Supporting Information

Photoredox Trifluoromethylation of Isocyanides to Access 2-Trifluoromethylated Quinolines and Indoles

Jin Wang,*† Yaohui Liu,† Jinhai Xu, Peiyuan Li, Xiaoxi Xu, Shuo Zhang, Jie Yang, and Xianxiu Xu*

College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan, 250014, P. R. China.

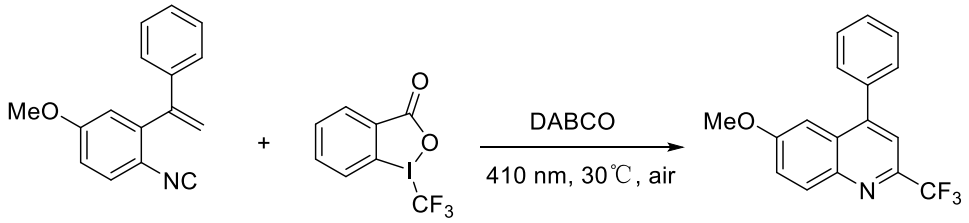
Table of Contents

I. General information

All reagents were commercially available and used without further purification, unless otherwise indicated. The *ortho*-vinylphenylisocyanides **1** and **4** were synthesized based on reported literature (*Org. Chem. Front.* **2022**, *9*, 6484; *Chem. Commun.*, **2023**, *59*, 14595-14598). Chromatography was carried out on flash silica gel (300−400 mesh). All reactions were monitored by TLC, performed on glass plates with precoated silica gel 60 (F254). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a 400 MHz Bruker instrument, with TMS as the internal standard. All chemical shifts are reported in ppm scale. High-resolution mass spectra (HRMS) were acquired using a Bruker microTOF II focusing spectrometer (ESI). UV-Vis analyses were conducted on a SHIMADZU UV-2700 220V, CH Spectrophotometer using a 1.0 cm path length quartz cuvette. The photochemical reaction was performed in the RLH-18CU 8-position photoreaction system.

II. Optimization of reaction conditions for quinoline compounds

Table 1. Optimization of reaction solvent [a].



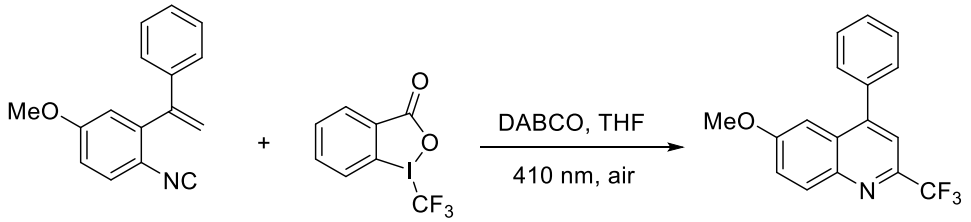
1a **2** **3a**

Entry	1a : 2	Solvent	Yield(%)[b]
1	1 : 3.0	THF	79
2	1 : 3.0	CH_3CN	70
3	1 : 3.0	DMF	68
4	1 : 3.0	1,4-dioxane	65
5	1 : 3.0	CH_3OH	46
6	1 : 3.0	DCE	53

7	1 : 3.0	DMSO	23
8[c]	1 : 3.0	Toluene	37
9	1 : 3.0	DMF+THF	52
10[d]	1 : 3.0	THF	54
11[e]	1 : 3.0	THF	76
12[f]	1 : 3.0	THF	76
13[g]	1 : 3.0	THF	76

a) Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DABCO (0.6 mmol) and solvent (2 mL) were reacted in a schlenk tube under 410 nm LED light at 30 ℃ for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) 10 h. d) Under N_2 atmosphere. e) Using Umemoto's reagent as CF_3 reagent. f) Using CF_3I as CF_3 reagent. g) Using CF_3SO_2Cl as CF_3 reagent.

Table 2. Optimization of reaction temperature [a].

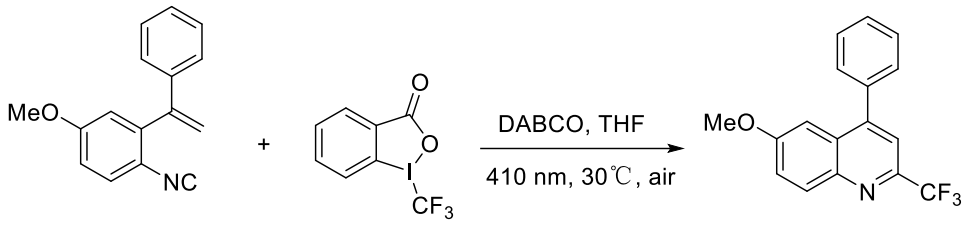


1a **2** **3a**

Entry	**1a** : **2**	Temperature (℃)	Yield (%)[b]
1	1 : 3.0	20	70
2	1 : 3.0	30	79
3	1 : 3.0	40	71
4	1 : 3.0	50	69
5	1 : 3.0	60	44

a) Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DABCO (0.6 mmol) and solvent (2 mL) were reacted in a schlenk tube under 410 nm LED light for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 3. Optimization of Togni's reagent amount [a].

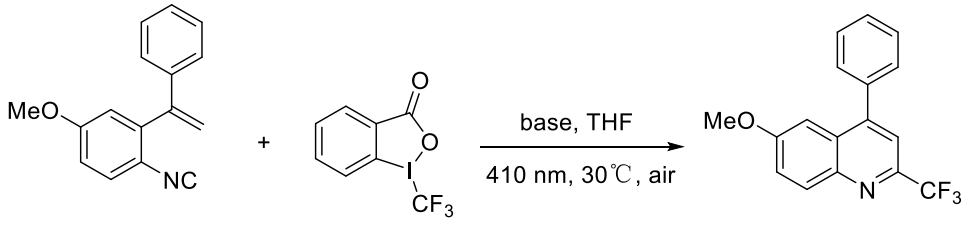


1a **2** **3a**

Entry	1a : 2	Temperature (℃)	Yield (%)[b]
1	1 : 1.0	30	40
2	1 : 1.5	30	41
3	1 : 2.0	30	58
4	1 : 3.0	30	79
5	1 : 4.0	30	70

a) Reaction conditions: **1a** (0.2 mmol), **2** (x mmol), DABCO (0.6 mmol) and solvent (2 mL) were reacted in a schlenk tube under 410 nm LED light at 30 ℃ for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 4. Optimization of base [a].



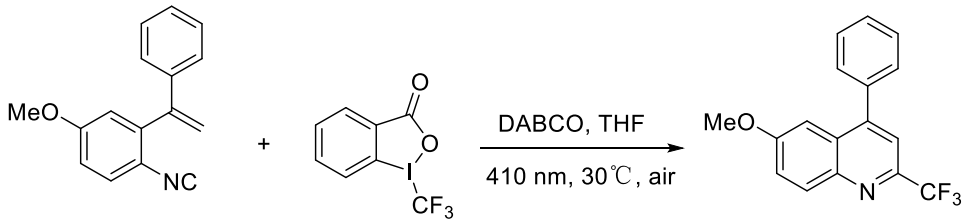
1a **2** **3a**

Entry	1a:2	Base	Yield (%)[b]
1[c]	1:3.0	K_2HPO_4	72
2[c]	1:3.0	*t*-BuOK	75
3[c]	1:3.0	DABCO	77
4	1:3.0	NaOH	44
5	1:3.0	Cs_2CO_3	45
6	1:3.0	NaH	42
7	1:3.0	DMAP	55
8	1:3.0	*t*-BuONa	46
9	1:3.0	*t*-BuOK	65
10	1:3.0	DBU	59
11	1:3.0	K_2HPO_4	72
12	1:3.0	Et_3N	39
13	1:3.0	NMM	64
14	1:3.0	Na_2CO_3	48
15	1:3.0	DABCO	79

16[d]	1:3.0	none	17

a) Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), base (0.6 mmol) and solvent (2 mL) were reacted in a schlenk tube under 410 nm LED light at 30 ℃ for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) Add 1 mol% photocatalyst Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6. d) Unreacted Togni's reagent **2** was filtered off upon work-up.

Table 5. Optimization of base amount [a].

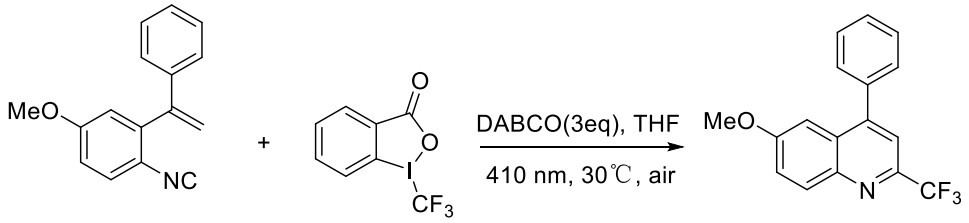


1a **2** **3a**

Entry	Base	Base amount	Yield(%)[b]
1	DABCO	1.5 eq	50
2	DABCO	2.0 eq	65
3	DABCO	3.0 eq	79
4	DABCO	4.0 eq	57

a) Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DABCO (x eq) and solvent (2 mL) were reacted in a schlenk tube under 410 nm LED light at 30 ℃ for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 6. Optimization of wavelength [a].



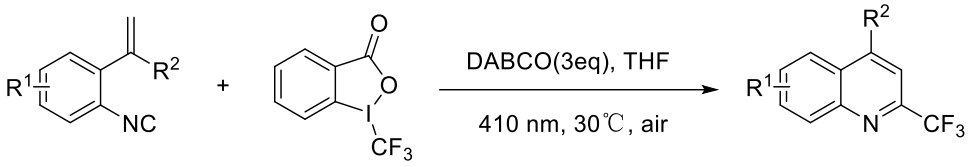
1a **2** **3a**

Entry	**1a**:**2**	Wavelength (nm)	Yield(%)[b]
1	1:3.0	365	61
2	1:3.0	390	59
3	1:3.0	410	79
4	1:3.0	430	56
5	1:3.0	450	65
6[c]	1:3.0	dark	0

a) Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DABCO (0.6 mmol) and solvent (2 mL) were reacted in a schlenk tube under different wavelength LED light at 30 ℃ for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) Unreacted Togni's reagent **2** was filtered off upon work-up.

III. Preparation and analytical data of quinoline 3

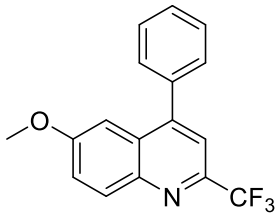
Typical synthetic procedure (with **3a** as an example)



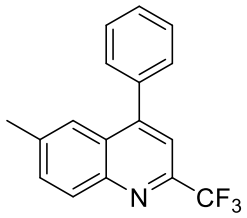
1 **2** **3**

1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1** (0.2 mmol, 47 mg), Togni's reagent **2a** (0.6 mmol, 3.0 eq, 190 mg) and DABCO (0.6 mmol, 3.0 eq, 47.1 mg) were dissolved in 2.0 mL THF in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 410 nm light source, and heated up at 30 ℃ for 3 h, until the complete consumption of isocyanide **1** as monitored by TLC. After this time, the mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 20mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=20:1) to give 6-methoxy-4-phenyl-2- (trifluoromethyl) quinoline **3a** (46.8 mg, 79 %).

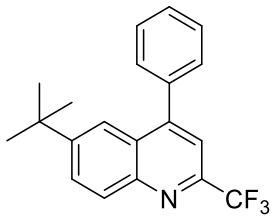
Analytical data of quinoline 3



6-methoxy-4-phenyl-2-(trifluoromethyl)quinoline (3a). Eluent: PE/EA (20:1), White solid, 46.8 mg, 79% yield, m.p.: 75 – 77 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.3 Hz, 1H), 7.62 (s, 1H), 7.58 – 7.49 (m, 5H), 7.44 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 149.0, 145.0 (q, *J* = 34.2 Hz), 143.8, 137.4, 131.8, 129.1, 128.9, 128.8, 128.6, 123.3, 121.8 (q, *J* = 273.0 Hz), 117.3 (q, *J* = 2.1 Hz), 103.3, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3NO^+$ 304.0944; found 304.0947.

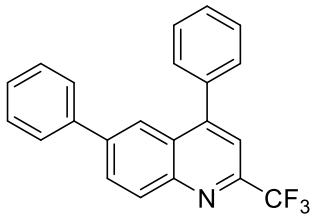


6-methyl-4-phenyl-2-(trifluoromethyl)quinolone (3b). Eluent: PE/EA (20:1), Colorless oil, 32.5 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.72 (s, 1H), 7.67 – 7.63 (m, 2H), 7.58 – 7.49 (m, 5H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 146.5, 146.4 (q, *J* = 34.6 Hz), 138.9, 137.4, 132.9, 130.2, 129.5, 128.9, 128.8, 127.4, 124.5, 123.2 (q, *J* = 274.3 Hz), 117.1 (q, *J* = 2.9 Hz), 22.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N^+$ 288.0995; found 288.1009.

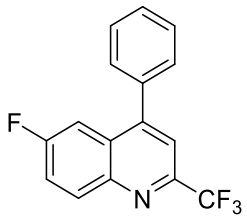


6-(tert-butyl)-4-phenyl-2-(trifluoromethyl)quinolone (3c). Eluent: PE/EA (20:1), White oil, 35.6 mg, 53% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.56 (s, 1H), 7.51 – 7.43 (m, 5H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 150.5, 146.9 (q, *J* = 34.1 Hz), 146.4, 137.4, 130.0, 129.6, 129.4, 128.9, 128.8, 127.0, 121.8 (q, *J* = 273.5 Hz), 120.7, 117.0 (q, *J* = 2.3 Hz), 35.3, 31.0.

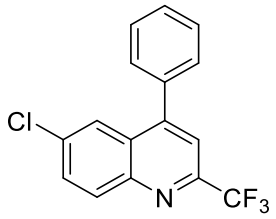
^{19}F NMR (376 MHz, $CDCl_3$) δ -67.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{19}F_3N^+$ 330.1464; found 330.1467.



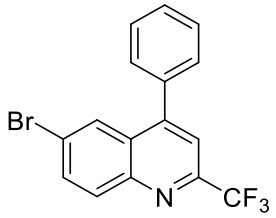
4,6-diphenyl-2-(trifluoromethyl)quinolone (3d). Eluent: PE/EA (20:1)， Bright yellow solid, 47.6 mg, 71% yield, m.p.: 171 – 173 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.71 (s, 1H), 7.65 – 7.55 (m, 7H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.40 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 147.3 (q, *J* = 34.2 Hz), 147.2, 141.4, 140.0, 137.1, 130.9, 130.4, 129.5, 129.1, 129.0, 128.9, 128.1, 127.6, 127.5, 123.4, 121.7 (q, *J* = 273.6 Hz), 117.4 (q, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{15}F_3N^+$ 350.1151; found 350.1140.



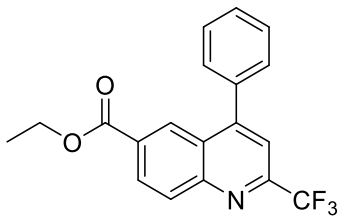
6-fluoro-4-phenyl-2-(trifluoromethyl)quinolone (3e). Eluent: PE/EA (20:1)， White solid, 32.0 mg, 55% yield, m.p.: 98 – 100 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 10.1, 5.5 Hz, 1H), 7.70 (s, 1H), 7.64 – 7.55 (m, 5H), 7.53 – 7.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 249.7 Hz), 150.4 (d, *J* = 5.9 Hz), 147.0 (q, *J* = 34.7 Hz), 144.9, 136.7, 133.2 (d, *J* = 9.4 Hz), 129.3, 129.0, 128.5 (d, *J* = 9.9 Hz), 121.5 (q, *J* = 273.7 Hz), 121.1 (d, *J* = 25.9 Hz), 117.6, 109.4 (d, *J* = 23.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.9, -67.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{10}F_4N^+$ 292.0744; found 292.0750.



6-chloro-4-phenyl-2-(trifluoromethyl)quinolone (3f). Eluent: PE/EA (20:1)， White solid, 38.0 mg, 62% yield, m.p.: 94 – 96 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 2.3 Hz, 1H), 7.76 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.70 (s, 1H), 7.63 – 7.47 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.2, 147.8 (q, *J* = 30.0 Hz), 146.2, 136.5, 134.9, 132.1, 131.6, 129.4, 129.3, 129.0, 128.1, 124.7, 121.5 (q, *J* = 273.8 Hz), 117.8 (q, *J* = 2.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{10}ClF_3N^+$ 308.0448; found 308.0443.

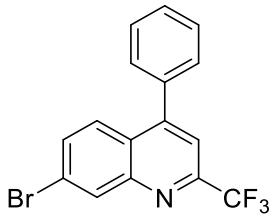


6-bromo-4-phenyl-2-(trifluoromethyl)quinolone (3g). Eluent: PE/EA (20:1)， White solid, 52.2 mg, 78% yield, m.p.: 81 – 83 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 2H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.69 (s, 1H), 7.62 – 7.47 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.1, 147.9 (q, *J* = 34.6 Hz), 146.4, 136.4, 134.2, 132.1, 129.4, 129.3, 129.0, 128.5, 128.1, 123.2, 121.5 (q, *J* = 273.8 Hz), 117.8 (q, *J* = 2.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{10}BrF_3N^+$ 351.9943; found 351.9932.

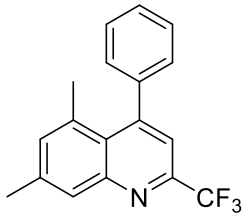


ethyl-4-phenyl-2-(trifluoromethyl)quinoline-6-carboxylate (3h). Eluent: PE/EA (20:1)， White solid, 47.4 mg, 67% yield, m.p.: 162 – 164 ℃. **^{1}H NMR** (400 MHz,

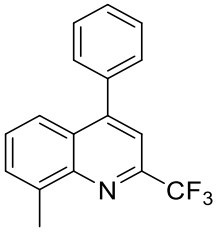
$CDCl_3$) δ 8.75 (d, *J* = 1.8 Hz, 1H), 8.41 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.34 – 8.32 (m, 1H), 7.74 (s, 1H), 7.64 – 7.50 (m, 5H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 152.5, 149.6, 149.3 (q, *J* = 34.6 Hz), 136.5, 130.8, 130.4, 130.0, 129.6, 129.5, 129.0, 128.9, 126.7, 121.4 (q, *J* = 274.0 Hz), 117.7 (q, *J* = 2.3 Hz), 61.6, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{15}F_3NO_2^+$ 346.1049; found 346.1030.



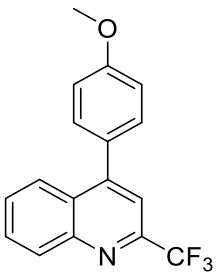
7-bromo-4-phenyl-2-(trifluoromethyl)quinolone (3i). Eluent: PE/EA (20:1)， White oil, 51.2 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.5 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7. 73 – 7.69 (m, 2H), 7.60 – 7.54 (m, 3H), 7.53 – 7.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 148.5 (q, *J* = 34.5 Hz), 148.4, 136.6, 132.7, 132.1, 129.4, 129.3, 129.0, 127.3, 126.1, 125.1, 121.4 (q, *J* = 273.9 Hz), 117.3 (q, *J* = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{10}BrF_3N^+$ 351.9943; found 351.9945.



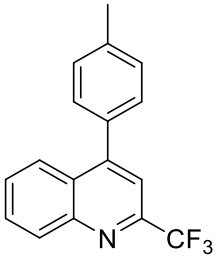
5,7-dimethyl-4-phenyl-2-(trifluoromethyl)quinolone (3j). Eluent: PE/EA (20:1)， White solid, 43.6 mg, 73% yield, m.p.: 123 – 125 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.49 – 7.43 (m, 4H), 7.34 – 7.31 (m, 2H), 7.24 (s, 1H), 2.52 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 149.3, 146.1 (q, *J* = 34.2 Hz), 141.6, 140.5, 135.3, 134.1, 128.6, 128.2, 128.1, 125.1, 121.6 (q, *J* = 273.7 Hz), 118.3 (q, *J* = 2.6 Hz), 24.2, 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{15}F_3N^+$ 302.1151; found 302.1161.



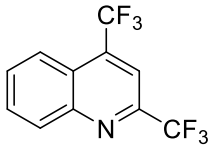
8-methyl-4-phenyl-2-(trifluoromethyl)quinolone (3k). Eluent: PE/EA (20:1)，White oil, 46.3 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.58 – 7.50 (m, 6H), 2.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 146.8, 146.2 (q, *J* = 34.2 Hz), 138.7, 137.7, 130.5, 129.5, 128.8, 128.7, 128.2, 127.4, 123.7, 121.8 (q, *J* = 273.5 Hz), 116.7 (q, *J* = 2.2 Hz), 18.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N^+$ 288.0995; found 288.0988.



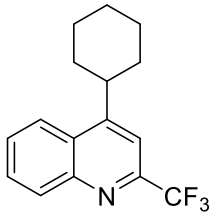
4-**(4-methoxyphenyl)-2-(trifluoromethyl)quinolone (3l).** Eluent: PE/EA (20:1)，White solid, 28.5 mg, 47% yield, m.p.: 85 – 87 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.77 (m, 1H), 7.69 – 7.54 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 150.6, 147.5 (q, *J* = 34.2 Hz), 130.9, 130.5, 130.5, 130.2, 130.2, 128.4, 125.9, 121.7 (q, *J* = 273.7 Hz), 116.9 (q, *J* = 2.3 Hz), 114.3, 113.7, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3NO^+$ 304.0944; found 304.0935.



4-**(p-tolyl)-2-(trifluoromethyl)quinolone (3m).** Eluent: PE/EA (20:1)，Colorless oil, 39.1 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.1 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.64 – 7.59 (m, 1H), 7. 46 – 7.41 (m, 2H), 7.39 – 7.36 (m, 2H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 147.8, 147.5 (q, *J* = 34.2 Hz), 139.1, 134.2, 130.5, 129.5, 129.4, 128.5, 127.5, 126.0, 121.7 (q, *J* = 273.7 Hz), 121.5, 116.9 (q, *J* = 2.3 Hz), 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3N^+$ 288.2995; found 288.0981.

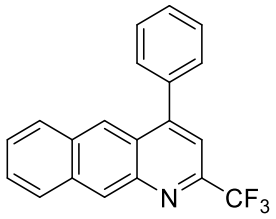


2,4-bis(trifluoromethyl)quinolone (3n). Eluent: PE/EA (20:1)，Bright yellow oil, 35.5 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 8.03 (s, 1H), 7.97 – 7.90 (m, 1H), 7.86 – 7.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 147.5 (q, *J* = 35.6 Hz), 136.5 (q, *J* = 32.5 Hz), 131.6, 131.1, 130.5, 124.2, 124.0 (q, *J* = 2.4 Hz), 123.8, 120.6 (q, *J* = 186.3 Hz), 114.2 – 114.0 (m). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.7, -61.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{11}H_{11}F_6N^+$ 266.0399; found 266.0410.



4-cyclohexyl-2-(trifluoromethyl)quinoline (3o). Eluent: PE/EA (20:1)，Yellow oil, 39.5 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.79 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.67 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.61 (s, 1H), 3.43 – 3.36 (m, 1H), 2.12 – 1.83 (m, 5H), 1.66 – 1.51 (m, 4H), 1.36 – 1.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 147.9 (q, *J* = 33.7 Hz), 147.4, 131.1, 130.0, 128.1, 127.5, 123.0, 121.8 (q, *J* = 273.7 Hz), 113.1 (q, *J* = 2.2 Hz), 39.2, 33.5,

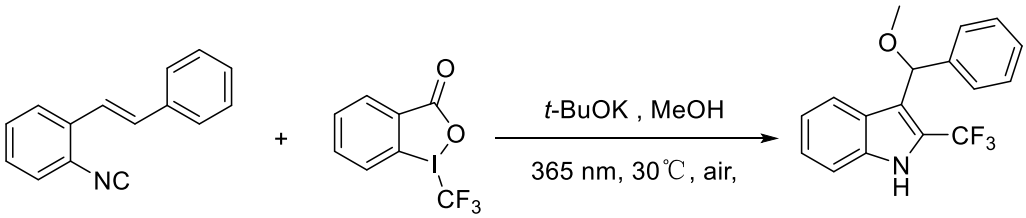
26.8, 26.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{17}F_3N^+$ 280.1308; found 280.1295.



4-phenyl-2-(trifluoromethyl)benzo[g]quinoline (3p). Eluent: PE/EA (20:1), Colorless oil, 35.4 mg, 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.02 (m, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.58 – 7.52 (m, 4H), 7.46 – 7.40 (m, 2H), 7.20 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 149.4, 146.1 (q, *J* = 34.5 Hz), 141.8, 133.5, 132.8, 129.5, 129.1, 128.8, 128.7, 128.5, 128.4, 128.1, 127.7, 126.0, 125.4, 121.7 (q, *J* = 273.3 Hz), 120.2 (q, *J* = 2.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{13}F_3N^+$ 324.0995; found 324.0986.

IV. Optimization of reaction conditions for indole compounds

Table 7. Optimization of Togni's reagent amount [a].

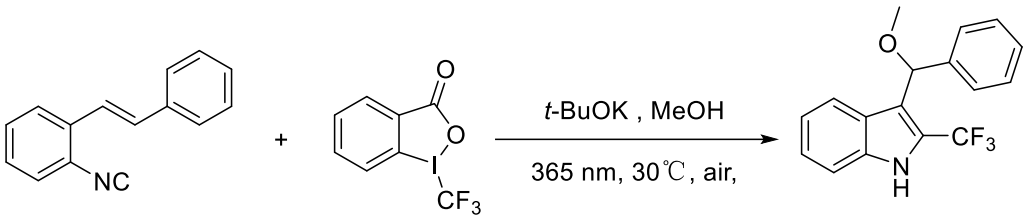


4a **2** **5a**

Entry	4a : 2	Yield(%)[b]
1	1 : 1.0	51
2	1 : 1.5	48
3	1 : 2.0	56
4	1 : 3.0	62
5	1 : 4.0	60

a) Reaction conditions: **4a** (0.2 mmol), **2** (x mmol), *t*-BuOK (0.3 mmol) and MeOH (2 mL) were reacted in a schlenk tube under 365 nm LED light at 30 ℃ for 1 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 8. Optimization of reaction temperature [a].

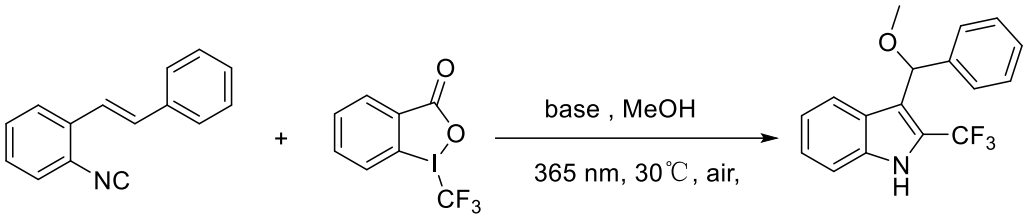


4a **2** **5a**

Entry	4a : 2a	Temperature (℃)	Yield (%)[b]
1	1 : 3.0	10	46
2	1 : 3.0	20	56
3	1 : 3.0	30	62
4	1 : 3.0	40	54
5	1 : 3.0	50	50

a) Reaction conditions: **4a** (0.2 mmol), **2** (0.6 mmol), *t*-BuOK (0.3 mmol) and MeOH (2 mL) were reacted in a schlenk tube under 365 nm LED light at different temprature for 1 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 9. Optimization of base [a].

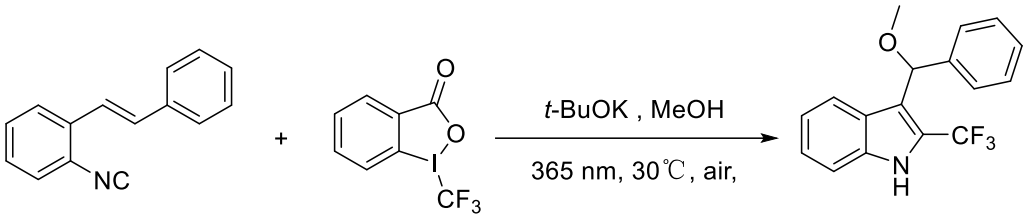


4a **2** **5a**

Entry	4a : 2	Base	Yield (%)[b]
1	1 : 3.0	*t*-BuOK	62
2	1 : 3.0	*t*-BuONa	51
3	1 : 3.0	*t*-BuOLi	46
4	1 : 3.0	Cs_2CO_3	40
5	1 : 3.0	Na_2CO_3	33
6	1 : 3.0	K_2HPO_4	45
7	1 : 3.0	DMAP	n.d.
8	1 : 3.0	DBU	n.d.
9	1 : 3.0	DABCO	21
10	1 : 3.0	NaH	40
11	1 : 3.0	NMM	33

a) Reaction conditions: **4a** (0.2 mmol), **2** (0.6 mmol), base (0.3 mmol) and MeOH (2 mL) were reacted in a schlenk tube under 365 nm LED light at 30 ℃ for 1 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 10. Optimization of base amount [a].



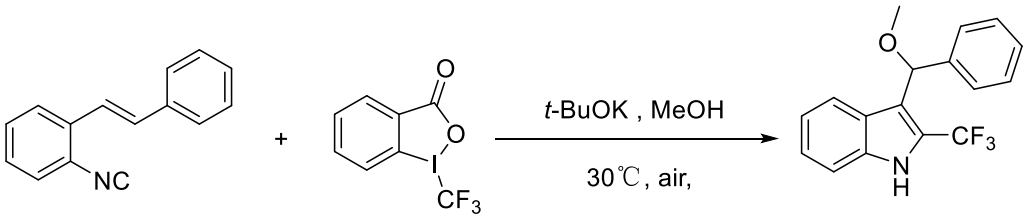
4a **2** **5a**

Entry	Base	Base amount	Yield (%)[b]
1	*t*-BuOK	1.5 eq	62
2	*t*-BuOK	2.0 eq	70
3	*t*-BuOK	3.0 eq	86(82[c])
4[d]	*t*-BuOK	3.0 eq	75
5[e]	*t*-BuOK	3.0 eq	n.d.
6[f]	*t*-BuOK	3.0 eq	<20

a) Reaction conditions: **4a** (0.2 mmol), **2** (0.6 mmol), *t*-BuOK (x mmol) and MeOH (2 mL) were reacted in a schlenk tube under 365 nm LED light at 30 ℃ for 1 h. b)

Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) Isolated yield. d) Under N_2. e) No light irradiation. f) Under natural light irradiation.

Table 11. Optimization of wavelength [a].



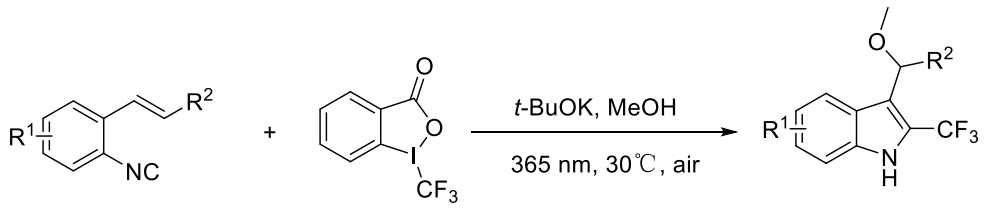
4a **2** **5a**

Entry	4a : 2	Wavelength (nm)	Yield(%)[b]
1	1 : 3.0	365	86(82[c])
2	1 : 3.0	390	61
3	1 : 3.0	410	40
4	1 : 3.0	430	55

a) Reaction conditions: **4a** (0.2 mmol), **2** (0.6 mmol), *t*-BuOK (0.6 mmol) and MeOH (2 mL) were reacted in a schlenk tube under different wavelength LED light at 30 ℃ for 1 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) Isolated yield.

V. Preparation and analytical data of indole 5

Typical synthetic procedure (with **5a** as an example)

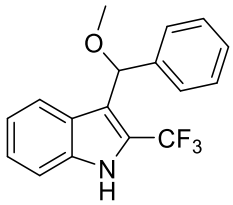


4 **2** **5**

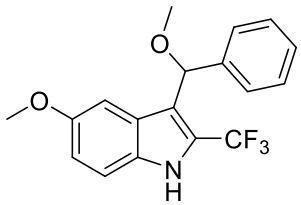
(*E*)-1-isocyano-2-styrylbenzene **4** (0.2 mmol, 41.1 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and *t*-BuOK (0.6 mmol, 3.0 eq, 73.2 mg) were dissolved in 2.0 mL CH_3OH in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 360 nm light source, and heated up at 30 ℃ for

1 h, until the complete consumption of isocyanide **4** as monitored by TLC. After this time, the mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 20mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=10:1) to give 3-(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole **5a** (40.1 mg, 82 %).

Analytical data of indole 5

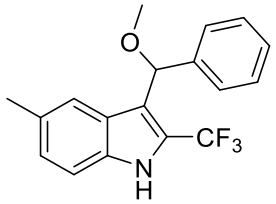


3-**(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole (5a).** Eluent: PE/EA (10:1)，White solid, 40.4 mg, 82% yield, m.p.: 105 – 107 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (br.s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.17 (m, 5H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.81 (s, 1H), 3.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 135.4, 128.2, 127.2, 126.4, 125.5, 124.9, 123.0 (q, *J* = 36.6 Hz), 122.9, 121.8 (q, *J* = 267.8 Hz), 121.0, 117.9 (q, *J* = 3.0 Hz), 111.6, 77.5, 56.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{15}F_3NO^+$ 306.1100; found 306.1084.

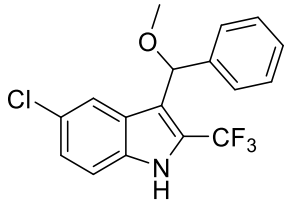


5-methoxy-3-(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole (5b). Eluent: PE/EA (10:1)，White oil, 39.2 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (br.s, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.13 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 5.78 (s, 1H), 3.73 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 141.2, 130.5, 128.2, 127.3, 126.4, 126.0, 123.1 (q, *J*

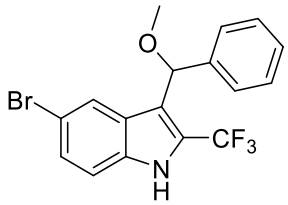
= 36.1 Hz), 121.7 (q, *J* = 267.4 Hz), 117.3 (q, *J* = 2.3 Hz), 116.1, 112.4, 103.4, 77.4, 56.9, 55.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO_2^+$ 336.1206; found 336.1208.



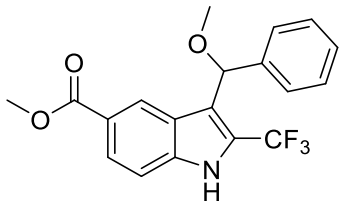
4-**(methoxy(phenyl)methyl)-5-methyl-2-(trifluoromethyl)-1H-indole (5c).** Eluent: PE/EA (10:1)，White solid, 26.4 mg, 54% yield, m.p.: 100 – 102 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (br.s, 1H), 7.53 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.18 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 1H), 5.78 (s, 1H), 3.40 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 133.8, 130.4, 128.2, 127.2, 126.8, 126.4, 125.7, 123.1 (q, *J* = 36.7 Hz), 122.2, 121.8 (q, *J* = 267.6 Hz), 117.2 (q, *J* = 2.7 Hz), 111.3, 77.5, 57.0, 21.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO^+$ 320.1257; found 320.1268.



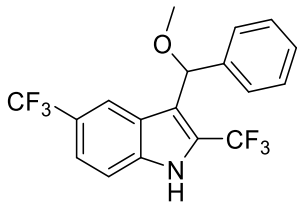
5-**chloro-3-(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole (5d).** Eluent: PE/EA (10:1)，White solid, 42.1 mg, 67% yield, m.p.: 121 – 123 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (br.s, 1H), 7.77 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 5.76 (s, 1H), 3.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.9, 133.7, 128.4, 127.5, 126.8, 126.4, 126.3, 125.6, 124.1 (q, *J* = 37.2 Hz), 122.3, 121.4 (q, *J* = 267.8 Hz), 117.8 (q, *J* = 2.8 Hz), 112.8, 77.4, 57.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{14}ClF_3NO^+$ 340.0711; found 340.0704.



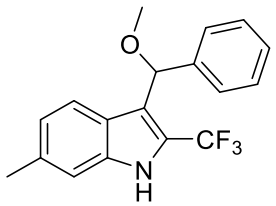
5-bromo-3-(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole (5e). Eluent: PE/EA (10:1)，White solid, 25.0 mg, 33% yield, m.p.: 189 – 191 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (br.s, 1H), 7.95 (s, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.29 (m, 4H), 7.24 (d, *J* = 4.0 Hz, 1H), 5.77 (s, 1H), 3.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.8, 134.0, 128.4, 128.1, 127.5, 127.0, 126.3, 125.3, 123.9 (q, *J* = 37.2 Hz), 121.4 (q, *J* = 268.0 Hz), 117.6 (q, *J* = 2.8 Hz), 114.4, 113.2, 77.4, 57.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{14}BrF_3NO^+$ 384.0205; found 384.0210.



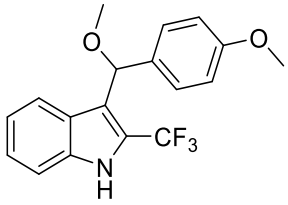
methyl-3-(methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole-5-carboxylate (5f). Eluent: PE/EA (10:1)，White solid, 40.4 mg, 62% yield, m.p.: 191 – 193 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (br.s, 1H), 8.59 (s, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.82 (s, 1H), 3.90 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.54, 140.89, 137.86, 128.36, 127.49, 126.39, 126.12, 125.97, 125.05, 124.1 (q, *J* = 37.2 Hz), 123.38, 121.4 (q, *J* = 267.8 Hz), 119.5 (q, *J* = 2.8 Hz), 111.53, 77.60, 57.12, 52.01. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{17}F_3NO_3^+$ 364.1155; found 364.1140.



3-(methoxy(phenyl)methyl)-2,5-bis(trifluoromethyl)-1H-indole (5g). Eluent: PE/EA (10:1)，White solid, 49.1 mg, 65% yield, m.p.: 114 – 116 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (br.s, 1H), 8.12 (s, 1H), 7.55 – 7.43 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 5.81 (s, 1H), 3.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.71, 136.66, 135.13, 128.5 (q, *J* = 5.1 Hz), 128.4, 127.6, 126.3, 124.4 (q, *J* = 37.3 Hz), 123.6 (q, *J* = 32.2 Hz), 121.7 (q, *J* = 3.4 Hz), 121.4 (q, *J* = 267.9 Hz), 120.9 (q, *J* = 4.6 Hz), 119.2 (q, *J* = 2.7 Hz), 112.2, 77.5, 57.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.8, -57.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{14}F_6NO^+$ 374.0974; found 374.0979.

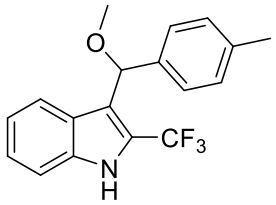


3-(methoxy(phenyl)methyl)-6-methyl-2-(trifluoromethyl)-1H-indole (5h). Eluent: PE/EA (10:1)，White solid, 39.1 mg, 63% yield, m.p.: 102 – 104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (br.s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.17 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.79 (s, 1H), 3.41 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.38, 135.93, 135.12, 128.18, 127.19, 126.36, 123.32, 123.05, 122.4 (q, *J* = 37.0 Hz), 122.49, 121.9 (q, *J* = 267.4 Hz), 117.9 (q, *J* = 2.7 Hz), 111.30, 77.42, 56.89, 21.76. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.9. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO^+$ 320.1257; found 320.1244.

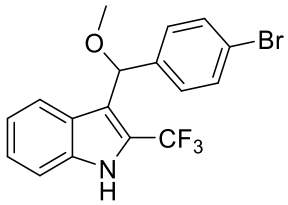


3-**(methoxy(4-methoxyphenyl)methyl)-2-(trifluoromethyl)-1H-indole (5i).** Eluent: PE/EA (10:1)，White solid, 45.4 mg, 66% yield, m.p.: 141 – 143 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (br.s, 1H), 7.81 (d, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 8.3, 3.2 Hz, 3H),

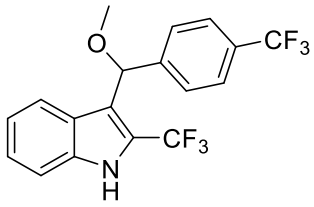
7.29 (t, *J* = 7.1 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.77 (s, 1H), 3.77 (s, 3H), 3.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 135.4, 133.6, 127.7, 125.5, 124.9, 123.0, 122.8 (q, *J* = 37.3 Hz), 121.8 (q, *J* = 267.6 Hz), 121.0, 118.2 (q, *J* = 2.7 Hz), 113.6, 111.6, 77.2, 56.9, 55.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO_2^+$ 336.1206; found 336.1201.



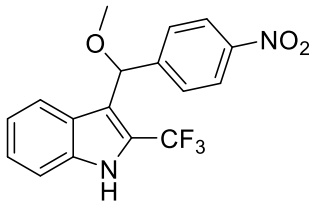
3-**(methoxy(p-tolyl)methyl)-2-(trifluoromethyl)-1H-indole (5j).** Eluent: PE/EA (10:1)，White solid, 43.3 mg, 67% yield, m.p.: 141 – 143 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (br.s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.08 (m, 3H), 5.78 (s, 1H), 3.40 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.3, 136.9, 135.4, 128.9, 126.3, 125.5, 124.9, 123.0, 122.9 (q, *J* = 37.3 Hz), 121.8 (q, *J* = 267.8 Hz), 121.0, 118.2 (q, *J* = 2.8 Hz), 111.6, 77.5, 56.9, 21.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{17}F_3NO^+$ 320.1275; found 320.1267.



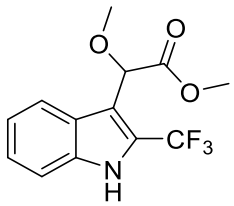
3-((4-bromophenyl)(methoxy)methyl)-2-(trifluoromethyl)-1H-indole (5k). Eluent: PE/EA (10:1)，White oil, 43.2 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (br.s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 9.3 Hz, 3H), 7.35 – 7.27 (m, 3H), 7.12 – 7.03 (m, 1H), 5.74 (s, 1H), 3.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.41, 135.44, 131.28, 128.09, 125.24, 125.10, 123.2 (q, *J* = 37.1 Hz), 122.65, 121.7 (q, *J* = 268.0 Hz), 121.20, 121.13, 117.2 (q, *J* = 2.8 Hz), 111.72, 76.68, 56.89. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{14}BrF_3NO^+$ 384.0205; found 384.0195.



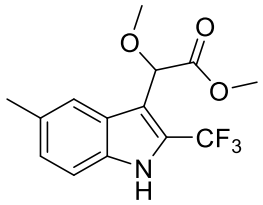
3-(methoxy(4-(trifluoromethyl)phenyl)methyl)-2-(trifluoromethyl)-1H-indole (5l). Eluent: PE/EA (10:1)，Bright yellow oil, 42.1 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (br.s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58 (q, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.85 (s, 1H), 3.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 135.5, 129.4 (q, *J* = 32.1 Hz), 126.6, 125.2, 125.2, 125.1, 124.2 (q, *J* = 270.3 Hz), 123.4 (q, *J* = 37.0 Hz), 122.5, 121.7 (q, *J* = 267.6 Hz), 121.3, 116.9 (q, *J* = 2.5 Hz), 111.8, 77.2, 56.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5, -56.9. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{14}F_6NO^+$ 374.0974; found 374.0977.



4-**(methoxy(4-nitrophenyl)methyl)-2-(trifluoromethyl)-1H-indole (5m).** Eluent: PE/EA (10:1)，Bright yellow oil, 46.1 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (br.s, 1H), 8.22 – 8.10 (m, 2H), 8.66 – 8.60 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.15 – 6.99 (m, 1H), 5.87 (s, 1H), 3.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.70, 147.04, 135.47, 127.07, 125.31, 125.01, 123.7 (q, *J* = 37.1 Hz), 123.45, 122.16, 121.7 (q, *J* = 267.7 Hz), 121.40, 116.1 (q, *J* = 2.8 Hz), 111.93, 76.17, 56.90. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{14}F_3N_2O_3^+$ 351.0951; found 351.0947.

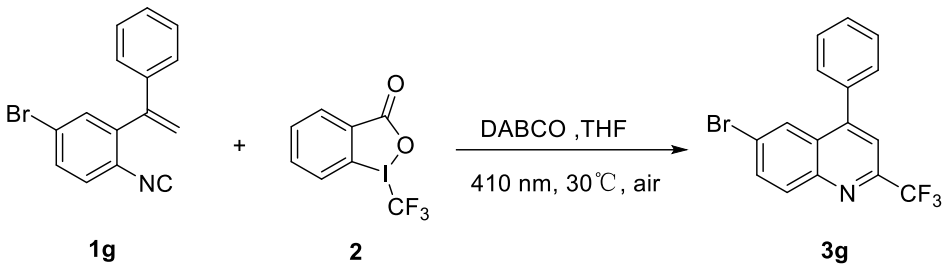


methyl-2-methoxy-2-(2-(trifluoromethyl)-1H-indol-3-yl)acetate (5n). Eluent: PE/EA (10:1)，White solid, 45.0 mg, 78% yield, m.p.: 130 – 132 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (br.s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.32 (s, 1H), 3.71 (s, 3H), 3.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 135.2, 125.4, 125.2, 124.1 (q, *J* = 37.3 Hz), 122.0, 121.6, 121.4 (q, *J* = 267.9 Hz), 112.1 (q, *J* = 2.8 Hz), 111.8, 74.4, 57.0, 52.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{13}H_{13}F_3NO_3^+$ 288.0842; found 288.0838.



methyl-2-methoxy-2-(5-methyl-2-(trifluoromethyl)-1H-indol-3-yl)acetate (5o). Eluent: PE/EA (10:1)，White solid, 42.1 mg, 70% yield, m.p.: 138 – 140 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (br.s, 1H), 7.70 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 5.26 (s, 1H), 3.71 (s, 3H), 3.39 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 133.5, 131.2, 127.2, 125.6, 124.0 (q, *J* = 37.2 Hz), 121.4 (q, *J* = 267.6 Hz), 121.3, 111.8 (q, *J* = 2.6 Hz), 111.4, 74.4, 57.0, 52.4, 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{14}H_{15}F_3NO_3^+$ 302.0999; found 302.0989.

