Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition-metal-catalyzed straightforward synthesis of *N*-trifluoromethyl indoles from 2-alkynylaryl isothiocyanates or 2-alkynylanilines†

Jianquan Hong,*[a] Chongbin Wei,[a] Ruilong Feng,[a] Kui Zhao,[a] Yi Zhu,[a] Chunxiang Li,[a] Xifei Chen,[a] Xinxin Gong,[a] Dejing Yin,[b] Changge Zheng*[a]

[a]Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China

[b]School of Biotechnology, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China

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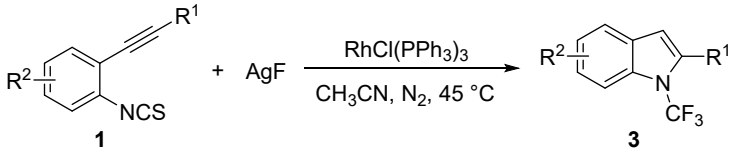
1. General Information

Unless otherwise noted, all commercially available materials were purchased from Energy Chemical and used without further purification. Column chromatography was carried out on silica gel 60 (200–300 mesh). Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates and visualized with short-wavelength UV light (254 nm). ^{1}H NMR, ^{13}C NMR, ^{19}F NMR were all recorded using $CDCl_3$ as a solvent on a Bruker 400 MHz spectrometer at 298 K (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F). Chemical shifts (δ) were measured in ppm relative to TMS $\delta = 0$ for ^{1}H or to chloroform $\delta = 77.0$ for ^{13}C as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, m = multiplet). Coupling constant J was reported in hertz (Hz).

2. General procedure for synthesis of *N*-trifluoromethyl indoles

Method A



To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added 2-alkynyl aryl isothiocyanate (0.5 mmol, 1.0 equiv.), AgF (3.2 equiv.), $RhCl(PPh_3)_3$ (1 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (5 mL) was then added by syringe. The reaction mixture was required to heat to 45 °C and then stirred for 3 h under N_2. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and wash with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent.

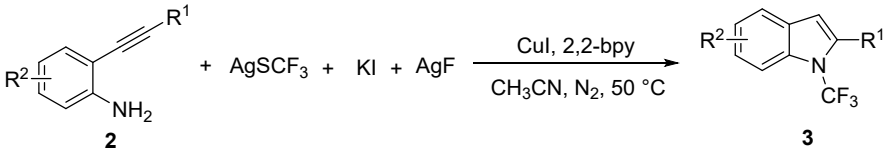
Table S1. Optimization of the reaction conditions[a]

Entry	Catalyst	Base	Solvent	Temp/°C	Yield/%[b]
1	-	-	CH_3CN	45	63
2	-	-	CH_3OH	45	0
3	-	-	DMSO	45	20
4	-	-	DMF	45	45
5	-	-	Dioxane	45	0
6	-	-	CH_2Cl_2	45	0
7	-	-	THF	45	0
8	-	-	NMP	45	20
9	-	-	Cyclohexane	45	0
10	-	-	Toluene	45	0

11	-	-	$CHCl_3$	45	0
12	-	-	Pyridine	45	0
13	-	Na_2CO_3	CH_3CN	45	40
14	-	NaOAc	CH_3CN	45	0
15	-	NEt_3	CH_3CN	45	45
16	-	$NaHSO_3$	CH_3CN	45	20
17	-	KH_2PO_4	CH_3CN	45	0
18	$ZnCl_2$	-	CH_3CN	45	50
19	$Cu(OAc)_2$	-	CH_3CN	45	30
20	CuI	-	CH_3CN	45	56
21	$(PPh_3)_3RhCl$	-	CH_3CN	45	89
22	$(PPh_3)_2NiCl_2$	-	CH_3CN	45	20
23	$(PPh_3)_2PdCl_2$	-	CH_3CN	45	23
24	$Ru(II)Cl_2$	-	CH_3CN	45	10
25	$Co(OAc)_2$	-	CH_3CN	45	0
26	$Fe(OAc)_2$	-	CH_3CN	45	15
27	$FeCl_3$	-	CH_3CN	45	10
28	$AlCl_3$	-	CH_3CN	45	5
29[c]	$(PPh_3)_3RhCl$	-	CH_3CN	45	90
30[c,d]	$(PPh_3)_3RhCl$		CH_3CN	45	83
31[c]	$(PPh_3)_3RhCl$		CH_3CN	rt	80
32[c]	$(PPh_3)_3RhCl$		CH_3CN	35	80
33[c]	$(PPh_3)_3RhCl$		CH_3CN	65	85
34[c]	$(PPh_3)_3RhCl$		CH_3CN	80	85
35[c,e]	$(PPh_3)_3RhCl$		CH_3CN	45	36

[a]Reaction conditions: under N_2, (2-phenylethynyl)phenyl isothiocyanate (0.1 mmol, 1.0 equiv), AgF (0.32 mmol, 3.2 equiv), catalyst (0.01 mmol, 10 mol%) and base (0.20 mmol, 2.0 equiv), solvent (1.5 mL), N_2, Temp., 3 h. [b]Reaction yield determined by ^{19}F NMR spectroscopy using 4,4-Difluorobiphenyl as internal standard based on (2-phenylethynyl)phenyl isothiocyanate. [c]Catalyst (0.001 mmol, 1 mol%). [d]AgF (0.5 mmol, 5.0 equiv). [e]Under air.

Method B



To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added 2-alkynyl arylamine (0.5 mmol, 1.0 equiv.), $AgSCF_3$ (1.5 equiv.), KI (1.5 equiv.), AgF (5.0 equiv.), CuI (20 mol%) and 2,2'-Bipyridine (20 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (5 mL) was then added by syringe. The reaction mixture was required to heat to 50 °C and then stirred for 4 h under N_2. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and wash with ethyl acetate, then concentrated under

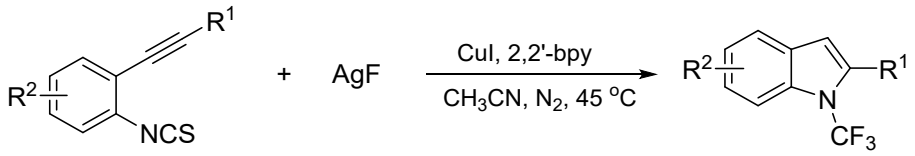
vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent.

Table S2. Optimization of the reaction conditions[a]

Entry	Catalyst	Ligand	Solvent	Temp./°C	Yield/%[b]
1	-	-	CH_3CN	25	58
2	-	-	THF	25	0
3	-	-	DMF	25	Trace
4	-	-	DMSO	25	0
5	-	-	DCE	25	0
6	-	-	DME	25	0
7[c]	-	-	CH_3CN	25	0
8[d]	-	-	CH_3CN	25	0
9	-	$RuCl_2$	CH_3CN	25	52
10	-	$RhCl(PPh_3)$	CH_3CN	25	37
11	-	$Pd(OAc)_2$	CH_3CN	25	46
12	-	CuI	CH_3CN	25	66
13	-	CuCl	CH_3CN	25	22
14	-	CuBr	CH_3CN	25	28
15	-	CuOAc	CH_3CN	25	Trace
16	-	$Cu(OAc)_2$	CH_3CN	25	Trace
17	-	$CuCl_2$	CH_3CN	25	Trace
18	-	CuF_2	CH_3CN	25	46
19	-	$Cu(TFA)_2$	CH_3CN	25	17
20	1,10-Phen	CuI	CH_3CN	25	36
21	2,2’-Bipyridine	CuI	CH_3CN	25	76
22	PPh_3	CuI	CH_3CN	25	48
23	Tricyclohexyl Phosphine	CuI	CH_3CN	25	44
24	DPEPhos	CuI	CH_3CN	25	46
25	4,4’-Bipyridine	CuI	CH_3CN	25	12
26	4,4’Di-Tert-Butyl-2,2’-Dipyridyl	CuI	CH_3CN	25	22
27	2,2’:6’,2’’-Terpyridine	CuI	CH_3CN	25	16
28	5,5'-Dimethyl-2,2'-Dipyridyl	CuI	CH_3CN	25	38
29	2,2’-Bipyridine	CuI	CH_3CN	30	64
30	**2,2’-Bipyridine**	CuI	**CH_3CN**	**50**	**88**
31	2,2’-Bipyridine	CuI	CH_3CN	70	83
32	2,2’-Bipyridine	CuI	CH_3CN	50	Trace

[a]Reaction conditions: 2-phenylethynyl aniline (0.10 mmol, 1.0 equiv), $AgSCF_3$ (0.15 mmol, 1.5 equiv), KI (0.15 mmol, 1.5 equiv), AgF (0.5 mmol, 5 equiv), catalyst (0.02 mmol, 20 mol%), ligand (0.02 mmol, 20 mol%), solvent (2 mL), N_2, Temp., 4 h. [b]Reaction yield determined by ^{19}F NMR spectroscopy using 4,4'-difluorobiphenyl as internal standard based on 2-phenylethynyl aniline. [c]KBr instead of KI. [d]KCl instead of KI. [e]Under air.

Method C

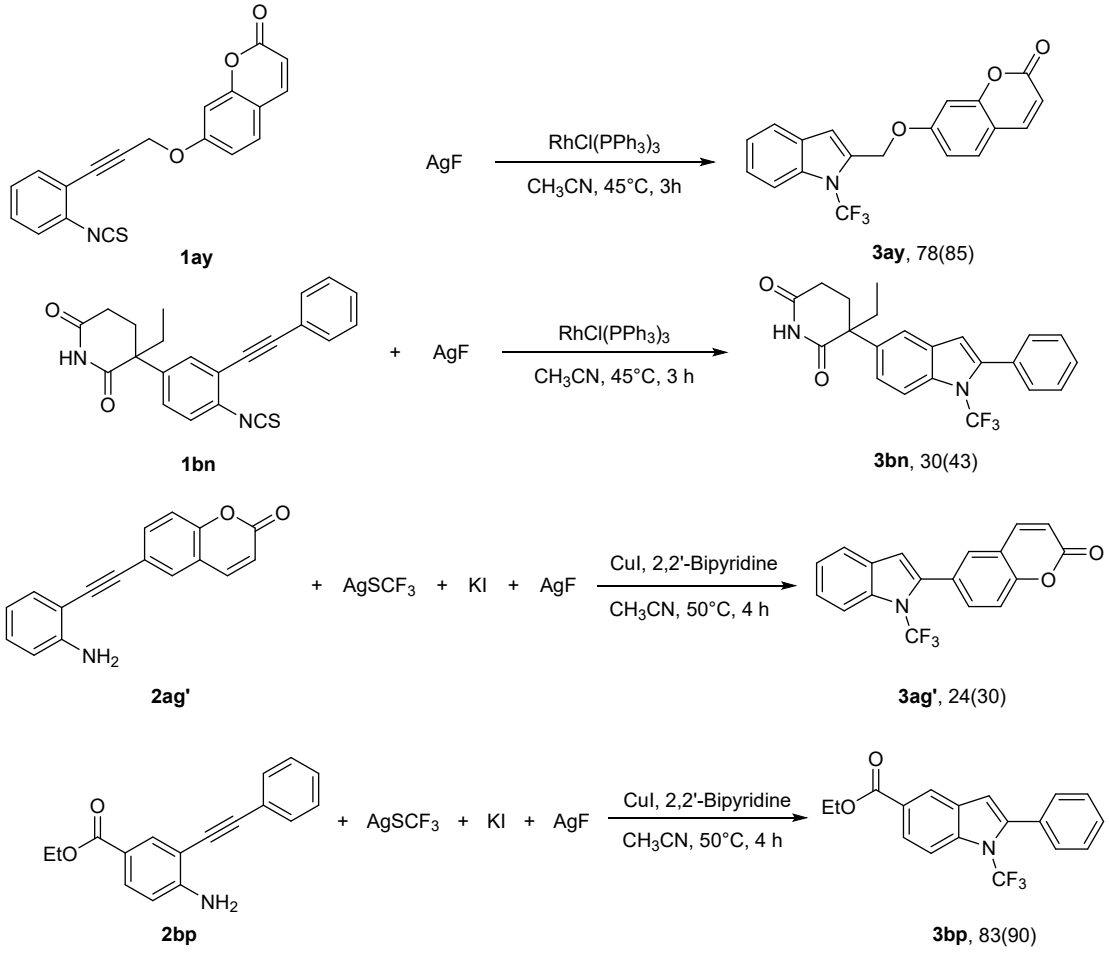


To an oven-dried 10 mL Schlenk tube equipped with a stir bar were added 2-alkynyl aryl isothiocyanate (0.5 mmol, 1.0 equiv.), AgF (3.2 equiv.), CuI (1 mol%) and 2,2'-bipyridine (1 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (1.5 mL) was then added by syringe. The reaction mixture was required to heat to 45 °C and then stirred for 6 h under N_2. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and wash with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent.

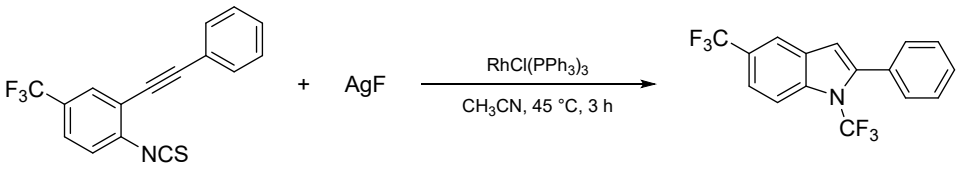
3. Modification of complex natural product and pharmaceutical molecules

(1) 2-Alkynyl aryl isothiocyanates **1ay** and **1bn** corresponding to products **3ay** and **3bn** were prepared according to the literature procedures.[1-4] 2-Alkynyl arylamines **2ag′** and **2bp** corresponding to products **3ag′** and **3bp** were prepared according to the literature procedures.[5-7]

(2) Target products were prepared according to the general procedure.

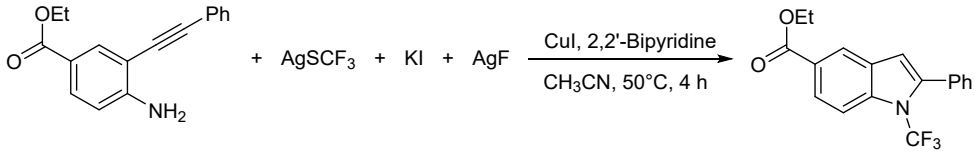


4. Synthesis of compounds 3bk and 3bp on 5.0 mmol scale



1bk, 5.0 mmol **3bk**, 1.299 g, 79%

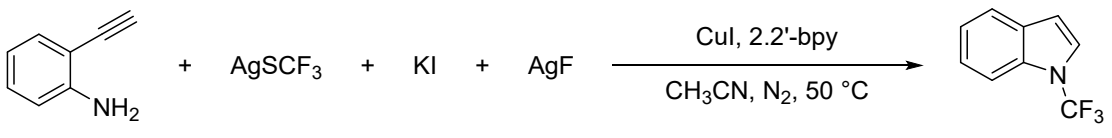
To an oven-dried 50 mL Schlenk tube equipped with a stir bar were added 1-isothiocyanato-2-(phenylethynyl)-4-(trifluoromethyl)benzene **1bk** (5.00 mmol, 1.520 g, 1.0 equiv.), AgF (16.00 mmol, 2.020 g, 3.2 equiv) and $RhCl(PPh_3)_3$ (0.05 mmol, 0.046 mg, 1 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (25 mL) was then added by syringe. The reaction mixture was required to heat to 45 °C and then stirred for 3 h under N_2. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and was with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent. to afford *N*-trifluoromethyl indole **3bk** (1.299 g, 79%).



2bp, 5.0 mmol **3bp**, 1.222 g, 77%

To an oven-dried 50 ml Schlenk tube equipped with a stir bar were added ethyl 4-amino-3-(phenylethynyl)benzoate **2bp** (5.00 mmol, 1.326 g, 1.0 equiv.), KI (7.5 mmol 1.245 g, 1.5 equiv.), $AgSCF_3$ (7.5 mmol, 1.567 g, 1.5 equiv.), AgF (25 mmol, 3.171 g, 5 equiv.), CuI (1 mmol, 0.190 g, 20 mmol%) and 2,2′-Bipyridine (1 mmol, 0.156 g, 20 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (30 ml) was then added by syringe. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and was with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent to afford *N*-trifluoromethyl indole **3bp** (1.222g, 77%).

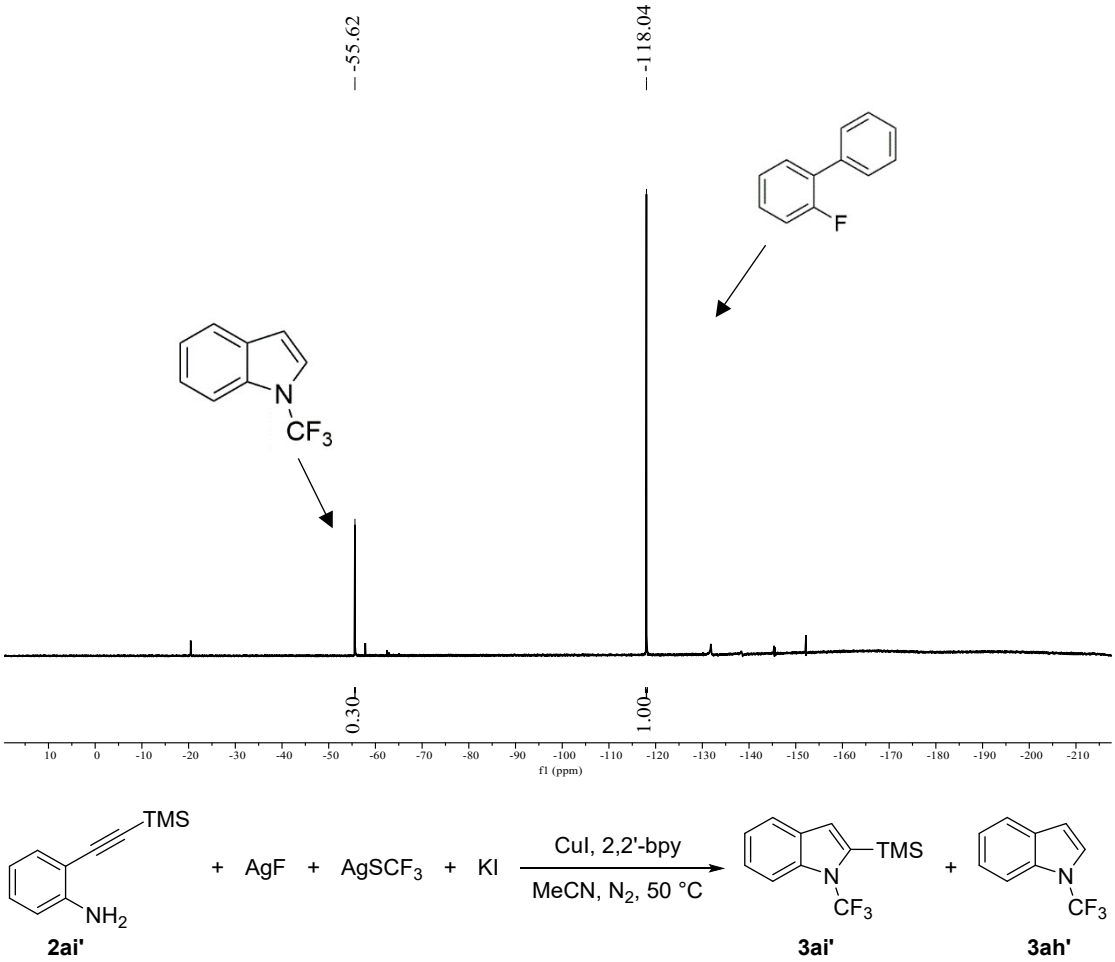
5. Test on desulfurization-fluorination/cyclization of some alkynyl arylamines



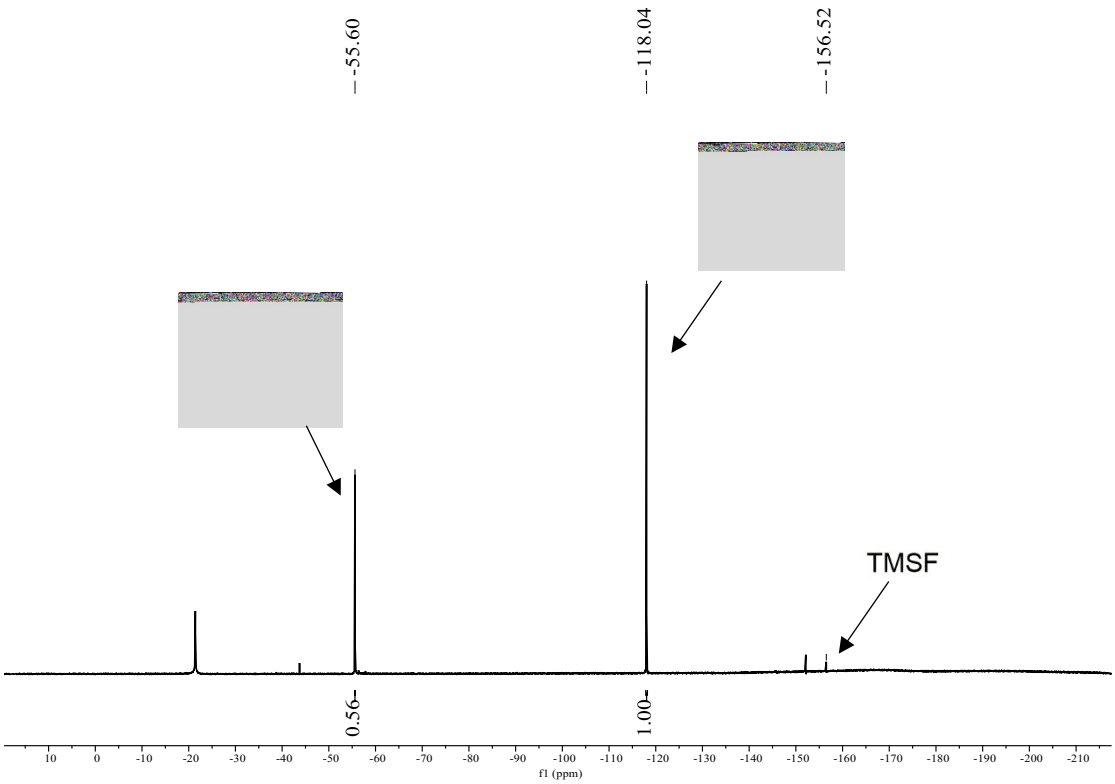
2ah' **3ah'**

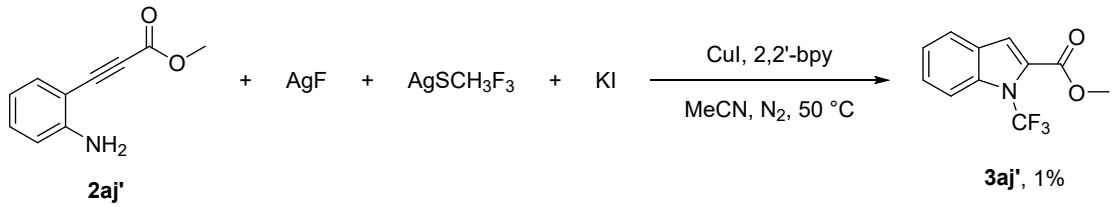
To an oven-dried 10 ml Schlenk tube equipped with a stir bar were added KI (0.15 mmol 24.9 mg, 1.5 equiv.), $AgSCF_3$ (0.15 mmol, 31.33 mg, 1.5 equiv.), AgF (0.5 mmol,

63.4 mg, 5 equiv.), CuI (0.02mmol, 3.82 mg, 20 mmol%) and 2,2′-Bipyridine (0.02mmol, 3.12 mg, 20 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (30 ml) and methyl 3-(2-aminophenyl)propiolate **2ah′** (0.1 mmol, 11.71 mg, 1.0 equiv.) was then added by syringe. The reaction mixture was required to heat to 50 °C and then stirred for 4 h. After cooling to room temperature, the raw product was analyzed by ^{19}F NMR using 4,4′-difluorobiphenyl (-115.0 ppm) as internal standard. The target product **3ah′** (-55.6 ppm)[8] was observed in 10% yield.



To an oven-dried 10 ml Schlenk tube equipped with a stir bar were added KI (0.15 mmol 24.9 mg, 1.5 equiv.), $AgSCF_3$ (0.15 mmol, 31.33 mg, 1.5 equiv.), AgF (0.5 mmol, 63.4 mg, 5 equiv.), CuI (0.02mmol, 3.82 mg, 20 mmol%) and 2,2′-Bipyridine (0.02mmol, 3.12 mg, 20 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (2 mL) and 2-((trimethylsilyl)ethynyl)aniline **2ai′** (0.1 mmol, 1.0 equiv. 18.9 mg) was then added by syringe. The reaction mixture was required to heat to 50 °C and then stirred for 4. After cooling to room temperature, the raw product was analyzed by ^{19}F NMR using 4,4′-difluorobiphenyl (-115.0 ppm) as internal standard. The product **3ah′** (-55.6 ppm) instead of **3ai′** was observed in18% yield. The signal of TMSF can also be observed at -156.6 ppm in ^{19}F NMR spectrum (Due to the volatility of this compound, the intensity of the signal is relatively weak in the spectrum).

