Supporting information

Difluorocarbene as a C-F source for the Construction of Fluorinated Thiazoles

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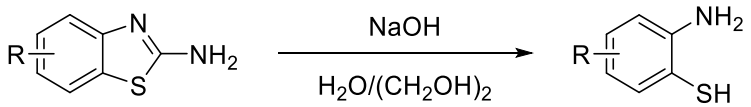
1. General Information

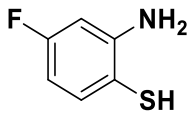
All reagents were commercially available and used without further purification unless indicated otherwise. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 500 MHz spectrometer. NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{19}F NMR: 565 MHz, ^{13}C: 150 MHz) , Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{19}F: 470 MHz) and JEOL ECZ 400MHz at ambient temperature. $CDCl_3$ was used as the NMR solvent. The chemical shifts for ^{1}H are given in ppm relative to tetramethylsilane (0.00) as a standard. The chemical shifts for ^{13}C are given in ppm relative to $CDCl_3$ (77.0 ppm) as a standard. The chemical shifts for ^{19}F NMR are given in ppm relative to trichlorofluoromethane (0.00) as a standard. ^{1}H, ^{13}C and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (td), triplet of triplet (tt), multiplet (m), quint (quintet), septet (sept), sextet (sext) and broad resonance (br). High resolution mass spectrometry (HRMS) was performed on a Waters Premier GC-TOF MS instrument with electron impact ionization mode (EI), time-of-flight mass spectrometer field ionization mode (FI), or on a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument with electrospray ionization mode (ESI). Unless noted, all reagents were bought from commercial suppliers and used without further purification. Compounds **4** for the synthesis of substrate **1** were bought from commercial suppliers or synthesized according to reported literature.[1]

2. General procedure for the synthesis of the substrates[2]



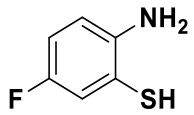
4 **1**

A solution of compound **4** (10 mmol) in a mixture of aqueous 50% NaOH and ethylene glycol (v/v = 1/1, 20 mL) was refluxed under a N_2 atmosphere until the starting material disappeared, as monitored by TLC (about 15 h). The mixture was then poured into ice water, acidified to pH = 3 with 3 M aqueous HCl, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to remove the solvent. The residue was subjected to flash chromatography on silica using hexane/EtOAc (v/v = 2/1 to 1/1) as an eluent to give substrate **1**.

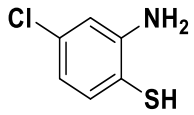


2-amino-4-fluorobenzenethiol (1b)[2]: yellow solid; 325.6 mg, 44% yield (5 mmol of **4b** was used).

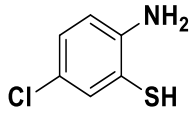
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 8.6, 6.5 Hz, 1H), 6.41 (dd, *J* = 10.6, 2.6 Hz, 1H), 6.29 (td, *J* = 8.5, 2.7 Hz, 1H), 4.49 (br, 2H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -108.42 – -108.50 (m, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 165.39 (d, *J* = 248.4 Hz), 150.41 (d, *J* = 12.2 Hz), 138.86 (d, *J* = 10.6 Hz), 113.72 (d, *J* = 2.6 Hz), 105.45 (d, *J* = 22.2 Hz), 101.64 (d, *J* = 25.3 Hz).**GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6FNS 143.0; Found 143.0.



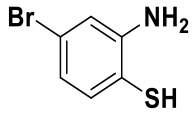
2-amino-5-fluorobenzenethiol (1c)[3]**:** yellow solid; yield: 515 mg (36%)**.**
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.95 – 6.88 (m, 2H), 6.66 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.18 (br, 2H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -126.26 (td, *J* = 8.3, 4.7 Hz, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 154.93 (d, *J* = 239.2 Hz), 144.92 (d, *J* = 2.0 Hz), 121.78 (d, *J* = 22.3 Hz), 118.96 (d, *J* = 7.3 Hz), 118.81 (d, *J* = 22.5 Hz), 116.08 (d, *J* = 7.4 Hz). **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6FNS 143.0; Found 143.0.



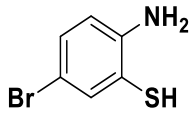
2-amino-4-chlorobenzenethiol (1d)[2]**:** yellow solid; yield: 206.7 mg (13%).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.42 (br, 2H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 149.47, 137.88, 137.66, 118.35, 116.64, 114.78. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6ClNS 159.0; Found 159.0.



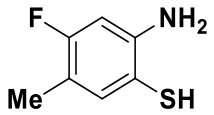
2-amino-5-chlorobenzenethiol (1e)[4]**:** yellow solid; yield: 397.5 mg (25%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 – 7.11 (m, 2H), 6.64 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.31 (br, 2H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 147.19, 135.66, 131.71, 122.21, 119.39, 116.25. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6ClNS 159.0; Found 159.0.



2-amino-4-bromobenzenethiol (1h)[3]**:** yellow solid; yield: 615.1 mg (30%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.41 (br, 2H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 149.59, 137.96, 126.01, 121.25, 117.72, 117.21. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6BrNS 204.9; Found 204.9.

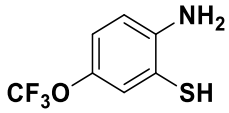


2-amino-5-bromobenzenethiol (1i)[4]**:** yellow solid; yield: 491.7 mg (24%).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28-7.25 (m, 2H), 6.62 (d, *J* = 9.1 Hz, 1H), 4.35 (br, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 147.61, 138.57, 134.52, 119.88, 116.65, 108.95. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_6H_6BrNS 204.9; Found 204.9.



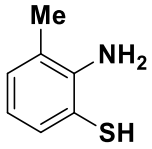
2-amino-4-fluoro-5-methylbenzenethiol (1j): yellow solid yellow solid (m.p. 110-111 ℃); yield: 596.6 mg (38%)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.88 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 11.2 Hz, 1H), 4.31 (br, 2H), 2.04 (d, *J* = 1.8 Hz, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -112.25 – -112.38 (m). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 163.60 (d, *J* = 247.9 Hz), 148.28 (d, *J* = 11.8 Hz), 139.79 (d, *J* = 7.7 Hz), 114.50 (d, *J* = 18.6 Hz), 113.77 (d, *J* = 2.8 Hz), 101.74 (d, *J* = 26.2 Hz), 13.35 (d, *J* = 3.1 Hz). **HRMS** (FI) calcd. for $C_7H_8FNS^+$ $[(M)]^+$:157.0361, found: 157.0356.



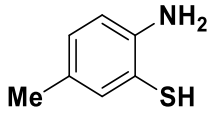
2-amino-5-(trifluoromethoxy)benzenethiol (1k)[5]**:**yellow solid; yield: 480.7 mg (23%)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.7 Hz, 1H), 7.47 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 5.42 (br, 2H), 1.78 (br, 1H). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -58.20 (s, 3F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 147.44, 140.06 (q, *J* = 2.1 Hz), 128.97, 125.26, 120.97 (q, *J* = 255.9 Hz), 118.18, 115.57. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_7H_6F_3NOS$ 209.0; Found 209.0.



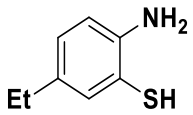
2-amino-3-methylbenzenethiol (1l)[2]**:** yellow solid; yield: 861.8 mg (62%)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 1H), 7.14 – 7.12 (m, 1H)， 7.04 (t, *J* = 7.6 Hz, 1H), 5.31 (br, 2H), 2.56 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.98, 134.67, 132.61, 122.49, 118.52, 117.58, 18.08. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_9NS 139.0; Found 139.0.

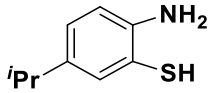


2-amino-5-methylbenzenethiol (1m)[6]**:** yellow solid; yield: 834 mg, 40% yield (15 mmol of **4m** was used)

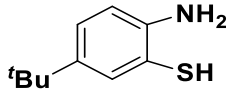
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.99-6.94 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.18 (br, 2H), 2.13 (s, 3H), 1.56 (br, 1H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.23, 137.06,132.34, 127.51, 118.94, 115.35, 20.08. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_9NS 139.0; Found 139.0.



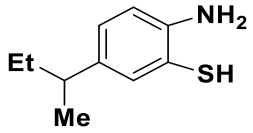
2-amino-5-ethylbenzenethiol (1n)[7]**:** yellow solid; yield: 627.3 mg (41%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.00 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 6.66 (d, *J* = 8.1 Hz), 4.21 (br, 2H), 2.42 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.40, 135.86, 134.16, 131.23, 118.73, 115.40, 27.62, 15.71. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_8H_{11}NS$ 153.1; Found 153.0.



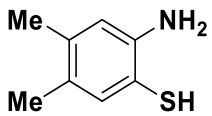
2-amino-5-isopropylbenzenethiol (1o)[7]**:** yellow solid; yield: 417.5 mg (25%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 4.21 (br, 2H), 2.69 (sept, *J* = 6.9 Hz, 1H), 1.11 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.45, 138.90, 134.39, 129.76, 118.52, 115.39, 32.91, 24.02. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_9H_{13}NS$ 167.1; Found 167.0.



2-amino-5-(tert-butyl)benzenethiol (1p)[8]**:** yellow solid; yield: 326.1 mg (18%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.16 (m, 2H), 6.66 (d, *J* = 6.7 Hz, 1H), 4.19 (br, 2H), 1.17 (s, 9H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.14, 141.33, 133.27, 128.75, 118.08, 115.17, 33.87, 31.36. **GC-MS** (EI) m/z: $[M]^+$Calcd for $C_{10}H_{15}NS$ 181.1; Found 181.1.

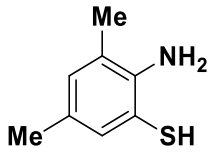


2-amino-5-(sec-butyl)benzenethiol (1q): yellow liquid; yield: 398.4 mg (22%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (s, 1H), 6.97 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 4.18 (br, 2H), 2.38 (sext, *J* = 7.0 Hz, 1H), 1.51 – 1.40 (m, 2H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.48, 137.81, 134.91, 130.24, 118.68, 115.37, 40.47, 31.17, 21.75, 12.21. **HRMS (FI)** calcd. for $C_{10}H_{15}NS^+$ $[(M)]^+$:181.0925, found: 181.0920.

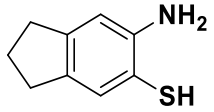


2-amino-4,5-dimethylbenzenethiol (1r)[9]**:** yellow solid; yield: 489.6 mg (32%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.93 (s, 1H), 6.54 (s, 1H), 3.97 (br, 2H), 2.17 (s, 3H), 2.05 (s, 3H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.57, 140.63, 137.50, 126.51,

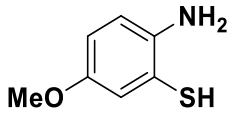
116.72, 116.50, 19.86, 18.35. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_8H_{11}NS$ 153.1; Found 153.0.



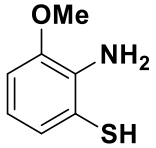
2-amino-3,5-dimethylbenzenethiol (1s)[9]**:** yellow solid; yield: 428.4 mg (28%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.90 (s, 1H), 6.86 (s, 1H), 4.17 (br, 2H), 2.15 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 144.51, 134.84, 133.54, 126.74, 122.55, 118.78, 20.04, 18.06. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_8H_{11}NS$ 153.1; Found 153.0.



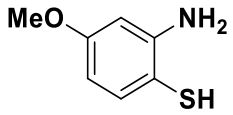
6-amino-2,3-dihydro-1H-indene-5-thiol (1t)[9]**:** yellow solid; yield: 214.6 mg (13%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.00 (s, 1H), 6.62 (s, 1H), 4.21 (br, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.01 (quint, *J* = 7.4 Hz, 2H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 148.73, 147.19, 134.19, 132.28, 117.00, 111.19, 33.08, 31.71, 25.66. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_9H_{11}NS$ 165.1; Found 165.0.



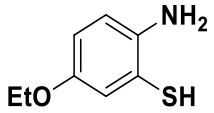
2-amino-5-methoxybenzenethiol (1u)[2]**:** yellow solid; yield: 465 mg, 20% yield (15 mmol of **4u** was used)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.71 – 6.64 (m, 2H), 4.06 (br, 2H), 3.60 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 151.82, 142.62, 120.03, 119.36, 119.26, 116.67, 55.76. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_9NOS 155.0; Found 155.0.



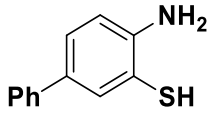
2-amino-3-methoxybenzenethiol (1v)[9]**:** yellow solid; yield: 697.5 mg (45%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.55 (t, *J* = 7.9 Hz, 1H), 4.49 (br, 2H), 3.85 (s, 3H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 146.97, 139.25, 128.11, 118.57, 116.71, 111.63, 55.77. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_9NOS 155.0; Found 155.0.



2-amino-4-methoxybenzenethiol (1w)[9]**:** yellow solid; yield:356.5 mg (45%).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.05 (d, *J* = 8.5 Hz, 1H), 6.24 (d, *J* = 2.6 Hz, 1H), 6.18 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.37 (br, 2H), 3.76 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 162.74, 150.17, 138.57, 110.82, 104.77, 99.94, 55.23. **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_9NOS 155.0; Found 155.0.

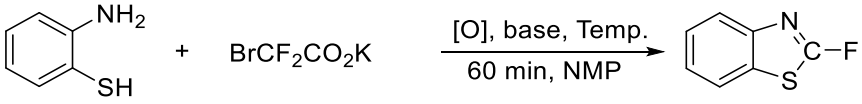


2-amino-5-ethoxybenzenethiol (1x)[7]**:** yellow solid; yield: 743.6 mg (44%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.79 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.01 (br, 2H), 3.80 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 151.14, 142.58, 120.95, 119.93, 119.33, 116.63, 64.09, 14.88. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_8H_{11}NOS$ 169.1; Found 169.0.



4-amino-[1,1'-biphenyl]-3-thiol (1y)[10]**:** yellow solid; yield: 241.6 mg (24%)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.38 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.47 (br, 2H).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 147.94, 140.10, 135.29, 131.55, 130.48, 128.76, 126.56, 126.33, 119.18, 115.77. **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}NS$ 201.1; Found 201.0.

3. Screening reaction conditions by using $BrCF_2CO_2K$ instead of PDFA



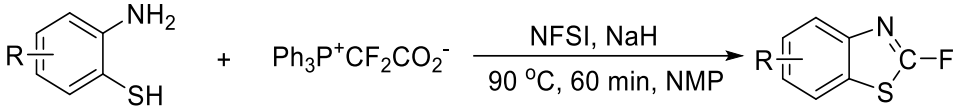
1a **5** **3a**

Entry	Molar Ratio[a]	Temp. (°C)	Solv.	Yield (%)[b]
1	1:2.5:2:3	50	NMP	27
2	1:2.5:2:3	70	NMP	15
3	1:2.5:2:3	90	NMP	12
4	1:2.5:2:3	110	NMP	33
5	1:2.5:1:3	110	NMP	30
6	1:2.5:2:3	110	DMF	24
7	1:2.5:2:3	110	THF	18
8	1:2.5:2:3	110	1,4 dioxane	ND
9	1:2.5:2:3	110	DMSO	ND

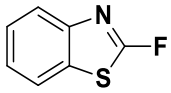
10	1:2.5:2:3	110	toloune	ND
11	1:2:2:3	110	NMP	30
12	1:3:2:3	110	NMP	39
13	1:3:2:2	110	NMP	27
14	1:3:2:1	110	NMP	39
15	1:3:2:0	110	NMP	27

Reaction conditions: Substrate **1a** (0.2 mmol), $BrCF_2CO_2K$ (**5**), NFSI, and NaH in a solvent (2 mL) under a N_2 atmosphere at the indicated temperature for 60 min. ND = not detected. [a]Molar ratio of **1a:5**:NFSI:NaH; [b]The yields were determined by ^{19}F NMR analysis.

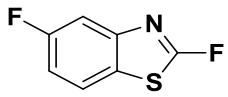
4. General procedure for the synthesis of fluorinated thiazoles



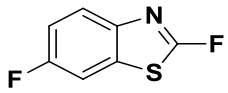
A sealed tube was charged with substrate **1** (0.5 mmol), $Ph_3P^+CF_2CO_2^-$ (2.5 equiv, 1.25 mmol, 445 mg), NFSI (2 equiv, 1.0 mmol, 315mg), NaH (60% purity, 3 equiv, 1.5 mmol, 60 mg) in NMP (5 mL) under a N_2 atmosphere at 90 °C for 60 min. When the reaction was completed, was quenched by slow addition of 1 mL of H_2O. Then the mixture was extracted with DCM. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using PE and EA as eluent) to obtain the final product **3**.



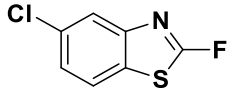
2-fluorobenzo[d]thiazole (3a)[12]**:** colorless liquid; yield: 49.7 mg (65%);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.49 (td, *J* = 7.8, 1.3 Hz, 1H), 7.41-7.37 (m, 1H). **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -72.31 (s, 1F).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.77 (d, *J* = 286.3 Hz), 146.28 (d, *J* = 18.3 Hz), 132.69, 126.91, 125.49 (d, *J* = 3.7 Hz), 122.91 (d, *J* = 2.7 Hz), 121.82. **HRMS**(EI) calcd. for $C_7H_4FNS^+$ $[(M)]^+$: 153.0048, found: 153.0053.



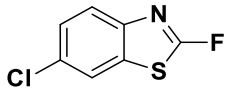
2,5-difluorobenzo[d]thiazole(3b): white solid (m.p.50-51℃); yield: 42.7 mg (50%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.68 (ddd, *J* = 8.9, 5.1, 1.5 Hz, 1H), 7.55 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.16 (td, *J* = 8.9, 2.5 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -68.94 (s, 1F), -113.65 – -113.76 (m, 1F).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 170.27 (d, *J* = 287.6 Hz), 162.06 (d, *J* = 244.5 Hz), 147.14 (dd, *J* = 18.7, 12.2 Hz), 127.86 (dd, *J* = 2.6, 1.2 Hz), 122.74 (d, *J* = 9.7 Hz), 114.09 (dd, *J* = 24.7, 3.9 Hz), 109.82 (dd, *J* = 24.4, 2.8 Hz). **HRMS** (EI) calcd. for $C_7H_3F_2NS^+$ $[(M)]^+$: 170.9954, found: 170.9949.



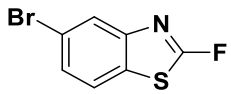
2,6-difluorobenzo[d]thiazole(3c)[11]**:** white solid; yield: 51.2 mg (60%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 (ddd, *J* = 8.9, 4.7, 1.4 Hz, 1H), 7.45 – 7.42 (m, 1H)), 7.21 (tdd, *J* = 9.0, 2.8, 1.4 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -71.38 (d, *J* = 10.1 Hz, 1F), -114.59 – -114.69 (m, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 167.83 (dd, *J* = 286.8, 2.5 Hz), 160.32 (dd, *J* = 245.8, 4.0 Hz), 142.64 (dd, *J* = 18.7, 2.2 Hz), 133.40 (dd, *J* = 11.0, 4.1 Hz), 124.04 (dd, *J* = 9.2, 3.3 Hz), 115.40 (d, *J* = 24.3 Hz), 108.41 (d, *J* = 27.3 Hz). **HRMS** (EI) calcd. for $C_7H_3F_2NS^+$ $[(M)]^+$: 170.9954, found: 170.9949.



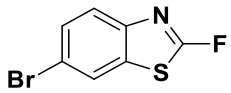
5-chloro-2-fluorobenzo[d]thiazole(3d): white solid (m.p. 47-48 ℃); yield: 37.4 mg (40%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.36 (dd, *J* = 8.6, 2.1 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -69.41(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 169.75 (d, *J* = 288.4 Hz), 147.03 (d, *J* = 18.6 Hz), 133.00, 130.78 (d, *J* = 4.1 Hz), 126.07 (d, *J* = 3.9 Hz), 122.97 (d, *J* = 2.9 Hz), 122.65. **HRMS** (ESI) calcd. for $C_7H_4ClNS^+$ $[(M+H)]^+$:187.9732, found: 187.9731.



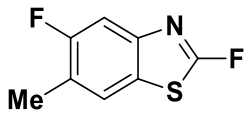
6-chloro-2-fluorobenzo[d]thiazole(3e)[11]**:** white solid; yield: 56.1 mg (60%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.7 Hz, 1H), 7.70 (t, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.1 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -70.82(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.65 (d, *J* = 288.0 Hz), 144.73 (d, *J* = 18.5 Hz), 133.67 (d, *J* = 4.1 Hz), 131.25 (d, *J* = 4.1 Hz), 127.74, 123.79 (d, *J* = 3.2 Hz), 121.49. **HRMS** (ESI) calcd. for $C_7H_4ClNS^+$ $[(M+H)]^+$:187.9732, found: 187.9731.



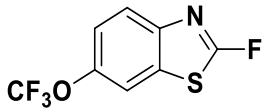
5-bromo-2-fluorobenzo[d]thiazole(3h): white solid (m.p.78-79 ℃); yield: 46.2mg (40%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.0 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -69.56(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 169.52 (d, *J* = 288.6 Hz), 147.29 (d, *J* = 18.6 Hz), 131.36 (d, *J* = 4.1 Hz), 128.73 (d, *J* = 4.0 Hz), 125.94 (d, *J* = 3.1 Hz), 122.94, 120.48. **HRMS** (ESI) calcd. for $C_7H_4BrNS^+$ $[(M+H)]^+$:231.9227, found: 231.9227.



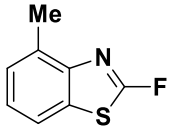
6-bromo-2-fluorobenzo[d]thiazole(3i): white solid (m.p.70-71 ℃); yield: 53.1 mg (46%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 8.7, 2.0 Hz, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -70.85(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.69 (d, *J* = 288.2 Hz), 145.10 (d, *J* = 18.7 Hz), 134.10 (d, *J* = 4.3 Hz), 130.48, 124.38, 124.17 (d, *J* = 3.3 Hz), 118.66 (d, *J* = 3.9 Hz). **HRMS** (ESI) calcd. for $C_7H_4BrNFS^+$ $[(M+H)]^+$:231.9227, found: 231.9227.



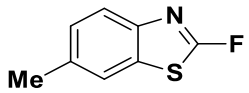
2,5-difluoro-6-methylbenzo[d]thiazole(3j): colorless liquid; yield: 44.4 mg (48%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 9.9 Hz, 1H), 2.38 (d, *J* = 2.2 Hz, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -70.88, -117.05 – -117.15 (m). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 169.42 (d, *J* = 286.9 Hz), 160.70 (d, *J* = 243.6 Hz), 145.09 (dd, *J* = 18.7, 12.4 Hz), 127.63 (dd, *J* = 3.9, 2.7 Hz), 124.09 (dd, *J* = 20.3, 3.9 Hz), 123.19 (d, *J* = 6.0 Hz), 109.13 (dd, *J* = 25.9, 2.7 Hz), 14.99 (d, *J* = 4.0 Hz). **HRMS** (EI) calcd. for $C_8H_5NF_2S^+$ $[(M)]^+$:185.0111, found: 185.0105.



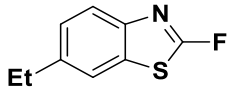
2-fluoro-6-(trifluoromethoxy)benzo[d]thiazole(3k): colorless liquid; yield: 59.2 mg (50%) ;^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.63 (s, 1H), 7.36 (dd, *J* = 8.8, 2.4, 1.1 Hz, 1H).**^{19}F NMR** (470 MHz, Chloroform-*d*) δ -58.17 (s, 3F), -69.68 (s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.91 (d, *J* = 288.1 Hz), 146.50 (q, *J* = 2.2 Hz), 144.83 (d, *J* = 18.7 Hz), 133.36 (d, *J* = 4.1 Hz), 123.93 (d, *J* = 3.2 Hz), 120.88, 120.46 (q, *J* = 257.8 Hz), 114.67. **HRMS** (EI) calcd. for $C_8H_3F_4NOS^+$ $[(M)]^+$:236.9871, found: 236.9866.



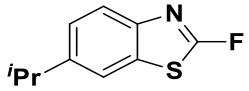
2-fluoro-4-methylbenzo[d]thiazole(3l): colorless liquid; yield: 52.6 mg (63%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (td, *J* = 4.6, 0.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 2.64 (s, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -72.99(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 167.81 (d, *J* = 285.1 Hz), 145.40 (d, *J* = 17.1 Hz), 132.87 (d, *J* = 3.2 Hz), 132.49 (d, *J* = 4.5 Hz), 127.60, 125.42 (d, *J* = 4.0 Hz), 119.17, 18.03. **HRMS** (EI) calcd. for $C_8H_6FNS^+$ $[(M)]^+$: 167.0205, found: 167.0199.



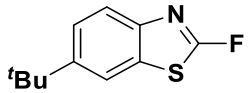
2-fluoro-6-methylbenzo[d]thiazole(3m)[12]**:** colorless liquid; yield: 55.9 mg (67%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.32 – 7.28 (m, 1H), 2.48 (s, 3H).**^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.55(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.14 (d, *J* = 285.7 Hz), 144.15 (d, *J* = 18.3 Hz), 135.72 (d, *J* = 3.9 Hz), 132.75 (d, *J* = 4.4 Hz), 128.37, 122.50 (d, *J* = 3.0 Hz), 121.69, 21.62. **HRMS** (EI) calcd. for $C_8H_6FNS^+$ $[(M)]^+$: 167.0205, found: 167.0199.



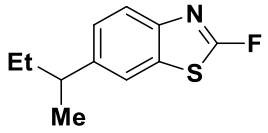
6-ethyl-2-fluorobenzo[d]thiazole(3n): colorless liquid; yield: 58.8 mg (65%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.30 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.38(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.11 (d, *J* = 285.8 Hz), 144.23 (d, *J* = 18.3 Hz), 142.06 (d, *J* = 4.0 Hz), 132.72 (d, *J* = 4.4 Hz), 127.22, 122.53 (d, *J* = 2.9 Hz), 120.46, 28.95, 15.78. **HRMS** (ESI) calcd. for $C_9H_9FNS^+$ $[(M+H)]^+$: 182.0435, found: 182.0435.



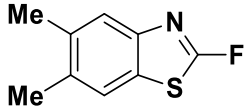
2-fluoro-6-isopropylbenzo[d]thiazole(3o)[12]**:** colorless liquid; yield: 66.3 mg (68%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.01 (sept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.25(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.14 (d, *J* = 285.6 Hz), 146.74 (d, *J* = 4.1 Hz), 144.34 (d, *J* = 18.3 Hz), 132.75 (d, *J* = 4.6 Hz), 125.89, 122.56 (d, *J* = 2.8 Hz), 119.05, 34.30, 24.15. **HRMS** (ESI) calcd. for $C_{10}H_{11}FNS^+$ $[(M+H)]^+$:196.0591, found: 196.0598.



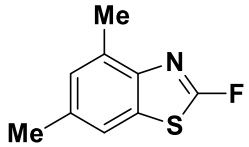
6-(tert-butyl)-2-fluorobenzo[d]thiazole(3p): colorless liquid; yield: 54.5 mg (52%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 1H), 7.72 (t, *J* = 1.6 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 1.37 (s, 9H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.02(s, 1F).**^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.30 (d, *J* = 285.9 Hz), 149.06 (d, *J* = 3.8 Hz), 143.99 (d, *J* = 18.2 Hz), 132.62 (d, *J* = 4.3 Hz), 124.84, 122.24 (d, *J* = 3.0 Hz), 118.05, 35.08, 31.49. **HRMS** (ESI) calcd for $C_{11}H_{13}FNS^+$ $[(M+H)]^+$:210.0748, found: 210.0750.



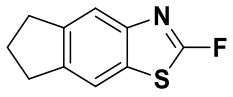
6-(sec-butyl)-2-fluorobenzo[d]thiazole(3q): colorless liquid; yield: 41.8 mg (40%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* =1.7 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.70 (sext, *J* = 7.0 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.37(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.12 (d, *J* = 285.7 Hz), 145.55 (d, *J* = 3.9 Hz), 144.39 (d, *J* = 18.3 Hz), 132.72 (d, *J* = 4.4 Hz), 126.33, 122.52 (d, *J* = 2.9 Hz), 119.75,41.85,31.32,22.04,12.20. **HRMS** (ESI) calcd for $C_{11}H_{13}FNS^{+}$ $[(M+H)]^{+}$:210.0748, found: 210.0750.



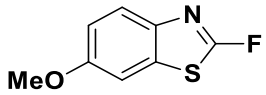
2-fluoro-5,6-dimethylbenzo[d]thiazole(3r): white solid (m.p. 217-218 ℃); yield: 55.2 mg (61%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.46 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H).. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.99(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.16 (d, *J* = 285.4 Hz), 144.59 (d, *J* = 18.1 Hz), 136.12, 134.83 (d, *J* = 4.1 Hz), 129.78 (d, *J* = 4.2 Hz), 123.20 (d, *J* = 2.7 Hz), 121.77, 20.13, 20.06. **HRMS** (EI) calcd. for $C_9H_8FNS^{+}$ $[(M)]^{+}$:181.0361, found: 181.0356



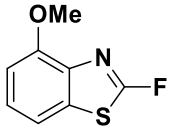
2-fluoro-4,6-dimethylbenzo[d]thiazole(3s): colorless liquid; yield: 36.2 mg (40%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 7.08 (s, 1H), 2.57 (s, 3H), 2.41 (s, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -74.18(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 167.13 (d, *J* = 284.6 Hz), 143.19 (d, *J* = 17.0 Hz), 135.47 (d, *J* = 4.0 Hz), 132.48 (d, *J* = 4.5 Hz), 132.26 (d, *J* = 3.2 Hz), 129.08, 118.95, 21.48, 17.95. **HRMS** (EI) calcd. for $C_9H_8FNS^{+}$ $[(M)]^{+}$:181.0361, found: 181.0356.



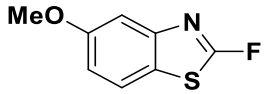
2-fluoro-6,7-dihydro-5H-indeno[5,6-d]thiazole(3t): colorless liquid; yield: 55.9 mg (58%); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.53 (s, 1H), 3.03-2.97 (m, 4H), 2.14 (quint, *J* = 7.4 Hz, 2H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.16(s, 1F).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.90 (d, *J* = 285.3 Hz), 144.71 (d, *J* = 17.5 Hz), 143.99, 142.37 (d, *J* = 4.0 Hz), 130.20 (d, *J* = 4.5 Hz), 118.45 (d, *J* = 2.7 Hz), 116.94, 32.87, 32.82, 26.04. **HRMS** (EI) calcd. For $C_{10}H_8NFS^{+}[(M)]^{+}$:193.0361, found: 193.0356.



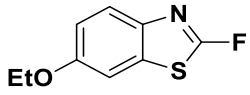
2-fluoro-6-methoxybenzo[d]thiazole(3u): white solid (m.p. 64-65 ℃); yield: 52.5 mg (58%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.9 Hz, 1H), 7.18 (dd, *J* = 2.7, 1.4 Hz, 2H), 7.04 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.84 (s, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -74.36(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 166.61 (d, *J* = 285.0 Hz), 157.70 (d, *J* = 3.8 Hz), 140.08 (d, *J* = 18.3 Hz), 133.67 (d, *J* = 4.4 Hz), 123.43 (d, *J* = 2.9 Hz), 115.43, 105.09, 55.79. **HRMS (ESI)** calcd. for $C_8H_7FNOS^+$ $[(M+H)]^+$:184.0227, found: 184.0227.



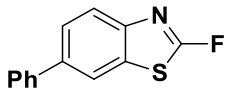
2-fluoro-4-methoxybenzo[d]thiazole(3v): white solid (m.p. 45-46 ℃); yield: 56.7 mg (62%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 6.92 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.99 (s, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.22(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 167.44 (d, *J* = 286.9 Hz), 153.06 (d, *J* = 3.3 Hz), 135.82 (d, *J* = 17.4 Hz), 133.90 (d, *J* = 4.3 Hz), 126.41 (d, *J* = 3.8 Hz), 113.67, 107.93, 56.06. **HRMS (ESI)** calcd. for $C_8H_7FNOS^+$ $[(M+H)]^+$:184.0227, found: 184.0227.



2-fluoro-5-methoxybenzo[d]thiazole(3w): white solid (m.p. 50-51 ℃); yield:45.7 mg (50%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.34 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.86 (s, 3H).**^{19}F NMR** (470 MHz, Chloroform-*d*) δ -73.22(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 169.74 (d, *J* = 286.2 Hz), 159.37, 147.32 (d, *J* = 18.2 Hz), 123.95 (d, *J* = 4.0 Hz), 122.18, 114.89 (d, *J* = 4.1 Hz), 106.33 (d, *J* = 2.3 Hz), 55.64. **HRMS (ESI)** calcd. for $C_8H_7FNOS^+$ $[(M+H)]^+$:184.0227, found: 184.0227.



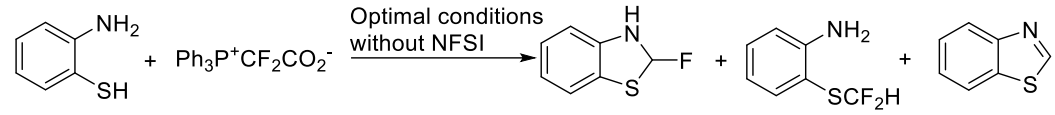
6-ethoxy-2-fluorobenzo[d]thiazole(3x): white solid (m.p. 54-55 ℃); yield: 59.1 mg (60%);**^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.9 Hz, 1H), 7.18 (s, 1H), 7.04 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -74.42(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 165.54 (d, *J* = 285.1 Hz), 156.01 (d, *J* = 3.8 Hz), 138.96 (d, *J* = 18.4 Hz), 132.60 (d, *J* = 4.3 Hz), 122.39 (d, *J* = 3.0 Hz), 114.87, 104.73, 63.13, 13.75. **HRMS (EI)** calcd. for $C_9H_8FNOS^+$ $[(M)]^+$:197.0311, found: 197.0305.



2-fluoro-6-phenylbenzo[d]thiazole(3y): white solid (m.p. 105-106 ℃); yield: 63.0 mg (55%);**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 1.5 Hz, 1H), 7.89 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.62-7.59 (m, 2H), 7.50 - 7.46 (m, 2H), 7.42 – 7.38 (m, 1H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -71.47(s, 1F). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 168.70 (d, *J* = 286.9 Hz), 145.49 (d, *J* = 18.3 Hz), 140.27, 139.13 (d, *J* = 3.8 Hz), 133.37 (d, *J* = 4.2 Hz), 129.01, 127.73, 127.31, 126.43, 123.02 (d, *J* = 3.0 Hz), 120.17. **HRMS (ESI)** calcd. for $C_{13}H_9FNS^+$ $[(M+H)]^+$:230.0435, found: 230.0437.

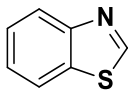
5. Mechanistic Investigations

5.1 The absence of NFSI



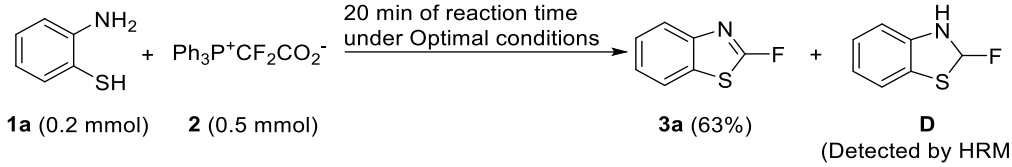
A sealed tube was charged with substrate **1a** (0.2 mmol), $Ph_3P^+CF_2CO_2^-$ (2.5 equiv, 0.5 mmol, 178 mg), NaH (60% purity, 3 equiv, 1.5 mmol, 24 mg) and NMP (2 mL) under a N_2 atmosphere. The resulting mixture was stirred at 90 ºC for 60 min. $PhCF_3$ (0.2 mmol) was added to the reaction system as an internal standard for the calculation of the ^{19}F NMR yield of **4a** (45%). The solution was diluted with CH_2Cl_2 and washed with water to remove the reaction solvent. The yield of **5a** was determined by ^{1}H NMR analysis of the residue (15%). Flash column chromatography ((using PE/EA = 50/1 ~ 30/1 as eluent) gave pure **4a** and **5a**. The purification of **4a** and **5a** is extremely difficult because they have very similar polarity. We tried our best and finally were successful to separate them from each other, but NMR yields rather than isolated yields would be suitable to convey the reaction results due to the loss during isolation.

2-((difluoromethyl)thio)aniline (4a)[13]**:** colorless liquid; 45% ^{19}F NMR yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.25-7.21 (m, 1H), 6.78 – 6.71 (m, 2H), 6.72 (t, *J* = 57.2 Hz, 1H), 4.41 (br, 2H). **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -91.01 (d, *J* = 57.3 Hz, 2F). **GC-MS** (EI) m/z: $[M]^+$ Calcd for $C_7H_7F_2NS$ 175.0; Found 175.1.



Benzo[d]thiazole (5a)[14]**:** colorless liquid; yield: 15% ^{1}H NMR yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.00 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.54-7.51 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H). **GC-MS** (EI) m/z: $[M]^+$ Calcd for C_7H_5NS 135.0; Found 135.0.

5.2 The observation of D by HRMS



A sealed tube was charged with substrate **1a** (0.2 mmol), $Ph_3P^+CF_2CO_2^-$ (2.5 equiv, 0.5 mmol, 178 mg), NaH (60% purity, 3 equiv, 1.5 mmol, 24 mg) and NMP (2 mL) under a N_2 atmosphere. The resulting mixture was stirred at 90 °C for 20 min. The reaction mixture was analyzed by high resolution mass spectrometer (EI) mode. Intermediate **D** was detected. **HRMS (EI)** calcd. for $C_7H_6FNS^+$ $[M]^+$: 155.0199, found: 155.0204.

