Supporting Information

General Remarks

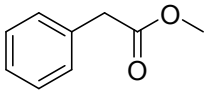
Most of chemicals were purchased from Sigma-Aldrich, Strem, Acros, TCI or Alfa, used as such unless stated otherwise and methyl benzylcarbamate was synthesized[10]. Solvents (Anhydrous and under inert atmosphere) were collected from The Solvent purification system by M BRAUN and used under standard schlenk technique. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR). Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) dd (doublet of doublet), m (multiplet) and br. s (broad singlet). GC-yields were calculated using isooctane as internal standard. All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

General Procedure

A 4 mL screw-cap vial was charged with $Pd(TFA)_2$ (1.66 mg, 2 mol%), DPPP (4.1 mg, 4 mol%), DMC/MeOH (1.5/1.0 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After benzyl alcohol (0.25 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and 20 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 135 ^{o}C for 24 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 100:1).

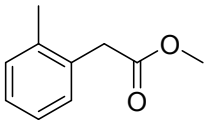
Analytic Data of Products

Methyl 2-phenylacetate



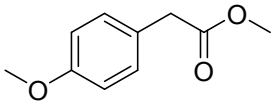
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 – 7.14 (m, 5H), 3.61 (s, 3H), 3.55 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.02, 134.01, 129.26, 128.60, 127.12, 52.04, 41.22.

Methyl 2-(*o*-tolyl)acetate



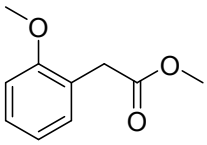
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 1.9 Hz, 4H), 3.70 (s, 3H), 3.65 (s, 2H), 2.32 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.95, 136.84, 132.72, 130.35, 130.16, 127.42, 126.14, 52.02, 39.06, 19.59.

Methyl 2-(4-methoxyphenyl)acetate



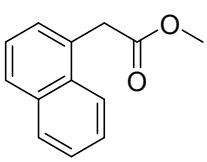
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 – 7.09 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.79 (d, *J* = 0.6 Hz, 3H), 3.68 (d, *J* = 0.6 Hz, 3H), 3.57 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.37, 158.70, 130.27, 126.04, 114.00, 55.25, 52.00, 40.28.

Methyl 2-(2-methoxyphenyl)acetate



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 1H), 7.10 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.89 – 6.74 (m, 2H), 3.73 (s, 3H), 3.61 (s, 3H), 3.56 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.31, 157.51, 130.86, 128.57, 123.01, 120.51, 110.50, 55.46, 51.90, 35.76.

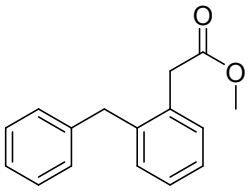
Methyl 2-(naphthalen-1-yl)acetate



^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 – 7.99 (m, 1H), 7.92 – 7.86 (m, 1H), 7.85 – 7.79 (m, 1H), 7.60 – 7.40 (m, 4H), 4.10 (s, 2H), 3.70 (s, 3H).

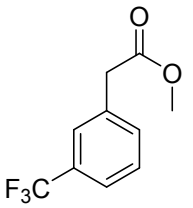
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.07, 133.86, 132.14, 130.55, 128.78, 128.15, 128.06, 126.45, 125.84, 125.53, 124.99, 123.81, 52.20, 39.10.

Methyl 2-(2-benzylphenyl)acetate



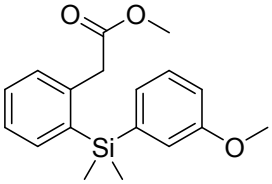
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 6.97 (m, 9H), 3.96 (s, 2H), 3.51 (d, *J* = 0.9 Hz, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.93, 140.13, 139.27, 132.96, 130.91, 130.80, 128.81, 128.50, 127.63, 126.86, 126.16, 52.02, 39.15, 38.77.

Methyl 2-(3-(trifluoromethyl)phenyl)acetate



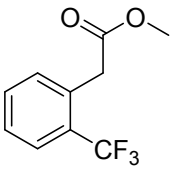
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.56 – 7.41 (m, 4H), 3.71 (s, 3H), 3.69 (s, 2H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.24 , 134.83 , 133.35 – 132.13 (m), 130.93 (d, *J* = 32.3 Hz), 129.01 , 126.31 – 125.52 (m), 124.05 (q, *J* = 3.9 Hz), 52.21 , 40.79 .

Methyl 2-(2-((3-methoxyphenyl)dimethylsilyl)phenyl)acetate



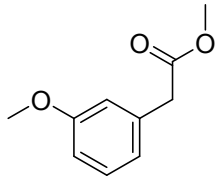
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (ddd, *J* = 7.3, 1.9, 0.8 Hz, 1H), 7.49 – 7.37 (m, 1H), 7.36 – 7.26 (m, 3H), 7.09 (dt, *J* = 7.2, 1.0 Hz, 1H), 7.05 (ddd, *J* = 2.7, 1.0, 0.5 Hz, 1H), 6.94 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.80 (s, 3H), 3.63 (s, 2H), 3.59 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 173.10, 160.15, 141.29, 141.00, 137.91, 136.78, 131.51, 130.88, 130.26, 127.54, 127.40, 120.61, 115.47, 56.13, 52.86, 42.35, 0.00.

Methyl 2-(2-(trifluoromethyl)phenyl)acetate



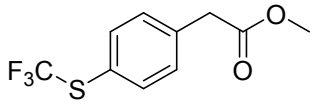
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 1H), 7.56 – 7.48 (m, 1H), 7.43 – 7.35 (m, 2H), 3.84 (p, *J* = 1.3 Hz, 2H), 3.71 (s, 3H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.13 , 132.51 , 131.92 (d, *J* = 1.4 Hz), 128.98 (d, *J* = 30.1 Hz), 127.41 , 126.09 (q, *J* = 5.5 Hz), 122.47 , 52.19 , 38.04 (d, *J* = 2.0 Hz).

Methyl 2-(3-methoxyphenyl)acetate



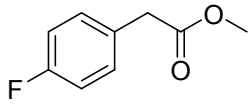
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.24 – 7.07 (m, 1H), 6.89 – 6.63 (m, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.52 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.89, 159.73, 135.40, 129.56, 121.60, 114.92, 112.65, 55.20, 52.06, 41.25.

Methyl 2-(4-((trifluoromethyl)thio)phenyl)acetate



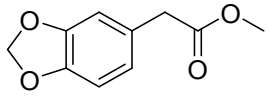
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 – 7.54 (m, 2H), 7.39 – 7.30 (m, 2H), 3.71 (s, 3H), 3.66 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.19, 137.11, 136.51, 131.60, 130.46, 127.52, 123.14, 123.11, 52.21, 40.77.

Methyl 2-(4-fluorophenyl)acetate



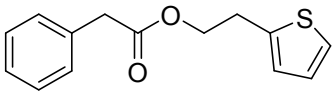
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 2H), 7.00 – 6.87 (m, 2H), 3.62 (s, 3H), 3.52 (d, *J* = 0.7 Hz, 2H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.87 , 162.04 (d, *J* = 245.4 Hz), 130.81 (d, *J* = 8.1 Hz), 129.67 (d, *J* = 3.3 Hz), 115.42 (d, *J* = 21.5 Hz), 52.08 , 40.28

Methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate



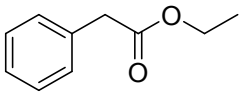
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.84 – 6.64 (m, 3H), 5.93 (s, 2H), 3.69 (s, 3H), 3.53 (t, *J* = 0.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.09, 147.77, 146.73, 127.54, 122.38, 109.71, 108.29, 101.03, 52.04, 40.78.

2-(Thiophen-2-yl)ethyl 2-phenylacetate

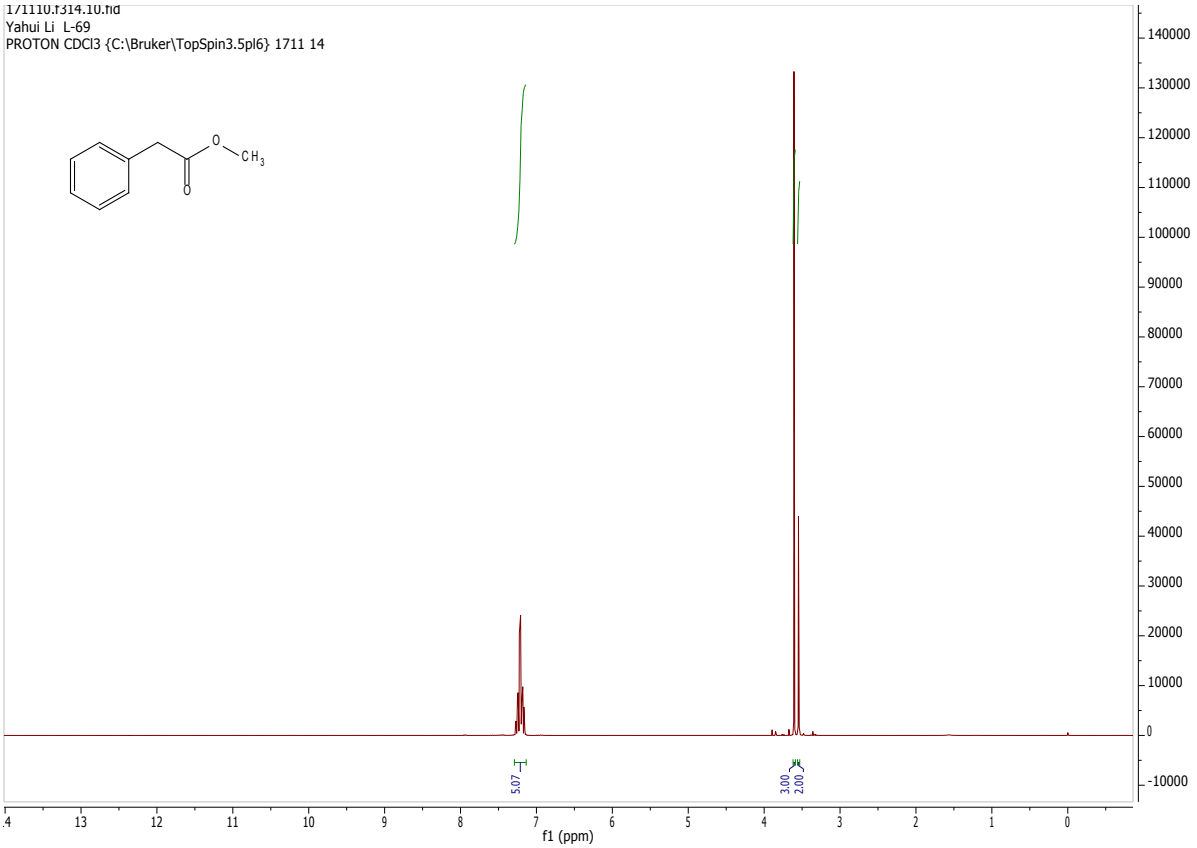


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.10 (m, 6H), 6.91 – 6.70 (m, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 3.54 (s, 2H), 2.94 – 2.75 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.46, 137.91, 133.99, 129.28, 128.59, 128.24, 127.09, 125.54, 121.63, 64.69, 41.48, 29.53.