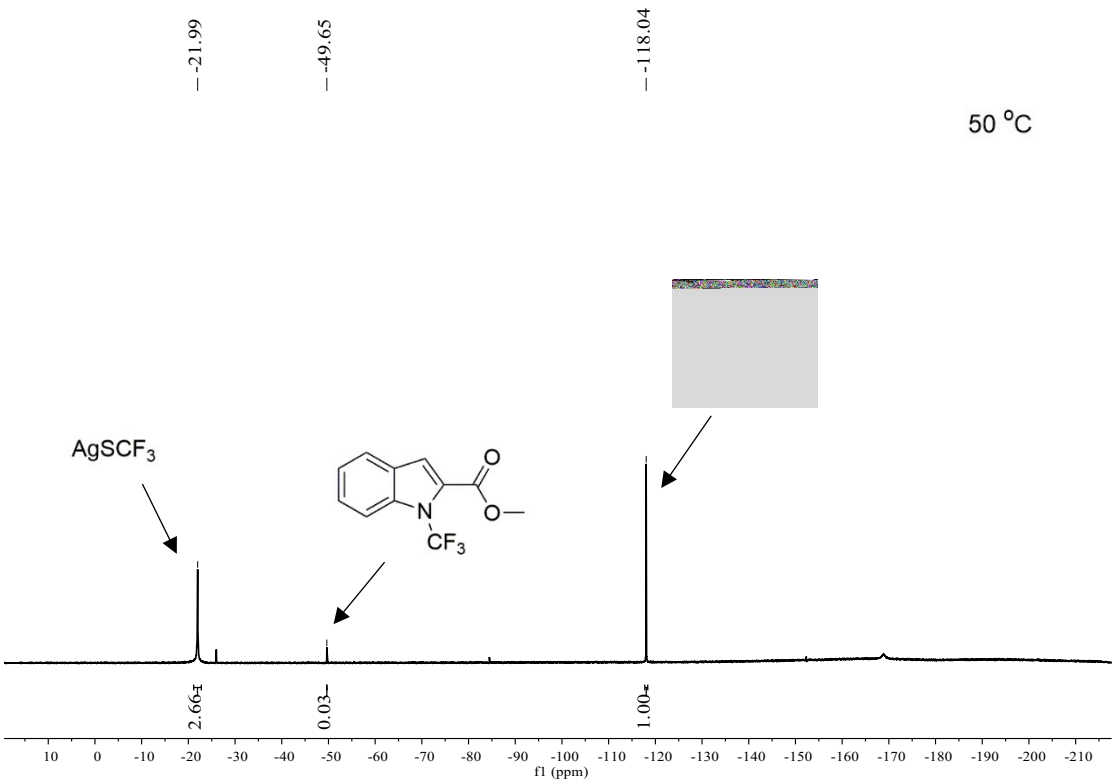


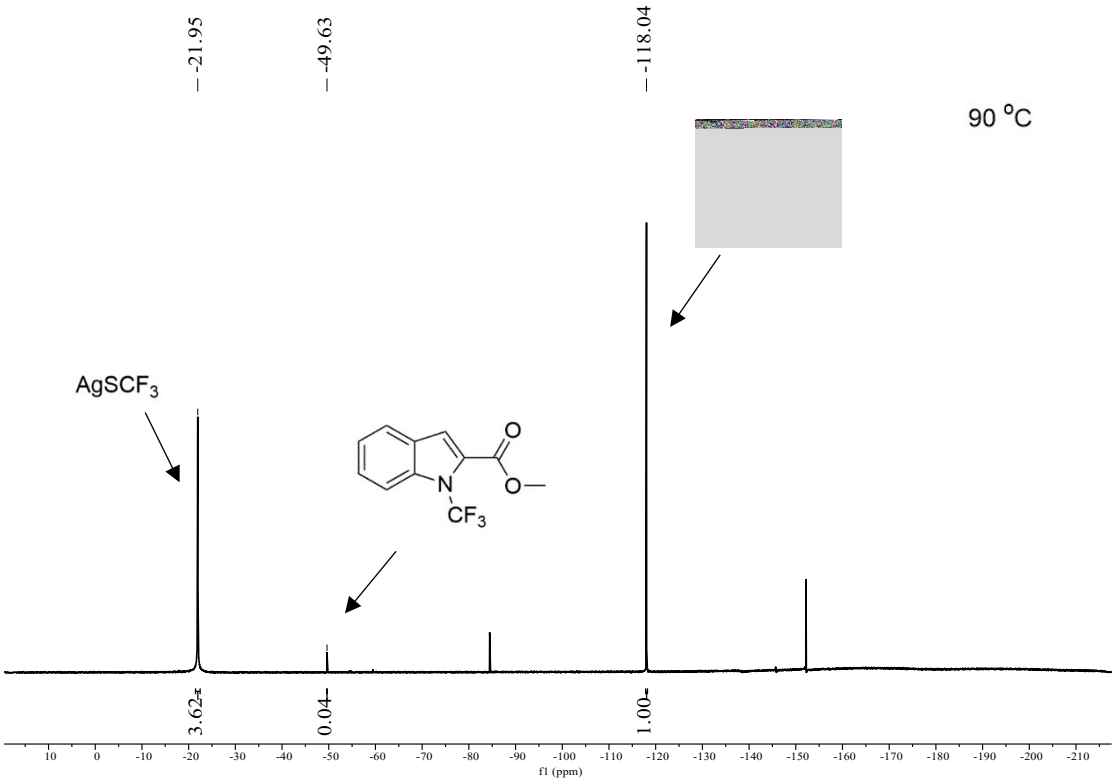


2aj'

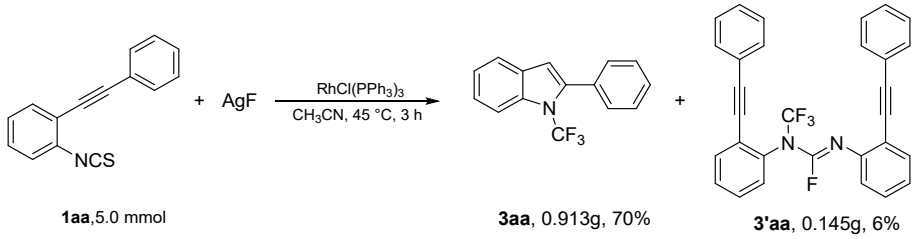
3aj', 1%

To an oven-dried 10 ml Schlenk tube equipped with a stir bar were added methyl 3-(2-aminophenyl)propiolate **2aj'** (0.1 mmol, 17.51 mg, 1.0 equiv.), KI (0.15 mmol 24.9 mg, 1.5 equiv.), $AgSCF_3$ (0.15 mmol, 31.33 mg, 1.5 equiv.), AgF (0.5 mmol, 63.4 mg, 5 equiv.), CuI (0.02mmol, 3.82 mg, 20 mmol%) and 2,2′-Bipyridine (0.02mmol, 3.12 mg, 20 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (30 ml) was then added by syringe. The reaction mixture was required to heat to 50 °C (or 90 °C) and then stirred for 4 h. After cooling to room temperature, the raw product was analyzed by ^{19}F NMR using 4,4′-difluorobiphenyl (-115.0 ppm) as internal standard. The target product was observed with a yield of 0.1%.


-21.99
-49.65
-118.04
50 °C
AgSCF3
O
O
N
CF3
2.66
0.03
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

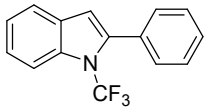

-21.95
-49.63
-118.04
90 °C
AgSCF3
O
O
N
CF3
3.62
0.04
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

6. Identification of byproduct in the synthesis of *N*-trifluoromethyl indole 3aa

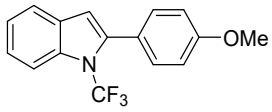


To an oven-dried 50 mL Schlenk tube equipped with a stir bar were added **1aa** (5.00 mmol, 1.180 g, 1.0 equiv.), AgF (16.00 mmol, 2.020 g, 3.2 equiv) and $RhCl(PPh_3)_3$ (0.05 mmol, 0.046 mg, 1 mol%). The Schlenk tube was evacuated and refilled with N_2 (three times). CH_3CN (25 mL) was then added by syringe. The reaction mixture was required to heat to 45 °C and then stirred for 3 h under N_2. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and was with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate as eluent to afford **3aa** (0.913 g, 70%) and **3′aa** (0.145 g, 6%). **3′aa**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.7, 1.5 Hz, 1H), 7.60–7.52 (m, 4H), 7.50 (dd, J = 7.7, 1.5 Hz, 1H), 7.41 (ddd, J = 14.3, 7.1, 1.6 Hz, 4H), 7.35 (qd, J = 5.2, 4.7, 2.6 Hz, 6H), 7.18 (td, J = 7.7, 1.6 Hz, 1H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -44.95 (s, 1F), -54.47 (d, J = 14.3 Hz, 3F).

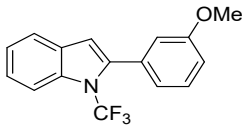
7. Characterization data for the products



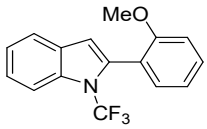
2-phenyl-1-(trifluoromethyl)-1H-indole (3aa). Following the general procedure of **Method A**, compound **3aa** was synthesized and isolated as a colorless oil (0.105 g, 80%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.093 g, 71%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.69 (m, 1H), 7.69–7.62 (m, 1H), 7.57 (dd, J = 6.5, 2.8 Hz, 2H), 7.52–7.44 (m, 3H), 7.43–7.30 (m, 2H), 6.69–6.61 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.82 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4 (s), 136.0 (s), 132.4 (s), 129.6 (s), 129.3 (s), 128.8 (s), 128.2 (s), 124.4 (s), 123.0 (s), 121.1 (s), 120.7 (q, J = 263.2 Hz), 113.2 (q, J = 4.3 Hz), 109.8 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{10}F_3NH$ $(M+H)^+$: 262.0838; found: 262.0835.



2-(4-methoxyphenyl)-1-(trifluoromethyl)-1H-indole (3ab). Following the general procedure of **Method A**, compound **3ab** was synthesized and isolated as a colorless solid (0.090 g, 62%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless solid (0.092 g, 66%) via **Method B**. mp 77-79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 1H), 7.61 (d, J = 7.3 Hz, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.37–7.32 (m, 1H), 7.29 (td, J = 7.5, 0.9 Hz, 1H), 7.02–6.94 (m, 1H), 6.57 (s, 1H), 3.88 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.86 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1 (s), 139.3 (s), 135.9 (s), 131.0–130.8 (m), 129.3 (s), 124,8–124.5 (m), 124.1 (s), 122.9 (s), 120.9 (s), 120.8 (q, J = 261.5 Hz), 113.7 (s), 113.1 (q, J = 4.5 Hz), 109.4 (s), 55.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NOH$ $(M+H)^+$: 292.0944; found: 292.0946.

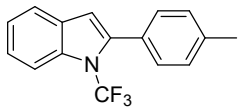


2-(3-methoxyphenyl)-1-(trifluoromethyl)-1H-indole (3ac). Following the general procedure of **Method A**, compound **3ac** was synthesized and isolated as a yellow oil (0.090 g, 62%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a yellow oil (0.074 g, 51%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.36 (td, J = 8.4, 1.6 Hz, 2H), 7.30 (td, J = 7.5, 1.1 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.08 (s, 1H), 7.00 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 6.63 (s, 1H), 3.87 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.86 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3 (s), 139.2 (s), 136.0 (s), 133.6 (s), 129.2 (d, J = 3.9 Hz), 124.4 (s), 123.0 (s), 122.2–121.9 (m), 121.1 (s), 120.7 (q, J = 261.6 Hz), 115.2 (s), 114.5 (s), 113.2 (q, J = 4.3 Hz), 109.8 (s), 55.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NOH$ $(M+H)^+$: 292.0944; found: 292.0949.

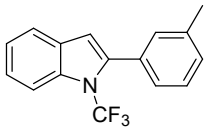


2-(2-methoxyphenyl)-1-(trifluoromethyl)-1H-indole (3ad). Following the general procedure of **Method A**, compound **3ad** was synthesized and isolated as a colorless oil (0.073 g, 50%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.070 g, 48%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.45 (td, J = 8.2, 1.7 Hz, 1H), 7.39 (dd, J = 7.4, 1.7 Hz, 1H), 7.35 (td, J = 8.4, 7.8, 1.3 Hz, 1H), 7.28 (td, J = 7.7, 1.0 Hz, 1H), 7.04 (td, J = 7.5, 0.9 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.60–6.53 (m, 1H), 3.81 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -53.52 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1 (s), 135.7 (d, J = 22.4Hz), 131.6 (s), 130.7 (s), 129.2 (s), 124.0 (s), 122.6 (s), 121.8 (s), 121.0 (s), 120.5 (q, J = 261.5 Hz), 120.3

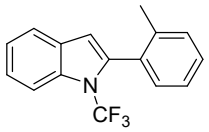
(s), 112.7 (q, J = 4.5 Hz), 110.5 (s), 109.1 (s), 55.5 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NOH$ $(M+H)^+$: 292.0944; found: 292.0956.



2-(p-tolyl)-1-(trifluoromethyl)-1H-indole (3ae). Following the general procedure of **Method A**, compound **3ae** was synthesized and isolated as a yellow oil (0.107 g, 78%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a yellow oil (0.095 g, 69%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62–7.56 (m, 1H), 7.55–7.50 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.29–7.24 (m, 1H), 7.22 (dd, J = 7.6, 1.1 Hz, 1H), 7.20–7.15 (m, 2H), 6.51 (s, 1H), 2.36 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.83 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6 (s), 138.8 (s), 136.0 (s), 129.6–129.4 (m), 129.3 (s), 128.9 (s), 124.2 (s), 123.0 (s), 121.0 (s), 120.7 (q, J = 263.4 Hz), 113.2 (q, J = 4.4 Hz), 109.5 (s), 21.5 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NH$ $(M+H)^+$: 276.0995; found: 276.0996.

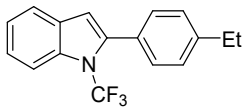


2-(m-tolyl)-1-(trifluoromethyl)-1H-indole (3af). Following the general procedure of **Method A**, compound **3af** was synthesized and isolated as a colorless oil (0.105 g, 76%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 1H), 7.64–7.60 (m, 1H), 7.39–7.29 (m, 5H), 7.29–7.25 (m, 1H), 6.61 (s, 1H), 2.44 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.87 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6 (s), 137.9 (s), 136.0 (s), 132.3 (s), 130.2 (s), 129.6 (s), 129.3 (s), 128.1 (s), 126.8–126.5 (m), 124.3 (s), 123.0 (s), 121.1 (s), 120.7 (q, J = 263.3 Hz), 113.2 (q, J = 4.3 Hz), 109.7 (s), 21.5 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NH$ $(M+H)^+$: 276.0995; found: 276.0989.

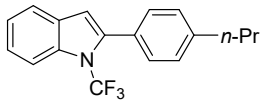


2-(o-tolyl)-1-(trifluoromethyl)-1H-indole (3ag). Following the general procedure of **Method A**, compound **3ag** was synthesized and isolated as a yellow oil (0.076 g, 55%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 1H), 7.66–7.63 (m, 1H), 7.38 (dtd, J = 8.3, 5.8, 5.3, 1.5 Hz, 3H), 7.32 (td, J = 7.6, 1.1 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 6.58–6.50 (m, 1H), 2.25 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.95 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1 (d, J = 34.9 Hz), 135.4 (s), 131.9 (s), 130.9 (s), 129.9 (s), 129.3 (d, J = 5.4 Hz), 125.4 (s), 124.2 (s), 122.9 (s), 121.0 (s), 120.6 (q, J = 263.3 Hz),

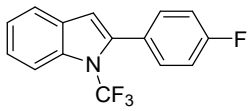
112.9 (q, J = 4.1 Hz), 109.3 (s), 20.0 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NH$ $(M+H)^+$: 276.0995; found: 276.0982.



2-(4-ethylphenyl)-1-(trifluoromethyl)-1H-indole (3ah). Following the general procedure of **Method A**, compound **3ah** was synthesized and isolated as a colorless oil (0.108 g, 75%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72–7.67 (m, 1H), 7.65–7.60 (m, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.39–7.34 (m, 1H), 7.31 (t, J = 7.3 Hz, 3H), 6.61 (s, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.83 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0 (s), 139.6 (s), 136.0 (s), 129.7 (s), 129.5 (d, J = 1.1 Hz), 129.3 (s), 127.7 (s), 124.2(s), 123.0 (s), 121.0 (s), 120.7 (q, J = 261.6 Hz), 113.2 (q, J = 4.4 Hz), 109.6 (s), 28.8 (s), 15.5 (s). **HRMS (ESI)** *m/z* calcd. for $C_{17}H_{14}F_3NH$ $(M+H)^+$: 290.1151; found: 290.1151.

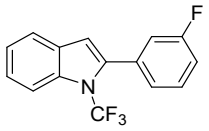


2-(4-propylphenyl)-1-(trifluoromethyl)-1H-indole (3ai). Following the general procedure of **Method A**, compound **3ai** was synthesized and isolated as a colorless oil (0.114 g, 75%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.038 g, 25%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73–7.65 (m, 1H), 7.66–7.59 (m, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.38–7.32 (m, 1H), 7.31 (dd, J = 7.6, 1.0 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 6.60 (s, 1H), 2.86–2.41 (m, 2H), 1.73 (m, J = 7.4 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.84 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5 (s), 139.6 (s), 136.0 (s), 129.7 (s), 129.5 – 129.3 (m), 129.3 (s), 128.3 (s), 124.2 (s), 123.0 (s), 121.0 (s), 120.7 (q, J = 261.8 Hz), 113.2 (q, J = 4.4 Hz), 109.5 (s), 38.0 (s), 24.6 (s), 14.0 (s). **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{16}F_3NH$ $(M+H)^+$: 304.1308; found: 304.1310.

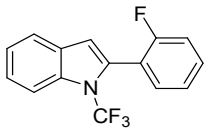


2-(4-fluorophenyl)-1-(trifluoromethyl)-1H-indole (3aj). Following the general procedure of **Method A**, compound **3aj** was synthesized and isolated as a colorless oil (0.089 g, 64%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.101 g, 72%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 1H), 7.62 (d, J = 7.3 Hz, 1H), 7.49 (dd, J = 8.5, 5.4 Hz, 2H), 7.41–7.26 (m, 2H), 7.18–7.08 (m, 2H), 6.60 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.89 (s, 3F), -112.57 (s, 1F). **^{13}C NMR** (101 MHz,

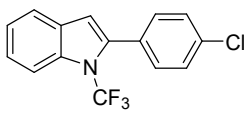
$CDCl_3$) δ 163.2 (d, J = 248.6 Hz), 136.0 (s), 131.5 – 131.2 (m), 129.1 (s), 124.5 (s), 123.1 (s), 121.1 (s), 120.7 (q, J = 263.1 Hz), 115.8 (d, J = 21.8 Hz), 113.2 (q, J = 4.4 Hz), 110.0 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_4NH$ $(M+H)^+$: 280.0744; found: 280.0738.



2-(3-fluorophenyl)-1-(trifluoromethyl)-1H-indole (3ak). Following the general procedure of **Method A**, compound **3ak** was synthesized and isolated as a colorless oil (0.098 g, 70%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.061 g, 44%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.43–7.35 (m, 2H), 7.34–7.28 (m, 2H), 7.24 (d, J = 9.5 Hz, 1H), 7.15 (tdd, J = 8.5, 2.6, 1.0 Hz, 1H), 6.64 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.92 (s, 3F), -113.14 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, J = 246.6 Hz), 137.8 (d, J = 2.3 Hz), 136.1 (s), 134.3 (d, J = 7.6 Hz), 129.8 (d, J = 8.5 Hz), 129.1 (s), 125.4 (dd, J = 2.8, 1.3 Hz), 124.7 (s), 123.2 (s), 121.3 (s), 120.6 (q, J = 261.8 Hz), 116.5 (d, J = 22.5 Hz), 115.8 (d, J = 21.1 Hz), 113.2 (q, J = 4.3 Hz), 110.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_4NH$ $(M+H)^+$: 280.0744; found: 280.0745.

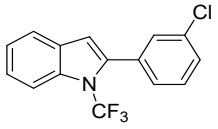


2-(2-fluorophenyl)-1-(trifluoromethyl)-1H-indole (3al). Following the general procedure of **Method A**, compound **3al** was synthesized and isolated as a colorless oil (0.073 g, 52%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.049 g, 35%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.50–7.42 (m, 2H), 7.38 (td, J = 8.4, 7.8, 1.3 Hz, 1H), 7.34–7.28 (m, 1H), 7.23 (td, J = 7.6, 1.0 Hz, 1H), 7.18 (t, J = 9.0 Hz, 1H), 6.67 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -52.61 (d, J = 5.1 Hz, 3F), -112.86 (q, J = 5.1 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6 (d, J = 249.4 Hz), 135.9 (s), 132.4 (s), 132.0 (d, J = 1.9 Hz), 131.1 (d, J = 8.1 Hz), 129.1 (s), 124.6 (s), 124.0 (d, J = 3.7 Hz), 123.0 (s), 121.2 (s), 120.5 (q, J = 262.6 Hz), 120.4 (d, J = 15.7 Hz), 115.6 (d, J = 21.6 Hz), 112.9 (q, J = 3.7 Hz), 110.7 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_4NH$ $(M+H)^+$: 280.0744; found: 280.0735.

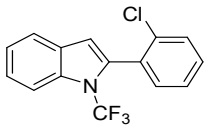


2-(4-chlorophenyl)-1-(trifluoromethyl)-1H-indole (3am). Following the general procedure of **Method A**, compound **3am** was synthesized and isolated as a colorless

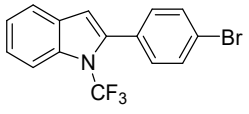
solid (0.074 g, 50%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless solid (0.075 g, 51%) via **Method B**. mp 23-24 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.36 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 7.30 (td, J = 7.6, 1.0 Hz, 1H), 6.61 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.88 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0 (s), 136.1 (s), 135.0 (s), 130.9 – 130.7 (m), 129.1 (s), 128.5 (s), 124.6 (s), 123.2 (s), 121.2 (s), 120.6 (q, J = 263.5 Hz), 113.2 (q, J = 4.3 Hz), 110.2 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9ClF_3NH$ $(M+H)^+$: 296.048; found: 296.0433.



2-(3-chlorophenyl)-1-(trifluoromethyl)-1H-indole (3an). Following the general procedure of **Method A**, compound **3an** was synthesized and isolated as a colorless oil (0.102 g, 69%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.44–7.34 (m, 4H), 7.31 (td, J = 7.7, 0.9 Hz, 1H), 6.63 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.93 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.7 (s), 136.1 (s), 134.1 (d, J = 10.1 Hz), 129.6–129.5 (m), 129.5 (s), 129.1 (s), 129.0 (s), 127.8 (d, J = 1.3 Hz), 124.8 (s), 123.2 (s), 121.3 (s), 120.6 (q, J = 261.8 Hz), 113.2 (q, J = 4.3 Hz), 110.5 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9ClF_3NH$ $(M+H)^+$: 296.0448; found: 296.0438.

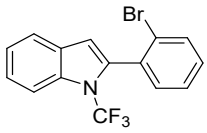


2-(2-chlorophenyl)-1-(trifluoromethyl)-1H-indole (3ao). Following the general procedure of **Method A**, compound **3ao** was synthesized and isolated as a colorless solid (0.087 g, 59%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 70-71 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72–7.63 (m, 2H), 7.51 (dd, J = 8.0, 1.1 Hz, 1H), 7.49–7.27 (m, 5H), 6.62 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -52.47 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.4 (s), 135.2 (s), 132.3 (s), 131.6 (s), 130.6 (s), 129.5 (s), 129.0 (s), 126.4 (s), 124.6 (s), 123.0 (s), 121.3 (s), 120.4 (q, J = 261.5 Hz), 112.8 (q, J = 3.7 Hz), 110.3–110.0 (m). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9ClF_3NH$ $(M+H)^+$: 296.0448; found: 296.0441.

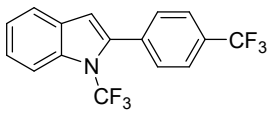


2-(4-bromophenyl)-1-(trifluoromethyl)-1H-indole (3ap). Following the general procedure of **Method A**, compound **3ap** was synthesized and isolated as a colorless oil

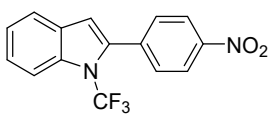
(0.116 g, 68%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.070 g, 41%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69–7.64 (m, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.60–7.56 (m, 2H), 7.41–7.34 (m, 3H), 7.30 (td, J = 7.6, 1.0 Hz, 1H), 6.61 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.87 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0 (s), 136.1 (s), 131.5 (s), 131.3 (s), 131.2–131.0 (m), 129.1 (s), 124.7 (s), 123.2 (d, J = 2.4 Hz), 121.2 (s), 120.6 (q, J = 261.8 Hz), 113.2 (q, J = 4.3 Hz), 110.2 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9BrF_3NH$ $(M+H)^+$: 339.9943; found: 339.9914.



2-(2-bromophenyl)-1-(trifluoromethyl)-1H-indole (3aq). Following the general procedure of **Method A**, compound **3aq** was synthesized and isolated as a colorless solid (0.099 g, 58%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 68-69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73–7.63 (m, 3H), 7.45 (dd, J = 7.5, 1.8 Hz, 1H), 7.42–7.36 (m, 2H), 7.36–7.29 (m, 2H), 6.62 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -52.18 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7 (s), 135.2 (s), 133.7 (s), 132.7 (s), 132.4 (s), 130.7 (s), 129.0 (s), 127.0 (s), 125.2 (s), 124.6 (s), 123.0 (s), 121.4 (s), 120.4 (q, J = 261.7 Hz), 112.8 (q, J = 3.7 Hz), 110.1 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9BrF_3NH$ $(M+H)^+$: 339.9943; found: 339.9943.

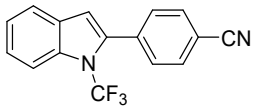


1-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-1H-indole (3ar). Following the general procedure of **Method A**, compound **3ar** was synthesized and isolated as a colorless solid (0.122 g, 74%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless solid (0.079 g, 48%) via **Method B**. mp 46-47 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.61 (m, 6H), 7.39 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.90 (s, 3F), -62.69 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.6 (s), 136.3 (s), 136.0 (s), 130.9 (q, J = 32.6 Hz), 129.8 (s), 129.1 (s), 125.3 (q, J = 3.7 Hz), 125.0 (s), 124.2 (q, J = 270.4 Hz), 123.4 (s), 121.4 (s), 120.6 (q, J = 261.7 Hz), 113.3 (q, J = 4.2 Hz), 110.9 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_9F_6NH$ $(M+H)^+$: 330.0712; found: 330.0710.

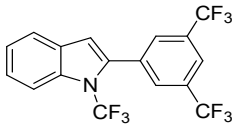


2-(4-nitrophenyl)-1-(trifluoromethyl)-1H-indole (3as). Following the general procedure of **Method A**, compound **3as** was synthesized and isolated as a yellow solid

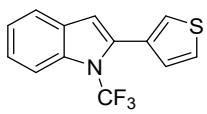
(0.081 g, 53%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (petroleum ether:ethyl acetate = 100:1) as eluent. This compound can also be obtained as a yellow solid (0.061 g, 40%) via **Method B**. mp 108-110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35–8.26 (m, 2H), 7.67 (dd, J = 15.0, 8.2 Hz, 3H), 7.45–7.36 (m, 1H), 7.38–7.29 (m, 1H), 6.74 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.87 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9 (s), 138.8 (s), 136.6 (d, J = 13.4 Hz), 130.3–130.0 (m), 129.0 (s), 125.4 (s), 123.6 (s), 121.6 (s), 120.5 (q, J = 262.1 Hz), 113.4 (q, J = 4.1 Hz), 111.8 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_3N_2O_2H$ $(M+H)^+$: 307.0689; found: 307.0682.



