Supporting Information

Iron Porphyrin-Catalyzed N-Trifluoroethylation of Anilines with 2,2,2-Trifluoroethylamine Hydrochloride in Aqueous Solution

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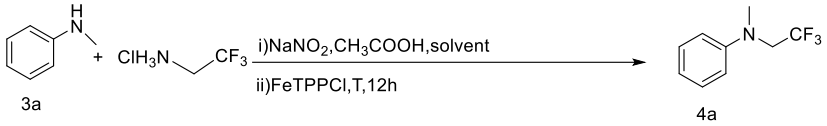
Table of Contents

1. General information

Unless otherwise noted, all reactions were carried out in Schlenk tubes. Reagents and solvents were obtained from commercial sources and used without further purification. The ^{1}H ,^{13}C and ^{9}F spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, 100 MHz and 377 MHz, and Chemical shifts are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt= doublet of triplets m = multiplet). Column chromatography was performed using silica gel of 300-400 μm. The electron ionization (EI) method was used for HRMS measurement, and the mass analyzer type is TOF for EI. The HRMS (EI) was recorded on an Esquire 3000 plus instrument. ESR measurements were carried out on a JEOL JES-FA-200 spectrometer at 77k or room temperature.

2. Optimization of reaction conditions for N-trifluoroethylation[a]



3a 4a

Entry	solvent	Tempeture [℃]	Yield [%]
1	H_2O:CH_2Cl_2=1:1	r.t	30
2	H_2O:CH_2ClCH_2Cl=1:1	40℃	46
3	H_2O:CH_2ClCH_2Cl=1:1	60℃	63
4	H_2O:CH_2ClCH_2Cl=1:1	80℃	72

[a]Reaction conditions： **3a** (0.3 mmol, 1.0 equiv.), trifluoroethylamine hydrochloride (0.6 mmol, 2 equiv.), FeTPPCl (0.9 mol %), $NaNO_2$ (0.6 mmol, 2 equiv.), CH_3COOH (0.6 mmol, 2 equiv.), solvent (4 mL), air atmosphere, 12 h

3. ESR spectra data of FeTPP(NO)

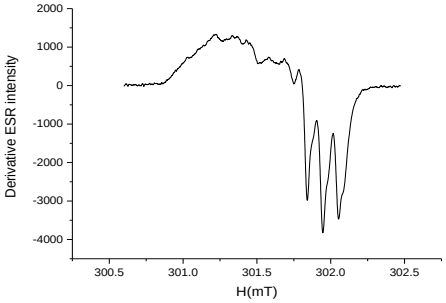


Fig.1 ESR spectrum of [FeTPP(NO)] in DMSO at 77K

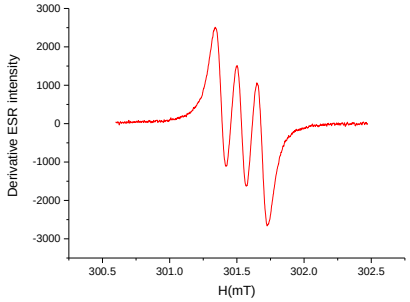
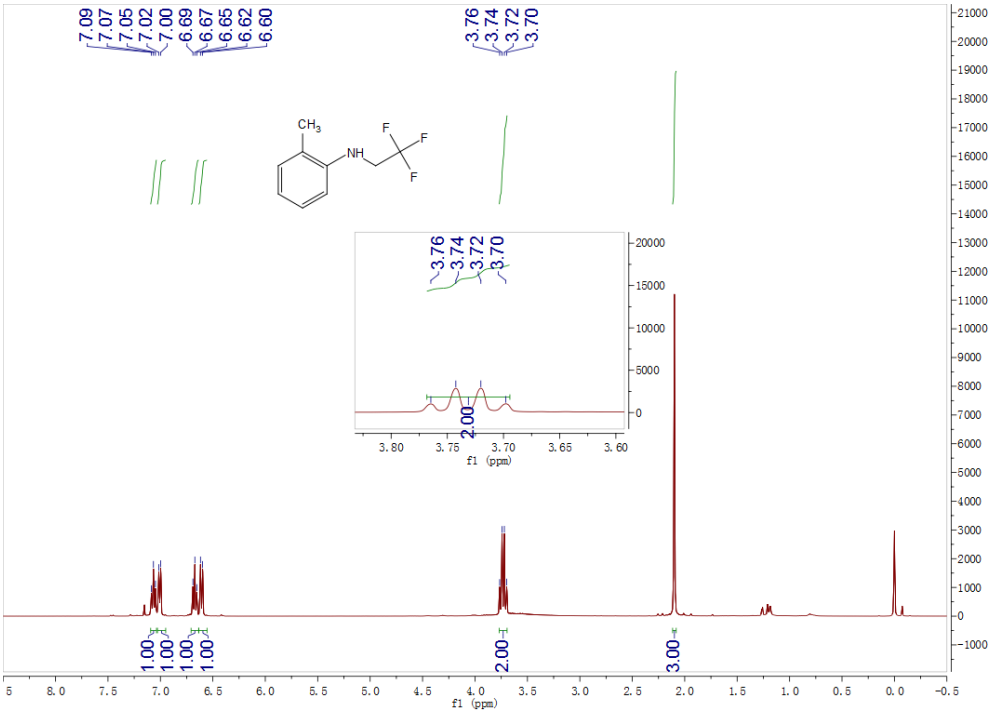
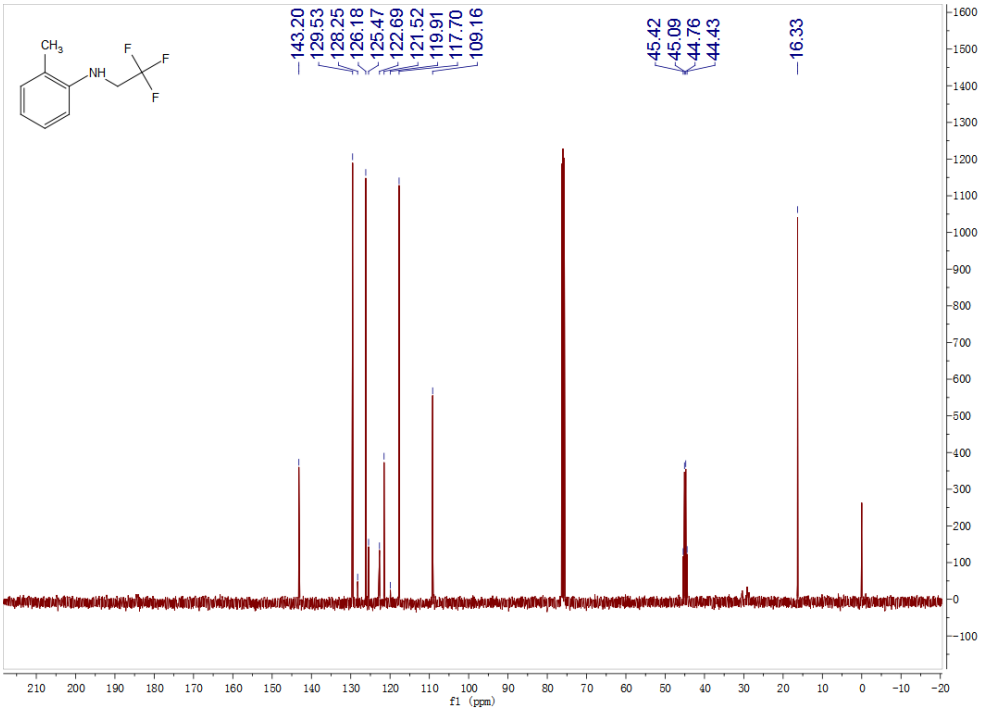


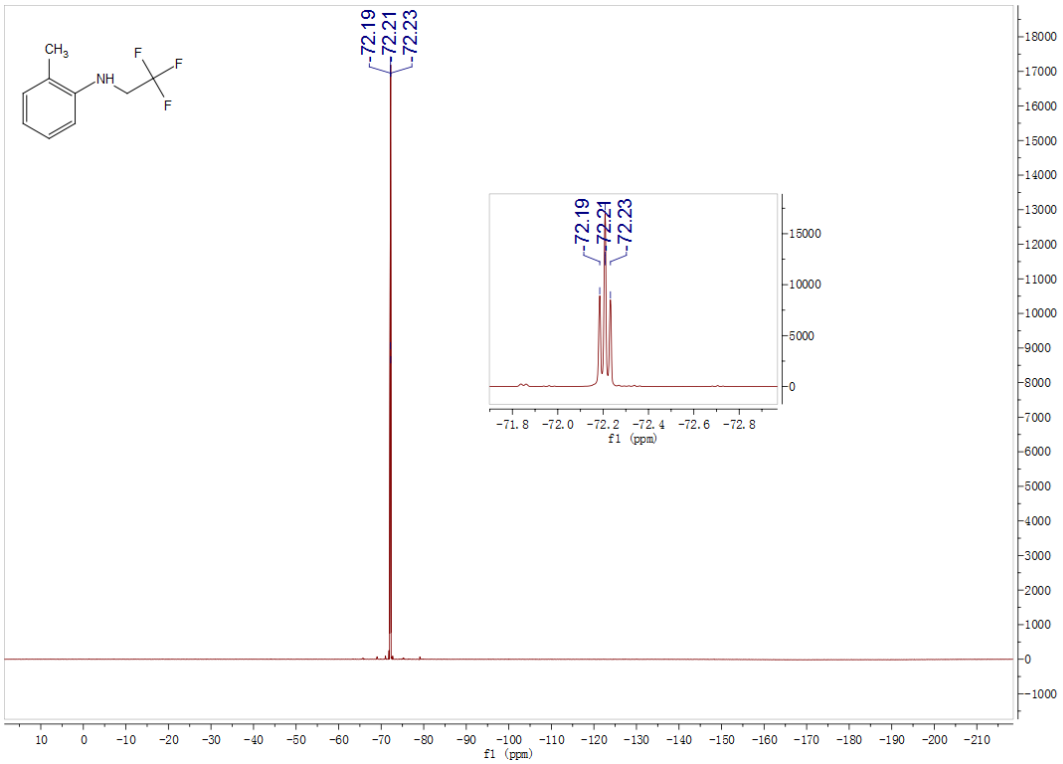
Fig.2 ESR spectrum of [FeTPP(NO)] in DMSO at room temperature

4. Spectra data of the products

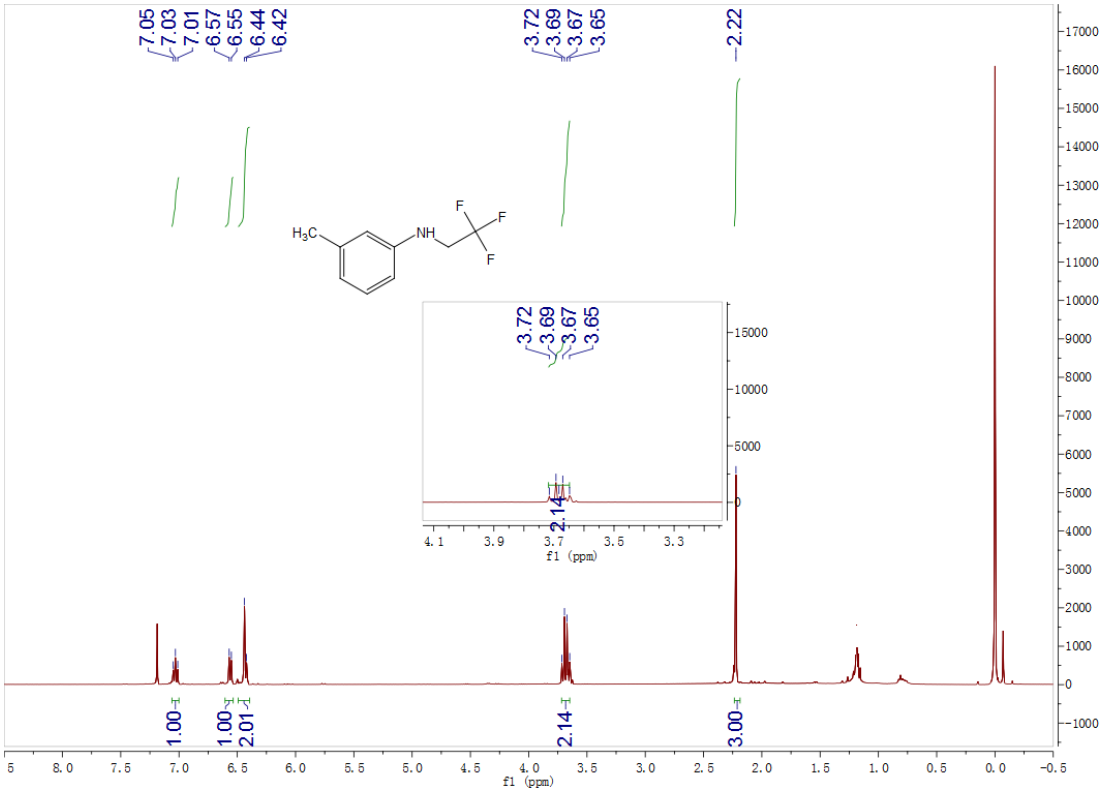
2-Methyl-N-(2,2,2-trifluoroethyl)benzenamine(2a) pale yellow liquid, 42.1 mg,74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, *J*=7.7 Hz, 1H), 7.01 (d, *J*=7.3 Hz, 1H), 6.67 (t, *J*=7.4 Hz, 1H), 6.61 (d, *J*=8.1 Hz, 1H), 3.73 (q, *J*=8.9 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) :δ 143.2, 129.6, 126.2, 124.1 (q,*J*=278.0 Hz), 121.5, 117.7, 109.2, 44.9 (q,*J*=33.0 Hz), 16.3. ^{19}F NMR (377MHz, $CDCl_3$) :δ-72.20 (t, *J*=8.7 Hz). HRMS (EI): calcd for $C_9H_{10}F_3N$: 189.0765; found: 189.0768

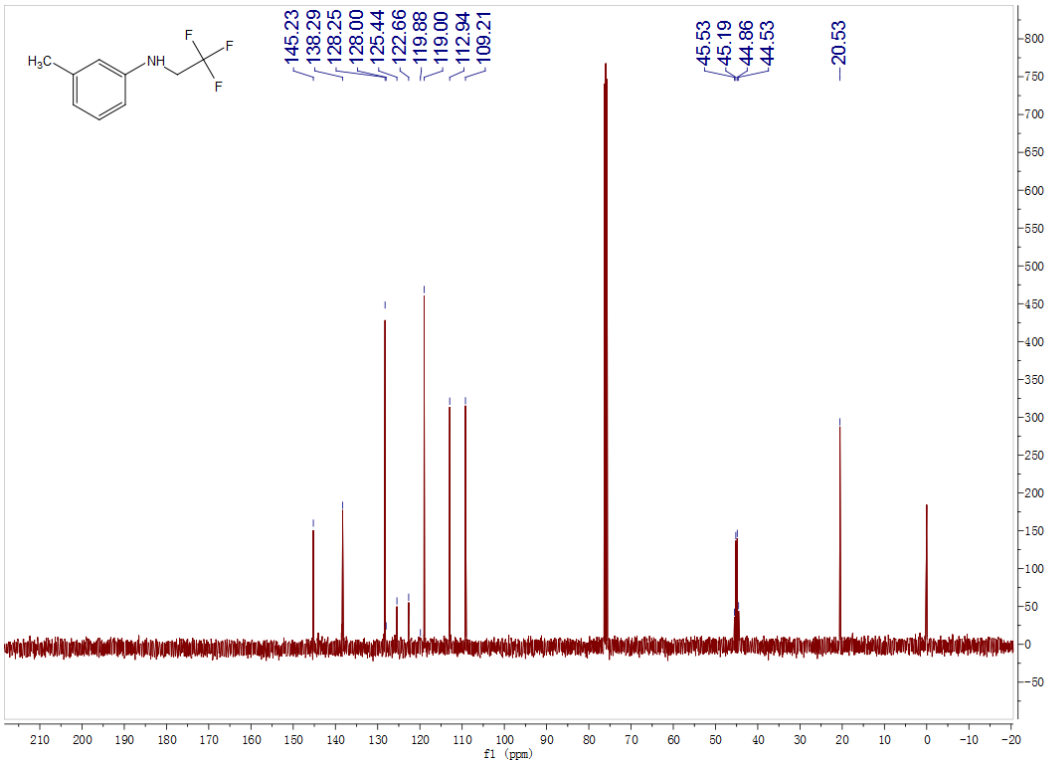






3-Methyl-N-(2,2,2-trifluoroethyl)benzenamine (2b) pale yellow liquid, 40.9 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, *J* = 7.8 Hz, 1H), 6.56 (d, *J*=7.5 Hz, 1H), 6.43 (d, *J*=7.2 Hz, 2H), 3.69 (t, *J*=9.0 Hz, 2H), 2.22 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =145.2, 138.3, 128.3, 124.1 (q, *J*=278.0 Hz), 119.0, 112.9, 109.2, 45.0 (q, *J*=33.0 Hz), 20.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.35 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_9H_{10}F_3N$: 189.0765; found: 189.0771

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128.00
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109.21
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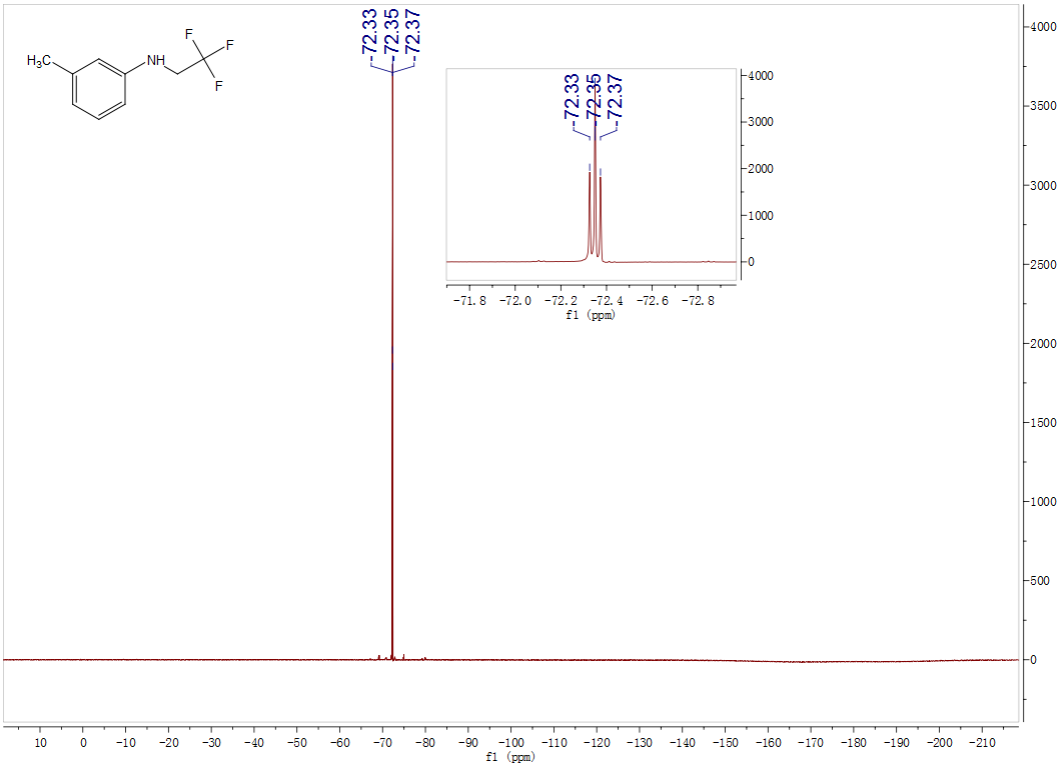
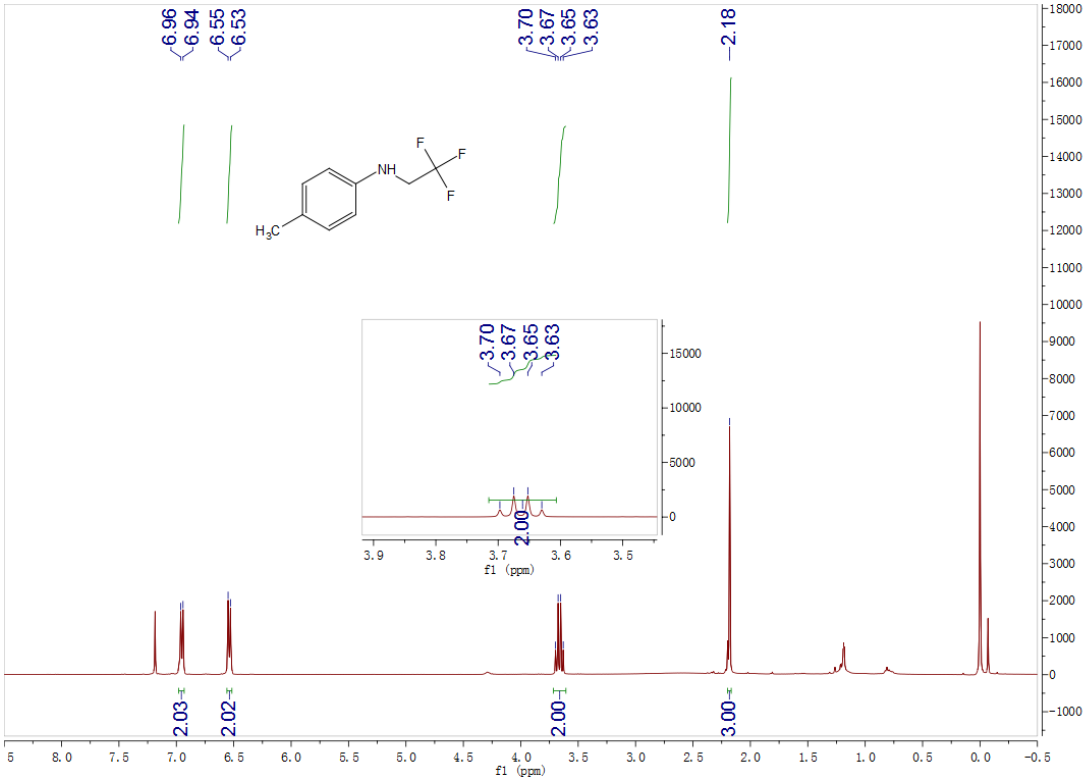
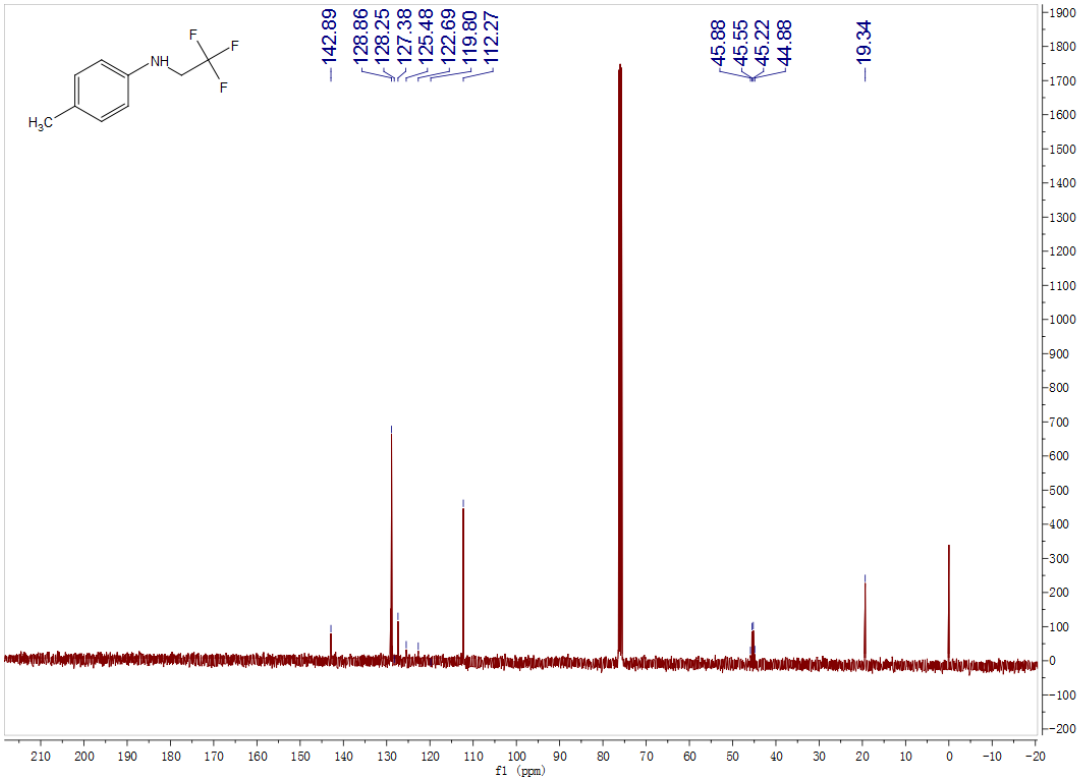
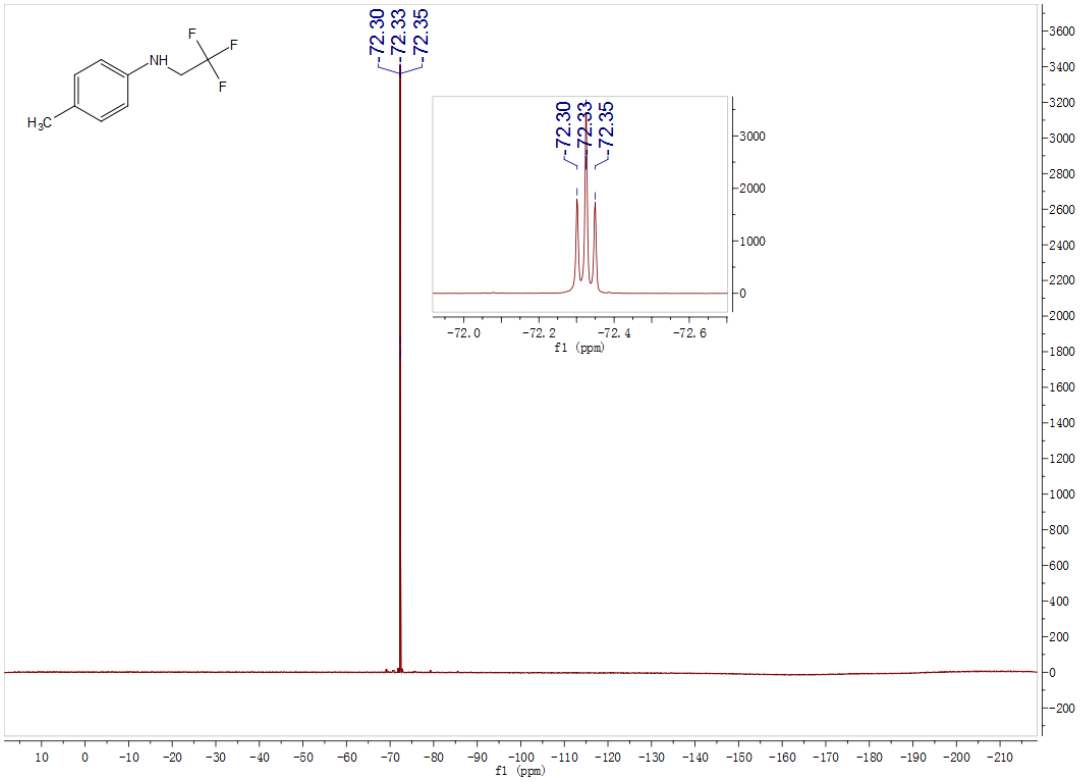
45.19
44.86
44.53
20.53
f1 (ppm)


72.33
72.35
72.37
f1 (ppm)

