Supplementary Information

for

Fe-Catalyzed B-H and N-H Insertion Reactions of Iodonium Ylides

Hejun An[1], Zhi Cui[1], Jinchao Liang[2], Xingxing Ma[1], Jinglong Chen[2,*], Qiuling Song[1,3,4,5*]

[1]Key Laboratory of Molecule Synthesis and Function Discovery, Fujian Province University, College of Chemistry at Fuzhou University, Fuzhou, Fujian 350108, China

[2]College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China

[3]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

[4]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

[5]Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Peking University, Beijing 100871, China

*e-mail: qsong@fzu.edu.cn; jchen@fzu.edu.cn

Table of Contents

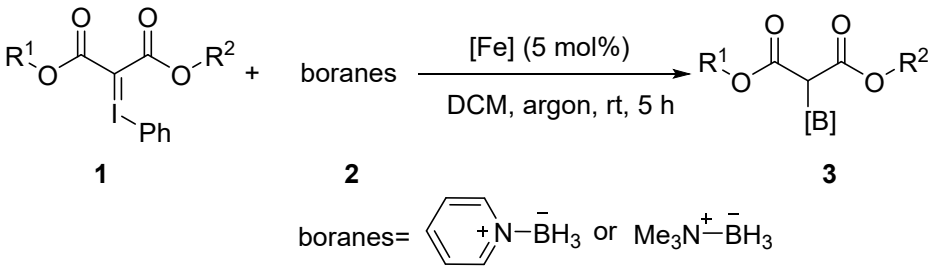
1. General information

General Experimental Procedures: All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Flash column chromatography was performed over silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm).

Materials: All chemicals were purchased from Adamas-beta®、Adamas-life® Reagent, Energy Chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd, Macklin reagent, LAAJOO reagent and Leyan (Shanghai, China) reagent. Unless otherwise stated, all experiments were conducted in a sealed tube under argon atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh). Material iodonium ylides **1** and [Fe] catalyst were prepared by methods reported in literature[1,2].

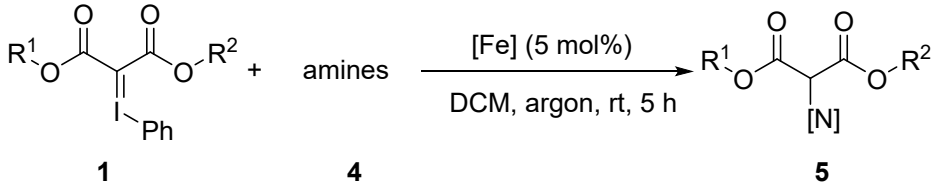
Instrumentation: ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, and ^{19}F NMR spectra were recorded at ambient temperature using Bruker Ascend^{TM} 400 (400 MHz) spectrometer or JNM-ECZ500R/S1 (500 or 600 MHz). Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) as an internal reference. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, m = multiplet. GC analysis was performed at Shimadzu GC-2030. HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source (Ion Trap) or Agilent 7250 QTOF with EI mode. The X-ray crystal structure was measured on the Bruker D8 venture.

2. General procedure 1: General procedure for Fe-Catalyzed B-H Insertion Reactions of Iodonium Ylides.



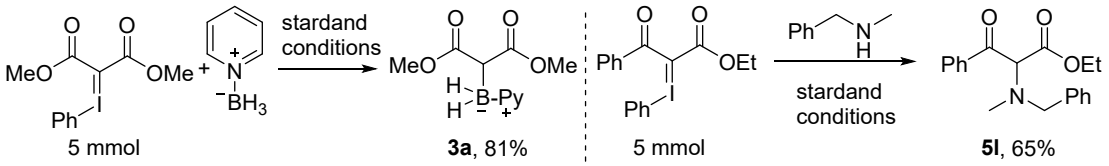
In an oven-dried 10 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with boranes **2** (0.2 mmol, 2.0 equiv), iodonium ylides **1** (0.1 mmol, 1.0 equiv), [Fe] catalyst(0.005 mmol, 5 mol%). After that, argon was pumped three times, and DCM (1 mL), was added. The reaction mixture was stirred at room temperature for 5 h. After complete reaction, concentrate under reduced pressure and purified by column flash chromatography on silica gel to afford the target products **3**.

3. General procedure for Fe-Catalyzed N-H Insertion Reactions of Iodonium Ylides.



In an oven-dried 10 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with amines **4** (if solid, 0.11 mmol, 1.1 equiv), iodonium ylides **1** (0.1 mmol, 1.0 equiv), [Fe] catalyst(0.005 mmol, 5 mol%). After that, argon was pumped three times, and DCM (1 mL), amines (if liquid, 0.11 mmol,1.1 equiv) was added. The reaction mixture was stirred at room temperature for 5 h. After complete reaction, concentrate under reduced pressure and purified by column flash chromatography on silica gel to afford the target products **5**.

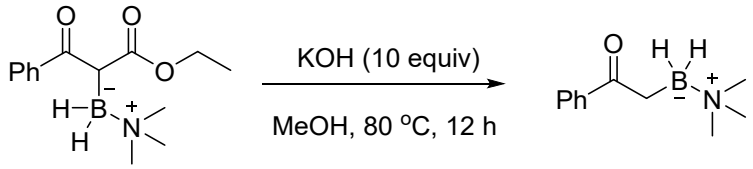
4. General Procedure for the Gram-Scale Synthesis 3a and 5l.



In an oven-dried 100 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with iodonium ylides (5 mmol, 1.0 equiv), Borane-pyridine complex (10 mmol, 2.0 equiv) or N-methyl-1-phenylmethanamine (5.5 mmol, 1.1 equiv), [Fe] catalyst(0.25 mmol, 5 mol%). After that,

argon was pumped three times, and DCM (30 mL) was added. The reaction mixture was stirred at room temperature for 5 h. After complete reaction, concentrate under reduced pressure and purified by column flash chromatography on silica gel to afford the target product **3a** or **5l**.

5. General Procedure for the Synthesis of 11 and 12.



4m **11**, 79%

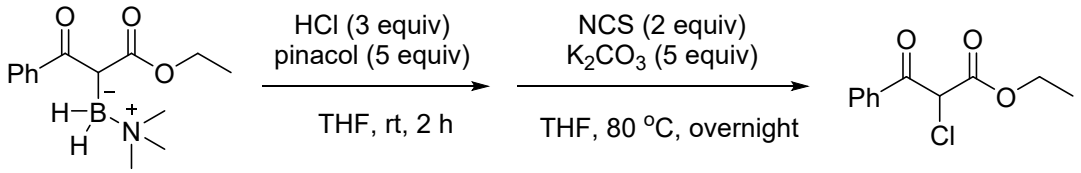
To a solution of **4m** (0.2 mmol, 1 equiv) in MeOH (2.0 ml) was added KOH (112mg, 2 mmol, 10 equiv) , The reaction mixture was stirred under nitrogen atmosphere for 12 hours at 80 °C, The reaction mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give 2-(trimethylamine-boranyl)-1-phenylethan-1-one **11** (30 mg, 0.15 mmol) in 78% yield as a yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 1H), 7.47 – 7.40 (m, 1H), 7.37 (td, *J* = 7.4, 7.0, 1.5 Hz, 1H), 2.57 (d, *J* = 1.6 Hz, 4H), 2.43 (d, *J* = 5.6 Hz, 1H), 1.98 (d, *J* = 155.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.8, 138.0, 131.7, 128.6, 128.0, 52.1.

^{11}B NMR (160 MHz, Chloroform-*d*) δ -4.59 (t, *J* = 101.6 Hz).

The data are in accordance with the literature.[3]



4m **12**, 62%

To a solution of **4m** (0.2 mmol, 1 equiv) in THF (2.0 ml) was added HCl (0.4 ml, 1 M in water, 2 equiv) and and pinacol (118.2 mg, 1.0 mmol,5equiv), The reaction mixture was stirred under nitrogen atmosphere for 2 hours at room temperature then Na_2CO_3 (136 mg, 1 mmol, 5 equiv) and NCS (55 mg, 0.4mmol, 2 equiv) was added. The reaction mixture was continued by stirring overnight at room temperature. The reaction mixture was extracted three times with ethyl acetate.

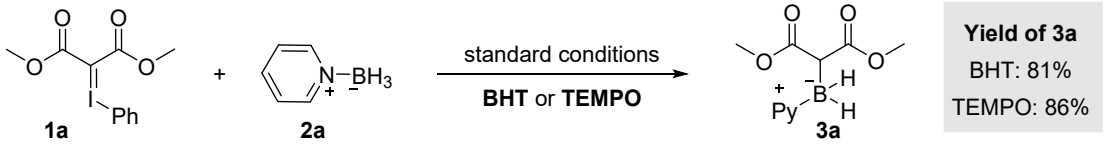
The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 5:1) to give Ethyl 2-chloro-3-oxo-3-phenylpropanoate **12** (28 mg, 0.12 mmol) in 62% yield as a pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 1H), 7.66 – 7.58 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 5.62 (s, 0H), 4.27 (q, *J* = 7.1 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.3, 165.3, 134.4, 133.4, 129.3, 129.0, 63.3, 58.1, 13.9.

The data are in accordance with the literature.[4]

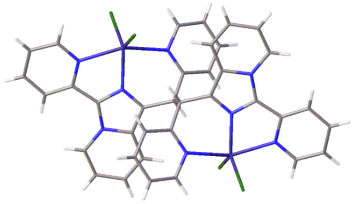
6. Mechanism investigations: General Procedure for Radical Experimrnts.



In an oven-dried 10 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with Borane-pyridine complex **2a** (0.2 mmol, 2.0 equiv), iodonium ylides **1a** (0.1 mmol, 1.0 equiv), [Fe] catalyst(0.005 mmol, 5 mol%), BHT (0.3 mmol, 3.0 equiv) or TEMPO (0.3 mmol, 3.0 equiv). After that, argon was pumped three times, and DCM (1 mL), was added. The reaction mixture was stirred at room temperature for 5 h. After complete reaction, concentrate under reduced pressure and purified by column flash chromatography on silica gel to afford the target product **3a**.

7. X-Ray Crystallographic Data

X-Ray Crystallographic Data for [Fe] catalyst.



CCDC: 2255651

Fe-checkcif

Table 1 Crystal data and structure refinement for Fe-checkcif.

Identification code	Fe-checkcif

Empirical formula	$C_{36}H_{26}Cl_4Fe_2N_8$
Formula weight	824.15
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.7255(5)
b/Å	13.0219(7)
c/Å	15.4500(7)
α/°	90
β/°	96.927(2)
γ/°	90
Volume/Å^3	1742.66(16)
Z	2
ρ_{calc}g/cm^3	1.571
μ/mm^{-1}	1.180
F(000)	836.0
Crystal size/mm^3	0.33 × 0.28 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.104 to 55.046
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	89855
Independent reflections	4011 [R_{int} = 0.0617, R_{sigma} = 0.0201]
Data/restraints/parameters	4011/890/302
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0723, wR_2 = 0.1754
Final R indexes [all data]	R_1 = 0.0871, wR_2 = 0.1849
Largest diff. peak/hole / e Å^{-3}	1.81/-0.98

X-Ray Crystallographic Data for 3p.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ljc_0m

X-ray of **3p** CCDC: 2255652

3p

Table 1 Crystal data and structure refinement for **3p**.

Identification code	3p
Empirical formula	$C_{20}H_{26}BNO_4$
Formula weight	355.23
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.6258(16)
b/Å	15.020(4)
c/Å	23.475(7)
α/°	90
β/°	95.160(11)
γ/°	90
Volume/Å^3	1975.6(10)
Z	4
ρ_{calc}g/cm^3	1.194
μ/mm^{-1}	0.081
F(000)	760.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.484 to 60.296
Index ranges	$-7 \leq h \leq 7$, $-21 \leq k \leq 21$, $-33 \leq l \leq 33$
Reflections collected	68809
Independent reflections	5794 [R_{int} = 0.0494, R_{sigma} = 0.0269]
Data/restraints/parameters	5794/0/248
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1125
Final R indexes [all data]	R_1 = 0.0611, wR_2 = 0.1206
Largest diff. peak/hole / e Å^{-3}	0.27/-0.26

8. References

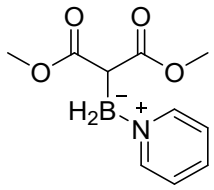
1. Yoshimura A, Zhdankin V V, Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem Rev*, **2016**, *116*, 3328-3435.
2. Chen, Y.; Li, L.; Chen, Z.; Liu, Y.; Hu, H.; Chen, W.; Liu, W.; Li, Y.; Lei, T.; Cao, Y.; Kang, Z.; Lin, M.; Li,W., Metal-Mediated Controllable Creation of Secondary, Tertiary, and Quaternary Carbon Centers: A Powerful Strategy for the Synthesis of Iron, Cobalt, and Copper Complexes with in Situ Generated Substituted 1-Pyridineimidazo[1,5-a]pyridine Ligands. *Inorg. Chem.* **2012**, *51*, 9705−9713.

3. Zhang, S. –S.; Xie, H.; Shu, B.; Che, T.; Wang, X. –T.; Peng, D.; Yang, F.; Zhang, L. Iridium-catalyzed B–H insertion of sulfoxonium ylides and borane adducts: a versatile platform to α-boryl carbonyls. *Chem. Commun.*, **2020**,*56*, 423-426.

4. Yue, X.; Li, Y.; Liu, M.; Sang, D.; Huang, Z.; Chen, F. Biocatalytic dynamic reductive kinetic resolution of aryl α-chloro β-keto esters: divergent, stereocontrolled synthesis of diltiazem, clentiazem, and siratiazem. *Chem. Commun.*, **2022**, *58*, 9010-9013.

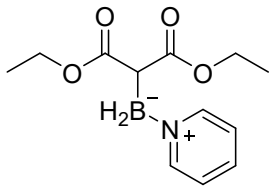
9. Product characterization

dimethyl 2-boranylmalonate-pyridine complex (3a)



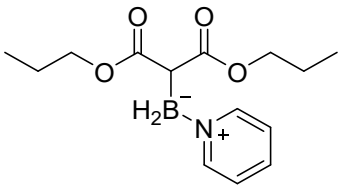
R_f = 0.3 (silica gel, PE: EtOAc = 2:1)
Yield: 90% (40 mg, 0.18mmol)
Physical state: yellow oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.0 Hz, 2H), 8.07 (t, *J* = 7.6, 7.6 Hz, 1H), 7.61 (t, *J* = 6.4 Hz, 2H), 3.59 (s, 6H), 3.28 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 147.9, 140.9, 125.4, 51.3, 31.4.
^{11}B NMR (160 MHz, $CDCl_3$) δ -5.92 (t, *J* = 100.8 Hz).
HRMS (ESI): calcd for $(M+H)^+$ $C_{10}H_{15}BNO_4^+$, 224.1089, found: 224.1085.

diethyl 2-boranylmalonate-pyridine complex (3b)



R_f = 0.3 (silica gel, PE: EtOAc = 2:1)
Yield: 87% (44mg, 0.17 mmol)
Physical state: yellow oil
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.55 (m, 2H), 8.03 (tt, *J* = 1.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 4.05 – 3.99 (m, 4H), 3.22 (s, 1H), 1.17 – 1.13 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 148.1, 140.6, 125., 59.8, 14.3.
^{11}B NMR (128 MHz, $CDCl_3$) δ -5.11 (t, *J* = 101.8 Hz).
HRMS (ESI): calcd for $(M+H)^+$ $C_{12}H_{19}BNO_4^+$, 252.1402, found: 252.1405.

dipropyl 2-boranylmalonate-pyridine complex (3c)



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

Yield: 80% (45mg, 0.16 mmol)

Physical state: yellow oil

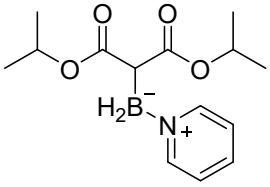
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.5 Hz, 2H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 6.6 Hz, 2H), 3.92 (t, *J* = 6.7 Hz, 4H), 3.24 (s, 1H), 1.55 (q, *J* = 7.1 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 148.1, 140.6, 125.2, 65.5, 22.1, 10.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.10 (t, *J* = 92.2 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{23}BNO_4^+$, 280.1715, found: 280.1716.

diisopropyl 2-boranylmalonate-pyridine complex (3d)



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

Yield: 79% (44mg, 0.16 mmol)

Physical state: yellow oil

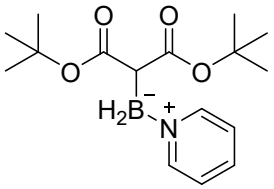
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.7 Hz, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 2H), 4.91 (p, *J* = 6.3 Hz, 2H), 3.15 (d, *J* = 4.0 Hz, 1H), 1.14 (d, *J* = 6.3 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 148.2, 140.5, 125.2, 66.6, 21.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.28 (t, *J* = 95.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{23}BNO_4^+$, 280.1715, found: 280.1719.

di-tert-butyl 2-boranylmalonate-pyridine complex (3e)



General procedure: L

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

Yield: 91% (56 mg, 0.18mmol)

Physical state: yellow oil

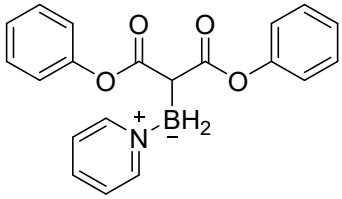
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.8 Hz, 2H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 2H), 3.04 (s, 1H), 1.36 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 148.4, 140.3, 125.0, 78.9, 28.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.39 (t, *J* = 96.6 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{27}BNO_4^+$, 308.2028, found: 308.2025.

diphenyl 2-boranylmalonate-pyridine complex (3f)



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

Yield: 92% (64 mg, 0.18 mg)

Physical state: colorless oil

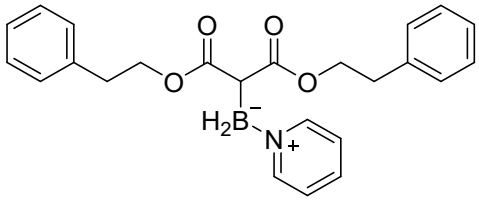
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.3 Hz, 2H), 8.02 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 6.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.13 (dd, *J* = 7.3 Hz, 6H), 3.72 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 151.1, 148.3, 141.0, 129.4, 125.6, 125.6, 121.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.12 (t, *J* = 100.5 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{20}H_{19}BNO_4^+$, 348.1402, found: 348.1045.

diphenethyl 2-boranylmalonate-pyridine complex (3g)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 71% (57 mg, 0.14 mmol)

Physical state: yellow oil

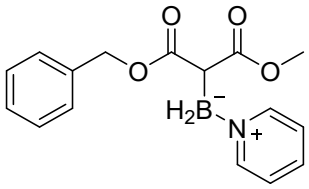
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 – 8.39 (m, 2H), 7.97 (tt, *J* = 1.6 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.31 – 7.28 (m, 2H), 7.23 – 7.20 (m, 3H), 4.24 – 4.15 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.26 (t, *J* = 4.1 Hz, 1H), 2.88 (t, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 148.0, 140.5, 138.4, 129.2, 128.5, 126.5, 125.2, 64.5, 35.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.19 (t, *J* = 97.3 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{24}H_{27}BNO_4^+$, 404.2028, found: 404.2026.

1-benzyl 3-methyl 2-boranylmalonate-pyridine complex (3h)



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

Yield: 72% (43 mg, 0.14 mmol)

Physical state: yellow oil

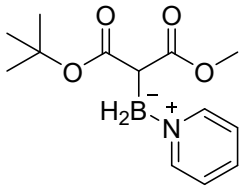
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.8 Hz, 2H), 7.96 (t, *J* = 7.4 Hz, 1H), 7.44 (s, 2H), 7.35 (s, 5H), 5.17 – 4.97 (m, 2H), 3.63 (s, 3H), 3.36 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 172.7, 148.0, 140.6, 136.8, 128.5, 128.5, 128.0, 125.3, 65.6, 51.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.22 (t, *J* = 76.8 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{19}BNO_4^+$, 300.1402, found: 300.1406.

1-(*tert*-butyl) 3-methyl 2-boranylmalonate-pyridine complex (3i)



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

Yield: 76% 9 (40 mg, 0.15 mmol)

Physical state: yellow oil

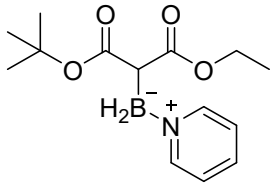
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 2H), 8.02 (s, 1H), 7.57 (t, *J* = 6.2 Hz, 2H), 3.56 (s, 3H), 3.16 (s, 1H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 172.4, 148.2, 140.6, 125.2, 79.3, 51.2, 28.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.19 (t, *J* = 105.0 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{21}BNO_4^+$, 266.1658, found: 266.1659.

1-(*tert*-butyl) 3-ethyl 2-boranylmalonate-pyridine complex (3j)



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

Yield: 75% (42 mg, 0.15 mmol)

Physical state: yellow oil

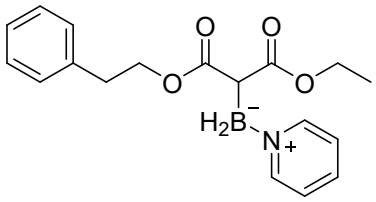
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9 Hz, 2H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 6.3 Hz, 2H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.13 (s, 1H), 1.35 (s, 9H), 1.16 (t, *J* = 7.0, 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 172.4, 148.2, 140.6, 125.2, 79.3, 51.2, 28.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.22 (t, *J* = 95.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{23}BNO_4^+$, 280.1715, found: 280.1711.

1-ethyl 3-phenethyl 2-boranylmalonate-pyridine complex (3k)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 64% (42 mg, 0.13 mmol)

Physical state: yellow oil

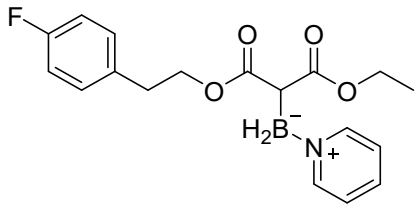
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.26 (m, 2H), 7.92 (tt, *J* = 1.6 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.30 (dd, *J* = 8.0, 6.6 Hz, 4H), 7.24 – 7.20 (m, 6H), 4.24 – 4.15 (m, 4H), 3.27 (t, *J* = 4.0 Hz, 1H), 2.88 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 148.1, 140.6, 138.4, 129.2, 128.5, 126.5, 125.2, 64.5, 59.9, 35.3, 14.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.40 (t, *J* = 95.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{23}BNO_4^+$, 328.1715, found: 328.1714.

1-ethyl 3-(4-fluorophenethyl) 2-boranylmalonate -pyridine complex (3l)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 72% (50 mg, 0.14 mmol)

Physical state: yellow oil

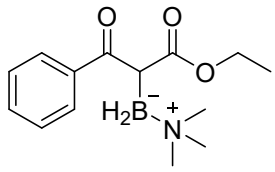
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.3 Hz, 2H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.18 (dd, *J* = 5.5 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 4.21 – 4.14 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.24 (t, *J* = 3.8 Hz, 1H), 2.86 (t, *J* = 6.9 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 160.7, 148.1, 140.6, 134.1, 130.6 (d, *J* = 7.6 Hz), 125.2, 115.3, 115.1, 64.5, 59.9, 34.5, 14.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.15 (t, *J* = 103 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{22}BFNO_4^+$, 346.1620, found: 346.1622.

ethyl 2-boranyl-3-oxo-3-phenylpropanoate-trimethylamine complex (3m)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 88% (46 mg, 0.18 mmol)

Physical state: colorless oil

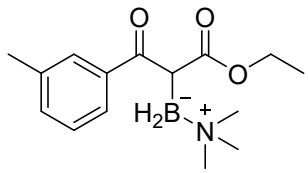
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.43 (dt, *J* = 7.3 Hz, 3H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 1H), 2.64 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 174.1, 138.1, 132.0, 129.0, 128.0, 60.1, 52.5, 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ -3.02 (t, *J* = 99.2 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{23}BNO_3^+$, 264.1766, found: 264.1765.

ethyl 2-boranyl-3-oxo-3-(m-tolyl)propanoate-trimethylamine complex (3n)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 72% (40 mg, 0.14 mg)

Physical state: yellow oil

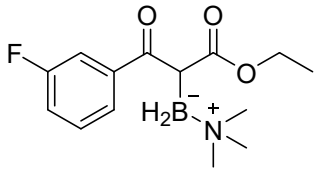
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.30 – 7.27 (m, 2H), 4.12 (qd, *J* = 4.0 Hz, 2H), 4.00 (dd, *J* = 2.0 Hz, 1H), 2.64 (s, 9H), 2.38 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 174.1, 138.2, 137.8, 132.7, 129.4, 127.9, 126.2, 60.1, 52.6, 21.5, 14.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ -3.05 (t, *J* = 100.5 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{25}BNO_3^+$, 278.1922, found: 278.1925.

ethyl 2-boranyl-3-(3-fluorophenyl)-3-oxopropanoate-trimethylamine complex (3o)



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

Yield: 65% (37 mg, 0.13 mmol)

Physical state: yellow oil

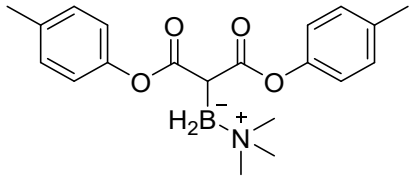
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.36 (td, *J* = 5.7 Hz, 1H), 7.16 (td, *J* = 2.2 Hz, 1H), 4.10 (qd, *J* = 2.9 Hz, 2H), 3.91 – 3.84 (m, 1H), 2.64 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 173.8, 163.6, 161.6, 140.2 (d, *J* = 6.0 Hz), 129.5 (d, *J* = 7.4 Hz), 124.8(d, *J* = 2.2 Hz), 117.3 (dd, *J* = 21.9 Hz), 60.2, 52.5, 14.3, 1.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ -3.29 (t, *J* = 95.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{22}BFNO_3^+$, 282.1671, found: 282.1674.

di-*p*-tolyl 2-boranylmalonate-trimethylamine complex (3p)



R_f = 0.5 (silica gel, PE: EtOAc = 2:1)

Yield: 74% (53 mg, 0.15 mmol)

Physical state: white solid

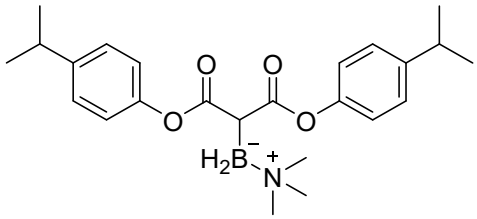
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.1 Hz, 4H), 7.03 – 6.99 (m, 4H), 2.76 (s, 9H), 2.33 (s, 6H).

^{19}C NMR (126 MHz, $CDCl_3$) δ 171.8, 149.0, 135.0, 129.8, 121.5, 52.6, 21.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.81 (t, *J* = 106.9 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{20}H_{27}BNO_4^+$, 356.2028, found: 356.2027.

bis(4-isopropylphenyl) 2-boranylmalonate-trimethylamine complex (3q)



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

Yield: 71% (58 mg, 0.14 mmol)

Physical state: yellow oil

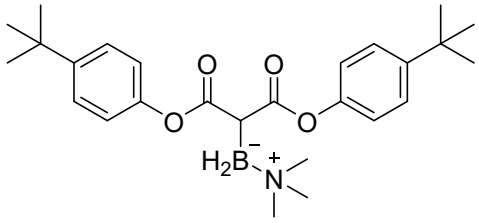
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 3.37 (s, 1H), 2.90 (hept, *J* = 6.9 Hz, 2H), 2.75 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 12H).

^{19}C NMR (126 MHz, $CDCl_3$) δ 198.4, 173.8, 163.6, 161.6, 140.2 (d, *J* = 6.0 Hz), 129.5 (d, *J* = 7.4 Hz), 124.8 (d, *J* = 2.2 Hz), 118.9, 118.8, 115.9, 115.7, 60.2, 52.5, 14.3, 1.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.78 (t, *J* = 141.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{24}H_{35}BNO_4^+$, 412.2654, found: 412.2654.

bis(4-(tert-butyl)phenyl) 2-boranylmalonate-trimethylamine complex (3r)



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

Yield: 81% (71 mg, 0.16 mmol)

Physical state: yellow oil

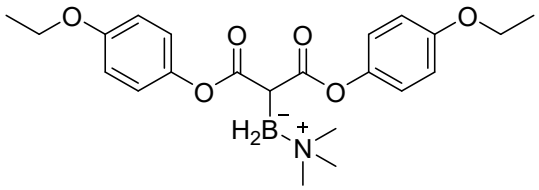
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 4H), 7.05 (d, *J* = 8.6 Hz, 4H), 3.38 (s, 1H), 2.76 (s, 9H), 1.31 (s, 18H).

^{19}C NMR (126 MHz, $CDCl_3$) δ 171.8, 148.9, 148.2, 126.2, 121.1, 52.6, 34.5, 31.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.94 (t, *J* = 116.5 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{26}H_{39}BNO_4^+$, 440.2967, found: 440.2966.

bis(4-ethoxyphenyl) 2-boranylmalonate-trimethylamine complex (3s)



R_f = 0.2 (silica gel, PE: EtOAc = 2:1)

Yield: 80% (66 mg, 0.16 mmol)

Physical state: yellow oil

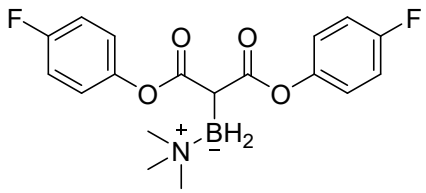
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 9.1 Hz, 4H), 6.85 (d, *J* = 9.1 Hz, 4H), 4.00 (q, *J* = 7.0 Hz, 4H), 3.36 (s, 1H), 2.76 (s, 9H), 1.39 (t, *J* = 7.0, 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 156.3, 144.6, 122.4, 114.9, 63.8, 52.5, 14.9, 1.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.94 (t, *J* = 116.5 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{22}H_{31}BNO_6^+$, 416.2239, found: 416.2233.

bis(4-fluorophenyl) 2-boranylmalonate-trimethylamine complex (3t)



R_f = 0.5 (silica gel, PE: EtOAc = 3:1)

Yield: 77% (56 mg, 0.15 mmol)

Physical state: brown oil

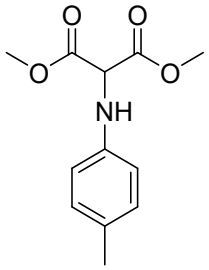
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.00 (m, 8H), 3.36 (s, 1H), 2.76 (s, 9H), 2.23 (d, *J* = 113.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 161.2, 159.2, 147.0, 123.2 (d, *J* = 8.4 Hz), 116.1, 115.9, 52.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ -2.72 (t, *J* = 134.4 Hz).

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{21}BF_2NO_4^+$, 364.1526, found: 364.1529.

dimethyl 2-(p-tolylamino)malonate (5a)



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

Yield: 79% (38 mg, 0.16 mmol)

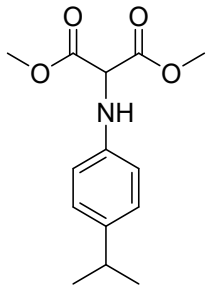
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 6.83 – 6.78 (m, 3H), 5.17 (d, *J* = 3.7 Hz, 1H), 3.80 (s, 6H), 3.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 148.9, 129.4, 118.9, 113.5, 65.8, 52.8, 35.8.

HRMS (ESI): calcd for $(M+H)^+$ $C_{12}H_{16}NO_4^+$, 238.1074, found: 238.1077.

dimethyl 2-((4-isopropylphenyl)amino)malonate (5b)



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

Yield: 71% (38 mg, 0.14 mmol)

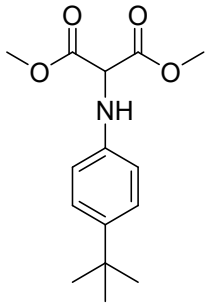
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 7.05 (m, 2H), 6.63 – 6.59 (m, 2H), 4.78 (s, 1H), 3.81 (s, 6H), 2.81 (hept, *J* = 7.0, 7.0, 7.0, 7.0, 7.0, 7.0 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 143.0, 142.0, 126.3, 113.3, 60.8, 53.4, 34.0, 31.6.

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{20}NO_4^+$, 266.1387, found: 266.1388.

dimethyl 2-((4-(tert-butyl)phenyl)amino)malonate (5c)



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

Yield: 75% (42 mg, 0.15 mmol)

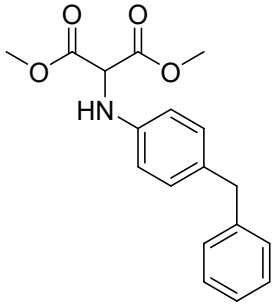
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.63 – 6.59 (m, 2H), 4.78 (d, *J* = 7.4 Hz, 1H), 3.82 (m, 6H), 1.27 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 143.3, 139.8, 127.4, 113.6, 60.9, 53.6, 33.3, 24.2.

HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{22}NO_4^+$, 280.1543, found: 280.1540.

dimethyl 2-((4-benzylphenyl)amino)malonate (5d)



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

Yield: 62% (39 mg, 0.12 mmol)

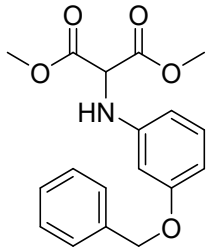
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.77 (s, 2H), 3.88 (s, 2H), 3.81 (s, 6H).

^{13}C NMR (126 MHz, CDCl3) δ 168.3, 143.6, 141.7, 131.9, 130.0, 128.9, 128.4, 126.0, 113.7, 60.7, 53.3, 41.1.

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{20}NO_4^+$, 314.1387, found: 314.1381.

dimethyl 2-((3-(benzyloxy)phenyl)amino)malonate (5e)



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

Yield: 68% (45 mg, 0.13 mmol)

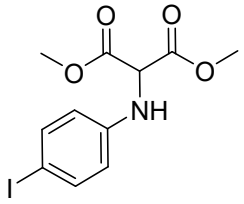
Physical state: yellow oil

^{1}H NMR (500 MHz, CDCl3) δ 7.47 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 7.10 (t, *J* = 8.0, 8.0 Hz, 1H), 6.44 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.34 – 6.25 (m, 1H), 5.03 (s, 2H), 4.85 (d, *J* = 7.4 Hz, 1H), 4.78 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 160.2, 146.7, 137.2, 130.4, 128.7, 128.0, 127.6, 106.6, 105.5, 100.7, 77.4, 77.1, 76.9, 69.9, 60.5, 53.4.

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{20}NO_4^+$, 330.1336, found: 330.1338.

dimethyl 2-((4-iodophenyl)amino)malonate (5f)



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

Yield: 69% (48 mg, 0.14 mmol)

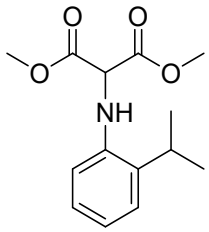
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ7.49 – 7.42 (m, 2H), 6.48 – 6.36 (m, 2H), 4.74 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ167.9, 138.2, 115.7, 60.2, 53.5.

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{11}NIO_4^+$, 349.9884, found: 349.9888.

ethyl dimethyl 2-((2-isopropylphenyl)amino)malonate (5g)



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

Yield: 75% (40 mg, 0.15 mmol)

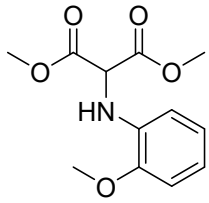
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.09 (td, *J* = 7.9, 7.8, 1.6 Hz, 1H), 6.82 (td, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.54 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.84 (d, *J* = 7.2 Hz), 3.83 (s, 6H), 3.05 (p, *J* = 6.8, 6.8, 6.8, 6.8 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 142.3, 133.4, 126.9, 125.6, 119.2, 111.1, 60.8, 53.4, 27.40, 22.4.

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{20}NO_4^+$, 266.1387, found: 266.1389.

dimethyl 2-((2-methoxyphenyl)amino)malonate (5h)



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

Yield: 73% (37 mg, 0.15 mmol)

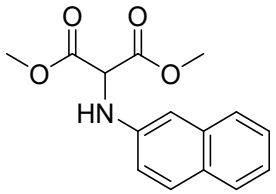
Physical state: brown oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 – 6.79 (m, 2H), 6.78 – 6.70 (m, 1H), 6.52 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.40 (d, *J* = 7.5 Hz, 1H), 4.81 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 147.3, 135.3, 121.2, 118.6, 110.6, 110.0, 60.5, 55.6, 53.34.

HRMS (ESI): calcd for $(M+H)^+$ $C_{12}H_{16}NO_5^+$, 254.1023, found: 254.1022.

dimethyl 2-(naphthalen-2-ylamino)malonate (5i)



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

Yield: 65% (36 mg, 0.13 mmol)

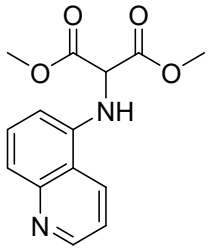
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.6, 7.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.02 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.86 – 6.82 (m, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 143.0, 134.9, 129.5, 128.3, 127.7, 126.6, 126.3, 123.0, 117.94, 105.78, 60.55, 53.51

HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{16}NO_4^+$, 274.1074, found: 274.1077.

dimethyl 2-(quinolin-5-ylamino)malonate (5j)



R_f = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 63% (35 mg, 0.13 mmol)

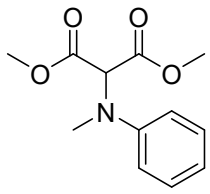
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.38 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.54 (d, *J* = 7.4 Hz, 1H), 5.59 (d, *J* = 7.0 Hz, 1H), 4.93 (d, *J* = 7.1 Hz, 1H), 3.84 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 150.4, 149.2, 140.8, 130.1, 129.1, 120.6, 120.0, 118.8, 105.8, 60.5, 53.6.

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{15}N_2O_4^+$, 275.1026, found: 275.1025.

dimethyl 2-(methyl(phenyl)amino)malonate (5k)



R_f = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 67% (37 mg, 0.13 mmol)

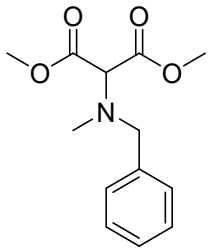
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 6.83 – 6.77 (m, 3H), 5.16 (s, 1H), 3.80 (s, 6H), 3.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 148.9, 129.4, 118.8, 113.5, 65.8, 52.8, 35.8.

HRMS (ESI): calcd for $(M+H)^+$ $C_{12}H_{16}NO_4^+$, 238.1074, found: 280.1072.

dimethyl 2-(benzyl(methyl)amino)malonate (5l)



$\mathbf{R_f}$ = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 71% (35 mg, 0.14 mmol)

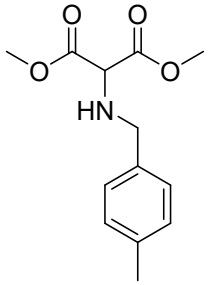
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 4.20 (s, 1H), 3.79 (s, 2H), 3.79 (s, 6H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 148.9, 129.4, 118.8, 113.5, 65.8, 52.8, 35.8.

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{18}NO_4^+$, 252.1230, found: 252.1233.

dimethyl 2-((4-methylbenzyl)amino)malonate (5m)



$\mathbf{R_f}$ = 0.5 (silica gel, PE: EtOAc = 5:1)

Yield: 75% (42 mg, 0.15 mmol)

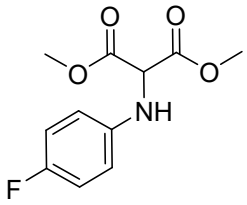
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.09 (s, 1H), 3.76 (s, 8H), 2.34 (d, *J* = 5.7 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 169.1 (s), 137.1 (s), 135.5 (s), 129.3 (s), 128.5 (s), 63.8 (s), 52.9 (s), 51.5 (s), 21.2 (s).

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{18}NO_4^+$, 252.1230, found: 252.1237.

dimethyl 2-((4-fluorophenyl)amino)malonate (5n)



$\mathbf{R_f}$ = 0.5 (silica gel, PE: EtOAc = 5:1)

Yield: 75% 36 mg, 0.15 mmol)

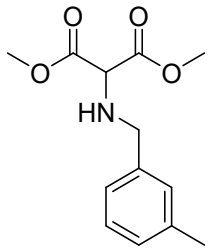
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.03 – 6.97 (m, 2H), 4.06 (s, 1H), 3.77 (d, *J* = 1.8 Hz, 6H).

^{13}C NMR (126 MHz, CDCl3) δ168.9, 134.3, 130.1 (d, *J* = 8.2 Hz), 115.4, 115.3, 63.7, 53.0, 51.0.

HRMS (ESI): calcd for $(M+H)^+$ $C_{11}H_{13}NFO_4^+$, 242.0823, found: 242.0825.

dimethyl 2-((3-methylbenzyl)amino)malonate (5o)



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

Yield: 60% (30 mg, 0.12 mmol)

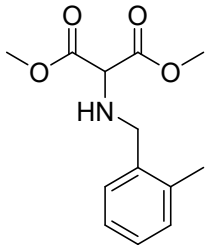
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5, 7.5 Hz, 1H), 7.17 – 7.04 (m, 3H), 4.10 (s, 1H), 3.79 – 3.73 (m, 8H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 138.5, 138.2, 129.2, 128.5, 128.2, 125.5, 63.9, 52.9, 51.8, 21.4.

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{18}NO_4^+$, 252.1230, found: 252.1235.

dimethyl 2-((2-methylbenzyl)amino)malonate (5p)



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

Yield: 62% (31 mg, 0.12 mmol)

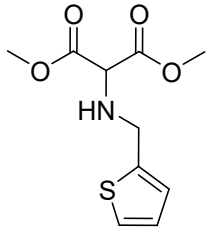
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.20 – 7.14 (m, 3H), 4.12 (s, 1H), 3.79 (s, 2H), 3.77 (s, 6H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 136.9, 136.6, 130.5, 129.0, 127.6, 126.0, 64.2, 52.9, 49.7, 19.0.

HRMS (ESI): calcd for $(M+H)^+$ $C_{13}H_{18}NO_4^+$, 252.1230, found: 252.1231.

dimethyl 2-((thiophen-2-ylmethyl)amino)malonate (5q)



General procedure: M

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

Yield: 61% (30 mg, 0.12 mmol)

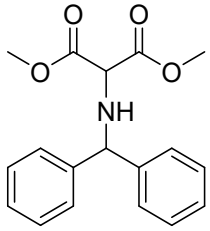
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 1H), 6.95 – 6.92 (m, 2H), 4.15 (s, 1H), 4.02 (s, 2H), 3.77 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 141.9, 126.7, 125.9, 125.2, 63.3, 52.9, 46.2.

HRMS (ESI): calcd for $(M+H)^+$ $C_{10}H_{14}NSO_4^+$, 244.0638, found: 244.0639.

dimethyl 2-(benzhydrylamino)malonate (5r)



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

Yield: 65% (41 mg, 0.13 mmol)

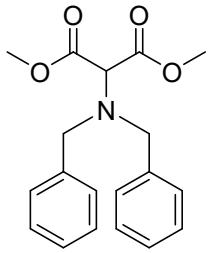
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.49 – 7.45 (m, 3H), 7.44 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.21 – 7.16 (m, 2H), 4.90 (s, 1H), 3.79 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 138.9, 135.4, 131.1, 129.3 (d, *J* = 8.5 Hz), 128.9, 128.2, 127.8, 69.5, 53.0.

HRMS (ESI): calcd for $(M+H)^+$ $C_{18}H_{20}NO_4^+$, 314.1387, found: 314.1382.

dimethyl 2-(dibenzylamino)malonate (5s)



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

Yield: 63% (41 mg, 0.12 mmol)

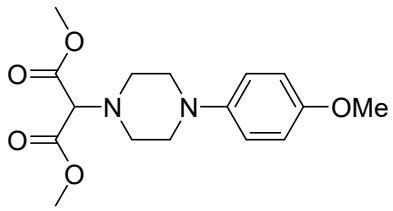
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 4H), 7.31 (td, *J* = 6.8, 6.4, 1.6 Hz, 4H), 7.26 – 7.21 (m, 2H), 4.21 (s, 1H), 3.83 (s, 4H), 3.77 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 148.9, 129.4, 118.8, 113.5, 65.8, 52.8, 35.8.

HRMS (ESI): calcd for $(M+H)^+$ $C_{19}H_{22}NO_4^+$, 328.1543, found: 328.1540.

dimethyl 2-(4-(4-methoxyphenyl)piperazin-1-yl)malonate (5t)



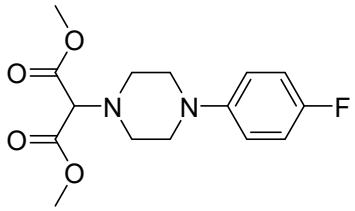
R_f = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 94% (61 mg, 0.19 mmol)

Physical state: yellow oil

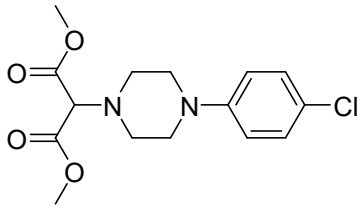
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 – 6.86 (m, 2H), 6.86 – 6.79 (m, 2H), 4.14 (s, 1H), 3.79 (s, 6H), 3.76 (s, 3H), 3.15 – 3.07 (m, 4H), 2.94 – 2.89 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 154.1, 145.6, 118.6, 114.5, 70.7, 55.6, 52.5, 51.1, 50.4.
HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{23}N_2O_5^+$, 323.1601, found: 323.1605.

dimethyl 2-(4-(4-fluorophenyl)piperazin-1-yl)malonate (5u)



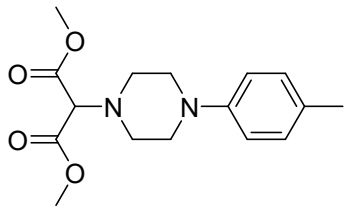
R_f = 0.5 (silica gel, PE: EtOAc = 5:1)
Yield: 76% (47 mg, 0.15 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 – 6.91 (m, 2H), 6.93 – 6.86 (m, 2H), 4.14 (s, 1H), 3.79 (s, 6H), 3.19 – 3.11 (m, 4H), 2.95 – 2.87 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 118.3 (d, J = 6.9 Hz), 115.8, 115.6, 70.5, 52.5, 50.8, 50.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -123.92.
HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{20}N_2FO_4^+$, 311.1402, found: 311.1405.

dimethyl 2-(4-(4-chlorophenyl)piperazin-1-yl)malonate (5v)



R_f = 0.5 (silica gel, PE: EtOAc = 5:1)
Yield: 90% (59 mg, 0.18 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 6.85 – 6.81 (m, 2H), 4.14 (s, 1H), 3.79 (s, 6H), 3.23 – 3.16 (m, 4H), 2.93 – 2.85 (m, 4H).
^{13}CNMR (126 MHz, $CDCl_3$) δ 167.4, 149.9, 129.1 (d, J = 12.4 Hz), 124.9, 117.6, 70.6, 52.5, 50.1, 49.6.
HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{20}N_2ClO_4^+$, 327.1206, found: 327.1205.

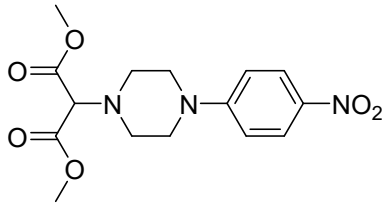
dimethyl 2-(4-(p-tolyl)piperazin-1-yl)malonate (5w)



R_f = 0.4 (silica gel, PE: EtOAc = 5:1)
Yield: 87% (53 mg, 0.17 mmol)
Physical state: yellow oil

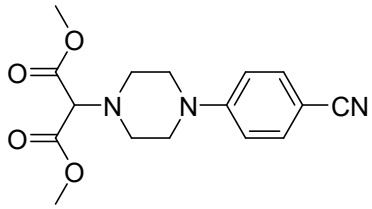
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.14 (s, 1H), 3.79 (s,6H), 3.24 – 3.15 (m, 4H), 3.00 – 2.88 (m, 4H), 2.27 (s, 3H).
^{13}CNMR (126 MHz, $CDCl_3$) δ 167.4, 149.2, 129.7, 116.8, 70.7, 52.5, 50.4, 50.2, 20.5.
HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{23}N_2O_4^+$, 307.1652, found: 307.1655.

dimethyl 2-(4-(4-nitrophenyl)piperazin-1-yl)malonate (5x)



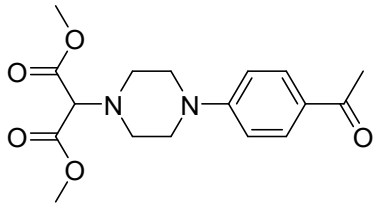
R_f = 0.3 (silica gel, PE: EtOAc = 5:1)
Yield: 65% (44 mg, 0.13 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 9.4, 2.3 Hz, 2H), 6.79 (dd, *J* = 9.2, 1.3 Hz, 2H), 4.14 (s, 1H), 3.77 (d, *J* = 1.4 Hz, 6H), 3.49 – 3.37 (m, 4H), 2.95 – 2.87 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 154.8, 138.7, 126.0, 112.9, 70.2, 52.6, 49.7, 47.4.
HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{20}N_3O_6^+$, 338.1347, found: 338.1348.

dimethyl 2-(4-(4-cyanophenyl)piperazin-1-yl)malonate (5y)



R_f = 0.3 (silica gel, PE: EtOAc = 5:1)
Yield: 68% (43 mg, 0.14 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 6.87 – 6.81 (m, 2H), 4.14(s, 1H), 3.78(s, 6H), 3.40 – 3.33 (m, 4H), 2.96 – 2.85 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 153.3, 133.5, 120.0, 114.3, 100.5, 70.2, 52.5, 49.7, 47.5.
HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{20}N_3O_4^+$, 318.1448, found: 318.1442.

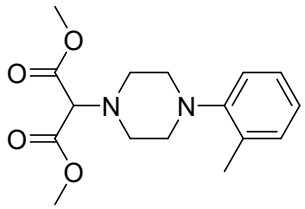
dimethyl 2-(4-(4-acetylphenyl)piperazin-1-yl)malonate (5z)



R_f = 0.3 (silica gel, PE: EtOAc = 5:1)
Yield: 72% (48 mg, 0.14 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.14 (s, 1H), 3.78 (s,6H), 3.41 – 3.26 (m, 4H), 2.93 – 2.83 (m, 4H), 2.50 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 167.3, 154.1, 130.5, 127.9, 113.6, 70.4, 52.5, 49.9, 47.7, 26.2.

HRMS (ESI): calcd for $(M+H)^+$ $C_{17}H_{23}N_2O_5^+$, 335.1601, found: 335.1604.

dimethyl 2-(4-(o-tolyl)piperazin-1-yl)malonate (5aa)



$\mathbf{R_f}$ = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 75% (46 mg, 0.15 mmol)

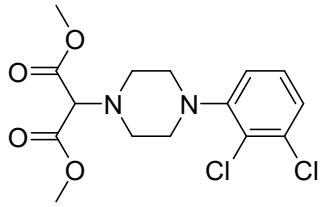
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.3, 7.3 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.4, 7.4 Hz, 1H), 4.16 (s, 1H), 3.81 (s, 6H), 3.02 – 2.99 (m, 4H), 2.93 (m, 4H), 2.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 151.4, 132.7, 131.1, 126.7, 123.4, 119.2, 70.8, 52.5, 51.9, 50.8, 18.0.

HRMS (ESI): calcd for $(M+H)^+$ $C_{16}H_{23}N_2O_4^+$, 307.1652, found: 307.1654.

dimethyl 2-(4-(2,3-dichlorophenyl)piperazin-1-yl)malonate (5ab)



$\mathbf{R_f}$ = 0.5 (silica gel, PE: EtOAc = 5:1)

Yield: 63% (45 mg, 0.13 mmol)

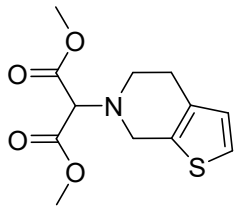
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 2H), 6.95 (dd, *J* = 7.1, 2.4 Hz, 1H), 4.15 (s, 1H), 3.81 (s, 6H), 3.18 – 3.06 (m, 4H), 2.93 (t, *J* = 4.8, 4.8 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 162.7, 151.2, 134.1, 127.6, 124.8, 118.8, 70.7, 53.5, 52.5, 51.5, 50.5.

HRMS (ESI): calcd for $(M+H)^+$ $C_{15}H_{19}N_2Cl_2O_4^+$, 361.0716, found: 361.0718.

dimethyl 2-(4,7-dihydrothieno[2,3-c]pyridin-6(5H)-yl)malonate (5ac)



$\mathbf{R_f}$ = 0.4 (silica gel, PE: EtOAc = 5:1)

Yield: 66% (36 mg, 0.13 mmol)

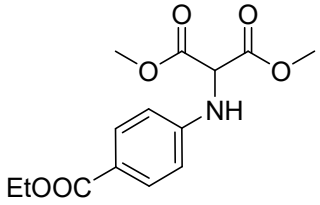
Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.0 Hz, 1H), 6.76 (d, *J* = 5.0 Hz, 1H), 4.33 (s, 1H), 4.03 (s, 2H), 3.79 (s, 6H), 3.06 (t, *J* = 5.8, 5.8 Hz, 2H), 2.78 (t, *J* = 5.7, 5.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 133.4, 132.3, 127.0, 122.5, 70.0, 52.5, 49.3, 47.7, 26.3.