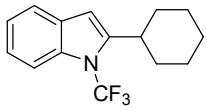
4-(1-(trifluoromethyl)-1H-indol-2-yl)benzonitrile (3at). Following the general procedure of **Method A**, compound **3at** was synthesized and isolated as a colorless solid (0.100 g, 70%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (petroleum ether: ethyl acetate = 50:1) as eluent. This compound can also be obtained as a colorless solid (0.109 g, 76%) via **Method B**. mp 101-102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.69–7.66 (m, 1H), 7.63 (t, J = 7.4 Hz, 3H), 7.42–7.37 (m, 1H), 7.35–7.29 (m, 1H), 6.69 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.90 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1 (s), 136.9 (s), 136.4 (s), 132.1 (s), 130.1–129.8 (m), 129.0 (s), 125.3 (s), 123.5 (s), 121.5 (s), 120.5 (q, J = 262.1 Hz), 118.6 (s), 113.3 (q, J = 4.2 Hz), 112.5 (s), 111.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_9F_3N_2H$ $(M+H)^+$: 287.0791; found: 287.0784.



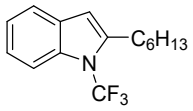
2-(3,5-bis(trifluoromethyl)phenyl)-1-(trifluoromethyl)-1H-indole (3au). Following the general procedure of **Method A**, compound **3au** was synthesized and isolated as a colorless oil (0.093 g, 47%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.9 Hz, 3H), 7.71–7.67 (m, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.4, 1.3 Hz, 1H), 7.37–7.31 (m, 1H), 6.76 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.06 (s, 3F), -63.00 (s, 6F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.5 (s), 135.7 (s), 134.5 (s), 131.9 (q, J = 33.7 Hz), 129.9–129.1 (m), 128.9 (s), 125.6 (s), 123.7 (s), 123.2 (q, J = 271.1 Hz), 122.6 (p, J = 3.8 Hz), 121.6 (s), 120.6 (q, J = 261.8 Hz), 113.4 (q, J = 4.2 Hz), 112.1 (s). **HRMS (ESI)** *m/z* calcd. for $C_{17}H_8F_9NH$ $(M+H)^+$: 398.0586; found: 398.0583.



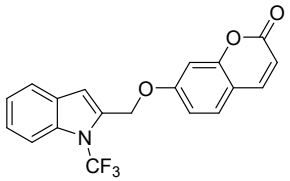
2-(thiophen-3-yl)-1-(trifluoromethyl)-1H-indole (3av). Following the general procedure of **Method A**, compound **3av** was synthesized and isolated as a colorless oil (0.107 g, 80%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.45 (dd, J = 2.9, 1.0 Hz, 1H), 7.36 (dd, J = 5.0, 3.0 Hz, 1H), 7.25 (dd, J = 14.1, 6.8 Hz, 2H), 6.63 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.23 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.9 (s), 134.0 (s), 132.1 (s), 129.0 (s), 129.0 – 128.6 (m), 125.4 (s), 125.3 (s), 124.4 (s), 123.0 (s), 121.0 (s), 120.7 (q, J = 261.3 Hz), 113.1 (q, J = 4.7 Hz), 109.9 (s). **HRMS (AP)** *m/z* calcd. for $C_{13}H_8F_3NS$ $(M)^+$: 267.0430; found: 267.0330.



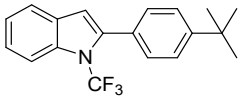
2-cyclohexyl-1-(trifluoromethyl)-1H-indole (3aw). Following the general procedure of **Method A**, compound **3aw** was synthesized and isolated as a colorless oil (0.104 g, 78%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 1H), 7.56–7.50 (m, 1H), 7.31–7.18 (m, 2H), 6.45 (s, 1H), 2.85 (s, 1H), 2.11 (t, J = 9.7 Hz, 2H), 1.89 (dd, J = 5.3, 2.5 Hz, 2H), 1.81 (ddt, J = 11.1, 3.0, 1.4 Hz, 1H), 1.45 (p, J = 11.7 Hz, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.35 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2 (s), 135.3 (s), 129.4 (s), 123.4 (s), 122.5 (s), 121.2 (q, J = 260.2 Hz), 120.5 (s), 112.7 (q, J = 5.1 Hz), 104.6 (s), 37.1 (q, J = 2.9 Hz), 34.3 (s), 26.8 (s), 26.3 (s). **HRMS (AP)** *m/z* calcd. for $C_{15}H_{16}F_3N$ $[M]^+$: 267.1380, found 267.1235.



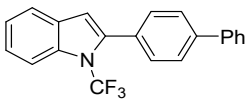
2-hexyl-1-(trifluoromethyl)-1H-indole (3ax). Following the general procedure of **Method A**, compound **3ax** was synthesized and isolated as a colorless oil (0.102 g, 76%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.035 g, 26%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63–7.56 (m, 1H), 7.53 (dd, J = 6.8, 1.8 Hz, 1H), 7.24 (pd, J = 7.2, 6.7, 1.4 Hz, 2H), 6.43 (s, 1H), 2.84 (t, J = 7.7 Hz, 2H), 1.77 (p, J = 7.5 Hz, 2H), 1.42 (ddq, J = 33.4, 7.1, 3.2 Hz, 6H), 1.01–0.88 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.89 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3 (s), 135.6 (s), 129.3 (s), 123.4 (s), 122.5 (s), 121.1 (q, J = 260.0 Hz), 120.4 (s), 112.5 (q, J = 4.8 Hz), 106.3 (s), 31.8 (s), 29.2 (s), 28.4 (s), 28.0 (q, J = 3.2 Hz), 22.8 (s), 14.2 (s). **HRMS (AP)** *m/z* calcd. for $C_{15}H_{18}F_3NH$ $(M+H)^+$: 270.1470; found: 270.1477.



7-((1-(trifluoromethyl)-1H-indol-2-yl)methoxy)-2H-chromen-2-one (3ay). Following the general procedure of **Method A**, compound **3ay** was synthesized and isolated as a colorless solid (0.140 g, 78%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (petroleum ether:ethyl acetate = 20:1) as eluent. mp 113-114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 14.8, 8.7 Hz, 3H), 7.43–7.32 (m, 2H), 7.30–7.25 (m, 1H), 6.92 (d, J = 7.5 Hz, 2H), 6.79 (s, 1H), 6.27 (d, J = 9.5 Hz, 1H), 5.28 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -53.21 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1 (s), 160.0 (s), 154.7 (s), 142.2 (s), 134.9 (s), 131.1 (s), 127.9 (s), 127.1 (s), 124.1 (s), 121.9 (s), 120.5 (s), 112.6 (s), 112.2 (s), 112.1 (s), 119.6 (q, J = 261.4 Hz), 111.5 (q, J = 4.2 Hz), 109.8 (s), 100.9 (s), 62.5 (q, J = 3.4 Hz). **HRMS (AP)** *m/z* calcd. for $C_{19}H_{12}F_3NO_3$ $(M)^+$: 359.0769; found: 359.0766.

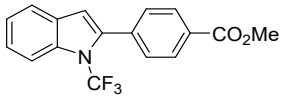


2-(4-(tert-butyl)phenyl)-1-(trifluoromethyl)-1H-indole (3az). Following the general procedure of **Method B**, compound **3az** was synthesized and isolated as a colorless solid (0.095 g, 60%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 52-54 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.Z1 Hz, 2H), 7.59 (d, J = 7.9 Hz, 1H), 7.43 (s, 4H), 7.36–7.26 (m, 2H), 6.57 (s, 1H), 1.37 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.32 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.76 (s), 139.43 (s), 135.85 (s), 129.93–128.66 (m), 124.98 (s), 124.04 (s), 122.80 (s), 119.49 (q), 120.85 (s), 113.01 (q, J = 4.4 Hz), 109.44 (s), 34.72 (s), 31.31 (s). **HRMS (AP)** *m/z* calcd. for $C_{19}H_{18}F_3NH$ $(M+H)^+$: 318.1480; found: 318.1481.

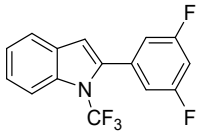


2-([1,1'-biphenyl]-4-yl)-1-(trifluoromethyl)-1H-indole (3aa′). Following the general procedure of **Method B**, compound **3aa′** was synthesized and isolated as a colorless solid (0.067 g, 40%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 114-115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dt, J = 5.6, 3.5 Hz, 5H), 7.63–7.56 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.41–7.26 (m, 3H), 6.64 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.27 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.94 (d, J = 108.1 Hz), 138.98 (s), 135.99 (s), 131.14 (s), 129.85–129.66 (m), 129.17 (s), 128.87 (s), 127.64 (s), 126.94 (d, J = 36.8 Hz), 124.27 (s), 122.93 (s), 120.97 (s), δ

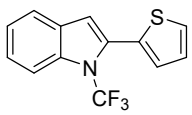
120.60 (q, J = 263.2 Hz), 113.08 (q, J = 4.3 Hz), 109.82 (s). **HRMS (AP)** *m/z* calcd. for $C_{21}H_{14}F_3NH$ $(M+H)^+$: 338.1157; found: 338.1142.



methyl 4-(1-(trifluoromethyl)-1H-indol-2-yl)benzoate (3ab′). Following the general procedure of **Method B**, compound **3ab′** was synthesized and isolated as a colorless solid (0.120 g, 75%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 54-55 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.60 (dd, J = 13.7, 7.9 Hz, 4H), 7.33 (dtd, J = 26.4, 7.3, 1.2 Hz, 2H), 6.66 (s, 1H), 3.95 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.41 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.65 (s), 138.05 (s), 136.45 (d, J = 51.9 Hz), 130.22 (s), 129.42 – 129.20 (m), 129.01 (s), 124.73 (s), 123.15 (s), 121.20 (s), δ 120.48 (q, J = 263.6 Hz), 113.14 (q, J = 4.2 Hz), 110.64 (s), 52.26 (s). **HRMS (AP)** *m/z* calcd. for $C_{17}H_{12}F_3NO_2H$ $(M+H)^+$: 320.0898; found: 320.0898.

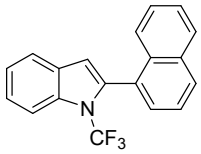


2-(3,5-difluorophenyl)-1-(trifluoromethyl)-1H-indole (3ac′). Following the general procedure of **Method B**, compound **3ac′** was synthesized and isolated as a colorless solid (0.030 g, 20%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 56-58 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 15.7, 8.1 Hz, 2H), 7.40 – 7.33 (m, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 5.9 Hz, 2H), 6.88 (tt, J = 8.9, 2.3 Hz, 1H), 6.64 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.53 (s, 3F), -109.18 (s, 2F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.74 (d, J = 12.9 Hz), 161.26 (d, J = 13.1 Hz), 136.51 (t, J = 2.8 Hz), 136.08 , 135.07 (d, J = 10.7 Hz), 128.74 (s), 124.11 (d, J = 172.7 Hz), 121.30 (s), δ 119.02 (q), 113.16 (q, J = 4.3 Hz), 112.73–112.33 (m), 104.22 (t, J = 25.2 Hz). **HRMS (AP)** *m/z* calcd. for $C_{15}H_8F_5NH$ $(M+H)^+$: 298.0655; found: 298.0652.

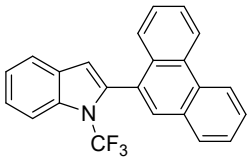


2-(thiophen-2-yl)-1-(trifluoromethyl)-1H-indole (3ad′). Following the general procedure of **Method B**, compound **3ad′** was synthesized and isolated as a brown oil (0.094 g, 70%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 6.0 Hz, 1H), 7.36–7.29 (m, 1H), 7.29–7.22 (m, 2H), 7.10 (dd, J = 5.1, 3.7 Hz, 1H), 6.74 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.36 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.91 (s), 131.97 (s), 131.13 (s), 128.92–128.77 (m),

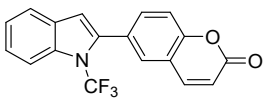
128.60 (s), 127.12 (d, J = 27.9 Hz), 124.72 (s), 122.94 (s), 121.05 (s), 120.51 (q, J = 263.3 Hz), 113.01 (q, J = 5.0 Hz), 111.54 (s). **HRMS (AP)** *m/z* calcd. for $C_{13}H_8F_3NSH$ $(M+H)^+$: 268.0408; found: 268.0401.



2-(naphthalen-1-yl)-1-(trifluoromethyl)-1H-indole (3ae′). Following the general procedure of **Method B**, compound **3ae′** was synthesized and isolated as a colorless solid (0.089 g, 57%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 39-41 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 18.1, 8.1 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.59–7.47 (m, 3H), 7.47–7.30 (m, 3H), 6.69 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.21 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.67 (s), 135.66 (s), 133.34 (d, J = 5.7 Hz), 129.87 (s), 129.67 (s), 129.34 (s), 128.80 (s), 128.29 (s), 126.50 (d, J = 52.1 Hz), 125.84 (s), 124.95 (s), 124.42 (s), 123.06 (s), 121.17 (s), 119.81 (q, J = 263.5 Hz). 112.97 (q, J = 4.0 Hz), 110.84(s). **HRMS (AP)** *m/z* calcd. for $C_{19}H_{12}F_3NH$ $(M+H)^+$: 312.1000; found: 312.1014.

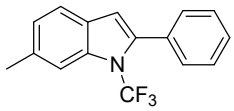


2-(phenanthren-9-yl)-1-(trifluoromethyl)-1H-indole (3af′). Following the general procedure of **Method B**, compound **3af′** was synthesized and isolated as a colorless solid (0.103 g, 57%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 47-49 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.78 – 8.71 (m, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.86 (s, 1H), 7.76 – 7.62 (m, 6H), 7.56 – 7.51 (m, 1H), 7.44 – 7.37 (m, 1H), 7.37 – 7.31 (m, 1H), 7.25 (s, 1H), 6.76 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -51.43 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.81 (s), 135.67 (s), 132.09 (s), 130.94 (d, J = 8.0 Hz), 130.21 (s), 129.99 (s), 129.37 (s), 129.17 (s), 128.76 (s), 127.69 (s), 127.11 (d, J = 7.0 Hz), 126.80 (d, J = 28.0 Hz), 124.50 (s), 123.10 (s), 122.85 (d, J = 10.7 Hz), 121.23 (s), 120.62 (q, J = 263.4 Hz), 112.95 (q, J = 3.8 Hz), 110.87 (s). **HRMS (AP)** *m/z* calcd. for $C_{23}H_{14}F_3NH$ $(M+H)^+$: 362.1157; found: 362.1170.

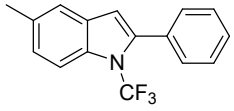


6-(1-(trifluoromethyl)-1H-indol-2-yl)-2H-chromen-2-one (3ag′). Following the general procedure of **Method B**, compound **3ag′** was synthesized and isolated as a yellow solid (0.040 g, 24%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (ether:ethyl acetate = 20:1) as eluent. mp 106-108 °C. **^{1}H**

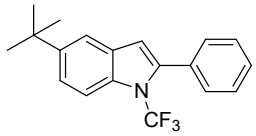
NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 9.6 Hz, 1H), 7.70 – 7.59 (m, 4H), 7.38 (dd, J = 13.7, 7.8 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 6.64 (s, 1H), 6.49 (d, J = 9.5 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.39 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.37 (s), 154.13 (s), 143.10 (s), 136.47 (d, J = 109.6 Hz), 132.89 (s), 128.96 – 128.54 (m), 124.76 (s), 123.21 (s), 121.14 (s), 121.67 (q) , 118.55 (s), 117.12 (d, J = 64.7 Hz), 113.09 (q, J = 4.3 Hz), 110.60 (s). **HRMS (AP)** *m/z* calcd. for $C_{18}H_{10}F_3NO_2H$ $[M+H]^+$: 330.0742; found: 330.0759.



6-methyl-2-phenyl-1-(trifluoromethyl)-1H-indole (3ba). Following the general procedure of **Method A**, compound **3ba** was synthesized and isolated as a colorless oil (0.084 g, 61%) via silica gel flash column chromatography using petroleum ether as eluent. This compound can also be obtained as a colorless oil (0.039 g, 28%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.46 (m, 4H), 7.46–7.40 (m, 3H), 7.13 (d, J = 8.1 Hz, 1H), 6.56 (s, 1H), 2.53 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.94 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8 (s), 136.5 (s), 134.4 (s), 132.6 (s), 129.5 (s), 128.6 (s), 128.2 (s), 127.1 (s), 124.6 (s), 120.7 (q, J = 261.4 Hz), 120.7 (s), 113.3 (q, J = 4.2 Hz), 109.7 (s), 22.1 (s). **HRMS (AP)** *m/z* calcd. for $C_{16}H_{12}F_3NH$ $(M)^+$: 276.0995; found: 276.1001.

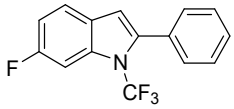


5-methyl-2-phenyl-1-(trifluoromethyl)-1H-indole (3bb). Following the general procedure of **Method A**, compound **3bb** was synthesized and isolated as a yellow oil (0.081 g, 59%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a yellow oil (0.045 g, 33%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (ddd, J = 13.6, 7.0, 1.9 Hz, 3H), 7.47–7.43 (m, 3H), 7.41 (s, 1H), 7.18 (dd, J = 8.5, 1.3 Hz, 1H), 6.55 (s, 1H), 2.49 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.03 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.5 (s), 134.3 (s), 132.7 (s), 132.6 (s), 132.5 (s), 129.7 – 129.3 (m), 128.7 (s), 128.2 (s), 125.8 (s), 120.9 (s), 120.8 (q, J = 261.3 Hz), 112.9 (q, J = 4.2 Hz), 109.6 (s), 21.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}F_3NH$ $(M+H)^+$: 276.0995; found: 276.0995.

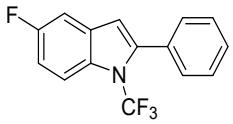


5-(tert-butyl)-2-phenyl-1-(trifluoromethyl)-1H-indole (3bc). Following the general procedure of **Method A**, compound **3bc** was synthesized and isolated as a colorless oil (0.090 g, 57%) via silica gel flash column chromatography using petroleum ether (60-

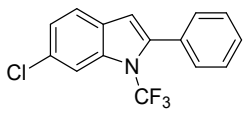
90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 11.6, 1.9 Hz, 2H), 7.50 (dd, J = 6.5, 2.9 Hz, 2H), 7.46–7.40 (m, 4H), 6.58 (s, 1H), 1.42 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.03 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2 (s), 139.5 (s), 134.2 (s), 132.5 (s), 129.6 (s), 129.2 (s), 128.7 (s), 128.2 (s), 122.5 (s), 120.8 (q, J = 261.4 Hz), 117.2 (s), 112.7 (q, J = 4.2 Hz), 110.0 (s), 34.8 (s), 31.9 (s). **HRMS (AP)** *m/z* calcd. for $C_{19}H_{18}F_3NH$ $(M+H)^+$: 318.1470; found: 318.1479.



6-fluoro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bd). Following the general procedure of **Method A**, compound **3bd** was synthesized and isolated as a colorless oil (0.091 g, 65%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.48 (m, 3H), 7.49–7.41 (m, 3H), 7.41–7.35 (m, 1H), 7.11–6.99 (m, 1H), 6.58 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.24 (s, 3F), -116.99 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8 (d, J = 241.0 Hz), 139.7 (d, J = 4.0 Hz), 136.0 (d, J = 12.4 Hz), 132.0 (s), 129.8–129.3 (m), 128.9 (s), 128.3 (s), 125.5 (s), 121.9 (d, J = 9.9 Hz), 120.5 (q, J = 262.0 Hz), 111.5 (d, J = 24.1 Hz), 109.4 (s), 100.6 (dq, J = 28.5, 4.6 Hz). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_4NH$ $(M+H)^+$: 280.0744; found: 280.0734.

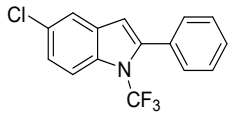


5-fluoro-2-phenyl-1-(trifluoromethyl)-1H-indole (3be): Following the general procedure of **Method A**, compound **3be** was synthesized and isolated as a colorless oil (0.108 g, 77%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless oil (0.081 g, 58%) via **Method B**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (ddd, J = 8.9, 4.1, 2.0 Hz, 1H), 7.51 (dd, J = 6.6, 2.9 Hz, 2H), 7.50–7.41 (m, 3H), 7.27 (dd, J = 8.6, 2.7 Hz, 1H), 7.08 (td, J = 9.1, 2.6 Hz, 1H), 6.59–6.55 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.10 (s, 3F), -120.68 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5 (d, J = 239.3 Hz), 141.1 (s), 132.2 (d, J = 36.8 Hz), 130.1 (d, J = 10.1 Hz), 129.5 (d, J = 1.0 Hz), 129.1 (s), 128.3 (s),120.6 (q, J = 261.6 Hz), 114.1 (dd, J = 9.3, 4.6 Hz), 112.4 (d, J = 25.7 Hz), 109.6 (d, J = 3.3 Hz), 106.4 (d, J = 23.8 Hz). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_4NH$ $(M+H)^+$: 280.0736; found: 280.0744.

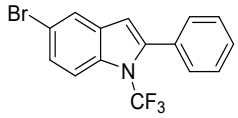


6-chloro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bf). Following the general procedure of **Method A**, compound **3bf** was synthesized and isolated as a colorless oil

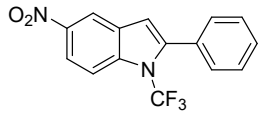
(0.096 g, 65%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.55–7.48 (m, 3H), 7.48–7.42 (m, 3H), 7.28 (dd, J = 8.4, 1.8 Hz, 1H), 6.58 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.97 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0 (s), 136.2 (s), 131.8 (s), 130.2 (s), 129.5 (s), 129.1 (s), 128.3 (s), 127.7 (s), 123.7 (s), 121.8 (s), 120.4 (q, J = 263.9 Hz), 113.4 (q, J = 4.7 Hz), 109.4 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9ClF_3NH$ $(M+H)^+$: 296.0448; found: 296.0437.



5-chloro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bg). Following the general procedure of **Method A**, compound **3bg** was synthesized and isolated as a colorless solid (0.109 g, 74%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless solid (0.064 g, 43%) via **Method B**. mp 61-63 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 9.4, 1.9 Hz, 2H), 7.51 (dd, J = 6.7, 2.9 Hz, 2H), 7.48–7.43 (m, 3H), 7.30 (dd, J = 8.9, 2.1 Hz, 1H), 6.55 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.98 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8 (s), 134.3 (s), 131.8 (s), 130.4 (s), 129.5 (d, J = 1.1 Hz), 129.1 (s), 128.8 (s), 128.3 (s), 124.6 (s), 120.6 (s), 120.5 (q, J = 262.1 Hz), 114.2 (q, J = 4.5 Hz), 109.1 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9ClF_3NH$ $(M+H)^+$: 296.0448; found: 296.0438.

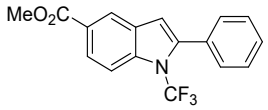


5-bromo-2-phenyl-1-(trifluoromethyl)-1H-indole (3bh). Following the general procedure of **Method A**, compound **3bh** was synthesized and isolated as a colorless solid (0.122 g, 72%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent to afford the product. This compound can also be obtained as a colorless solid (0.122 g, 72%) via **Method B**. mp 57-59 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 1.9 Hz, 1H), 7.56–7.48 (m, 3H), 7.47–7.41 (m, 4H), 6.55 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.95 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6 (s), 134.6 (s), 131.7 (s), 130.9 (s), 129.8–129.3 (m), 129.1 (s), 128.3 (s), 127.2 (s), 123.7 (s), 120.4 (q, J = 262.2 Hz), 116.3 (s), 114.6 (q, J = 4.5 Hz), 108.9 (s). **HRMS (AP)** *m/z* calcd. for $C_{15}H_9BrF_3NH$ $(M+H)^+$: 339.9949; found: 339.9955.

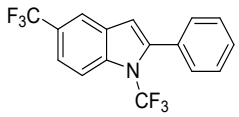


5-nitro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bi). Following the general procedure of **Method A**, compound **3bi** was synthesized and isolated as a yellow solid

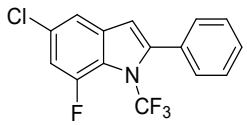
(0.110 g, 72%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (petroleum ether:ethyl acetate = 100:1) as eluent. This compound can also be obtained as a yellow solid (0.031 g, 20%) via **Method B**. mp 84-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, J = 2.2 Hz, 1H), 8.23 (dd, J = 9.2, 2.3 Hz, 1H), 7.73 (dd, J = 9.2, 1.8 Hz, 1H), 7.49 (qd, J = 6.6, 5.4, 3.3 Hz, 5H), 6.75 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.81 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0 (s), 142.4 (s), 138.5 (s), 131.0 (s), 129.6 (s), 129.6–129.4 (m), 128.9 (s), 128.5 (s), 120.1 (q, J = 265.0 Hz), 119.5 (s), 117.4 (s), 113.3 (q, J = 4.8 Hz), 110.1 (s). **HRMS (ESI)** *m/z* calcd. for $C_{15}H_9F_3N_2O_2H$ $(M+H)^+$: 307.0689; found: 307.0681.



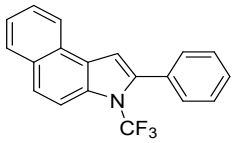
methyl 2-phenyl-1-(trifluoromethyl)-1H-indole-5-carboxylate (3bj). Following the general procedure of **Method A**, compound **3bj** was synthesized and isolated as a colorless oil (0.118 g, 74%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.55–7.40 (m, 5H), 6.67 (s, 1H), 3.96 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.83 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4 (s), 140.6 (s), 138.3 (s), 131.7 (s), 129.7–129.4 (m), 129.1 (s), 128.9 (s), 128.3 (s), 125.6 (s), 125.2 (s), 123.5 (s), 120.4 (q, J = 262.5 Hz), 12.8 (q, J = 4.5 Hz), 110.0 (s), 52.2 (s). **HRMS (AP)** *m/z* calcd. for $C_{17}H_{12}F_3NO_2H$ $(M+H)^+$: 320.0893; found: 320.0997.



