Electronic Supplementary Material (ESI) for ChemComm.

Nickel-Catalyzed Thiolation of Unactivated Aryl C–H Bonds: An Efficient Access to Diverse Aryl Sulfides

Sheng-Yi Yan,[‡] Yue-Jin Liu,[‡] Bin Liu, Yan-Hua Liu, Bing-Feng Shi[*]

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Supporting Information

Table of Contents:

1. General information S2

2. Experimental Section S2

2.1 Preparation of substrate S2

2.2 Optimization of Reaction Conditions S5

2.3 Screening of Other Directing Groups S6

2.4 General Procedure for the Thiolation S6

2.5 Gram-Scale Experiment S19

2.6 Mechanistic Investigation S19

3. References S22

4. Spectra S23

1. General Information

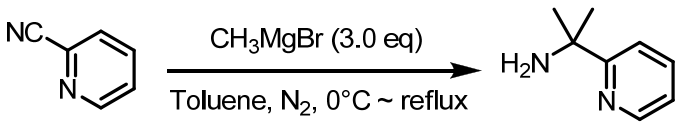
All the materials and solvents were purchased from Adamas-beta and other commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

2. Experimental Section

2.1 Preparation of Substrates

Compounds **1a-1h, 1j-1p, 1a-*d*$_5$,** were known compounds.[1, 2, 3] Compounds **1i, 1q, 1r** were prepared following **typical method A or method B**.

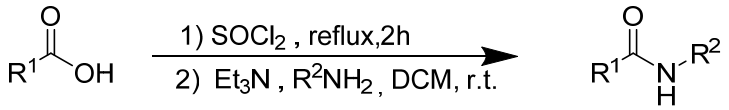
Preparation of 2-(Pyridin-2-yl)isopropyl (PIP) Amine



An improvement of the work-up procedure to the literature[4] was used: To a solution of 2-cyanopyridine (33.0 g, 0.32 mol) in 500 ml of toluene was added CH_3MgBr (3.2M in 2-methyl tetrahydrofuran, 300ml, 0.96 mol) dropwise at 0 ^{o}C in a nitrogen atmosphere by vigorous magnetometric stirring. Upon completion of addition, the mixture was refluxed overnight. The reaction was quenched by adding saturated aqueous NH_4Cl dropwise at 0 ^{o}C until the dark mixture changed to yellow. The suspension was filtrated through a pad of celite and the filtration was acidified by aqueous HCl (6 M, 10 ml). The resulting water phase combined with the filter residue was basified by saturated aqueous NaOH until the yellow colored mixture turned dark

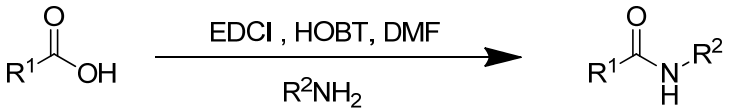
brown with slurry sticky to the bottom. The mixture was washed with dichloromethane (500 ml × 4) carefully and the organic phase was combined and concentrated using a rotary evaporator. The crude product was further purified by distillation under reduced pressure. The target product was obtained as a light yellow liquid (>98% purity. 24 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.2 Hz, 1 H), 7.63 (td, J = 7.8, 1.8 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.12 (ddd, J = 7.4, 4.8, 0.8 Hz, 1 H), 1.87 (s, 2 H), 1.50 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.32, 148.78, 136.55, 121.41, 118.53, 54.14, 31.35.

General Procedure for the Preparation of Starting Materials (Method A):

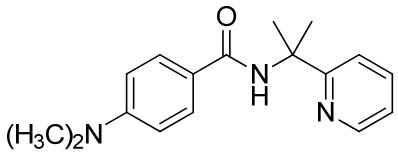


A solution of an acid (5 mmol) was refluxed in 5 mL $SOCl_2$ for 2h and cooled to RT. The excess of $SOCl_2$ was removed under vacuum to give corresponding acid choloride. The acid choloride was then re-dissolved in 5 mL dry CH_2Cl_2 and added dropwiseto a 20 mL dry CH_2Cl_2 solution containing amine (5 mmol) and Et_3N (10 mmol) at 0 ^{o}C. After stirring for 6h at ambient temperature, the resulting mixture was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.

General Procedure for the Preparation of Starting Materials (Method B):

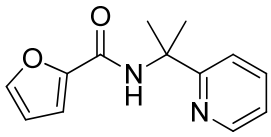


A mixture of amine (5 mmol), 6-bromohexanoic acid (5 mmol), EDCI (5.5 mmol) and HOBT (5.5 mmol) in anhydrous DMF (20 mL) was stirred at room temperature overnight. Water was added and the mixture was extracted with diethyl ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product.



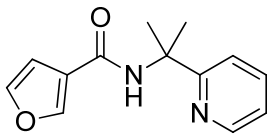
4-(dimethylamino)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 1i

The title compound **1i** was prepared according to the general procedure (Method A). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.2 Hz, 1H), 8.52 (br, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.72 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.20 (ddd, *J* = 7.2, 4.8, 0.8 Hz, 1H), 6.71 – 6.69 (m, 2H), 3.02 (s, 6H), 1.87 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.47, 165.32, 152.40, 147.73, 137.16, 128.50, 123.14, 121.85, 119.67, 111.24, 56.57, 40.30, 27.90. **HRMS** (EI-TOF) calcd for $C_{17}H_{21}N_3O$ (M^+): 283.1685, found: 283.1687.



***N*-(2-(pyridin-2-yl)propan-2-yl)furan-2-carboxamide 1q**

The title compound **1q** was prepared according to the general procedure (Method B). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (br, 1H), 8.59 (d, *J* = 4.4 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.22 (dd, *J* = 6.4, 5.2 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.49 – 6.48 (m, 1H), 1.86 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.46, 157.79, 149.31, 147.93, 143.70, 137.25, 122.05, 119.54, 113.53, 112.02, 56.83, 27.80. **HRMS** (EI-TOF) calcd for $C_{13}H_{14}N_2O_2$ (M^+): 230.1055, found: 230.1058.

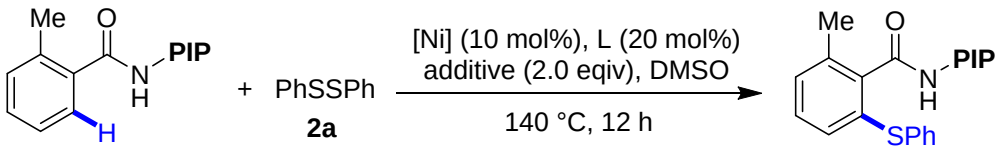


***N*-(2-(pyridin-2-yl)propan-2-yl)furan-3-carboxamide 1r**

The title compound **1q** was prepared according to the general procedure (Method B). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 8.46 (br, 1H), 7.97 (s, 1H), 7.77 – 7.73 (m, 1H), 7.45 (d, *J* = 9.6 Hz, 2H), 7.23 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.73 (s,

1H), 1.85 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.58, 161.88, 147.67, 144.60, 143.61, 137.41, 124.32, 122.11, 119.67, 108.73, 56.65, 27.73. **HRMS** (EI-TOF) calcd for $C_{13}H_{14}N_2O_2$ (M^+): 230.1055, found: 230.1051.

2.2 Optimization of Reaction Conditions[a]



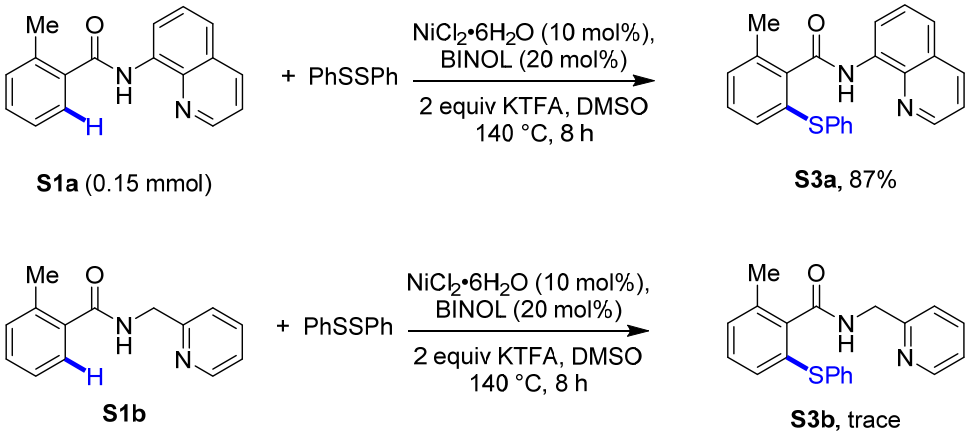
1a **3a**

entry	[Ni]	ligand	additive (equiv)	solvent	yield
1	$Ni(OTf)_2$	PPh_3	Na_2CO_3 (2.0)	toluene	8%
2	$Ni(OTf)_2$	PPh_3	Na_2CO_3 (2.0)	t-AmylOH	trace
3	$Ni(OTf)_2$	PPh_3	Na_2CO_3 (2.0)	1,4-dioxane	trace
4	$Ni(OTf)_2$	PPh_3	Na_2CO_3 (2.0)	DMF	15%
5	$Ni(OTf)_2$	PPh_3	Na_2CO_3 (2.0)	DMSO	45%
6	$NiBr_2$	PPh_3	Na_2CO_3 (2.0)	DMSO	27%
7	$Ni(acac)_2$	PPh_3	Na_2CO_3 (2.0)	DMSO	46%
8	$NiCl_2$	PPh_3	Na_2CO_3 (2.0)	DMSO	50%
9	$NiCl_2·6H_2O$	PPh_3	Na_2CO_3 (2.0)	DMSO	59%
10	$NiCl_2·6H_2O$	TMEDA	Na_2CO_3 (2.0)	DMSO	50%
11	$NiCl_2·6H_2O$	dppp	Na_2CO_3 (2.0)	DMSO	46%
12	$NiCl_2·6H_2O$	dppb	Na_2CO_3 (2.0)	DMSO	72%
13	$NiCl_2·6H_2O$	dppe	Na_2CO_3 (2.0)	DMSO	60%
14	$NiCl_2·6H_2O$	PCy_3	Na_2CO_3 (2.0)	DMSO	49%
15	$NiCl_2·6H_2O$	BINOL	Na_2CO_3 (2.0)	DMSO	78%
16	$NiCl_2·6H_2O$	BINOL	K_2CO_3 (2.0)	DMSO	76%
17	$NiCl_2·6H_2O$	BINOL	$NaHCO_3$ (2.0)	DMSO	66%
18	$NiCl_2·6H_2O$	BINOL	$KHCO_3$ (2.0)	DMSO	55%
19	$NiCl_2·6H_2O$	BINOL	K_3PO_4 (2.0)	DMSO	75%

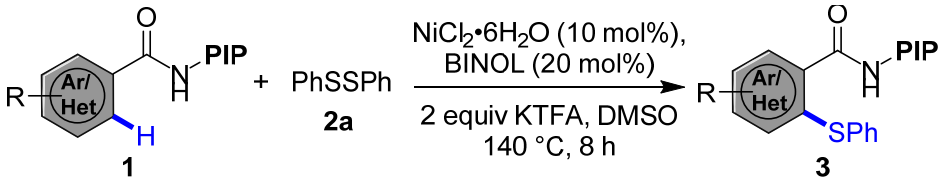
20	$NiCl_2·6H_2O$	BINOL	NaTFA (2.0)	DMSO	67%
21	$NiCl_2·6H_2O$	BINOL	KTFA (2.0)	DMSO	88%
22	—	—	KTFA (2.0)	DMSO	trace
23	$NiCl_2·6H_2O$	—	KTFA (2.0)	DMSO	49%
24[b]	$NiCl_2·6H_2O$	BINOL	KTFA (2.0)	DMSO	88% (84%)[c]
25	$Cu(OAc)_2$	BINOL	KTFA (2.0)	DMSO	trace

[a]^{1}H NMR yield using CH_2Br_2 as the internal standard. [b]8 h. [c]Isolated yield in parenthesis.

2.3 Screening of Other Directing Groups

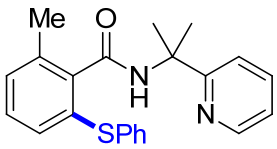


2.4 General Procedure for the Thiolation



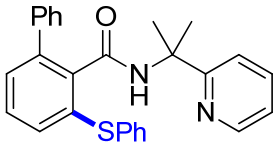
To a 50 mL Schlenk tube was added substrate (0.15 mmol), ArSSAr (0.3 mmol), $NiCl_2·6H_2O$ (3.6 mg, 0.015 mmol), BINOL (8.6 mg, 0.03 mmol), KTFA (45.6 mg, 0. 3 mmol), and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm), and stirred at 140 °C for 8 h. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate (3×20 mL). The combined phase was then washed with brine, if necessary it can be washed with NaOH solution to remove the ligand BINOL and dried with anhydrous magnesium sulfate. After concentration, the

resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the prcoduct.



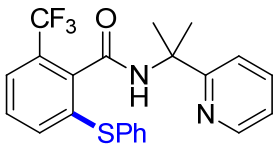
6-Methyl-2-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)benzamide 3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.90 (br, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.17 - 7.13 (m, 4H), 2.41 (s, 3H), 1.86 (s, 6H);; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.47, 164.35, 147.56, 141.44, 137.11, 136.94, 136.23, 131.75, 131.06, 130.44, 129.83, 129.19, 126.70, 121.88, 119.59, 57.44, 27.46, 19.45; **HRMS** (EI-TOF) calcd for $C_{22}H_{22}N_2OS$ (M^+): 362.1453, found: 362.1458.



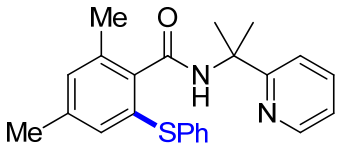
6-Phenyl-2-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)benzamide 3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 4.0 Hz, 1H), 7.63 (br, 1H), 7.57 (td, *J* = 8.4, 1.6 Hz, 1H), 7.52 (d, *J* = 6.8 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 - 7.27 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 6.4, 4.8 Hz, 1H), 1.56 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.74, 164.23, 147.40, 140.63, 140.15, 139.26, 136.94, 135.69, 134.66, 132.16, 130.72, 129.34, 129.22, 129.15, 128.68, 128.17, 127.55, 127.45, 121.67, 119.44, 57.31, 27.07; **HRMS** (EI-TOF) calcd for $C_{27}H_{24}N_2OS$ (M^+): 424.1609, found: 424.1603.



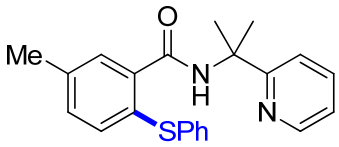
6-trifluoromethyl-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br, 1H), 8.40 (d, *J* = 4.8 Hz, 1H), 7.72 (td, *J* = 8.0, 1.6 Hz, 1H), 7.55 -7.53 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.17 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.92 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.46, 164.12, 147.37, 137.66, 137.30, 137.16, 135.06, 134.43, 132.76, 129.58, 129.23, 128.35, 128.11, 124.62 (q, *J* = 4.9 Hz), 123.71 (q, *J* = 272.8 Hz), 122.01, 119.62, 57.70, 27.10; **HRMS** (EI-TOF) calcd for $C_{22}H_{19}F_3N_2OS$ (M^+): 416.1170, found: 416.1174.



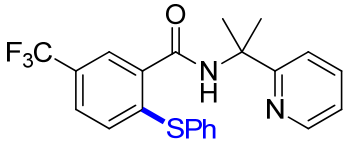
4,6-Dimethyl-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.0 Hz, 1H), 7.82 (br, 1H), 7.67 (td, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.14 – 7.10 (m, 2H), 6.99 (d, *J* = 13.6 Hz, 2H), 2.38 (s, 3H), 2.25 (s, 3H), 1.83 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.67, 164.38, 147.53, 139.17, 139.09, 137.38, 137.04, 136.10, 131.90, 130.96, 130.92, 129.90, 129.11, 126.40, 121.80, 119.56, 57.36, 27.43, 21.15, 19.38; **HRMS** (EI-TOF) calcd for $C_{23}H_{24}N_2OS$ (M^+): 376.1609, found: 376.1609.



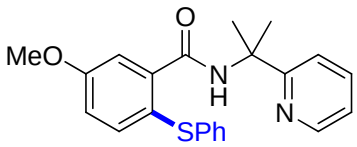
5-Methyl-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.0, 0.8 Hz, 1H), 8.34 (br, 1H), 7.66 (td, *J* = 8.0, 1.6 Hz, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.17 (m, 6H), 7.16 – 7.13 (m, 2H), 2.36 (s, 3H), 1.77 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.15, 164.47, 147.75, 139.30, 138.02, 137.03, 136.66, 133.76, 131.34, 130.18, 129.83, 129.29, 129.12, 126.77, 121.80, 119.50, 57.48, 27.52, 21.07; **HRMS** (EI-TOF) calcd for $C_{22}H_{22}N_2OS$ (M^+): 362.1453, found: 362.1456.



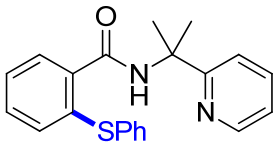
5-trifluoromethyl-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (br, 1H), 8.50 (d, *J* = 4.0 Hz, 1H), 7.83 (s, 1H), 7.75 (td, *J* = 8.0, 1.6 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.43 – 7.38 (m, 4H), 7.21 (dd, *J* = 6.4, 4.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 1.90 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.02, 164.18, 147.69, 142.39, 137.40, 136.60, 134.32, 132.60, 129.91, 129.36, 129.04, 127.78 (q, *J* = 32.8 Hz), 126.70 (q, *J* = 3.4 Hz), 125.06 (q, *J* = 3.7 Hz), 123.95 (q, *J* = 270.5 Hz), 122.15, 119.60, 57.55, 27.53; **HRMS** (EI-TOF) calcd for $C_{22}H_{19}F_3N_2OS$ (M^+): 416.1170, found: 416.1174.



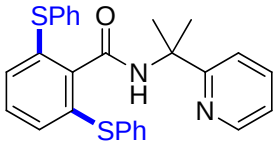
5-Methoxy-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.0 Hz, 2H), 7.63 (td, *J* = 8.0, 1.6 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.33 (t, *J* = 3.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15 – 7.10 (m, 4H), 6.94 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.85 (s, 3H), 1.72 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.57, 164.45, 160.23, 147.85, 142.17, 138.11, 137.55, 136.98, 129.24, 128.21, 126.09, 121.78, 121.06, 119.46, 117.29, 114.66, 57.66, 55.75, 27.51; **HRMS** (EI-TOF) calcd for $C_{22}H_{22}N_2O_2S$ (M^+): 378.1402, found: 378.1400.



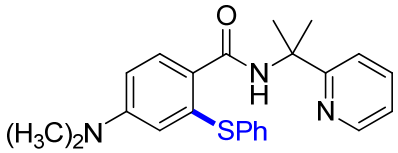
2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.0 Hz, 1H), 8.43 (br, 1H), 7.72 -7.65(m, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.32 - 7.25 (m, 5H), 7.19 – 7.16 (m, 2H), 1.83 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.16, 164.56, 147.75, 138.19, 137.15, 135.37, 134.81, 132.02, 131.85, 130.43, 129.47, 128.75, 127.56, 126.89, 121.92, 119.58, 57.48, 27.59; **HRMS** (EI-TOF) calcd for $C_{21}H_{20}N_2OS$ (M^+): 348.1296, found: 348.1300.



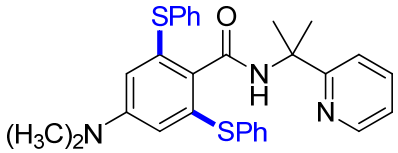
2,6-bis(diphenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)benzamide 3h'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.4 Hz, 1H), 8.08 (br, 1H), 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.39 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.15 – 7.06 (m, 4H), 1.87 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.71, 164.20, 147.40, 141.43, 137.08, 135.31, 134.82, 131.90, 130.73, 129.67, 129.36, 127.51, 121.80, 119.61, 57.73, 27.41; **HRMS** (EI-TOF) calcd for $C_{27}H_{24}N_2OS_2$ (M^+): 456.1330, found: 456.1332.



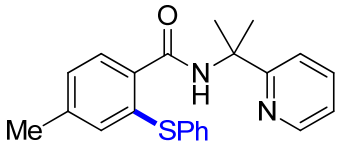
4-Dimethylamino-6-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)benzamide 3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 8.48 (d, *J* = 4.0 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 5H), 7.23 – 7.20 (m, 1H), 7.13 (dd, *J* = 6.4, 5.2 Hz, 1H), 6.61 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 2.89 (s, 6H), 1.72 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.57, 165.13, 151.80, 147.84, 136.97, 136.25, 134.46, 131.48, 130.60, 129.37, 127.01, 121.64, 119.61, 116.02, 110.75, 57.38, 40.10, 27.83; **HRMS** (EI-TOF) calcd for $C_{23}H_{25}N_3OS$ (M^+): 391.1718, found: 391.1720.



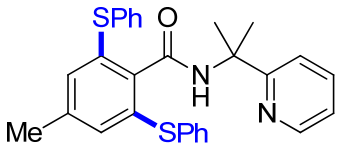
4-Dimethylamino-2,6-bis(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)benzamide 3i'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.4 Hz, 1H), 7.63 (td, *J* = 8.4, 1.2 Hz, 1H), 7.59 (br, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.28 – 7.27 (m, 1H), 7.26 – 7.24 (m, 3H),7.17 (t, *J* = 7.6 Hz, 2H), 7.10 (dd, *J* = 6.4, 4.8 Hz, 1H), 6.50 (s, 2H), 2.76 (s, 6H), 1.74 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.39, 164.58, 150.82, 147.57, 136.84, 136.66, 134.38, 131.33, 130.77, 129.22, 126.86, 121.58, 119.71, 115.68, 57.73, 40.13, 27.45; **HRMS** (EI-TOF) calcd for $C_{29}H_{29}N_3OS_2$ (M^+): 499.1752, found: 499.1754.



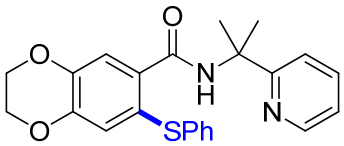
4-Methyl-2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 1H), 8.43 (br, 1H), 7.67 (td, *J* = 8.0, 1.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 - 7.27 (m, 4H), 7.25 - 7.21 (m, 1H), 7.16 (ddd, *J* = 7.2, 4.8, 0.8 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 2.27 (s, 3H), 1.78 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.06, 164.66, 147.79, 140.80, 137.07, 135.88, 133.64, 133.11, 131.21, 129.41, 129.14, 128.15, 127.23, 121.84, 119.56, 57.47, 27.61, 21.34; **HRMS** (EI-TOF) calcd for $C_{22}H_{22}N_2OS$ (M^+): 362.1453, found: 362.1457.



4-Methyl-2,6-bis(phenylthio)*N*-(2-(pyridin-2-yl)propan-2-yl benzamide 3j'

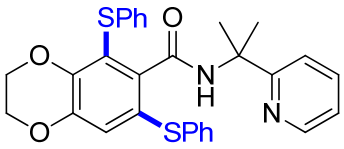
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.4 Hz, 1H), 7.93 (br, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 4H), 7.21 – 7.17 (m, 2H), 7.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 6.97 (s, 2H), 2.15 (s, 3H), 1.83 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.93, 164.34, 147.44, 139.93, 137.01, 135.92, 134.00, 132.34, 131.37, 129.31, 127.22, 121.73, 119.62, 57.73, 27.41, 21.21; **HRMS** (EI-TOF) calcd for $C_{28}H_{26}N_2OS_2$ (M^+): 470.1487, found: 470.1491.



7-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine -6-carboxamide 3k

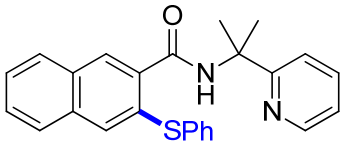
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2H), 7.64 (td, *J* = 8.0, 1.6 Hz, 1H), 7.35 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 4H), 7.18 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.14 (dd, *J* = 6.4, 4.8 Hz, 1H), 6.88 (s, 1H), 4.26 (s, 4H), 1.72 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.99, 164.58, 147.79, 145.25, 143.57, 137.03, 136.88, 132.66,

129.64, 129.35, 126.72, 124.20, 123.01, 121.76, 119.52, 119.03, 64.59, 64.47, 57.50, 27.57; **HRMS** (EI-TOF) calcd for $C_{23}H_{22}N_2O_3S$ (M^+): 406.1351, found: 406.1357.



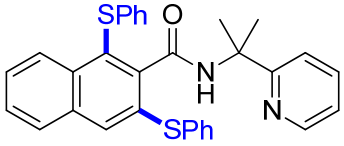
5,7-bis(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)- 2,3-dihydrobenzo[*b*][1,4]dio xine-6-carboxamide 3k'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.4 Hz, 1H), 7.69 (br, 1H), 7.61 (t, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 7H), 7.10 – 7.03 (m, 2H), 7.00 (s, 1H), 4.21 (d, *J* = 2.8 Hz, 4H), 1.75 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.52, 164.26, 147.37, 145.10, 144.54, 141.25, 137.28, 137.03, 136.91, 130.22, 129.23, 128.86, 127.68, 126.77, 125.66, 124.52, 124.21, 121.62, 119.57, 118.80, 64.95, 64.14, 57.71, 27.33; **HRMS** (EI-TOF) calcd for $C_{29}H_{26}N_2O_3S_2$ (M^+): 514.1385, found: 514.1385.



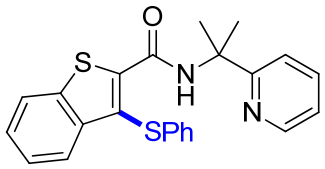
3-(phenylthio)-*N*-(2-(pyridine-2-yl)propan-2-yl)2-naphthamide 3l

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (br, 1H), 8.47 (d, *J* = 4.8 Hz, 1H), 8.20 (s, 1H), 7.88 – 7.85 (m, 1H), 7.71 – 7.65 (m, 3H), 7.50 – 7.47 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36 - 7.34 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.18 – 7.15 (m, 1H), 1.81 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.01, 164.51, 147.77, 137.14, 136.18, 135.82, 134.14, 131.95, 131.92, 131.12, 130.74, 129.48, 129.08, 128.39, 127.70, 127.32, 127.26, 126.88, 121.90, 119.57, 57.56, 27.52; **HRMS** (EI-TOF) calcd for $C_{25}H_{22}N_2OS$ (M^+): 398.1453, found: 398.1457.



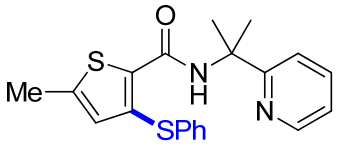
1,3-bis(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)-2-naphthamide 3l'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.42 (m, 1H), 8.24 (d, *J* = 4.0 Hz, 1H), 7.91 (br, 1H), 7.86 (t, *J* = 5.2 Hz, 1H), 7.81 (s, 1H), 7.70 - 7.68 (m, 1H), 7.63 (td, *J* = 8.0, 1.6 Hz, 1H), 7.48 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 3H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.07 (m, 4H), 7.01 – 6.97 (m, 1H), 1.82 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.03, 164.16, 147.32, 145.31, 138.29, 136.98, 135.54, 134.32, 134.22, 133.84, 131.65, 131.58, 129.48, 129.04, 128.16, 128.09, 127.52, 127.26, 127.08, 126.98, 125.41, 121.66, 119.53, 57.82, 27.32; **HRMS** (EI-TOF) calcd for $C_{31}H_{26}N_2OS_2$ (M^+): 506.1487, found: 506.1491.



3-(phenylthio)-*N*-(2-(pyridin2-yl)propan-2-yl)benzo[*b*]thiophene-2-carboxamide 3m

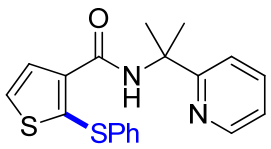
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (br, 1H), 8.38 (d, *J* = 4.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.62 (td, *J* = 8.0, 1.6 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 6.4 Hz, 2H), 7.13 (t, *J* = 6.8 Hz, 4H), 1.79 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.25, 160.61, 147.99, 146.80, 141.32, 139.33, 136.94, 135.60, 129.34, 127.11, 126.77, 126.34, 125.31, 124.59, 122.82, 121.87, 120.78, 119.33, 58.32, 27.76; **HRMS** (EI-TOF) calcd for $C_{23}H_{20}N_2OS_2$ (M^+): 404.1017, found: 404.1018.



5-Methyl-3-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-2-carboxamide 3n

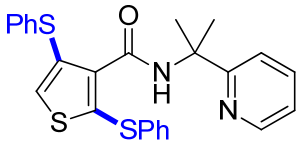
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (br, 1H), 8.46 (d, *J* = 4.8 Hz, 1H), 7.62 (td, *J* = 8.0, 1.6 Hz, 1H), 7.30 – 7.25 (m, 5H), 7.24 - 7.20 (m, 1H), 7.13 (ddd, *J* = 7.2, 4.8, 0.8 Hz, 1H), 6.61 (d, *J* = 0.8 Hz, 1H), 2.42 (s, 3H), 1.75 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.54, 160.61, 147.99, 143.37, 137.88, 136.88, 135.64, 131.71, 129.34,

129.32, 128.63, 127.06, 121.75, 119.35, 57.86, 27.88, 15.73; **HRMS** (EI-TOF) calcd for $C_{20}H_{20}N_2OS_2$ (M^+): 368.1017, found: 368.1022.



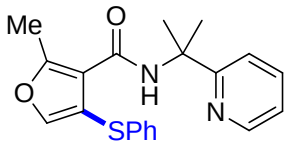
2-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-3-carboxamide 3o

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (br, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 7.62 (td, *J* = 7.6, 1.6 Hz, 1H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.32 – 7.23 (m, 7H), 7.13 (dd, *J* = 7.2, 4.8 Hz, 1H), 1.74 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.60, 161.79, 147.94, 139.89, 136.95, 136.31, 130.46, 129.49, 128.97, 127.82, 127.44, 121.80, 119.42, 57.52, 27.78; **HRMS** (EI-TOF) calcd for $C_{19}H_{18}N_2OS_2$ (M^+): 354.0861, found: 354.0865.



2,6-bis(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)thiophene-3-carboxamide 3o'

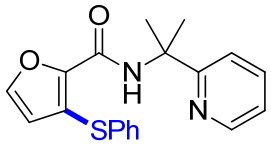
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (br, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.35 (d, *J* = 6.8 Hz, 3H), 7.28 – 7.17 (m, 6H), 7.13 - 7.10 (m, 2H), 1.64 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.51, 162.03, 147.92, 136.86, 135.85, 134.88, 132.20, 129.64, 129.43, 129.28, 129.17, 128.66, 126.96, 121.67, 119.39, 100.12, 57.81, 27.66; **HRMS** (EI-TOF) calcd for $C_{25}H_{22}N_2OS_3$ (M^+): 462.0894, found: 462.0896.



