Thiourea participation in [3+2] cycloaddition with donor-acceptor cyclopropanes: a domino process to 2-amino-dihydrothiophenes

Ming-Sheng Xie, Guo-Feng Zhao, Tao Qin, Yong-Bo Suo, Gui-Rong Qu, and Hai-Ming Guo*

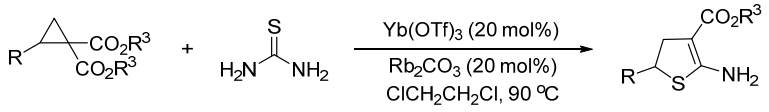
Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.
E-mail: ghm@htu.edu.cn

Contents

1. General information.

^{1}H NMR spectra were recorded on commercial instruments (400/600 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quaternary, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100/150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel OD-H in comparison with the authentic racemates. Chiral HPLC analysis recorded on Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Toluene and THF were freshly distilled from a sodium benzophenone ketyl. CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled over calcium hydride prior to use. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use.

2. General procedure for the reaction of D-A cyclopropanes with thiourea

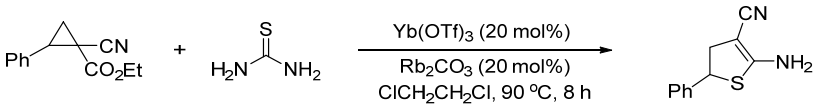


1a-1s **2a** **3aa-3sa**

R^1 = Alkyl, Aryl
R^3 = Me, Et, Bn

In a test tube, cyclopropane **1a-1s** (0.2 mmol),[1] thiourea **2a** (2 equiv, 0.4 mmol, 30.5 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 10/1 to 2/1) to afford the 2-amino-dihyddrothiophene adduct.

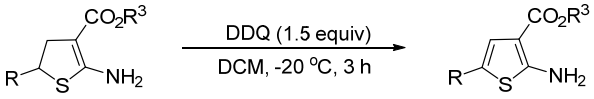
3. Synthesis of 2-amino-3-cyano-4,5-dihydrothiophene 3ta



1t **2a** **3ta**: 56% yield

In a test tube, cyclopropane **1t** (0.2 mmol, 43 mg), thiourea **2a** (2 equiv, 0.4 mmol, 30.5 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1) to afford the product **3ta** as a white solid (22.6 mg, 56% yield).

4. Synthesis of 2-amino thiophenes 5



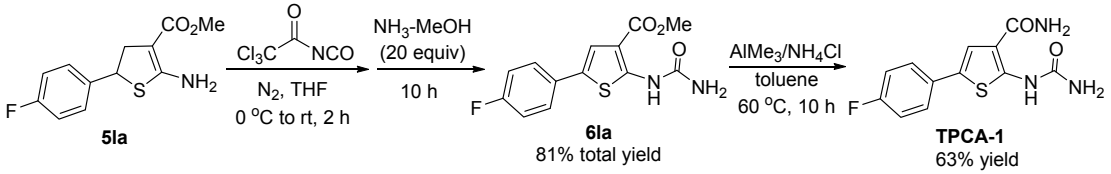
3 **5**

3aa: R = Ph, R^3 = Me — **5aa**: 78% yield
3la: R = 4-FC_6H_4, R^3 = Me — **5la**: 75% yield
3ra: R = Ph, R^3 = Et — **5ra**: 78% yield
3sa: R = Ph, R^3 = Bn — **5sa**: 43% yield

In a test tube containing dihydrothiophene **3** (0.1 mmol), DCM (2.0 mL) was added, and the reaction was carried out at -20 °C. Subsequently, 2,3-dichloro-4,5-dicyanoquinone (DDQ, 34.1 mg, 0.15 mmol, 1.5 equiv) was added. The reaction was carried out at -20 °C for 2 hours. At the end of the reaction, the mixture was quenched with saturated sodium sulfite, and then extracted three times with EtOAc. The combined organic phases were washed with brine,

dried over Na_2SO_4, and the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel to afford the oxidation product **5**.[2]

5. Synthesis of TPCA-1

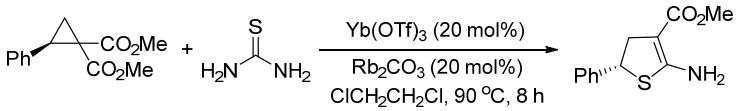


In a test tube, **5Ia** (0.1 mmol, 25.1 mg) was added, and the tube was filled with N_2 gas. Then, THF (1.0 mL) was added, and the reaction was carried out at 0 °C. Subsequently, trichloroacetyl isocyanate (0.1 mmol, 18.8 mg in 0.5 mL THF) was added. The reaction mixture was stirred for 2 hours at rt. At the end of the reaction, the mixture was concentrated on a rotary evaporator and the crude product was obtained. Next, in a seal tube containing the crude product, methanol (1.0 mL) was added, and then NH_3-CH_3OH (20 equiv.) was added. The reaction was carried out at 80 °C for 10 hours. The crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel to afford the **6Ia** as a white solid (23.8 mg, 81% total yield).

In a test tube, NH_4Cl (0.3 mmol, 16.0 mg) was added, and the tube was filled with N_2 gas. Then, toluene (1.0 mL) was added, and the reaction was carried out at 0 °C. Subsequently, $AlMe_3$ (0.3 mmol, 1.6 mol/L in toluene) was added. The reaction mixture was stirred for 2 hours at rt, then **6Ia** (0.1 mmol, 29.4 mg) was added. The reaction mixture was stirred for 10 hours at 60 °C. At the end of the reaction, the mixture was quenched with saturated water and then extracted three times with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography to afford the **TPCA-1** as a white solid (17.6 mg, 63% yield).

6. Stereospecificity experiments

6.1 Synthesis of chiral 2-amino-4,5-dihydrothiophene (*S*)-3aa



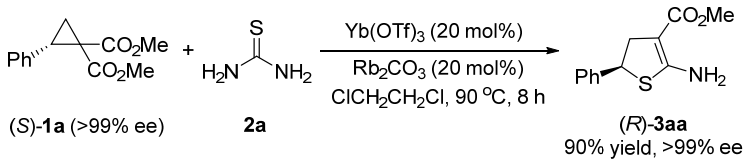
In a test tube, cyclopropane (*R*)-**1a** (0.2 mmol, 47 mg),[3] thiourea **2a** (2 equiv, 0.4 mmol, 30.5 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end

of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1) to afford product (*S*)-**3aa** as a white solid (43.2 mg, 92% yield, 99% ee).

The ee value was determined by HPLC and the absolute configuration of (*S*)-**3aa** was unambiguously determined by X-ray analysis.

(*S*)-**3aa**: HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, λ = 250 nm, retention time: 22.009 min (minor), 37.428 min (major). $[\alpha]_D^{25.5}$ = -227.1 (c = 0.34, CH_2Cl_2).

6.2 Synthesis of chiral 2-amino-4,5-dihydrothiophene (*R*)-3aa



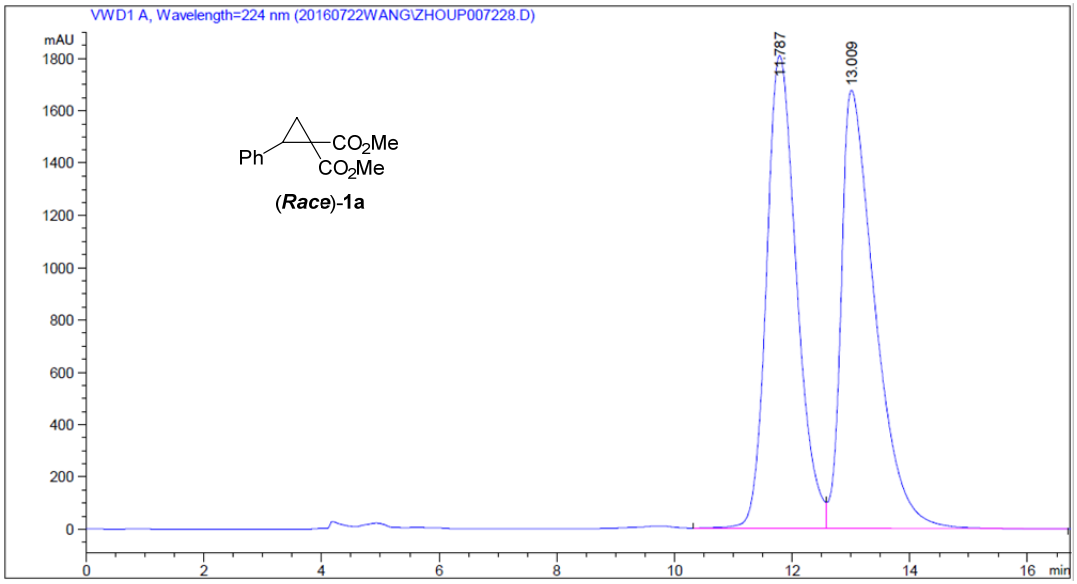
(*S*)-**1a** (>99% ee) **2a** (*R*)-**3aa** 90% yield, >99% ee

In a test tube, cyclopropane (*S*)-**1a** (0.2 mmol, 47 mg),[3] thiourea **2a** (2 equiv, 0.4 mmol, 30.5 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) was added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1) to afford product (*R*)-**3aa** as a white solid (42.3 mg, 90% yield, 99% ee).

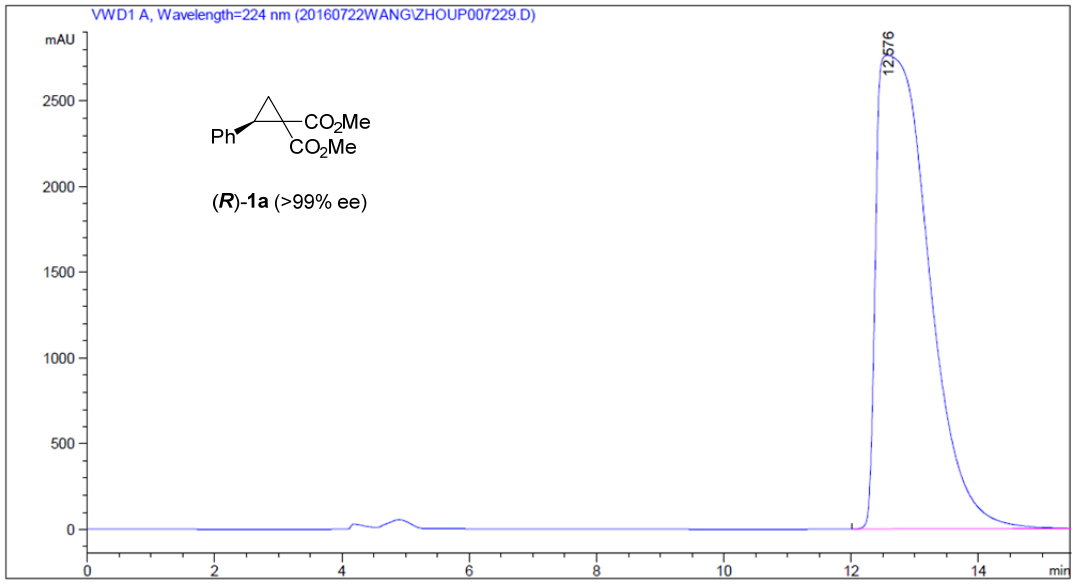
The ee value was determined by HPLC analysis.

(*R*)-**3aa**: HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, λ = 250 nm, retention time: 22.229 min (major), 40.140 min (minor). $[\alpha]_D^{25.5}$ = +225.3 (c = 0.35, CH_2Cl_2).

6.3. Copies of HPLC spectra for 1a



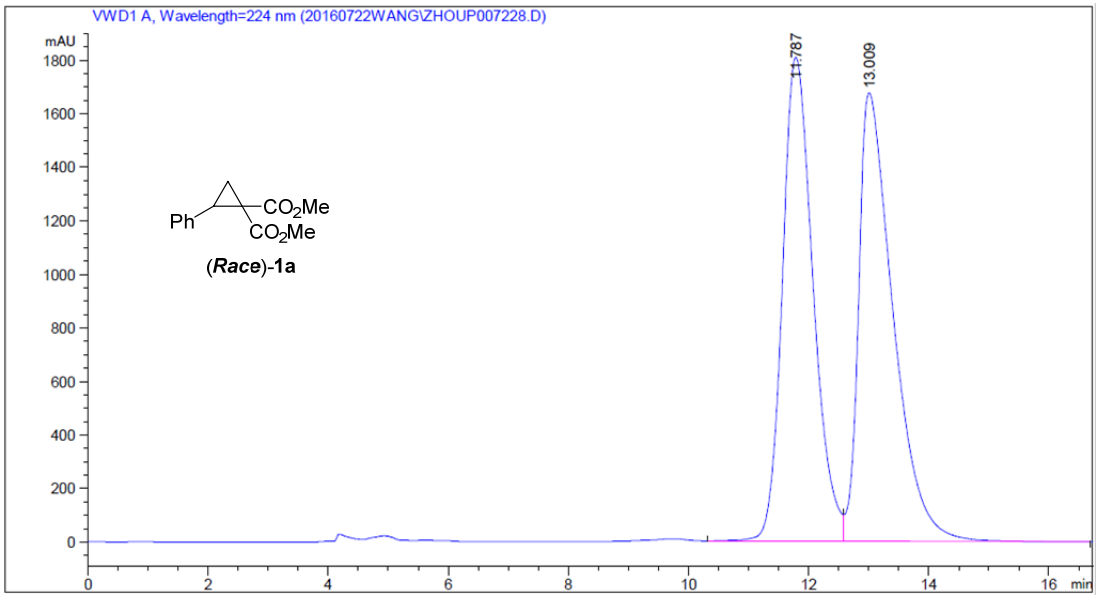
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.787	BV	0.5442	6.42209e4	1807.25903	49.0863
2	13.009	VBA	0.5919	6.66118e4	1675.51978	50.9137



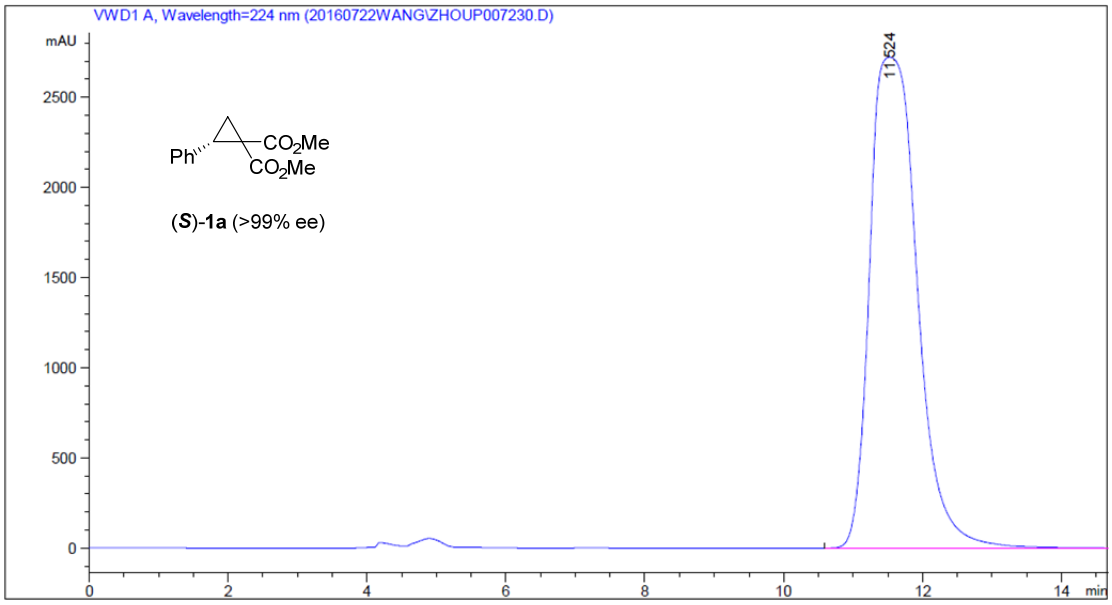
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.576	BBA	0.8936	1.58250e5	2764.23608	100.0000

The ee value of (*R*)-**1a** was determined by HPLC analysis.

HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 99/1, flow rate = 0.8 mL/min, λ = 224 nm, retention time: 12.576 min (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.787	BV	0.5442	6.42209e4	1807.25903	49.0863
2	13.009	VBA	0.5919	6.66118e4	1675.51978	50.9137

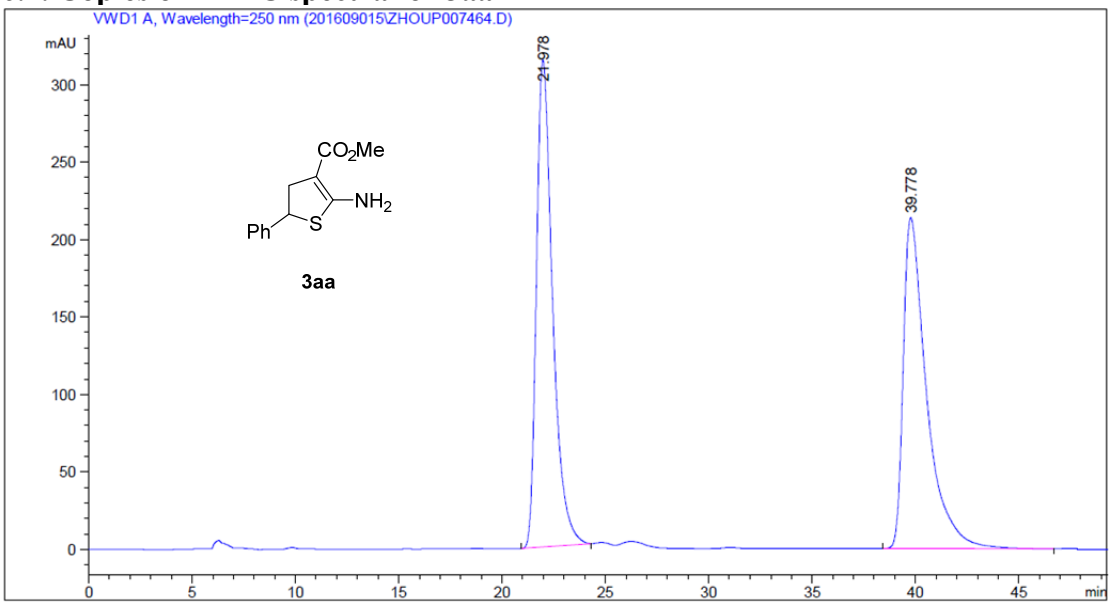


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.524	BBA	0.7384	1.29195e5	2723.44653	100.0000

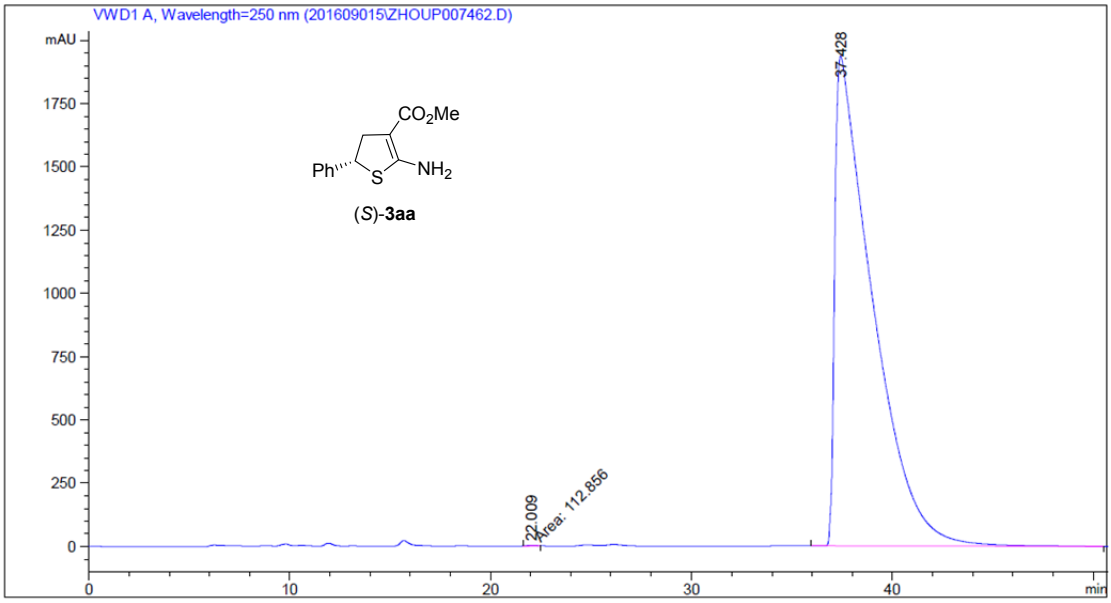
The ee value of (*S*)-**1a** was determined by HPLC analysis.

HPLC CHIRALCEL OD-H, n-hexane/2-propanol = 99/1, flow rate = 0.8 mL/min, λ = 224 nm, retention time: 11.524 min (major).

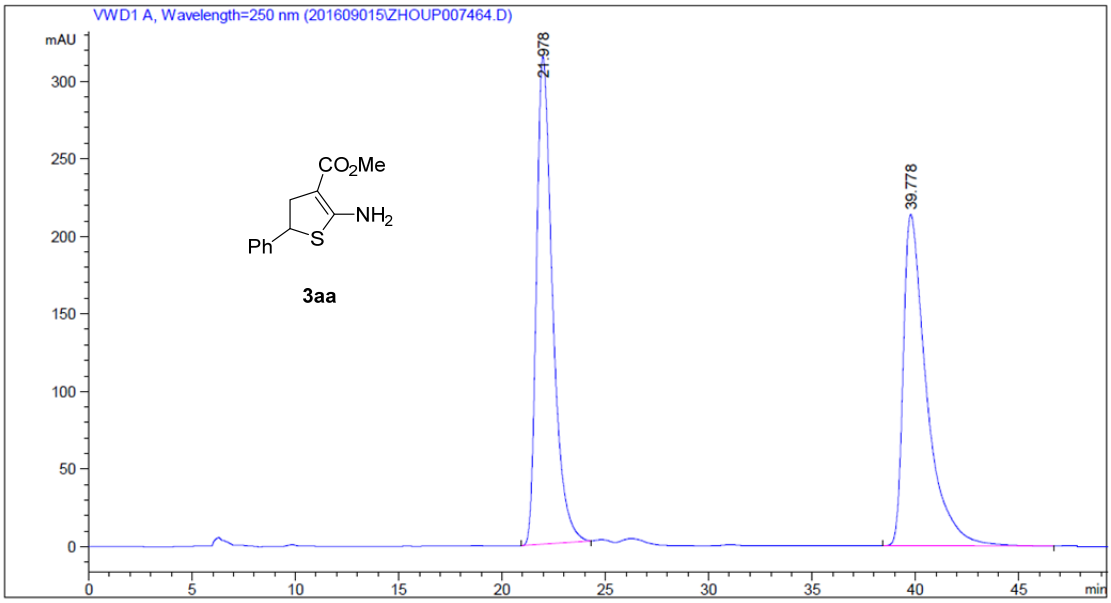
6.4. Copies of HPLC spectra for 3aa



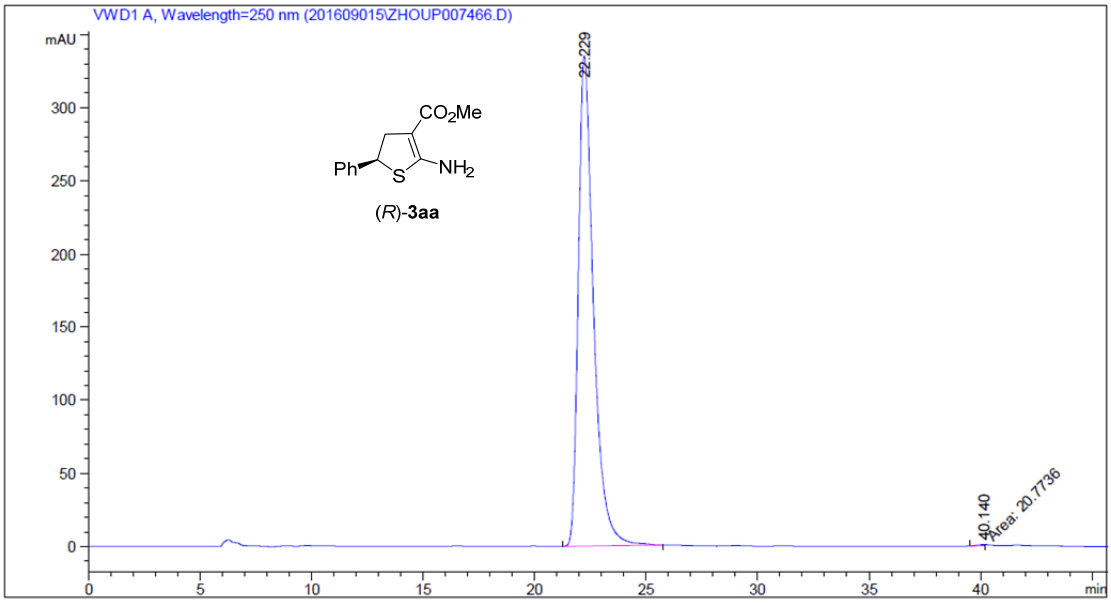
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.978	BB	0.8164	1.71066e4	314.61096	50.5080
2	39.778	BB	1.1501	1.67625e4	213.57420	49.4920



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.009	MM	0.4998	112.85564	3.76369	0.0447
2	37.428	BB	1.6845	2.52432e5	1937.56384	99.9553



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.978	BB	0.8164	1.71066e4	314.61096	50.5080
2	39.778	BB	1.1501	1.67625e4	213.57420	49.4920

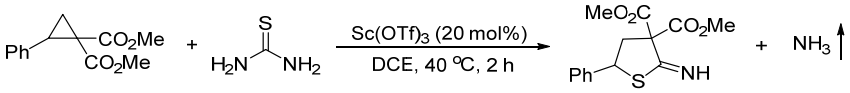


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.229	BB	0.7145	1.58800e4	335.11588	99.8694
2	40.140	MM	0.5099	20.77356	4.87168e-1	0.1306

7. Preliminary mechanistic studies

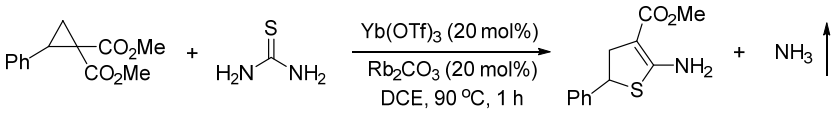
7.1 Experiments for [3+2] cycloaddition/deamination step

6.1.1 The generation of germinal diester **4aa** and detection of NH_3



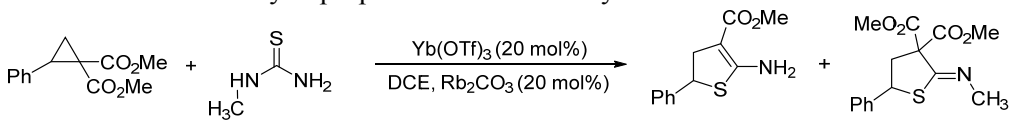
1a **2a** **4aa**, 42 % yield

6.1.2 The detection of NH_3 in the model reaction



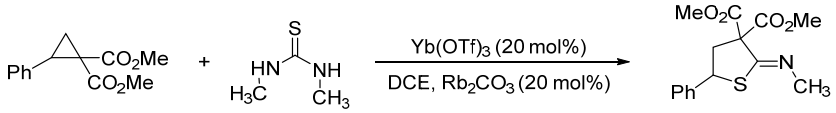
1a **2a** **3aa**

6.1.3 The reaction of cyclopropane **1a** with 1-methylthiourea **2b**



1a **2b** **3aa**, 43% yield **4ab**, 36% yield

6.1.4 The reaction of cyclopropane **1a** with 1,3-dimethylthiourea **2c**

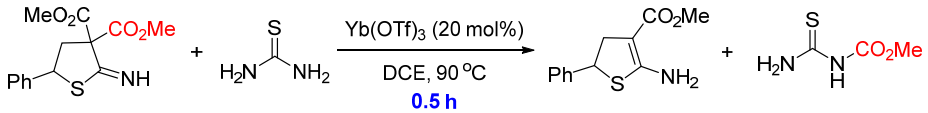


1a **2c** **4ab**, 63% yield

7.2 Experiments for decarbalkoxylation step

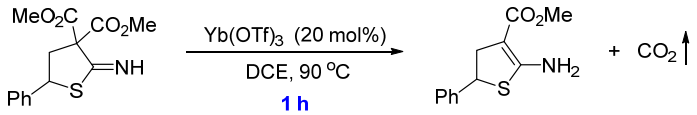
6.2.1 Comparison the reaction rates in the decarbalkoxylation step

a) With thiourea



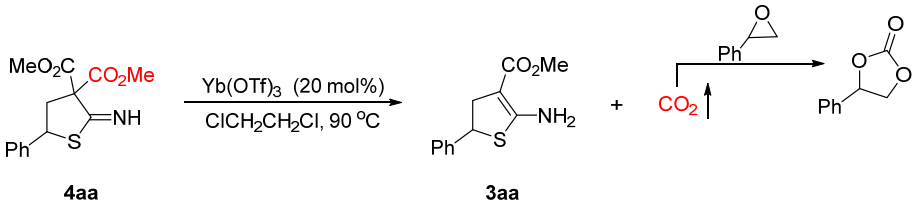
4aa **2a** **3aa**, 87% yield **7aa**, 52% yield

b) Without thiourea



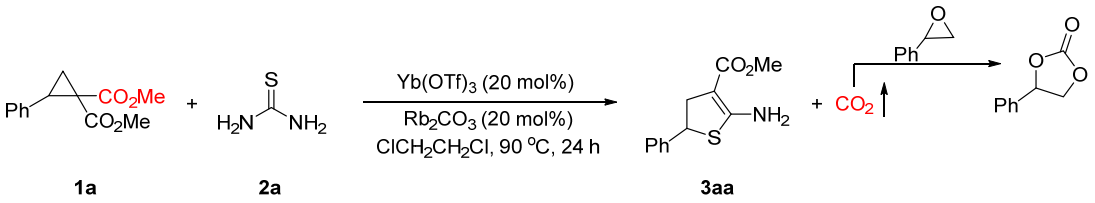
4aa **3aa**, 85% yield

6.2.2 Capture CO_2 experiments



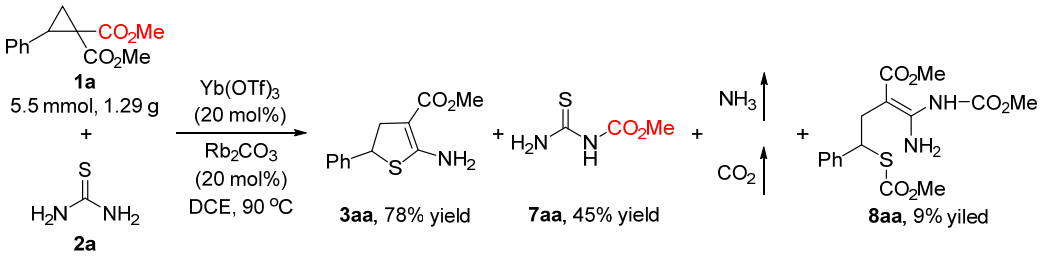
4aa **3aa**

6.2.3 The CO_2 was captured by model reaction

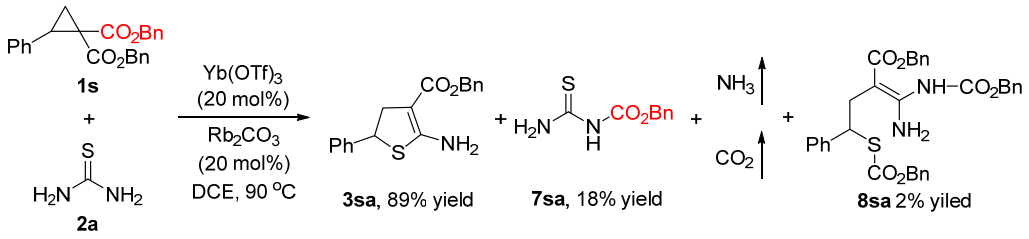


7.3 [3+2] cycloaddition/deamination/decarbalkoxylation process

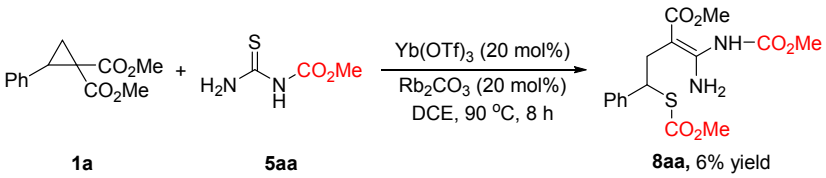
6.3.1 The reaction of cyclopropane **1a** with thiourea **2a**



6.3.2 The reaction of cyclopropane **1s** with thiourea **2a**

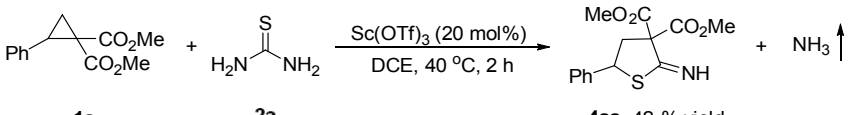


7.4 The reaction of 1a with esterified 5aa



7.1 Experiments for [3+2] cycloaddition/deamination step

7.1.1 The generation of germinal diester **4aa** and detection of NH_3



1a **2a** **4aa**, 42 % yield

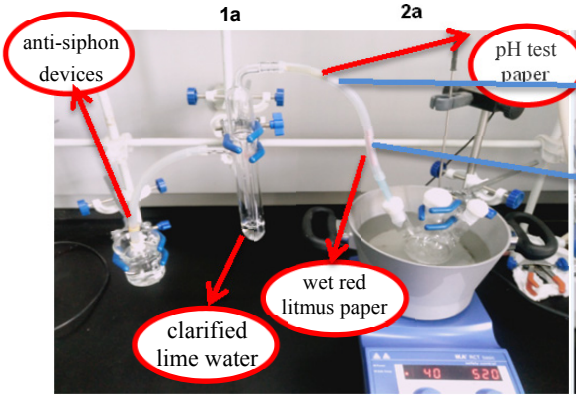


Figure S1. Before the reaction

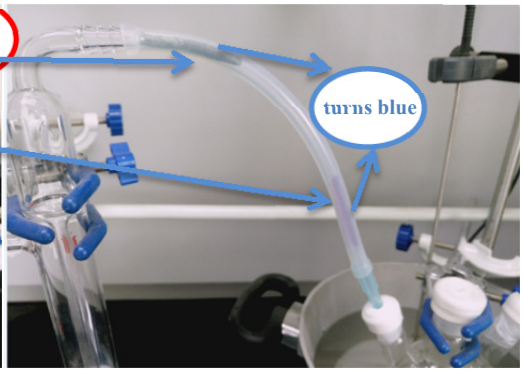


Figure S2. 2 hours later (Partial magnification)

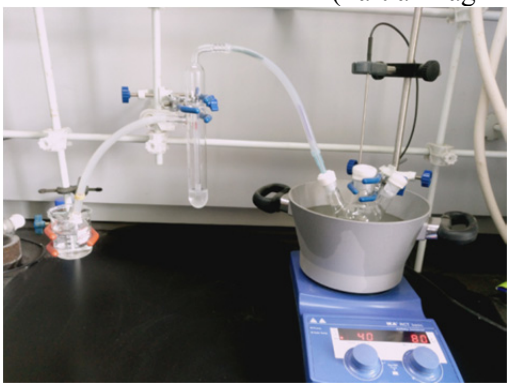
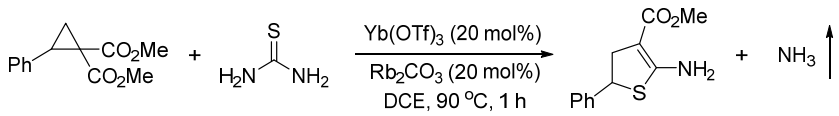


Figure S3. 2 hours later (Full view)

To a 50 mL three-necked bottle with a stir bar, cyclopropanes **1a** (5.5 mmol, 1.2884 g), thiourea **2a** (2 equiv, 11 mmol, 0.8370 g), and $Sc(OTf)_3$ (20 mol%, 1.1 mmol, 0.5410 g) were added. Then DCE (25 mL) was added to the bottle. The reaction was carried out at 40 °C. Meanwhile, the reaction bottle was connected to the clarified lime water and an anti-siphon device (Figure S1). Two hours later, as shown in Figure S2, the pH test paper and wet red litmus paper turned blue. Thus, NH_3 gas was detected to be released in the reaction. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 3/1) to afford the germinal diester **4aa** product as a colorless oil (676 mg, 2.3 mmol, 42% yield).