VI. Scale-up experiment

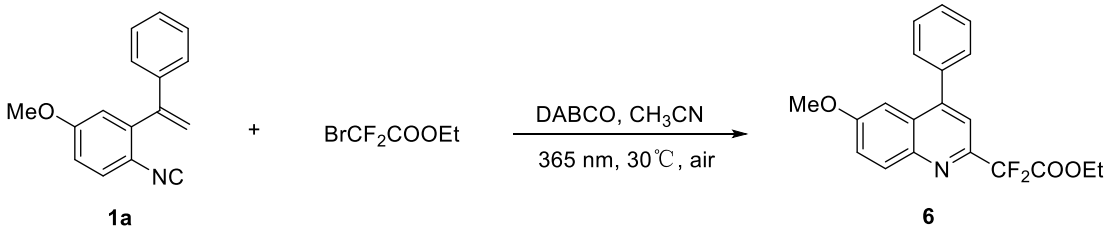


1g **2** **3g**

In a 100 mL round bottom flask equipped was added 4-bromo-1-isocyano-2-(1-phenylvinyl)benzene (5 mmol, 1.4108 g) **1g**, Togni's reagent **2** (15 mmol, 3.0 eq, 4.7402 g), DABCO (15 mmol, 3.0 eq, 1.6825 g) and THF (5 mL). The reaction (open to air) was placed in a metal bath, irradiated with a 410 nm light source and heated up at 30 ℃ for 3 h, until the complete consumption of isocyanide **1g** as monitored by TLC. After this time, the mixture was quenched with H_2O and extracted three times with CH_2Cl_2. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=20:1) to give 6-bromo-4-phenyl-2-(trifluoromethyl)quinolone **3g** (1.127 g, 64 %).

VII. Synthetic utility of quinolines and indoles

Synthesis of quinoline 6

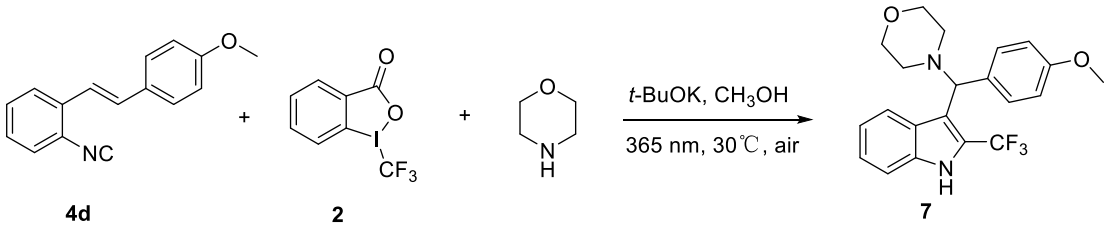


1a **6**

Ethyl 2,2-difluoro-2-(6-methoxy-4-phenylquinolin-2-yl)acetate (6): 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg) and ethyl 2-

bromo-2,2-difluoroacetate **2b** (0.6 mmol, 3.0 eq, 121.1 mg) were dissolved in 2.0 mL CH_3CN in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 365 nm light source, and heated at 30 ℃ for 2 h, until the complete consumption of isocyanide **1a** as monitored by TLC. After this time, the mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 20mL). The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=20:1) to give ethyl 2,2-difluoro-2-(6-methoxy-4-phenylquinolin-2-yl)acetate **6**. Yellow oil, 41.8 mg, 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.3 Hz, 1H), 7.68 (s, 1H), 7.60 – 7.48 (m, 5H), 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7 (t, *J* = 64.8 Hz), 159.1, 148.8, 148.7 (t, *J* = 56.3 Hz), 143.8, 137.8, 131.9, 129.3, 128.8, 128.7, 127.4 (t, *J* = 222.6 Hz), 122.8, 117.6 (t, *J* = 5.2 Hz), 112.8 (t, *J* = 500.5 Hz), 103.4, 63.2, 55.5, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{20}H_{18}F_2NO_3^+$ 358.1249; found 358.1206.

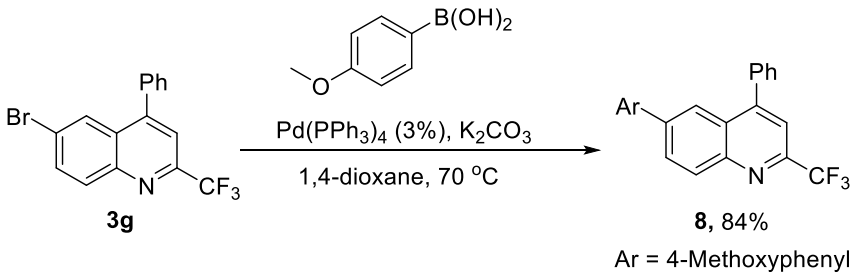
Synthesis of indole 7



5-**((4-methoxyphenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methyl)morpholine (7)**: (*E*)-1-isocyano-2-(4-methoxystyryl)benzene **4d** (0.2 mmol, 47.1 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg), *t*-BuOK (0.6 mmol, 3.0 eq, 73.2 mg) and morpholine (1.0 mL, 58 eq) were dissolved in 1.0 mL CH_3OH in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 365 nm light source, and heated up at 30 ℃ for 1 h, until the complete consumption of isocyanide **4d** as monitored by TLC. After this time, the mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried

over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=10:1) to give 4-((4-methoxyphenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methyl)morpholine **7**. Note: when the quinoline **5a** was used to react with morpholine directly, no product **7** was obtained. Yellow oil, 47.2 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.1 Hz, 1H), 8.33 (br.s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.68 (s, 1H), 3.73 (s, 3H), 3.71 (d, *J* = 5.4 Hz, 4H), 2.56 – 2.34 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 135.4, 133.7, 129.3, 125.6, 124.8, 123.7, 122.1 (q, *J* = 36.5 Hz), 121.8 (q, *J* = 267.7 Hz), 120.9, 119.4 (q, *J* = 2.3 Hz), 113.8, 111.7, 67.5, 67.3, 55.2, 52.8.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -56.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{21}H_{22}F_3N_2O_2^+$ 391.1628; found 391.1616.

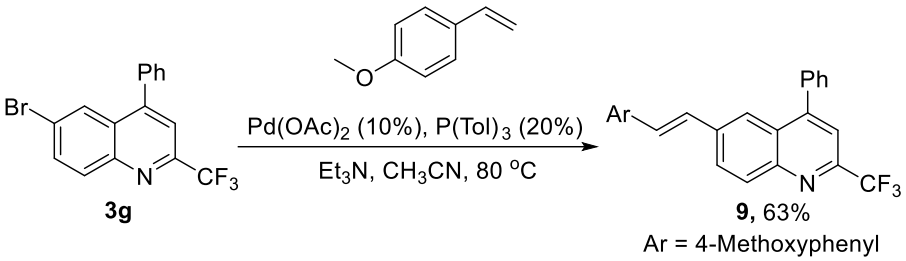
Synthesis of quinoline 8



6-(4-methoxyphenyl)-4-phenyl-2-(trifluoromethyl)quinoline (8): A round bottom flask was charged with the mixture of 6-bromo-4-phenyl-2-(trifluoromethyl)quinoline **3g** (0.2 mmol), K_2CO_3 (0.4 mmol), $Pd(PPh_3)_4$ (3 %) and (4-methoxyphenyl)boronic acid (0.2 mmol) in 1,4-dioxane (2.0 mL). The reaction was kept at 70 ℃ for 12 h under nitrogen atmosphere. After completion, H_2O (5.0 mL) was added and the mixture was extracted with CH_2Cl_2 (5.0 mL × 3). The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA=20:1) to give 6-(4-methoxyphenyl)-4-phenyl-2-(trifluoromethyl)quinoline **8**. White solid, 63.2 mg, 84% yield, m.p. 105 – 107 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.13

– 8.03 (m, 2H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.60 – 7.51 (m, 7H), 6.99 (d, *J* = 7.4 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 150.7, 147.0 (q, *J* = 34.2 Hz), 146.9, 140.9, 137.3, 132.3, 130.8, 130.1, 129.5, 129.0, 128.9, 128.6, 127.7, 122.5, 121.7 (q, *J* = 273.6 Hz), 117.4 (q, *J* = 2.3 Hz), 114.5, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{17}F_3NO^+$ 380.1257; found 380.1241.

Synthesis of quinoline 9

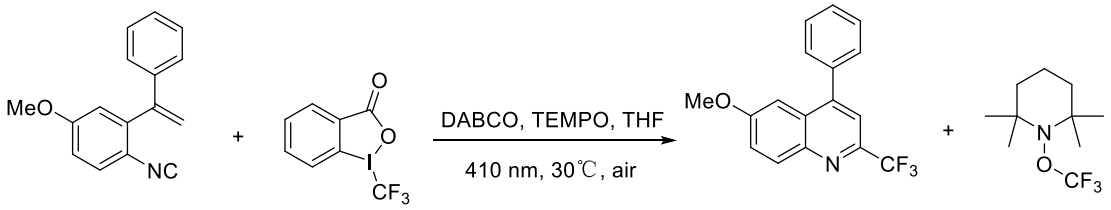


(*E*)-6-(4-methoxystyryl)-4-phenyl-2-(trifluoromethyl)quinoline (9): To a solution of 6-bromo-4-phenyl-2-(trifluoromethyl)quinoline **3g** (0.2 mmol) in dry acetonitrile was added palladium acetate (10 %), tri-*ortho*-tolyl phosphine (20 %), triethylamine (6 eq) and 1-methoxy-4-vinylbenzene (1.2 eq) under nitrogen atmosphere. The reaction was stirred under reflux in oil bath for 16 h. After cooling to room temperature, the crude solution was filtered using celite plug and washed with ethyl acetate. The filtrate was concentrated under vacuum and the resulting mixture was purified by flash column chromatography on silica gel using a mixture of PE/EA = 70/30 as eluent to afford the corresponding (*E*)-6-(4-methoxystyryl)-4-phenyl-2-(trifluoromethyl)quinoline **9**. Yellow solid, 51.0 mg, 63% yield, m.p. 121 – 123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.9 Hz, 1H), 8.09 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.65 (s, 1H), 7.63 – 7.54 (m, 5H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 16.3 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 150.3, 147.4, 147.2 (q, *J* = 46.8 Hz), 138.0, 137.3, 130.9, 130.7, 129.5, 129.5, 129.0, 128.9, 128.1, 127.9, 125.5, 123.6, 121.7 (q, *J*

= 273.6 Hz), 120.4, 117.5 (q, *J* = 2.3 Hz), 114.3, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{25}H_{19}F_3NO^+$ 406.1413; found 406.1429.

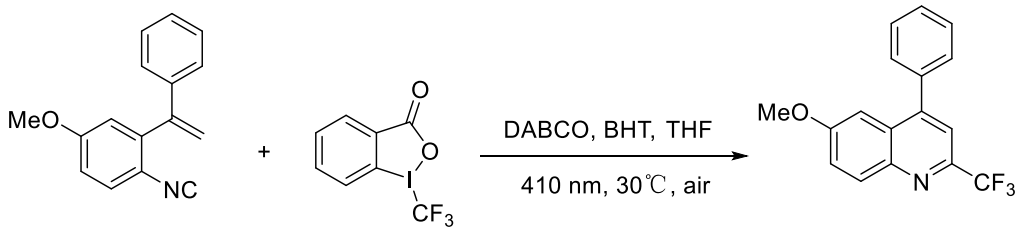
VIII. Mechanistic investigation

Radical trapping experiment



1a **2** **3a** not detected 44 %

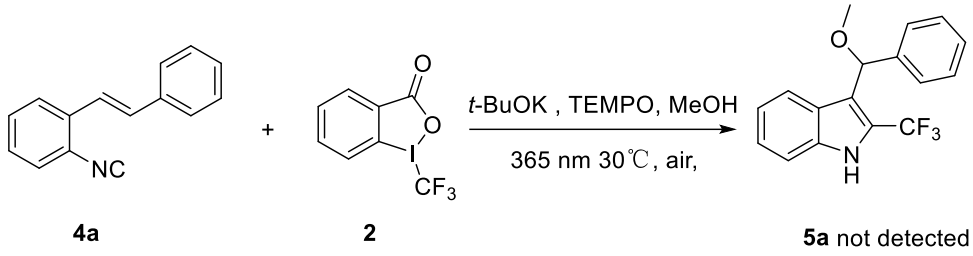
1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and DABCO (0.6 mmol, 3.0 eq, 47.1 mg) and TEMPO (0.6 mmol, 3.0 eq, 93.7 mg) were dissolved in THF (2.0 mL) in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 410 nm light source, and heated up at 30 ℃ for 3 h. No desired product **3a** was detected; only a large amount of starting material **1a** was recovered. TEMPO-CF_3 trapping product was formed in 44% as indicated by ^{19}F NMR with $PhCF_3$ (0.1 mmol) as internal standard.



1a **2** **3a** not detected

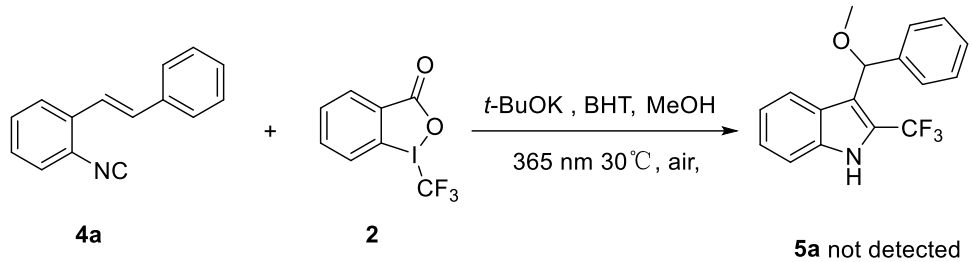
1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and DABCO (0.6 mmol, 3.0 eq, 47.1 mg) and

BHT (0.6 mmol, 3.0 eq, 132.2 mg) were dissolved in THF (2.0 mL) in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 410 nm light source, and heated up at 30 ℃ for 3 h. No desired product **3a** was detected; only a large amount of starting material **1a** was recovered.



4a **2** **5a** not detected

(*E*)-1-isocyano-2-styrylbenzene **4a** (0.2 mmol, 41.1 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and *t*-BuOK (0.6 mmol, 3.0 eq, 73.2 mg) and TEMPO (0.6 mmol, 3.0 eq, 93.7 mg) were dissolved in CH_3OH (2.0 mL) in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 365 nm light source, and heated up at 30 ℃ for 3 h. No desired product **5a** was detected; only a large amount of starting material **4a** was recovered.



4a **2** **5a** not detected

(*E*)-1-isocyano-2-styrylbenzene **4a** (0.2 mmol, 41.1 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and *t*-BuOK (0.6 mmol, 3.0 eq, 73.2 mg) and BHT (0.6 mmol, 3.0 eq, 132.2 mg) were dissolved in CH_3OH (2.0 mL) in a schlenk tube. The reaction was placed in the RLH-18CU 8-position photoreaction system, irradiated with a 365 nm light source, and heated up at 30 ℃ for 3 h. No desired product **5a** was detected; only a large amount of starting material **4a** was recovered.

UV-Vis Absorption Spectroscopy Studies

The UV-Vis absorption spectra of **1a**, **2**, **4a** and base (DABCO or *t*-BuOK) were measured at room temperature in THF or MeOH in an attempt to show a possible shift in absorbance caused by the formation of an EDA complex. The data in Figure S3 and Figure S6 suggested EDA complexes were formed by Togni's reagent **2** and DABCO as well as **2** and *t*-BuOK. On the other hand, no EDA complexes were observed when mixing **1a** and **2**, **1a** and DABCO, **4a** and **2**, **4a** and *t*-BuOK.

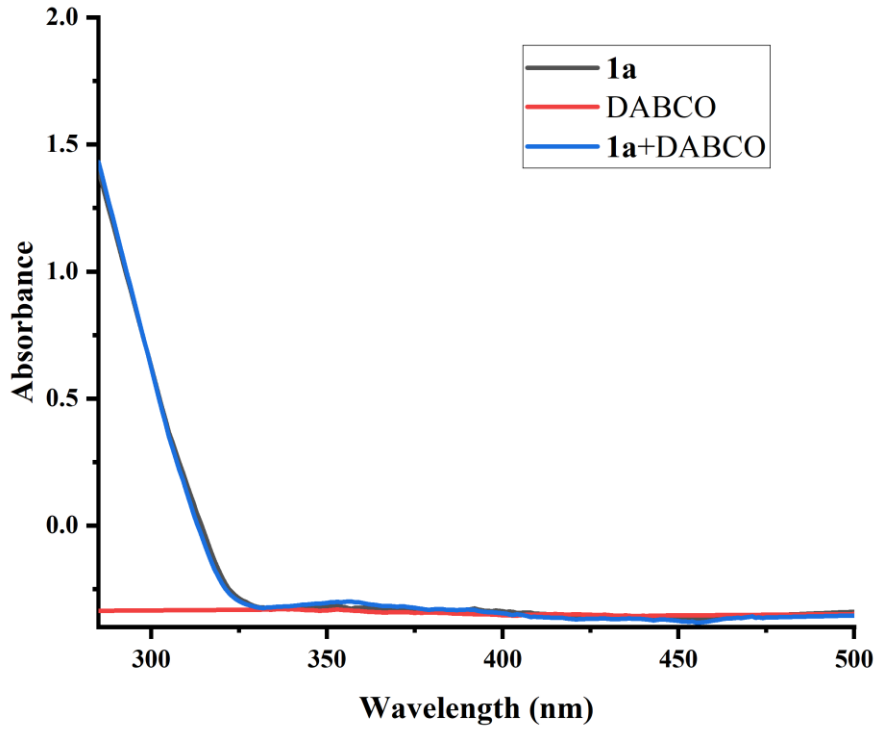


Figure S1. UV/Vis spectrum (recorded 0.1 mmol in THF) of **1a**, DABCO and 1:1 mixture of **1a** and DABCO

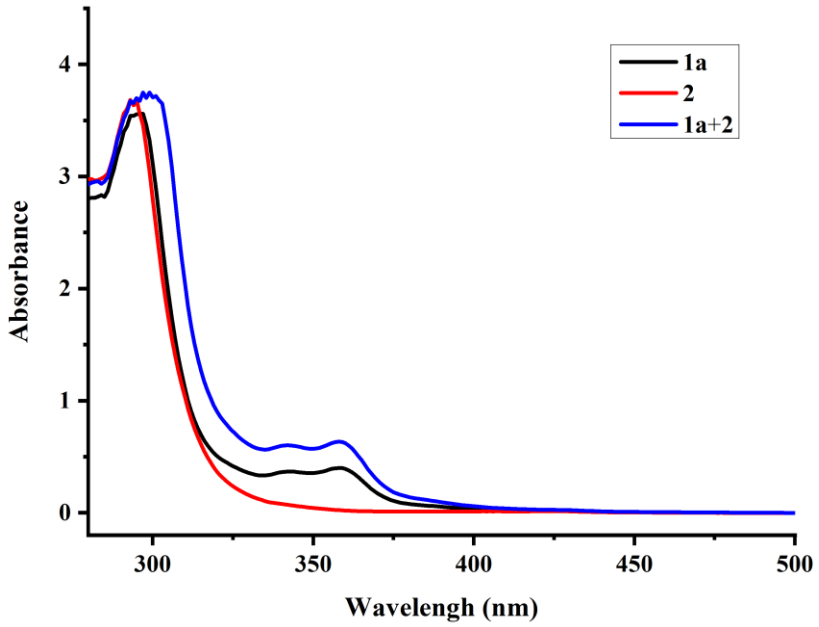


Figure S2. UV/Vis spectrum (recorded 0.1 mmol in THF) of **1a**, **2** and 1:1 mixture of **1a** and **2**

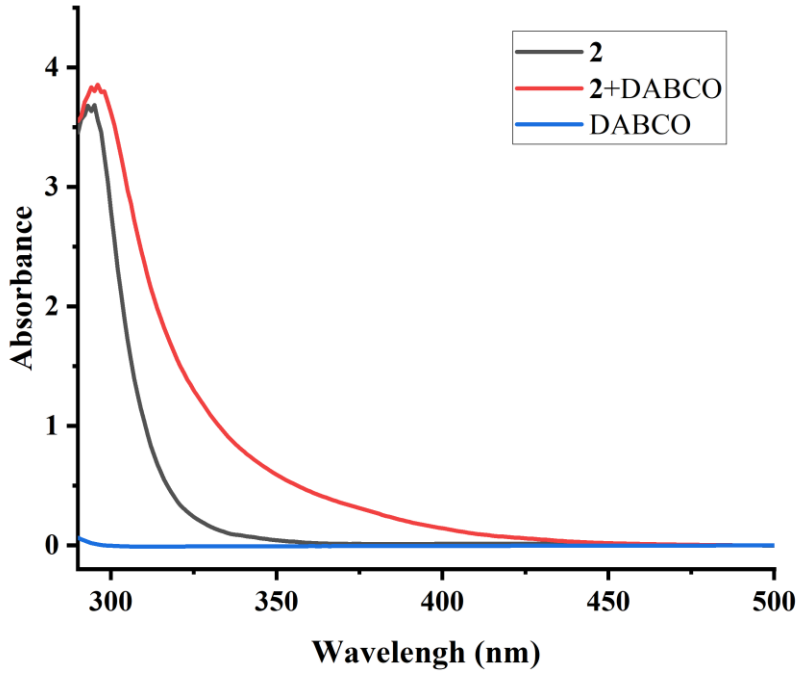


Figure S3. UV/Vis spectrum (recorded 0.1 mmol in THF) of **2**, DABCO and 1:1 mixture of **2** and DABCO

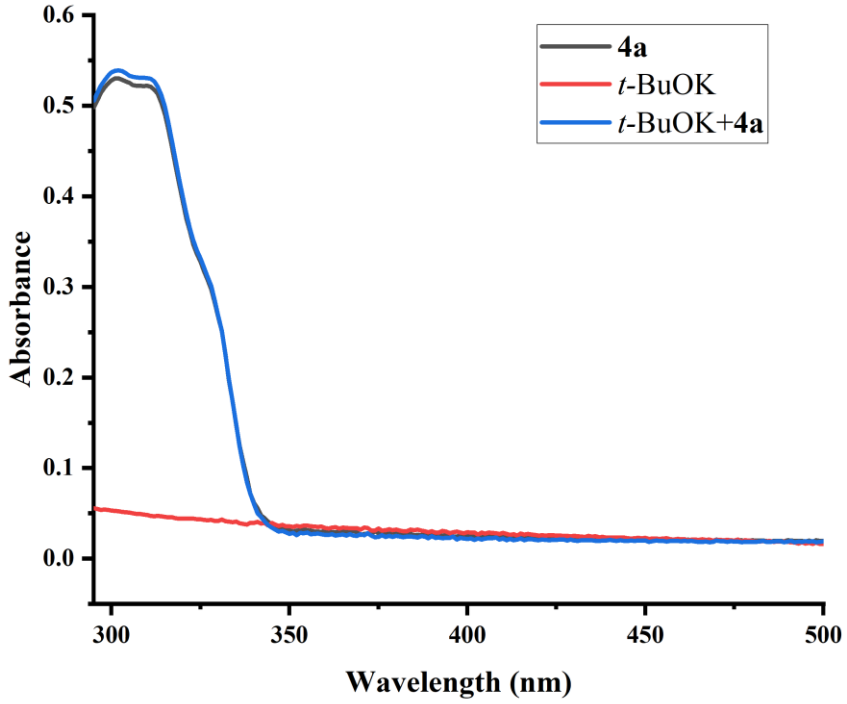


Figure S4. UV/Vis spectrum (recorded 0.1 mmol in THF) of **4a**, *t*-BuOK and 1:1 mixture of **4a** and *t*-BuOK

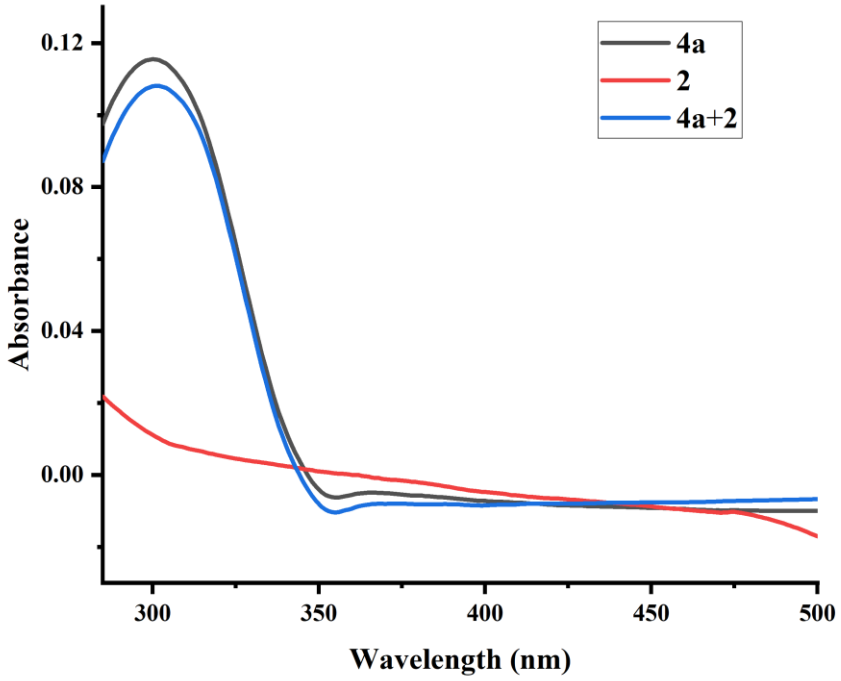


Figure S5. UV/Vis spectrum (recorded 0.1 mmol in THF) of **4a**, **2** and 1:1 mixture of **4a** and **2**

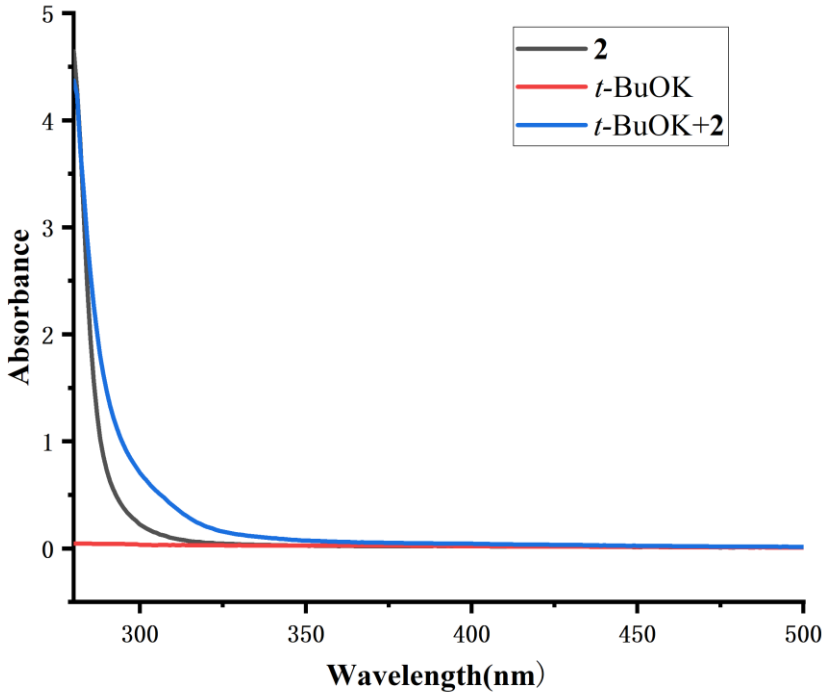
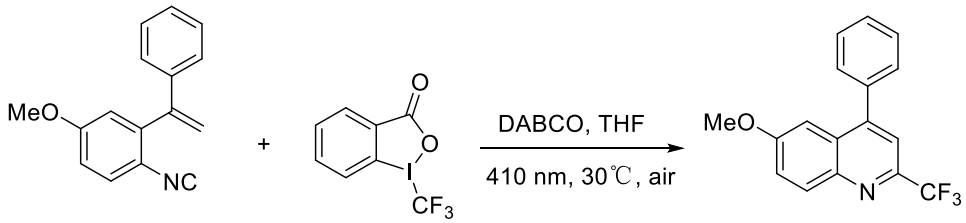


Figure S6. UV/Vis spectrum (recorded 0.1 mmol in THF) of **2**, *t*-BuOK and 1:1 mixture of **2** and *t*-BuOK

Light on/off experiments



1a **2** **3a**

1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), Togni's reagent **2** (0.6 mmol, 3.0 eq, 190 mg) and DABCO (0.6 mmol, 3.0 eq, 47.1 mg) were dissolved in 2.0 mL THF in a schlenk tube. Irradiate the reaction with a 410 nm LED light and maintain the temperature at 30 ℃. For light-off operations, wrap the entire schlenk tube with tin foil. After given time, 100 μL the reaction solution was taken and dissolved in $CDCl_3$ as crude NMR sample. Yields were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

Reaction time (min)	Light (on/off)	Yield of 3a (%)
0 - 20	on	33

20 - 40	off	34
40 - 60	on	48
60 - 80	off	50
80 - 100	on	55
100 - 120	on	55

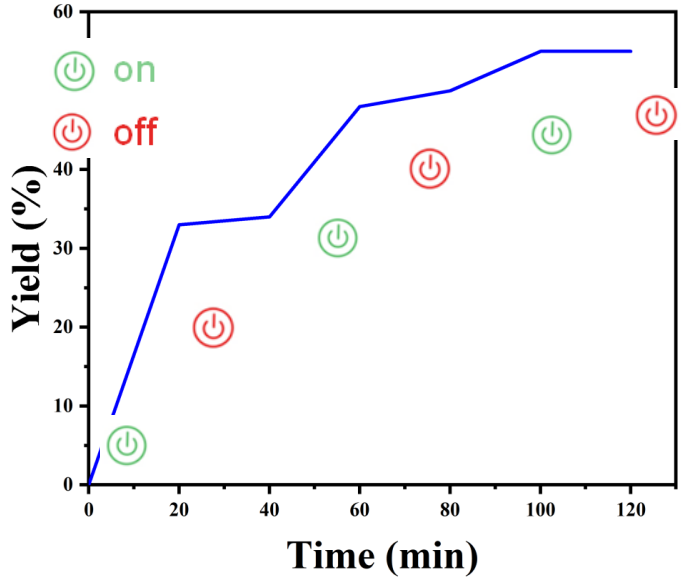


Figure S7. Light on/off Experiments

Proposed mechanism for formation of 2-CF_3 substituted indole 5

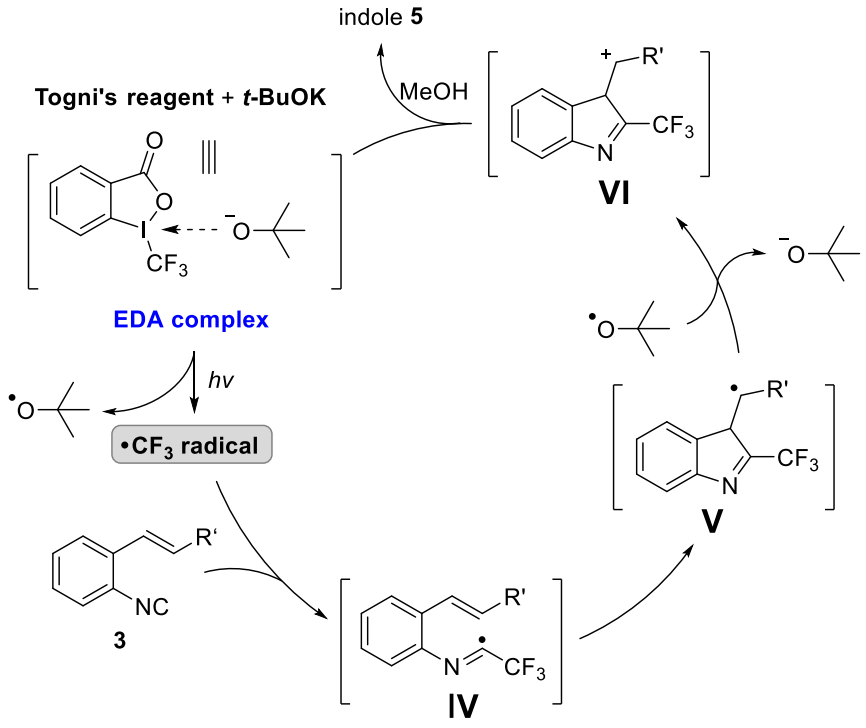


Figure S8. Proposed mechanism for indole 5 formation

IX. X-ray Crystallographic Data of compounds 3a, 5a

X-ray Crystallographic Data of compound 3a

Sample preparation

30 mg of **3a** was dissolved in CH_2Cl_2 and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.

Crystal measurement for compound 3a

Suitable single crystals of complex **3a** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 293K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.

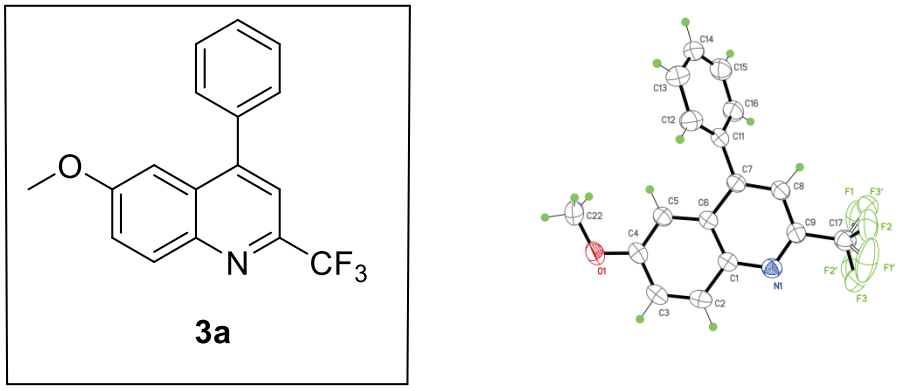


Figure S8. Crystal measurement for compound **3a**

3a CCDC 2339671, displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for 3a

Empirical formula	$C_{17}H_{12}NF_3O$
Formula weight	303.28
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.6930(7)
b/Å	7.2066(4)
c/Å	19.6695(11)

α/°	90.00
β/°	104.091(7)
γ/°	90.00
Volume/Å^3	1470.13(15)
Z	4
ρ_{calc}mg/mm^3	1.370
m/mm^{-1}	0.954
F(000)	624.0
Crystal size/mm^3	0.25 × 0.2 × 0.15
2Θ range for data collection	8.66 to 134.1°
Index ranges	-11 ≤ h ≤ 12, -6 ≤ k ≤ -8, -23 ≤ l ≤ 23
Reflections collected	5973
Independent reflections	2606[R(int) = 0.0320]
Data/restraints/parameters	2606/0/228
Goodness-of-fit on F^2	1.157
Final R indexes [I>=2σ (I)]	R_1 = 0.0702, wR_2 = 0.1976
Final R indexes [all data]	R_1 = 0.1176, wR_2 = 0.2266
Largest diff. peak/hole / e Å^{-3}	0.17/-0.21

X-ray Crystallographic Data of compound 5a

Sample preparation

30 mg of **5a** was dissolved in CH_2Cl_2 and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.

Crystal measurement for compound 5a

Suitable single crystals of complex **5a** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 113.15 K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.

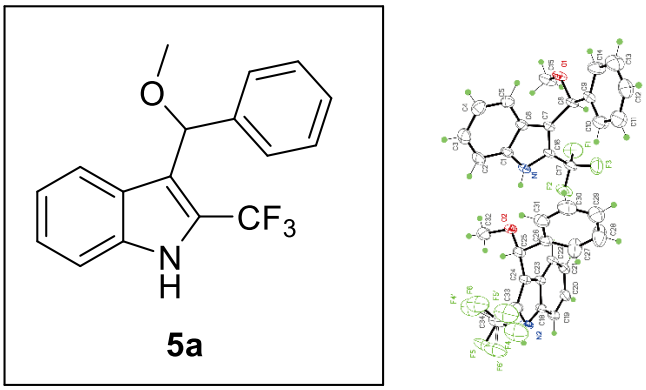


Figure S9. Crystal measurement for compound 5**a**

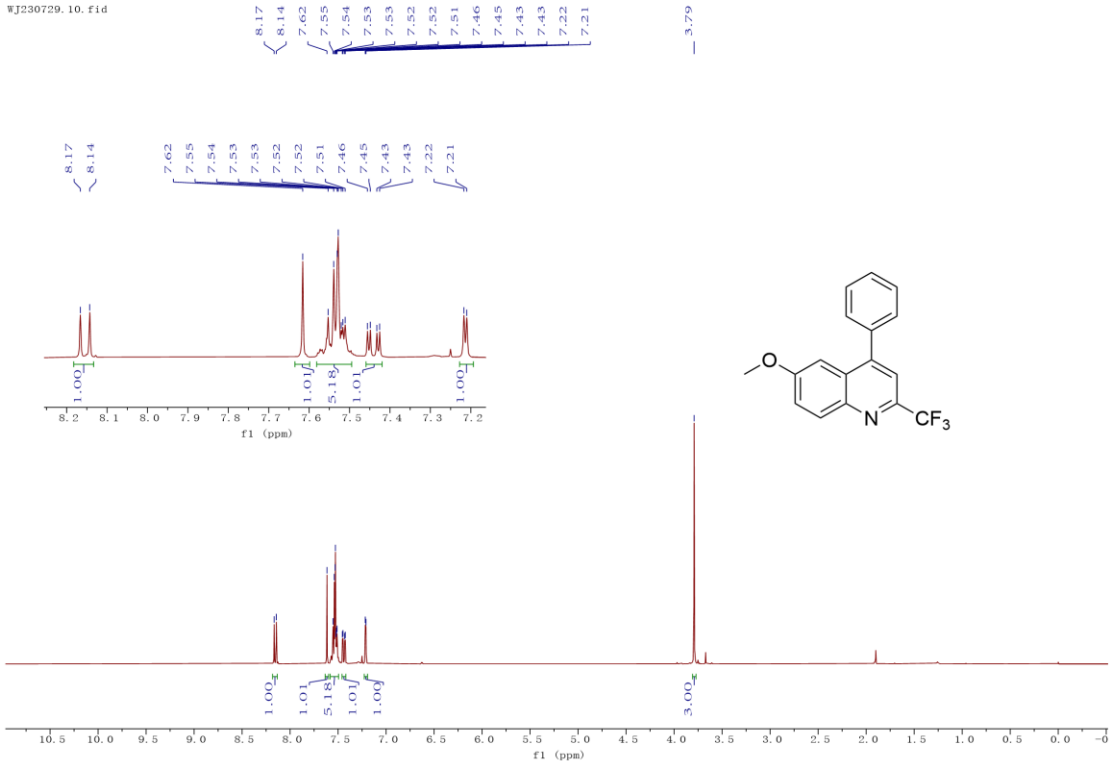
5a CCDC 2339666, displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for 3m

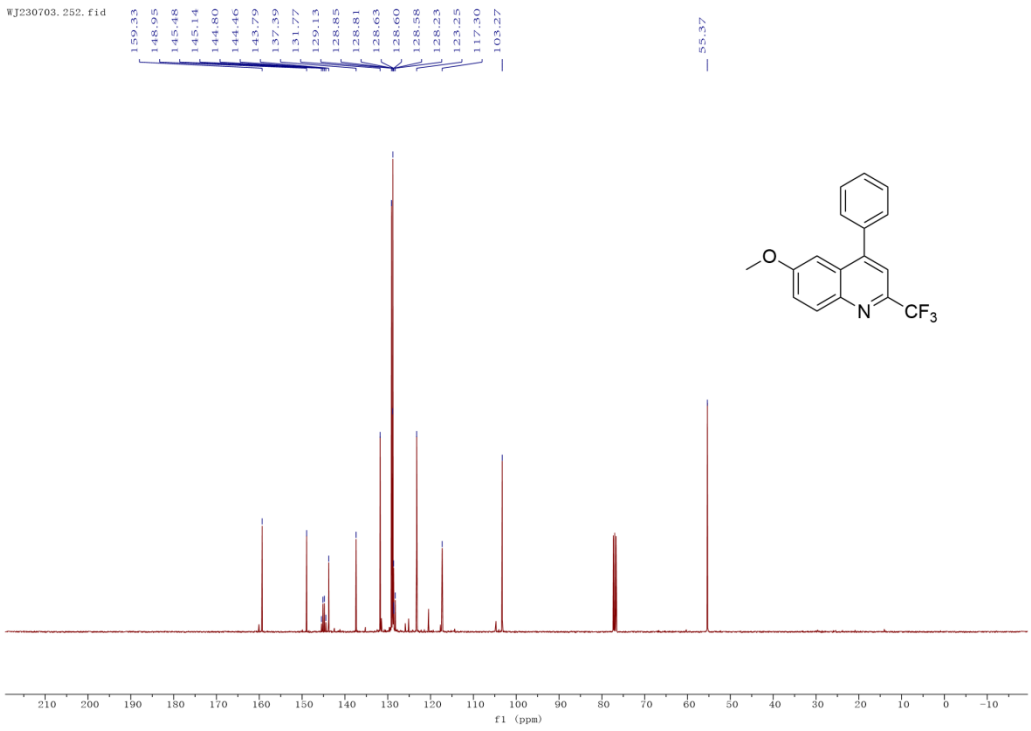
Empirical formula	$C_{17}H_{14}NOF_3$
Formula weight	305.29
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.6371(4)
b/Å	12.8598(5)
c/Å	16.1477(5)
α/°	90.00
β/°	94.065(3)
γ/°	90.00
Volume/Å^3	3031.84(17)
Z	8
ρ_{calc}mg/mm^3	1.338
m/mm^{-1}	0.926
F(000)	1264.0
Crystal size/mm^3	0.12 × 0.08 × 0.05
2Θ range for data collection	7.88 to 134.14°
Index ranges	-16 ≤ h ≤ 17, -15 ≤ k ≤ 11, -19 ≤ l ≤ 18
Reflections collected	13414
Independent reflections	5326[R(int) = 0.0500]
Data/restraints/parameters	5326/36/427
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0735, wR_2 = 0.1975
Final R indexes [all data]	R_1 = 0.1056, wR_2 = 0.2268
Largest diff. peak/hole / e Å^{-3}	0.44/-0.41

X. NMR spectra of compounds 3, 5, 6, 7, 8 and 9

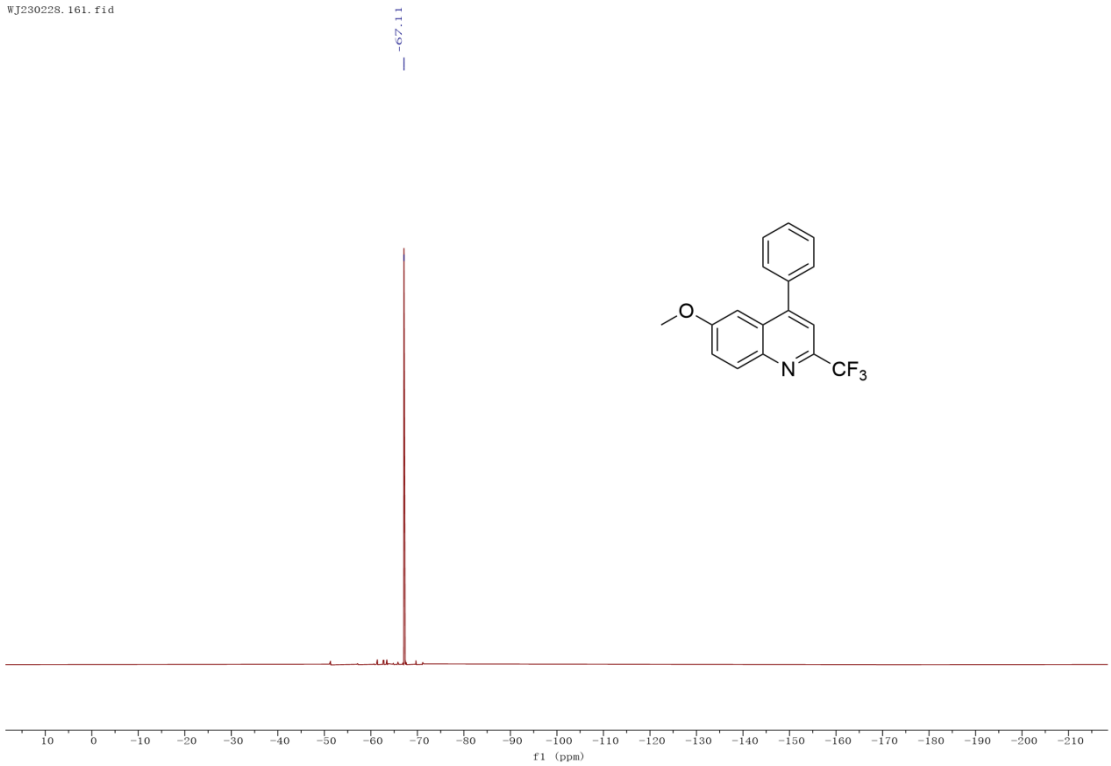
^{1}H NMR (400 MHz, $CDCl_3$) for **3a**



