Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Palladium-Catalyzed Monoselective C-H Borylation of Acetanilides under Acidic Conditions

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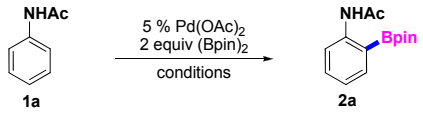
General Remark:

$PhCF_3$ (>99%) and BQ was purchased from Aldrich and used without further treatment. $(Bpin)_2$ was recrystallized from EtOAc/Petroleum Ether (1:50) before being used. The 12% TsOH solution in HOAc was purchased from Acros. Analytical TLC was done on pre-coated ***acidic alumina*** plates (iPr_2O/EtOH 8:1). Column chromatography was conducted with 300-400 mesh ***acidic alumina***. ^1H NMR spectra were recorded on 400 MHz spectrometers. ^{13}C NMR spectra were recorded on 100 MHz spectrometers. High-resolution mass spectra (HRMS) were recorded on a Thermo LTQ ORBITRAP XL spectrometer with ESI mode unless otherwise stated.

Table S1 Optimization of the reaction conditions.[a].



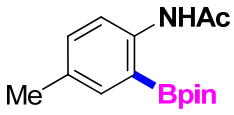
Entry	Additive	Oxidant	Solvent	T	Yield %[b]
1	$TsOH•H_2O$	benzoquinone	toluene	80 °C	7
2	$TsOH•H_2O$+HOAc	benzoquinone	toluene	80 °C	14
3	$TsOH•H_2O$+HOAc	benzoquinone	toluene	40 °C	55
4	$TsOH•H_2O$+HOAc	*o*-chloranil	toluene	80 °C	23
5	$TsOH•H_2O$+HOAc	*o*-chloranil	toluene	40 °C	0
6	12% TsOH in HOAc	benzoquinone	toluene	40 °C	66
7	12% TsOH in HOAc	benzoquinone	DCE	40 °C	67
8	12% TsOH in HOAc	benzoquinone	dioxane	40 °C	trace
9	12% TsOH in HOAc	benzoquinone	DMF	40 °C	0
10	12% TsOH in HOAc	benzoquinone	mesitylene	40 °C	77
11	12% TsOH in HOAc	benzoquinone	$PhCF_3$	40 °C	80
12	12% TsOH in HOAc	$Cu(OAc)_2$	$PhCF_3$	40 °C	0
13	12% TsOH in HOAc	AgOAc	$PhCF_3$	40 °C	0
14	TFA	benzoquinone	$PhCF_3$	40 °C	trace
15	TFA	AgOAc	$PhCF_3$	40 °C	trace
16	12% TsOH in HOAc	benzoquinone	$PhCF_3$	30 °C	87(70[c])
17	12% TsOH in HOAc	benzoquinone	$PhCF_3$	25 °C	76

[a] All the reactions were carried out in 0.3 mmol scale with 0.1 mmol of additive (TsOH or TFA) and 2 equiv of oxidant in 0.4 mL solvent and 0.1 mL HOAc (if used). [b] GC yields with benzophenone as an internal standard. [c] Isolated yield.

General Procedure for The Synthesis of 2a-2x:

To a 10 mL vial was sequentially added $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), acetanilide (0.3 mmol), B_2pin_2 (152 mg, 0.6 mmol), BQ (65 mg, 0.6 mmol) and $PhCF_3$ (0.4 mL). After the reaction was stirred at room temperature for 2 min, TsOH (12% in HOAc, 133uL, 0.1 mmol) was added. The vial was stirred at the 30 ^oC for 36-48 h. The reaction mixture was diluted with 0.5 mL $CHCl_3$-EtOH (20:1) and then loaded onto the top of a short (diameter of 2 cm, 10 cm long) ***acidic alumina*** column slurry-packed with $CHCl_3$-EtOH (20:1). The crude product containing un-reacted starting material was soon obtained by eluting with $CHCl_3$-EtOH (20:1). The solution of crude product was evaporated, and then 10 mL EtOAc/Petroleum ether (1:5, for most of substrates, and 1:10 for **2e**, **2r**, **2u-2x**) was added. After sedimentation for 1 hour at room temperature, the desired product was filtered out as white or light pink solid.

The procedure for gram-scale synthesis of **2y** is similar to **2a-x**. A 25 mL round-bottomed flask was used instead of a 10 mL vial. Column chromatography was conducted with ***acidic alumina*** column (diameter of 5 cm, 15 cm long).

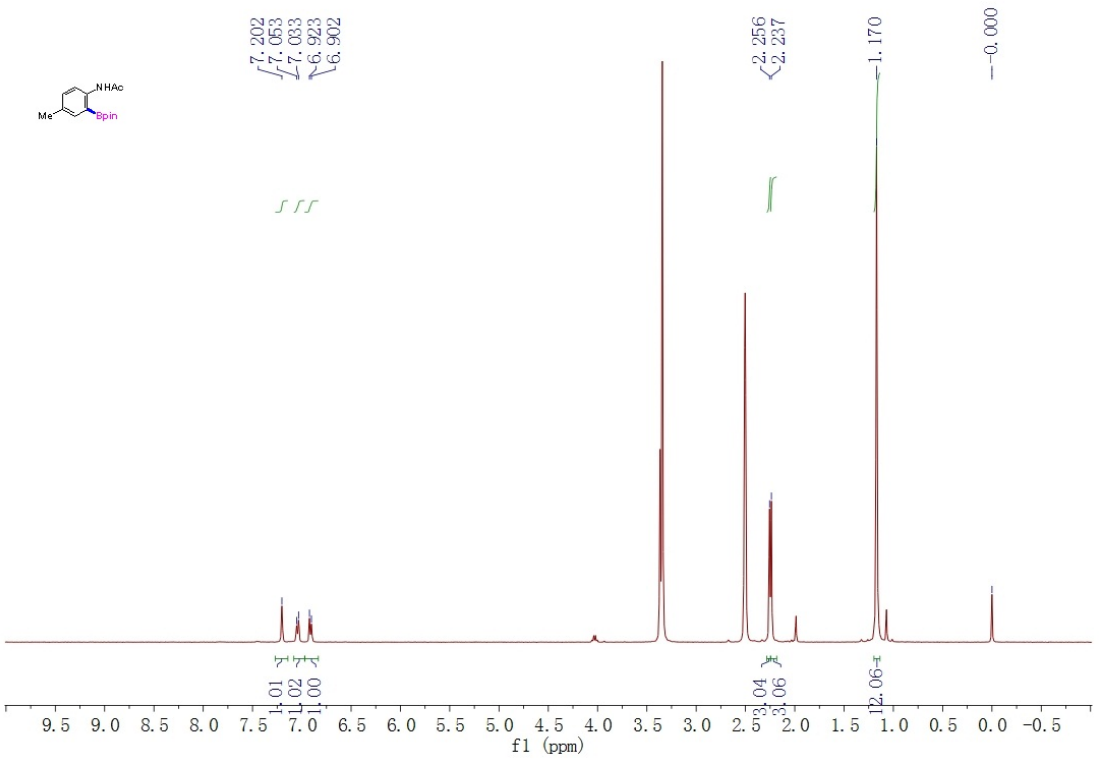


N-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.20 (s, 1H), 7.04 (d, J = 8.0, 1H), 6.91 (d, J = 8.0, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.17 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 169.04, 135.71, 133.78, 132.92, 128.00, 115.40, 79.49, 25.95, 21.61, 20.82.

HRMS requires $[C15H22BNO3+H]^+$ 276.1766, found ESI $[M+H]^+$ 276.1764.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Me
Bpin
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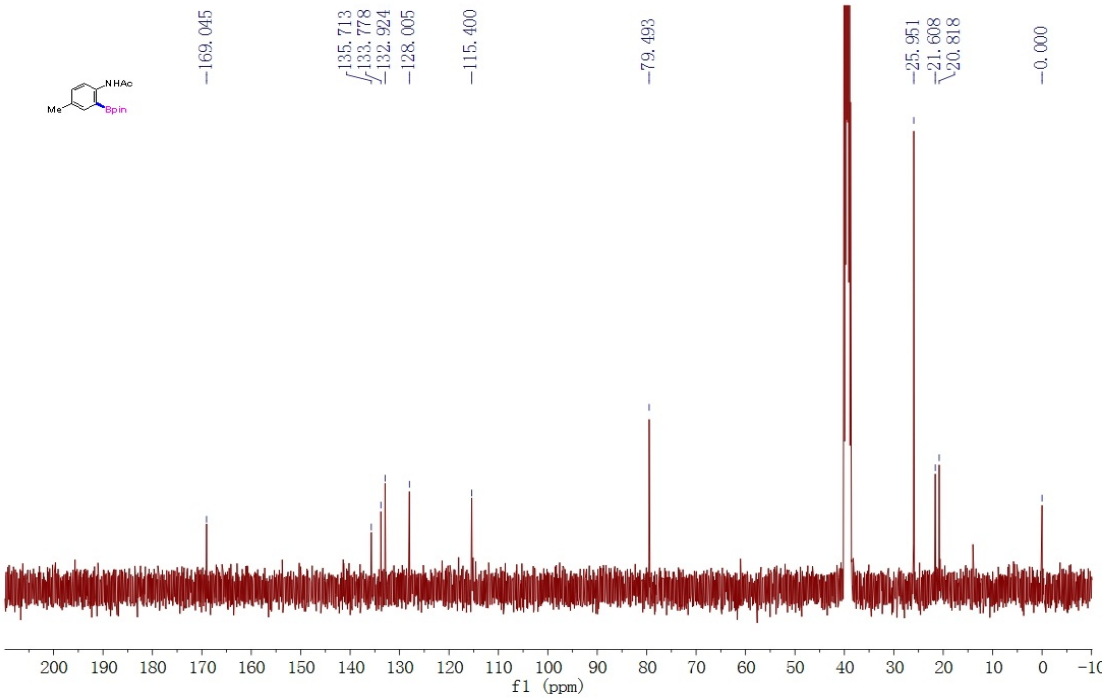
1.02
1.00
3.04
3.06
12.06
f1 (ppm)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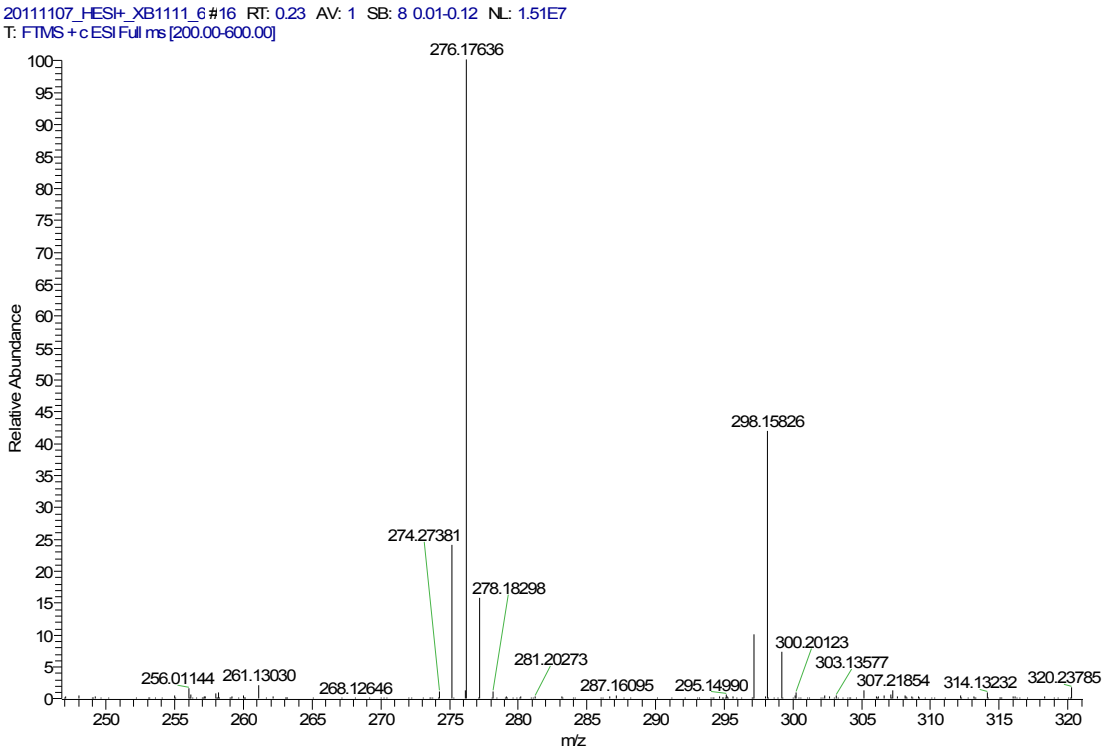
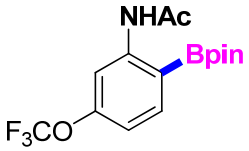
Me
Bpin
f1 (ppm)



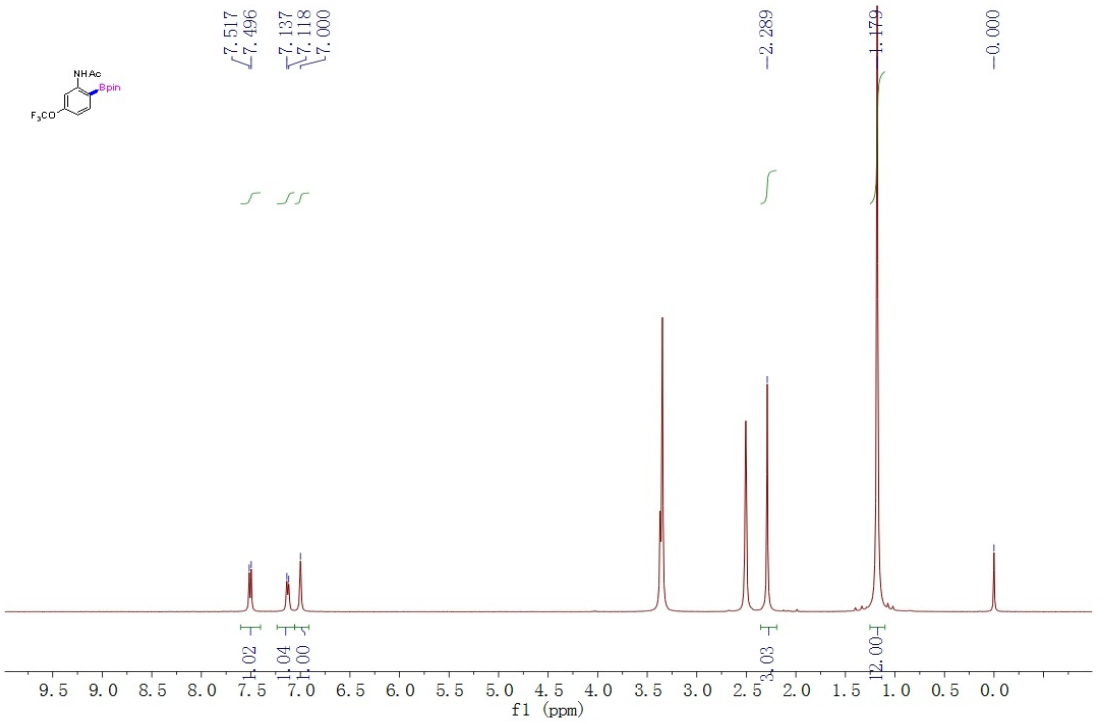


N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethoxy)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.51 (d, *J* = 8.2, 1H), 7.13 (d, *J* = 7.7, 1H), 7.00 (s, 1H), 2.29 (s, 3H), 1.18 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 170.74, 147.64, 139.10, 134.66, 120.01, 117.46, 107.80, 79.86, 25.87, 21.88.

HRMS requires $[C15H19BF3NO4+H]^{+}$ 346.1432, found ESI $[M+H]^{+}$ 346.1434.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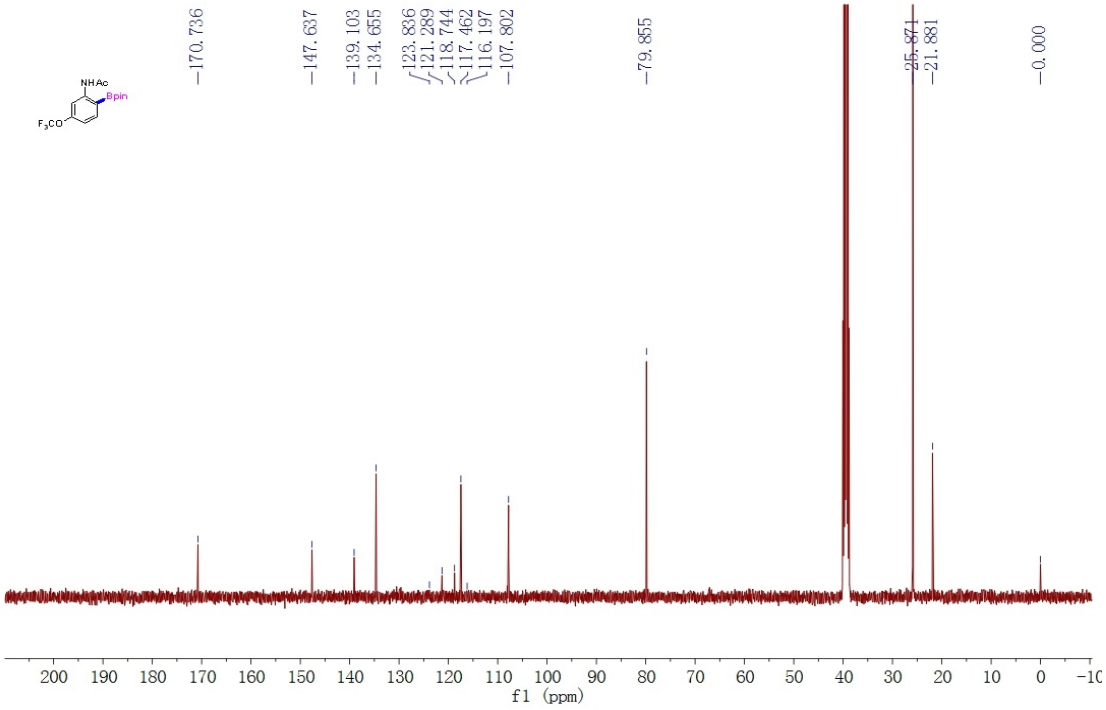
2.289
1.179
0.000
1.02
1.04
1.00
3.03
12.00
f1 (ppm)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147.637
139.103
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0.000
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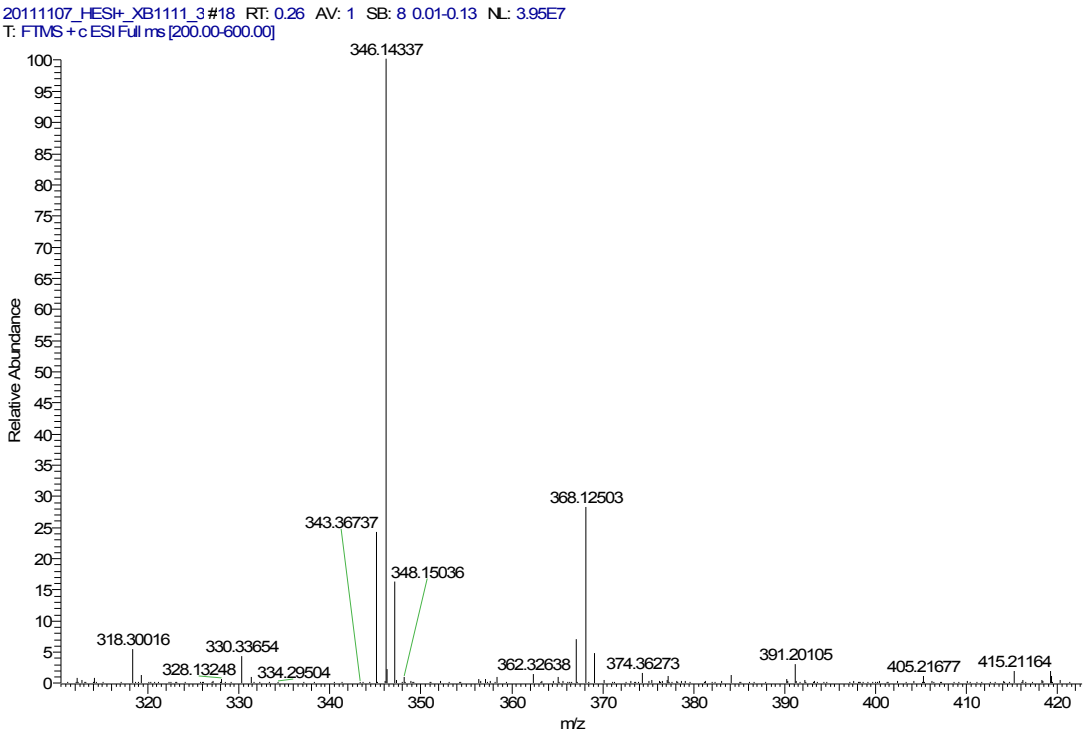
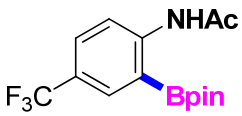


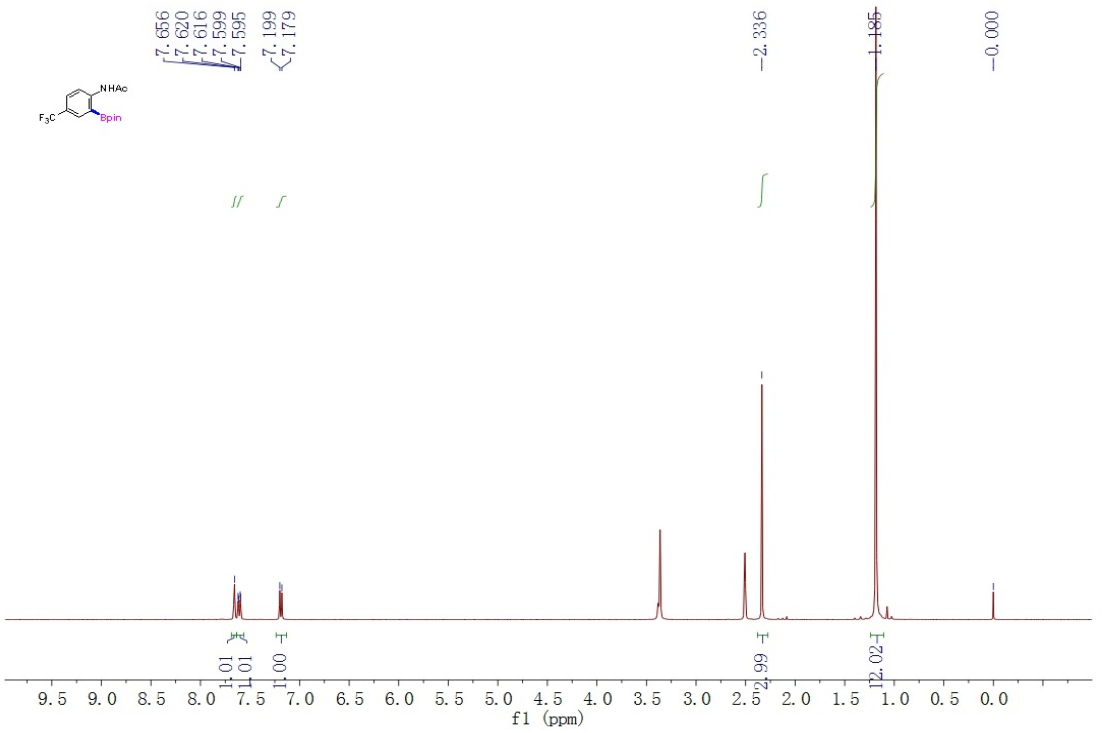


N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.66 (s, 1H), 7.61 (dd, J = 8.4, 1.7, 1H), 7.19 (d, J = 8.4, 1H), 2.34 (s, 3H), 1.19 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 171.37, 140.86, 129.14 (q, J = 4 Hz), 125.55 (q, J = 31 Hz) (126.01, 125.70, 125.39, 125.08.), 124.49 (q, J = 4 Hz), 124.48 (q, J = 270 Hz) (128.53, 125.83, 123.13, 120.43), 116.12, 79.75, 25.92, 21.82.

HRMS requires $[C15H19BF3NO3+H]^{+}$ 330.1483, found ESI $[M+H]^{+}$ 330.1483.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7.616
7.599
7.595
7.199
7.179
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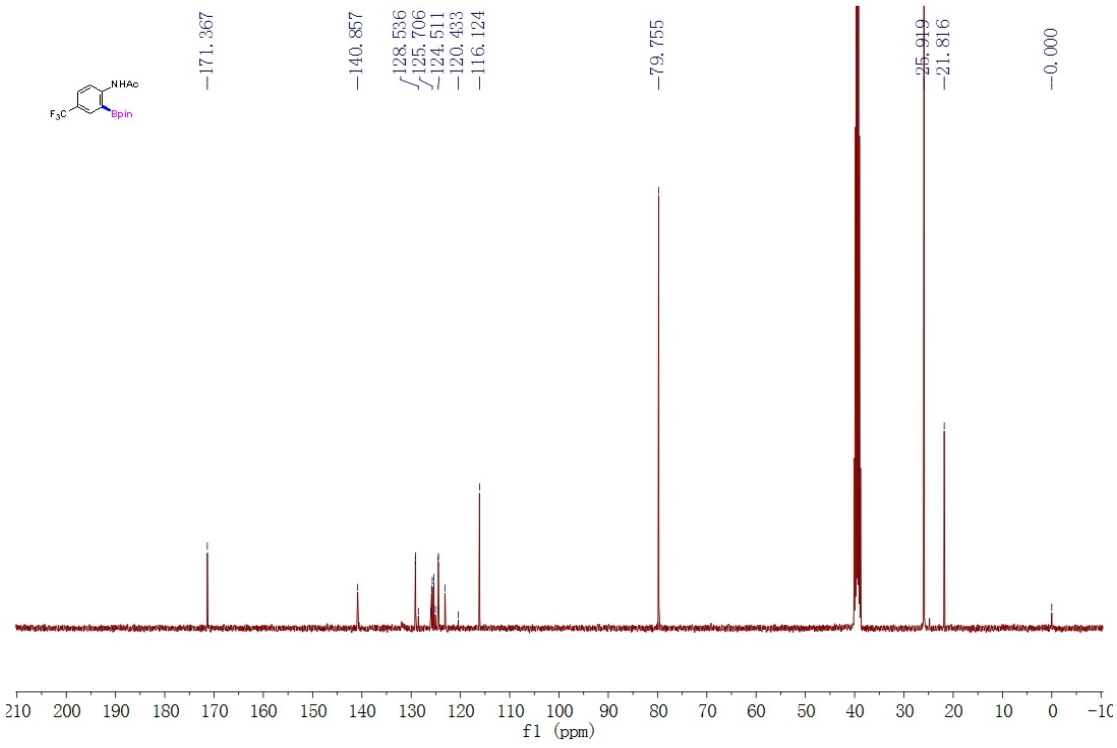
Bpin
1.01
1.01
1.00
2.99
12.02
f1 (ppm)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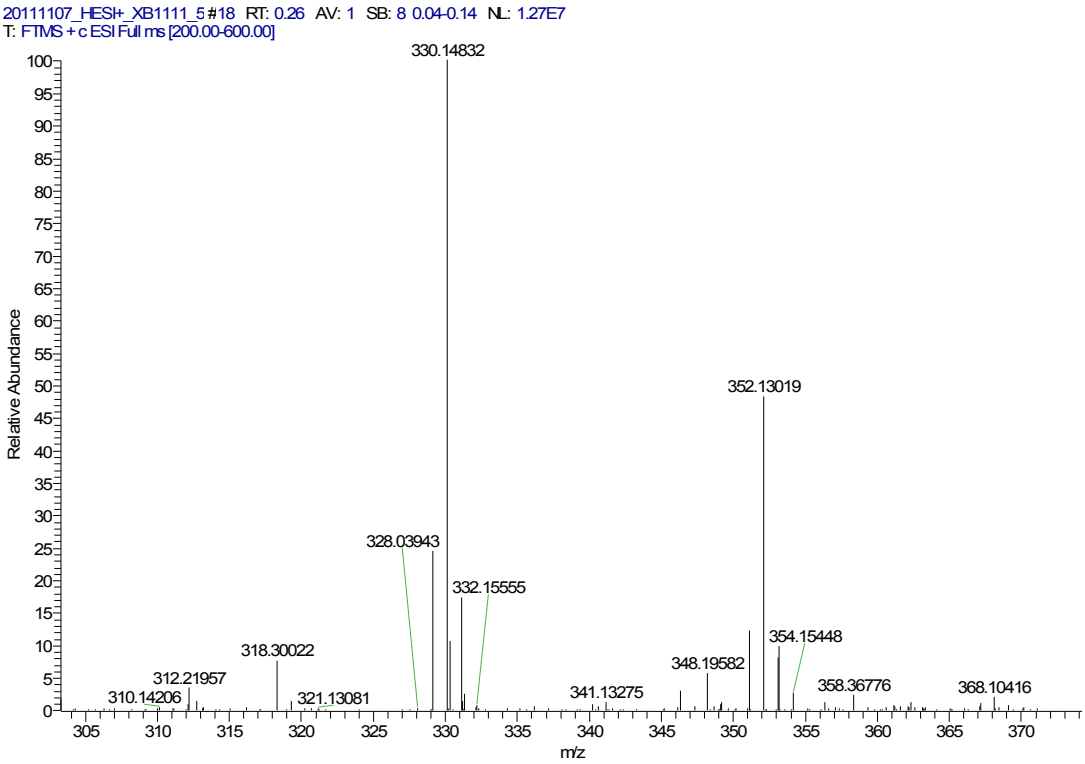
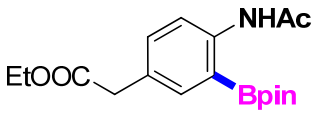
F3C
Bpin
f1 (ppm)



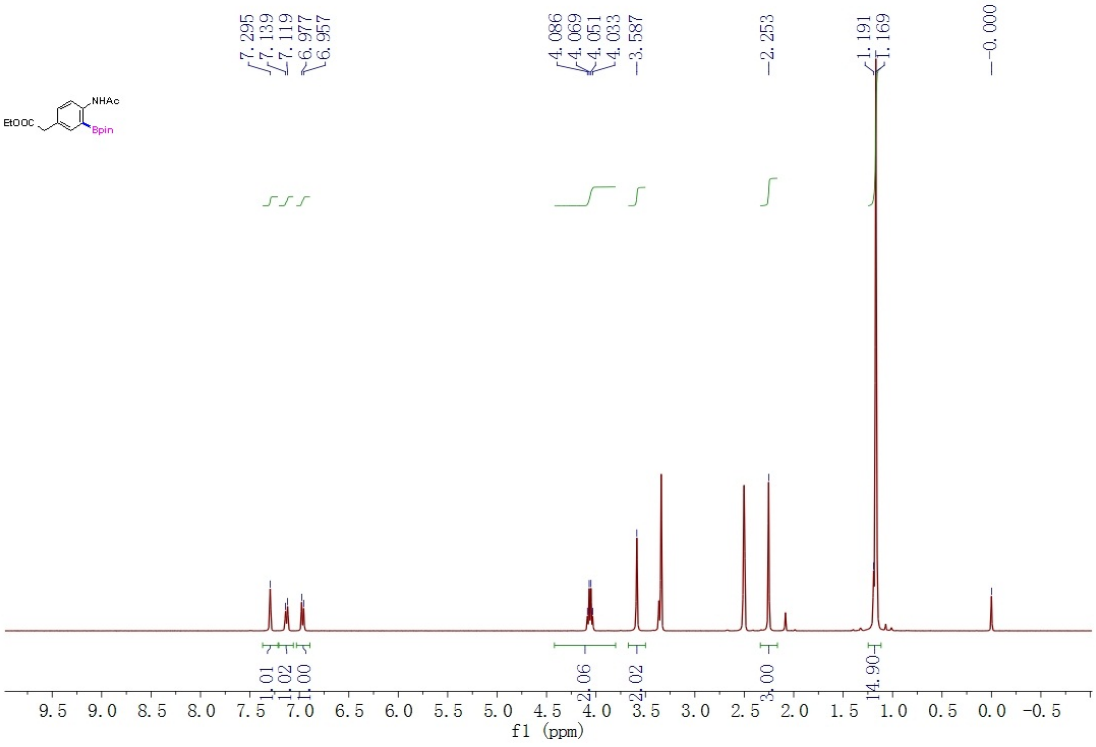


ethyl 2-(4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetate

^{1}H NMR (400 MHz, DMSO) δ 7.30 (s, 1H), 7.13 (d, J = 8.1, 1H), 6.97 (d, J = 8.1, 1H), 4.06 (q, J = 7.0, 2H), 3.59 (s, 2H), 2.25 (s, 3H), 1.18 (m, 15H).

13C NMR (100 MHz, DMSO) δ 171.19, 169.52, 136.78, 133.21, 130.96, 128.36, 115.53, 79.54, 60.08, 40.29, 25.93, 21.63, 13.96.

HRMS requires $[C18H26BNO5+H]^+$ 348.1977, found ESI $[M+H]^+$ 348.1977.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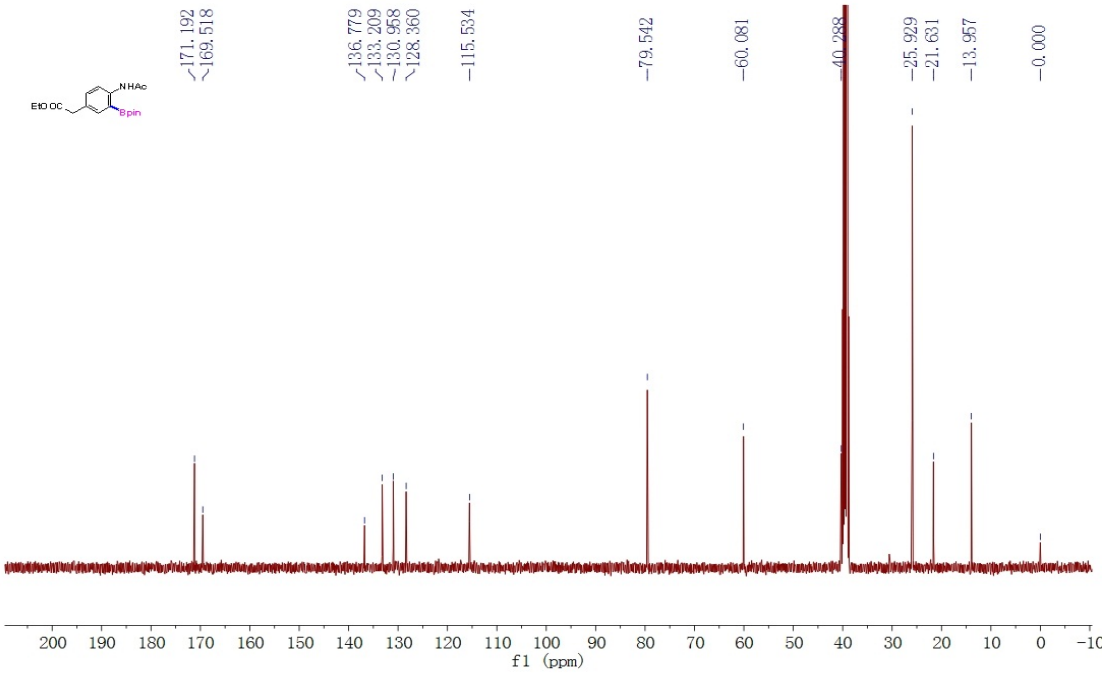
7.139
7.119
6.977
6.957
4.086
4.069
4.051
4.033
3.587
2.253
1.191
1.169
0.000
NHAc
EtOOC
Bpin
1.01
1.02
1.00
2.06
2.02
3.00
14.90
f1 (ppm)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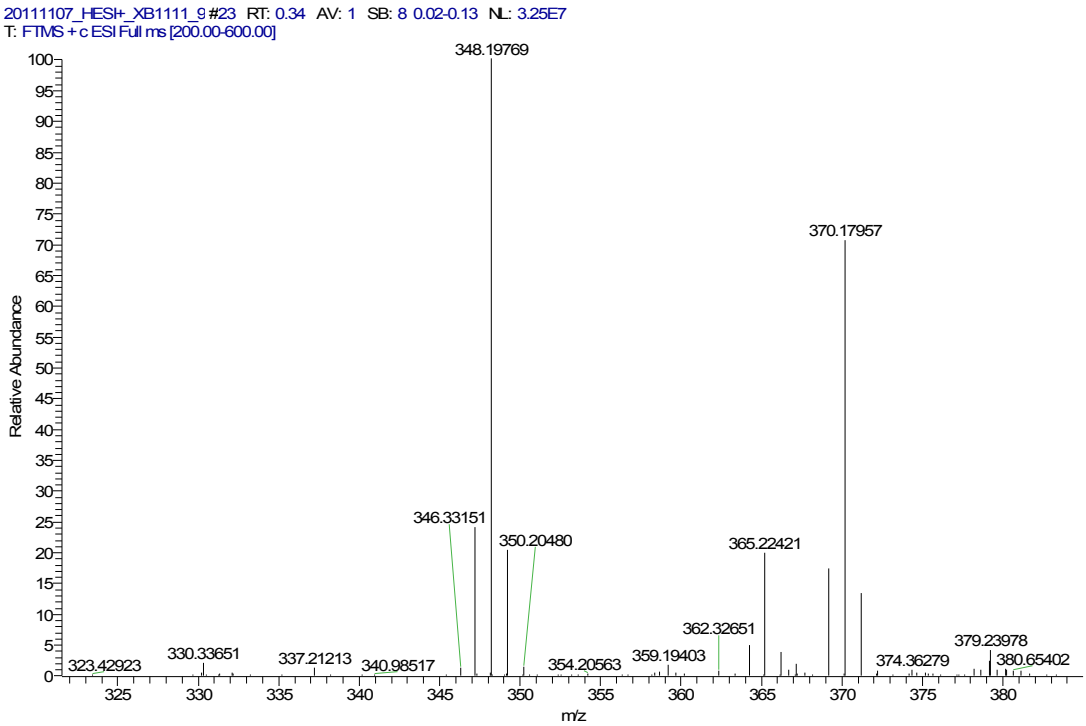
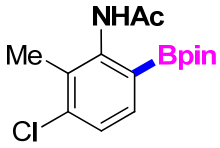
0.000
NHAc
EtO OC
Bpin
f1 (ppm)



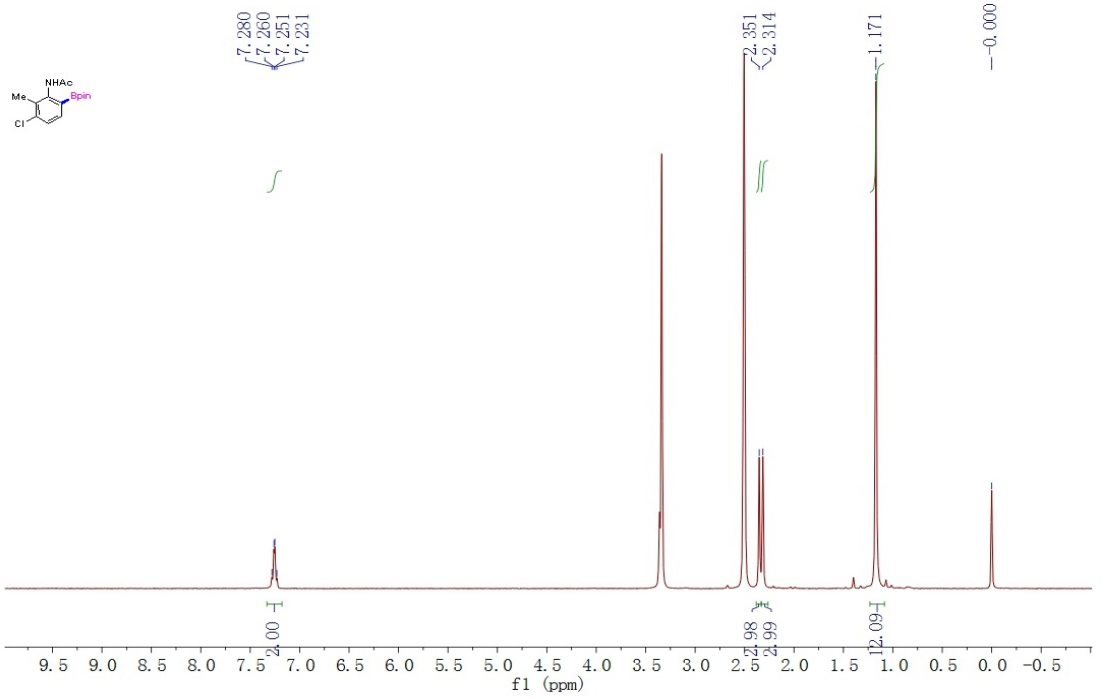


N-(3-chloro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.26 (m, 2H), 2.35 (s,3H), 2.31 (s, 3H), 1.17 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 171.30, 140.28, 138.15, 133.08, 131.21, 125.86, 123.61, 80.19, 25.66, 22.10, 14.14.