6. References

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7. Copies of NMR Spectra

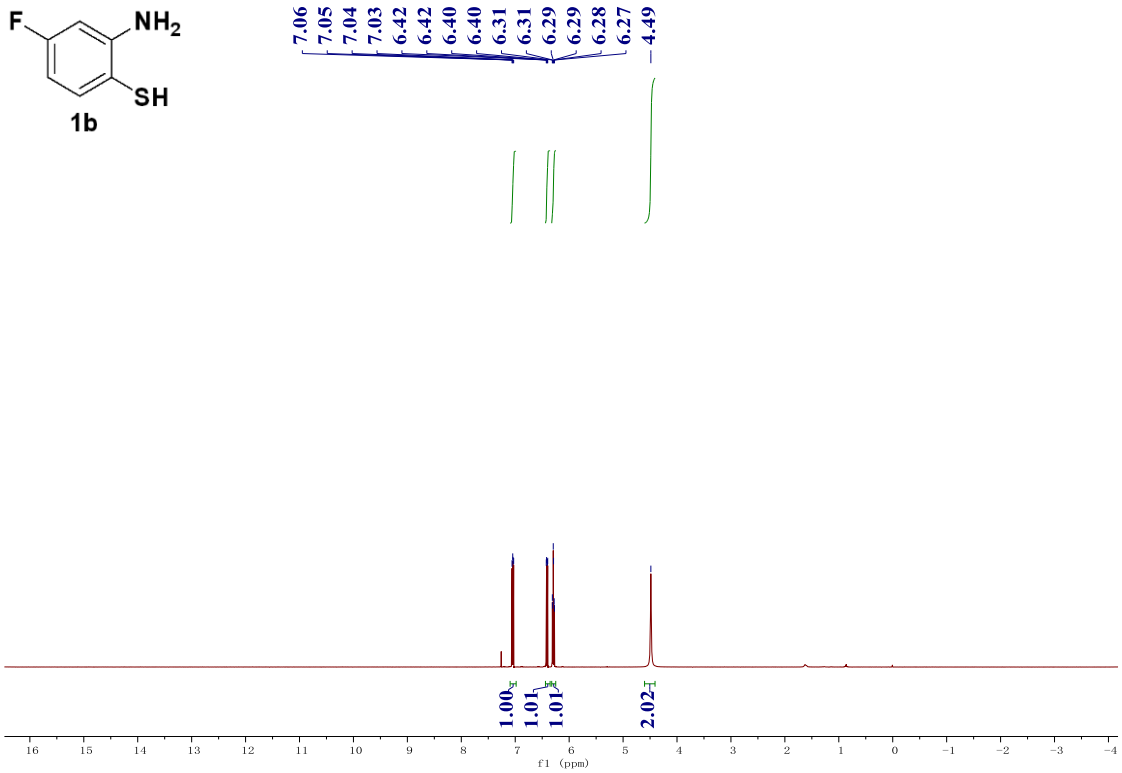

Fig. 1 ^{1}H NMR of **1b** in $CDCl_3$

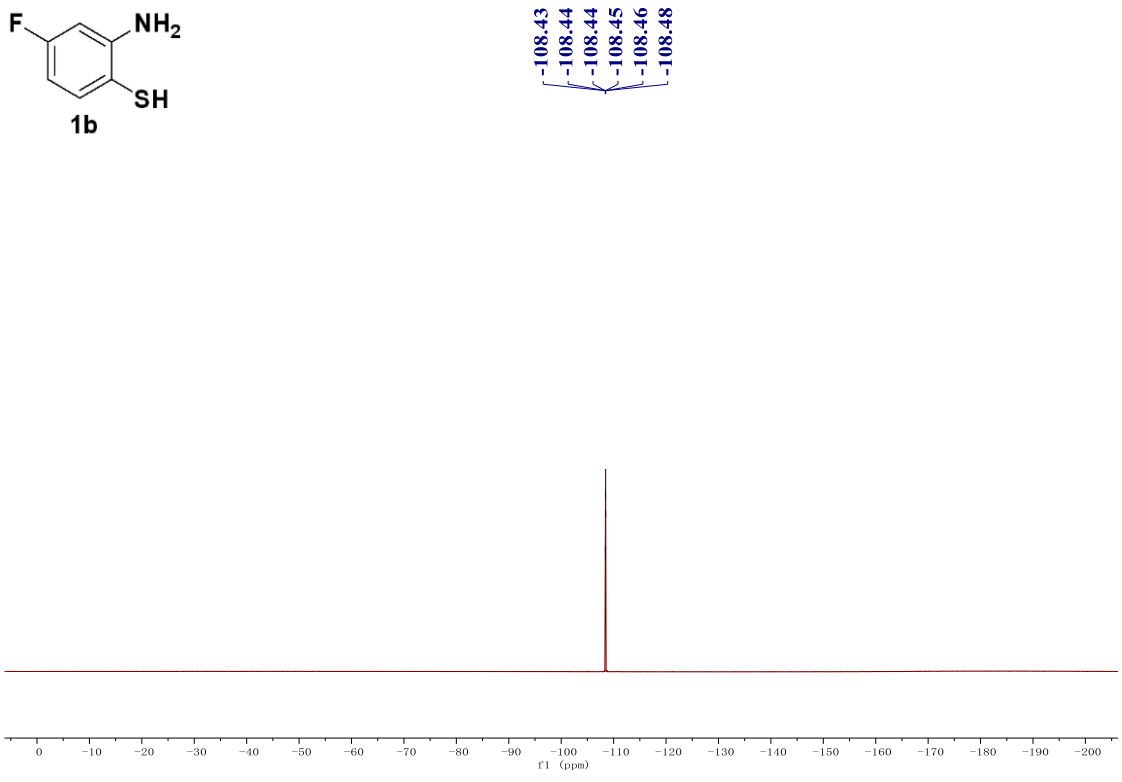

Fig. 2 ^{19}F NMR of **1b** in $CDCl_3$

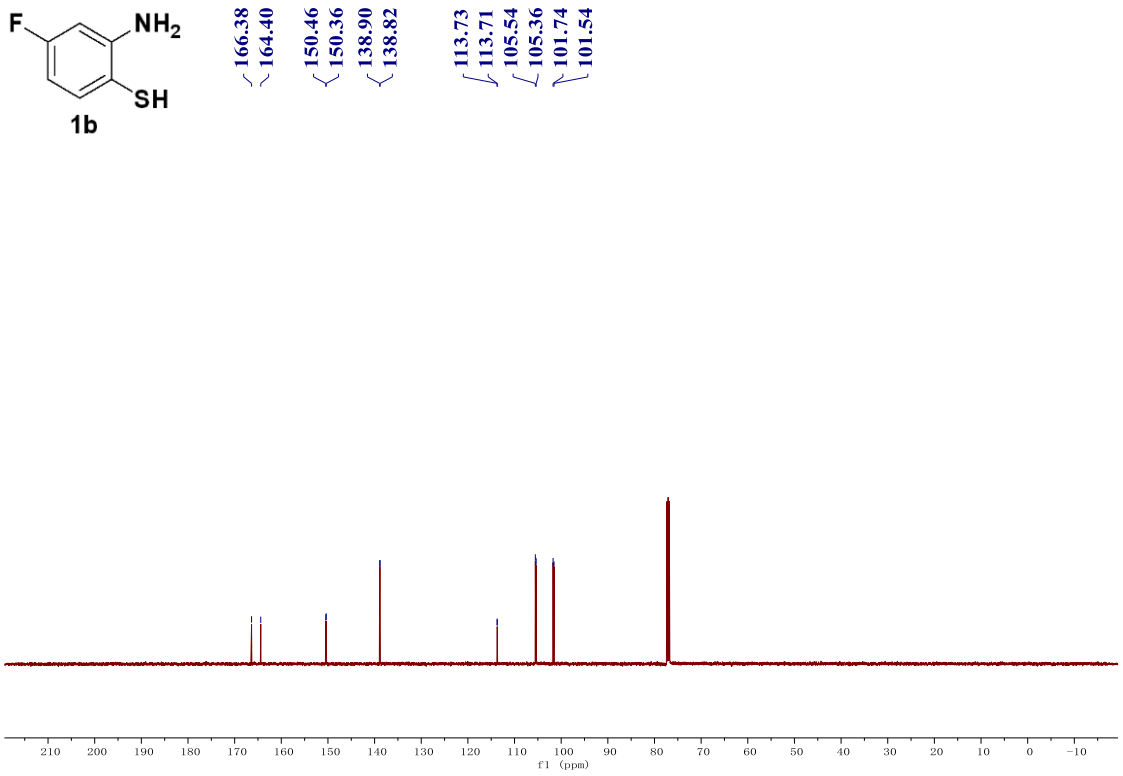

Fig. 3 ^{13}C NMR of **1b** in $CDCl_3$

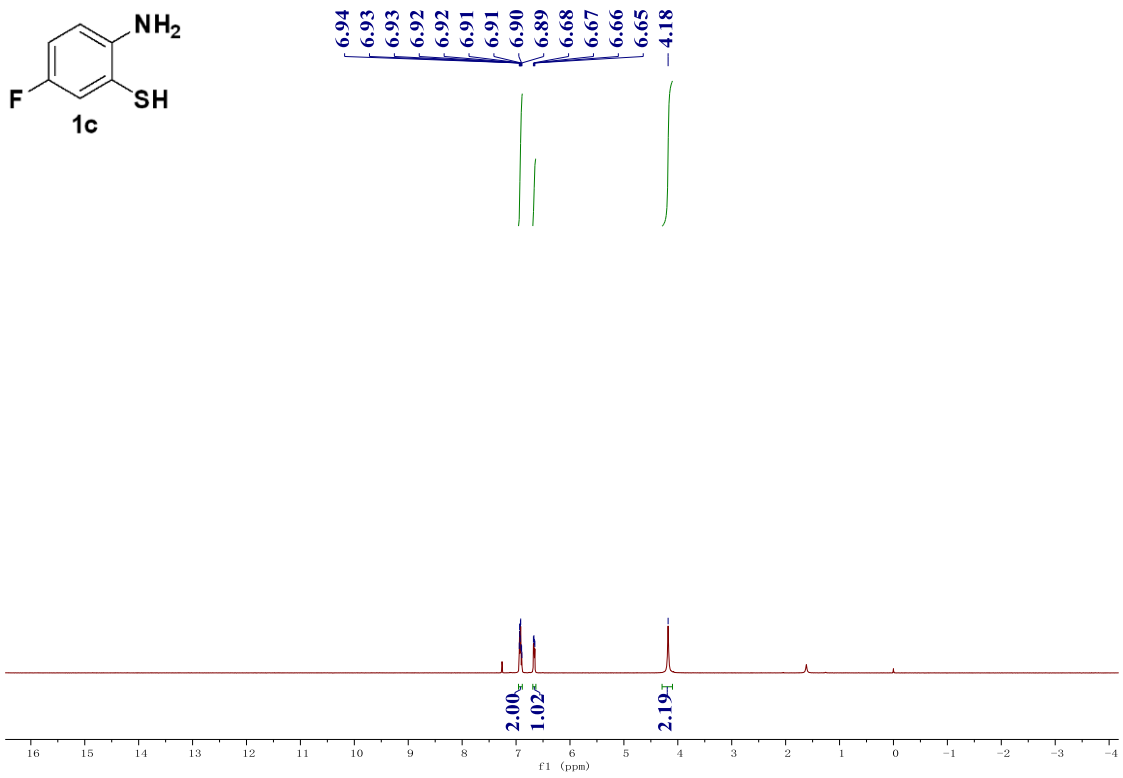

Fig.4 ^{1}H NMR of **1c** in $CDCl_3$

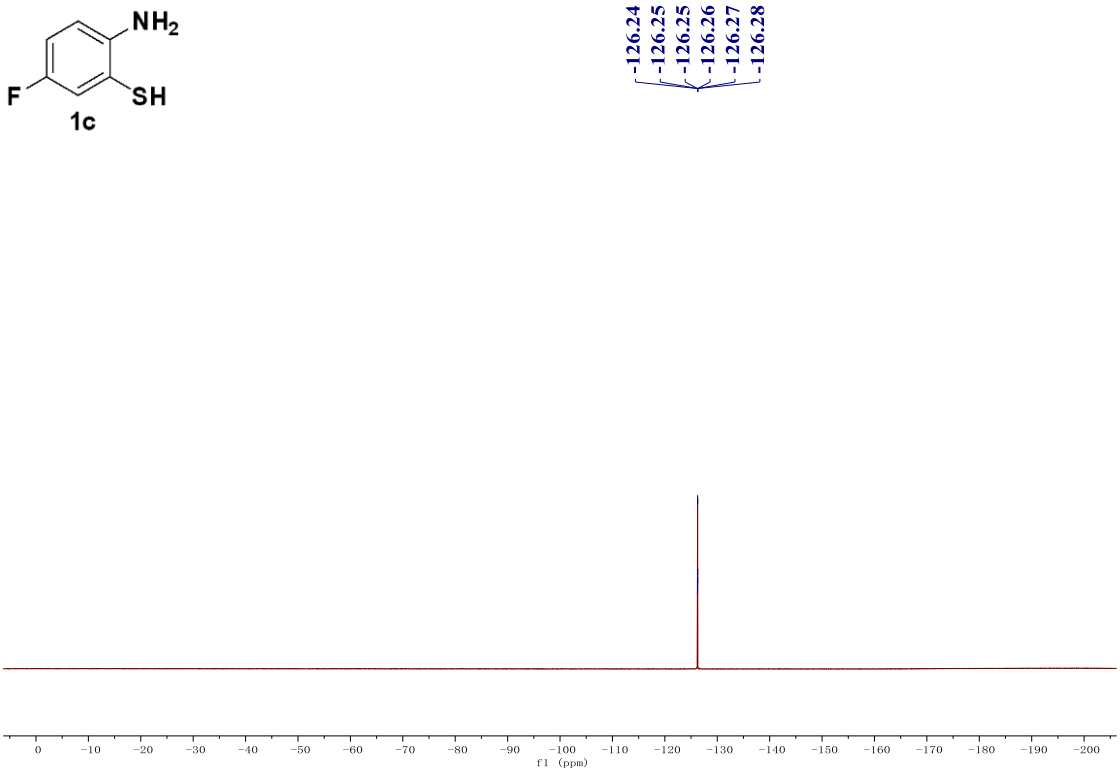

Fig. 5 ^{13}C NMR of **1c** in $CDCl_3$

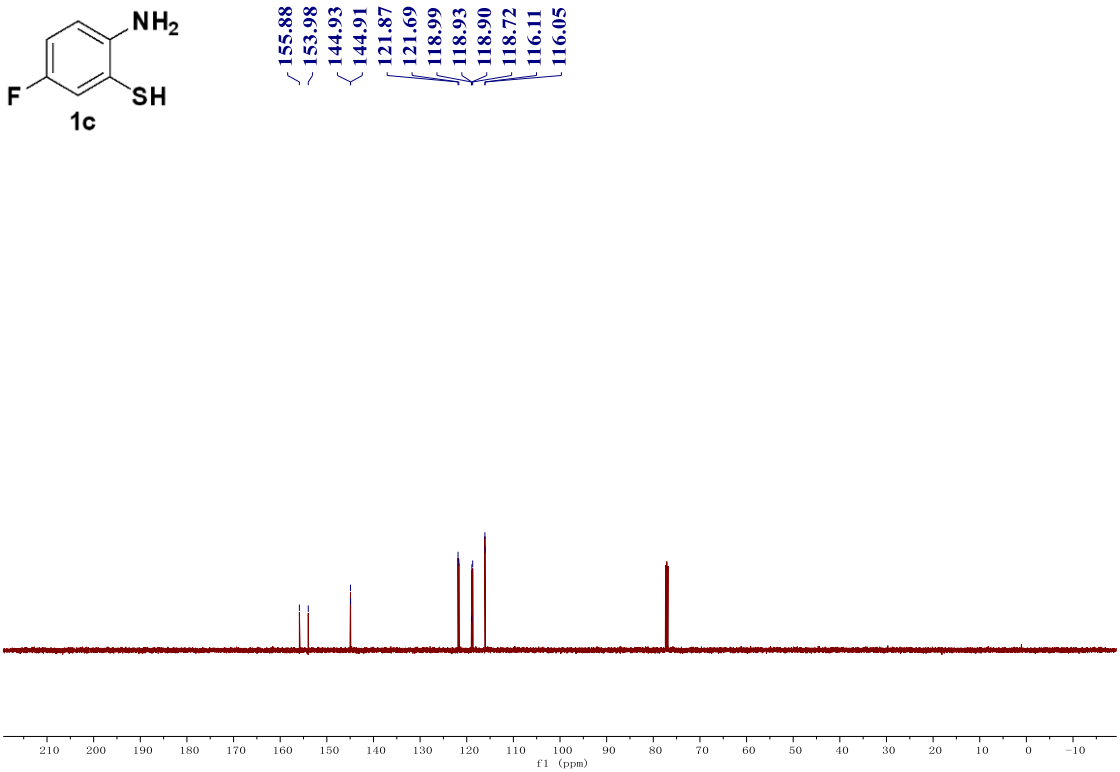

Fig. 6 ^{13}C NMR of **1c** in $CDCl_3$

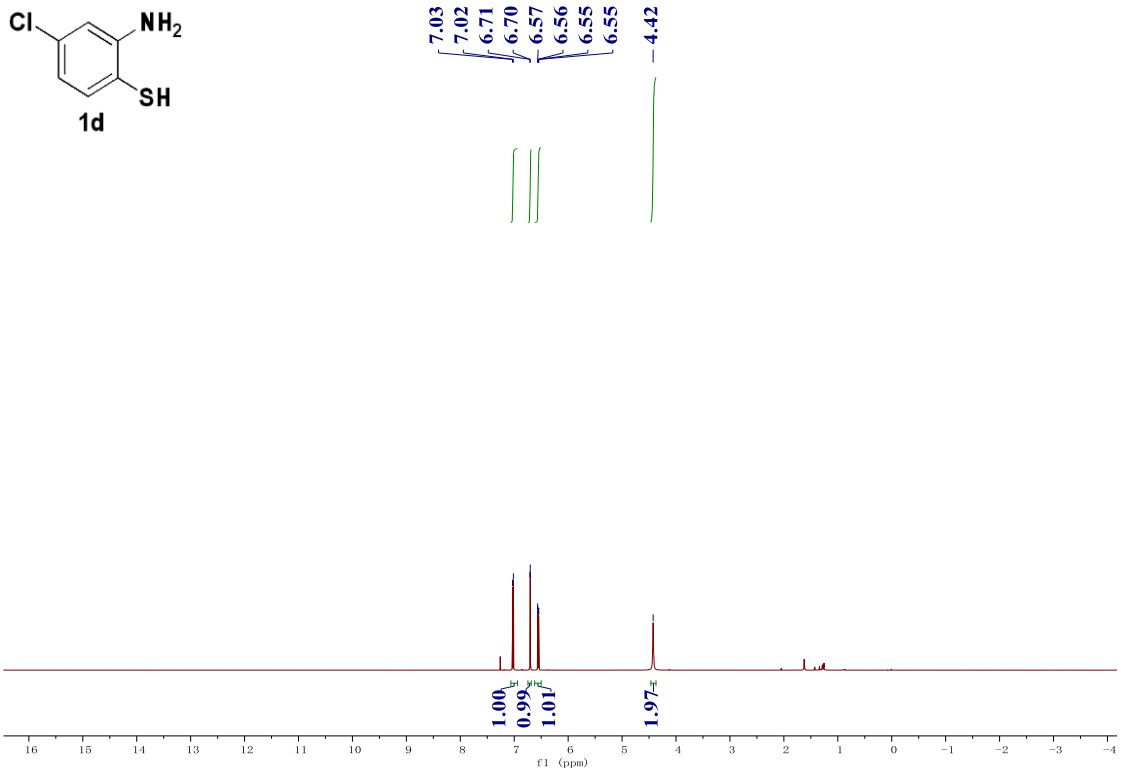

Fig. 7 ^{1}H NMR of **1d** in $CDCl_3$

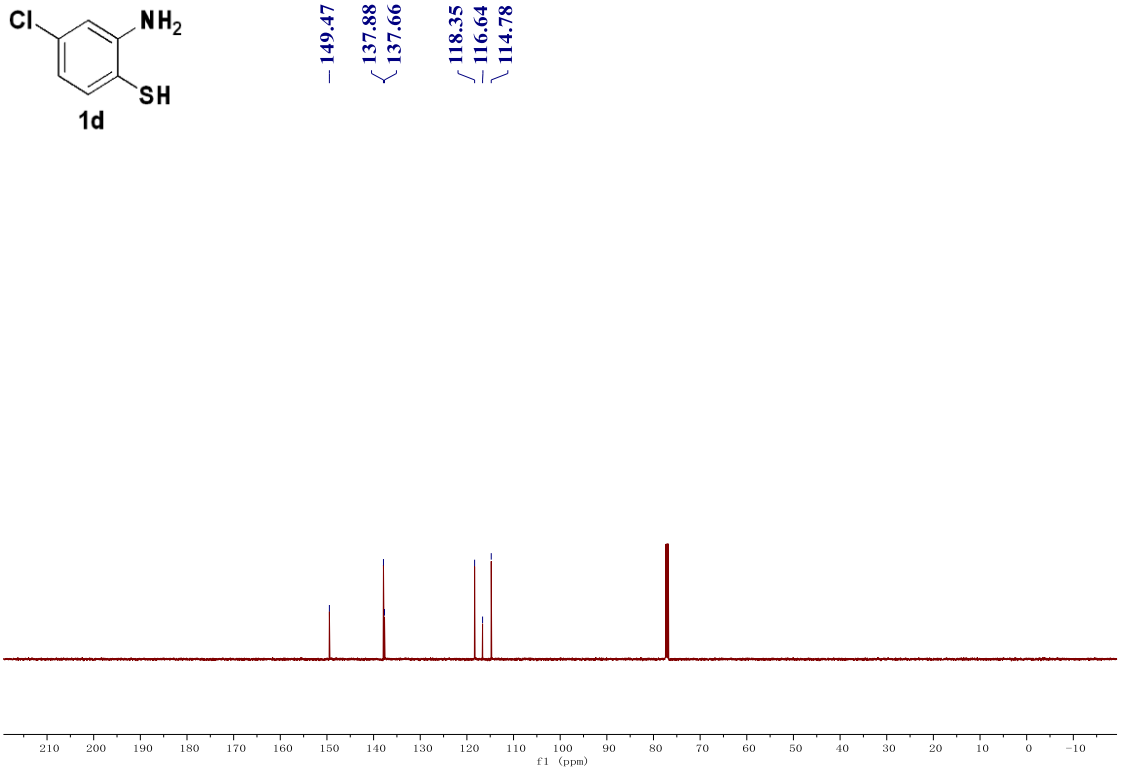

Fig. 8 ^{13}C NMR of **1d** in $CDCl_3$

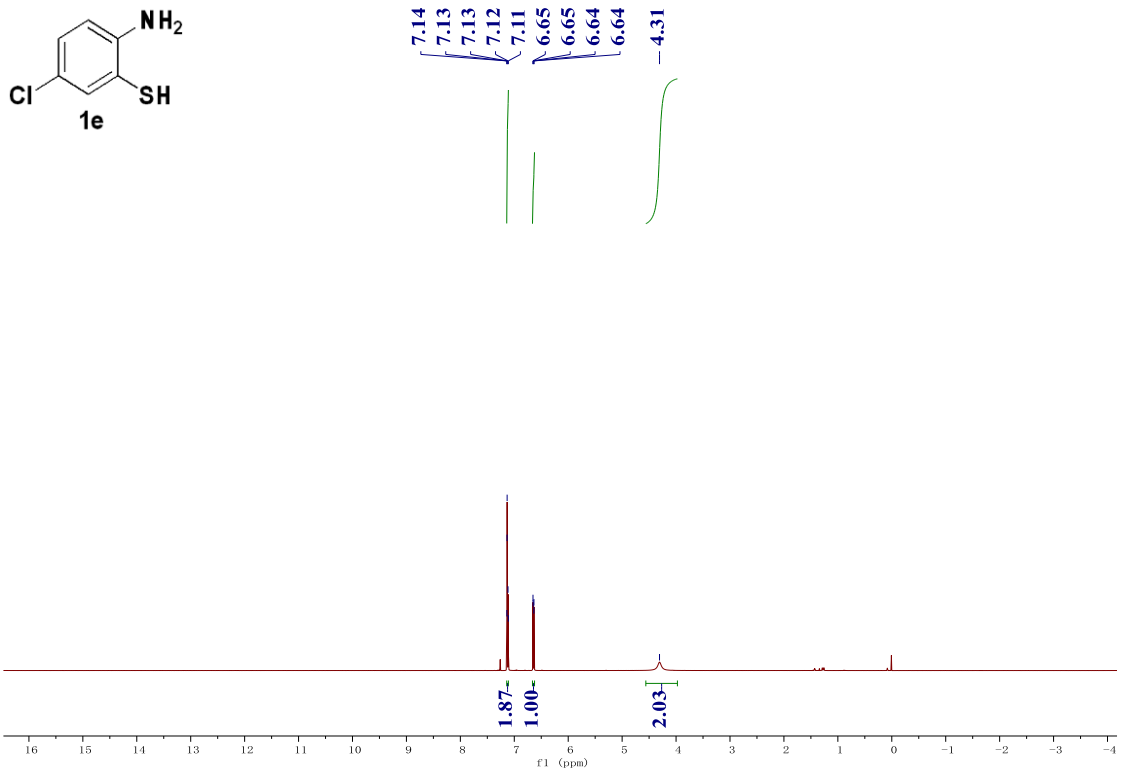

Fig. 9 ^{1}H NMR of **1e** in $CDCl_3$

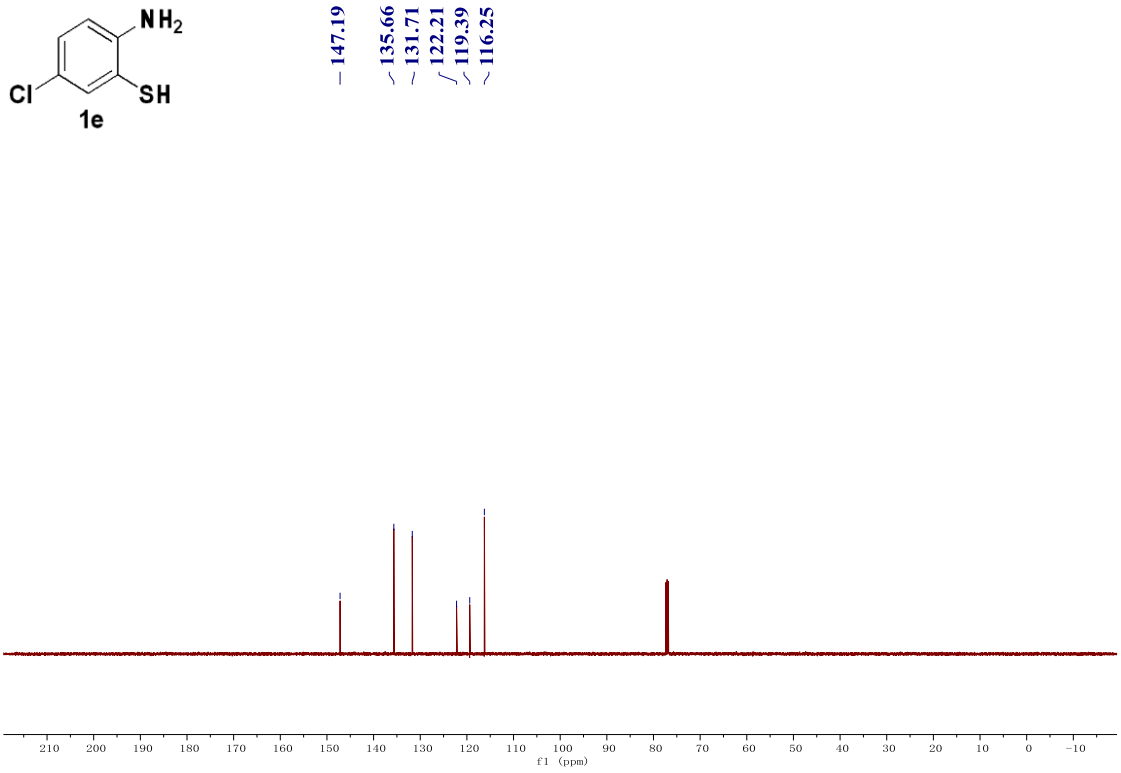

Fig. 10 ^{13}C NMR of **1e** in $CDCl_3$

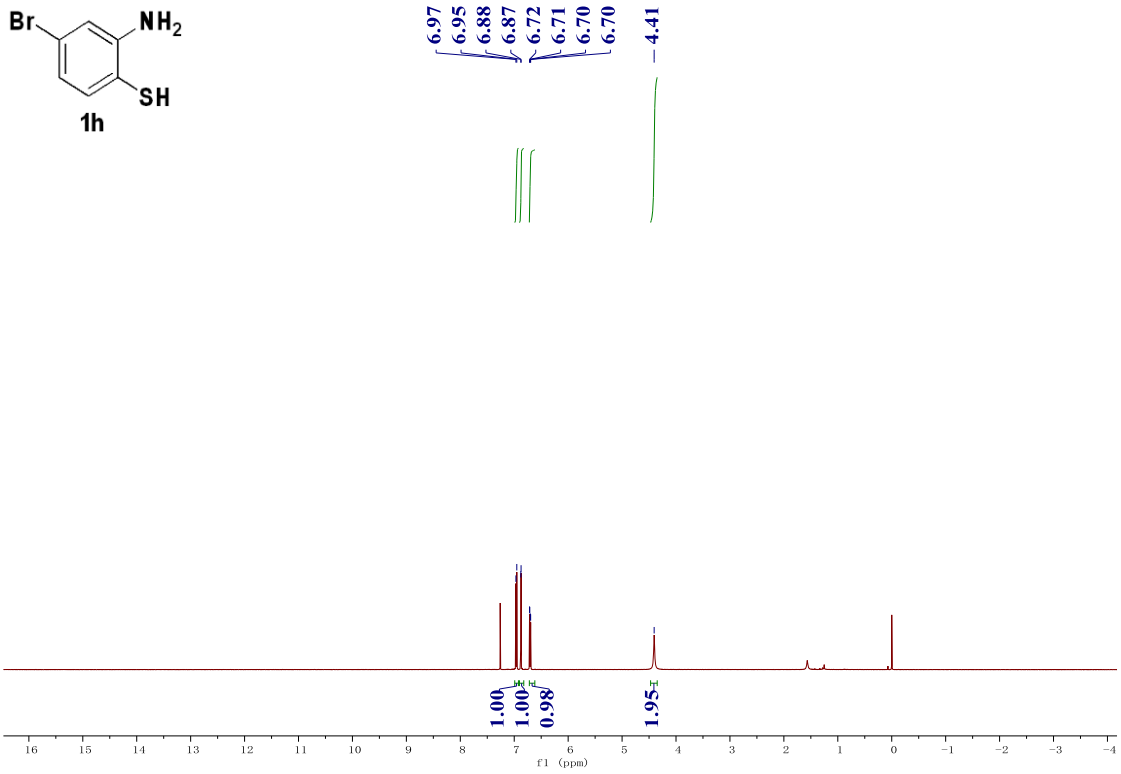

Fig. 11 ^{1}H NMR of **1h** in $CDCl_3$

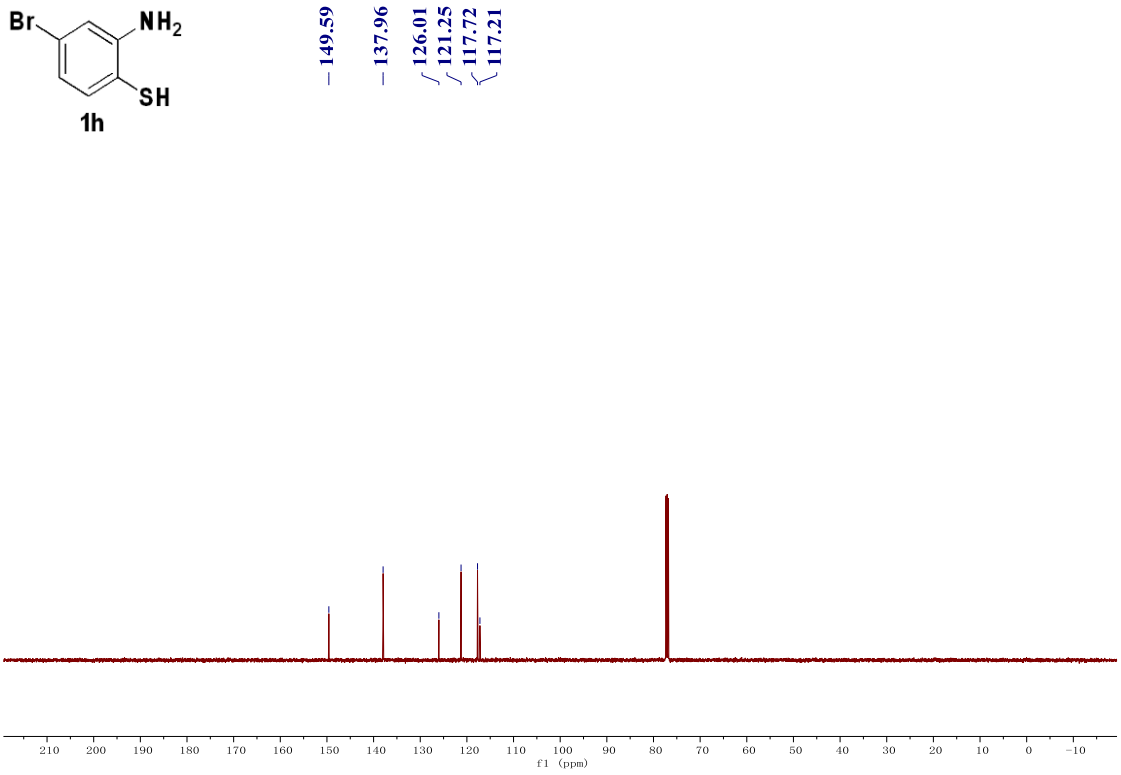

Fig. 12 ^{13}C NMR of **1h** in $CDCl_3$

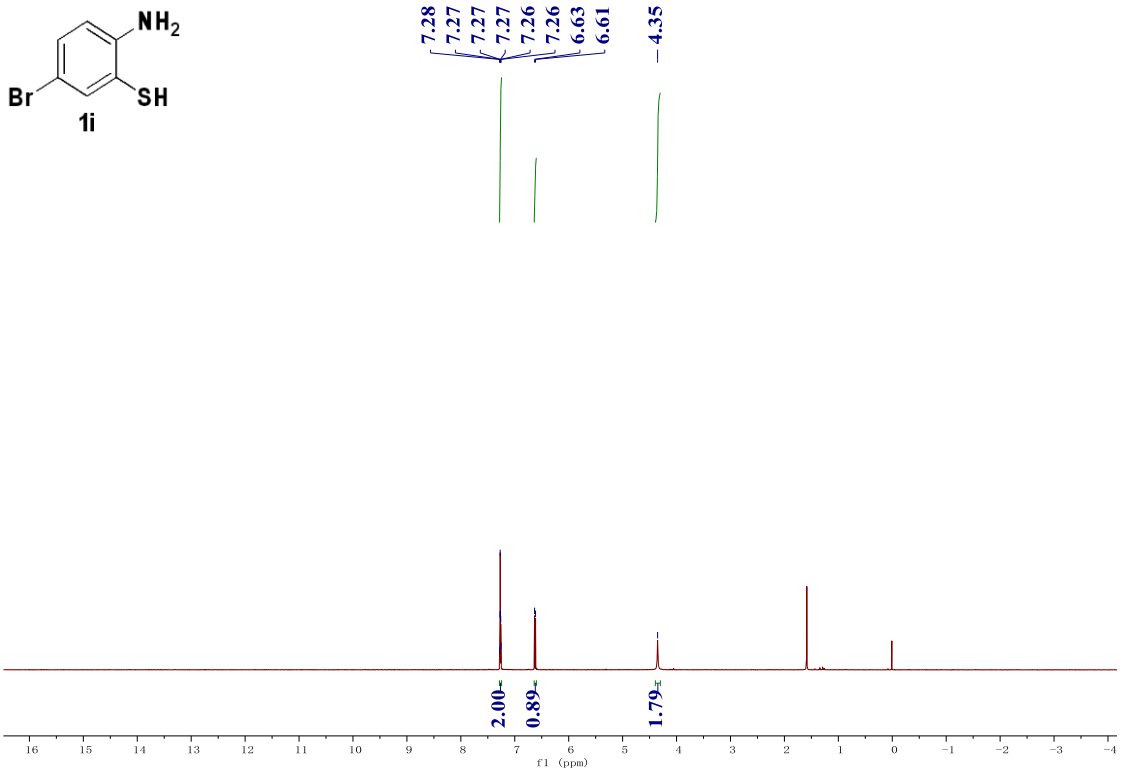

Fig. 13 ^{1}H NMR of **1i** in $CDCl_3$

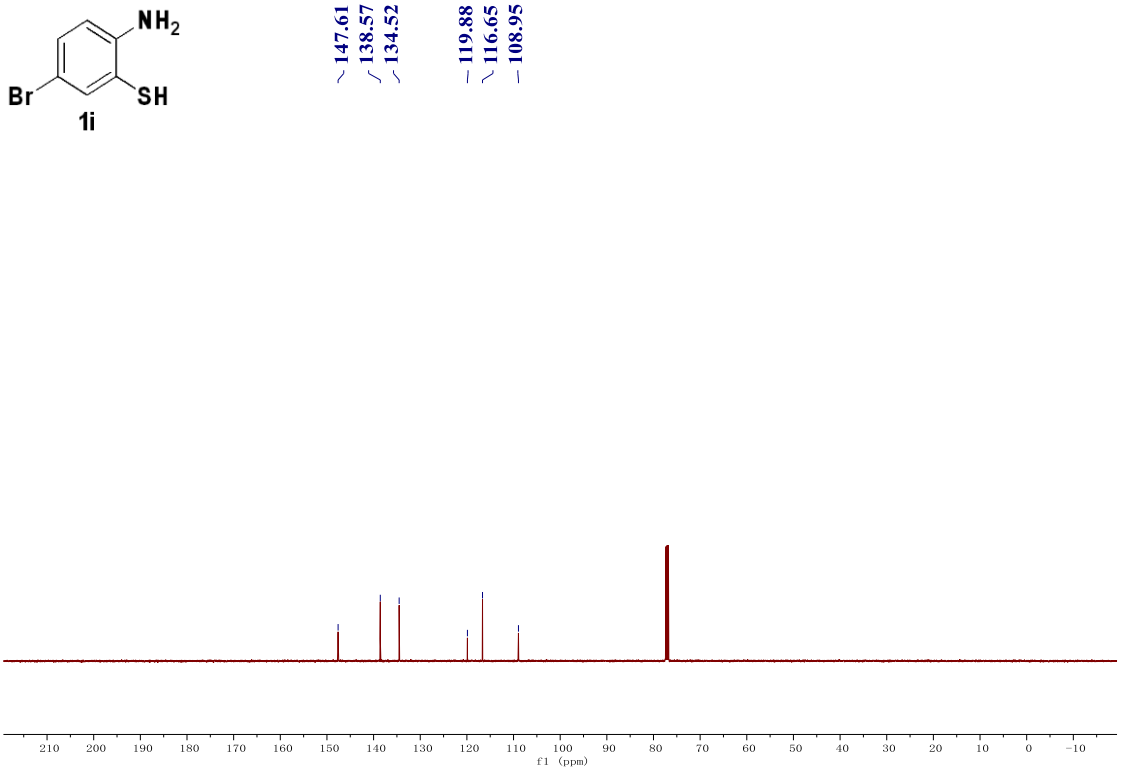

Fig. 14 ^{13}C NMR of **1i** in $CDCl_3$

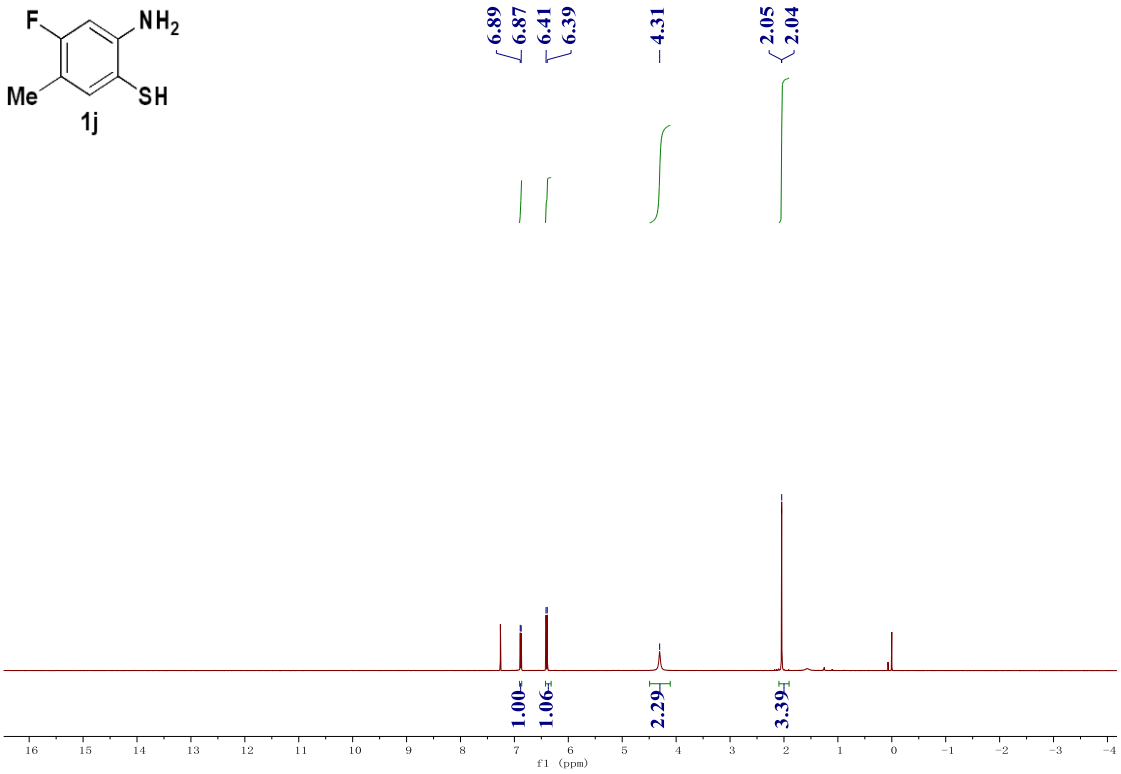

Fig. 15 ^{1}H NMR of **1j** in $CDCl_3$

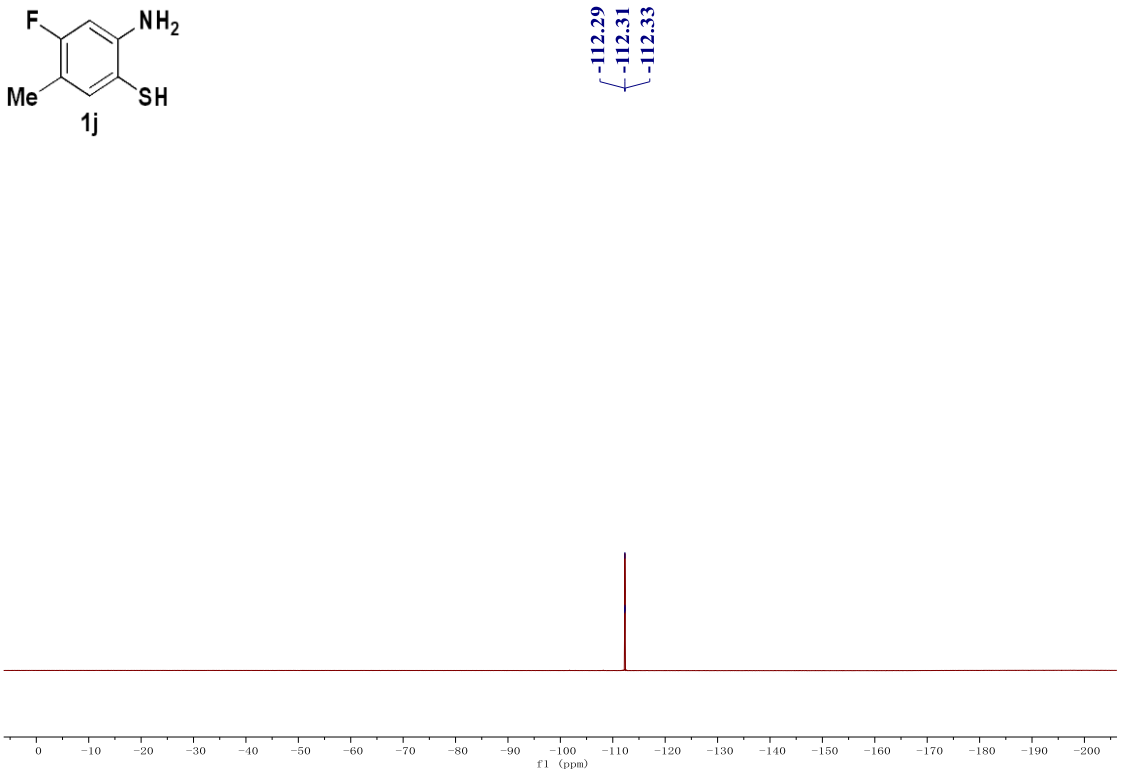

Fig.16 ^{19} NMR of **1j** in $CDCl_3$

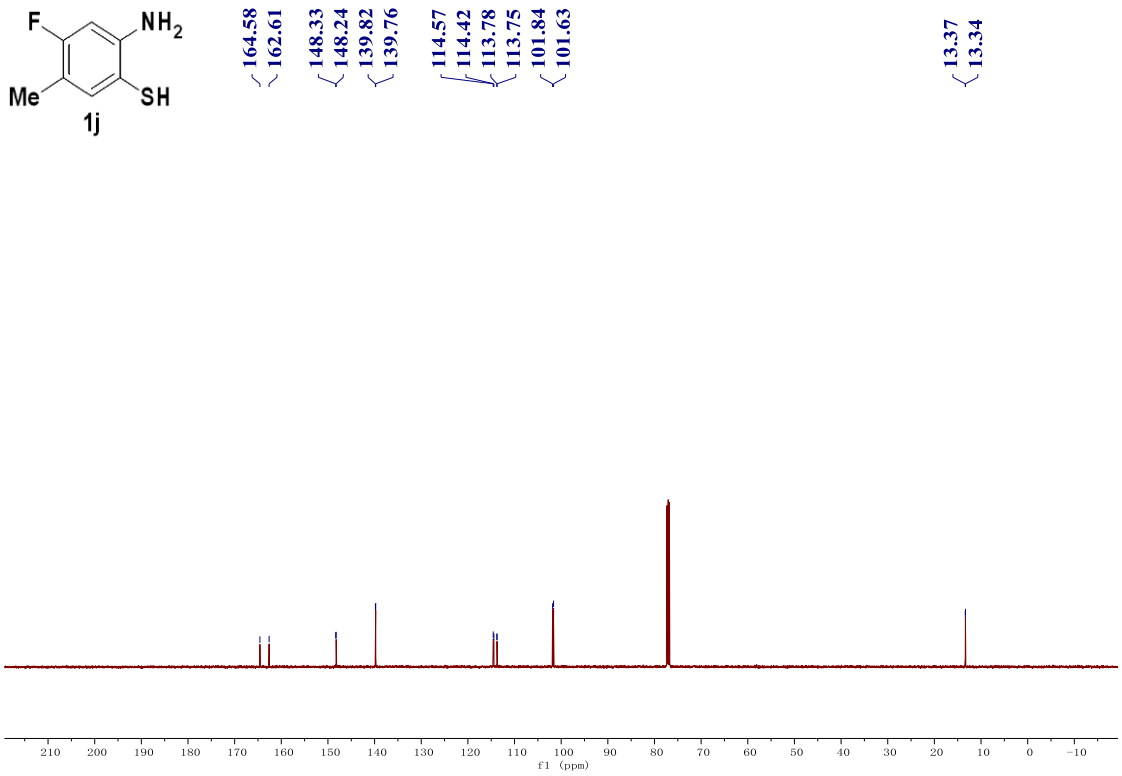