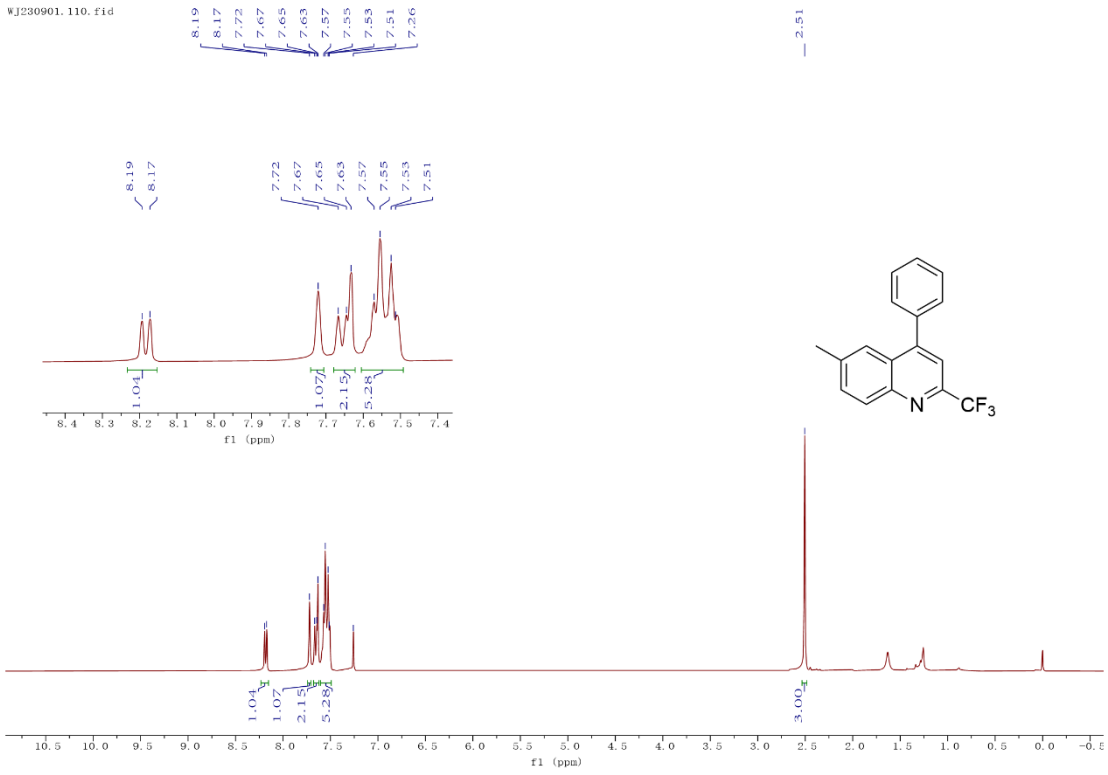
^{13}C NMR (100 MHz, $CDCl_3$) for **3a**



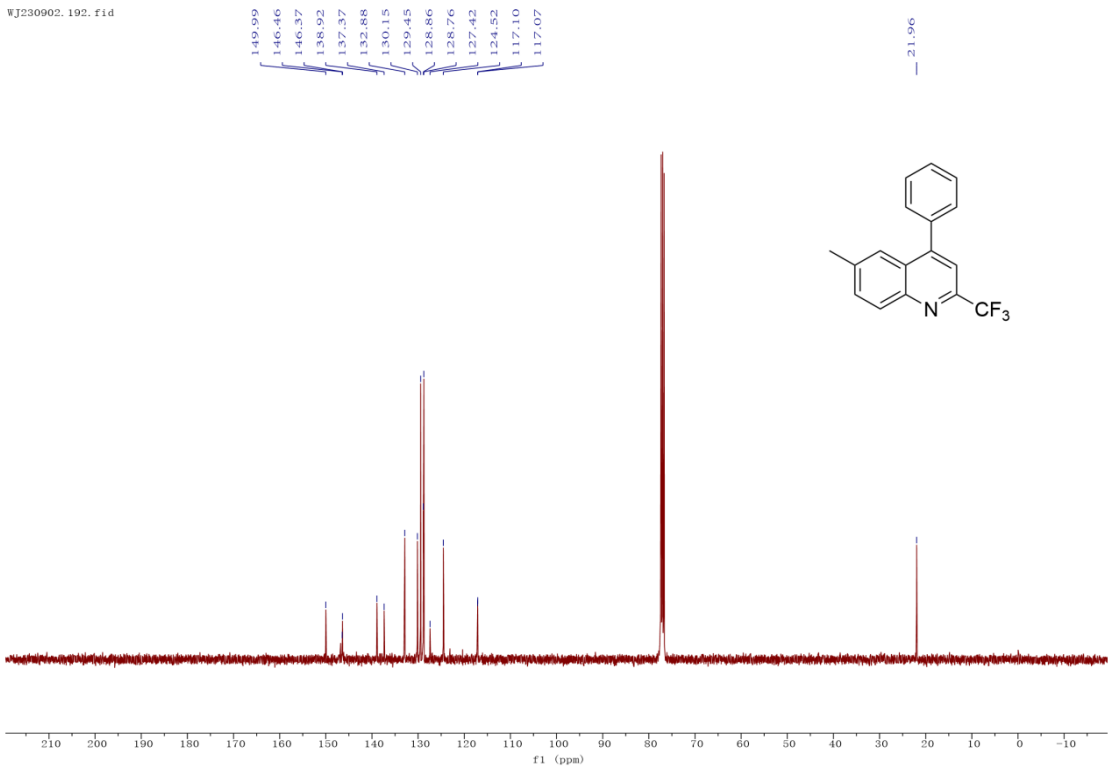
^{19}F NMR (376 MHz, $CDCl_3$) for **3a**



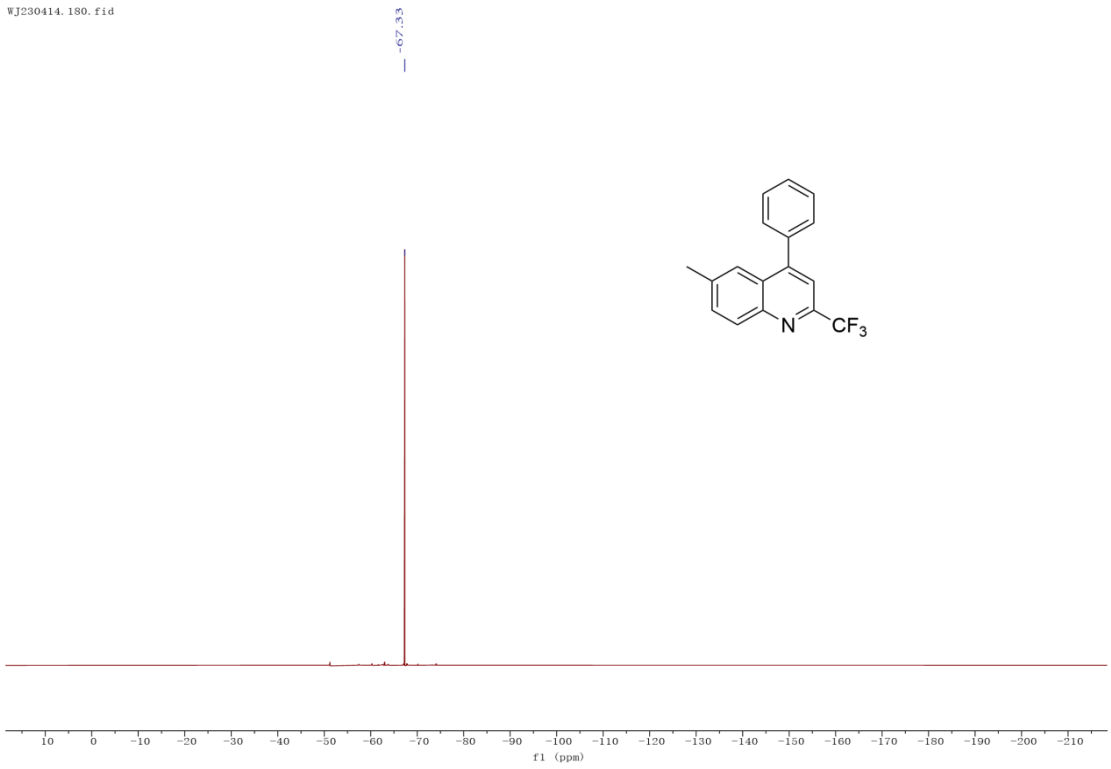
^{1}H NMR (400 MHz, $CDCl_3$) for **3b**



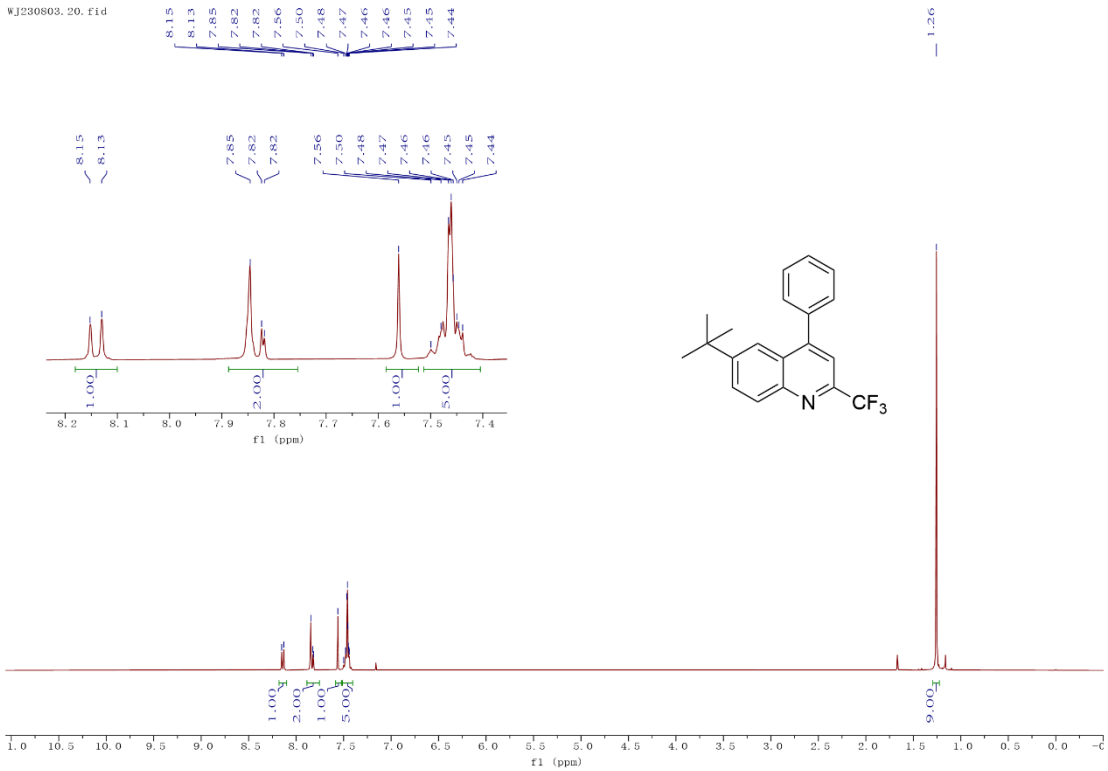
^{13}C NMR (100 MHz, $CDCl_3$) for **3b**



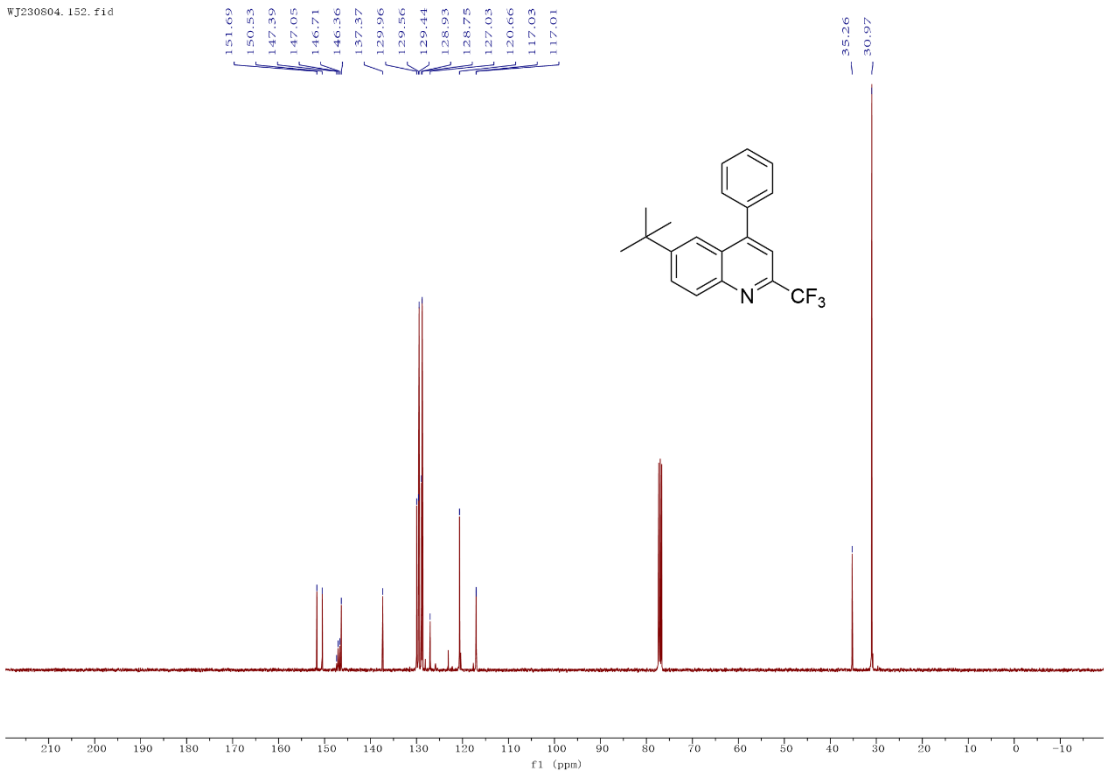
^{19}F NMR (376 MHz, $CDCl_3$) for **3b**



^{1}H NMR (400 MHz, $CDCl_3$) for **3c**

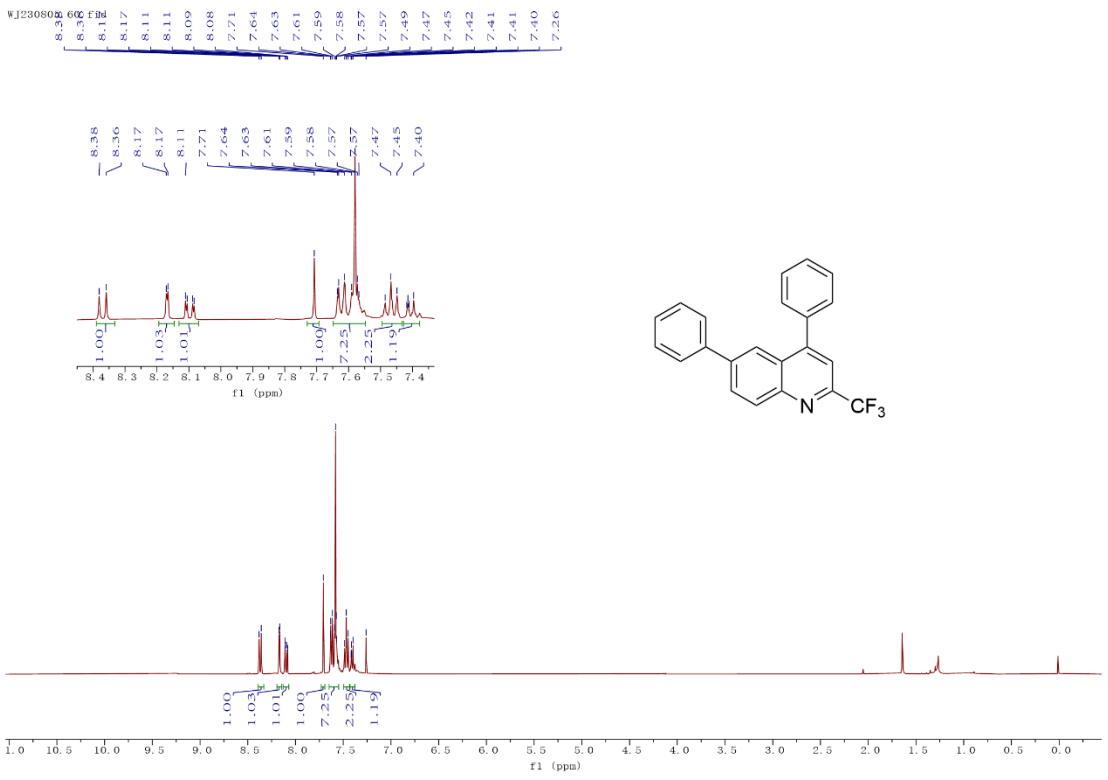


^{13}C NMR (100 MHz, $CDCl_3$) for **3c**

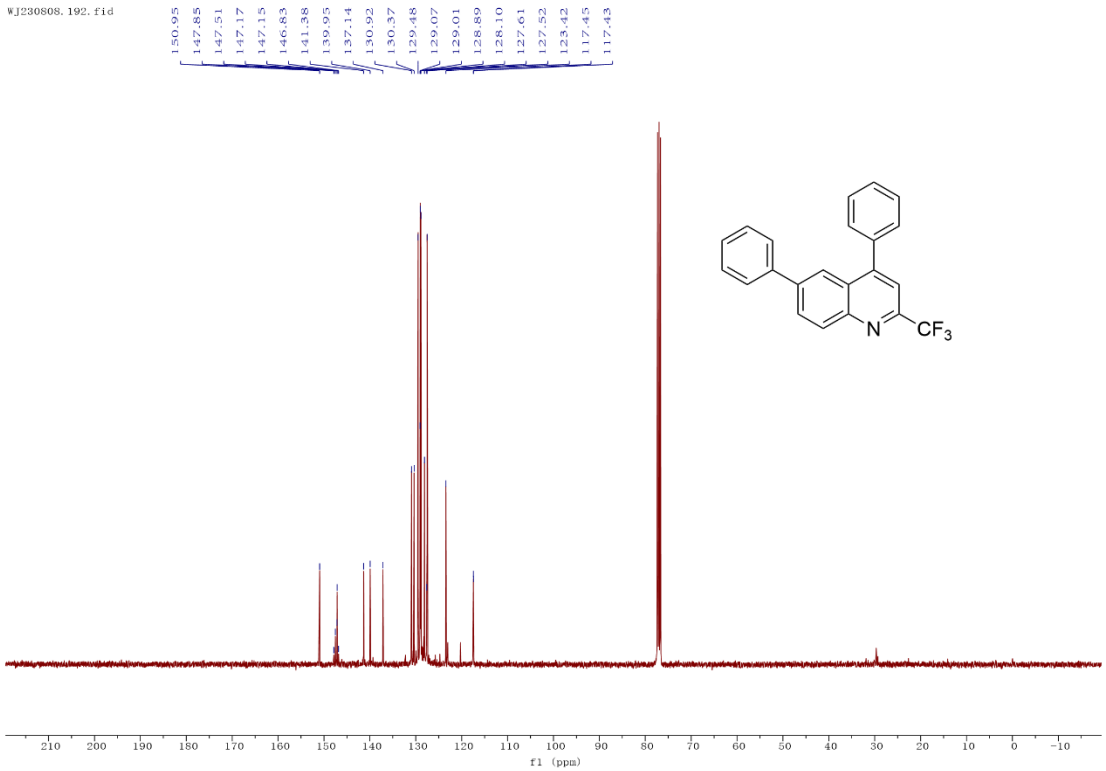


^{19}F NMR (376 MHz, $CDCl_3$) for **3c**

^{1}H NMR (400 MHz, $CDCl_3$) for **3d**

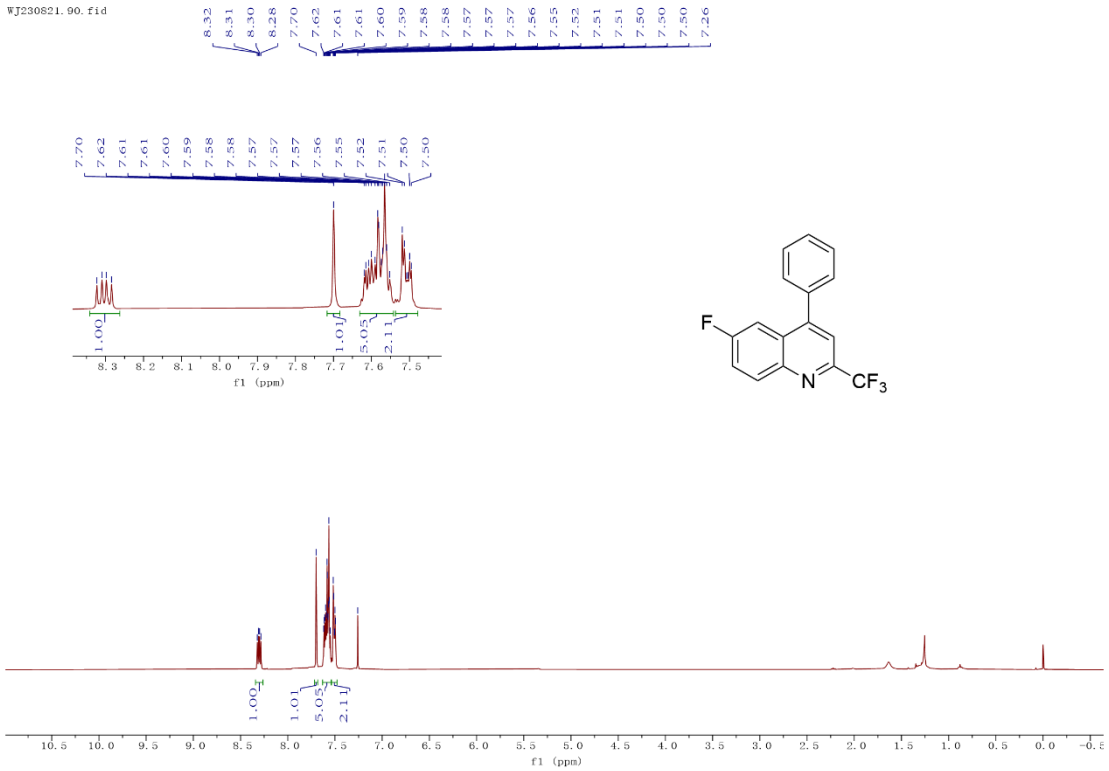


^{13}C NMR (100 MHz, $CDCl_3$) for **3d**

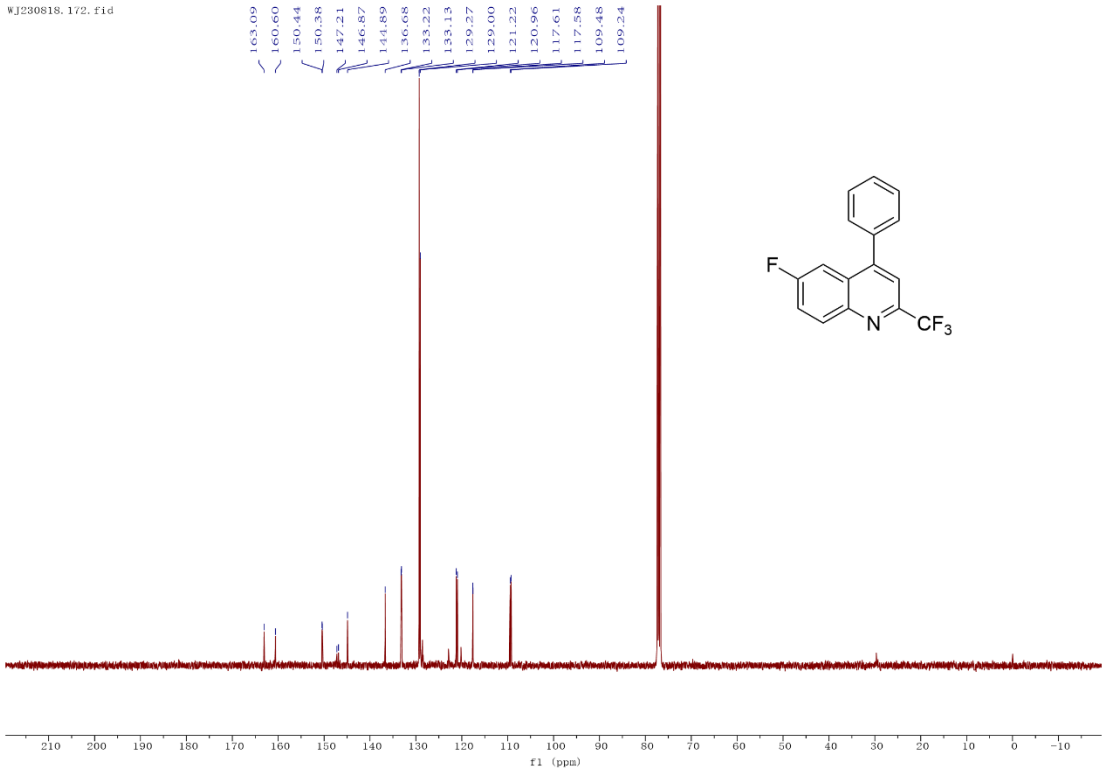


^{19}F NMR (376 MHz, $CDCl_3$) for **3d**

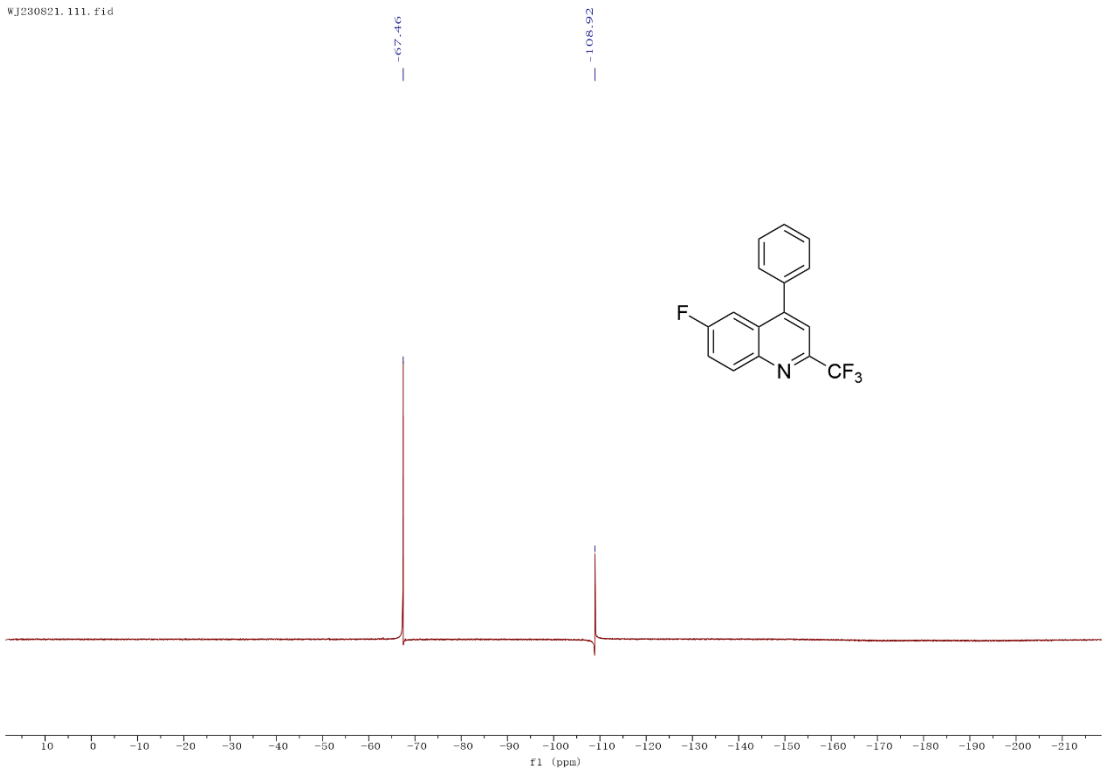
^{1}H NMR (400 MHz, $CDCl_3$) for **3e**



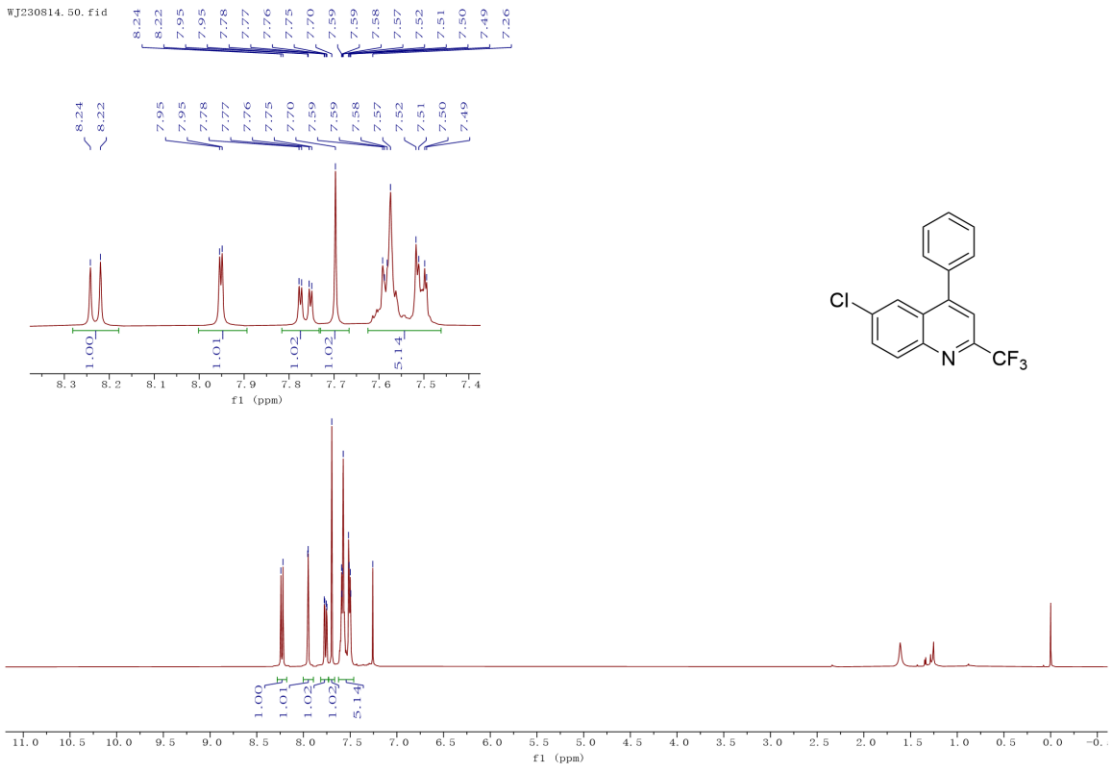
^{13}C NMR (100 MHz, $CDCl_3$) for **3e**



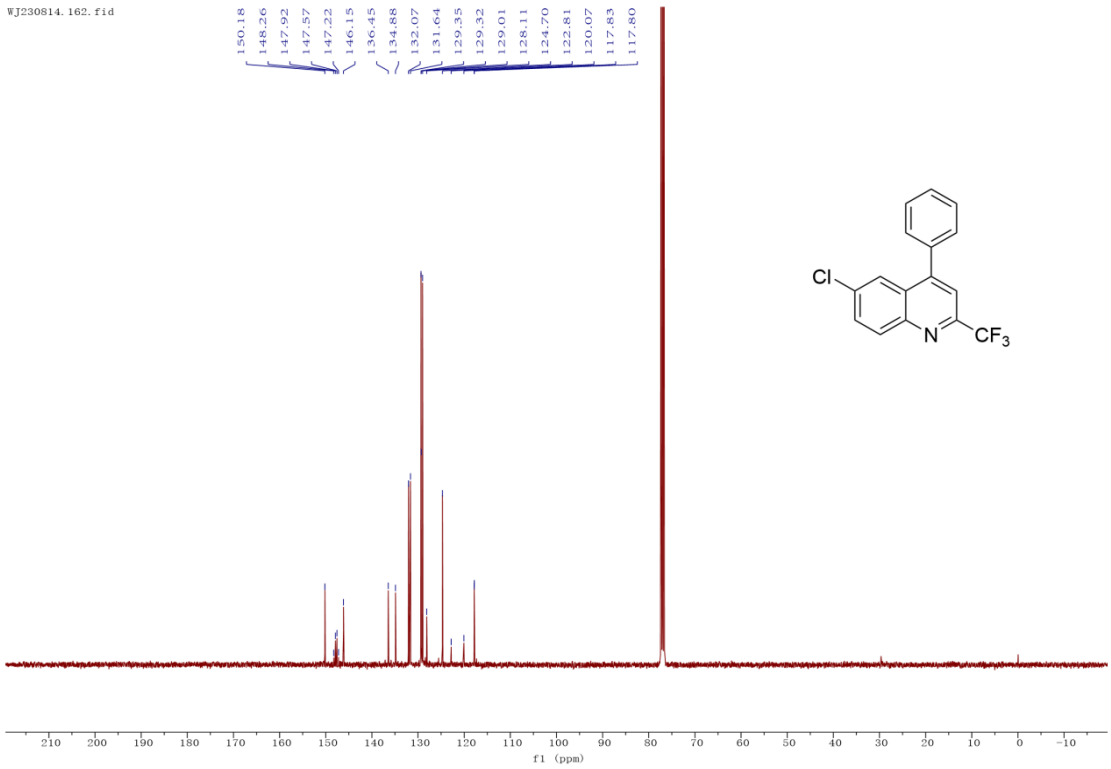
^{19}F NMR (376 MHz, $CDCl_3$) for **3e**



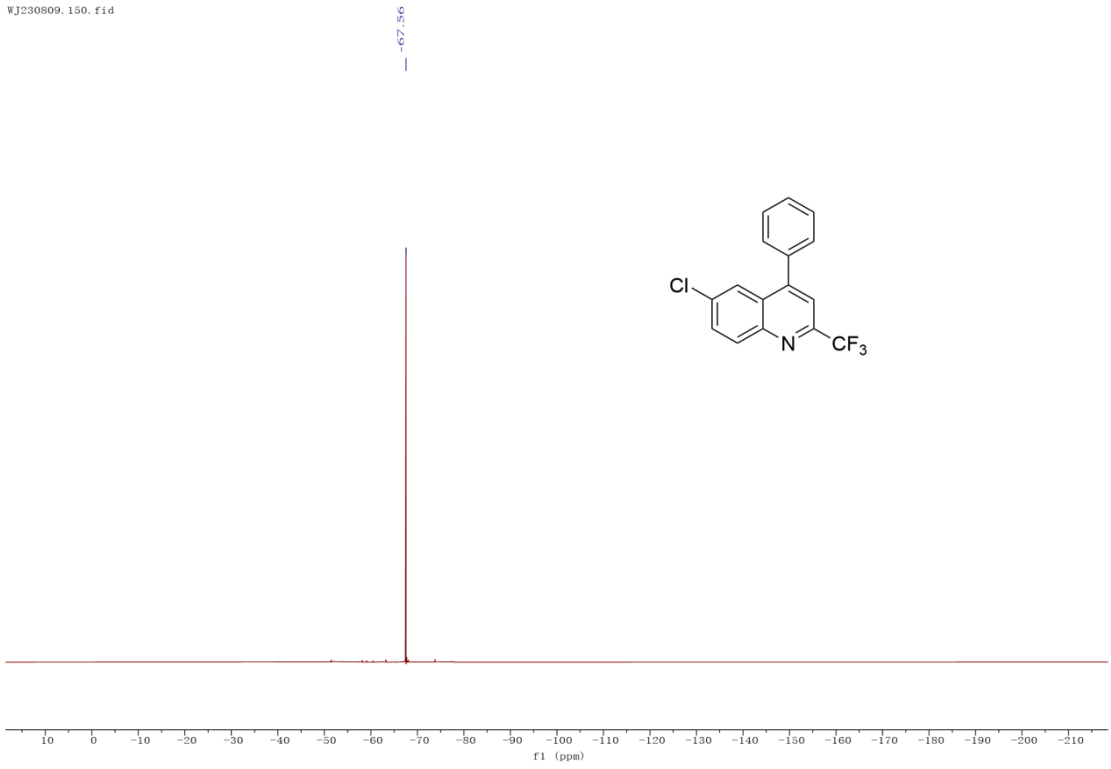
^{1}H NMR (400 MHz, $CDCl_3$) for **3f**



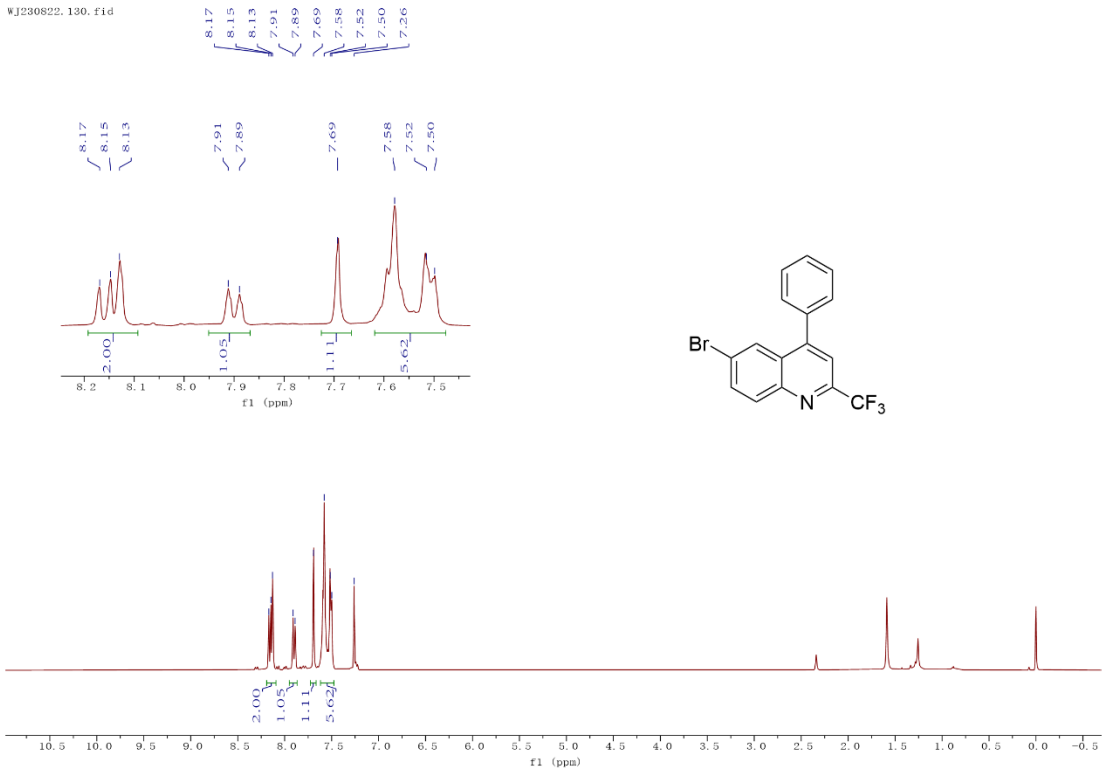
^{13}C NMR (100 MHz, $CDCl_3$) for **3f**



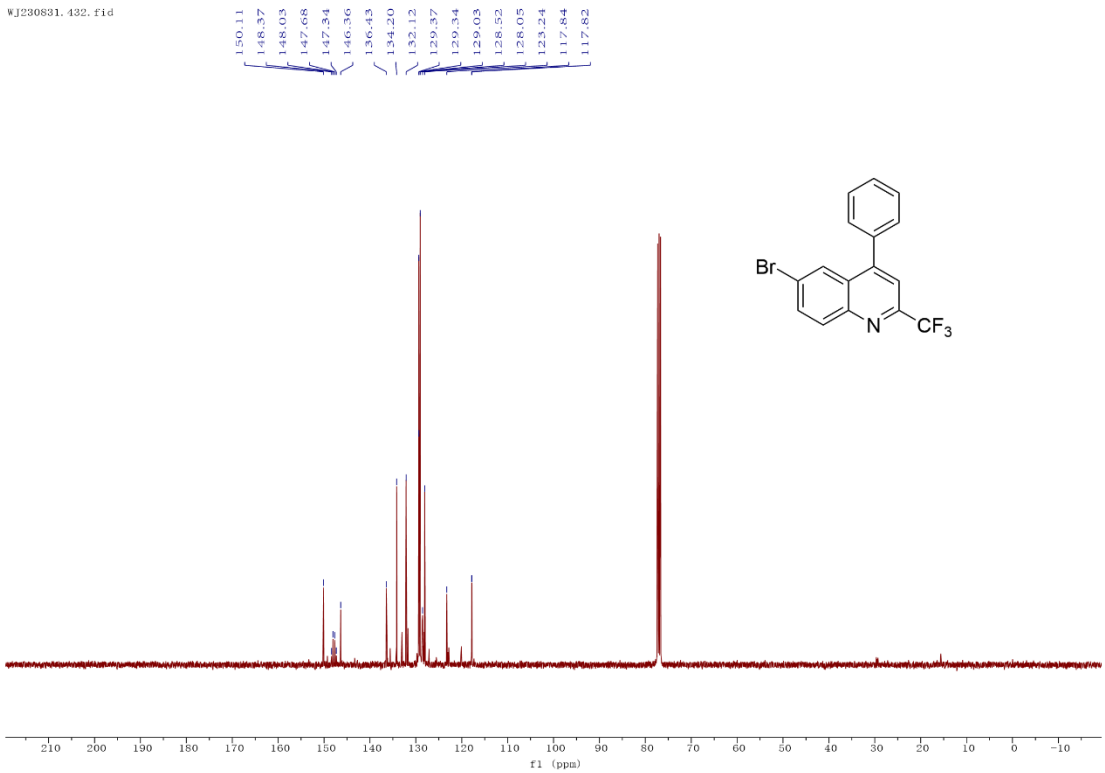
^{19}F NMR (376 MHz, $CDCl_3$) for **3f**



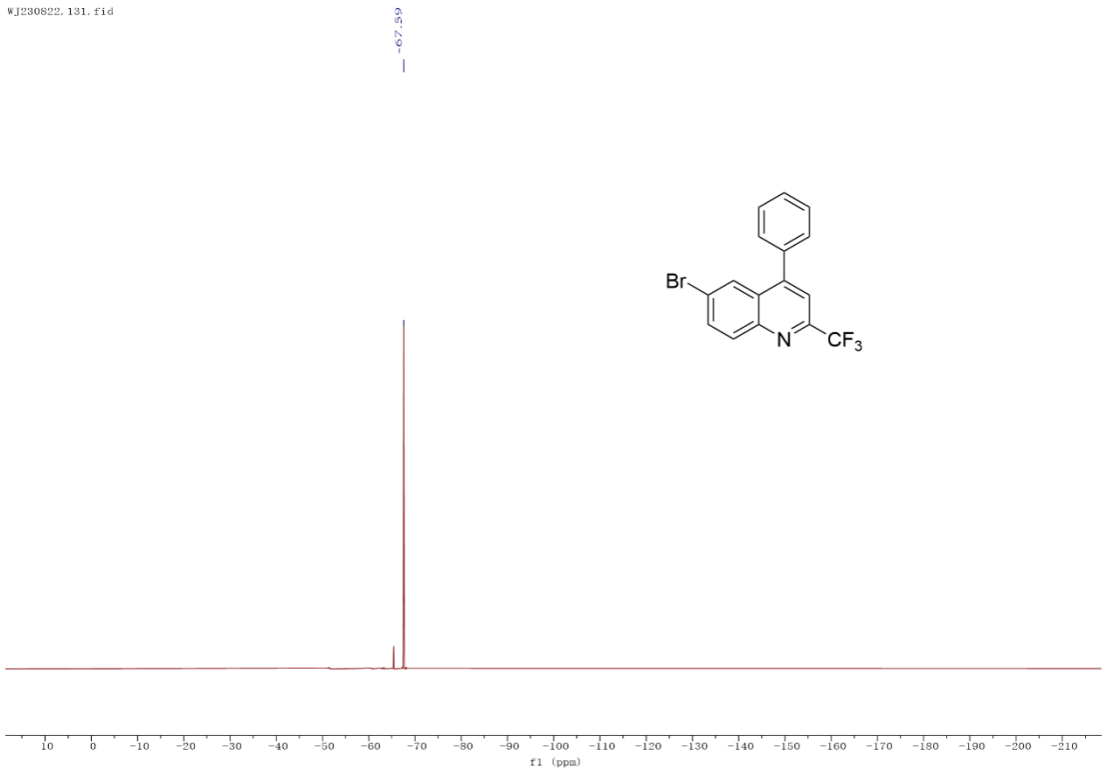
^{1}H NMR (400 MHz, $CDCl_3$) for **3g**