HRMS requires $[C15H21BClNO3+H]^{+}$ 310.1376, found ESI $[M+H]^{+}$ 310.1374 .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Me
Bpin
Cl
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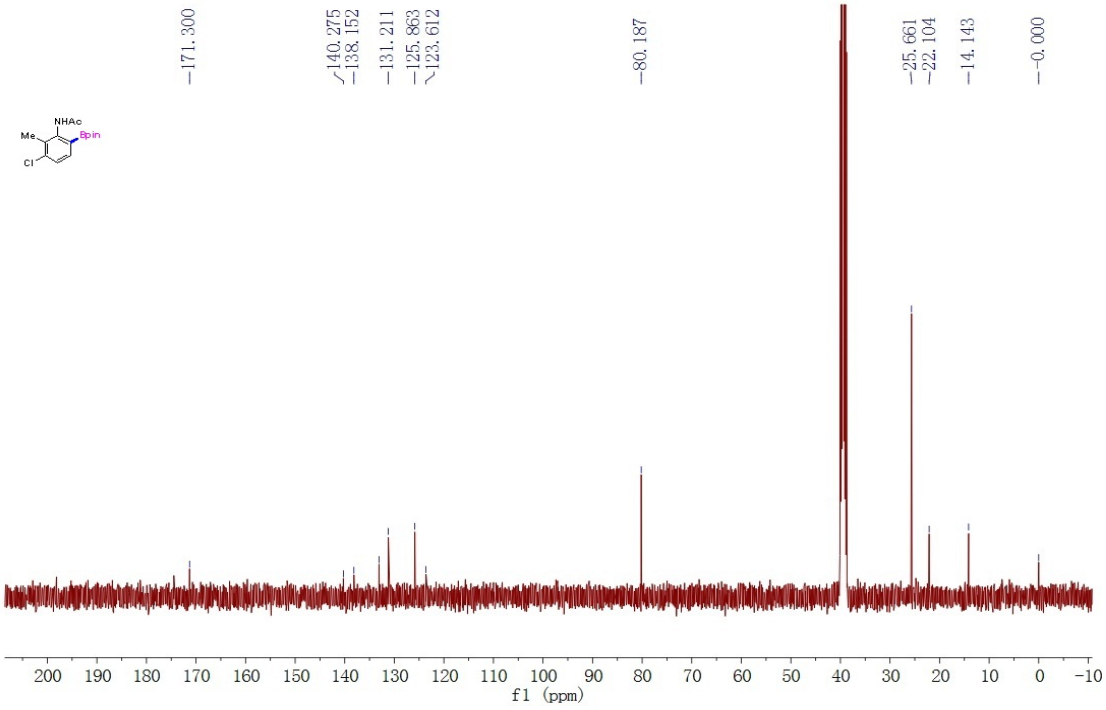
2.99
12.09
f1 (ppm)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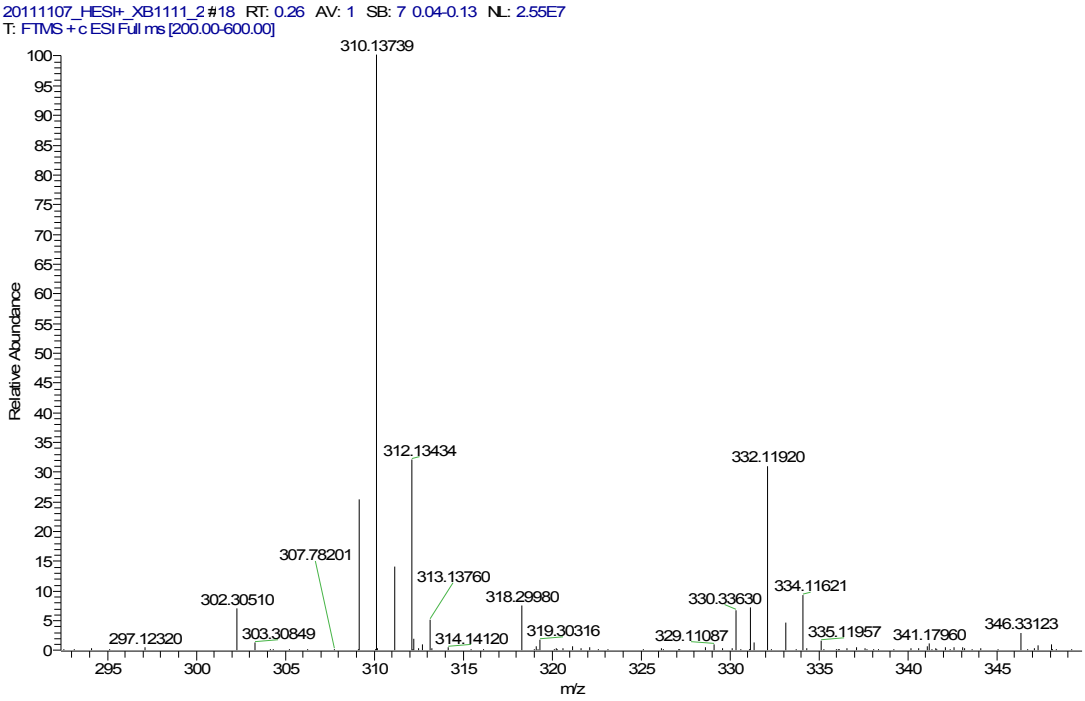
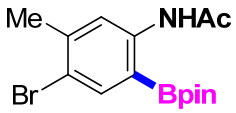
NHAc
Me
Bpin
Cl
f1 (ppm)



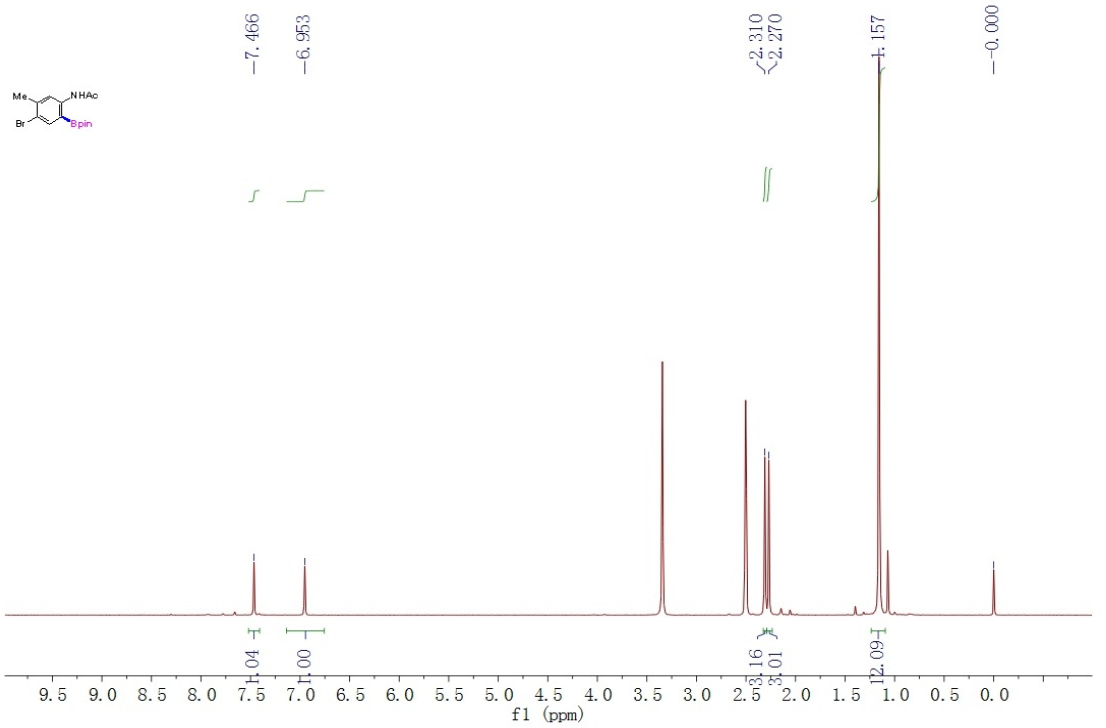


N-(4-bromo-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.47 (s, 1H), 6.95 (s, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.16 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 170.19, 137.33, 137.22, 136.03, 135.66, 120.59, 118.00, 79.54, 25.91, 22.29, 21.68.

HRMS requires $[C15H21BBrNO3+H]^{+}$ 354.0871, found ESI $[M+H]^{+}$ 354.0870 .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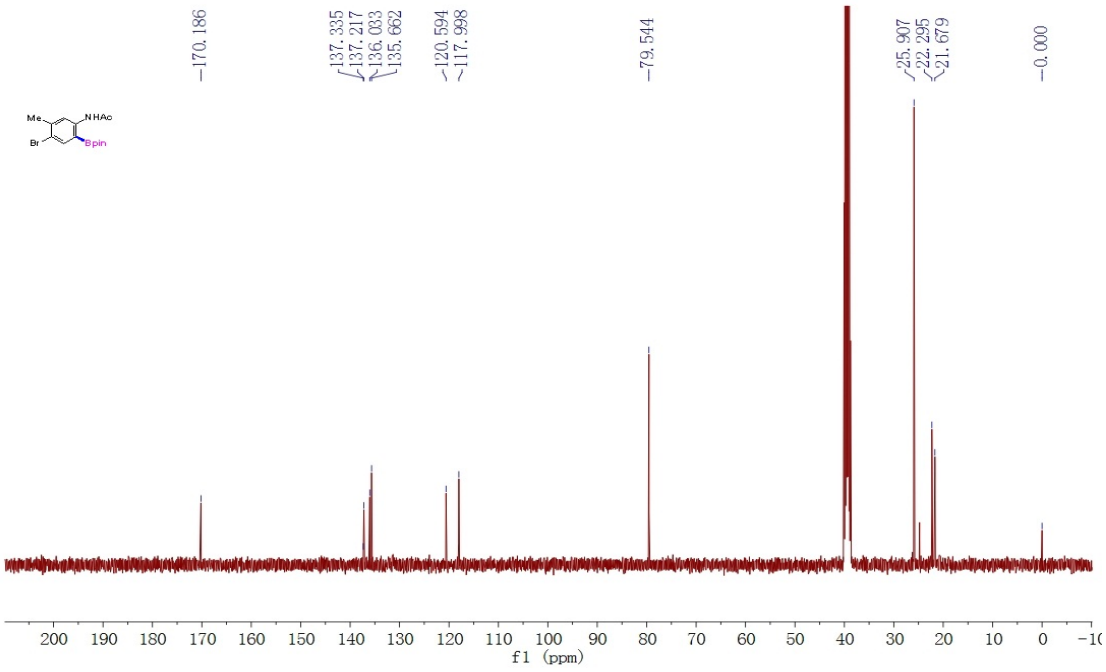
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22.295
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0.000
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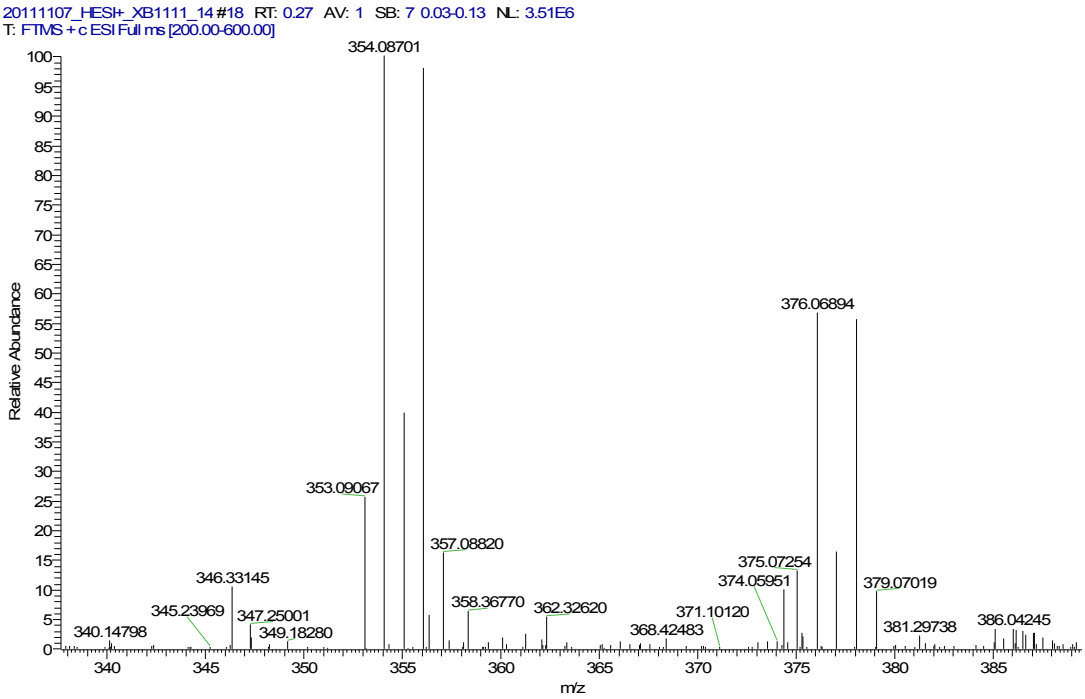
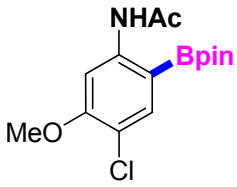


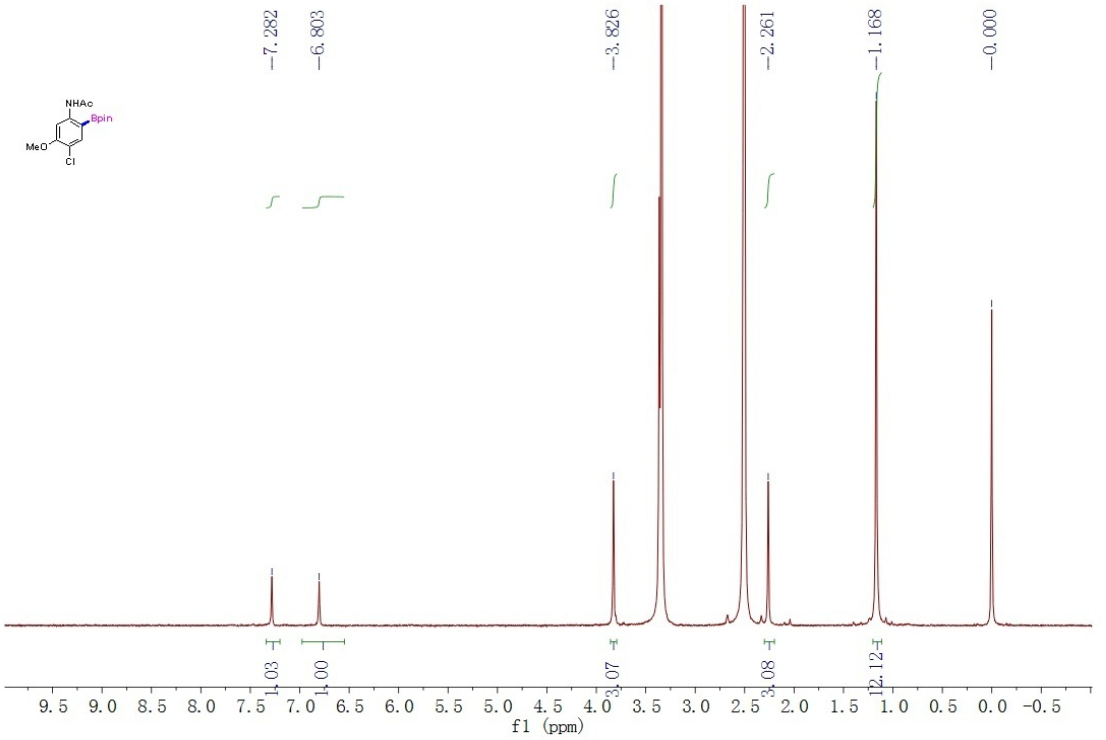


N-(4-chloro-5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

^{1}H NMR (400 MHz, DMSO) δ 7.28 (s, 1H), 6.80 (s, 1H), 3.83 (s, 3H), 2.26 (s, 3H), 1.17 (s, 12H).

^{13}C NMR (100 MHz, DMSO) δ 170.06, 153.86, 137.93, 133.41, 117.59, 100.64, 79.79, 55.77, 25.81, 21.88.

HRMS requires $[C15H21BClNO4+H]^{+}$ 326.1325, found ESI $[M+H]^{+}$ 326.1324 .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3.826
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Bpin
MeO
Cl
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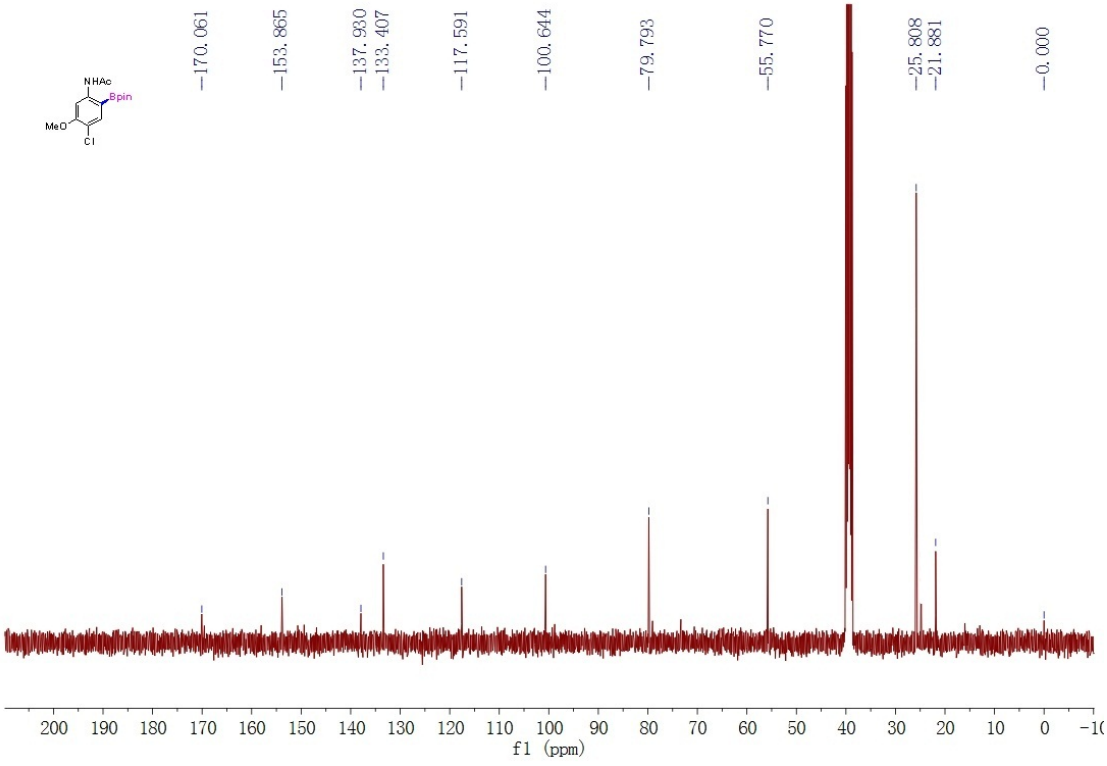
1.00
3.07
3.08
12.12
f1 (ppm)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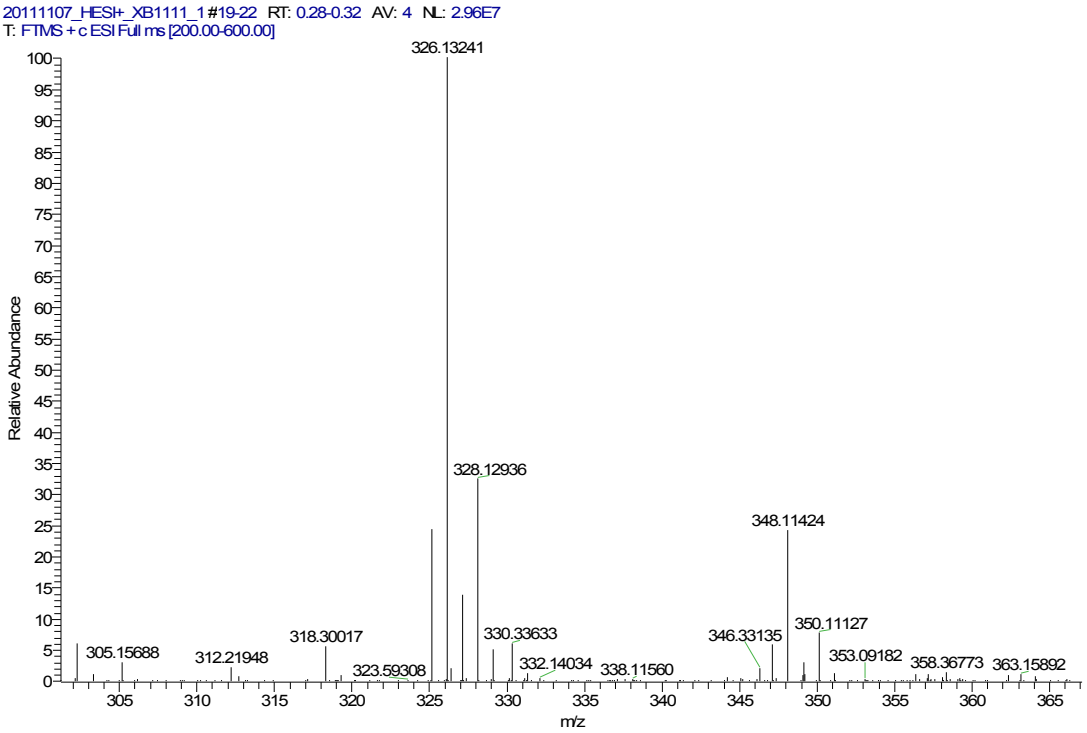
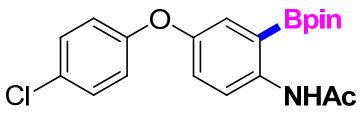
MeO
Cl
f1 (ppm)



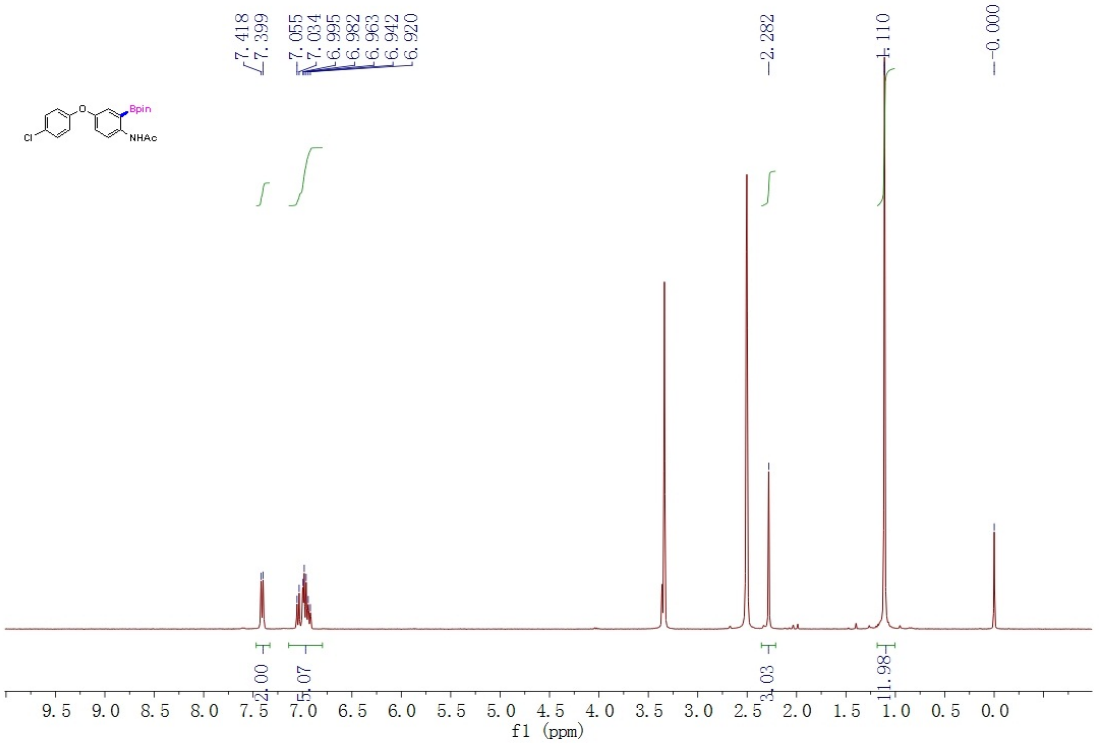


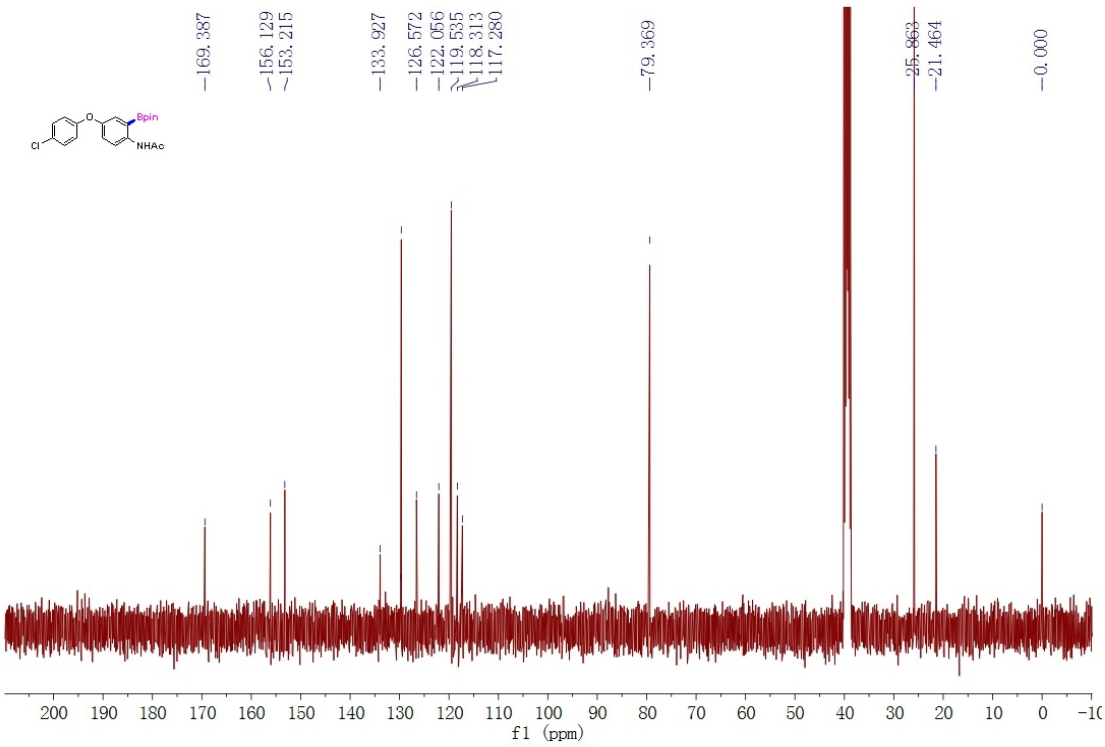
N-(4-(4-chlorophenoxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

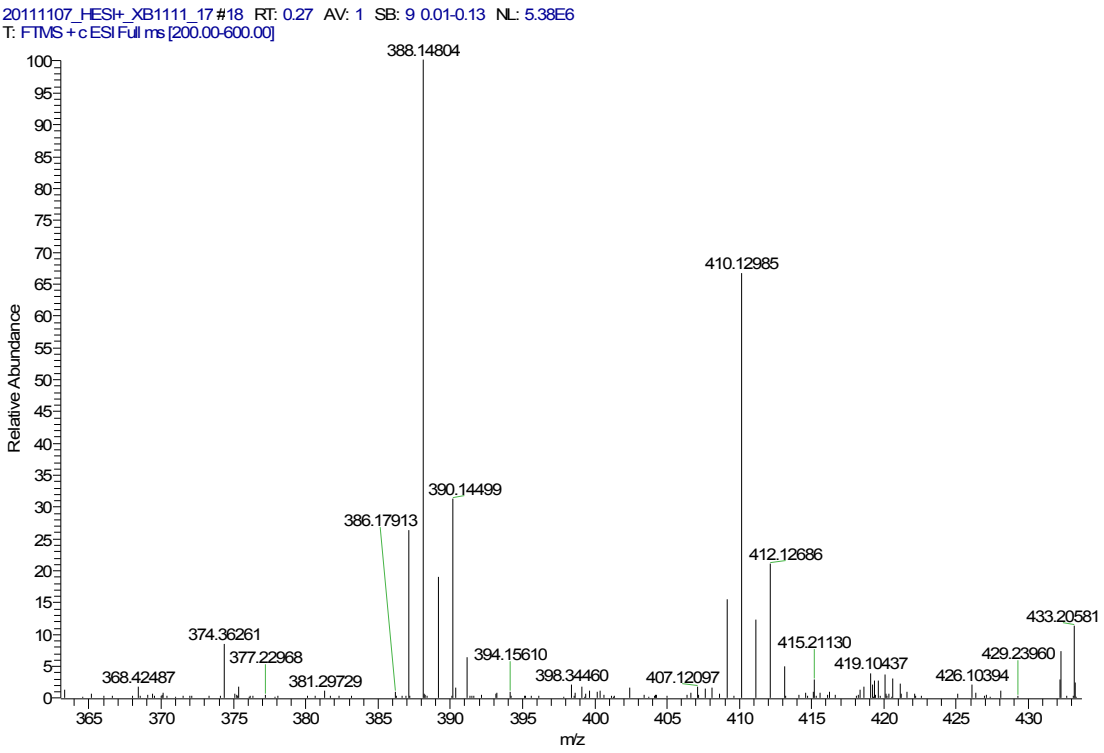
^{1}H NMR (400 MHz, DMSO) δ 7.41 (d, *J* = 7.7, 2H), 7.19 – 6.74 (m, 5H), 2.28 (s, 3H), 1.11 (s, 12H).

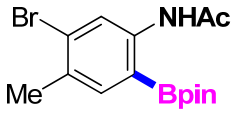
^{13}C NMR (100 MHz, DMSO) δ 169.39, 156.13, 153.22, 133.93, 129.71, 129.65, 126.57, 122.06, 119.53, 118.31, 117.28, 79.37, 25.86, 21.46.

HRMS requires $[C20H23BClNO4+H]^{+}$ 388.1481, found ESI $[M+H]^{+}$ 388.1480 .