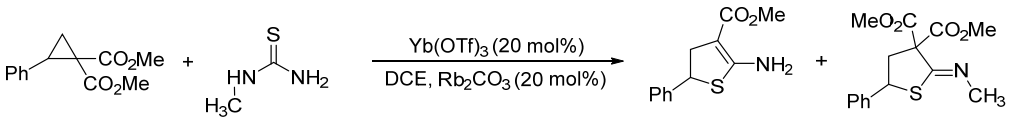
7.1.2 The detection of NH_3 in the model reaction



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

In a 100 mL two-necked bottle with a stir bar, cyclopropane **1a** (5.5 mmol, 1.2884 g), thiourea **2a** (2 equiv, 11 mmol, 0.8370 g), $Yb(OTf)_3$ (20 mol%, 1.1 mmol, 0.6822 g), and Rb_2CO_3 (20 mol%, 1.1 mmol, 0.2540 g) were added. The reaction was performed in DCE (40 mL) at 90 °C. The reaction bottle was connected to clarified lime water and anti-siphon devices. The pH test paper and wet red litmus paper turned blue. So we can prove that NH_3 was released in the reaction. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1) to afford product **3aa** as a white solid (0.6720 g, 2.86 mmol, 52% yield).

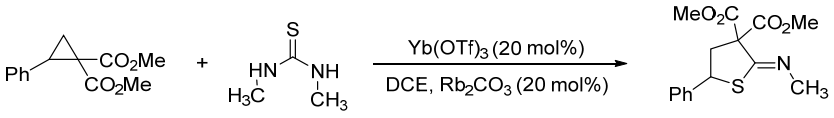
7.1.3 The reaction of cyclopropane 1a with 1-methylthiourea 2b



1a **2b** **3aa**, 43% yield **4ab**, 36% yield

In a test tube, cyclopropane **1a** (0.2 mmol, 46.8 mg), 1-methylthiourea **2b** (2 equiv, 0.4 mmol, 36.0 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 4/1) to afford monoester **3aa** as a white solid (20.2 mg, 43% yield) and germinal diester **4ab** as a colorless oil (22.1 mg, 36% yield).

7.1.4 The reaction of cyclopropane 1a with 1,3-dimethylthiourea 2c



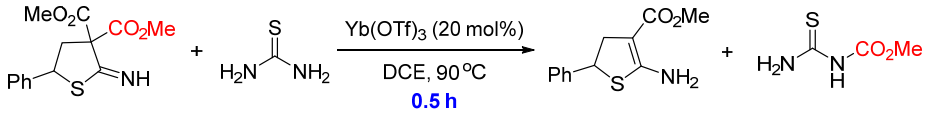
1a **2c** **4ab**, 63% yield

In a test tube, cyclopropane **1a** (0.2 mmol, 46.8 mg), 1,3-dimethylthiourea **2c** (2 equiv, 0.4 mmol, 41.6 mg), $Yb(OTf)_3$ (20 mol %, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol %, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 5/1) to afford germinal diester **4ab** as a colorless oil (38.6 mg, 63% yield).

7.2 Experiments for decarbalkoxylation step

7.2.1 Comparison the reaction rates in the decarbalkoxylation step

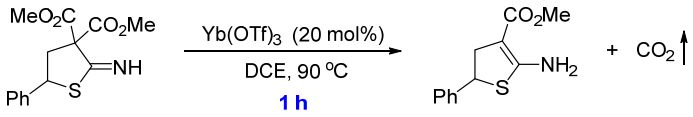
a) With thiourea



4aa **2a** **3aa**, 87% yield **7aa**, 52% yield

In a test tube, germinal diester **4aa** (0.2 mmol, 58.6 mg), thiourea **2b** (2 equiv, 0.4 mmol, 30.4 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 0.5 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1 to 3/1) to afford products **3aa** as a white solid (40.8 mg, 87% yield) and **7aa** as a white solid (13.9 mg, 52% yield).

b) Without thiourea



4aa **3aa**, 85% yield

In a test tube, germinal diester **4aa** (0.2 mmol, 58.6 mg) and $Yb(OTf)_3$ (20 mol%, 0.02 mmol, 25 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 1 hour. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 7/1) to afford the product **3aa** as a white solid (40.0 mg, 85% yield).

7.2.2 Capture CO_2 experiments

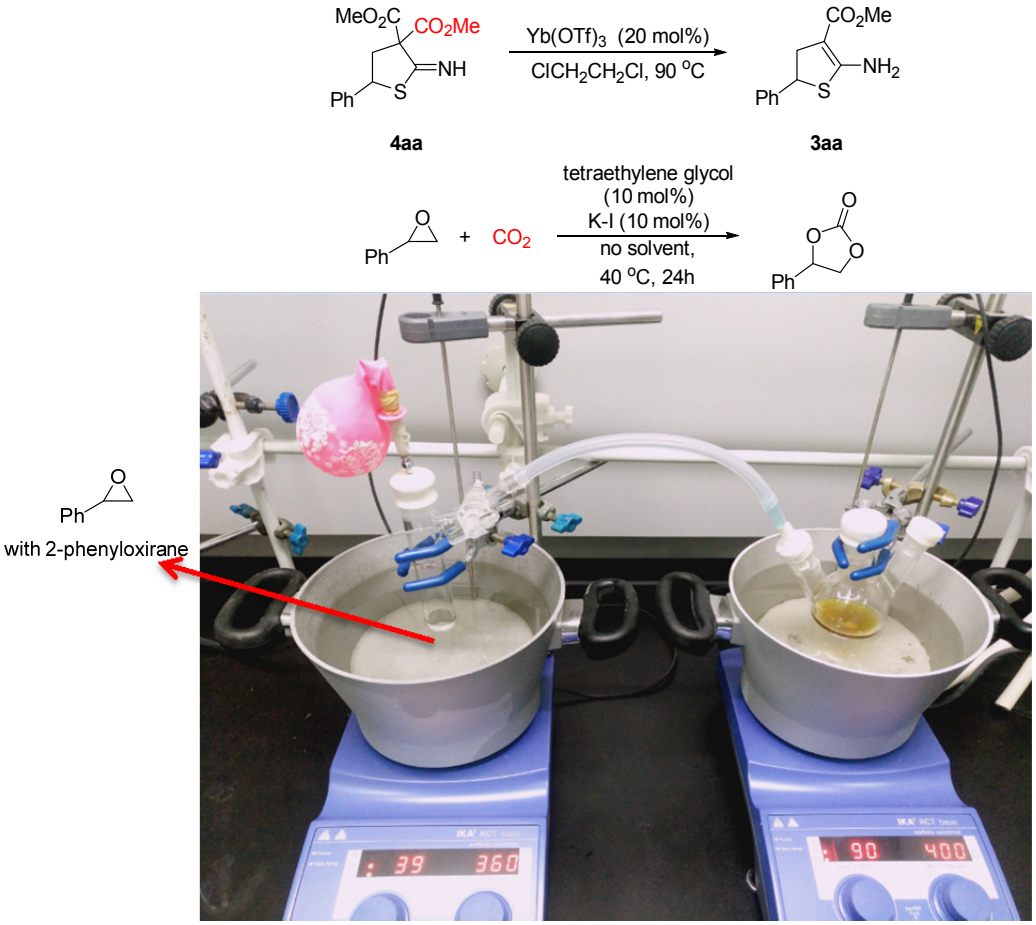
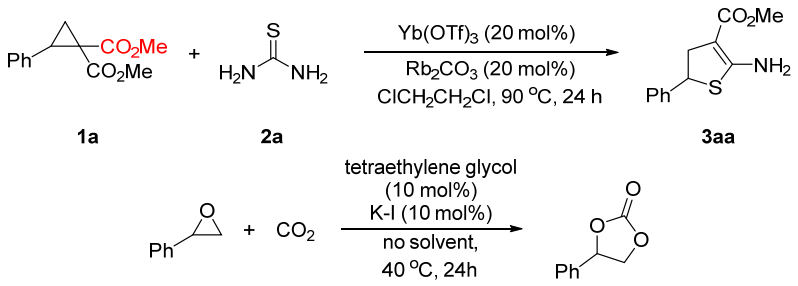


Figure S4

In a 50 mL three-necked bottle with a stir bar, germinal diester **4aa** (2.51 mmol, 735 mg) and $Yb(OTf)_3$ (20 mol%, 0.5 mmol, 311 mg) were added. The reaction was performed in DCE (25 mL) at 90 °C. As shown in Figure S4, styrene oxide (0.570 mL, 5 mmol), tetraethylene glycol (86.3 μL, 0.5 mmol, 10 mol%), and potassium iodide (83.0 mg, 0.5 mmol, 10 mol%) were added to the schlenk tube heated at 40 °C. The air of the installation was removed by the N_2 gas. After 24 hours, the reaction was determined by TLC. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 8/1) to afford the cyclic carbonate product as a colorless oil (128 mg, 0.78 mmol, 16% yield). So we can prove that CO_2 was captured in the reaction.[4] The **3aa** was directly purified by flash chromatography on silica gel (PE/EA = 7/1) as a white solid (501 mg, 2.13 mmol, 85% yield).

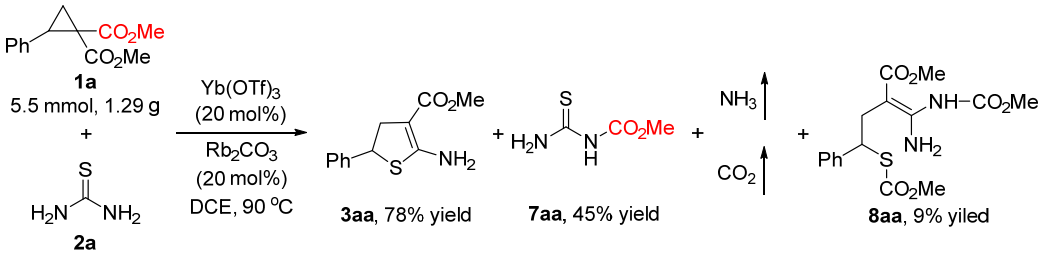
7.2.3 The CO_2 was captured by model reaction



In a two-necked bottle with a stir bar, cyclopropane **1a** (5.5 mmol, 1.2884 g), thiourea **2a** (2 equiv, 11 mmol, 0.8372 g), $Yb(OTf)_3$ (20 mol%, 1.1 mmol, 0.6822 g), and Rb_2CO_3 (20 mol%, 1.1 mmol, 0.2540 g) were added. The reaction was performed in DCE (40 mL) at 90 °C. Then, another side was connected the Schlenk tube with a stir bar, styrene oxide (0.570 mL, 5.00 mmol), tetraethylene glycol (86.3 μL, 0.500 mmol, 10 mol%), and potassium iodide (83.0 mg, 0.500 mmol, 10 mol%) were heated at 40 °C then at one end of the two neck bottle. The air of the installation was removed by the N_2 gas. As the figure S10 above shows After 24 hours, determined by TLC, at the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 8/1) to afford the cyclic carbonate product with colorless oil (32.9 mg, 0.2 mmol). So we can prove that CO_2 was released in the reaction.[4] The **3aa** was directly purified by flash chromatography on silica gel (PE/EA = 7/1) to afford as a white soild (1.02 g, 4.3 mmol, 78% yield).

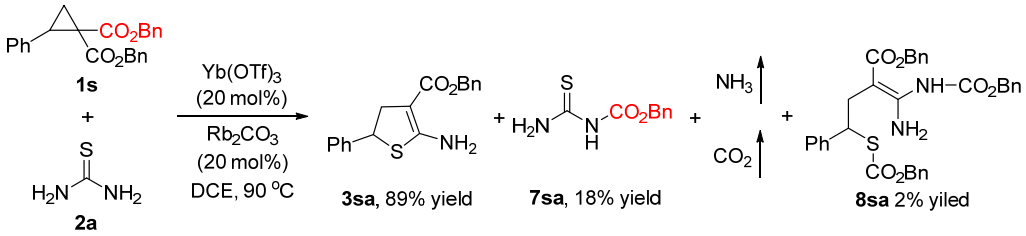
7.3 [3+2] cycloaddition/deamination/decarbalkoxylation process

7.3.1 The reaction of cyclopropane 1a with thiourea 2a



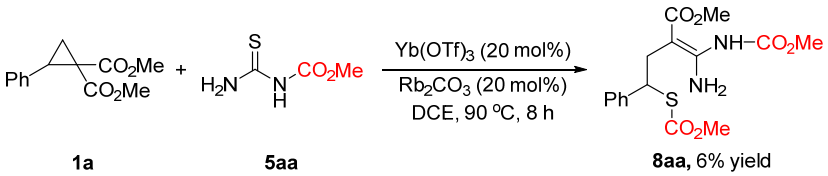
In a 100 mL two-necked bottle with a stir bar, cyclopropane **1a** (5.5 mmol, 1.2884 g), thiourea **2a** (2 equiv, 11.0 mmol, 0.8372 g), $Yb(OTf)_3$ (20 mol%, 1.1 mmol, 0.6822 g), and Rb_2CO_3 (20 mol%, 1.1 mmol, 0.2540 g) were added. The reaction was performed in DCE (40 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 8/1 to 3/1) to afford product **3aa** as a white solid (1.0092 g, 78% yield), **7aa** as a white solid (0.334 g, 45% yield), and **8aa** as a white solid (0.1830 g, 9% yield).

7.3.2 The reaction of cyclopropanes 1s with thiourea 2a



In a test tube, cyclopropane **1s** (0.2 mmol, 77.2 mg), thiourea **2a** (2 equiv, 0.4 mmol, 30.5 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 10/1 to 3/1) to afford products **3sa** as a white solid (50.4 mg, 89% yield), **7sa** as a colorless oil (7.6 mg, 18% yield) and **8sa** as a colorless oil (2.4 mg, 2% yield).

7.4 The reaction of 1a with esterified 5aa

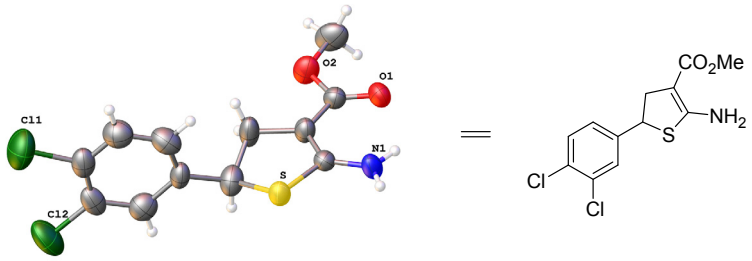


In a test tube, cyclopropane **1a** (0.2 mmol, 46.8 mg), methyl carbamothioylcarbamate **5aa** (2 equiv, 0.4 mmol, 53.6 mg), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 25 mg), and Rb_2CO_3 (20 mol%, 0.04 mmol, 9.2 mg) were added. The reaction was performed in DCE (3 mL) at 90 °C for 8 hours. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash chromatography on silica gel (PE/EA = 8/1) to afford product **8aa** as a white solid (4.4 mg, 6% yield).

8. The X-ray crystallographic data

8.1 The X-ray crystallographic data of 3na

Recrystallization in petroleum ether and ethyl acetate afforded crystals suitable for X-ray analysis**.**



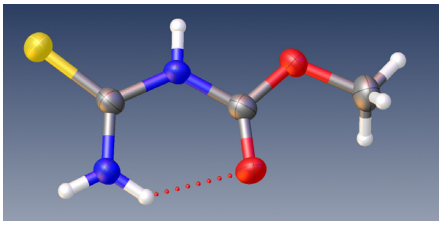
CCDC number (**3na**): 1849437

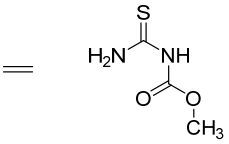
Table 1 Crystal data and structure refinement for 3na.

Identification code	T
Empirical formula	$C_{12}H_{11}Cl_2NO_2S$
Formula weight	304.20
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.687(2)
b/Å	9.6570(19)
c/Å	11.950(2)
α/°	90
β/°	96.80(3)
γ/°	90
Volume/Å^3	1339.2(5)
Z	4
ρ_{calc}g/cm^3	1.5087
μ/mm^{-1}	0.633
F(000)	625.9
Crystal size/mm^3	0.3 × 0.25 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.44 to 49.98
Index ranges	$-15 \le h \le 15$, $-10 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	11542
Independent reflections	2347 [R_{int} = 0.0235, R_{sigma} = 0.0240]
Data/restraints/parameters	2347/7/164
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0954, wR_2 = 0.2761
Final R indexes [all data]	R_1 = 0.1062, wR_2 = 0.2893
Largest diff. peak/hole / e Å^{-3}	1.34/-0.88

8.2 The X-ray crystallographic data of 7aa

Recrystallization in petroleum ether and ethyl acetate afforded crystals suitable for X-ray analysis**.**





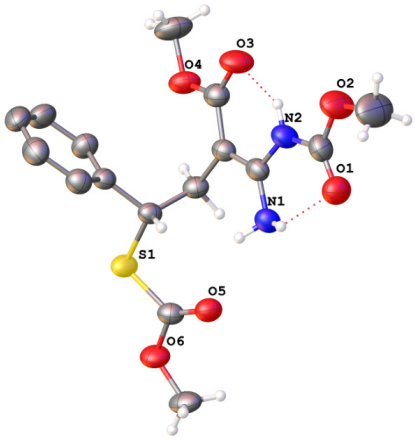
CCDC number (**7aa**): 1852129

Table 1 Crystal data and structure refinement for zgf-20180104.

Identification code	zgf-20180104
Empirical formula	$C_3H_6N_2O_2S$
Formula weight	134.16
Temperature/K	293.67(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.3625(4)
b/Å	9.5369(4)
c/Å	16.9216(7)
α/°	90
β/°	94.933(4)
γ/°	90
Volume/Å^3	1183.76(10)
Z	8
ρ_{calc}g/cm^3	1.5054
μ/mm^{-1}	0.456
F(000)	561.2
Crystal size/mm^3	0.5 × 0.4 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	7 to 50
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 12$, $-22 \le l \le 22$
Reflections collected	8001
Independent reflections	2081 [R_{int} = 0.0299, R_{sigma} = 0.0367]
Data/restraints/parameters	2081/0/147
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.0882
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	0.22/-0.25

8.3 The X-ray crystallographic data of 8aa

Recrystallization in petroleum ether and ethyl acetate afforded crystals suitable for X-ray analysis**.**



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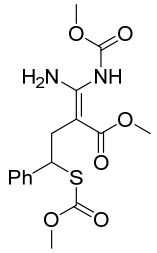


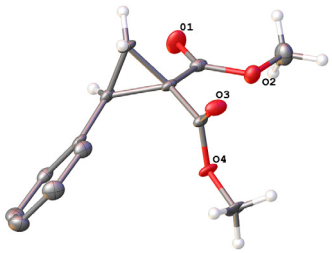
CCDC number (**8aa**): 1852131

zgf-20171208

Table 1 Crystal data and structure refinement for zgf-20171208.

Identification code	zgf-20171208
Empirical formula	C16H20N2O6S
Formula weight	368.41
Temperature/K	291.37(11)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.0809(10)
b/Å	12.1296(5)
c/Å	21.4422(10)
α/°	90
β/°	90
γ/°	90
Volume/Å3	3662.2(4)
Z	8
ρcalcg/cm3	1.3363
μ/mm-1	0.210
F(000)	1553.9
Crystal size/mm3	0.5 × 0.4 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	6.7 to 50
Index ranges	-14 ≤ h ≤ 18, -16 ≤ k ≤ 11, -28 ≤ l ≤ 23
Reflections collected	12723
Independent reflections	3212 [Rint = 0.0368, Rsigma = 0.0379]
Data/restraints/parameters	3212/0/230
Goodness-of-fit on F2	1.048
Final R indexes [I>=2σ (I)]	R1 = 0.0474, wR2 = 0.1241
Final R indexes [all data]	R1 = 0.0628, wR2 = 0.1385
Largest diff. peak/hole / e Å-3	0.31/-0.36

8.4 The X-ray crystallographic data of (*R*)-1a



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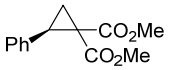
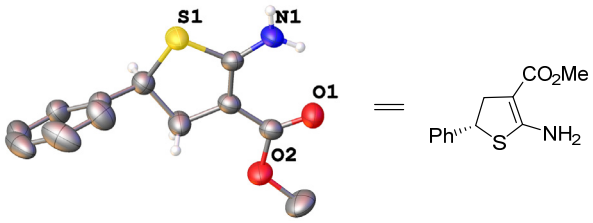


CCDC number (*R*-**1a**): 1852130

Table 1 Crystal data and structure refinement for syb-yuanliao-r -.

Identification code	syb-yuanliao-r -
Empirical formula	$C_{13}H_{14}O_4$
Formula weight	234.24
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.91560(10)
b/Å	9.8147(2)
c/Å	15.3289(2)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1190.89(3)
Z	4
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	0.804
F(000)	496.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.7 to 145.68
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 12$, $-18 \le l \le 18$
Reflections collected	33543
Independent reflections	2353 [R_{int} = 0.0507, R_{sigma} = 0.0168]
Data/restraints/parameters	2353/0/157
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0856
Largest diff. peak/hole / e Å^{-3}	0.27/-0.23
Flack parameter	0.01(17)

8.5 The X-ray crystallographic data of (*S*)-3aa



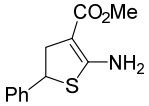
CCDC number (*S*-**3aa**): 1852128

Table 1 Crystal data and structure refinement for SYB-CHANWU-1.

Identification code	SYB-CHANWU-1
Empirical formula	$C_{12}H_{13}NO_2S$
Formula weight	235.29
Temperature/K	294
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.5830(2)
b/Å	6.1506(1)
c/Å	25.4866(5)
α/°	90
β/°	95.003(2)
γ/°	90
Volume/Å^3	1184.17(4)
Z	2
ρ_{calc}g/cm^3	1.3198
μ/mm^{-1}	2.310
F(000)	498.8
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.96 to 146.08
Index ranges	$-9 \le h \le 8$, $-7 \le k \le 7$, $-31 \le l \le 31$
Reflections collected	22056
Independent reflections	4627 [R_{int} = 0.0467, R_{sigma} = 0.0374]
Data/restraints/parameters	4627/1/291
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0453, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23
Flack parameter	0.007(18)

9. The analytical and spectral characterization data for the products

Methyl 2-amino-5-phenyl-4,5-dihydrothiophene-3-carboxylate (3aa)



White solid. 39.5 mg, 84% yield. m.p. 114～115 °C;

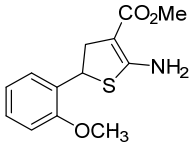
TLC: R_f = 0.55 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.44 (m, 2H), 7.30-7.36 (m, 2H), 7.26-7.30 (m, 1H), 6.16 (br, 2H), 4.85 (t, *J* = 8.4 Hz, 1H), 3.69 (s, 3H), 3.39 (dd, *J* = 13.8, 8.4 Hz, 1H), 3.15 (dd, *J* = 14.4, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 162.6, 141.6, 128.7, 127.8, 127.2, 90.6, 51.4, 50.6, 41.5.

HRMS: exact mass calcd for $C_{12}H_{13}NO_2S$ $(M+Na)^+$: requires m/z 258.0559, found m/z 258.0549.

Methyl 2-amino-5-(2-methoxyphenyl)-4,5-dihydrothiophene-3-carboxylate (3ba)



White solid. 40.3 mg, 76% yield. m.p. 106～107 °C;

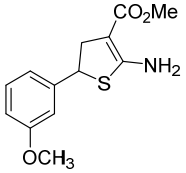
TLC: R_f = 0.50 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.26-7.22 (m, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.05 (br, 2H), 5.15 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.35 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.17 (dd, *J* = 14.4, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 163.0, 156.5, 130.1, 128.8, 127.0, 120.8, 110.4, 91.0, 55.6, 50.6, 44.1, 38.7.

HRMS: exact mass calcd for $C_{13}H_{15}NO_3S$ $(M+H)^+$: requires m/z 266.0845, found m/z 266.0835.

Methyl 2-amino-5-(3-methoxyphenyl)-4,5-dihydrothiophene-3-carboxylate (3ca)



White solid. 34.5 mg, 65% yield. m.p. 97～98 °C;

TLC: R_f = 0.60 (petroleum ether: ethyl acetate = 4:1) [UV].

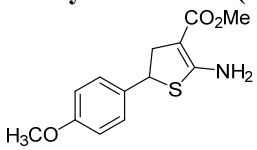
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.8 Hz, 1H), 7.01-6.95 (m, 2H), 6.81 (dd, *J* = 8.4,

1.8 Hz, 1H), 6.11 (br, 2H), 4.82 (t, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.38 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.14 (dd, *J* = 14.4, 7.8 Hz, H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 162.4, 159.9, 143.2, 129.8, 119.7, 113.2, 113.1, 90.9, 55.4, 51.5, 50.6, 41.5.

HRMS: exact mass calcd for $C_{13}H_{15}NO_3S$ $(M+H)^+$: requires m/z 266.0845, found m/z 266.0848.

Methyl 2-amino-5-(4-methoxyphenyl)-4,5-dihydrothiophene-3-carboxylate (3da)



White solid. 43.5 mg, 82% yield. m.p. 85～86 °C;

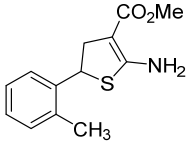
TLC: R_f = 0.51 (petroleum ether: ethyl acetate = 5:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.37 (m, 2H), 6.82-6.89 (m, 2H), 6.08 (br, 2H), 4.83 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.35 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.13 (dd, *J* = 14.4, 7.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 162.6, 159.3, 133.6, 128.5, 114.2, 90.9, 55.4, 51.3, 50.6, 41.7.

HRMS: exact mass calcd for $C_{13}H_{15}NO_3S$ $(M+H)^+$: requires m/z 266.0845, found m/z 266.0836.

Methyl 2-amino-5-(2-bromophenyl)-4,5-dihydrothiophene-3-carboxylate (3ea)



White solid. 40.8 mg, 82% yield. m.p. 103～104 °C;

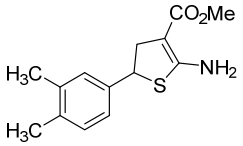
TLC: R_f = 0.43 (petroleum ether: ethyl acetate = 3:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.23-7.14 (m, 3H), 6.12 (br, 2H), 5.05 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.70 (s, 3H), 3.38 (dd, *J* = 14.4, 9.0 Hz, 1H), 3.16 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 162.6, 139.5, 135.4, 130.6, 127.7, 126.7, 126.6, 91.0, 50.6, 47.5, 40.1, 19.7.

HRMS: exact mass calcd for $C_{13}H_{15}NO_2S$ $(M+Na)^+$: requires m/z 272.0716, found m/z 272.0725.

Methyl 2-amino-5-(3,4-dimethylphenyl)-4,5-dihydrothiophene-3-carboxylate (3fa)



White solid. 43.7 mg, 83% yield. m.p. 116～117 °C;

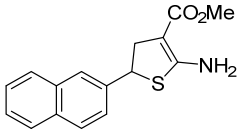
TLC: R_f = 0.55 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (s, 1H), 7.13-7.17 (m, 1H), 7.06-7.11 (m, 1H), 6.09 (br, 2H), 4.83 (t, *J* = 7.8 Hz, 1H), 3.69 (s, 3H), 3.36 (dd, *J* = 13.8, 8.4 Hz, 1H), 3.15 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 162.7, 138.9, 137.0, 136.4, 130.0, 128.6, 124.7, 90.9, 51.5, 50.6, 41.5, 19.9, 19.5.

HRMS: exact mass calcd for $C_{14}H_{17}NO_2S$ $(M+H)^+$: requires m/z 264.1053, found m/z 264.1061.

Methyl 2-amino-5-(naphthalen-2-yl)-4,5-dihydrothiophene-3-carboxylate (3ga)



White solid. 48.4 mg, 85% yield. m.p. 126～127 °C;

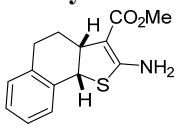
TLC: R_f = 0.44 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 6.15 (br, 2H), 5.63 - 5.54 (m, 1H), 3.71 (s, 3H), 3.54 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.38 (dd, *J* = 14.4, 6.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 162.7, 136.5, 134.0, 130.9, 129.2, 128.5, 126.5, 125.9, 125.6, 124.3, 123.0, 91.1, 50.7, 47.4, 39.7.

HRMS: exact mass calcd for $C_{16}H_{15}NO_2S$ $(M+Na)^+$: requires m/z 308.0716, found m/z 308.0713.

Methyl 2-amino-3a,4,5,9b-tetrahydronaphtho[1,2-*b*]thiophene-3-carboxylate (3ha)



White solid. 22.4 mg, 43% yield, >20:1 dr. m.p. 84～85 °C;

TLC: R_f = 0.55 (petroleum ether: ethyl acetate = 5:1) [UV].

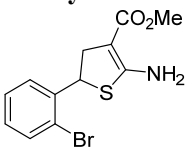
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21-7.19 (m, 1H), 7.15-7.13 (m, 2H), 6.98-6.96 (d, *J* = 7.8 Hz, 1H), 6.29 (br, 2H), 4.64 (d, *J* = 12.6 Hz, 1H), 3.73 (s, 3H), 3.11-3.06 (m, 1H), 3.03-3.00 (m, 2H), 2.93-2.89 (m, 1H), 1.78-1.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 165.1, 136.6, 135.3, 129.0, 127.5, 126.4, 125.9, 96.2,

57.0, 50.7, 50.4, 29.0, 28.0.

HRMS: exact mass calcd for $C_{14}H_{15}NO_2S$ $(M+H)^+$: requires m/z 262.0896, found m/z 262.0895.

Methyl 2-amino-5-(2-bromophenyl)-4,5-dihydrothiophene-3-carboxylate (3ia)



White solid. 49.4 mg, 79% yield. m.p. 115～116 °C;

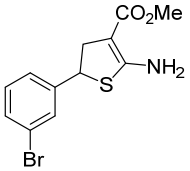
TLC: R_f = 0.50 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.08 (br, 2H), 5.13 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.70 (s, 3H), 3.45 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.12 (dd, *J* = 14.4, 4.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 162.2, 141.2, 133.0, 129.2, 128.1, 128.0, 123.9, 90.7, 50.7, 49.5, 39.5.

HRMS: exact mass calcd for $C_{12}H_{12}BrNO_2S$ $(M+Na)^+$: requires m/z 335.9664, found m/z 335.9674.

Methyl 2-amino-5-(3-bromophenyl)-4,5-dihydrothiophene-3-carboxylate (3ja)



White solid. 45.6 mg, 73% yield. m.p. 101～102 °C;

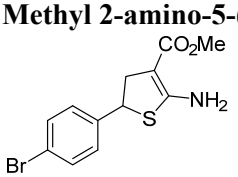
TLC: R_f = 0.62 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.10 (br, 2H), 4.73-4.82 (m, 1H), 3.69 (s, 3H), 3.40 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.10 (dd, *J* = 14.0, 6.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 162.0, 144.2, 131.0, 130.4, 130.4, 125.9, 122.8, 90.5, 50.7, 50.5, 41.6.

HRMS: exact mass calcd for $C_{12}H_{12}BrNO_2S$ $(M+Na)^+$: requires m/z 335.9664, found m/z 335.9664.

Methyl 2-amino-5-(4-bromophenyl)-4,5-dihydrothiophene-3-carboxylate (3ka)



White solid. 46.9 mg, 75% yield. m.p. 144～145 °C;

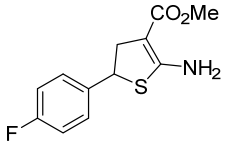
TLC: R_f = 0.56 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.47 (m, 2H), 7.26-7.31 (m, 2H), 6.11 (br, 2H), 4.80-4.74 (m, 1H), 3.68 (s, 3H), 3.39 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.09 (dd, *J* = 14.0, 6.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 162.1, 140.9, 131.9, 129.0, 121.7, 90.5, 50.7, 50.6, 41.5.

HRMS: exact mass calcd for $C_{12}H_{12}BrNO_2S$ $(M+Na)^+$: requires m/z 355.9664, found m/z 355.9675.

Methyl 2-amino-5-(4-fluorophenyl)-4,5-dihydrothiophene-3-carboxylate (3la)



White solid. 36.4 mg, 72% yield. m.p. 95～96 °C;

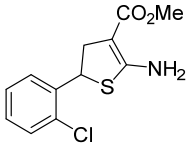
TLC: R_f = 0.45 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.34 (m, 2H), 7.04 - 6.95 (m, 2H), 6.12 (br, 2H), 4.81 (t, *J* = 8.0, 1H), 3.69 (s, 3H), 3.39 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.10 (dd, *J* = 14.4, 7.2 Hz, 1H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 163.2, 162.3, 161.5, 137.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.0 Hz), 90.6, 50.7, 41.8.

