Supporting Information

for

Photoredox-Catalyzed Intermolecular Dearomative Trifluoromethycarboxylation of Indoles and Heteroanalogues with CO_2 and Fluorinated Radical Precursors

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1. General information and procedure

1.1 General information

All reactions were carried out in dried Schlenk tube. All solvents were dried before use according to the standard methods. Unless otherwise noted, the starting materials were commercially available and used without further purification. Glass 0.25 mm silica gel plates were employed for thin layer chromatography (TLC). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether, ethyl acetate, and alcohol.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR data were recorded on a 400 MHz spectrometer with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and D-solvent peaks, respectively. Abbreviations used for signal multiplicity. ^{1}H and ^{19}F NMR: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublets of doublets, and m = multiplet.

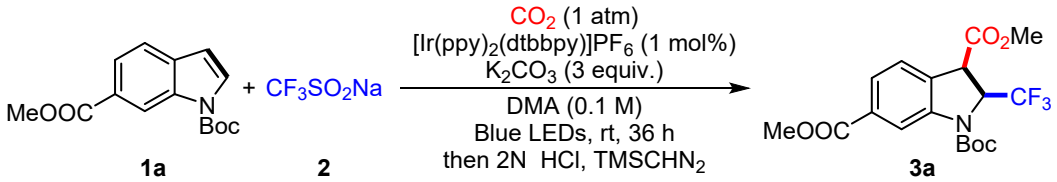
Information about the photoreactor: the photoreactor (Type H106065) used in this research was purchased from GeAo Chem, Wuhan, China. The photoreactor was made up of 8 blue LED bulbs (5 W for each) with a cooler fan to keep room temperature. Spectral distribution: 415 - 430 nm. In the reaction, each Schlenk tube is mainly irradiated by one of the light bulbs. The approximate distance of the tube to the closest light bulb is 2 cm. A magnetic stirrer is placed under the photoreactor to keep the reaction being stirred.

1.2 General procedure for synthesis of starting materials[1]

A mixture of indole (5.0 mmol), Boc_2O (1.2 g, 5.5 mmol) and DMAP (61 mg, 0.50 mmol) in THF (20 mL) was stirred at room temperature for 12 h. H_2O was then added, and the product was extracted with ethyl acetate. After washed with sat. aq. $NaHCO_3$ and brine, the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under reduce pressure. The purification of the crude mixture by silica gel

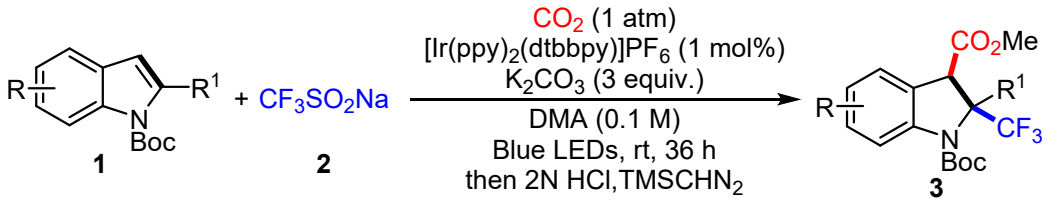
column chromatography provided Boc-protected indoles **1** (>90% yield).

1.3 Typical procedure for reaction optimization



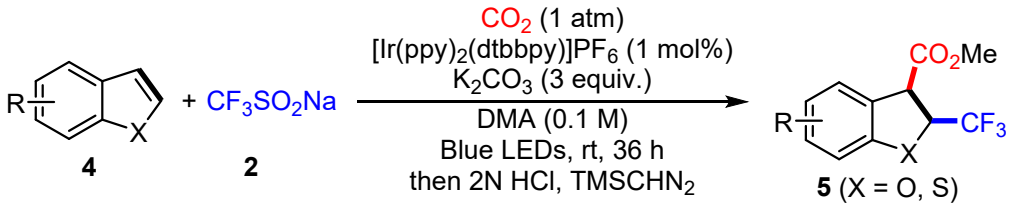
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA (1 mL, bubbled with CO_2 for 5 min before use) and **1a** (27.5 mg, 0.1 mmol) were added to the tube under a CO_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the yields were determined by crude ^1H NMR using CH_2Br_2 as internal standard.

1.4 General procedure for evaluation of substrate scope

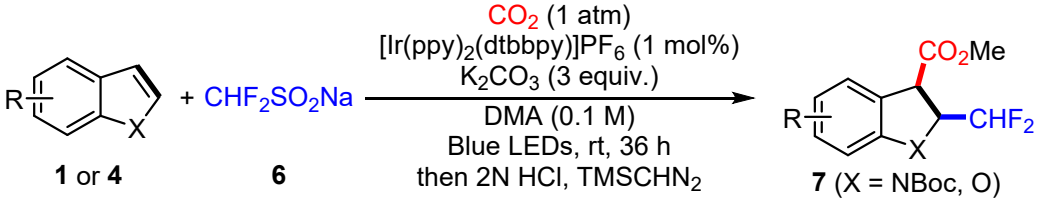


To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (2 mg, 0.002 mmol), CF_3SO_2Na (78.0 mg, 0.5 mmol) and K_2CO_3 (83.0 mg, 0.6 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA (2 mL, bubbled with CO_2 for 5 min before use) and **1** (0.2 mmol) were added to the tube under a CO_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 M HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and

concentrated under reduced pressure. After esterification, the reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to afford the desired product **3**. All of the products were characterized by NMR techniques.



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (2 mg, 0.002 mmol), CF_3SO_2Na (78.0 mg, 0.5 mmol) and K_2CO_3 (83.0 mg, 0.6 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA (2 mL, bubbled with CO_2 for 5 min before use) and **4** (0.2 mmol) were added to the tube under a CO_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 M HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to afford the desired product **5**. All of the products were characterized by NMR techniques.



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (2 mg, 0.002 mmol), CHF_2SO_2Na (110.4 mg, 0.8 mmol) and K_2CO_3 (83.0 mg, 0.6 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA (2 mL, bubbled with CO_2 for 5 min before use) and **1** or **4** (0.2 mmol) were added to the tube under a CO_2 atmosphere. The reaction tube was

sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 M HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to afford the desired product **7**. All of the products were characterized by NMR techniques.

2. Mechanistic studies

2.1 Radical termination with TEMPO

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA (1 mL, bubbled with CO_2 for 5 min before use), **1a** (27.5 mg, 0.1 mmol) and TEMPO (46.9 mg, 0.3 mmol) were added to the tube under a CO_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the yields were determined by crude ^1H NMR using CH_2Br_2 as internal standard. Also, the crude product was tested by ESI.

2.2 Isotope labelling experiments with D_2O

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol), the tube was evacuated and filled N_2 for three times. Then the anhydrous DMA (1 mL, bubbled with CO_2 for 5 min before use), **1a** (27.5 mg, 0.1 mmol) and D_2O were added to the tube under a N_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent, the deuterium ratio was determined by ^1H NMR.

^{1}H NMR (10 equiv. D_2O)

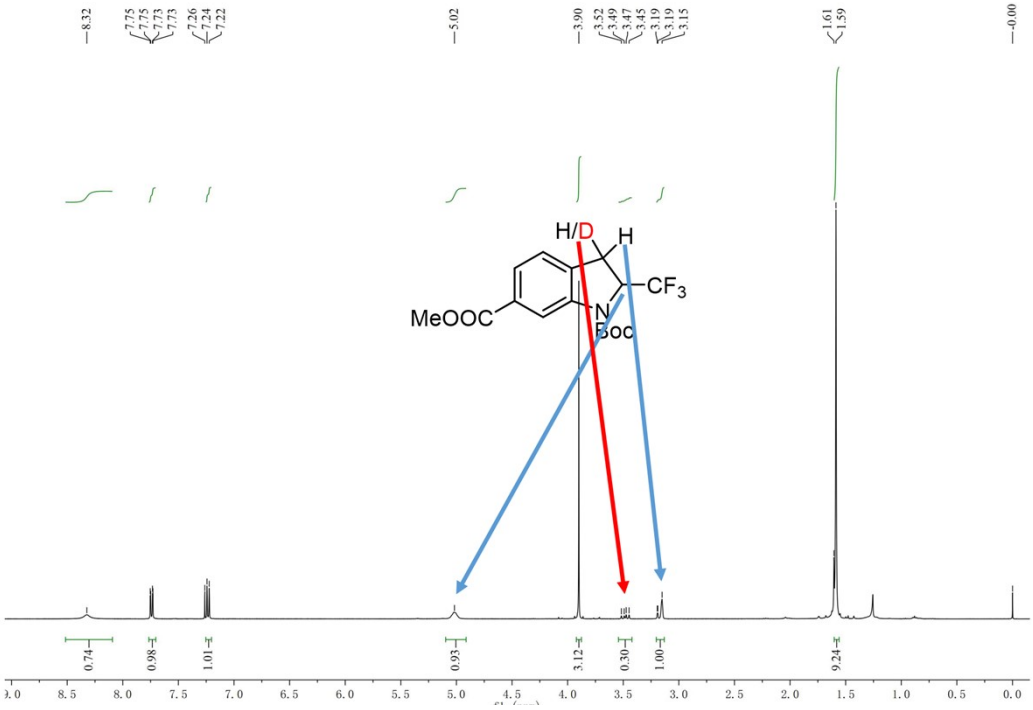


Figure S1

^{1}H NMR (20 equiv. D_2O)

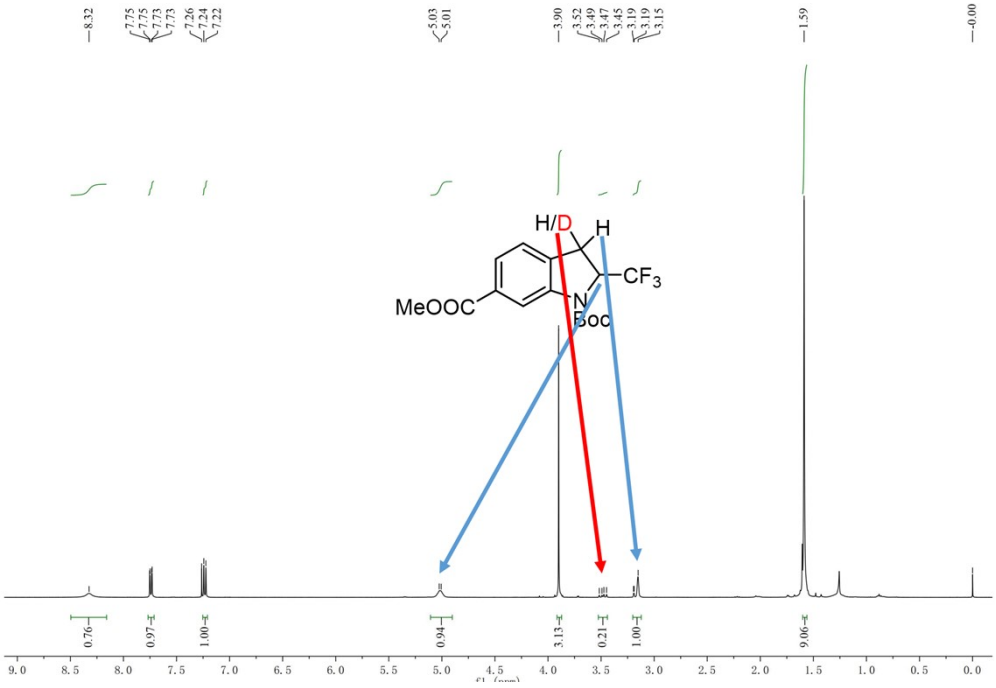


Figure S2

2.3 Using aldehyde as electrophile instead of CO_2

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol), the tube was evacuated and filled N_2 for three times. Then the anhydrous DMA (1 mL, bubbled with CO_2 for 5 min before use), **1a** (27.5 mg, 0.1 mmol) and aldehyde (42.4 mg, 0.4mmol) were added to the tube under a N_2 atmosphere. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to afford the desired product **9a**. Then the product was characterized by NMR techniques.

2.4 Reaction with $^{13}CO_2$

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol), the tube was evacuated and filled CO_2 for three times. Then the anhydrous DMA and **1a** (27.5 mg, 0.1 mmol) were added to the tube under a CO_2 atmosphere. Next, $^{13}CO_2$ was bubbled to the solvent by a 5 mL injection syringe for 3 times. The reaction tube was sealed and stirred at room temperature under blue LEDs (5 W) for 36 h. After completion, the reaction was carefully quenched with 2 N HCl and the mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the crude mixture was determined by ^{13}C NMR.

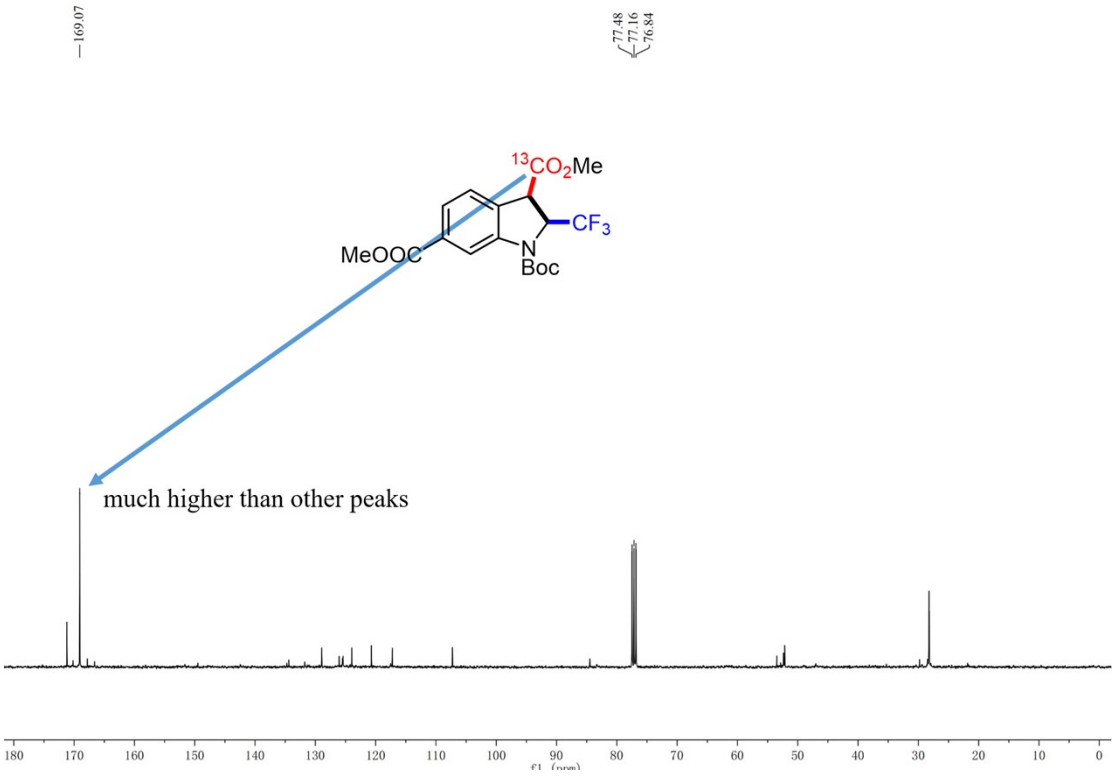


Figure S3

2.5 Stern-Volmer Fluorescence quenching experiments[2]

Fluorescence quenching experiments were tested on a LS (PERKINELMER(HK)LTD) Spectrofluorophotometer with a 4 mL quartz cuvette with a cap. $Ir(ppy)_2(dtbbpy)PF_6$ was irradiated at 435 nm and the emission intensity at about 575 nm was observed. In a typical experiment, the emission spectrum of a 2×10^{-5} M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in anhydrous DMA was collected.

CF_3SO_2Na: A stock solution of CF_3SO_2Na (1×10^{-2} M) was prepared. Then, different amounts of this stock solution were added to 3 mL of $Ir(ppy)_2(dtbbpy)PF_6$ in DMA (2×10^{-5} M).

1a: A stock solution of **1a** (0.5 M) was prepared. Then, different amounts of this stock solution were added to 2.5 mL of $Ir(ppy)_2(dtbbpy)PF_6$ in DMA (2×10^{-5} M).

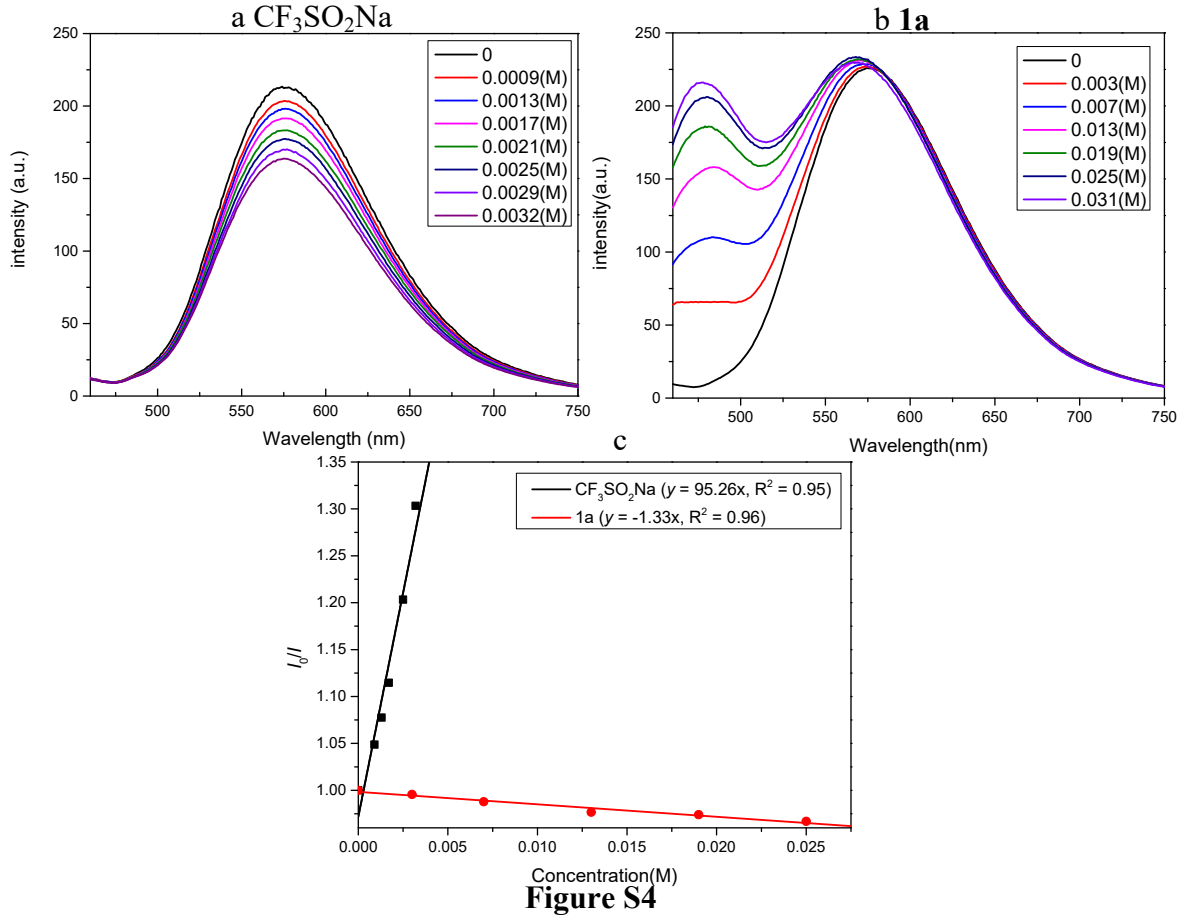


Figure S4

a. Steady-state Stern–Volmer experiment of $Ir(ppy)_2(dtbbpy)PF_6$ and CF_3SO_2Na.

b. Steady-state Stern–Volmer experiment of $Ir(ppy)_2(dtbbpy)PF_6$ and **1a**.

c. Comparison of quenching efficiency of CF_3SO_2Na and **1a**.

2.6 Light on-off experiments

To six 25 mL-Schlenk tubes equipped with a magnetic stir bar were added $Ir(ppy)_2(dtbbpy)PF_6$ (1 mg, 0.001 mmol), CF_3SO_2Na (39.0 mg, 0.25 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) respectively, the tubes were evacuated and filled CO_2 for three times. Then the anhydrous DMA (1 mL, bubbled with CO_2 for 5 min before use) and **1a** (27.5 mg, 0.1 mmol) were added to the tubes under a CO_2 atmosphere. The reaction tubes were sealed and stirred at room temperature under blue LEDs (5 W). Turn on/off the blue LEDs every 2 hours and quenched one reaction with 2 N HCl at the same time until all the reactions were quenched. Each reaction mixture was extracted with ethyl acetate (3 x 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After esterification, the yields were determined by crude ^1H NMR using CH_2Br_2 as internal standard.

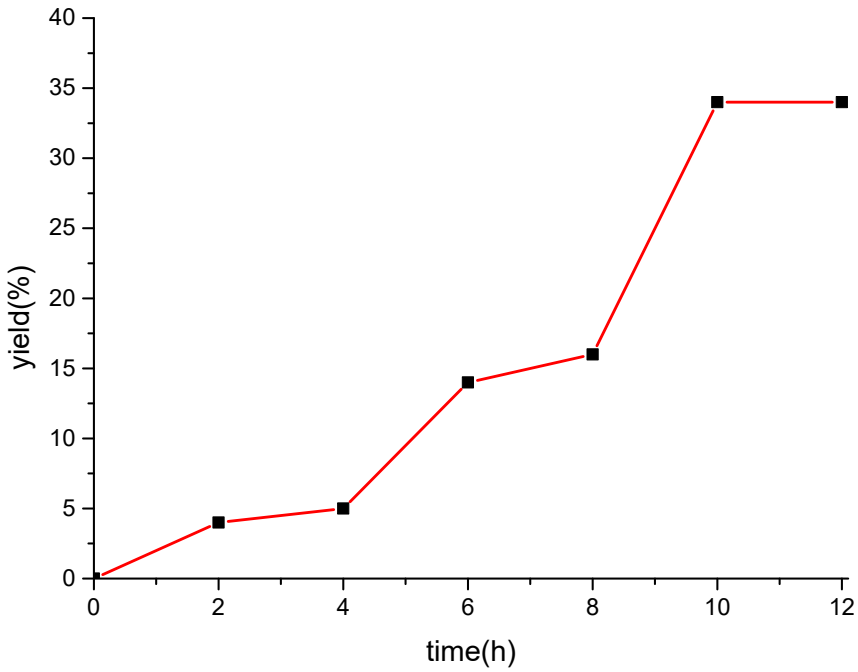


Figure S5. Light On-off Curve

2.7 Characterization with UV-Vis spectroscopy

The UV-Vis spectra of $Ir(ppy)_2(dtbbpy)PF_6$ with/without **1a** in DMA were collected by using the following parameter set: scan rate 600 nm·min^{-1}, band width 2.0 nm, baseline correction.

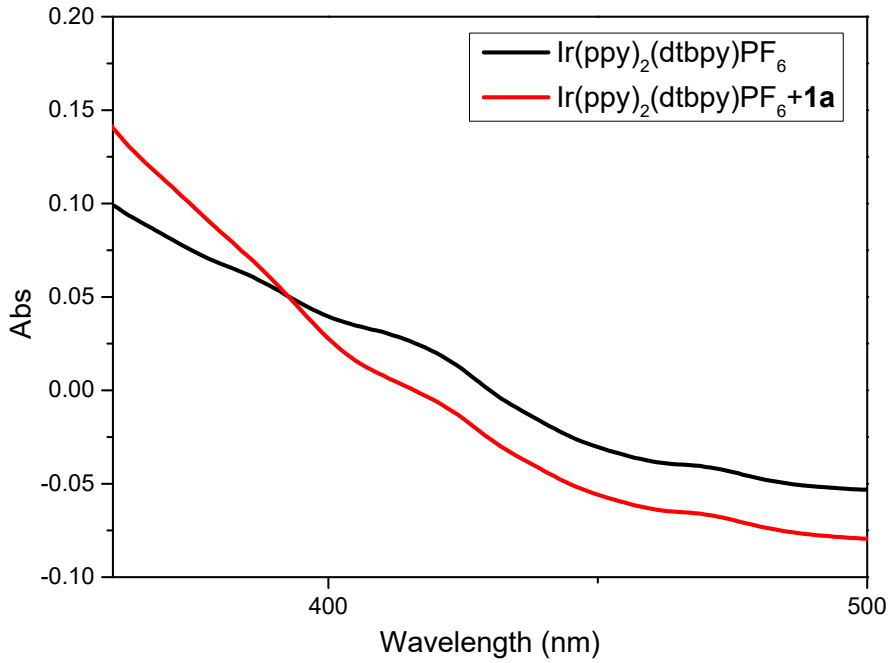
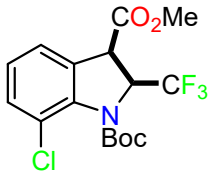


Figure S6. UV-Vis spectra

3. X-ray crystallographic data

X-ray crystallographic data of 3p (CCDC 2190100)



3p

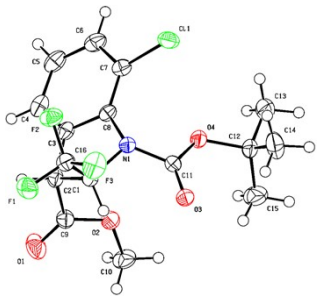
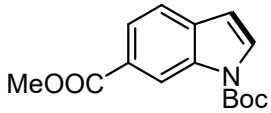


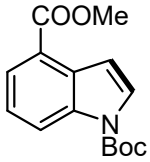
Table S1 Crystal data and structure refinement for 3p

Identification code	**3p**
Empirical formula	$C_{16}H_{17}ClF_3NO_4$
Formula weight	379.76
Temperature/K	170.00(11)
Crystal system	triclinic
Space group	P-1
a/Å	9.1441(2)
b/Å	10.1797(3)
c/Å	10.2607(3)
α/°	114.406(3)
β/°	94.673(2)
γ/°	99.133(2)
Volume/Å^3	847.16(4)
Z	2
ρ_{calc}g/cm^3	1.489
μ/mm^{-1}	2.496
F(000)	392.0
Crystal size/mm^3	0.3 × 0.25 × 0.17
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.594 to 154.694
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	9766
Independent reflections	3386 [R_{int} = 0.0216, R_{sigma} = 0.0207]
Data/restraints/parameters	3386/0/231
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0921
Final R indexes [all data]	R_1 = 0.0353, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

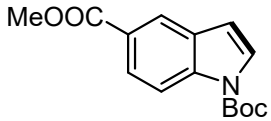
4. NMR data of starting materials



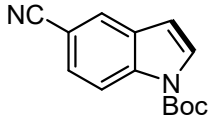
1a (1-(*tert*-butyl) 6-methyl 1*H*-indole-1,6-dicarboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 3.8 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 3.94 (s, 3H), 1.70 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 149.4, 134.6, 134.3, 128.8, 125.9, 123.8, 120.6, 117.1, 107.2, 84.3, 52.1, 28.1. GC-MS: *m*/*z* = 275. m.p. = 79 ± 1°C.



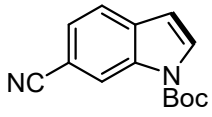
1c (1-(*tert*-butyl) 4-methyl 1*H*-indole-1,4-dicarboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 3.8 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 3.8 Hz, 1H), 3.94 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 149.2, 135.7, 130.3, 127.4, 125.2, 123.3, 121.7, 119.5, 107.7, 83.8, 51.6, 27.9. GC-MS: *m*/*z* = 275.



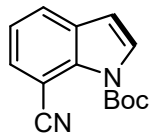
1d (1-(*tert*-butyl) 5-methyl 1*H*-indole-1,5-dicarboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 8.17 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 3.9 Hz, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 3.92 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 149.2, 137.7, 130.2, 127.0, 125.4, 124.5, 123.1, 114.7, 107.6, 84.1, 51.8, 28.0. GC-MS: *m*/*z* = 275. m.p. = 50 ± 1°C.



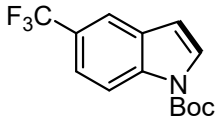
1e (*tert*-butyl 5-cyano-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 3.7 Hz, 1H), 7.55 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.62 (d, *J* = 3.7 Hz, 1H), 1.69 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 137.1, 130.6, 128.2, 127.4, 125.9, 119.9, 116.1, 107.0, 106.1, 85.0, 28.2. GC-MS: *m*/*z* = 242. m.p. = 75 ± 1.5°C.



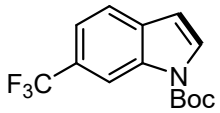
1f (*tert*-butyl 6-cyano-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.76 (d, *J* = 3.7 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.46 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 1.69 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 134.3, 133.9, 129.3, 125.8, 121.8, 120.1, 119.8, 107.3, 107.1, 85.1, 28.2. GC-MS: *m*/*z* = 242. m.p. = 78 ± 1°C.



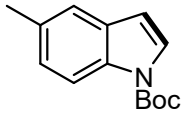
1g (*tert*-butyl 7-cyano-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 3.8 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 3.9 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 132.8, 132.5, 131.7, 128.4, 126.1, 122.7, 118.1, 107.2, 99.7, 85.6, 28.0. GC-MS: *m*/*z* = 242. m.p. = 82 ± 1°C.



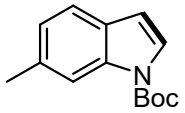
1h (*tert*-butyl 5-(trifluoromethyl)-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.8 Hz, 1H), 7.82 (s, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.54 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 1.68 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 136.9, 130.3, 127.7, 125.1 (q, *J* = 32.1 Hz), 125.0 (q, *J* = 271.7 Hz), 121.1 (q, *J* = 3.9 Hz), 118.5 (q, *J* = 4.2 Hz) 115.6, 107.4, 84.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.88. GC-MS: *m*/*z* = 285. m.p. = 64 ± 1.5°C.



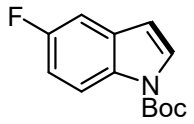
1i (*tert*-butyl 6-(trifluoromethyl)-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.70 (d, *J* = 3.8 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 1.68 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 134.5, 133.1, 128.4, 126.3 (q, *J* = 31.9 Hz), 125.1 (q, *J* = 271.8 Hz), 121.3, 119.5 (q, *J* = 3.5 Hz), 112.9 (q, *J* = 4.5 Hz), 107.1, 84.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.83. GC-MS: *m*/*z* = 285. m.p. = 68 ± 1°C.



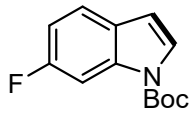
1j (*tert*-butyl 5-methyl-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 3.8 Hz, 1H), 7.31 (s, 1H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.46 (d, *J* = 3.7 Hz, 1H), 2.42 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9, 133.5, 132.1, 130.9, 126.0, 125.6, 120.9, 114.9, 107.1, 83.5, 28.3, 21.4. GC-MS: *m*/*z* = 231.



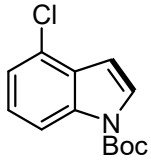
1k (*tert*-butyl 6-methyl-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.49 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 2.47 (s, 3H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9, 135.7, 134.2, 128.3, 125.3, 124.2, 120.5, 115.5, 107.2, 83.4, 28.2, 22.0. GC-MS: *m*/*z* = 231.



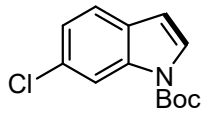
1l (*tert*-butyl 5-fluoro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.61 (d, *J* = 3.8 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.02 (td, *J* = 9.2, 2.7 Hz, 1H), 6.50 (d, *J* = 3.7 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3 (d, *J* = 238.2 Hz), 149.6, 131.7, 131.5 (d, *J* = 9.9 Hz), 127.5, 116.2 (d, *J* = 8.8 Hz), 112.1 (d, *J* = 25.0 Hz), 107.1 (d, *J* = 3.9 Hz), 106.4 (d, *J* = 23.9 Hz) 84.0, 28.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.07. GC-MS: *m*/*z* = 235.



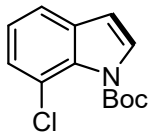
1m (*tert*-butyl 6-fluoro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 10.4 Hz, 1H), 7.55 (d, *J* = 3.8 Hz, 1H), 7.44 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.97 (td, *J* = 9.0, 2.5 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0 (d, *J* = 239.8 Hz), 149.6, 135.5 (d, *J* = 12.0 Hz), 126.9, 126.3 (d, *J* = 3.9 Hz), 121.5 (d, *J* = 9.7 Hz), 111.0 (d, *J* = 24.3 Hz), 107.1, 102.6 (d, *J* = 28.4 Hz), 84.2, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.56. GC-MS: *m*/*z* = 235.



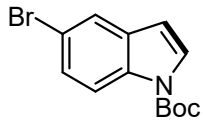
1n (*tert*-butyl 4-chloro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (t, *J* = 4.6 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.20 (m, 2H), 6.67 (d, *J* = 3.7 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 136.0, 129.4, 126.5, 126.2, 124.9, 122.5, 113.8, 105.4, 84.3, 28.2. GC-MS: *m*/*z* = 252.



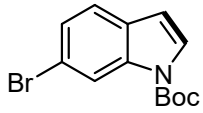
1o (*tert*-butyl 6-chloro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.54 (d, *J* = 3.7 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.50 (d, *J* = 3.8 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 135.6, 130.2, 129.1, 126.5, 123.3, 121.6, 115.6, 107.1, 84.2, 28.2. GC-MS: *m*/*z* = 252.



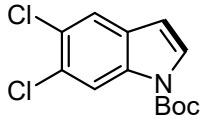
1p (*tert*-butyl 7-chloro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 3.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 134.2, 132.1, 129.5, 126.5, 123.8, 120.5, 119.7, 107.0, 84.4, 28.0. GC-MS: *m*/*z* = 252.



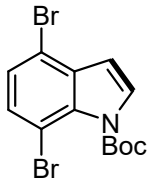
1q (*tert*-butyl 5-bromo-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 9.1 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.56 (s, 1H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.46 (d, *J* = 3.7 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 134.0, 132.3, 127.1, 123.6, 116.6, 116.0, 106.5, 84.1, 28.2. GC-MS: *m*/*z* = 296.



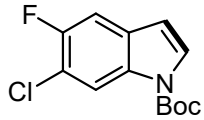
1r (*tert*-butyl 6-bromo-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.53 (d, *J* = 3.7 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.49 (d, *J* = 3.9 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 135.9, 129.4, 126.4, 125.9, 122.0, 118.4, 118.0, 107.1, 84.3, 28.2. GC-MS: *m*/*z* = 296.



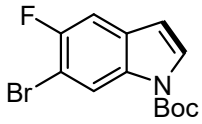
1s (*tert*-butyl 5,6-dichloro-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.54 (d, *J* = 3.7 Hz, 1H), 7.49 (s, 1H), 6.40 (d, *J* = 3.7 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 133.8, 130.0, 128.0, 127.5, 126.6, 121.6, 116.8, 106.3, 84.5, 28.1. GC-MS: *m*/*z* = 286. m.p. = 74 ± 1°C.



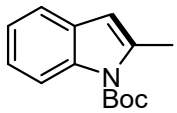
1t (*tert*-butyl 4,7-dibromo-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 3.7 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.2, 134.3, 134.0, 130.4, 130.0, 126.8, 114.1, 107.0, 106.9, 85.0, 28.0. GC-MS: *m*/*z* = 375.



1u (*tert*-butyl 6-chloro-5-fluoro-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.24 (d, *J* = 9.2 Hz, 1H), 6.47 (d, *J* = 3.7 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.5 (d, *J* = 241.8 Hz), 149.2, 131.4, 129.7 (d, *J* = 9.1 Hz), 127.7, 117.6 (d, *J* = 20.6 Hz), 116.9, 107.2 (d, *J* = 23.4 Hz), 106.8 (d, *J* = 3.8 Hz), 84.5, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -122.63. GC-MS: *m*/*z* = 270.

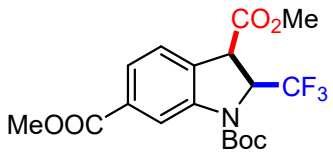


1v (*tert*-butyl 6-bromo-5-fluoro-1*H*-indole-1-carboxylate). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.58 (d, *J* = 4.1 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 6.47 (d, *J* = 3.7 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3 (d, *J* = 240.2 Hz), 149.2, 132.0, 130.5 (d, *J* = 8.7 Hz), 127.8, 119.7, 107.1 (d, *J* = 24.8 Hz), 106.9 (d, *J* = 3.8 Hz), 105.3 (d, *J* = 24.0 Hz) 84.5, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.83. GC-MS: *m*/*z* = 314. m.p. = 70 ± 1℃.

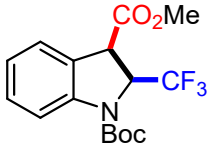


1w (*tert*-butyl 2-methyl-1*H*-indole-1-carboxylate). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.27 – 7.11 (m, 2H), 6.28 (s, 1H), 2.58 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 137.9, 136.6, 129.5, 123.2, 122.7, 119.6, 115.6, 108.1, 83.7, 28.4, 17.2. GC-MS: *m*/*z* = 231.

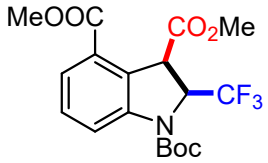
5. NMR data of products



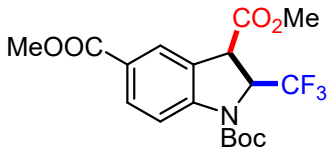
3a (1-(*tert*-butyl) 3,6-dimethyl 2-(trifluoromethyl)indoline-1,3,6-tricarboxylate). Colorless oil. 58.1 mg, 72% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.79 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 5.50 (q, *J* = 7.5 Hz, 1H), 4.18 (d, *J* = 2.2 Hz, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 166.6, 151.6, 142.4, 131.7, 131.1, 125.5, 125.4, 124.6 (q, *J* = 282.5 Hz), 117.5, 83.3, 62.0 (q, *J* = 31.9 Hz), 53.5, 52.4, 47.0, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.00. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{18}H_{19}F_3NO_6$]$^{-}$: 402.1170, found: 402.1174.



3b (1-(*tert*-butyl) 3-methyl 2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 40.1 mg, 58% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.46 (q, *J* = 7.3 Hz, 1H), 4.14 (s, 1H), 3.77 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.8, 151.9, 142.2, 129.5, 126.4, 125.5, 124.8 (q, *J* = 282.6 Hz), 123.7, 116.7, 82.8, 61.8 (q, *J* = 31.6 Hz), 53.3, 47.0, 28.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.96. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{16}H_{17}F_3NO_4$]$^{-}$: 344.1115, found: 344.1110.

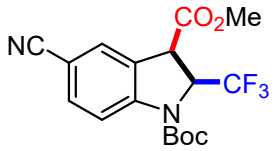


3c (1-(*tert*-butyl) 3,4-dimethyl 2-(trifluoromethyl)indoline-1,3,4-tricarboxylate). Colorless oil. 56.5 mg, 70% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 5.25 – 5.06 (m, 1H), 4.73 (d, *J* = 2.2 Hz, 1H), 3.89 (s, 3H), 3.75 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 166.3, 151.5, 143.7, 129.7, 127.5, 125.1, 124.5 (q, *J* = 283.4 Hz), 120.5, 83.3, 62.9 (q, *J* = 33.9, 31.0 Hz), 53.1, 52.2, 47.2, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.41. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{18}H_{19}F_3NO_6$]$^{-}$: 402.1170, found: 402.1165.

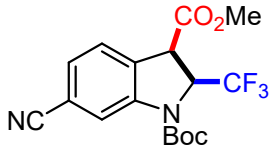


3d (1-(*tert*-butyl) 3,5-dimethyl 2-(trifluoromethyl)indoline-1,3,5-tricarboxylate). Colorless oil. 41.9 mg, 52% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*)

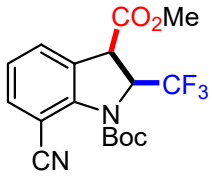
δ 8.08 (s, 1H), 8.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.79 (s, 1H), 5.49 (q, *J* = 7.1 Hz, 1H), 4.17 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 166.5, 151.4, 146.0, 131.9, 127.1, 126.6, 125.7, 124.6 (q, *J* = 282.6 Hz), 116.0, 83.6, 62.2 (q, *J* = 32.4 Hz), 53.5, 52.2, 46.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.85. HRMS (ESI): calculated m/z [M-H]$^-$ for $[C_{18}H_{19}F_3NO_6]^-$: 402.1170, found: 402.1172.



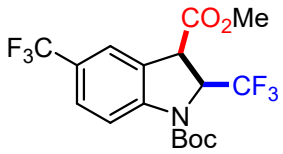
3e (1-(*tert*-butyl) 3-methyl 5-cyano-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 53.3 mg, 72% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.71 (s, 1H), 7.61 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.55 – 5.47 (m, 1H), 4.19 (s, 1H), 3.83 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 151.0, 145.8, 134.3, 129.4, 127.3, 124.4 (q, *J* = 284.8 Hz), 118.8, 116.8, 107.0, 84.1, 62.0 (q, *J* = 32.5 Hz), 53.7, 46.4, 28.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.86. HRMS (ESI): calculated m/z [M-H]$^-$ for $[C_{17}H_{16}F_3N_2O_4]^-$: 369.1067, found: 369.1063.



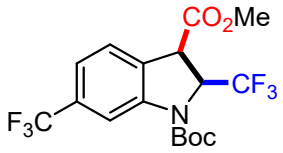
3f (1-(*tert*-butyl) 3-methyl 6-cyano-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 59.3 mg, 80% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.49 (q, *J* = 7.1 Hz, 1H), 4.21 (s, 1H), 3.81 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 151.2, 142.7, 131.2, 127.8, 126.4, 124.4 (q, *J* = 282.7 Hz), 119.6, 118.5, 113.4, 83.9, 61.8 (q, *J* = 31.8 Hz), 53.6, 47.1, 28.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.96. HRMS (ESI): calculated m/z [M-H]$^-$ for $[C_{17}H_{16}F_3N_2O_4]^-$: 369.1067, found: 369.1065.



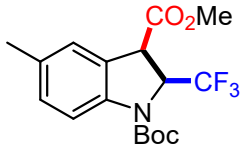
3g (1-(*tert*-butyl) 3-methyl 7-cyano-2-(trifluoromethyl)indoline-1,3-dicarboxylate). White solid. 37.8 mg, 51% yield (PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.49 (qd, *J* = 7.4, 1.6 Hz, 1H), 4.08 (s, 1H), 3.79 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 151.8, 143.8, 134.1, 130.5, 129.8, 125.2, 124.3 (q, *J* = 283.8 Hz), 116.8, 103.8, 85.0, 63.8 (q, *J* = 32.9 Hz), 53.5, 46.9, 28.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.54 (d, *J* = 6.6 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for $[C_{17}H_{16}F_3N_2O_4]^-$: 369.1067, found: 369.1068. m.p. = 109 ± 1°C.



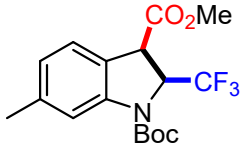
3h (1-(*tert*-butyl) 3-methyl 2,5-bis(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 61.2 mg, 74% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.66 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 5.51 (q, *J* = 6.4 Hz, 1H), 4.18 (s, 1H), 3.81 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 151.4, 145.1, 127.2 (q, *J* = 3.9 Hz), 126.0 (q, *J* = 33.3 Hz), 124.6 (q, *J* = 282.4 Hz), 124.0 (q, *J* = 272.7 Hz), 122.8, 122.8, 116.5, 83.7, 62.2 (q, *J* = 32.4 Hz), 53.6, 46.7, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.64 (s, 3H), -76.98 (s, 3H). HRMS (ESI): calculated m/z [M-H]$^{-}$ for $[C_{17}H_{16}F_6NO_4]^-$: 412.0989, found: 412.0986.



3i (1-(*tert*-butyl) 3-methyl 2,5-bis(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 62.0 mg, 75% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.6 Hz, 1H), 5.51 (q, *J* = 7.5 Hz, 1H), 4.20 (s, 1H), 3.79 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 151.5, 142.7, 132.1 (q, *J* = 32.3 Hz), 130.0, 125.9, 124.6 (q, *J* = 282.2 Hz), 124.0 (q, *J* = 272.3 Hz), 120.8 (q, *J* = 4.1 Hz), 113.7, 83.6, 62.0 (q, *J* = 32.0 Hz), 53.5, 46.9, 28.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.47 (s, 3H), -77.03 (s, 3H). HRMS (ESI): calculated m/z [M-H]$^{-}$ for $[C_{17}H_{16}F_6NO_4]^-$: 412.0989, found: 412.0990.

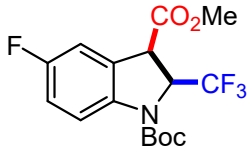


3j (1-(*tert*-butyl) 3-methyl 5-methyl-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 23.0 mg, 32% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.09 (dd, *J* = 8.3, 1.8 Hz, 1H), 5.43 (q, *J* = 7.5 Hz, 1H), 4.09 (d, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 2.32 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 152.0, 139.9, 133.5, 130.1, 126.3, 125.9, 124.9 (q, *J* = 282.9 Hz), 116.4, 82.6, 61.9 (q, *J* = 32.5 Hz), 53.3, 47.0, 28.3, 21.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.98. HRMS (ESI): calculated m/z [M-H]$^{-}$ for $[C_{17}H_{19}F_3NO_4]^-$: 358.1271, found: 358.1275.

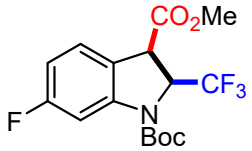


3k (1-(*tert*-butyl) 3-methyl 6-methyl-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 25.2 mg, 35% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.44 (q, *J* = 6.7, 6.3 Hz, 1H), 4.10 (d, *J* = 2.1 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H), 1.57 (s, 9H). ^{13}C NMR

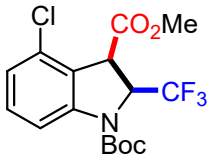
(101 MHz, Chloroform-*d*) δ 170.0, 152.0, 142.2, 139.8, 125.0, 124.8 (q, *J* = 282.8 Hz), 124.5, 123.4, 117.3, 82.7, 62.1 (q, *J* = 31.8 Hz), 53.2, 46.7, 28.2, 21.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.93. HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{17}H_{19}F_3NO_4$]$^-$: 358.1271, found: 358.1270.



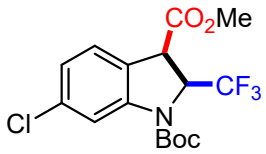
3l (1-(*tert*-butyl) 3-methyl 5-fluoro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 50.1 mg, 69% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.13 (dd, *J* = 7.8, 2.8 Hz, 1H), 6.99 (td, *J* = 8.9, 2.7 Hz, 1H), 5.47 (q, *J* = 6.9 Hz, 1H), 4.11 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 159.3 (d, *J* = 242.6 Hz), 151.8, 138.3, 127.8 (d, *J* = 6.0 Hz), 124.7 (q, *J* = 283.0 Hz), 117.5 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 23.1 Hz), 112.9 (d, *J* = 25.2 Hz), 83.0, 62.1 (q, *J* = 31.7 Hz), 53.5, 46.9, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.08 (s, 3H), -119.32 (s, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{16}F_4NO_4$]$^-$: 362.1021, found: 362.1023.



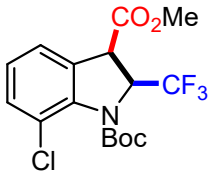
3m (1-(*tert*-butyl) 3-methyl 6-fluoro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 43.6 mg, 60% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.33 (dd, *J* = 8.5, 5.4 Hz, 1H), 6.74 (td, *J* = 8.6, 2.5 Hz, 1H), 5.47 (q, *J* = 7.4 Hz, 1H), 4.10 (s, 1H), 3.78 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 163.8 (d, *J* = 245.1 Hz), 151.5, 143.6 (d, *J* = 11.4 Hz), 126.2 (d, *J* = 9.9 Hz), 124.7 (q, *J* = 282.4 Hz), 121.7, 110.5 (d, *J* = 23.4 Hz), 104.9 (d, *J* = 29.5 Hz), 83.4, 62.5 (q, *J* = 32.0 Hz), 53.4, 46.3, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.99 (s, 3H), -111.25 (s, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{16}F_4NO_4$]$^-$: 362.1021, found: 362.1024.



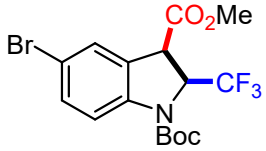
3n (1-(*tert*-butyl) 3-methyl 4-chloro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 34.2 mg, 45% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.24 (t, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 5.21 (q, *J* = 7.2 Hz, 1H), 4.20 (d, *J* = 1.8 Hz, 1H), 3.78 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 151.5, 143.9, 131.2, 130.9, 124.4 (q, *J* = 283.5 Hz), 124.2, 115.0, 83.4, 62.9 (q, *J* = 32.4 Hz), 53.2, 46.3, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.25. HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{16}ClF_3NO_4$]$^-$: 378.0725, found: 378.0728.



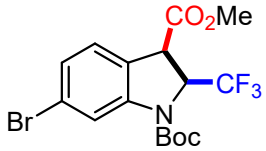
3o (1-(*tert*-butyl) 3-methyl 6-chloro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 47.8 mg, 63% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.46 (q, *J* = 7.1 Hz, 1H), 4.10 (s, 1H), 3.78 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 151.5, 143.2, 135.5, 126.2, 124.7, 124.6 (q, *J* = 282.9 Hz), 123.8, 117.1, 83.4, 62.2 (q, *J* = 32.0 Hz), 53.4, 46.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.25. δ -76.95. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{16}H_{16}ClF_3NO_4$]$^{-}$: 378.0725, found: 378.0723.



3p (1-(*tert*-butyl) 3-methyl 7-chloro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). White solid. 53.2 mg, 70% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.17 – 6.91 (m, 1H), 5.41 (qd, *J* = 7.6, 1.2 Hz, 1H), 4.02 (s, 1H), 3.76 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 152.7, 140.3, 131.7, 131.2, 126.4, 125.3, 124.5 (q, *J* = 281.4 Hz), 123.5, 83.3, 64.8 (q, *J* = 32.6 Hz), 53.3, 47.8, 28.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.56 (d, *J* = 8.6 Hz). HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{16}H_{16}ClF_3NO_4$]$^{-}$: 378.0725, found: 378.0720. m.p. = 102 ± 1.5℃.

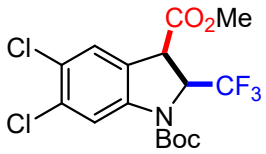


3q (1-(*tert*-butyl) 3-methyl 5-bromo-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 62.8 mg, 74% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.41 (dd, *J* = 8.6, 2.1 Hz, 1H), 5.45 (q, *J* = 7.4 Hz, 1H), 4.11 (s, 1H), 3.80 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 151.6, 141.4, 132.5, 128.5, 128.3, 124.6 (q, *J* = 282.5 Hz), 118.0, 116.1, 83.2, 62.0 (q, *J* = 32.1 Hz), 53.5, 46.7, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.97. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{16}H_{16}BrF_3NO_4$]$^{-}$: 422.0220, found: 422.0222.

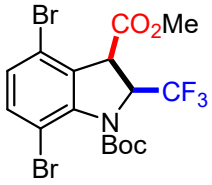


3r (1-(*tert*-butyl) 3-methyl 6-bromo-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 47.5 mg, 56% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.29 – 7.23 (m, 1H), 7.19 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.44 (q, *J* = 7.2 Hz,

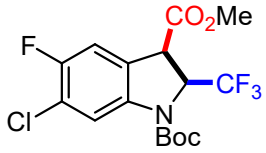
1H), 4.08 (d, J = 2.2 Hz, 1H), 3.78 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 151.5, 143.4, 126.8, 126.6, 125.3, 124.6 (q, J = 282.9 Hz), 123.4, 119.9, 83.4, 62.1 (q, J = 32.1 Hz), 53.4, 46.6, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.93. HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{16}BrF_3NO_4$]$^-$: 422.0220, found: 422.0224.



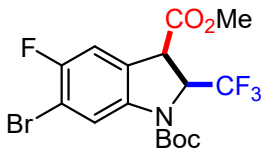
3s (1-(*tert*-butyl) 3-methyl 5,6-dichloro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 53.8 mg, 65% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.47 (s, 1H), 5.45 (q, J = 7.3 Hz, 1H), 4.10 (s, 1H), 3.81 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 151.3, 141.6, 133.7, 127.1, 126.9, 126.2, 124.5 (q, J = 282.8 Hz), 118.3, 83.7, 62.3 (q, J = 32.6 Hz), 53.7, 46.5, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.93. HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{15}Cl_2F_3NO_4$]$^-$: 412.0335, found: 412.0339.



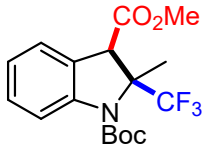
3t (1-(*tert*-butyl) 3-methyl 4,7-dibromo-2-(trifluoromethyl)indoline-1,3-dicarboxylate). White solid. 62.4 mg, 62% yield (PE:EA = 70:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 5.20 (q, J = 7.3 Hz, 1H), 4.05 (s, 1H), 3.77 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 152.5, 143.8, 135.4, 132.8, 130.1, 124.1 (q, J = 281.5 Hz), 118.1, 112.9, 83.9, 65.6 (q, J = 33.0 Hz), 53.2, 49.1, 28.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.62 (d, J = 8.4 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{15}Br_2F_3NO_4$]$^-$: 499.9325, found: 499.9320. m.p. = 120 ± 1°C.



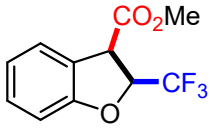
3u (1-(*tert*-butyl) 3-methyl 6-chloro-5-fluoro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 35.0 mg, 44% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.21 (dd, J = 8.1, 1.0 Hz, 1H), 5.46 (q, J = 7.2 Hz, 1H), 4.10 (s, 1H), 3.80 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 154.7 (d, J = 245.5 Hz), 151.5, 138.6, 126.0, 124.6 (q, J = 282.4 Hz), 122.0 (d, J = 19.1 Hz), 118.3, 113.7 (d, J = 24.6 Hz), 83.5, 62.2 (q, J = 32.5 Hz), 53.6, 46.7, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.04 (s, 3H), -120.62 (s, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{15}ClF_4NO_4$]$^-$: 396.0631, found: 396.0628.



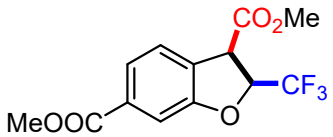
3v (1-(*tert*-butyl) 3-methyl 6-bromo-5-fluoro-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 42.5 mg, 48% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 5.46 (q, *J* = 7.3, 6.9 Hz, 1H), 4.08 (s, 1H), 3.80 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 155.7 (d, *J* = 243.7 Hz), 151.5, 138.9, 126.9 (d, *J* = 3.0 Hz), 124.5 (q, *J* = 282.8 Hz), 121.0, 113.6 (d, *J* = 26.1 Hz), 109.9 (d, *J* = 22.3 Hz), 83.5, 62.2 (q, *J* = 32.3 Hz), 53.6, 46.7, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.01 (s, 3H), -112.68 (s, 1H). HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{16}H_{15}BrF_4NO_4$]$^{-}$: 440.0126, found: 440.0128.



3w (1-(*tert*-butyl) 3-methyl 2-methyl-2-(trifluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 15.8 mg, 22% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.22 (m, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.00 (td, *J* = 7.3, 0.8 Hz, 1H), 4.28 (s, 1H), 3.73 (s, 3H), 1.88 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 151.6, 144.1, 129.3, 126.1, 123.9, 123.4, 116.7, 116.2, 82.7, 69.5 (q, *J* = 28.9 Hz), 54.0, 52.6, 28.4, 17.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.80. HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{17}H_{19}F_3NO_4$]$^{-}$: 358.1271, found: 358.1267.

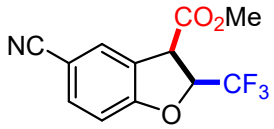


5a (methyl 2-(trifluoromethyl)-2,3-dihydrobenzofuran-3-carboxylate). Colorless oil. 30.5 mg, 62% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.56 – 5.45 (m, 1H), 4.43 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 158.5, 130.3, 125.4, 123.8 (q, *J* = 280.0 Hz), 122.1, 110.5, 80.3 (q, *J* = 33.5 Hz), 53.3, 48.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.35 (d, *J* = 6.5 Hz). HRMS (ESI): calculated m/z [M-H]$^{-}$ for [$C_{11}H_8F_3O_3$]$^{-}$: 245.0431, found: 245.0427.

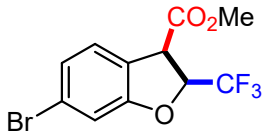


5b (dimethyl 2-(trifluoromethyl)-2,3-dihydrobenzofuran-3,6-dicarboxylate). Colorless oil. 35.3 mg, 58% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55 (d, *J* = 1.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 5.56 (dt, *J*

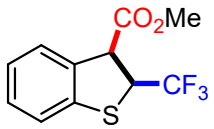
= 12.6, 6.6 Hz, 1H), 4.46 (d, *J* = 5.5 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 166.3, 158.7, 132.6, 127.2, 125.3, 123.9, 123.6 (q, *J* = 280.3 Hz), 111.4, 80.7 (q, *J* = 33.7 Hz), 53.6, 52.5, 48.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.38 (d, *J* = 6.5 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{13}H_{10}F_3O_5$]$^-$: 303.0486, found: 303.0490.



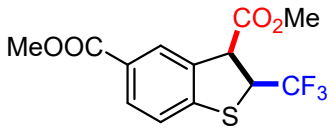
5c (methyl 5-cyano-2-(trifluoromethyl)-2,3-dihydrobenzofuran-3-carboxylate). White solid. 27.1 mg, 50% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 1.5 Hz, 1H), 7.60 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 5.61 (p, *J* = 6.5 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 161.7, 135.3, 130.0, 123.9, 123.3 (q, *J* = 280.1 Hz), 118.6, 111.6, 106.1, 81.2 (q, *J* = 34.4 Hz), 53.9, 47.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.32 (d, *J* = 6.5 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{12}H_7F_3NO_3$]$^-$: 270.0383, found: 270.0384. m.p. = 118 ± 1°C.