7.418
7.399
7.055
7.034
6.995
6.982
6.963
6.942
6.920
2.282
1.110
0.000
Bpin
Cl
NHAc
2.00
5.07
3.03
11.98
f1 (ppm)


169.387
156.129
153.215
133.927
126.572
122.056
119.535
118.313
117.280
79.369
25.863
21.464
0.000
Bpin
Cl
NHAc
f1 (ppm)



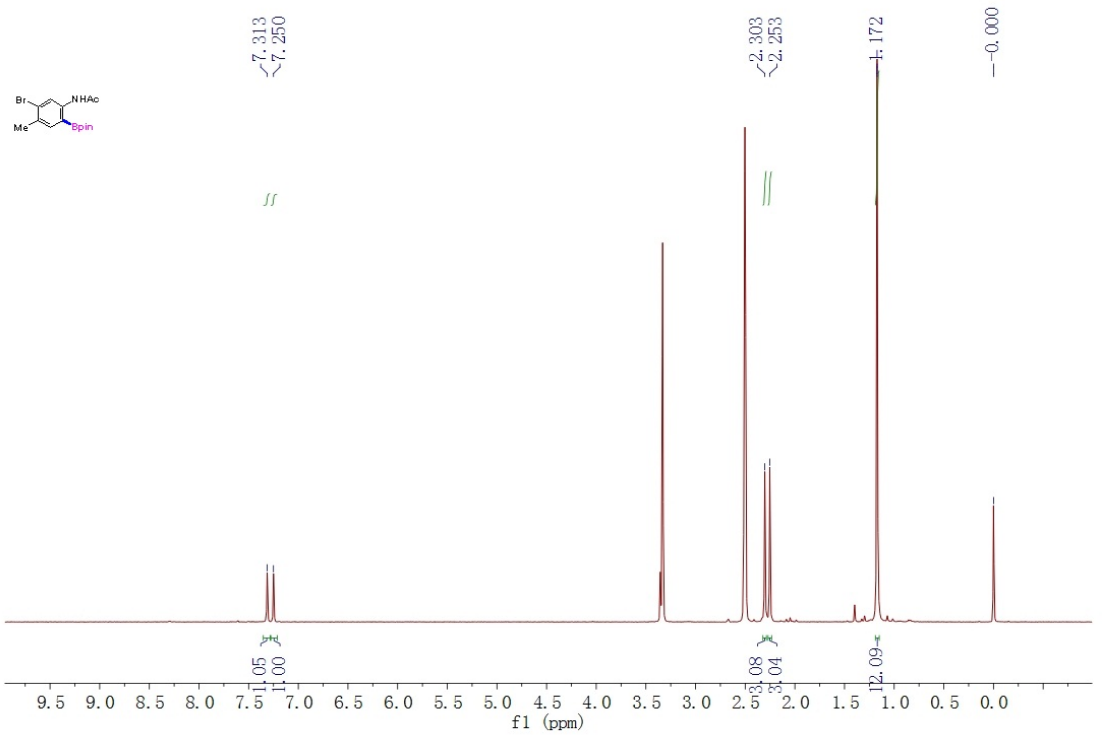


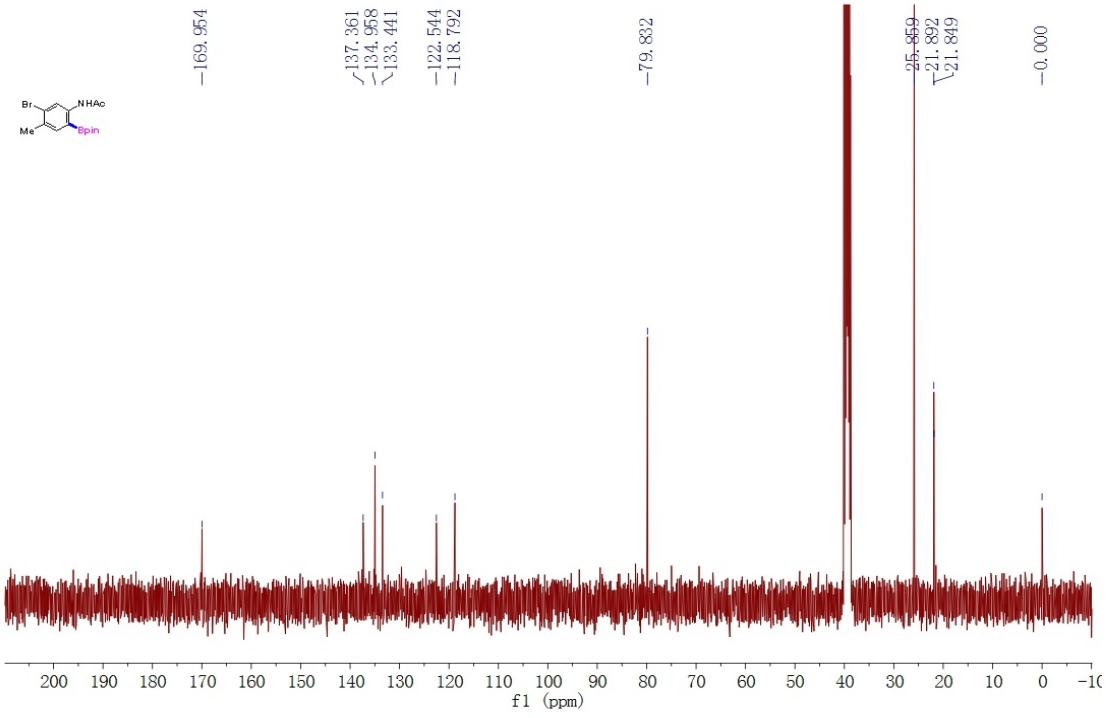
N-(5-bromo-4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

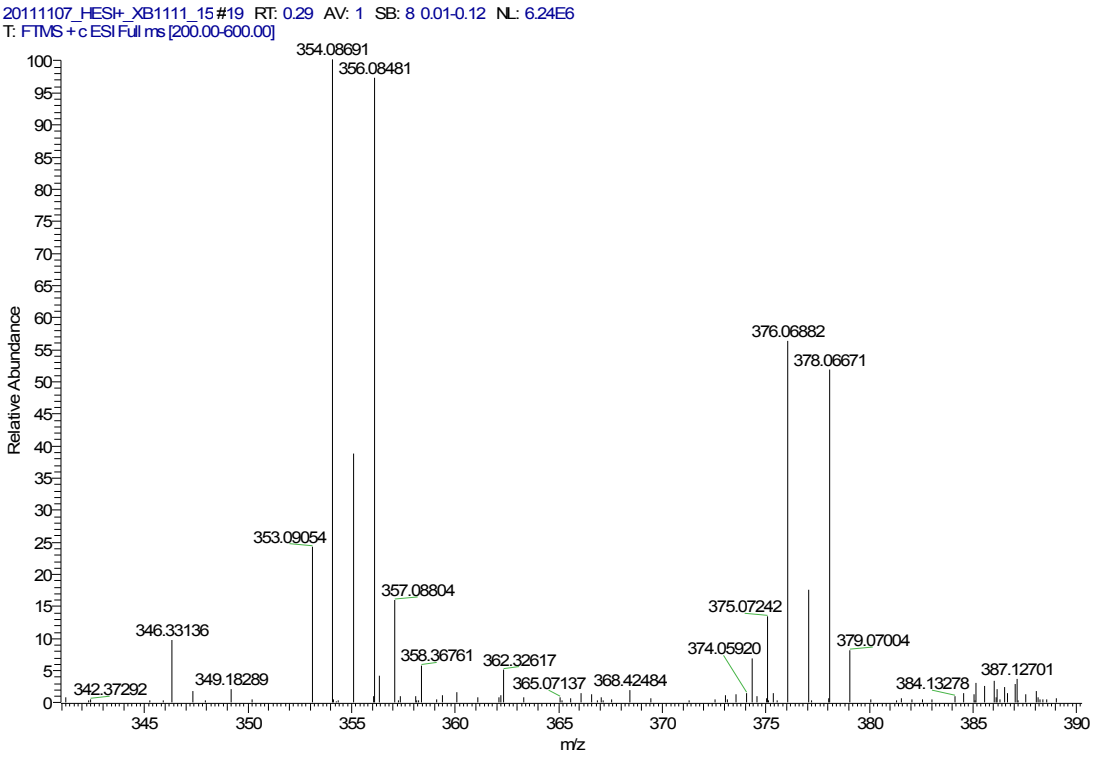
^{1}H NMR (400 MHz, DMSO) δ 7.31 (s, 1H), 7.25 (s, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 1.17 (s, 12H).

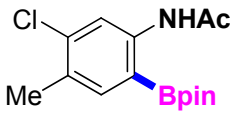
^{13}C NMR (100 MHz, DMSO) δ 169.95, 137.36, 134.96, 133.44, 122.54, 118.79, 79.83, 25.86, 21.89, 21.85.

HRMS requires $[C15H21BBrNO3+H]^{+}$ 354.0871, found ESI $[M+H]^{+}$ 354.0869 .


7.313
7.250
2.303
2.253
1.172
0.000
1.05
1.00
3.08
3.04
12.09
f1 (ppm)


169.954
137.361
134.958
133.441
122.544
118.792
79.832
25.859
21.892
21.849
0.000
f1 (ppm)



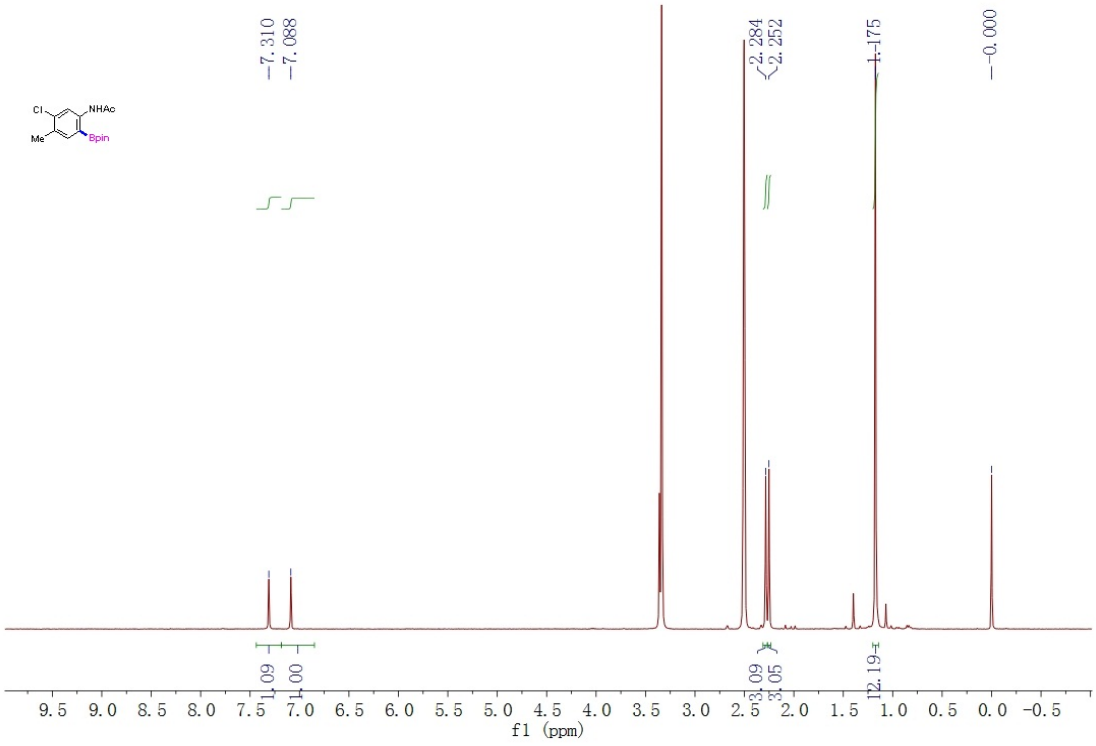


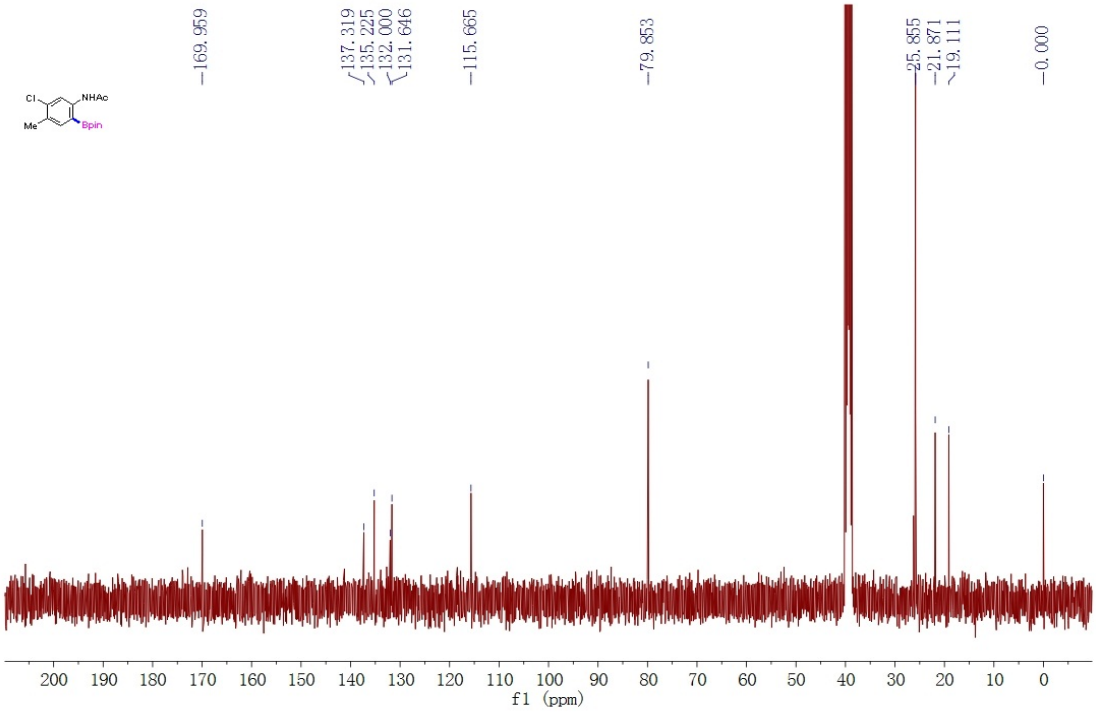
N-(5-chloro-4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

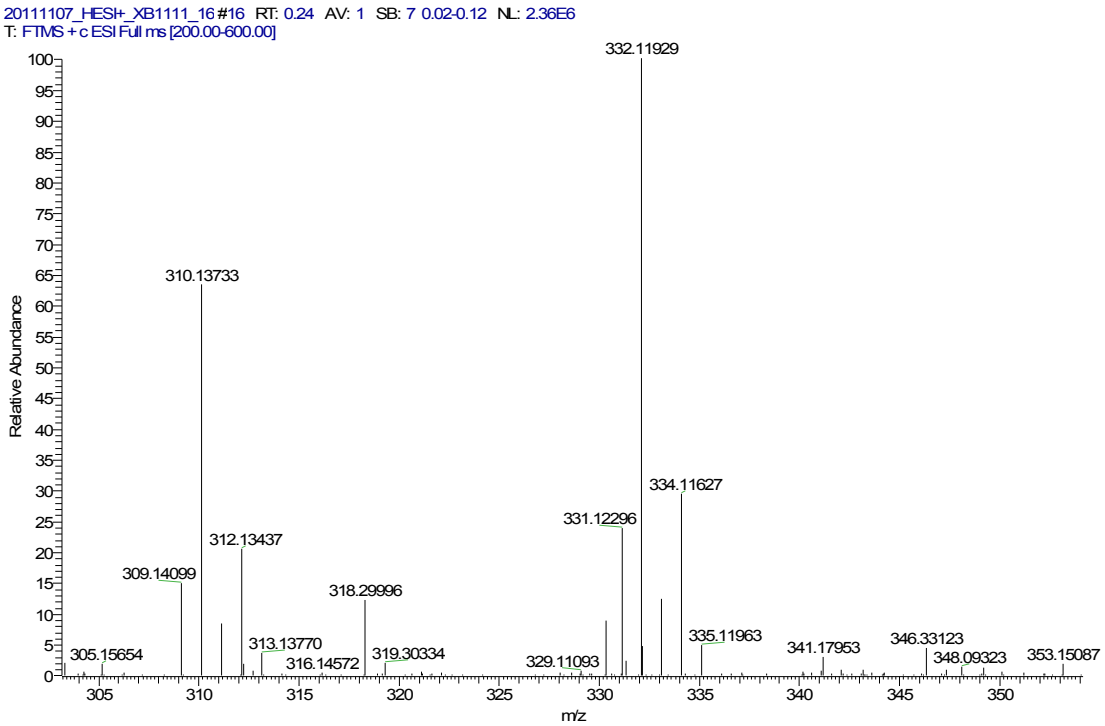
^{1}H NMR (400 MHz, DMSO) δ 7.31 (s, 1H), 7.09 (s, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 1.17 (s, 12H).

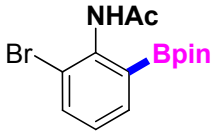
^{13}C NMR (100 MHz, DMSO) δ 169.96, 137.32, 135.22, 132.00, 131.65, 115.67, 79.85, 25.86, 21.87, 19.11.

HRMS requires $[C15H21BClNO3+H]^{+}$ 310.1376, found ESI $[M+H]^{+}$ 310.1373 .


7.310
7.088
2.284
2.252
1.175
0.000
1.09
1.00
3.09
3.05
12.19
f1 (ppm)


169.959
137.319
135.225
132.000
131.646
115.665
79.853
25.855
21.871
19.111
0.000
f1 (ppm)



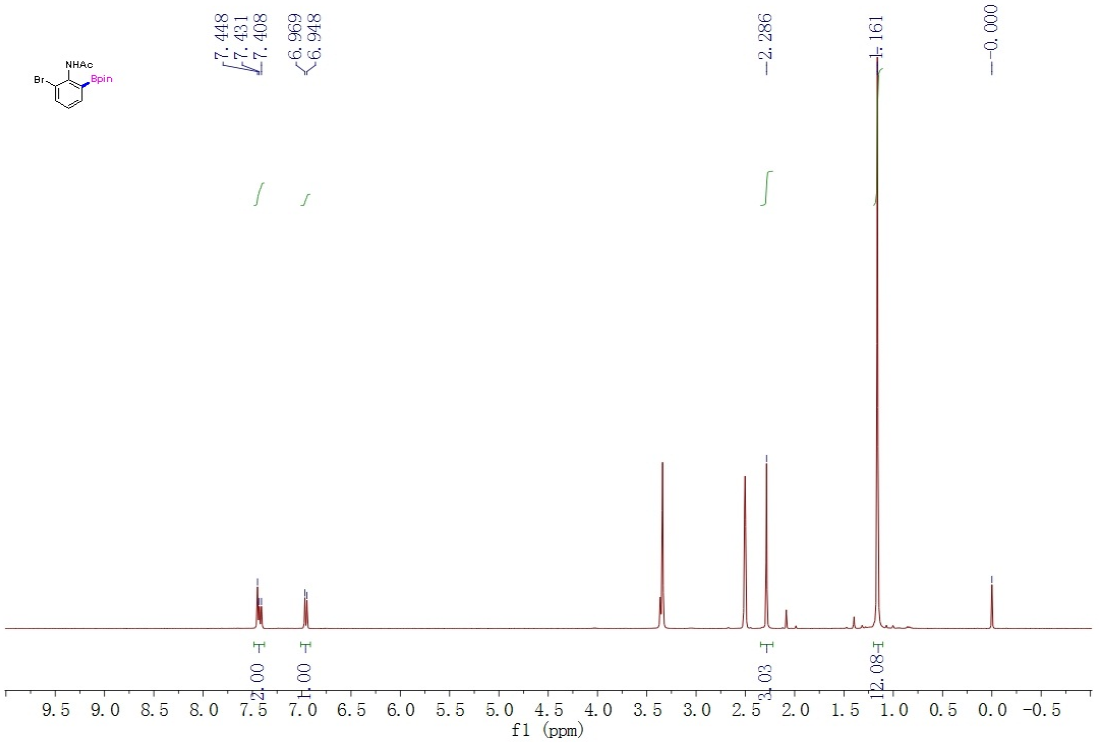


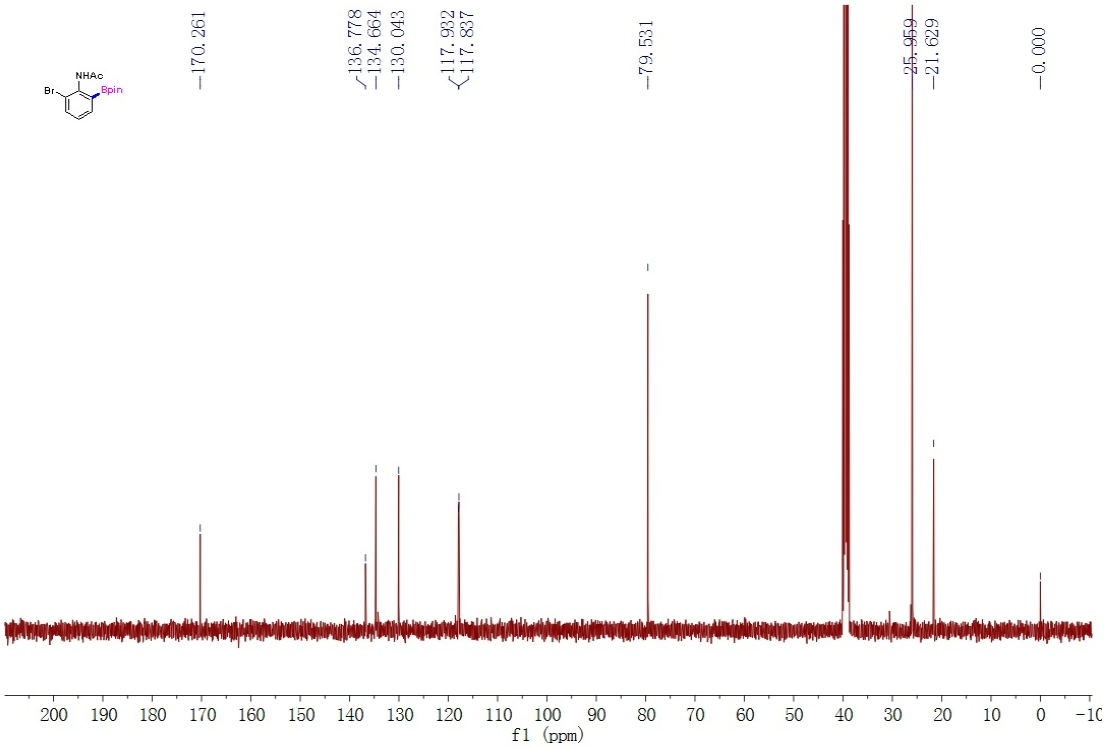
N-(2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

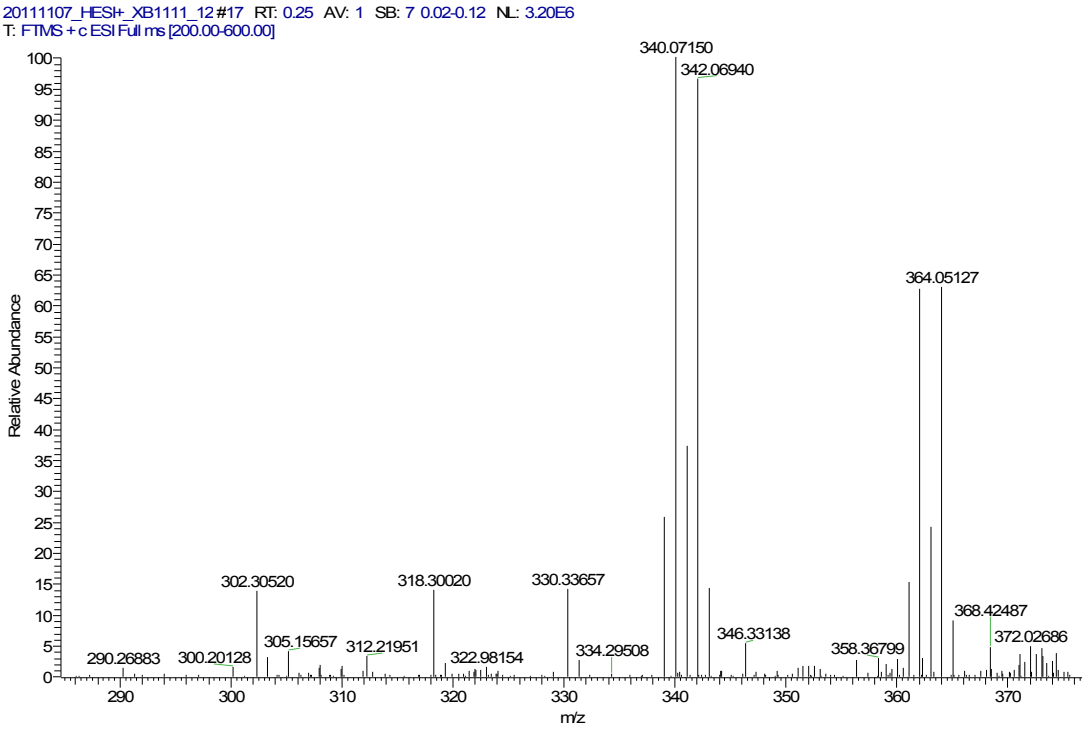
^{1}H NMR (400 MHz, DMSO) δ 7.52 – 7.32 (m, 2H), 6.96 (d, J = 8.4, 1H), 2.29 (s, 3H), 1.16 (s, 12H).

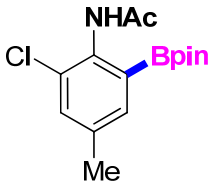
^{13}C NMR (100 MHz, DMSO) δ 170.26, 136.78, 134.66, 130.04, 117.93, 117.84, 79.53, 25.96, 21.63.

HRMS requires $[C14H19BBrNO3+H]^{+}$ 340.0714, found ESI $[M+H]^{+}$ 340.0715.


NHAc
Br
Bpin
7.448
7.431
7.408
6.969
6.948
2.286
1.161
0.000
2.00
1.00
3.03
12.08
f1 (ppm)


NHAc
Br
Bpin
170.261
136.778
134.664
130.043
117.932
117.837
79.531
25.959
21.629
0.000
f1 (ppm)



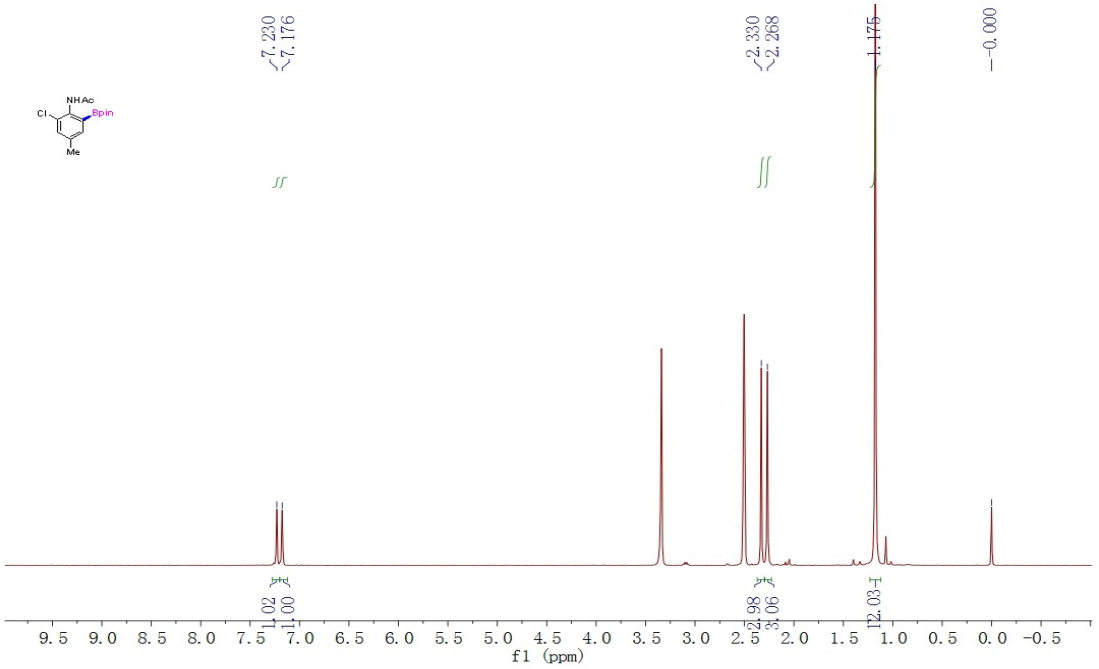


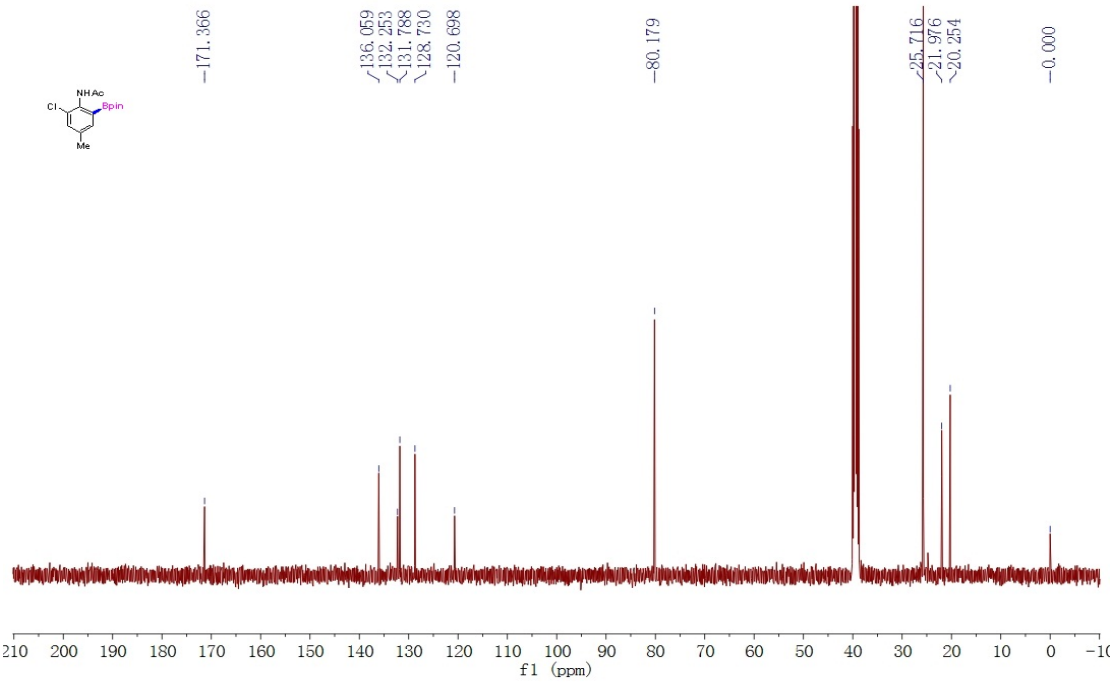
N-(2-chloro-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

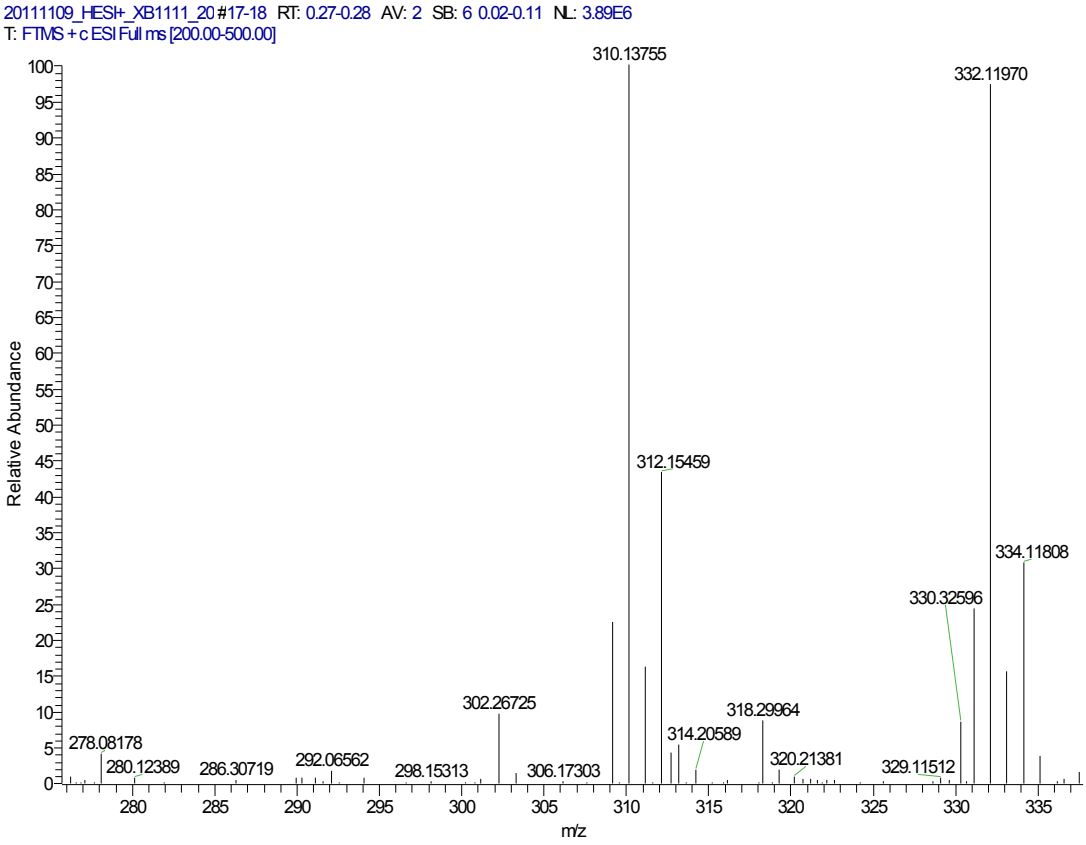
^{1}H NMR (400 MHz, DMSO) δ 7.23 (s, 1H), 7.18 (s, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.18 (s, 12H).

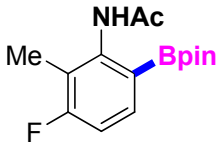
^{13}C NMR (100 MHz, DMSO) δ 171.37, 136.06, 132.25, 131.79, 128.73, 120.70, 80.18, 25.72, 21.98, 20.25.

HRMS requires $[C15H21BClNO3+H]^{+}$ 310.1376, found ESI $[M+H]^{+}$ 310.1376 .


7.230
7.176
2.330
2.268
1.175
-0.000
1.02
1.00
2.98
3.06
12.03
f1 (ppm)


171.366
136.059
132.253
131.788
128.730
120.698
80.179
25.716
21.976
20.254
0.000
f1 (ppm)



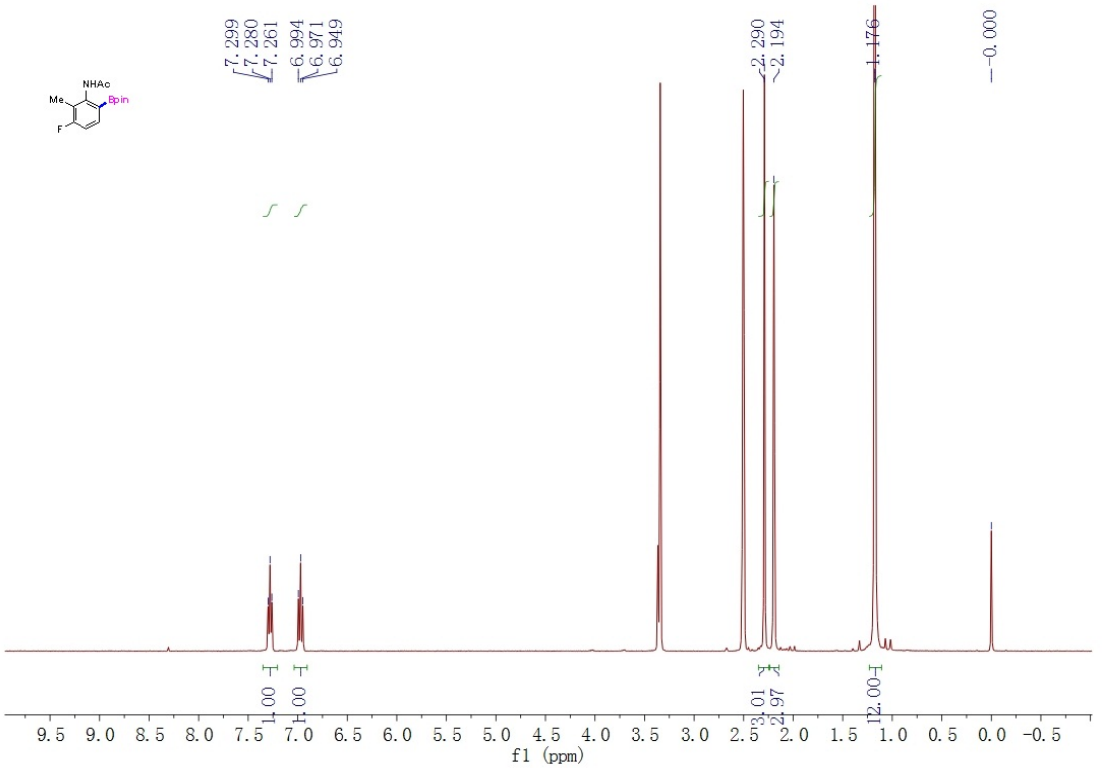


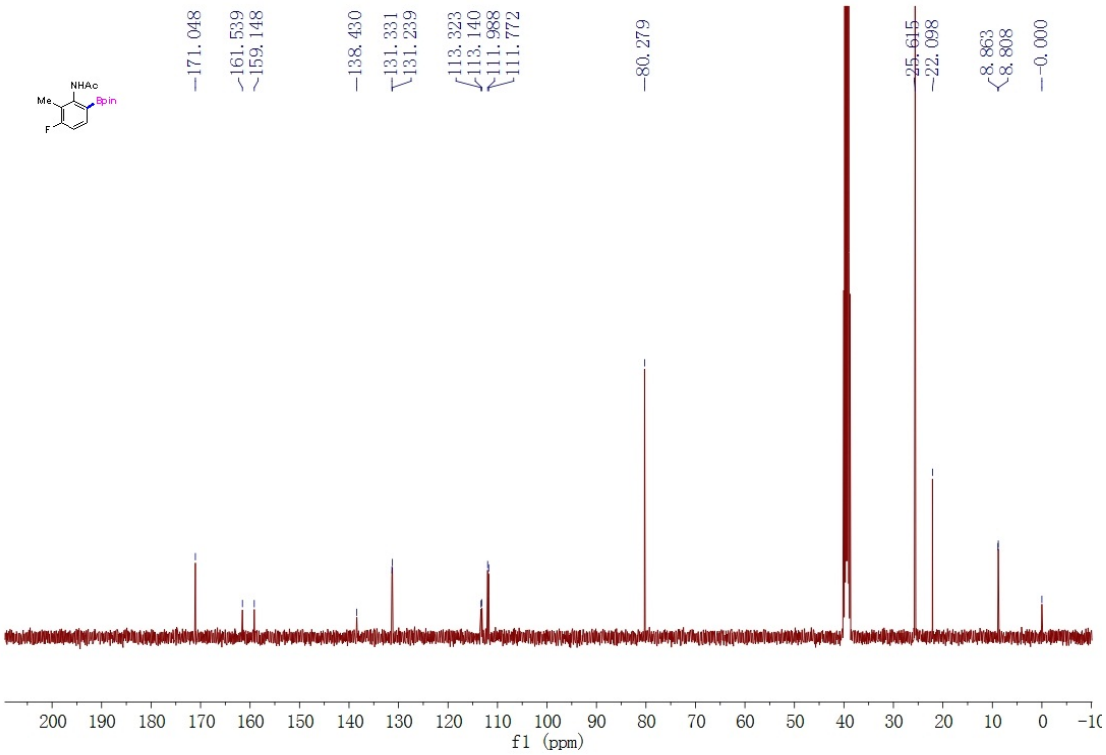
N-(3-fluoro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

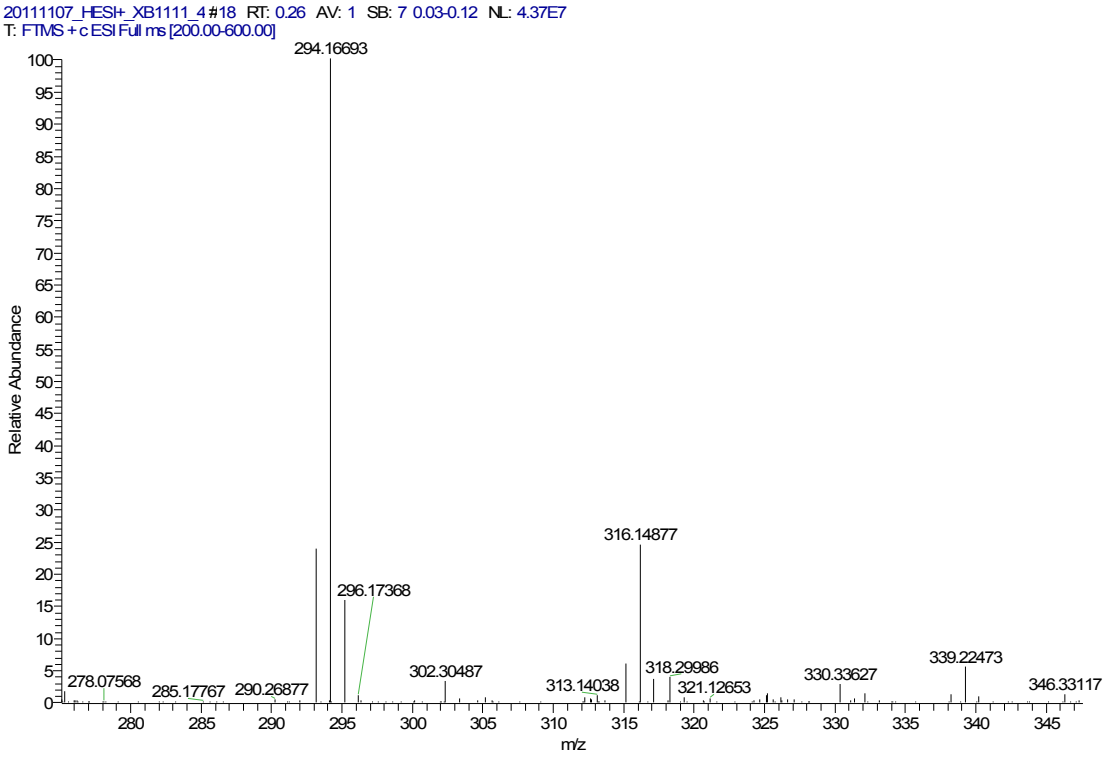
^{1}H NMR (400 MHz, DMSO) δ 7.28 (t, J = 7.5, 1H), 6.97 (t, J = 8.9, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 1.18 (s, 12H).

