Supporting Information *for*

Trifluoromethylation of (Hetero)Aryl Iodides and Bromides with Copper (I) Chlorodifluoroacetate Complexes

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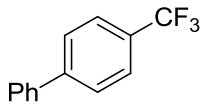
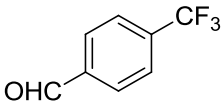
Data for Compounds 3a-3r, 5a-5o, and 7.



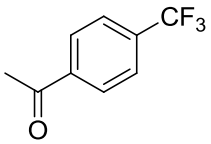
4-Trifluoromethyl-1,1'-biphenyl (3a)[1]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3a** was produced in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.66 – 7.60 (m, 2H), 7.54 – 7.44 (m, 2H), 7.46 – 7.30 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 (q, *J* = 1.1 Hz), 139.8 (s), 129.3 (q, *J* = 32.6 Hz), 129.0 (s), 128.2 (s), 127.4 (s), 127.3 (s), 125.7 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.8 Hz). GC-MS m/z 221 (M^+-H).



4-(Trifluoromethyl)benzaldehyde (3b)[2]

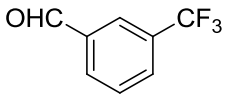
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3b** was produced in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1 (s), 138.7 (s), 135.6 (q, *J* = 32.9 Hz), 129.9 (s), 126.1 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 273.9 Hz). GC-MS m/z 173 (M^+-H).



1-(4-Trifluoromethyl)phenyl)ethanone (3c)[1]

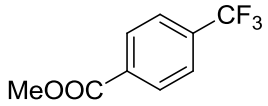
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3c** was produced in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2

Hz, 2H), 2.67 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (s), 139.7 (q, *J* = 1.3 Hz), 134.4 (q, *J* = 32.8 Hz), 128.6 (s), 125.7 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 273.7 Hz), 26.8 (s). GC-MS m/z 188 (M^+).



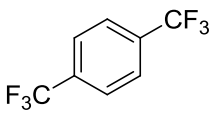
3-(Trifluoromethyl)benzaldehyde (3d)[3]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3d** was produced in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.16 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7 (s), 136.8 (s), 132.6 (q, *J* = 1.2 Hz), 131.8 (q, *J* = 33.6 Hz), 130.8 (q, *J* = 3.6 Hz), 129.8 (s), 126.4 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 273.5 Hz). GC-MS m/z 173 (M^+-H).



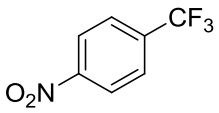
Methyl 4-(trifluoromethyl)benzoate (3e)[1]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3e** was produced in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 3.96 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (s), 134.4 (q, *J* = 32.6 Hz), 133.3 (s), 130.0 (s), 125.4 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 273.7 Hz), 52.5 (s). GC-MS m/z 203 (M^+-H).



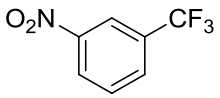
1,4-Bis(trifluoromethyl)benzene (3f)[4]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3f** was produced in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (s, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0 (q, *J* = 33.3 Hz), 126.0 – 125.7 (m), 123.4 (q, *J* = 273.7 Hz). GC-MS m/z 214 (M^+).



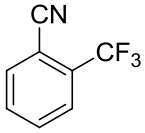
1-Nitro-4-(trifluoromethyl)benzene (3g)[2]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3g** was produced in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (s), 136.1 (q, *J* = 33.3 Hz), 126.9 – 126.6 (m), 124.1 (s), 123.0 (q, *J* = 274.1 Hz). GC-MS m/z 191 (M^+).



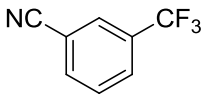
1-Nitro-3-(trifluoromethyl)benzene (3h)[1]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3h** was produced in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.46 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3 (s), 132.3 (q, *J* = 33.8 Hz), 131.1 (q, *J* = 3.5 Hz), 130.4 (s), 126.7 (s), 122.8 (q, *J* = 273.8 Hz), 120.8 (q, *J* = 3.9 Hz). GC-MS m/z 191 (M^+).



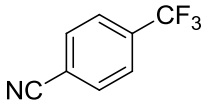
2-(Trifluoromethyl)benzonitrile (3i)[1]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3i** was produced in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.75 – 7.69 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7 (s), 132.9 (q, *J* = 32.9 Hz), 132.9 (s), 132.2 (q, *J* = 1.0 Hz), 126.7 (q, *J* = 4.7 Hz), 122.4 (q, *J* = 274.9 Hz), 115.4 (s), 110.3 (q, *J* = 2.2 Hz). GC-MS m/z 171 (M^+).



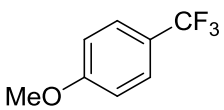
3-(Trifluoromethyl)benzonitrile (3j)[5]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3j** was produced in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.92 – 7.87 (bs, 2H), 7.68 (t, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3 (s), 132.0 (q, *J* = 33.7 Hz), 130.0 (s), 129.5 (q, *J* = 3.6 Hz), 129.0 (q, *J* = 3.9 Hz), 122.9 (t, *J* = 272.7 Hz), 117.3 (s), 113.5 (s). GC-MS m/z 171 (M^+).



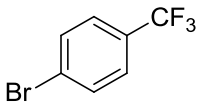
4-(Trifluoromethyl)benzonitrile (3k)[2]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3k** was produced in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (d, *J* = 33.6 Hz), 132.7 (s), 126.2 (t, *J* = 3.7 Hz), 123.1 (d, *J* = 274.0 Hz), 117.4 (s), 116.1 (q, *J* = 1.4 Hz). GC-MS m/z 171 (M^+).



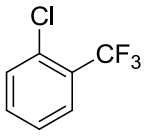
1-Methoxy-4-(trifluoromethyl)benzene (3l) [2]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3l** was produced in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (s), 126.9 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 270.9 Hz), 122.8 (q, *J* = 32.5 Hz), 113.9 (s), 55.4 (s). GC-MS m/z 176 (M^+).



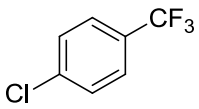
1-Bromo-4-(trifluoromethyl)benzene (3m) [2]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3m** was produced in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1 (s), 129.7 (s), 126.9 (q, *J* = 3.8 Hz), 126.5 (q, *J* = 1.8 Hz), 123.9 (q, *J* = 273.1 Hz). GC-MS m/z 225 (M^+).



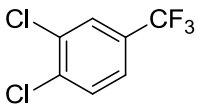
1-Chloro-2-(trifluoromethyl)benzene (3n)[6]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3n** was produced in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.38 – 7.32 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9 (q, *J* = 1.0 Hz), 132.4 (q, *J* = 1.9 Hz), 131.4 (s), 128.5 (q, *J* = 31.5 Hz), 127.5 (q, *J* = 5.5 Hz), 126.6 (s), 122. 9 (d, *J* = 274.1 Hz). GC-MS m/z 180 (M^+).



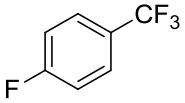
1-Chloro-4-(trifluoromethyl)benzene (3o)[7]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3o** was produced in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 (q, *J* = 1.7 Hz), 129.1 (s), 129.0 (q, *J* = 32.8 Hz), 126.7 (q, *J* = 3.8 Hz), 123.8 (d, *J* = 270.3 Hz). GC-MS m/z 180 (M^+).



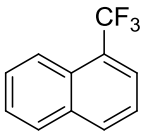
1,2-Dichloro-4-(trifluoromethyl)benzene (3p)[8]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3p** was produced in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6 (q, *J* = 1.1 Hz), 133.5 (s), 131.0 (s), 130.4 (q, *J* = 33.6 Hz), 127.6 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 273.9 Hz). GC-MS m/z 214 (M^+-H).



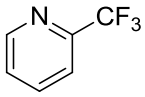
1-Fluoro-4-(trifluoromethyl)benzene (3q)[9]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3q** was produced in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.16 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.1 (s, 3F), -107.6 – -107.9 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6 (d, *J* = 248.4), 127.6 (m), 126.8 (qd, *J* = 33.0, 3.4 Hz), 123.8 (q, *J* = 272.7 Hz), 115.9 (d, *J* = 22.4 Hz). GC-MS m/z 163 (M^+-H).



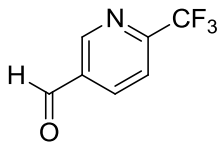
1-(Trifluoromethyl)naphthalene (3r) [1]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **3r** was produced in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0 (s), 132.8 (s), 129.0 (s), 128.8 (s), 127.7 (s), 126.6 (s), 126.1 (q, *J* = 30.1 Hz), 124.8 (q, *J* = 274.5 Hz), 124.7 (q, *J* = 6.0 Hz), 124.3 (q, *J* = 2.4 Hz), 124.2 (s). GC-MS m/z 196 (M^+).



2-(Trifluoromethyl)pyridine (5a)[10]

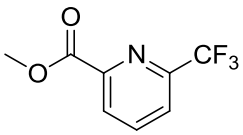
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5a** was produced in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.4 Hz, 1H), 7.89 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.48 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (s), 148.2 (s), 137.4 (s), 126.4 (q, *J* = 1.0 Hz), 121.5 (q, *J* = 275.0 Hz), 120.4 (q, *J* = 2.7 Hz). GC-MS m/z 147 (M^+).



6-(Trifluoromethyl)nicotinaldehyde (5b)[11]

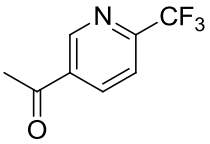
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5b** was

produced in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.22 (s, 1H), 8.39 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3 (s), 152.3 (q, *J* = 35.4 Hz), 151.7 (s), 137.7 (s), 133.1 (q, *J* = 0.9 Hz), 121.0 (q, *J* = 2.7 Hz), 120.9 (q, *J* = 275.8 Hz). HRMS (EI) calcd for $C_7H_4F_3NO$: 175.0245; Found: 175.0246.



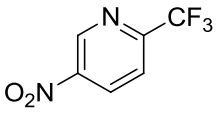
Methyl 6-(trifluoromethyl)picolinate (5c)[12]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5c** was produced in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.98 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (s), 148.6 (s), 148.5 (q, *J* = 35.5 Hz), 138.8 (s), 127.6 (q, *J* = 1.0 Hz), 123.5 (q, *J* = 2.6 Hz), 121.0 (q, *J* = 274.8 Hz), 53.3 (s). GC-MS m/z 205 (M^+).



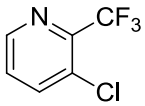
1-(6-(Trifluoromethyl)pyridin-3-yl)ethanone (5d)[13]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5d** was produced in 72% yield. ^{1}H NMR (400 MHz,) δ 9.27 (s, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 2.72 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4 (s), 151.3 (q, *J* = 35.3 Hz), 149.9 (s), 137.2 (s), 134.2 (q, *J* = 0.9 Hz), 121.1 (q, *J* = 275.6 Hz), 120.5 (q, *J* = 2.7 Hz), 27.0 (s). GC-MS m/z 189 (M^+).



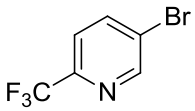
5-Nitro-2-(trifluoromethyl)pyridine (5e) [12]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5e** was produced in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, *J* = 2.3 Hz, 1H), 8.72 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6 (q, *J* = 36.0 Hz), 145.5 (s), 145.4 (s), 133.0 (s), 121.2 (q, *J* = 2.6 Hz), 120.5 (q, *J* = 276.0 Hz). GC-MS m/z 192 (M^+).



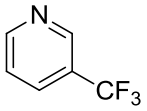
3-Chloro-2-(trifluoromethyl)pyridine (5f)[14]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5f** was produced in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.7 Hz, 1H), 7.91 (d, *J* = 12.7 Hz, 1H), 7.49 (dd, *J* = 8.2, 4.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (s), 144.8 (q, *J* = 34.3 Hz), 139.6 (s), 130.6 (s), 127.3 (s), 121.0 (q, *J* = 276.2 Hz). GC-MS m/z 181 (M^+-H).



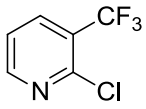
5-Bromo-2-(trifluoromethyl)pyridine (5g)[15]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5g** was produced in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.7 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.7 Hz 1H), 7.61 (d, *J* = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4 (s), 146.7 (q, *J* = 35.7 Hz), 140.1 (s), 124.0 (q, *J* = 1.2 Hz), 121.7 (q, *J* = 2.7 Hz) , 121.3 (q, *J* = 275.1 Hz). GC-MS m/z 226 (M^+).



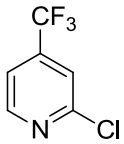
3-(Trifluoromethyl)pyridine (5h) [9]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5h** was produced in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.82 (d, *J* = 4.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.40 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0 (q, *J* = 1.5 Hz), 146.7 (q, *J* = 4.1 Hz), 133.0 (q, *J* = 3.6 Hz), 126.8 (q, *J* = 33.0 Hz), 123.4 (q, *J* = 273.4 Hz), 123.3 (s). GC-MS m/z 147 (M^+).



2-Chloro-3-(trifluoromethyl)pyridine (5i) [15]

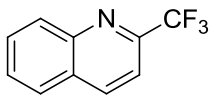
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5i** was produced in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.8 Hz, 1H), 8.04 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.45 – 7.35 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3 (q, *J* = 1.2 Hz), 149.1 (q, *J* = 1.6 Hz), 136.6 (q, *J* = 5.0 Hz), 125.5 (q, *J* = 33.4 Hz), 122.1 (q, *J* = 273.8 Hz), 122.0 (s). GC-MS m/z 182 (M^++H).



2-Chloro-4-(trifluoromethyl)pyridine (5j) [15]

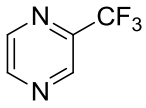
Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5j** was produced in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.1 Hz, 1H), 7.58 (s, 1H), 7.46 (d, *J* = 5.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, 3F). ^{13}C NMR (101

MHz, $CDCl_3$) δ 152.7 (s), 150.9 (s), 141.0 (q, *J* = 34.8 Hz), 122.0 (q, *J* = 274.7 Hz), 120.6 (q, *J* = 3.9 Hz), 118.1 (q, *J* = 3.4 Hz). GC-MS m/z 182 (M^++H).



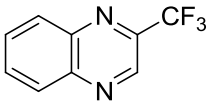
2-Chloro-4-(trifluoromethyl)pyridine (5k) [3]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5k** was produced in 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.79 – 7.75 (d, *J* = 8.5 Hz, 1H), 7.71 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.5 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9 (q, *J* = 34.7 Hz), 147.2 (s), 138.1 (s), 130.8 (s), 130.1 (s), 128.9 (q, *J* = 0.8 Hz), 128.6 (s), 127.7 (s), 121.7 (q, *J* = 276.1 Hz), 116.8 (d, *J* = 2.2 Hz). GC-MS m/z 197 (M^+).



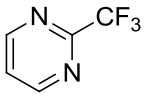
2-(Trifluoromethyl)pyrazine (5l) [10]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5l** was produced in 73% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.86 (d, *J* = 2.4 Hz, 1H), 8.77 – 8.73 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8 (q, *J* = 1.3 Hz), 147.7 (q, *J* = 1.7 Hz), 144.4 (s), 141.9 (q, *J* = 3.2 Hz), 121.0 (q, *J* = 275.4 Hz). GC-MS m/z 149 (M^++H).



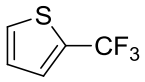
2-(Trifluoromethyl)quinoxaline (5m) [12]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5m** was produced in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.30 – 8.20 (m, 2H), 8.03 – 7.87 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.0 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7 (q, *J* = 1.0 Hz), 142.8 (q, *J* = 35.4 Hz), 141.0 – 140.7 (m), 132.3 (s), 131.5 (s), 130.0 (s), 129.5 (s), 121.1 (q, *J* = 276.5 Hz). GC-MS m/z 198 (M^+).



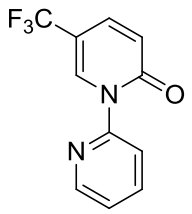
2-(Trifluoromethyl)pyrimidine (5n)[16]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5n** was produced in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 4.9 Hz, 2H), 7.56 (t, *J* = 4.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (s), 157.0 (q, *J* = 37.0 Hz), 123.2 (s) , 119.4 (q, *J* = 276.6 Hz). GC-MS m/z 148 (M^+).



2-(Trifluoromethyl)thiophene (5o)[17]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **5o** was produced in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.13 – 7.05 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4 (q, *J* = 38.3 Hz), 128.9 (q, *J* = 1.3 Hz), 128.5 (q, *J* = 3.7 Hz), 126.8 (s), 122.6 (d, *J* = 269.4 Hz). GC-MS m/z 151 (M^+-H).



5-(Trifluoromethyl)-2*H*-[1,2'-bipyridin]-2-one (7)[18]

Quantitative ^{19}F NMR analysis of the reaction mixture indicated that **7** was produced in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.6 Hz, 1H), 8.43 – 8.32 (m, 1H), 8.03 – 7.86 (m, 2H), 7.54 (d, *J* = 9.6 Hz, 1H), 7.44 – 7.36 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (s), 150.8 (s), 149.1 (s), 138.1 (s), 136.0 (q, *J* = 5.7 Hz), 135.5 (q, *J* = 2.3 Hz), 123.8 (s), 123.3 (q, *J* = 269.8 Hz), 122.7 (s), 121.1 (s), 110.4 (q, *J* = 35.0 Hz). GC-MS m/z 240 (M^+).

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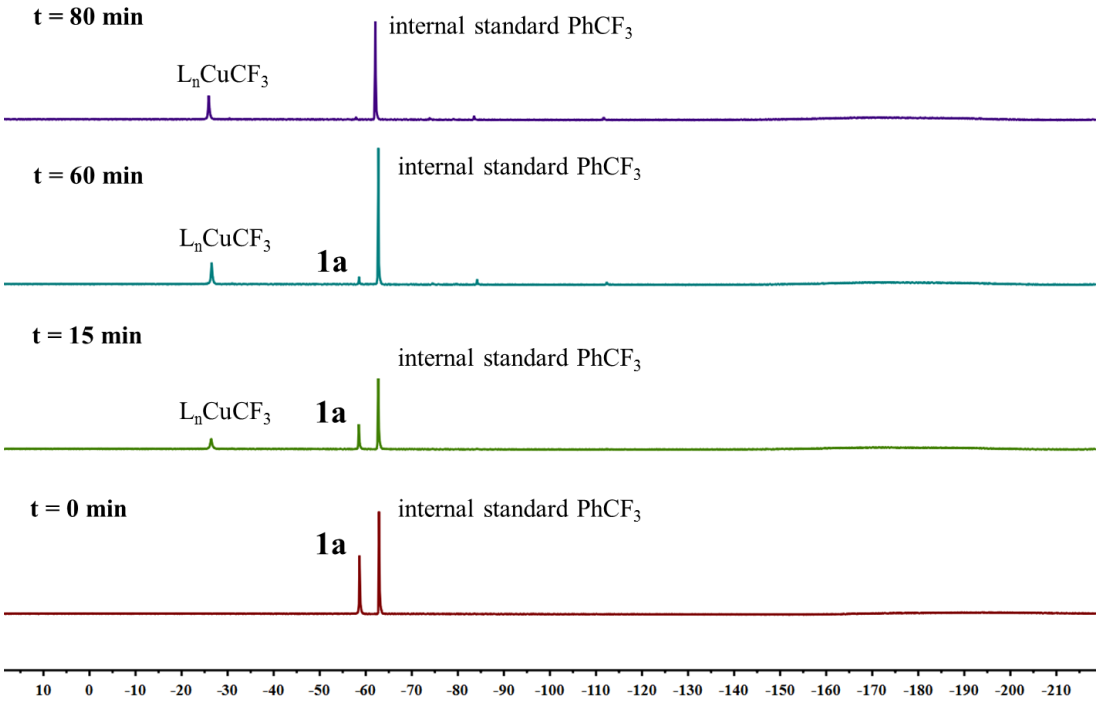
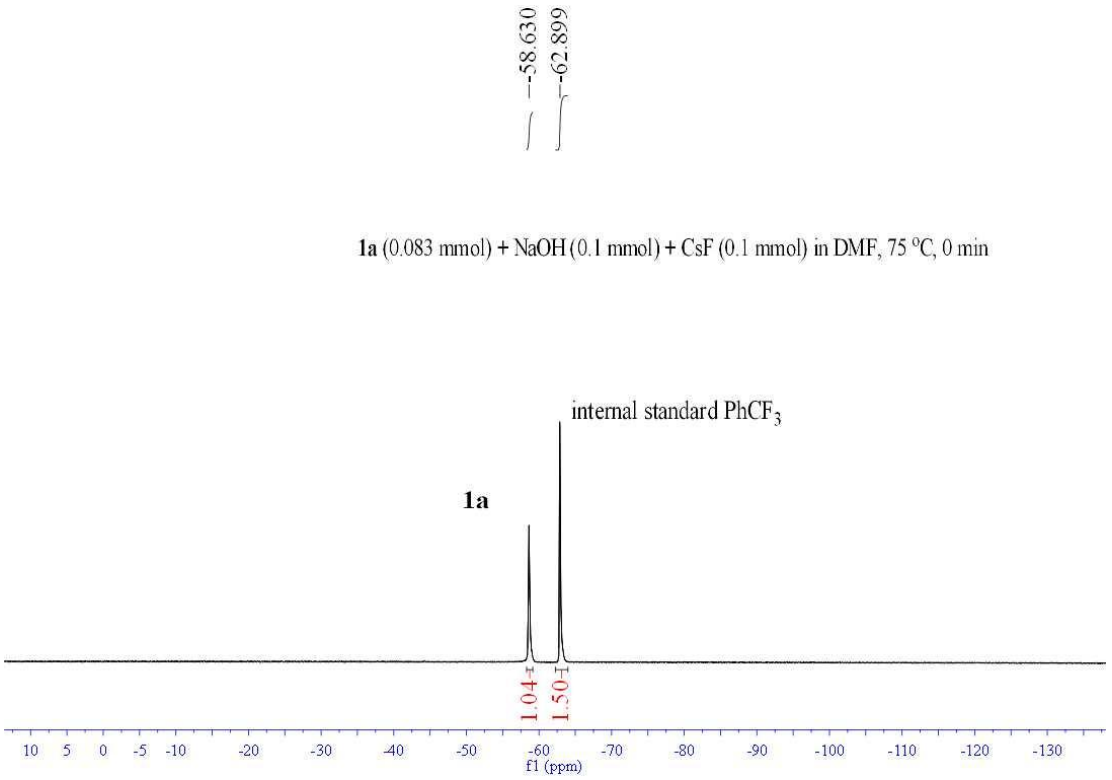
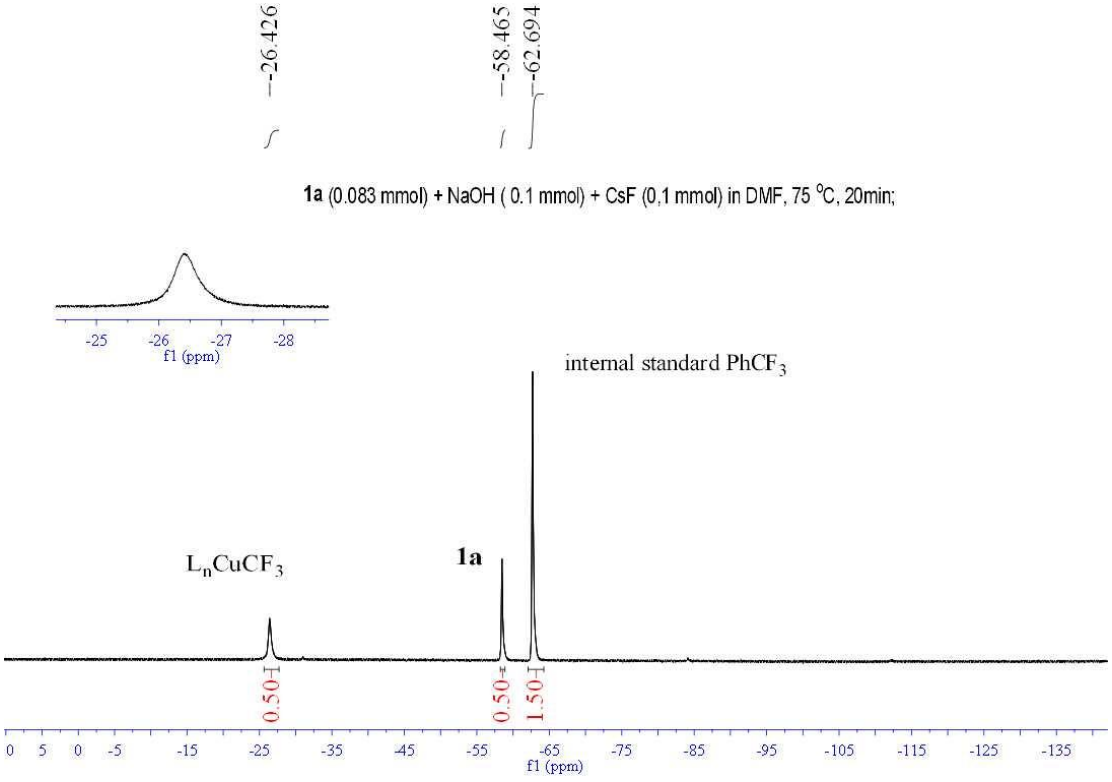
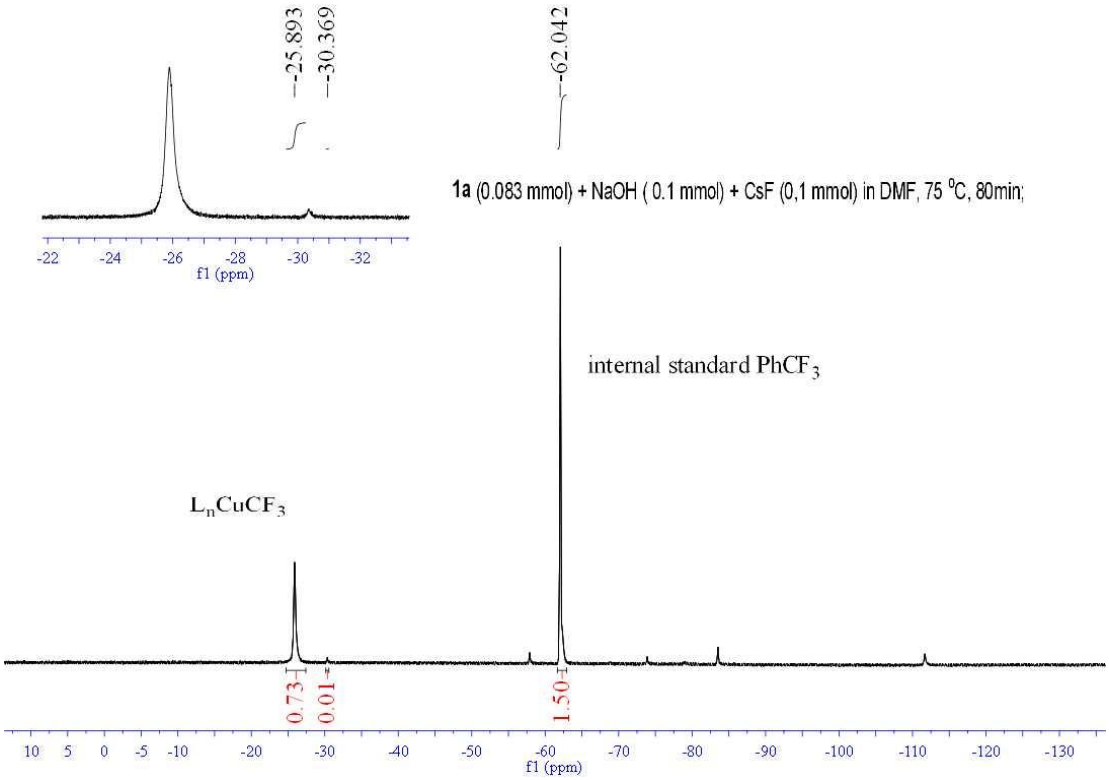
Generation of L_nCuCF_3 species from reaction of 1a with CsF in the presence of NaOH in DMF at 75 ℃.

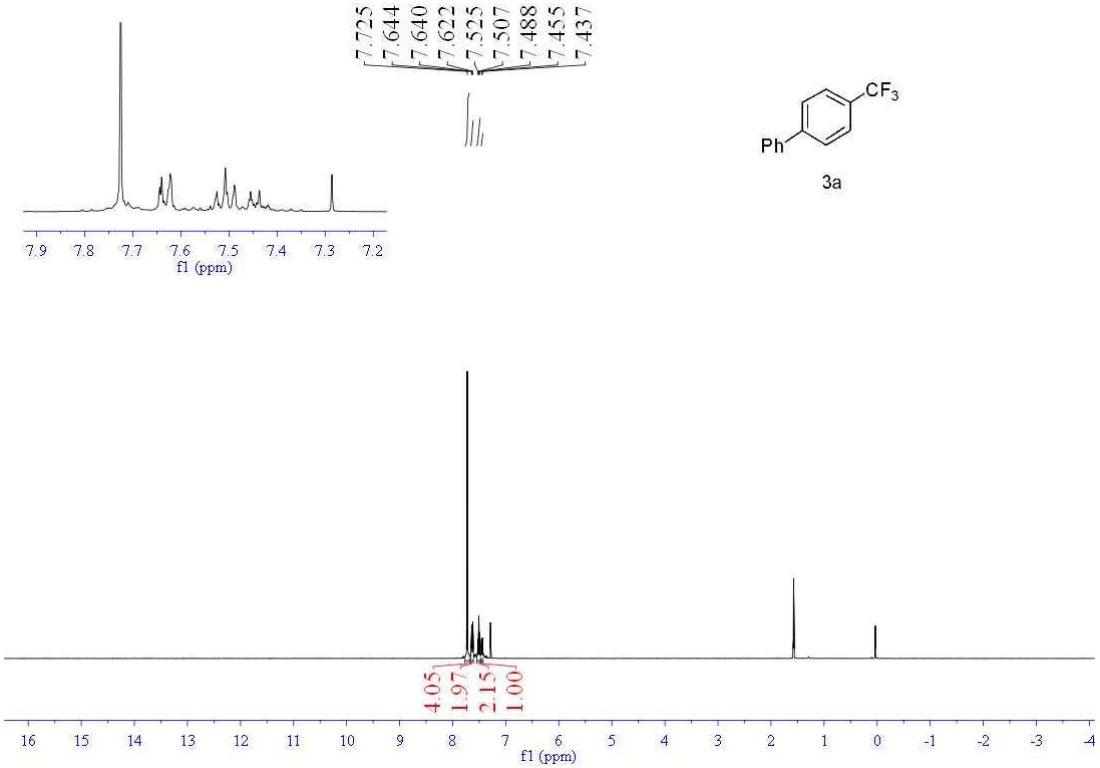



-58.630
-62.899
1a (0.083 mmol) + NaOH (0.1 mmol) + CsF (0.1 mmol) in DMF, 75 °C, 0 min
internal standard PhCF3
1a
1.04
1.50
10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

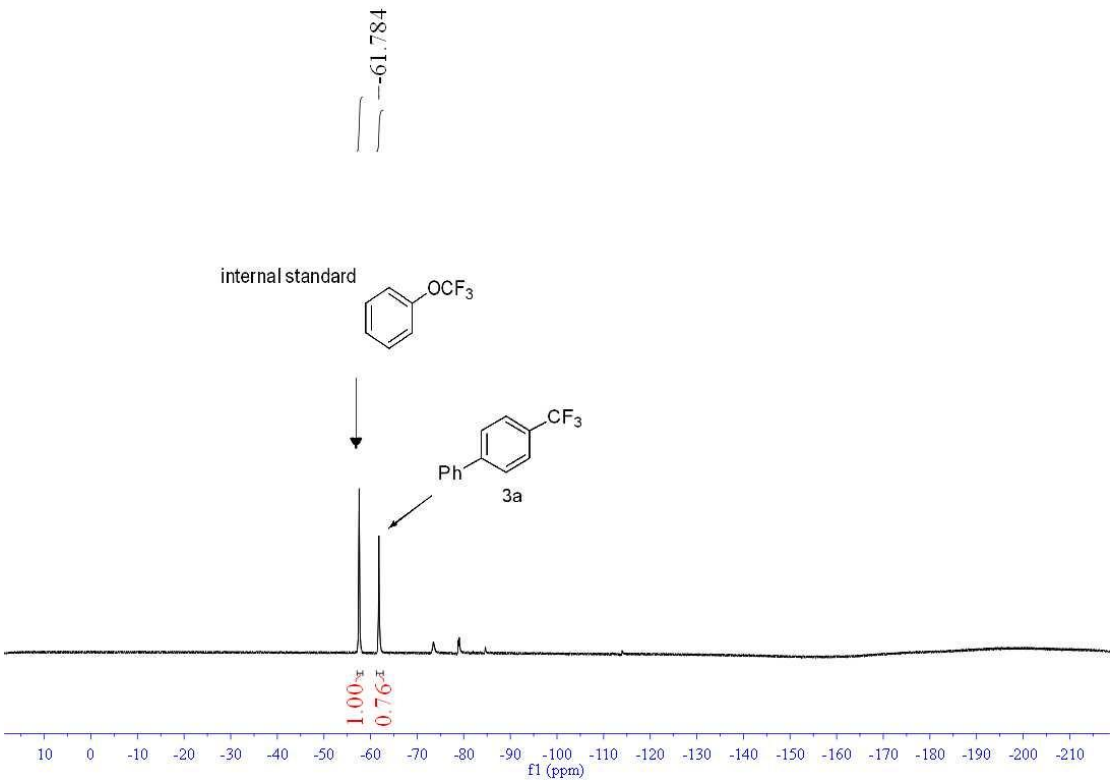

-26.426
-58.465
-62.694
1a (0.083 mmol) + NaOH (0.1 mmol) + CsF (0,1 mmol) in DMF, 75 °C, 20min;
-25 -26 -27 -28
f1 (ppm)
internal standard PhCF3
LnCuCF3
1a
0.50
0.50
1.50
0 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135
f1 (ppm)


-25.893
-30.369
-62.042
1a (0.083 mmol) + NaOH (0.1 mmol) + CsF (0,1 mmol) in DMF, 75 °C, 80min;
f1 (ppm)
internal standard PhCF3
LnCuCF3
0.73
0.01
1.50
f1 (ppm)

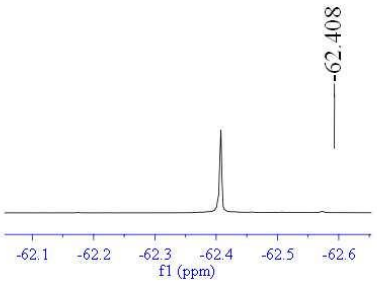
^{1}H NMR spectrum of **3a** in $CDCl_3$

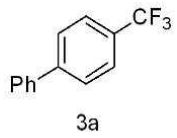


^{19}F NMR spectrum of **3a** (unlocked)

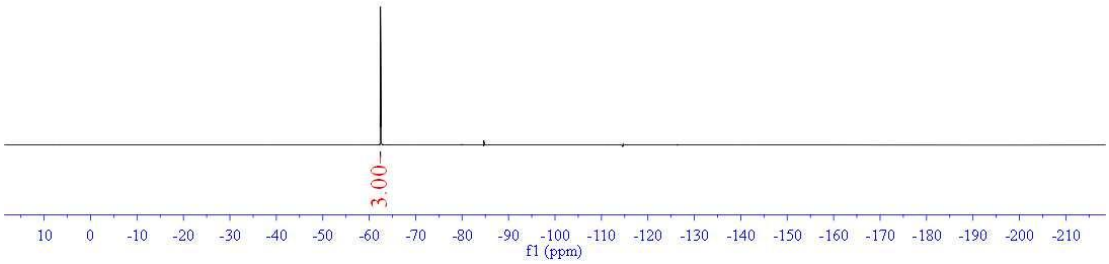


^{19}F NMR spectrum of **3a** in $CDCl_3$

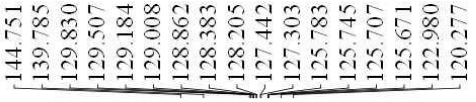


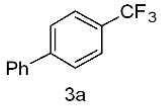


3a

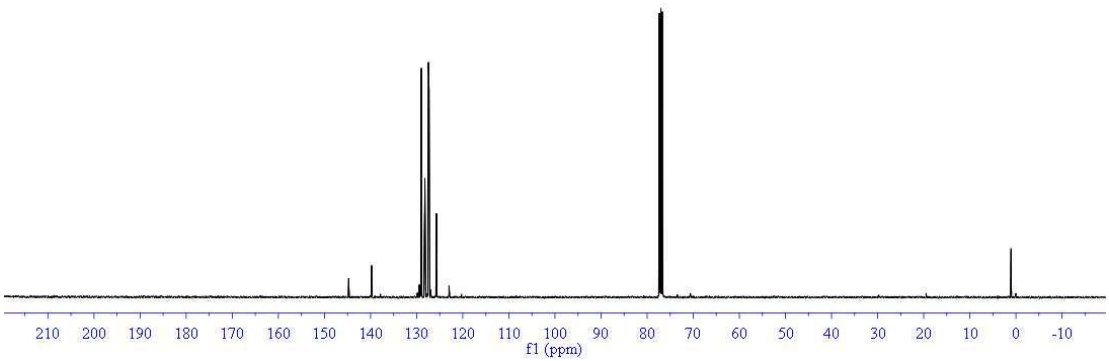


^{13}C NMR spectrum of **3a** in $CDCl_3$

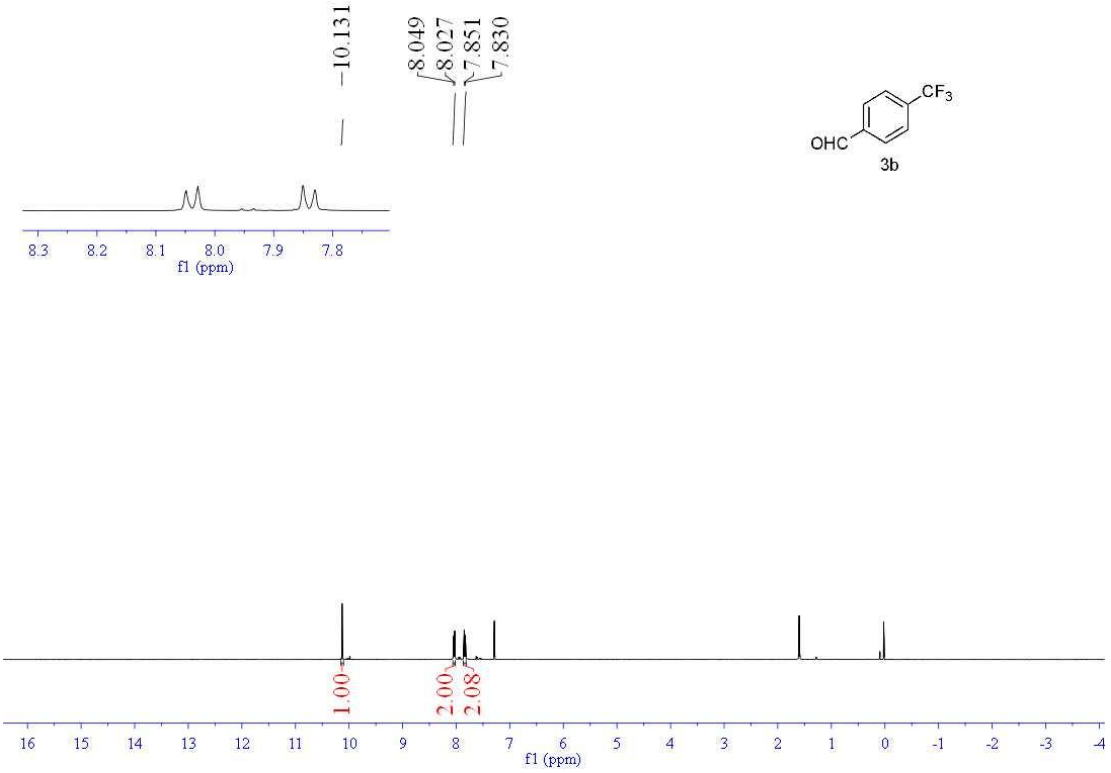




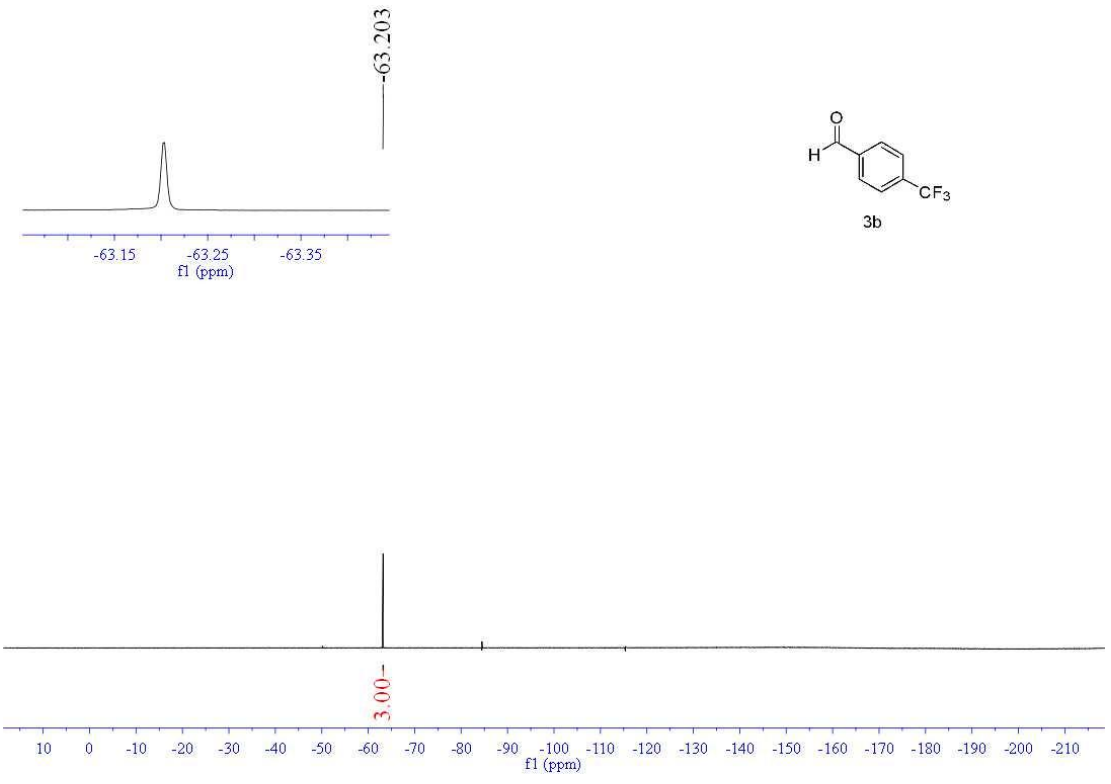
3a



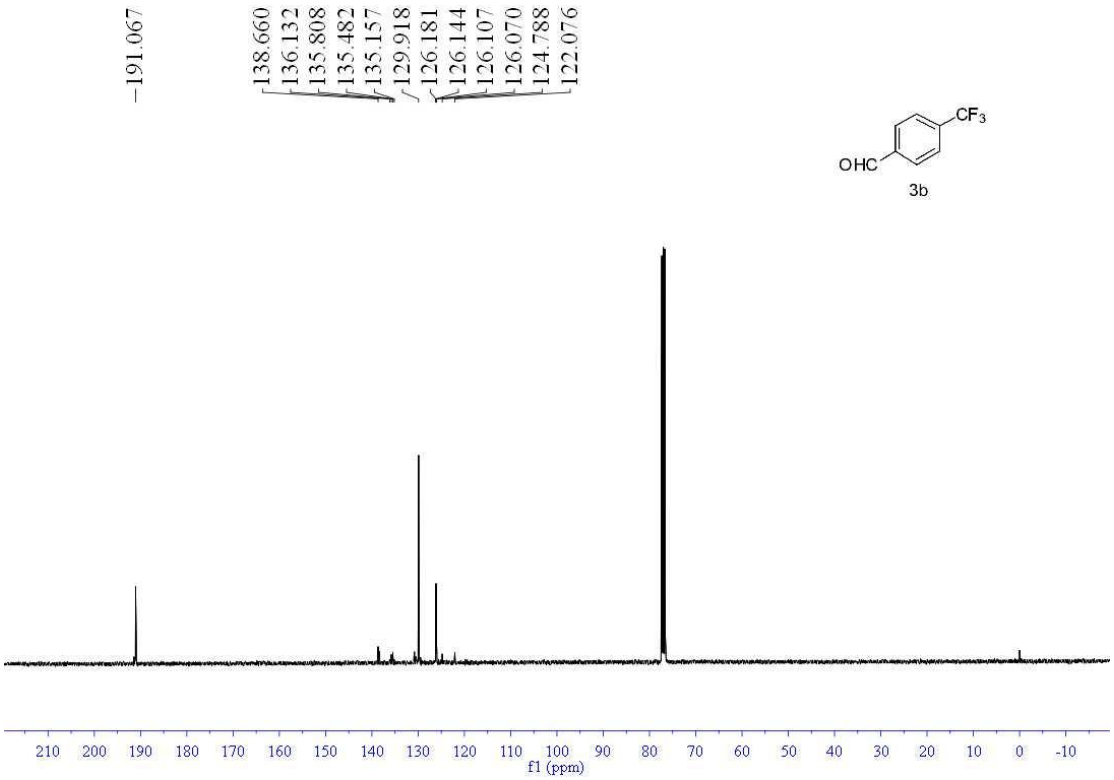
^{1}H NMR spectrum of **3b** in $CDCl_3$



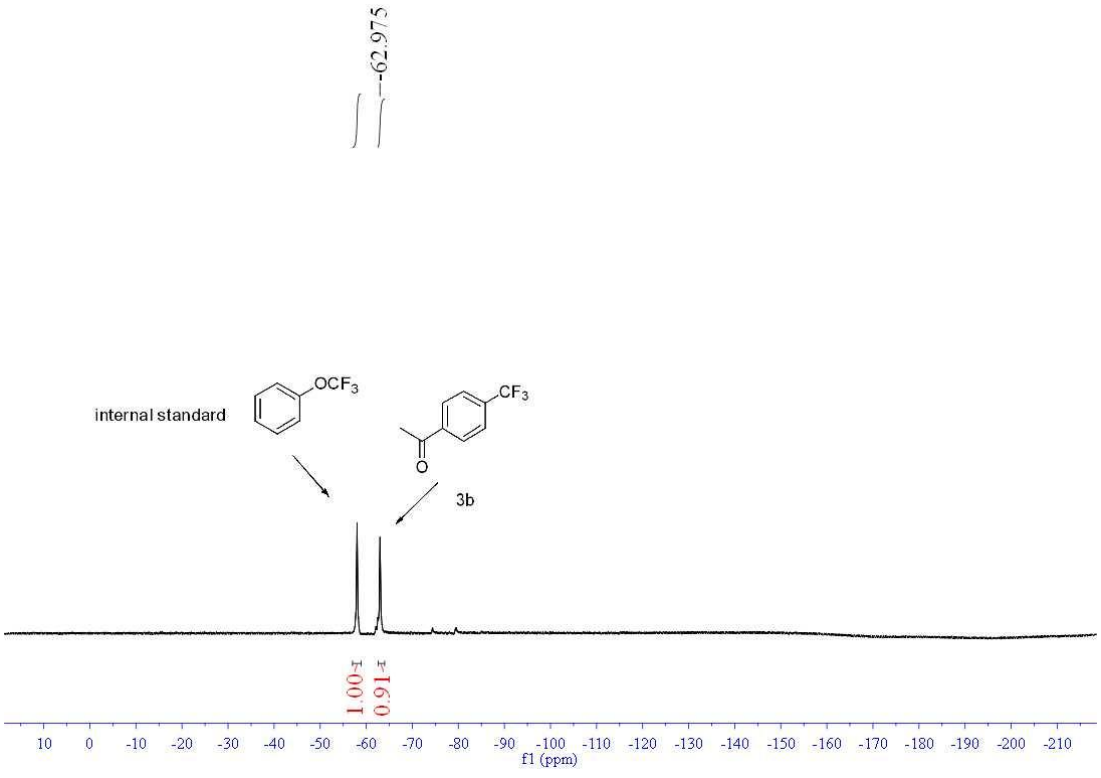
^{19}F NMR spectrum of **3b** in $CDCl_3$