HRMS (ESI): calcd for $(M+H)^+$ $C_{12}H_{16}NSO_4^+$, 270.0795, found: 270.0798.

dimethyl 2-((4-(ethoxycarbonyl)phenyl)amino)malonate (6)



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

Yield: 71% (42 mg, 0.14 mmol)

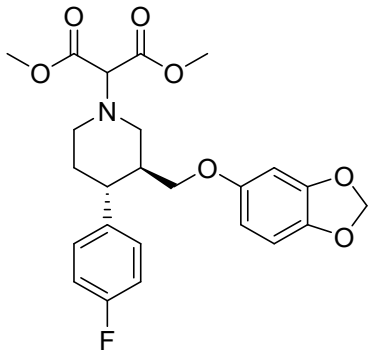
Physical state: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 2H), 5.22 (d, *J* = 7.3 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 6H), 1.36 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 166.5, 148.9, 131.6, 120.8, 112.3, 60.4, 59.7, 53.5, 14.4.

HRMS (ESI): calcd for $(M+H)^+$ $C_{14}H_{18}NO_6^+$, 296.1129, found: 296.1127.

dimethyl 2-((3S,4R)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)malonate (7)



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

Yield: 70% (64 mg, 0.14 mmol)

Physical state: yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 6.96 (t, *J* = 8.7, 8.7 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 2.5 Hz, 1H), 6.11 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.87 (s, 2H), 4.22 (s, 1H), 3.81 (s, 6H), 3.55 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.43 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.20 – 3.09 (m, 1H), 2.70 – 2.58 (m, 2H), 2.51 (td, *J* = 11.9, 11.8, 3.9 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.07 – 1.90 (m, 1H), 1.83 (dd, *J* = 13.4, 3.5 Hz, 1H).

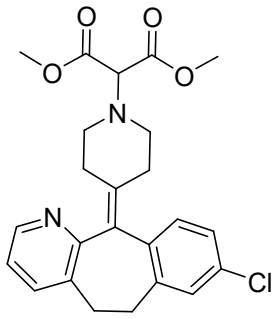
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 162.6, 160.7, 154.3, 148.2, 141.7, 139.3, 128.9 (d, *J* = 7.8 Hz), 115.5, 107.9, 105.6, 101.2, 98.1, 70.9, 69.3, 54.8, 52.6 (d, *J* = 11.1 Hz), 50.9, 43.7, 42.3, 34.2.

^{19}F NMR (126 MHz, $CDCl_3$) δ -116.25.

HRMS (ESI): calcd for $(M+H)^+$ $C_{24}H_{27}NFO_7^+$, 460.1766, found: 460.1769.

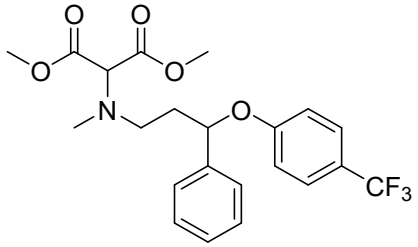
dimethyl

2-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)malonate (8)



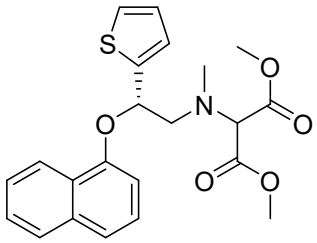
R_f = 0.3 (silica gel, PE: EtOAc = 5:1)
Yield: 83% (73 mg, 0.17 mmol)
Physical state: white solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.13 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.11 (t, *J* = 1.4 Hz, 2H), 7.07 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.10 (s, 1H), 3.74 (s, 6H), 3.43 – 3.30 (m, 2H), 2.93 – 2.87 (m, 2H), 2.85 – 2.73 (m, 2H), 2.60 – 2.43 (m, 4H), 2.41 – 2.33 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 157.6, 146.7, 139.6, 138.1, 137.7, 137.4, 133.5, 133.2, 132.8, 130.9, 129.1, 126.1, 122.2, 70.8, 52.4, 52.4, 51.9, 51.8, 31.9, 31.5, 31.3, 31.1.
HRMS (ESI): calcd for $(M+H)^+$ $C_{24}H_{26}N_2ClO_4^+$, 441.1576, found: 441.1572.

dimethyl 2-(methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)amino)malonate (9)



R_f = 0.5 (silica gel, PE: EtOAc = 5:1)
Yield: 65% (57 mg, 0.13 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.29 (d, *J* = 3.9 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.35 (dd, *J* = 8.7, 4.4 Hz, 1H), 4.16 (s, 1H), 3.76 (s, 3H), 3.70 (s, 2H), 2.86 (qt, *J* = 12.9, 6.8 Hz, 2H), 2.51 (s, 2H), 2.21 (dq, *J* = 14.2, 7.2 Hz, 1H), 2.10 – 1.97 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 160.7, 141.1, 128.8, 127.9, 126.8 (d, *J* = 3.6 Hz), 125.9, 115.9, 78.3, 58.6, 53.2, 51.6, 42.4, 36.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.56.
HRMS (ESI): calcd for $(M+H)^+$ $C_{22}H_{25}NF_3O_5^+$, 440.1679, found: 440.1675.

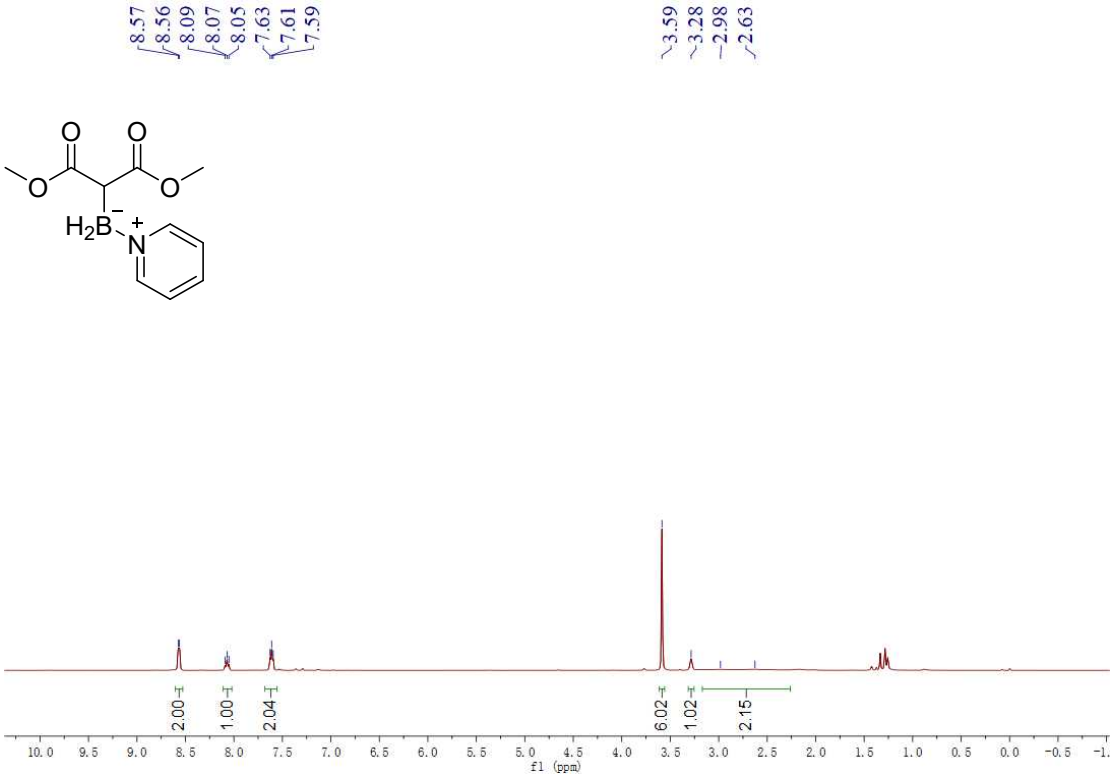
dimethyl (S)-2-(methyl(2-(naphthalen-1-yloxy)-2-(thiophen-2-yl)ethyl)amino)malonate (10)



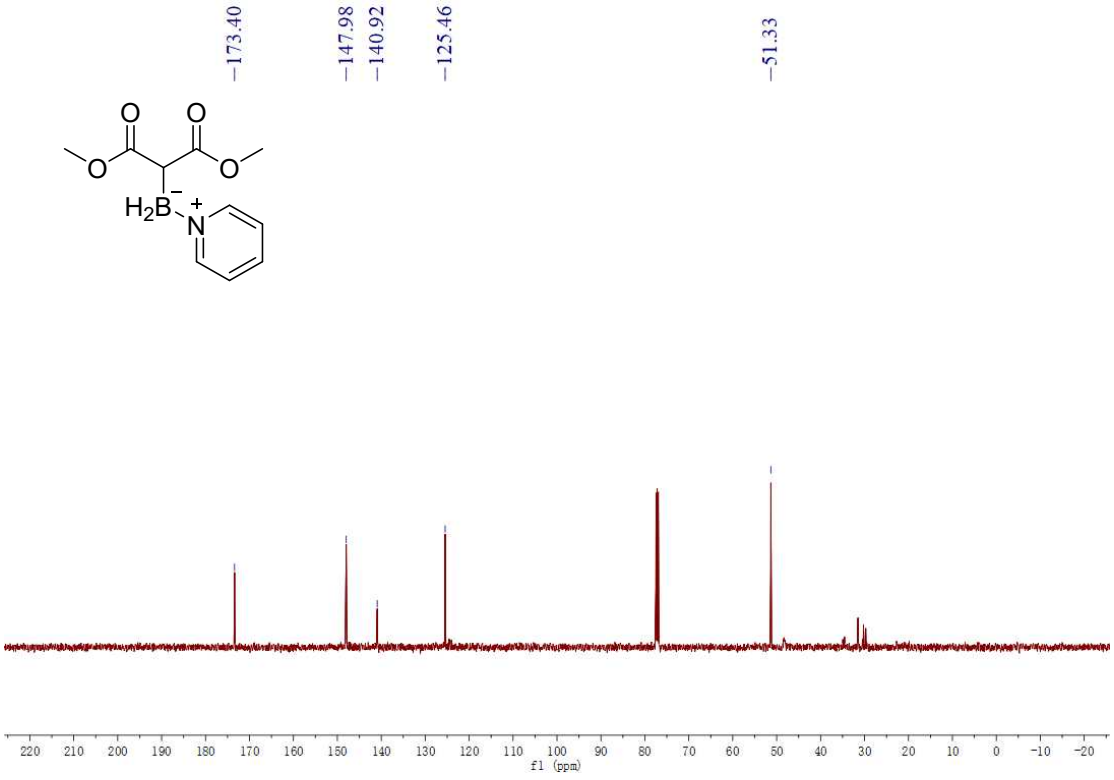
R_f = 0.5 (silica gel, PE: EtOAc = 5:1)
Yield: 68% (56 mg, 0.14 mmol)
Physical state: yellow oil
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 1H), 7.81 – 7.74 (m, 1H), 7.53 – 7.45 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.21 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.93 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.81 (dd, *J* = 7.9, 5.0 Hz, 1H), 4.15 (s, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 2.97 – 2.86 (m, 2H), 2.51 (s, 3H), 2.50 – 2.42 (m, 1H), 2.24 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1 (d, *J* = 4.4 Hz), 153.5, 145.4, 134.6, 127.5, 126.6, 126.4, 126.2, 125.8, 125.3, 124.8 (d, *J* = 3.5 Hz), 122.2, 120.6, 107.1, 74.0, 70.1, 52.3, 51.5, 39.1, 37.4.
HRMS (ESI): calcd for $(M+H)^+$ $C_{22}H_{24}NSO_5^+$, 414.1370, found: 414.1375.

10. NMR spectra of products

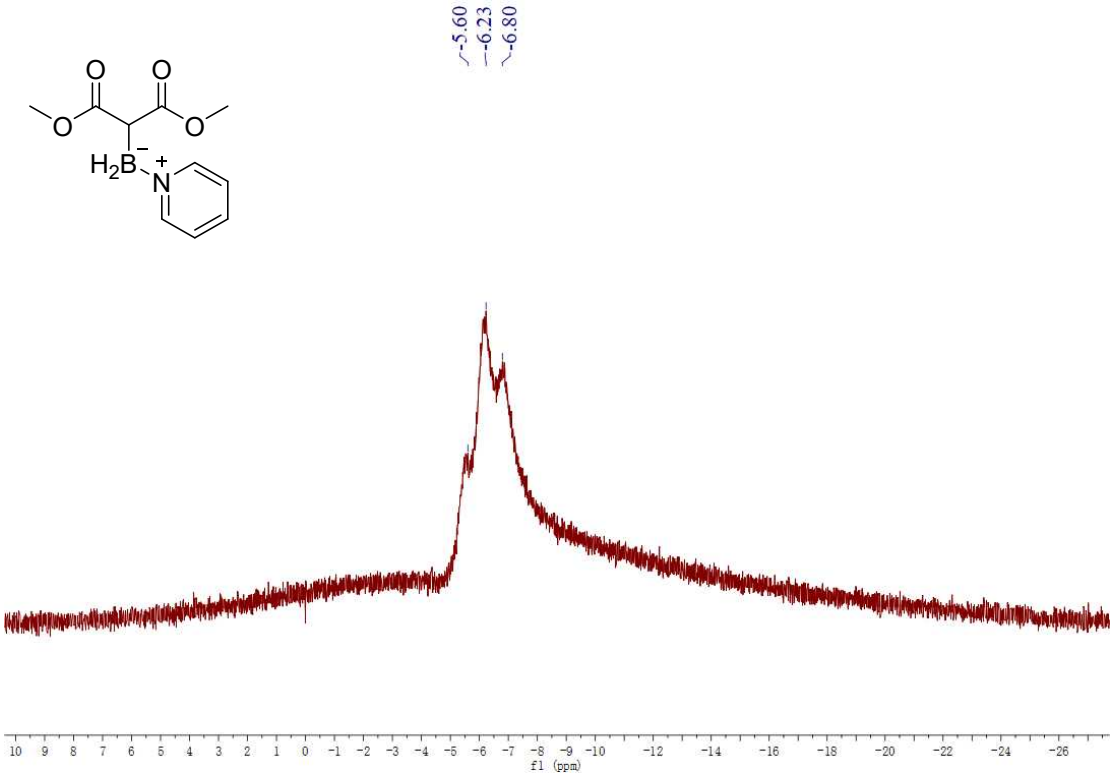
^{1}H NMR of dimethyl 2-boranylmalonate-pyridine complex (3a)



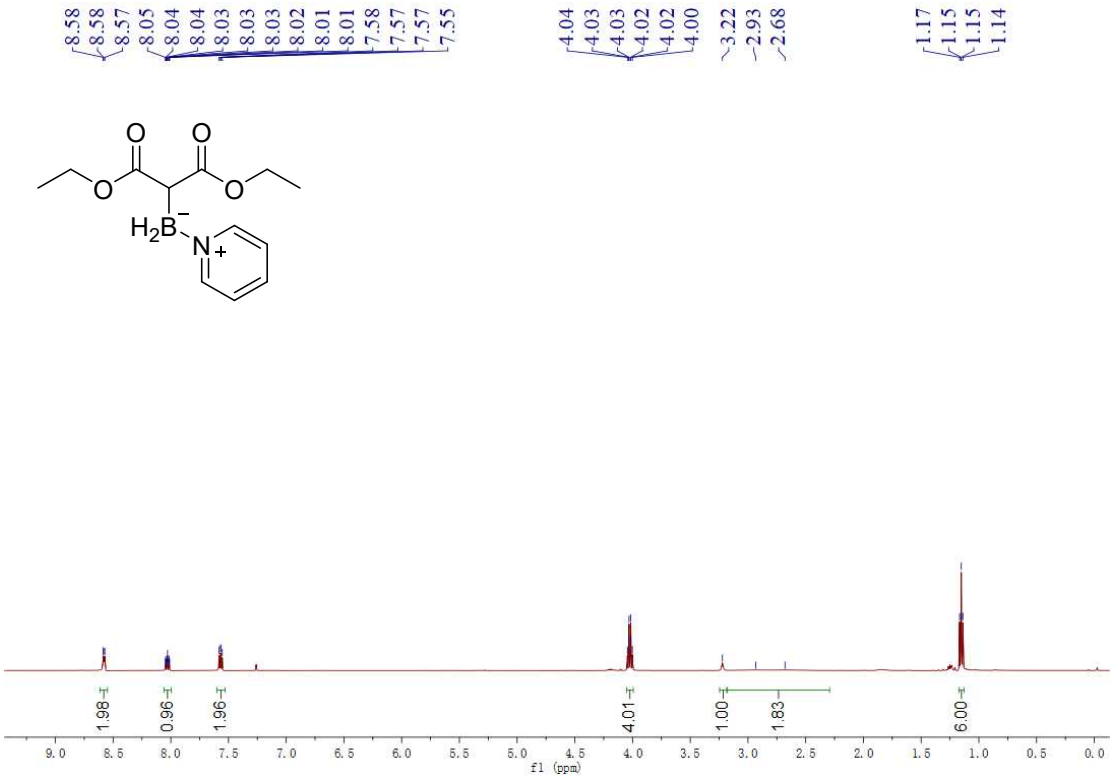
^{13}C NMR of dimethyl 2-boranylmalonate-pyridine complex (3a)



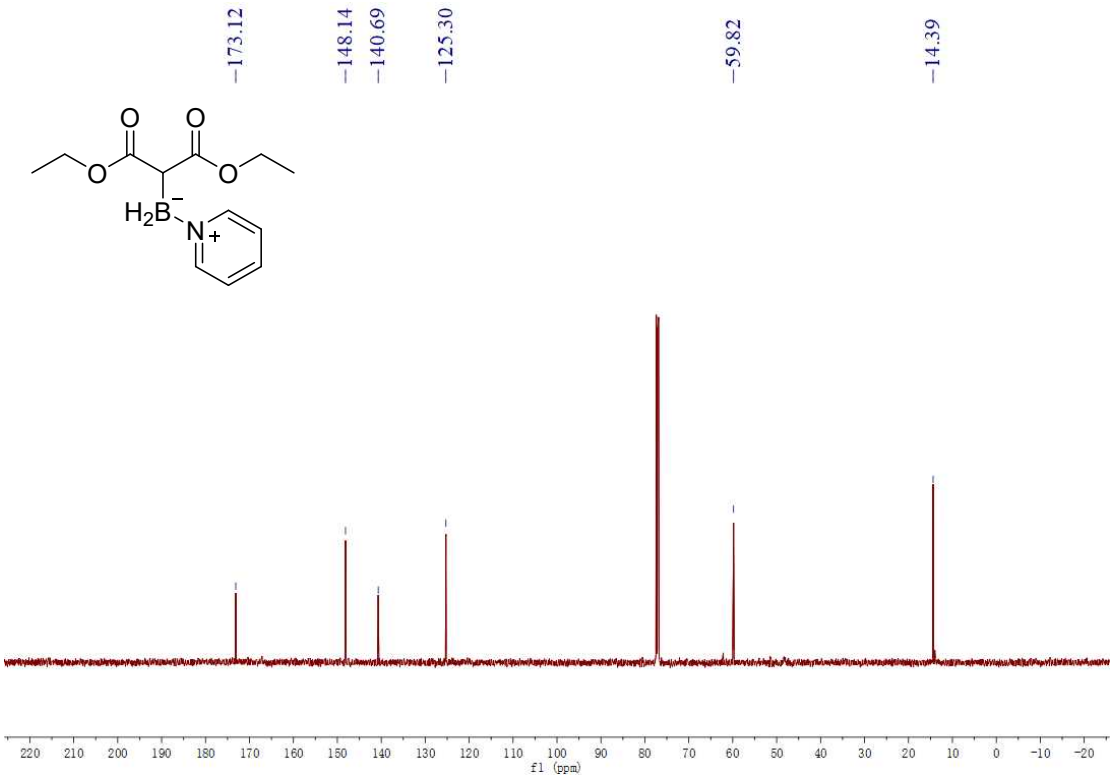
^{11}B NMR of dimethyl 2-boranylmalonate-pyridine complex (3a)



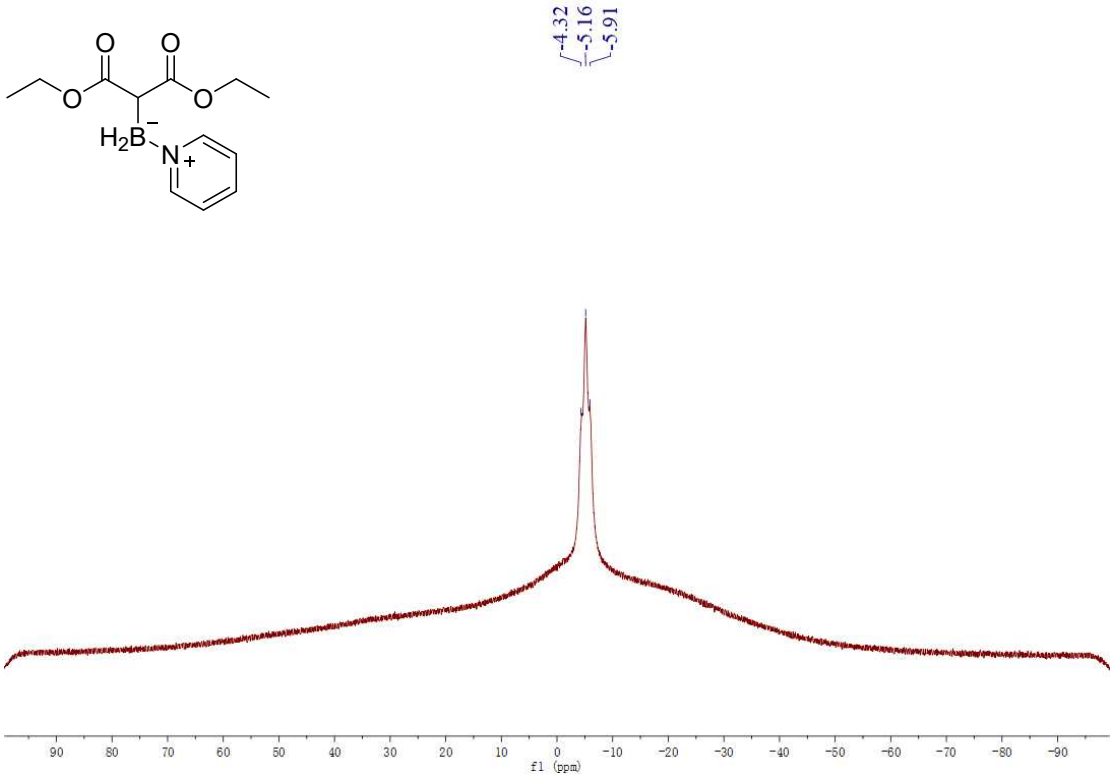
^{1}H NMR of diethyl 2-boranylmalonate-pyridine complex (3b)



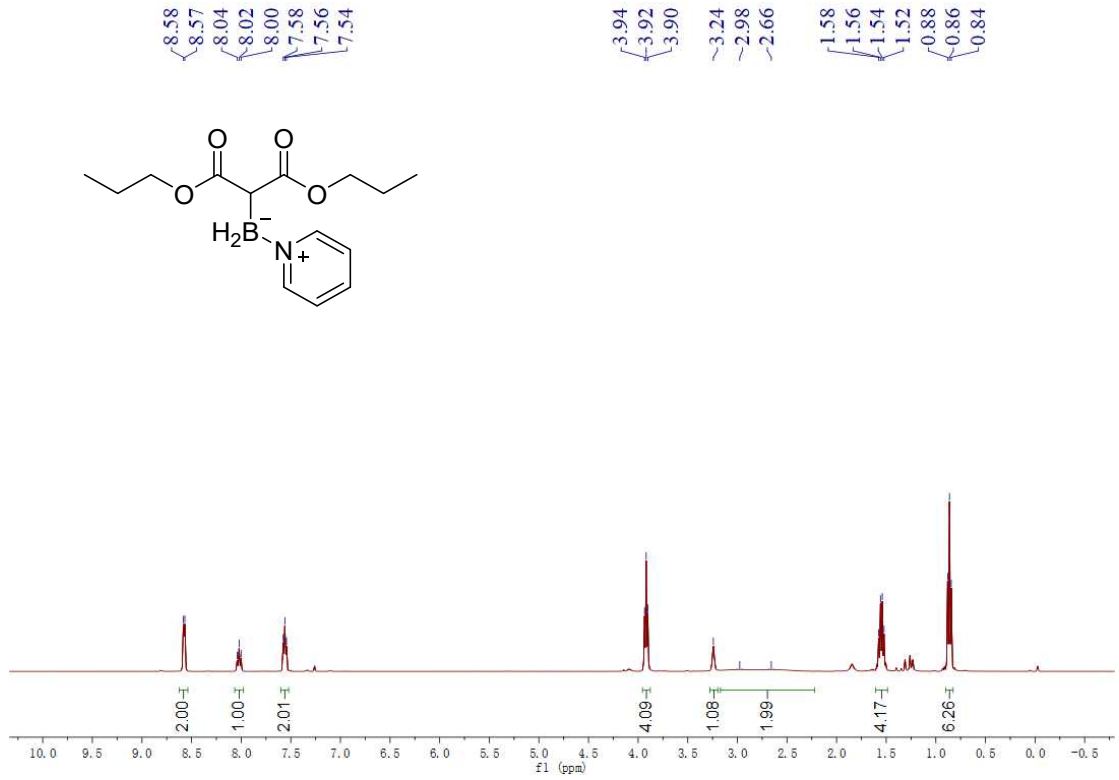
^{13}C NMR of diethyl 2-boranylmalonate-pyridine complex (3b)



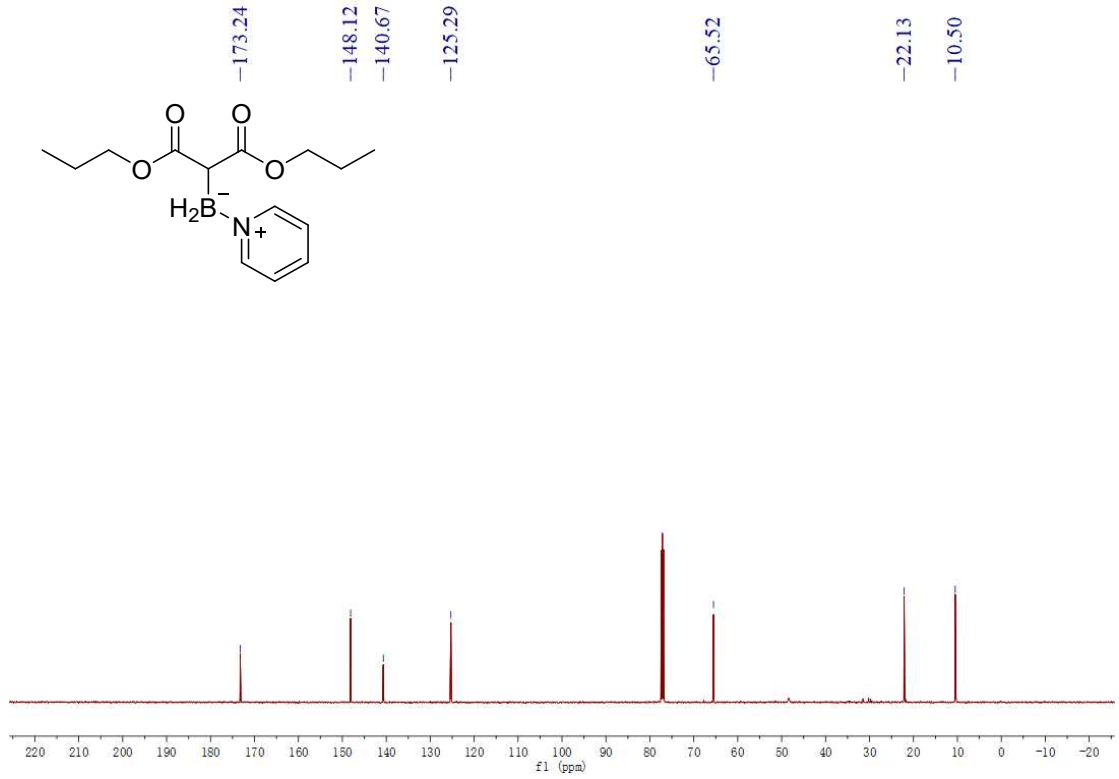
^{11}B NMR of diethyl 2-boranylmalonate-pyridine complex (3b)



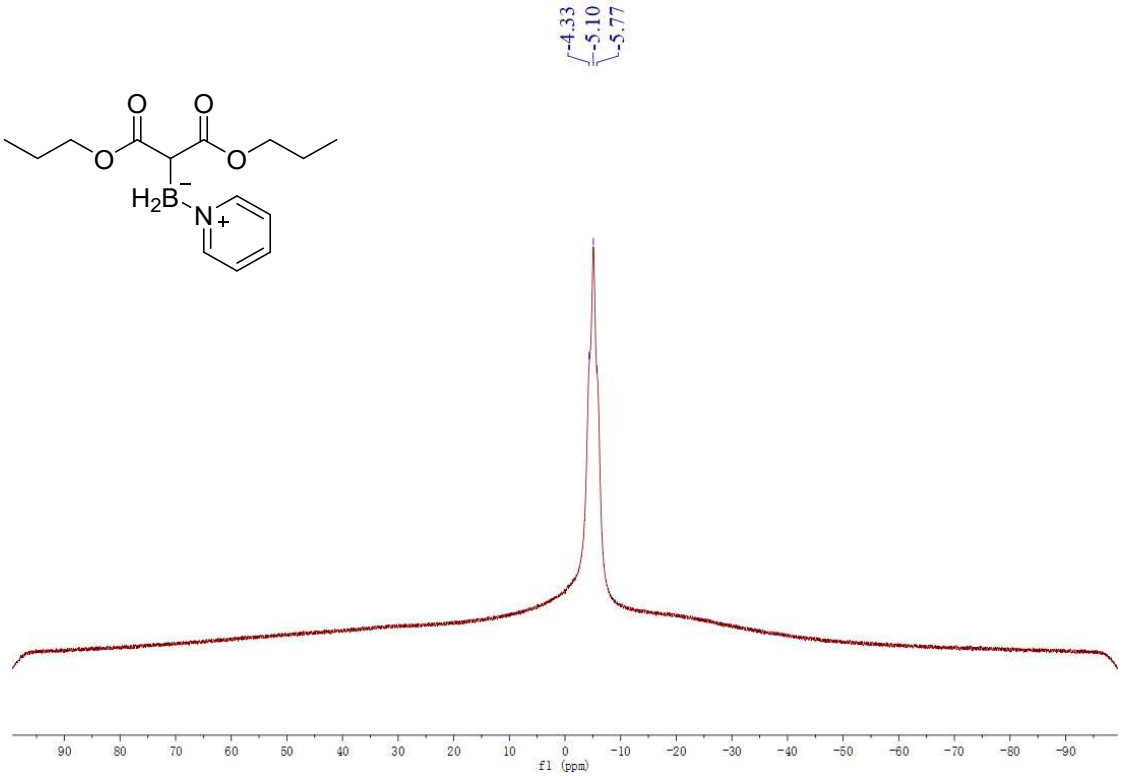
^{1}H NMR of diisopropyl 2-boranylmalonate-pyridine complex (3c)



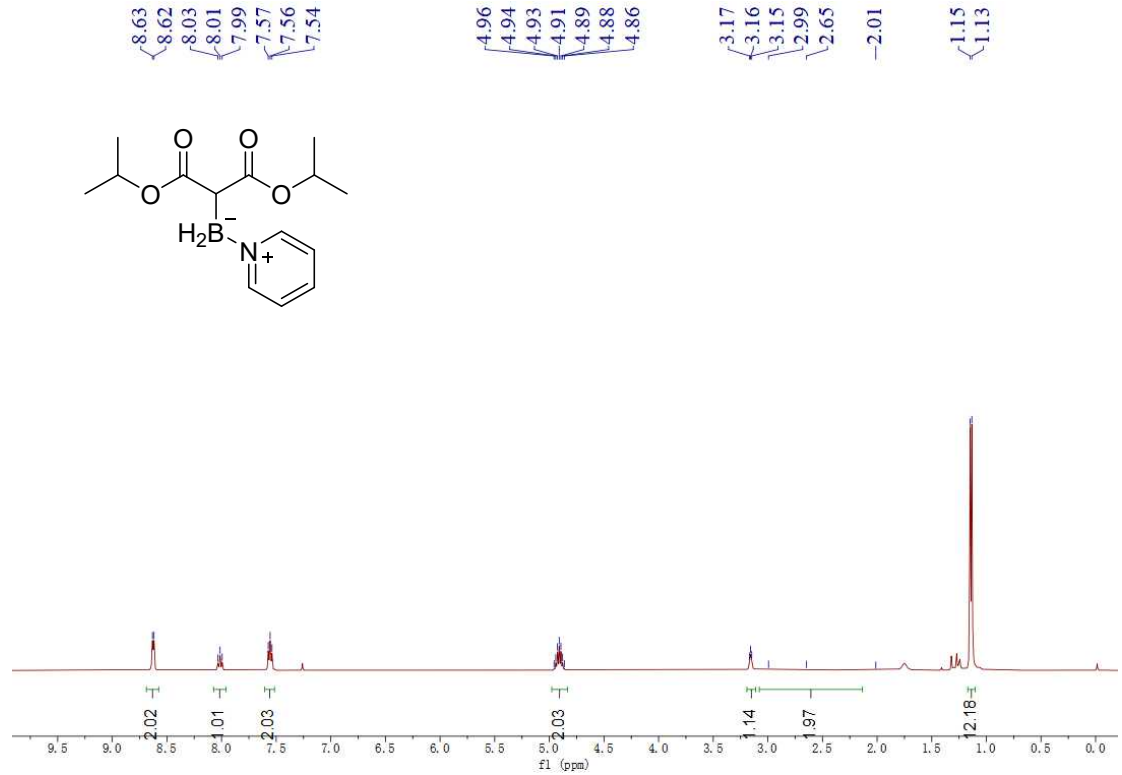
^{13}C NMR of diisopropyl 2-boranylmalonate-pyridine complex (3c)



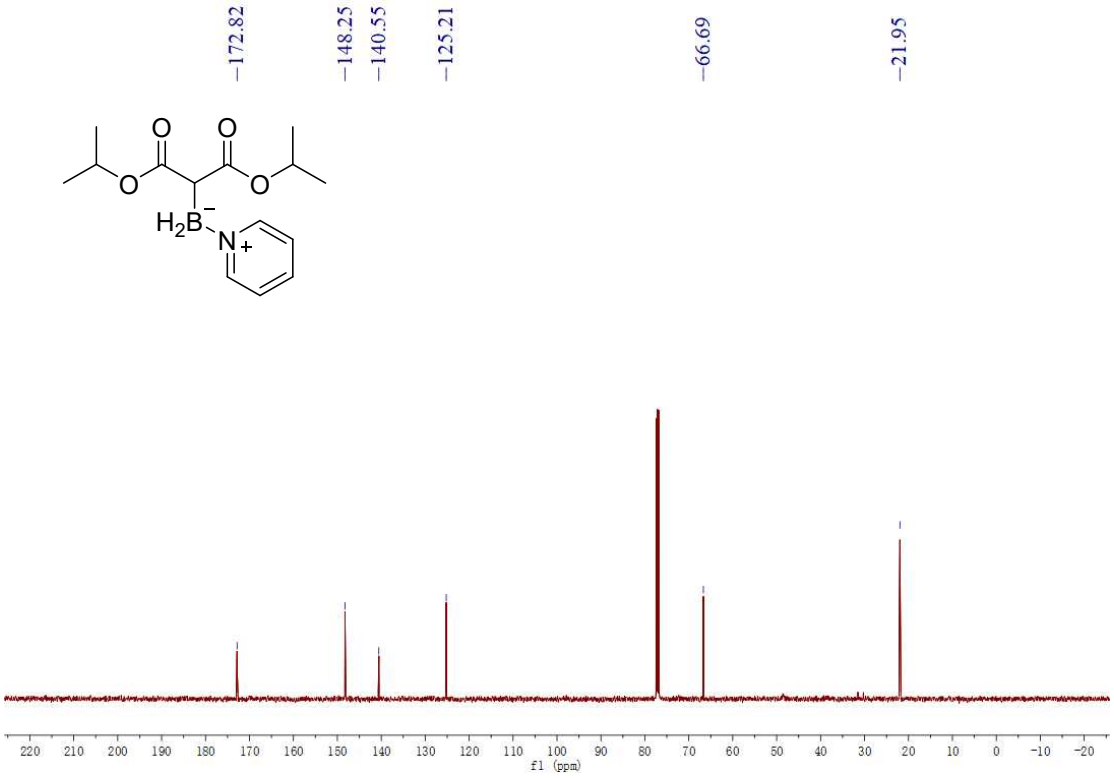
^{11}B NMR of diisopropyl 2-boranylmalonate-pyridine complex (3c)



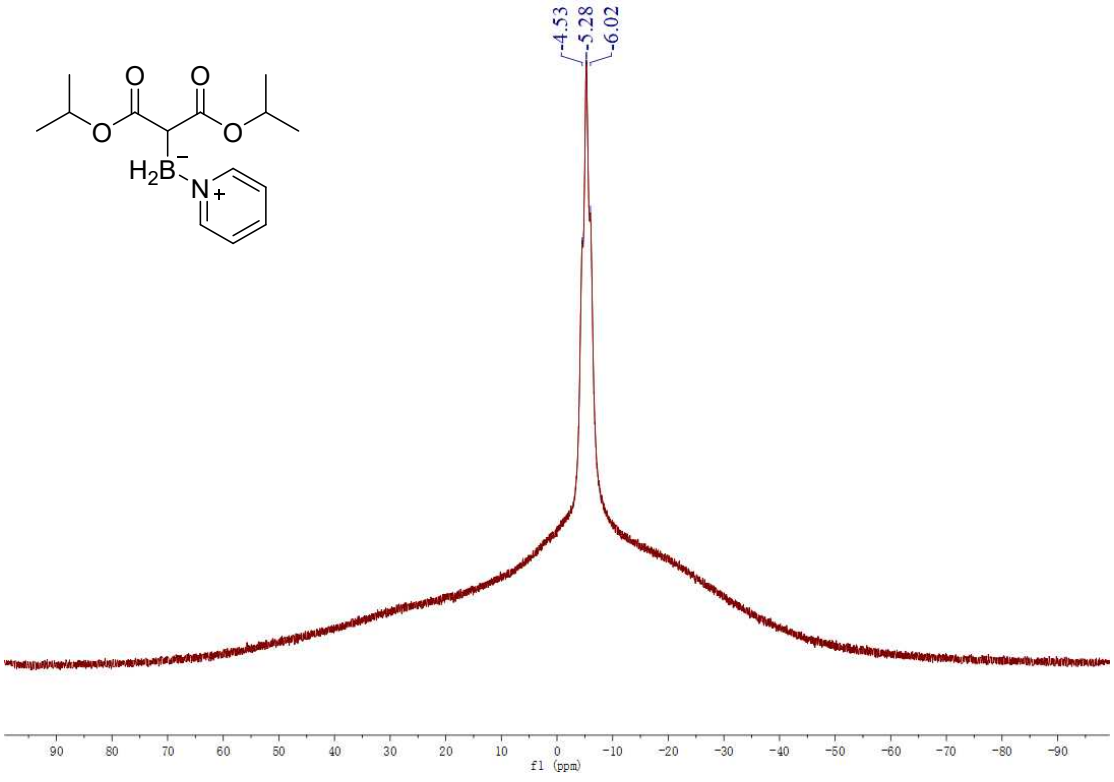
[1]H NMR of di-tert-butyl 2-boranylmalonate-pyridine complex (3d)



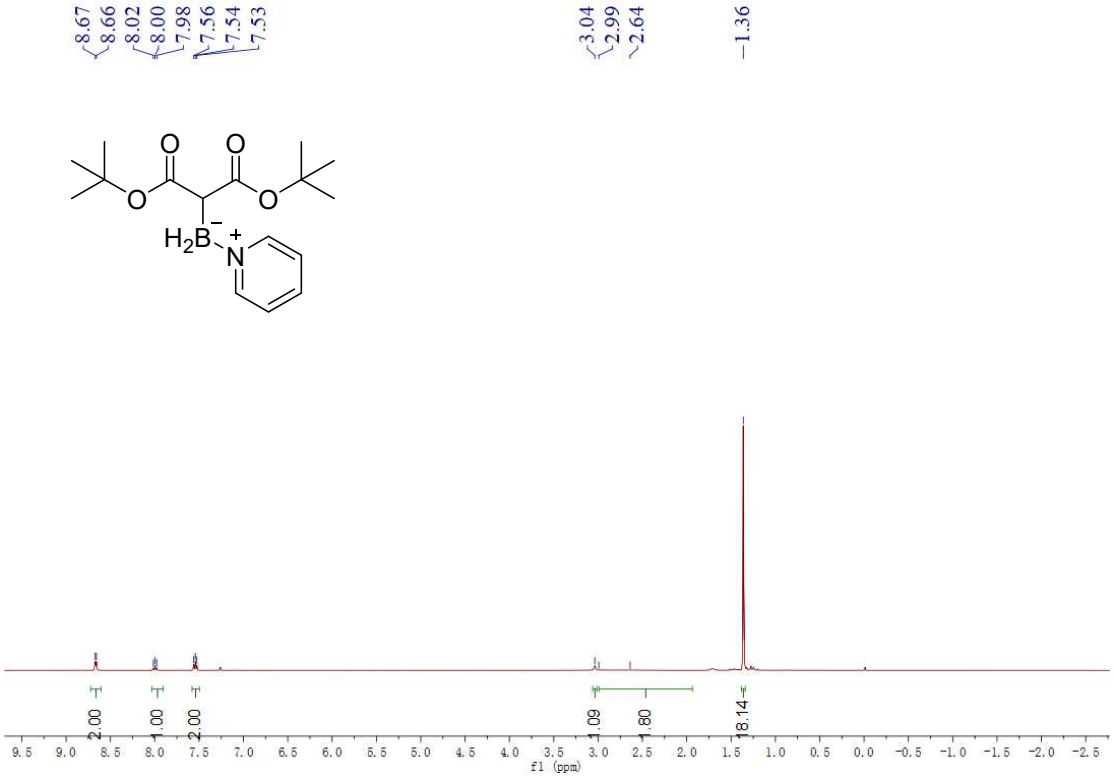
[13]C NMR of di-tert-butyl 2-boranylmalonate-pyridine complex (3d)



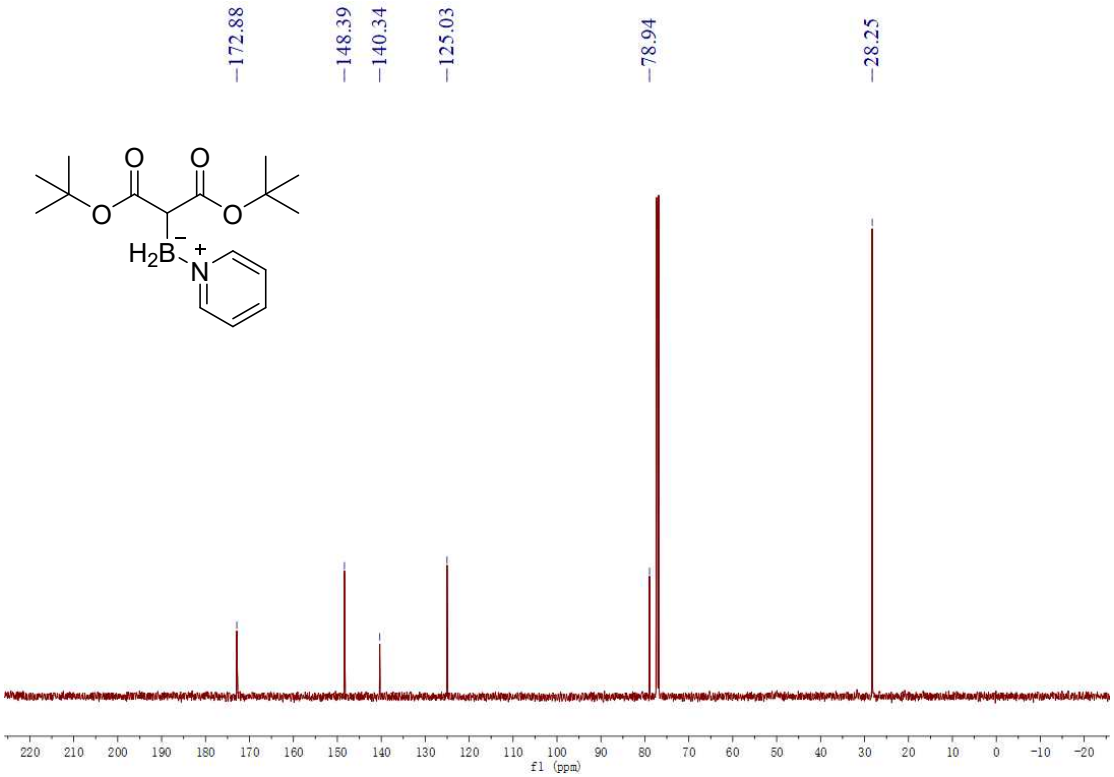
^{11}B NMR of di-tert-butyl 2-boranylmalonate-pyridine complex (3d)



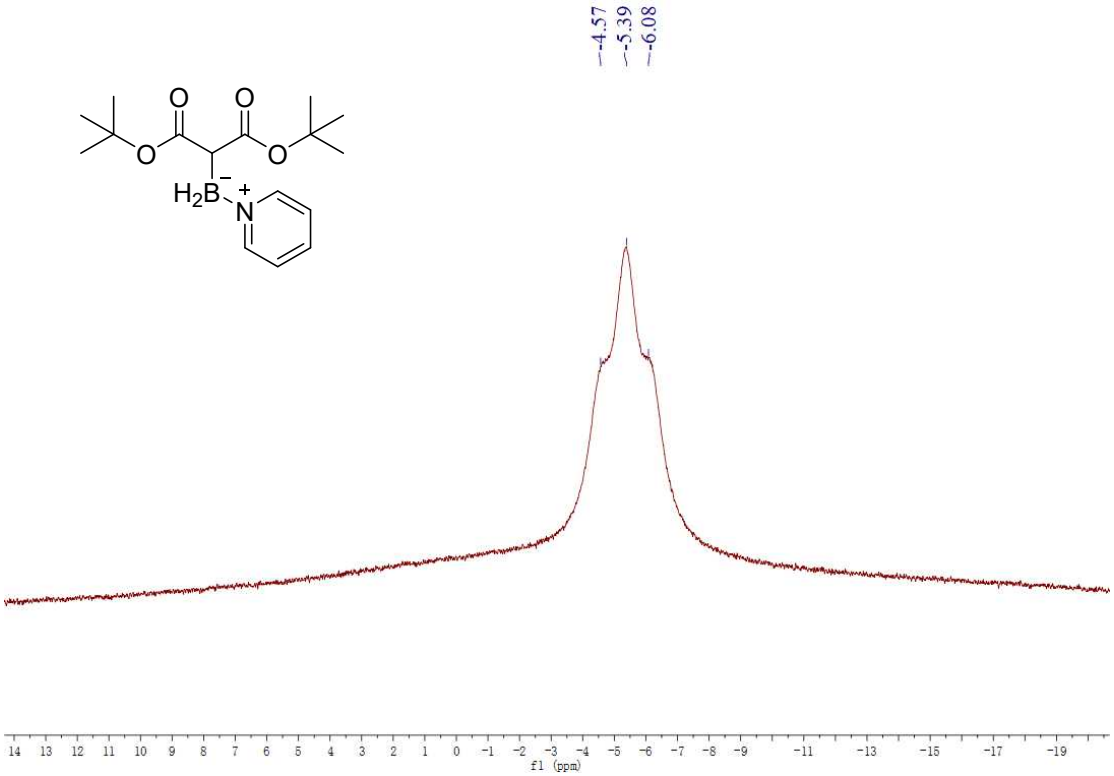
^{1}H NMR of dipropyl 2-boranylmalonate-pyridine complex (3e)



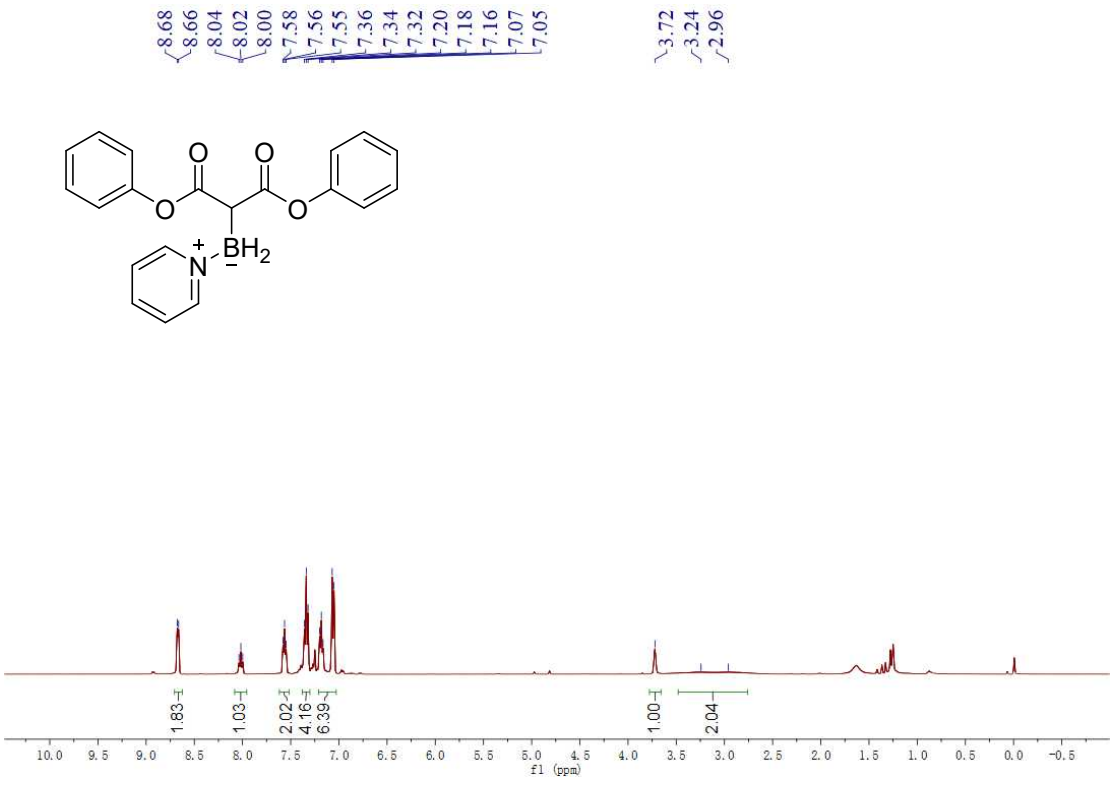
^{13}C NMR of dipropyl 2-boranylmalonate-pyridine complex (3e)



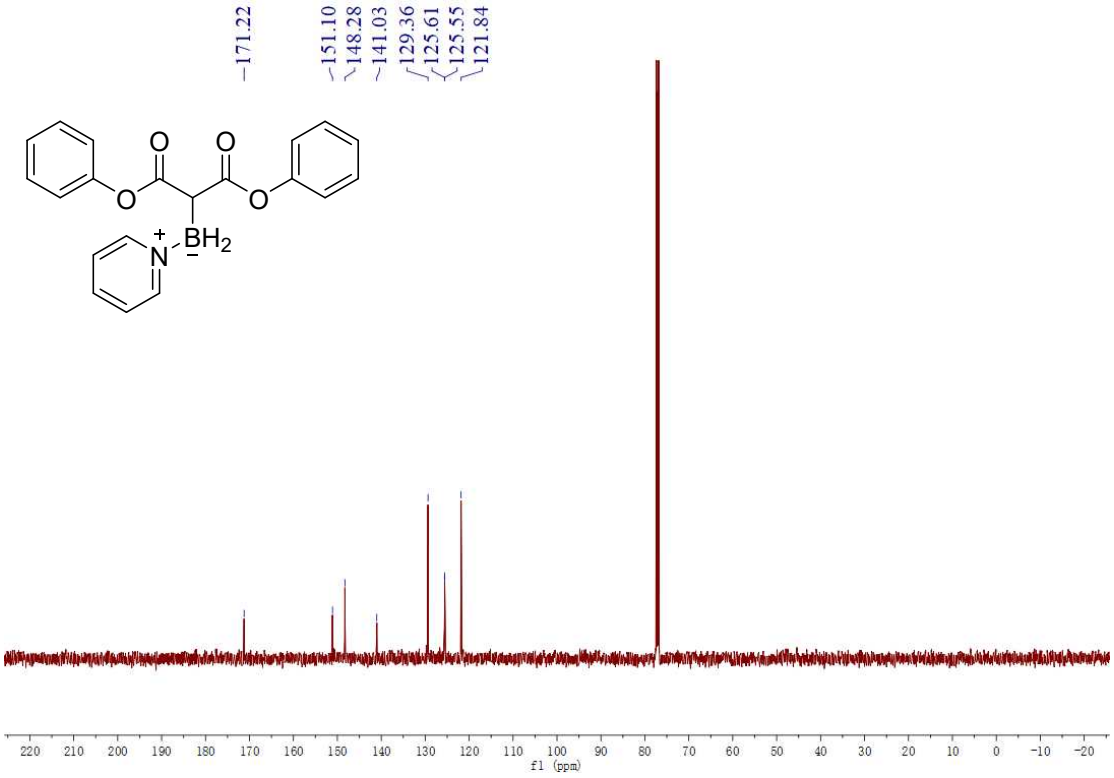
^{11}B NMR of dipropyl 2-boranylmalonate-pyridine complex (3e)