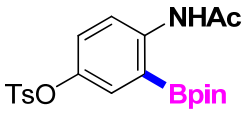
^{13}C NMR (100 MHz, DMSO) δ 171.05, 160.34 (d, J = 239 Hz), 138.43, 131.28 (d, J = 9.2 Hz), 113.23 (d, J = 18 Hz), 111.88 (d, J = 22 Hz), 80.28, 25.62, 22.10, 8.83.

HRMS requires $[C15H21BFNO3+H]^{+}$ 294.1671, found ESI $[M+H]^{+}$ 294.1669.


7.299
7.280
7.261
6.994
6.971
6.949
2.290
2.194
1.176
-0.000
NHAc
Me
Bpin
F
1.00
1.00
3.01
2.97
12.00
f1 (ppm)


171.048
161.539
159.148
138.430
131.331
131.239
113.323
113.140
111.988
111.772
80.279
25.615
22.098
8.863
8.808
-0.000
NHAc
Me
Bpin
F
f1 (ppm)



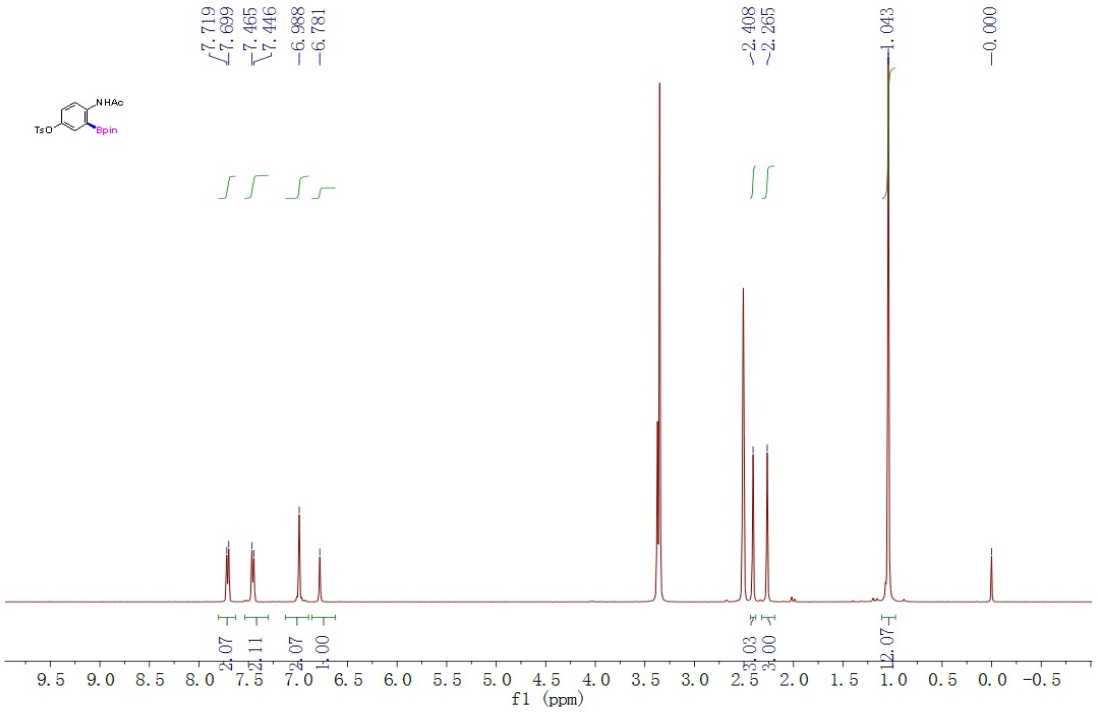


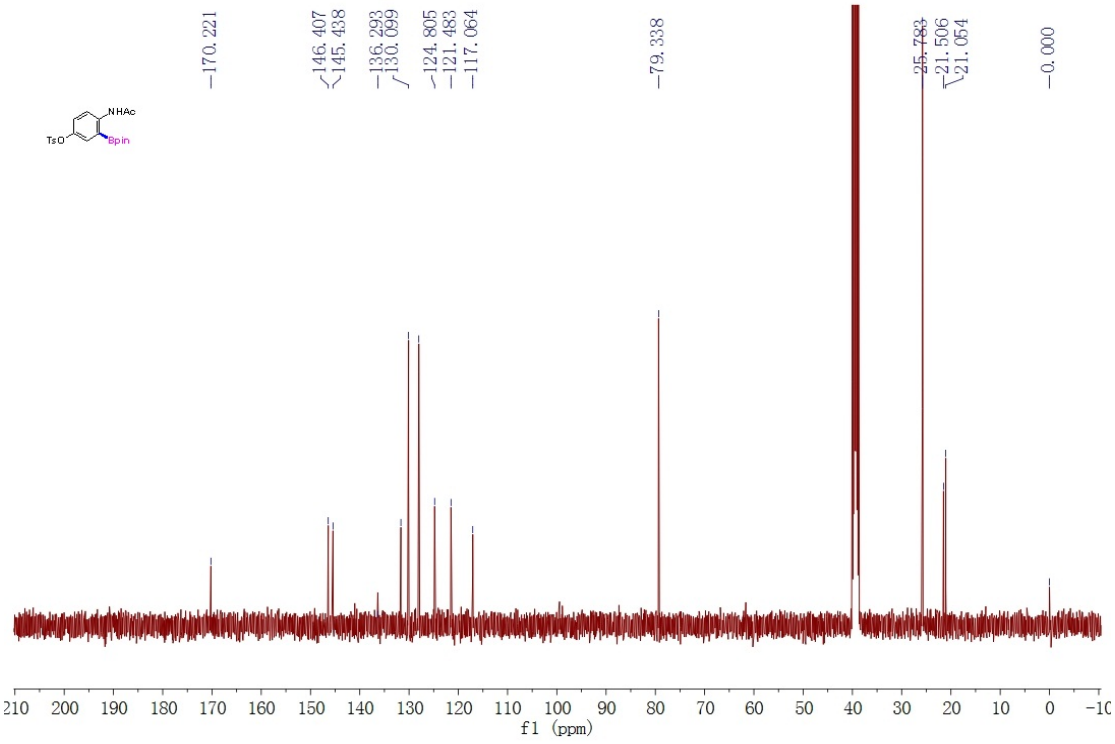
4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 4-methylbenzenesulfonate

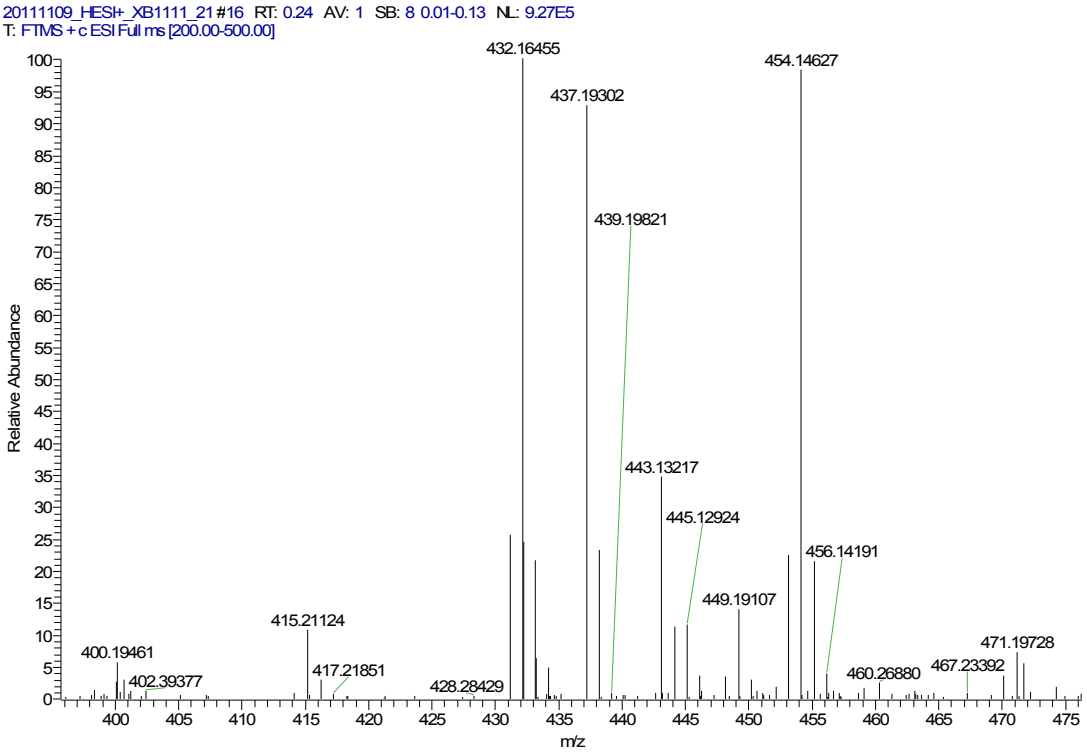
^{1}H NMR (400 MHz, DMSO) δ 7.71 (d, J = 8.0, 2H), 7.46 (d, J = 7.7, 2H), 6.99 (s, 2H), 6.78 (s, 1H), 2.41 (s, 3H), 2.26 (s, 3H), 1.04 (s, 12H).

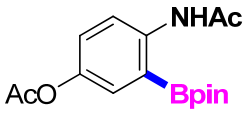
^{13}C NMR (100 MHz, DMSO) δ 170.22, 146.41, 145.44, 136.29, 131.65, 130.10, 128.02, 124.80, 121.48, 117.06, 79.34, 25.78, 21.51, 21.05.

HRMS requires $[C_{21}H_{26}BNO_6S+H]^+$ 432.1647, found ESI $[M+H]^+$ 432.1646.


7.719
7.699
7.465
7.446
6.988
6.781
2.408
2.265
1.043
0.000
NHAc
TsO
Bpin
2.07
2.11
2.07
1.00
3.03
3.00
12.07
f1 (ppm)


170.221
146.407
145.438
136.293
130.099
124.805
121.483
117.064
79.338
25.783
21.506
21.054
0.000
NHAc
TsO
Bpin
f1 (ppm)



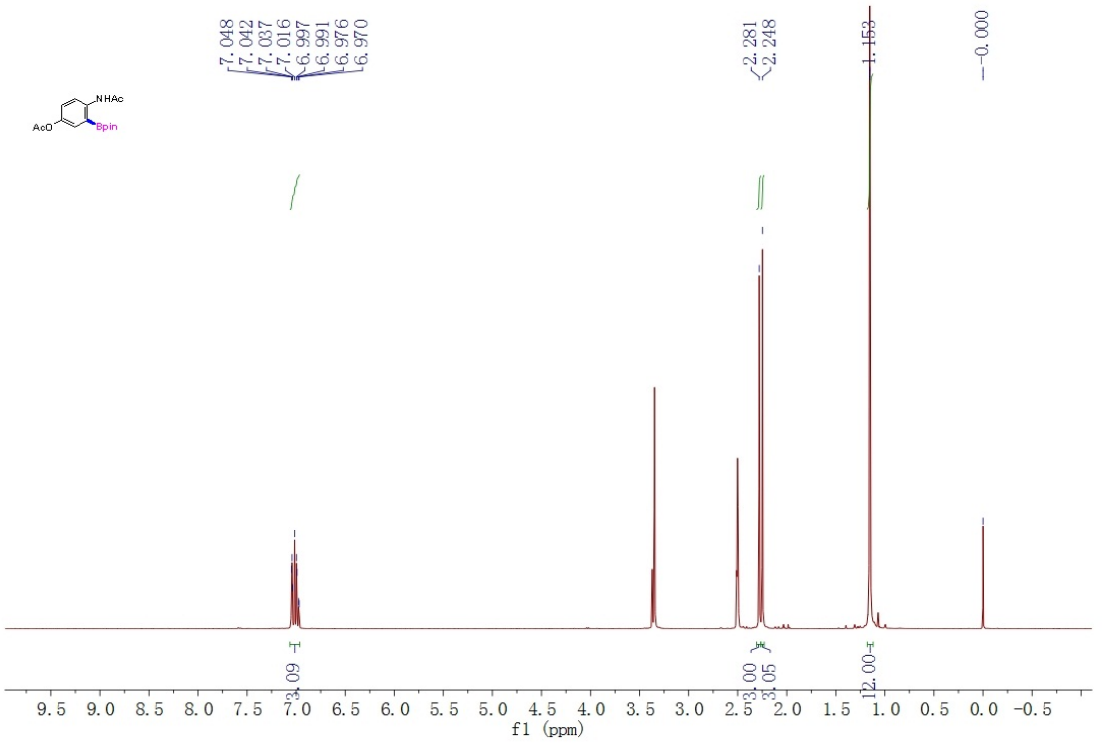


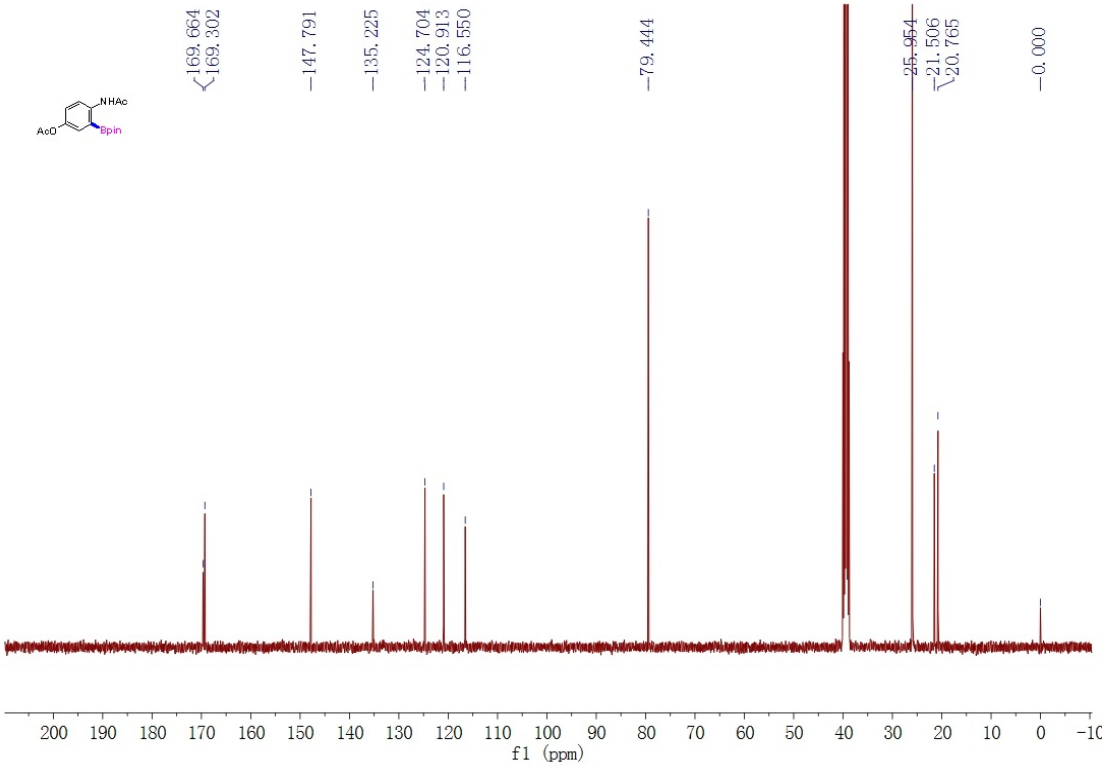
4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acetate

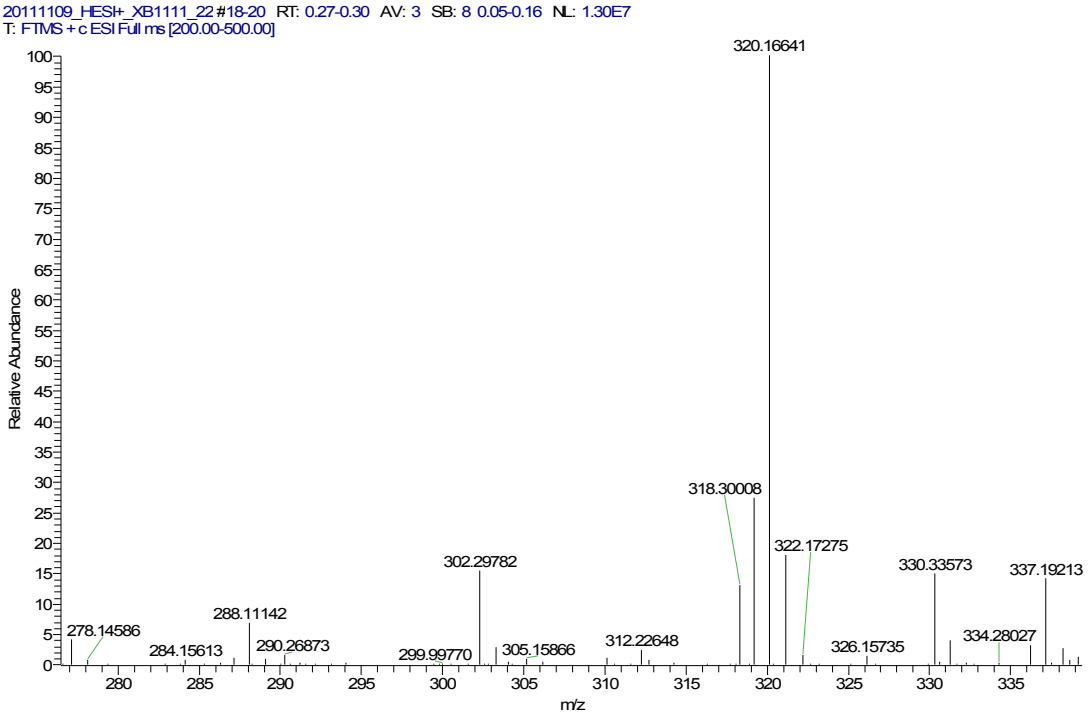
^{1}H NMR (400 MHz, DMSO) δ 7.01 (m, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 1.15 (s, 12H).

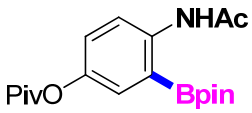
^{13}C NMR (100 MHz, DMSO) δ 169.66, 169.30, 147.79, 135.23, 124.70, 120.91, 116.55, 79.44, 25.95, 21.51, 20.76.

HRMS requires $[C16H22BNO5+H]^{+}$ 320.1664, found ESI $[M+H]^{+}$ 320.1664.


7.048
7.042
7.037
7.016
6.997
6.991
6.976
6.970
2.281
2.248
1.153
0.000
NHAc
AcO
Bpin
3.09
3.00
3.05
12.00
f1 (ppm)


169.664
169.302
147.791
135.225
124.704
120.913
116.550
79.444
25.964
21.506
20.765
0.000
NHAc
AcO
Bpin
f1 (ppm)



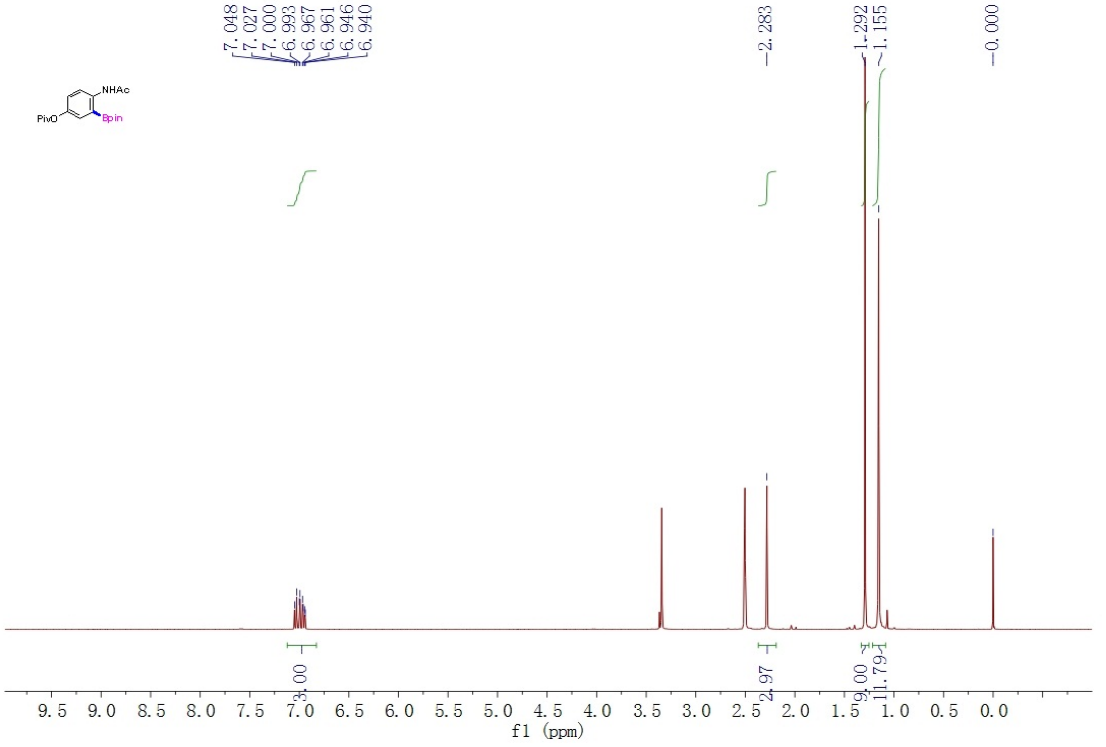


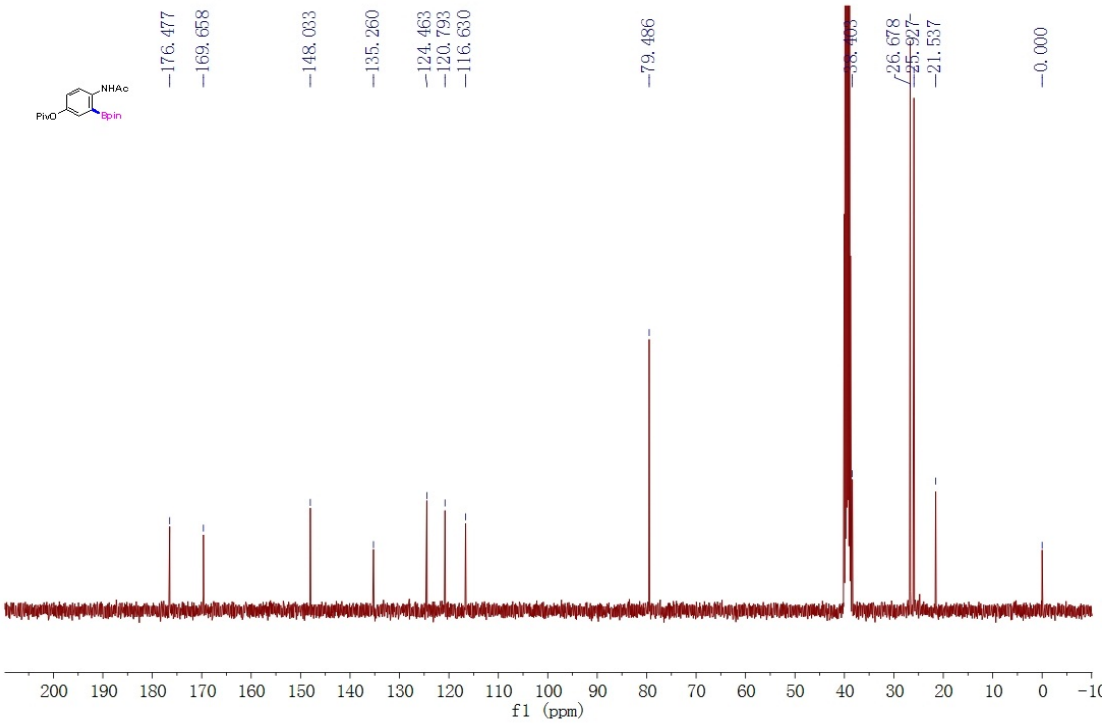
4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl pivalate

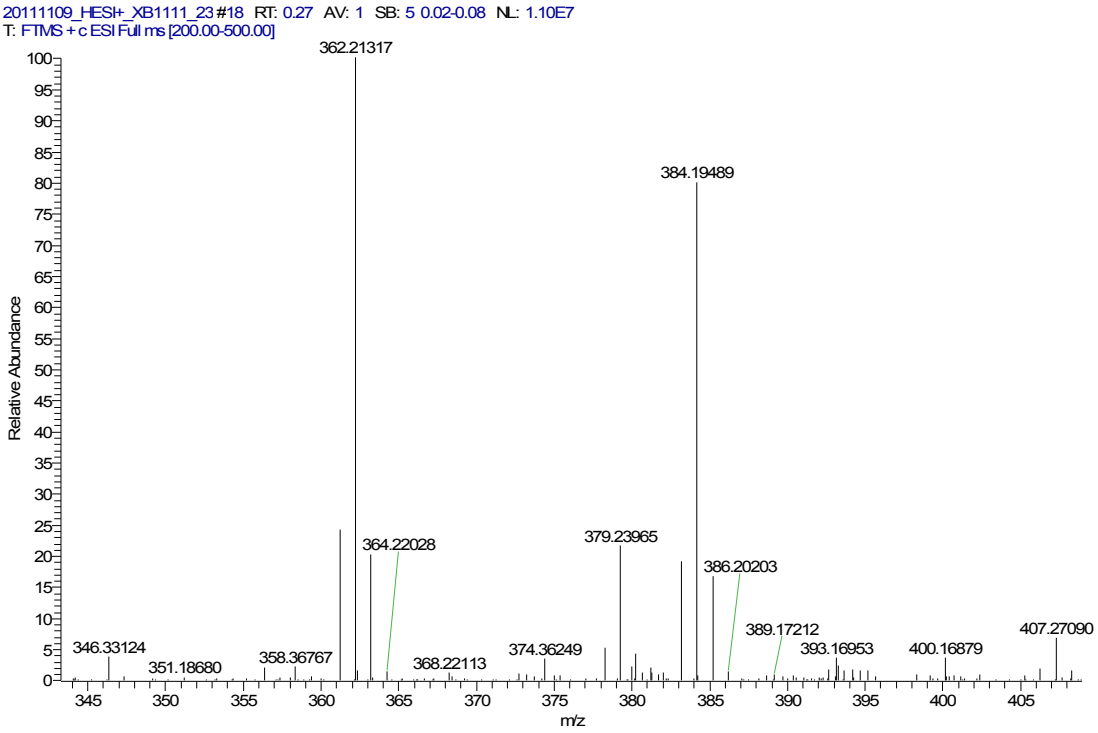
^{1}H NMR (400 MHz, DMSO) δ 6.99 (m, 3H), 2.28 (s, 3H), 1.29 (s, 9H), 1.15 (s, 12H).

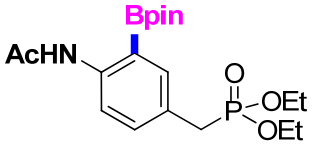
^{13}C NMR (100 MHz, DMSO) δ 176.48, 169.66, 148.03, 135.26, 124.46, 120.79, 116.63, 79.49, 38.40, 26.68, 25.93, 21.54.

HRMS requires $[C19H28BNO5+H]^{+}$ 362.2133, found ESI $[M+H]^{+}$ 362.2132.


7.048
7.027
7.000
6.993
6.967
6.961
6.946
6.940
2.283
1.292
1.155
0.000
NHAc
PivO
Bpin
3.00
2.97
9.00
11.79
f1 (ppm)


176.477
169.658
148.033
135.260
124.463
120.793
116.630
79.486
38.403
26.678
25.927
21.537
0.000
NHAc
PivO
Bpin
f1 (ppm)



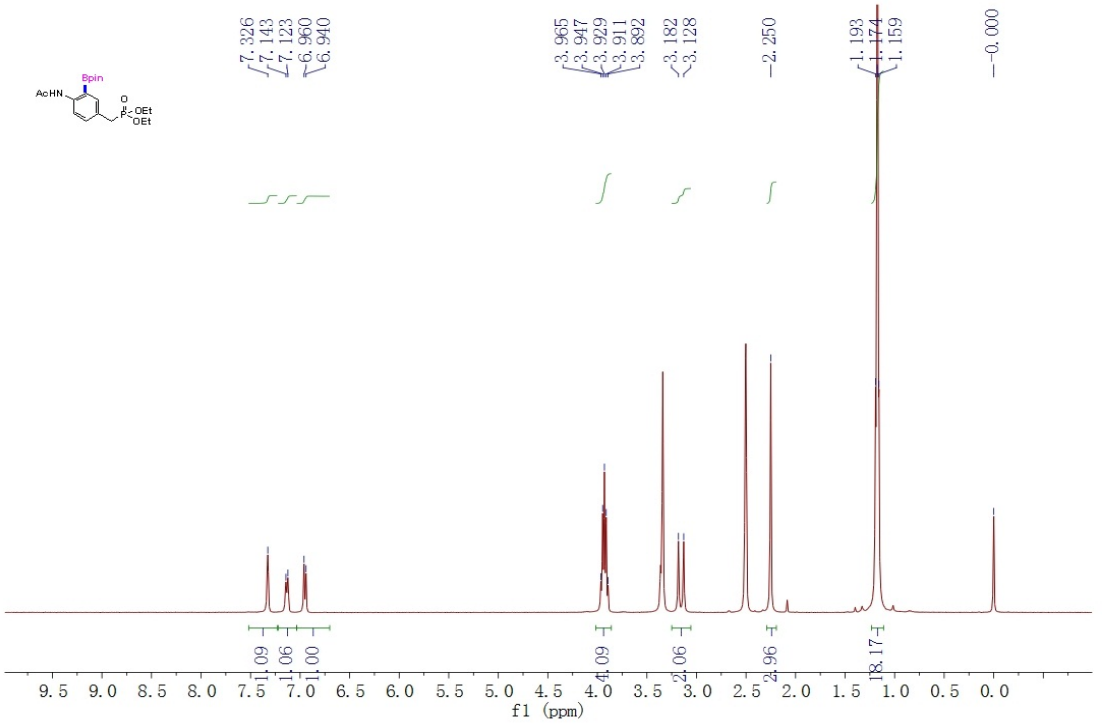


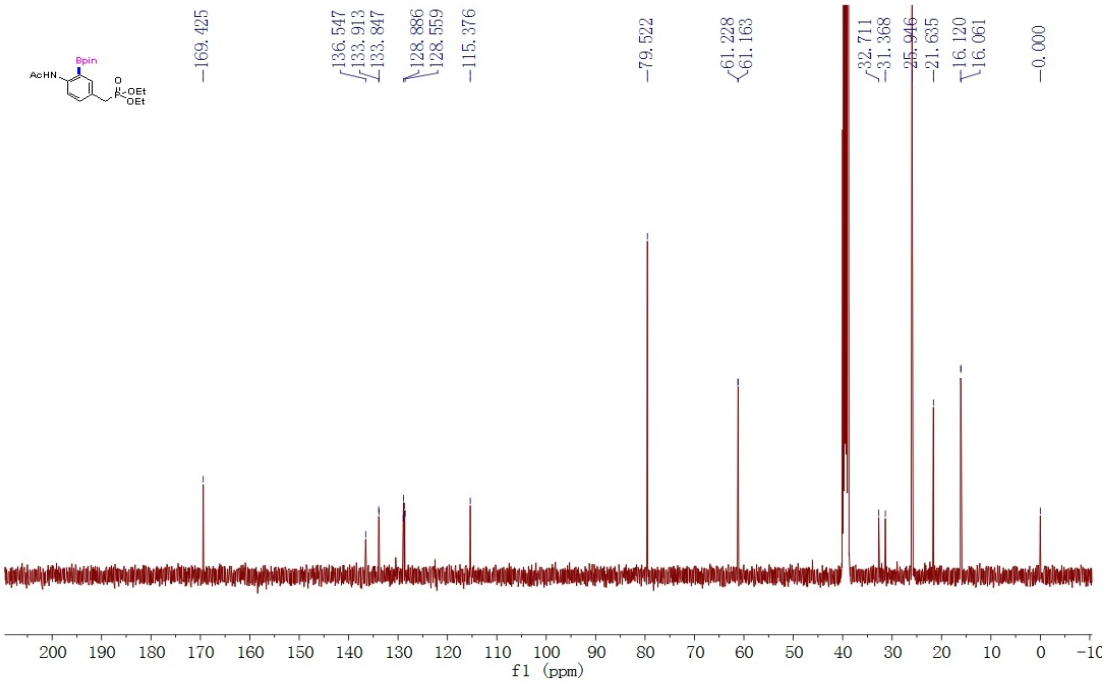
diethyl 4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylphosphonate

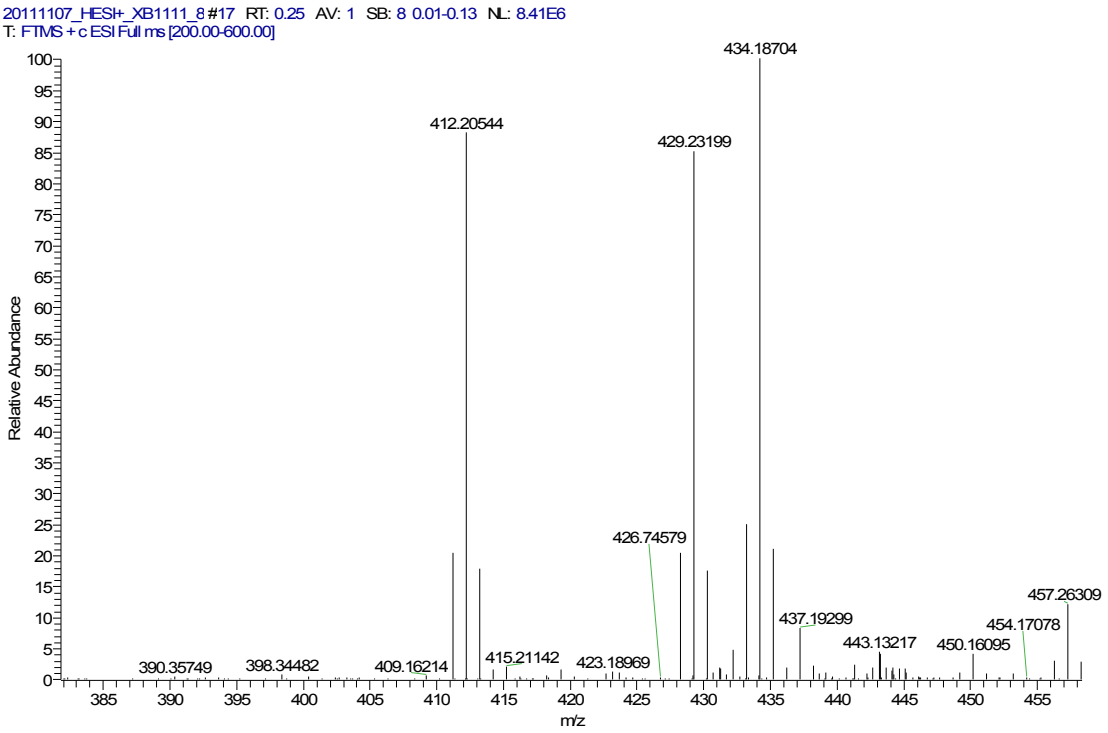
^{1}H NMR (400 MHz, DMSO) δ 7.33 (s, 1H), 7.13 (d, J = 8.0, 1H), 6.95 (d, J = 8.0, 1H), 4.29 – 3.65 (m, 4H), 3.15 (d, J = 21.3, 2H), 2.25 (s, 3H), 1.17 (m, 18H).