HRMS: exact mass calcd for $C_{12}H_{12}FNO_2S$ $(M+H)^+$: requires m/z 254.0646, found m/z 264.0645.

Methyl 2-amino-5-(2-chlorophenyl)-4,5-dihydrothiophene-3-carboxylate (3ma)



White solid. 33.4 mg, 62% yield. m.p. 119～120 °C;

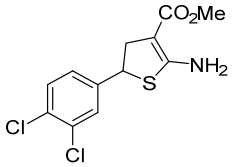
TLC: R_f = 0.55 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.26-7.30 (m, 1H), 77.20-7.24 (m, 1H), 6.11 (br, 2H), 5.18 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.72 (s, 3H), 3.45 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.14 (dd, *J* = 14.4, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 162.2, 139.5, 133.2, 129.6, 128.9, 127.9, 127.5, 90.7, 50.7, 46.8, 39.4.

HRMS: exact mass calcd for $C_{12}H_{12}ClNO_2S$ $(M+H)^+$: requires m/z 270.0350, found m/z 270.0342.

Methyl 2-amino-5-(3, 4-dichlorophenyl)-4,5-dihydrothiophene-3-carboxylate (3na)



White solid. 52.1 mg, 86% yield. m.p. 123～124 °C;

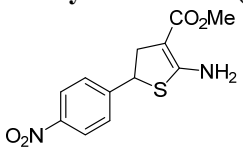
TLC: R_f = 0.40 (petroleum ether: ethyl acetate = 7:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.21-7.26 (m, 1H), 6.12 (br, 2H), 4.73 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.68 (s, 3H), 3.40 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.08 (dd, *J* = 14.4, 6.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 161.7, 142.3, 132.8, 131.9, 130.8, 129.3, 126.6, 90.3, 50.7, 49.8, 41.5.

HRMS: exact mass calcd for $C_{12}H_{11}Cl_2NO_2S$ $(M+Na)^+$: requires m/z 325.9780, found m/z 325.9775.

Methyl 2-amino-5-(4-nitrophenyl)-4,5-dihydrothiophene-3-carboxylate (3oa)



Red solid. 37.5 mg, 67% yield. m.p. 75～76 °C

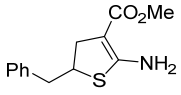
TLC: R_f = 0.44 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.13 (br, 2H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.69 (s, 3H), 3.49 (dd, *J* = 14.4, 9.0 Hz, 1H), 3.11 (dd, *J* = 14.4, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5, 161.4, 149.5, 147.5, 128.1, 124.2, 90.3, 50.8, 49.9, 41.4.

HRMS: exact mass calcd for $C_{12}H_{12}N_2O_4S$ $(M+Na)^+$: requires m/z 303.0410, found m/z 303.0412.

Methyl 2-amino-5-benzyl-4,5-dihydrothiophene-3-carboxylate (3pa)



Colorless oil, 39.8 mg, 80% yield;

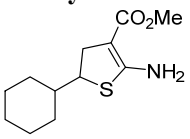
TLC: R_f = 0.33 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.39 (m, 2H), 7.27-7.31 (m, 1H), 7.20-7.25 (m, 2H), 6.08 (br, 2H), 3.91-4.01 (m, 1H), 3.72 (s, 3H), 2.97-3.15 (m, 3H), 2.82 (dd, *J* = 14.0, 6.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 162.6, 139.1, 129.1, 128.6, 126.8, 90.9, 50.5, 50.0, 42.4, 38.5.

HRMS: exact mass calcd for $C_{13}H_{15}NO_2S$ $(M+H)^+$: requires m/z 250.0896, found m/z 250.0892.

Methyl 2-amino-5-cyclohexyl-4, 5-dihydrothiophene-3-carboxylate (3qa)



White solid. 39.5 mg, 82% yield. m.p. 63～64 °C;

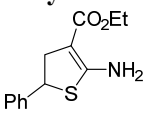
TLC: R_f = 0.42 (petroleum ether: ethyl acetate = 10:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (br, 2H), 3.66 (s, 3H), 3.59 (q, *J* = 8.4 Hz, 1H), 3.02 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.73 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.63-1.82 (m, 5H), 1.47-1.57 (m, 1H), 0.90-1.26 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 163.0, 91.7, 55.6, 50.5, 43.4, 36.9, 31.7, 30.8, 26.3, 26.1, 26.0.

HRMS: exact mass calcd for $C_{12}H_{19}NO_2S$ $(M+Na)^+$: requires m/z 264.1029, found m/z 264.1033.

Ethyl 2-amino-5-phenyl-4,5-dihydrothiophene-3-carboxylate (3ra)



White solid. 43.3 mg, 87% yield. m.p. 85～86 °C;

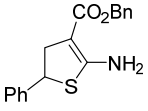
TLC: R_f = 0.46 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.47 (m, 2H), 7.26-7.37 (m, 2H), 6.11 (br, 2H), 4.86 (t, *J* = 8.4 Hz, 1H), 4.22-4.09 (m, 2H), 3.40 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.15 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 162.2, 141.6, 128.8, 127.9, 127.3, 91.6, 59.2, 51.5, 41.7, 14.7.

HRMS: exact mass calcd for $C_{13}H_{15}NO_2S$ $(M+H)^+$: requires m/z 250.0896, found m/z 250.0888.

Phenyl 2-amino-5-phenyl-4,5-dihydrothiophene-3-carboxylate (3sa)



White solid. 55.4 mg, 89% yield. m.p. 58～59 °C;

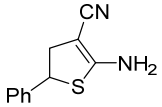
TLC: R_f = 0.52 (petroleum ether: ethyl acetate = 4:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.44 (m, 2H), 7.27-7.37 (m, 8H), 6.10 (br, 2H), 5.15 (q, *J* = 12.6 Hz, 2H), 4.88 (t, *J* = 7.8 Hz, 1H), 3.45 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.19 (dd, *J* = 14.4, 7.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 163.0, 141.4, 137.2, 128.8, 128.6, 127.96, 127.91, 127.8, 127.4, 90.8, 65.0, 51.7, 41.7.

HRMS: exact mass calcd for $C_{18}H_{17}NO_2S$ $(M+Na)^+$: requires m/z 334.0872, found m/z 334.0872.

2-amino-5-phenyl-4,5-dihydrothiophene-3-carbonitrile (3ta)



White solid. 22.6 mg, 56% yield. m.p. 78～80 °C;

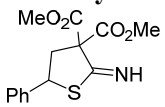
TLC: R_f = 0.32 (petroleum ether: ethyl acetate = 6:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.44 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.33-7.28 (m, 1H), 4.98 (t, *J* = 7.8 Hz, 1H), 4.72 (s, 2H), 3.31 (dd, *J* = 13.8, 8.4 Hz, 1H), 3.13 (dd, *J* = 13.8, 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 140.1, 129.0, 128.4, 127.3, 117.7, 70.1, 53.6, 42.3.

HRMS: exact mass calcd for $C_{11}H_{10}N_2S$ $(M+Na)^+$: requires m/z 225.0457, found m/z 225.0457.

Dimethyl 2-imino-5-phenyldihydrothiophene-3,3(2*H*)-dicarboxylate (4aa)



Colorless oil, 676.0 mg, 42% yield.

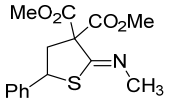
TLC: R_f = 0.30 (petroleum ether: ethyl acetate = 2:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (br, 1H), 7.40-7.48 (m, 2H), 7.29-7.40 (m, 3H), 4.84 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.14 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.97 (br, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 129.1, 128.6, 127.8, 90.6, 54.0, 53.7, 45.5.

HRMS: exact mass calcd for $C_{14}H_{15}NO_4S$ $(M+Na)^+$: requires m/z 316.0614, found m/z 316.0605.

Dimethyl (*Z*)-2-(methylimino)-5-phenyldihydrothiophene-3,3(2*H*)-dicarboxylate (4ab)



Colorless oil, 22.1 mg, 36% yield

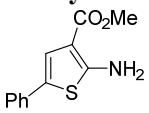
TLC: R_f = 0.32 (petroleum ether: ethyl acetate = 5:1) [UV];

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.46 (m, 2H), 7.35-7.39 (m, 2H), 7.29-7.34 (m, 1H), 4.72 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.25 (s, 3H), 3.12 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.91 (t, *J* = 12.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 168.2, 167.9, 138.0, 129.0, 128.6, 127.8, 70.8, 53.9, 53.8, 50.9, 44.7, 44.0.

HRMS: exact mass calcd for $C_{15}H_{17}NO_4S$ $(M+Na)^+$: requires m/z 330.0770, found m/z 330.0752.

Methyl 2-amino-5-phenylthiophene-3-carboxylate (5aa)



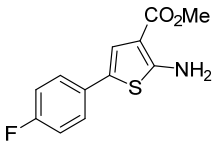
Yellow solid, 18.2 mg, 78% yield. [Known compound, see reference 2 in SI]

TLC: R_f = 0.40 (petroleum ether: ethyl acetate = 8:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.47 (m, 2H), 7.30-7.36 (m, 2H), 7.17-7.24 (m, 2H), 6.02 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 162.3, 134.0, 129.0, 126.8, 125.1, 124.8, 121.2, 107.7, 51.3.

Methyl 2-amino-5-(4-fluorophenyl)thiophene-3-carboxylate (5la)



White solid. 17.7 mg, 75% yield. m.p. 193～194 °C;

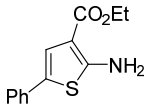
TLC: R_f = 0.35 (petroleum ether: ethyl acetate = 15:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.32 (m, 2H), 7.14 (s, 1H), 7.07-6.97 (m, 2H), 6.02 (s, 2H), 3.83 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 162.3, 161.8 (d, $J_{C\text{-}F}$ = 244.5 Hz), 130.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 126.4 (d, $J_{C\text{-}F}$ = 9.0 Hz), 124.0, 121.2, 115.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 107.7, 51.3.

HRMS: exact mass calcd for $C_{12}H_{11}NFO_2S$ $(M+H)^+$: requires m/z 252.0489, found m/z 252.0483.

Ethyl 2-amino-5-phenylthiophene-3-carboxylate (5ra)



White solid. 19.3 mg, 78% yield. m.p. 194～195 °C;

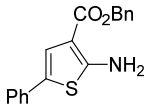
TLC: R_f = 0.31 (petroleum ether: ethyl acetate = 15:1) [UV].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.35-7.31 (m, 2H), 7.25 (s, 1H), 7.23-7.19 (m, 1H), 6.03 (s, 2H), 4.31 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 162.2, 134.1, 128.9, 126.7, 125.0, 124.8, 121.3, 108.0, 60.0, 14.7.

HRMS: exact mass calcd for $C_{13}H_{14}NO_2S$ $(M+H)^+$: requires m/z 248.0740, found m/z 248.0733.

Benzyl 2-amino-5-phenylthiophene-3-carboxylate (5sa)



White solid. 13.3 mg, 43% yield. m.p. 78～79 °C;

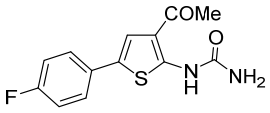
TLC: R_f = 0.56 (petroleum ether: ethyl acetate = 15:1) [UV].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.41 (m, 5H), 7.39-7.30 (m, 5H), 7.20 (t, J = 7.2 Hz, 1H), 6.03 (s, 2H), 5.30 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.6, 136.6, 134.0, 128.9, 128.7, 128.3, 128.2, 126.8, 125.1, 124.9, 121.3, 107.7, 65.7.

HRMS: exact mass calcd for $C_{18}H_{16}NO_2S$ $(M+H)^+$: requires m/z 310.0896, found m/z 310.0898.

1-(3-Acetyl-5-(4-fluorophenyl)thiophen-2-yl)urea (6la)



White solid. 24.1 mg, 82% yield. m.p. 210-211 °C;

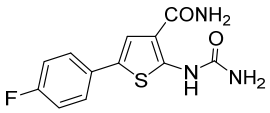
TLC: R_f = 0.44 (petroleum ether: ethyl acetate = 5:1) [UV].

^{1}H NMR (400 MHz, d^6-DMSO) δ 10.12 (s, 1H), 7.64-7.61 (m, 2H), 7.39 (s, 1H), 7.23-6.93 (m, 4H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, d^6-DMSO) δ 164.5, 161.3 (d, $J_{C\text{-}F}$ = 243.0 Hz), 154.3, 151.0, 130.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.5, 129.5, 126.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 119.2, 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 109.9, 51.5.

HRMS: exact mass calcd for $C_{13}H_{11}FN_2NaO_3S$ $(M+Na)^+$: requires m/z 317.0367, found m/z 317.0364.

5-(4-Fluorophenyl)-2-ureidothiophene-3-carboxamide (TPCA-1)



White solid. 17.6 mg, 63% yield. m.p. 221-223 °C;

TLC: R_f = 0.35 (DCM: MeOH = 15:1) [UV].

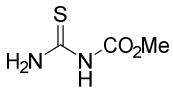
^{1}H NMR (400 MHz, d^6-DMSO) δ 10.99 (s, 1H), 7.68 (s, 2H), 7.57-7.50 (m, 2H), 7.32 (s, 1H), 7.27-7.21 (m, 2H), 6.98 (s, 2H).

^{13}C NMR (150 MHz, d^6-DMSO) δ 166.8, 161.1 (d, $J_{C\text{-}F}$ = 243.0 Hz), 154.4, 148.8, 130.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.6, 126.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 119.5, 116.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.0.

HRMS: exact mass calcd for $C_{12}H_{10}FN_3NaO_2S$ (M+Na)+: requires m/z 302.0370 found m/z

302.0373.

Methyl carbamothioylcarbamate (7aa)



White solid, 334.0 mg, 45% yield. m.p. 65～66 °C;

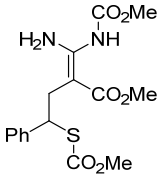
TLC: R_f = 0.42 (petroleum ether: ethyl acetate = 2:1) [UV];

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (br, 1H), 8.20 (br, 1H), 6.99 (br, 1H), 3.82 (s, 3H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 181.6, 152.9, 53.7;

HRMS: exact mass calcd for $C_3H_6N_2O_2S$ $(M+H)^+$: requires m/z 135.0223, found m/z 135.0228.

Methyl (*Z*)-2-(amino((methoxycarbonyl)amino)methylene)-4-((methoxycarbonyl)thio)-4-phenylbutanoate (8aa)



White solid, 183.0 mg, 9% yield. m.p. 135～136 °C;

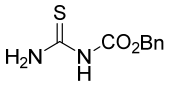
TLC: R_f = 0.60 (petroleum ether: ethyl acetate = 5:1) [UV];

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.0 (s, 1H), 7.20-7.25 (m, 5H), 4.31 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.17-3.25 (m, 1H), 3.12 (s, 3H), 2.70 (dd, *J* = 15.2, 3.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 170.7, 155.1, 155.0, 138.4, 128.5, 128.1, 127.7, 76.8, 54.0, 52.6, 50.0, 49.1, 33.5;

HRMS: exact mass calcd for $C_{16}H_{20}N_2O_6S$ $(M+H)^+$: requires m/z 369.1115, found m/z 369.1117.

***N*-(Benzyloxycarbonyl)thiourea (7sa)**



Colorless oil, 7.6 mg, 18% yield.

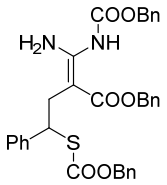
TLC: R_f = 0.22 (petroleum ether: ethyl acetate = 3:1) [UV];

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.15 (br, 1H), 8.13 (s, 1H), 7.32-7.43 (m, 5H), 6.94 (br, 1H), 5.20 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 160.1, 152.2, 134.4, 129.2, 129.0, 128.6, 68.7.

HRMS: exact mass calcd for $C_9H_{10}N_2O_2S$ $(M+H)^+$: requires m/z 211.0536, found m/z 211.0545.

Benzyl (*Z*)-2-(amino(((benzyloxy)carbonyl)amino)methylene)-4-(((benzyloxy)carbonyl) thio)-4-phenylbutanoate (8sa)



Colorless oil, 2.4 mg, 2% yield.

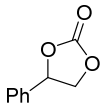
TLC: R_f = 0.33 (petroleum ether: ethyl acetate = 6:1) [UV];

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.11 (s, 1H), 7.28-7.39 (m, 13H), 7.08-7.19 (m, 7H), 5.24-5.31 (m, 2H), 5.14-5.20 (m, 2H), 4.93 (d, *J* = 12.6 Hz, 1H), 4.30-4.39 (m, 2H), 3.29-3.37 (m, 1H), 2.69-2.74 (m, 1H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.1, 170.2, 155.5, 154.5, 138.2, 137.1, 135.4, 135.0, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.7, 69.4, 67.5, 64.9, 49.0, 33.5;

HRMS: exact mass calcd for $C_{34}H_{32}N_2O_6S$ $(M+H)^+$: requires m/z 597.2054, found m/z 597.2063

4-phenyl-1,3-dioxolan-2-one



Colorless oil

TLC: R_f = 0.42 (petroleum ether: ethyl acetate = 10:1) [UV];

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.48 (m, 5H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.0 Hz, 1H), 4.34 (t, *J* = 8.0 Hz, 1H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 154.9, 135.9, 129.8, 129.3, 126.0, 78.1, 71.3.

10. References

1 (*a*) F. Gonzalez-Bobes, M. D. B. Fenster, S. Kiau, L. Kolla, S. Kolotuchin and M. Soumeillant, *Adv. Synth. Catal.*, 2008, **350**, 813; (*b*) M. K. Ghorai, R. Talukdar and D. P. Tiwari, *Org. Lett.*, 2014, **16**, 2204; (*c*) S. Racine, F. de Nanteuil, E. Serrano and J. Waser, *Angew. Chem., Int. Ed.,* 2014, **53**, 8484; (*d*) F. de Nanteuil and J. Waser, *Angew. Chem., Int. Ed.,* 2011, **50**, 12075; (*e*) D.-C. Wang, M.-S. Xie, H.-M. Guo, G.-R. Qu, M.-C. Zhang and S.-L. You, *Angew. Chem., Int. Ed.,* 2016, **55**, 14111.

2 P. Gopinath and S. Chandrasekaran, *J. Org. Chem.,* 2011, **76**, 700.

3 P. D. Pohlhaus, S. D. Sanders, A. T. Parsons, W. Li and J. S. Johnson, *J. Am. Chem. Soc.,* 2008, **130**, 8642.

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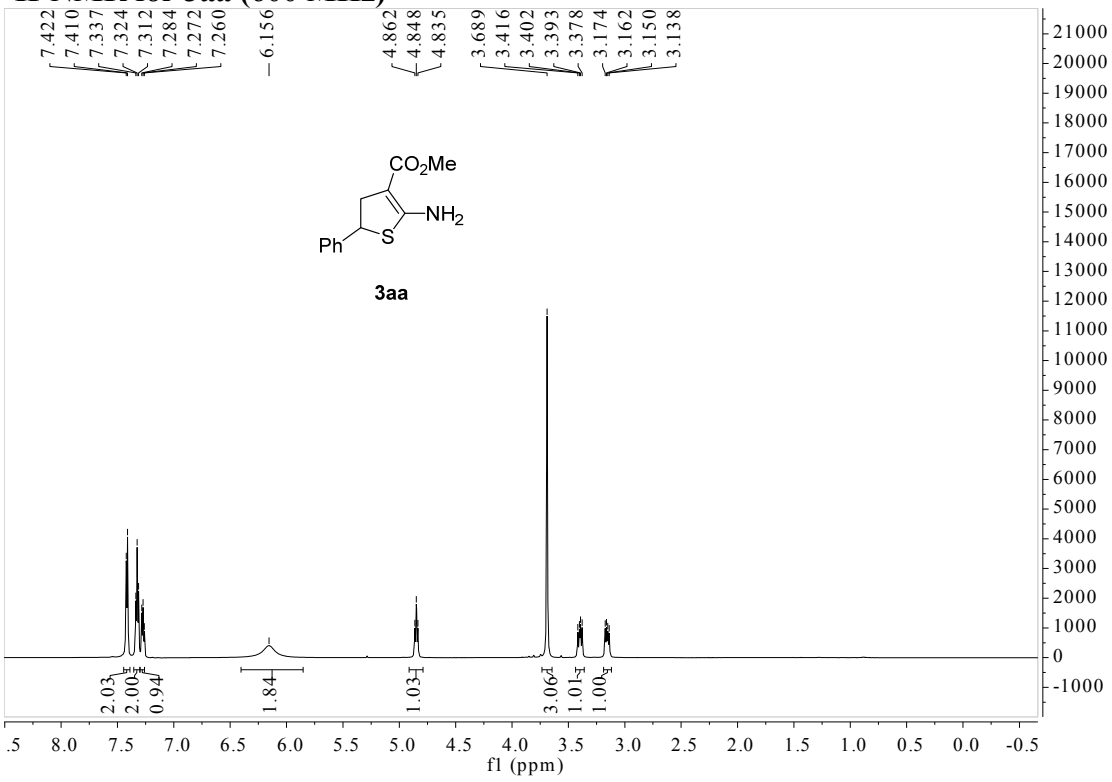
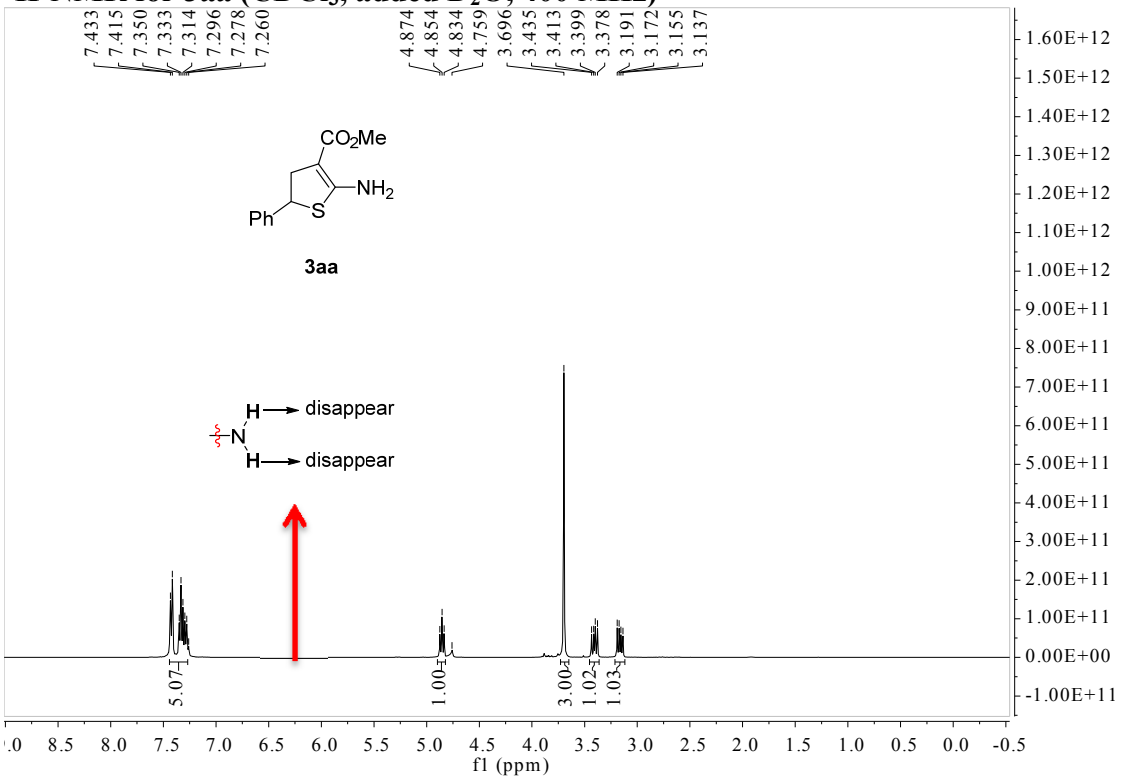
11. Copies of ^{1}H and ^{13}C NMR spectra

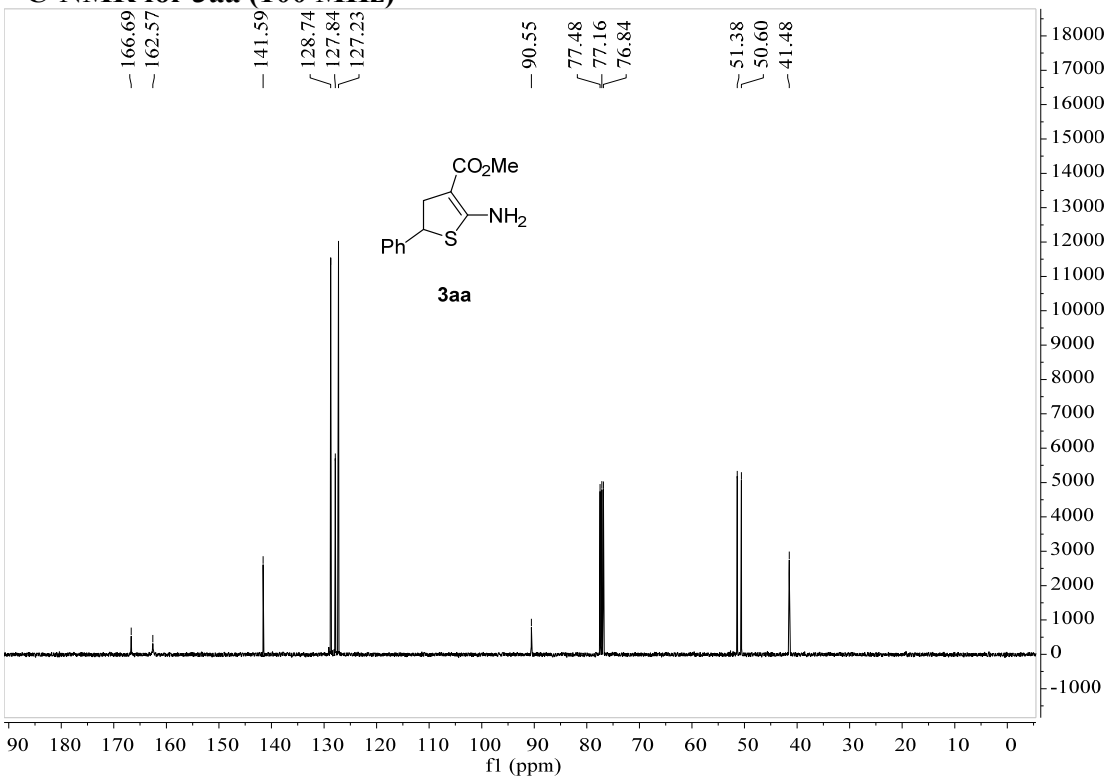
^{1}H-NMR for 3aa (600 MHz)



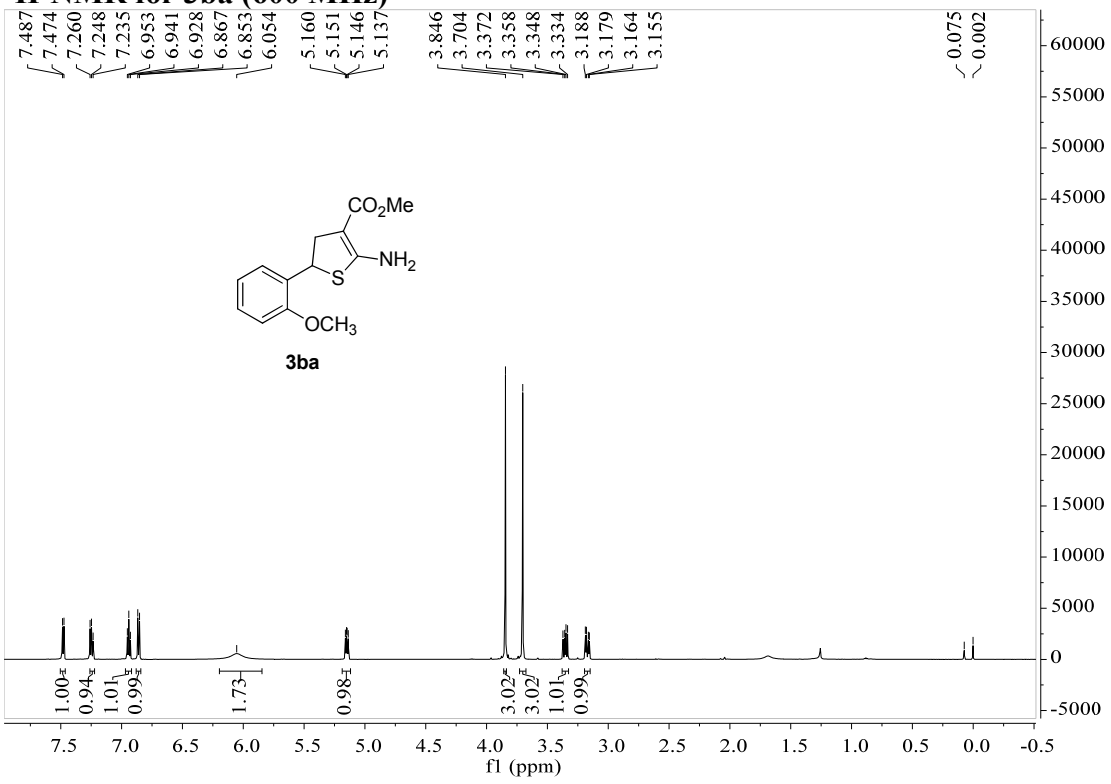
^{1}H-NMR for 3aa ($CDCl_3$, added D_2O, 400 MHz)



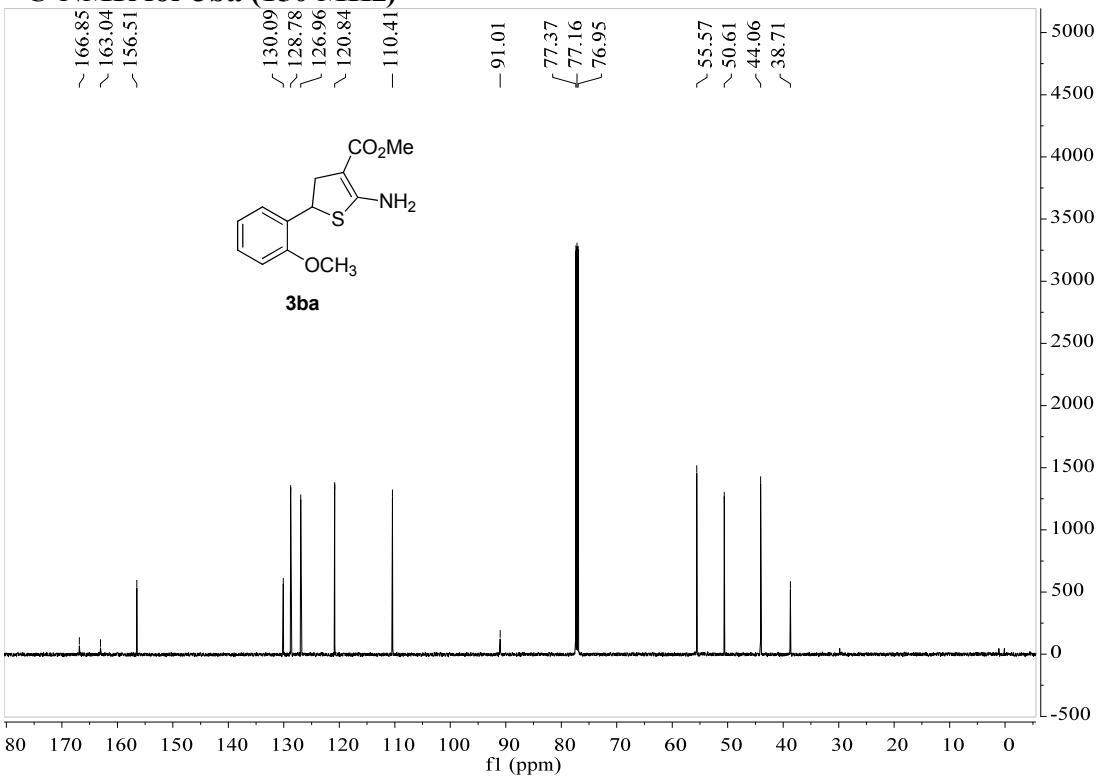
^{13}C-NMR for 3aa (100 MHz)



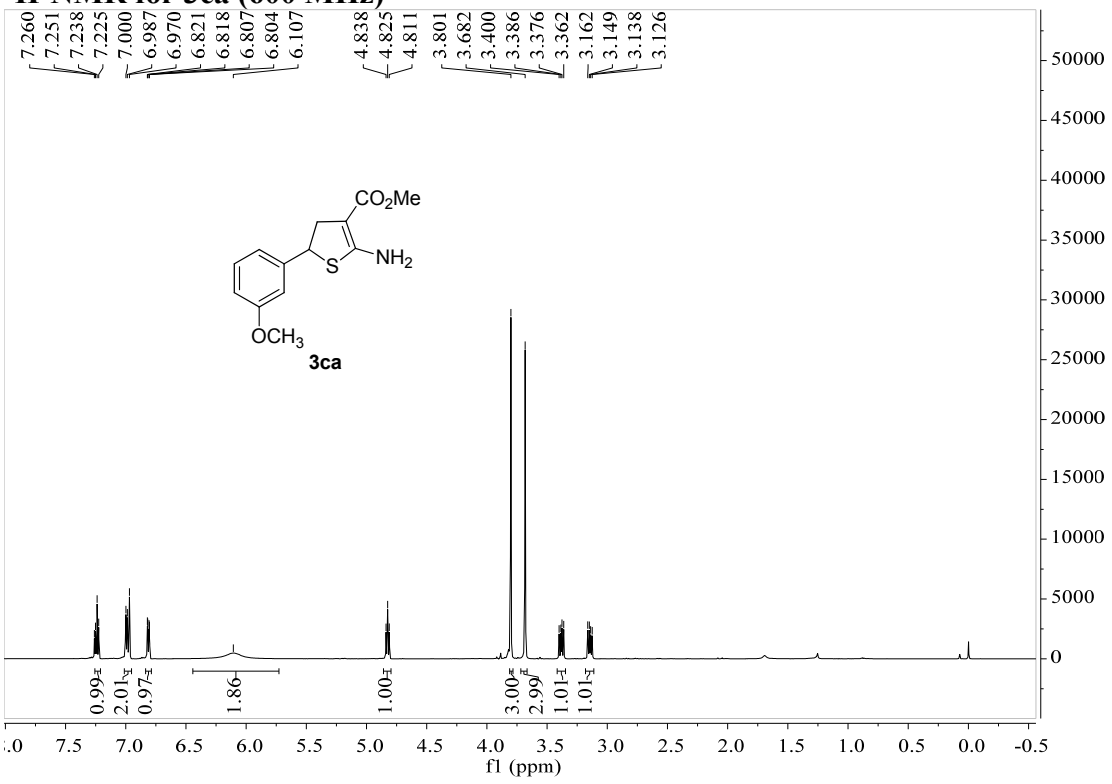
^{1}H-NMR for 3ba (600 MHz)