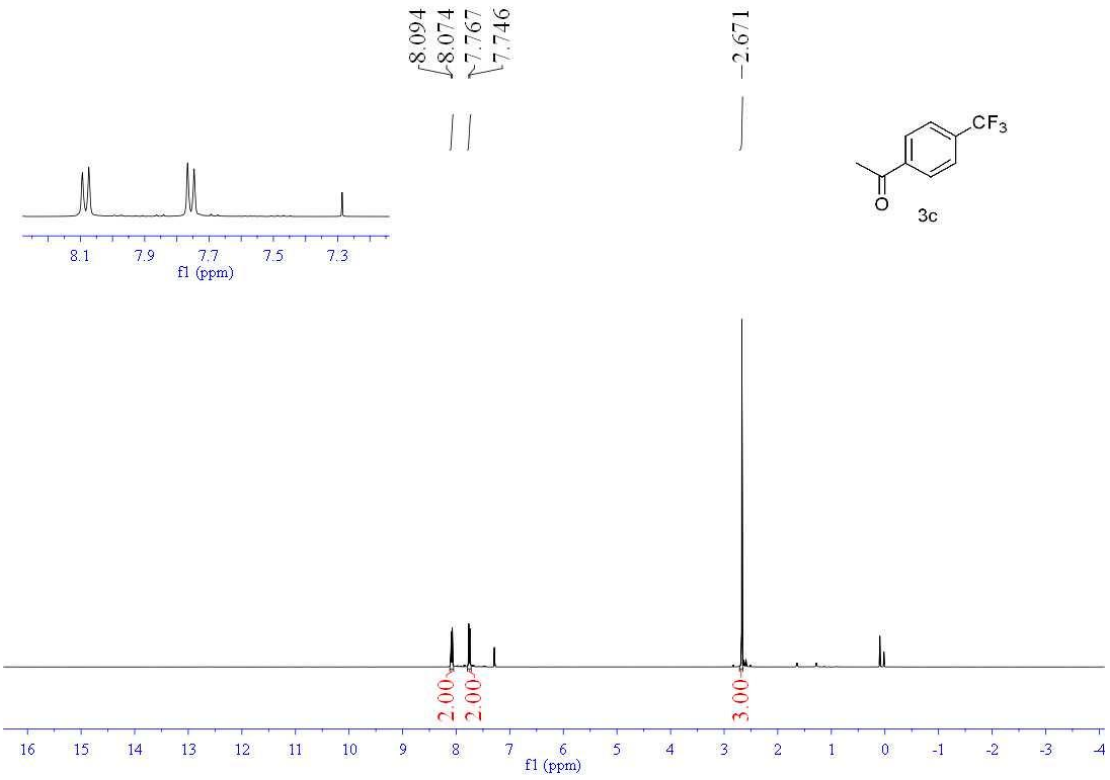
^{13}C NMR spectrum of **3b** in $CDCl_3$



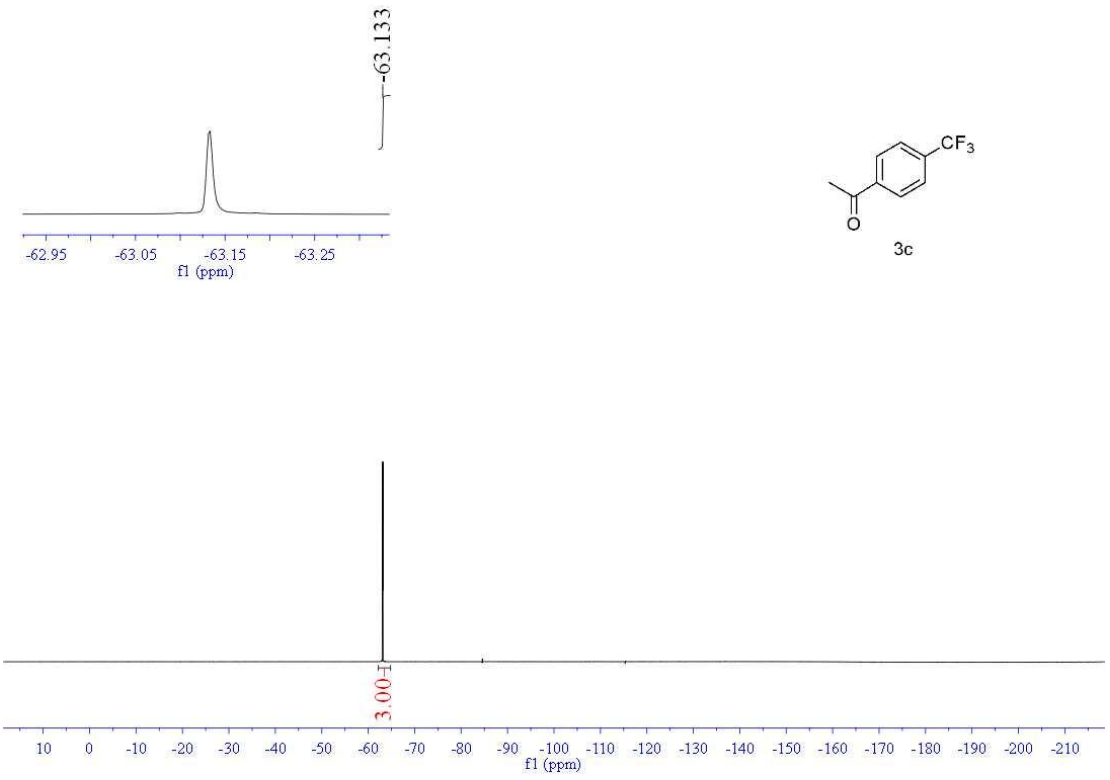
^{19}F NMR spectrum of **3b** (unlocked)



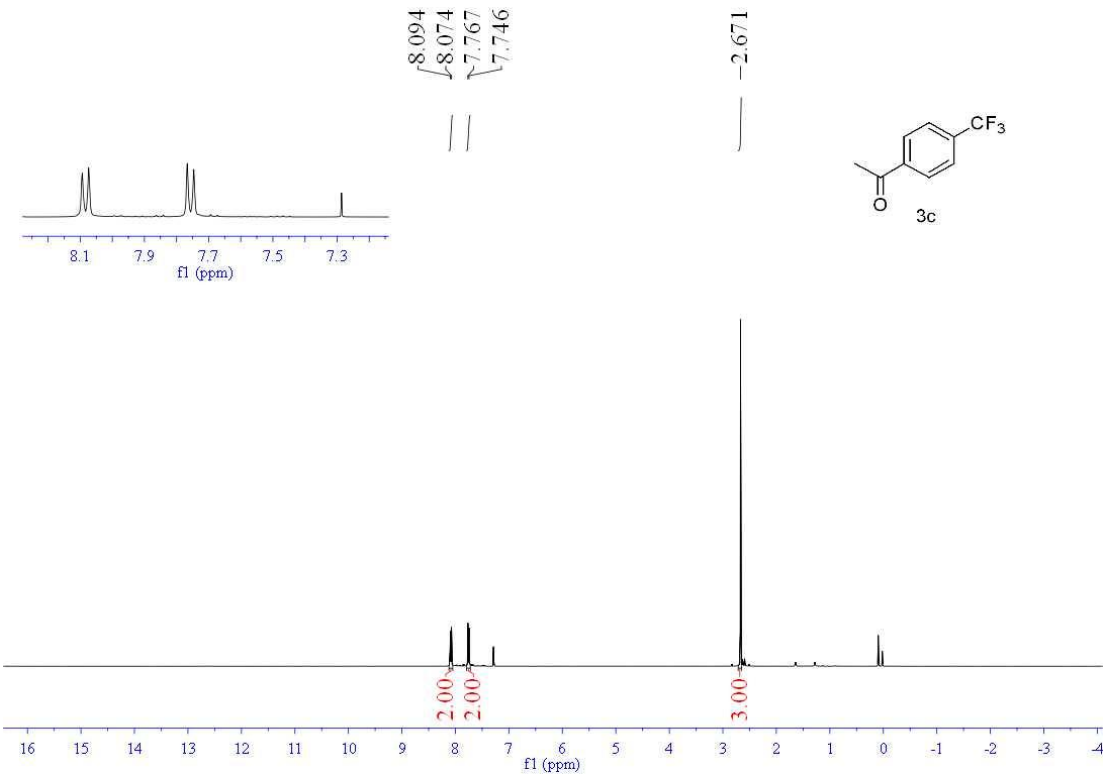
^{1}H NMR spectrum of **3c** in $CDCl_3$



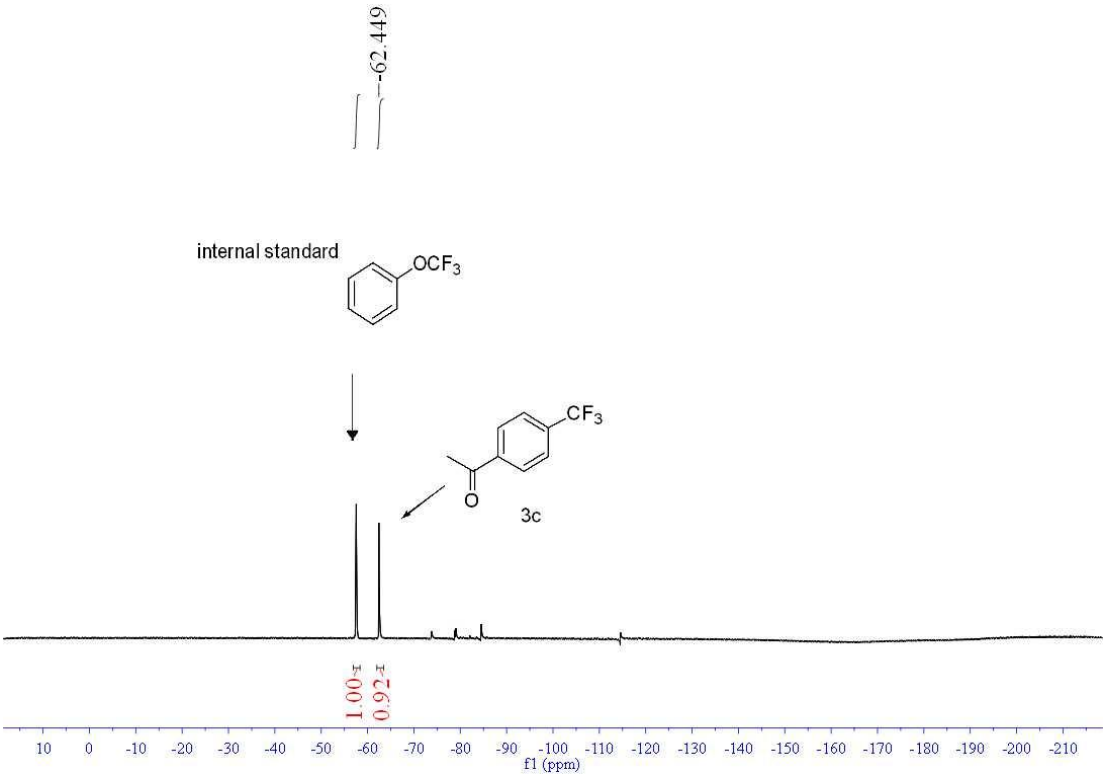
^{19}F NMR spectrum of **3c** in $CDCl_3$



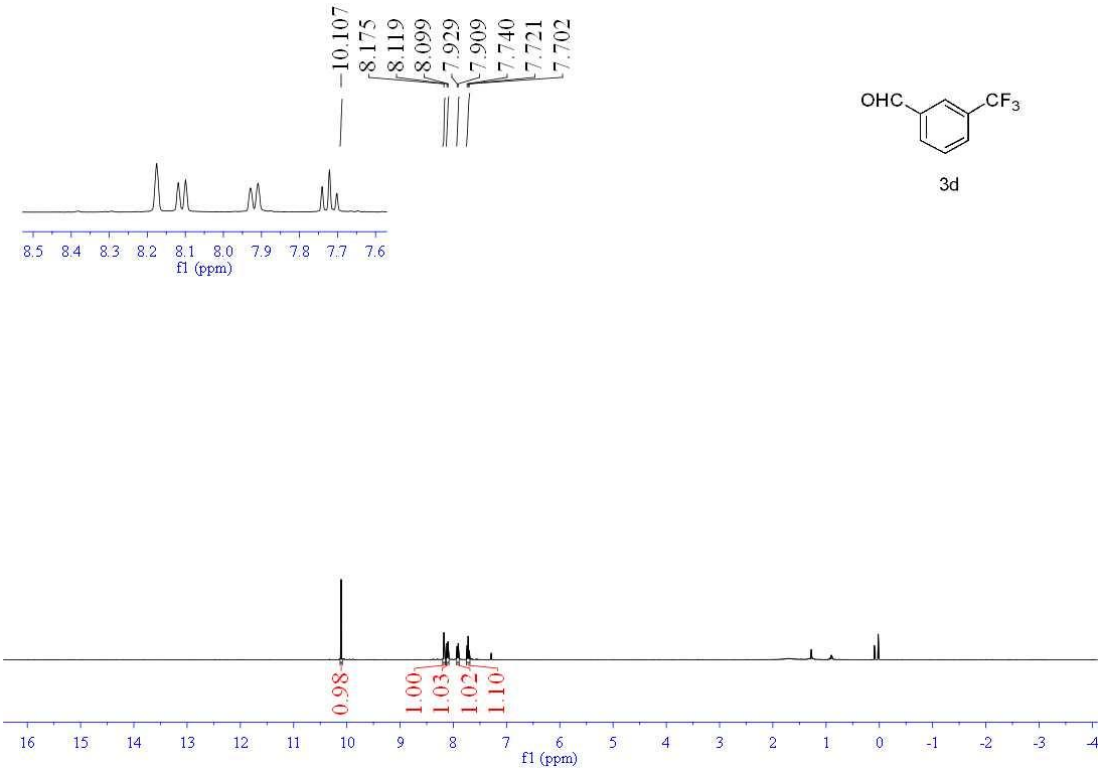
^{13}C NMR spectrum of **3c** in $CDCl_3$



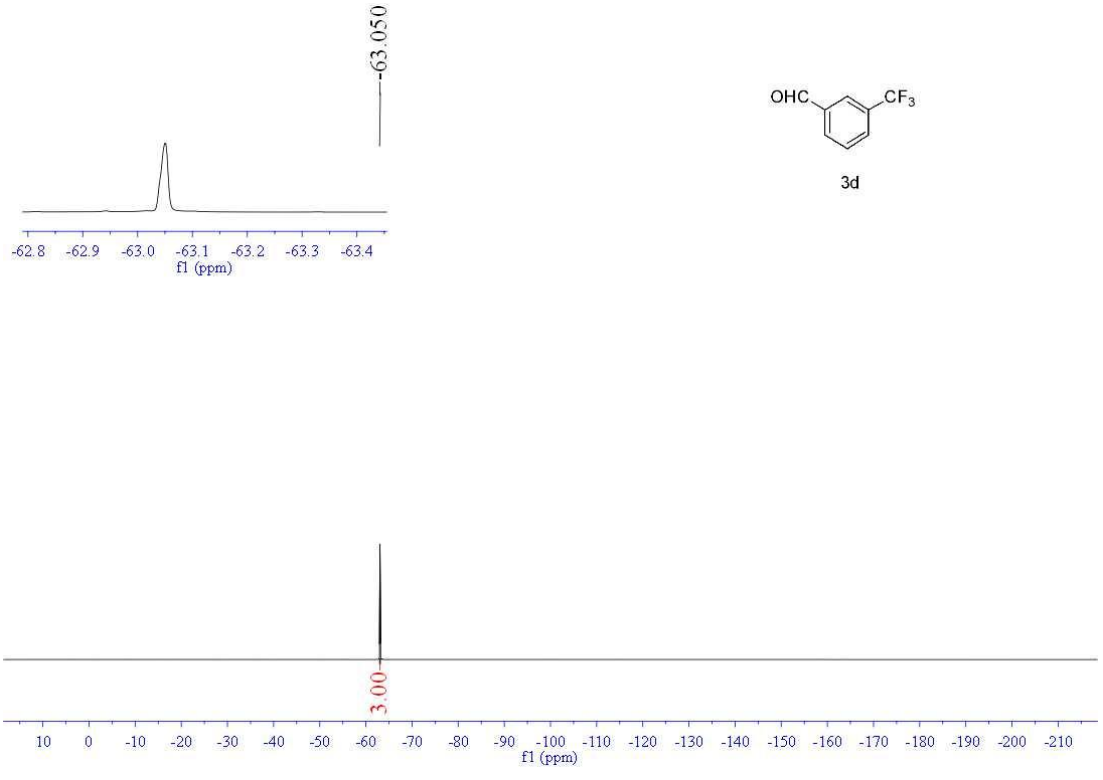
^{19}F NMR spectrum of **3c** (unlocked)



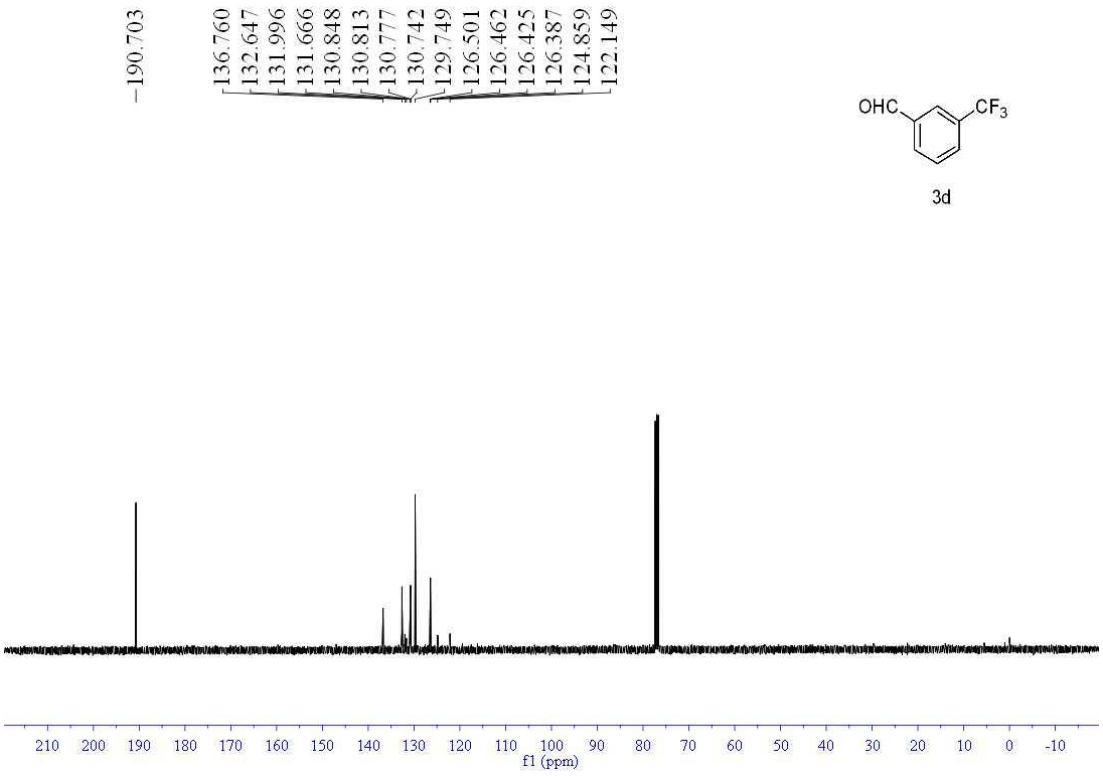
^{1}H NMR spectrum of **3d** in $CDCl_3$



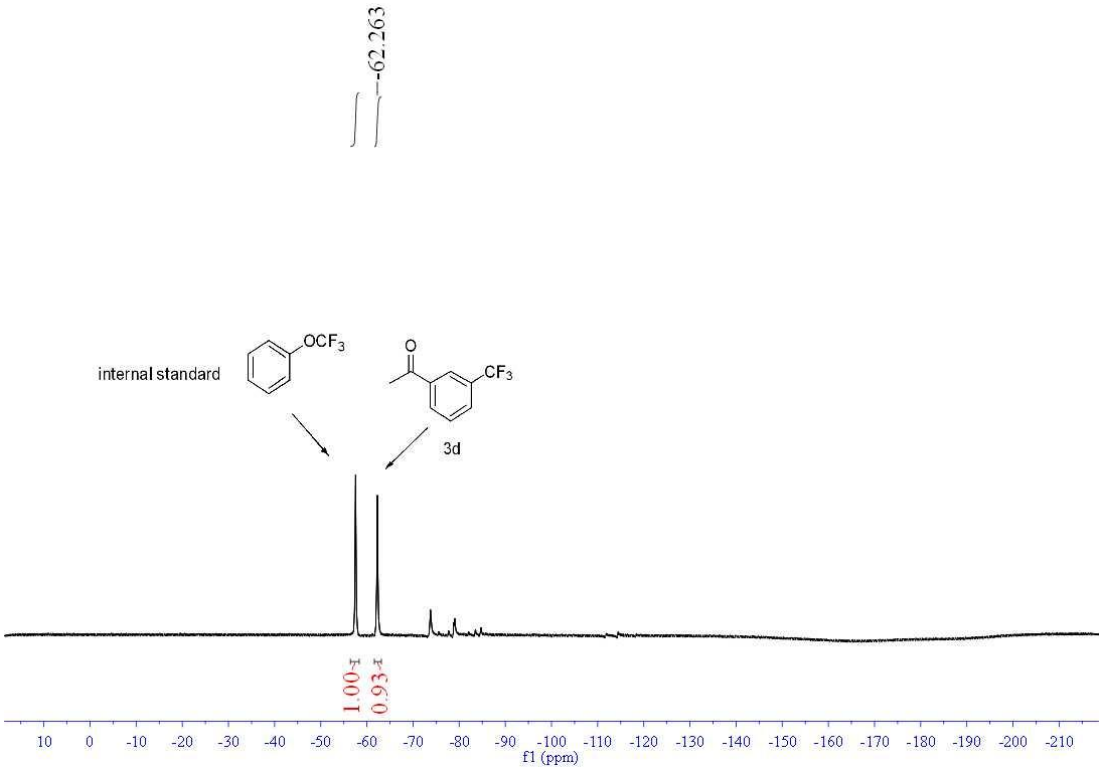
^{19}F NMR spectrum of **3d** in $CDCl_3$



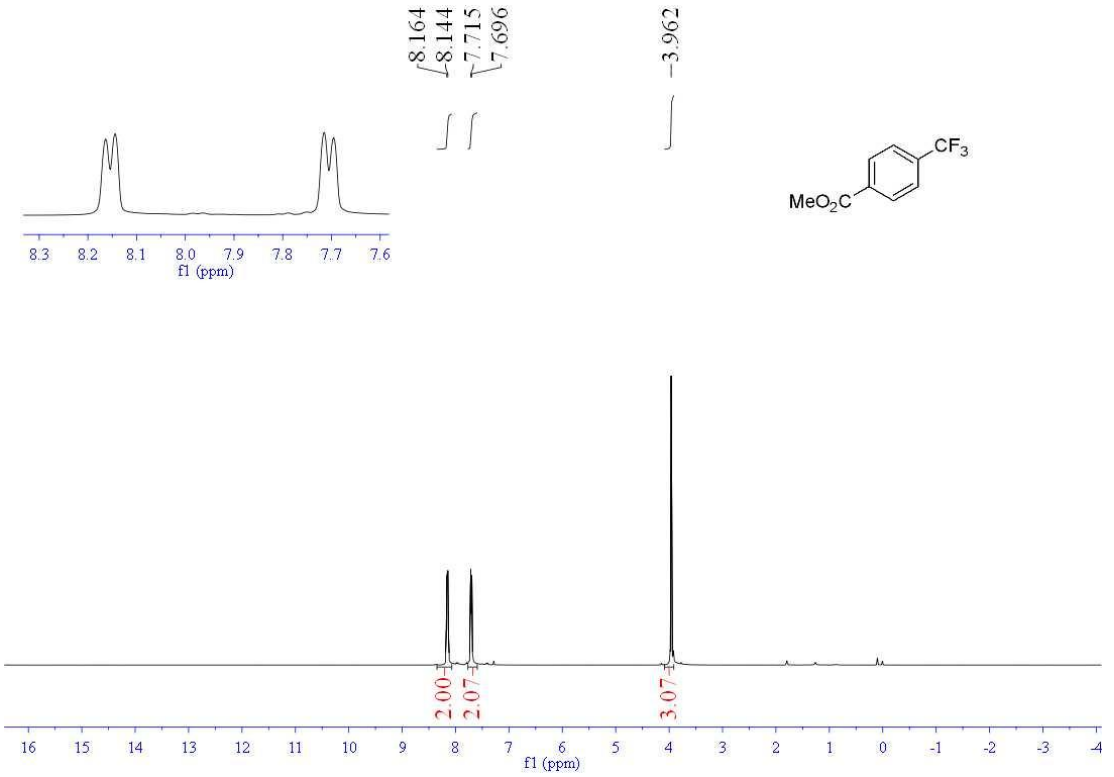
^{13}C NMR spectrum of **3d** in $CDCl_3$



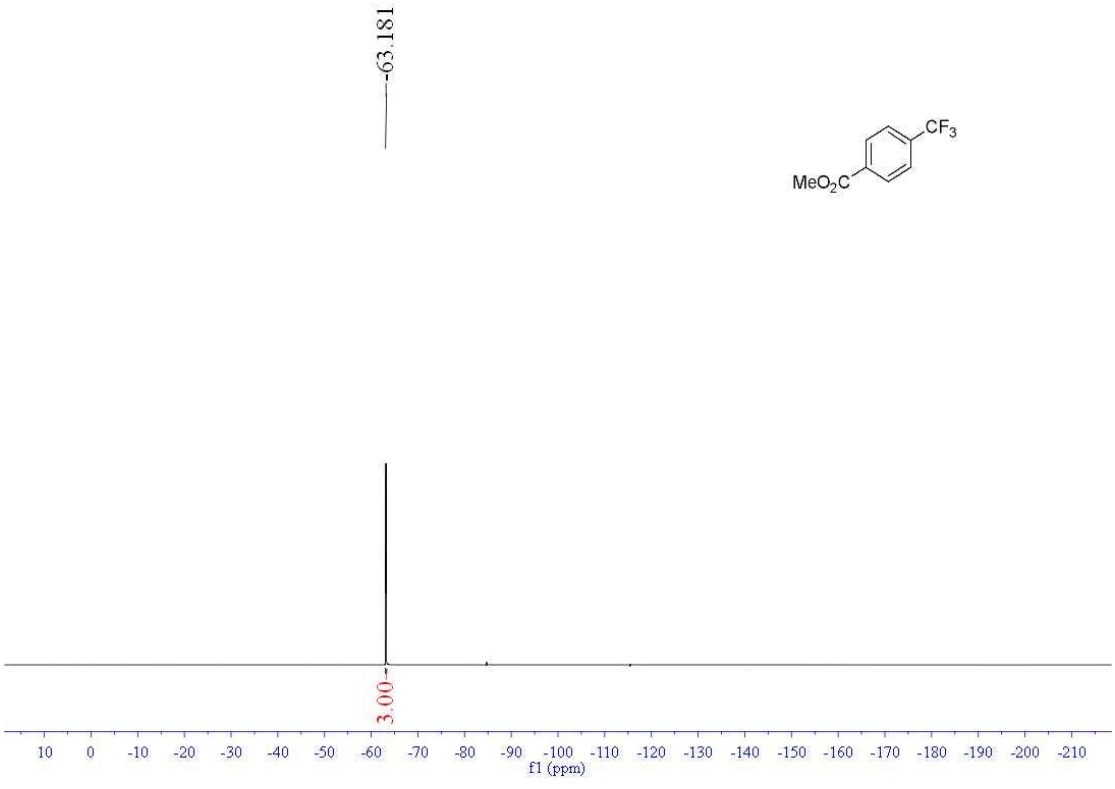
^{19}F NMR spectrum of **3d** (unlocked)



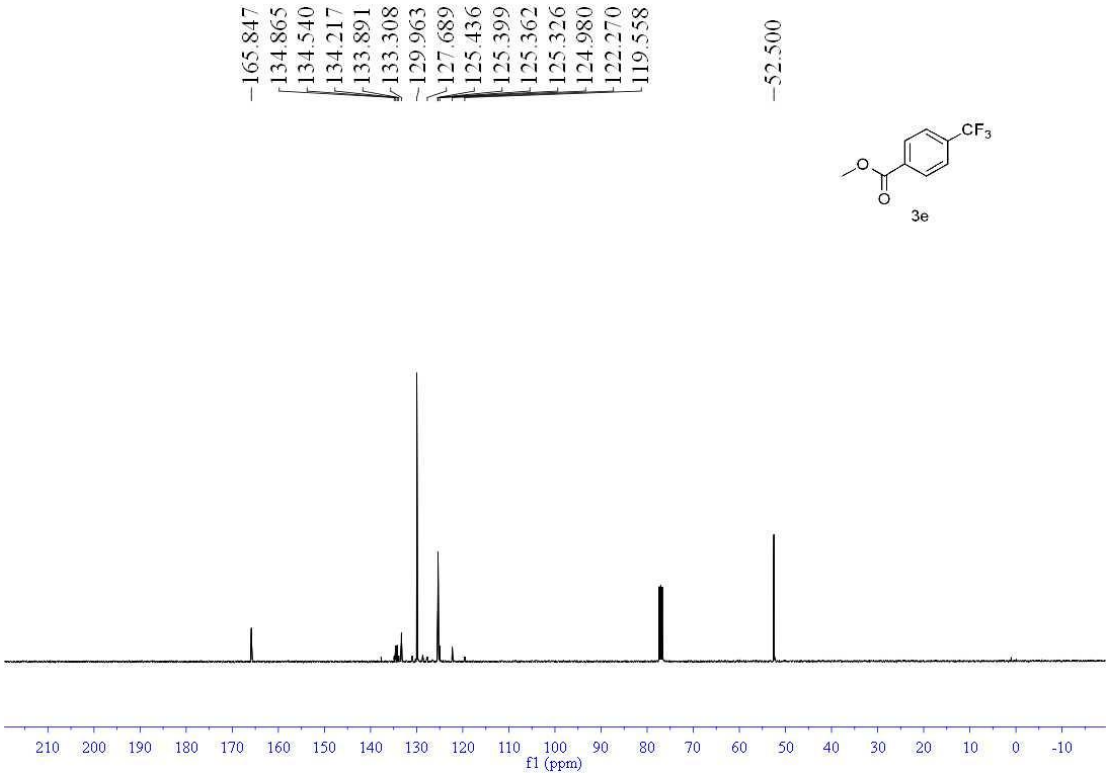
^{1}H NMR spectrum of **3e** in $CDCl_3$



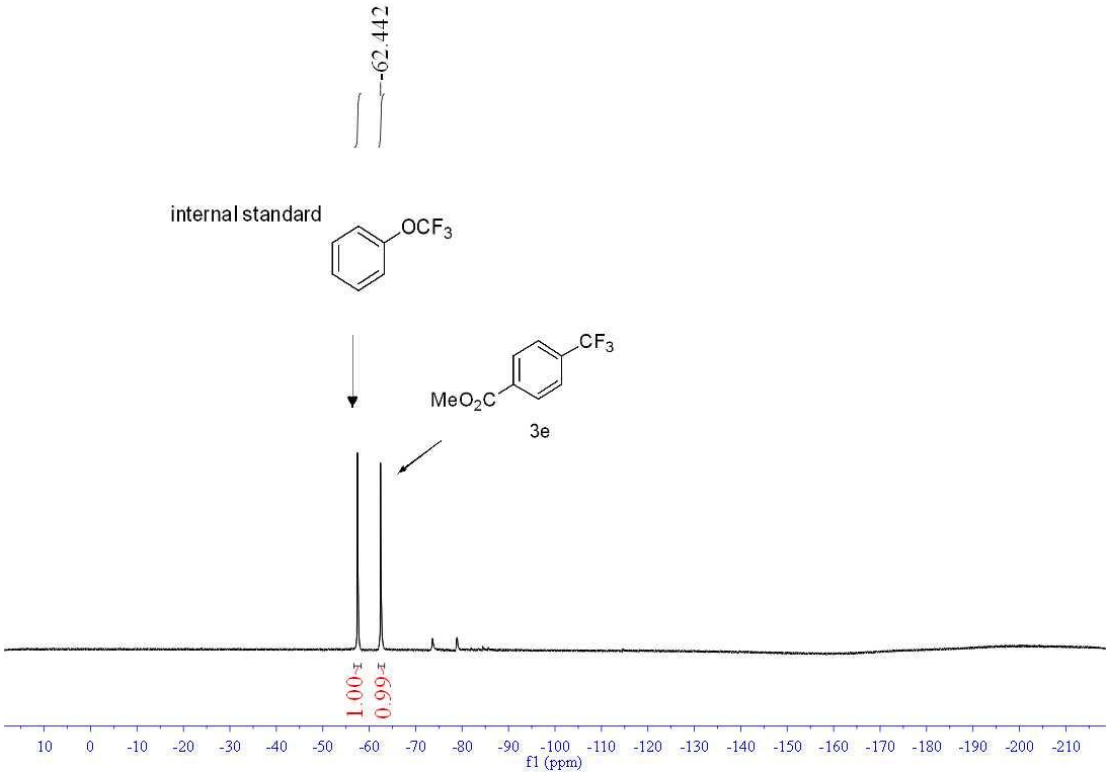
^{19}F NMR spectrum of **3e** in $CDCl_3$



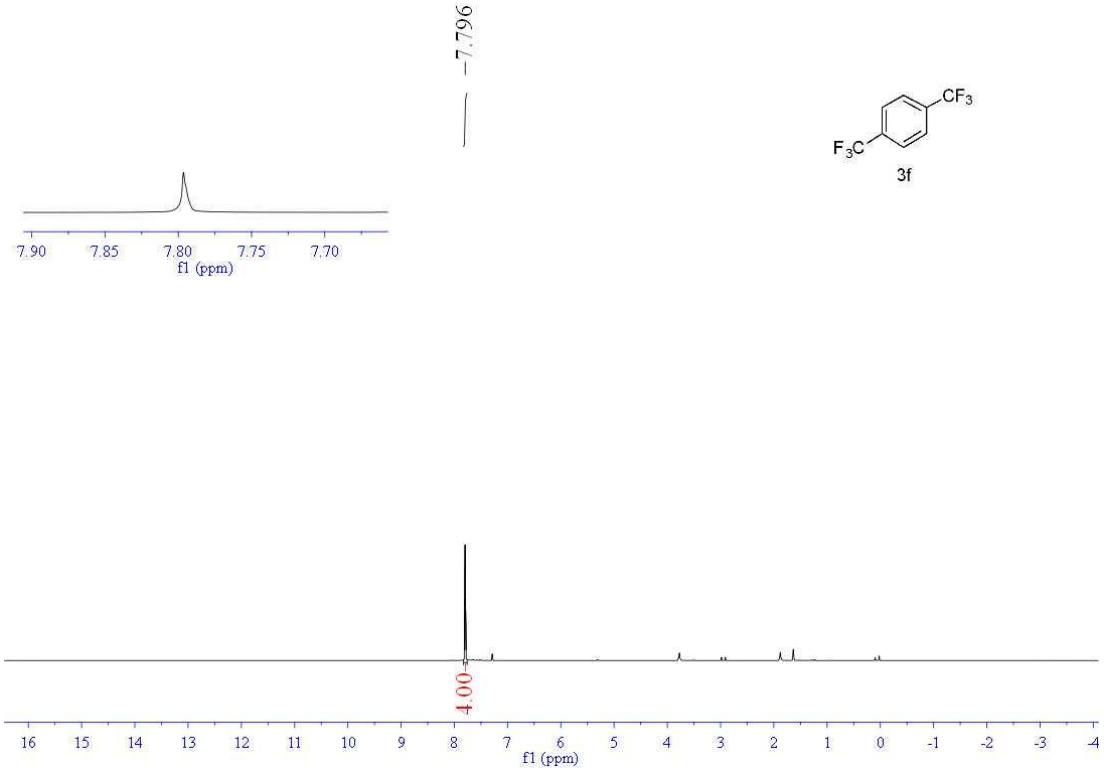
^{13}C NMR spectrum of **3e** in $CDCl_3$



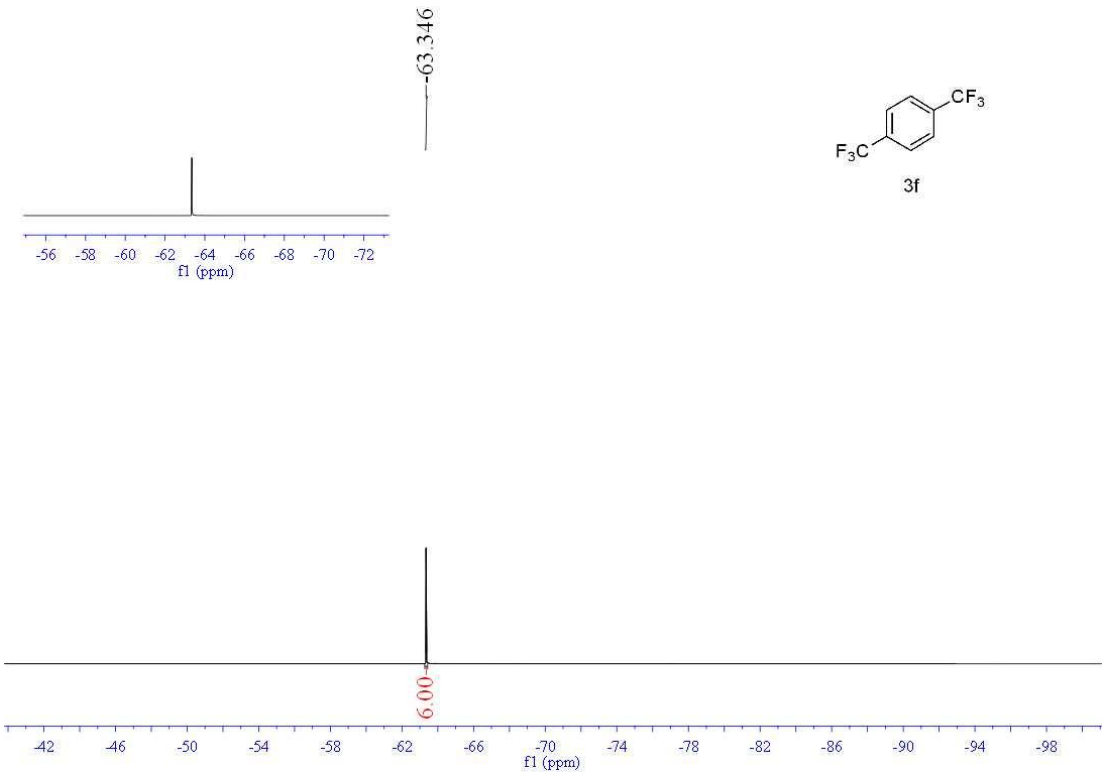
^{19}F NMR spectrum of **3e** (unlocked)



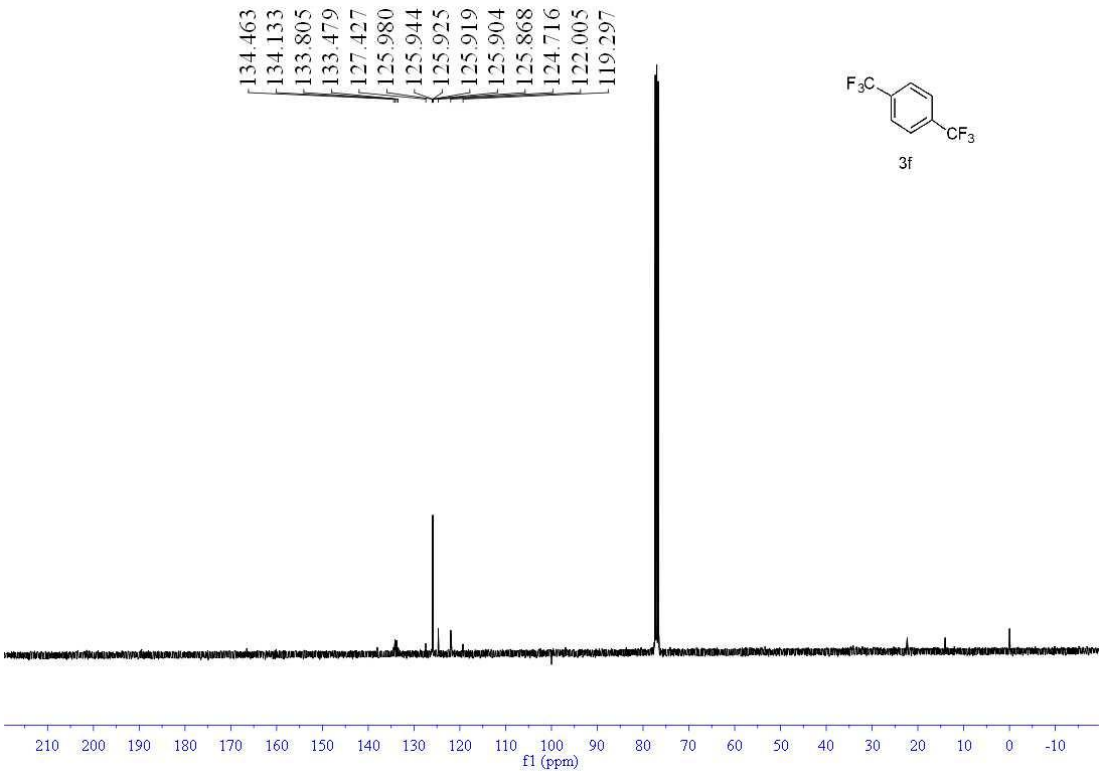
^{1}H NMR spectrum of **3f**



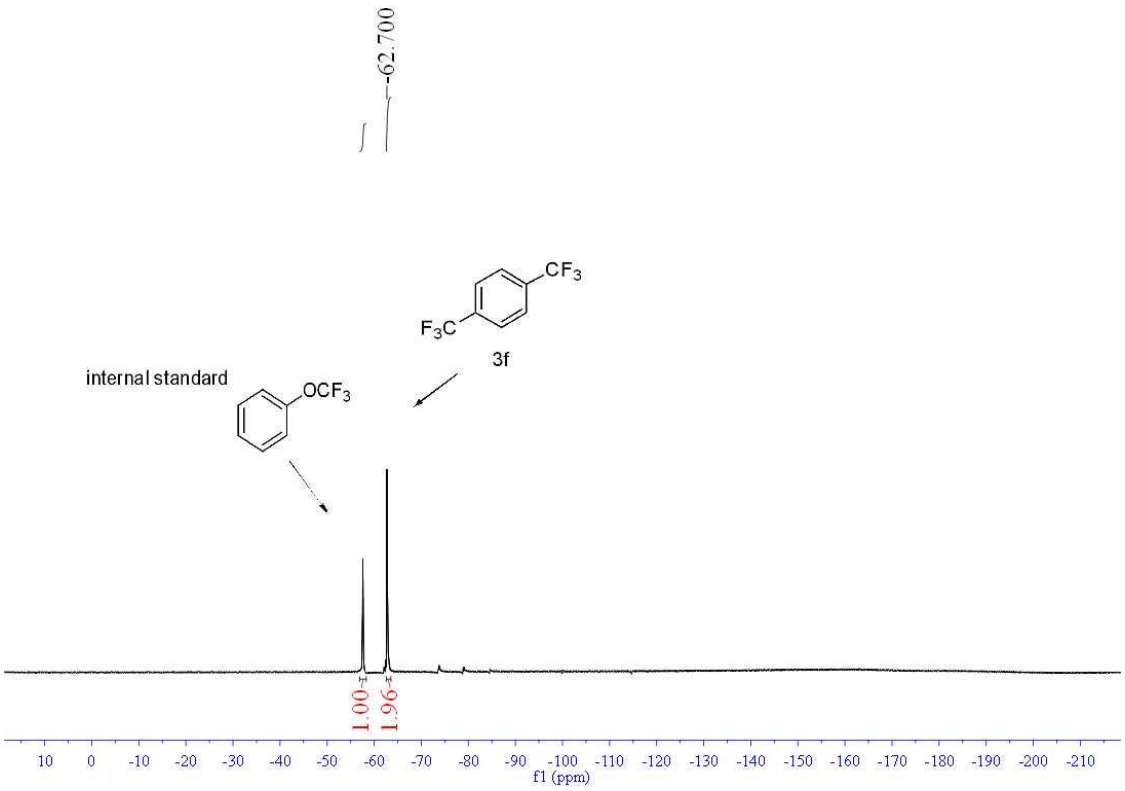
^{19}F NMR spectrum of **3f**



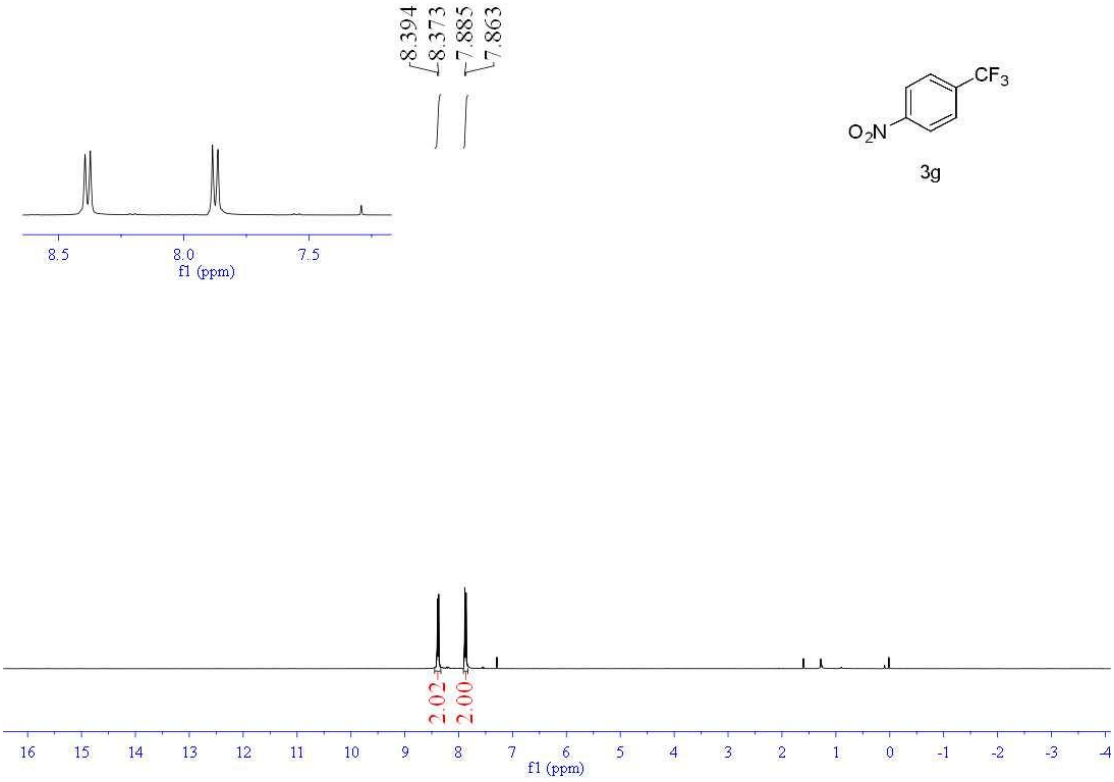
^{13}C NMR spectrum of **3f**



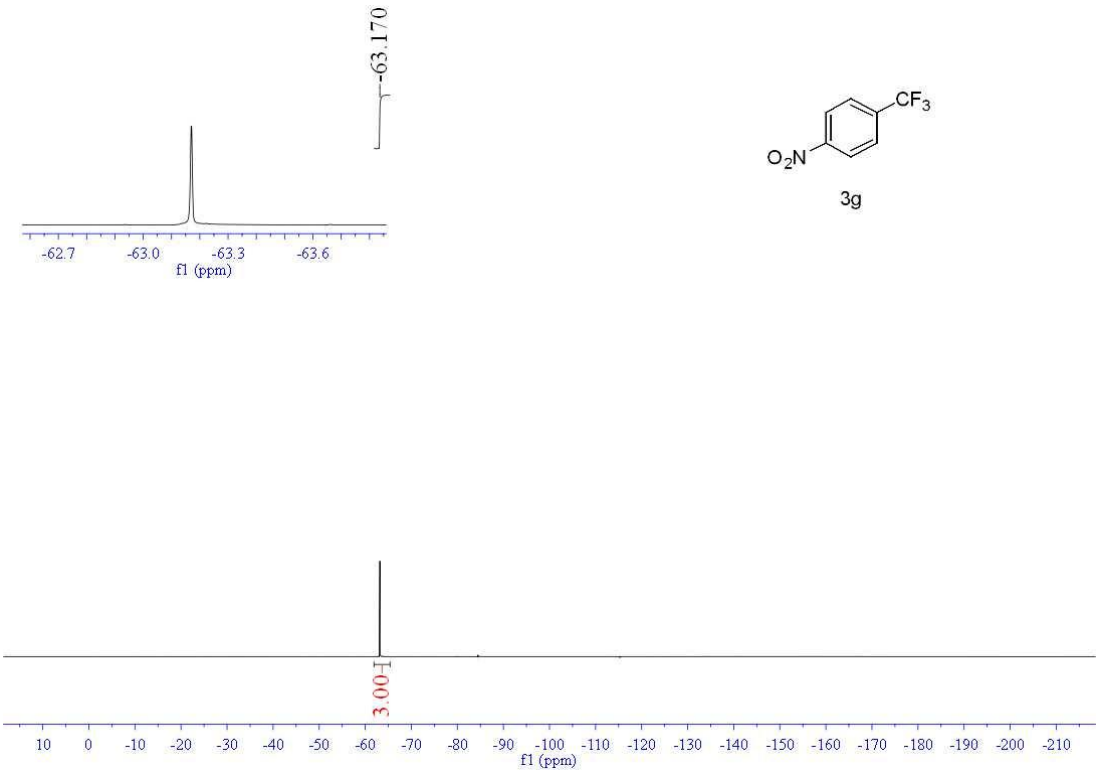
^{19}F NMR spectrum of **3f** (unlocked)