Fig. 17 ^{13}C NMR of **1j** in $CDCl_3$

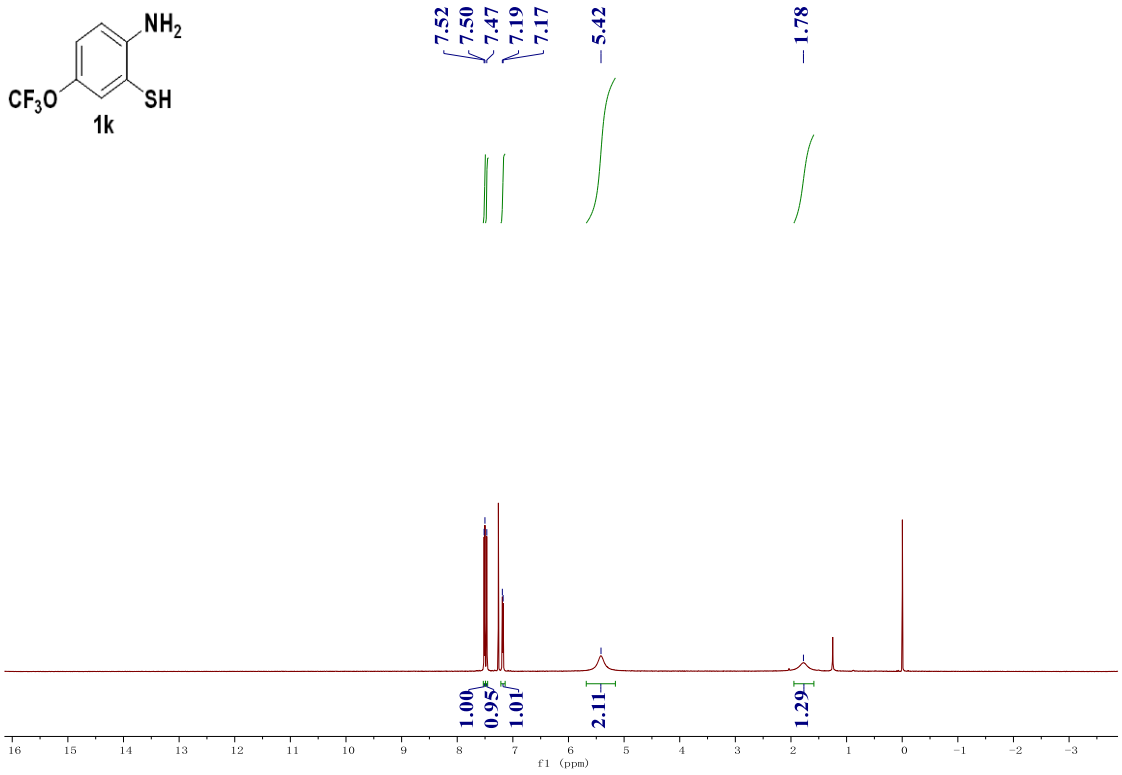

Fig. 18 ^{1}H NMR of **1k** in $CDCl_3$

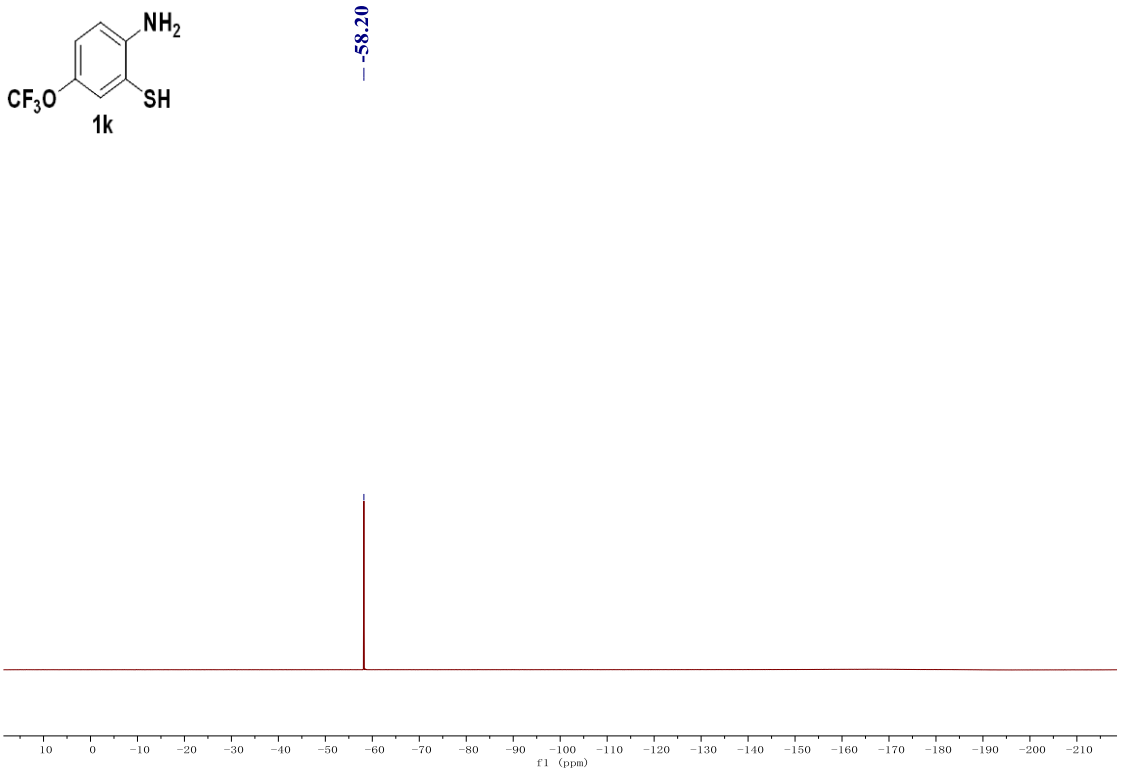

Fig. 19 ^{19} NMR of **1k** in $CDCl_3$

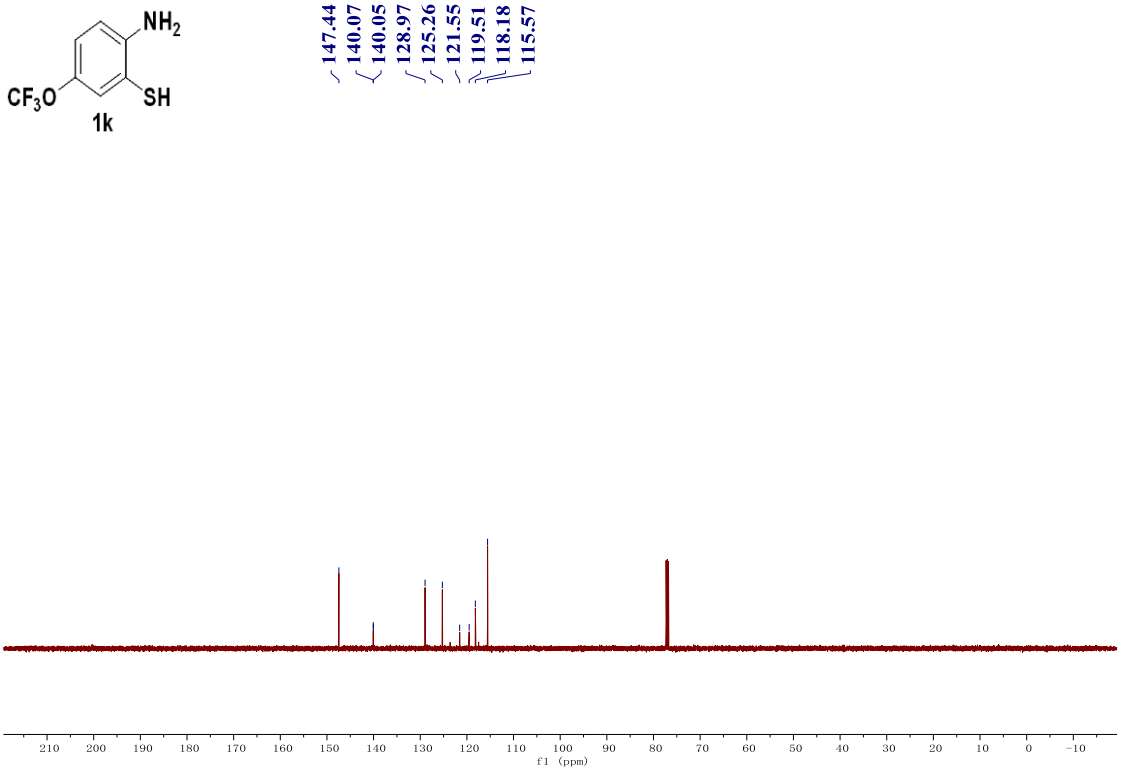

Fig. 20 ^{13}C NMR of **1k** in $CDCl_3$

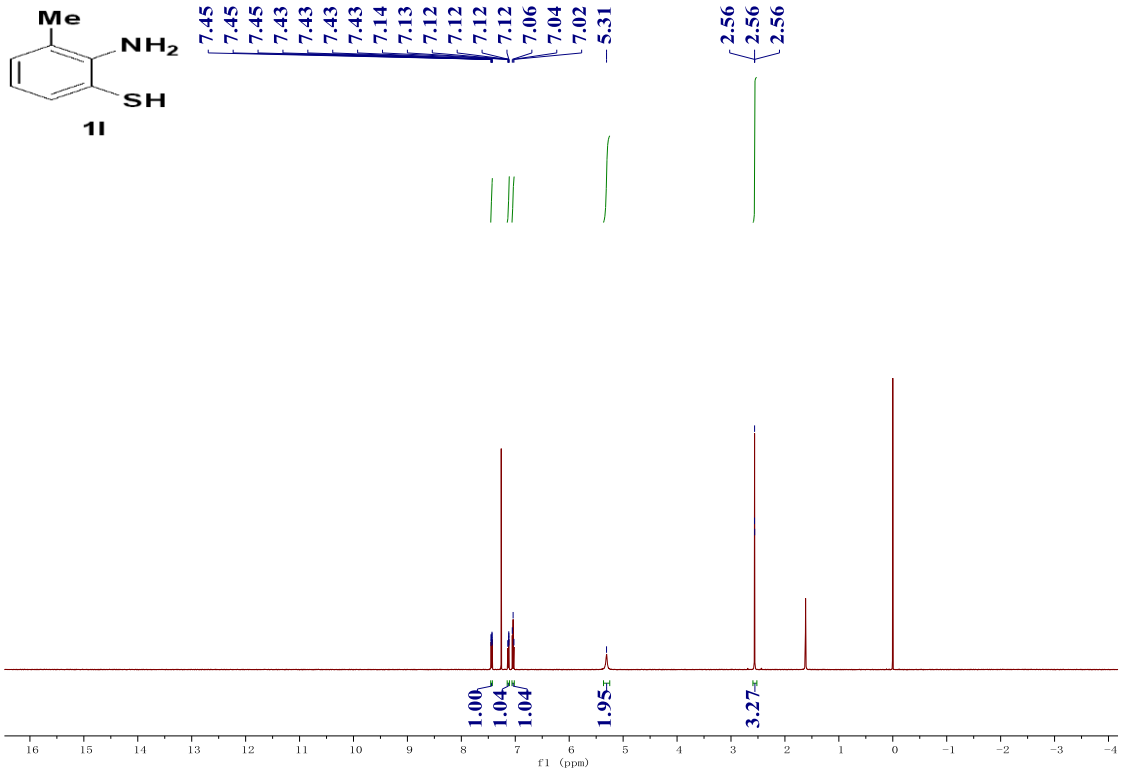

Fig. 21 ^{1}H NMR of **1l** in $CDCl_3$

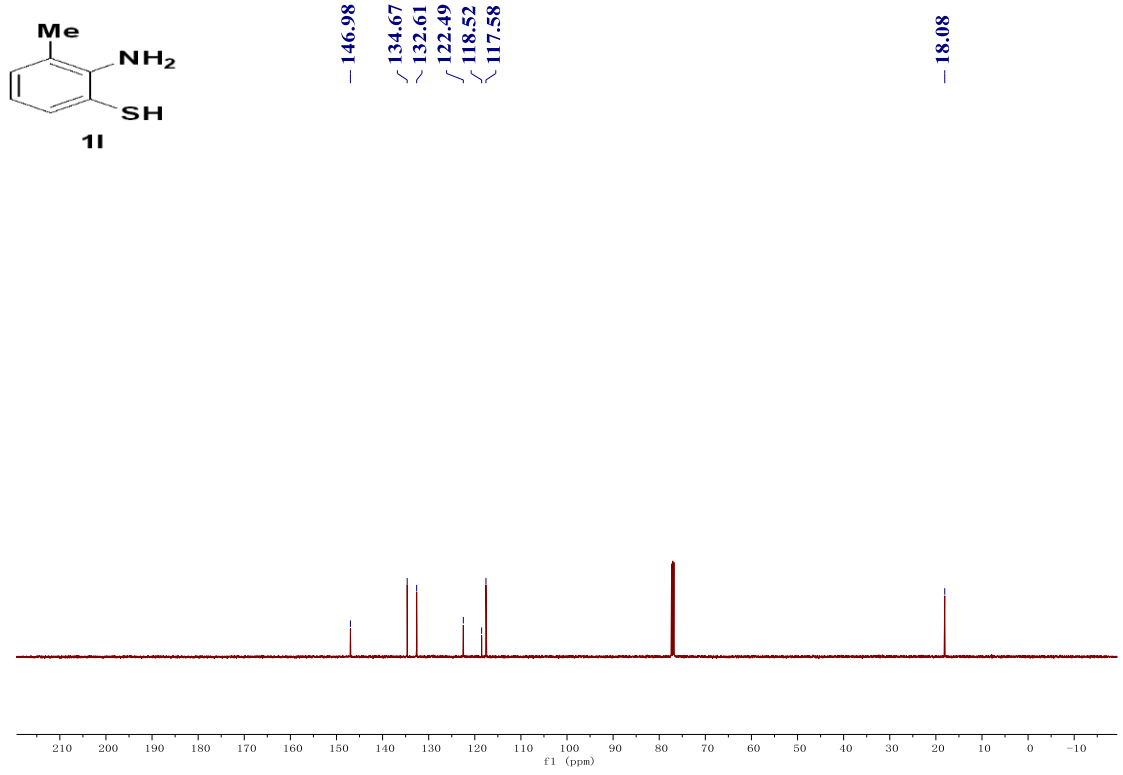

Fig. 22 ^{13}C NMR of **1l** in $CDCl_3$

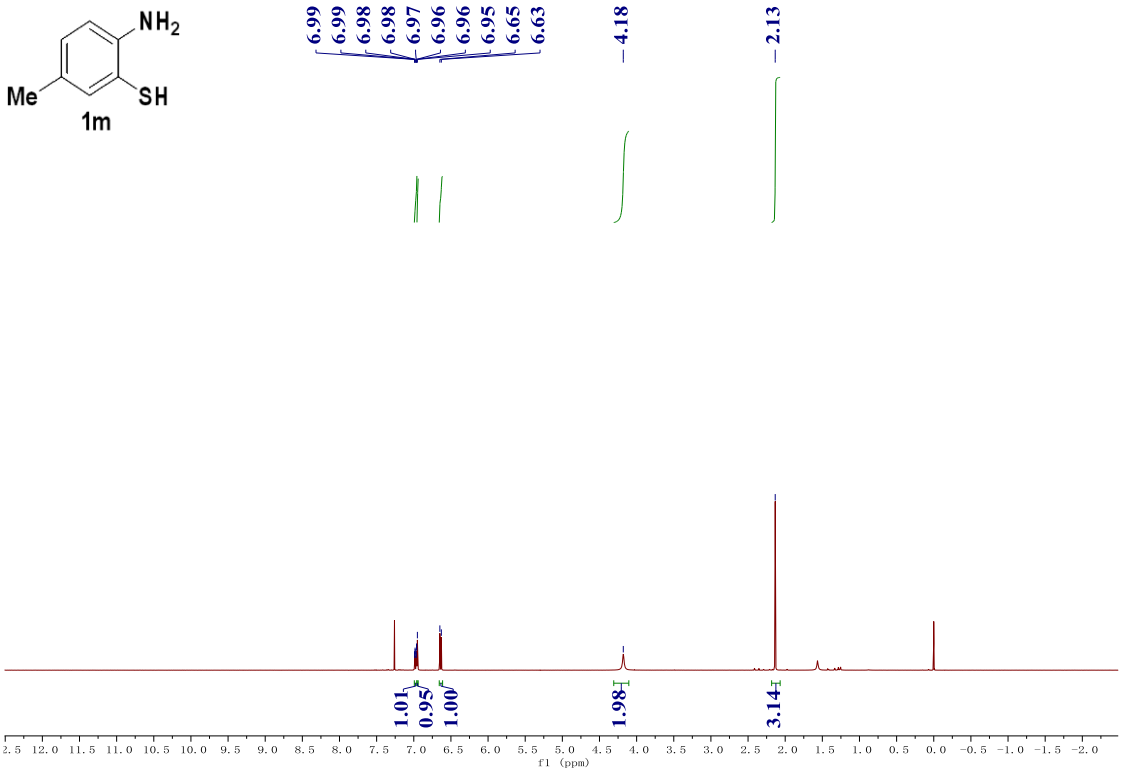

Fig. 23 ^{1}H NMR of **1m** in $CDCl_3$

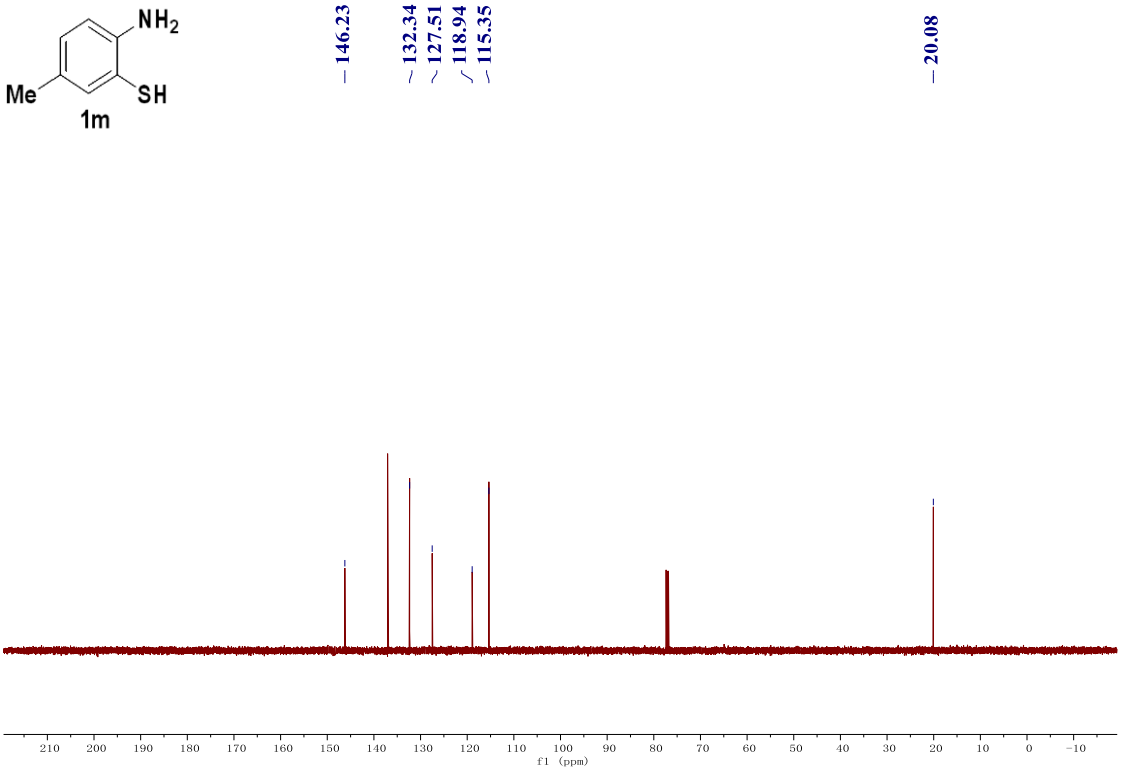

Fig. 24 ^{13}C NMR of **1m** in $CDCl_3$

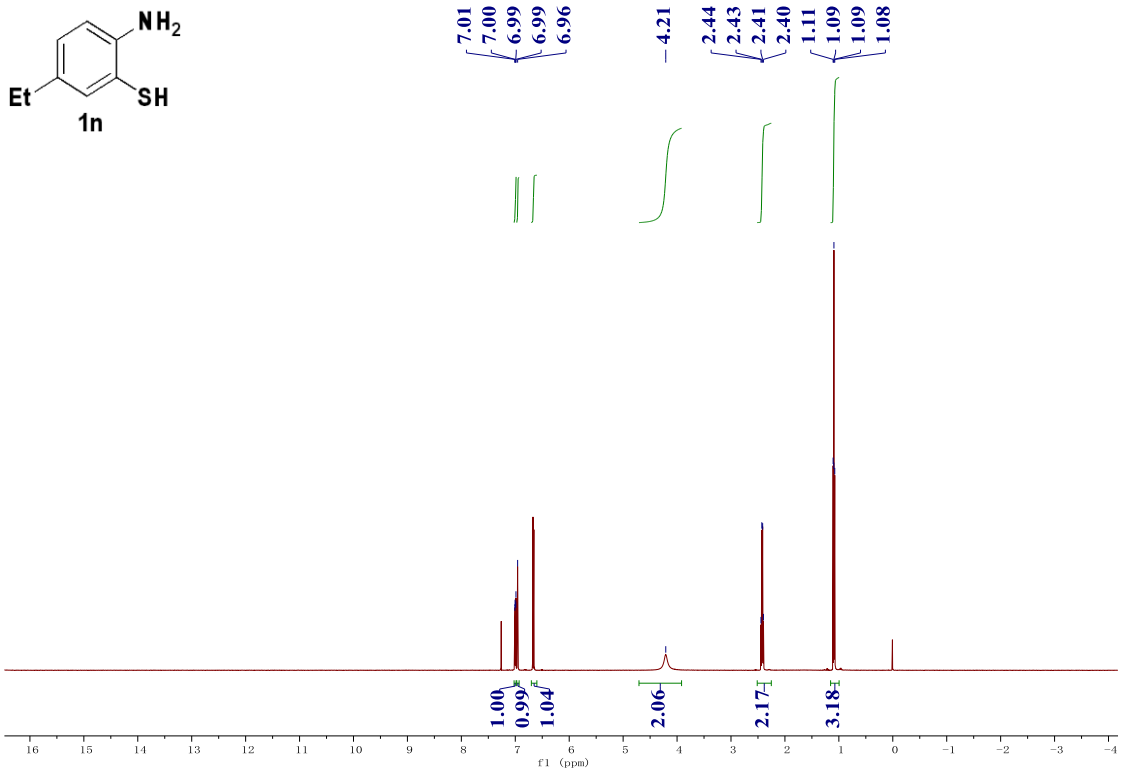

Fig. 25 ^{1}H NMR of **1n** in $CDCl_3$

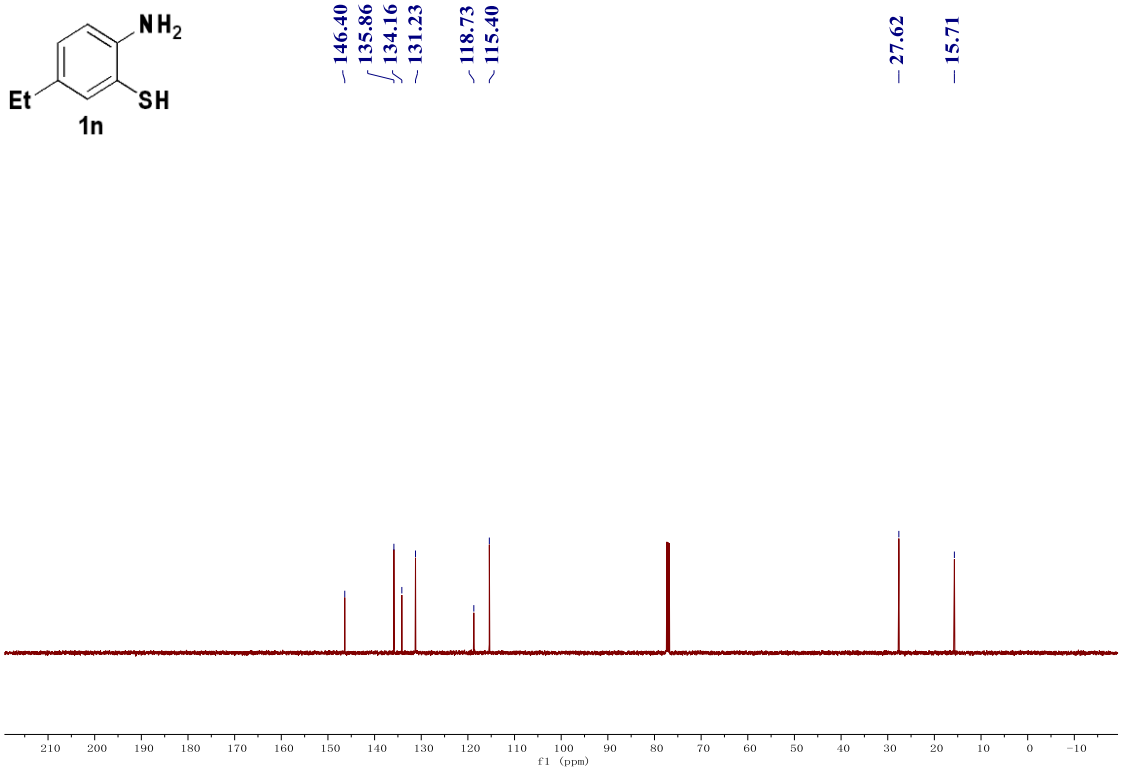

Fig. 26 ^{13}C NMR of **1n** in $CDCl_3$

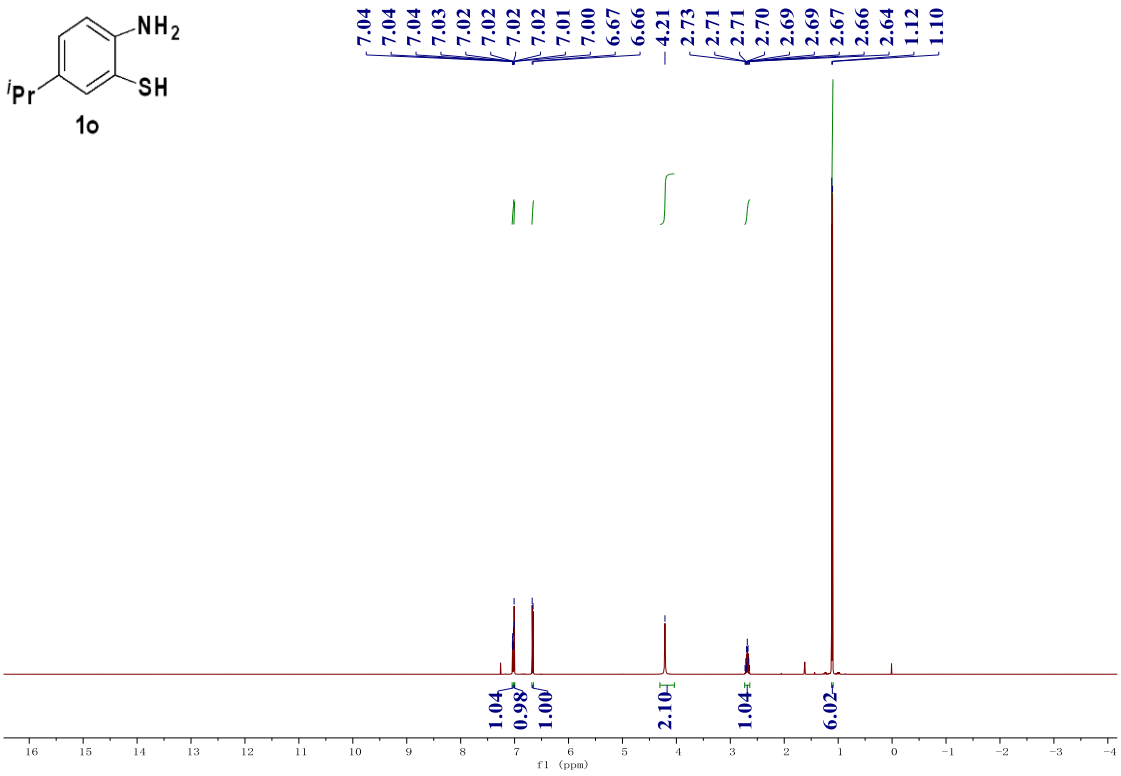

Fig. 27 ^{1}H NMR of **1o** in $CDCl_3$

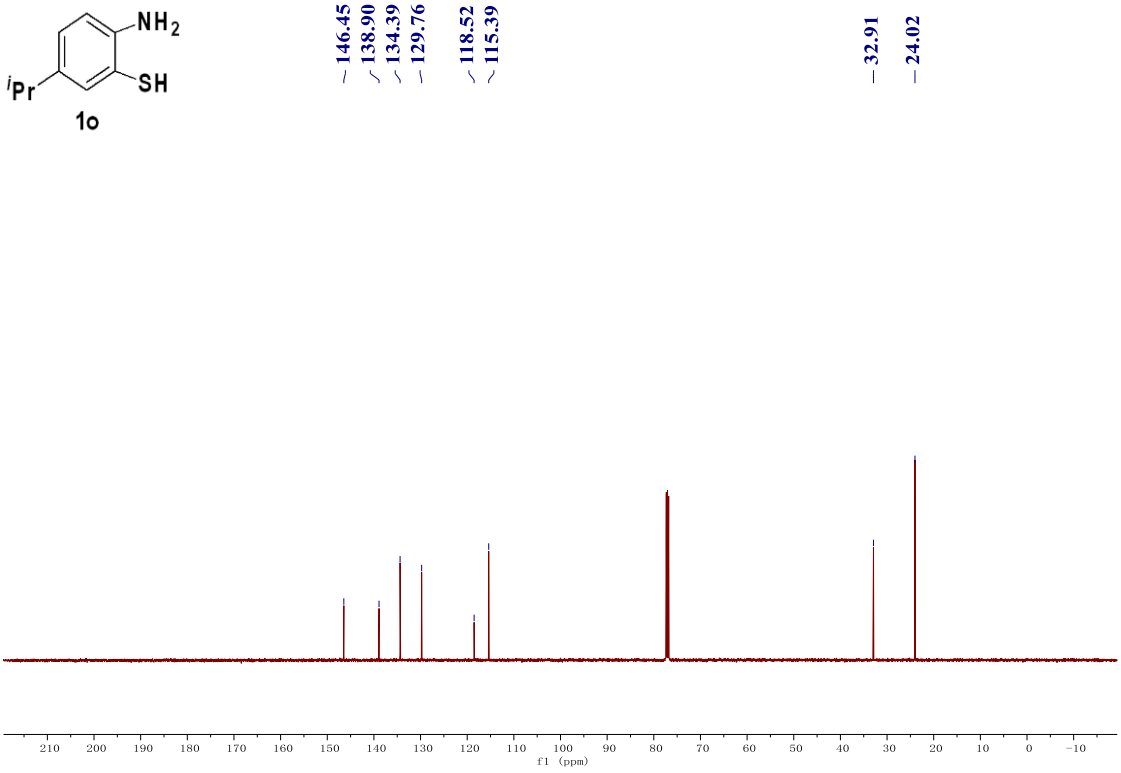

Fig. 28 ^{13}C NMR of **1o** in $CDCl_3$

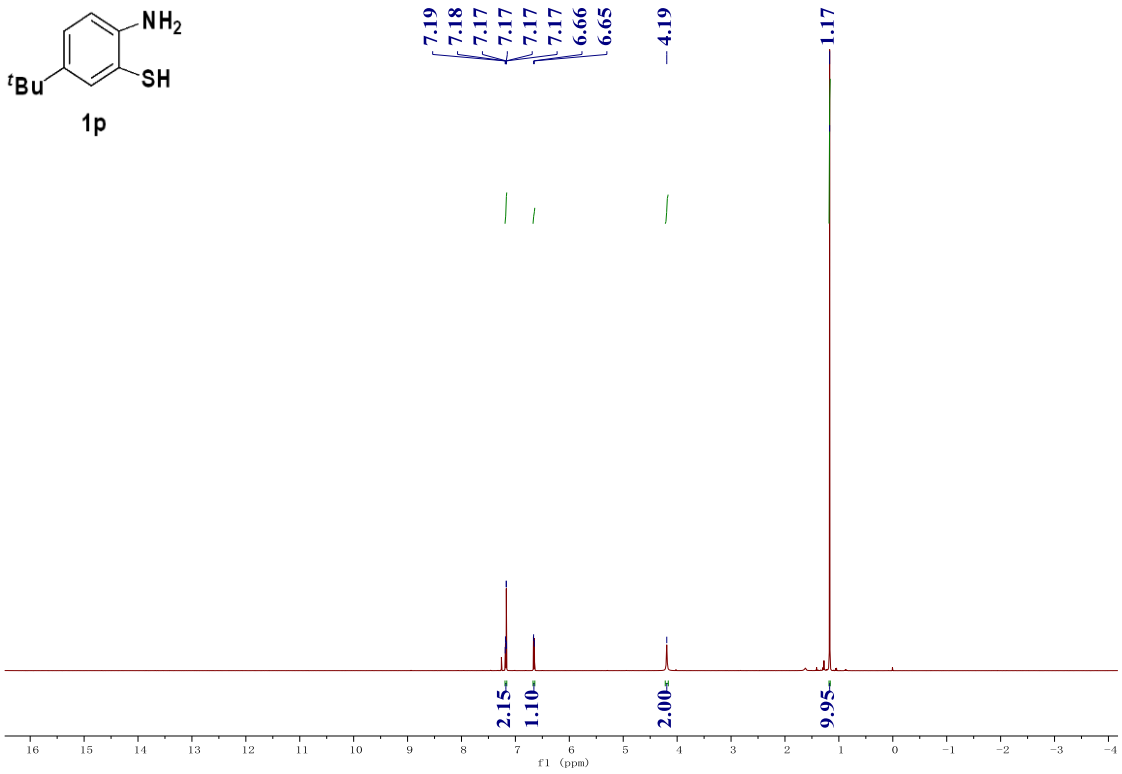

Fig. 29 ^{1}H NMR of **1p** in $CDCl_3$

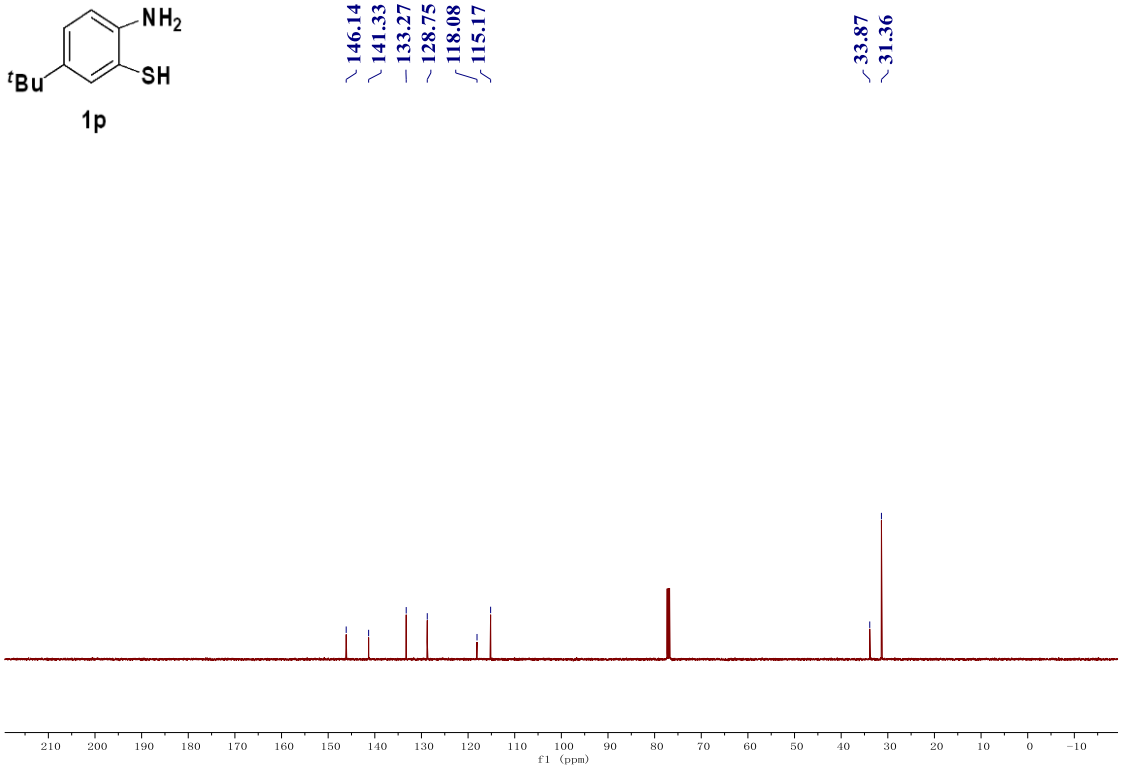

Fig. 30 ^{13}C NMR of **1p** in $CDCl_3$

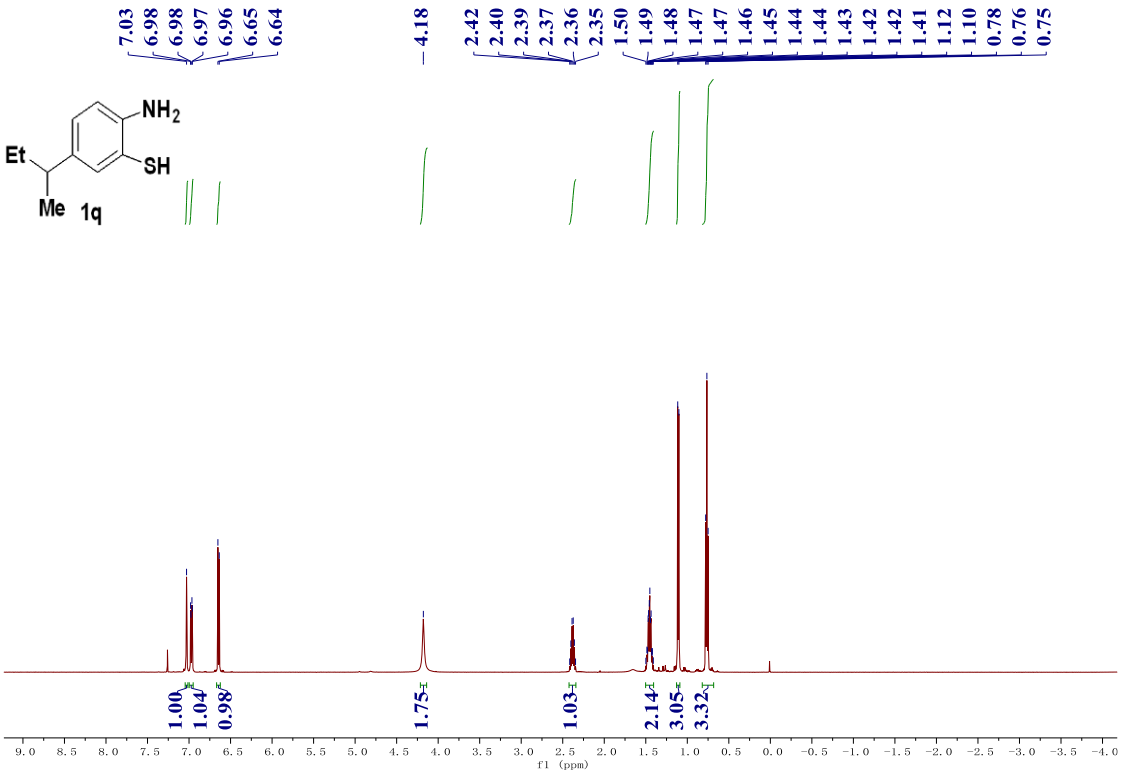

Fig. 31 ^{1}H NMR of **1q** in $CDCl_3$

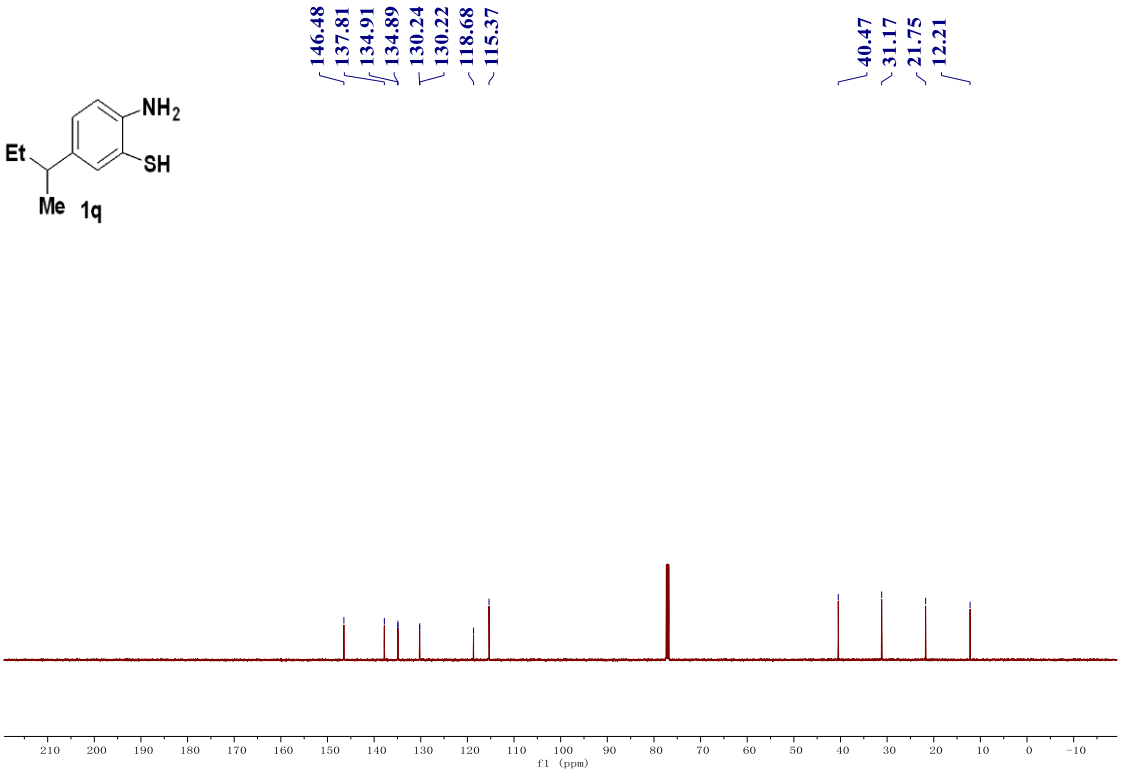

Fig. 32 ^{13}C NMR of **1q** in $CDCl_3$

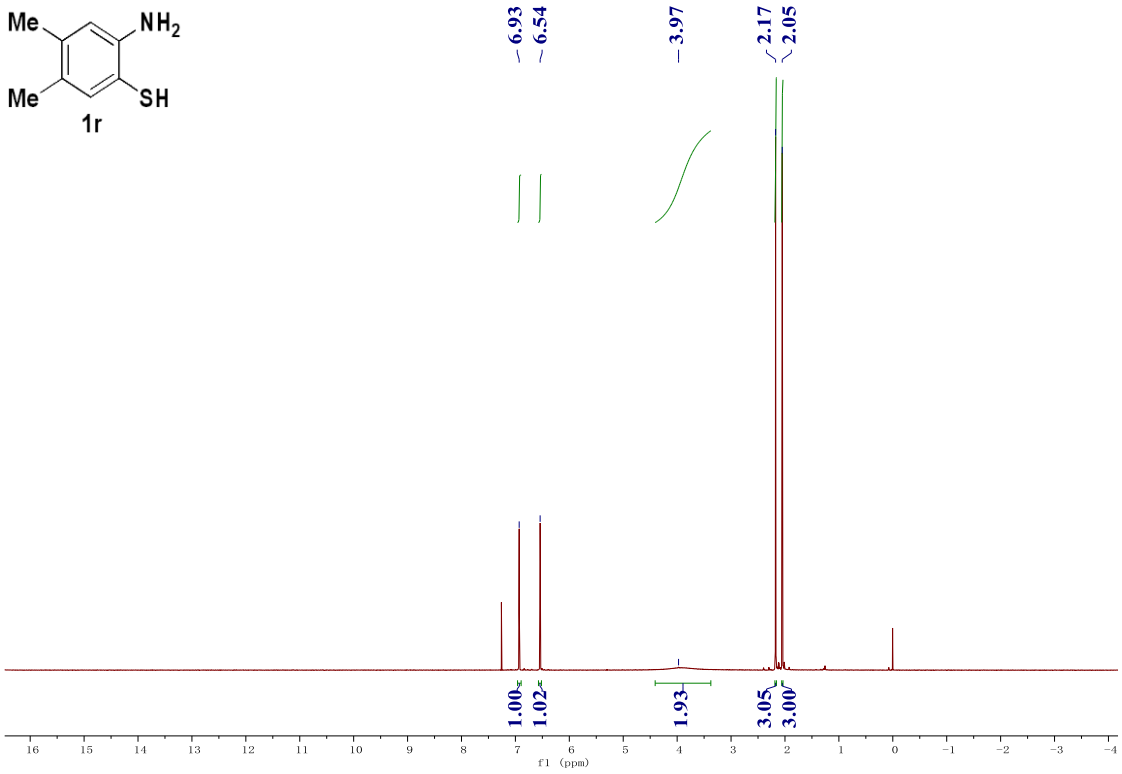

Fig. 33 ^{1}H NMR of **1r** in $CDCl_3$

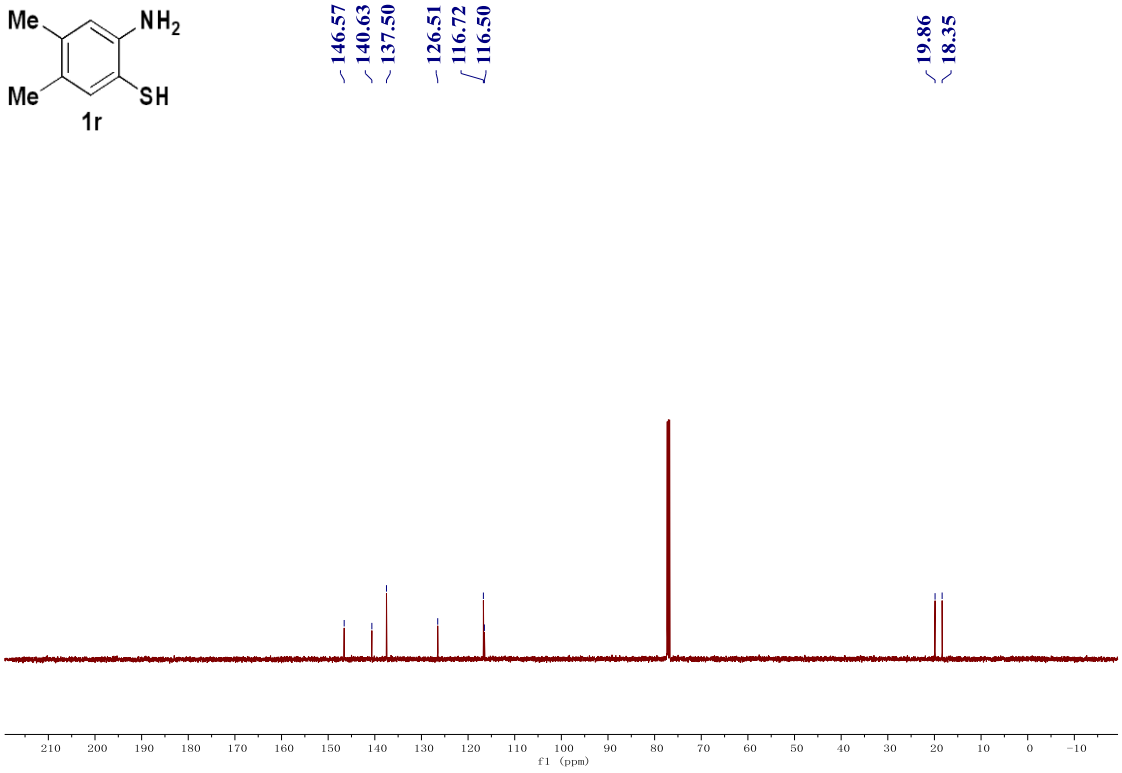