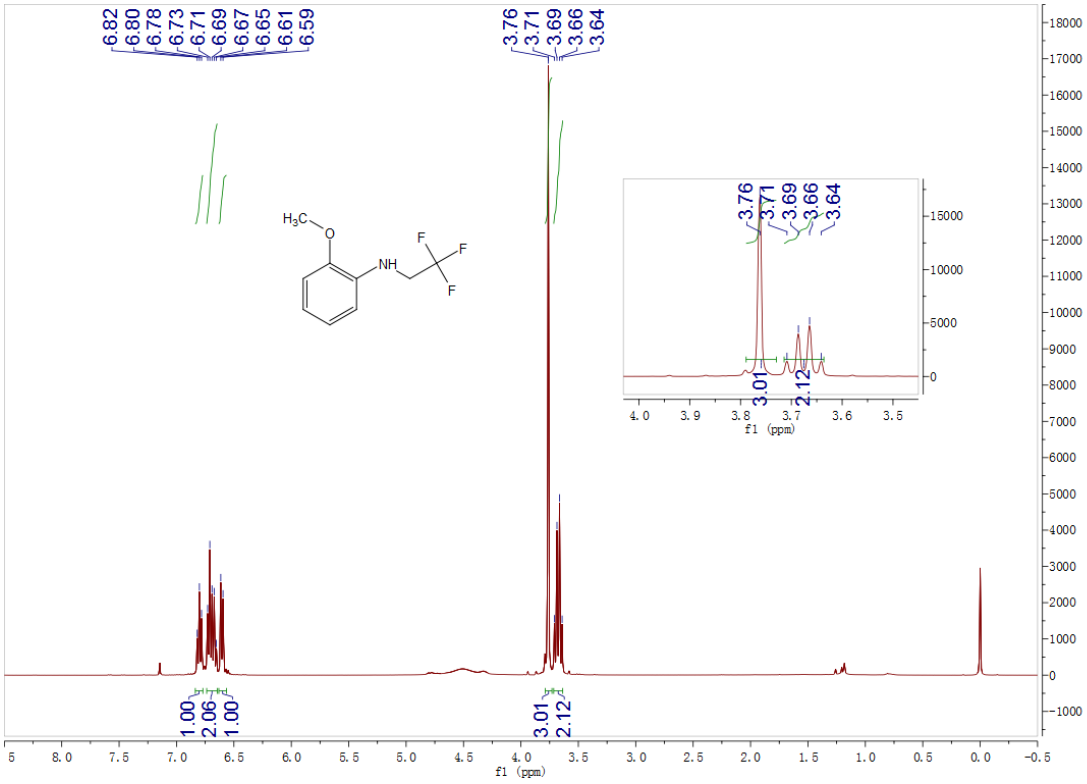
4-Methyl-N-(2,2,2-trifluoroethyl)benzenamine(2c) pale yellow liquid, 40.7 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.89 (m, 2H), 6.65 (d, *J*=8.1 Hz, 1H), 3.83 (q, *J*=8.9 Hz, 2H), 2.29 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.9, 131.4, 128.0, 127.5, 125.2 (q, *J*=278.0 Hz), 122.7, 110.6, 46.3 (q, *J*=33.0 Hz), 20.3, 17.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.24 (t, *J*=8.9Hz). HRMS (EI): calcd for $C_9H_{10}F_3N$: 189.0765; found: 189.0759

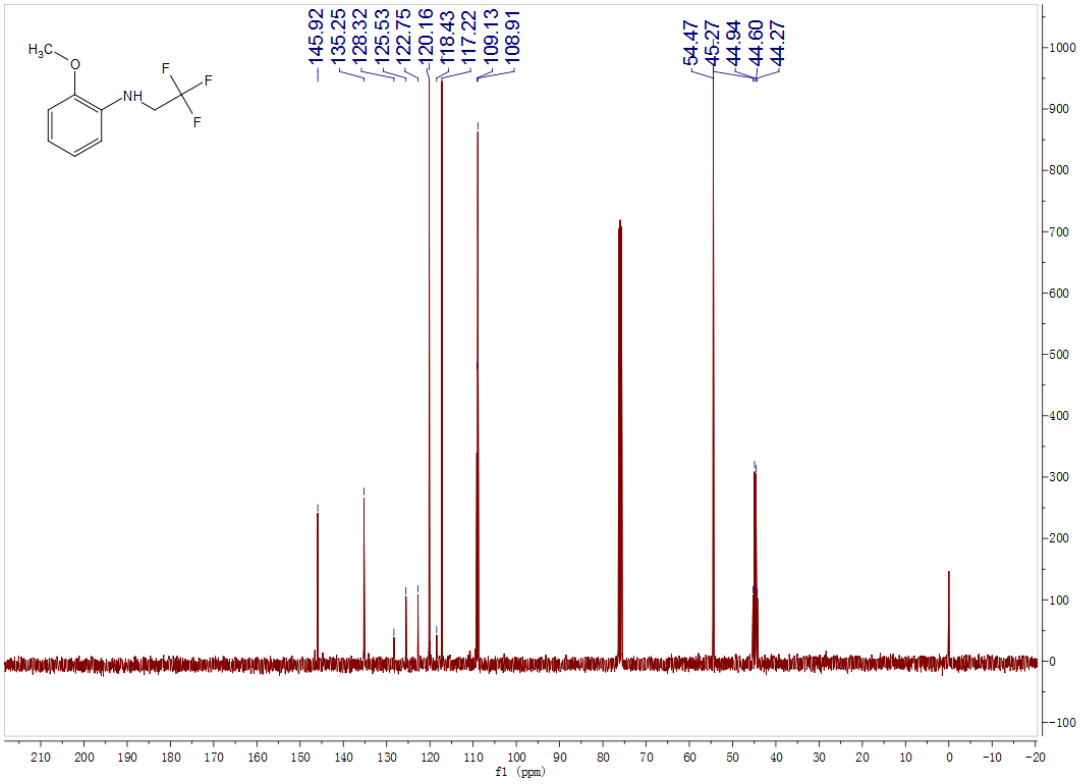






2-Methoxy-N-(2,2,2-trifluoroethyl)benzenamine(2d) pale yellow liquid, 42.5 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (t, *J*=7.5 Hz, 1H), 6.69 (dt, *J*=15.1, 7.6 Hz, 2H), 6.60 (d, *J*=7.8 Hz, 1H), 3.76 (s, 3H), 3.67 (q, *J*=9.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=145.9, 135.3, 124.1(q, *J* =278.0 Hz), 120.2, 117.2, 109.1, 108.9, 54.8, 44.7 (q, *J*=34.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.29 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_9H_{10}F_3NO$: 205.0714; found: 205.0711

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135.25
128.32
125.53
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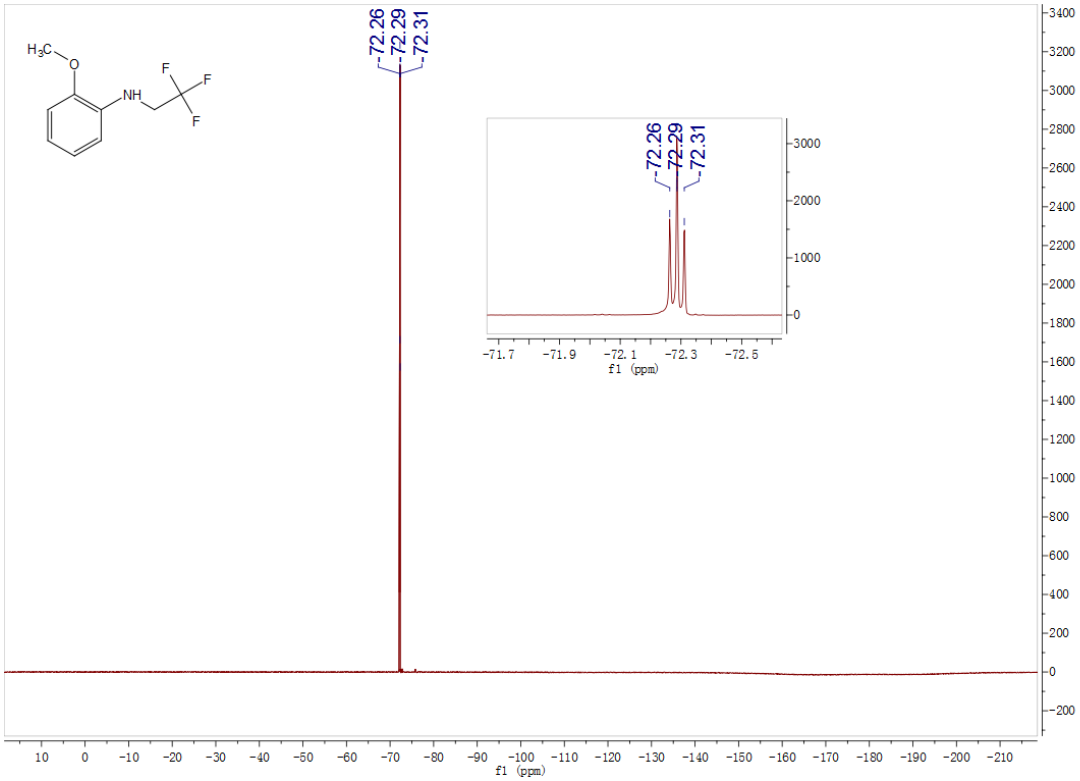
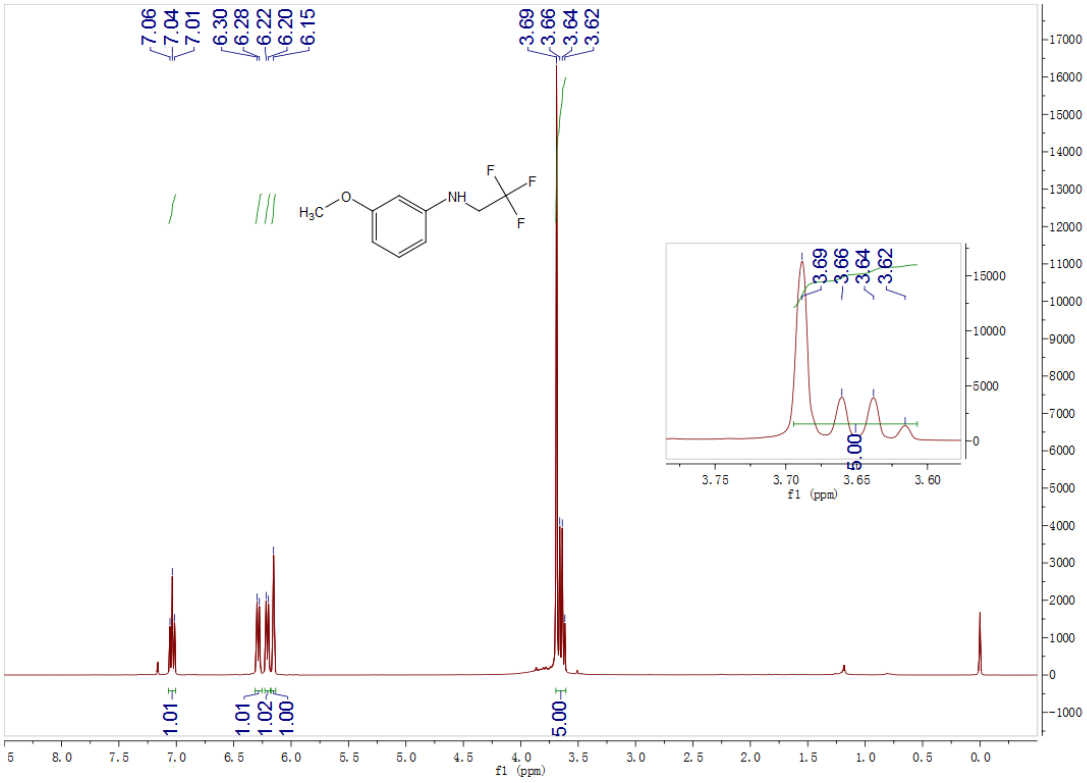
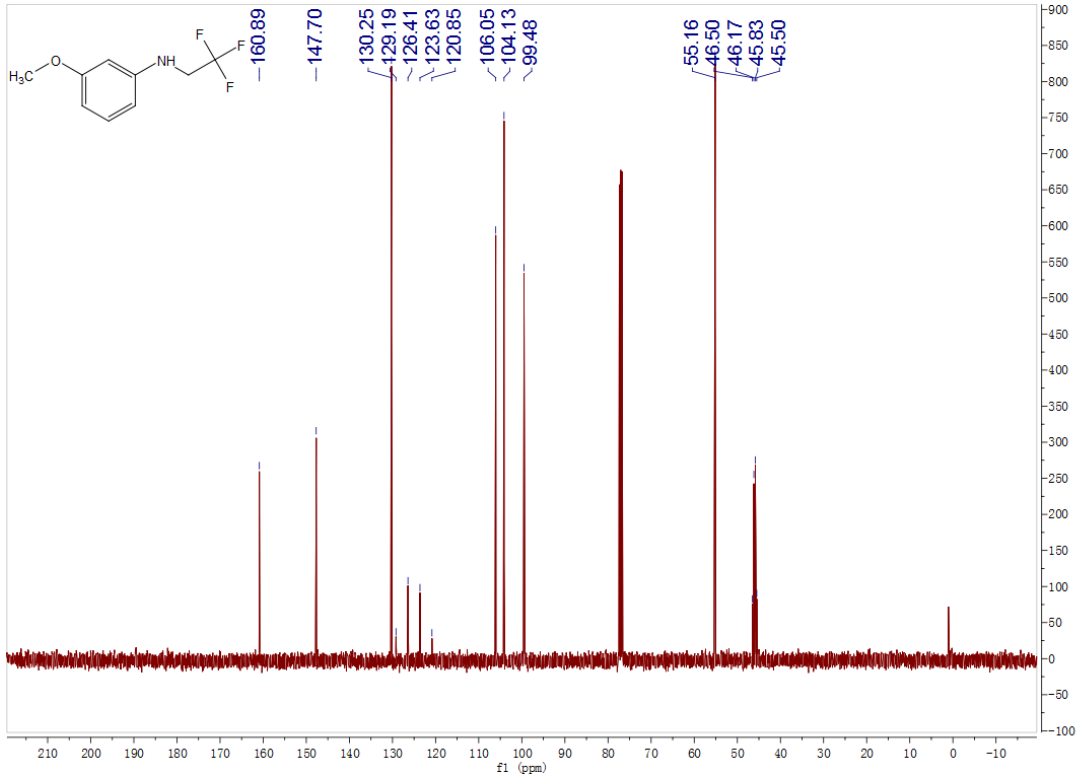
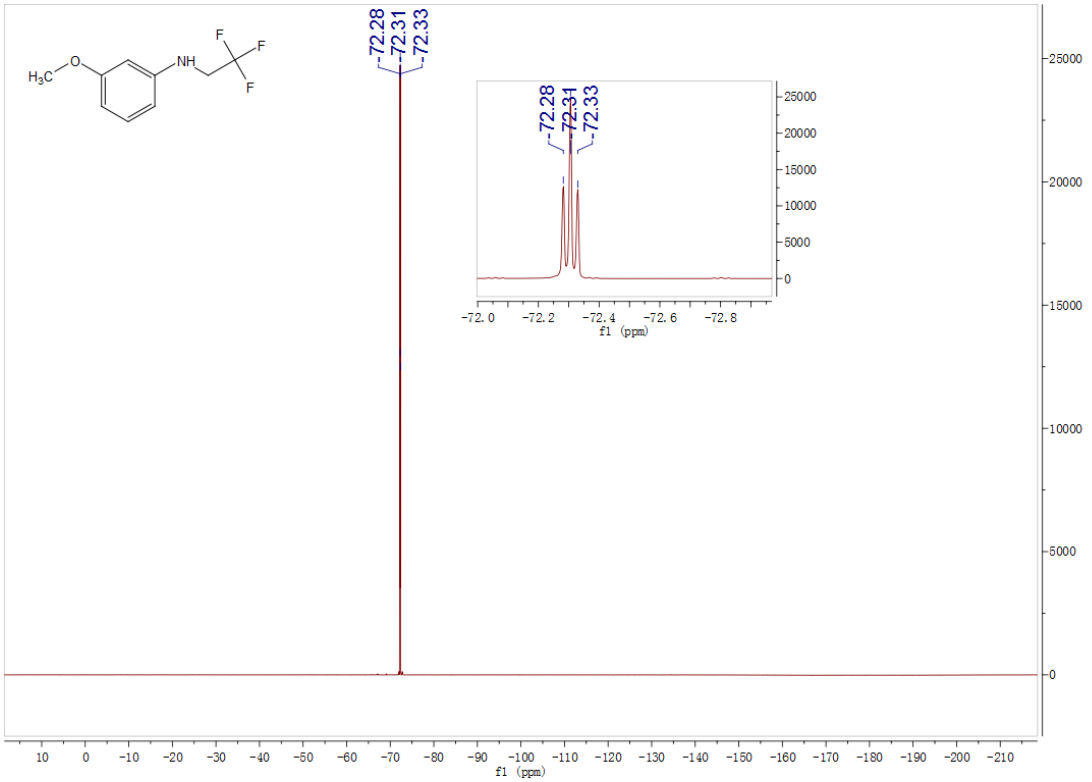
118.43
117.22
109.13
108.91
54.47
45.27
44.94
44.60
44.27
f1 (ppm)


72.26
72.29
72.31
f1 (ppm)

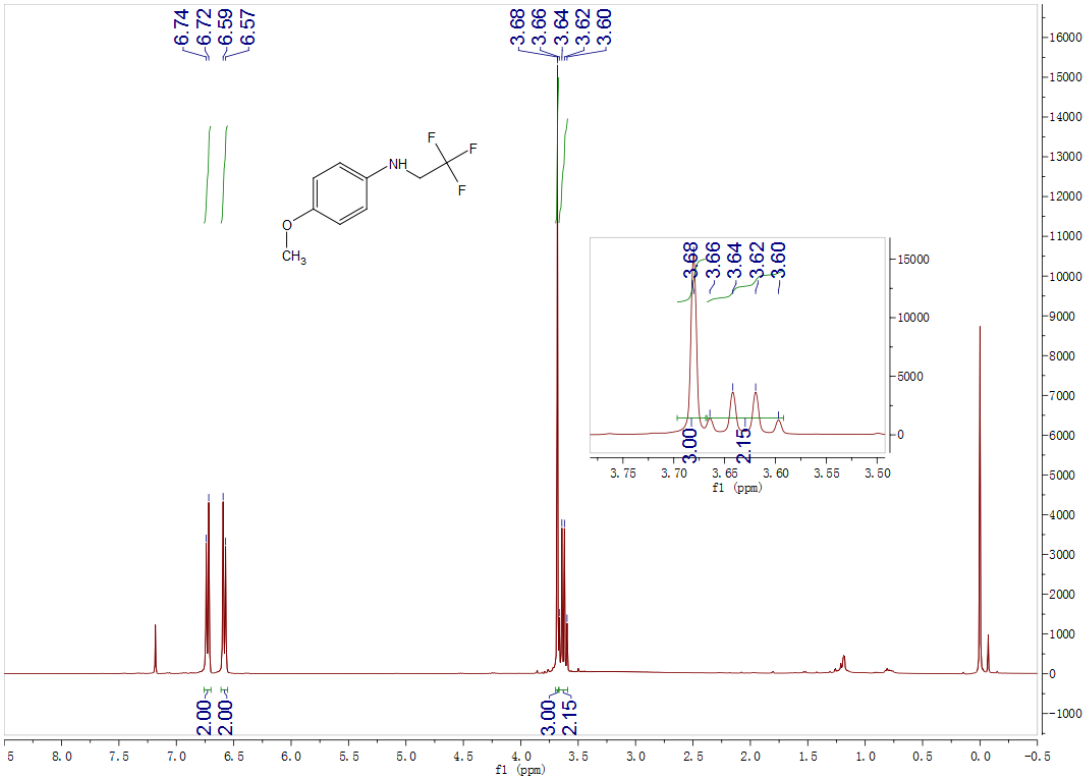
3-Methoxy-N-(2,2,2-trifluoroethyl)benzenamine(2e) pale yellow liquid, 38.2 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J*=8.1 Hz, 1H), 6.29 (d, *J*=8.2 Hz, 1H), 6.21 (d, *J*=8.1 Hz, 1H), 6.15 (s, 1H), 3.69-3.61 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =160.9, 147.7, 130.3, 125.0 (q,*J*=278.0 Hz), 106.1, 104.1, 99.5, 55.2, 46.0 (q,*J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.31 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_9H_{10}F_3NO$: 205.0714; found: 205.0716

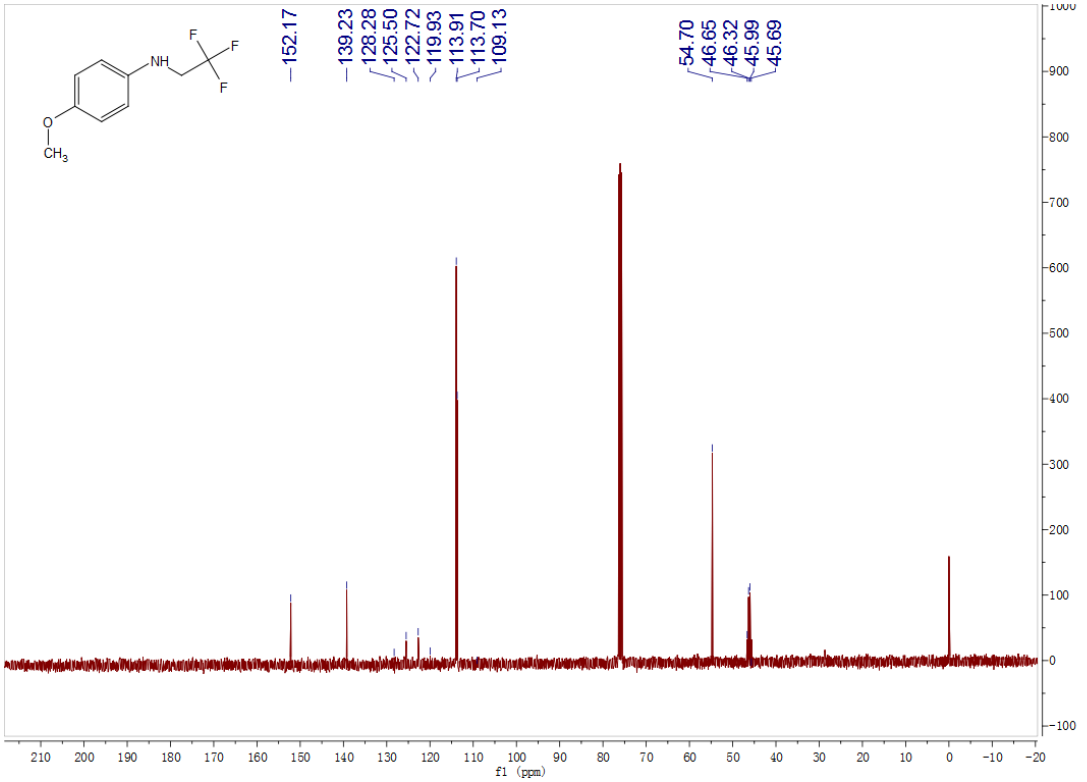






4-Methoxy-N-(2,2,2-trifluoroethyl)benzenamine(2f) pale yellow liquid, 44.9 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J*=8.8 Hz, 2H), 6.58 (d, *J*=8.8 Hz, 2H), 3.68 (s, 3H), 3.63 (q, *J*=9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 139.2, 124.1 (q, *J*=278.0 Hz), 113.9, 113.7, 54.7, 46.2 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.32 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_9H_{10}F_3NO$: 205.0714; found: 205.0718




152.17
139.23
128.28
125.50
122.72
119.93
113.91
113.70
109.13
54.70
46.65
46.32
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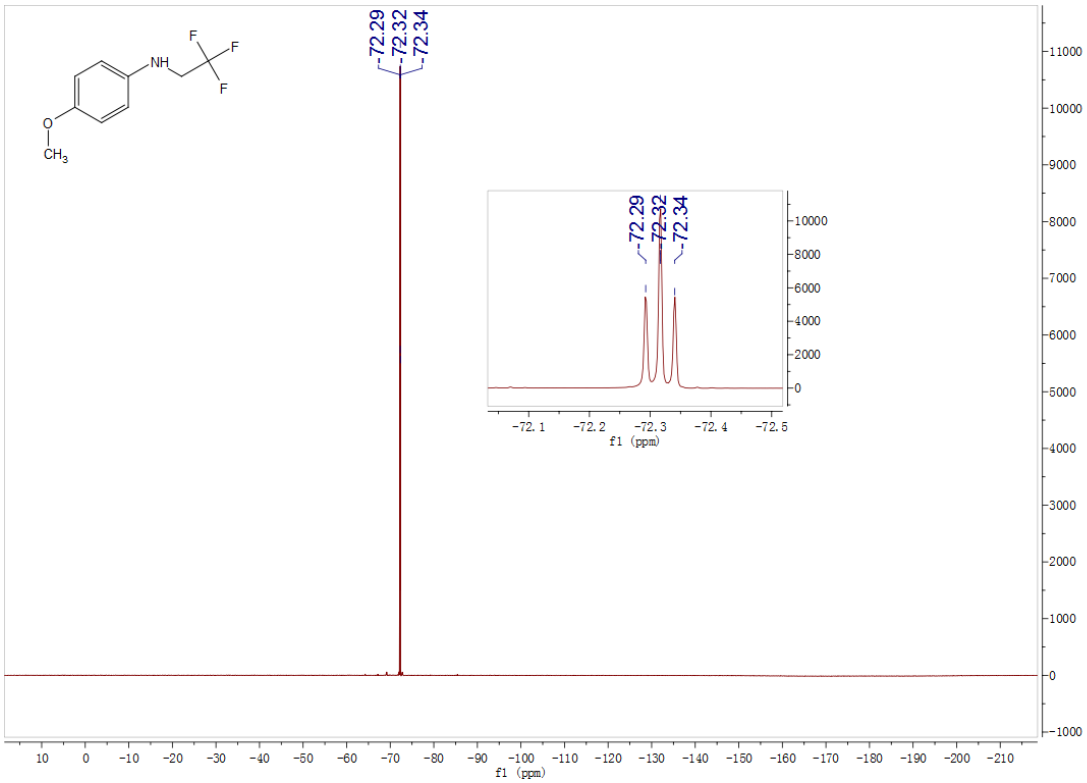
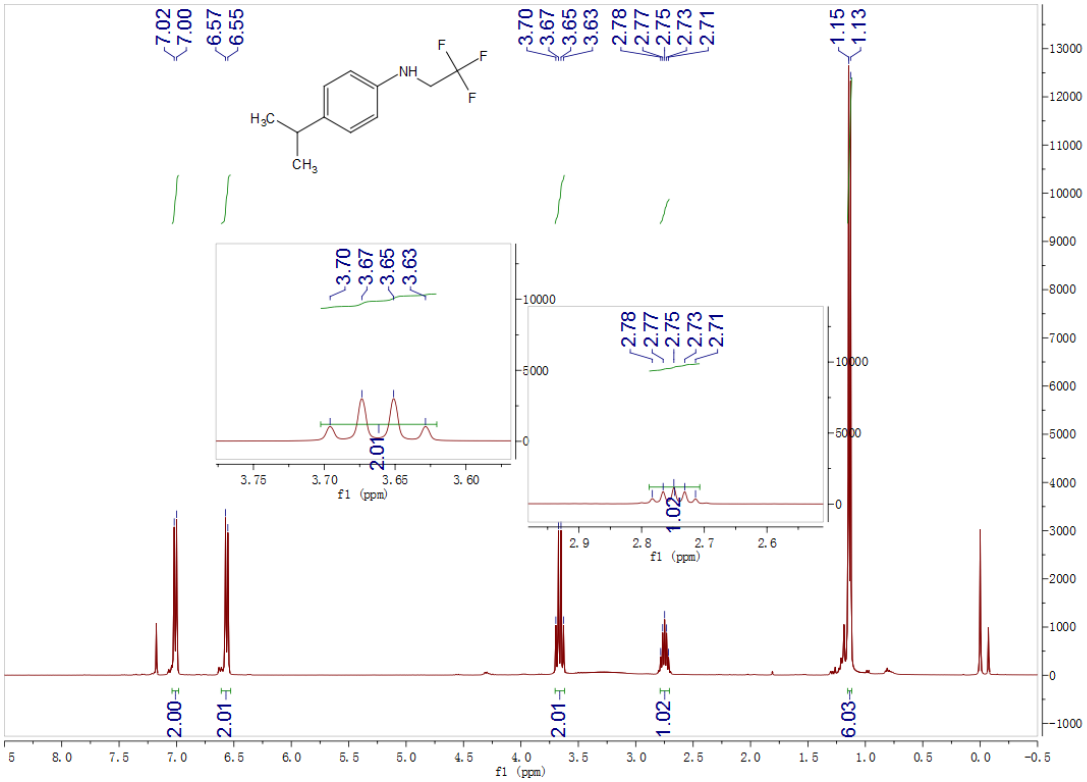
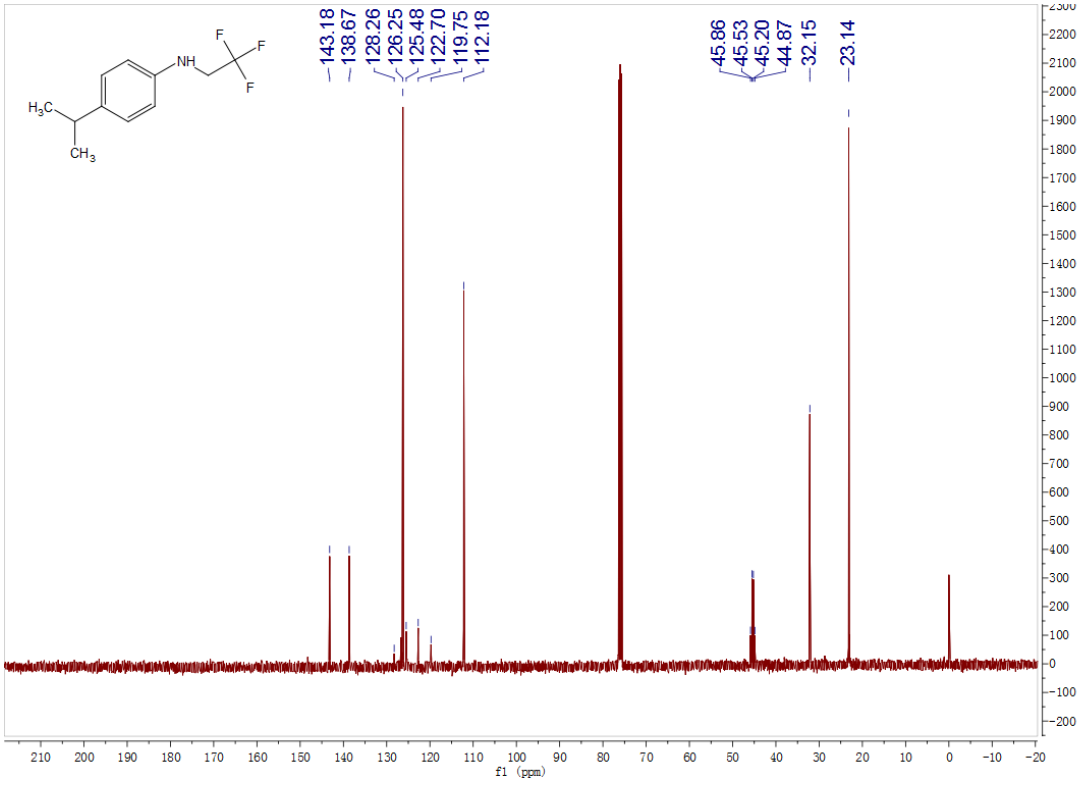
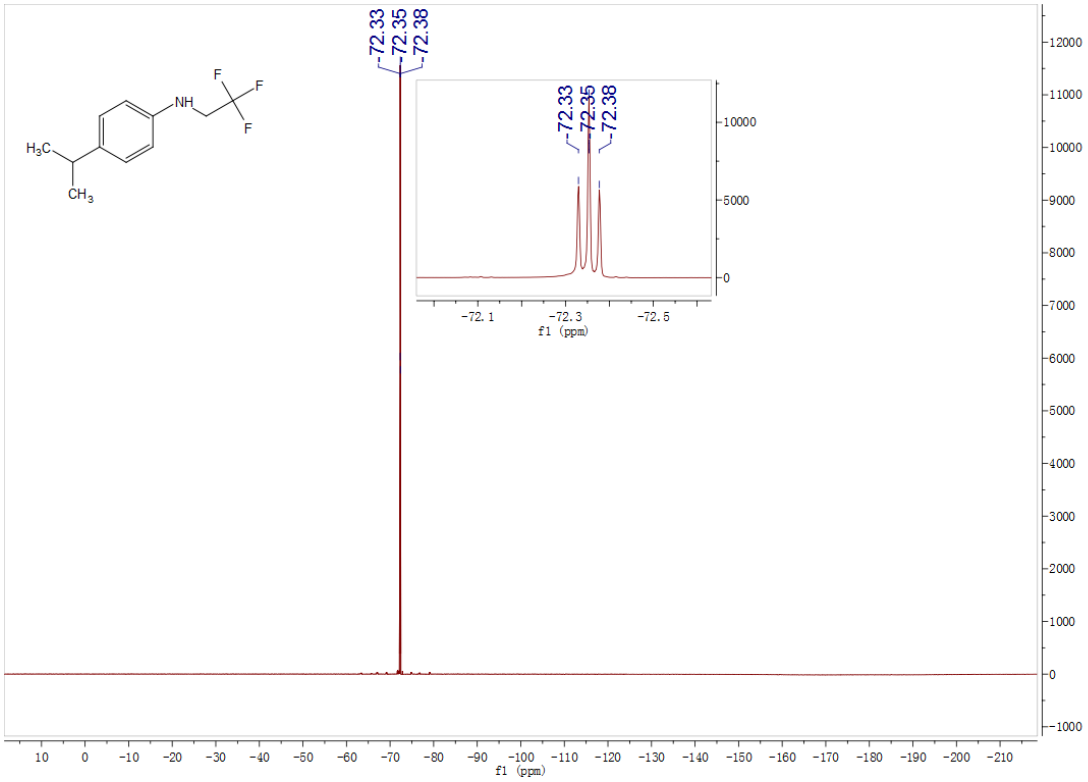
45.69
NH
F
F
F
O
CH3
f1 (ppm)