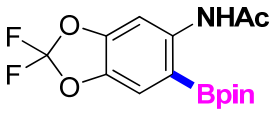
^{13}C NMR (100 MHz, DMSO) δ 169.43, 136.55, 133.88, 128.92, 128.60, 115.38, 79.52, 61.19, 32.04, 25.95, 21.64, 16.90.

HRMS requires $[C19H31BNO6P+H]^{+}$ 412.2055, found ESI $[M+H]^{+}$ 412.2054.


7.326
7.143
7.123
6.960
6.940
3.965
3.947
3.929
3.911
3.892
3.182
3.128
2.250
1.193
1.174
1.159
0.000
1.09
1.06
1.00
4.09
2.06
2.96
18.17
f1 (ppm)


169.425
136.547
133.913
133.847
128.886
128.559
115.376
79.522
61.228
61.163
32.711
31.368
26.946
21.635
16.120
16.061
0.000
f1 (ppm)



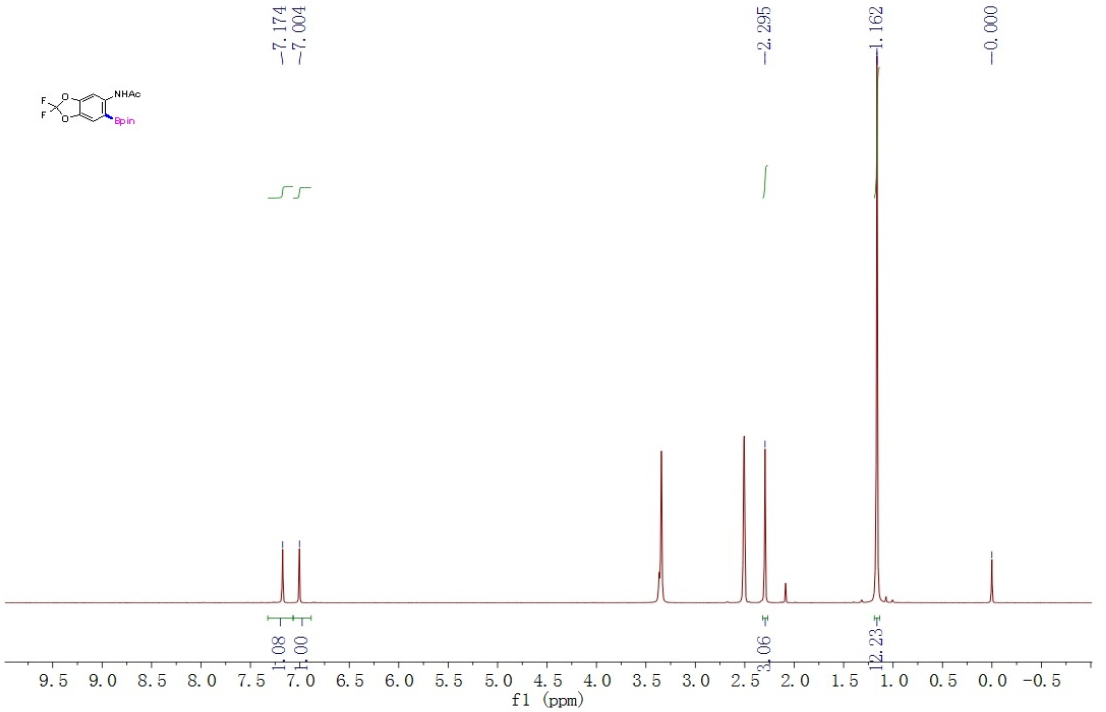


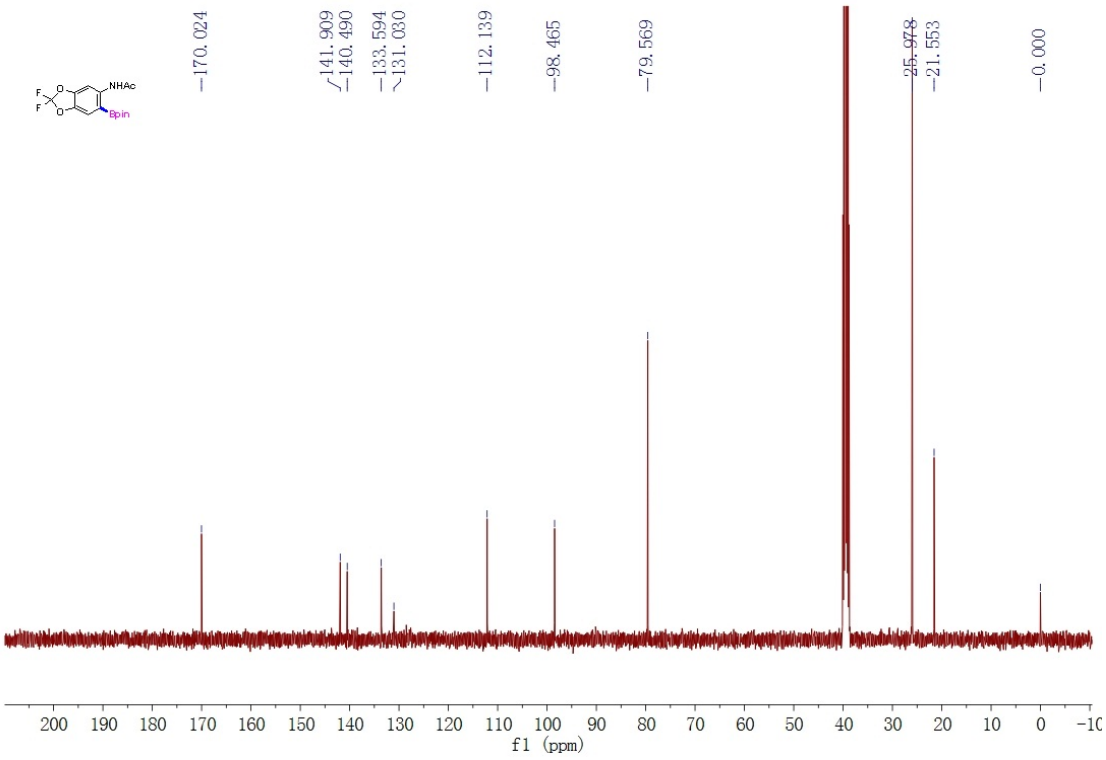
N-(2,2-difluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*d*][1,3]dioxol-5-yl)acetamide

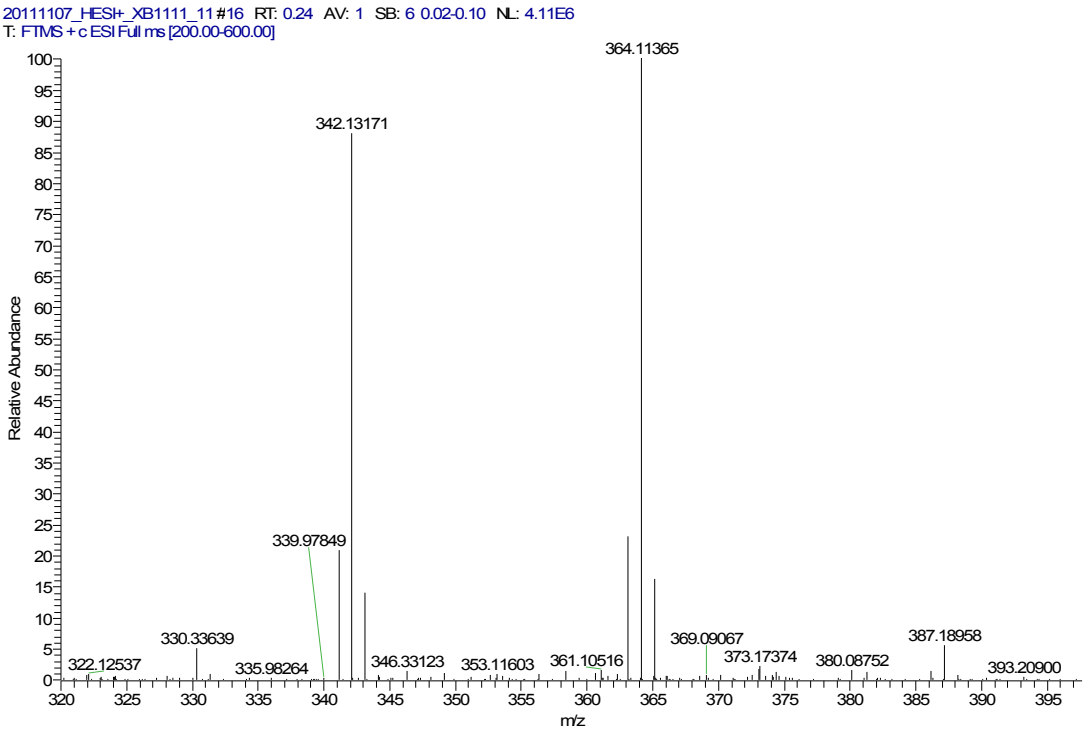
^{1}H NMR (400 MHz, DMSO) δ 7.17 (s, 1H), 7.00 (s, 1H), 2.29 (s, 3H), 1.16 (s, 12H).

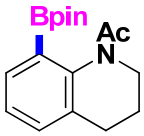
^{13}C NMR (100 MHz, DMSO) δ 170.02, 141.91, 140.49, 133.59, 131.03, 112.14, 98.47, 79.57, 25.98, 21.55.

HRMS requires $[C15H18BF2NO5+H]^{+}$ 342.1319, found ESI $[M+H]^{+}$ 342.1317.


7.174
7.004
2.295
1.162
0.000
NHAc
Bpin
1.08
1.00
2.06
12.23
f1 (ppm)


170.024
141.909
140.490
133.594
131.030
112.139
98.465
79.569
25.978
21.553
0.000
NHAc
Bpin
f1 (ppm)



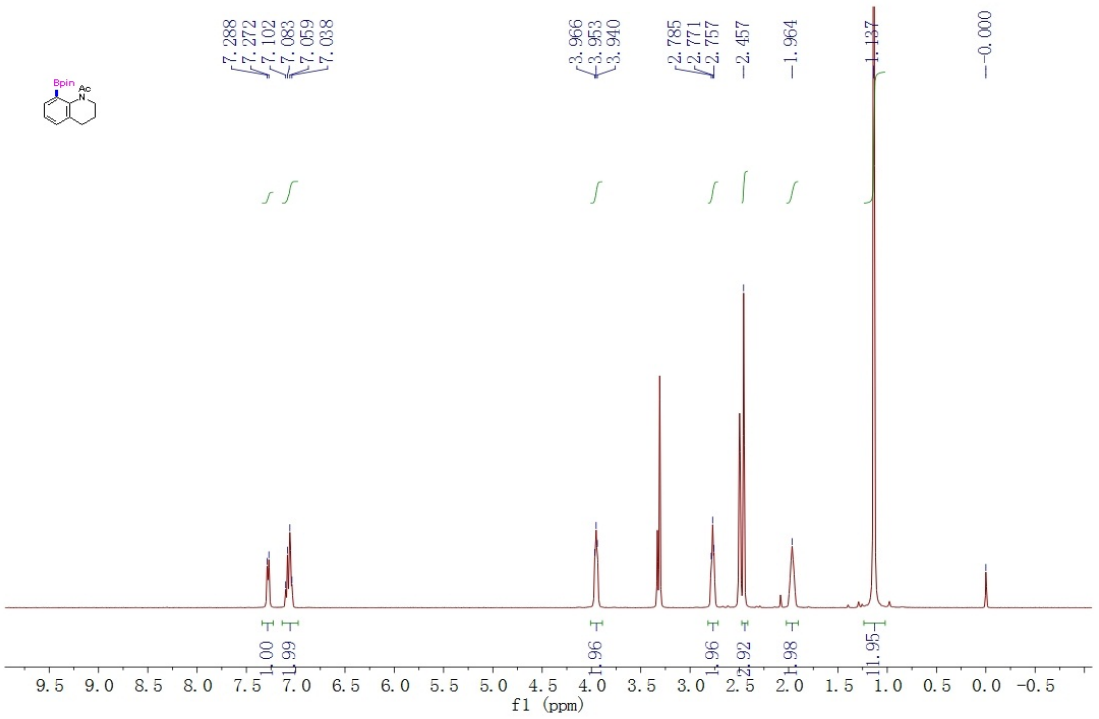


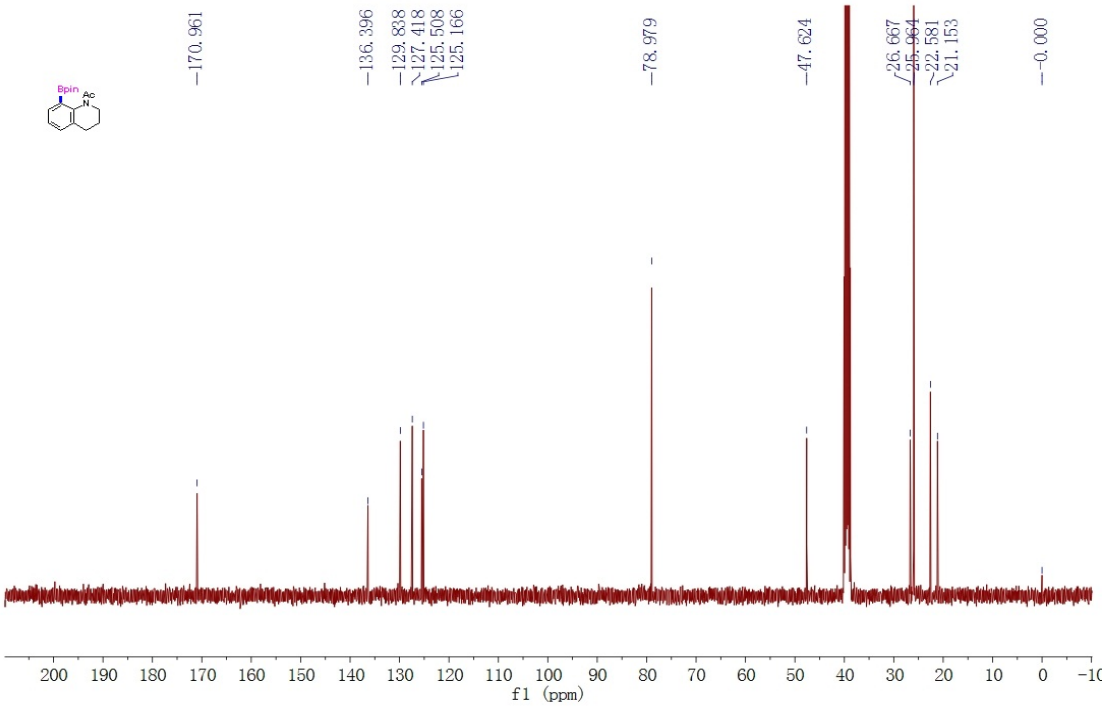
1-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinolin-1(2*H*)-yl)ethanone

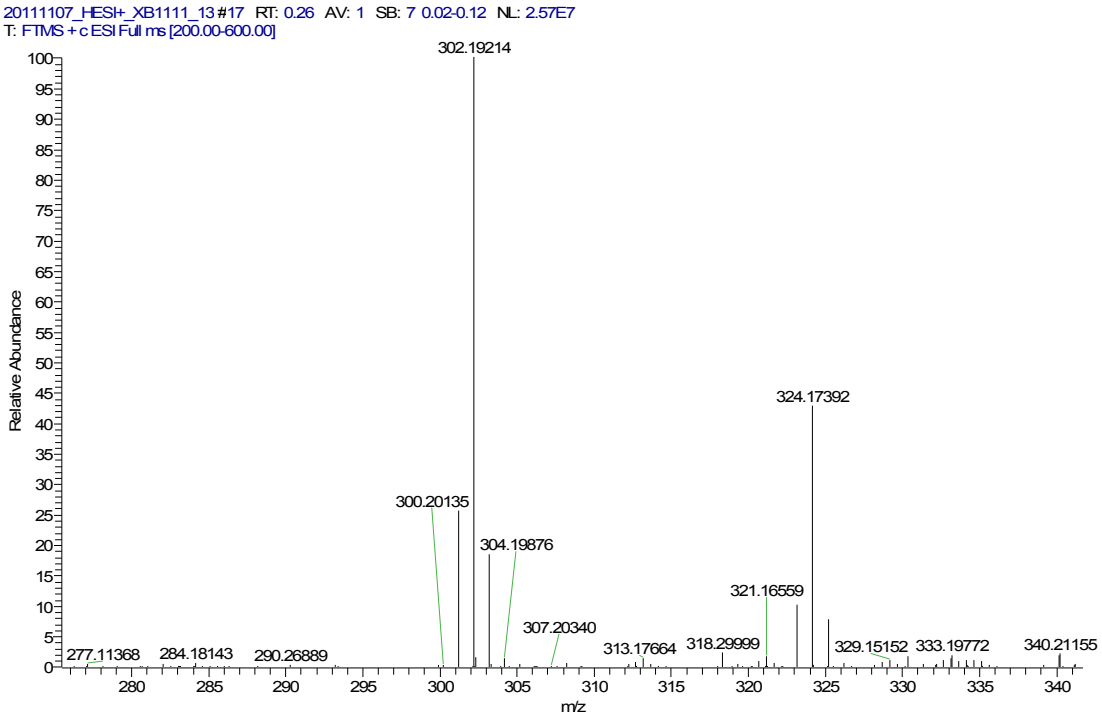
^{1}H NMR (400 MHz, DMSO) δ 7.28 (d, *J* = 6.7, 1H), 7.16 – 6.78 (m, 2H), 4.35 – 3.71 (t, *J* =5.5, 2H), 2.77 (t, *J* = 5.5, 2H), 2.46 (s, 3H), 1.96 (q, *J* = 5.5, 2H), 1.14 (s, 12H).

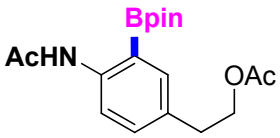
^{13}C NMR (100 MHz, DMSO) δ 170.96, 136.40, 129.84, 127.42, 125.51, 125.17, 78.98, 47.62, 26.67, 25.96, 22.58, 21.15.

HRMS requires $[C17H24BNO3+H]^{+}$ 302.1922, found ESI $[M+H]^{+}$ 302.1921.


7.288
7.272
7.102
7.083
7.059
7.038
3.966
3.953
3.940
2.785
2.771
2.757
2.457
1.964
1.137
-0.000
Bpin
Ac
N
1.00
1.99
1.96
1.96
2.92
1.98
11.95
f1 (ppm)


170.961
136.396
129.838
127.418
125.508
125.166
78.979
47.624
26.667
25.964
22.581
21.153
-0.000
Bpin
Ac
N
f1 (ppm)



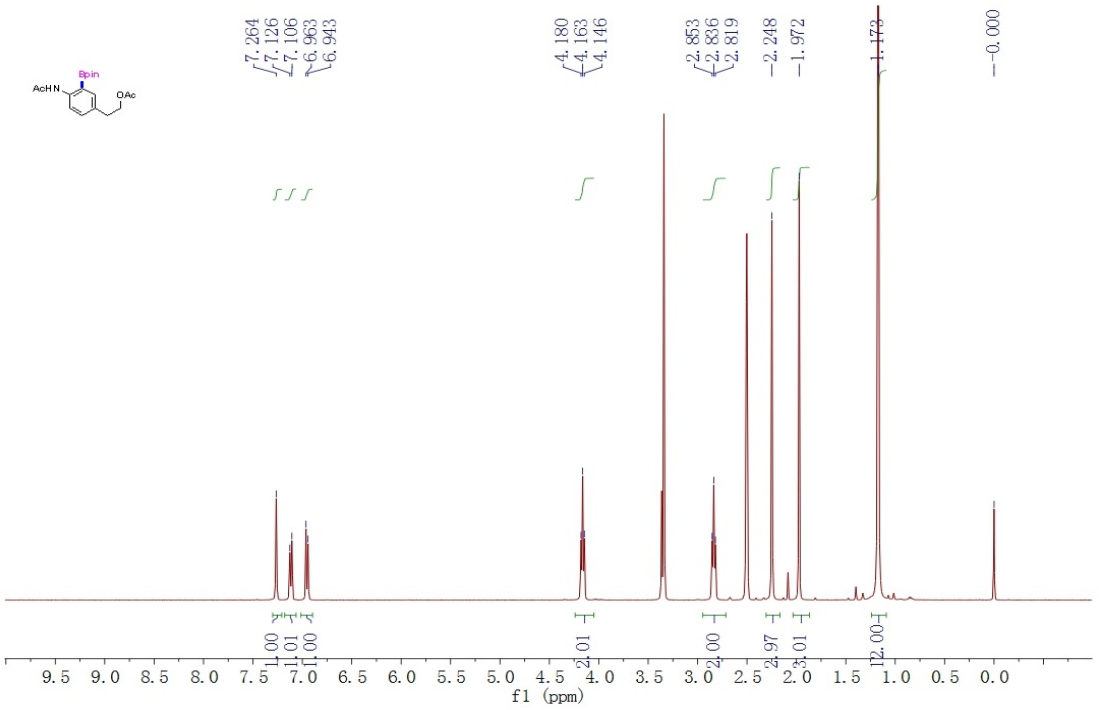


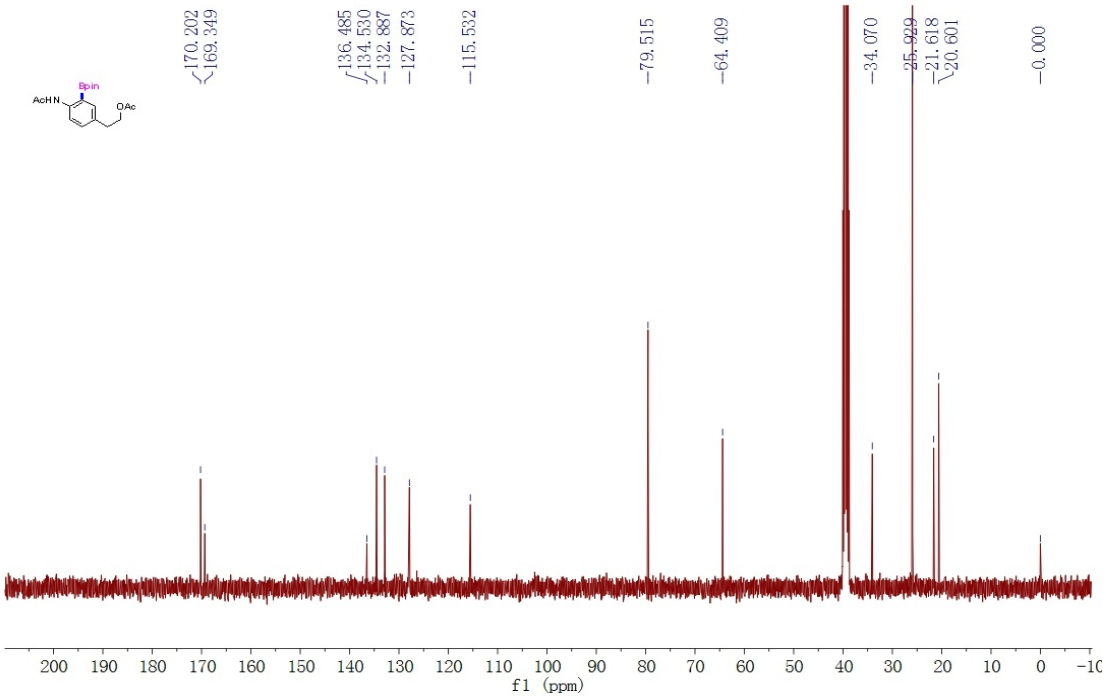
4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl acetate

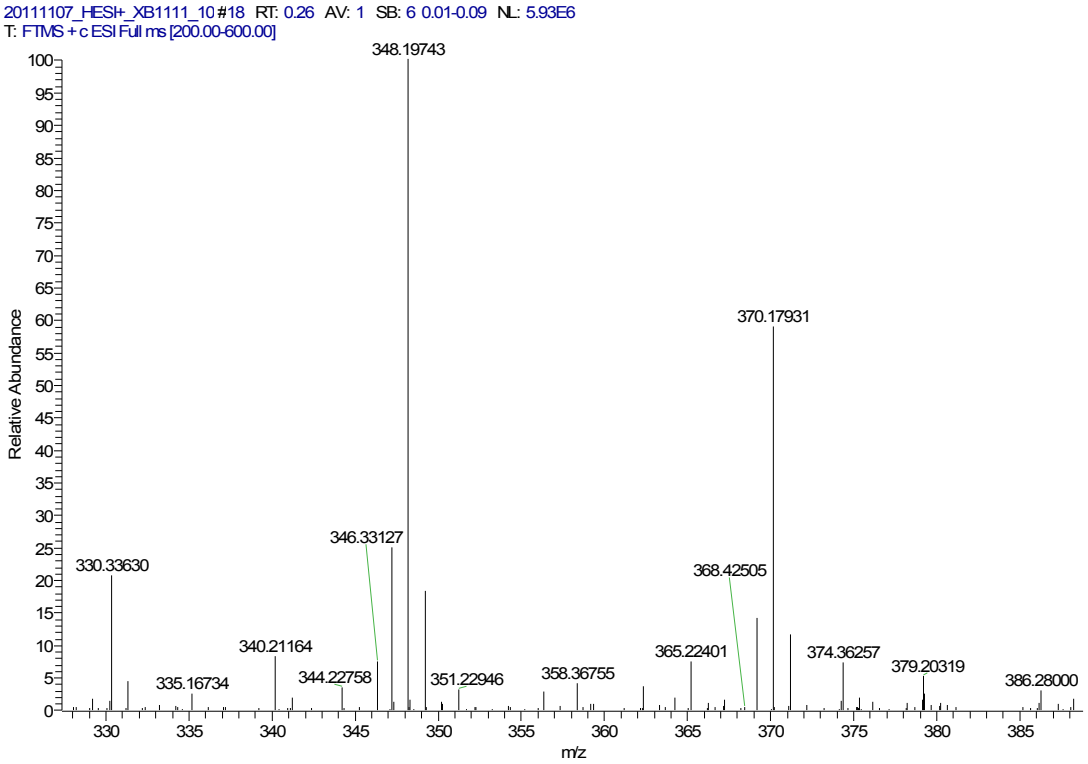
^{1}H NMR (400 MHz, DMSO) δ 7.26 (s, 1H), 7.12 (d, J = 8.1, 1H), 6.95 (d, J = 8.1, 1H), 4.16 (t, J = 6.7, 2H), 2.84 (t, J = 6.7, 2H), 2.25 (s, 3H), 1.97 (s, 3H), 1.17 (s, 12H).

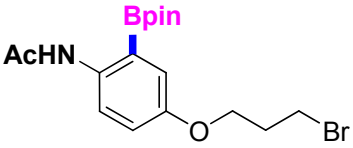
^{13}C NMR (100 MHz, DMSO) δ 170.20, 169.35, 136.49, 134.53, 132.89, 127.87, 115.53, 79.51, 64.41, 34.07, 25.93, 21.62, 20.60.

HRMS requires $[C18H26BNO5+H]^{+}$ 348.1977, found ESI $[M+H]^{+}$ 348.1974.


7.264
7.126
7.106
6.963
6.943
4.180
4.163
4.146
2.853
2.836
2.819
2.248
1.972
1.173
-0.000
1.00
1.01
1.00
2.01
2.00
2.97
3.01
12.00
f1 (ppm)


170.202
169.349
136.485
134.530
132.887
127.873
115.532
79.515
64.409
34.070
25.929
21.618
20.601
-0.000
f1 (ppm)



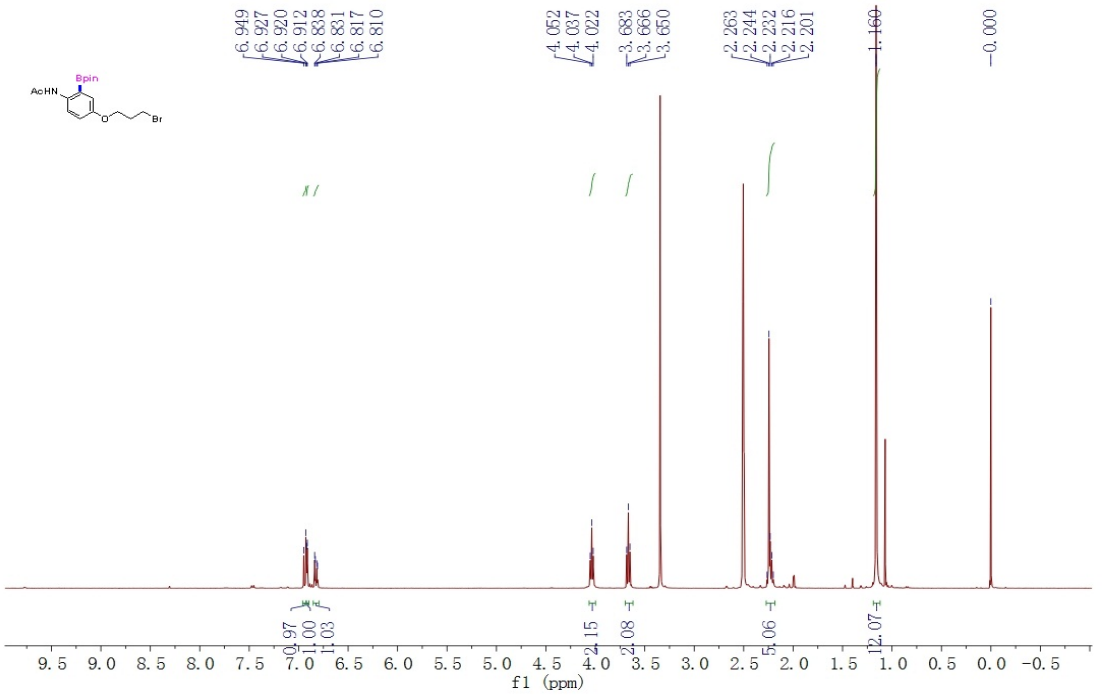


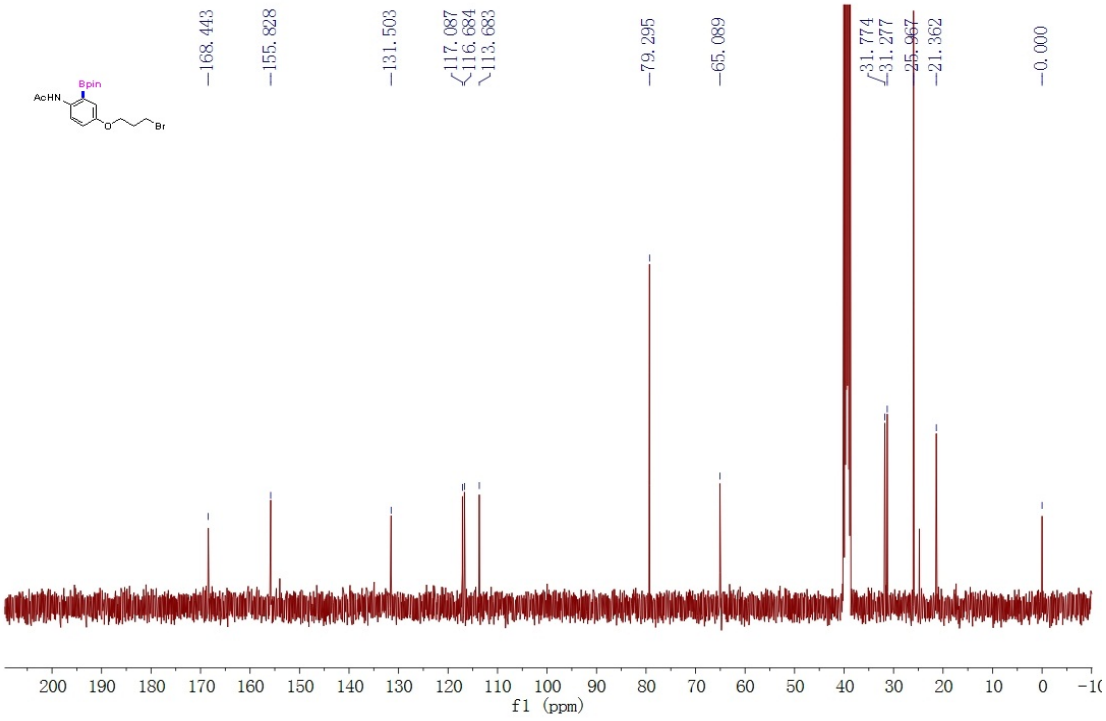
N-(4-(3-bromopropoxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

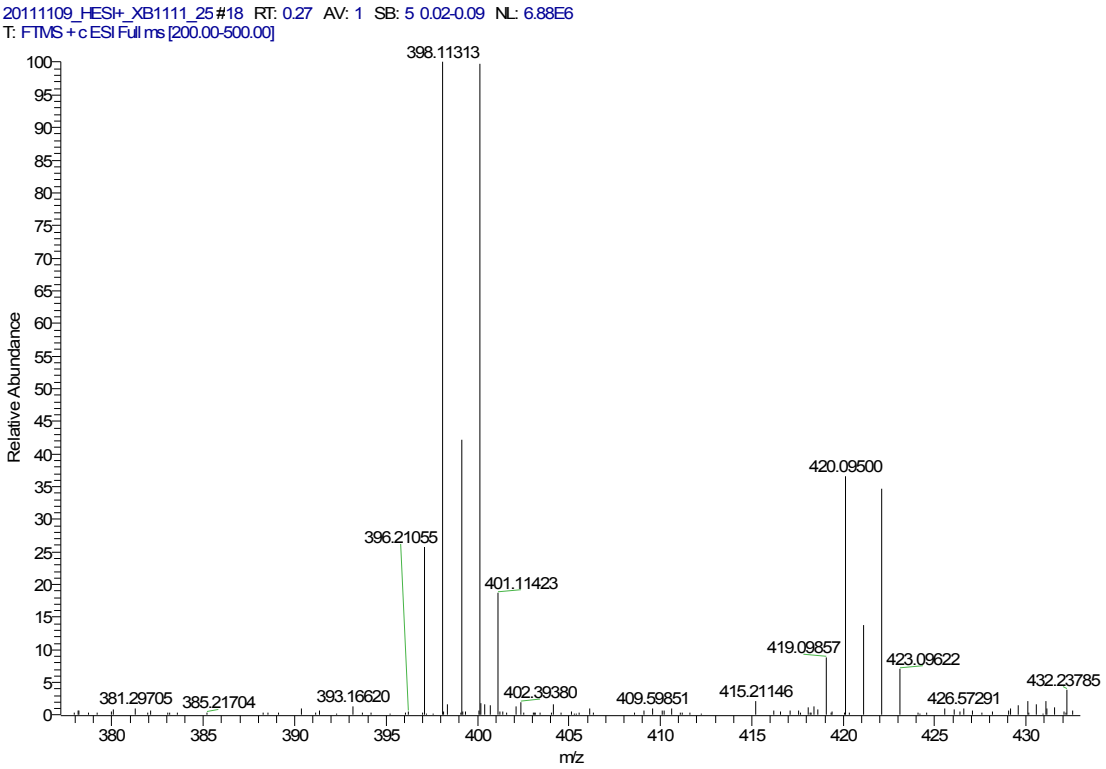
^{1}H NMR (400 MHz, DMSO) δ 6.94 (d, *J* = 8.6, 1H), 6.92 (d, *J* = 2.8, 1H), 6.82 (dd, *J* = 8.6, 2.8, 1H), 4.04 (t, *J* = 6.0, 2H), 3.67 (t, *J* = 6.5, 2H), 2.33 – 2.13 (m, 5H), 1.16 (s, 12H).

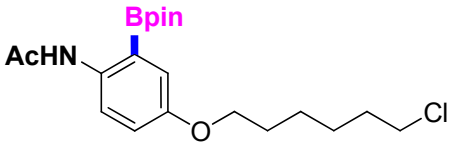
^{13}C NMR (100 MHz, DMSO) δ 168.44, 155.83, 131.50, 117.09, 116.68, 113.68, 79.29, 65.09, 31.77, 31.28, 25.97, 21.36.

HRMS requires $[C17H25BBrNO4+H]^{+}$ 398.1133, found ESI $[M+H]^{+}$ 398.1131.