2-Methyl-4-(phenylthio)-*N*-(2-(pyridin-2-yl)propan-2-yl)furan-3-carboxamide 3p

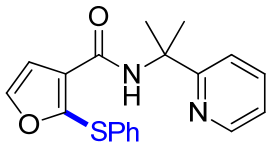
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.0 Hz, 1H), 8.29 (br, 1H), 7.54 (s, 1H), 7.50 (td, *J* = 8.0, 1.6 Hz, 1H), 7.25 -7.22 (m, 2H), 7.17 – 7.06 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 1H), 2.61 (s, 3H), 1.55 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.73, 161.74,

160.61, 148.12, 145.78, 136.50, 136.04, 129.20, 126.39, 126.08, 121.39, 119.03, 116.43, 110.24, 57.37, 27.77, 14.45; **HRMS** (EI-TOF) calcd for $C_{20}H_{20}N_2O_2S$ (M^+): 352.1245, found: 352.1241.



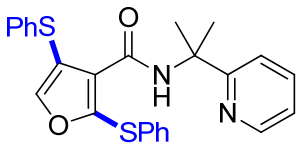
3-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)furan-2-carboxamide 3q

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (br, 1H), 8.55 (dd, *J* = 4.4, 0.8 Hz, 1H), 7.73 (td, *J* = 8.0, 1.6 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.20 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.03 (d, *J* = 2.0 Hz, 1H), 1.87 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.54, 158.08, 147.88, 143.04, 142.24, 137.24, 133.31, 133.17, 129.42, 128.43, 125.55, 122.01, 119.55, 113.42, 57.05, 27.96; **HRMS** (EI-TOF) calcd for $C_{19}H_{18}N_2O_2S$ (M^+): 338.1089, found: 338.1093.



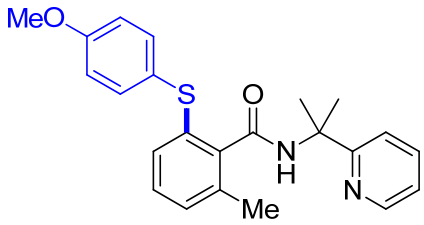
2-(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)furan-3-carboxamide 3r

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (br, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.32 - 7.29 (m, 3H), 7.27 - 7.22 (m, 2H), 7.16 (dd, *J* = 6.4, 4.8 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 1.79 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.52, 160.95, 147.76, 145.48, 142.90, 137.21, 133.92, 129.50, 129.08, 127.55, 121.94, 119.54, 113.12, 57.48, 27.84; **HRMS** (EI-TOF) calcd for $C_{19}H_{18}N_2O_2S$ (M^+): 338.1089, found: 338.1086.



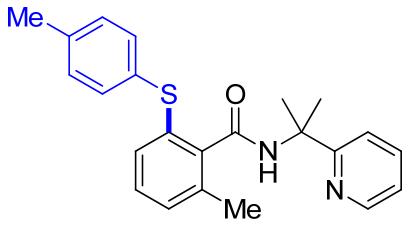
2,4-bis(phenylthio)-*N*-(2-(Pyridin-2-yl)propan-2-yl)furan-3-carboxamide 3r'

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (br, 1H), 8.45 (d, *J* = 3.2 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.49 (d, *J* = 3.6 Hz, 2H), 7.39 (s, 1H), 7.34 (d, *J* = 4.4 Hz, 3H), 7.24 (d, *J* = 7.2 Hz, 4H), 7.20 – 7.14 (m, 3H), 1.65 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.51, 162.03, 147.92, 136.86, 135.85, 134.88, 132.20, 129.64, 129.43, 129.28, 129.17, 128.66, 126.96, 121.67, 119.39, 100.12, 57.81, 27.66; **HRMS** (EI-TOF) calcd for $C_{25}H_{22}N_2O_2S_2$ (M^+): 446.1123, found: 446.1125.



2-(4-(methoxyphenyl)thio)-6-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 5a

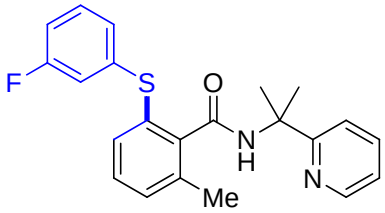
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 1H), 8.05 (br, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 6.4, 4.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 2.39 (s, 3H), 1.93 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.64, 164.41, 159.69, 147.57, 139.12, 137.19, 135.72, 135.00, 134.96, 128.97, 128.37, 127.96, 125.38, 121.95, 119.67, 115.00, 57.48, 55.43, 27.55, 19.36; **HRMS** (EI-TOF) calcd for $C_{23}H_{24}N_2O_2S$ (M^+): 392.1558, found: 392.1554.



2-Methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)-6-(*p*-tolylthio)benzamide 5b

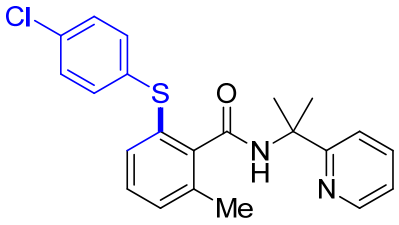
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.4 Hz, 1H), 7.97 (br, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.15 – 7.05 (m, 6H), 2.40 (s, 3H), 2.28 (s, 3H), 1.89(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.53, 164.36, 147.51, 140.45, 137.14, 137.11, 135.94, 133.17, 132.44, 131.66, 130.03, 129.72,

129.12, 129.03, 121.84, 119.60, 57.42, 27.47, 21.16, 19.38; **HRMS** (EI-TOF) calcd for $C_{23}H_{24}N_2OS$ (M^+): 376.1609, found: 376.1608.



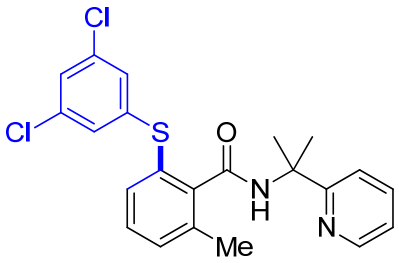
2-((3-fluorophenyl)thio)-6-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 5c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.4 Hz, 1H), 7.97 (br, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.12 (dd, *J* = 12.4, 6.4 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 9.6 Hz, 1H), 6.75 (td, *J* = 8.4, 1.6 Hz, 1H), 2.43 (s, 3H), 1.84 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.24, 164.14, 163.11 (d, *J* = 246.6 Hz,), 147.43, 142.72, 140.43 (d, *J* = 7.8 Hz), 137.14, 136.56, 132.62, 130.93, 130.20 (d, *J* = 8.5 Hz), 129.48, 129.39, 124.48 (d, *J* = 2.9 Hz), 121.89, 119.44, 115.72 (d, *J* = 23.4 Hz), 113.03 (d, *J* = 21.2 Hz), 57.33, 27.35, 19.43; **HRMS** (EI-TOF) calcd for $C_{22}H_{21}FN_2OS$ (M^+): 380.1359, found: 380.1362.



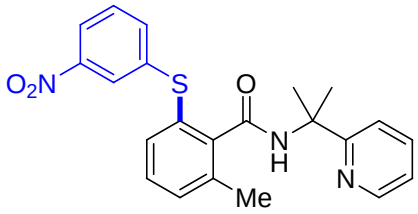
2-((4-chlorophenyl)thio)-6-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 5d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.8 Hz, 1H), 8.00 (br, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.14 (m, 8H), 2.42 (s, 3H), 1.87 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.30, 164.14, 147.46, 142.03, 137.20, 136.41, 135.97, 132.45, 131.68, 131.13, 130.73, 130.41, 129.30, 129.23, 121.94, 119.50, 57.36, 27.39, 19.42; **HRMS** (EI-TOF) calcd for $C_{22}H_{21}ClN_2OS$ (M^+): 396.1063, found: 396.1067.



2-((3,5-dichlorophenyl)thio)-6-methyl-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 4.8, 0.8 Hz, 1H), 8.03 (br, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 - 7.27 (m, 3H), 7.15 (dd, *J* = 6.4, 4.8 Hz, 1H), 6.99 (s, 3H), 2.44 (s, 3H), 1.85 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.02, 163.98, 147.40, 143.30, 142.27, 137.24, 136.85, 135.28, 133.29, 131.67, 129.59, 127.97, 126.15, 125.95, 121.97, 119.37, 57.29, 27.30, 19.45; **HRMS** (EI-TOF) calcd for $C_{22}H_{20}Cl_2N_2OS$ (M^+): 430.0673, found: 430.0676.



6-Methyl-2-((3-nitrophenyl)thio)-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide 5f

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.8 Hz, 1H), 8.05 (br, 1H), 7.96 (s, 1H), 7.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.14 (dd, *J* = 6.4, 5.2 Hz, 1H), 2.45 (s, 3H), 1.83 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.05, 163.95, 148.63, 147.30, 143.44, 141.46, 137.34, 136.88, 133.97, 133.32, 131.83, 129.71, 129.61, 127.97, 122.62, 122.04, 120.62, 119.48, 57.28, 27.31, 19.46; **HRMS** (EI-TOF) calcd for $C_{22}H_{21}N_3O_3S$ (M^+): 407.1304, found: 407.1300.

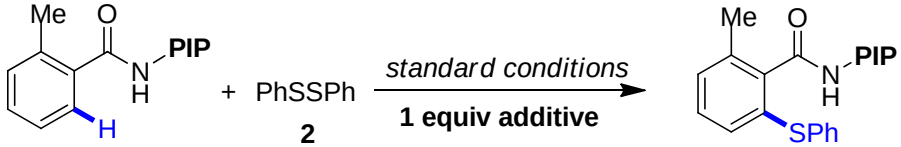
2.5 Gram-Scale Experiment

1a (4 mmol, 1.02 g)

3a, 57%

2.6 Mechanistic Investigation

Radical Scavenger Reactions



1a **3a**

Additive (1.0 equiv)	Yield
---------	84%[a]
1,4-dinitrobenzene	95%[b]
TEMPO	86%[b]
1,4-diphenylethylene	78%[b]

[a]Isolated yield. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard.

To a 50 mL Schlenk tube was added substrate **1a** (0.15 mmol), PhSSPh (0.3 mmol), additive (0.15 mmol), $NiCl_2 \cdot 6H_2O$ (3.6 mg, 0.015 mmol), BINOL (8.6 mg, 0.03 mmol), KTFA (45.6 mg, 0.3 mmol), and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm), and stirred at 140 °C for 8 h. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate (3×20 mL). The combined phase was then washed with brine and dried with anhydrous magnesium sulfate. After concentration, the resulting residue was analyzed with NMR using CH_2Br_2 as the internal standard.

Deuterium Labeling Experiment

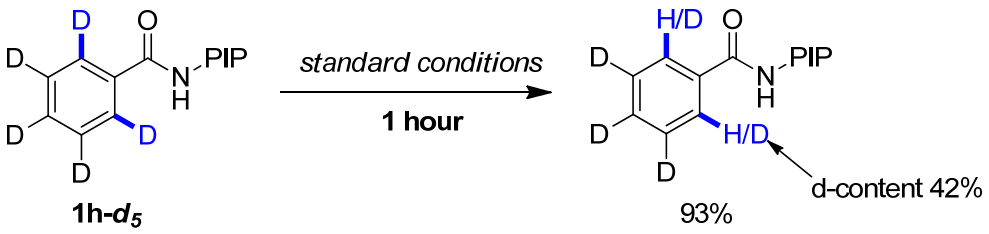
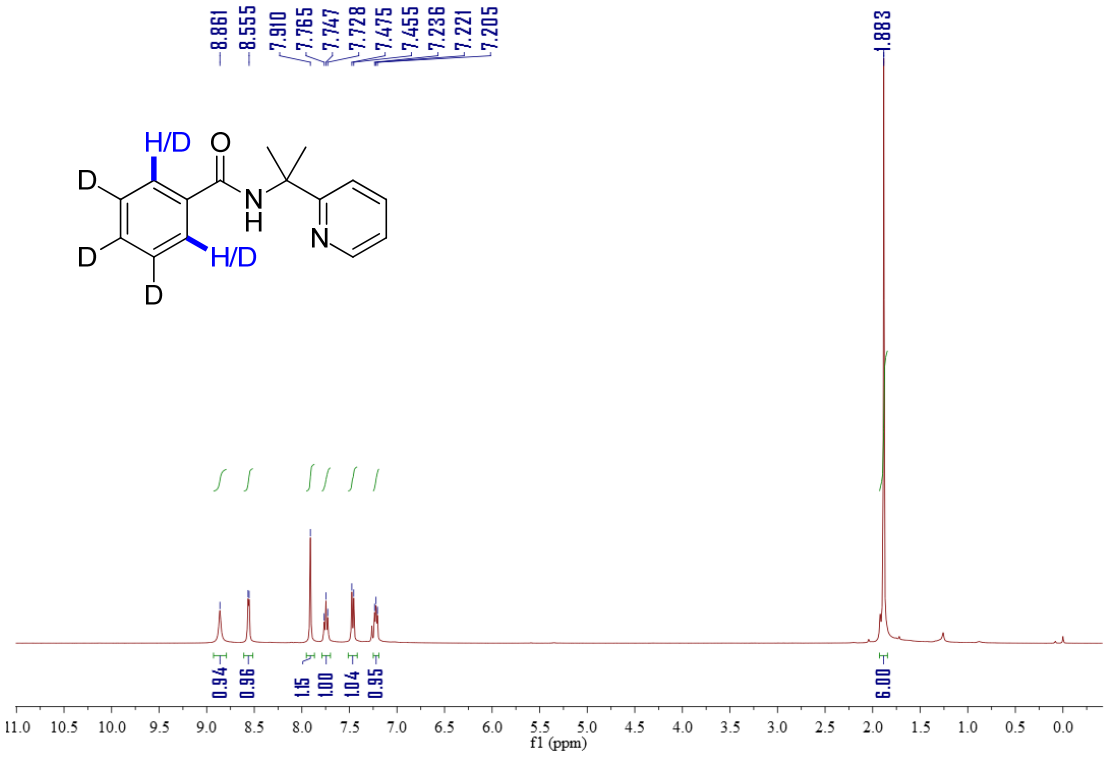
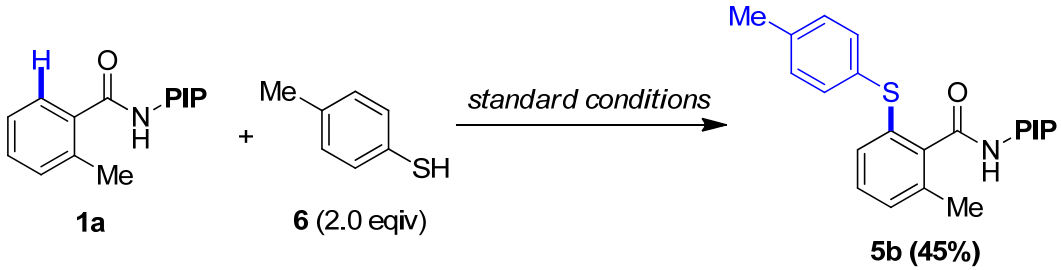


Figure S1. ^{1}H NMR spectrum of product for the deuterium labeling experiment.



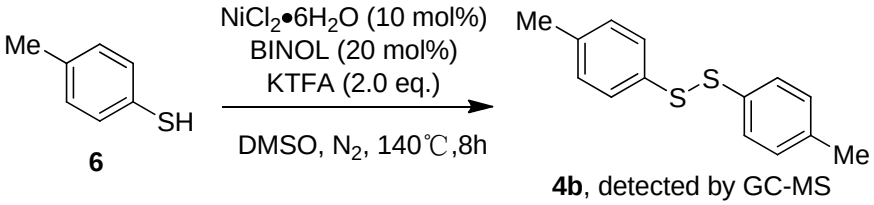
Thiolation with 4-methylbenzenethiol 6



To a 50 mL Schlenk tube was added substrate **1a** (0.15 mmol), 4-methylbenzenethiol (0.3 mmol), $NiCl_2 \cdot 6H_2O$ (3.6 mg, 0.015 mmol), BINOL (8.6 mg, 0.03 mmol), KTFA (45.6 mg, 0.3 mmol), and DMSO (1 mL). The vial was evacuated and filled with N_2

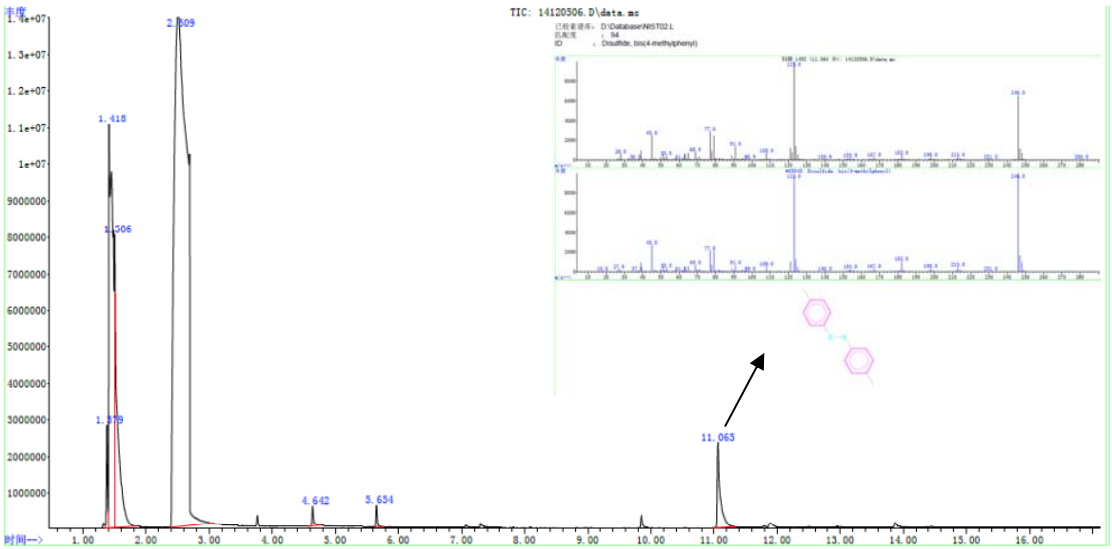
(1 atm), and stirred at 140 °C for 8 h. The mixture was then cooled to room temperature, diluted with water, extracted with ethyl acetate (3×20 mL). The combined phase was then washed with NaOH solution to remove the ligand BINOL and dried with anhydrous magnesium sulfate. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

Oxidation of 4-methylbenzenethiol 6 to disulfide 4b



To a 50 mL Schlenk tube was added substrate 4-methylbenzenethiol (0.15 mmol), $NiCl_2 \cdot 6H_2O$ (3.6 mg, 0.015 mmol), BINOL (8.6 mg, 0.03 mmol), KTFA (45.6 mg, 0. 3 mmol), and DMSO (1 mL). The vial was evacuated and filled with N_2 (1 atm), and stirred at 140 °C for 8 h. The mixture was then cooled to room temperature, diluted with 10 mL CH_2Cl_2 and filtered through a pad of Celite. The filtrate was then analyzed with GC-MS.

Figure S2. GC-MS for the oxidation of 4-methylbenzenethiol.

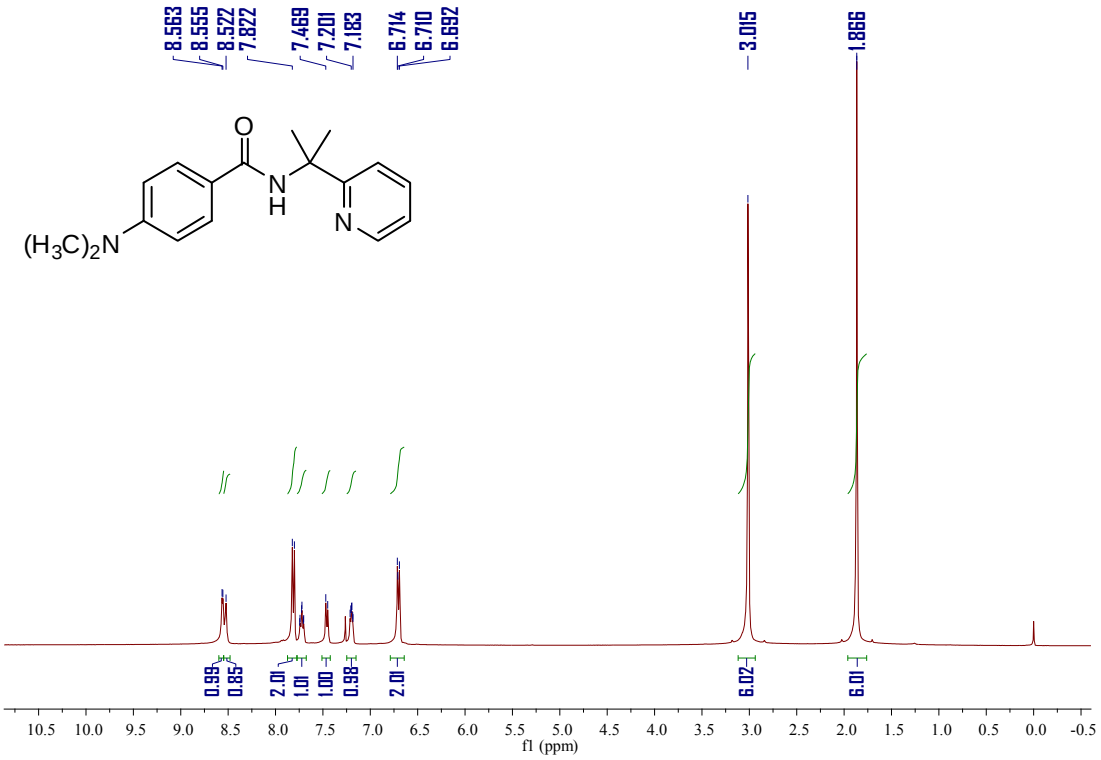


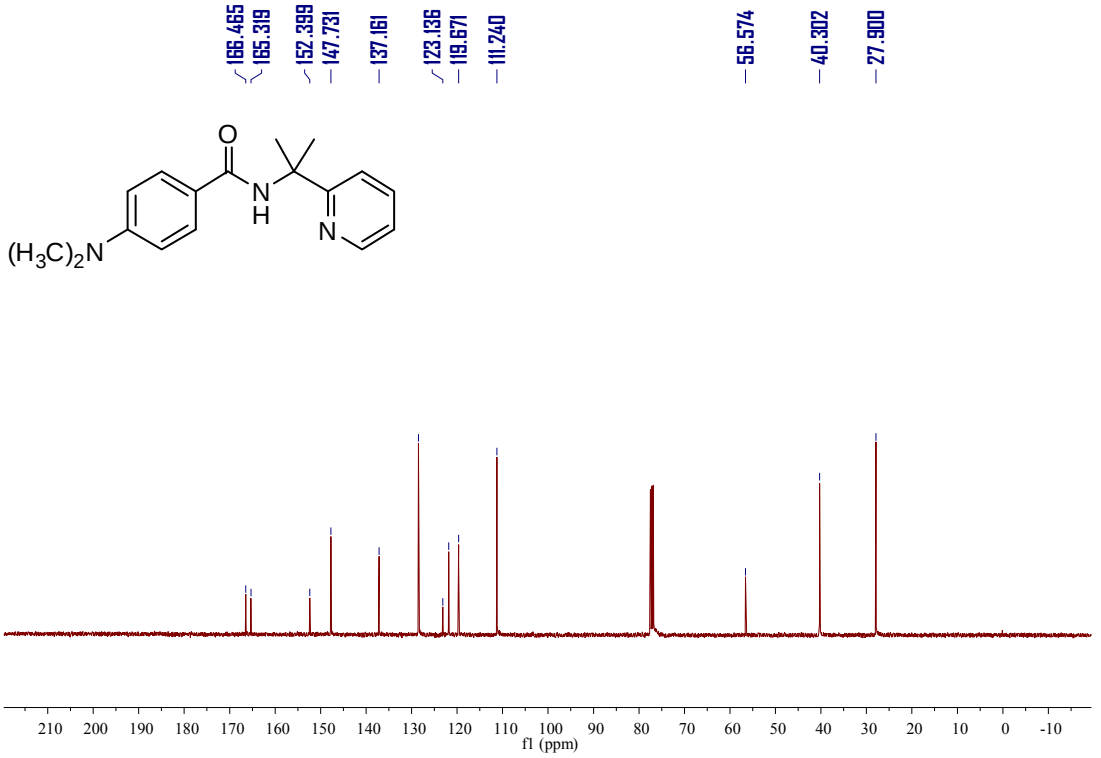
3. References:

1. Chen, F.-J.; Liao, G.; Li, X.; Wu, J.; Shi, B.-F. *Org. Lett.* **2014,** *16*, 5644-5647.
2. Li, X.; Liu, Y.-H.; Gu, W.-J.; Li, B.; Chen, F.-J.; Shi, B.-F. *Org. Lett.* **2014**, *16*, 3904-3907.
3. Liu, Y.-J.; Liu, Y.-H.; Yin, X.-S.; Gu, W.-J.; Shi, B.-F. *Chem. Eur. J.* **2014**, 20, 1.
4. Yager, K. M.; Plaza, E. A.; Kumar, D. V.; Kim, I. C. US Pat., 20080207573 A1.

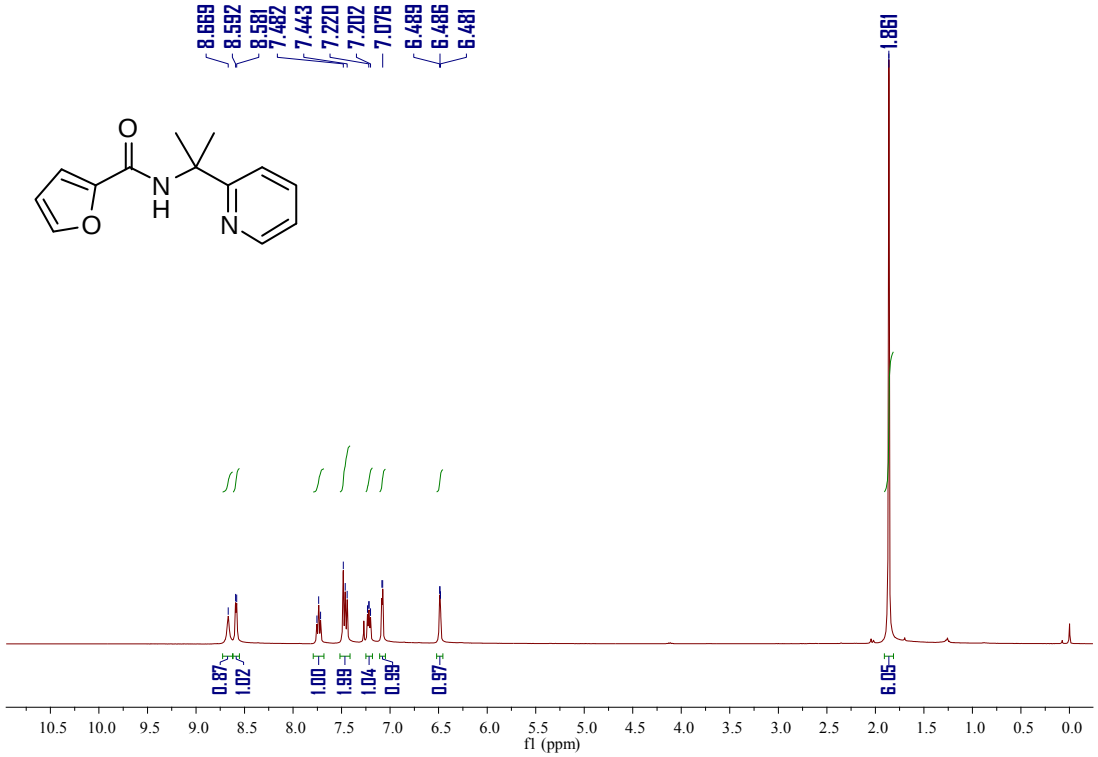
4. NMR Spectra

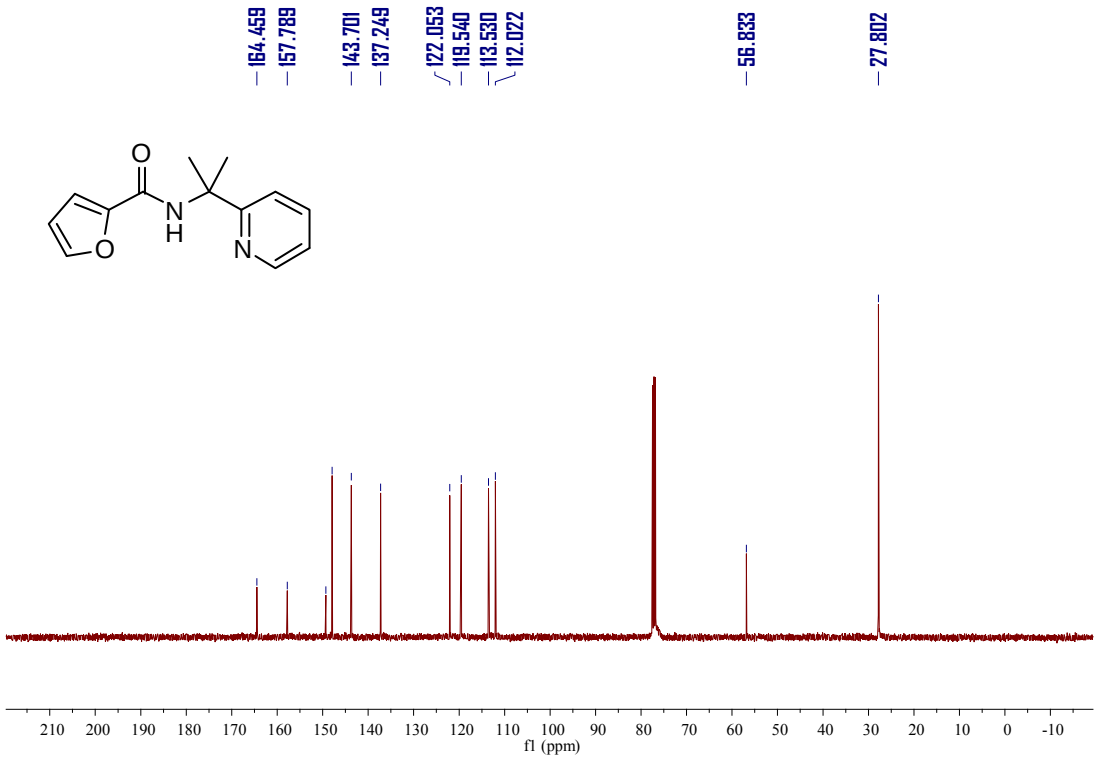
1i



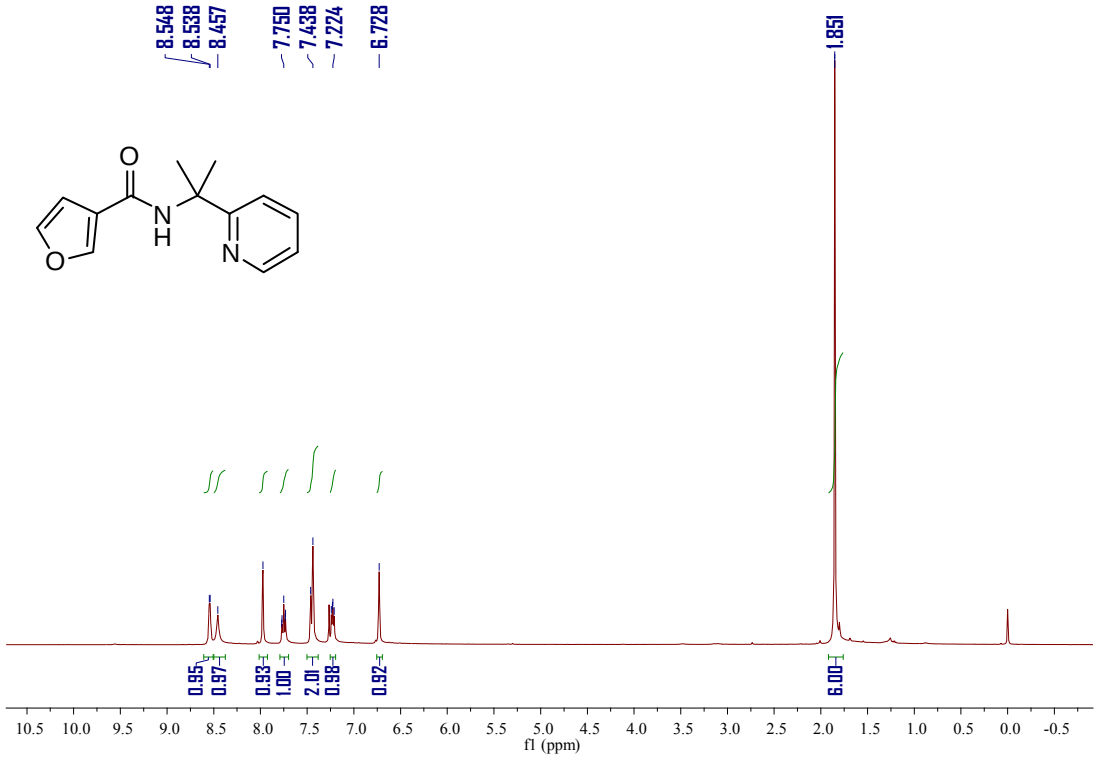


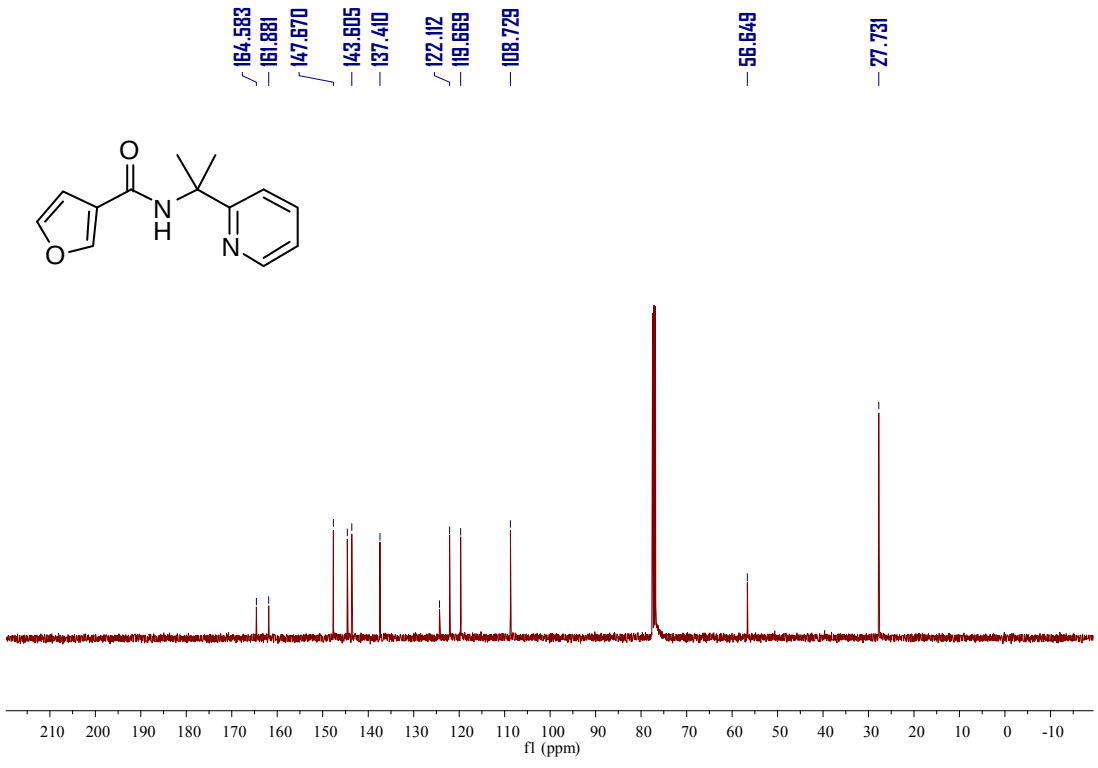
1q


8.669
8.592
8.581
7.482
7.443
7.220
7.202
7.076
6.489
6.486
6.481
1.861
0.87
1.02
1.00
1.99
1.04
0.99
0.97
6.05
O
N
H
O
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