-72.29
-72.32
-72.34
NH
F
F
F
O
CH3
f1 (ppm)

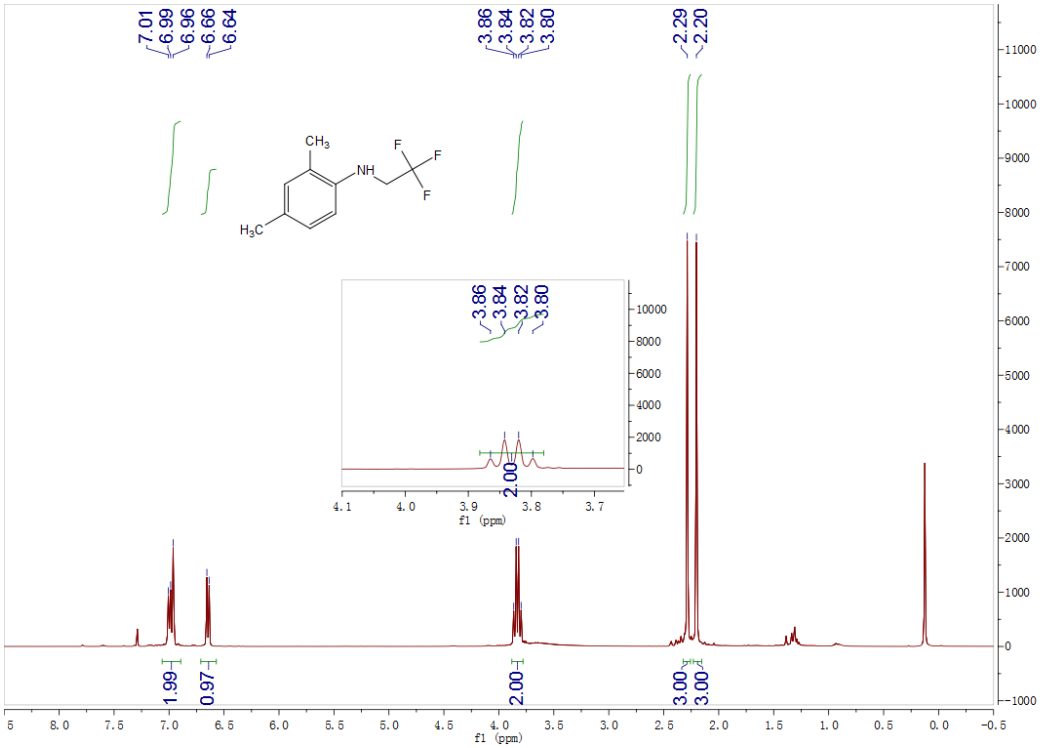
4-(1-Methylethyl)-N-(2,2,2-trifluoroethyl)benzenamine(2g) pale yellow liquid,48.2 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J*=8.4 Hz, 2H), 6.56 (d, *J*=8.3 Hz, 2H), 3.66 (q, *J*=9.0 Hz, 2H), 2.75 (dt, *J*=13.8, 6.9 Hz, 1H), 1.14 (d, *J*=6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.7, 126.3, 124.1 (q, *J*=278.0 Hz) 112.2, 45.4 (q, *J*=33.0 Hz), 32.2, 23.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.35 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_{11}H_{14}F_3N$: 217.1078; found: 217.1085

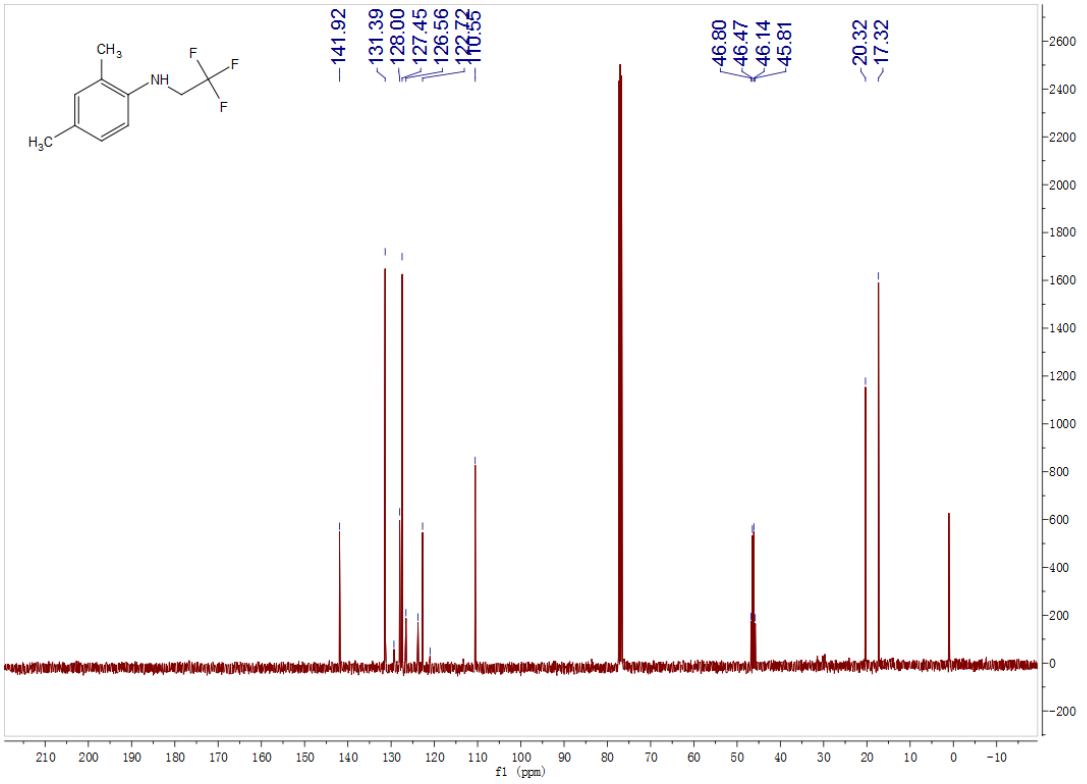






2,4-dimethyl-N-(2,2,2-trifluoroethyl)benzenamine(2h) pale yellow liquid, 53.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.89 (m, 2H), 6.65 (d, *J*=8.1 Hz, 1H), 3.83 (q, *J*=8.9 Hz, 2H), 2.29 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.9, 131.4, 128.0, 127.5, 125.2 (q, *J*=278.0 Hz), 122.7, 110.6, 46.3 (q, *J*=33.0 Hz), 20.3, 17.3 ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.24 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3N$: 203.0922; found: 203.0927

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127.45
126.56
122.72
110.55
46.80
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46.14
45.81
20.32
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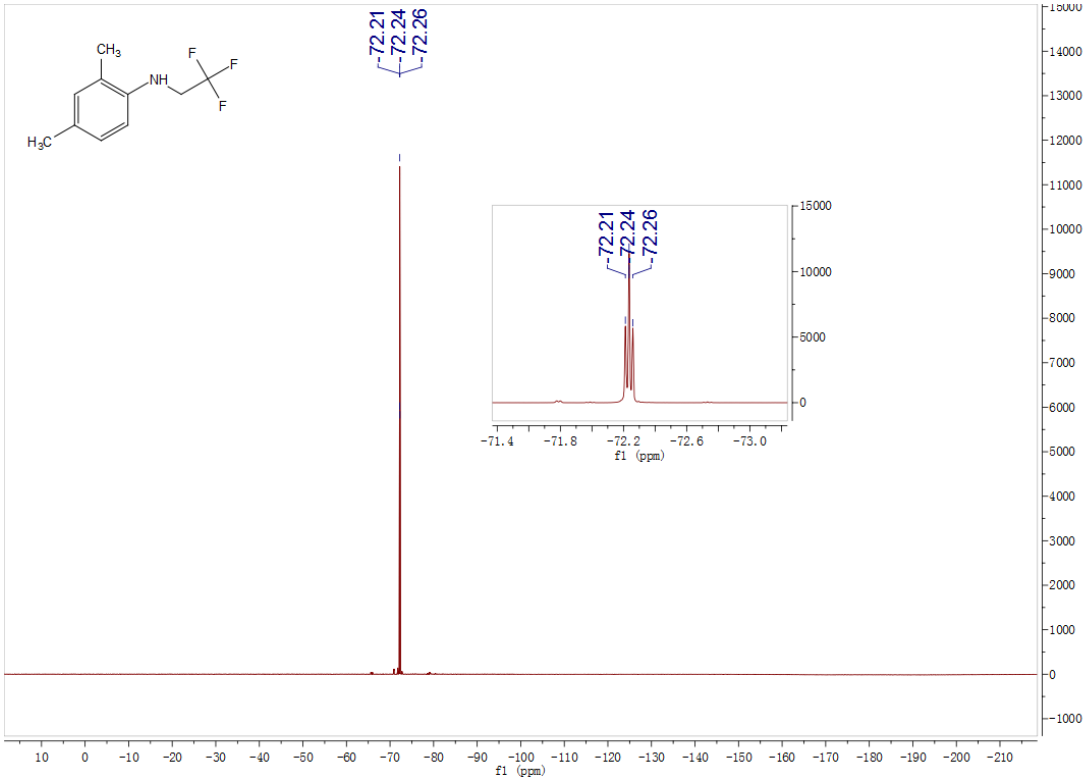
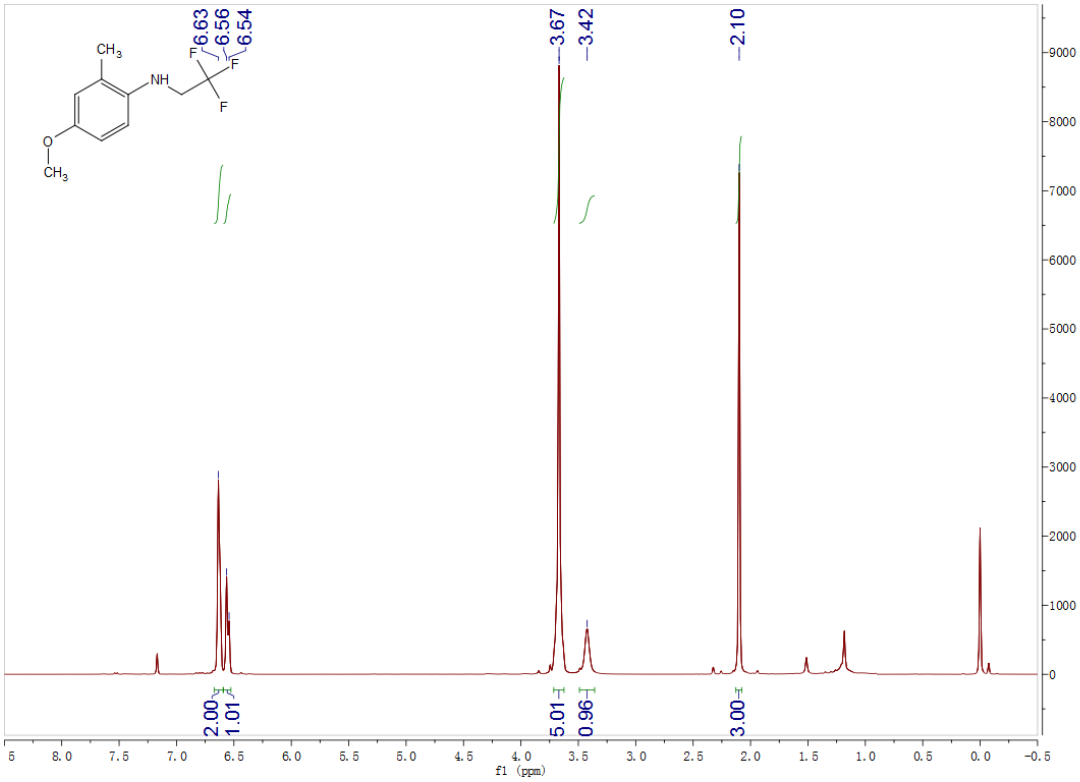
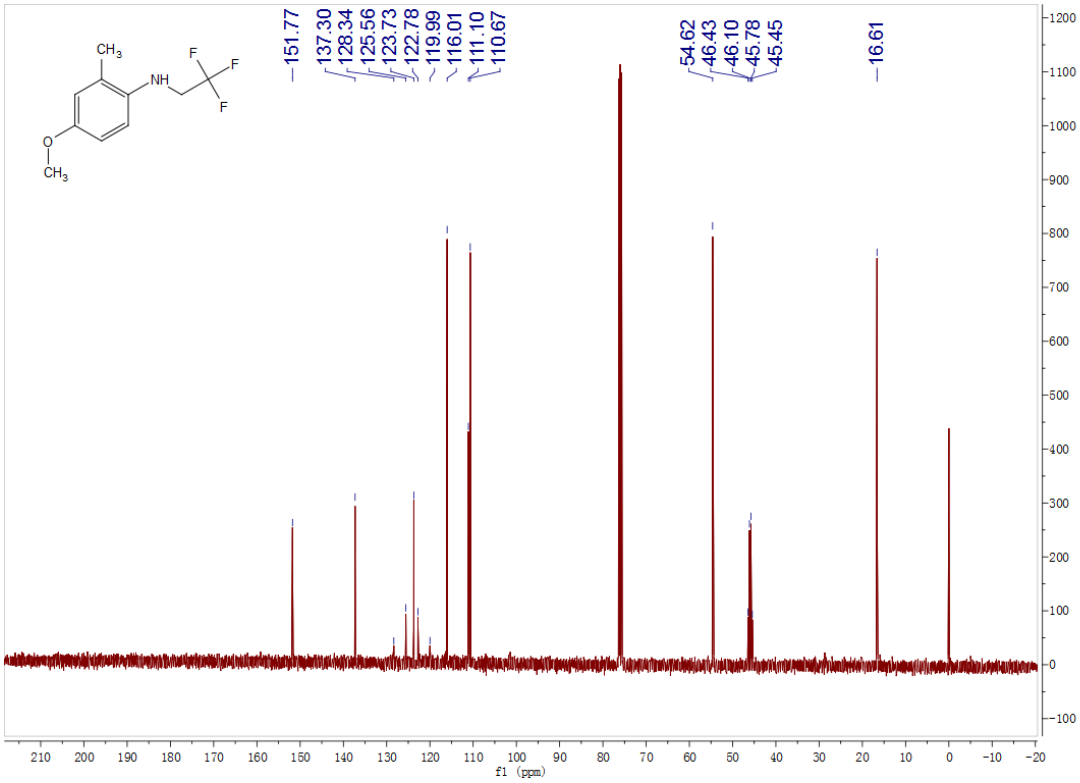
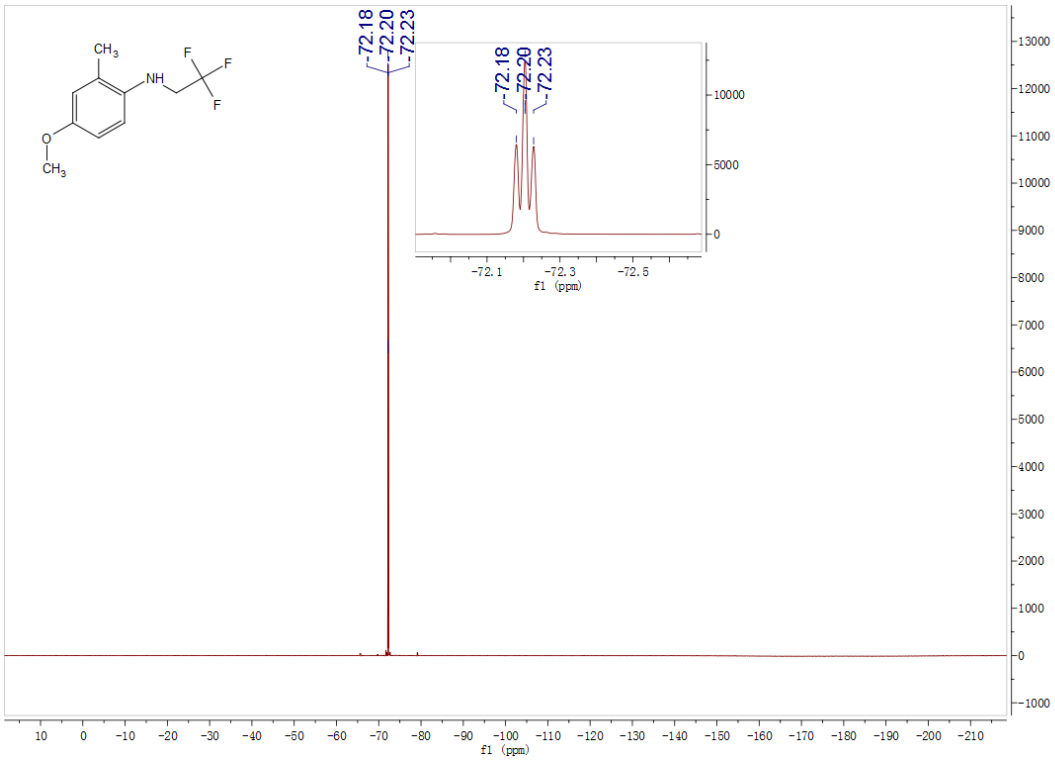
CH3
NH
F
F
F
H3C
f1 (ppm)


72.21
72.24
72.26
CH3
NH
F
F
F
H3C
f1 (ppm)

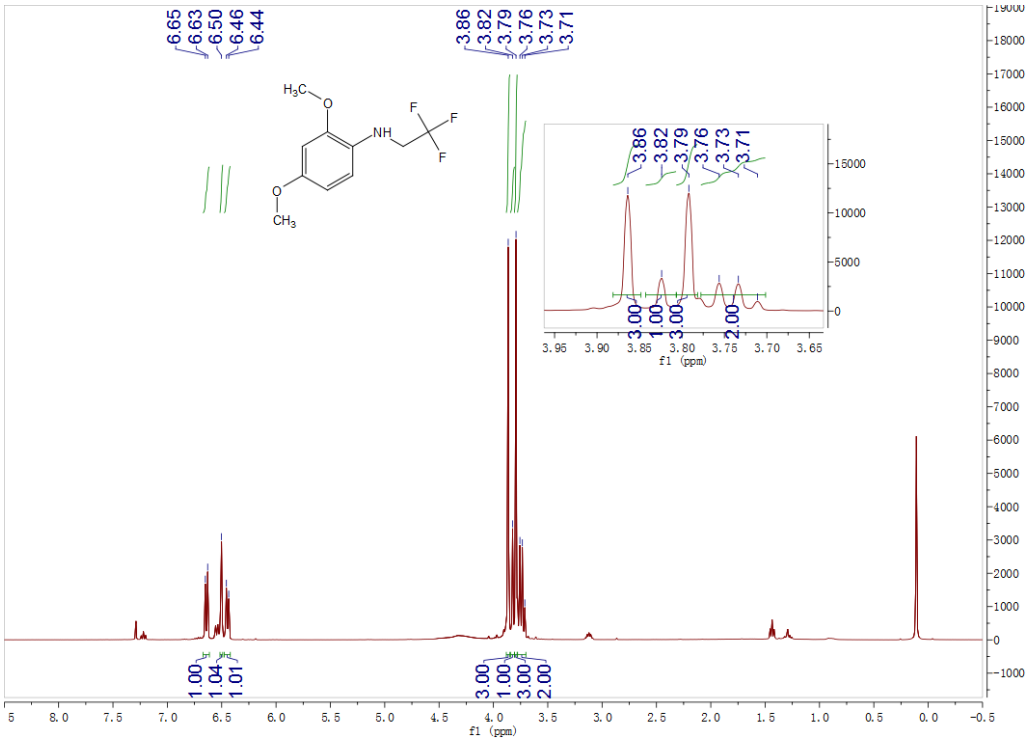
4-methoxy-2-methyl-N-(2,2,2-trifluoroethyl)benzenamine(2i), pale yellow liquid, 61.2 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*=8.5 Hz, 2H), 6.40 (d, *J*=8.5 Hz, 2H), 3.91 (s, 1H), 3.66 (q, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=151.8, 137.3, 124.2 (q, *J*=278.0 Hz), 123.7, 116.0, 111.1, 110.7, 54.6, 45.9 (q, *J*=32.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.20 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3NO$: 219.0871; found: 219.0877

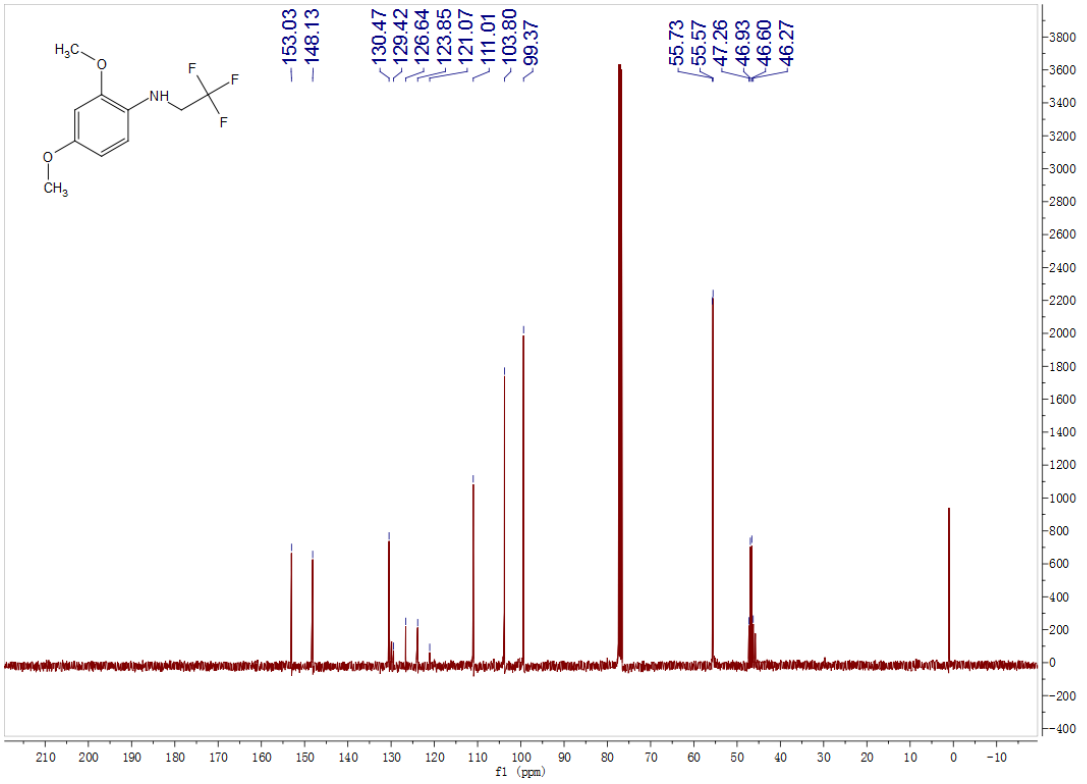






2,4-dimethoxy-N-(2,2,2-trifluoroethyl)benzenamine(2j) ,pale yellow liquid,57.9mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J*=8.5 Hz, 1H), 6.50 (s, 1H), 6.45 (d, *J*=8.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 1H), 3.79 (s, 3H), 3.78-3.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=153.0, 148.1, 130.5, 125.3 (q, *J*=278.0 Hz), 111.0, 103.8, 99.4, 55.7, 55.6, 46.7 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.28 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3NO_2$: 235.0820; found: 219.0814