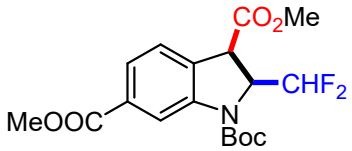
5d (methyl 6-bromo-2-(trifluoromethyl)-2,3-dihydrobenzofuran-3-carboxylate). Colorless oil. 29.9 mg, 46% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.12 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.08 (d, *J* = 1.7 Hz, 1H), 5.74 – 5.37 (m, 1H), 4.35 (dd, *J* = 5.5, 1.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 159.3, 126.5, 125.4, 123.6, 123.6 (q, *J* = 279.9 Hz), 121.5, 114.2, 80.9 (q, *J* = 33.8 Hz), 53.5, 47.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.98. HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{11}H_7BrF_3O_3$]$^-$: 322.9533, found: 322.9538.



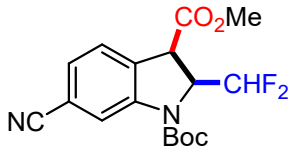
5e (methyl 2-(trifluoromethyl)-2,3-dihydrobenzo[b]thiophene-3-carboxylate). Colorless oil. 10.5 mg, 20% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 6.6 Hz, 1H), 7.11 (td, *J* = 7.3, 1.4 Hz, 1H), 4.82 (qd, *J* = 8.5, 3.5 Hz, 1H), 4.50 (d, *J* = 3.3 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 138.9, 134.4, 129.5, 126.3, 125.9 (q, *J* = 277.2 Hz), 125.3, 122.0, 53.4, 53.3, 51.0 (q, *J* = 31.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.02 (d, *J* = 8.7 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{11}H_8F_3O_2S$]$^-$: 261.0202, found: 261.0198.



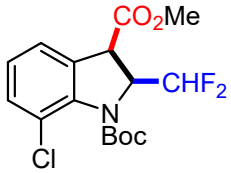
5f (methyl 2-(trifluoromethyl)-2,3-dihydrobenzo[b]thiophene-3-carboxylate). Colorless oil. 16.0 mg, 25% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (t, *J* = 1.2 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 4.87 (qd, *J* = 8.3, 3.0 Hz, 1H), 4.53 (d, *J* = 3.1 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 166.5, 145.4, 134.9, 131.0, 127.8, 127.4, 125.7 (q, *J* = 278.2 Hz), 121.8, 53.6, 52.8, 52.4, 51.6 (q, *J* = 31.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.16 (d, *J* = 7.1 Hz). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{13}H_{10}F_3O_4S$]$^-$: 319.0257, found: 319.0261.



7a (1-(*tert*-butyl) 3,6-dimethyl 2-(difluoromethyl)indoline-1,3,6-tricarboxylate). Colorless oil. 50.1 mg, 65% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 6.26 (t, *J* = 55.2 Hz, 1H), 5.18 (d, *J* = 25.1 Hz, 1H), 4.35 (d, *J* = 3.6 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 166.7, 151.6, 142.2, 131.5, 125.4, 125.0, 116.6, 113.2 (t, *J* = 243.9 Hz), 83.3, 62.7 (dd, *J* = 31.1, 20.8 Hz), 53.3, 52.3, 44.4, 28.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.95 (dd, *J* = 437.3, 289.1 Hz, 1H), -135.82 (dd, *J* = 672.1, 291.0 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{18}H_{20}F_2NO_6$]$^-$: 384.1264, found: 384.1270.

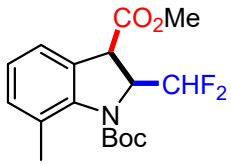


7b (1-(*tert*-butyl) 3-methyl 2-(difluoromethyl)-5-isocyanoindoline-1,3-dicarboxylate). Colorless oil. 28.2 mg, 40% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.70 (s, 1H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.24 (t, *J* = 55.8 Hz, 1H), 5.18 (d, *J* = 23.5 Hz, 1H), 4.33 (d, *J* = 3.3 Hz, 1H), 3.83 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 151.1, 145.7, 134.1, 129.4, 127.7, 119.0, 116.0, 112.9 (t, *J* = 246.4 Hz), 106.5, 84.2, 62.8 (dd, *J* = 31.3, 20.6 Hz), 53.5, 43.9, 28.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -127.07 (t, *J* = 341.3 Hz, 1H), -135.81 (dd, *J* = 643.7, 298.6 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{17}H_{17}F_2N_2O_4$]$^-$: 351.1162, found: 351.1161.

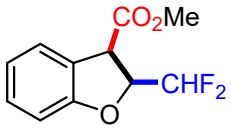


7c (1-(*tert*-butyl) 3-methyl 7-chloro-2-(difluoromethyl)indoline-1,3-dicarboxylate). Colorless oil. 22.4 mg, 31% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.23 (m, 2H), 7.10 – 7.00 (m, 1H), 5.93 (ddd, *J* = 57.0, 54.6, 3.0 Hz, 1H), 5.15 (dddd, *J* = 21.9, 4.9, 2.9, 1.6 Hz, 1H), 4.05 (s, 1H), 3.75 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 153.0, 140.1, 132.5, 131.0, 126.0, 124.8, 123.6,

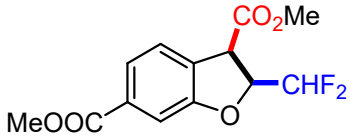
114.4 (dd, J = 247.2, 245.0 Hz), 83.0, 65.5 (dd, J = 29.4, 22.1 Hz), 53.1, 46.1, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -125.56 (ddd, J = 288.1, 54.6, 5.4 Hz, 1H), -133.70 (ddd, J = 286.2, 56.5, 21.8 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{16}H_{17}ClF_2NO_4$]$^-$: 360.0819, found: 360.0816.



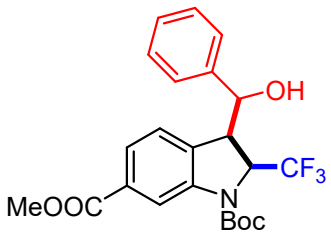
7d (1-(*tert*-butyl) 3-methyl 2-(difluoromethyl)-7-methylindoline-1,3-dicarboxylate). Colorless oil. 19.1 mg, 28% yield (PE:EA = 40:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, J = 7.3 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.05 – 5.61 (m, 1H), 5.23 – 5.05 (m, 1H), 3.99 (s, 1H), 3.73 (s, 3H), 2.29 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 153.7, 141.1, 131.8, 129.8, 129.0, 125.2, 122.5, 114.5 (t, J = 245.7 Hz), 82.2, 65.1 (dd, J = 28.4, 23.1 Hz), 53.0, 46.1, 28.3, 20.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -125.50 (ddd, J = 286.0, 54.3, 6.5 Hz, 1H), -132.50 (ddd, J = 285.8, 56.5, 19.6 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{17}H_{20}F_2NO_4$]$^-$: 340.1366, found: 340.1371.



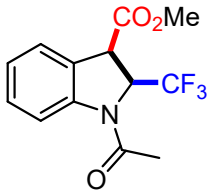
7e (methyl 2-(difluoromethyl)-2,3-dihydrobenzofuran-3-carboxylate). Colorless oil. 20.1 mg, 44% yield (PE:EA = 80:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dt, J = 7.5, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.99 – 6.92 (m, 1H), 6.87 (d, J = 8.1 Hz, 1H), 5.95 (ddd, J = 55.9, 54.4, 3.4 Hz, 1H), 5.34 (dddd, J = 15.3, 7.6, 5.9, 3.5 Hz, 1H), 4.40 (d, J = 5.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 158.7, 130.1, 125.5, 122.9, 121.8, 113.6 (t, J = 244.6 Hz), 110.4, 81.7 (dd, J = 27.8, 25.0 Hz), 53.2, 47.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -128.75 (ddd, J = 295.2, 54.5, 7.5 Hz, 1H), -133.19 (ddd, J = 292.9, 55.5, 15.3 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{11}H_9F_2O_3$]$^-$: 227.0525, found: 227.0522.



7f (dimethyl 2-(difluoromethyl)-2,3-dihydrobenzofuran-3,6-dicarboxylate). Colorless oil. 35.5 mg, 62% yield (PE:EA = 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, J = 7.9, 1.4 Hz, 1H), 7.50 (d, J = 1.4 Hz, 1H), 7.46 (dd, J = 7.8, 1.2 Hz, 1H), 5.99 (ddd, J = 55.9, 54.1, 3.1 Hz, 1H), 5.40 (dddd, J = 16.1, 7.0, 5.8, 2.9 Hz, 1H), 4.45 (dd, J = 5.8, 1.1 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 166.4, 158.8, 132.3, 128.0, 125.3, 123.5, 113.3 (t, J = 245.4 Hz), 111.2, 82.1 (dd, J = 28.6, 24.3 Hz), 53.3, 52.4, 46.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -129.29 (ddd, J = 291.4, 54.5, 7.5 Hz, 1H), -133.69 (ddd, J = 294.8, 56.1, 16.3 Hz, 1H). HRMS (ESI): calculated m/z [M-H]$^-$ for [$C_{13}H_{11}F_2O_5$]$^-$: 285.0580, found: 285.0582.

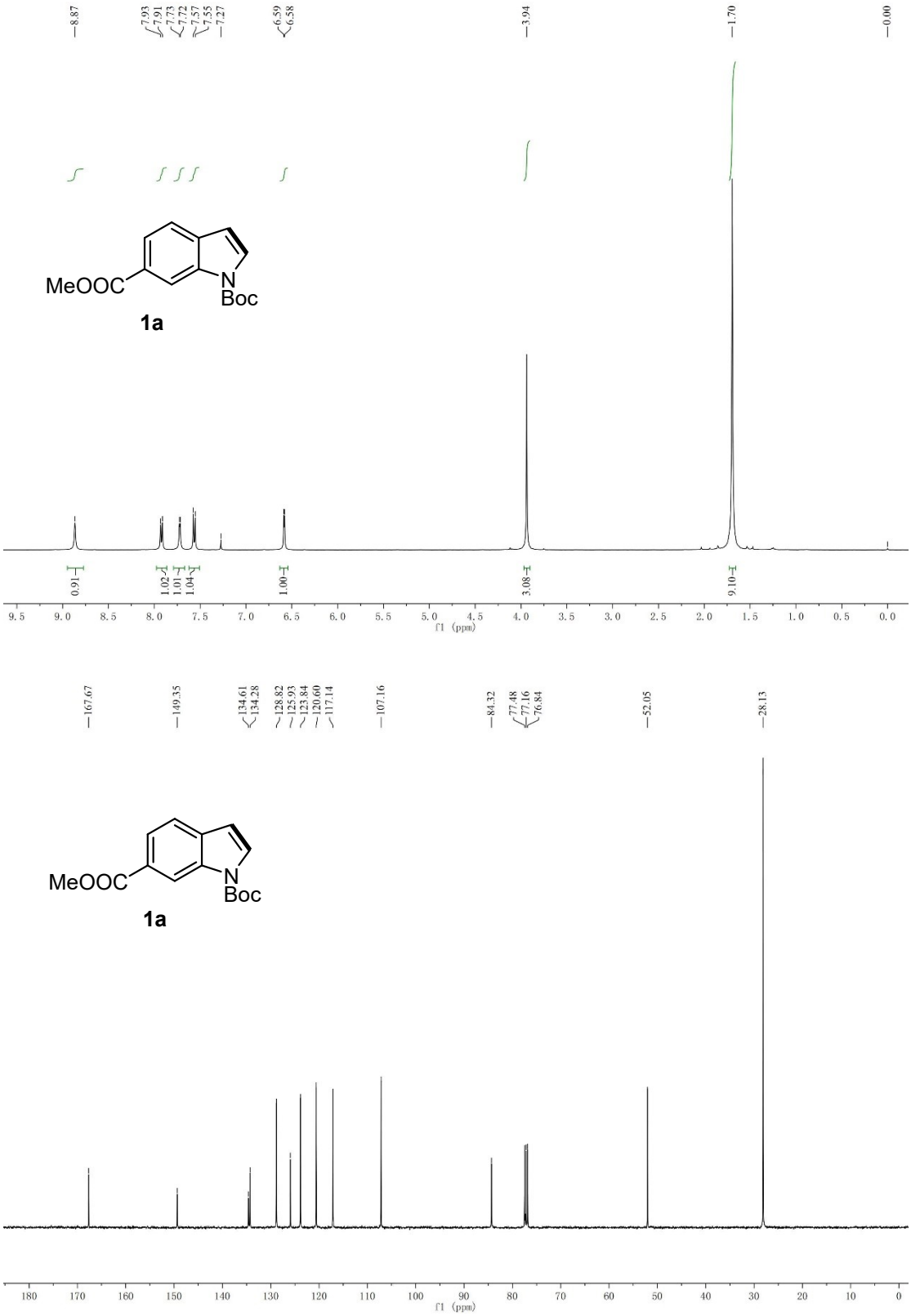


9a (1-(*tert*-butyl) 6-methyl 3-(hydroxy(phenyl)methyl)-2-(trifluoromethyl)indoline-1,6-dicarboxylate) Colorless oil. 58.7 mg, 65% yield (PE:EA = 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.40 – 7.13 (m, 6H), 6.58 (s, 1H), 5.10 (s, 1H), 4.69 (d, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 3.59 (dd, *J* = 7.3, 1.4 Hz, 1H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 151.9, 143.3, 140.1, 131.0, 128.9, 128.8, 126.9, 126.4, 125.5, 124.9, 123.6, 117.0, 82.8, 75.4, 62.2, 52.3, 49.6, 28.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.93. HRMS (ESI): calculated m/z [M-H]$^{-}$ for $[C_{23}H_{23}F_3NO_5]^{-}$: 450.1534, found: 450.1535.

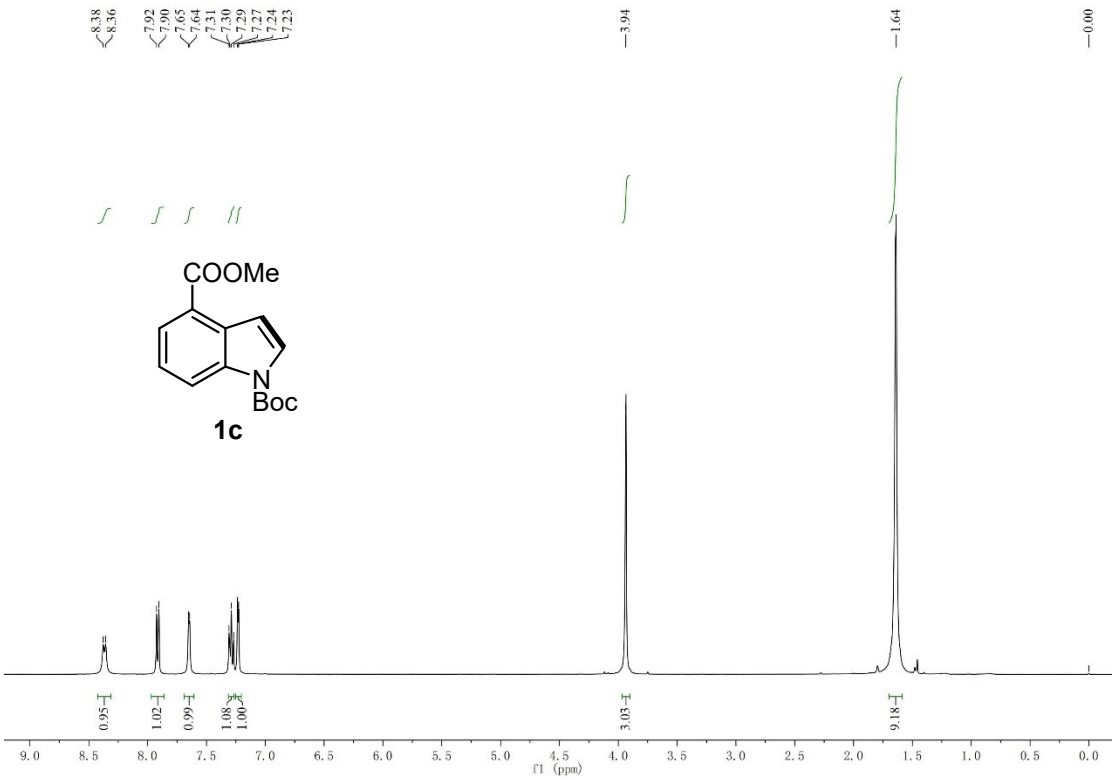


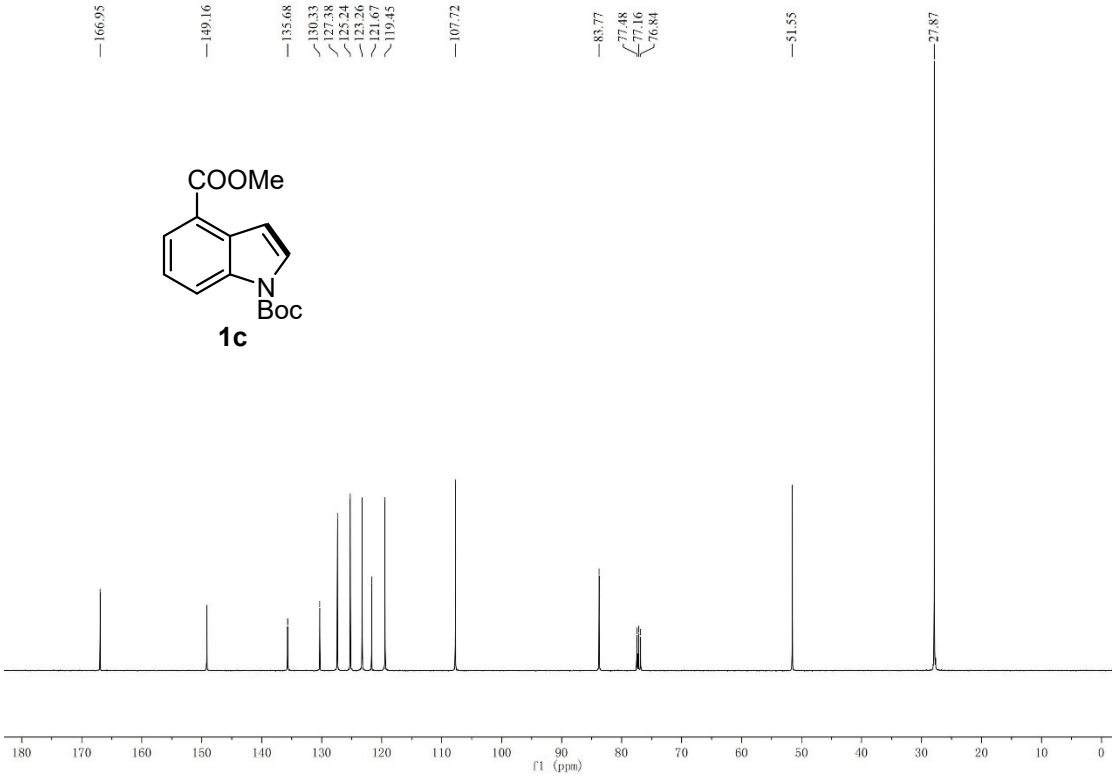
3b′ (Methyl -1-acetyl-2-(trifluoromethyl) indoline-3-carboxylate) Colorless oil. 11.5 mg, 20% yield (PE:EA = 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 (s, 1H), 7.5 (d, *J* = 7.5 Hz, 1H), 7.3 (td, *J* = 7.9, 1.4 Hz, 1H), 7.1 (td, *J* = 7.5, 1.2 Hz, 1H), 5.4 (s, 1H), 4.2 (s, 1H), 3.8 (s, 3H), 2.4 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.5, 169.4, 142.1, 129.6, 126.1, 124.9, 123.3, 53.4, 23.5. (Due to the small amount of the product, the peaks could not completely display) ^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.32. HRMS (ESI): calculated m/z [M-H]$^{-}$ for $[C_{13}H_{11}F_3NO_3]^{-}$: 286.0696, found: 286.0670.

6. NMR spectra of starting materials

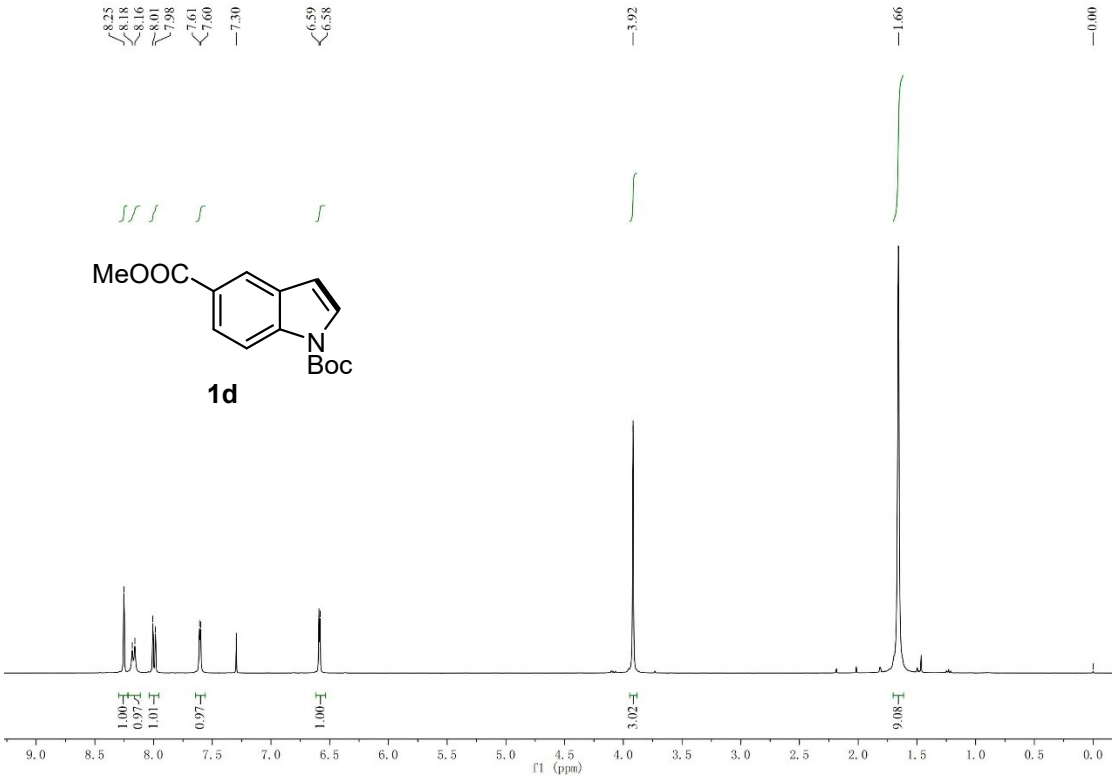


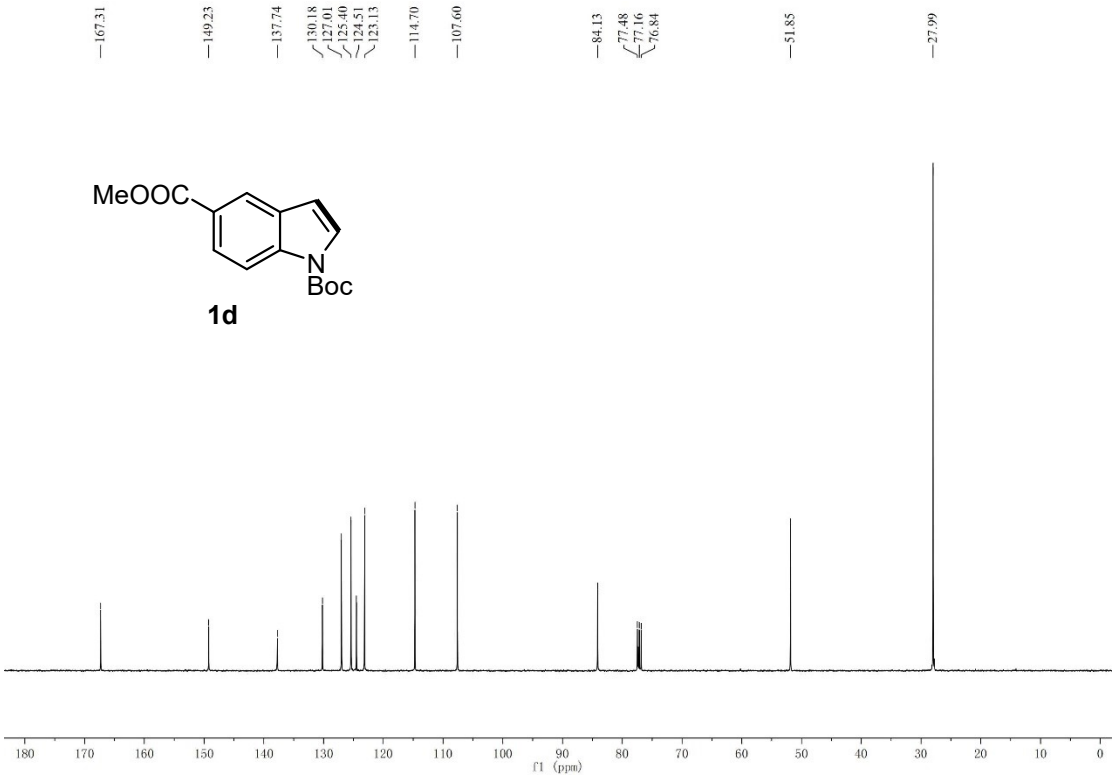
^{1}H NMR and ^{13}C NMR spectrum of **1a**



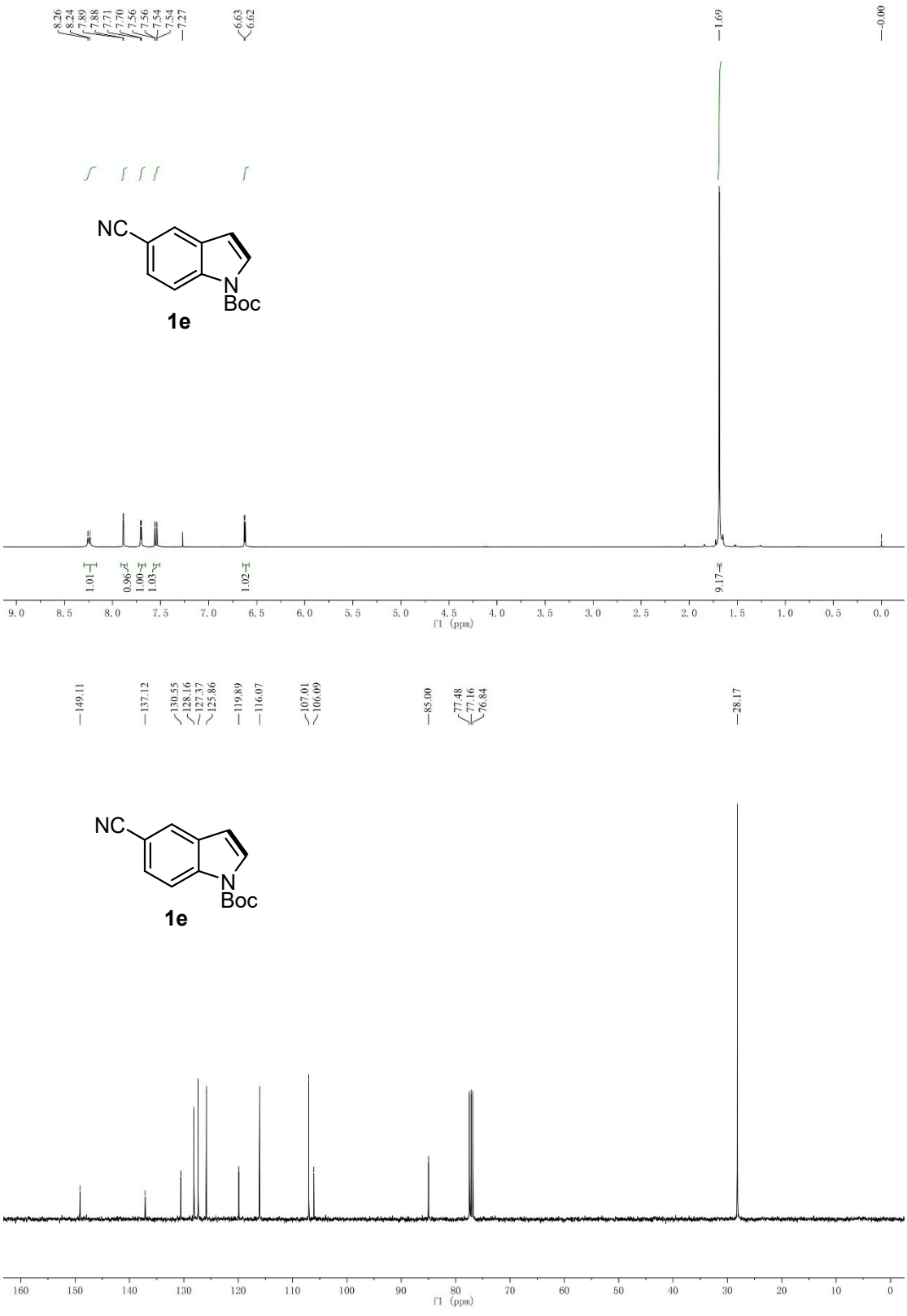


^{1}H NMR and ^{13}C NMR spectrum of **1c**

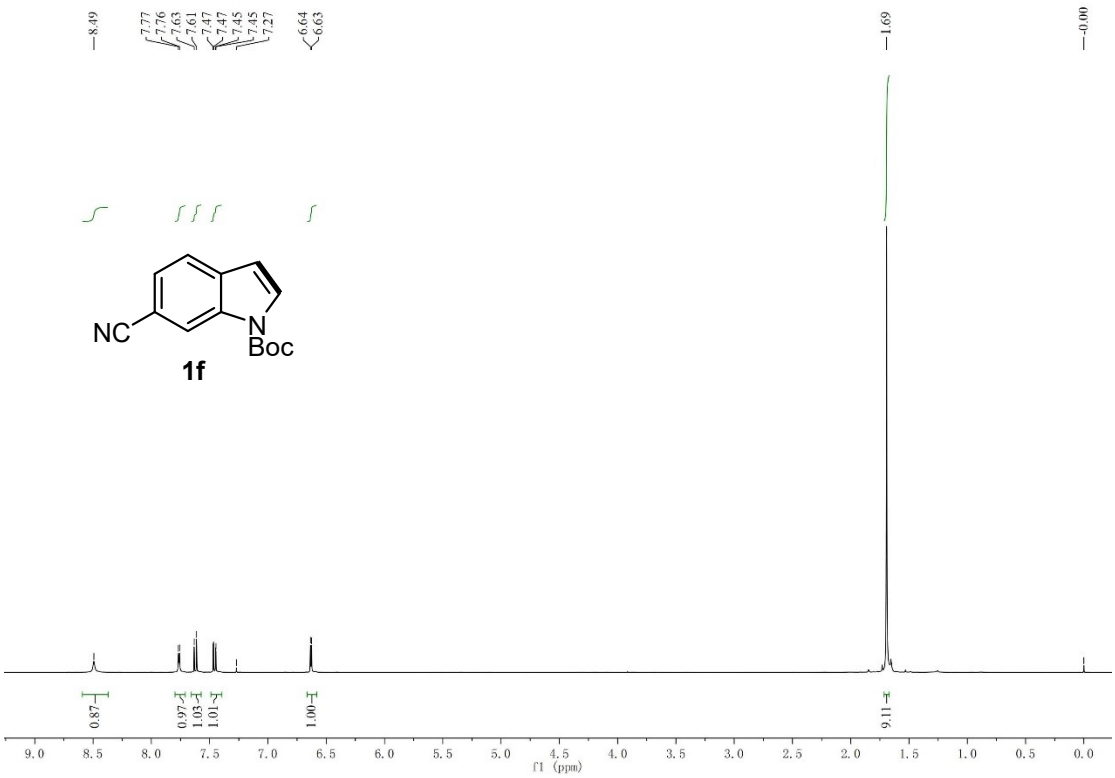


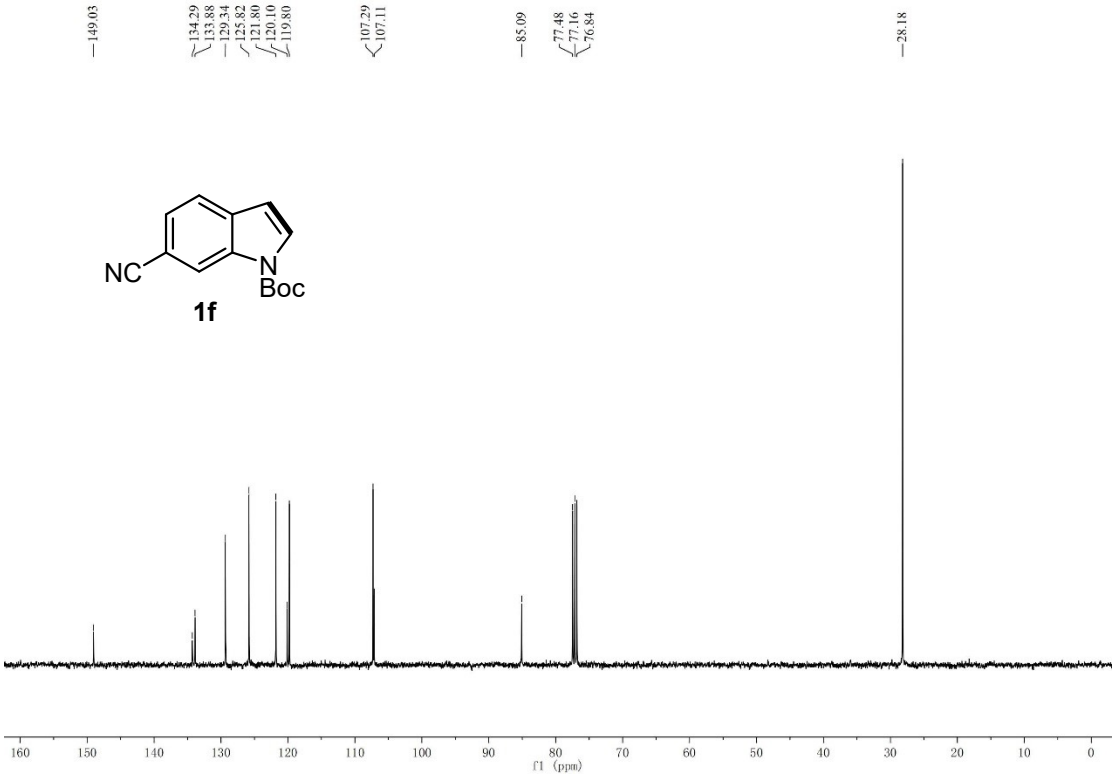


^{1}H NMR and ^{13}C NMR spectrum of **1d**

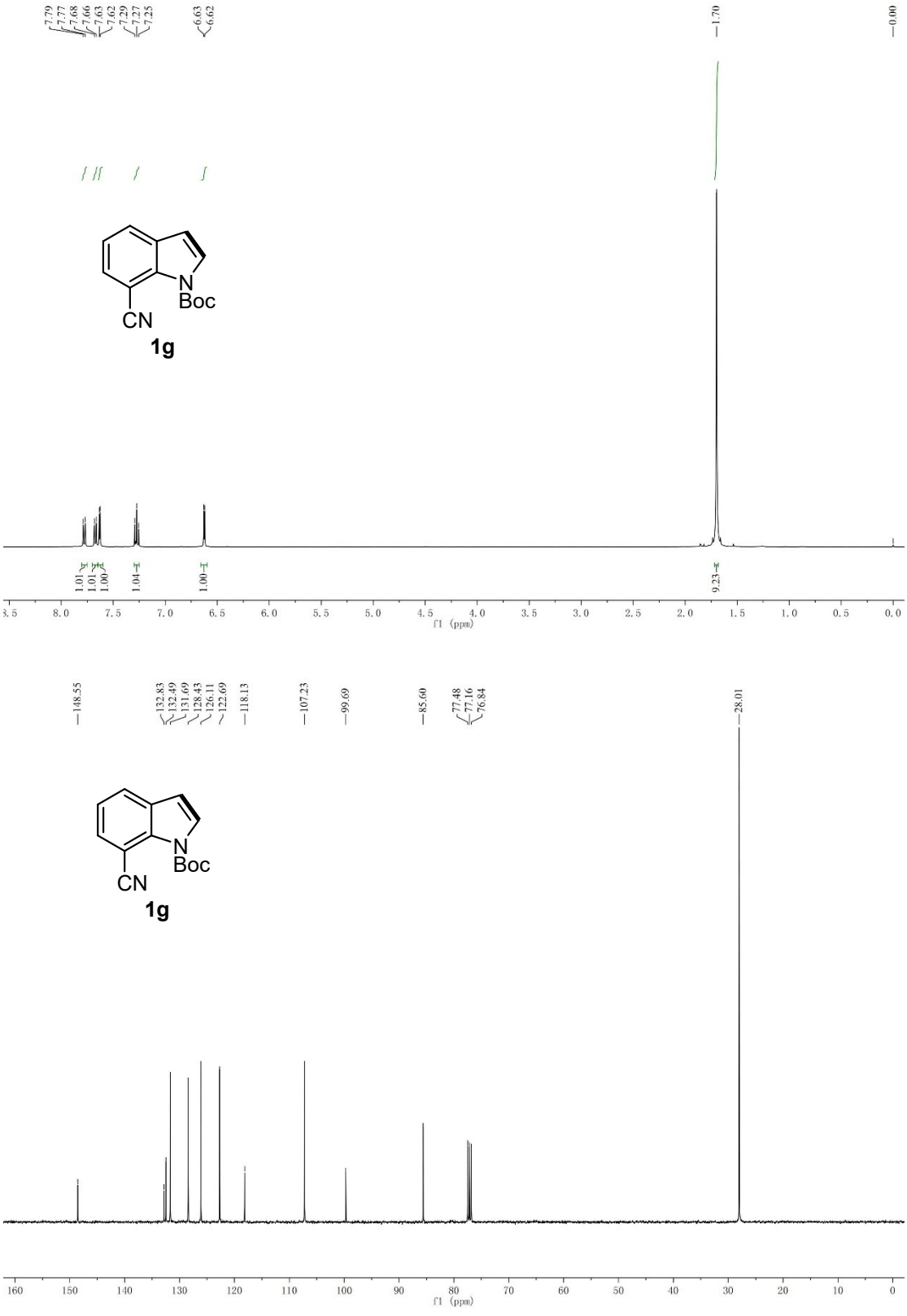


^{1}H NMR and ^{13}C NMR spectrum of **1e**

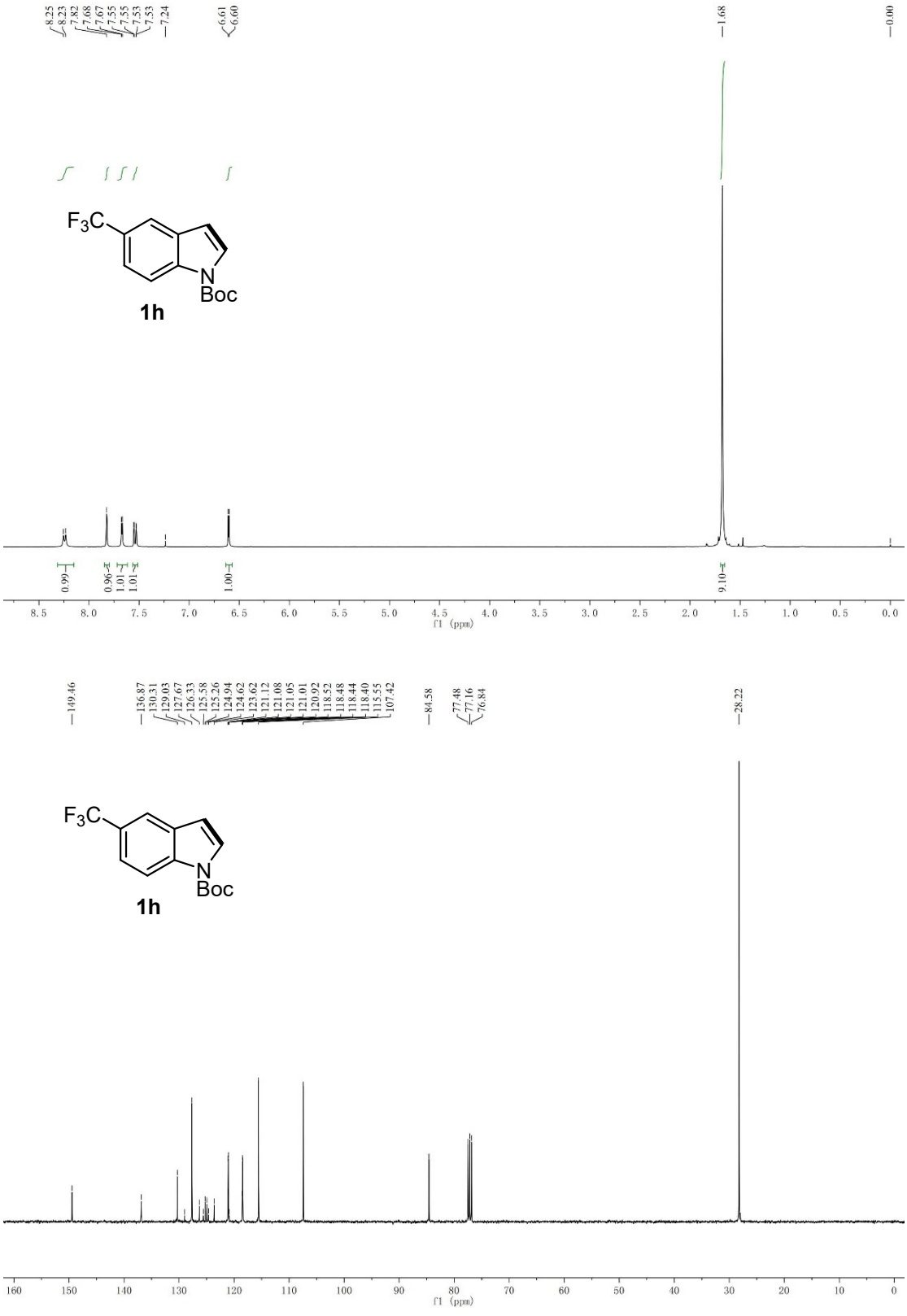




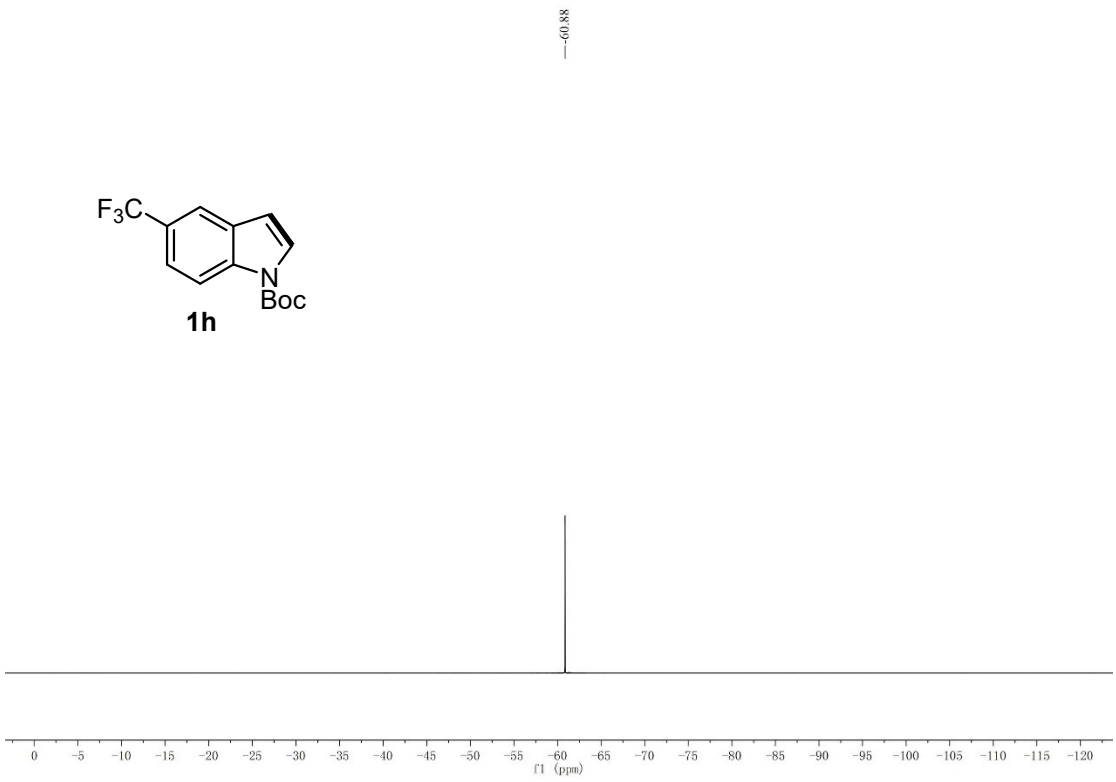
^{1}H NMR and ^{13}C NMR spectrum of **1f**



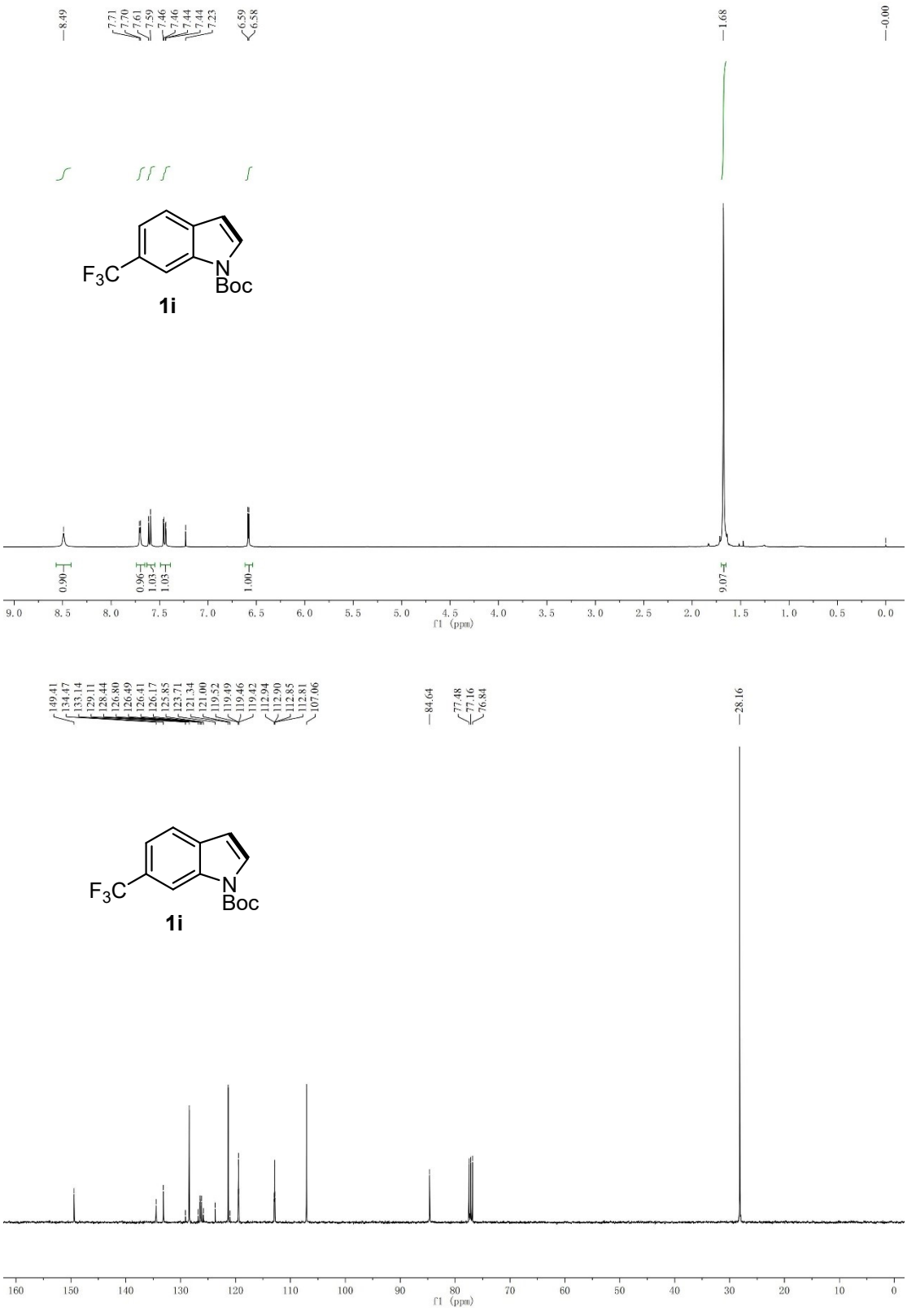
^{1}H NMR and ^{13}C NMR spectrum of **1g**



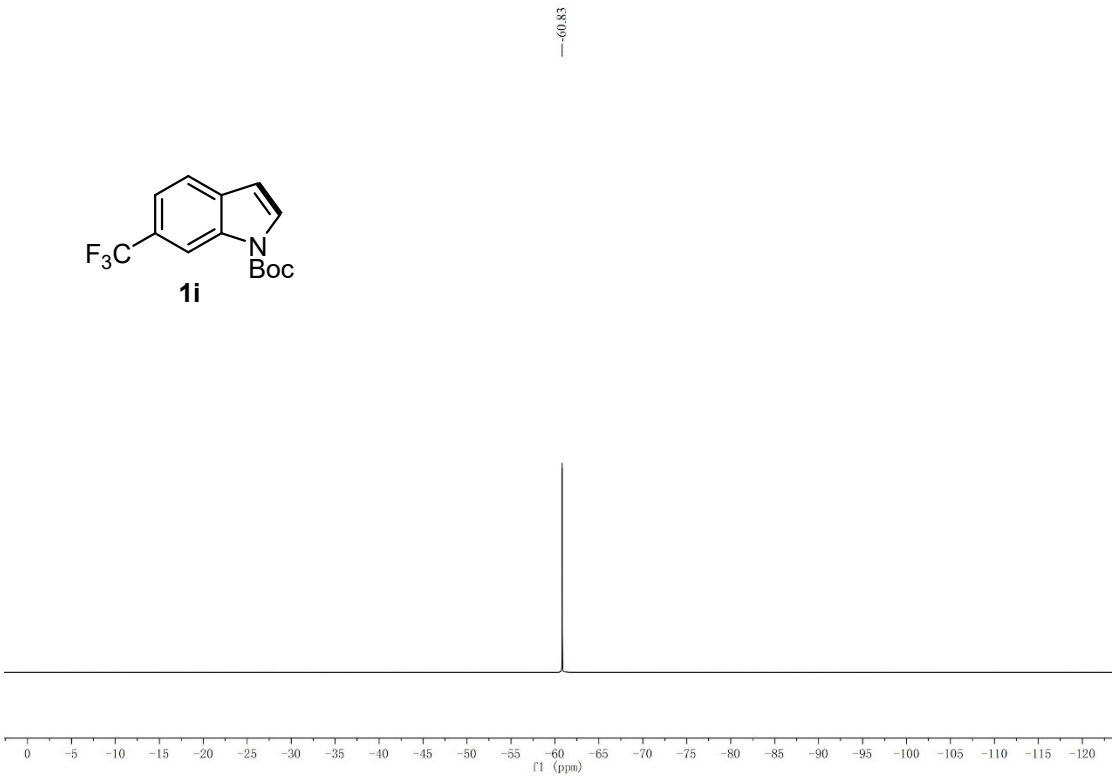
^{1}H NMR and ^{13}C NMR spectrum of **1h**



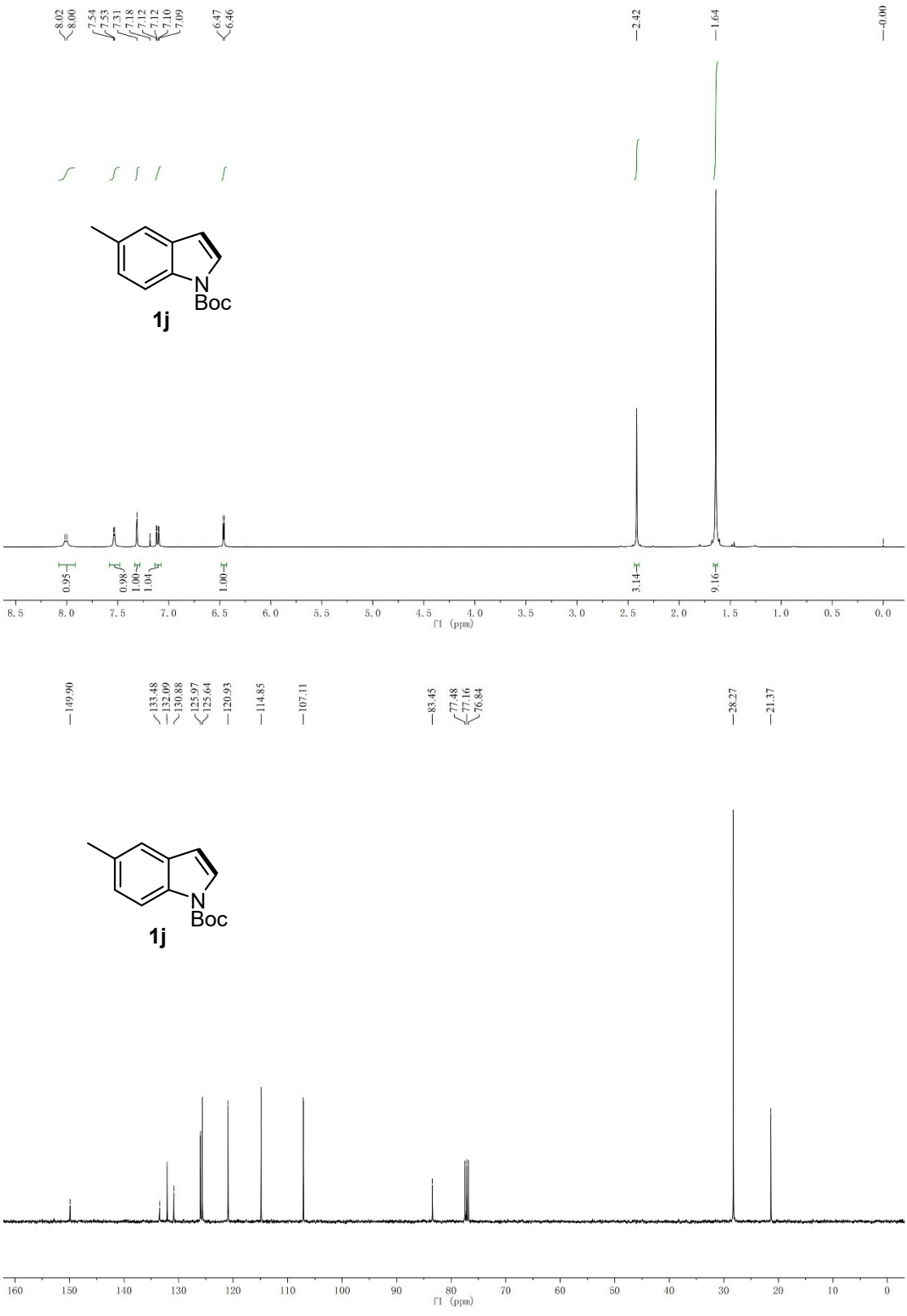
^{19}F NMR spectrum of **1h**



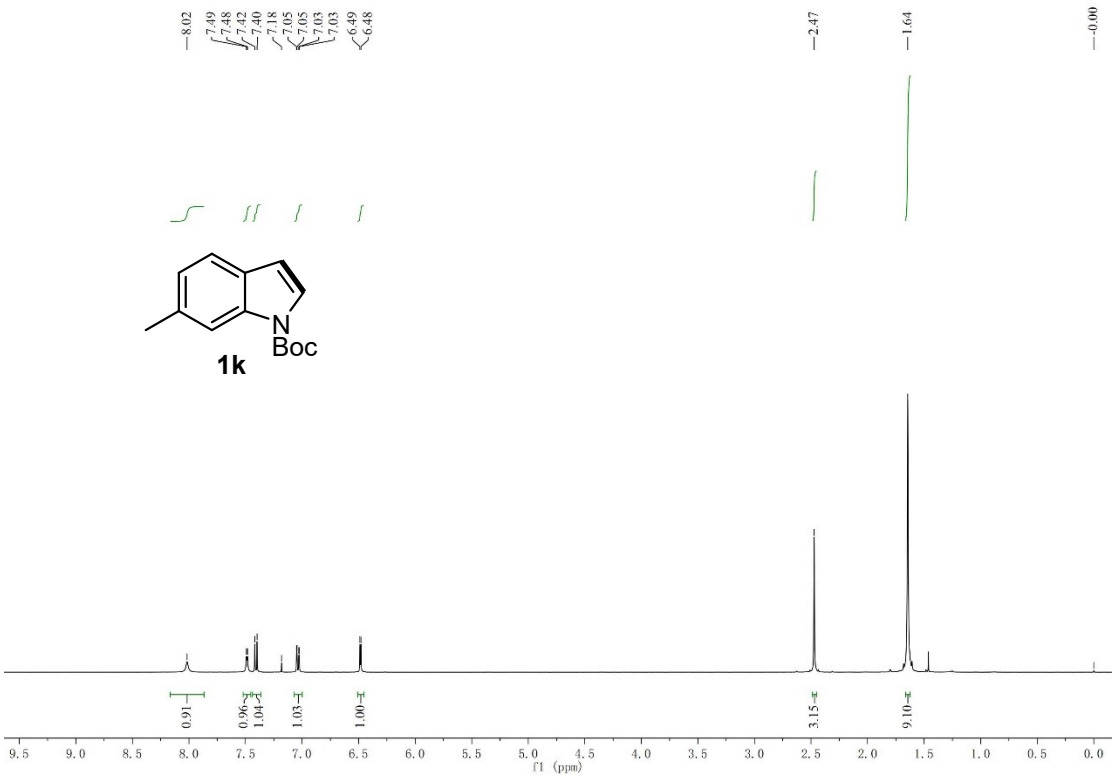
^{1}H NMR and ^{13}C NMR spectrum of **1i**