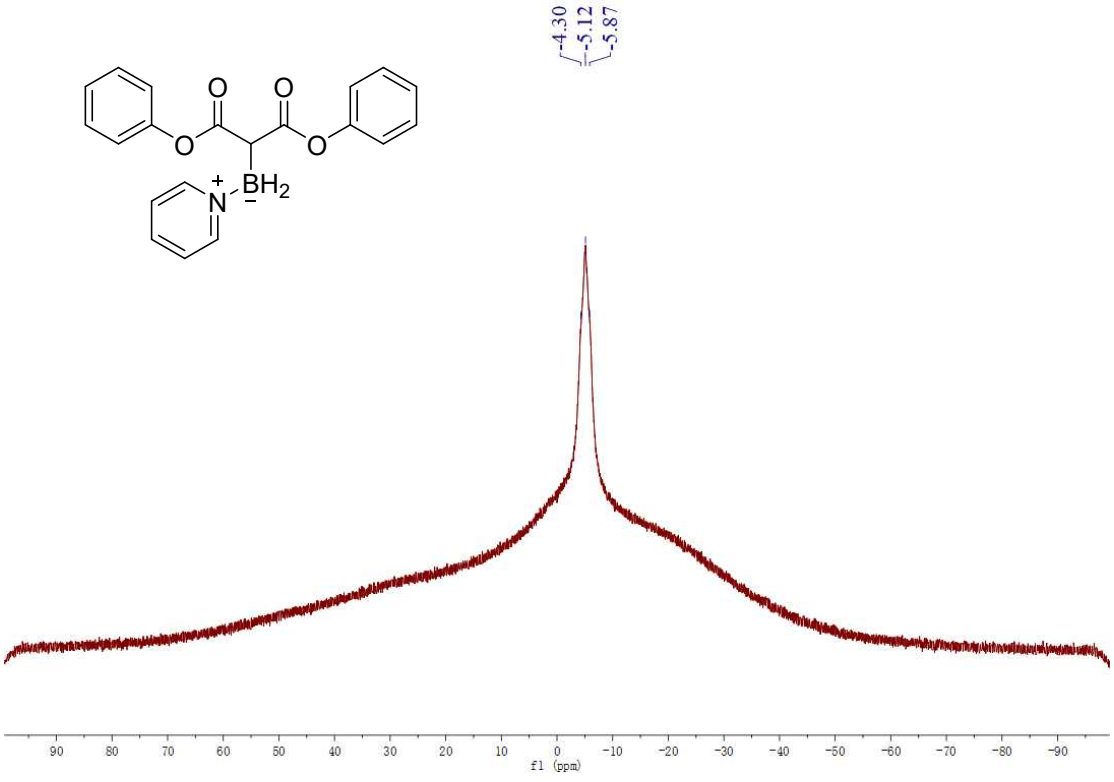
^{1}H NMR of diphenyl 2-boranylmalonate-pyridine complex (3f)



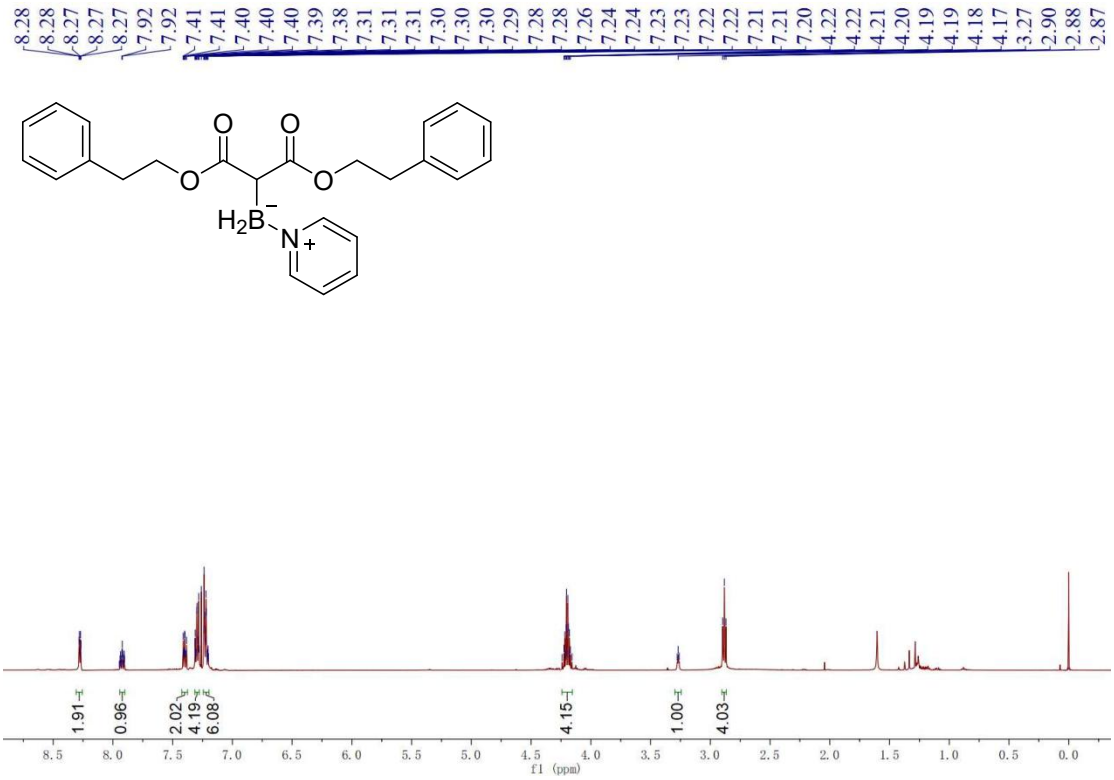
^{13}C NMR of diphenyl 2-boranylmalonate-pyridine complex (3f)



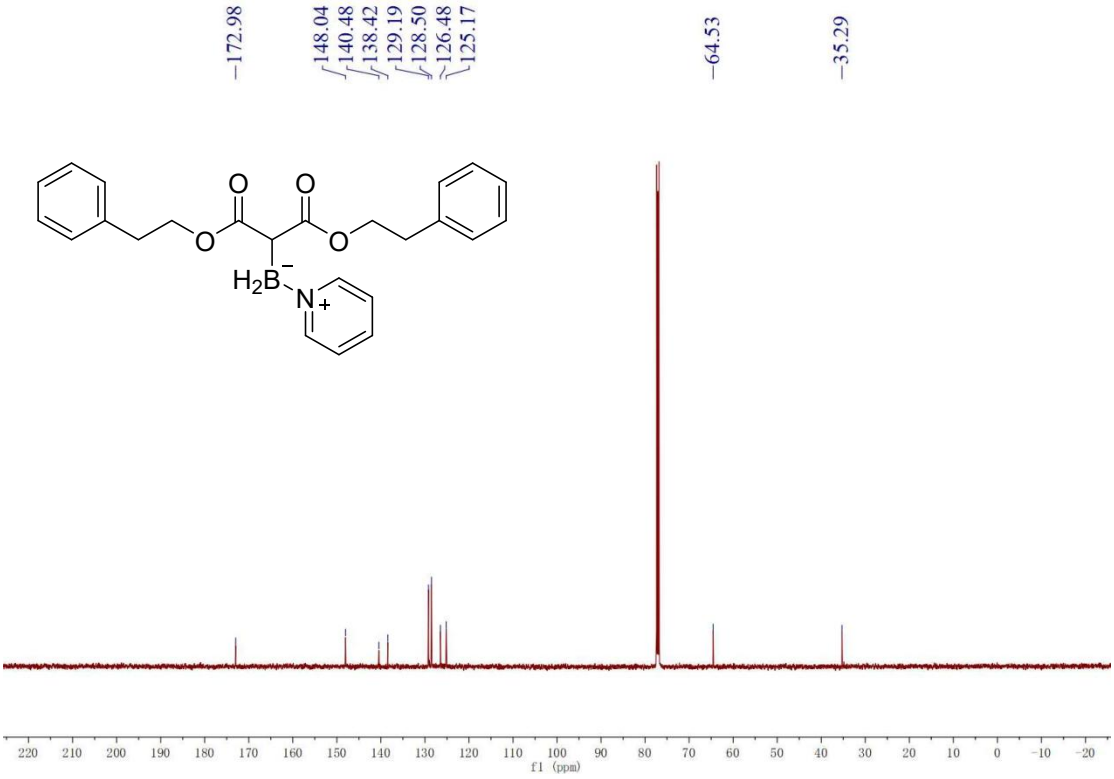
^{11}B NMR of diphenyl 2-boranylmalonate-pyridine complex (3f)



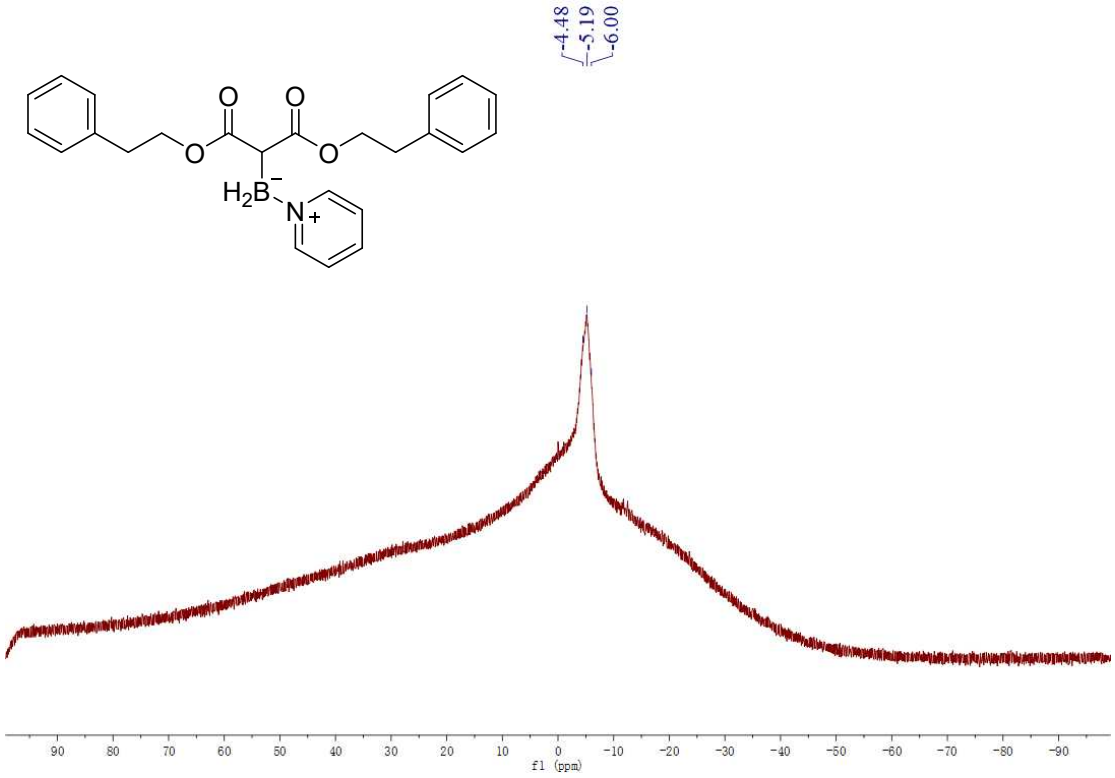
^{1}H NMR of 1-(tert-butyl) 3-methyl 2-boranylmalonate-pyridine complex (3g)



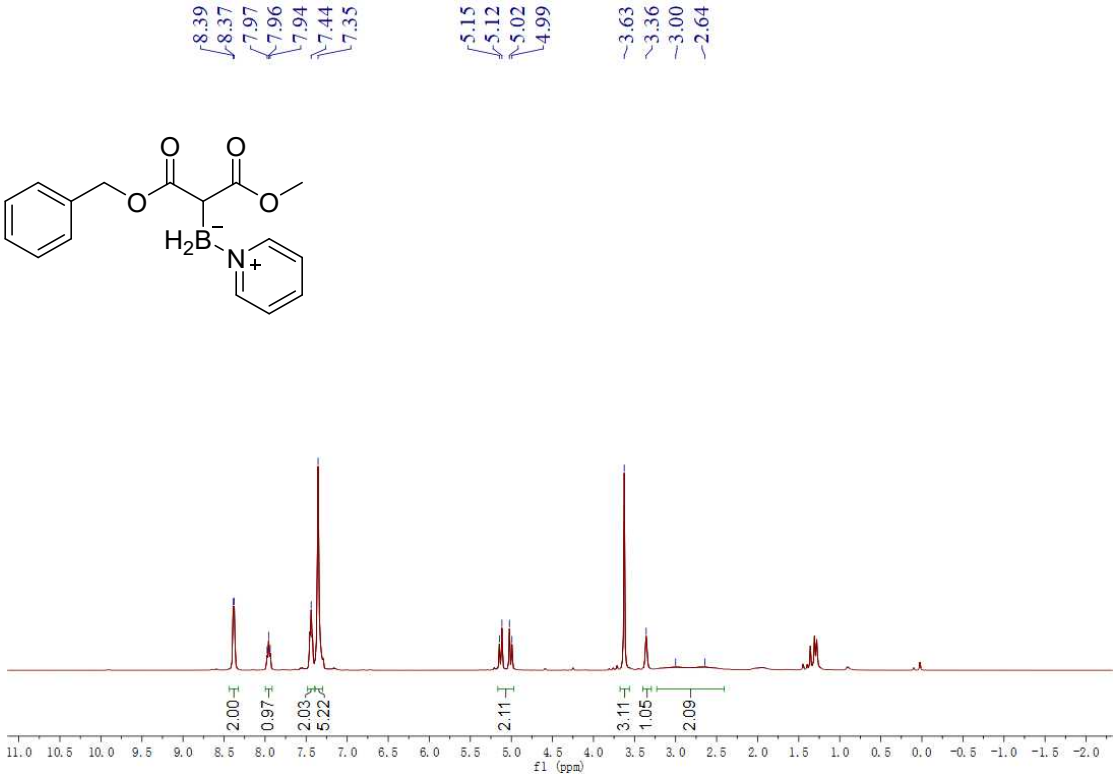
^{13}C NMR of 1-(tert-butyl) 3-methyl 2-boranylmalonate-pyridine complex (3g)



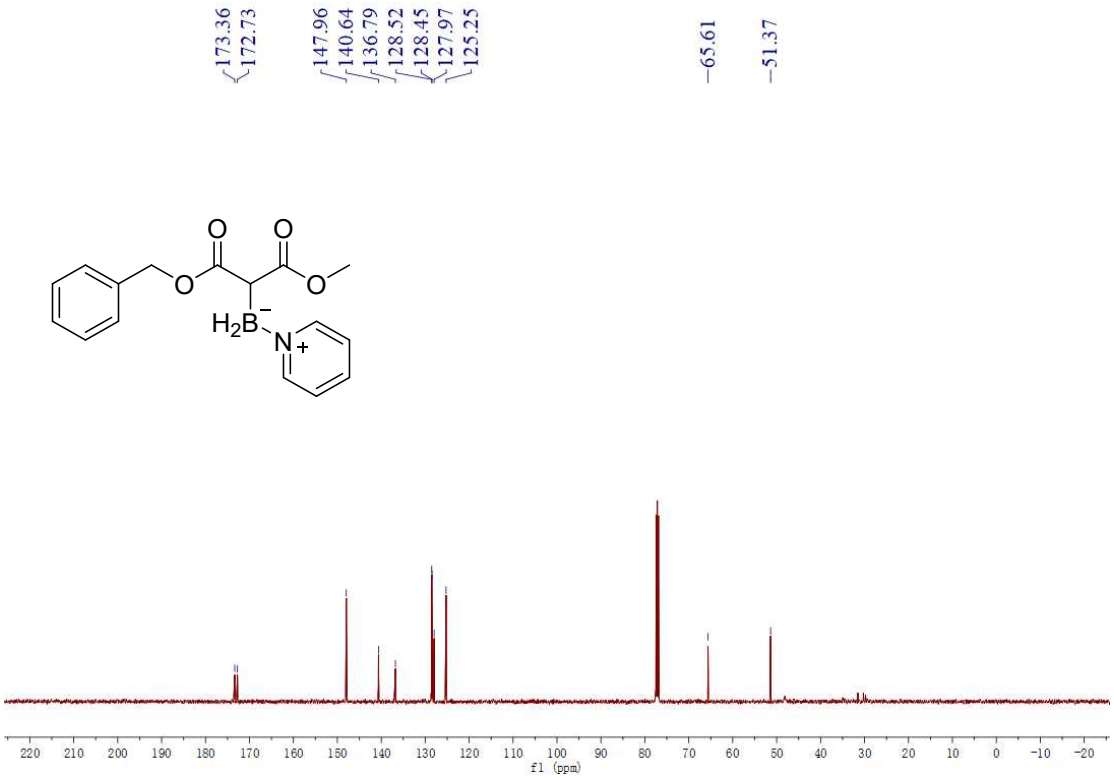
^{11}B NMR of 1-(tert-butyl) 3-methyl 2-boranylmalonate-pyridine complex (3g)



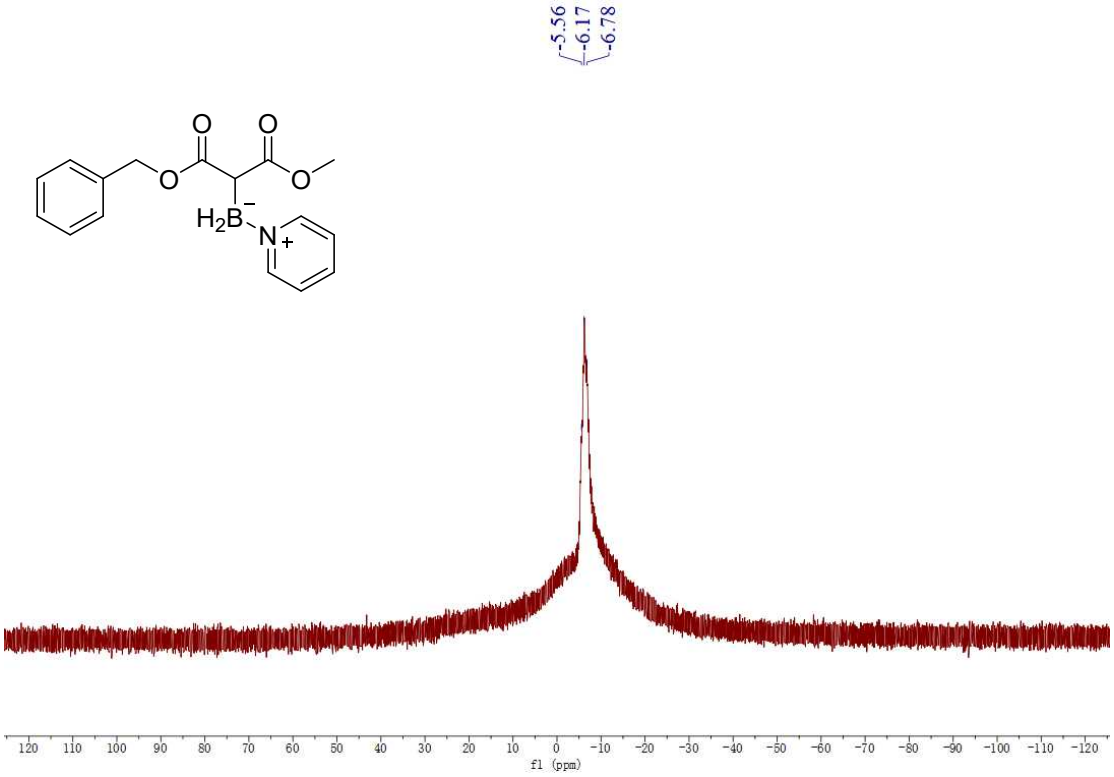
^{1}H NMR of 1-(tert-butyl) 3-ethyl 2-boranylmalonate-pyridine complex (3h)



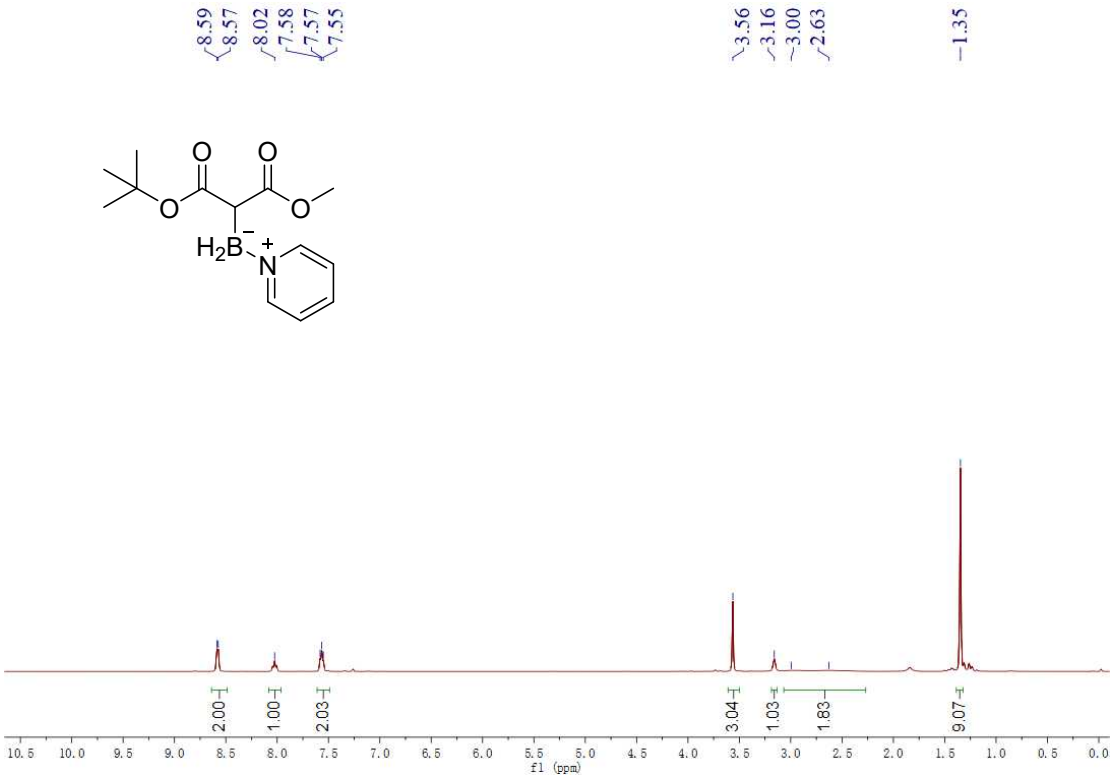
^{13}C NMR of 1-(tert-butyl) 3-ethyl 2-boranylmalonate-pyridine complex (3h)



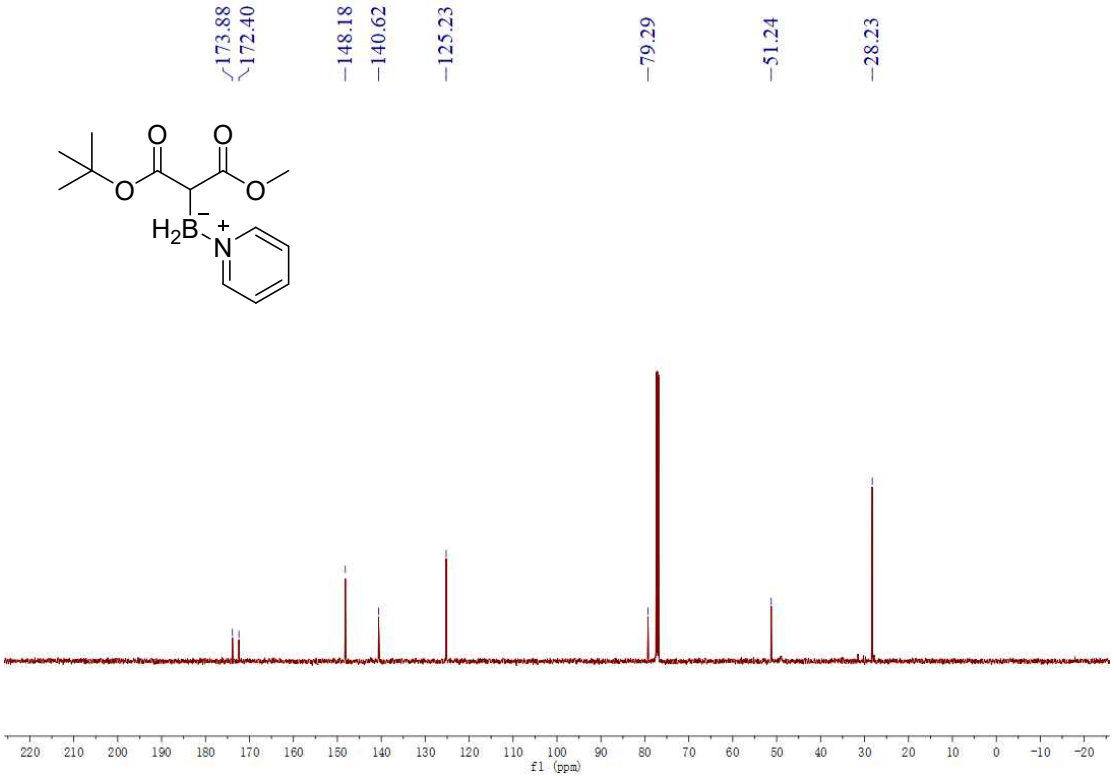
^{11}B NMR of 1-(tert-butyl) 3-ethyl 2-boranylmalonate-pyridine complex (3h)



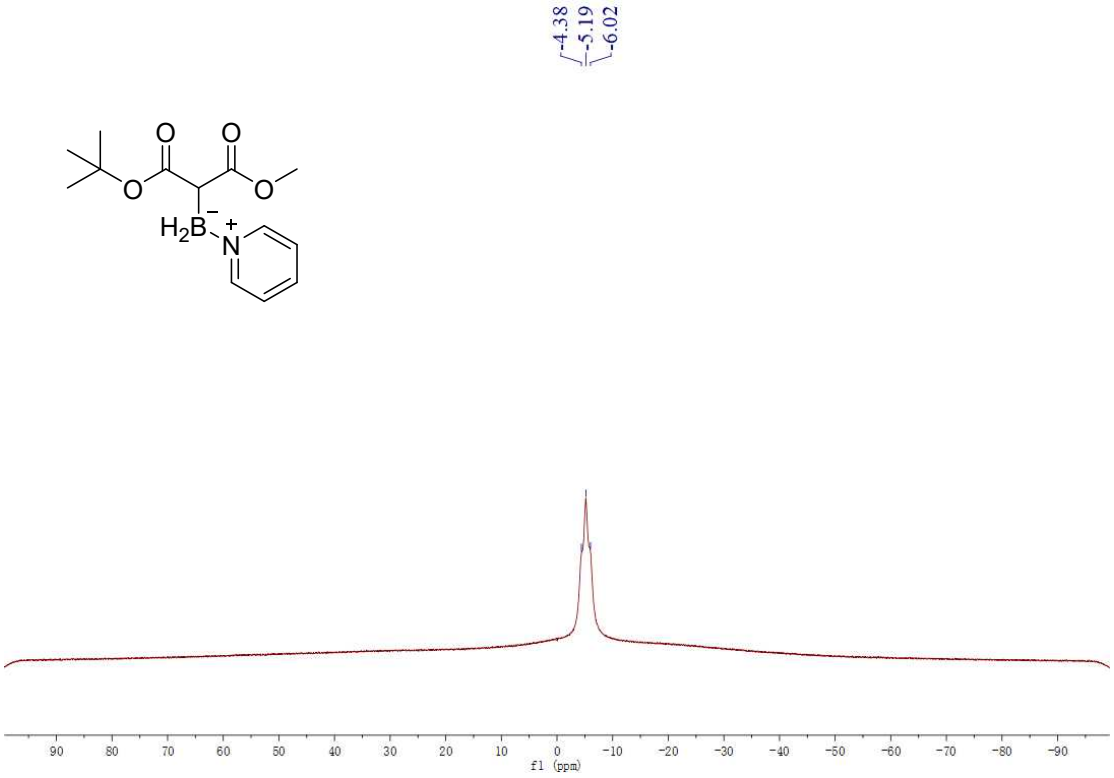
^{1}H NMR of 1-benzyl 3-methyl 2-boranylmalonate-pyridine complex (3i)



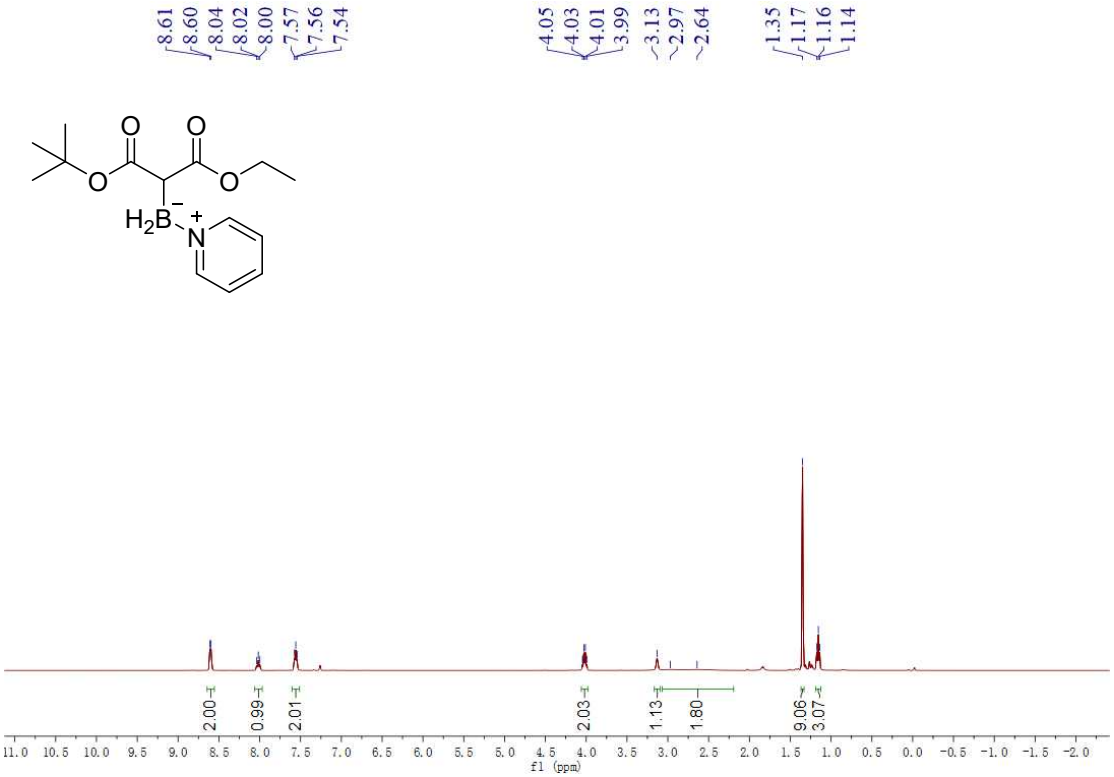
^{13}C NMR of 1-benzyl 3-methyl 2-boranylmalonate-pyridine complex (3i)



^{11}B NMR of 1-benzyl 3-methyl 2-boranylmalonate-pyridine complex (3i)

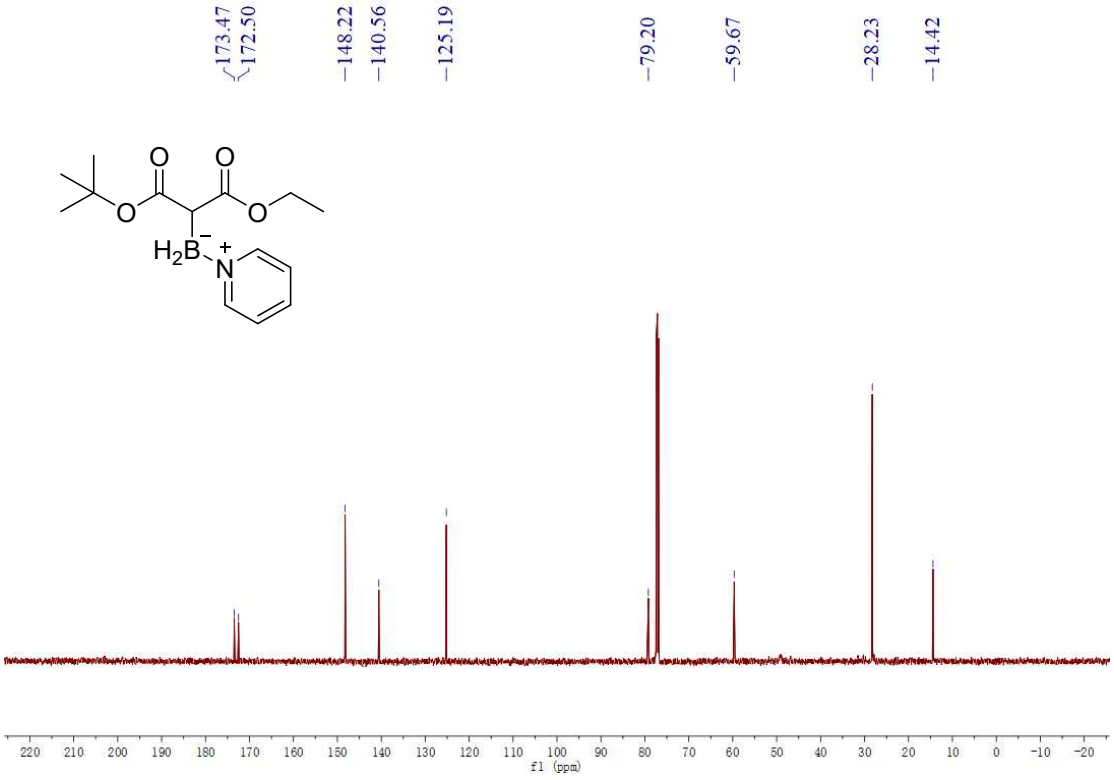


^{1}H NMR of 1-ethyl 3-(4-fluorophenethyl) 2-boranylmalonate -pyridine complex (3j)

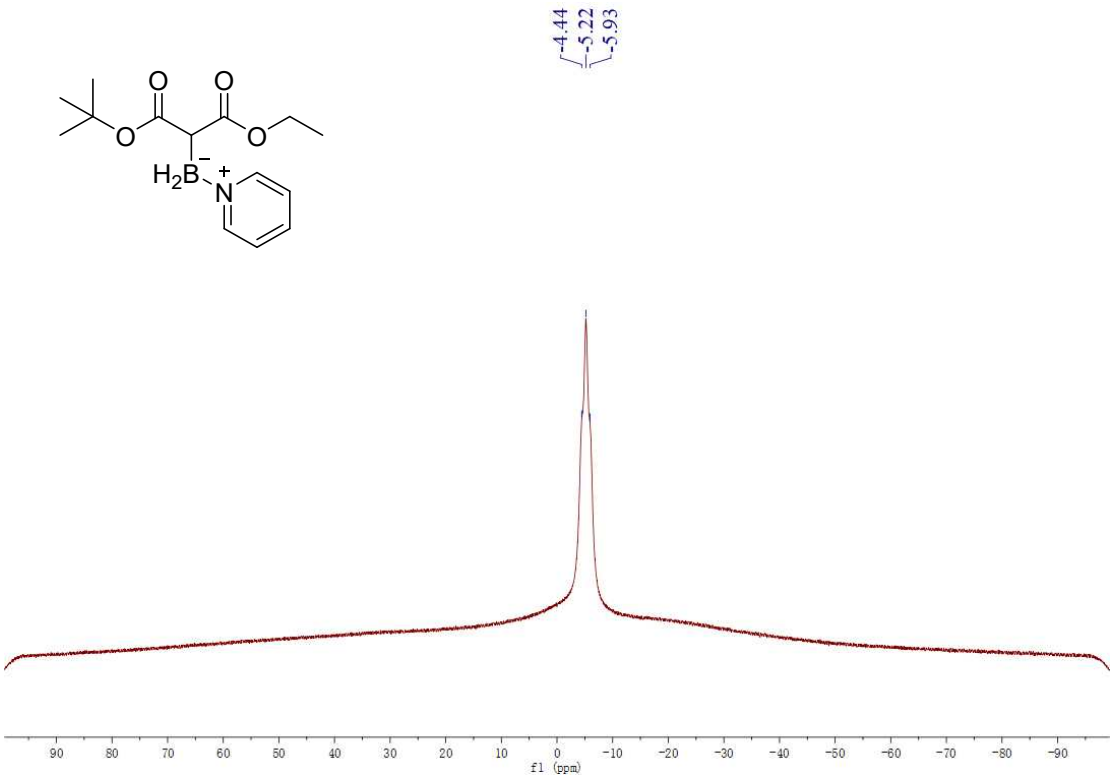


^{13}C NMR of 1-ethyl 3-(4-fluorophenethyl) 2-boranylmalonate -pyridine complex

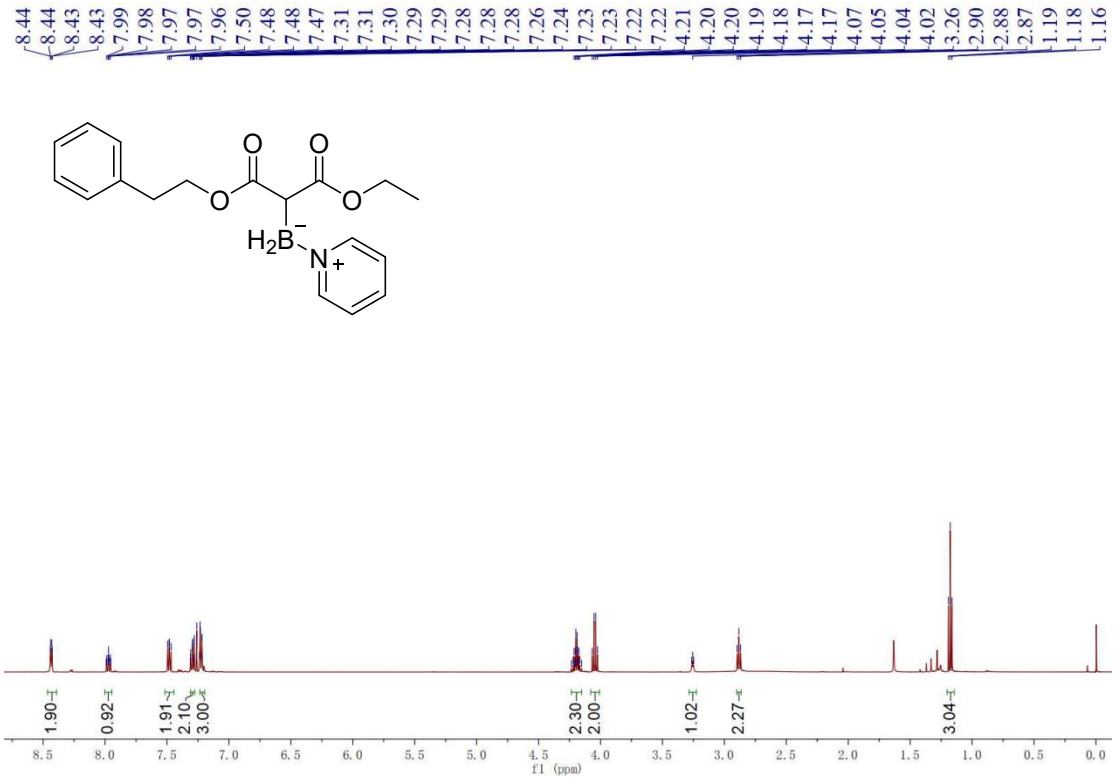
(3j)



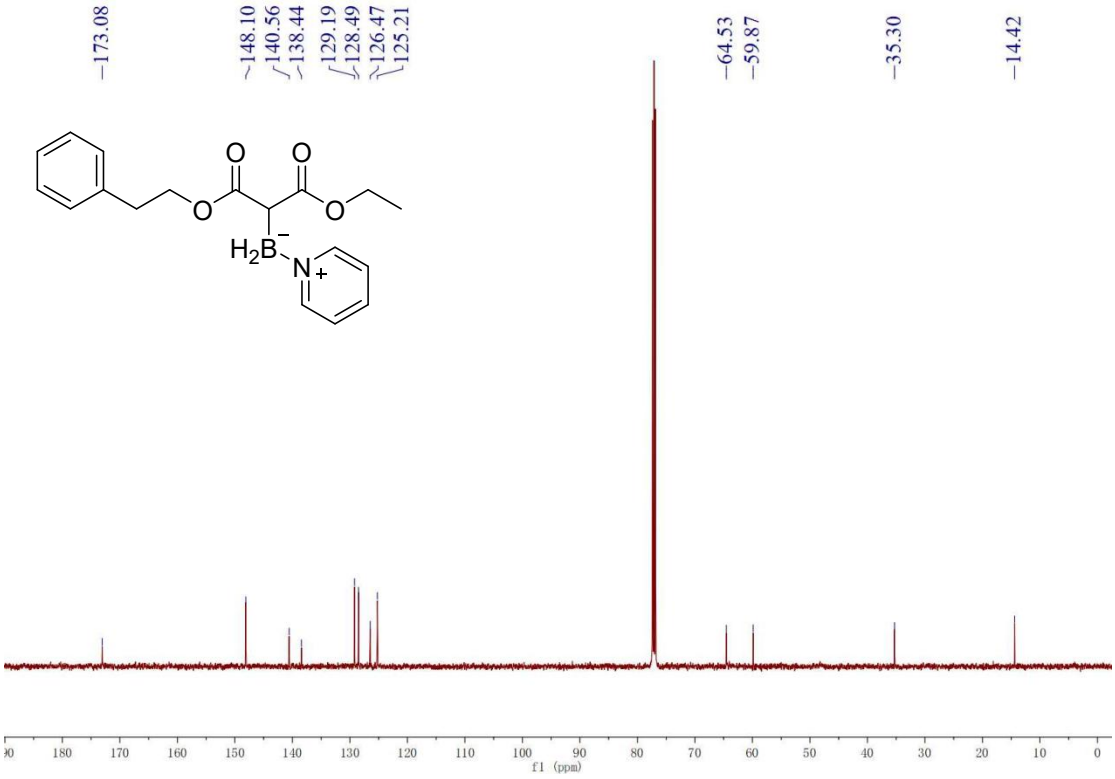
^{11}B NMR of 1-ethyl 3-(4-fluorophenethyl) 2-boranylmalonate -pyridine complex (3j)



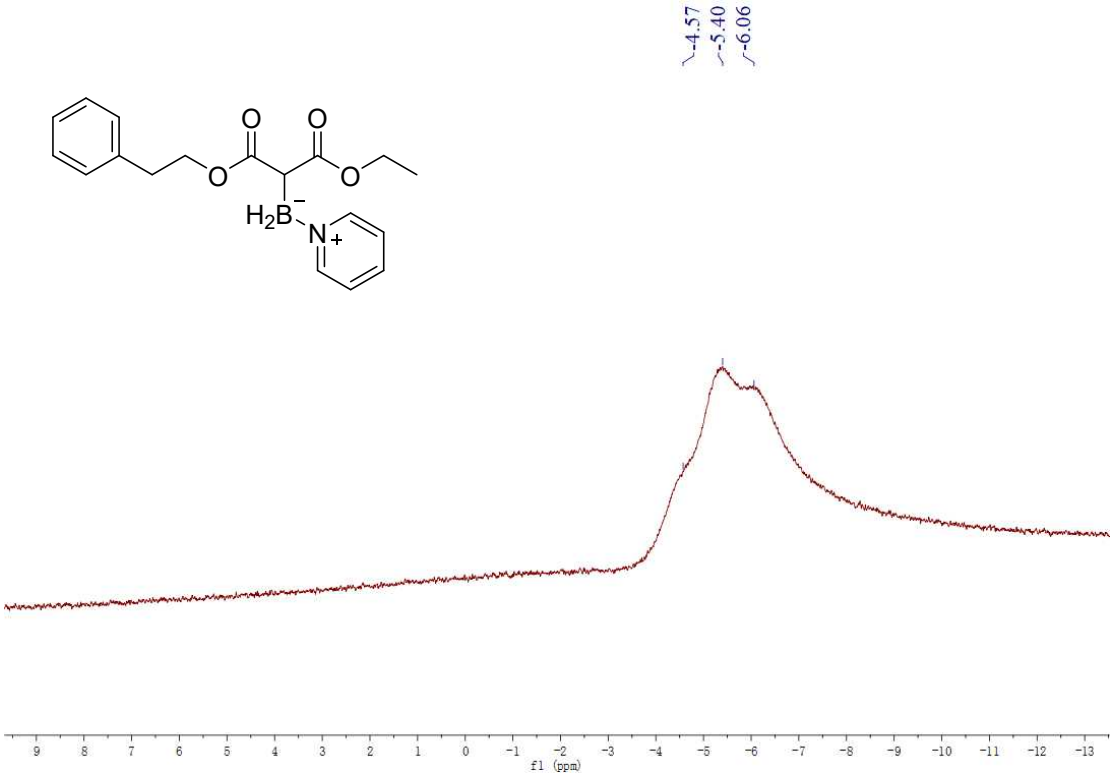
^{1}H NMR of 1-ethyl 3-phenethyl 2-boranylmalonate-pyridine complex (3k)



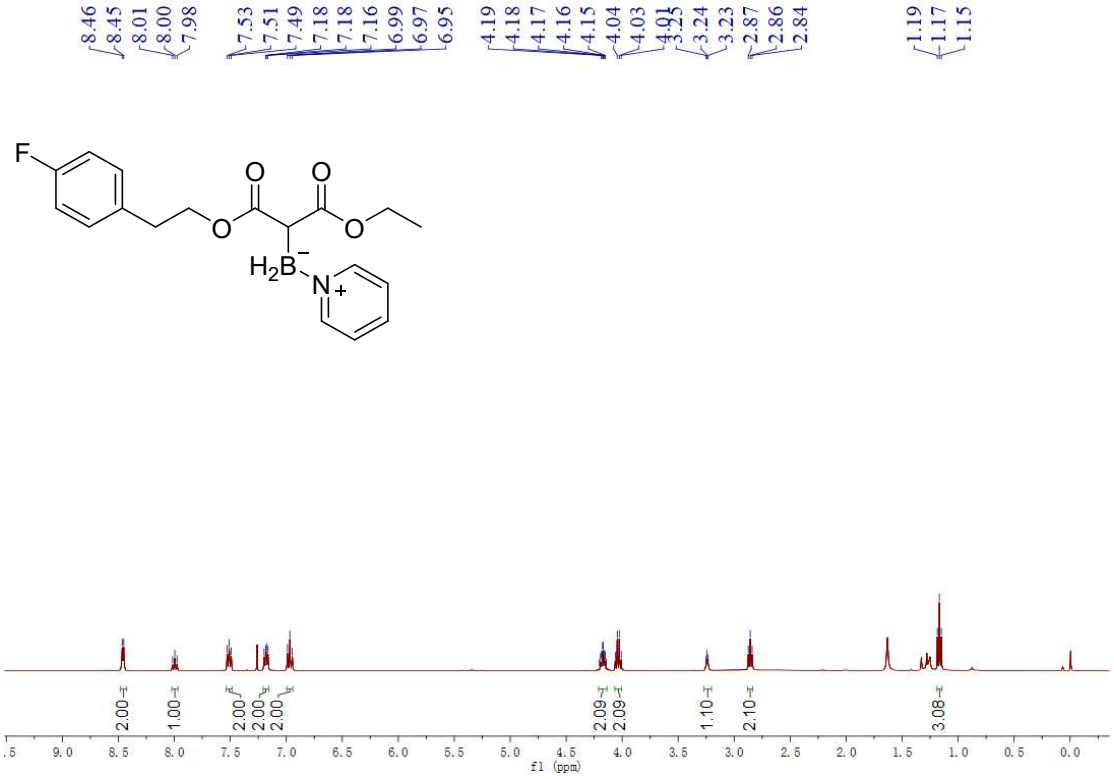
^{13}C NMR of 1-ethyl 3-phenethyl 2-boranylmalonate-pyridine complex (3k)



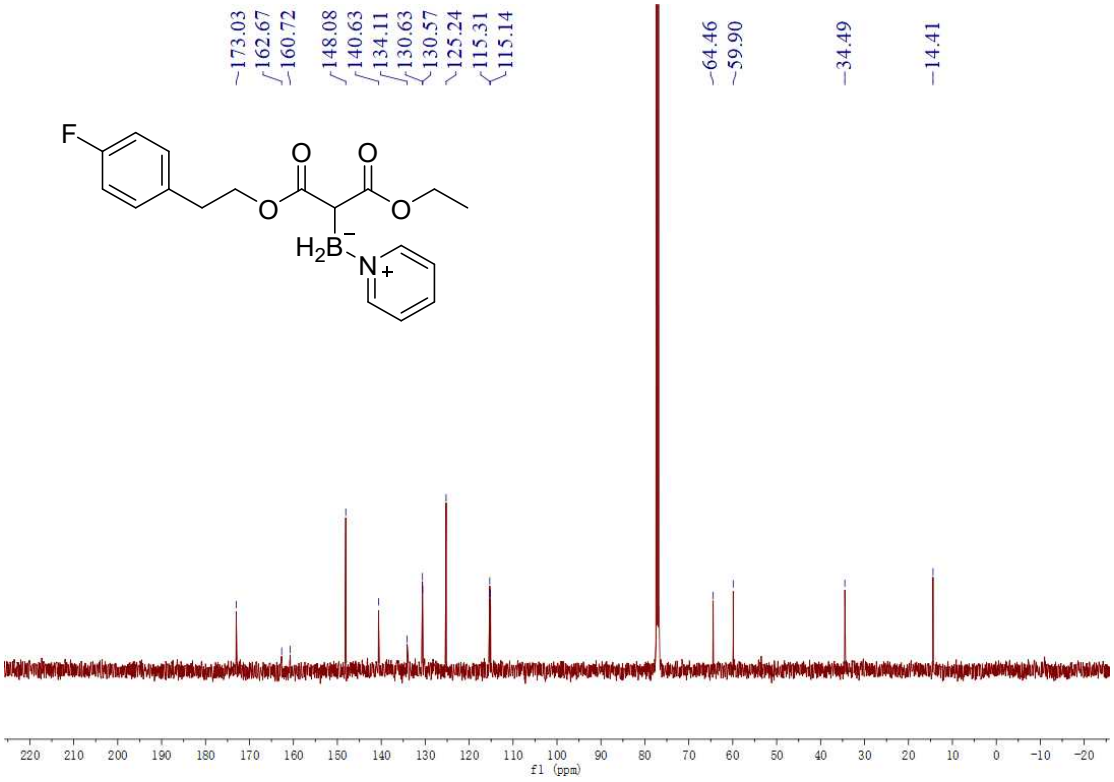
^{11}B NMR of 1-ethyl 3-phenethyl 2-boranylmalonate-pyridine complex (3k)



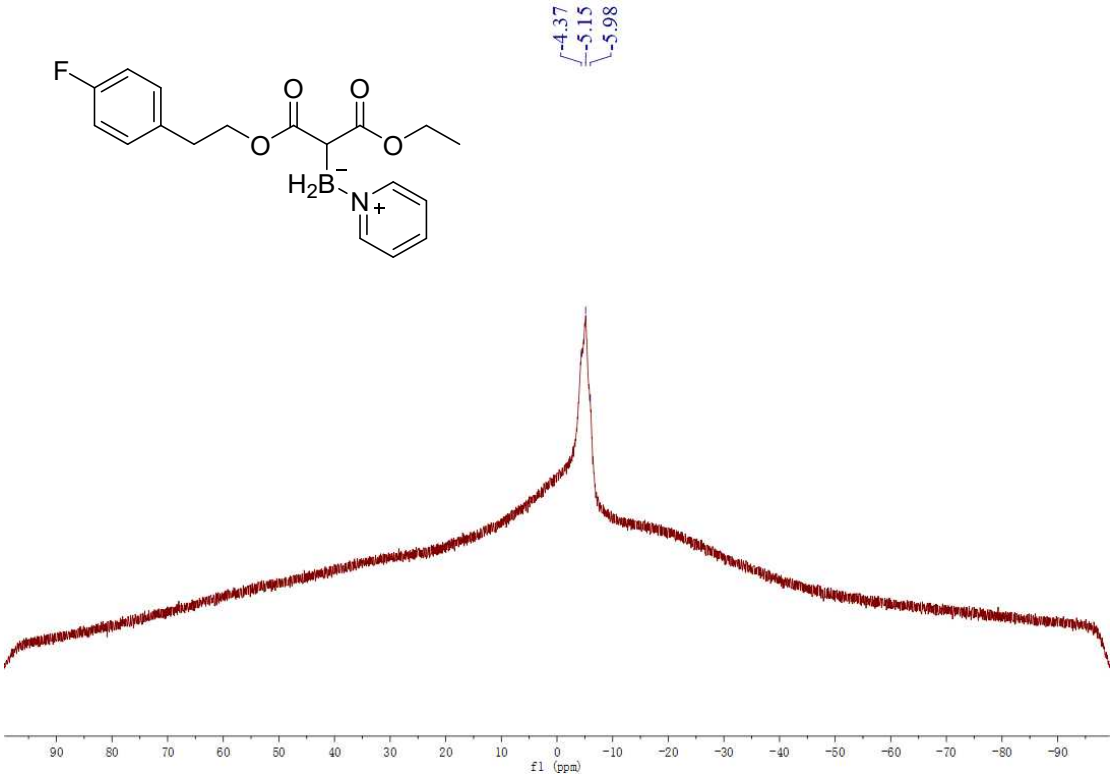
^{1}H NMR of diphenethyl 2-boranylmalonate-pyridine complex (3l)