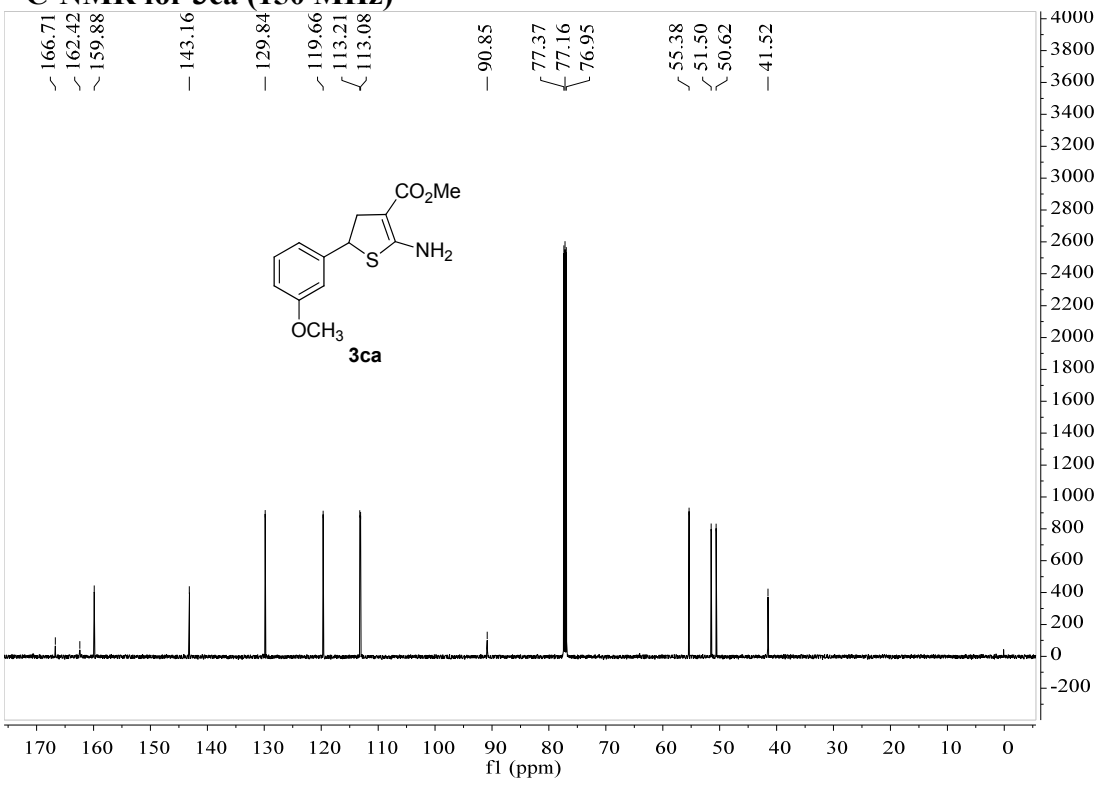
^{13}C-NMR for 3ba (150 MHz)



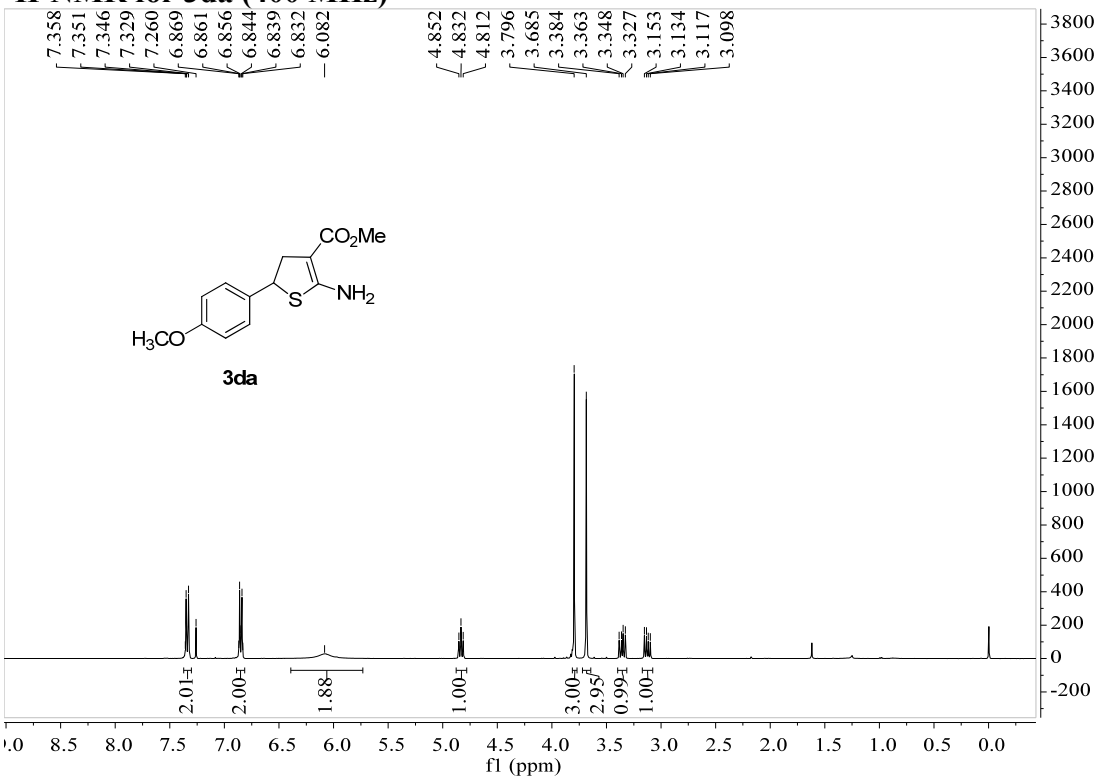
^{1}H-NMR for 3ca (600 MHz)



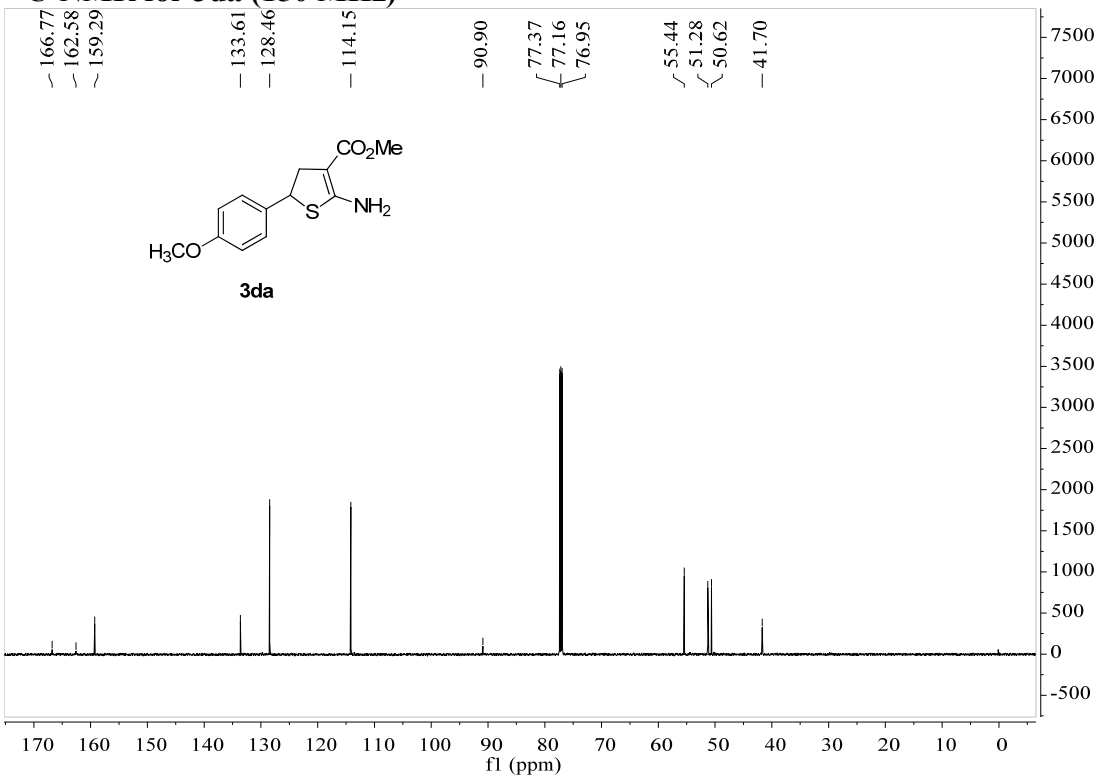
^{13}C-NMR for 3ca (150 MHz)



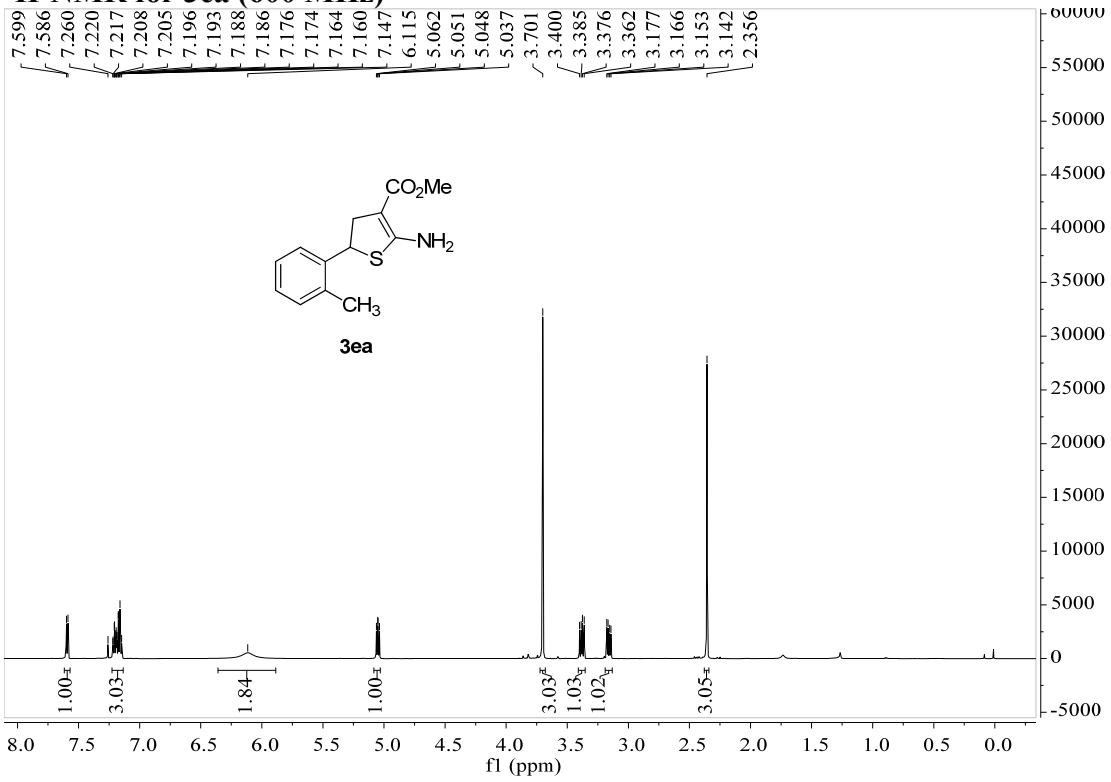
^{1}H-NMR for 3da (400 MHz)



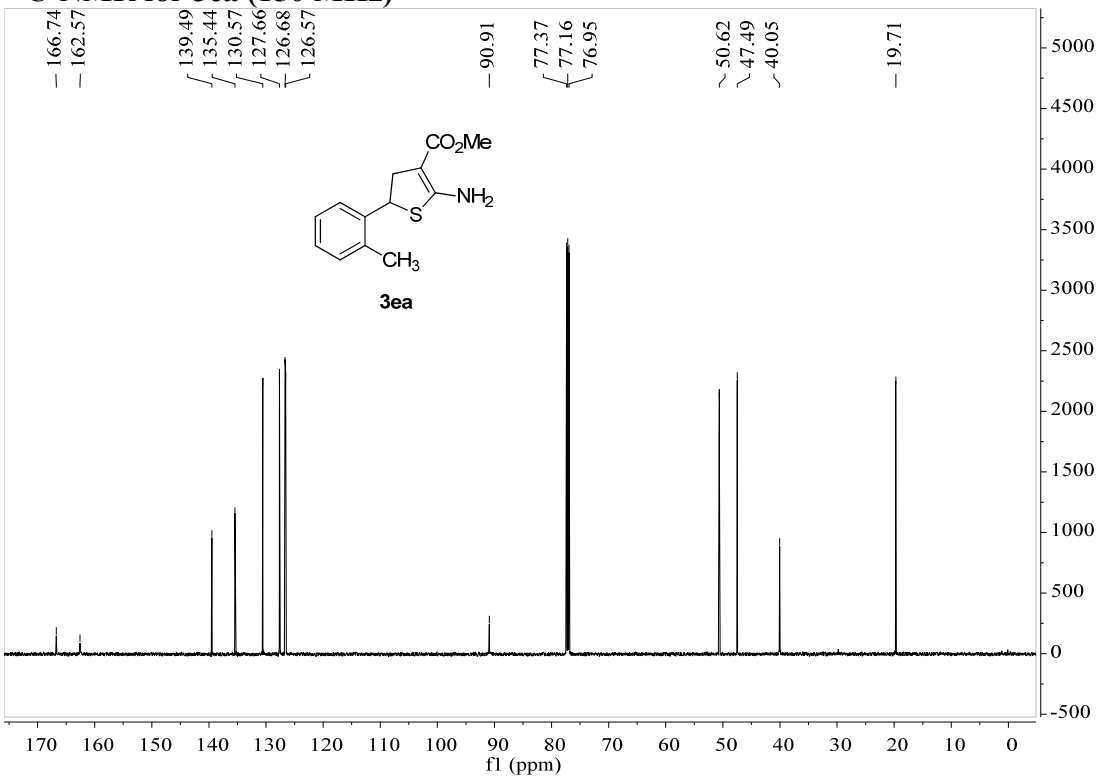
^{13}C-NMR for 3da (150 MHz)



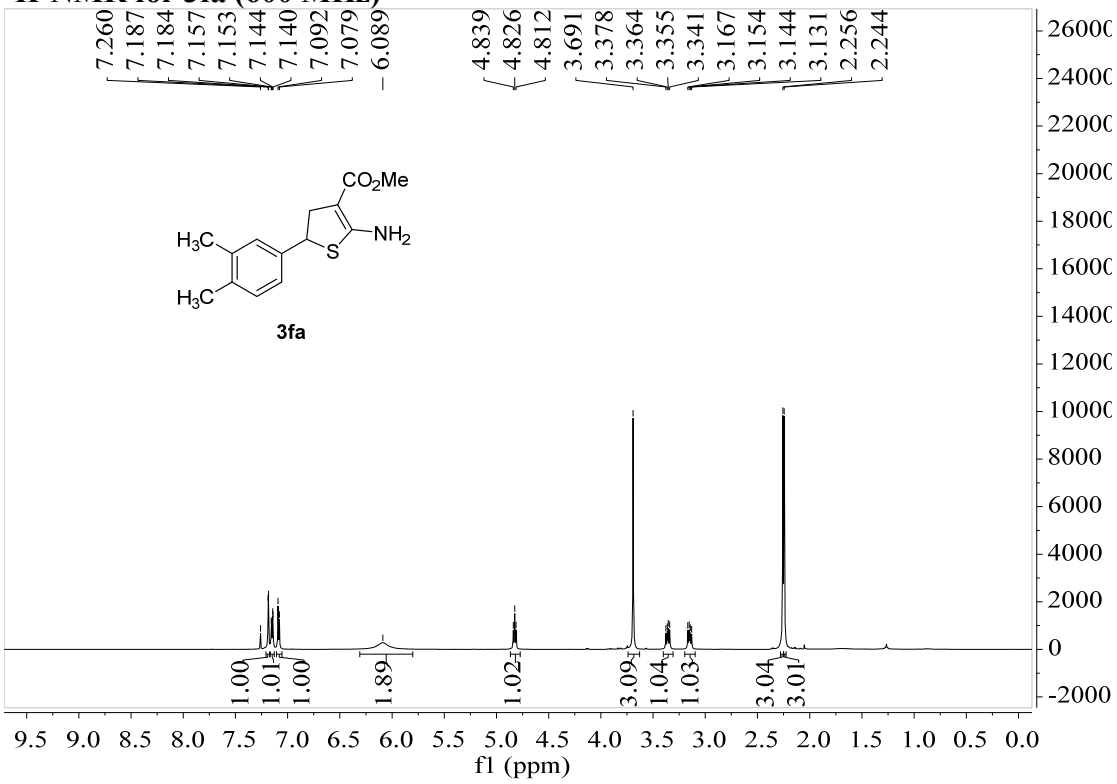
^{1}H-NMR for 3ea (600 MHz)



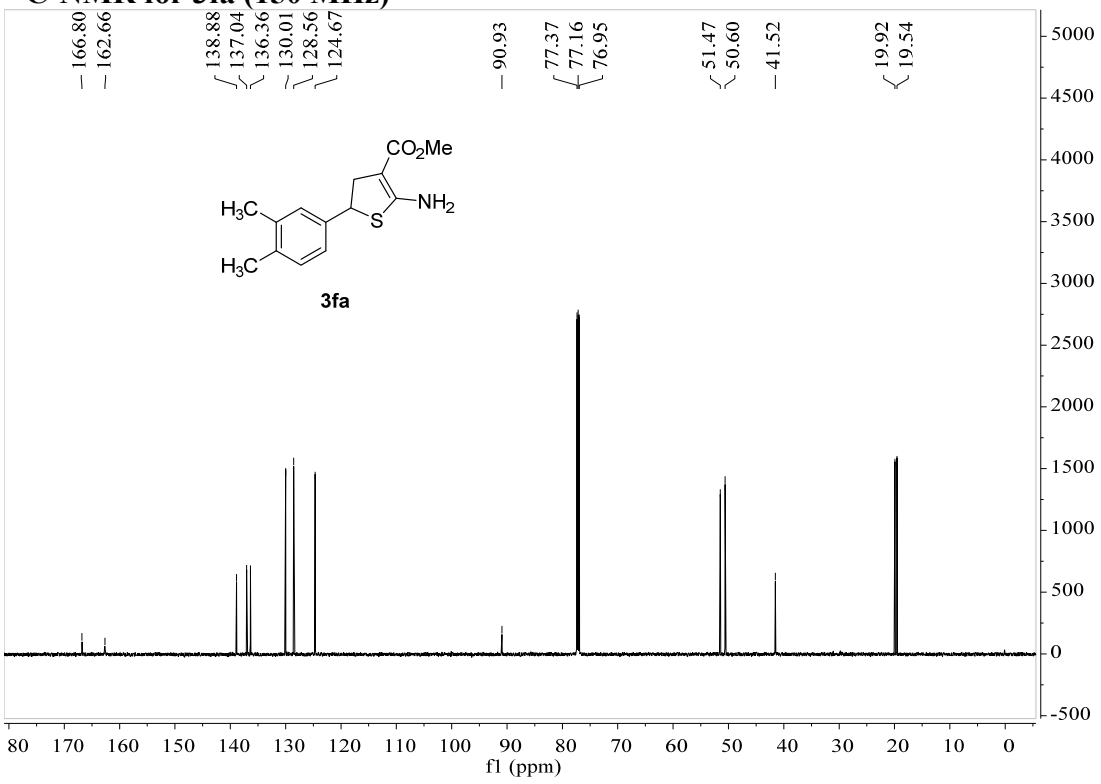
^{13}C-NMR for 3ea (150 MHz)



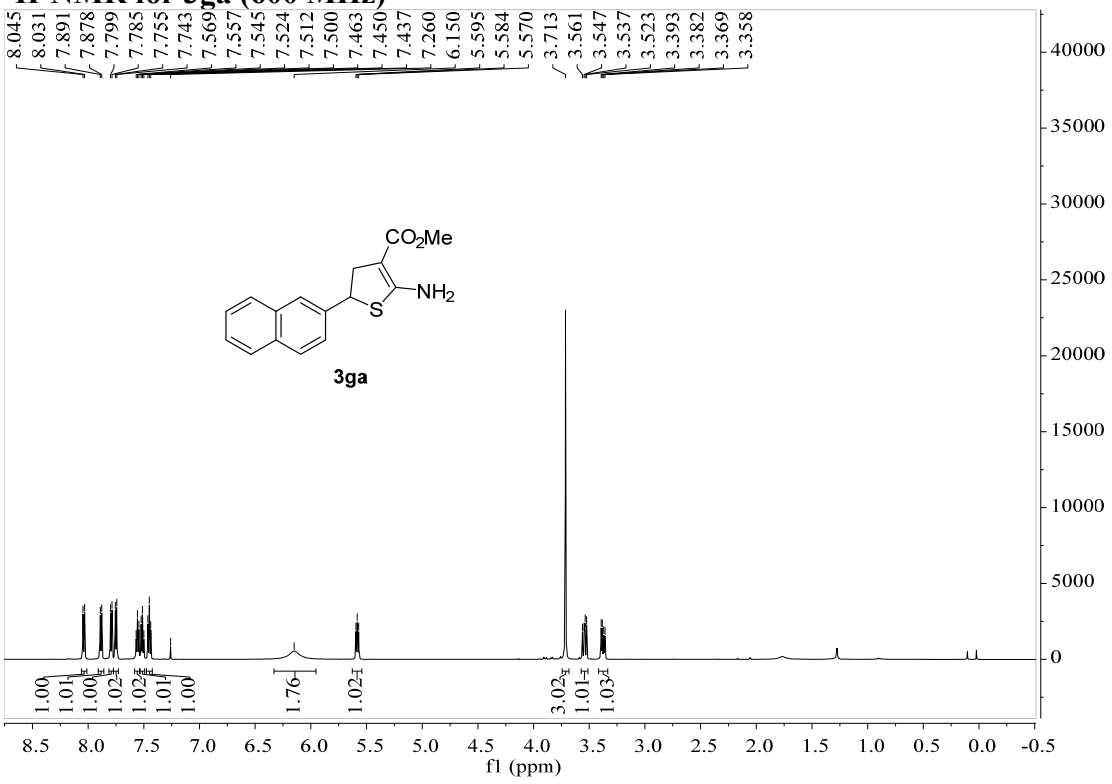
^{1}H-NMR for 3fa (600 MHz)



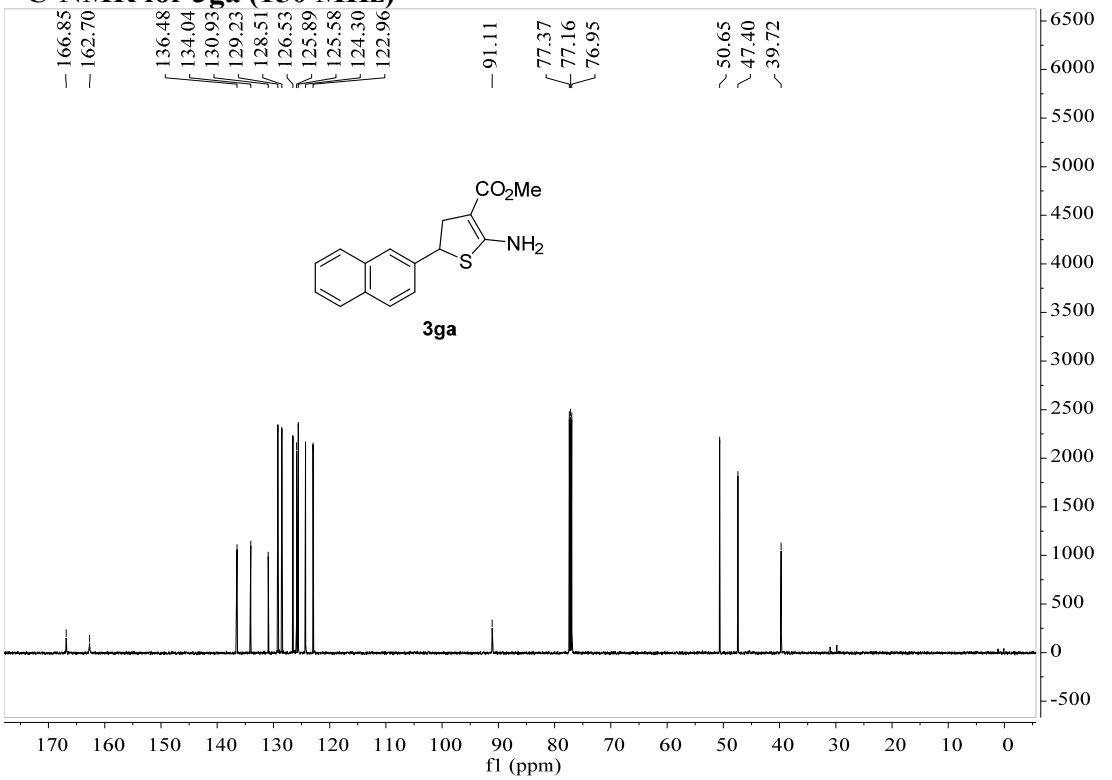
^{13}C-NMR for 3fa (150 MHz)



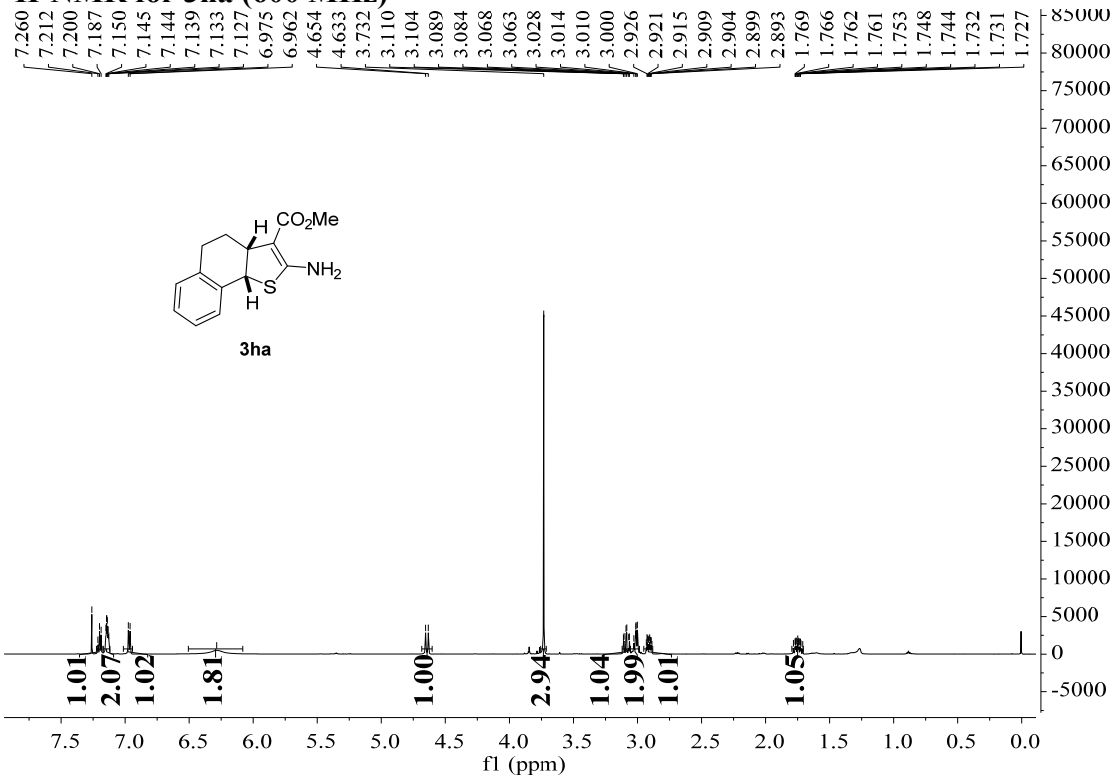
^{1}H-NMR for 3ga (600 MHz)



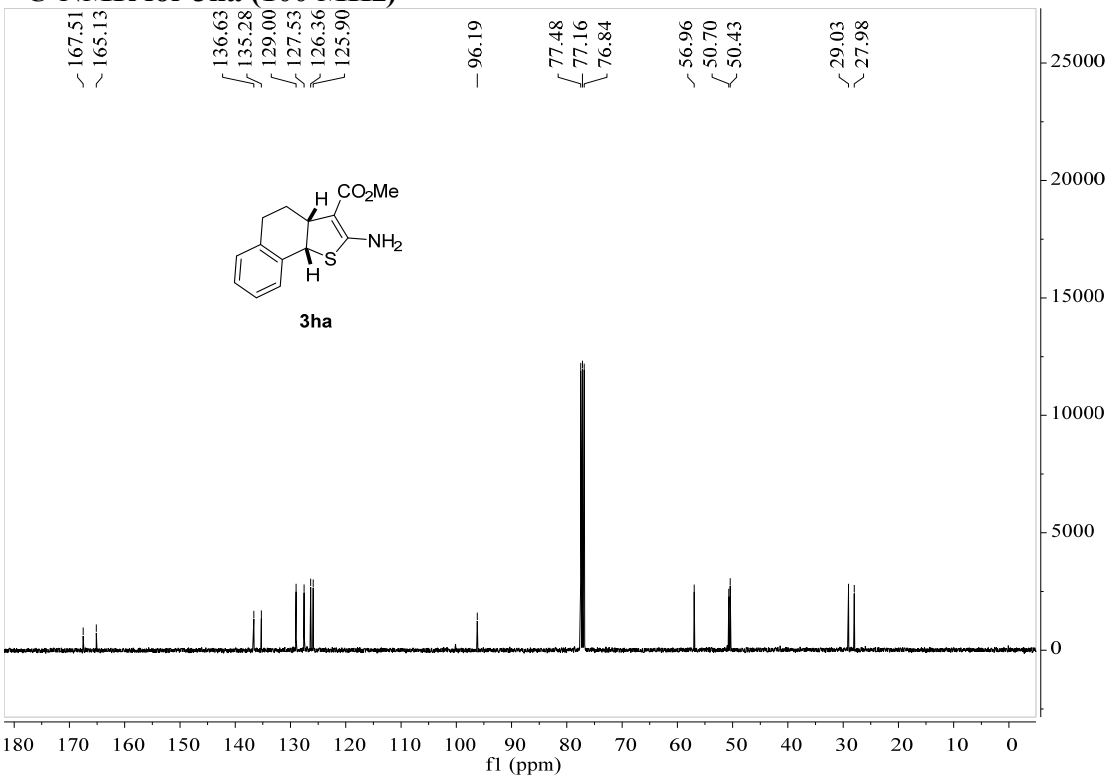
^{13}C-NMR for 3ga (150 MHz)



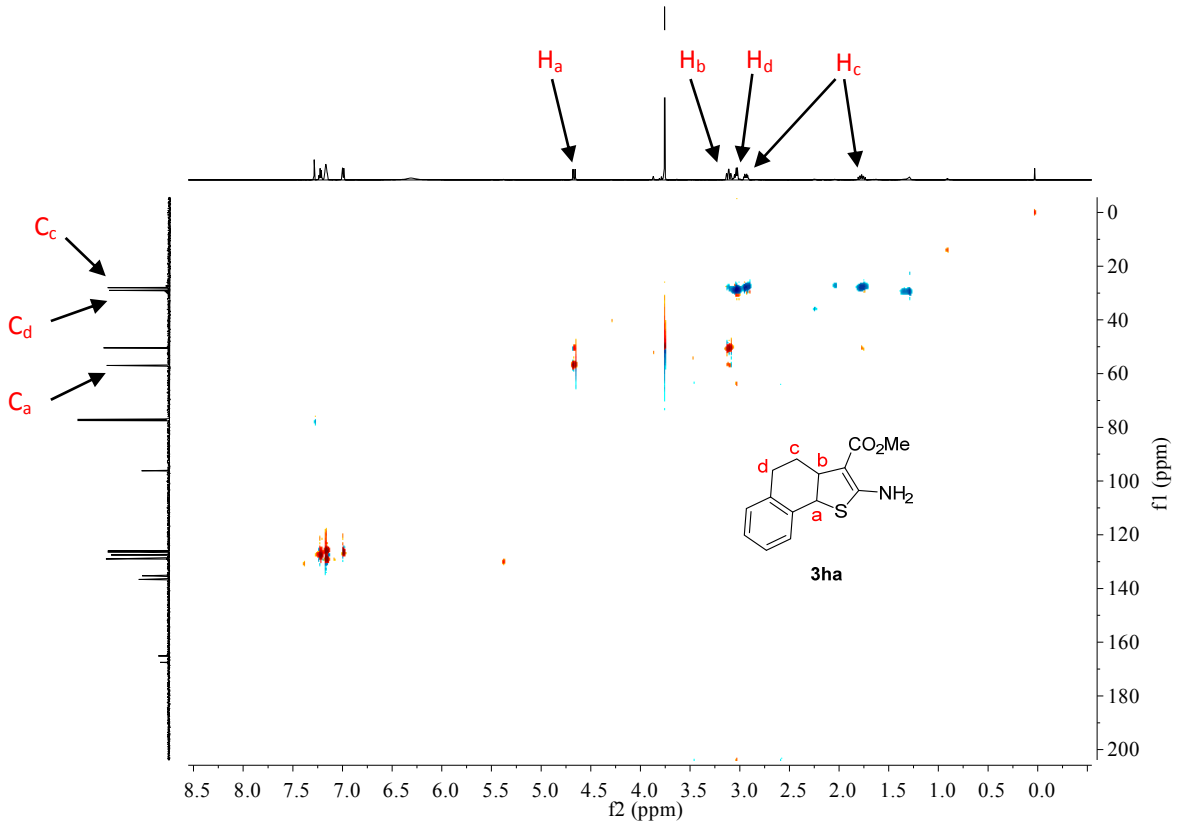
^{1}H-NMR for 3ha (600 MHz)