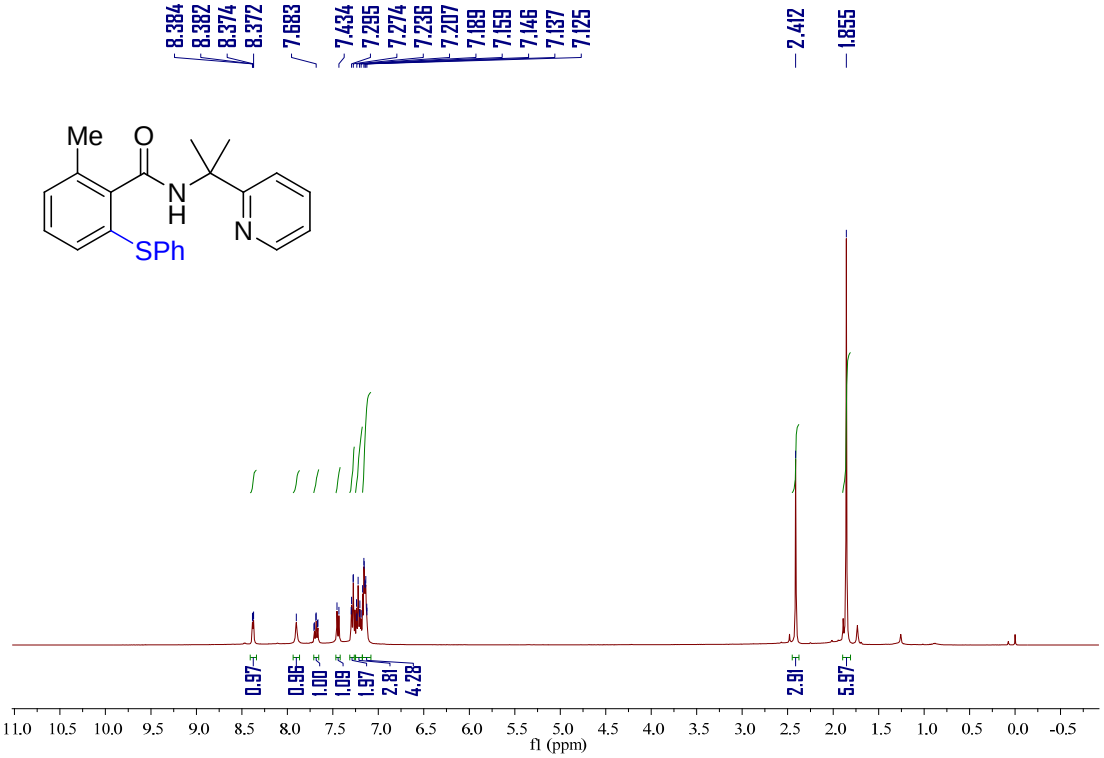

164.459
157.789
143.701
137.249
122.053
119.540
113.530
112.022
56.833
27.802
O
N
H
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

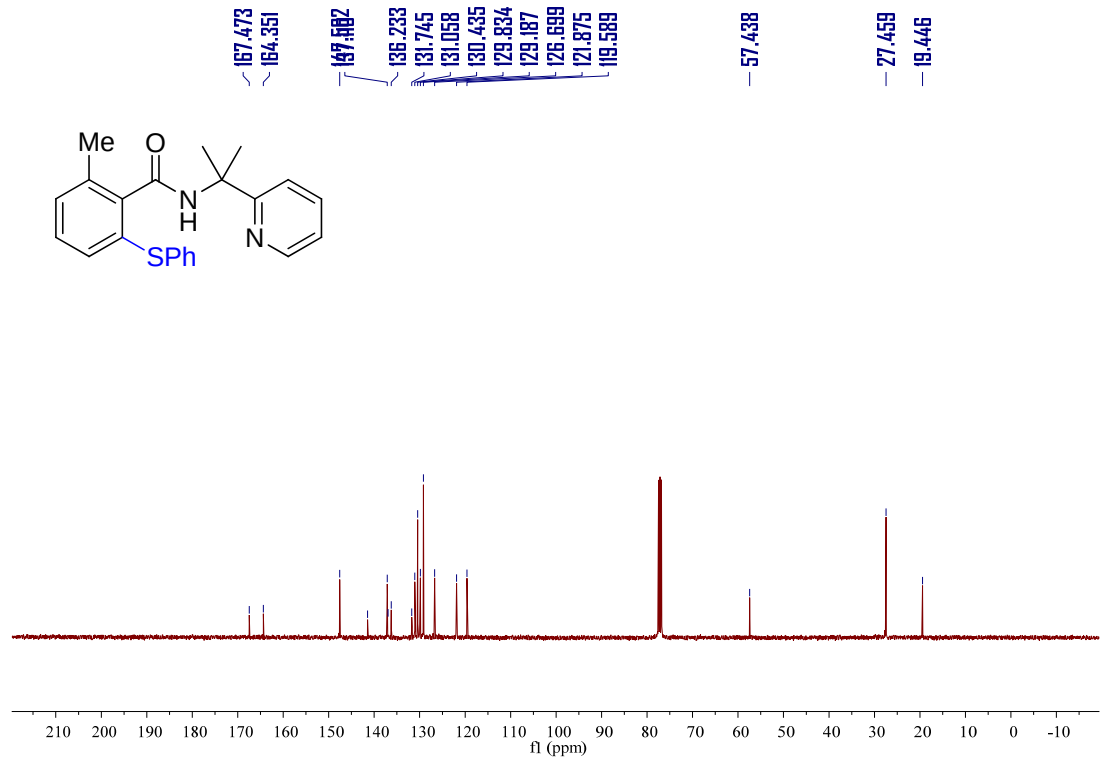
1r


8.548
8.538
8.457
7.750
7.438
7.224
6.728
1.851
O
N
H
O
N
0.95
0.97
0.93
1.00
2.01
0.98
0.92
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

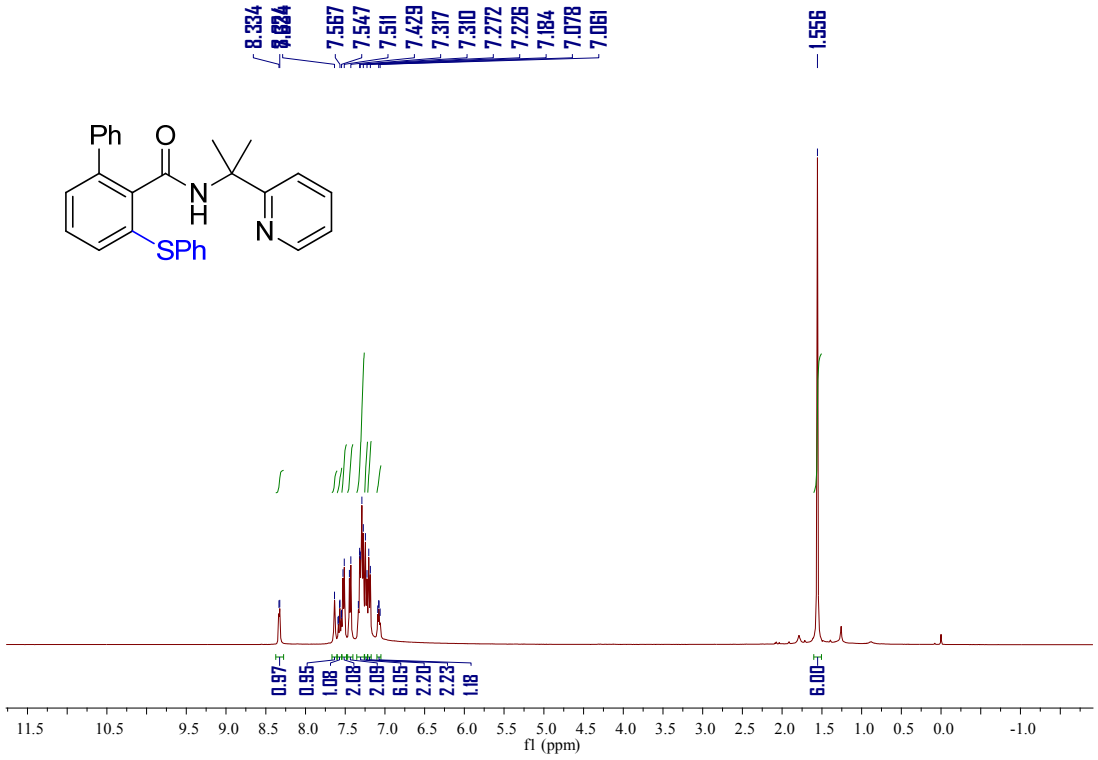

164.583
161.881
147.670
143.605
137.410
122.112
119.669
108.729
56.649
27.731
O
N
H
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

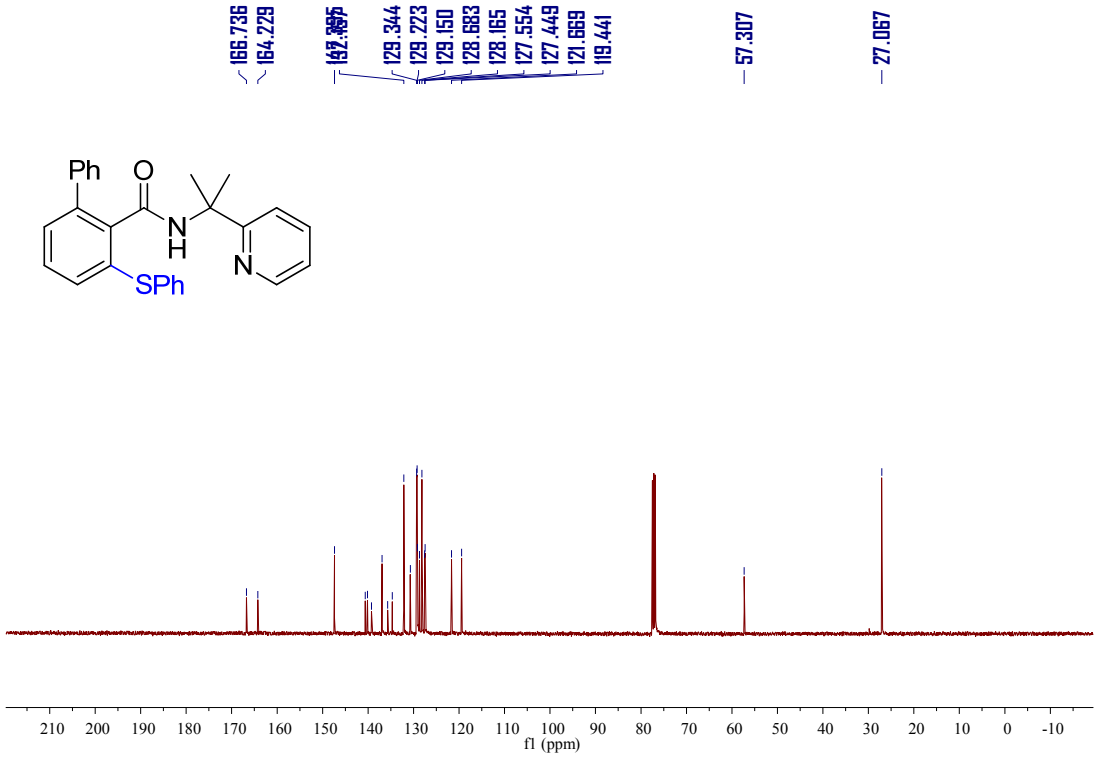
3a


8.384
8.382
8.374
8.372
7.683
7.434
7.295
7.274
7.236
7.207
7.189
7.159
7.146
7.137
7.125
2.412
1.855
Me
O
N
H
N
SPh
0.97
0.96
1.00
1.09
1.97
2.81
4.29
2.91
5.97
f1 (ppm)

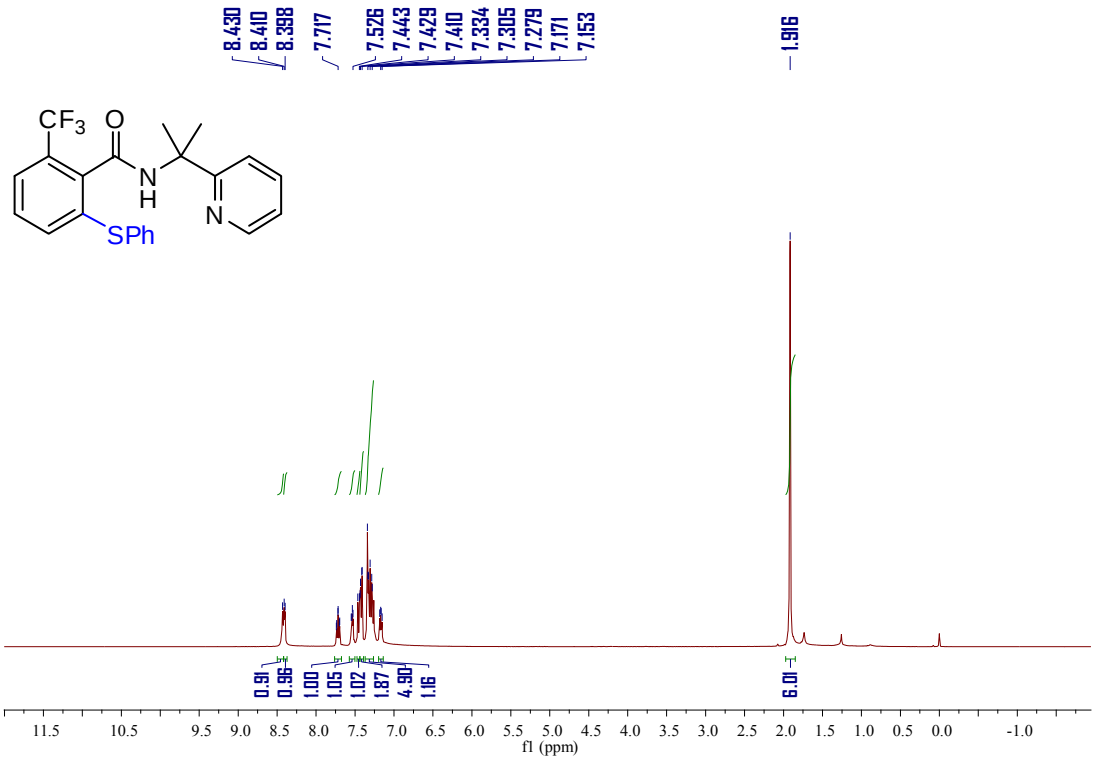

167.473
164.351
136.233
131.745
131.058
130.435
129.834
129.187
126.699
121.875
119.589
57.438
27.459
19.446
Me
O
N
H
N
SPh
f1 (ppm)

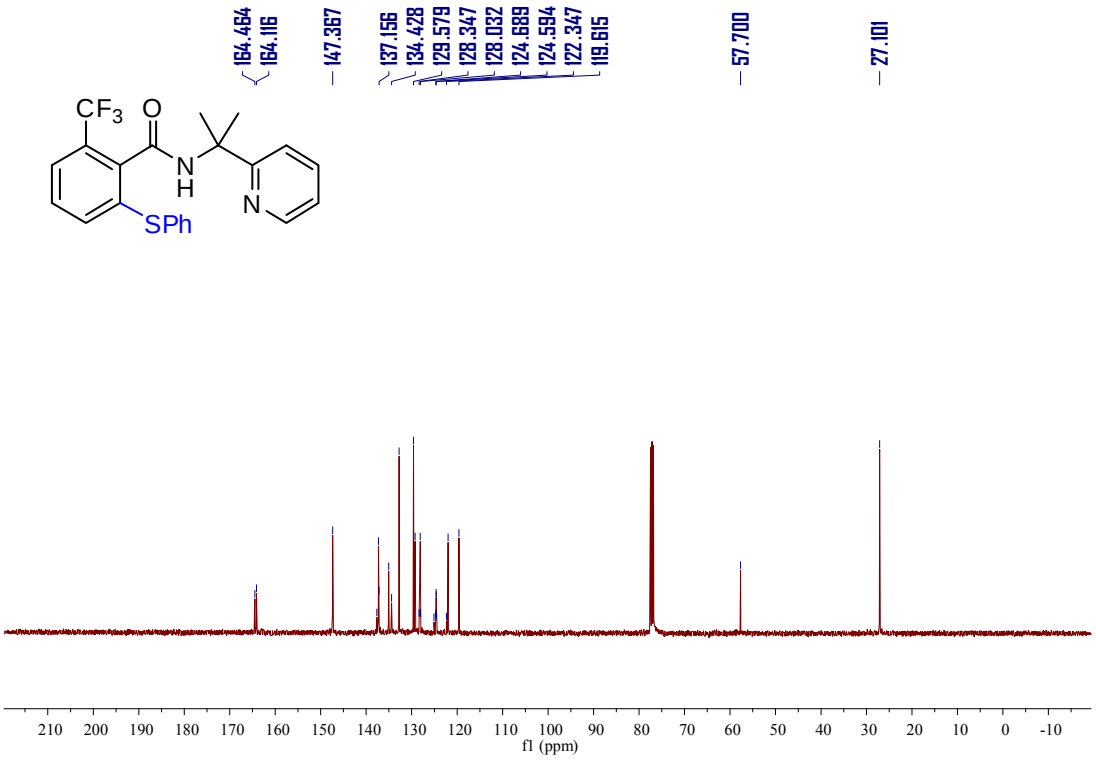
3b


8.334
7.567
7.547
7.511
7.429
7.317
7.310
7.272
7.226
7.184
7.078
7.061
1.556
Ph
O
N
H
N
SPh
0.97
0.95
1.08
2.08
2.09
6.05
2.20
2.23
1.18
6.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

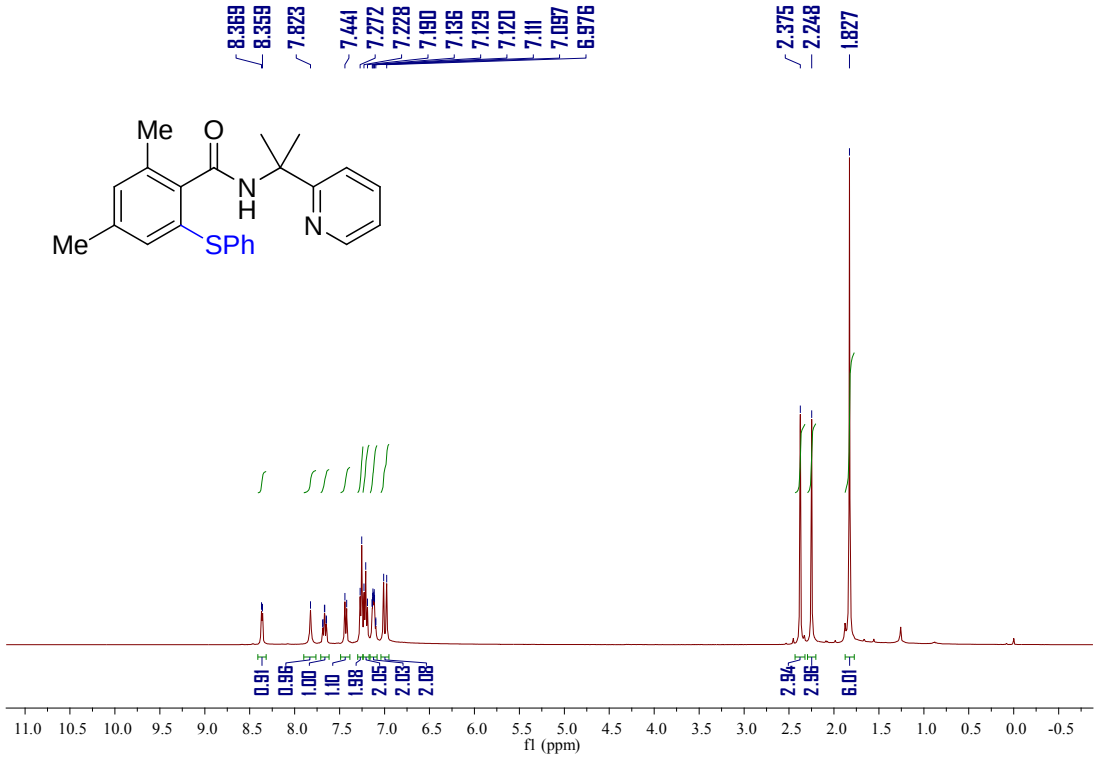

166.736
164.229
129.344
129.223
129.150
128.883
128.165
127.554
127.449
121.669
119.441
57.307
27.067
Ph
O
N
H
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

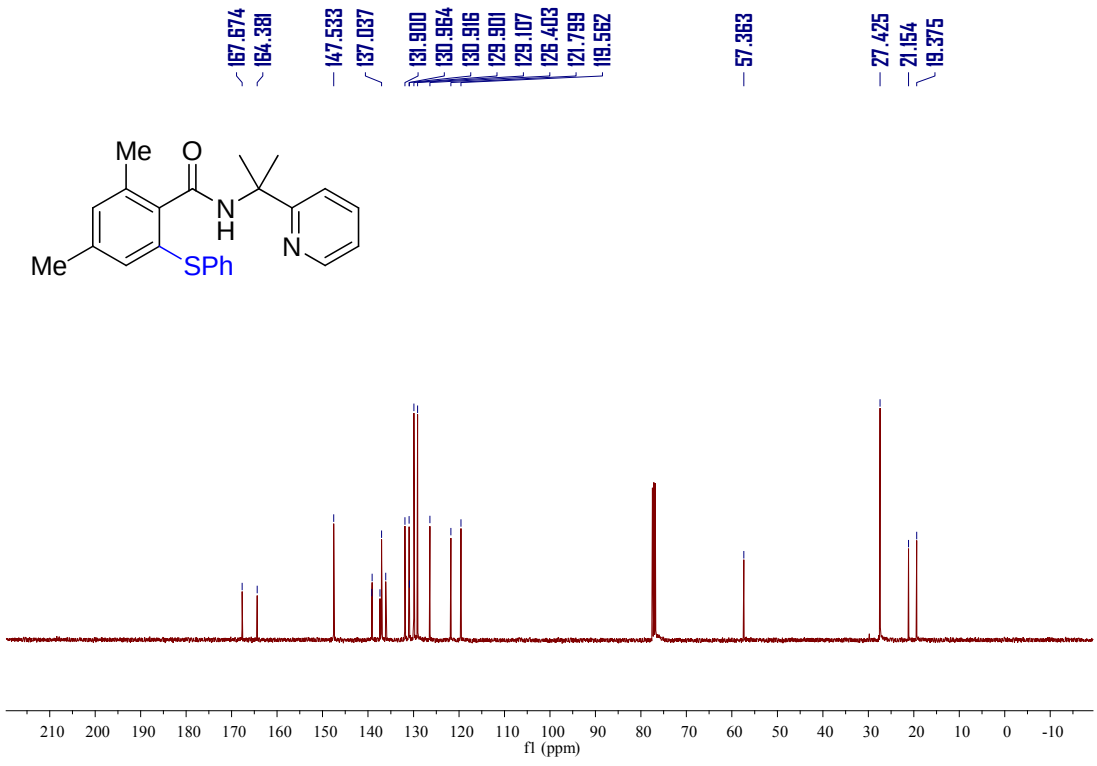
3c


8.430
8.410
8.398
7.717
7.526
7.443
7.429
7.410
7.334
7.305
7.279
7.171
7.153
1.916
CF3
O
N
H
N
SPh
0.91
0.96
1.00
1.05
1.02
1.87
4.90
1.16
6.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

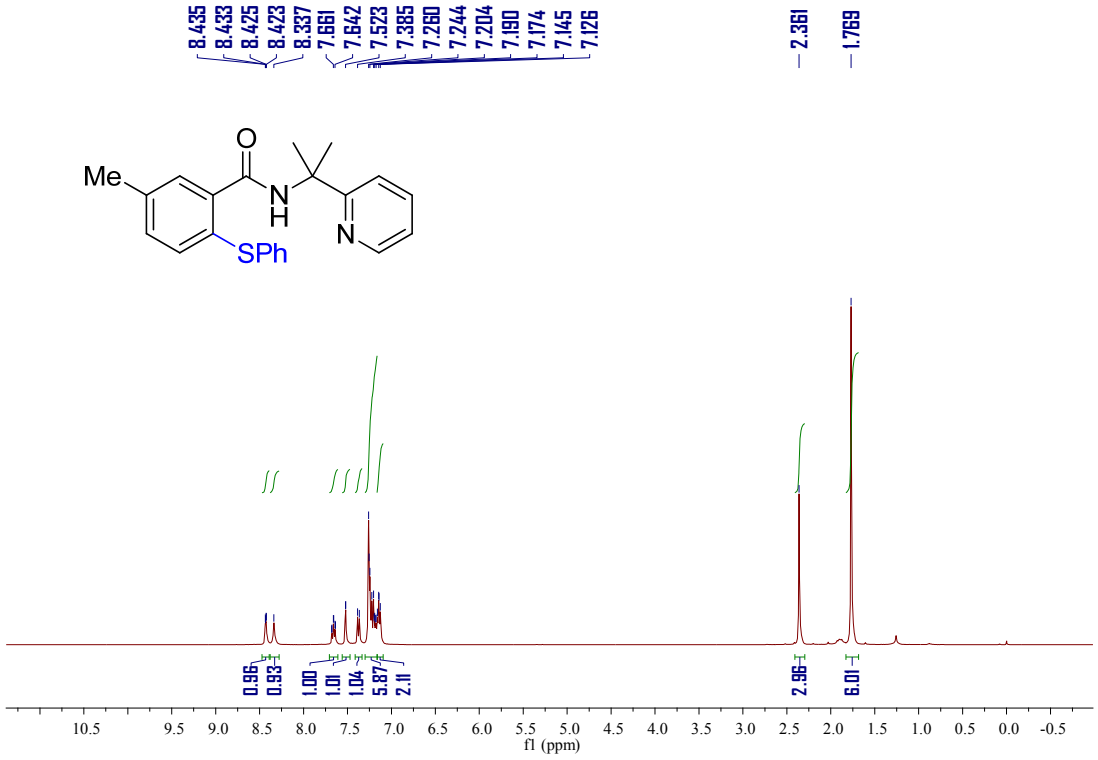

164.464
164.116
147.367
137.156
134.423
129.579
128.347
128.032
124.689
124.594
122.347
119.615
57.700
27.101
CF3
O
N
H
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