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129.42
126.64
123.85
121.07
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103.80
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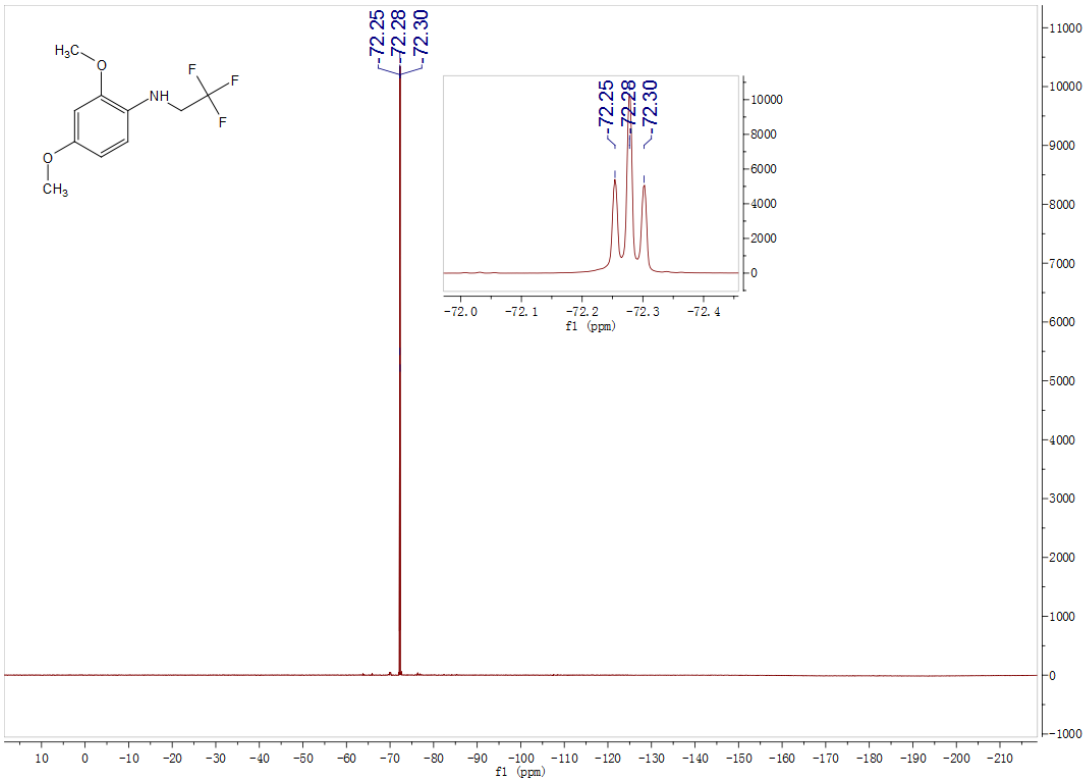
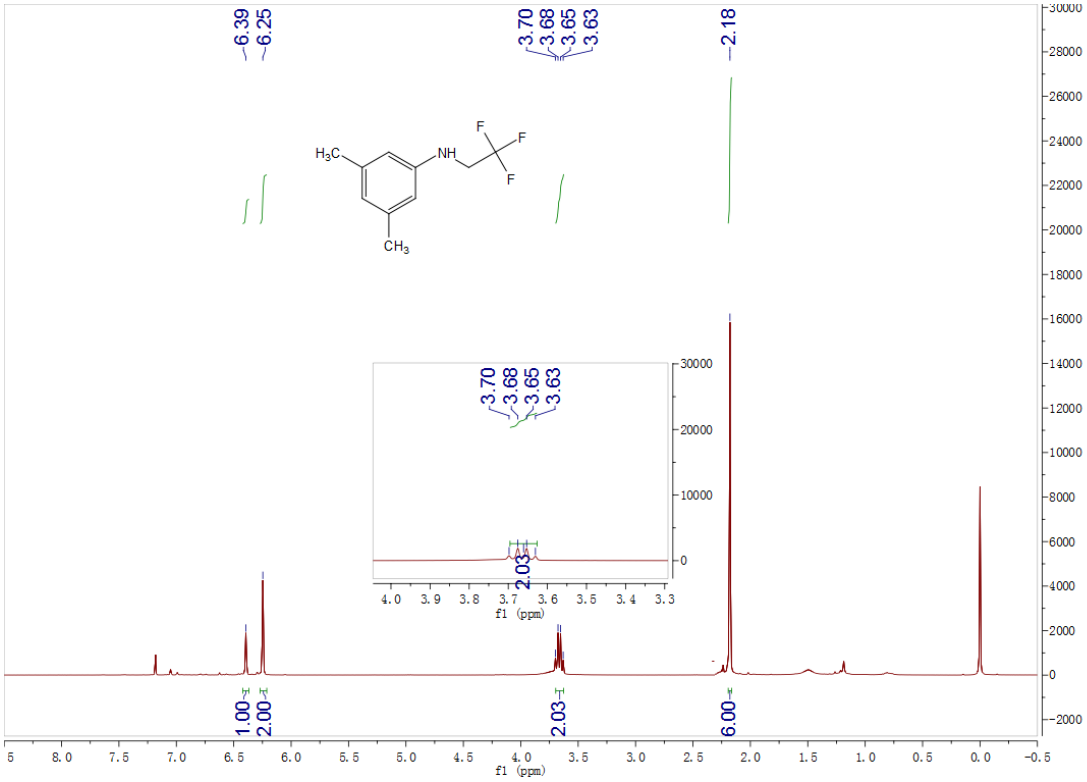
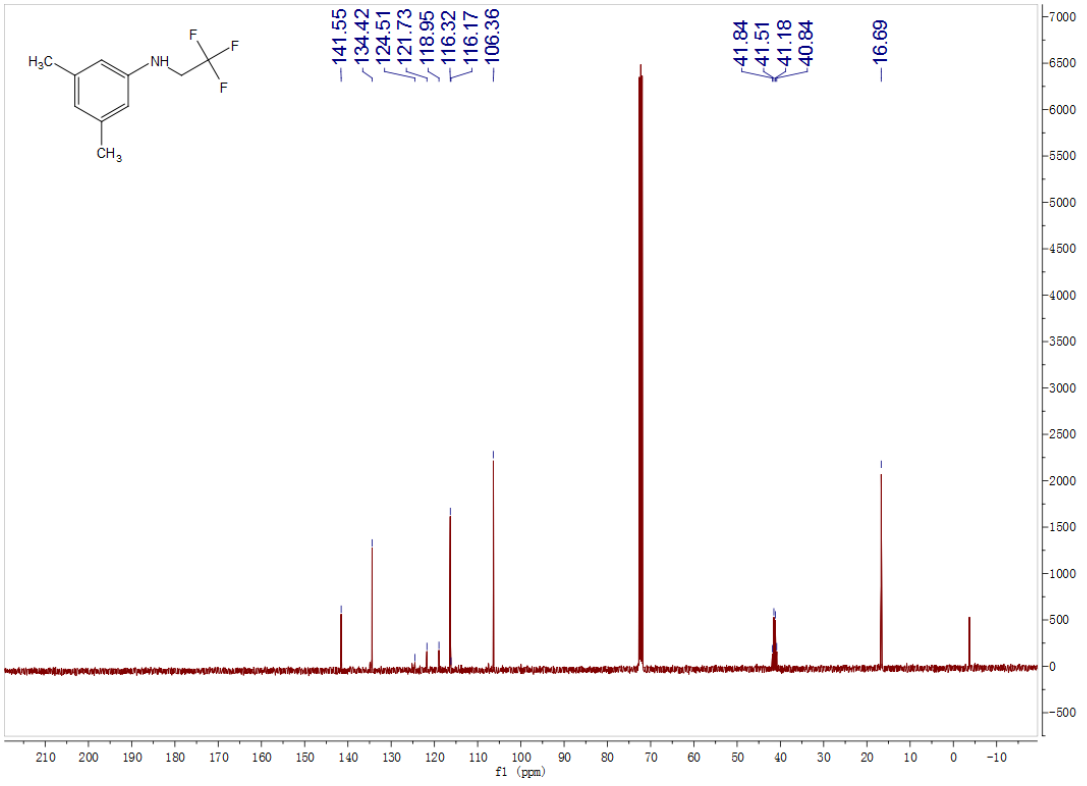
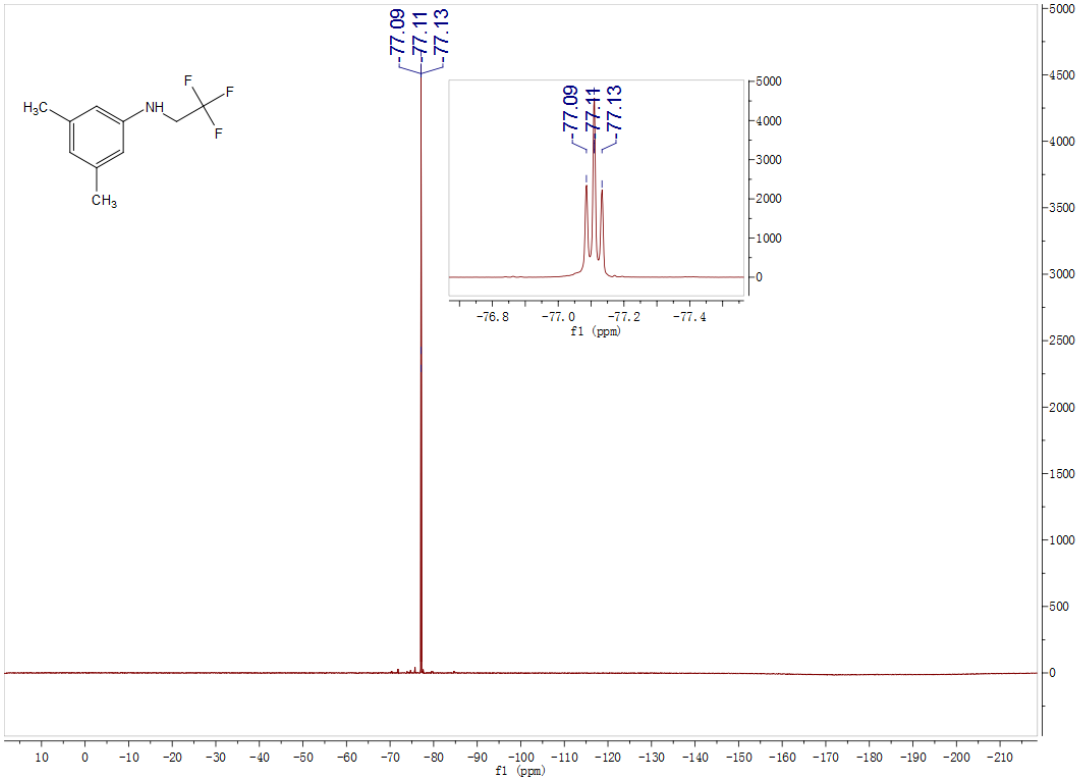
55.57
47.26
46.93
46.60
46.27
f1 (ppm)


72.25
72.28
72.30
f1 (ppm)

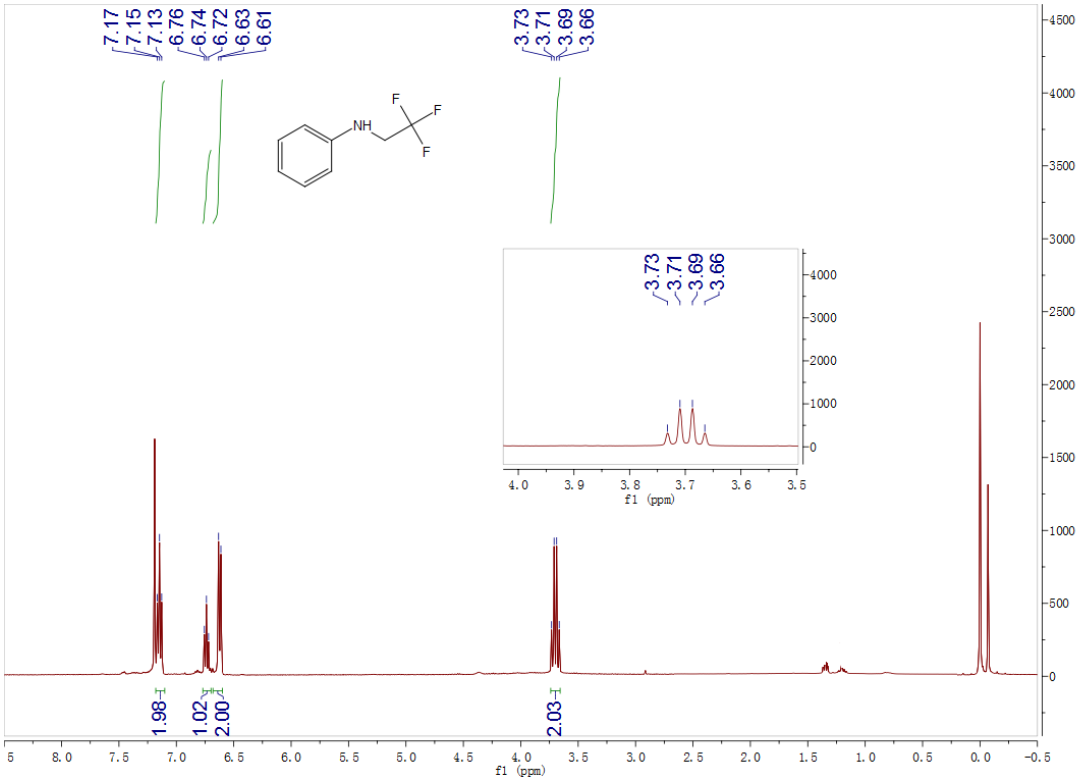
3, 5-Dimethyl-N-(2, 2, 2-trifluoroethyl)benzenamine(2k), pale yellow liquid, 51.8 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 -6.89 (m, 2H), 6.65 (d, *J*=8.1 Hz, 1H), 3.83 (q, *J*=8.9 Hz, 2H), 2.29 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.9, 131.4, 128.0, 127.5, 125.2 (q, *J*=278.0 Hz), 122.7, 110.6, 46.3 (q, *J*=33.0 Hz), 20.3, 17.3 ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.24 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3N$: 203.0922; found: 203.0926

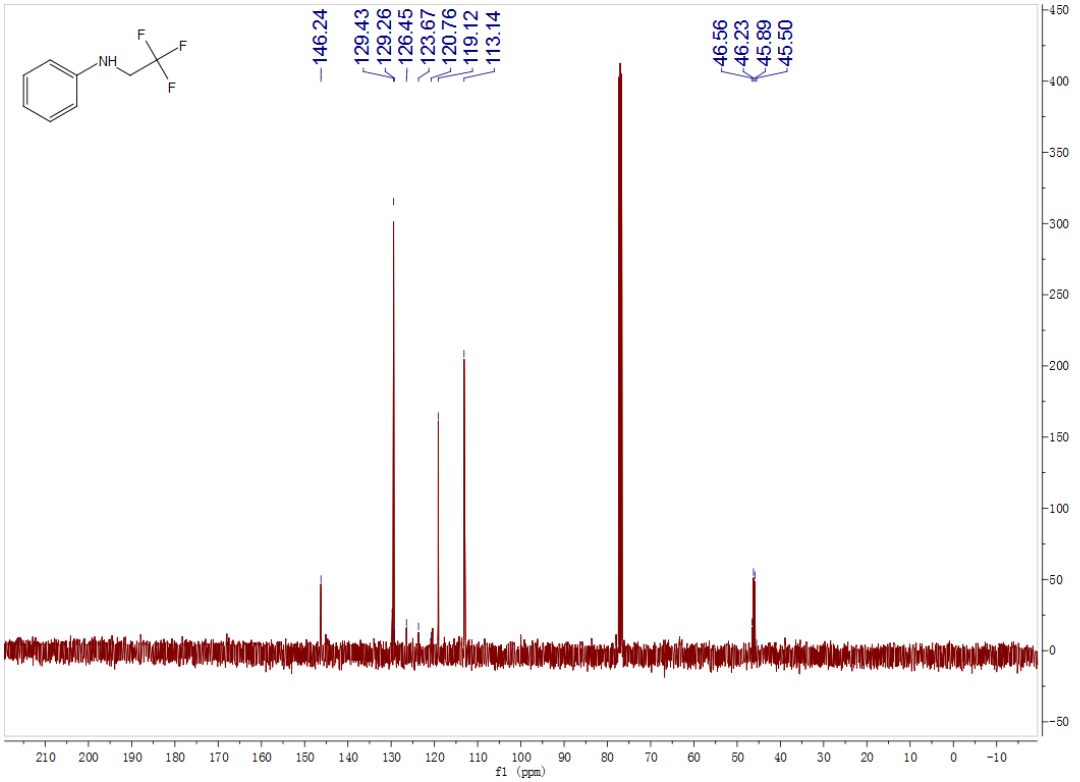


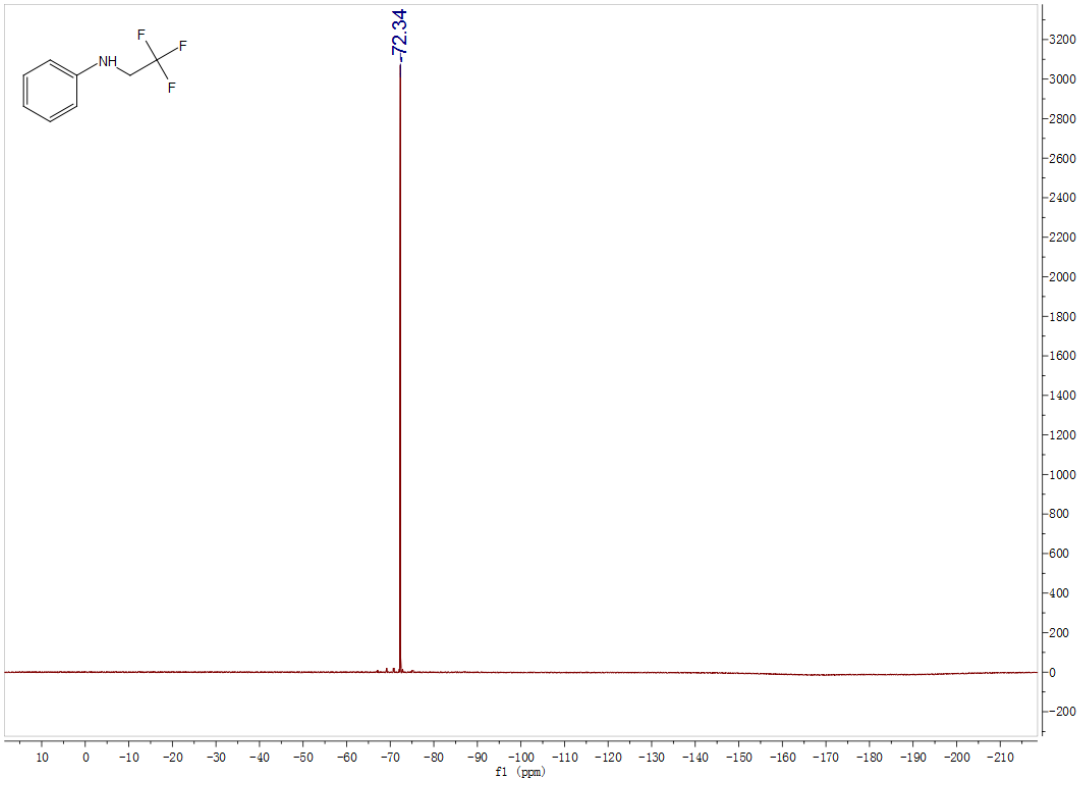




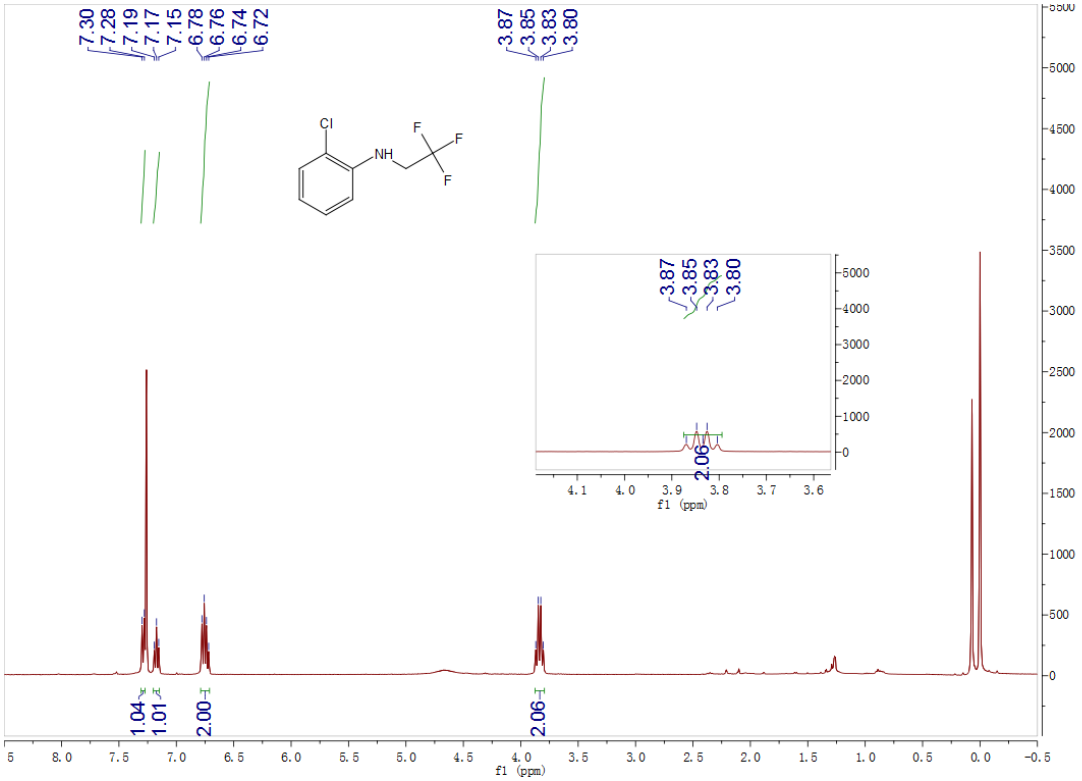
N-(2, 2, 2-Trifluoroethyl)benzenamine(2l) pale yellow liquid, 34.2 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J*=7.6 Hz, 2H), 6.74 (t, *J*=7.3 Hz, 1H), 6.62 (d, *J*=8.0 Hz, 2H), 3.70 (q, *J*=8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 129.4, 125.1 (q, *J*=280.0 Hz), 119.1, 113.1, 46.1 (q, *J*=34.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.33 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_8H_8F_3N$: 175.0609; found: 175.0612

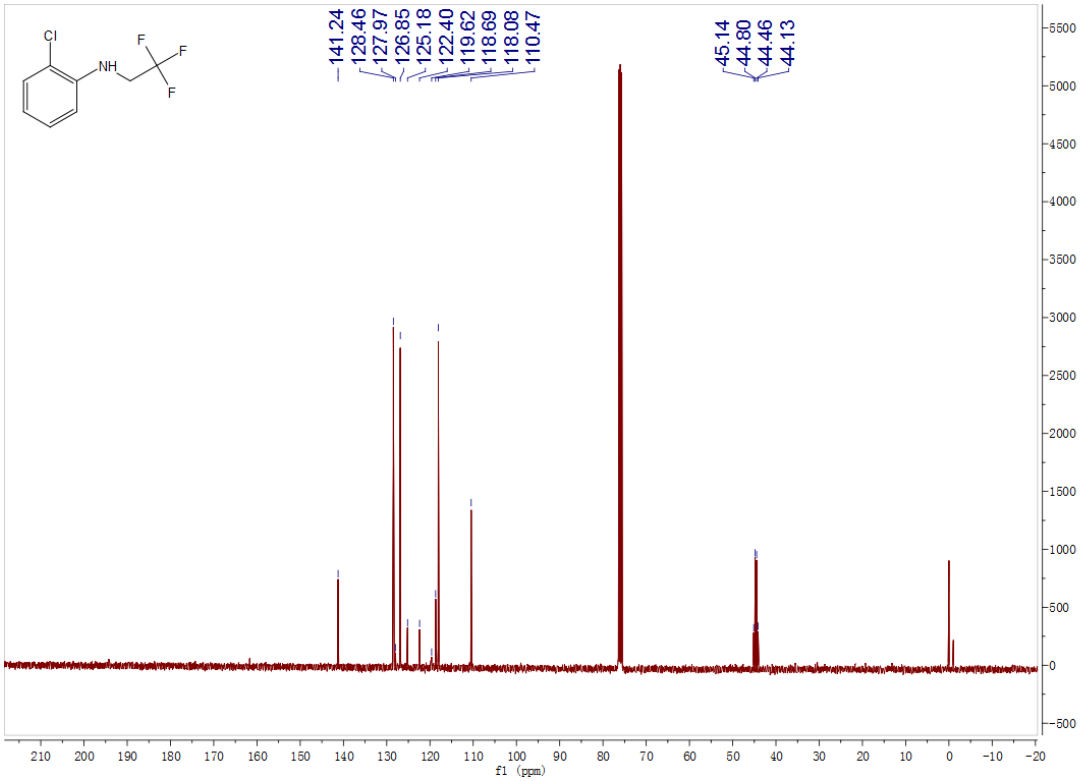


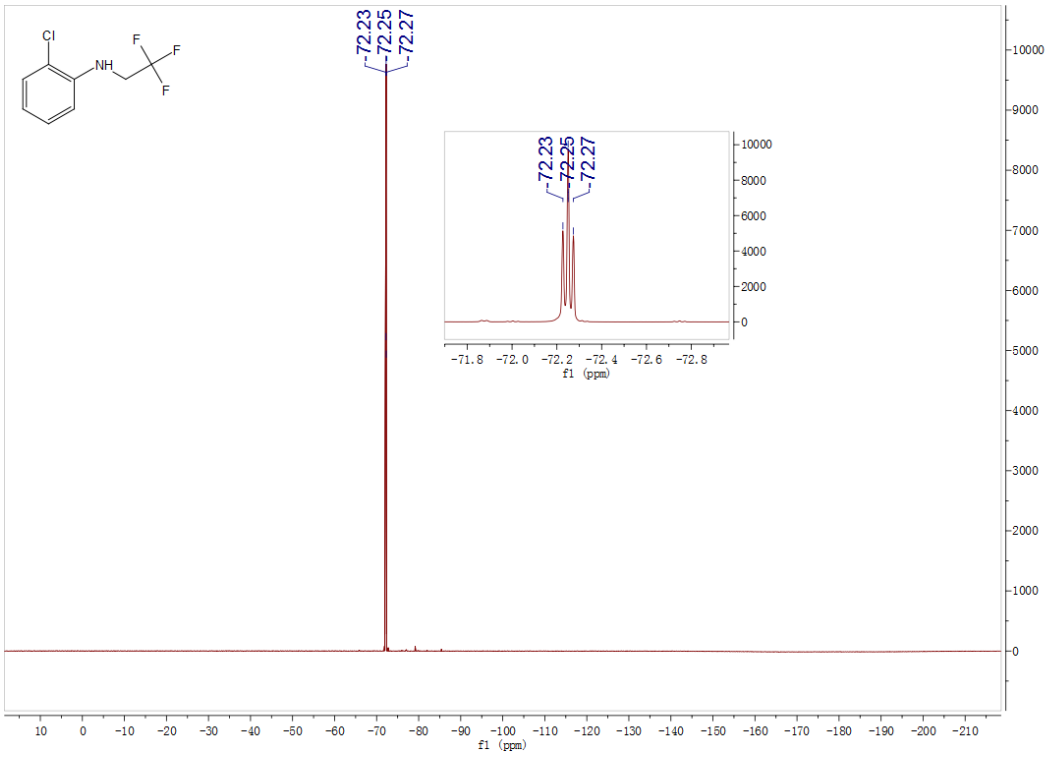

146.24
129.43
129.26
126.45
123.67
120.76
119.12
113.14
46.56
46.23
45.89
45.50
NH
F
F
F
f1 (ppm)


-72.34
NH
F
F
F
f1 (ppm)