Fig. 34 ^{13}C NMR of **1r** in $CDCl_3$

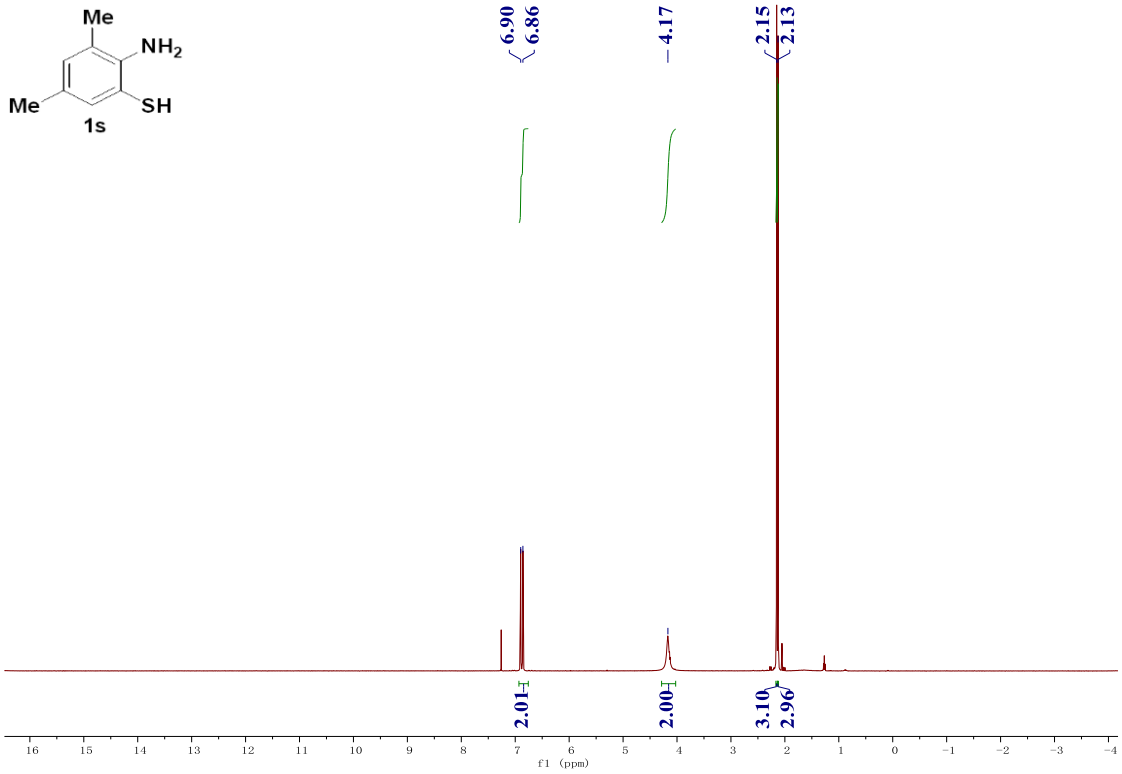

Fig. 35 ^{1}H NMR of **1s** in $CDCl_3$

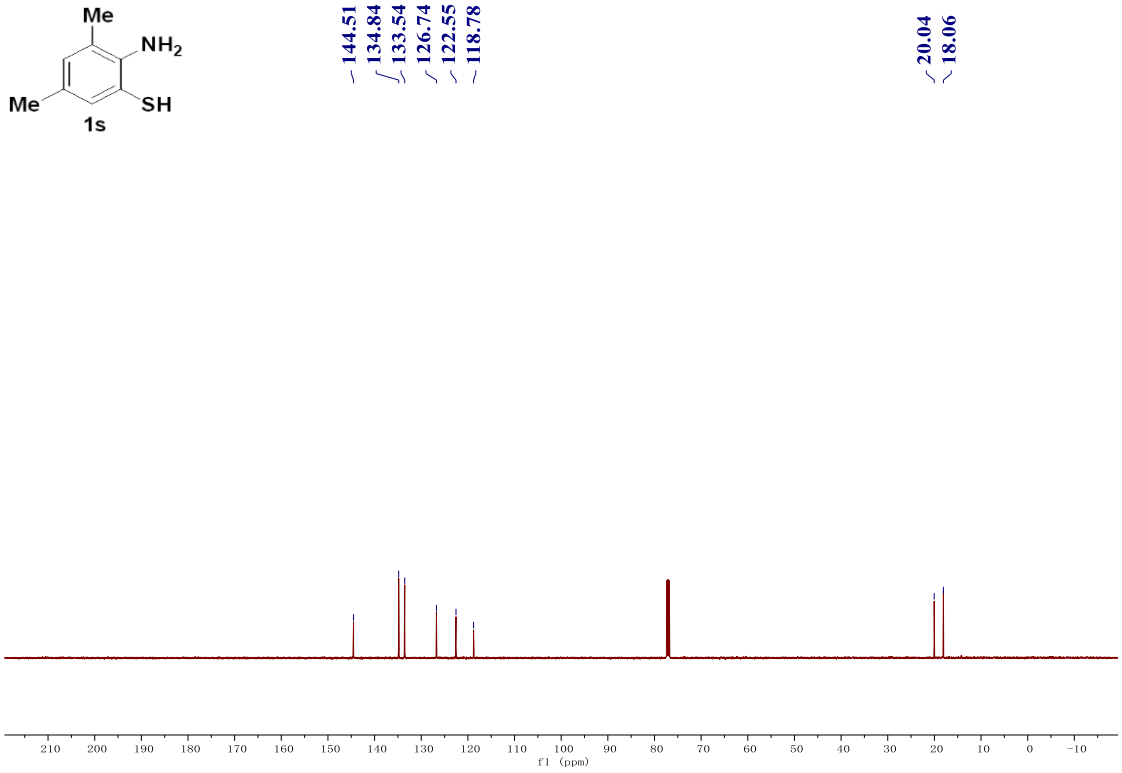

Fig. 36 ^{13}C NMR of **1s** in $CDCl_3$

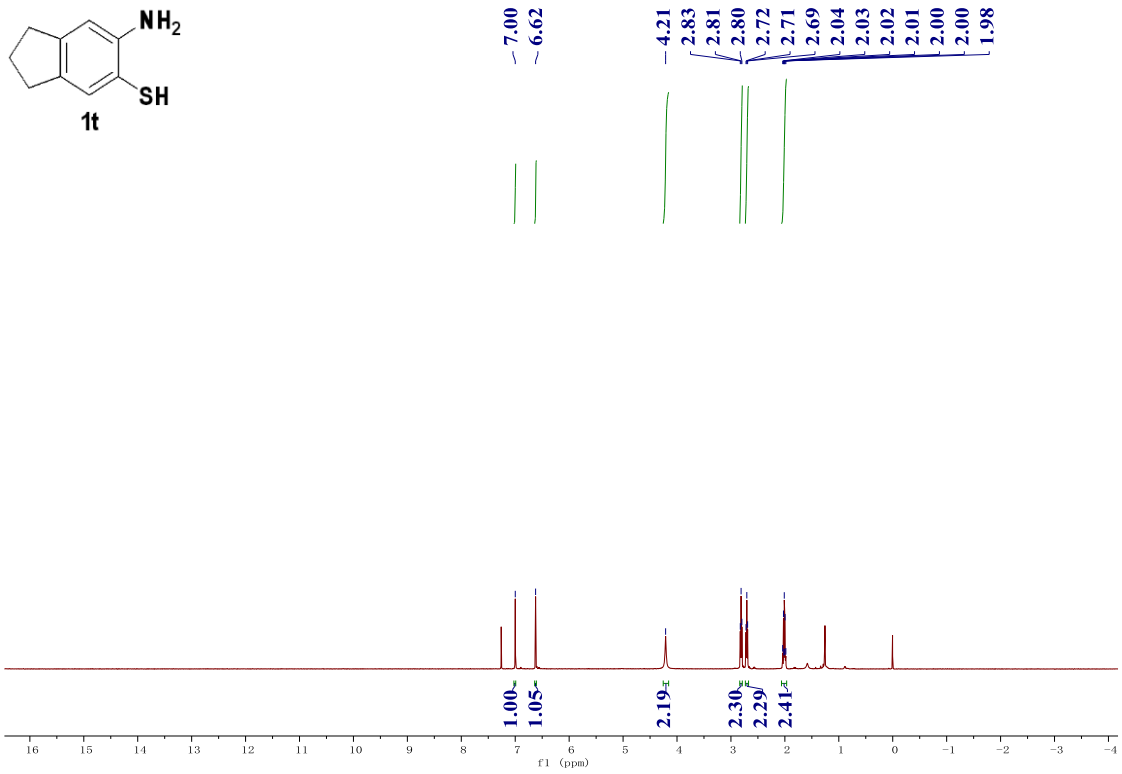

Fig. 37 ^{1}H NMR of **1t** in $CDCl_3$

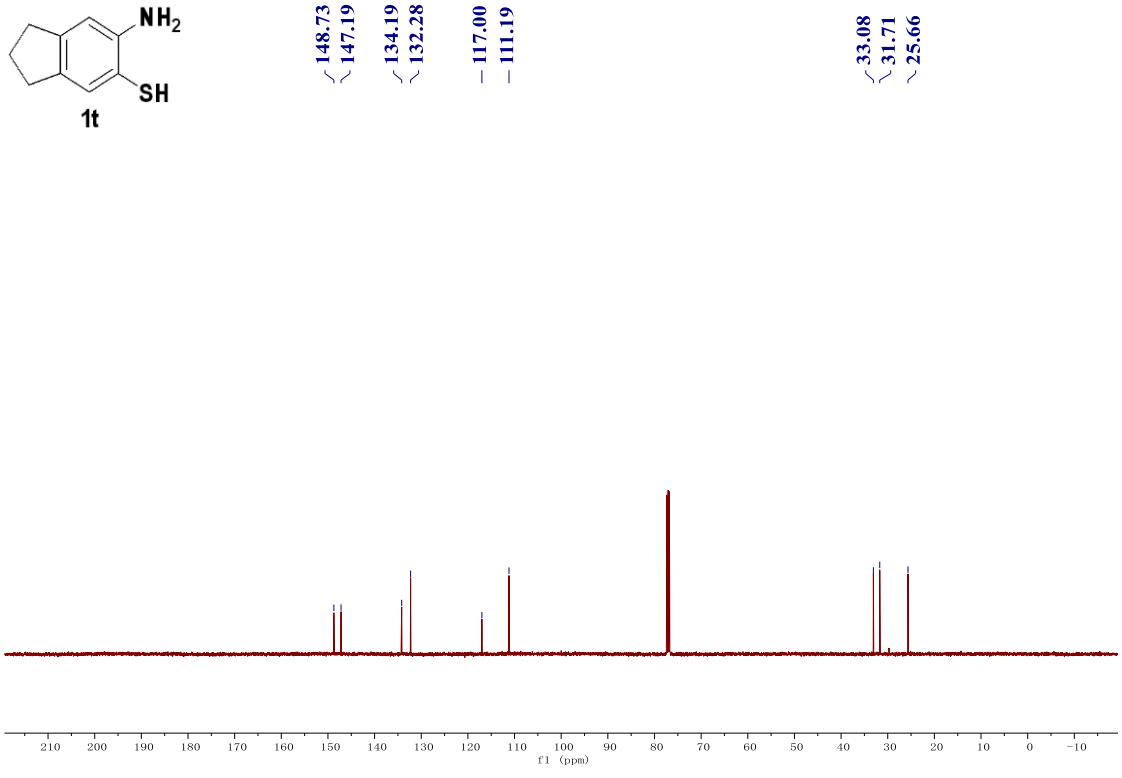

Fig. 38 ^{13}C NMR of **1t** in $CDCl_3$

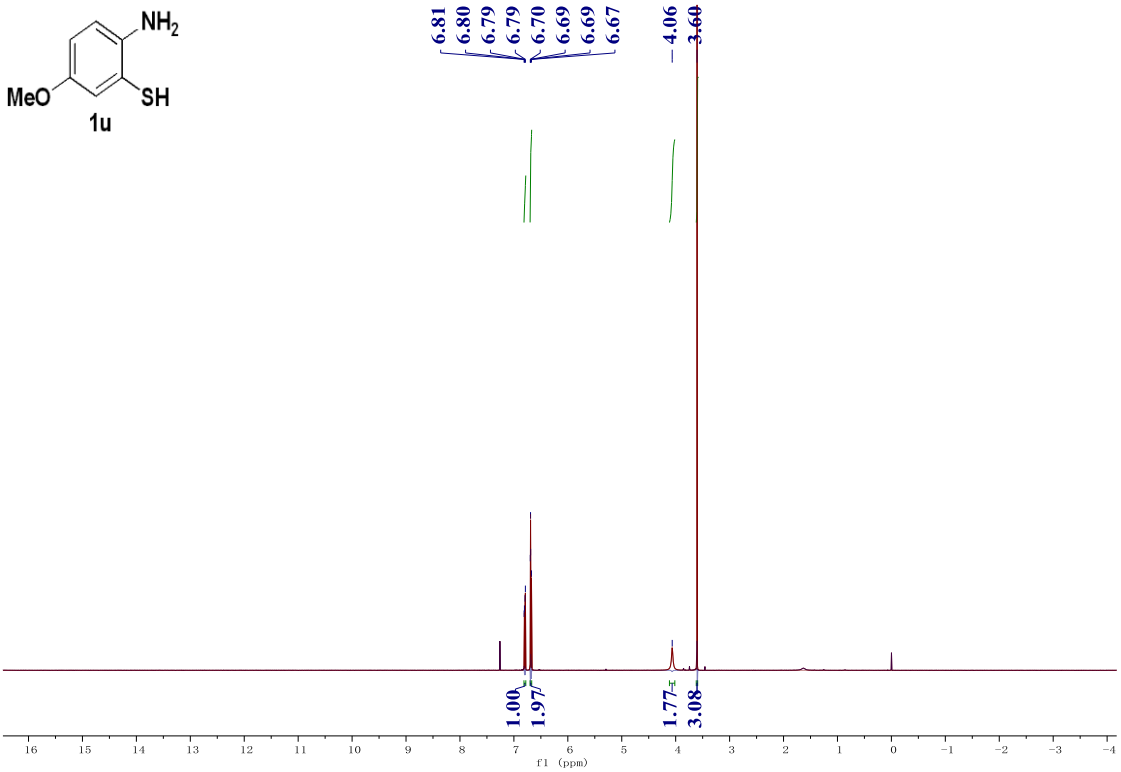

Fig. 39 ^{1}H NMR of **1u** in $CDCl_3$

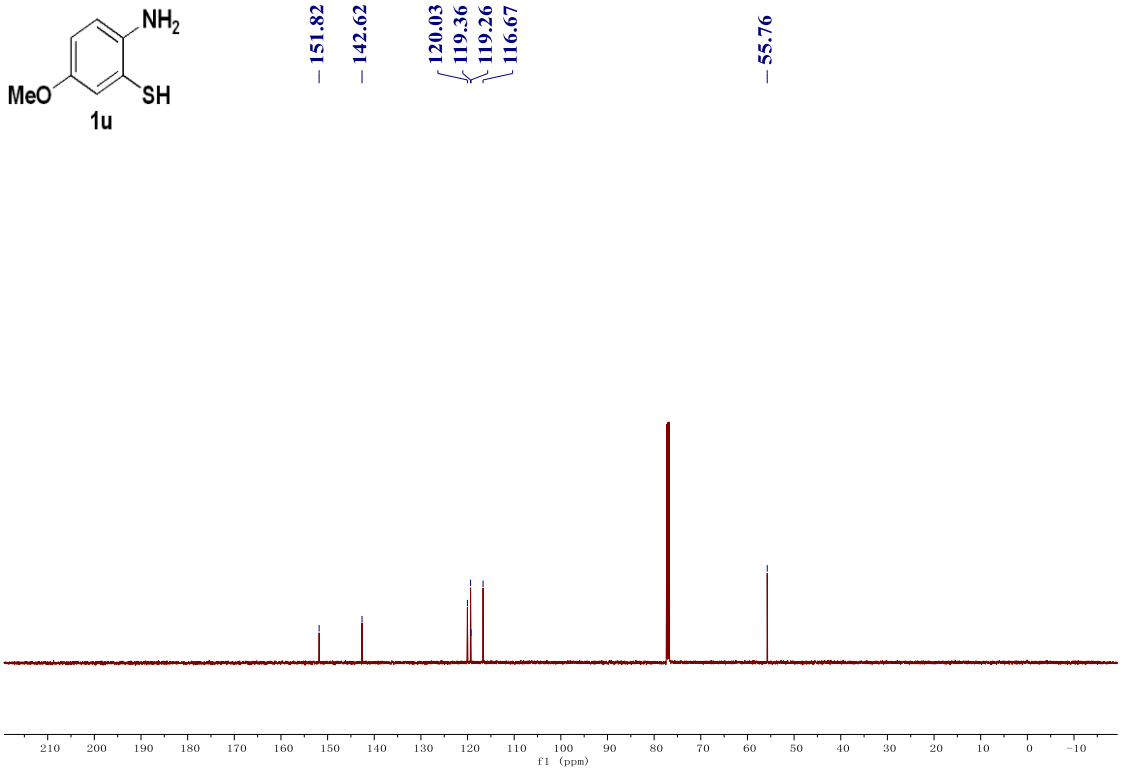

Fig. 40 ^{13}C NMR of **1u** in $CDCl_3$

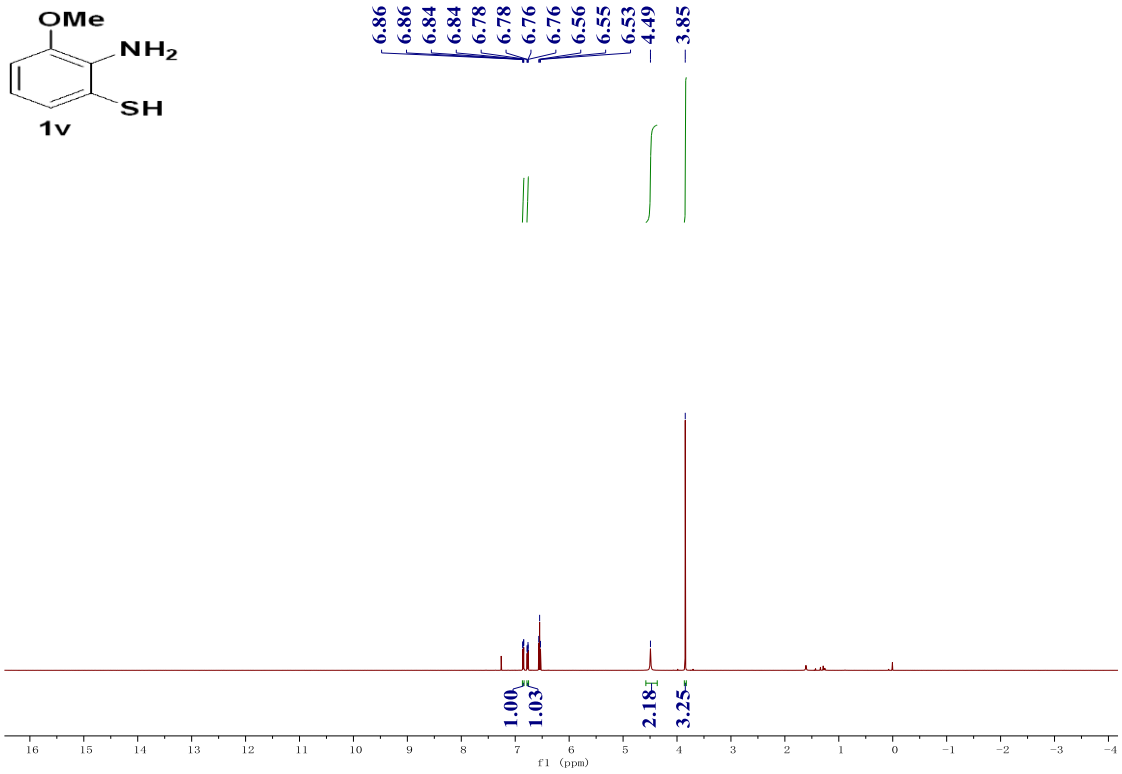

Fig. 41 ^{1}H NMR of **1v** in $CDCl_3$

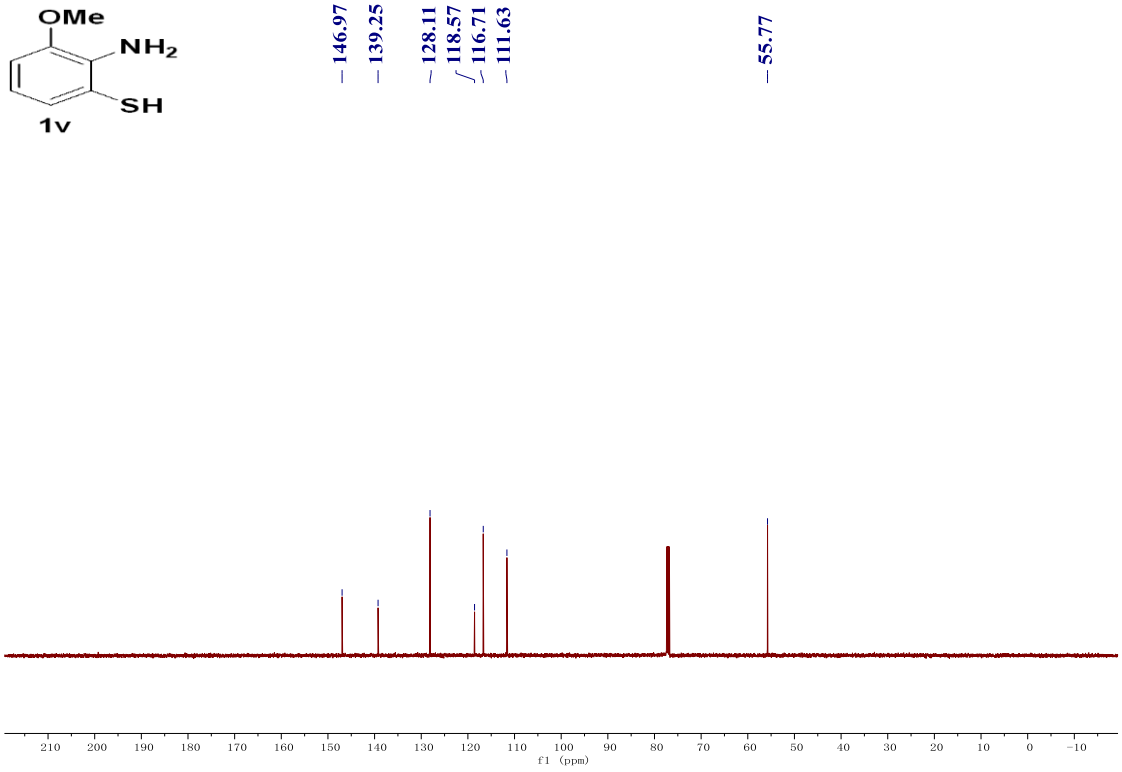

Fig. 42 ^{13}C NMR of **1v** in $CDCl_3$

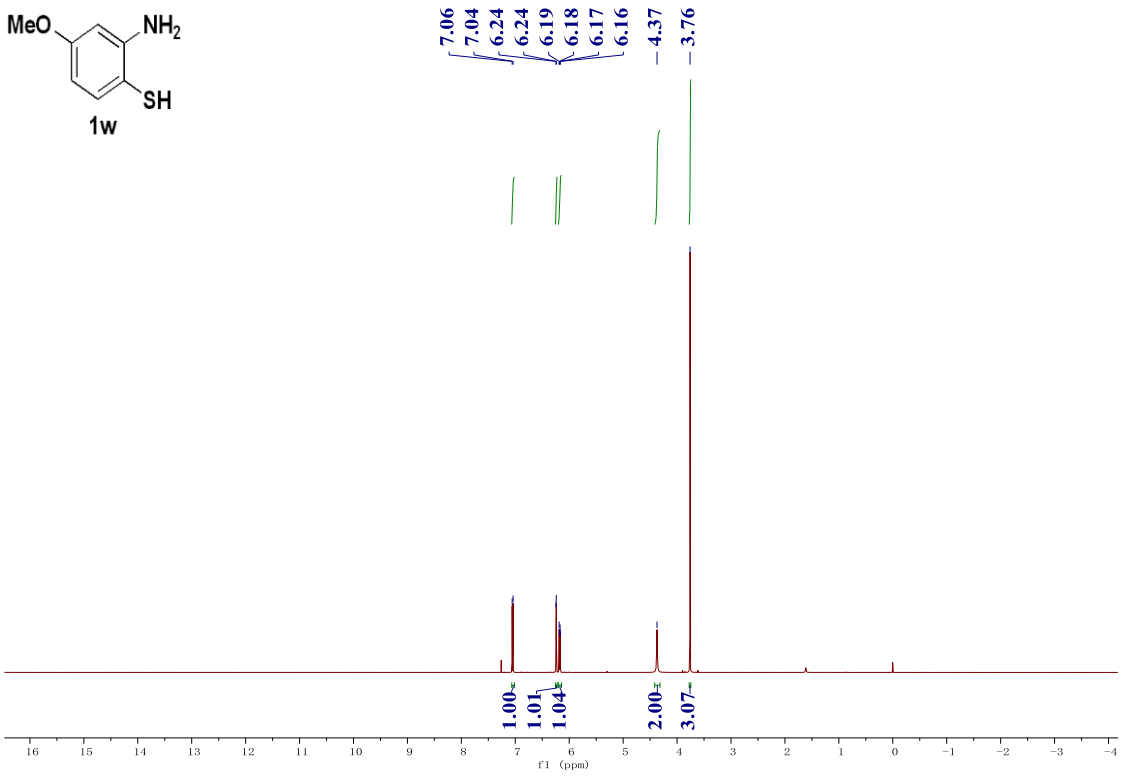

Fig. 43 ^{1}H NMR of **1w** in $CDCl_3$

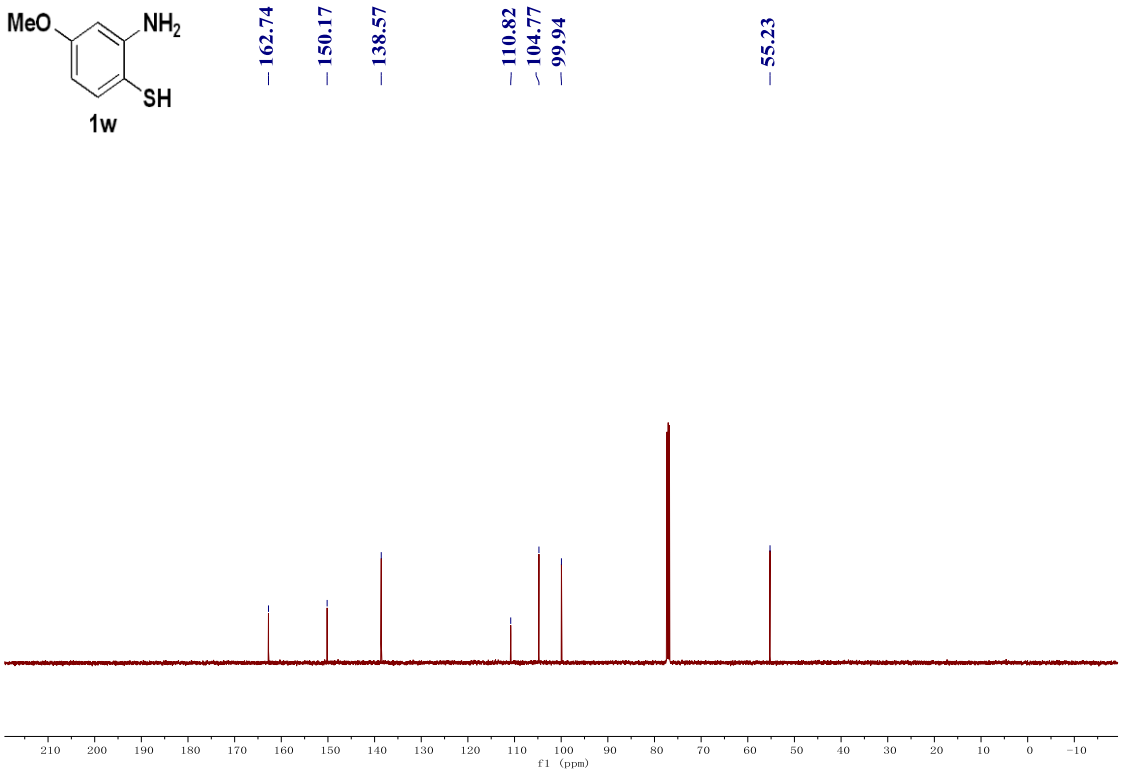

Fig. 44 ^{13}C NMR of **1w** in $CDCl_3$

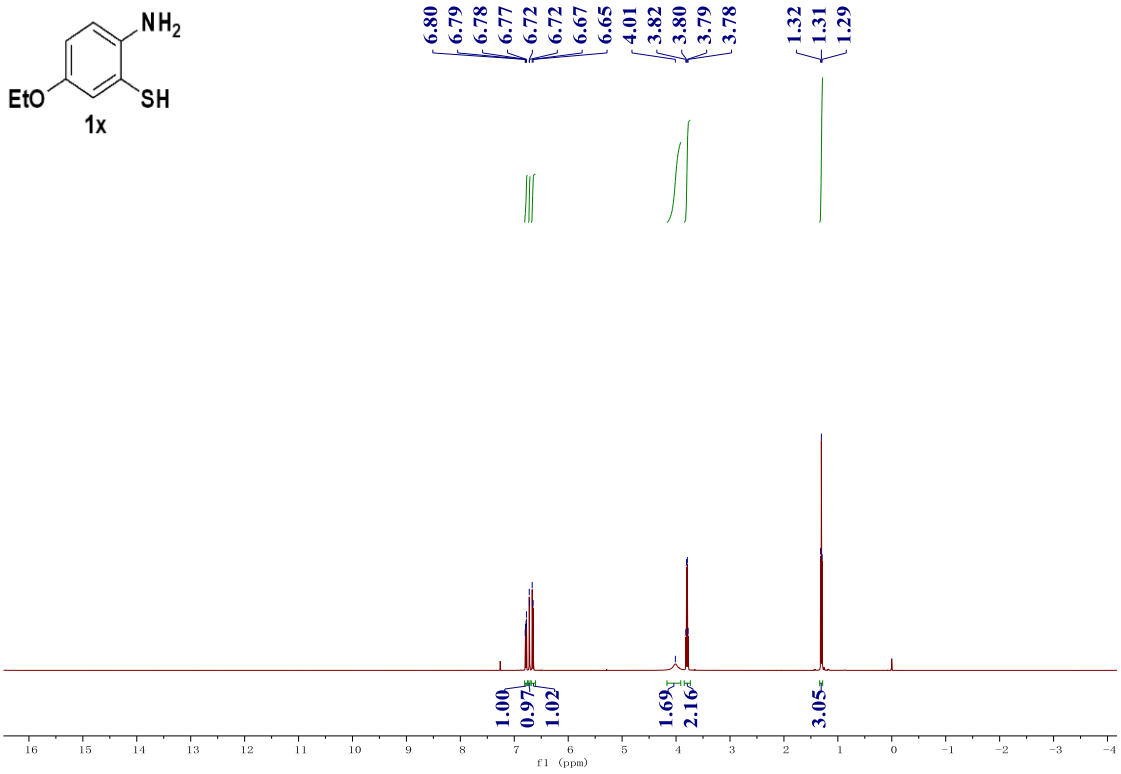

Fig. 45 ^{1}H NMR of **1x** in $CDCl_3$

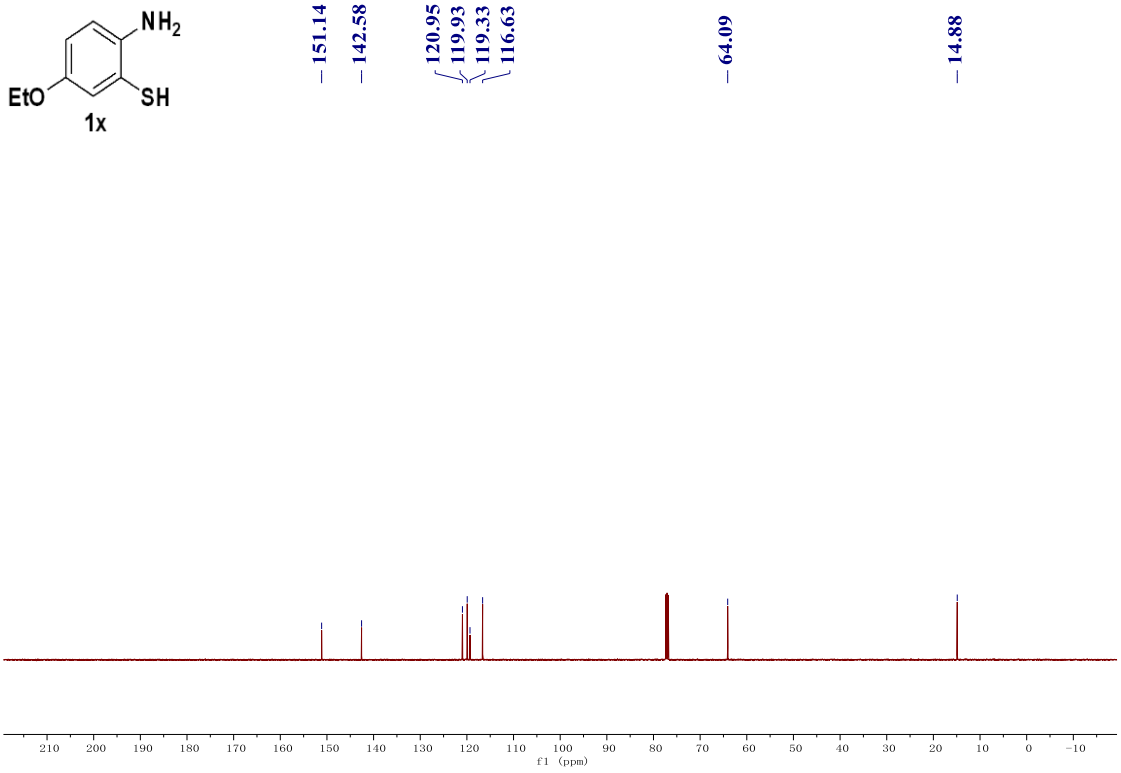

Fig. 46 ^{13}C NMR of **1x** in $CDCl_3$

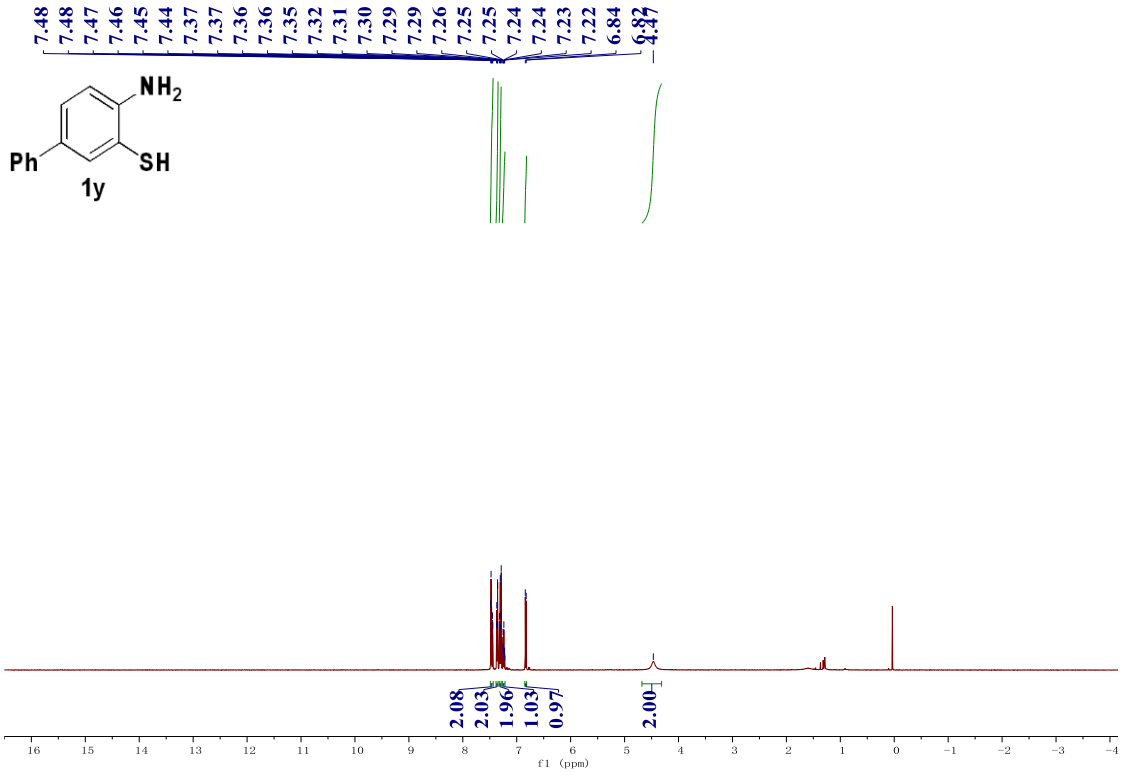

Fig. 47 ^{1}H NMR of **1y** in $CDCl_3$

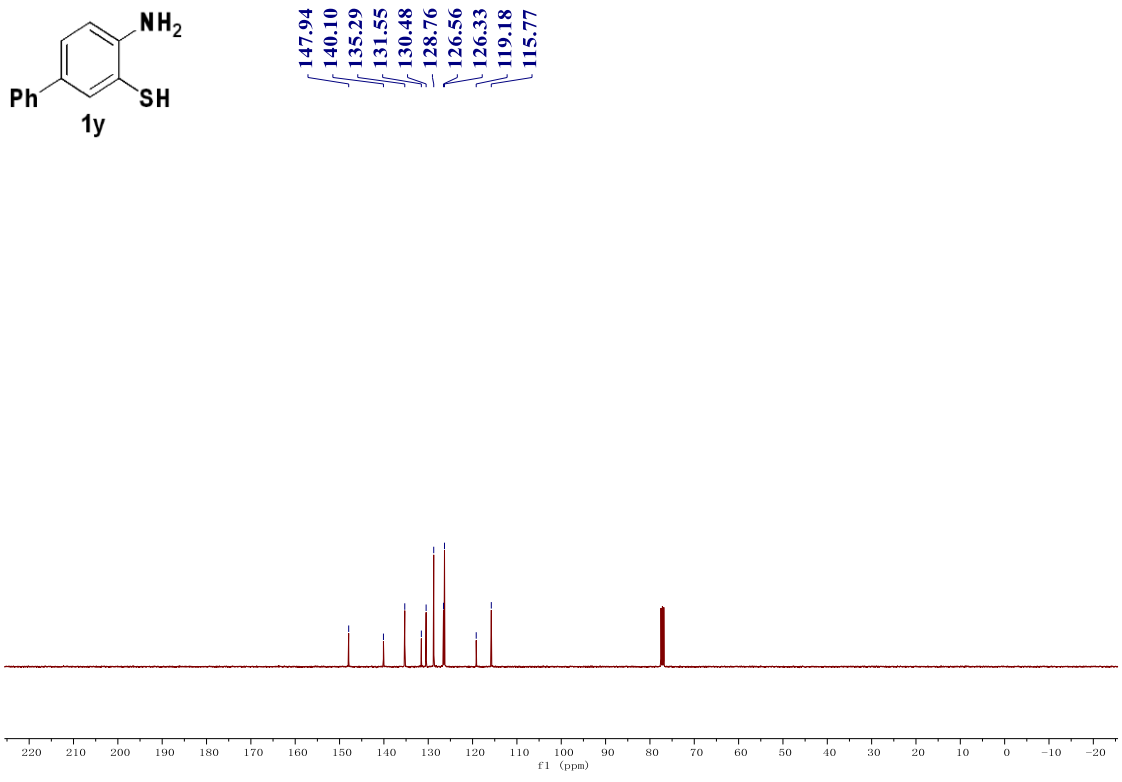

Fig. 48 ^{13}C NMR of **1y** in $CDCl_3$

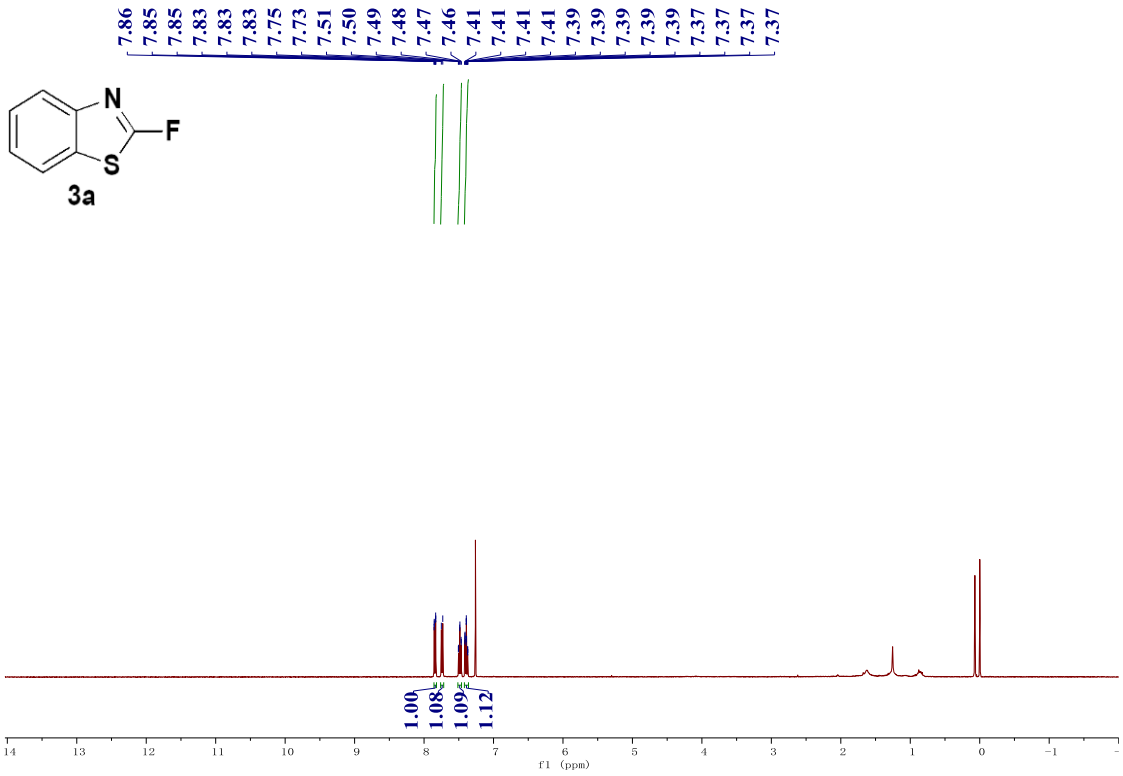

Fig. 49 ^{1}H NMR of **3a** in $CDCl_3$

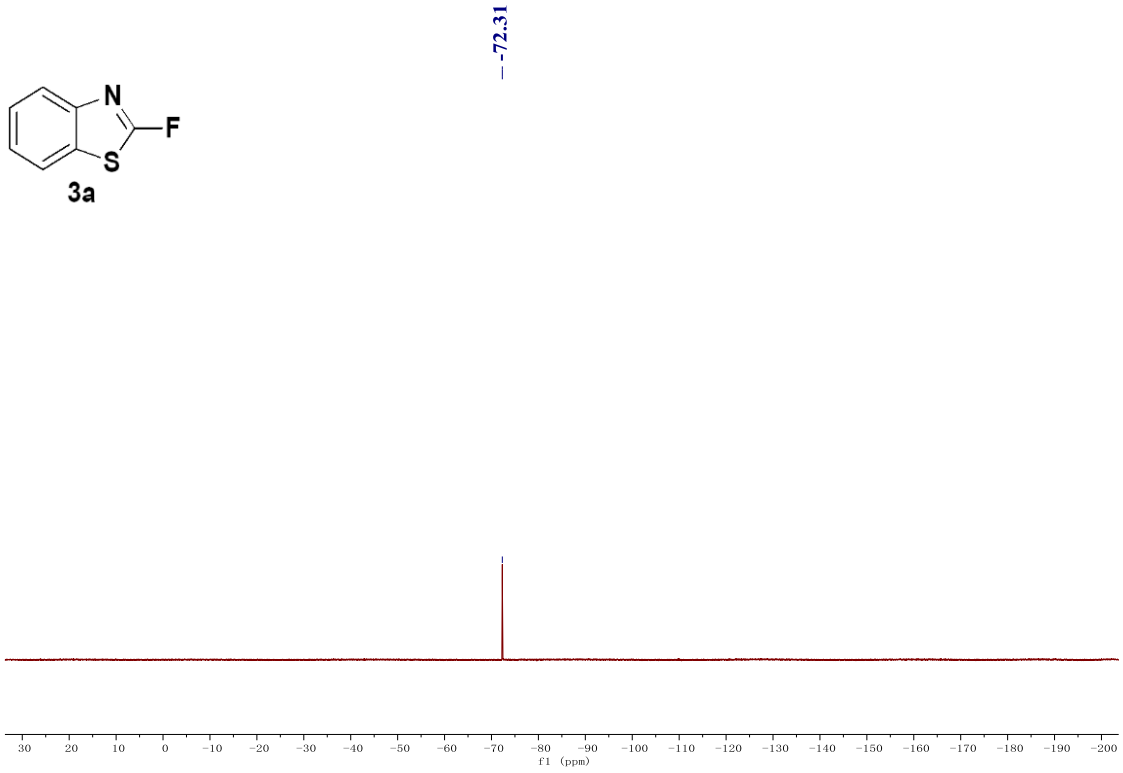

Fig. 50 ^{19}F NMR of **3a** in $CDCl_3$

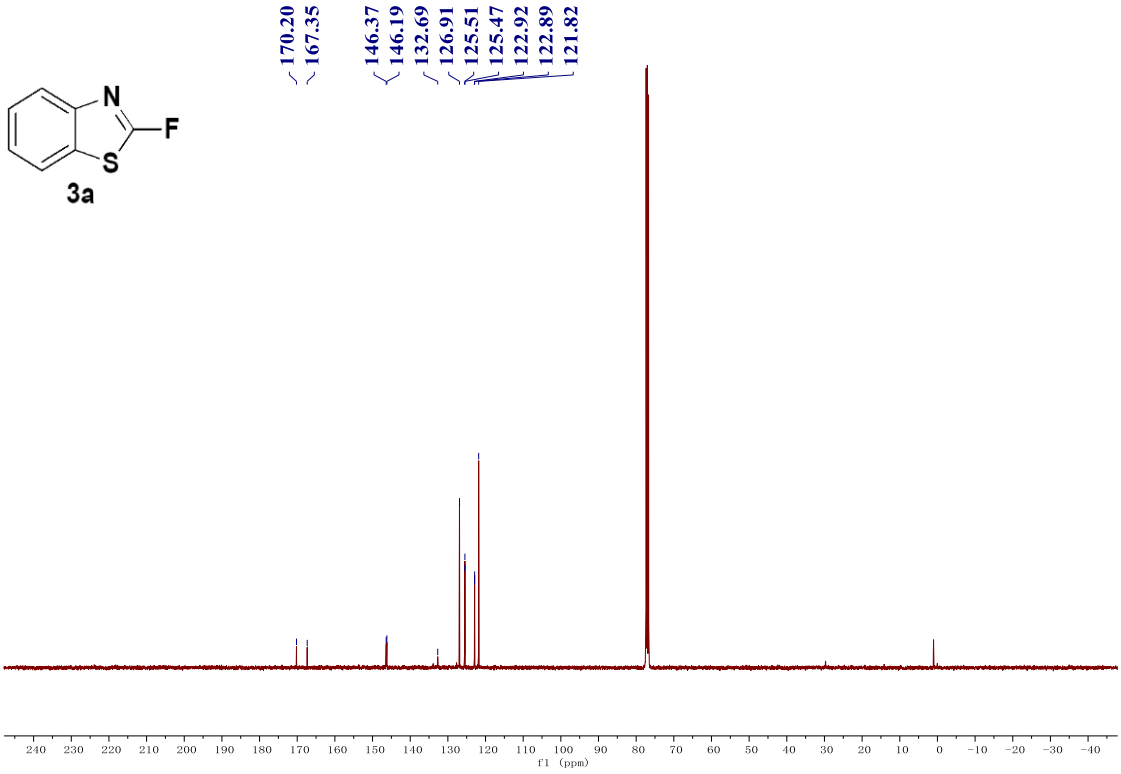

Fig. 51 ^{13}C NMR of **3a** in $CDCl_3$