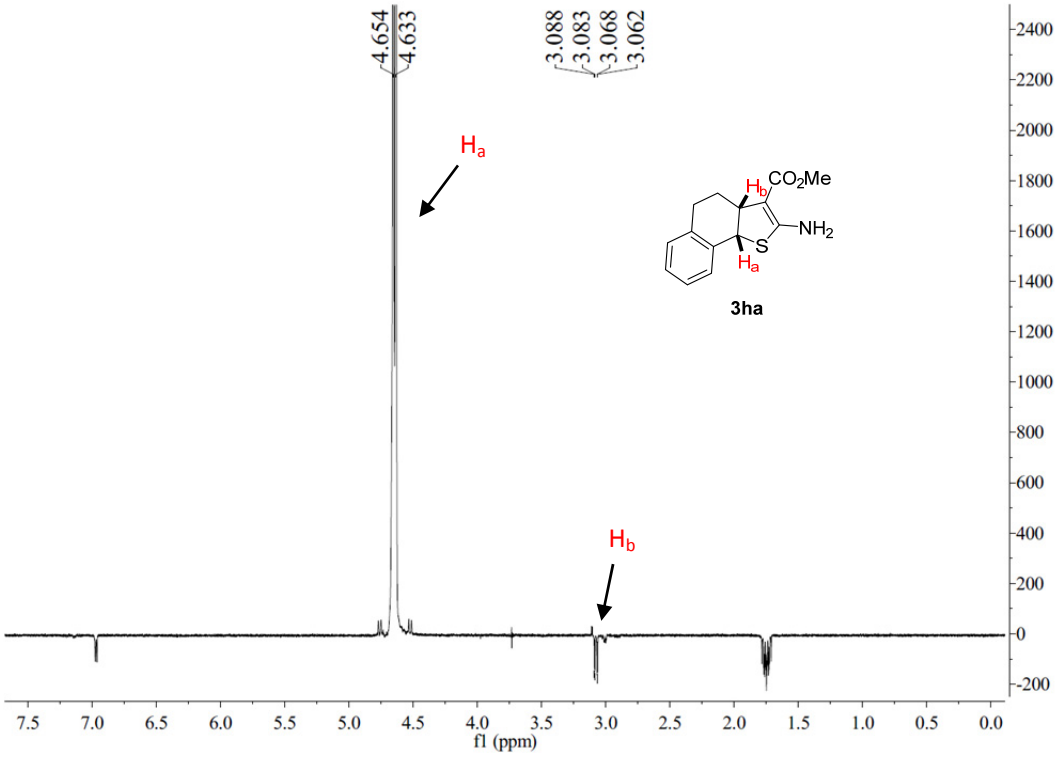
^{13}C-NMR for 3ha (100 MHz)



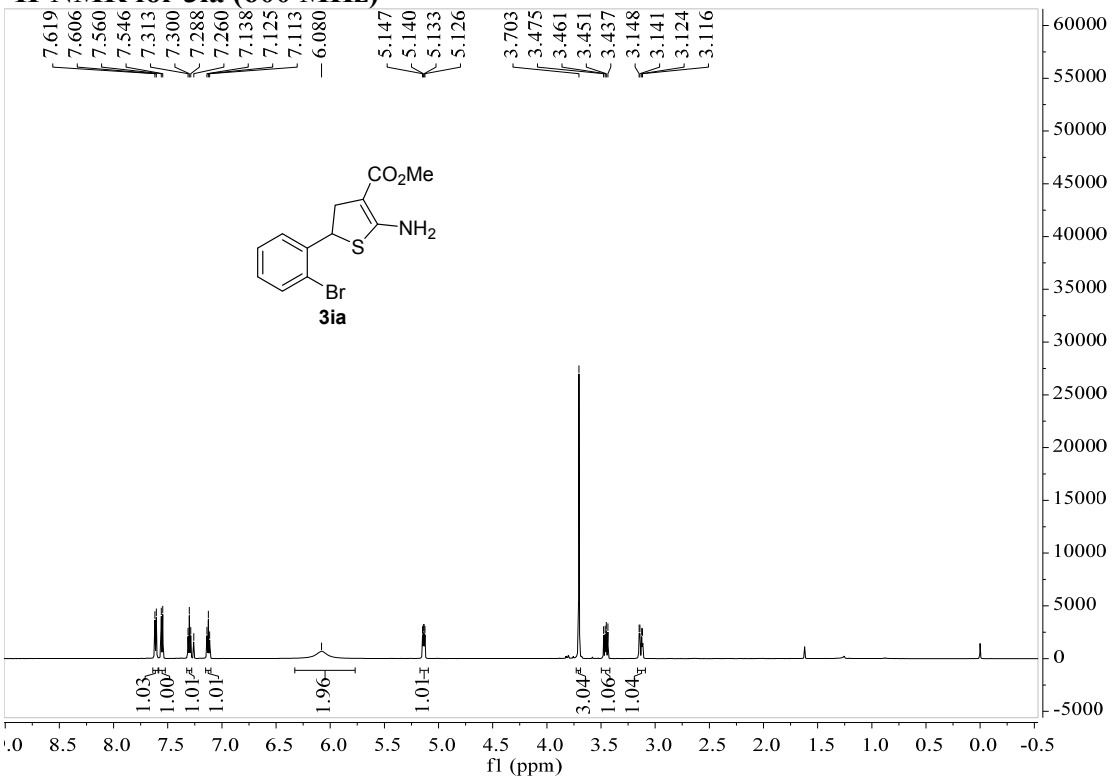
HSQC for 3ha



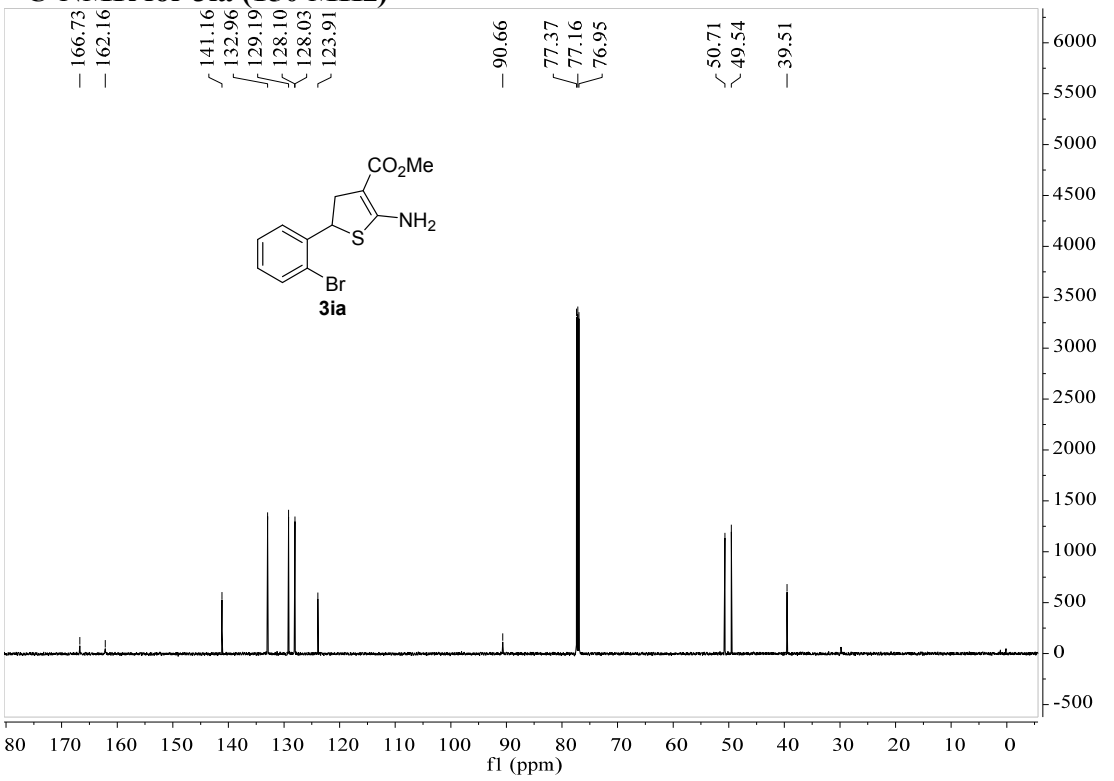
1D Selective Gradient NOESY for 3ha



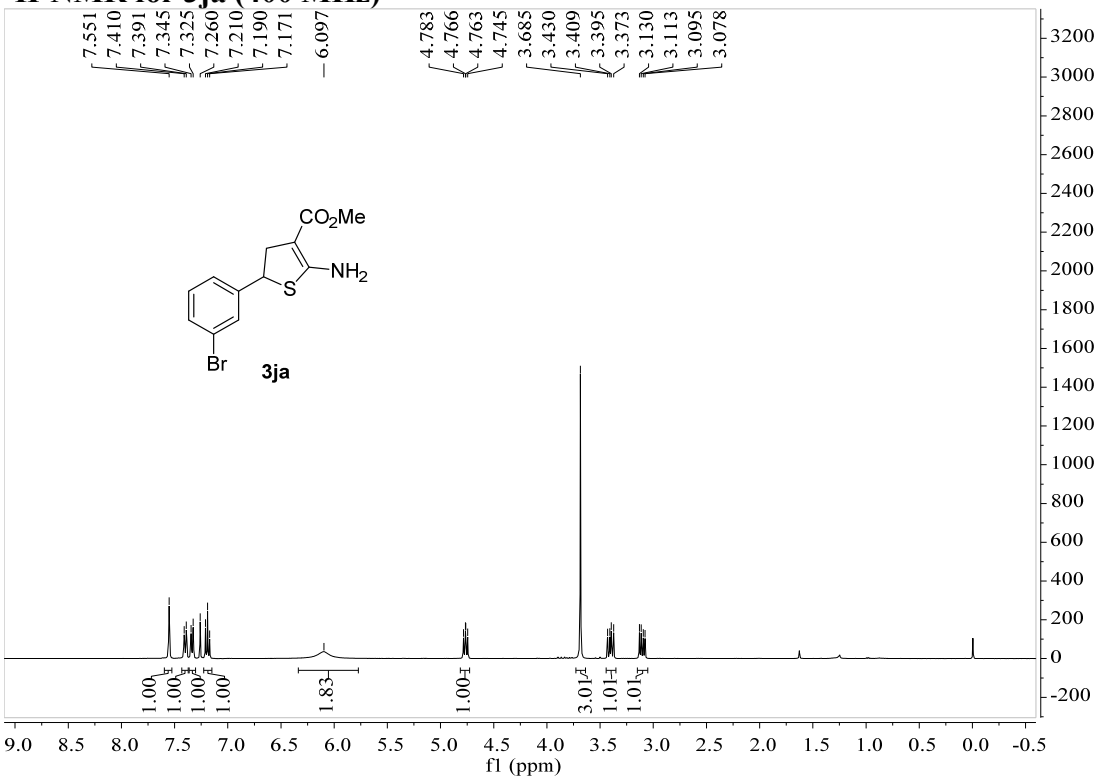
^{1}H-NMR for 3ia (600 MHz)



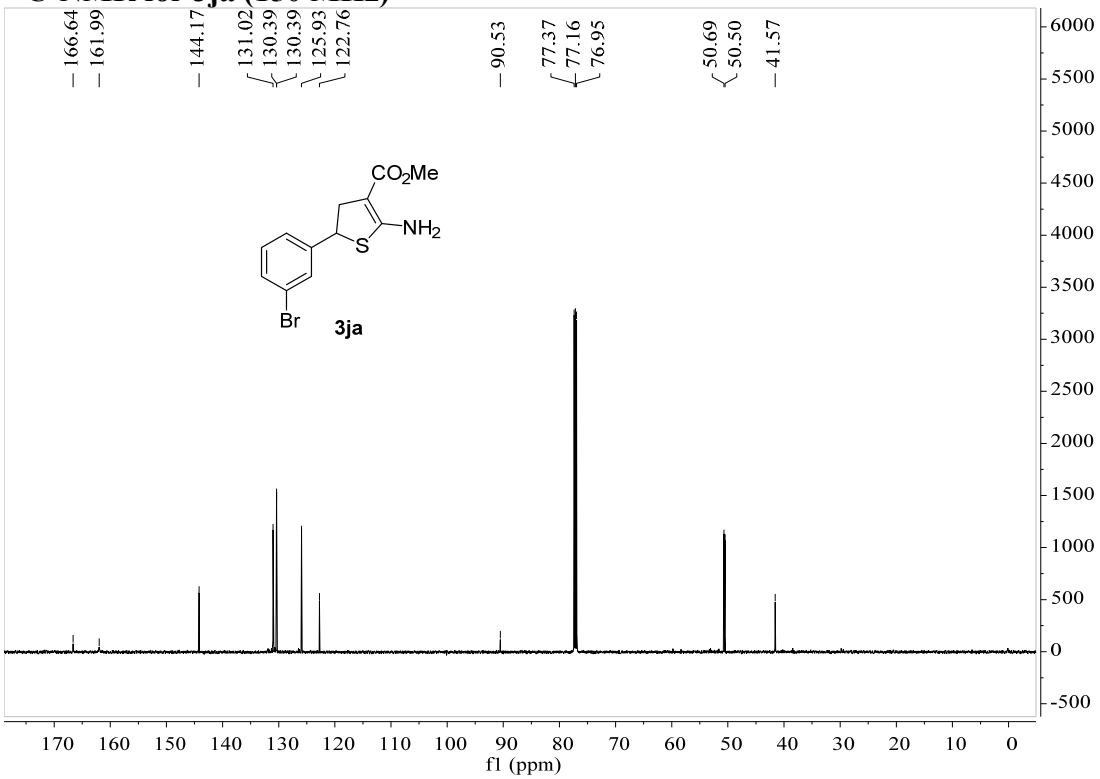
^{13}C-NMR for 3ia (150 MHz)



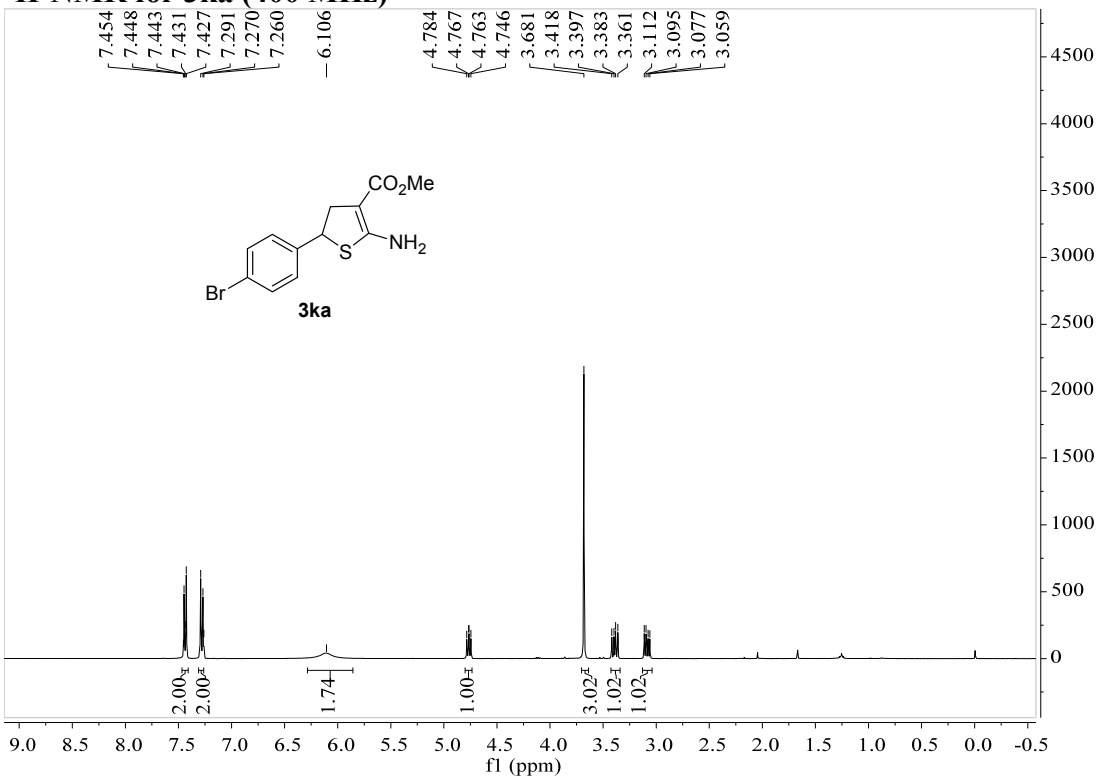
^{1}H-NMR for 3ja (400 MHz)



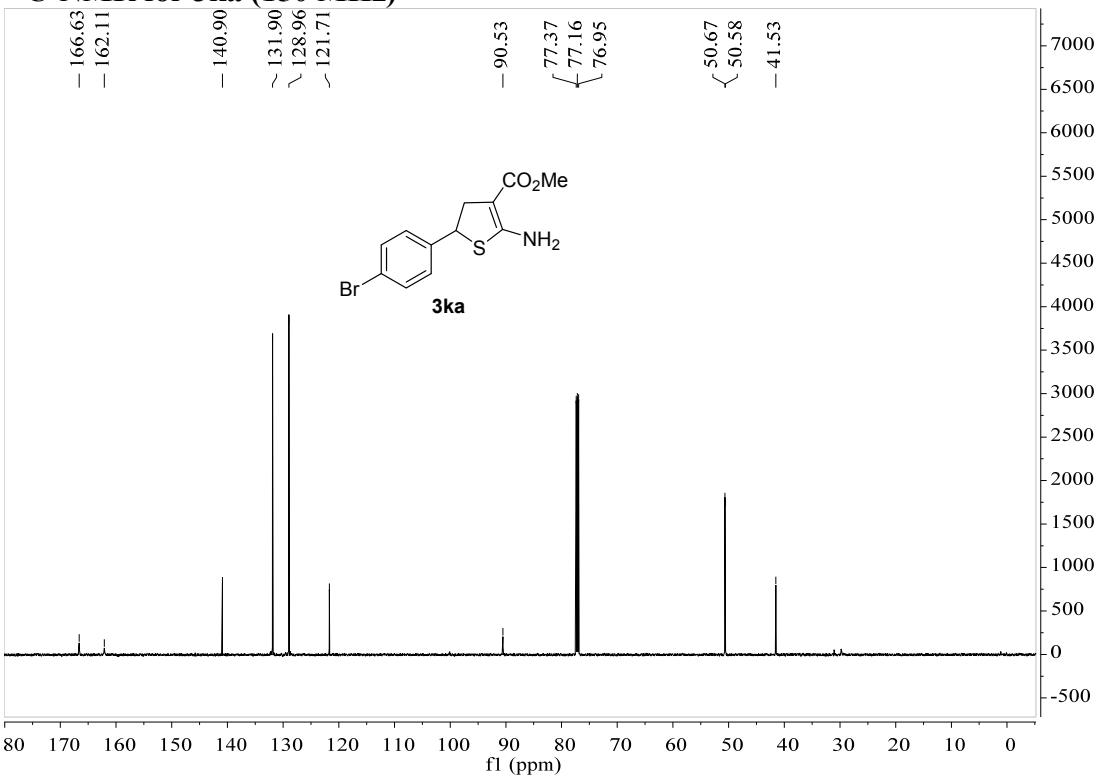
^{13}C-NMR for 3ja (150 MHz)



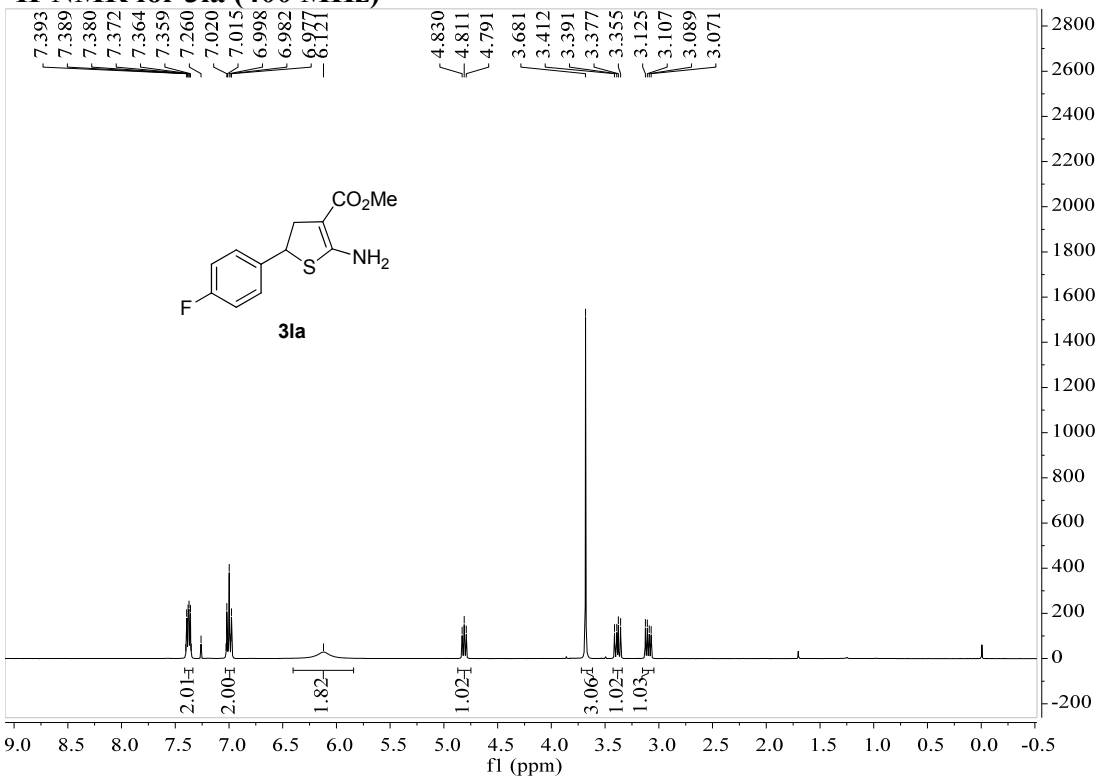
^{1}H-NMR for 3ka (400 MHz)



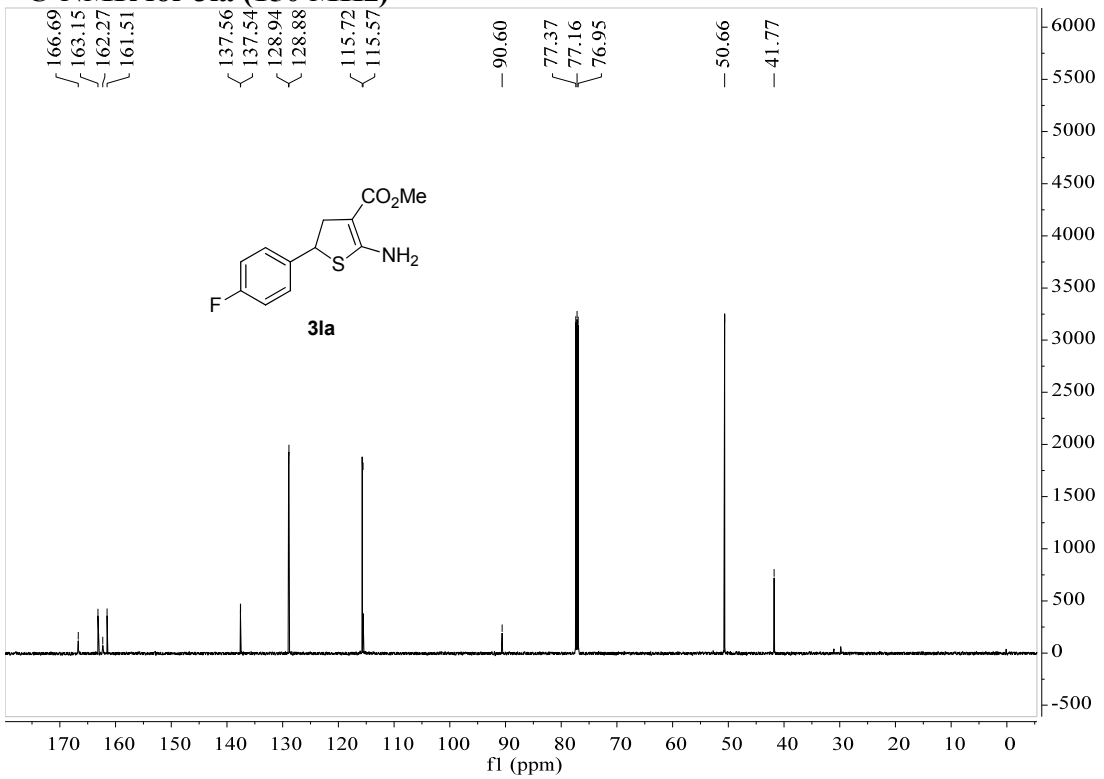
^{13}C-NMR for 3ka (150 MHz)



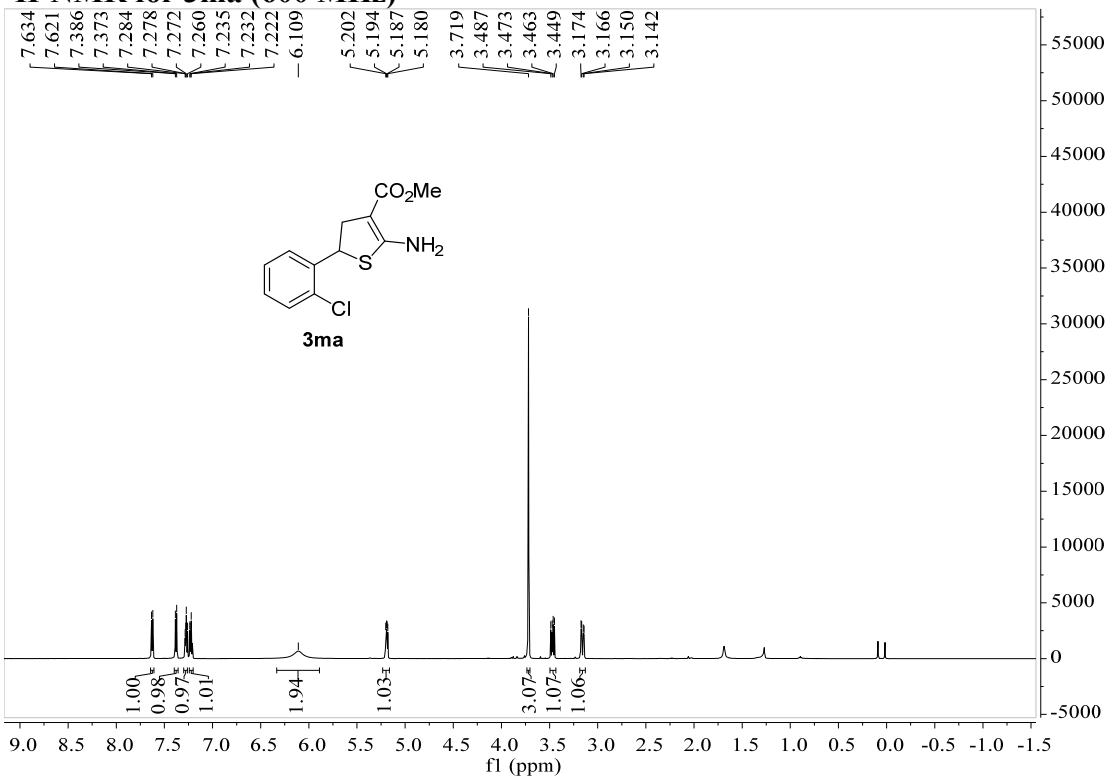
^{1}H-NMR for 3la (400 MHz)



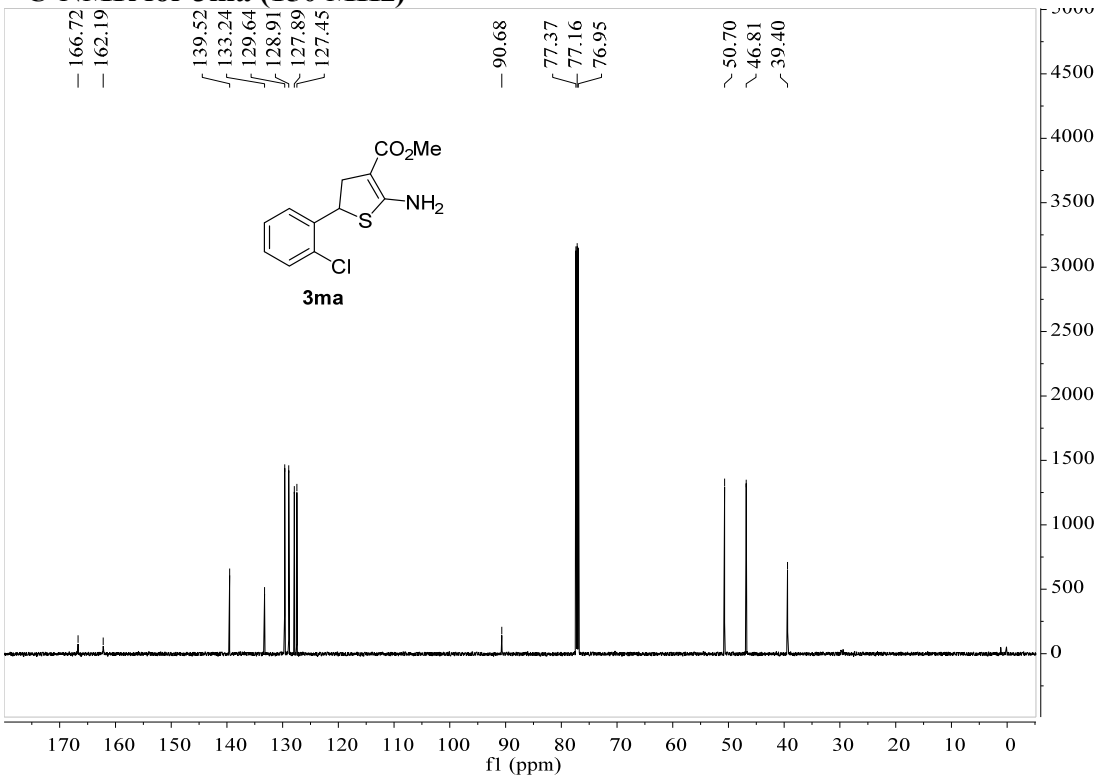
^{13}C-NMR for 3la (150 MHz)



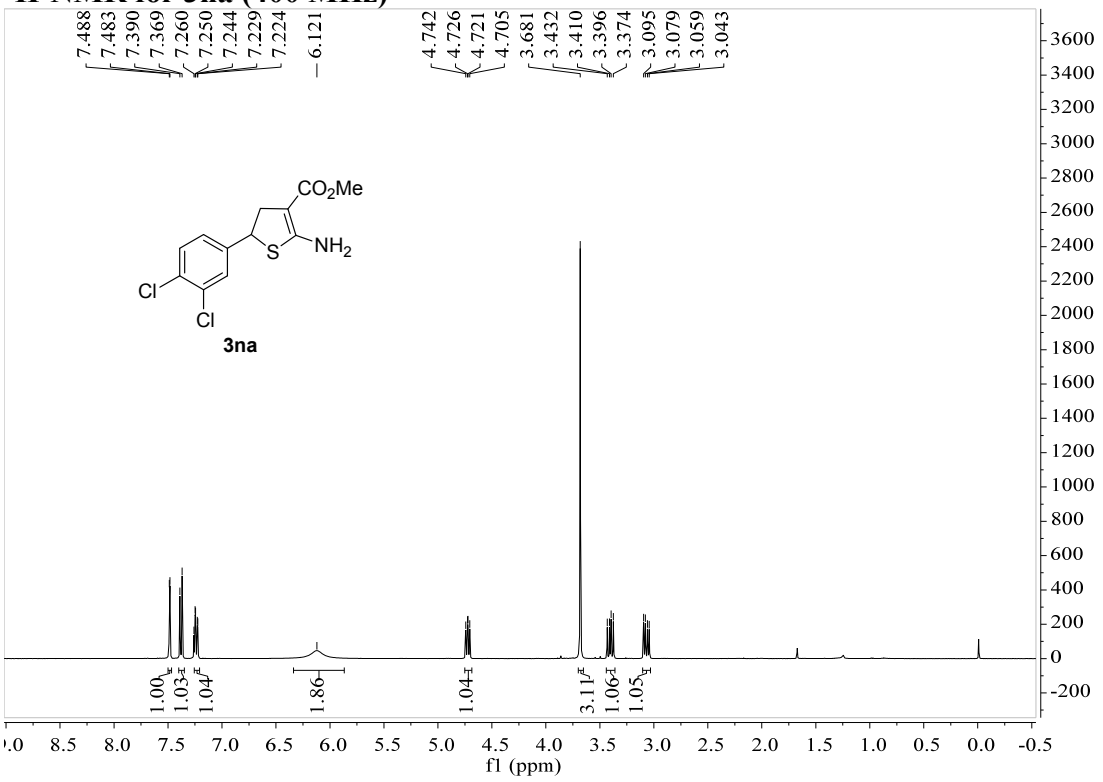
^{1}H-NMR for 3ma (600 MHz)



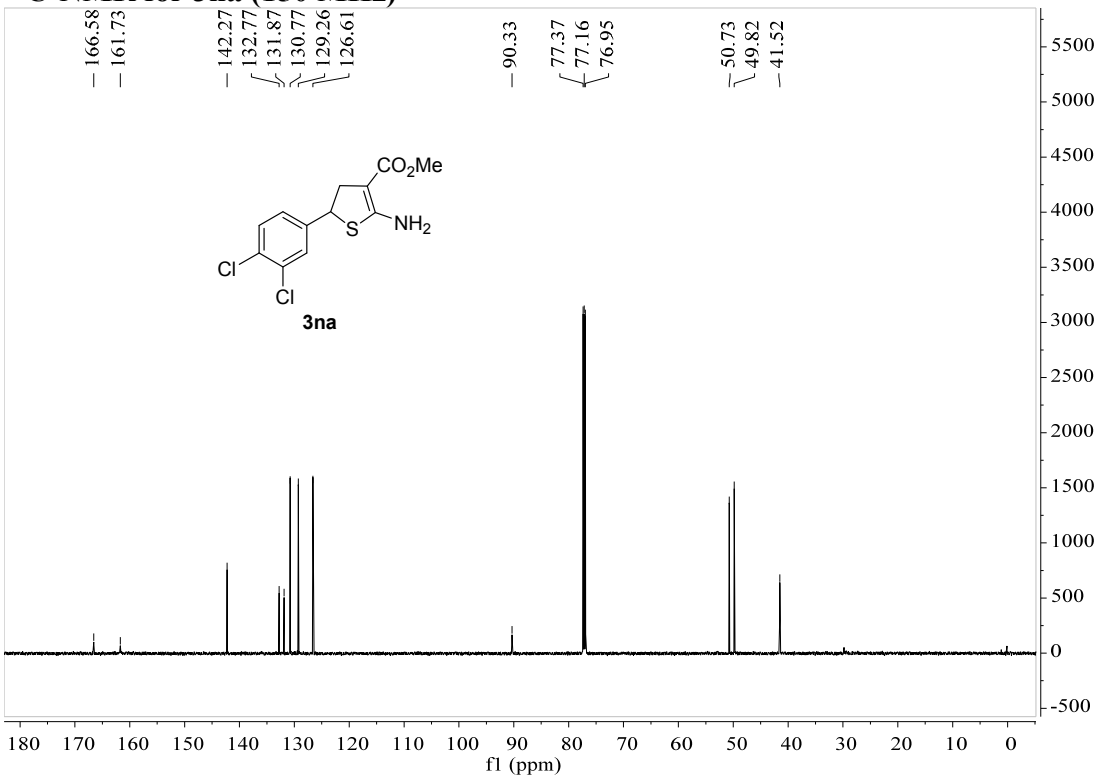
^{13}C-NMR for 3ma (150 MHz)