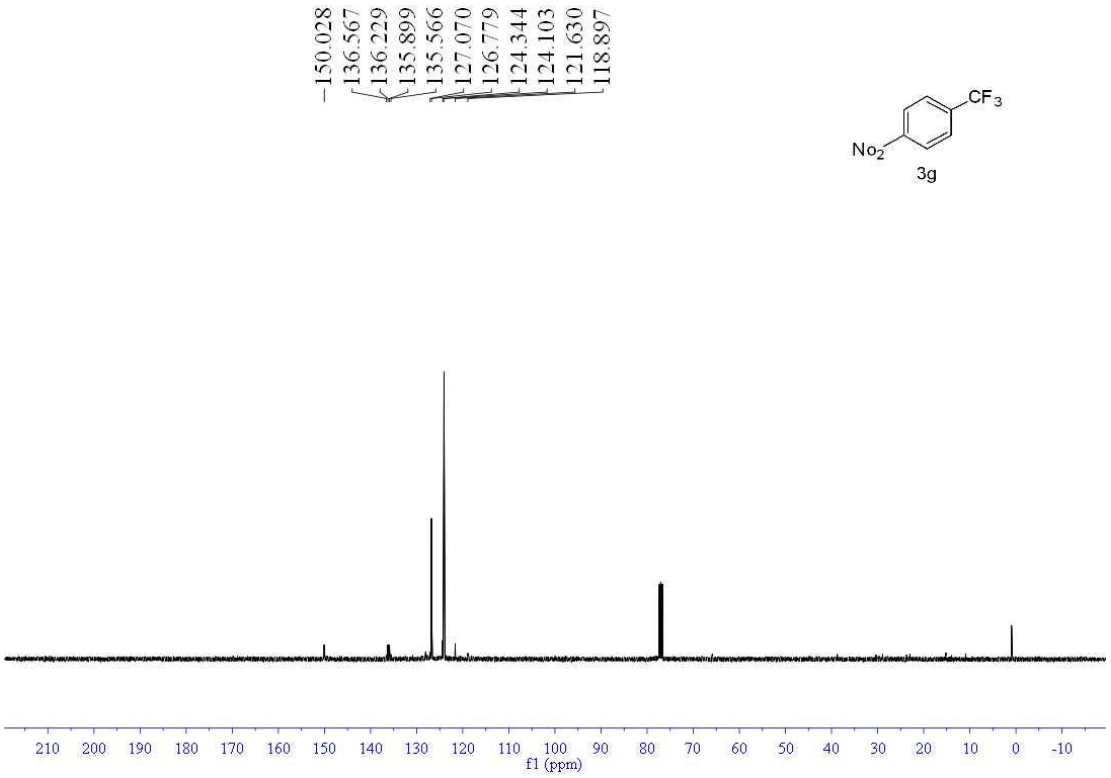
^{1}H NMR spectrum of **3g** in $CDCl_3$



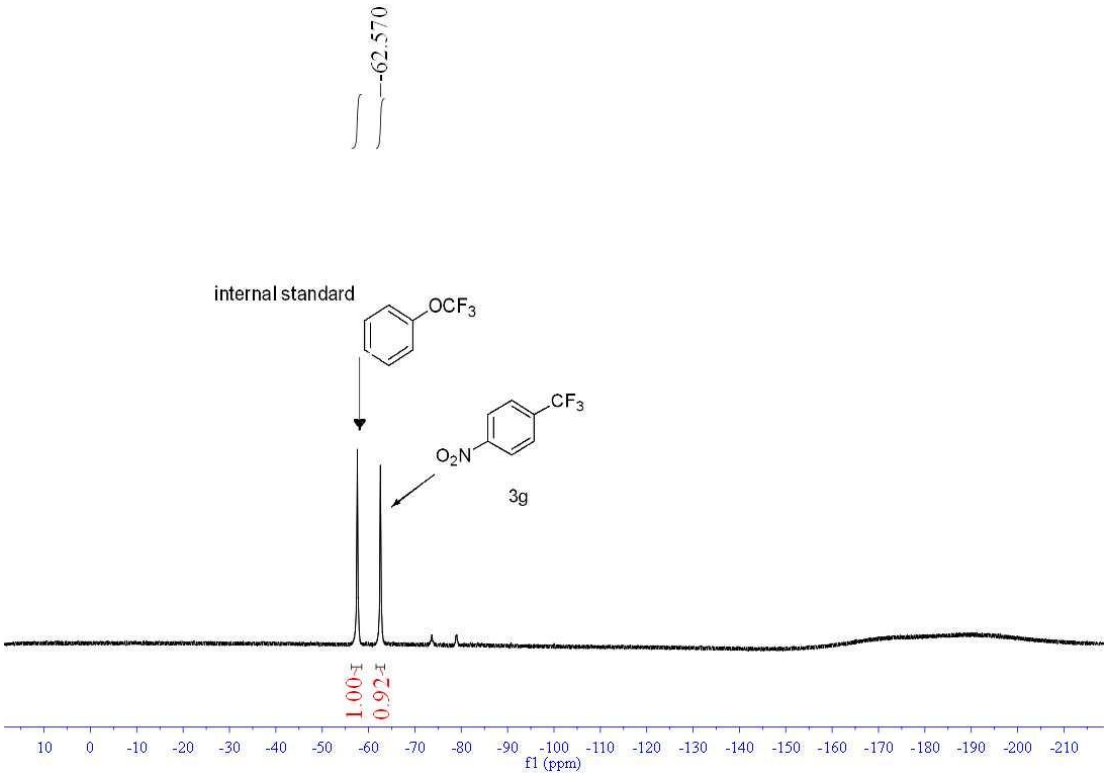
^{19}F NMR spectrum of **3g** in $CDCl_3$



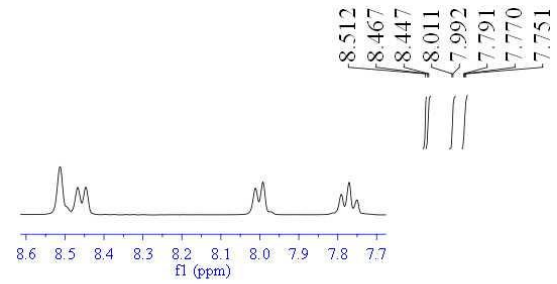
^{13}C NMR spectrum of **3g** in $CDCl_3$

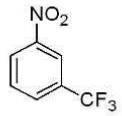


^{19}F NMR spectrum of **3g** (unlocked)

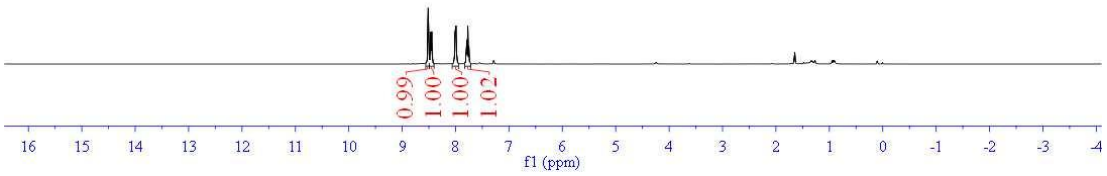


^{1}H NMR spectrum of **3h** in $CDCl_3$

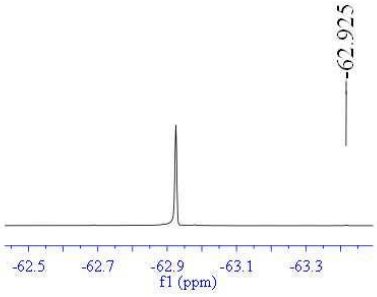


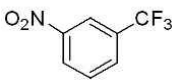


3h

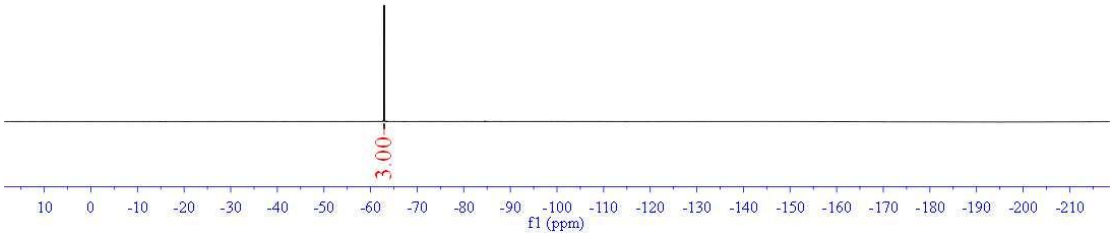


^{19}F NMR spectrum of **3h** in $CDCl_3$

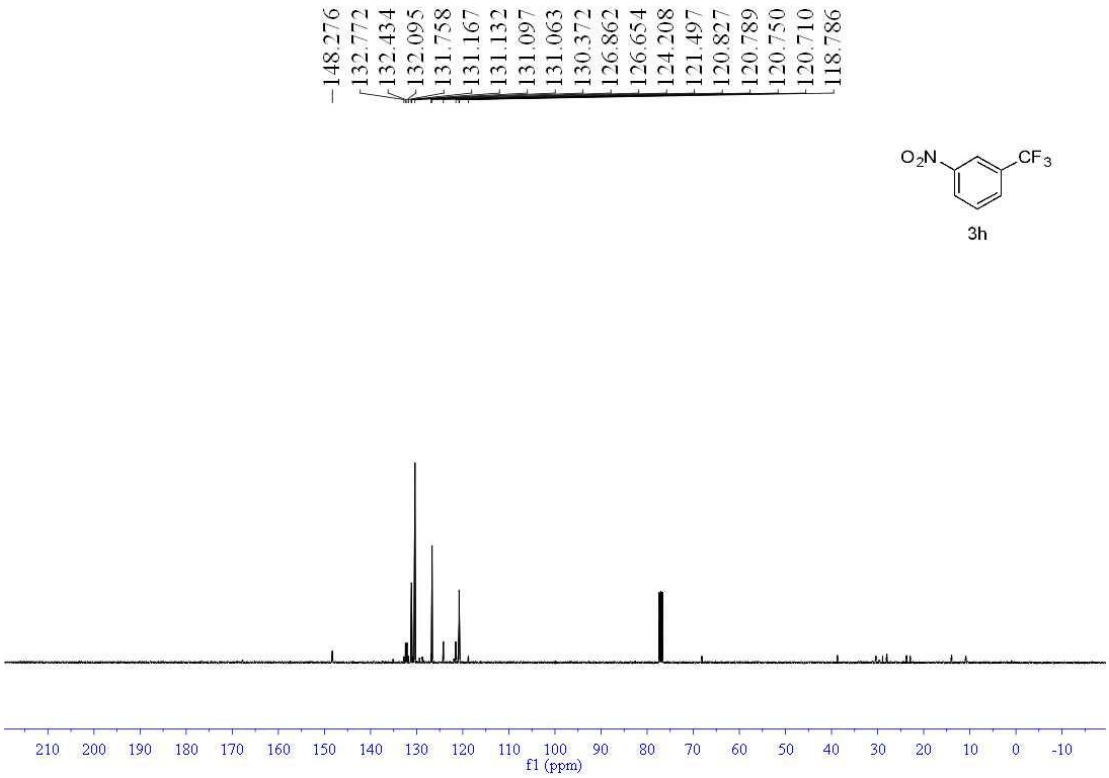




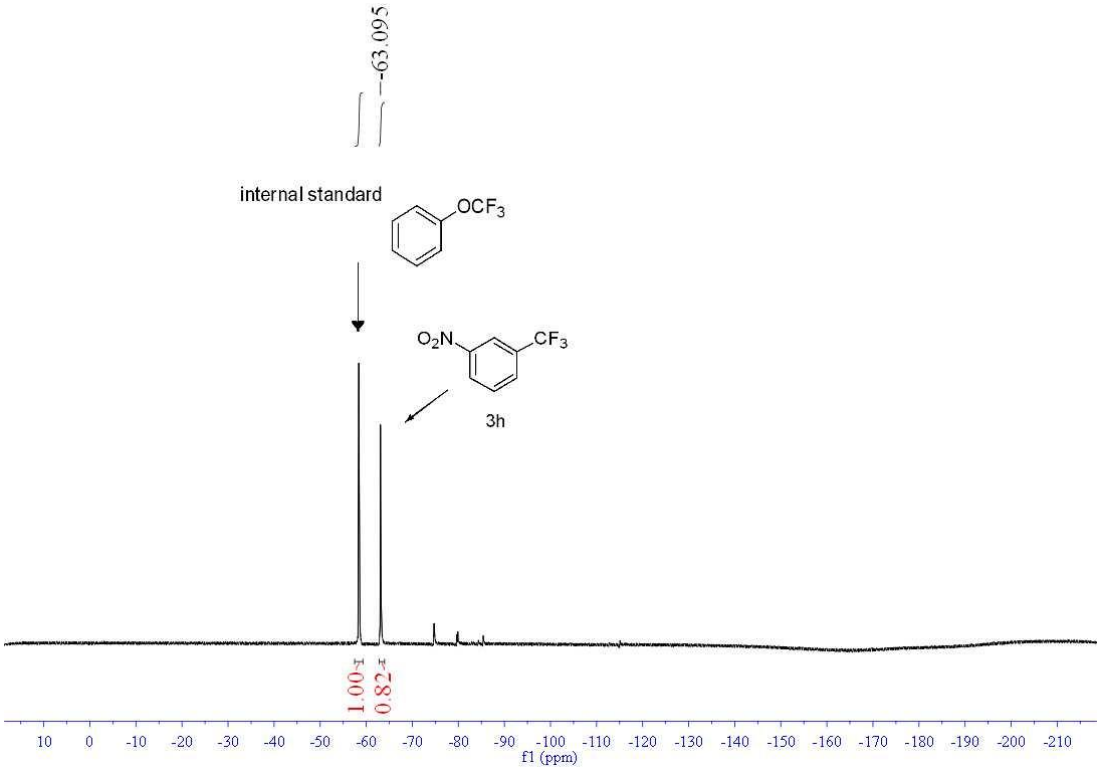
3h



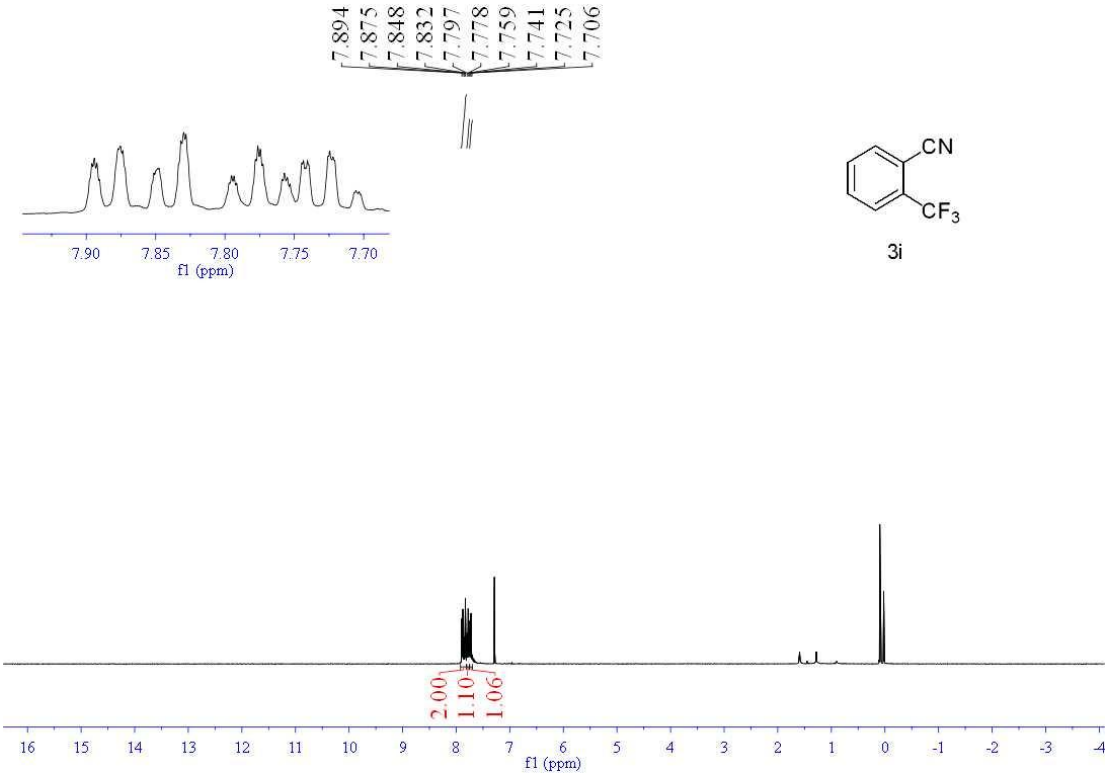
^{13}C NMR spectrum of **3h** in $CDCl_3$



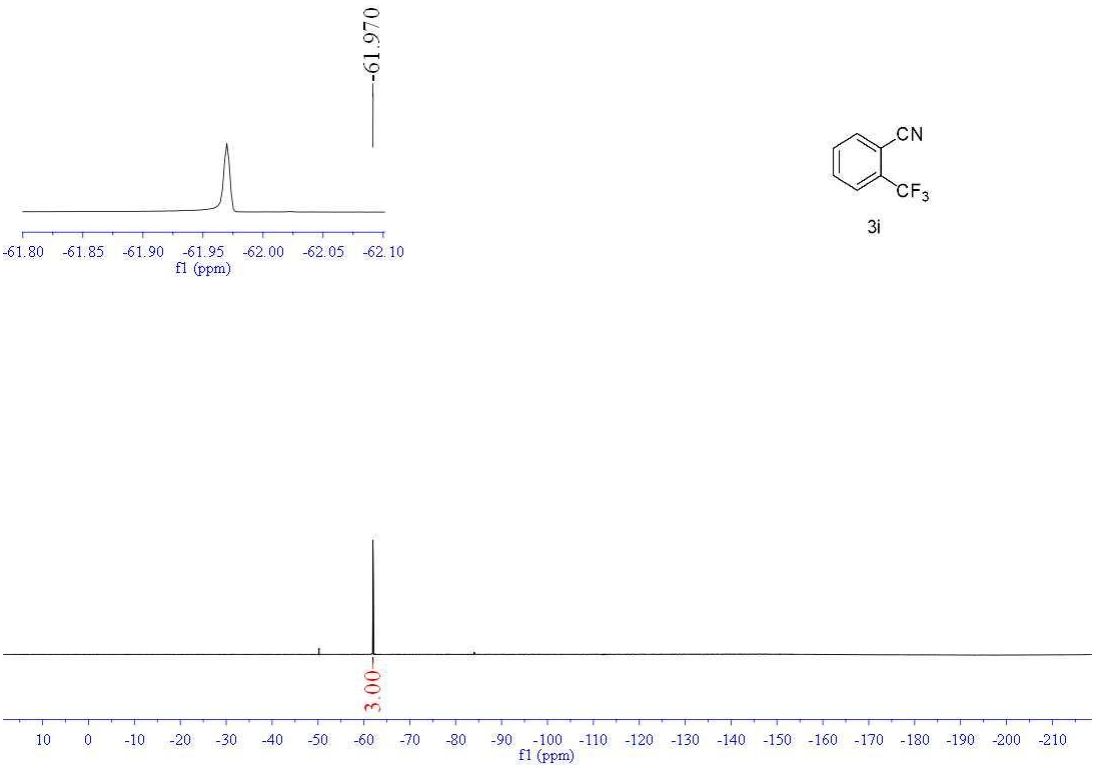
^{19}F NMR spectrum of **3h** (unlocked)



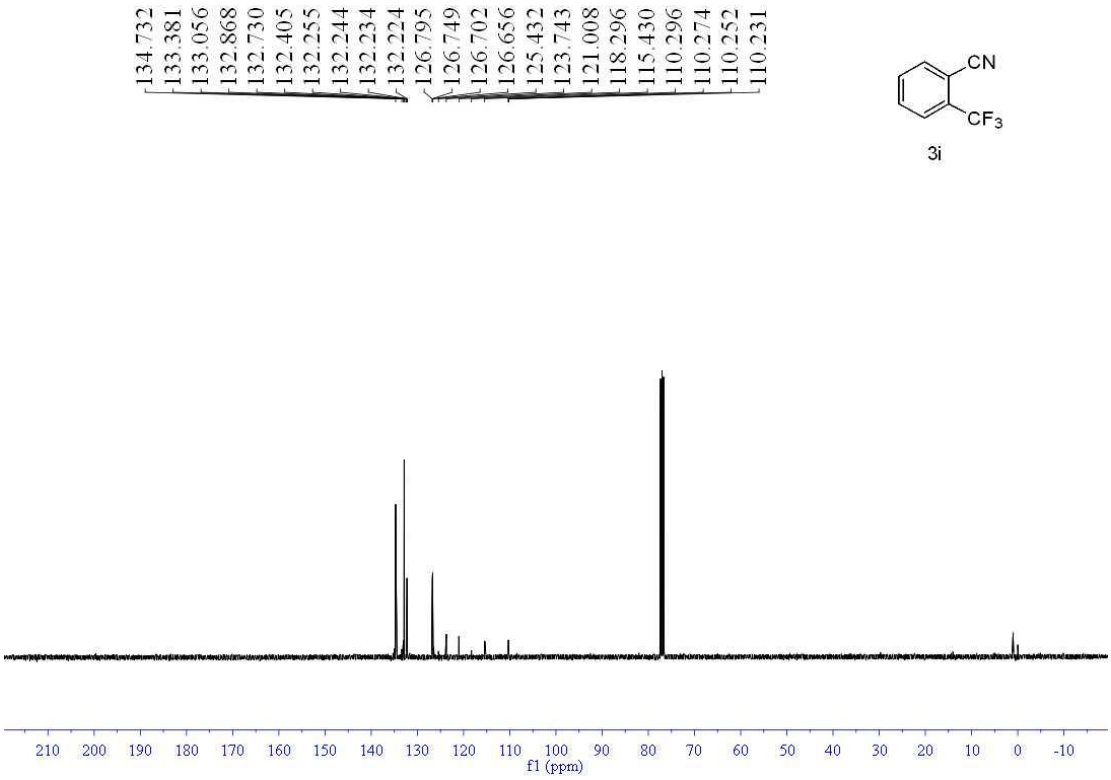
^{1}H NMR spectrum of **3i** in $CDCl_3$



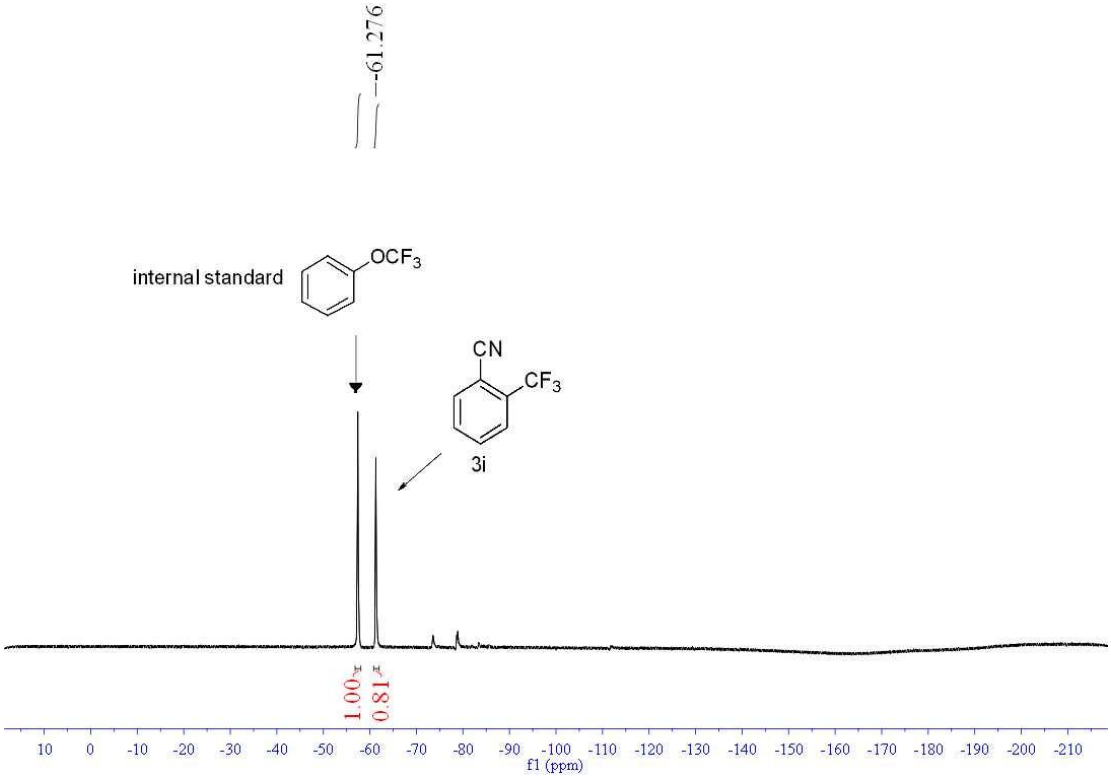
^{19}F NMR spectrum of **3i** in $CDCl_3$



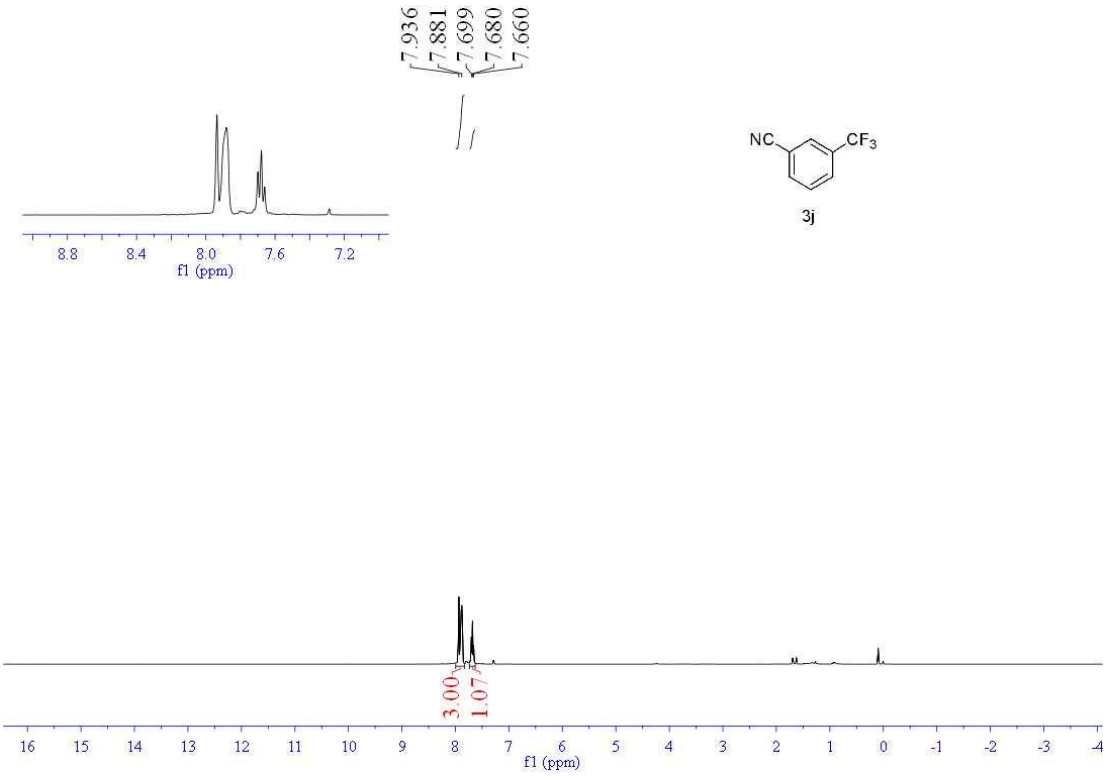
^{13}C NMR spectrum of **3i** in $CDCl_3$



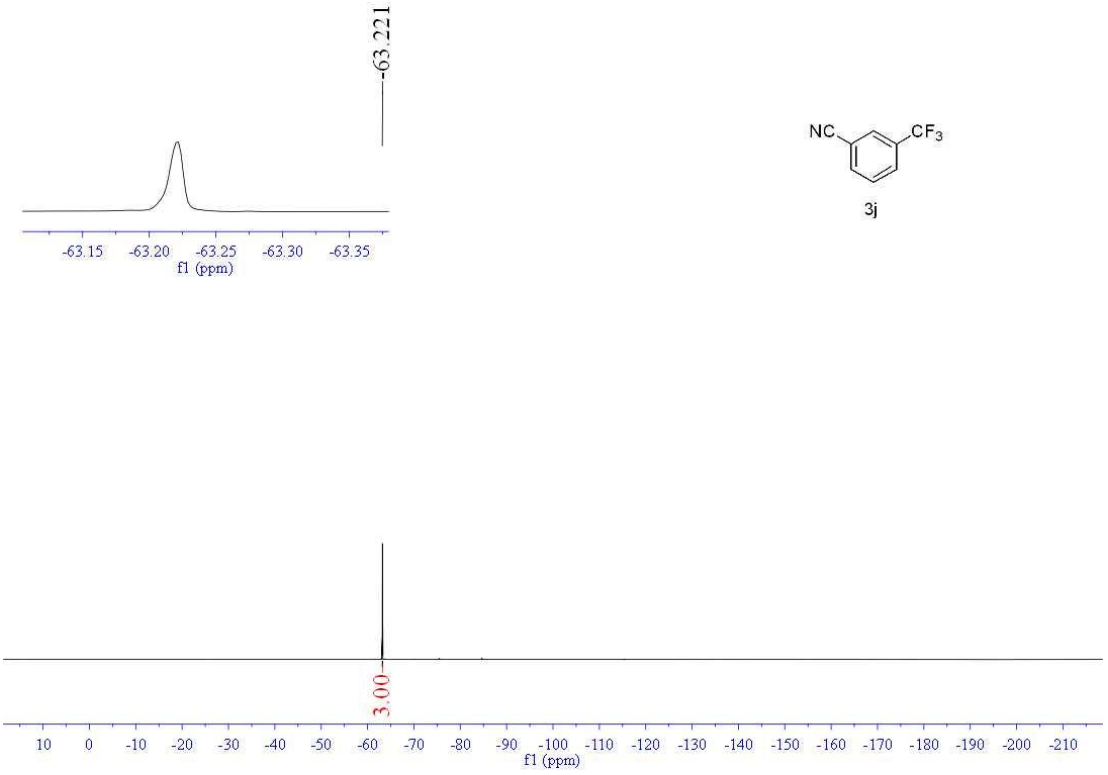
^{19}F NMR spectrum of **3i** (unlocked)



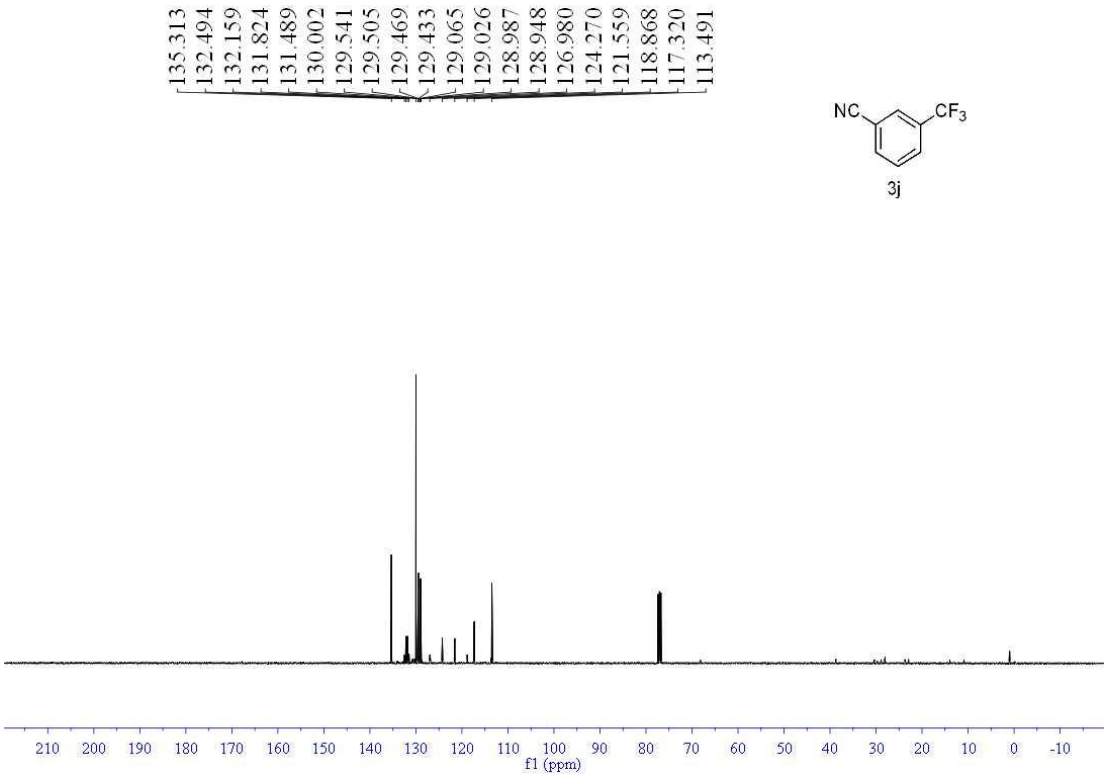
^{1}H NMR spectrum of **3j** in $CDCl_3$



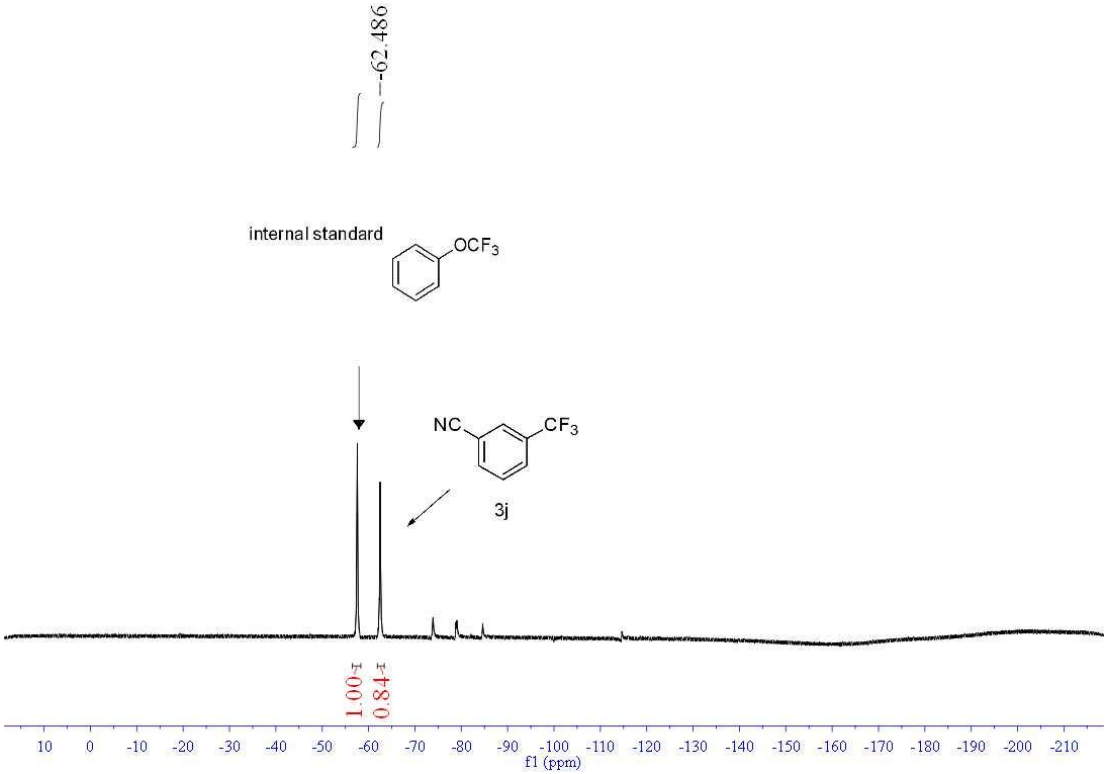
^{19}F NMR spectrum of **3j** in $CDCl_3$



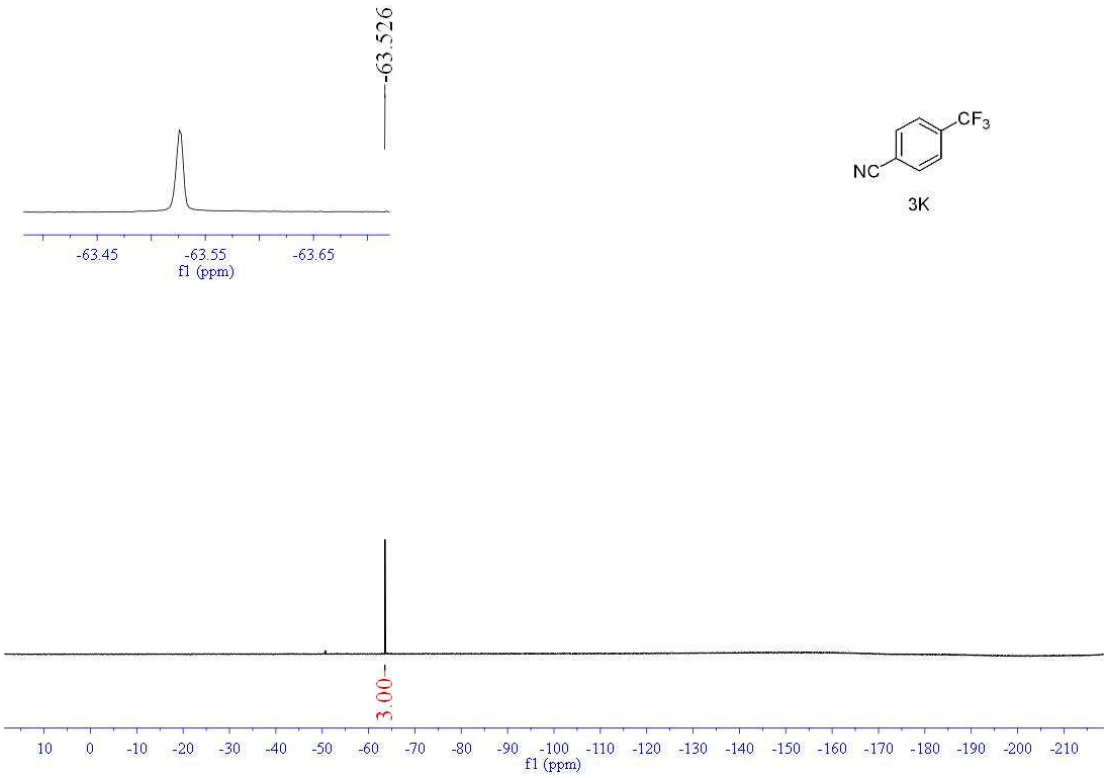
^{13}C NMR spectrum of **3j** in $CDCl_3$



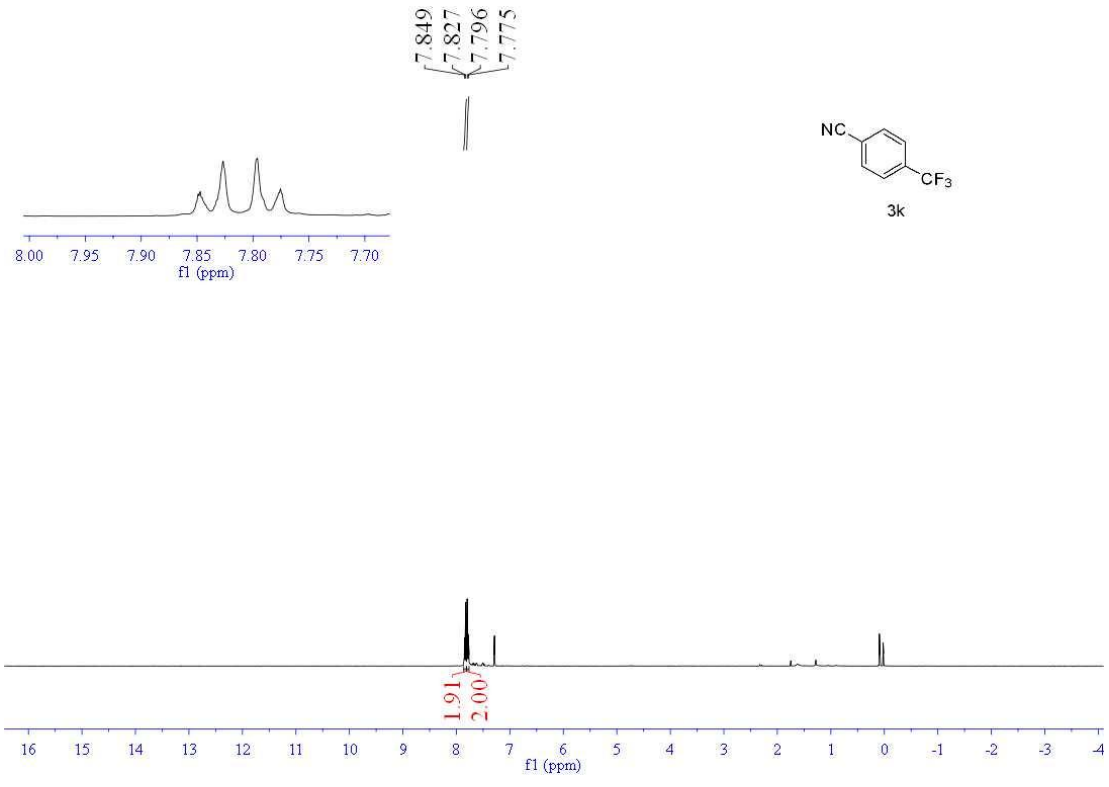
^{19}F NMR spectrum of **3j** (unlocked)



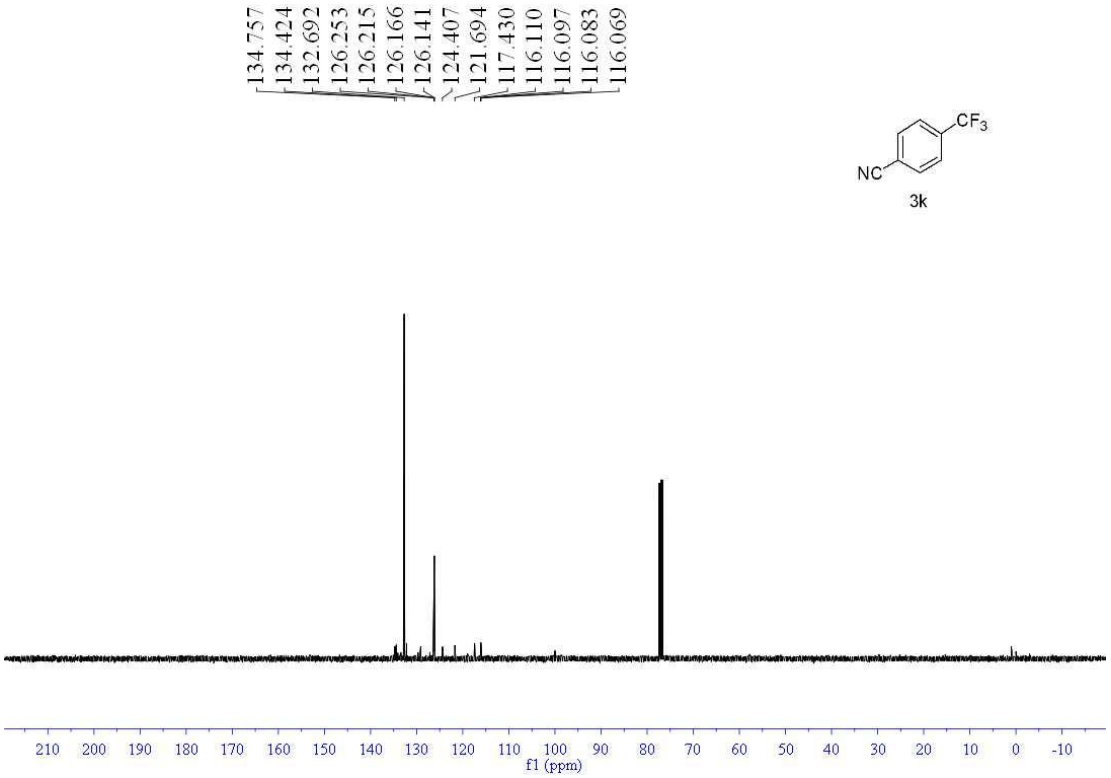
^{19}F NMR spectrum of **3k** in $CDCl_3$



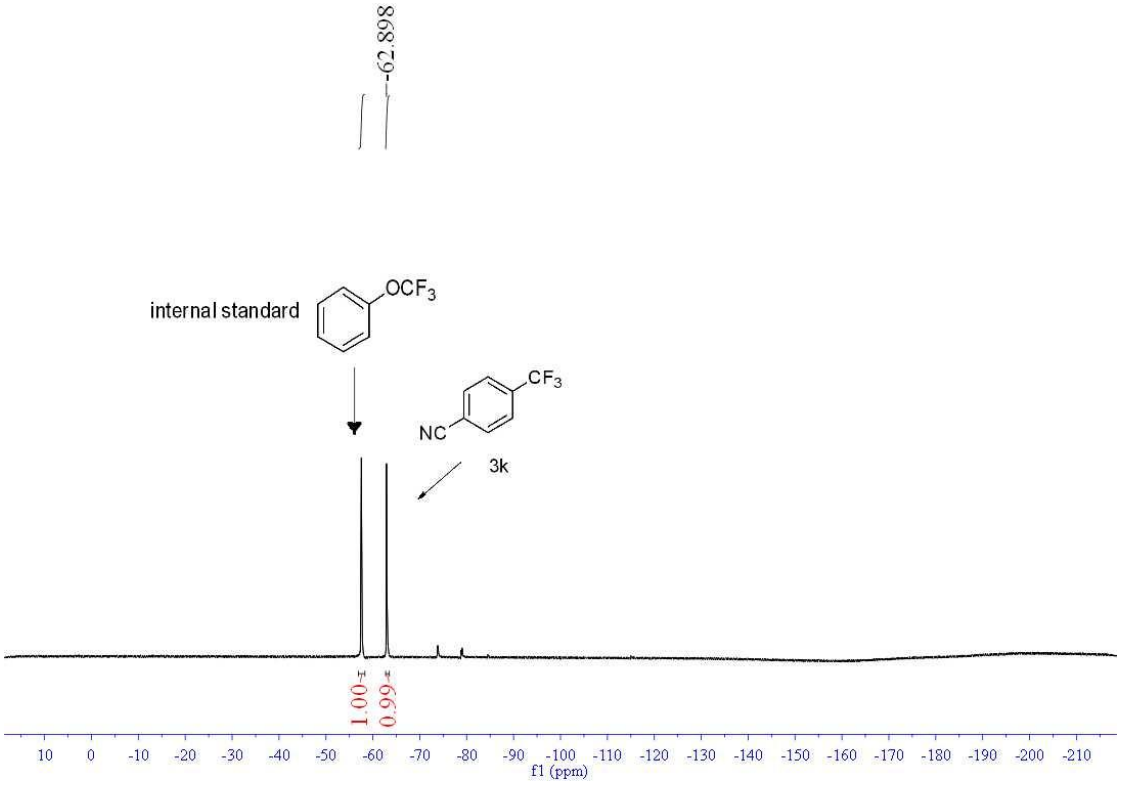
^{1}H NMR spectrum of **3k** in $CDCl_3$



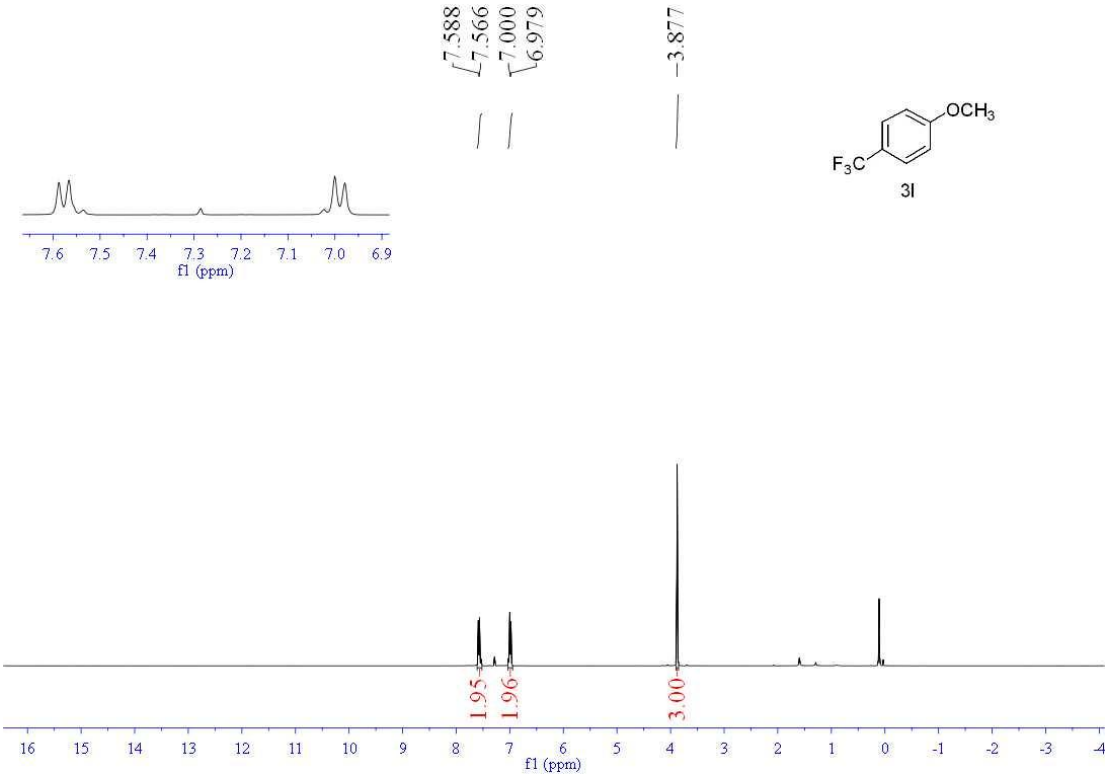
^{13}C NMR spectrum of **3k** in $CDCl_3$



