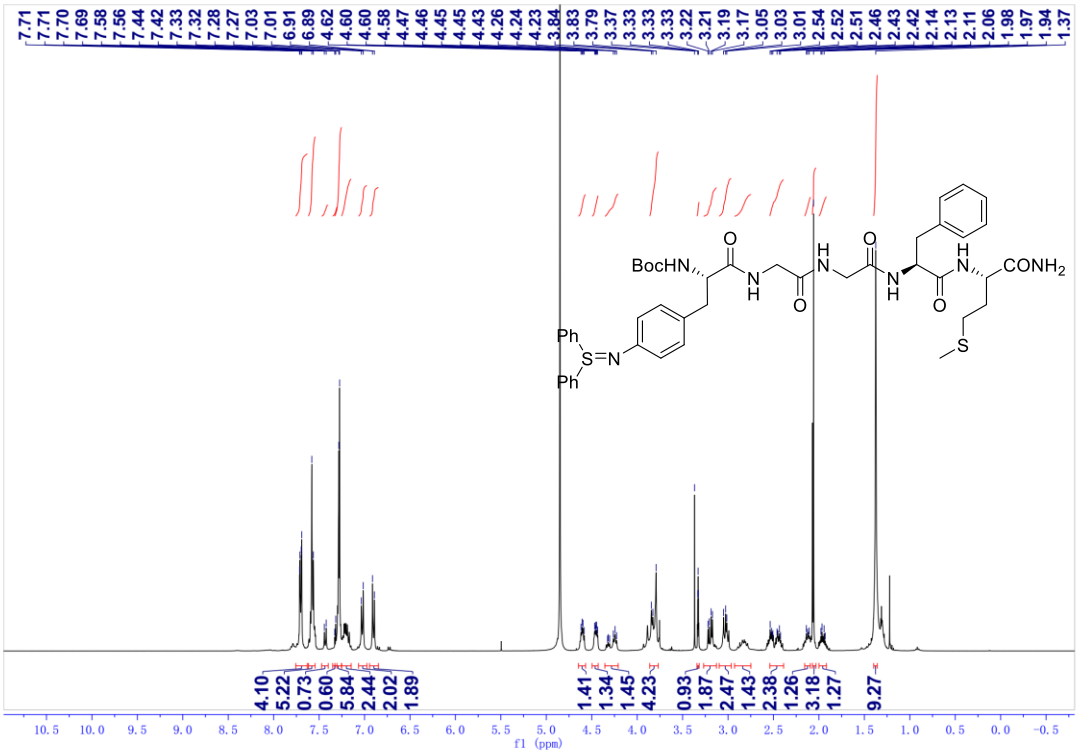
^{1}H NMR (400 MHz, $CDCl_3$) of Boc-Tyr^{s}-Pro-Trp-Phe-$CONH_2$ (6as)



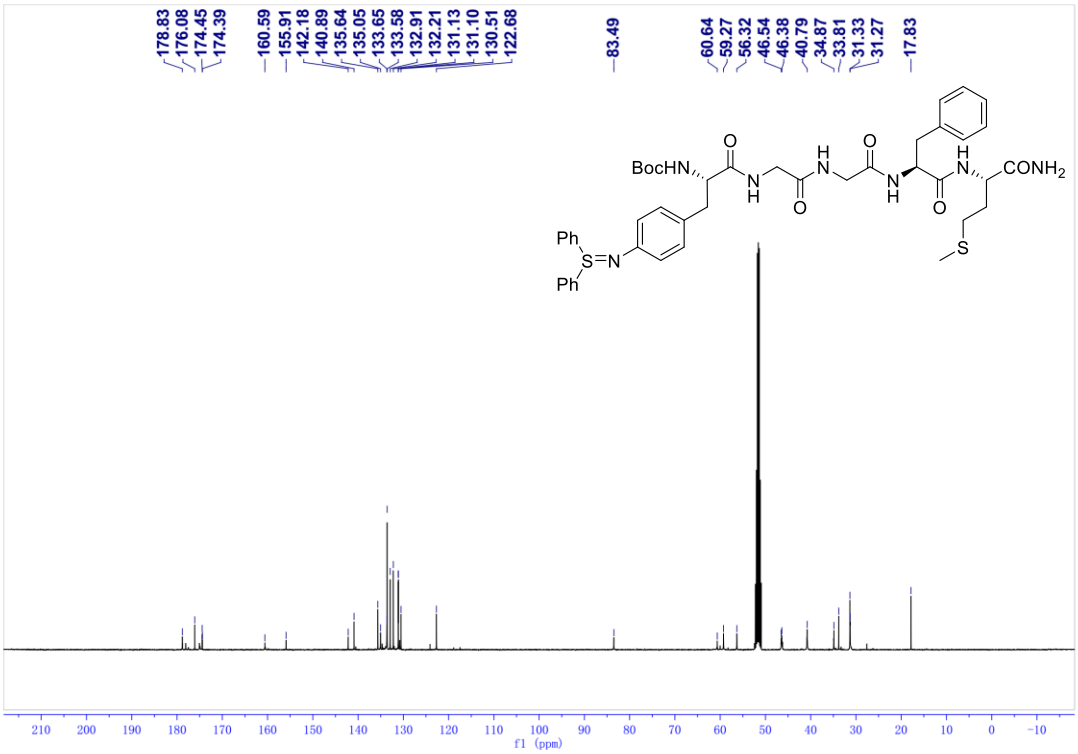
^{13}C NMR (100 MHz, $CDCl_3$) of Boc-Tyr^{s}-Pro-Trp-Phe-$CONH_2$ (6as)