6.949
6.927
6.920
6.912
6.838
6.831
6.817
6.810
4.052
4.037
4.022
3.683
3.666
3.650
2.263
2.244
2.232
2.216
2.201
1.160
0.000
Bpin
AcHN
Br
0.97
1.00
1.03
2.15
2.08
5.06
12.07
f1 (ppm)


168.443
155.828
131.503
117.087
116.684
113.683
79.295
65.089
31.774
31.277
25.967
21.362
0.000
Bpin
AcHN
Br
f1 (ppm)



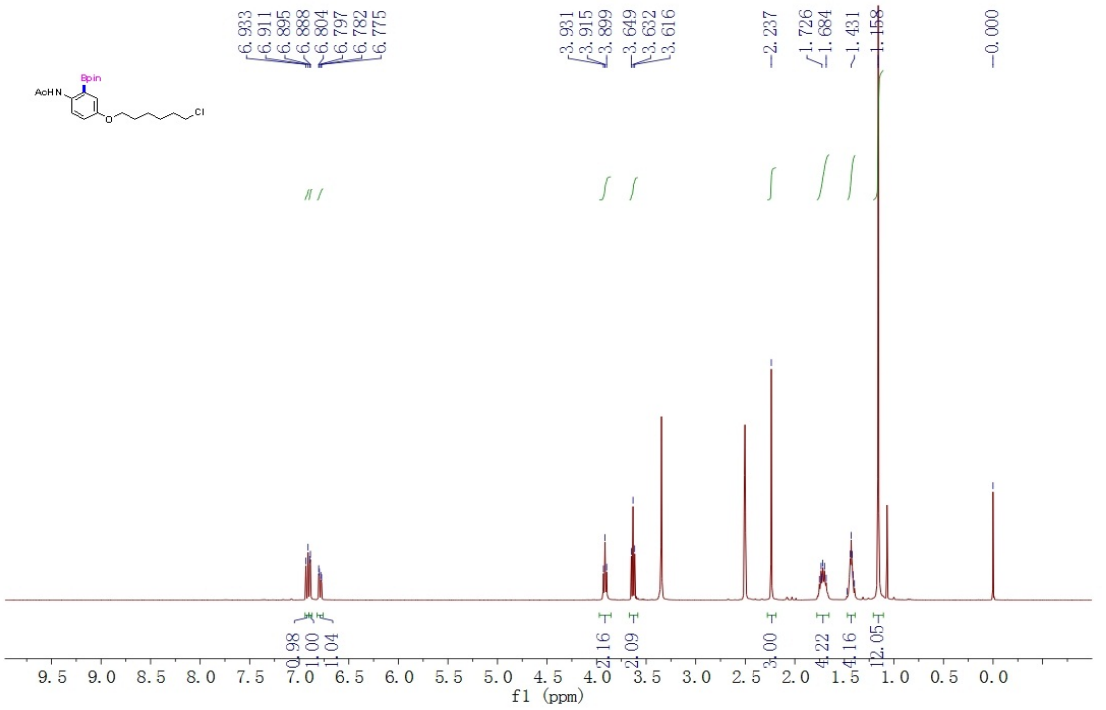


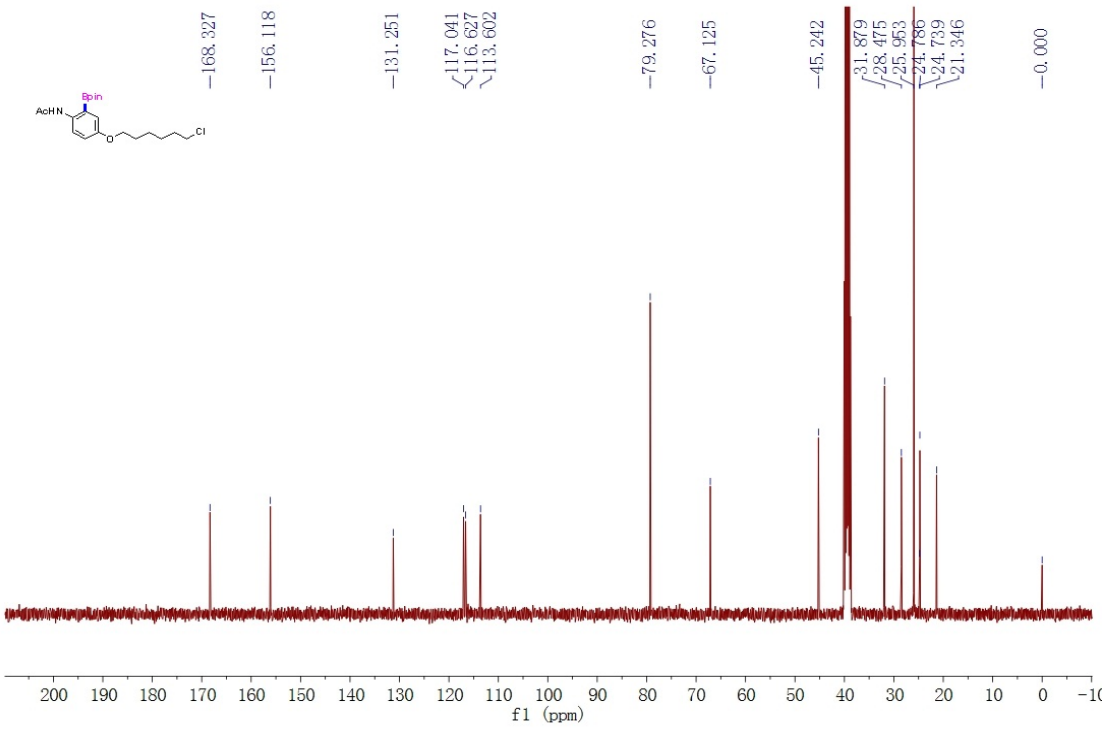
N-(4-(6-chlorohexyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

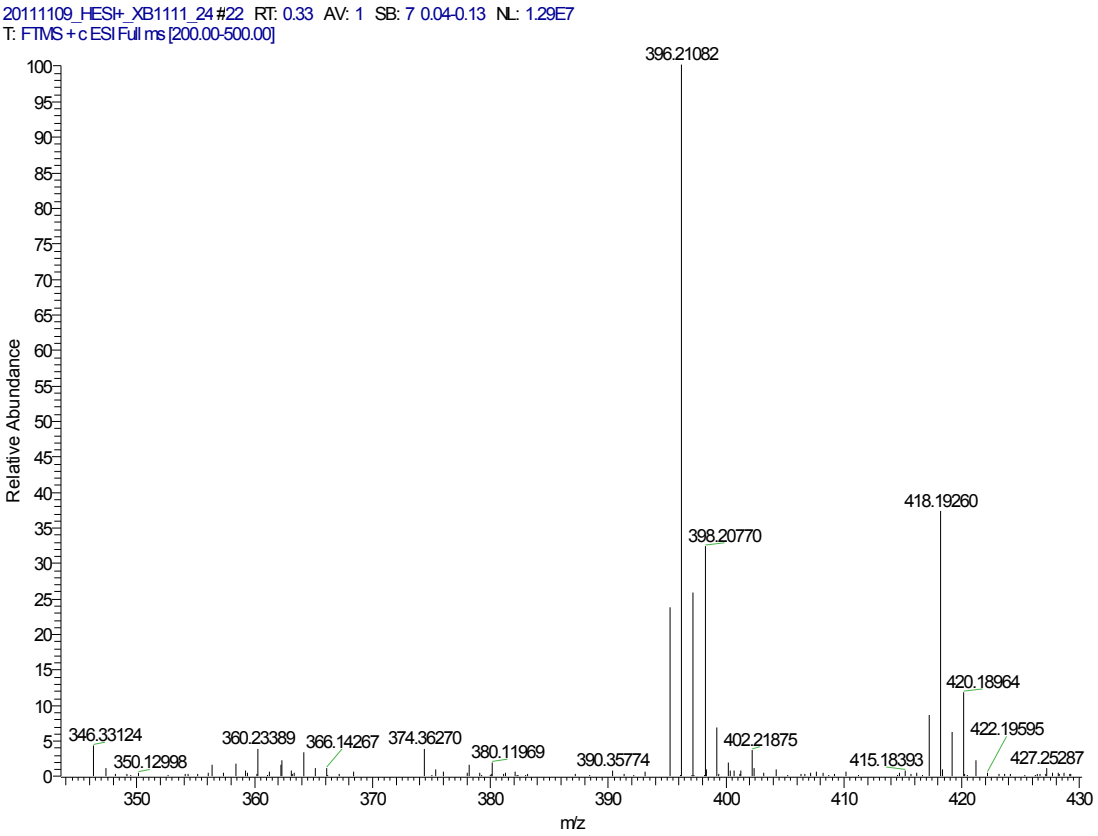
^{1}H NMR (400 MHz, DMSO) δ 6.92 (d, *J* = 8.6, 1H), 6.89 (d, *J* = 2.8, 1H), 6.79 (dd, *J* = 8.6, 2.8, 1H), 3.91 (t, *J* = 6.4, 2H), 3.63 (t, *J* = 6.6, 2H), 2.24 (s, 3H), 1.72 (m, 4H), 1.52 – 1.32 (m, 4H), 1.16 (s, 12H).

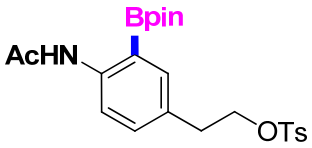
^{13}C NMR (100 MHz, DMSO) δ 168.33, 156.12, 131.25, 117.04, 116.63, 113.60, 79.28, 67.12, 45.24, 31.88, 28.47, 25.95, 24.79, 24.74, 21.35.

HRMS requires $[C20H31BClNO4+H]^{+}$ 396.2107, found ESI $[M+H]^{+}$ 396.2108.


6.933
6.911
6.895
6.888
6.804
6.797
6.782
6.775
3.931
3.915
3.899
3.649
3.632
3.616
2.237
1.726
1.684
1.431
1.158
0.000
AcHN
Bpin
Cl
0.98
1.00
1.04
2.16
2.09
3.00
4.22
4.16
12.05
f1 (ppm)


168.327
156.118
131.251
117.041
116.627
113.602
79.276
67.125
45.242
31.879
28.475
25.963
24.786
24.739
21.346
0.000
AcHN
Bpin
Cl
f1 (ppm)



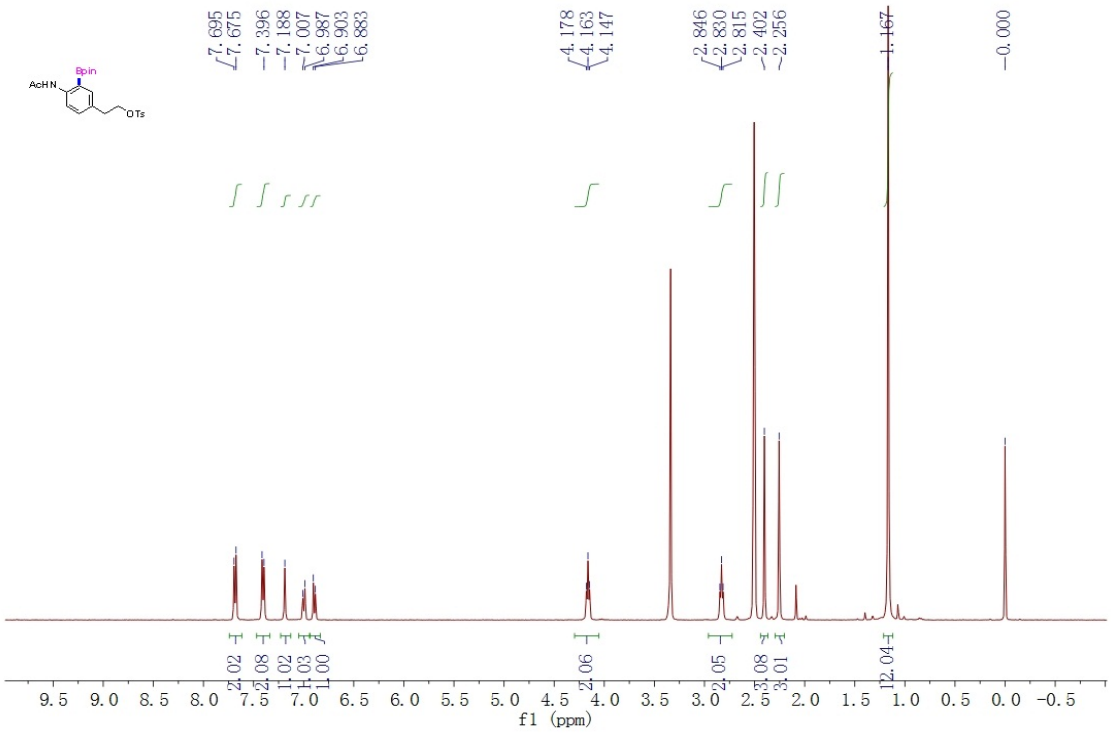


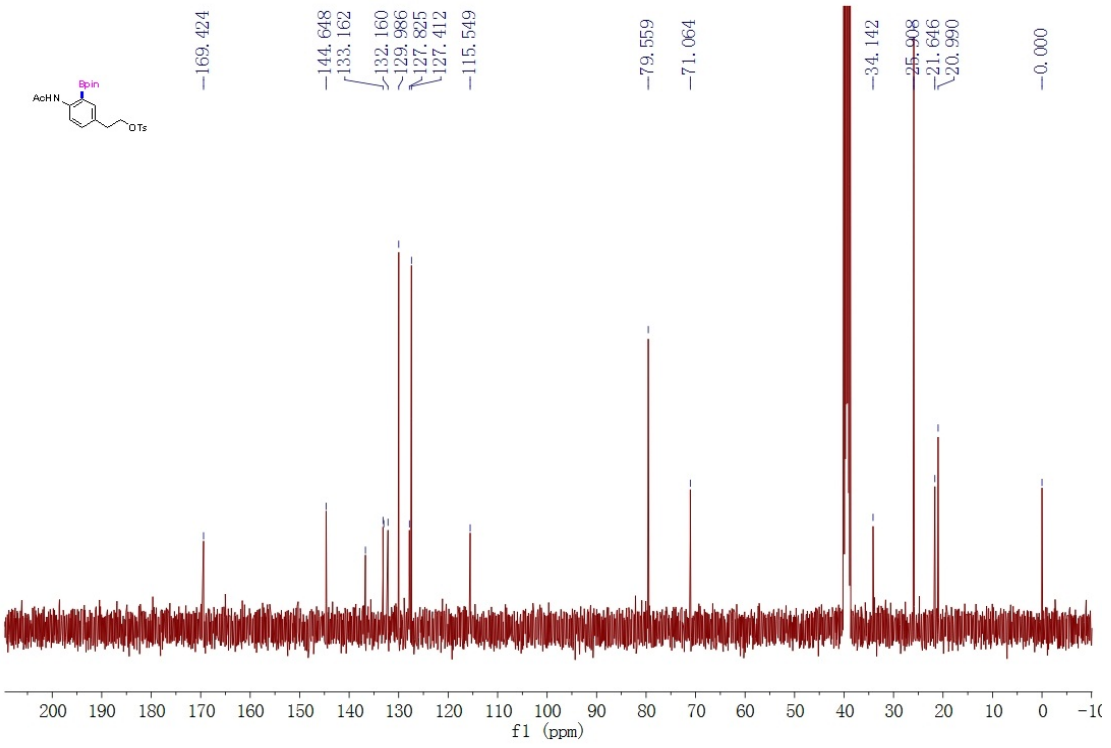
4-acetamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl 4-methylbenzenesulfonate

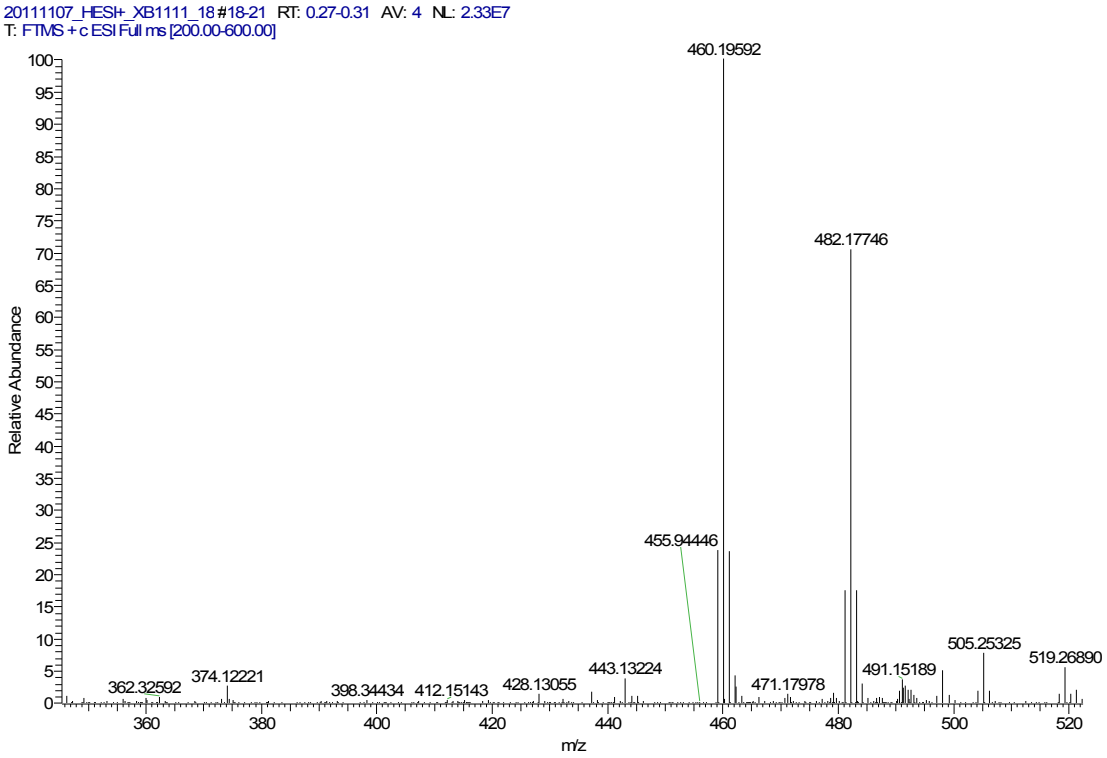
^{1}H NMR (400 MHz, DMSO) δ 7.68 (d, J = 8.0, 2H), 7.41 (d, J = 8.0, 2H), 7.19 (s, 1H), 7.00 (d, J = 8.1, 1H), 6.89 (d, J = 8.1, 1H), 4.16 (t, J = 6.4, 2H), 2.83 (t, J = 6.4, 2H), 2.40 (s, 3H), 2.26 (s, 3H), 1.17 (s, 12H).

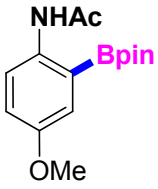
^{13}C NMR (100 MHz, DMSO) δ 169.42, 144.65, 136.71, 133.16, 133.00, 132.16, 129.99, 127.82, 127.41, 115.55, 79.56, 71.06, 34.14, 25.91, 21.65, 20.99.

HRMS requires $[C23H30BNO6S+H]^{+}$ 460.1960, found ESI $[M+H]^{+}$ 460.1959.


7.695
7.675
7.396
7.188
7.007
6.987
6.903
6.883
4.178
4.163
4.147
2.846
2.830
2.815
2.402
2.256
1.167
0.000
AcHN
Bpin
OTs
2.02
2.08
1.02
1.03
1.00
2.06
2.05
3.08
3.01
12.04
f1 (ppm)


169.424
144.648
133.162
132.160
129.986
127.825
127.412
115.549
79.559
71.064
34.142
25.908
21.646
20.990
0.000
AcHN
Bpin
OTs
f1 (ppm)



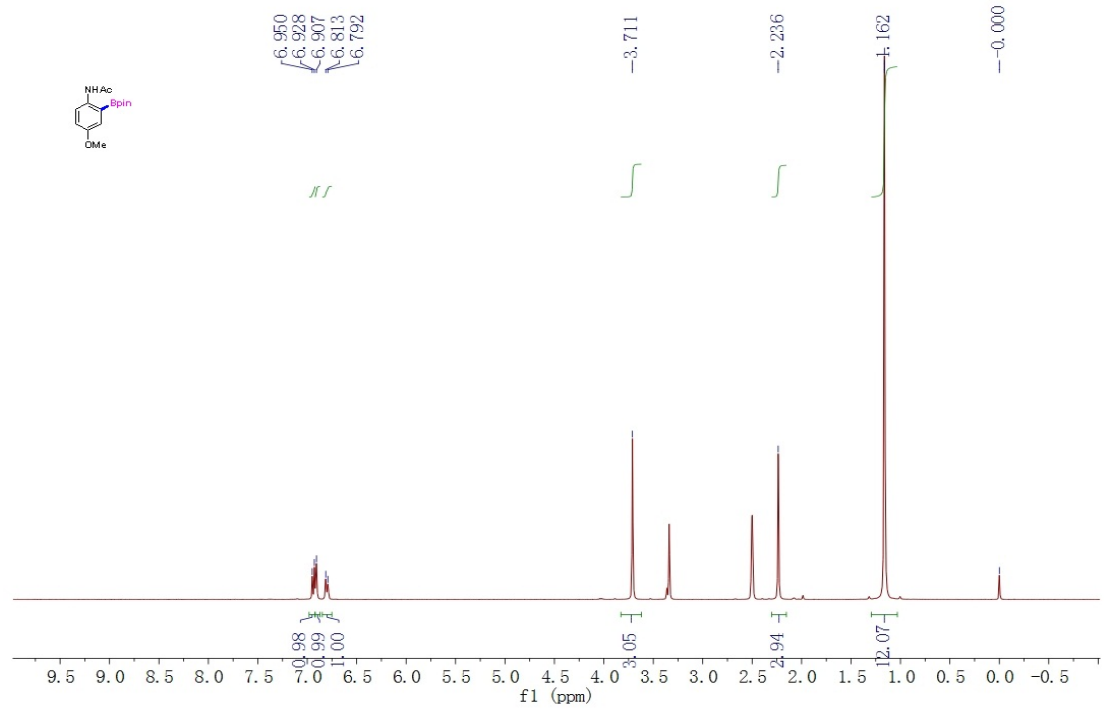


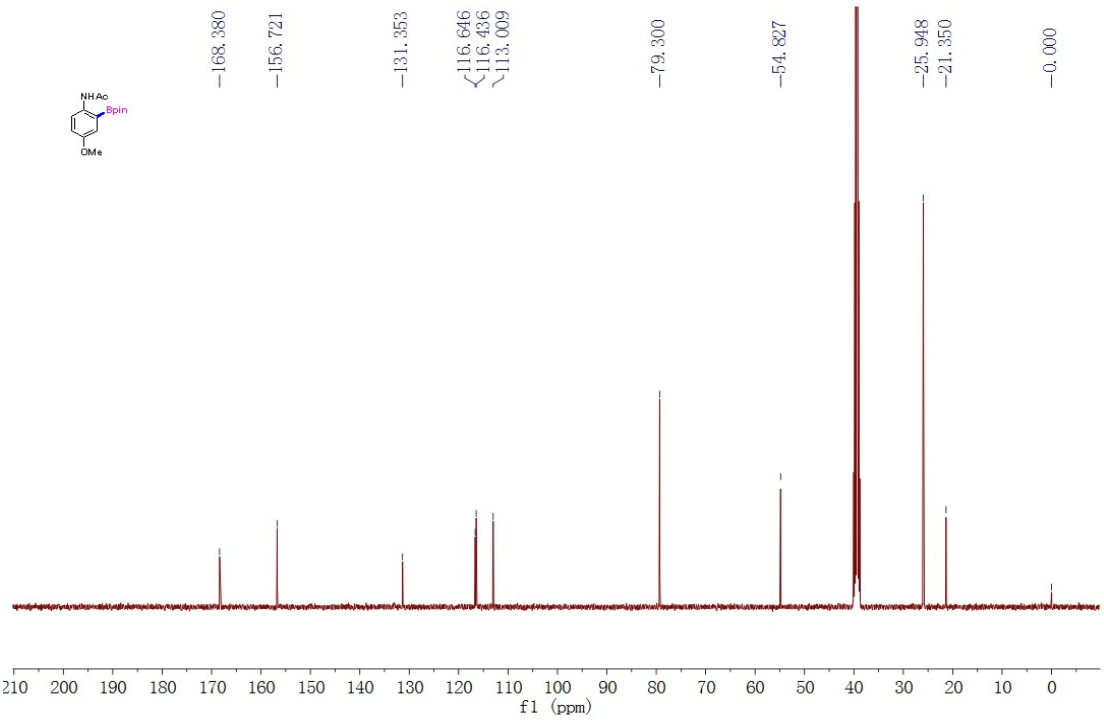
N-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide

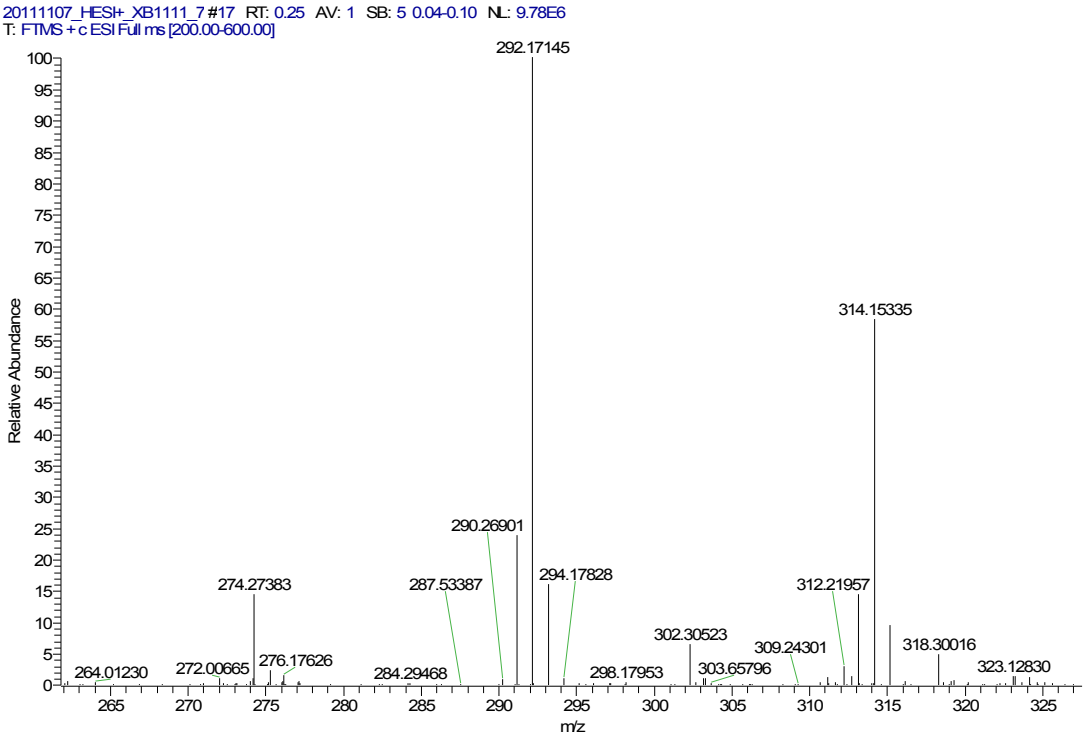
^{1}H NMR (400 MHz, DMSO) δ 6.94 (d, *J* = 8.6, 1H), 6.91 (s, 1H), 6.80 (d, *J* = 8.6, 1H), 3.71 (s, 3H), 2.24 (s, 3H), 1.16 (s, 12H).

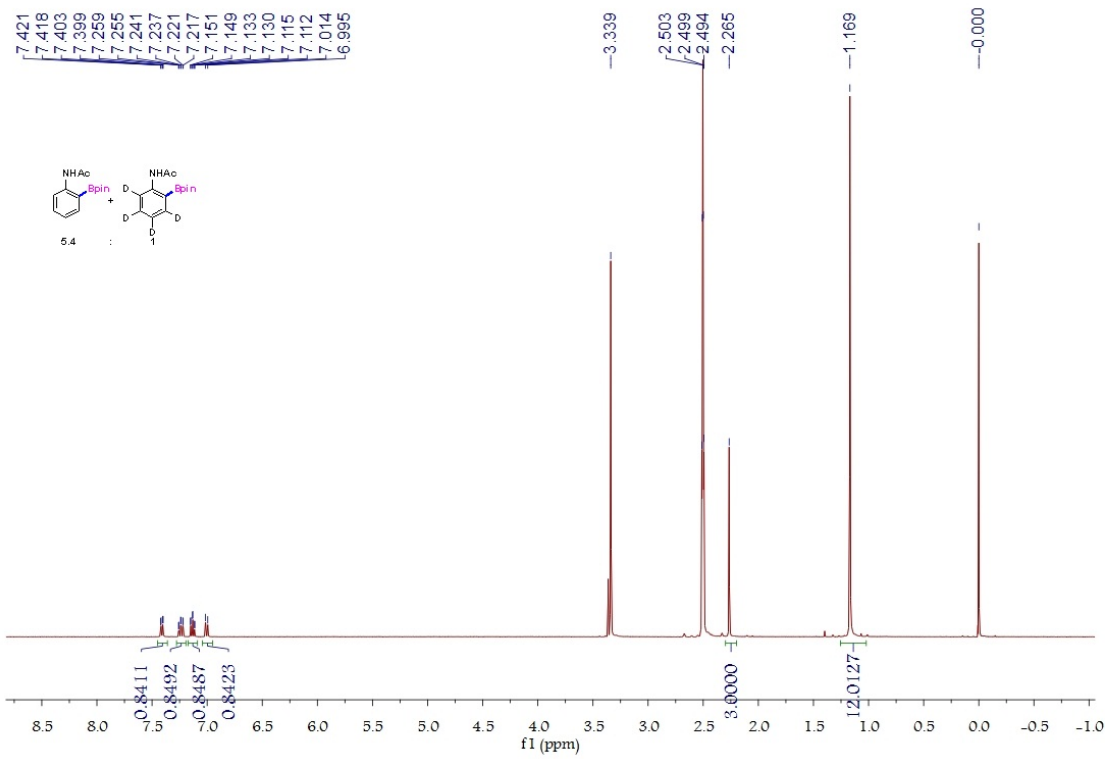
^{13}C NMR (101 MHz, DMSO) δ 168.38, 156.72, 131.35, 116.65, 116.44, 113.01, 79.30, 54.83, 25.95, 21.35.

HRMS requires $[C19H28BNO5+H]^{+}$ 292.1715, found ESI $[M+H]^{+}$ 292.1715.


6.950
6.928
6.907
6.813
6.792
3.711
2.236
1.162
0.000
NHAc
Bpin
OMe
0.98
0.99
1.00
3.05
2.94
12.07
f1 (ppm)

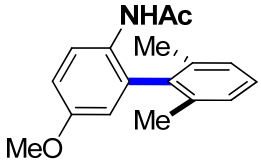

168.380
156.721
131.353
116.646
116.436
113.009
79.300
54.827
25.948
21.350
0.000
NHAc
Bpin
OMe
f1 (ppm)


20111107_HESI+_XB1111_7 #17 RT: 0.25 AV: 1 SB: 5 0.04-0.10 NL: 9.78E6
T: FTMS + c ESI Full ms [200.00-600.00]
Relative Abundance
m/z
292.17145
314.15335
290.26901
294.17828
274.27383
287.53387
312.21957
302.30523
309.24301
318.30016
276.17626
272.00665
264.01230
284.29468
298.17953
303.65796
323.12830



Synthesis of 3a and 3b via Suzuki Coupling:

N-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (**2y**) (73 mg, 0.25 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), S-Phos (8.2 mg, 0.02 mmol) and K_2CO_3 (104 mg, 0.75 mmol) were placed in a vial under Ar. Aryl-Br (0.2 mmol) and then a mixed solvent of 0.4 mL toluene, 0.4 mL EtOH and 0.2 mL H_2O was added. The mixture was violently stirred at 100 ^oC overnight and cooled to room temperature. The organic phase was purified by flash chromatography to give desired product as white solid.

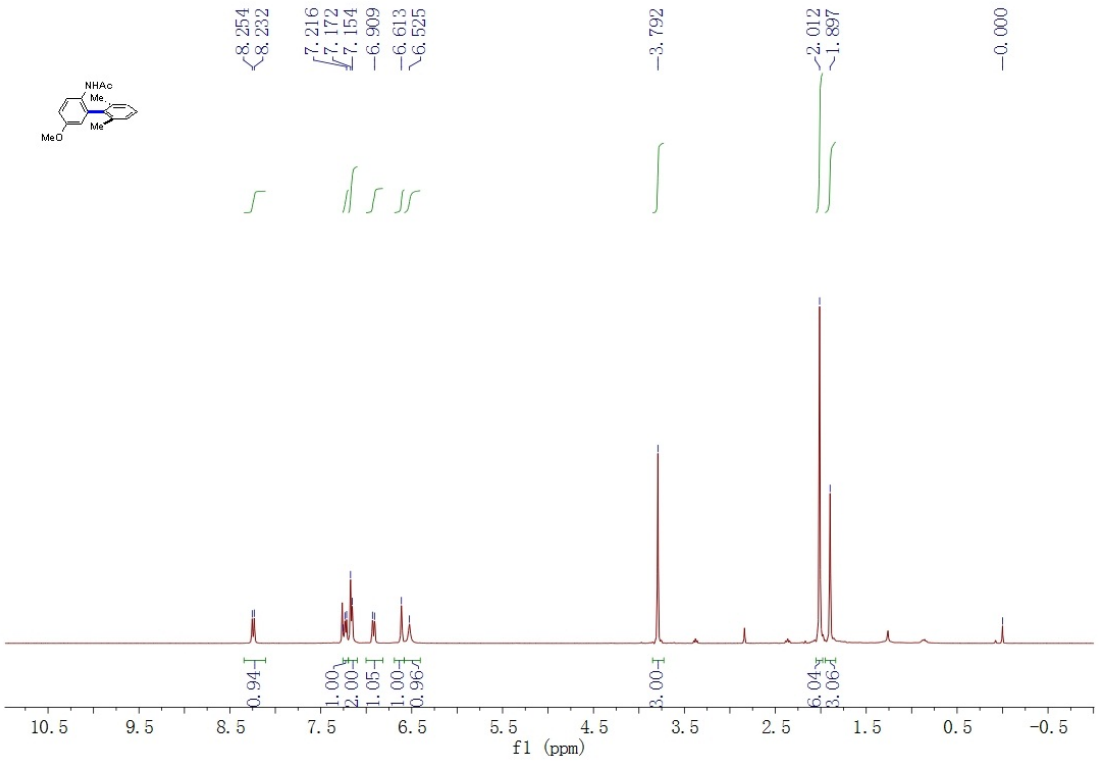


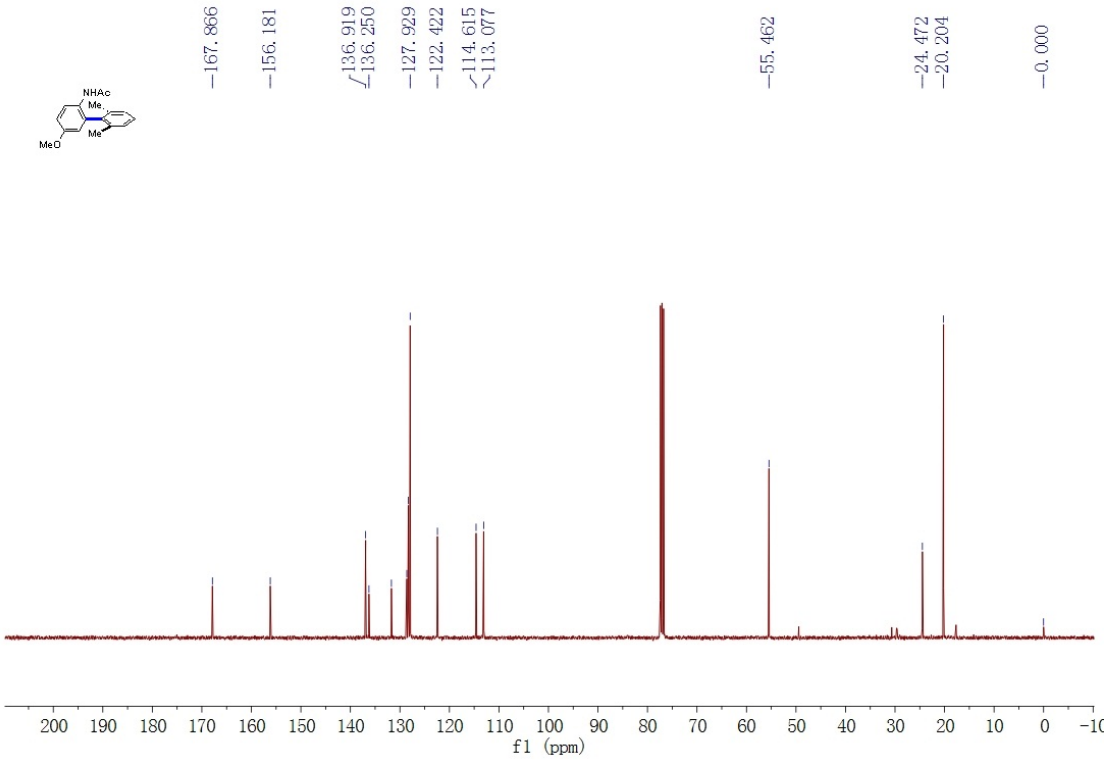
(*s*)-*N*-(5-methoxy-2',6'-dimethylbiphenyl-2-yl)acetamide

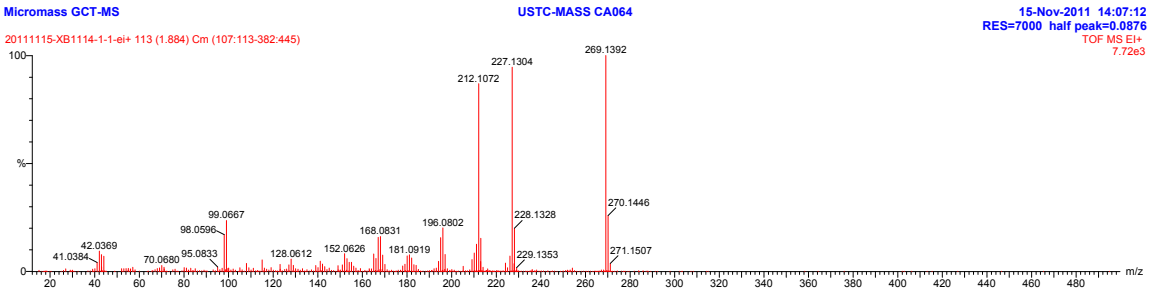
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.0, 1H), 7.23 (t, *J* = 7.3, 1H), 7.16 (d, *J* = 7.3, 2H), 6.92 (d, *J* = 9.0, 1H), 6.61 (s, 1H), 6.53 (s, 1H), 3.79 (s, 3H), 2.01 (s, 6H), 1.90 (s, 3H).