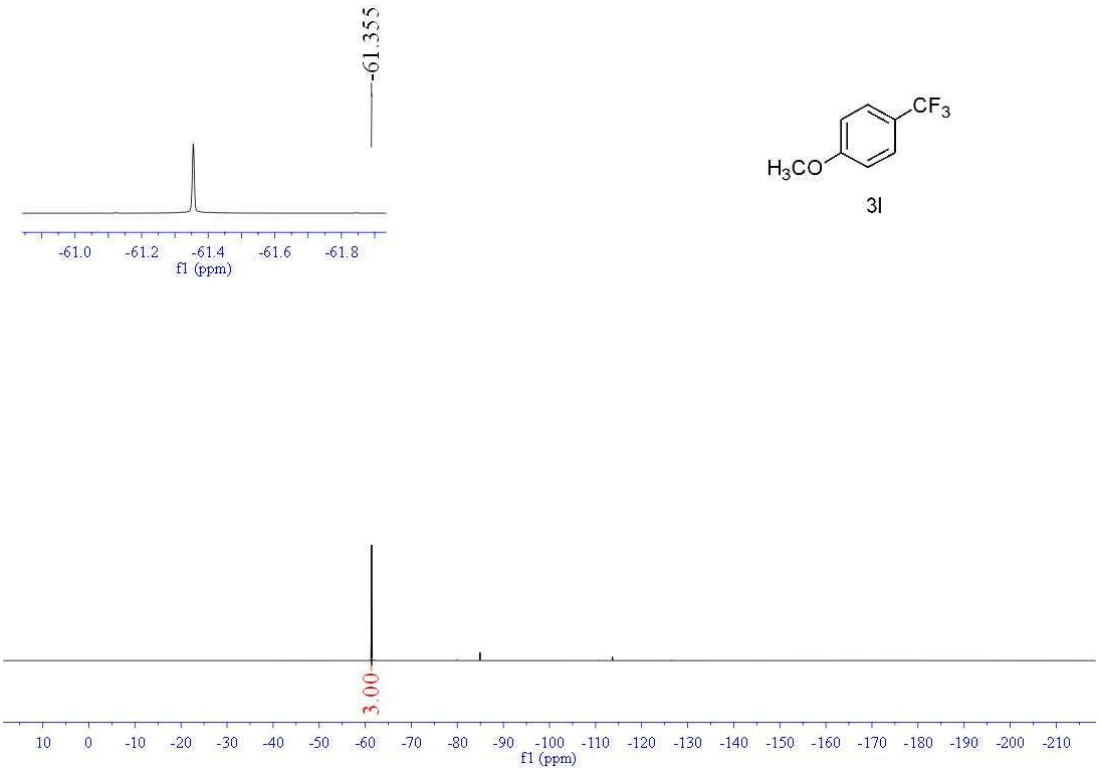
^{19}F NMR spectrum of **3k** (unlocked)



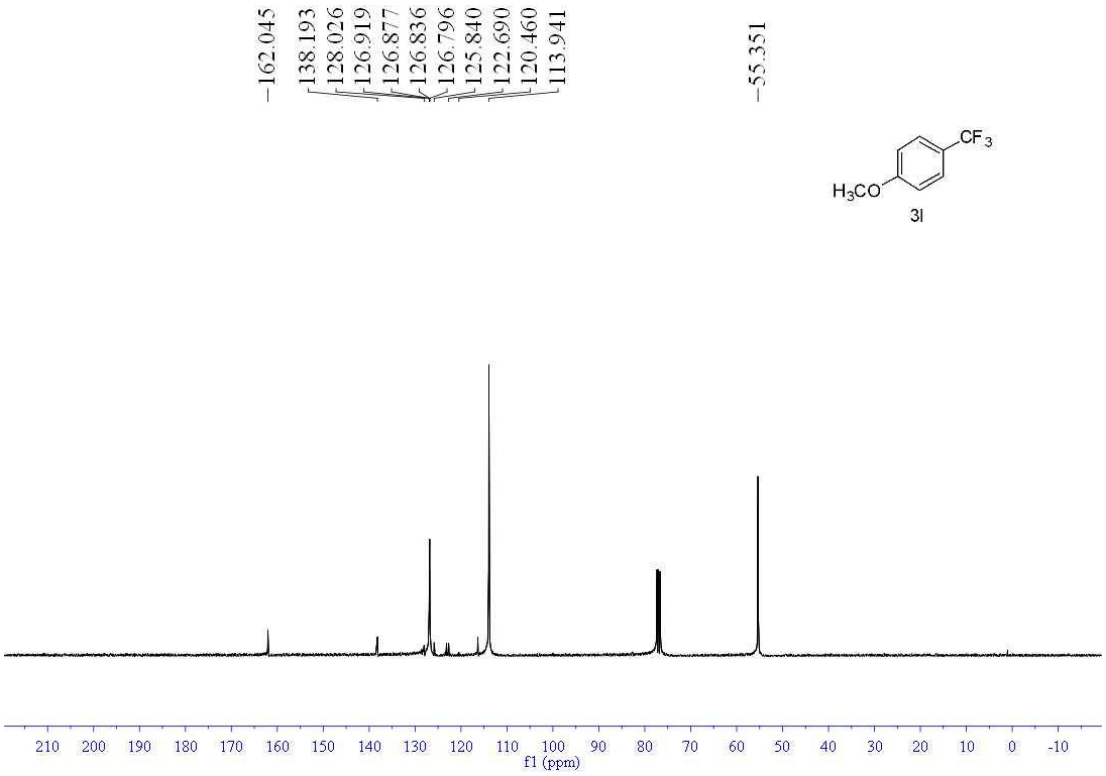
^{1}H NMR spectrum of **3l** in $CDCl_3$



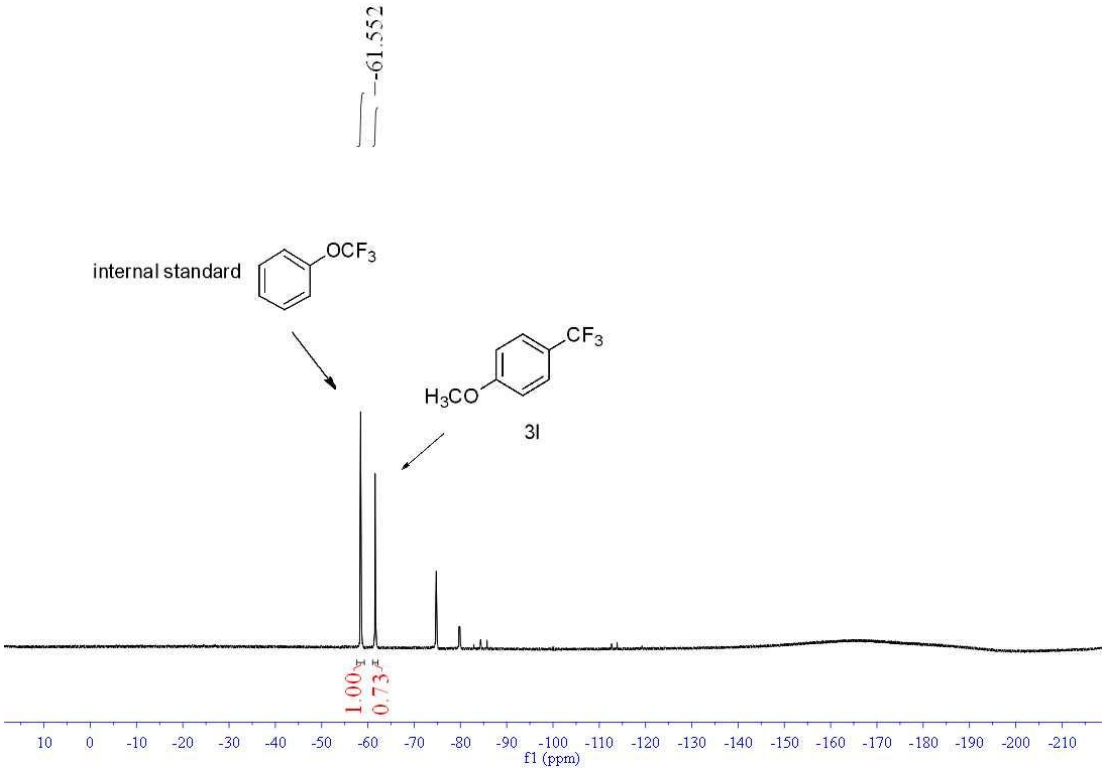
^{19}F NMR spectrum of **3l** in $CDCl_3$



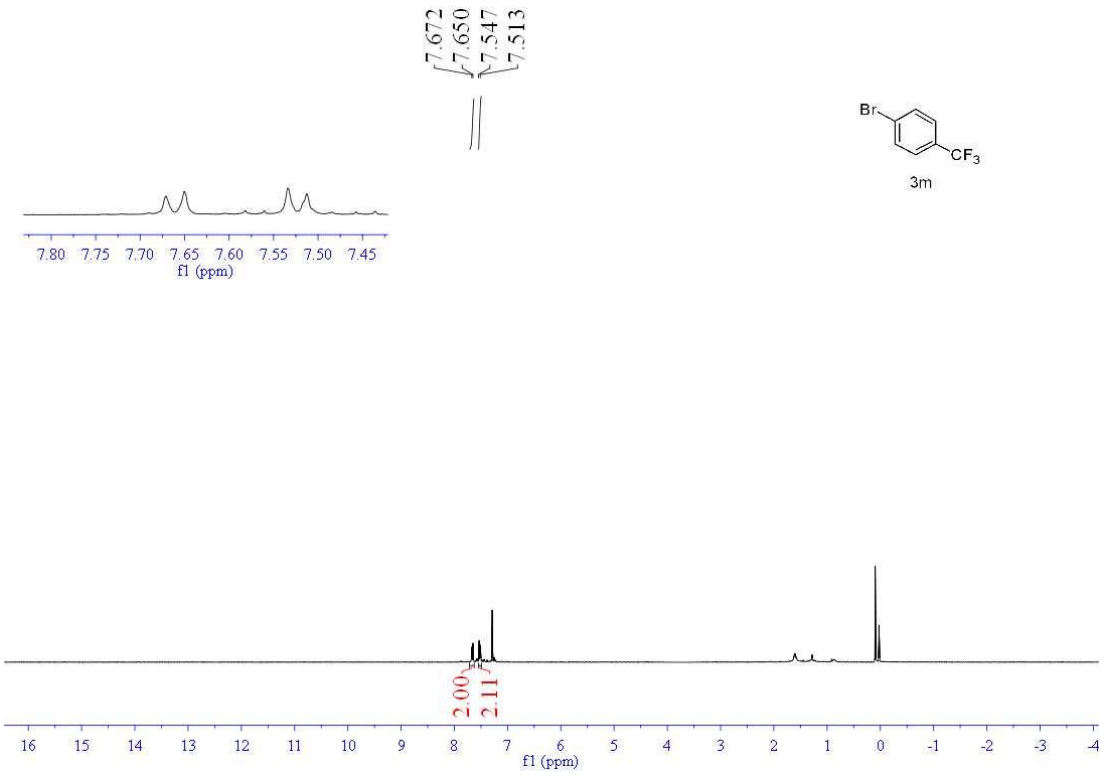
^{13}C NMR spectrum of **3l** in $CDCl_3$



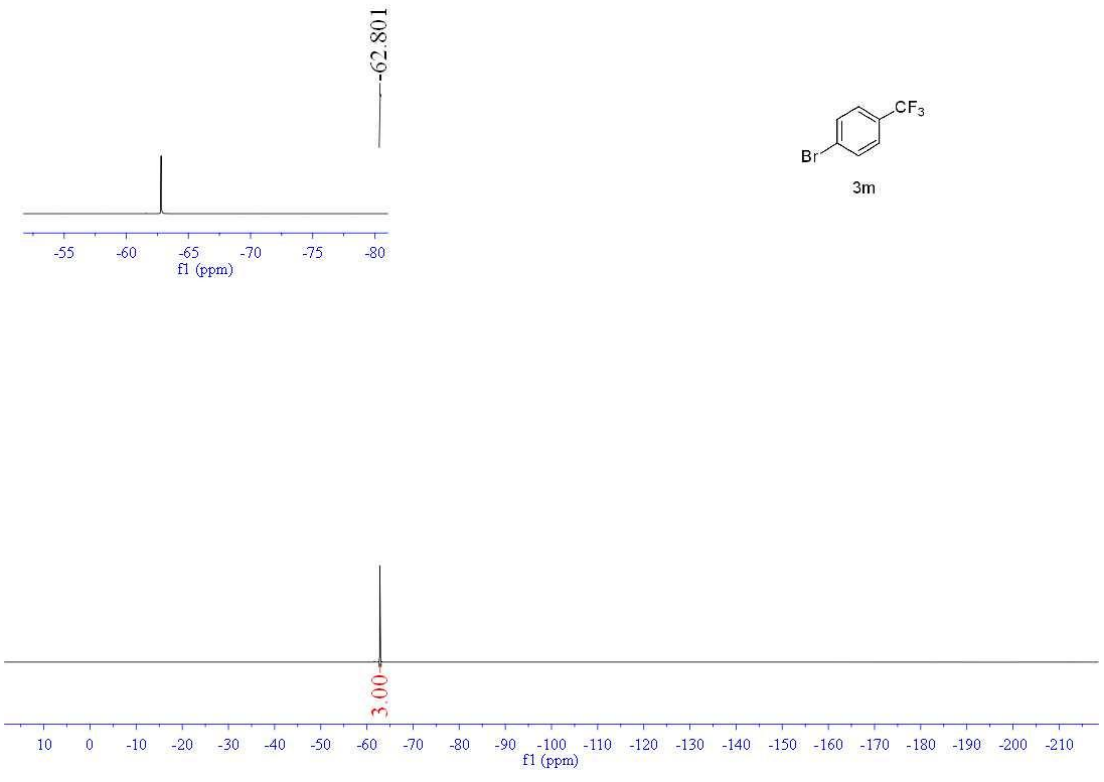
^{19}F NMR spectrum of **3l** (unlocked)



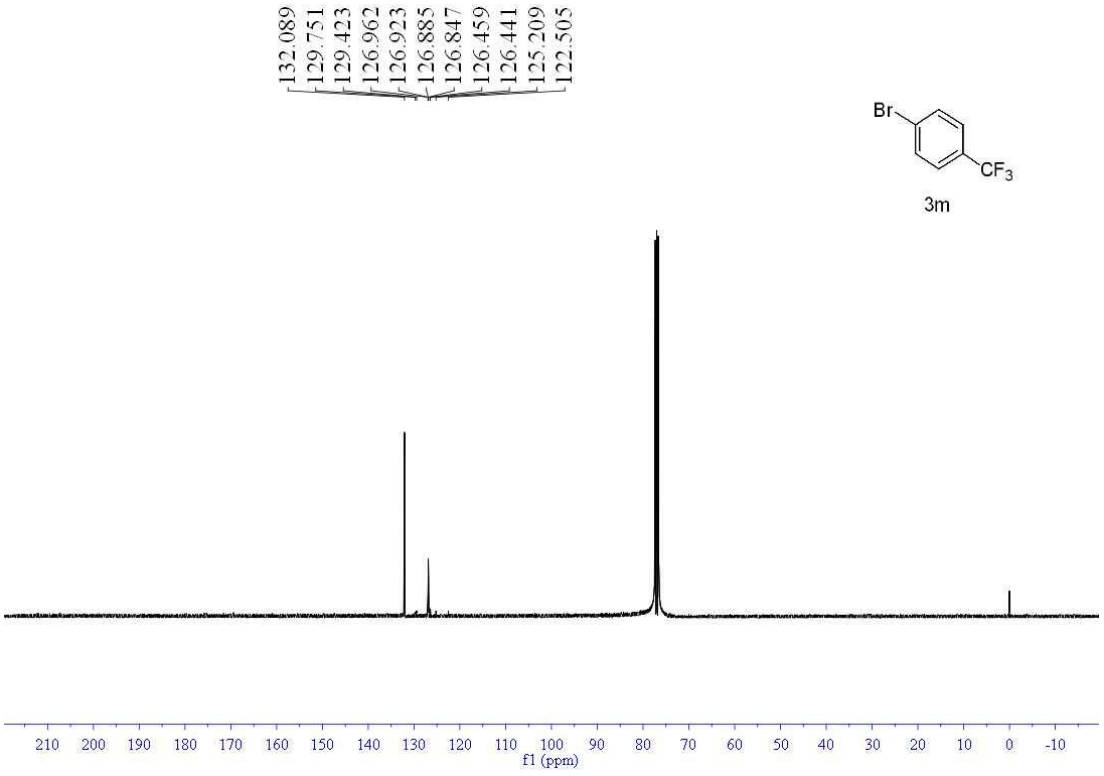
^{1}H NMR spectrum of **3m** in $CDCl_3$



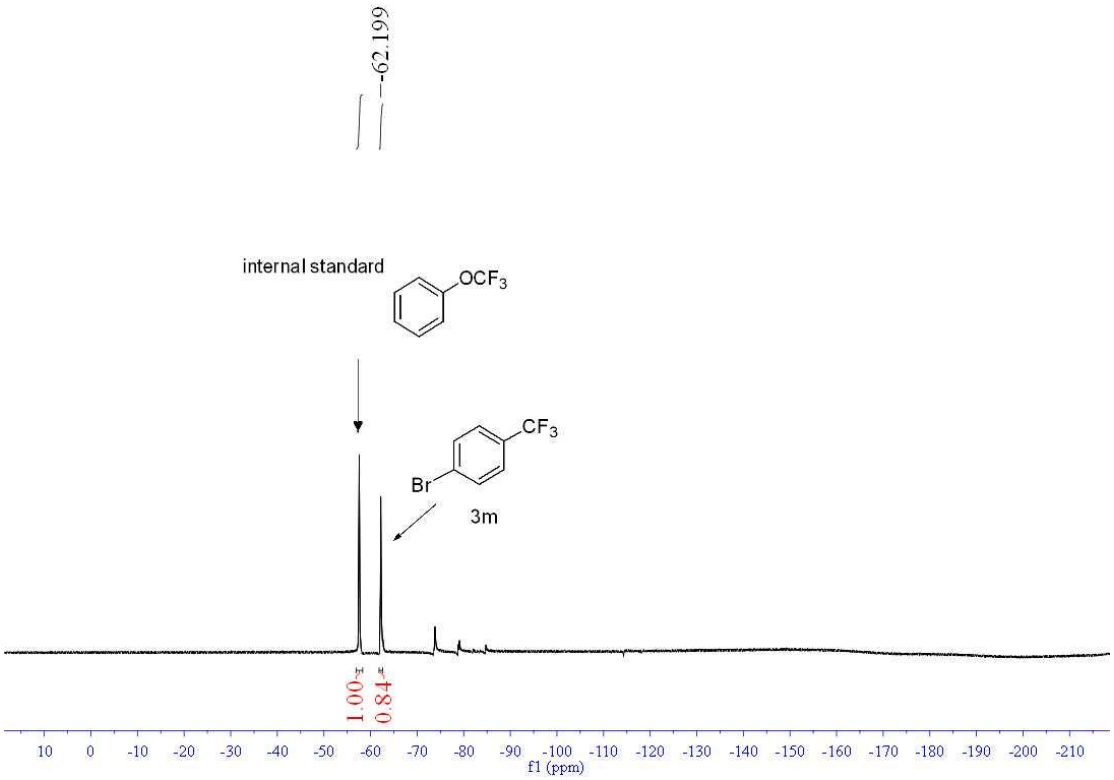
^{19}F NMR spectrum of **3m** in $CDCl_3$



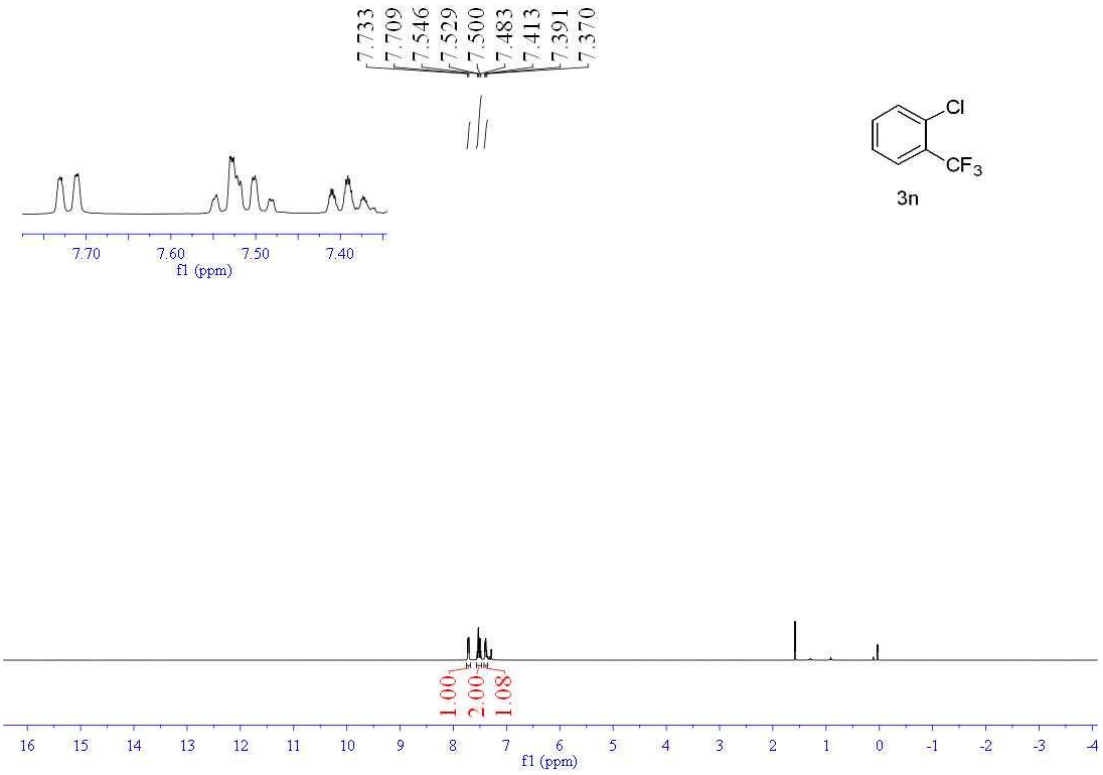
^{13}C NMR spectrum of **3m** in $CDCl_3$



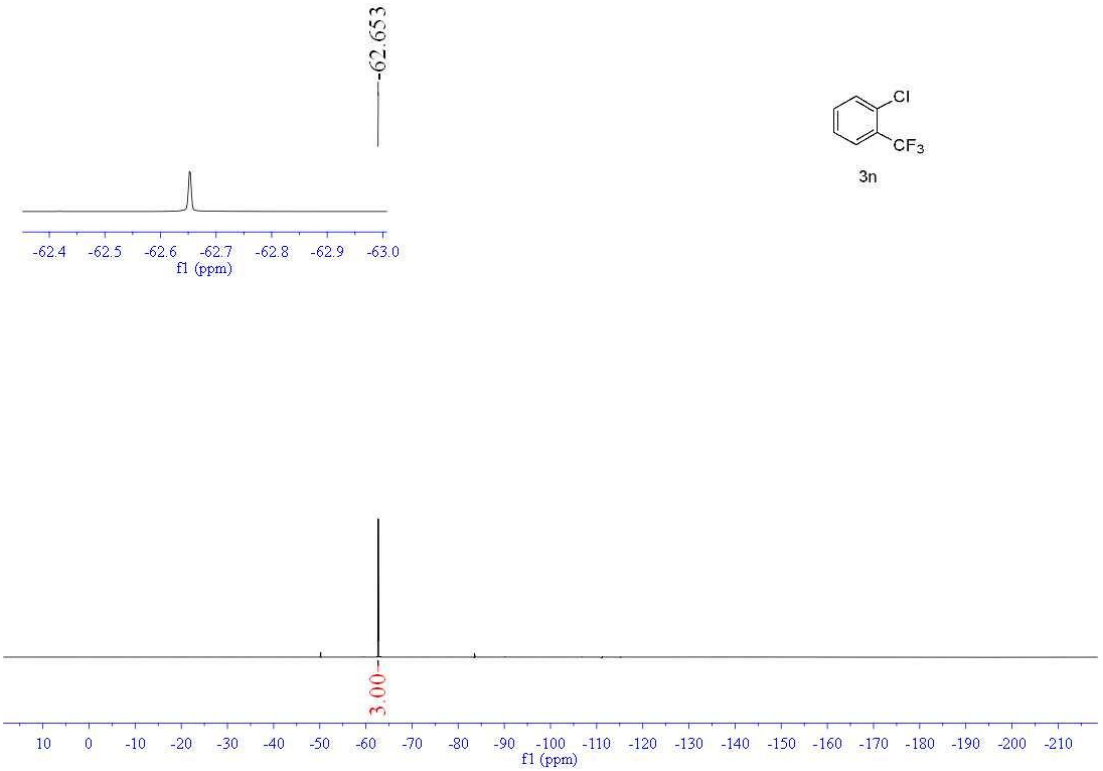
^{19}F NMR spectrum of **3m** (unlocked)



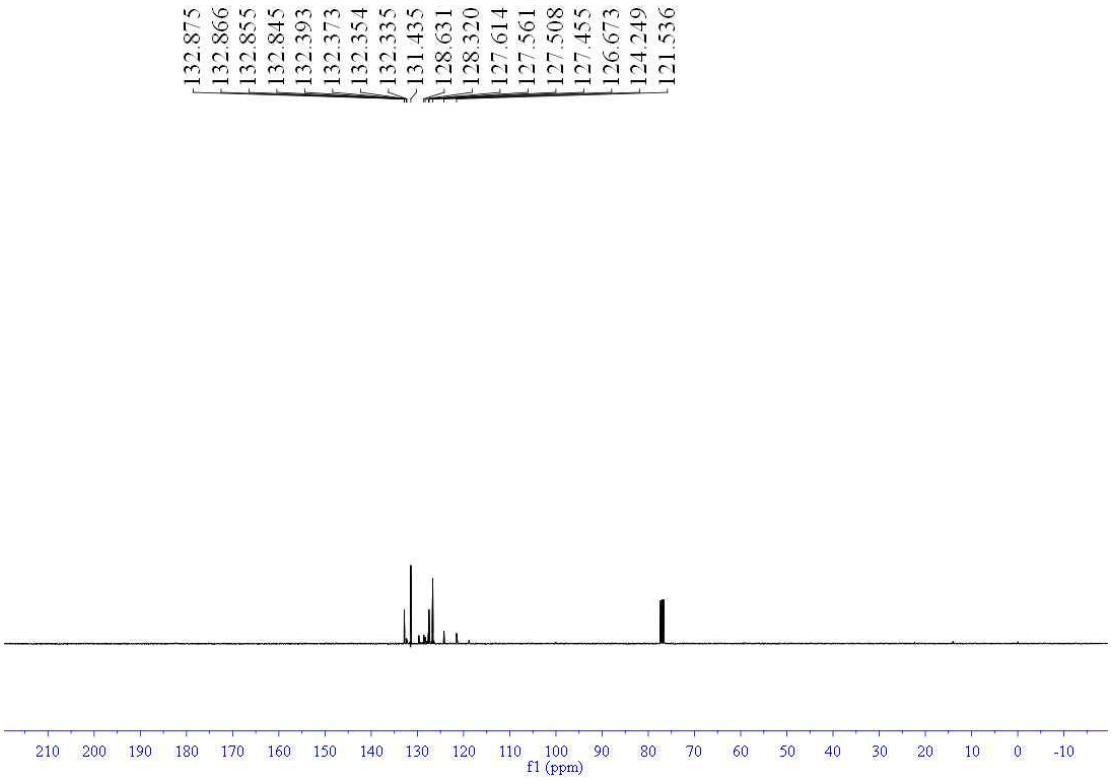
^{1}H NMR spectrum of **3n** in $CDCl_3$



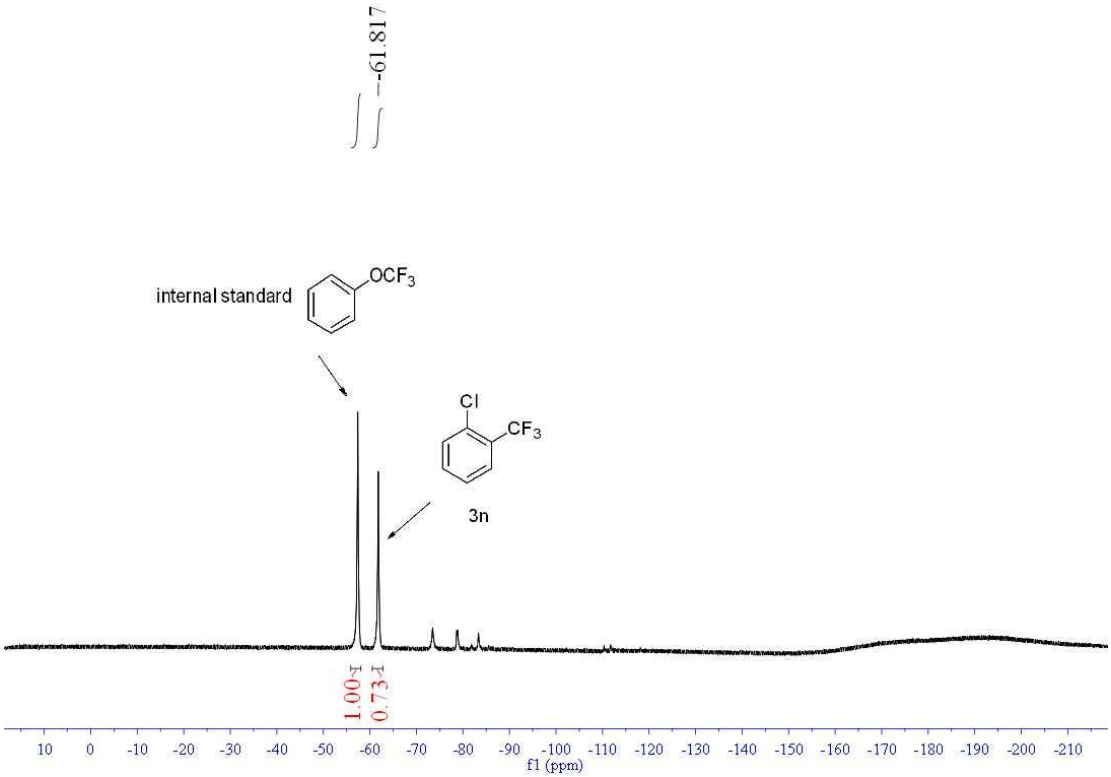
^{19}F NMR spectrum of **3n** in $CDCl_3$



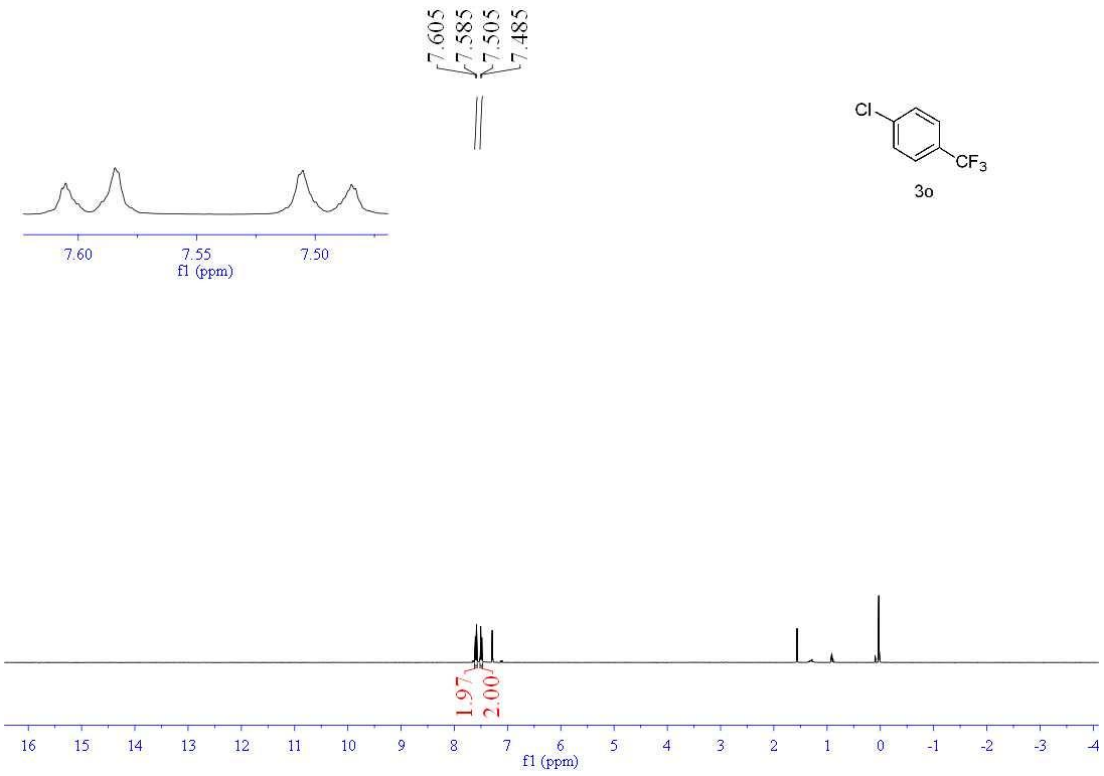
^{13}C NMR spectrum of **3n** in $CDCl_3$



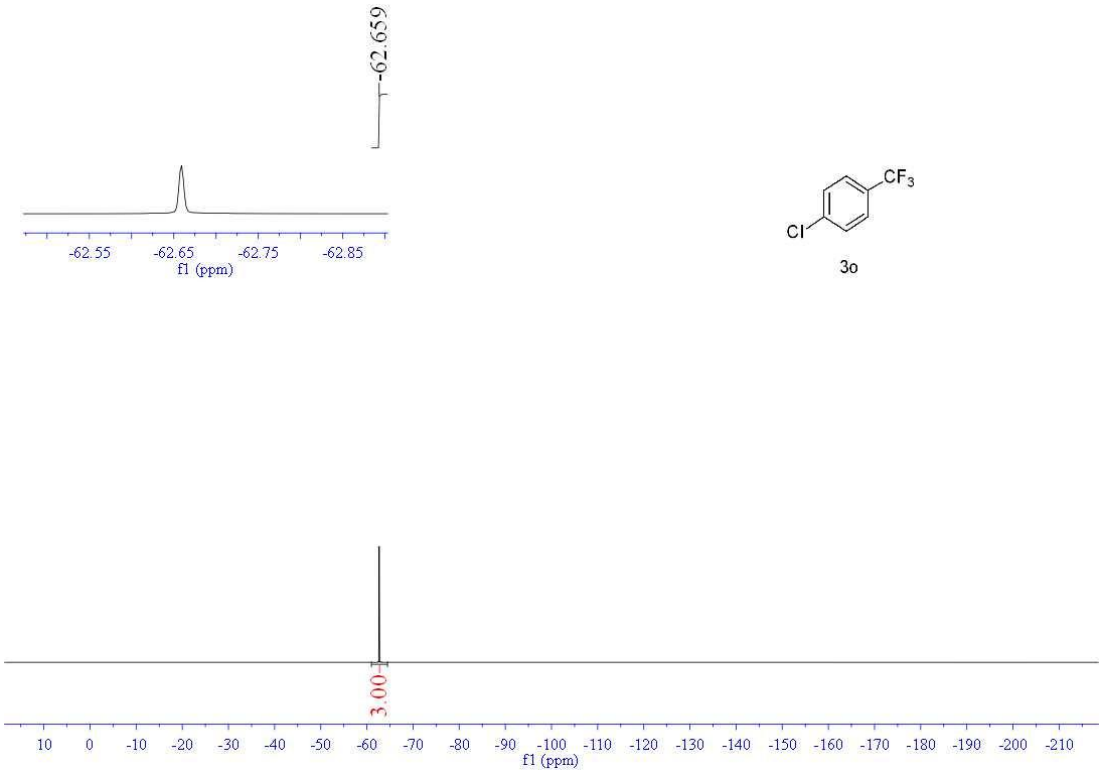
^{19}F NMR spectrum of **3n** (unlocked)



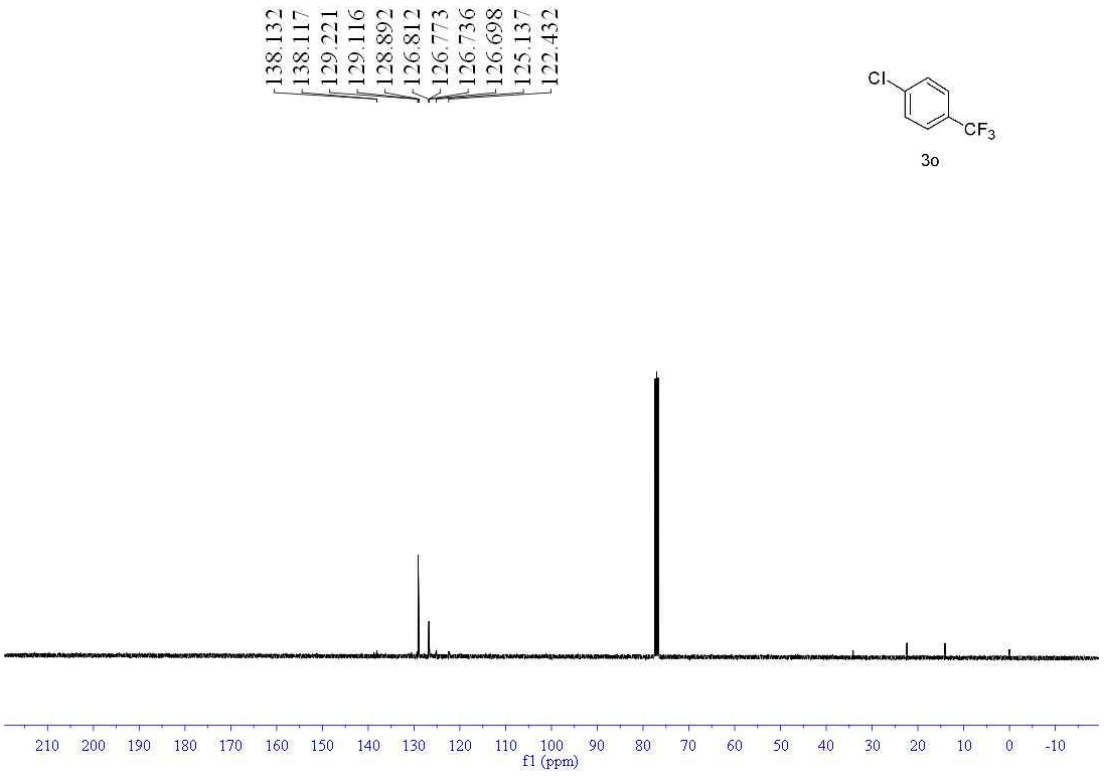
^{1}H NMR spectrum of **3o** in $CDCl_3$



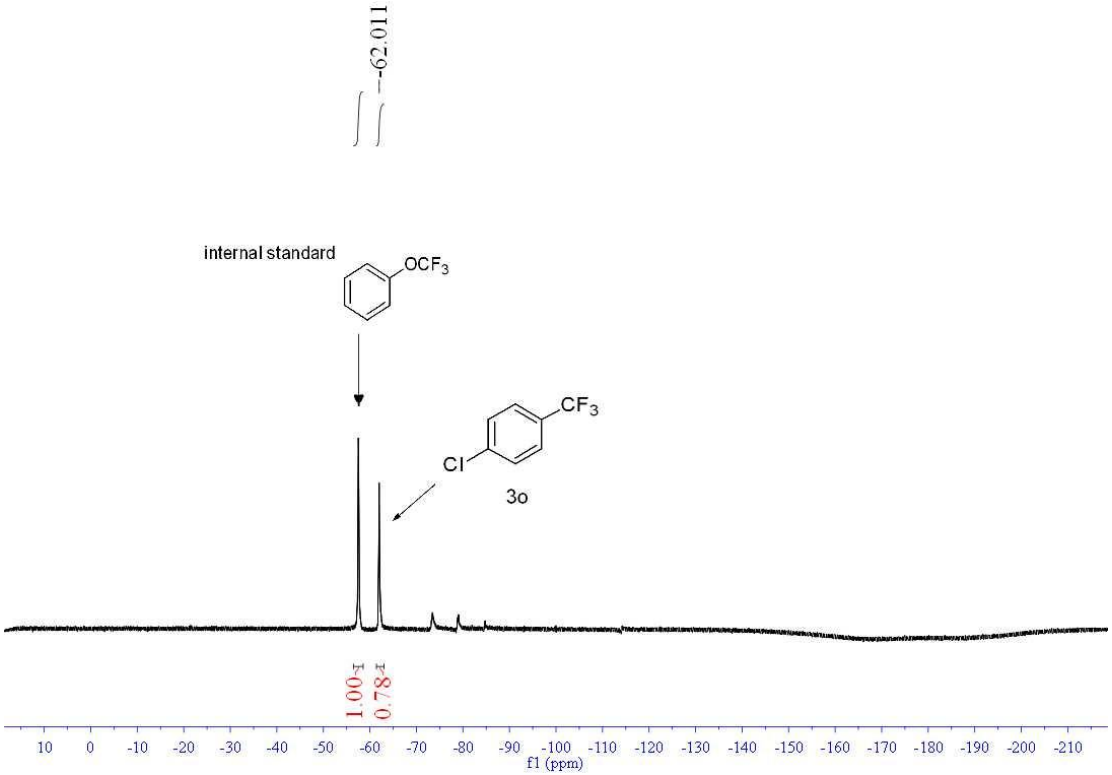
^{19}F NMR spectrum of **3o** in $CDCl_3$



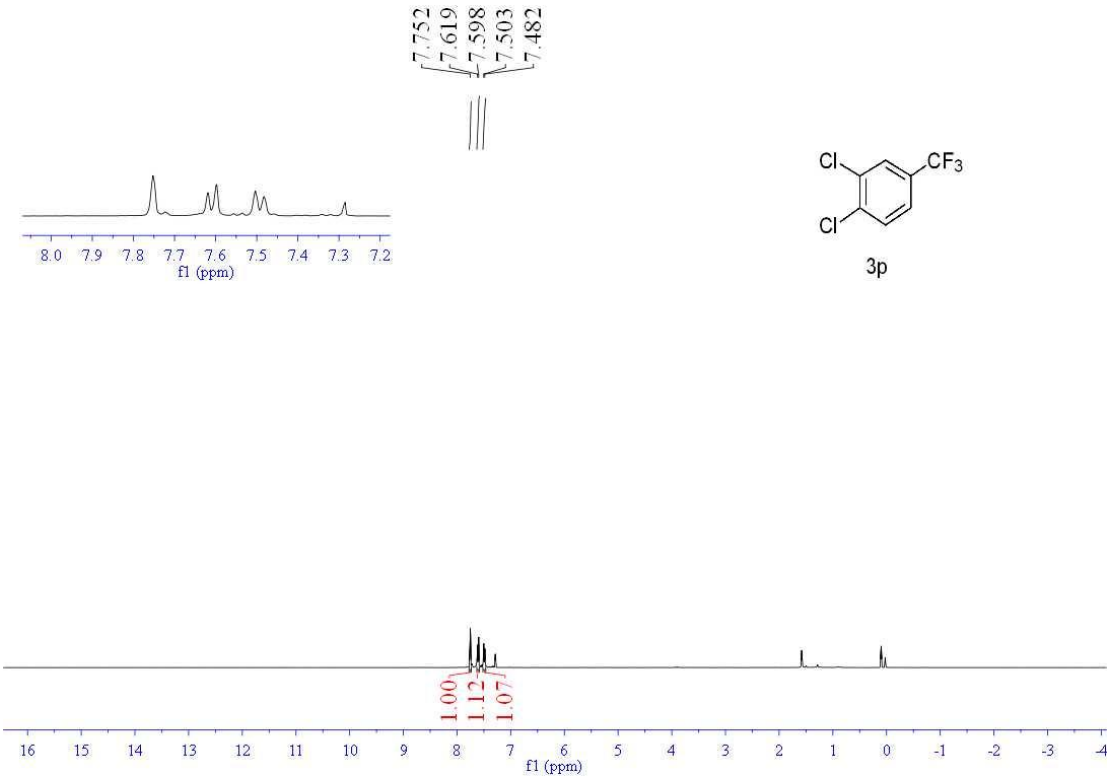
^{13}C NMR spectrum of **3o** in $CDCl_3$



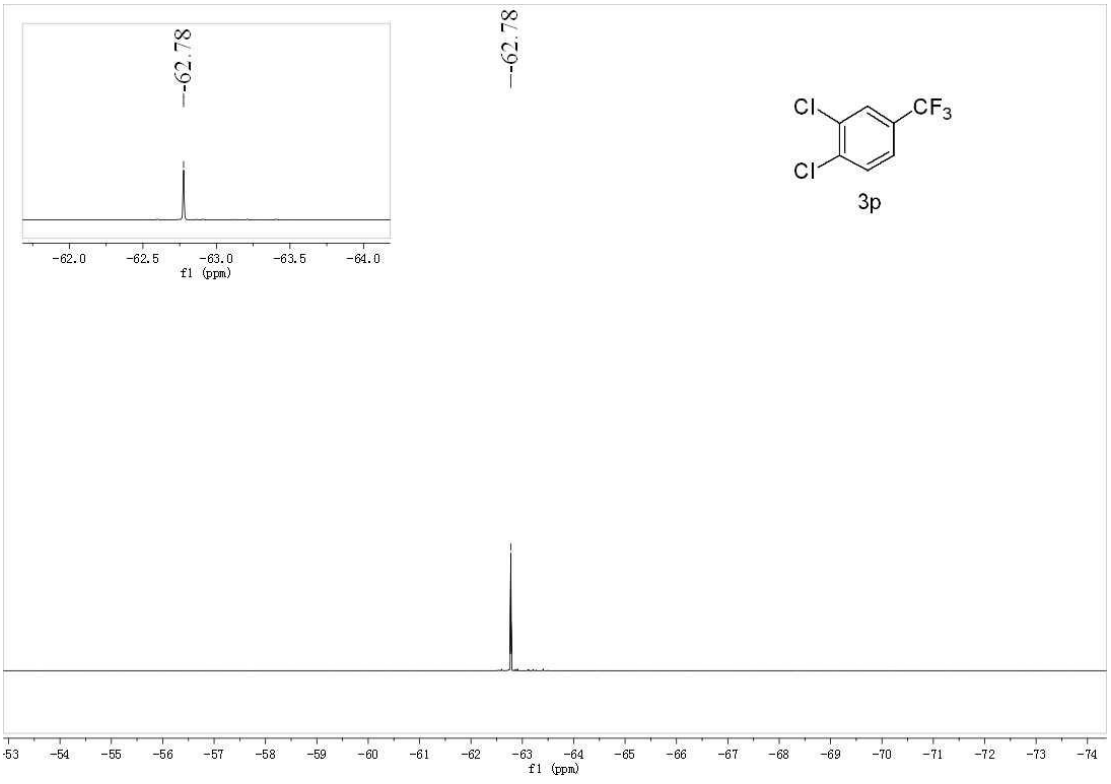
^{19}F NMR spectrum of **3o** (unlocked)