Ethyl 2-phenylacetate



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 – 7.08 (m, 5H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 2H), 1.18 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.61, 134.17, 129.24, 128.54, 127.03, 60.85, 41.45, 14.18.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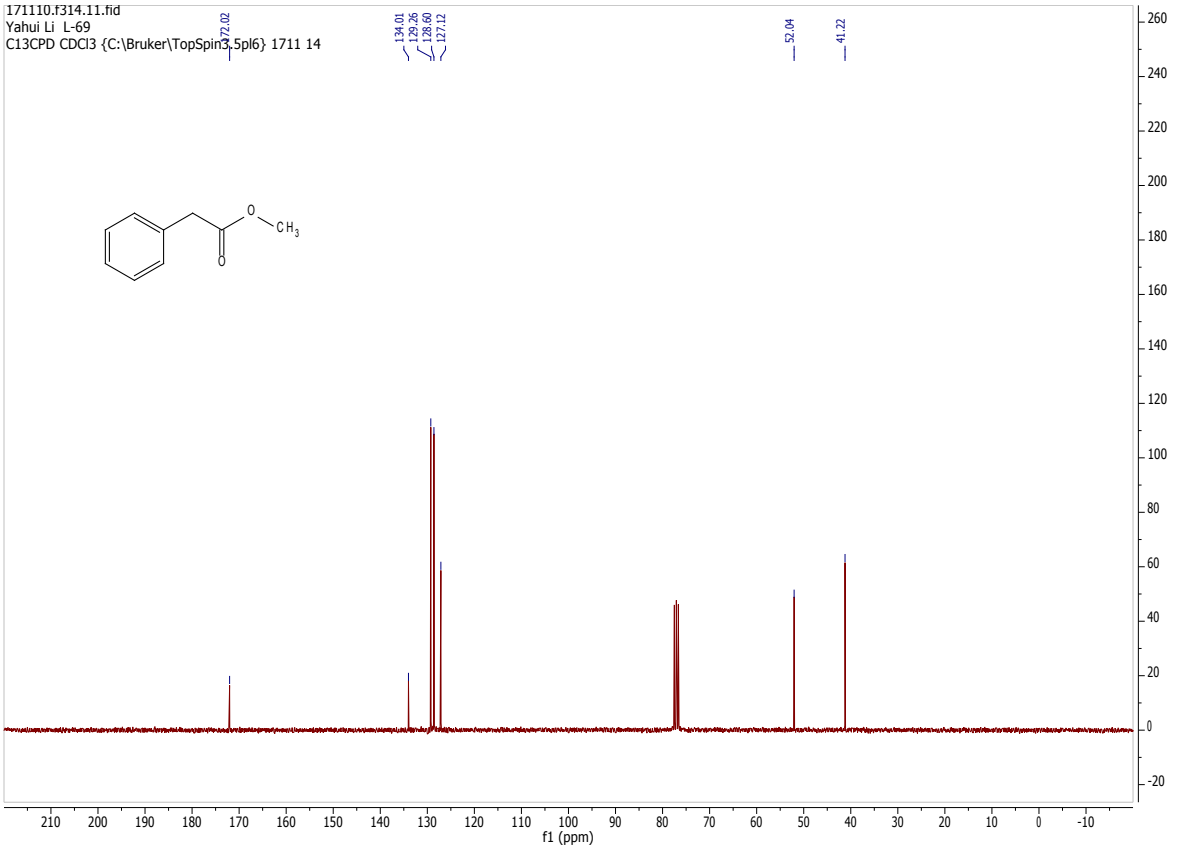
2.00
f1 (ppm)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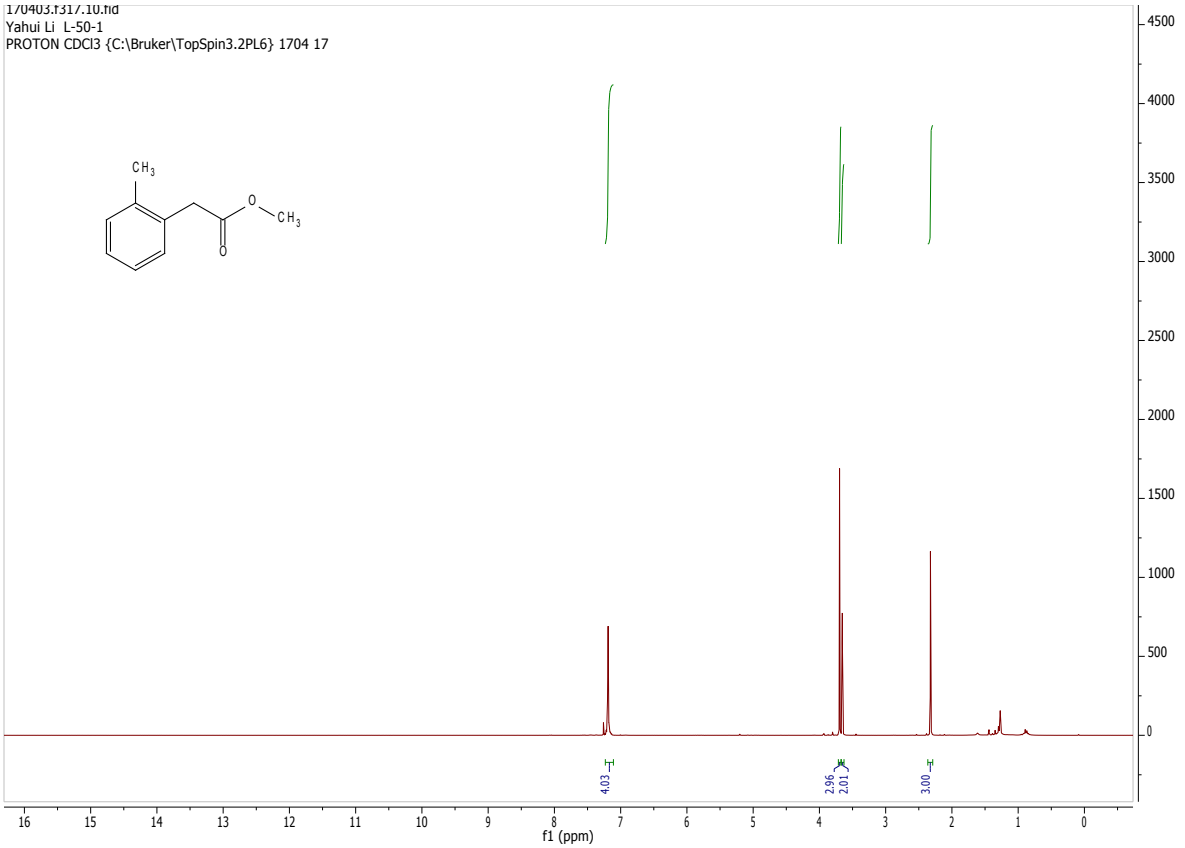
O
f1 (ppm)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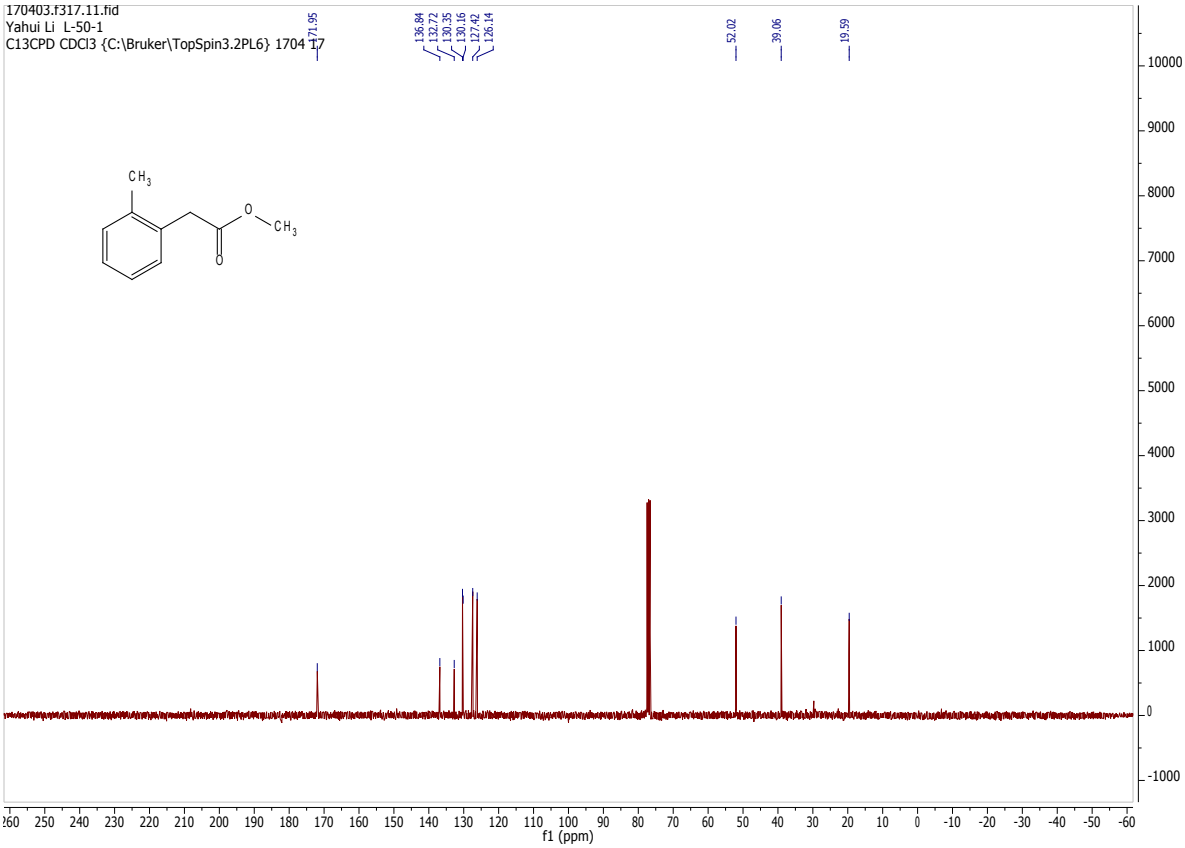