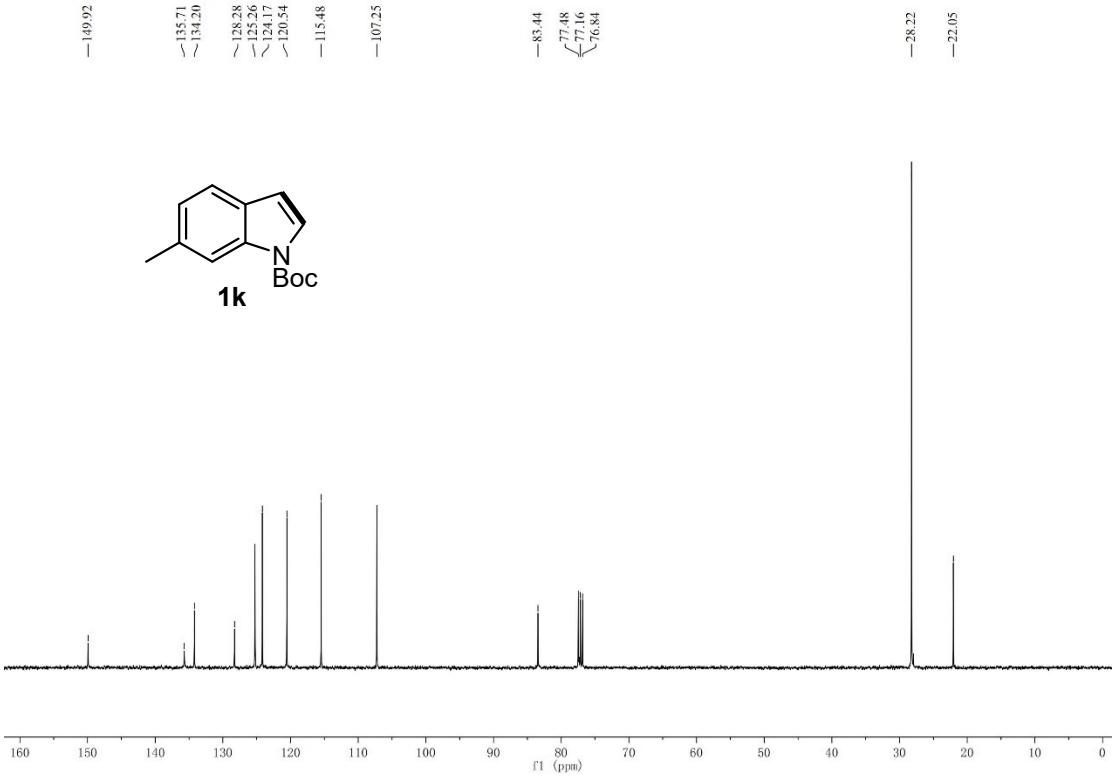


^{19}F NMR spectrum of **1i**

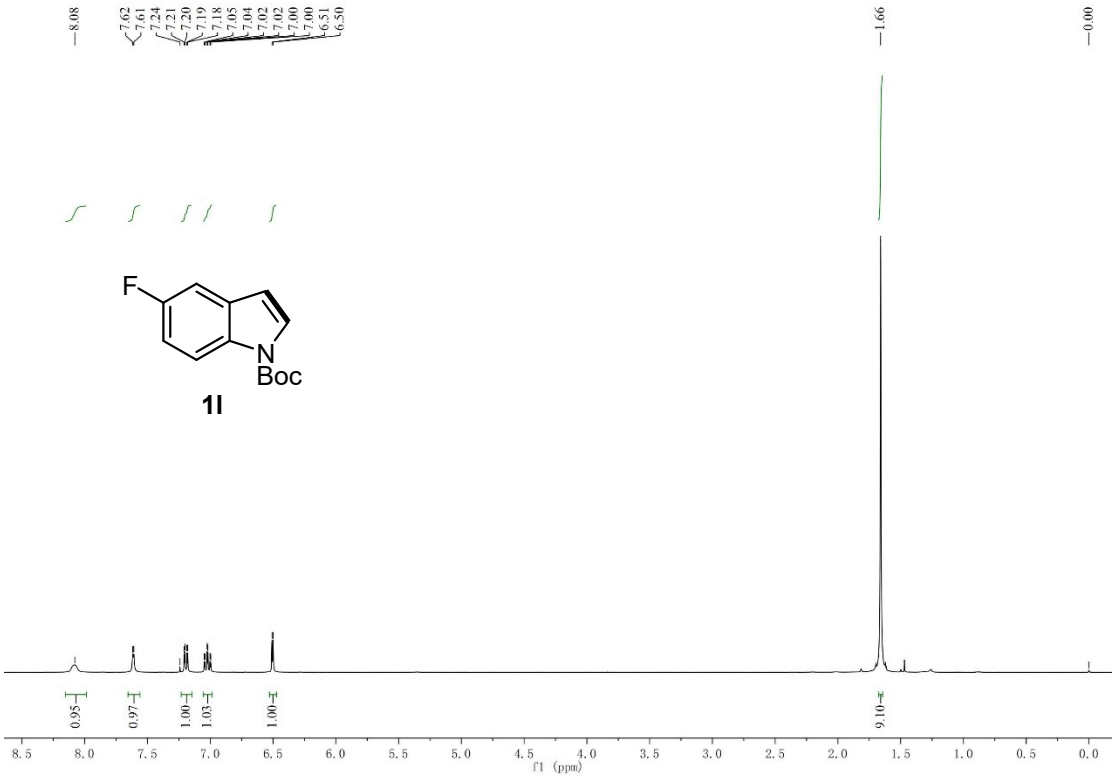


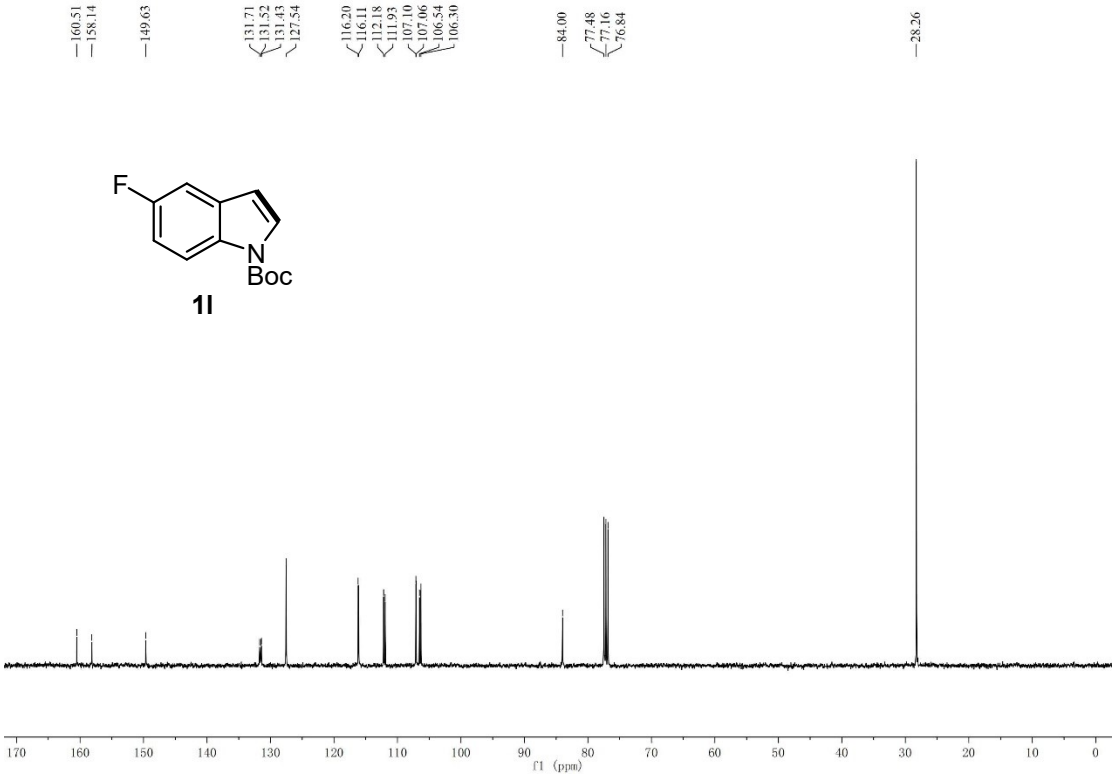
^{1}H NMR and ^{13}C NMR spectrum of **1j**



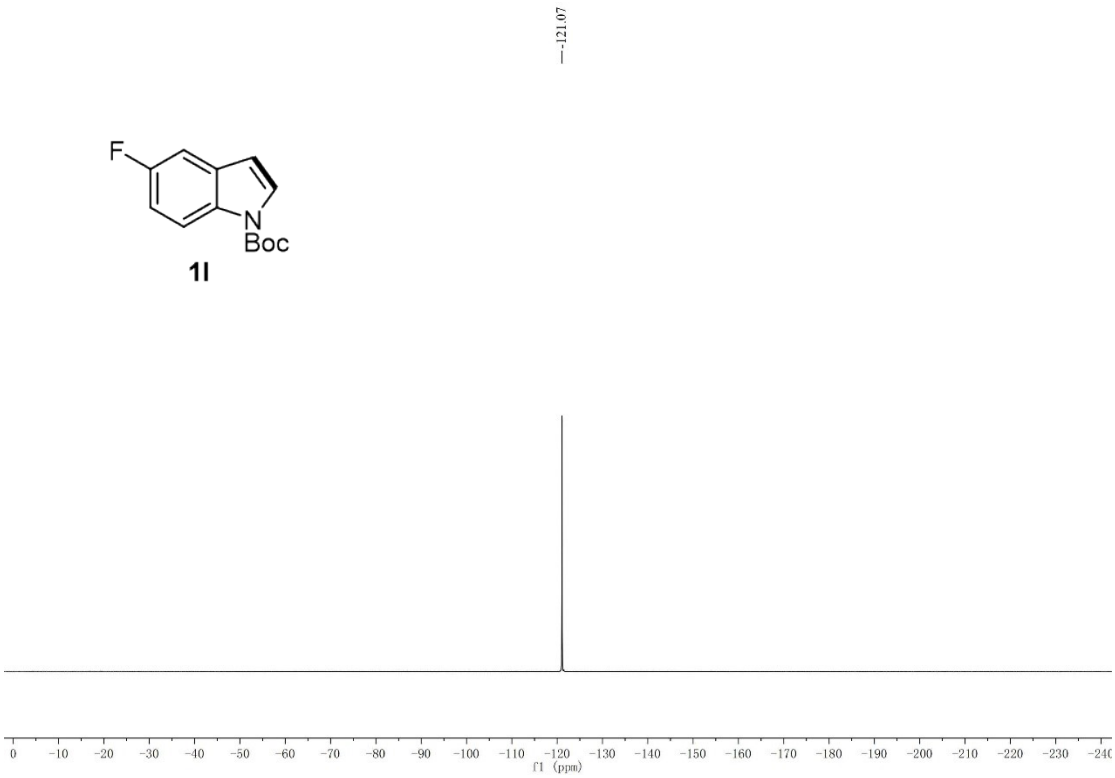


^{1}H NMR and ^{13}C NMR spectrum of **1k**

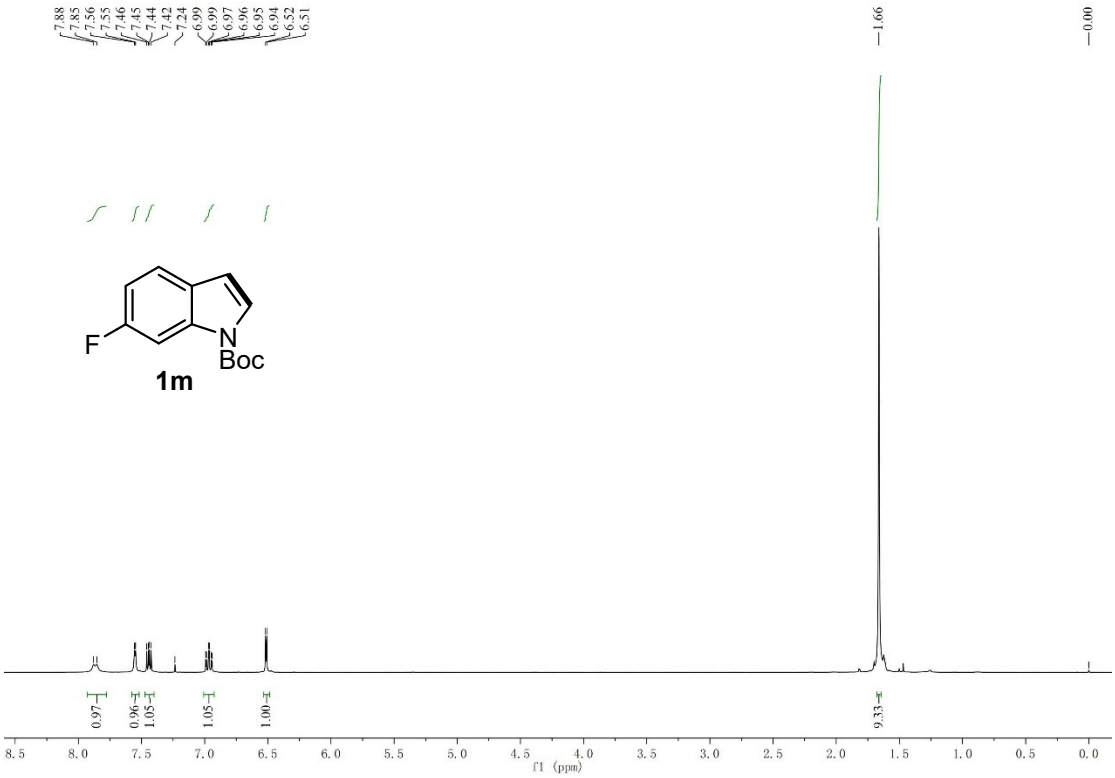


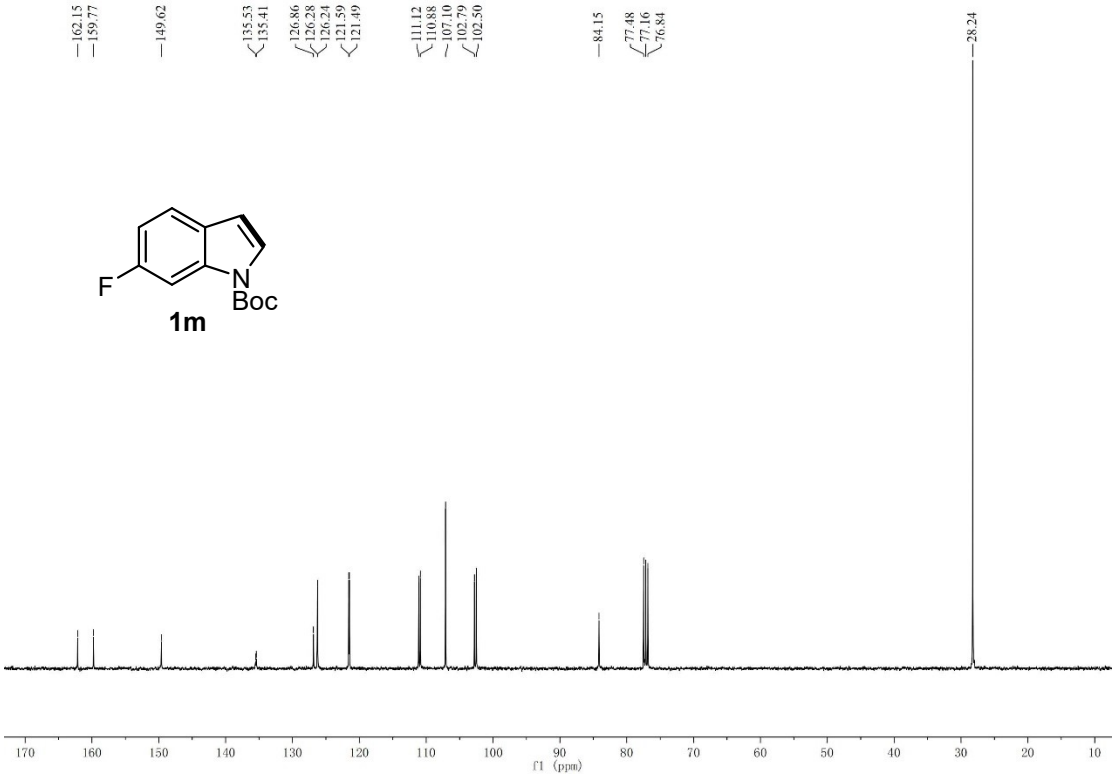


^{1}H NMR and ^{13}C NMR spectrum of **1l**



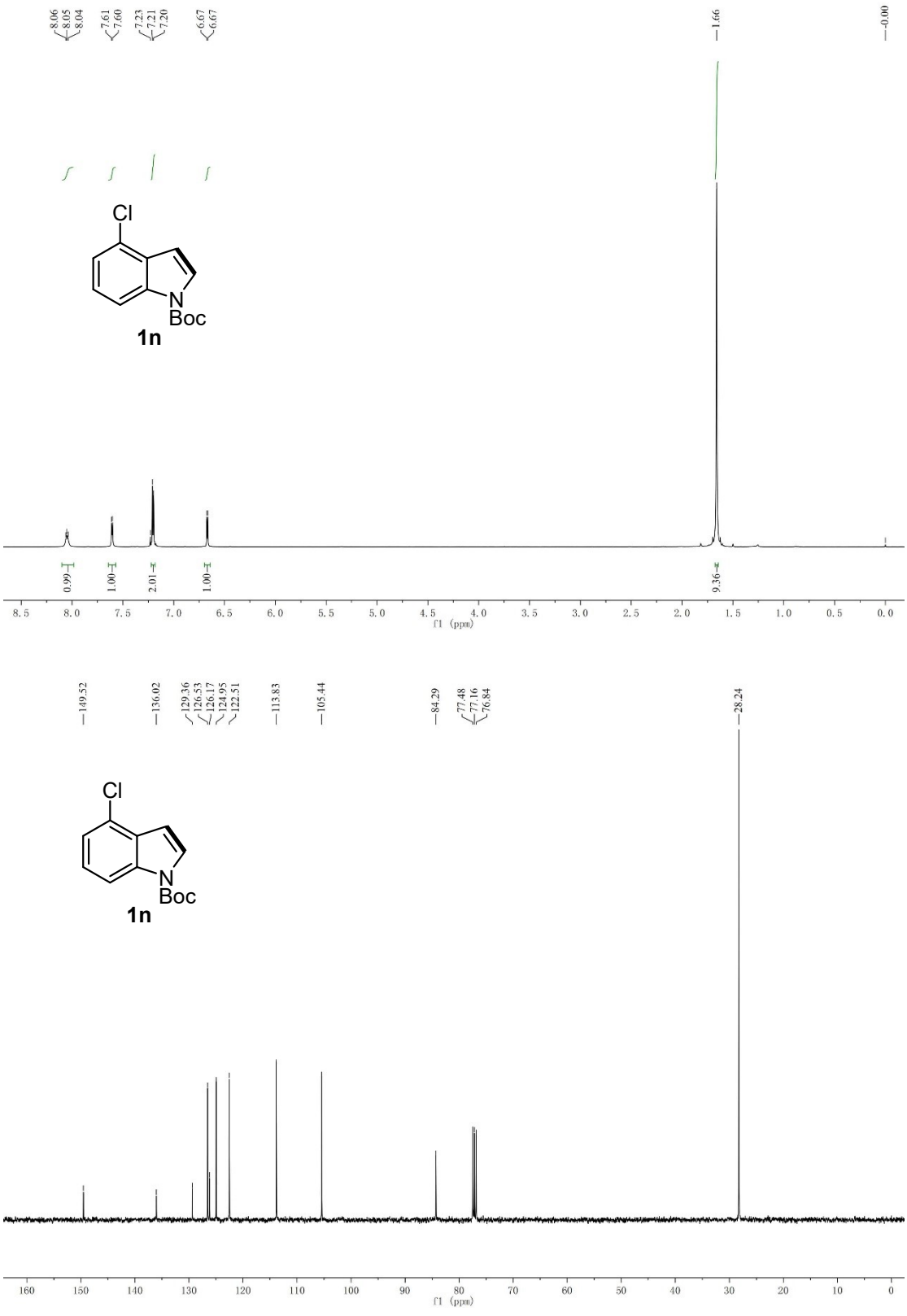
^{19}F NMR spectrum of **1l**



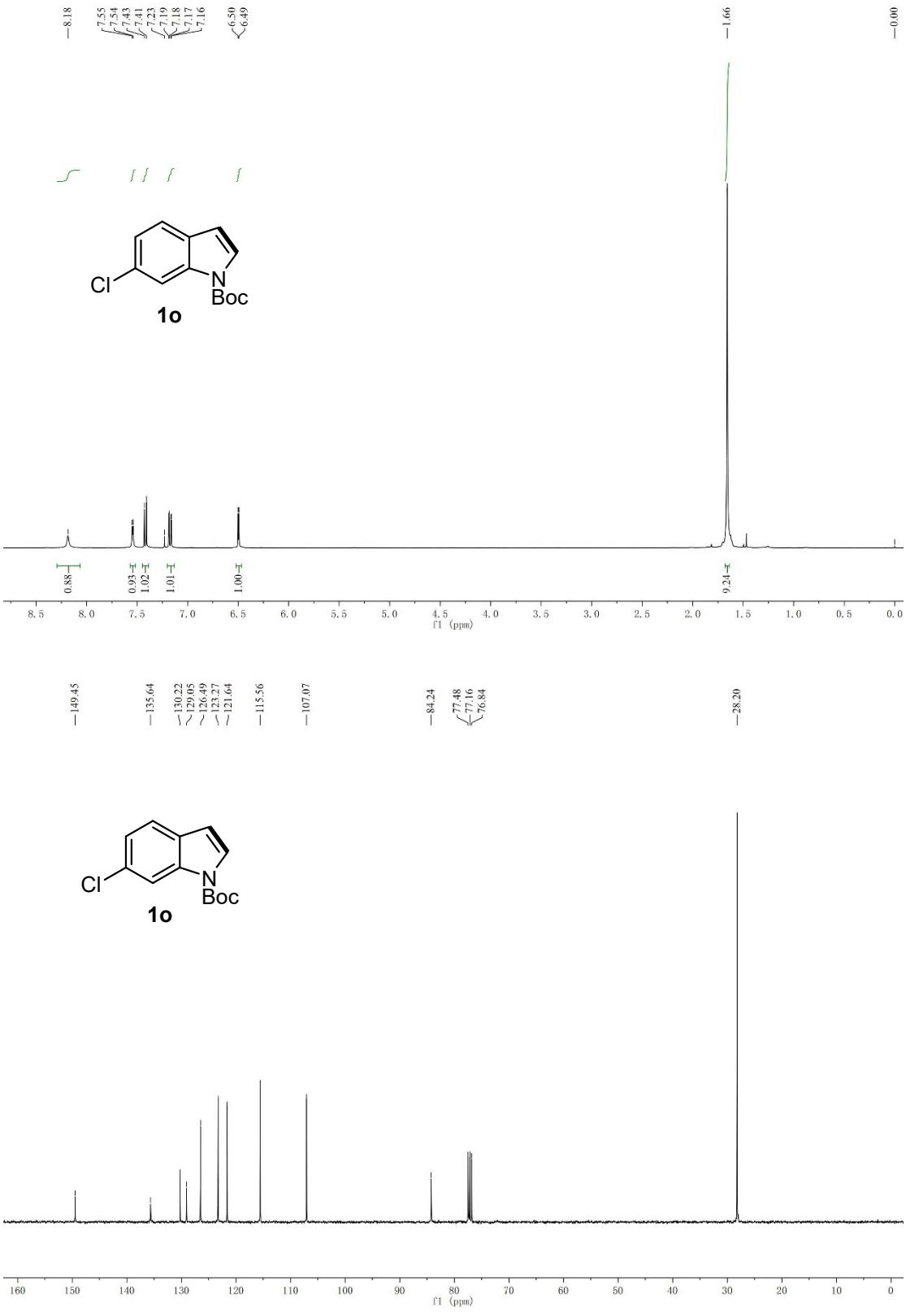


^{1}H NMR and ^{13}C NMR spectrum of **1m**

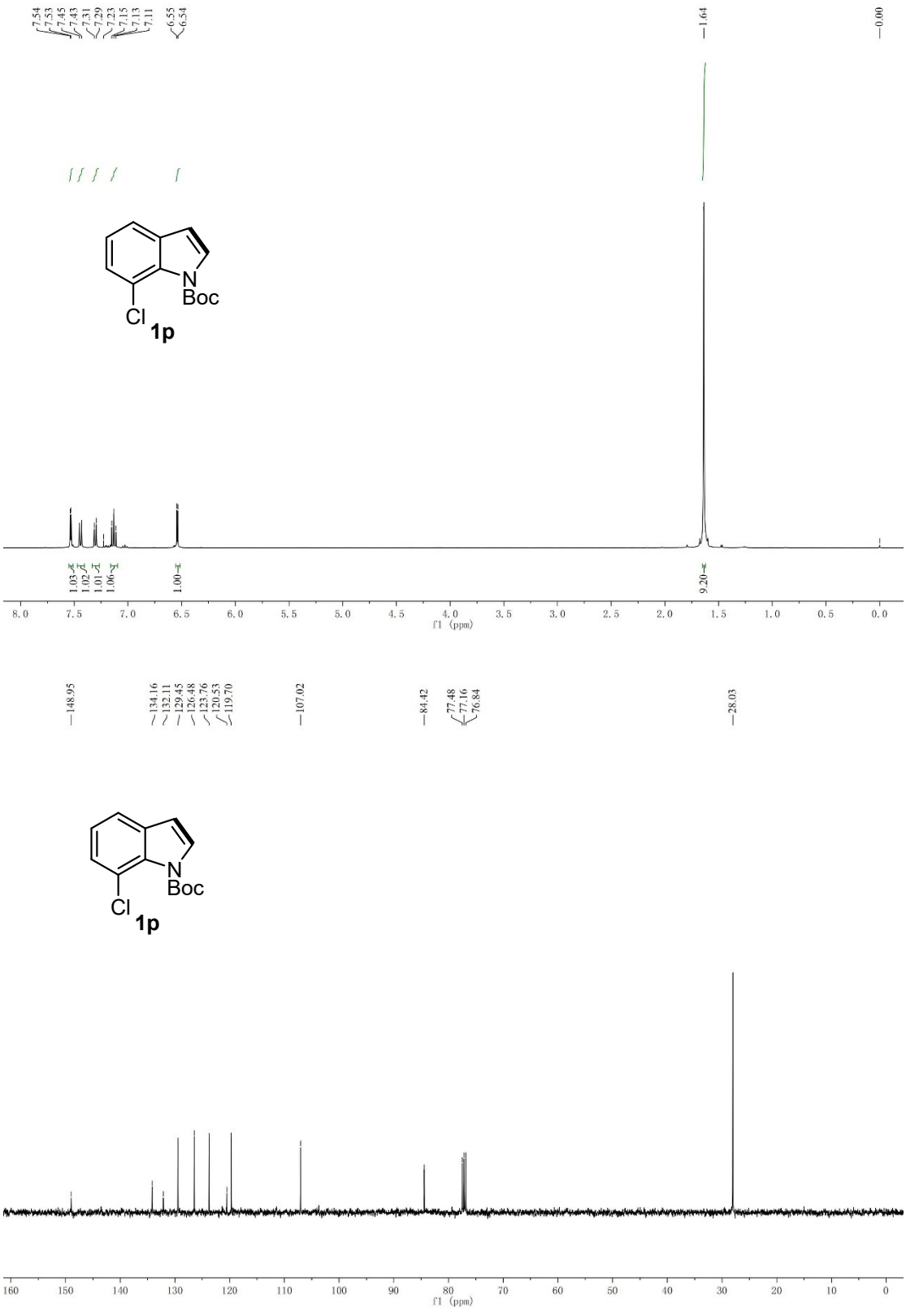
^{19}F NMR spectrum of **1m**



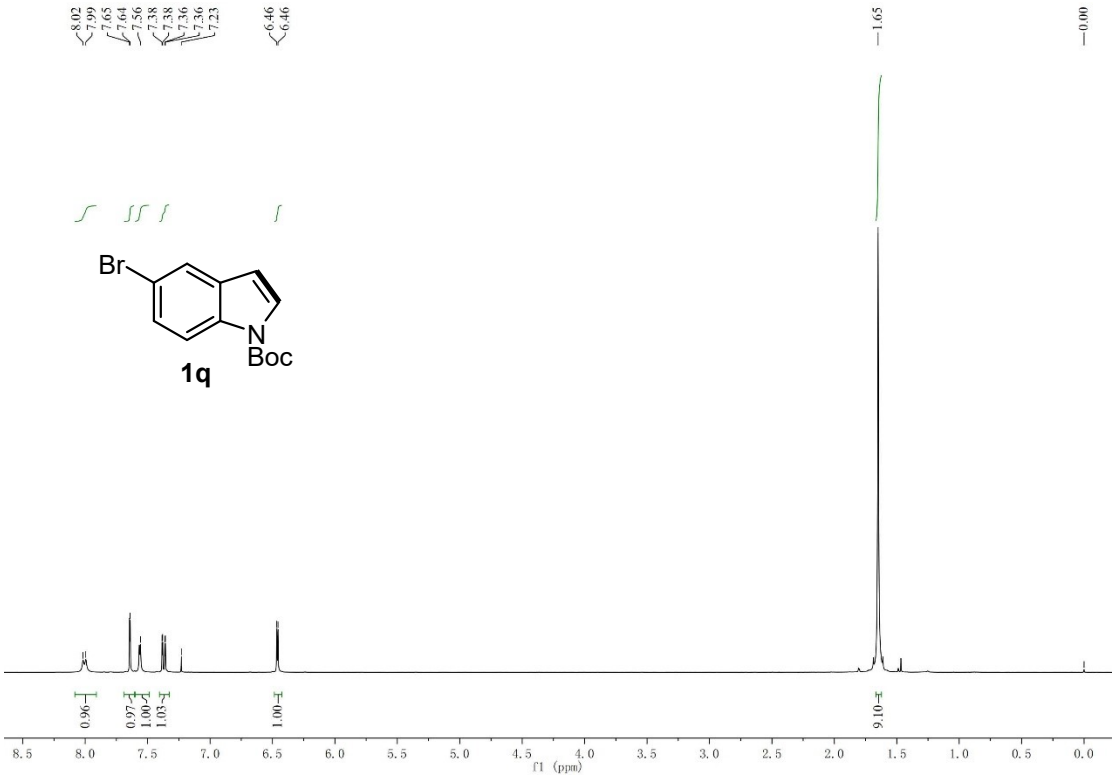
^{1}H NMR and ^{13}C NMR spectrum of **1n**

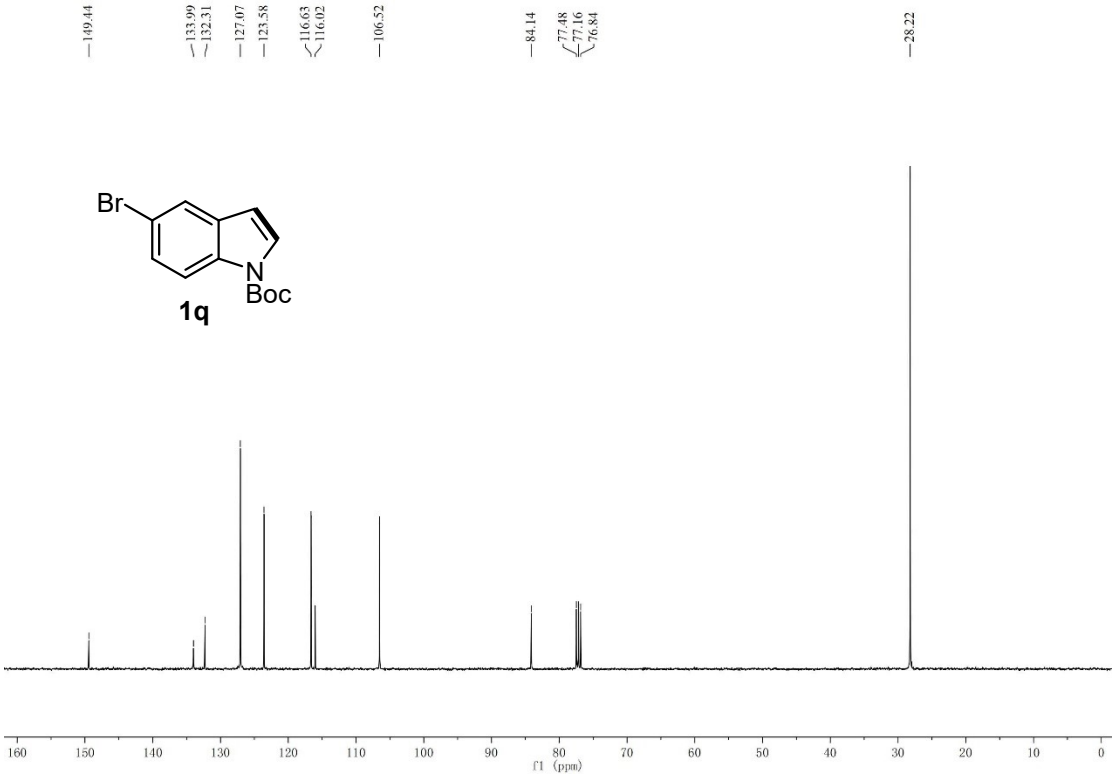


^{1}H NMR and ^{13}C NMR spectrum of **1o**

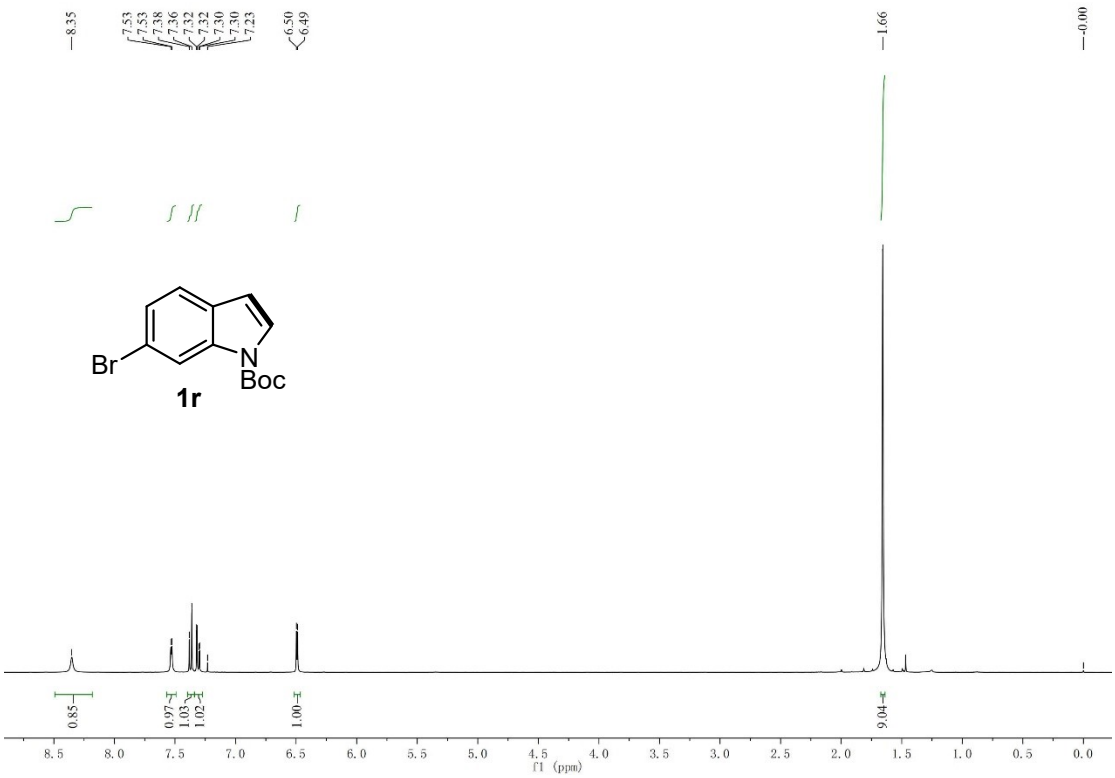


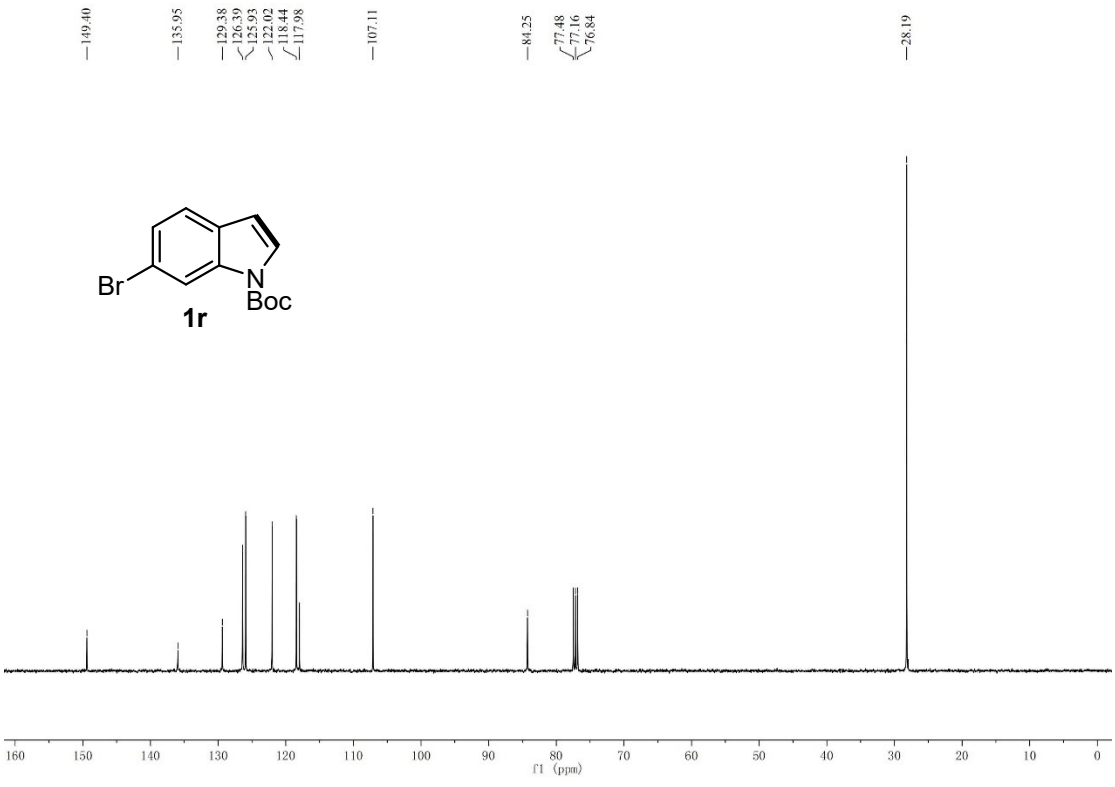
^{1}H NMR and ^{13}C NMR spectrum of **1p**



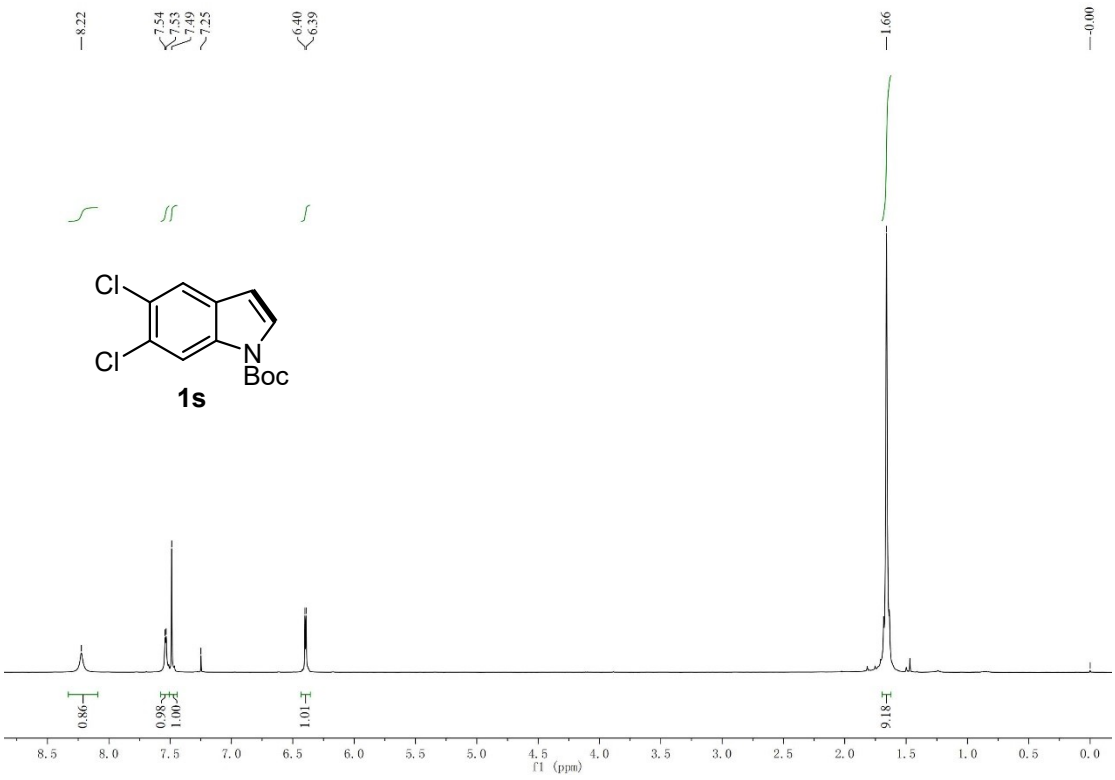


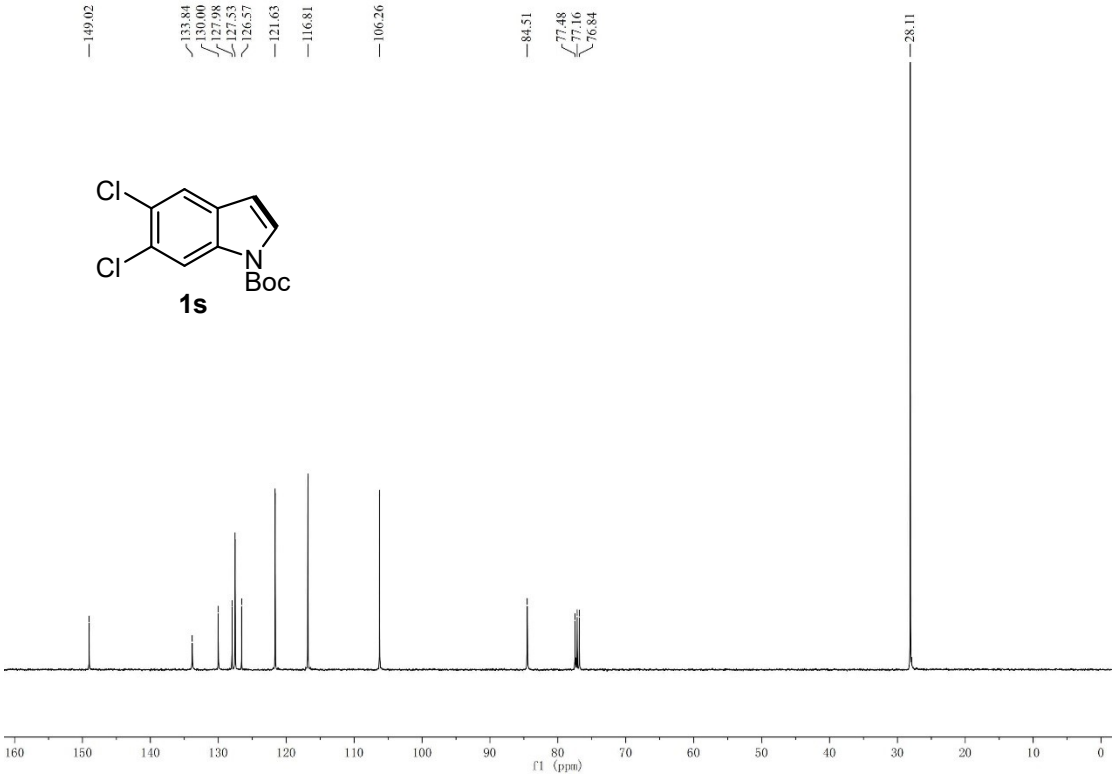
^{1}H NMR and ^{13}C NMR spectrum of **1q**



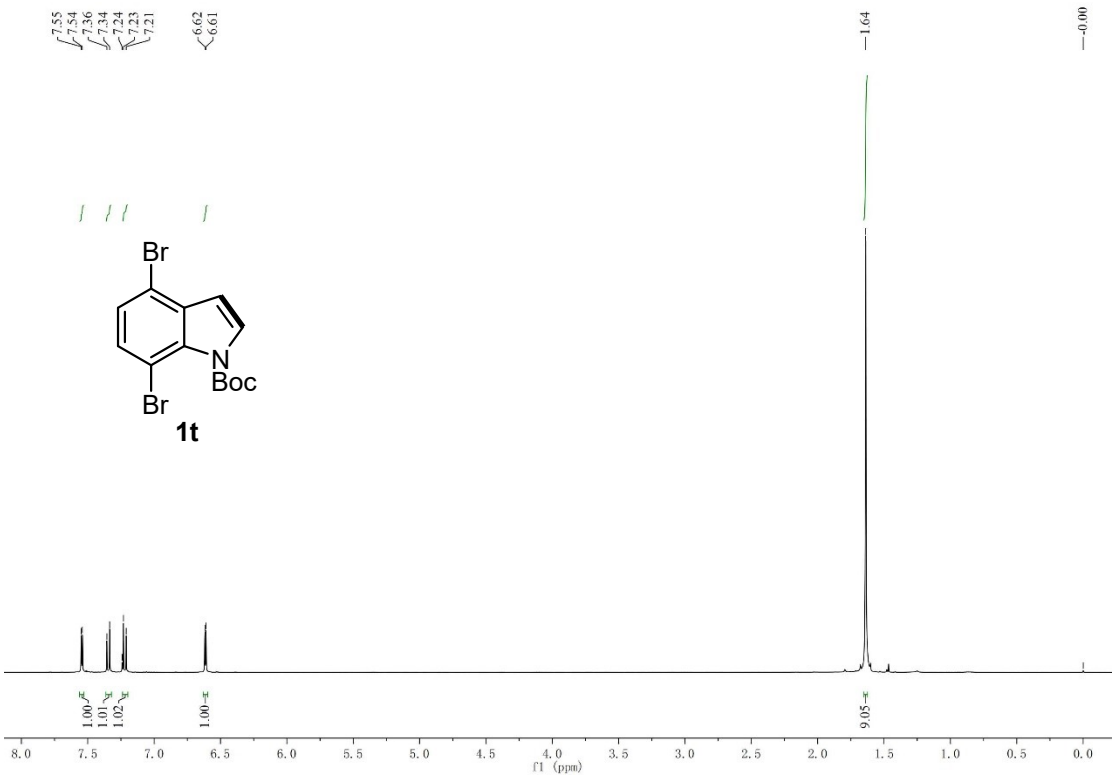


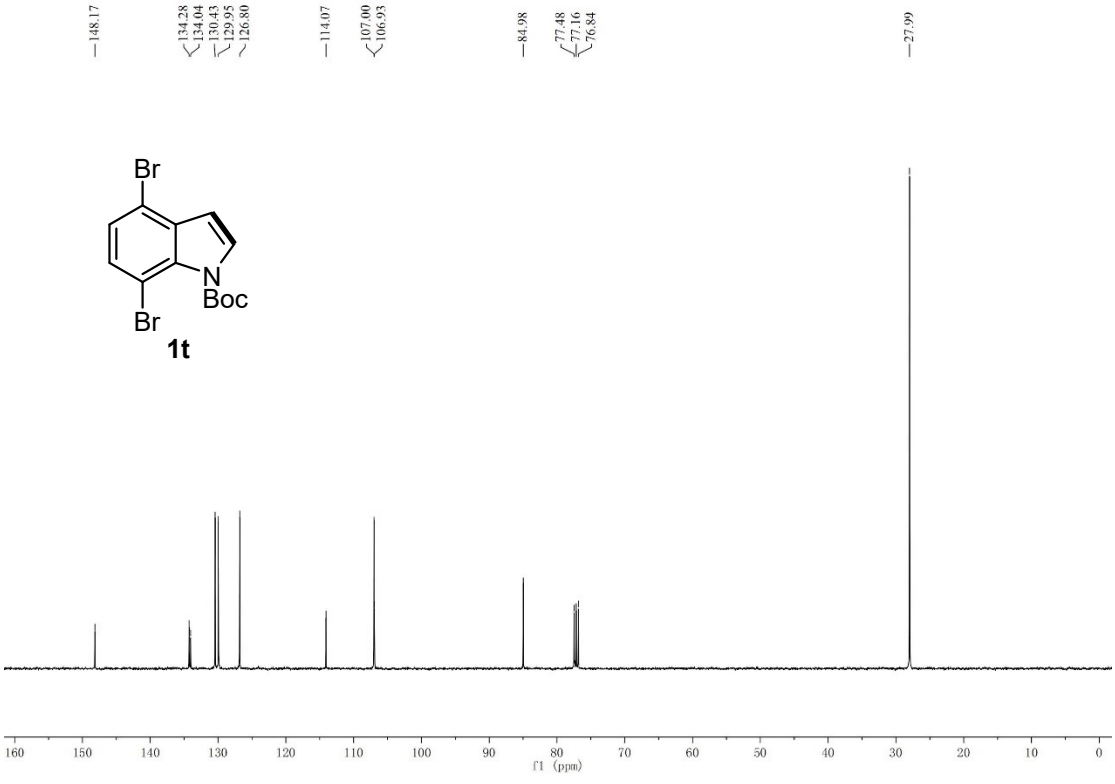
^{1}H NMR and ^{13}C NMR spectrum of **1r**



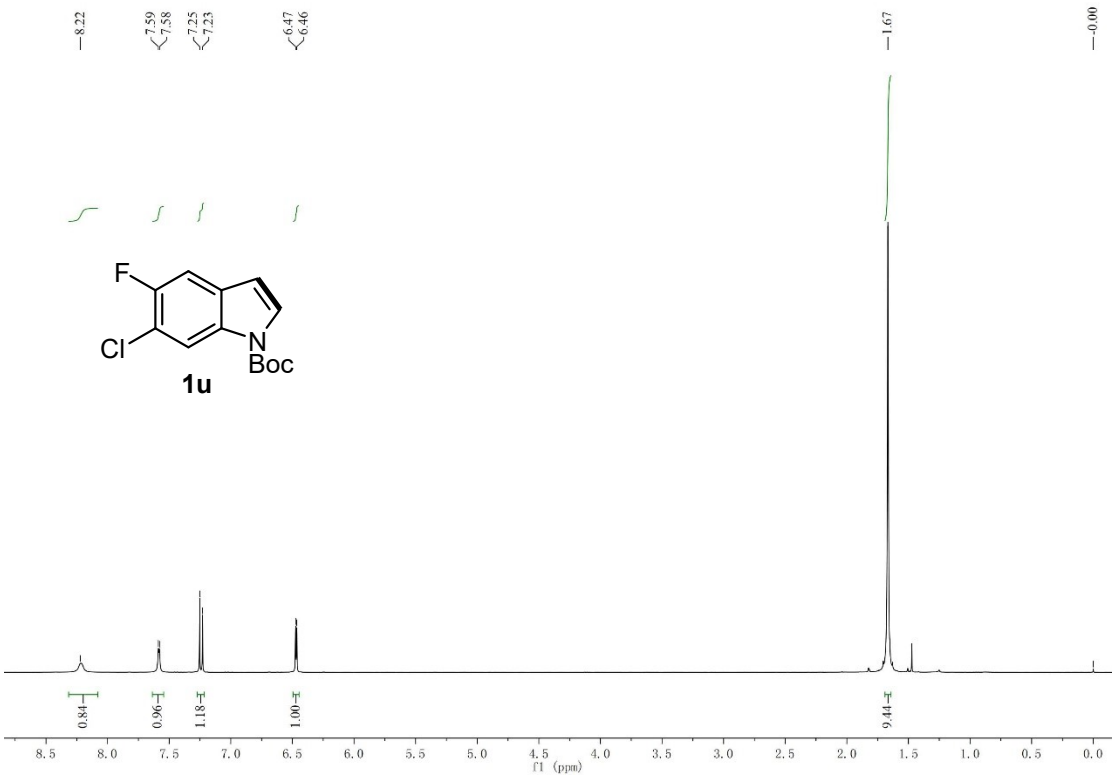


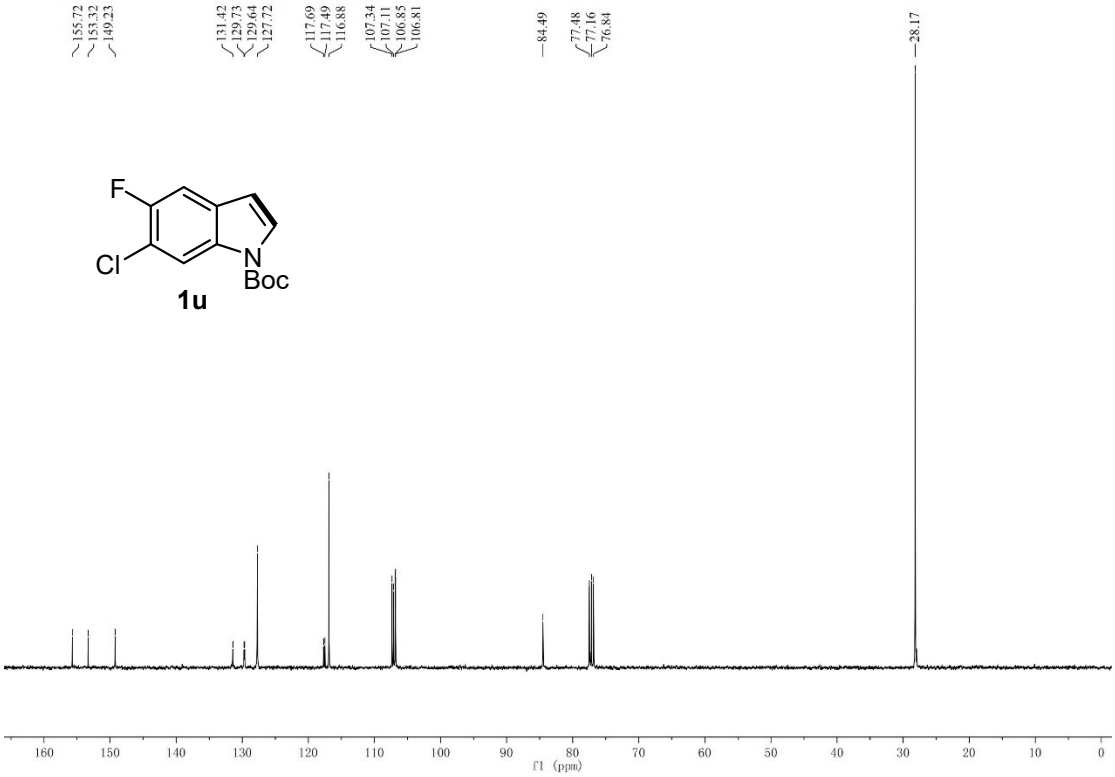
^{1}H NMR and ^{13}C NMR spectrum of **1s**