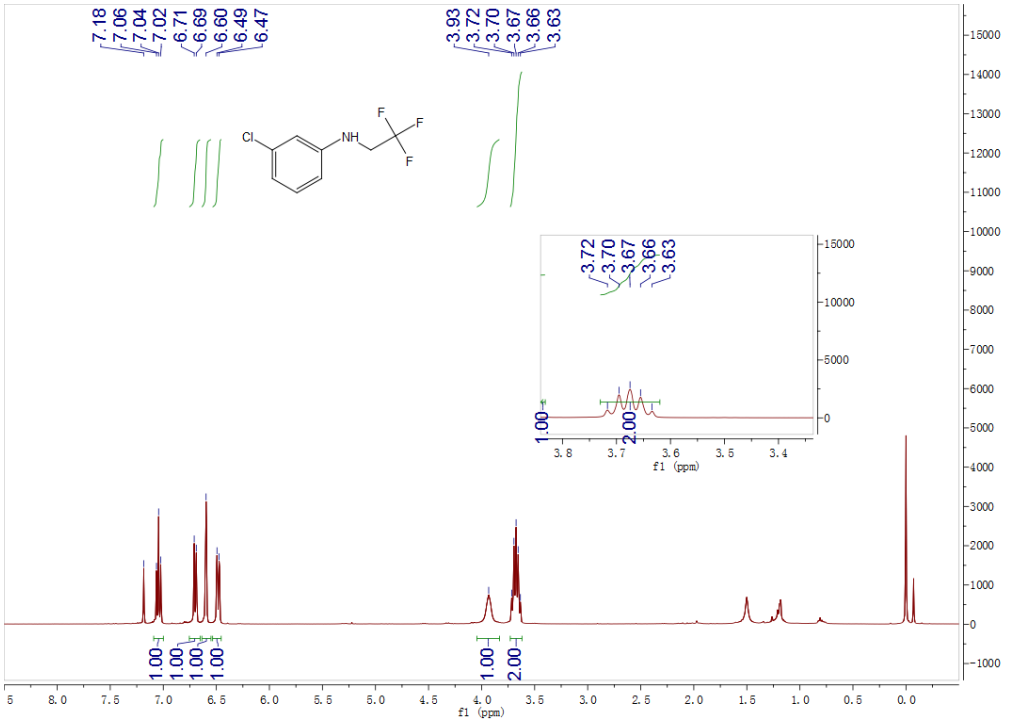
2-chloro-N-(2, 2, 2-trifluoroethyl)benzenamine(2m), pale yellow liquid, 28.3 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J*=7.9 Hz, 1H), 7.17 (t, *J*=7.7 Hz, 1H), 6.75 (dd, *J*=15.6, 7.9 Hz, 2H), 3.84 (q, *J*=8.7 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ =141.2, 128.5, 128.0, 123.8 (q, *J*=278.0 Hz), 118.7, 118.1, 110.5, 44.6 (q, *J* =34.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.25 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_8H_7ClF_3N$: 209.0219; found: 209.0215

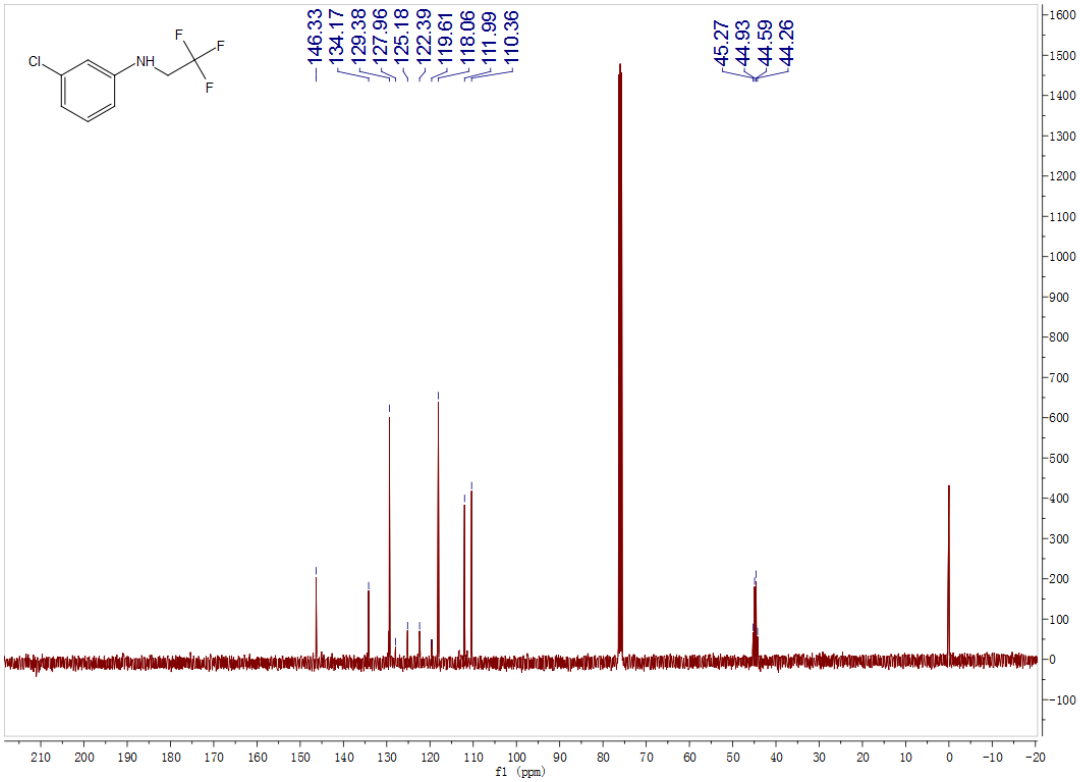


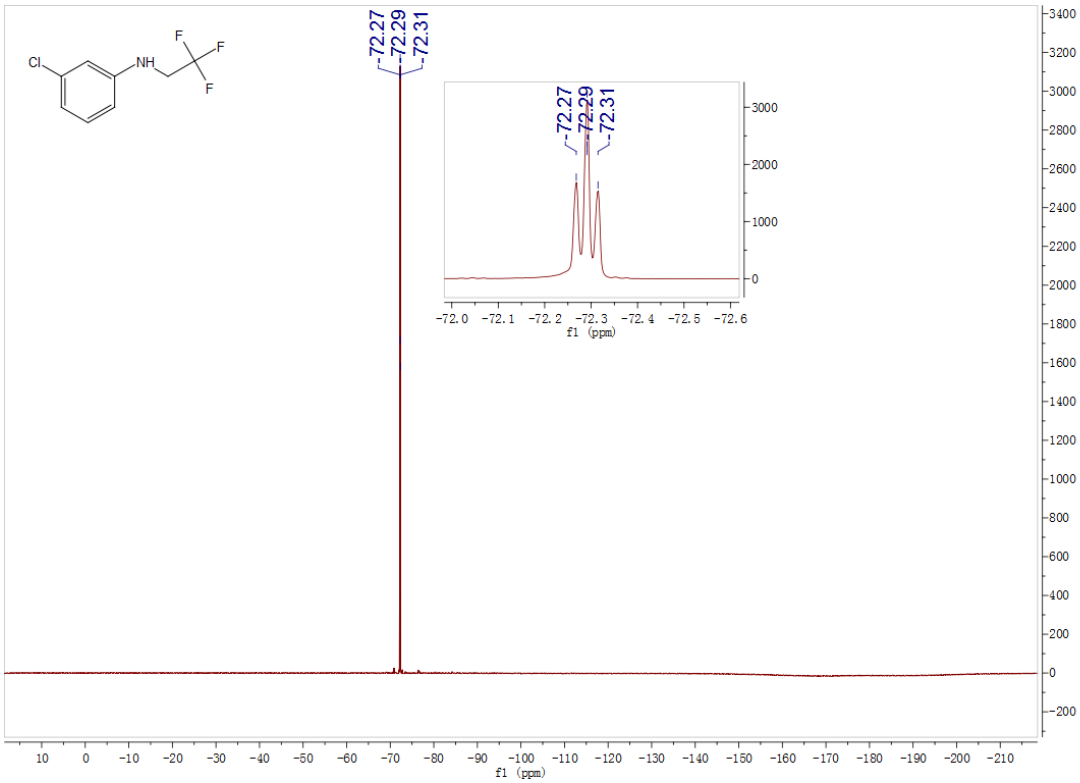




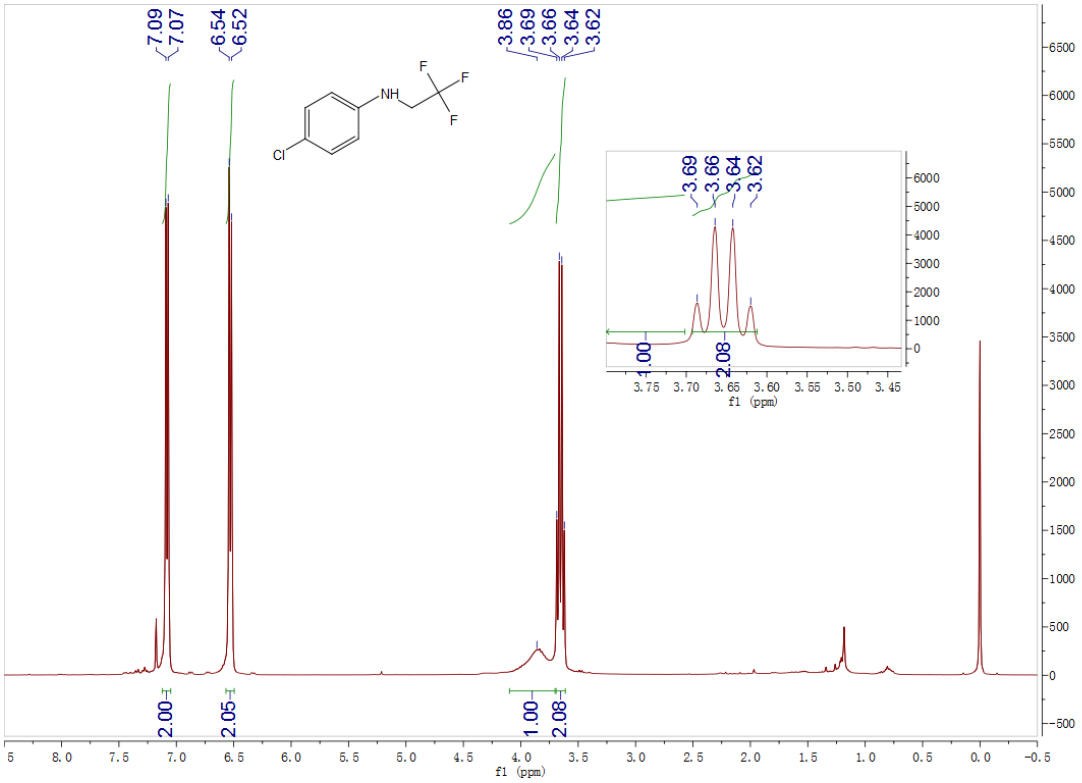
3-chloro-N-(2,2,2-trifluoroethyl)benzenamine(2n), pale yellow liquid, 29.6 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J*=8.0 Hz, 1H), 6.70 (d, *J*=7.9 Hz, 1H), 6.60 (s, 1H), 6.48 (d, *J*=8.2 Hz, 1H), 3.93 (s, 1H), 3.73-3.62 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ=146.3, 134.2, 129.4, 123.8 (q, *J*=279.0 Hz), 118.1, 112.0, 110.4, 44.8 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.29 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_8H_7ClF_3N$: 209.0219; found: 209.0224

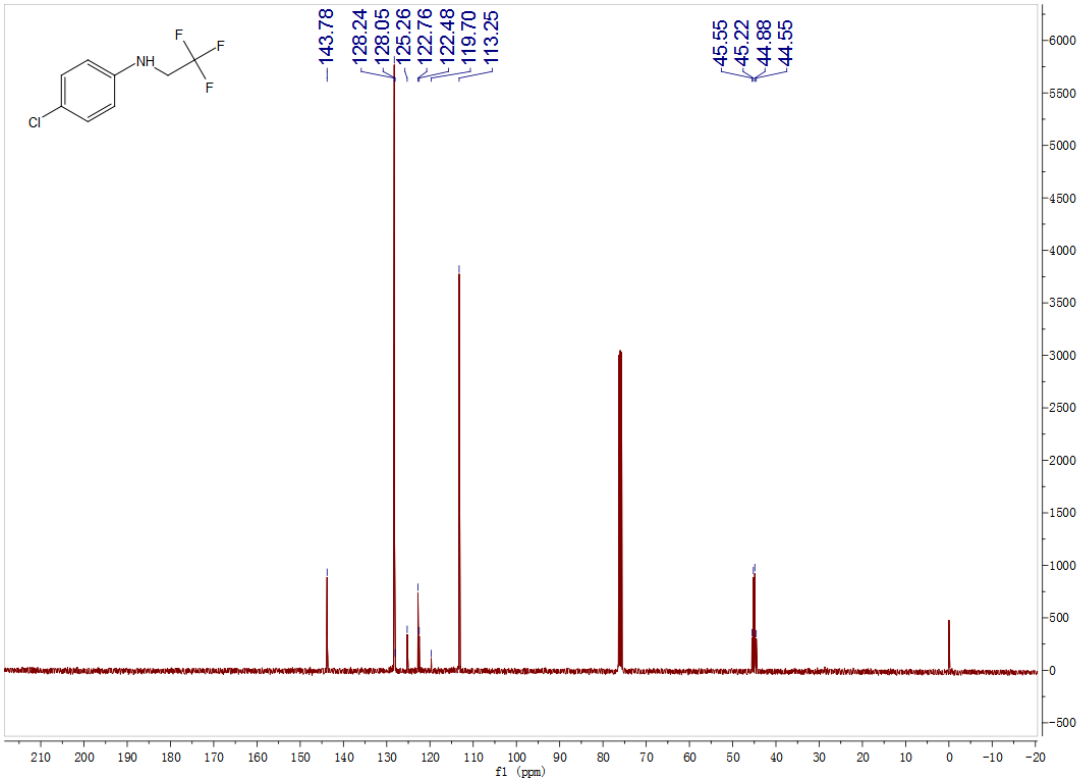


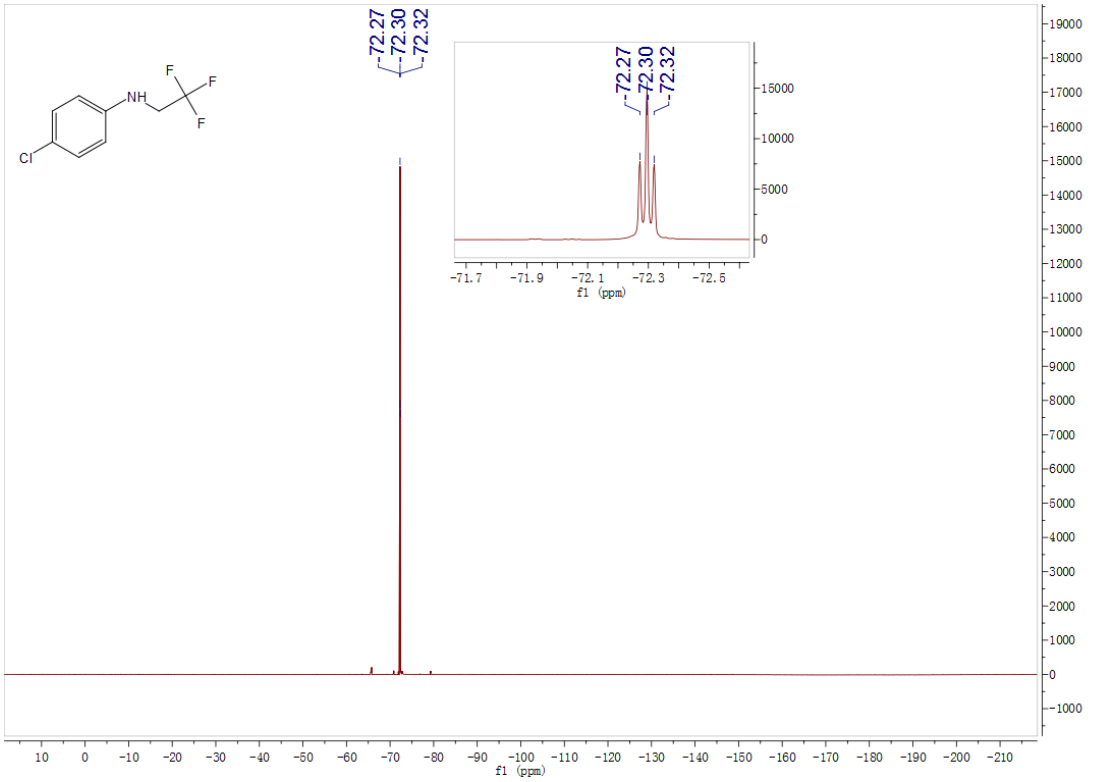

Cl
NH
F
F
F
146.33
134.17
129.38
127.96
125.18
122.39
119.61
118.06
111.99
110.36
45.27
44.93
44.59
44.26
f1 (ppm)


Cl
NH
F
F
F
-72.27
-72.29
-72.31
f1 (ppm)

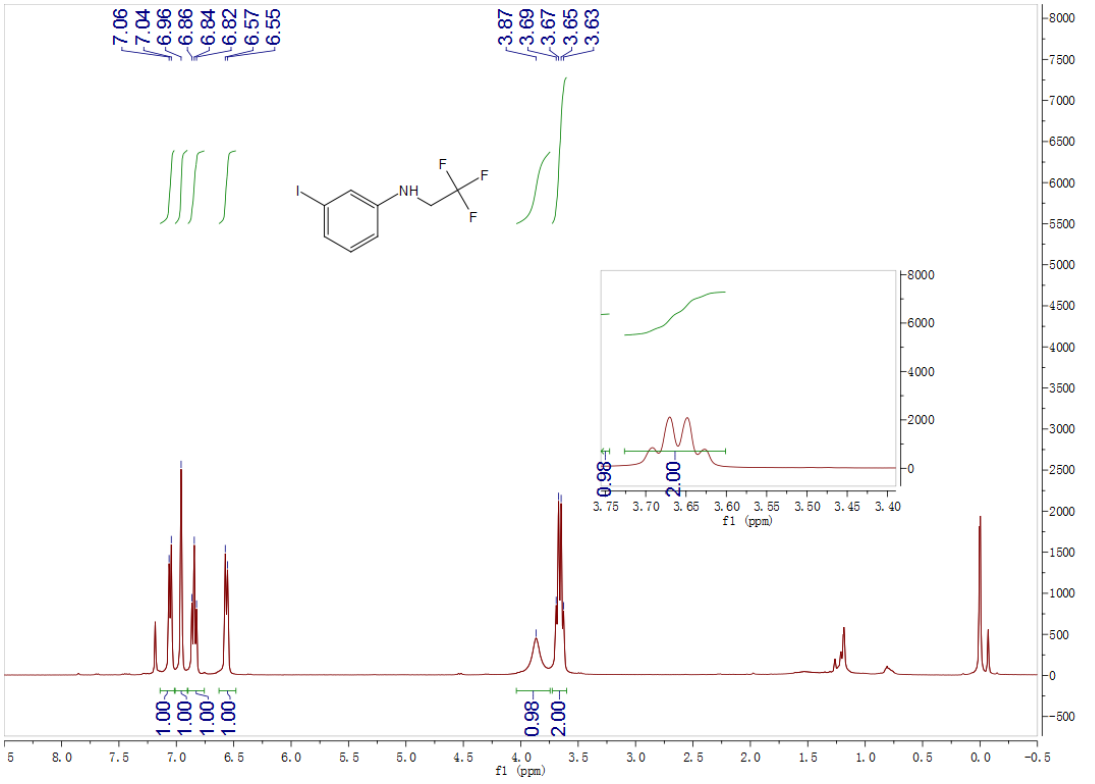
4-chloro-N-(2, 2, 2-trifluoroethyl)benzenamine(2o) pale yellow liquid, 34.0 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J*=8.1 Hz, 2H), 6.53 (d, *J*=8.1 Hz, 2H), 3.65 (q, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 128.2, 122.8, 123.9 (q, *J*=278.0 Hz),113.2, 45.1 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.30 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_8H_7ClF_3N$: 209.0219; found: 209.0223

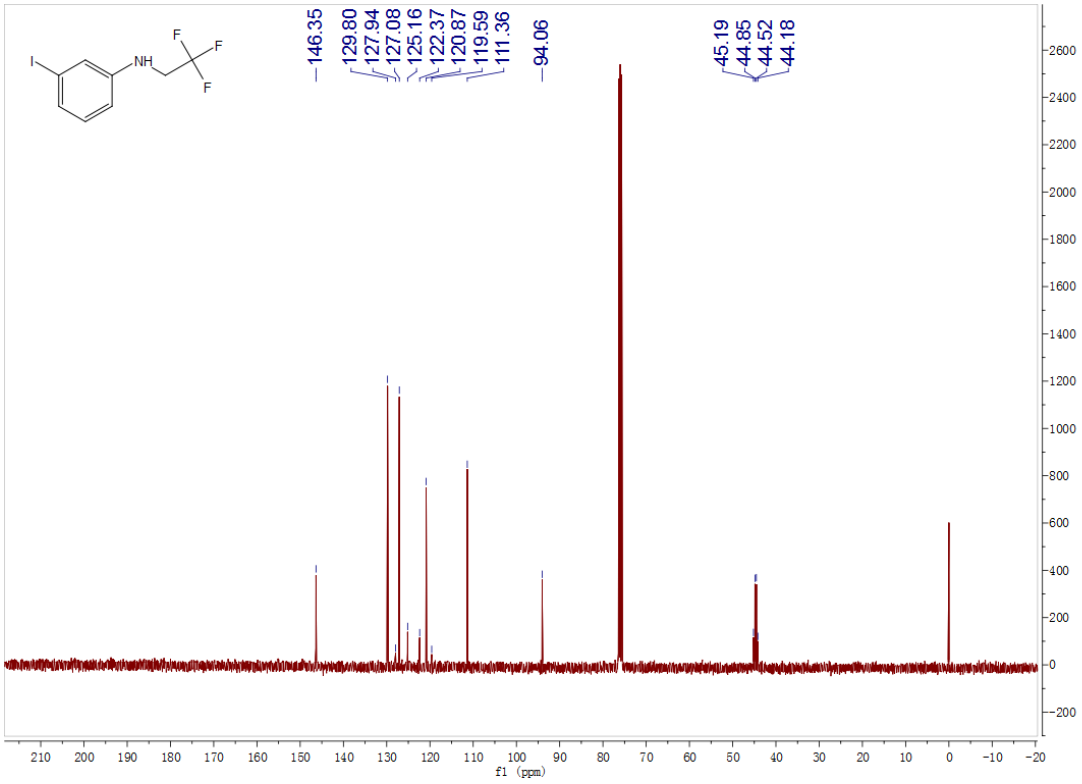


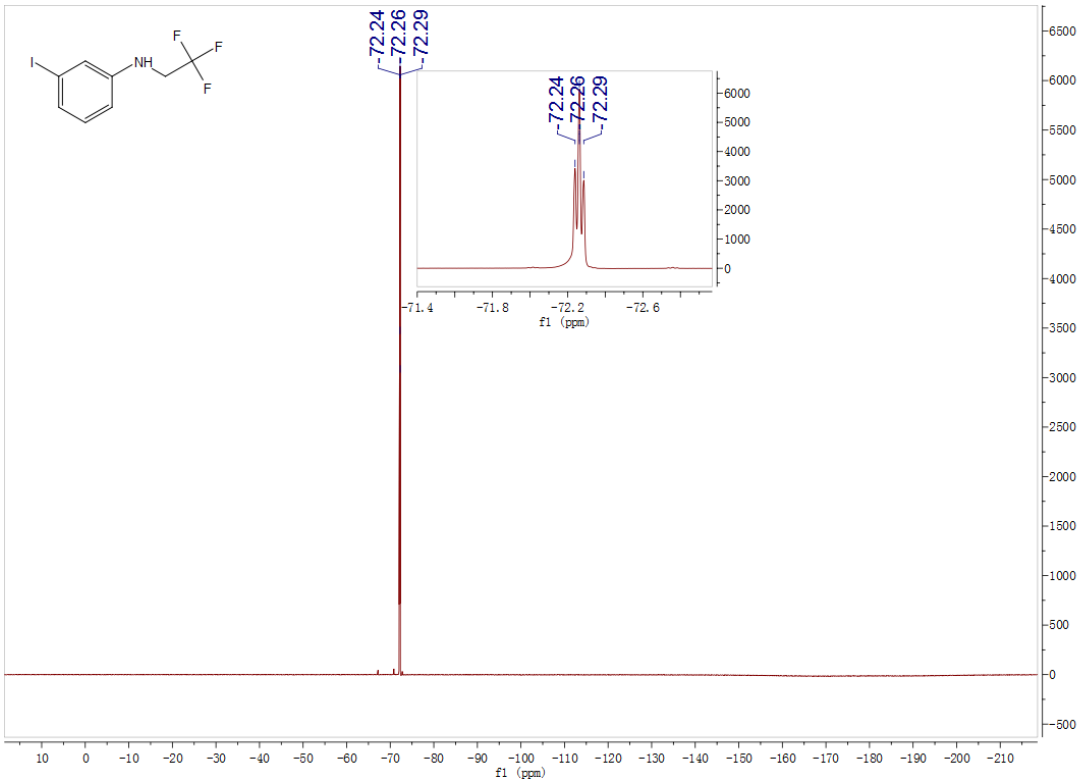




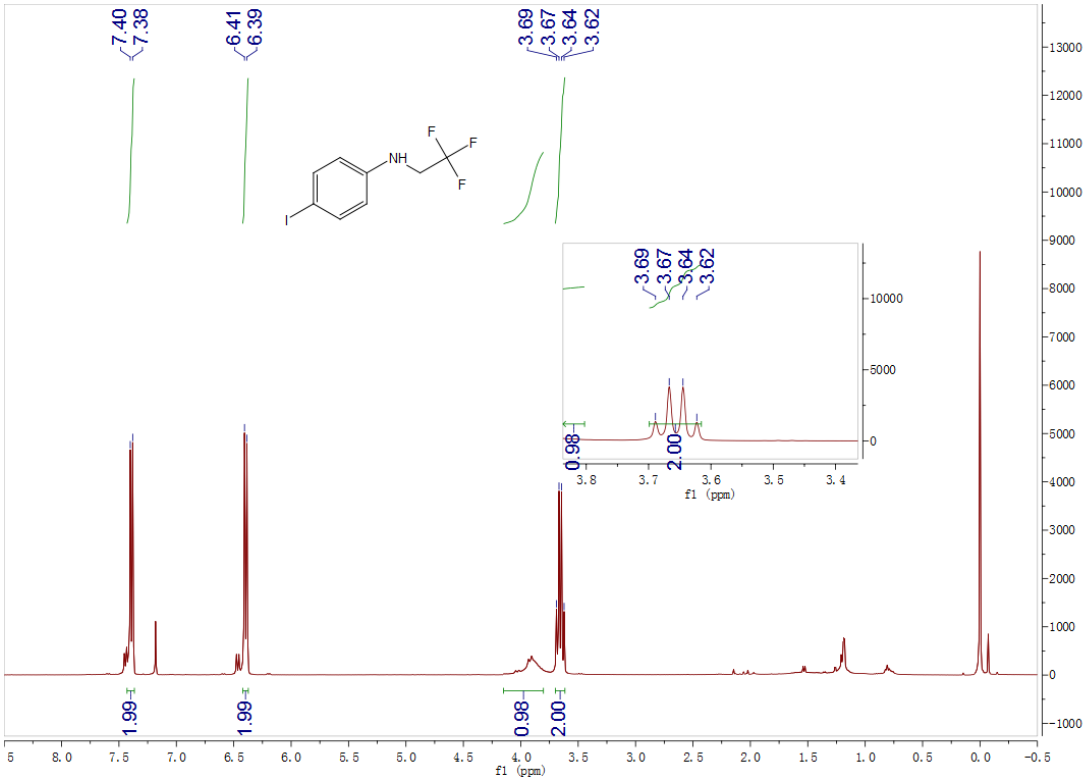
3-iodo-N-(2, 2, 2-trifluoroethyl)benzenamine(2p), pale yellow liquid, 58.7 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J*=7.6 Hz, 1H), 6.96 (s, 1H), 6.84 (t, *J*=7.9 Hz, 1H), 6.56 (d, *J*=8.1 Hz, 1H), 3.87 (s, 1H), 3.66 (q, *J*=8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 129.9, 127.1, 123.8 (q, *J*=279.0 Hz), 120.9, 111.4, 94.1, 44.7 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.26 (t, *J*=8.7 Hz). HRMS (EI): calcd for $C_8H_7F_3IN$: 300.9575; found: 300.9569