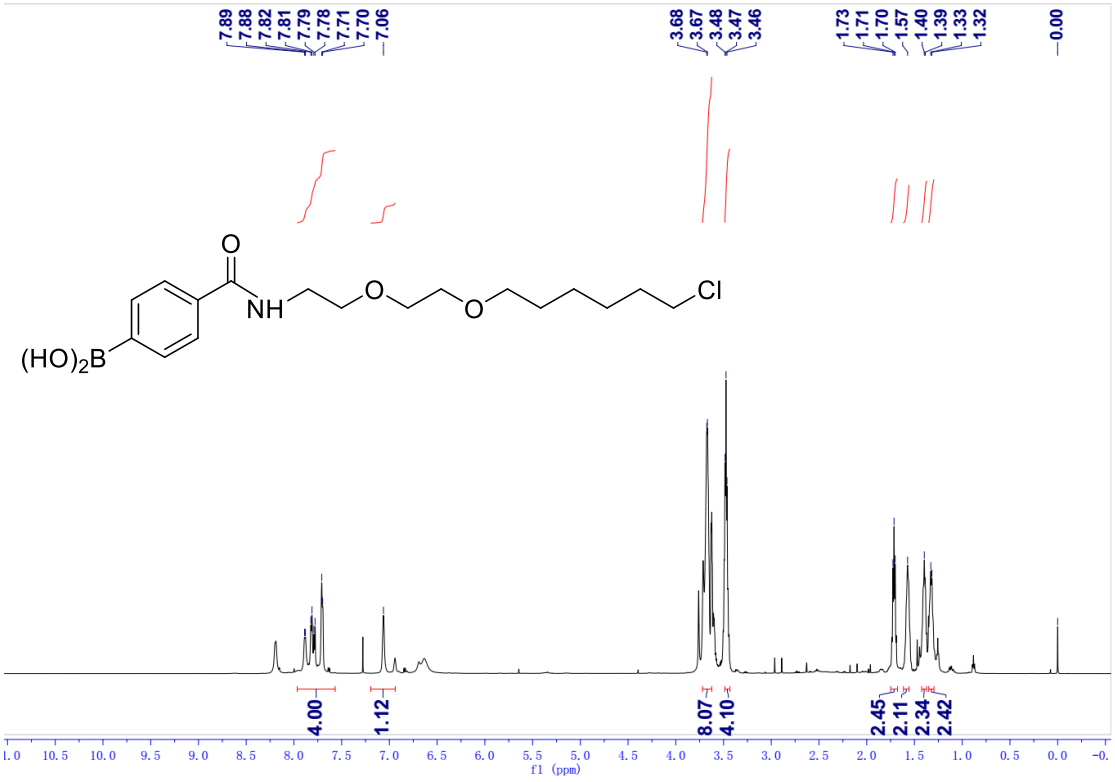
^{1}H NMR (400 MHz, CD_3OD) of Boc-Tyr^{s}-Gly-Gly-Phe-Met-$CONH_2$ (6at)



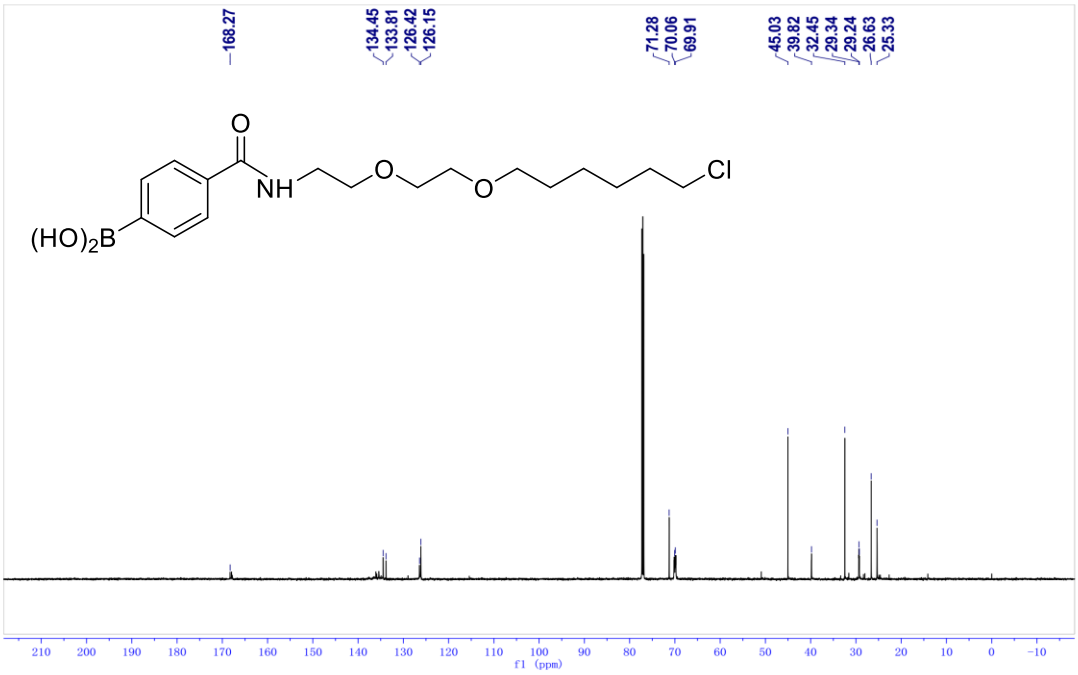
^{13}C NMR (100 MHz, CD_3OD) of Boc-Tyr^{s}-Gly-Gly-Phe-Met-$CONH_2$ (6at)