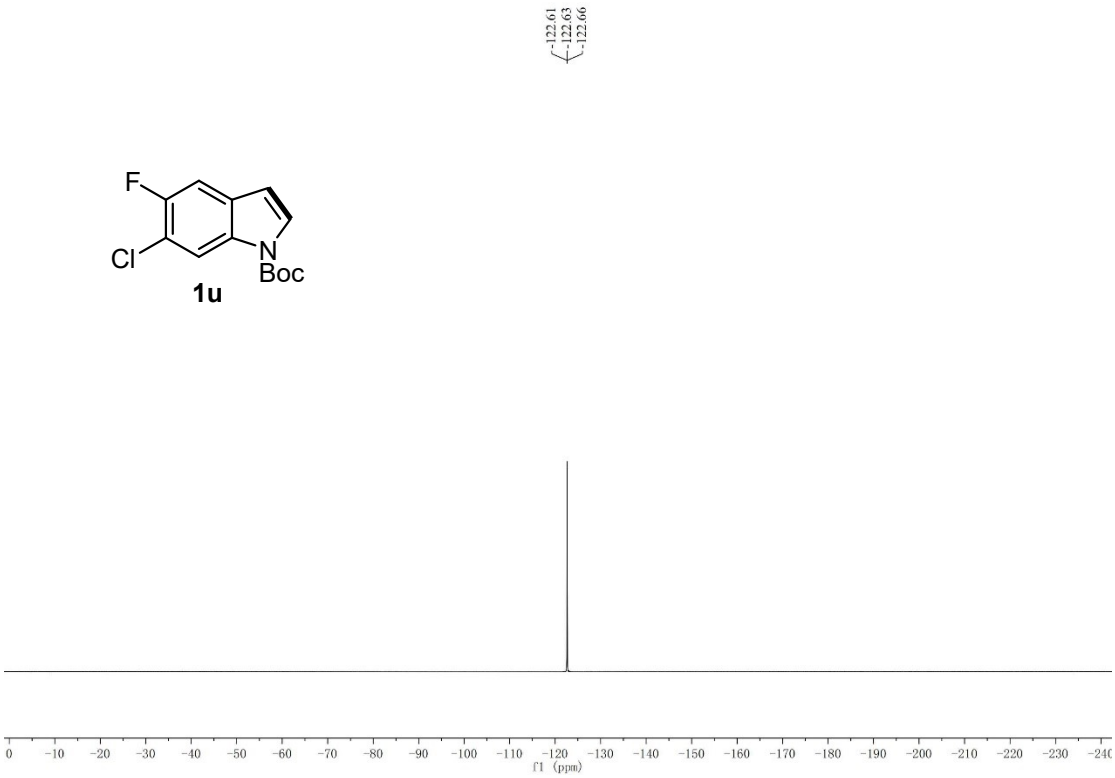


^{1}H NMR and ^{13}C NMR spectrum of **1t**

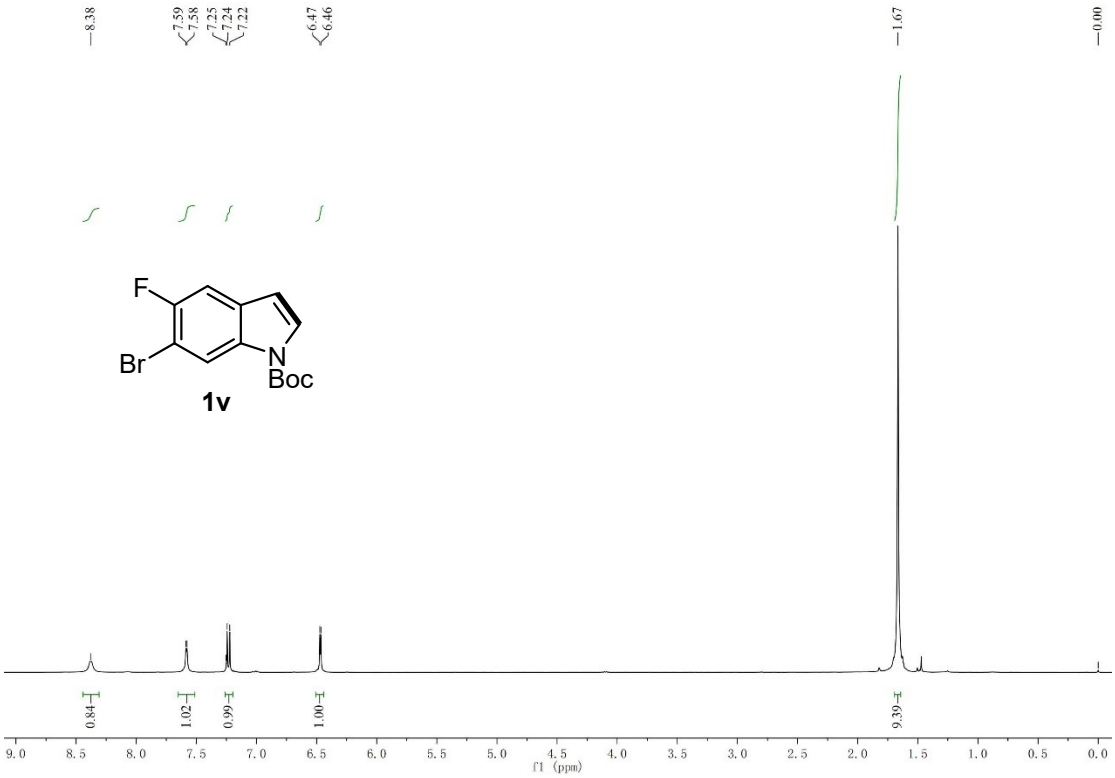


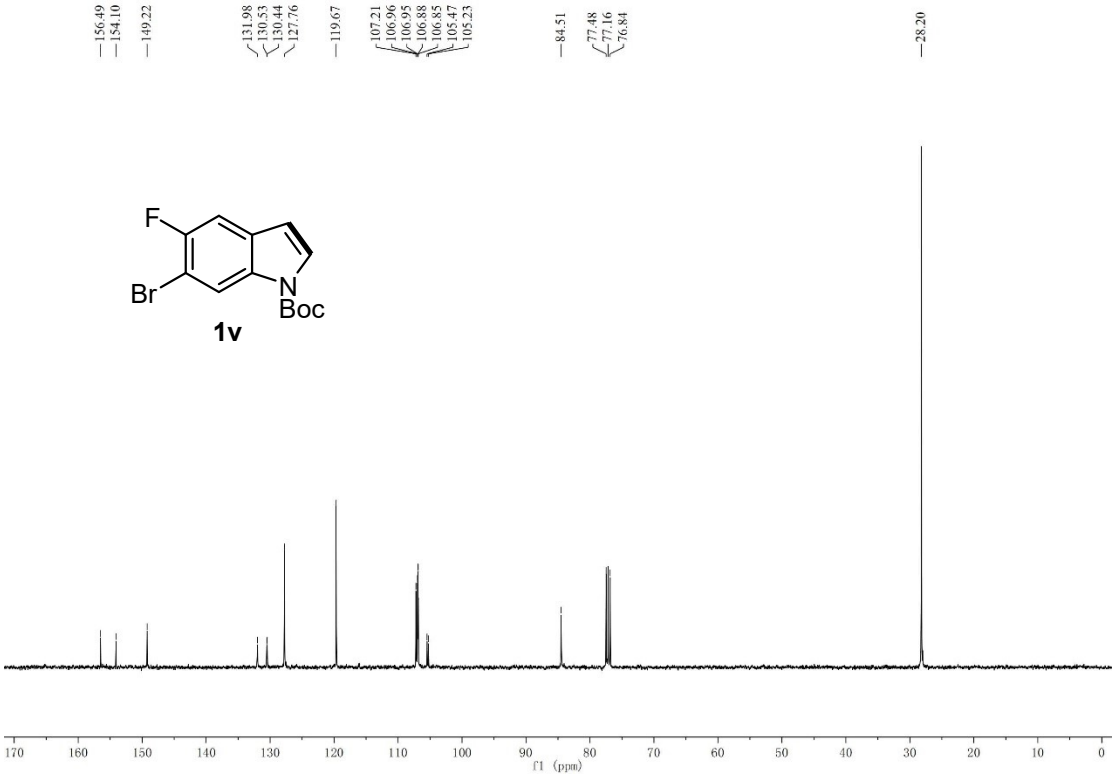


^{1}H NMR and ^{13}C NMR spectrum of **1u**

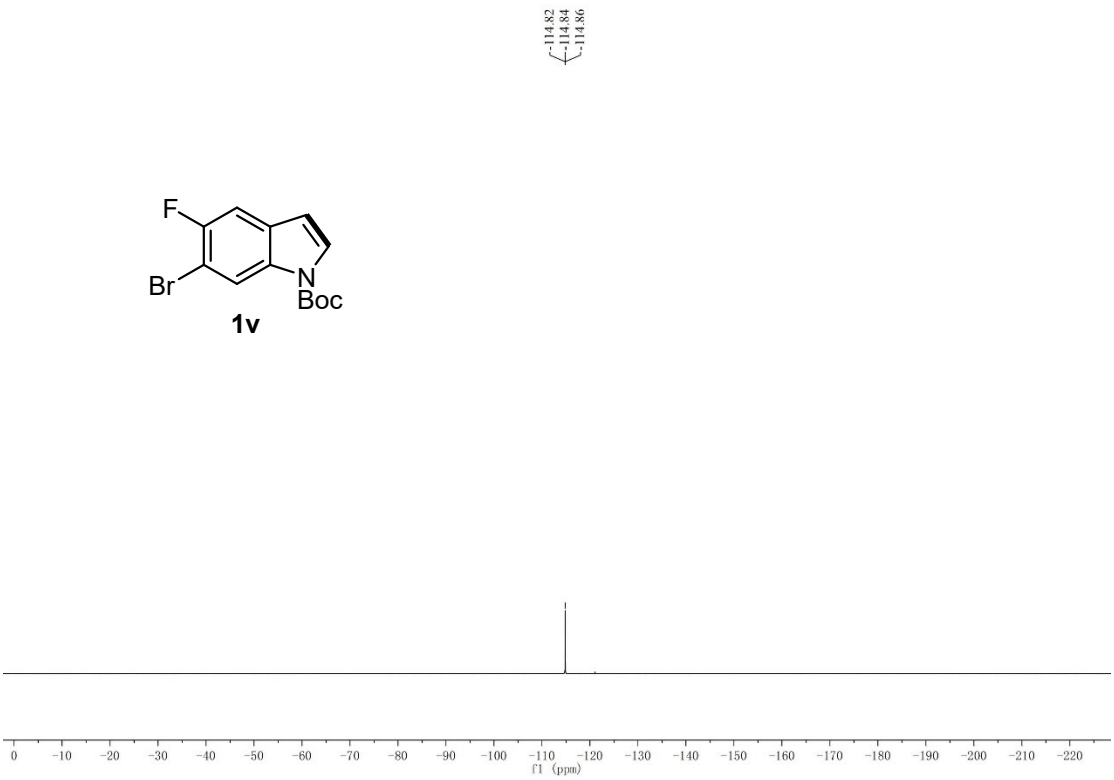


^{19}F NMR spectrum of **1u**

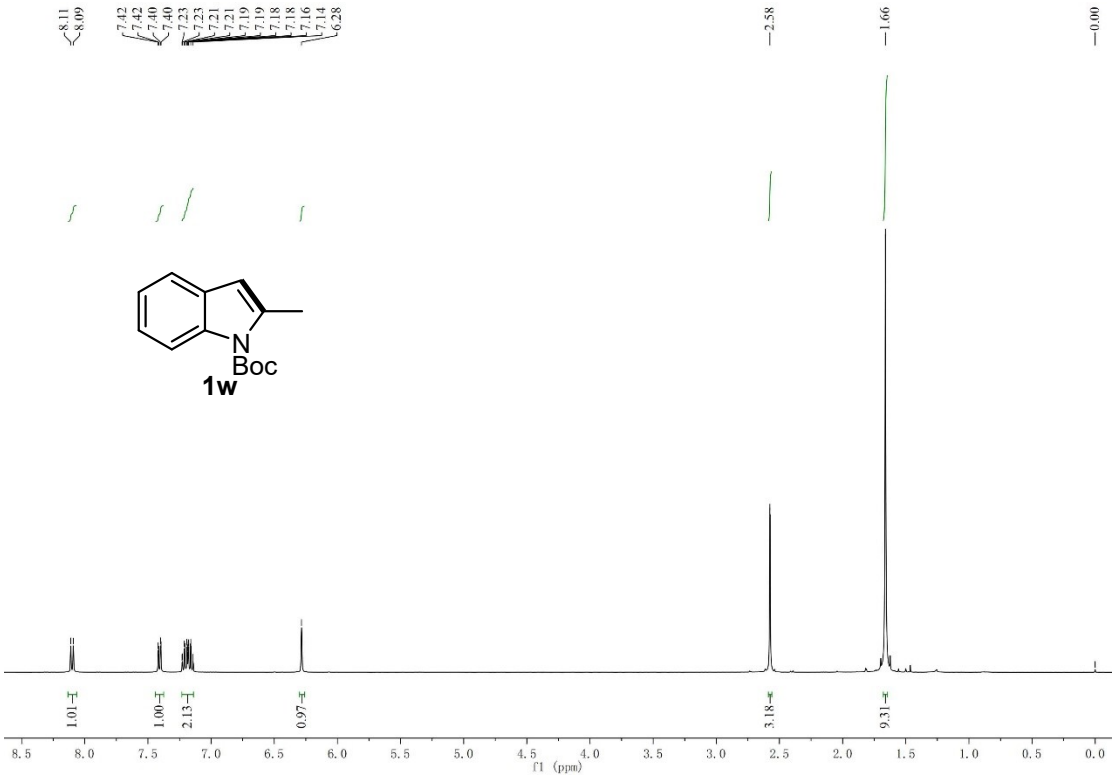


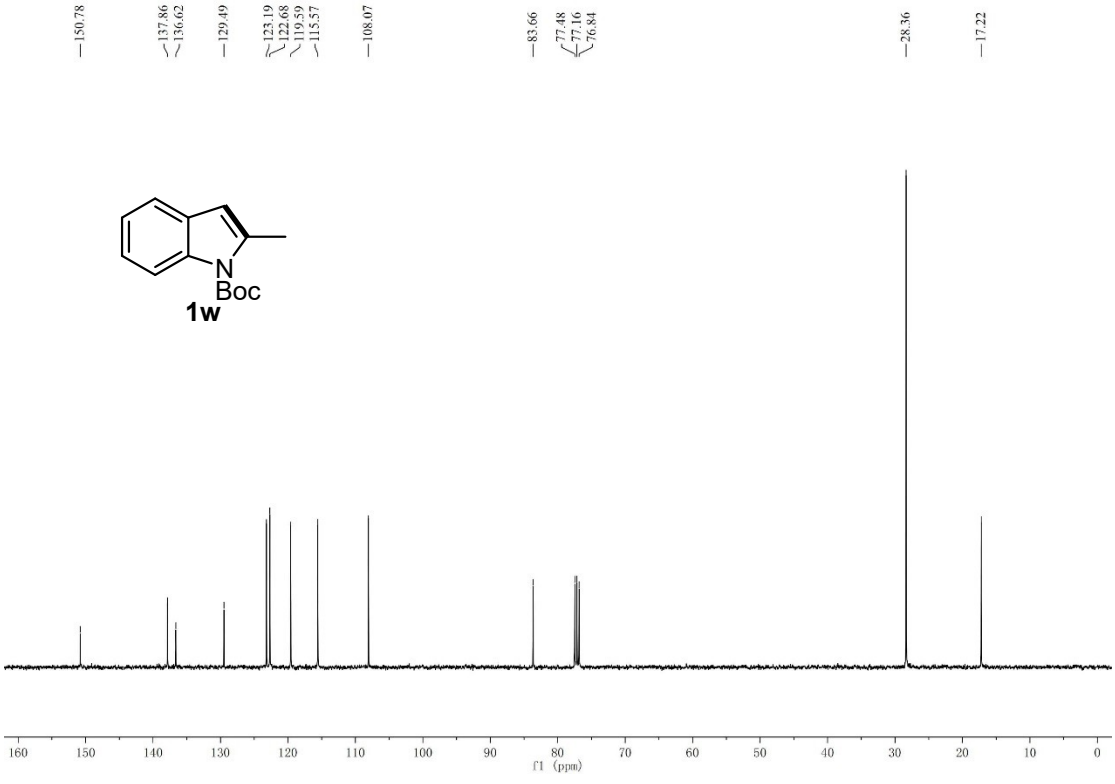


^{1}H NMR and ^{13}C NMR spectrum of **1v**



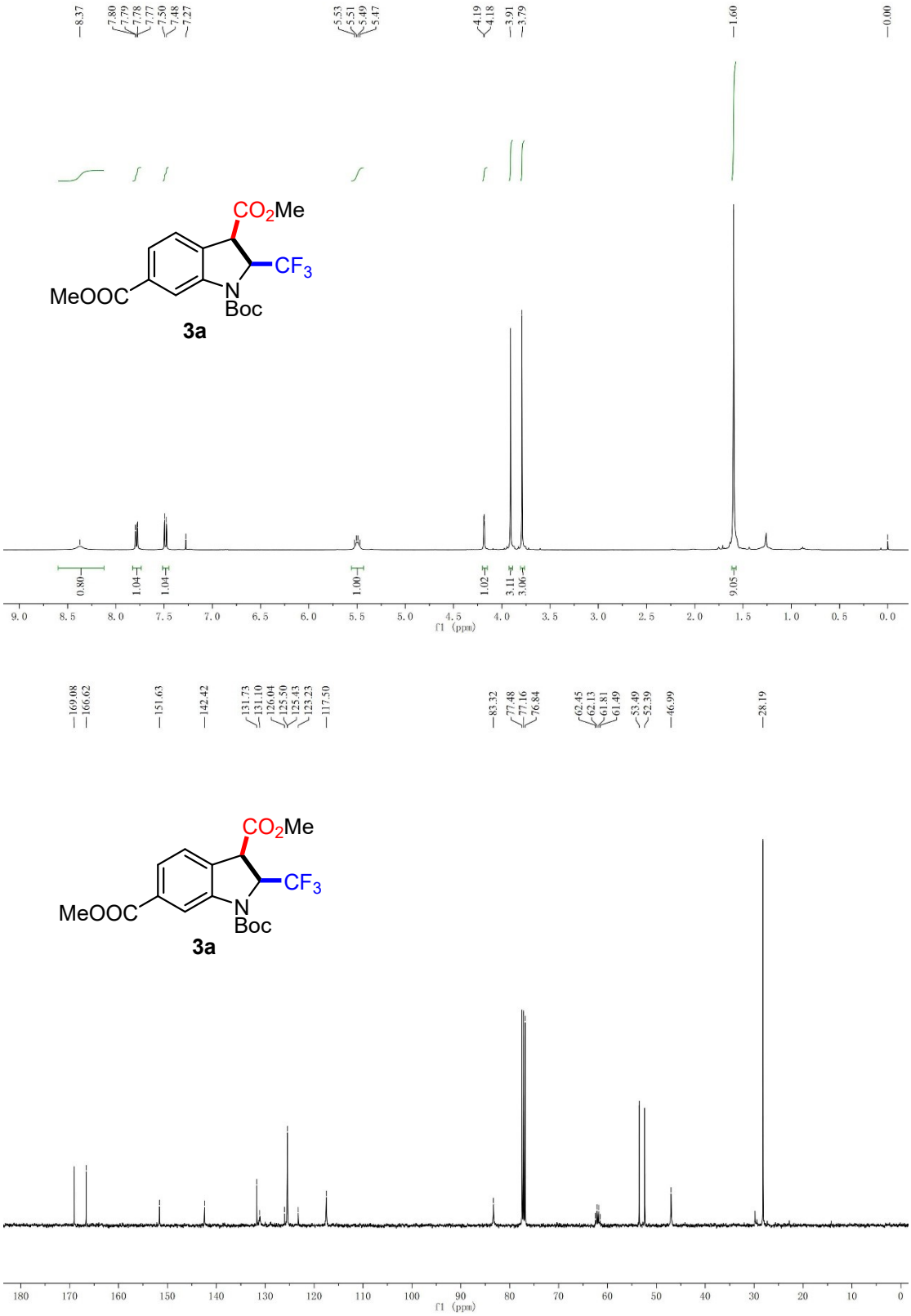
^{19}F NMR spectrum of **1v**



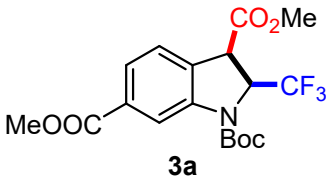


^{1}H NMR and ^{13}C NMR spectrum of **1w**

7. NMR Spectra of Products

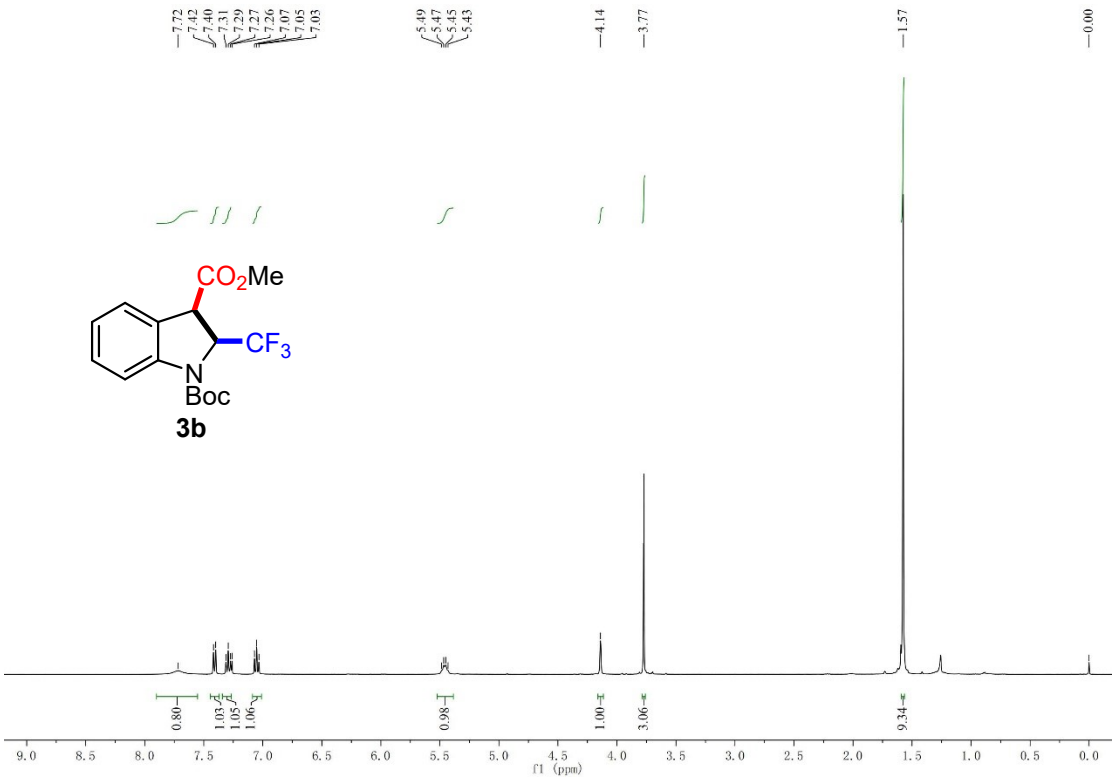


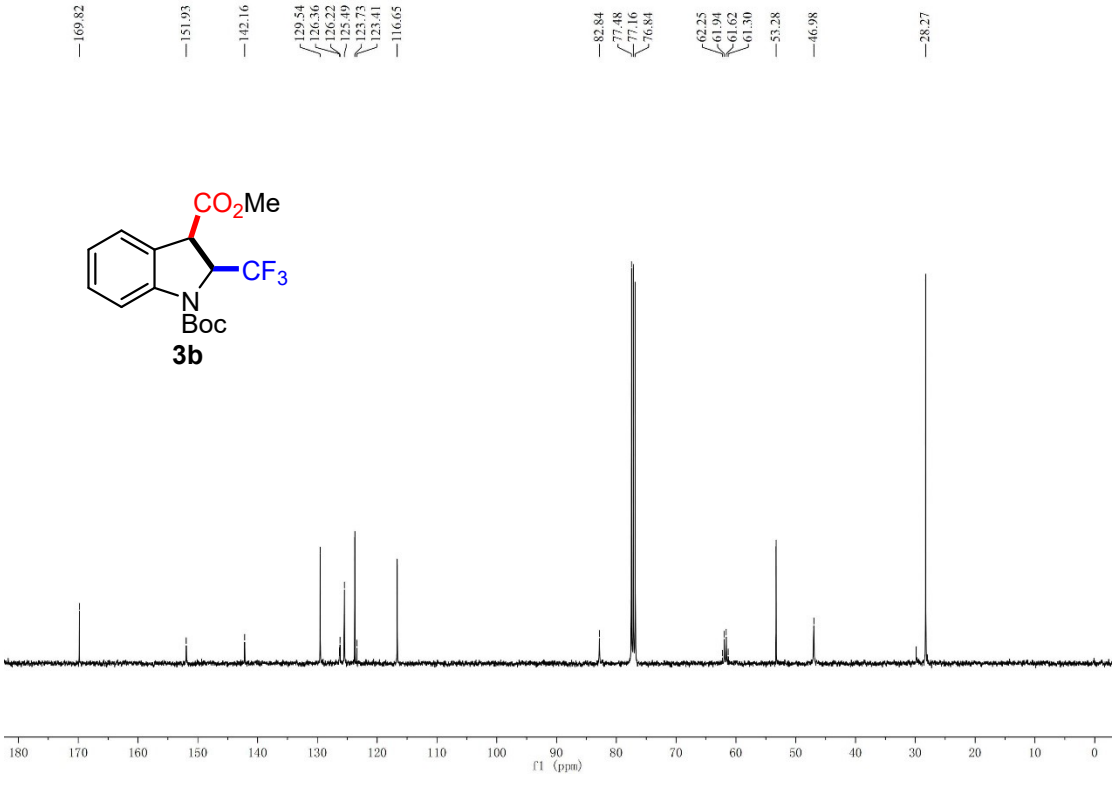
^{1}H NMR and ^{13}C NMR spectrum of **3a**



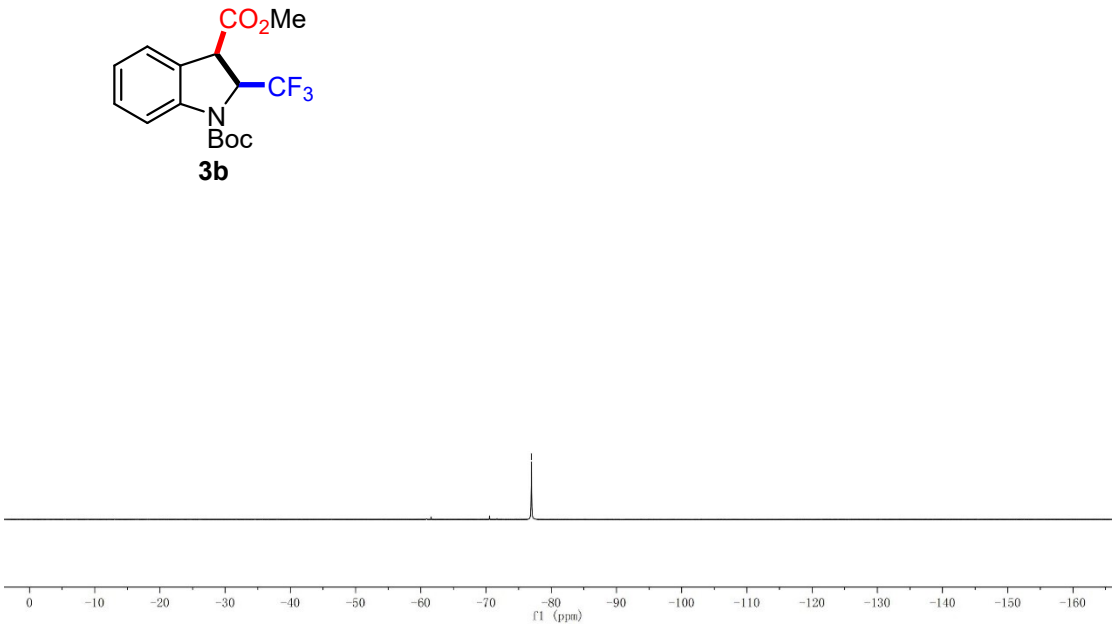
3a

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

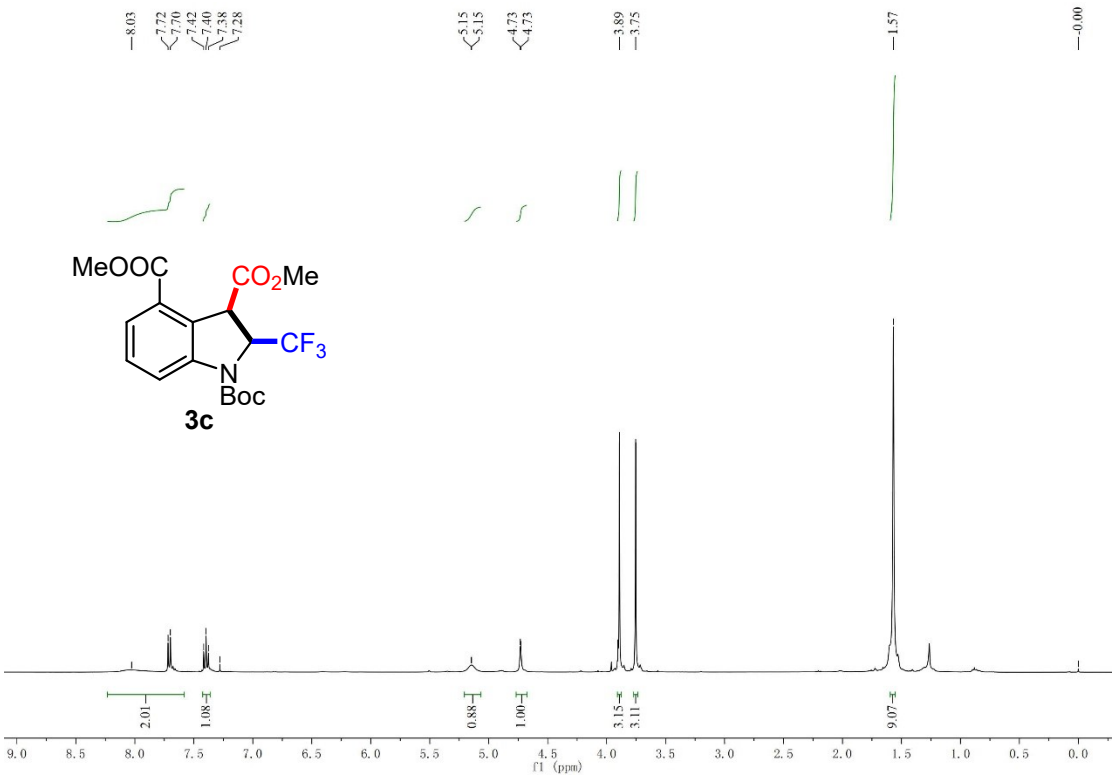


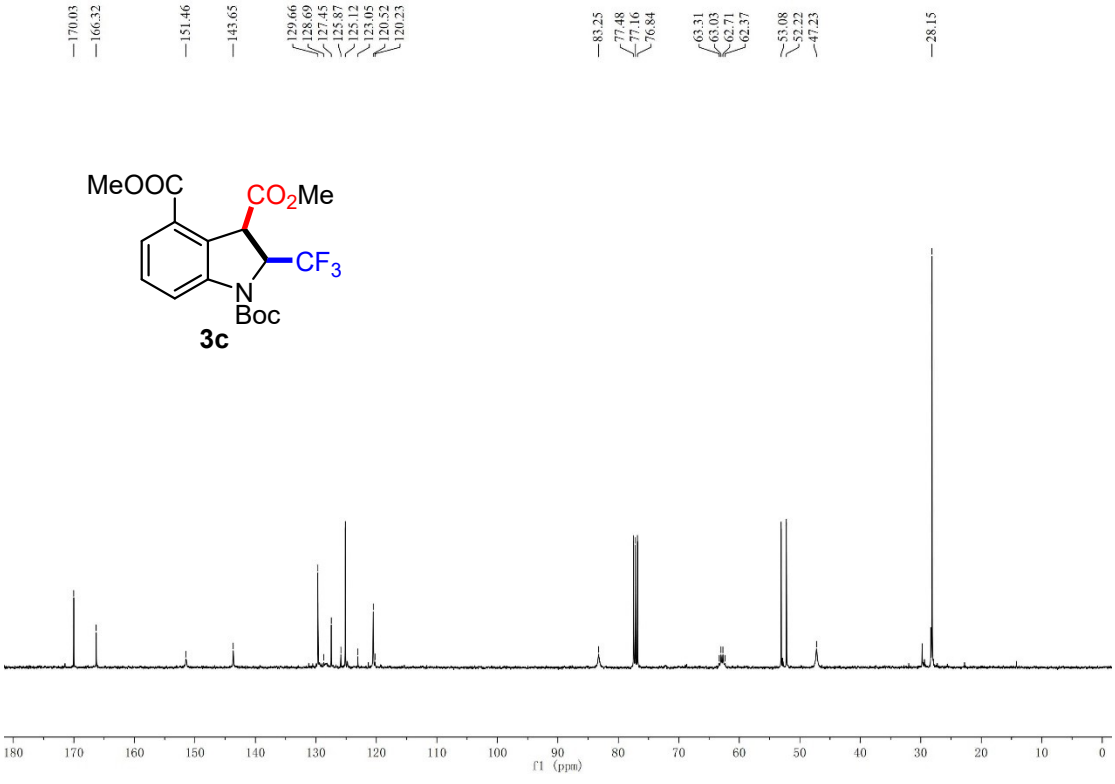


^{1}H NMR and ^{13}C NMR spectrum of **3b**

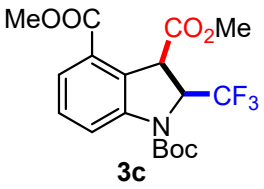


^{19}F NMR spectrum of **3b**



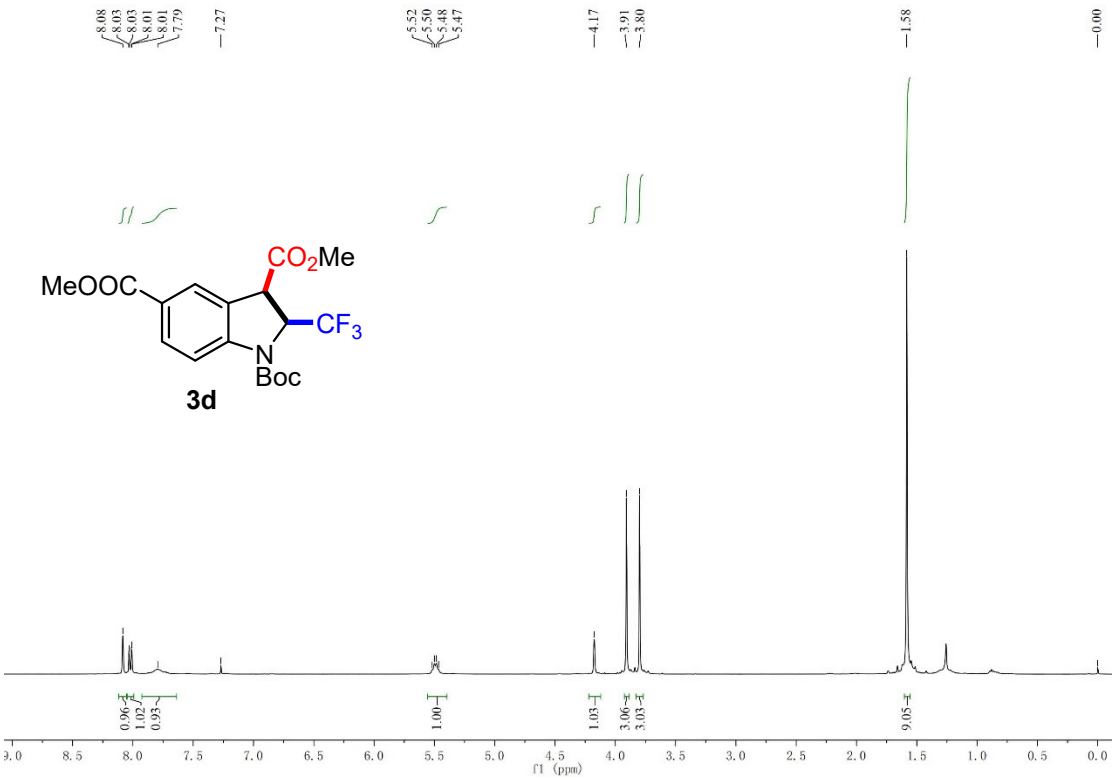


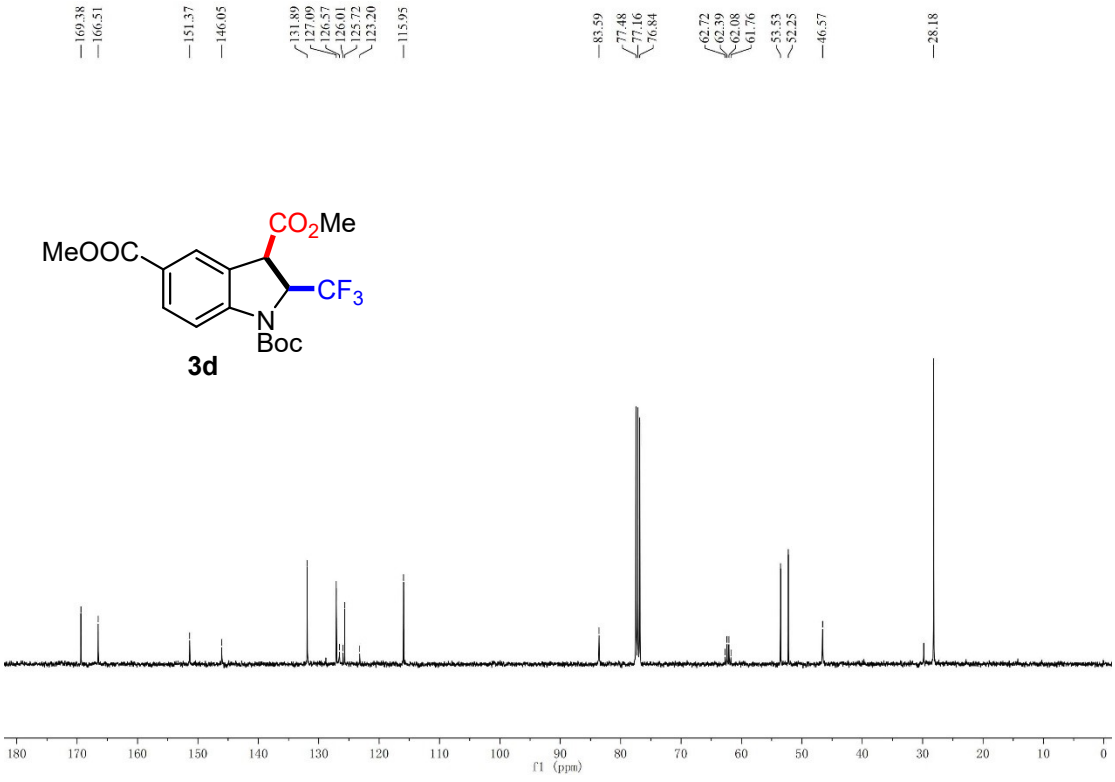
^{1}H NMR and ^{13}C NMR spectrum of **3c**



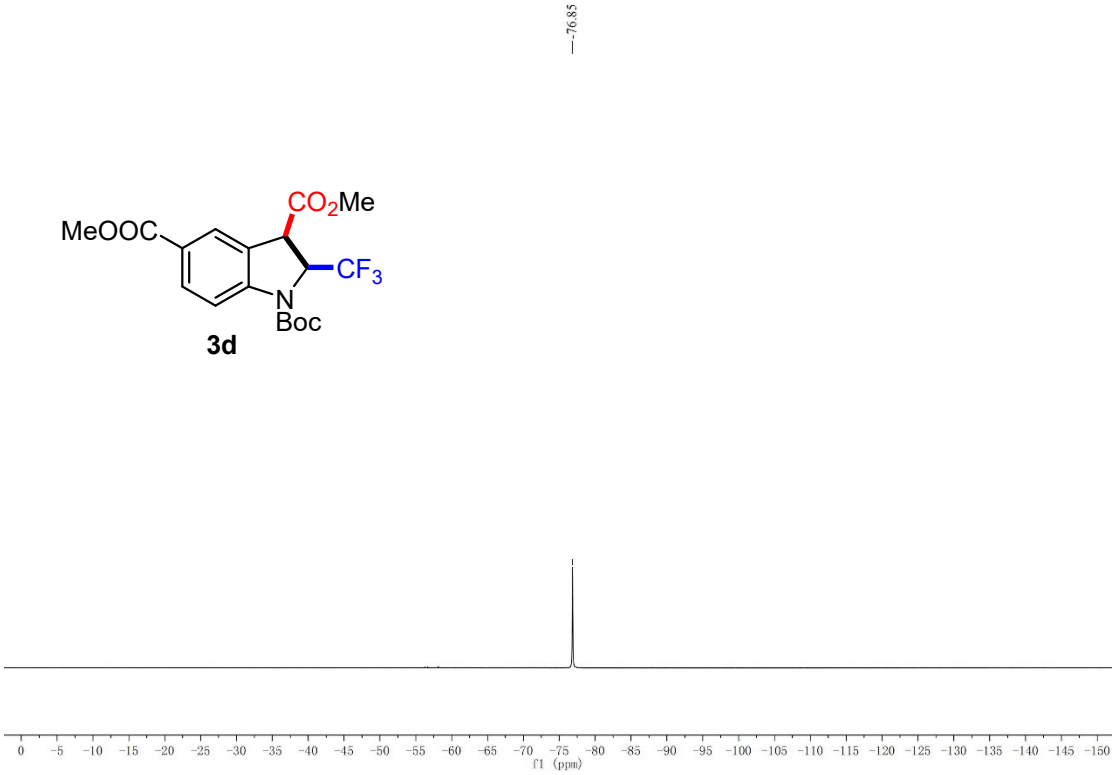
3c

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

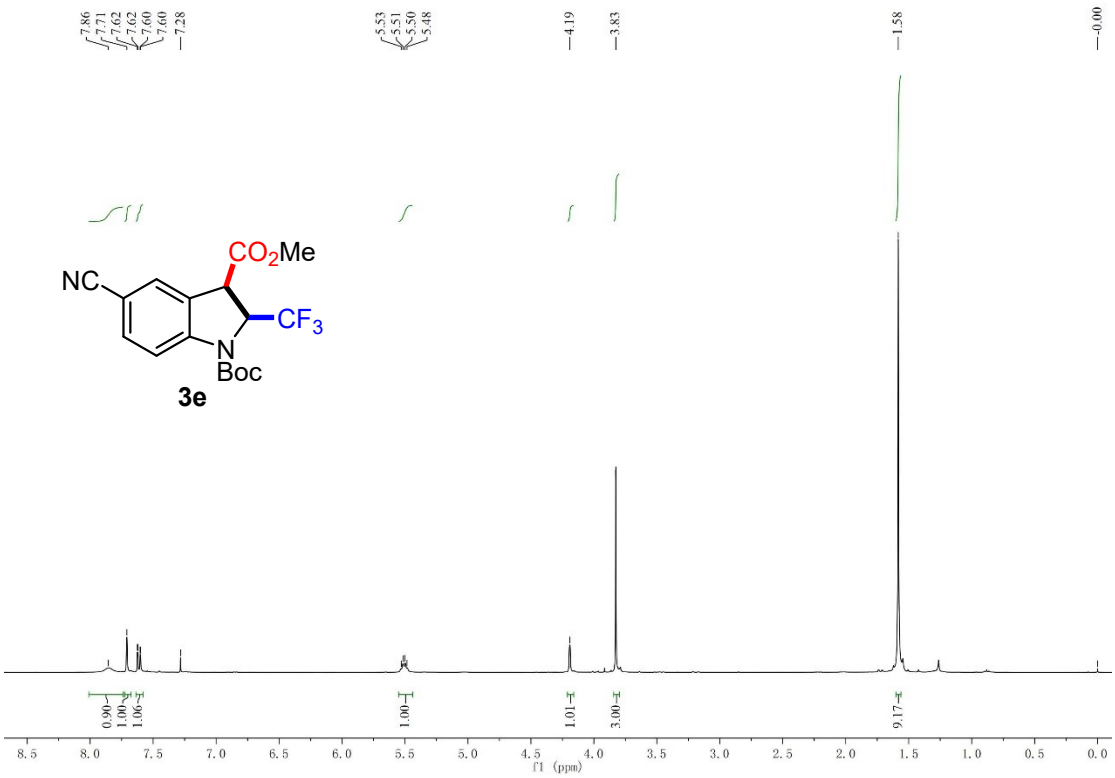


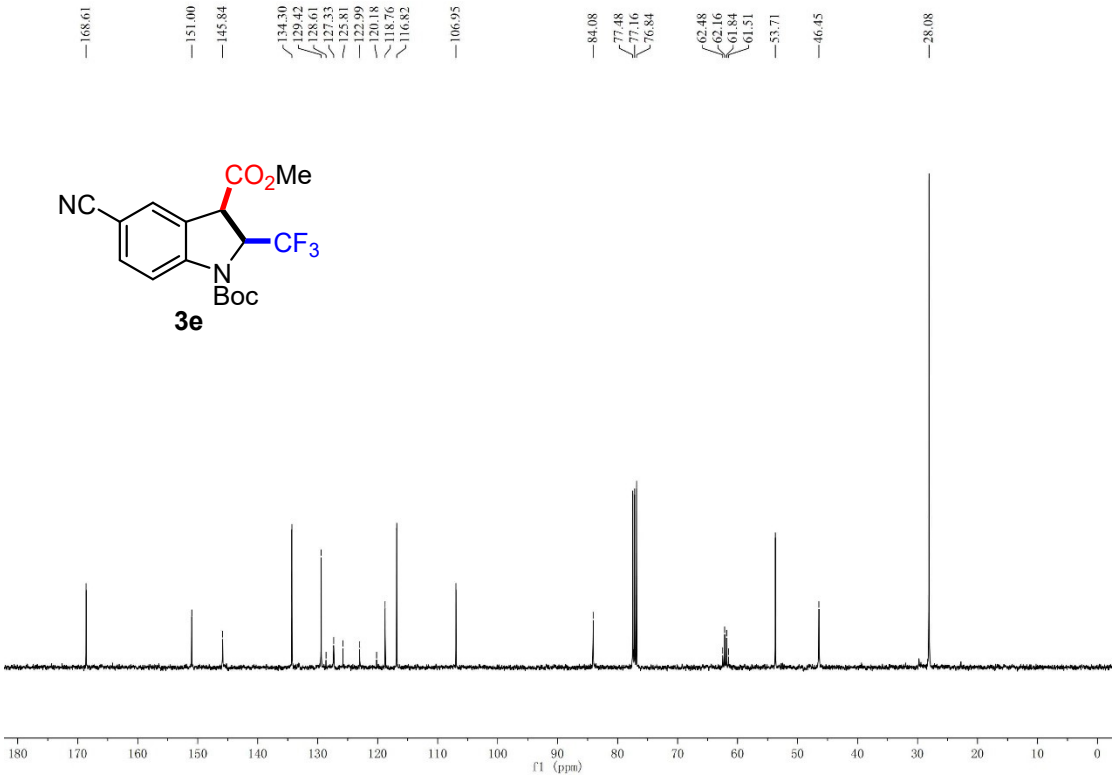


^{1}H NMR and ^{13}C NMR spectrum of **3d**

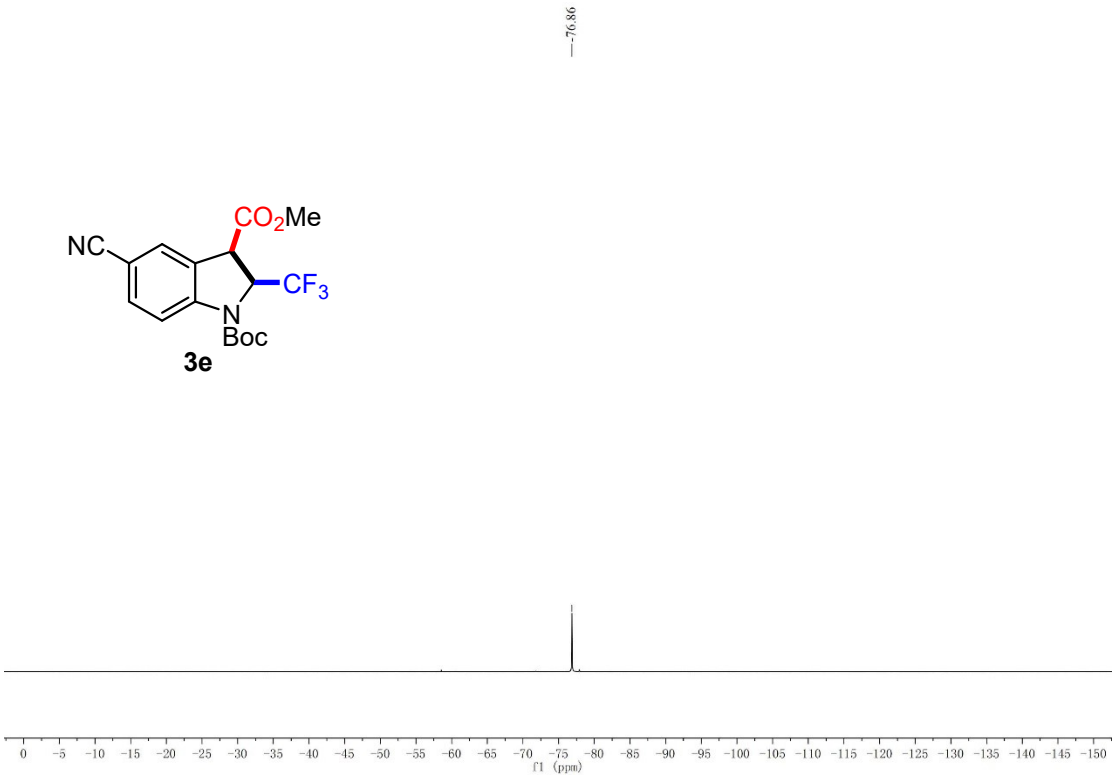


^{19}F NMR spectrum of **3d**

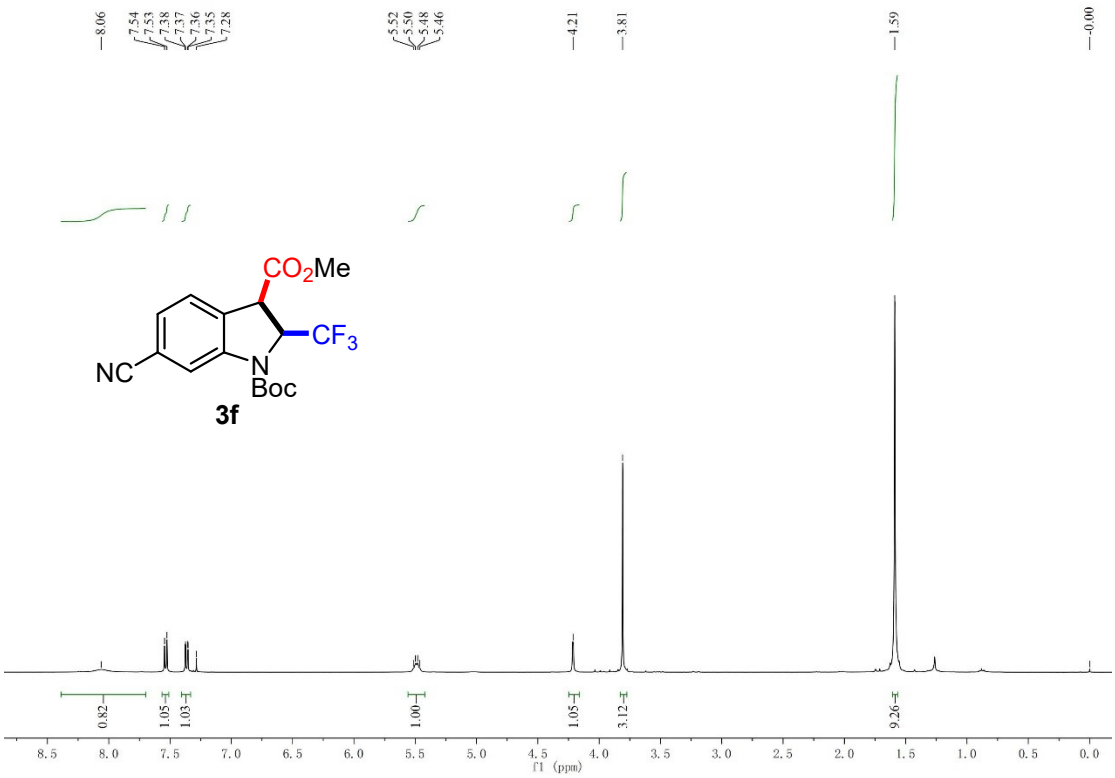


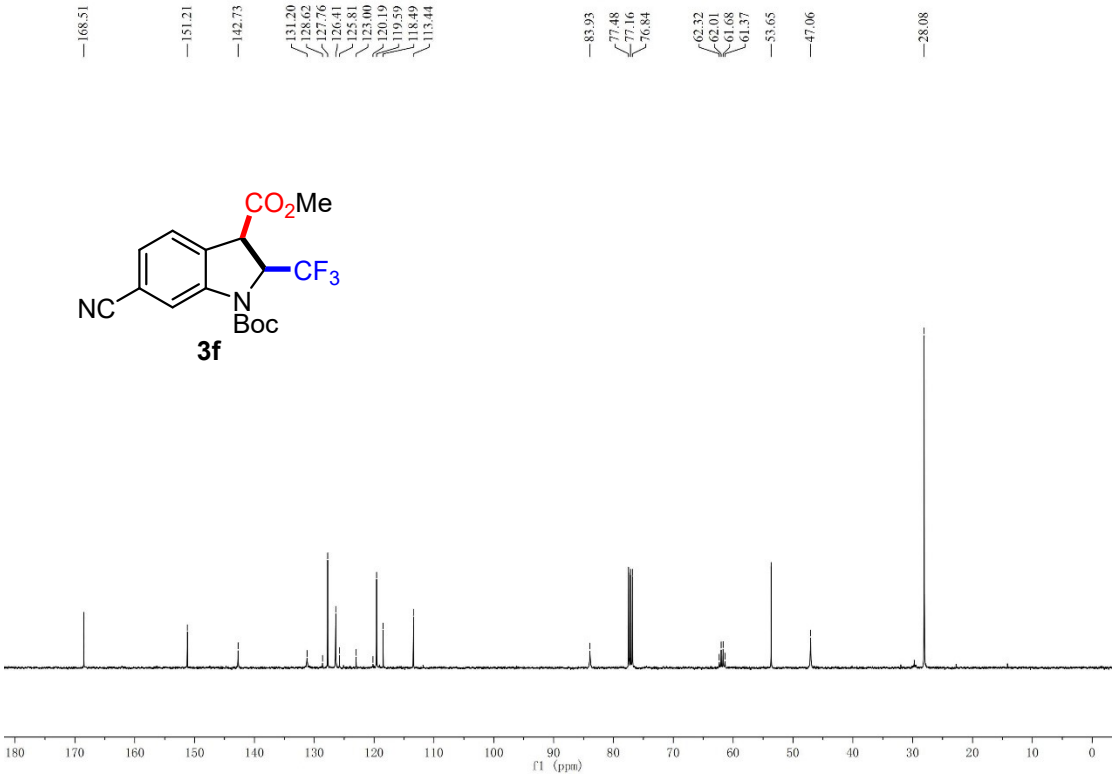


^{1}H NMR and ^{13}C NMR spectrum of **3e**

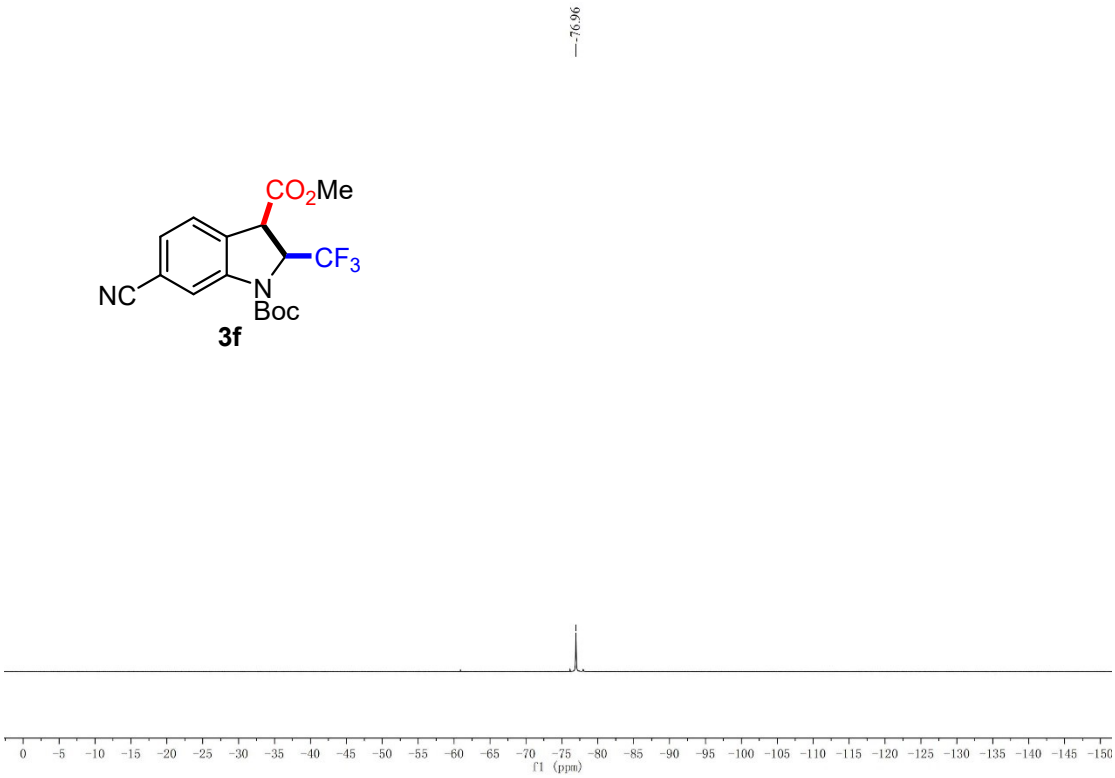


^{19}F NMR spectrum of **3e**

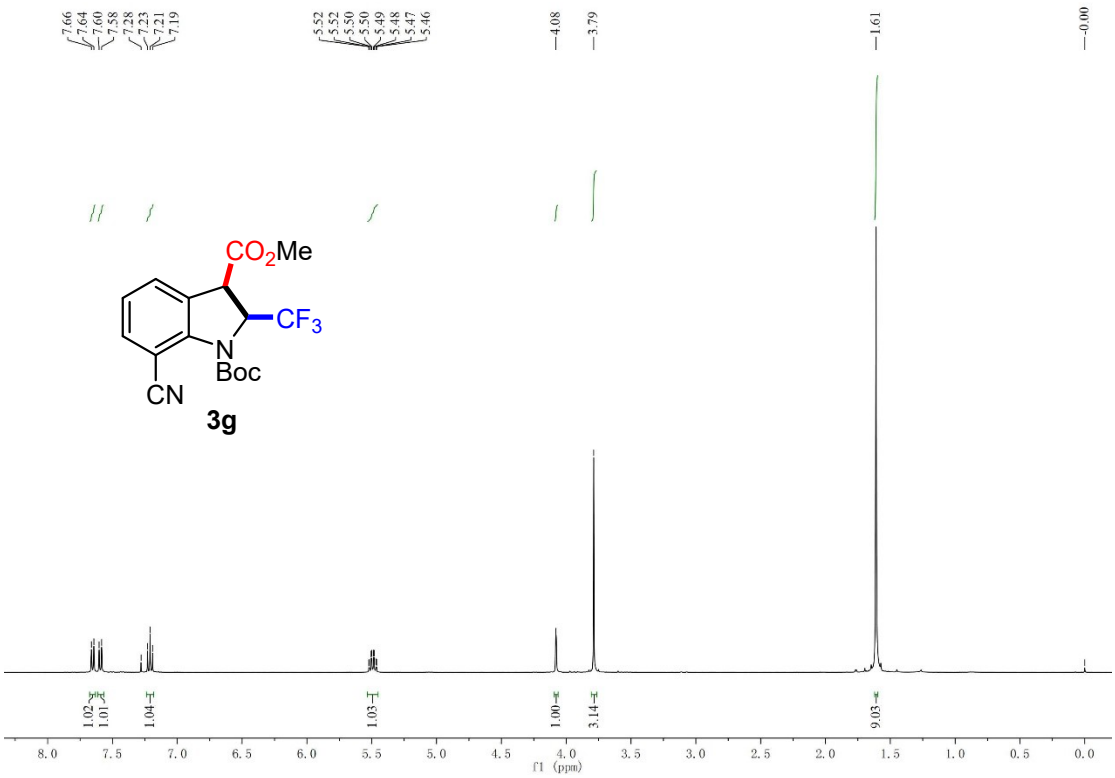


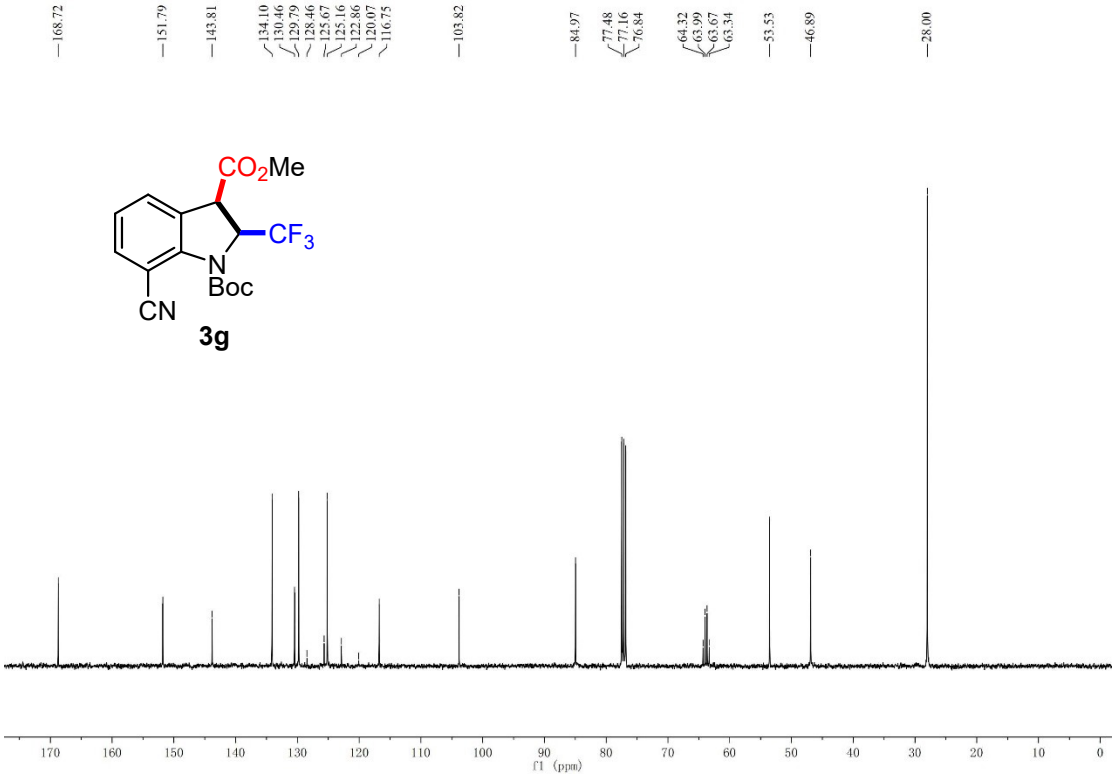


^{1}H NMR and ^{13}C NMR spectrum of **3f**

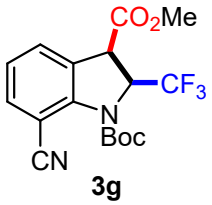


^{19}F NMR spectrum of **3f**

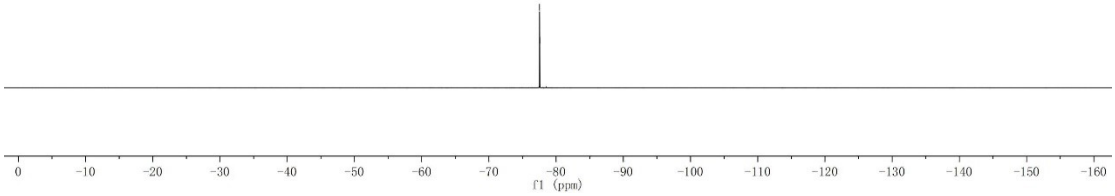




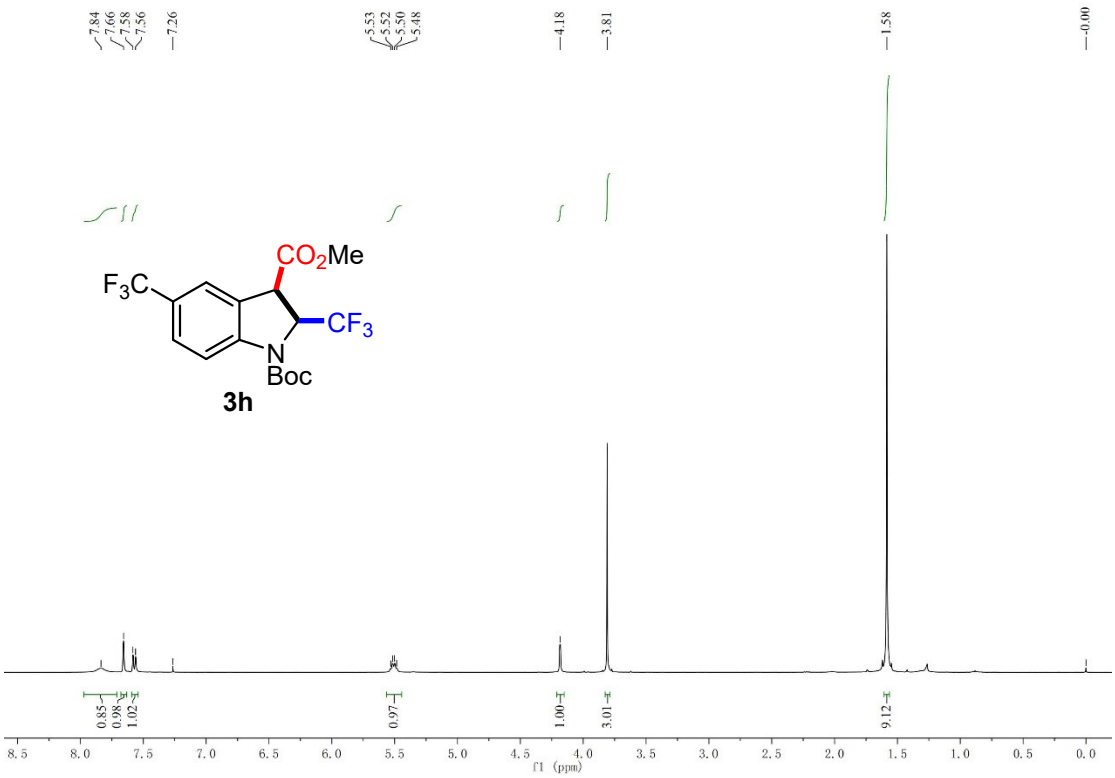
^{1}H NMR and ^{13}C NMR spectrum of **3g**