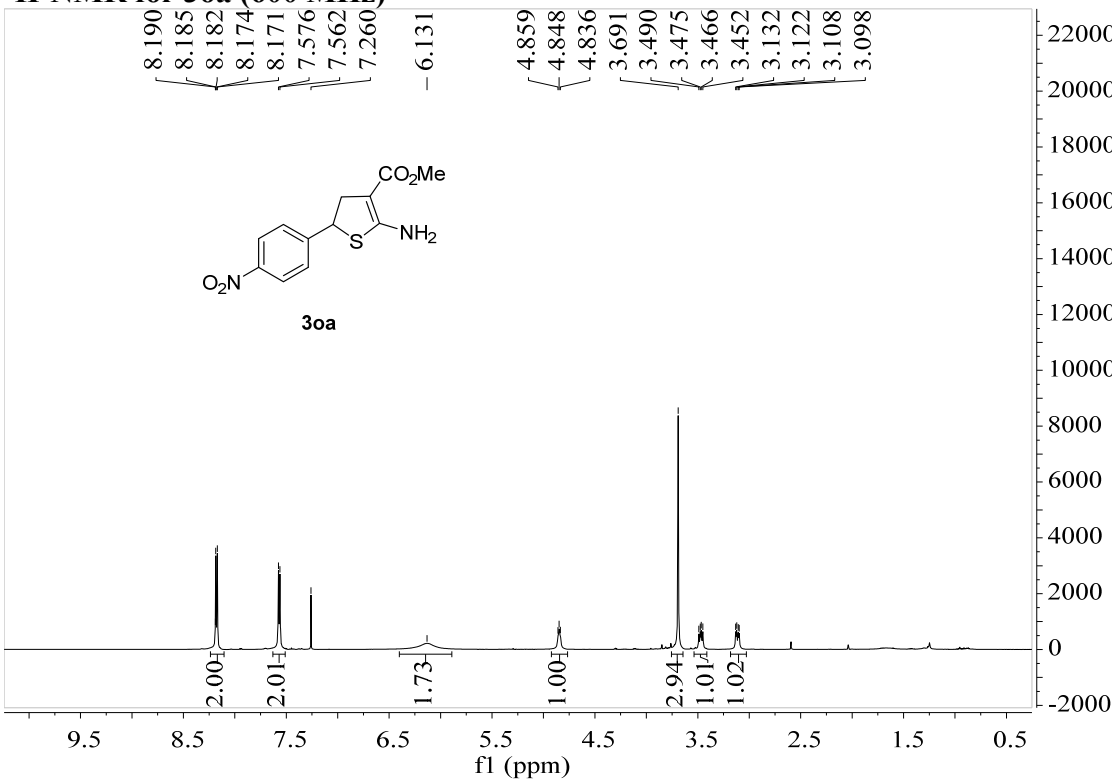
^{1}H-NMR for 3na (400 MHz)



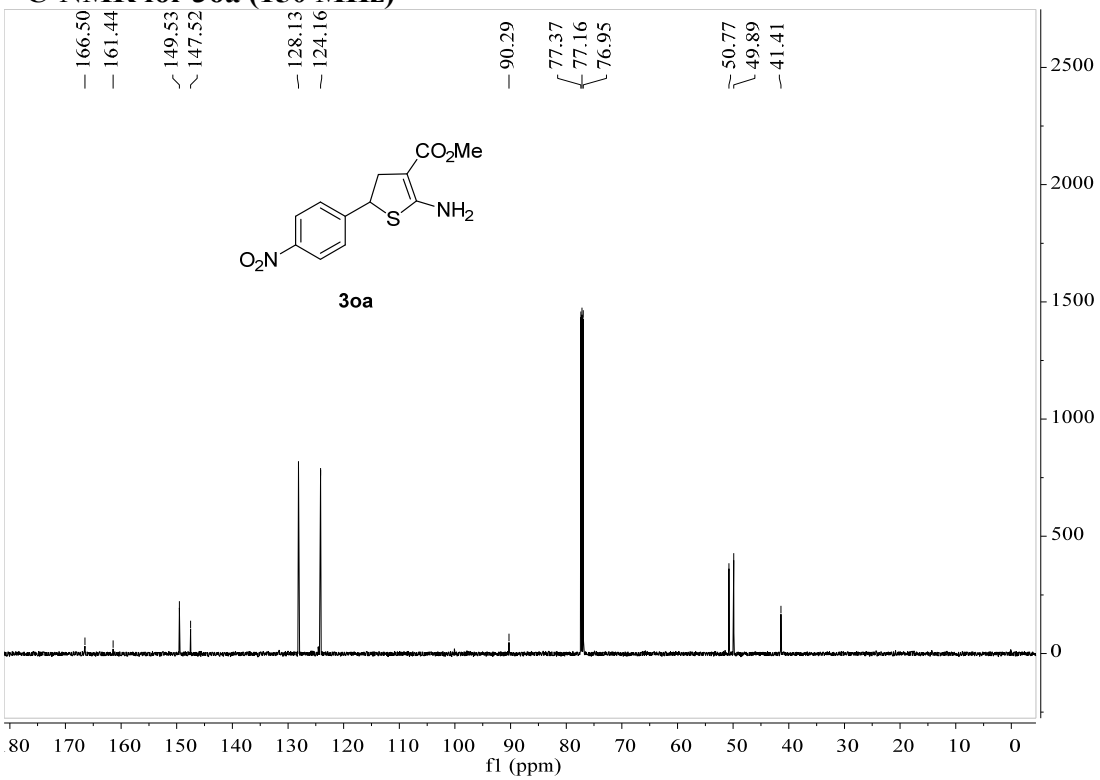
^{13}C-NMR for 3na (150 MHz)



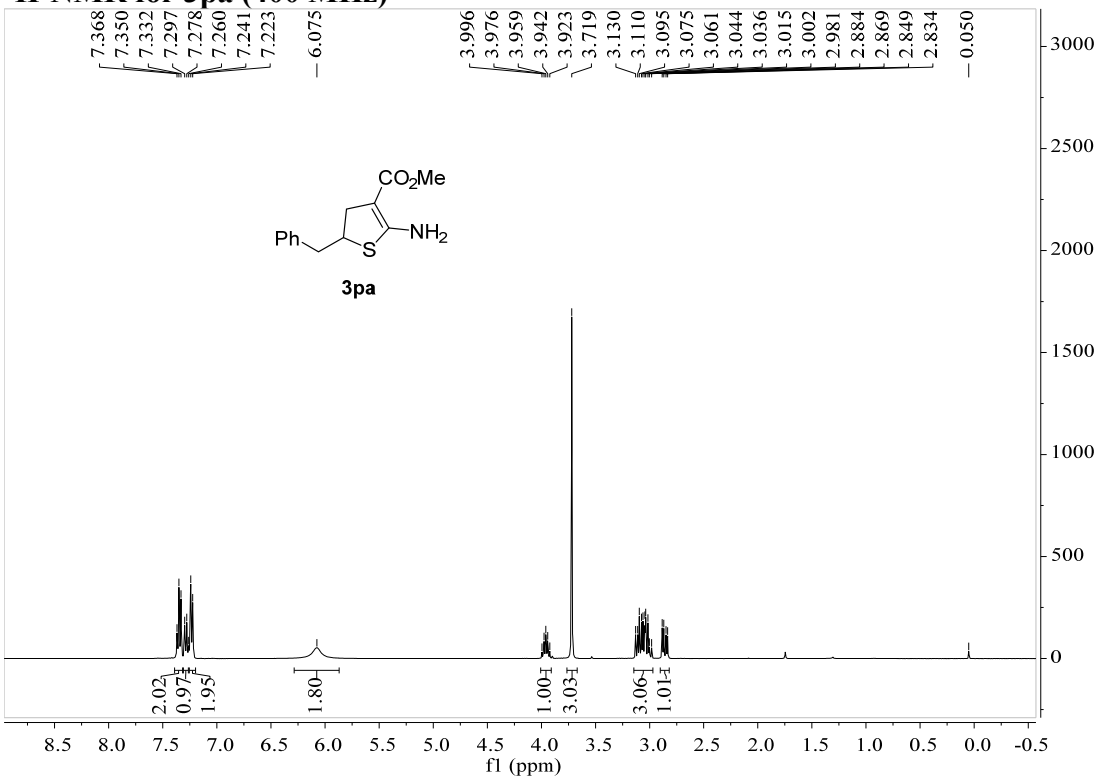
^{1}H-NMR for 3oa (600 MHz)



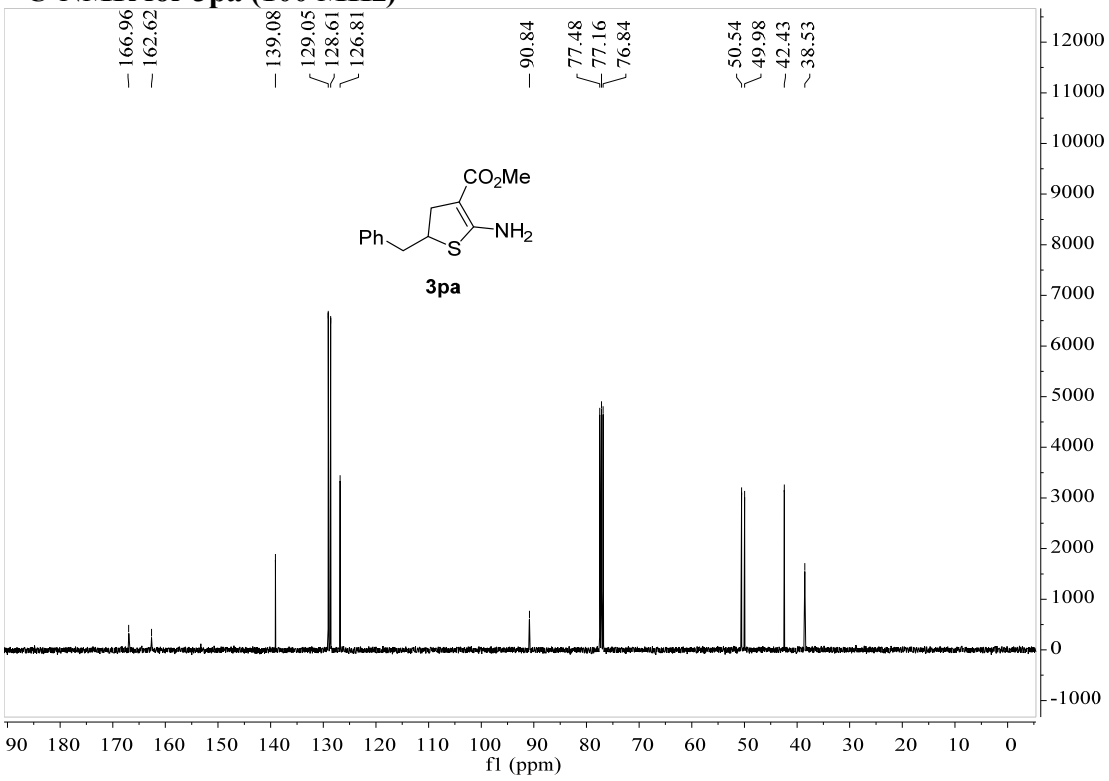
^{13}C-NMR for 3oa (150 MHz)



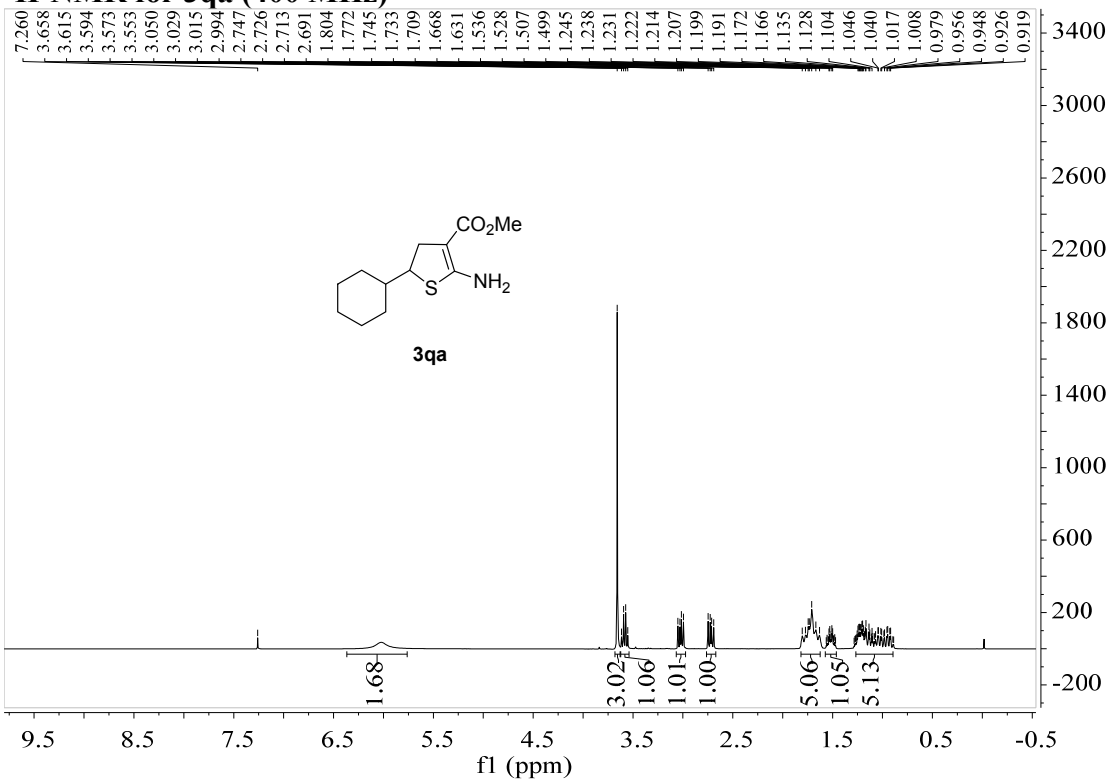
^{1}H-NMR for 3pa (400 MHz)



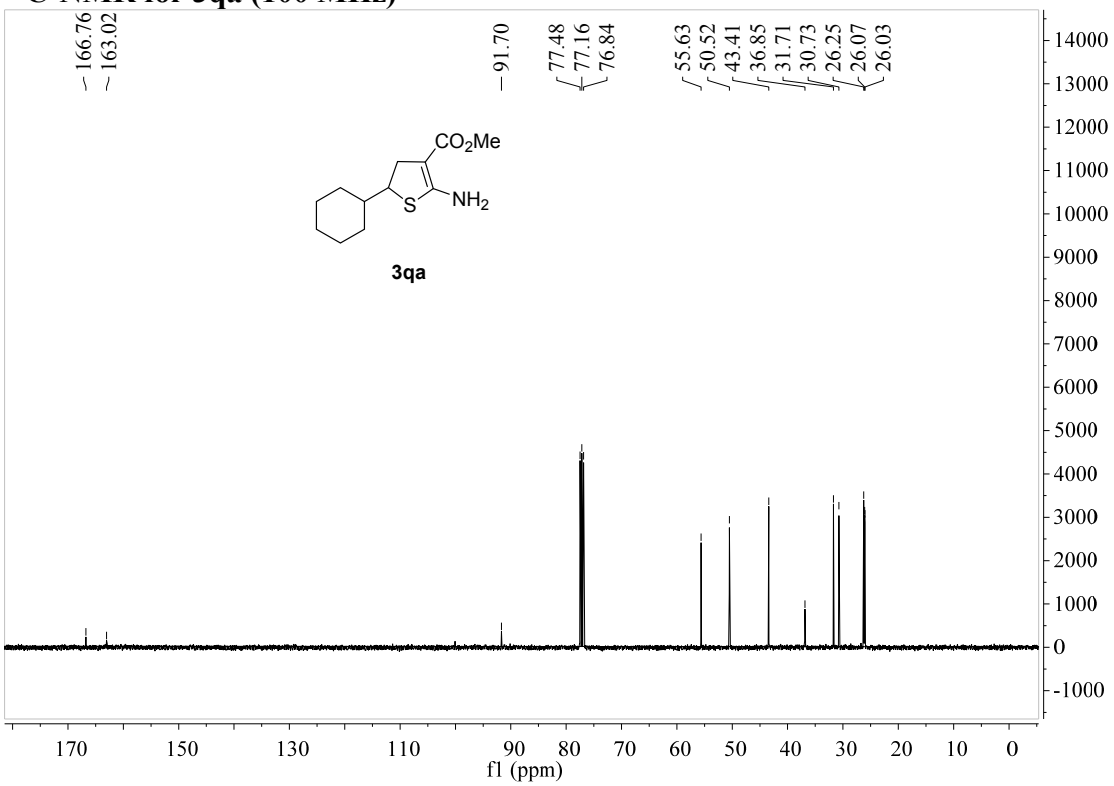
^{13}C-NMR for 3pa (100 MHz)



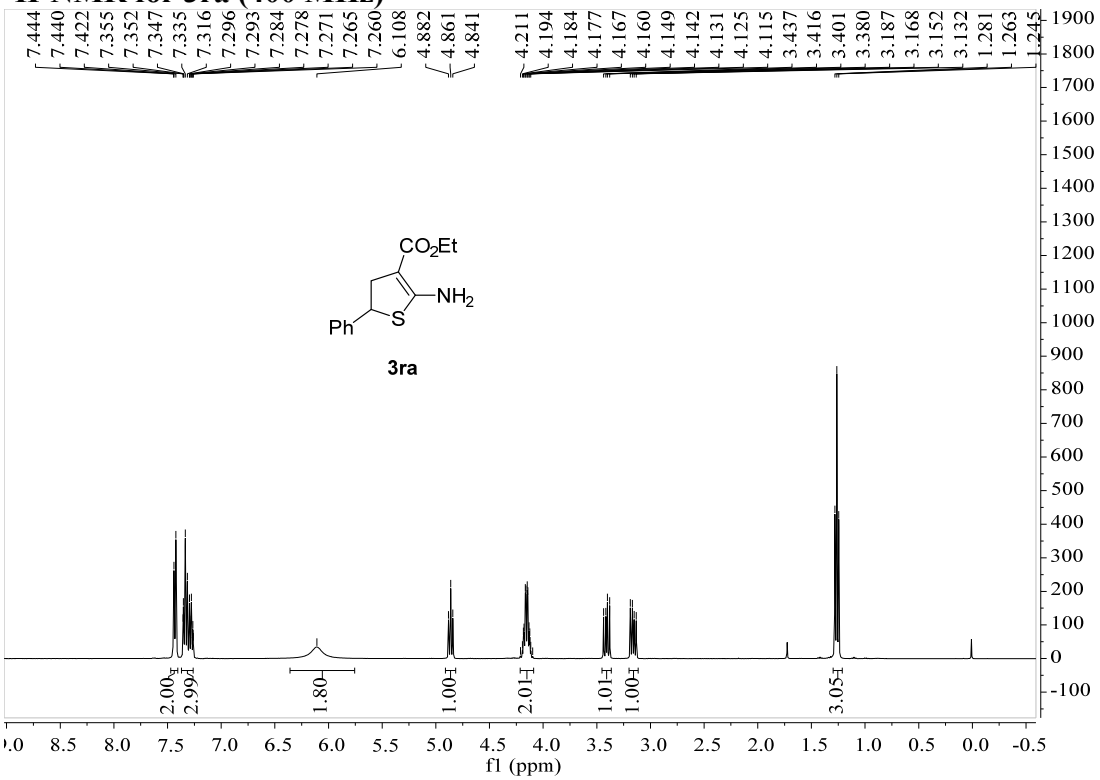
^{1}H-NMR for 3qa (400 MHz)



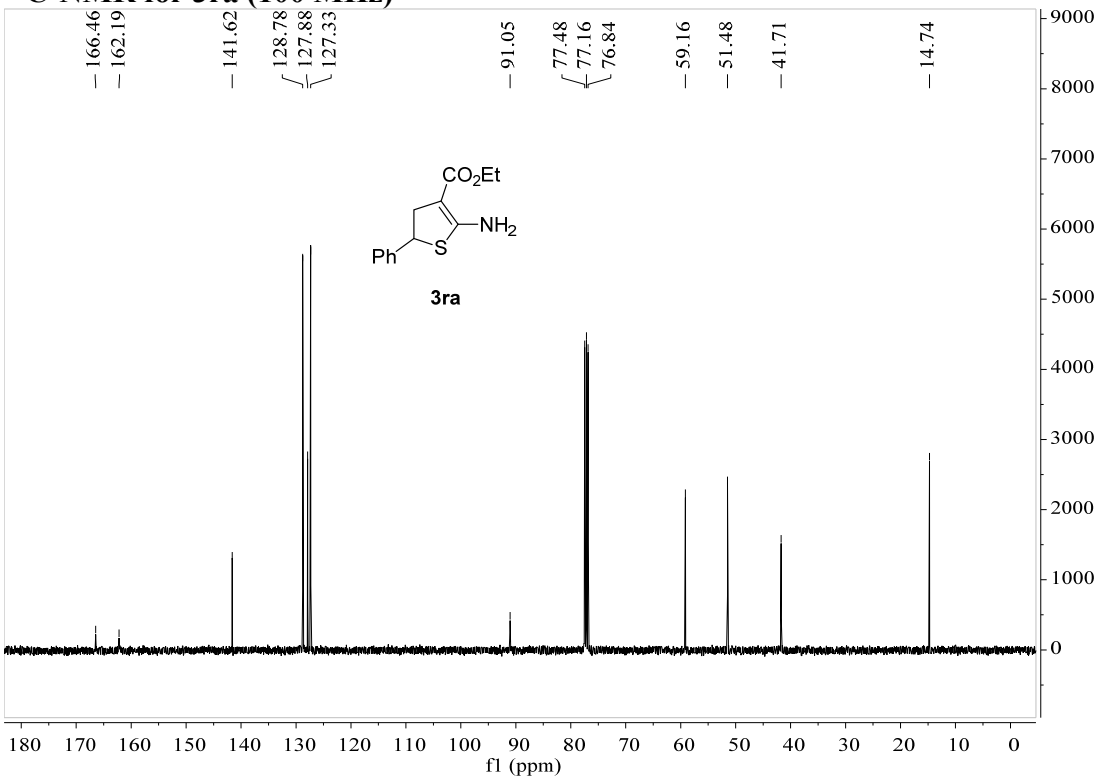
^{13}C-NMR for 3qa (100 MHz)



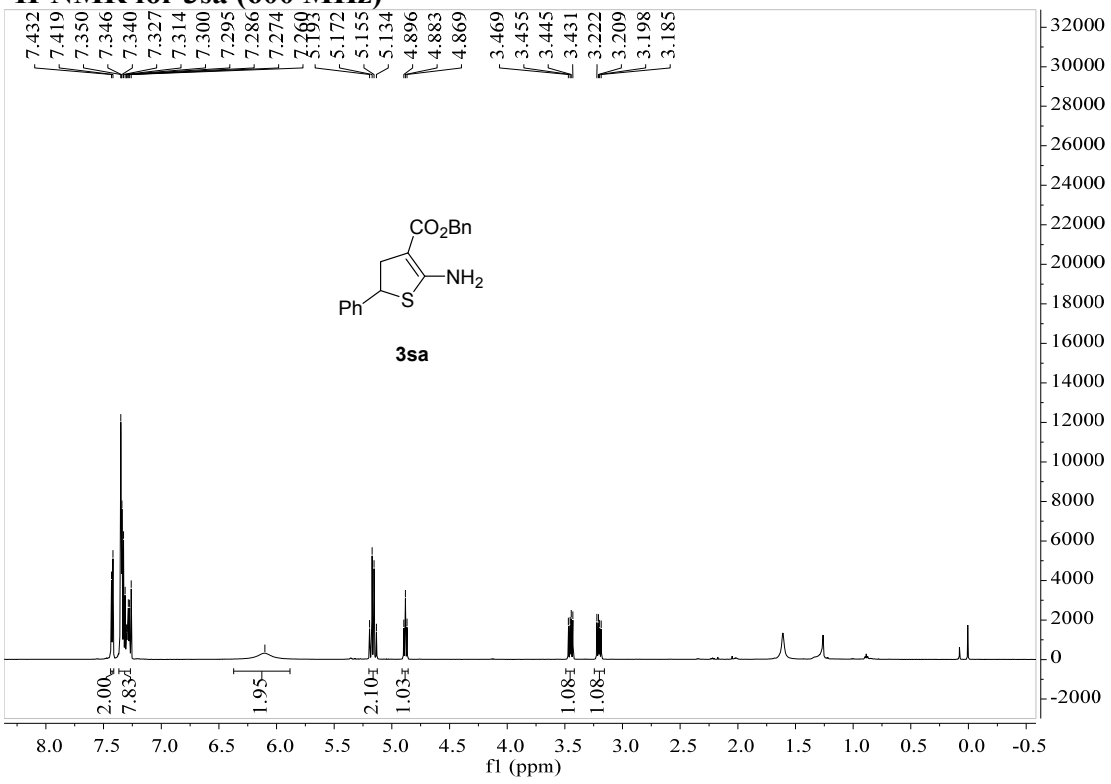
^{1}H-NMR for 3ra (400 MHz)



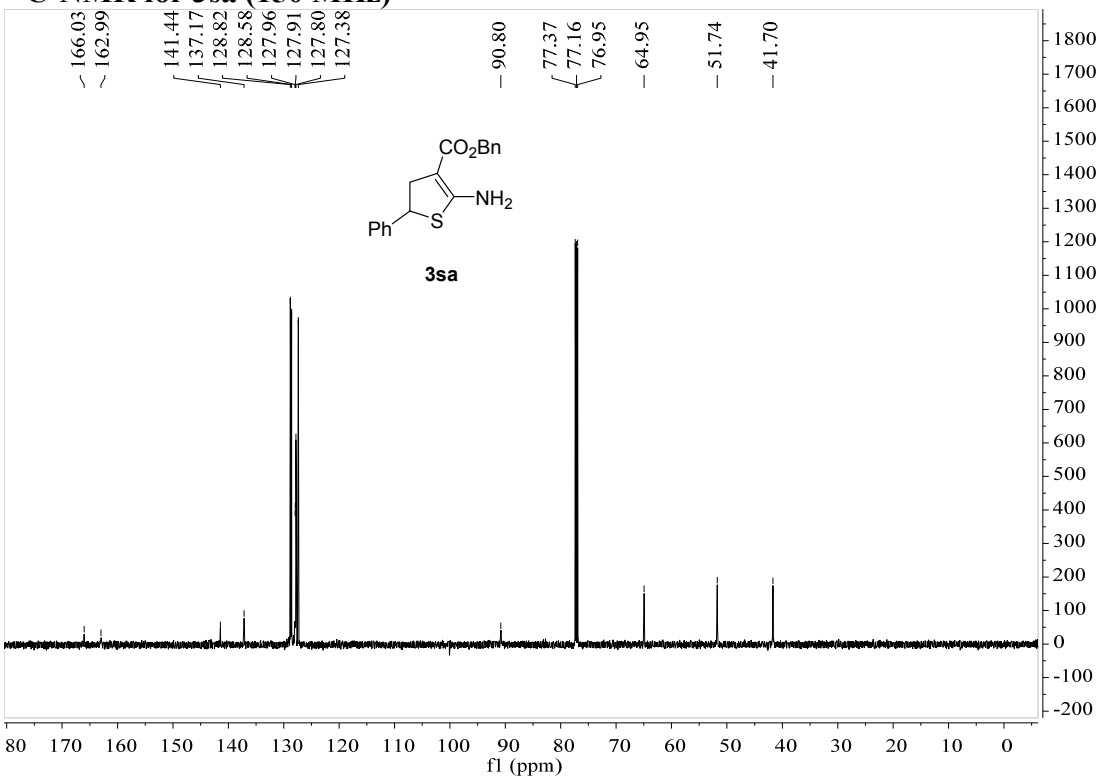
^{13}C-NMR for 3ra (100 MHz)



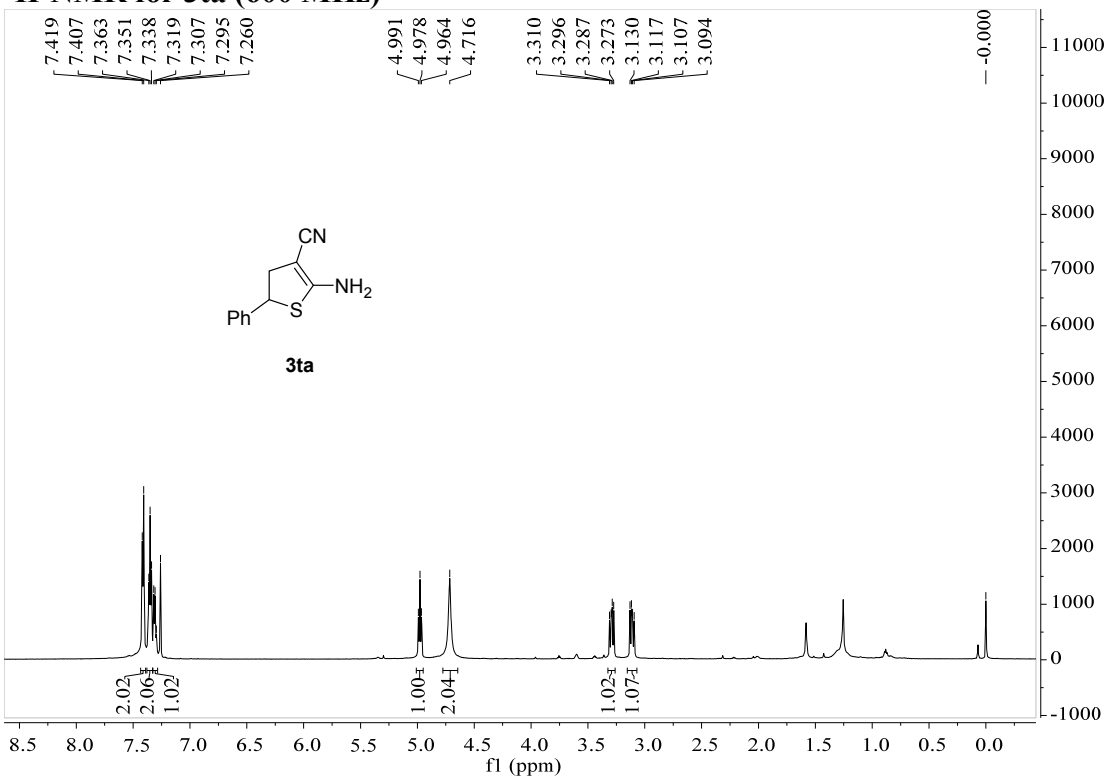
^{1}H-NMR for 3sa (600 MHz)



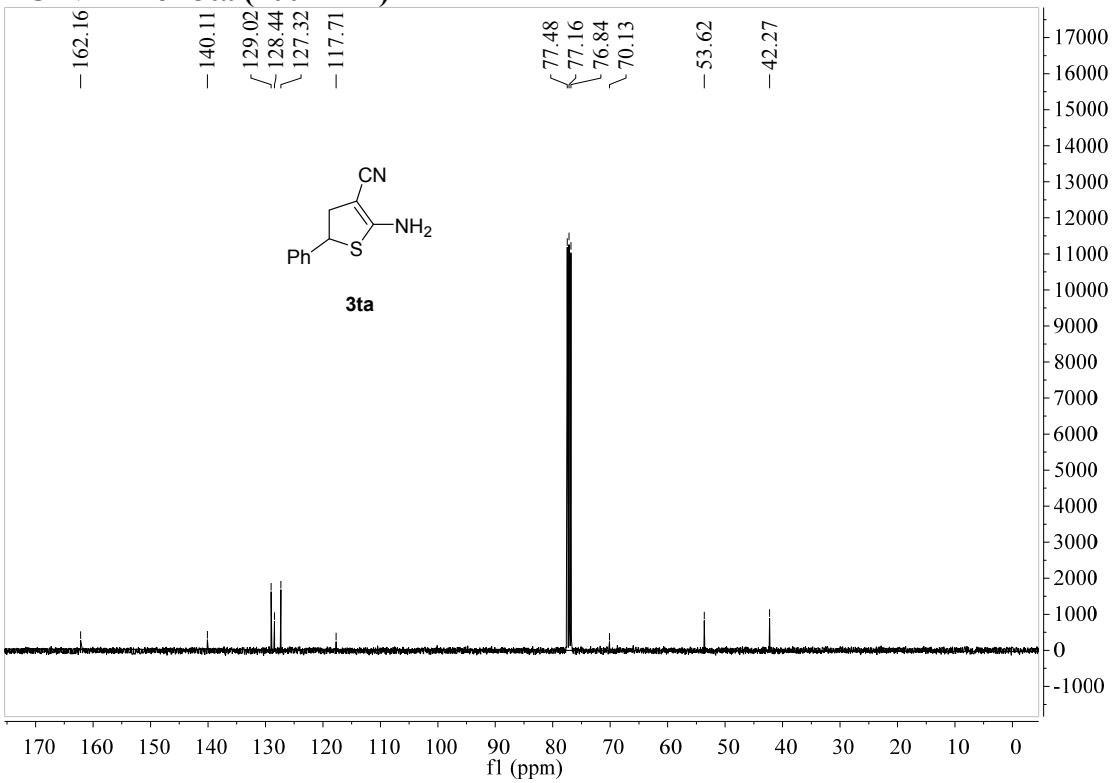
^{13}C-NMR for 3sa (150 MHz)