^{13}C NMR of diphenethyl 2-boranylmalonate-pyridine complex (3l)

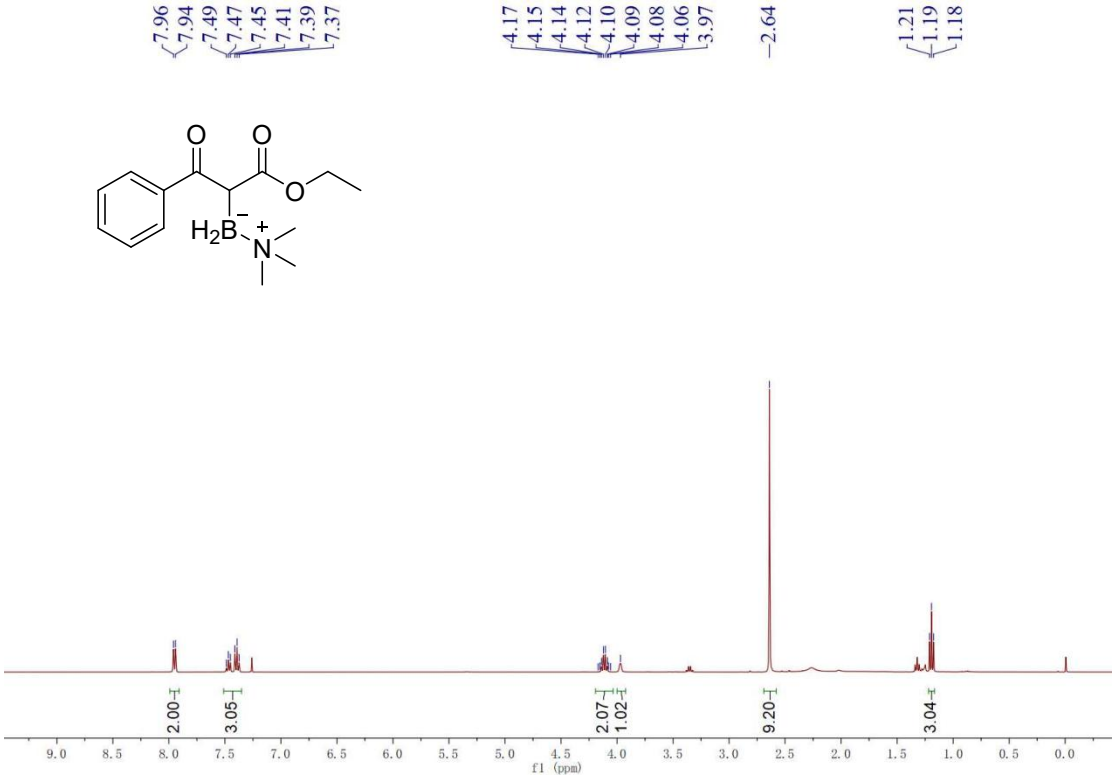


^{11}B NMR of diphenethyl 2-boranylmalonate-pyridine complex (3l)

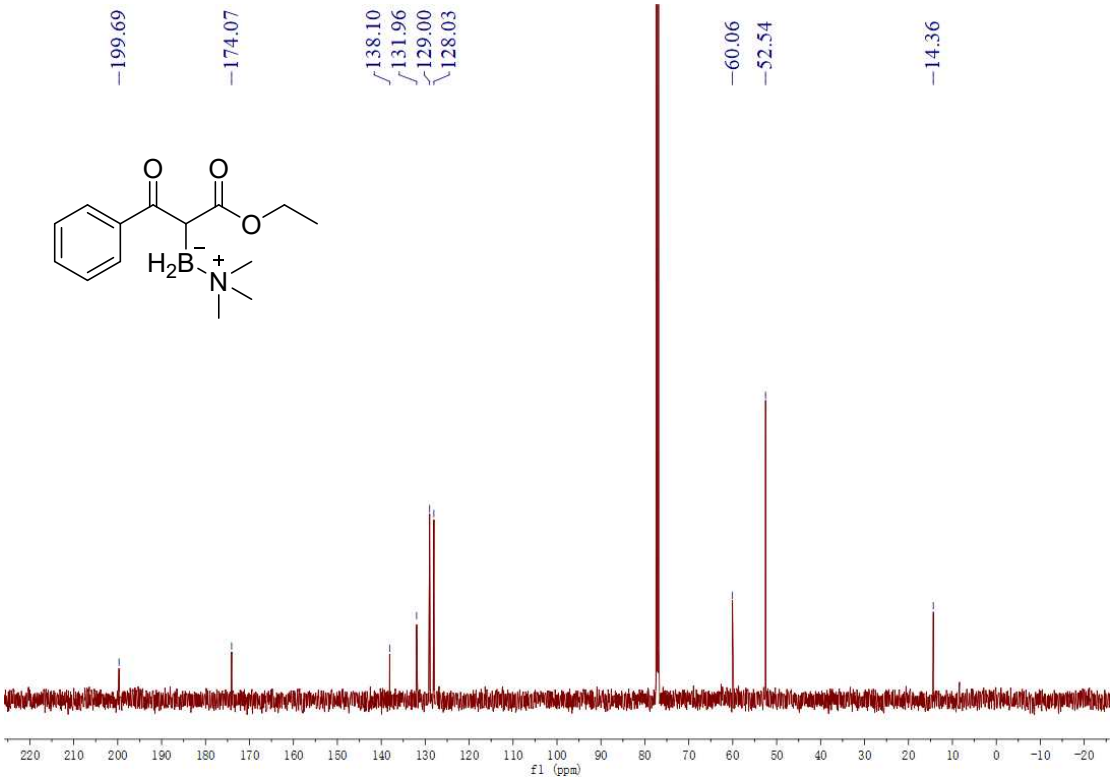


^{1}H NMR of ethyl 2-boranyl-3-oxo-3-phenylpropanoate-trimethylamine complex

(3m)

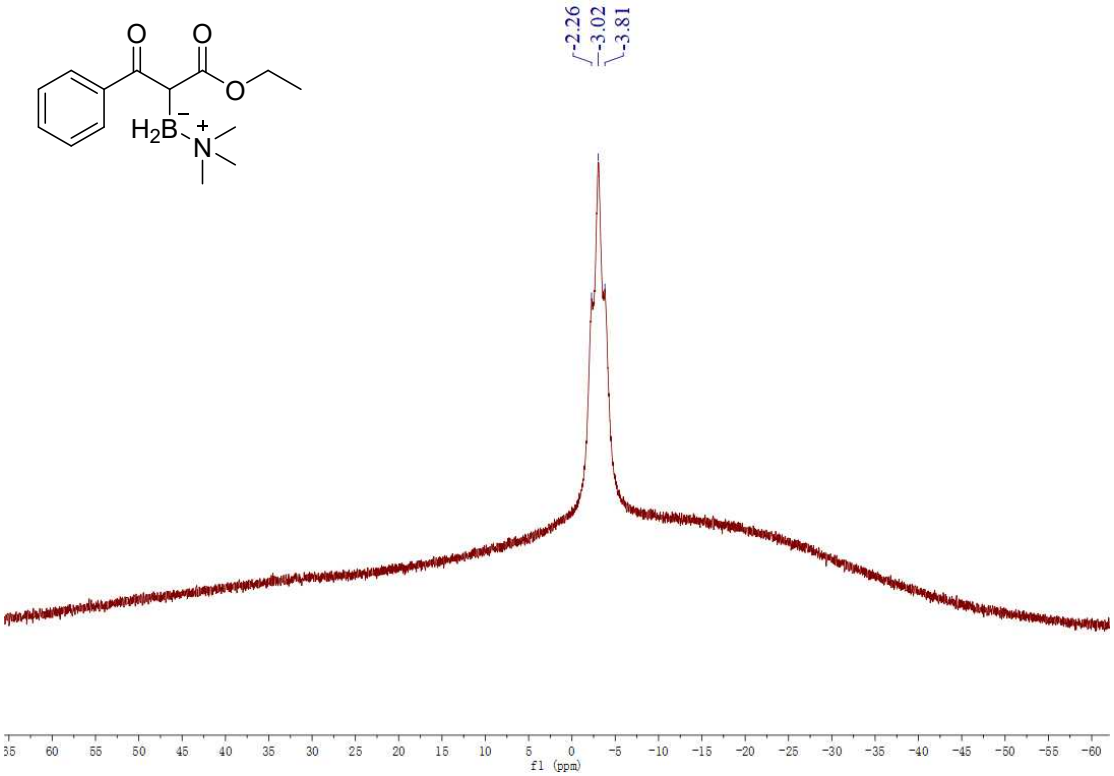


^{13}C NMR of ethyl 2-boranyl-3-oxo-3-phenylpropanoate-trimethylamine complex (3m)

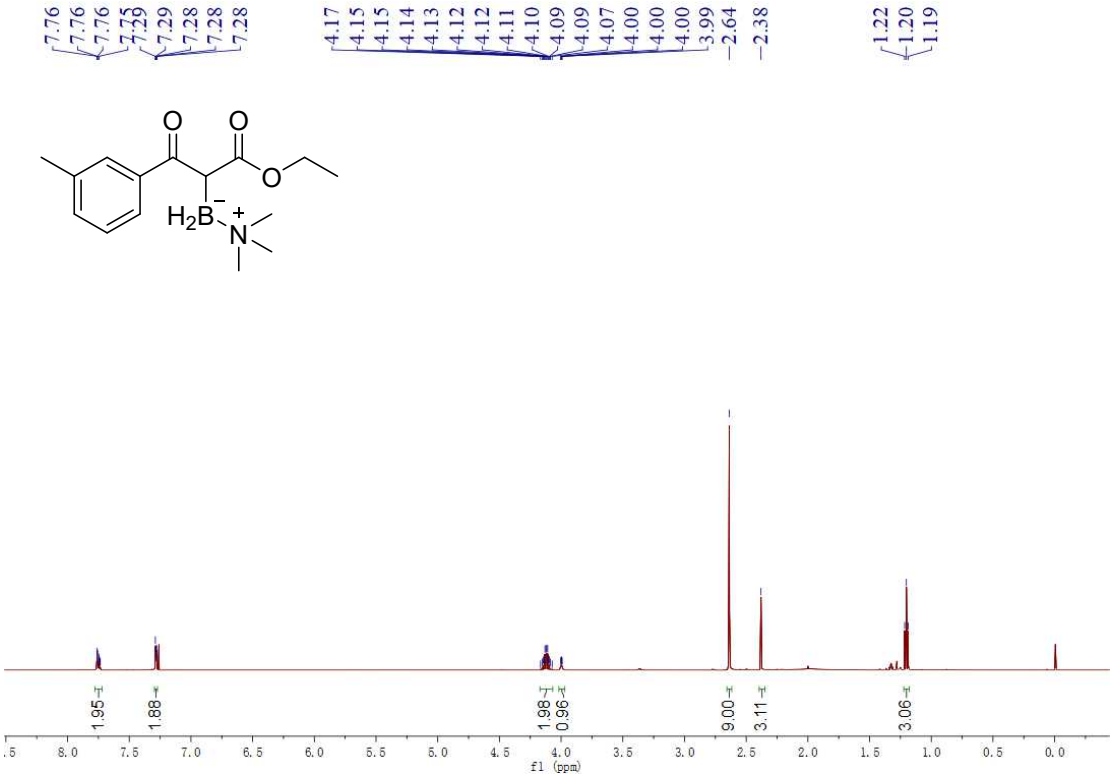


^{11}B NMR of ethyl 2-boranyl-3-oxo-3-phenylpropanoate-trimethylamine complex

(3m)

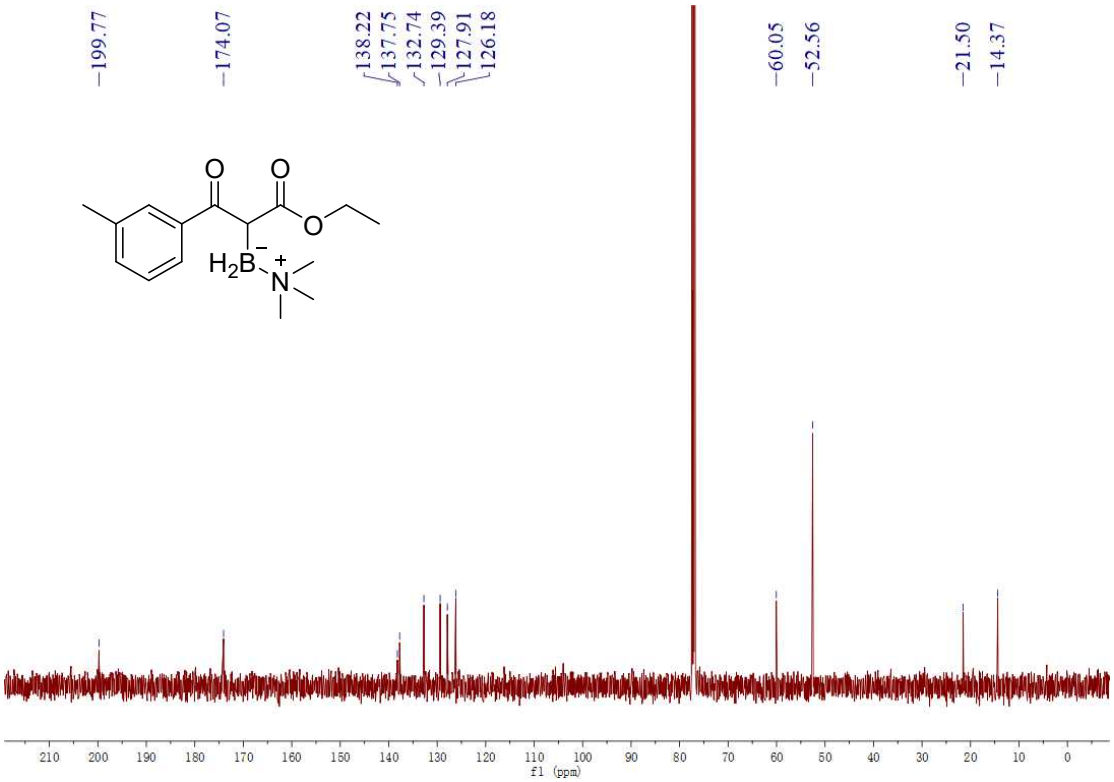


^{1}H NMR of ethyl 2-boranyl-3-oxo-3-(m-tolyl)propanoate-trimethylamine complex (3n)

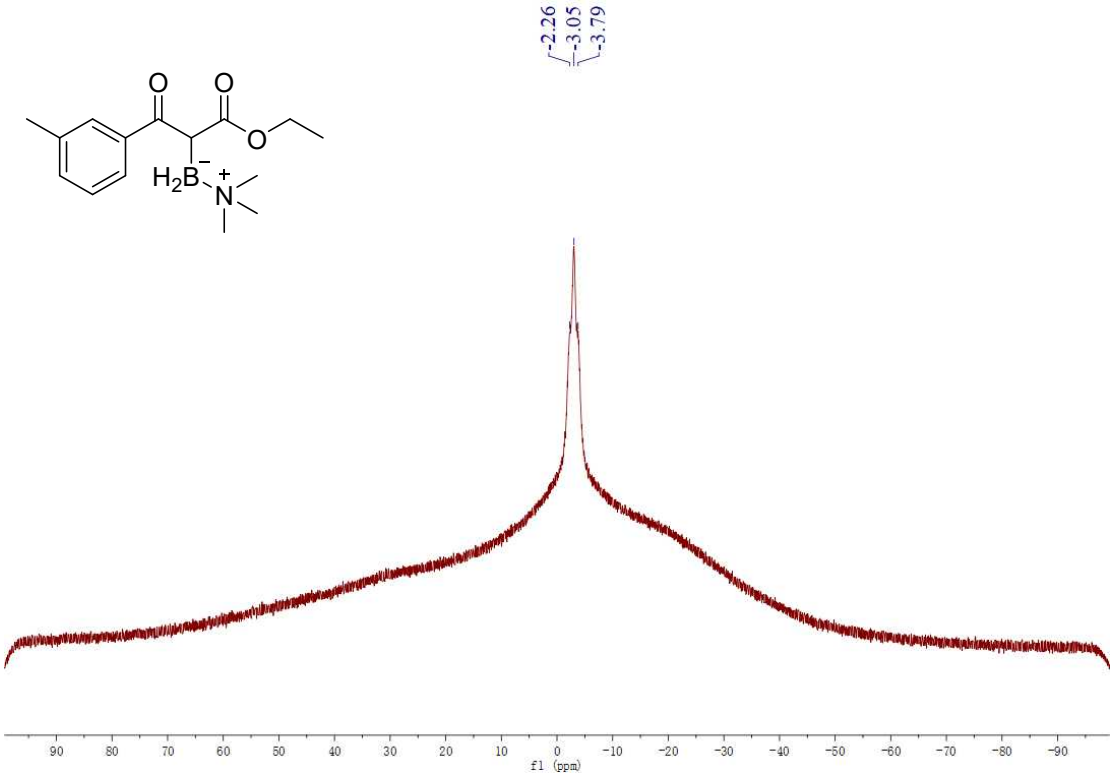


^{13}C NMR of ethyl 2-boranyl-3-oxo-3-(m-tolyl)propanoate-trimethylamine

complex (3n)

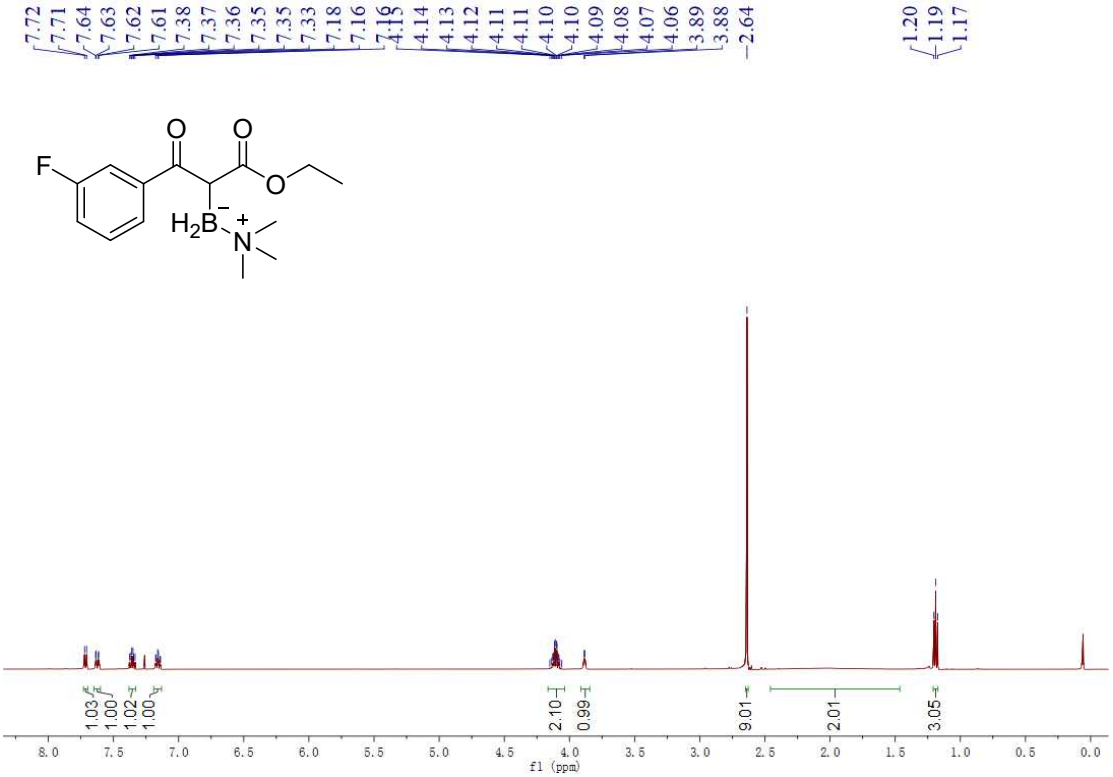


^{11}B NMR of ethyl 2-boranyl-3-oxo-3-(m-tolyl)propanoate-trimethylamine complex (3n)

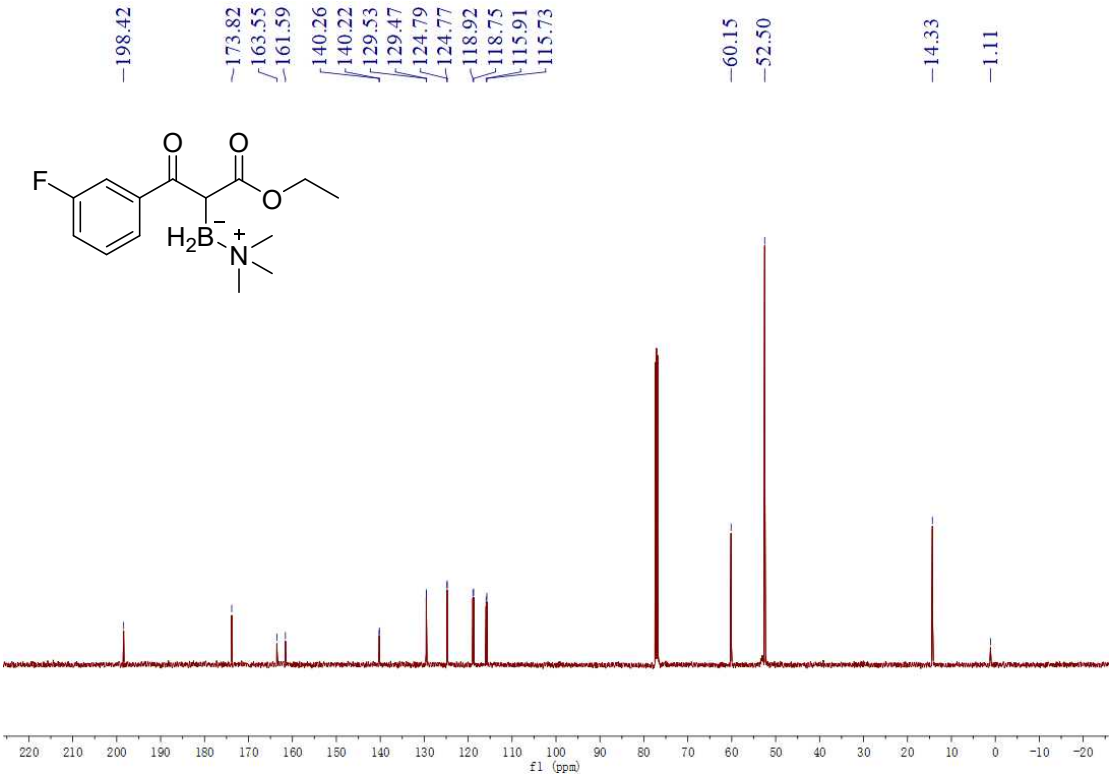


^{1}H NMR of ethyl 2-boranyl-3-(3-fluorophenyl)-3-oxopropanoate-trimethylamine

complex (3o)

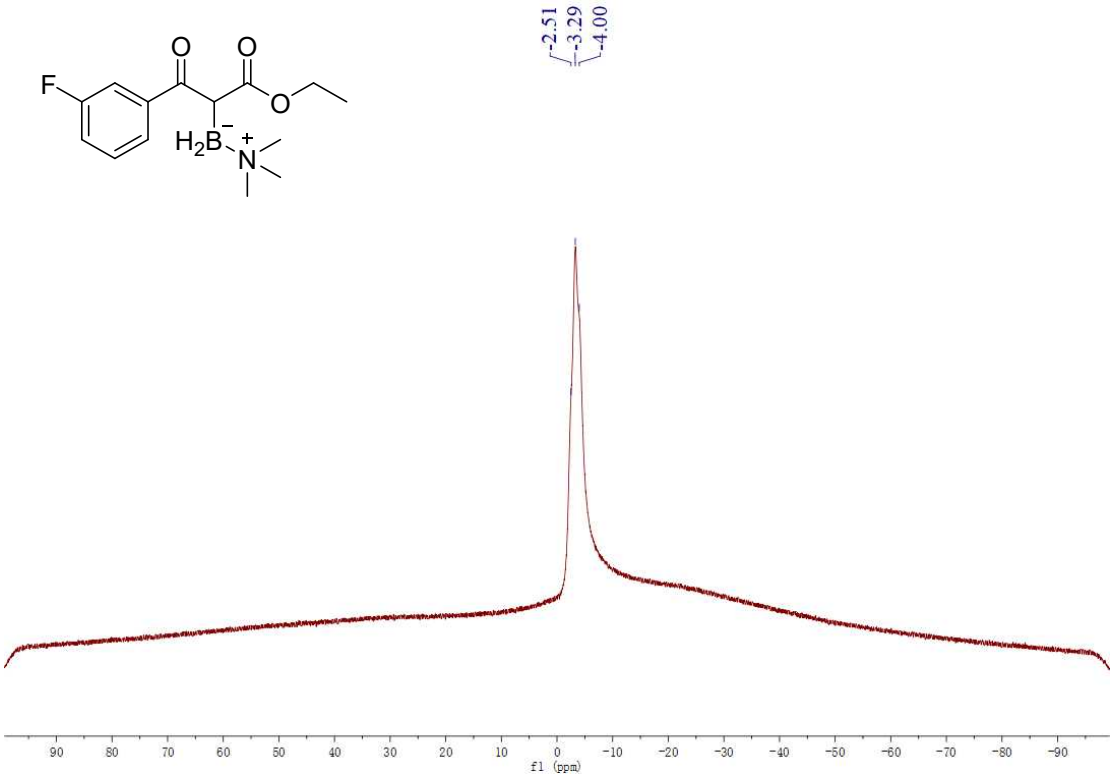


^{13}C NMR of ethyl 2-boranyl-3-(3-fluorophenyl)-3-oxopropanoate-trimethylamine complex (3o)

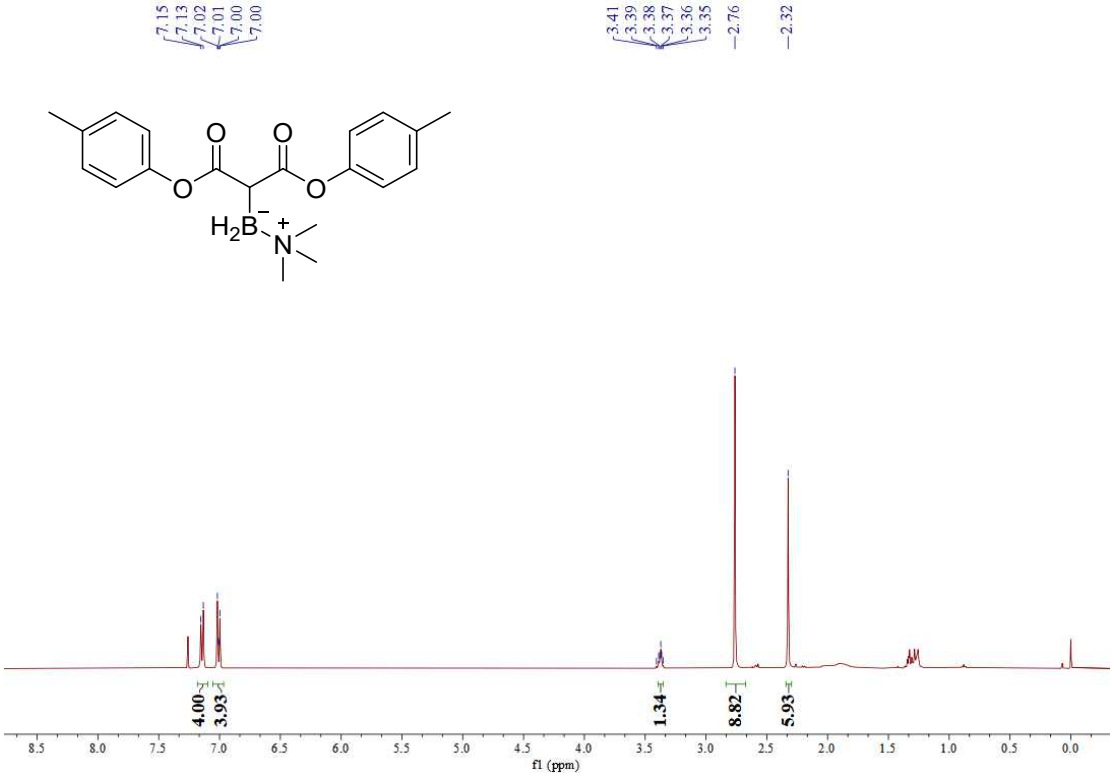


^{11}B NMR of ethyl 2-boranyl-3-(3-fluorophenyl)-3-oxopropanoate-trimethylamine

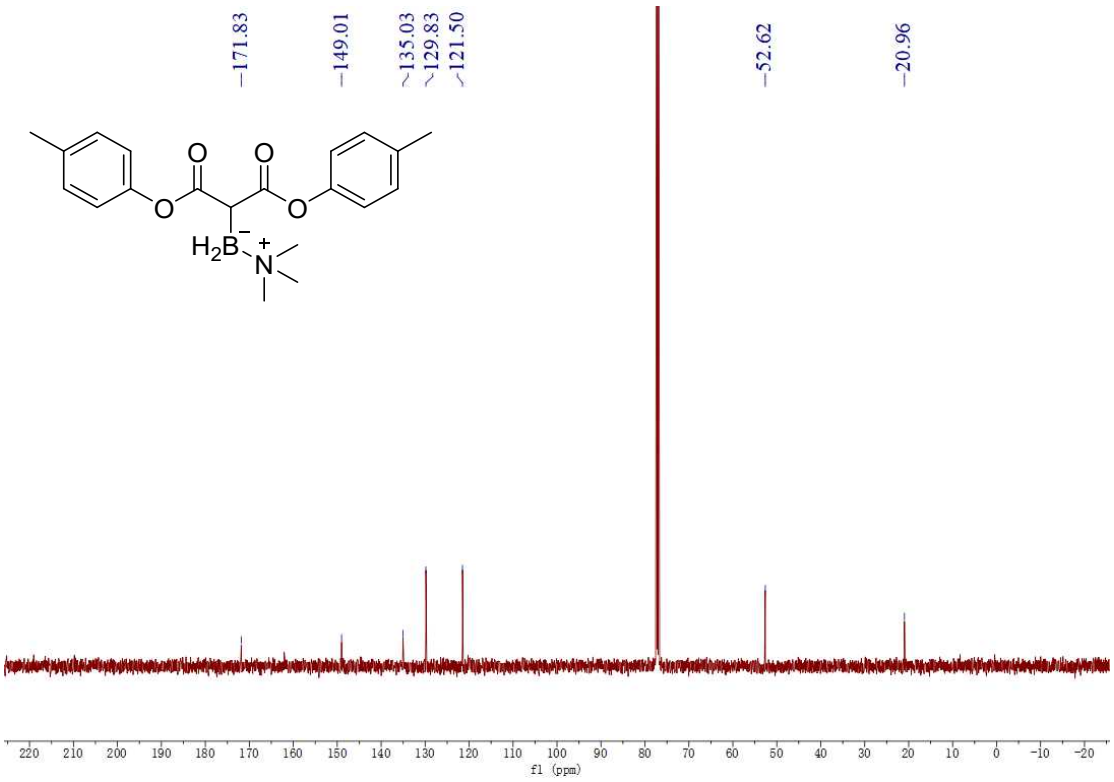
complex (3o)



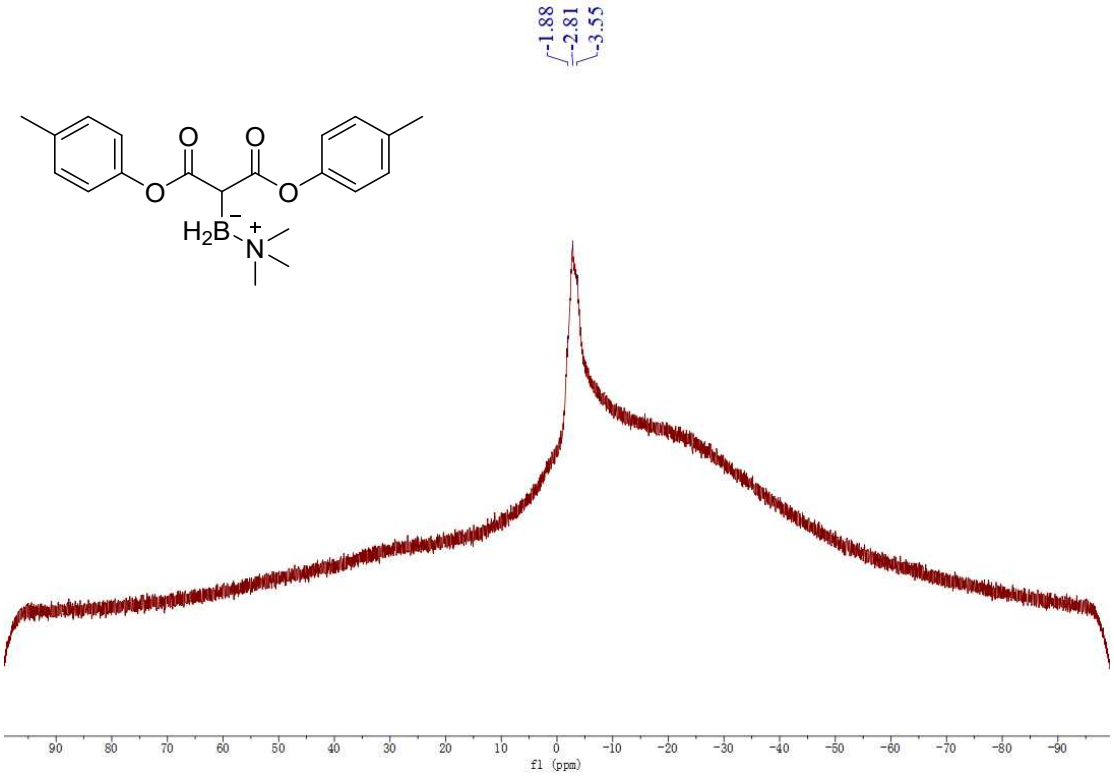
^{1}H NMR of di-p-tolyl 2-boranylmalonate-trimethylamine complex (3p)



^{13}C NMR of di-p-tolyl 2-boranylmalonate-trimethylamine complex (3p)

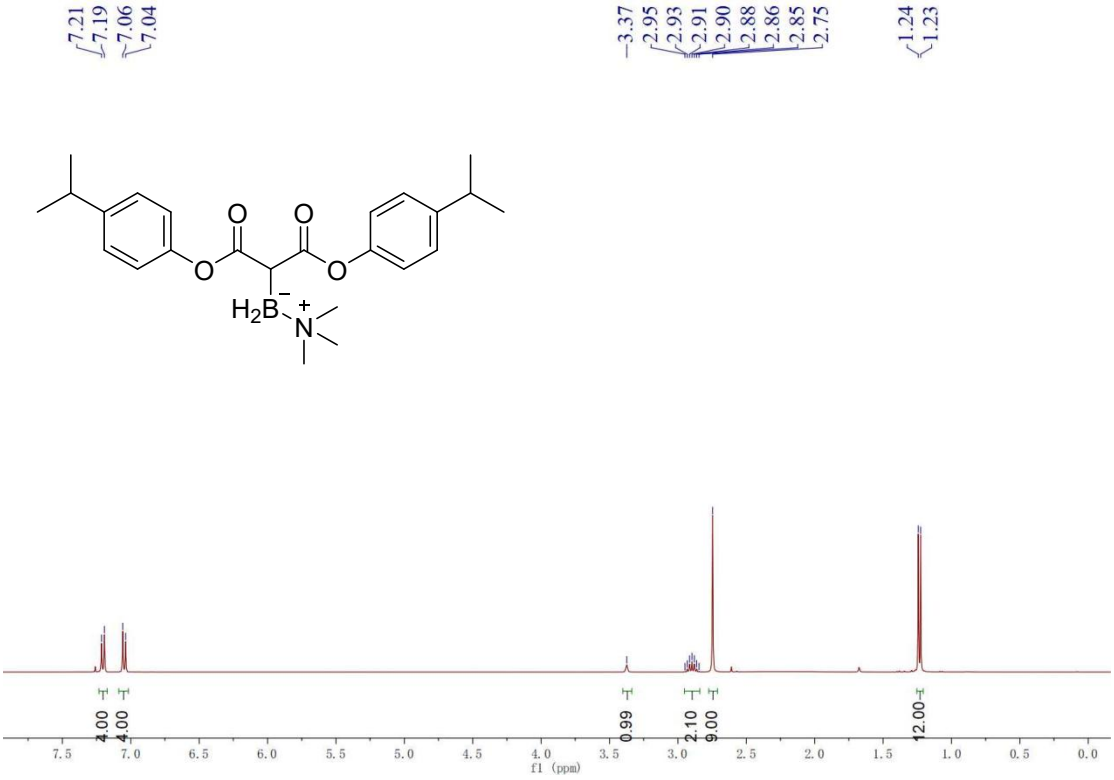


^{11}B NMR of di-p-tolyl 2-boranylmalonate-trimethylamine complex (3p)

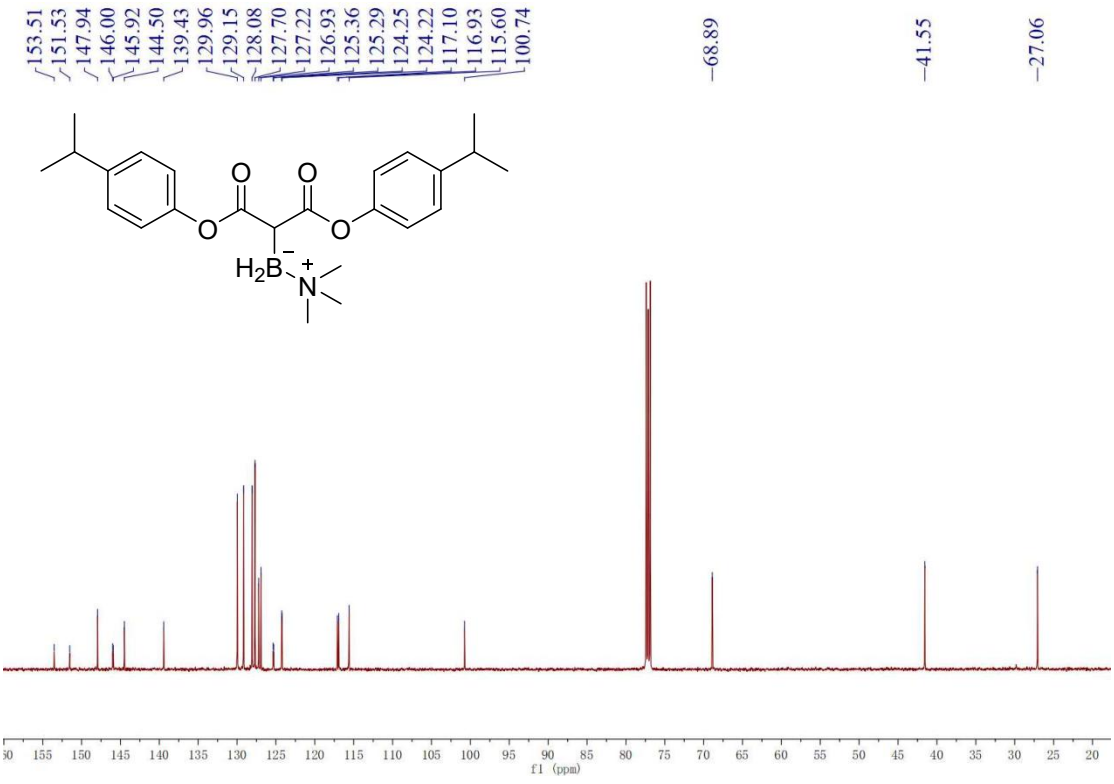


^{1}H NMR of bis(4-isopropylphenyl) 2-boranylmalonate-trimethylamine complex

(3q)

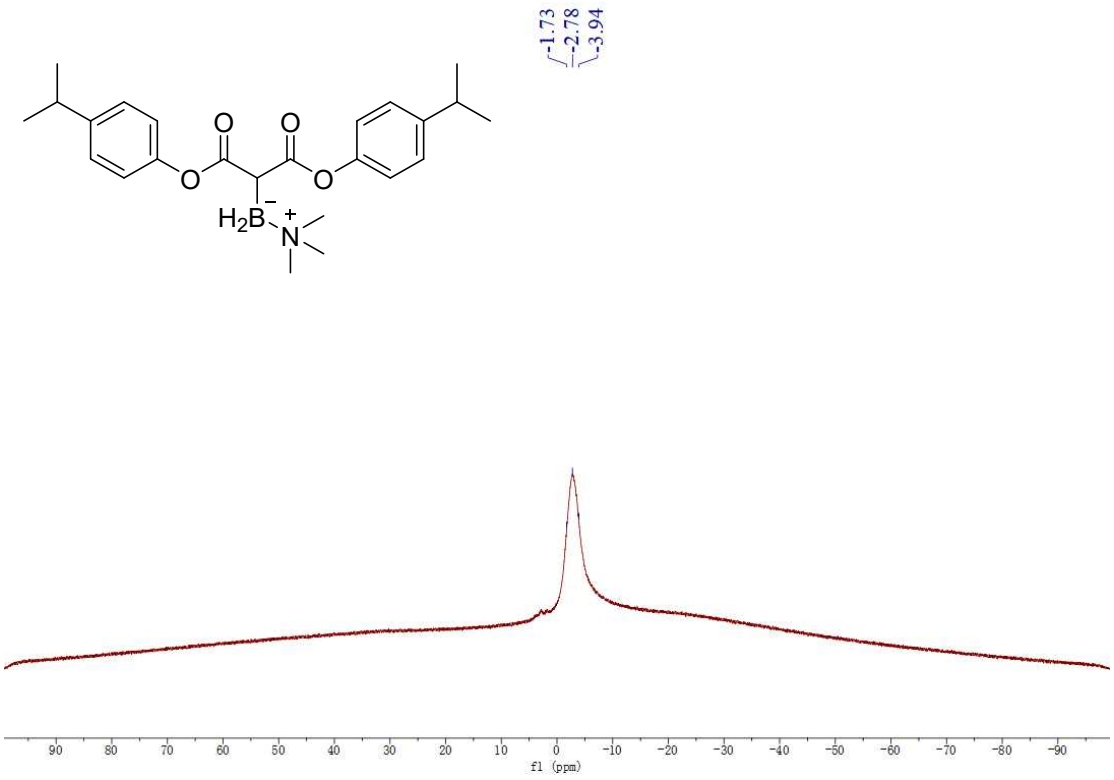


^{13}C NMR of bis(4-isopropylphenyl) 2-boranylmalonate-trimethylamine complex (3q)

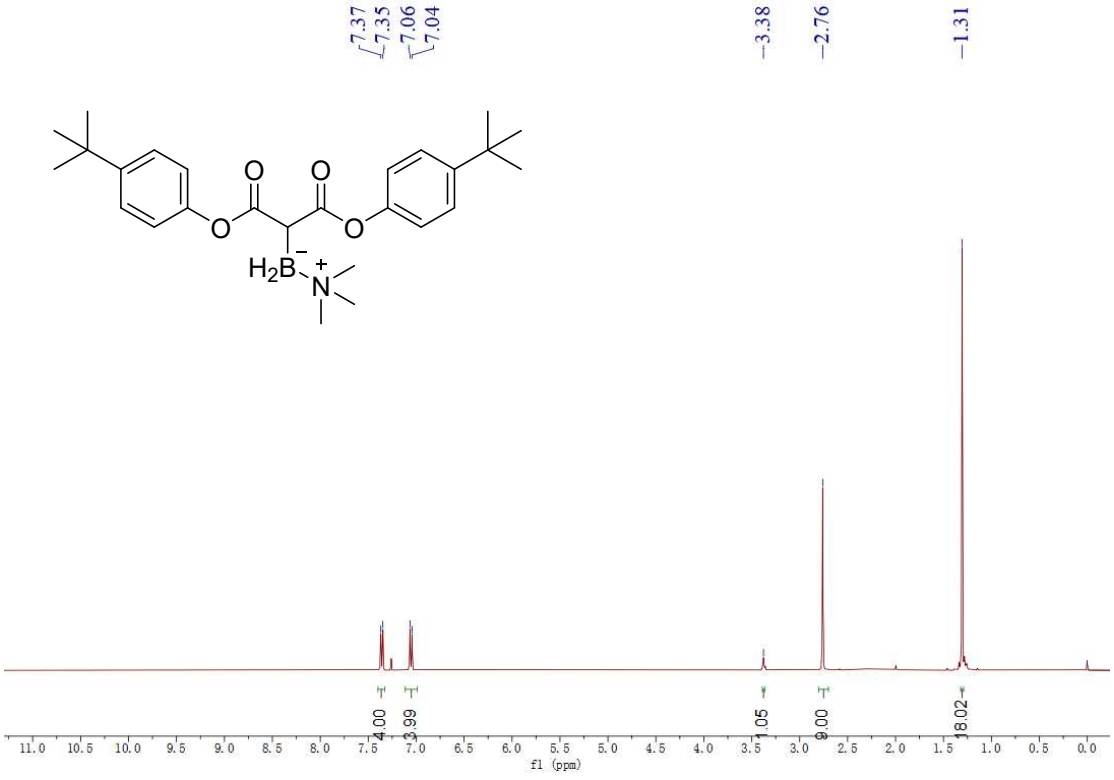


^{11}B NMR of bis(4-isopropylphenyl) 2-boranylmalonate-trimethylamine complex

(3q)

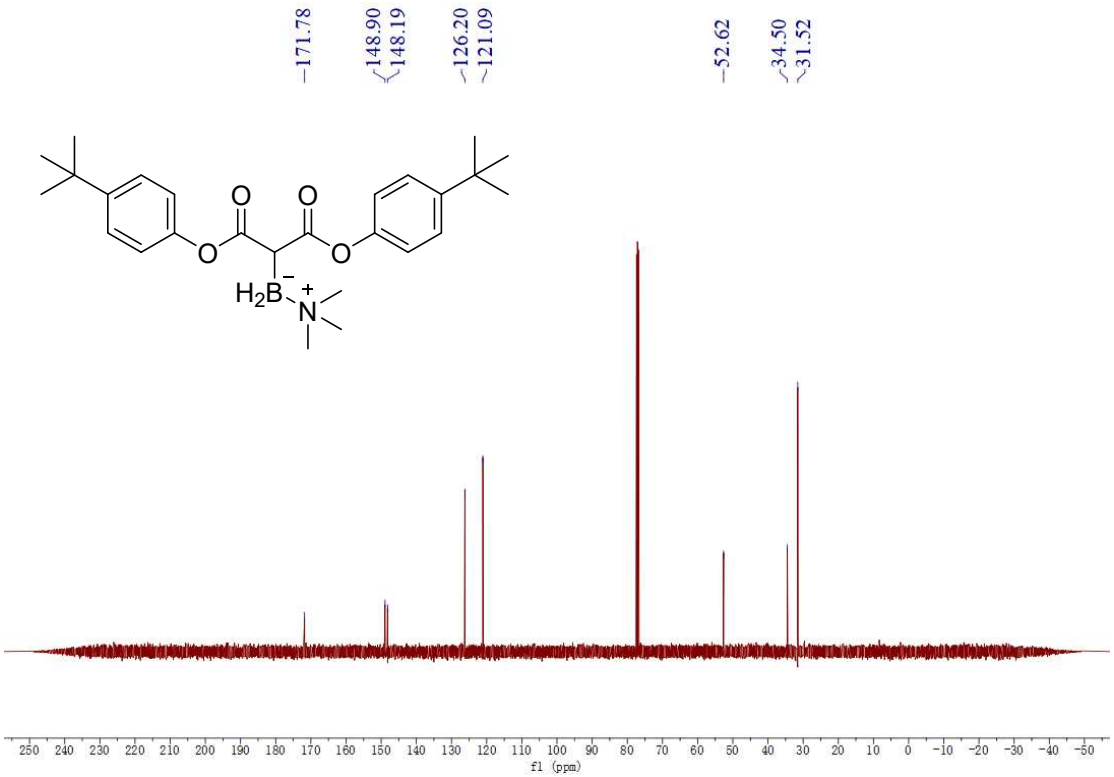


^{1}H NMR of bis(4-(tert-butyl)phenyl) 2-boranylmalonate-trimethylamine complex (3r)

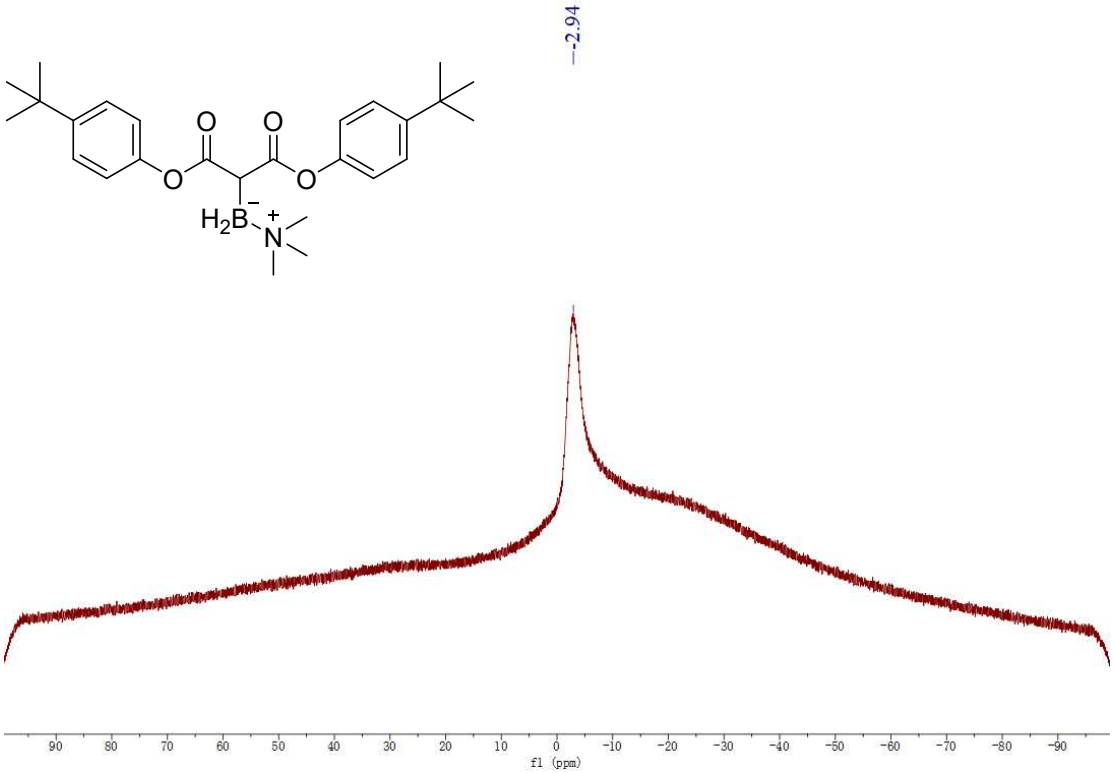


^{13}C NMR of bis(4-(tert-butyl)phenyl) 2-boranylmalonate-trimethylamine complex

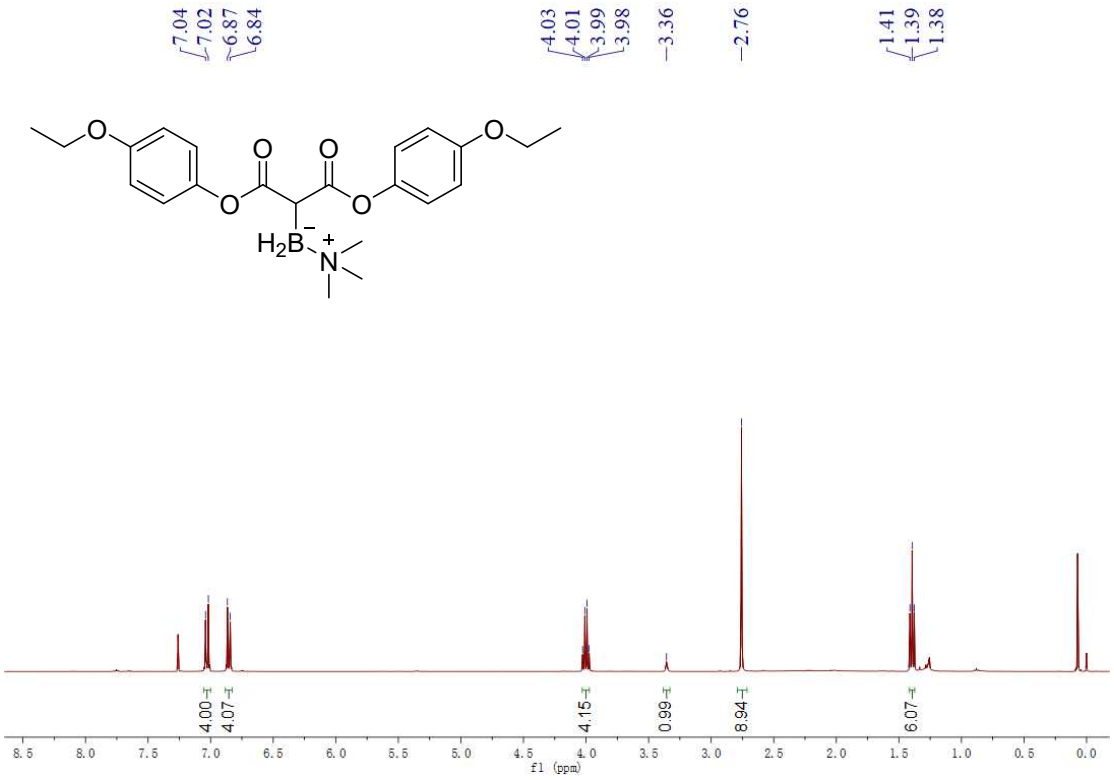
(3r)