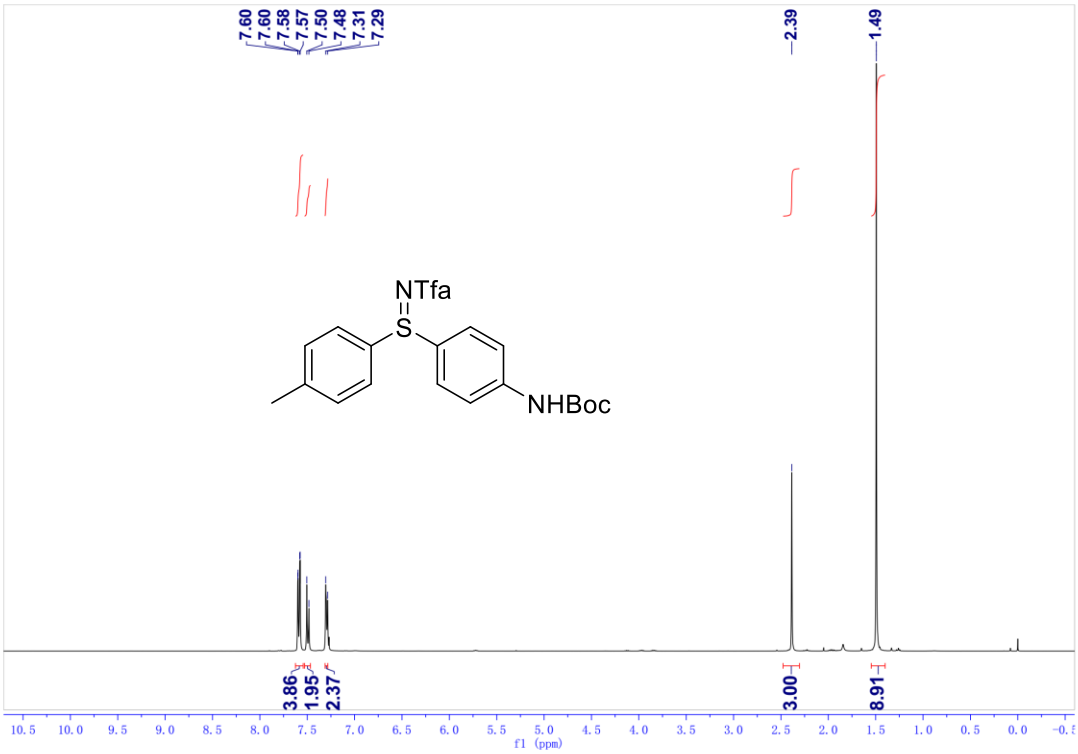
^{1}H NMR (600 MHz, $CDCl_3$) of (4-((2-(2-((6-Chlorohexyl)oxy)ethoxy)ethyl)carbamoyl)phenyl) boronic acid (B3)