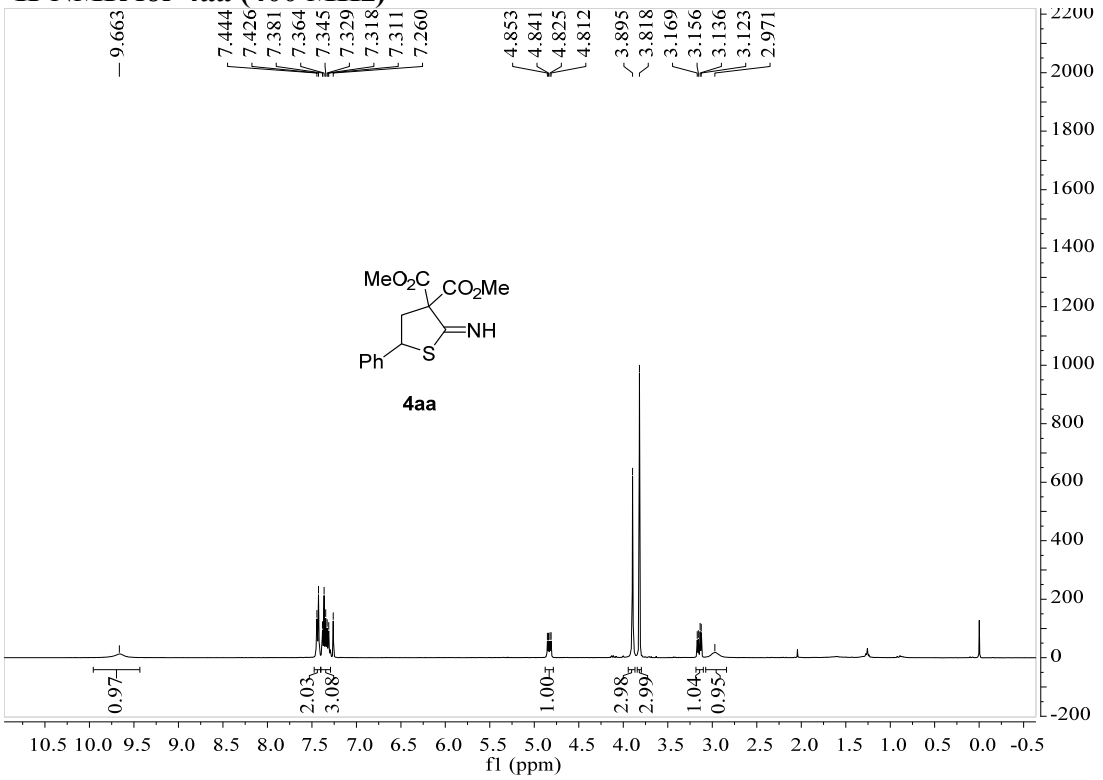
^{1}H-NMR for 3ta (600 MHz)



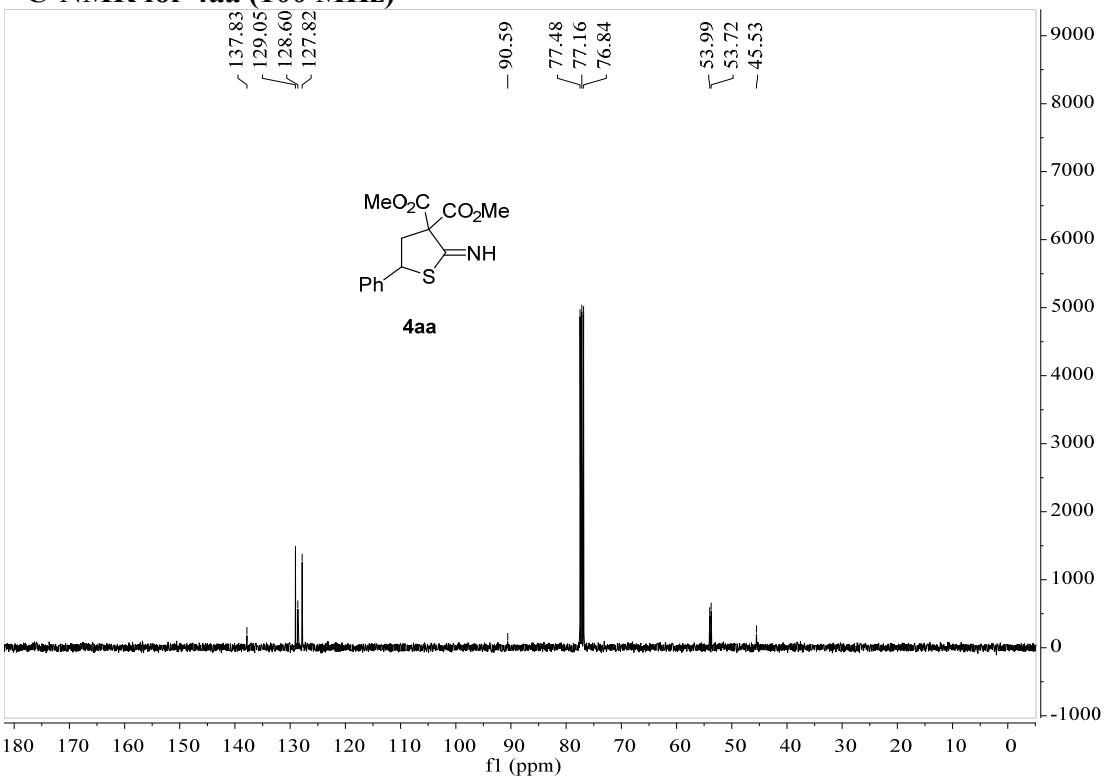
^{13}C-NMR for 3ta (100 MHz)



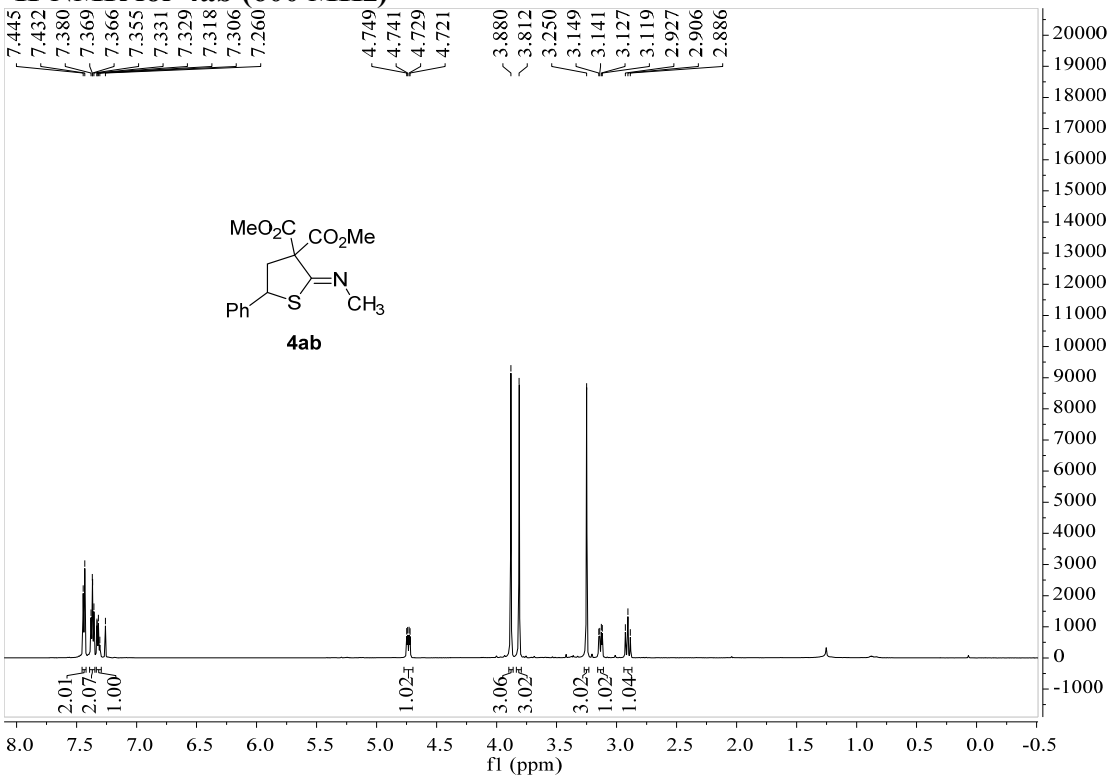
^{1}H-NMR for 4aa (400 MHz)



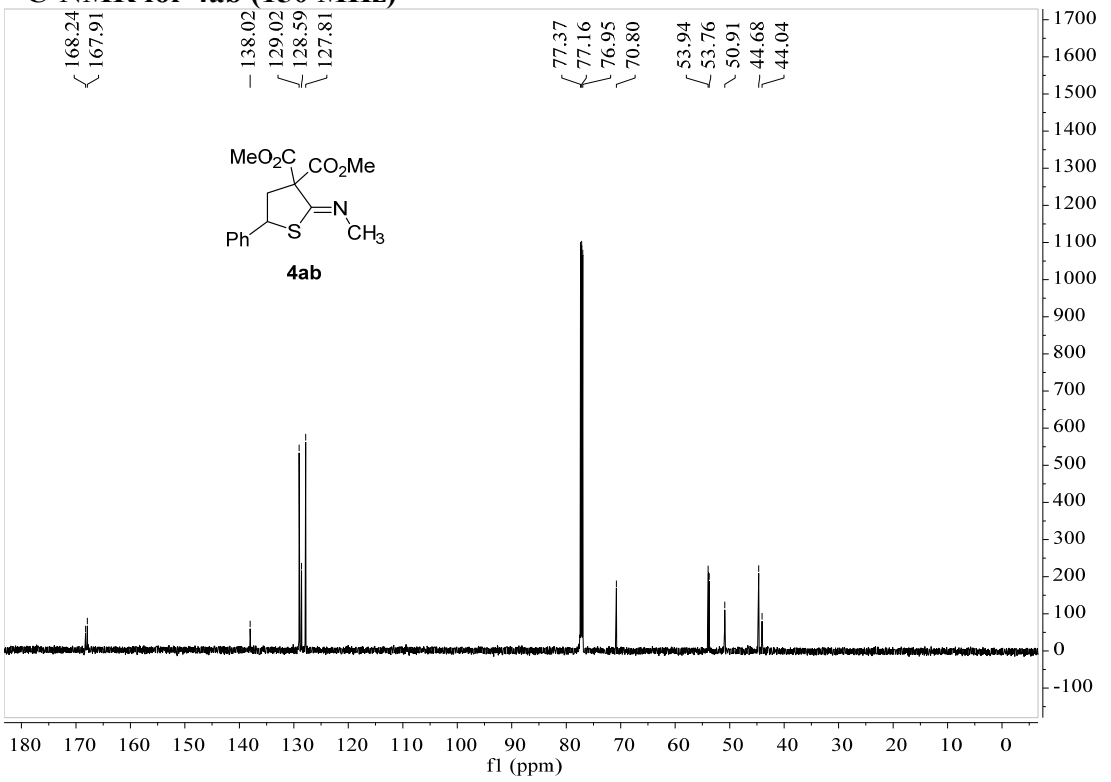
^{13}C-NMR for 4aa (100 MHz)



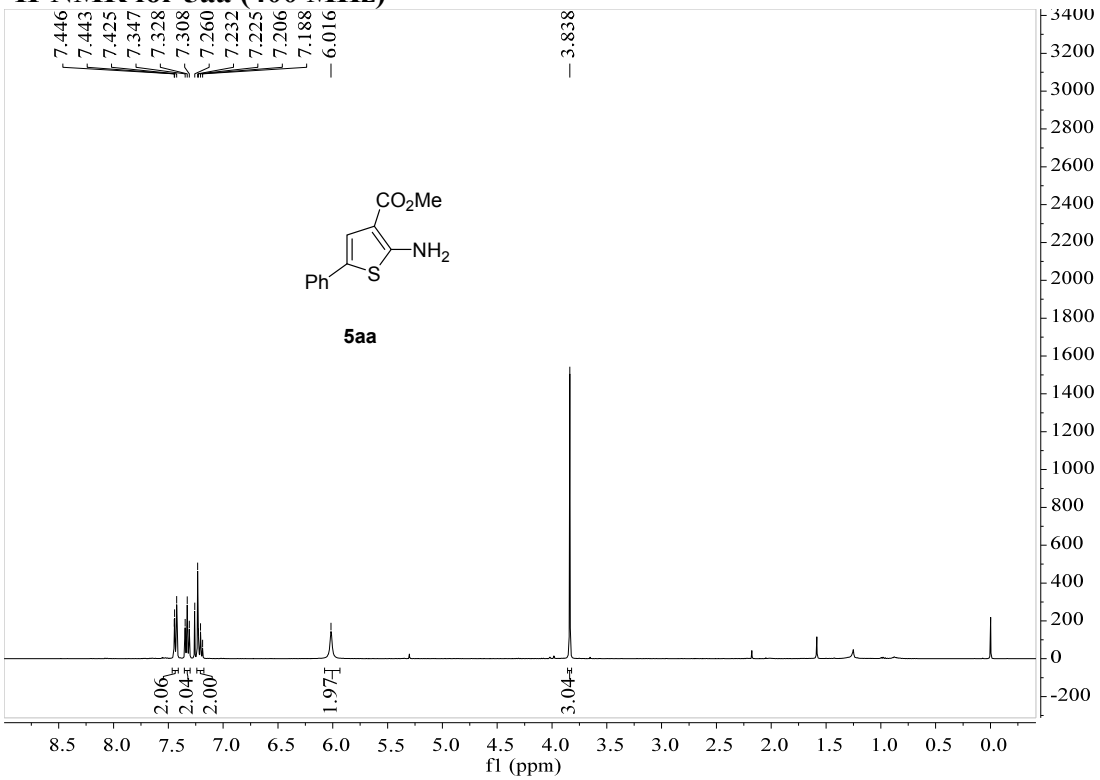
^{1}H-NMR for 4ab (600 MHz)



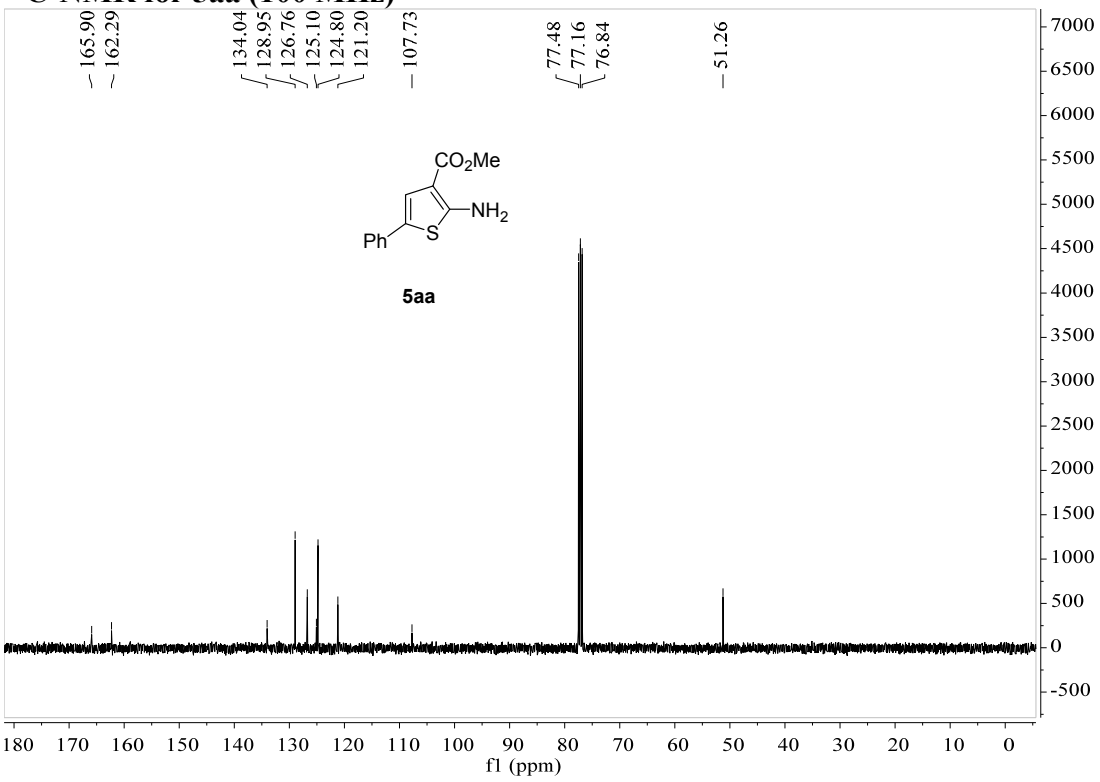
^{13}C-NMR for 4ab (150 MHz)



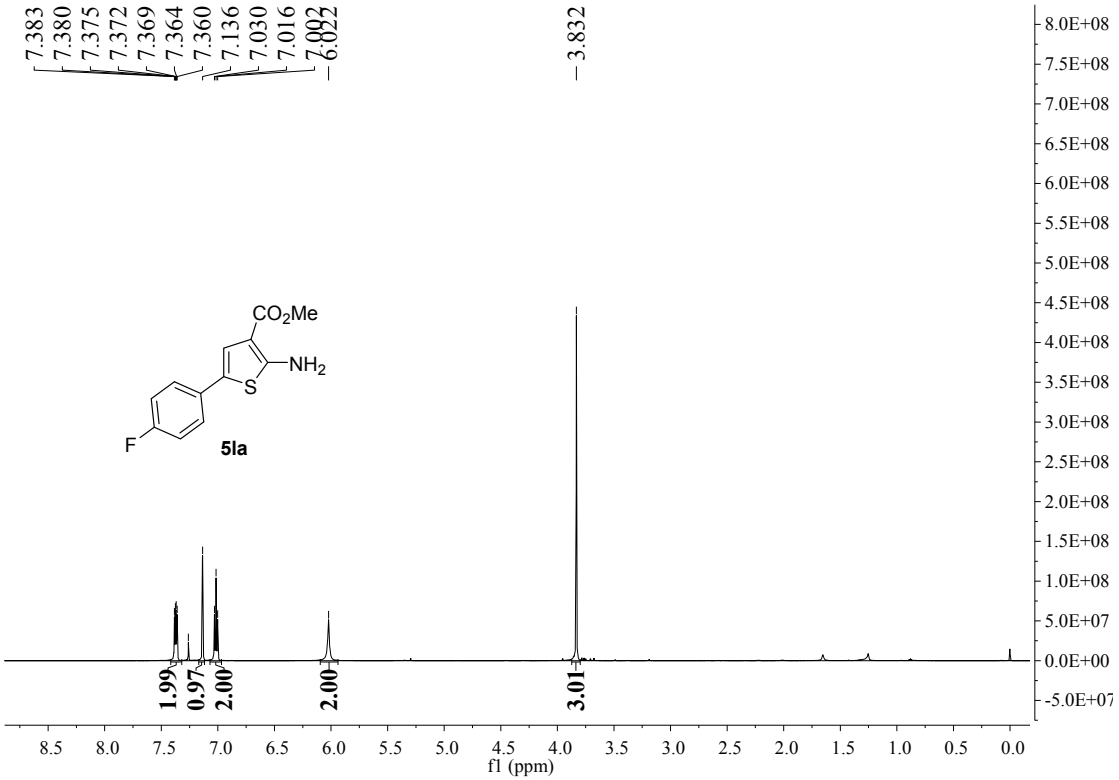
^{1}H-NMR for 5aa (400 MHz)



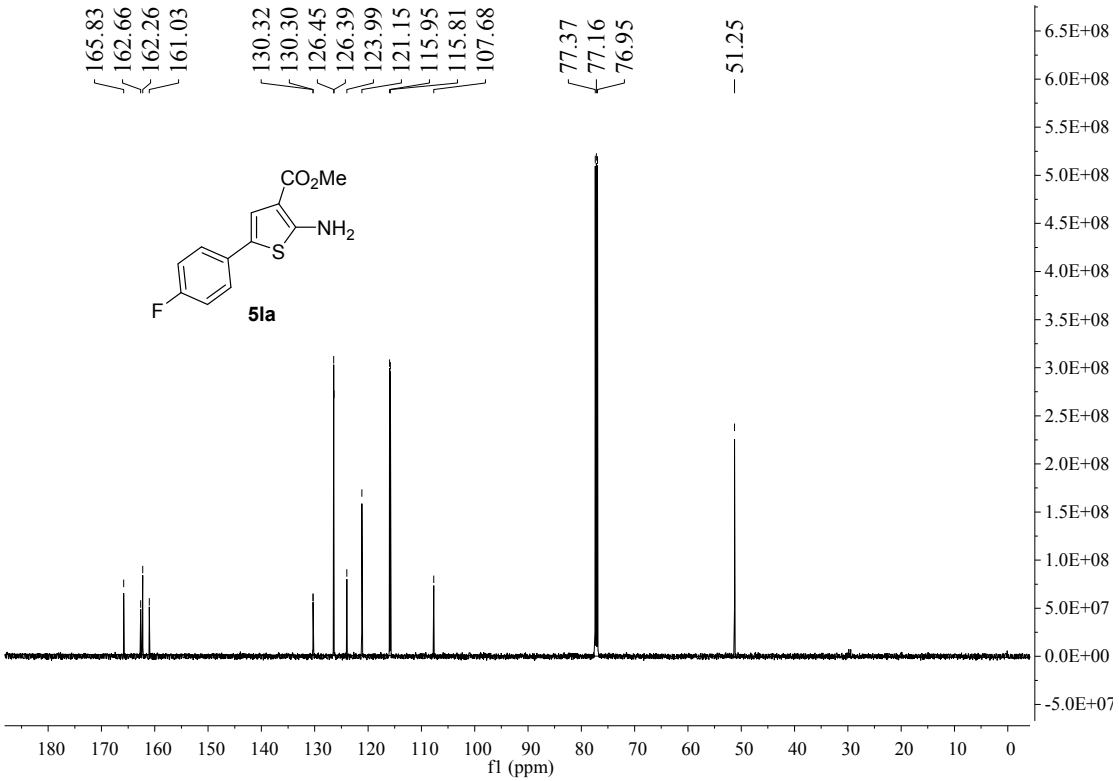
^{13}C-NMR for 5aa (100 MHz)



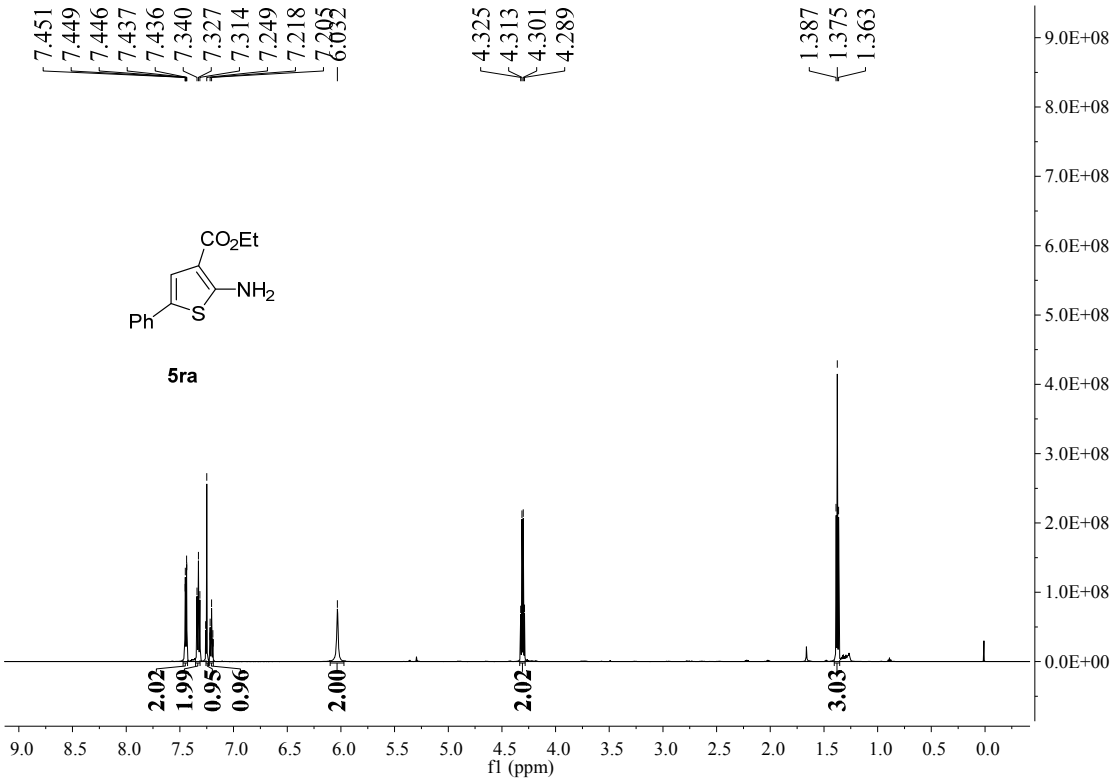
^{1}H-NMR for 5la (600 MHz)



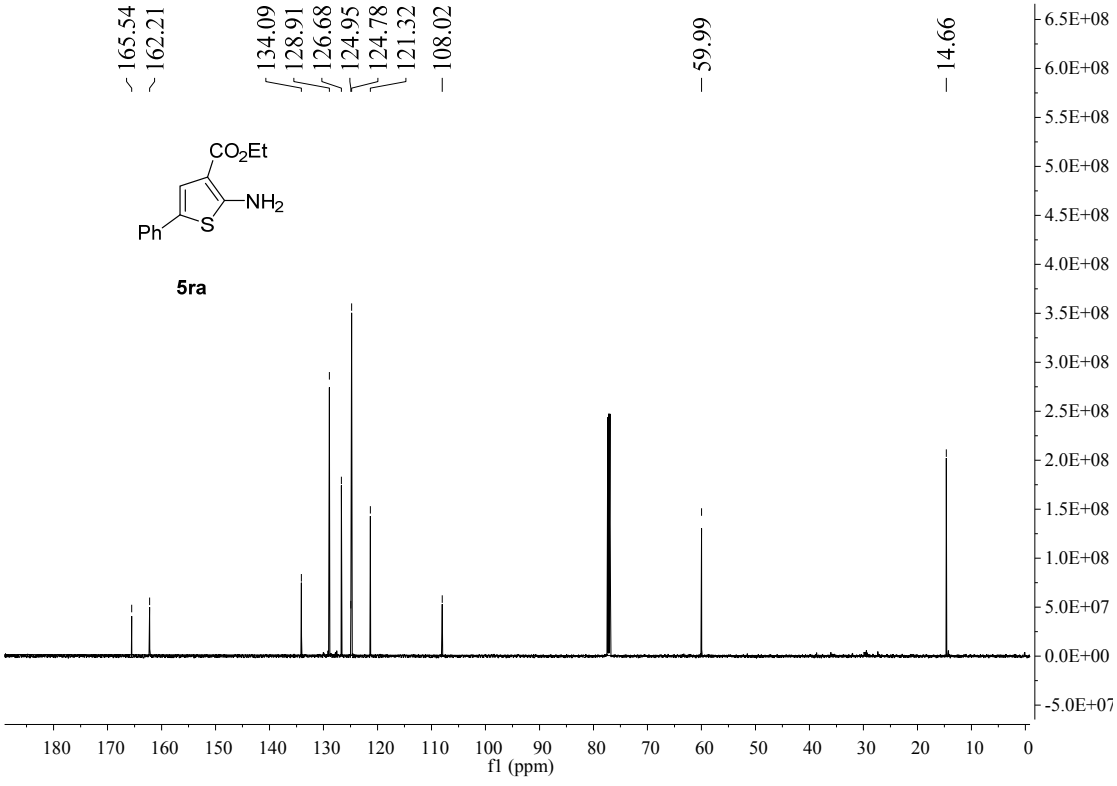
^{13}C-NMR for 5la (150 MHz)



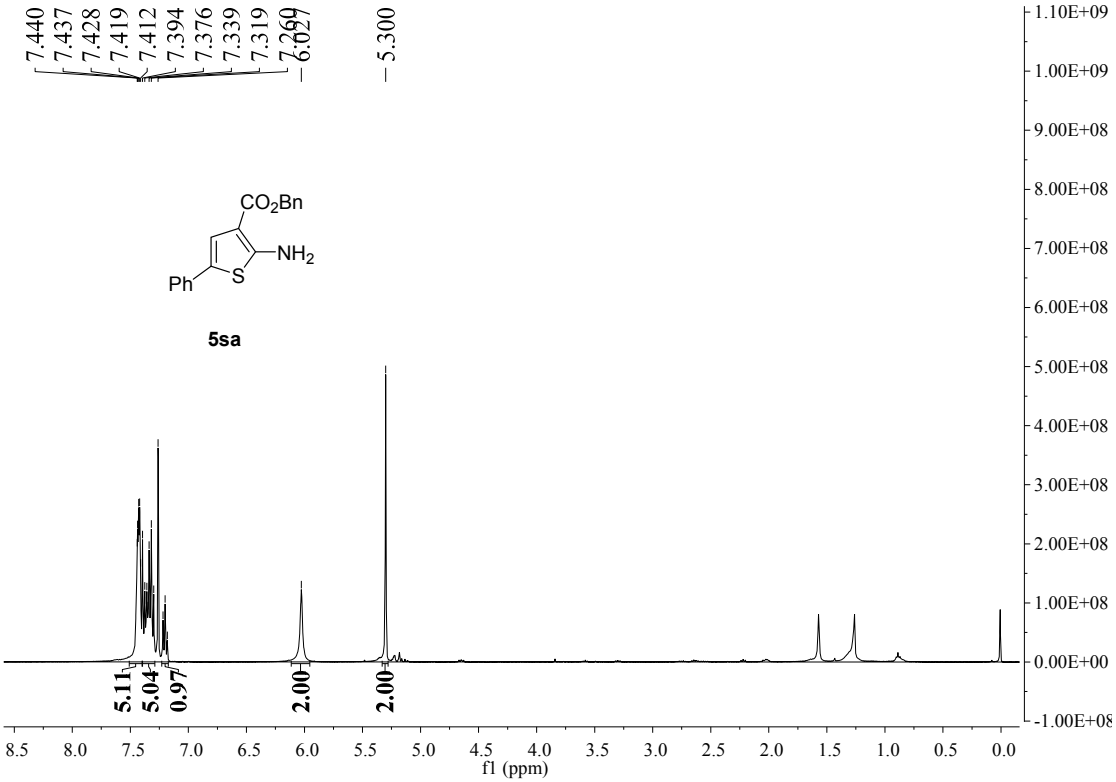
^{1}H-NMR for 5ra (600 MHz)



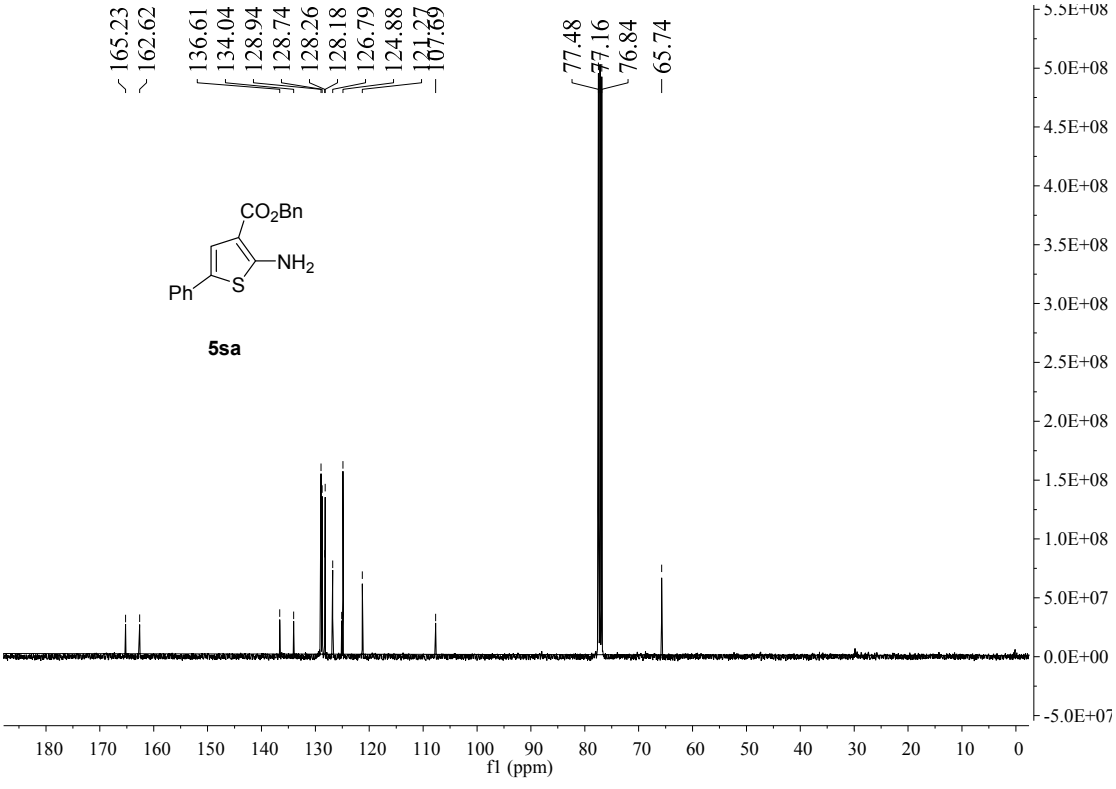
^{13}C-NMR for 5ra (150 MHz)



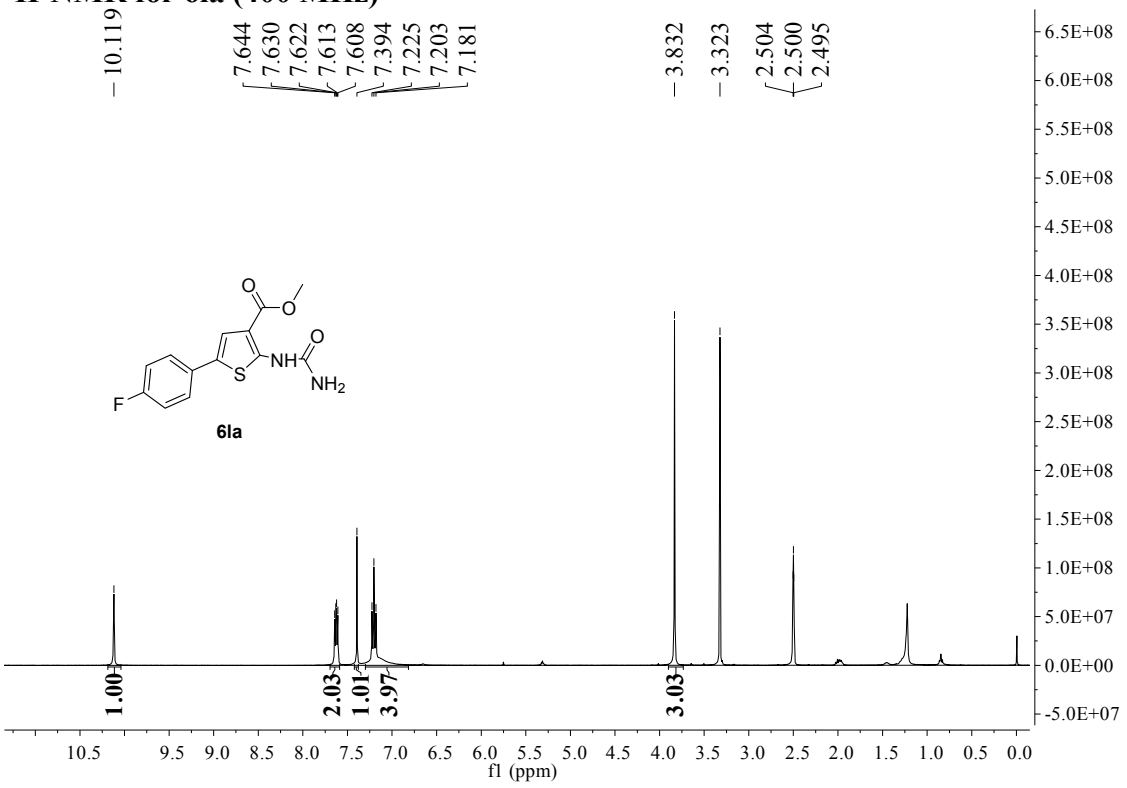
^{1}H-NMR for 5sa (400 MHz)