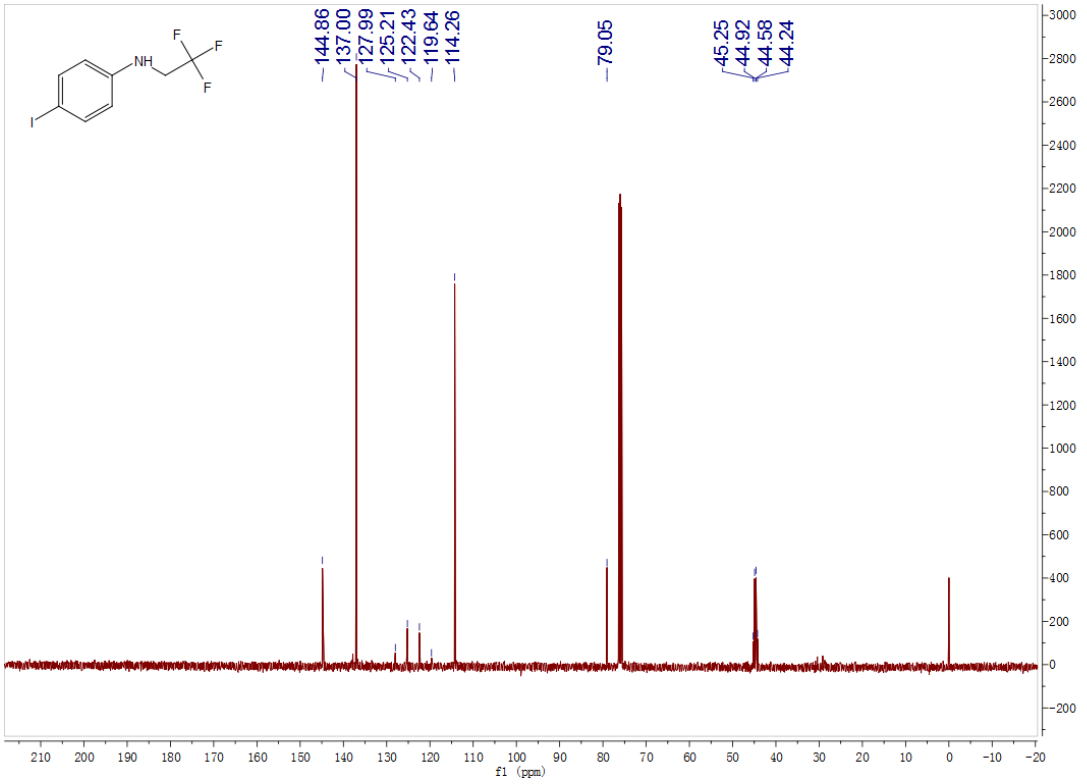


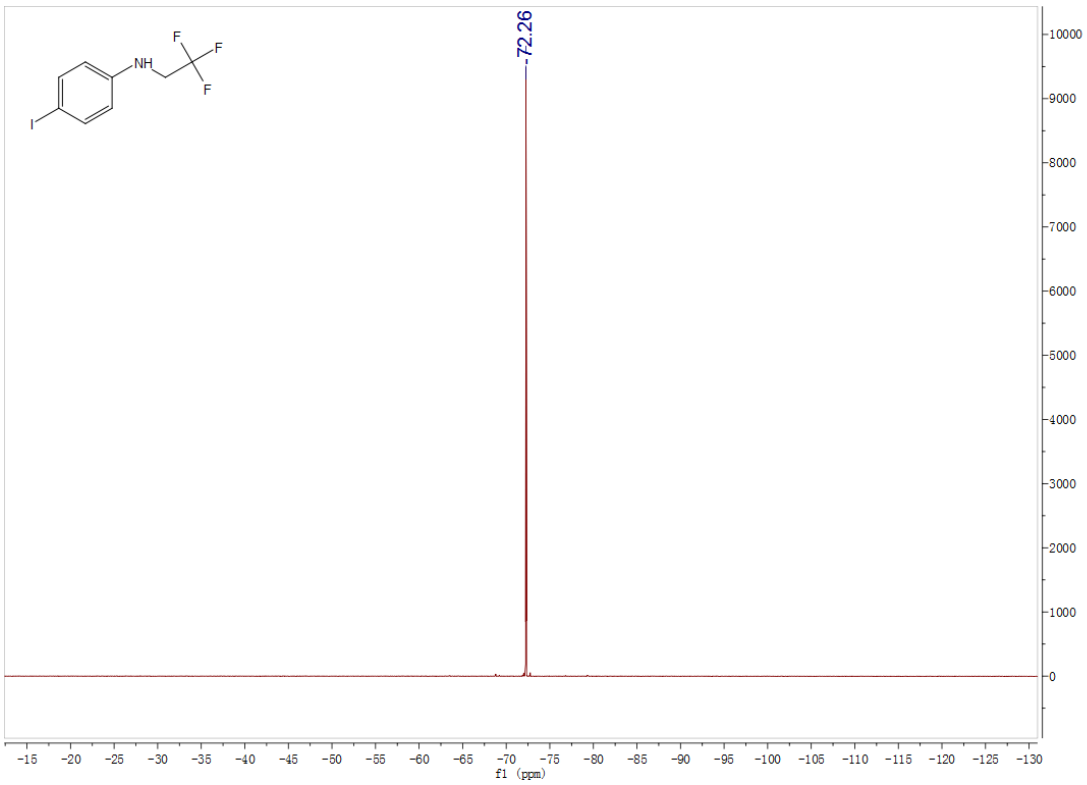

146.35
129.80
127.94
127.08
125.16
122.37
120.87
119.59
111.36
94.06
45.19
44.85
44.52
44.18
f1 (ppm)

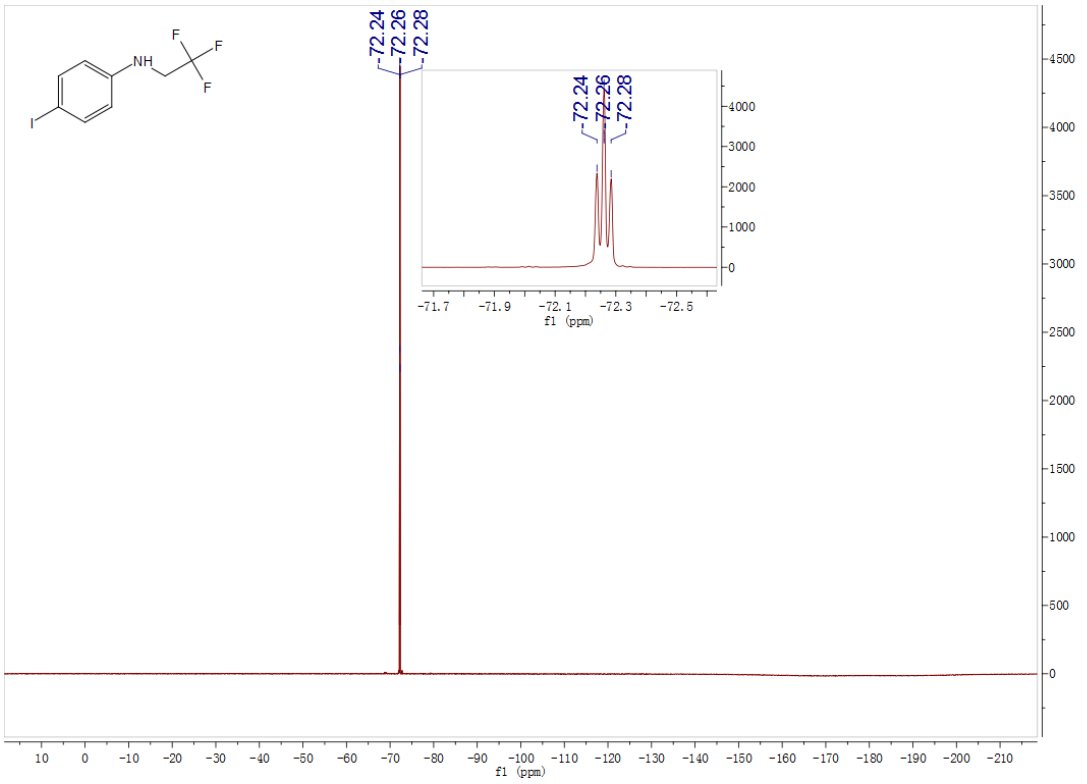

72.24
72.26
72.29
f1 (ppm)

4-iodo-N-(2, 2, 2-trifluoroethyl)benzenamine(2q), pale yellow liquid, 56.9 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*=8.5 Hz, 2H), 6.40 (d, *J*=8.5 Hz, 2H), 3.91 (s, 1H), 3.66 (q, *J*=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.0, 123.82 (q, *J*=278.0 Hz), 114.3, 79.1, 44.8 (q, *J*=34.0 Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.26 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_8H_7F_3IN$: 300.9575; found: 300.9582

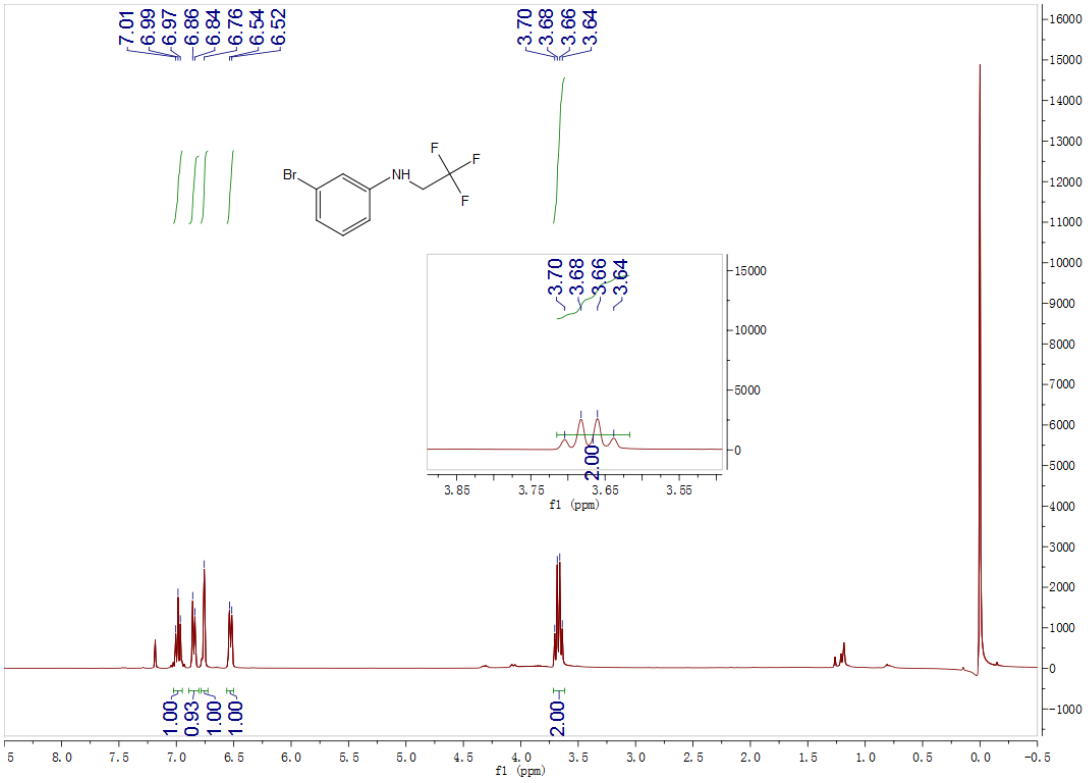


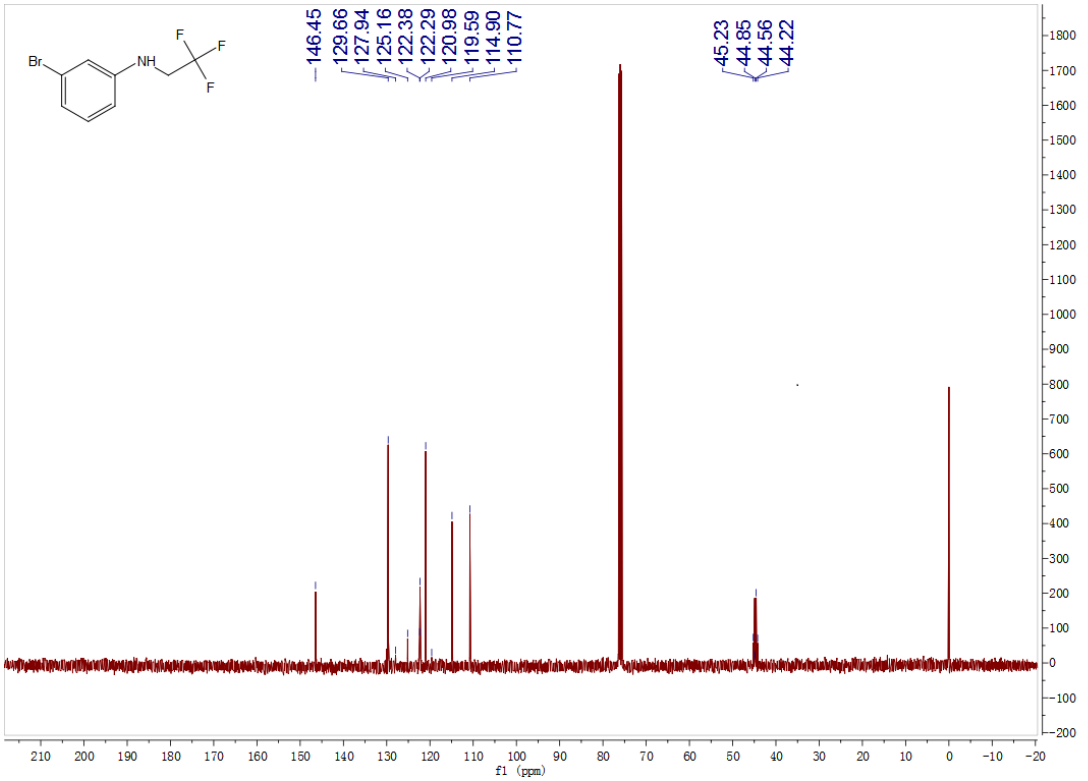


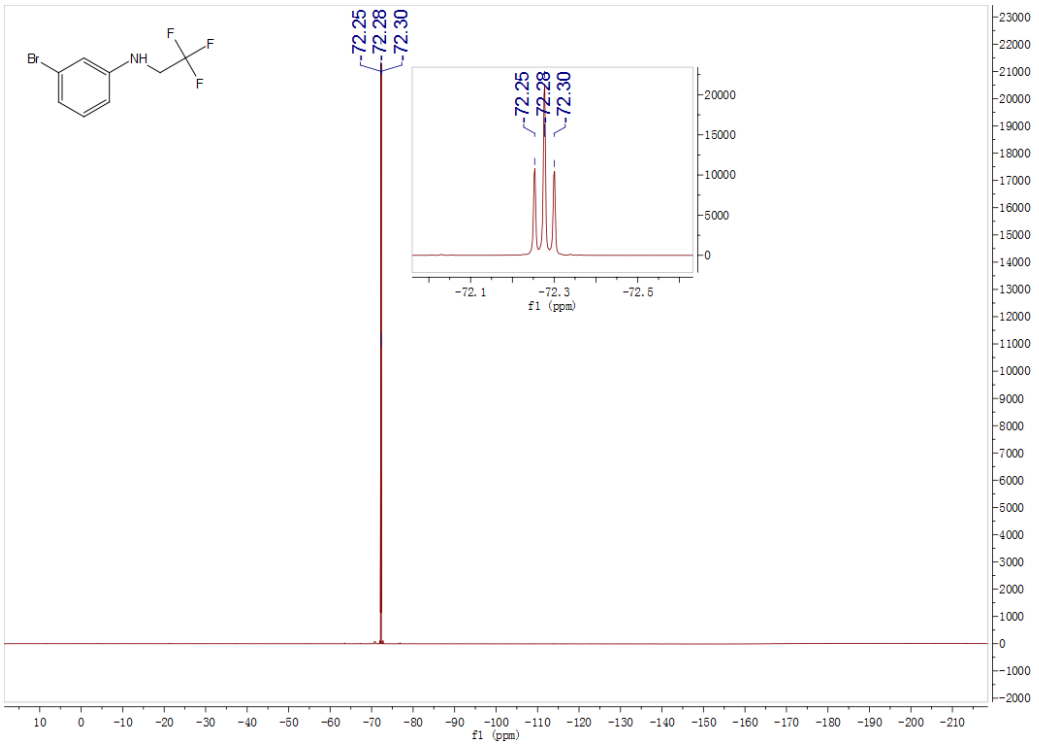

F
F
F
NH
I
-72.26
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)


F
F
F
NH
I
-72.24
-72.26
-72.28
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
-72.24
-72.26
-72.28
4000
3000
2000
1000
0
-71.7 -71.9 -72.1 -72.3 -72.5
f1 (ppm)

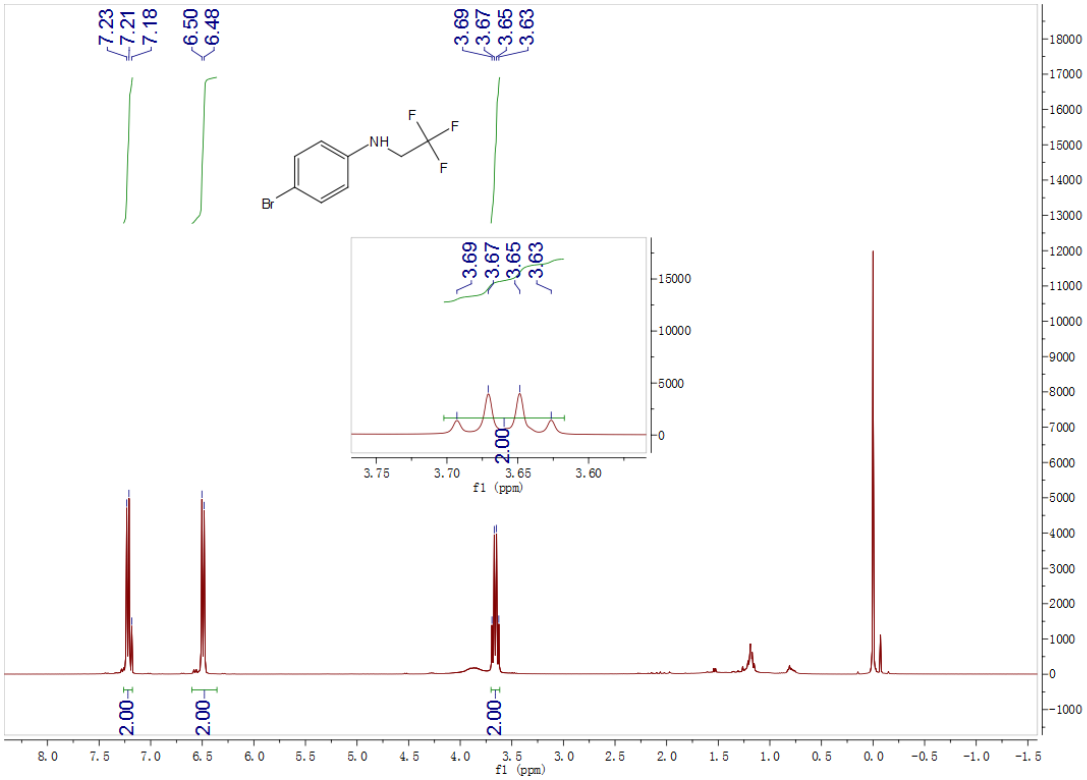
3-bromo-N-(2, 2, 2-trifluoroethyl)benzenamine(2r), pale yellow liquid, 48.0 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, *J*=8.0 Hz, 1H), 6.85 (d, *J*=7.8 Hz, 1H), 6.76 (s, 1H), 6.53 (d, *J*= 8.1 Hz, 1H), 3.67 (q, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 129.7, 123.8 (q, *J*=278.0 Hz), 122.3, 121.0, 114.9, 110.8, 44.8(q, *J*=34.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.28 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_8H_7BrF_3N$: 252.9714; found: 252.9719

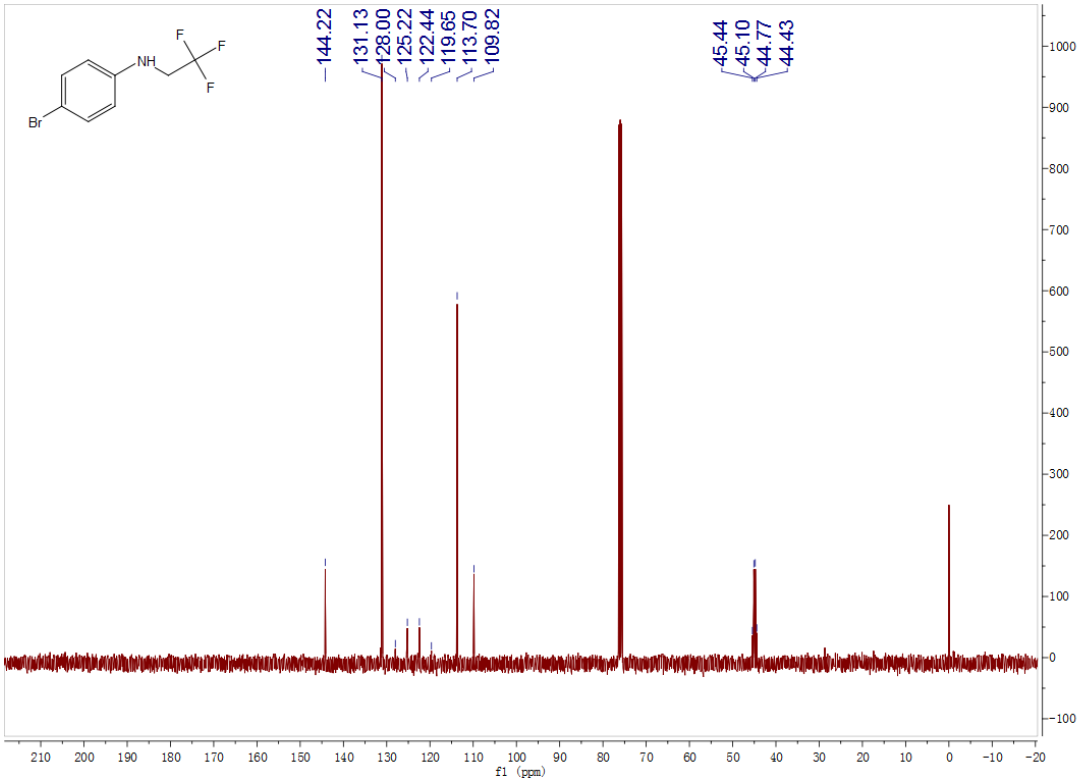


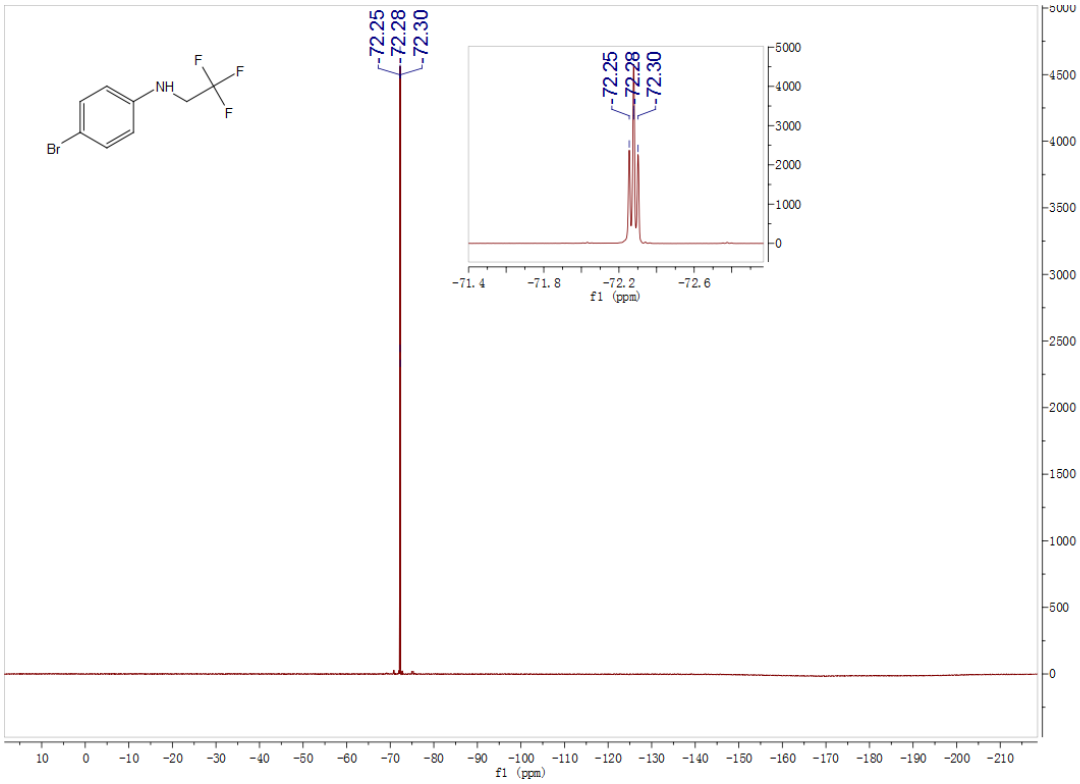




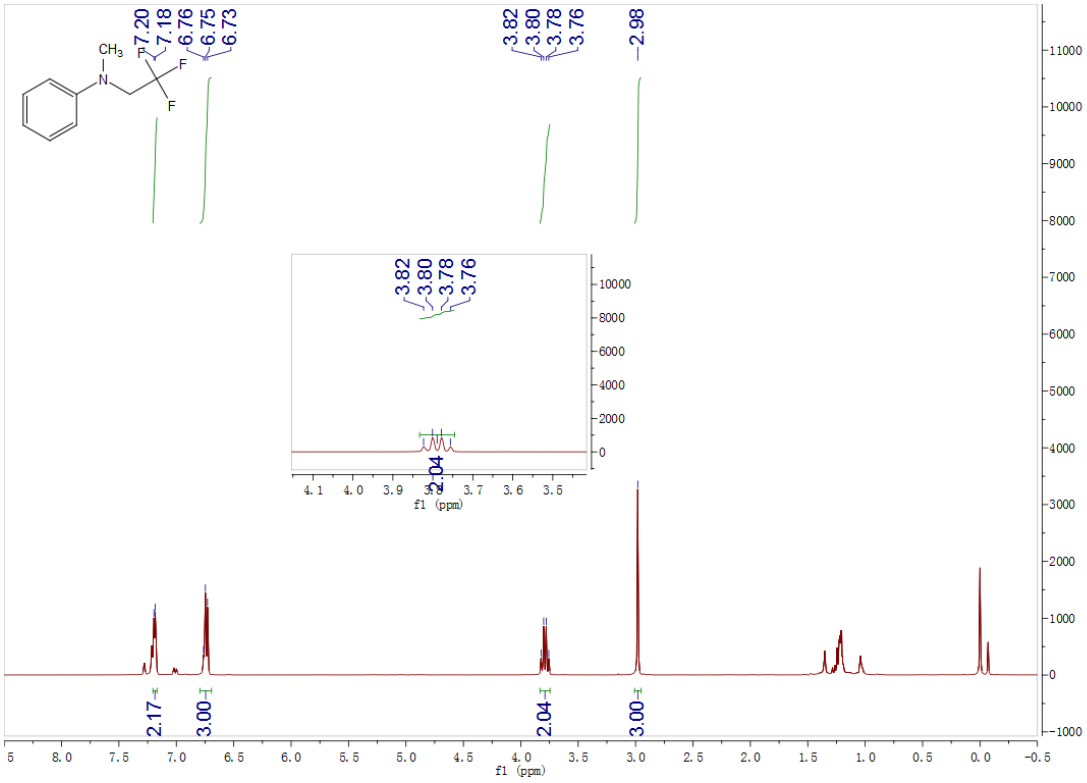
4-bromo-N-(2, 2, 2-trifluoroethyl)benzenamine(2s), pale yellow liquid,51.8 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J*=9.7 Hz, 2H), 6.49 (d, *J*=8.7 Hz, 2H), 3.66 (q, *J*=8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 131.1, 123.8 (q, *J*=278.0 Hz), 113.7, 109.8, 44.9 (q, *J*=33.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ-72.28 (t, *J* =8.8 Hz). HRMS (EI): calcd for $C_8H_7BrF_3N$: 252.9714; found: 252.9718