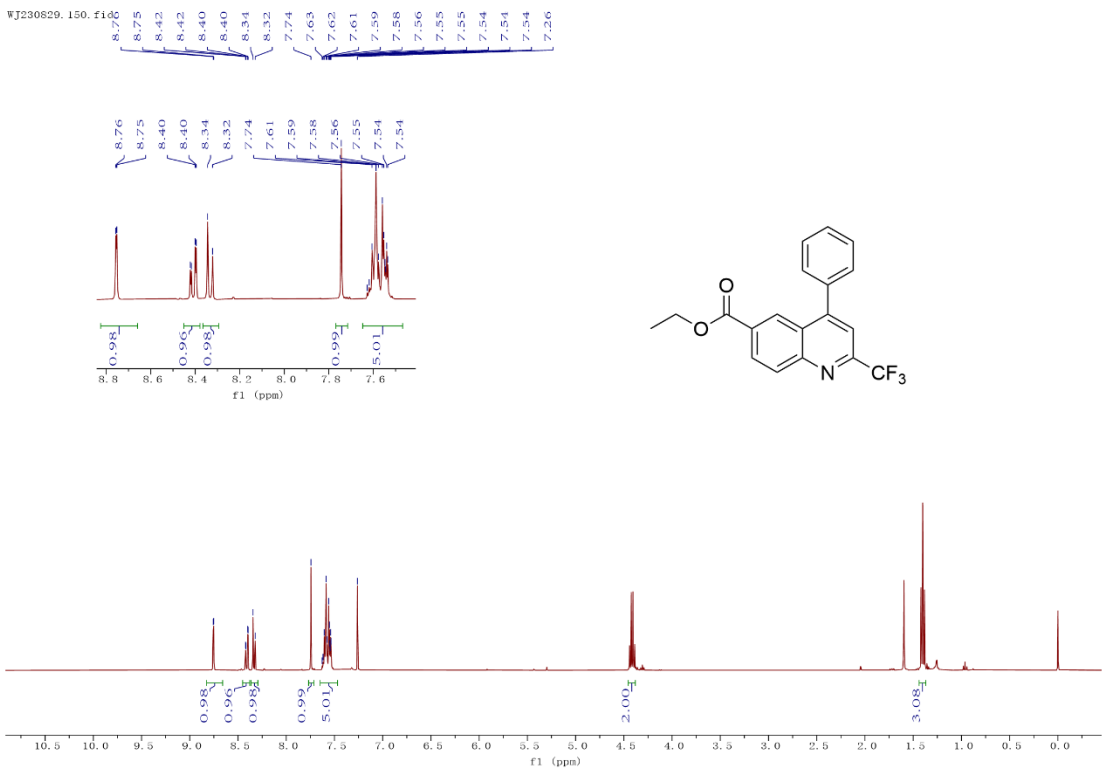
^{13}C NMR (100 MHz, $CDCl_3$) for **3g**



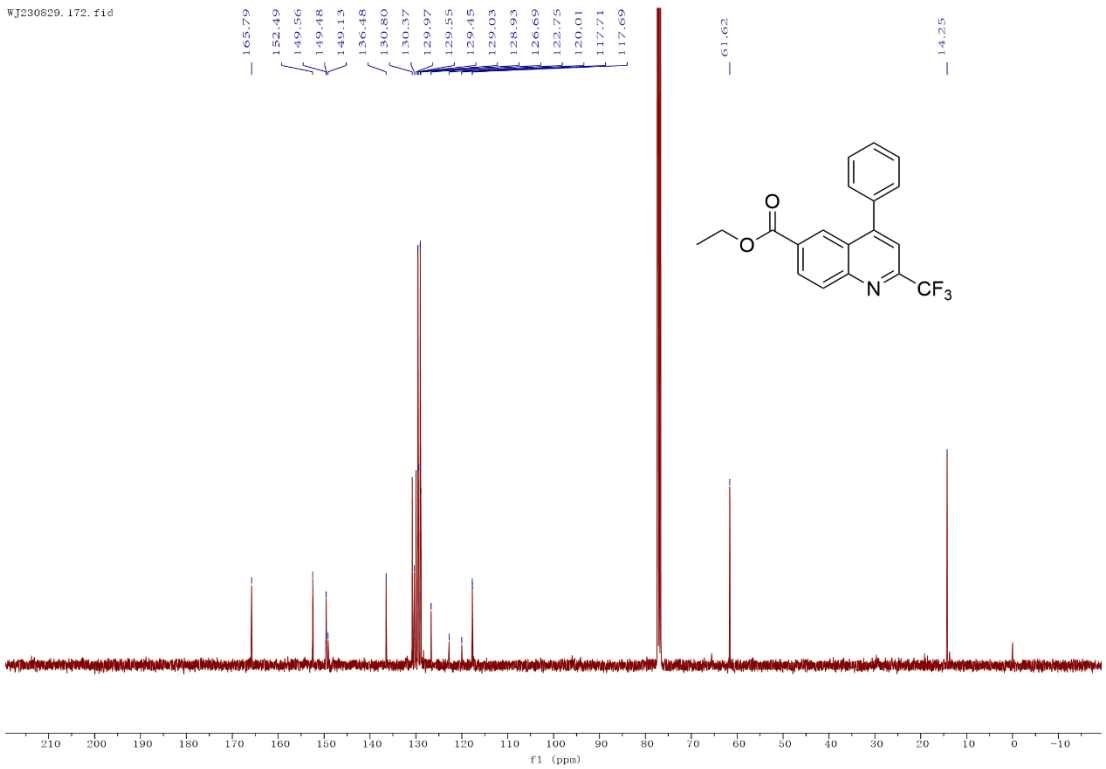
^{19}F NMR (376 MHz, $CDCl_3$) for **3g**



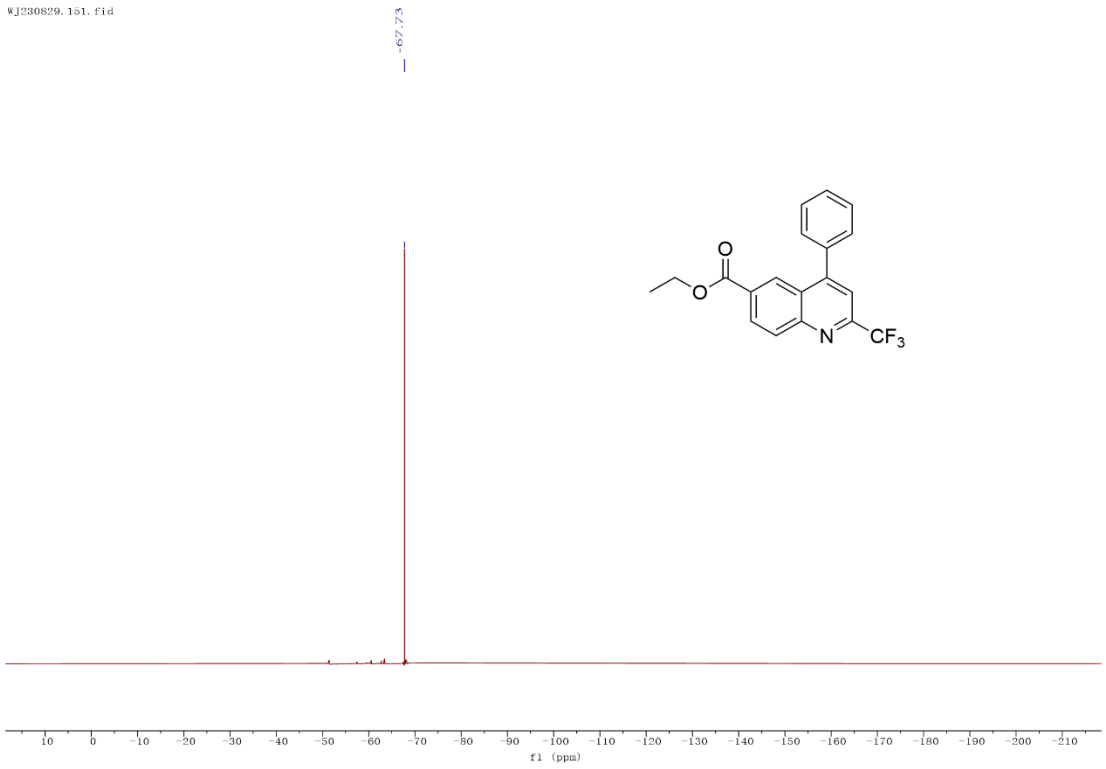
^{1}H NMR (400 MHz, $CDCl_3$) for **3h**



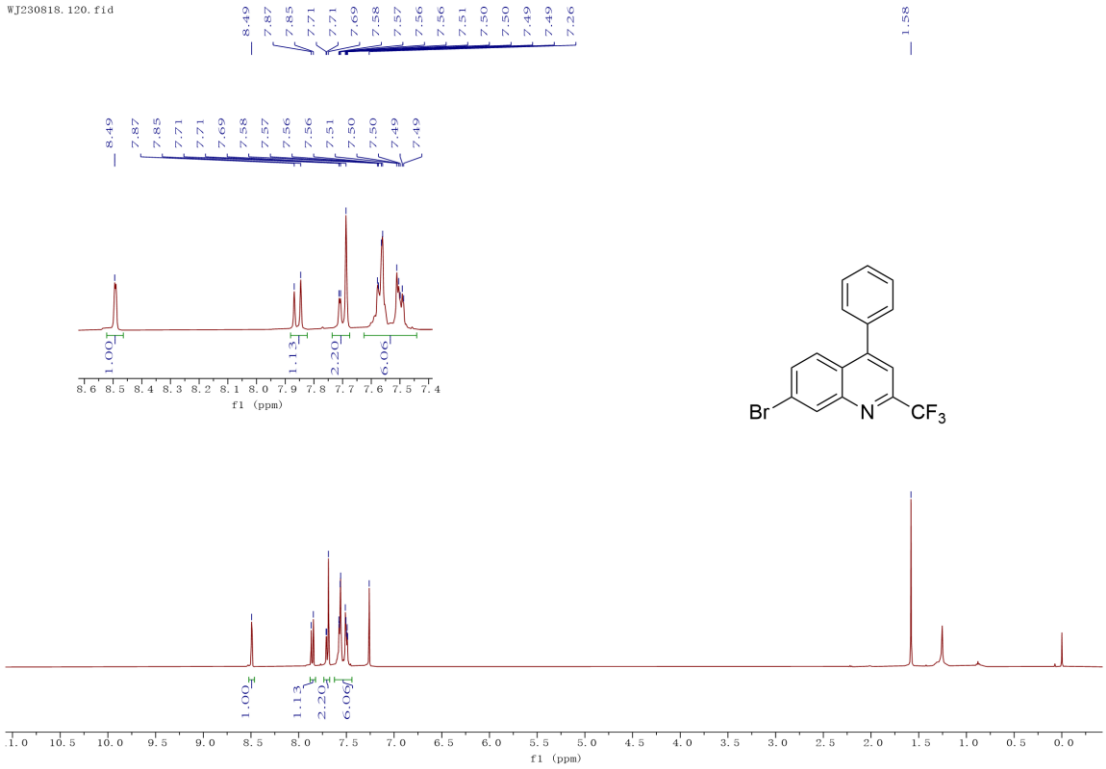
^{13}C NMR (100 MHz, $CDCl_3$) for **3h**



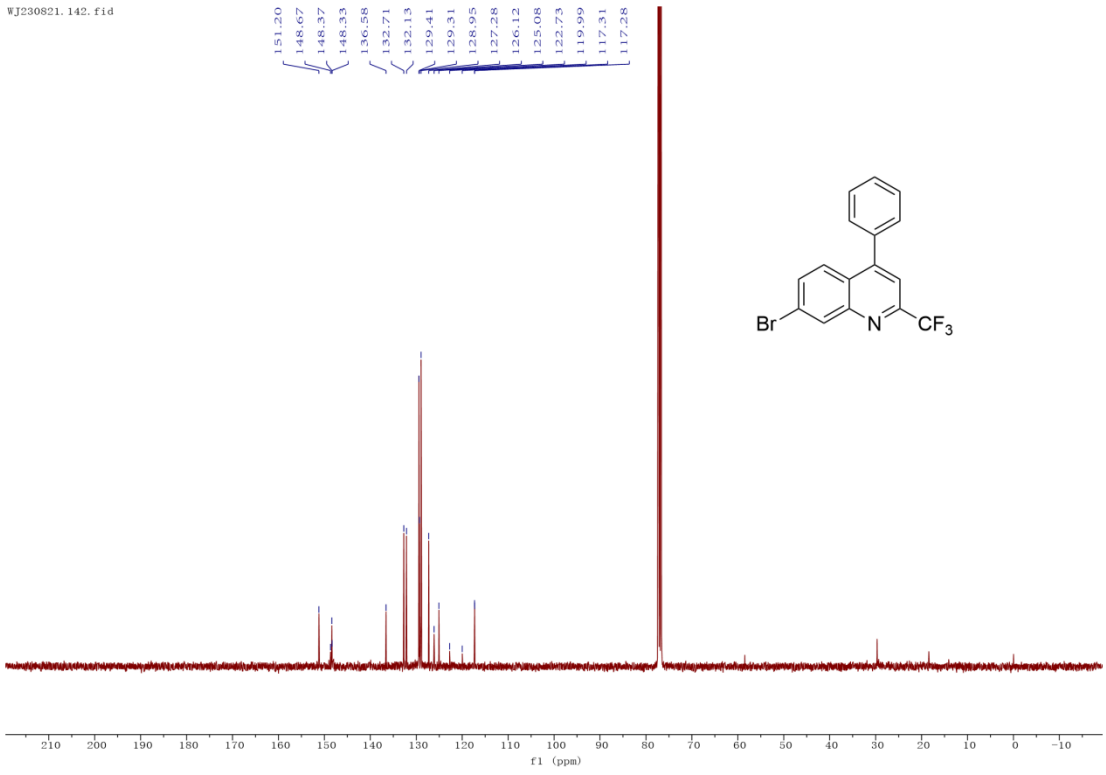
^{19}F NMR (376 MHz, $CDCl_3$) for **3h**



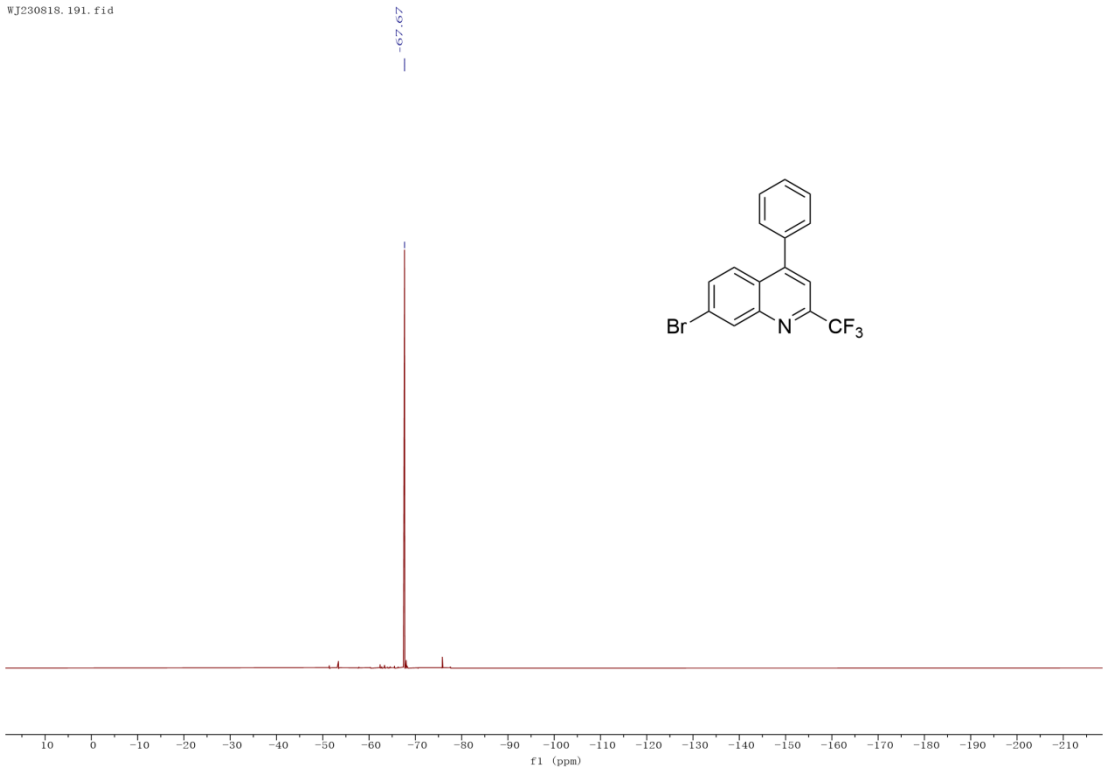
^{1}H NMR (400 MHz, $CDCl_3$) for **3i**



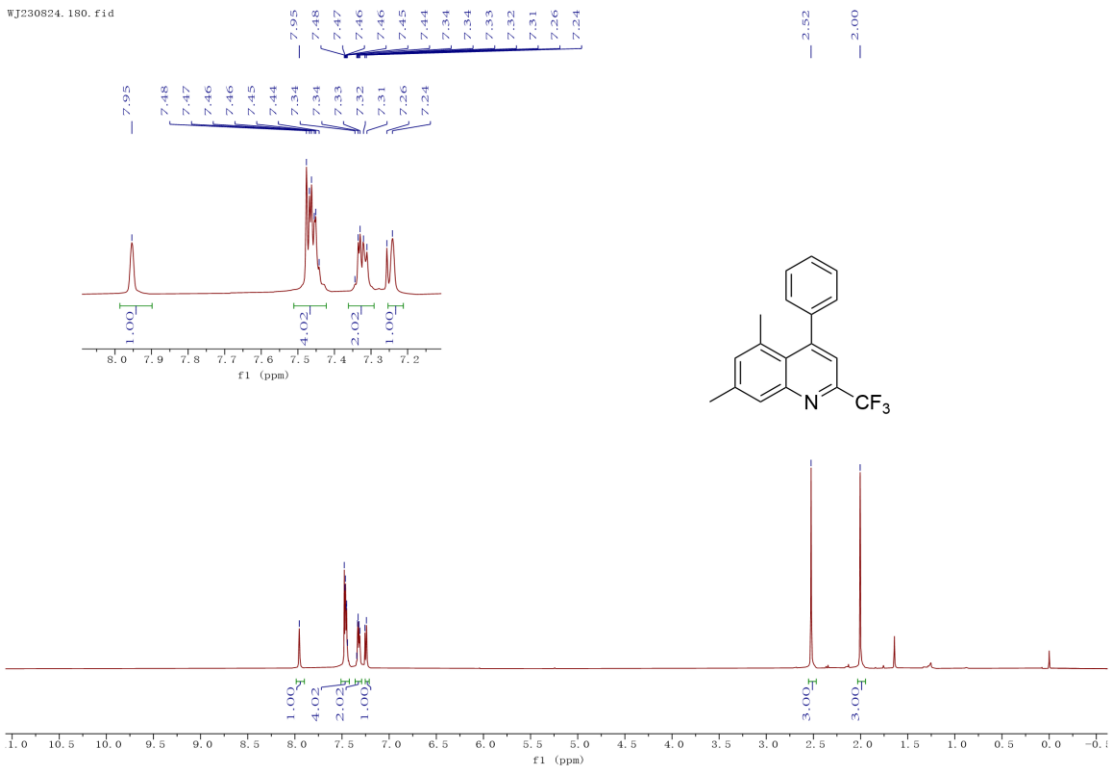
^{13}C NMR (100 MHz, $CDCl_3$) for **3i**



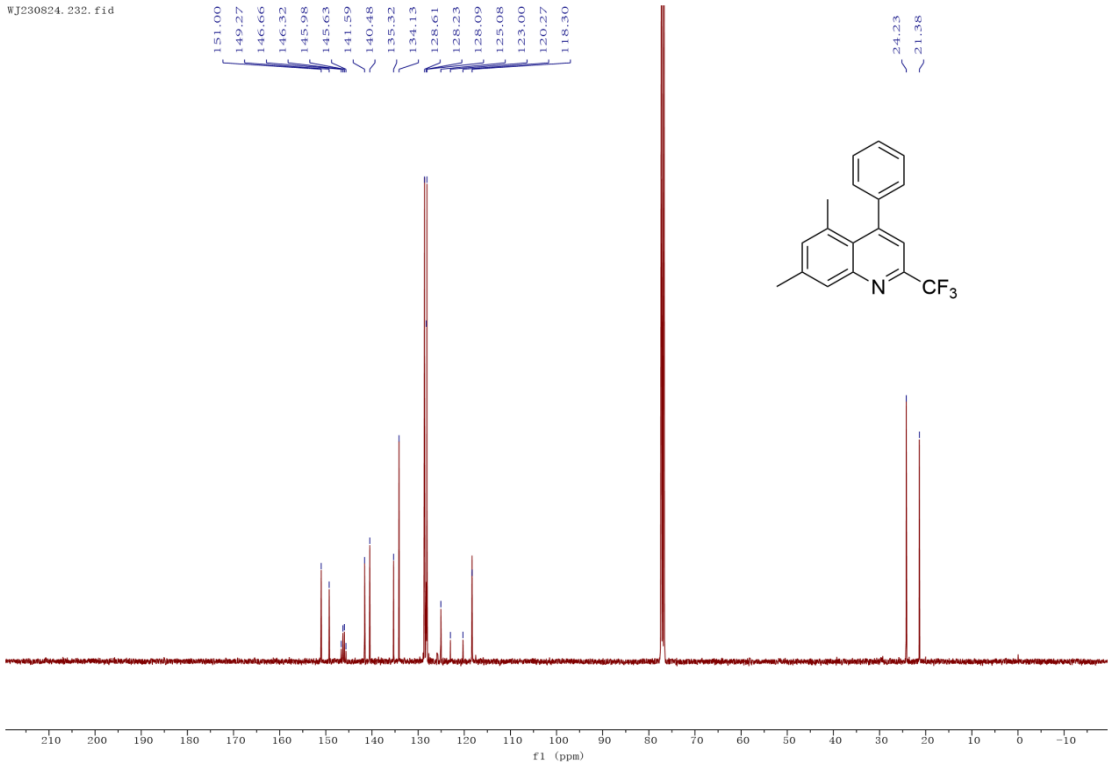
^{19}F NMR (376 MHz, $CDCl_3$) for **3i**



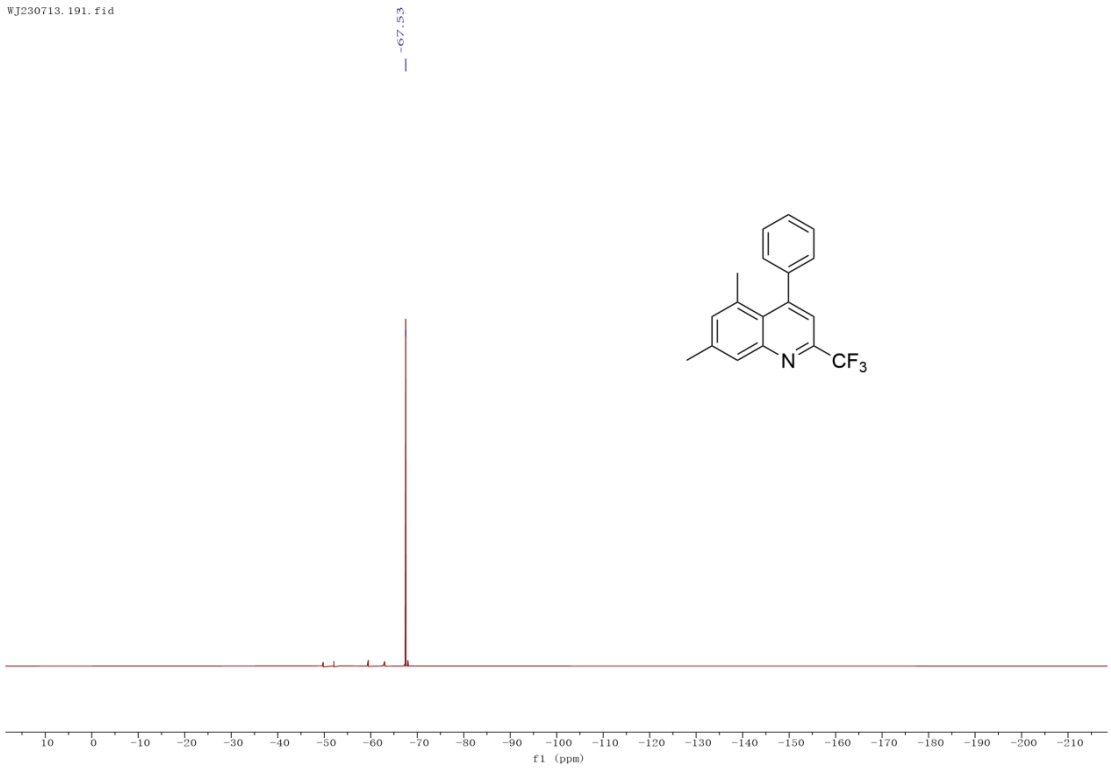
^{1}H NMR (400 MHz, $CDCl_3$) for **3j**



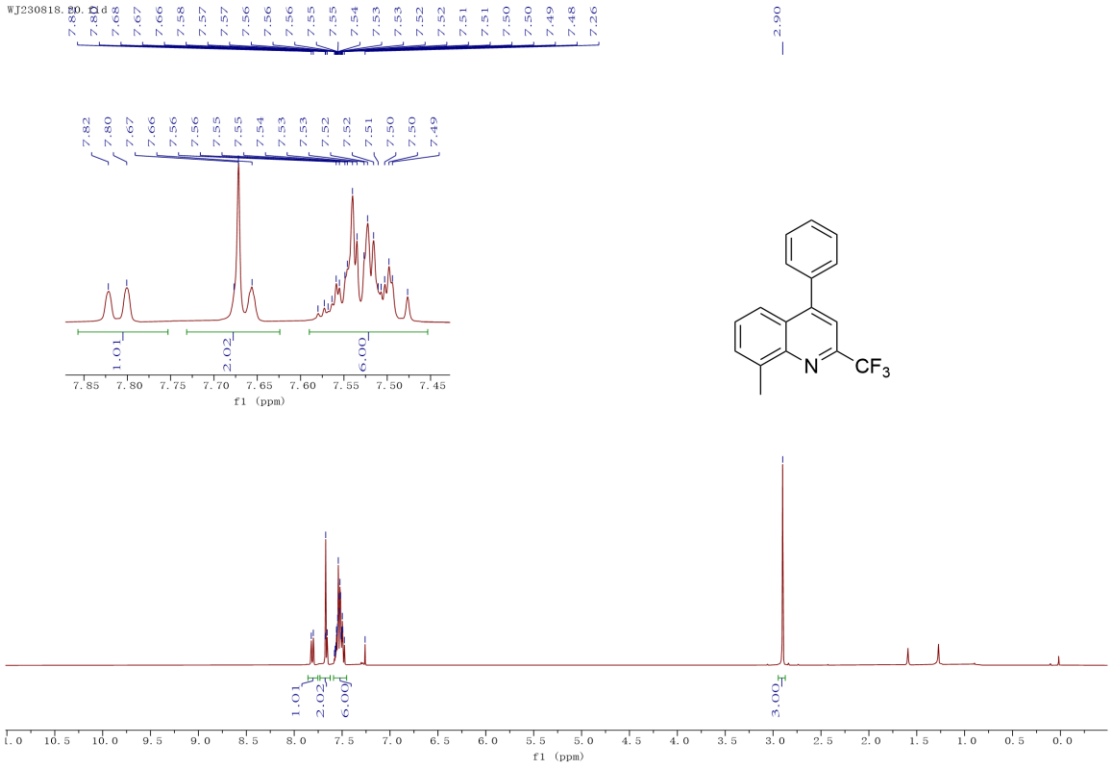
^{13}C NMR (100 MHz, $CDCl_3$) for **3j**



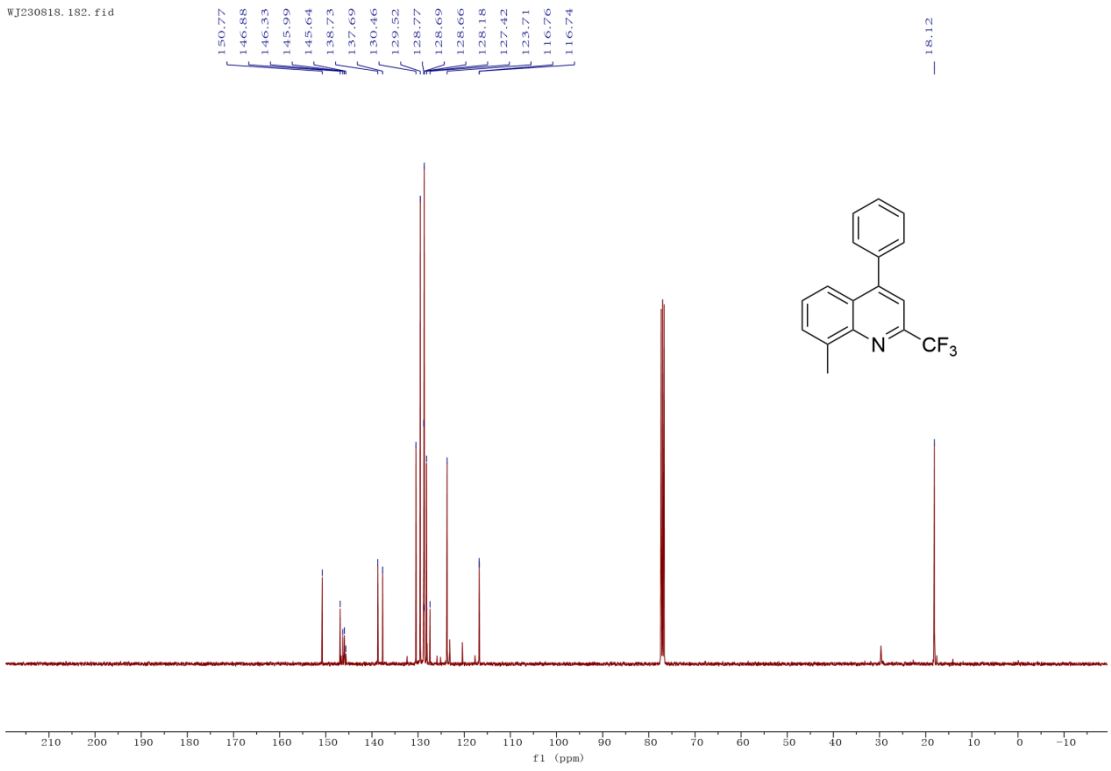
^{19}F NMR (376 MHz, $CDCl_3$) for **3j**



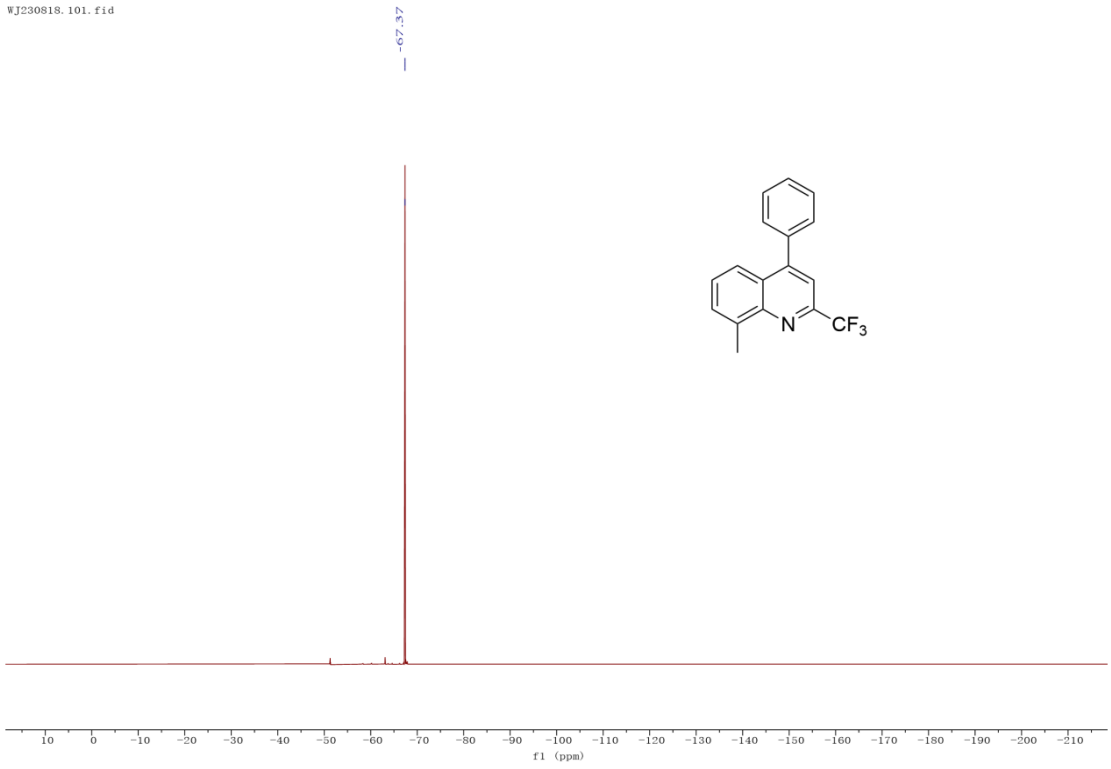
^{1}H NMR (400 MHz, $CDCl_3$) for **3k**



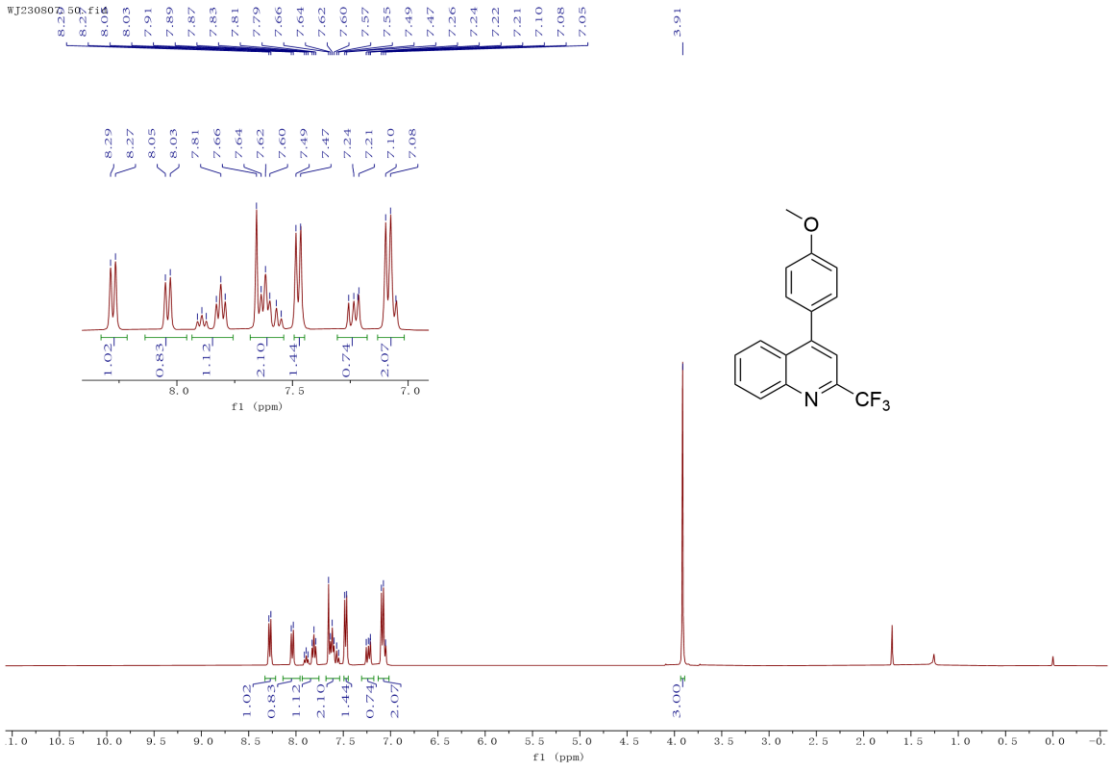
^{13}C NMR (100 MHz, $CDCl_3$) for **3k**



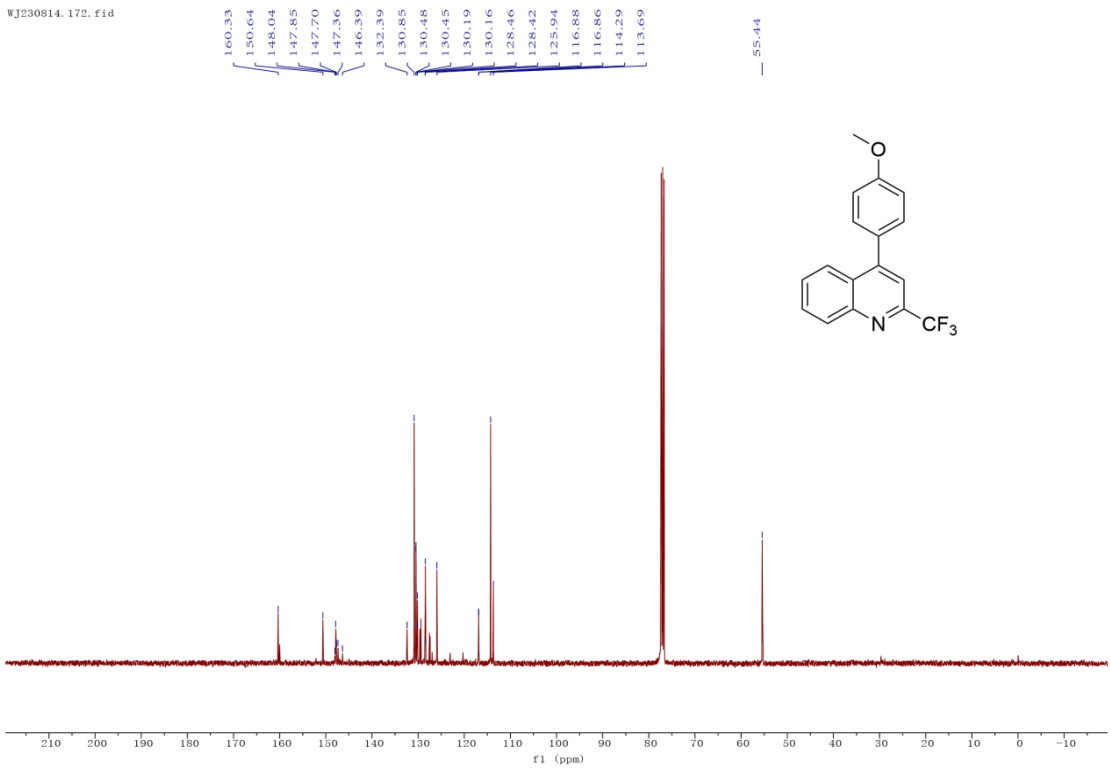
^{19}F NMR (376 MHz, $CDCl_3$) for **3k**



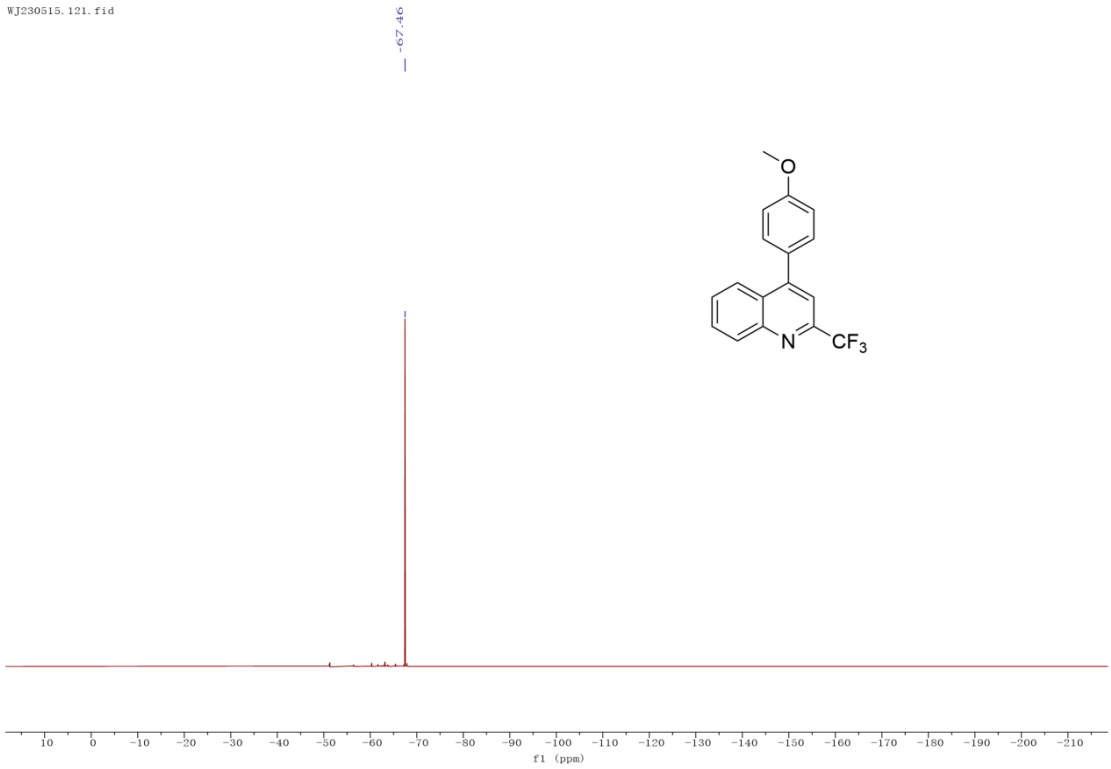
^{1}H NMR (400 MHz, $CDCl_3$) for **3l**



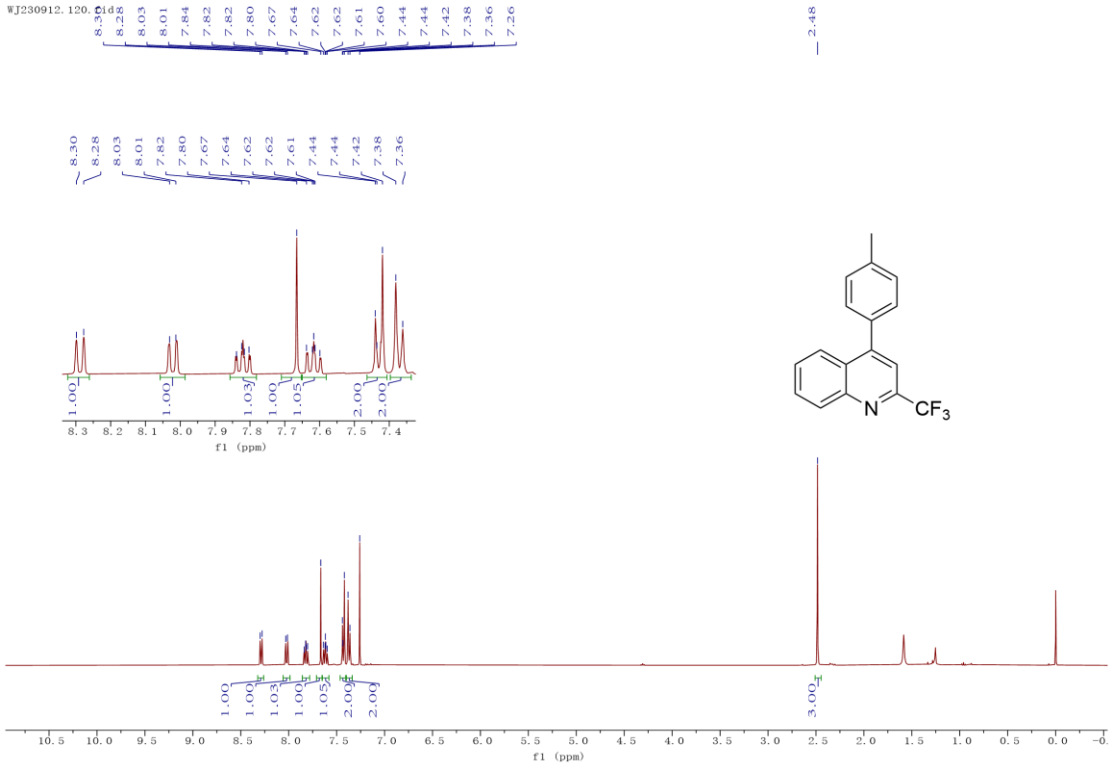
^{13}C NMR (100 MHz, $CDCl_3$) for **3l**



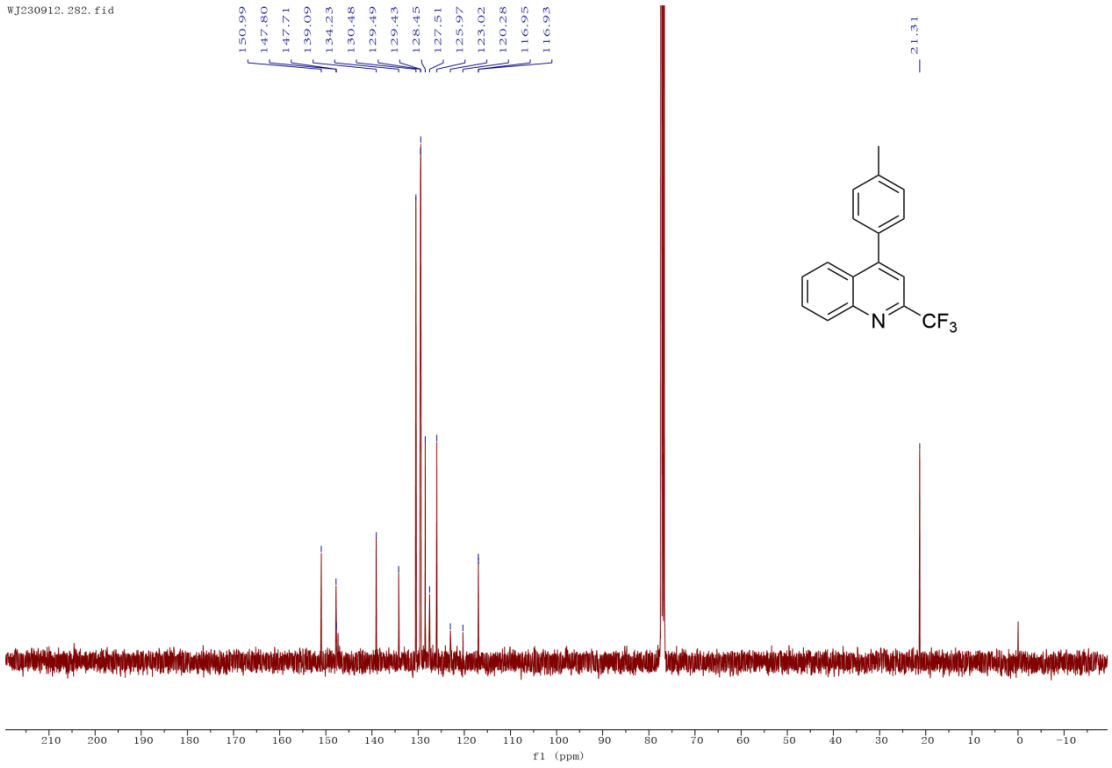
^{19}F NMR (376 MHz, $CDCl_3$) for **3l**