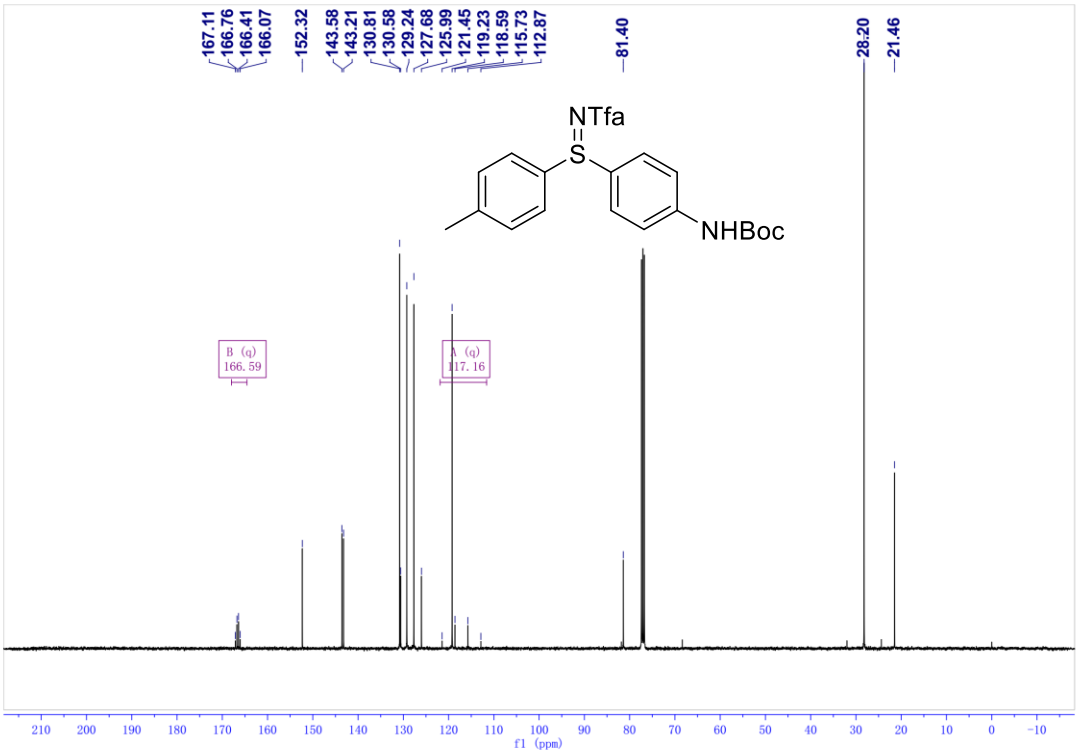
^{13}C NMR (150 MHz, $CDCl_3$) of (4-((2-(2-((6-Chlorohexyl)oxy)ethoxy)ethyl)carbamoyl)phenyl) boronic acid (B3)



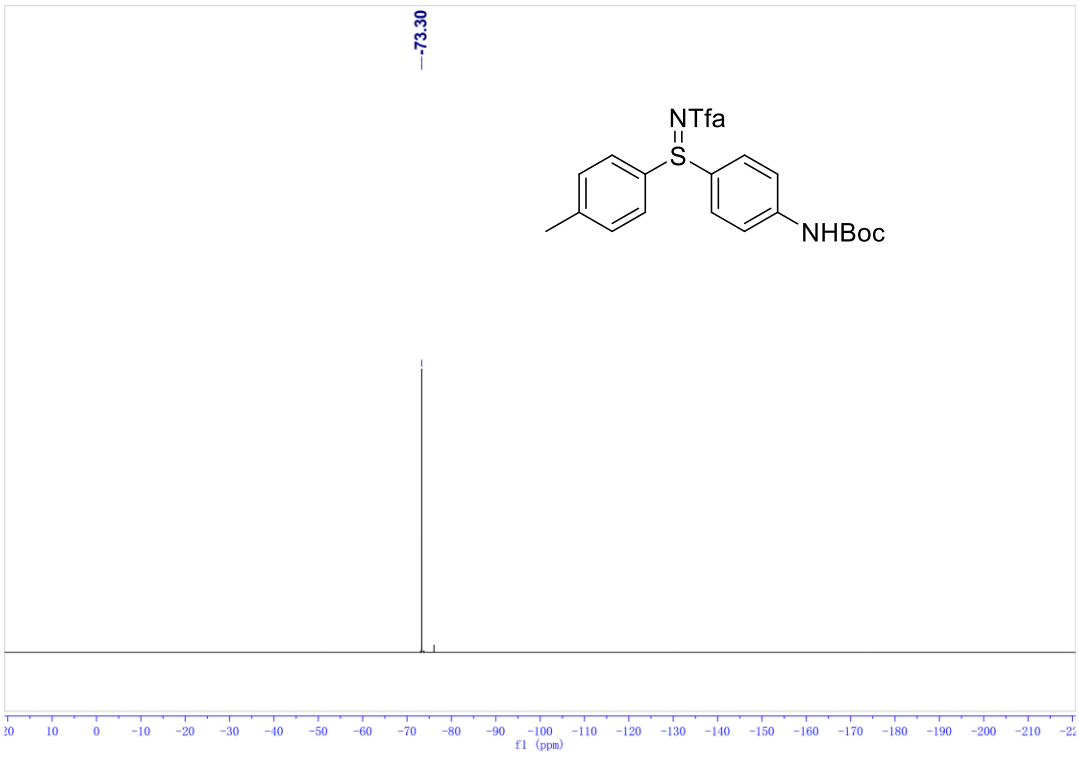
^{1}H NMR (400 MHz, $CDCl_3$) of *tert*-Butyl (*E*)-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl) sulfinimidoyl)phenyl)carbamate (C3)