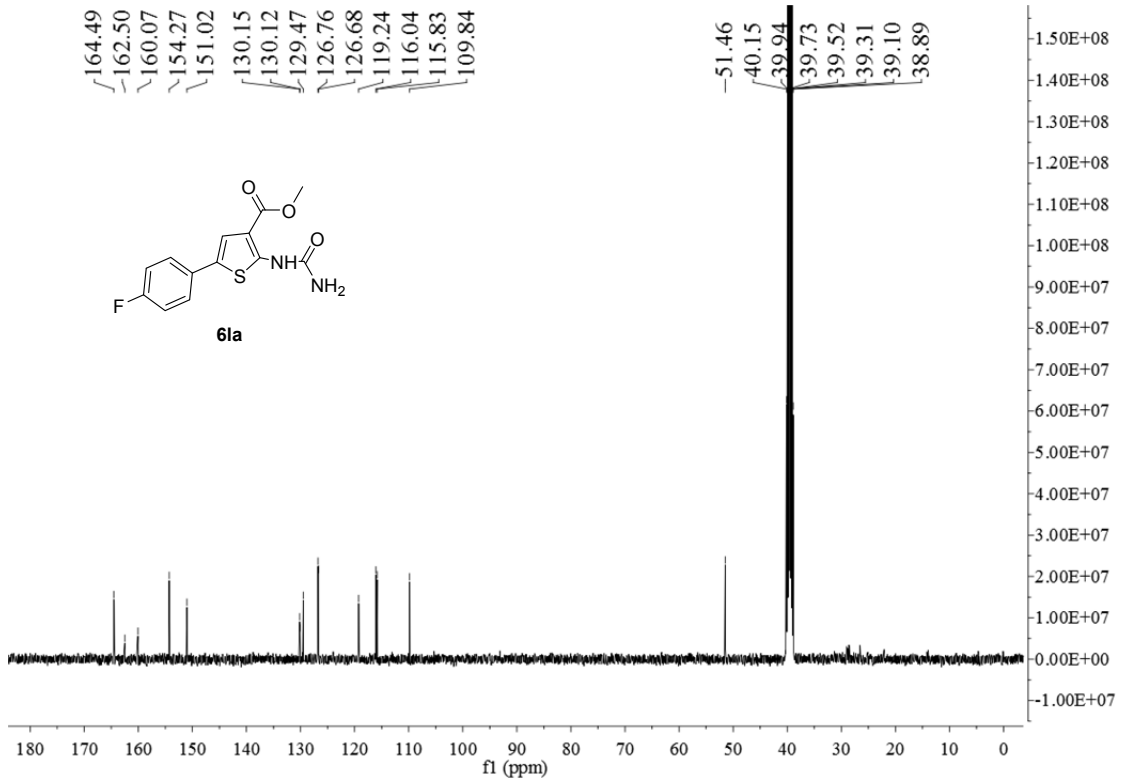
^{13}C-NMR for 5sa (100 MHz)



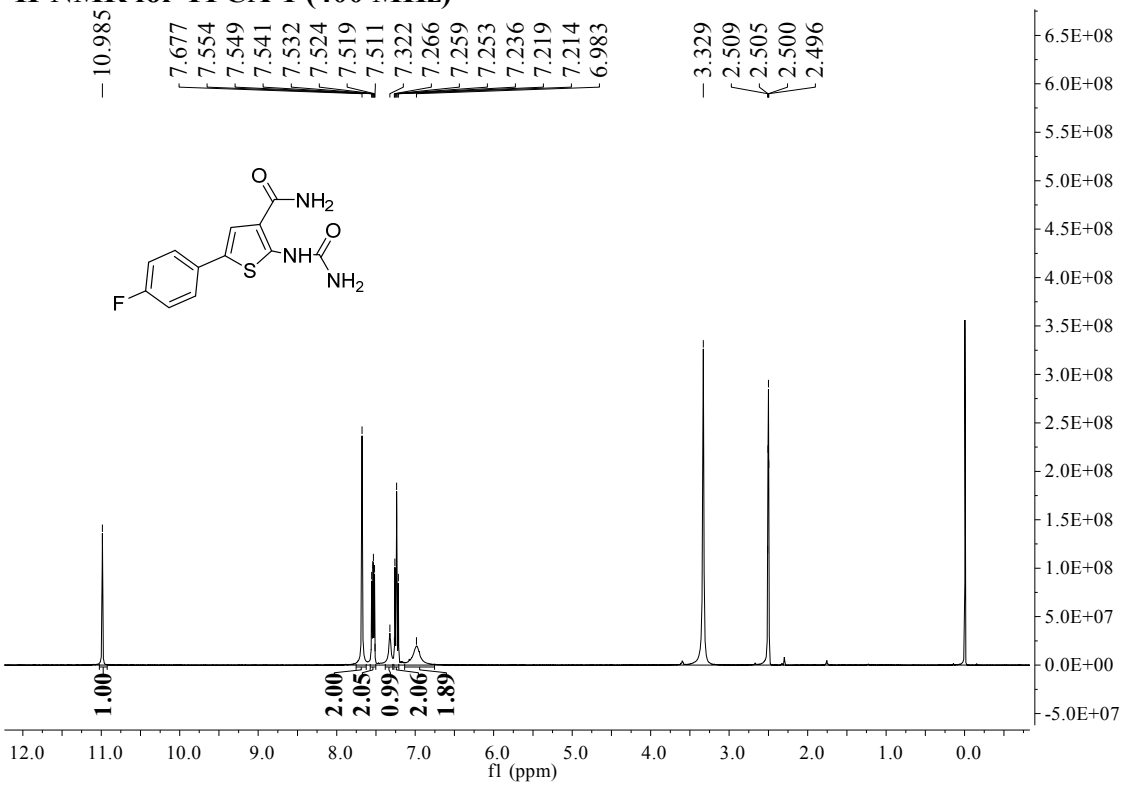
^{1}H-NMR for 6la (400 MHz)



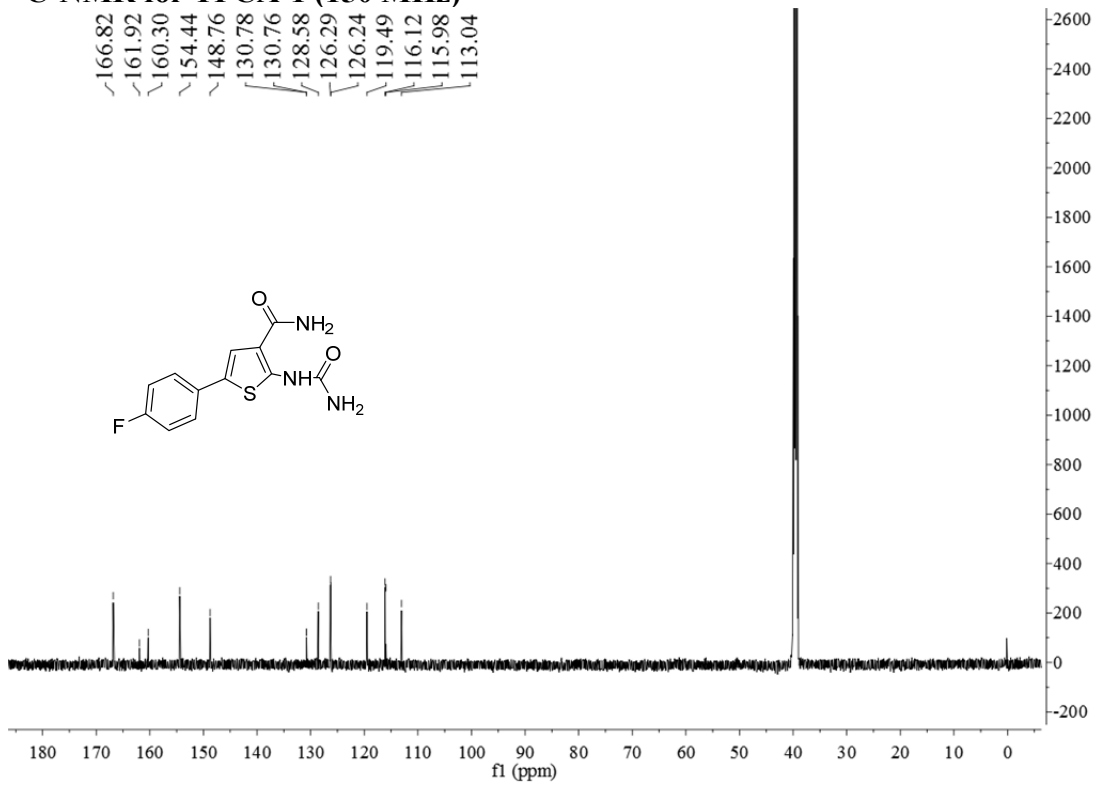
^{13}C-NMR for 6la (100 MHz)



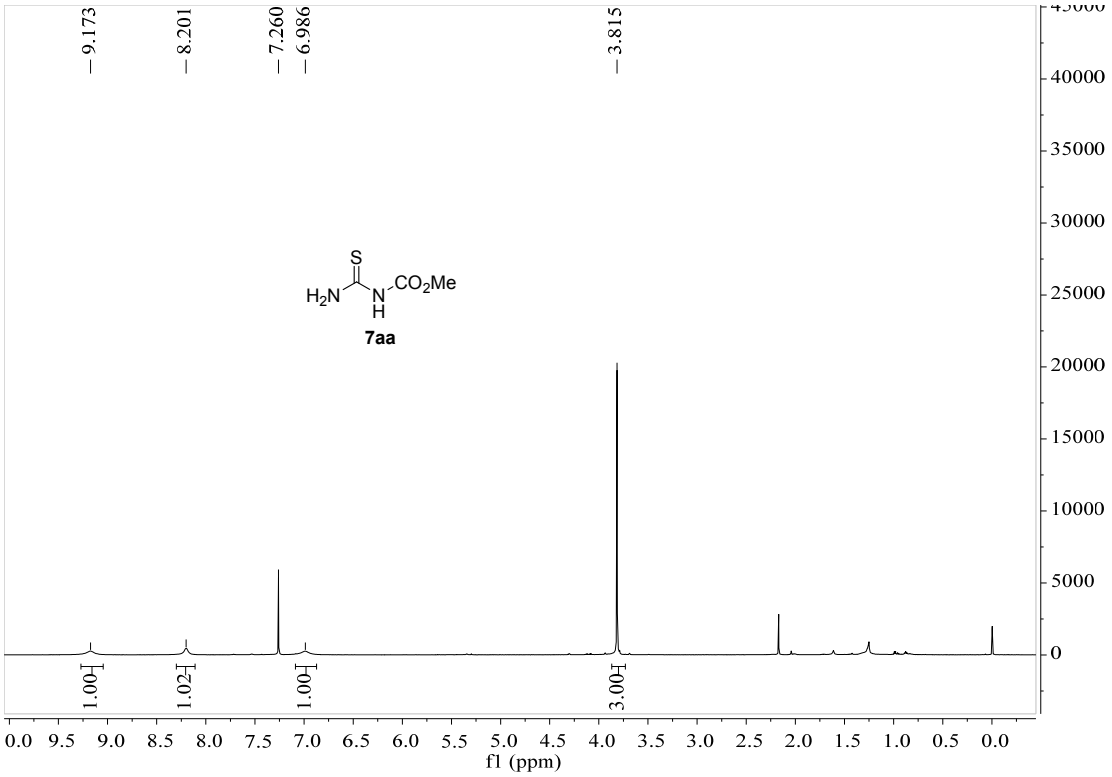
^{1}H-NMR for TPCA-1 (400 MHz)



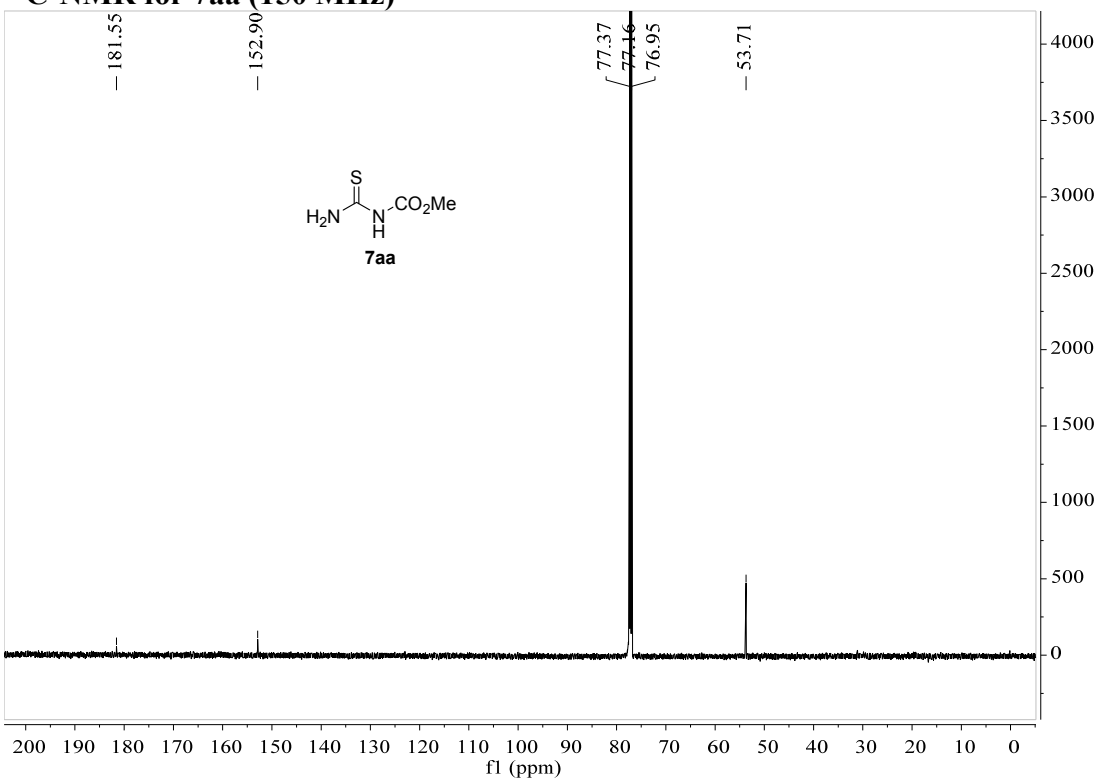
^{13}C-NMR for TPCA-1 (150 MHz)



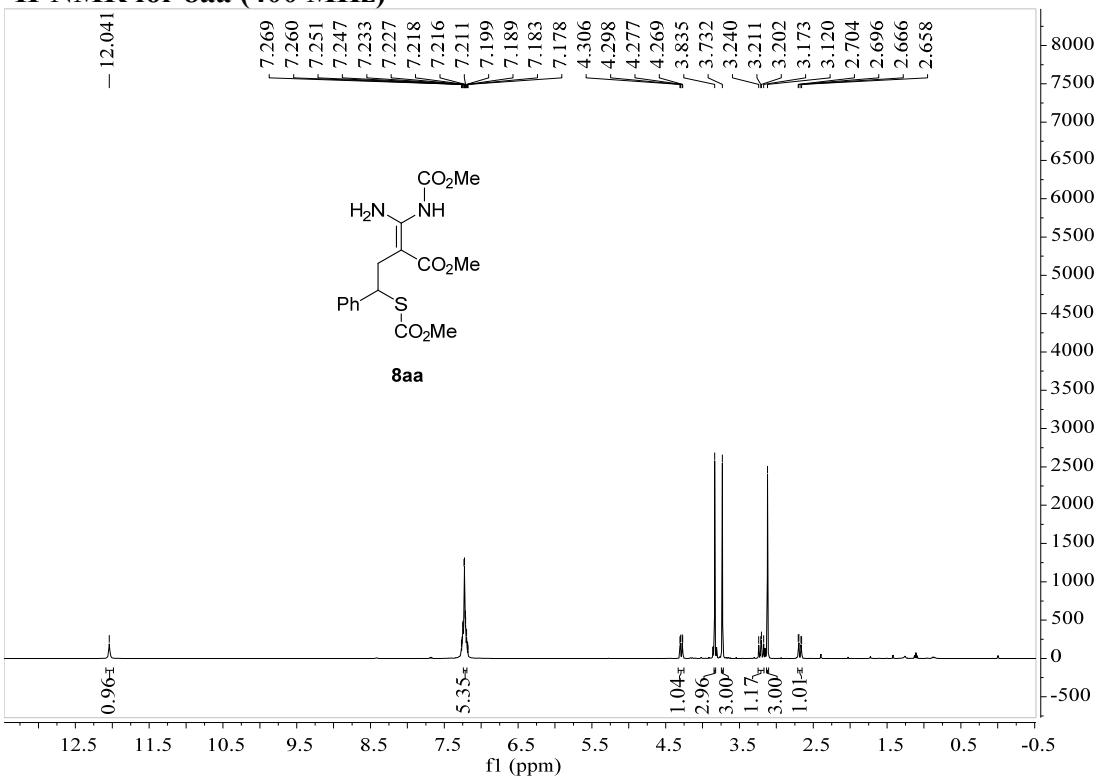
^{1}H-NMR for 7aa (600 MHz)



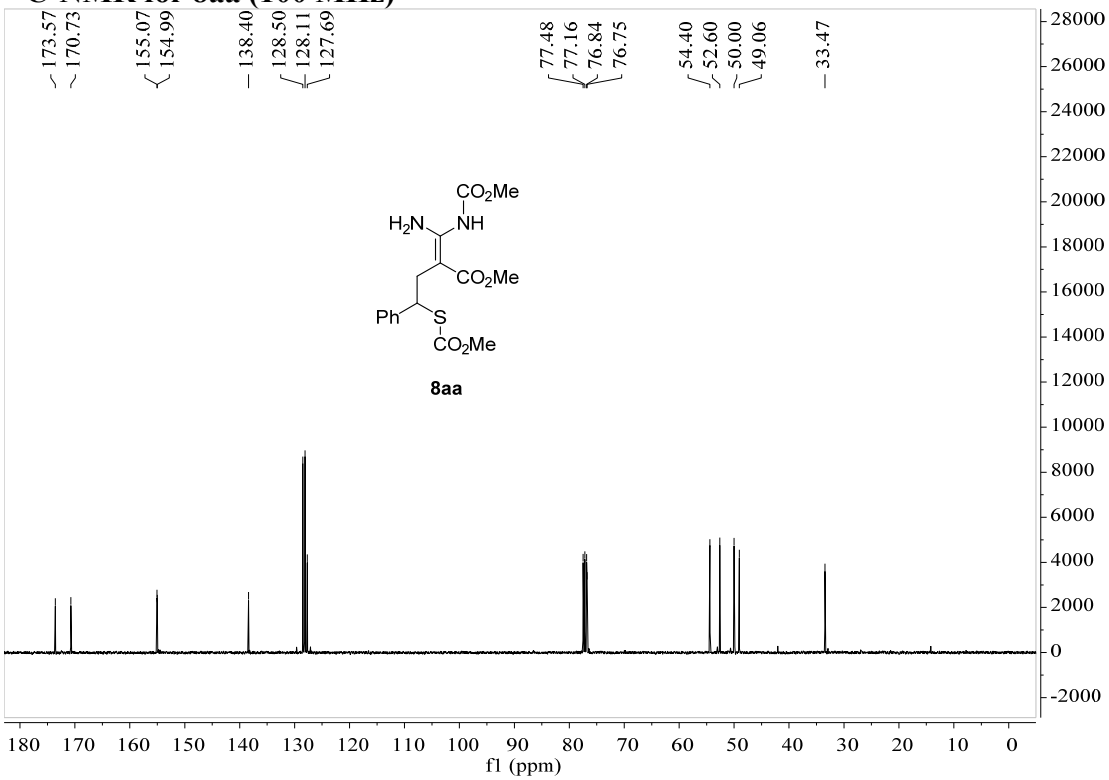
^{13}C-NMR for 7aa (150 MHz)



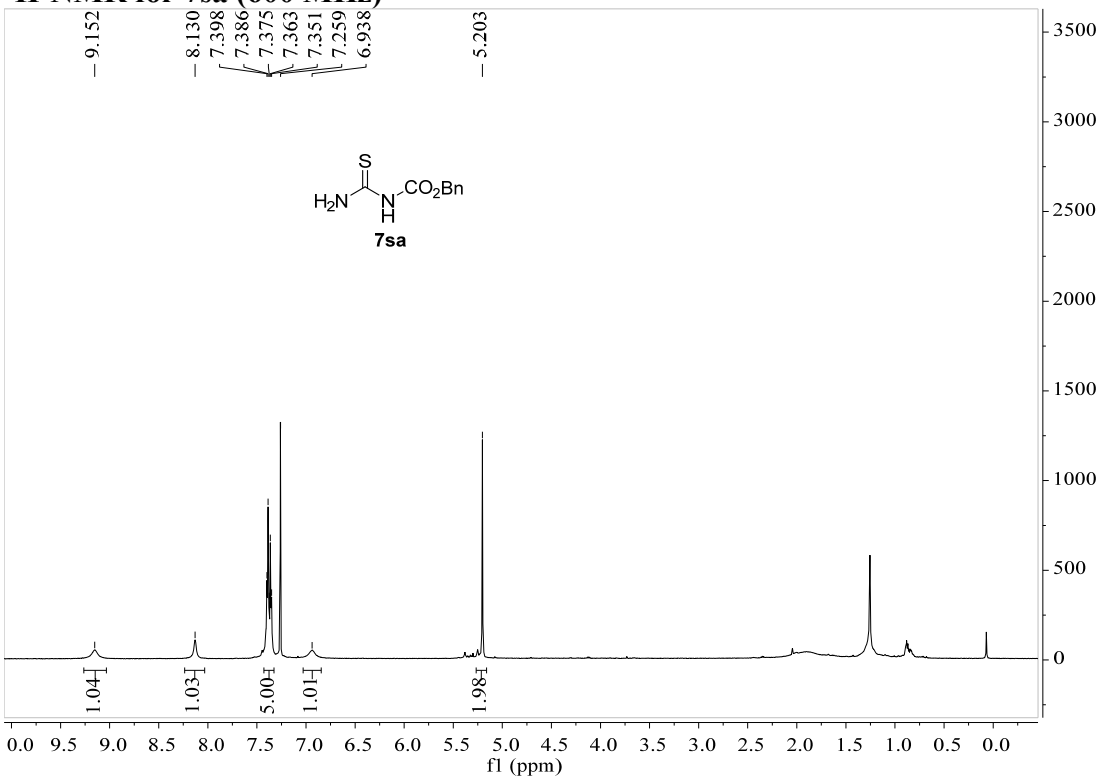
^{1}H-NMR for 8aa (400 MHz)



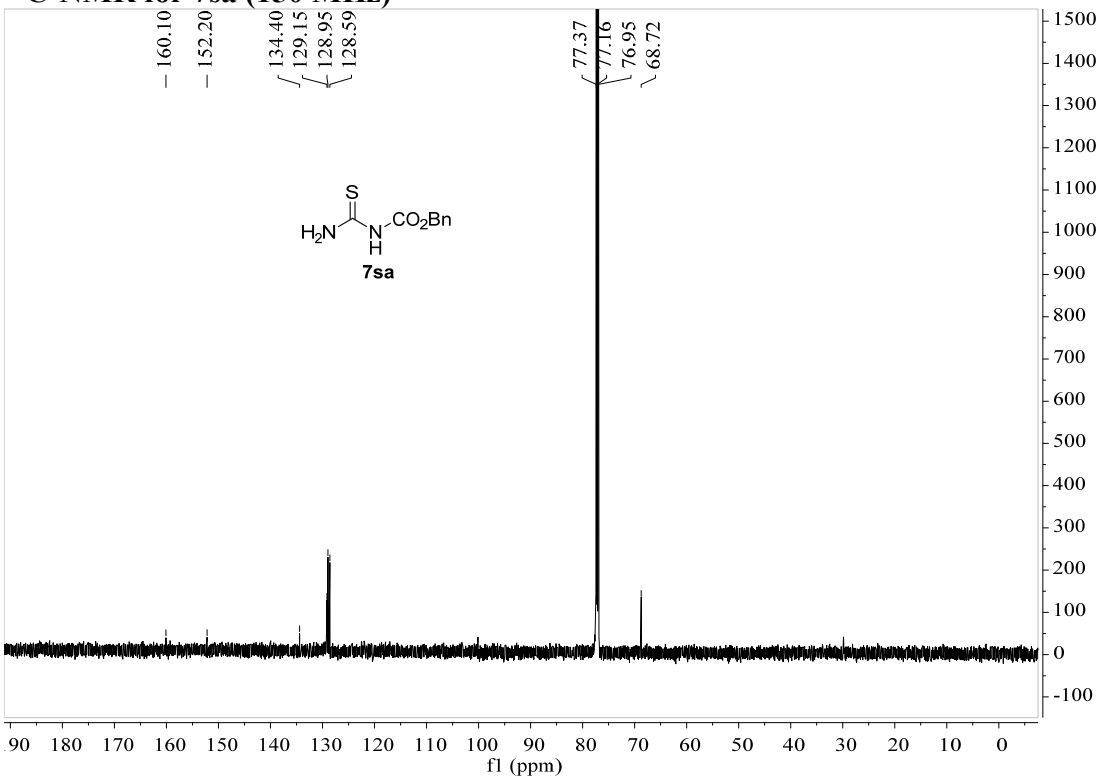
^{13}C-NMR for 8aa (100 MHz)



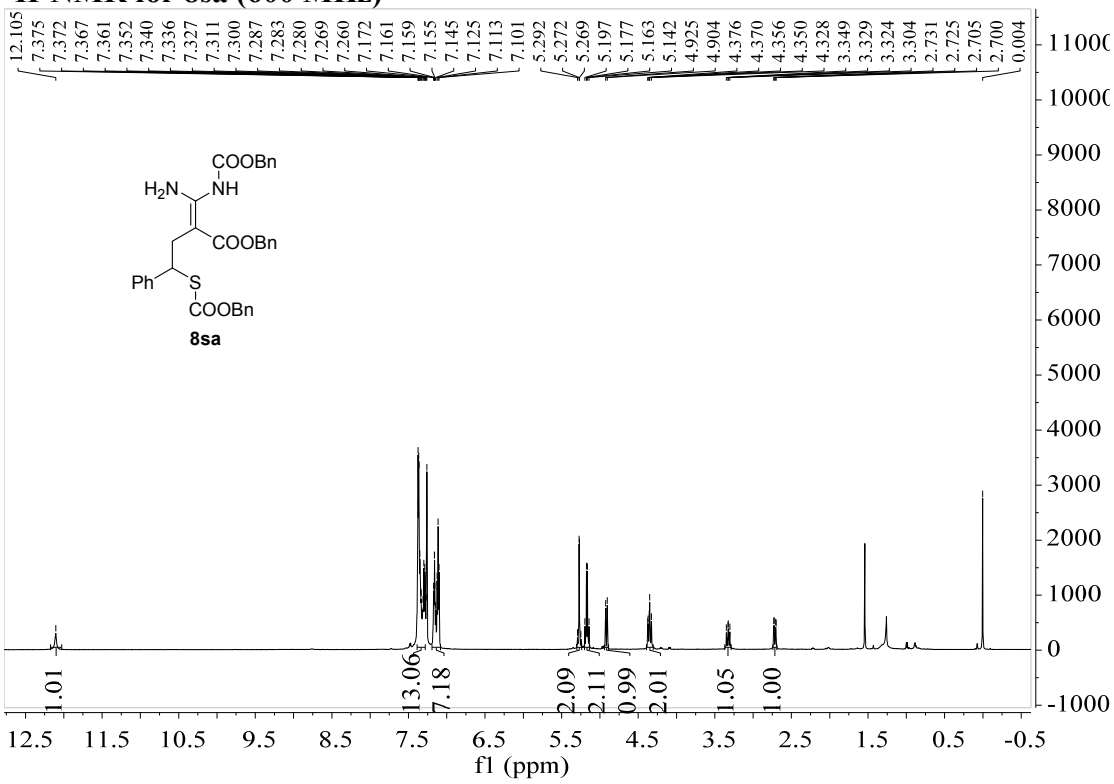
^{1}H-NMR for 7sa (600 MHz)



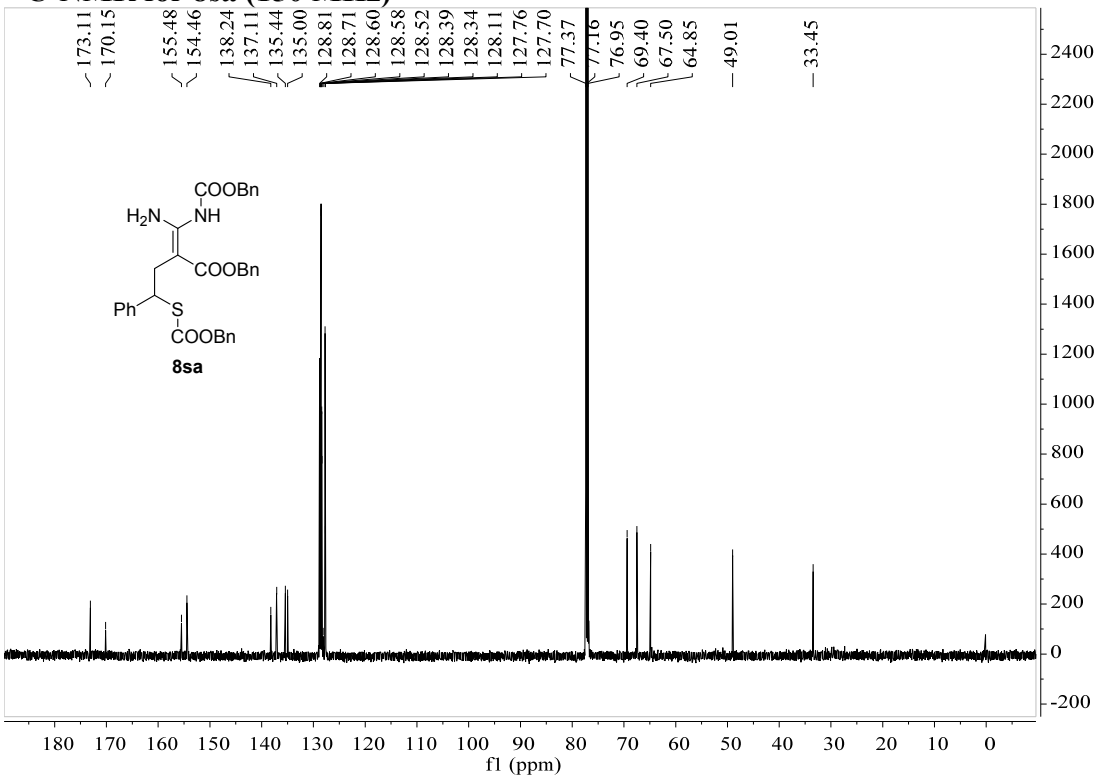
^{13}C-NMR for 7sa (150 MHz)



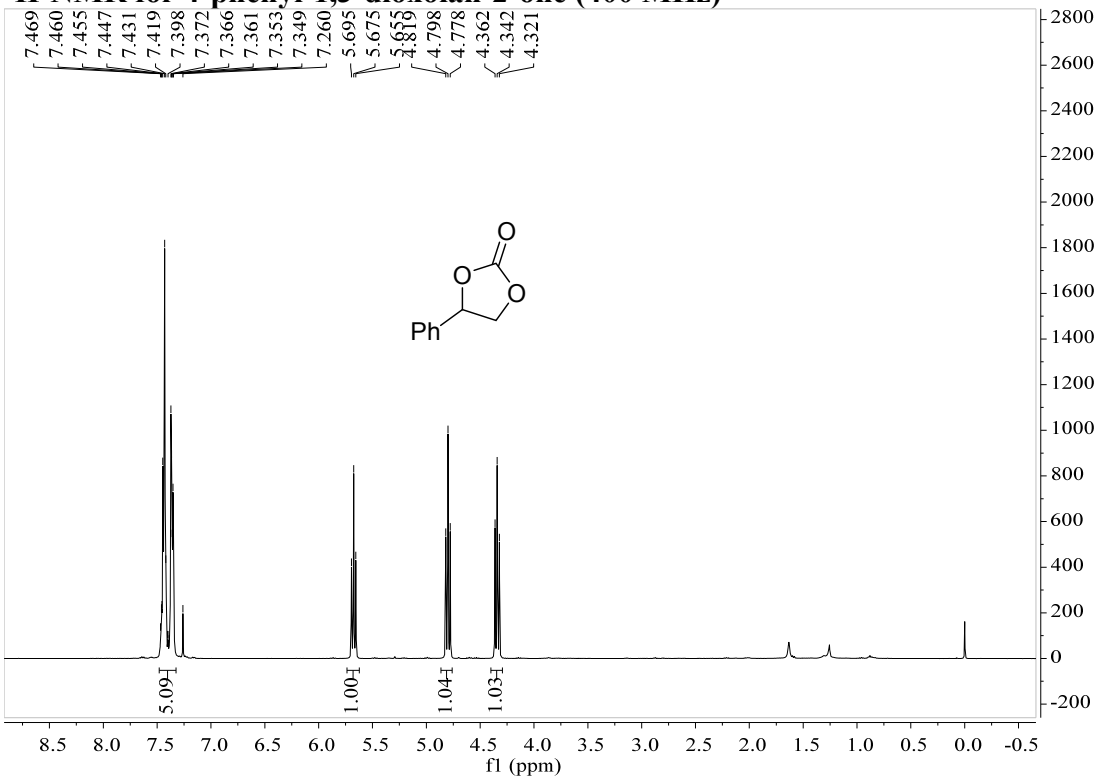
^{1}H-NMR for 8sa (600 MHz)



^{13}C-NMR for 8sa (150 MHz)



[1]H-NMR for 4-phenyl-1,3-dioxolan-2-one (400 MHz)



[13]C-NMR for 4-phenyl-1,3-dioxolan-2-one (150 MHz)