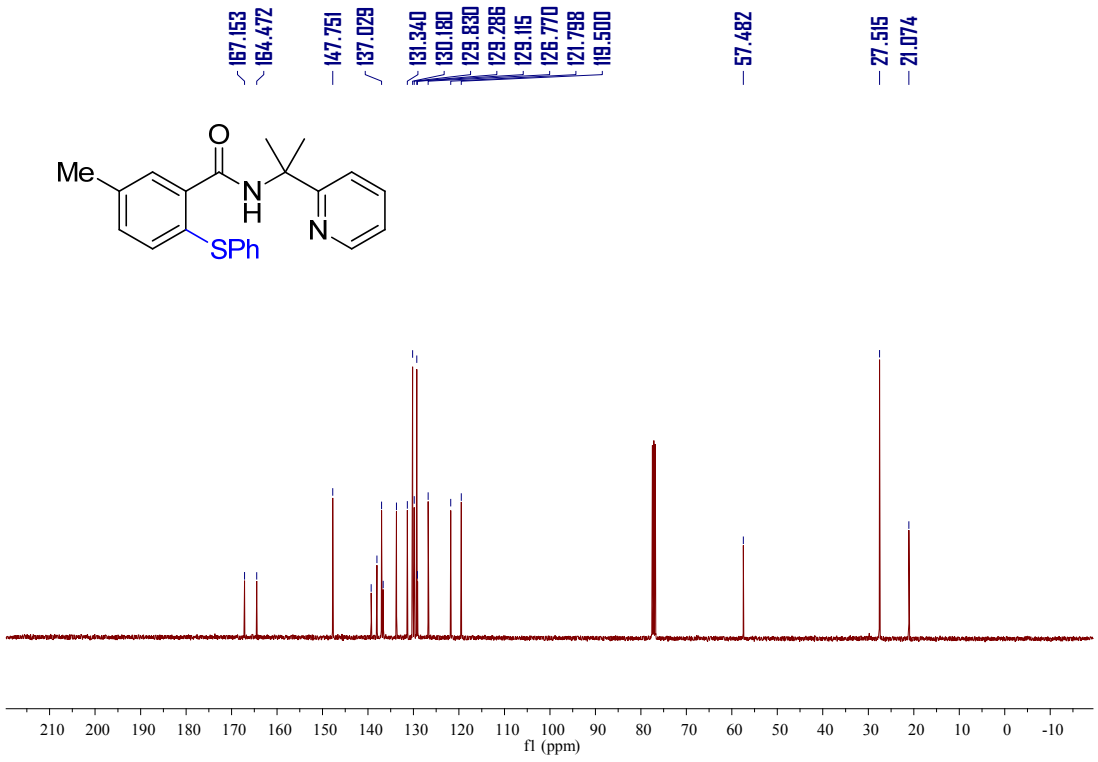
3d


8.369
8.359
7.823
7.441
7.272
7.228
7.190
7.136
7.129
7.120
7.111
7.097
6.976
2.375
2.248
1.827
Me
O
N
H
Me
SPh
N
0.91
0.96
1.00
1.10
1.98
2.05
2.03
2.08
2.94
2.96
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

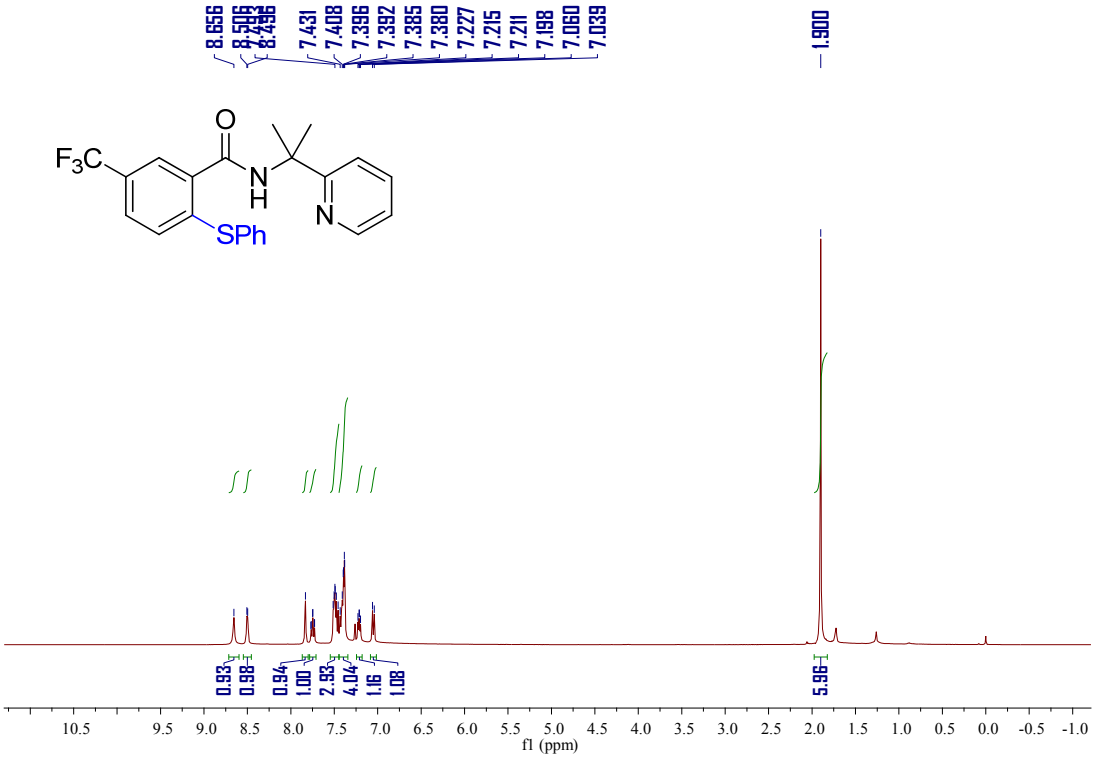

167.674
164.381
147.533
137.037
131.900
130.964
130.916
129.901
129.107
126.403
121.799
119.562
57.363
27.425
21.154
19.375
Me
O
N
H
Me
SPh
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

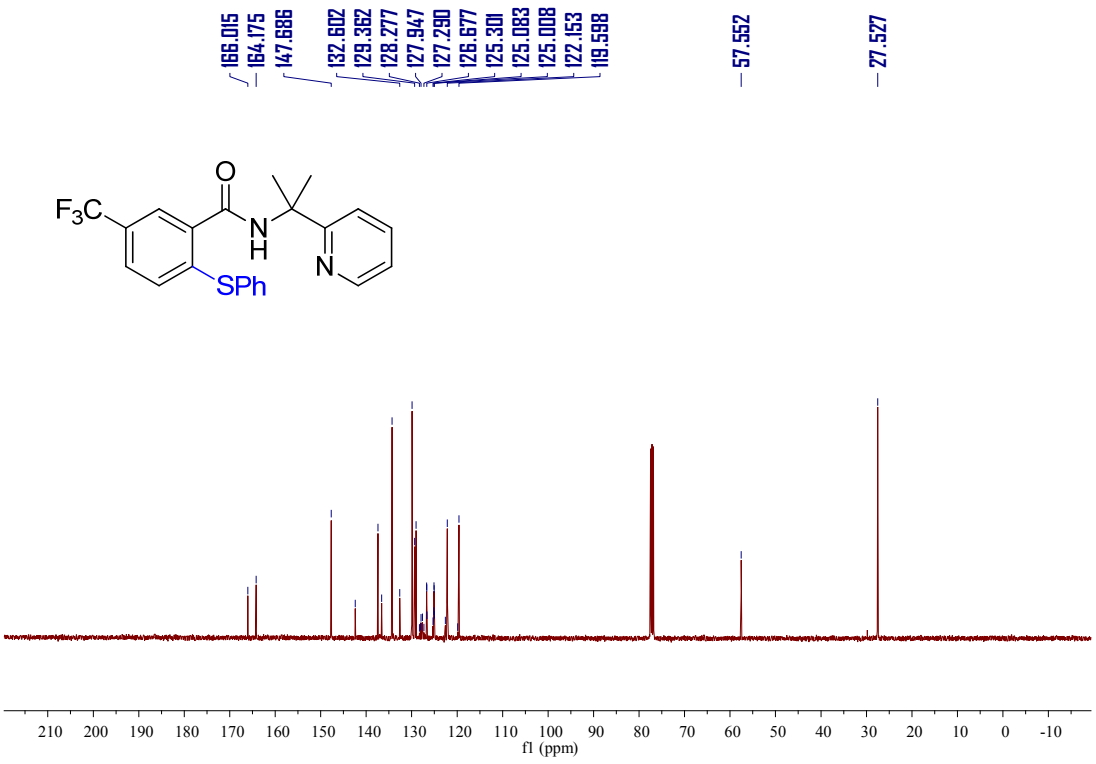
3e


8.435
8.433
8.425
8.423
8.337
7.661
7.642
7.523
7.385
7.260
7.244
7.204
7.190
7.174
7.145
7.126
2.361
1.769
Me
O
N
H
N
SPh
0.96
0.93
1.00
1.01
1.04
5.87
2.11
2.96
6.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

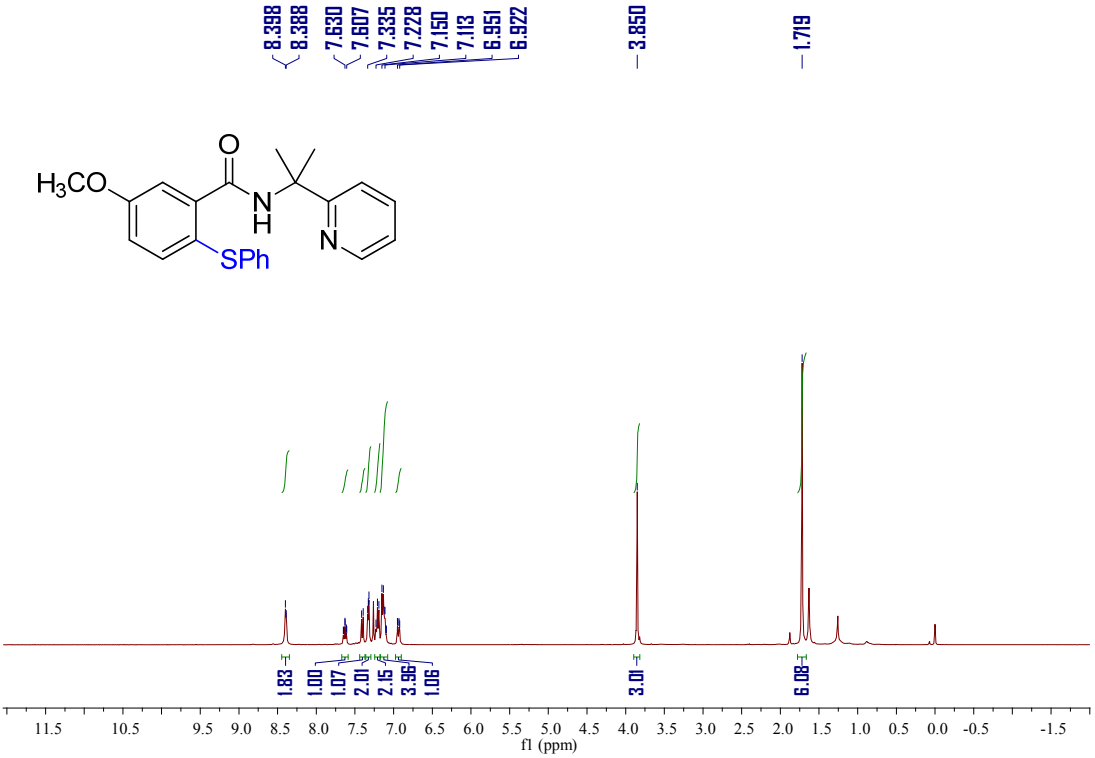

167.153
164.472
147.751
137.029
131.340
130.180
129.830
129.286
129.115
126.770
121.798
119.500
57.482
27.515
21.074
Me
O
N
H
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

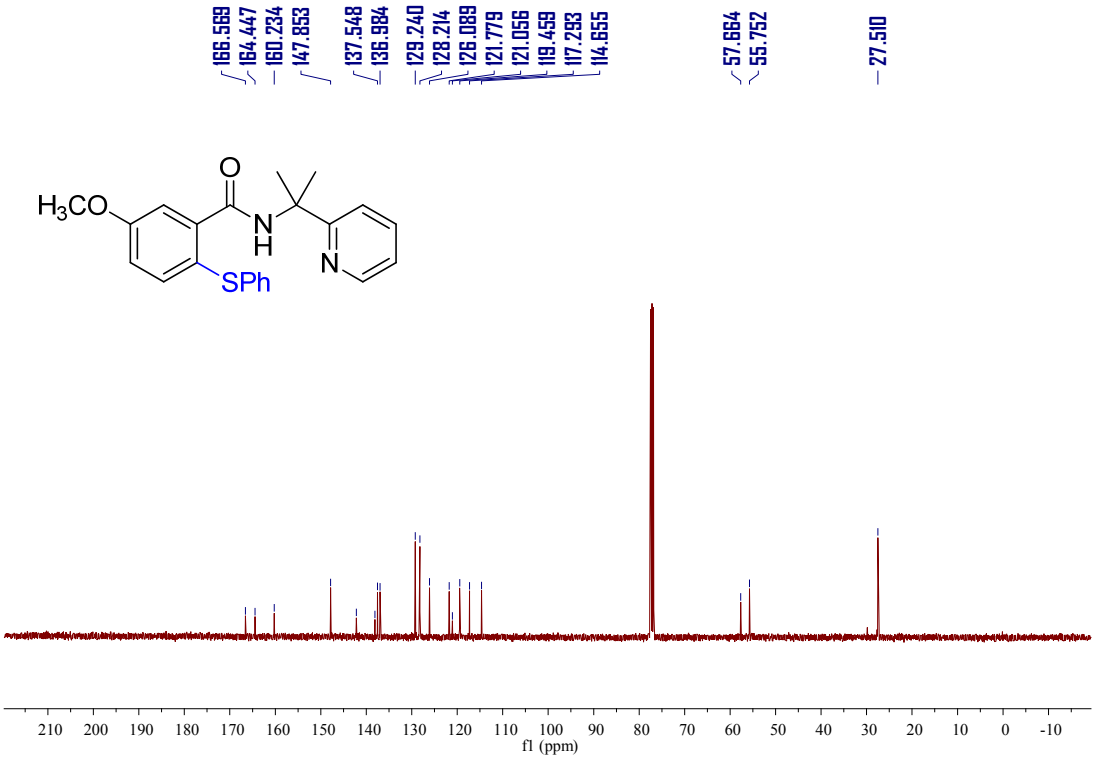
3f


8.656
8.505
7.431
7.408
7.396
7.392
7.385
7.380
7.227
7.215
7.211
7.198
7.060
7.039
1.900
F3C
O
N
H
N
SPh
0.93
0.98
0.94
1.00
2.93
4.04
1.16
1.08
5.96
fl (ppm)

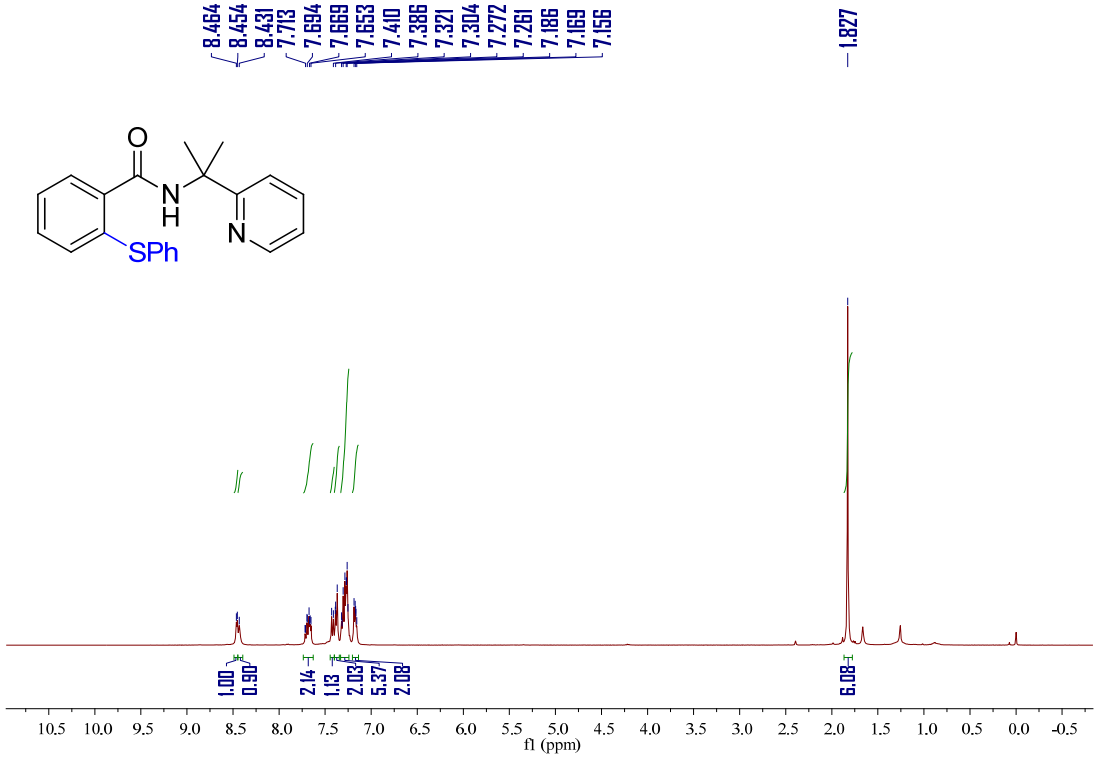

166.015
164.175
147.686
132.602
129.362
128.277
127.947
127.290
126.677
125.301
125.083
125.008
122.153
119.598
57.552
27.527
F3C
O
N
H
N
SPh
fl (ppm)

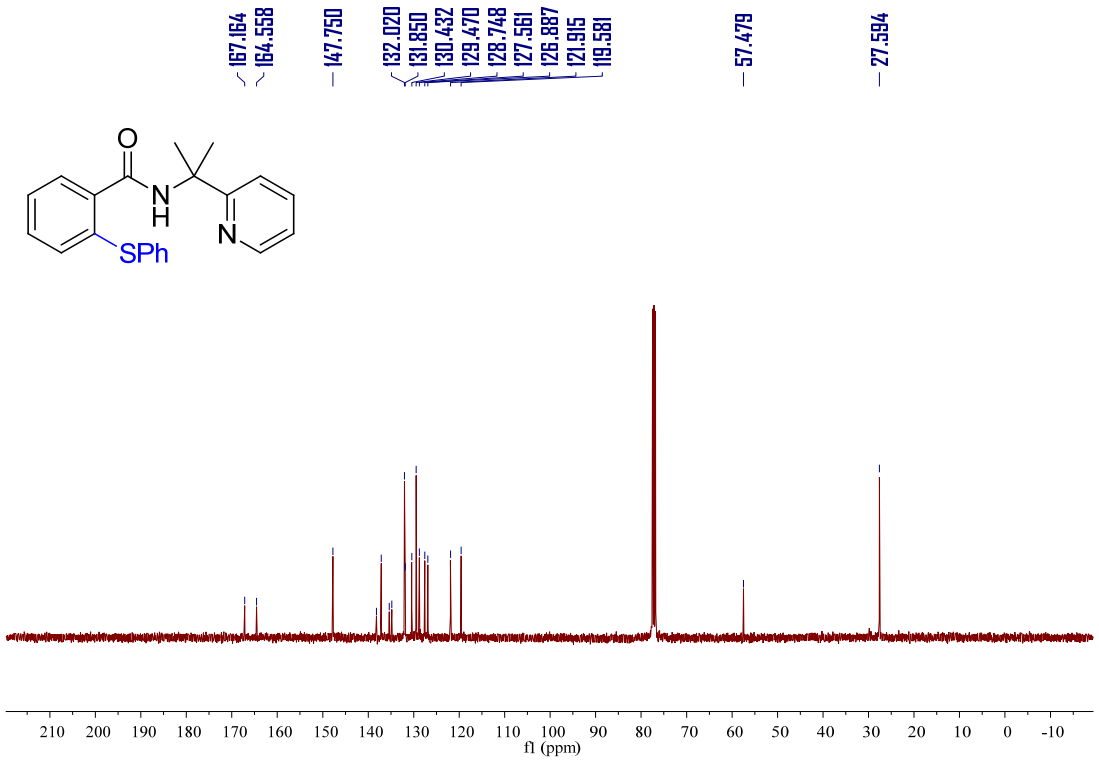
3g


8.398
8.388
7.630
7.607
7.335
7.228
7.150
7.113
6.951
6.922
3.850
1.719
O
H3CO
N
H
N
SPh
1.83
1.00
1.07
2.01
2.15
3.95
1.06
3.01
6.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)

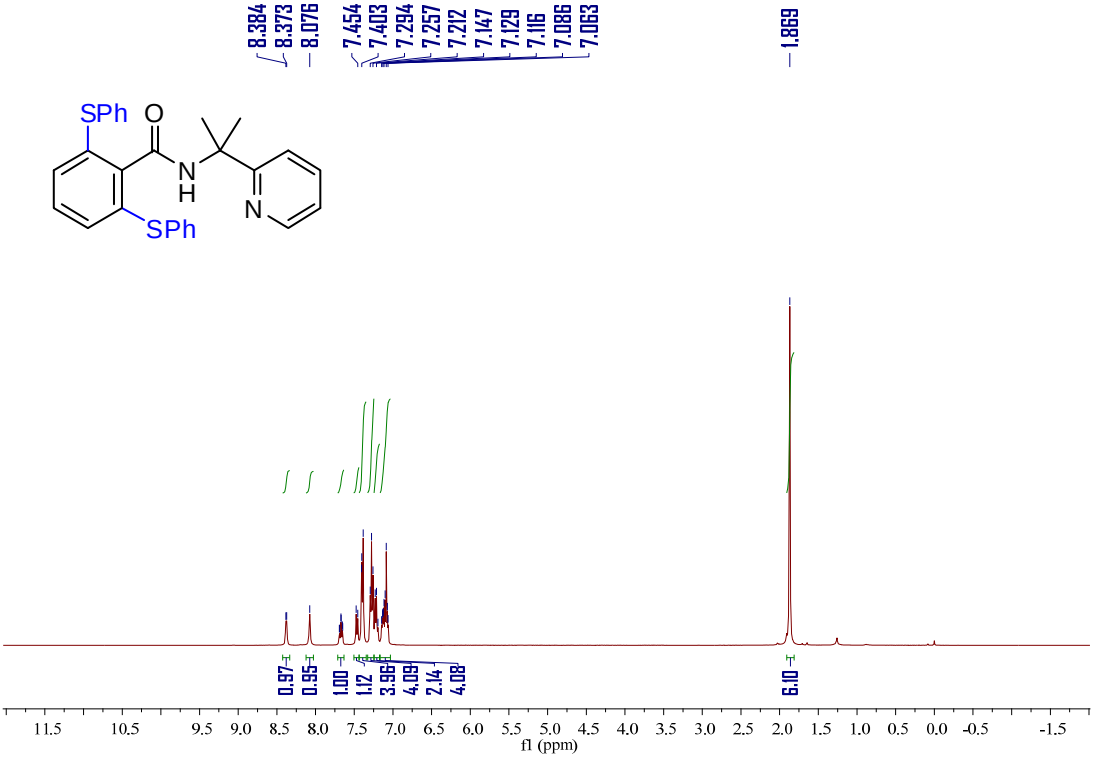

166.569
164.447
160.234
147.853
137.548
136.984
129.240
128.214
126.089
121.779
121.056
119.459
117.293
114.655
57.664
55.752
27.510
O
H3CO
N
H
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

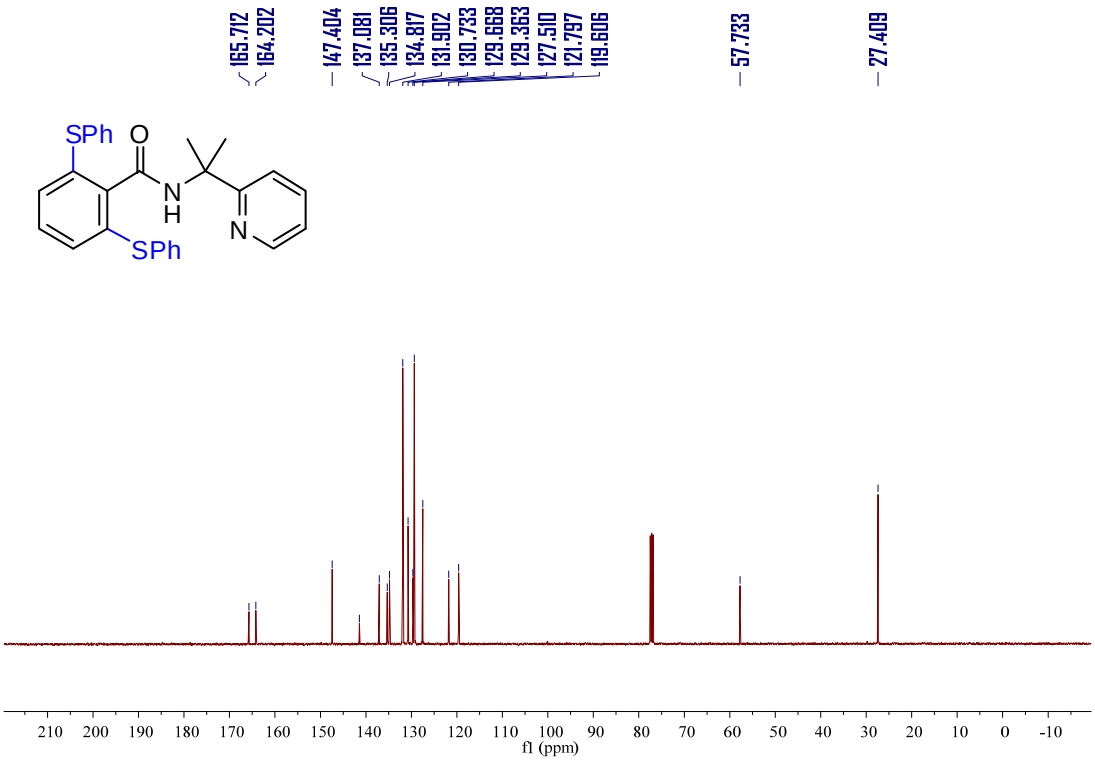
3h


8.464
8.454
8.431
7.713
7.694
7.669
7.653
7.410
7.386
7.321
7.304
7.272
7.261
7.186
7.169
7.156
1.827
O
N
H
N
SPh
1.00
0.90
2.14
1.13
2.03
5.37
2.08
6.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

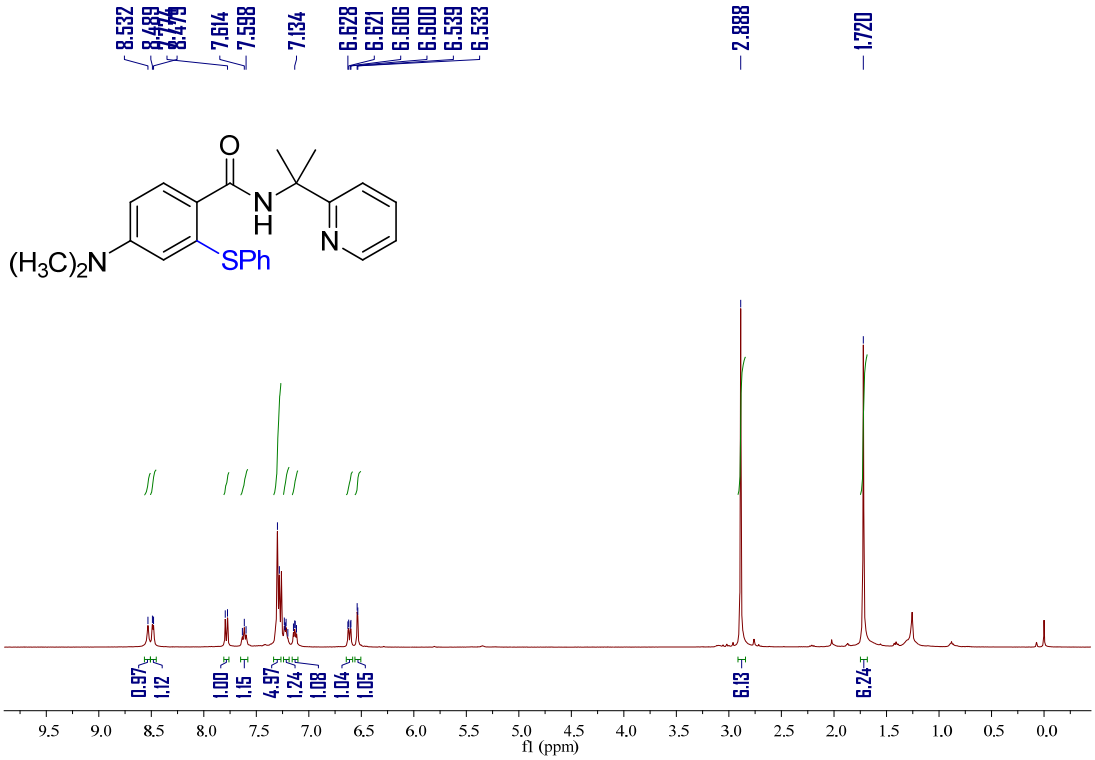

167.164
164.558
147.750
132.020
131.850
130.432
129.470
128.748
127.561
126.887
121.915
119.581
57.479
27.594
O
N
H
N
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

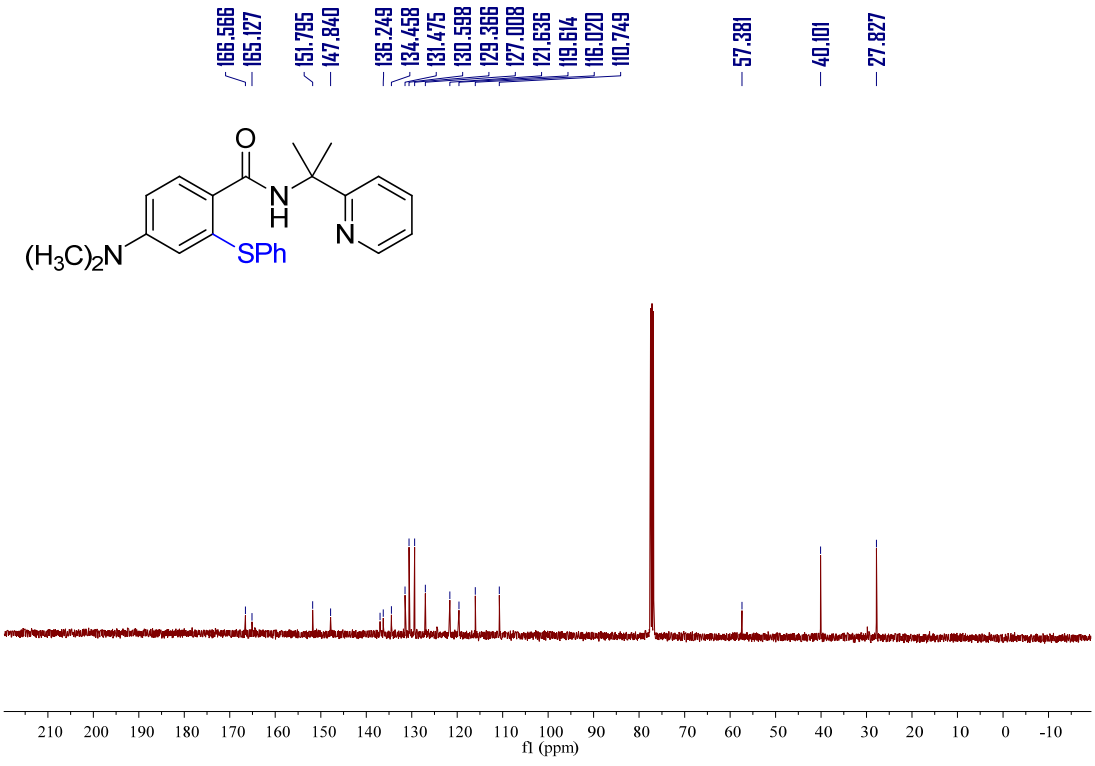
3h’