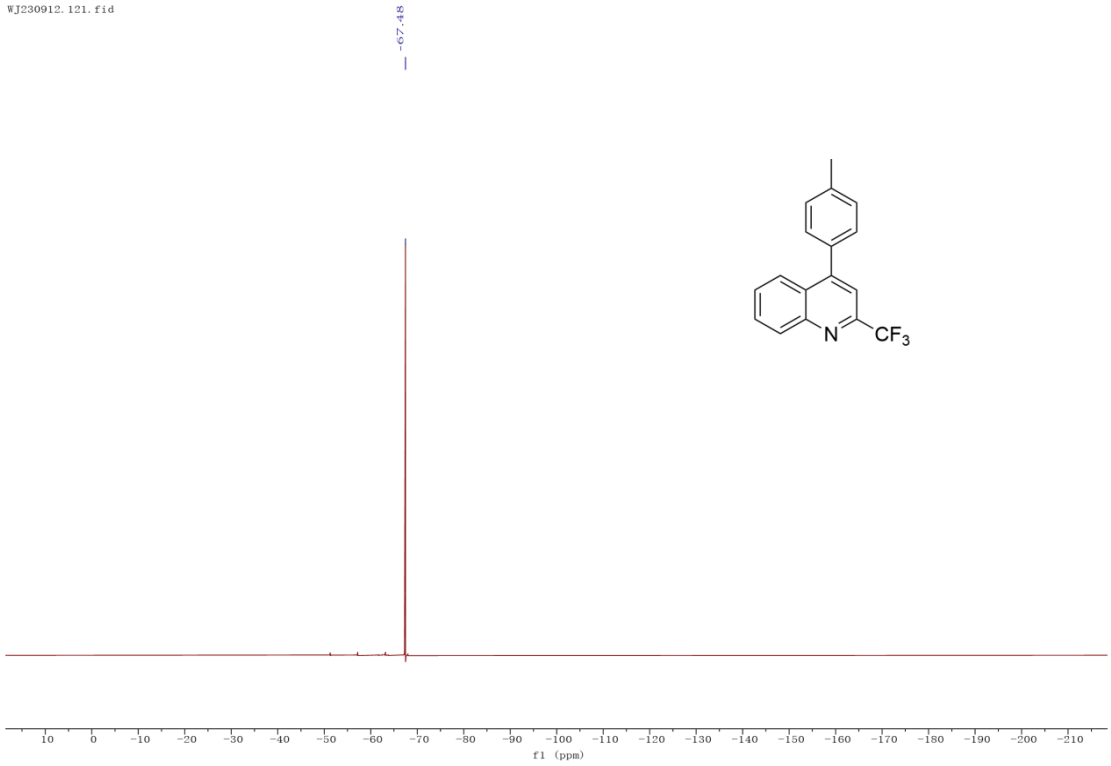
^{1}H NMR (400 MHz, $CDCl_3$) for **3m**



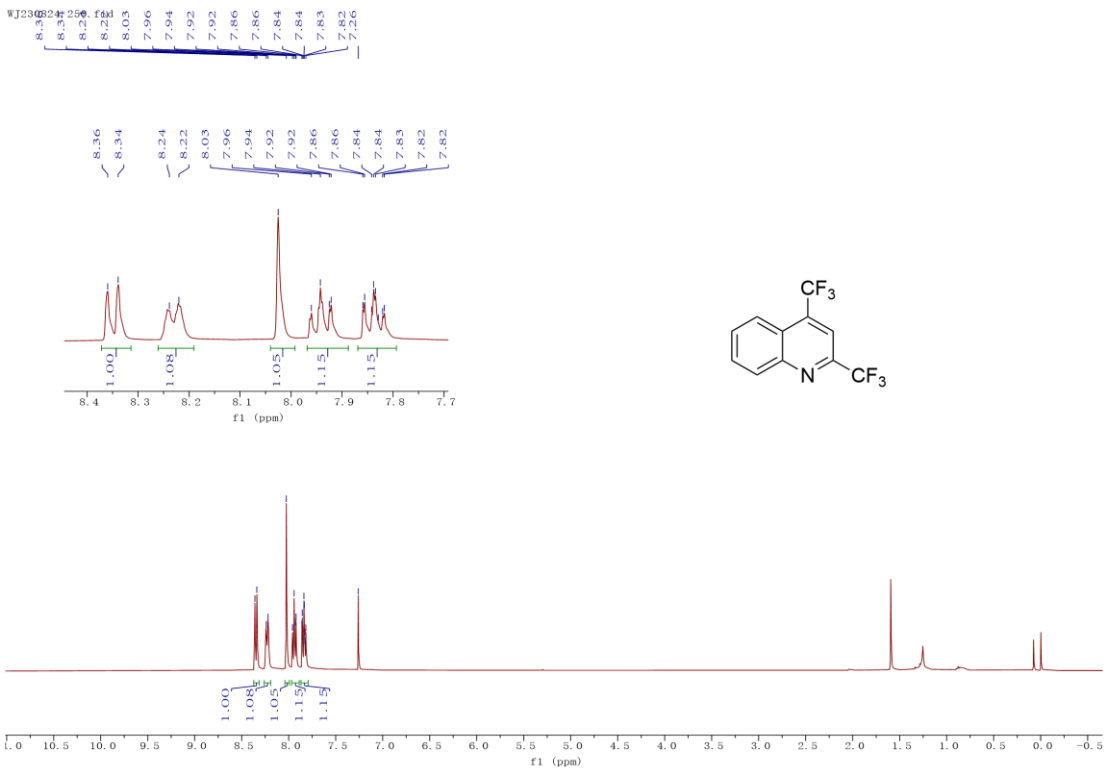
^{13}C NMR (100 MHz, $CDCl_3$) for **3m**



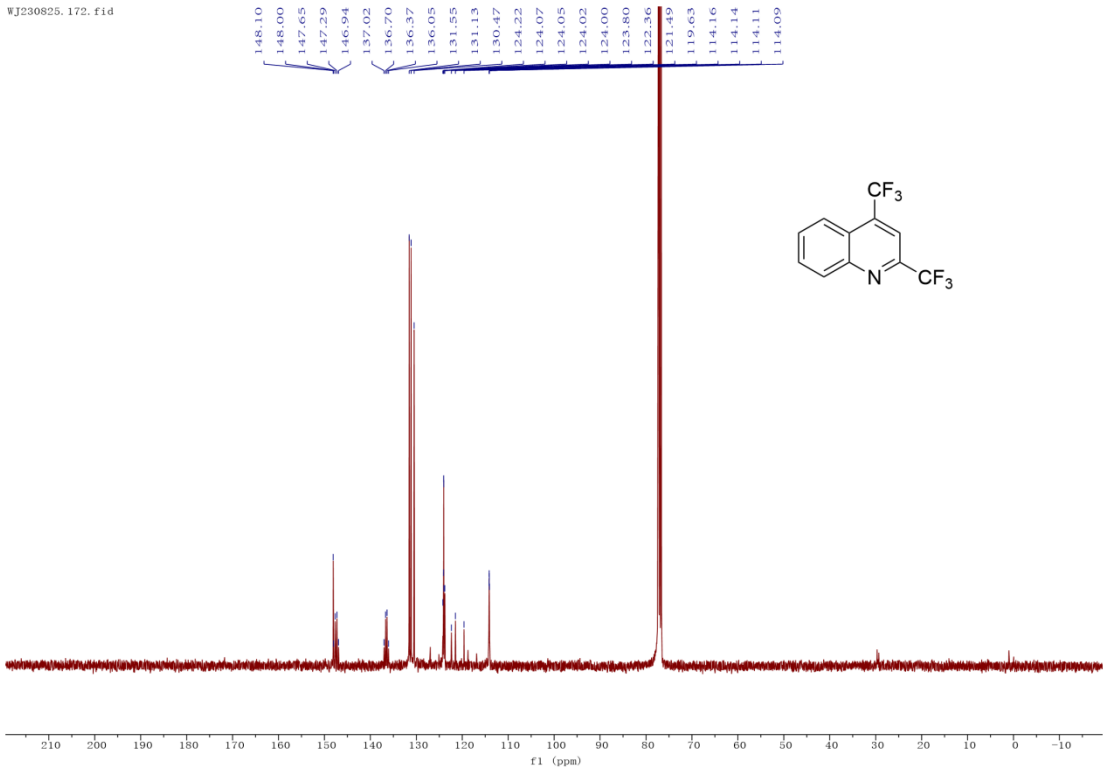
^{19}F NMR (376 MHz, $CDCl_3$) for **3m**



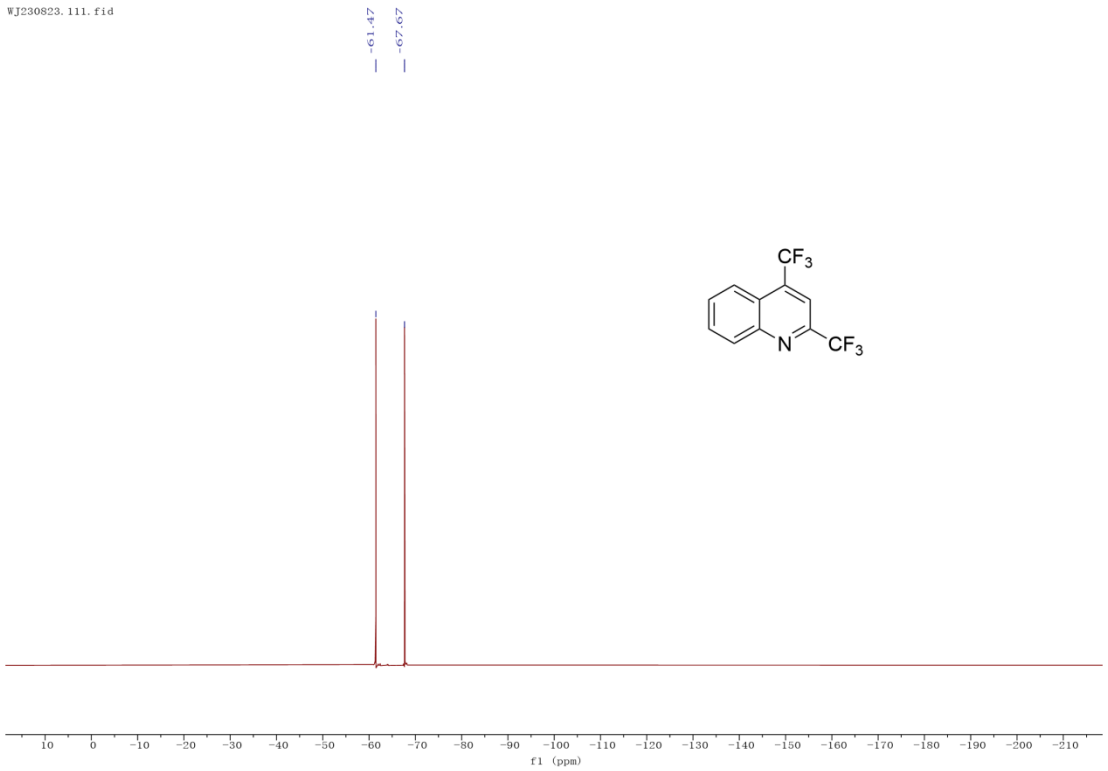
^{1}H NMR (400 MHz, $CDCl_3$) for **3n**



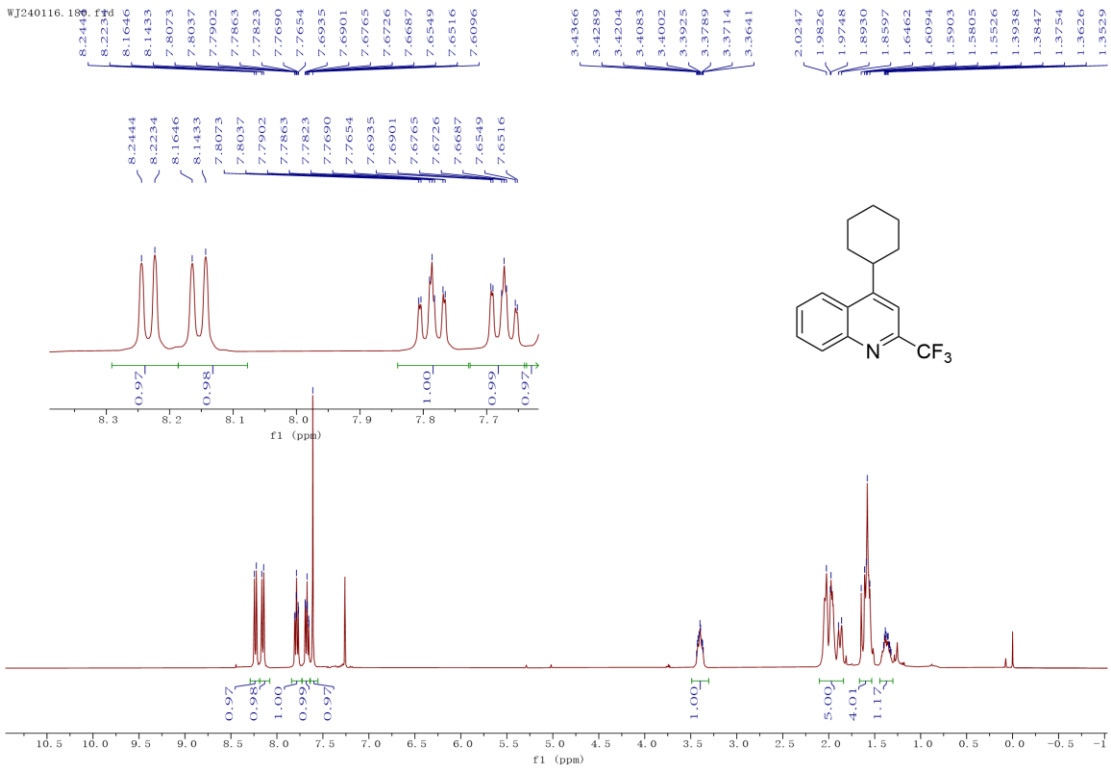
^{13}C NMR (100 MHz, $CDCl_3$) for **3n**



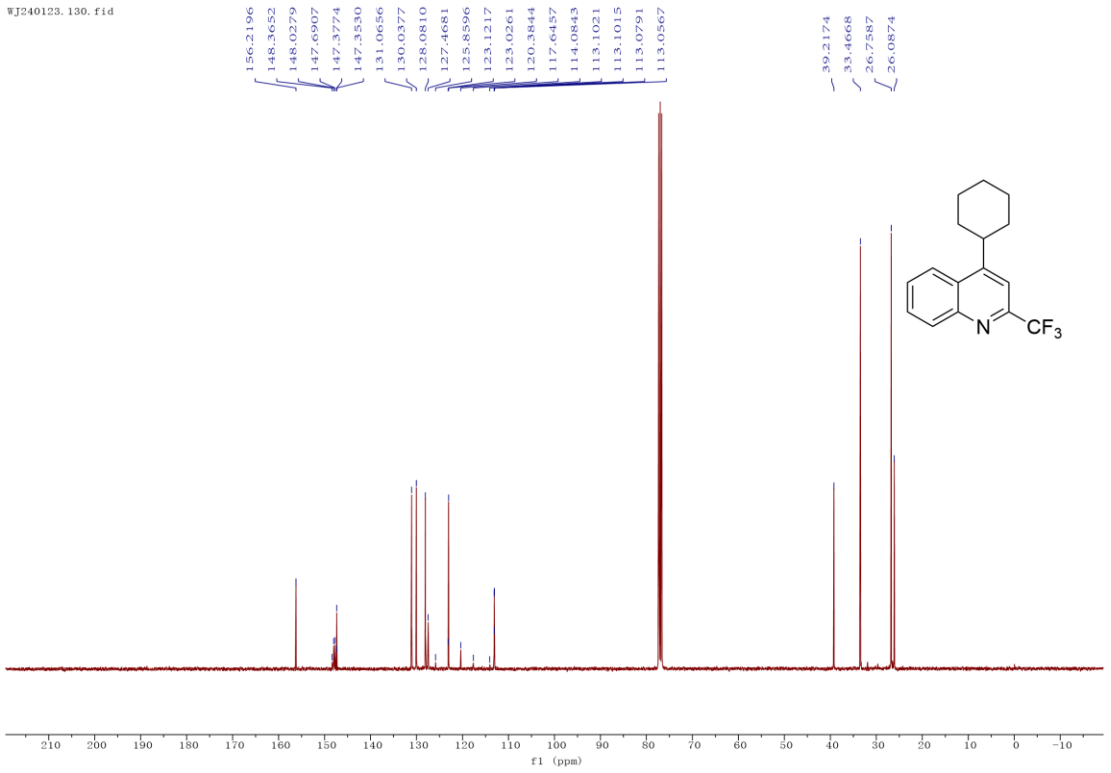
^{19}F NMR (376 MHz, $CDCl_3$) for **3n**



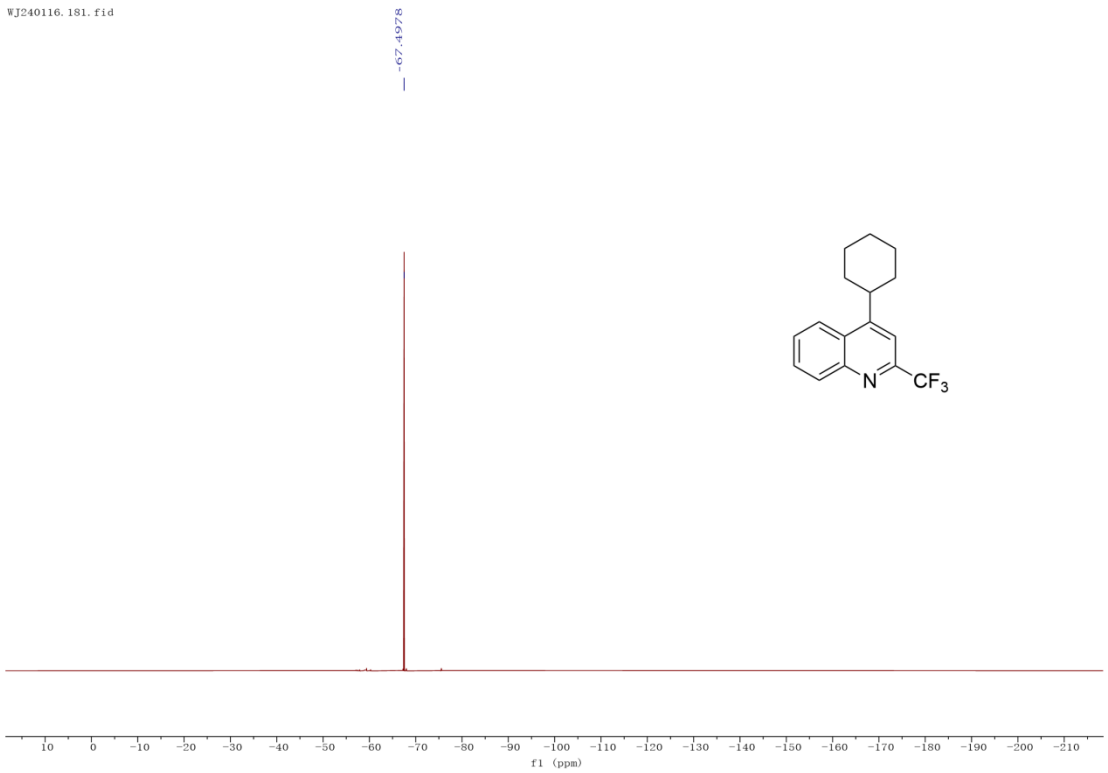
^{1}H NMR (400 MHz, $CDCl_3$) for **3o**



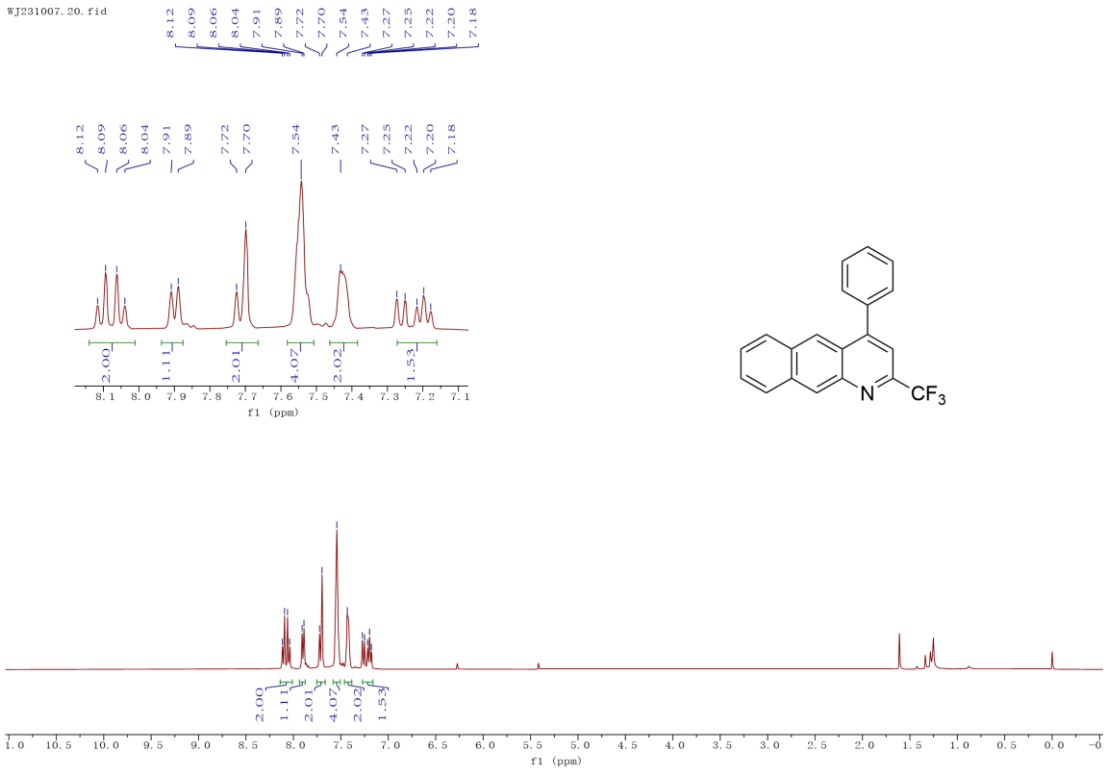
^{13}C NMR (100 MHz, $CDCl_3$) for **3o**



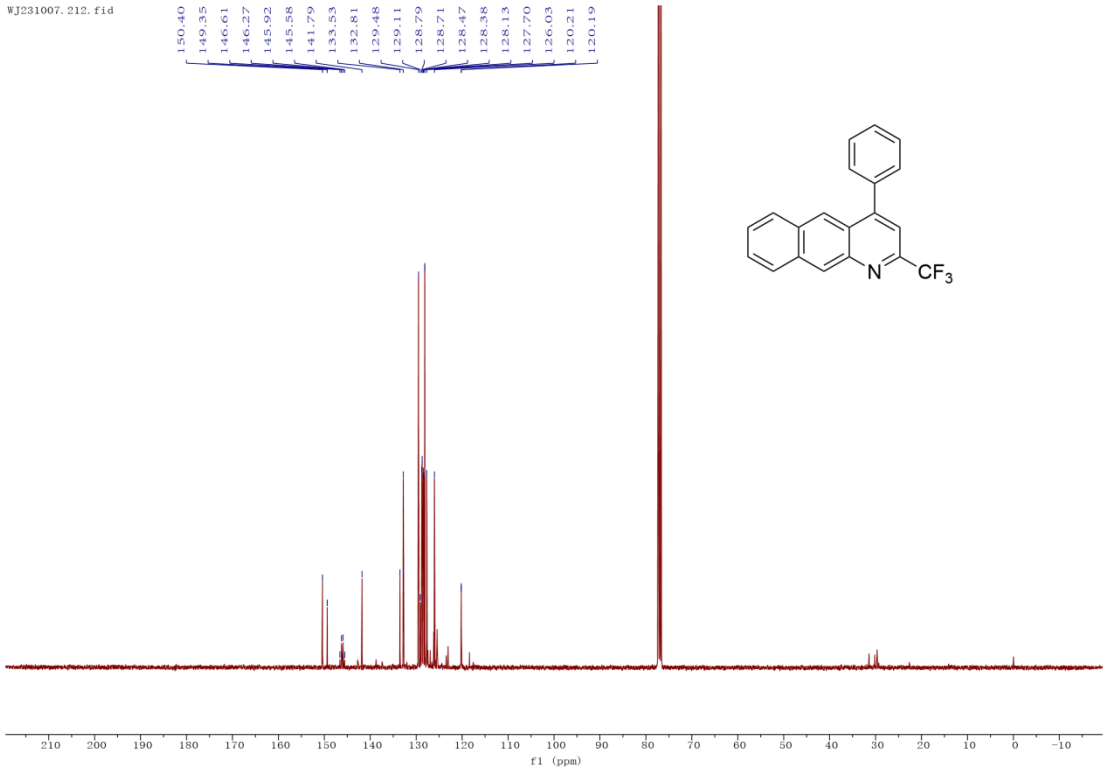
^{19}F NMR (376 MHz, $CDCl_3$) for **3o**



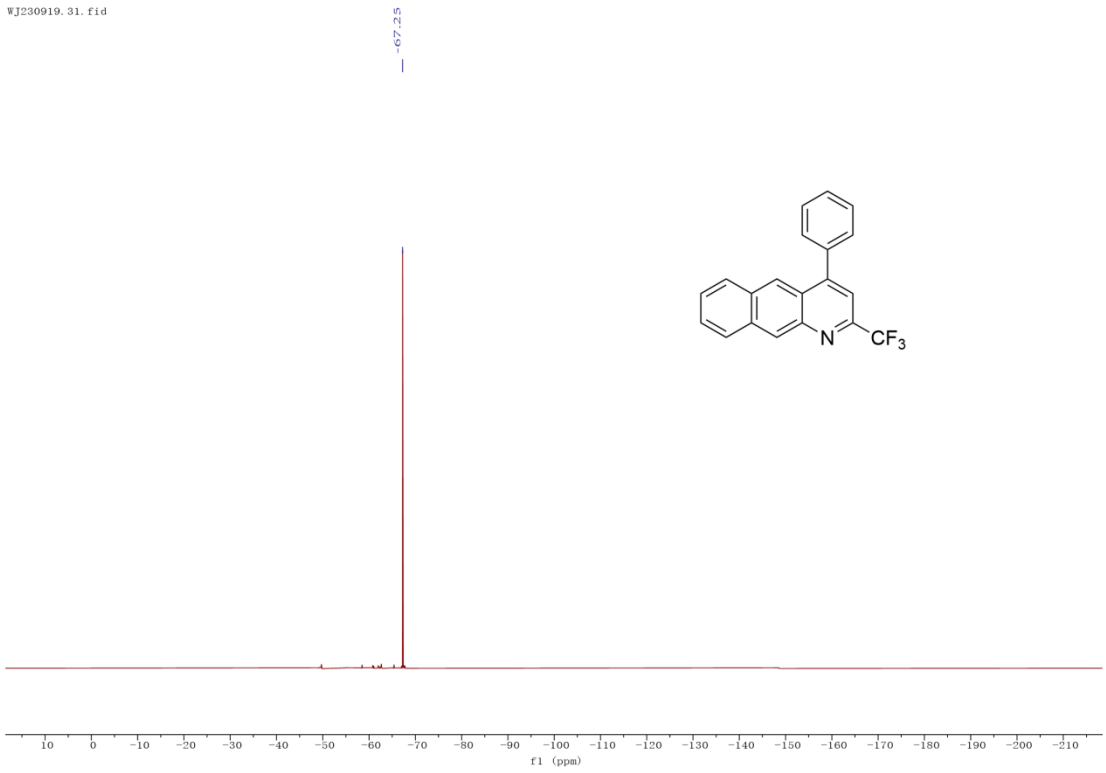
^{1}H NMR (400 MHz, $CDCl_3$) for **3p**



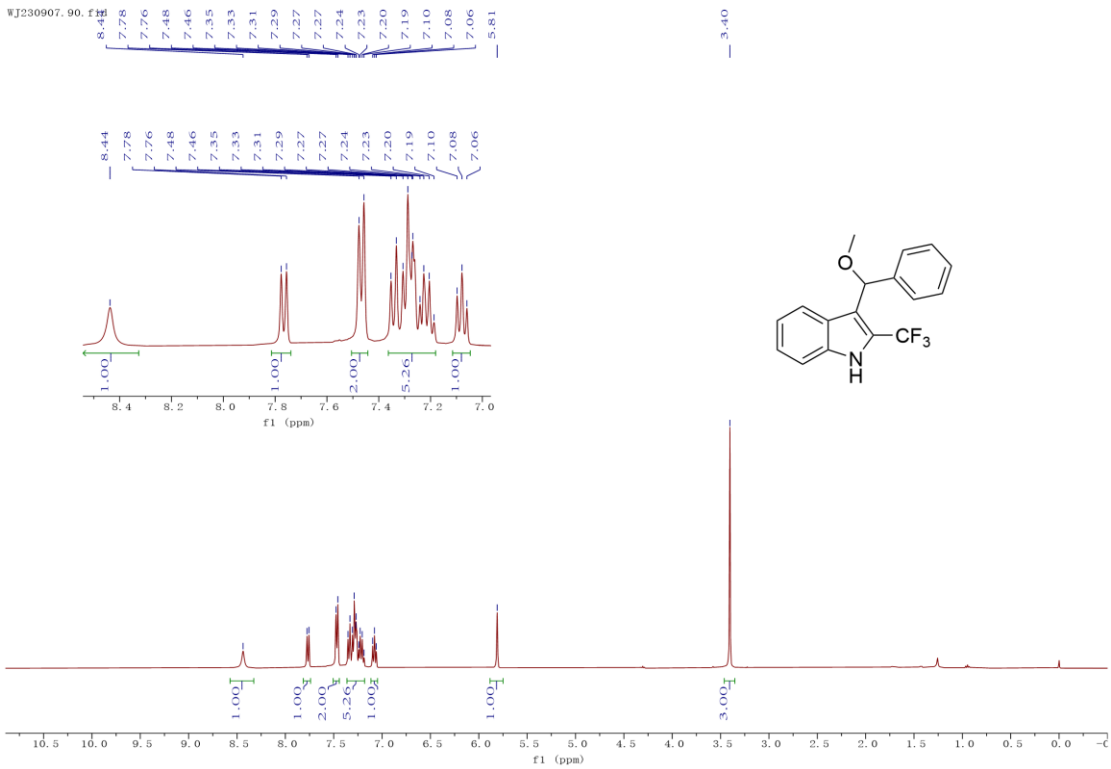
^{13}C NMR (100 MHz, $CDCl_3$) for **3p**



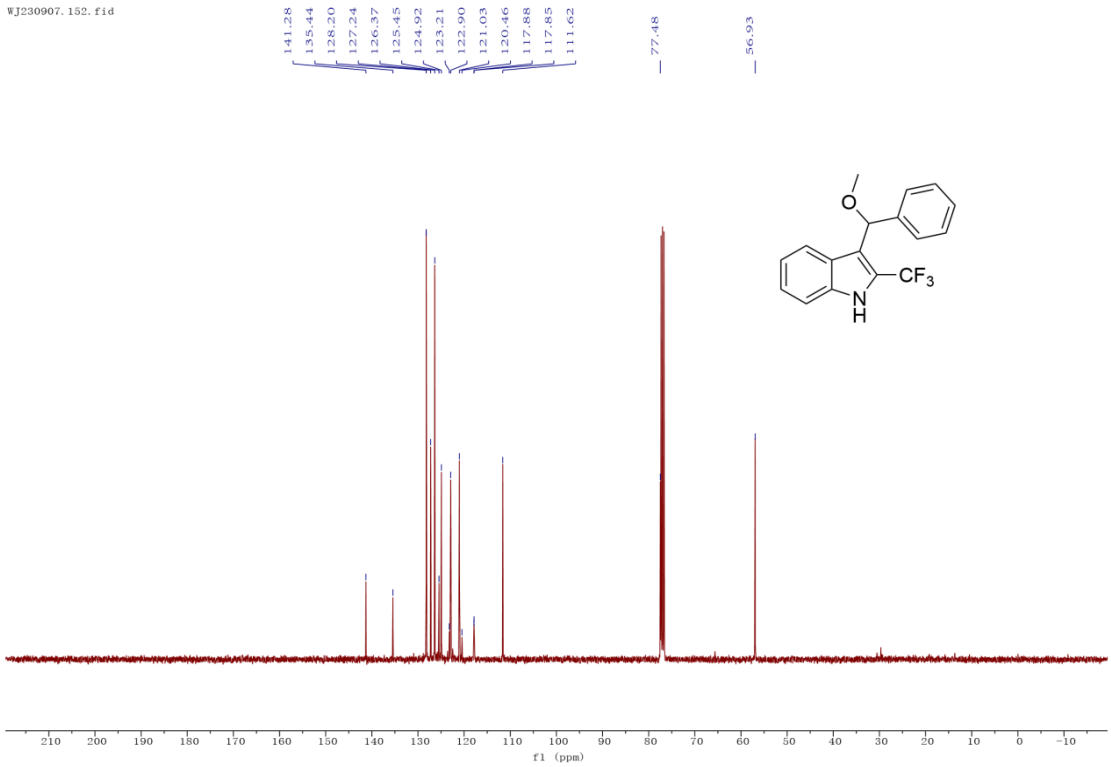
^{19}F NMR (376 MHz, $CDCl_3$) for **3p**



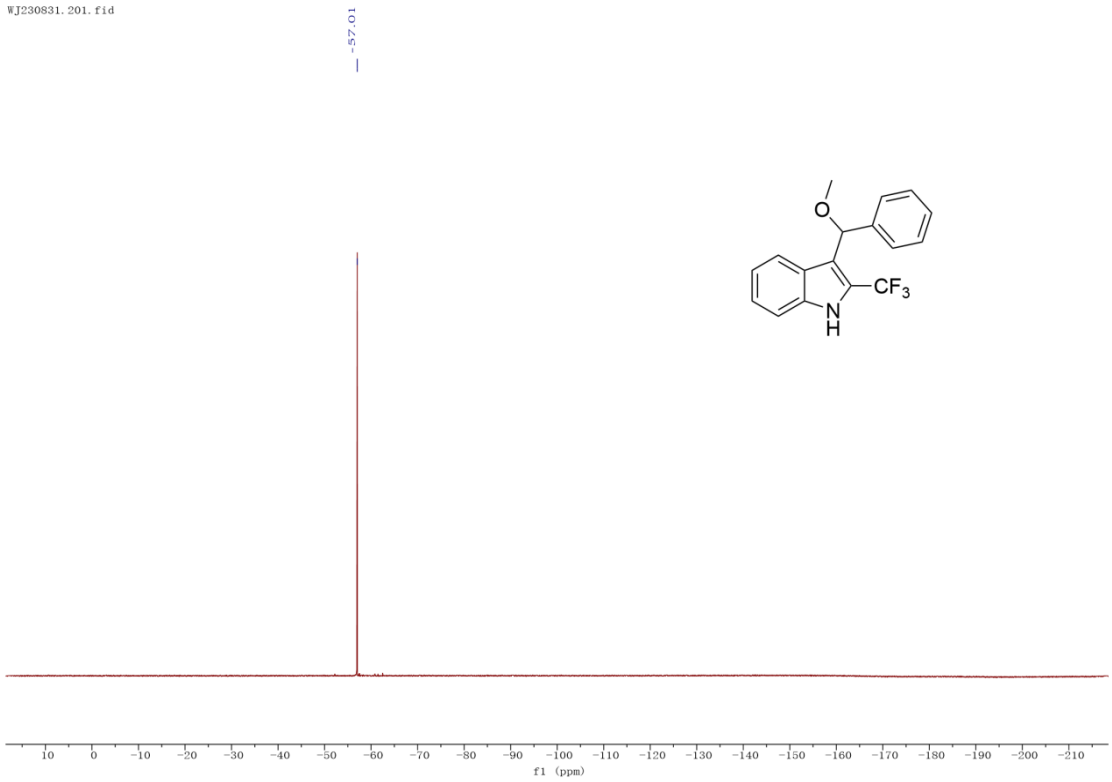
^{1}H NMR (400 MHz, $CDCl_3$) for **5a**



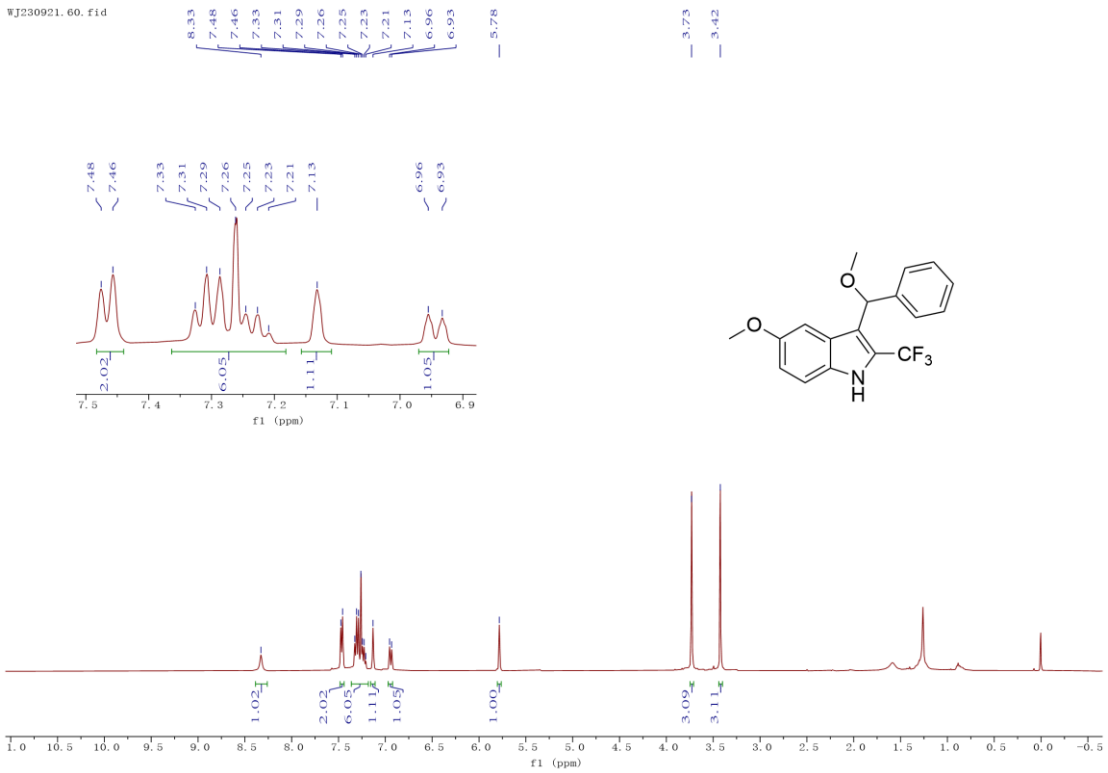
^{13}C NMR (100 MHz, $CDCl_3$) for **5a**



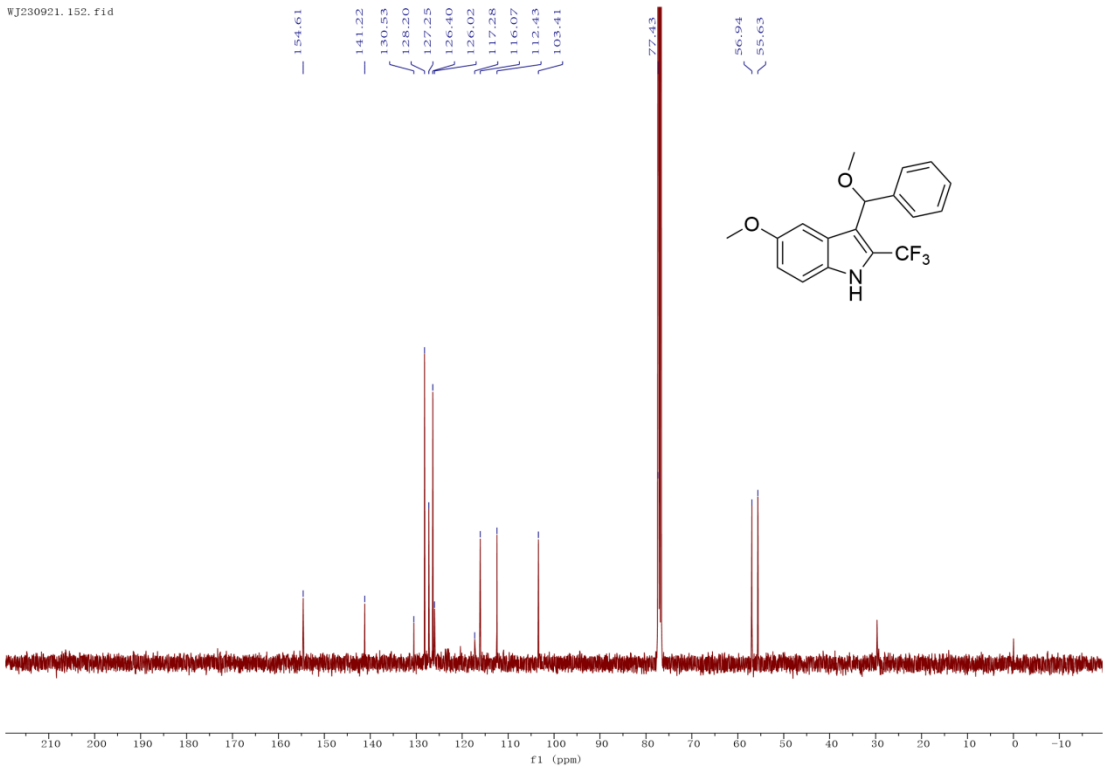
^{19}F NMR (376 MHz, $CDCl_3$) for **5a**



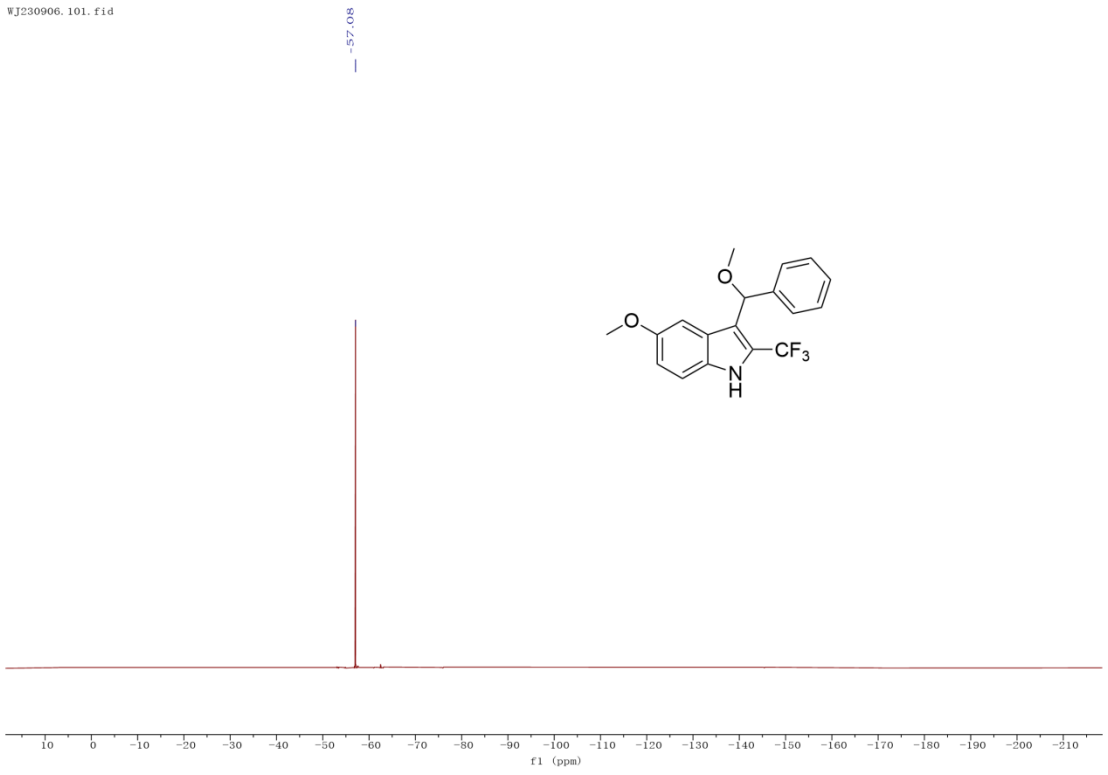
^{1}H NMR (400 MHz, $CDCl_3$) for **5b**