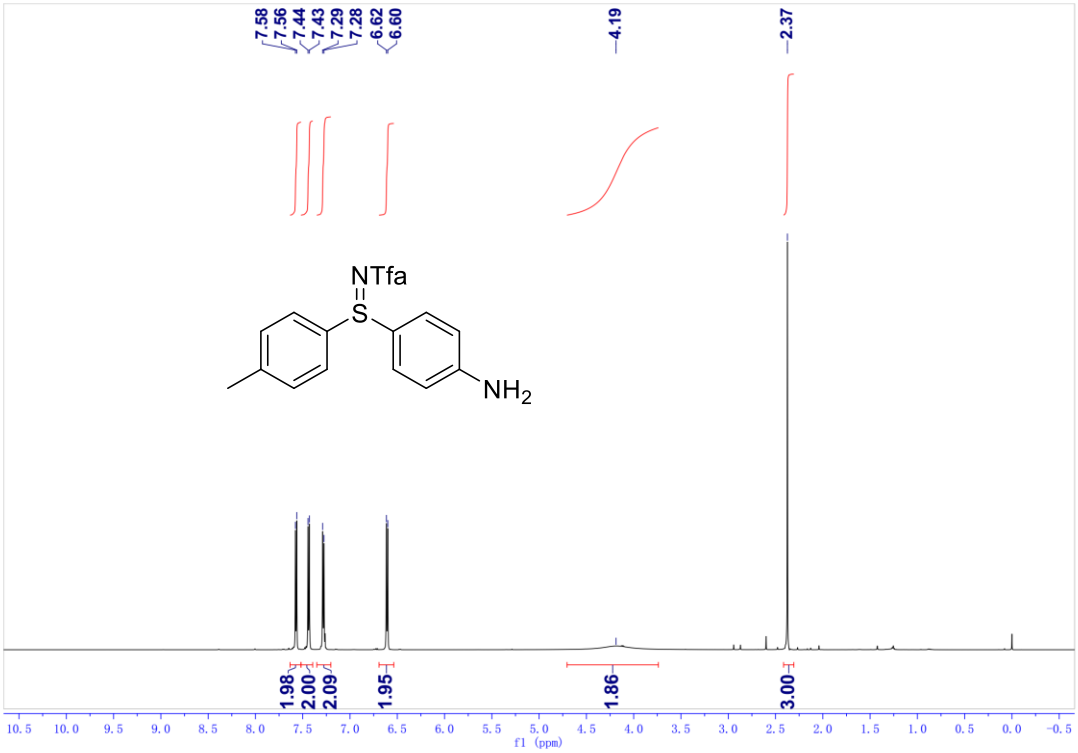
^{13}C NMR (100 MHz, $CDCl_3$) of *tert*-Butyl (*E*)-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl) sulfinimidoyl)phenyl)carbamate (C3)



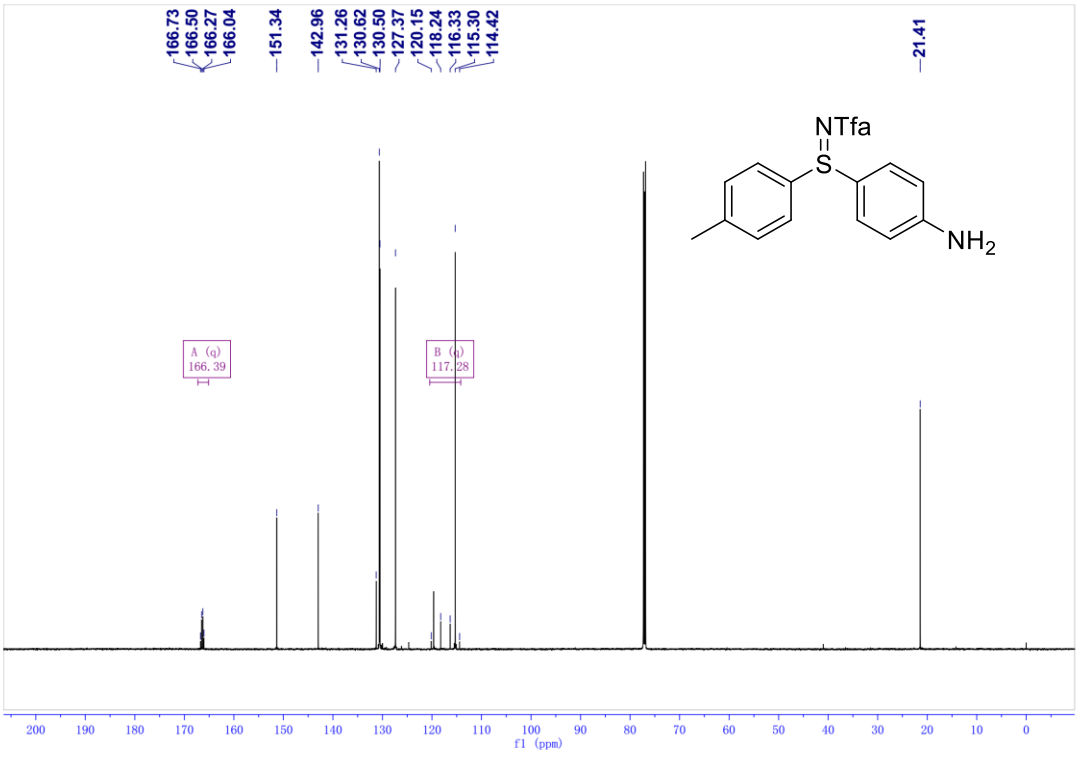
^{19}F NMR (376 MHz, $CDCl_3$) of *tert*-Butyl (*E*)-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl) sulfinimidoyl)phenyl)carbamate (C3)