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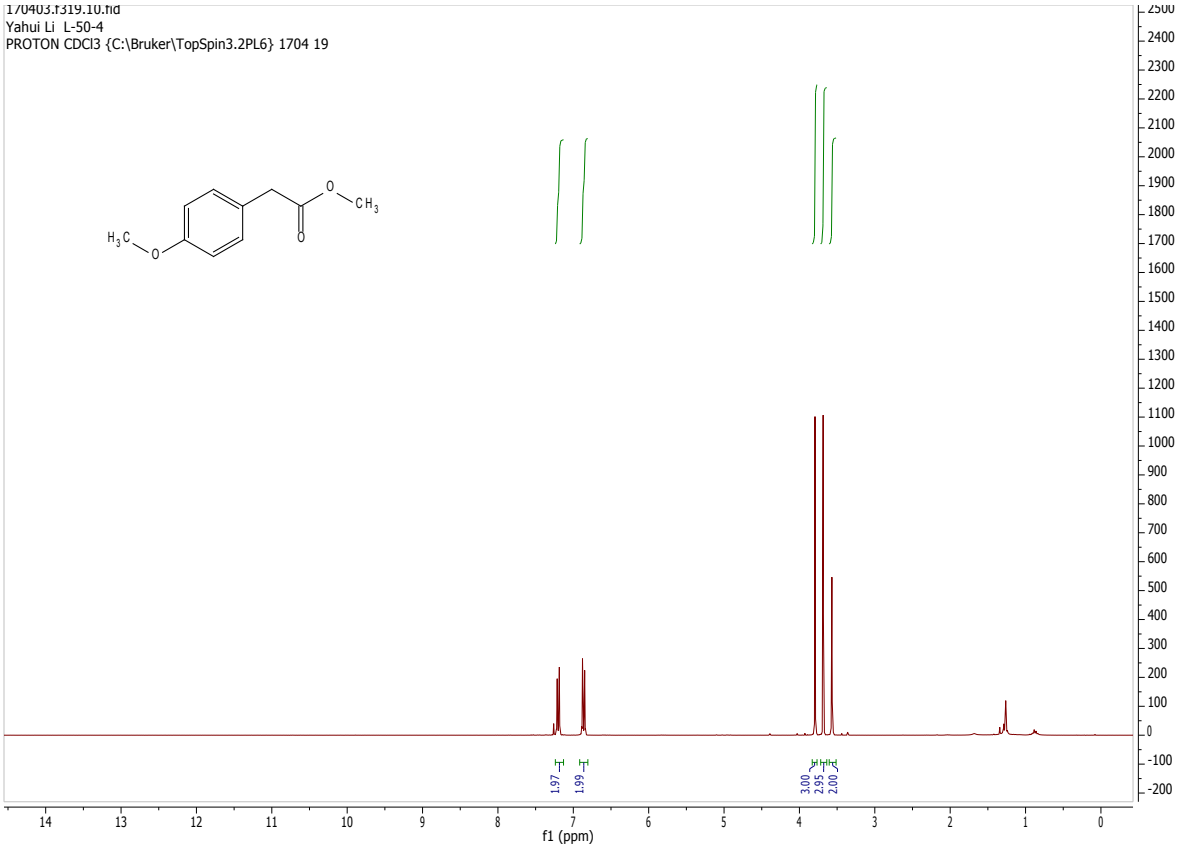
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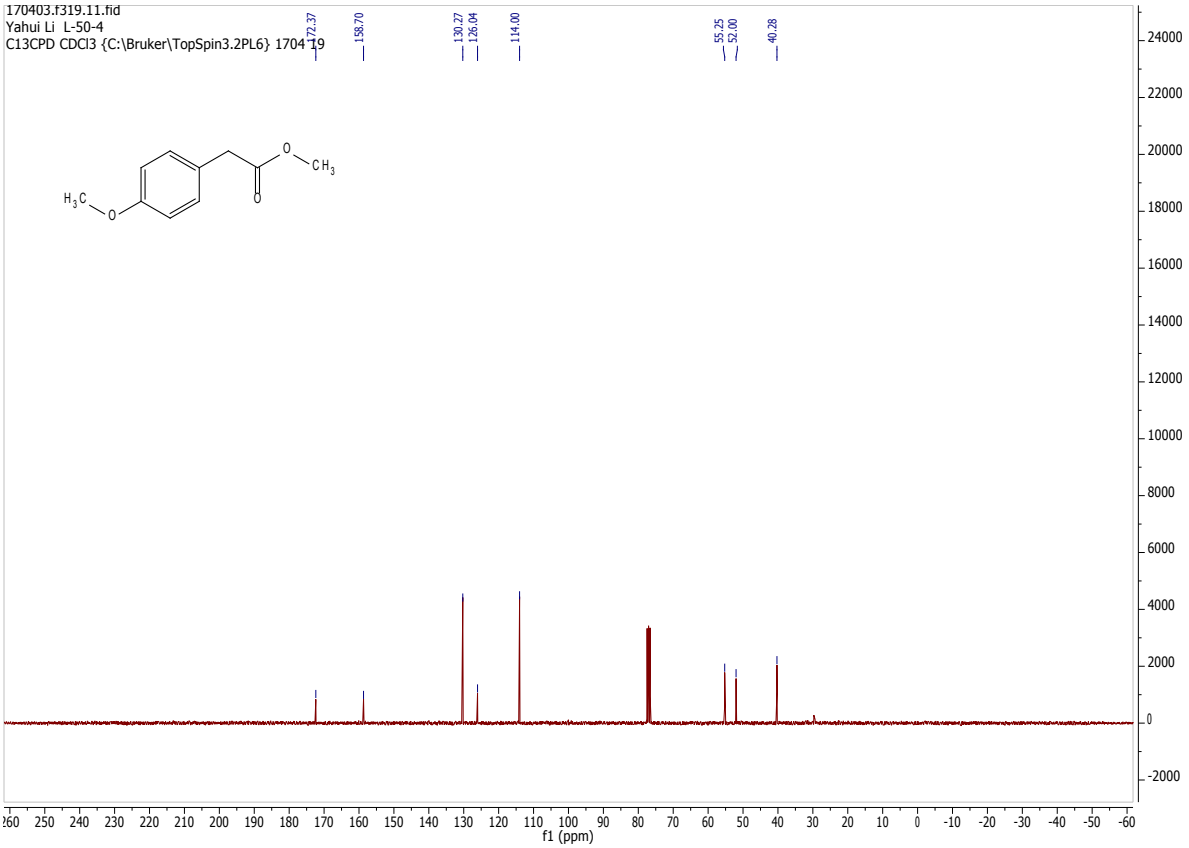
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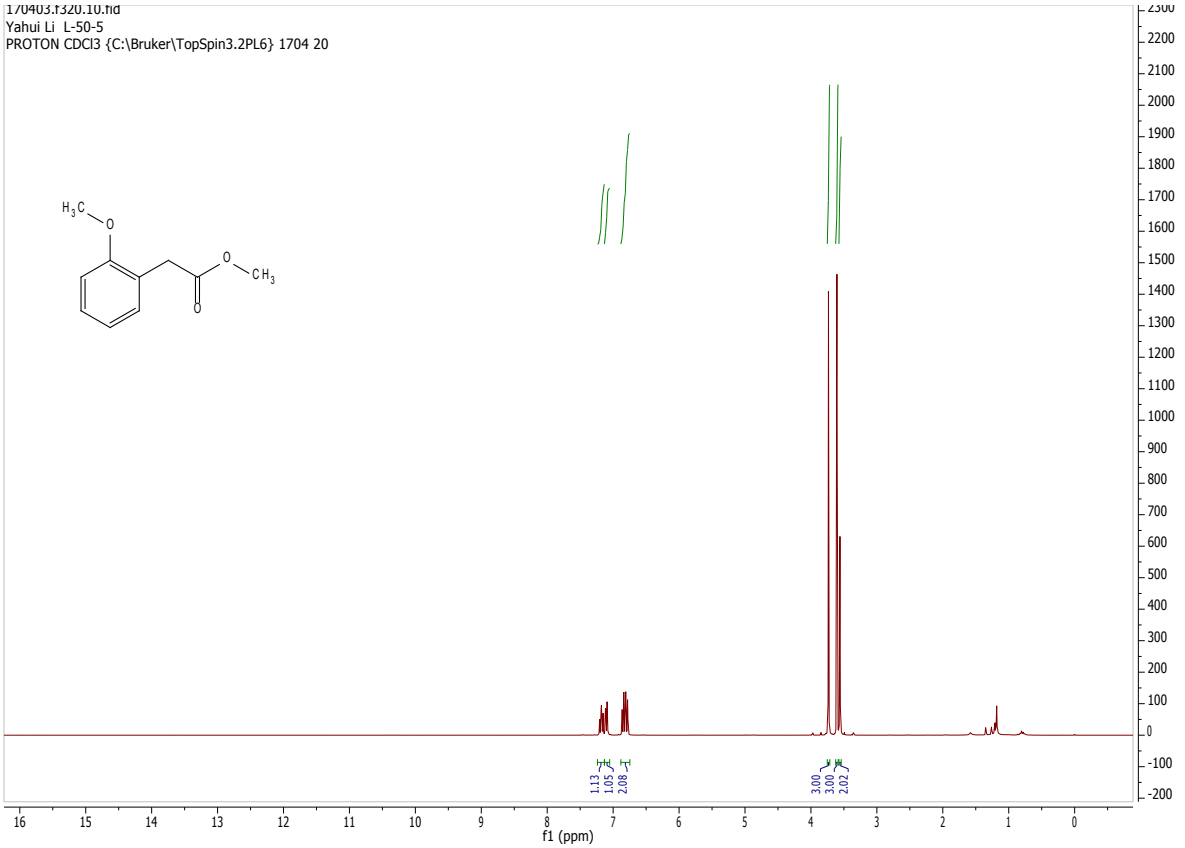
O
f1 (ppm)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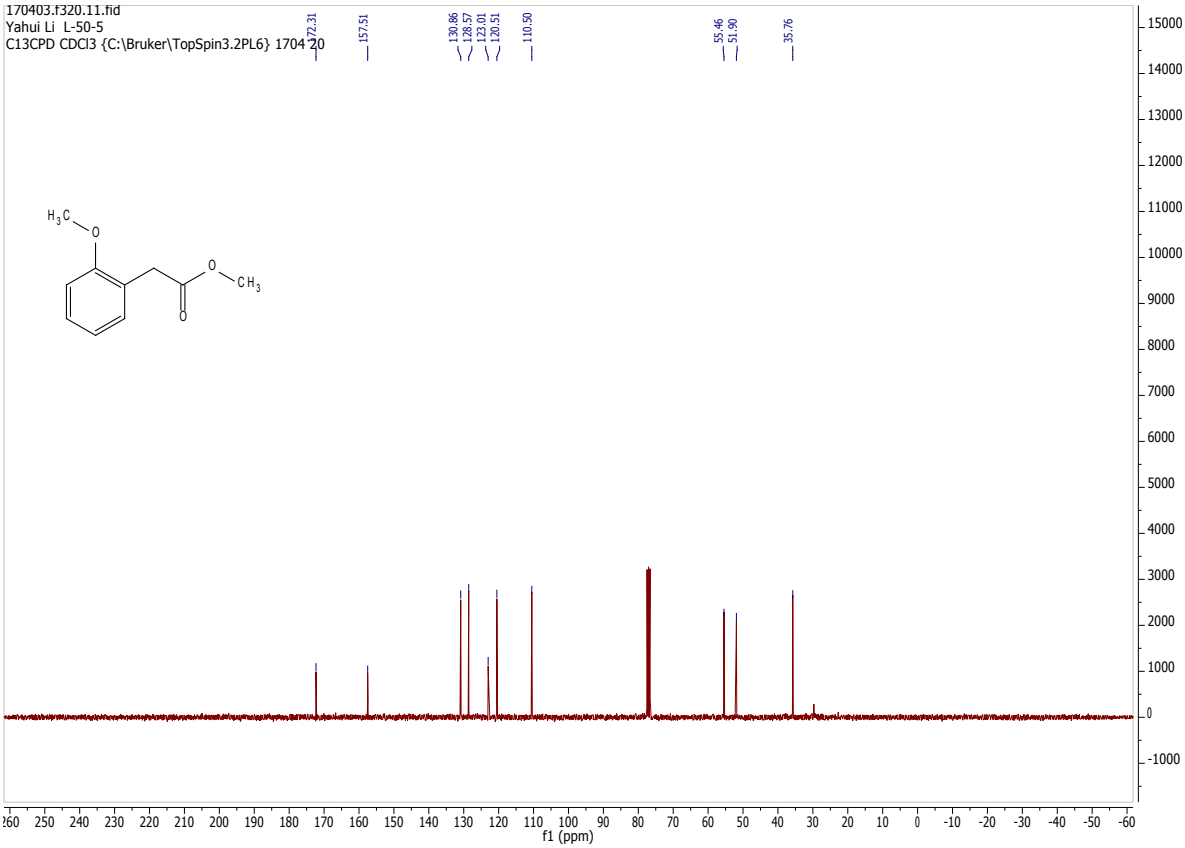
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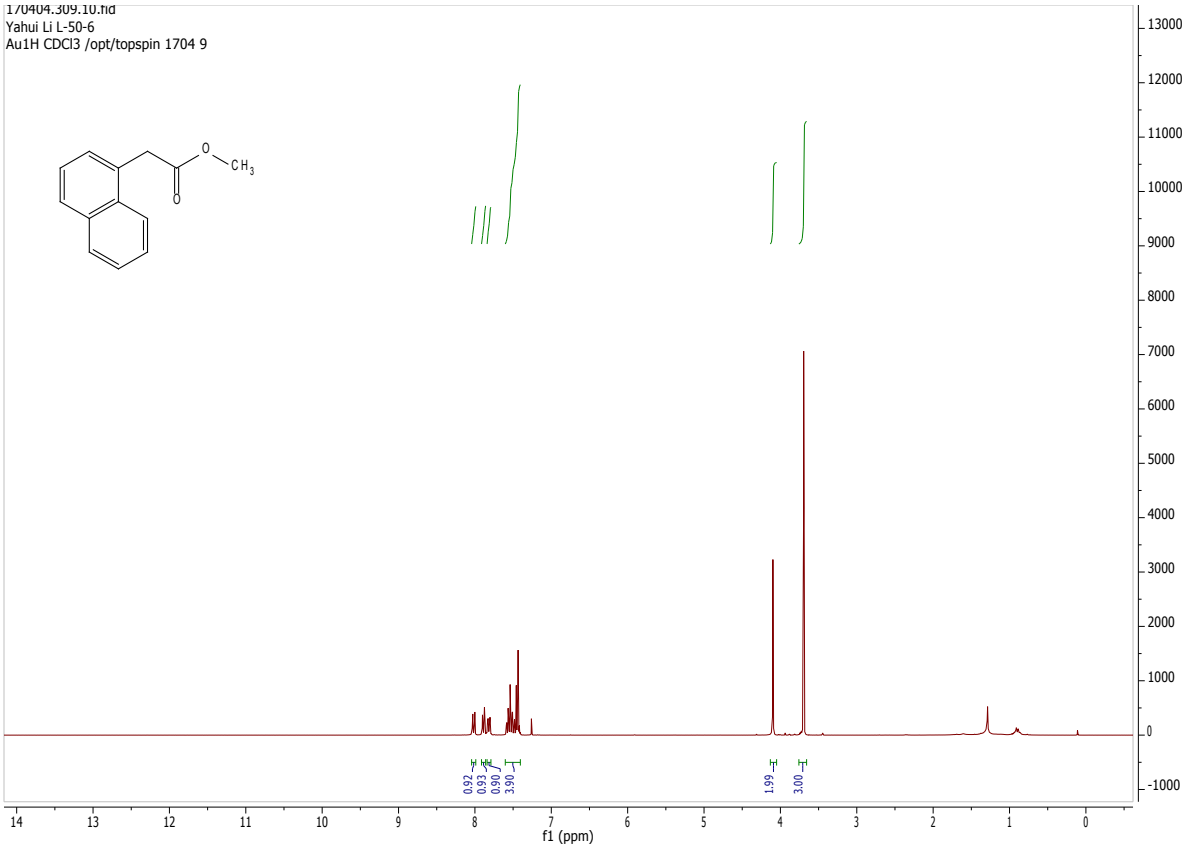
35.76
f1 (ppm)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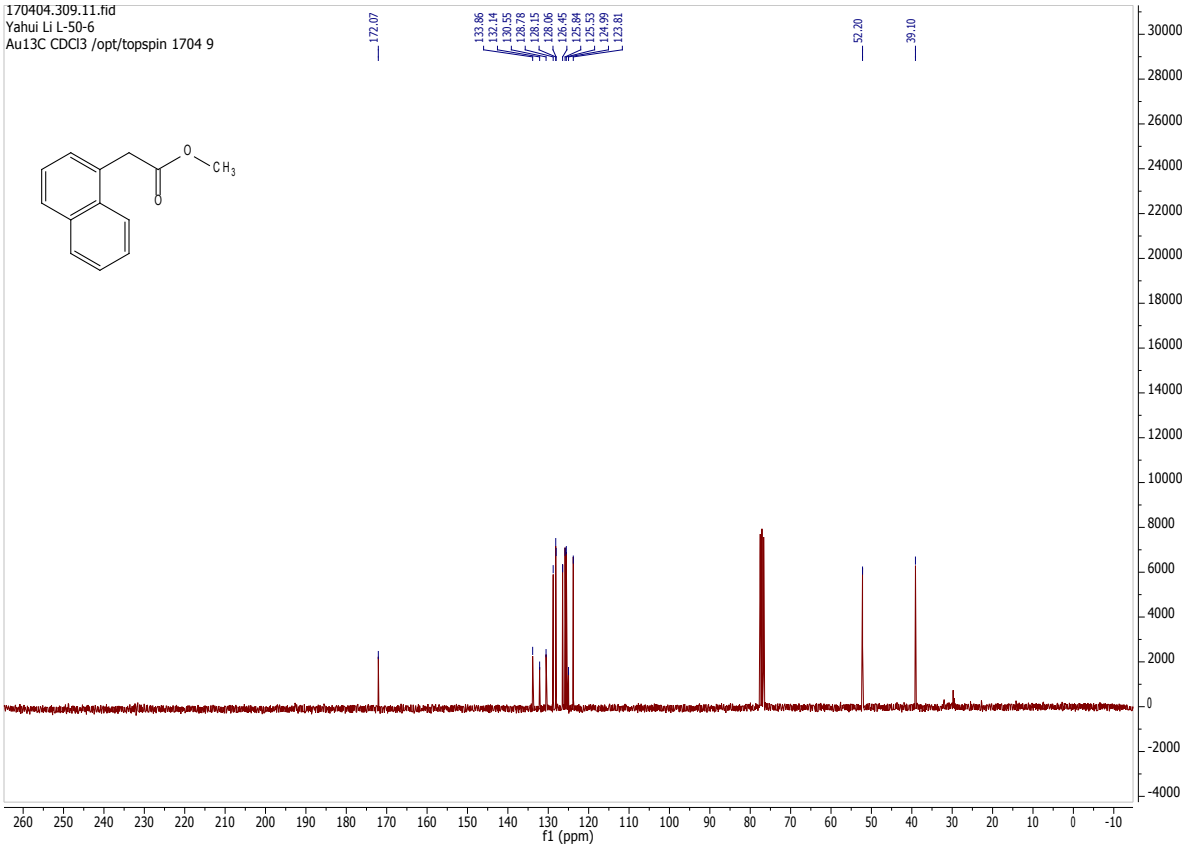