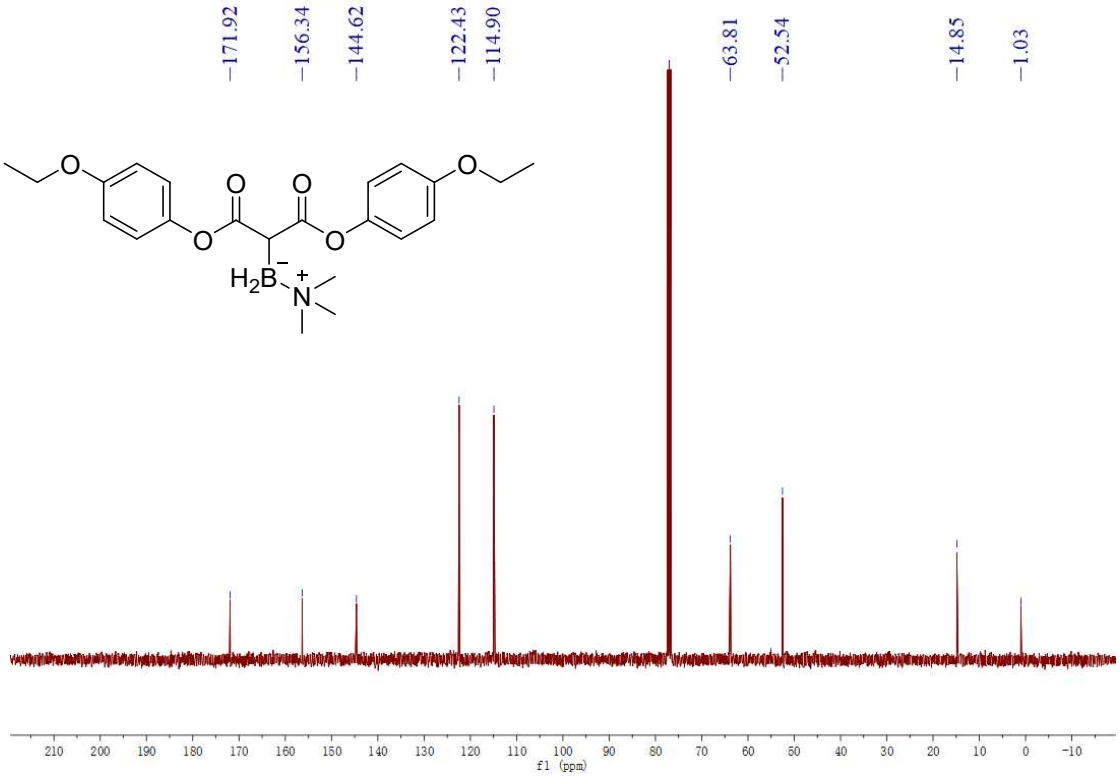
^{11}B NMR of bis(4-(tert-butyl)phenyl) 2-boranylmalonate-trimethylamine complex (3r)



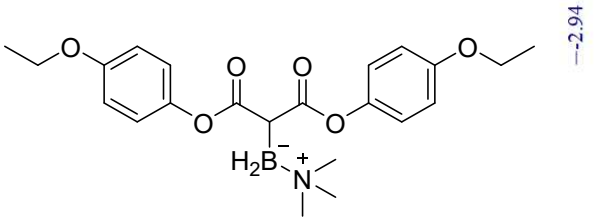
^{1}H NMR of bis(4-ethoxyphenyl) 2-boranylmalonate-trimethylamine complex (3s)



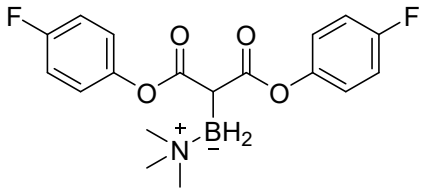
^{13}C NMR of bis(4-ethoxyphenyl) 2-boranylmalonate-trimethylamine complex (3s)

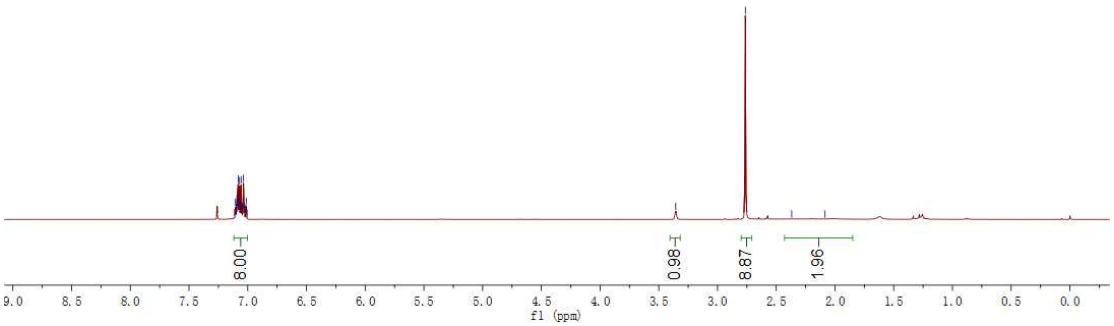


^{11}B NMR of bis(4-ethoxyphenyl) 2-boranylmalonate-trimethylamine complex (3s)

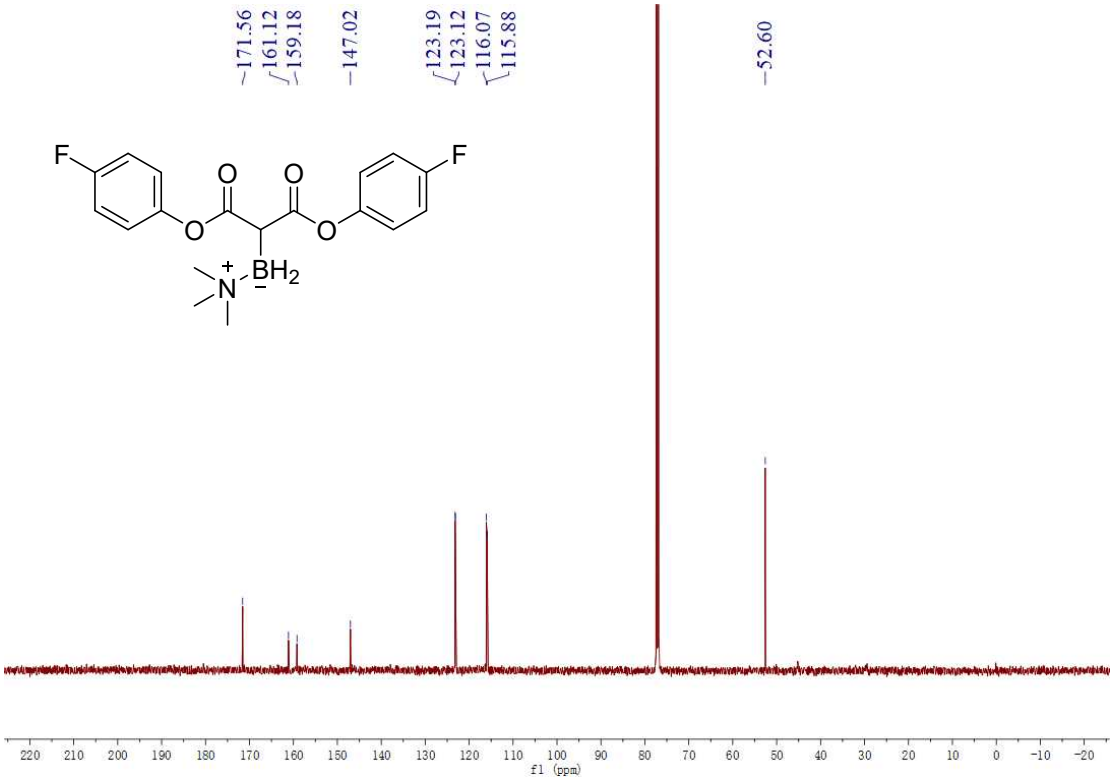


^{1}H NMR of bis(4-fluorophenyl) 2-boranylmalonate-trimethylamine complex (3t)

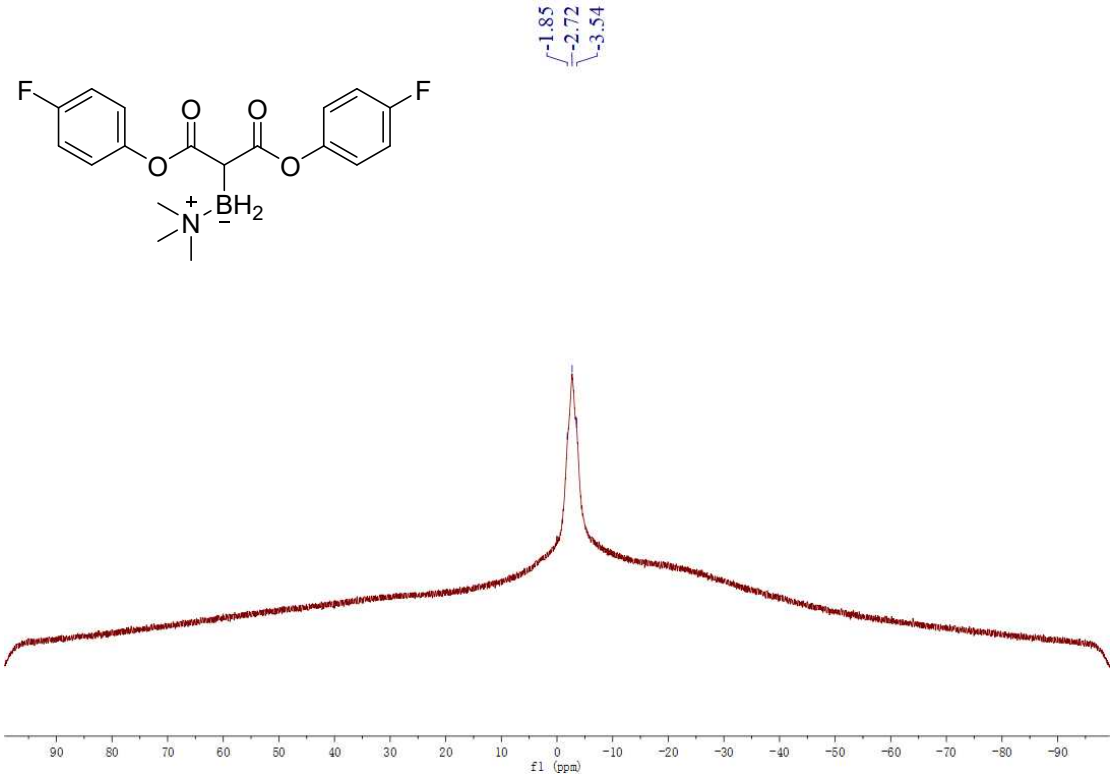




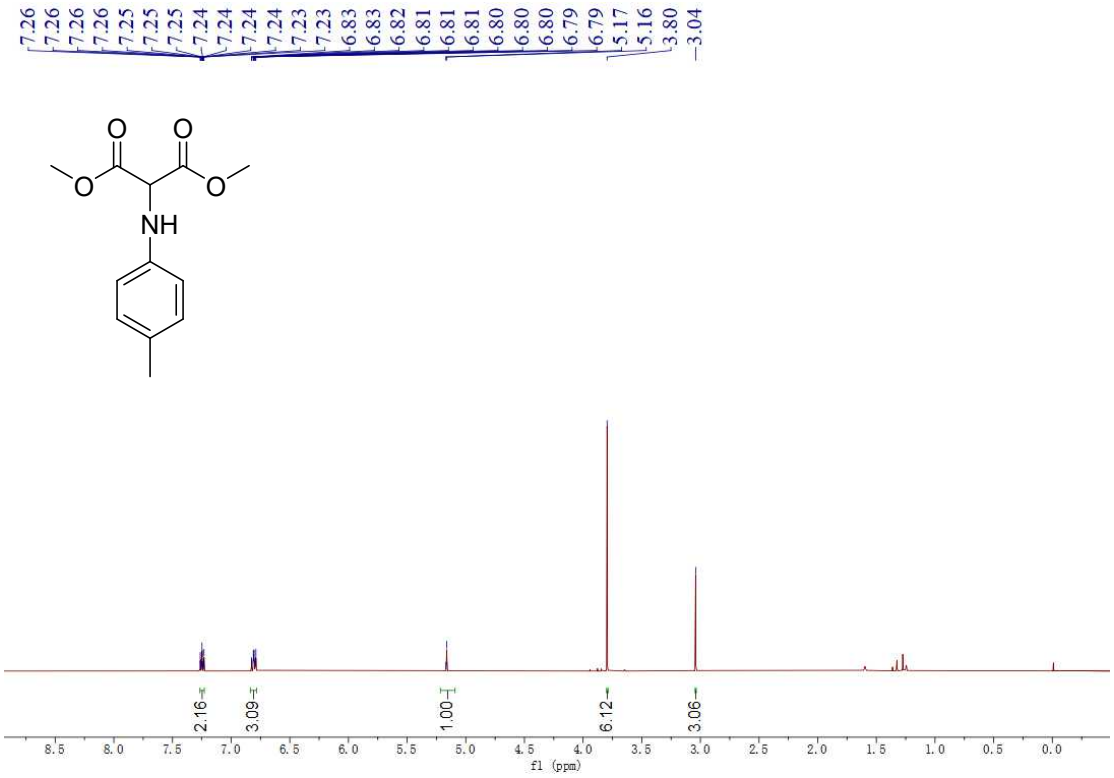
^{13}C NMR of bis(4-fluorophenyl) 2-boranylmalonate-trimethylamine complex (3t)



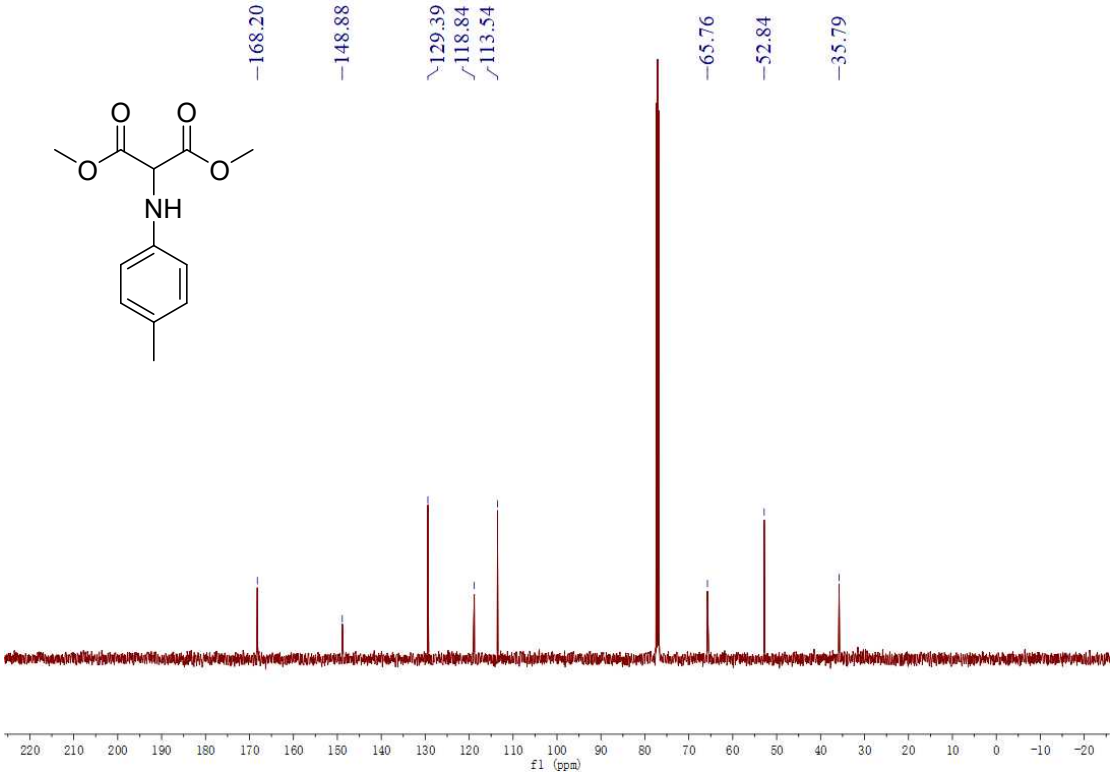
^{11}B NMR of bis(4-fluorophenyl) 2-boranylmalonate-trimethylamine complex (3t)



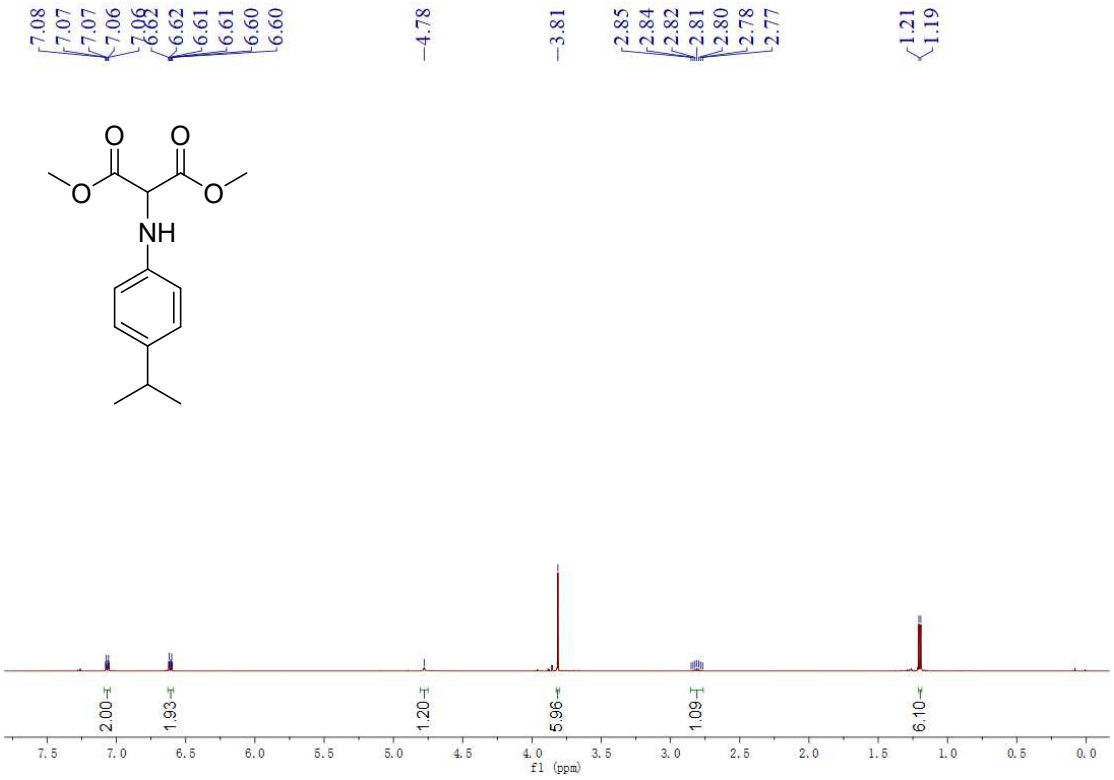
^{1}H NMR of dimethyl 2-(p-tolylamino)malonate (5a)



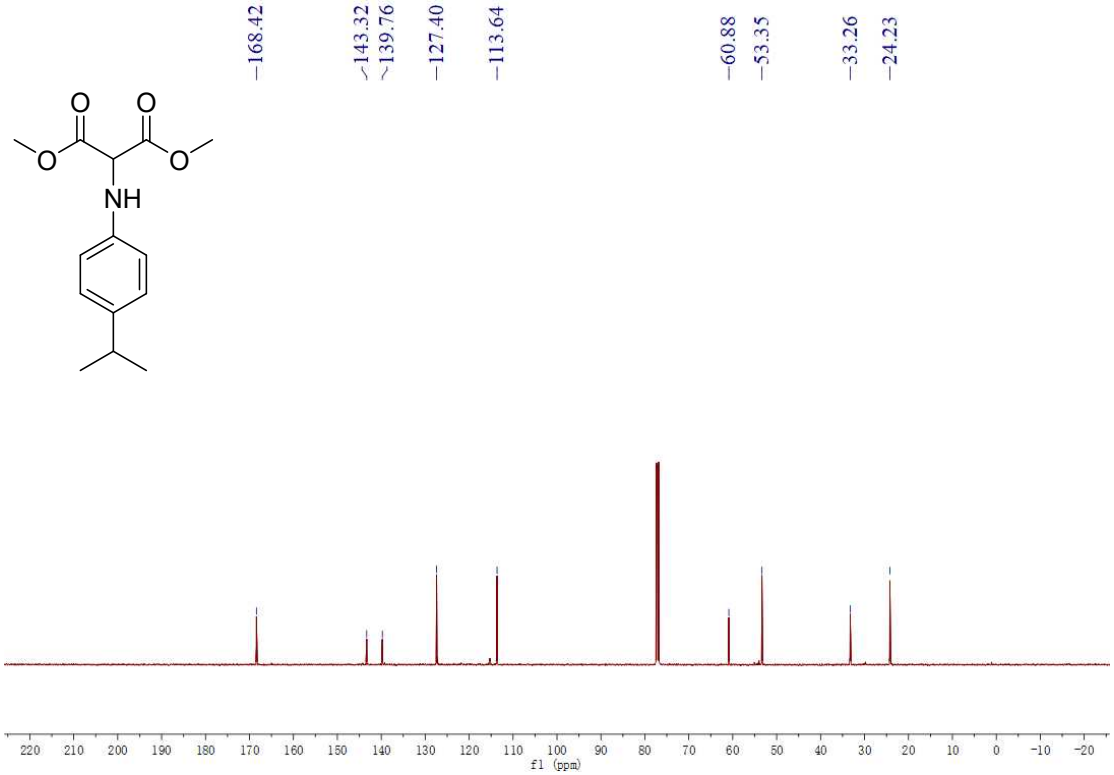
^{13}C NMR of dimethyl 2-(p-tolylamino)malonate (5a)



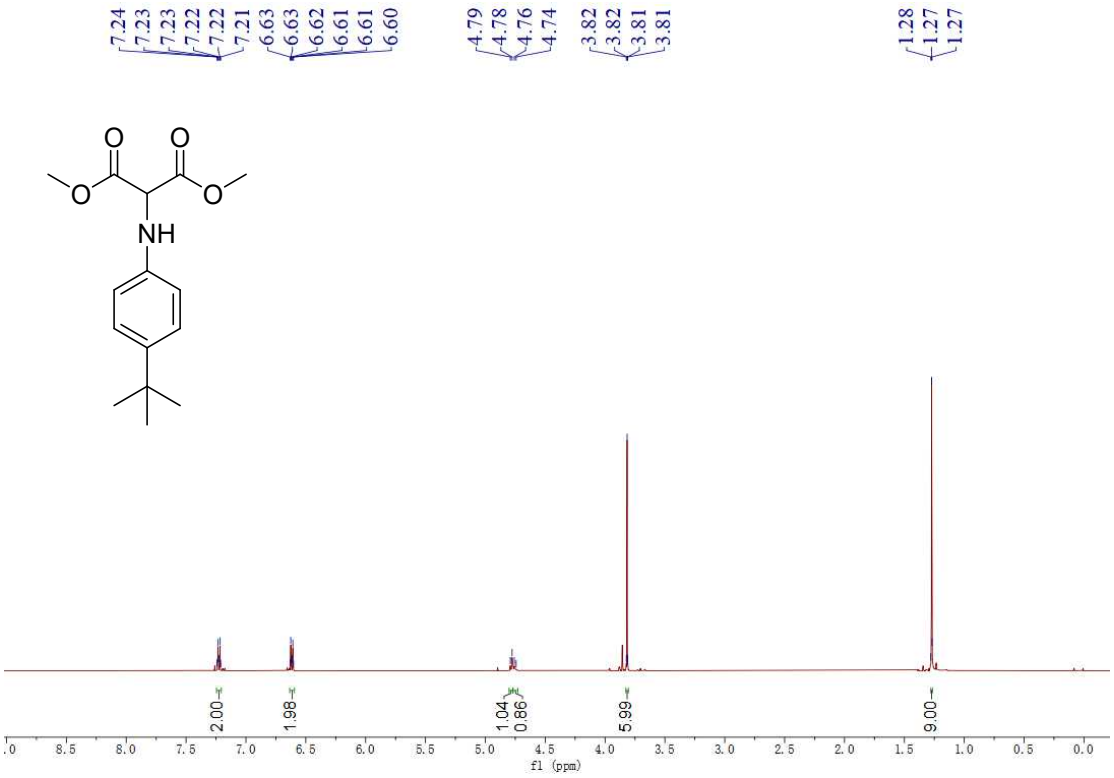
^{1}H NMR of dimethyl 2-((4-isopropylphenyl)amino)malonate (5b)



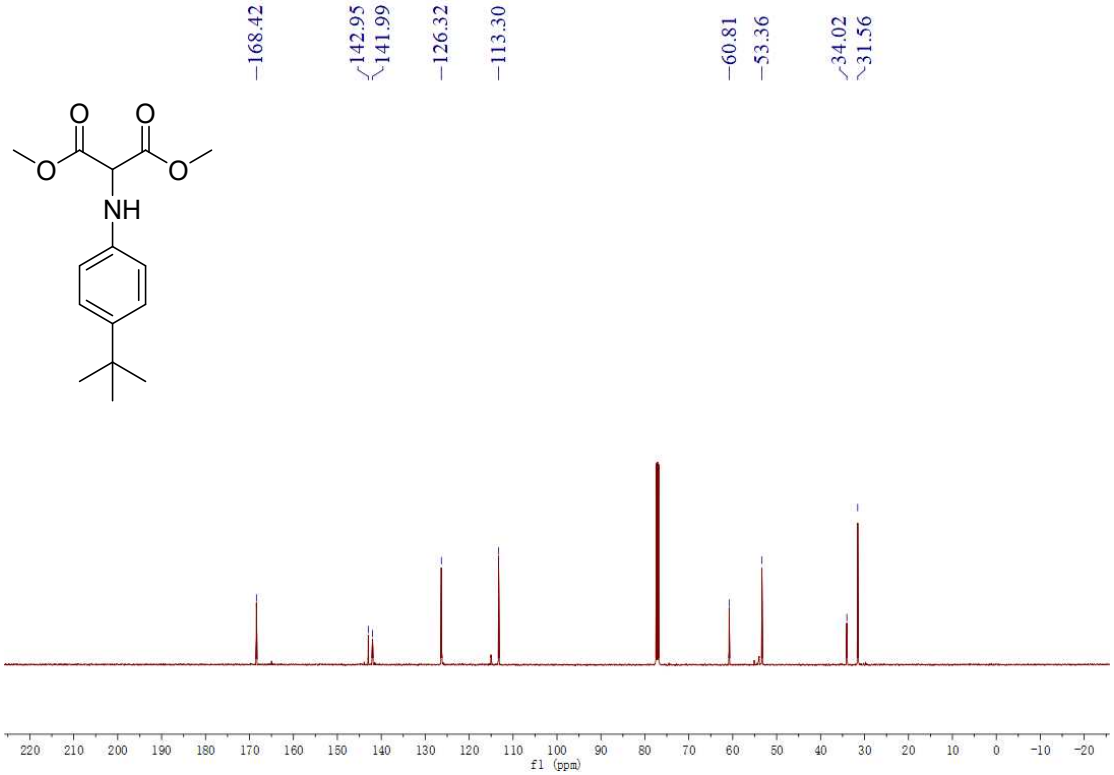
^{13}C NMR of dimethyl 2-((4-isopropylphenyl)amino)malonate (5b)



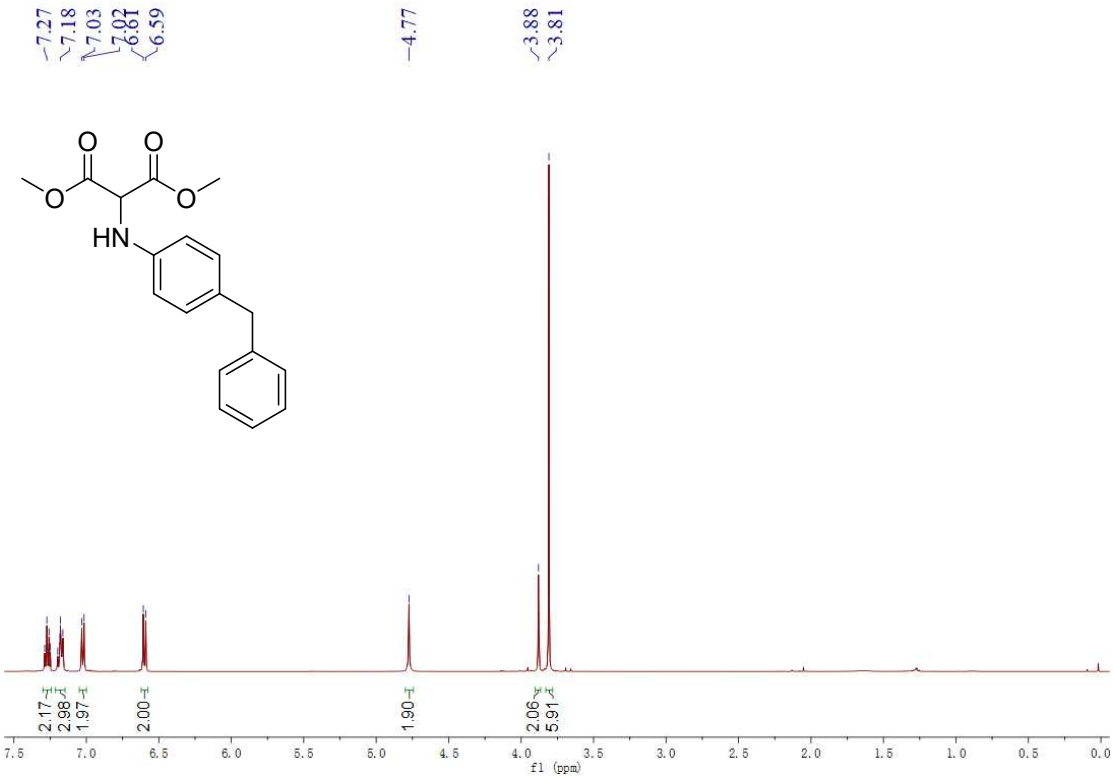
^{1}H NMR of dimethyl 2-((4-(tert-butyl)phenyl)amino)malonate (5c)



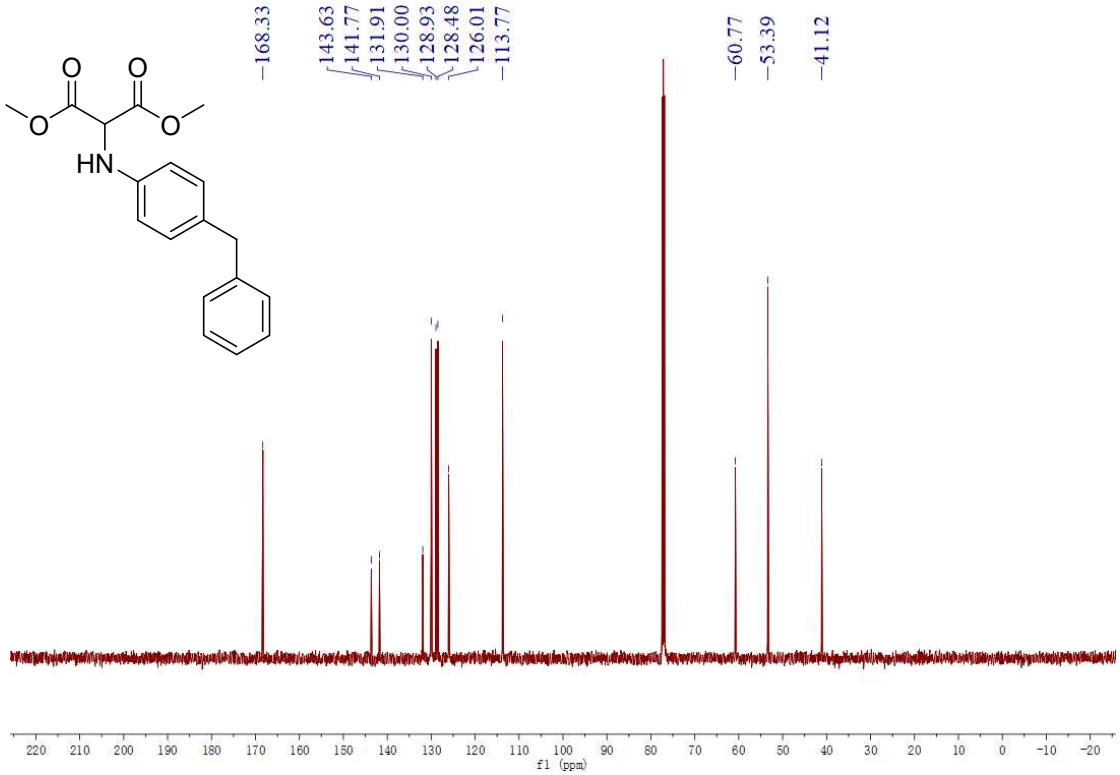
^{13}C NMR of dimethyl 2-((4-(tert-butyl)phenyl)amino)malonate (5c)



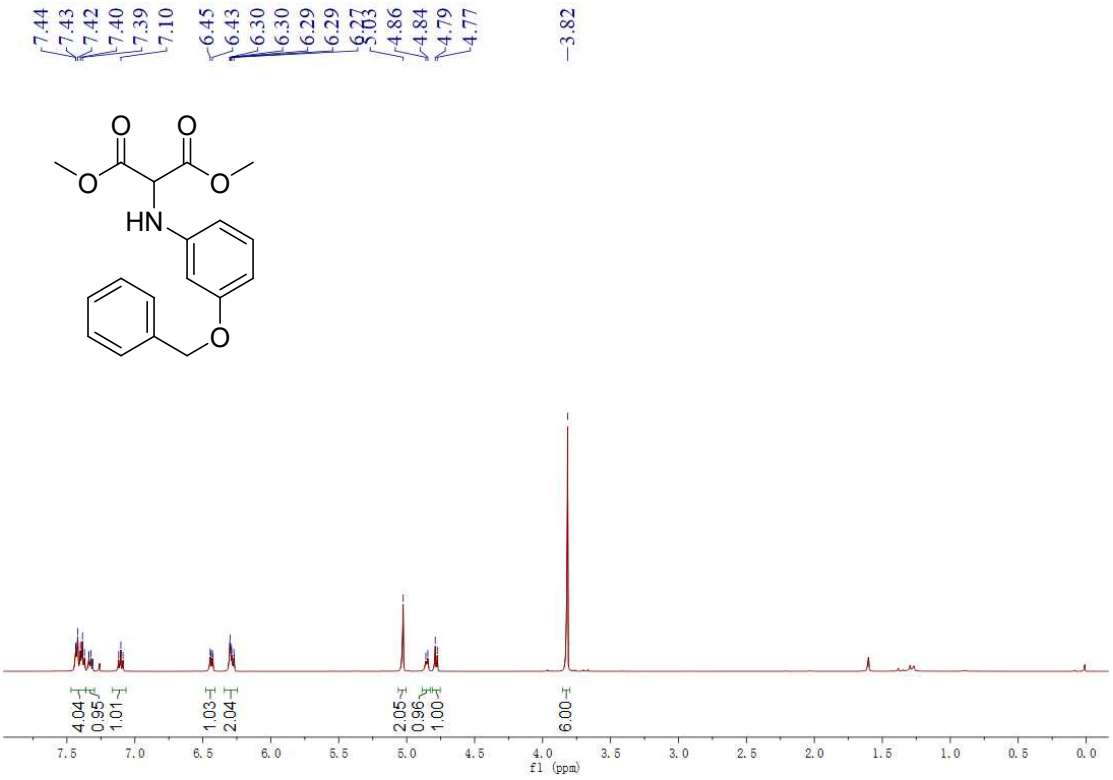
^{1}H NMR of dimethyl 2-((4-benzylphenyl)amino)malonate (5d)



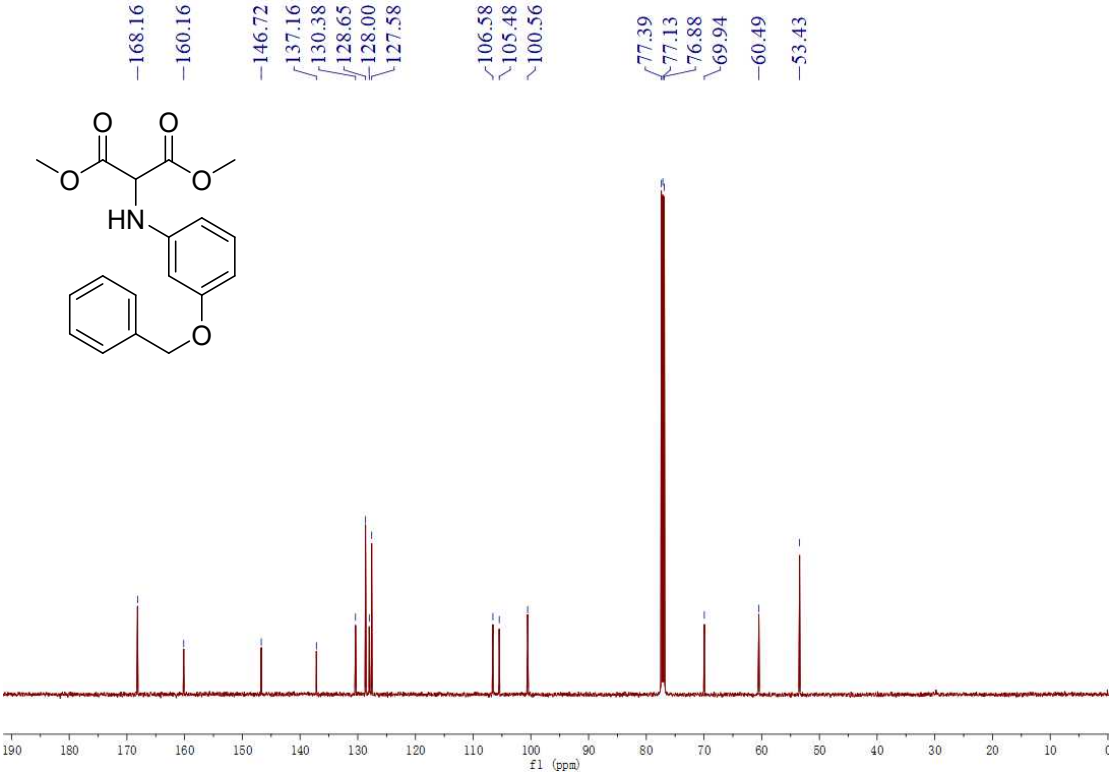
^{13}C NMR of dimethyl 2-((4-benzylphenyl)amino)malonate (5d)



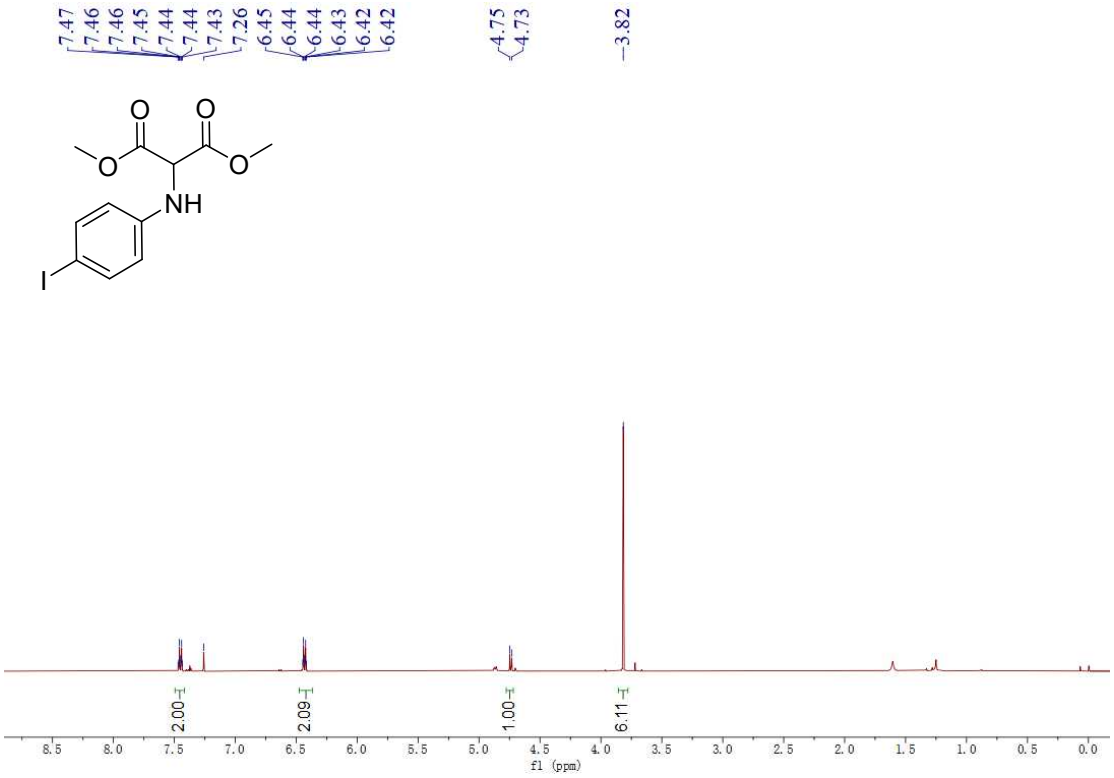
^{1}H NMR of dimethyl 2-((3-(benzyloxy)phenyl)amino)malonate (5e)



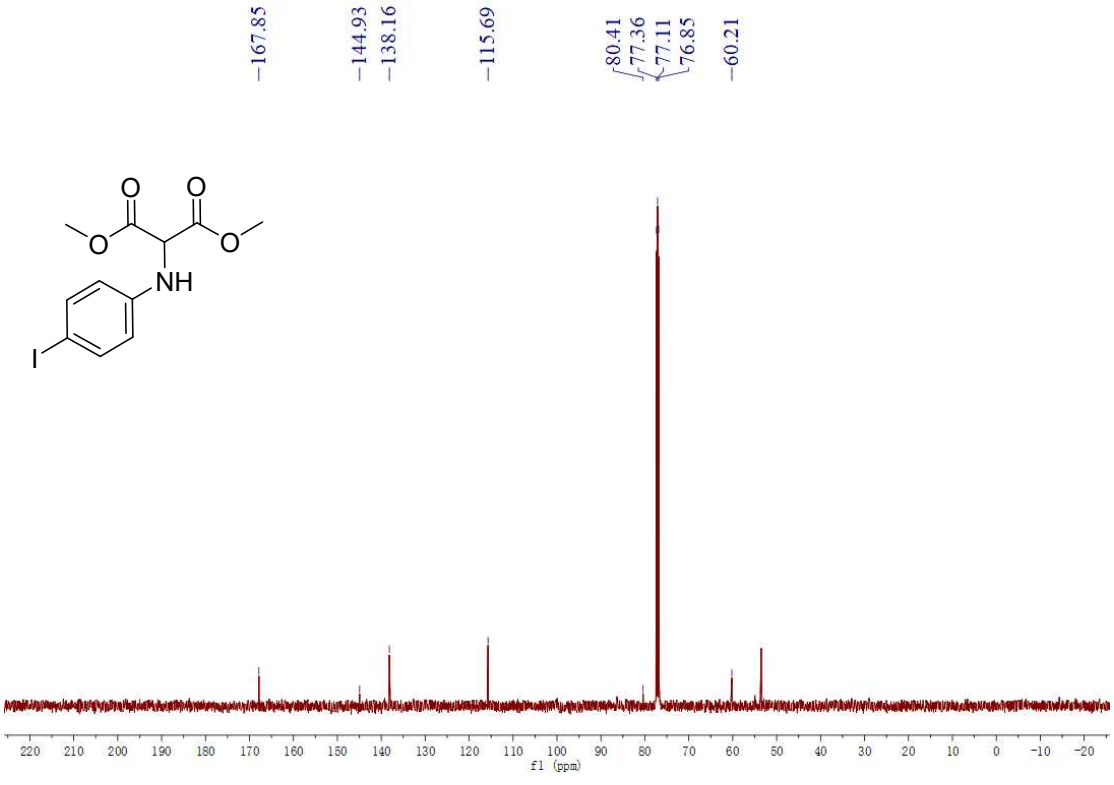
^{13}C NMR of dimethyl 2-((3-(benzyloxy)phenyl)amino)malonate (5e)



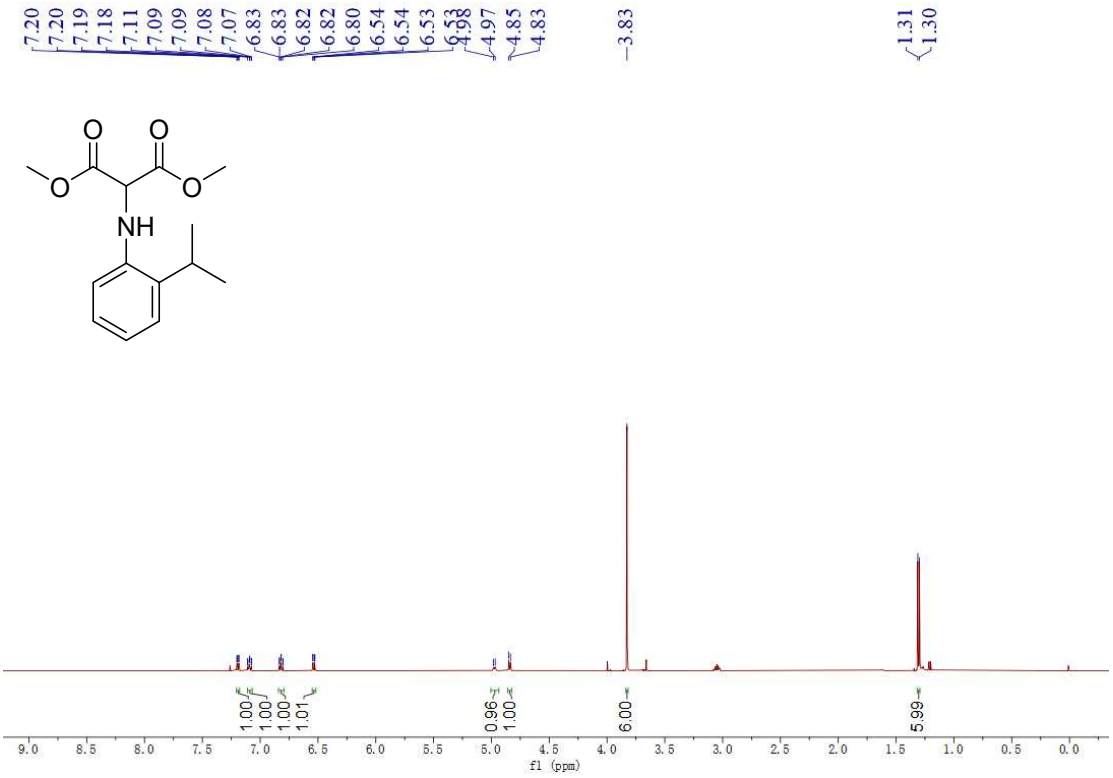
^{1}H NMR of dimethyl 2-((4-iodophenyl)amino)malonate (5f)



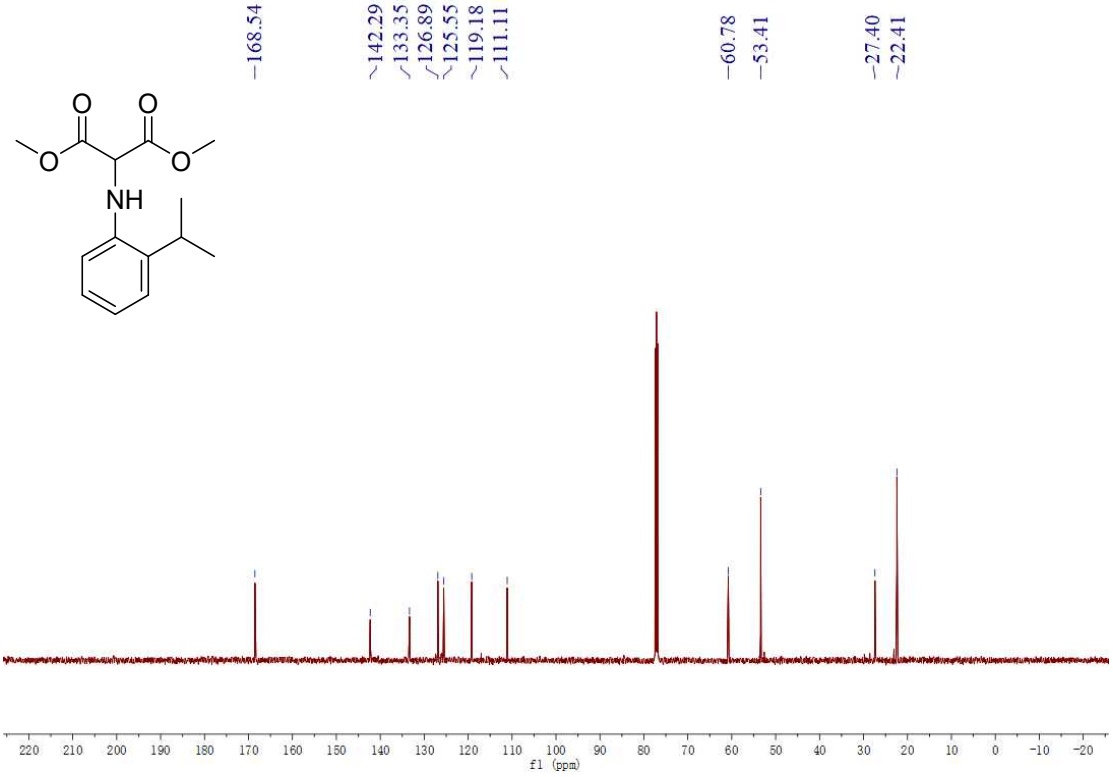
^{13}C NMR of dimethyl 2-((4-iodophenyl)amino)malonate (5f)



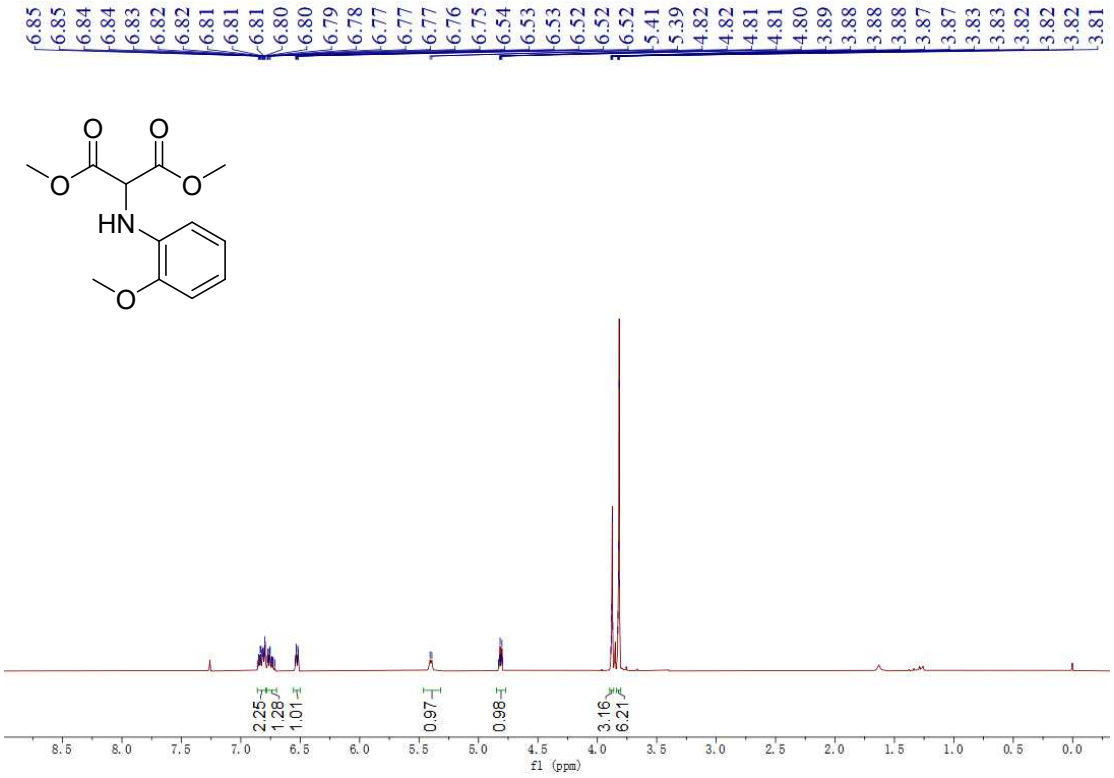
^{1}H NMR of ethyl dimethyl 2-((2-isopropylphenyl)amino)malonate (5g)