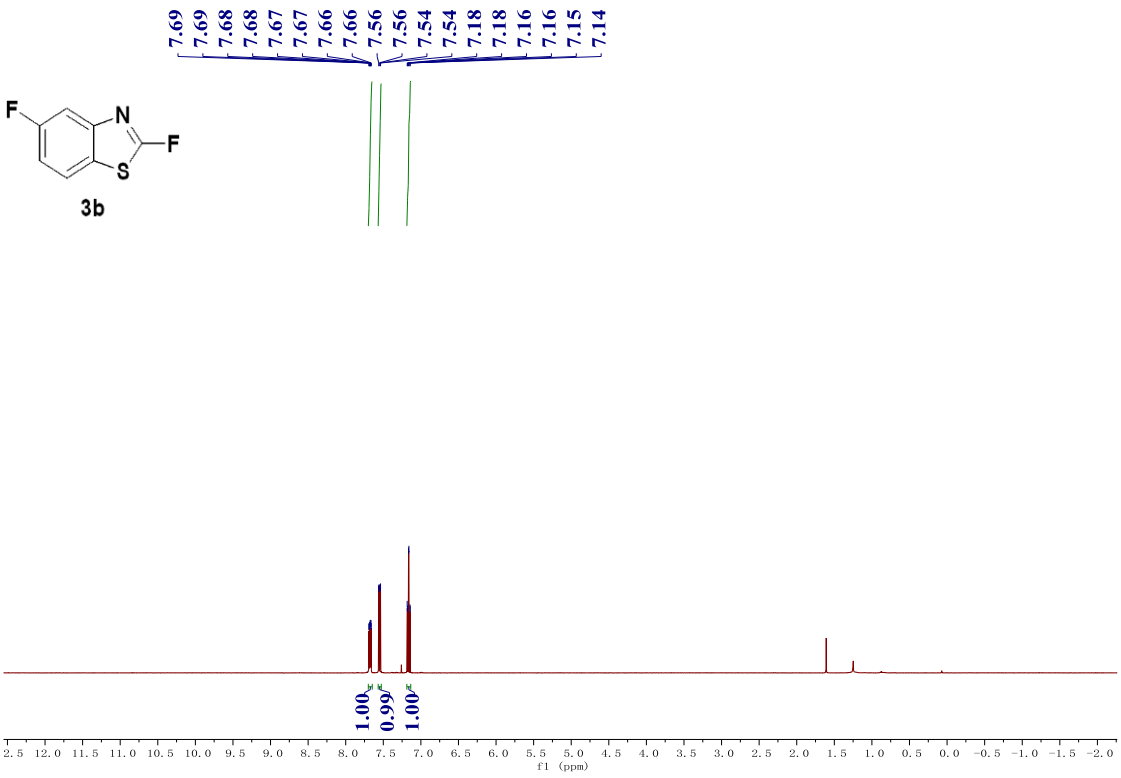

Fig. 52 ^{1}H NMR of **3b** in $CDCl_3$

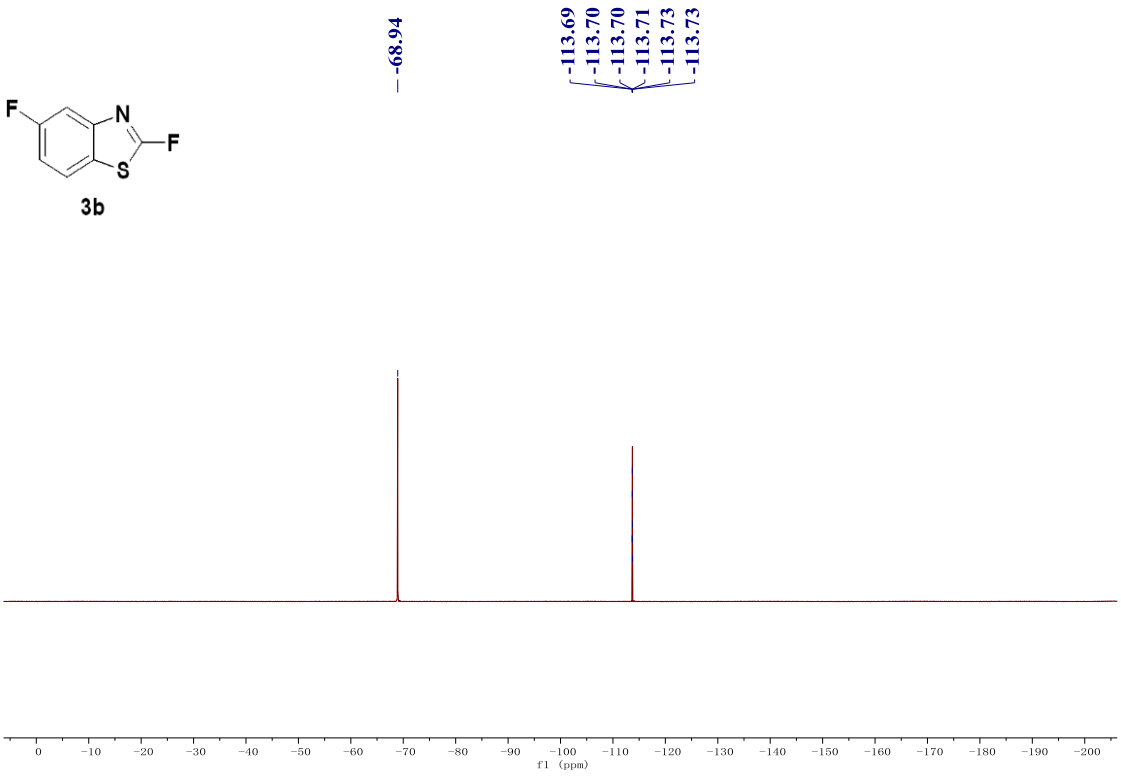

Fig. 53 ^{19}F NMR of **3b** in $CDCl_3$

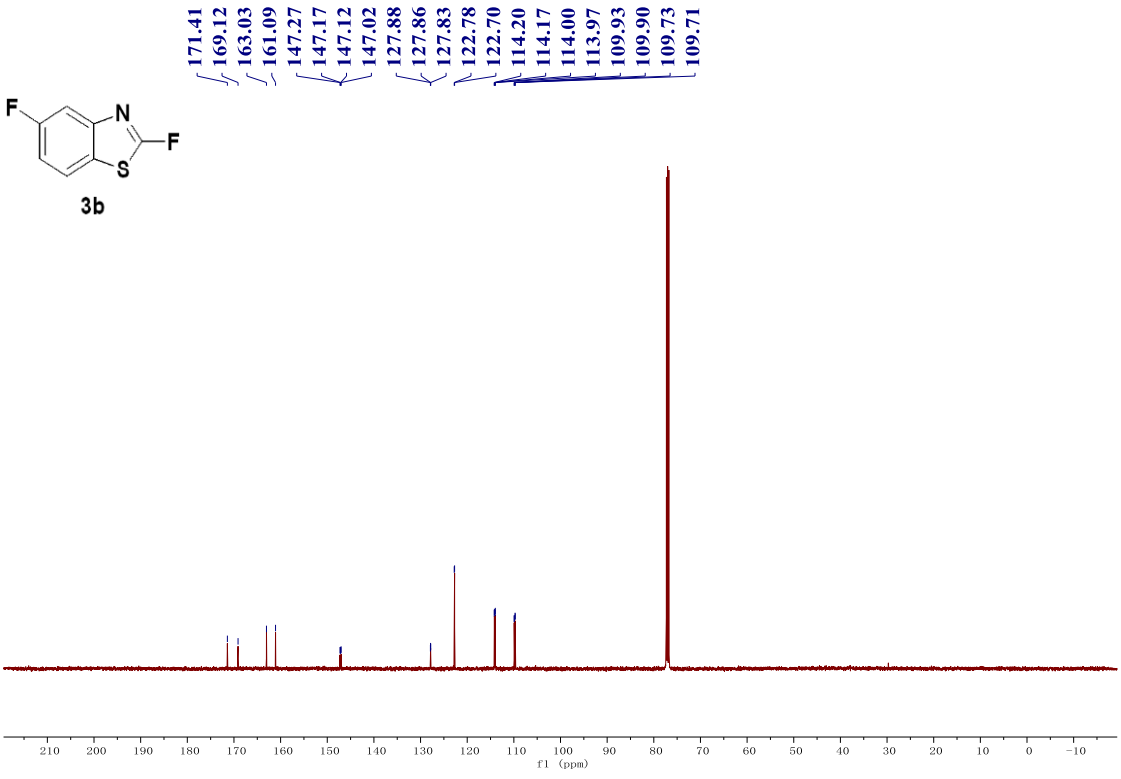

Fig. 54 ^{13}C NMR of **3b** in $CDCl_3$

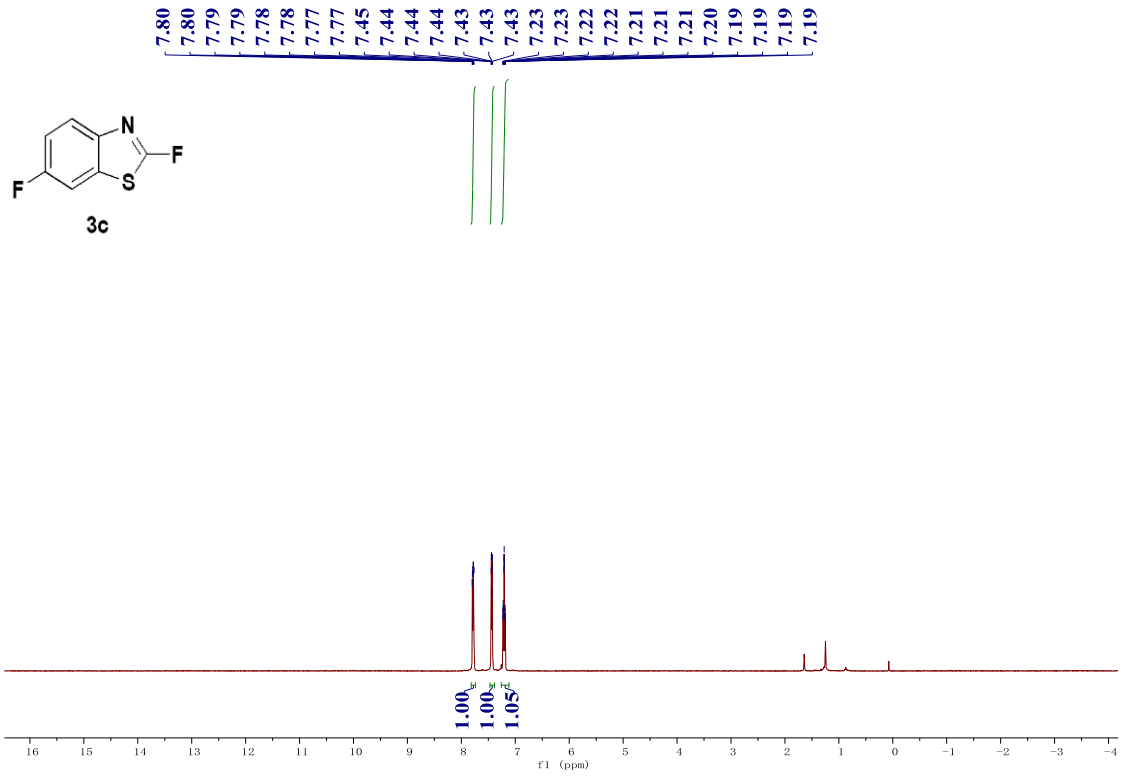

Fig. 55 ^{1}H NMR of **3c** in $CDCl_3$

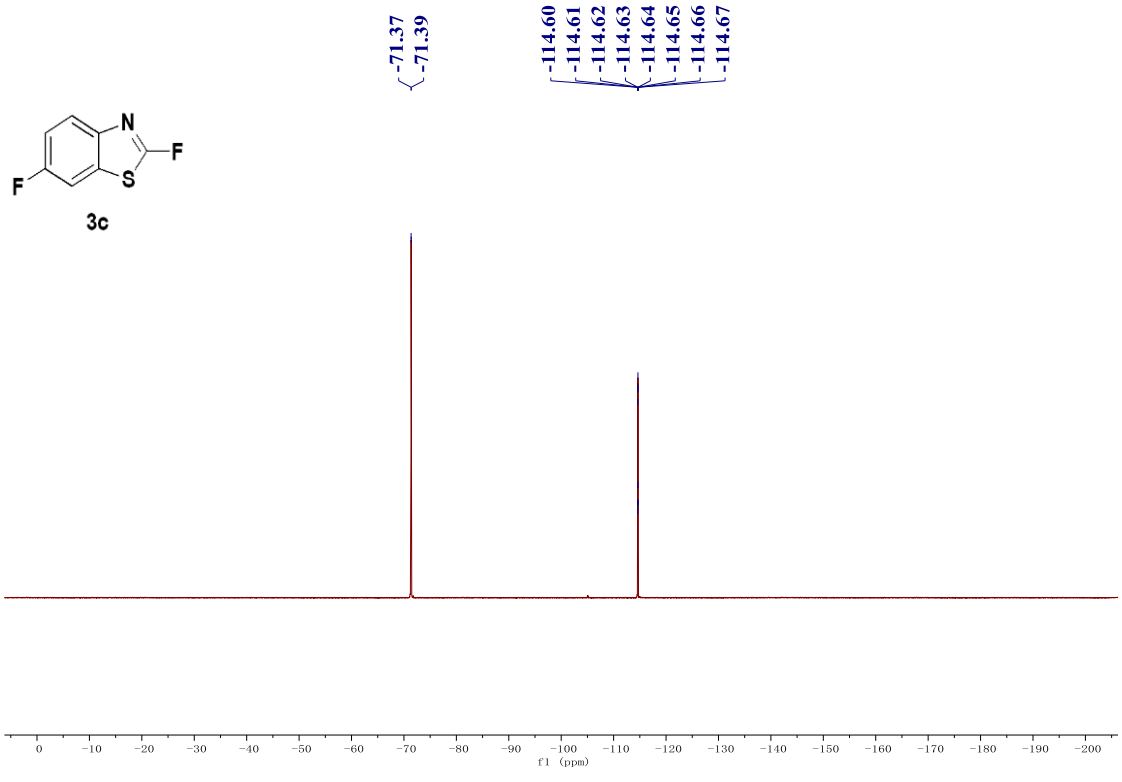

Fig. 56 ^{19}F NMR of **3c** in $CDCl_3$

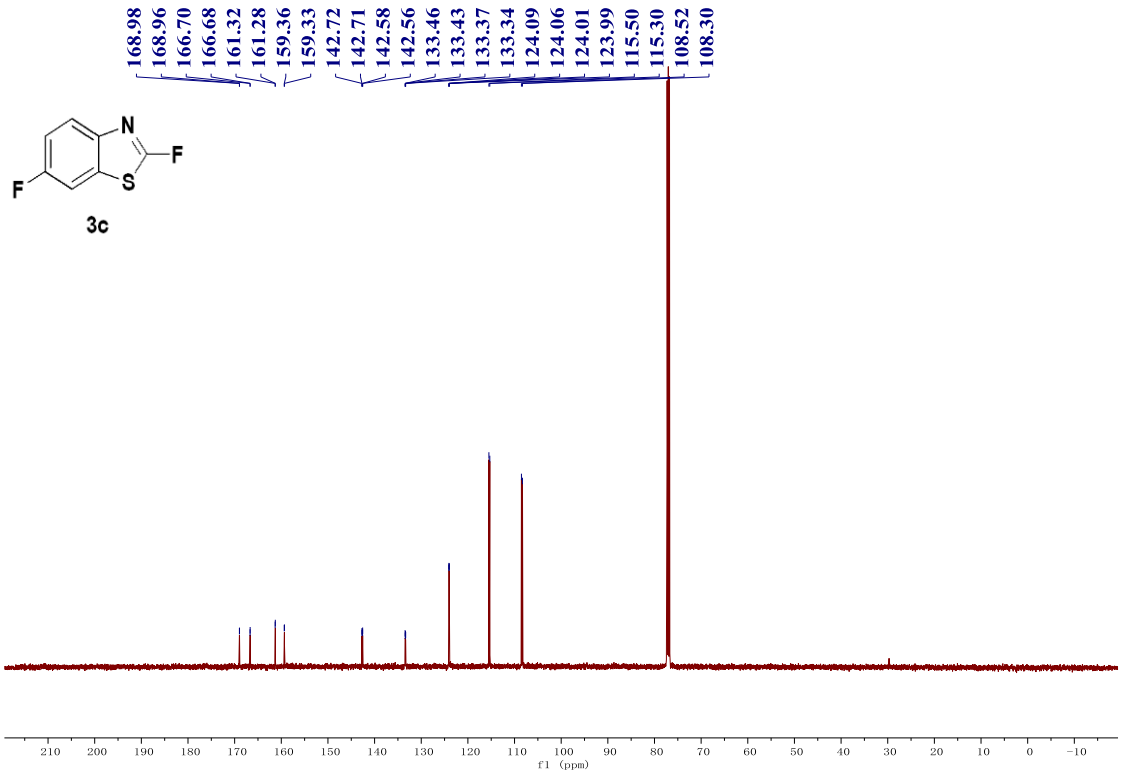

Fig. 57 ^{13}C NMR of **3c** in $CDCl_3$

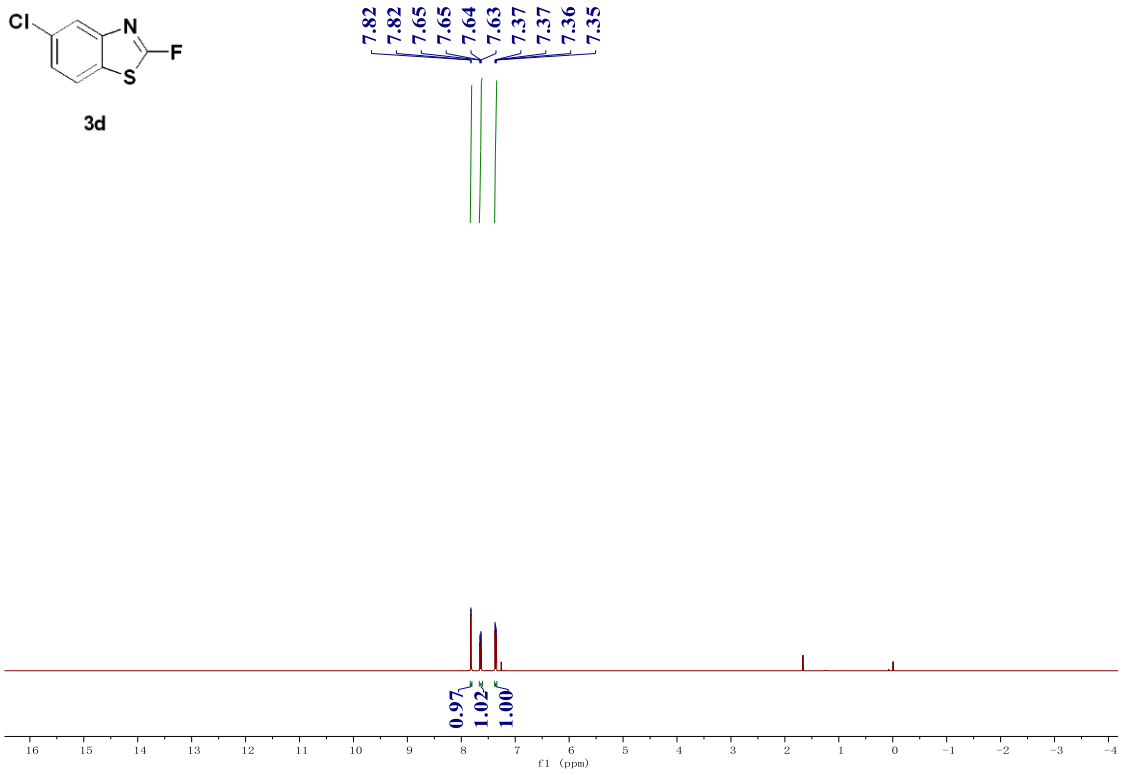

Fig. 58 ^{1}H NMR of **3d** in $CDCl_3$

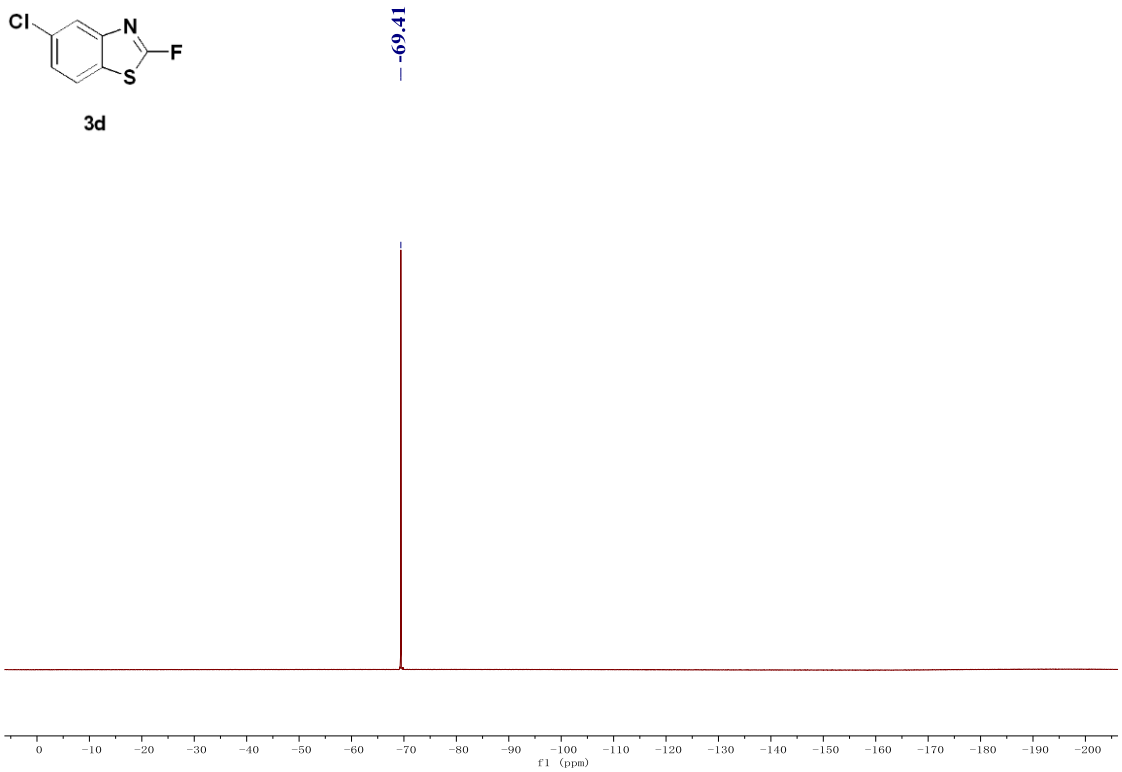

Fig. 59 ^{19}F NMR of **3d** in $CDCl_3$

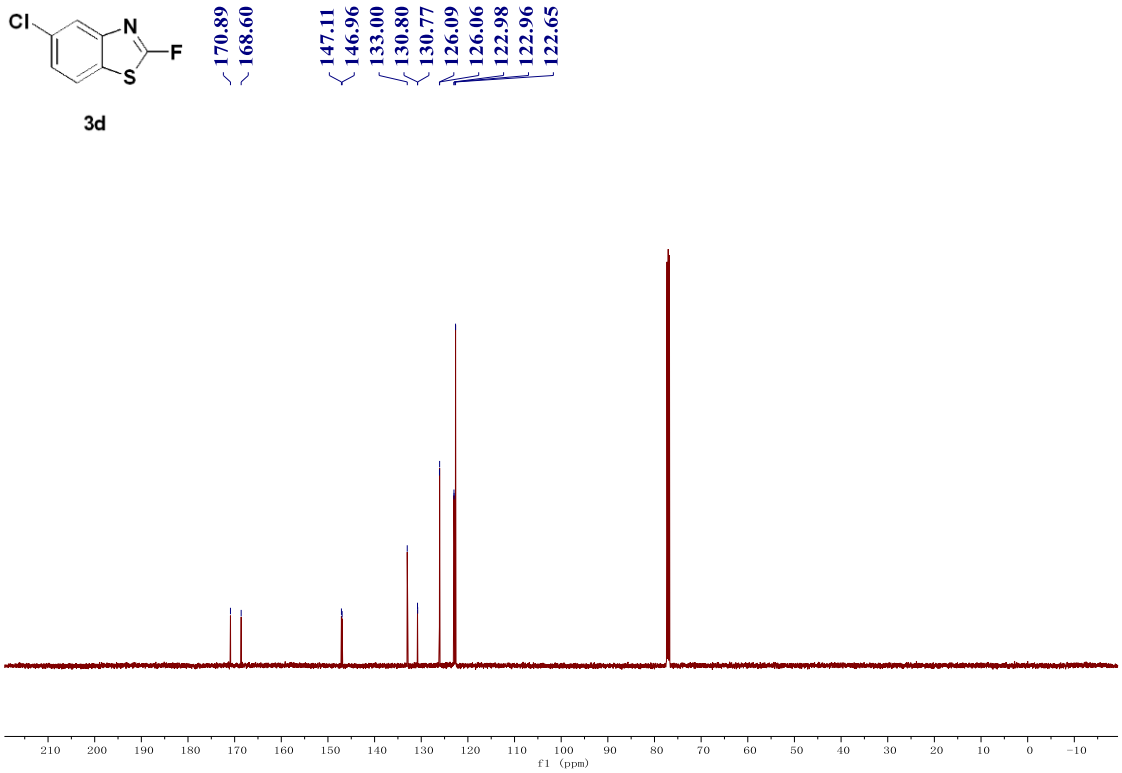

Fig. 60 ^{13}C NMR of **3d** in $CDCl_3$

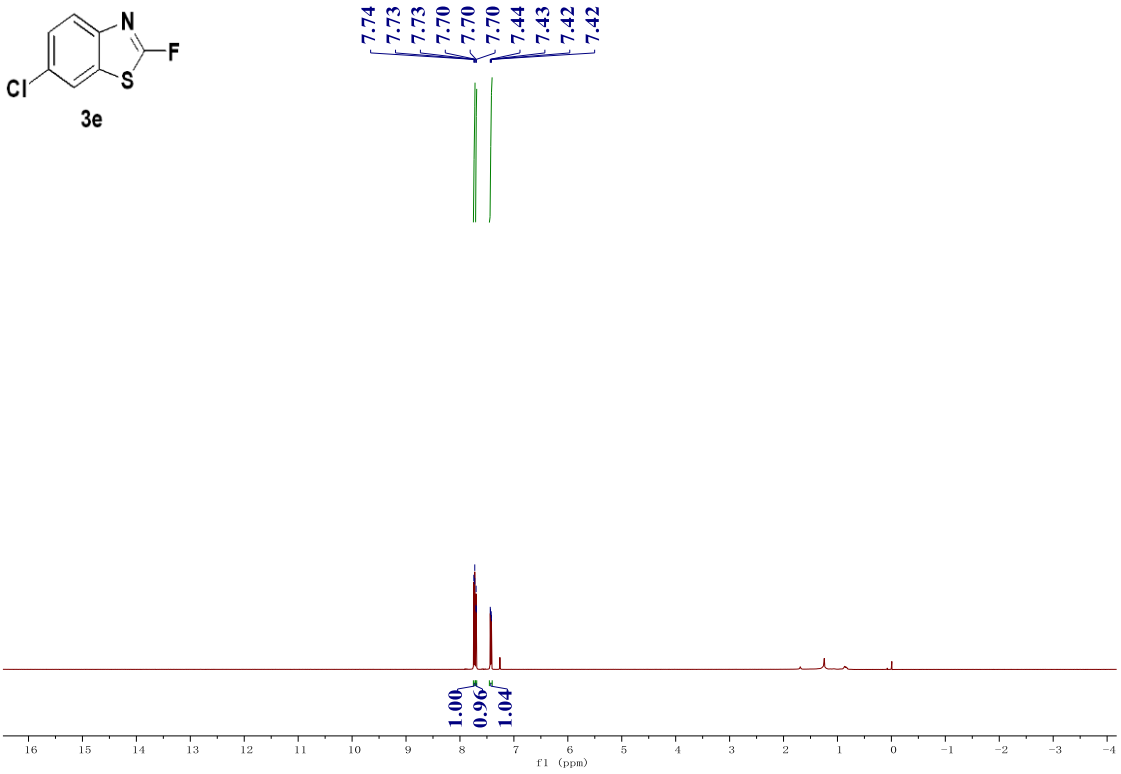

Fig. 61 ^{1}H NMR of **3e** in $CDCl_3$

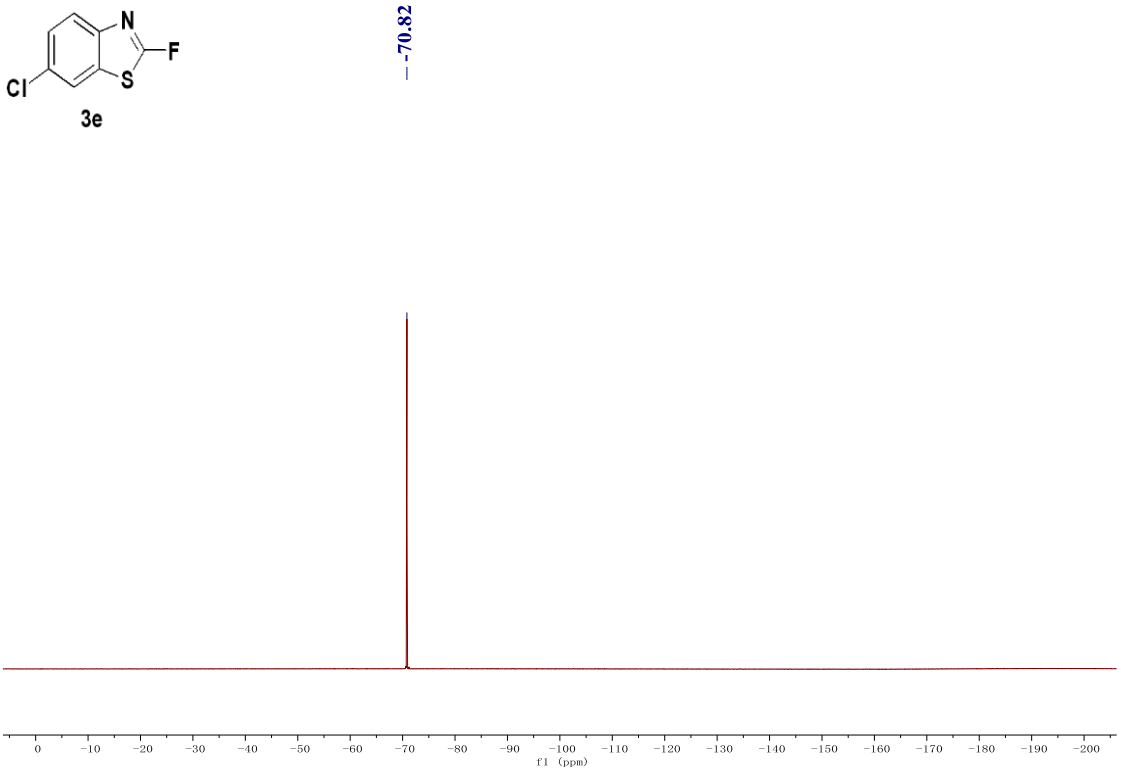

Fig. 62 ^{19}F NMR of **3e** in $CDCl_3$

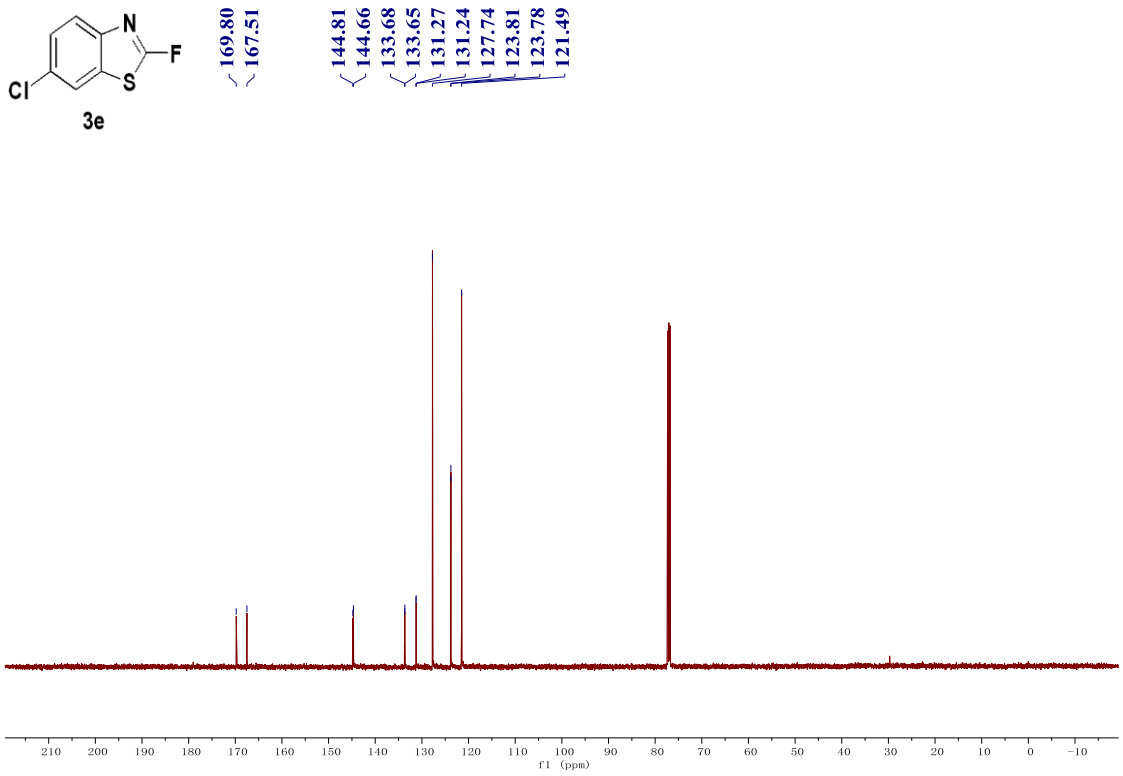

Fig. 63 ^{13}C NMR of **3e** in $CDCl_3$

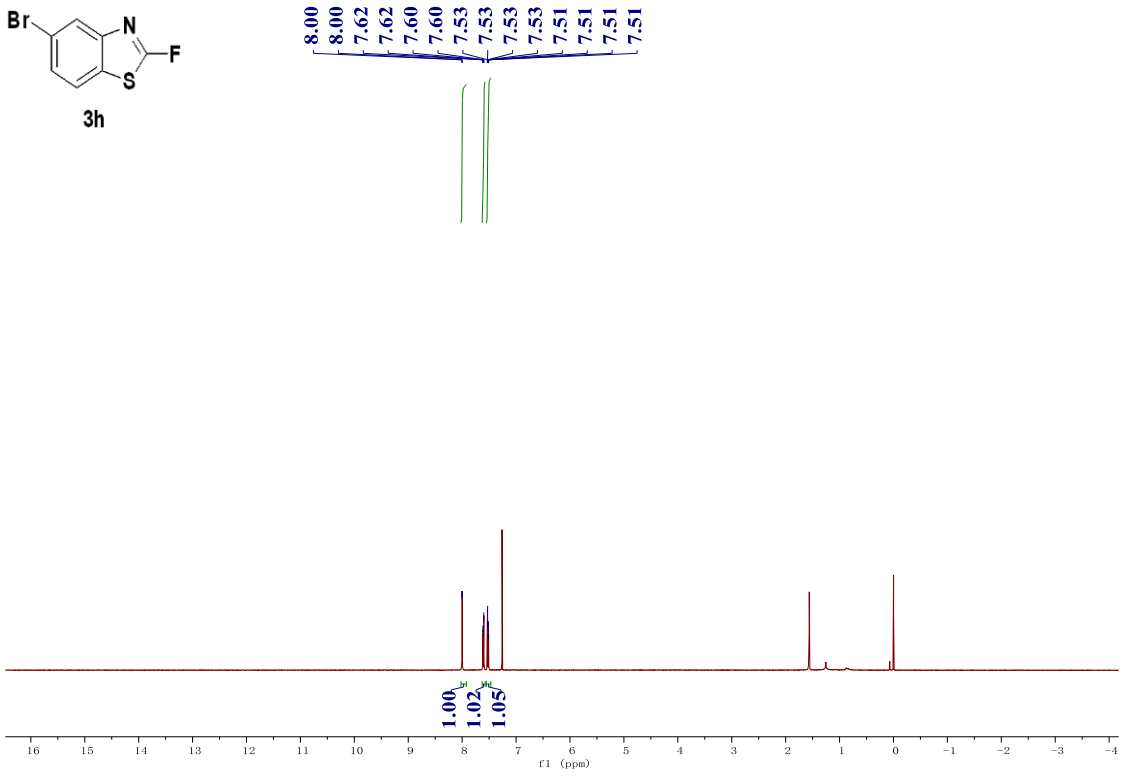

Fig. 64 ^{1}H NMR of **3h** in $CDCl_3$

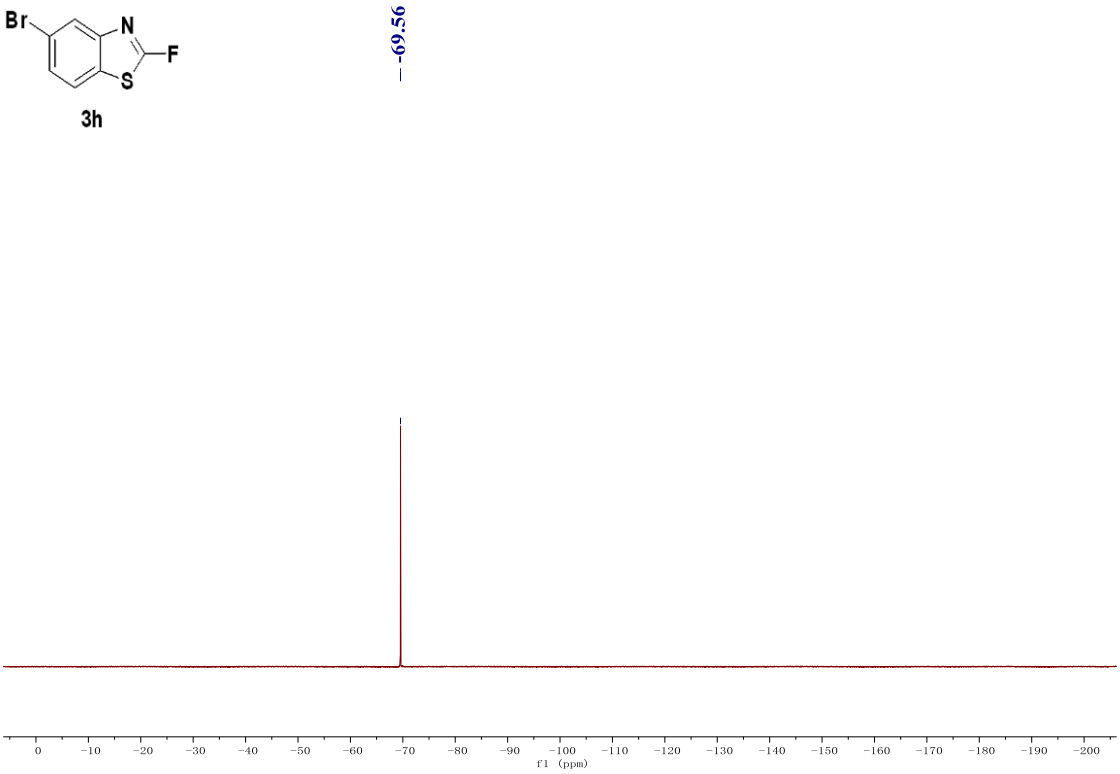

Fig. 65 ^{19}F NMR of **3h** in $CDCl_3$

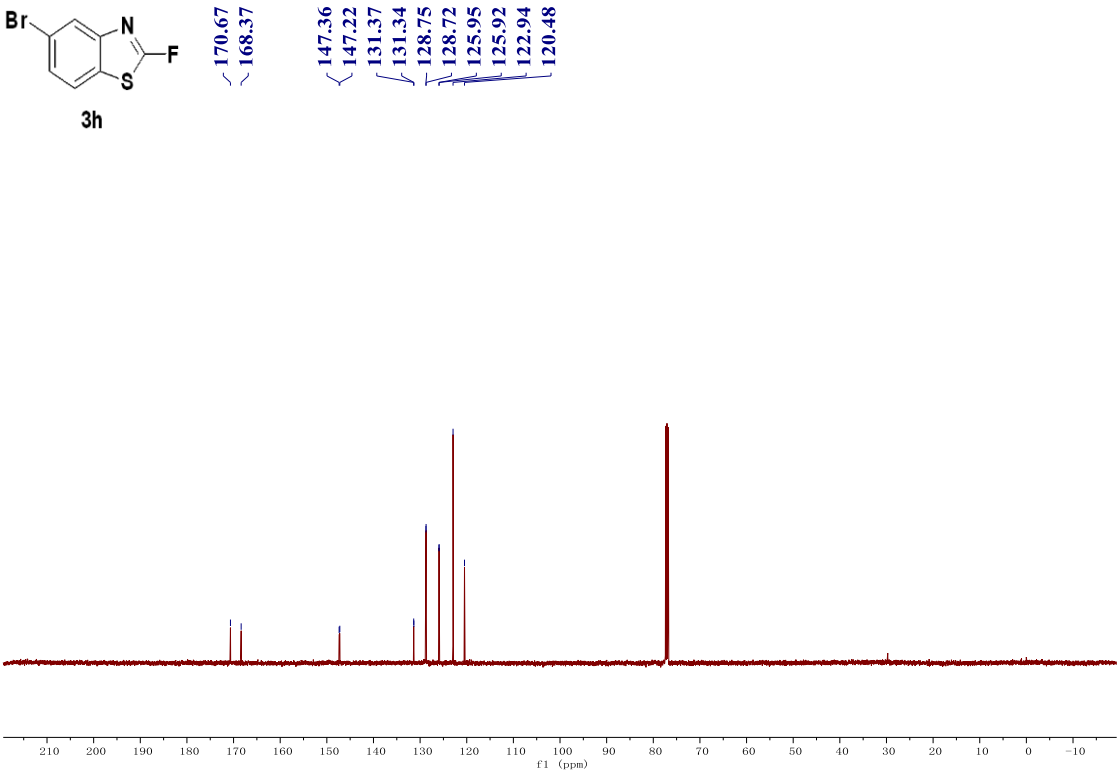

Fig. 66 ^{13}C NMR of **3h** in $CDCl_3$

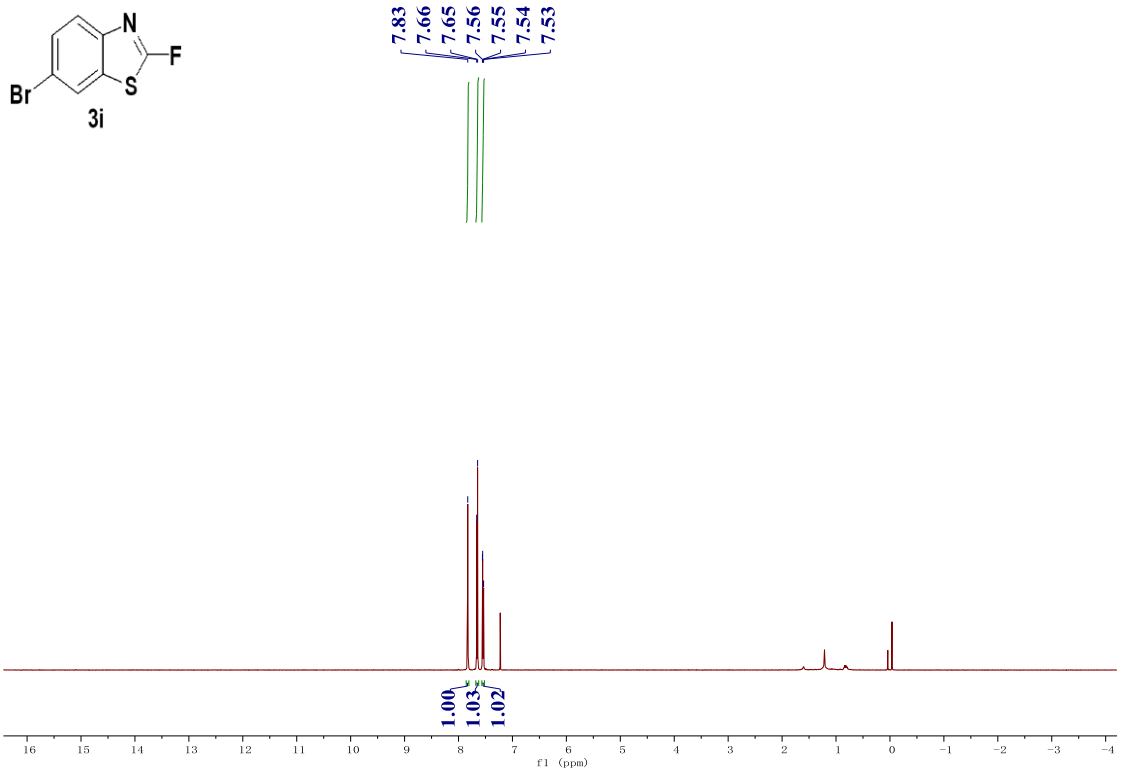

Fig. 67 ^{1}H NMR of **3i** in $CDCl_3$

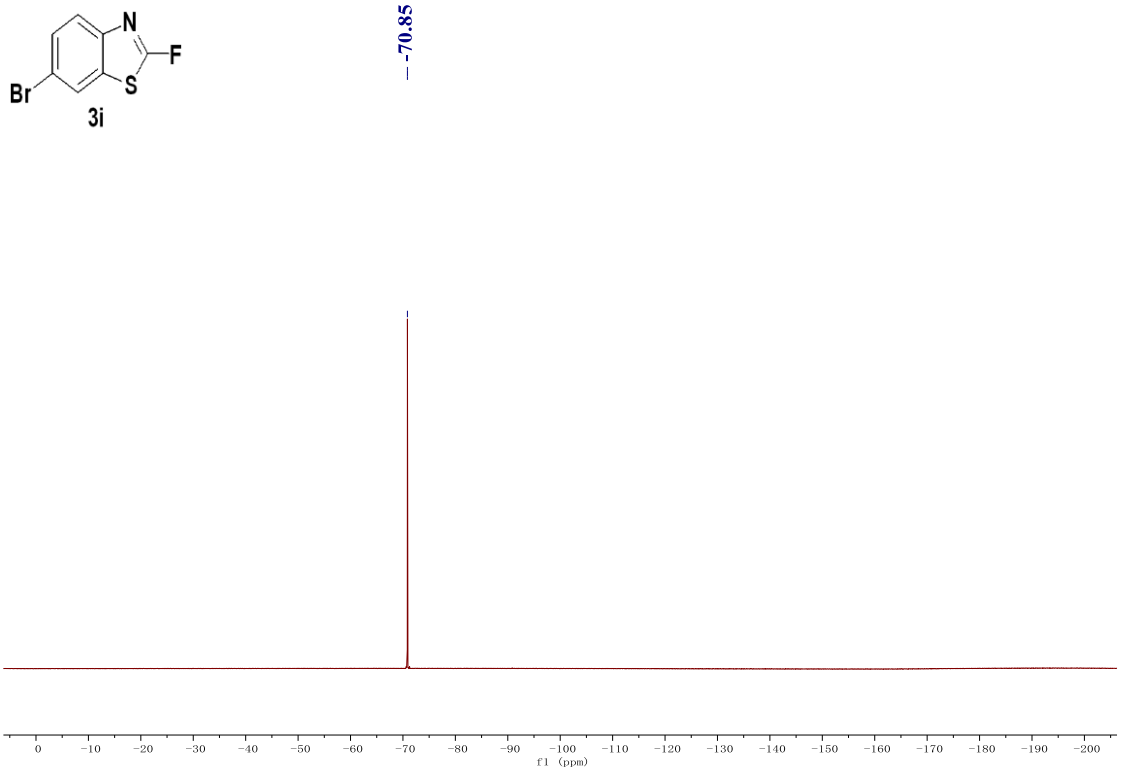

Fig. 68 ^{19}F NMR of **3i** in $CDCl_3$

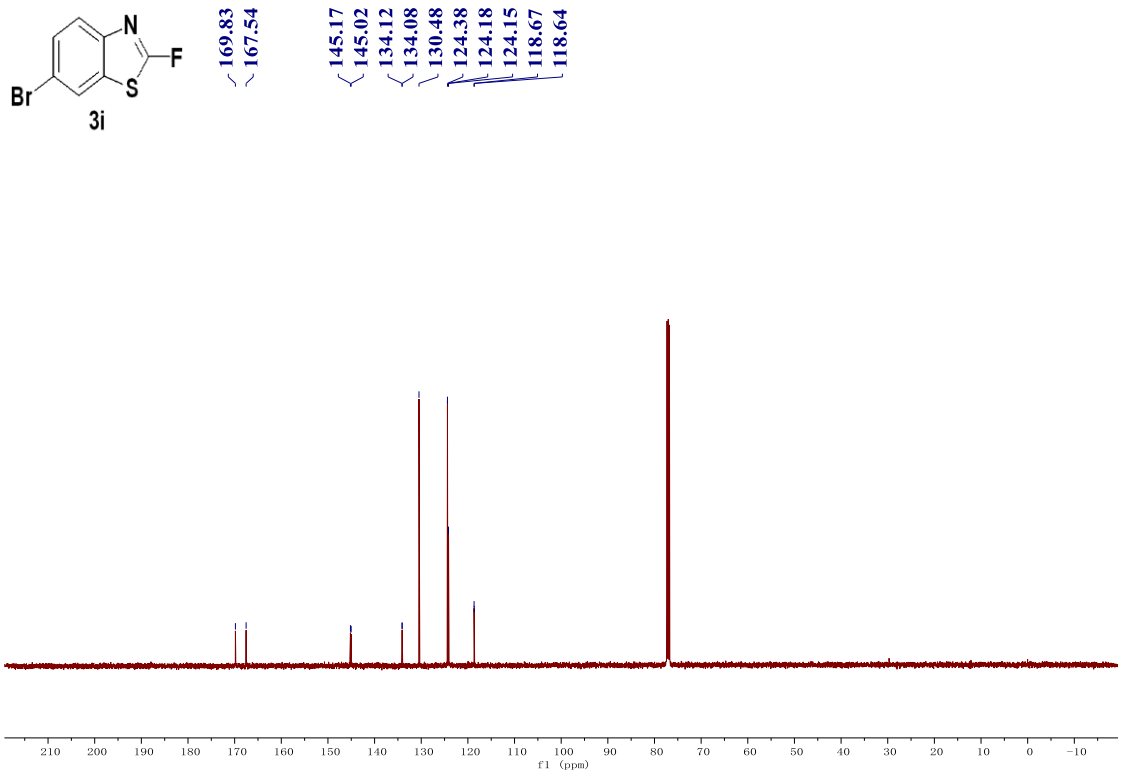