3.00
f1 (ppm)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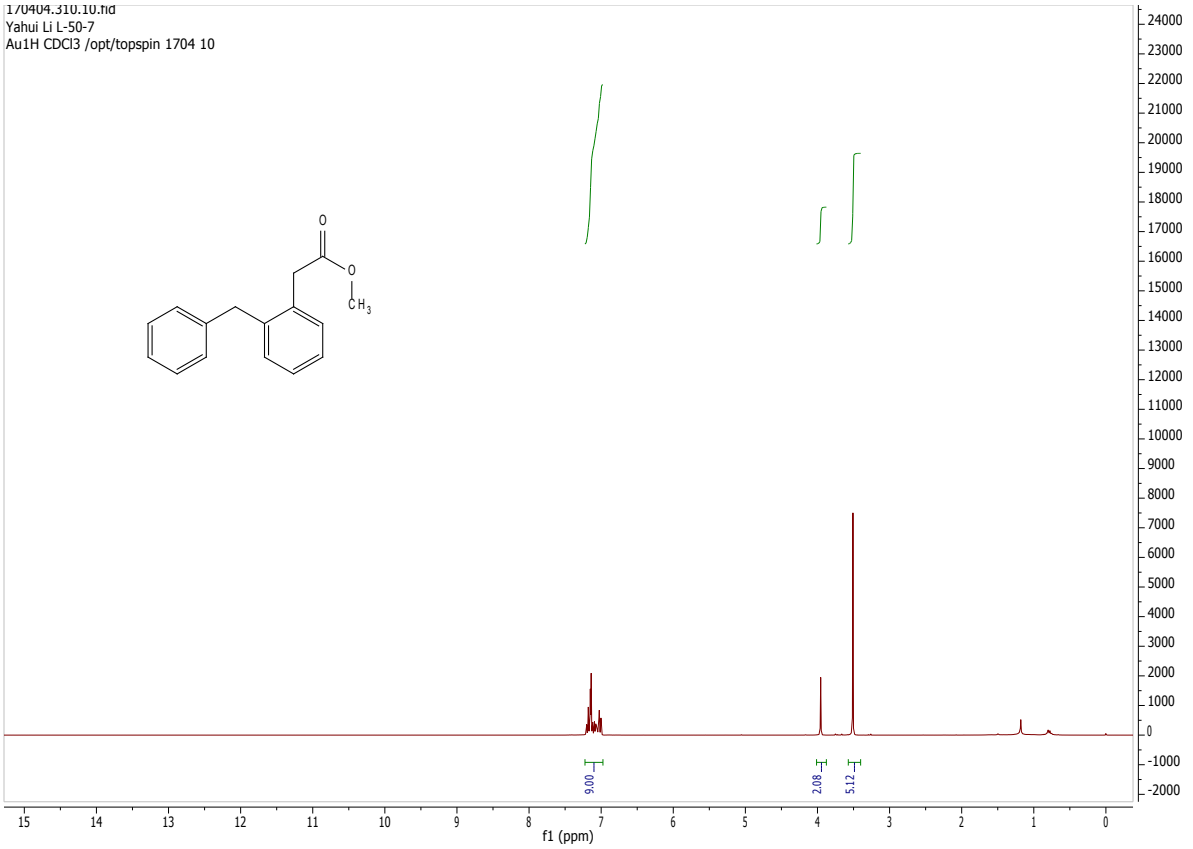
52.20
39.10
O
CH3
O
f1 (ppm)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CH3
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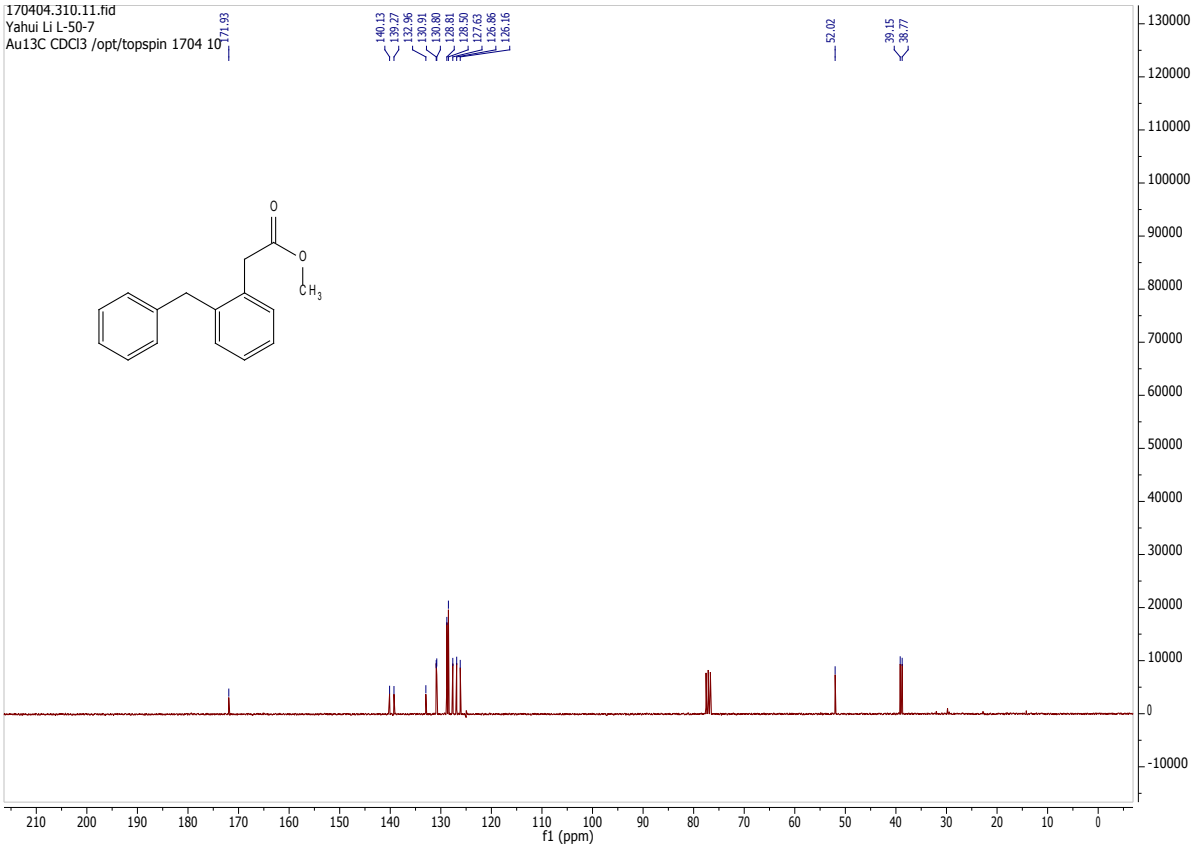
5.12
f1 (ppm)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127.63
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126.16
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O
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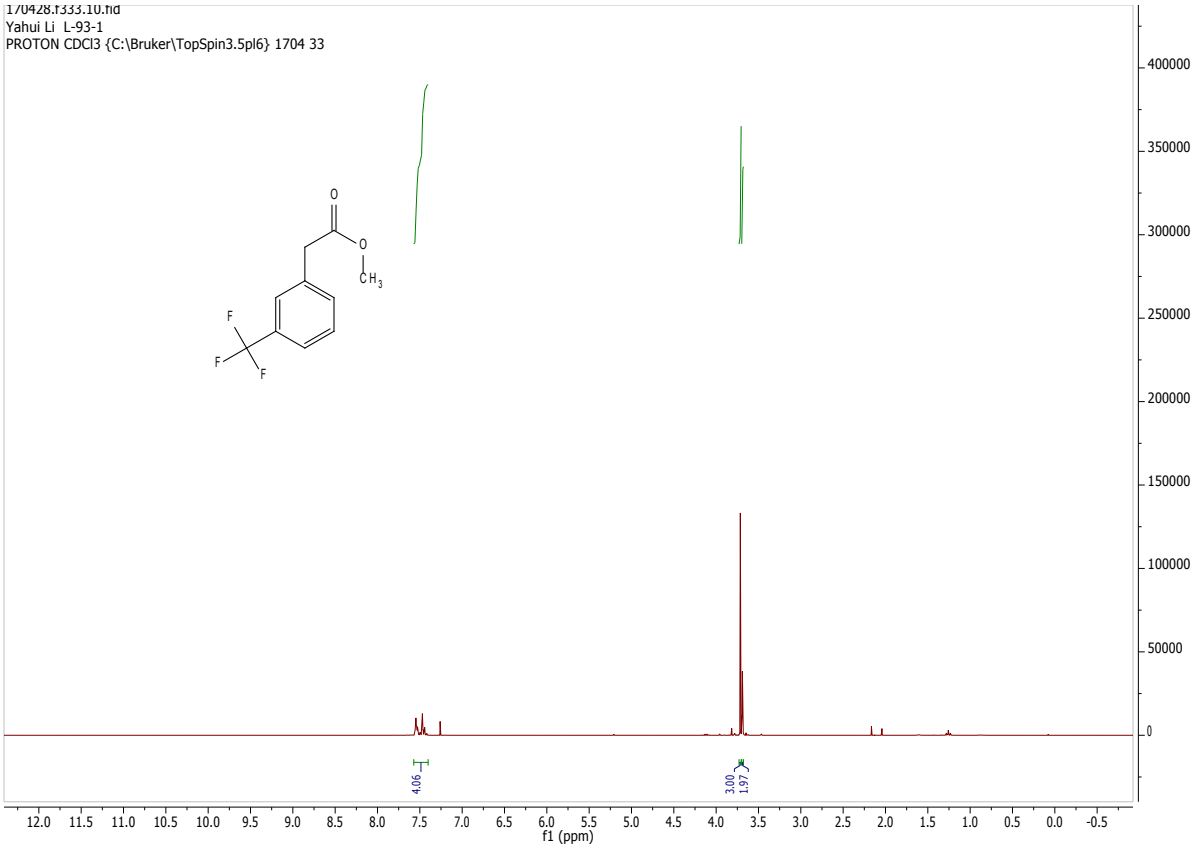