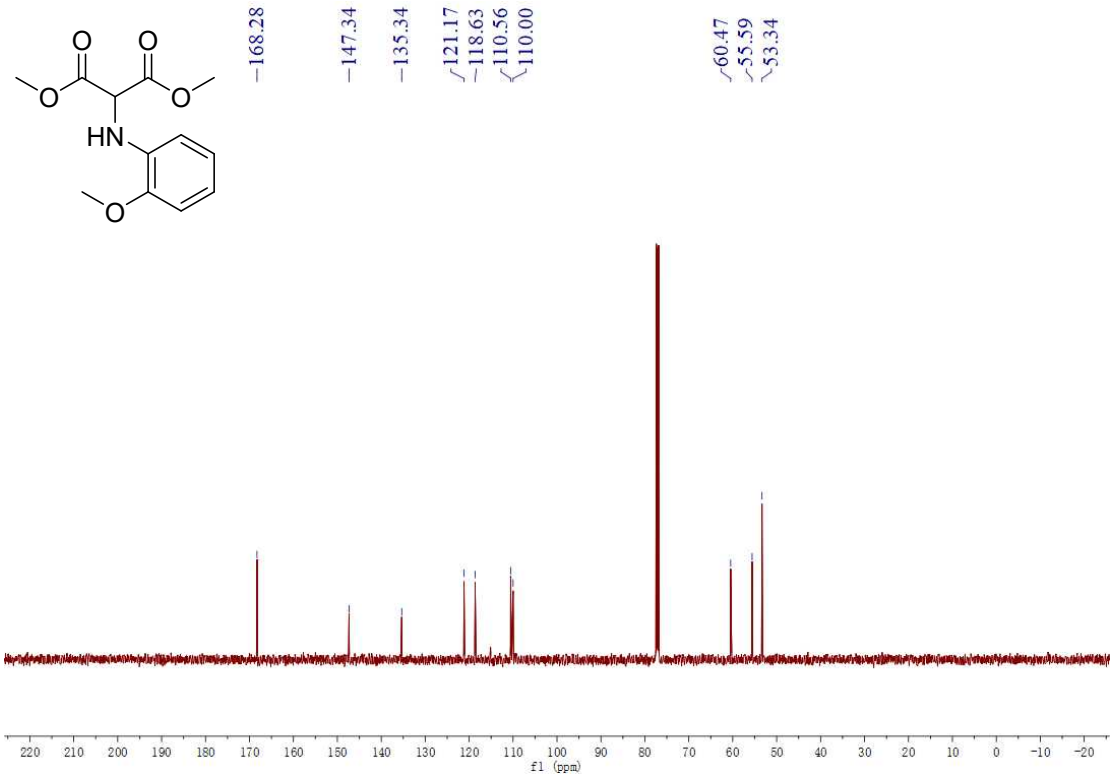
^{13}C NMR of ethyl dimethyl 2-((2-isopropylphenyl)amino)malonate (5g)



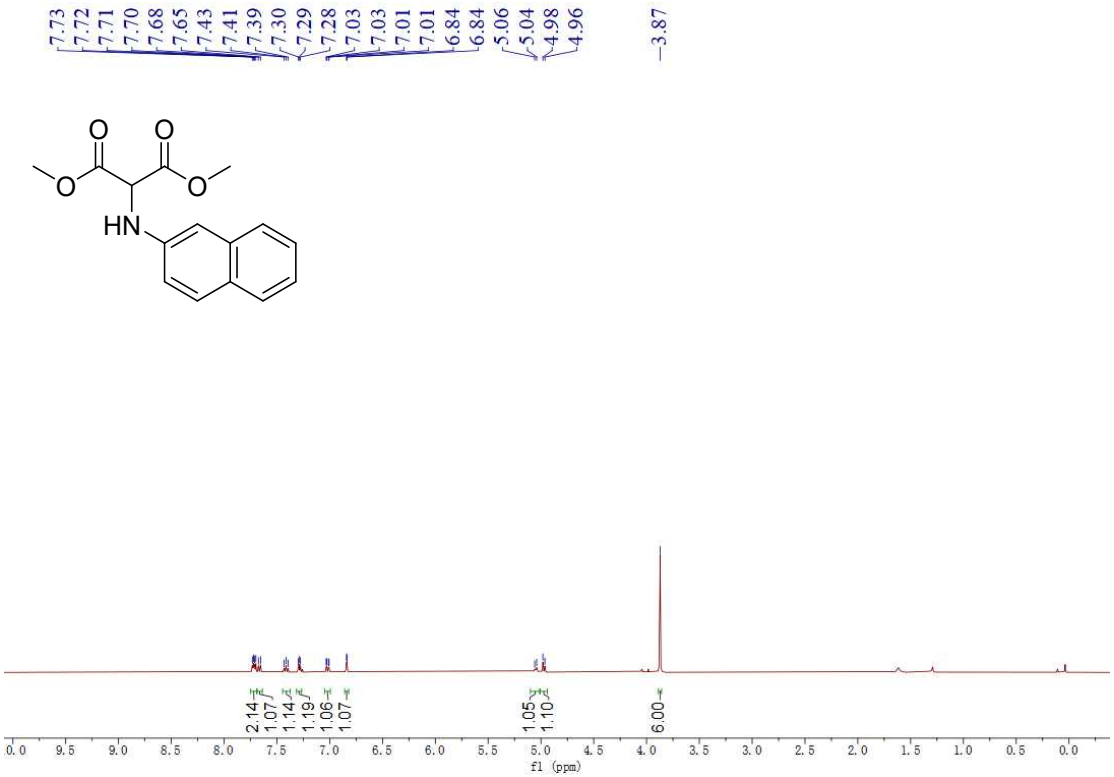
^{1}H NMR of dimethyl 2-((2-methoxyphenyl)amino)malonate (5h)



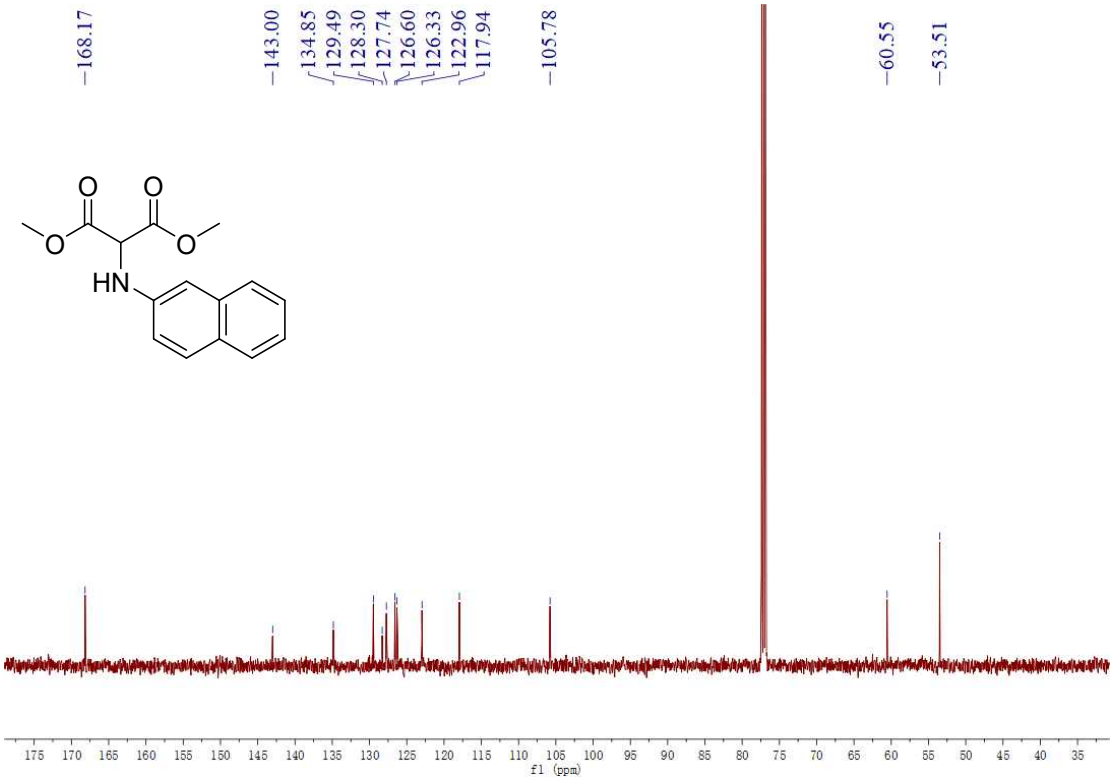
^{13}C NMR of dimethyl 2-((2-methoxyphenyl)amino)malonate (5h)



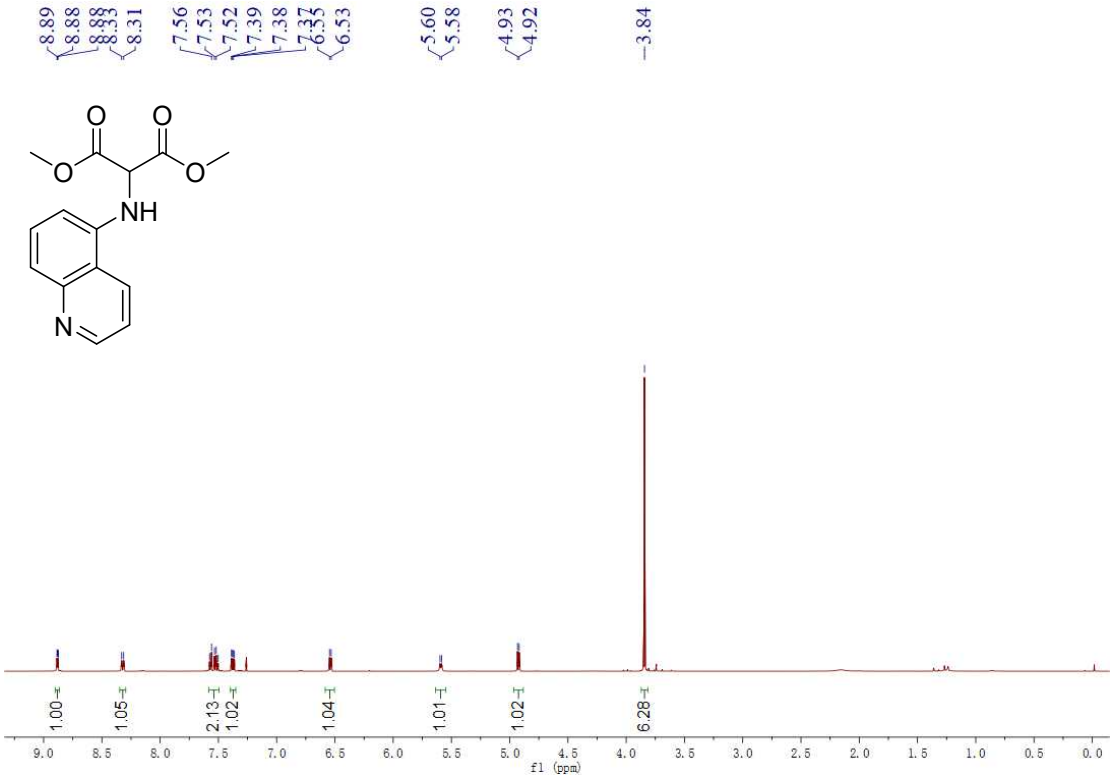
^{1}H NMR of dimethyl 2-(naphthalen-2-ylamino)malonate (5i)



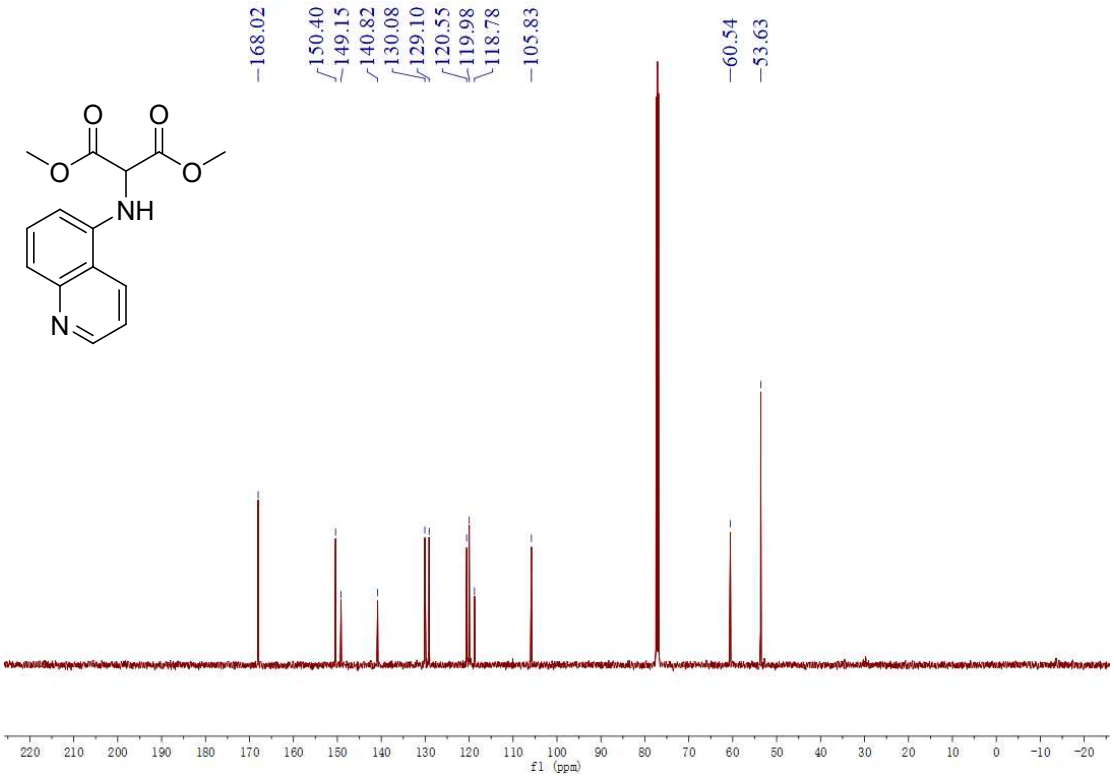
^{13}C NMR of dimethyl 2-(naphthalen-2-ylamino)malonate (5i)



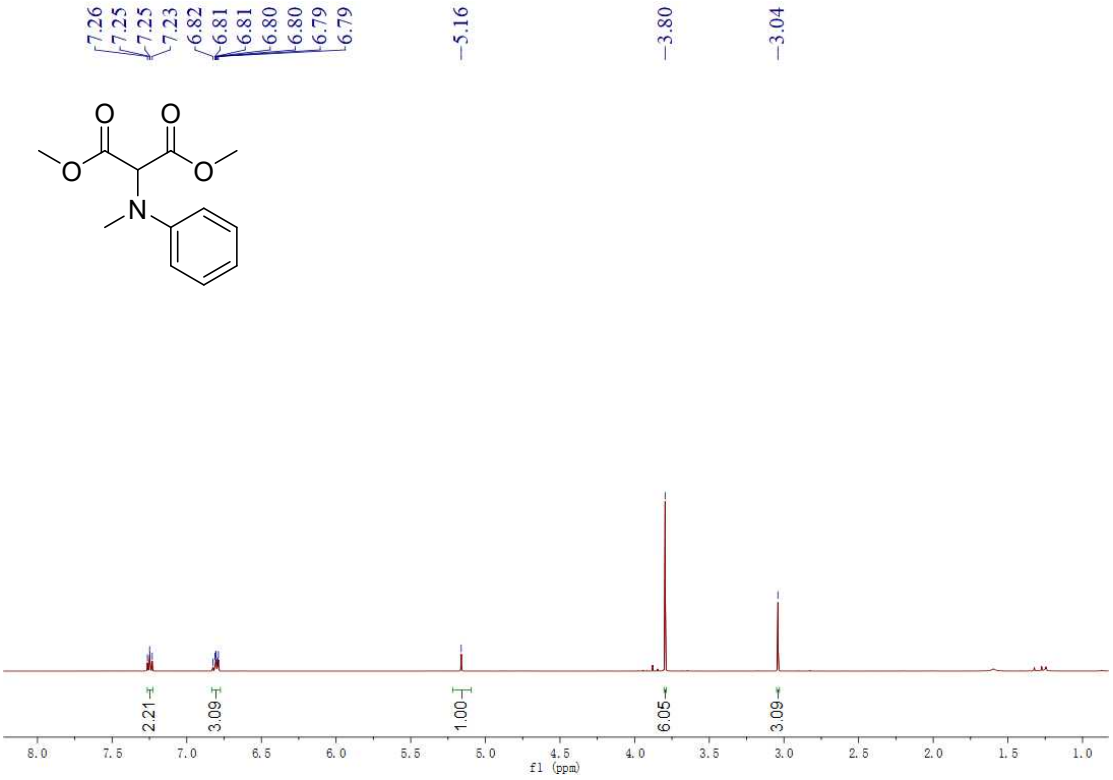
^{1}H NMR of dimethyl 2-(quinolin-5-ylamino)malonate (5j)



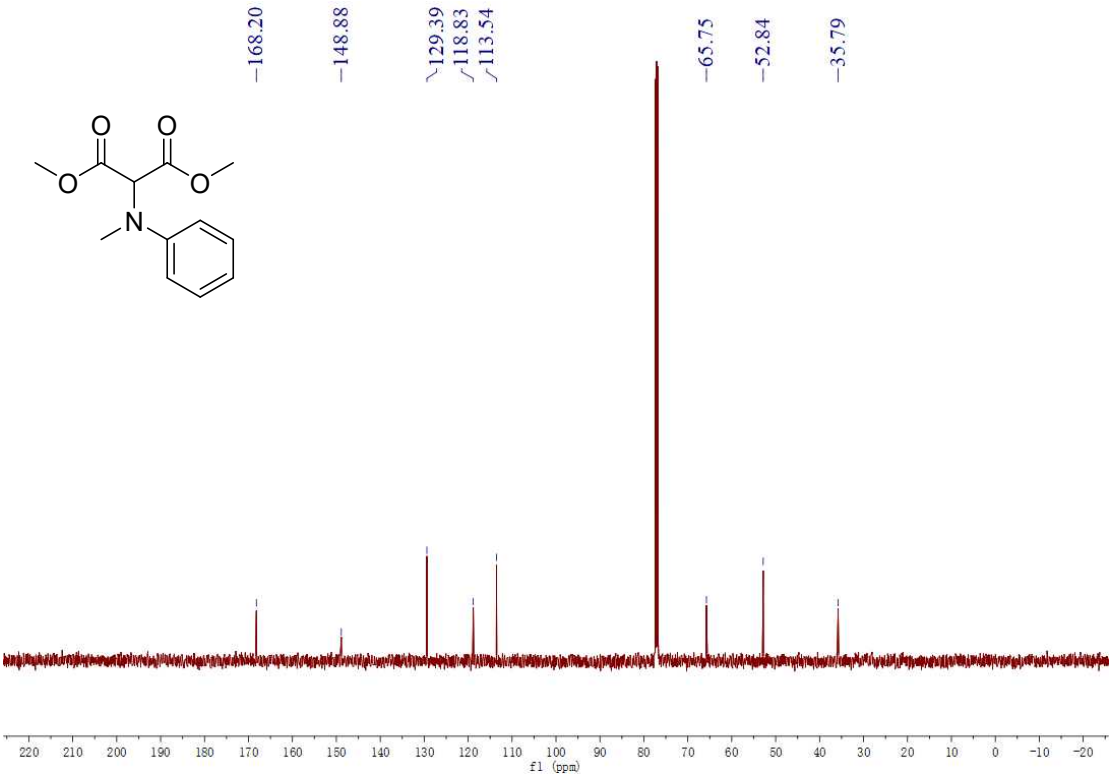
^{13}C NMR of dimethyl 2-(quinolin-5-ylamino)malonate (5j)



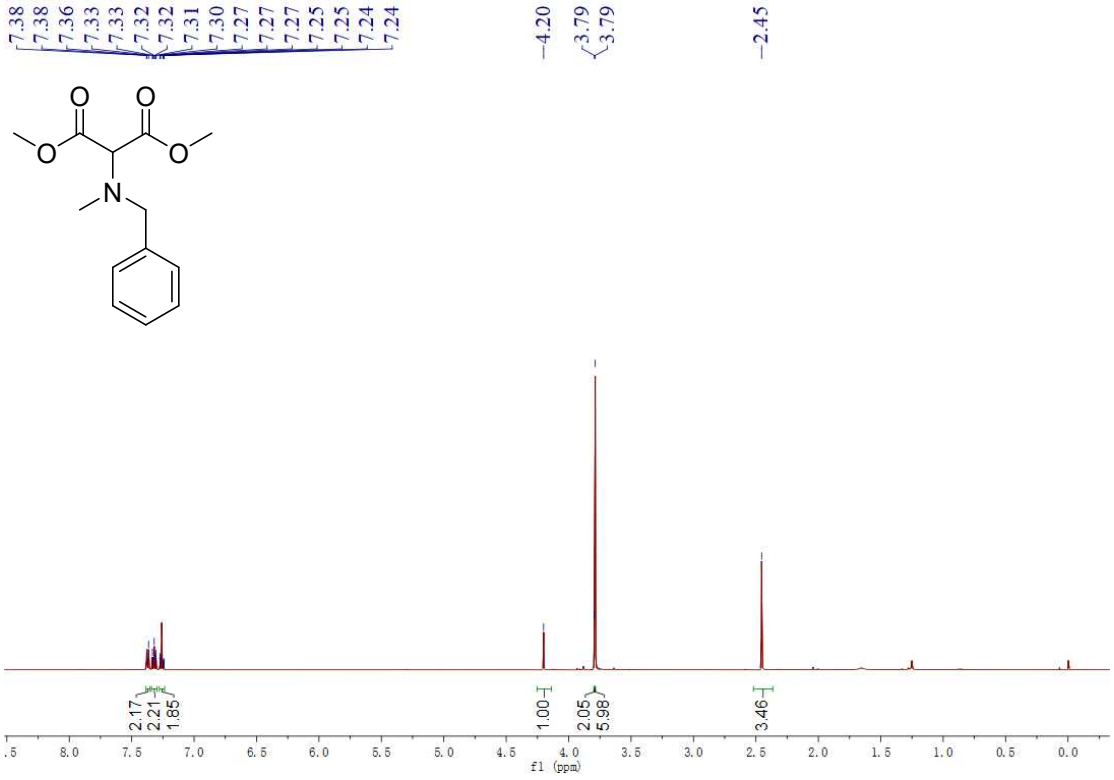
^{1}H NMR of dimethyl 2-(methyl(phenyl)amino)malonate (5k)



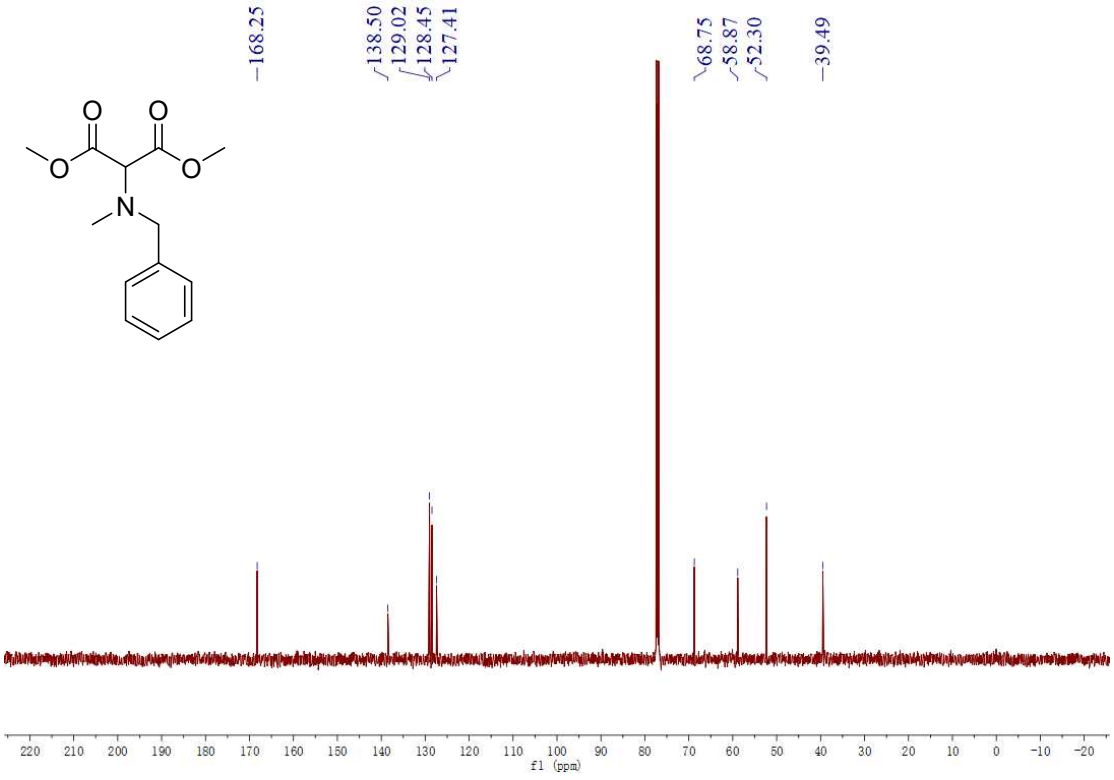
^{13}C NMR of dimethyl 2-(methyl(phenyl)amino)malonate (5k)



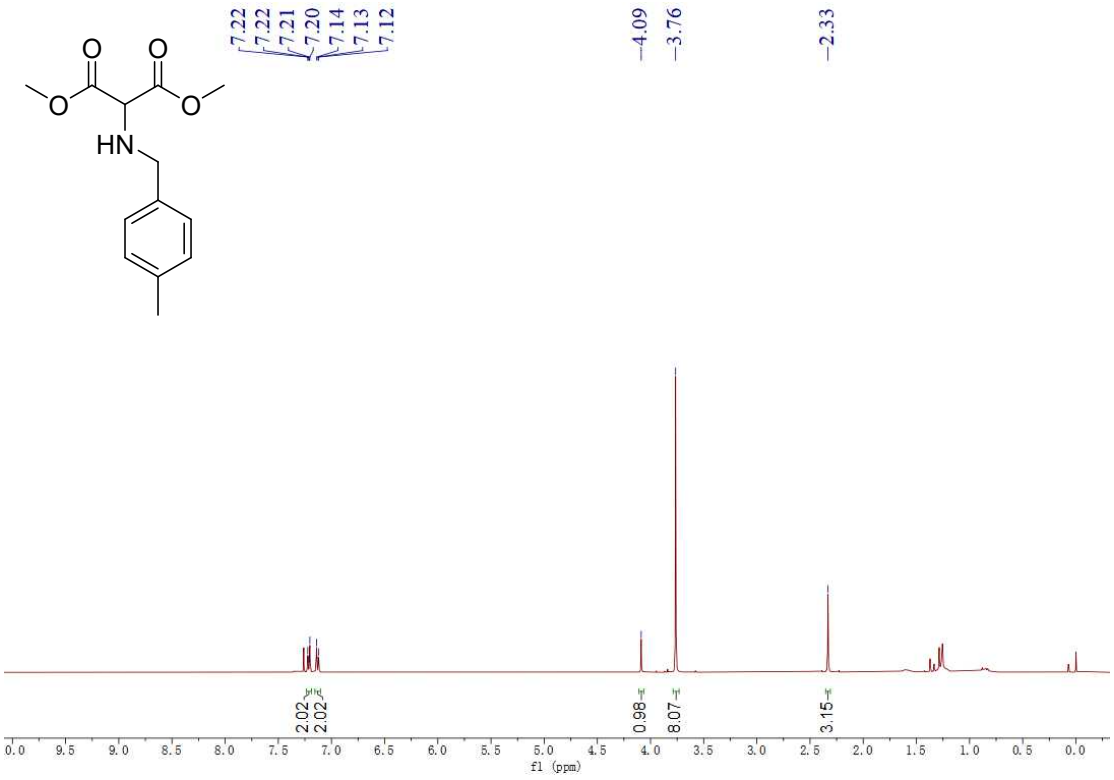
^{1}H NMR of dimethyl 2-(benzyl(methyl)amino)malonate (5l)



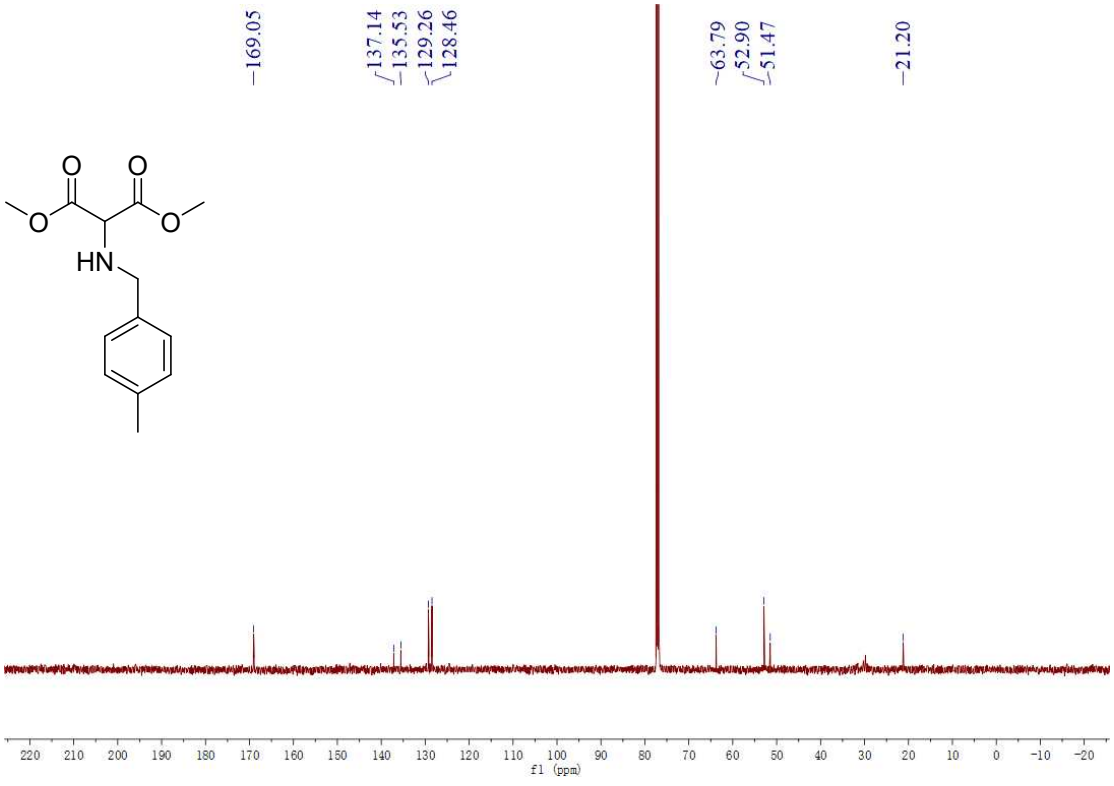
^{13}C NMR of dimethyl 2-(benzyl(methyl)amino)malonate (5l)



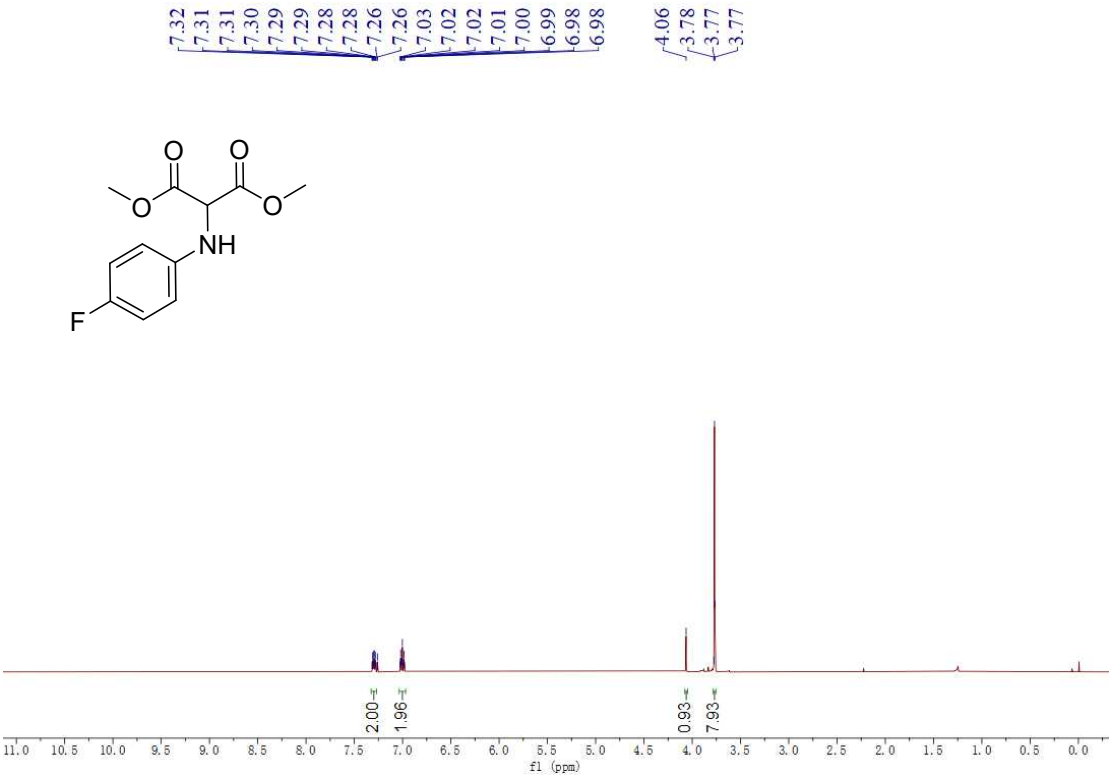
^{1}H NMR of dimethyl 2-((4-methylbenzyl)amino)malonate (5m)



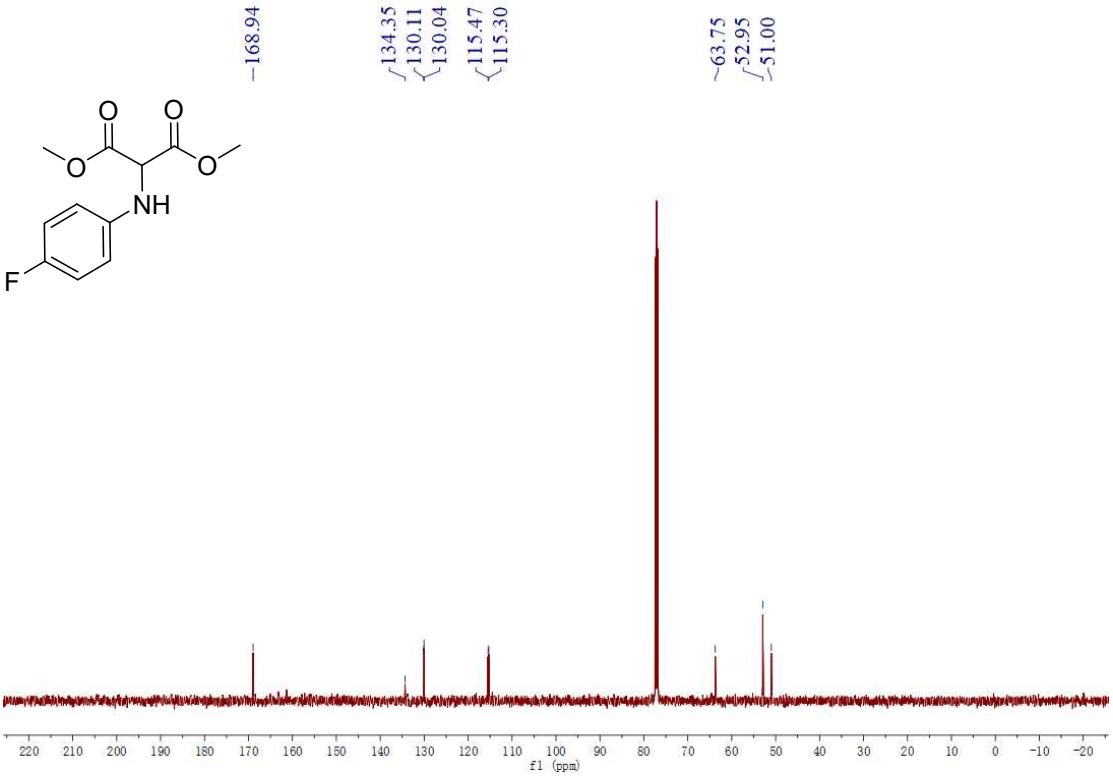
^{13}C NMR of dimethyl 2-((4-methylbenzyl)amino)malonate (5m)



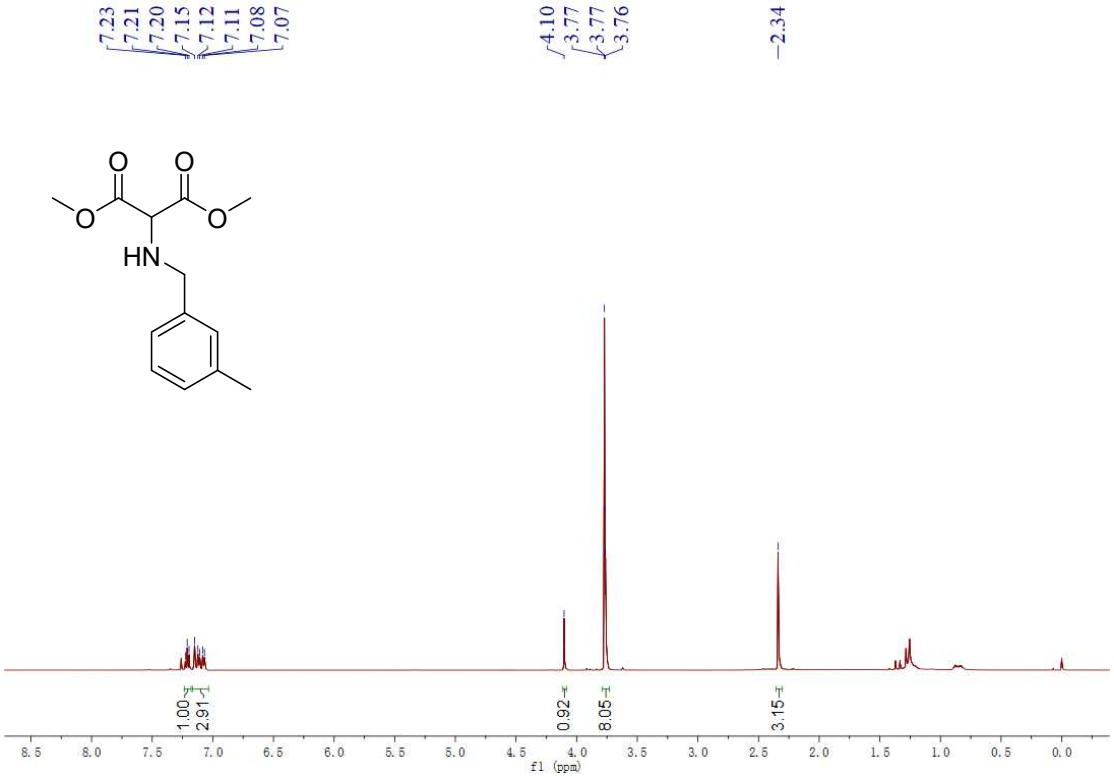
^{1}H NMR of dimethyl 2-((4-fluorobenzyl)amino)malonate (5n)



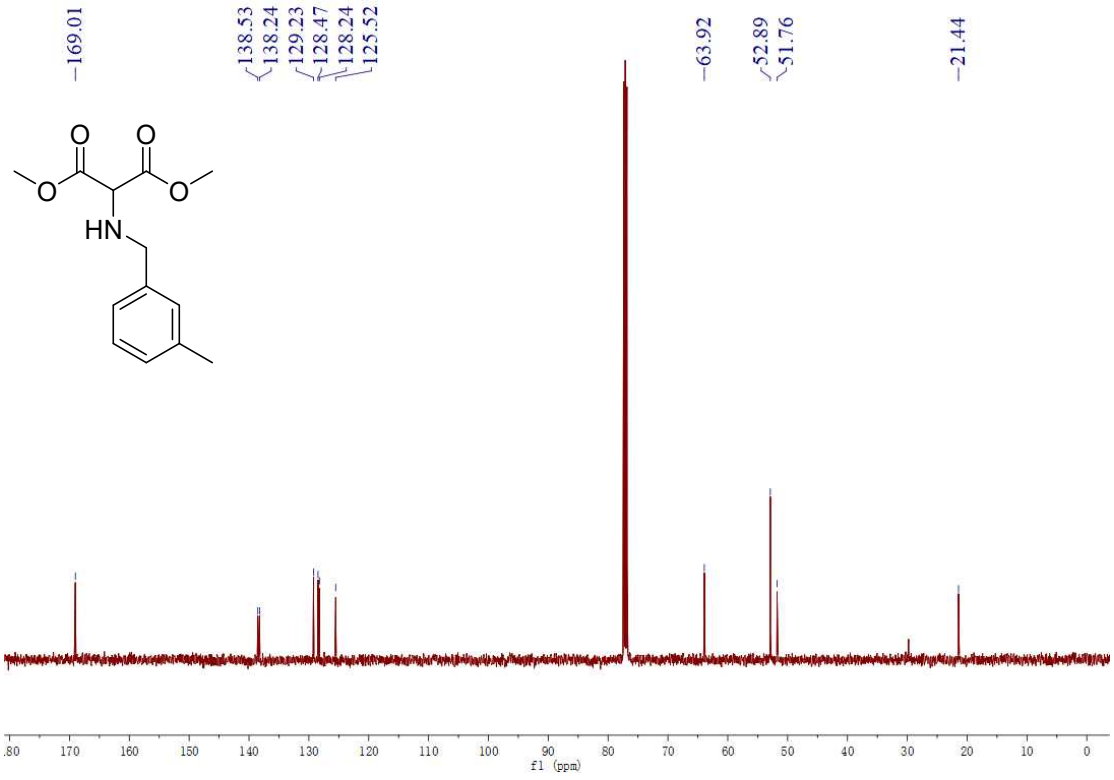
^{13}C NMR of dimethyl 2-((4-fluorobenzyl)amino)malonate (5n)



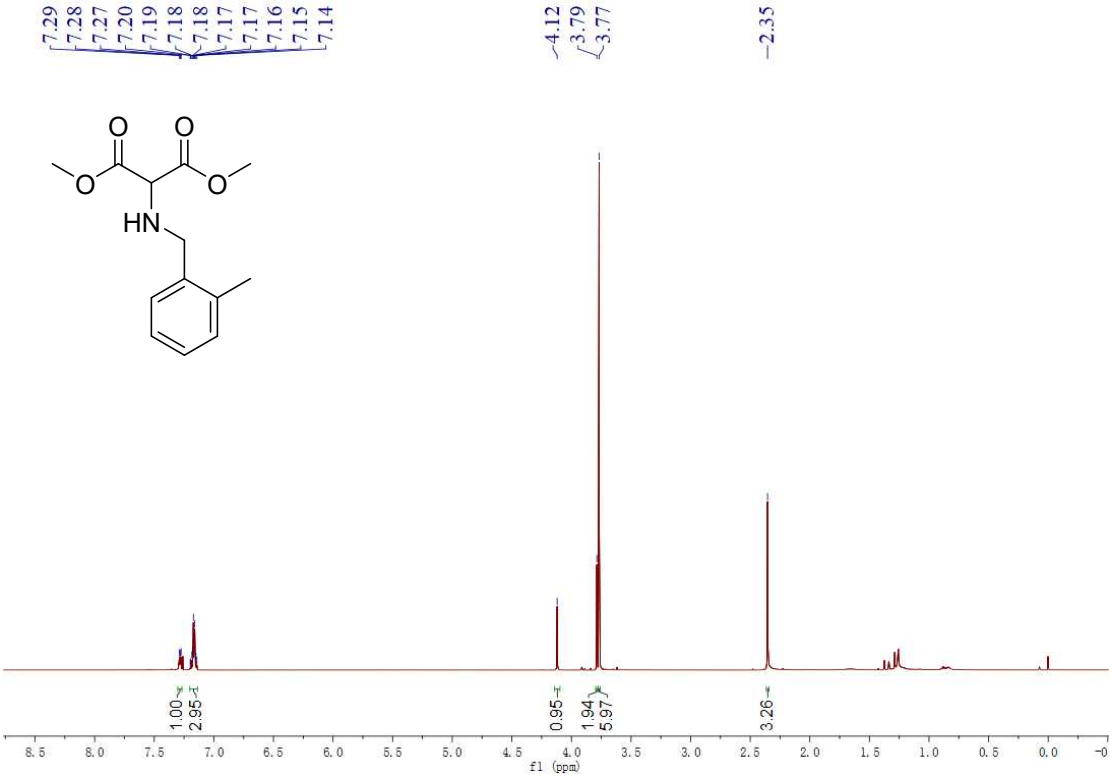
^{1}H NMR of dimethyl 2-((3-methylbenzyl)amino)malonate (5o)



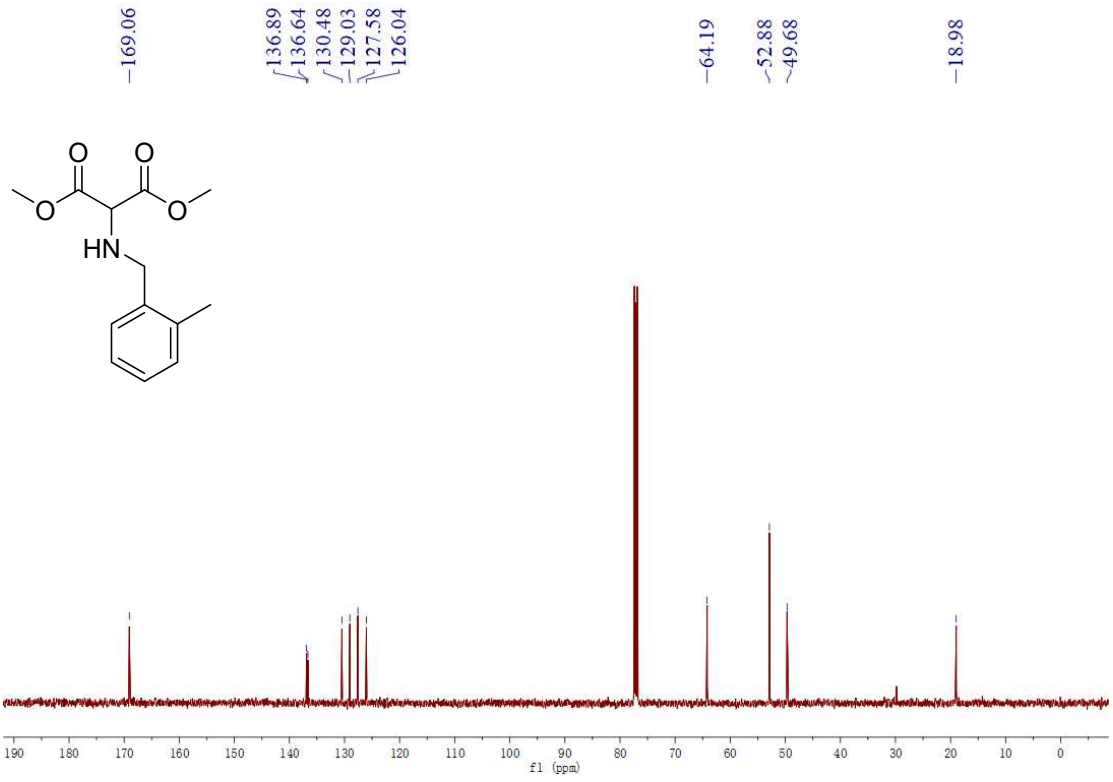
^{13}C NMR of dimethyl 2-((3-methylbenzyl)amino)malonate (5o)



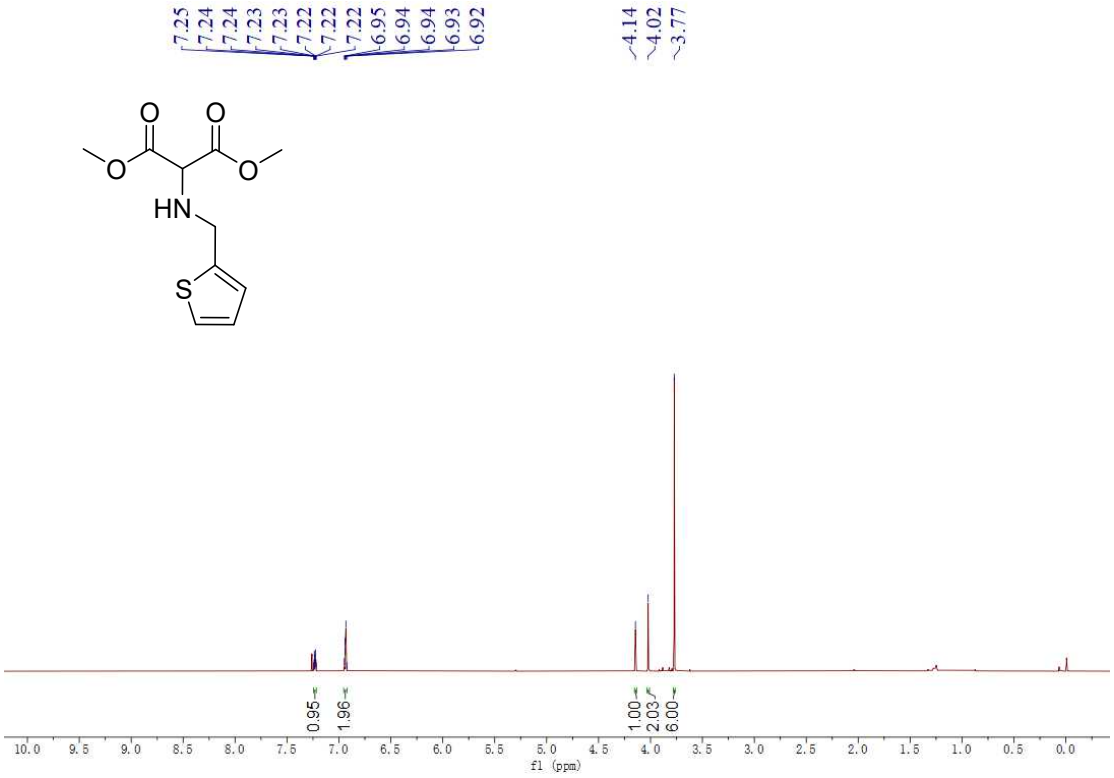
^{1}H NMR of dimethyl 2-((2-methylbenzyl)amino)malonate (5p)