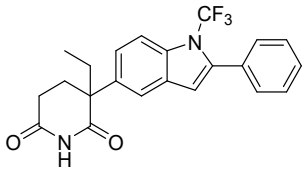
2-phenyl-1,5-bis(trifluoromethyl)-1H-indole (3bk). Following the general procedure of **Method A**, compound **3bk** was synthesized and isolated as a colorless oil (0.115 g, 70%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.81–7.67 (m, 1H), 7.59 (dd, J = 8.8, 1.4 Hz, 1H), 7.52 (dd, J = 6.8, 2.9 Hz, 2H), 7.47 (dt, J = 4.8, 2.1 Hz, 3H), 6.68 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.86 (s, 3F), -61.20 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1 (s), 137.2 (s), 131.6 (s), 129.6 (d, J = 1.1 Hz), 129.3 (s), 128.8 (s), 128.4 (s), 125.6 (q, J = 32.4 Hz), 124.8 (q, J = 270.2 Hz), 121.1 (q, J = 3.2 Hz), 120.4 (q, J = 264.1 Hz), 118.7 (q, J = 4.2 Hz), 113.4 (q, J = 4.6 Hz), 109.7 (s). **HRMS (ESI)** *m/z* calcd. for $C_{16}H_9F_6NH$ $(M+H)^+$: 330.0712; found: 330.0717.



5-chloro-7-fluoro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bl). Following the general procedure of **Method A**, compound **3bl** was synthesized and isolated as a colorless solid (0.110 g, 70%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. This compound can also be obtained as a colorless solid (0.069g, 44%) via **Method B**. mp 76-77 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.48–7.41 (m, 3H), 7.40–7.33 (m, 1H), 7.13–7.06 (m, 1H), 6.55 (d, J = 1.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -48.37 (d, J = 30.0 Hz, 3F), -123.17 (q, J = 30.0 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2 (s), 147.7 (s), 142.5 (s), 133.4 (d, J = 4.2 Hz), 131.9 (s), 129.2 (s), 128.9 (d, J = 8.9 Hz), 128.8 – 128.6 (m), 128.5 (s), 122.2 (d, J = 10.6 Hz), 119.7 (q, J = 263.6Hz), 116.5 (d, J = 4.0 Hz), 112.0 (d, J = 23.8 Hz), 109.0 (s). **HRMS (AP)** *m/z* calcd. for $C_{15}H_8ClF_4NH$ $(M+H)^+$: 314.0354; found: 314.0392.

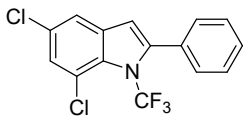


2-phenyl-3-(trifluoromethyl)-3H-benzo[e]indole (3bm). Following the general procedure of **Method A**, compound **3bm** was synthesized and isolated as a colorless solid (0.092 g, 59%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 44-46 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.76 (q, J = 8.5 Hz, 2H), 7.63–7.39 (m, 7H), 7.12 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.30 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1 (s), 132.6 (d, J = 11.1 Hz), 130.2 (s), 129.9–129.5 (m), 128.7 (d, J = 10.9 Hz), 128.2 (s), 127.4 (s), 126.6 (s), 125.2 (s), 125.0 (s), 124.8 (s), 123.2 (s), 120.6 (q, J = 262.3 Hz), 113.4 (q, J = 4.4 Hz), 108.3 (s). **HRMS (AP)** *m/z* calcd. for $C_{19}H_{12}F_3NH$ $(M+H)^+$: 312.0995; found: 311.1061.

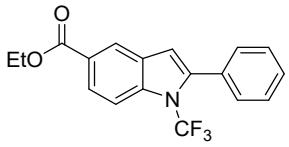


3-ethyl-3-(2-phenyl-1-(trifluoromethyl)-1H-indol-5-yl)piperidine-2,6-dione (3bn). Following the general procedure of **Method A**, compound **3bn** was synthesized and isolated as a colorless solid (0.060 g, 30%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 123-124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.69–7.60 (m, 1H), 7.53–7.42 (m, 6H), 7.30–7.25 (m, 1H), 6.57 (s, 1H), 2.63 (dd, J = 15.8, 4.7 Hz, 1H), 2.54–2.38 (m, 2H), 2.36–2.23 (m, 1H), 2.06 (ddt, J = 41.5, 14.1, 7.3 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -49.94 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5 (s), 172.3 (s), 140.3 (s), 135.1 (s), 133.5 (s), 132.0 (s), 129.7 (s), 129.6–129.4 (m), 129.0 (s), 128.3 (s), 122.2 (s), 120.5

(q, J = 261.8 Hz), 119.0 (s), 113.7 (q, J = 4.4 Hz), 109.6 (s), 51.2 (s), 33.4 (s), 29.5 (s), 27.6 (s), 9.3 (s). **HRMS (AP)** *m/z* calcd. for $C_{22}H_{19}F_3N_2O_2H$ $(M+H)^+$: 401.1477; found: 401.1474.

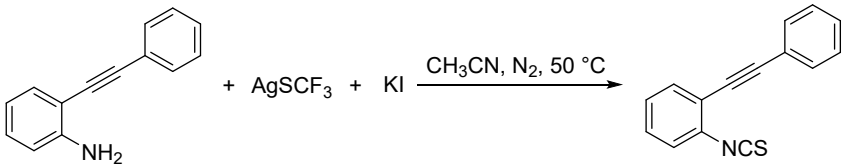


5,7-dichloro-2-phenyl-1-(trifluoromethyl)-1H-indole (3bo). Following the general procedure of **Method B**, compound **3bo** was synthesized and isolated as a colorless solid (0.033 g, 20%) via silica gel flash column chromatography using petroleum ether (60-90 °C) as eluent. mp 80-82 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.48–7.42 (m, 4H), 7.35 (s, 1H), 6.57 (s, 1H), 7.38 (dt, J = 24.4, 6.9 Hz, 2H), 6.77 (s, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$ δ -42.90 (s, 3F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.81 (s), 133.56 (s), 132.59 (s), 132.43 (d, J = 1.8 Hz), 129.41 (s), 129.07 (s), 128.68 (s), 128.05 (s), 126.39 (s), 120.33 (s), 119.35 (s), 119.81 (q, J = 266.1 Hz). 109.33 (s). **HRMS (AP)** *m/z* calcd. for $C_{15}H_8Cl_2F_3NH$ $(M+H)^+$: 330.0064; found: 330.0057.



ethyl 2-phenyl-1-(trifluoromethyl)-1H-indole-5-carboxylate (3bp). Following the general procedure of **Method B**, compound **3bp** was synthesized and isolated as a colorless solid (0.138 g, 83%) via silica gel flash column chromatography using petroleum ether/ethyl acetate (petroleum ether:ethyl acetate = 100:1) as eluent. mp 41-42 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 (d, J = 1.7 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 7.0 Hz, 2H), 7.47 (dt, J = 33.3, 3.8 Hz, 3H), 6.66 (s, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -49.21(s, 3F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.80 (s), 140.42 (s), 138.18 (s), 131.64 (s), 129.43 (s), 129.00 (s), 128.75 (s), 128.17 (s), 125.42 (d, J = 8.3 Hz), 123.27 (s), 120.28 (q, J = 264.1 Hz), 112.64 (q, J = 4.6 Hz), 109.92 (s), 60.97 (s), 14.40 (s). **HRMS (AP)** *m/z* calcd. for $C_{18}H_{14}F_3NO_2H$ $(M+H)^+$: 334.1055; found: 334.1058.

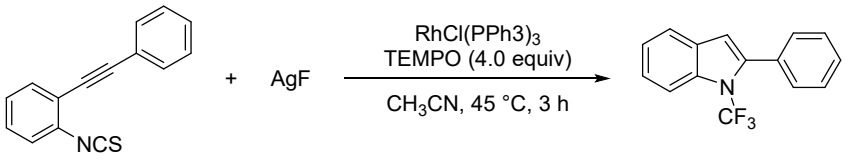
8. Mechanism study



2aa **1aa**, 0.102g, 87%

To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added 2-alkynyl arylamine **2aa** (0.5 mmol, 1.0 equiv.), $AgSCF_3$ (1.5 equiv.), KI (1.5 equiv.). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). CH_3CN (5 mL)

was then added by syringe. The reaction mixture was required to heat to 50 °C and then stirred for 1 h under nitrogen. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, filtered through a plug of celite and was with ethyl acetate, then concentrated under vacuum and purified by silica gel flash column chromatography (200-300 mesh) using petroleum ether (60-90 °C) as eluent to afford 2-alkynyl arylisothiocyanate **1aa** (0.102 g, 87% yield).

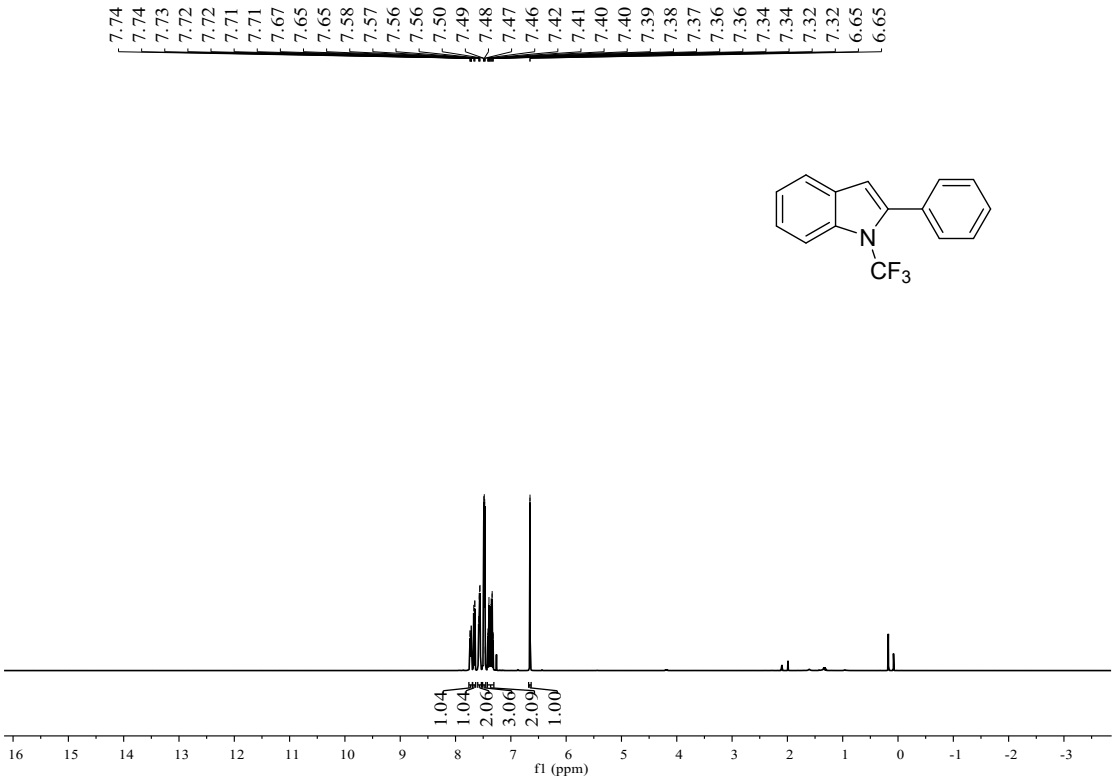


1aa **3aa**, 60%

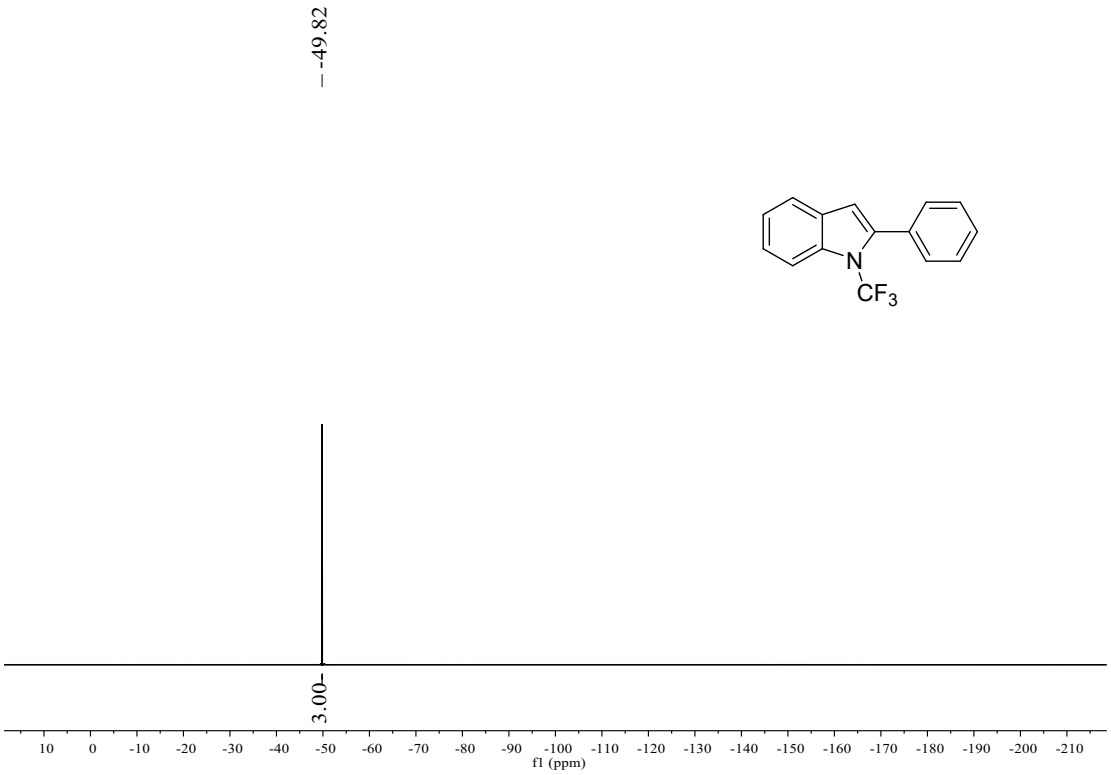
To an oven-dried 25 mL Schlenk tube equipped with a stir bar were added 2-alkynyl arylisothiocyanate **1aa** (0.5 mmol, 1.0equiv.), AgF (3.2 equiv.), TEMPO (4.0 equiv.), $RhCl(PPh_3)_3$ (1 mol%). The Schlenk tube was evacuated and refilled with dry nitrogen (three times). CH_3CN (5 mL) was then added by syringe. The reaction mixture was required to heat to 45 °C and then stirred for 3 h under nitrogen. After cooling to room temperature, the reaction mixture was diluted with dichloromethane. The raw product was analyzed by ^{19}F NMR using 4,4′-difluorobiphenyl (-115.0 ppm) as internal standard. The final product **3aa** is obtained with a yield of 60%.

9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products

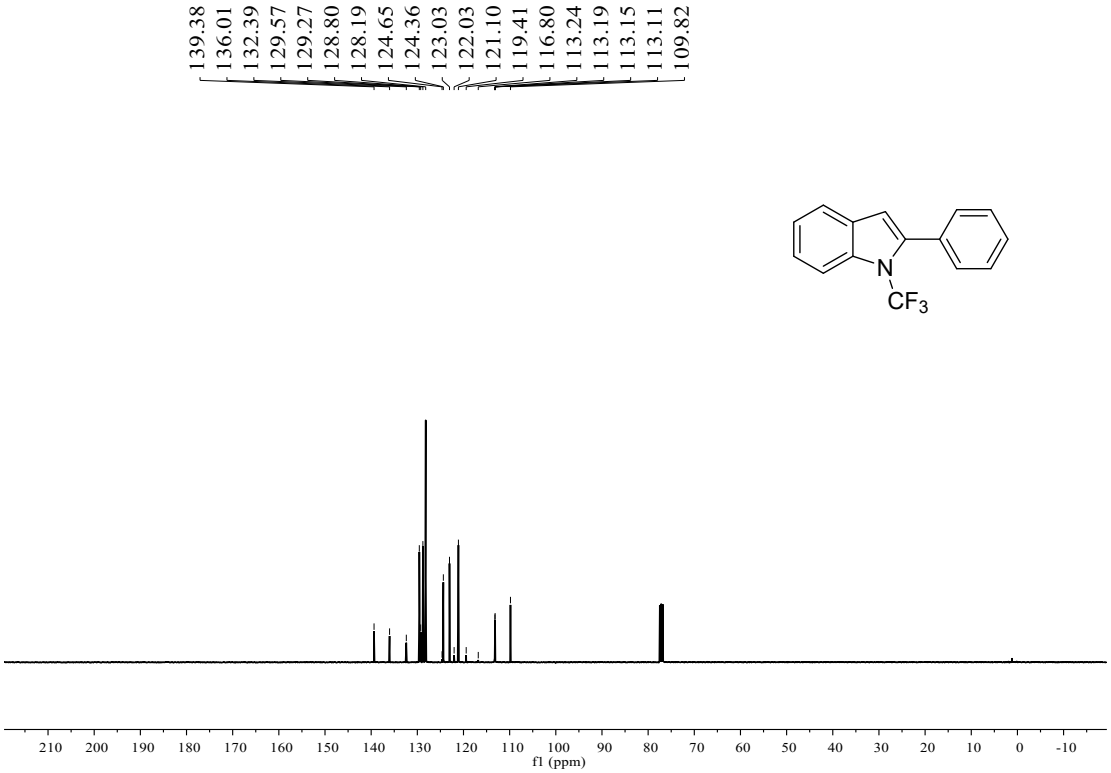
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



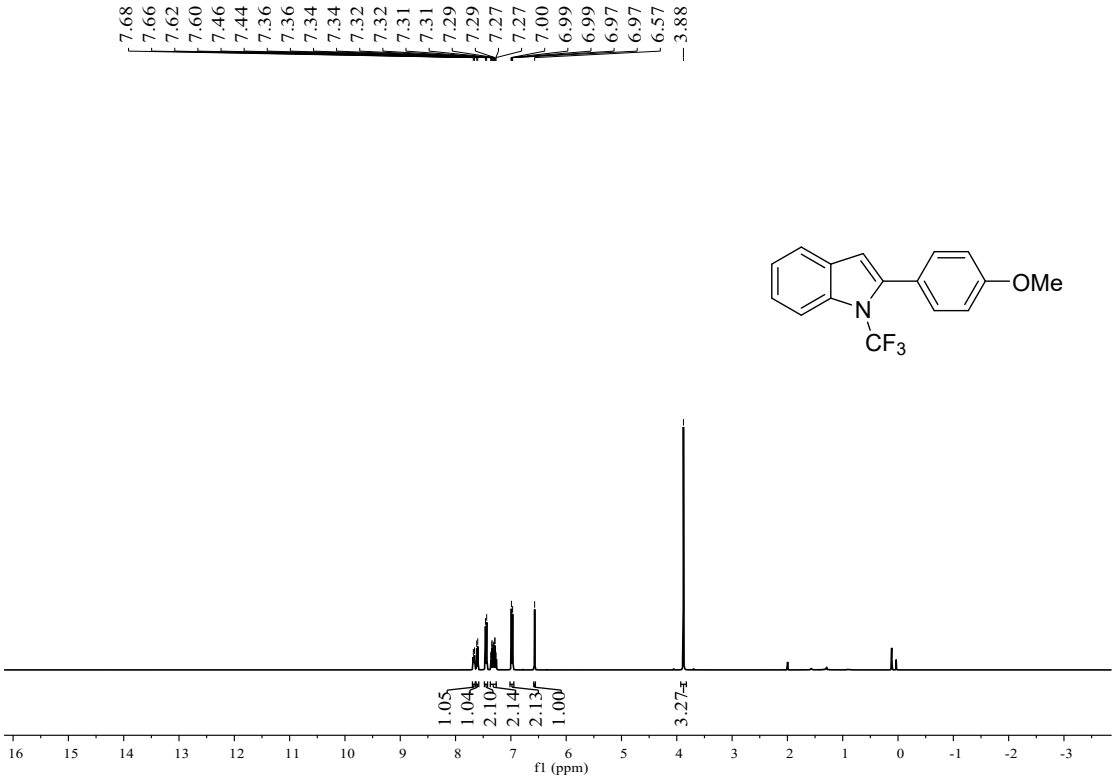
^{19}F NMR Spectrum of **3aa** (376 MHz, $CDCl_3$)



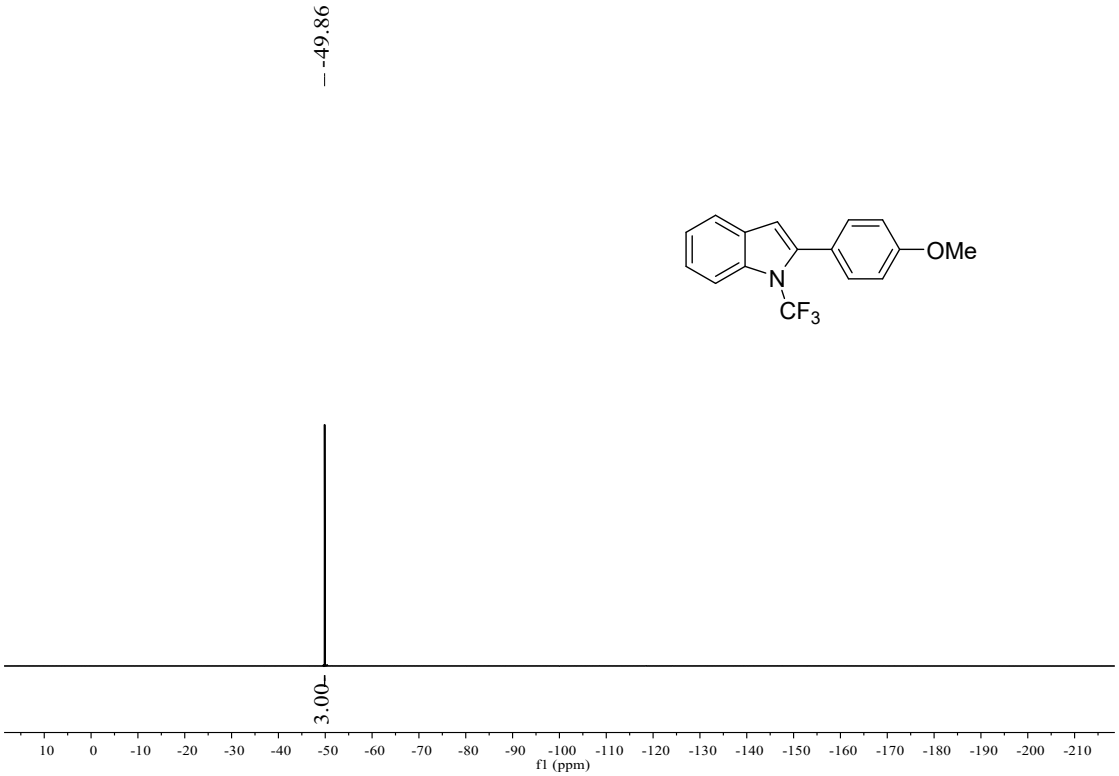
^{13}C NMR Spectrum of **3aa** (101 MHz, $CDCl_3$)



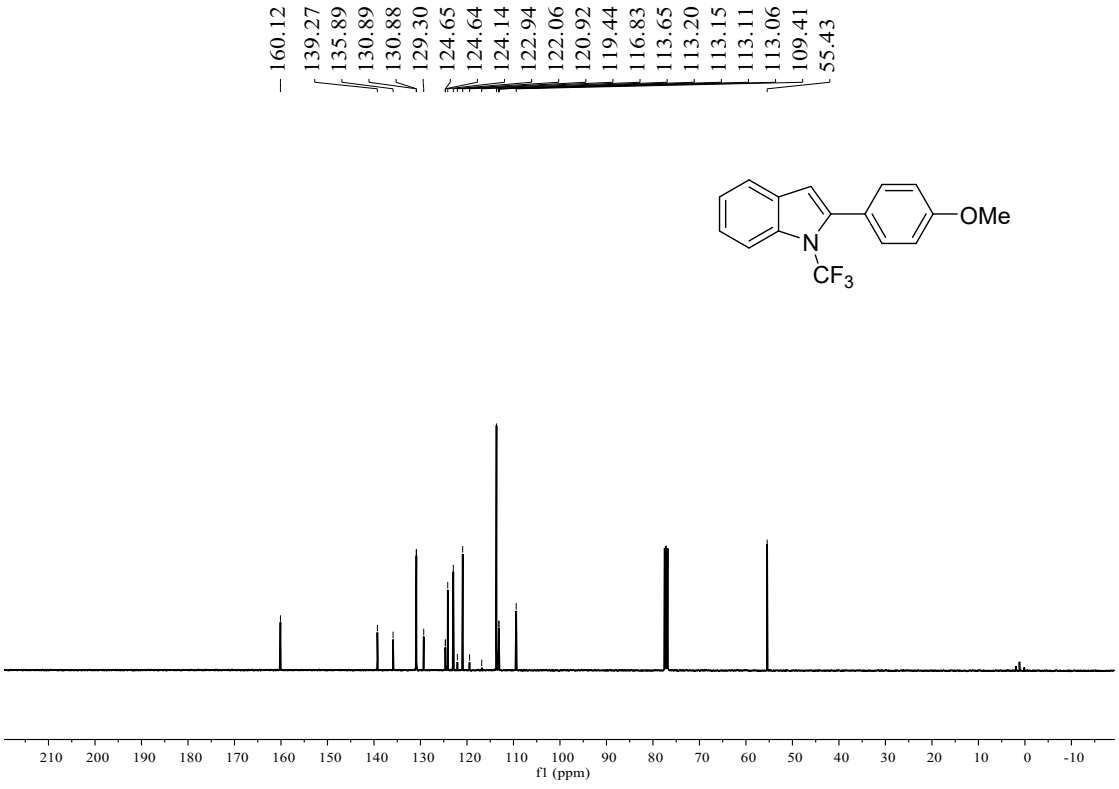
^{1}H NMR Spectrum of **3ab** (400 MHz, $CDCl_3$)