f1 (ppm)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F
F
F
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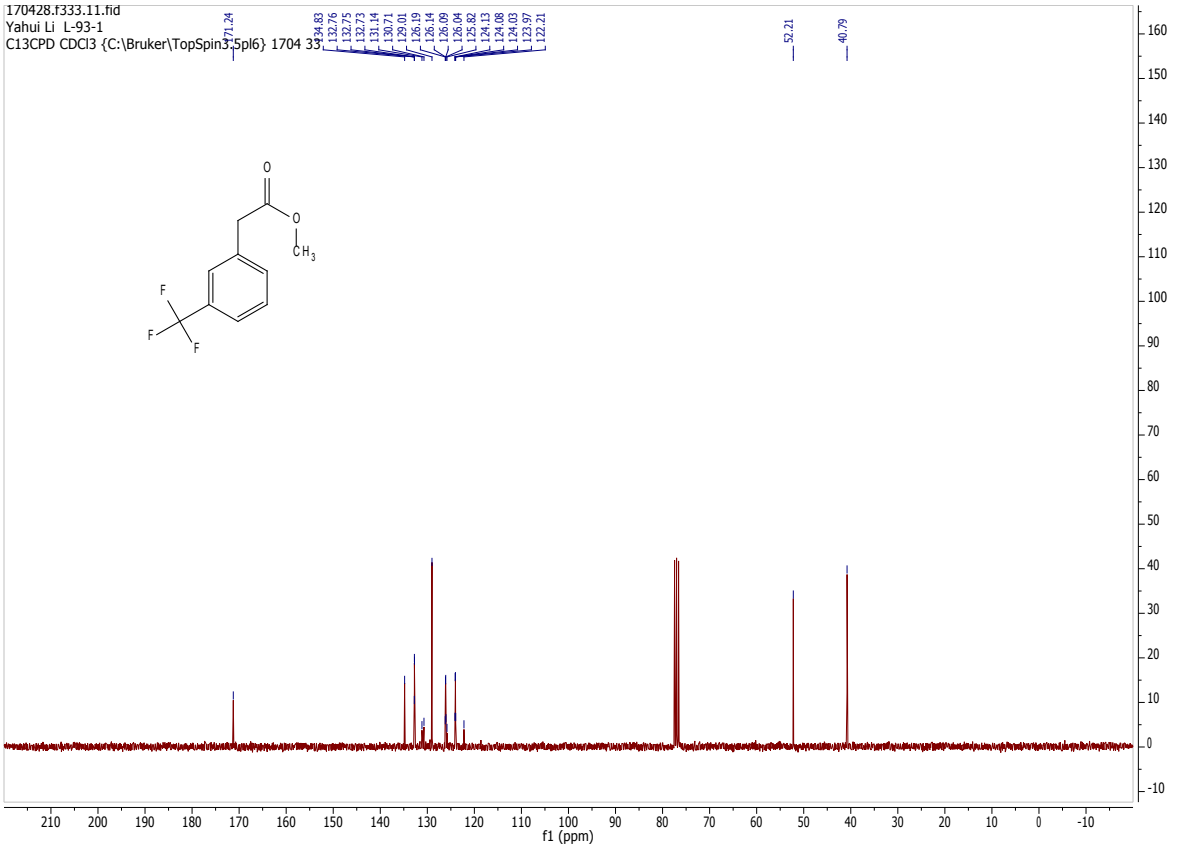
3.00
1.97
f1 (ppm)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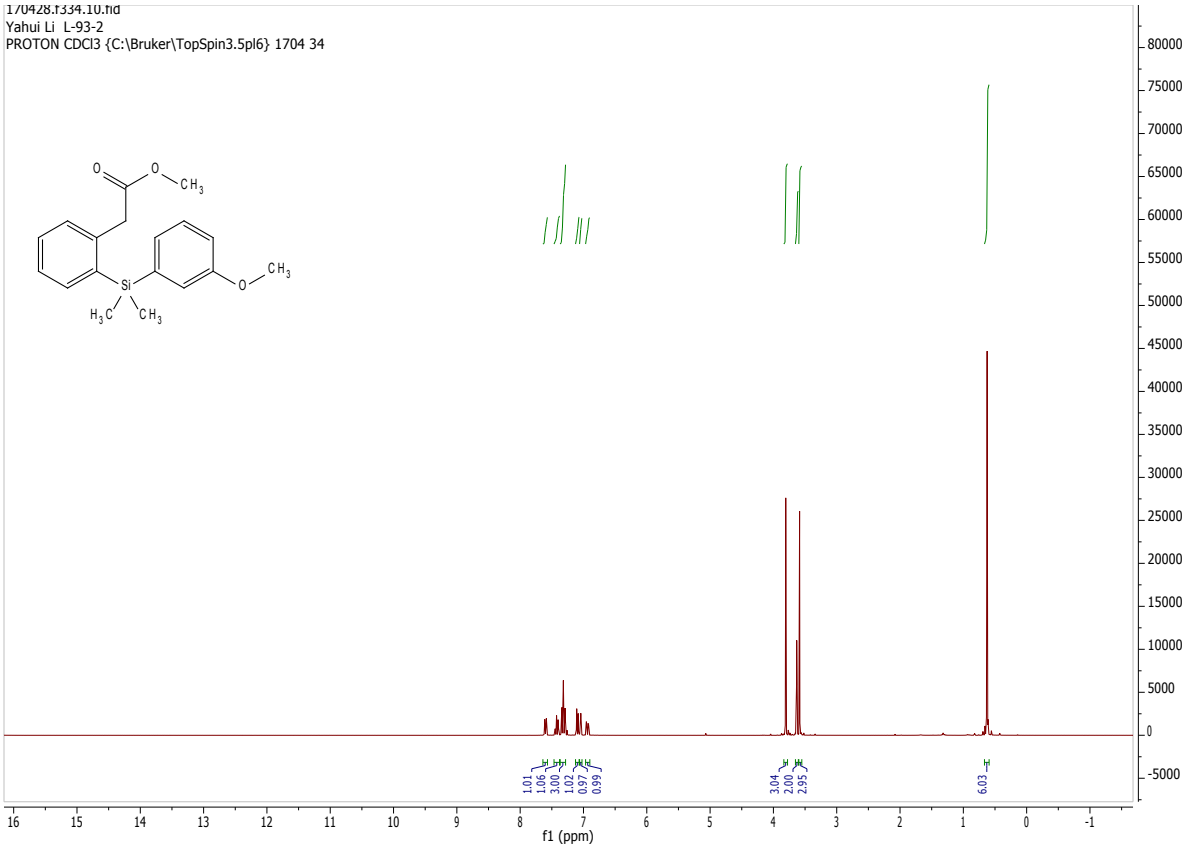
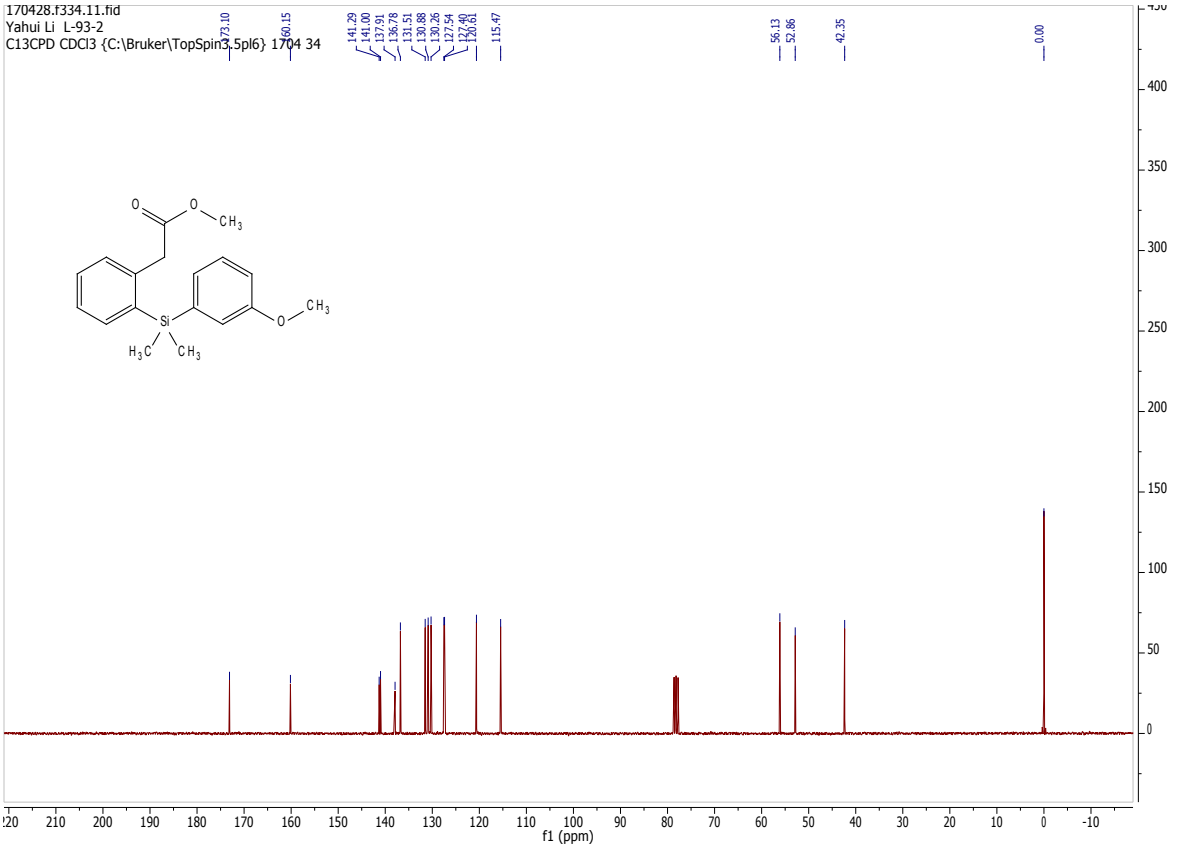
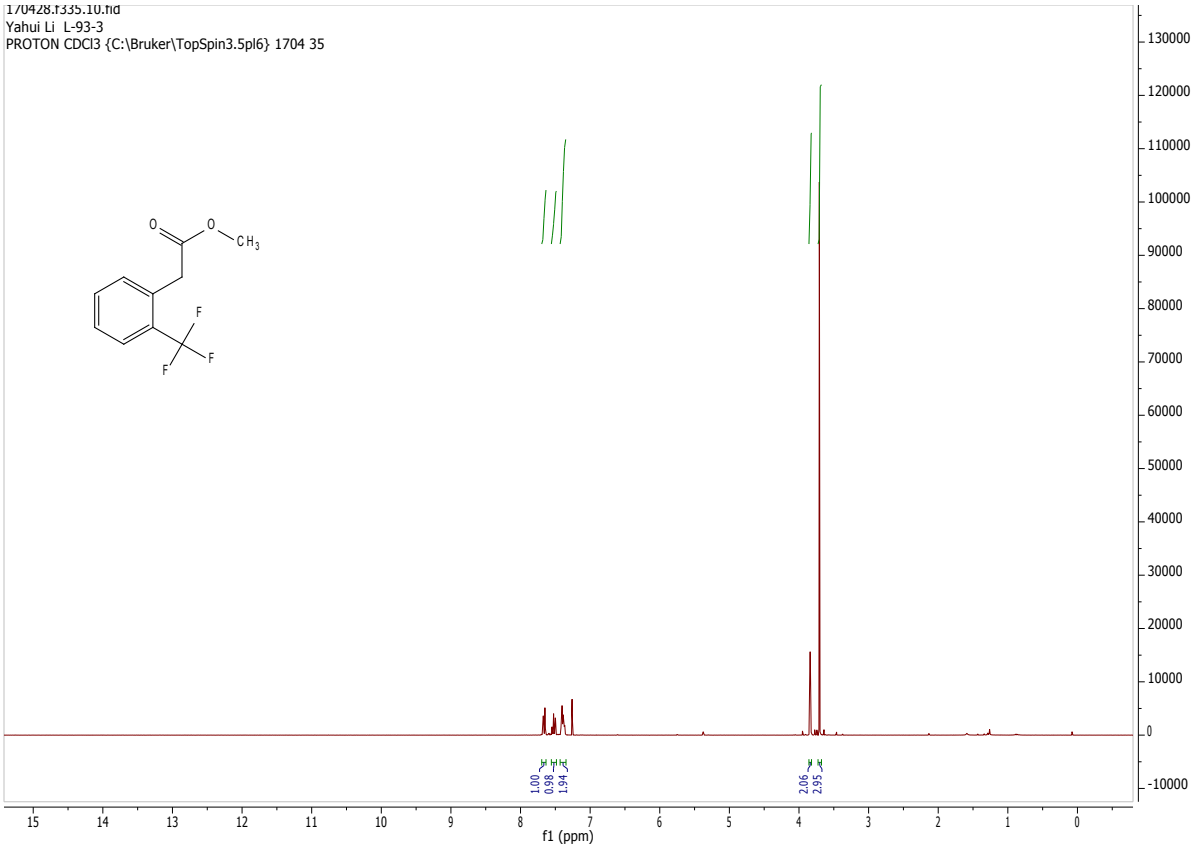
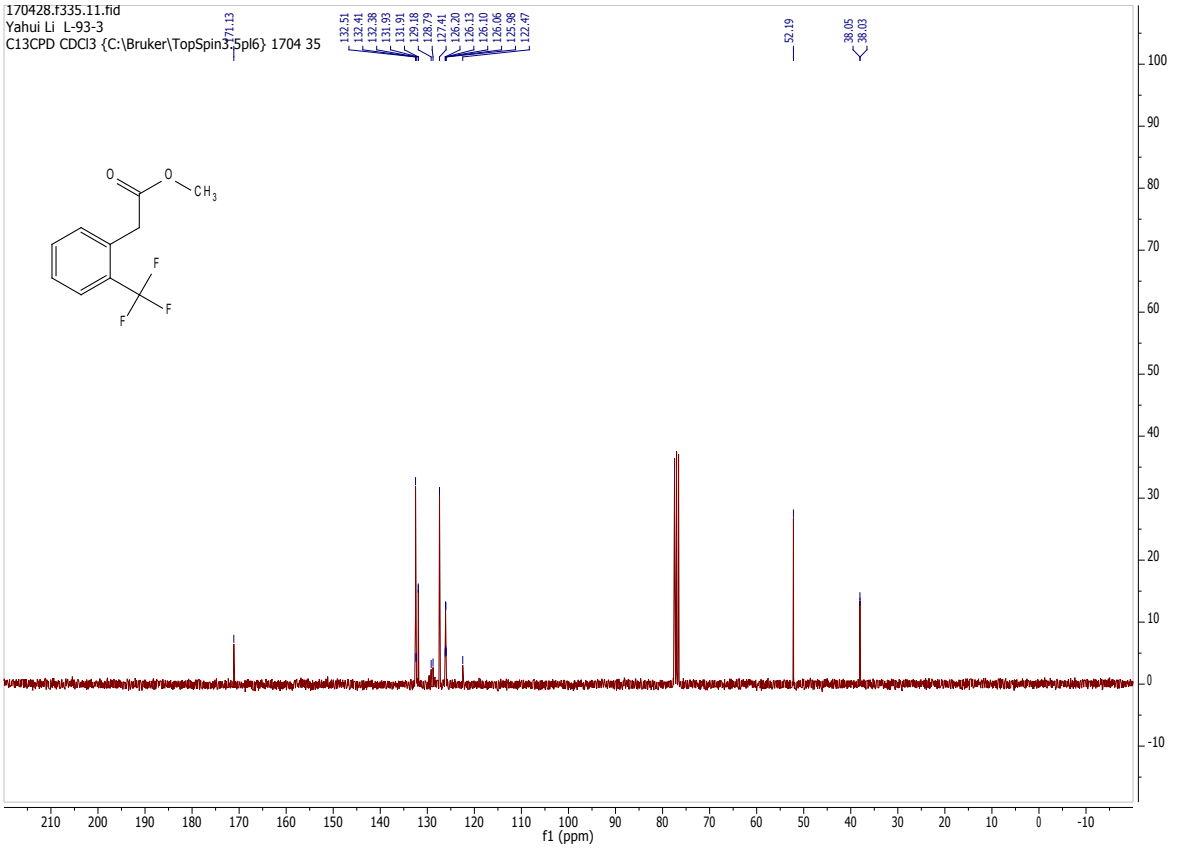
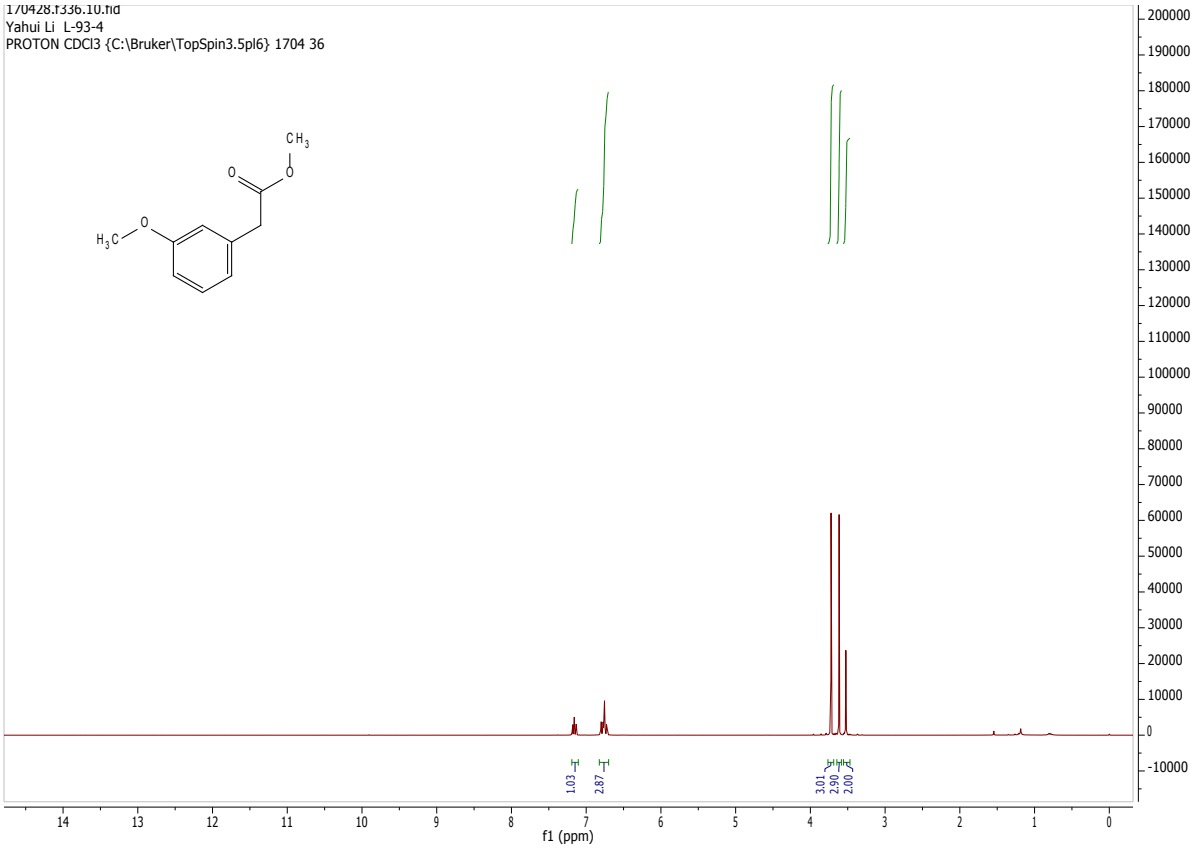
126.19
126.14
126.09
126.04
125.82
124.13
124.08
124.03
123.97
122.21
52.21
40.79
O
O
CH3
F
F
F
f1 (ppm)