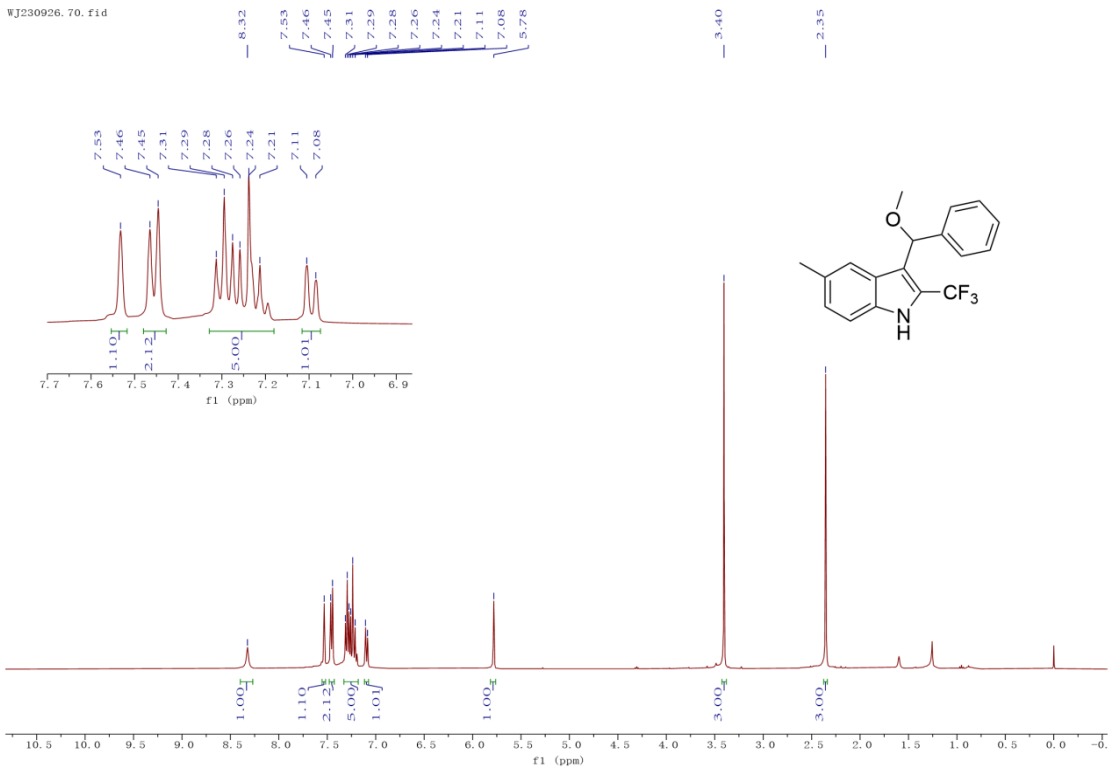
^{13}C NMR (100 MHz, $CDCl_3$) for **5b**



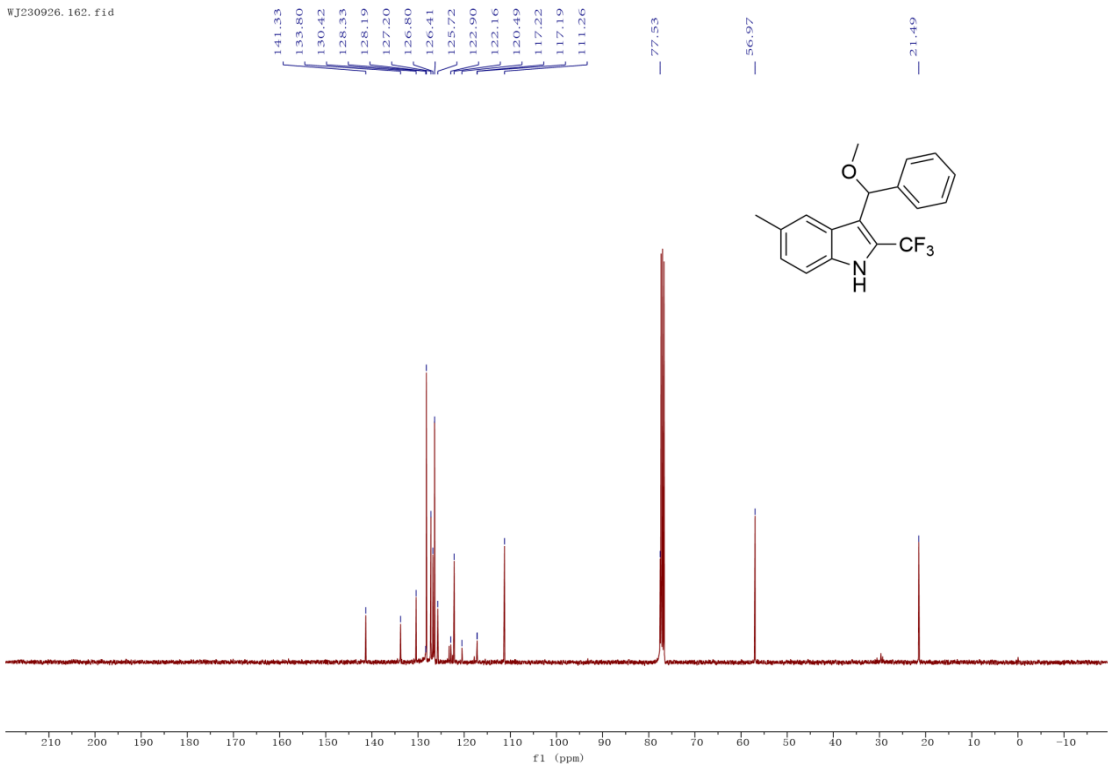
^{19}F NMR (376 MHz, $CDCl_3$) for **5b**



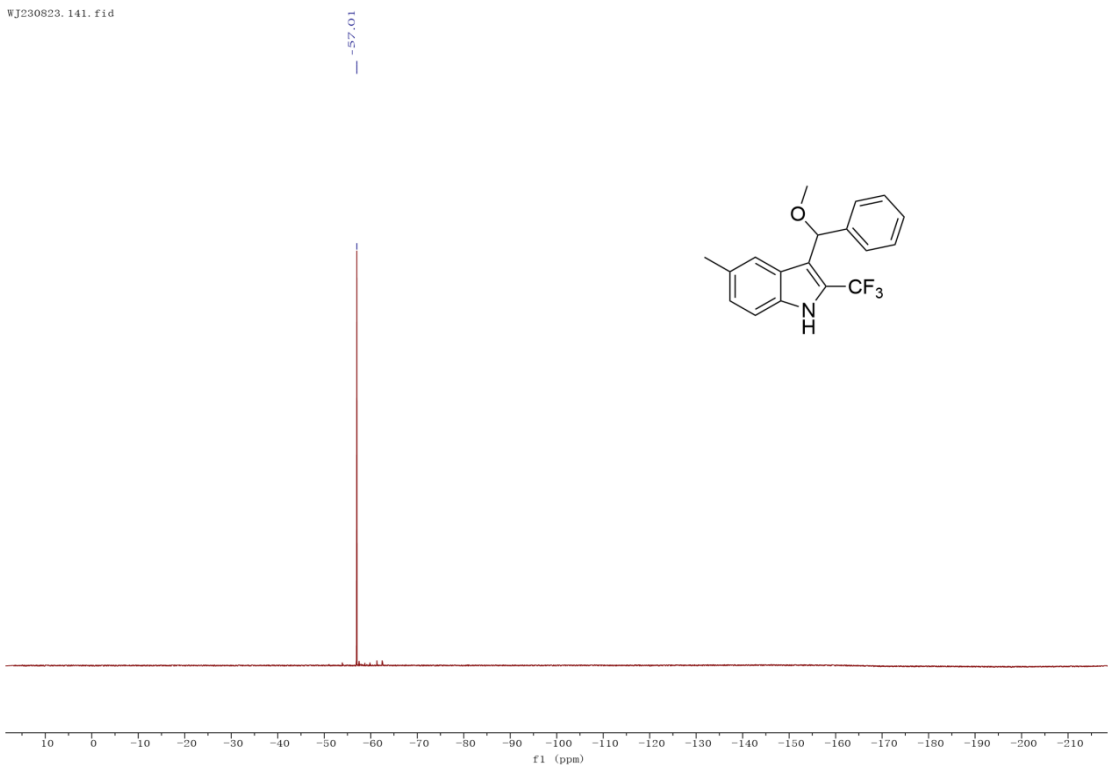
^{1}H NMR (400 MHz, $CDCl_3$) for **5c**



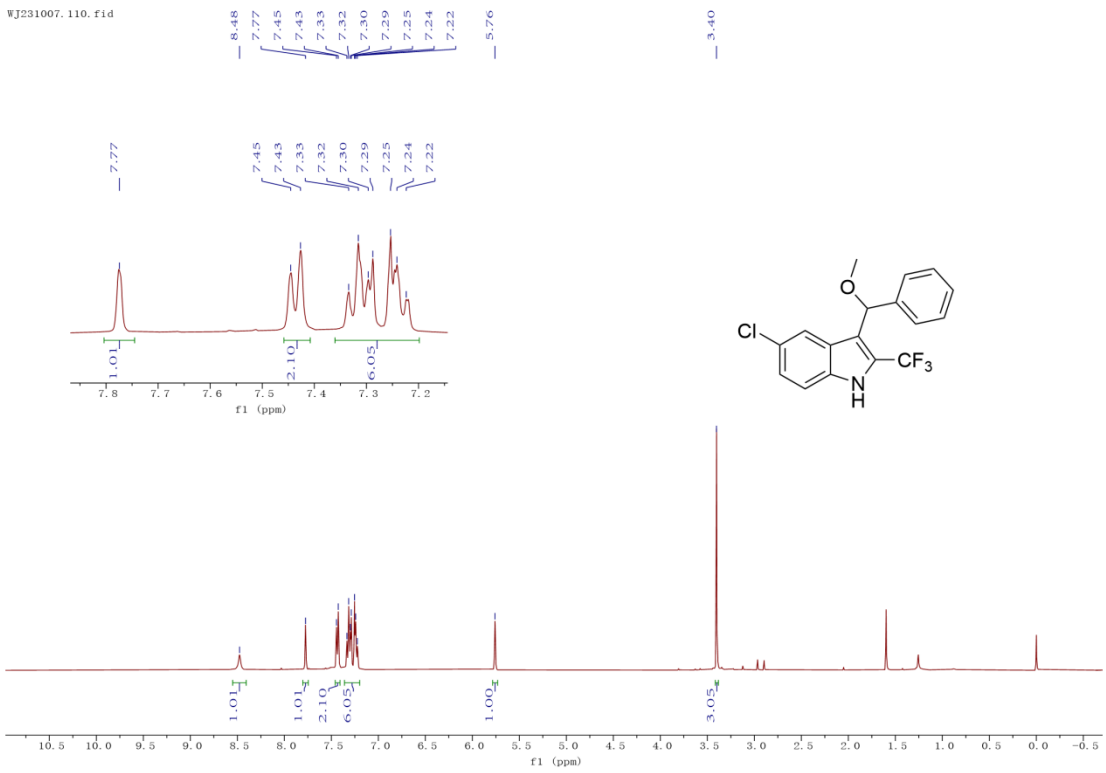
^{13}C NMR (100 MHz, $CDCl_3$) for **5c**



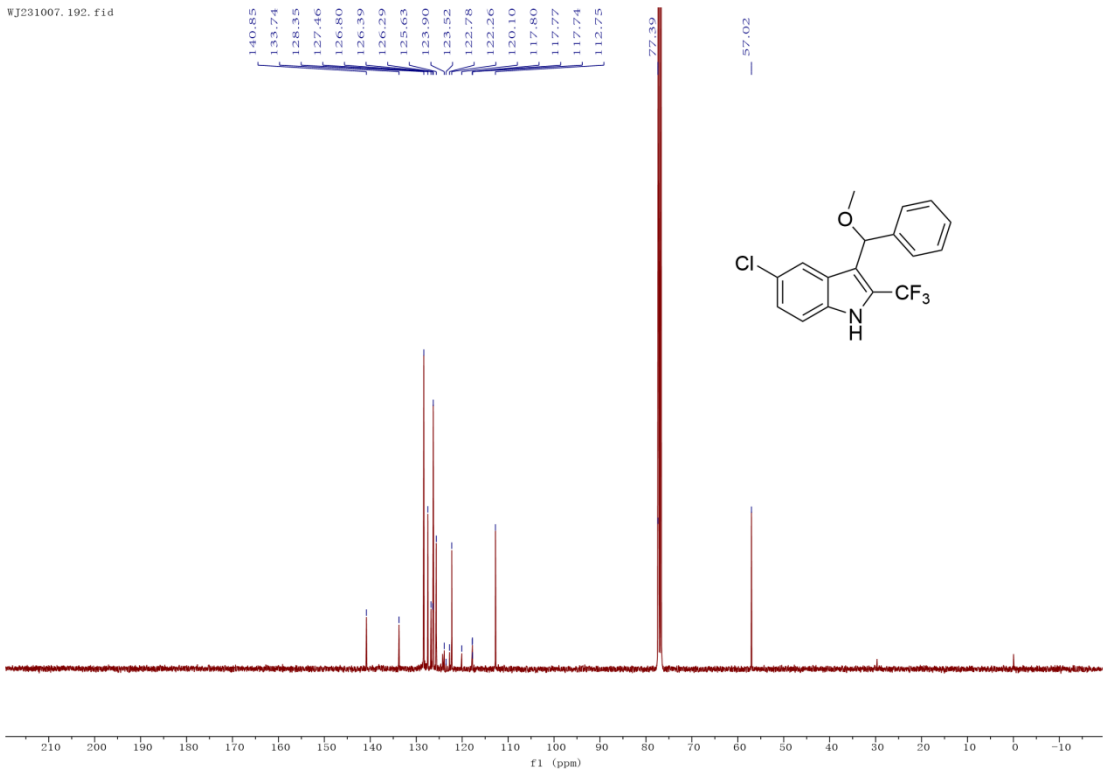
^{19}F NMR (376 MHz, $CDCl_3$) for **5c**



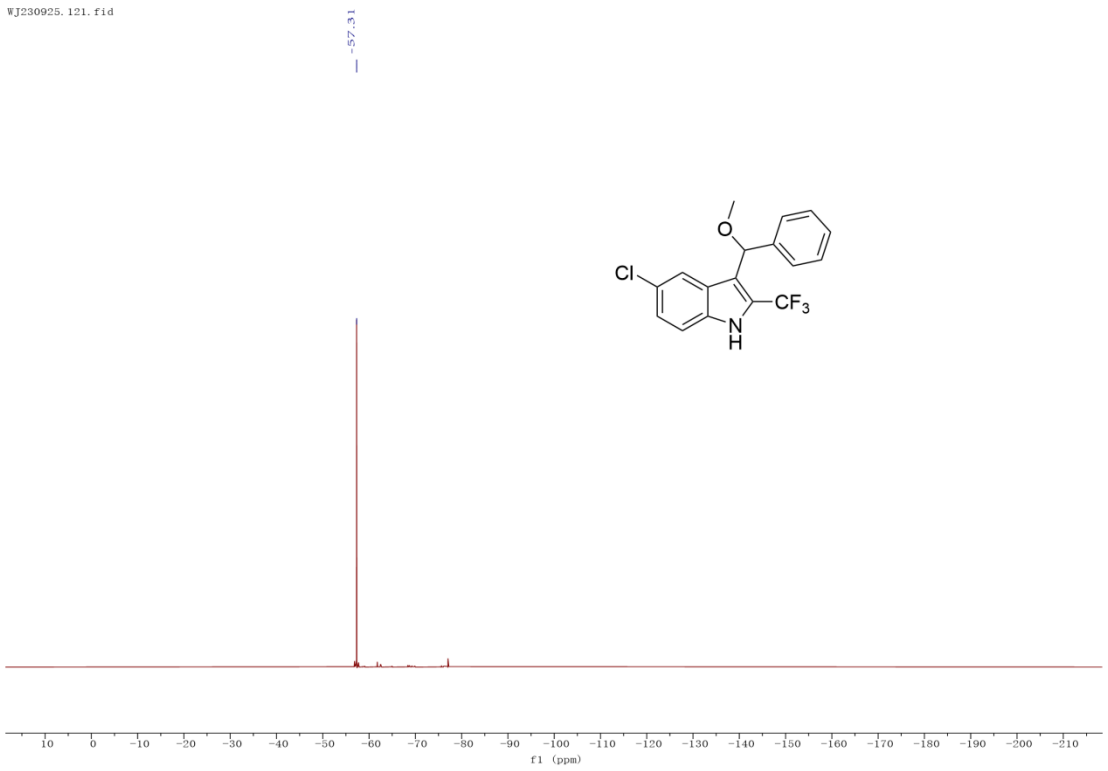
^{1}H NMR (400 MHz, $CDCl_3$) for **5d**



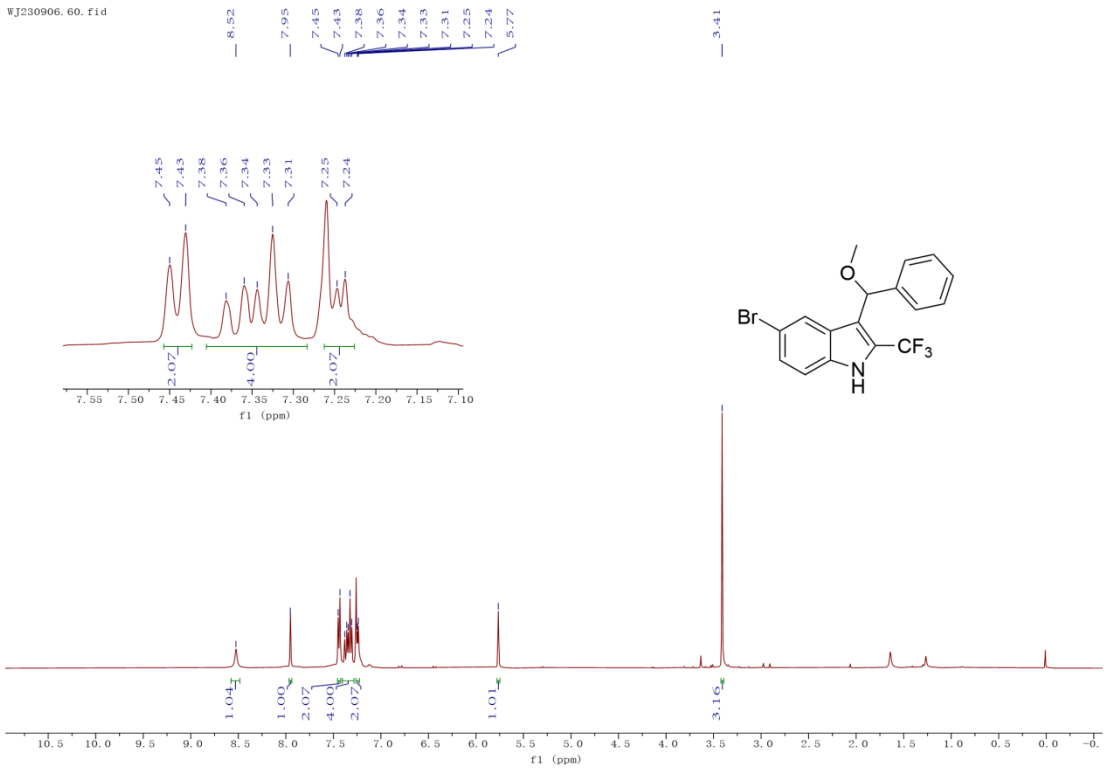
^{13}C NMR (100 MHz, $CDCl_3$) for **5d**



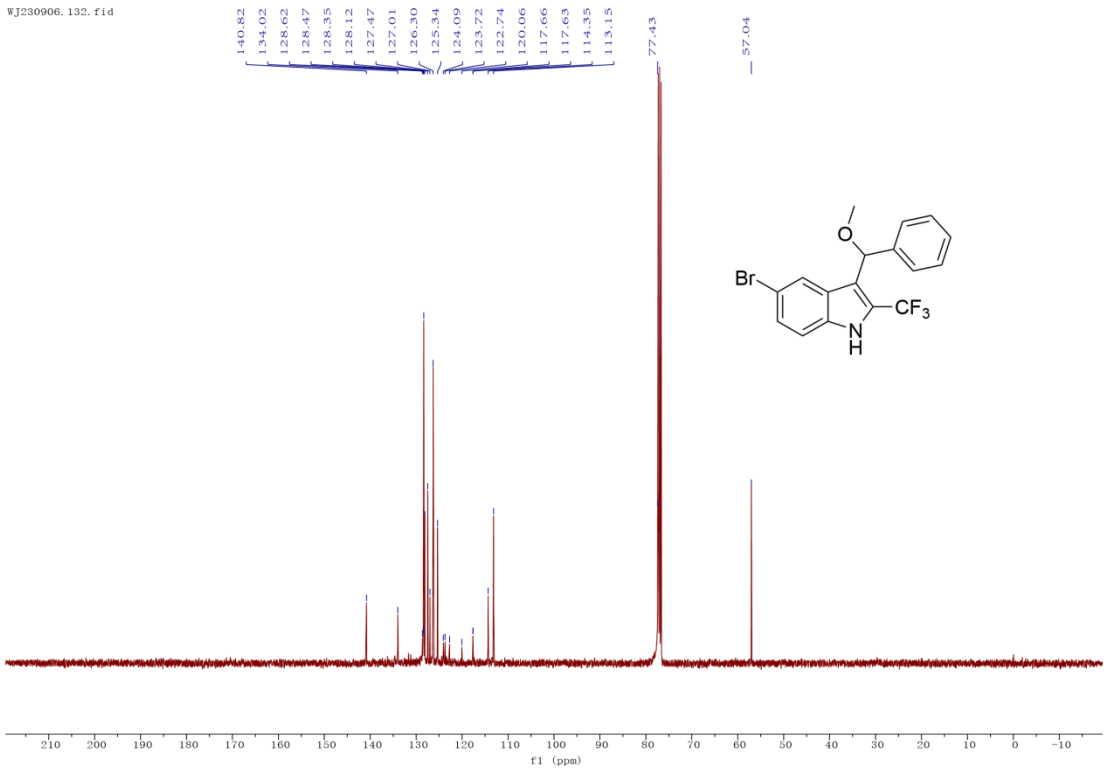
^{19}F NMR (376 MHz, $CDCl_3$) for **5d**



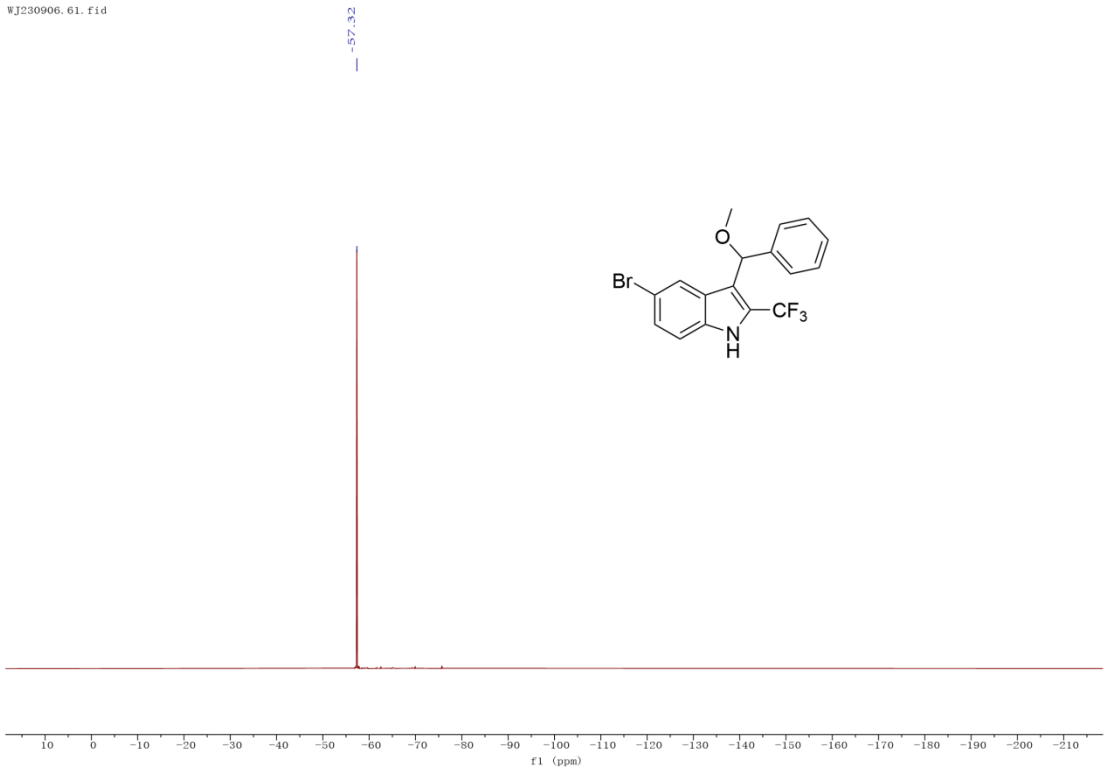
^{1}H NMR (400 MHz, $CDCl_3$) for **5e**



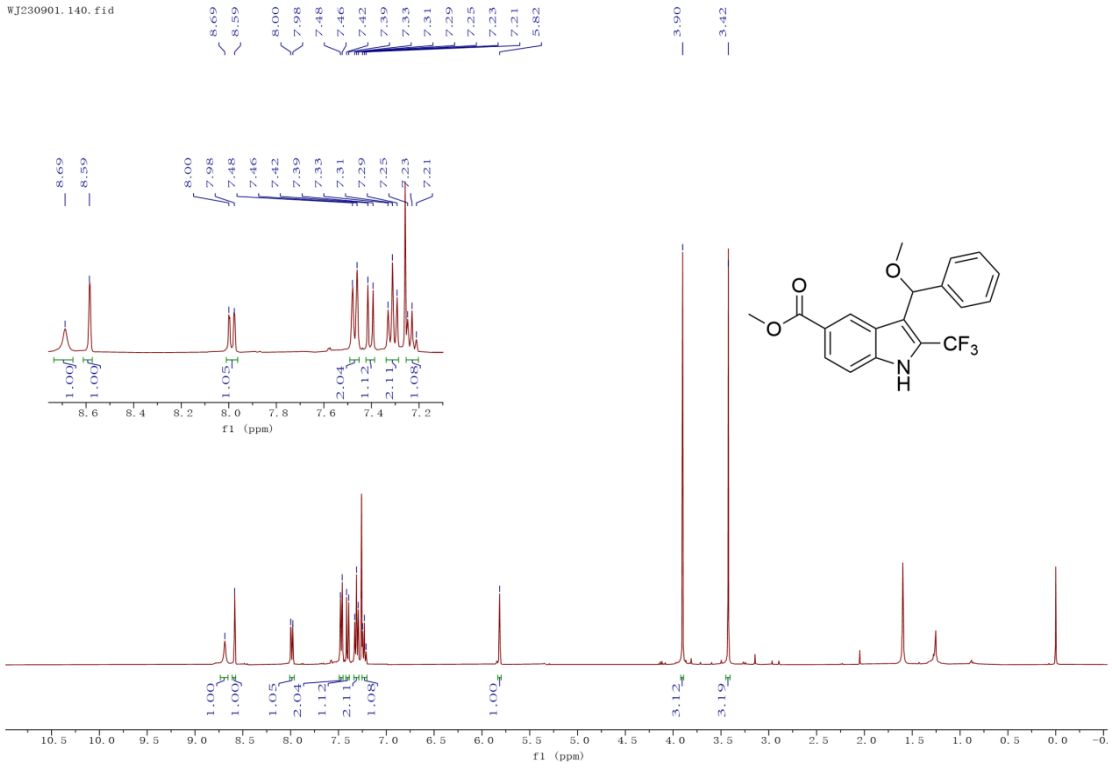
^{13}C NMR (100 MHz, $CDCl_3$) for **5e**



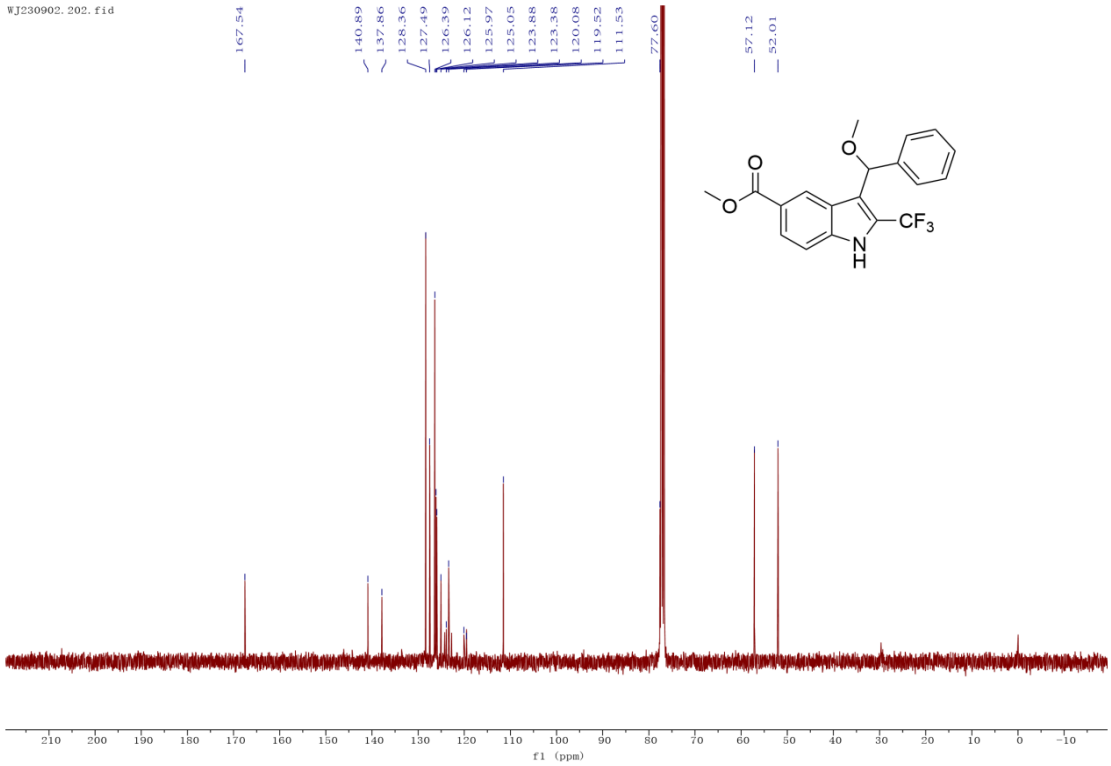
^{19}F NMR (376 MHz, $CDCl_3$) for **5e**



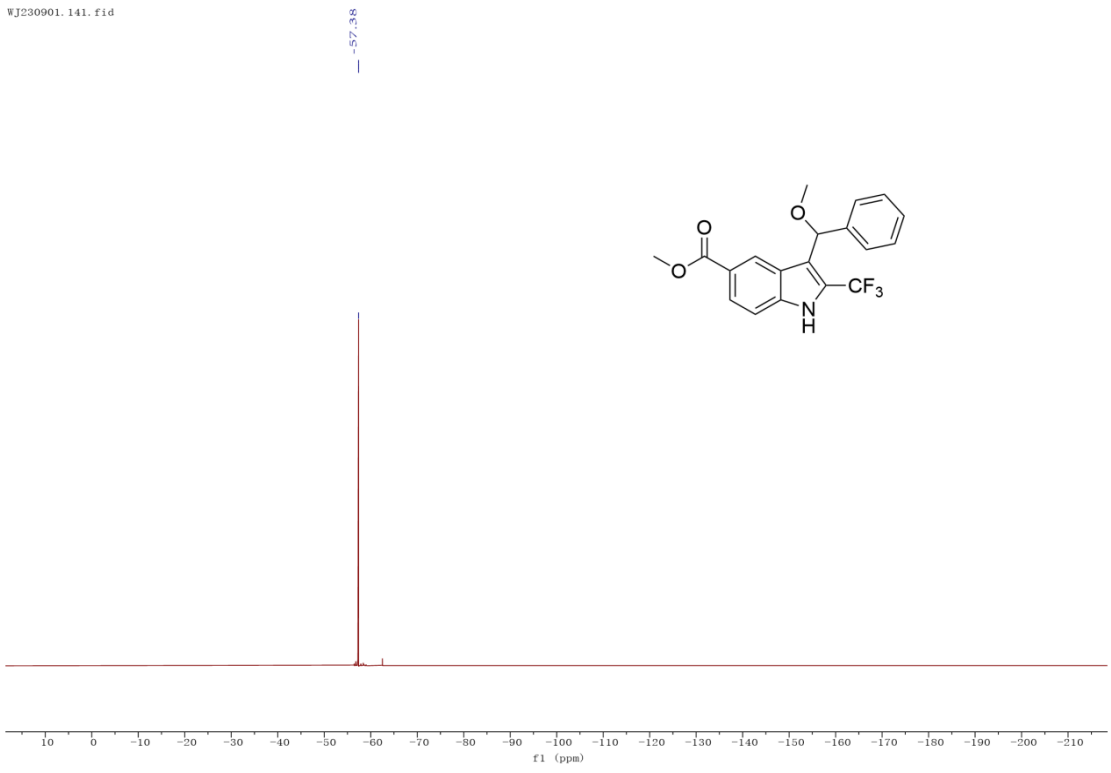
^{1}H NMR (400 MHz, $CDCl_3$) for **5f**



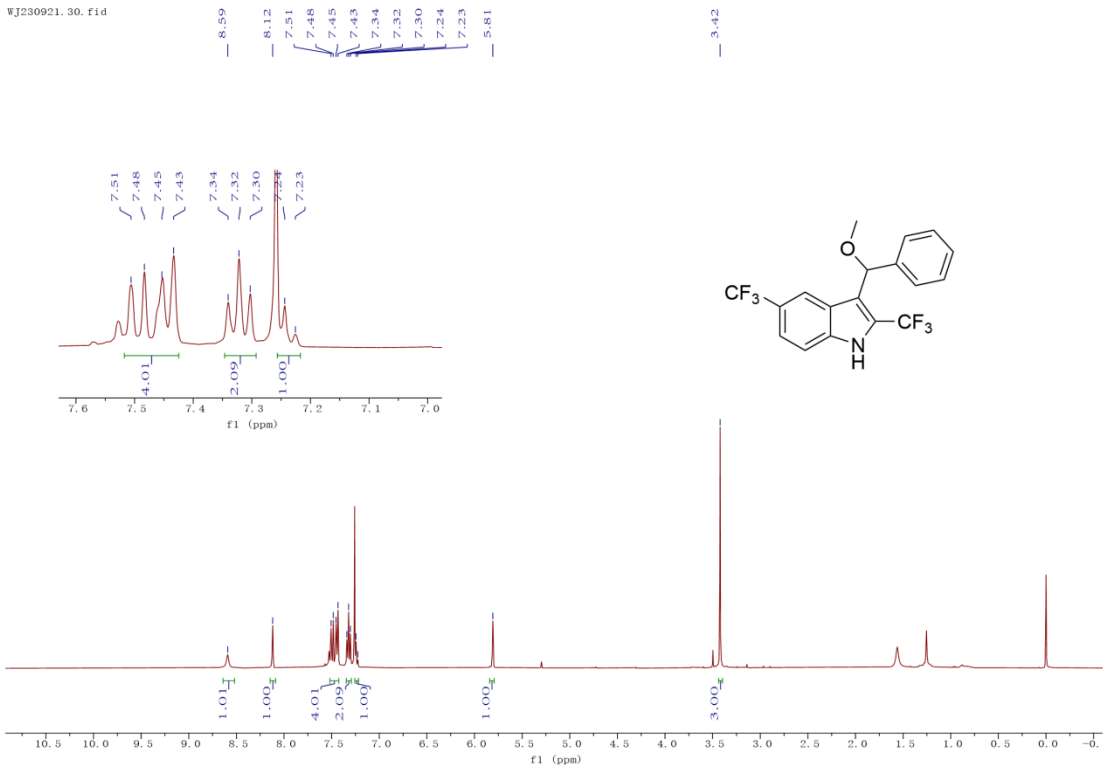
^{13}C NMR (100 MHz, $CDCl_3$) for **5f**



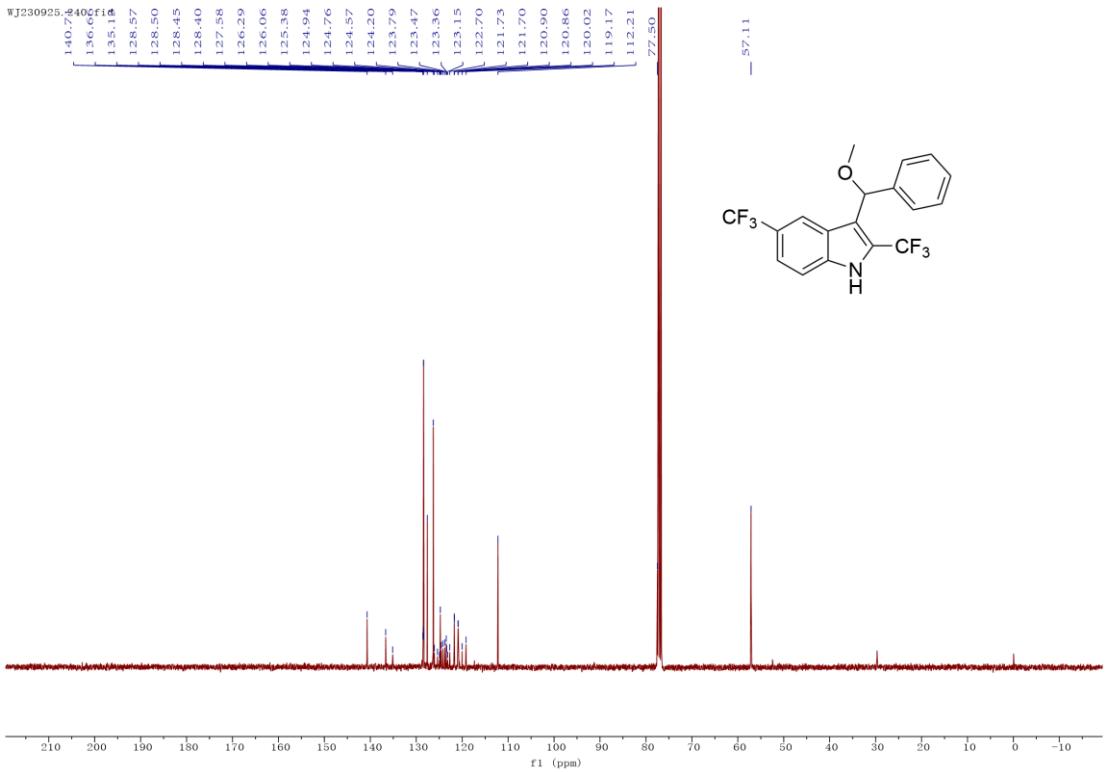
^{19}F NMR (376 MHz, $CDCl_3$) for **5f**



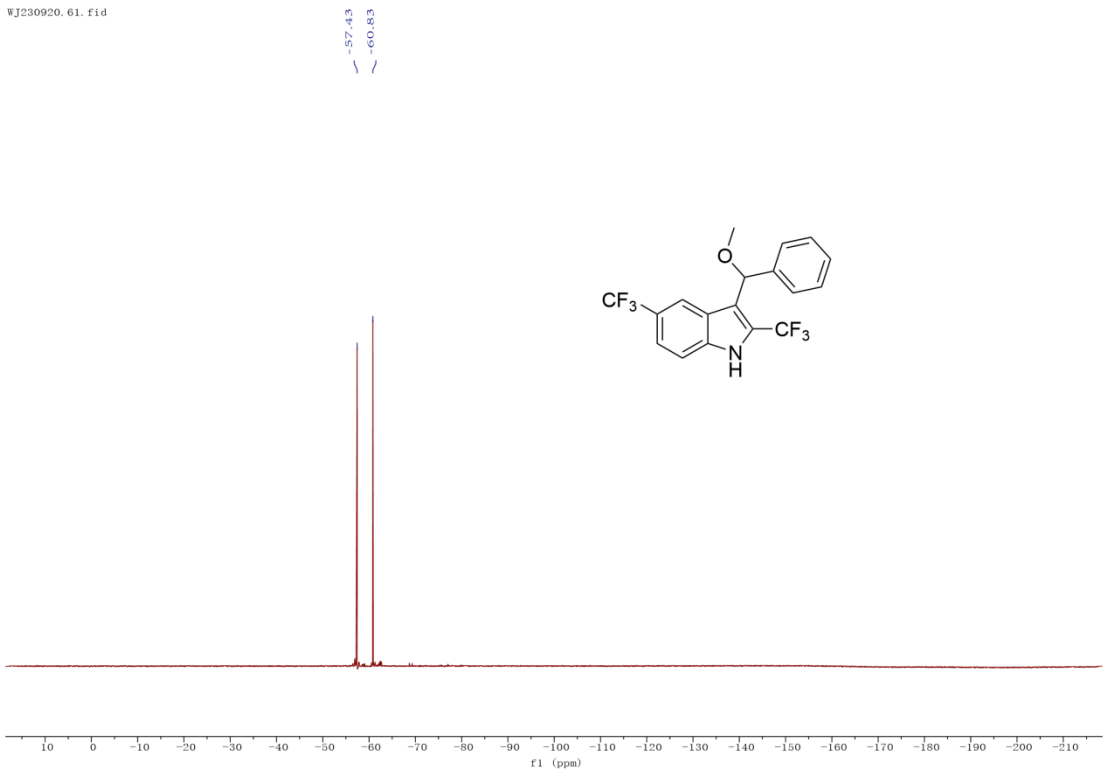
^{1}H NMR (400 MHz, $CDCl_3$) for **5g**



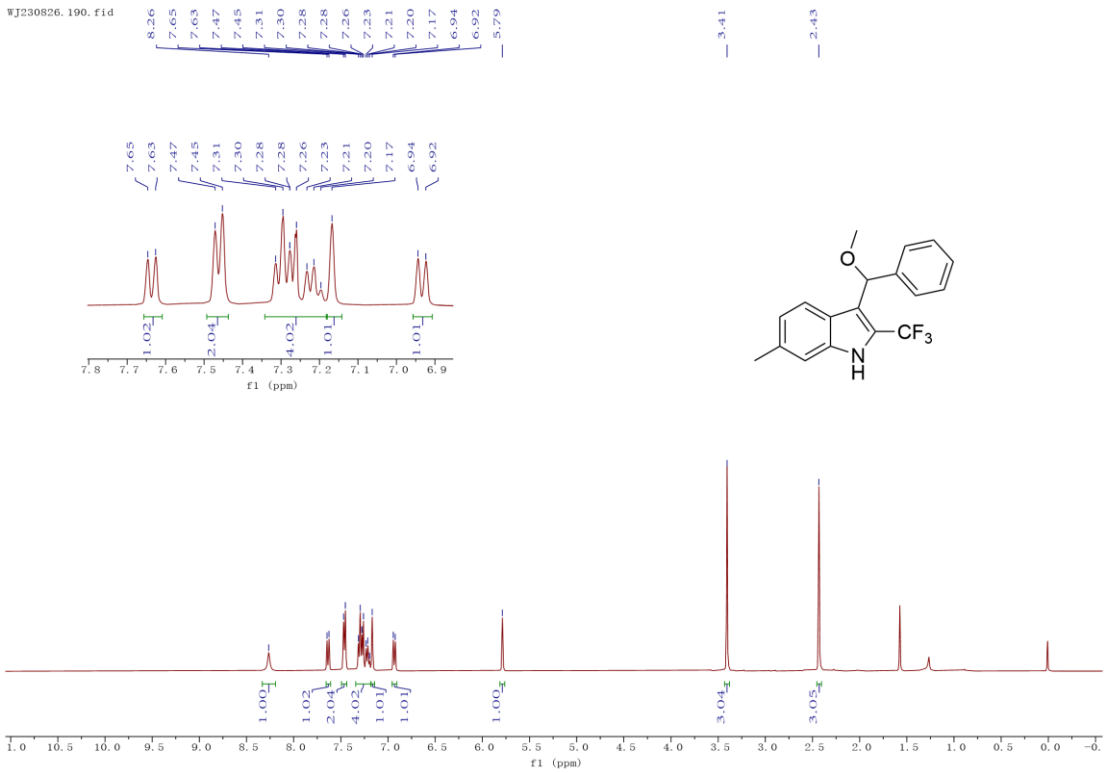
^{13}C NMR (100 MHz, $CDCl_3$) for **5g**