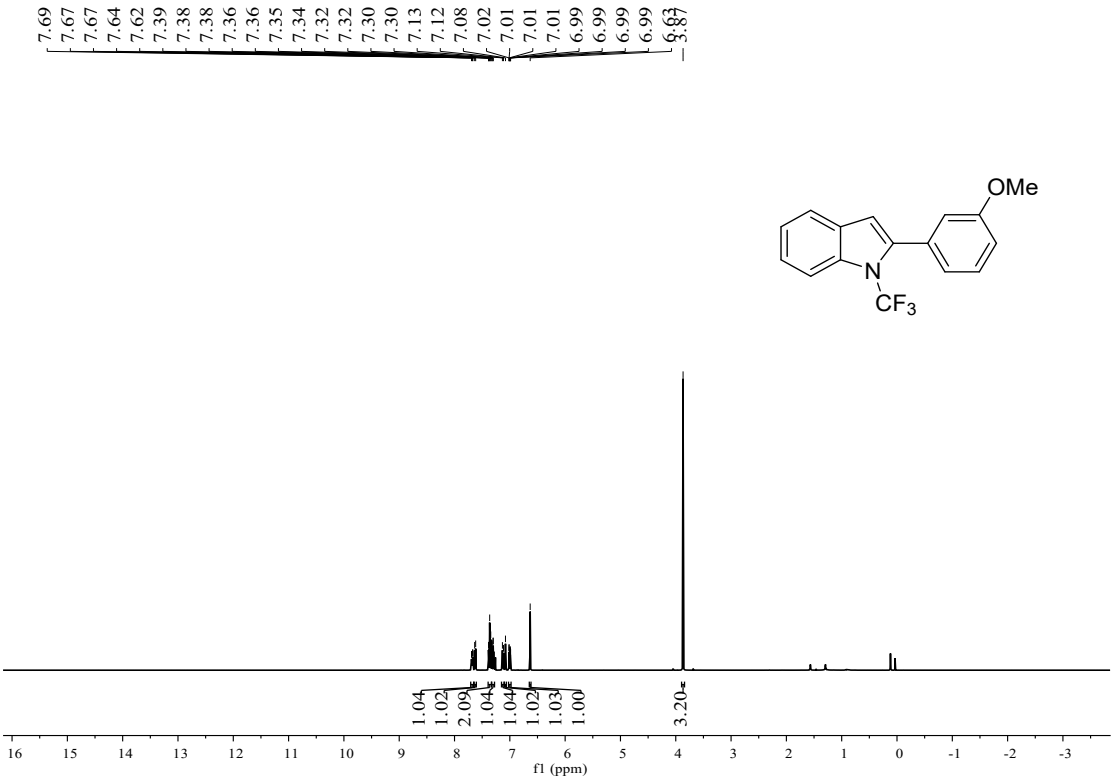
^{19}F NMR Spectrum of **3ab** (376 MHz, $CDCl_3$)



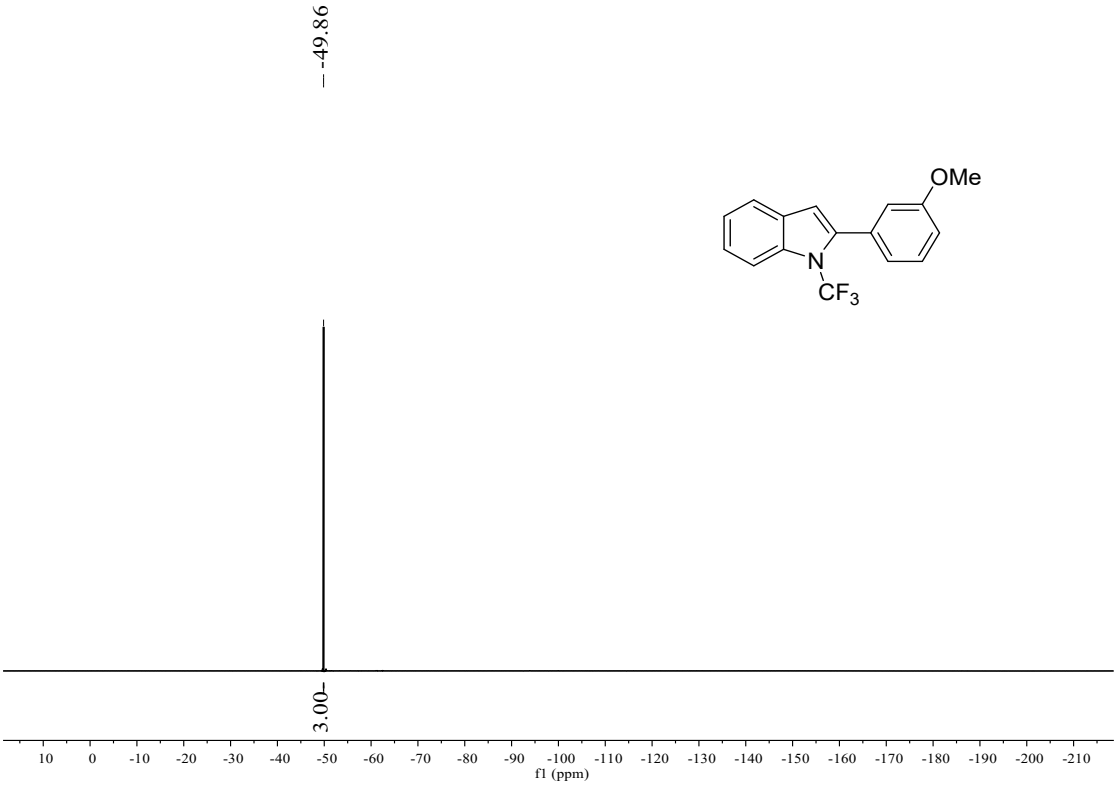
^{13}C NMR Spectrum of **3ab** (101 MHz, $CDCl_3$)



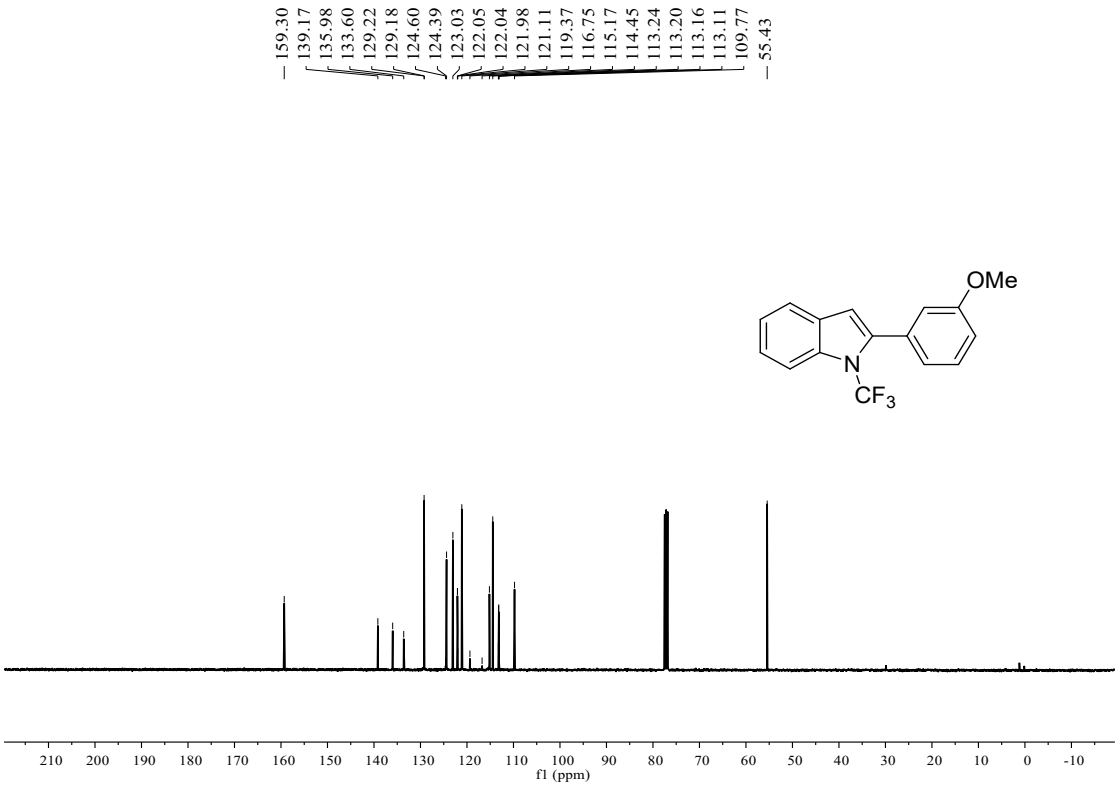
^{1}H NMR Spectrum of **3ac** (400 MHz, $CDCl_3$)



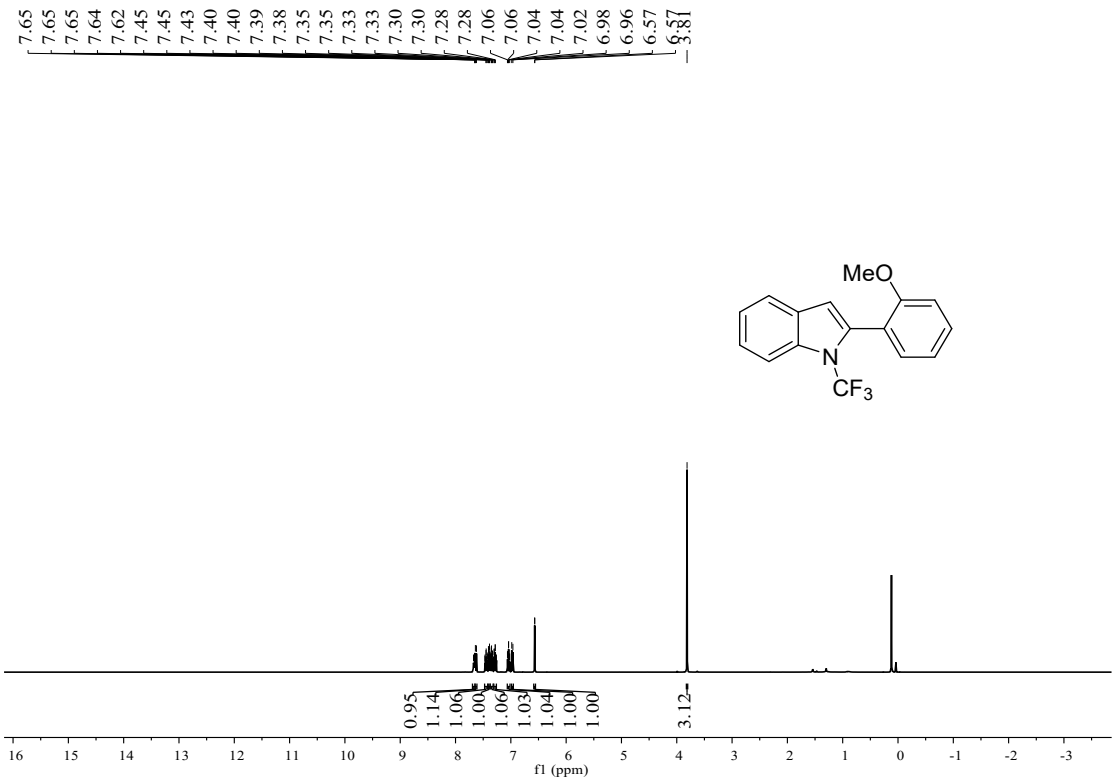
^{19}F NMR Spectrum of **3ac** (376 MHz, $CDCl_3$)



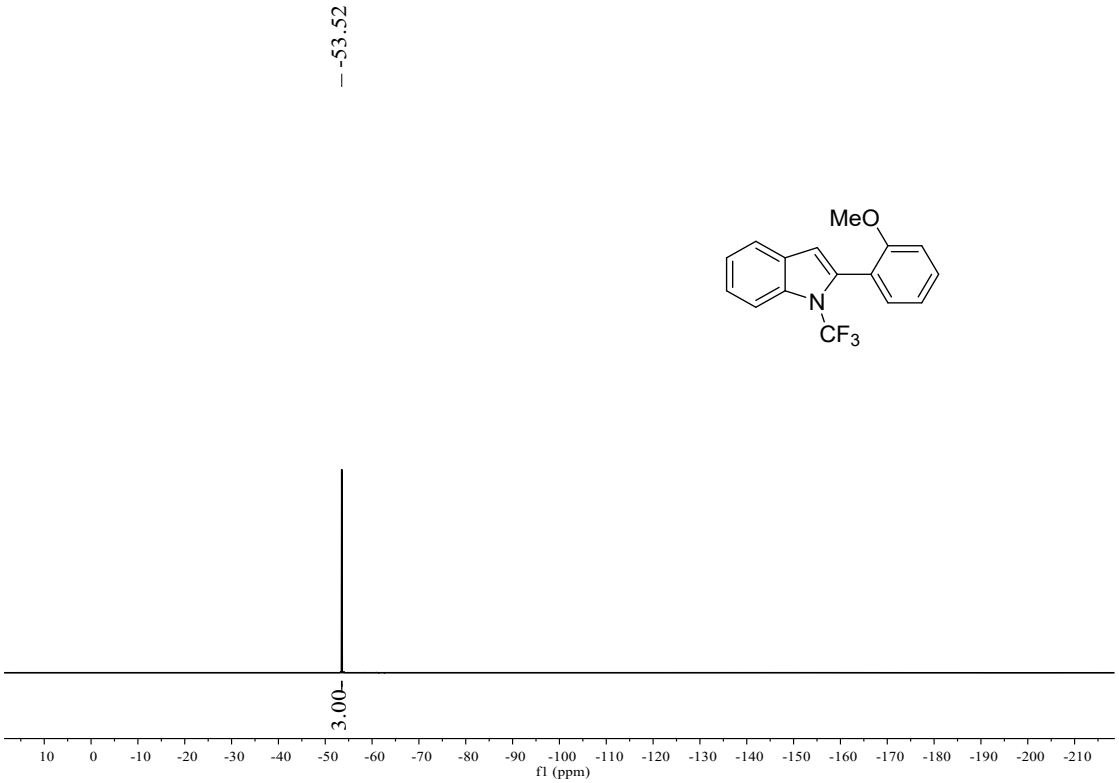
^{13}C NMR Spectrum of **3ac** (101 MHz, $CDCl_3$)



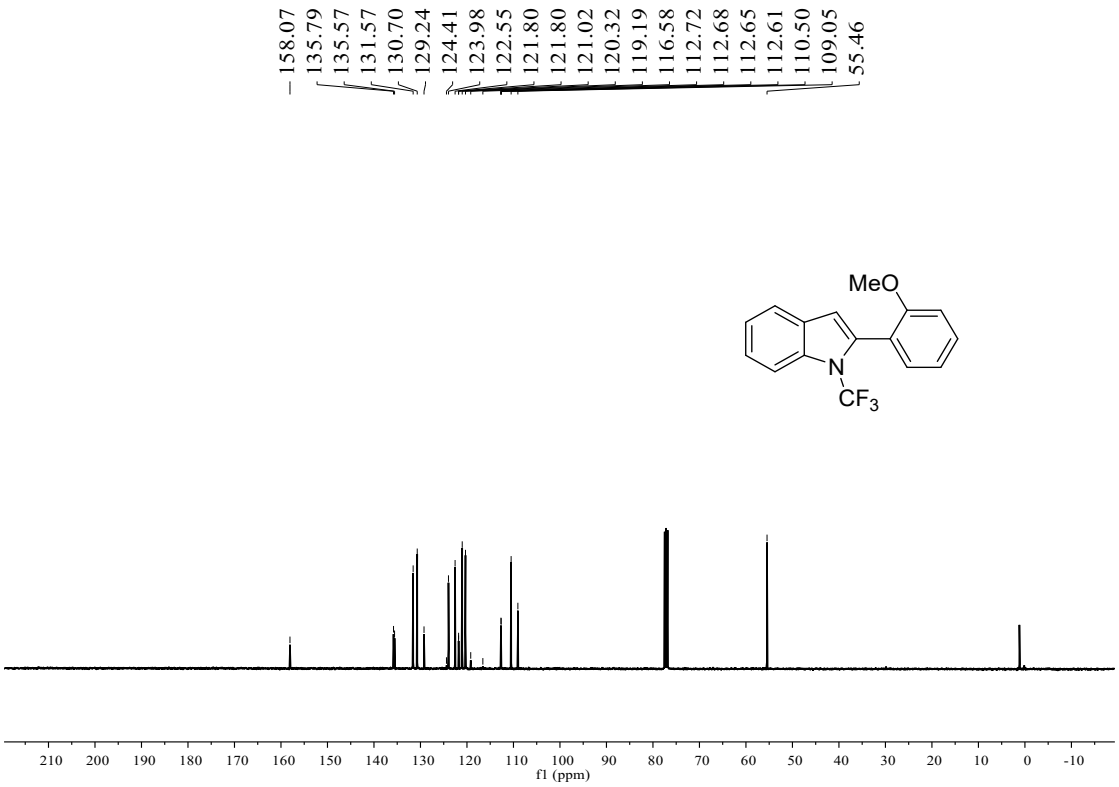
^{1}H NMR Spectrum of **3ad** (400 MHz, $CDCl_3$)



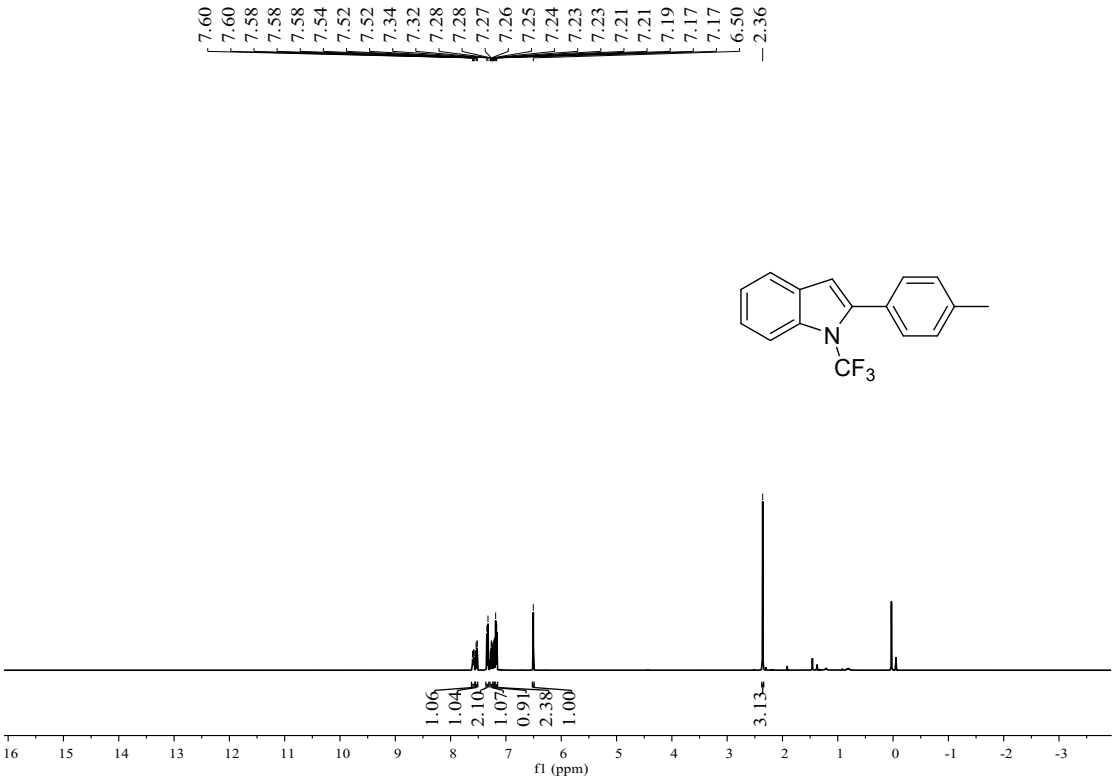
^{19}F NMR Spectrum of **3ad** (376 MHz, $CDCl_3$)



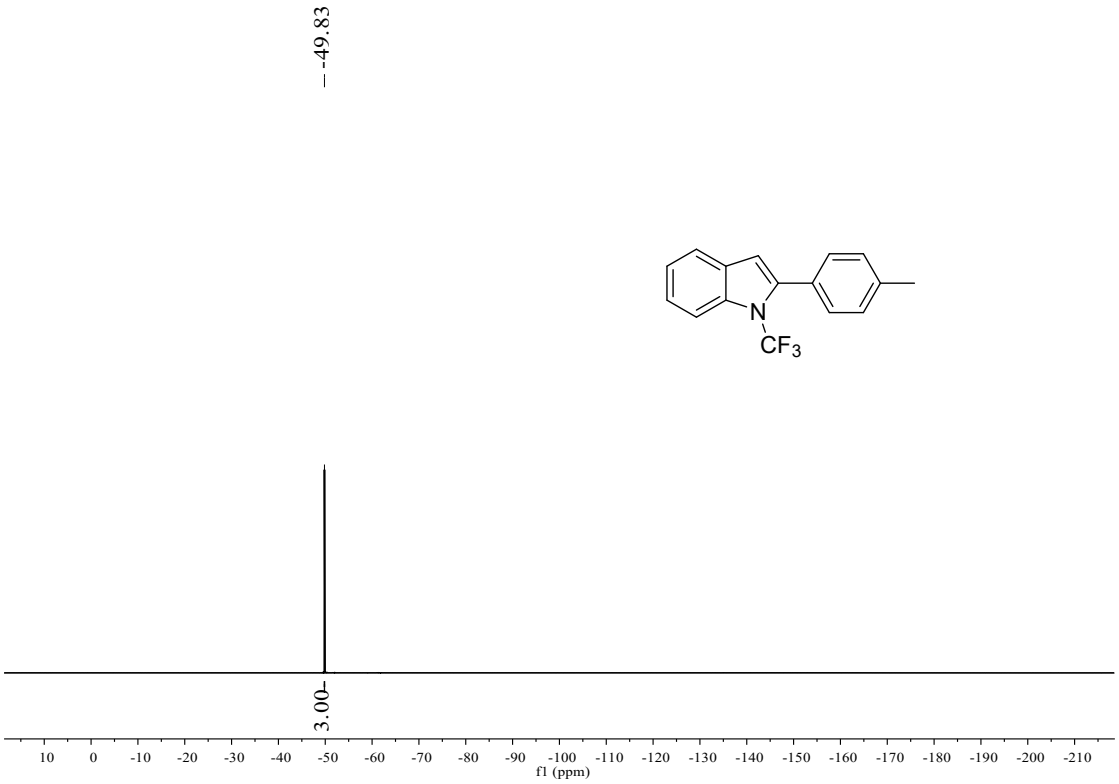
^{13}C NMR Spectrum of **3ad** (101 MHz, $CDCl_3$)



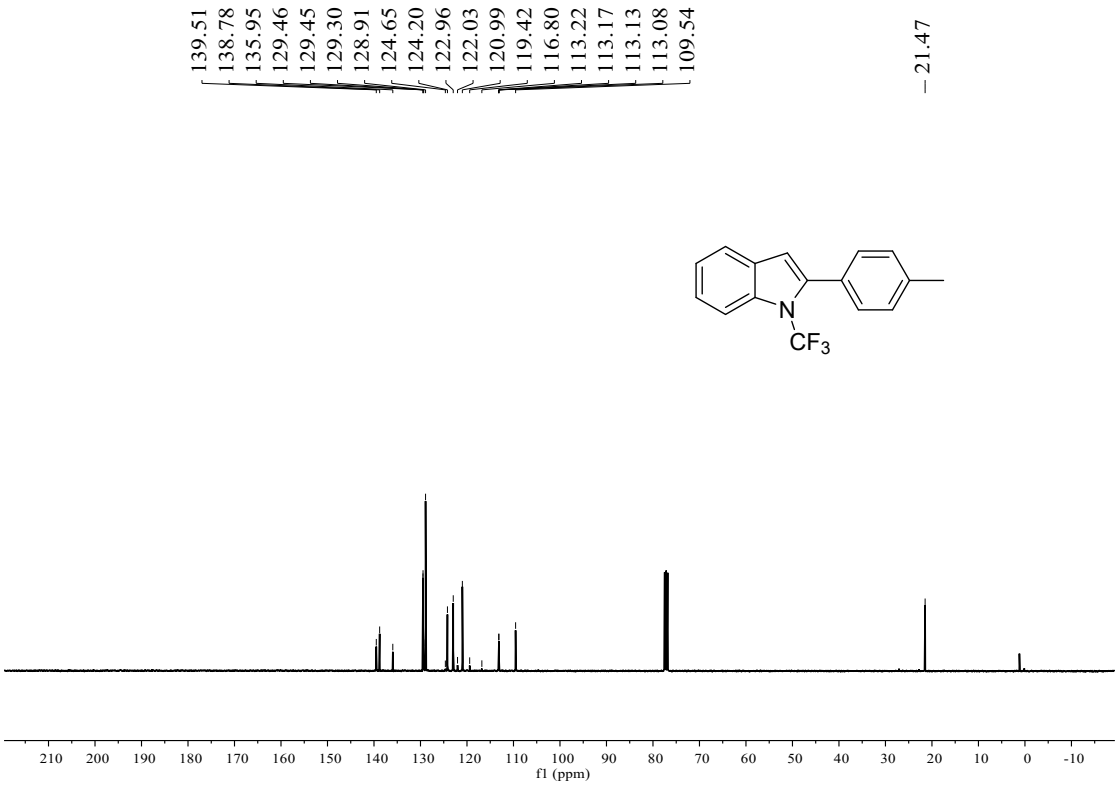
^{1}H NMR Spectrum of **3ae** (400 MHz, $CDCl_3$)



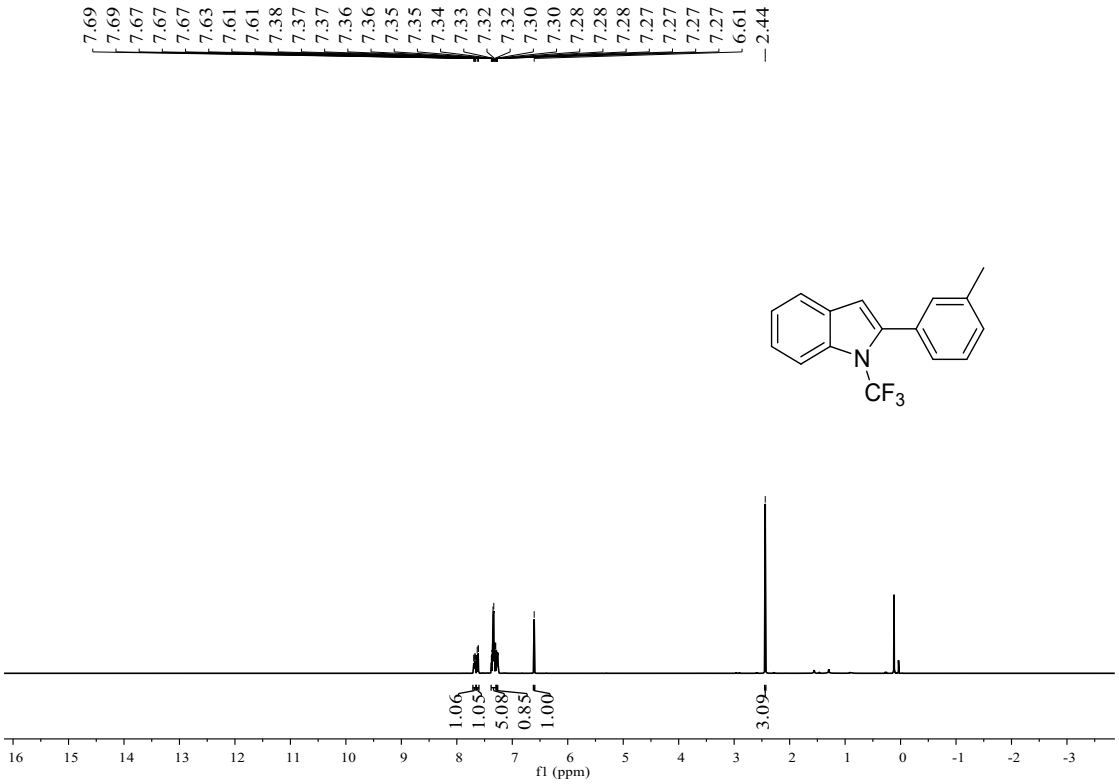
^{19}F NMR Spectrum of **3ae** (376 MHz, $CDCl_3$)