8.384
8.373
8.076
7.454
7.403
7.294
7.257
7.212
7.147
7.129
7.116
7.086
7.063
1.869
SPh
O
N
H
N
SPh
0.97
0.95
1.00
1.12
3.98
4.09
2.14
4.08
6.10
f1 (ppm)

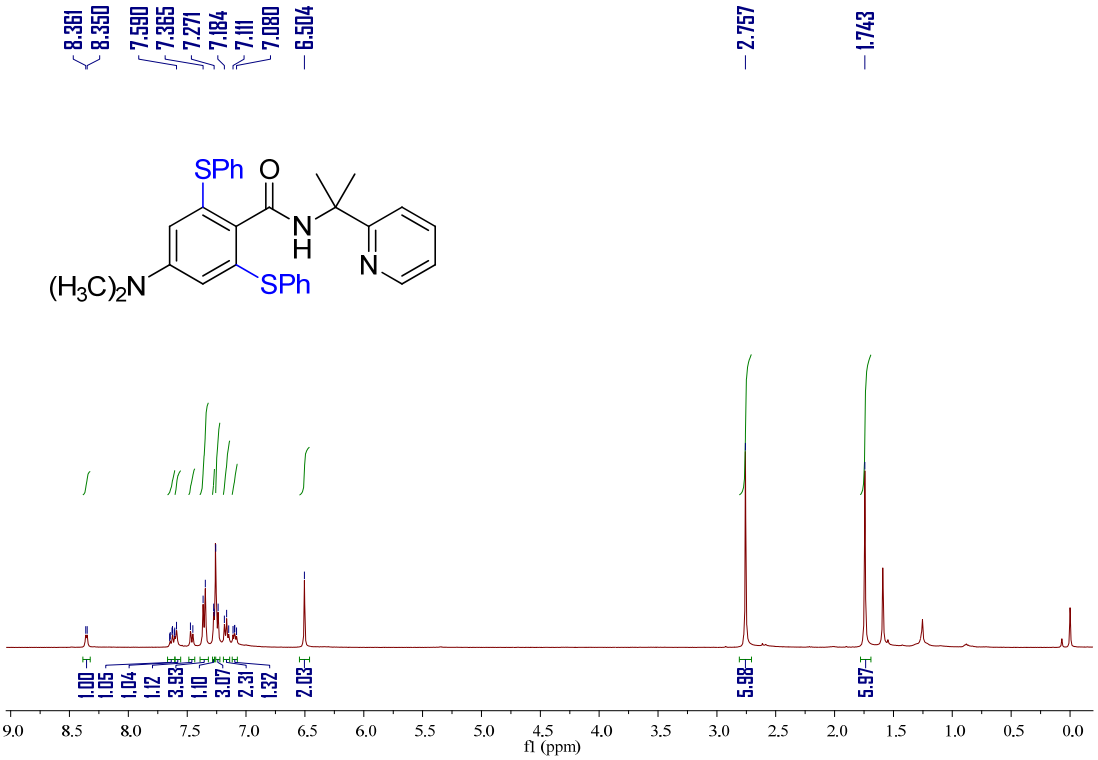

165.712
164.202
147.404
137.081
135.306
134.817
131.902
130.733
129.668
129.363
127.510
121.797
119.606
57.733
27.409
SPh
O
N
H
N
SPh
f1 (ppm)

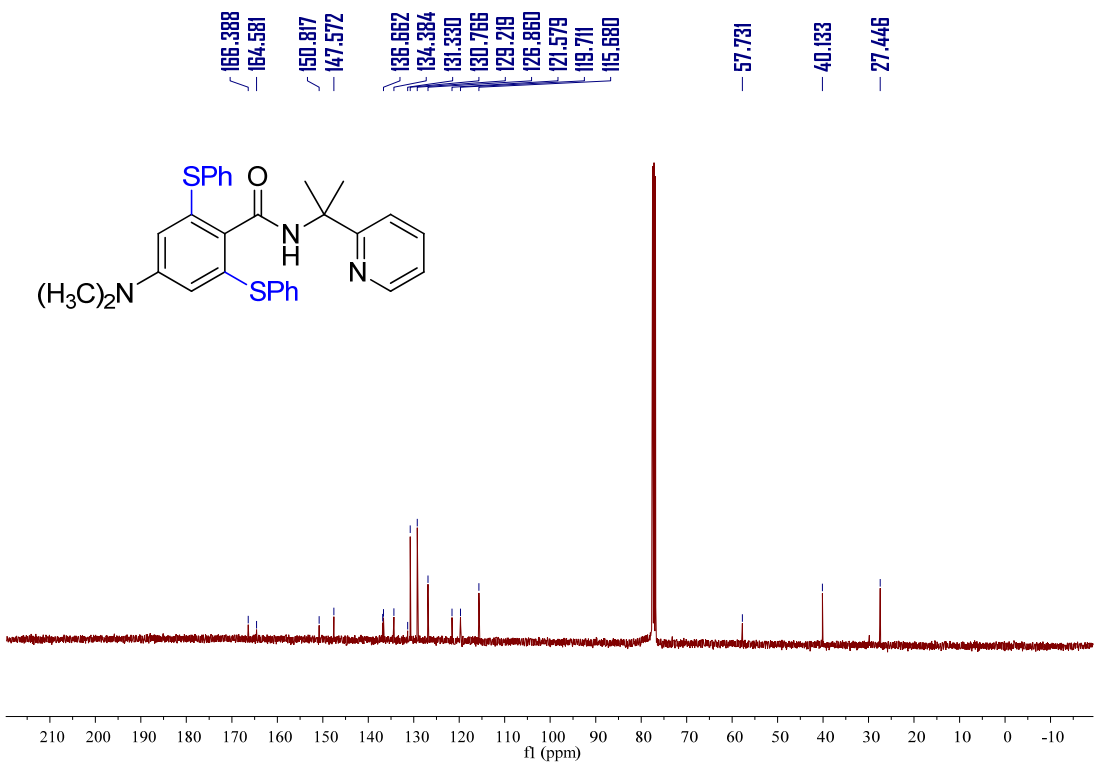
3i


8.532
8.488
8.479
7.614
7.598
7.134
6.628
6.621
6.606
6.600
6.539
6.533
2.888
1.720
O
N
H
N
(H3C)2N
SPh
0.97
1.12
1.00
1.15
4.97
1.24
1.08
1.04
1.05
6.13
6.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

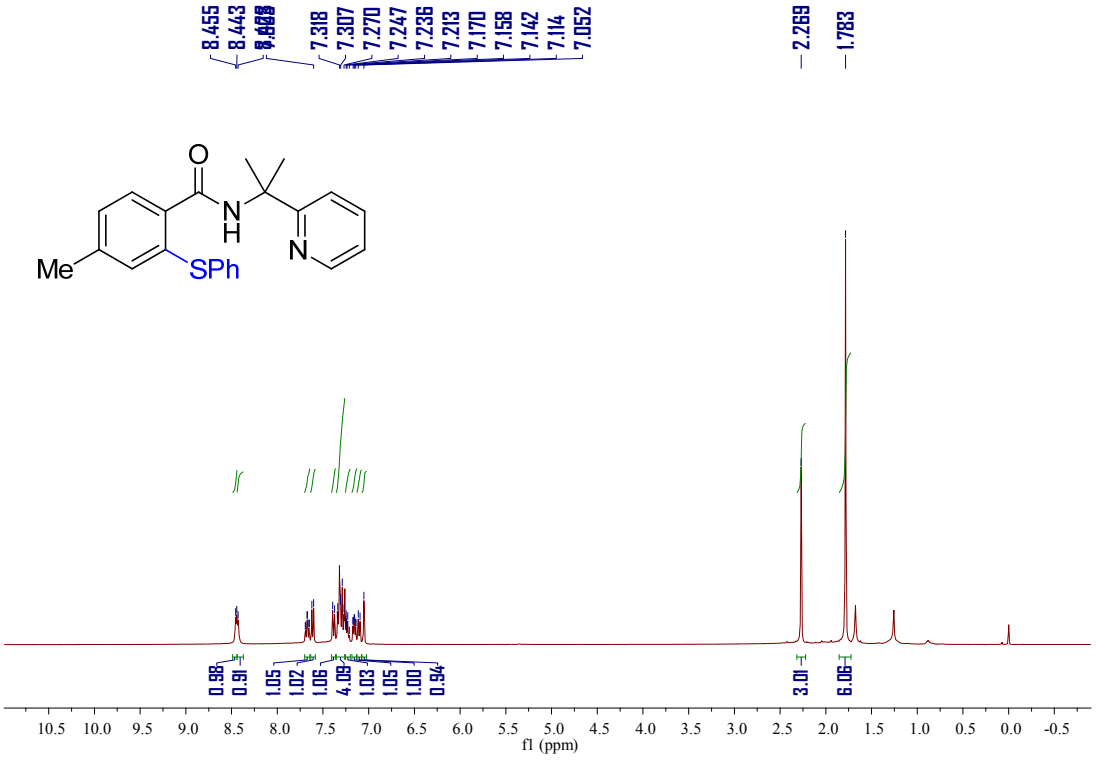

166.566
165.127
151.795
147.840
136.249
134.458
131.475
130.598
129.366
127.008
121.636
119.614
116.020
110.749
57.381
40.101
27.827
O
N
H
N
(H3C)2N
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

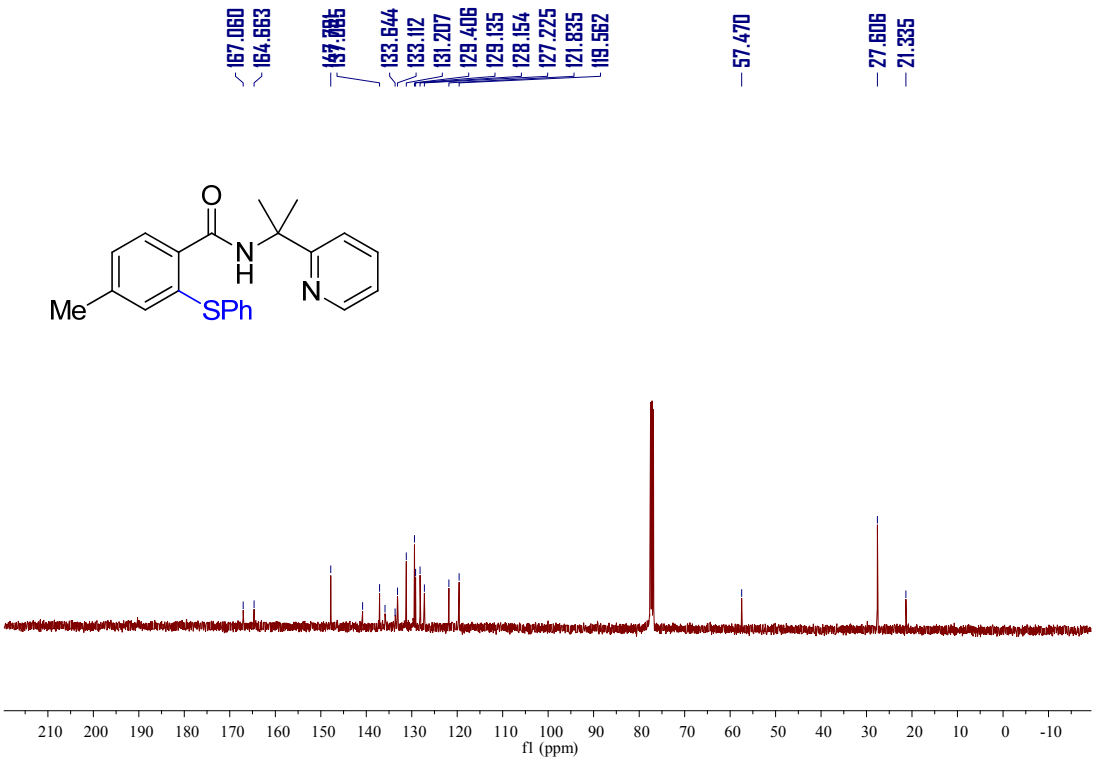
3i’


8.361
8.350
7.590
7.365
7.271
7.184
7.111
7.080
6.504
2.757
1.743
SPh
O
N
H
N
SPh
(H3C)2N
1.00
1.05
1.04
1.12
3.93
1.10
3.07
2.31
1.32
2.03
5.98
5.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

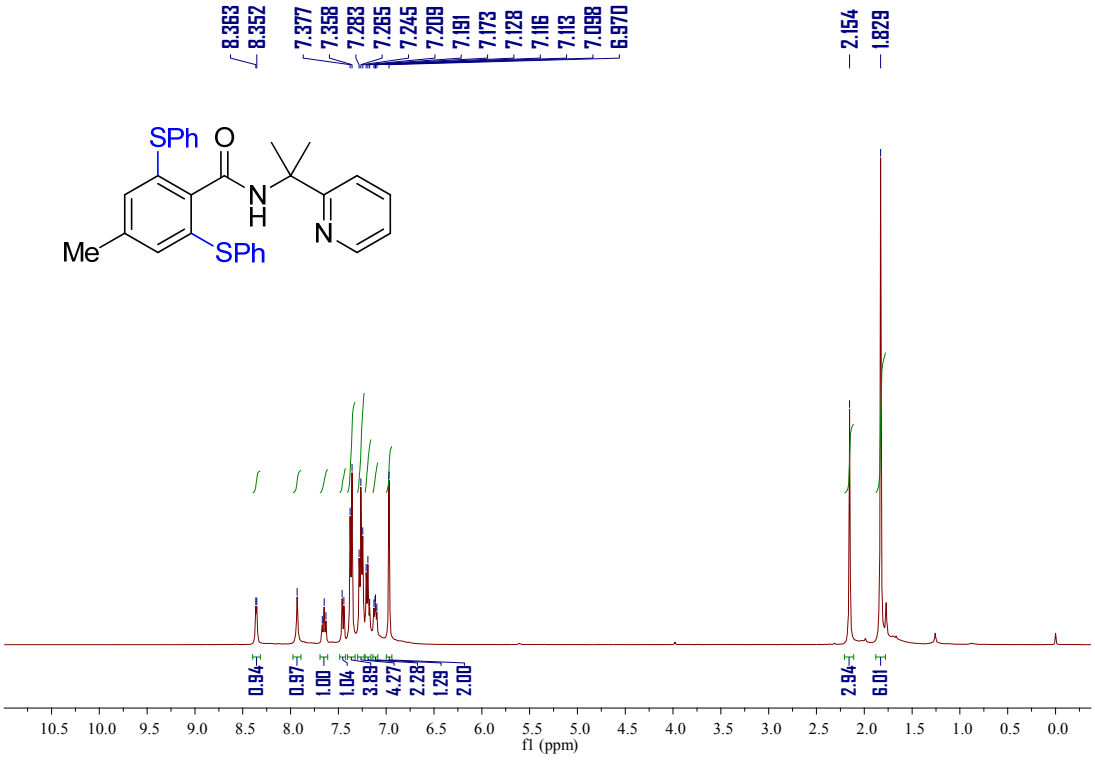

166.388
164.581
150.817
147.572
136.662
134.384
131.330
130.766
129.219
126.860
121.579
119.711
115.680
57.731
40.133
27.446
SPh
O
N
H
N
SPh
(H3C)2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

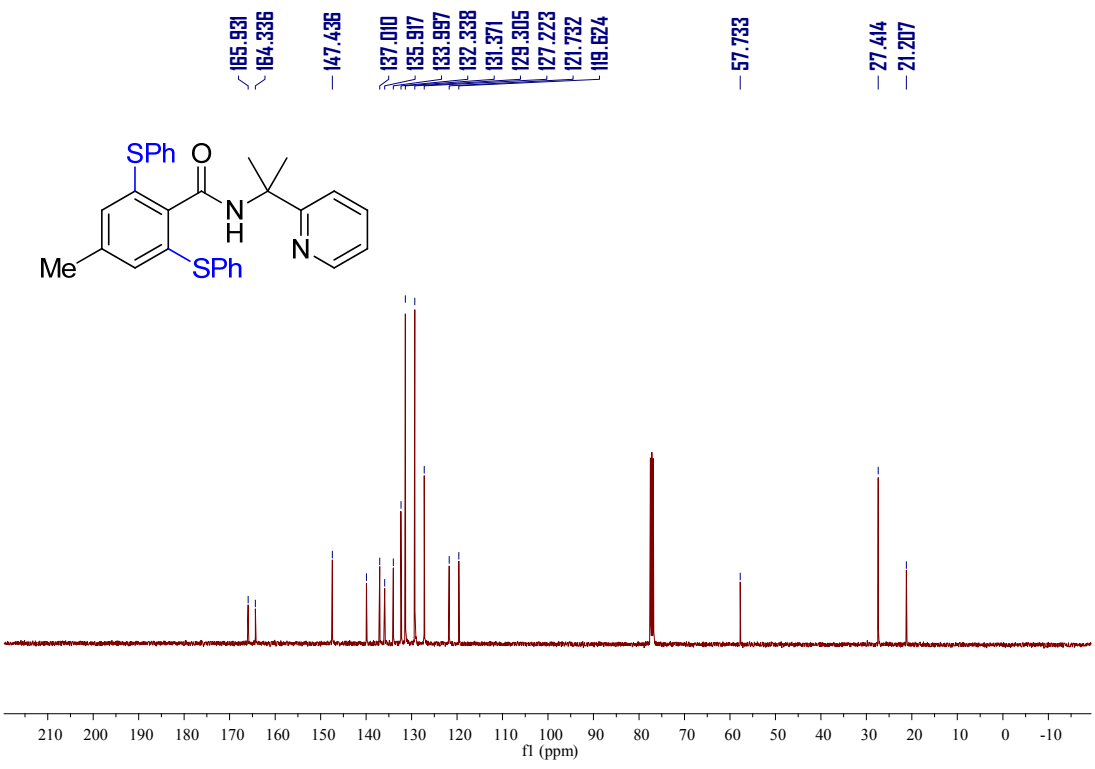
3j


8.455
8.443
7.318
7.307
7.270
7.247
7.236
7.213
7.170
7.158
7.142
7.114
7.052
2.269
1.783
O
N
H
N
Me
SPh
0.98
0.91
1.05
1.02
1.06
4.09
1.03
1.05
1.00
0.94
3.01
6.06
f1 (ppm)

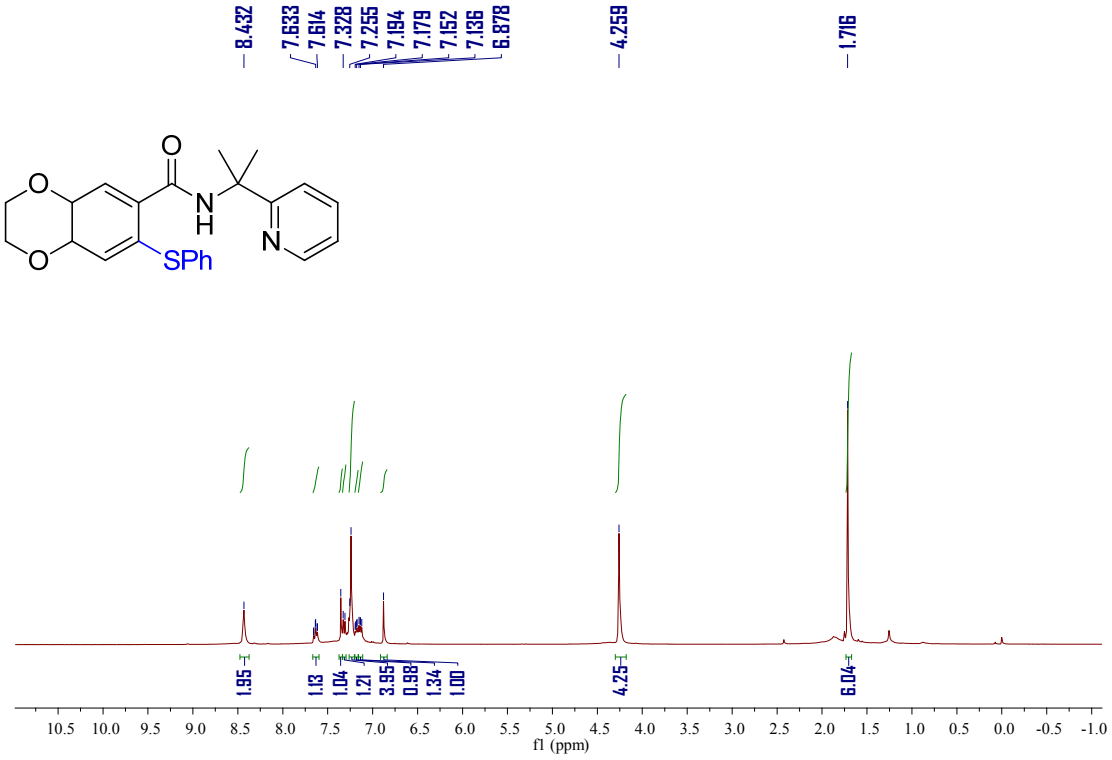

167.060
164.663
133.644
133.112
131.207
129.406
129.135
128.154
127.225
121.835
119.562
57.470
27.606
21.335
O
N
H
N
Me
SPh
f1 (ppm)

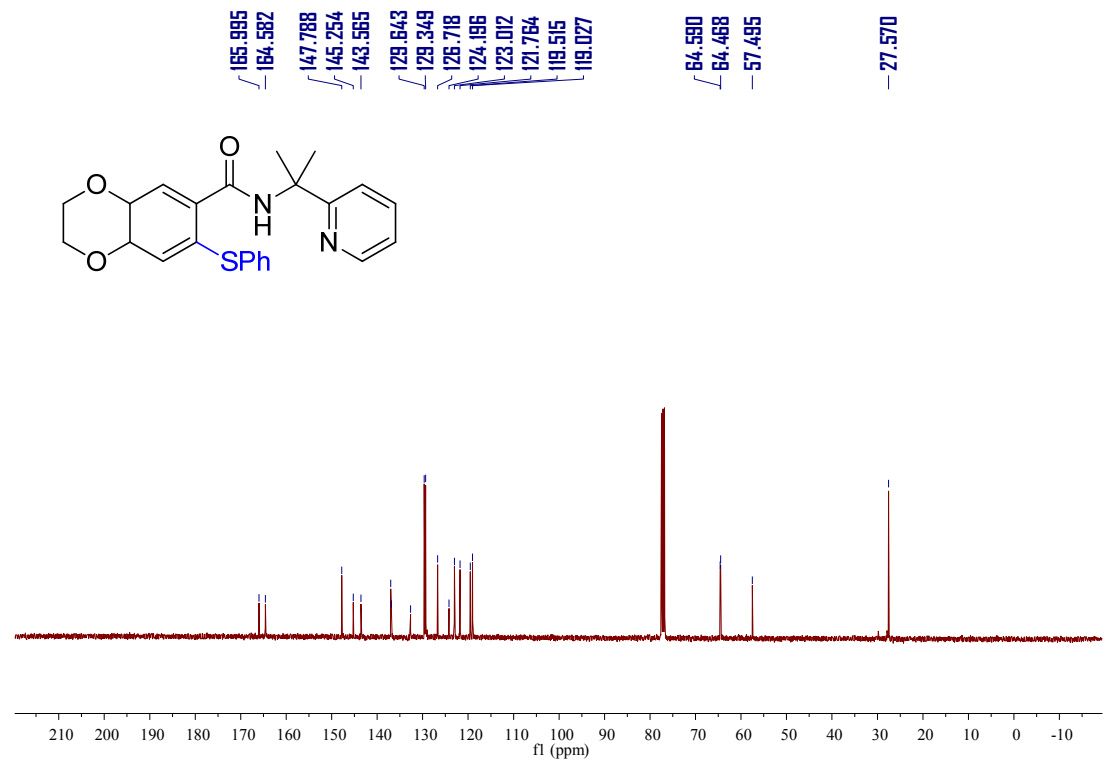
3j’


8.363
8.352
7.377
7.358
7.283
7.265
7.245
7.209
7.191
7.173
7.128
7.116
7.113
7.088
6.970
2.154
1.829
SPh
O
N
H
N
Me
SPh
0.94
0.97
1.00
1.04
3.89
4.27
2.28
1.29
2.00
2.94
6.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

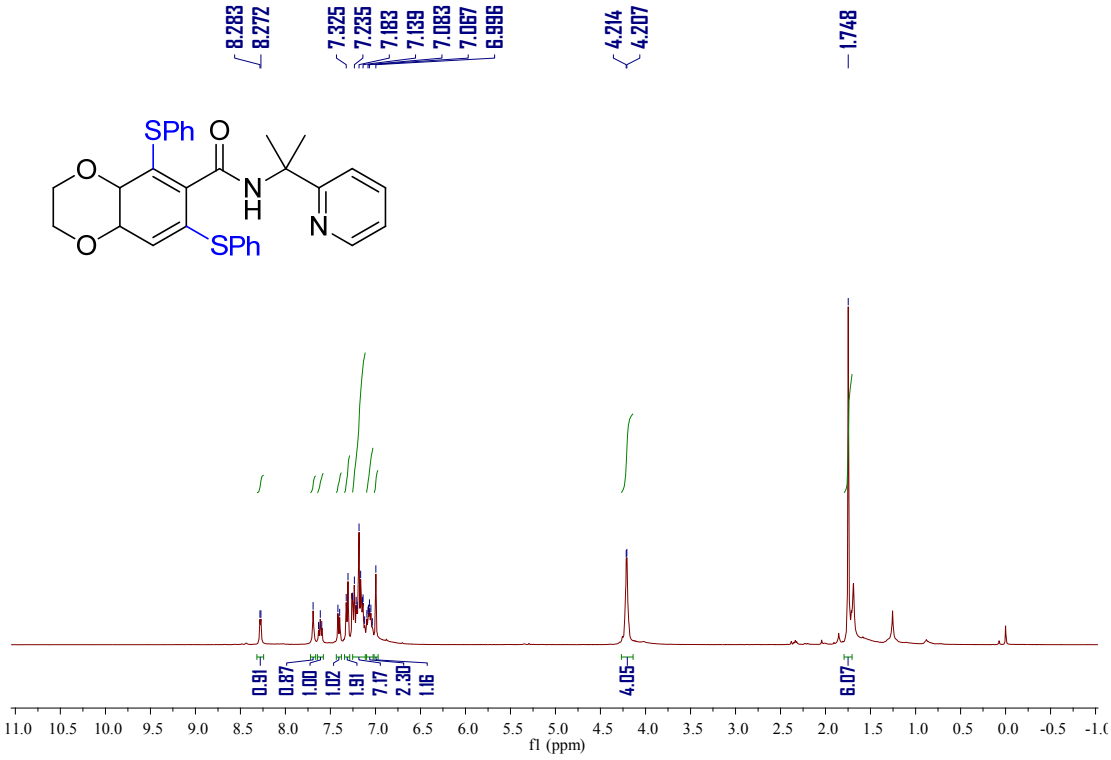

165.931
164.336
147.436
137.010
135.917
133.957
132.338
131.371
129.305
127.223
121.732
119.624
57.733
27.414
21.207
SPh
O
N
H
N
Me
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

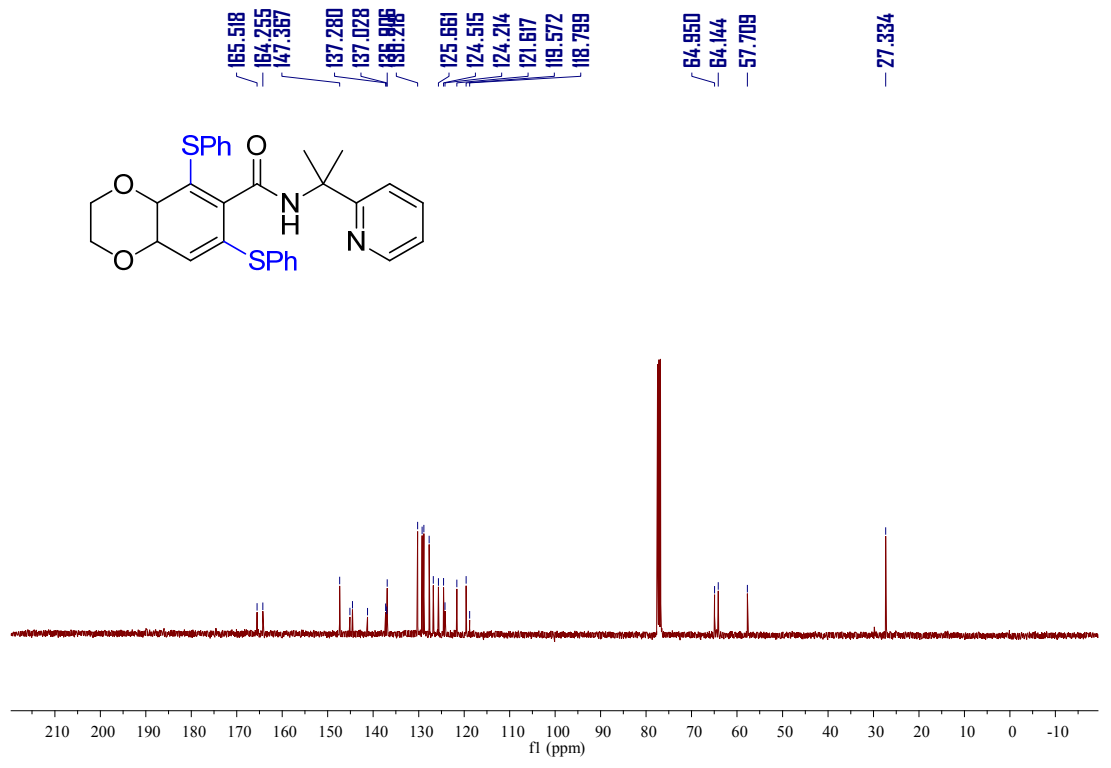
3k


8.432
7.633
7.614
7.328
7.255
7.194
7.179
7.152
7.136
6.878
4.259
1.716
O
O
O
N
H
N
SPh
1.95
1.13
1.04
1.21
3.95
0.98
1.34
1.00
4.25
6.04
f1 (ppm)