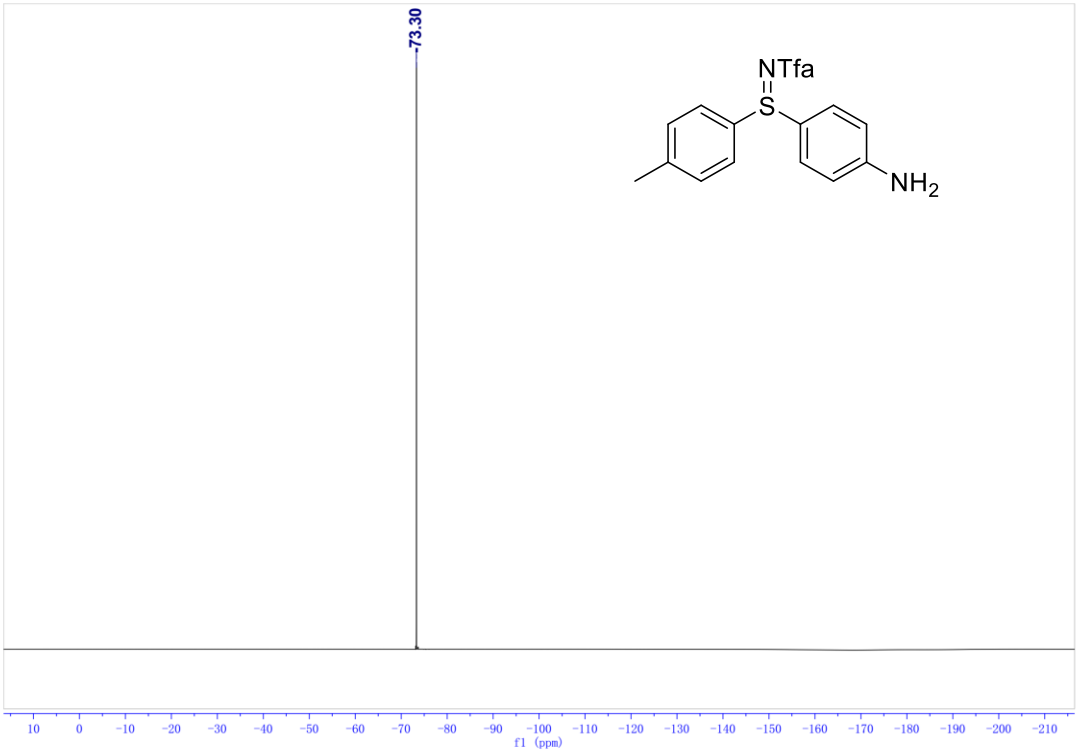
^{1}H NMR (600 MHz, $CDCl_3$) of (*Z*)-*N*-((4-Aminophenyl)(*p*-tolyl)- γ^4-sulfanylidene)-2,2,2-trifluoroacetamide (C4)



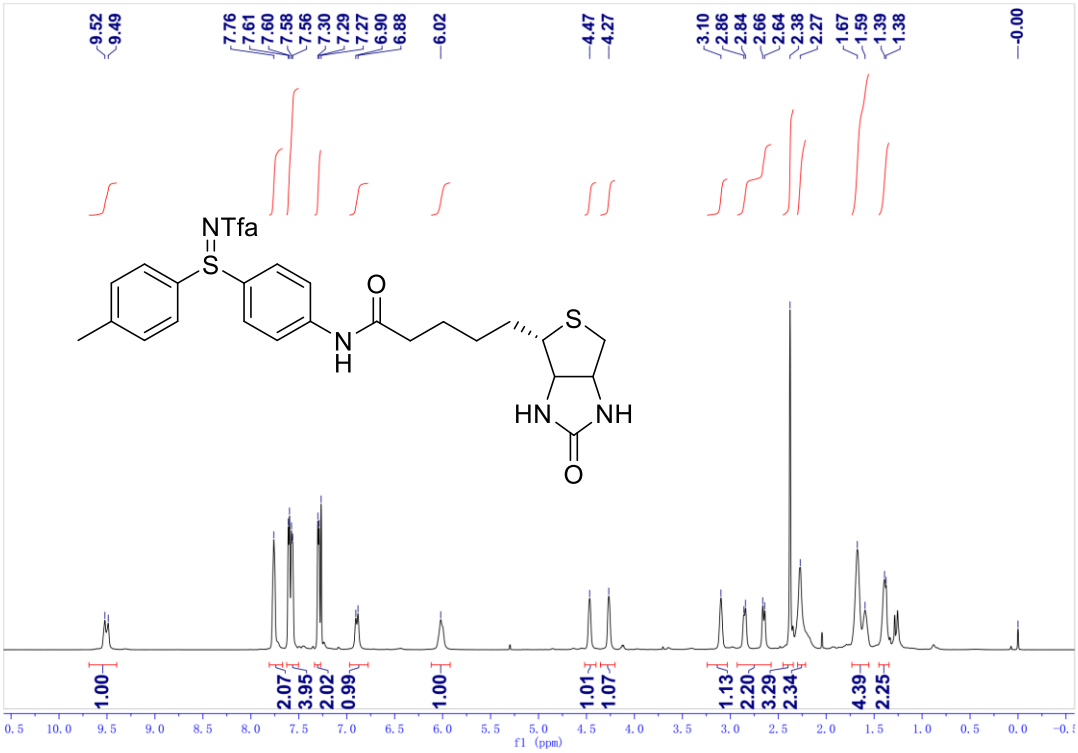
^{13}C NMR (150 MHz, $CDCl_3$) of (*Z*)-*N*-((4-Aminophenyl)(*p*-tolyl)- γ^4-sulfanylidene)-2,2,2-trifluoroacetamide (C4)