Fig. 69 ^{13}C NMR of **3i** in $CDCl_3$

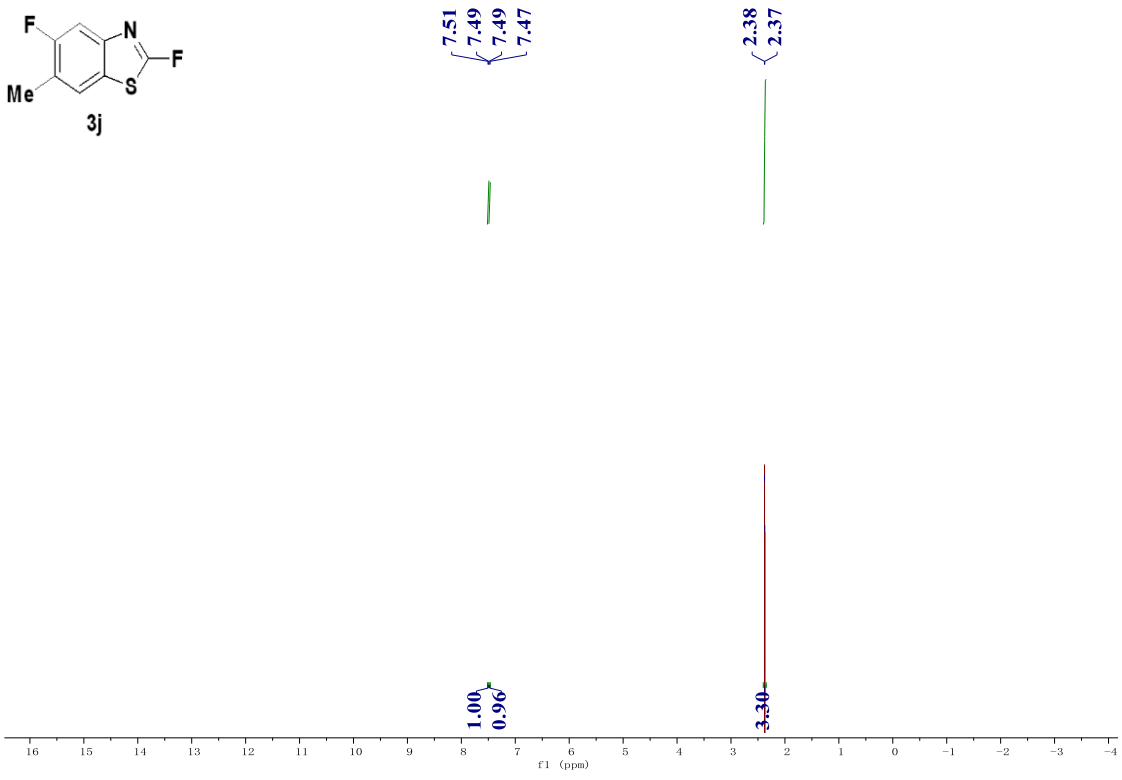

Fig. 70 ^{1}H NMR of **3j** in $CDCl_3$

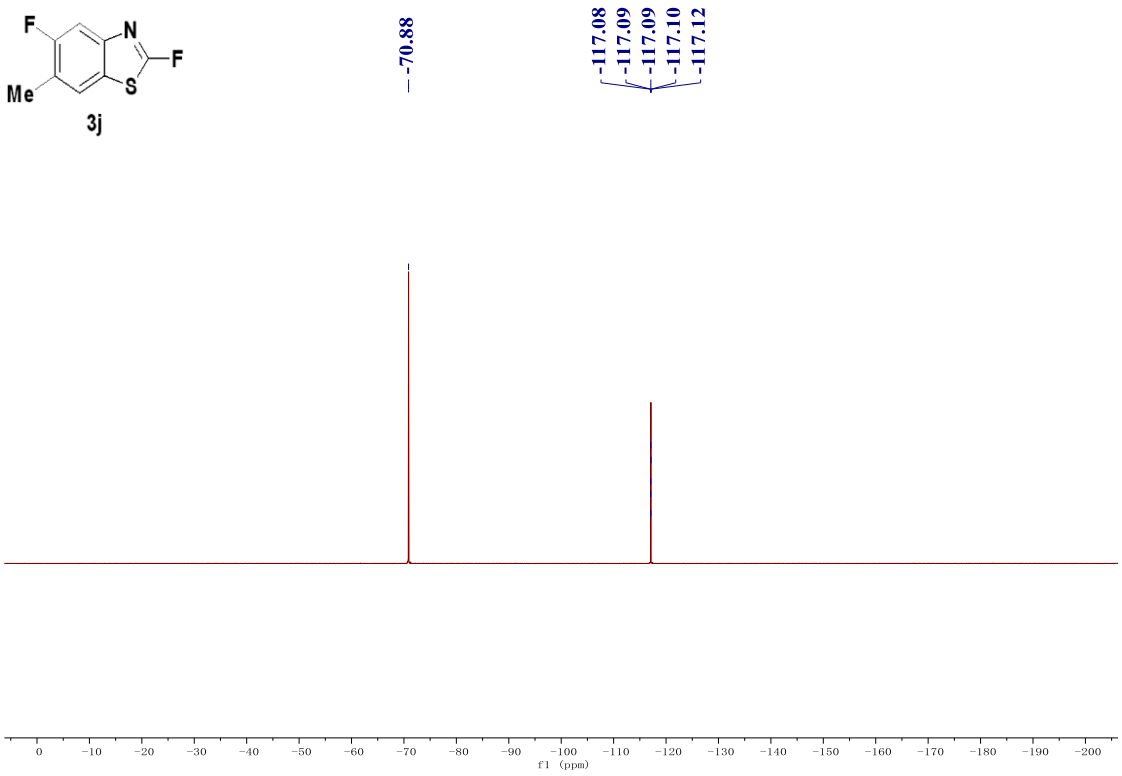

Fig. 71 ^{19}F NMR of **3j** in $CDCl_3$

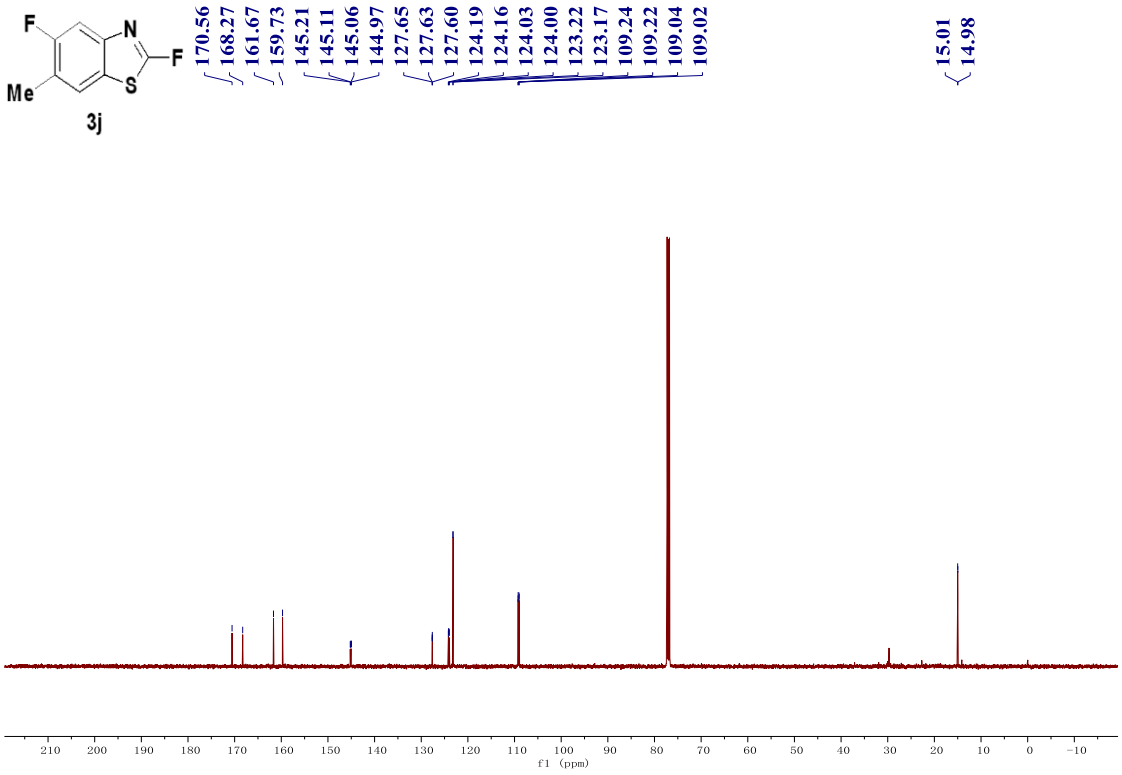

Fig. 72 ^{13}C NMR of **3j** in $CDCl_3$

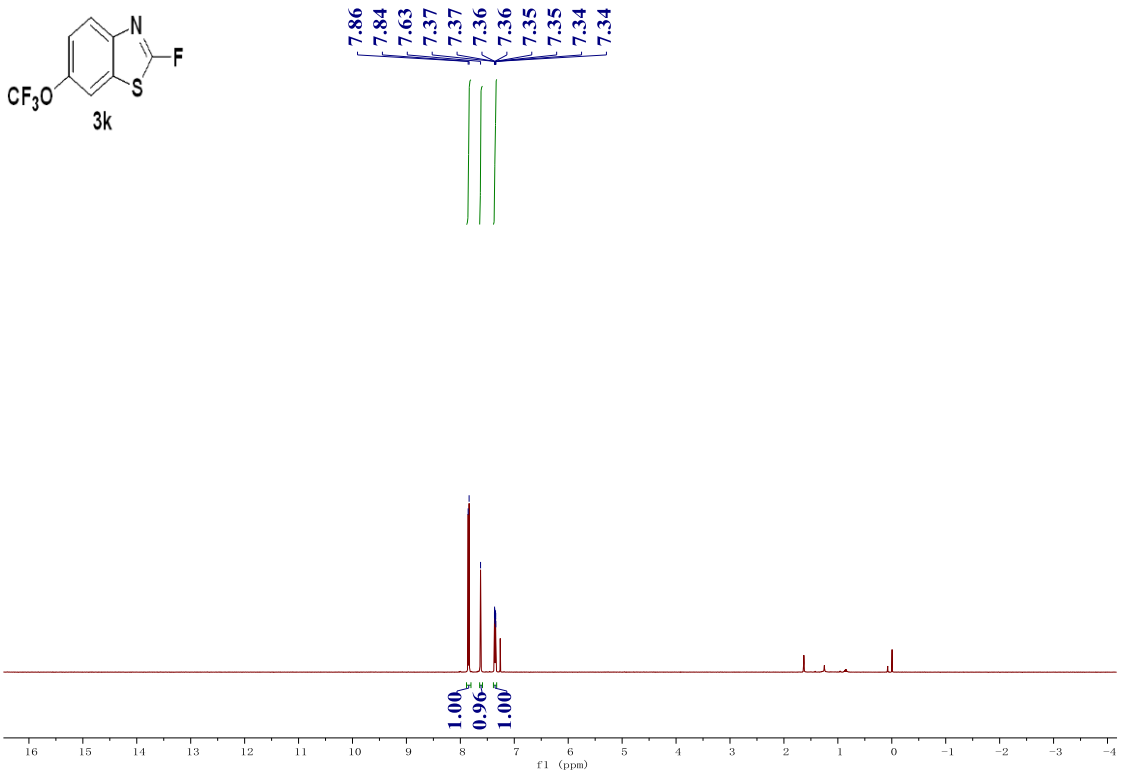

Fig. 73 ^{1}H NMR of **3k** in $CDCl_3$

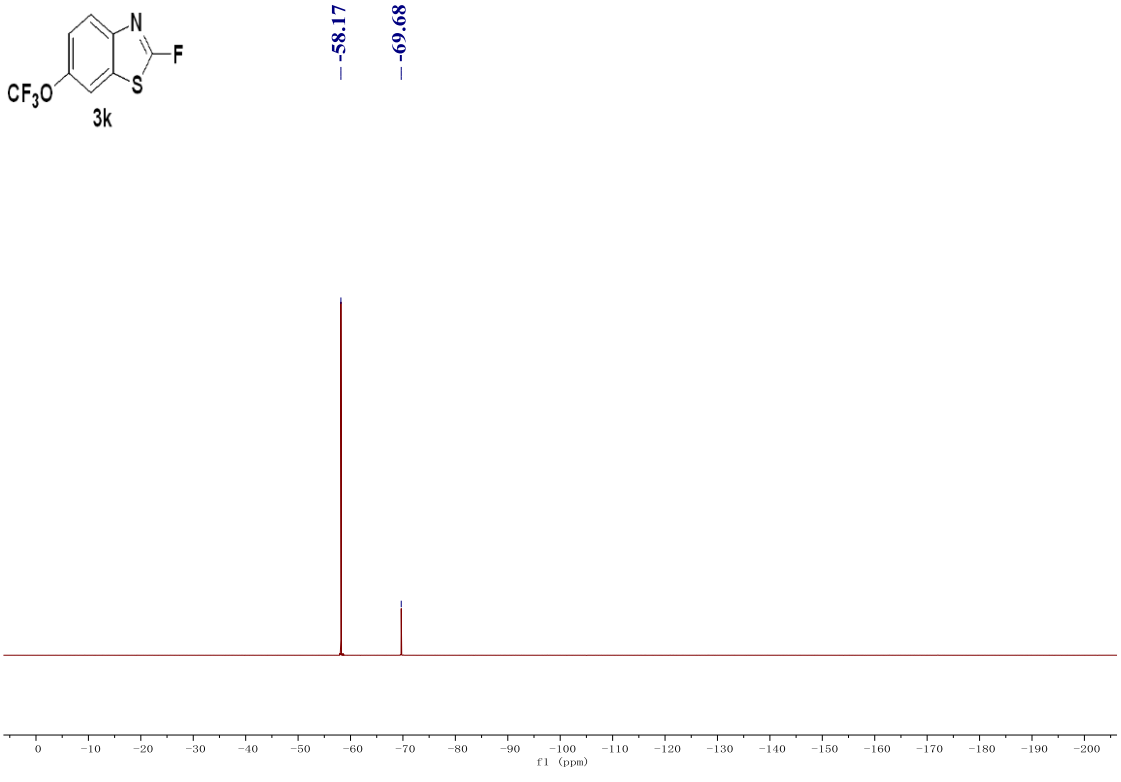

Fig. 74 ^{19}F NMR of **3k** in $CDCl_3$

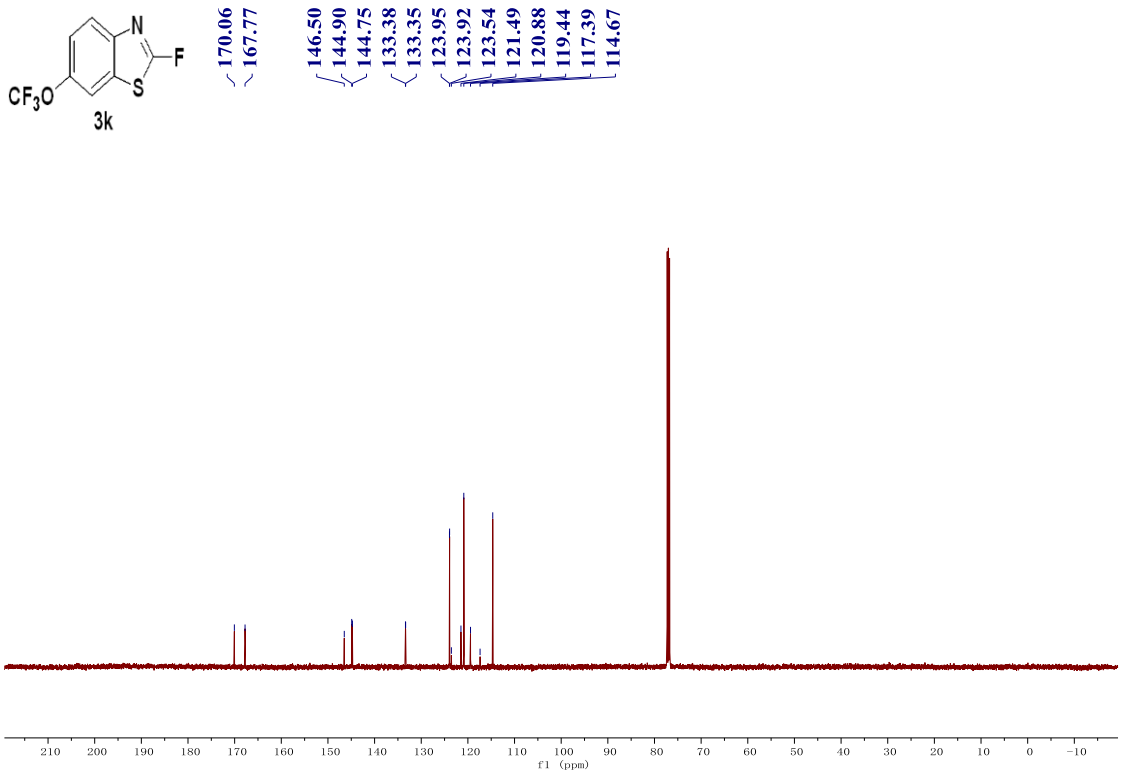

Fig. 75 ^{13}C NMR of **3k** in $CDCl_3$

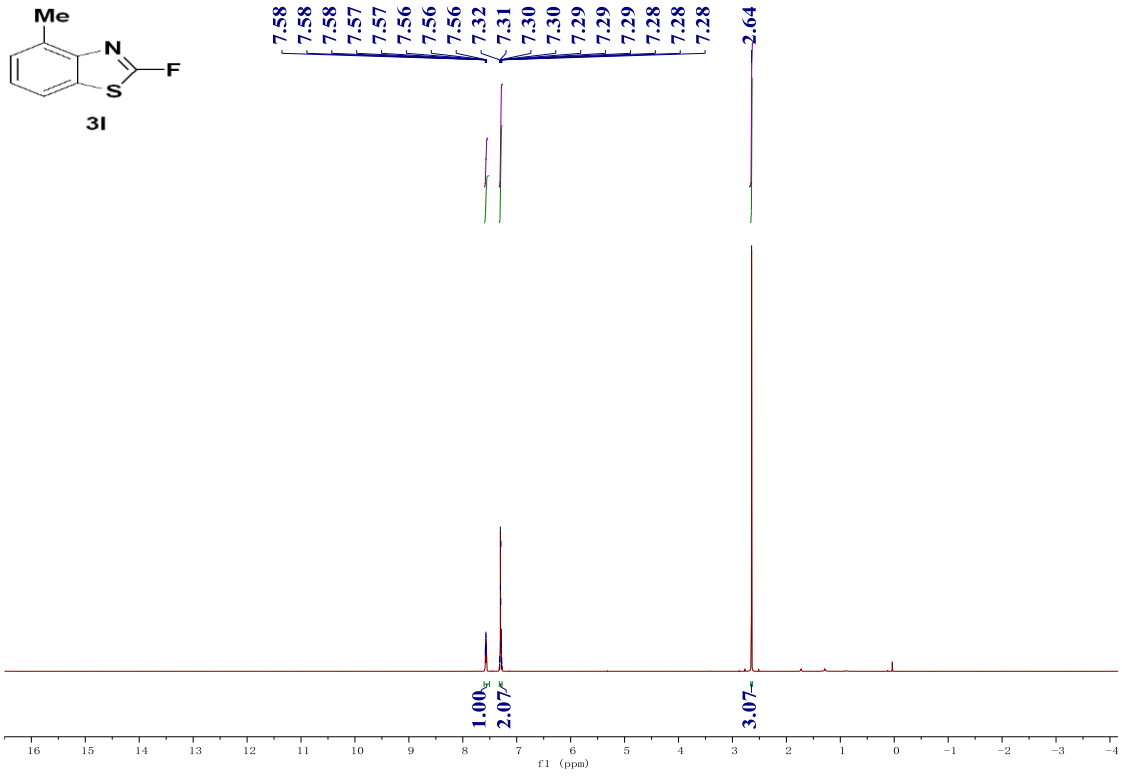

Fig. 76 ^{1}H NMR of **3l** in $CDCl_3$

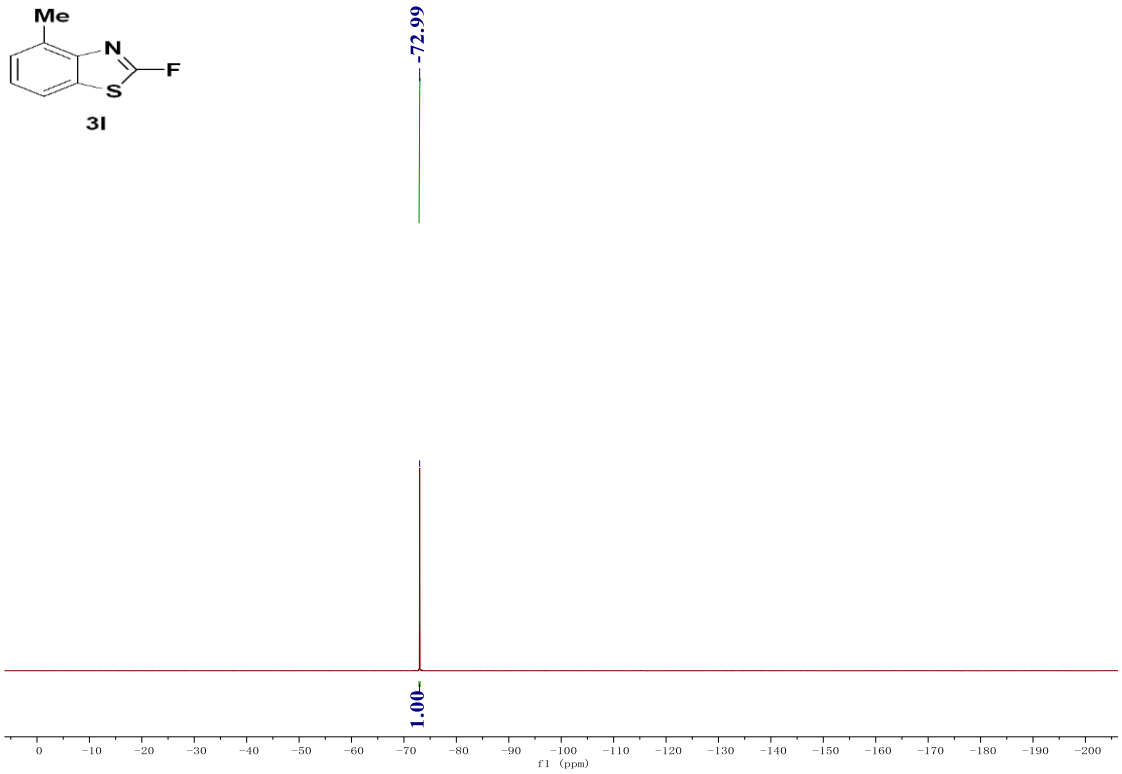

Fig. 77 ^{19}F NMR of **3l** in $CDCl_3$

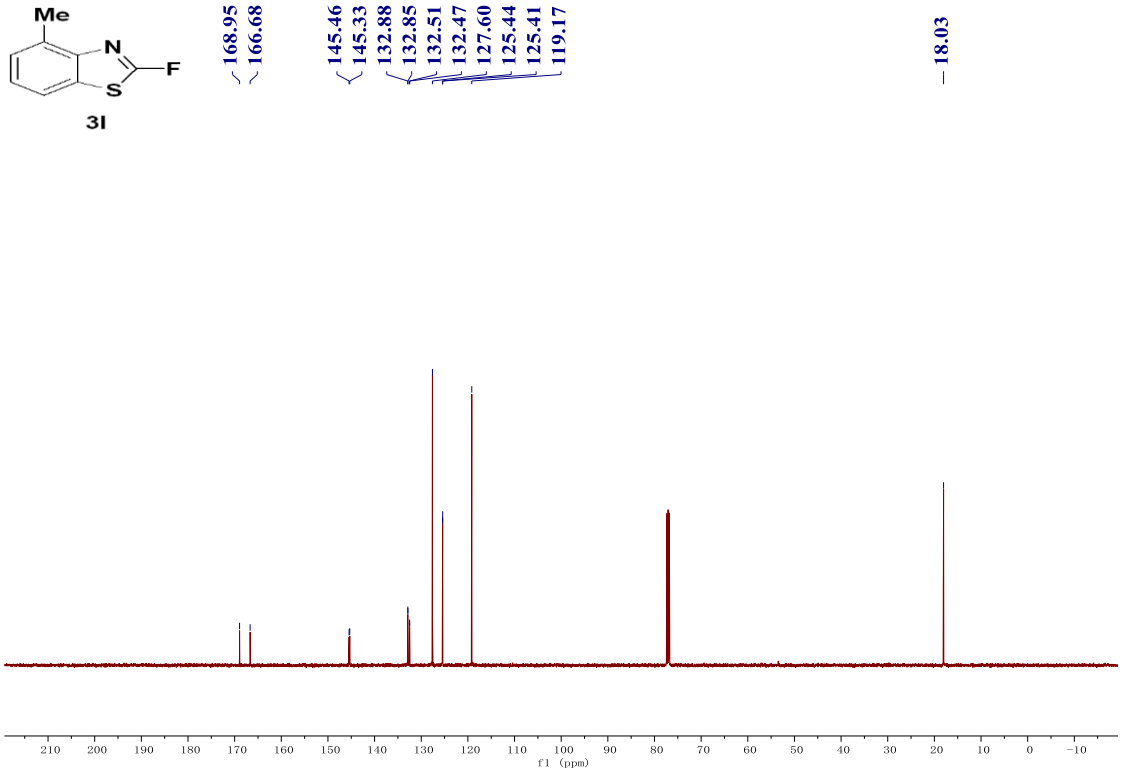

Fig. 78 ^{13}C NMR of **3l** in $CDCl_3$

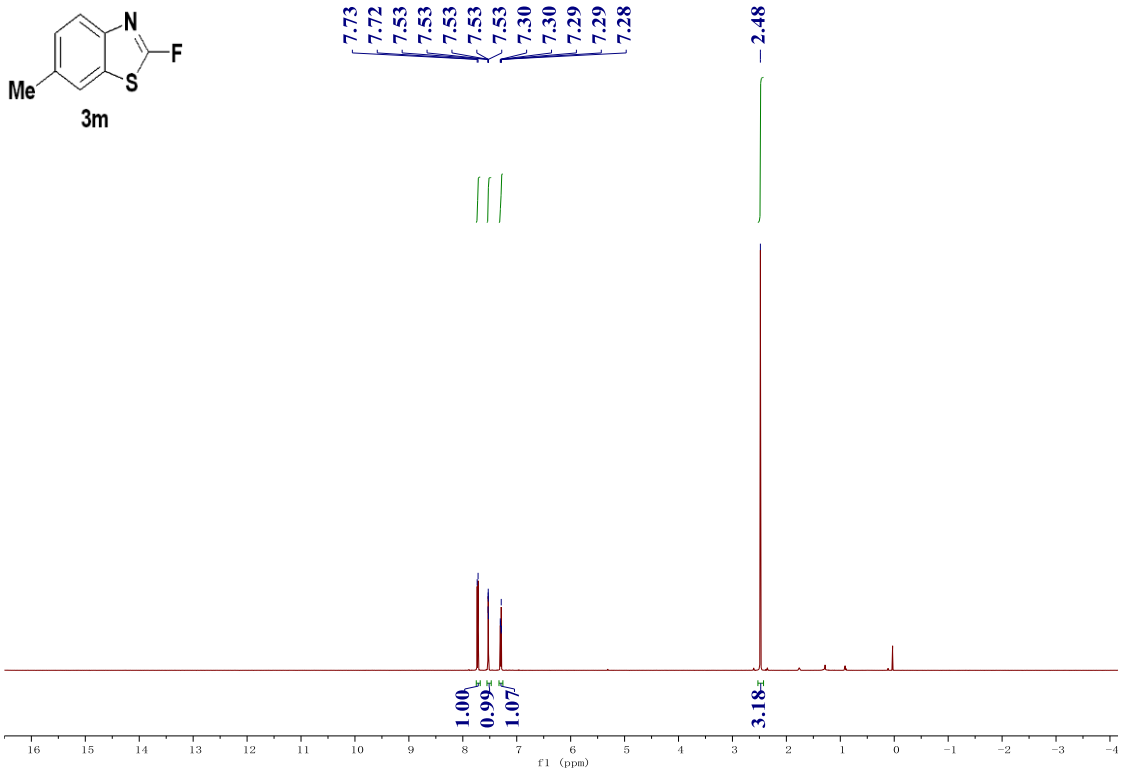

Fig. 79 ^{1}H NMR of **3m** in $CDCl_3$

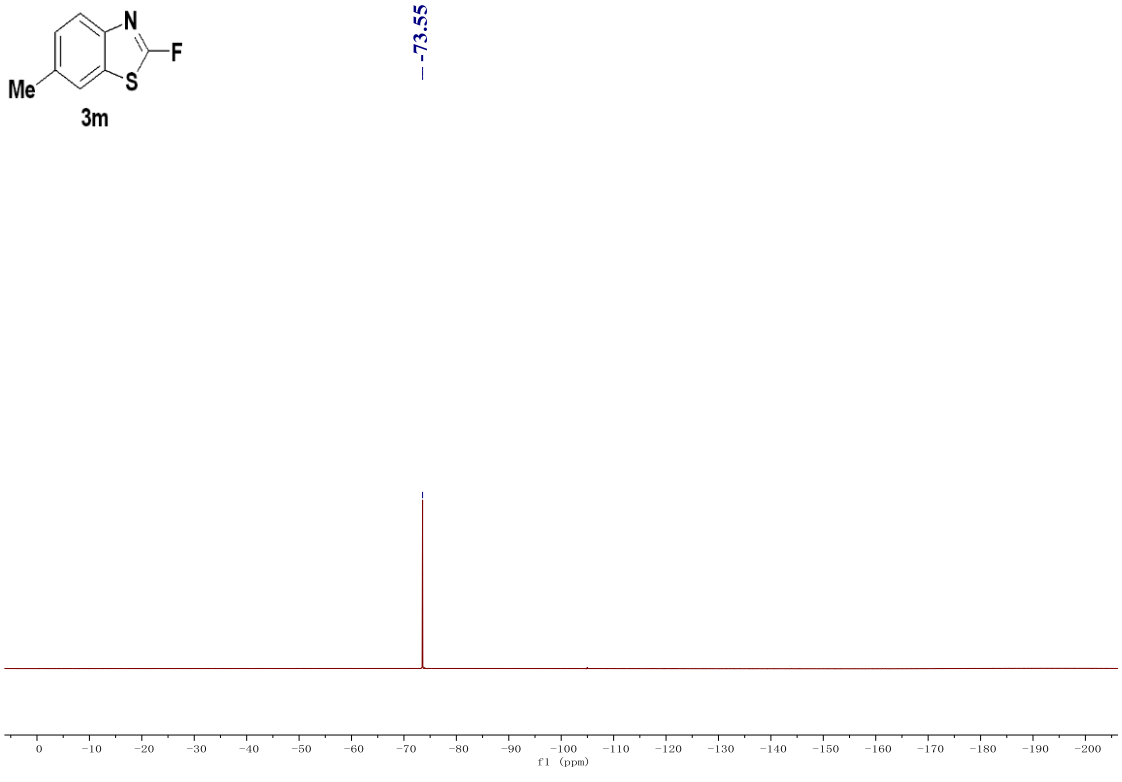

Fig. 80 ^{19}F NMR of **3m** in $CDCl_3$

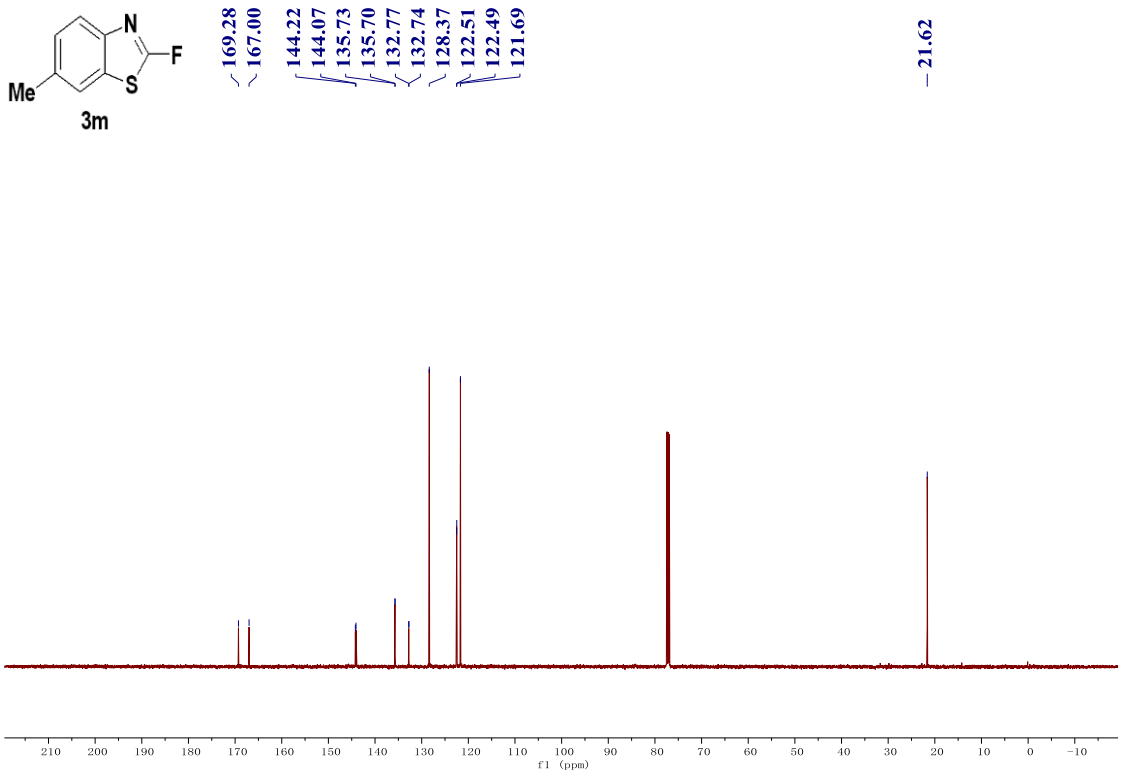

Fig. 81 ^{13}C NMR of **3m** in $CDCl_3$

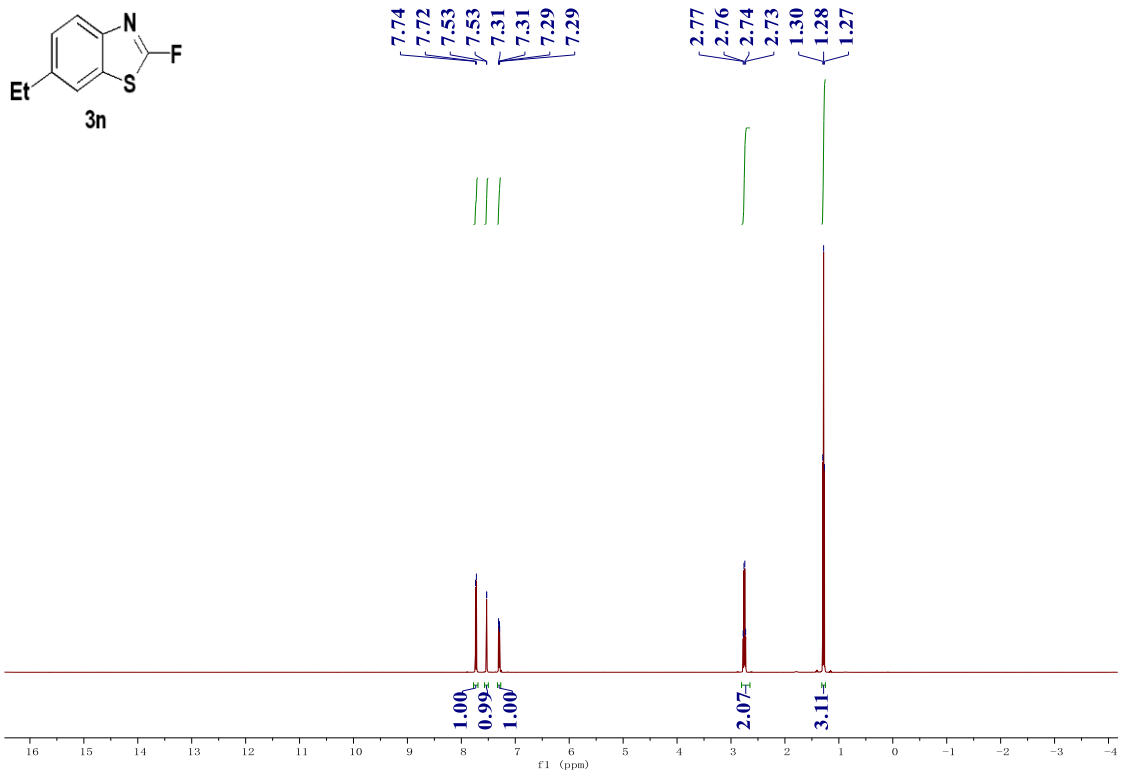

Fig. 82 ^{1}H NMR of **3n** in $CDCl_3$

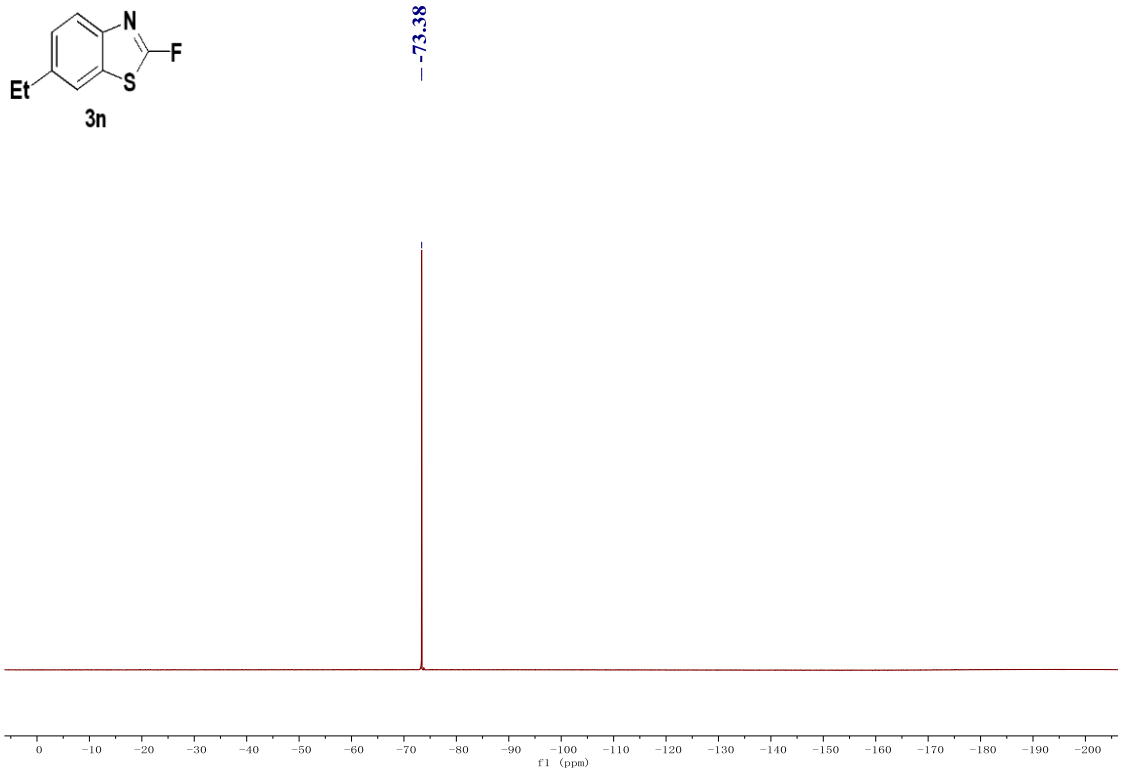

Fig. 83 ^{19}F NMR of **3n** in $CDCl_3$

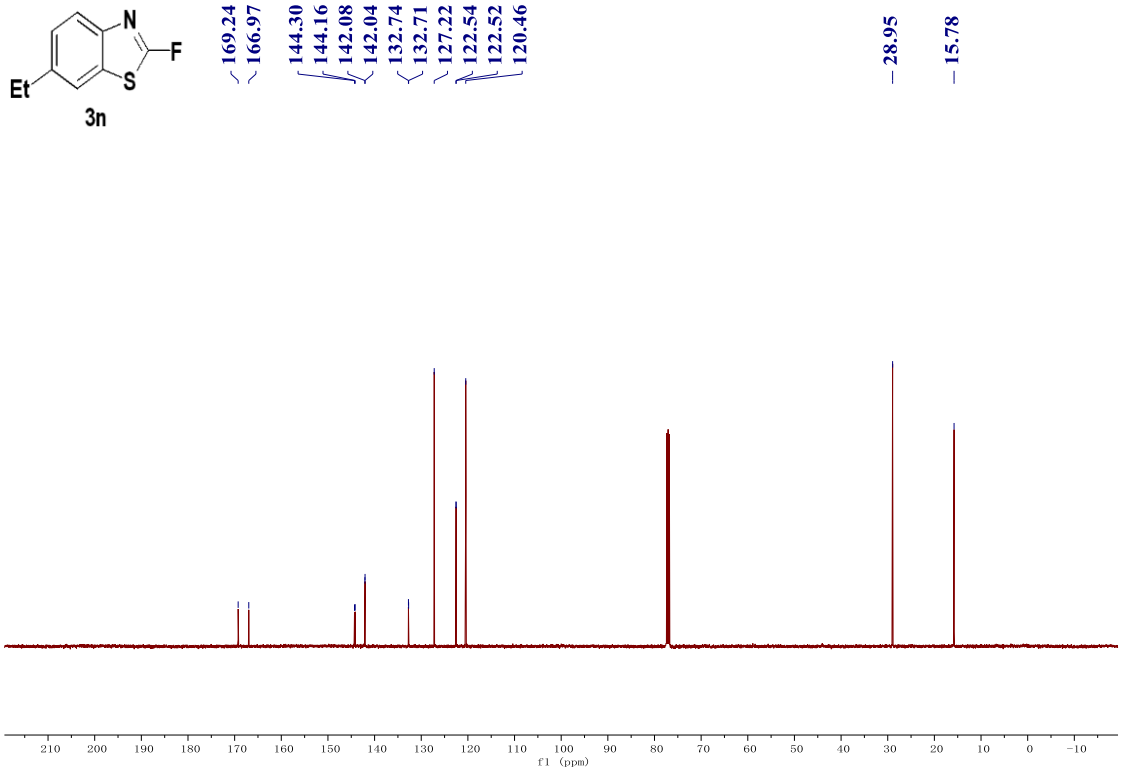

Fig. 84 ^{13}C NMR of **3n** in $CDCl_3$

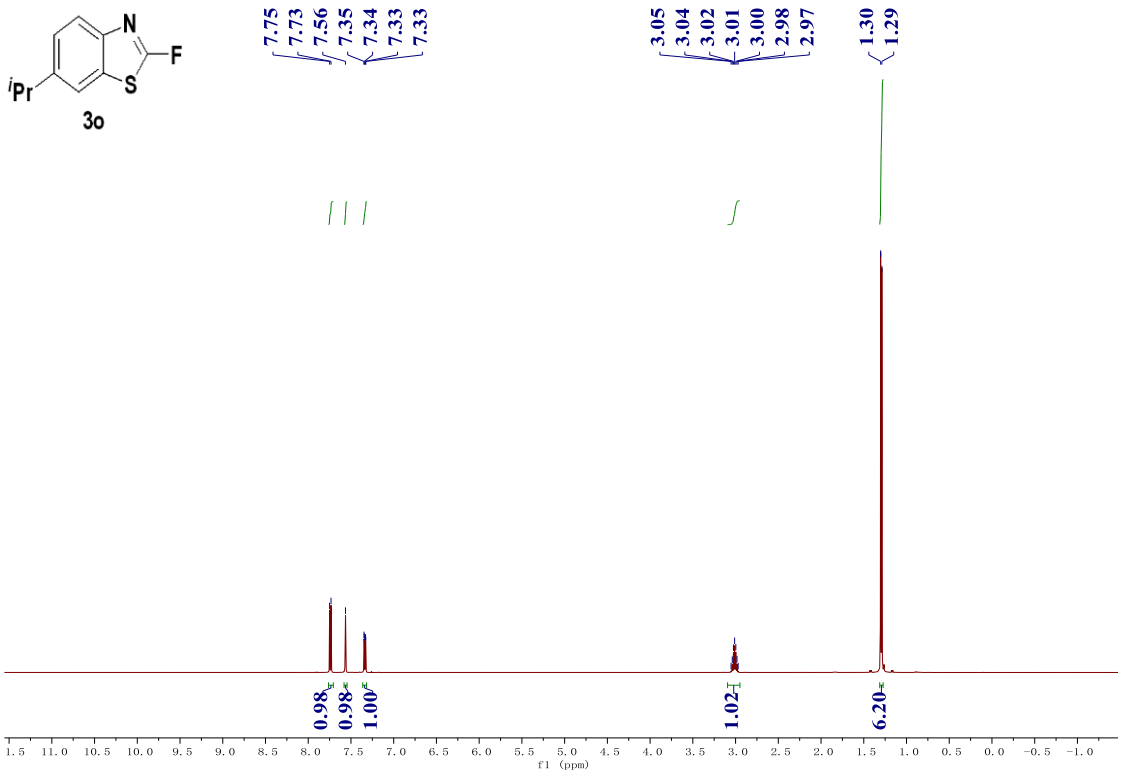

Fig. 85 ^{1}H NMR of **3o** in $CDCl_3$

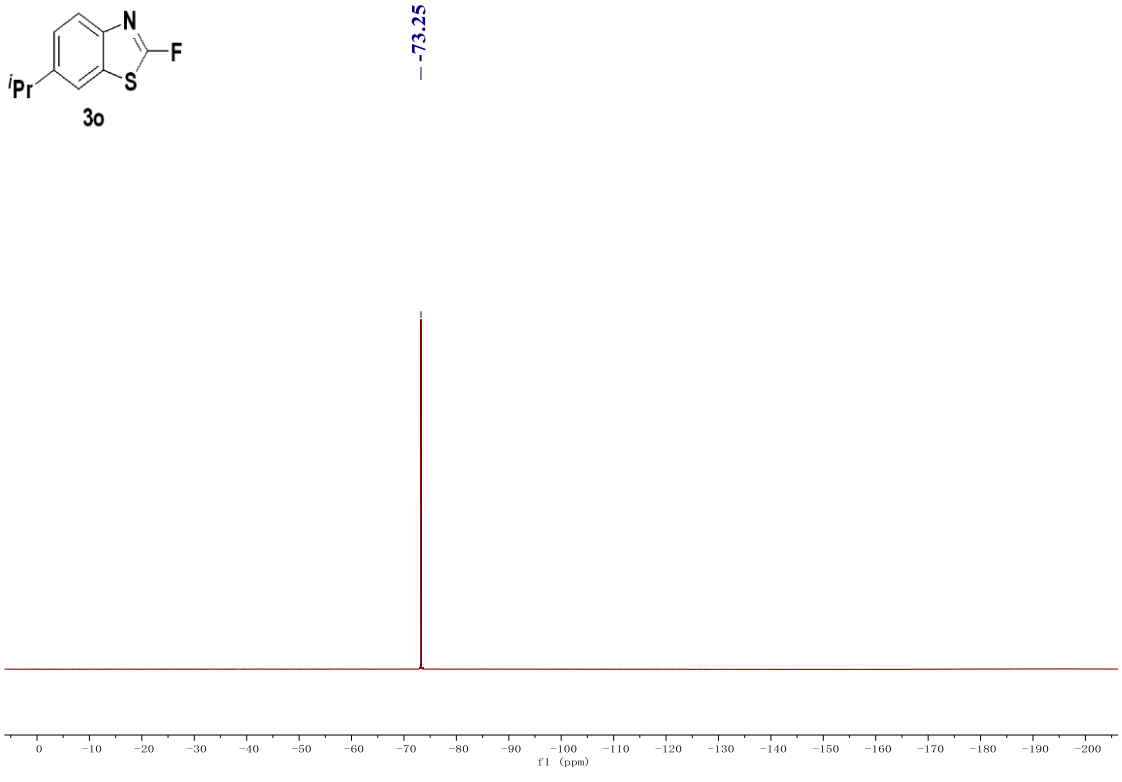