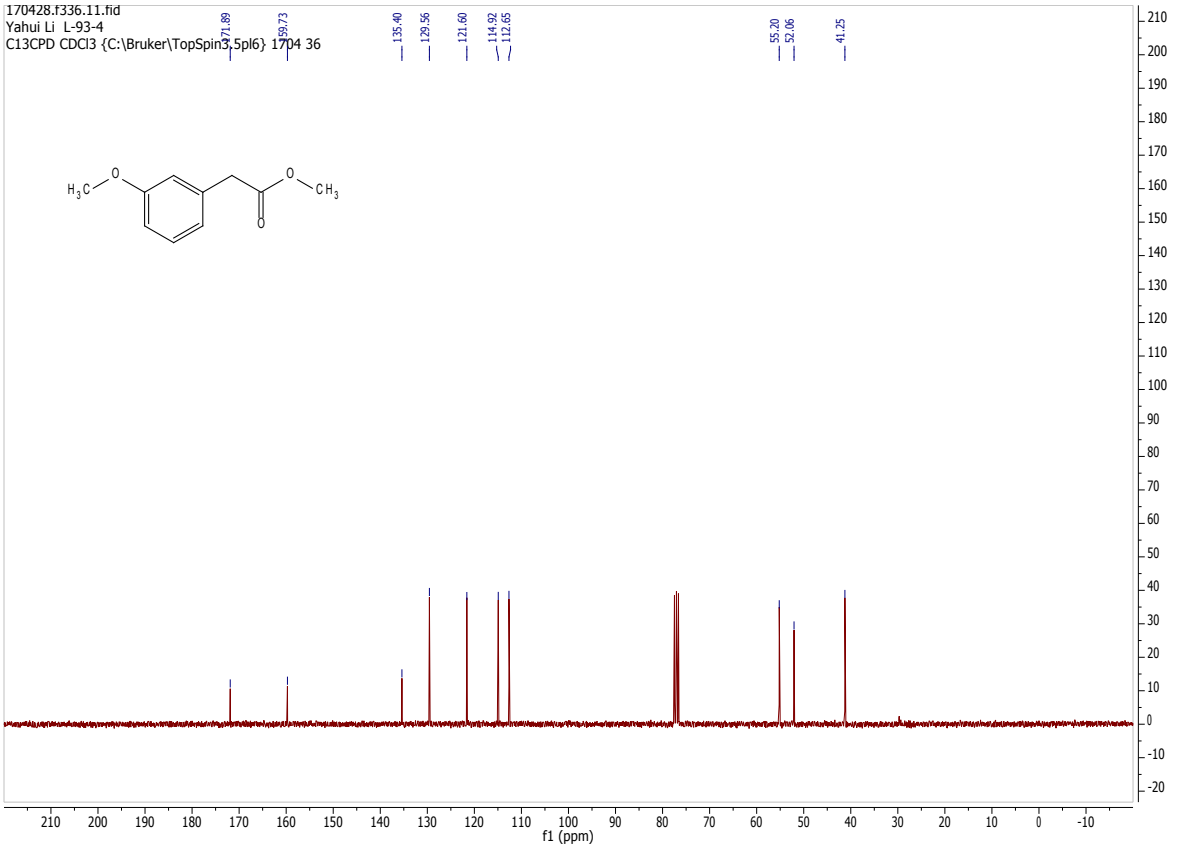

170428.f334.10.fid
Yahui Li L-93-2
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 34
1.01
1.06
3.00
1.02
0.97
0.99
3.04
2.00
2.95
6.03
f1 (ppm)

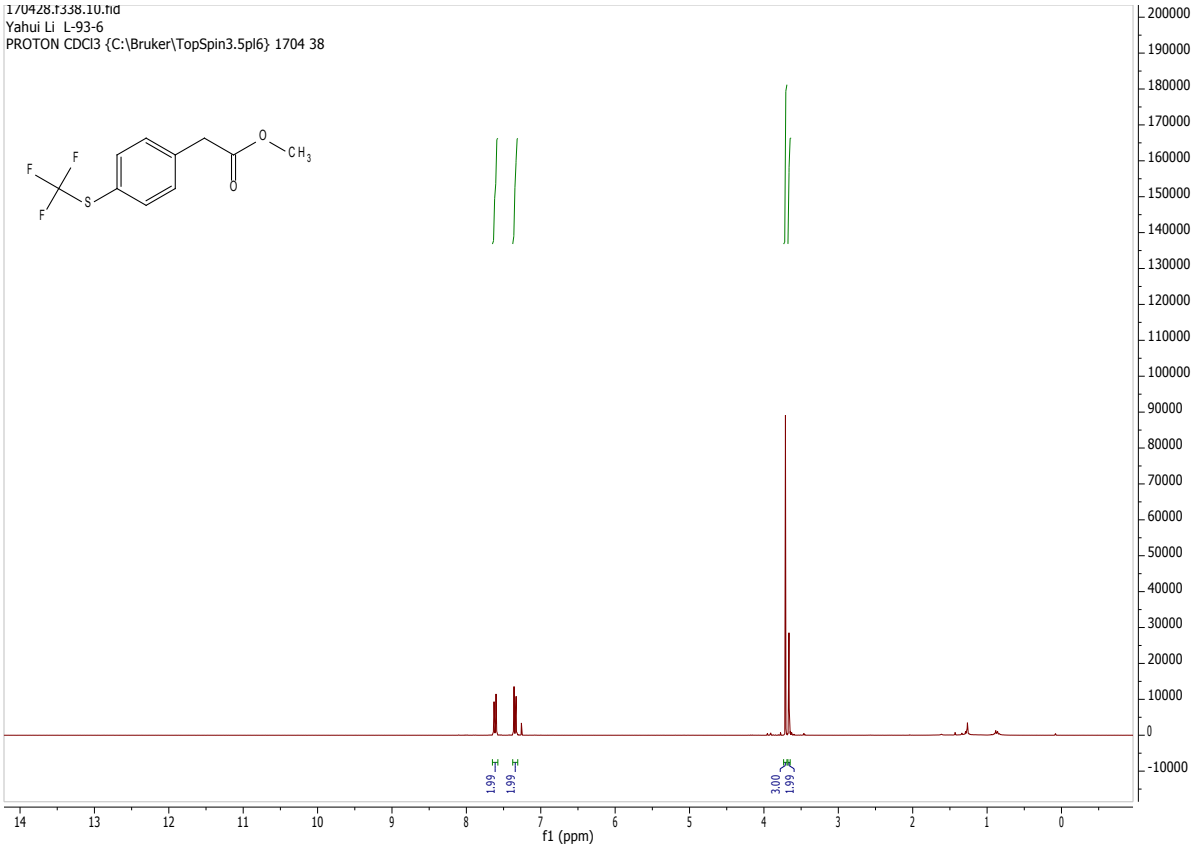

170428.f334.11.fid
Yahui Li L-93-2
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 34
173.10
160.15
141.29
141.00
137.91
136.78
131.51
130.88
130.26
127.54
127.40
120.61
115.47
56.13
52.86
42.35
0.00
f1 (ppm)

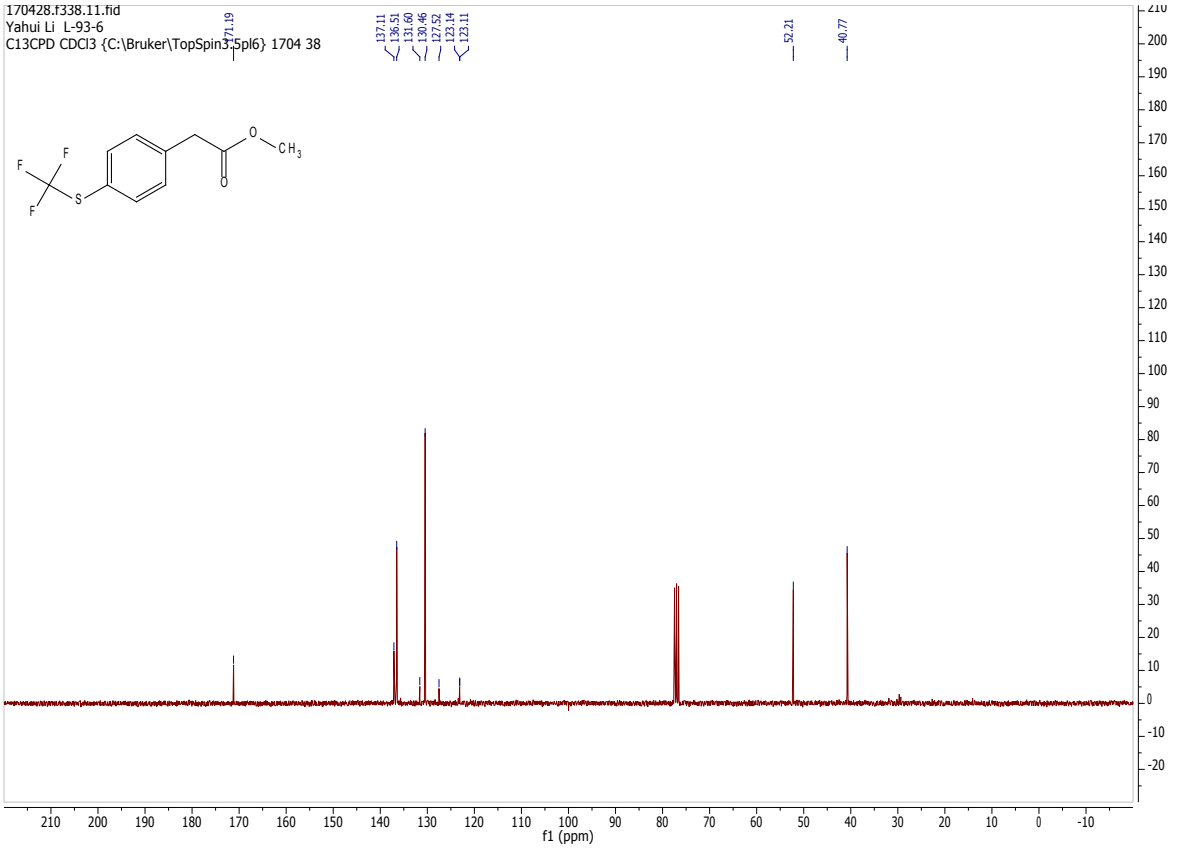

170428.f335.10.fid
Yahui Li L-93-3
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 35
1.00
0.98
1.94
2.06
2.95
f1 (ppm)