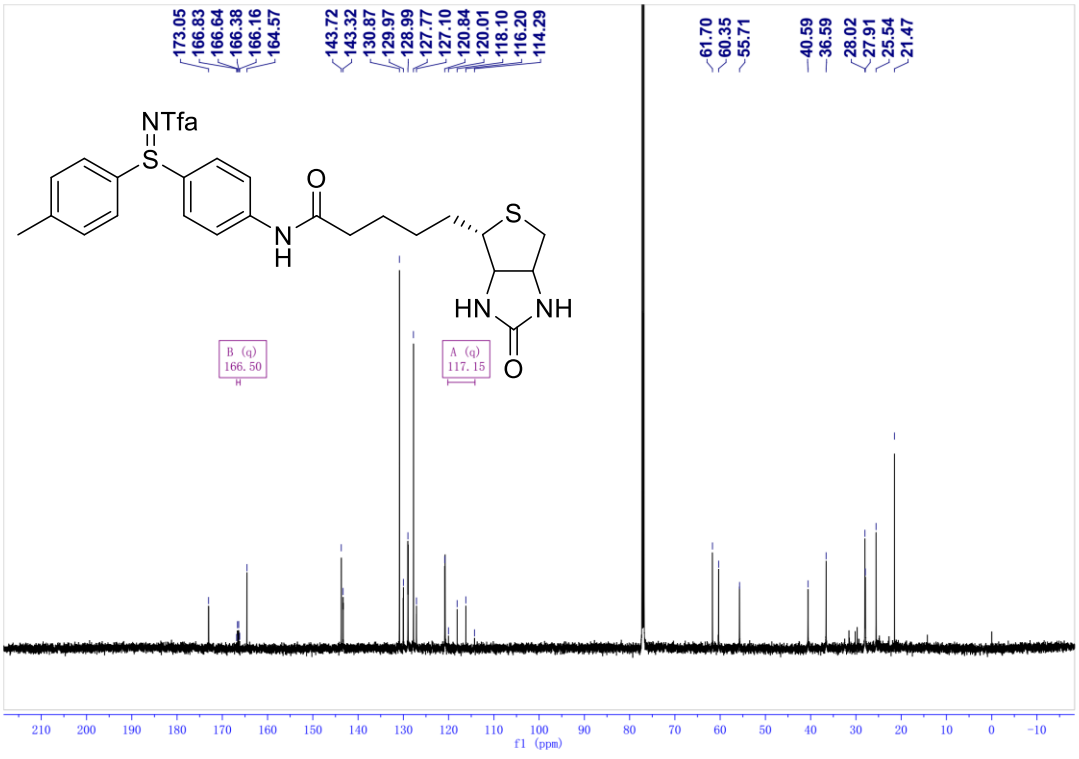
^{19}F NMR (565 MHz, $CDCl_3$) of (*Z*)-*N*-((4-Aminophenyl)(*p*-tolyl)- γ^4-sulfanylidene)-2,2,2-trifluoroacetamide (C4)