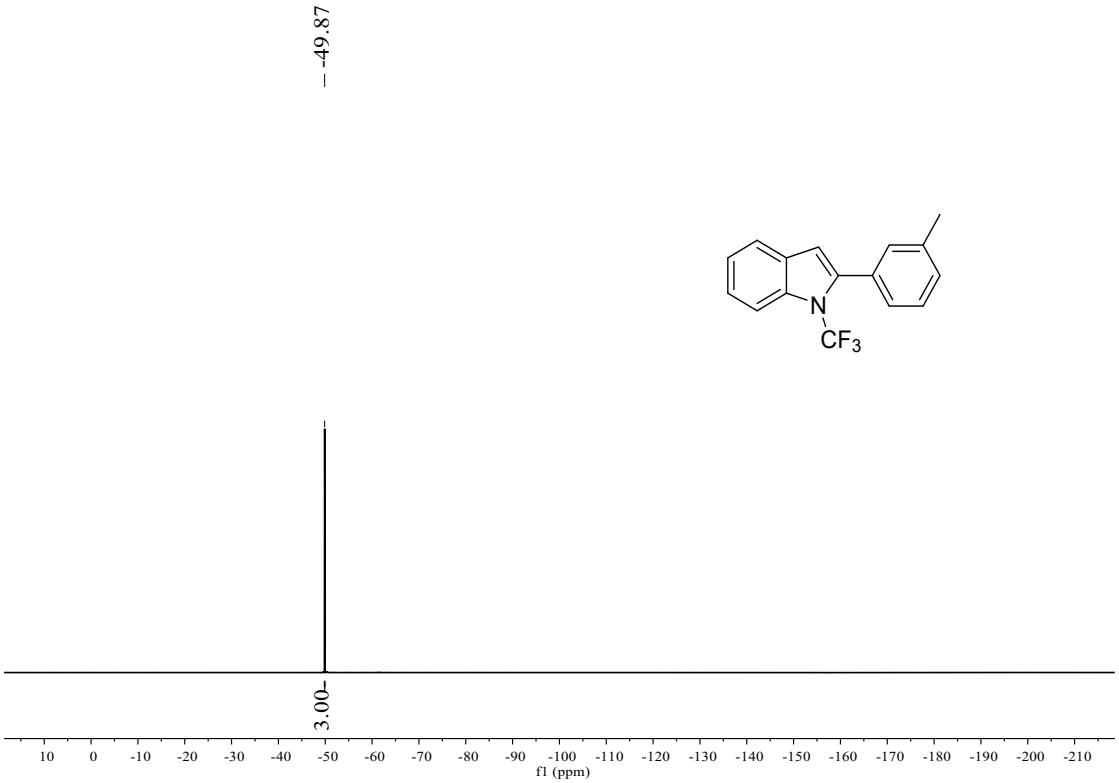
^{13}C NMR Spectrum of **3ae** (101 MHz, $CDCl_3$)



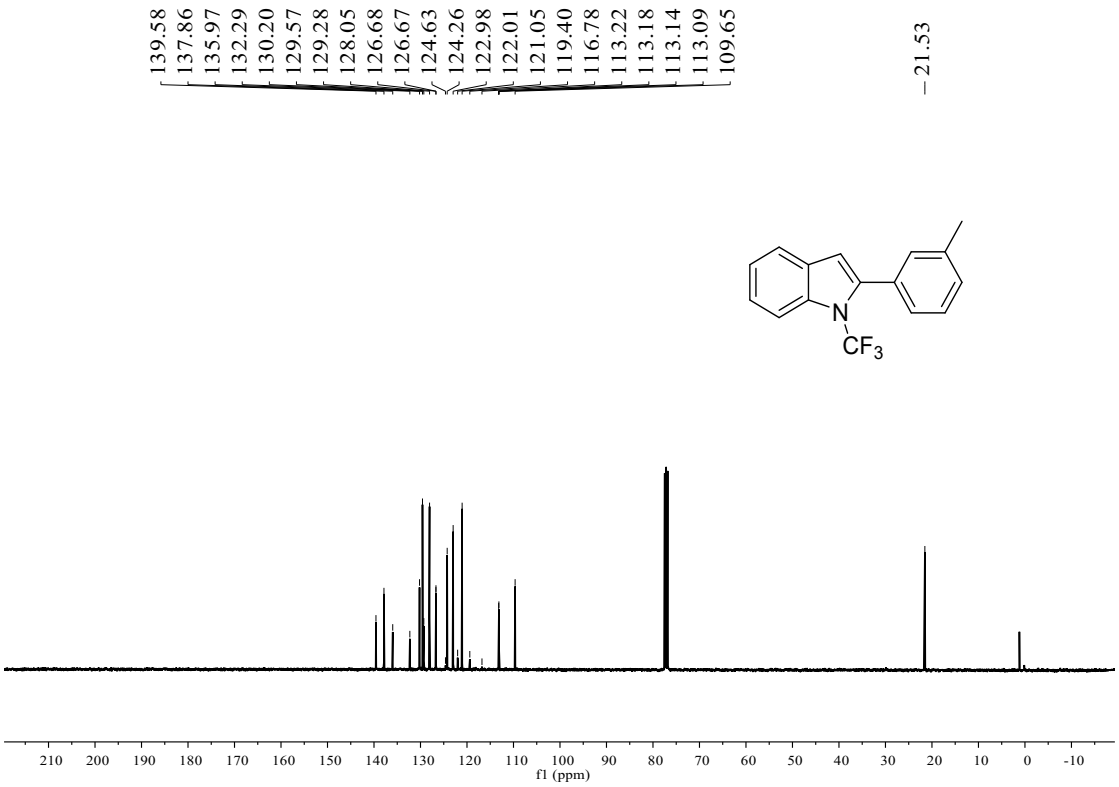
^{1}H NMR Spectrum of **3af** (400 MHz, $CDCl_3$)



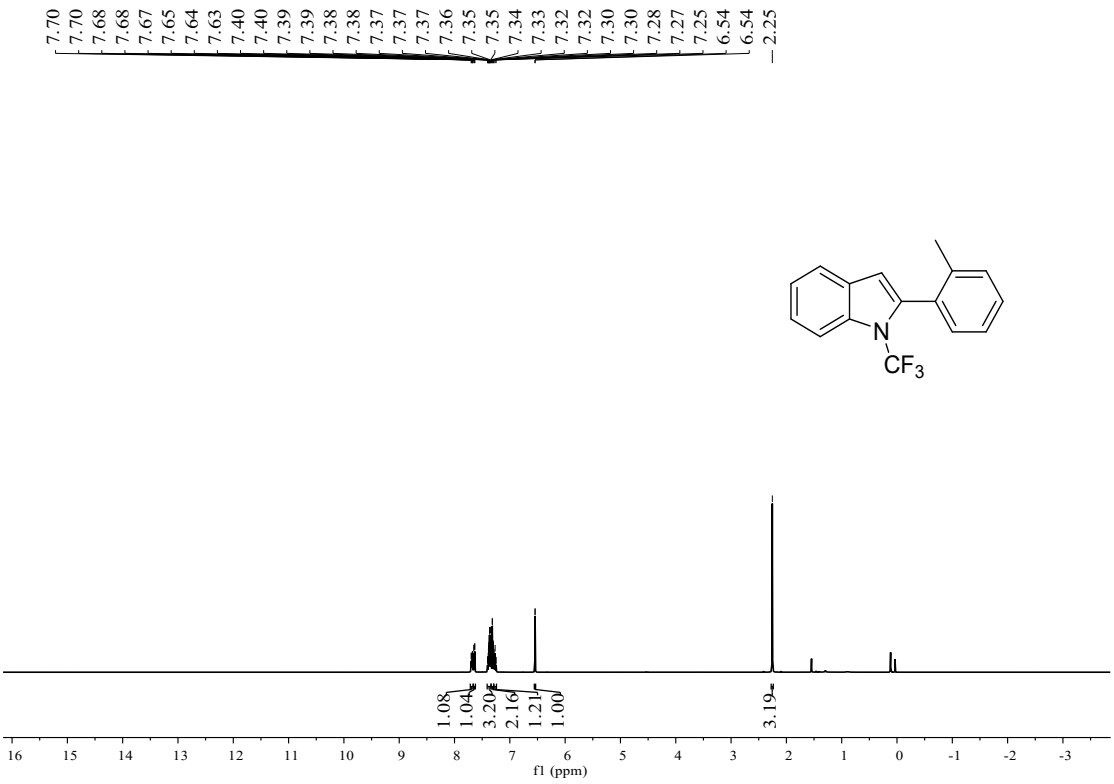
^{19}F NMR Spectrum of **3af** (376 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3af** (101 MHz, $CDCl_3$)

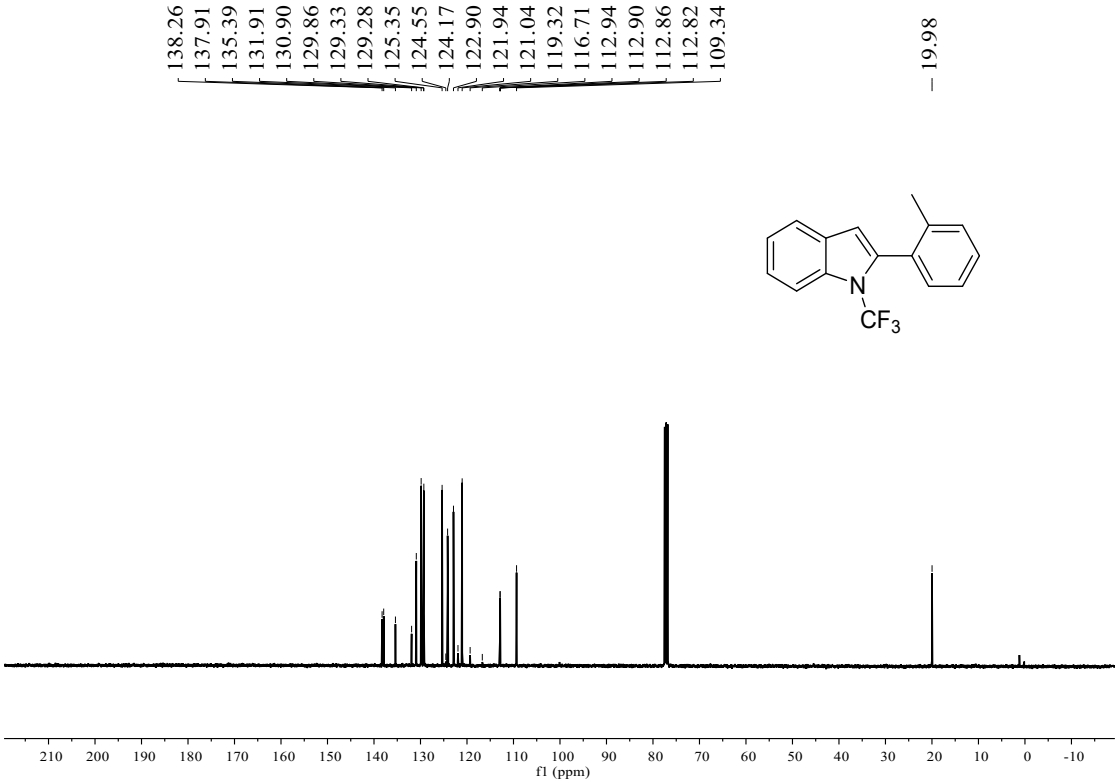


^{1}H NMR Spectrum of **3ag** (400 MHz, $CDCl_3$)

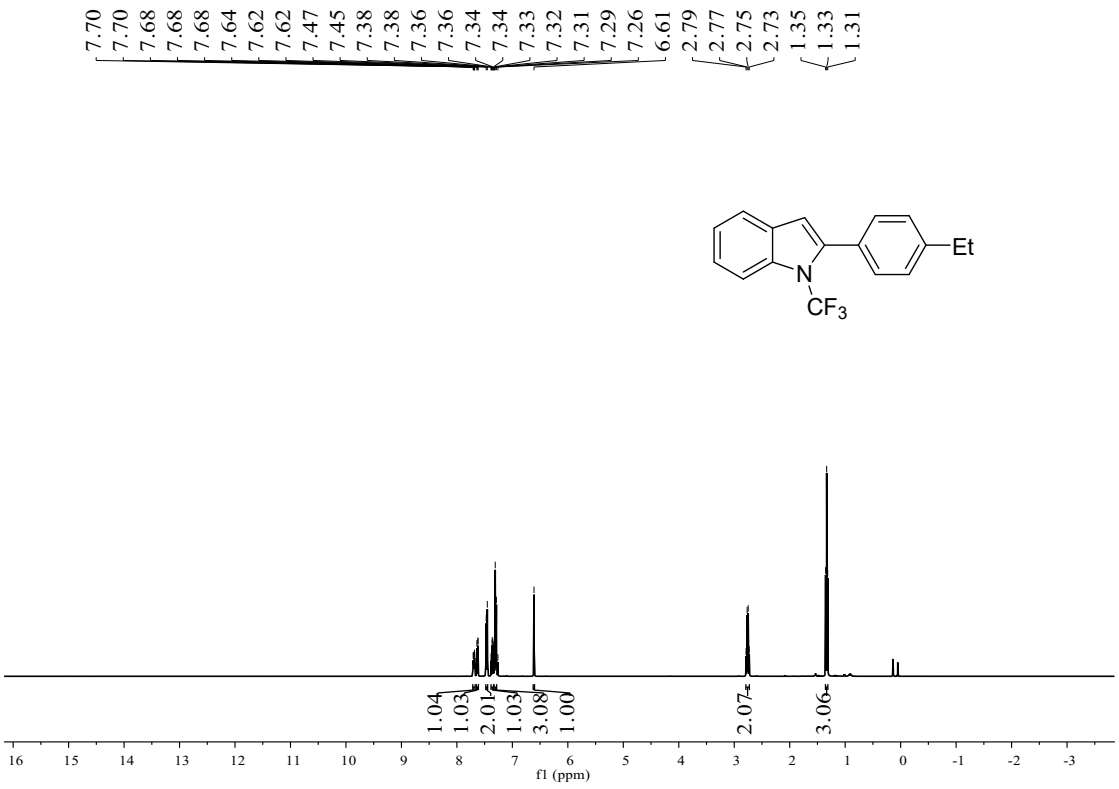


^{19}F NMR Spectrum of **3ag** (376 MHz, $CDCl_3$)

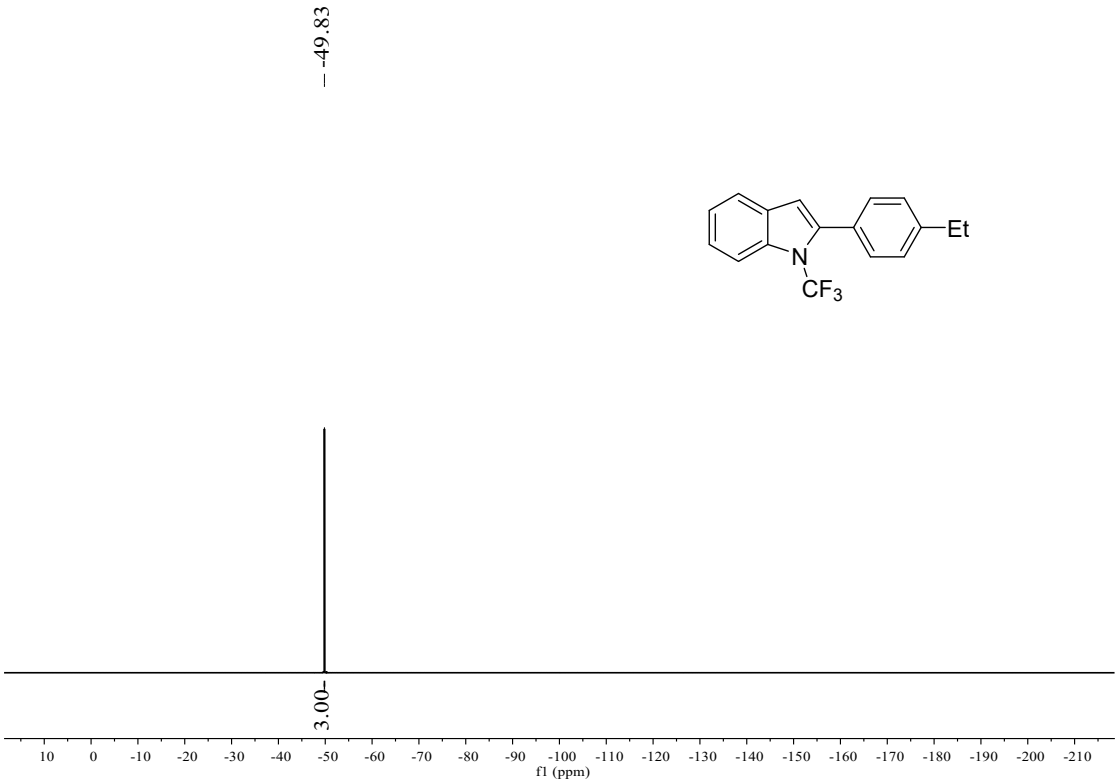
^{13}C NMR Spectrum of **3ag** (101 MHz, $CDCl_3$)



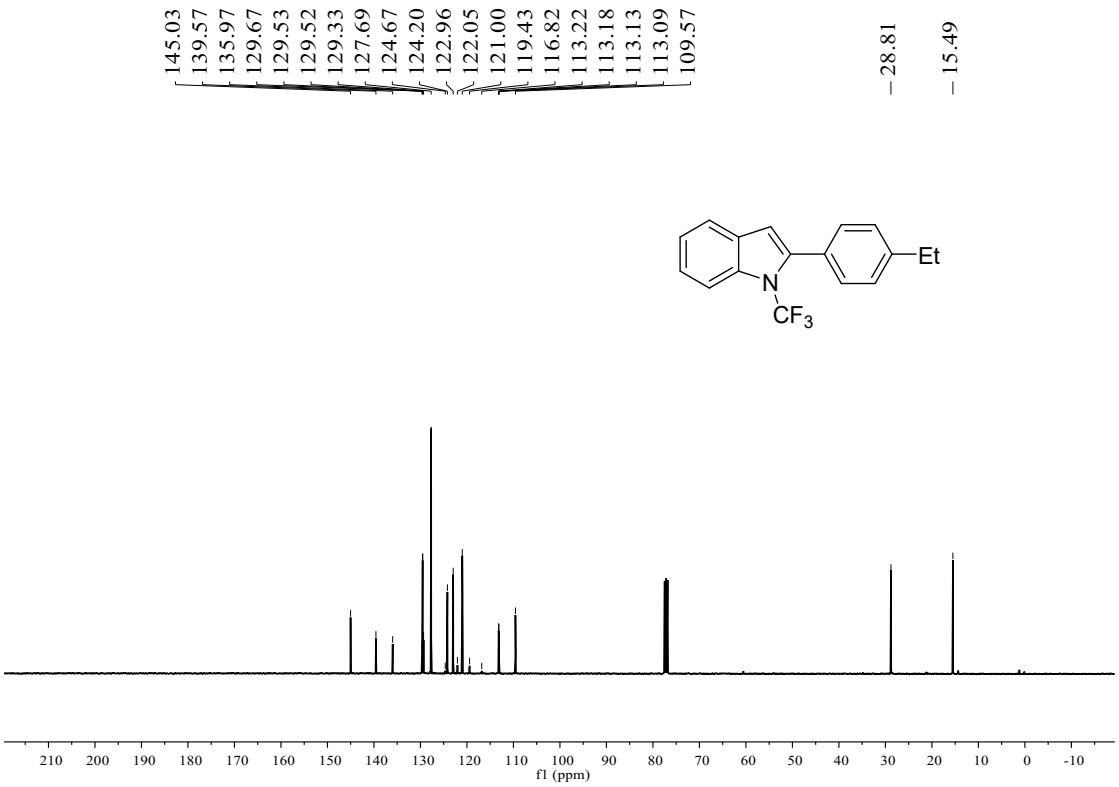
^{1}H NMR Spectrum of **3ah** (400 MHz, $CDCl_3$)



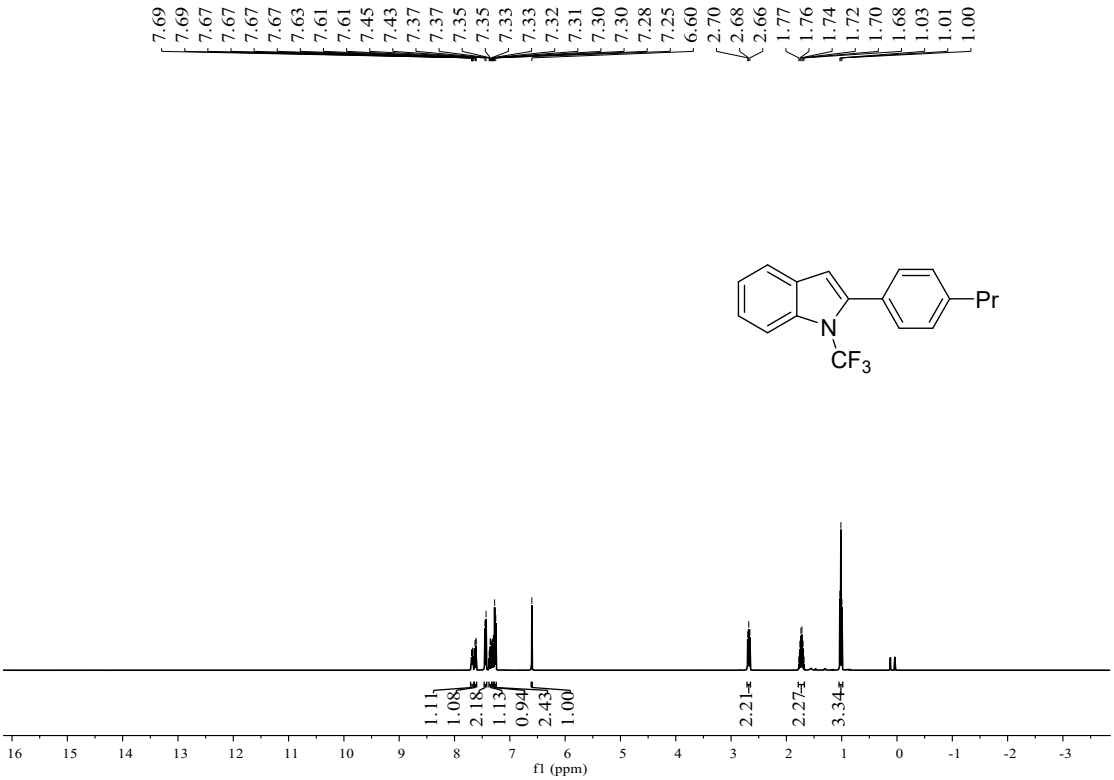
^{19}F NMR Spectrum of **3ah** (376 MHz, $CDCl_3$)



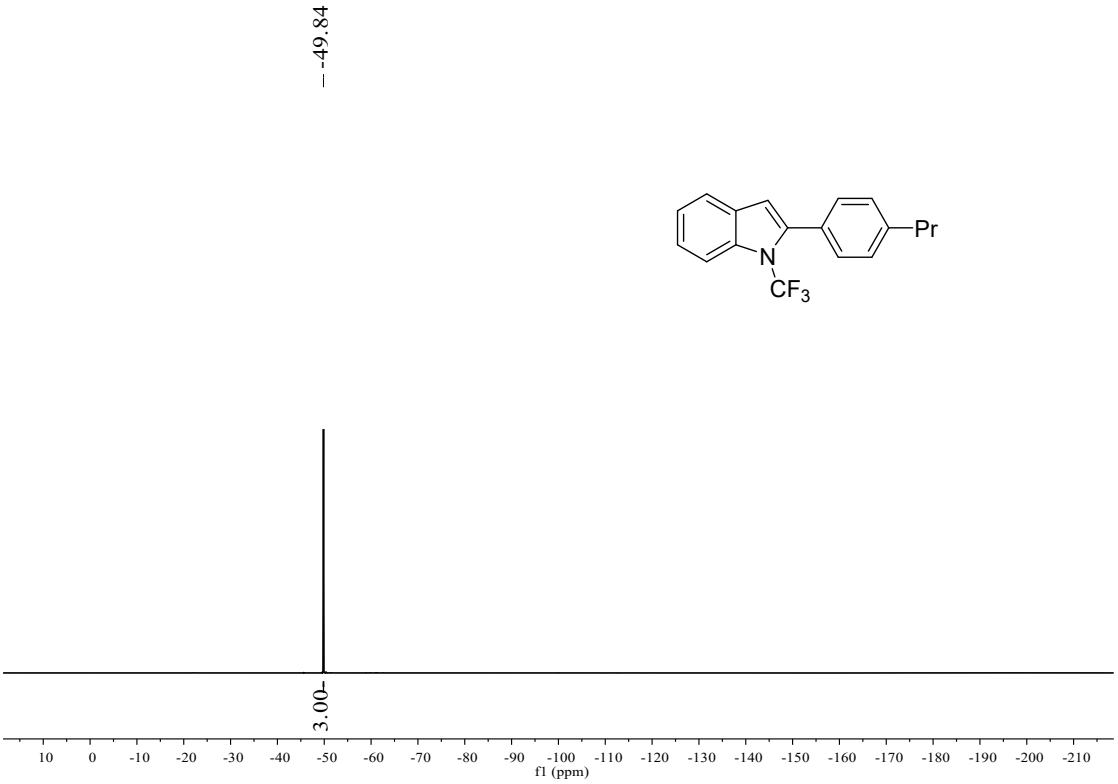
^{13}C NMR Spectrum of **3ah** (101 MHz, $CDCl_3$)