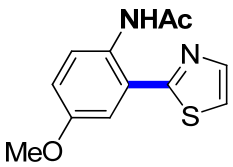
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.87, 156.18, 136.92, 136.25, 131.72, 128.61, 128.29, 127.93, 122.42, 114.62, 113.08, 55.46, 24.47, 20.20.

HRMS (EI) calcd for C17H19NO2: 269.1416; found: 269.1392.







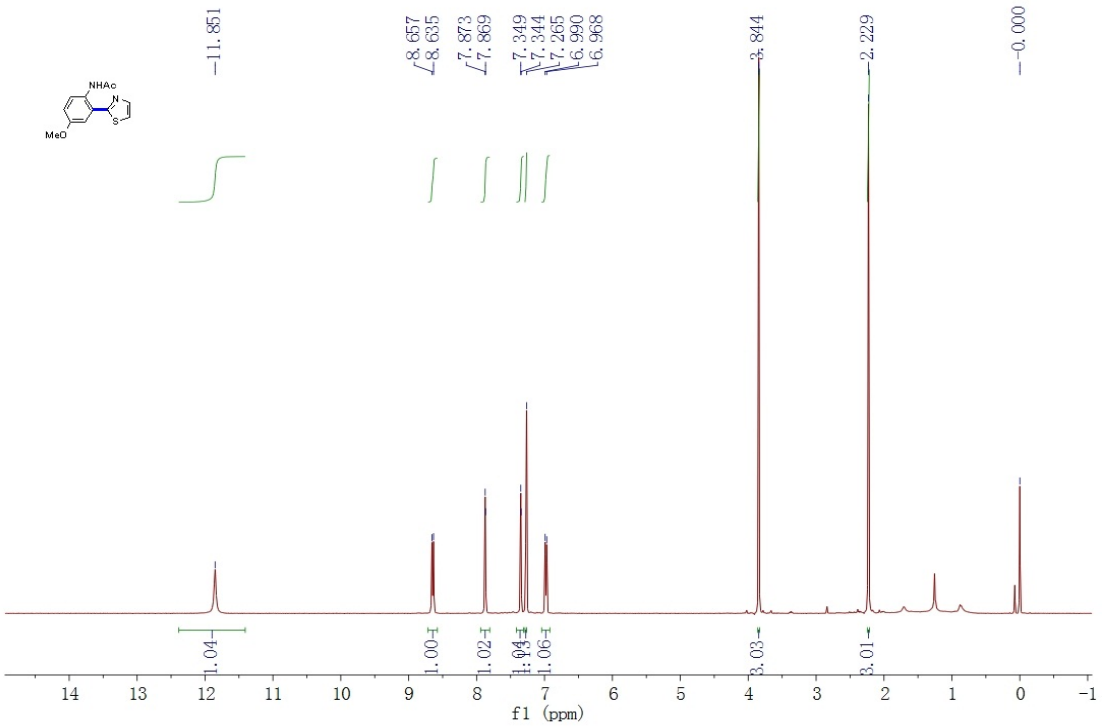


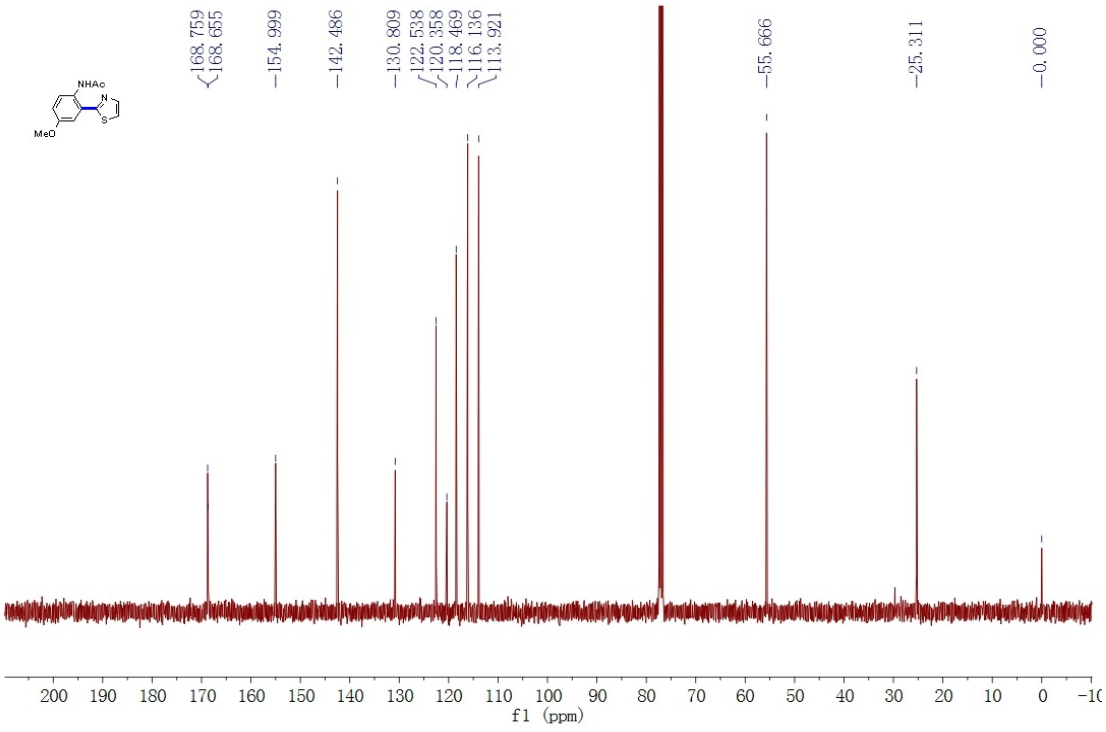
N-(4-methoxy-2-(thiazol-2-yl)phenyl)acetamide

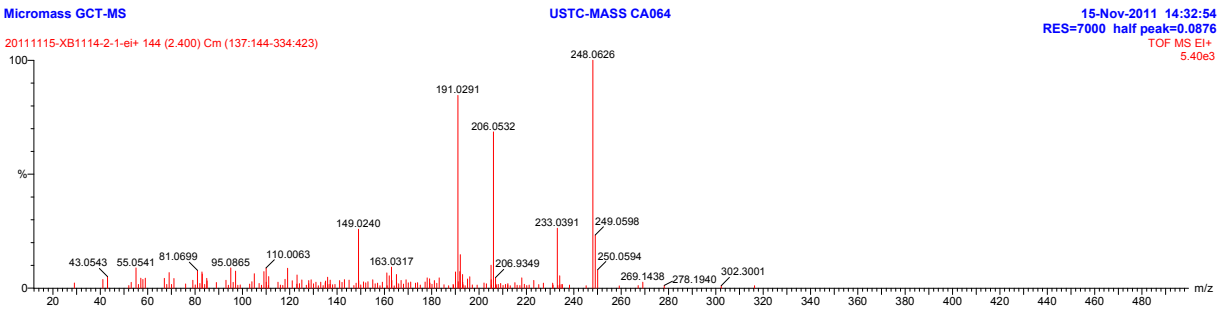
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.65 (d, J = 9.1, 1H), 7.87 (d, J = 2.0, 1H), 7.35 (d, J = 2.0, 1H), 7.26 (s, 1H), 6.98 (d, J = 9.1, 1H), 3.84 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.71, 155.00, 142.49, 130.81, 122.54, 120.36, 118.47, 116.14, 113.92, 55.67, 25.31.

HRMS (EI) calcd for C12H12N2O2S: 248.0619; found: 248.0626.

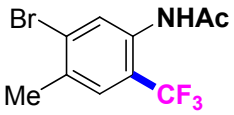

11.851
8.657
8.635
7.873
7.869
7.349
7.344
7.265
6.990
6.968
3.844
2.229
0.000
NHAc
MeO
1.04
1.00
1.02
1.03
1.04
1.06
3.03
3.01
f1 (ppm)


168.759
168.655
154.999
142.486
130.809
122.538
120.358
118.469
116.136
113.921
55.666
25.311
0.000
NHAc
MeO
f1 (ppm)


Micromass GCT-MS
USTC-MASS CA064
15-Nov-2011 14:32:54
RES=7000 half peak=0.0876
TOF MS EI+
5.40e3
20111115-XB1114-2-1-ei+ 144 (2.400) Cm (137:144-334:423)
248.0626
191.0291
206.0532
149.0240
233.0391
249.0598
43.0543
55.0541
81.0699
95.0865
110.0063
163.0317
206.9349
250.0594
269.1438
278.1940
302.3001
%
m/z

Synthesis of 4a-g:

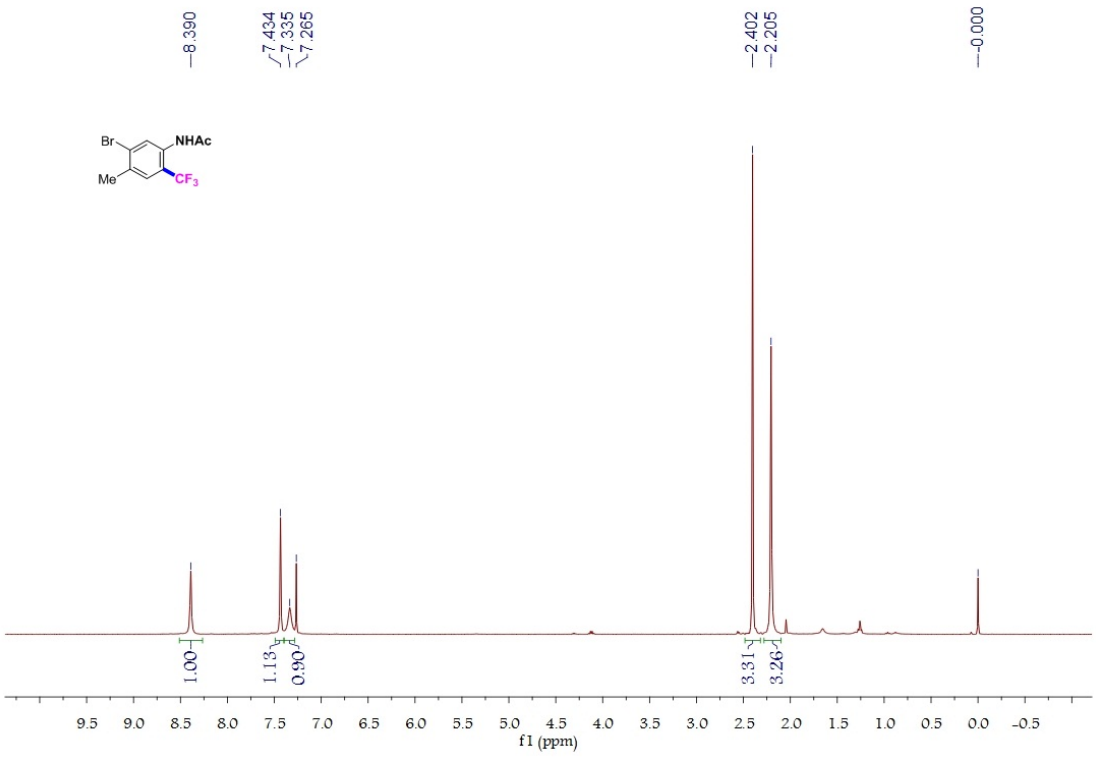
2 (0.2 mmol), CuTc (7.6 mg, 0.04 mmol), 5-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (81.6 mg, 0.24 mmol), 2,4,6-Collidine (24.2 mg, 0.2 mmol) and KOH (16.8 mg, 0.3 mmol) were placed in a vial. 1.0 mL DMAc was added. The mixture was stirred at 80 ^{o}C for 8 h and cooled to room temperature. EtOAc and H_2O was added and then the organic phase was purified by flash chromatography to give desired product as white solid.

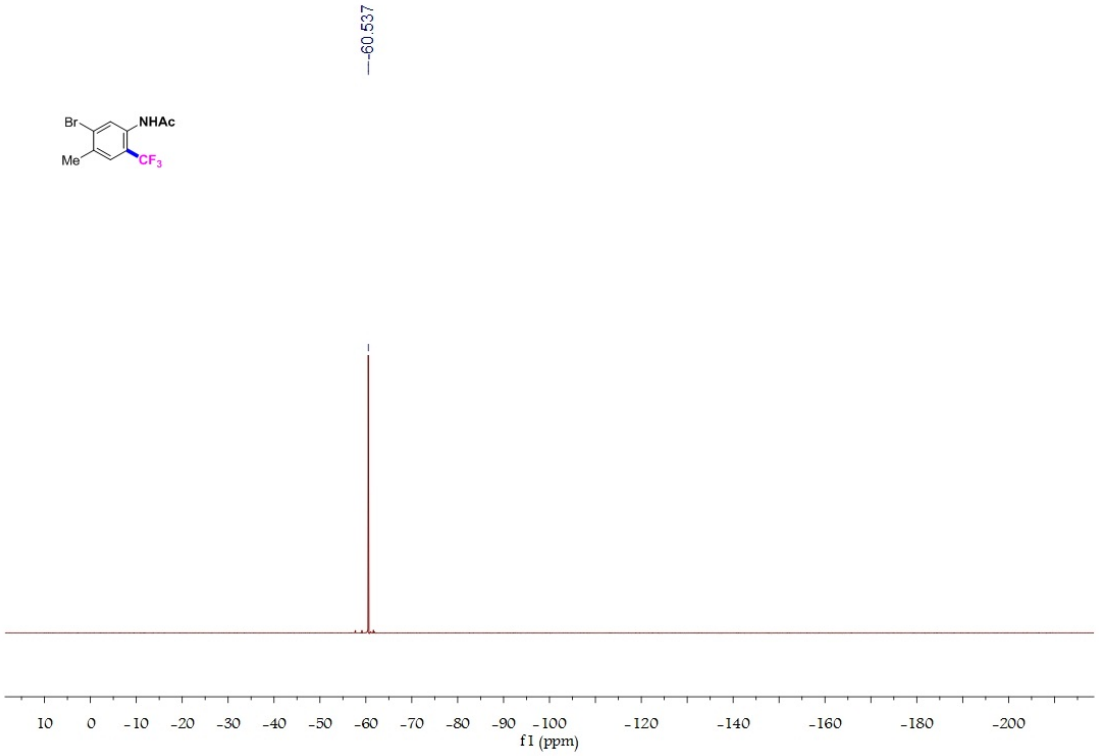


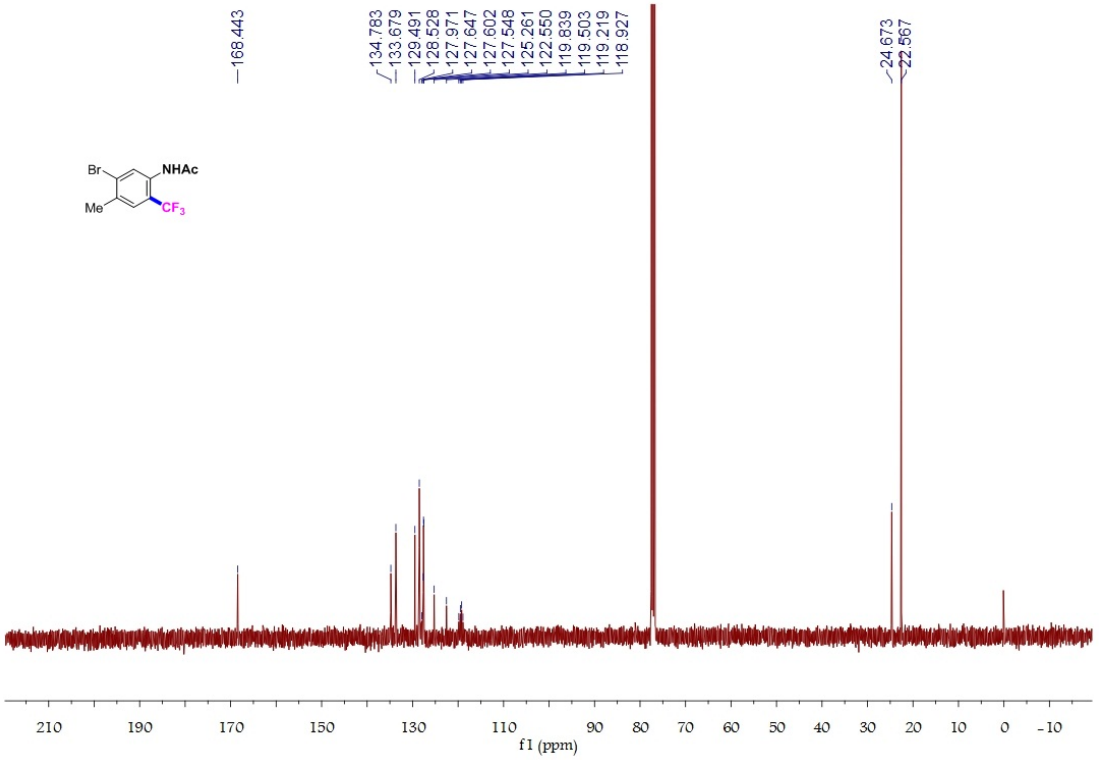
Chemical Formula: $C_{10}H_9BrF_3NO$
Exact Mass: 294.9820

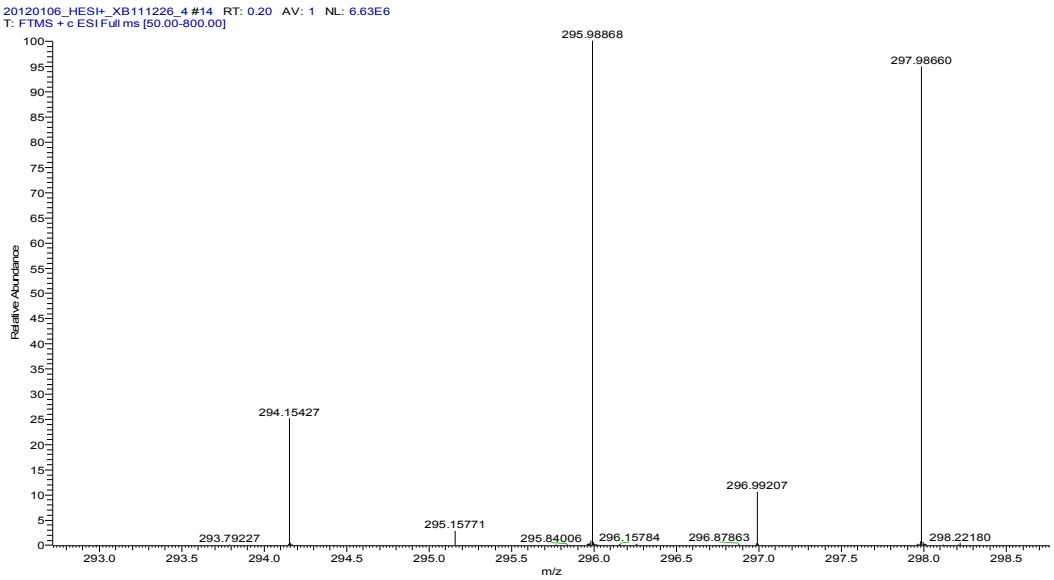
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.43 (s, 1H), 7.34 (s, 1H), 7.27 (s, 1H), 2.40 (s, 3H), 2.21 (s, 3H).

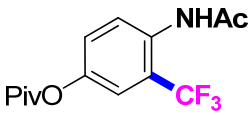
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.44, 134.78, 133.68, 129.49, 128.53, 127.58 (q, J = 5.4 Hz), 123.90 (q, J = 271 Hz) (127.97, 125.26, 122.55, 119.84), 119.36 (q, J = 28.4 Hz) (119.81, 119.50, 119.22, 118.93), 24.67, 22.57.




-60.537
Br
NHAc
Me
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


168.443
134.783
133.679
129.491
128.528
127.971
127.647
127.602
127.548
125.261
122.550
119.839
119.503
119.219
118.927
24.673
22.567
Br
NHAc
Me
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

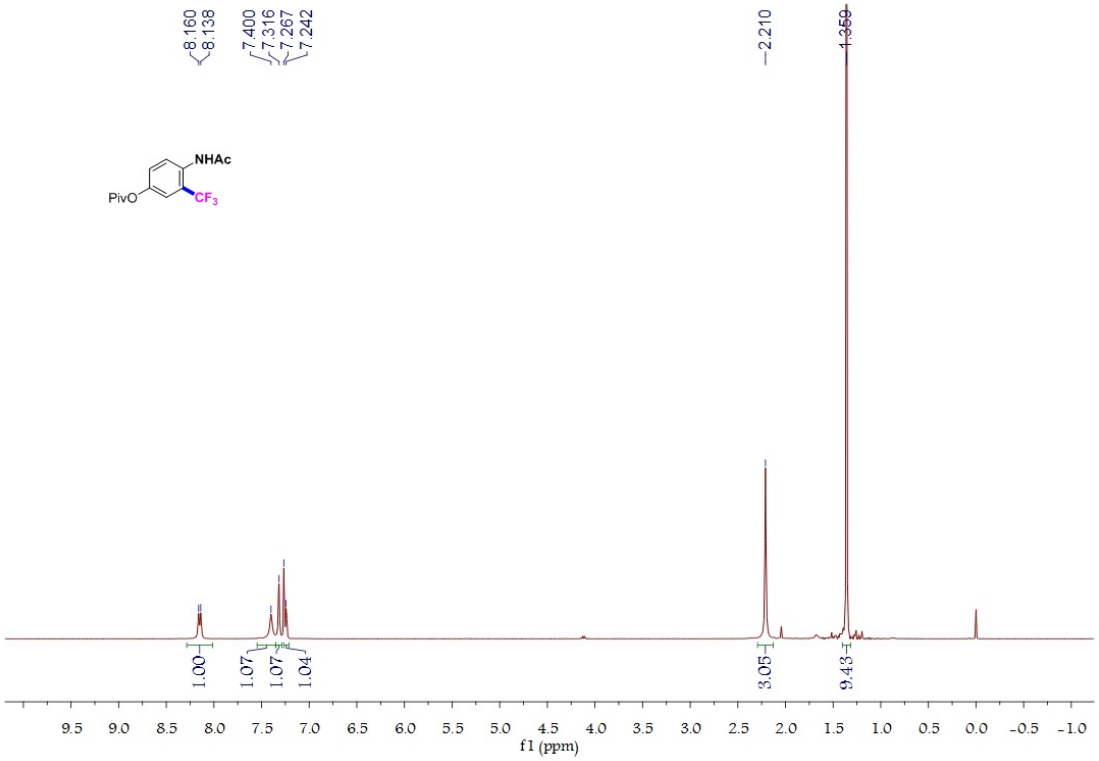


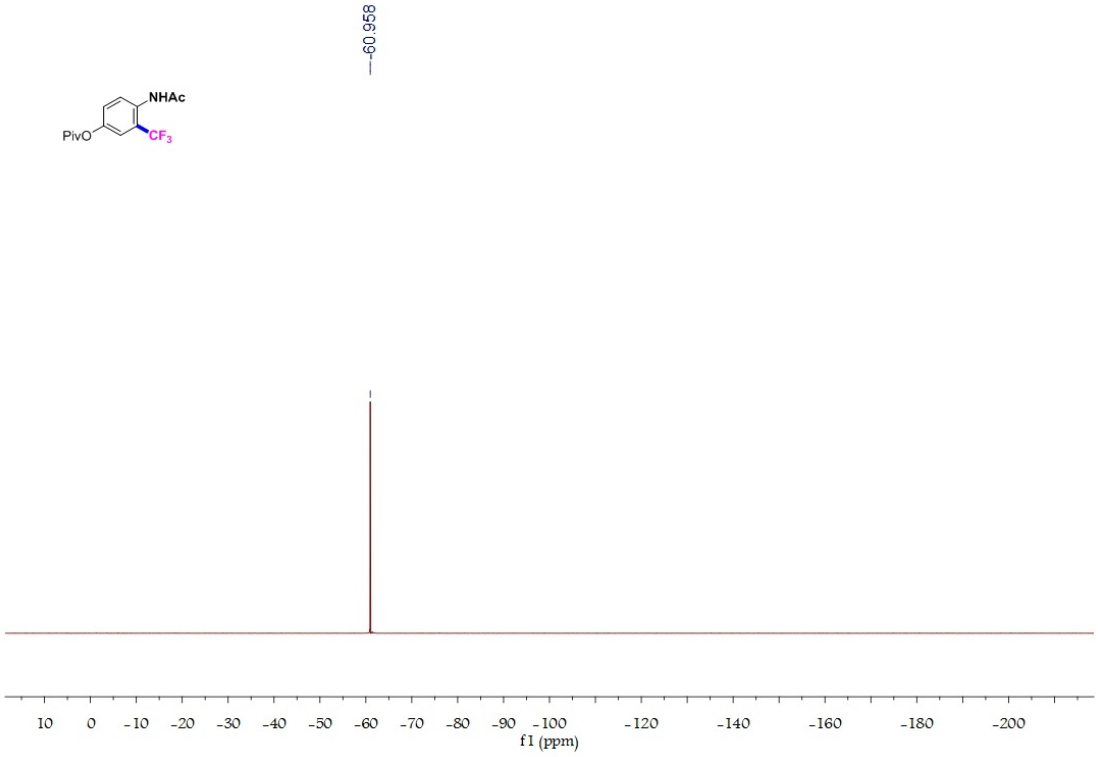


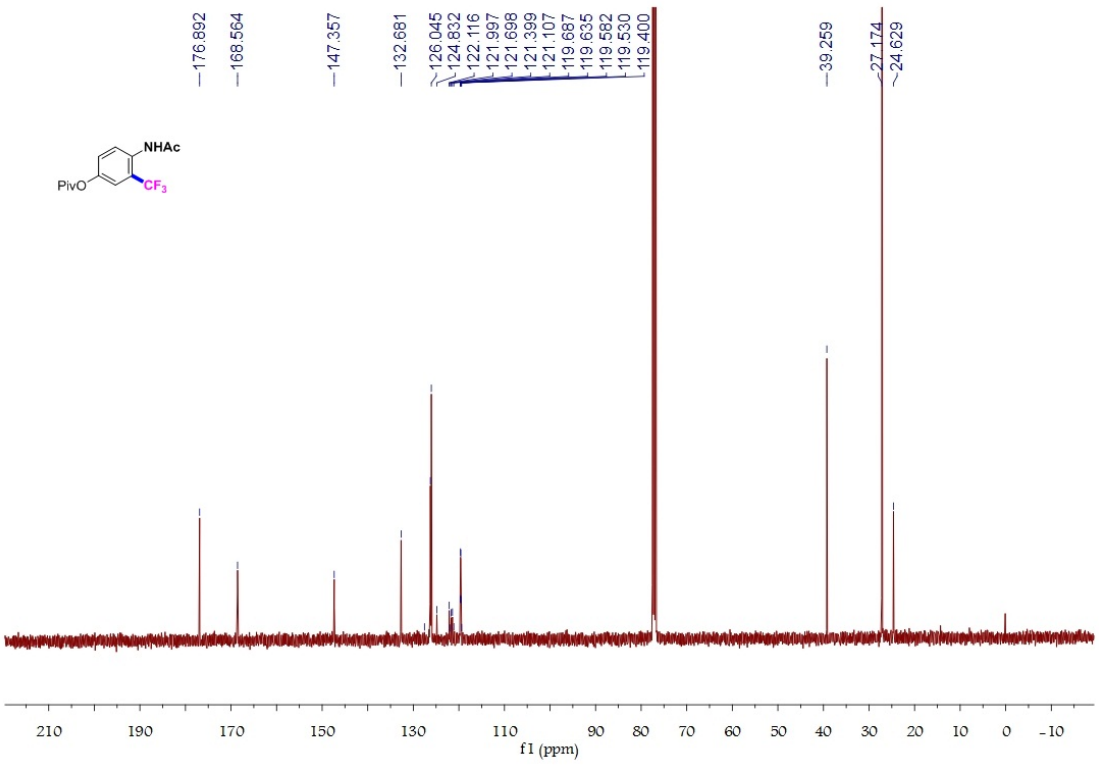
Chemical Formula: $C_{14}H_{16}F_3NO_3$
Exact Mass: 303.1082

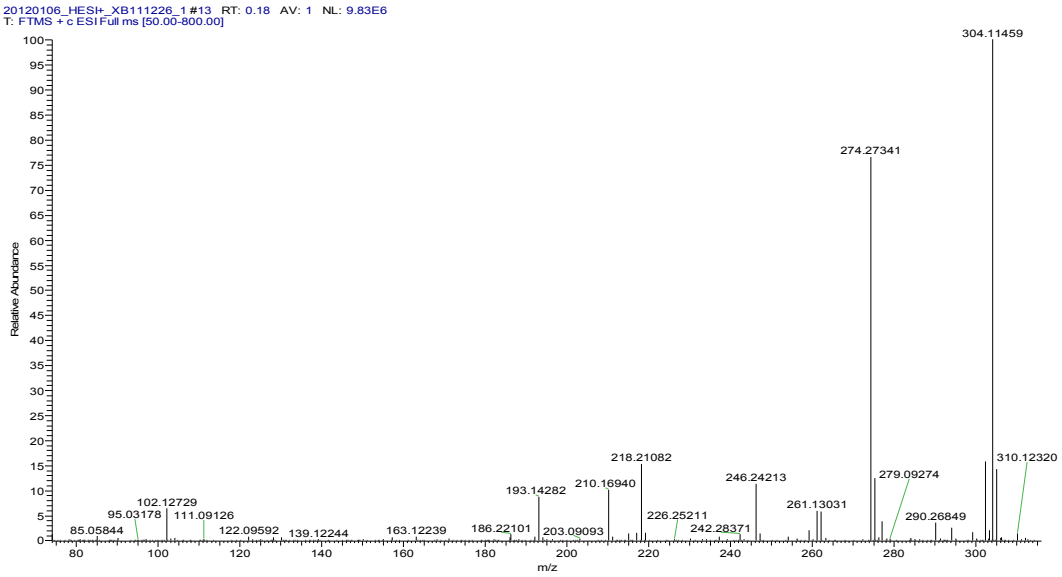
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7, 1H), 7.40 (s, 1H), 7.32 (s, 1H), 7.25 (d, J = 8.7, 1H), 2.21 (s, 3H), 1.36 (s, 9H).

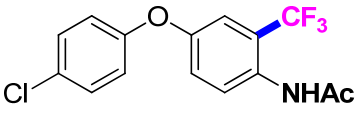
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.89, 168.56, 147.36, 132.68, 126.26, 126.04, 123.47 (q, J = 271 Hz) (127.55, 124.83, 122.12, 119.40), 121.55 (q, J = 30.0 Hz) (122.00, 121.70, 121.40, 121.11), 119.55 (119.69, 119.64, 119.58, 119.53), 39.26, 27.17, 24.63.




-60.958
NHAc
PivO
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


176.892
168.564
147.357
132.681
126.045
124.832
122.116
121.997
121.698
121.399
121.107
119.687
119.635
119.582
119.530
119.400
39.259
27.174
24.629
NHAc
PivO
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

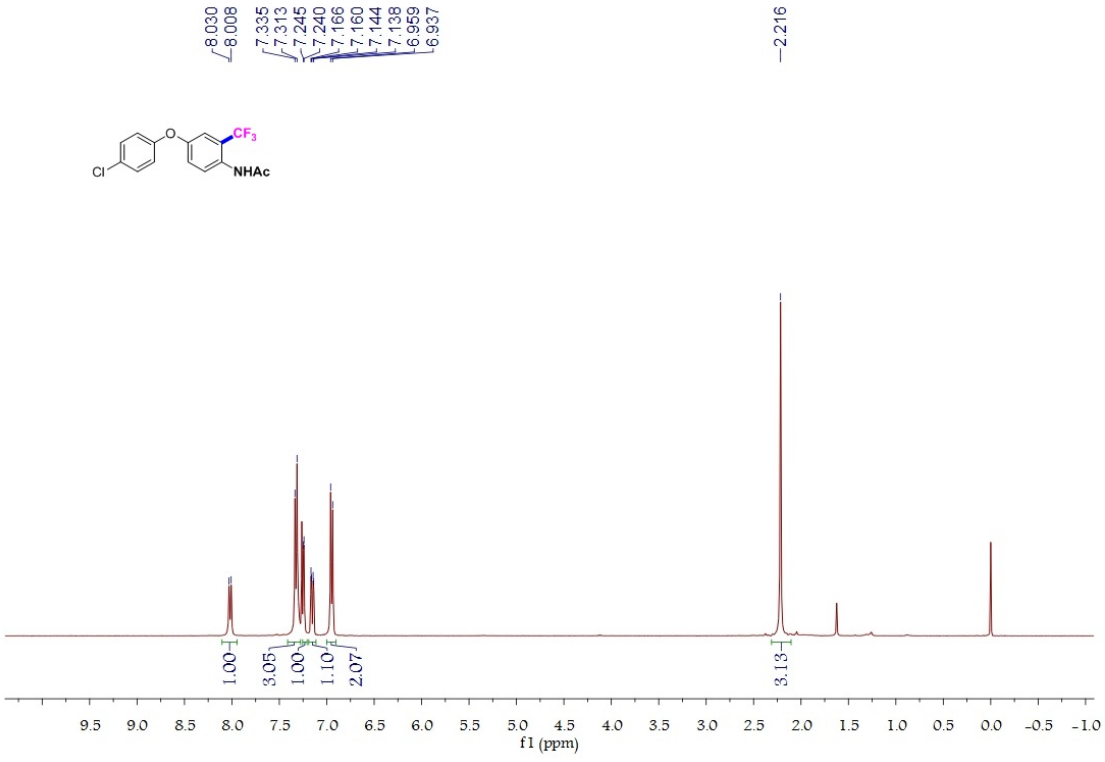


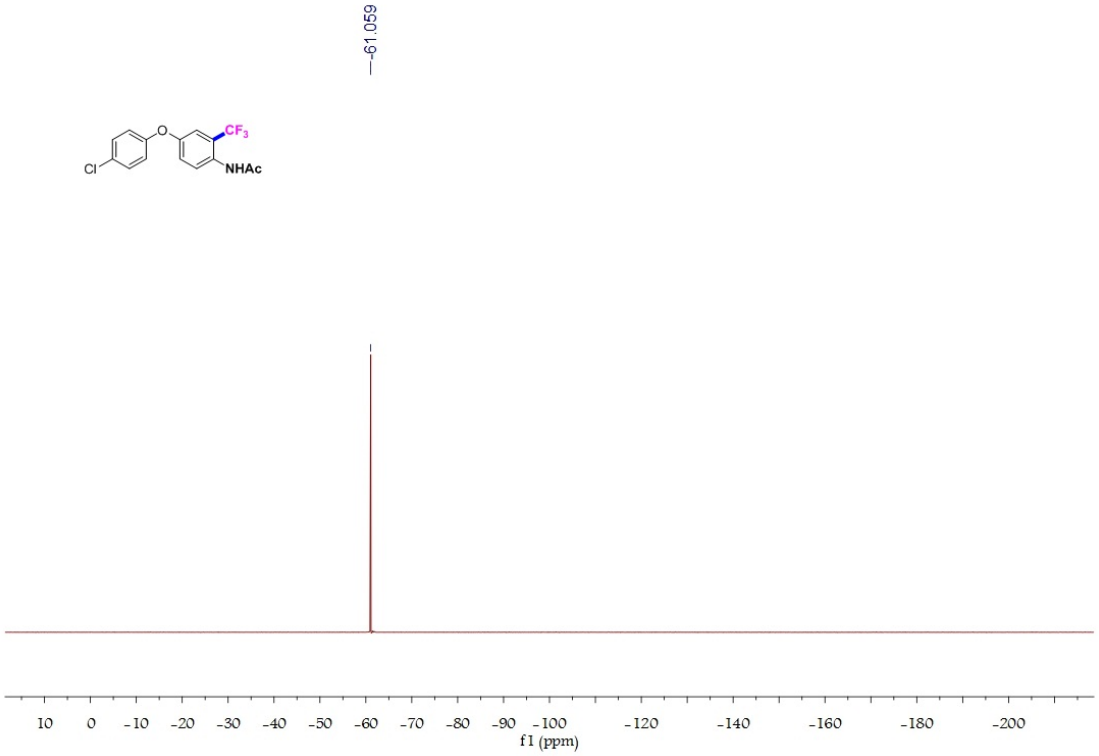


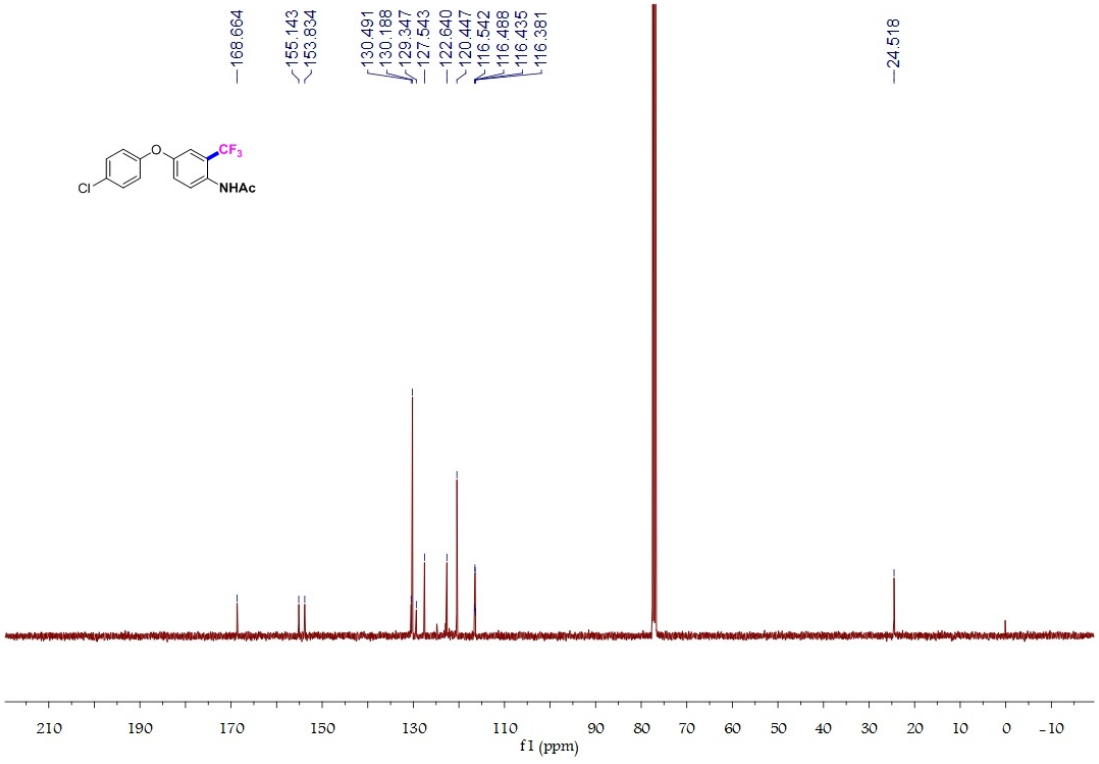
Chemical Formula: $C_{15}H_{11}ClF_3NO_2$
Exact Mass: 329.0430

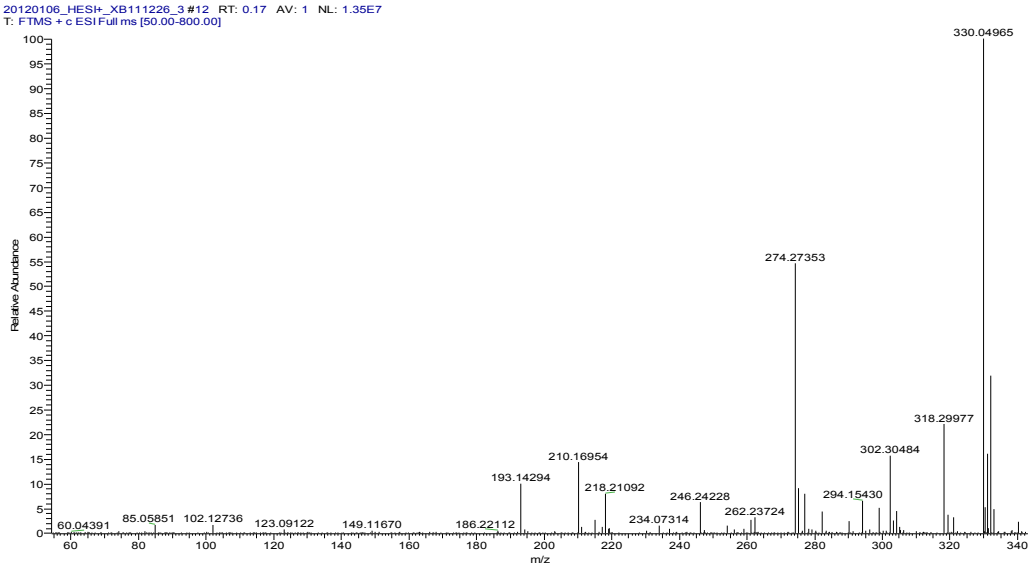
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.32 (m, 3H), 7.24 (m, 1H), 7.14 (m, 1H), 6.95 (m, 2H), 2.22 (s, 3H).