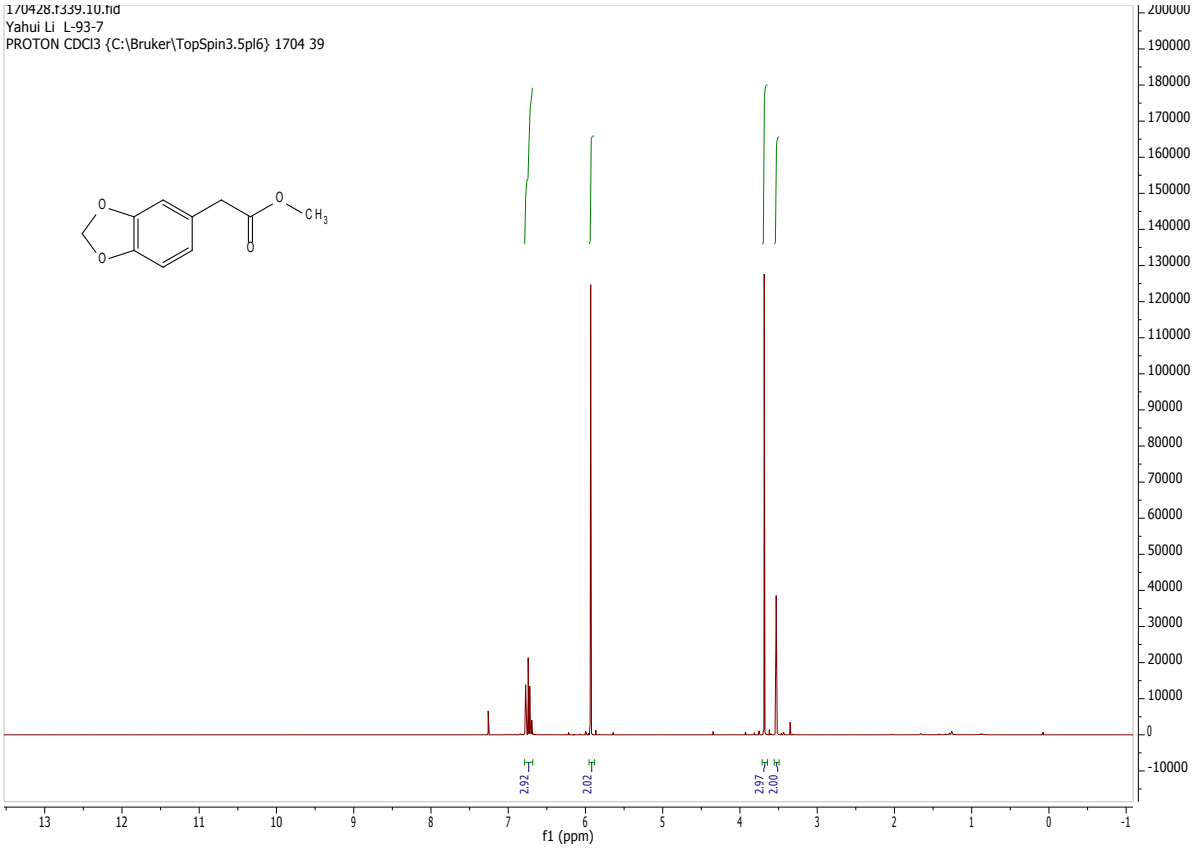

170428.f335.11.fid
Yahui Li L-93-3
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 35
171.13
132.51
132.41
132.38
131.93
131.91
129.18
128.79
127.41
126.20
126.13
126.10
126.06
125.98
122.47
52.19
38.05
38.03
f1 (ppm)

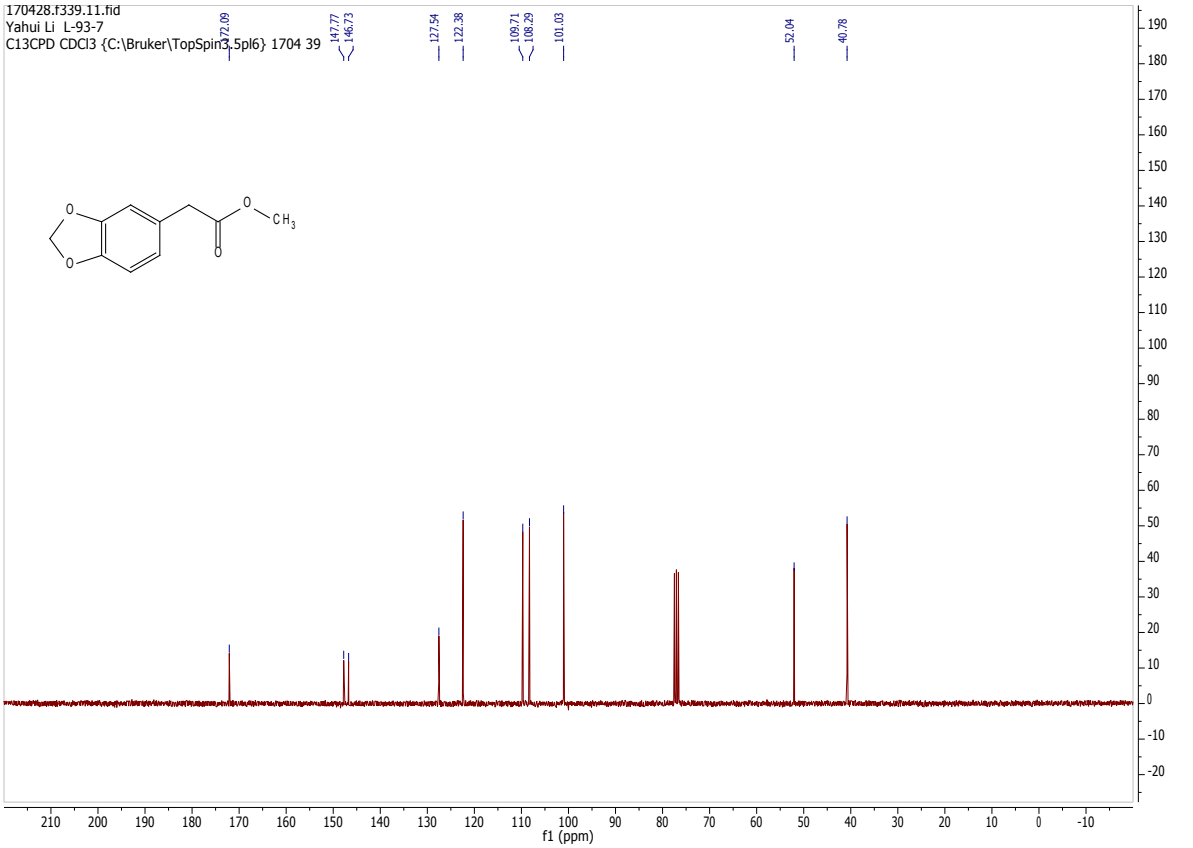

170428.f336.10.fid
Yahui Li L-93-4
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 36
1.03
2.87
3.01
2.90
2.00
f1 (ppm)

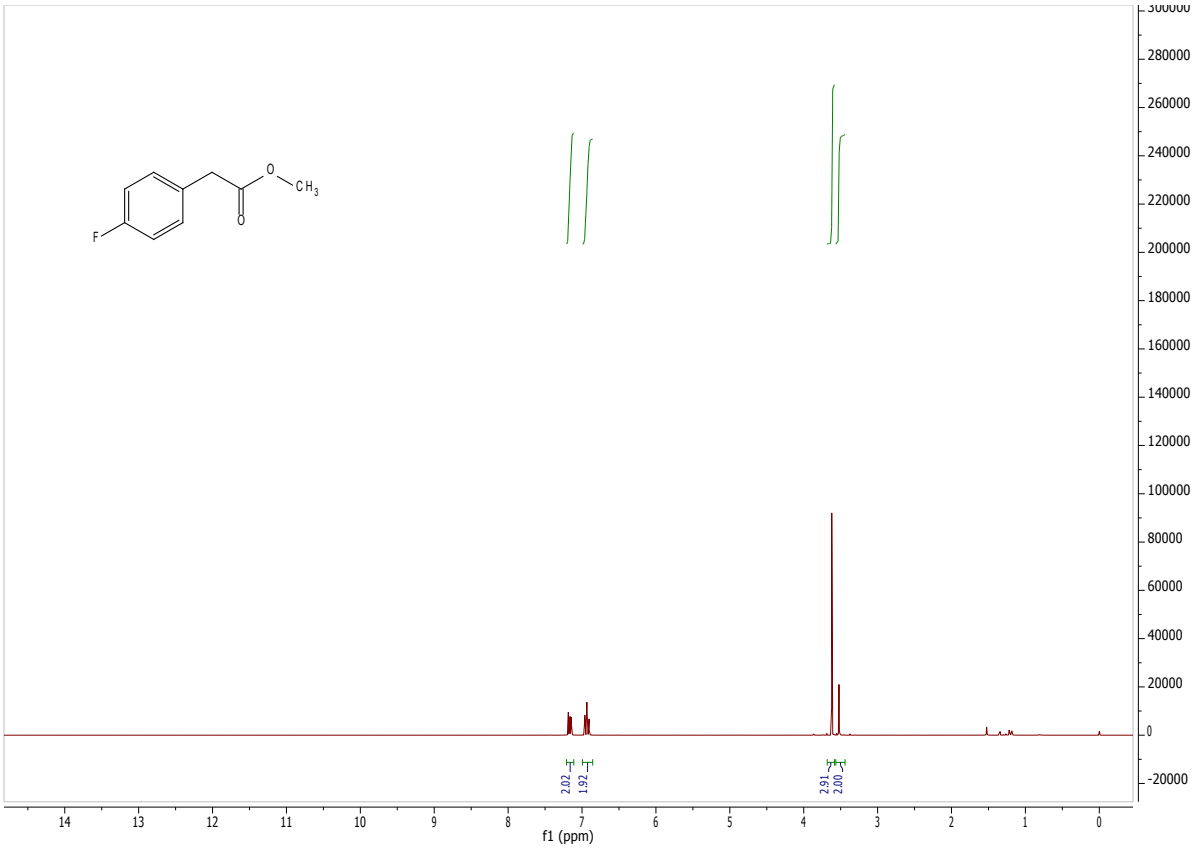

170428.f336.11.fid
Yahui Li L-93-4
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 36
171.89
159.73
135.40
129.56
121.60
114.92
112.65
55.20
52.06
41.25
f1 (ppm)

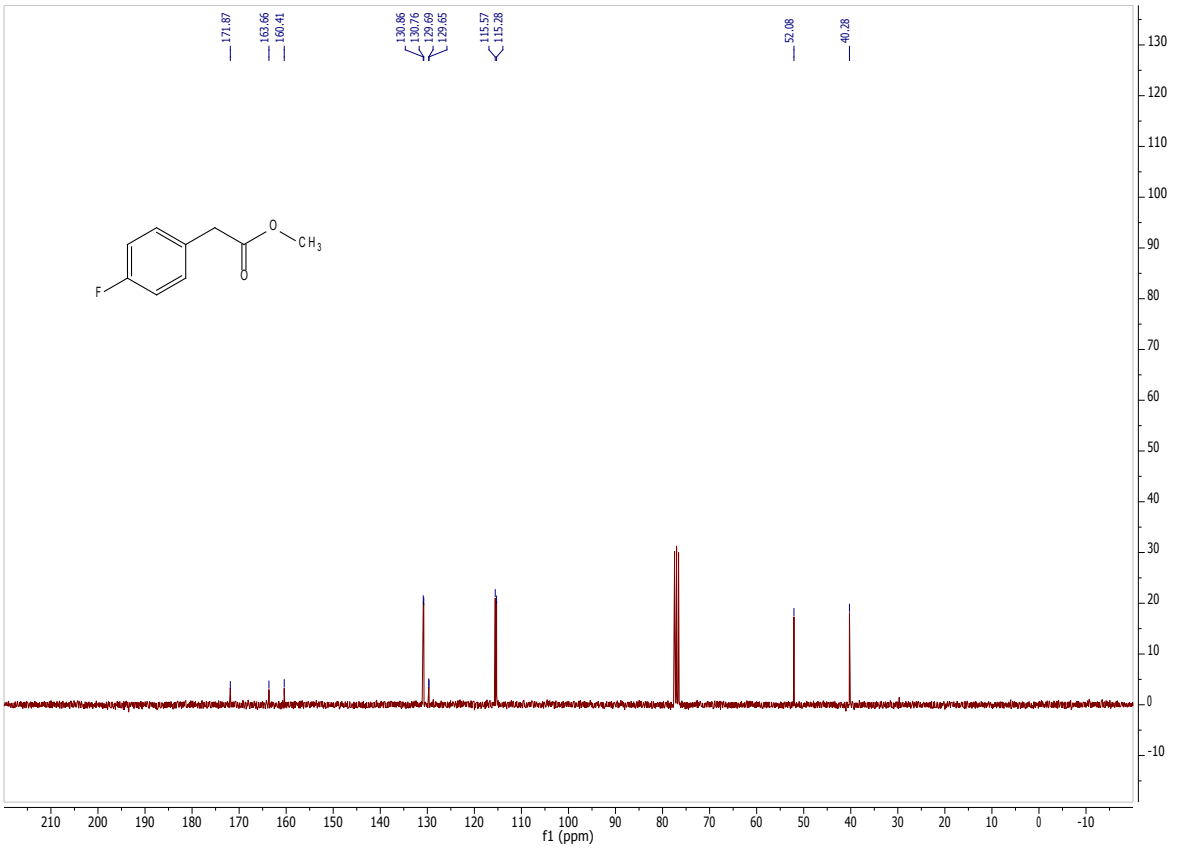

170428.f338.10.fid
Yahui Li L-93-6
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 38
F
F
F
S
O
O
CH3
1.99
1.99
3.00
1.99
f1 (ppm)