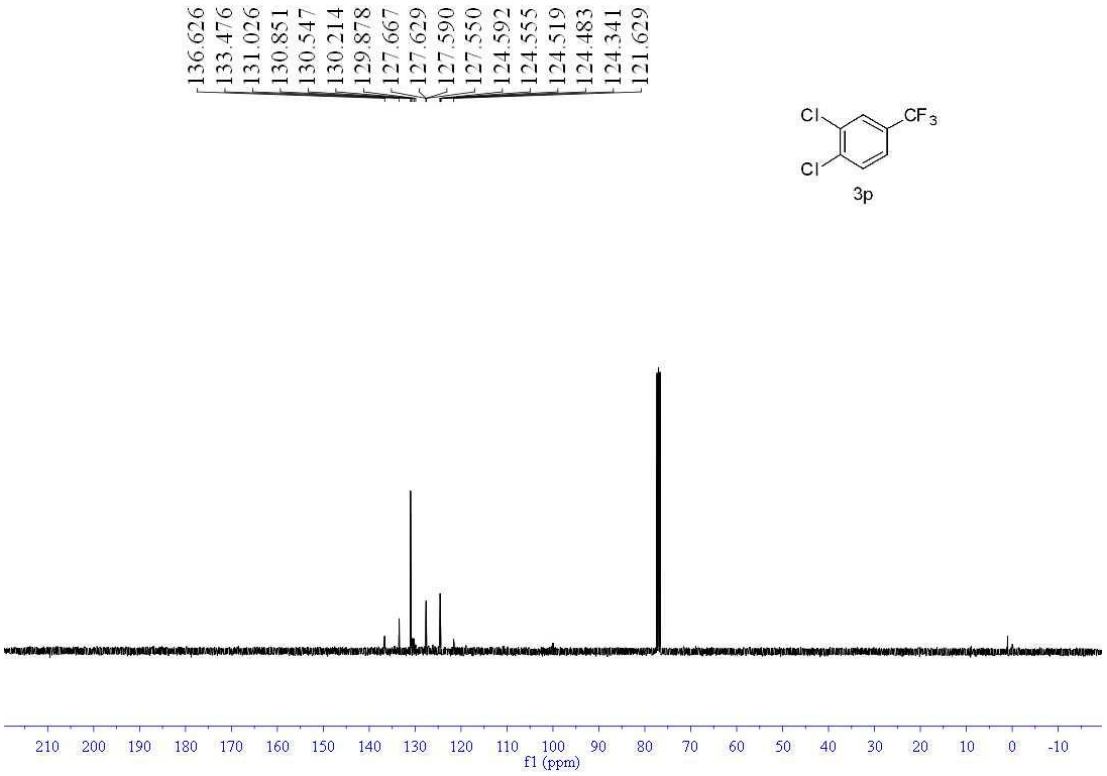
^{1}H NMR spectrum of **3p** in $CDCl_3$



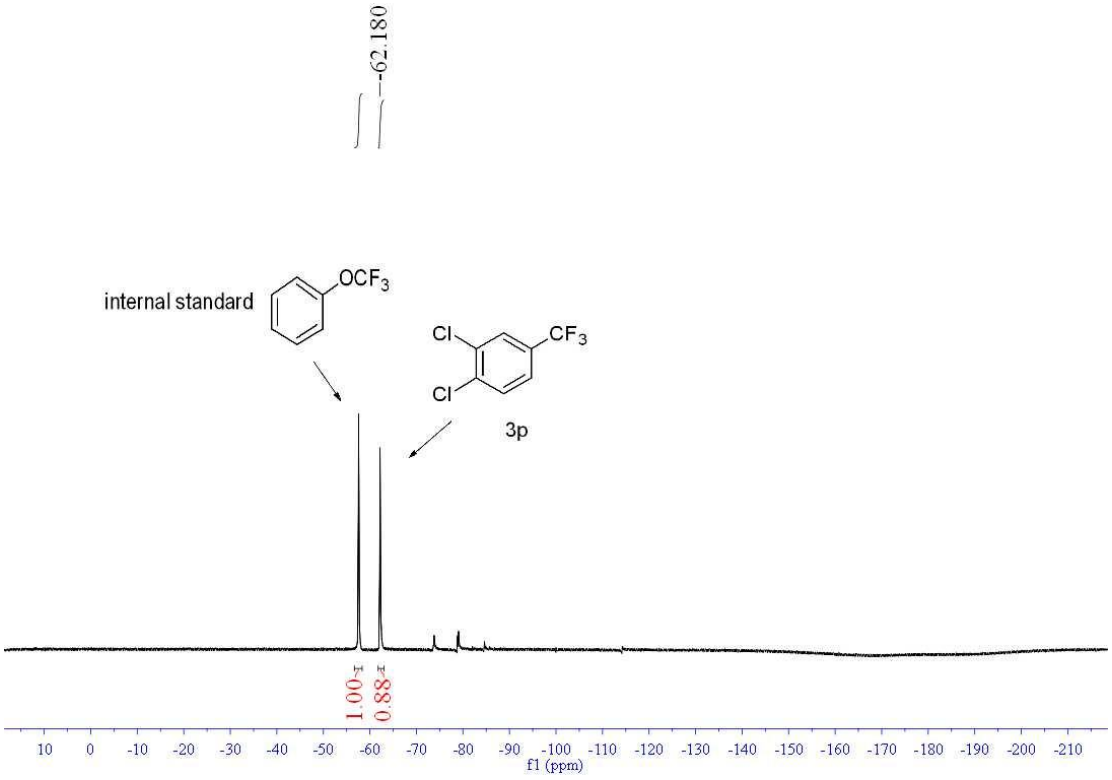
^{19}F NMR spectrum of **3p** in $CDCl_3$



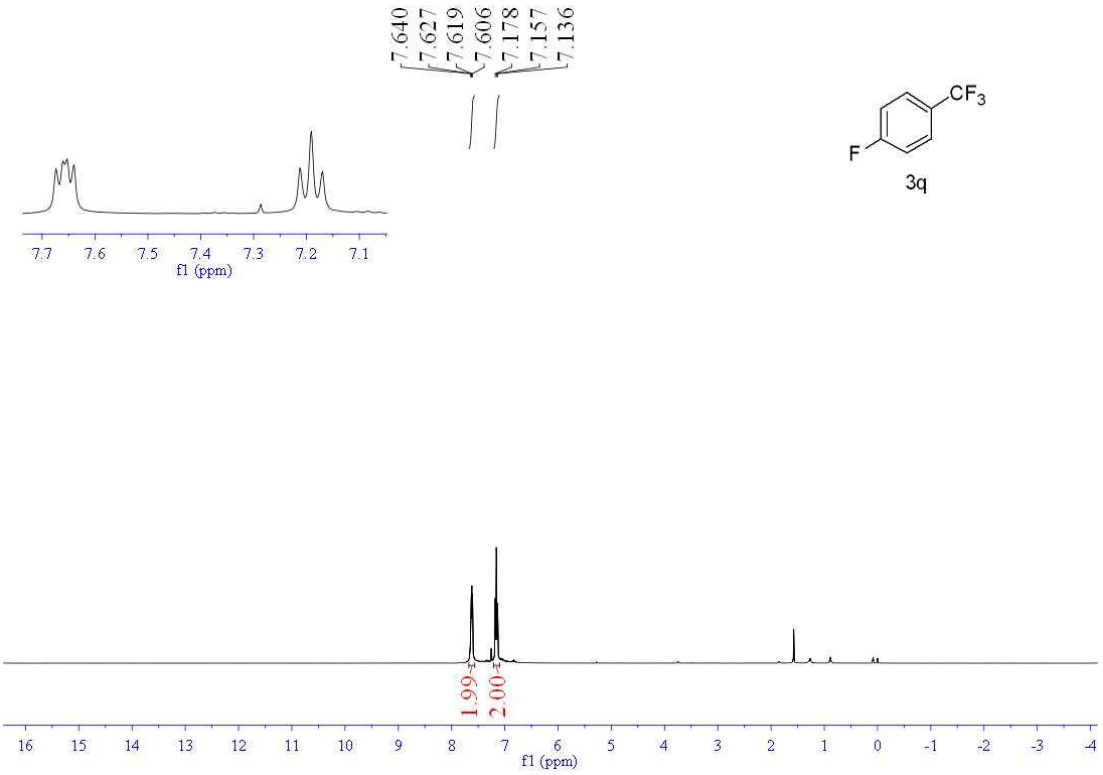
^{13}C NMR spectrum of **3p** in $CDCl_3$



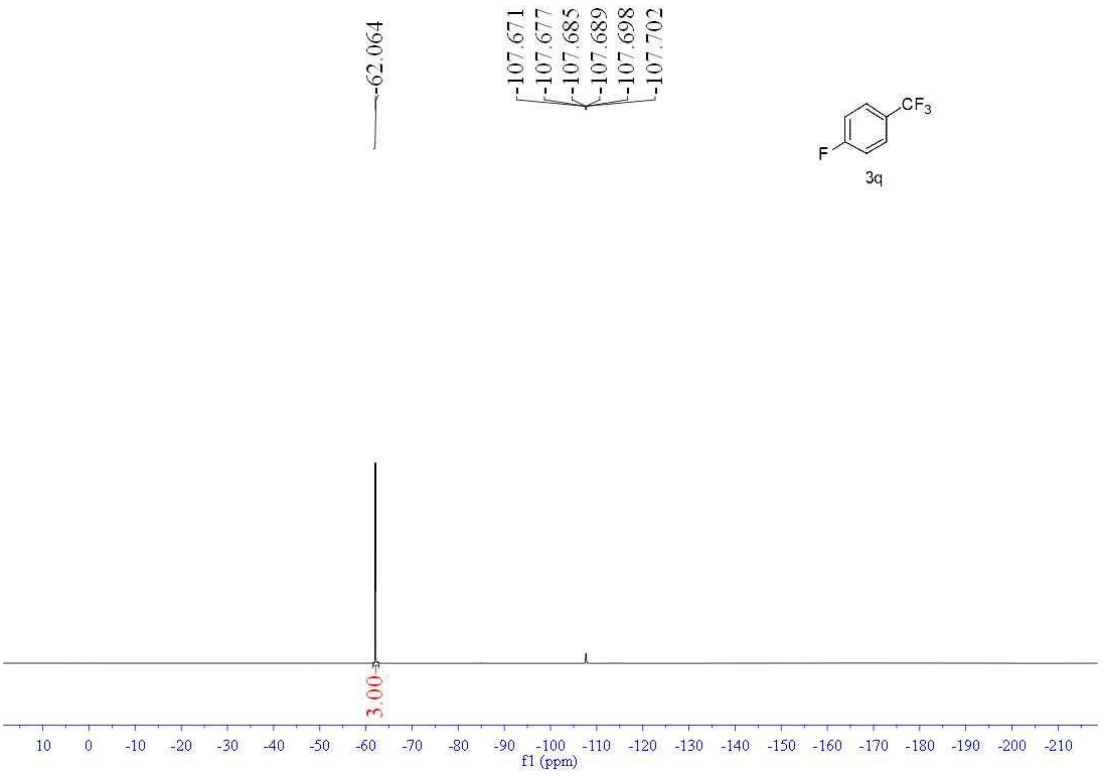
^{19}F NMR spectrum of **3p** (unlocked)



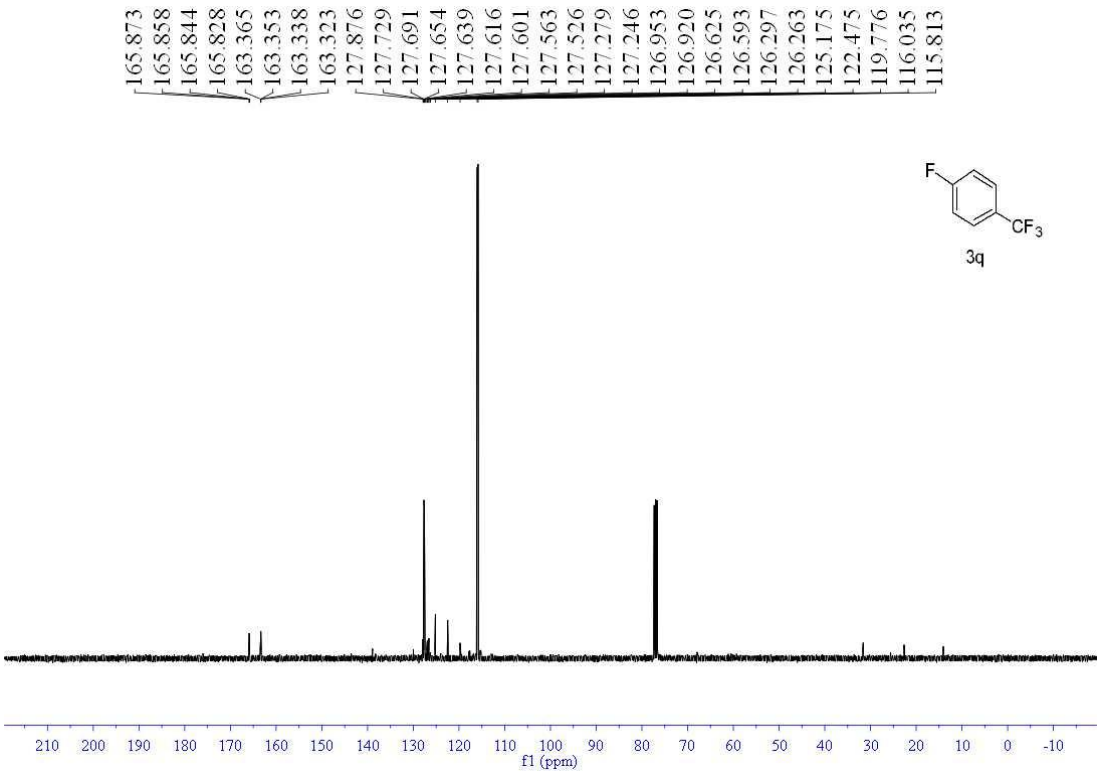
^{1}H NMR spectrum of **3q** in $CDCl_3$



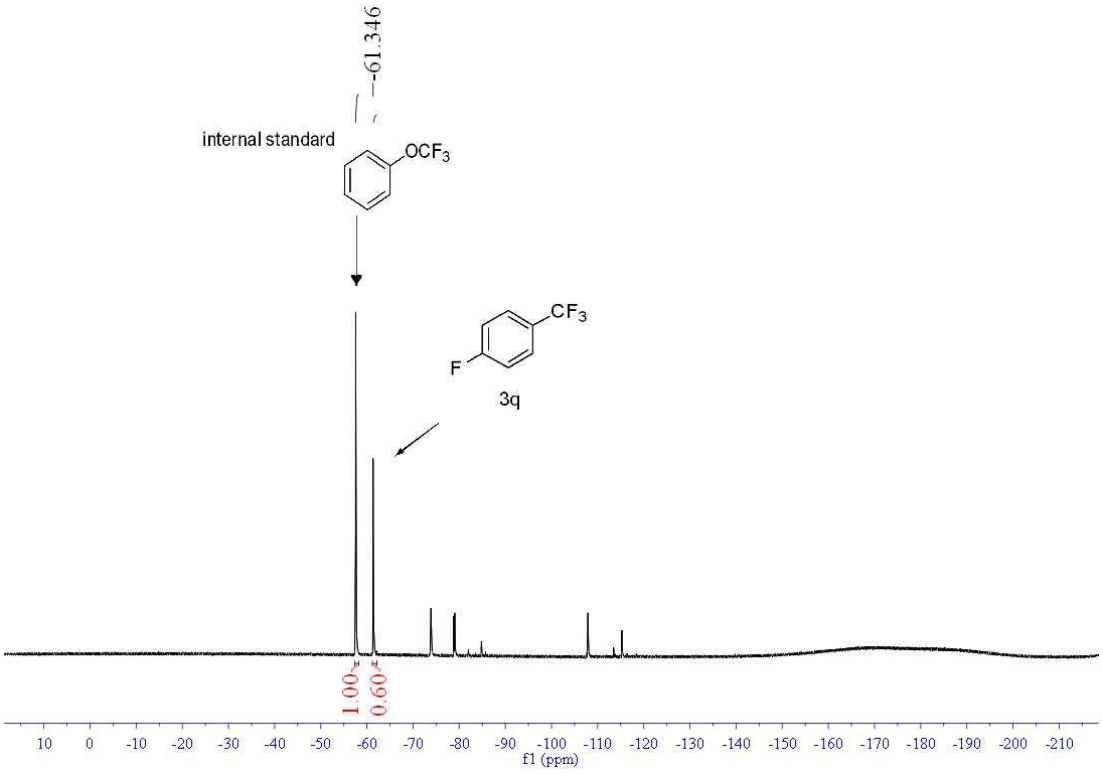
^{19}F NMR spectrum of **3q** in $CDCl_3$



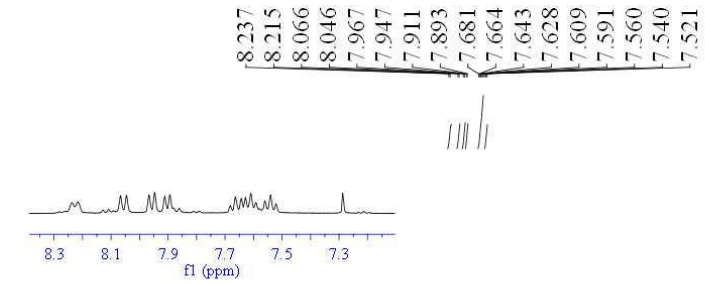
^{13}C NMR spectrum of **3q** in $CDCl_3$

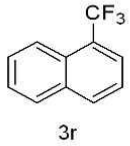


^{19}F NMR spectrum of **3q** (unlocked)

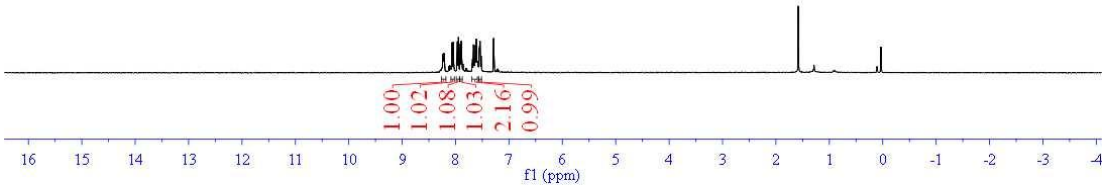


^{1}H NMR spectrum of **3r** in $CDCl_3$

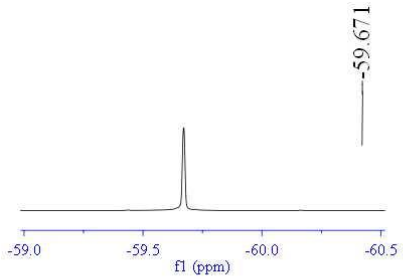


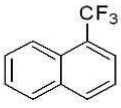


3r

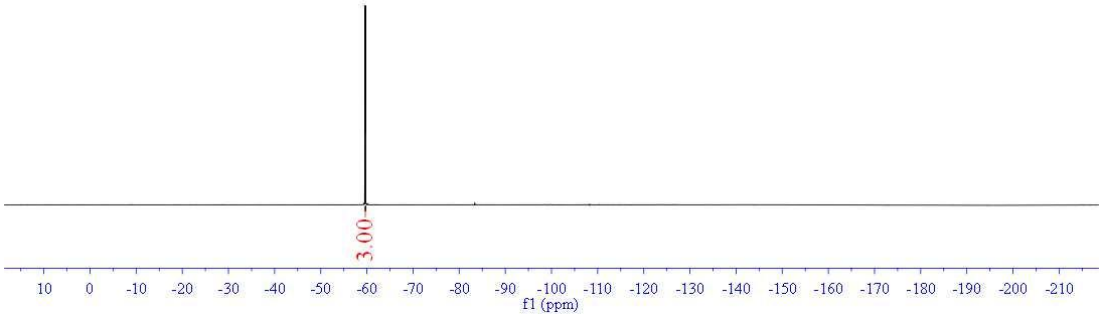


^{19}F NMR spectrum of **3r** in $CDCl_3$

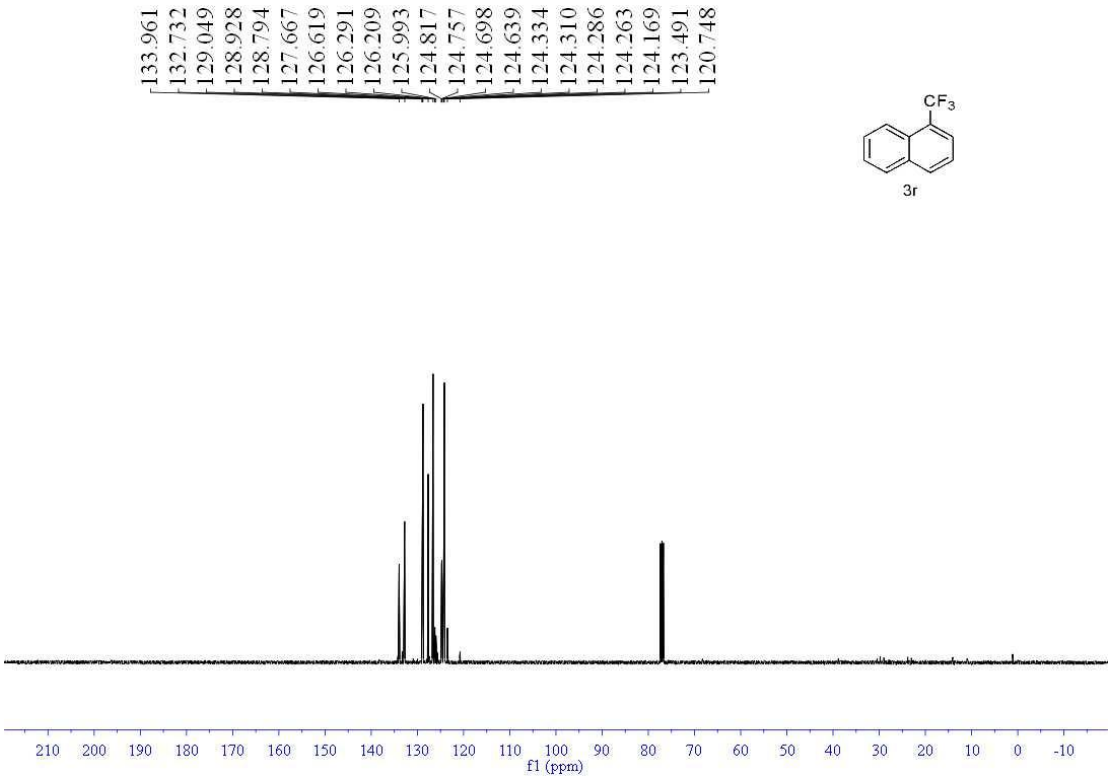




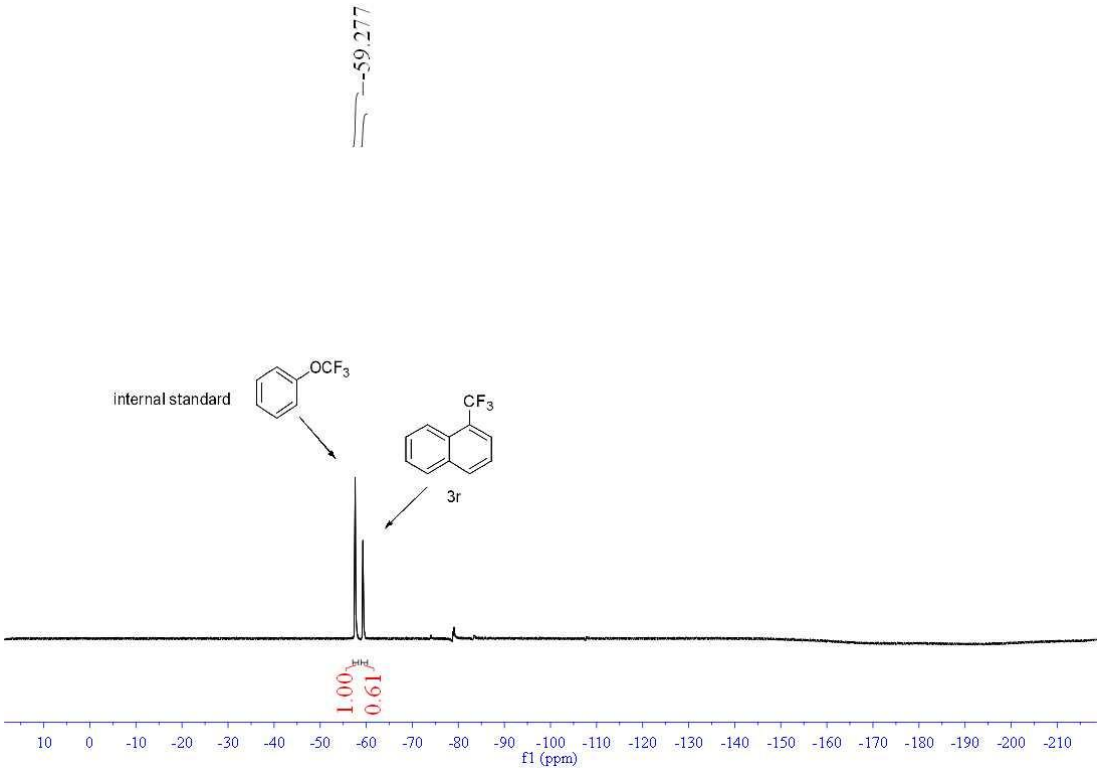
3r



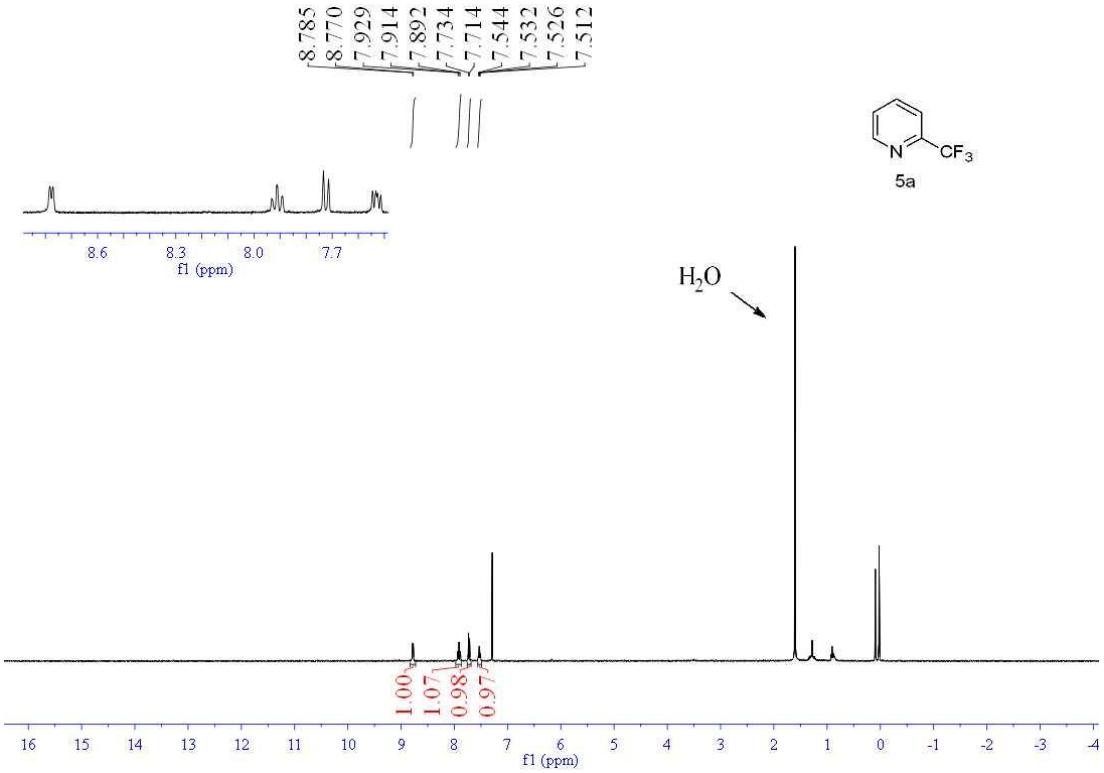
^{13}C NMR spectrum of **3r** in $CDCl_3$



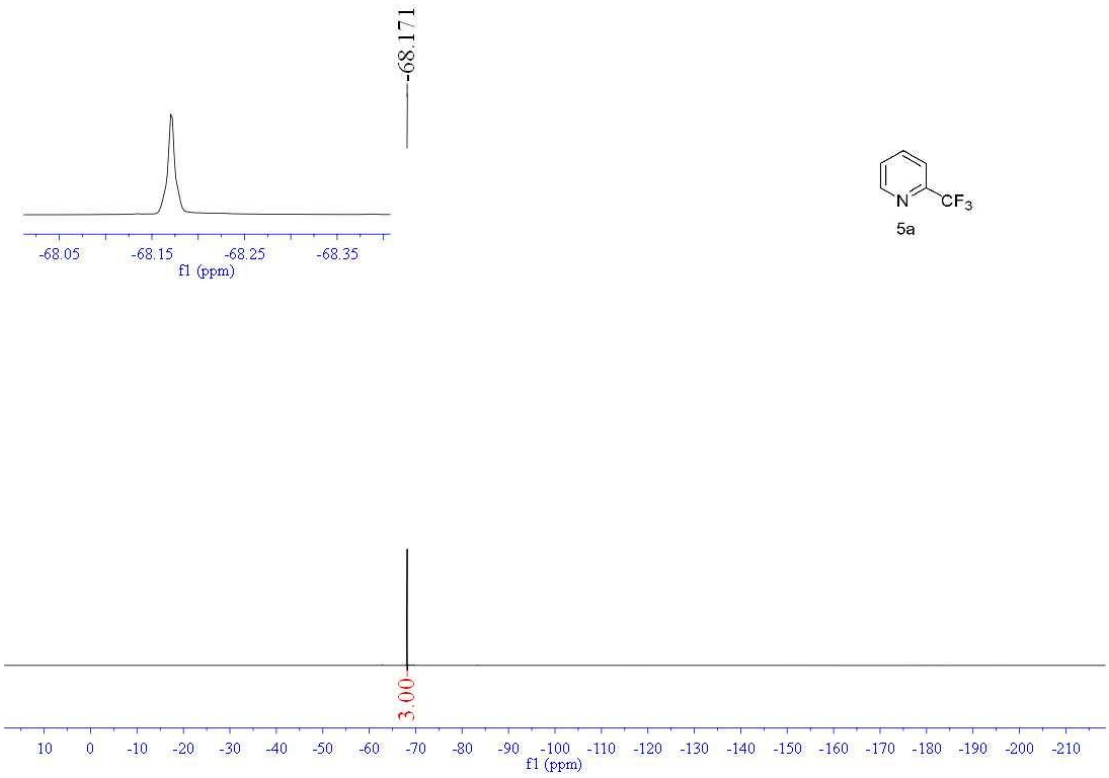
^{19}F NMR spectrum of **3r** (unlocked)



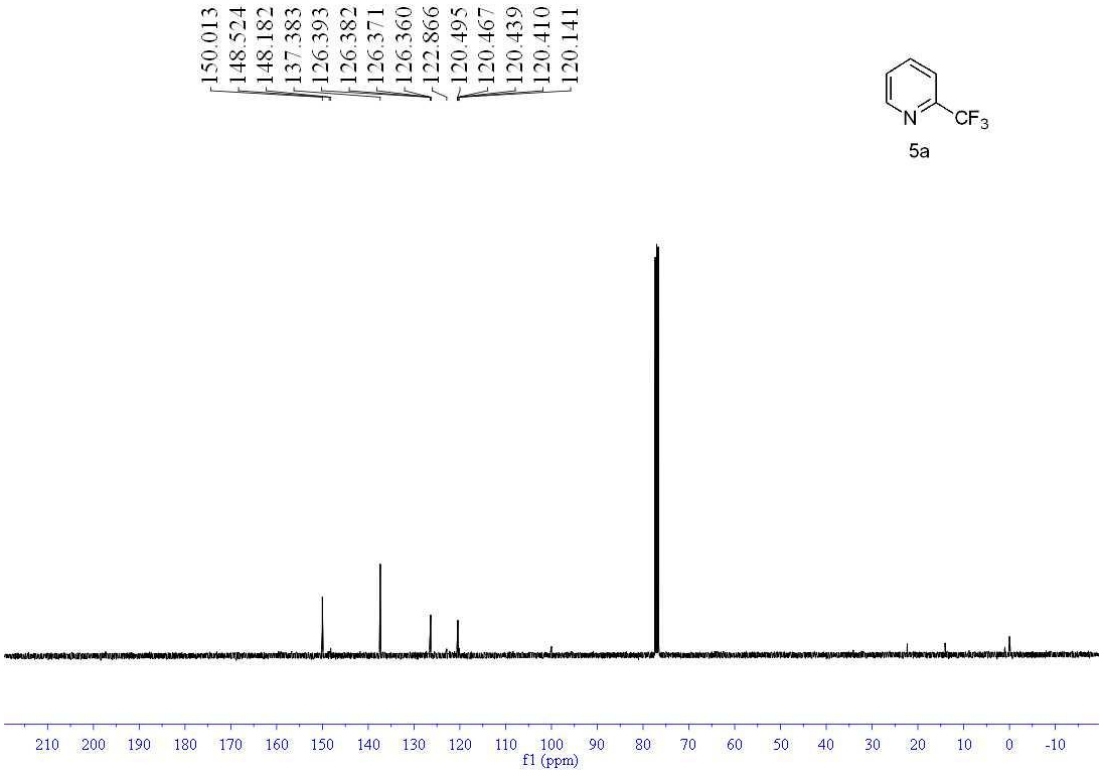
^{1}H NMR spectrum of **5a** in $CDCl_3$



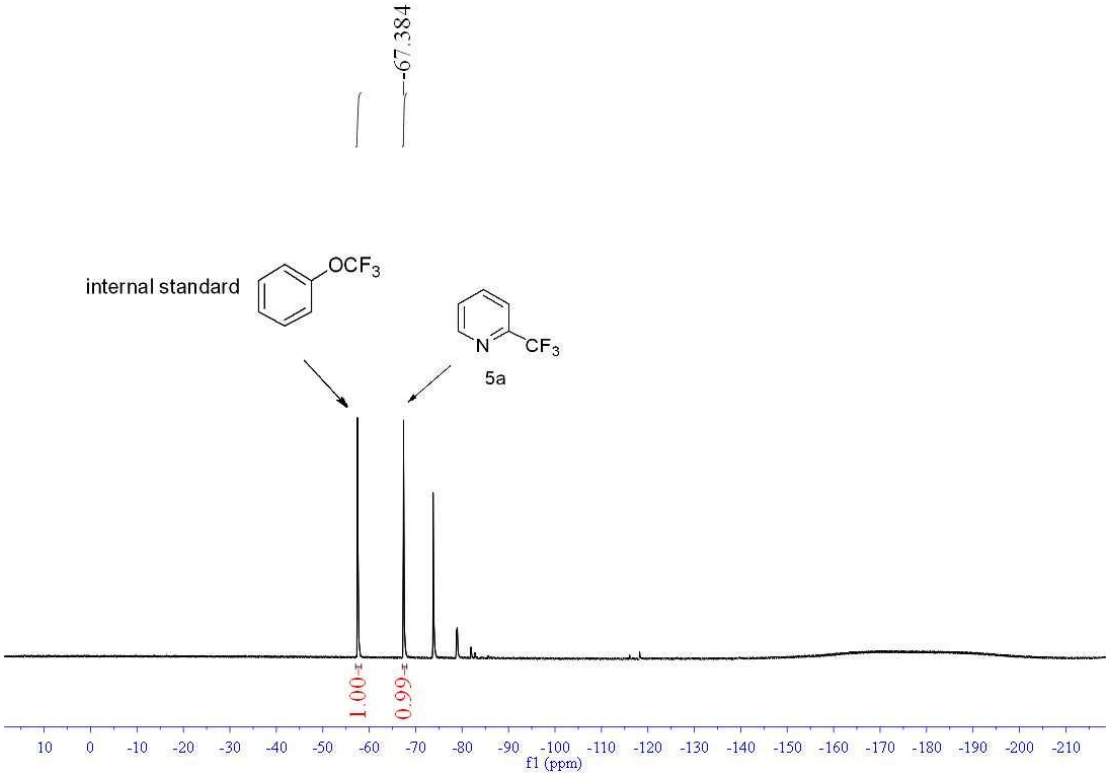
^{19}F NMR spectrum of **5a** in $CDCl_3$



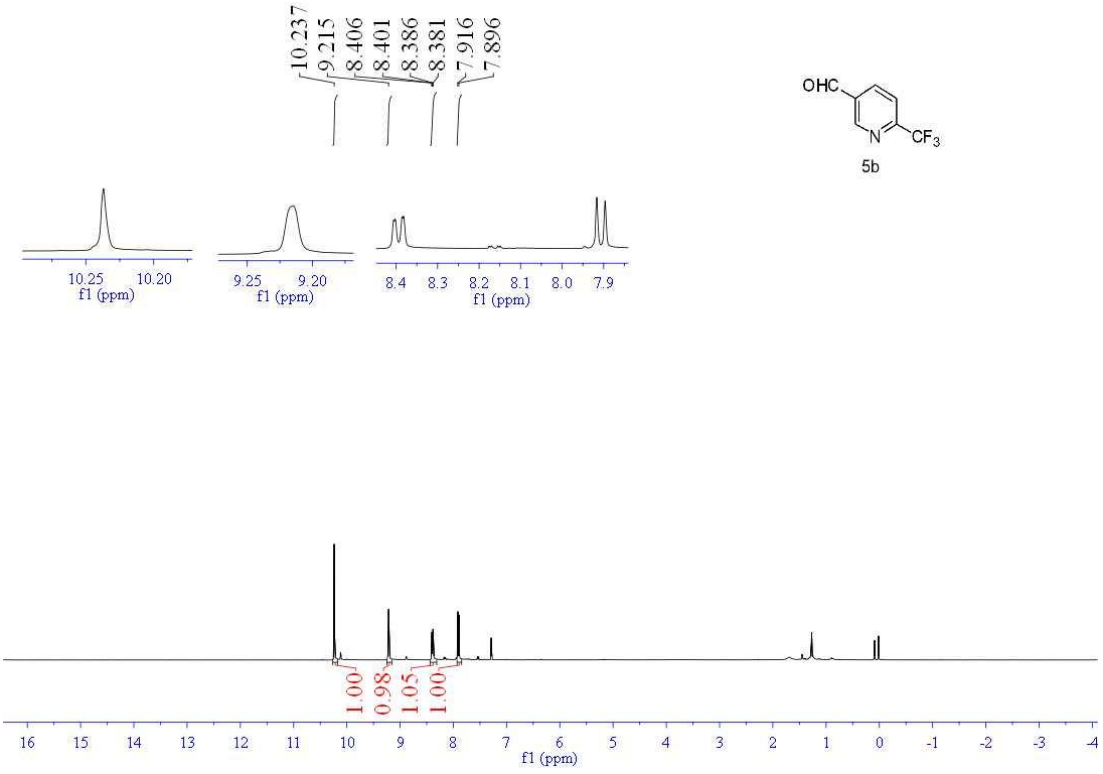
^{13}C NMR spectrum of **5a** in $CDCl_3$



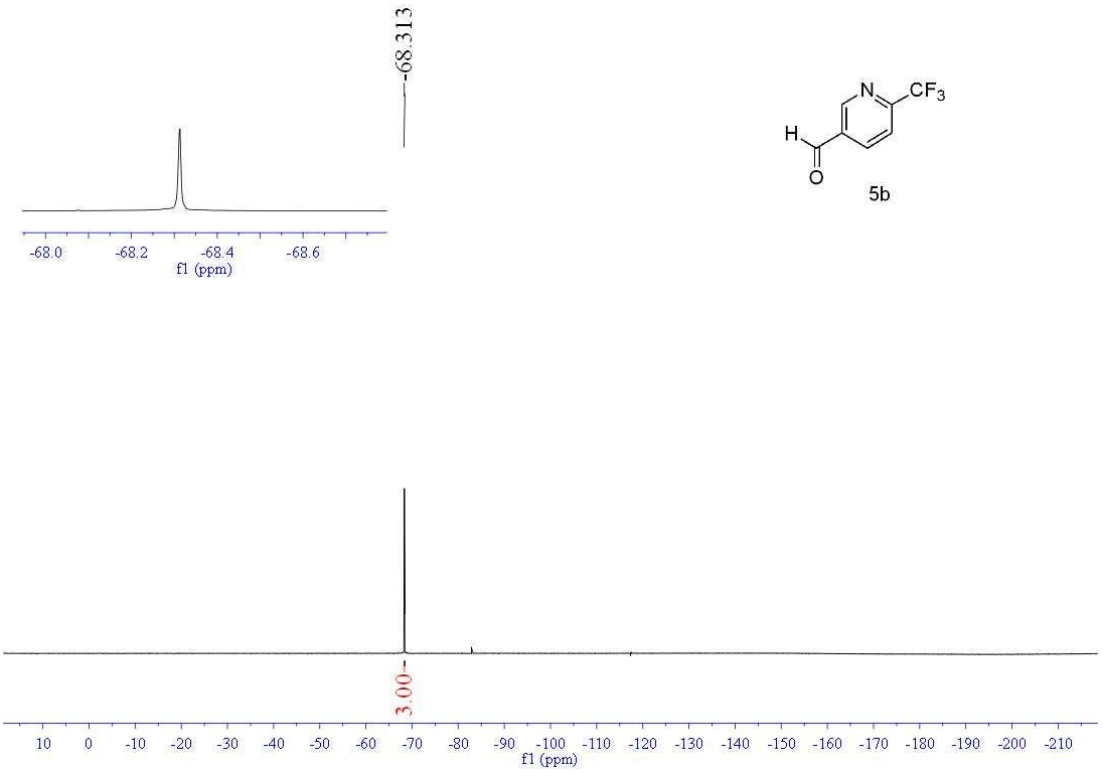
^{19}F NMR spectrum of **5a** (unlocked)



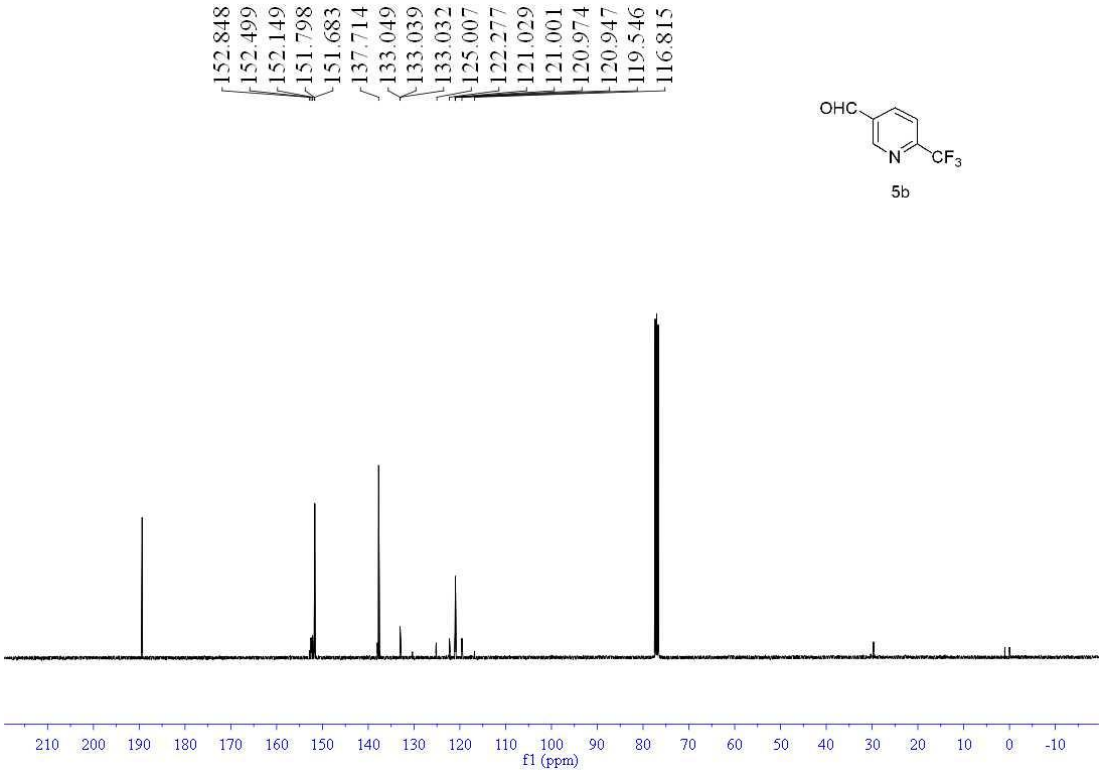
^{1}H NMR spectrum of **5b** in $CDCl_3$



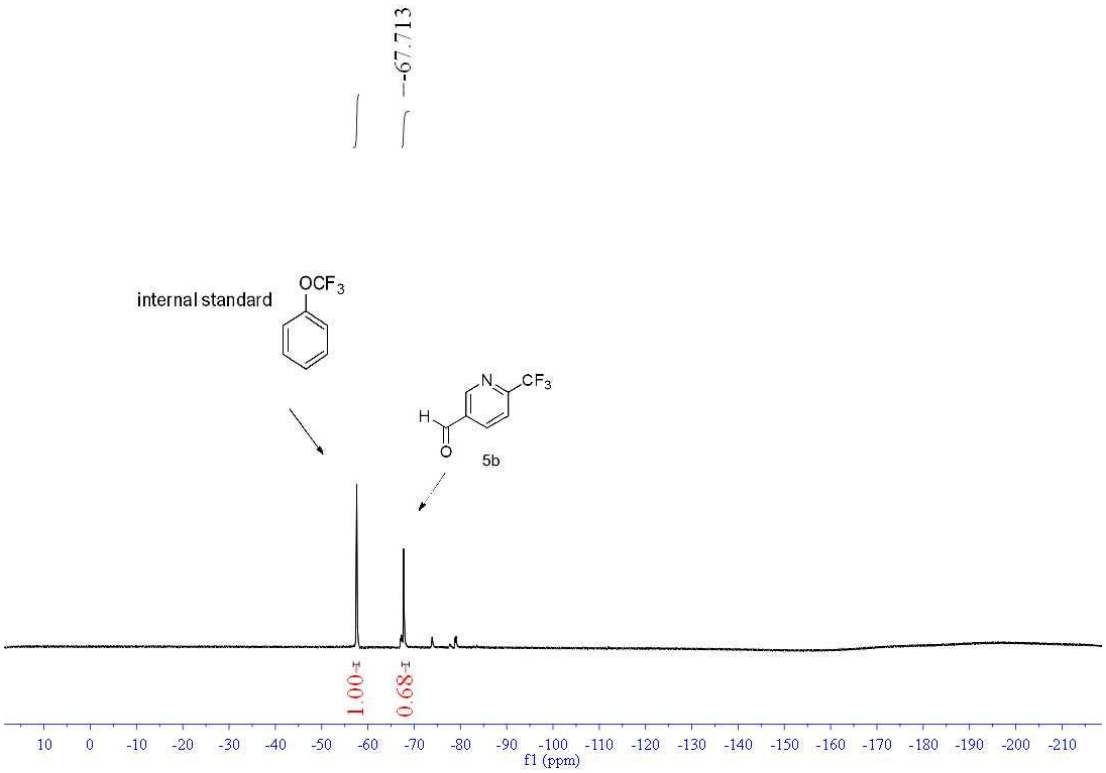
^{19}F NMR spectrum of **5b** in $CDCl_3$



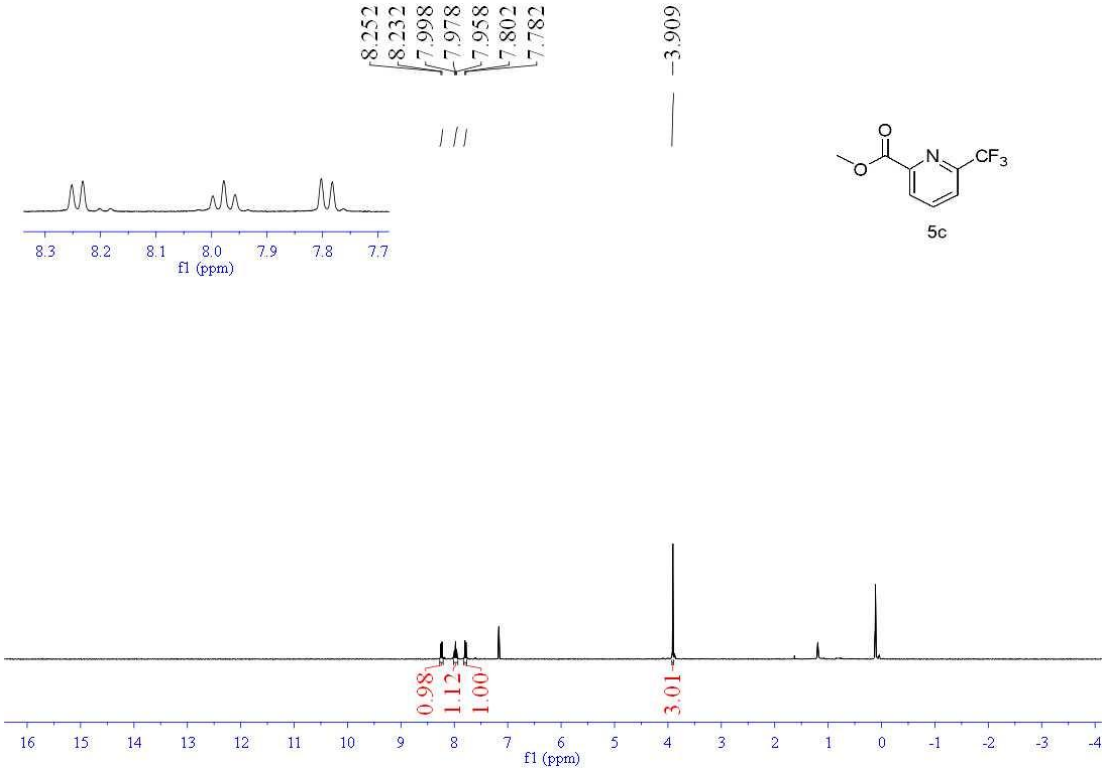
^{13}C NMR spectrum of **5b** in $CDCl_3$