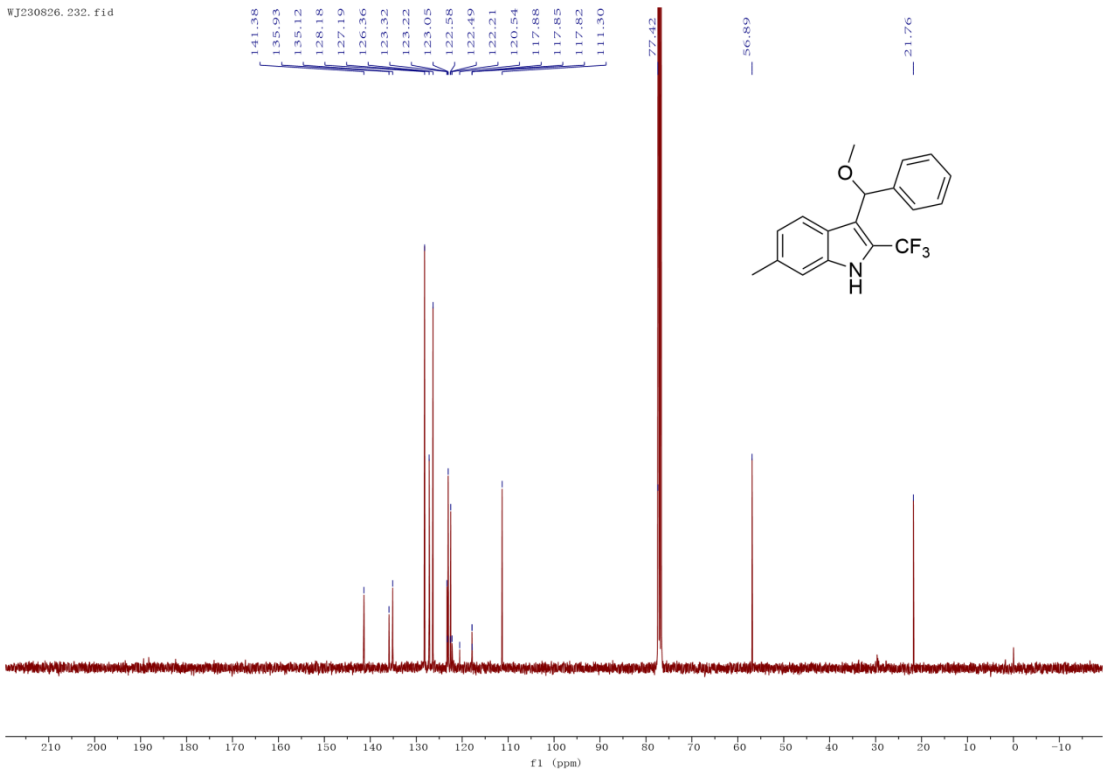
^{19}F NMR (376 MHz, $CDCl_3$) for **5g**



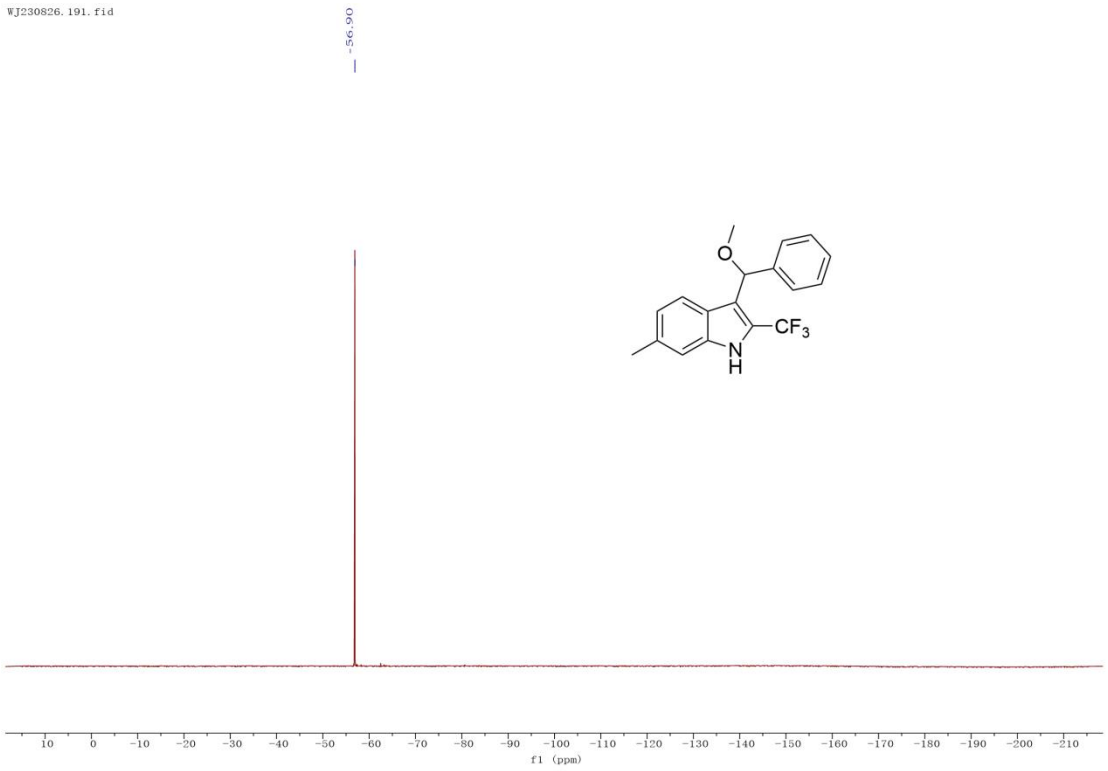
^{1}H NMR (400 MHz, $CDCl_3$) for **5h**



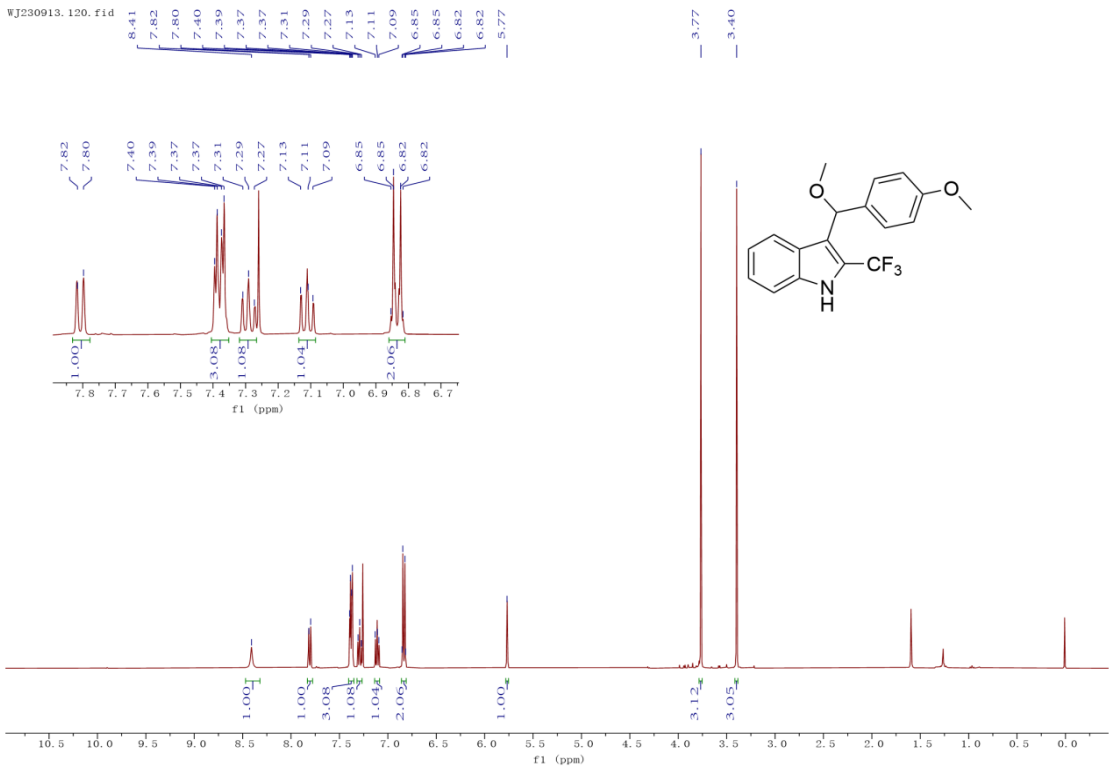
^{13}C NMR (100 MHz, $CDCl_3$) for **5h**



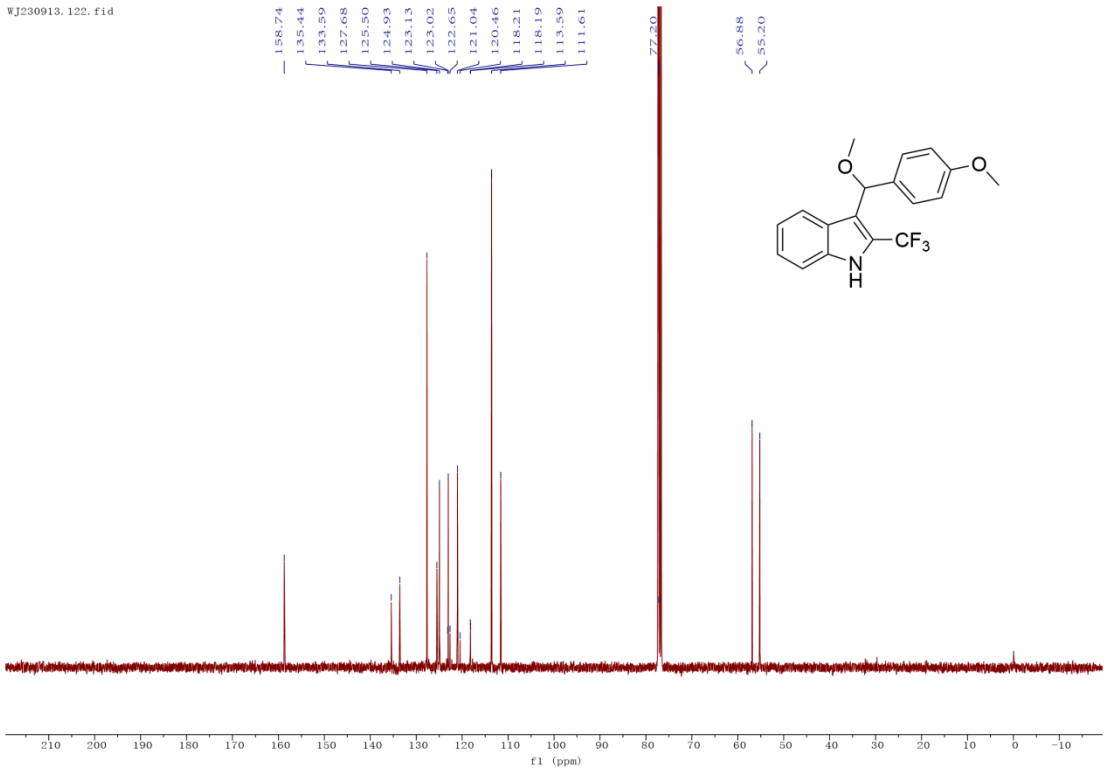
^{19}F NMR (376 MHz, $CDCl_3$) for **5h**



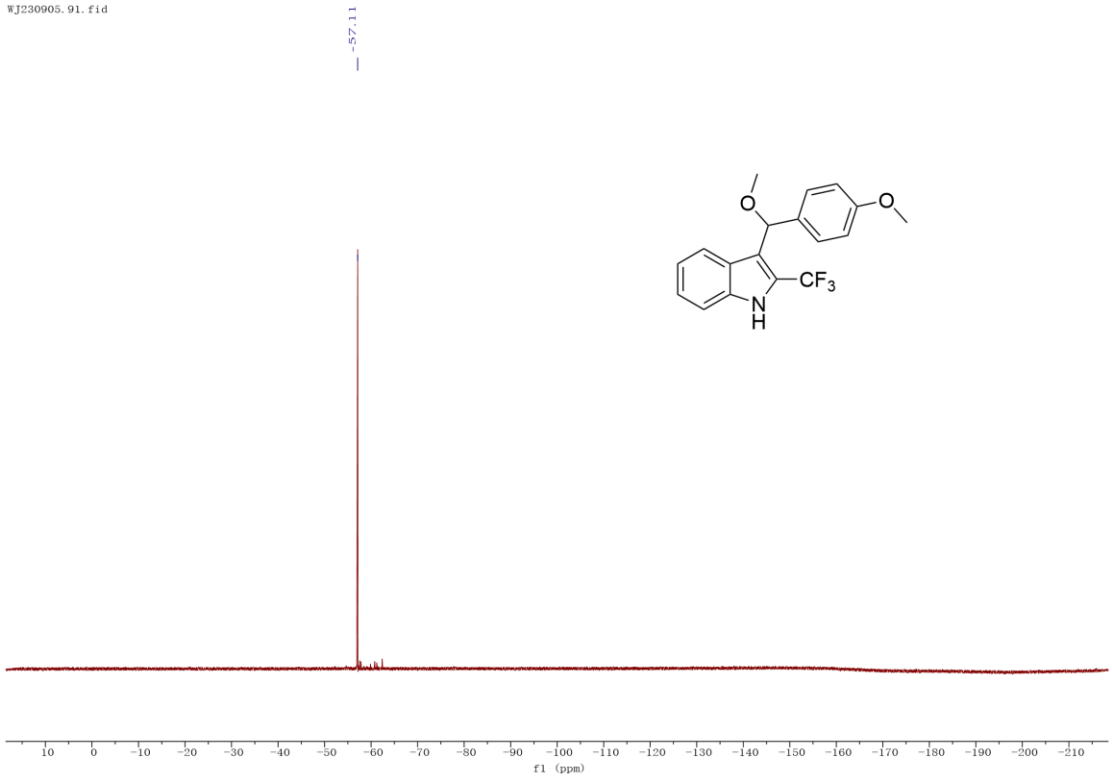
^{1}H NMR (400 MHz, $CDCl_3$) for **5i**



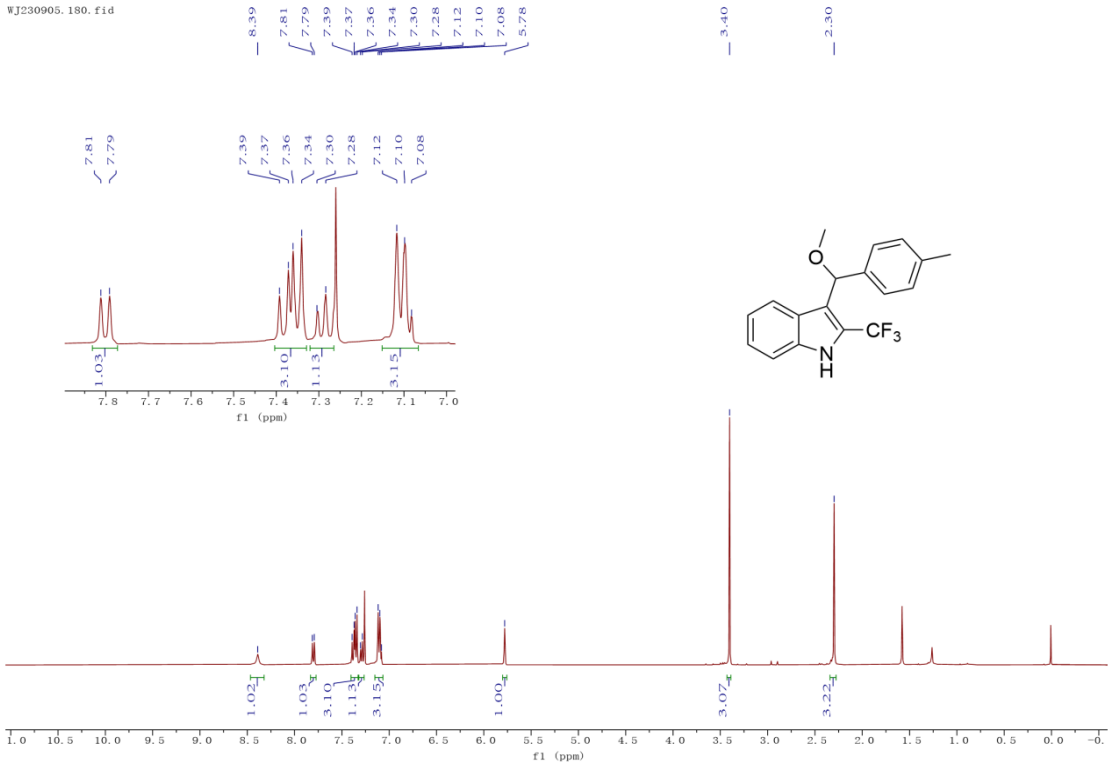
^{13}C NMR (100 MHz, $CDCl_3$) for **5i**



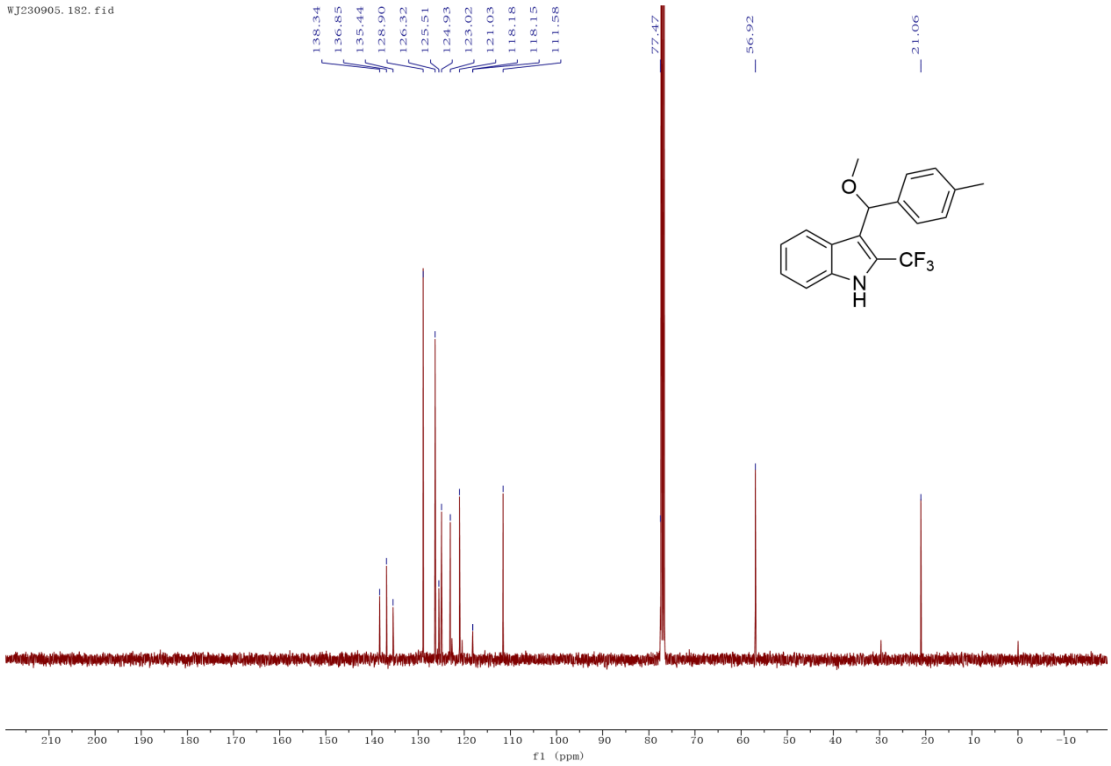
^{19}F NMR (376 MHz, $CDCl_3$) for **5i**



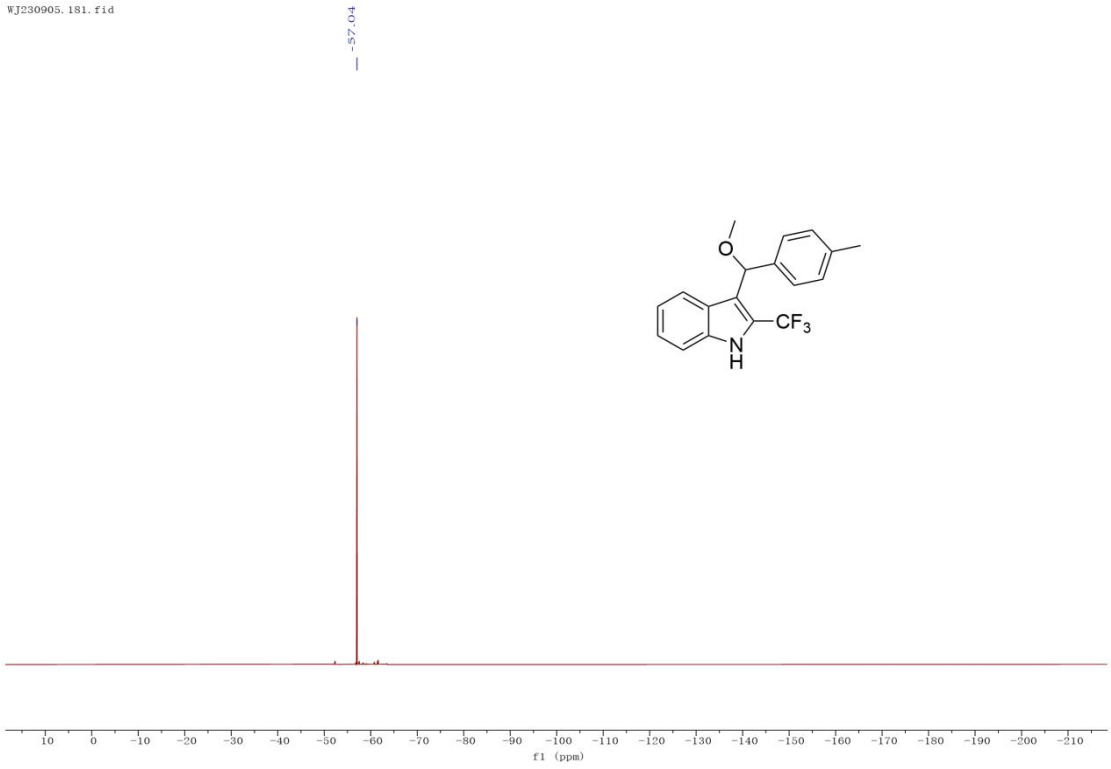
^{1}H NMR (400 MHz, $CDCl_3$) for **5j**



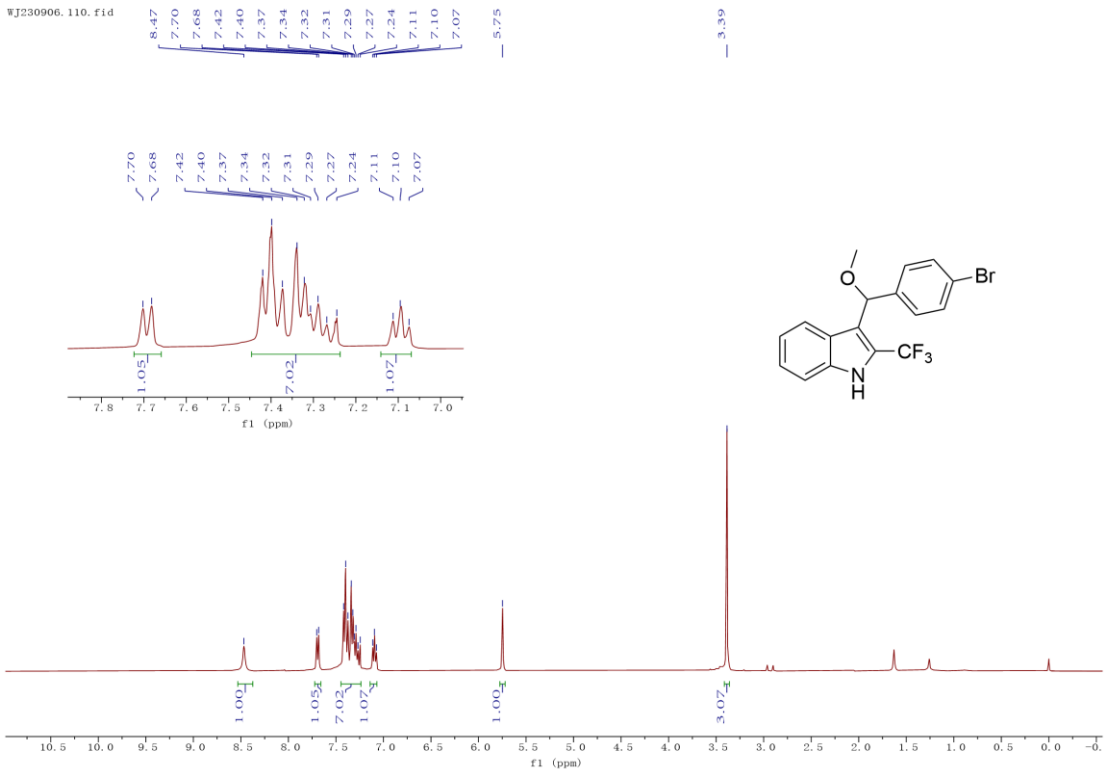
^{13}C NMR (100 MHz, $CDCl_3$) for **5j**



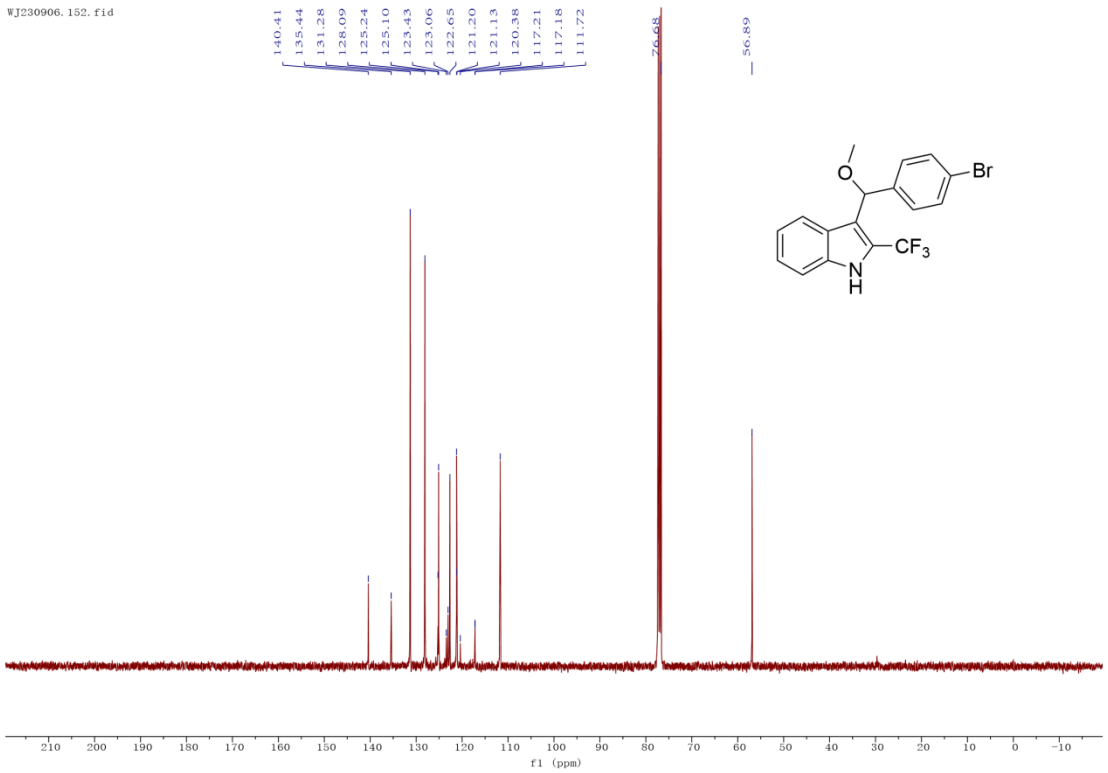
^{19}F NMR (376 MHz, $CDCl_3$) for **5j**



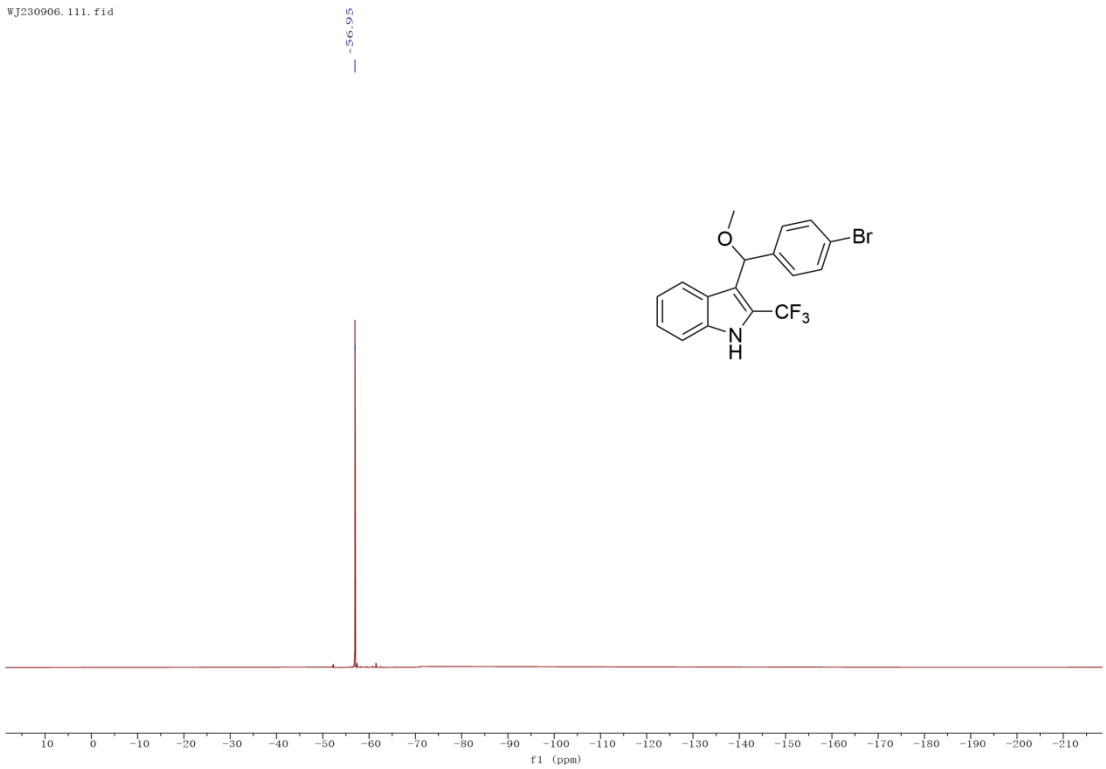
^{1}H NMR (400 MHz, $CDCl_3$) for **5k**



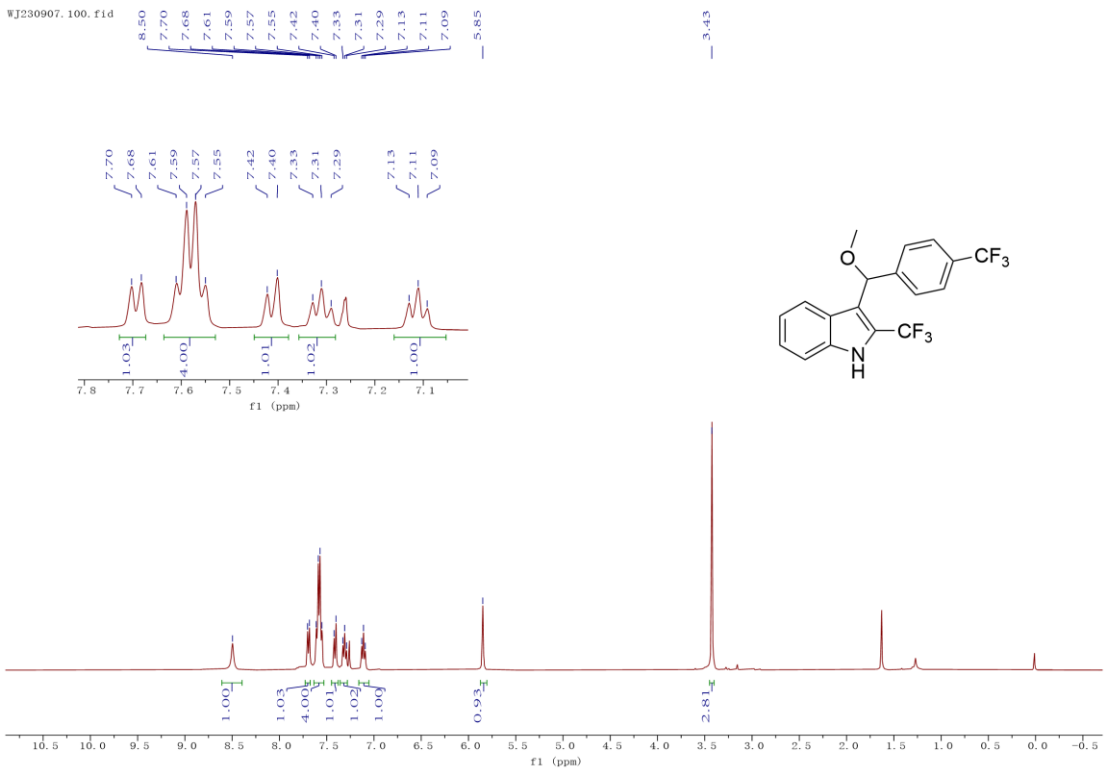
^{13}C NMR (100 MHz, $CDCl_3$) for **5k**



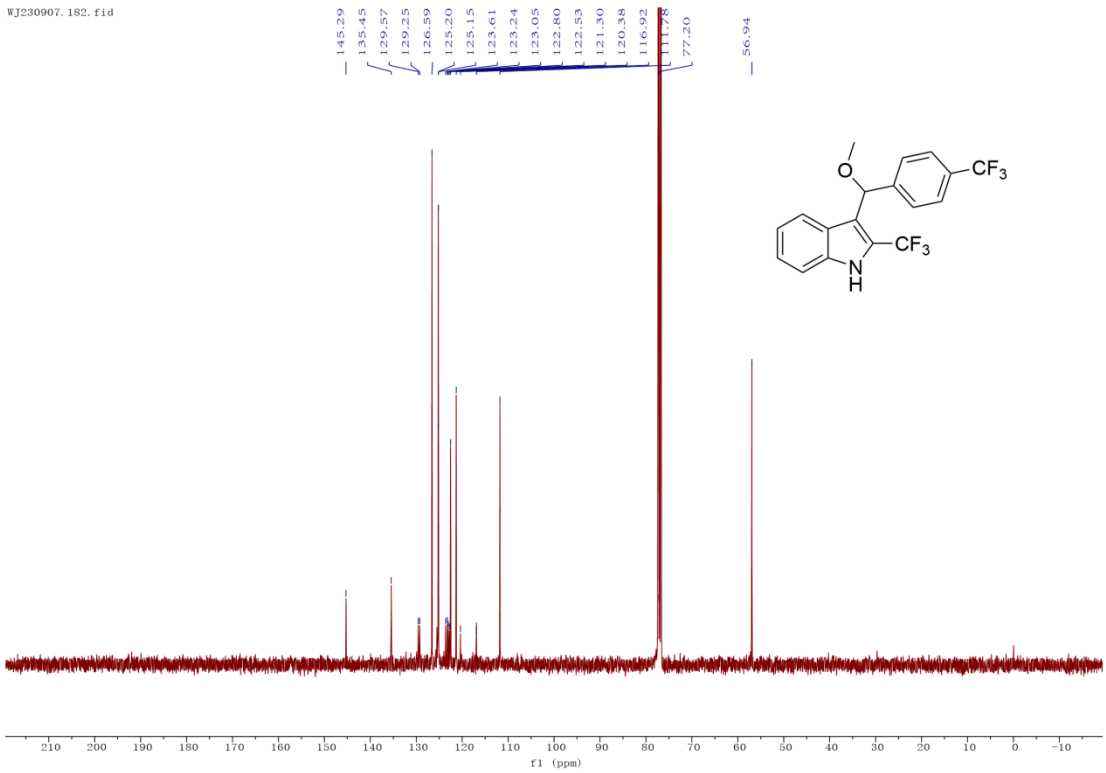
^{19}F NMR (376 MHz, $CDCl_3$) for **5k**



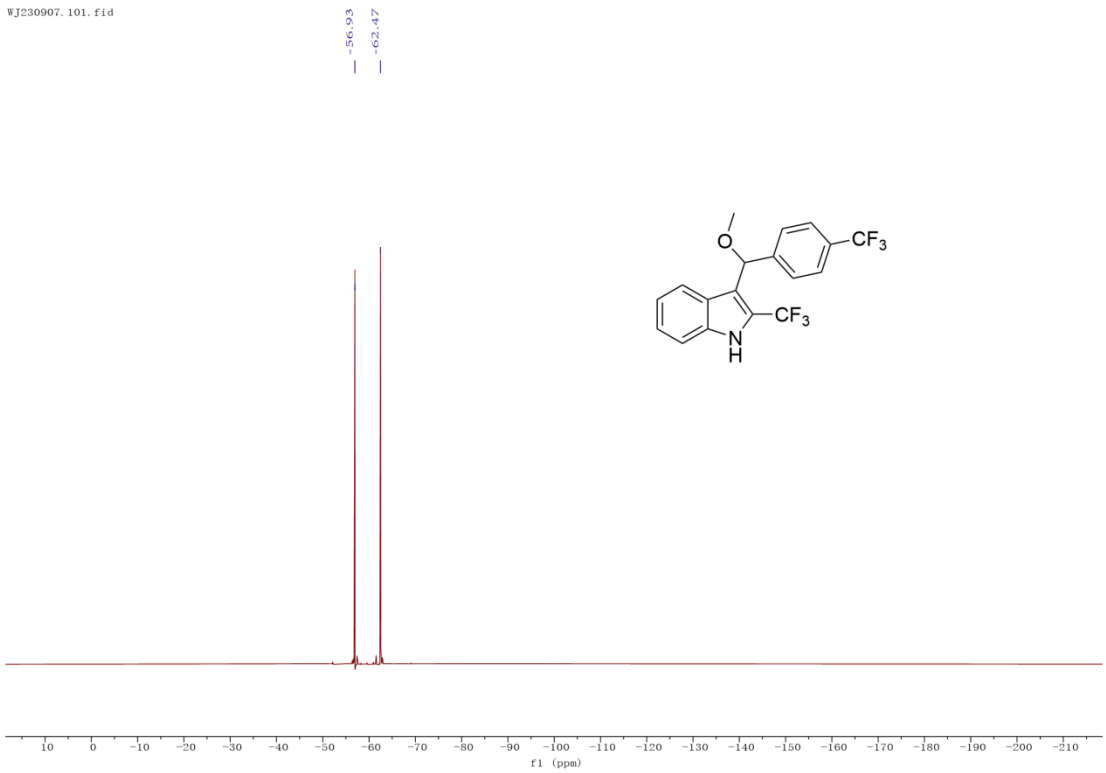
^{1}H NMR (400 MHz, $CDCl_3$) for **5l**



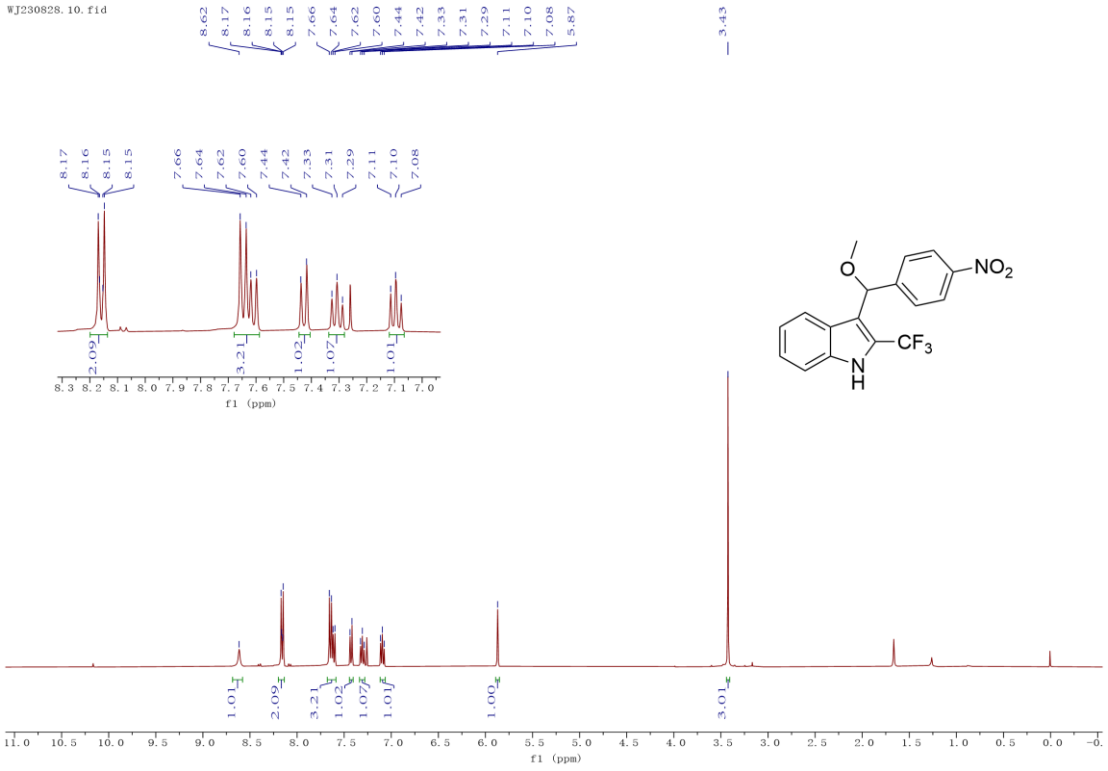
^{13}C NMR (100 MHz, $CDCl_3$) for **5l**



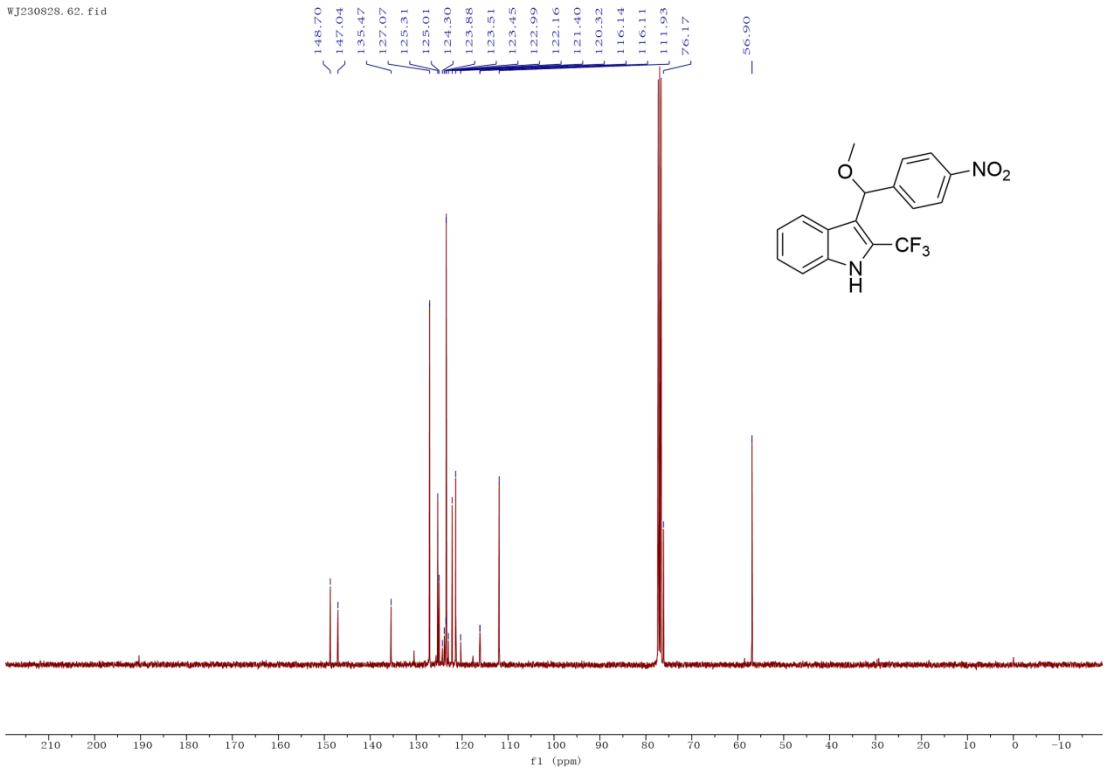
^{19}F NMR (376 MHz, $CDCl_3$) for **5l**



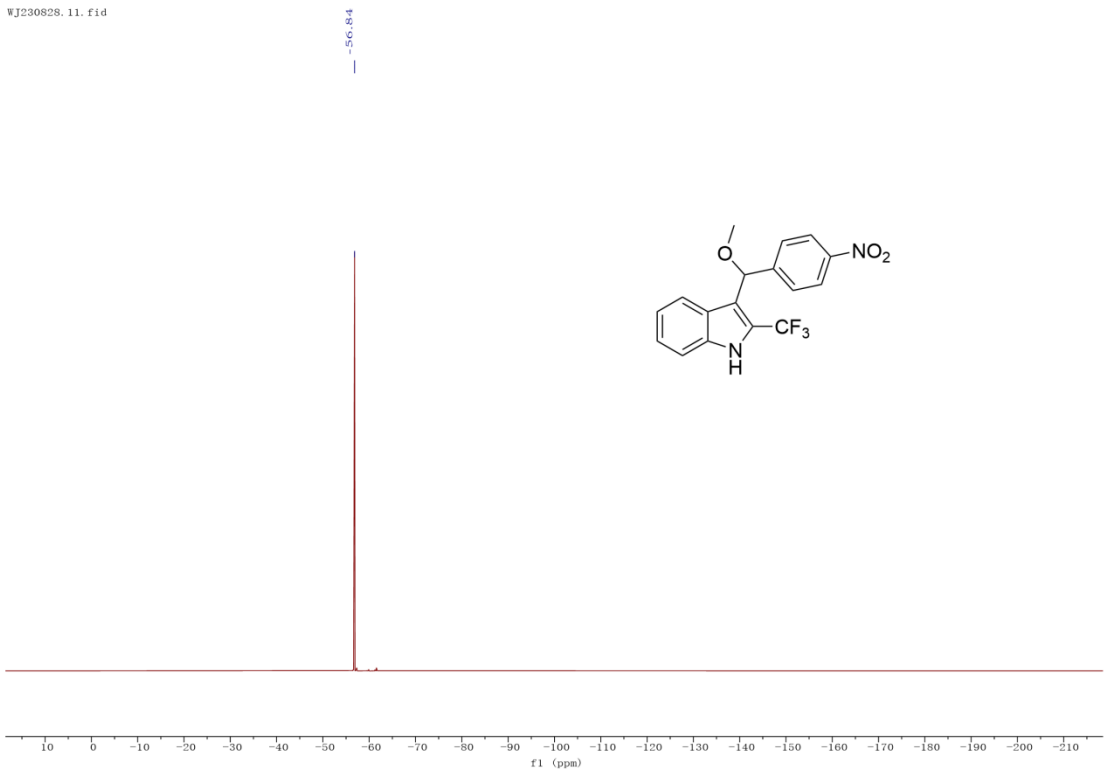
^{1}H NMR (400 MHz, $CDCl_3$) for **5m**