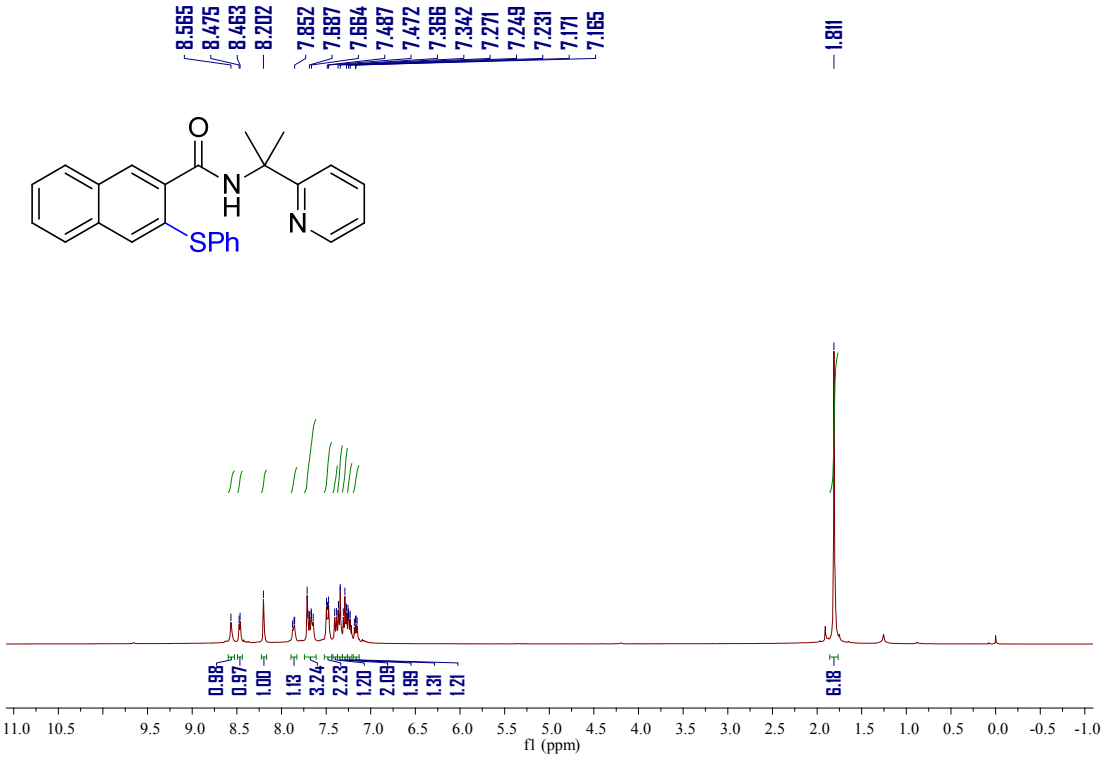

165.995
164.582
147.788
145.254
143.565
129.643
129.349
126.718
124.196
123.012
121.784
119.515
119.027
64.590
64.468
57.495
27.570
O
O
O
N
H
N
SPh
f1 (ppm)

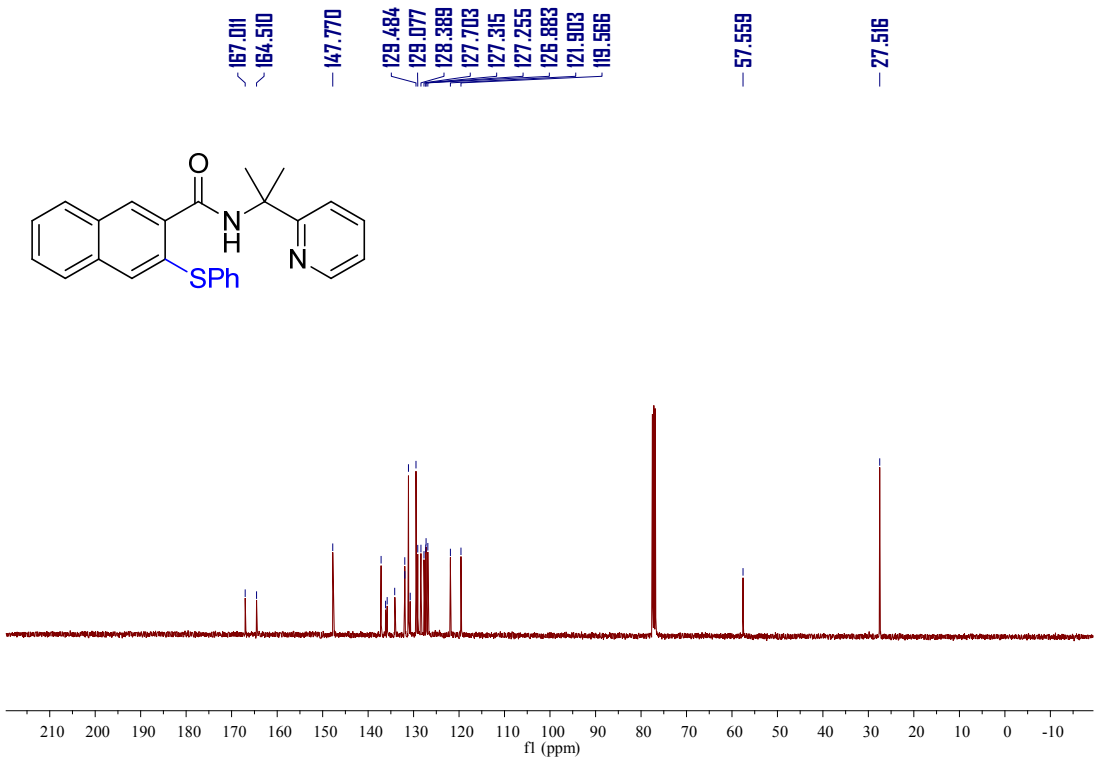
3k’


8.283
8.272
7.325
7.235
7.183
7.139
7.083
7.067
6.996
4.214
4.207
1.748
SPh
O
N
H
O
O
N
SPh
0.91
0.87
1.00
1.02
1.91
7.17
2.30
1.16
4.05
6.07
f1 (ppm)

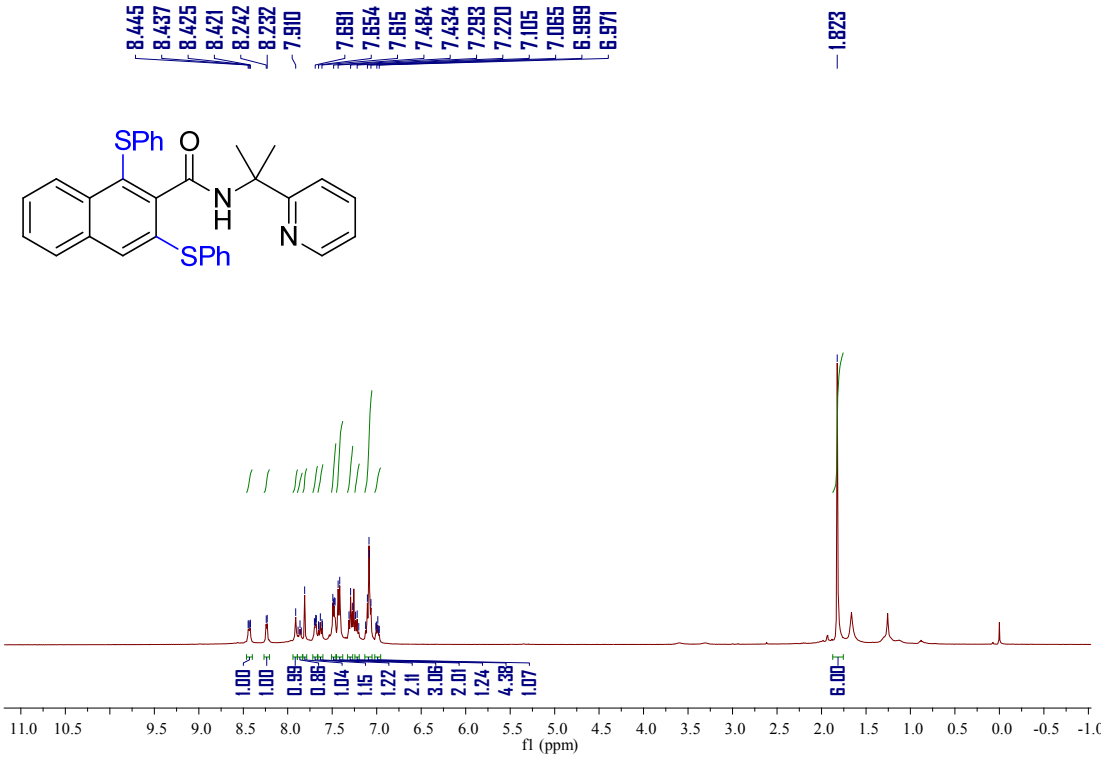

165.518
164.255
147.357
137.280
137.028
125.661
124.515
124.214
121.617
119.572
118.799
64.950
64.144
57.709
27.334
SPh
O
N
H
O
O
N
SPh
f1 (ppm)

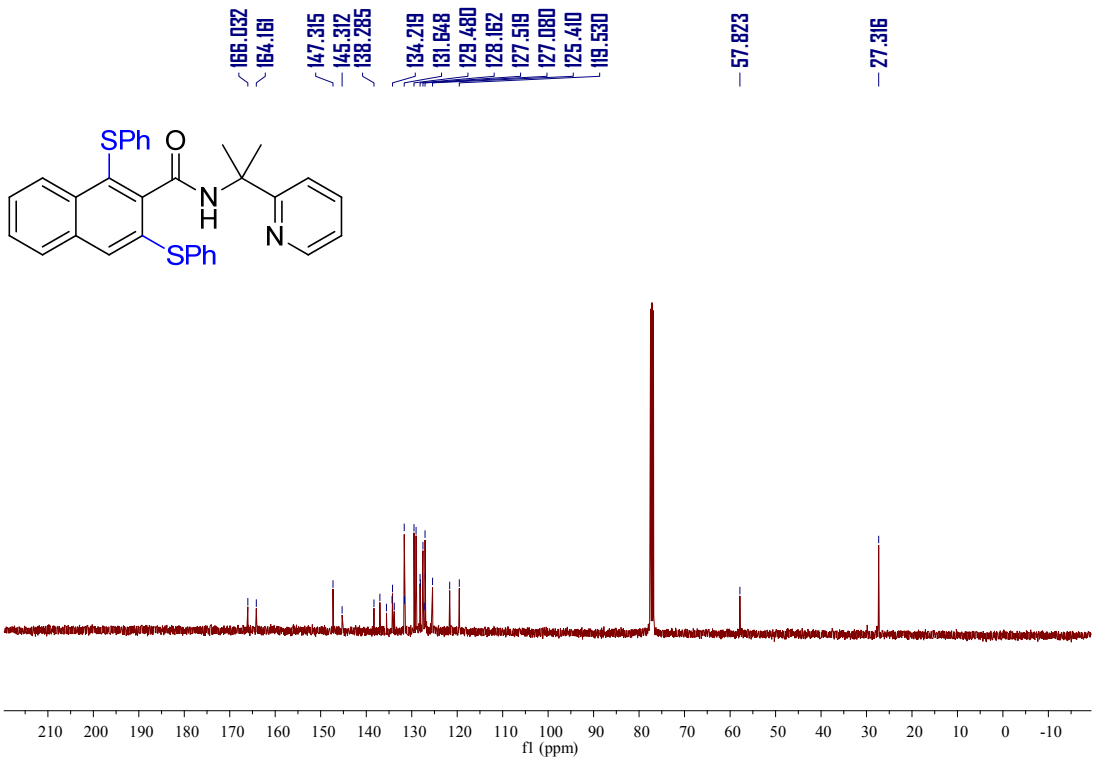
3l


8.565
8.475
8.463
8.202
7.852
7.687
7.664
7.487
7.472
7.366
7.342
7.271
7.249
7.231
7.171
7.165
1.811
O
N
H
N
SPh
0.98
0.97
1.00
1.13
3.24
2.23
1.20
2.09
1.99
1.31
1.21
6.18
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

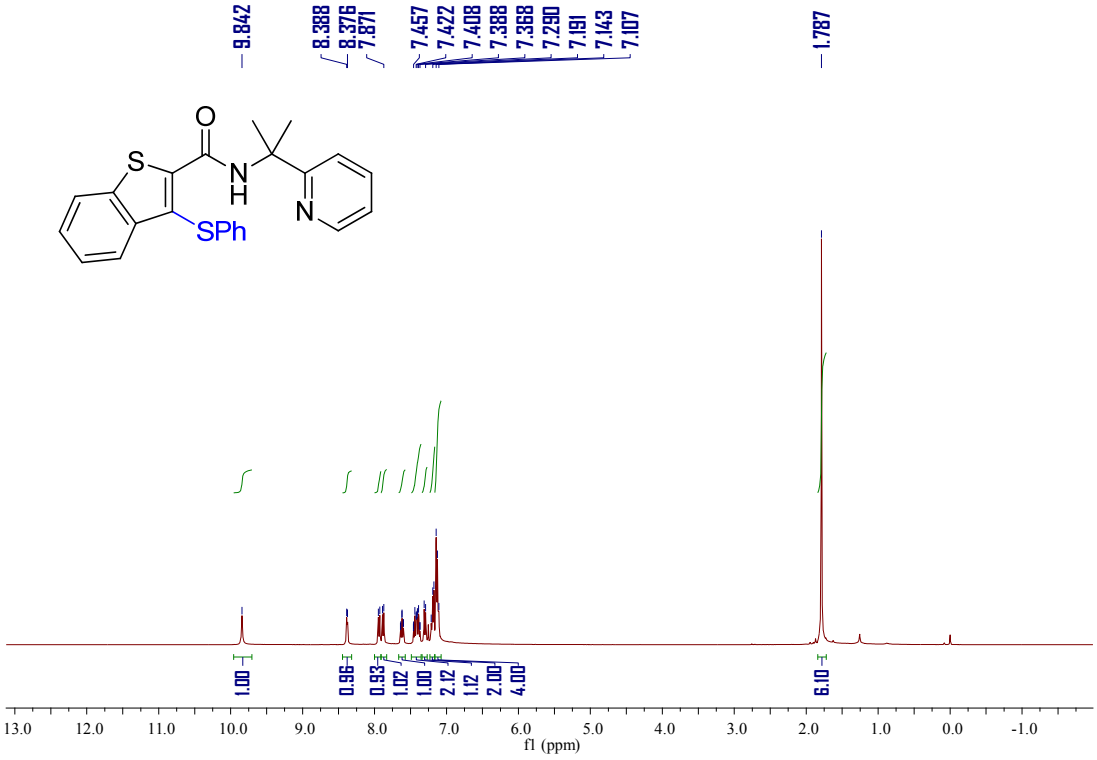

167.011
164.510
147.770
129.484
129.077
128.389
127.703
127.315
127.255
126.883
121.903
119.566
57.559
27.516
O
N
H
N
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

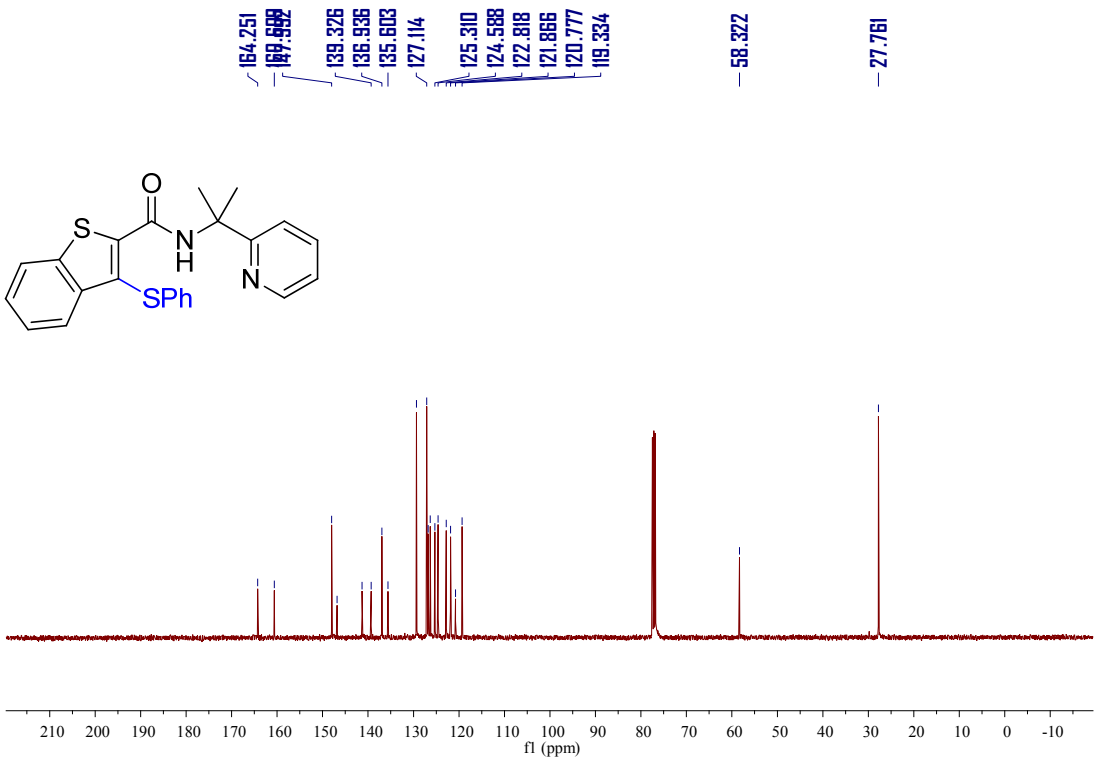
3l’


8.445
8.437
8.425
8.421
8.242
8.232
7.910
7.691
7.654
7.615
7.484
7.434
7.293
7.220
7.105
7.065
6.999
6.971
1.823
SPh
O
N
H
N
SPh
1.00
1.00
0.99
0.88
1.04
1.15
1.22
2.11
3.06
2.01
1.24
4.38
1.07
6.00
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

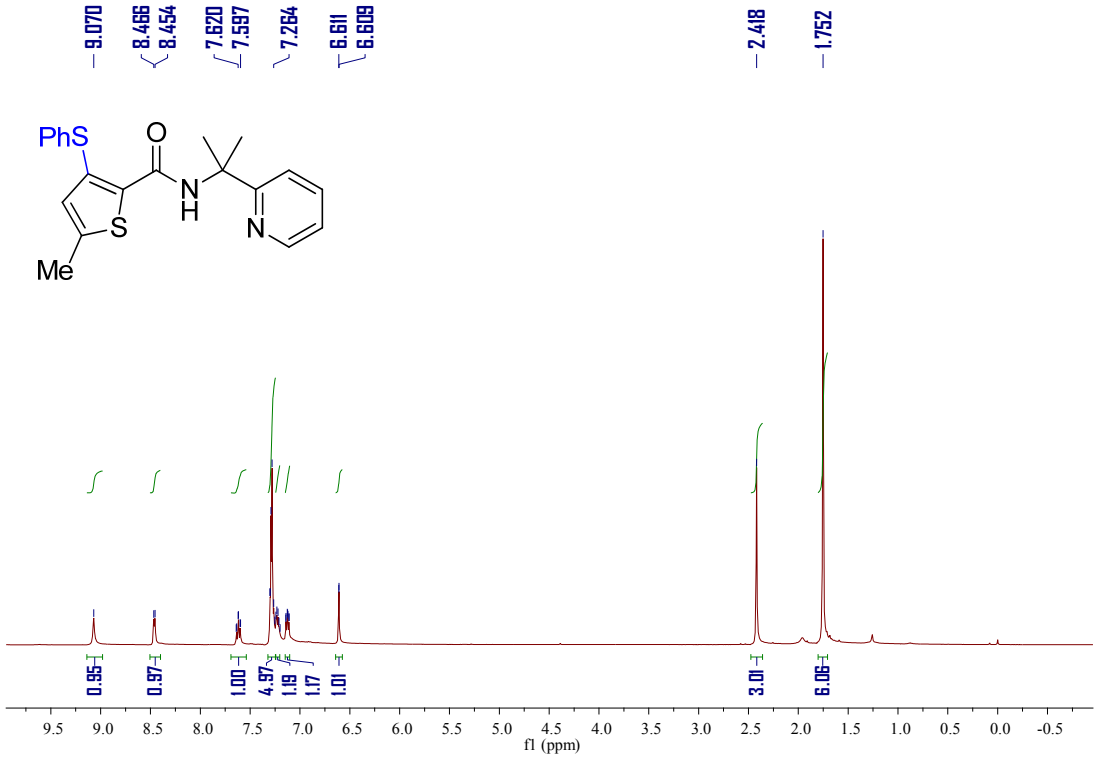

166.032
164.161
147.315
145.312
138.285
134.219
131.648
129.480
128.162
127.519
127.080
125.410
119.530
57.823
27.316
SPh
O
N
H
N
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

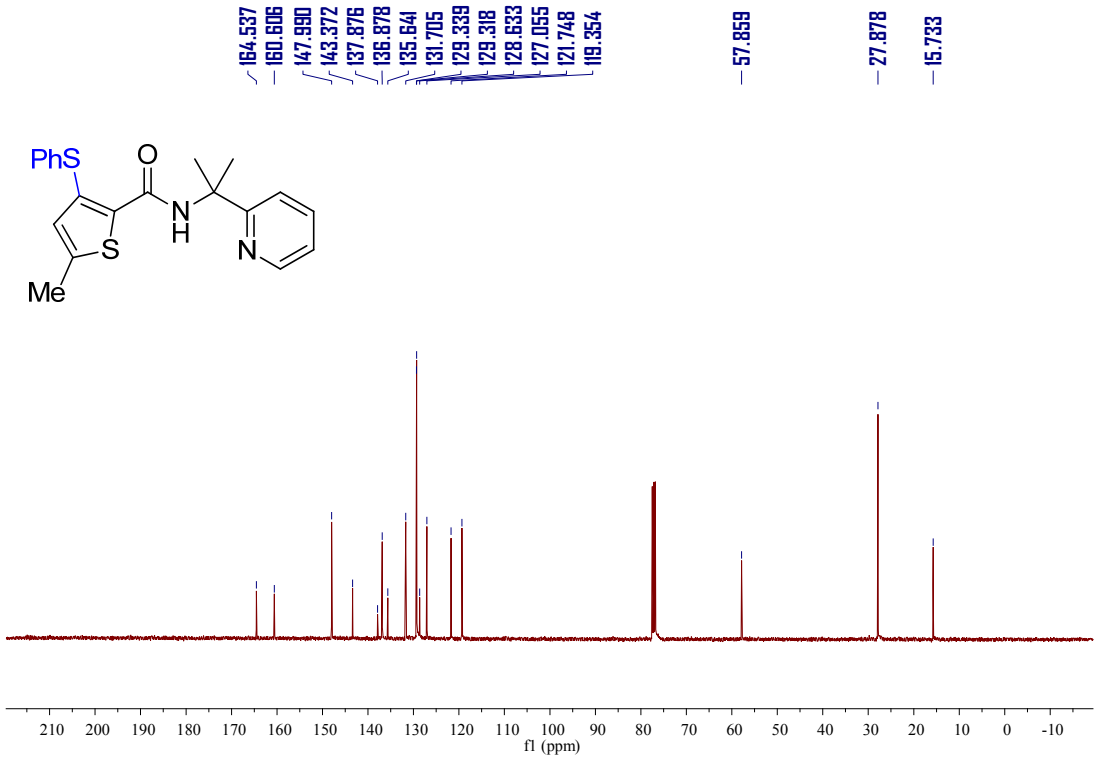
3m


9.842
8.388
8.376
7.871
7.457
7.422
7.408
7.388
7.368
7.290
7.191
7.143
7.107
1.787
O
S
N
H
N
SPh
1.00
0.96
0.93
1.02
1.00
2.12
1.12
2.00
4.00
6.10
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

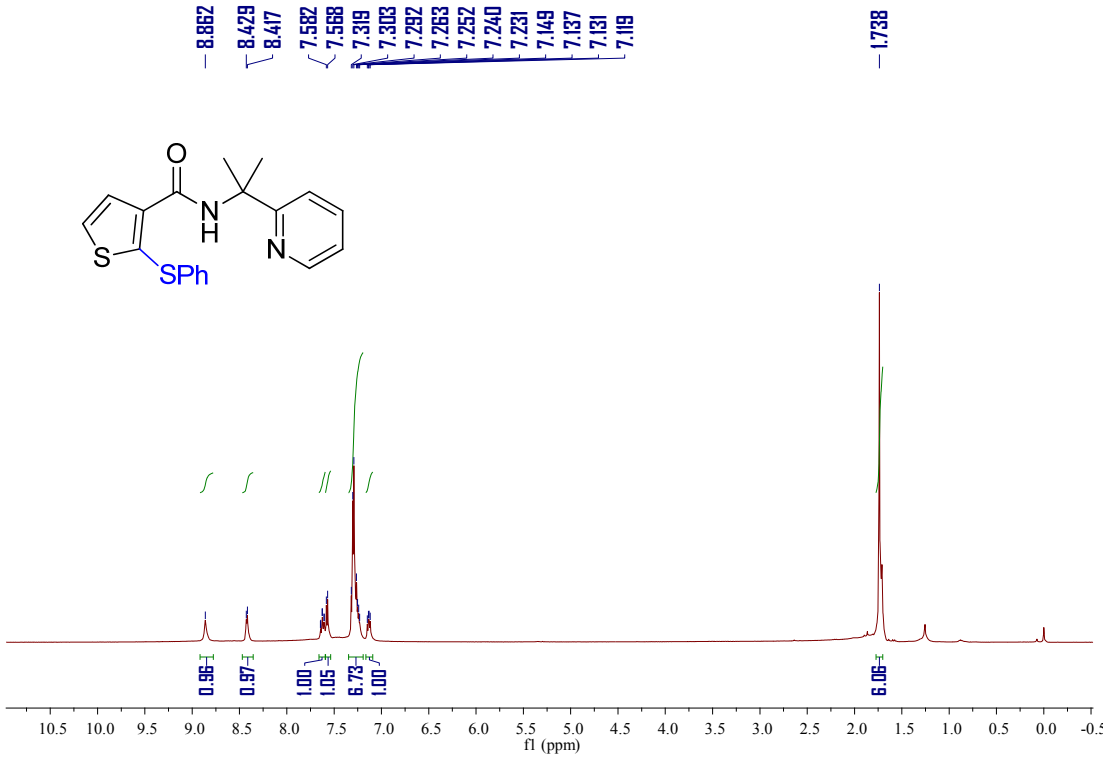

164.251
139.326
136.936
135.603
127.114
125.310
124.588
122.818
121.866
120.777
119.334
58.322
27.761
O
S
N
H
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

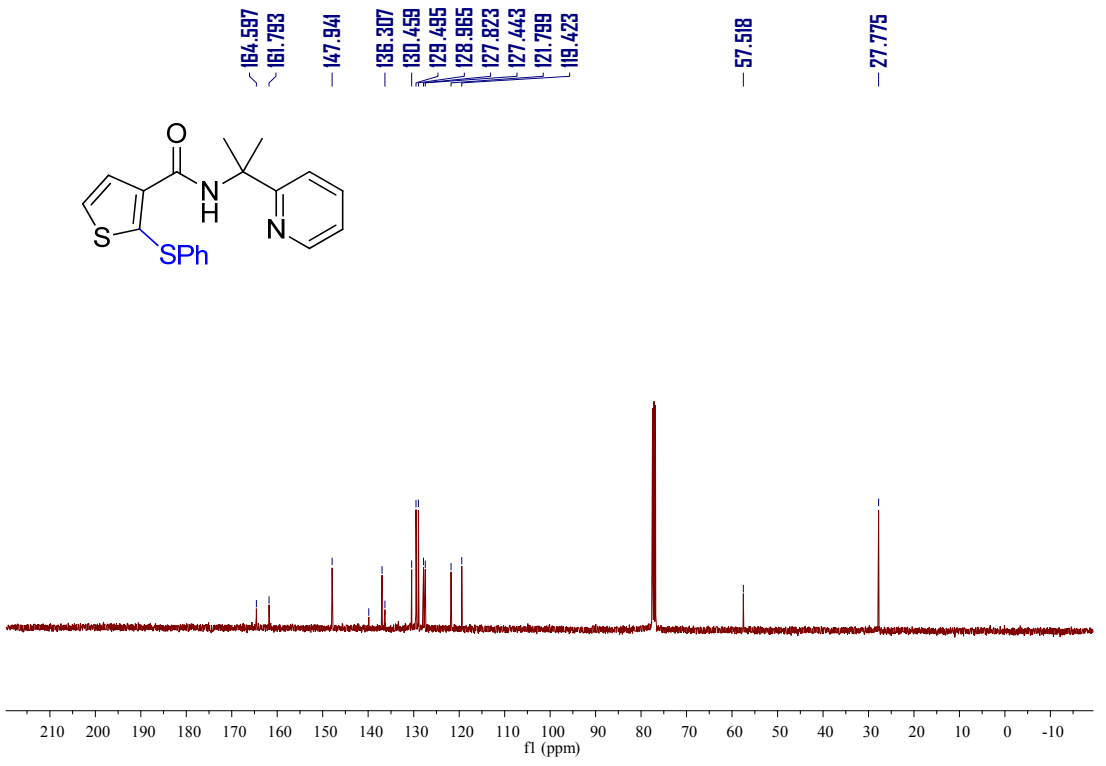
3n


9.070
8.466
8.454
7.620
7.597
7.264
6.611
6.609
2.418
1.752
PhS
O
N
H
S
N
Me
0.95
0.97
1.00
4.97
1.19
1.17
1.01
3.01
6.06
f1 (ppm)

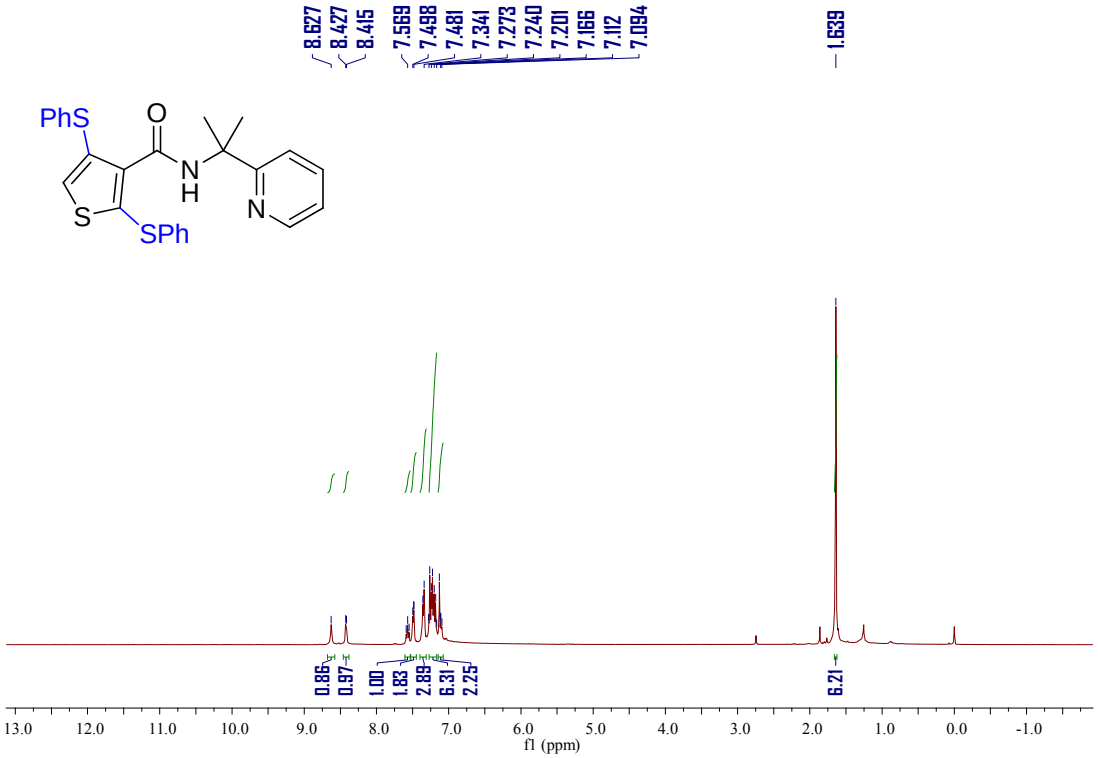

164.537
160.606
147.990
143.372
137.876
136.878
135.641
131.705
129.339
129.318
128.633
127.055
121.748
119.354
57.859
27.878
15.733
PhS
O
N
H
S
N
Me
f1 (ppm)