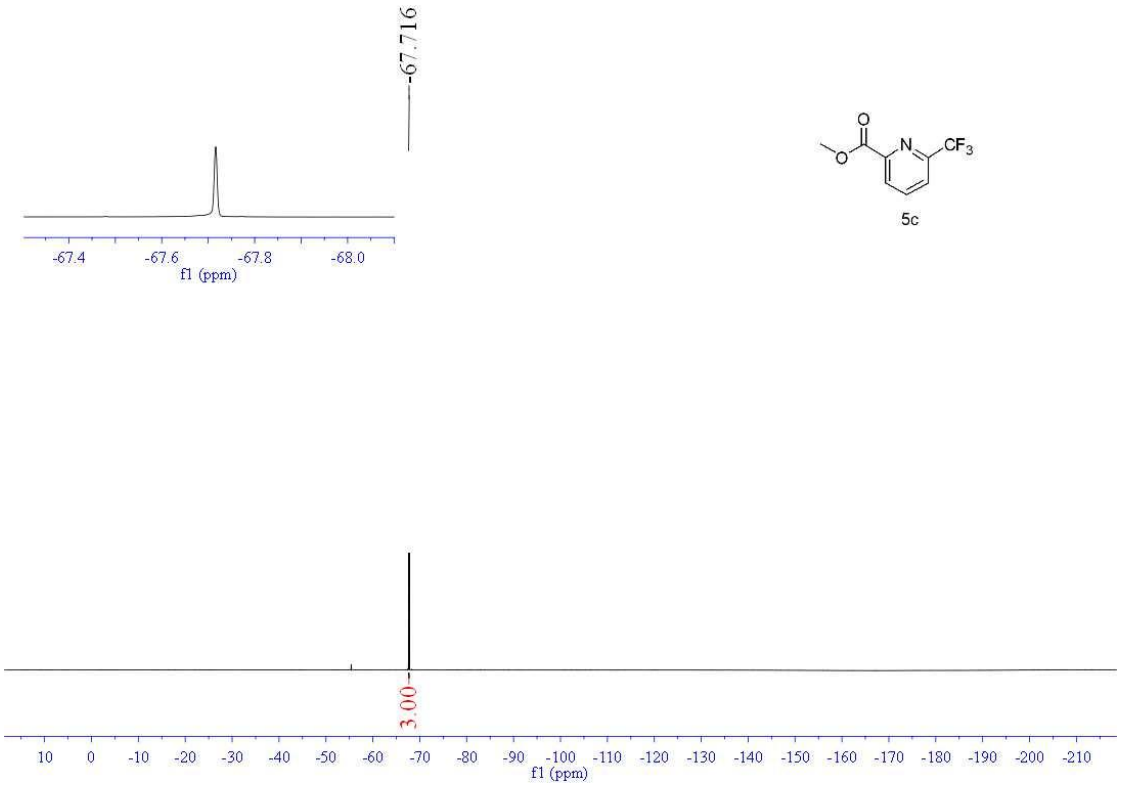
^{19}F NMR spectrum of **5b** (unlocked)



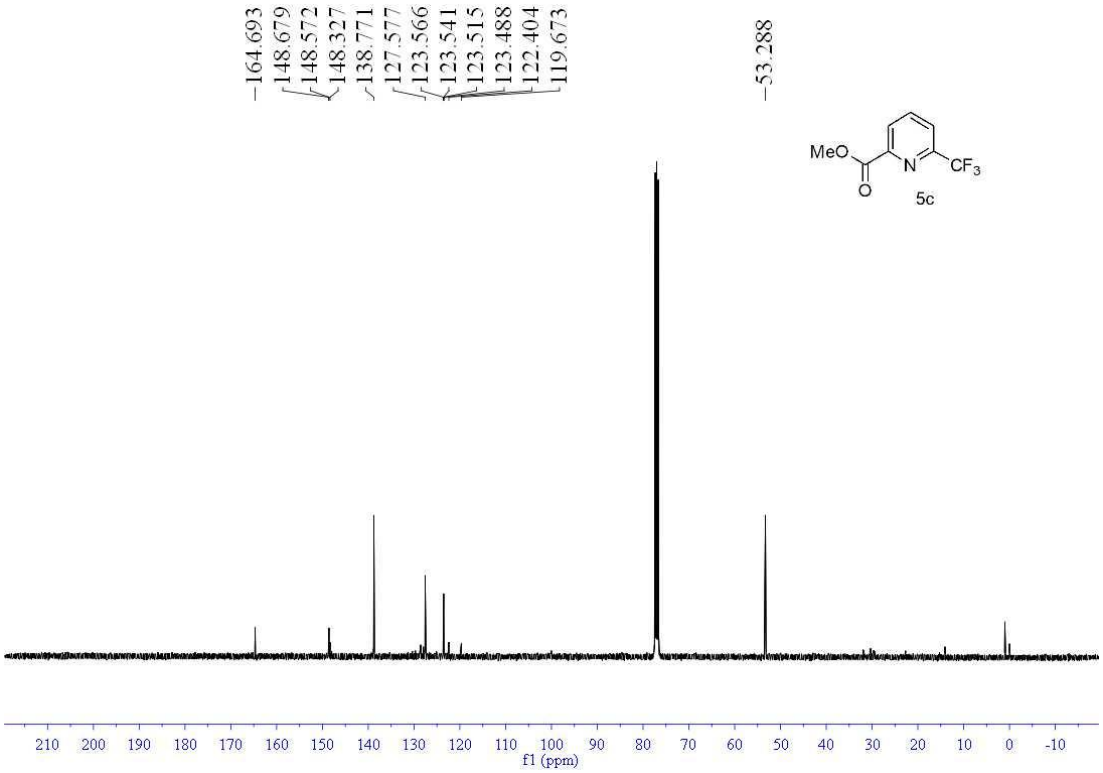
^{1}H NMR spectrum of **5c** in $CDCl_3$



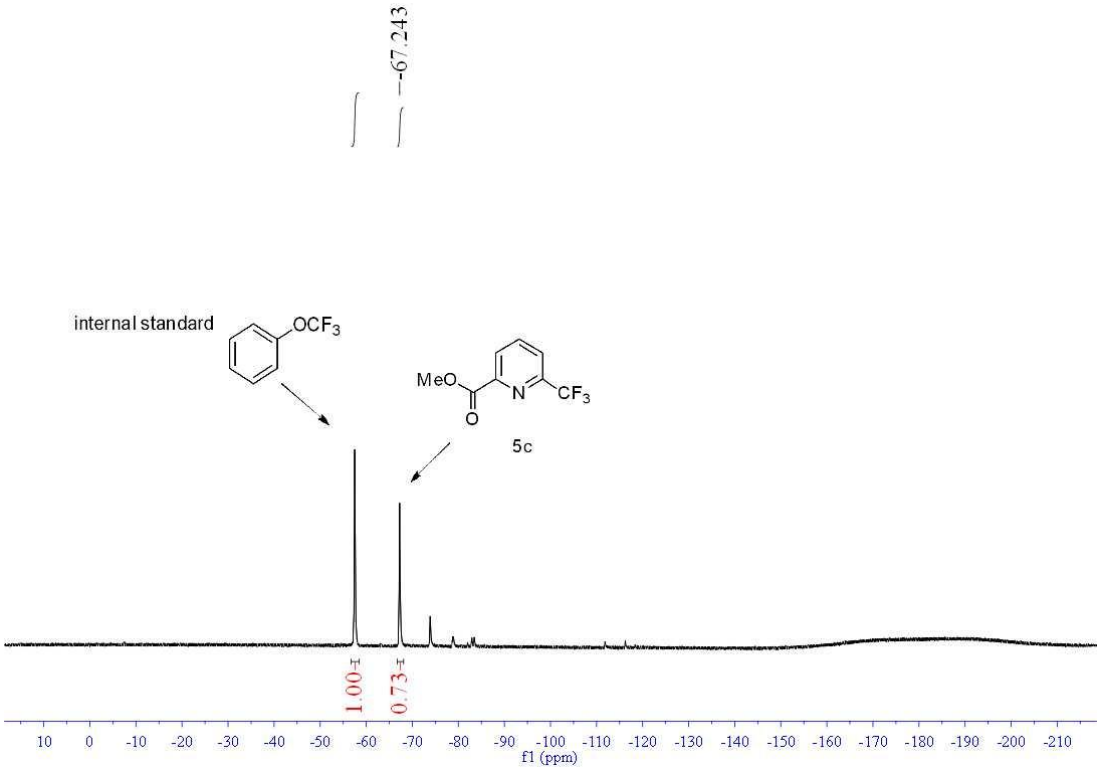
^{19}F NMR spectrum of **5c** in $CDCl_3$



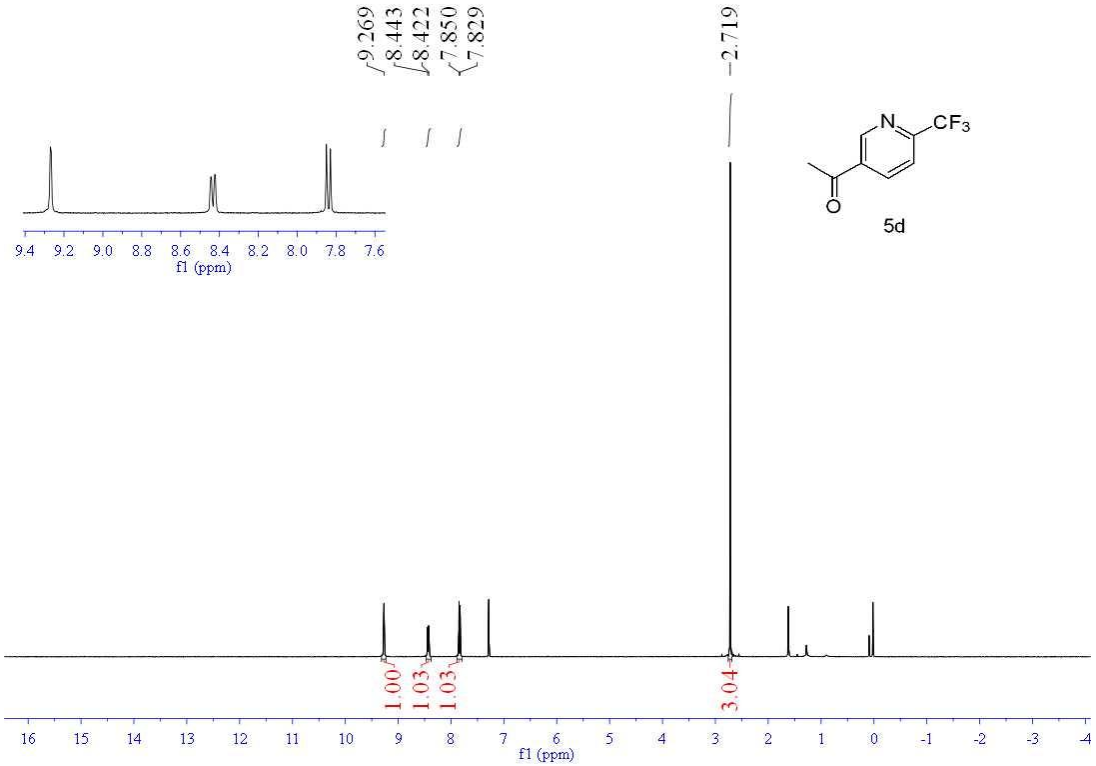
^{13}C NMR spectrum of **5c** in $CDCl_3$



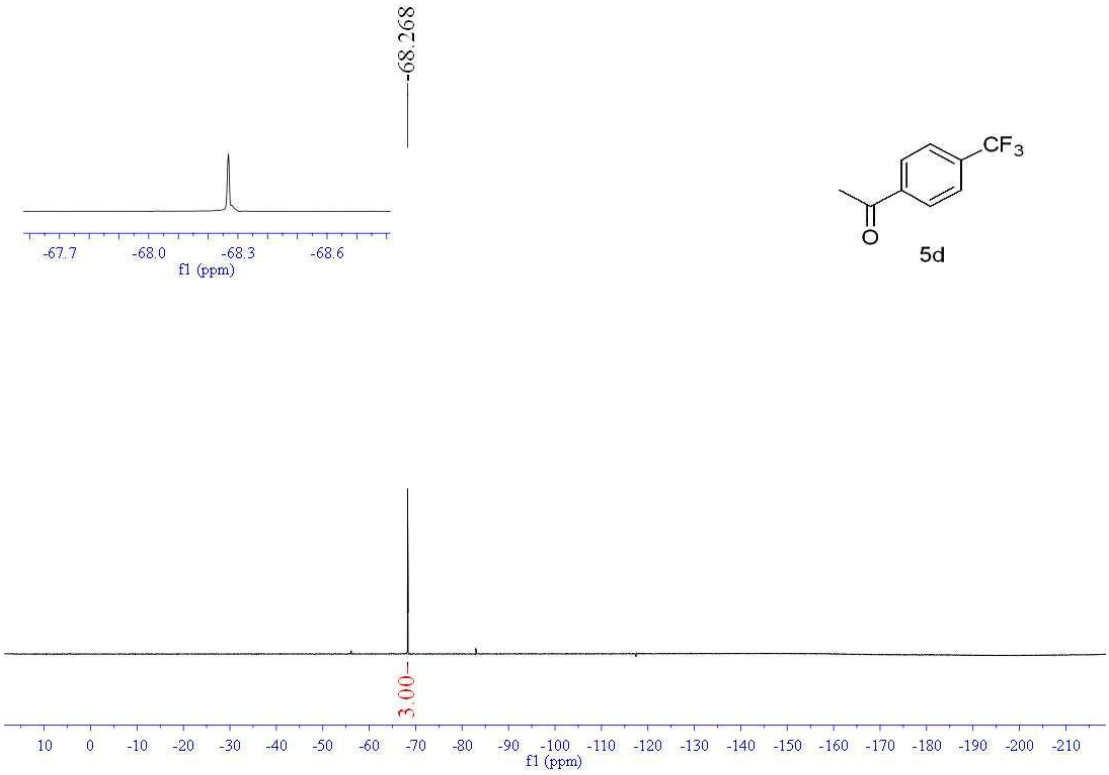
^{19}F NMR spectrum of **5c** (unlocked)



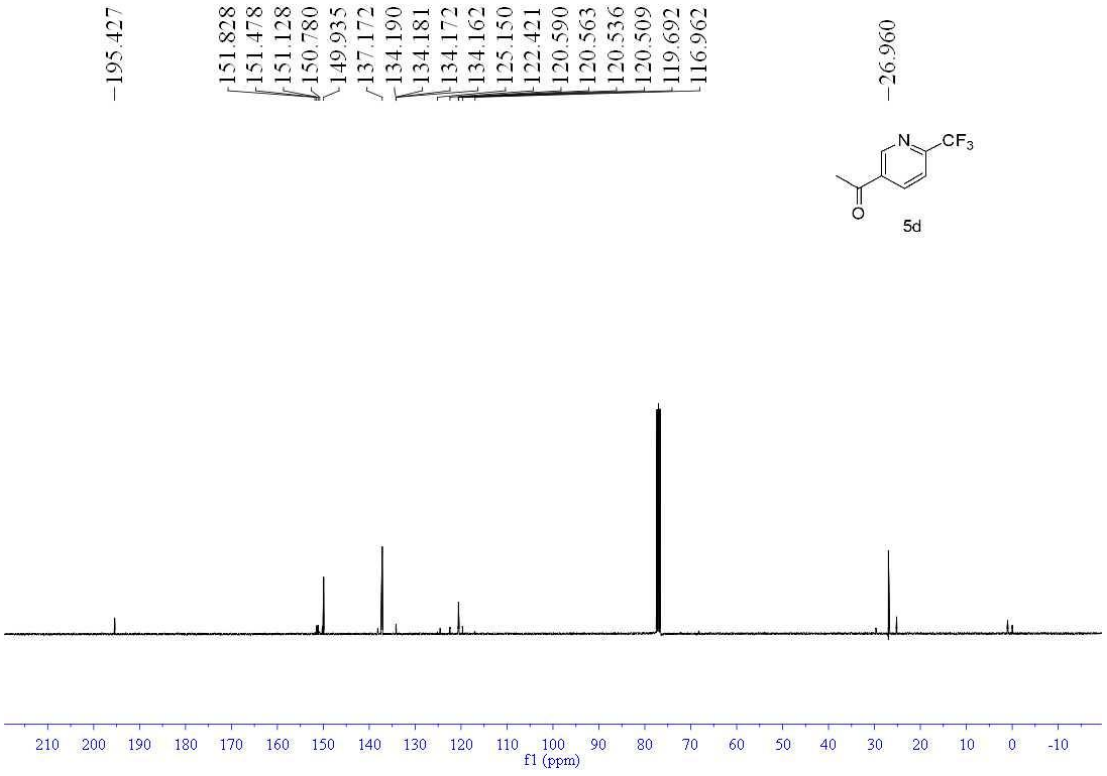
^{1}H NMR spectrum of **5d** in $CDCl_3$



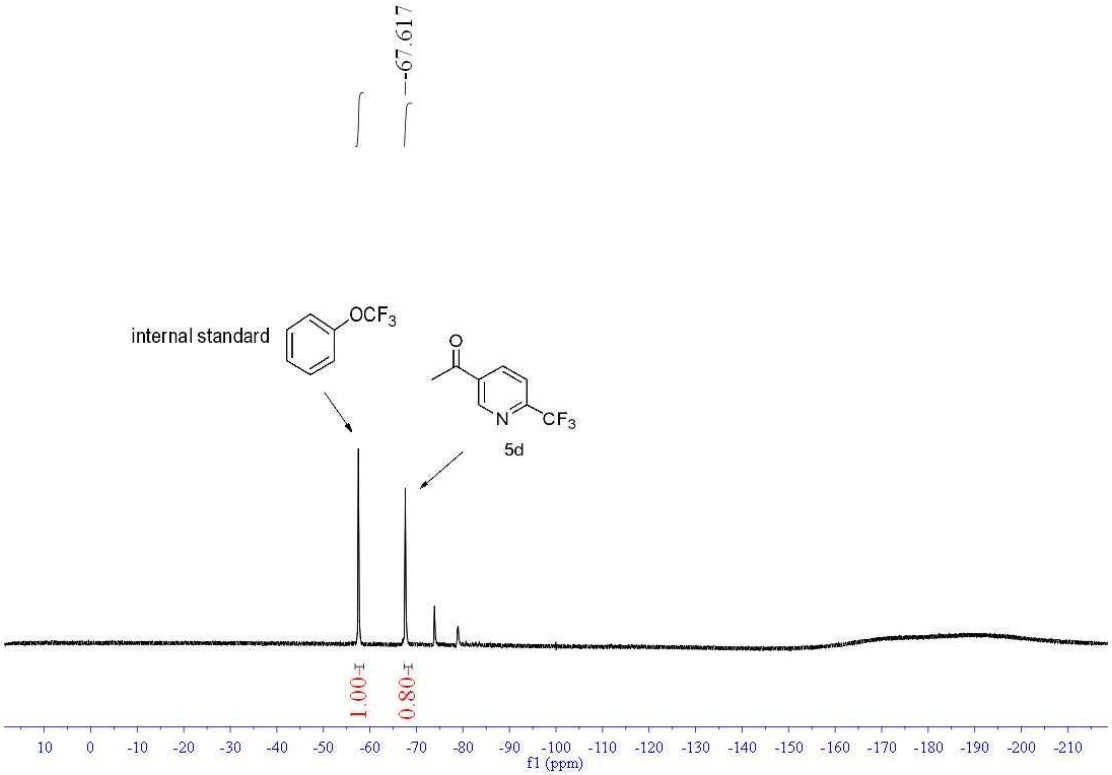
^{19}F NMR spectrum of **5d** in $CDCl_3$



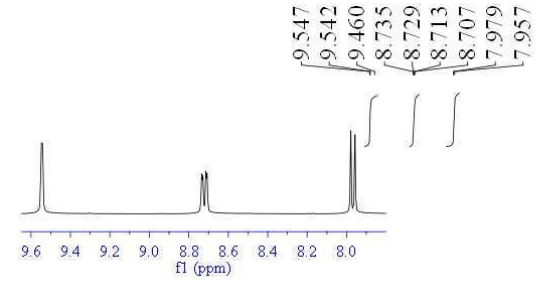
^{13}C NMR spectrum of **5d** in $CDCl_3$



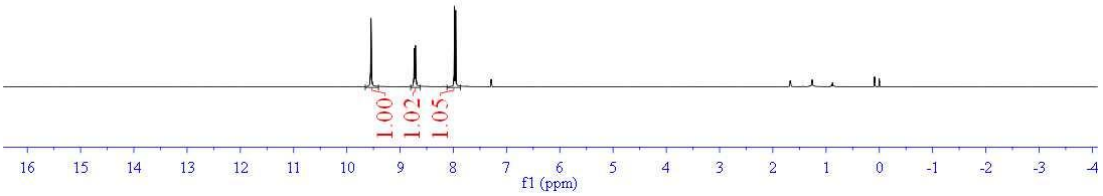
^{19}F NMR spectrum of **5d** (unlocked)



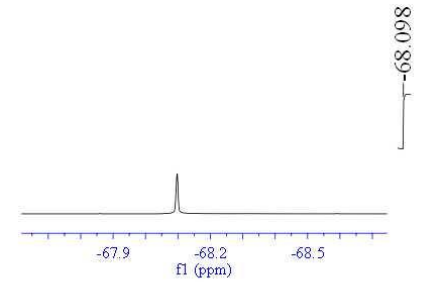
^{1}H NMR spectrum of **5e** in $CDCl_3$

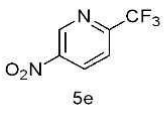


5e

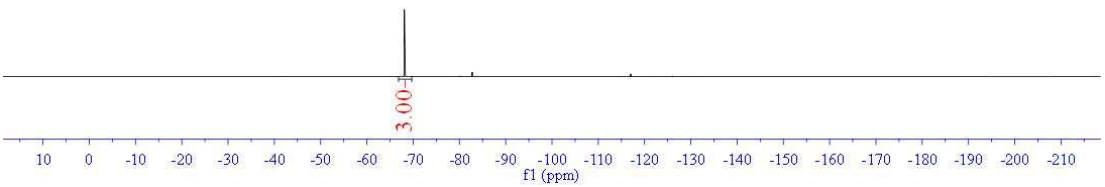


^{19}F NMR spectrum of **5e** in $CDCl_3$

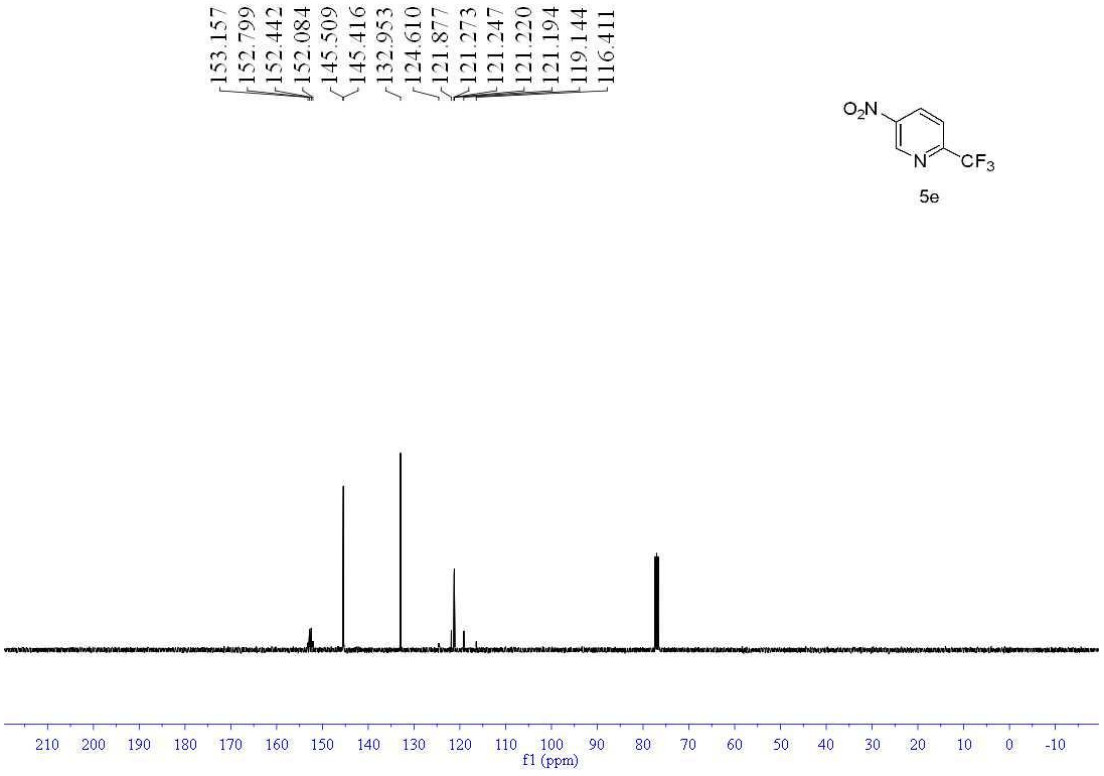




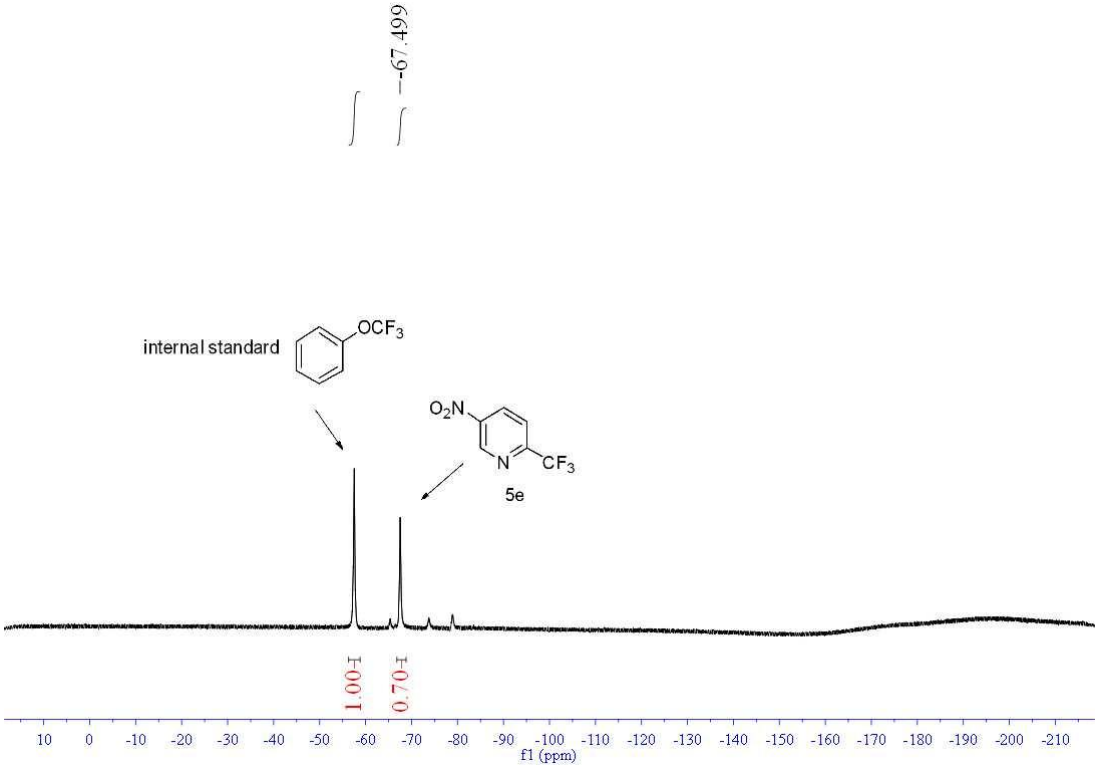
5e



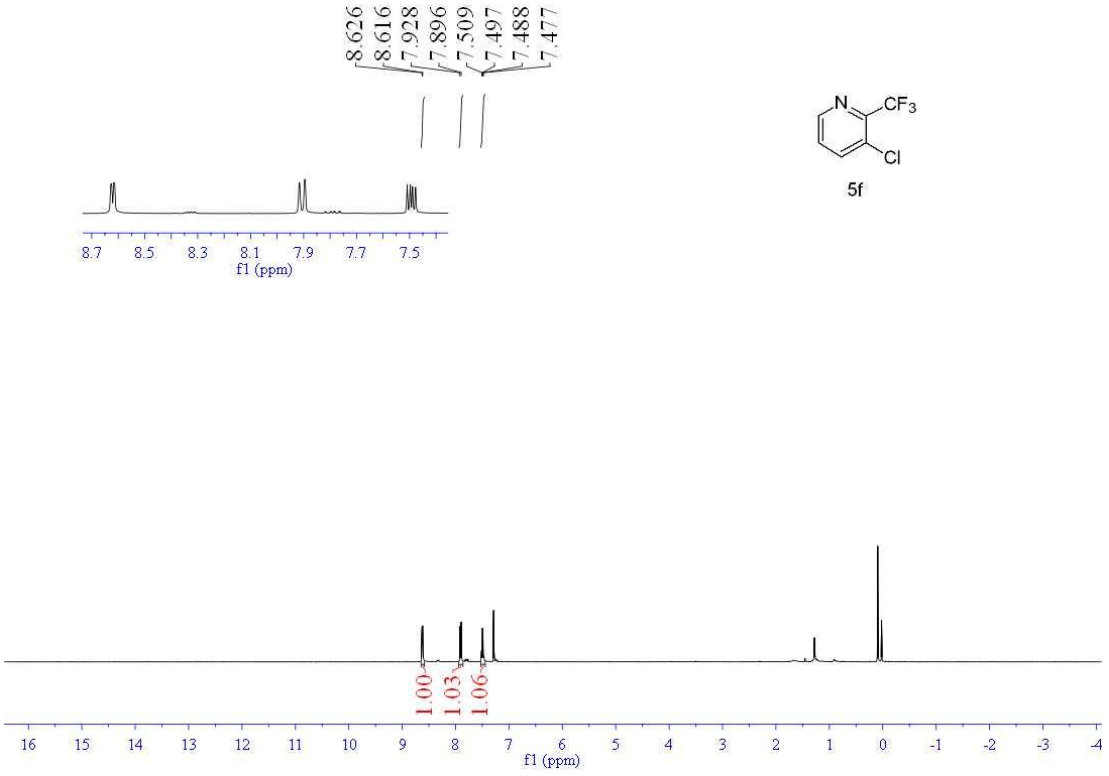
^{13}C NMR spectrum of **5e** in $CDCl_3$



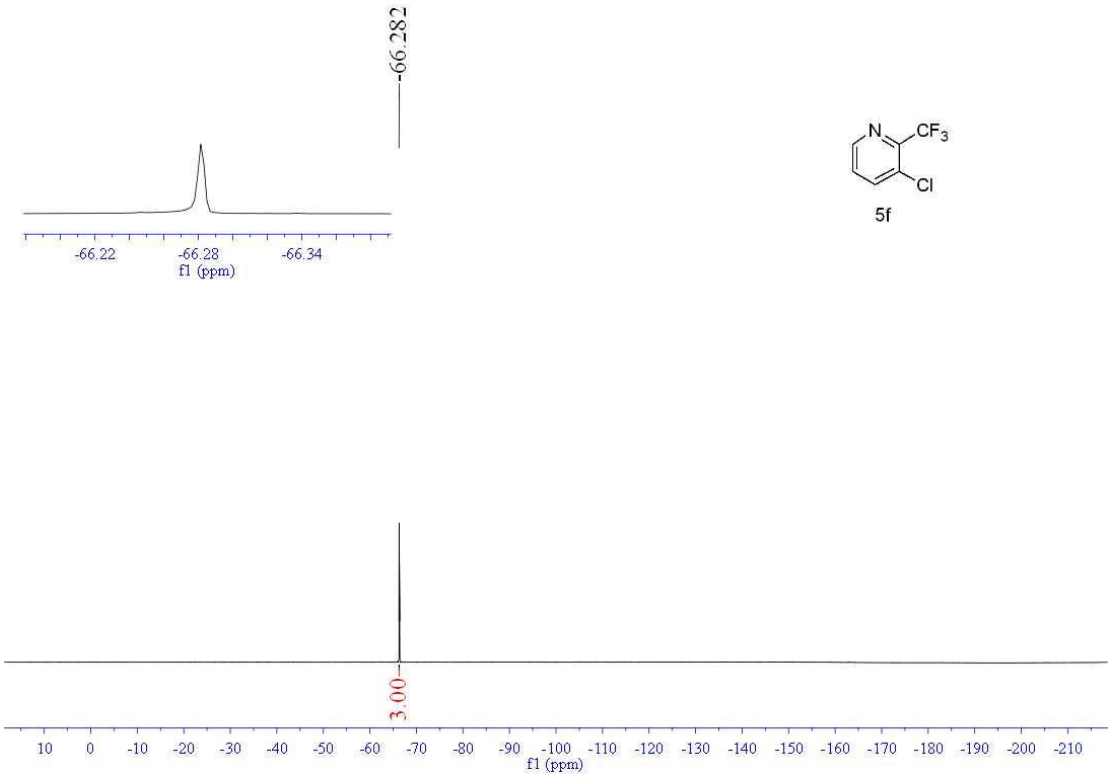
^{19}F NMR spectrum of **5e** (unlocked)



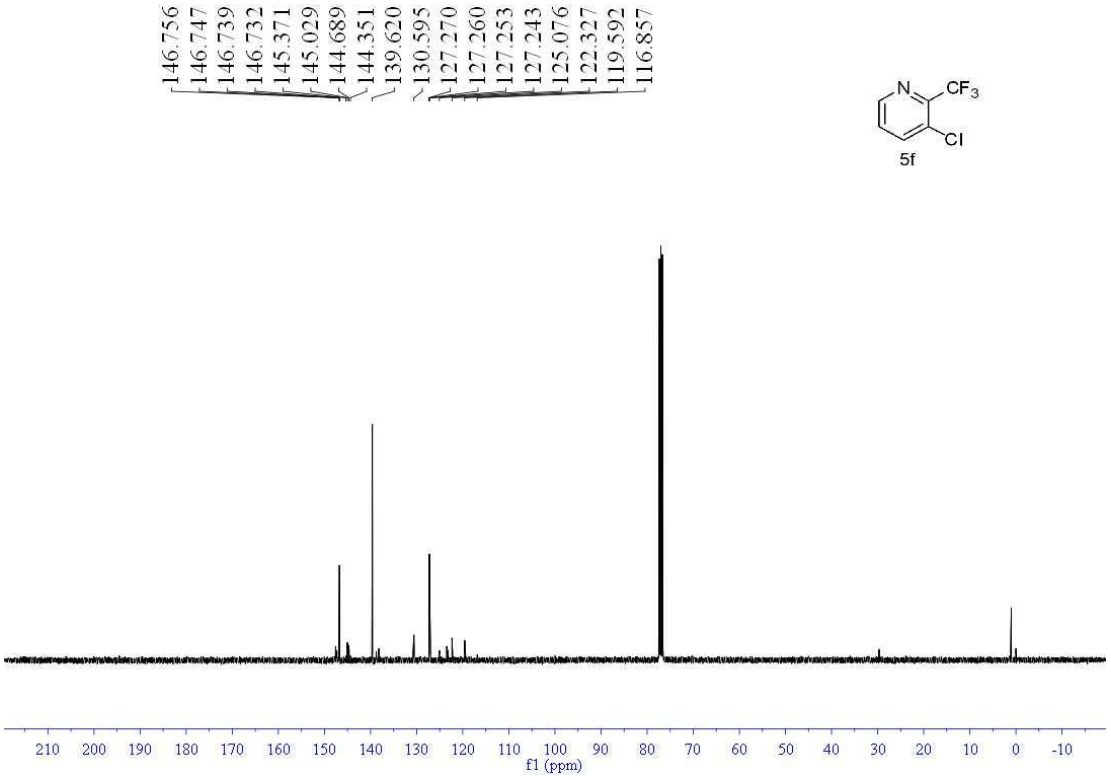
^{1}H NMR spectrum of **5f** in $CDCl_3$



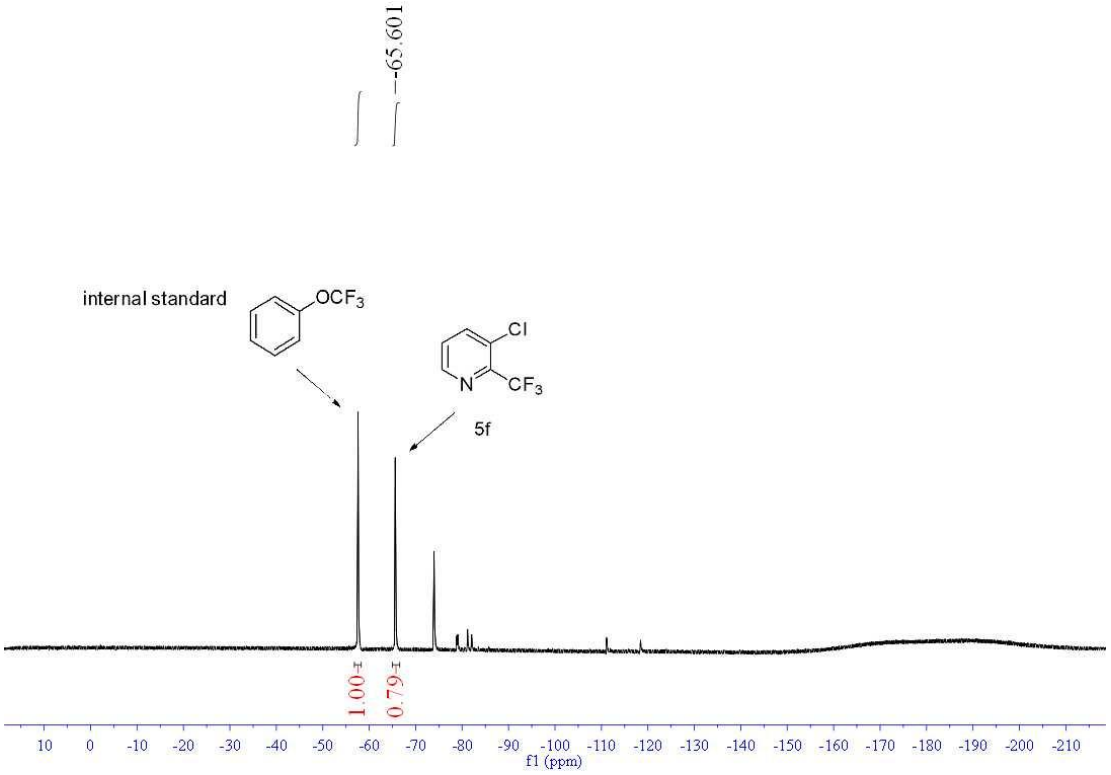
^{19}F NMR spectrum of **5f** in $CDCl_3$



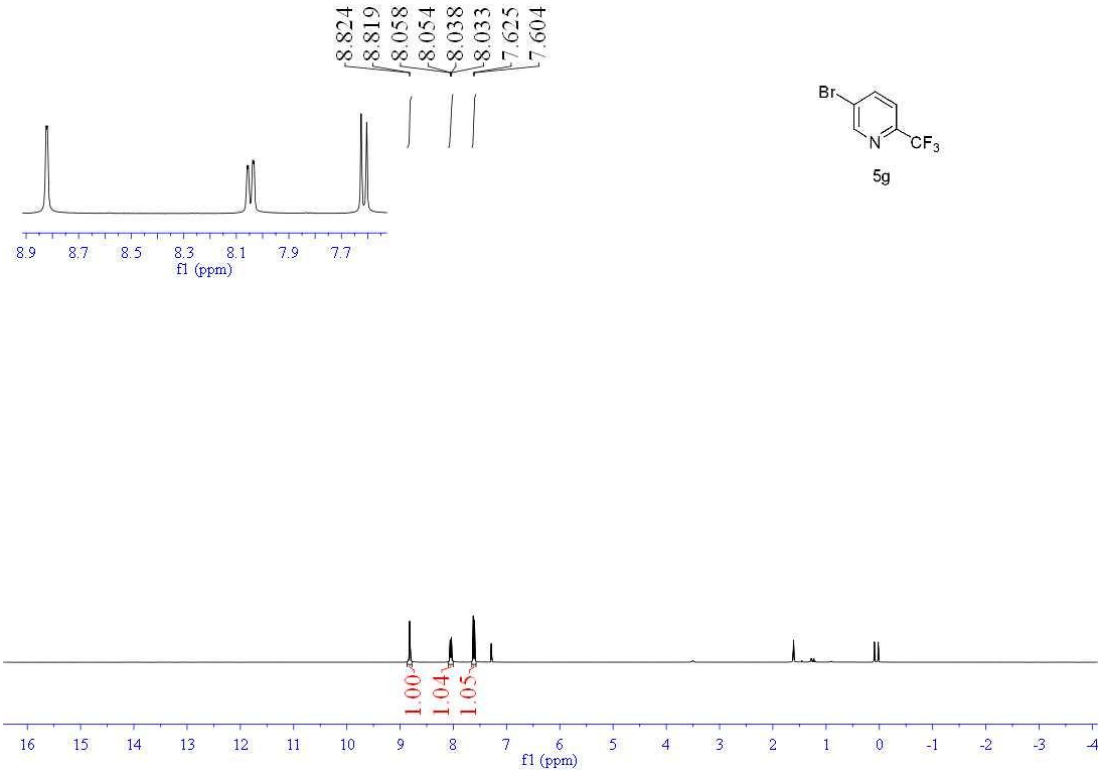
^{13}C NMR spectrum of **5f** in $CDCl_3$



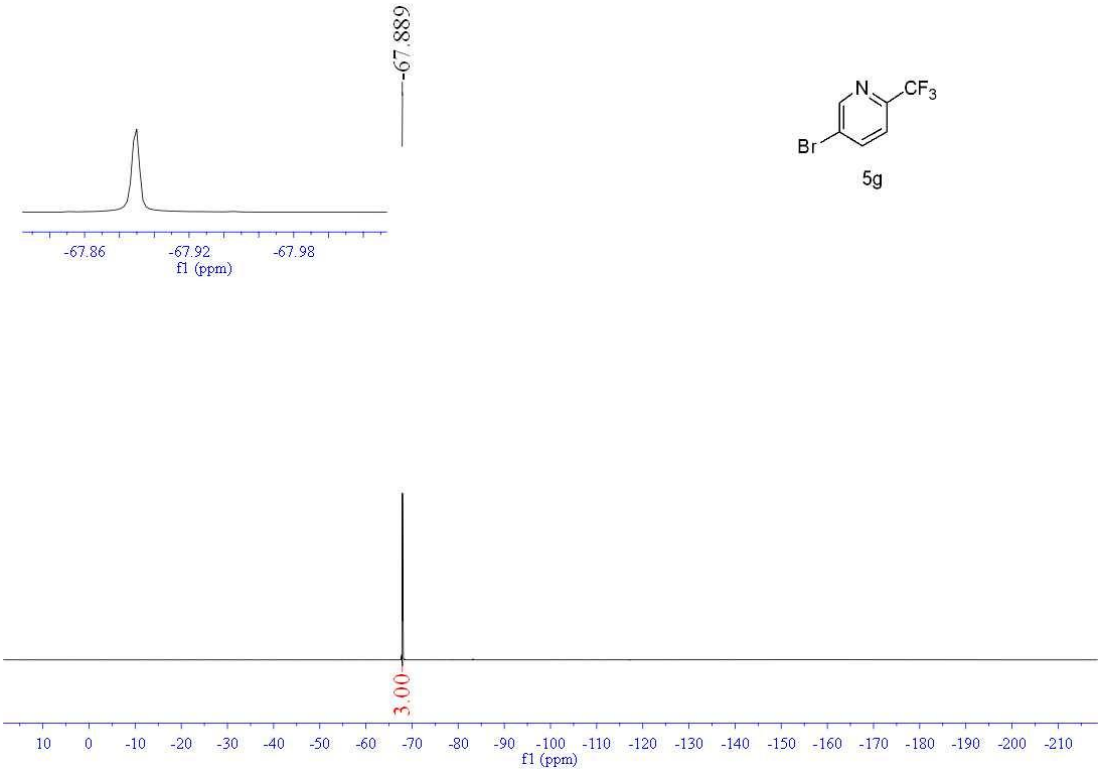
^{19}F NMR spectrum of **5f** (unlocked)



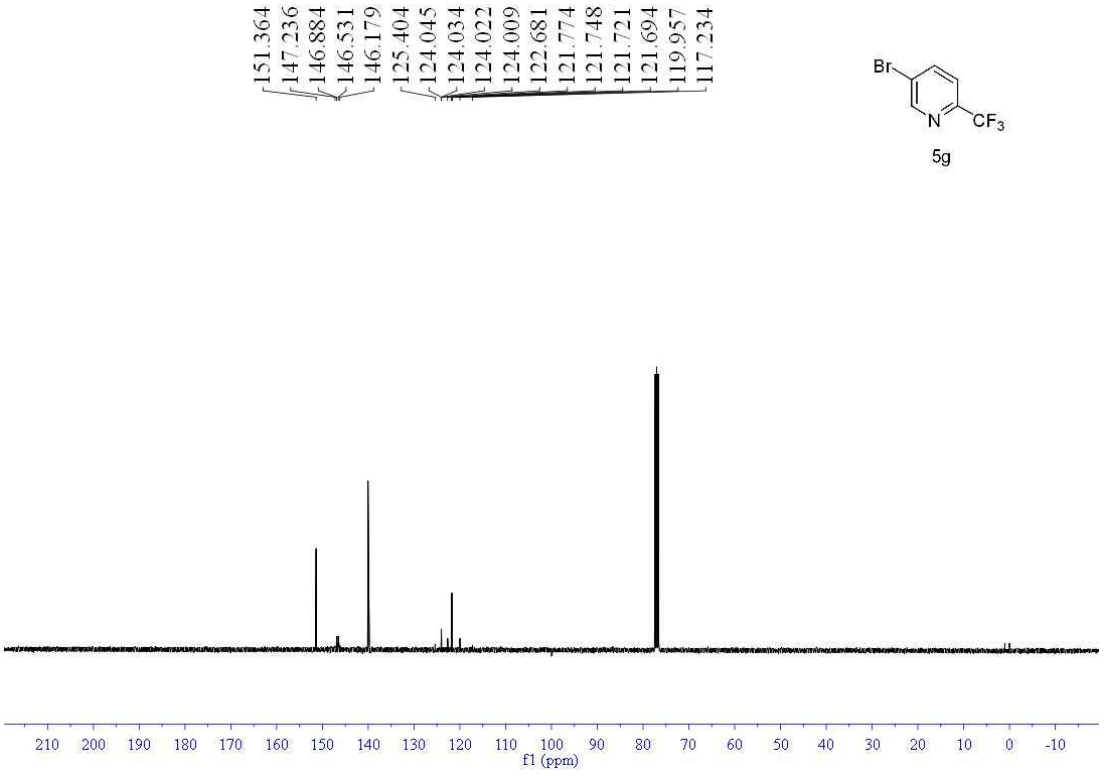
^{1}H NMR spectrum of **5g** in $CDCl_3$



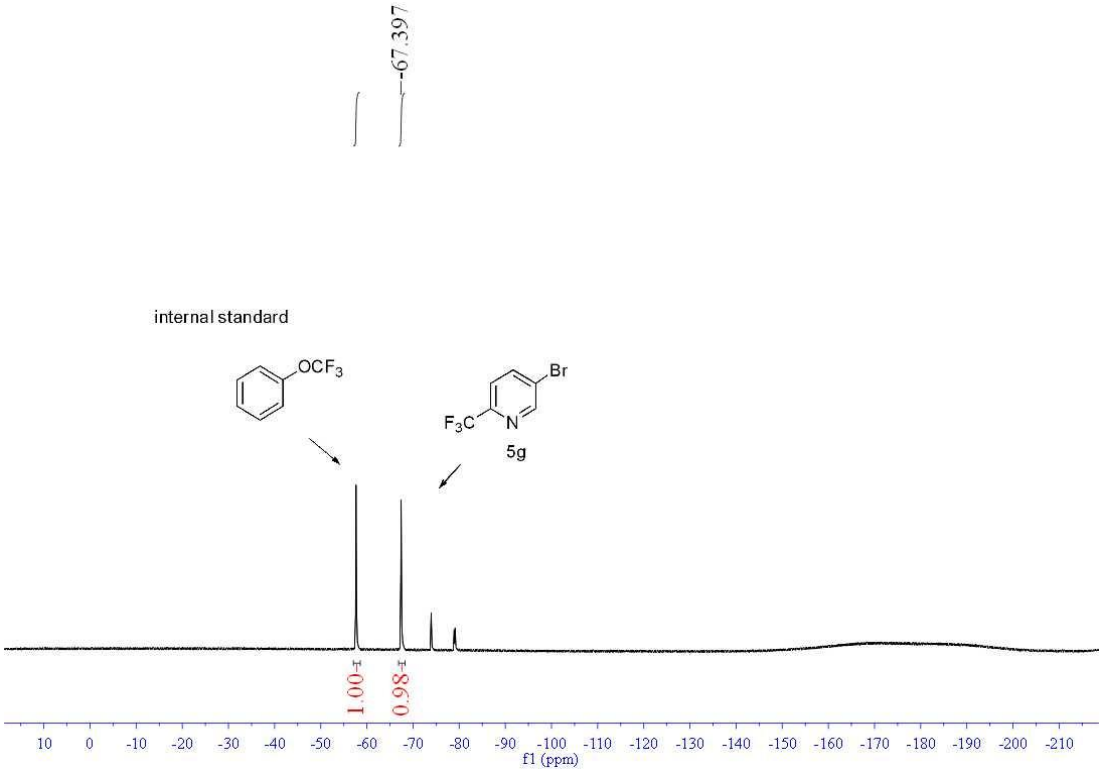
^{19}F NMR spectrum of **5g** in $CDCl_3$