Fig. 86 ^{19}F NMR of **3o** in $CDCl_3$

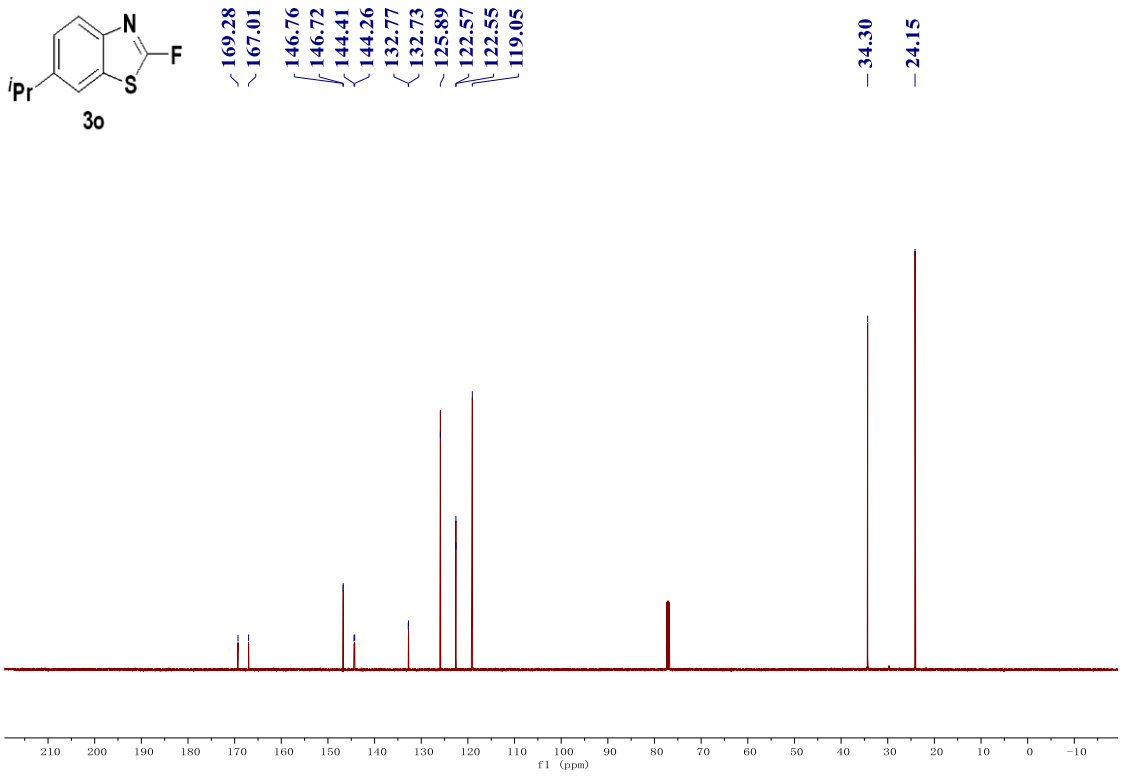

Fig. 87 ^{13}C NMR of **3o** in $CDCl_3$

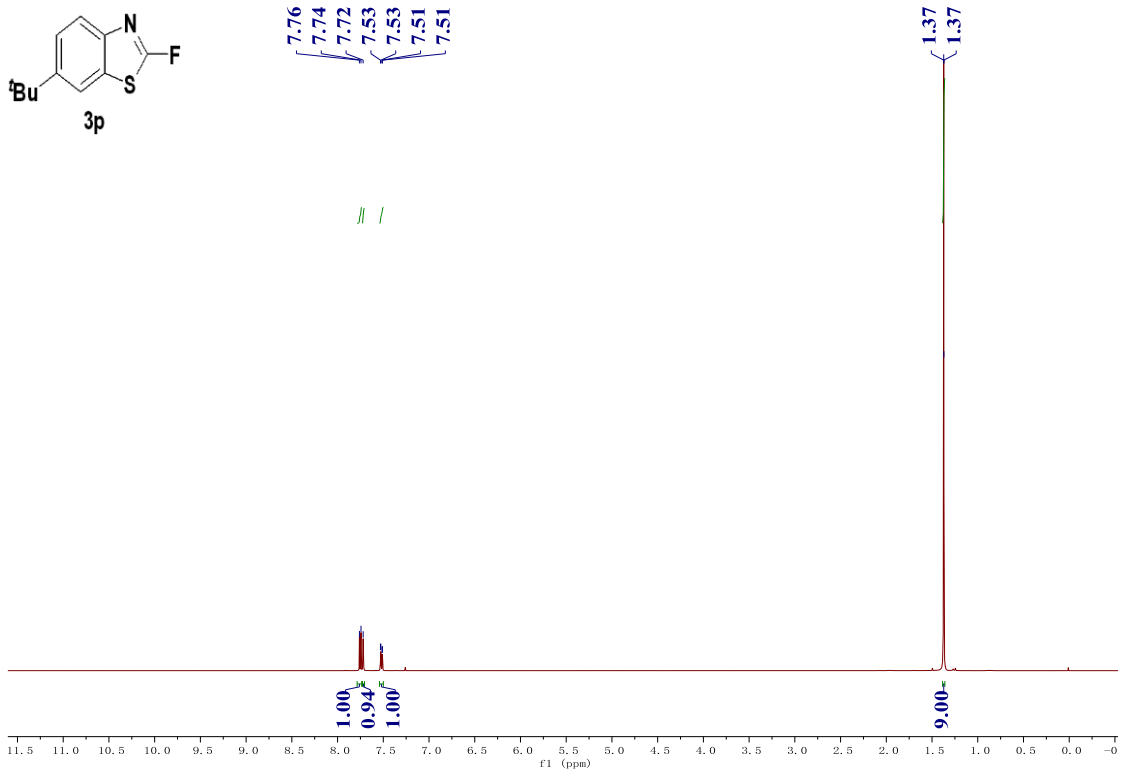

Fig. 88 ^{1}H NMR of **3p** in $CDCl_3$

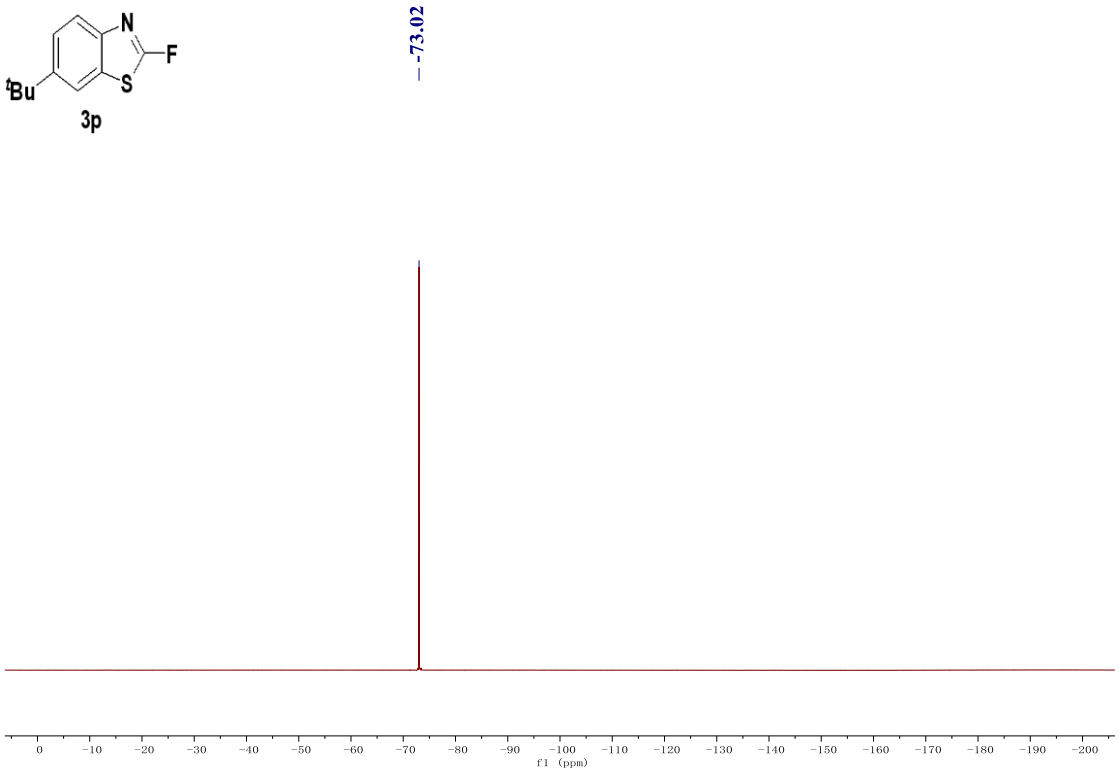

Fig. 89 ^{19}F NMR of **3p** in $CDCl_3$

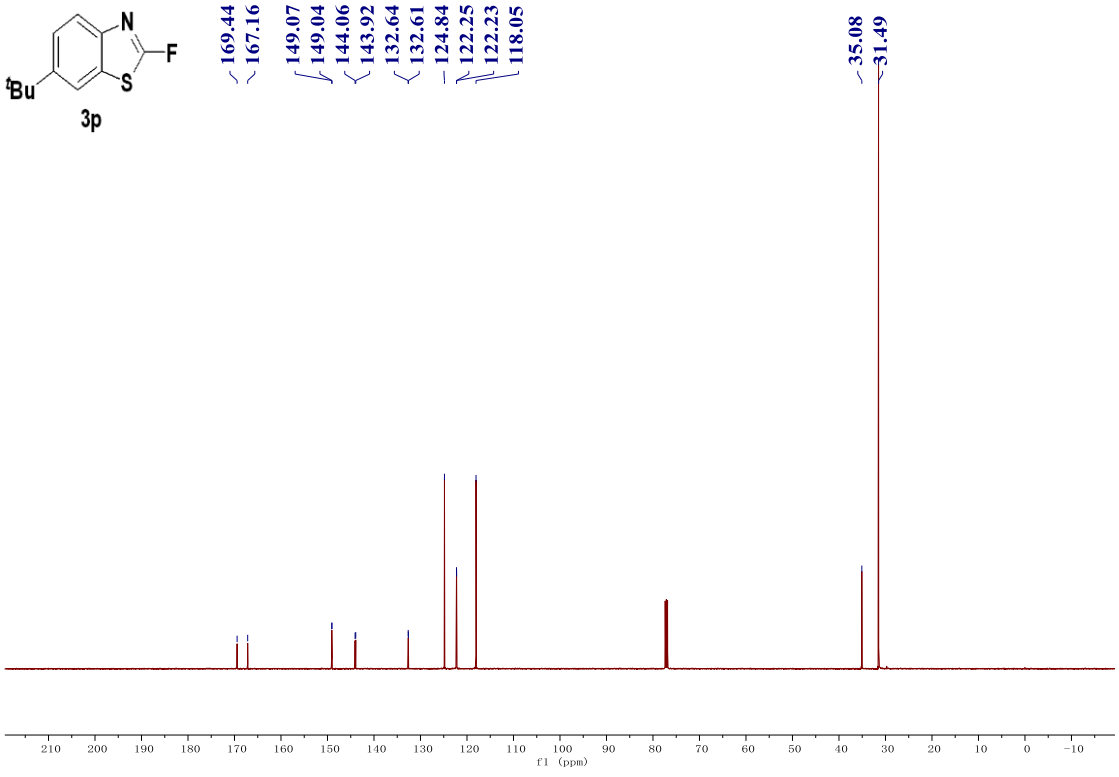

Fig. 90 ^{13}C NMR of **3p** in $CDCl_3$

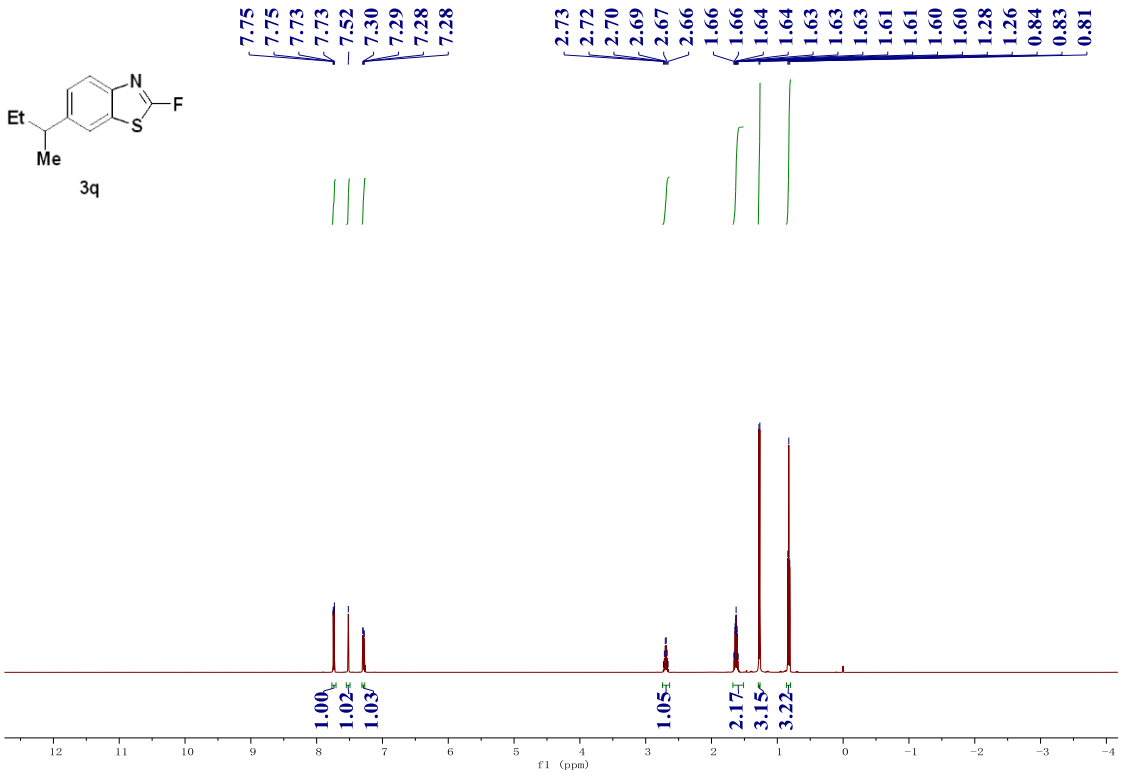

Fig. 91 ^{1}H NMR of **3q** in $CDCl_3$

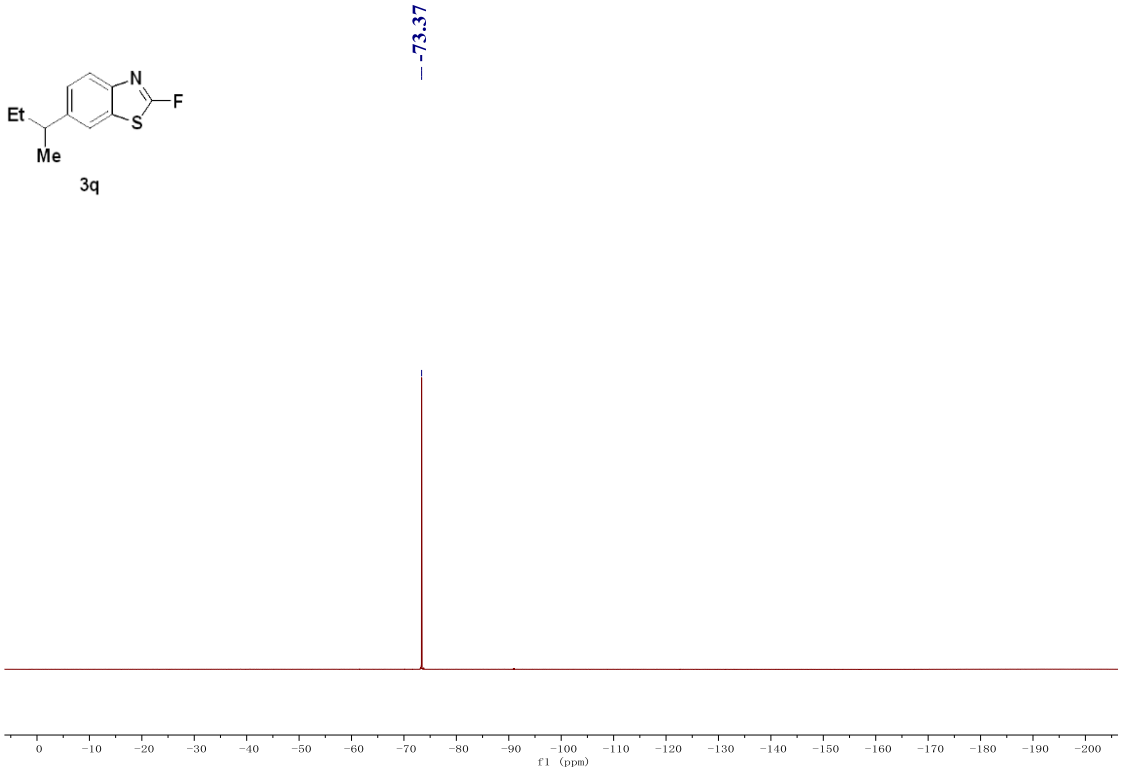

Fig. 92 ^{19}F NMR of **3q** in $CDCl_3$

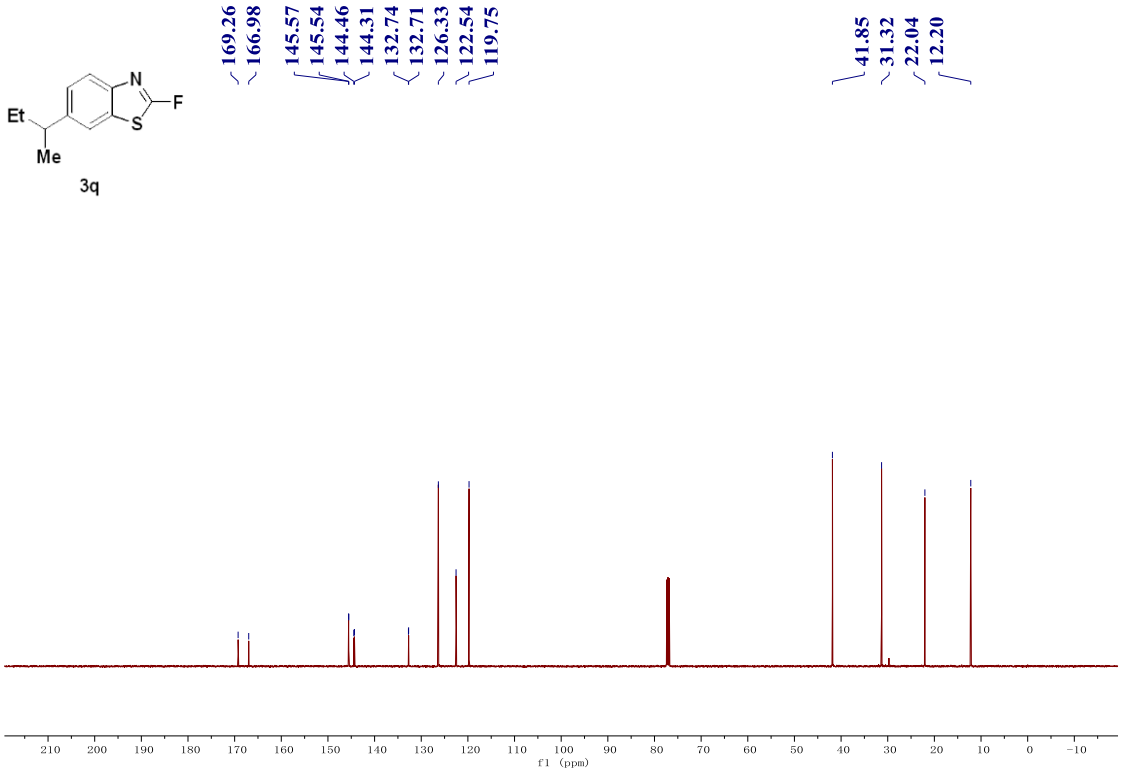

Fig. 93 ^{13}C NMR of **3q** in $CDCl_3$

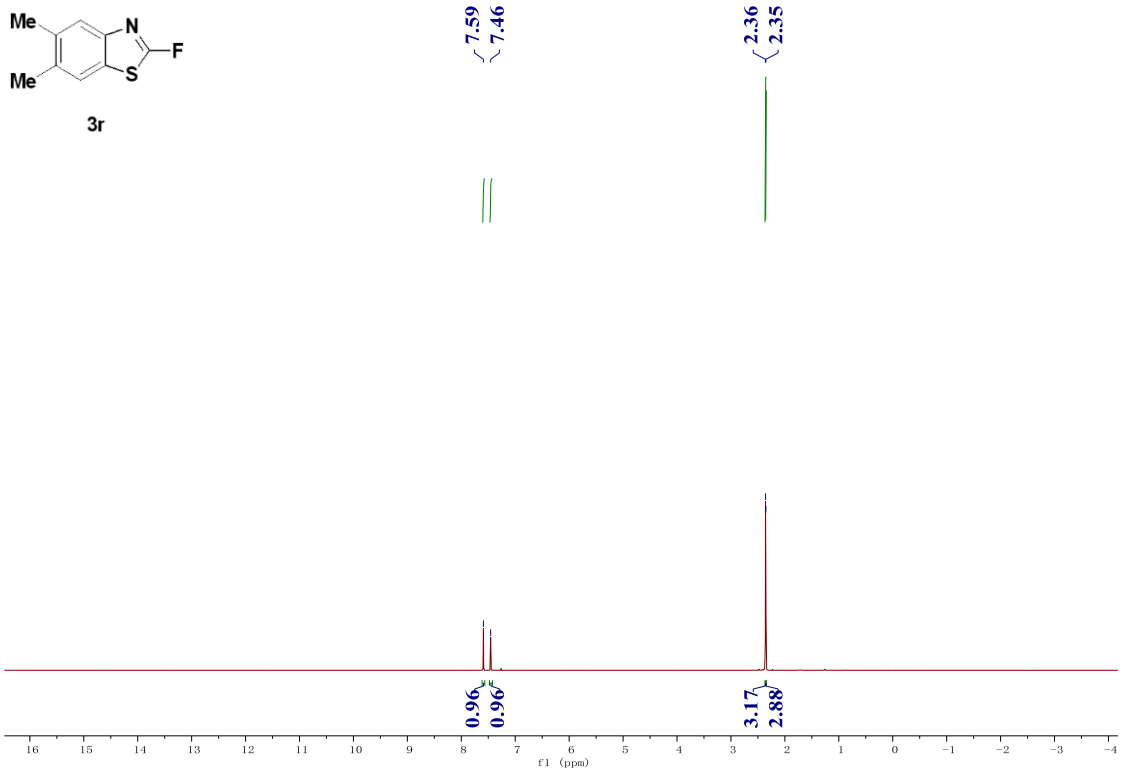

Fig. 94 ^{1}H NMR of **3r** in $CDCl_3$

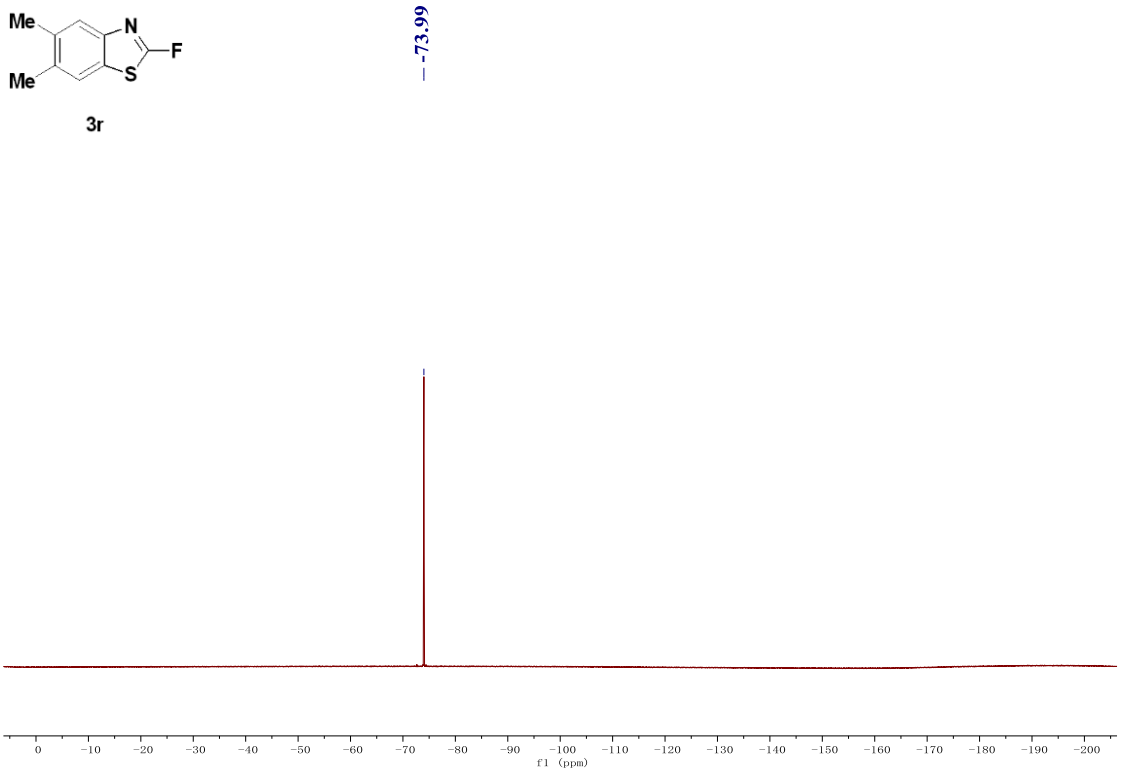

Fig. 95 ^{19}F NMR of **3r** in $CDCl_3$

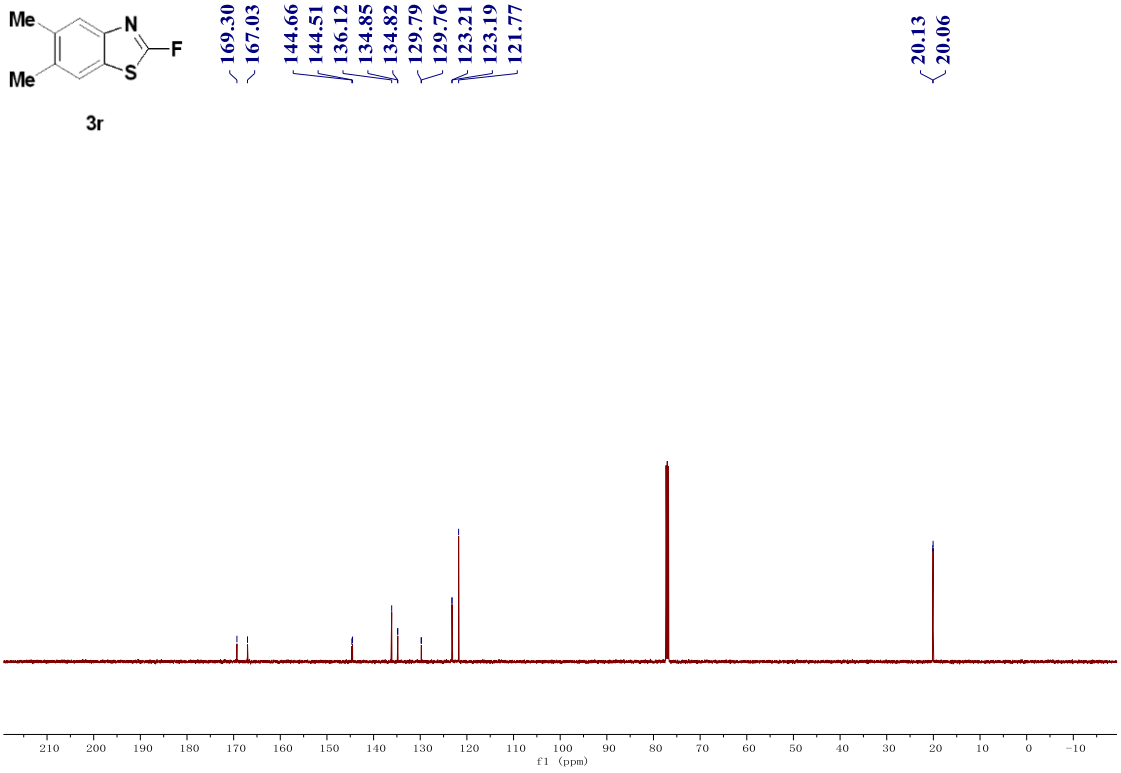

Fig. 96 ^{13}C NMR of **3r** in $CDCl_3$

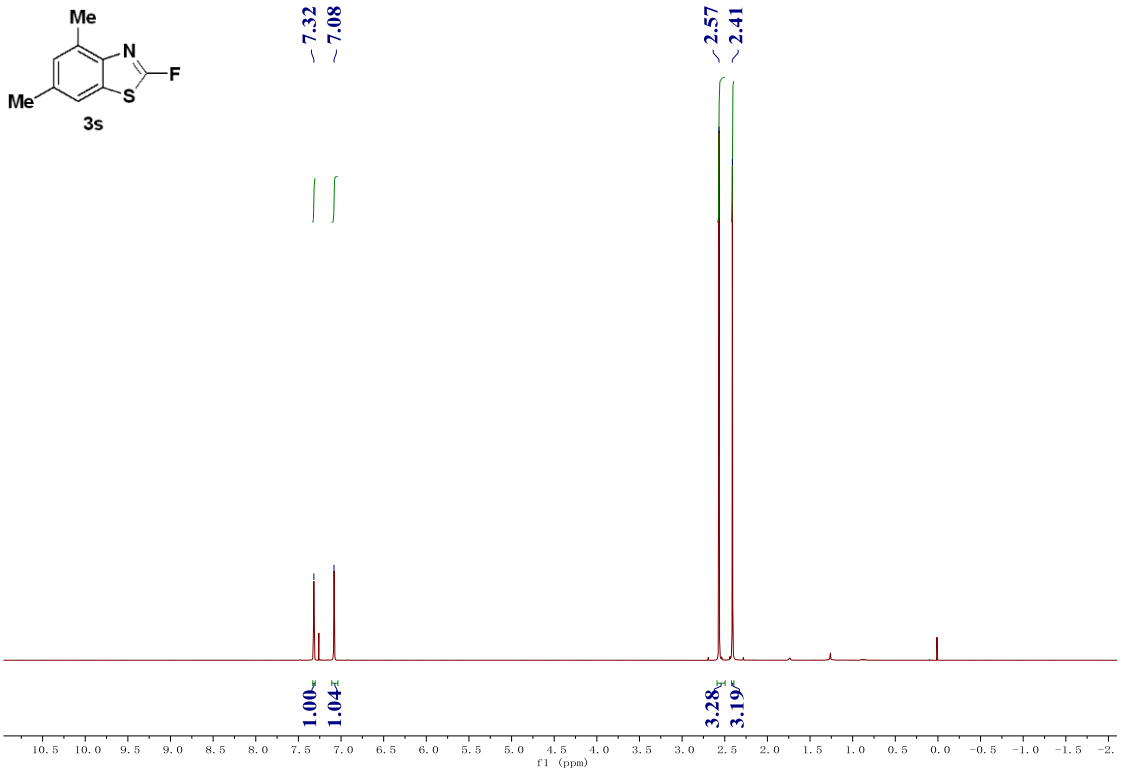

Fig. 97 ^{1}H NMR of **3s** in $CDCl_3$

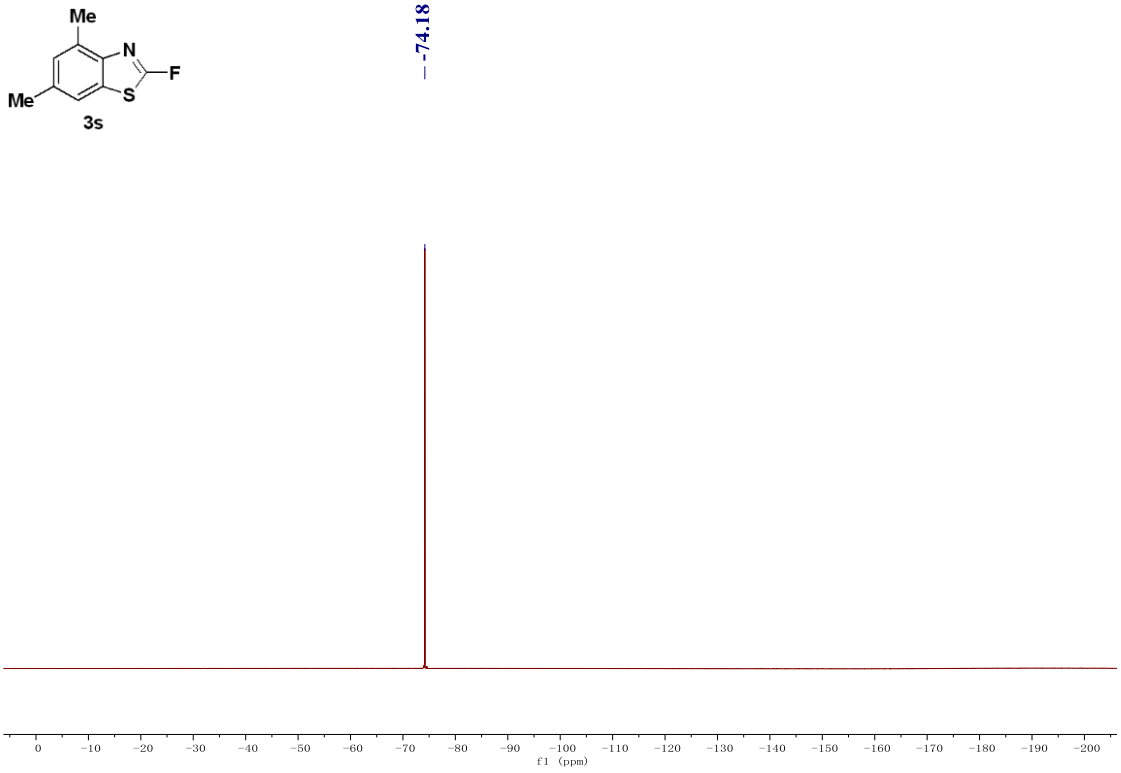

Fig. 98 ^{19}F NMR of **3s** in $CDCl_3$

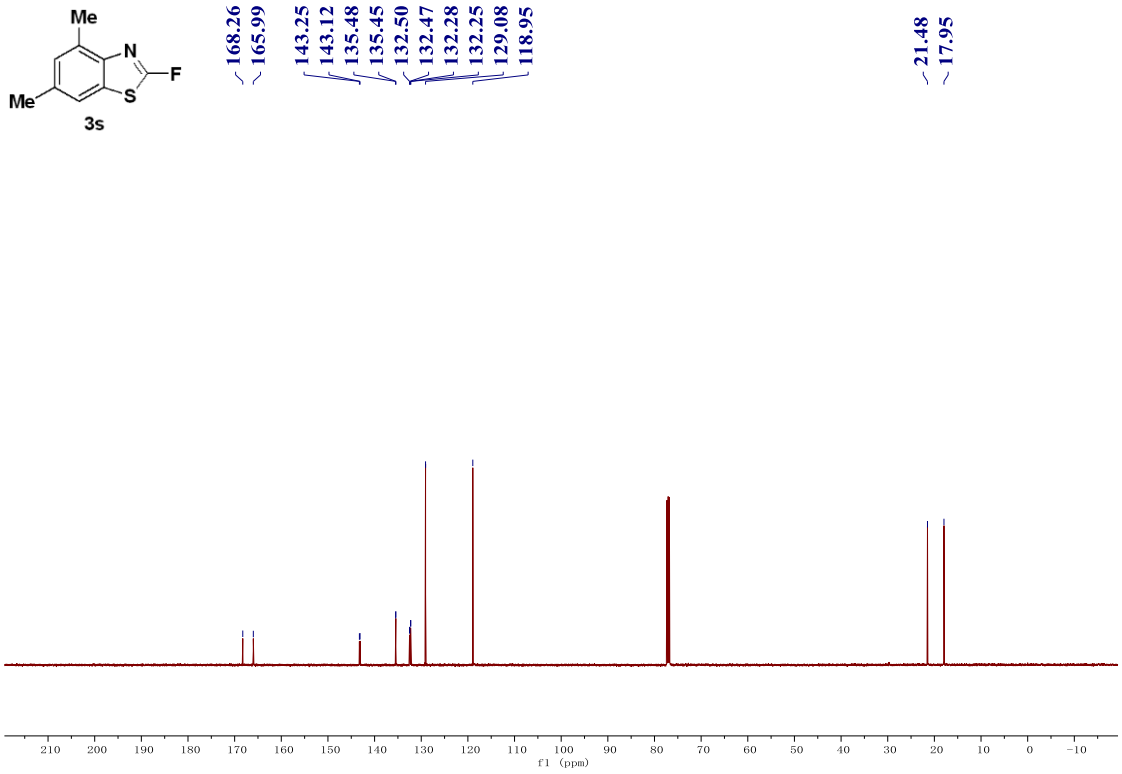

Fig. 99 ^{13}C NMR of **3s** in $CDCl_3$

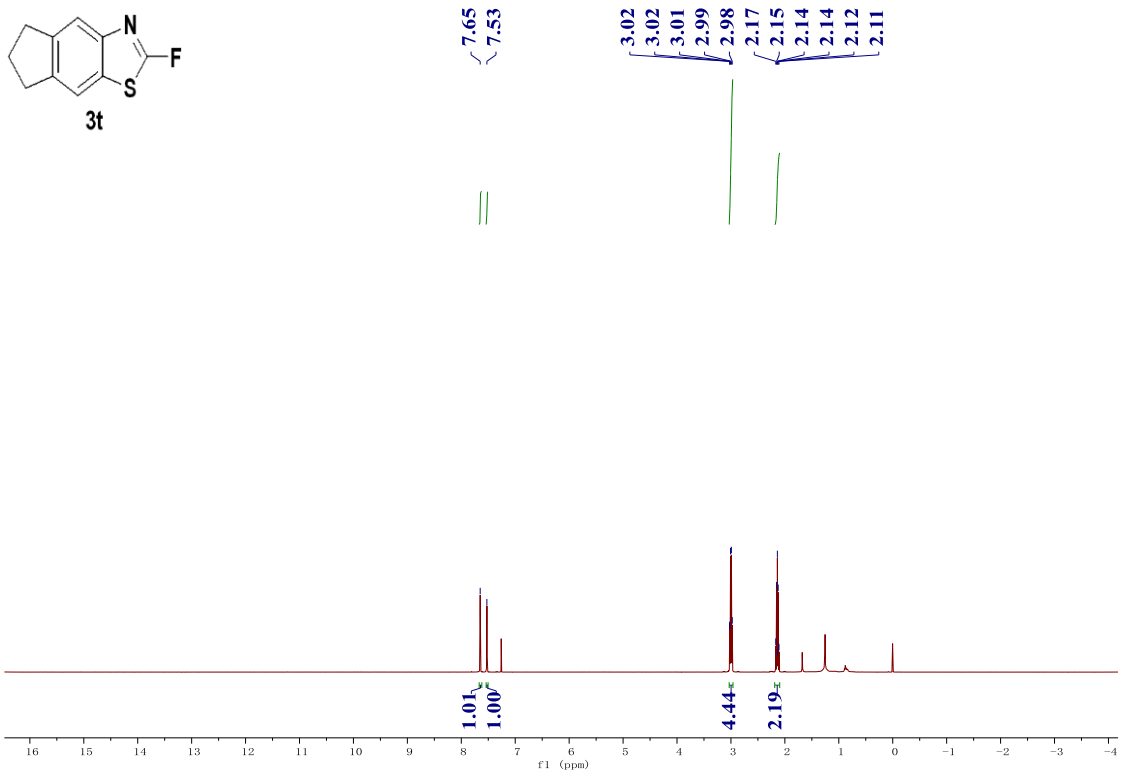

Fig. 100 ^{1}H NMR of **3t** in $CDCl_3$

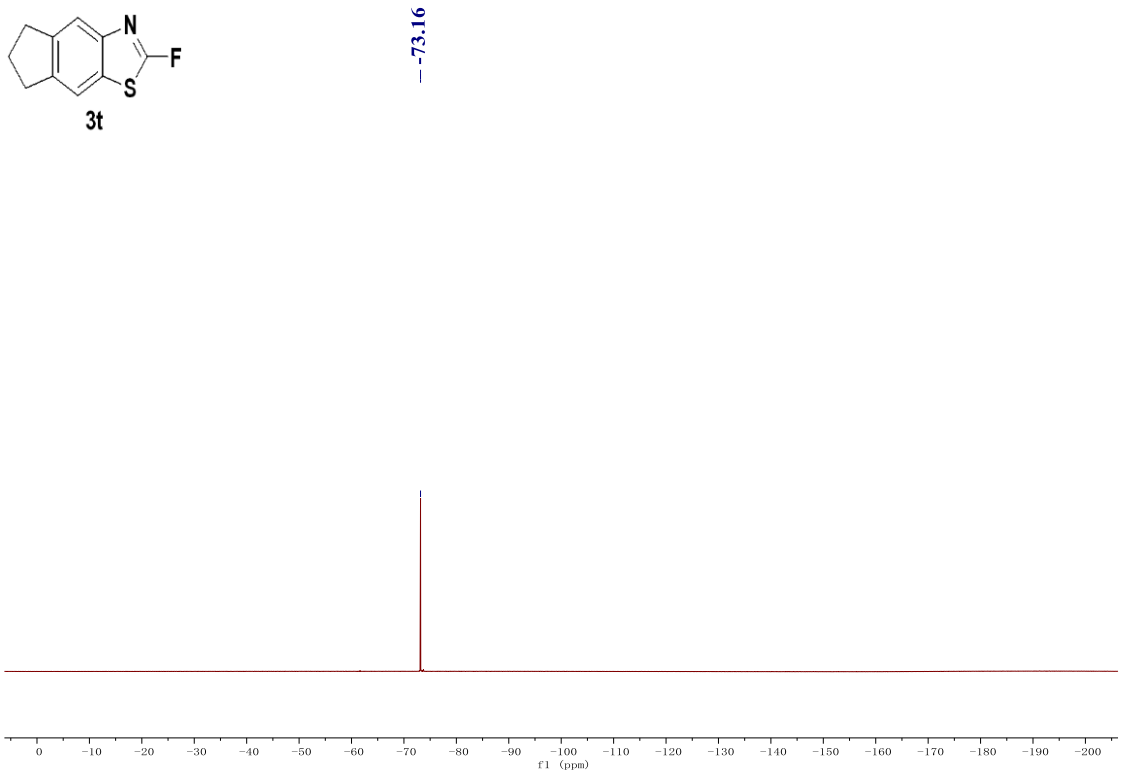

Fig. 101 ^{19}F NMR of **3t** in $CDCl_3$

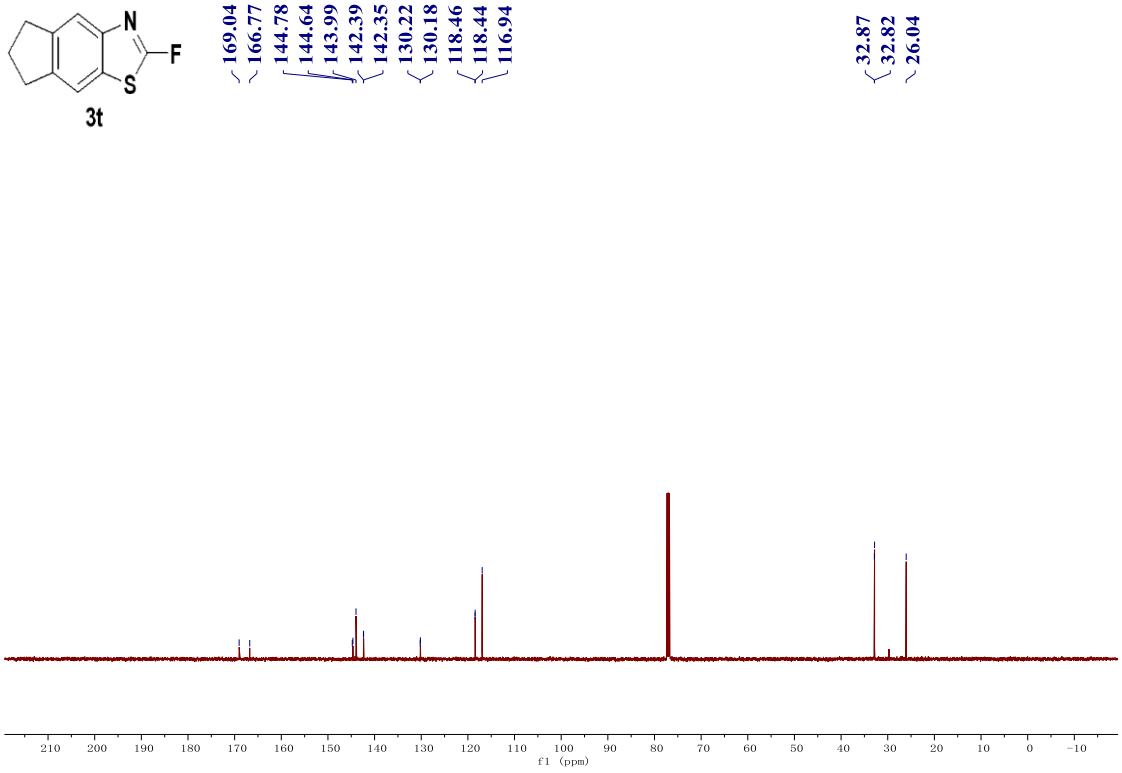

Fig. 102 ^{13}C NMR of **3t** in $CDCl_3$

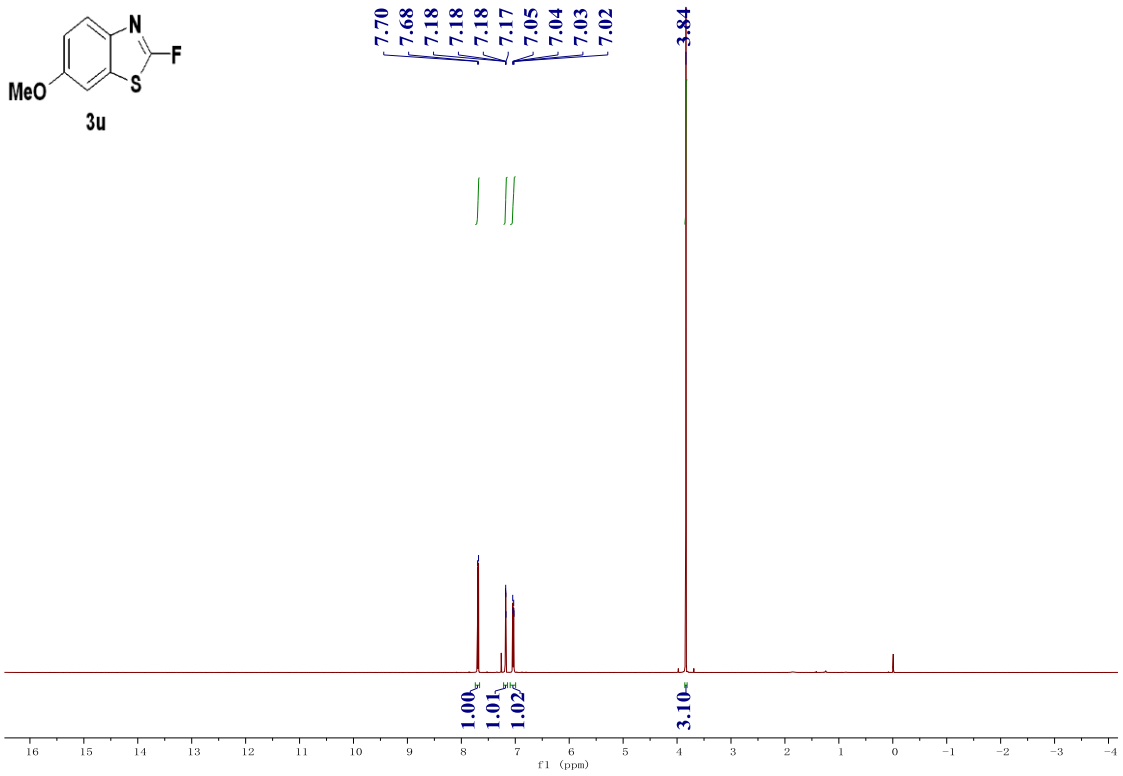

Fig. 103 ^{1}H NMR of **3u** in $CDCl_3$