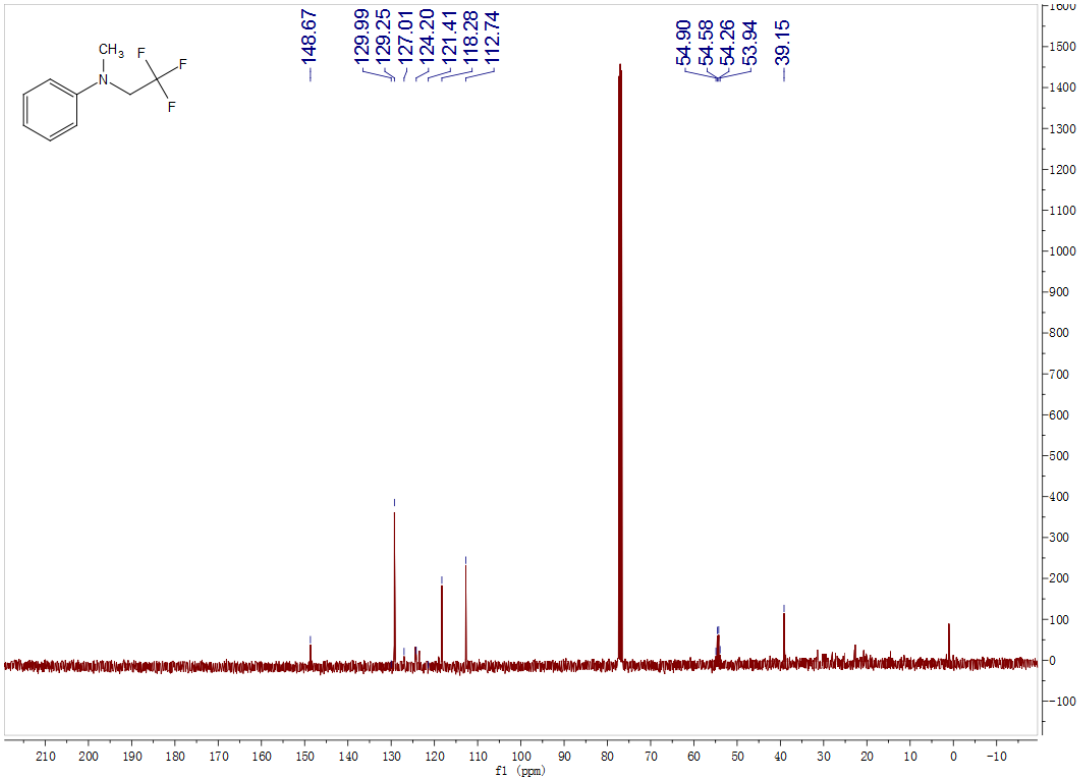


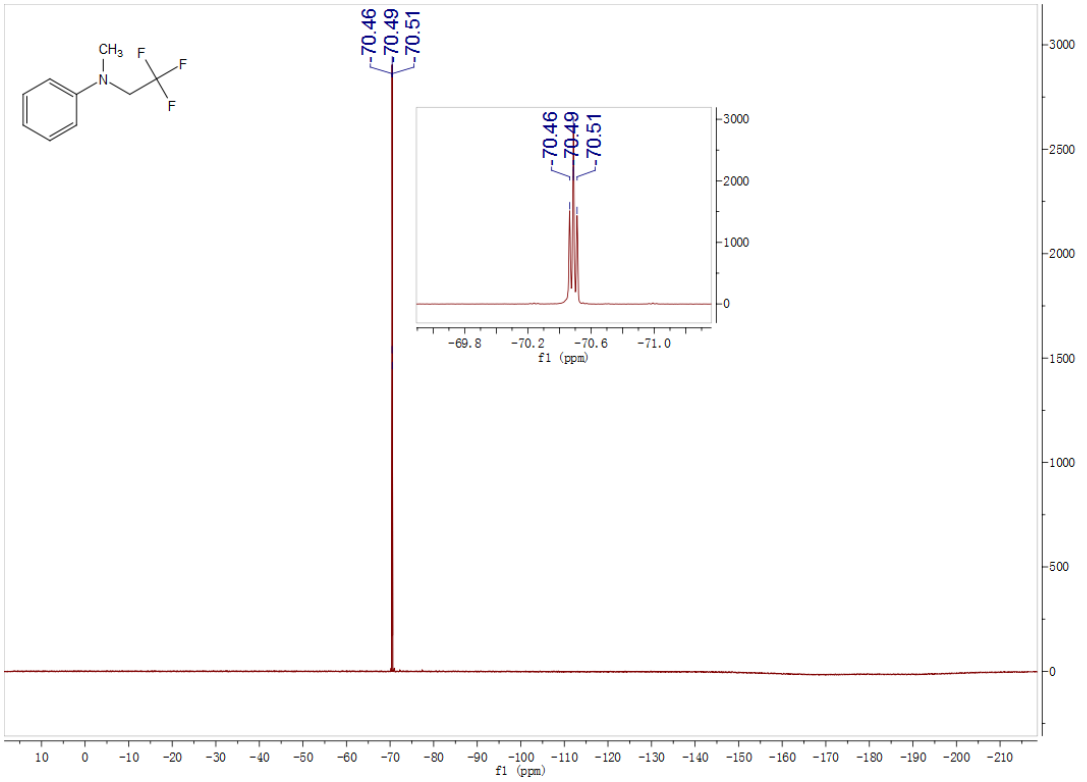

144.22
131.13
128.00
125.22
122.44
119.65
113.70
109.82
45.44
45.10
44.77
44.43
NH
F
F
F
Br
f1 (ppm)


72.25
72.28
72.30
NH
F
F
F
Br
f1 (ppm)

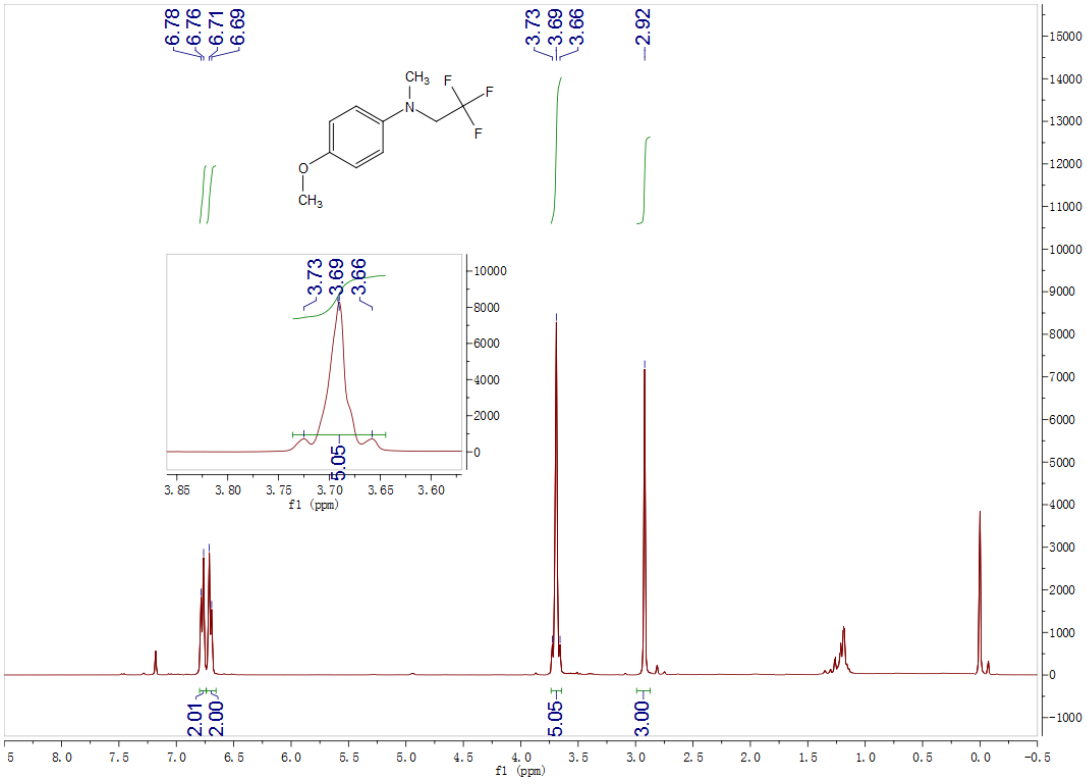
N-Methyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4a), pale yellow liquid, 40.9 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J*=4.5 Hz, 2H), 6.75 (t, *J*=6.9 Hz, 3H), 3.79 (q, *J*=8.9 Hz, 2H), 2.98 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =148.7,130.0,125.6(q, *J*=281.0 Hz),118.3,112.7,54.4(q, *J*=32.0 Hz),39.2.^{19}F NMR (377 MHz, $CDCl_3$) δ -70.49 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_9H_{10}F_3N$: 189.0765; found: 189.0772

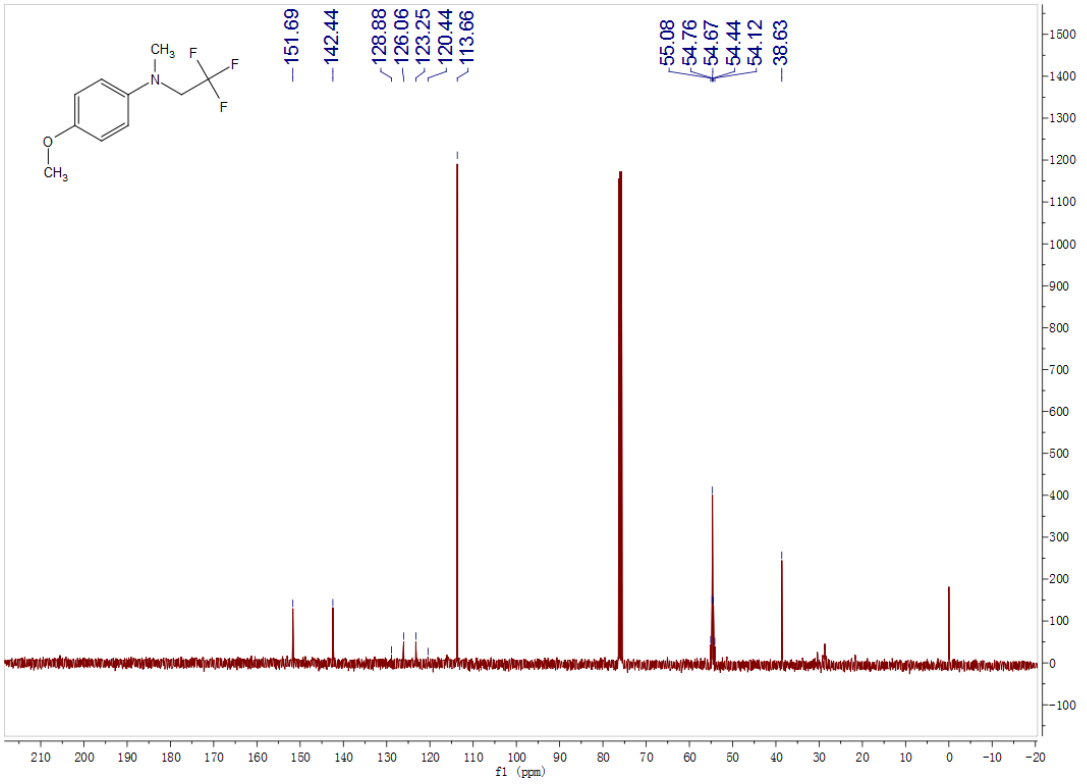






4-methoxy-N-methyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4b), pale yellow liquid, 49.3 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J*=8.8 Hz, 2H), 6.70 (d, *J*=8.3 Hz, 2H), 3.74-3.64 (m, 5H), 2.92 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ=151.7, 142.4, 123.7(q, *J*=281.0 Hz),113.7, 54.6(q, *J*=32.0 Hz),54.7, 38.6. ^{19}F NMR (377MHz, $CDCl_3$) δ -77.53 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3NO$: 219.0871; found: 219.0866




151.69
142.44
128.88
126.06
123.25
120.44
113.66
55.08
54.76
54.67
54.44
54.12
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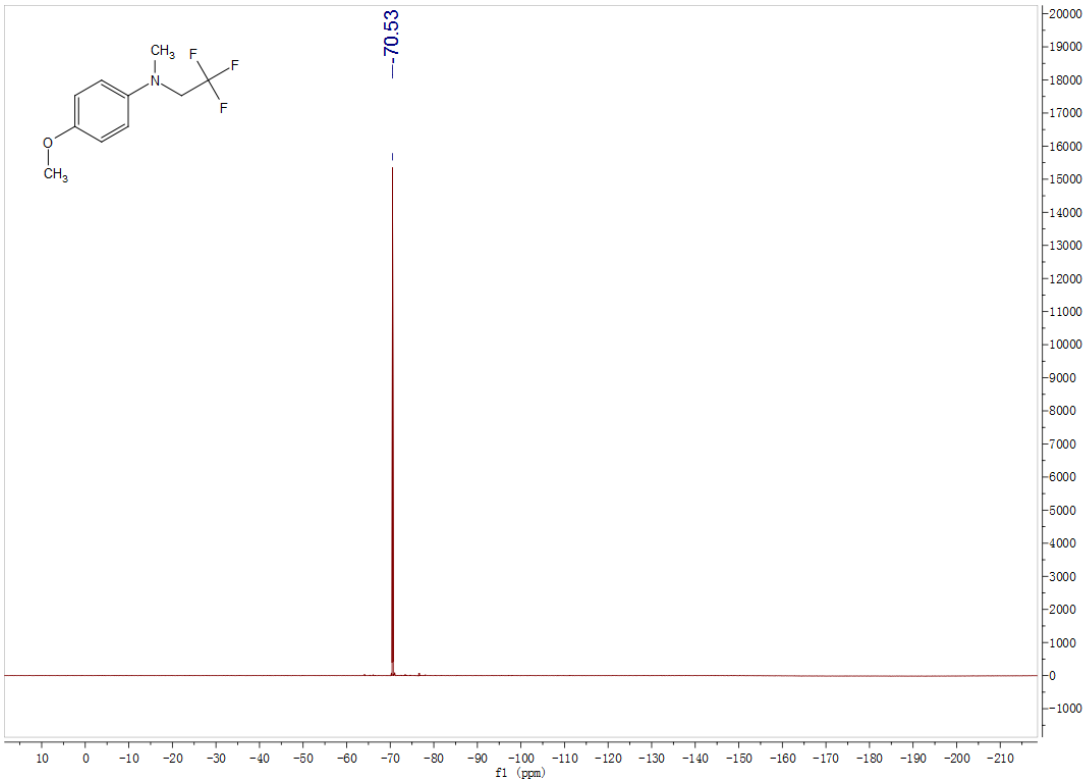
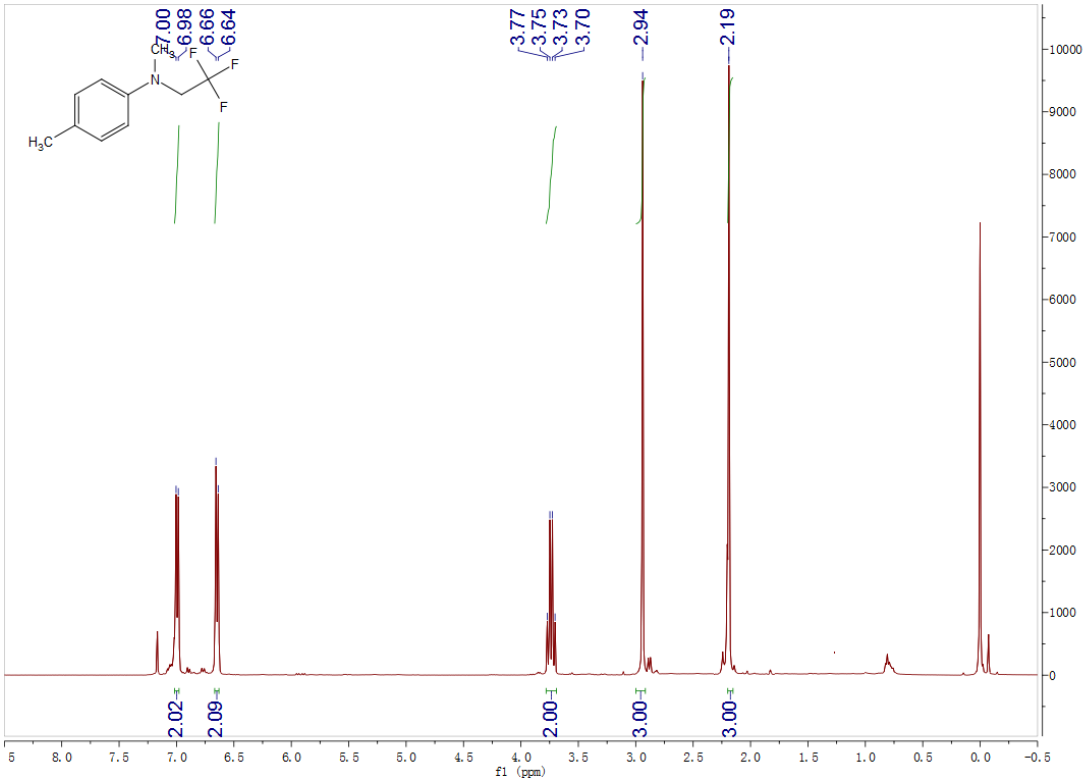
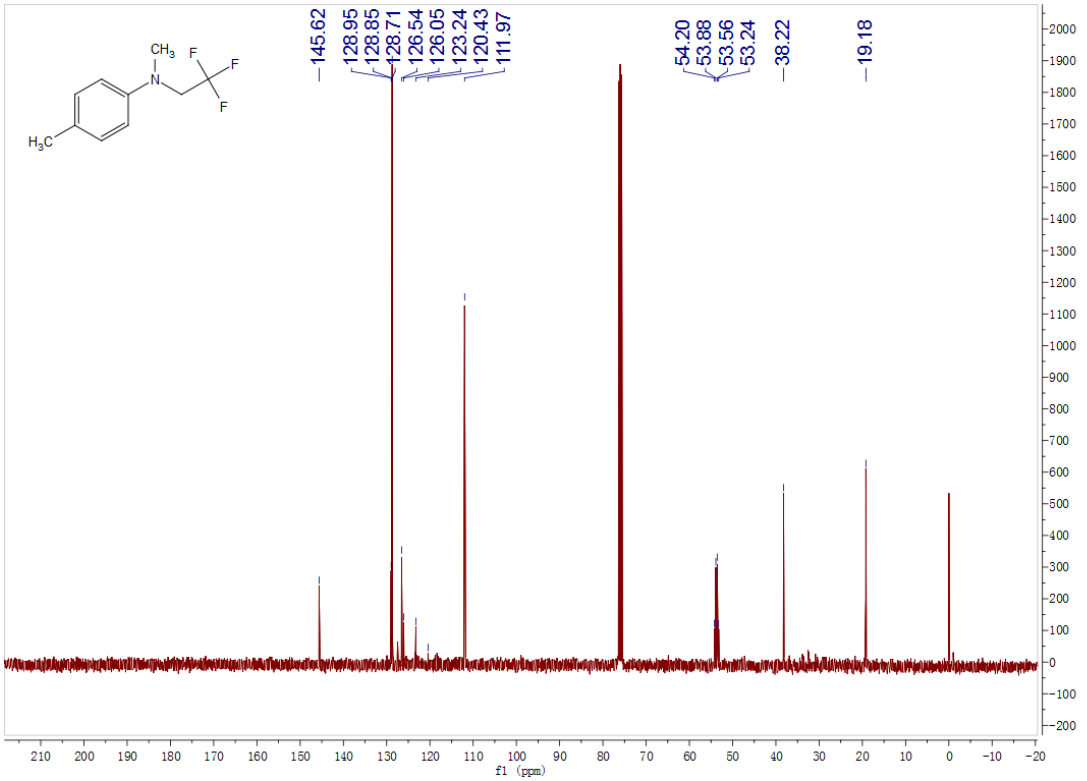
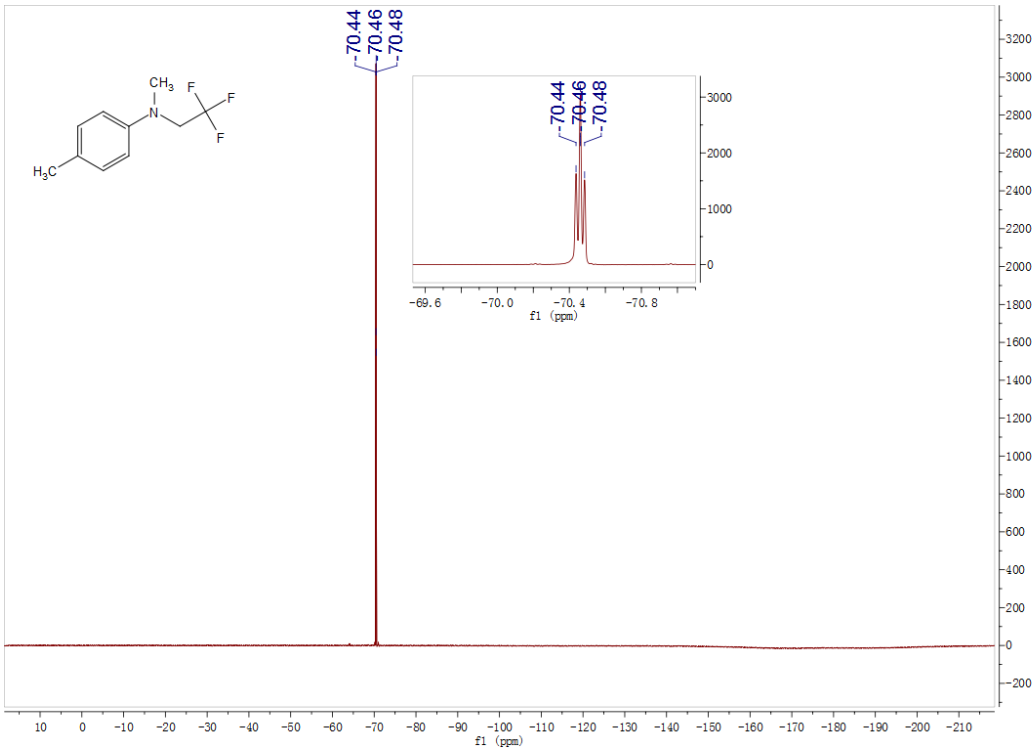
CH3
F
F
F
N
O
CH3
f1 (ppm)


70.53
CH3
F
F
F
N
O
CH3
f1 (ppm)

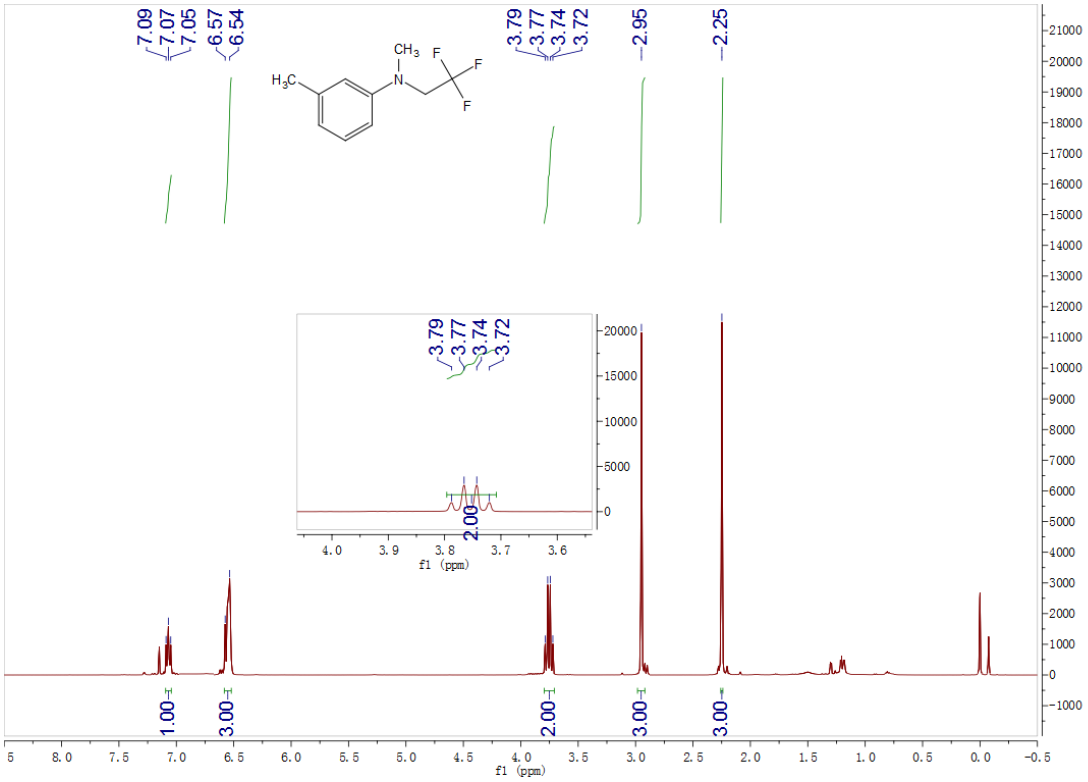
N,4-dimethyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4c), pale yellow liquid, 44.5 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J*=7.9 Hz, 2H), 6.65 (d, *J*=7.9 Hz, 2H), 3.74 (q, *J*=9.0 Hz, 2H), 2.94 (s, 3H), 2.19 (s, 3H).^{13}C NMR (100 MHz,$CDCl_3$) δ=145.6, 128.7, 126.5, 124.6(q, *J*=281.0 Hz), 112.0, 53.7(q, *J*=32.0 Hz), 38.2, 19.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.46 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3N$: 203.0922; found: 203.0918