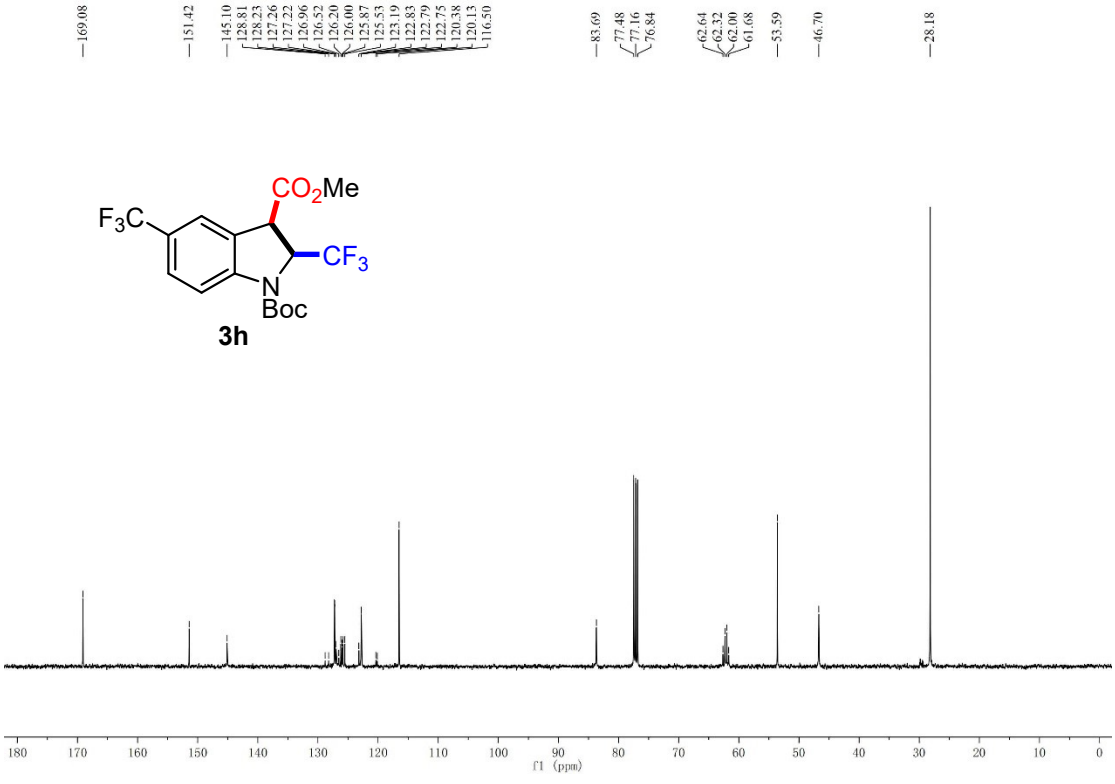


3g

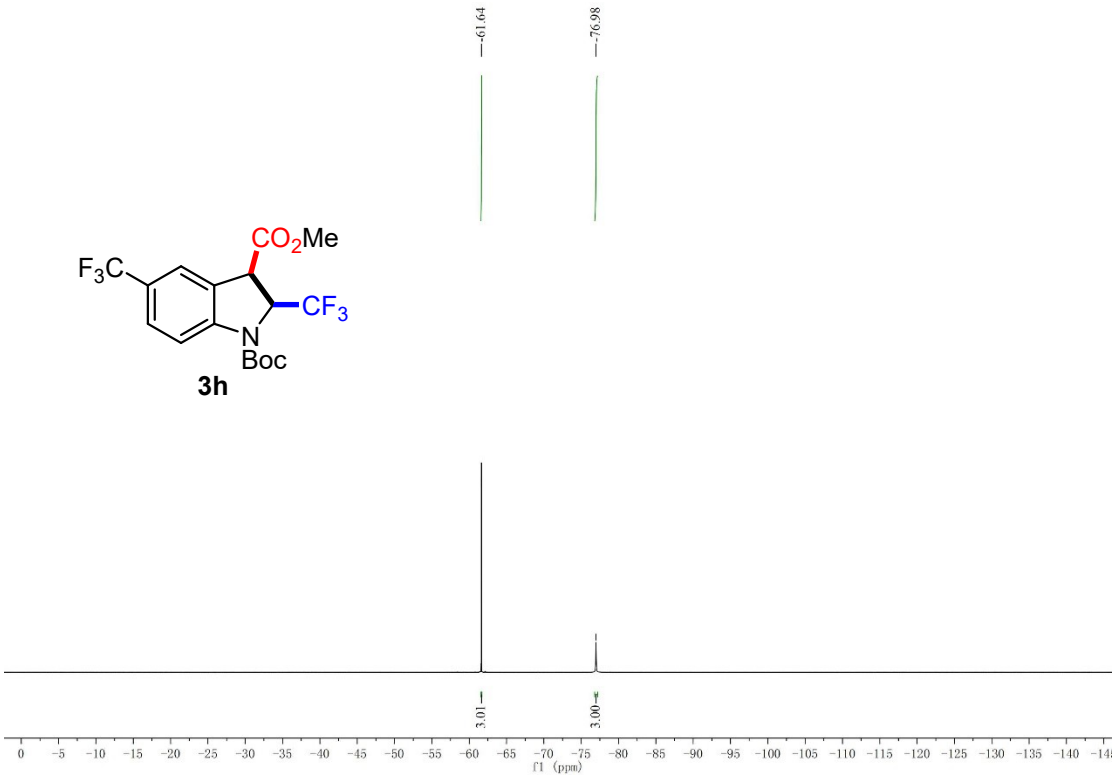


^{19}F NMR spectrum of **3g**

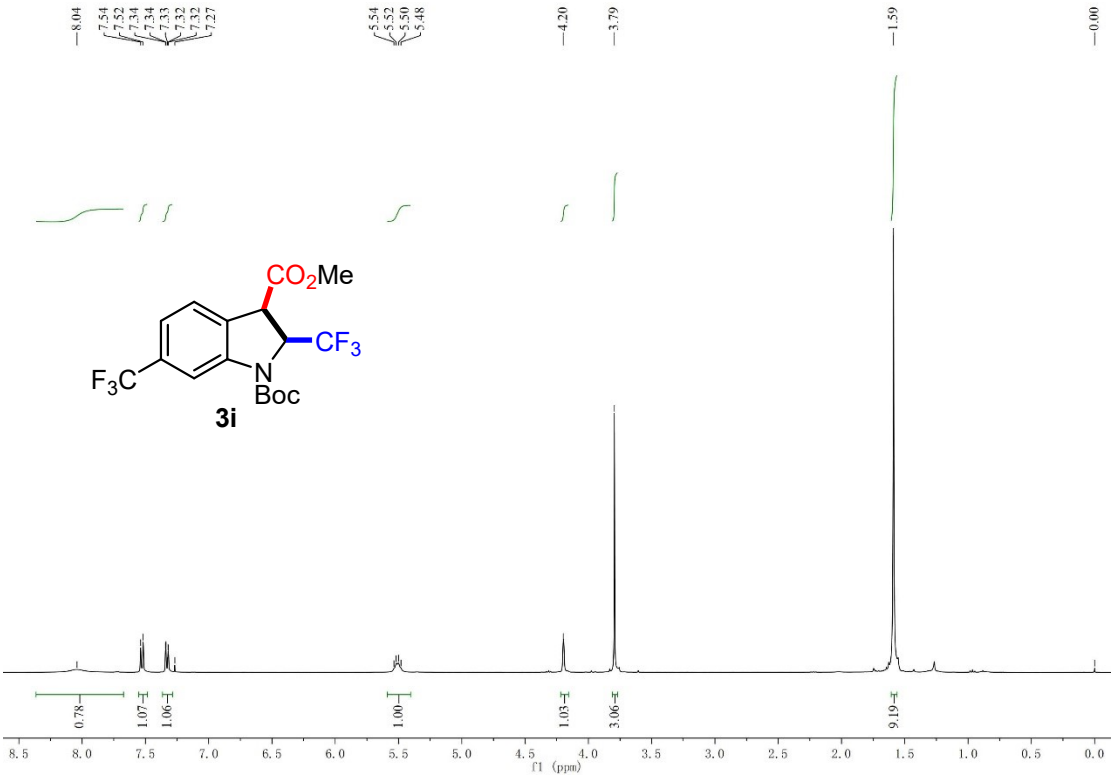


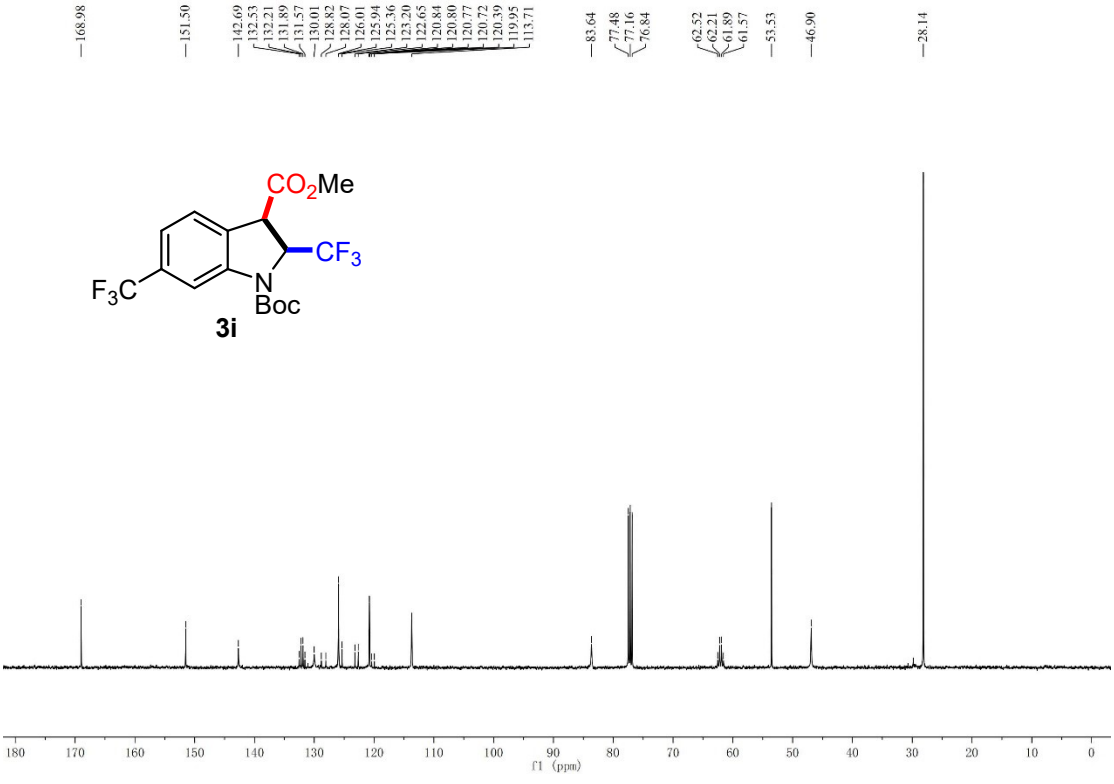


^{1}H NMR and ^{13}C NMR spectrum of **3h**

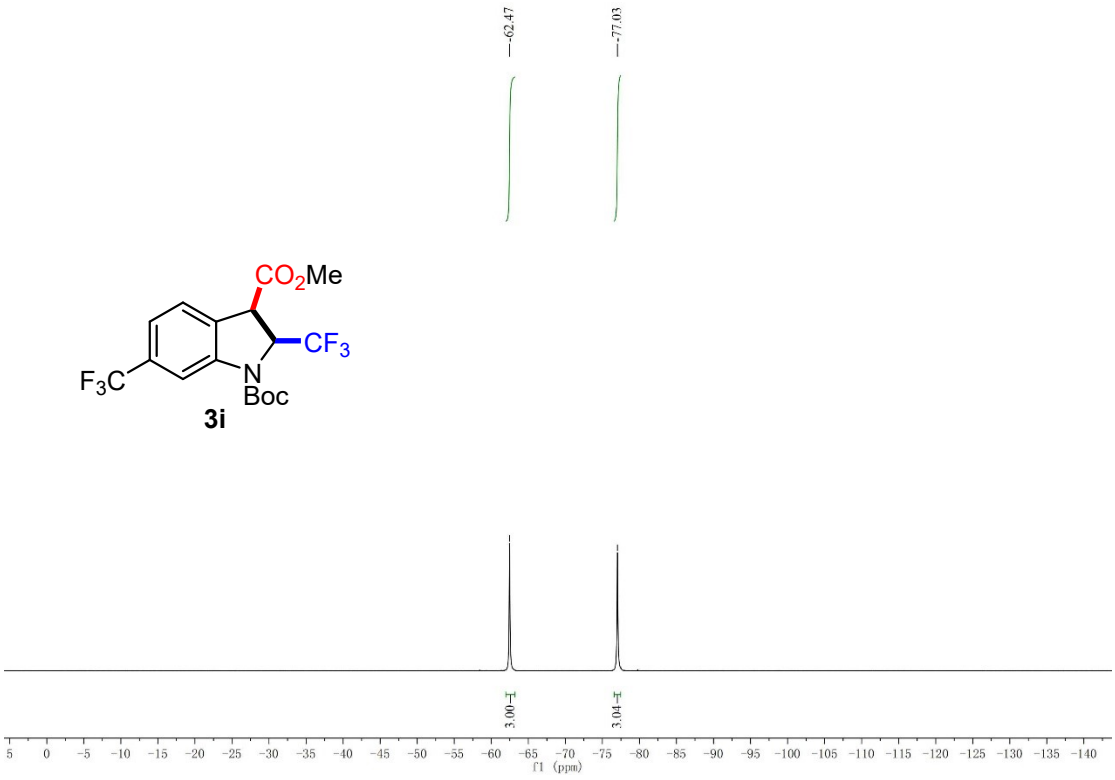


^{19}F NMR spectrum of **3h**

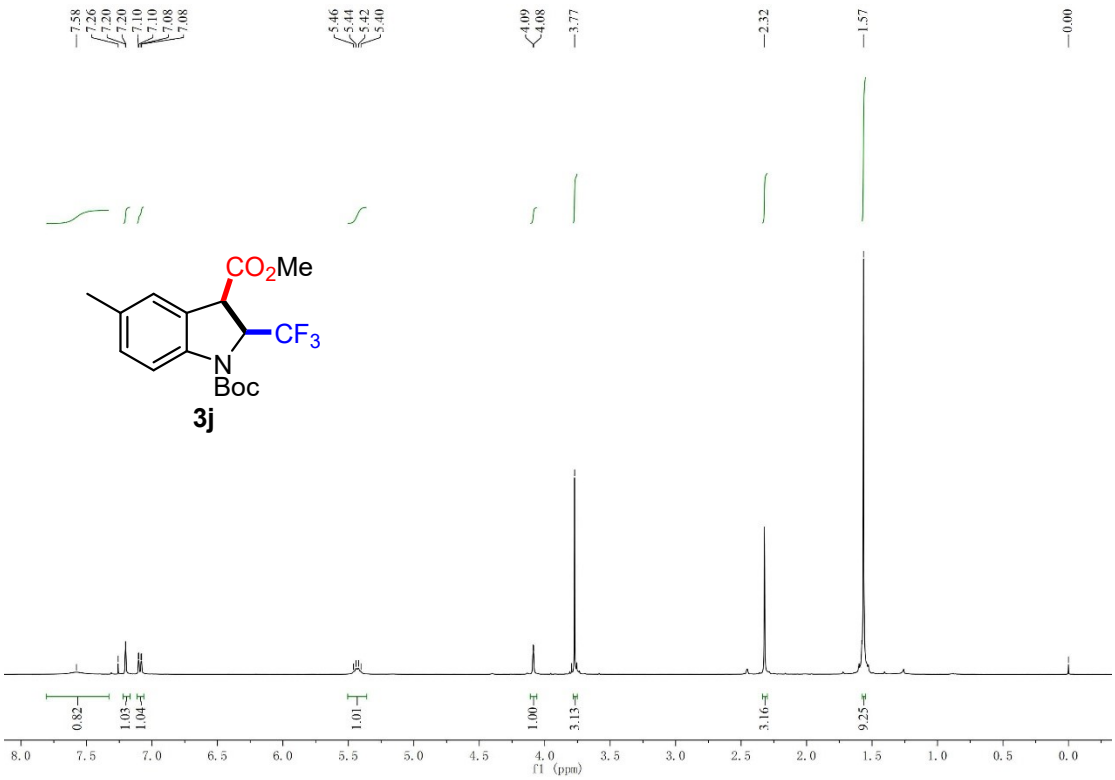


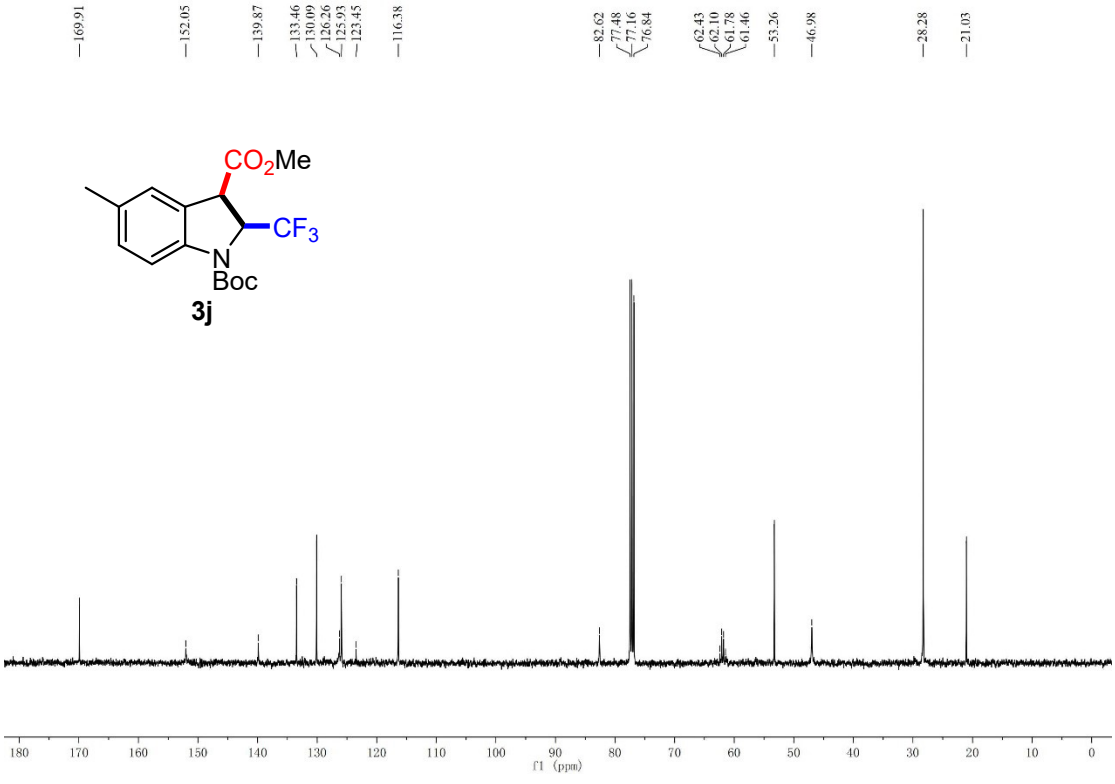


^{1}H NMR and ^{13}C NMR spectrum of **3i**

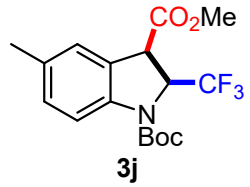


^{19}F NMR spectrum of **3i**

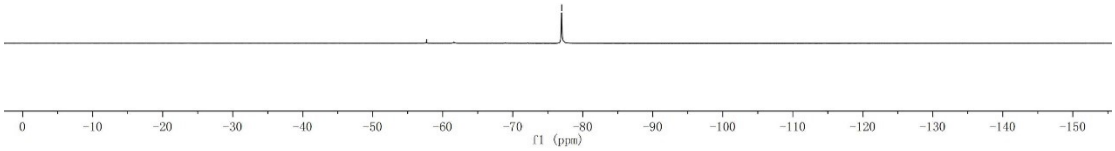




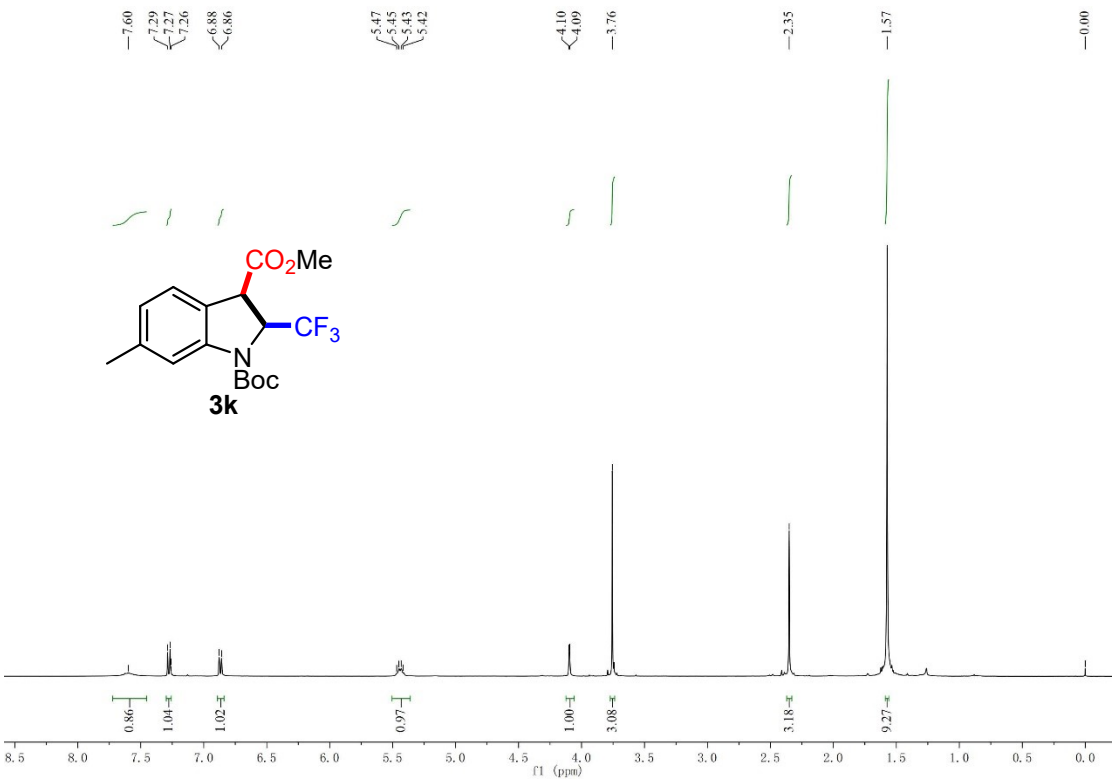
^{1}H NMR and ^{13}C NMR spectrum of **3j**

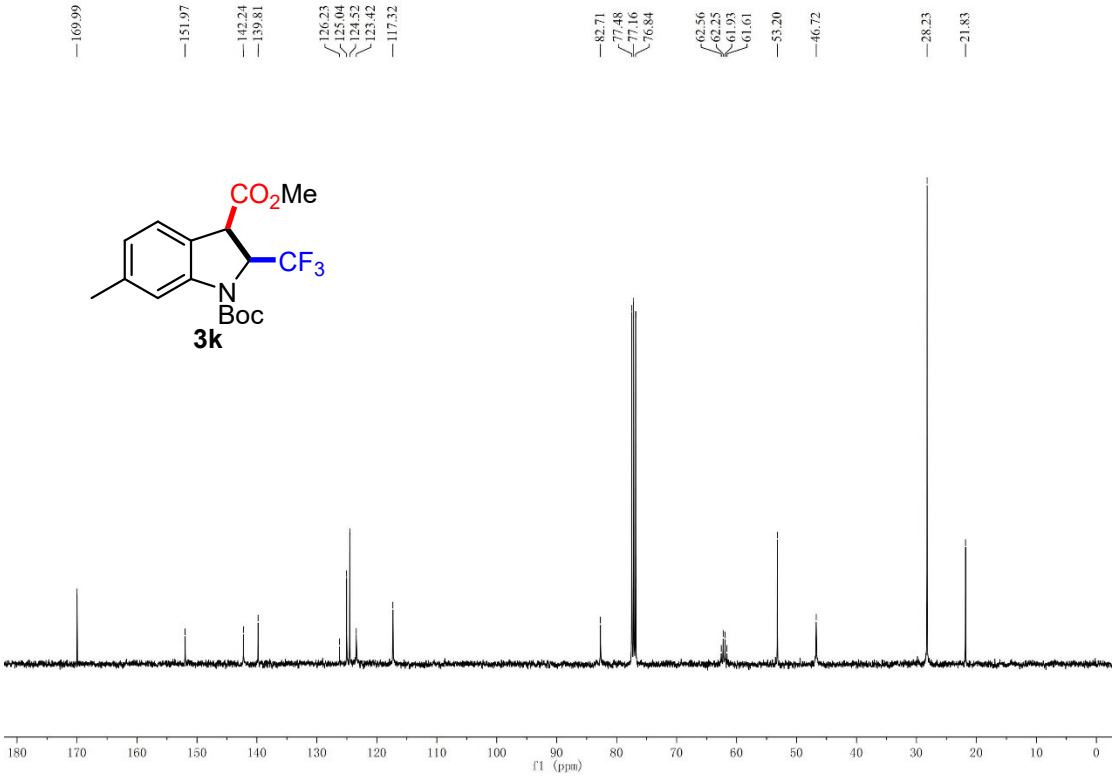


3j

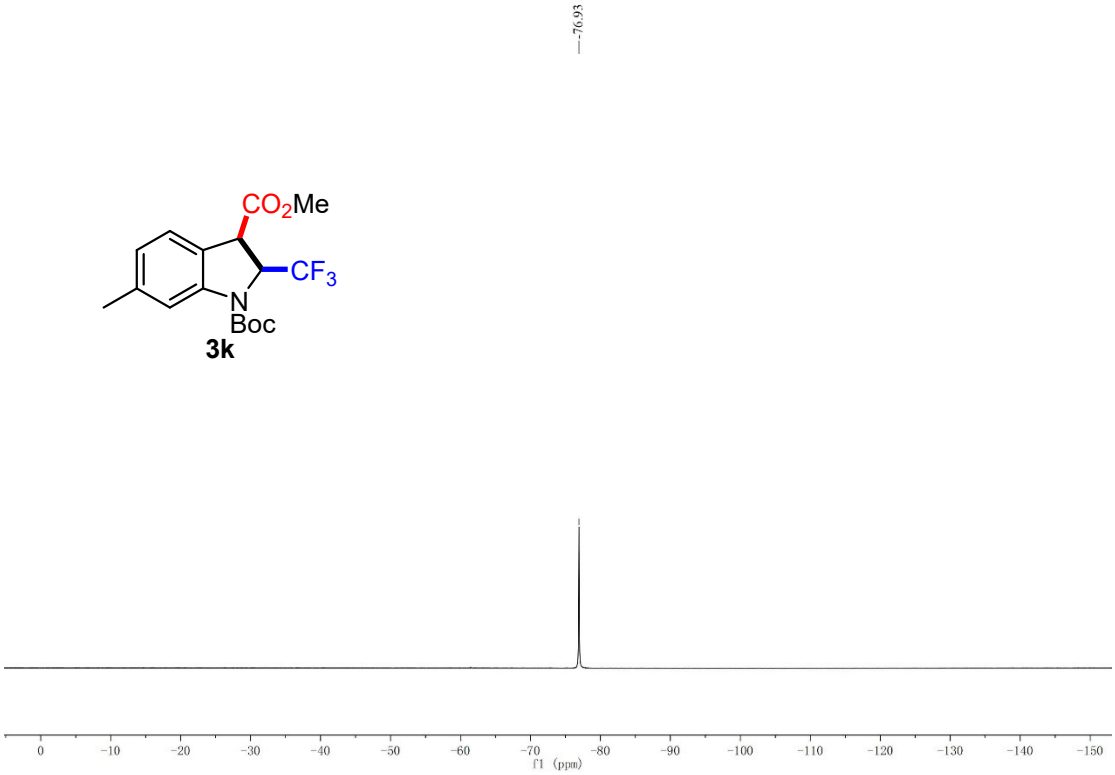


^{19}F NMR spectrum of **3j**

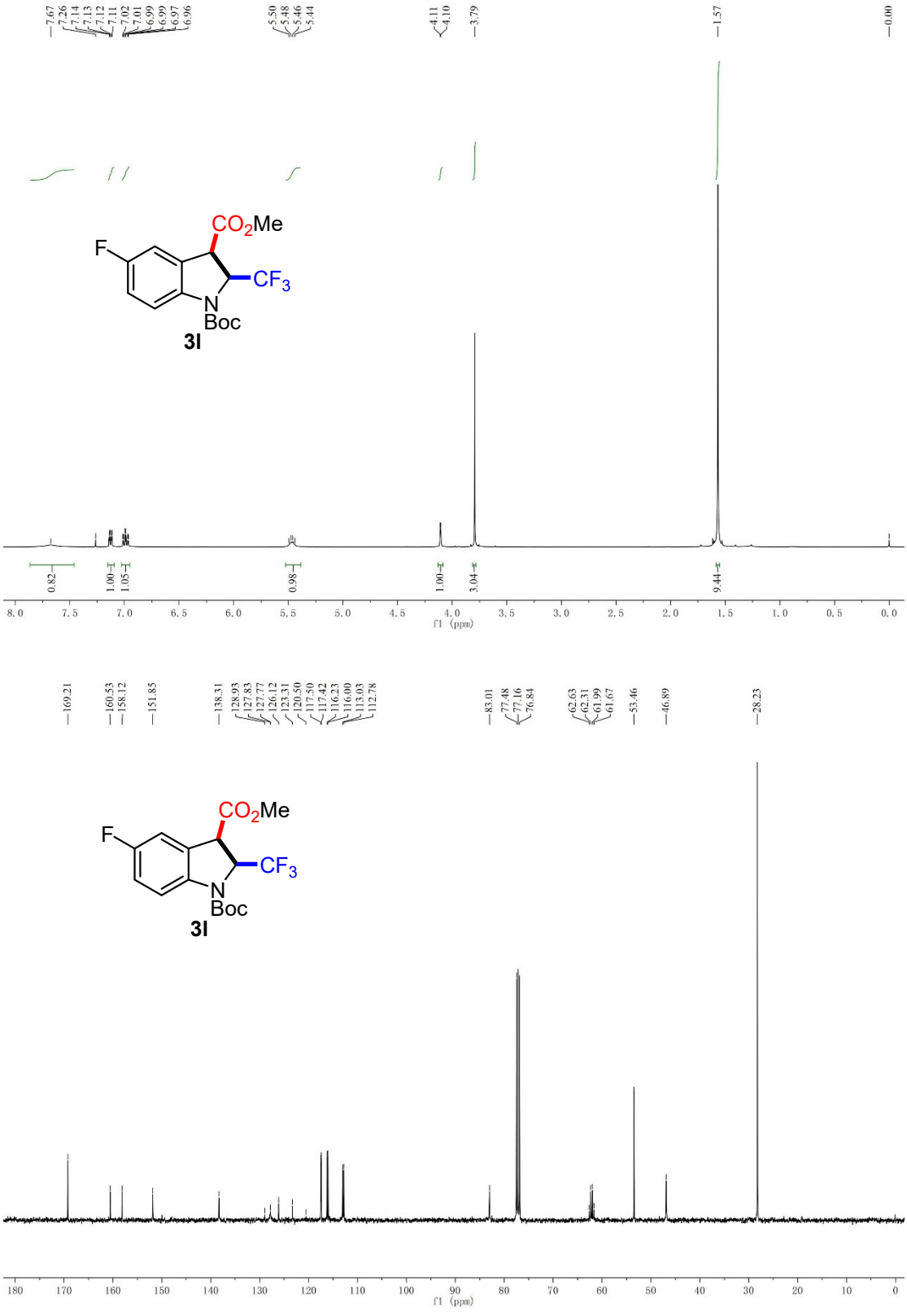




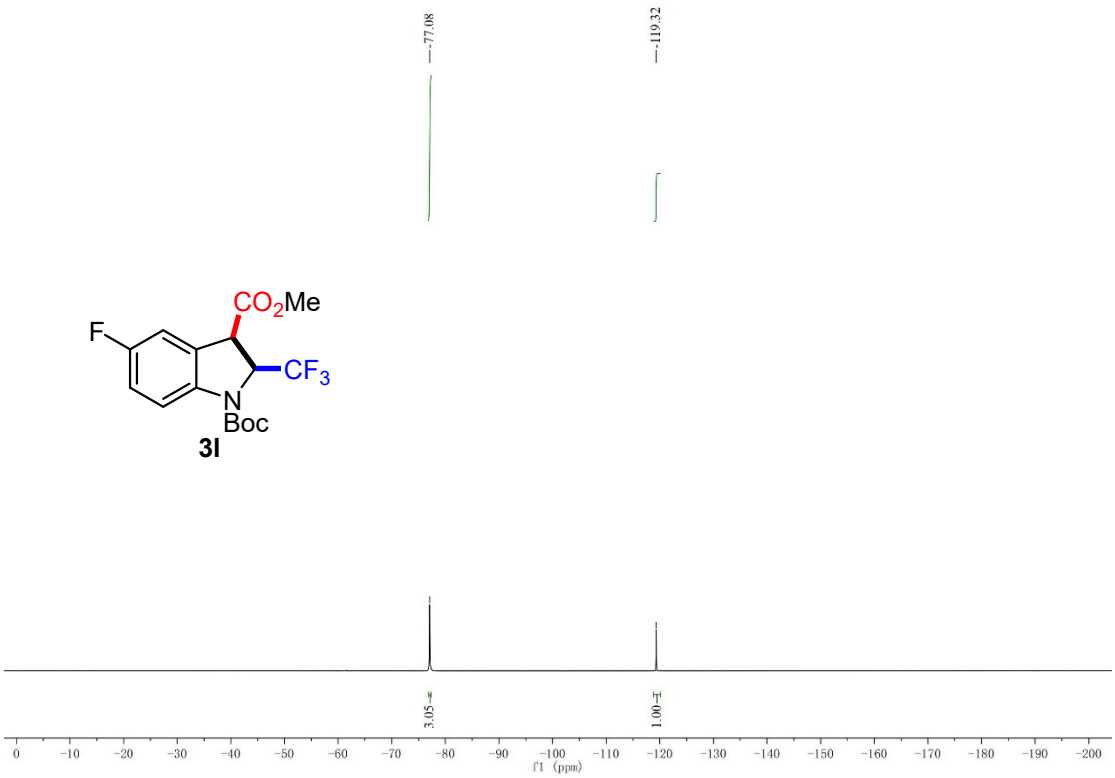
^{1}H NMR and ^{13}C NMR spectrum of **3k**



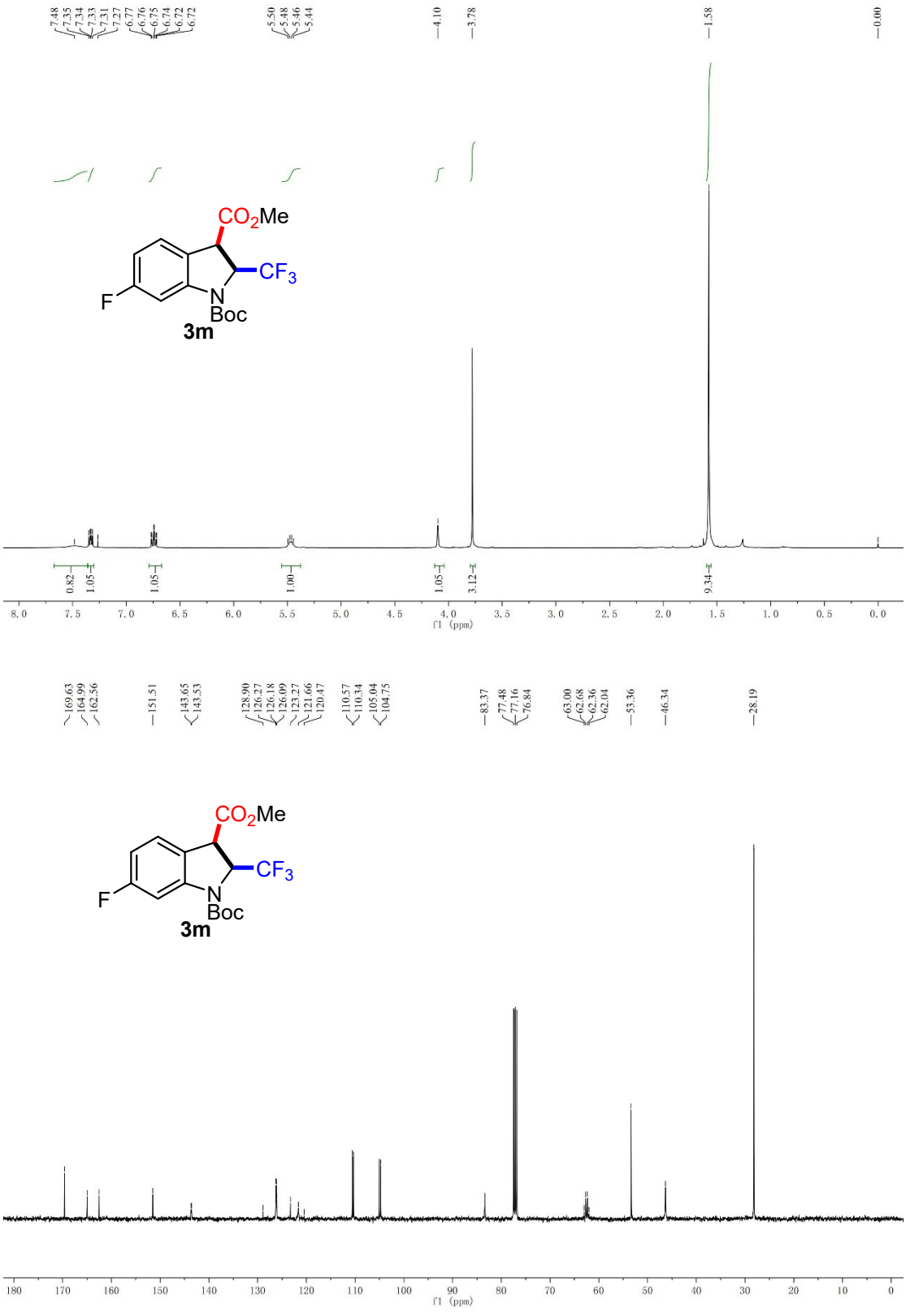
^{19}F NMR spectrum of **3k**



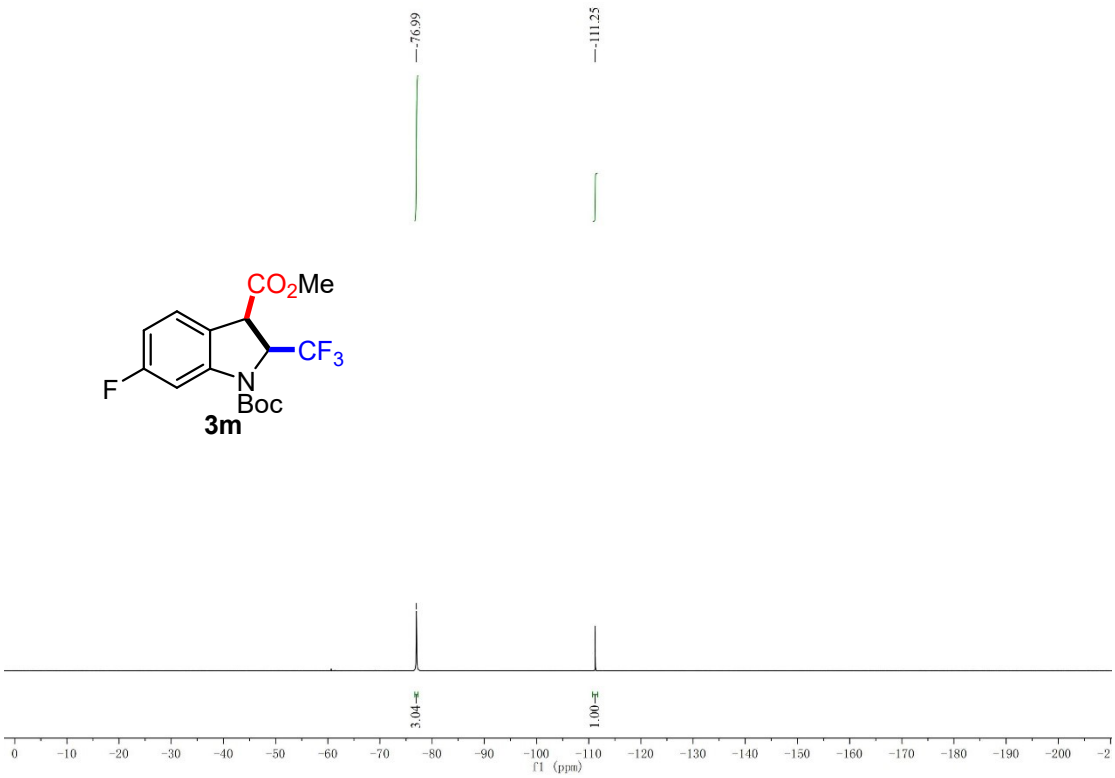
^{1}H NMR and ^{13}C NMR spectrum of **3l**