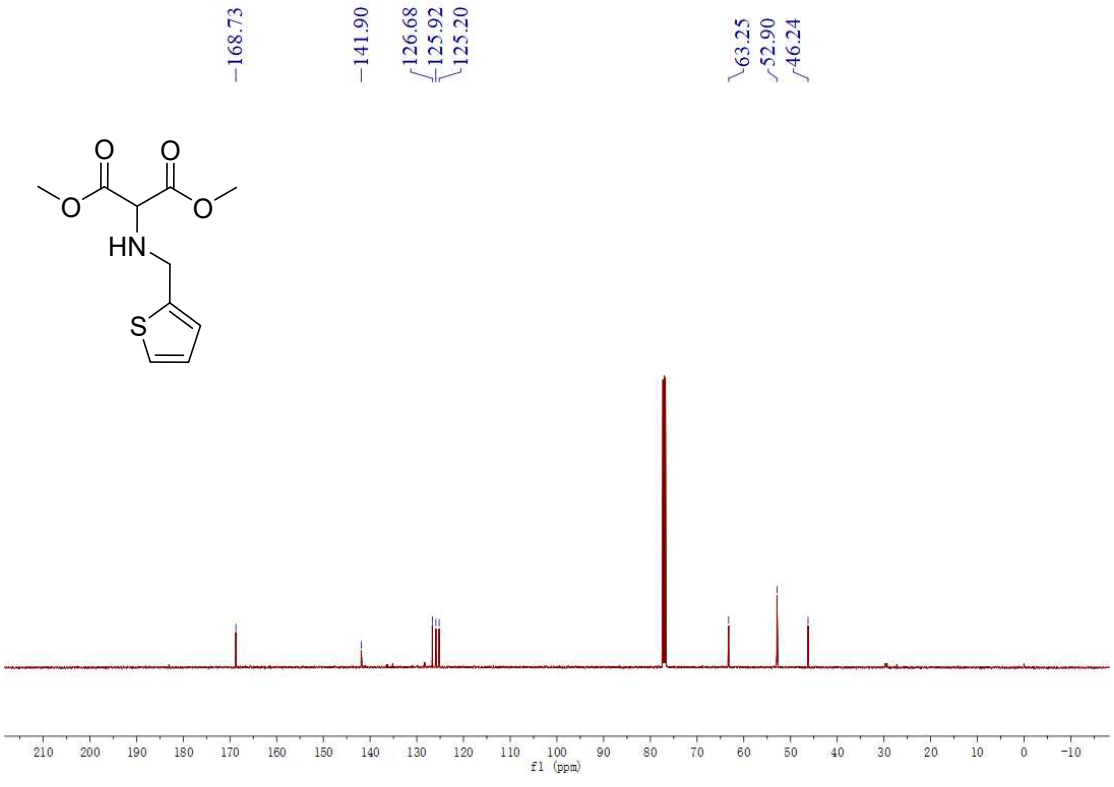
^{13}C NMR of dimethyl 2-((2-methylbenzyl)amino)malonate (5p)



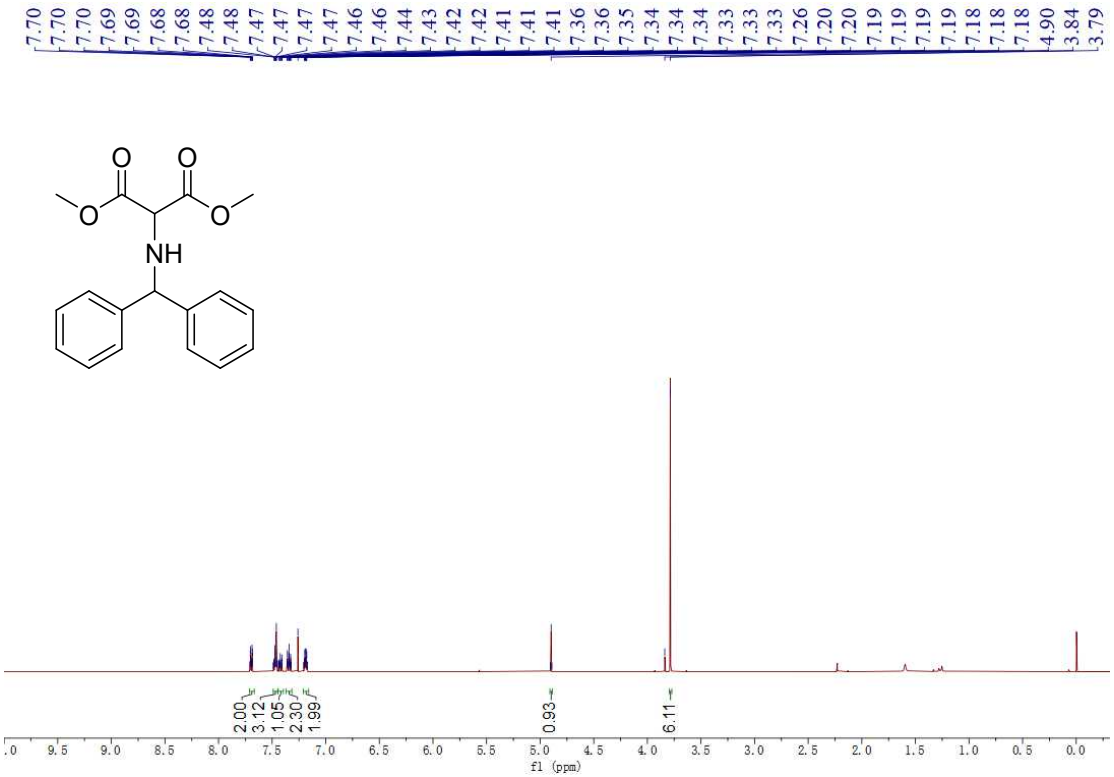
^{1}H NMR of dimethyl 2-((thiophen-2-ylmethyl)amino)malonate (5q)



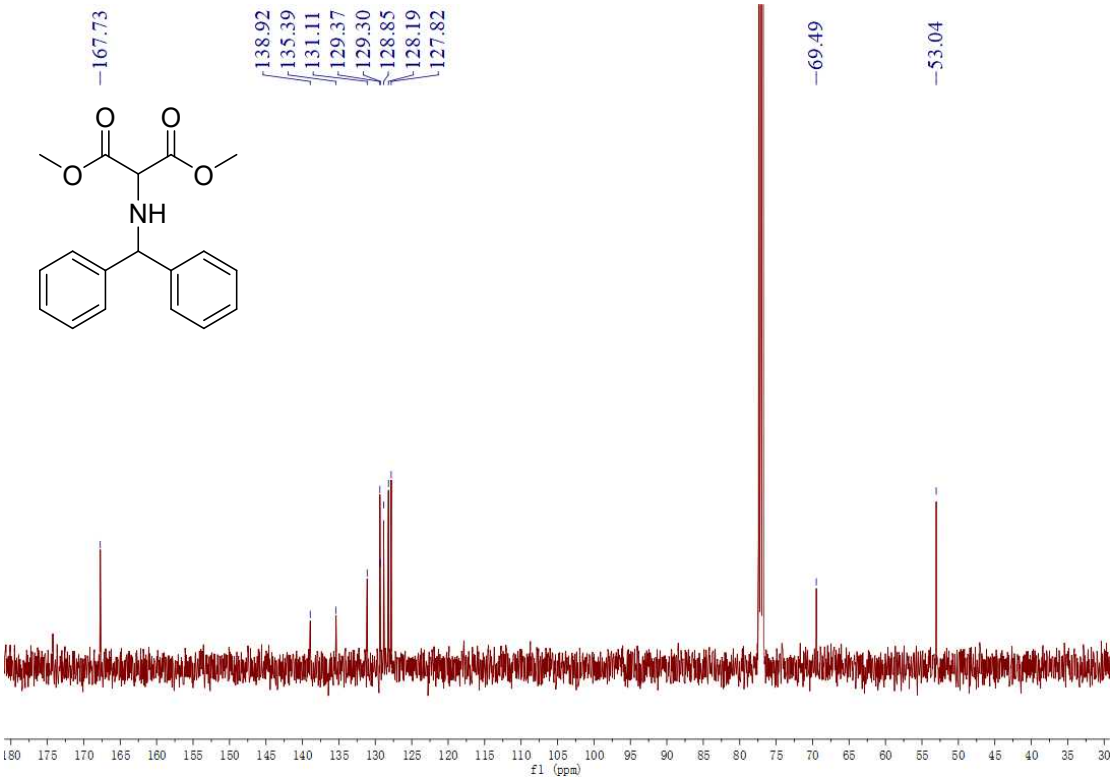
^{13}C NMR of dimethyl 2-((thiophen-2-ylmethyl)amino)malonate (5q)



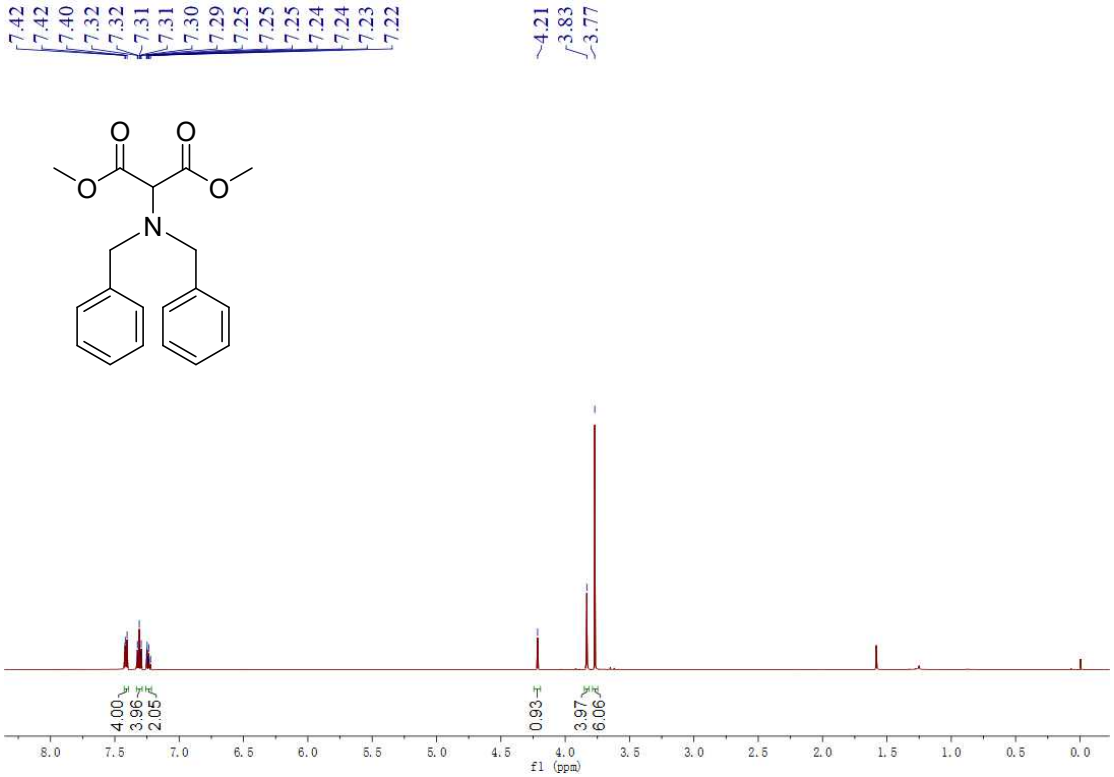
^{1}H NMR of dimethyl 2-(benzhydrylamino)malonate (5r)



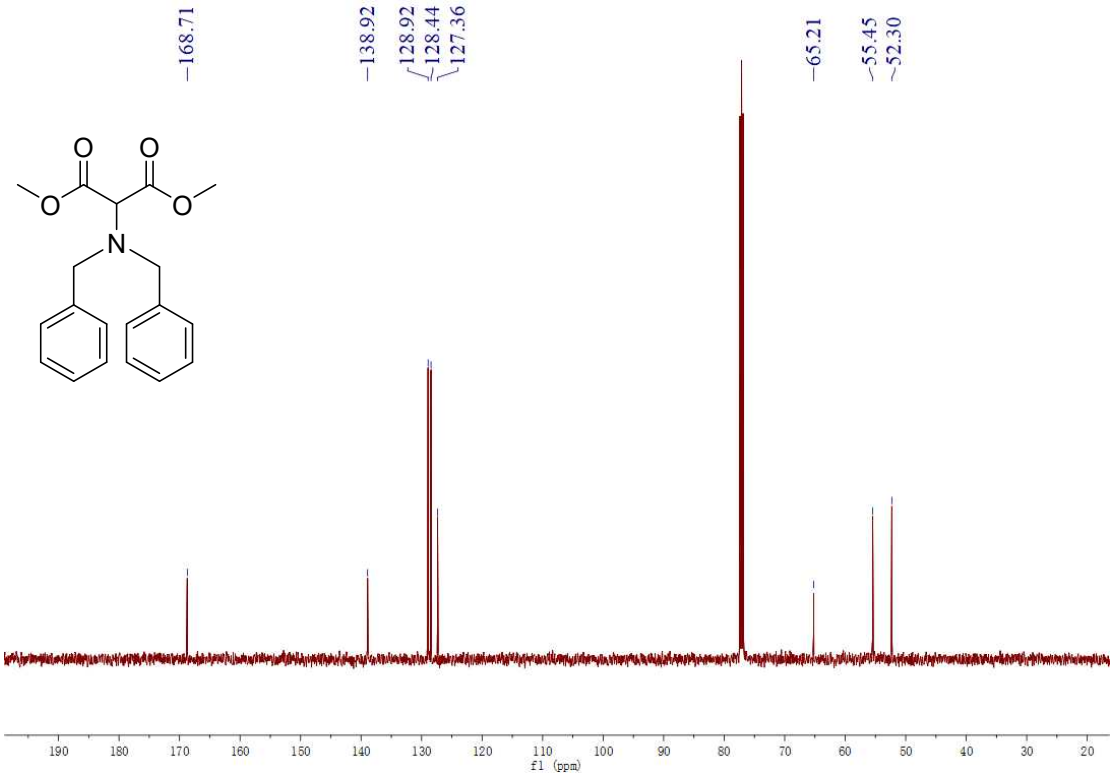
^{13}C NMR of dimethyl 2-(benzhydrylamino)malonate (5r)



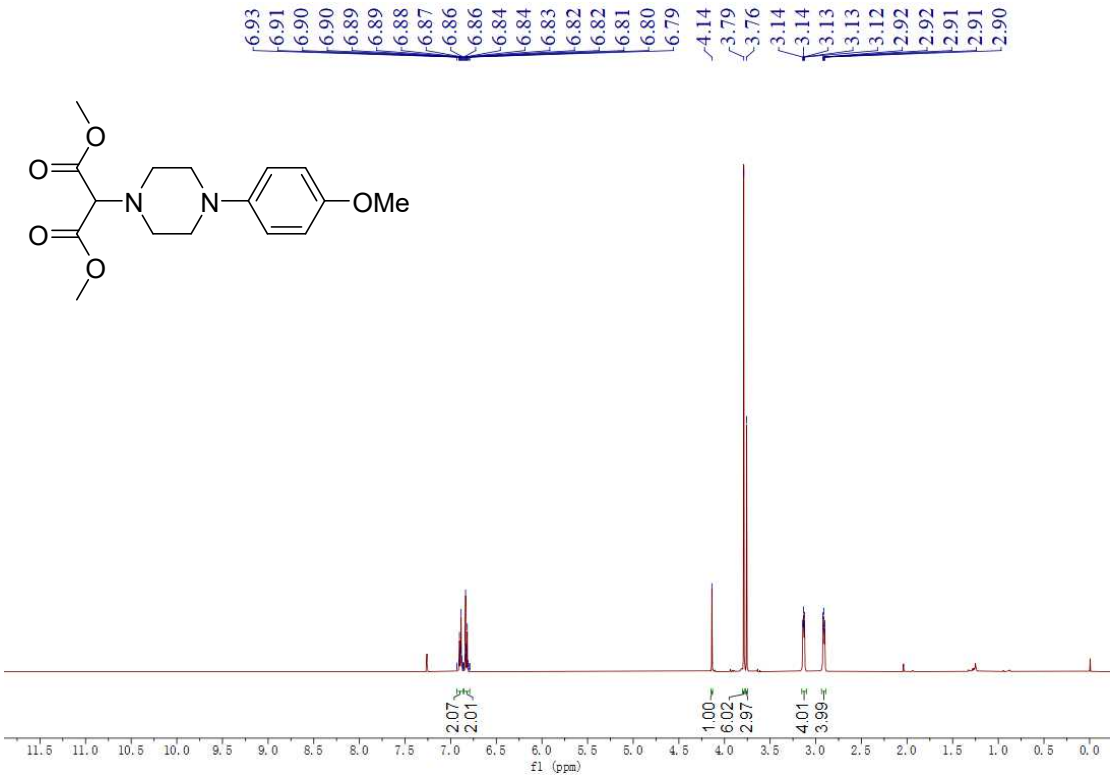
^{1}H NMR of dimethyl 2-(dibenzylamino)malonate (5s)



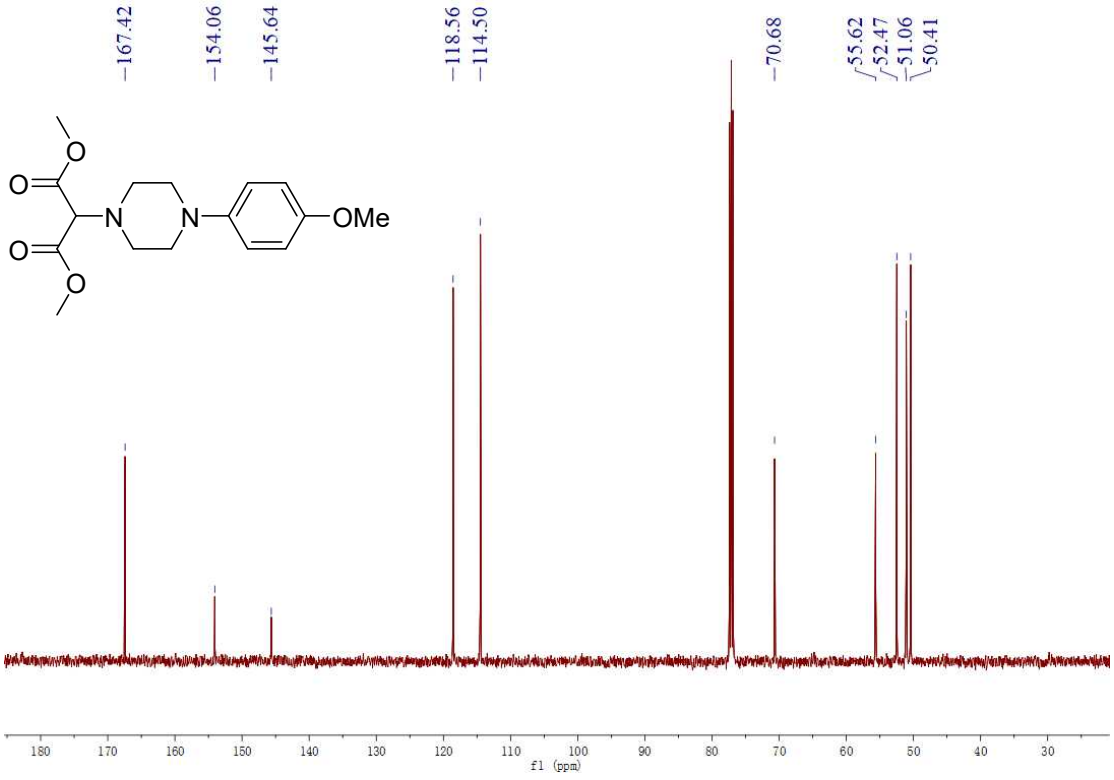
^{13}C NMR of dimethyl 2-(dibenzylamino)malonate (5s)



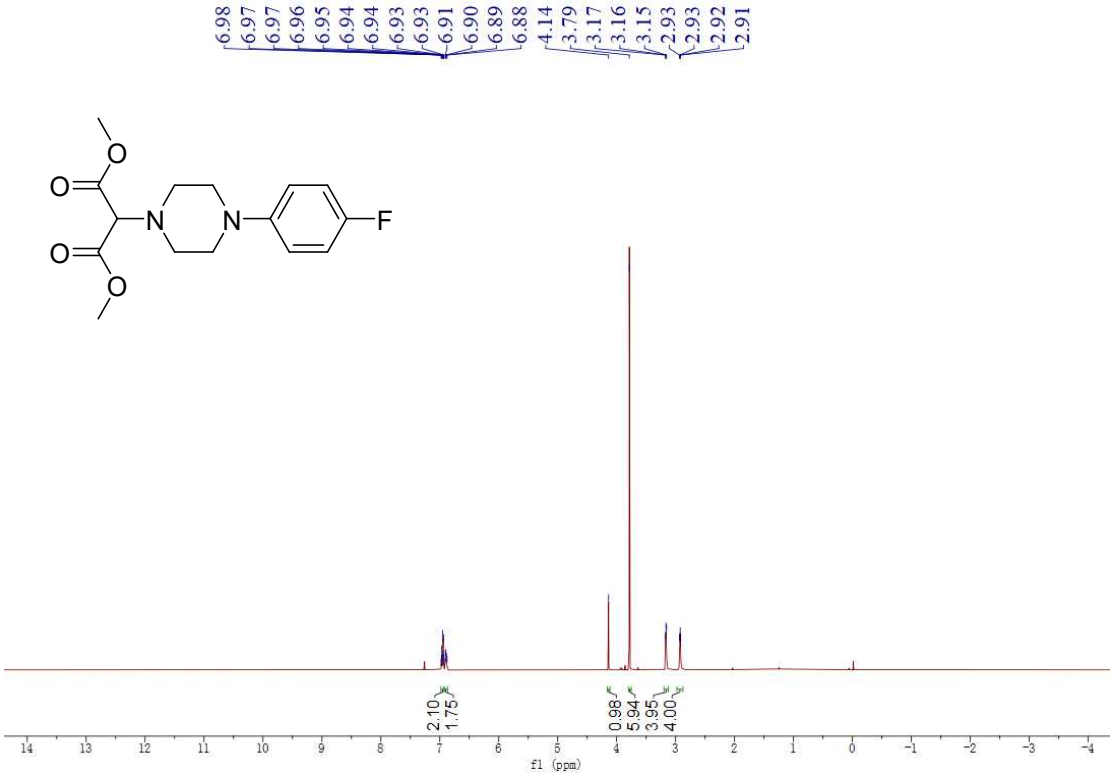
^{1}H NMR of dimethyl 2-(4-(4-methoxyphenyl)piperazin-1-yl)malonate (5t)



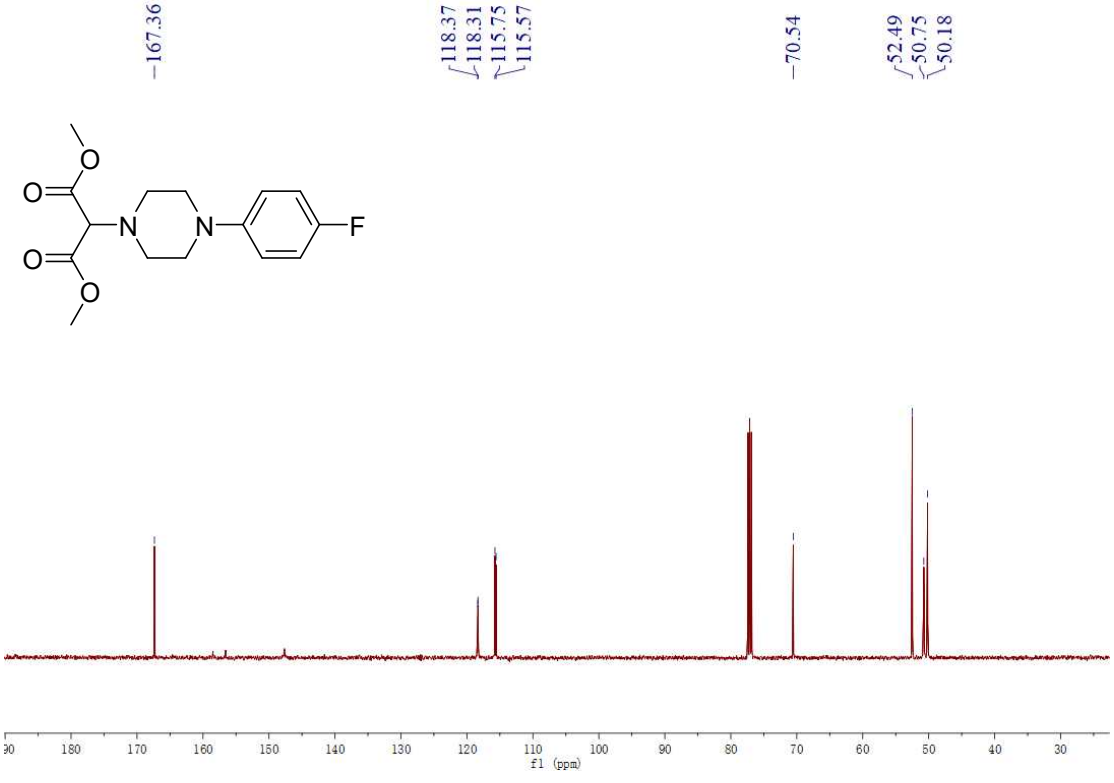
^{13}C NMR of dimethyl 2-(4-(4-methoxyphenyl)piperazin-1-yl)malonate (5t)



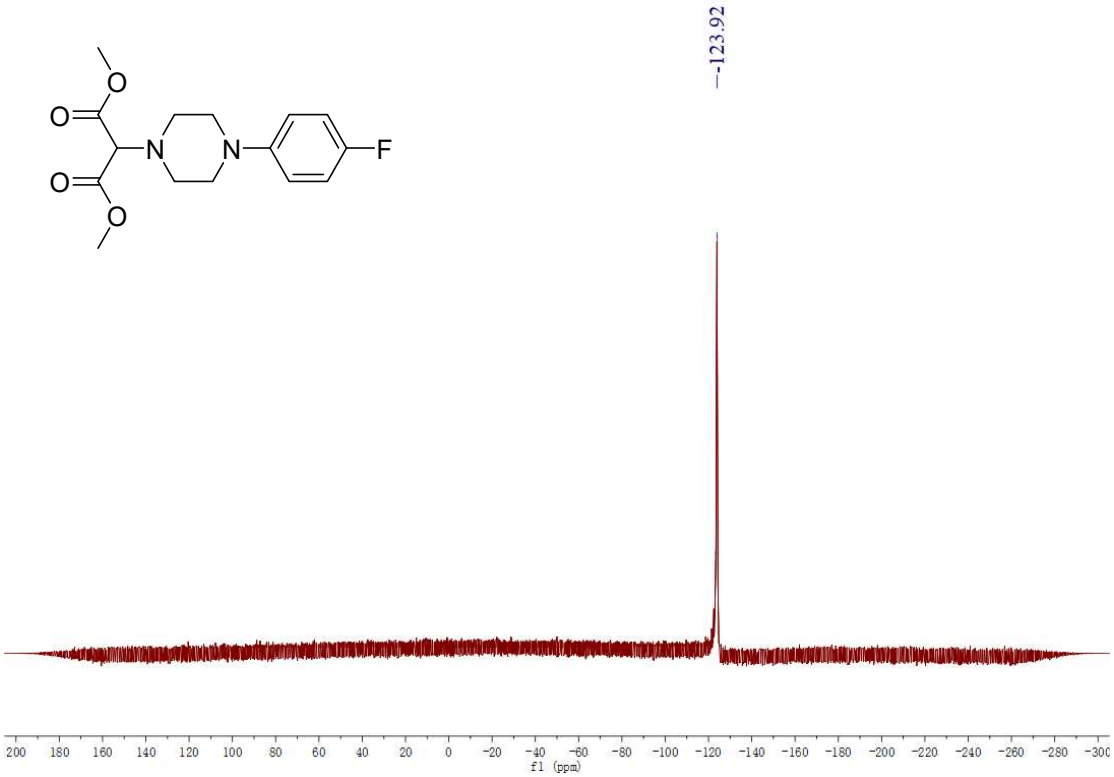
^{1}H NMR of dimethyl 2-(4-(4-fluorophenyl)piperazin-1-yl)malonate (5u)



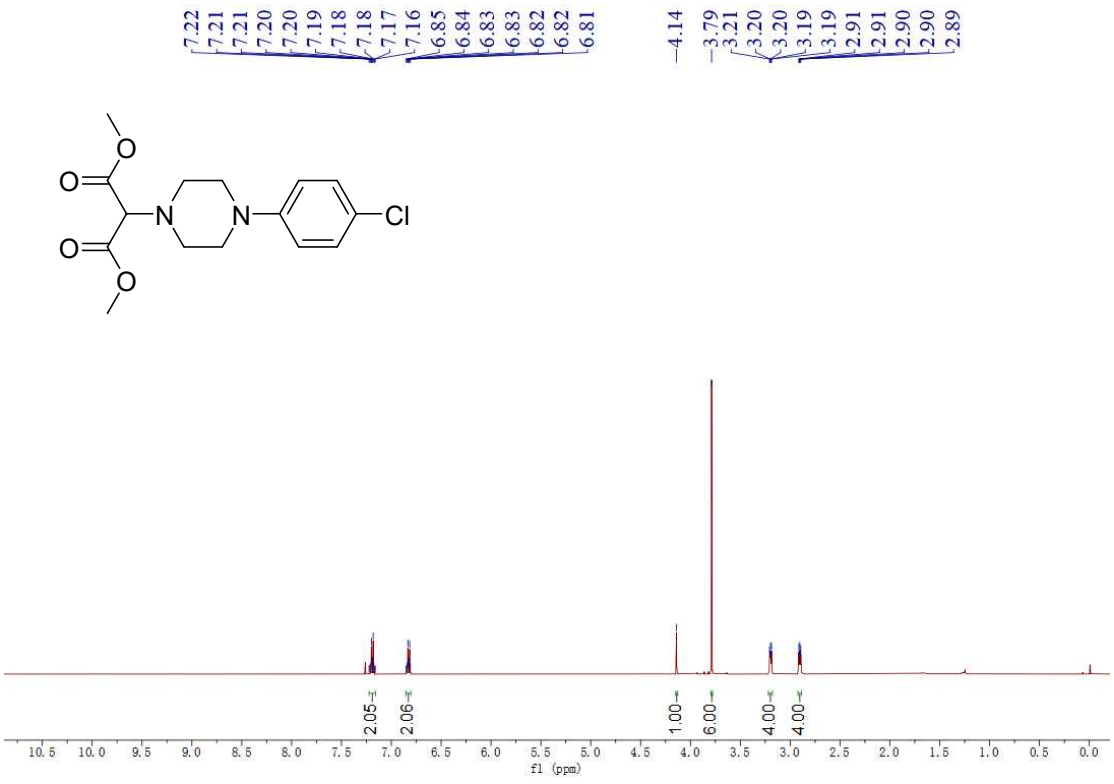
^{13}C NMR of dimethyl 2-(4-(4-fluorophenyl)piperazin-1-yl)malonate (5u)



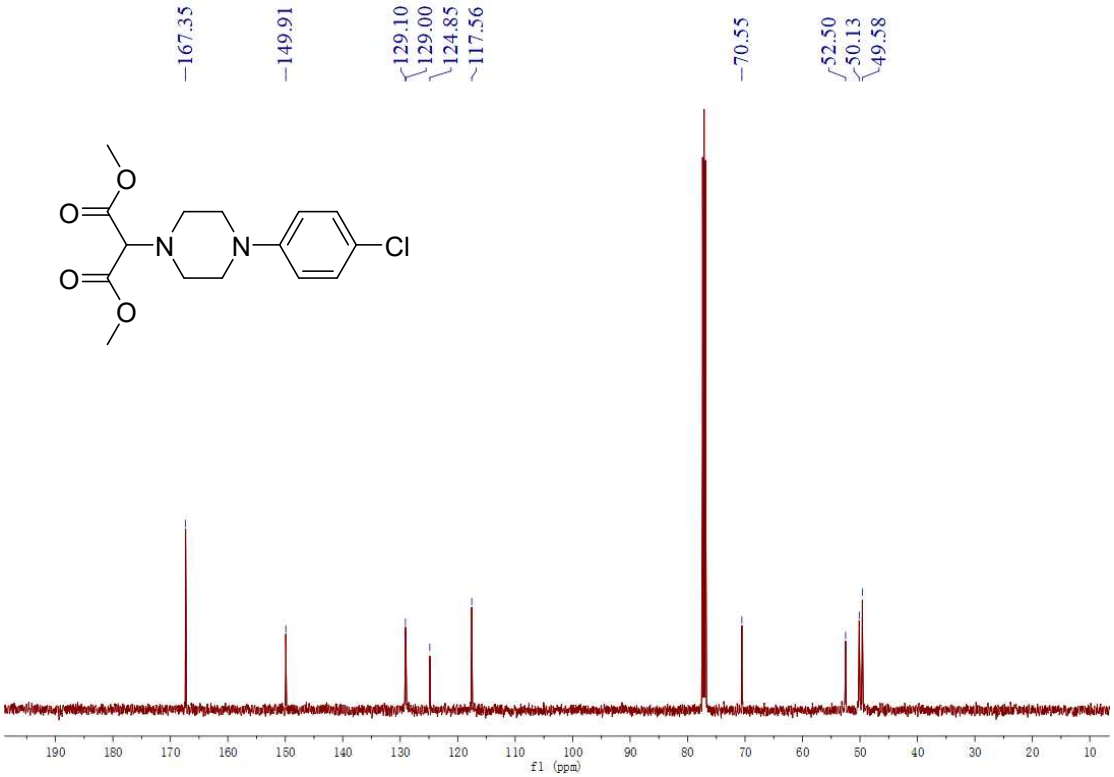
^{19}F NMR of dimethyl 2-(4-(4-fluorophenyl)piperazin-1-yl)malonate (5u)



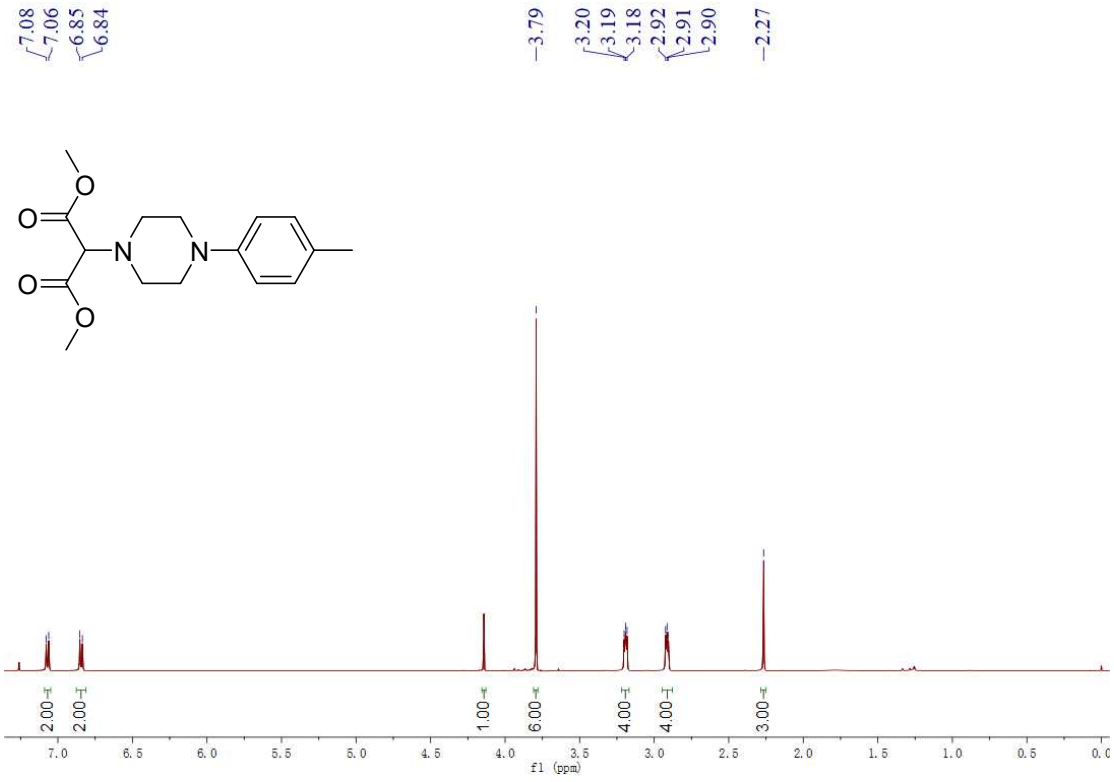
^{1}H NMR of dimethyl 2-(4-(4-chlorophenyl)piperazin-1-yl)malonate (5v)



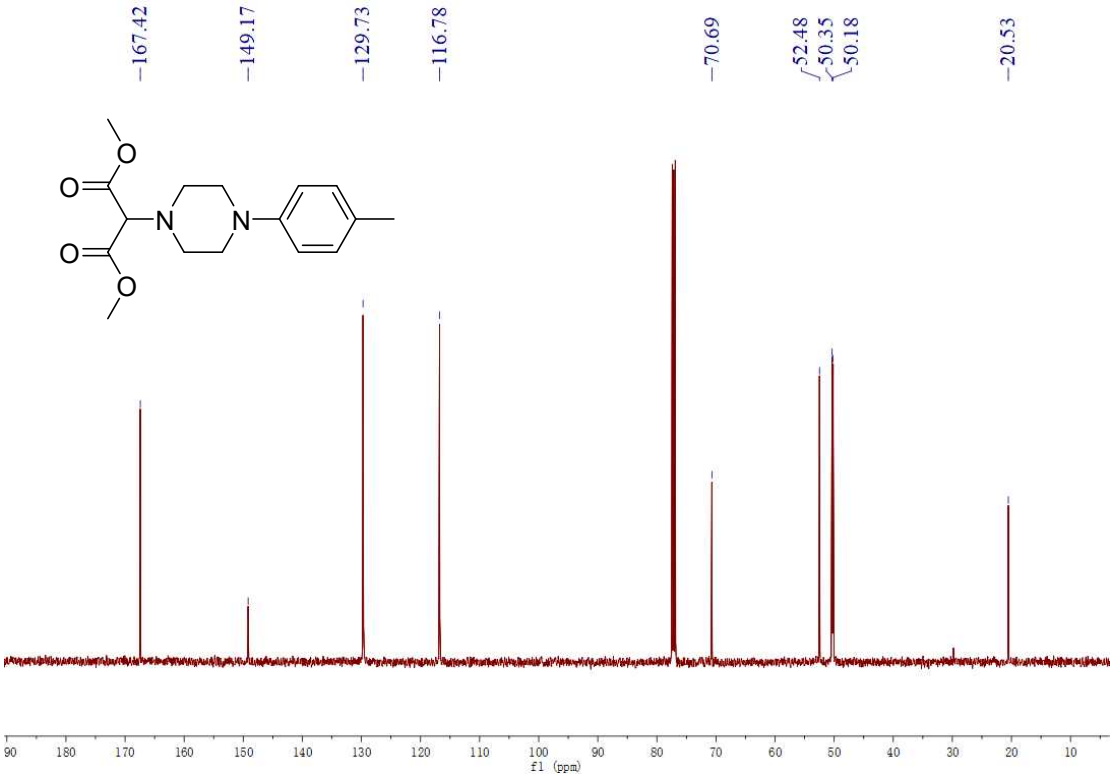
^{13}C NMR of dimethyl 2-(4-(4-chlorophenyl)piperazin-1-yl)malonate (5v)



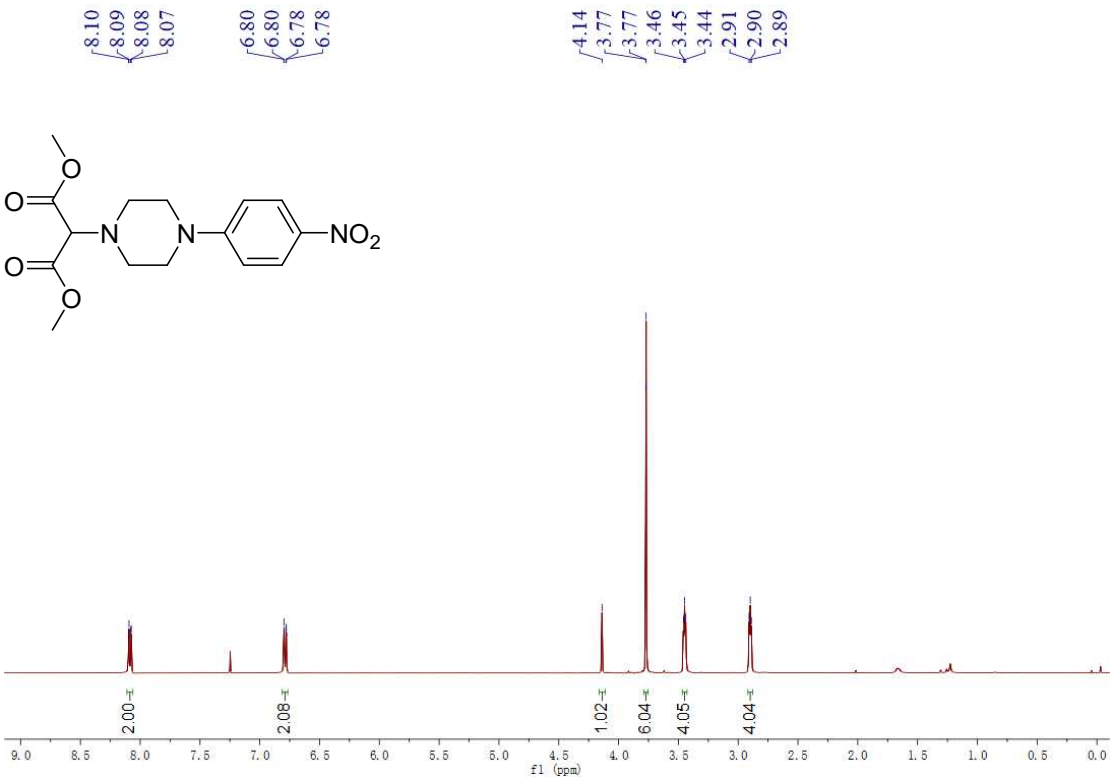
^{1}H NMR of dimethyl 2-(4-(p-tolyl)piperazin-1-yl)malonate (5w)



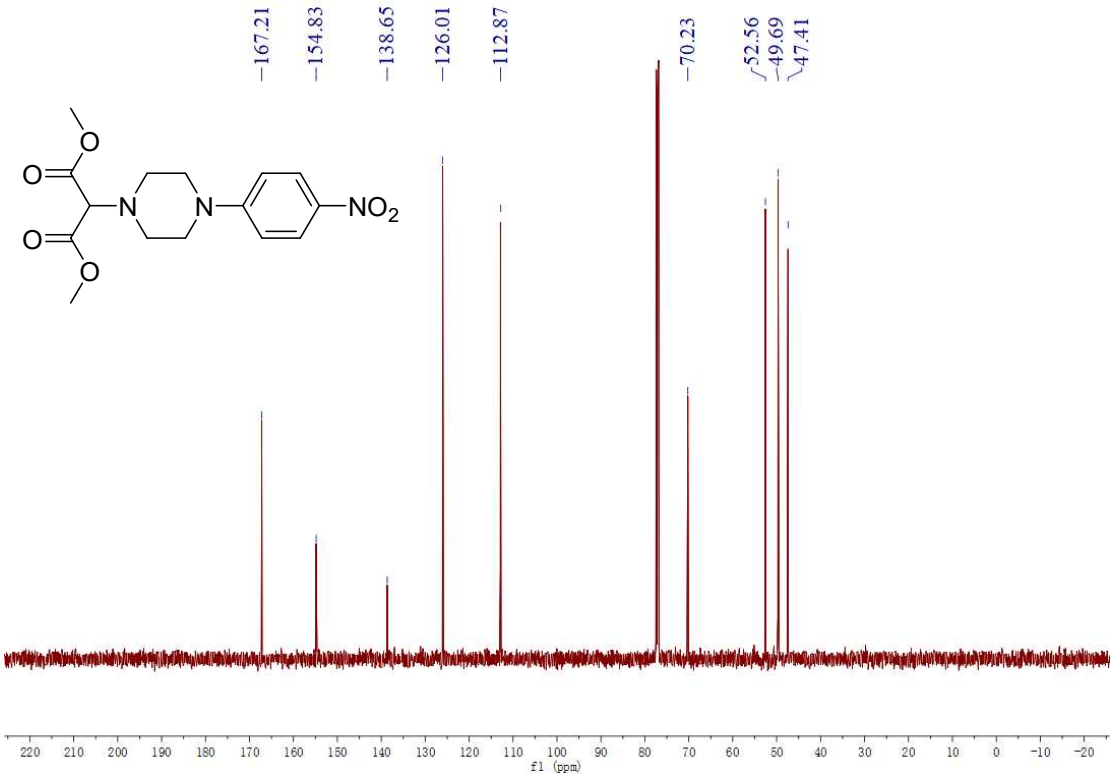
^{13}C NMR of dimethyl 2-(4-(p-tolyl)piperazin-1-yl)malonate (5w)



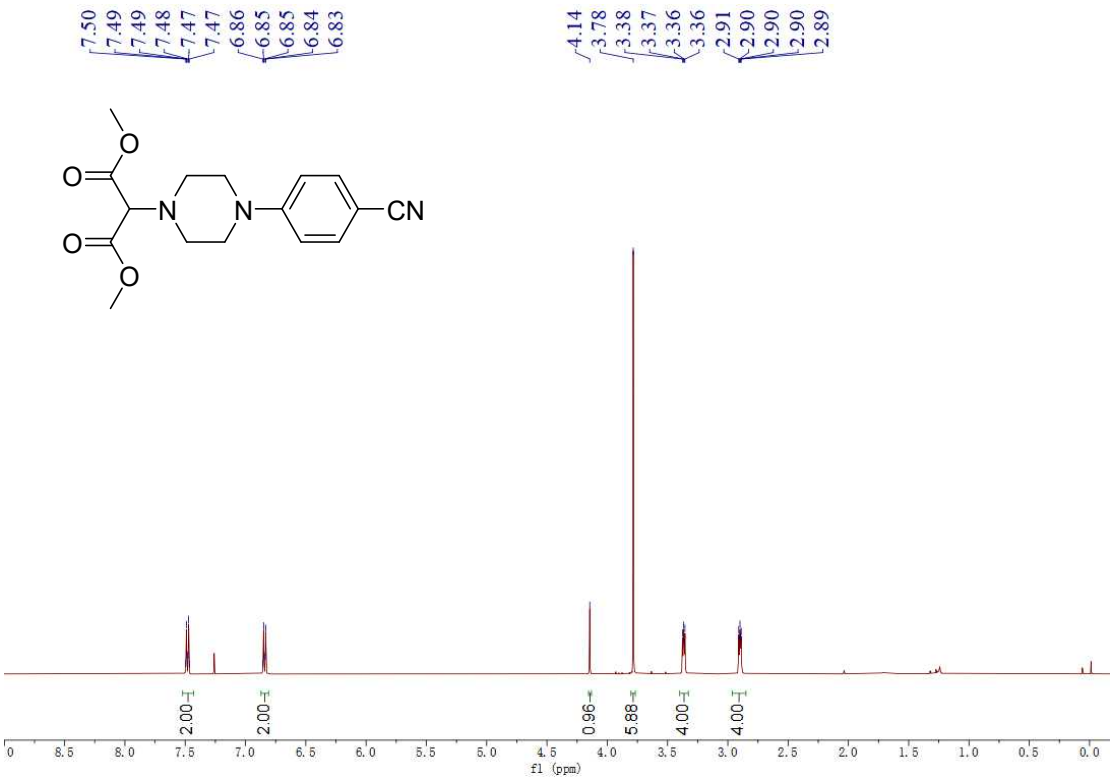
^{1}H NMR of dimethyl 2-(4-(4-nitrophenyl)piperazin-1-yl)malonate (5x)



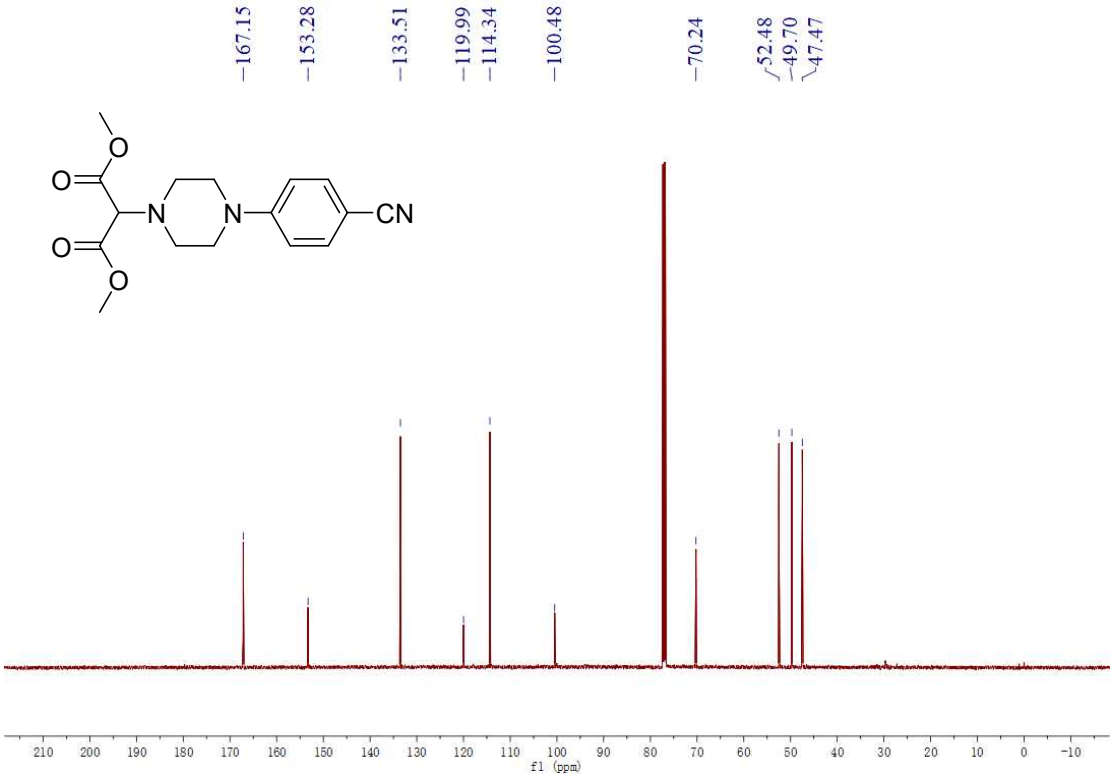
^{13}C NMR of dimethyl 2-(4-(4-nitrophenyl)piperazin-1-yl)malonate (5x)



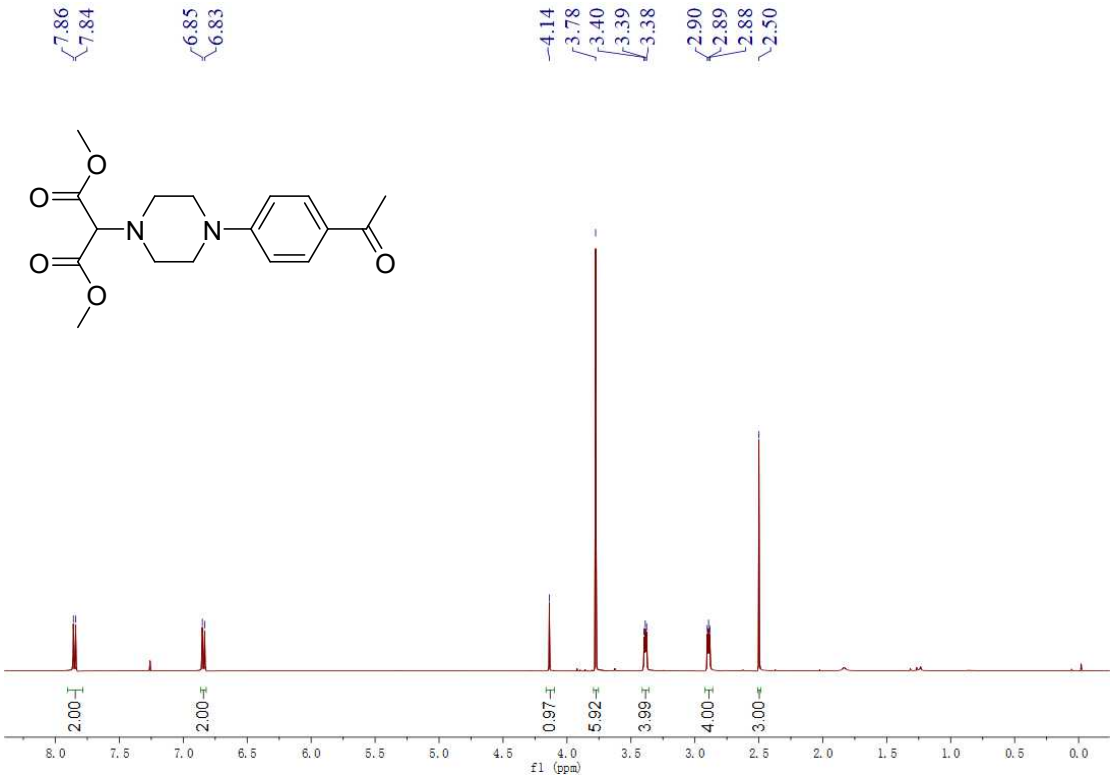
^{1}H NMR of dimethyl 2-(4-(4-cyanophenyl)piperazin-1-yl)malonate (5y)