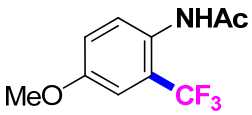
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66, 155.14, 153.83, 130.49, 130.19, 129.35, 127.54, 122.64, 120.45, 116.46 (q, J = 5.4 Hz) (116.54, 116.49, 116.43, 116.38), 24.52.




-61.059
CF3
O
Cl
NHAc
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


168.664
155.143
153.834
130.491
130.188
129.347
127.543
122.640
120.447
116.542
116.488
116.435
116.381
24.518
CF3
O
Cl
NHAc
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



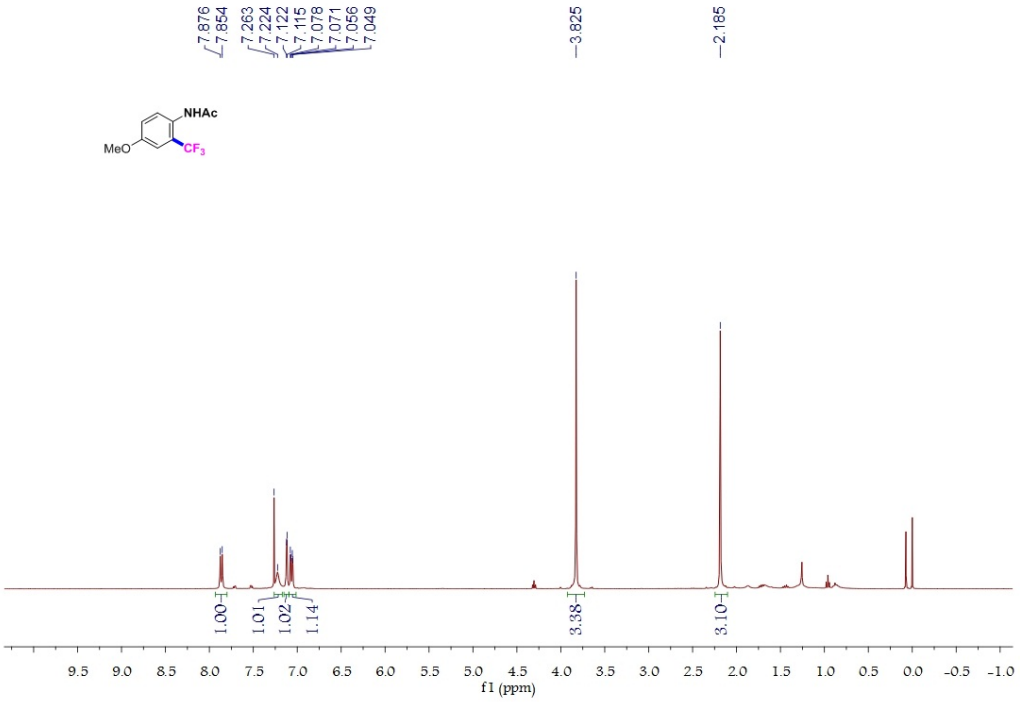


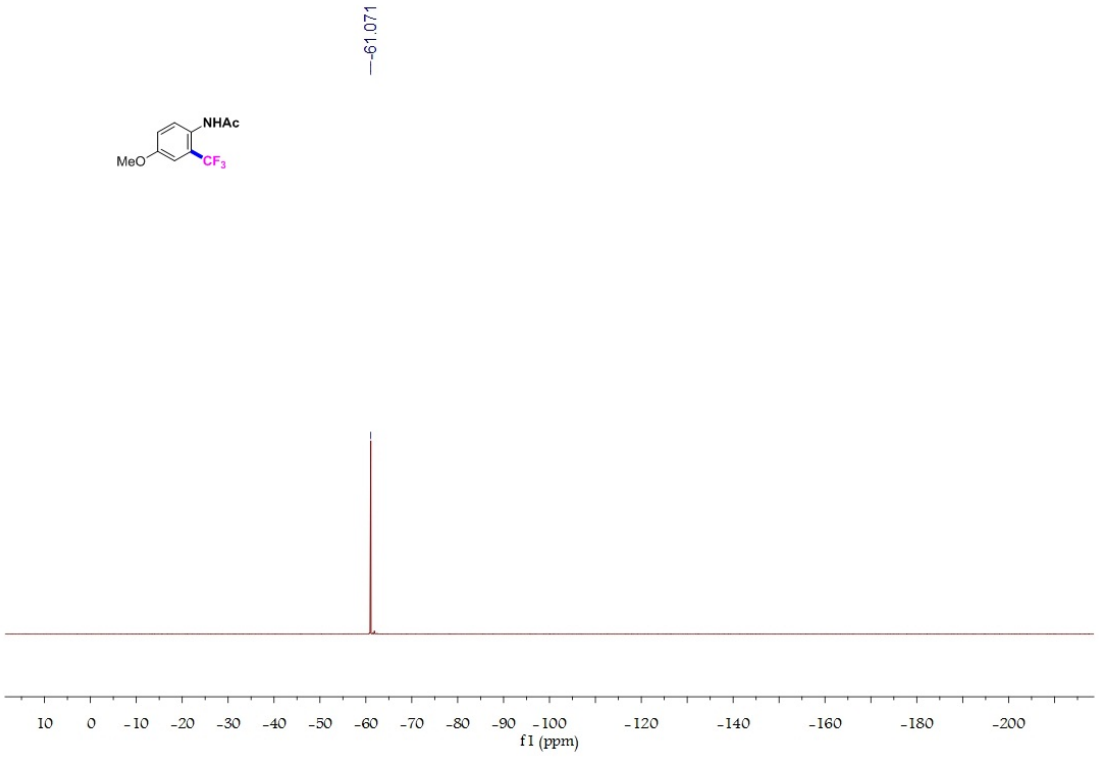
Chemical Formula: $C_{10}H_{10}F_3NO_2$
Exact Mass: 233.0664

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.9, 1H), 7.22 (s, 1H), 7.12 (d, J = 2.7, 1H), 7.06 (dd, J = 8.9, 2.8, 1H), 3.83 (s, 4H), 2.19 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.07.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 156.78, 127.95, 127.82, 123.77 (q, J = 271 Hz) (127.64, 125.13, 122.41, 119.78), 123.14 (q, J = 30 Hz) (123.59, 123.29, 123.00, 122.69), 117.82, 111.84, 111.78, 55.84, 24.31.




-61.071
NHAc
MeO
CF3
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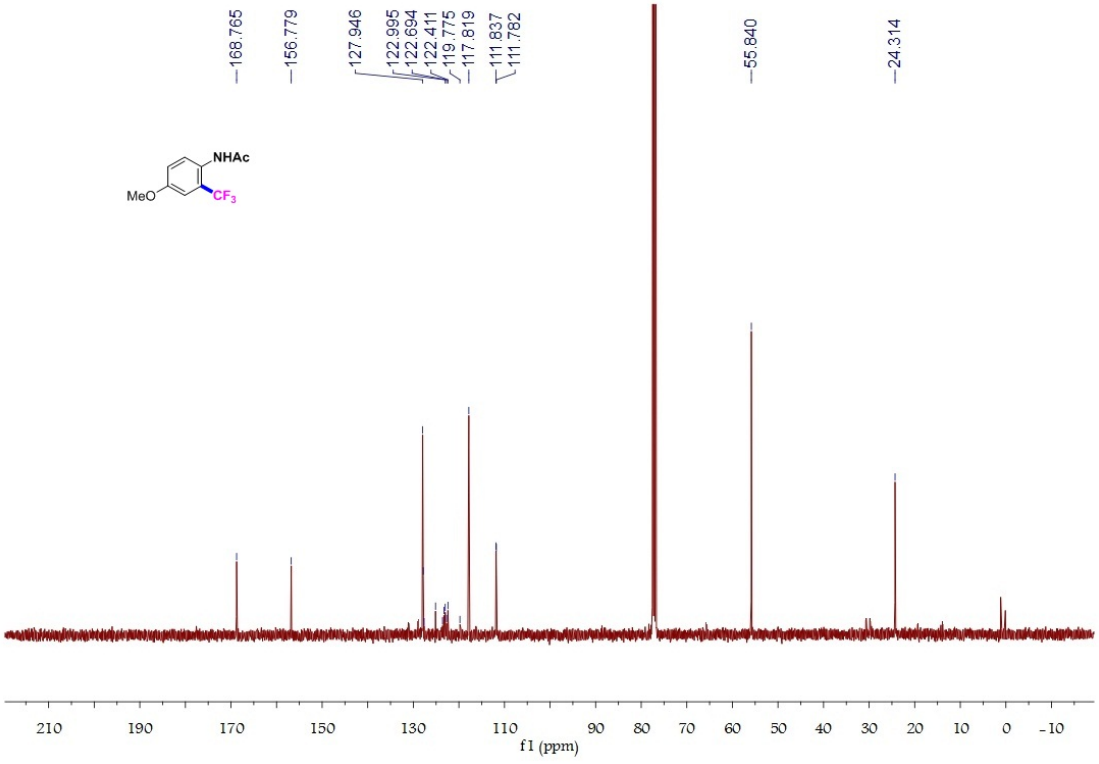
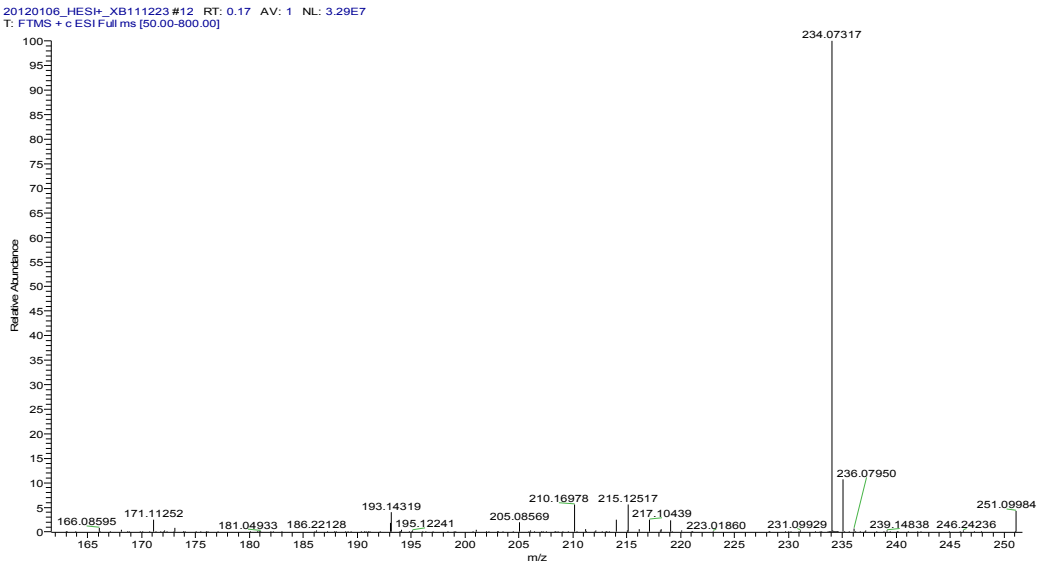
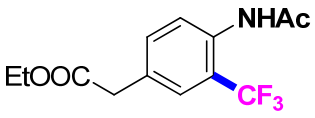
f1 (ppm)


168.765
156.779
127.946
122.995
122.694
122.411
119.775
117.819
111.837
111.782
55.840
24.314
NHAc
MeO
CF3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



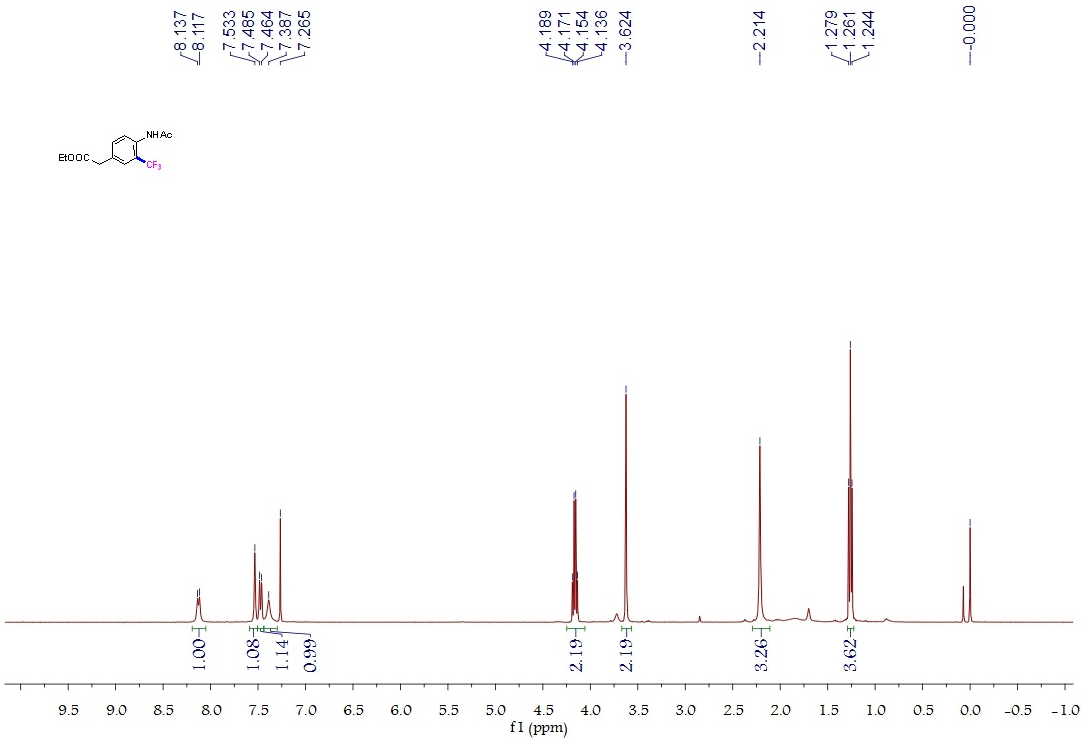


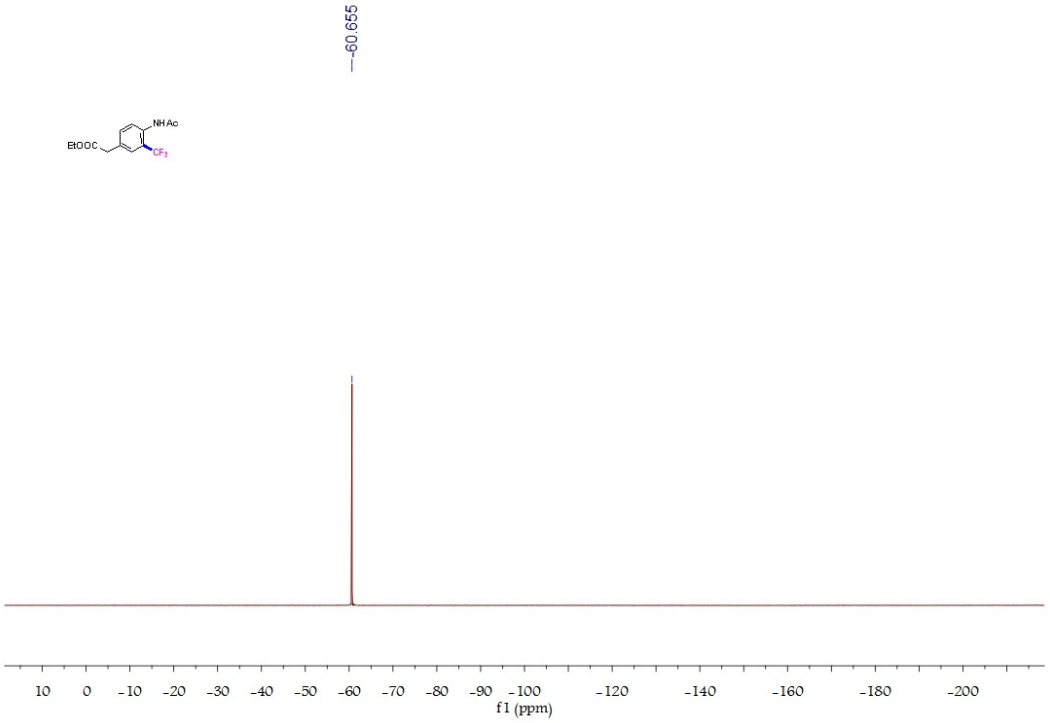
Chemical Formula: $C_{13}H_{14}F_3NO_3$
Exact Mass: 289.0926

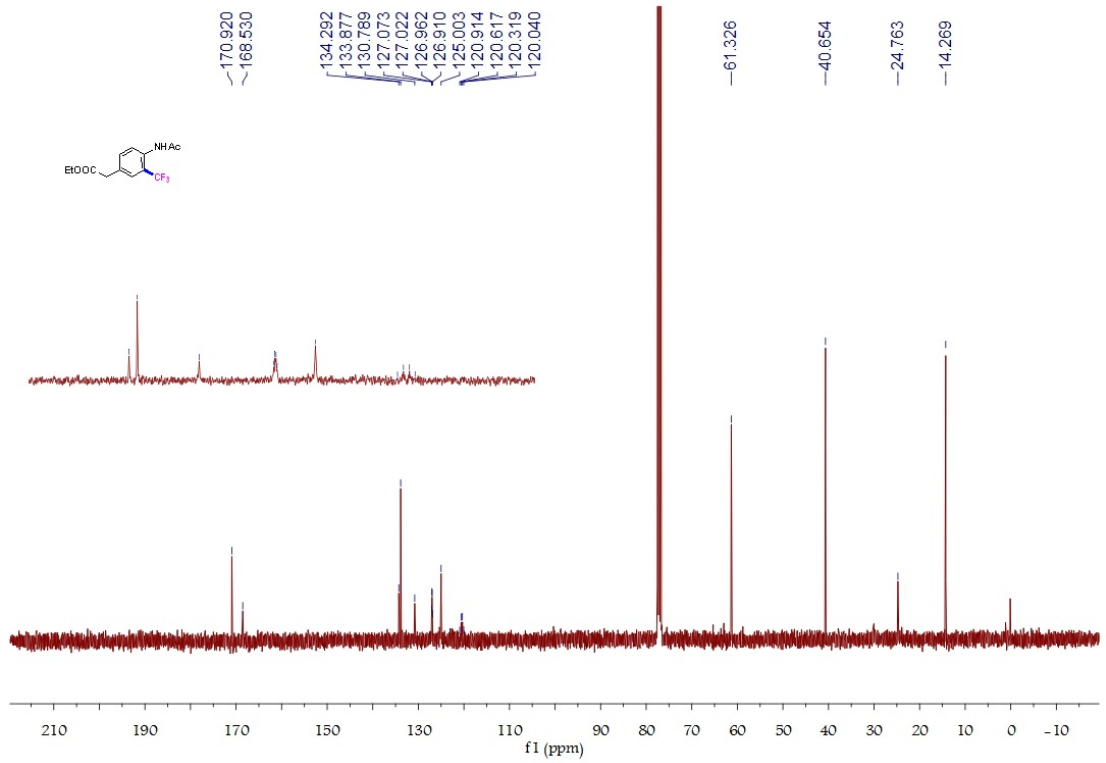
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1, 1H), 7.53 (s, 1H), 7.47 (d, J = 8.4, 1H), 7.39 (s, 1H), 4.16 (q, J = 7.1, 2H), 3.62 (s, 2H), 2.21 (s, 3H), 1.26 (t, J = 7.1, 3H).

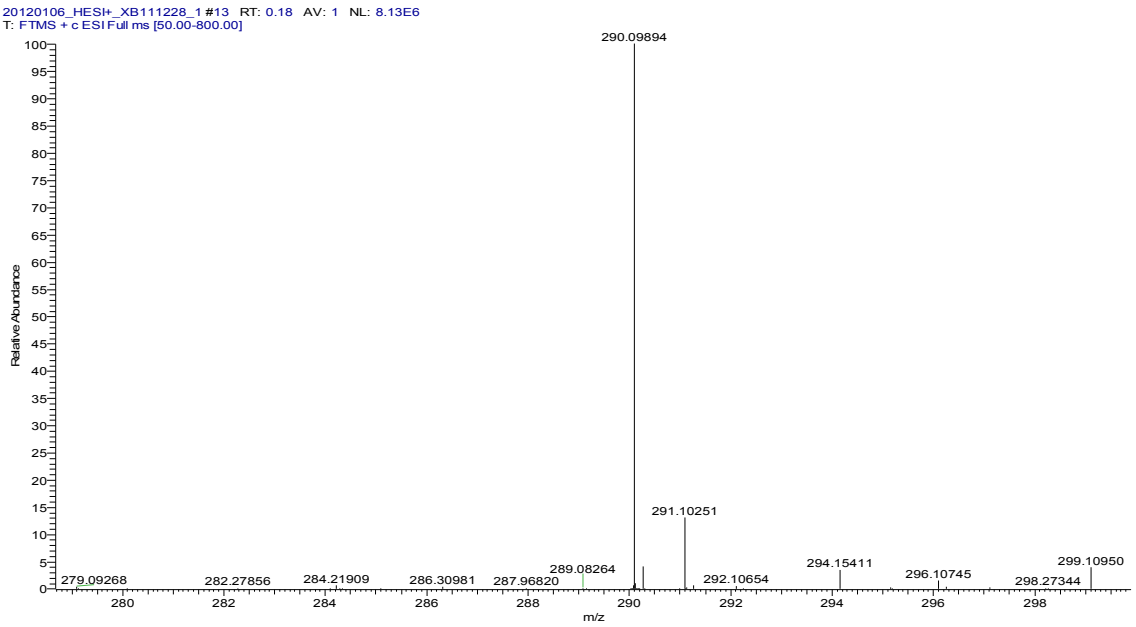
^{19}F NMR (376 MHz, $CDCl_3$) δ -60.65.

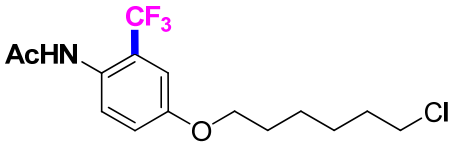
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.92, 168.53, 134.29, 133.88, 130.79, 126.99 (q, J = 5.4 Hz) (127.07, 127.02, 126.96, 126.91), 125.00, 120.47 (q, J = 30 Hz), 61.33, 40.65, 24.76, 14.27.


8.137
8.117
7.533
7.485
7.464
7.387
7.265
4.189
4.171
4.154
4.136
3.624
2.214
1.279
1.261
1.244
0.000
NHAc
EtOOC
CF3
1.00
1.08
1.14
0.99
2.19
2.19
3.26
3.62
f1 (ppm)


-60.655
NHAc
EtOOC
CF3
f1 (ppm)





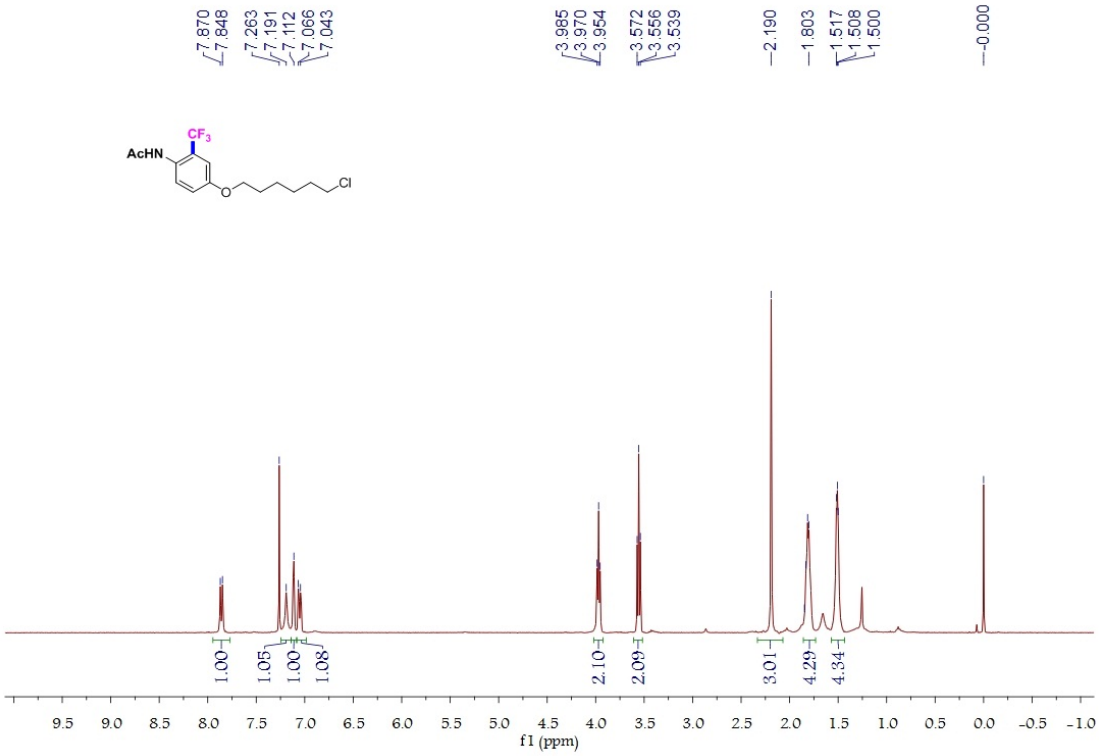


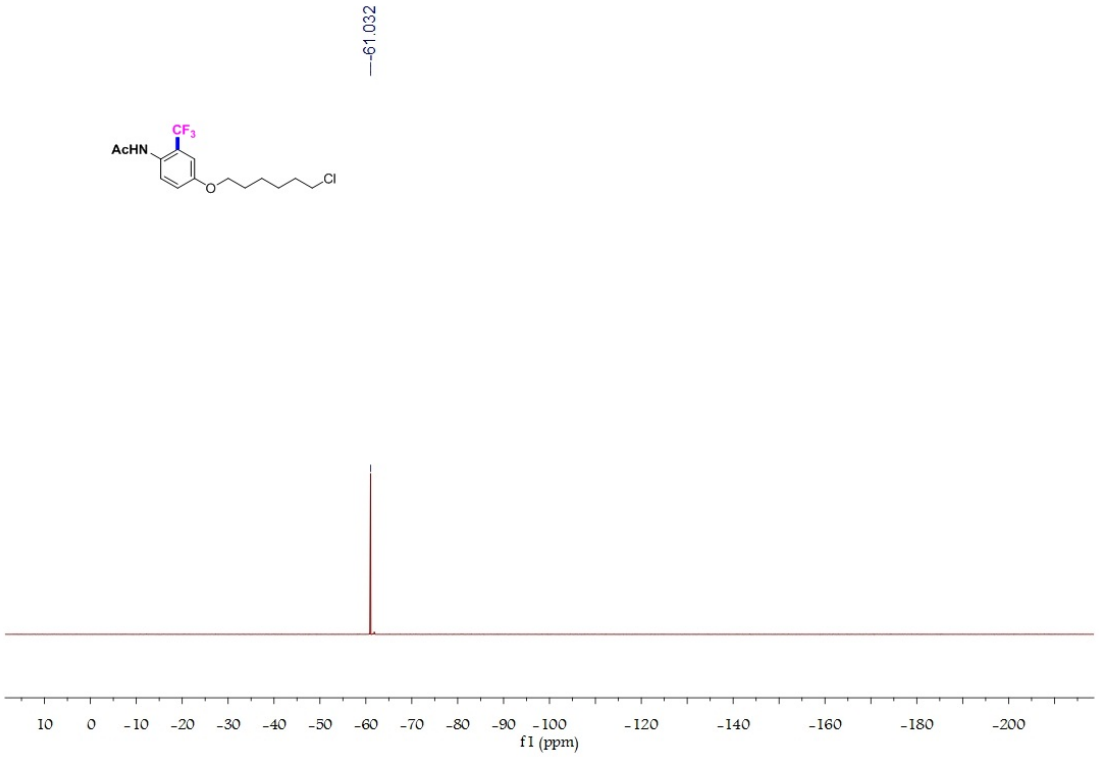
Chemical Formula: $C_{15}H_{19}ClF_3NO_2$
Exact Mass: 337.1056

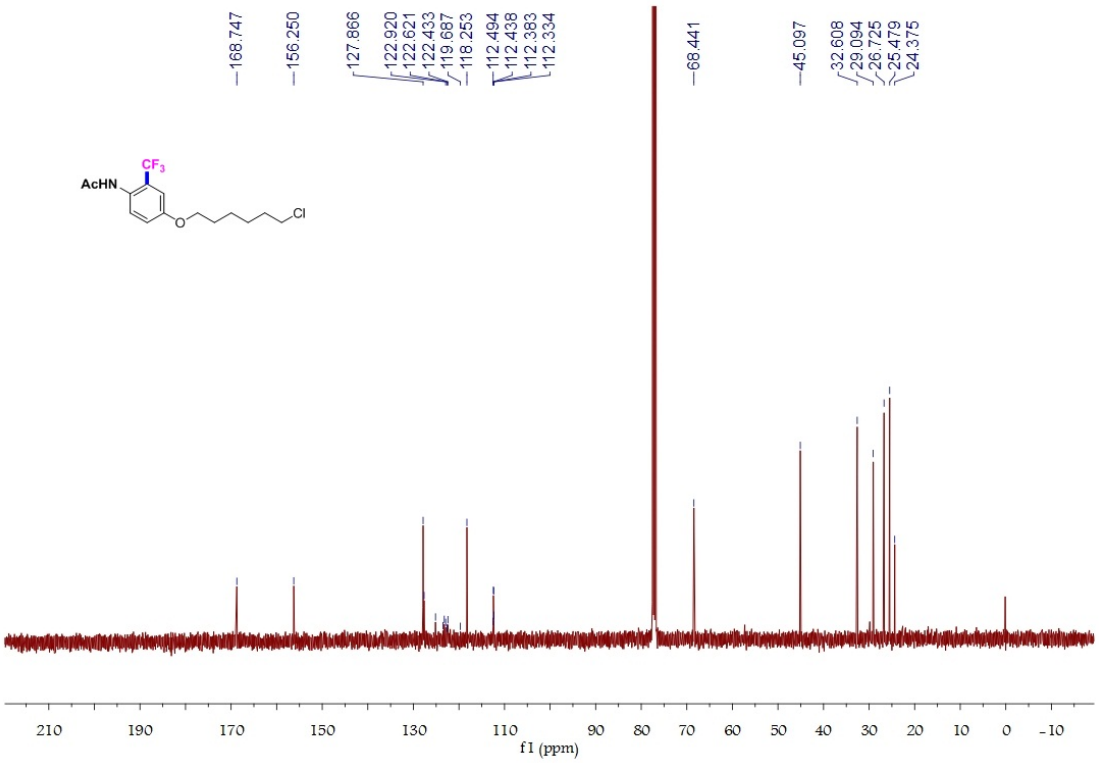
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.9, 1H), 7.19 (s, 1H), 7.11 (s, 1H), 7.05 (d, J = 8.9, 1H), 3.97 (t, J = 6.3, 2H), 3.56 (t, J = 6.6, 2H), 2.19 (s, 3H), 1.82 (m, 4H), 1.54 – 1.47 (m, 4H).

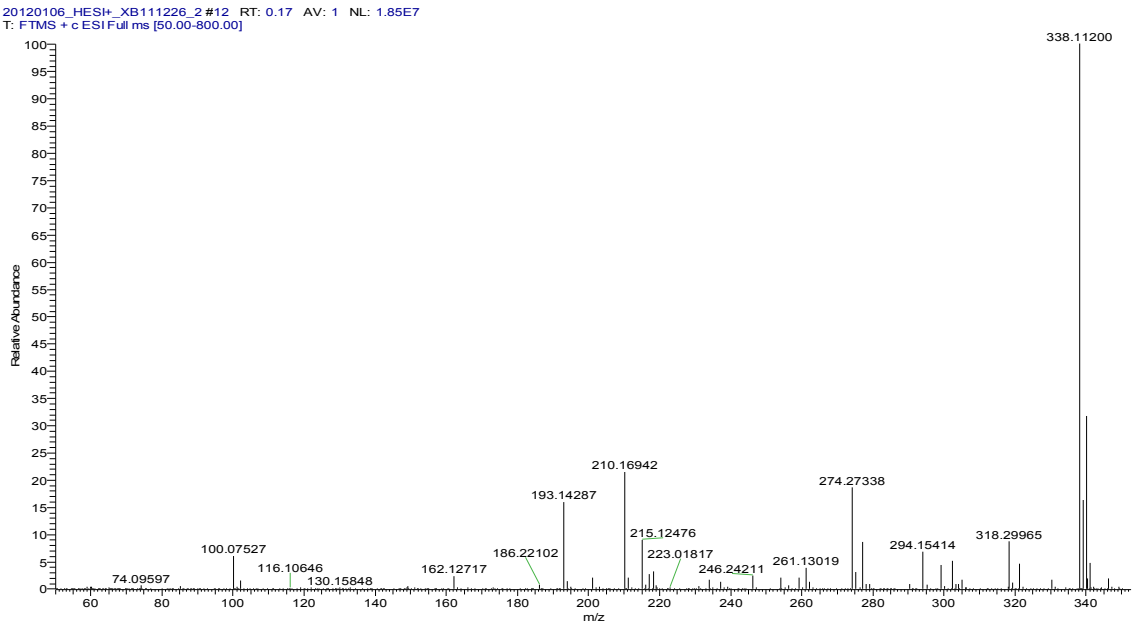
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.03.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.75, 156.25, 127.87, 127.65, 123.79 (q, J = 271 Hz), 123.07 (q, J = 30 Hz) 119.69, 118.25, 112.41 (q, J = 5.4 Hz) (112.49, 112.44, 112.38, 112.33), 68.44, 45.10, 32.61, 29.09, 26.73, 25.48, 24.37.






168.747
156.250
127.866
122.920
122.621
122.433
119.687
118.253
112.494
112.438
112.383
112.334
68.441
45.097
32.608
29.094
26.725
25.479
24.375
AcHN
CF3
Cl
O
f1 (ppm)


20120106_HESI+_XB111226_2 #12 RT: 0.17 AV: 1 NL: 1.85E7
T: FTMS + c ESI Full ms [50.00-800.00]
Relative Abundance
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338.11200
210.16942
193.14287
274.27338
215.12476
223.01817
294.15414
318.29965
100.07527
186.22102
116.10646
162.12717
261.13019
246.24211
74.09597
130.15848