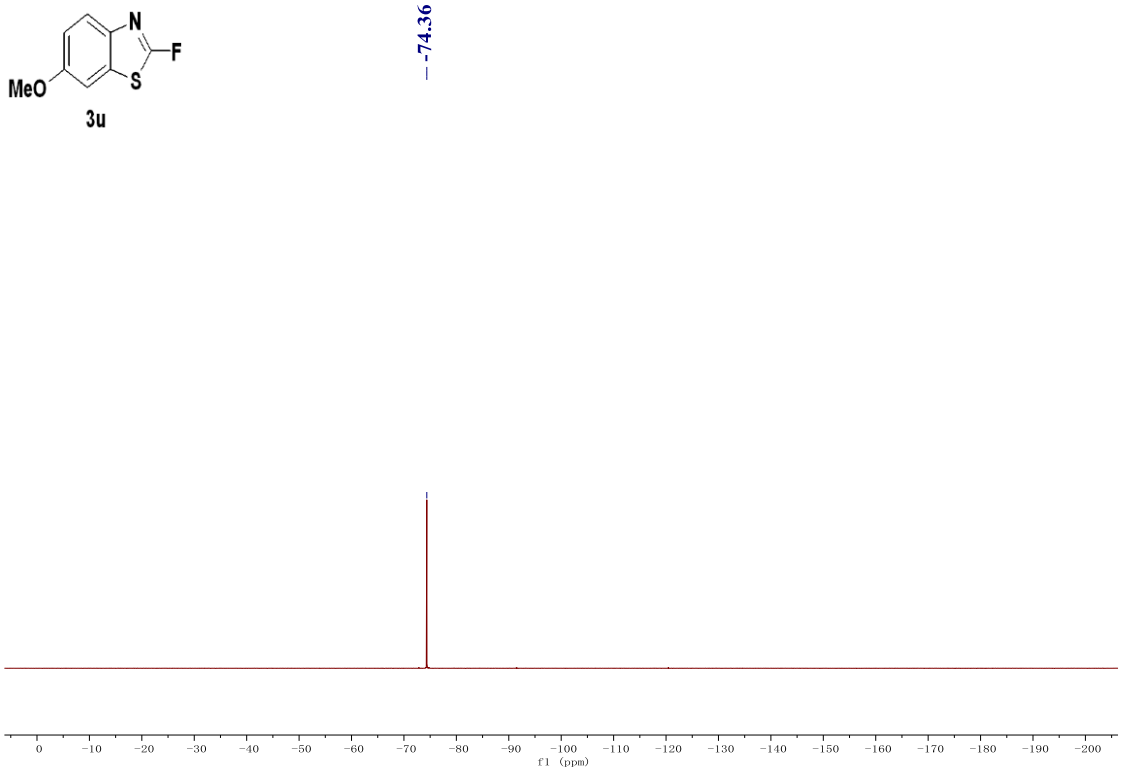

Fig. 104 ^{19}F NMR of **3u** in $CDCl_3$

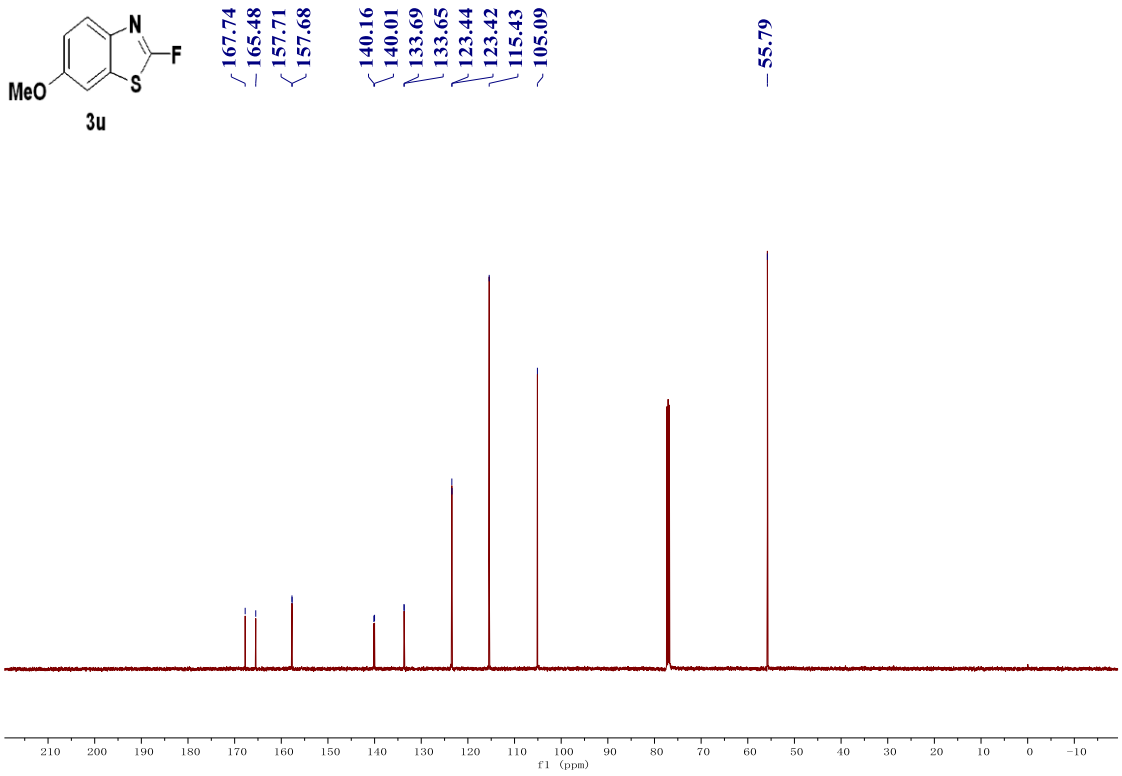

Fig. 105 ^{13}C NMR of **3u** in $CDCl_3$

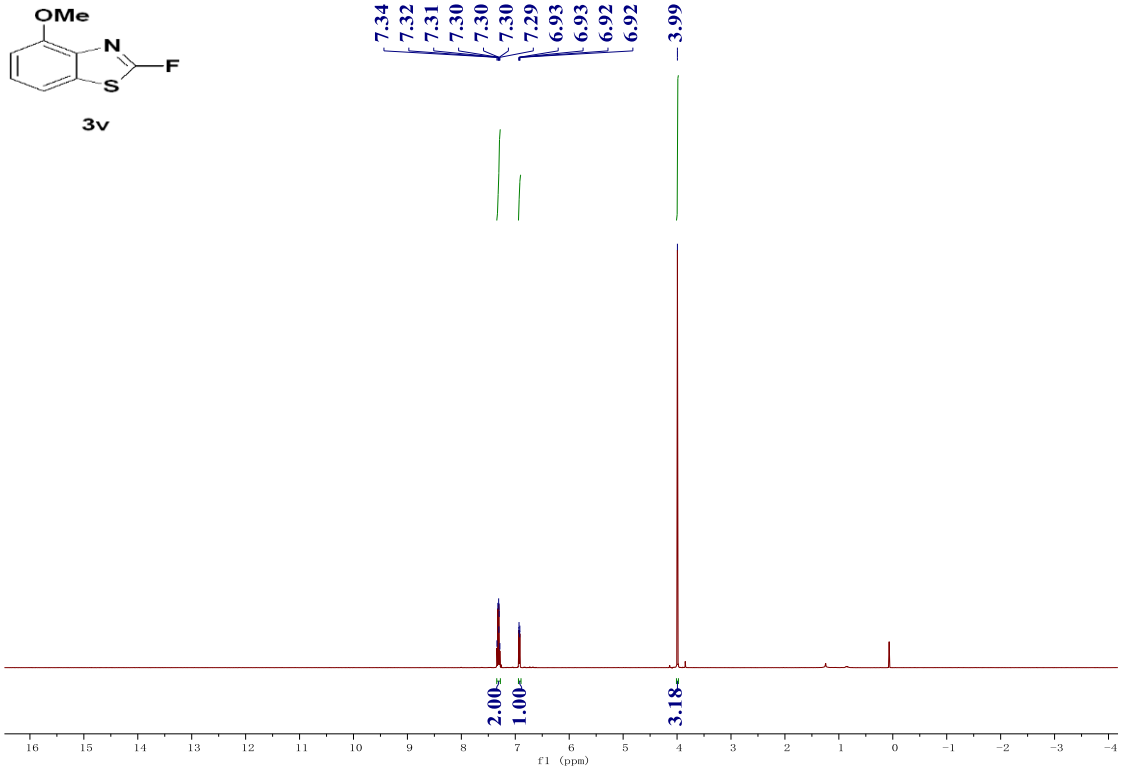

Fig. 106 ^{1}H NMR of **3v** in $CDCl_3$

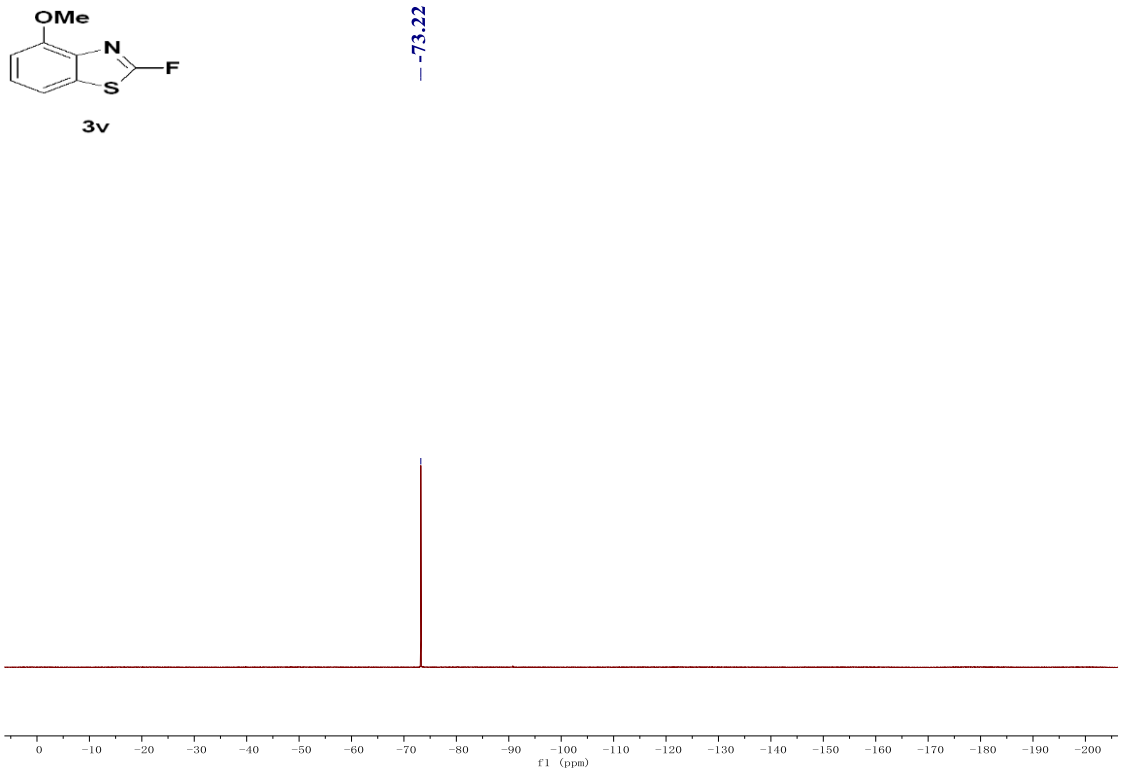

Fig. 107 ^{19}F NMR of **3v** in $CDCl_3$

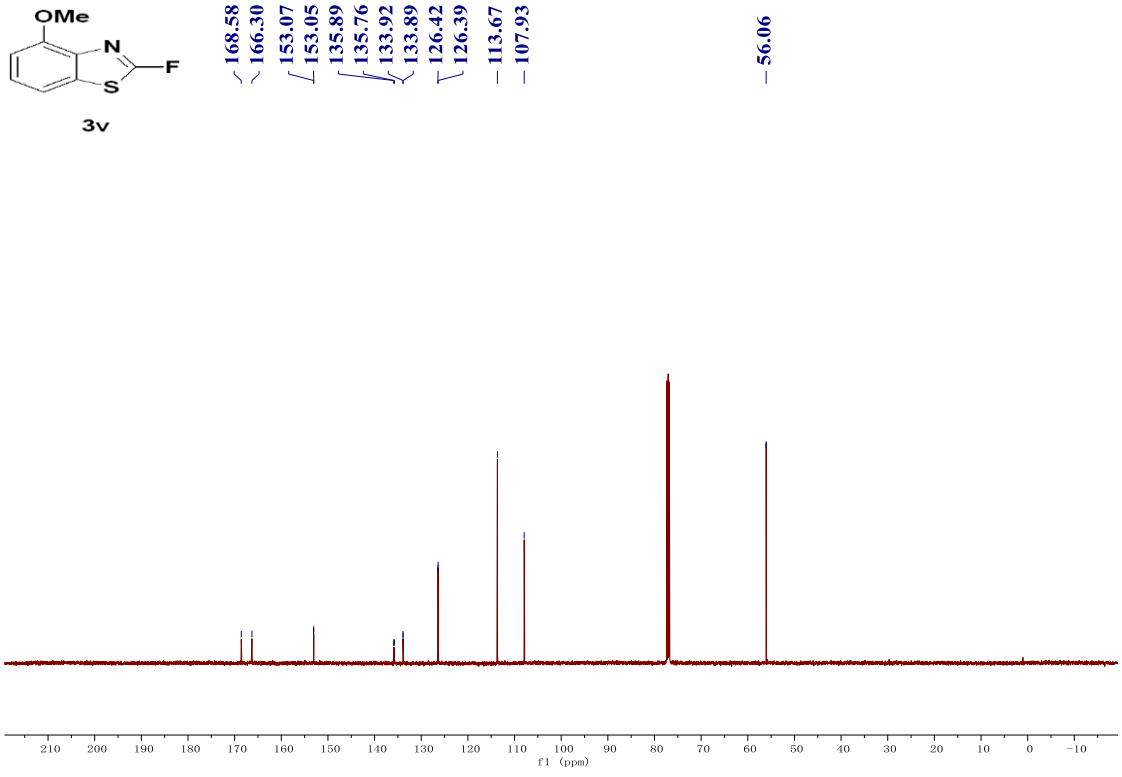

Fig. 108 ^{13}C NMR of **3v** in $CDCl_3$

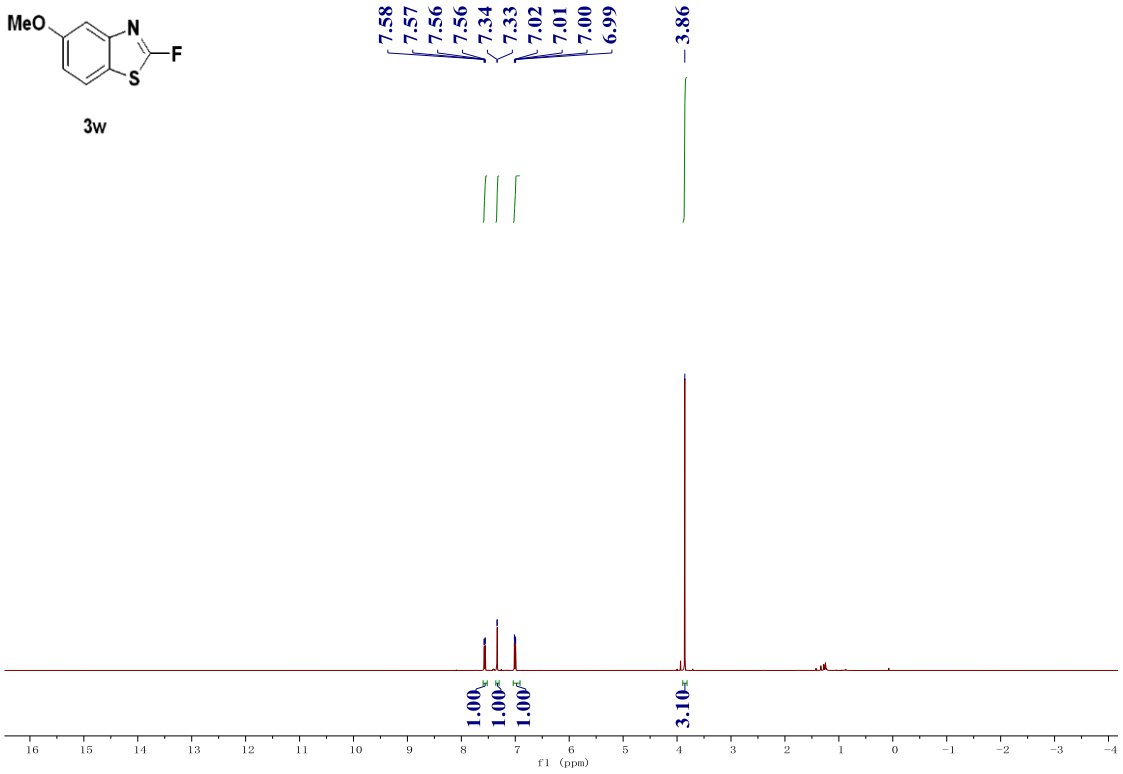

Fig. 109 ^{1}H NMR of **3w** in $CDCl_3$

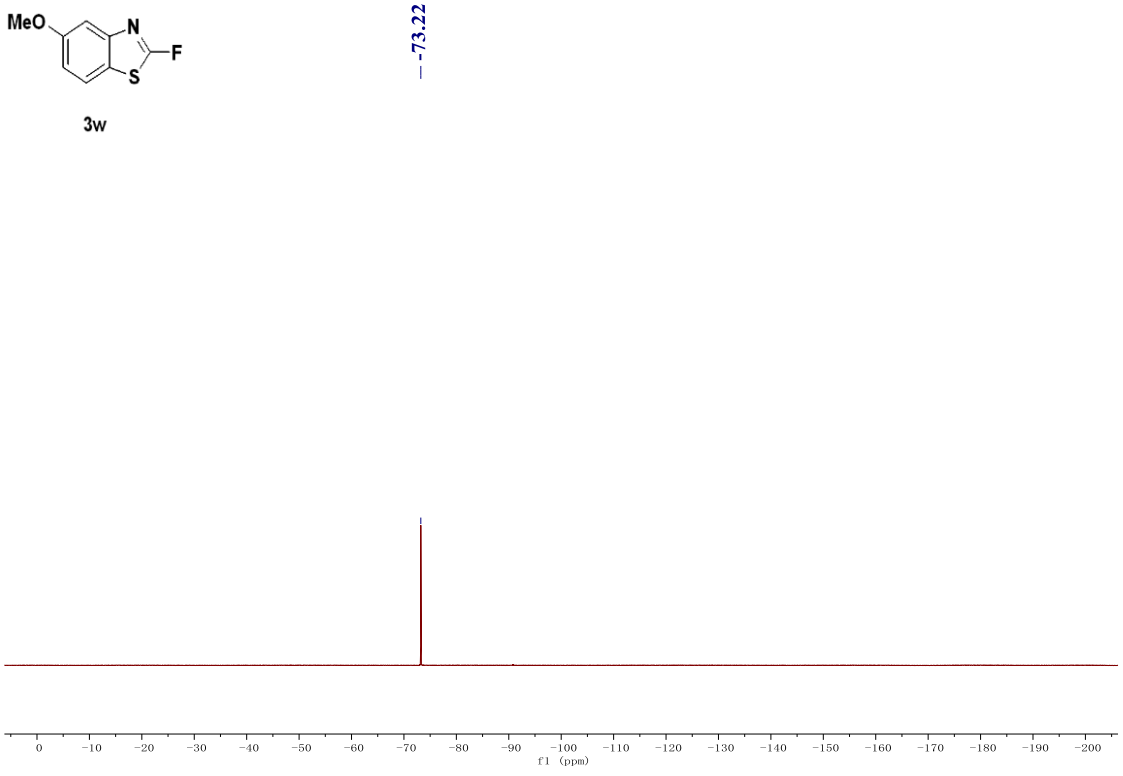

Fig. 120 ^{19}F NMR of **3w** in $CDCl_3$

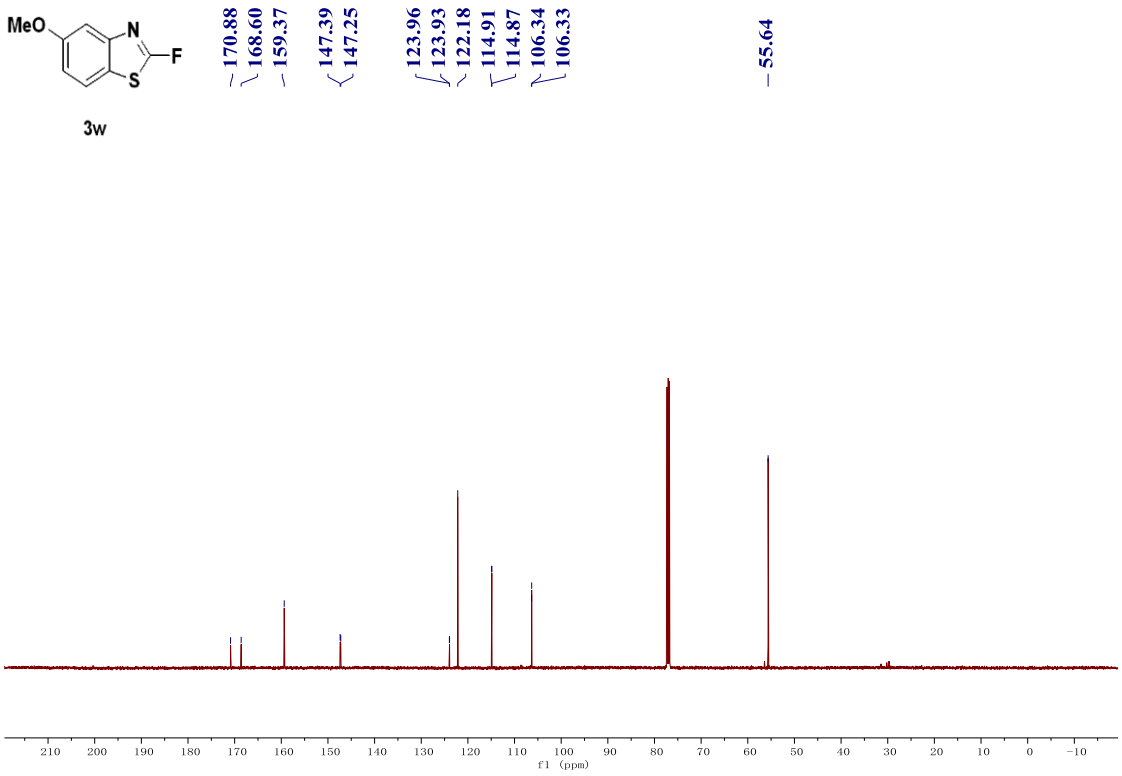

Fig. 121 ^{13}C NMR of **3w** in $CDCl_3$

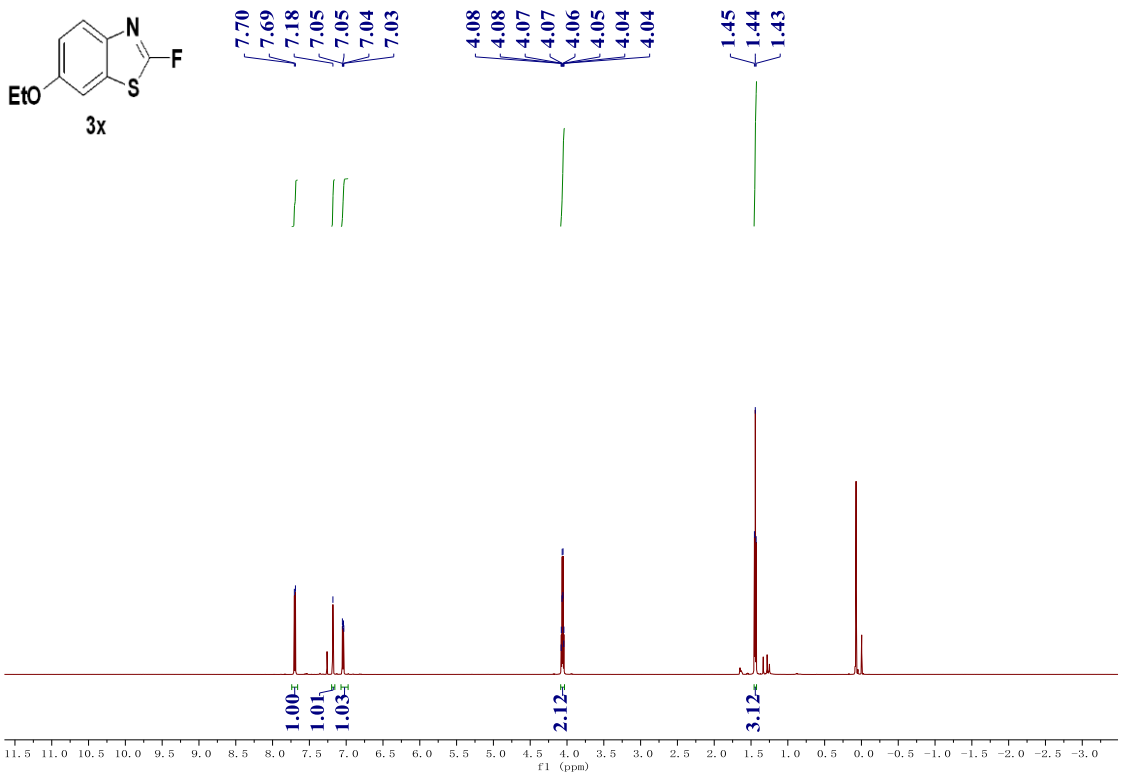

Fig. 122 ^{1}H NMR of **3x** in $CDCl_3$

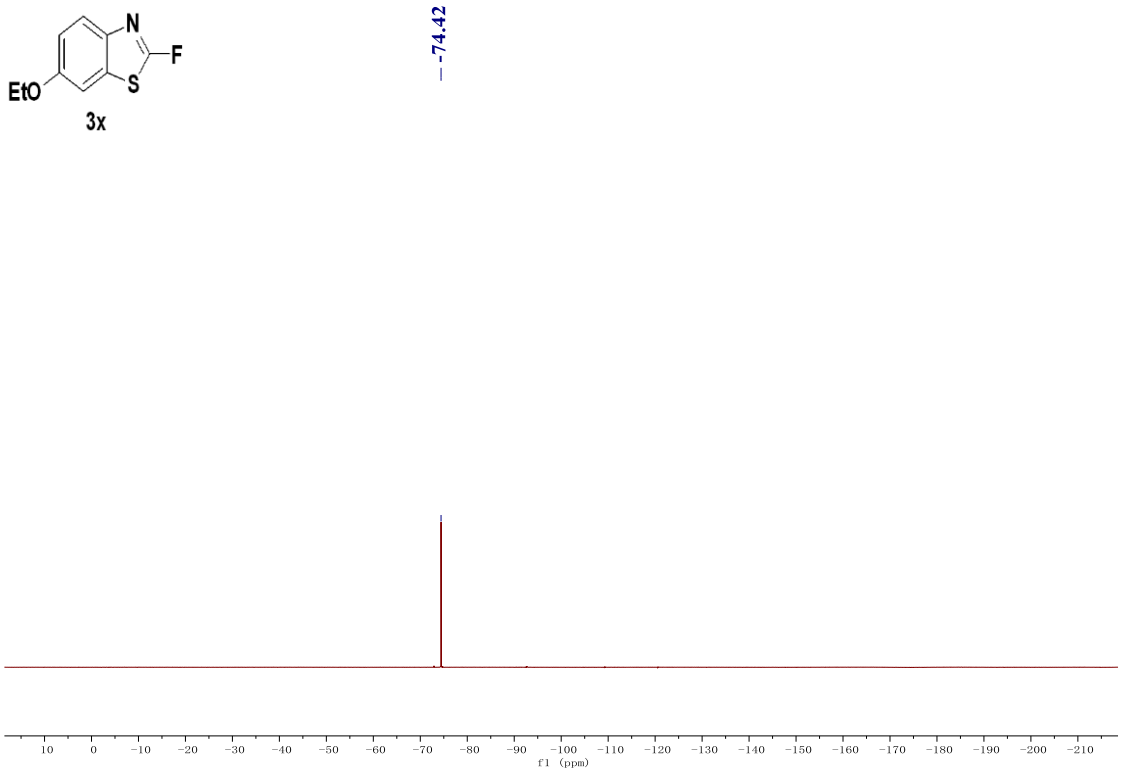

Fig. 123 ^{19}F NMR of **3x** in $CDCl_3$

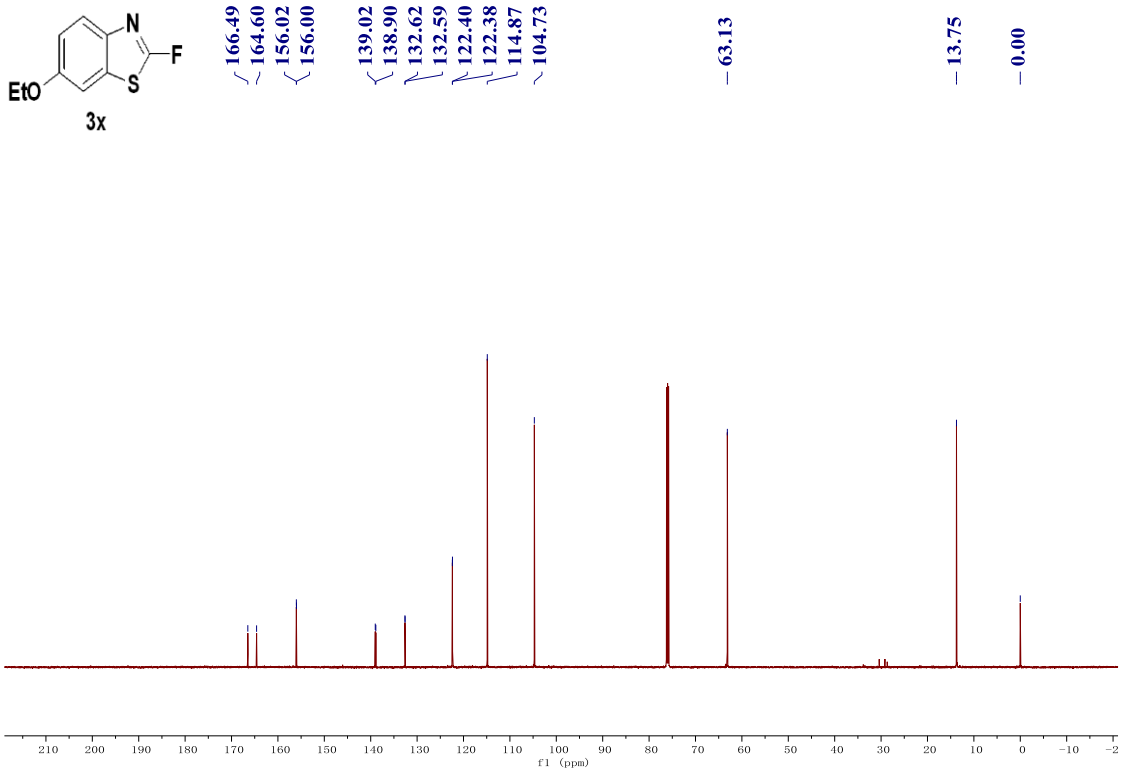

Fig. 124 ^{13}C NMR of **3x** in $CDCl_3$

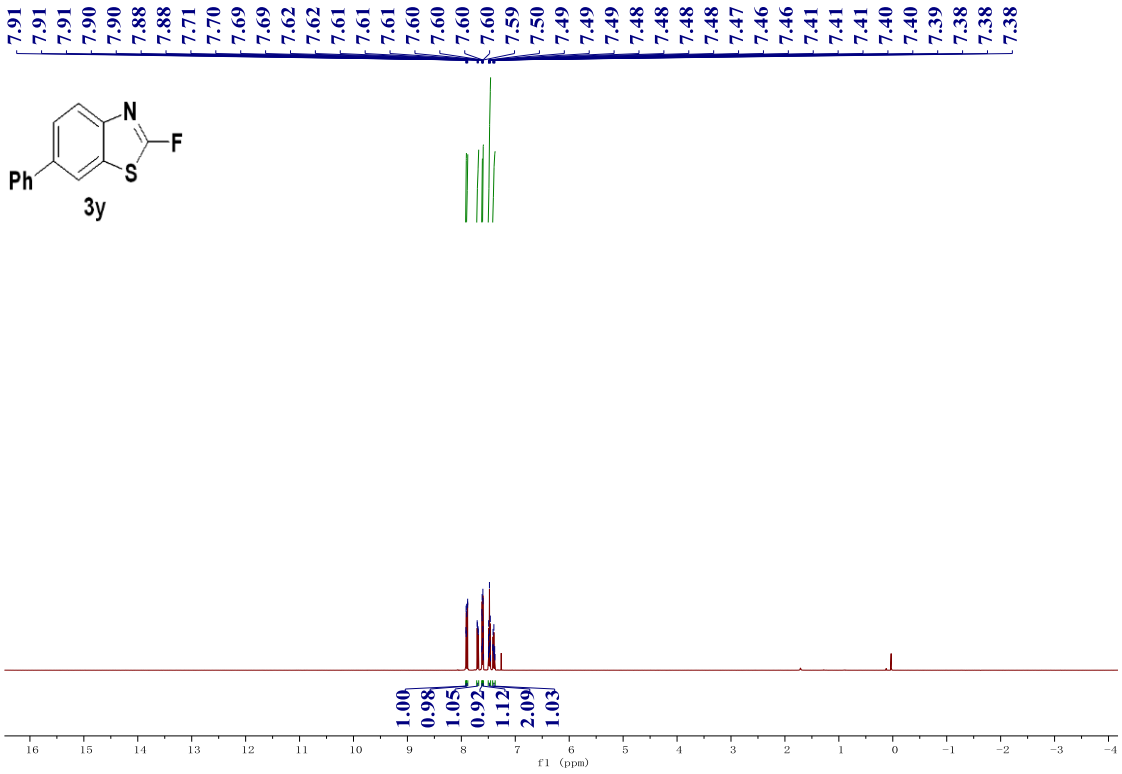

Fig. 125 ^{1}H NMR of **3y** in $CDCl_3$

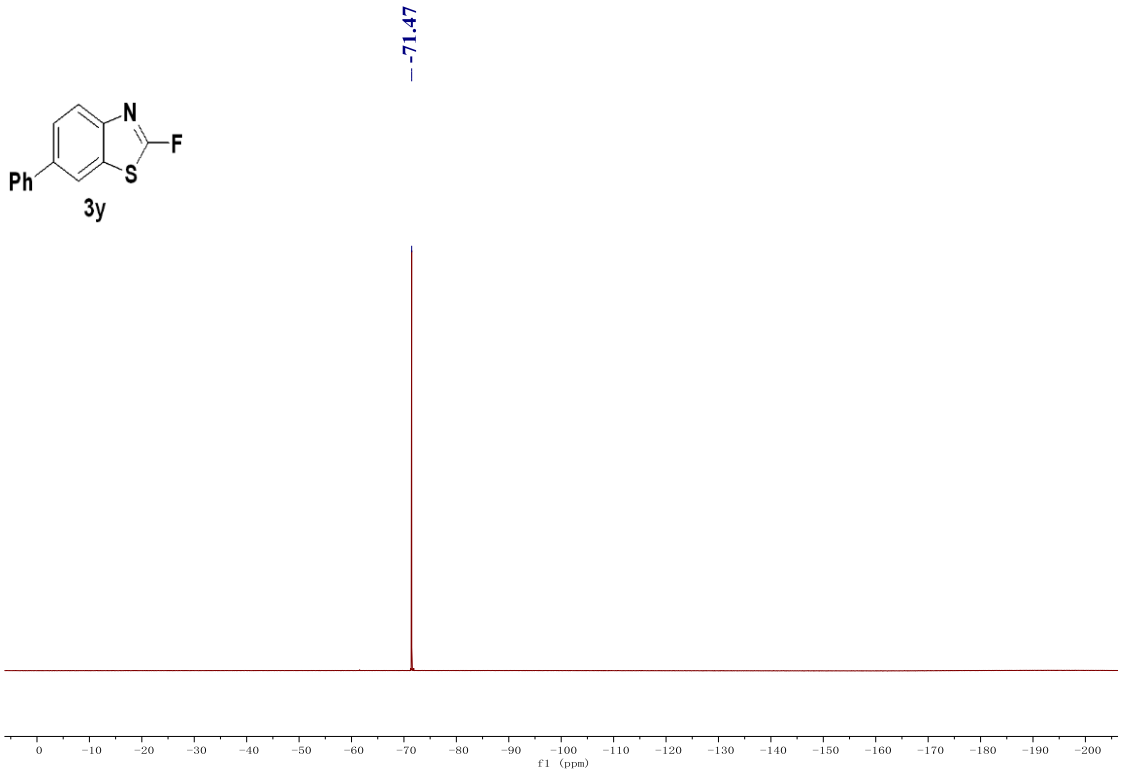

Fig. 126 ^{19}F NMR of **3y** in $CDCl_3$

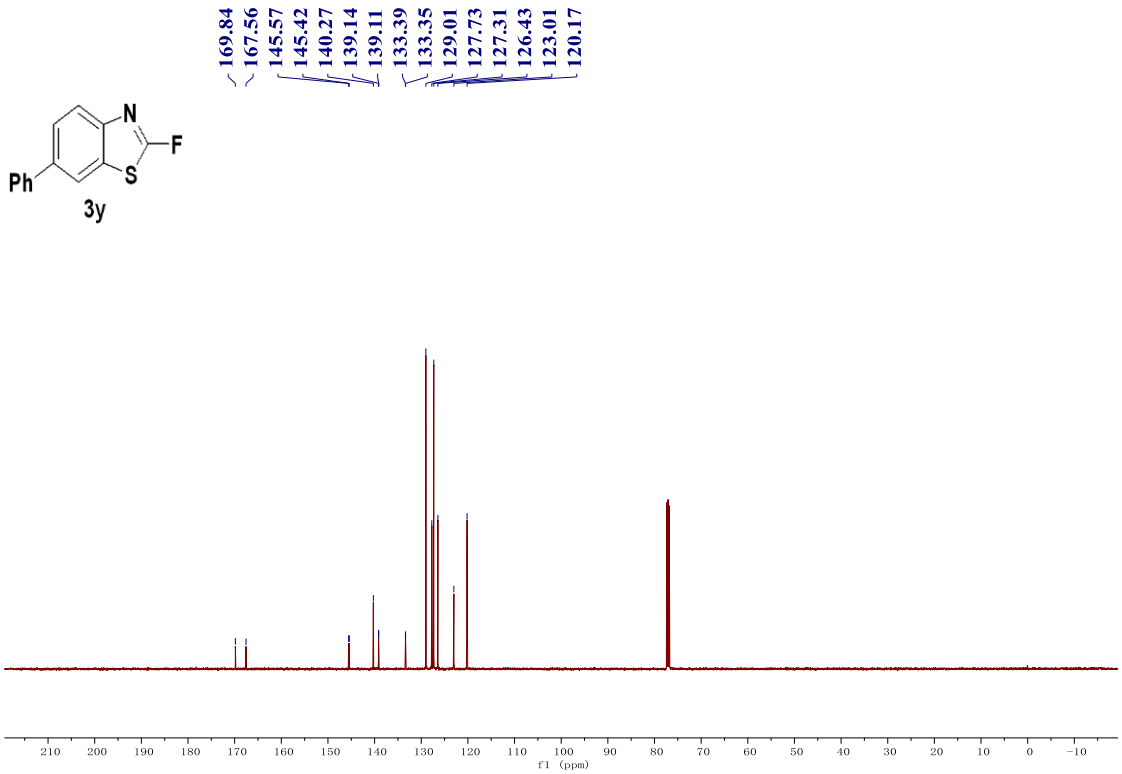

Fig. 127 ^{13}C NMR of **3y** in $CDCl_3$

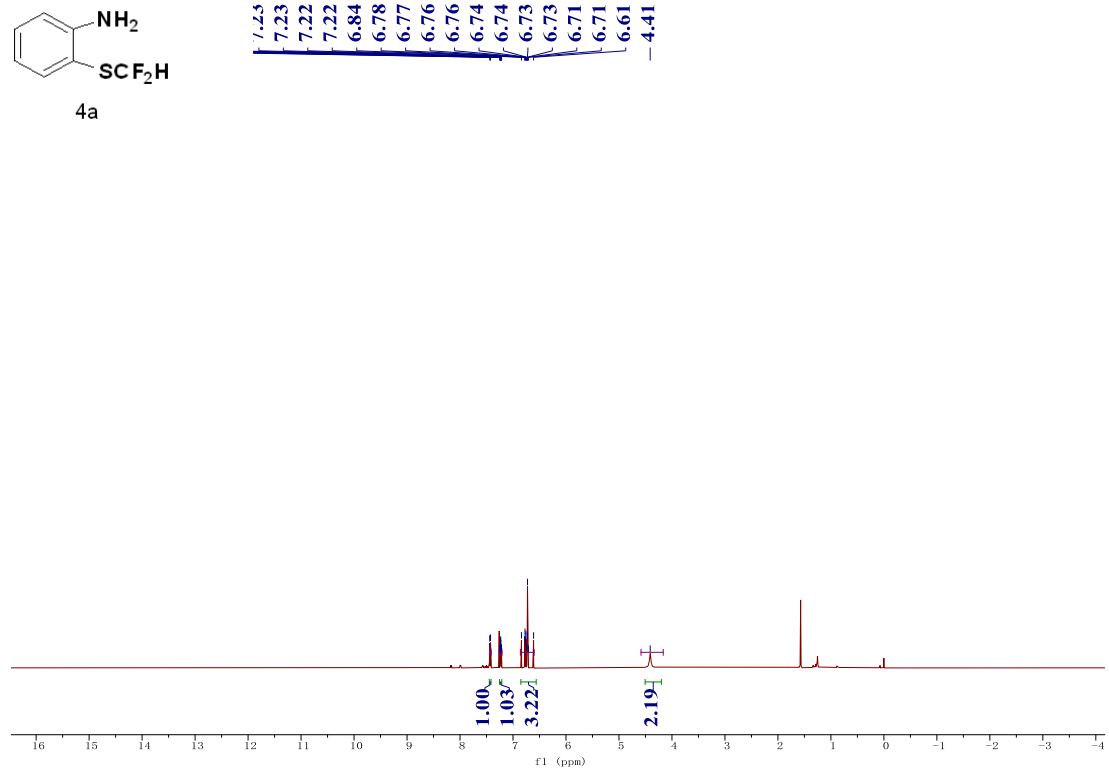

Fig. 128 ^{1}H NMR of **4a** in $CDCl_3$

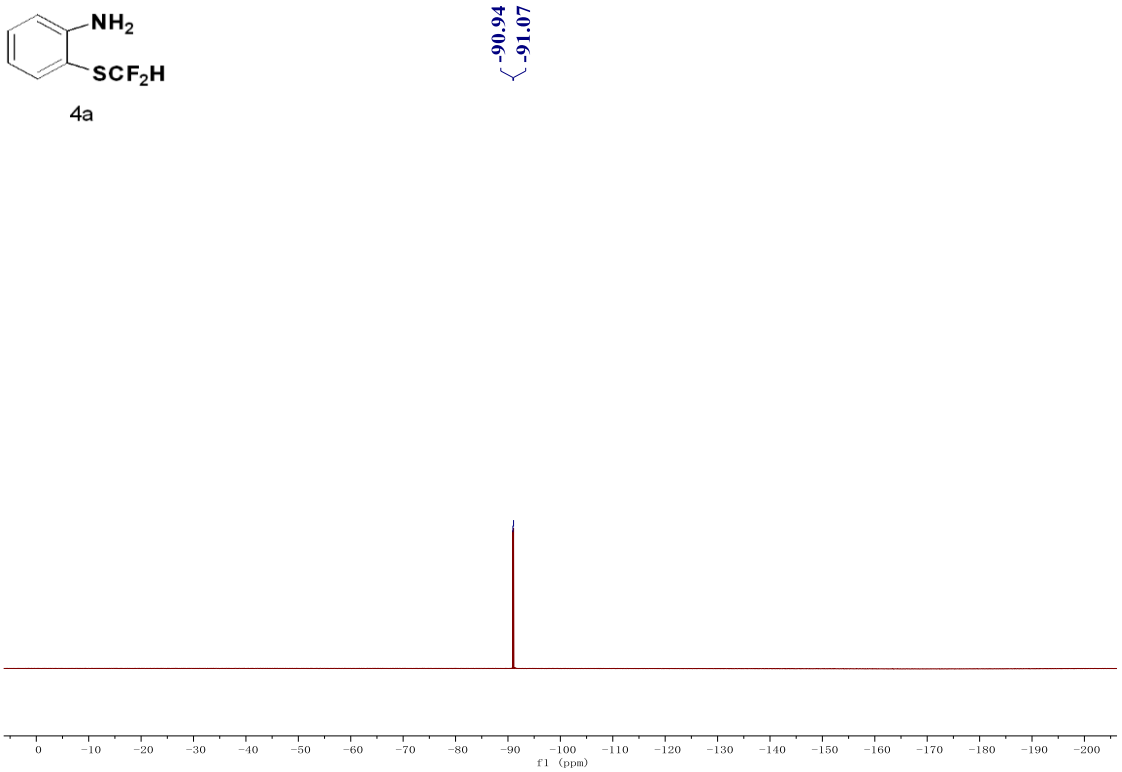

Fig. 129 ^{19}F NMR of **4a** in $CDCl_3$

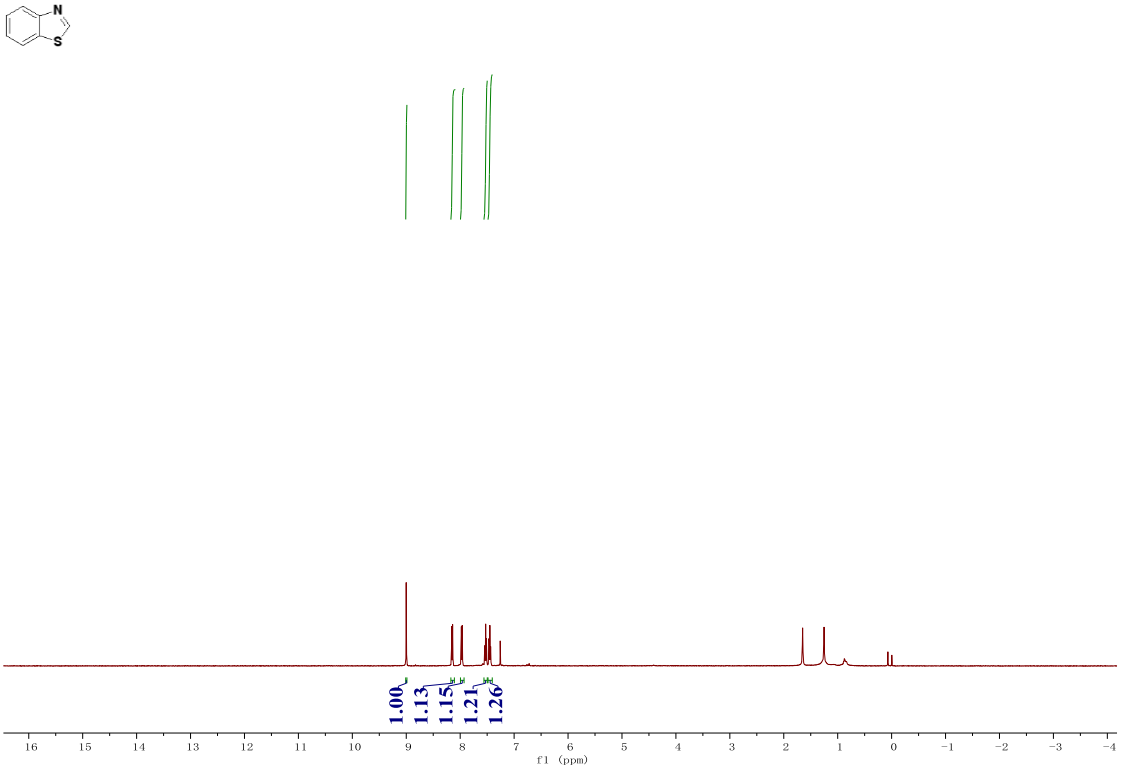

Fig. 130 ^{1}H NMR of **5a** in $CDCl_3$