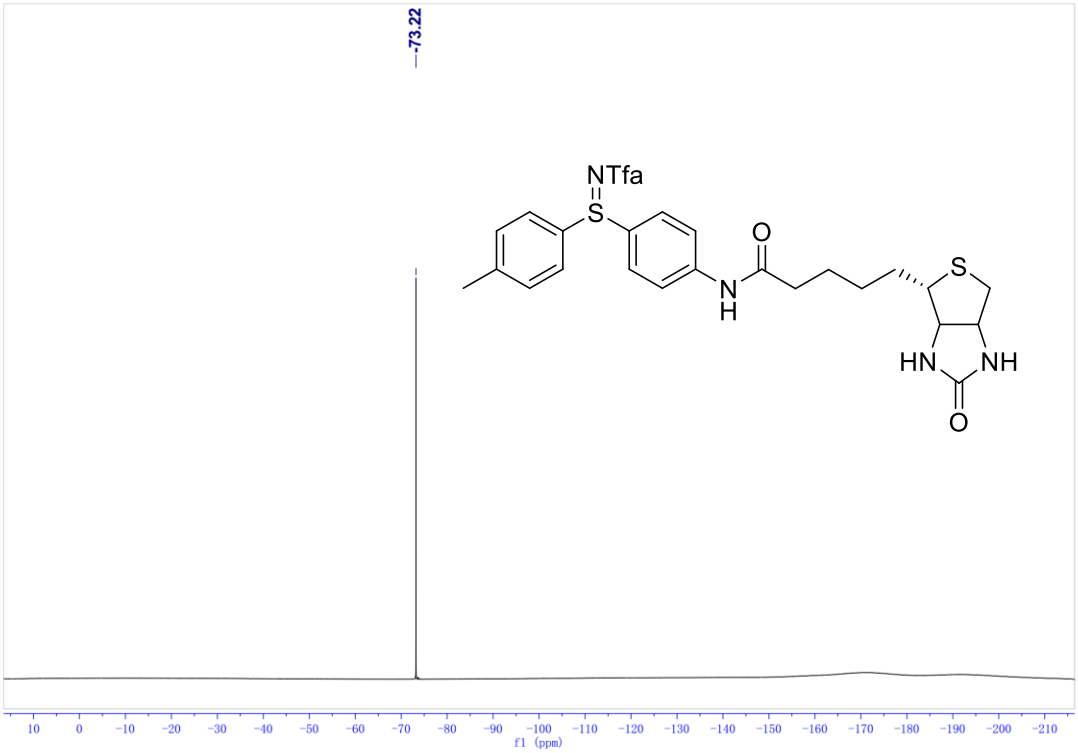
^{1}H NMR (600 MHz, $CDCl_3$) of (*E*)-5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl)sulfinimidoyl)phenyl)pentanamide (C5)



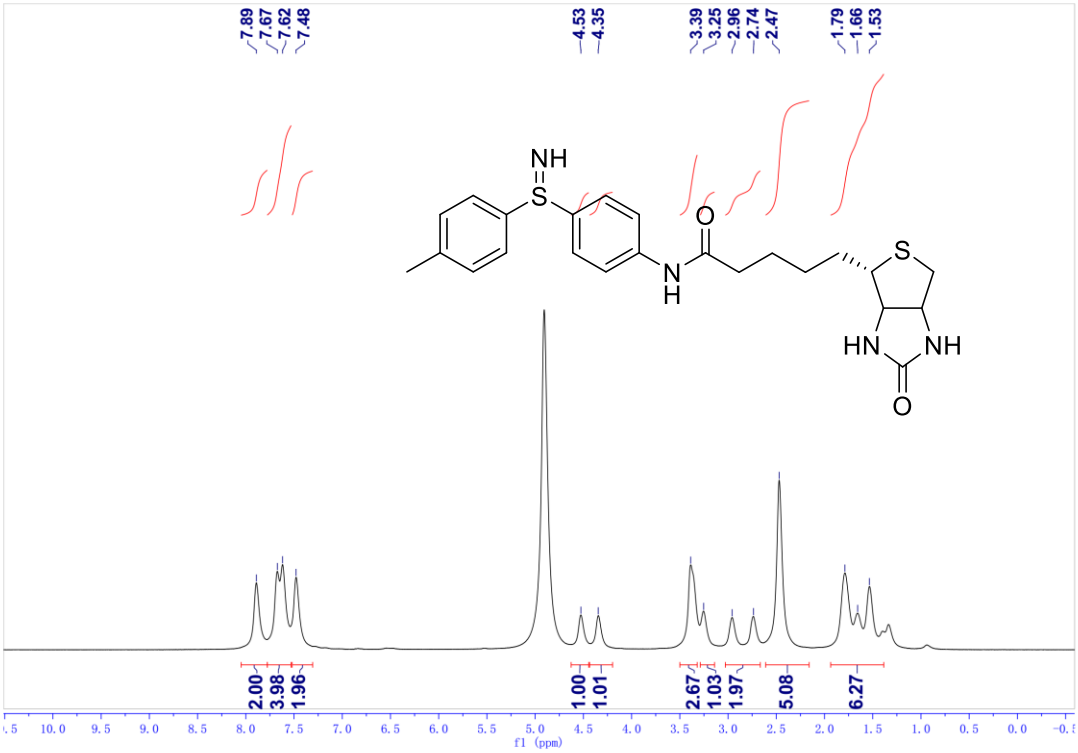
^{13}C NMR (150 MHz, $CDCl_3$) of (*E*)-5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl)sulfinimidoyl)phenyl)pentanamide (C5)



^{19}F NMR (565 MHz, $CDCl_3$) of (*E*)-5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)-*N*-(2,2,2-trifluoroacetyl)sulfinimidoyl)phenyl)pentanamide (C5)



^{1}H NMR (600 MHz, CD_3OD) of 5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)sulfinimidoyl)phenyl)pentanamide (1q)



^{13}C NMR (150 MHz, CD_3OD) of 5-(2-Oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)-*N*-(4-(*S*-(*p*-tolyl)sulfinimidoyl)phenyl)pentanamide (1q)