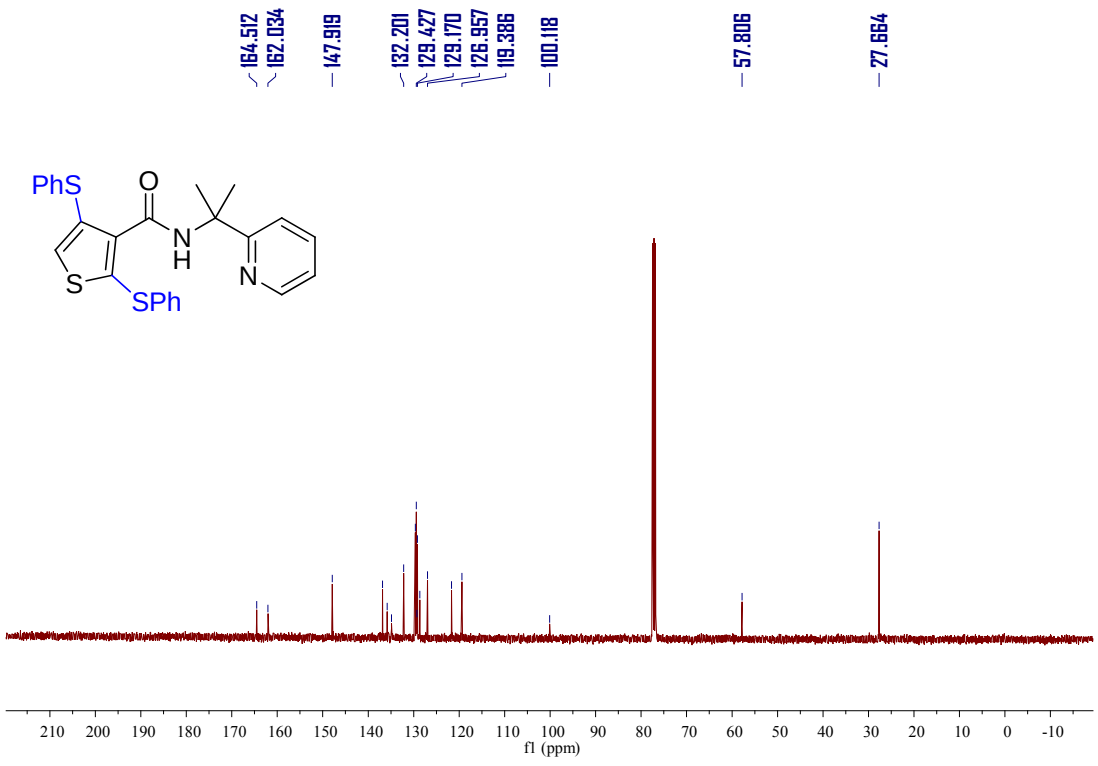
3o


8.862
8.429
8.417
7.582
7.568
7.319
7.303
7.292
7.263
7.252
7.240
7.231
7.149
7.137
7.131
7.119
1.738
O
N
H
S
SPh
N
0.96
0.97
1.00
1.05
6.73
1.00
6.06
f1 (ppm)

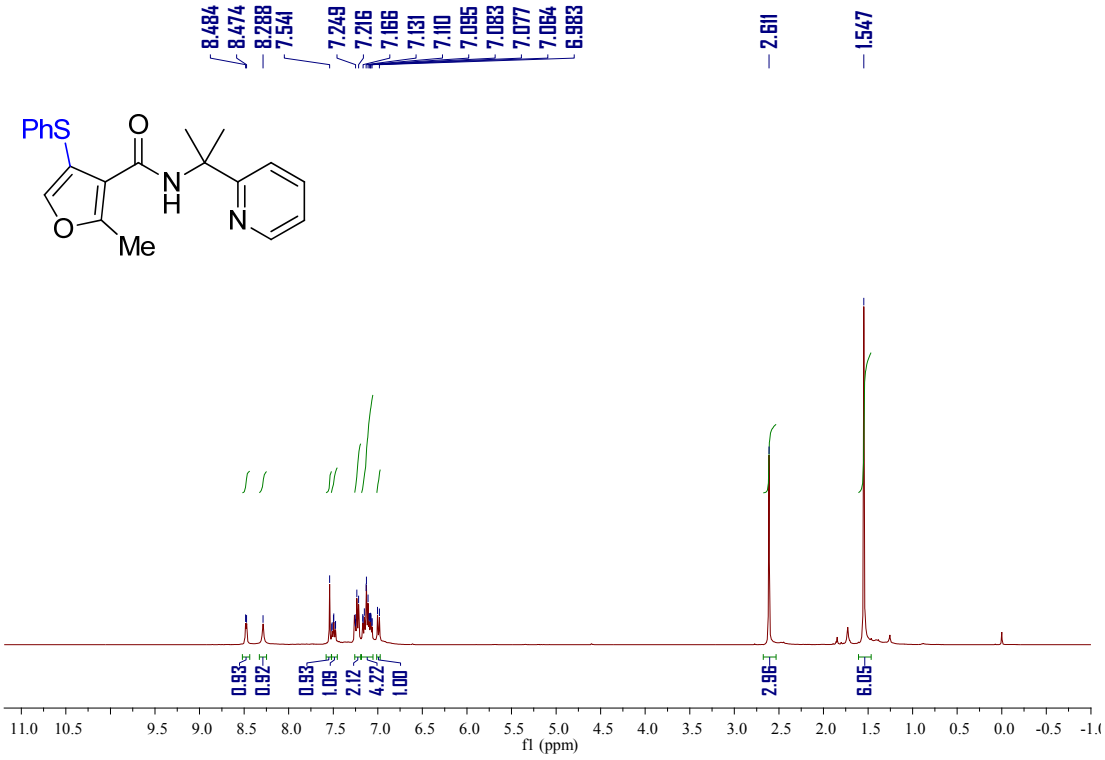

164.597
161.793
147.941
136.307
130.459
129.495
128.965
127.823
127.443
121.799
119.423
57.518
27.775
O
N
H
S
SPh
N
f1 (ppm)

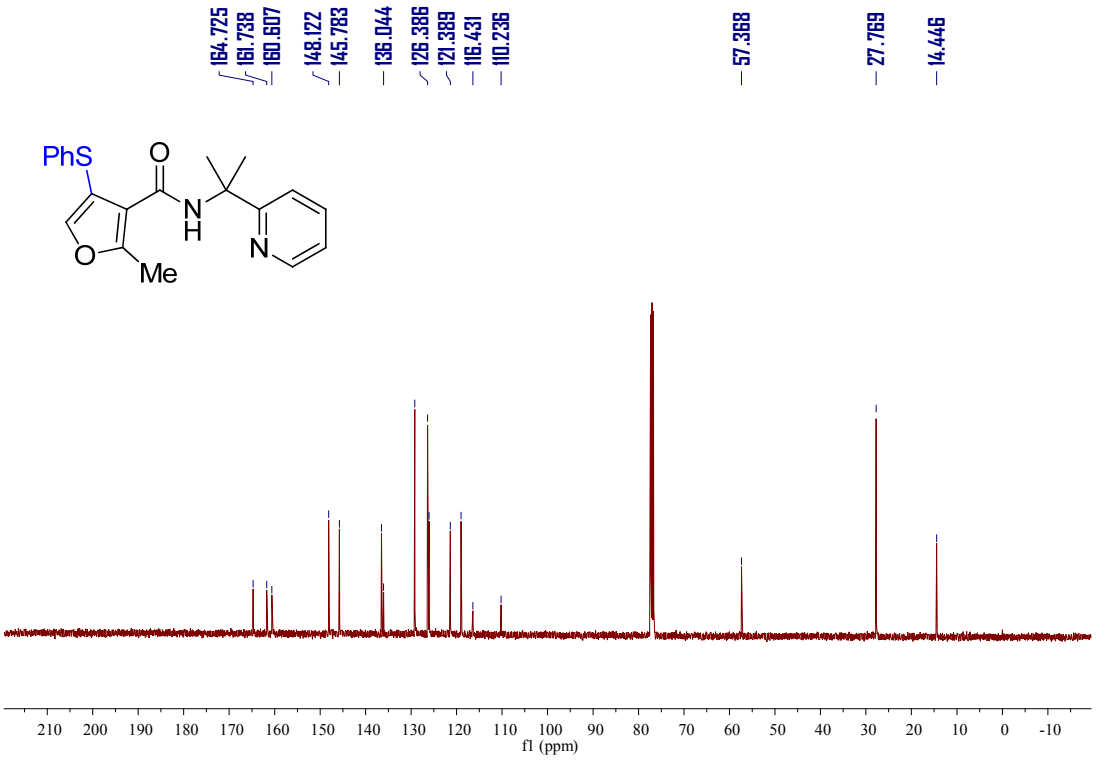
3o’


8.627
8.427
8.415
7.569
7.498
7.481
7.341
7.273
7.240
7.201
7.166
7.112
7.094
1.639
PhS
O
N
H
S
SPh
N
0.86
0.97
1.00
1.83
2.89
6.31
2.25
6.21
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

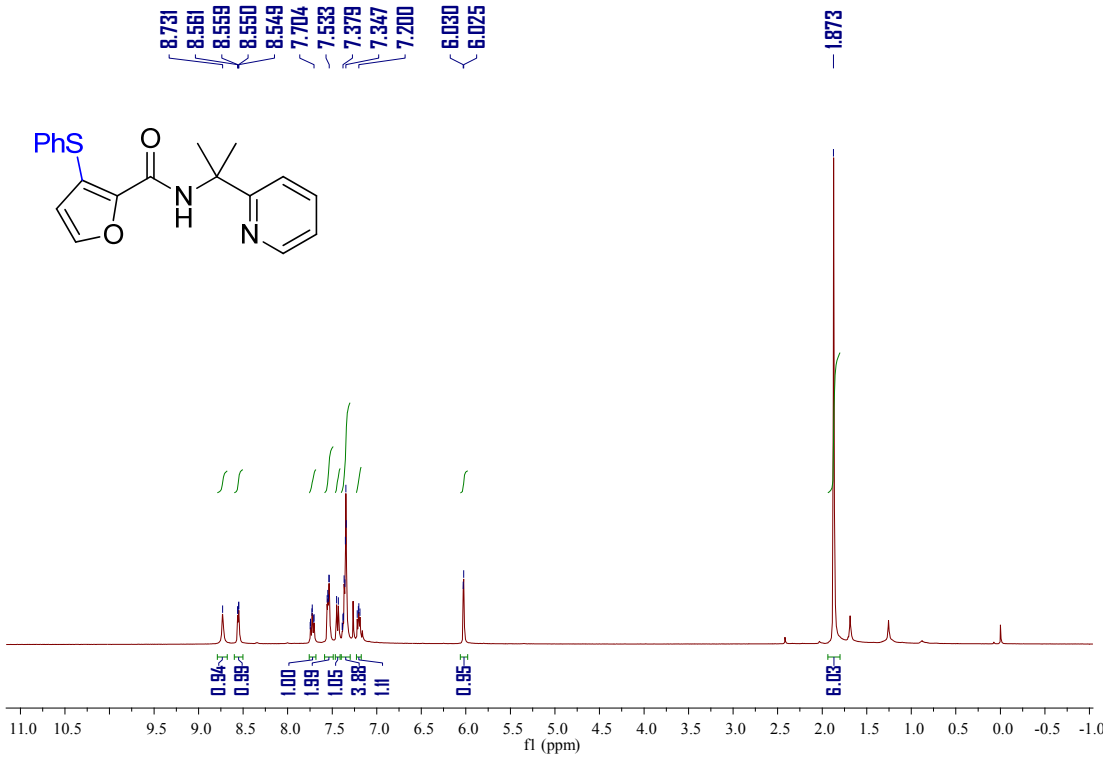

164.512
162.034
147.919
132.201
129.427
129.170
126.957
119.386
100.118
57.806
27.664
PhS
O
N
H
S
SPh
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

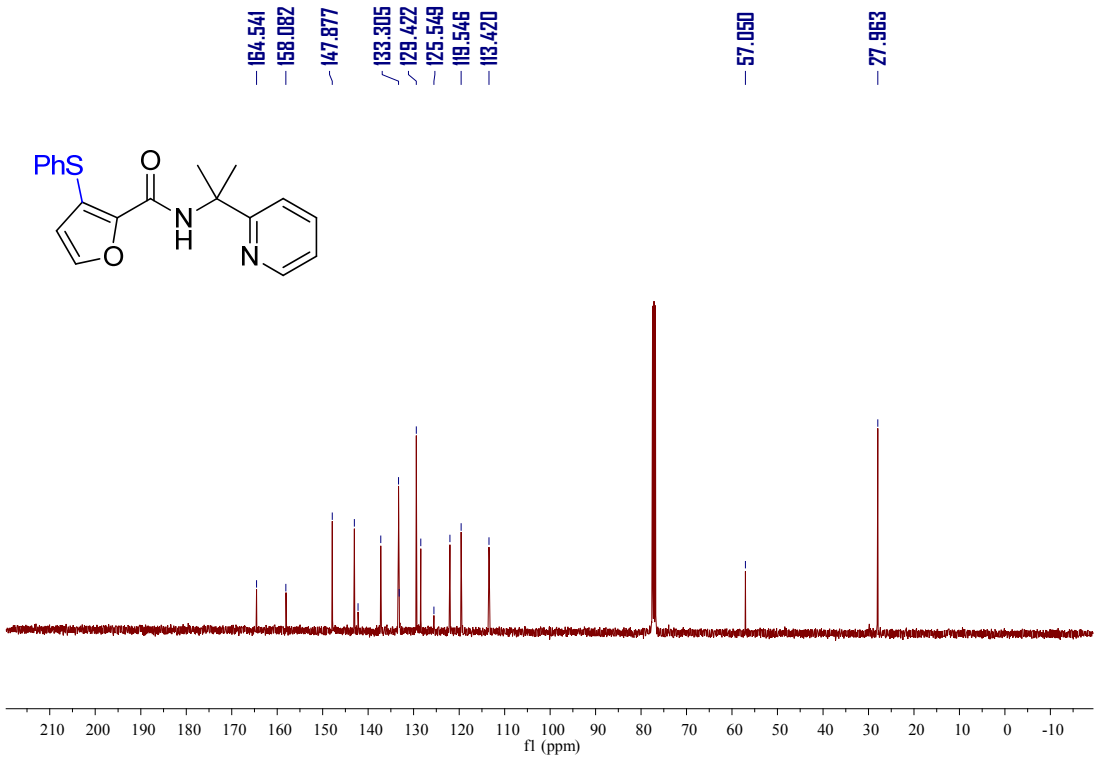
3p


8.484
8.474
8.288
7.541
7.249
7.216
7.166
7.131
7.110
7.095
7.083
7.077
7.064
6.983
2.611
1.547
PhS
O
N
H
O
Me
N
0.93
0.92
0.93
1.09
2.12
4.22
1.00
2.96
6.05
f1 (ppm)

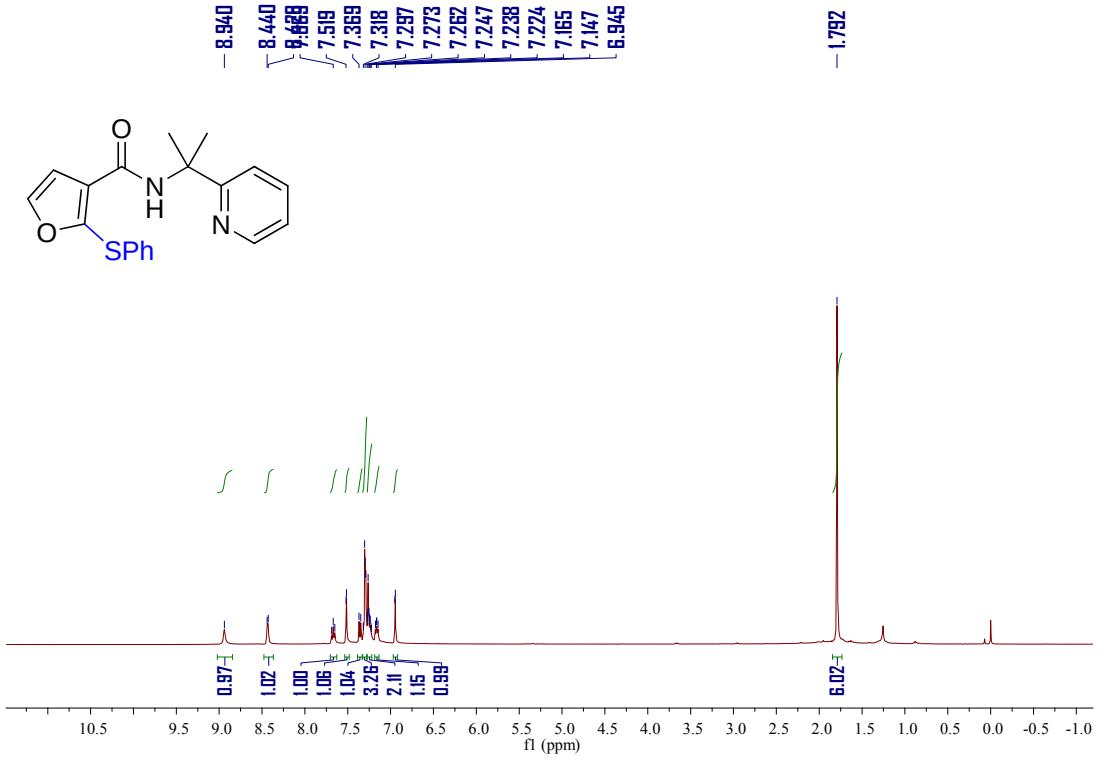

164.725
161.738
160.607
148.122
145.783
136.044
126.386
121.389
116.431
110.236
57.368
27.769
14.446
PhS
O
N
H
O
Me
N
f1 (ppm)

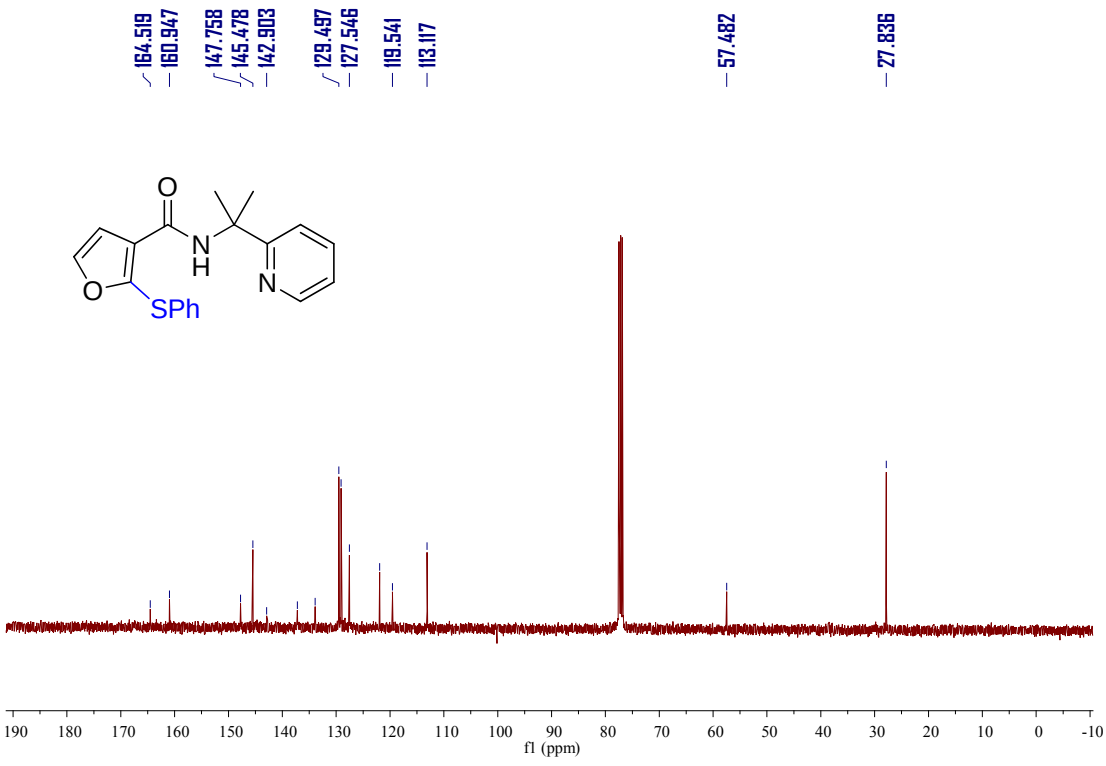
3q


8.731
8.561
8.559
8.550
8.549
7.704
7.533
7.379
7.347
7.200
6.030
6.025
1.873
PhS
O
N
H
O
N
0.94
0.99
1.00
1.99
1.05
3.88
1.11
0.95
6.03
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

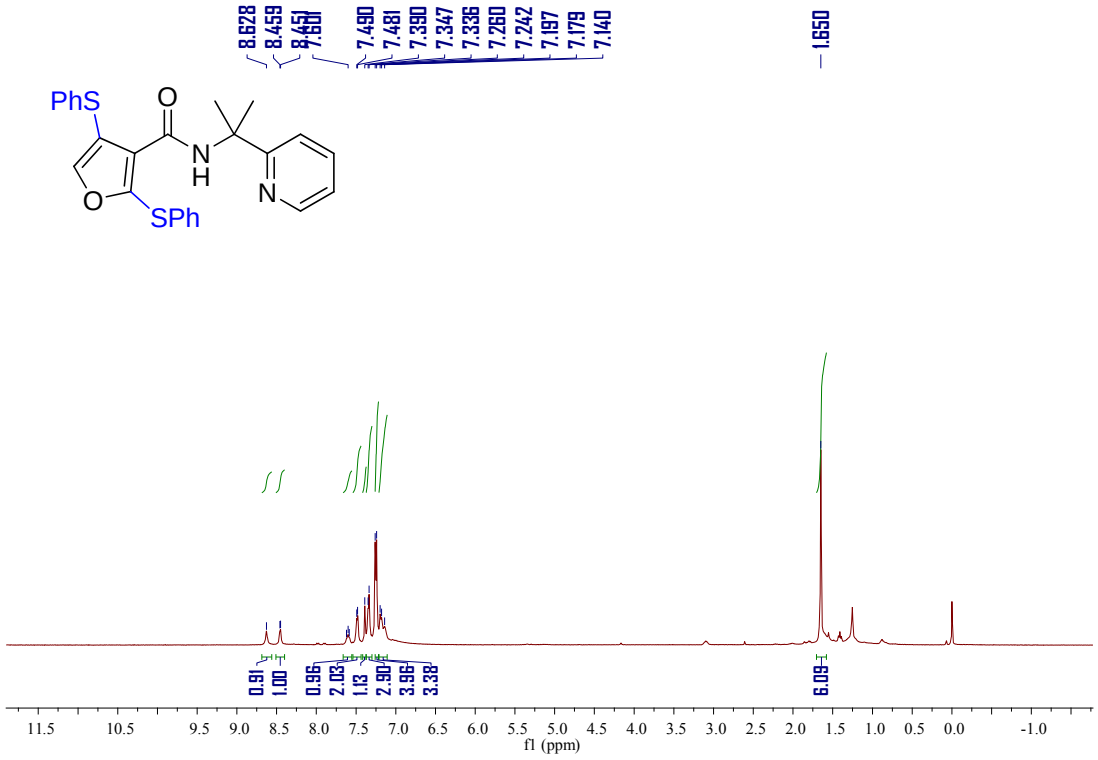

164.541
158.082
147.877
133.305
129.422
125.549
119.546
113.420
57.050
27.963
PhS
O
N
H
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

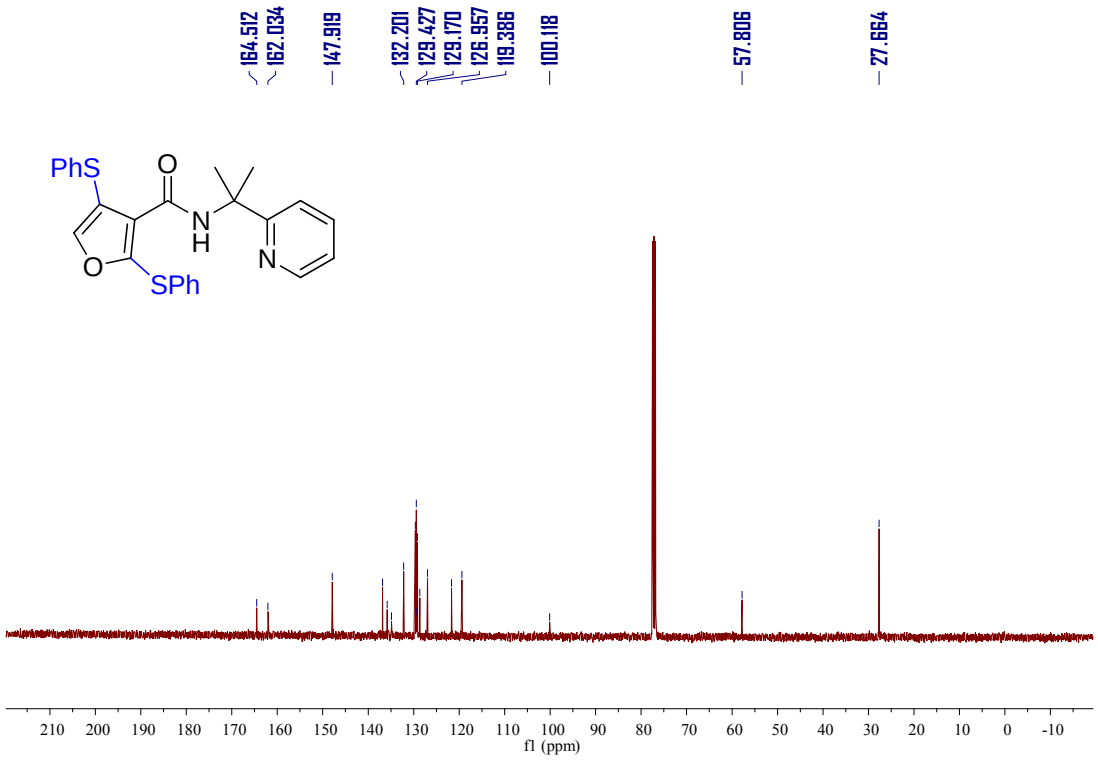
3r


8.940
8.440
7.519
7.369
7.318
7.297
7.273
7.262
7.247
7.238
7.224
7.165
7.147
6.945
1.792
O
N
H
O
N
SPh
0.97
1.02
1.00
1.06
1.04
3.26
2.11
1.15
0.99
6.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

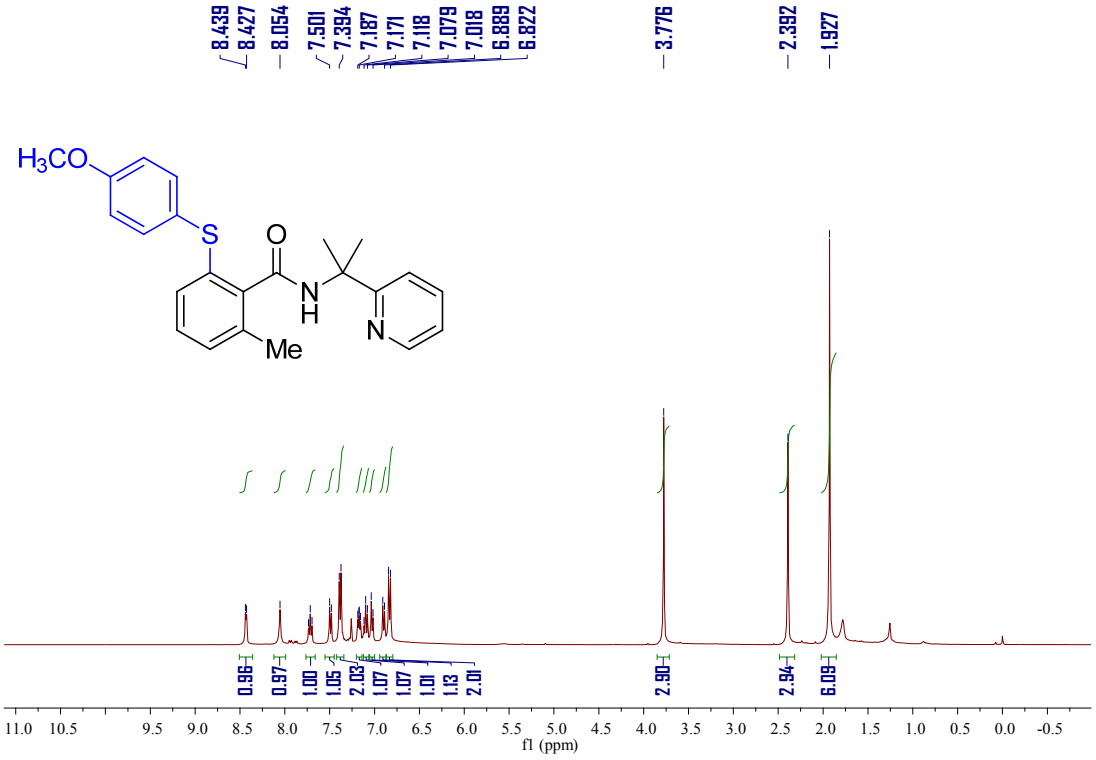

164.519
160.947
147.758
145.478
142.903
129.497
127.546
119.541
113.117
57.482
27.836
O
N
H
O
N
SPh
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

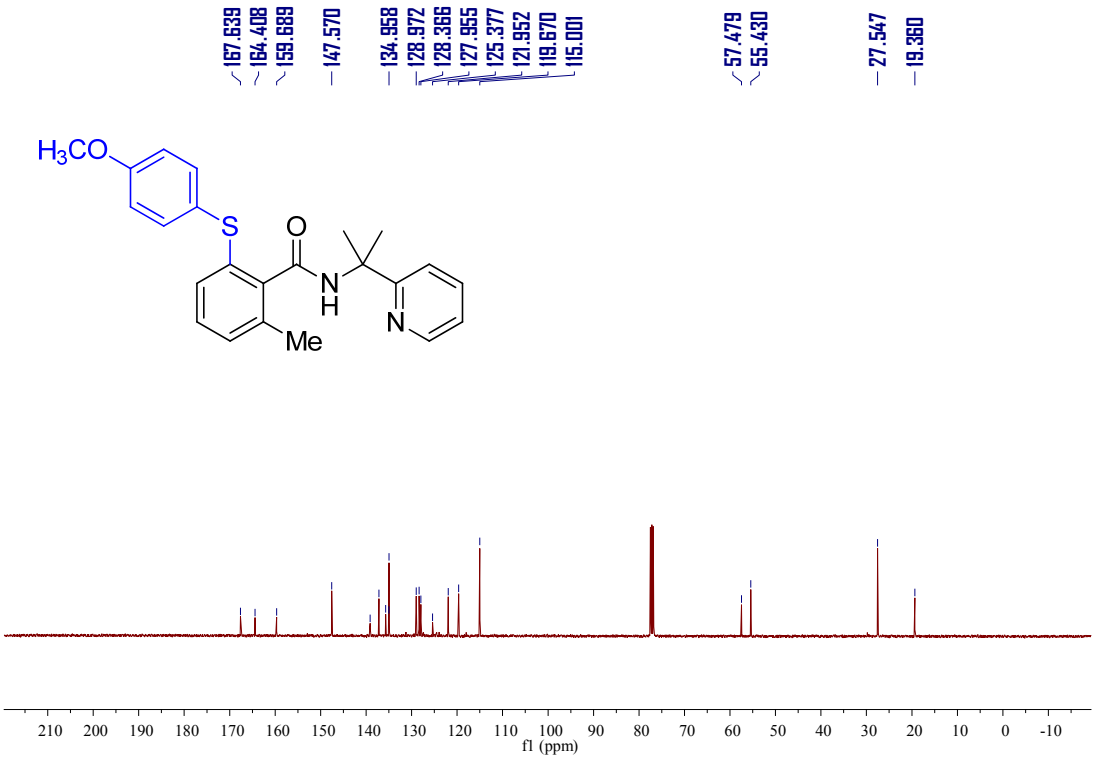
3r’