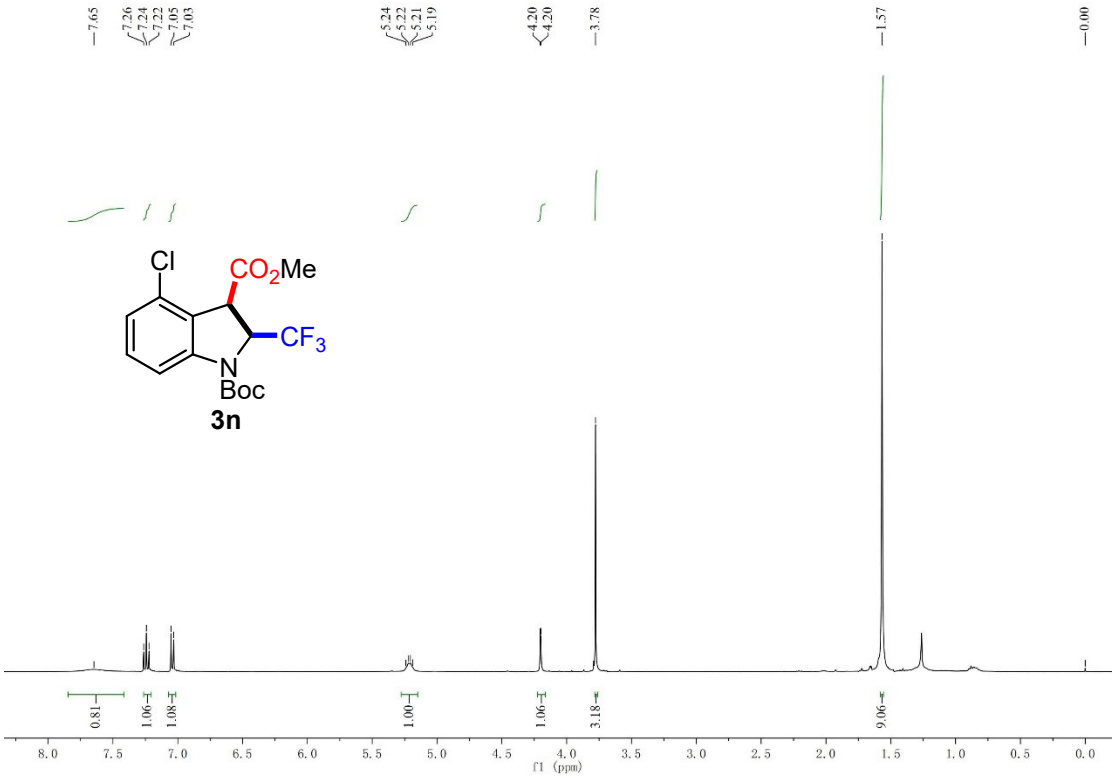
^{19}F NMR spectrum of **3l**

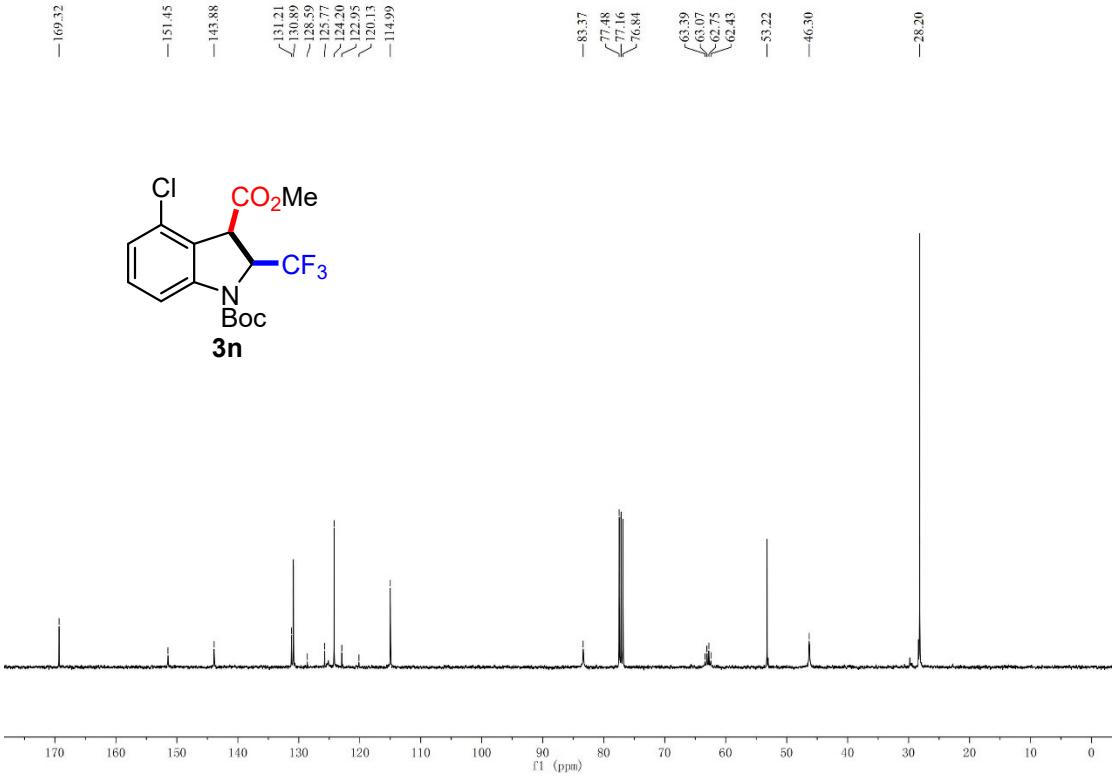


^{1}H NMR and ^{13}C NMR spectrum of **3m**

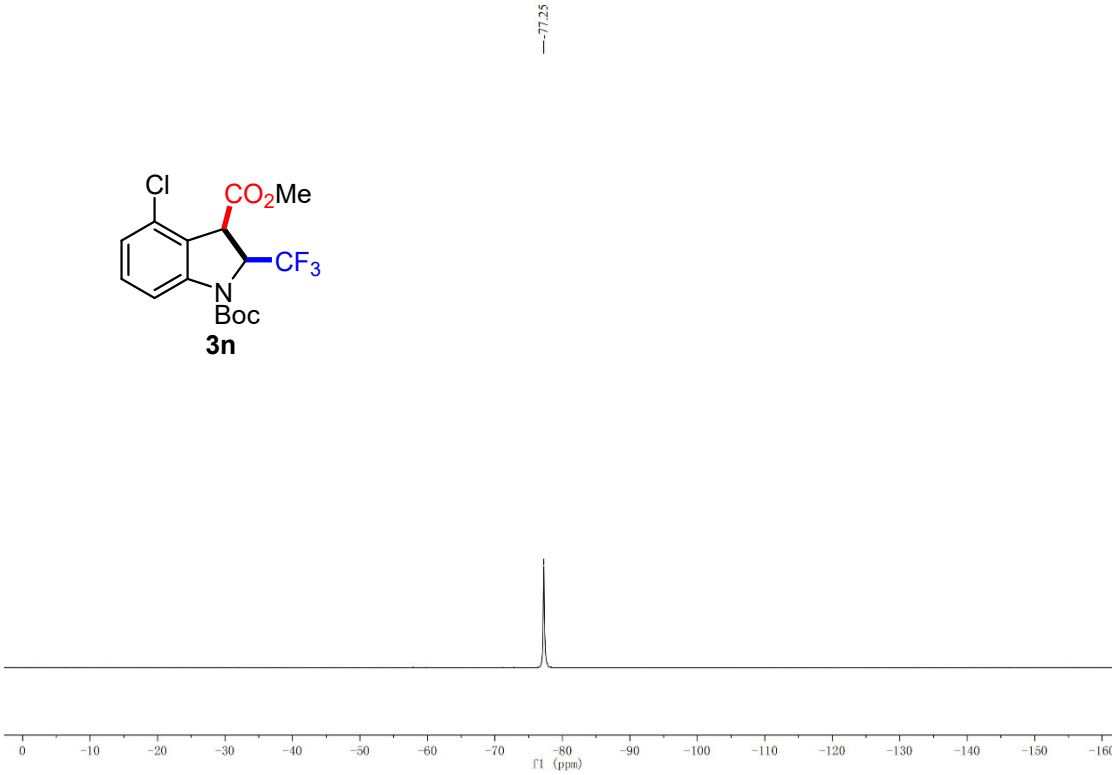


^{19}F NMR spectrum of **3m**

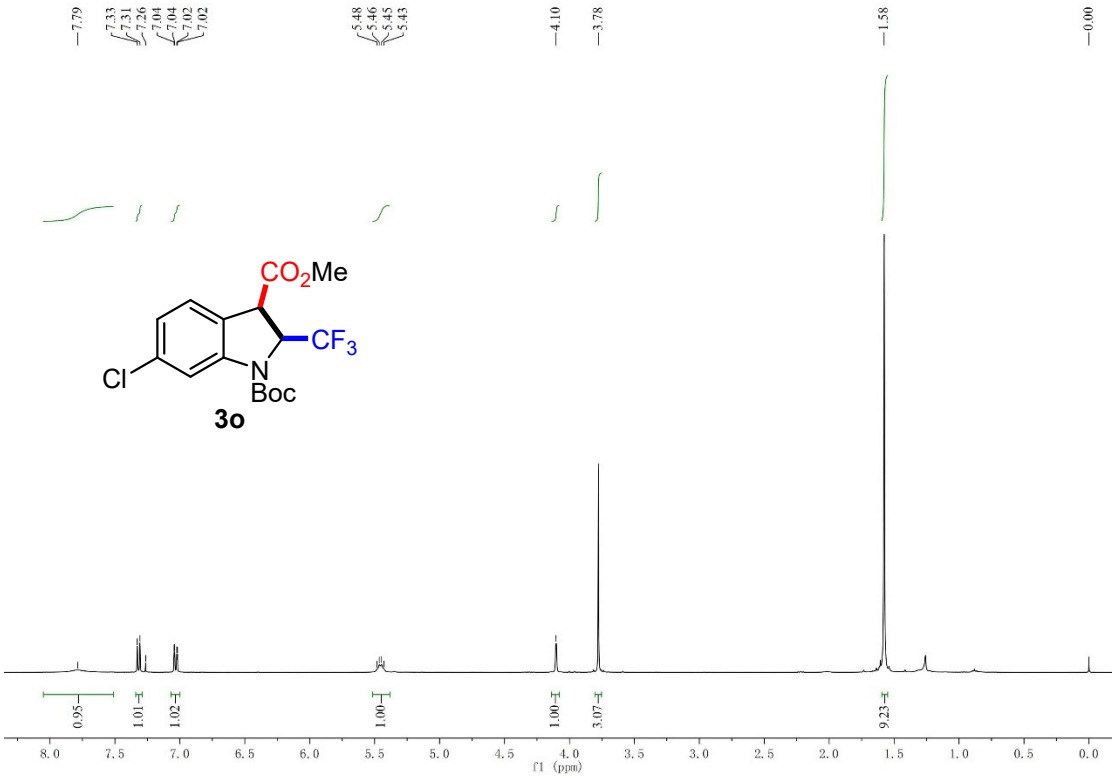


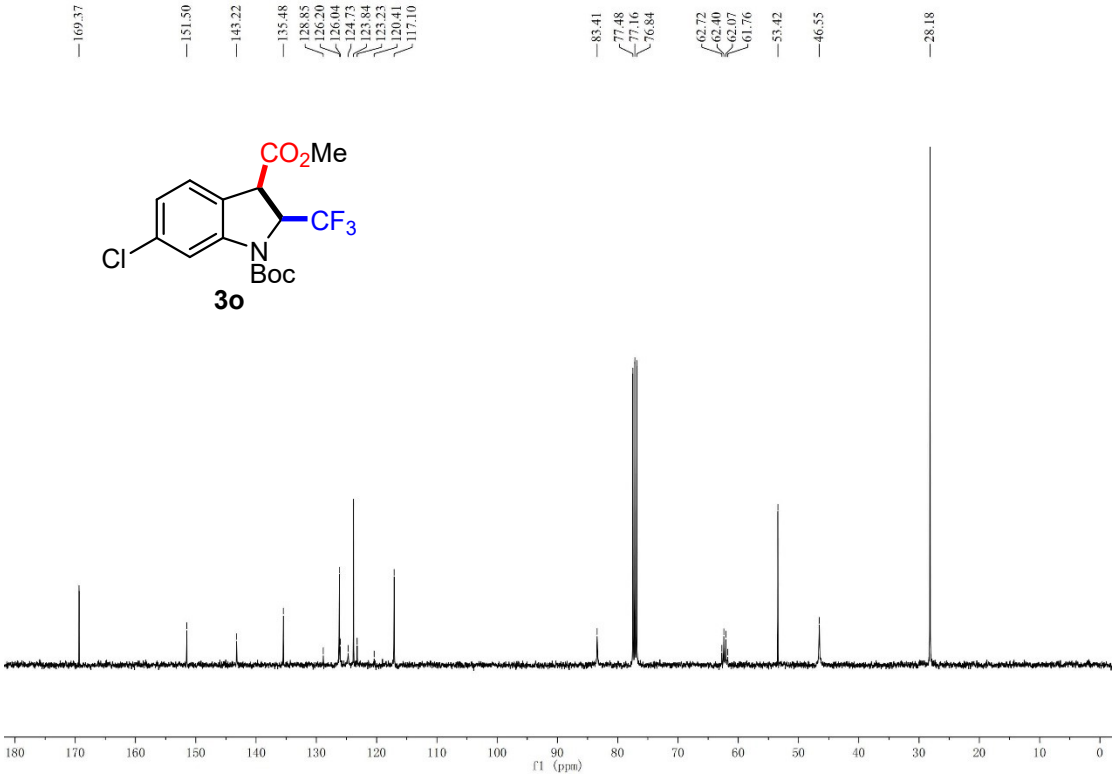


^{1}H NMR and ^{13}C NMR spectrum of **3n**

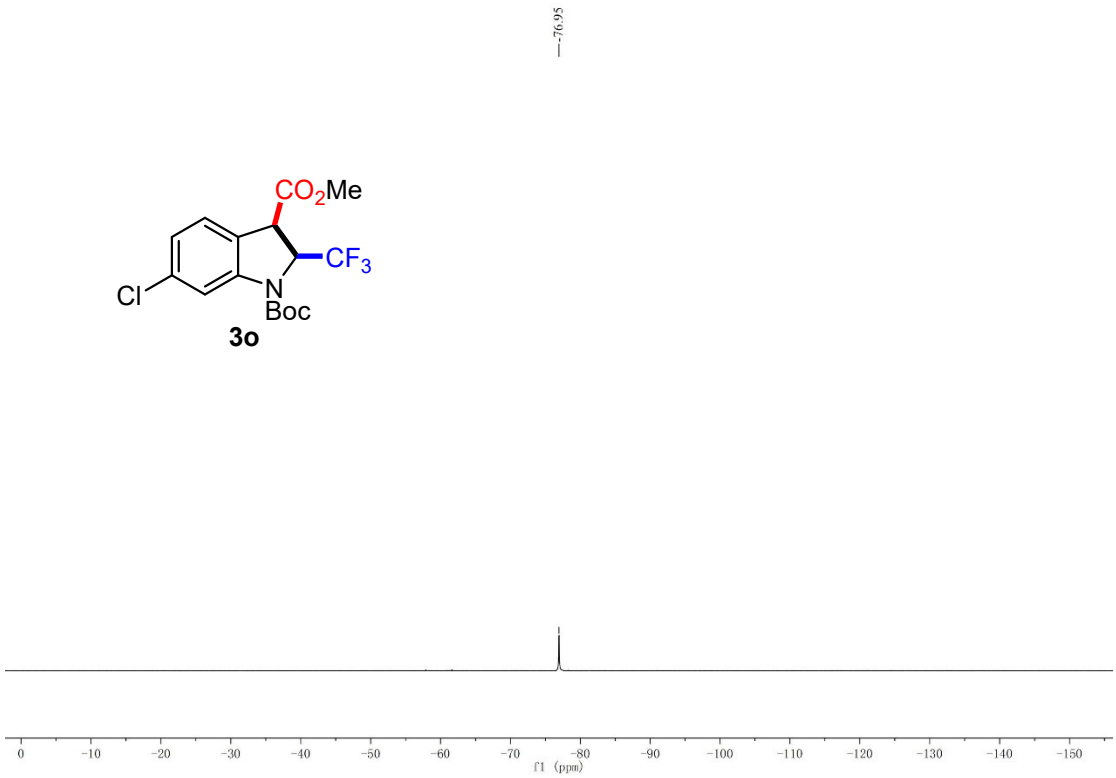


^{19}F NMR spectrum of **3n**

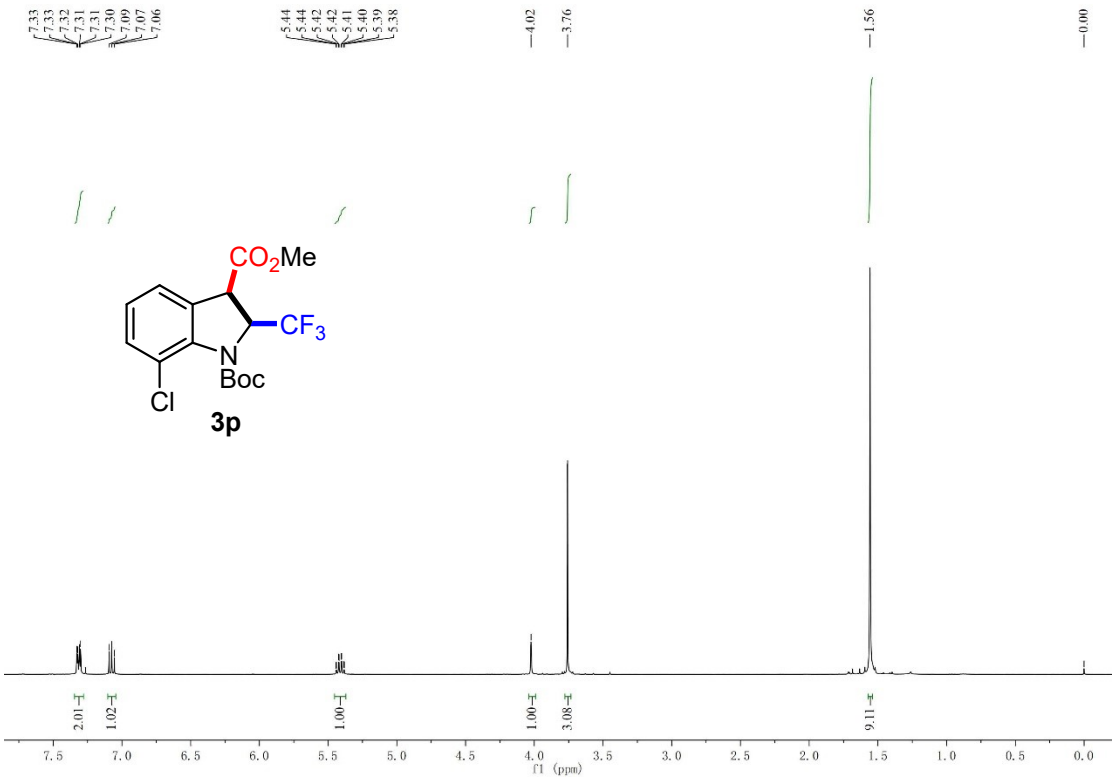


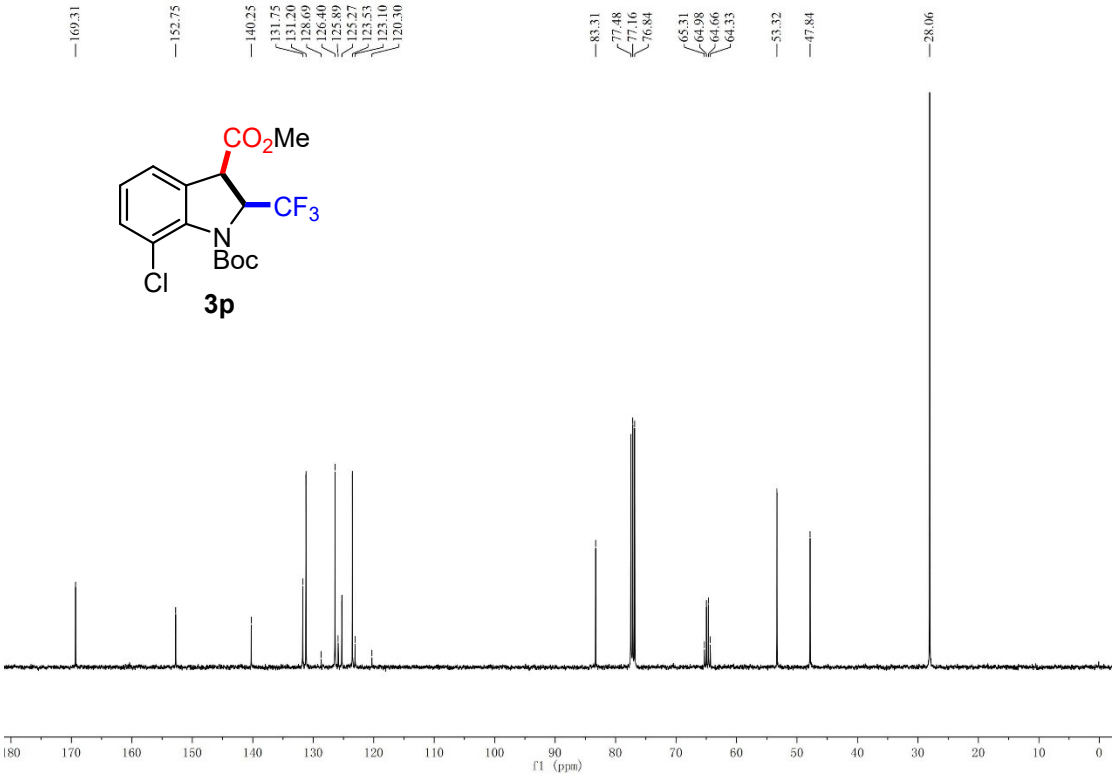


^{1}H NMR and ^{13}C NMR spectrum of **3o**

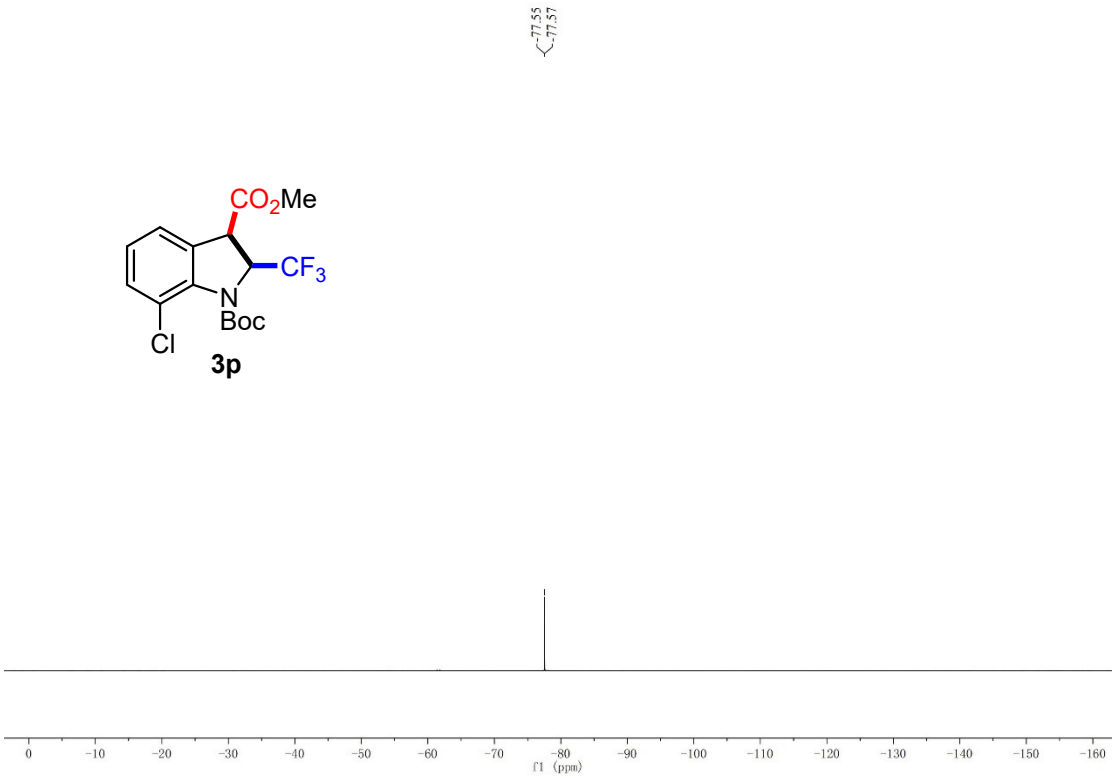


^{19}F NMR spectrum of **3o**

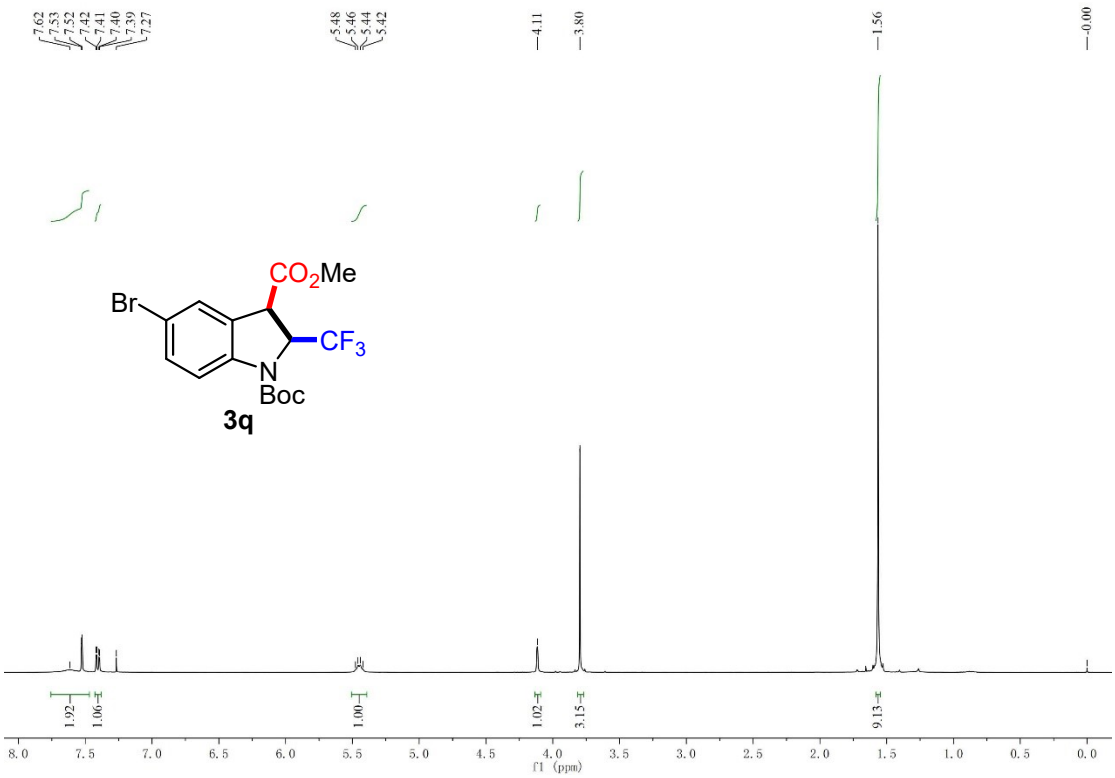


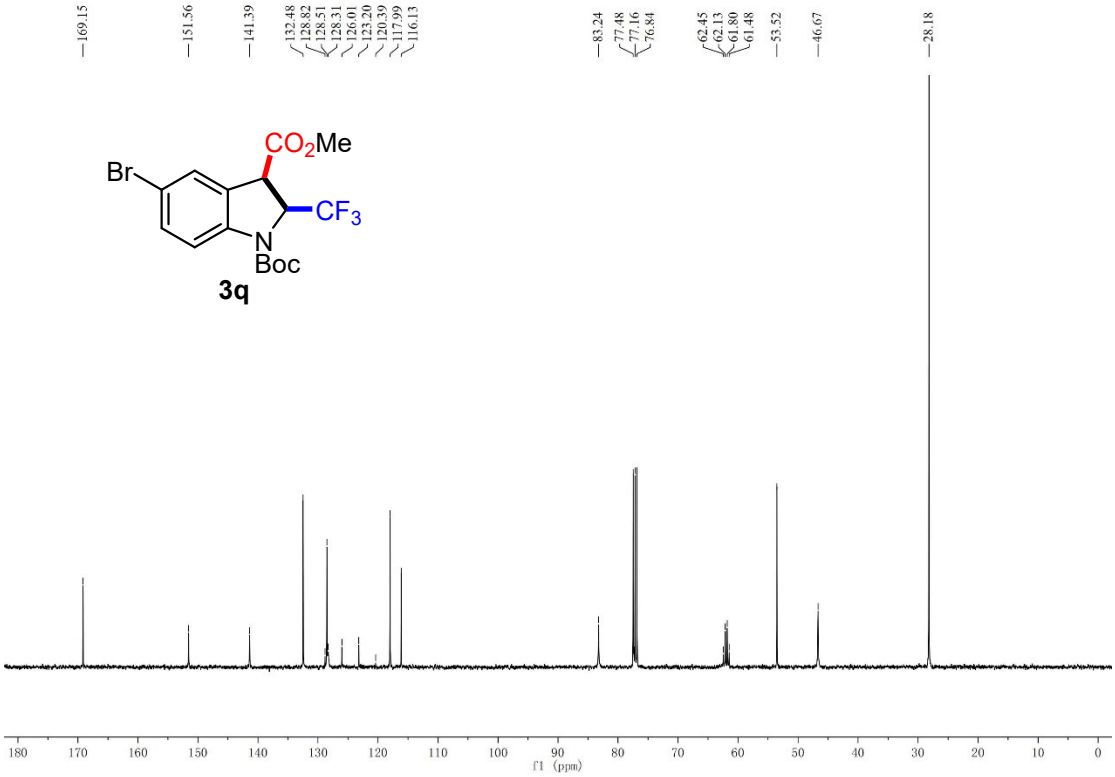


^{1}H NMR and ^{13}C NMR spectrum of **3p**

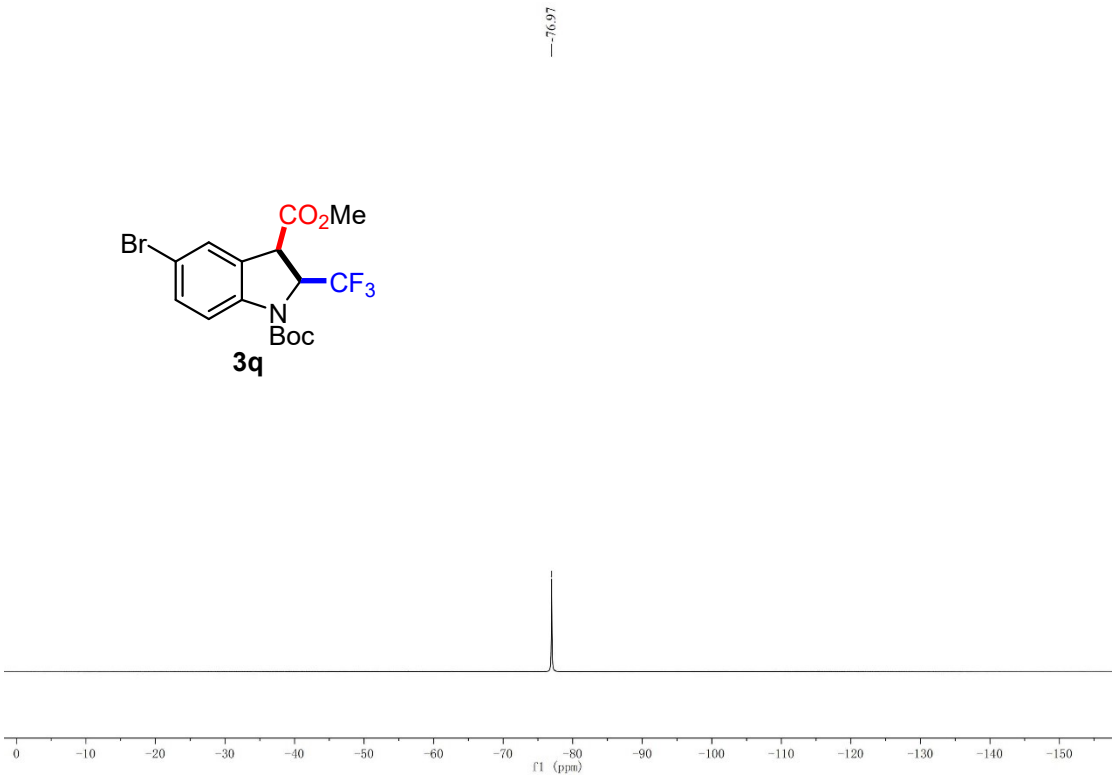


^{19}F NMR spectrum of **3p**

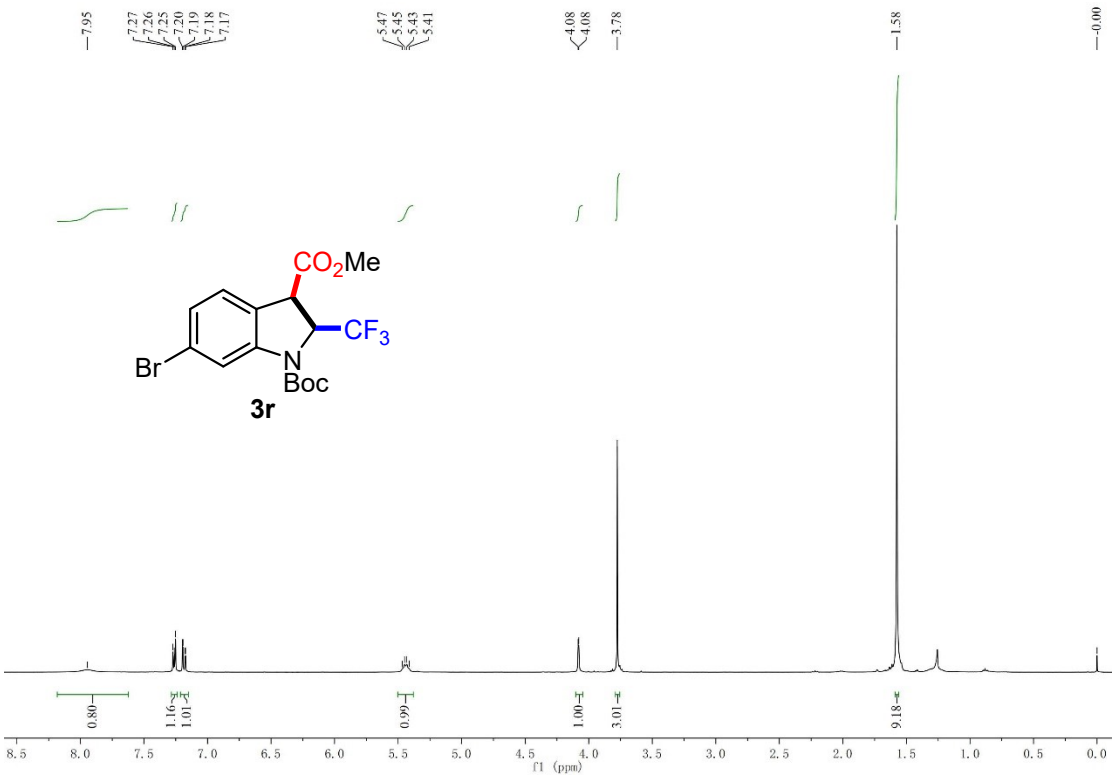


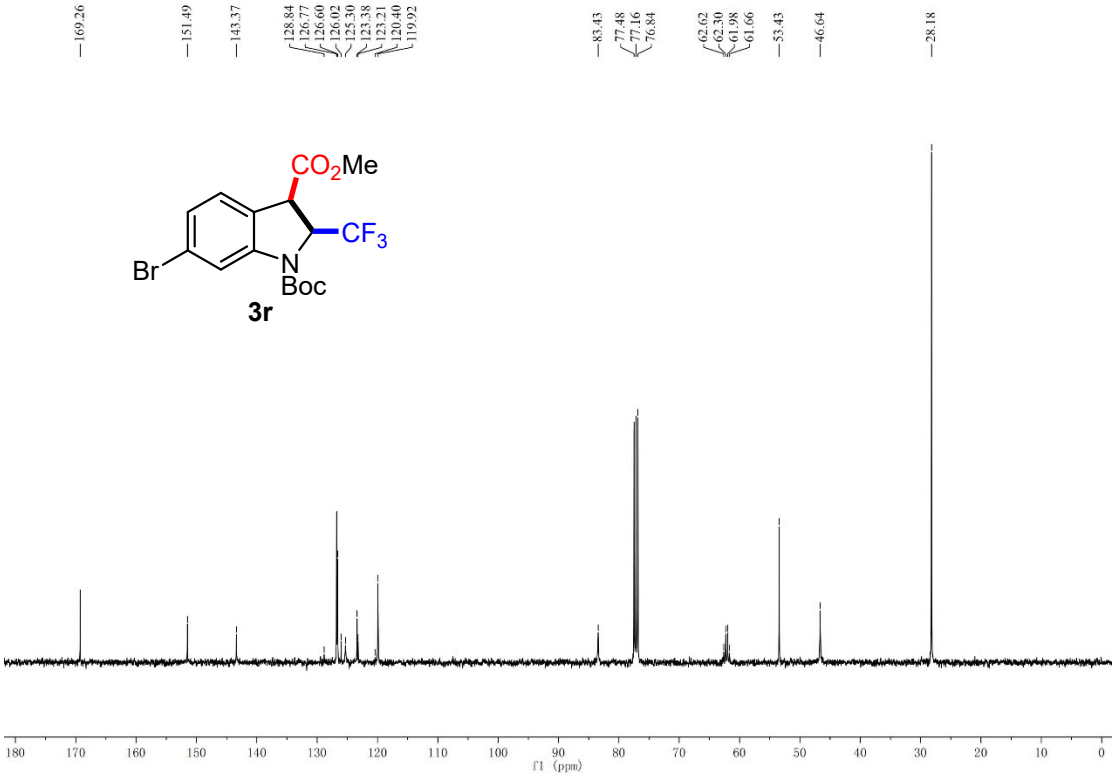


^{1}H NMR and ^{13}C NMR spectrum of **3q**

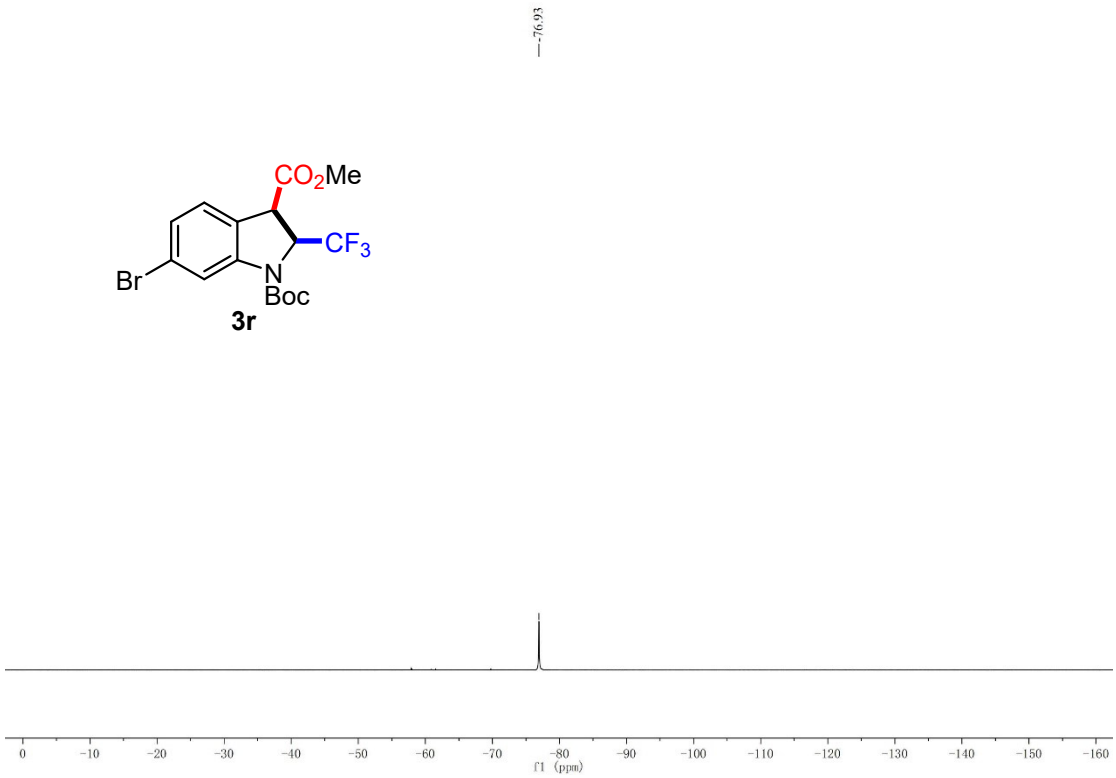


^{19}F NMR spectrum of **3q**

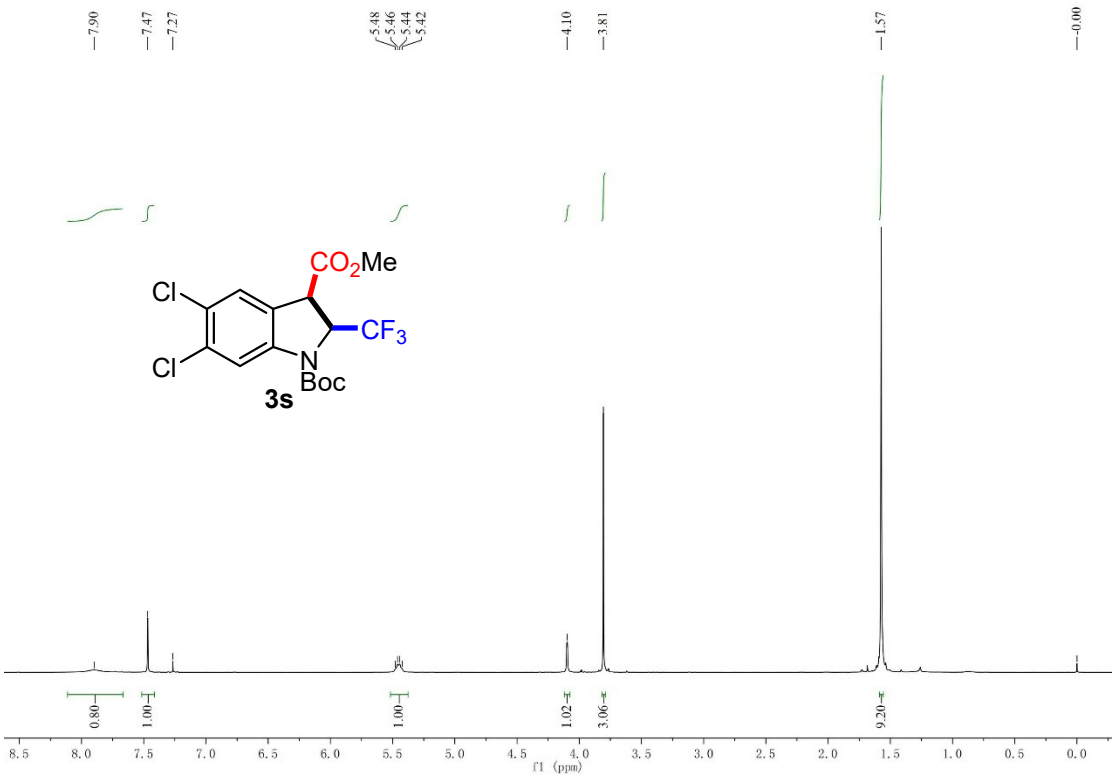


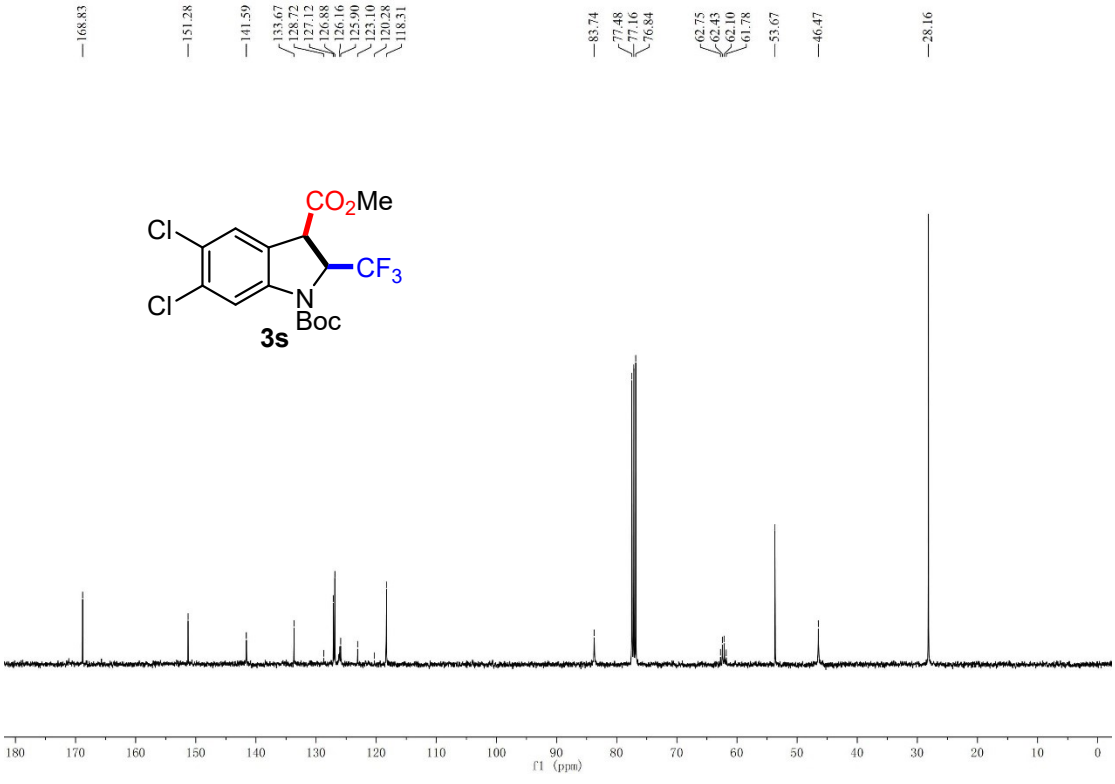


^{1}H NMR and ^{13}C NMR spectrum of **3r**

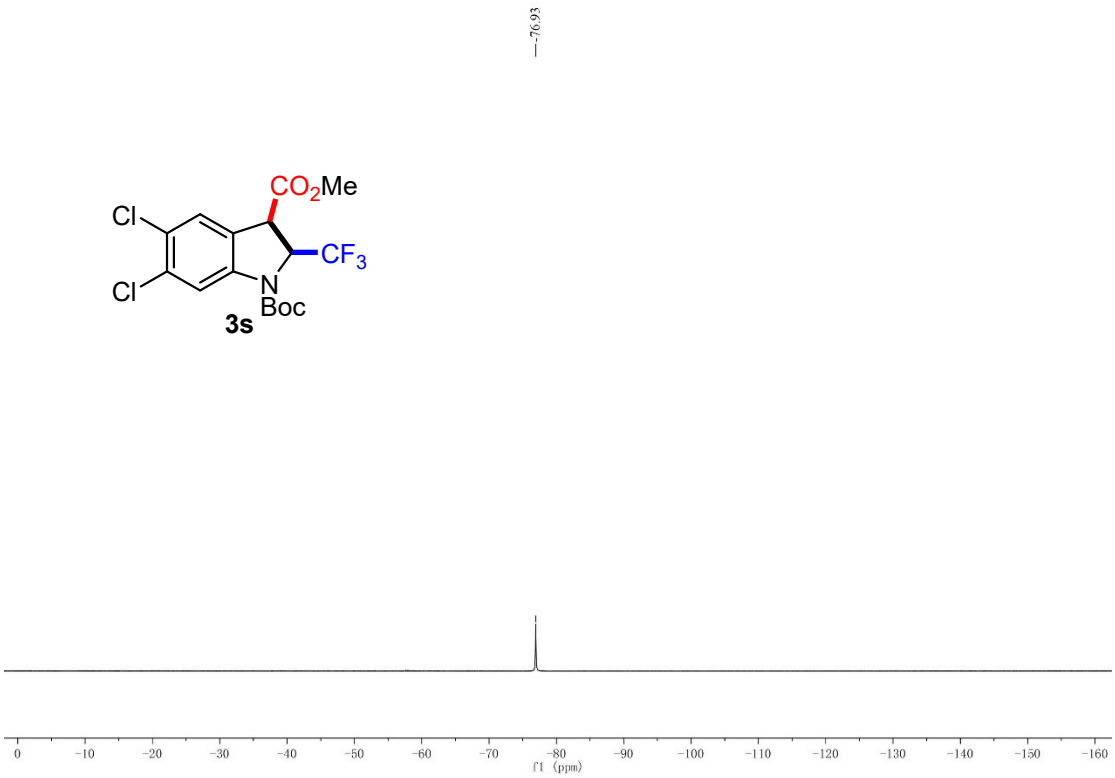


^{19}F NMR spectrum of **3r**

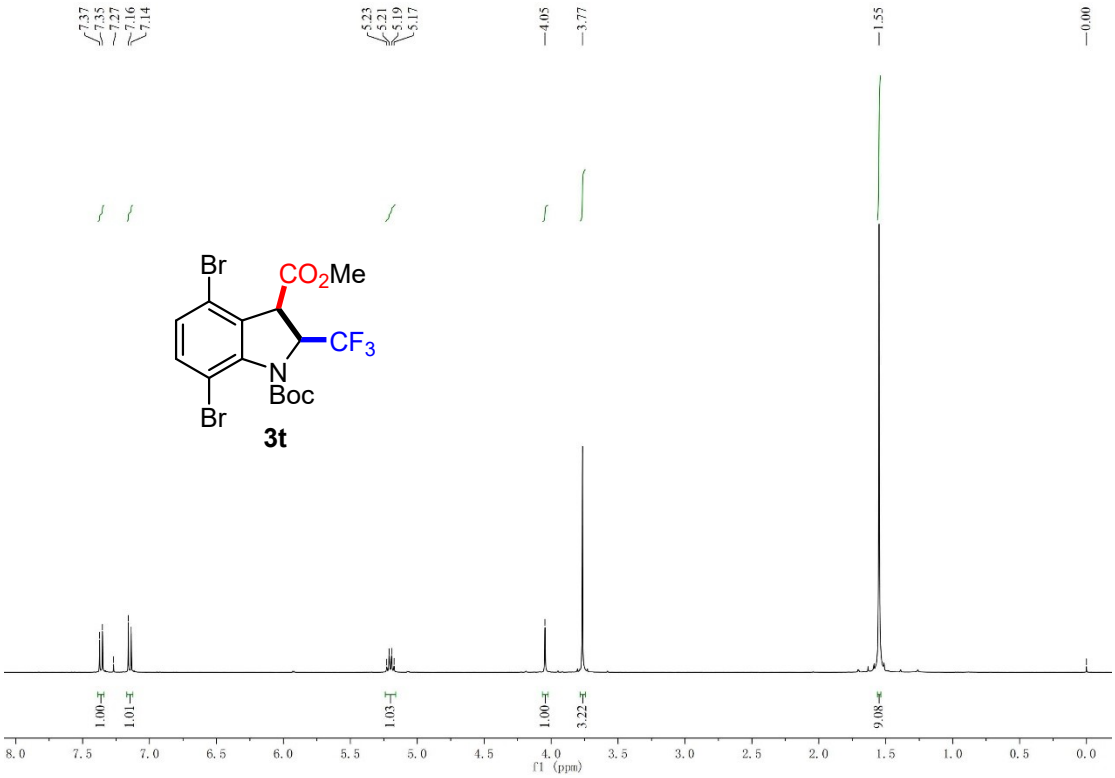


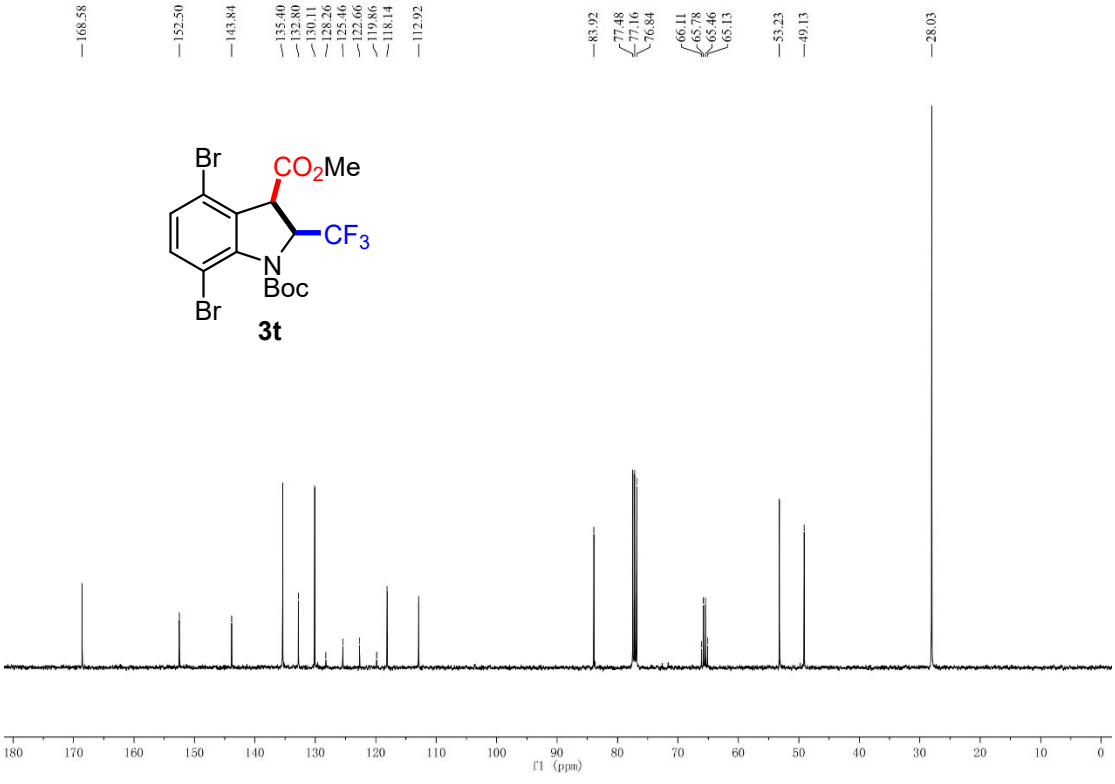


^{1}H NMR and ^{13}C NMR spectrum of **3s**

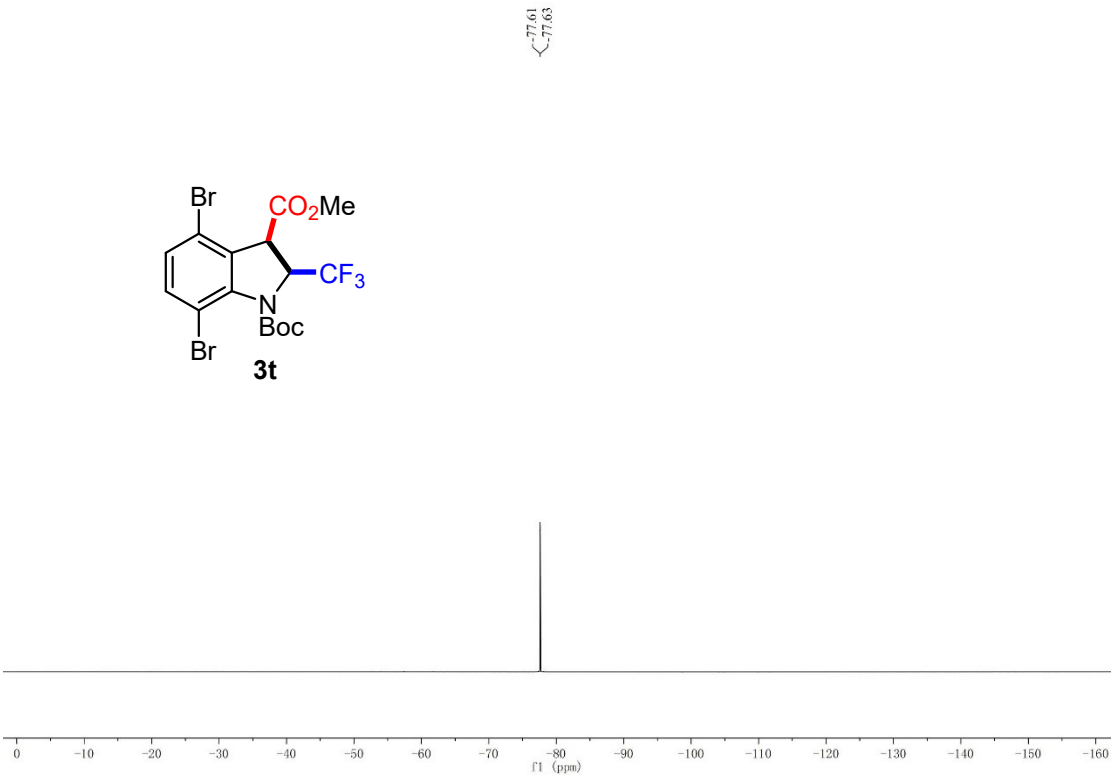


^{19}F NMR spectrum of **3s**

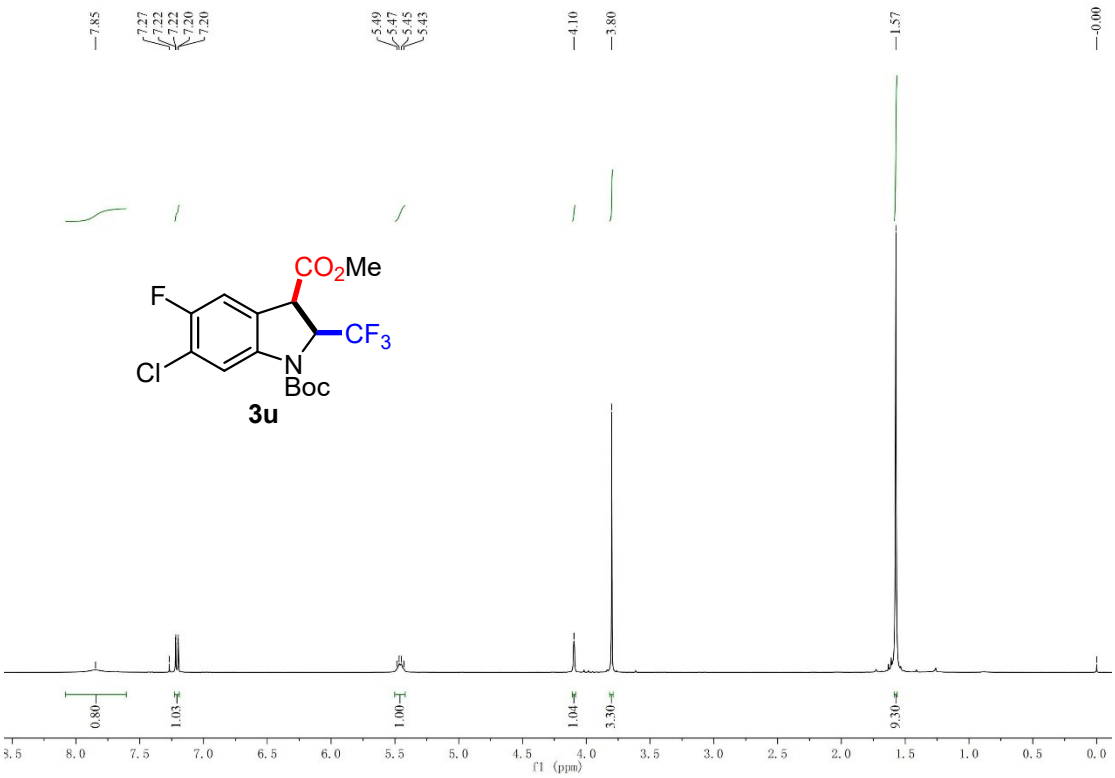


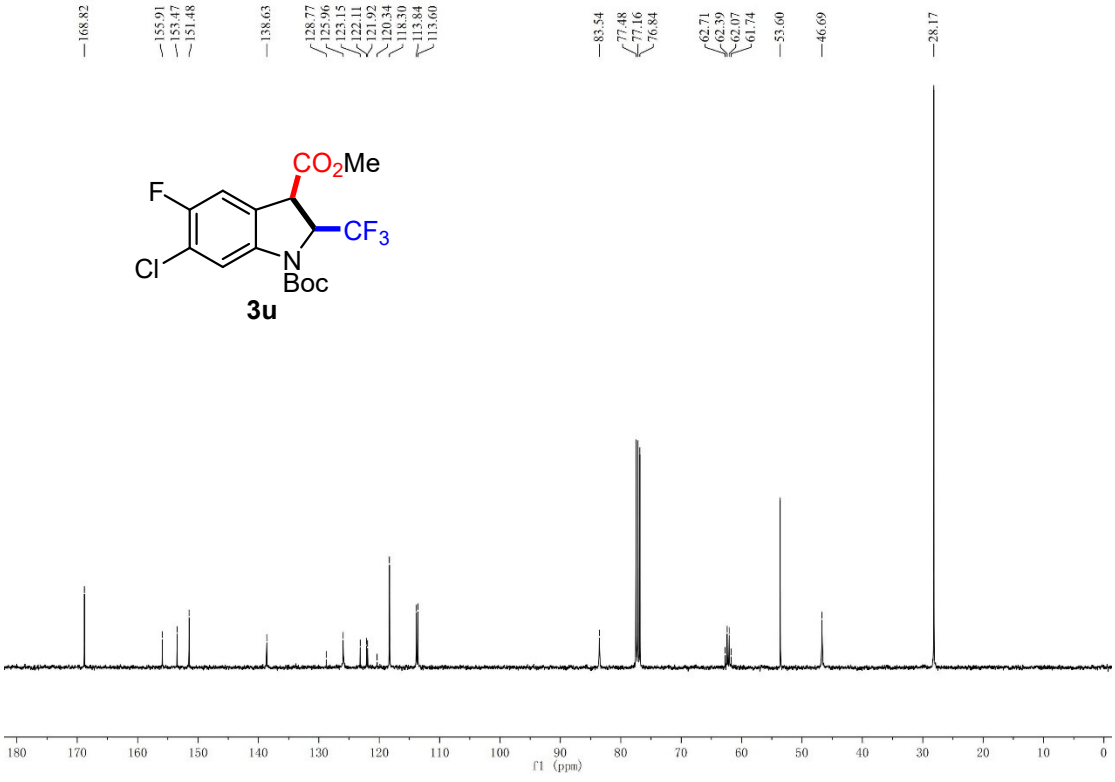


^{1}H NMR and ^{13}C NMR spectrum of **3t**

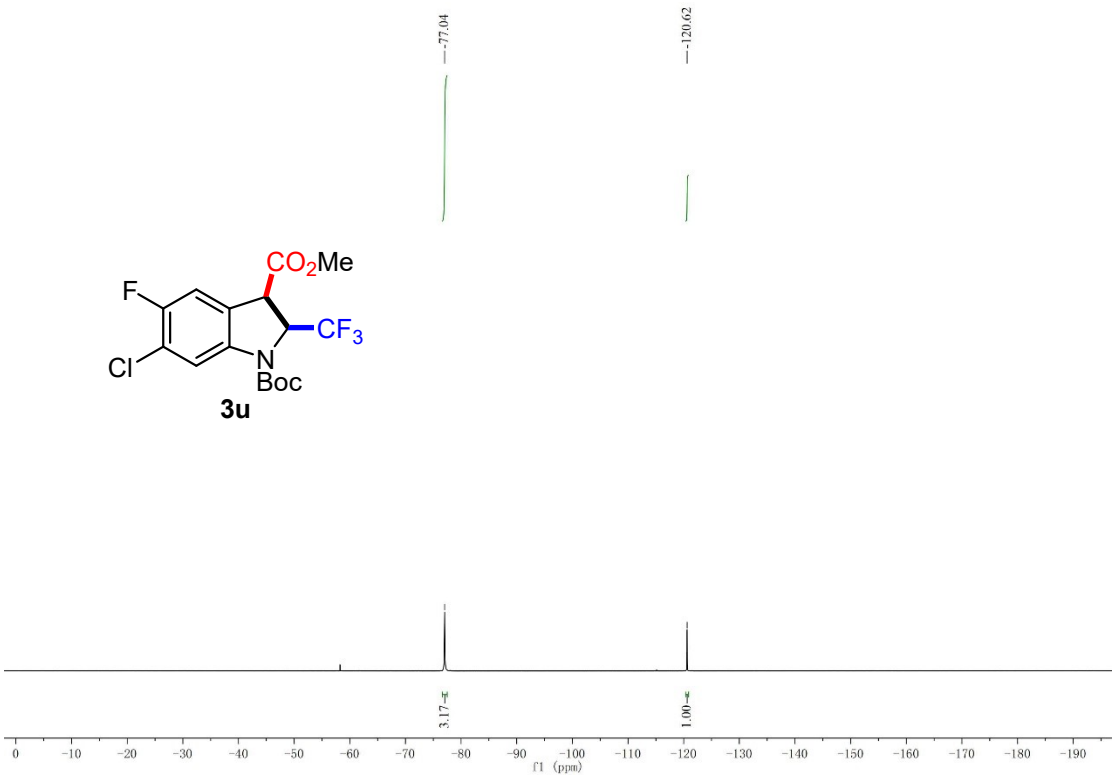


^{19}F NMR spectrum of **3t**