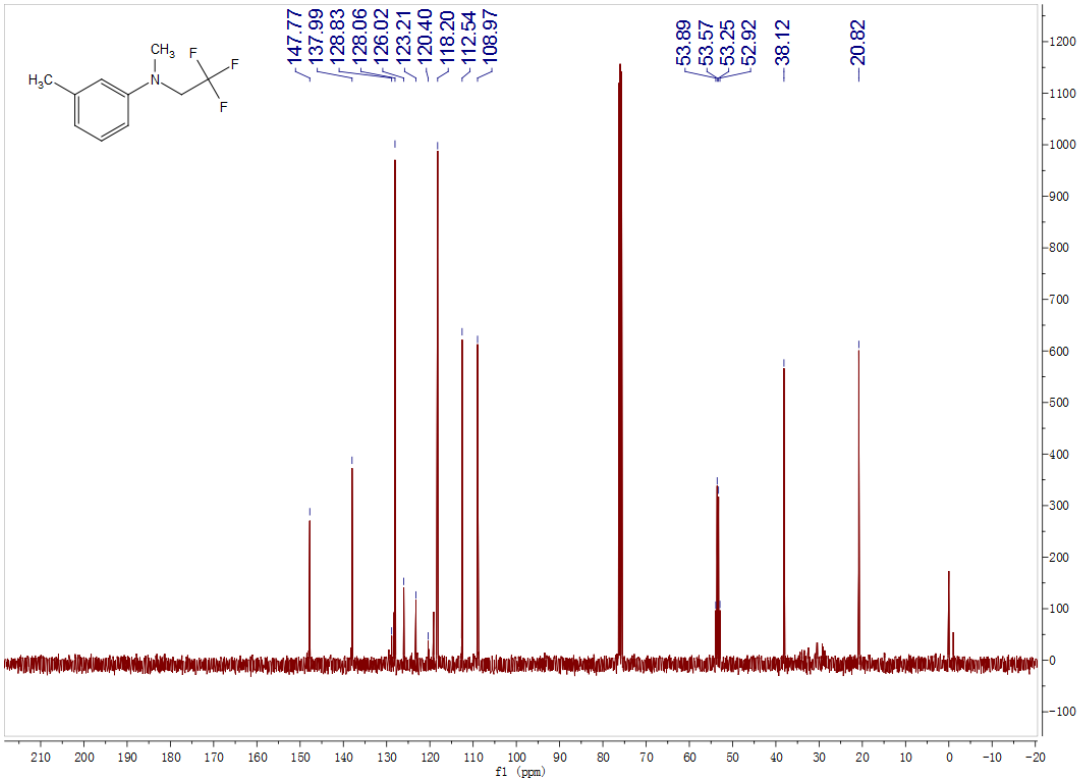


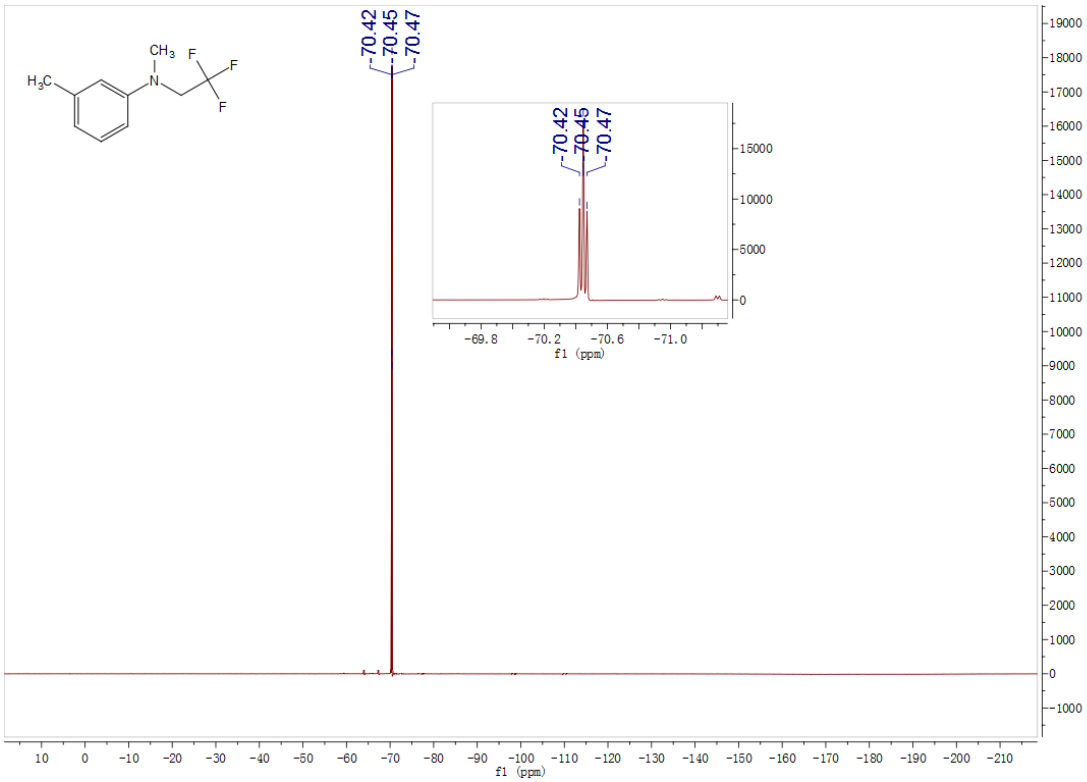




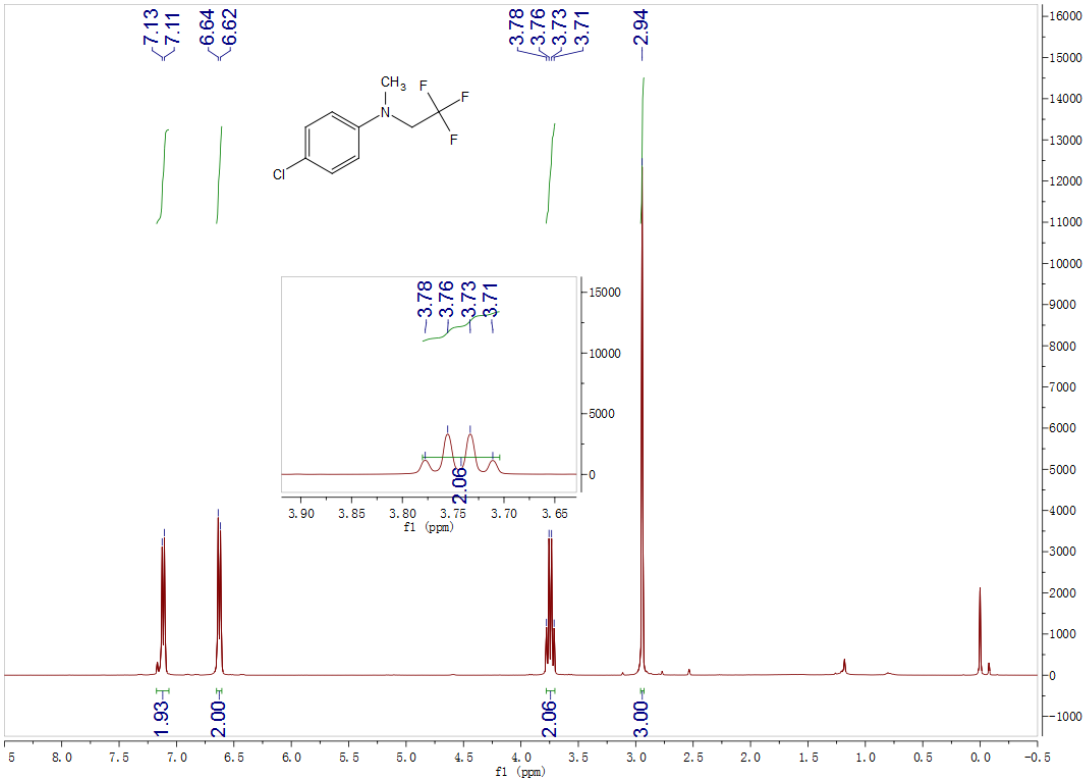
N,3-dimethyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4d), pale yellow liquid, 43.9 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J*=8.2 Hz, 1H), 6.56 (d, *J*=15.7 Hz, 3H), 3.75 (q, *J*=9.0 Hz, 2H), 2.95 (s, 3H), 2.25 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 138.0, 128.1, 124.6(q, *J*=281.0 Hz), 118.2, 112.5, 109.0, 53.4(q, *J*=32.0 Hz), 38.1, 20.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.45 (t, *J*=9.0 Hz). HRMS (EI): calcd for $C_{10}H_{12}F_3N$: 203.0922; found: 203.0926

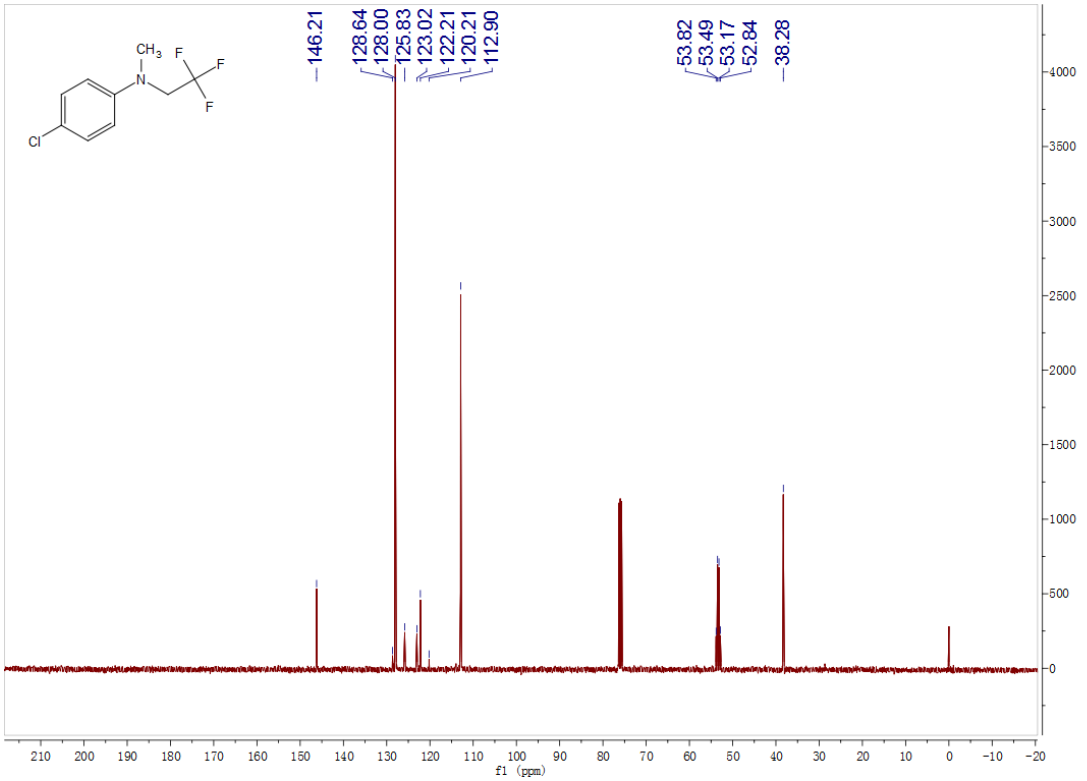


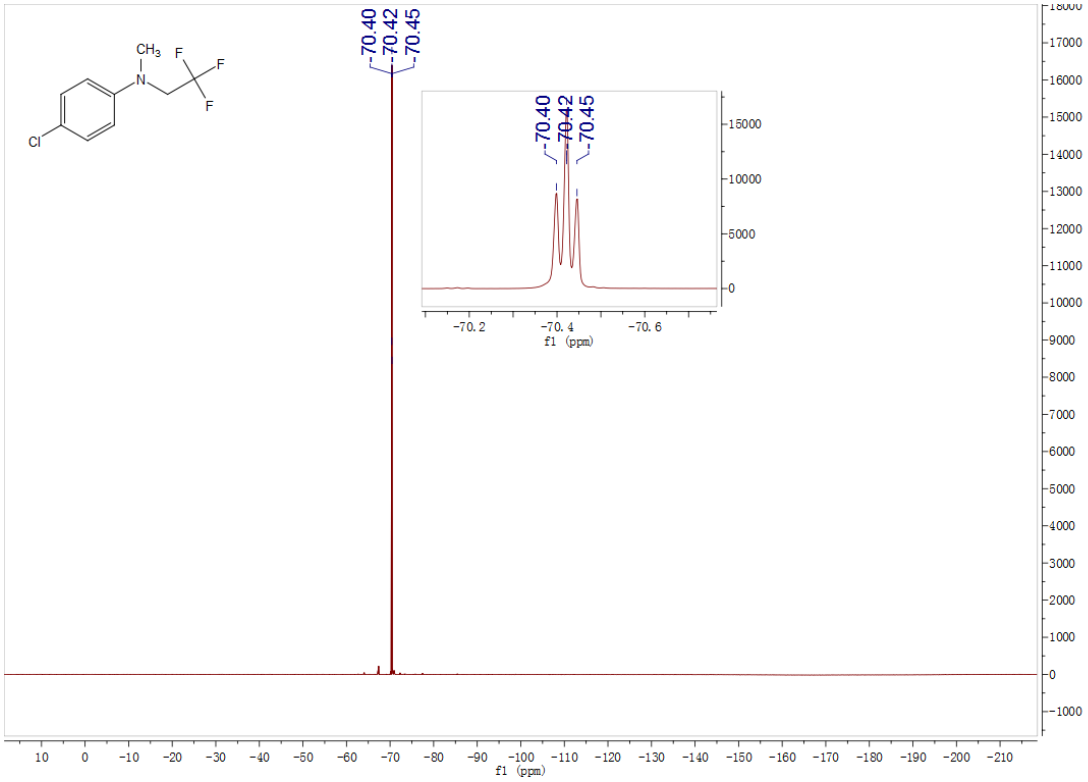

147.77
137.99
128.83
128.06
126.02
123.21
120.40
118.20
112.54
108.97
53.89
53.57
53.25
52.92
38.12
20.82
f1 (ppm)


70.42
70.45
70.47
f1 (ppm)

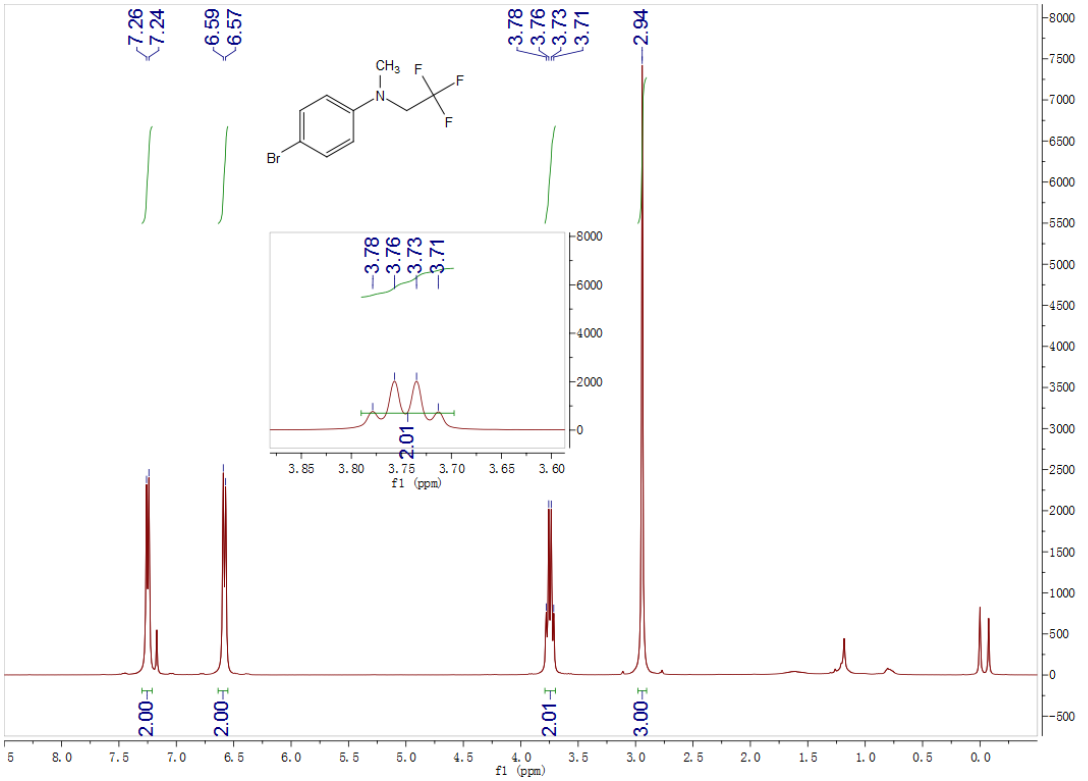
4-chloro-N-methyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4e), pale yellow liquid, 47.0mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J*=7.9 Hz, 2H), 6.63 (d, *J*=8.2 Hz, 2H), 3.74 (q, *J*=8.9 Hz, 2H), 2.94 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 128.0, 124.4 (q, *J*=281.0Hz), 122.2, 112.9, 53.3(q, *J*=33.0 Hz), 38.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.42 (t, *J*=8.9 Hz). HRMS (EI): calcd for $C_9H_9ClF_3N$: 223.0376; found: 223.0378

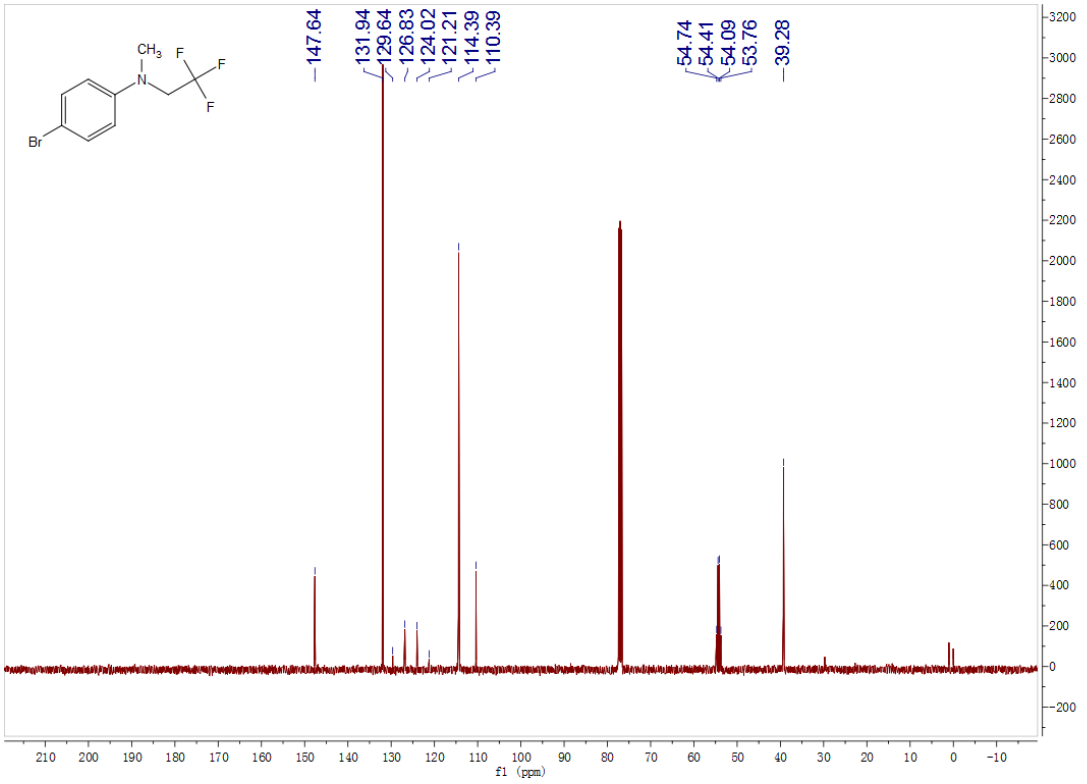


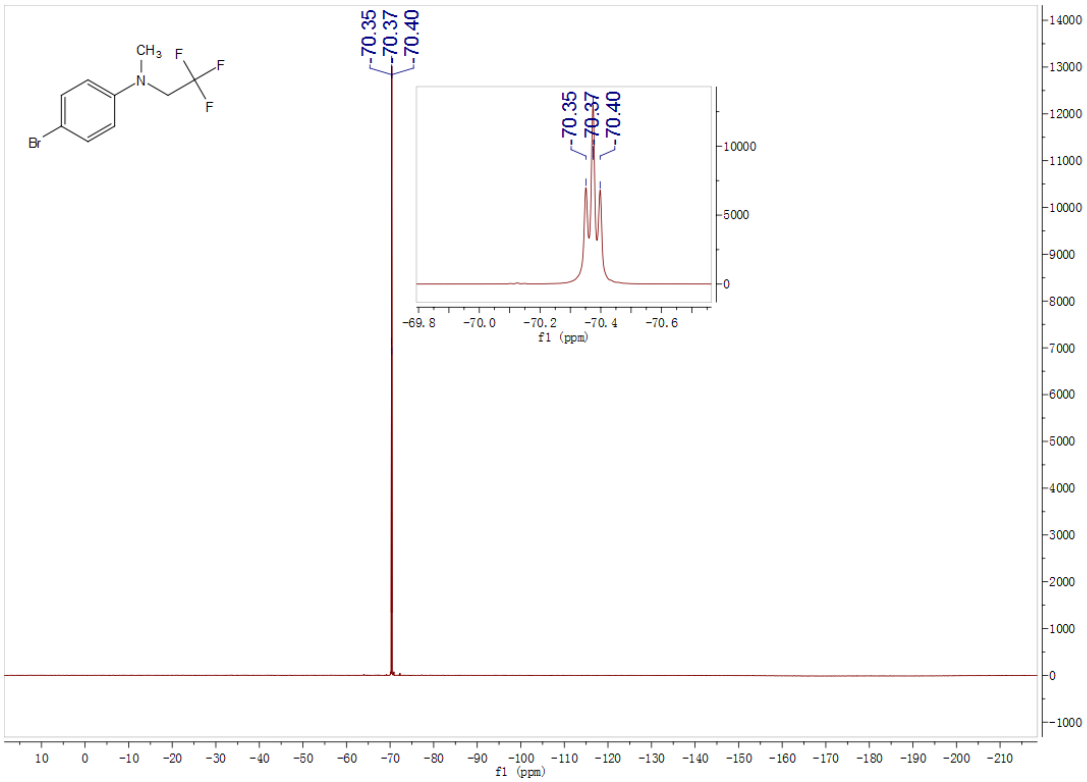




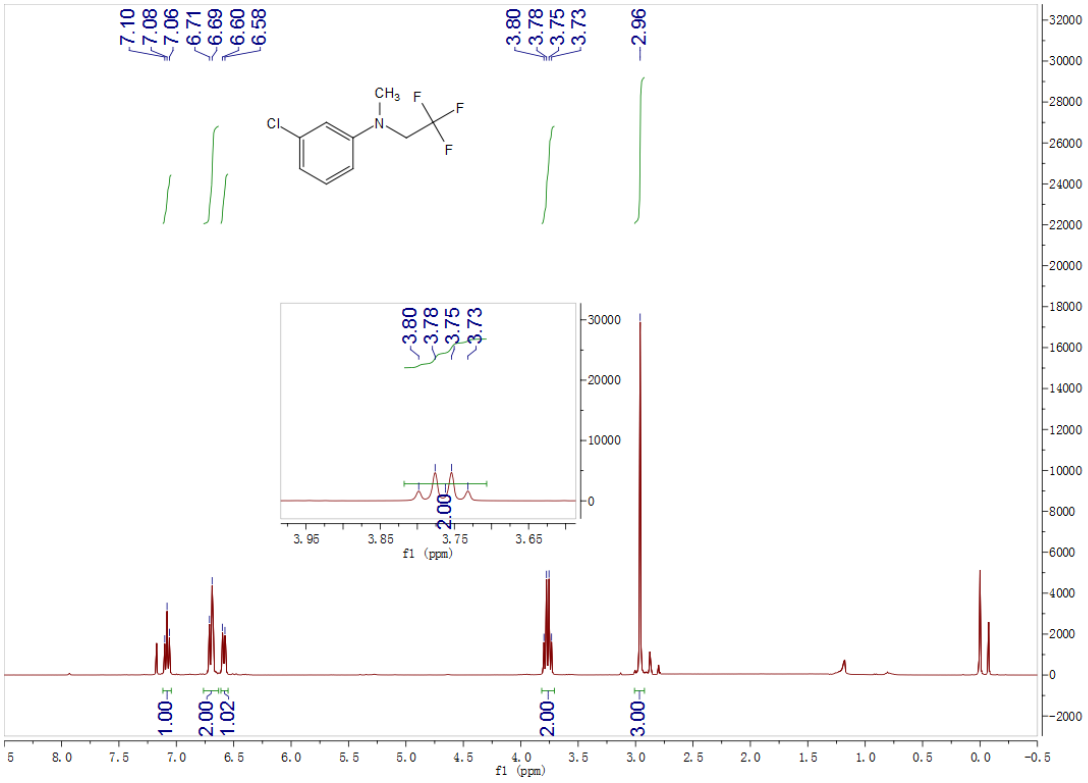
4-bromo-N-methyl-N-(2,2,2-trifluoroethyl)benzenamine(4f), pale yellow liquid, 58.7mg, 73% yield. ^{1}H NMR (400 MHz, CDCl3) δ 7.25 (d, *J*=8.2 Hz, 2H), 6.58 (d, *J*=8.3 Hz, 2H), 3.75 (q, *J*=8.7 Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 131.9, 125.4 (q, *J*=281.0Hz), 114.4, 110.4, 54.2(q, *J*=32.0 Hz), 39.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.37 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_9H_9BrF_3N$: 266.9870; found: 266.9866

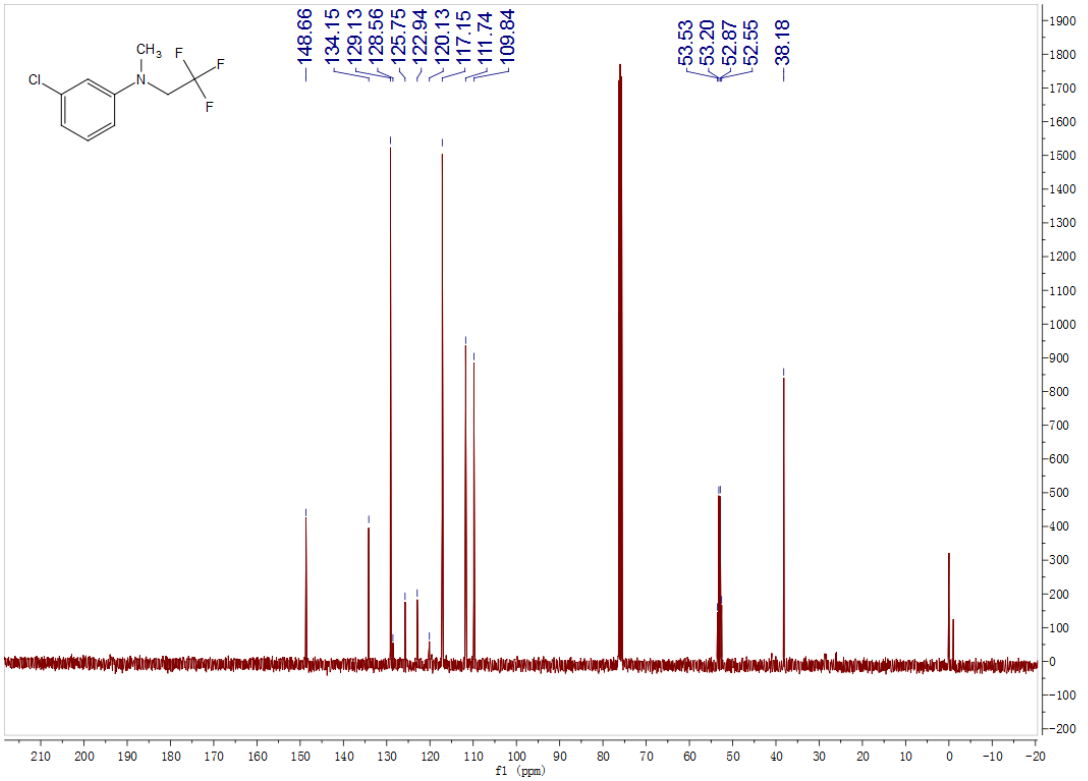


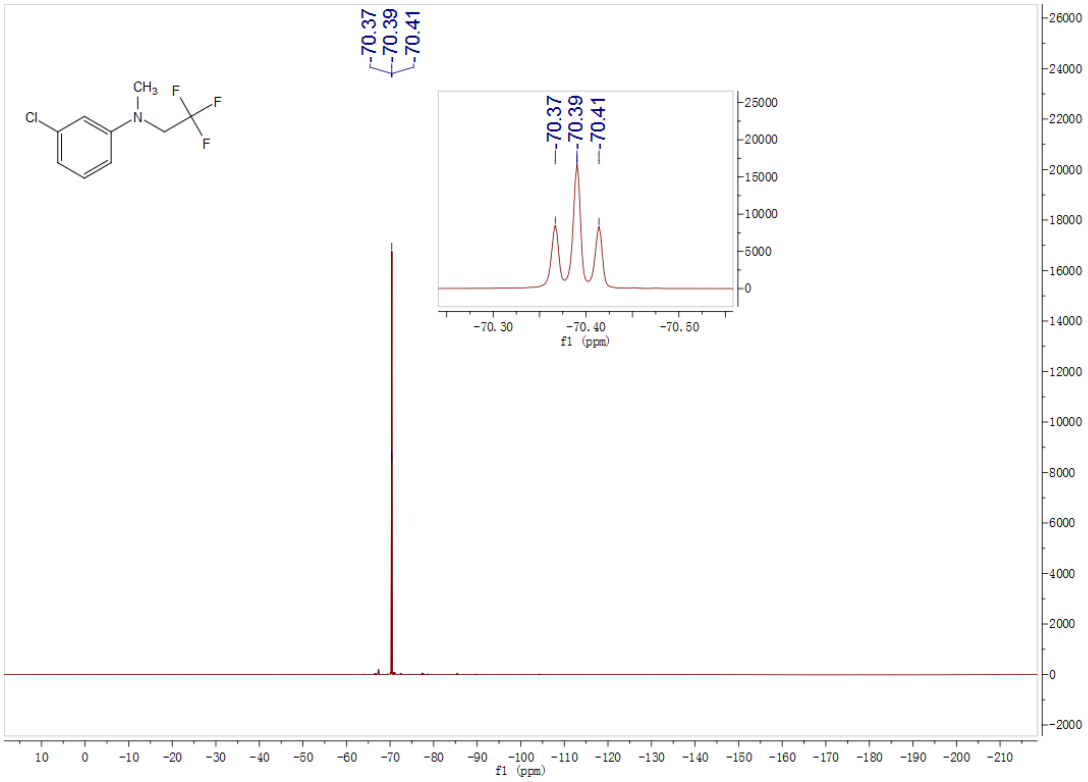

147.64
131.94
129.64
126.83
124.02
121.21
114.39
110.39
54.74
54.41
54.09
53.76
39.28
CH3
F
F
F
N
Br
f1 (ppm)


-70.35
-70.37
-70.40
CH3
F
F
F
N
Br
f1 (ppm)

3-chloro-N-methyl-N-(2, 2, 2-trifluoroethyl)benzenamine(4g), pale yellow liquid, 48.3mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J*=8.1 Hz, 1H), 6.70 (d, *J*=9.0 Hz, 2H), 6.59 (d, *J*=8.5 Hz, 2H), 2.96 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 134.2, 129.1, 124.3(q, *J*=281.0 Hz), 117.2, 111.7, 109.8, 53.0(q, *J*=33.0 Hz), 38.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.39 (t, *J*=8.8 Hz). HRMS (EI): calcd for $C_9H_9ClF_3N$: 223.0376; found: 223.0373






-70.37
-70.39
-70.41
Cl
N
CH3
F
F
F
-70.37
-70.39
-70.41
f1 (ppm)
f1 (ppm)