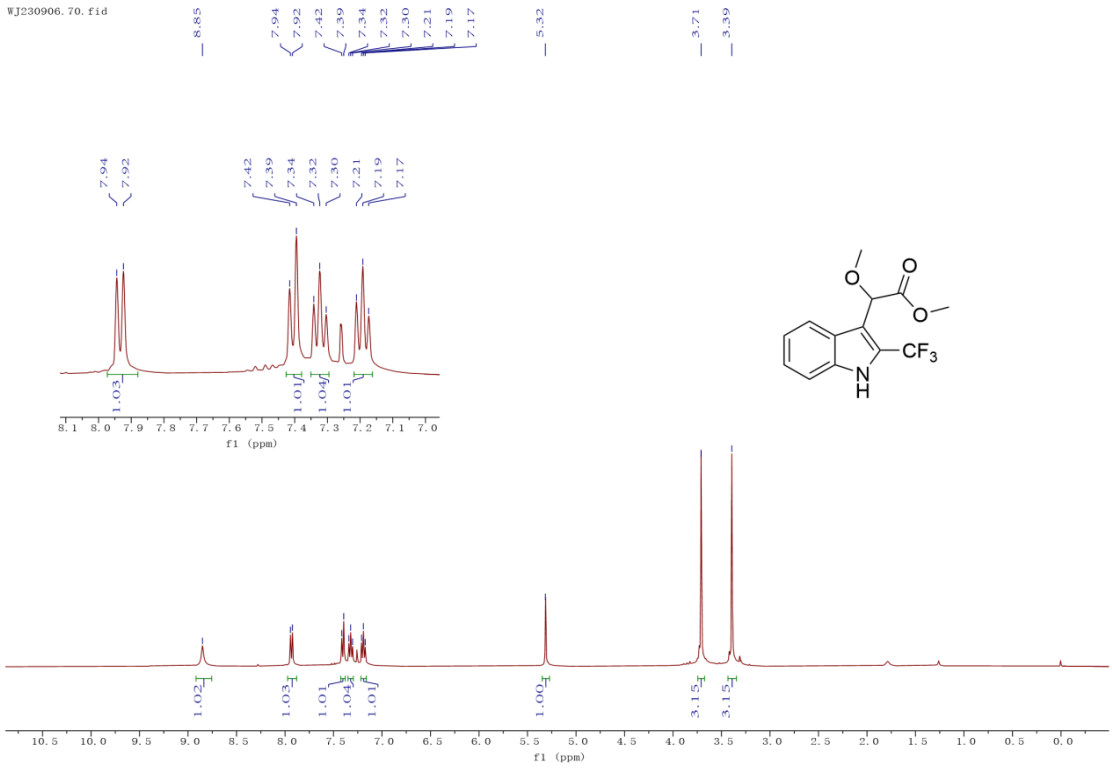
^{13}C NMR (100 MHz, $CDCl_3$) for **5m**



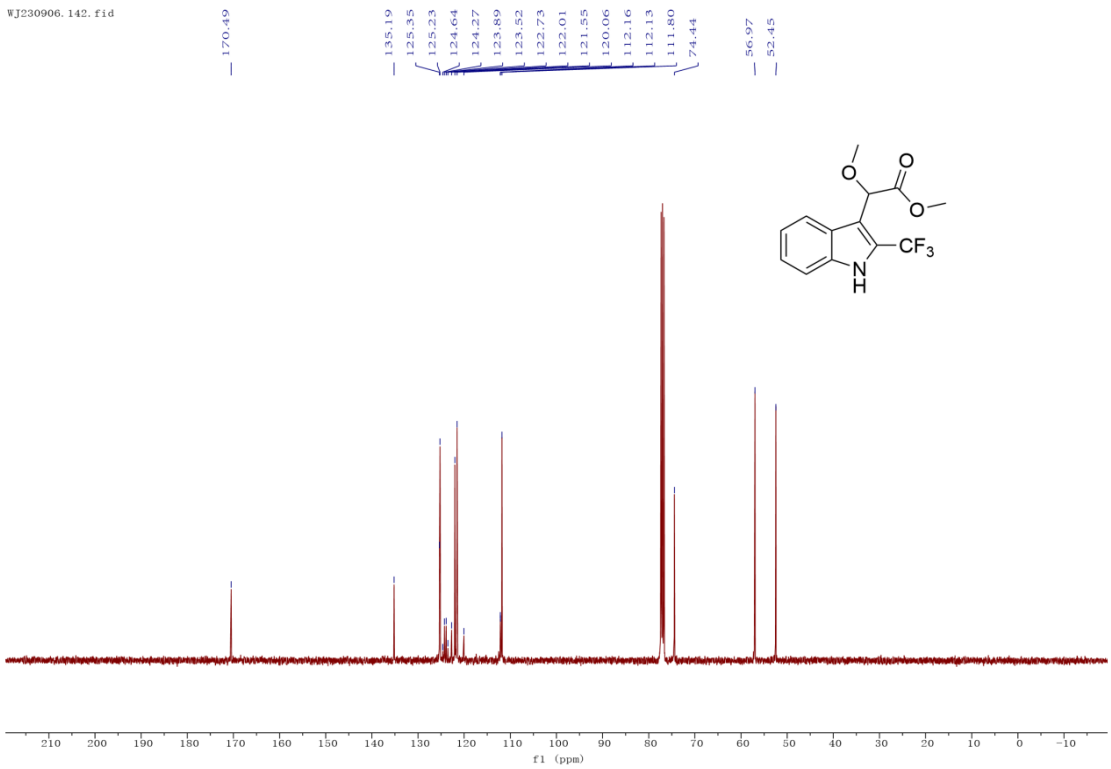
^{19}F NMR (376 MHz, $CDCl_3$) for **5m**



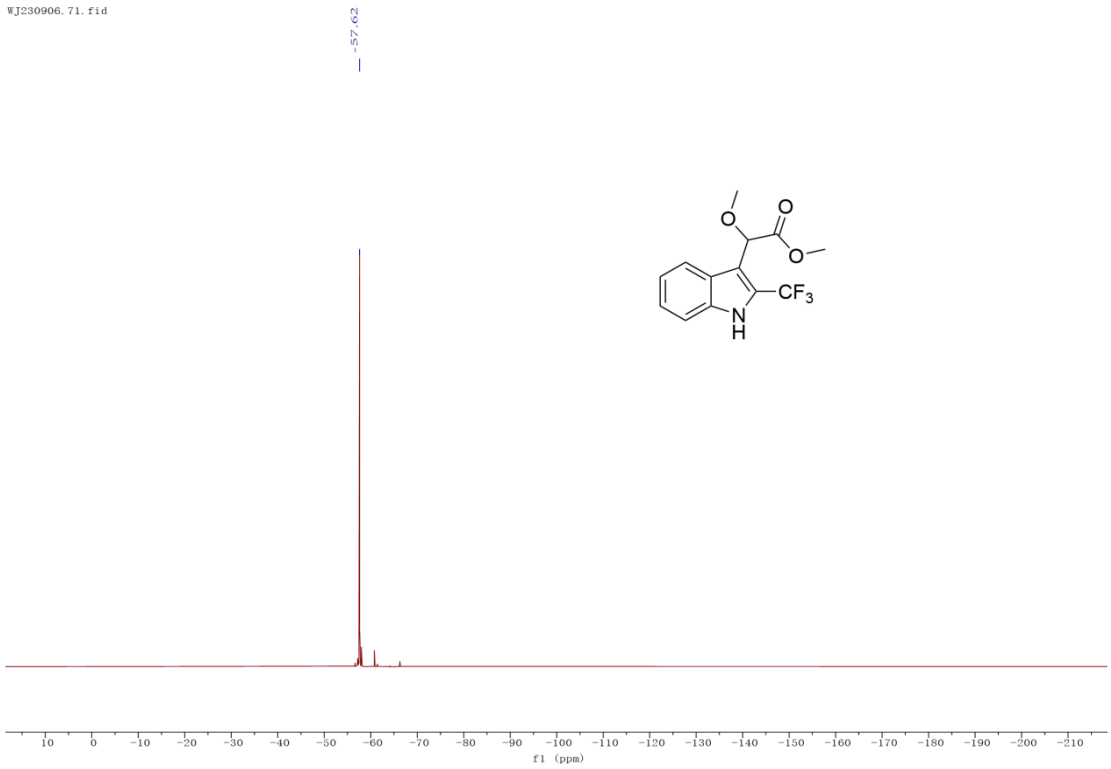
^{1}H NMR (400 MHz, $CDCl_3$) for **5n**



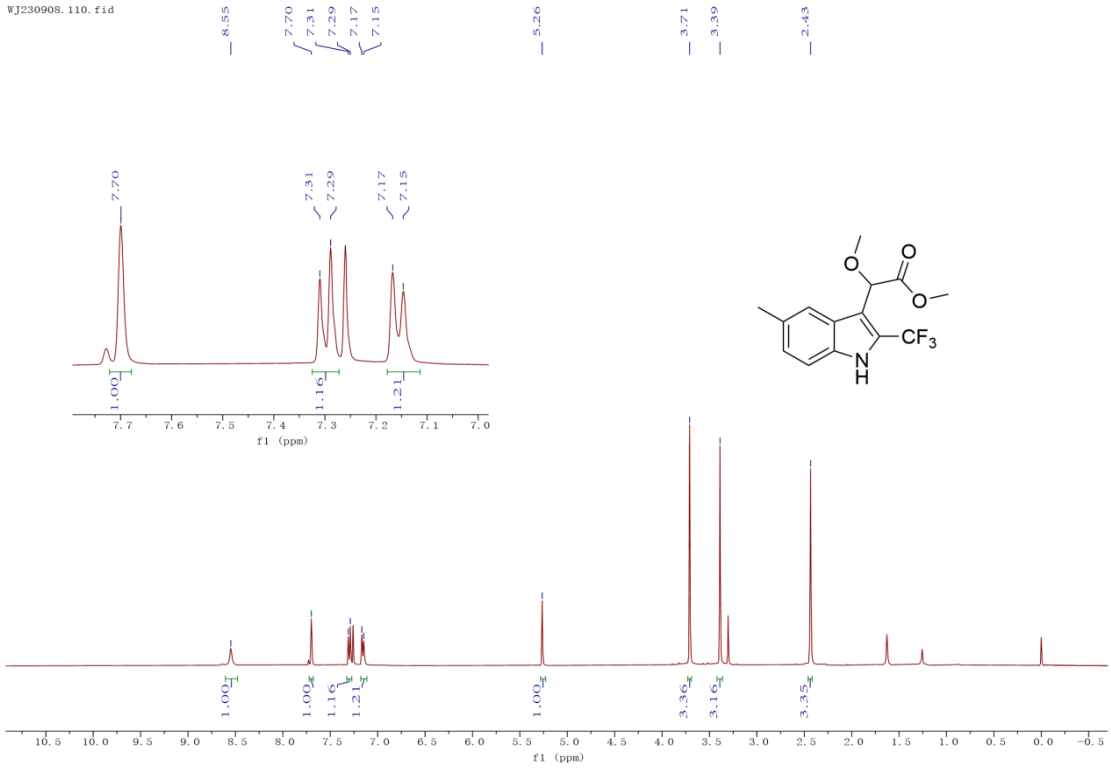
^{13}C NMR (100 MHz, $CDCl_3$) for **5n**



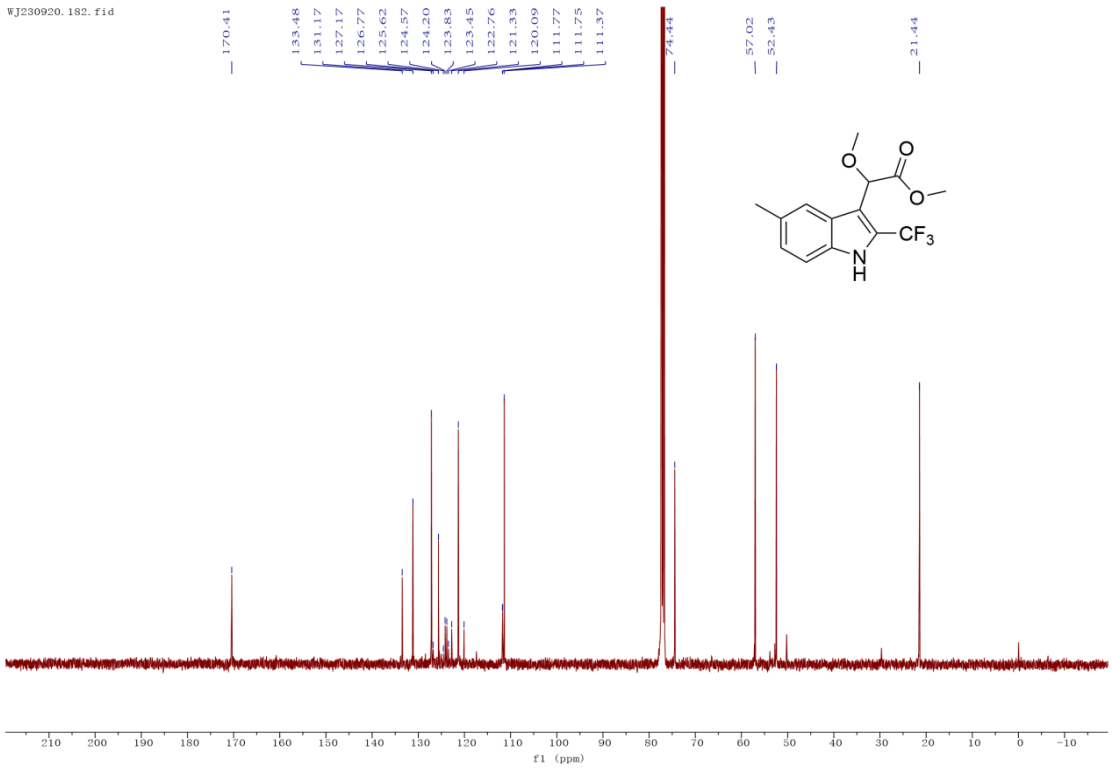
^{19}F NMR (376 MHz, $CDCl_3$) for **5n**



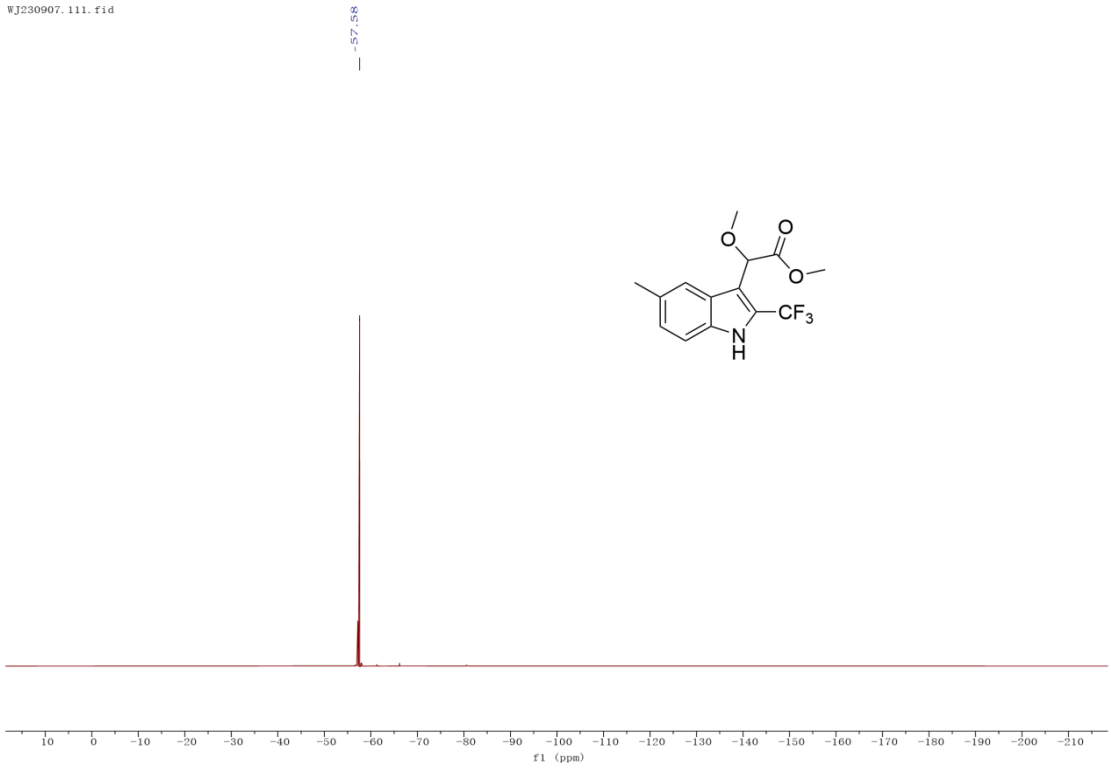
^{1}H NMR (400 MHz, $CDCl_3$) for **5o**



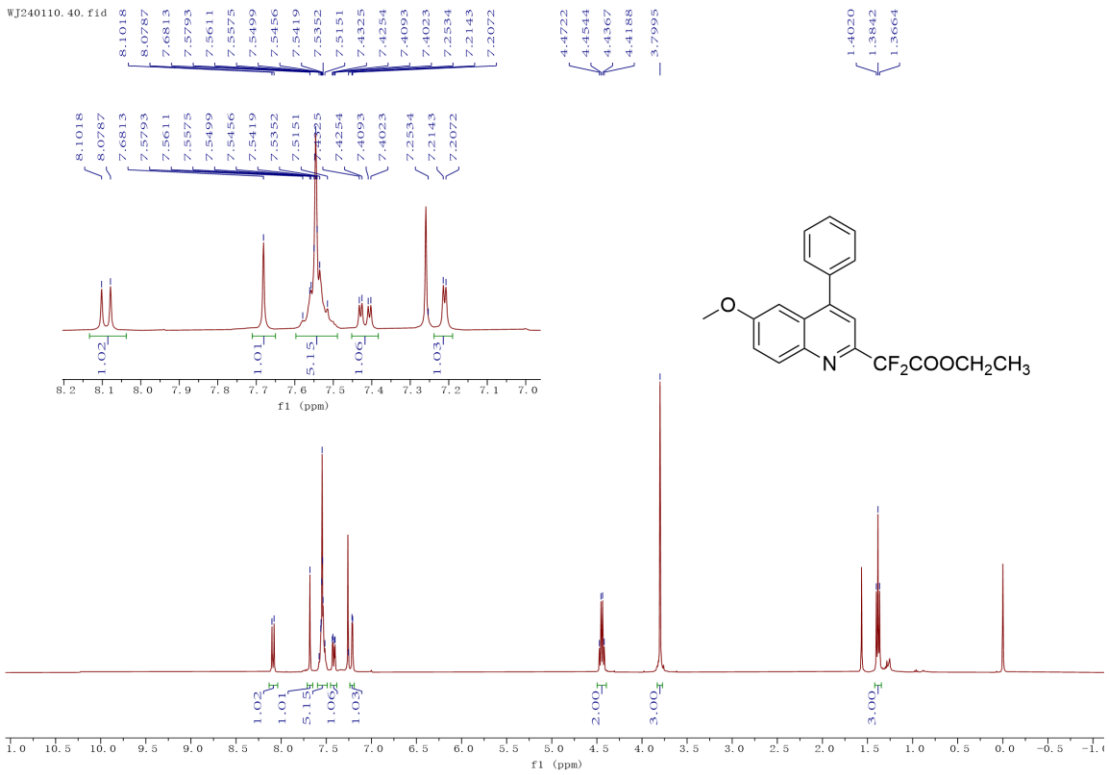
^{13}C NMR (100 MHz, $CDCl_3$) for **5o**



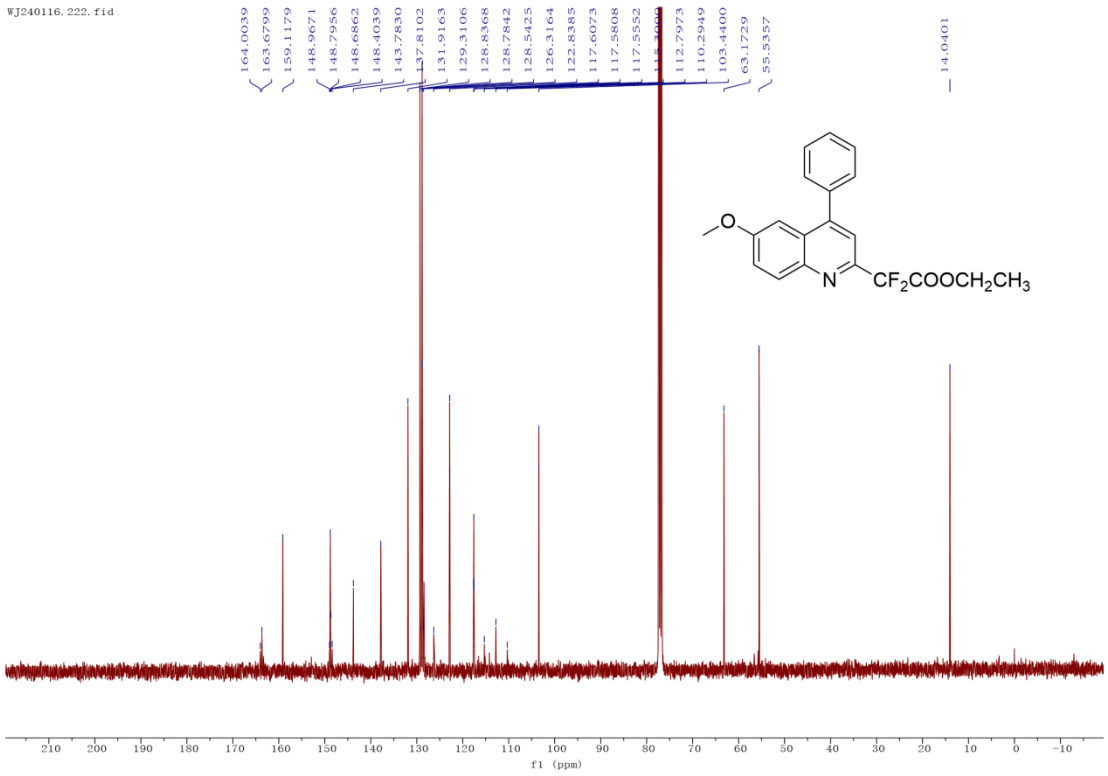
^{19}F NMR (376 MHz, $CDCl_3$) for **5o**



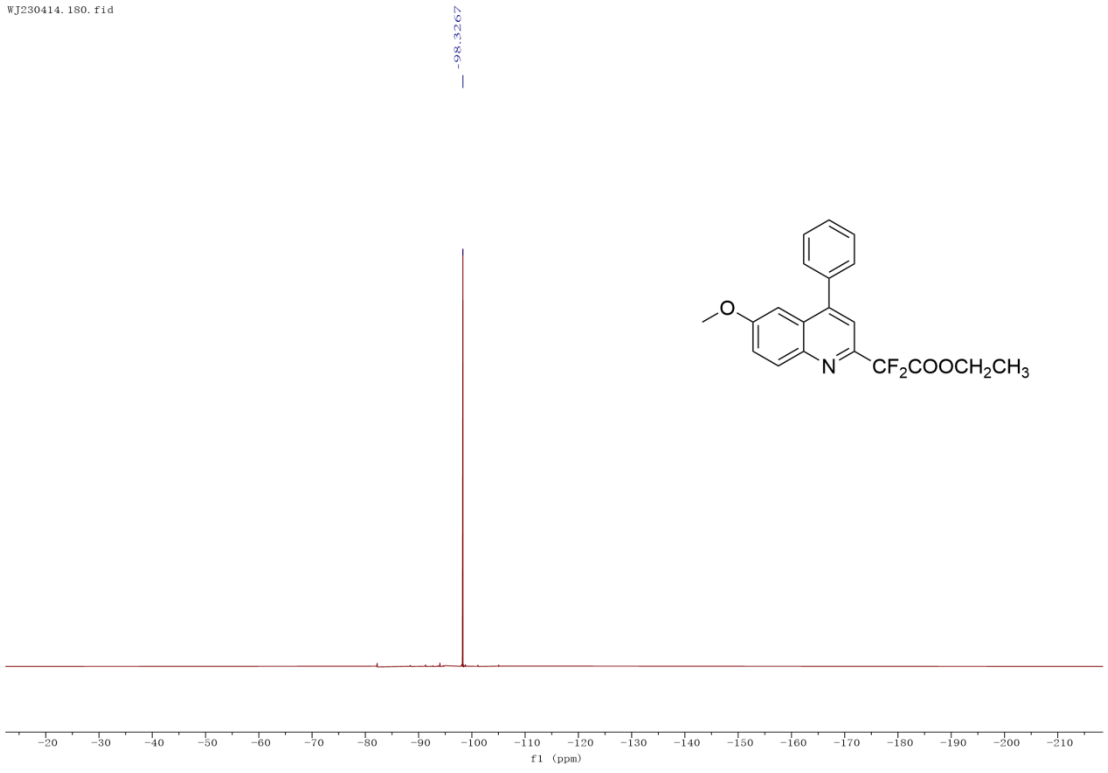
^{1}H NMR (400 MHz, $CDCl_3$) for **6**



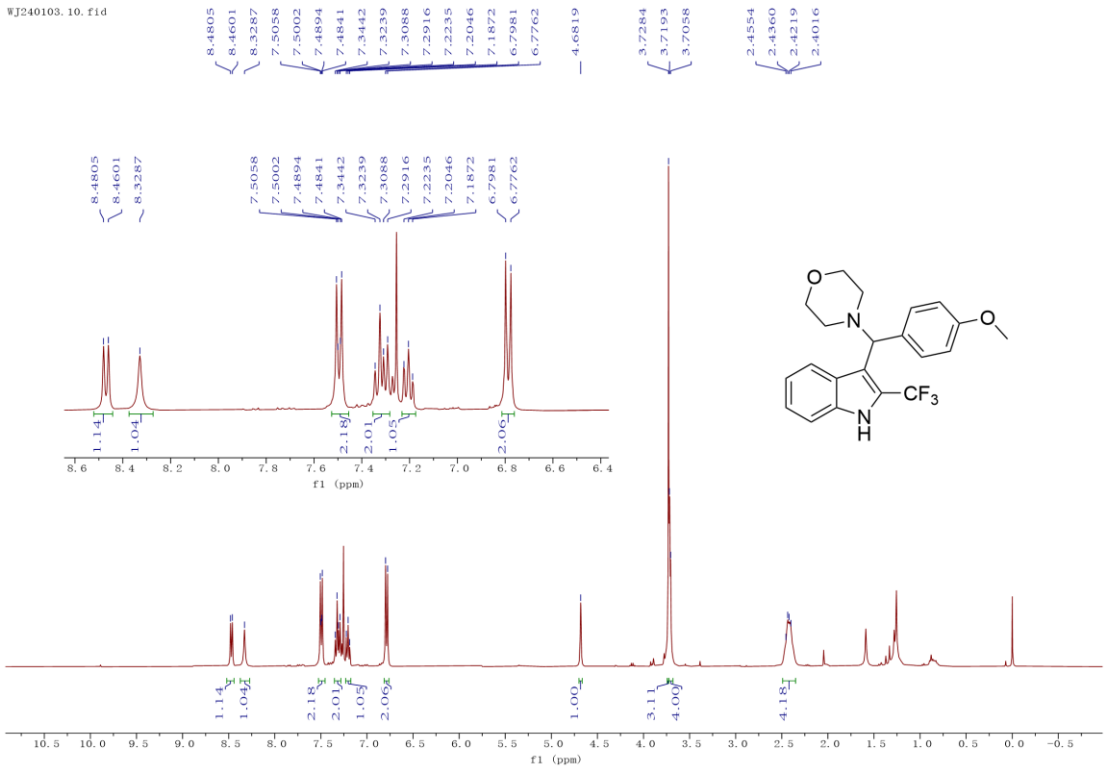
^{13}C NMR (100 MHz, $CDCl_3$) for **6**



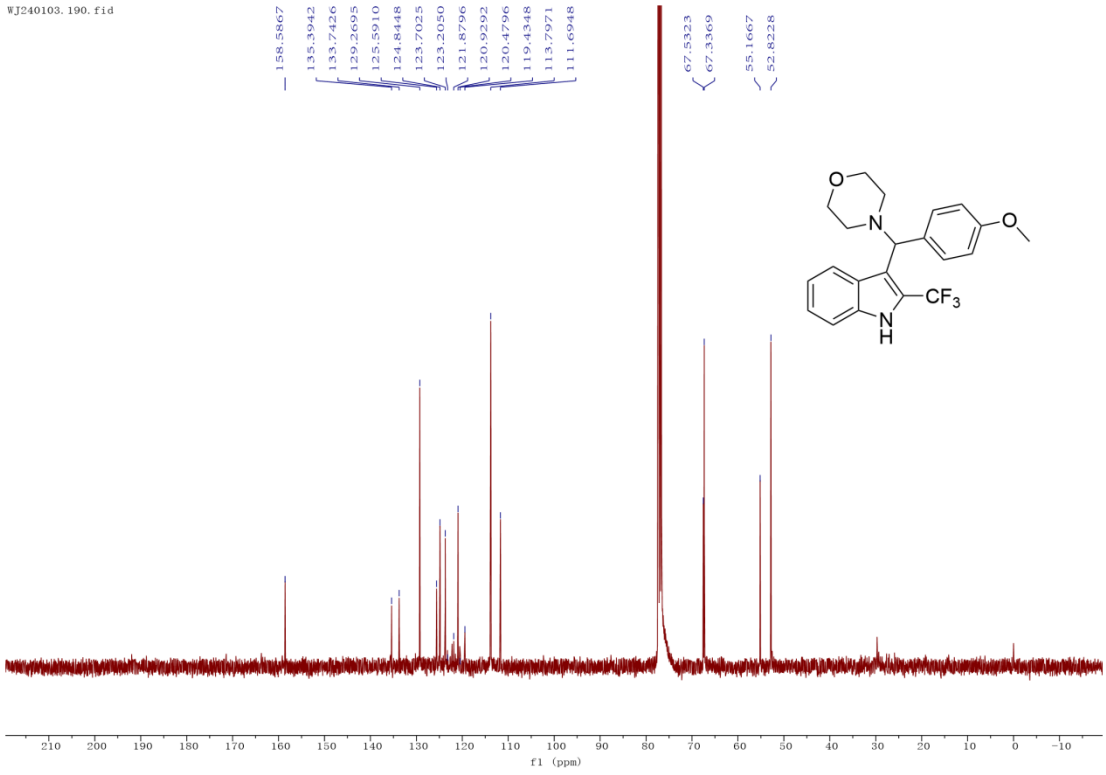
^{19}F NMR (376 MHz, $CDCl_3$) for **6**



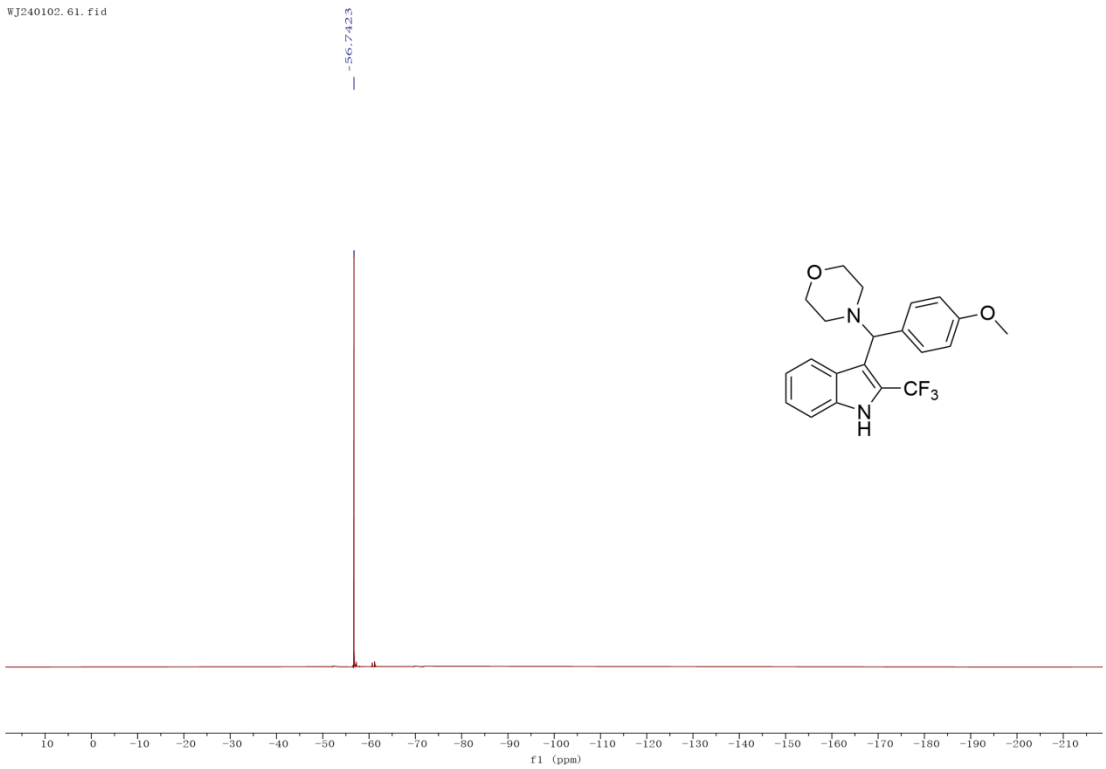
^{1}H NMR (400 MHz, $CDCl_3$) for **7**



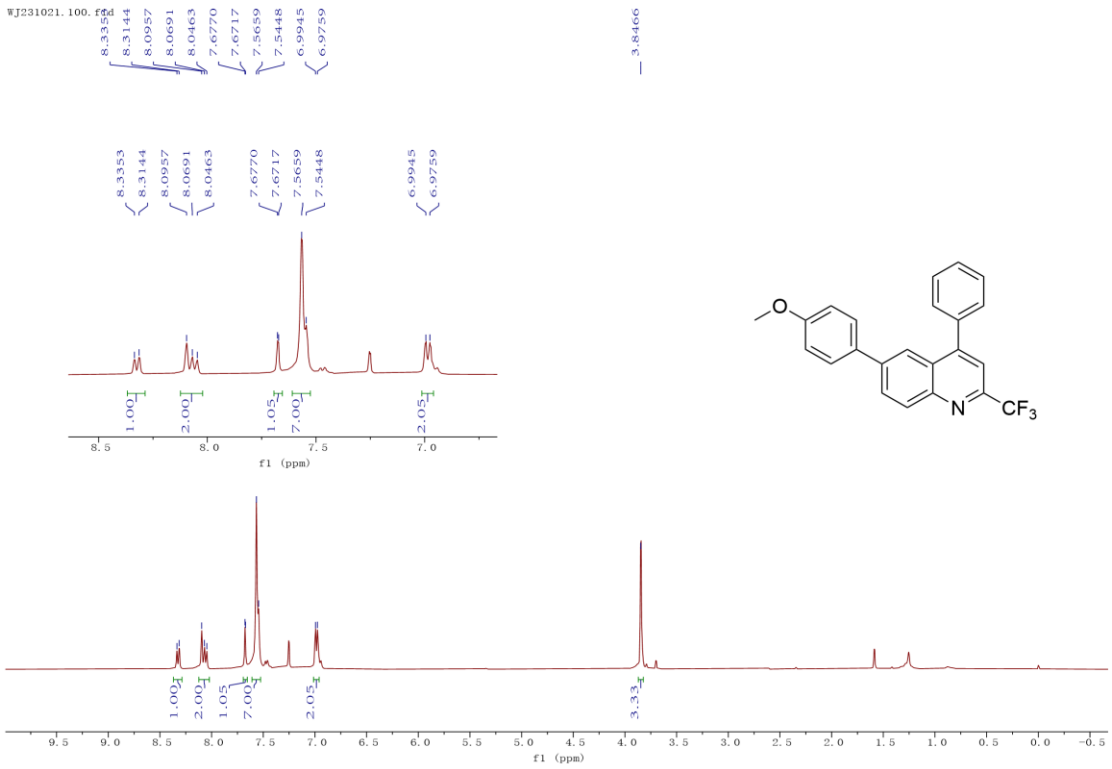
^{13}C NMR (100 MHz, $CDCl_3$) for **7**



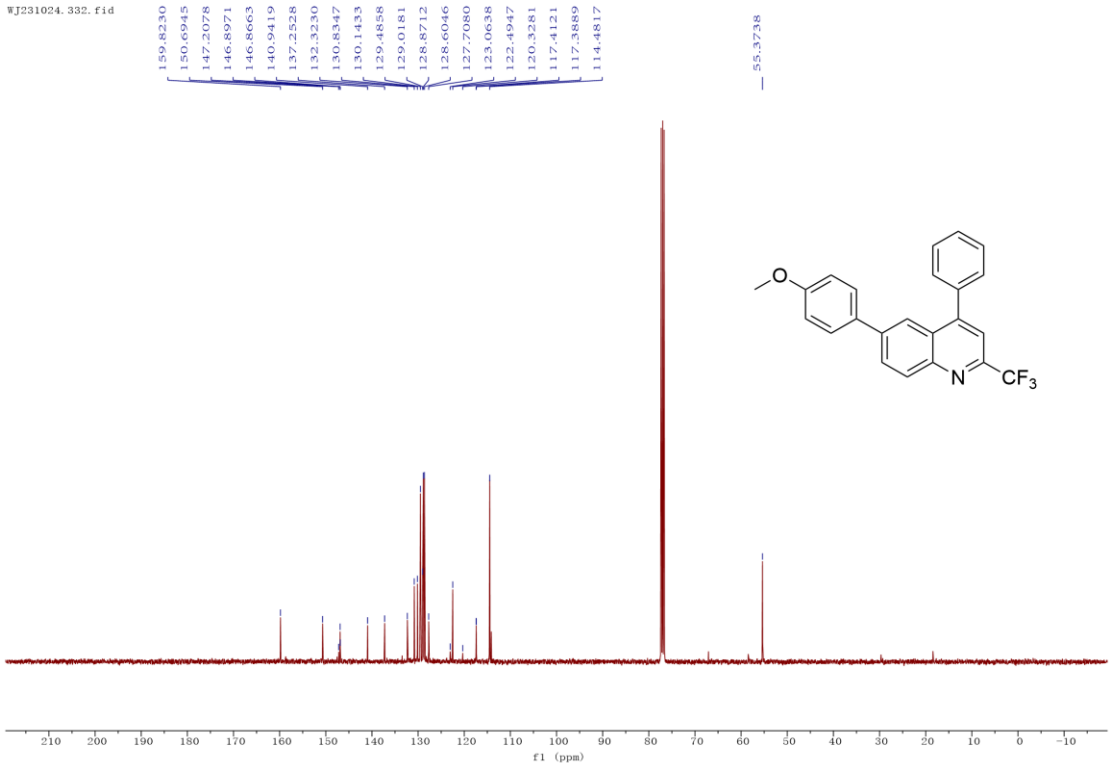
^{19}F NMR (376 MHz, $CDCl_3$) for **7**



^{1}H NMR (400 MHz, $CDCl_3$) for **8**

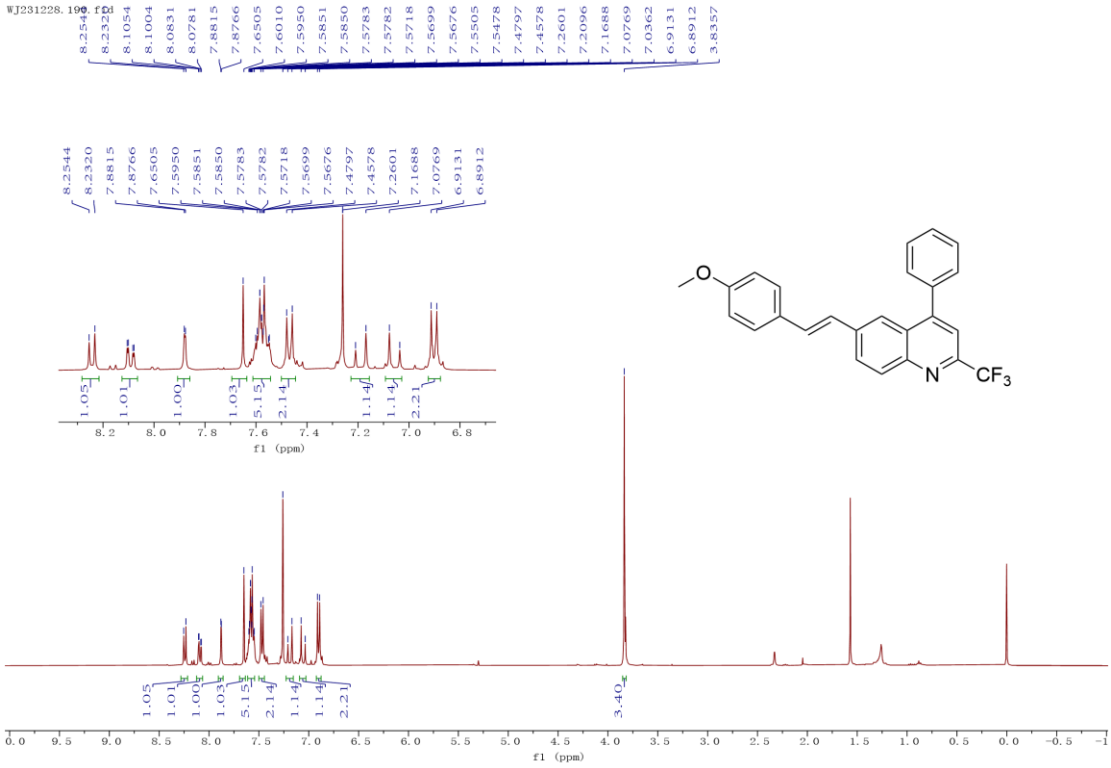


^{13}C NMR (100 MHz, $CDCl_3$) for **8**

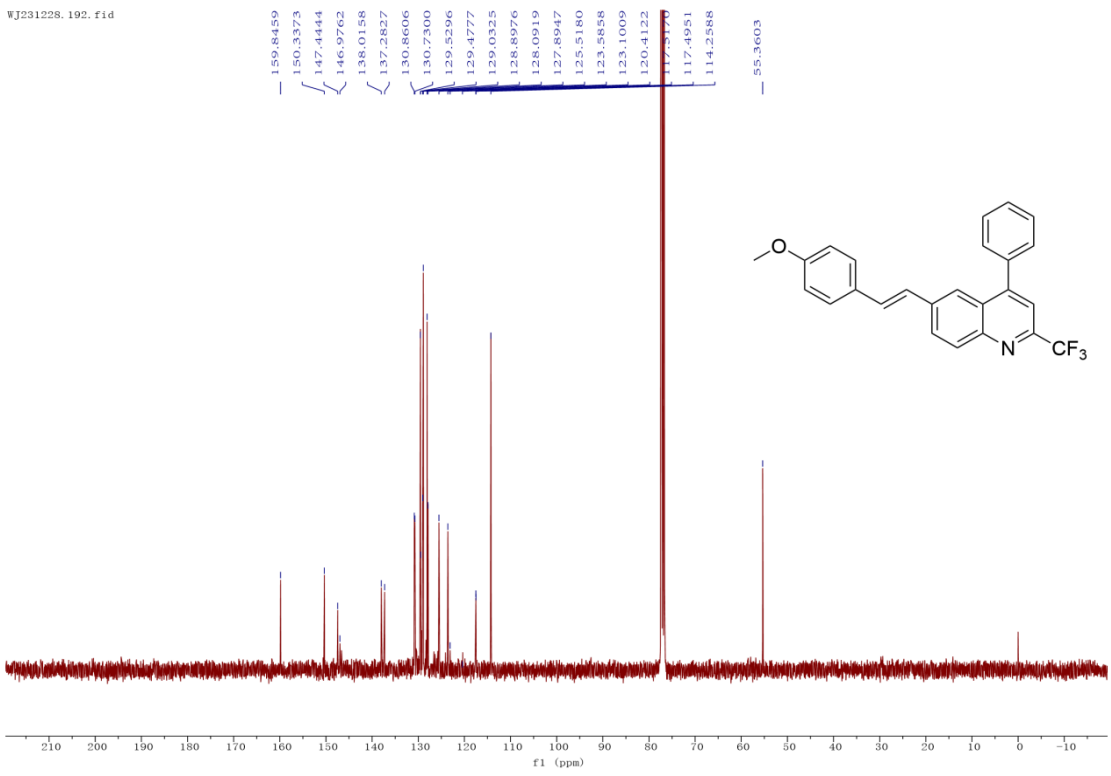


^{19}F NMR (376 MHz, $CDCl_3$) for **8**

^{1}H NMR (400 MHz, $CDCl_3$) for **9**



^{13}C NMR (100 MHz, $CDCl_3$) for **9**



^{19}F NMR (376 MHz, $CDCl_3$) for **9**