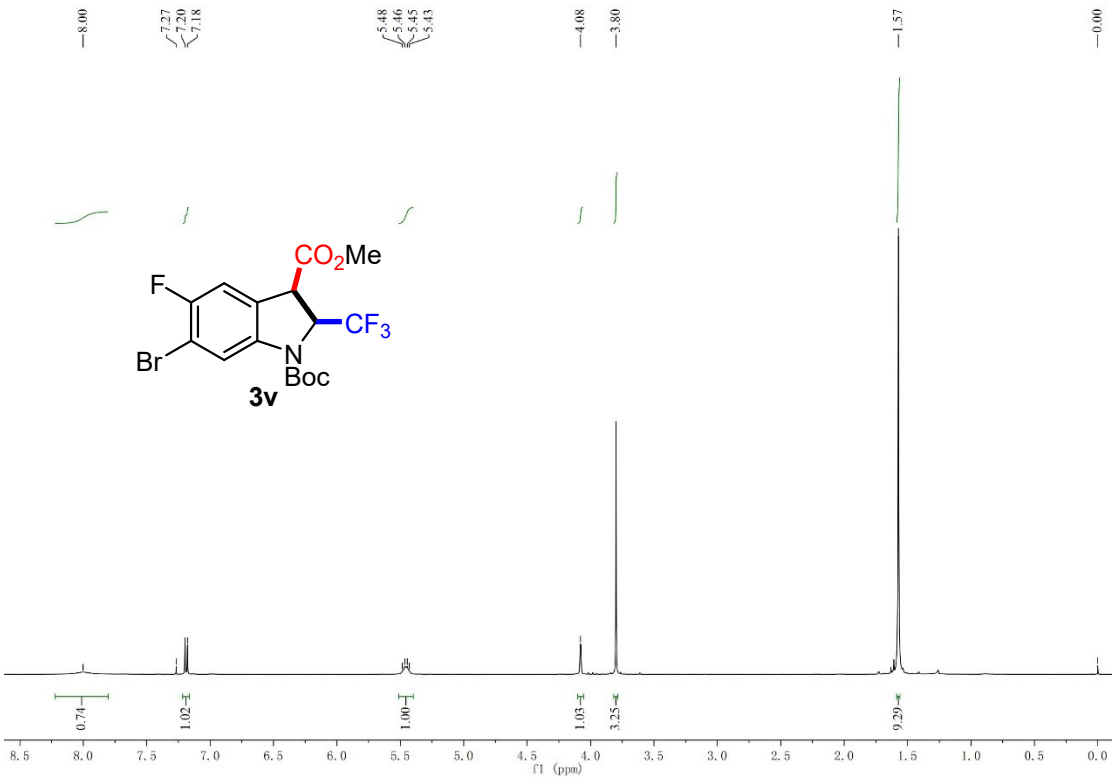


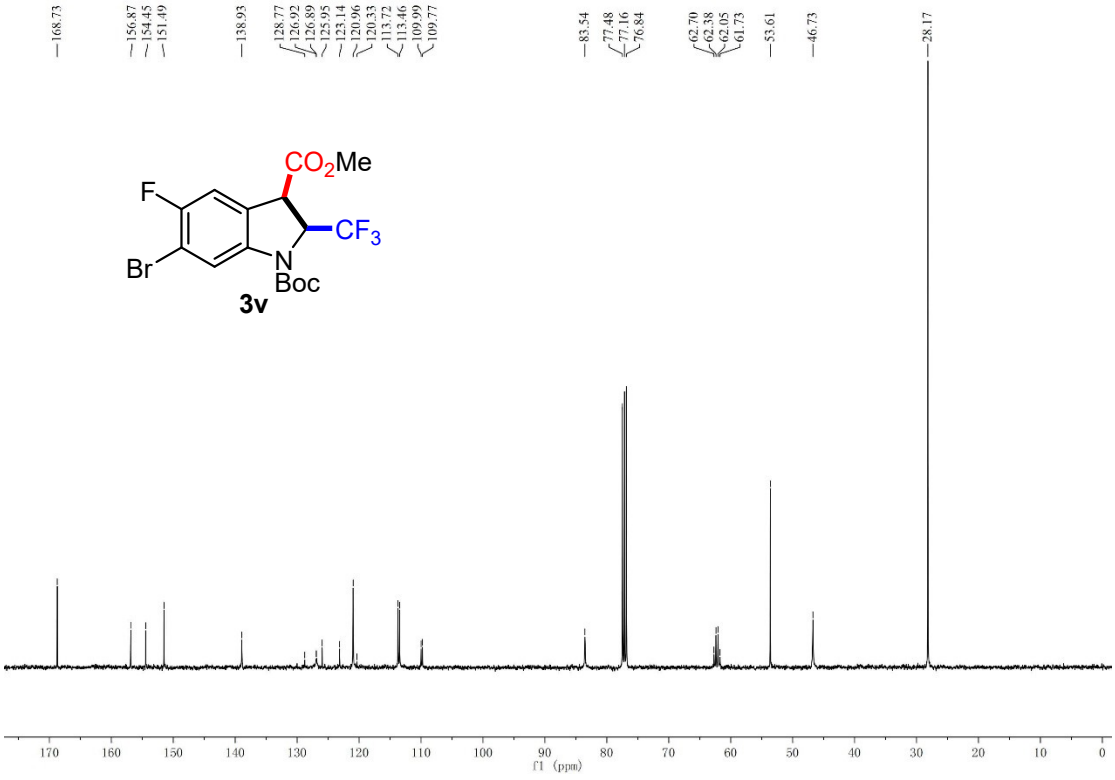


^{1}H NMR and ^{13}C NMR spectrum of **3u**

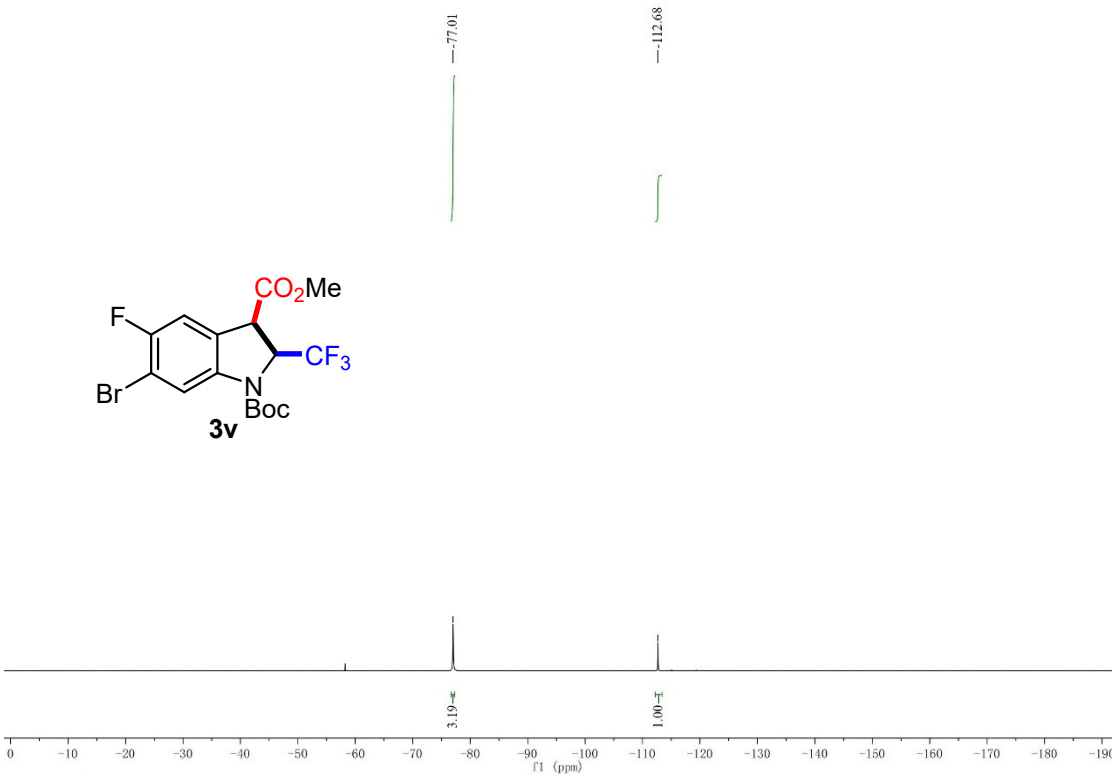


^{19}F NMR spectrum of **3u**

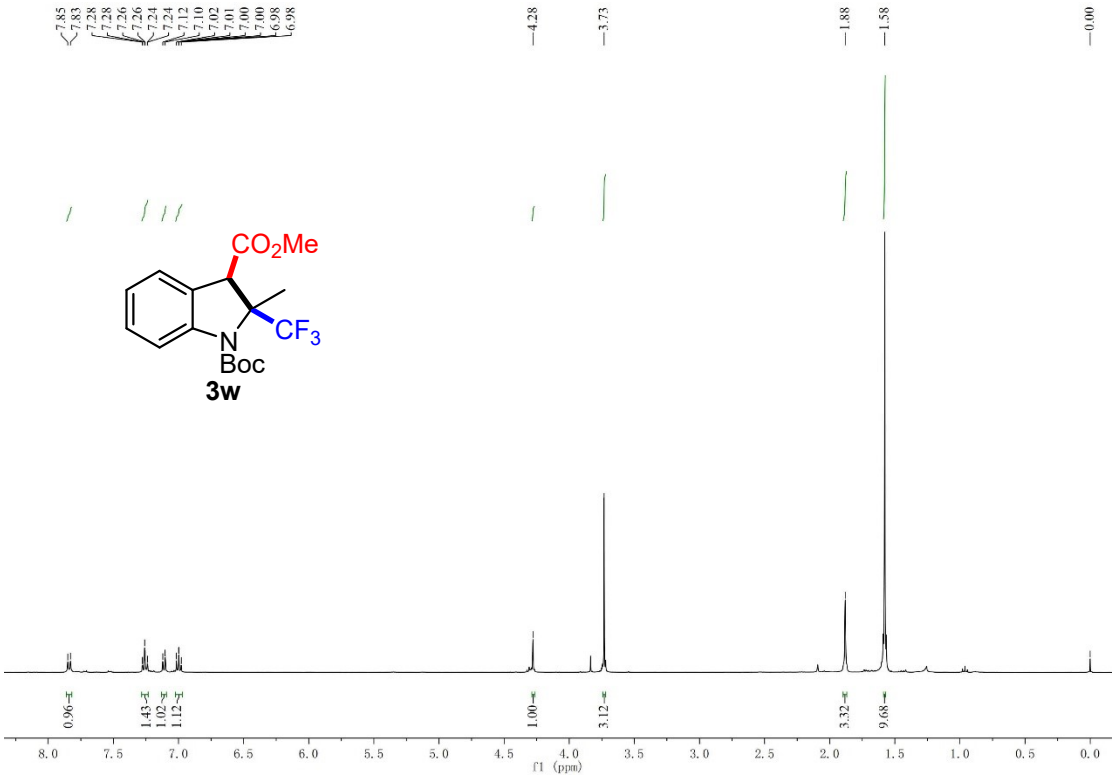


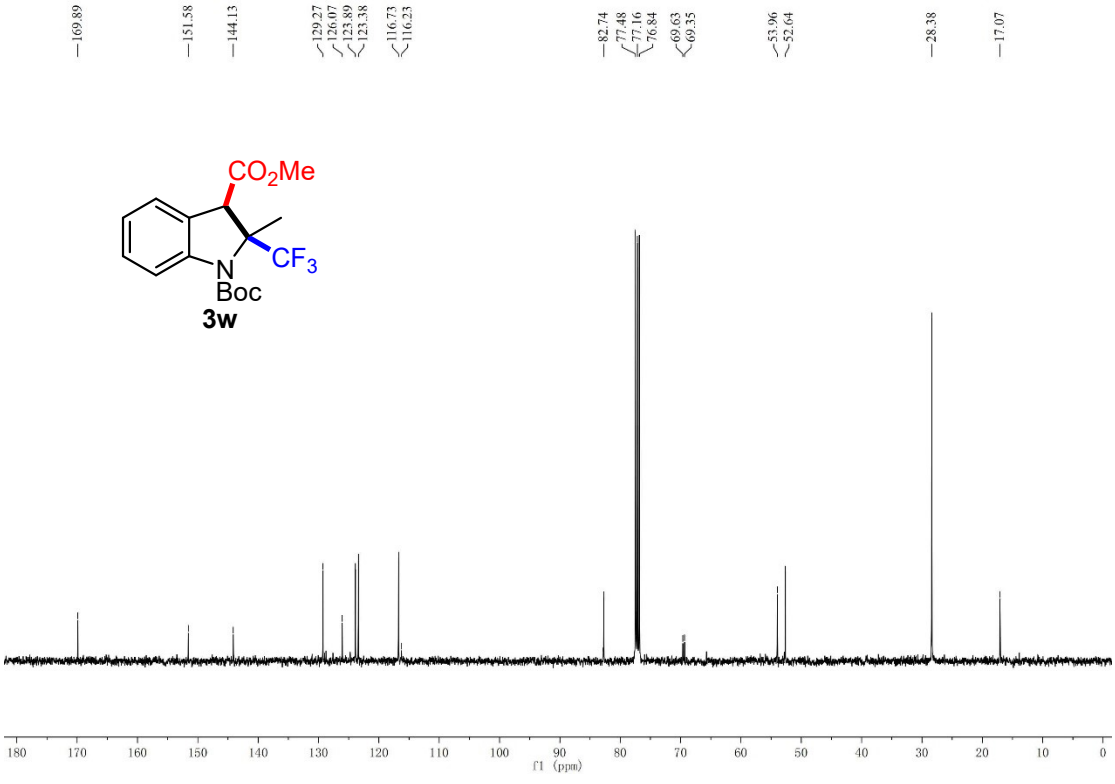


^{1}H NMR and ^{13}C NMR spectrum of **3v**

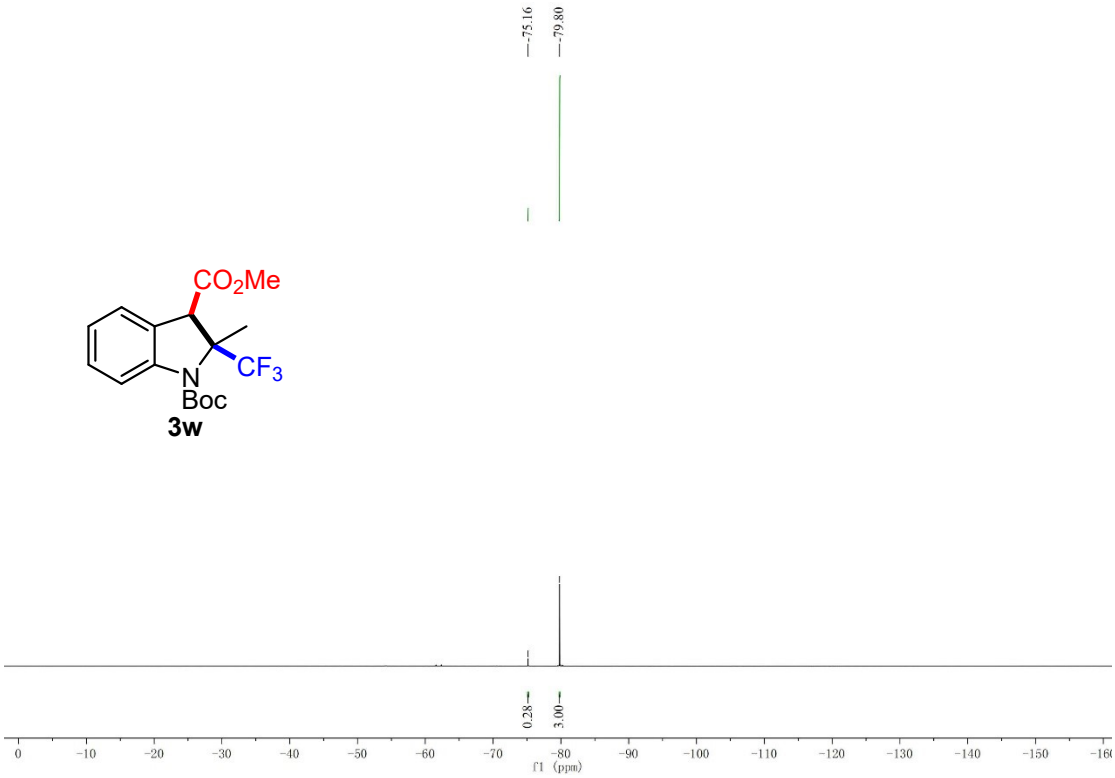


^{19}F NMR spectrum of **3v**

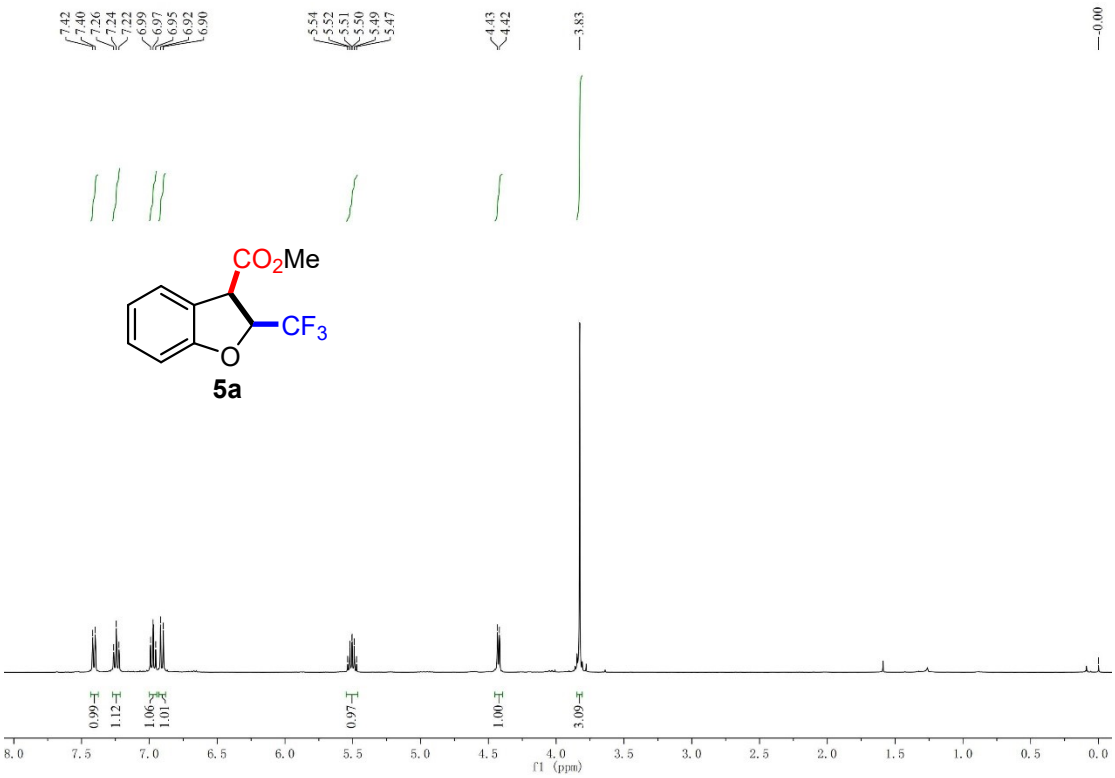


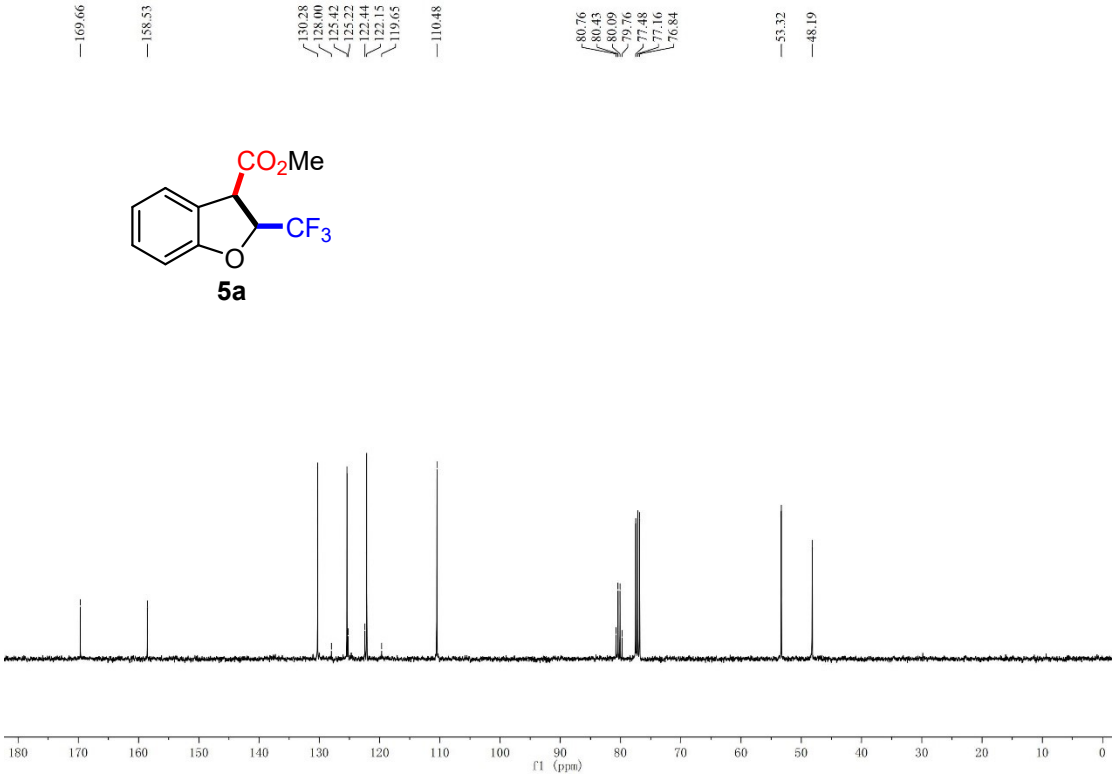


^{1}H NMR and ^{13}C NMR spectrum of **3w**

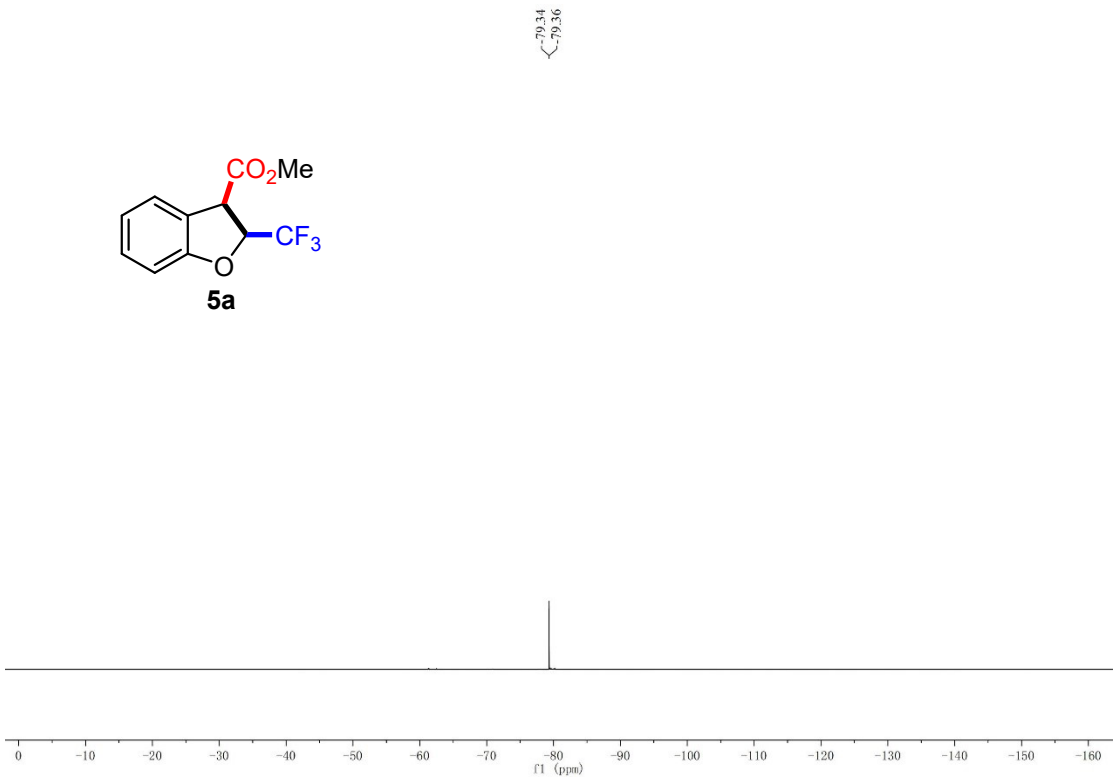


^{19}F NMR spectrum of **3w**

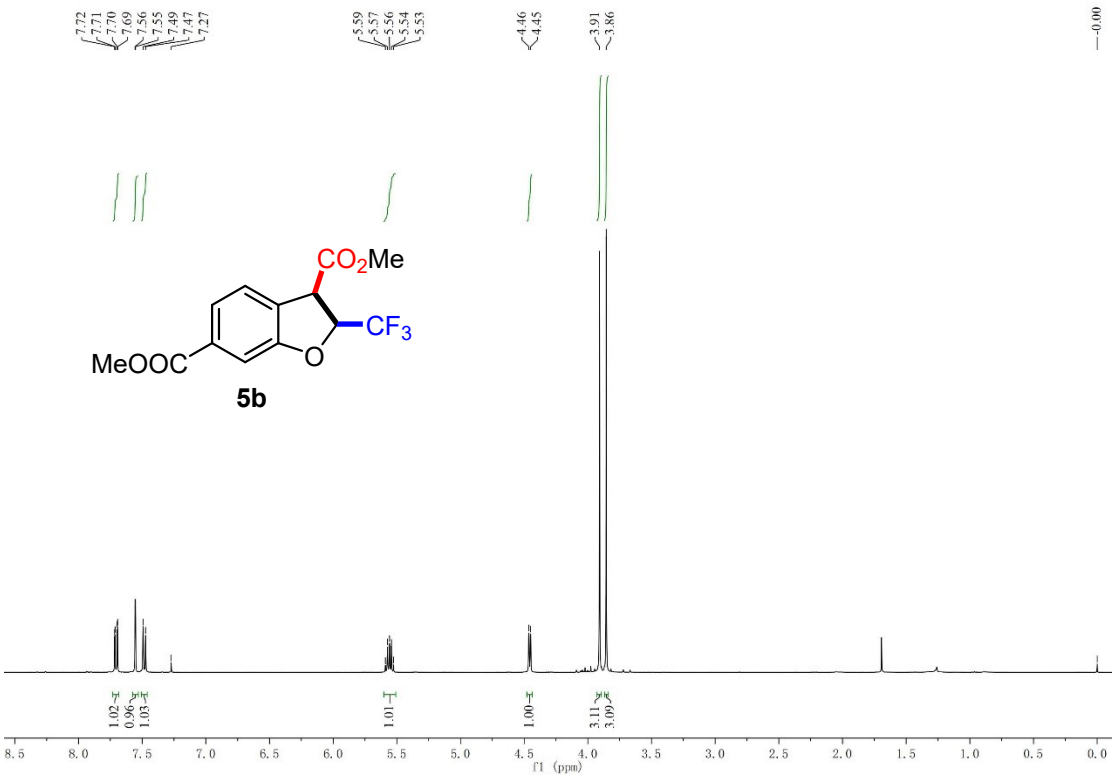


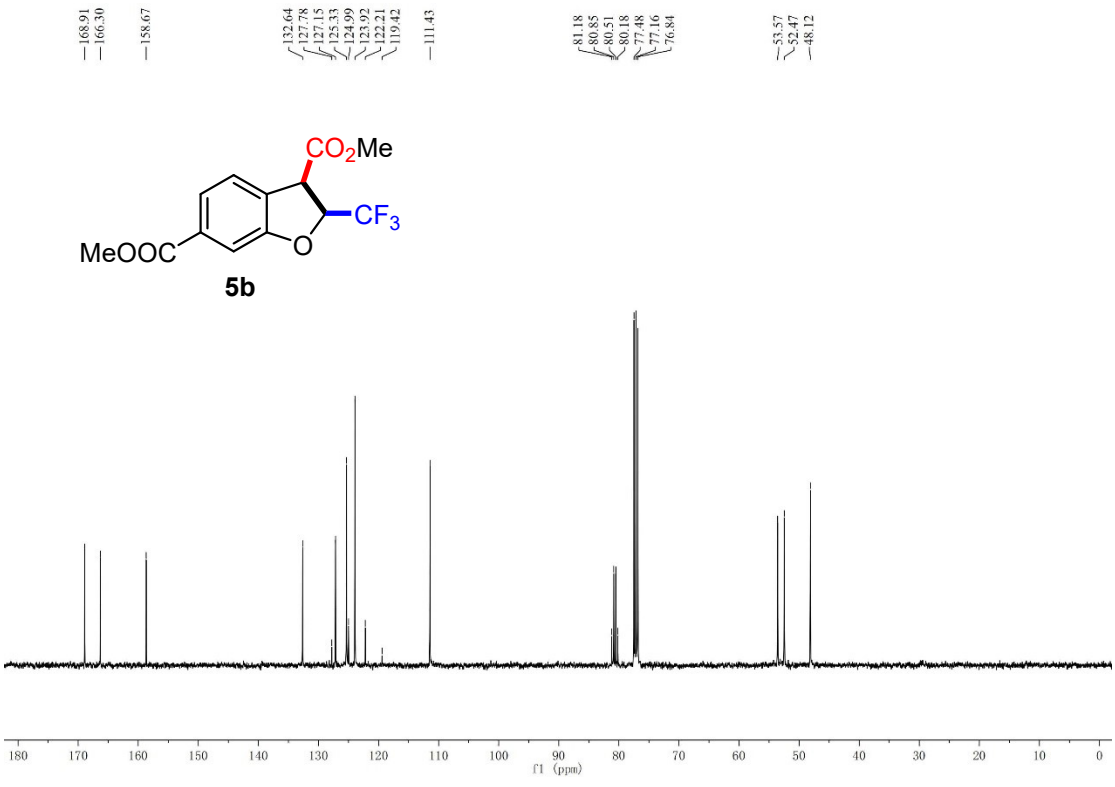


^{1}H NMR and ^{13}C NMR spectrum of **5a**

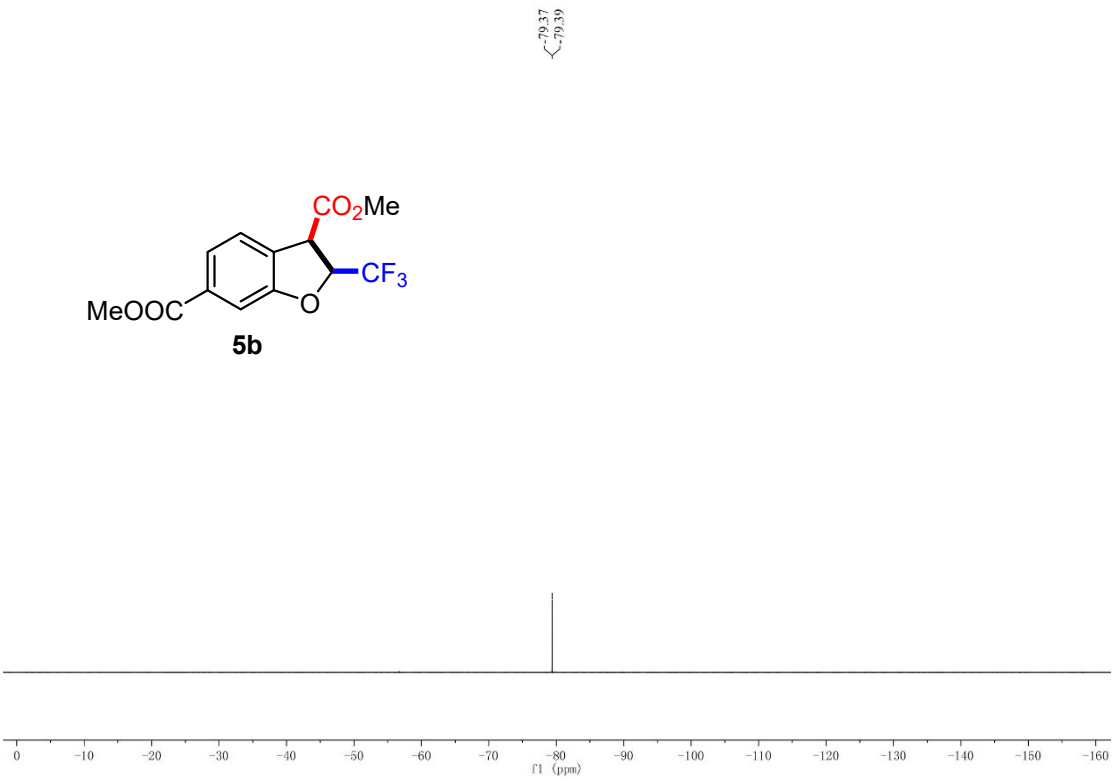


^{19}F NMR spectrum of **5a**

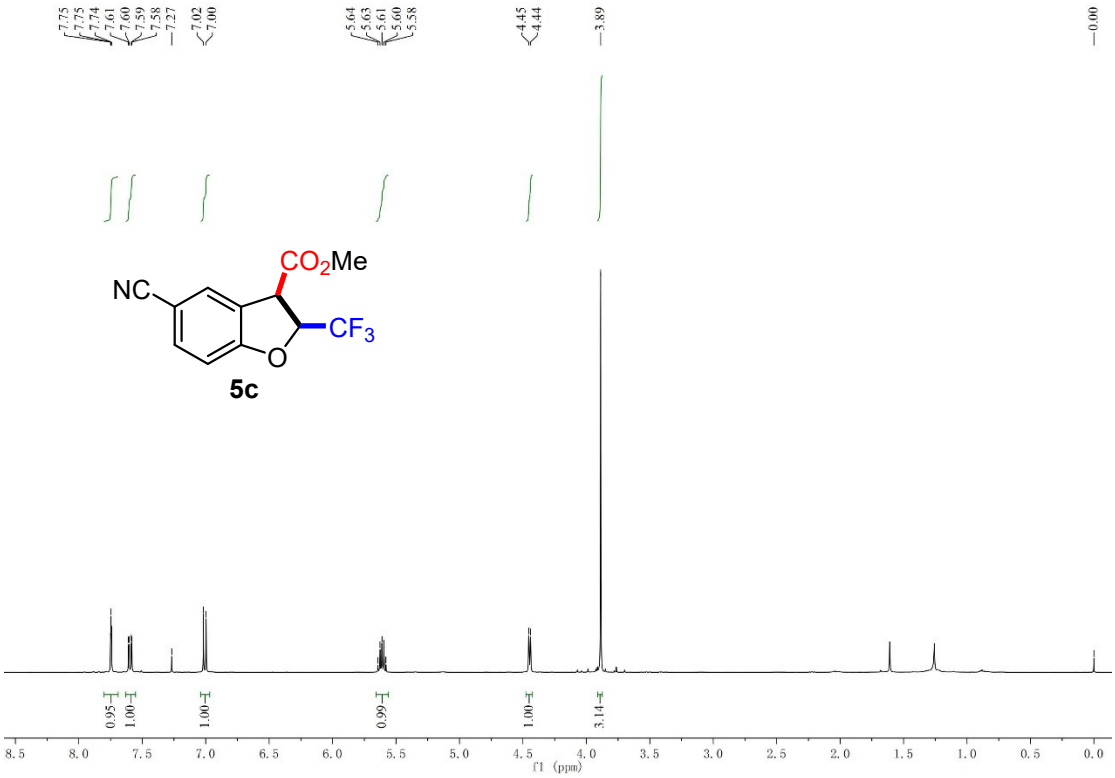


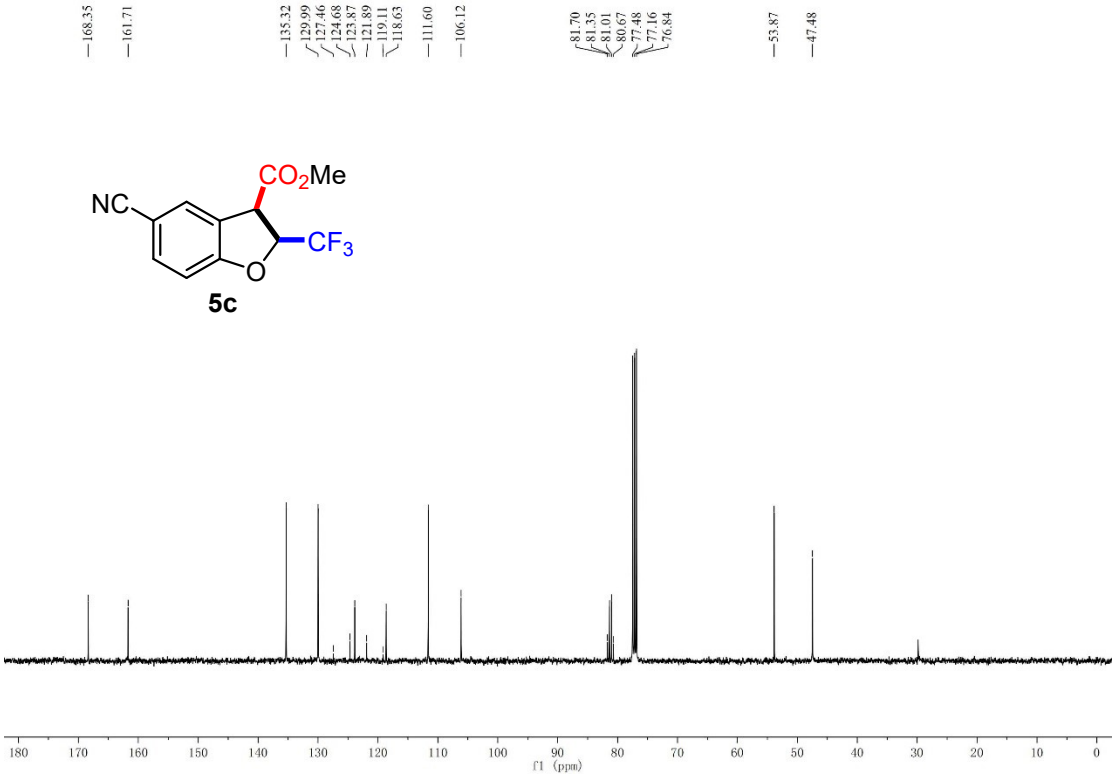


^{1}H NMR and ^{13}C NMR spectrum of **5b**

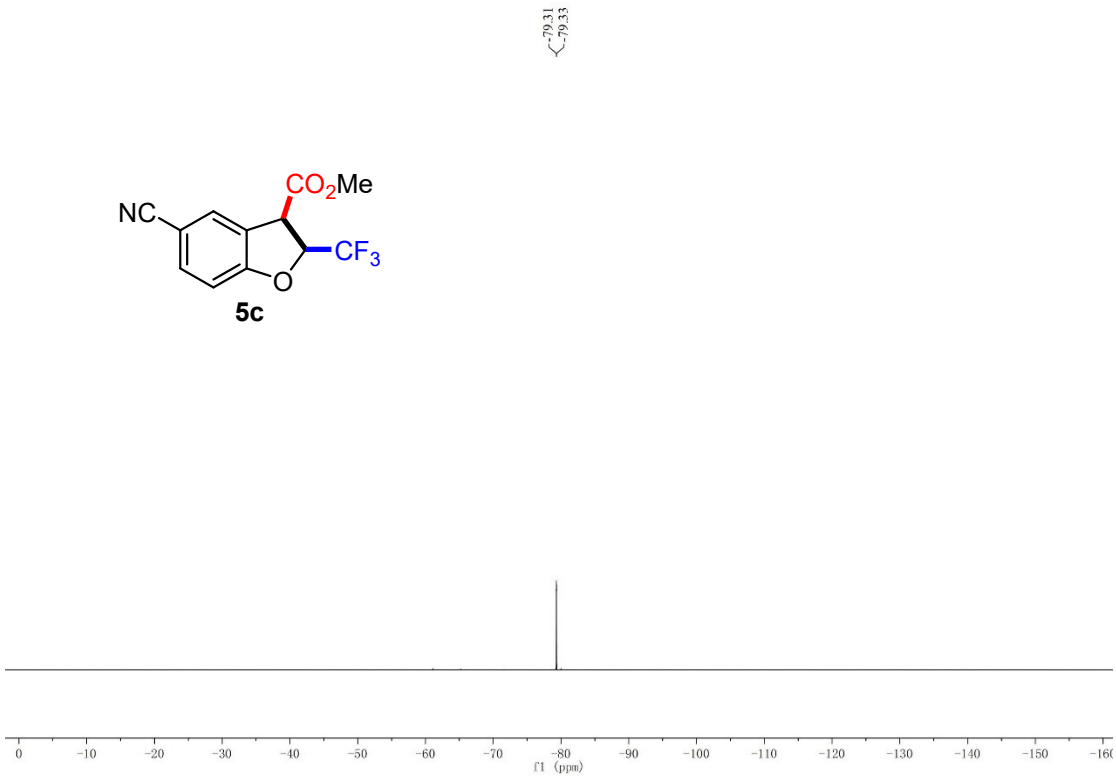


^{19}F NMR spectrum of **5b**

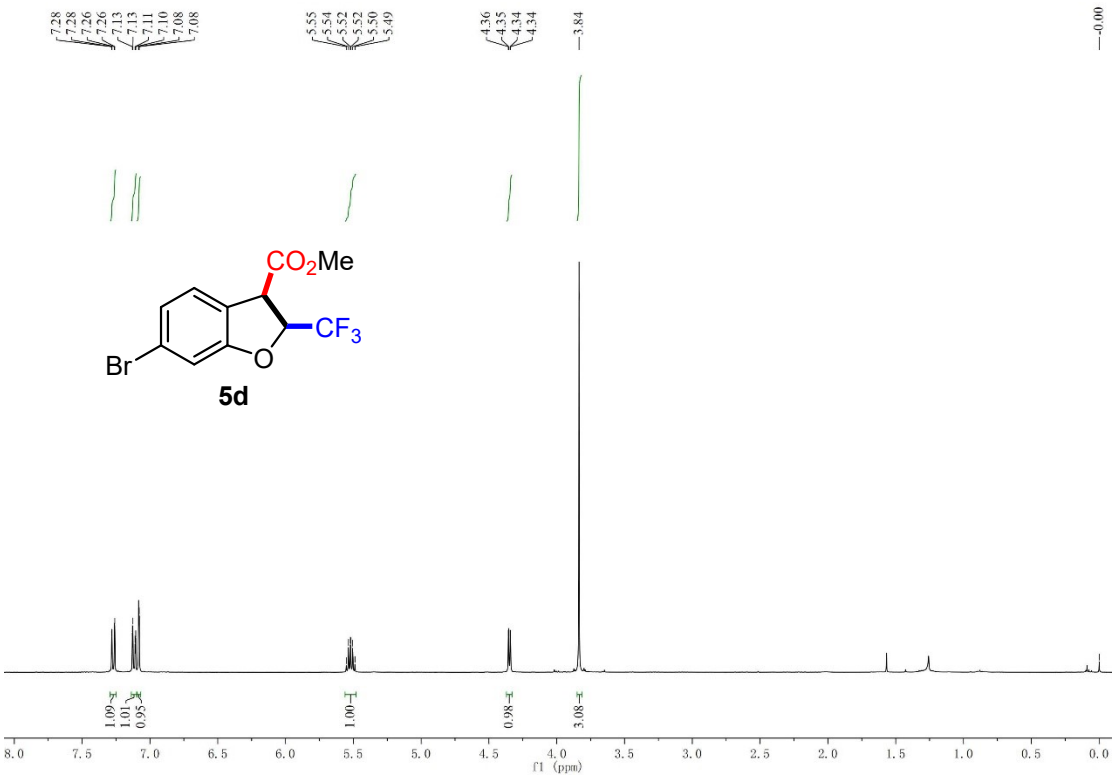


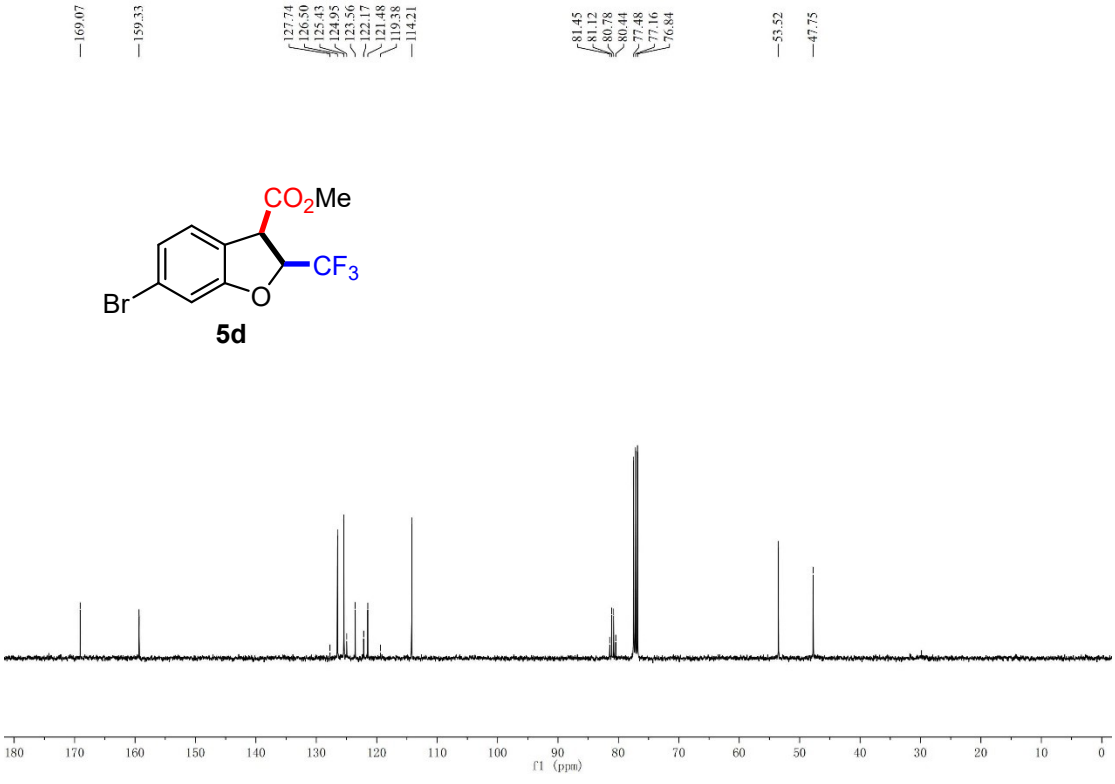


^{1}H NMR and ^{13}C NMR spectrum of **5c**

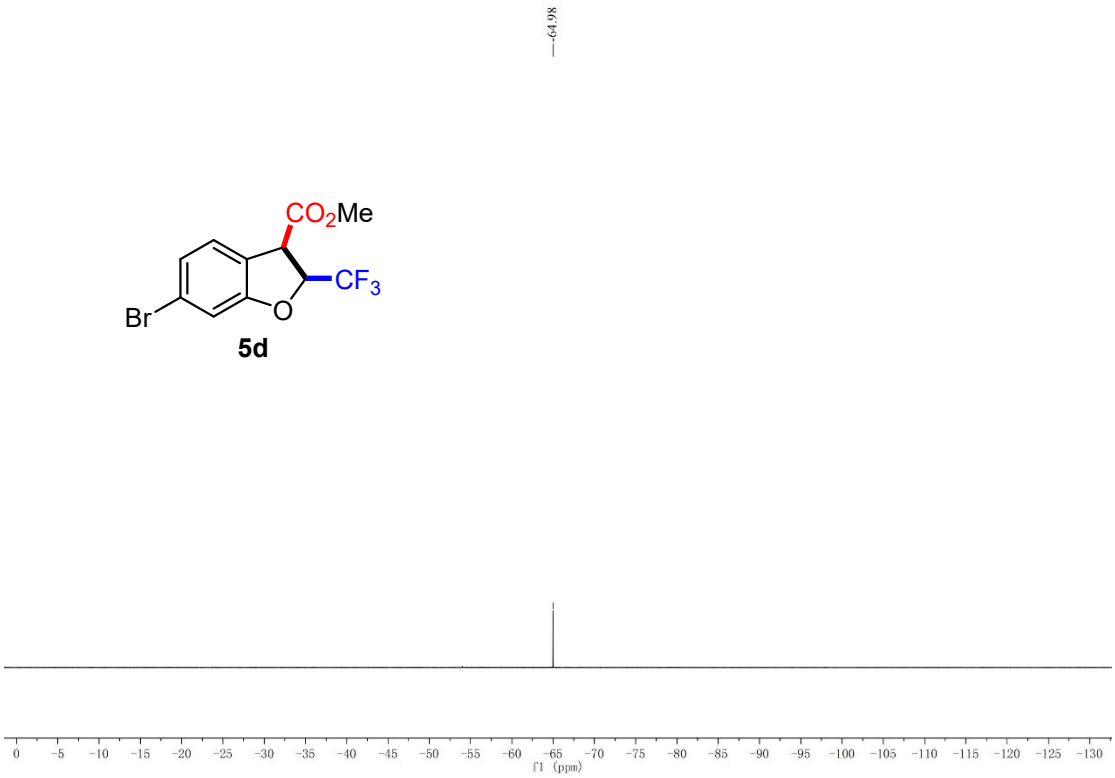


^{19}F NMR spectrum of **5c**

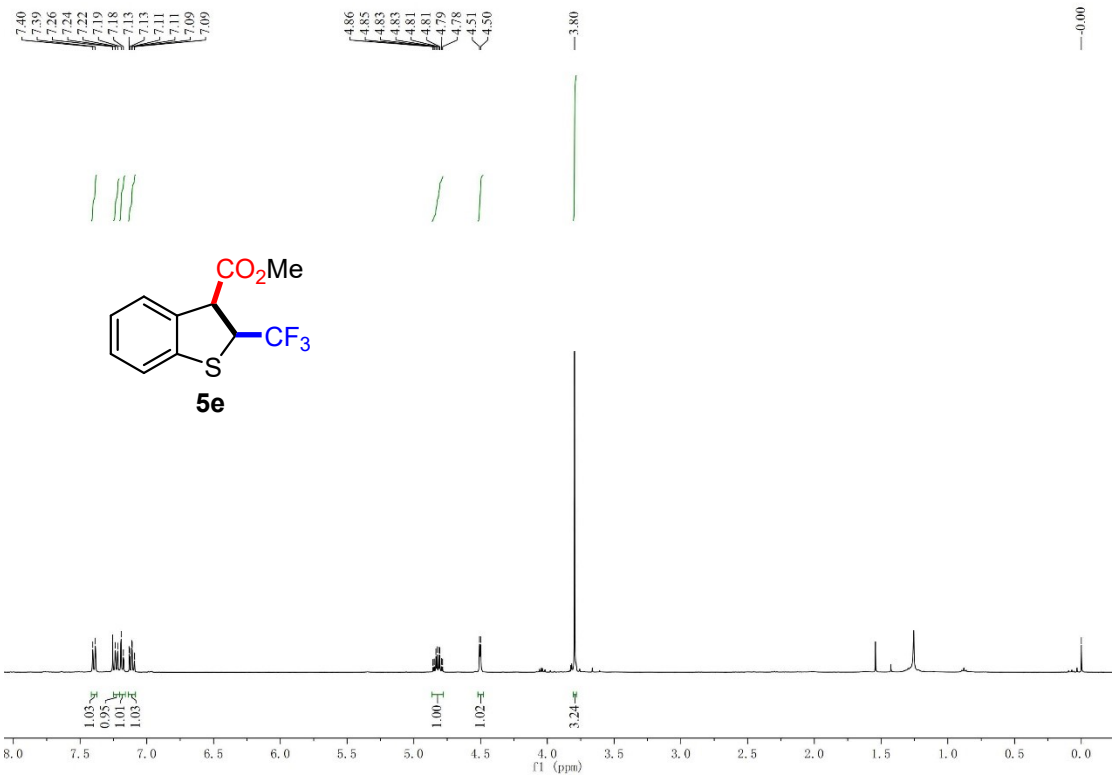


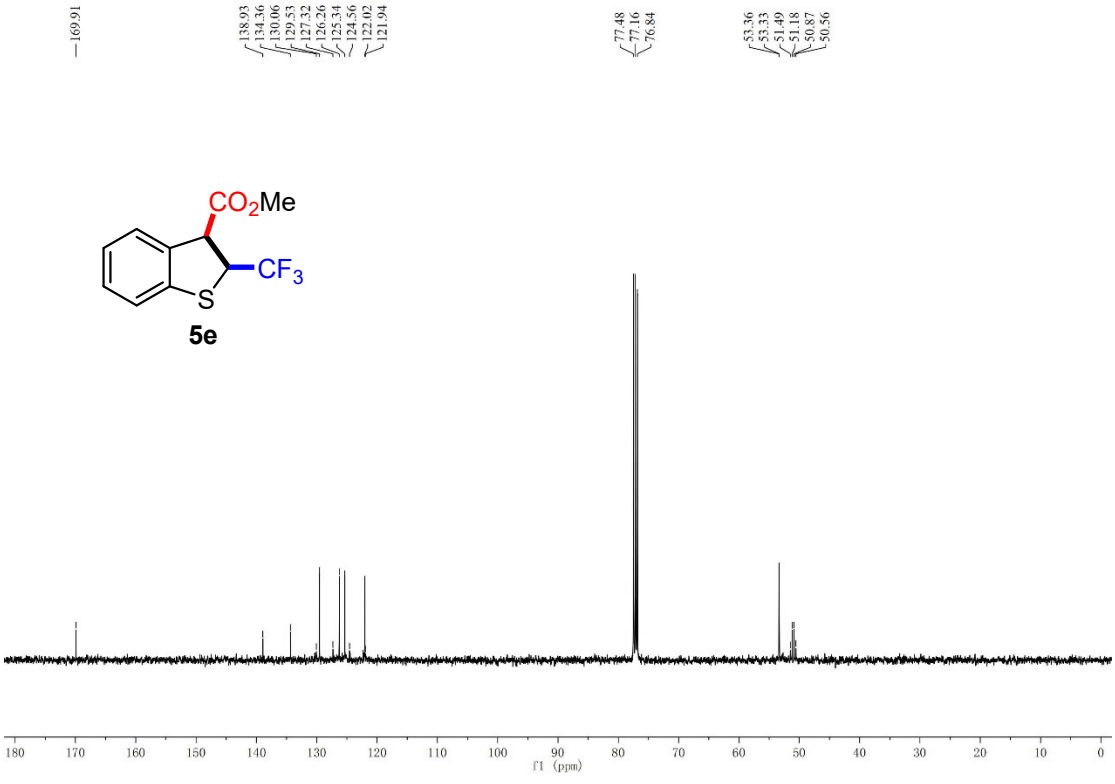


^{1}H NMR and ^{13}C NMR spectrum of **5d**

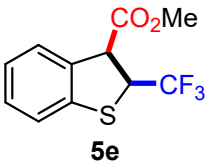


^{19}F NMR spectrum of **5d**





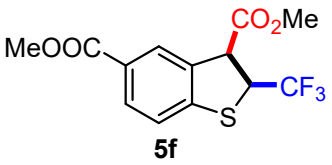
^{1}H NMR and ^{13}C NMR spectrum of **5e**



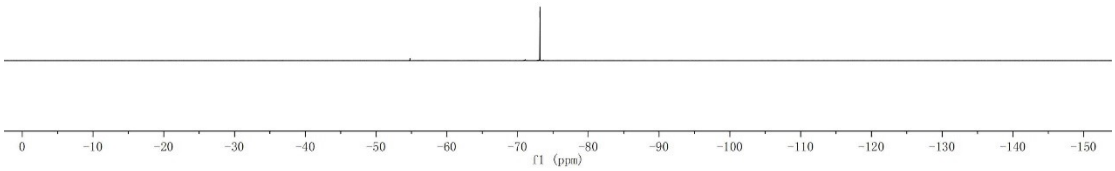
5e

^{19}F NMR spectrum of **5e**

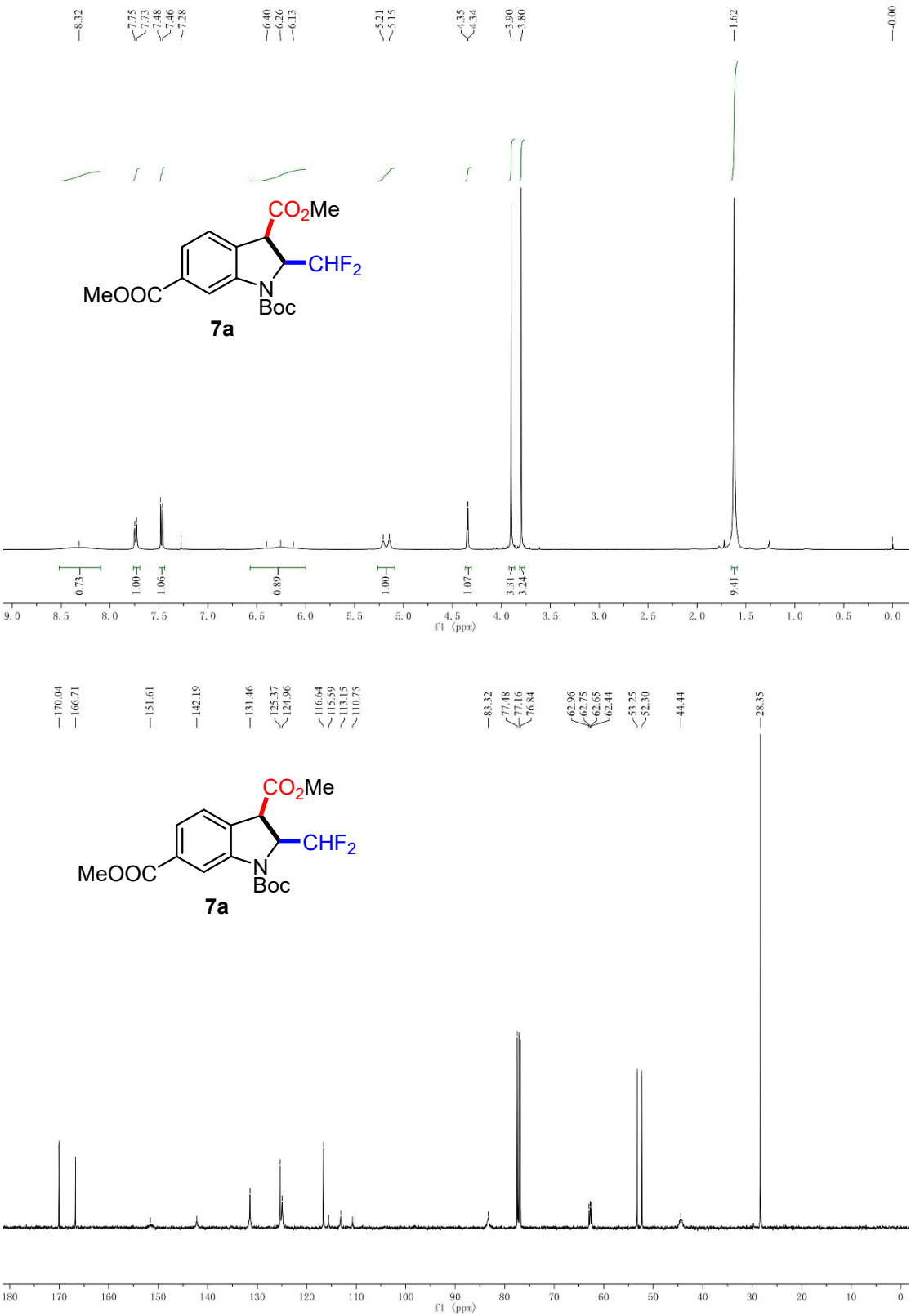
^{1}H NMR and ^{13}C NMR spectrum of **5f**