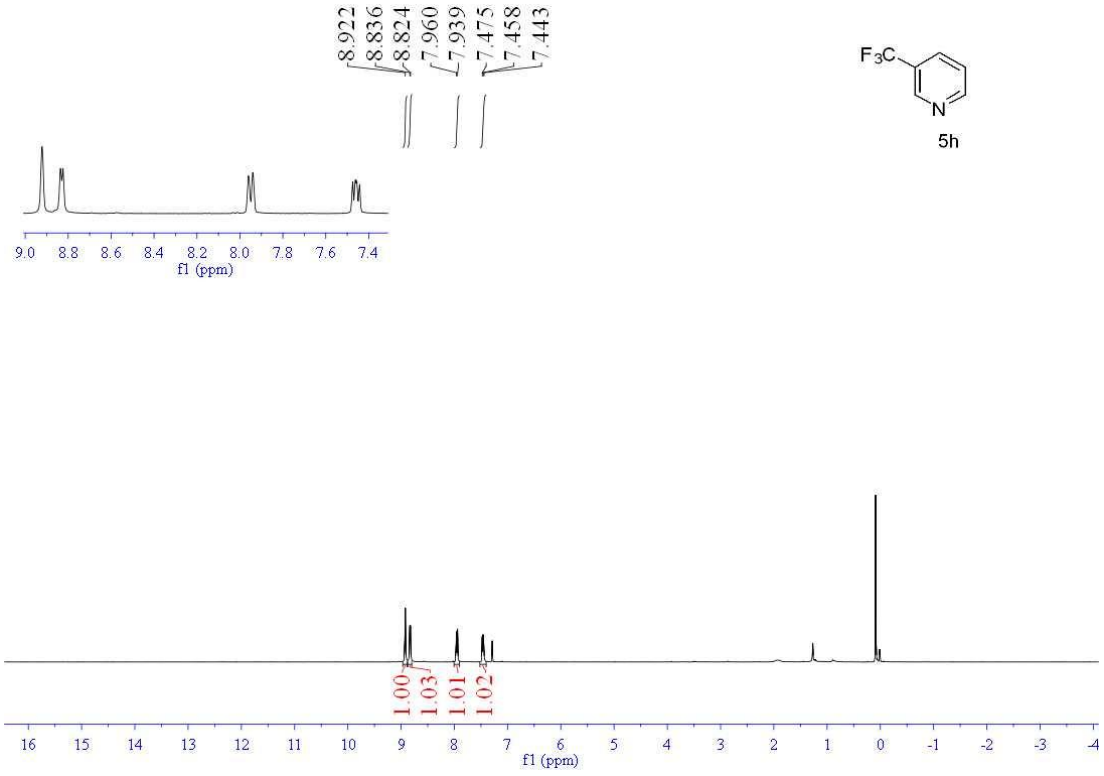
^{13}C NMR spectrum of **5g** in $CDCl_3$



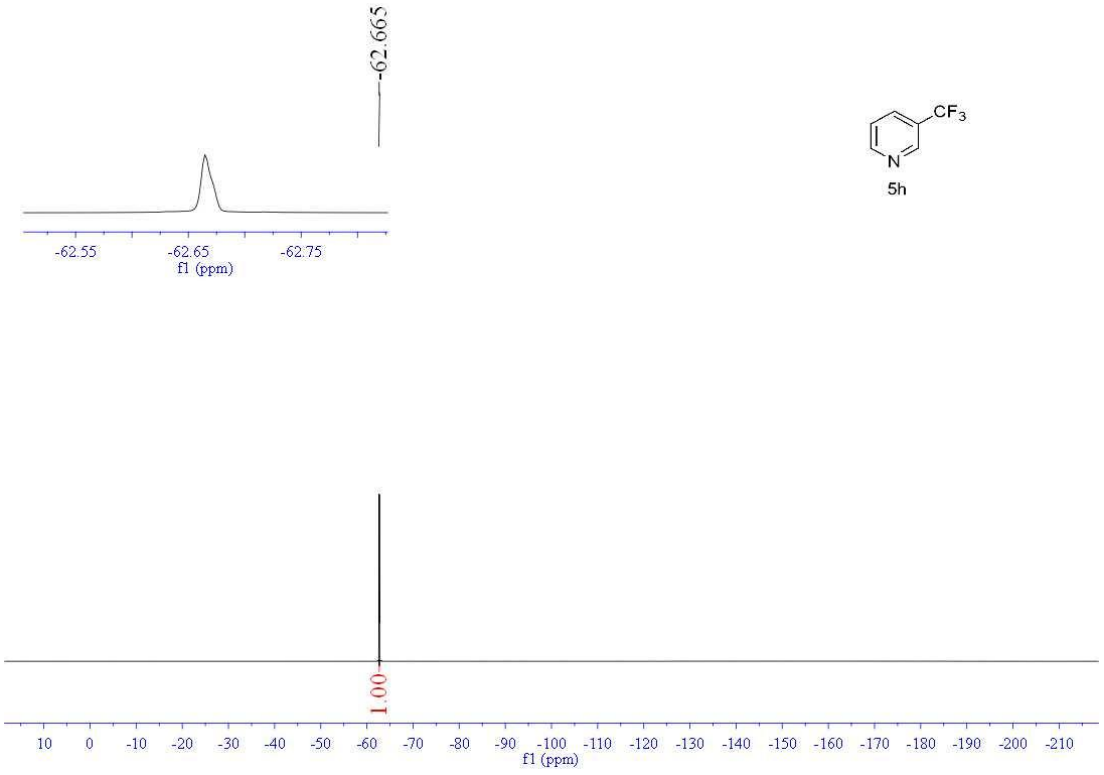
^{19}F NMR spectrum of **5g** (unlocked)



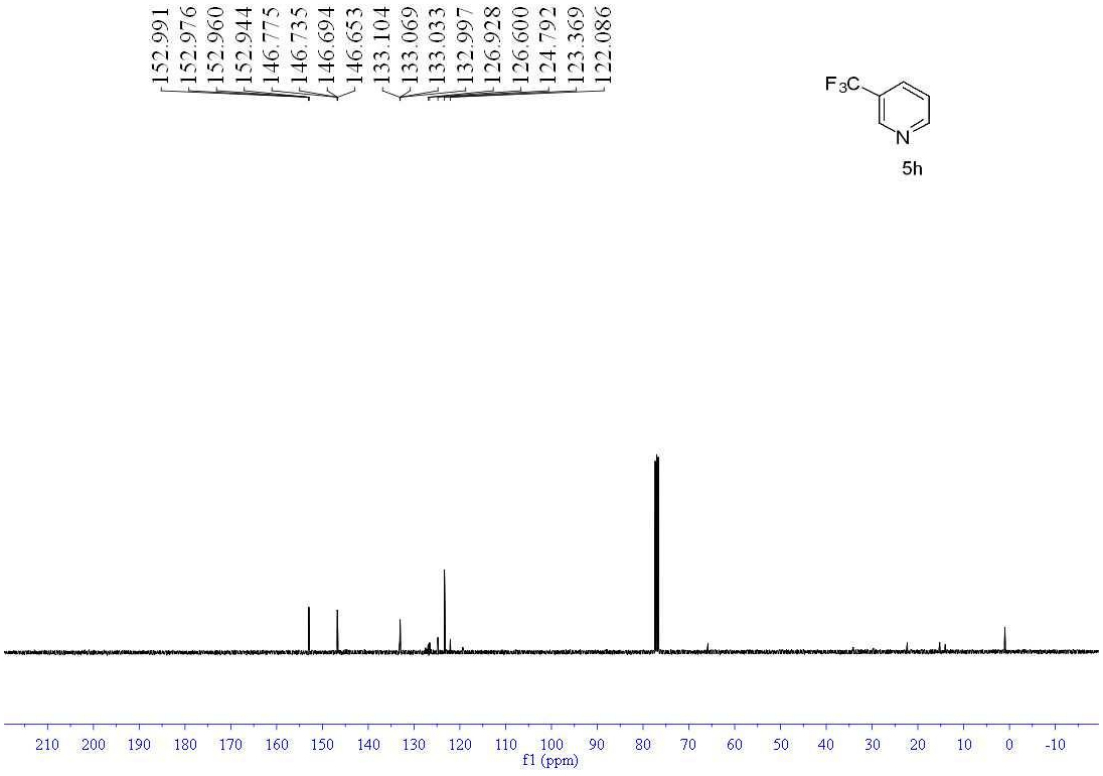
^{1}H NMR spectrum of **5h** in $CDCl_3$



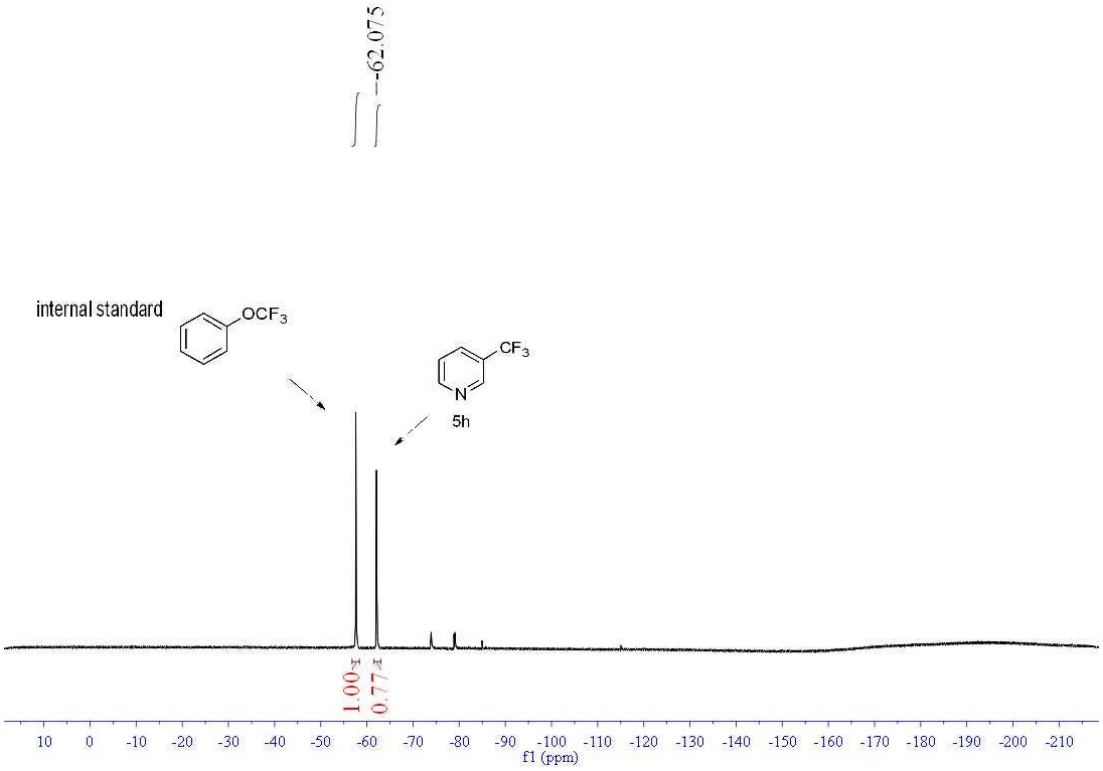
^{19}F NMR spectrum of **5h** in $CDCl_3$



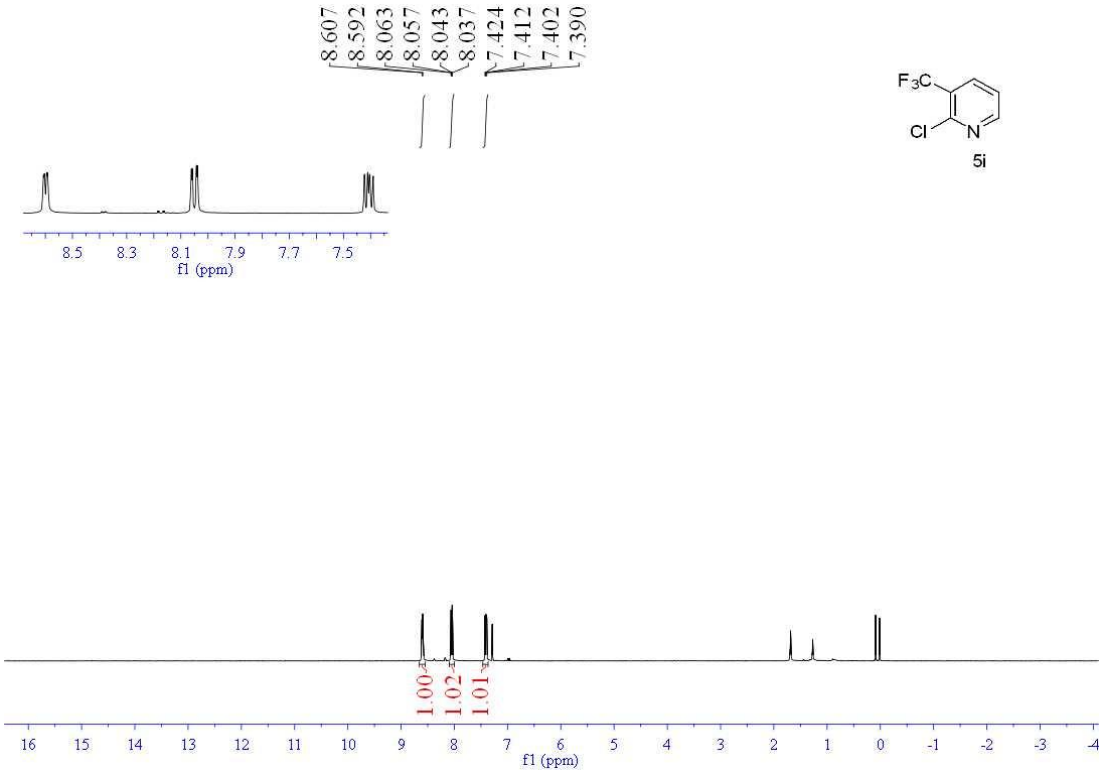
^{13}C NMR spectrum of **5h** in $CDCl_3$



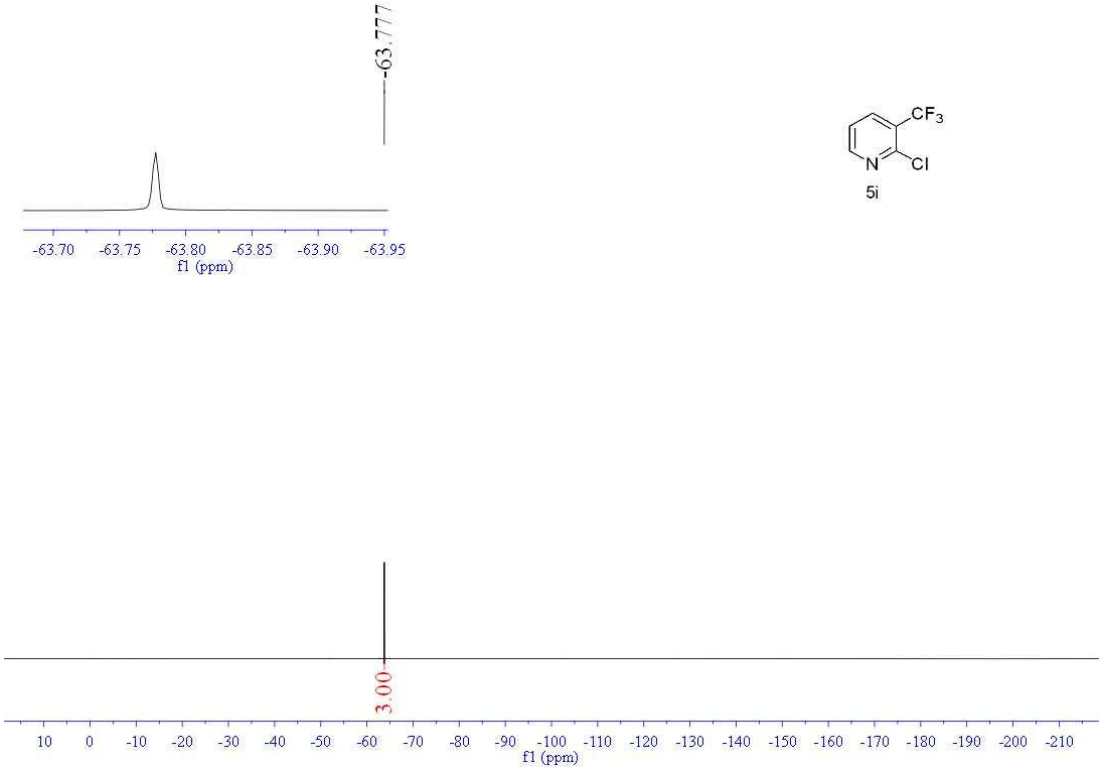
^{19}F NMR spectrum of **5h** (unlocked)



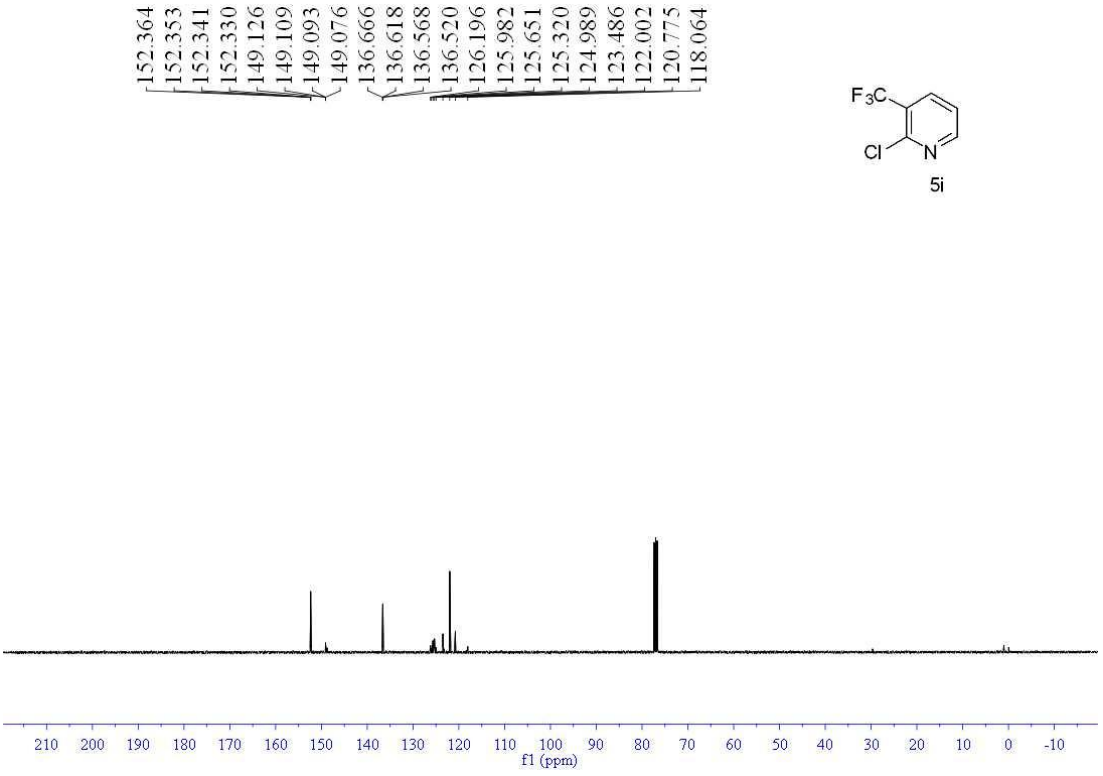
^{1}H NMR spectrum of **5i** in $CDCl_3$



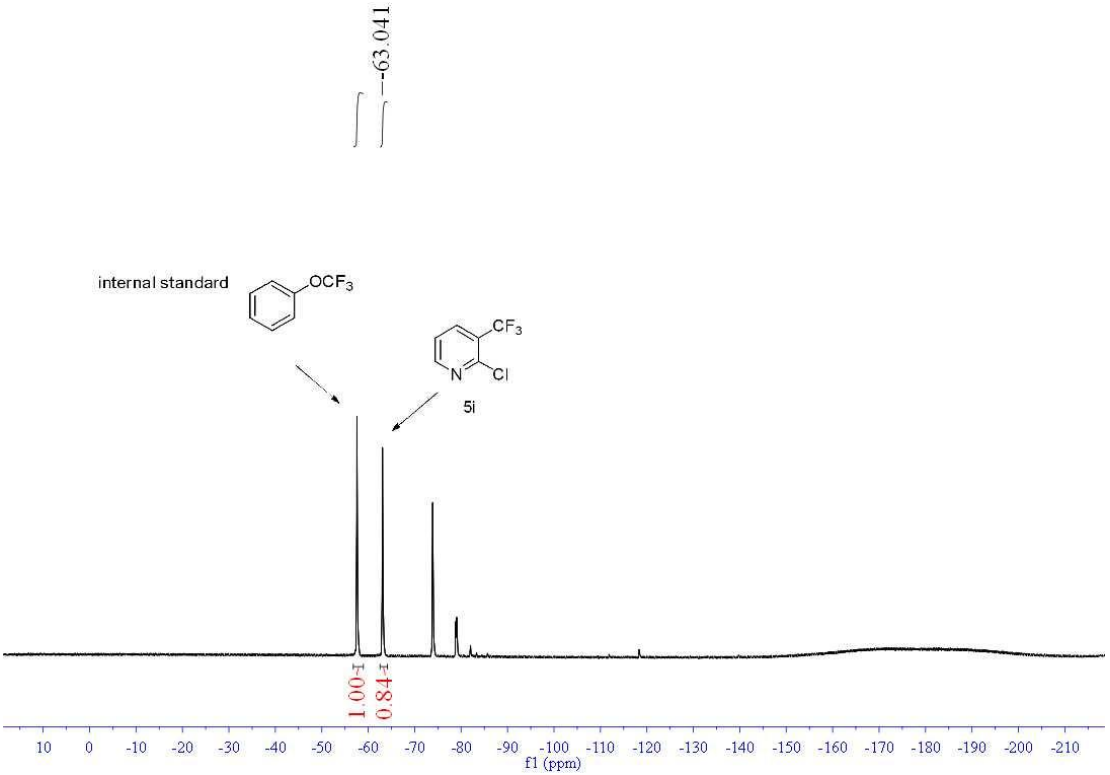
^{19}F NMR spectrum of **5i** in $CDCl_3$



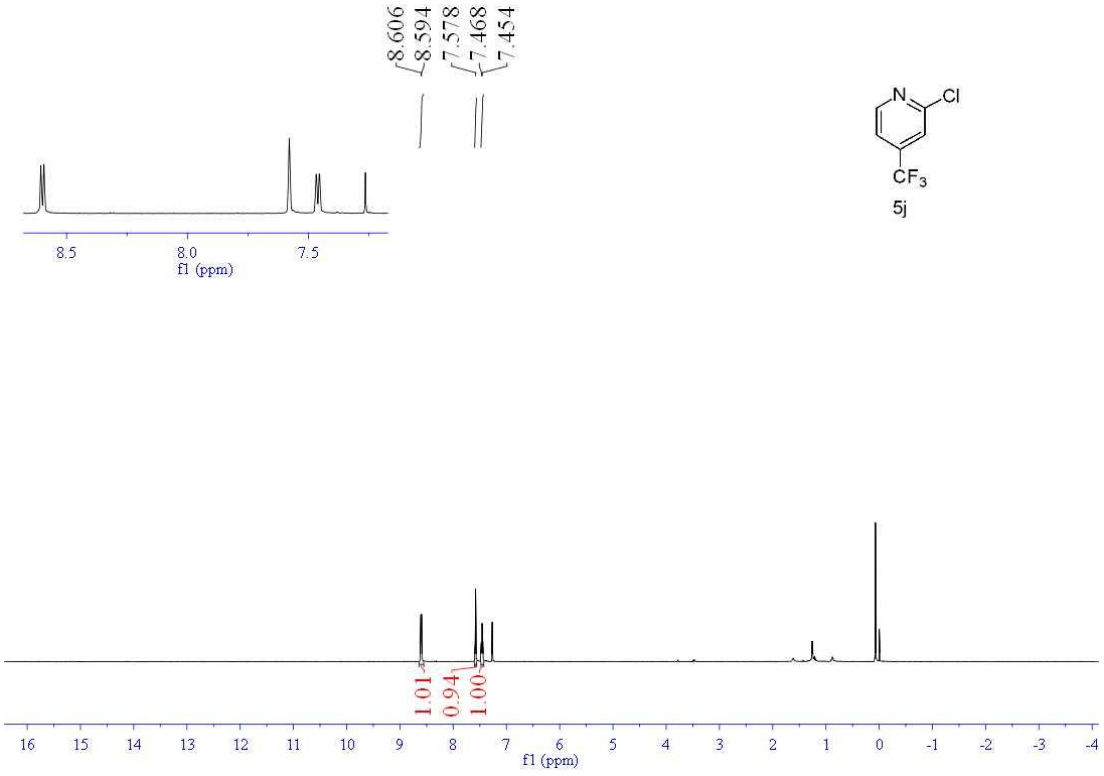
^{13}C NMR spectrum of **5i** in $CDCl_3$



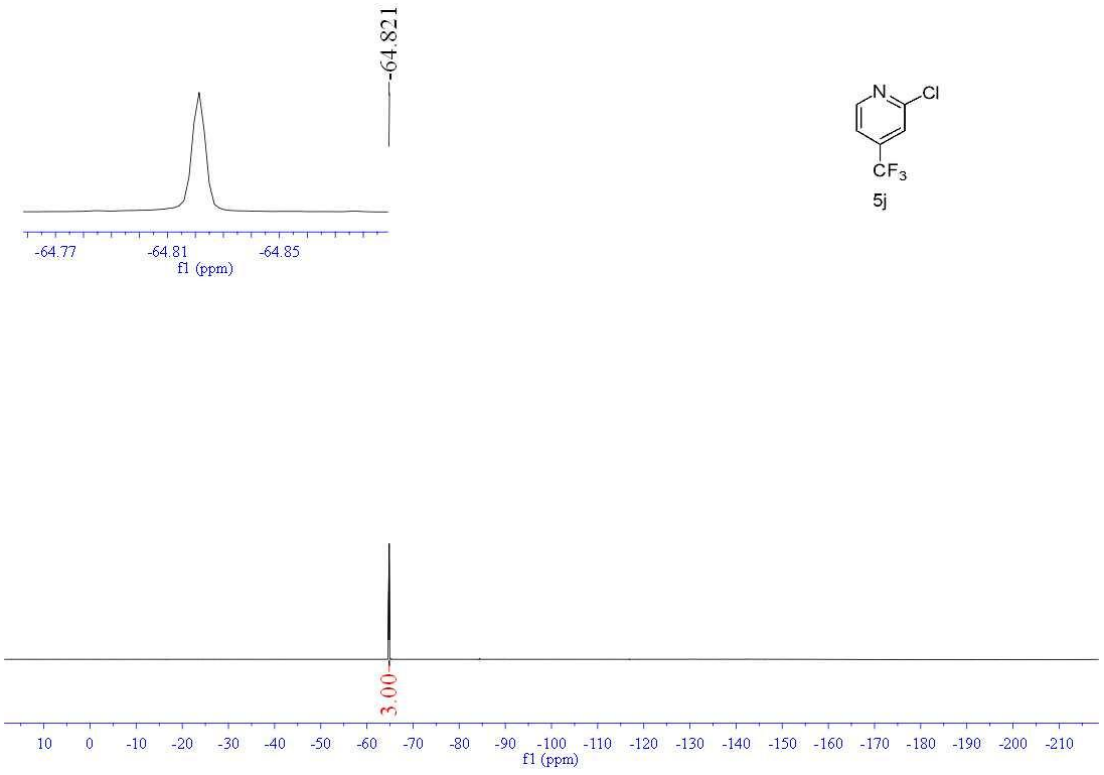
^{19}F NMR spectrum of **5i** (unlocked)



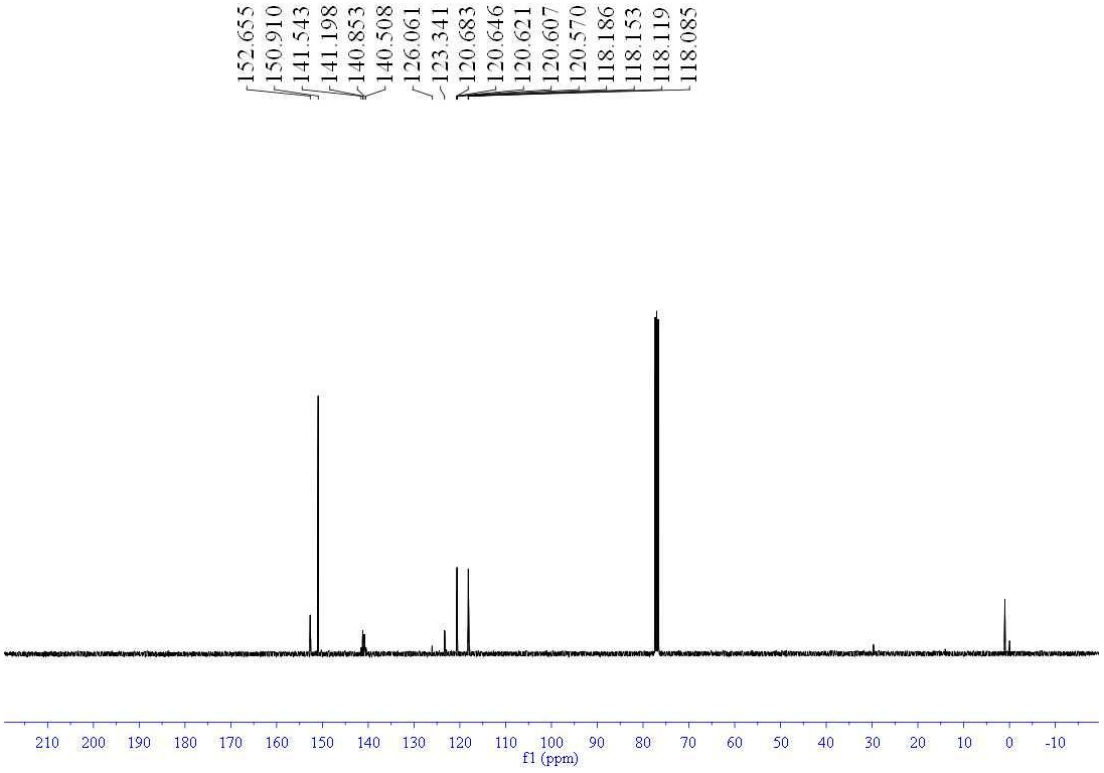
^{1}H NMR spectrum of **5j** in $CDCl_3$



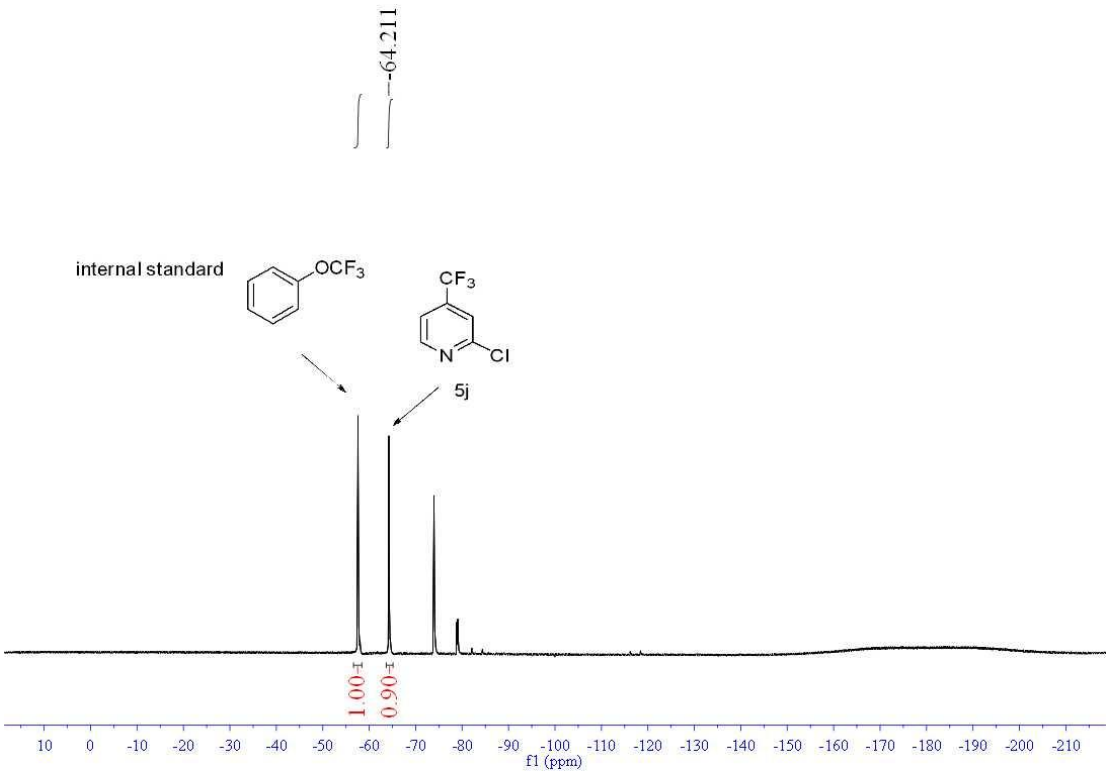
^{19}F NMR spectrum of **5j** in $CDCl_3$



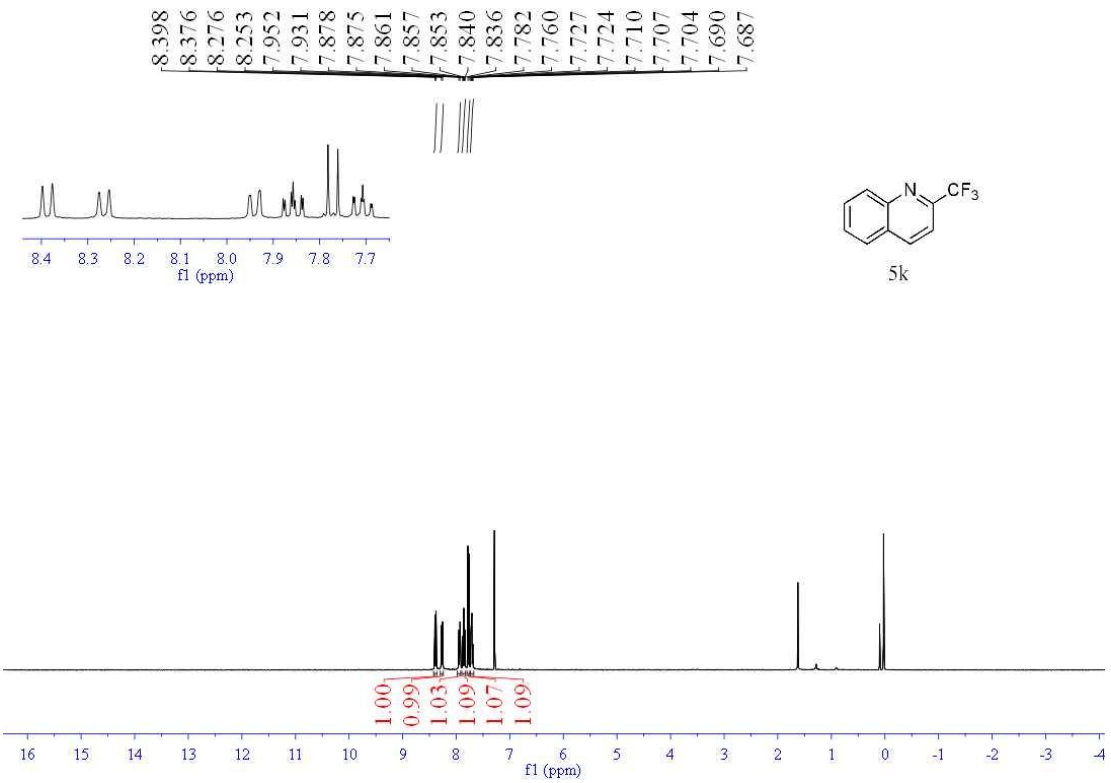
^{13}C NMR spectrum of **5j** in $CDCl_3$



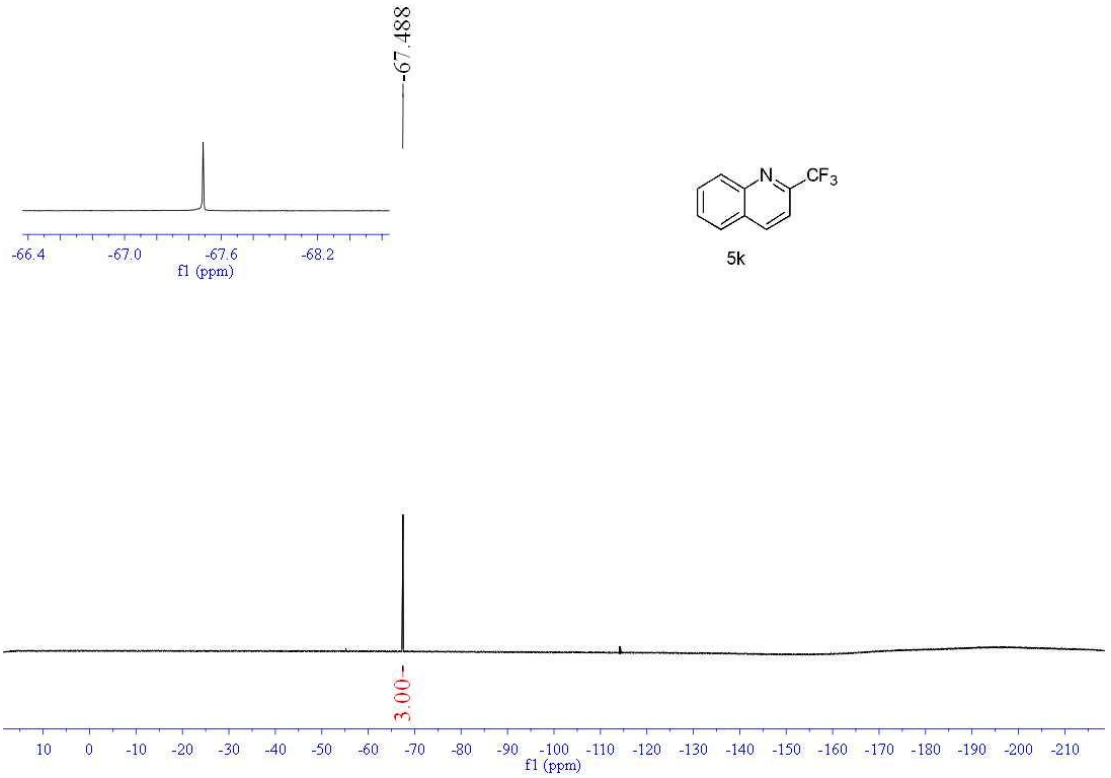
^{19}F NMR spectrum of **5j** (unlocked)



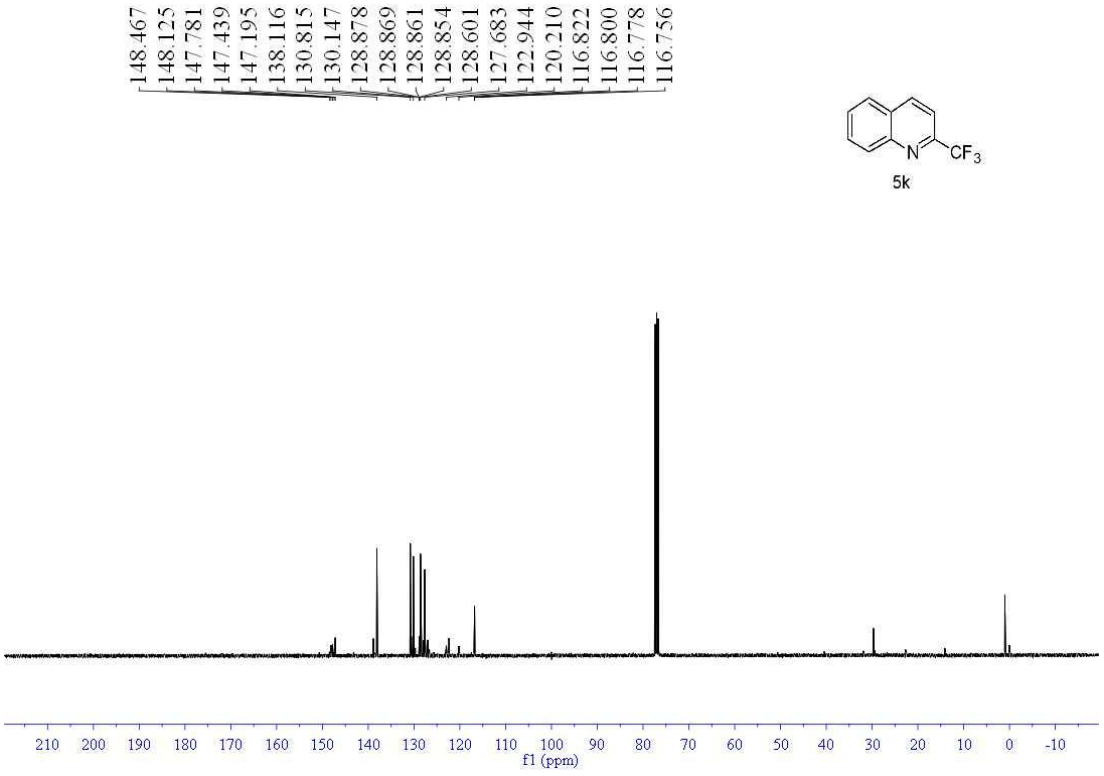
^{1}H NMR spectrum of **5k** in $CDCl_3$



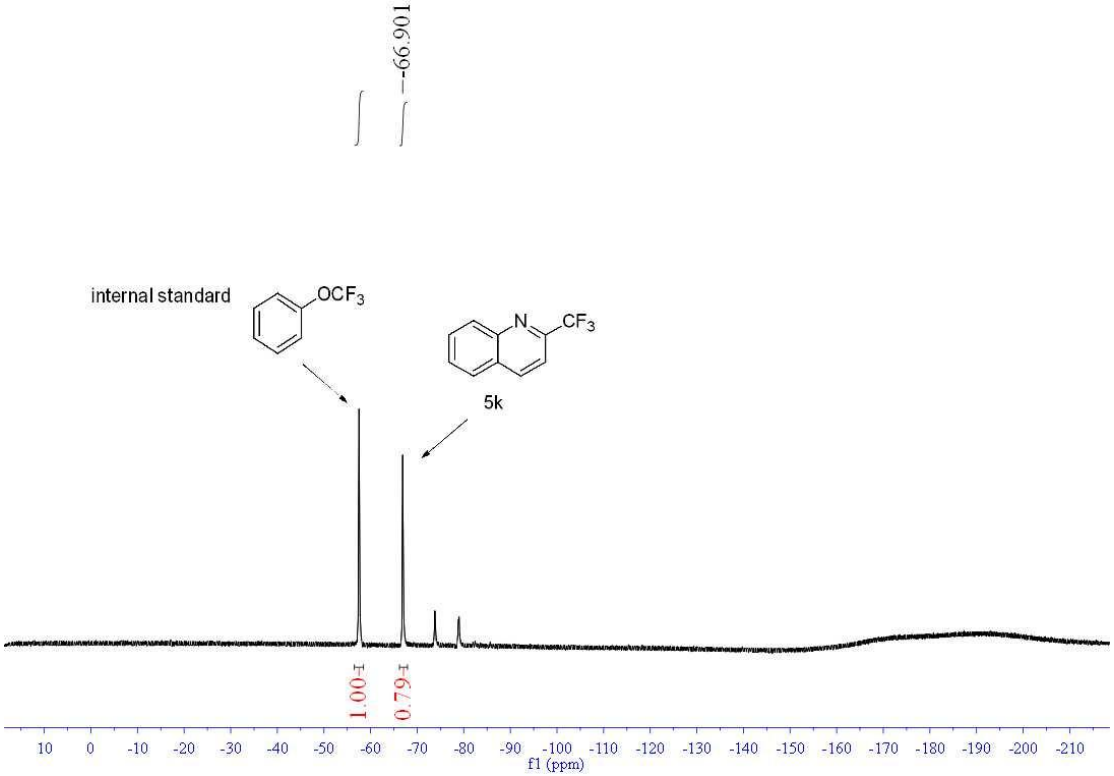
^{19}F NMR spectrum of **5k** in $CDCl_3$



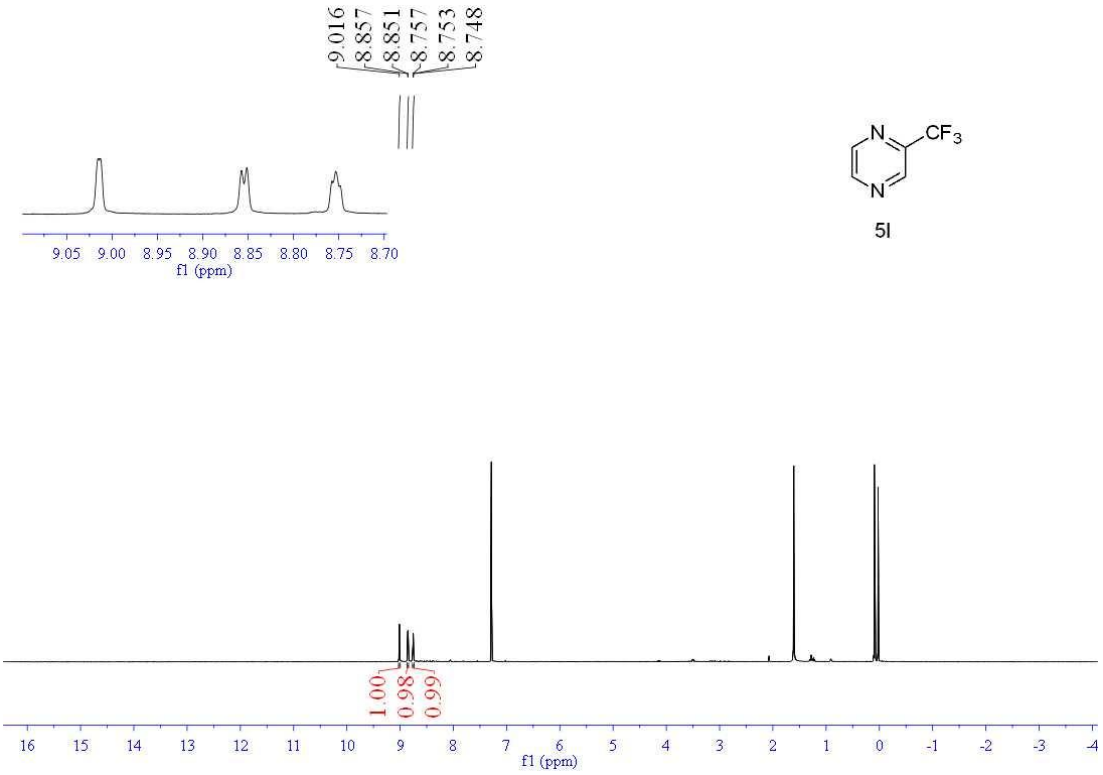
^{13}C NMR spectrum of **5k** in $CDCl_3$