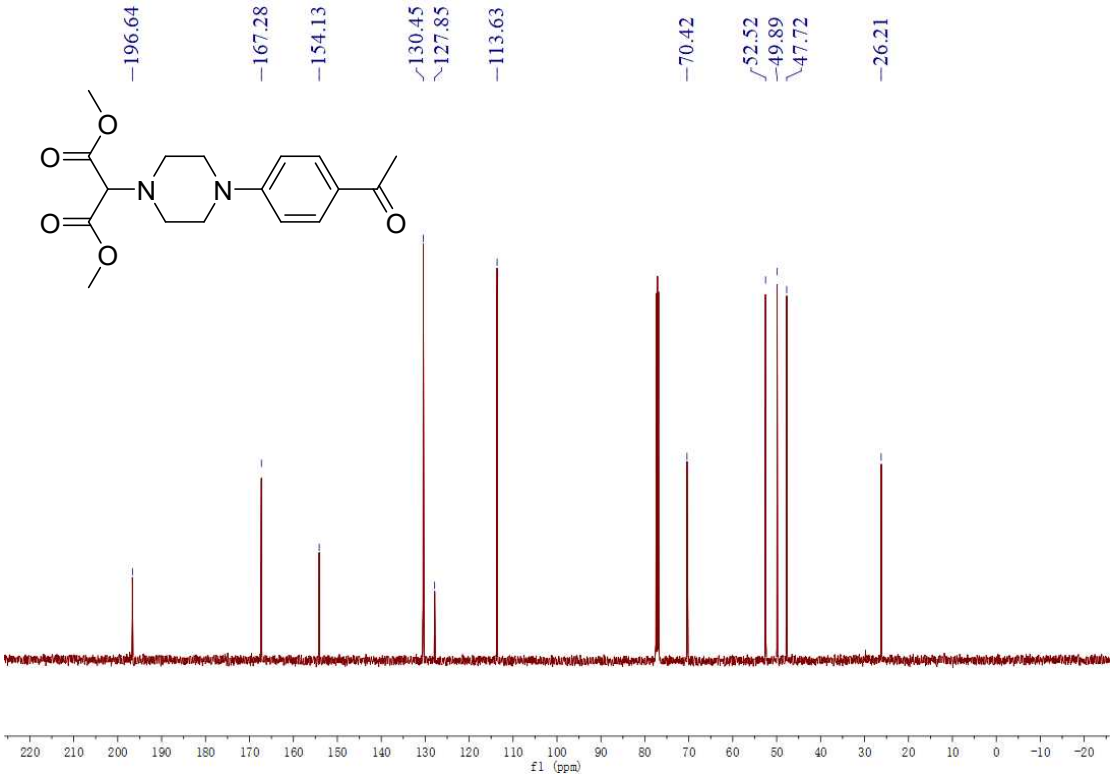
^{13}C NMR of dimethyl 2-(4-(4-cyanophenyl)piperazin-1-yl)malonate (5y)



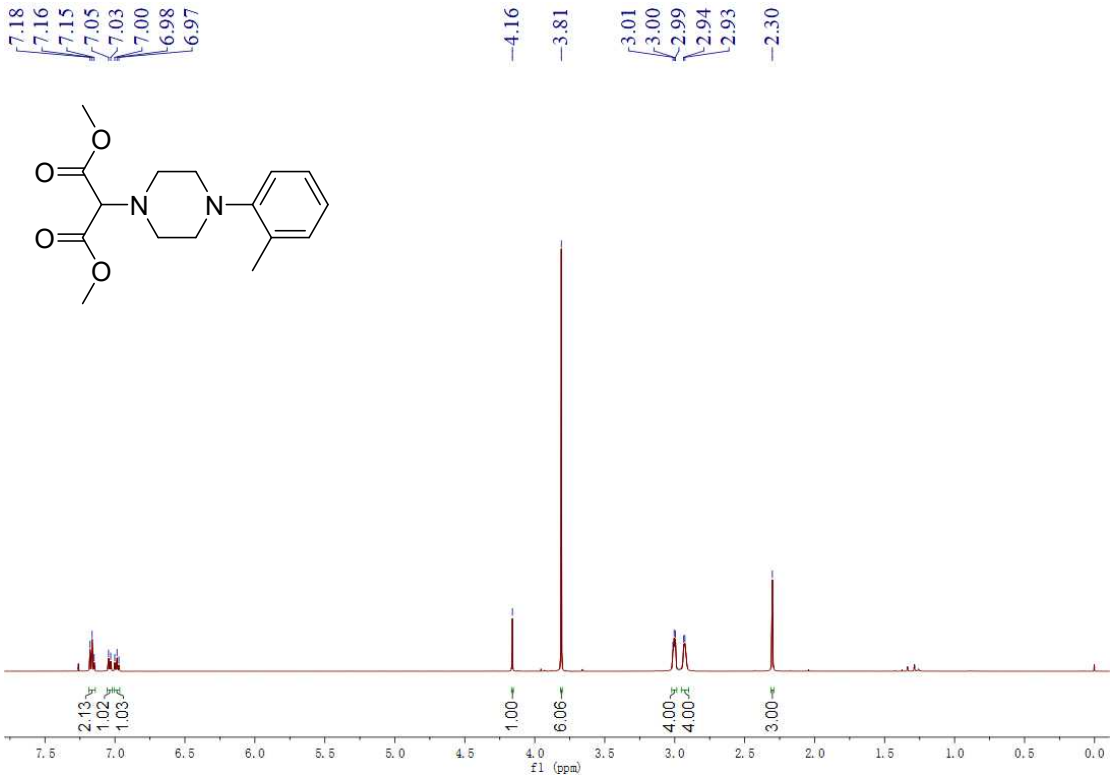
^{1}H NMR of dimethyl 2-(4-(4-acetylphenyl)piperazin-1-yl)malonate (5z)



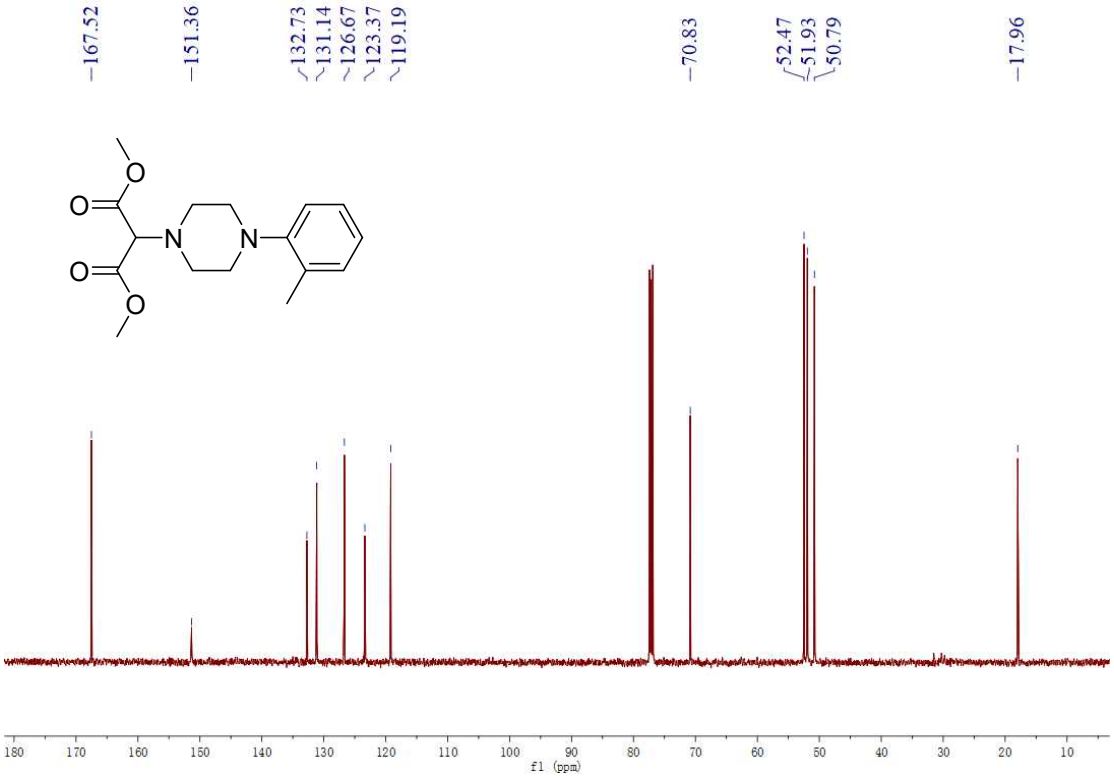
^{13}C NMR of dimethyl 2-(4-(4-acetylphenyl)piperazin-1-yl)malonate (5z)



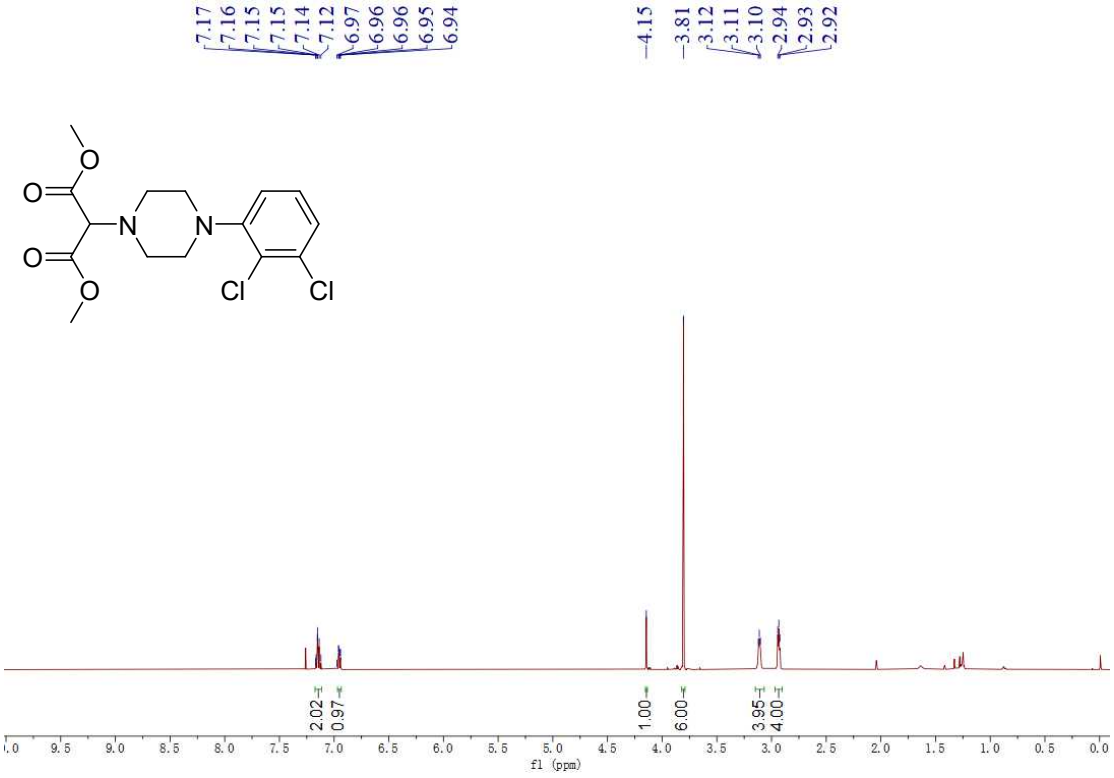
^{1}H NMR of dimethyl 2-(4-(o-tolyl)piperazin-1-yl)malonate (5aa)



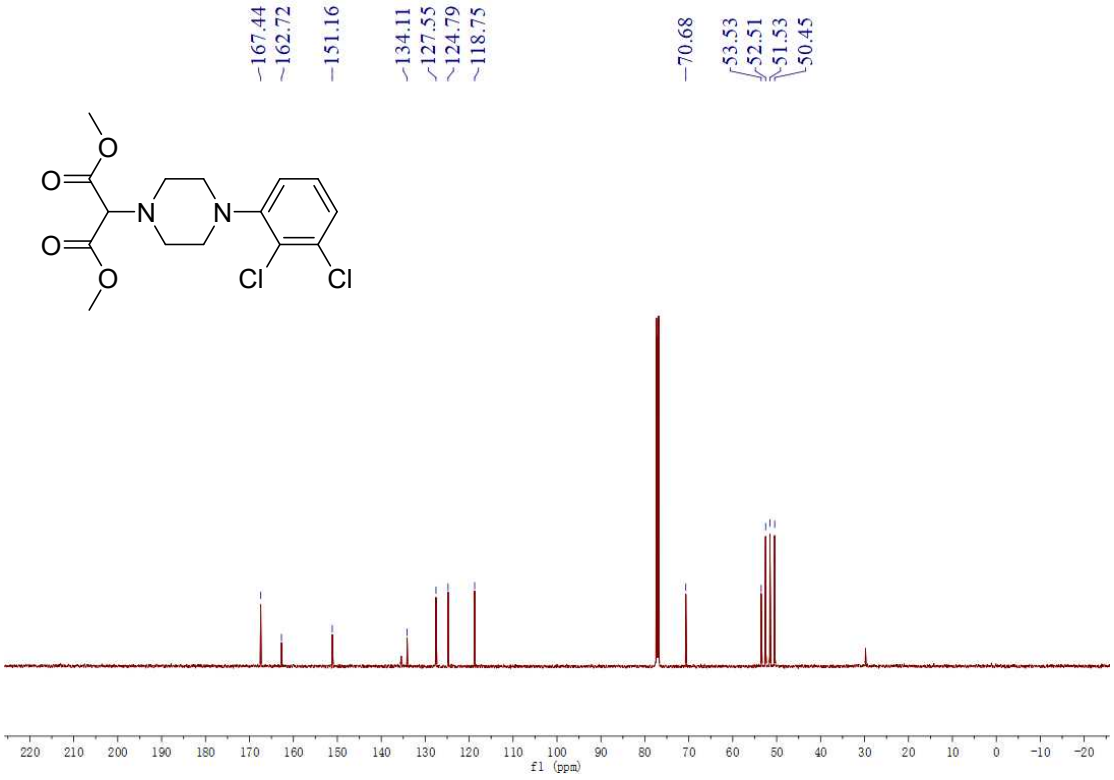
^{13}C NMR of dimethyl 2-(4-(o-tolyl)piperazin-1-yl)malonate (5aa)



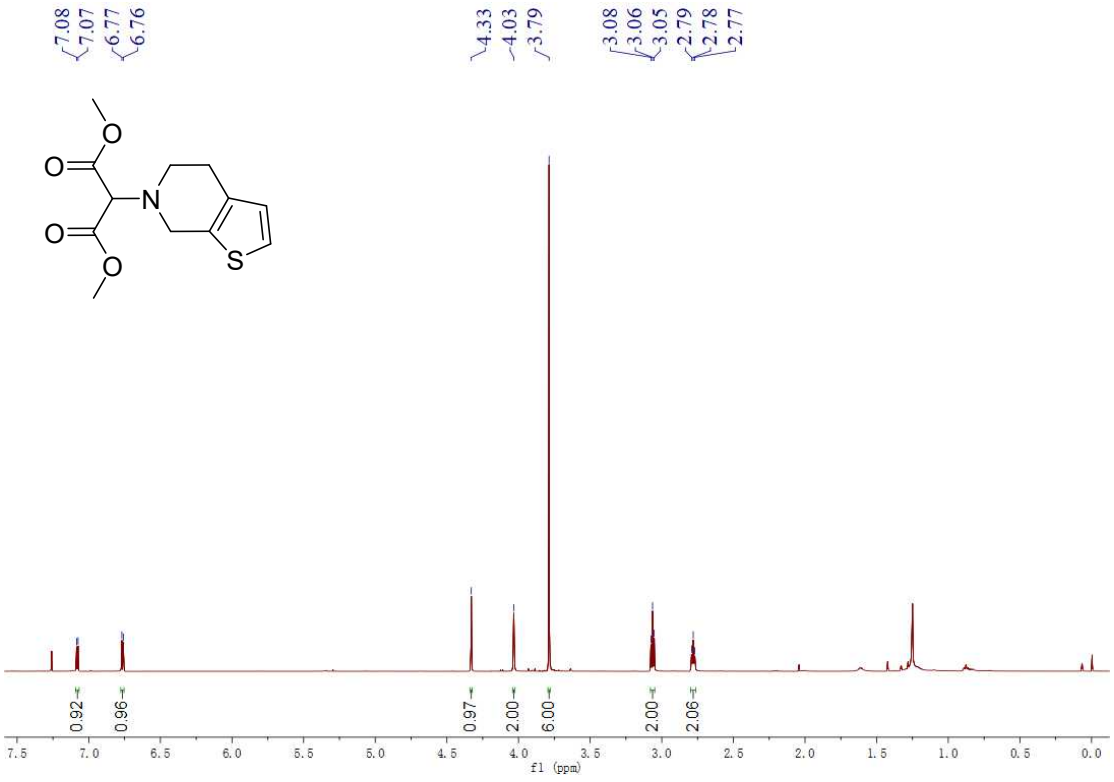
^{1}H NMR of dimethyl 2-(4-(2,3-dichlorophenyl)piperazin-1-yl)malonate (5ab)



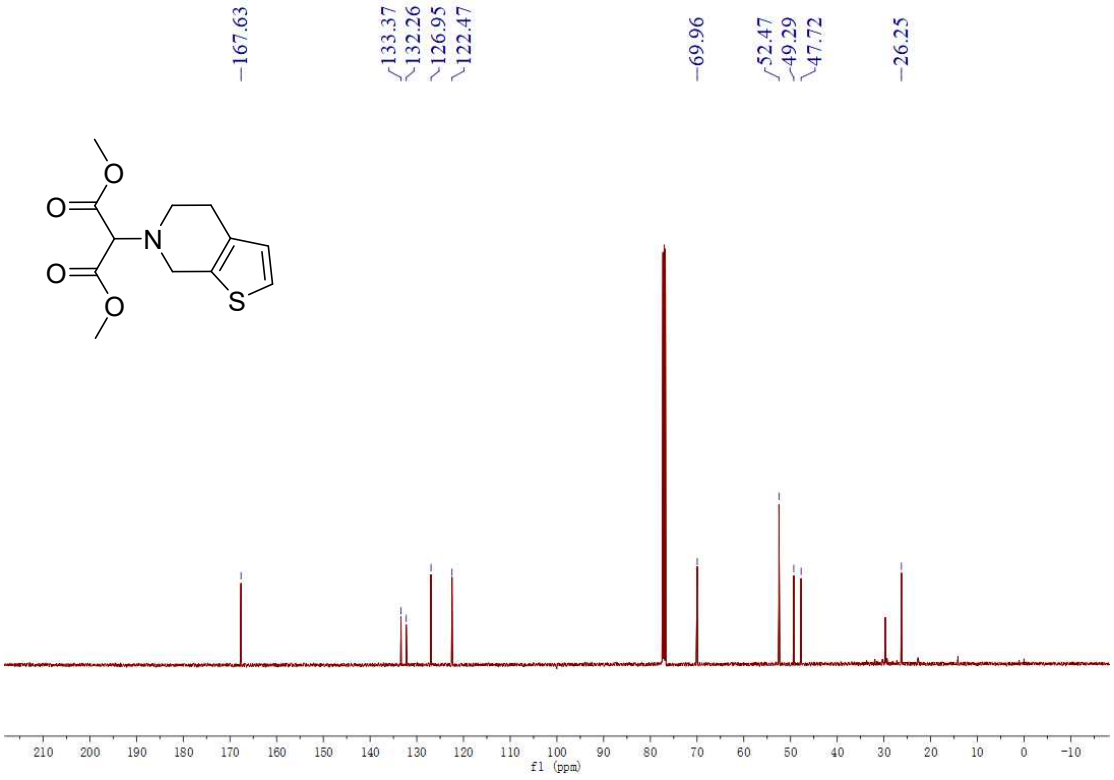
^{13}C NMR of dimethyl 2-(4-(2,3-dichlorophenyl)piperazin-1-yl)malonate (5ab)



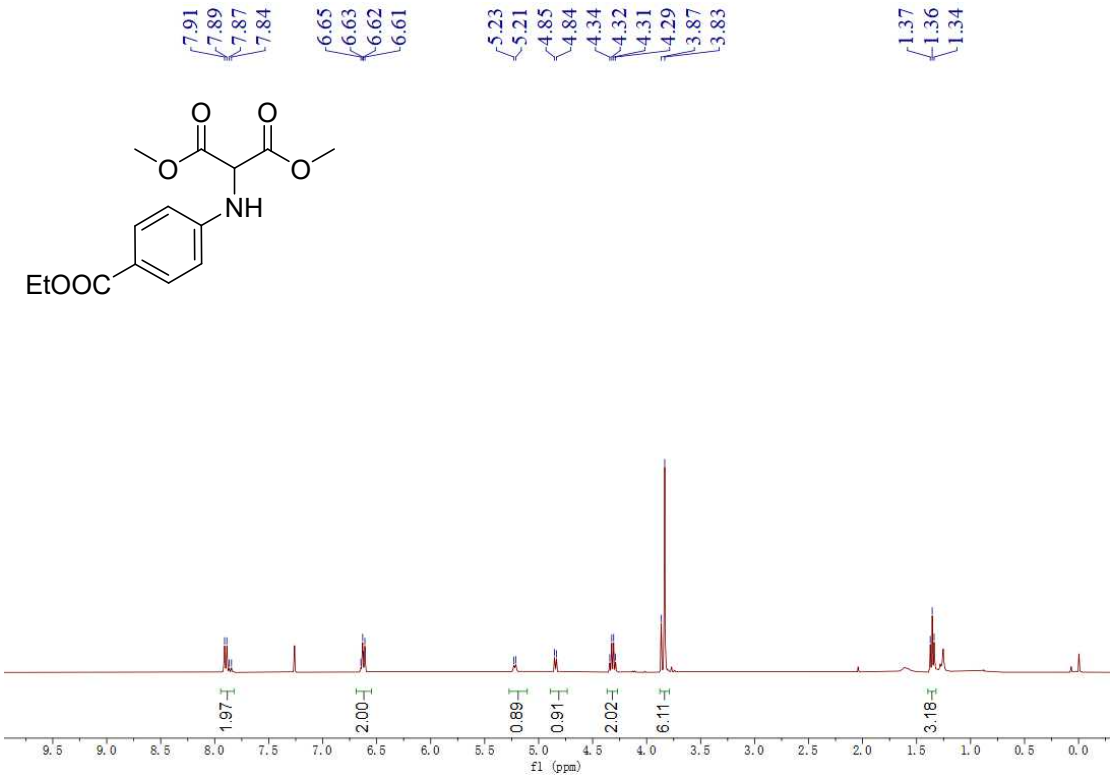
^{1}H NMR of dimethyl 2-(4,7-dihydrothieno[2,3-c]pyridin-6(5H)-yl)malonate (5ac)



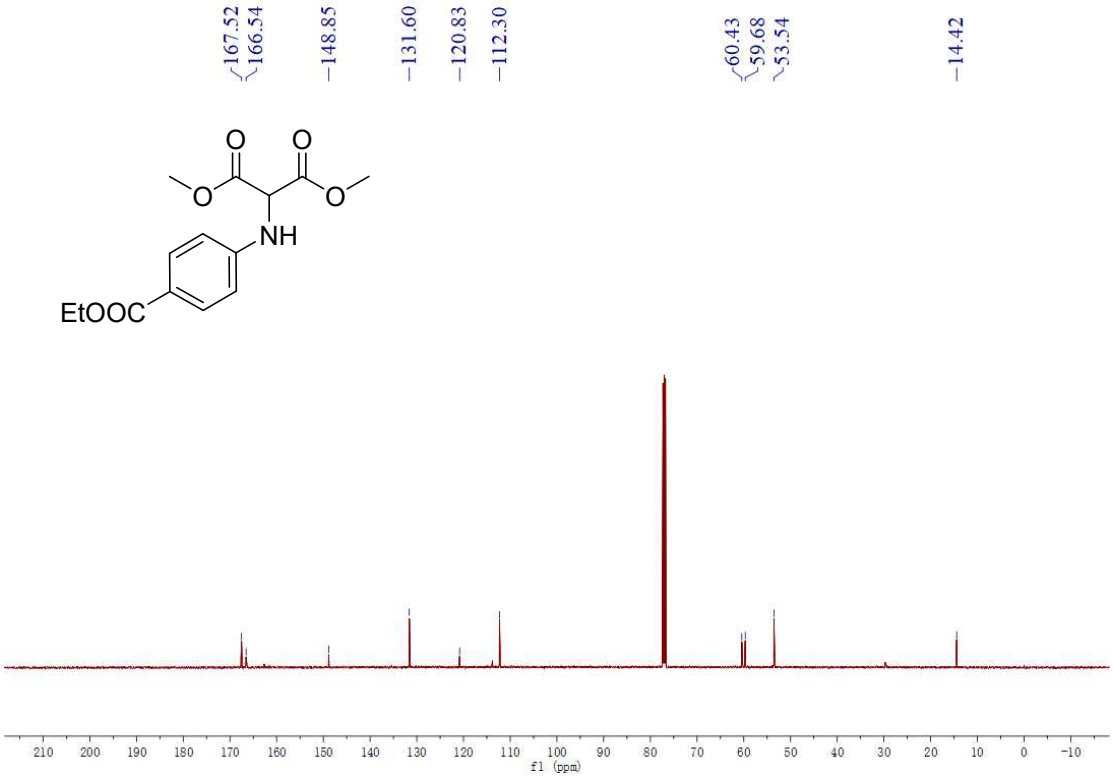
^{13}C NMR of dimethyl 2-(4,7-dihydrothieno[2,3-c]pyridin-6(5H)-yl)malonate (5ac)



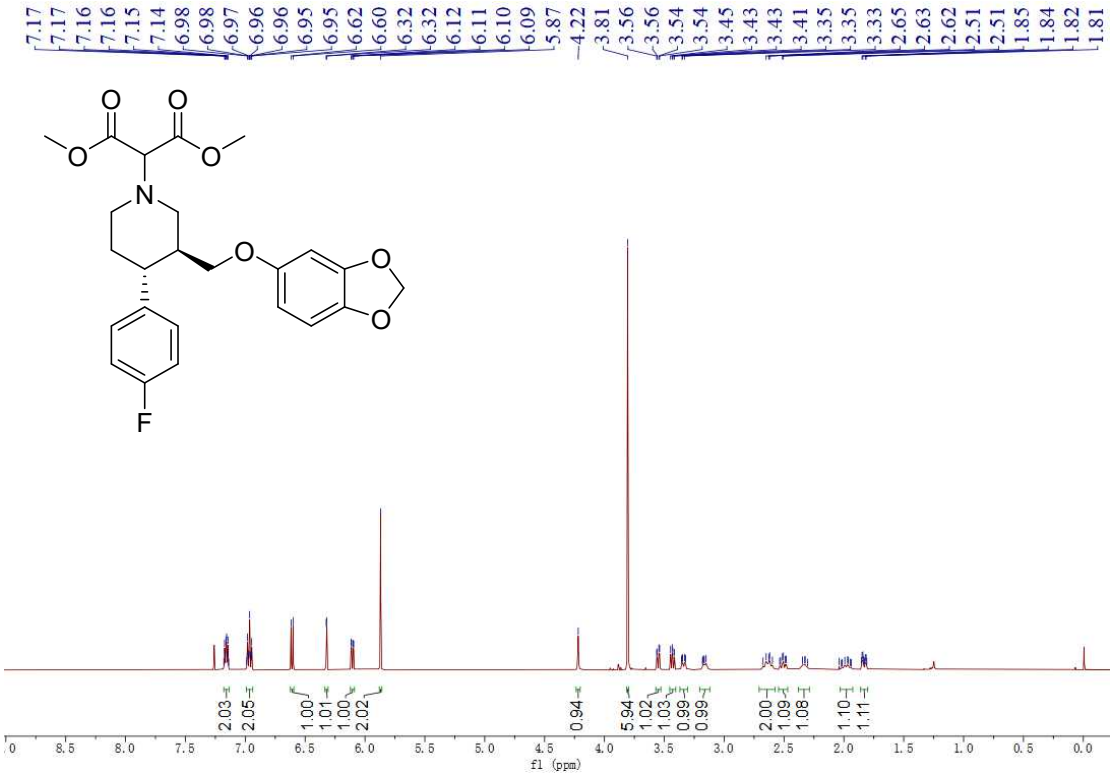
^{1}H NMR of dimethyl 2-((4-(ethoxycarbonyl)phenyl)amino)malonate (6)



^{13}C NMR of dimethyl 2-((4-(ethoxycarbonyl)phenyl)amino)malonate (6)

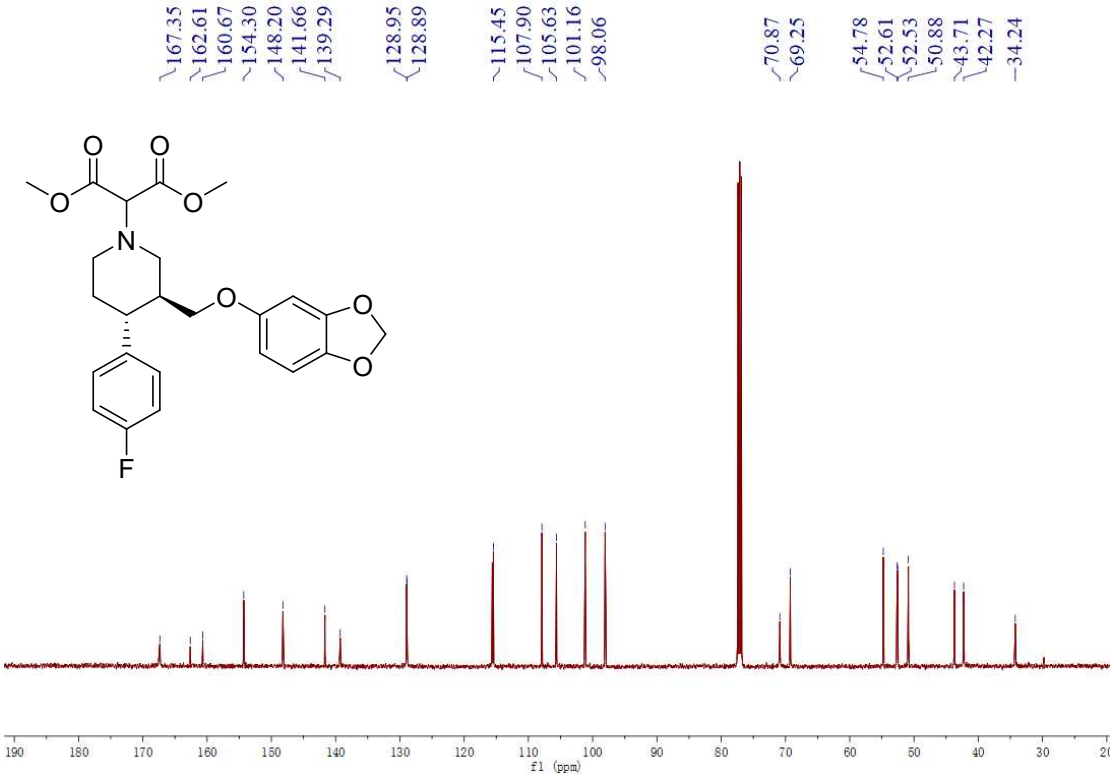


^{1}H NMR of 2-((3S,4R)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)malonate (7)

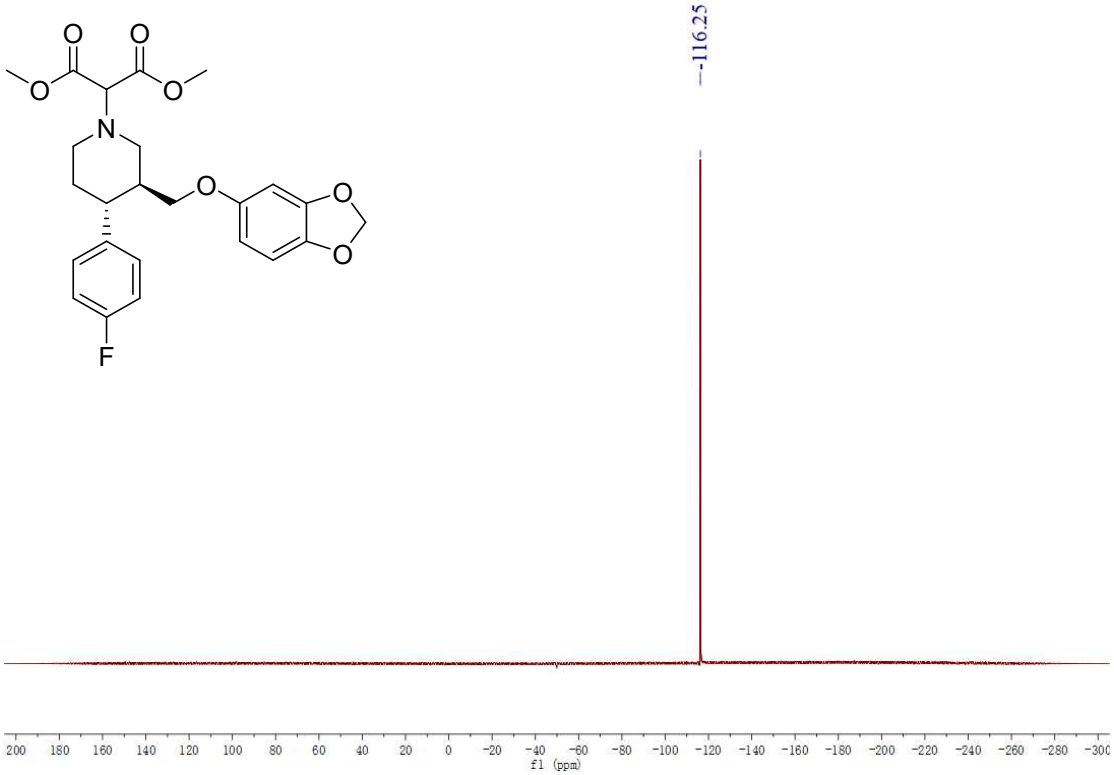


^{13}C NMR of 2-((3S,4R)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-

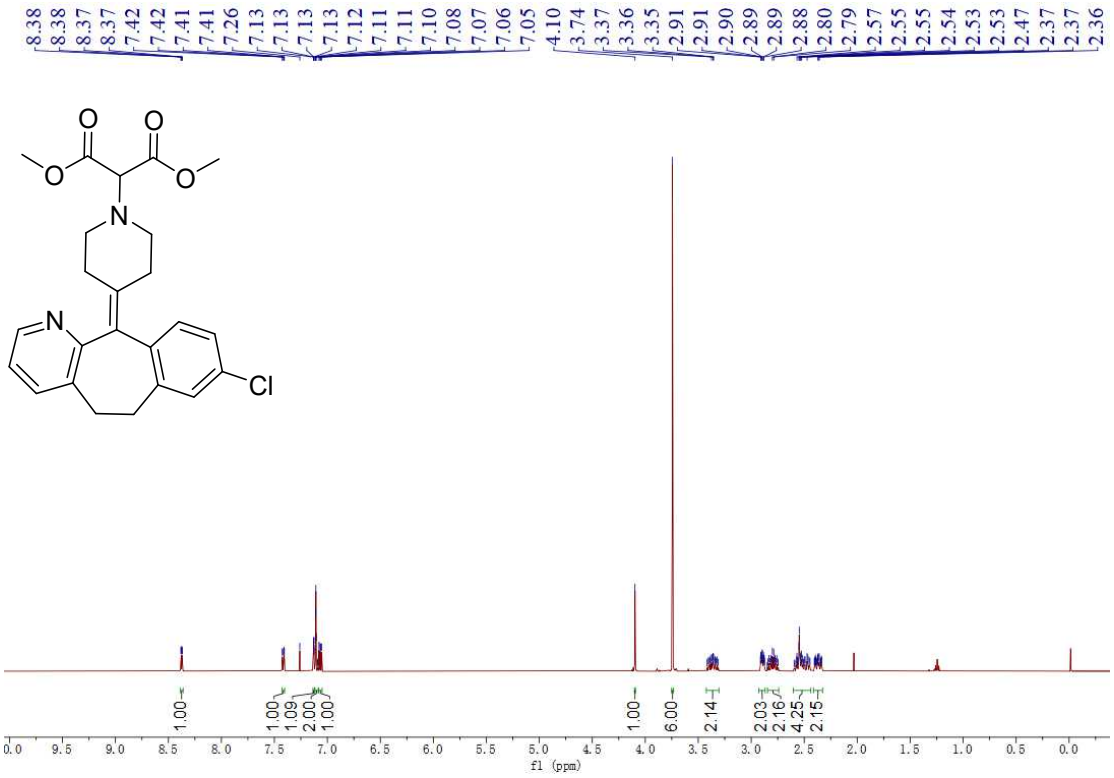
fluorophenyl)piperidin-1-yl)malonate (7)



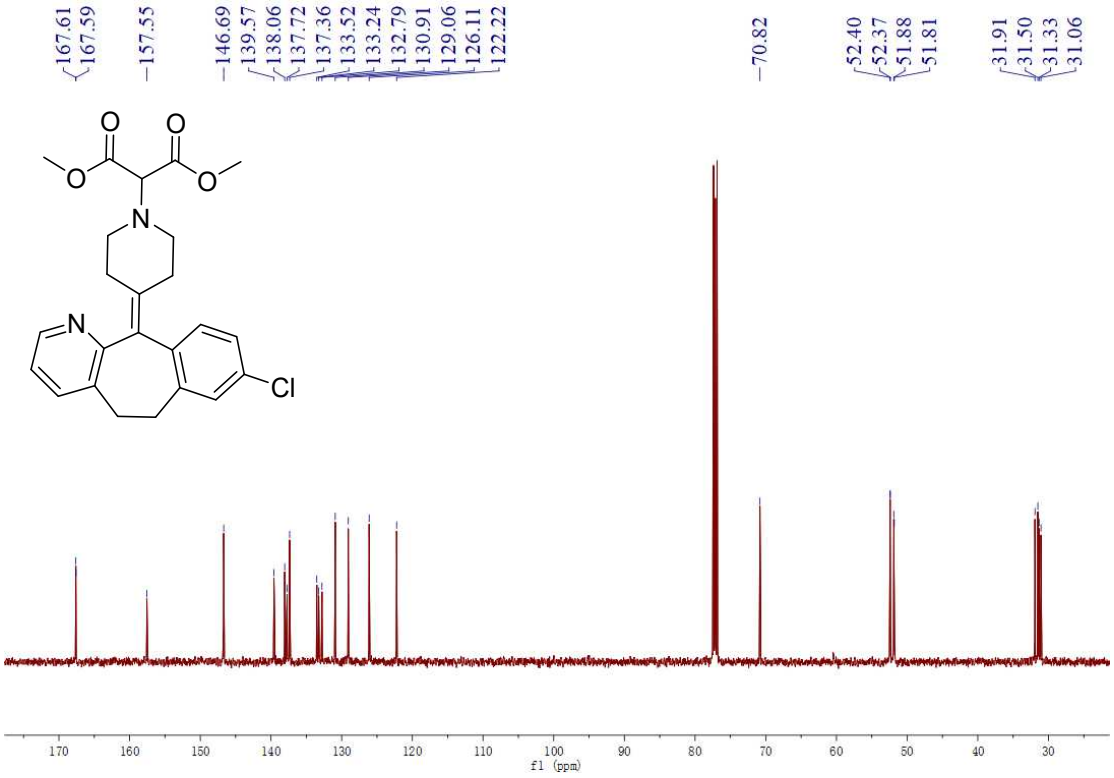
^{19}F NMR of 2-((3S,4R)-3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)malonate (7)



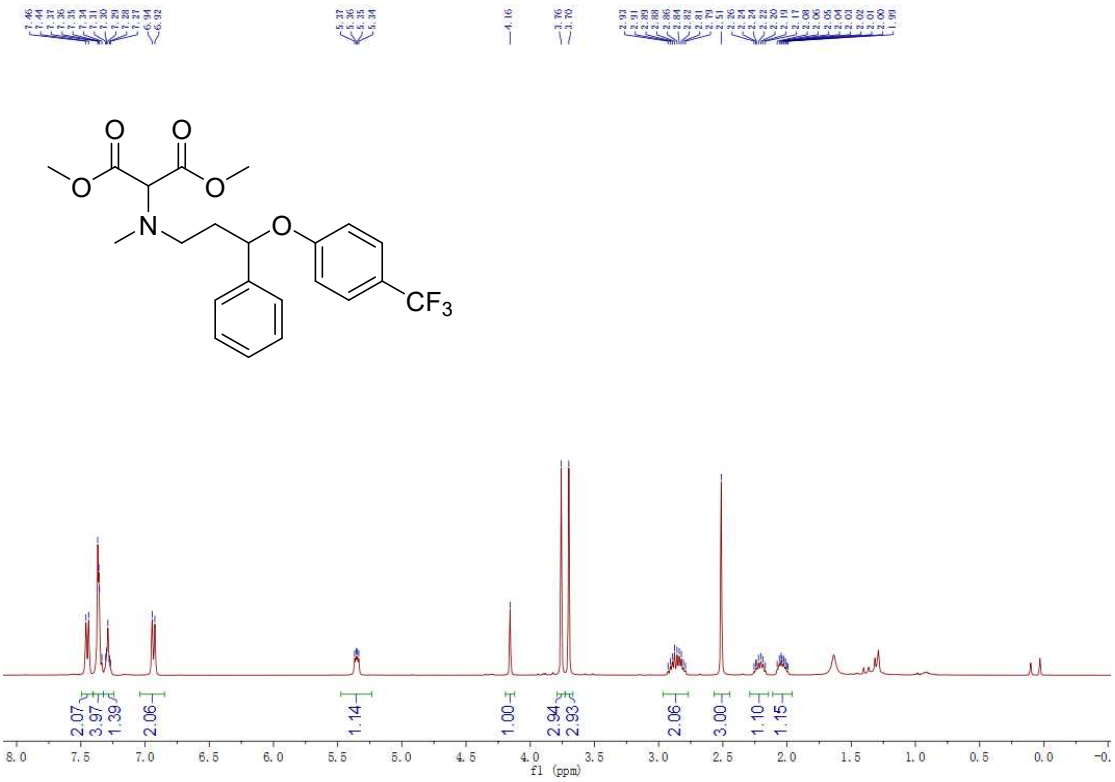
^{1}H NMR of 2-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)malonate (8)



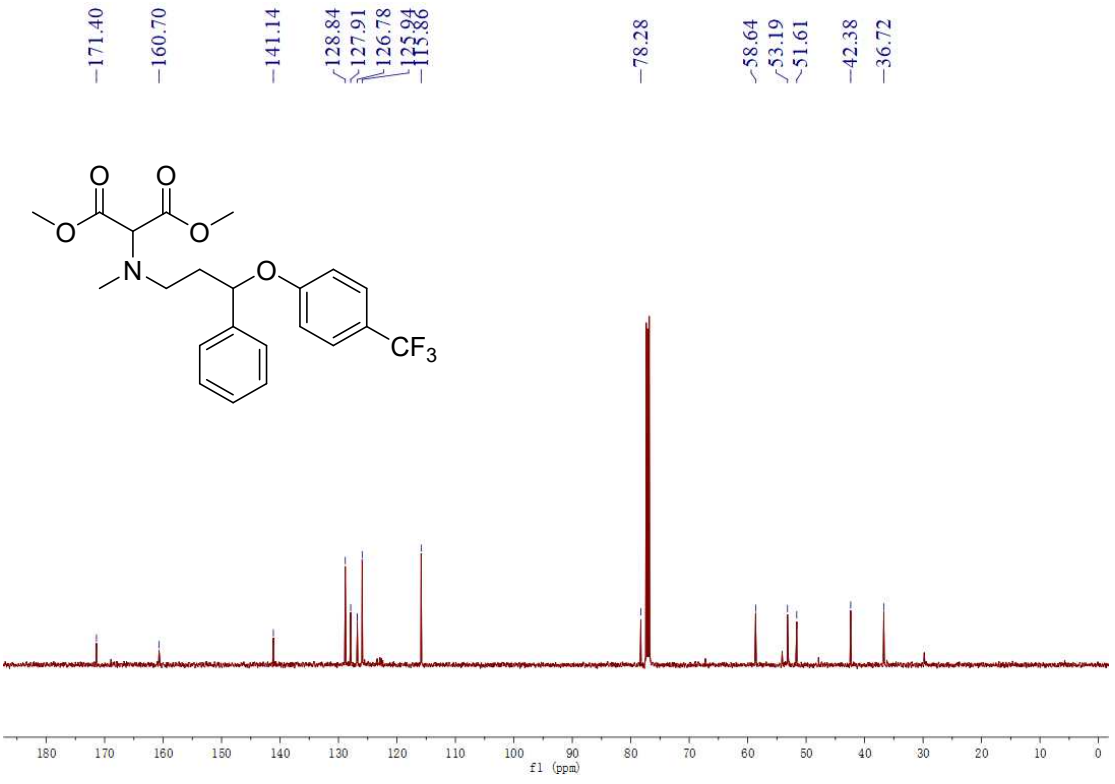
^{13}C NMR of 2-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)malonate (8)



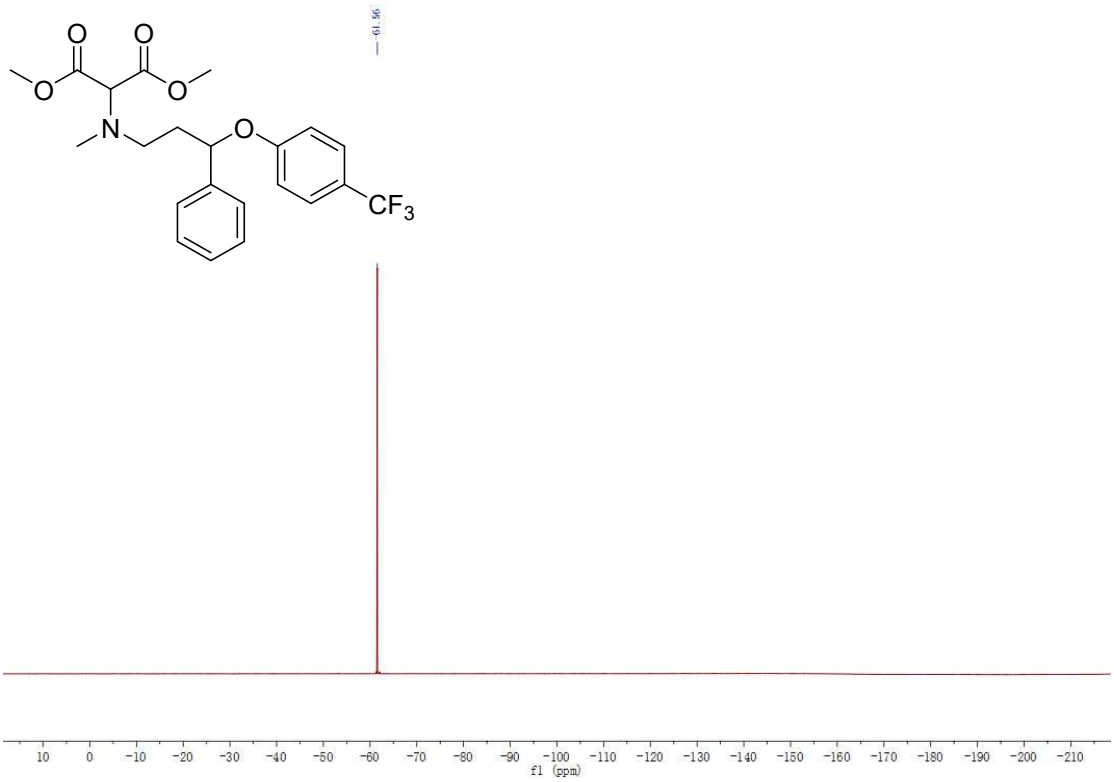
^{1}H NMR of dimethyl 2-(methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)amino)malonate (9)



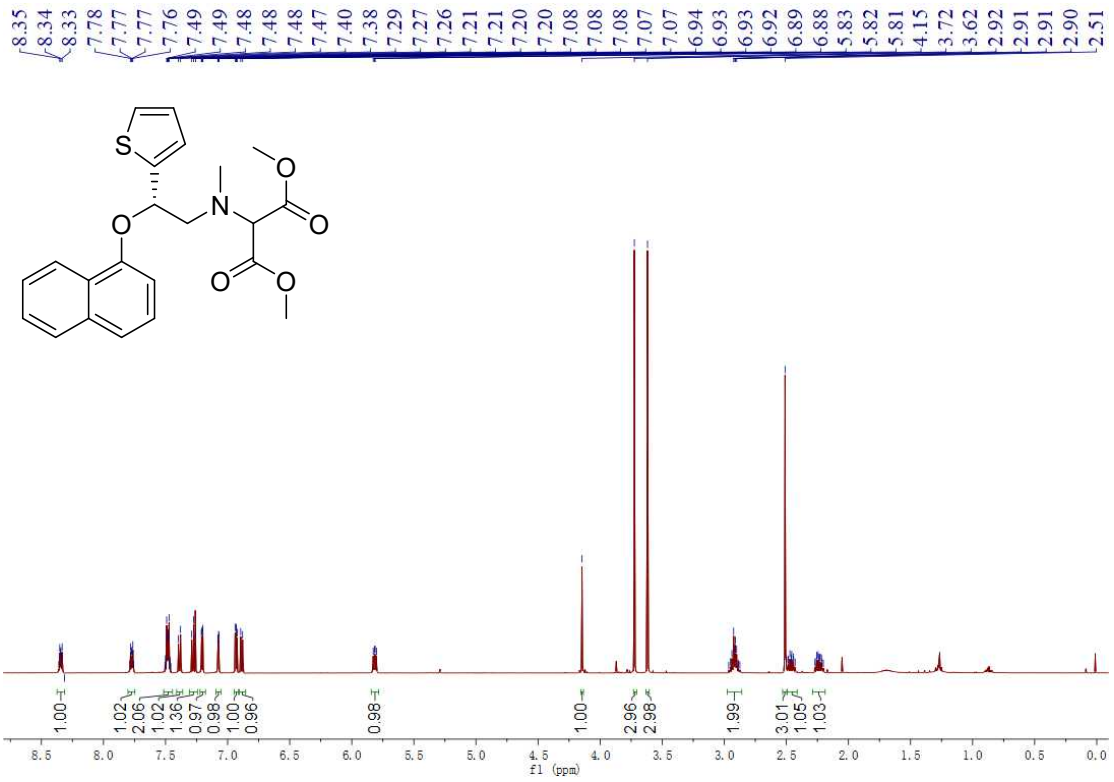
^{13}C NMR of dimethyl 2-(methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)amino)malonate (9)



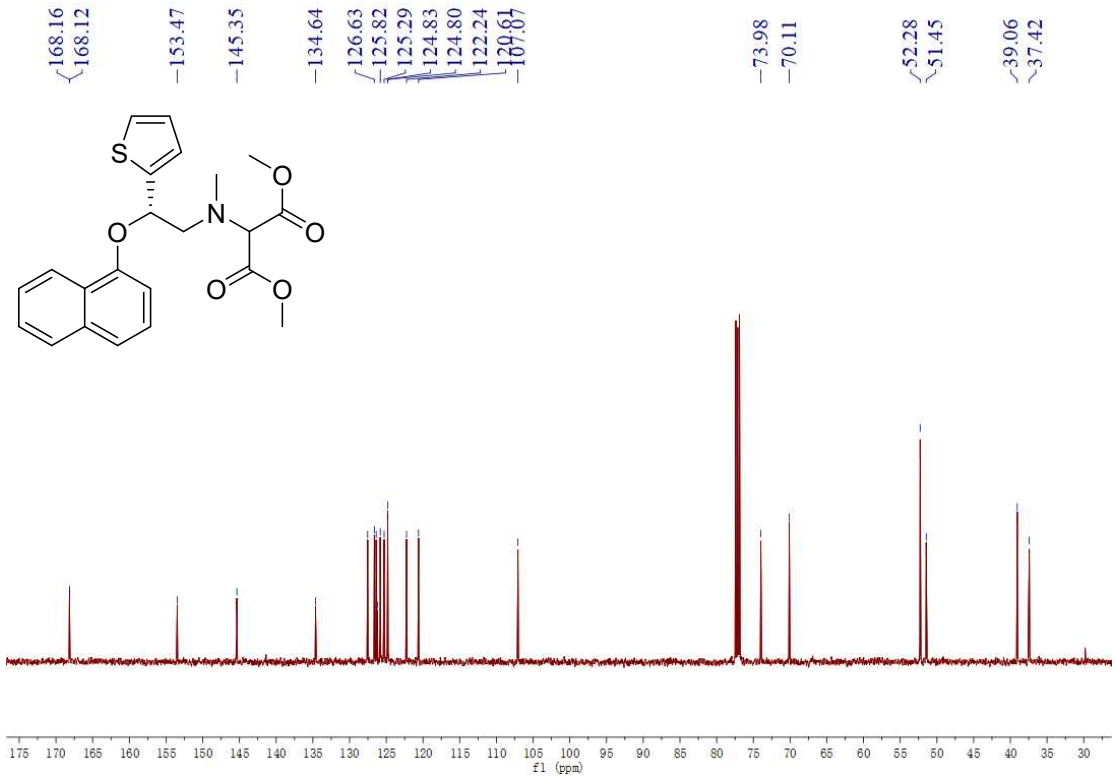
^{19}F NMR of dimethyl 2-(methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)amino)malonate (9)



^{1}H NMR of dimethyl (S)-2-(methyl(2-(naphthalen-1-yloxy)-2-(thiophen-2-yl)ethyl)amino)malonate (10)



^{13}C NMR of dimethyl (S)-2-(methyl(2-(naphthalen-1-yloxy)-2-(thiophen-2-yl)ethyl)amino)malonate (10)


168.16
168.12
153.47
145.35
134.64
126.63
125.82
125.29
124.83
124.80
122.24
120.61
107.07
73.98
70.11
52.28
51.45
39.06
37.42
S
O
N
O
O
O
O
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)