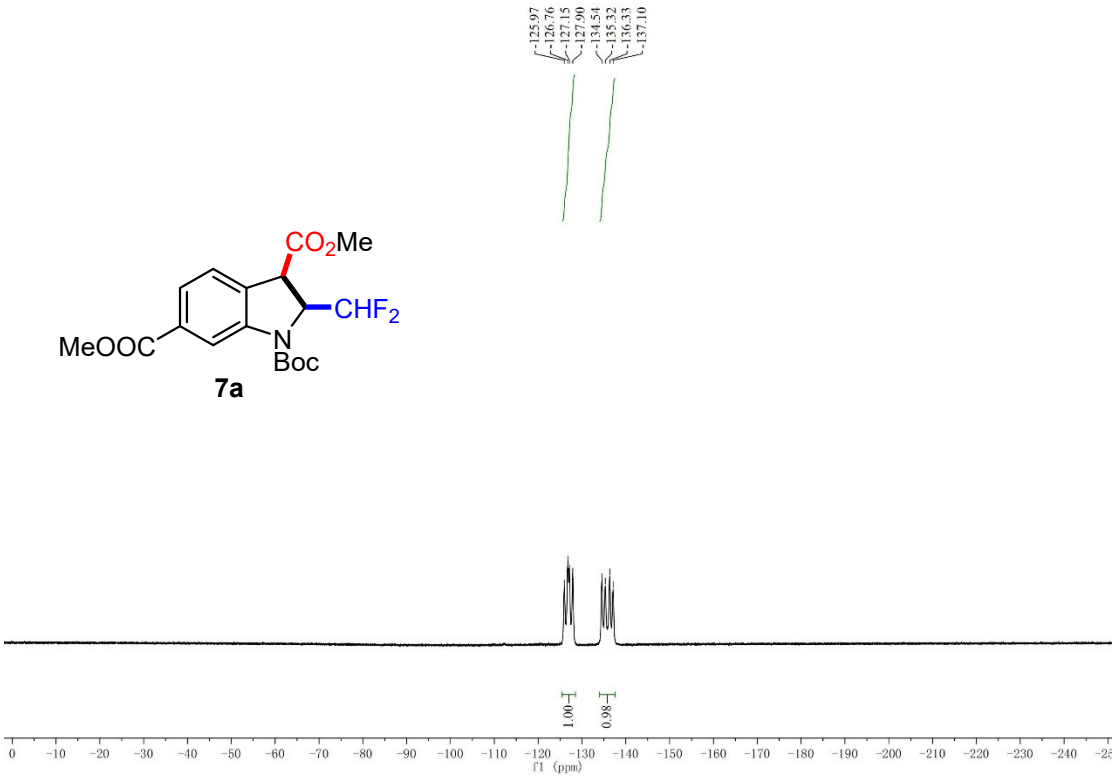
5f



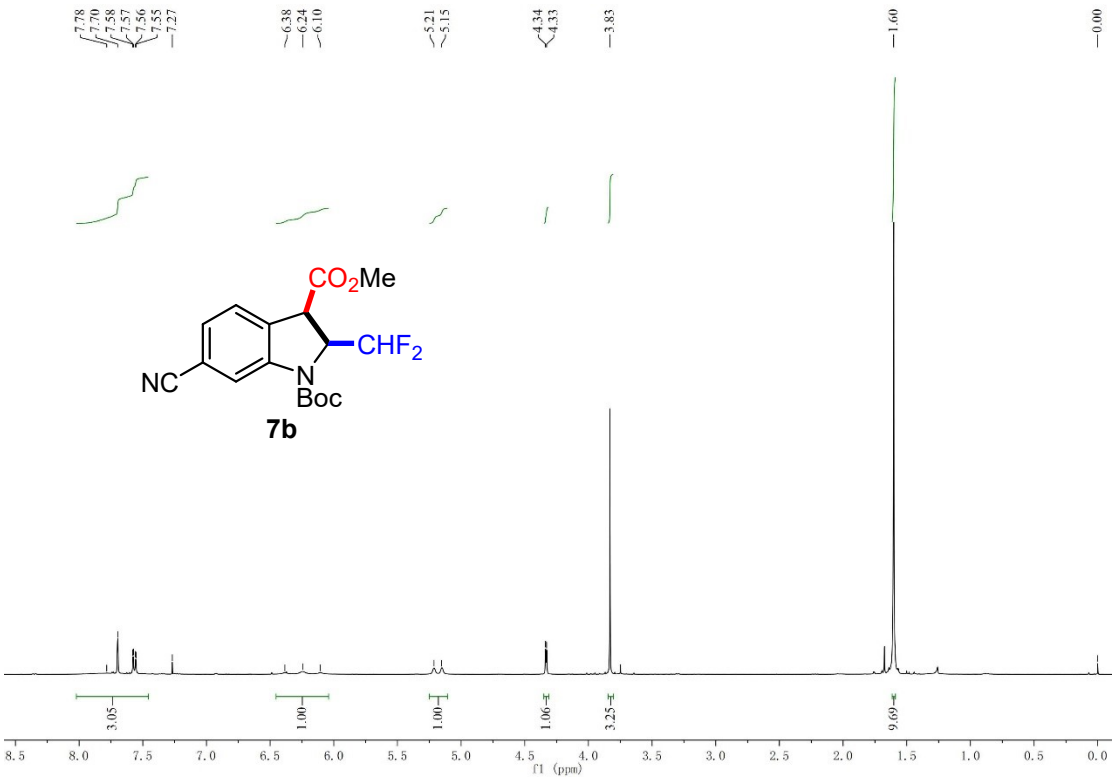
^{19}F NMR spectrum of **5f**

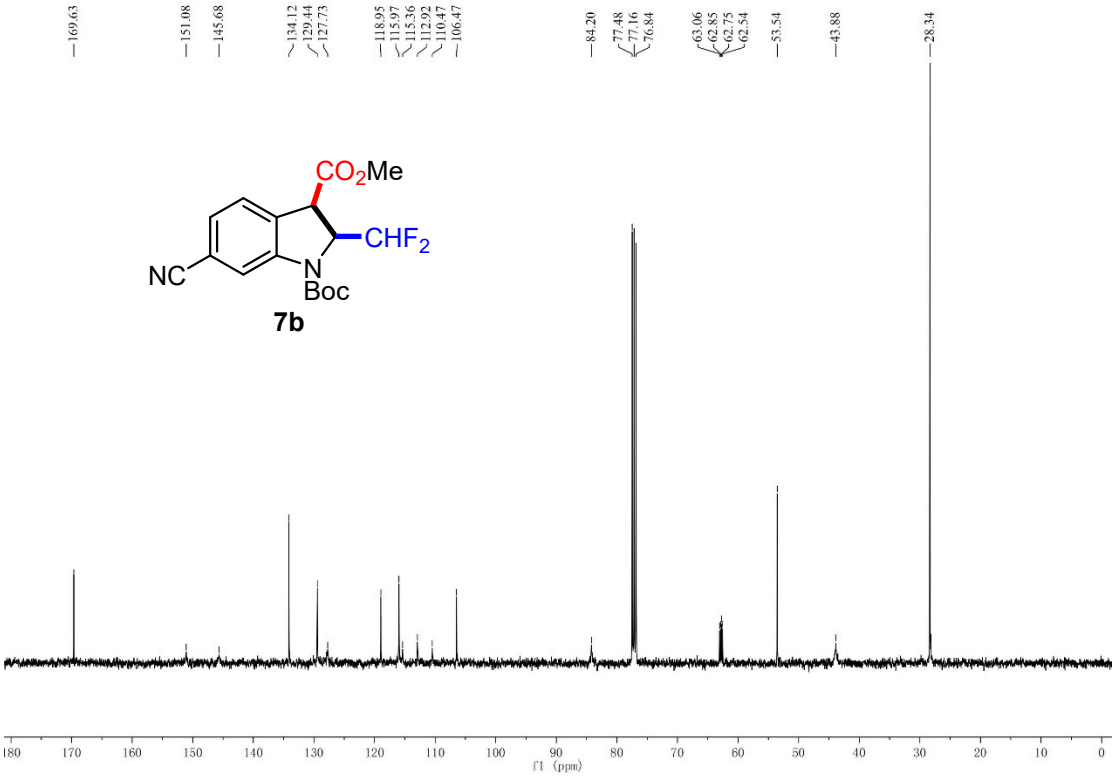


^{1}H NMR and ^{13}C NMR spectrum of **7a**

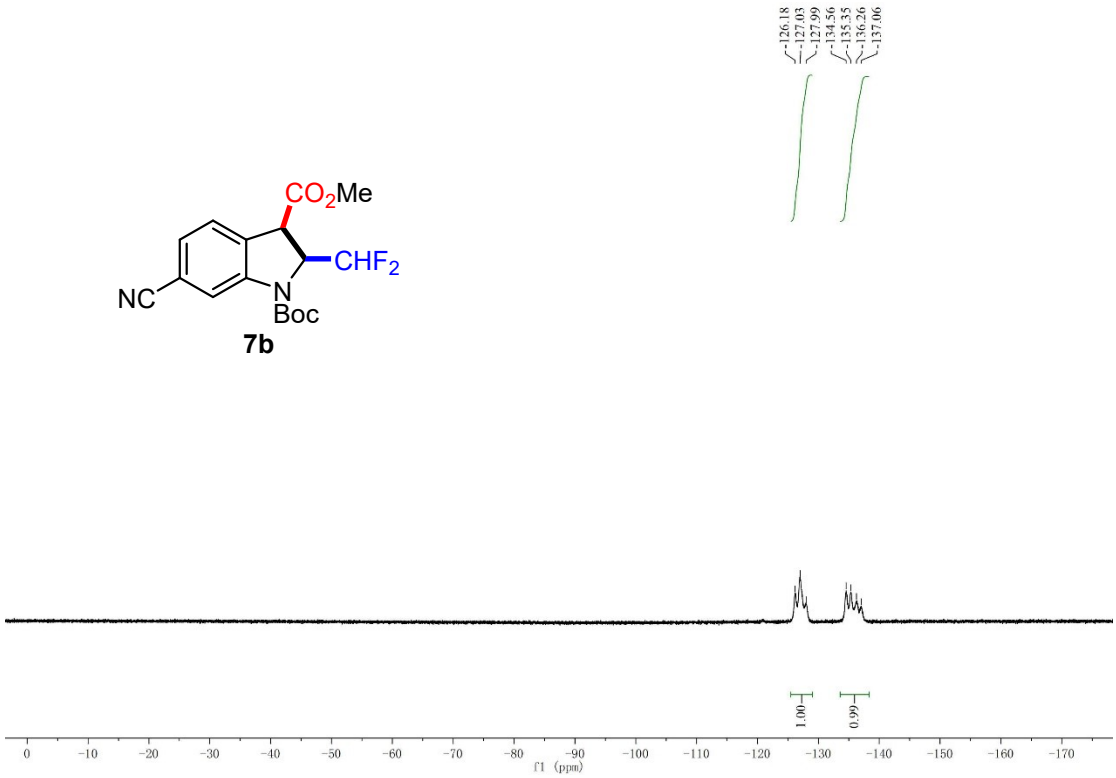


^{19}F NMR spectrum of **7a**

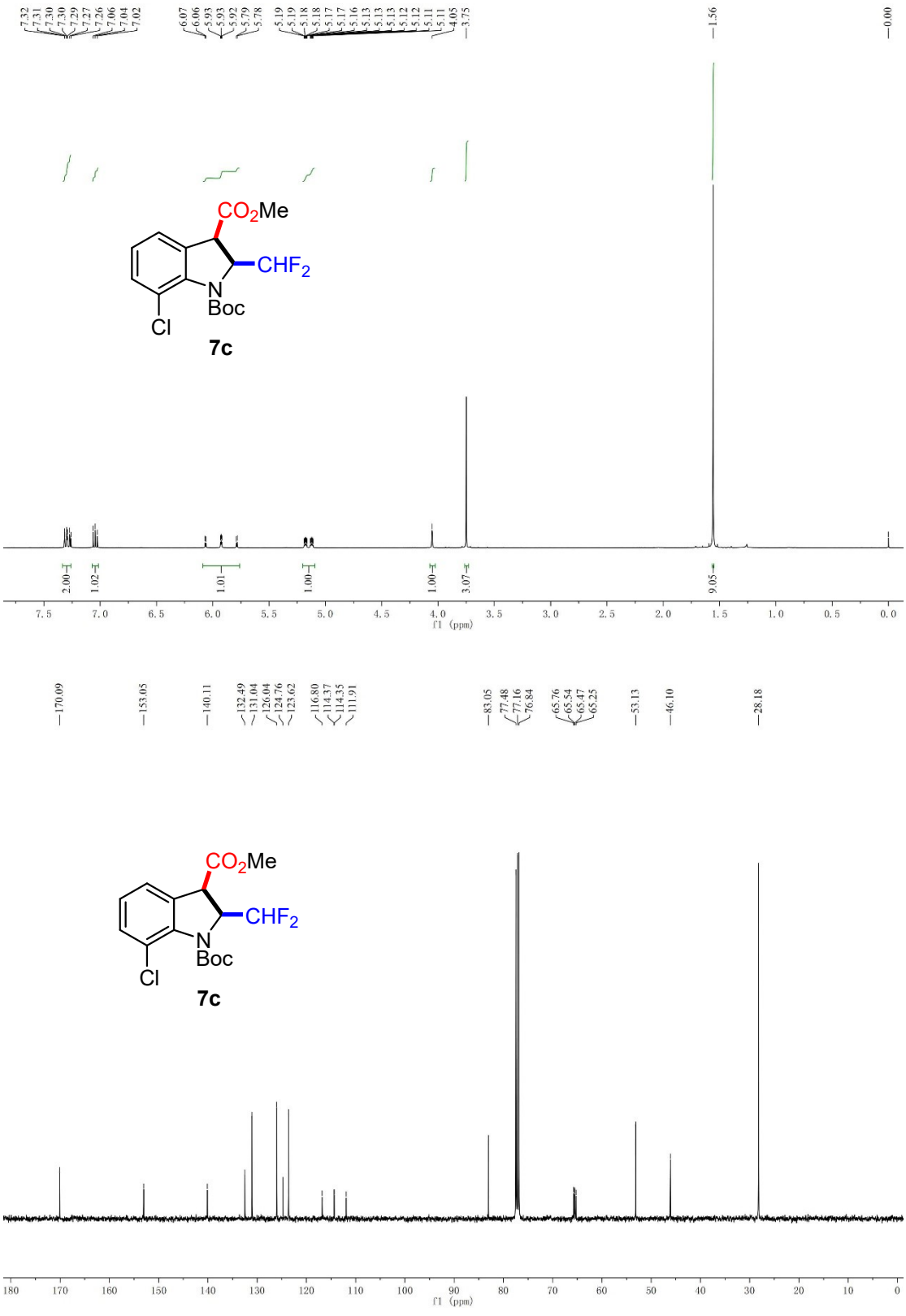




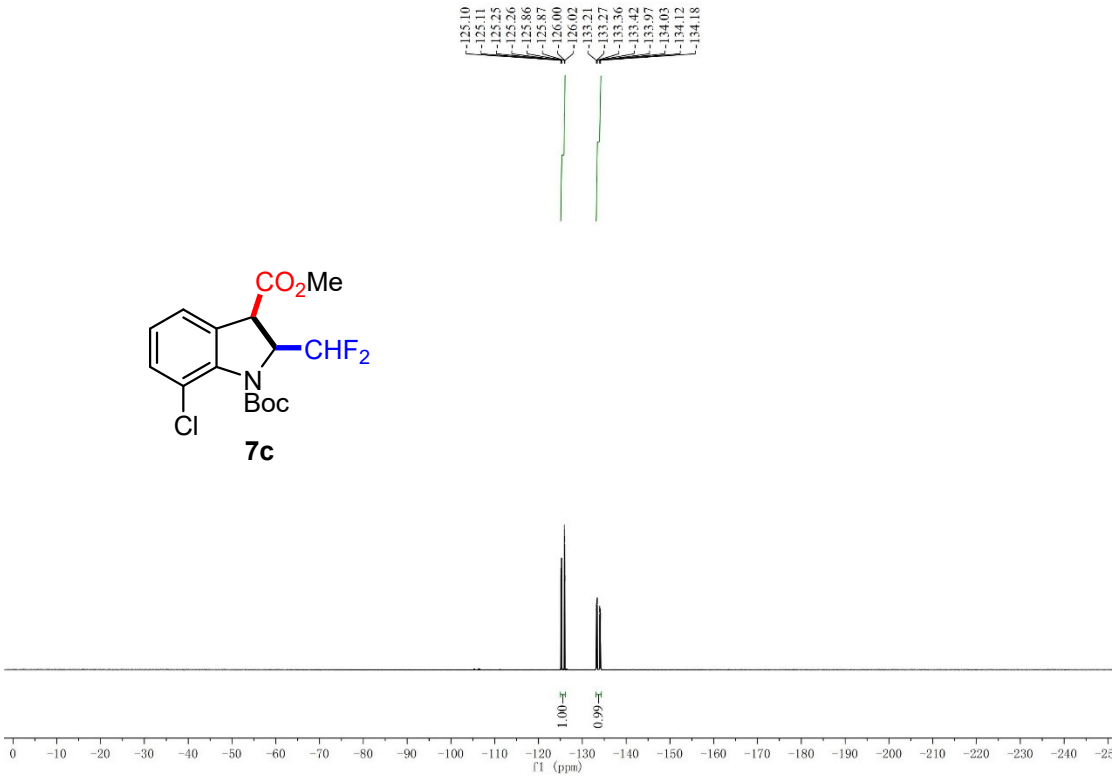
^{1}H NMR and ^{13}C NMR spectrum of **7b**



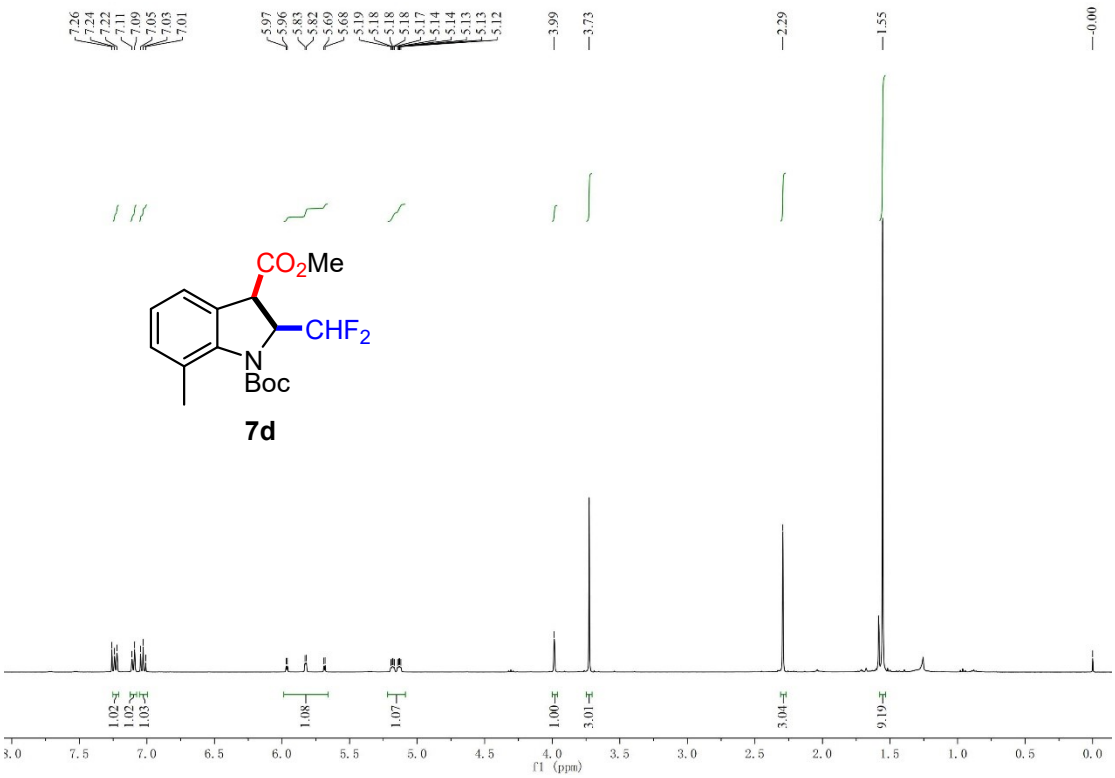
^{19}F NMR spectrum of **7b**

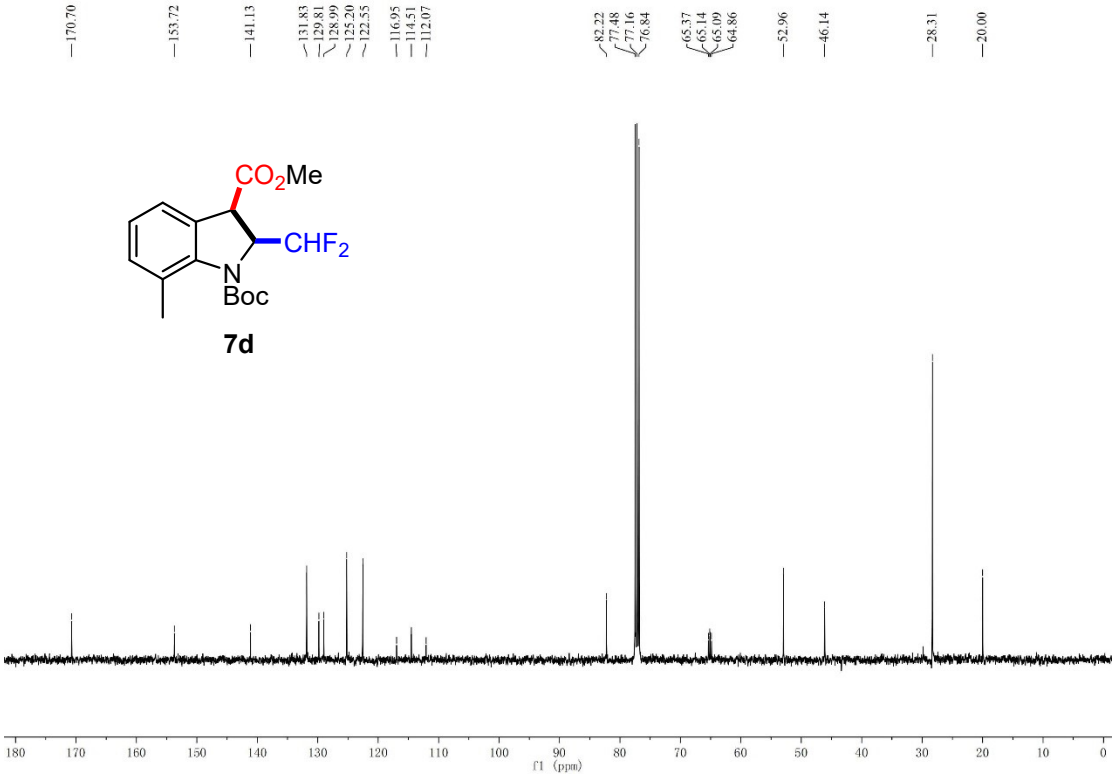


^{1}H NMR and ^{13}C NMR spectrum of **7c**

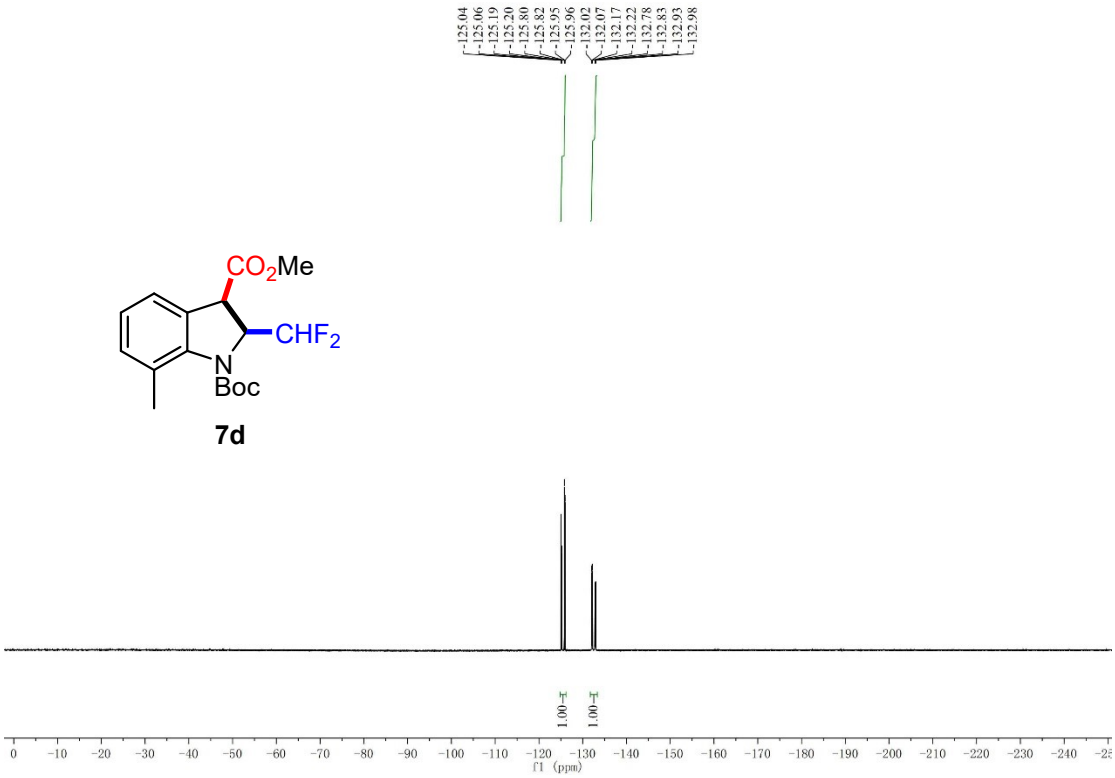


^{19}F NMR spectrum of **7c**

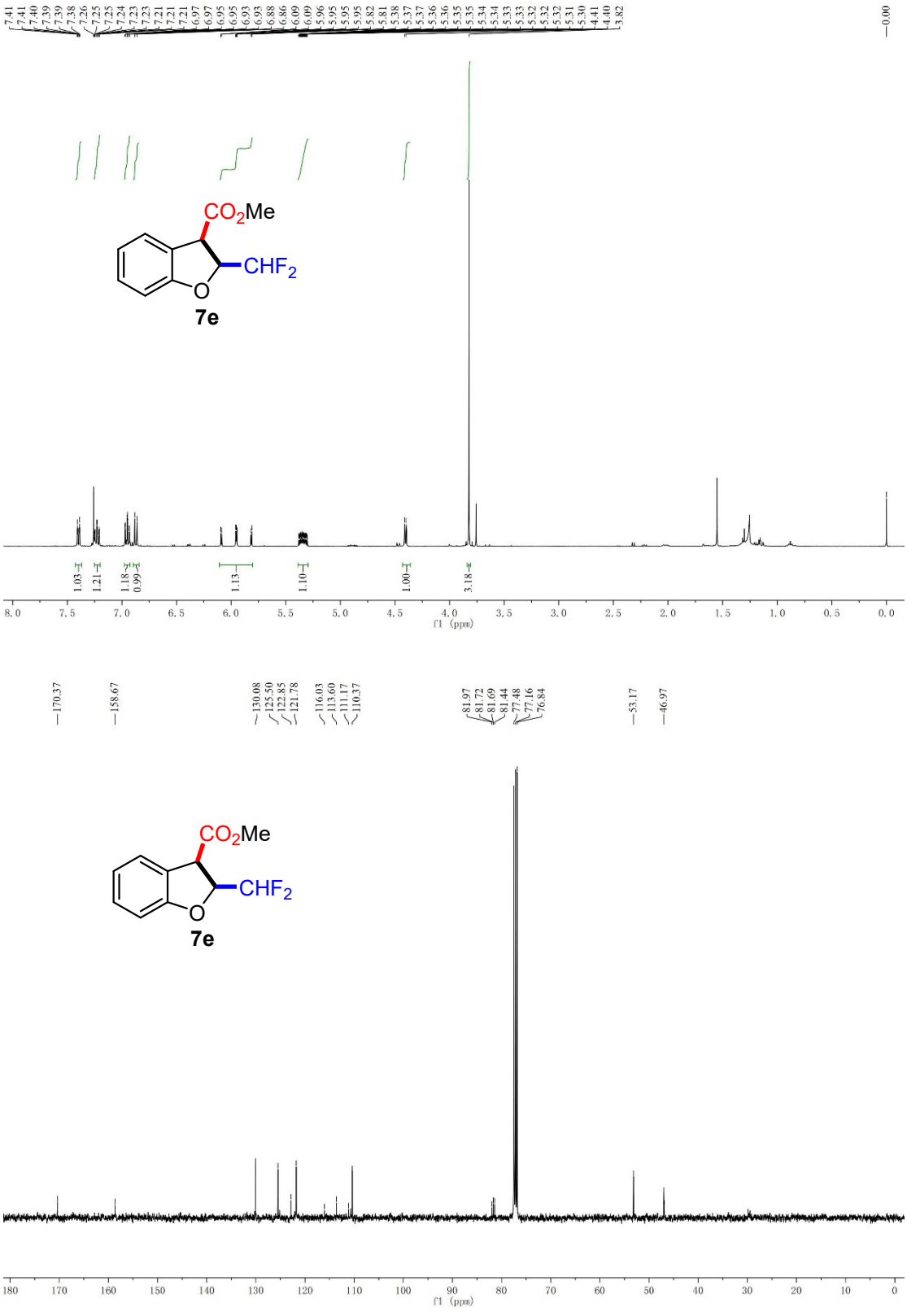




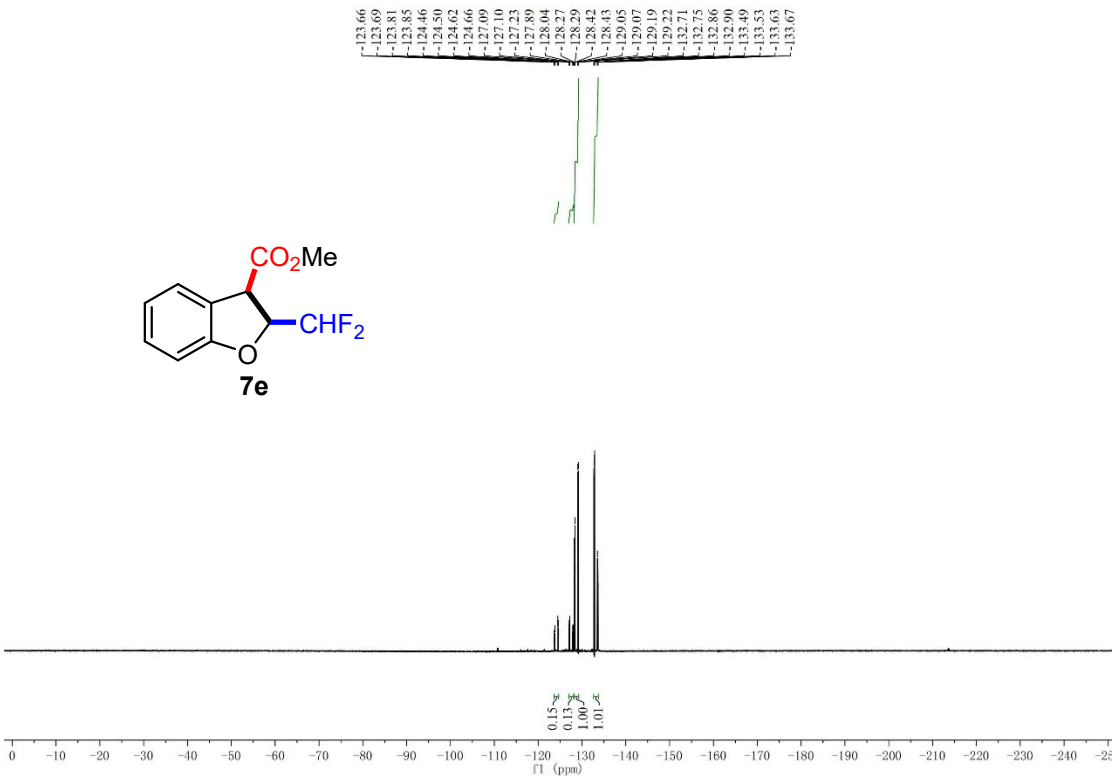
^{1}H NMR and ^{13}C NMR spectrum of **7d**



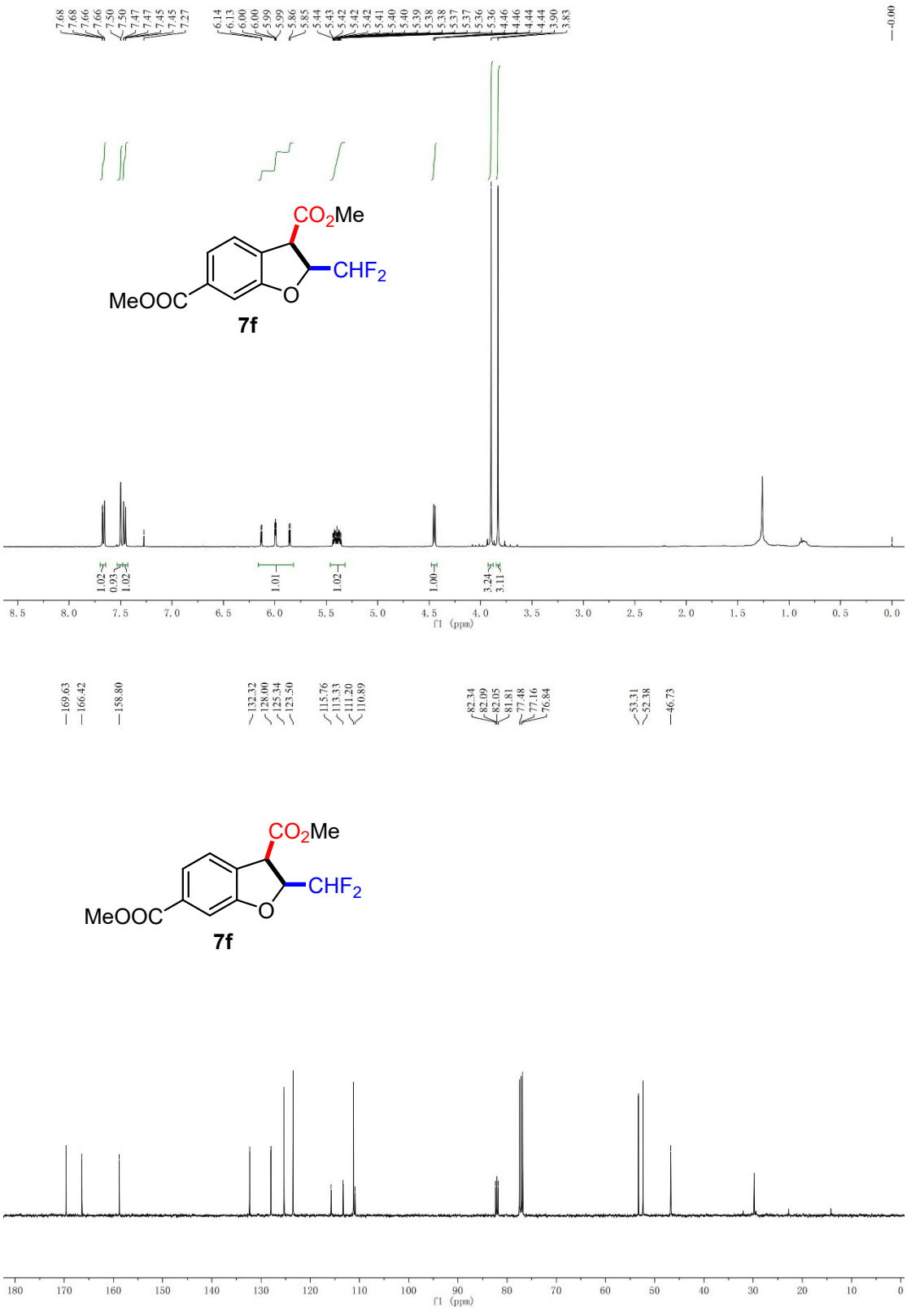
^{19}F NMR spectrum of **7d**



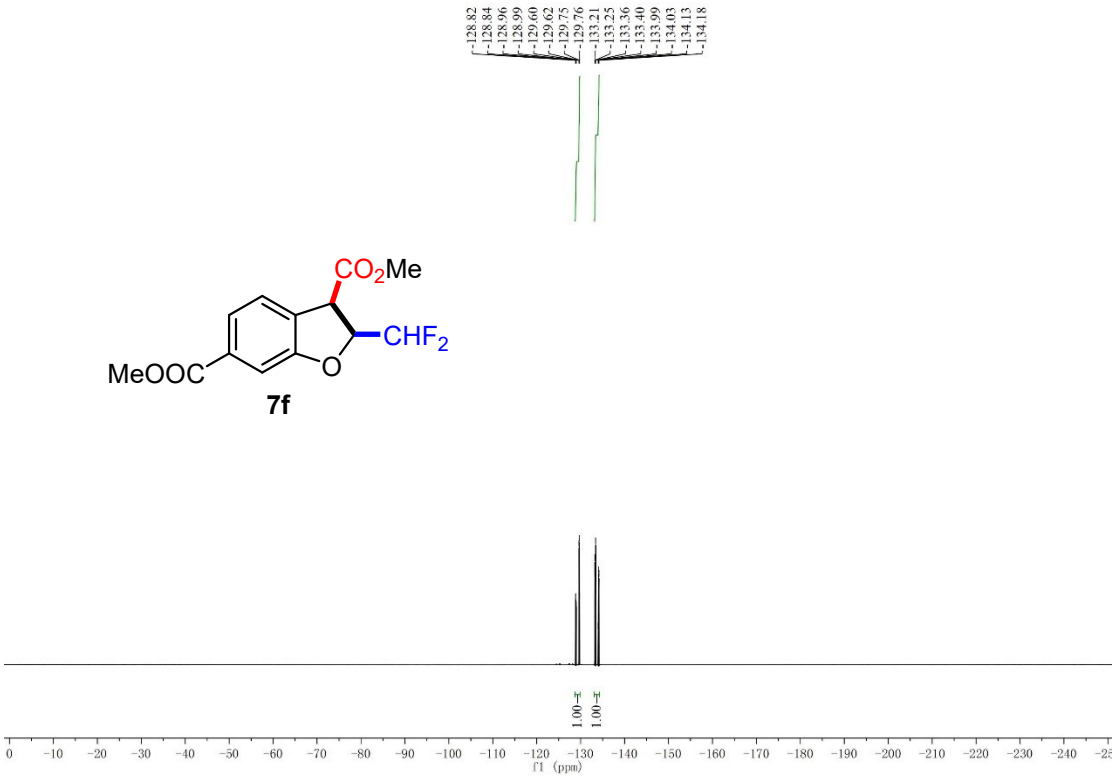
^{1}H NMR and ^{13}C NMR spectrum of **7e**



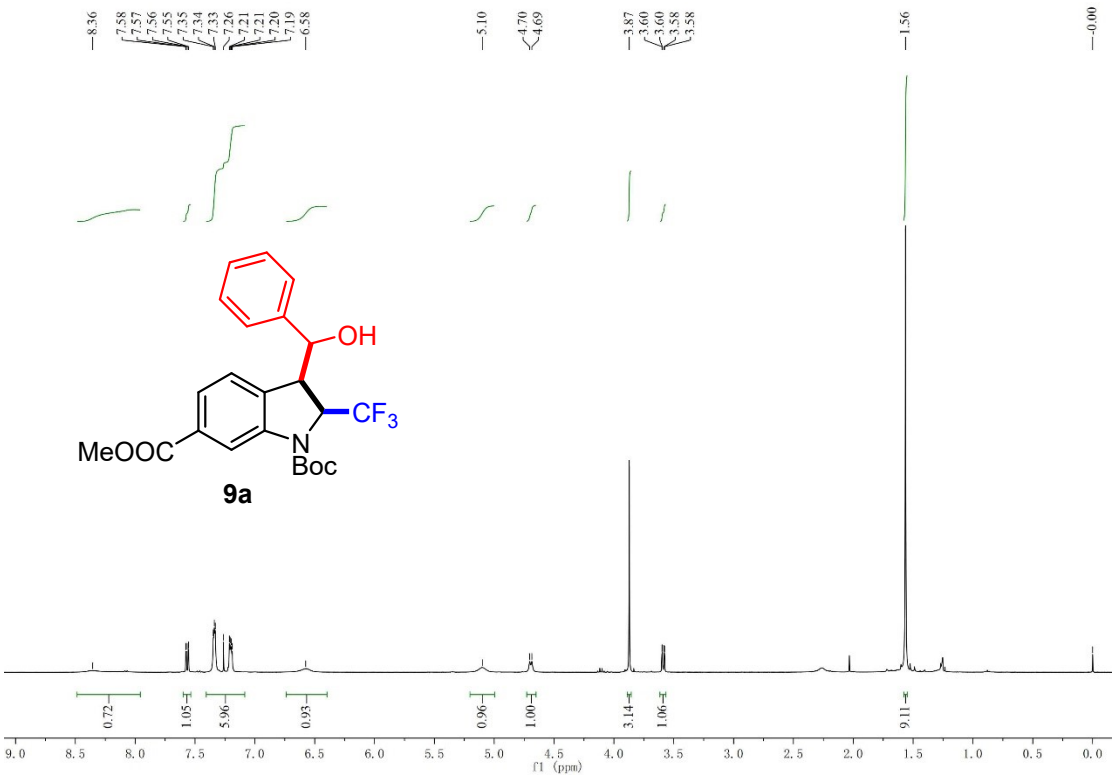
^{19}F NMR spectrum of **7e**

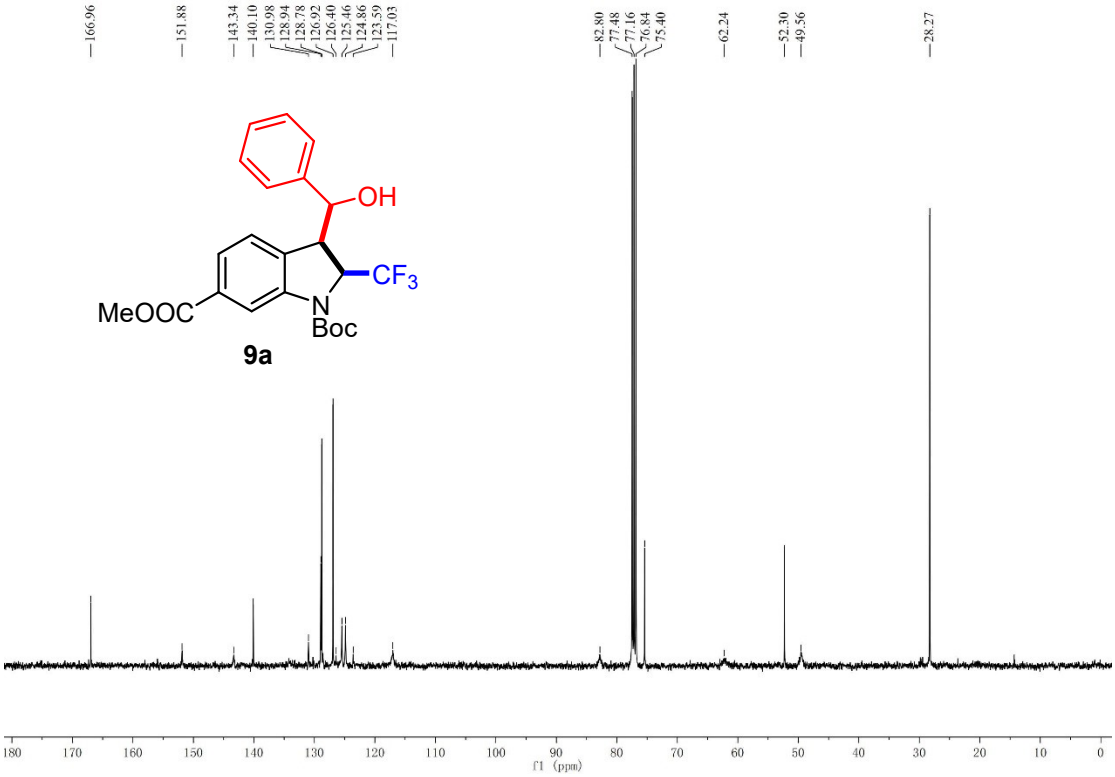


^{1}H NMR and ^{13}C NMR spectrum of **7f**

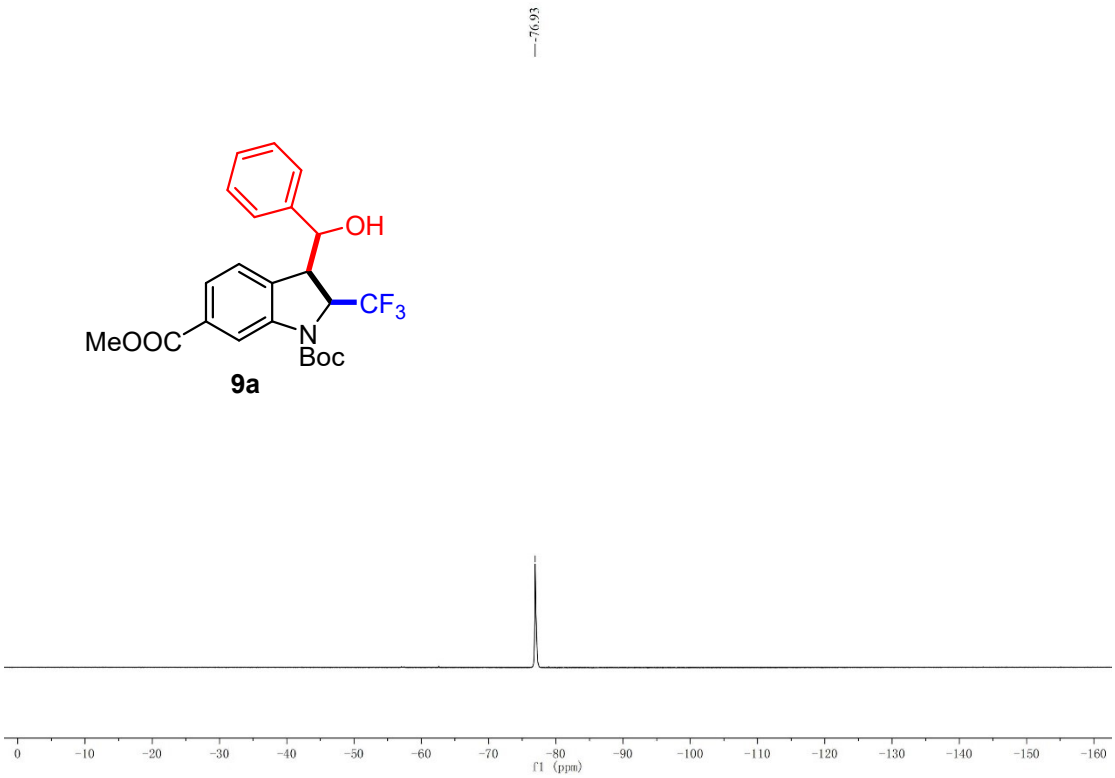


^{19}F NMR spectrum of **7f**

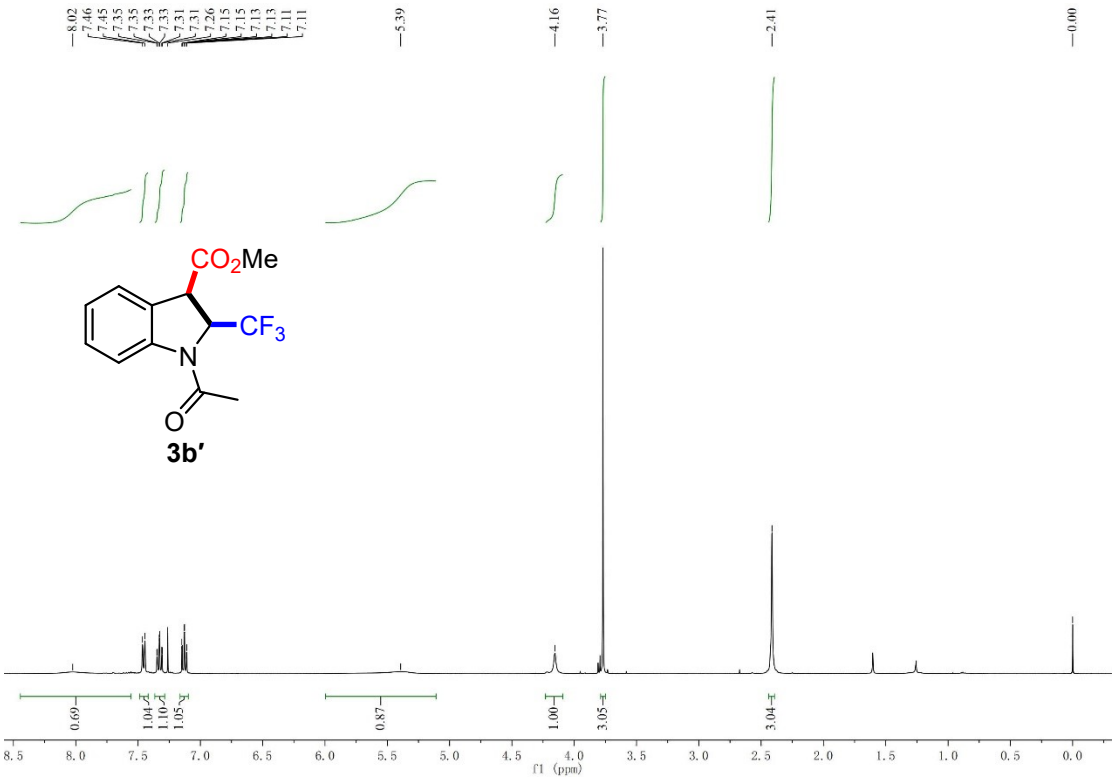


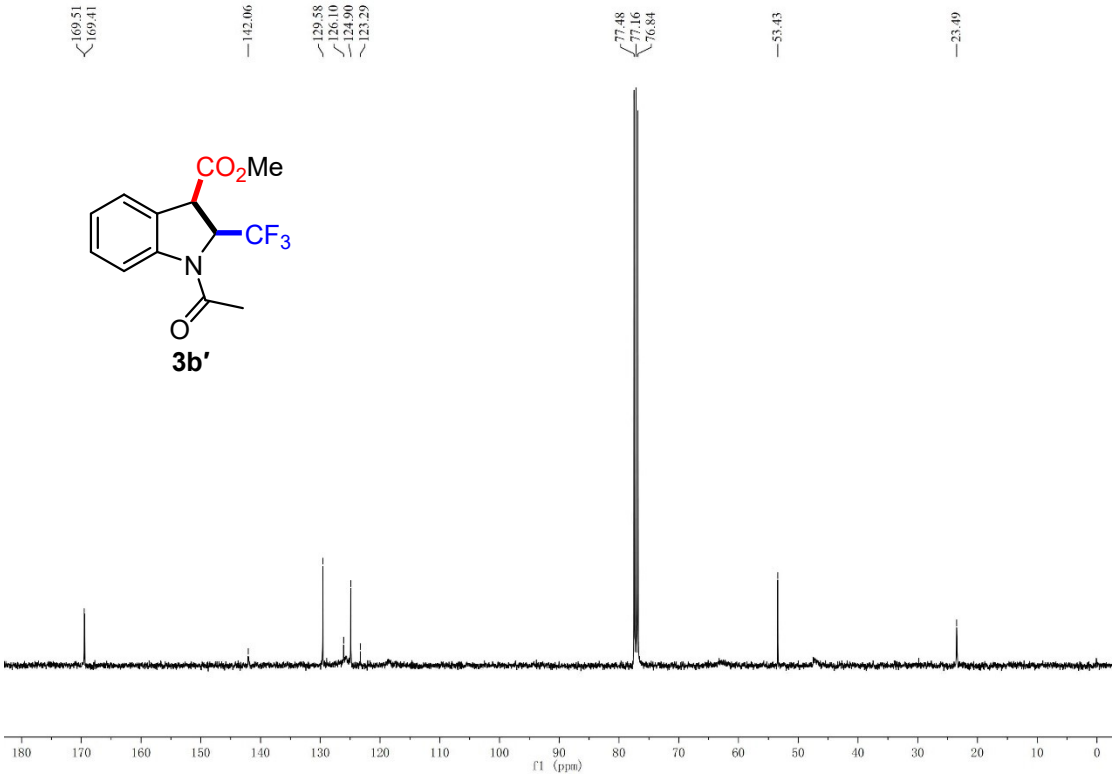


^{1}H NMR and ^{13}C NMR spectrum of **9a**

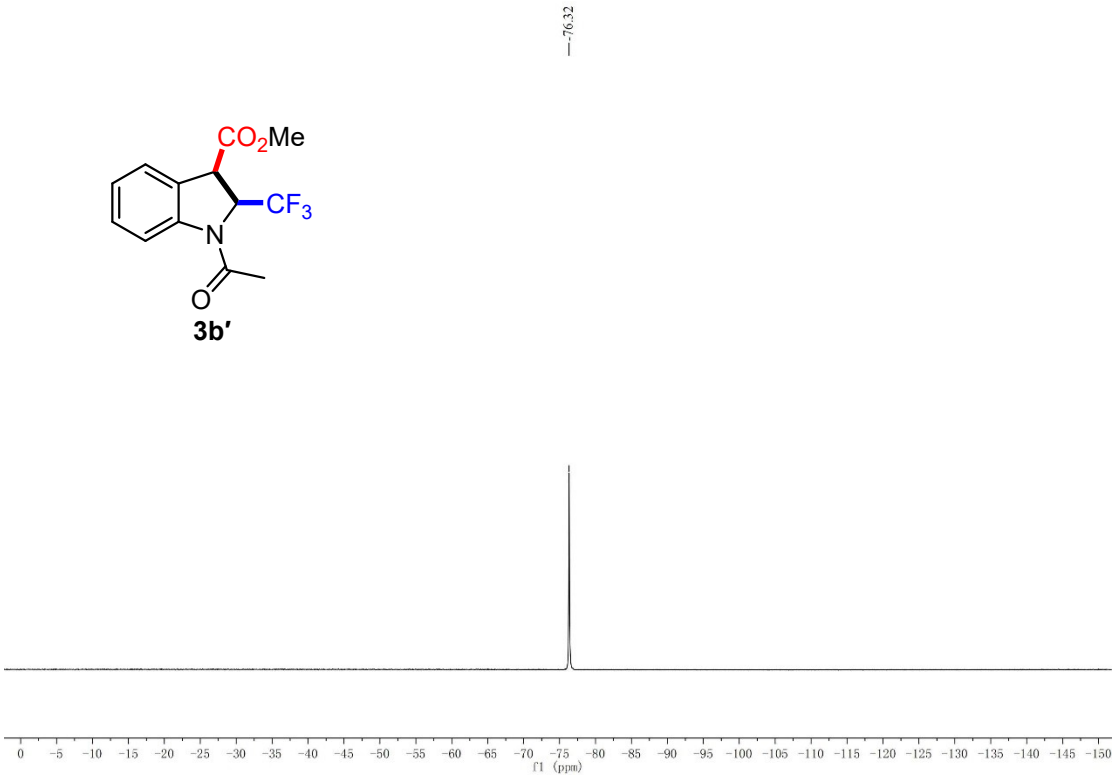


^{19}F NMR spectrum of **9a**





^{1}H NMR and ^{13}C NMR spectrum of **3b′**



^{19}F NMR spectrum of **3b′**

8. References

1 A. Kondoh, R. Ojima and M. Terada, *Org. Lett.*, 2021**, 23**, 7894-7899.

2 W.-J. Zhou, Z.-H. Wang, L.-L. Liao, Y.-X. Jiang, K.-G. Cao, T. Ju, Y. Li, G.-M. Cao and D.-G. Yu, *Nat. Commun.*, 2020, **11**, 3263.