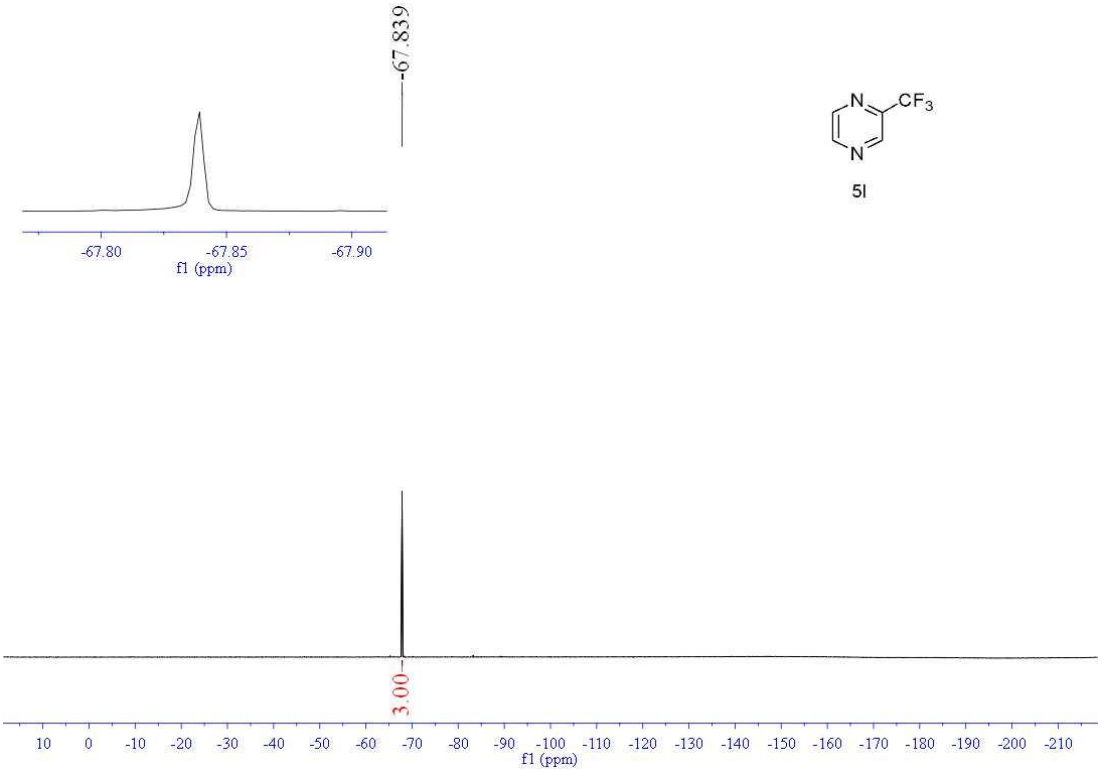
^{19}F NMR spectrum of **5k** (unlocked)



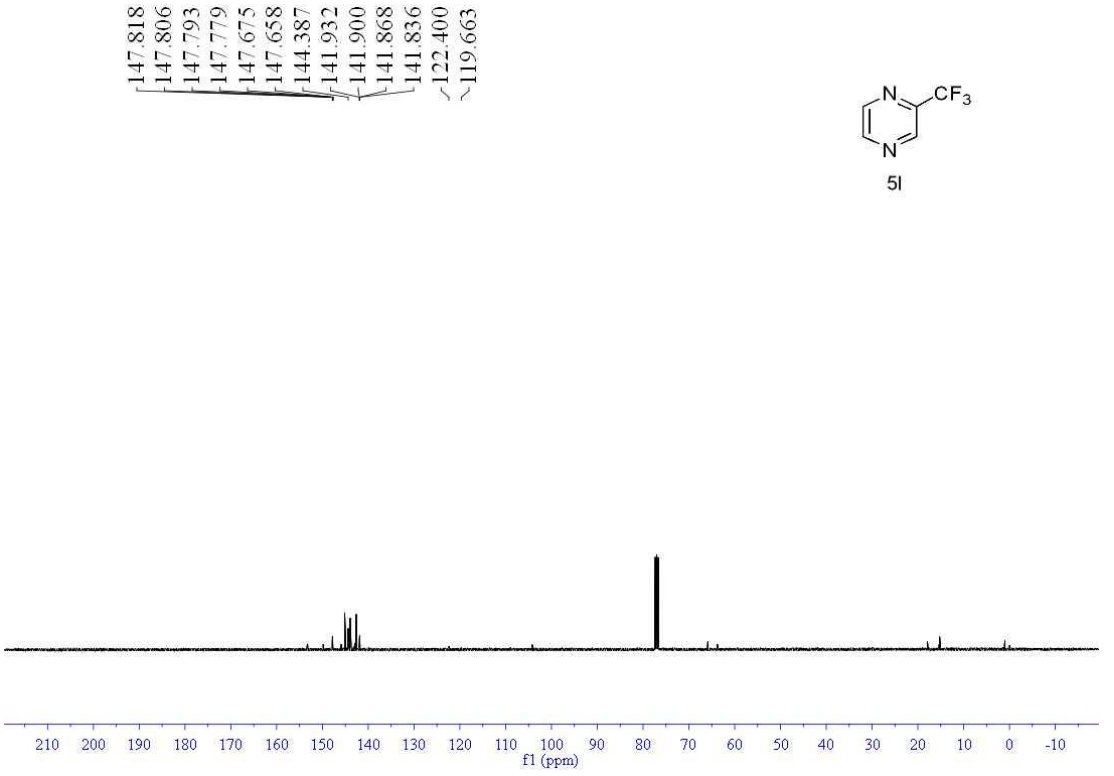
^{1}H NMR spectrum of **5l** in $CDCl_3$



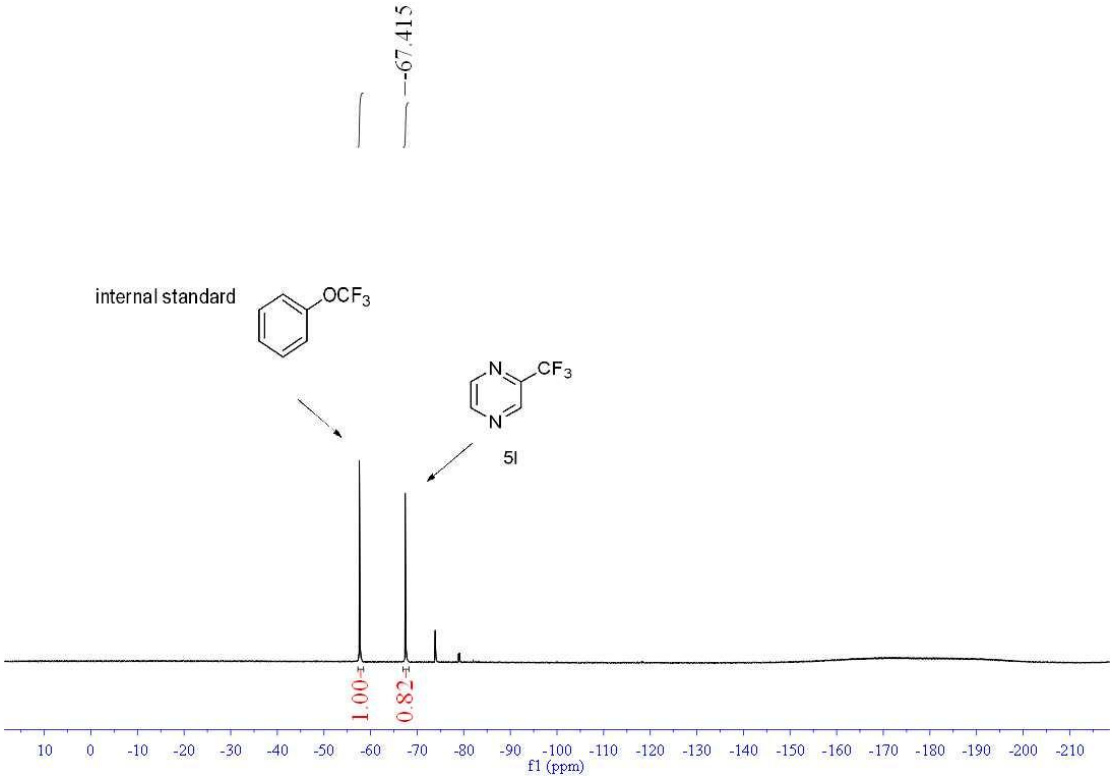
^{19}F NMR spectrum of **5l** in $CDCl_3$



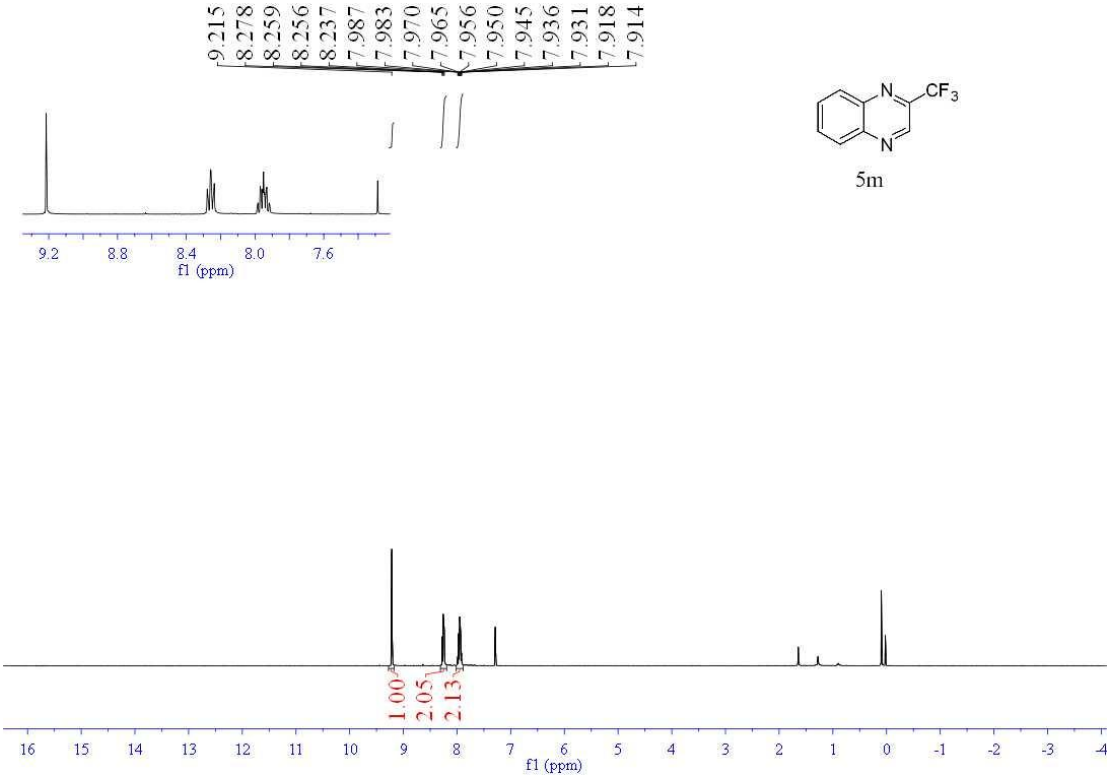
^{13}C NMR spectrum of **5l** in $CDCl_3$



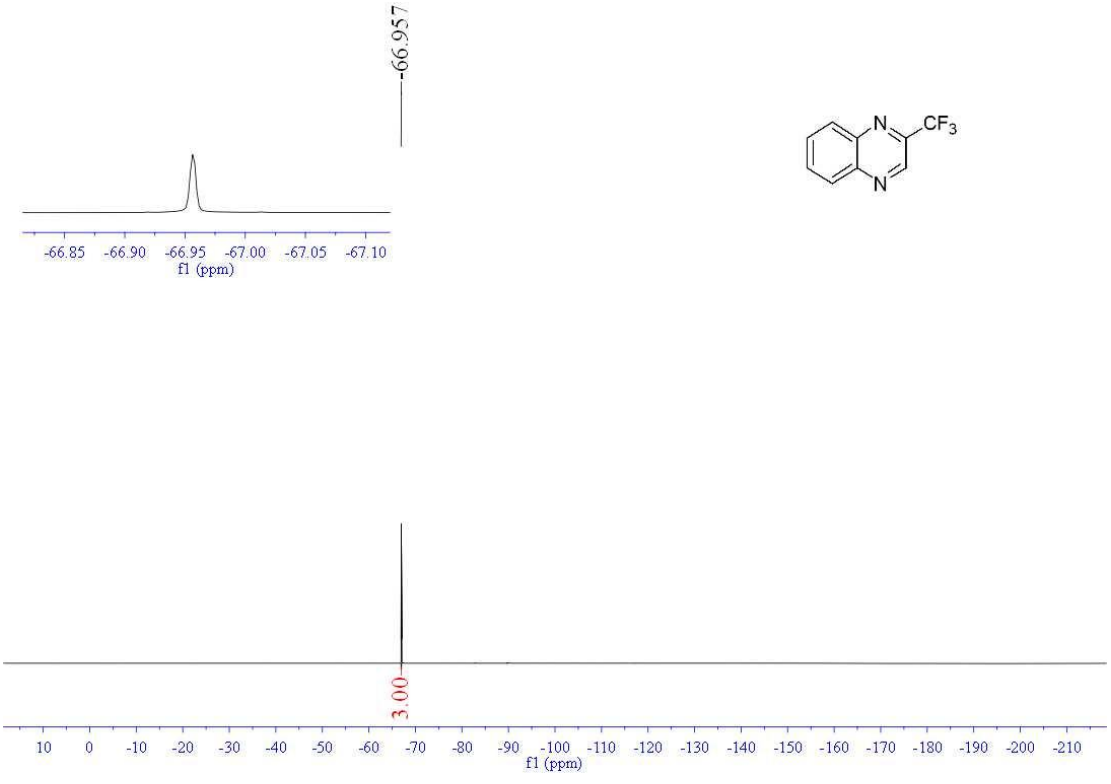
^{19}F NMR spectrum of **5l** (unlocked)



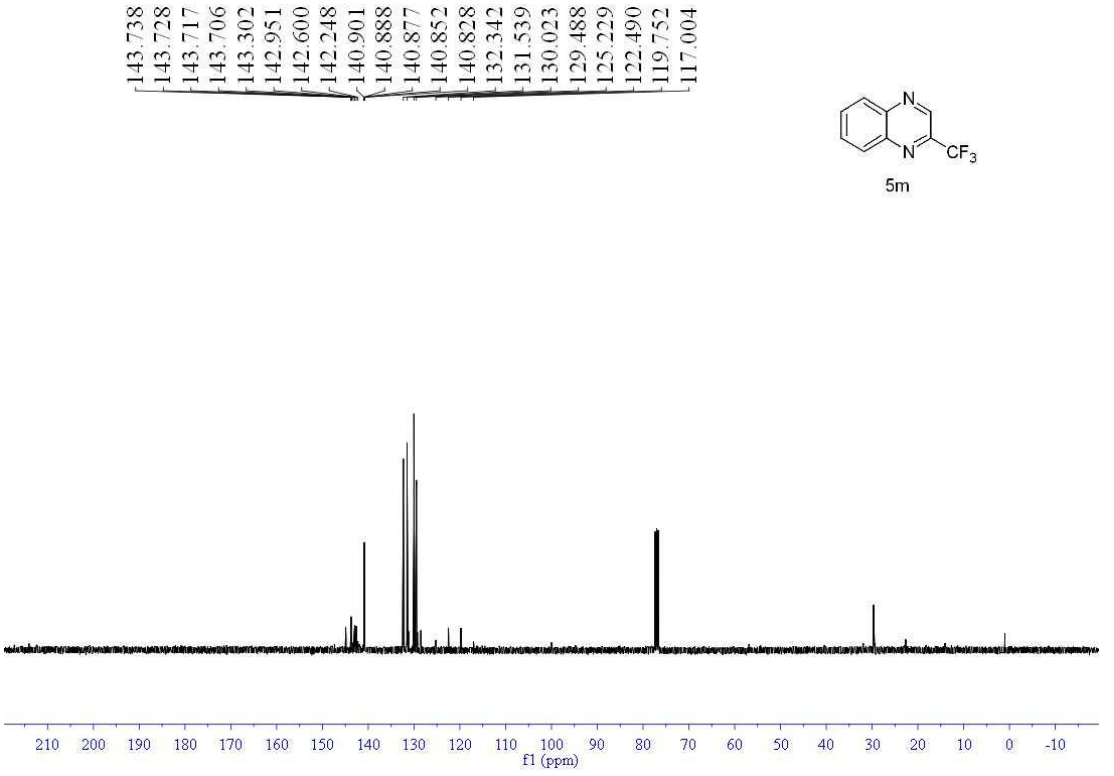
^{1}H NMR spectrum of **5m** in $CDCl_3$



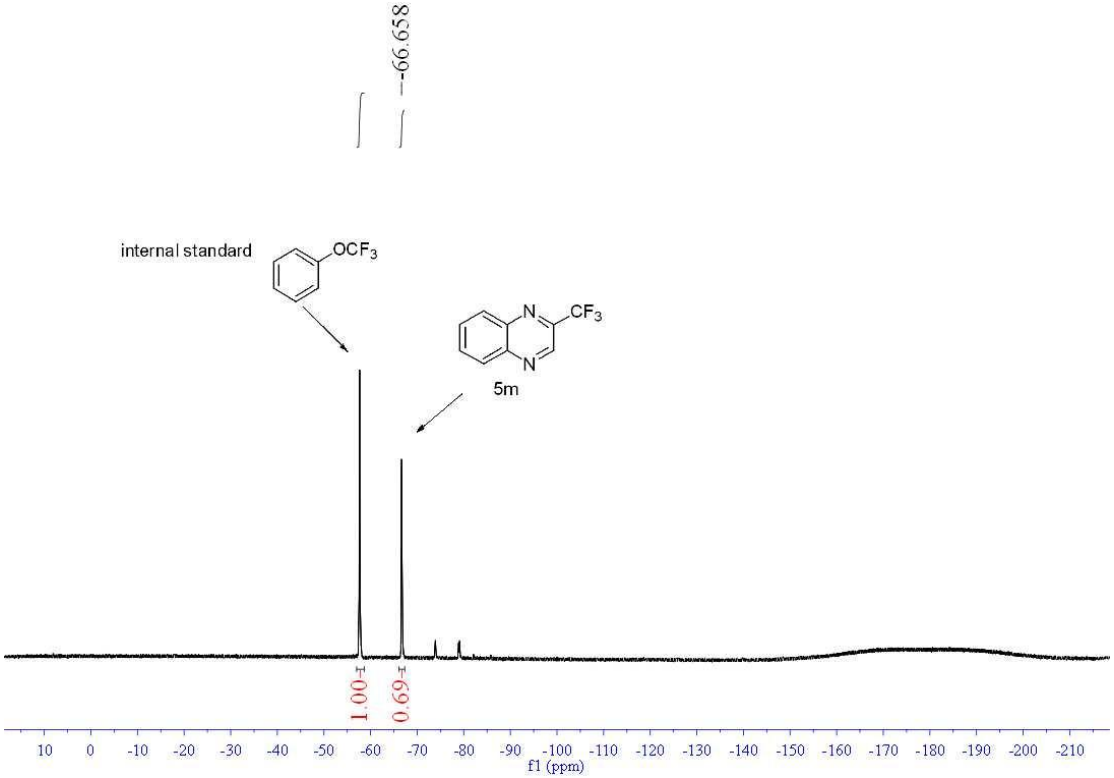
^{19}F NMR spectrum of **5m** in $CDCl_3$



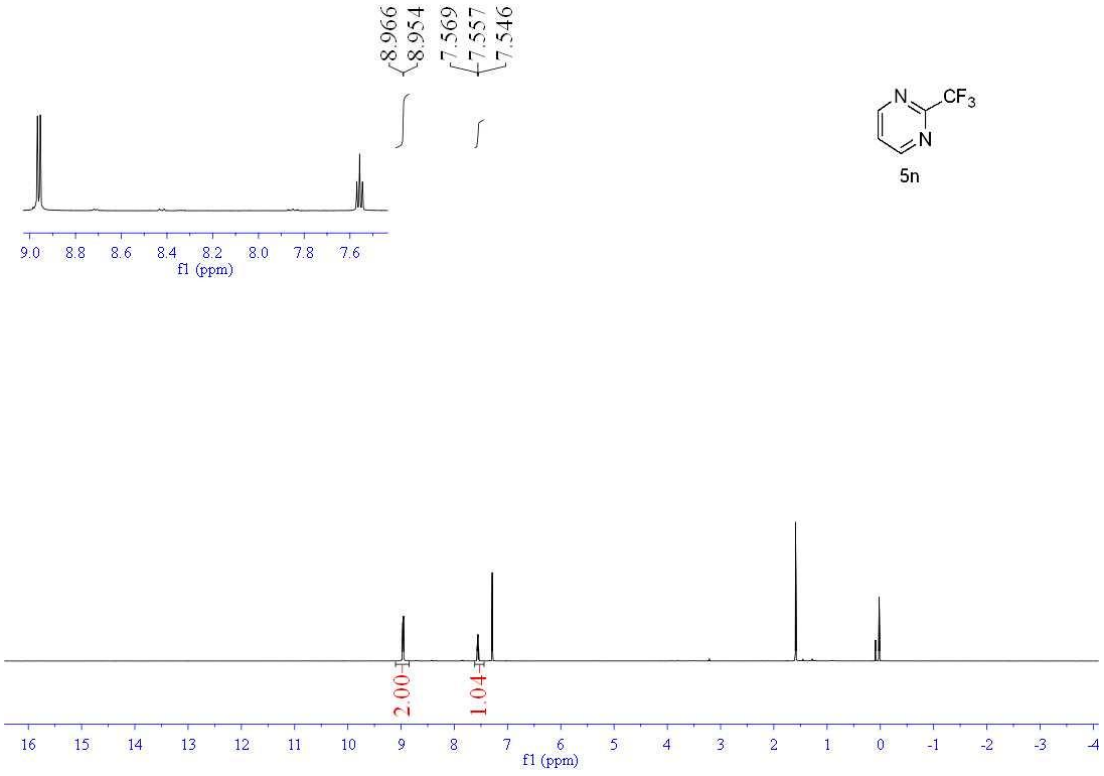
^{13}C NMR spectrum of **5m** in $CDCl_3$



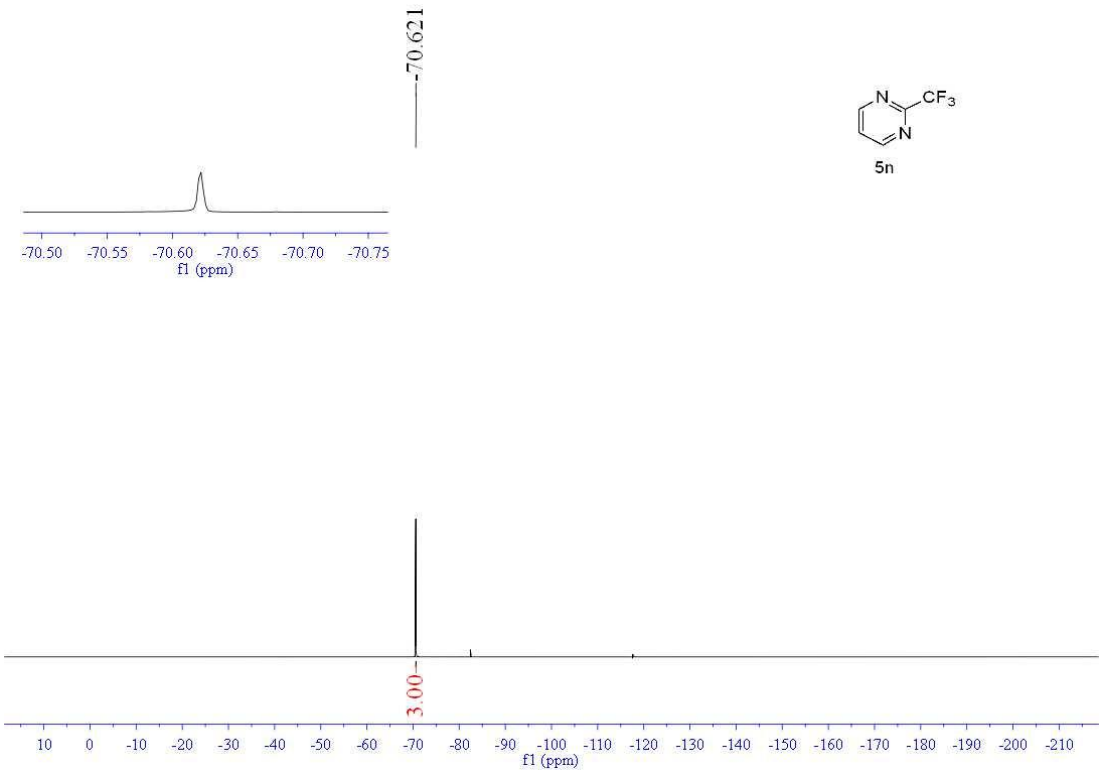
^{19}F NMR spectrum of **5m** (unlocked)



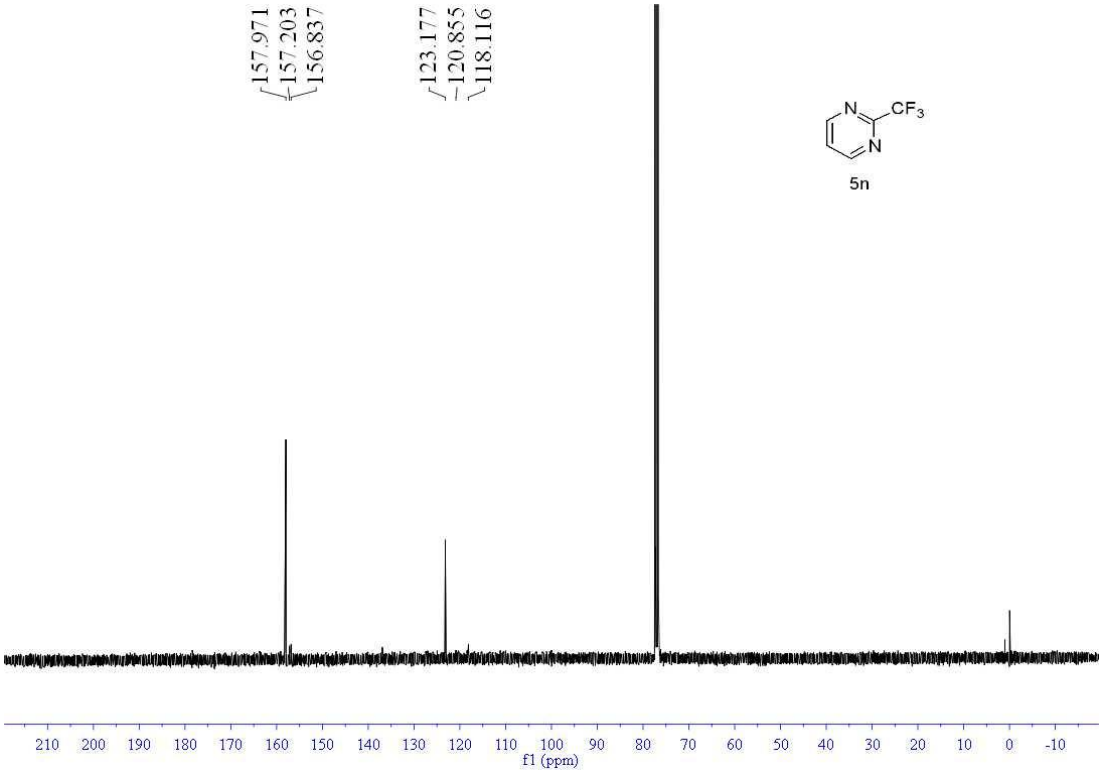
^{1}H NMR spectrum of **5n** in $CDCl_3$



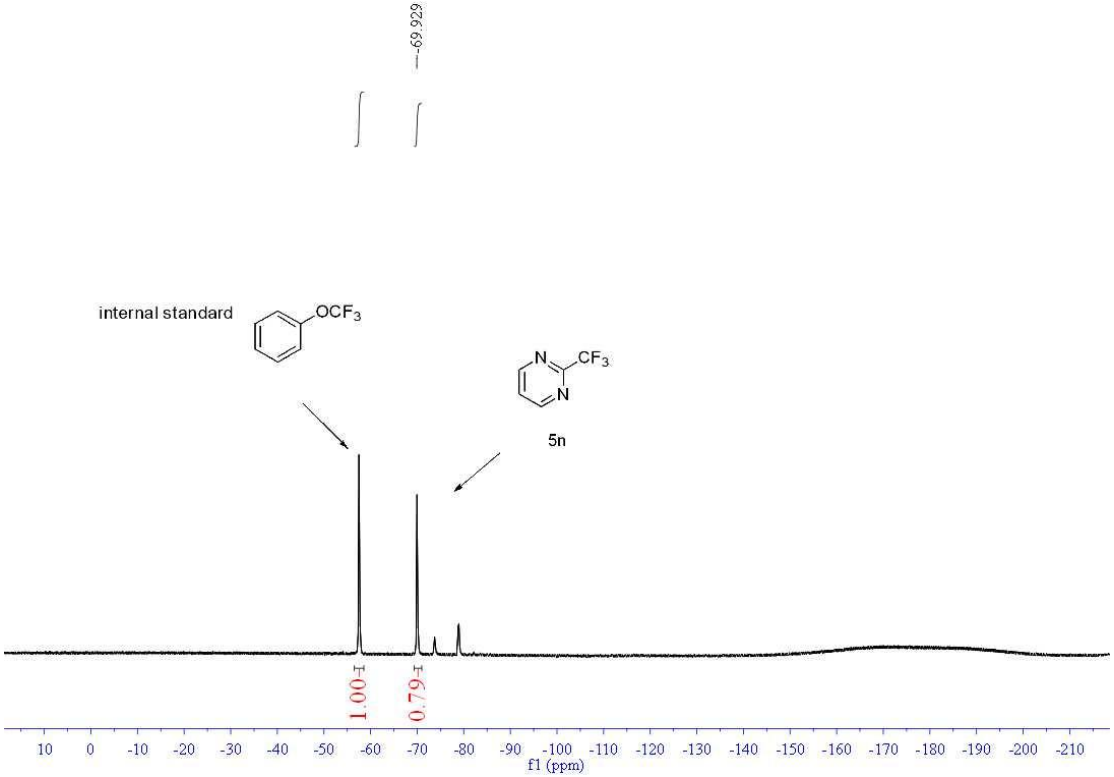
^{19}F NMR spectrum of **5n** in $CDCl_3$



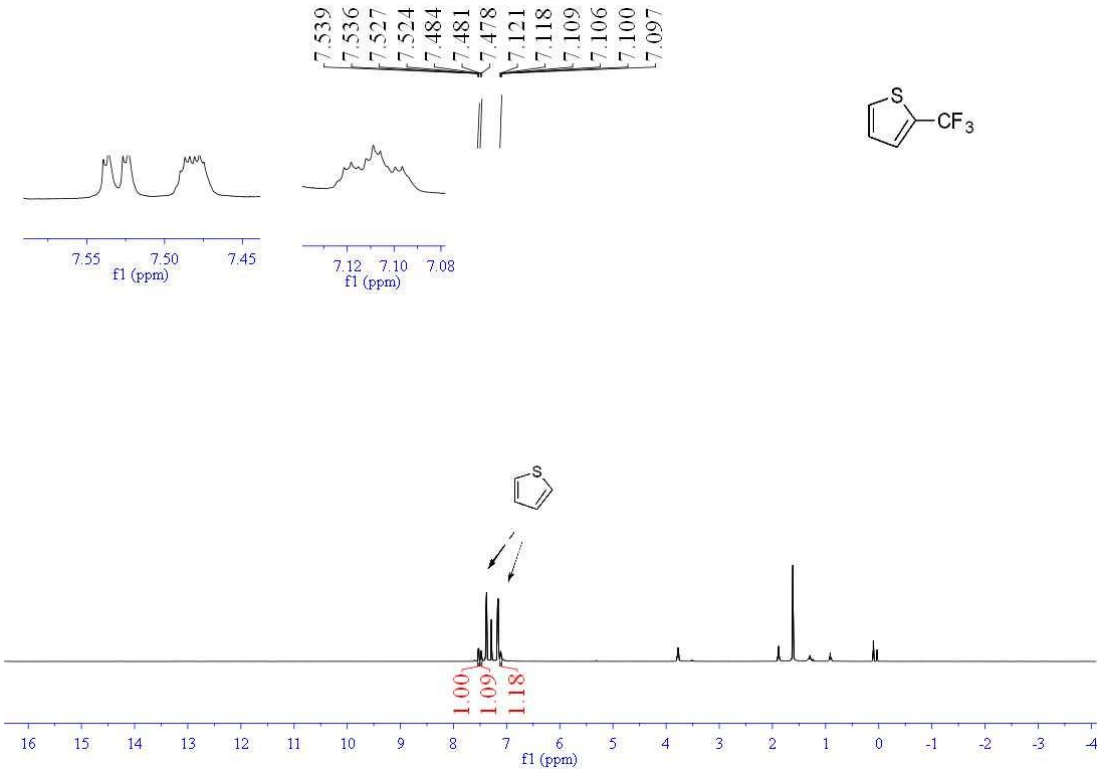
^{13}C NMR spectrum of **5n** in $CDCl_3$



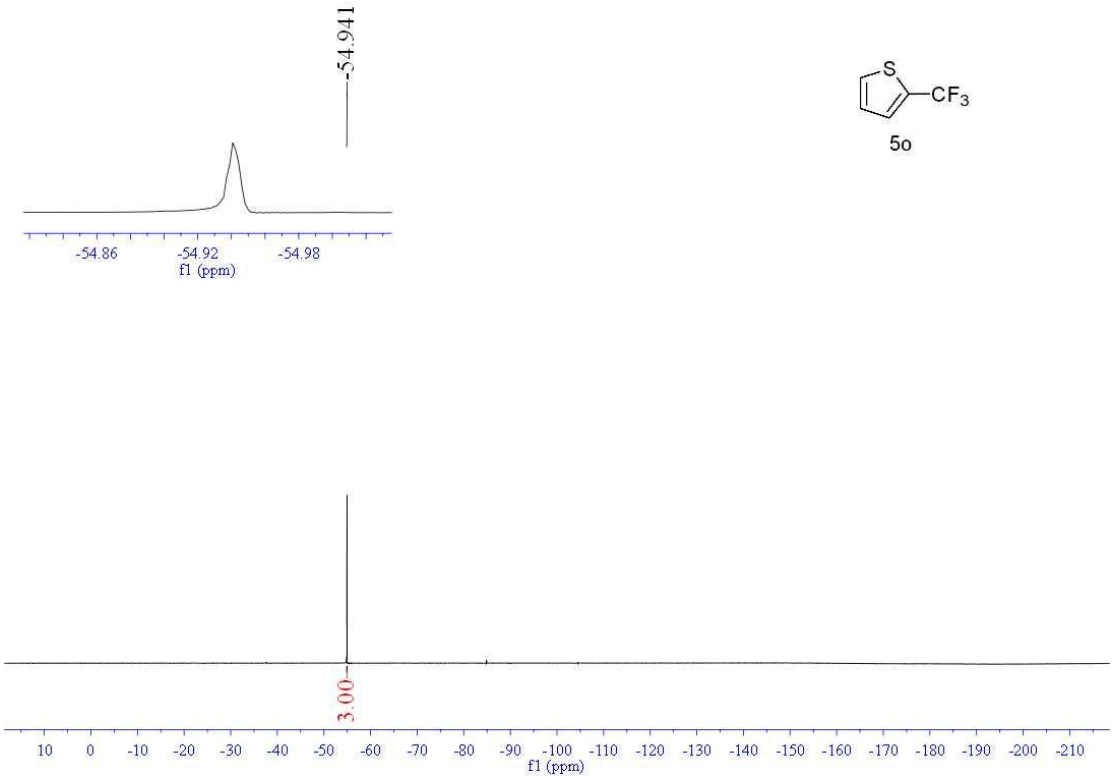
^{19}F NMR spectrum of **5n** (unlocked)



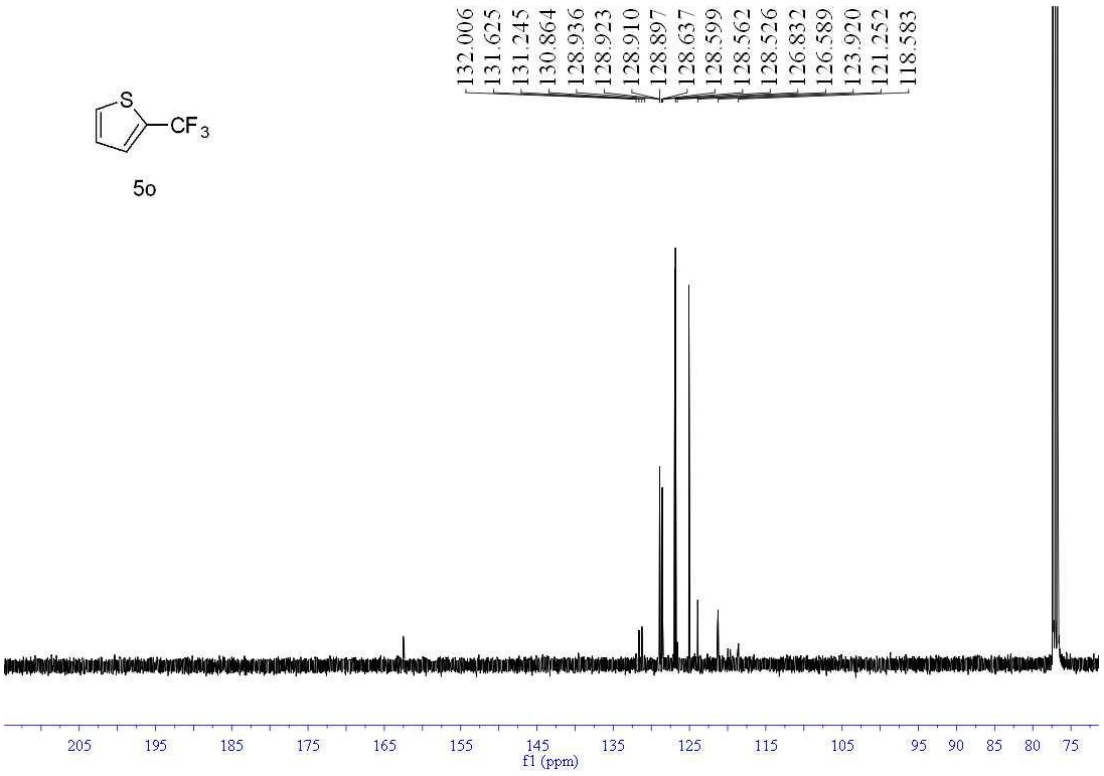
^{1}H NMR spectrum of **5o** in $CDCl_3$



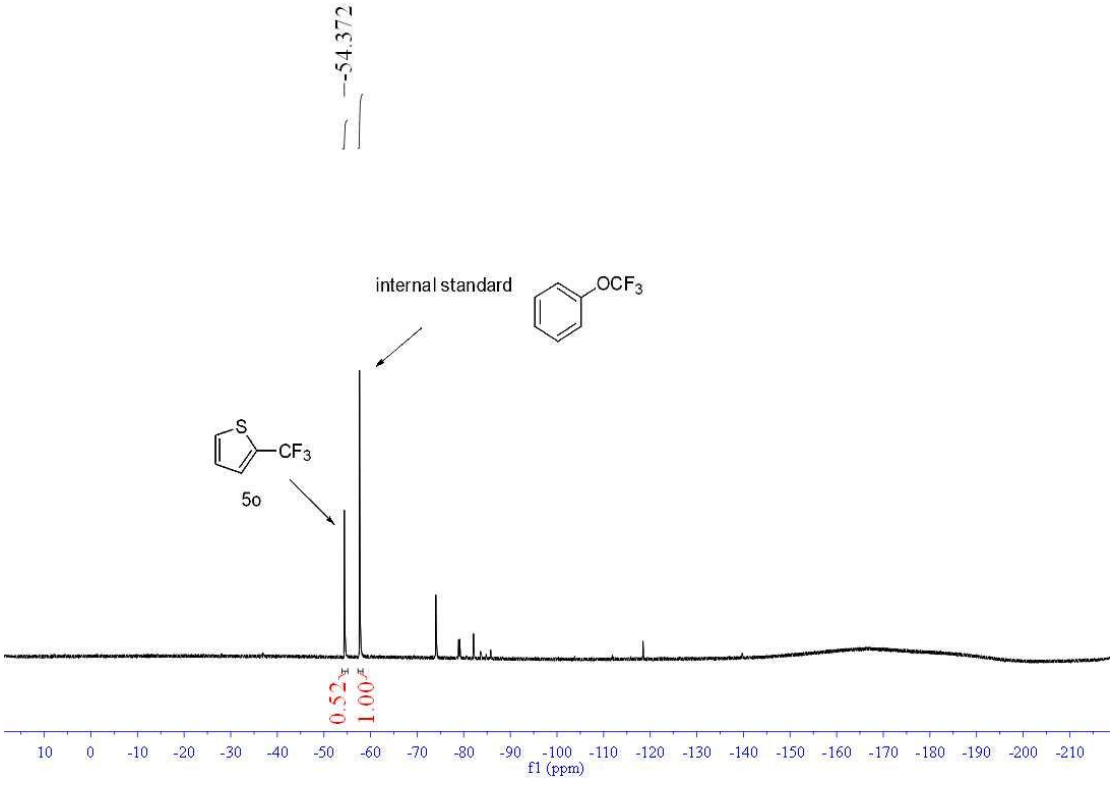
^{19}F NMR spectrum of **5o** in $CDCl_3$



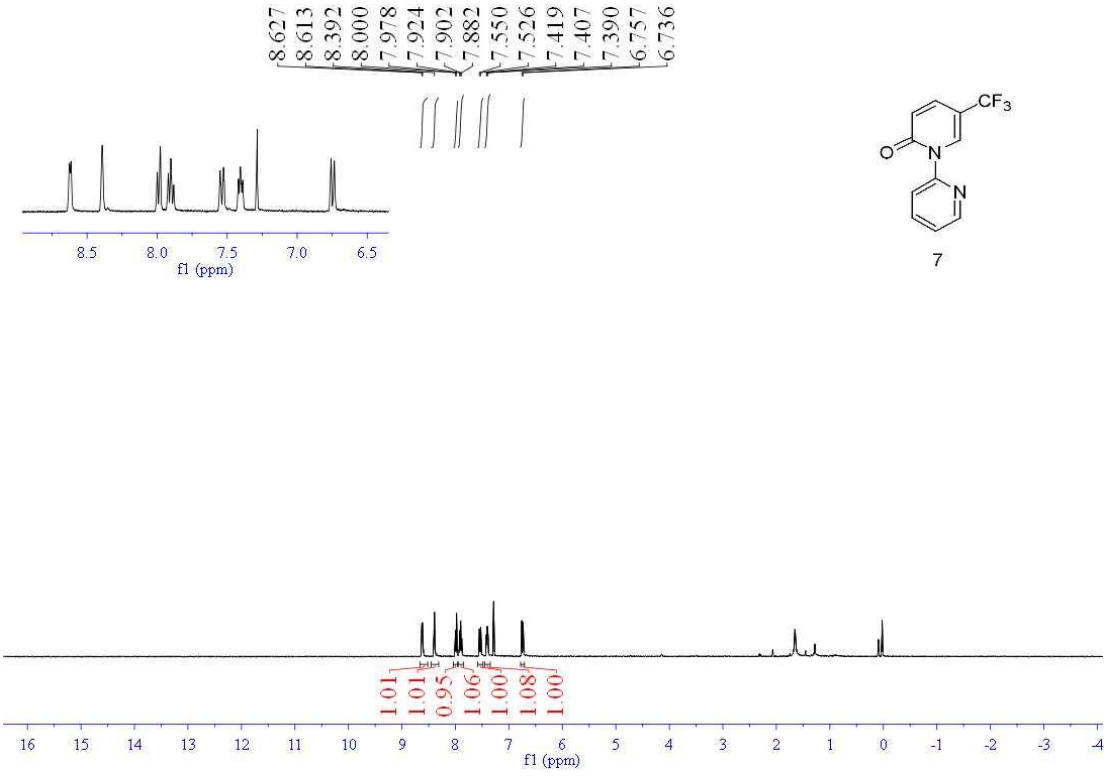
^{13}C NMR spectrum of **5o** in $CDCl_3$



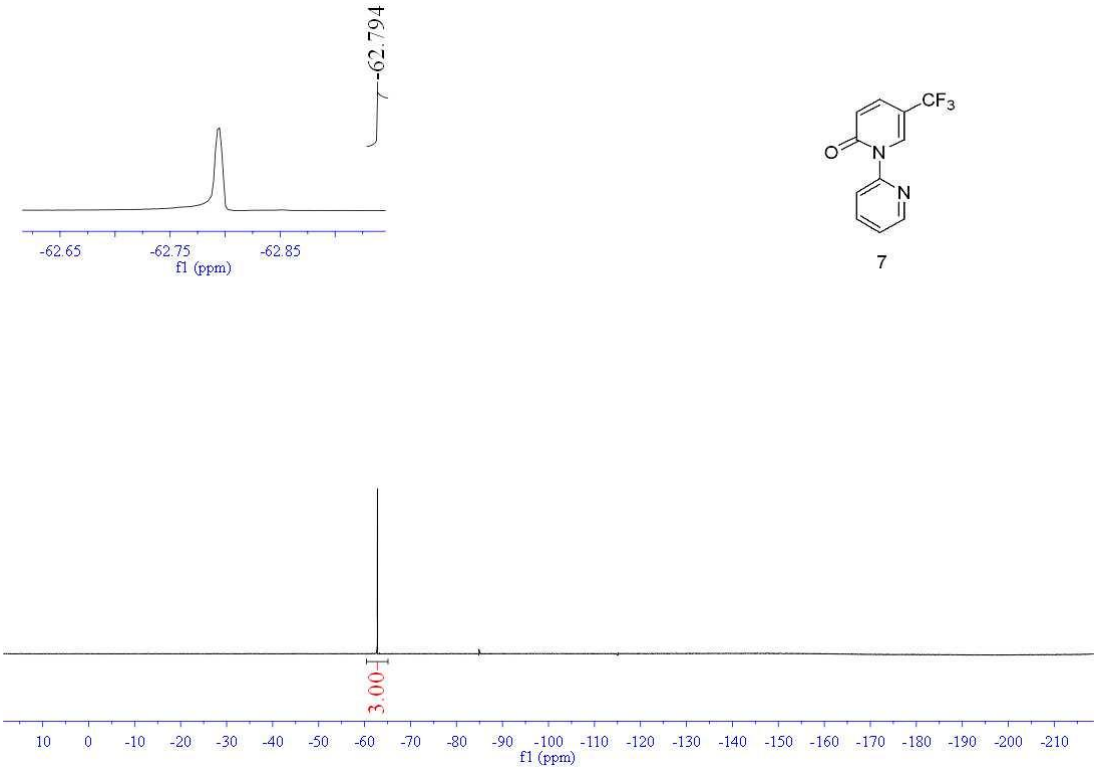
^{19}F NMR spectrum of **5o** (unlocked)



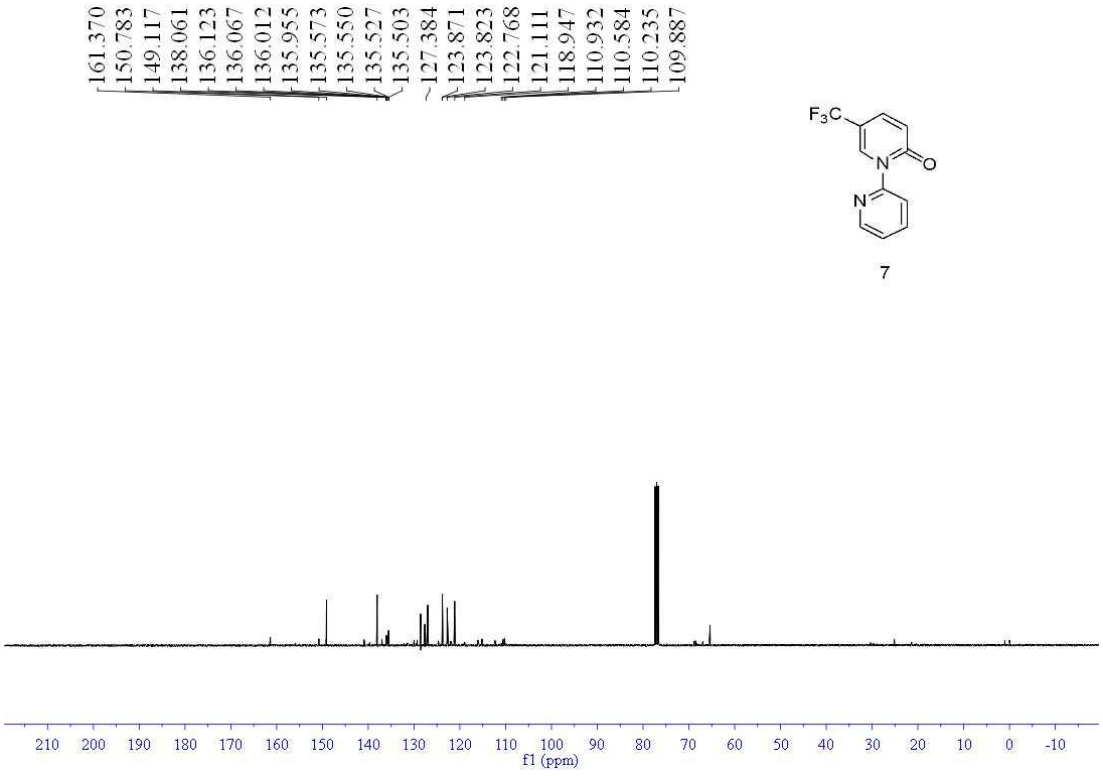
^{1}H NMR spectrum of **7** in $CDCl_3$



^{19}F NMR spectrum of **7** in $CDCl_3$



^{13}C NMR spectrum of **7** in $CDCl_3$



^{19}F NMR spectrum of **7** (unlocked)