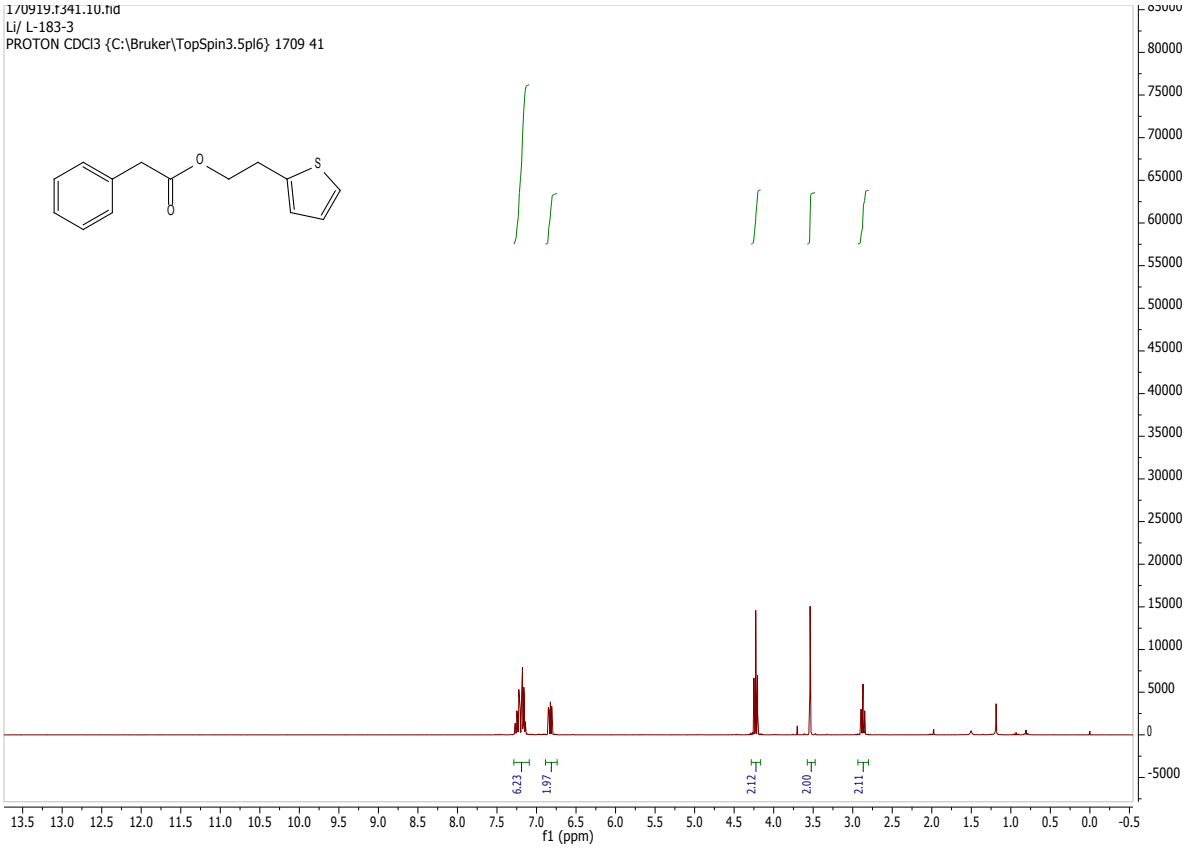

170428.f338.11.fid
Yahui Li L-93-6
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 38
171.19
137.11
136.51
131.60
130.46
127.52
123.14
123.11
52.21
40.77
F
F
F
S
O
O
CH3
f1 (ppm)

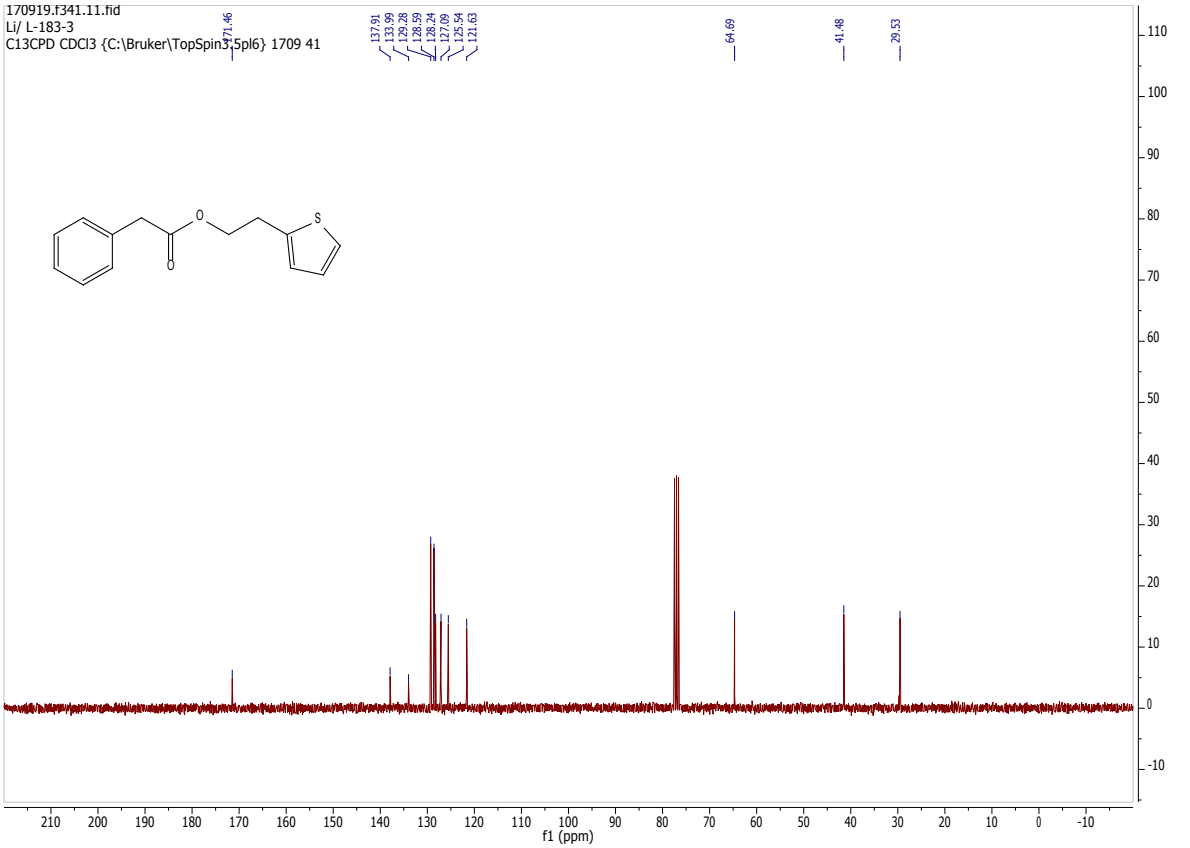

170428.f339.10.fid
Yahui Li L-93-7
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 39
O
O
O
O
CH3
2.92
2.02
2.97
2.00
f1 (ppm)

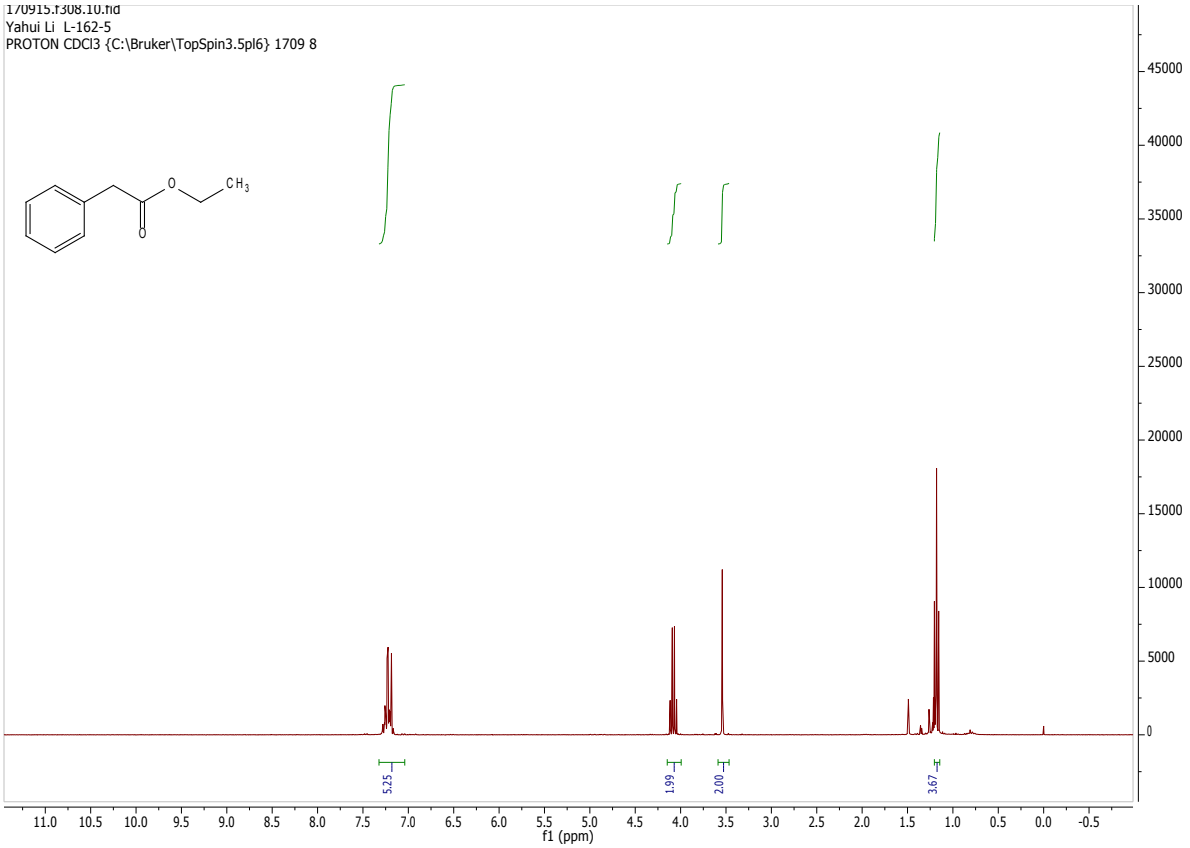

170428.f339.11.fid
Yahui Li L-93-7
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1704 39
172.09
147.77
146.73
127.54
122.38
109.71
108.29
101.03
52.04
40.78
O
O
O
O
CH3
f1 (ppm)

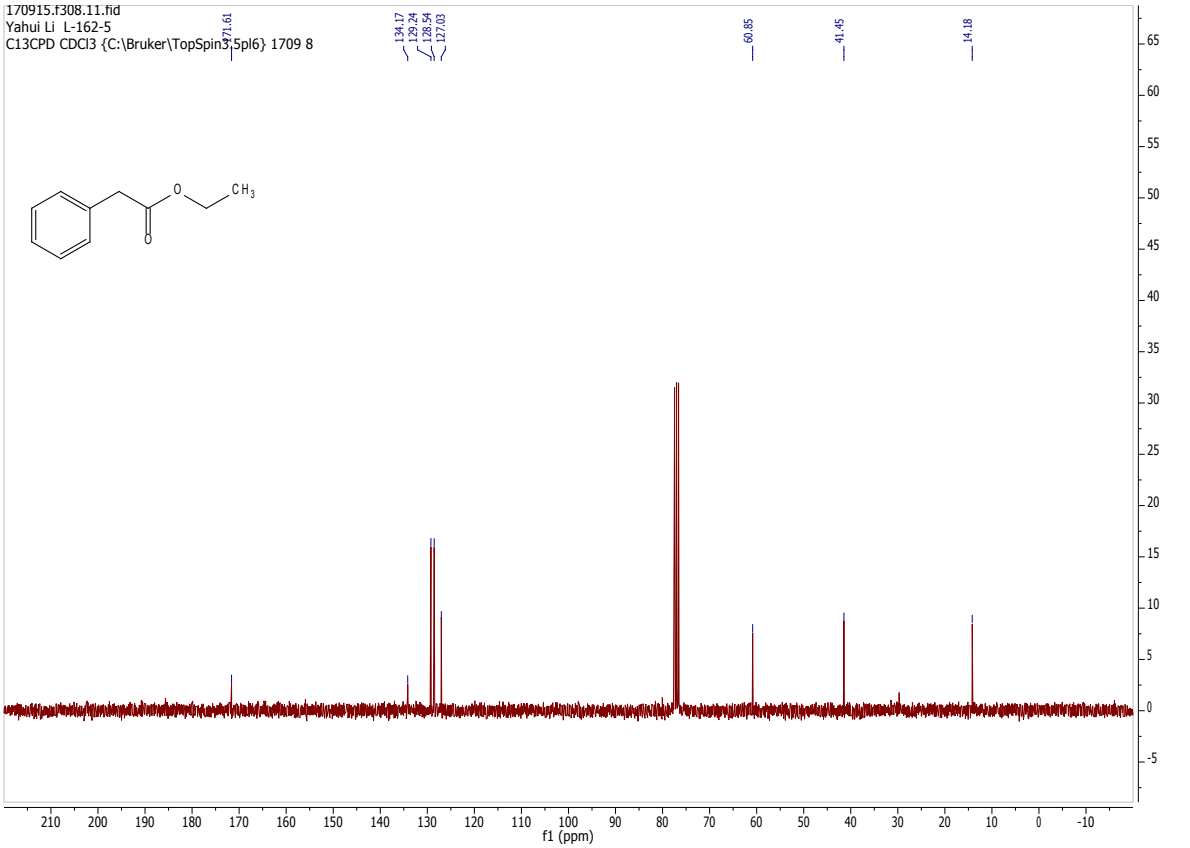

O
CH3
O
F
2.02
1.92
2.91
2.00
f1 (ppm)


171.87
163.66
160.41
130.86
130.76
129.69
129.65
115.57
115.28
52.08
40.28
O
CH3
O
F
f1 (ppm)


170919.f341.10.fid
Li/ L-183-3
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 41
O
O
S
6.23
1.97
2.12
2.00
2.11
f1 (ppm)


170919.f341.11.fid
Li/ L-183-3
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 41
171.46
137.91
133.99
129.28
128.59
128.24
127.09
125.54
121.63
64.69
41.48
29.53
O
O
S
f1 (ppm)


170915.f308.10.fid
Yahui Li L-162-5
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 8
O
O
CH3
5.25
1.99
2.00
3.67
f1 (ppm)


170915.f308.11.fid
Yahui Li L-162-5
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 8
171.61
134.17
129.24
128.54
127.03
60.85
41.45
14.18
O
O
CH3
f1 (ppm)