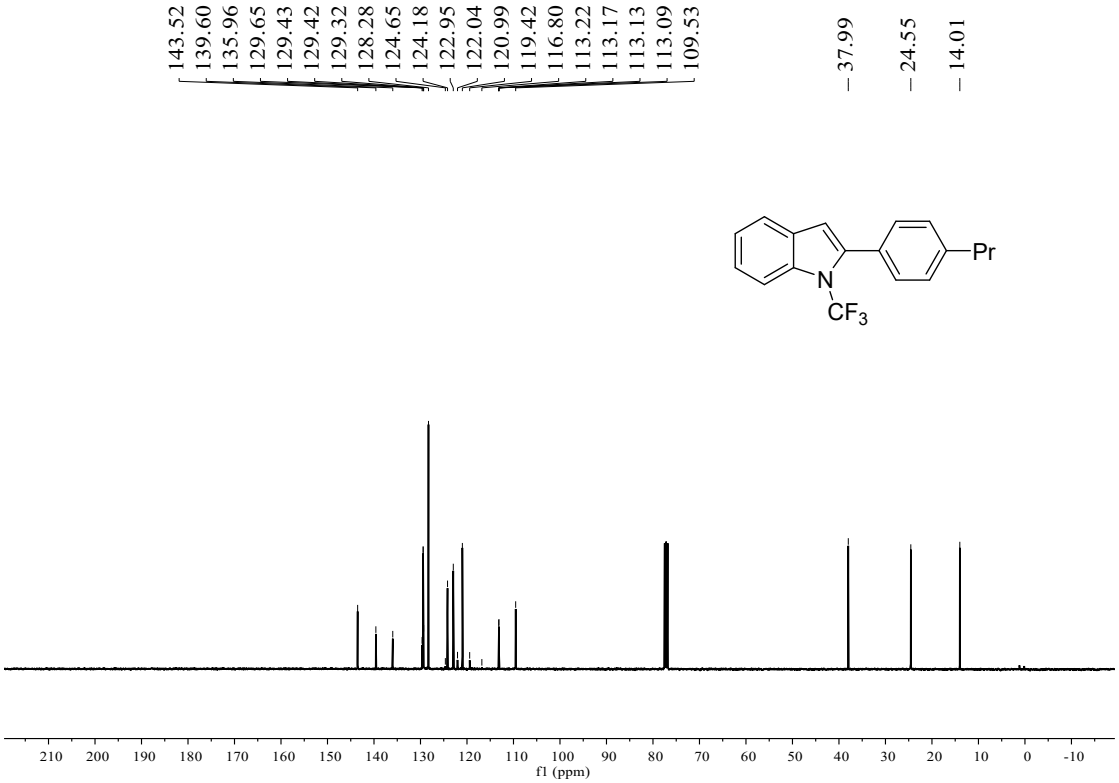
^{1}H NMR Spectrum of **3ai** (400 MHz, $CDCl_3$)



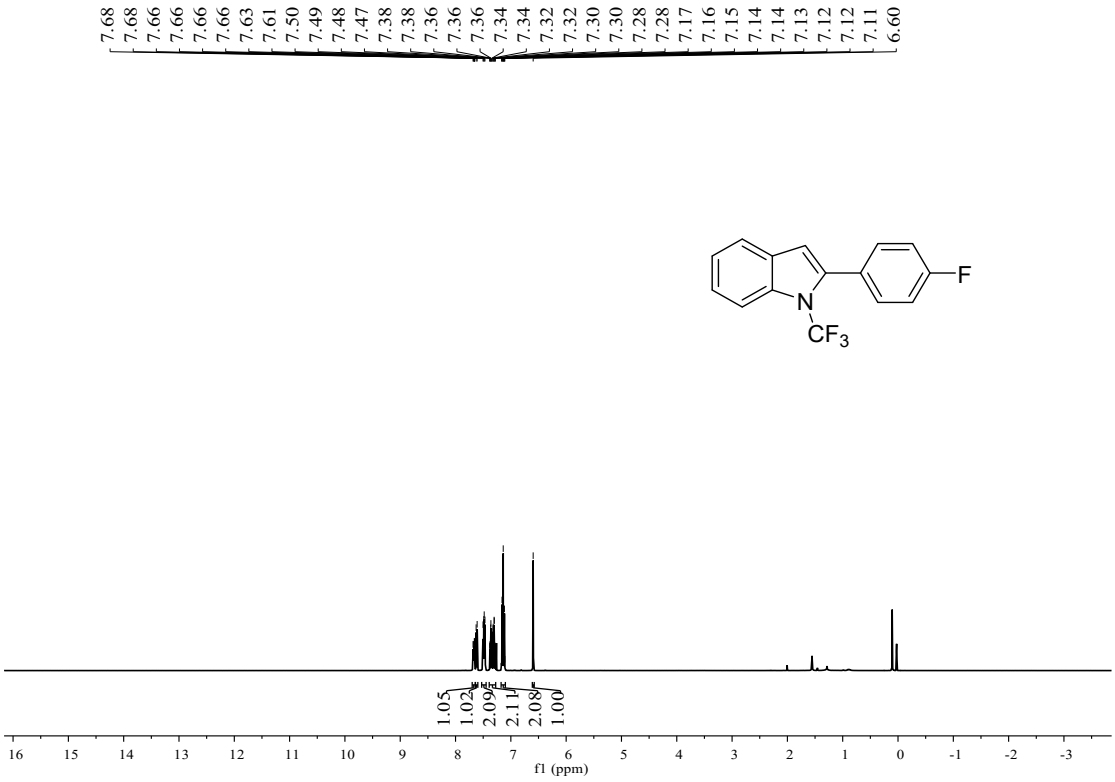
^{19}F NMR Spectrum of **3ai** (376 MHz, $CDCl_3$)



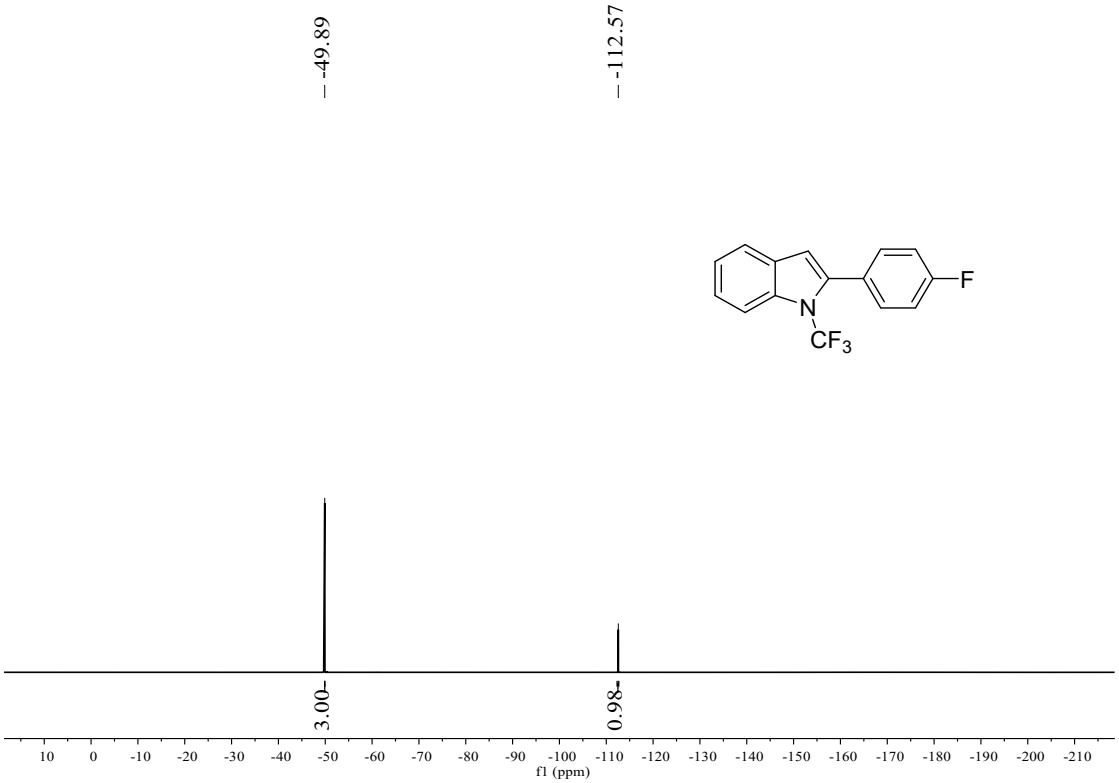
^{13}C NMR Spectrum of **3ai** (101 MHz, $CDCl_3$)



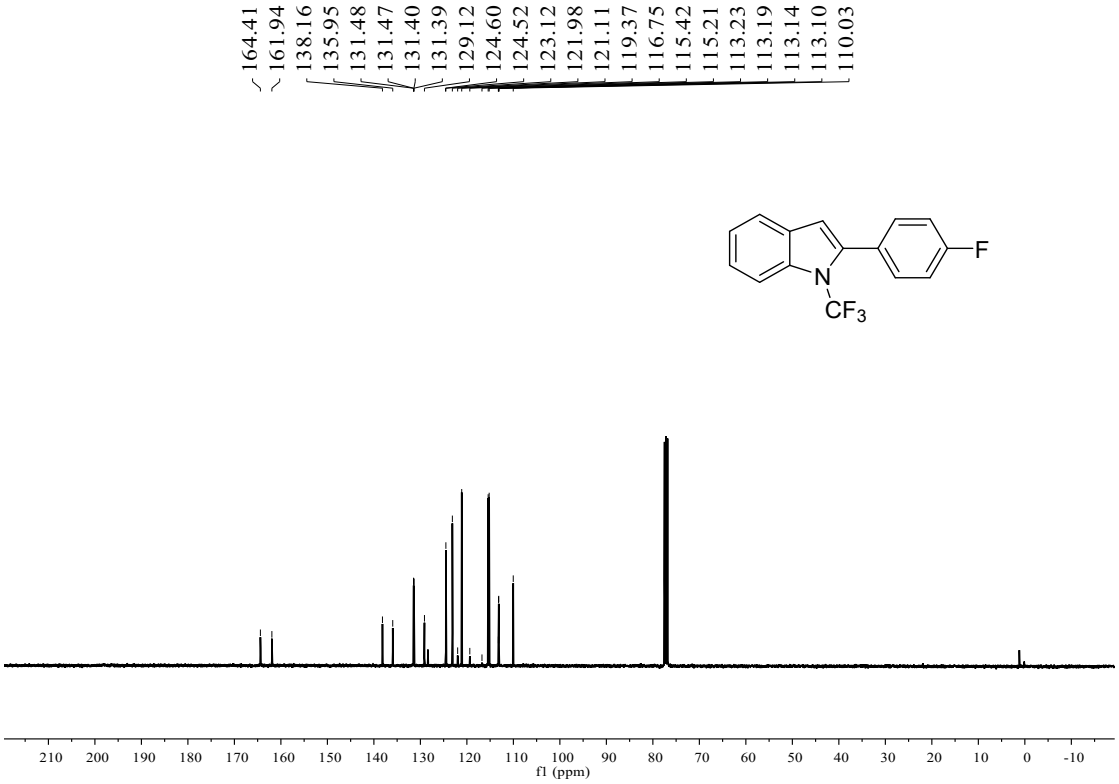
^{1}H NMR Spectrum of **3aj** (400 MHz, $CDCl_3$)



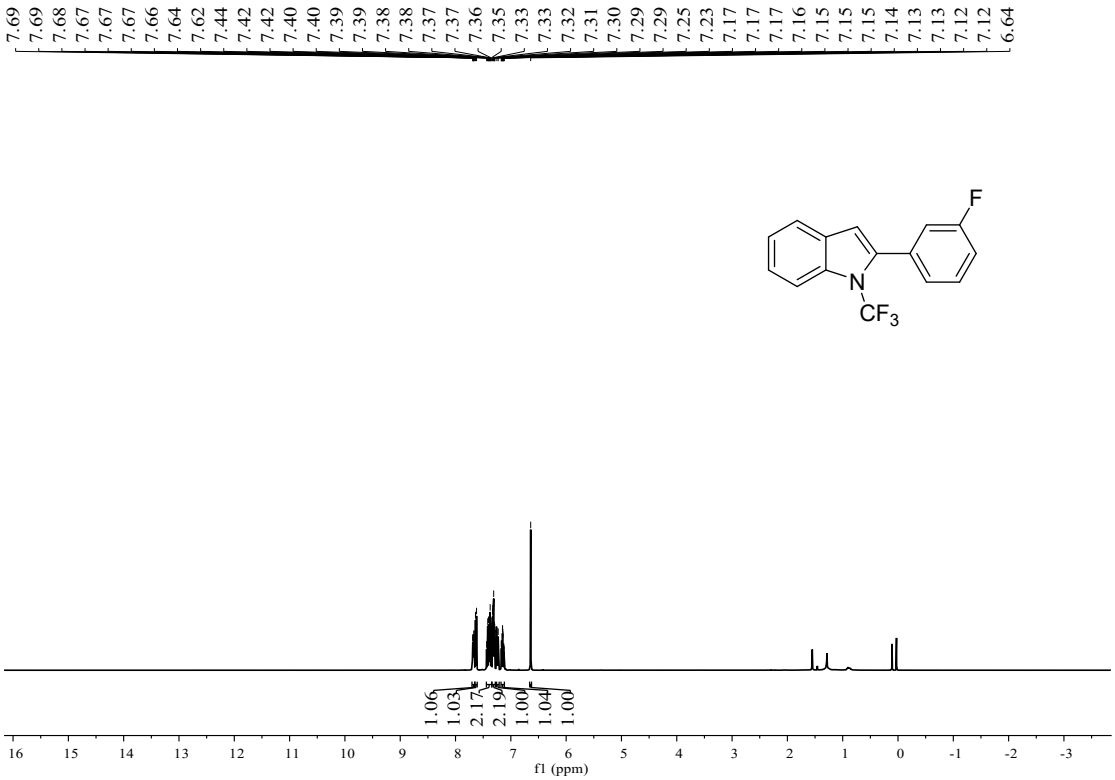
^{19}F NMR Spectrum of **3aj** (376 MHz, $CDCl_3$)



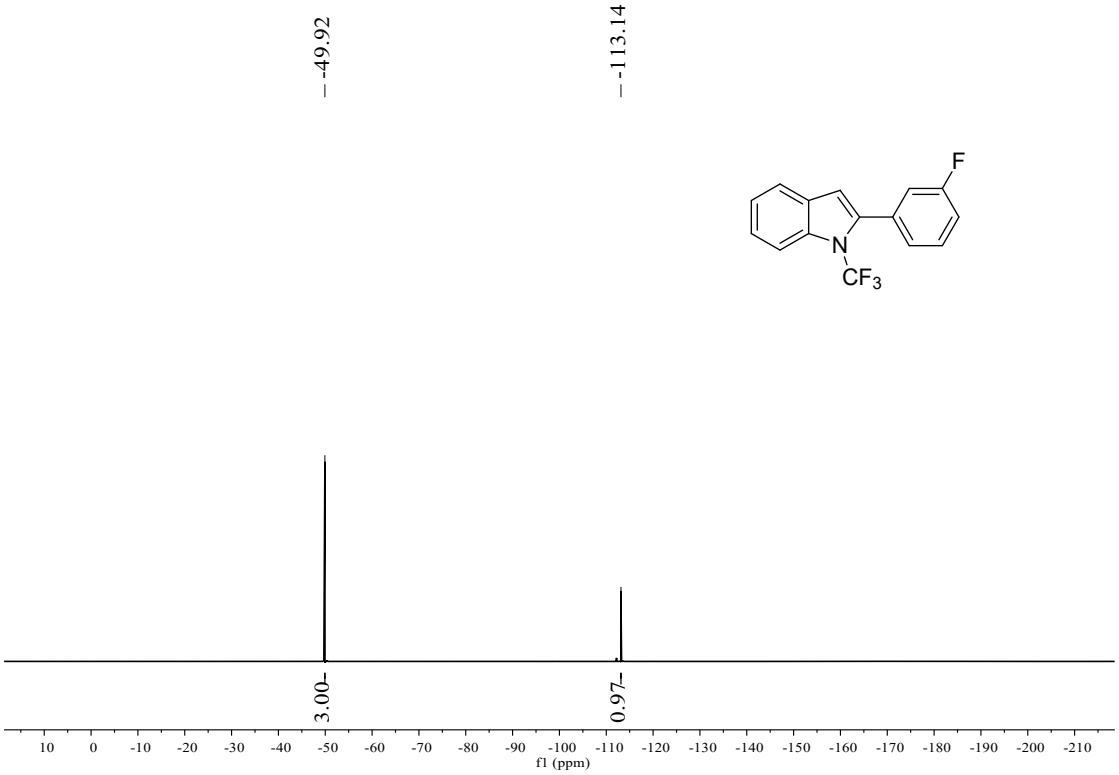
^{13}C NMR Spectrum of **3aj** (101 MHz, $CDCl_3$)



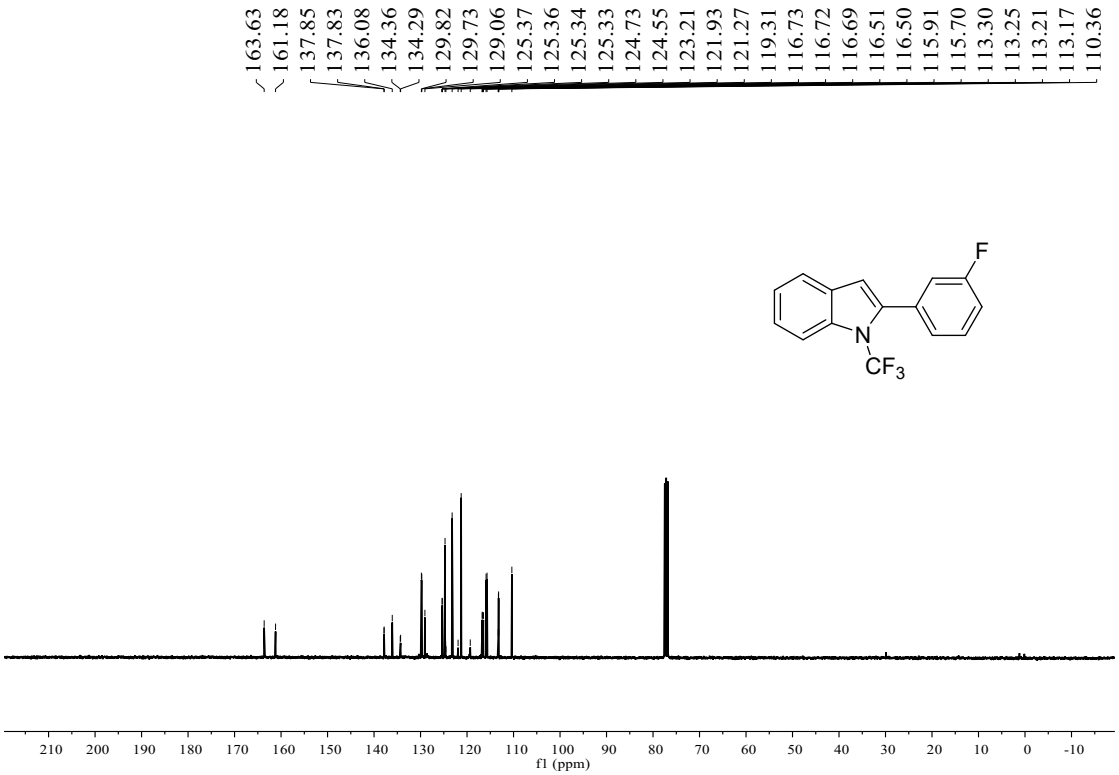
^{1}H NMR Spectrum of **3ak** (400 MHz, $CDCl_3$)



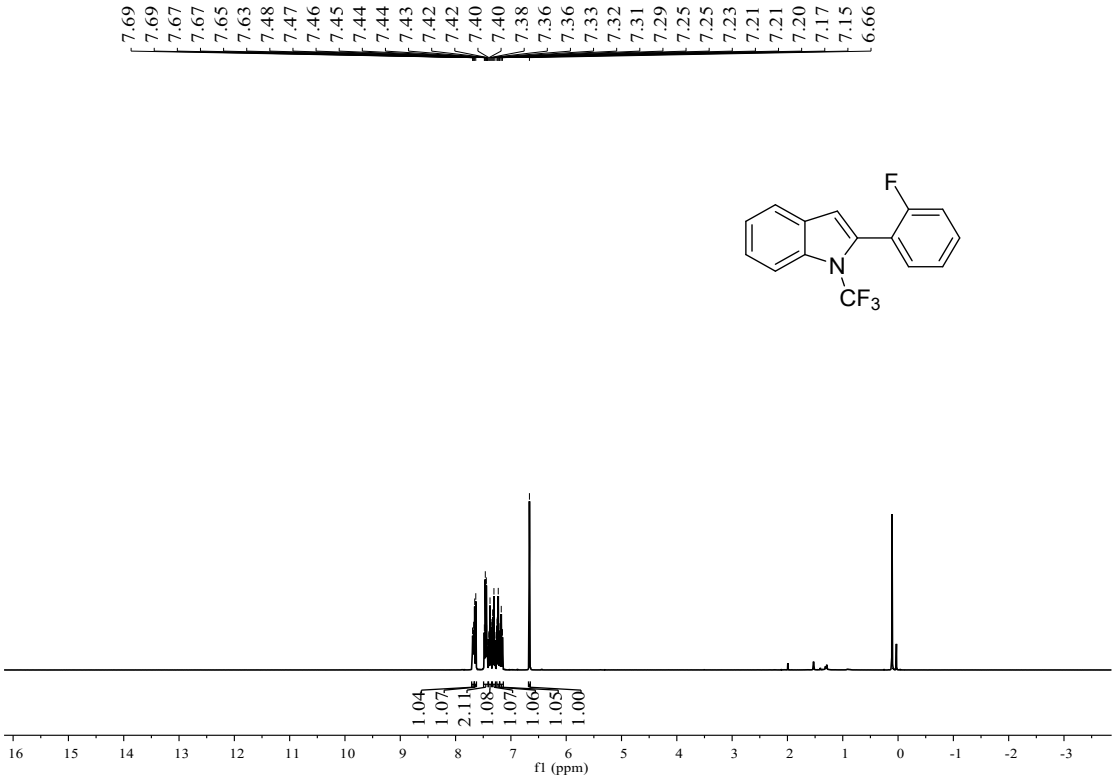
^{19}F NMR Spectrum of **3ak** (376 MHz, $CDCl_3$)



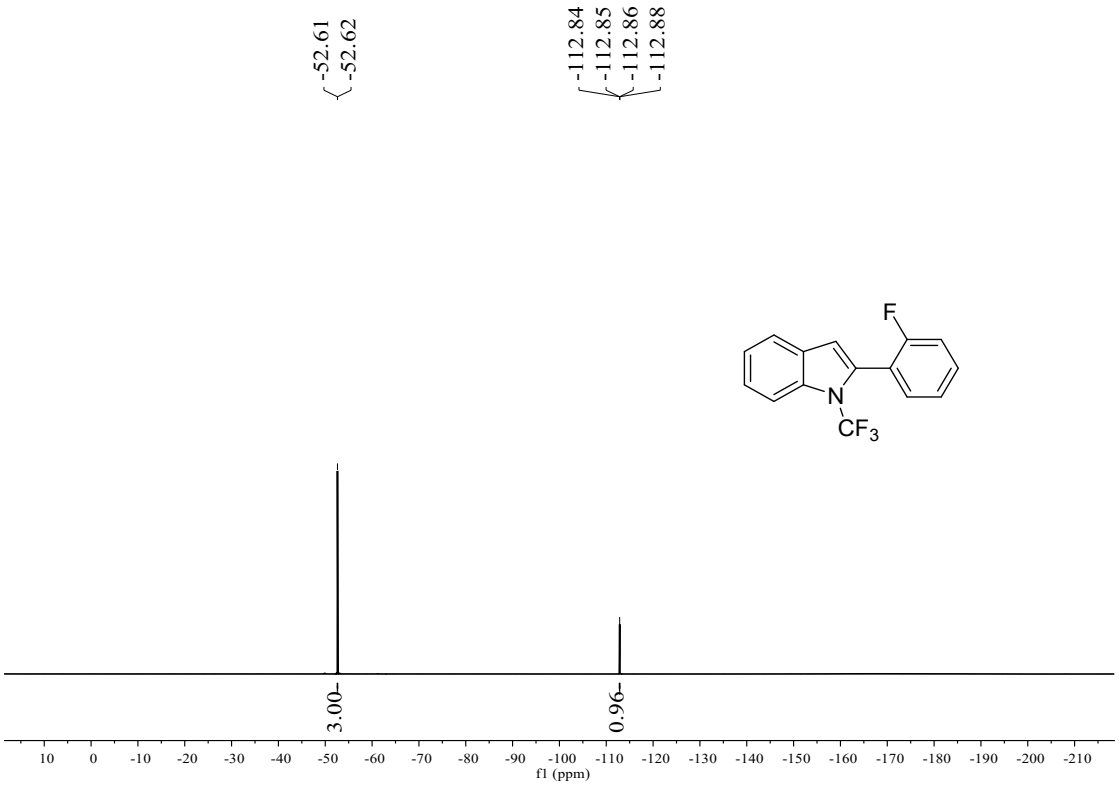
^{13}C NMR Spectrum of **3ak** (101 MHz, $CDCl_3$)



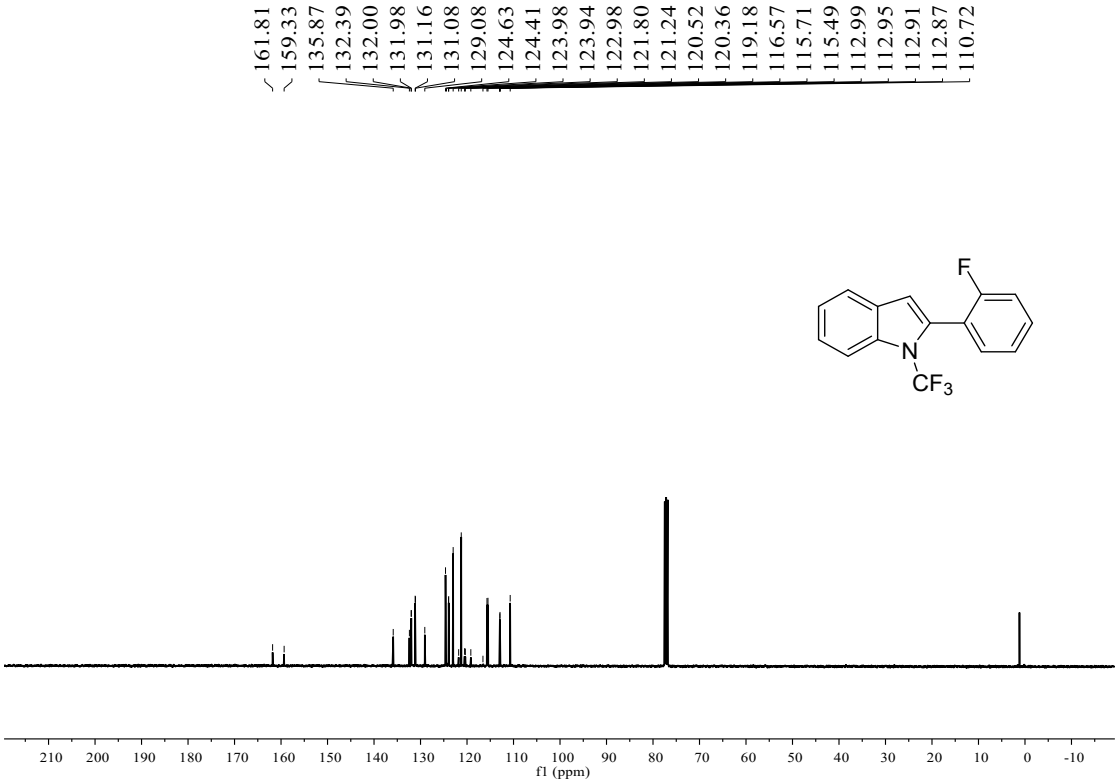
^{1}H NMR Spectrum of **3al** (400 MHz, $CDCl_3$)