8.628
8.459
8.451
7.490
7.481
7.390
7.347
7.336
7.260
7.242
7.197
7.179
7.140
1.650
PhS
O
N
H
O
N
SPh
0.91
1.00
0.96
2.03
1.13
2.90
3.96
3.38
6.09
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

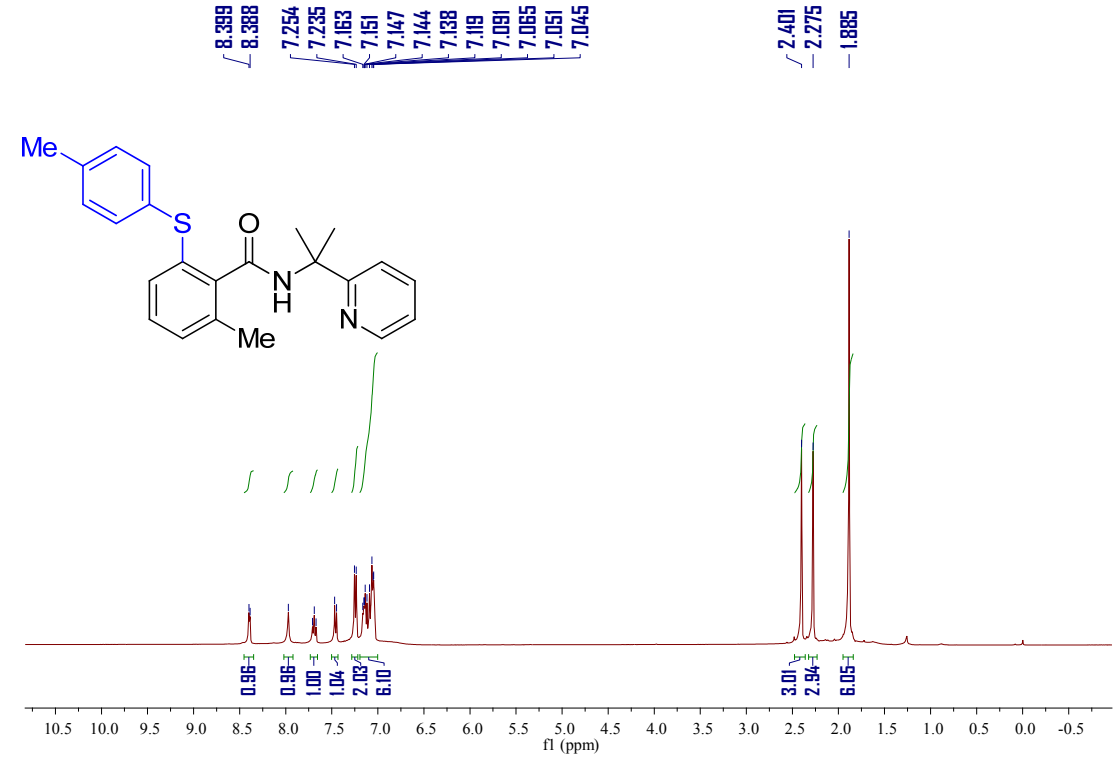

164.512
162.034
147.919
132.201
129.427
129.170
126.957
119.386
100.118
57.806
27.664
PhS
O
N
H
O
N
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

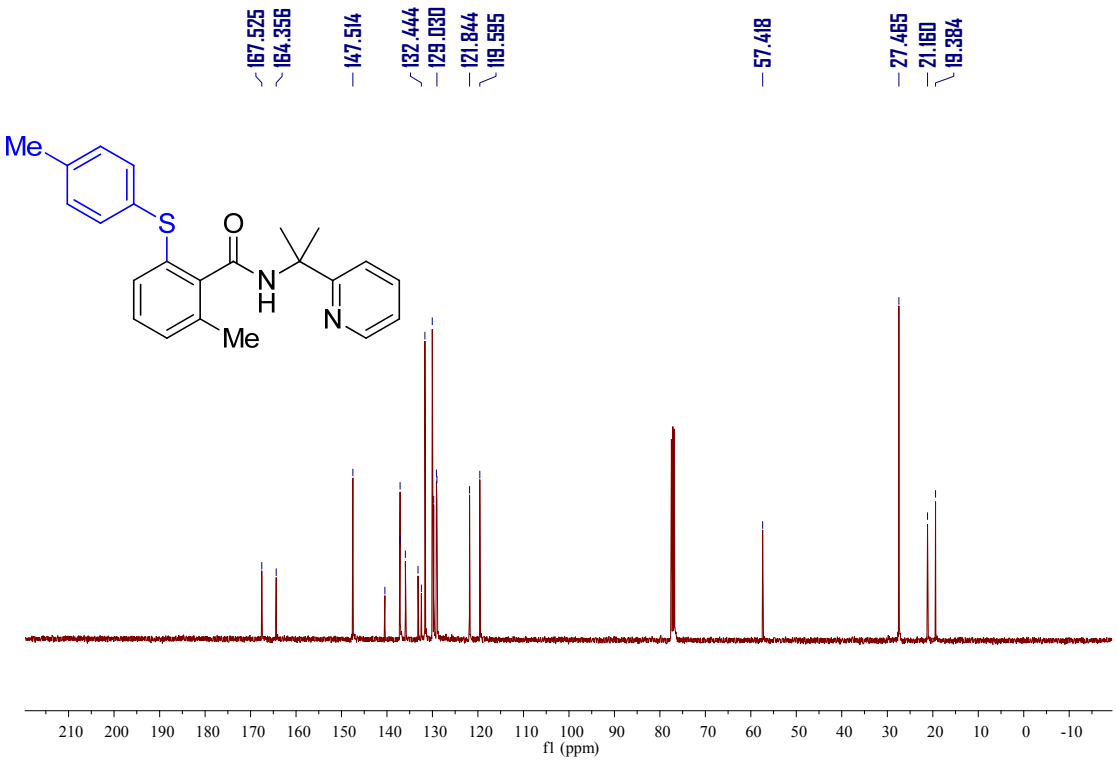
5a


8.439
8.427
8.054
7.501
7.394
7.187
7.171
7.118
7.079
7.018
6.889
6.822
3.776
2.392
1.927
H3CO
S
O
N
H
N
Me
0.96
0.97
1.00
1.05
2.03
1.07
1.07
1.01
1.13
2.01
2.90
2.94
6.09
f1 (ppm)

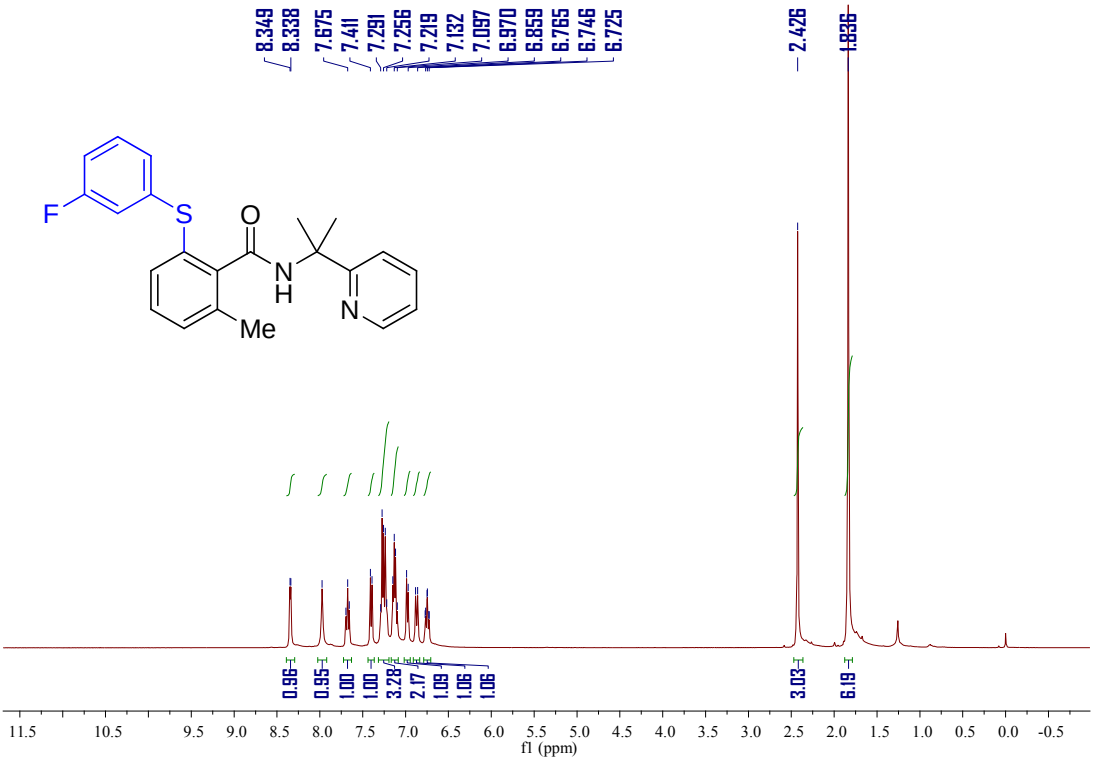

167.639
164.408
159.689
147.570
134.958
128.972
128.366
127.955
125.377
121.952
119.670
115.001
57.479
55.430
27.547
19.360
H3CO
S
O
N
H
N
Me
f1 (ppm)

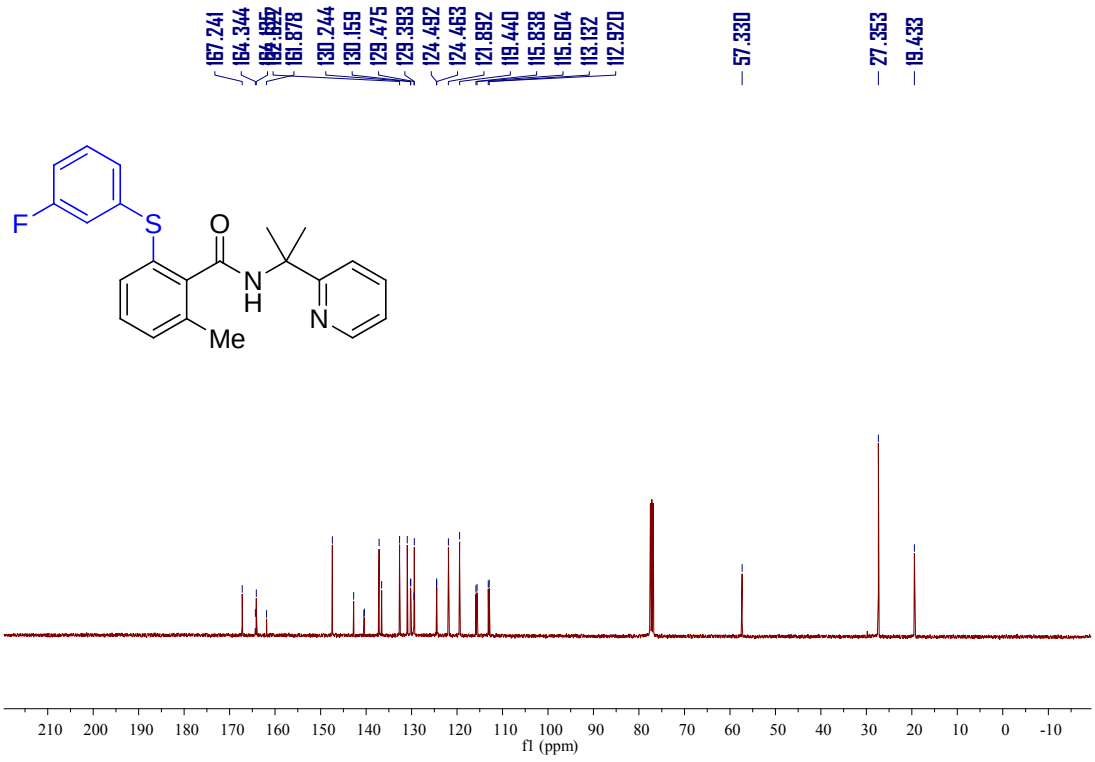
5b


8.399
8.388
7.254
7.235
7.163
7.151
7.147
7.144
7.138
7.119
7.091
7.065
7.051
7.045
2.401
2.275
1.885
Me
S
O
N
H
N
Me
0.96
0.96
1.00
1.04
2.03
6.10
3.01
2.94
6.05
f1 (ppm)

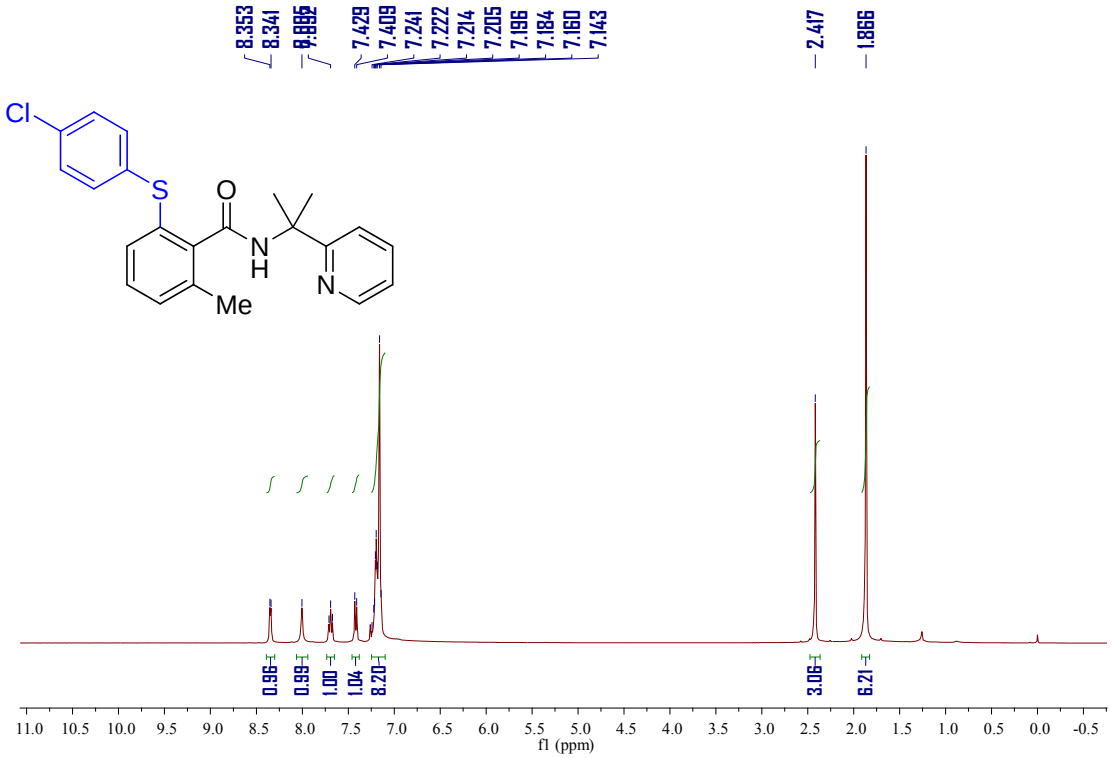

167.525
164.356
147.514
132.444
129.030
121.844
119.595
57.418
27.465
21.160
19.384
Me
S
O
N
H
N
Me
f1 (ppm)

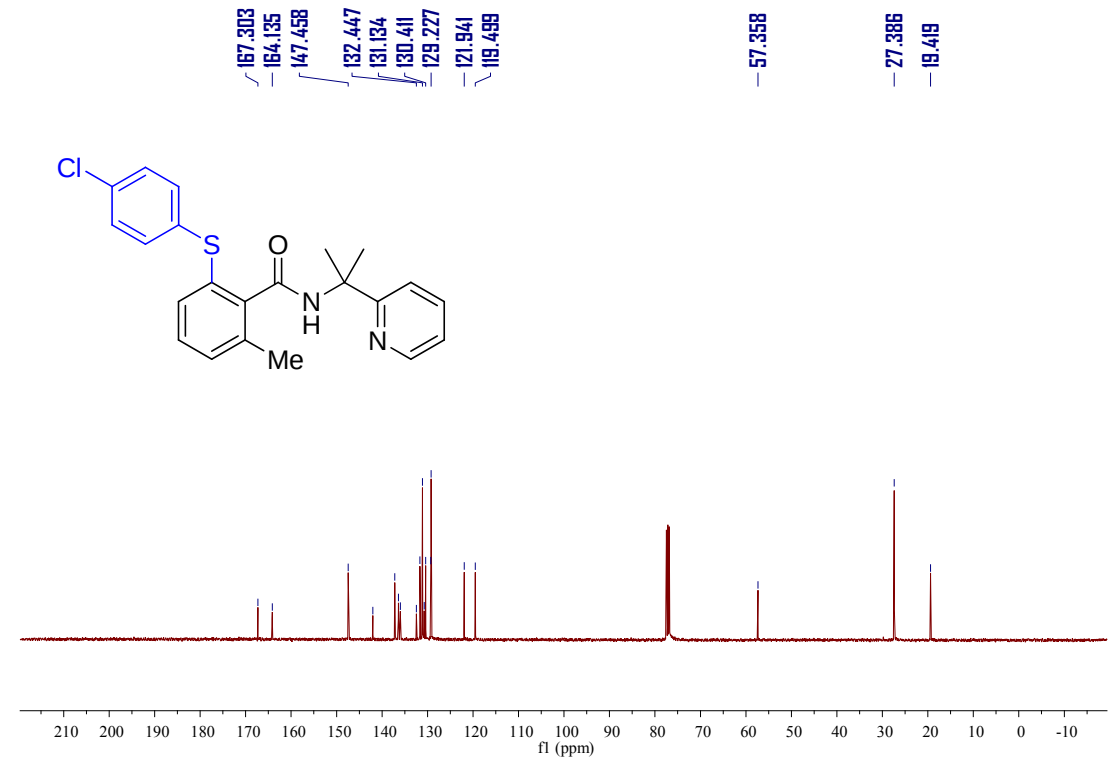
5c


8.349
8.338
7.675
7.411
7.291
7.256
7.219
7.132
7.097
6.970
6.859
6.765
6.746
6.725
2.426
1.836
F
S
O
N
H
N
Me
0.96
0.95
1.00
1.00
3.28
2.17
1.09
1.06
1.06
3.03
6.19
f1 (ppm)

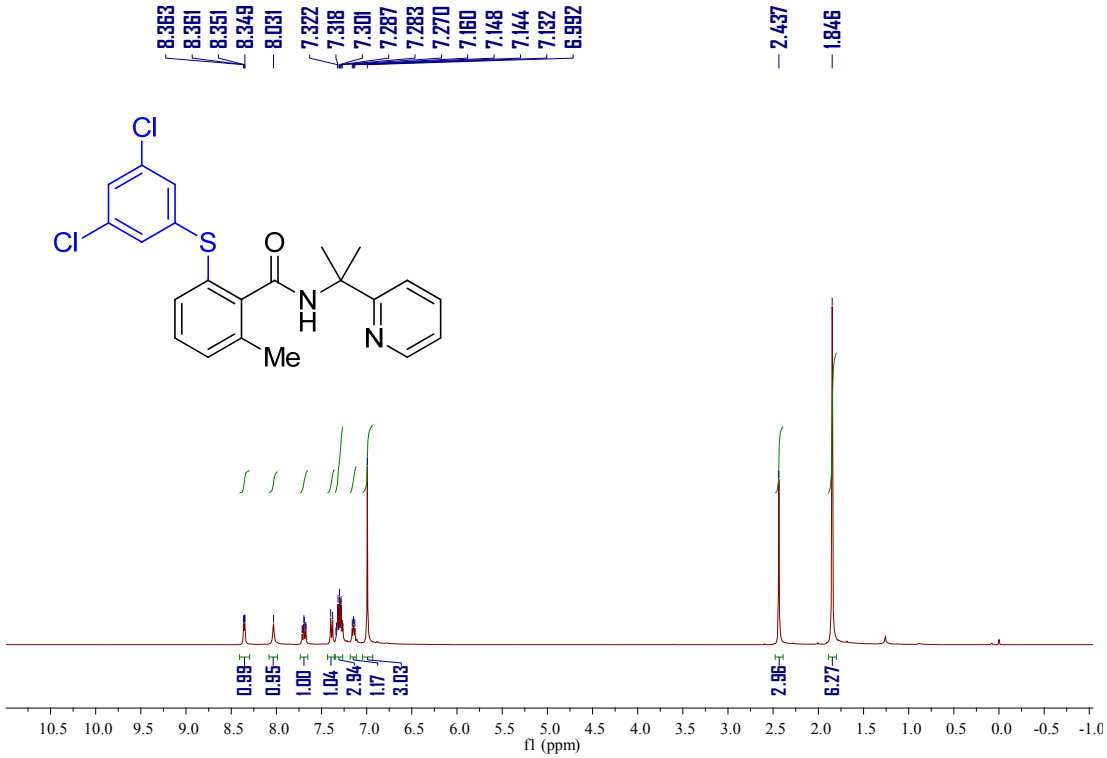

167.241
164.344
161.878
130.244
130.159
129.475
129.393
124.492
124.463
121.892
119.440
115.838
115.604
113.132
112.920
57.330
27.353
19.433
F
S
O
N
H
N
Me
f1 (ppm)

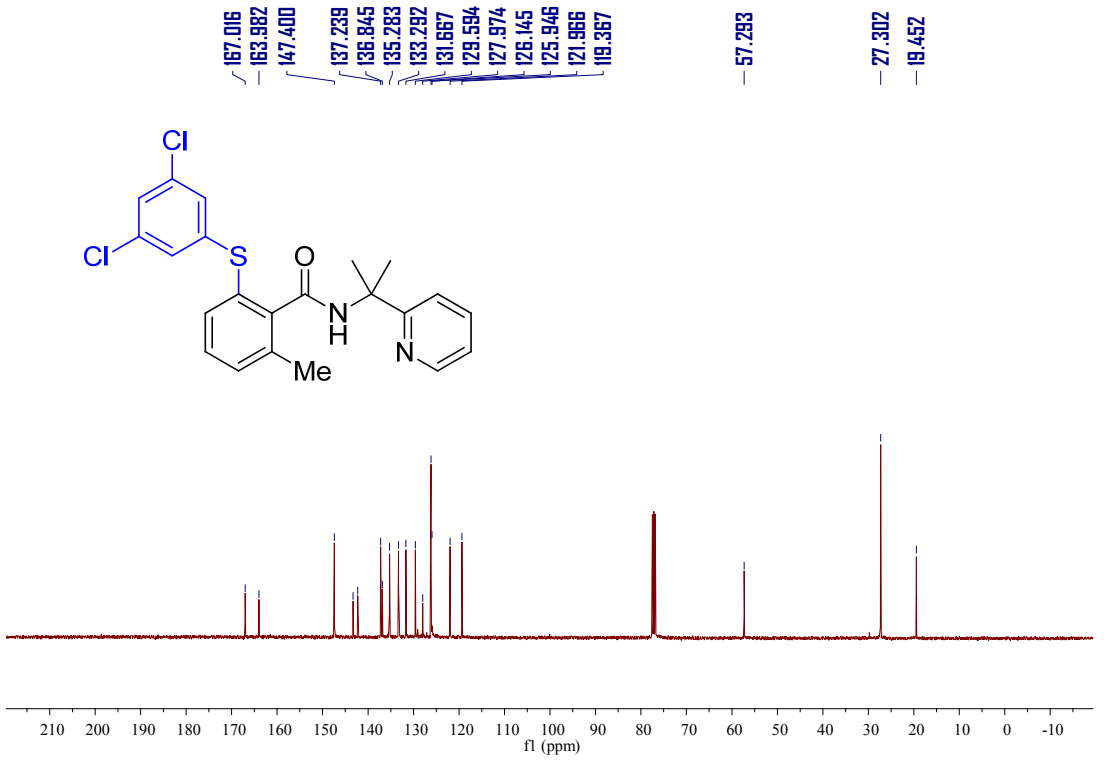
5d


8.353
8.341
7.429
7.409
7.241
7.222
7.214
7.205
7.196
7.184
7.160
7.143
2.417
1.866
Cl
S
O
N
H
N
Me
0.96
0.99
1.00
1.04
8.20
3.06
6.21
f1 (ppm)

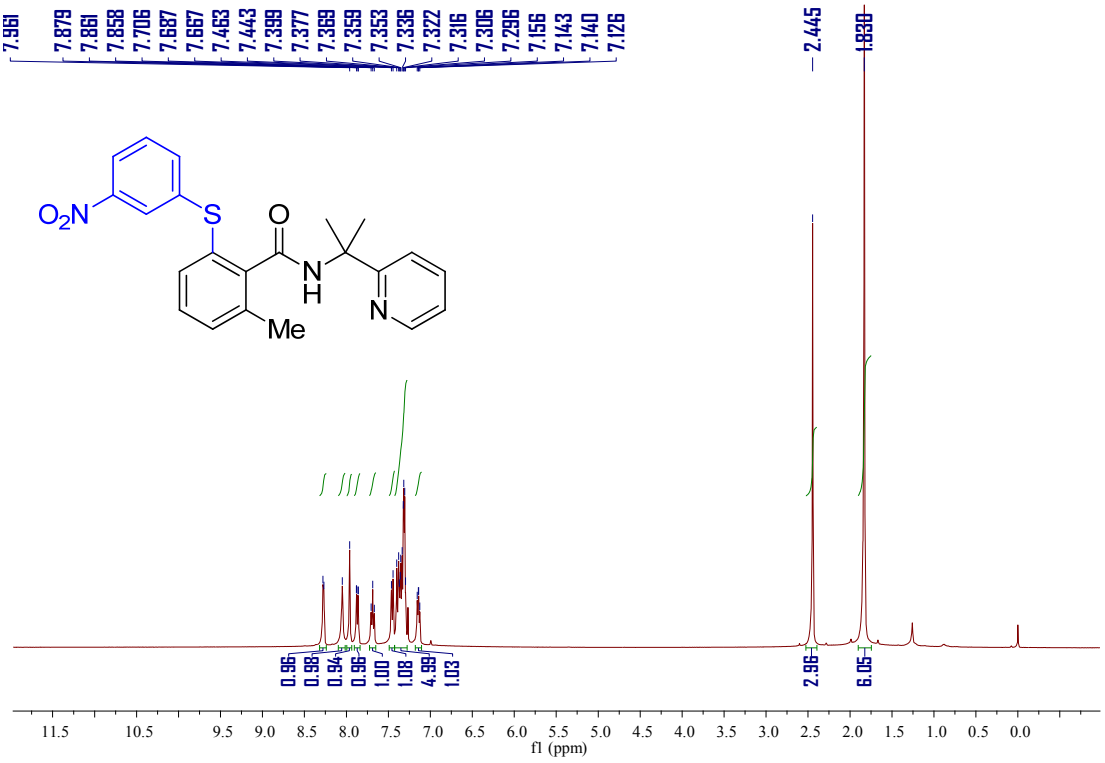

167.303
164.135
147.458
132.447
131.134
130.411
129.227
121.941
119.499
57.358
27.386
19.419
Cl
S
O
N
H
N
Me
f1 (ppm)

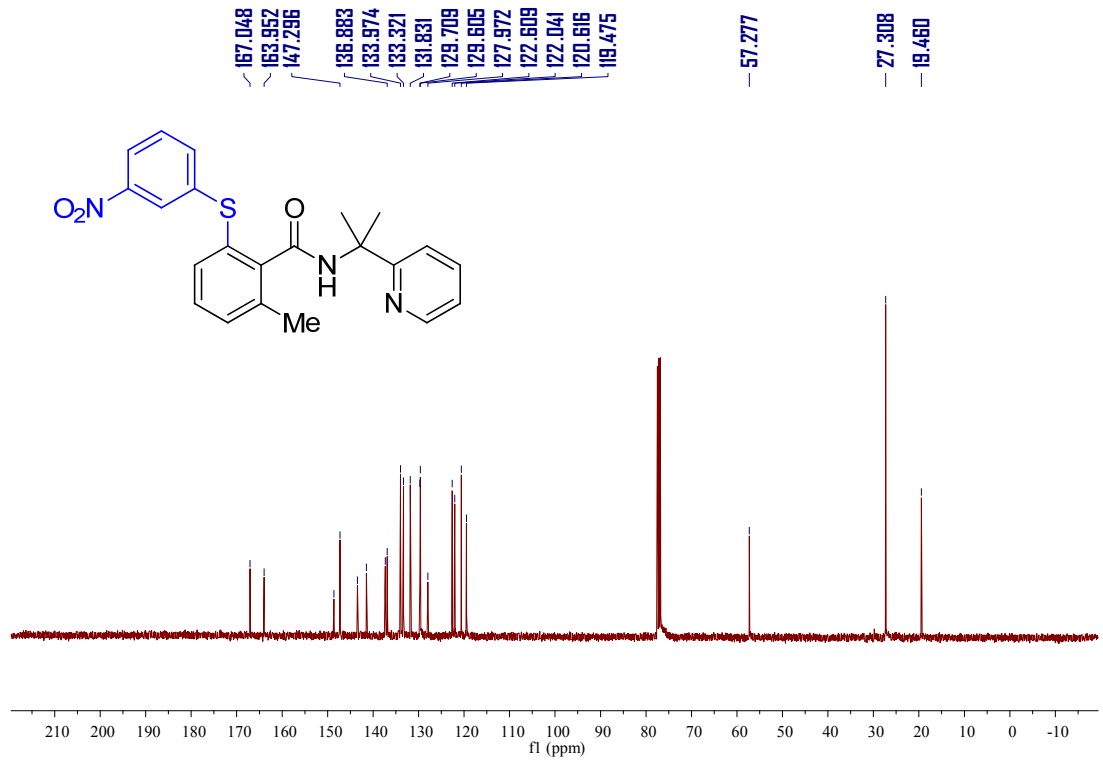
5e


8.363
8.361
8.351
8.349
8.031
7.322
7.318
7.301
7.287
7.283
7.270
7.160
7.148
7.144
7.132
6.992
2.437
1.846
Cl
Cl
S
O
N
H
N
Me
0.99
0.95
1.00
1.04
2.94
1.17
3.03
2.96
6.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.016
163.982
147.400
137.239
136.845
135.283
133.292
131.667
129.594
127.974
126.145
125.946
121.986
119.367
57.293
27.302
19.452
Cl
Cl
S
O
N
H
N
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5f


7.961
7.879
7.861
7.858
7.706
7.687
7.667
7.463
7.443
7.399
7.377
7.369
7.359
7.353
7.336
7.322
7.316
7.306
7.296
7.156
7.143
7.140
7.126
2.445
1.830
O2N
S
O
N
H
N
Me
0.96
0.98
0.94
0.96
1.00
1.08
4.89
1.03
2.96
6.05
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.048
163.952
147.296
136.883
133.974
133.321
131.831
129.709
129.605
127.972
122.609
122.041
120.616
119.475
57.277
27.308
19.460
O2N
S
O
N
H
N
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)