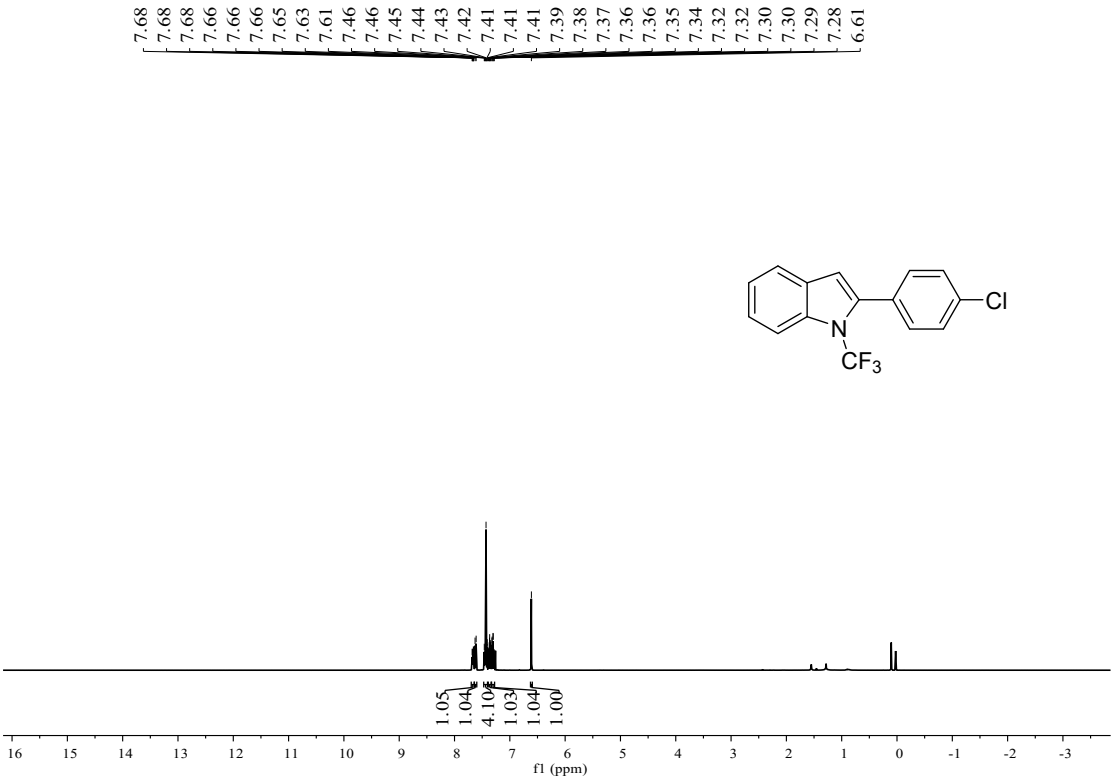
^{19}F NMR Spectrum of **3al** (376 MHz, $CDCl_3$)



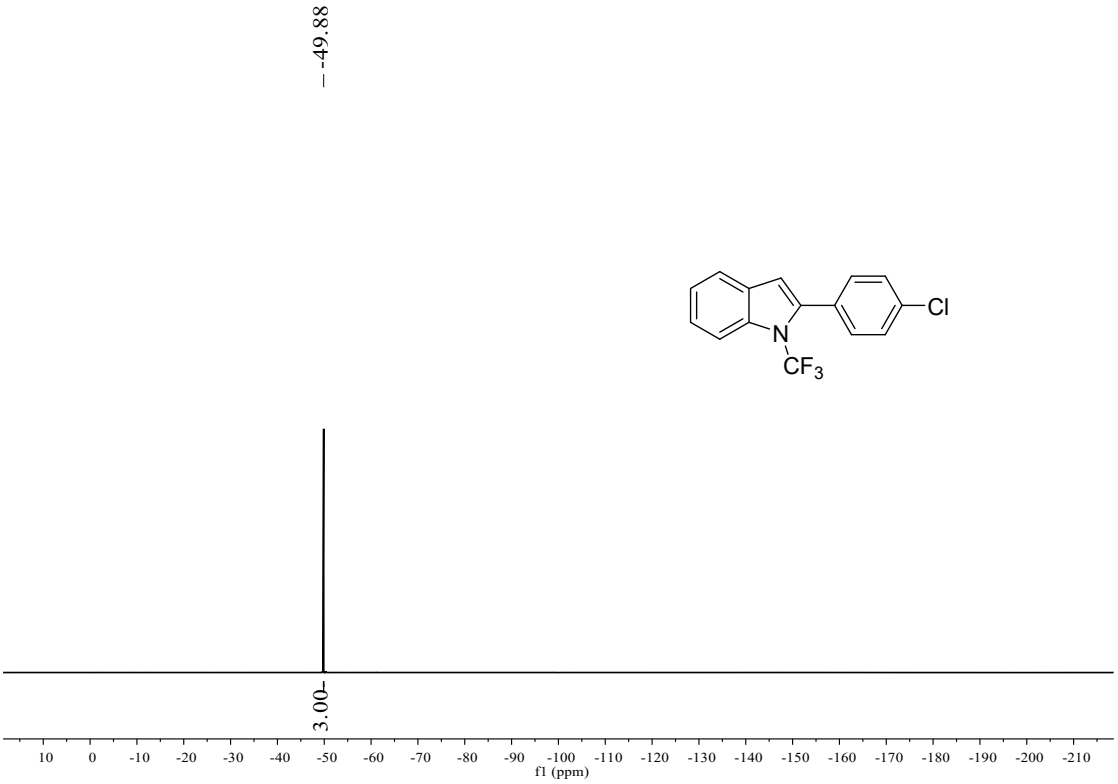
^{13}C NMR Spectrum of **3al** (101 MHz, $CDCl_3$)



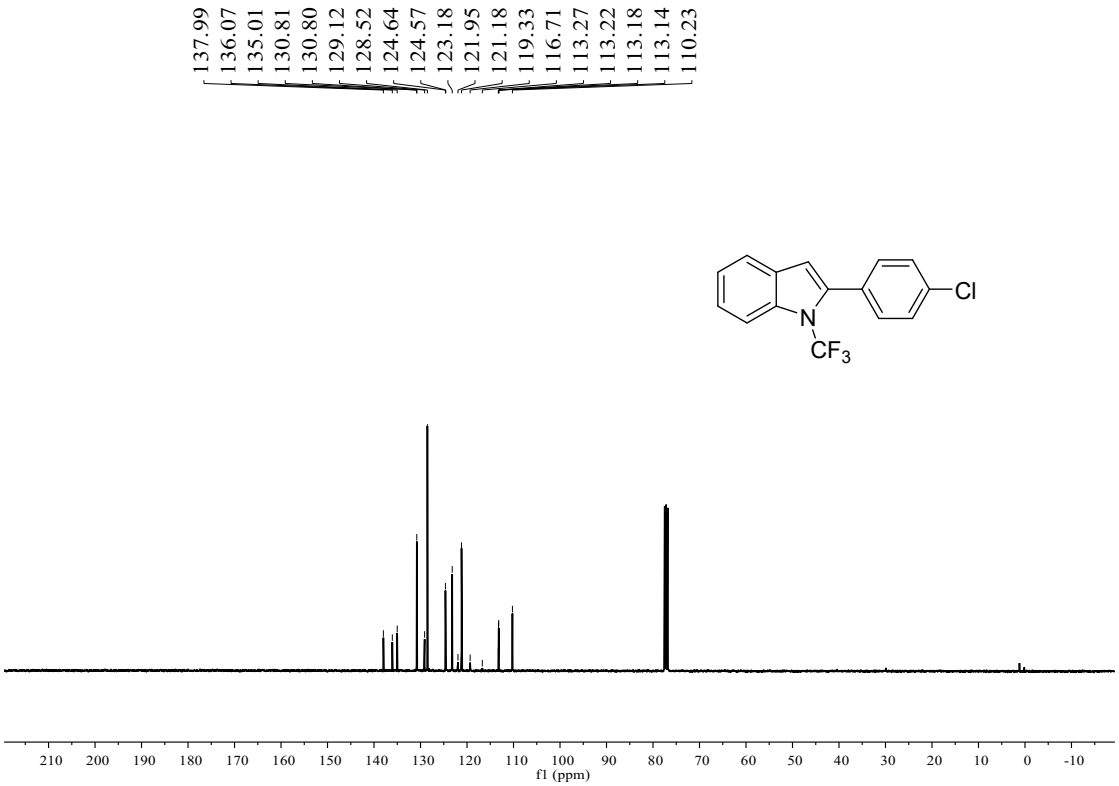
^{1}H NMR Spectrum of **3am** (400 MHz, $CDCl_3$)



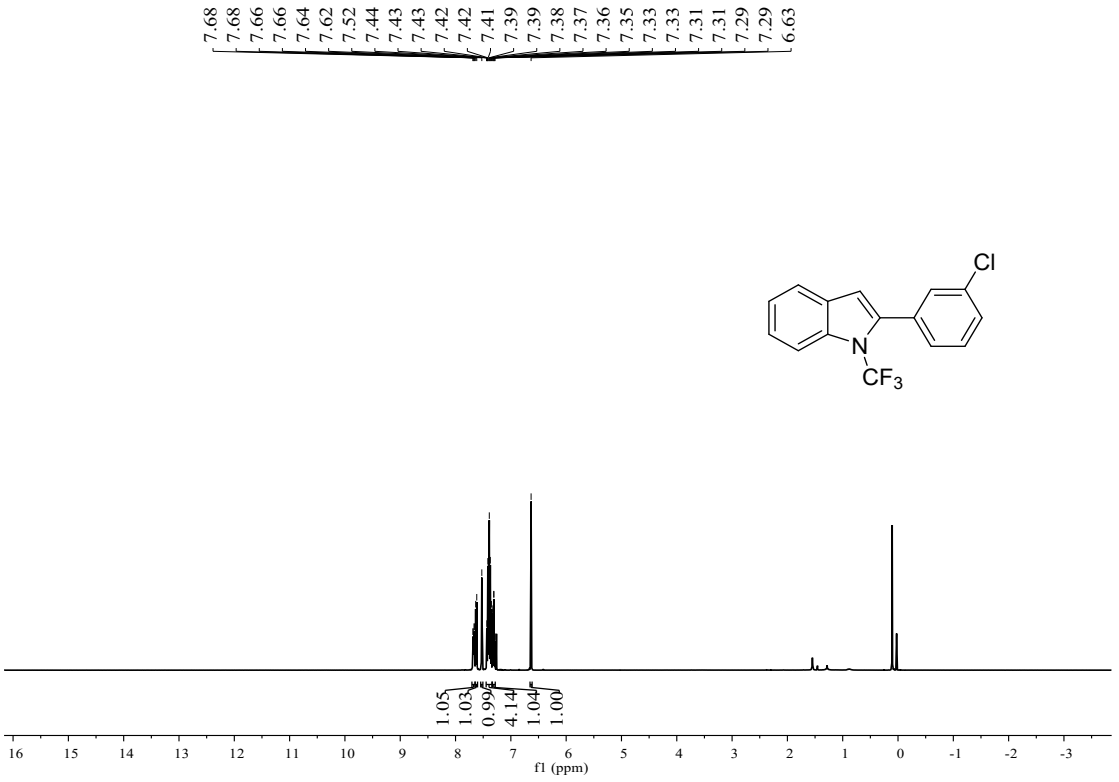
^{19}F NMR Spectrum of **3am** (376 MHz, $CDCl_3$)



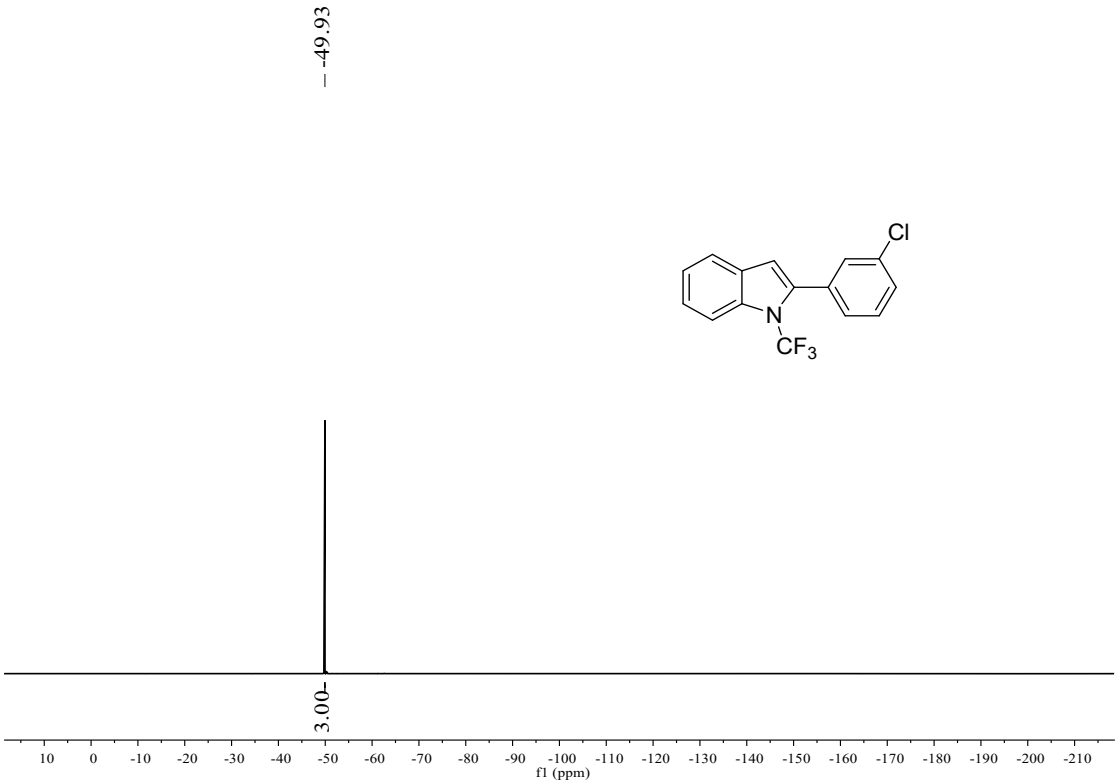
^{13}C NMR Spectrum of **3am** (101 MHz, $CDCl_3$)



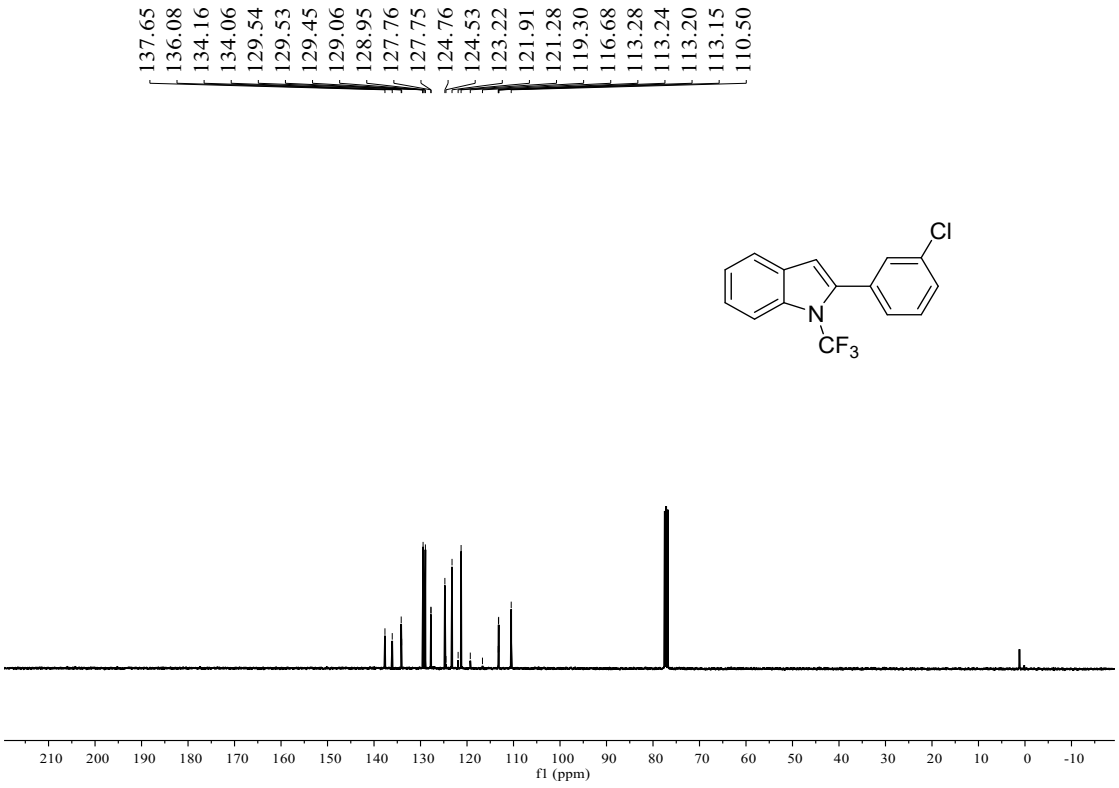
^{1}H NMR Spectrum of **3an** (400 MHz, $CDCl_3$)



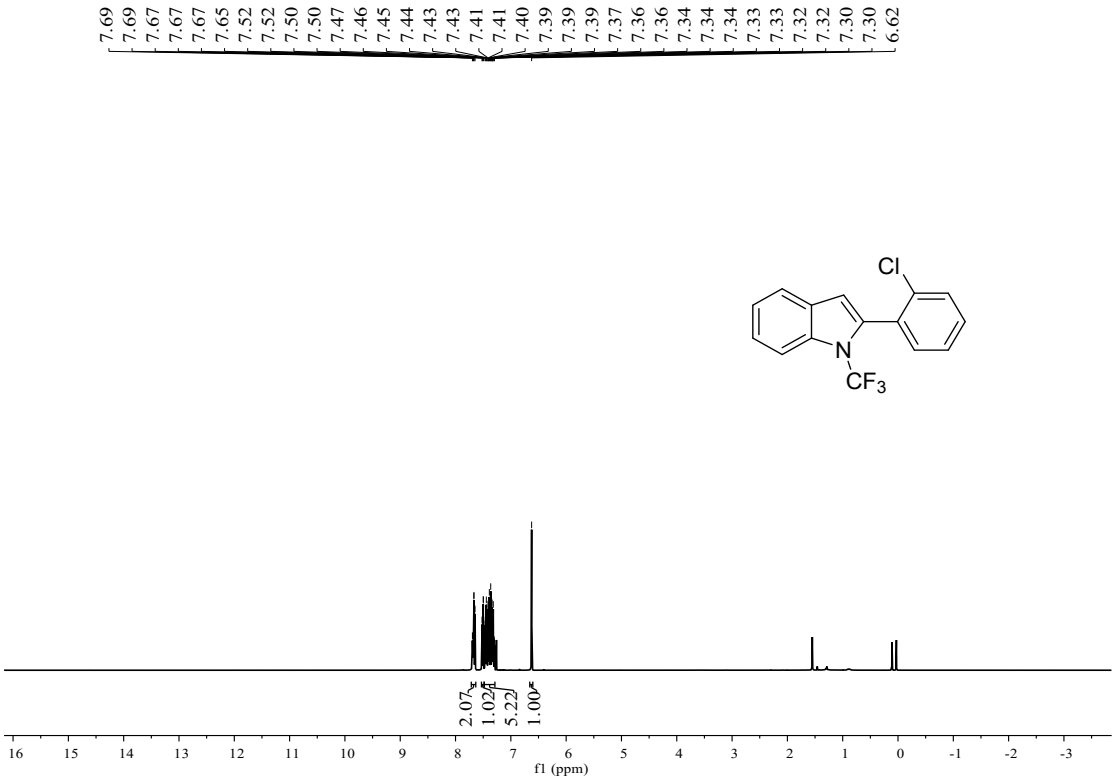
^{19}F NMR Spectrum of **3an** (376 MHz, $CDCl_3$)



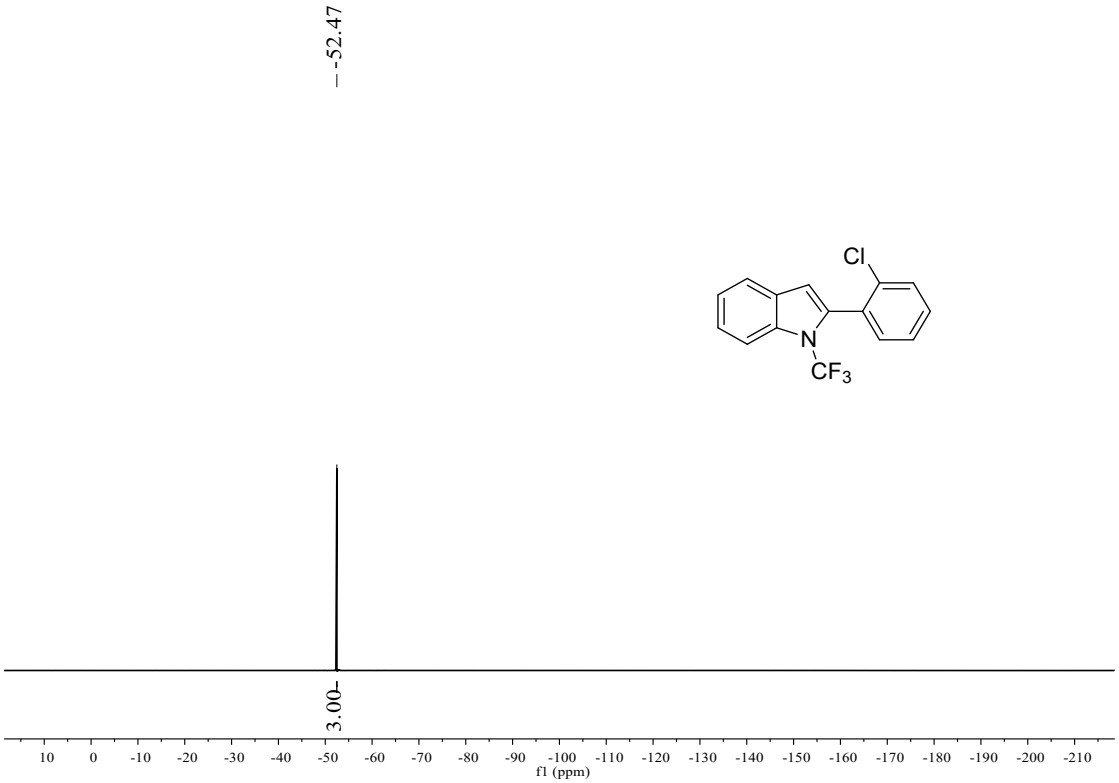
^{13}C NMR Spectrum of **3an** (101 MHz, $CDCl_3$)



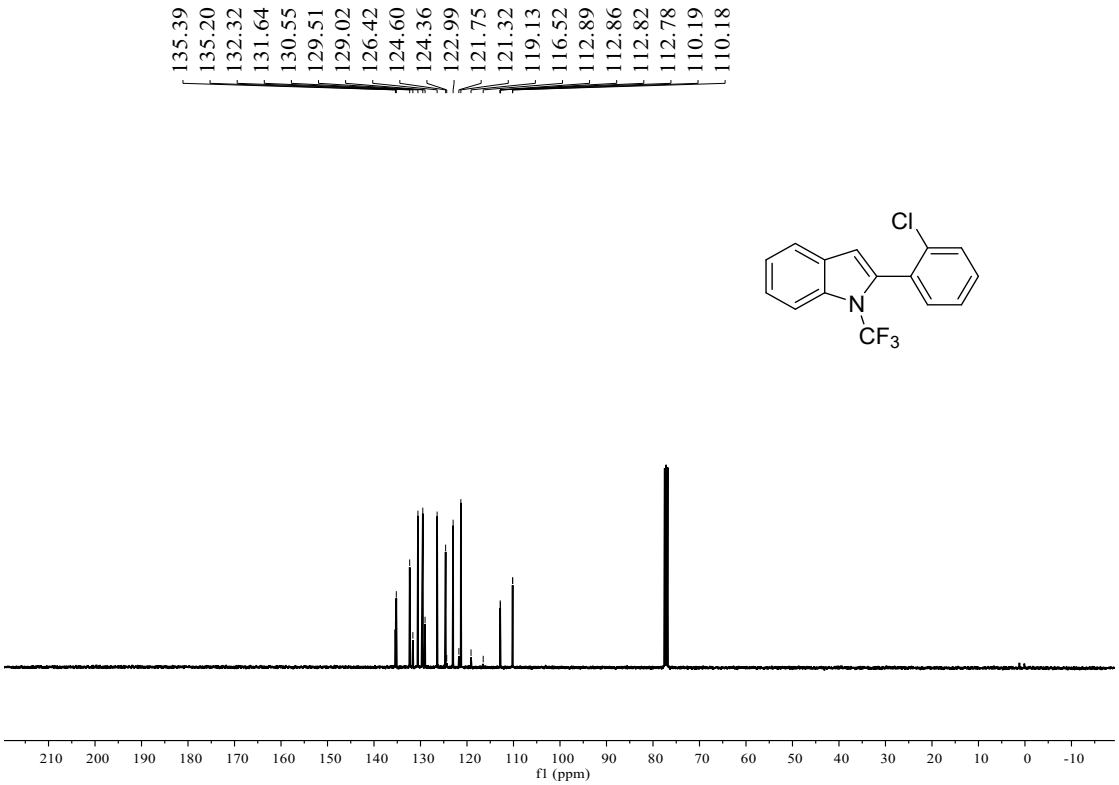
^{1}H NMR Spectrum of **3ao** (400 MHz, $CDCl_3$)



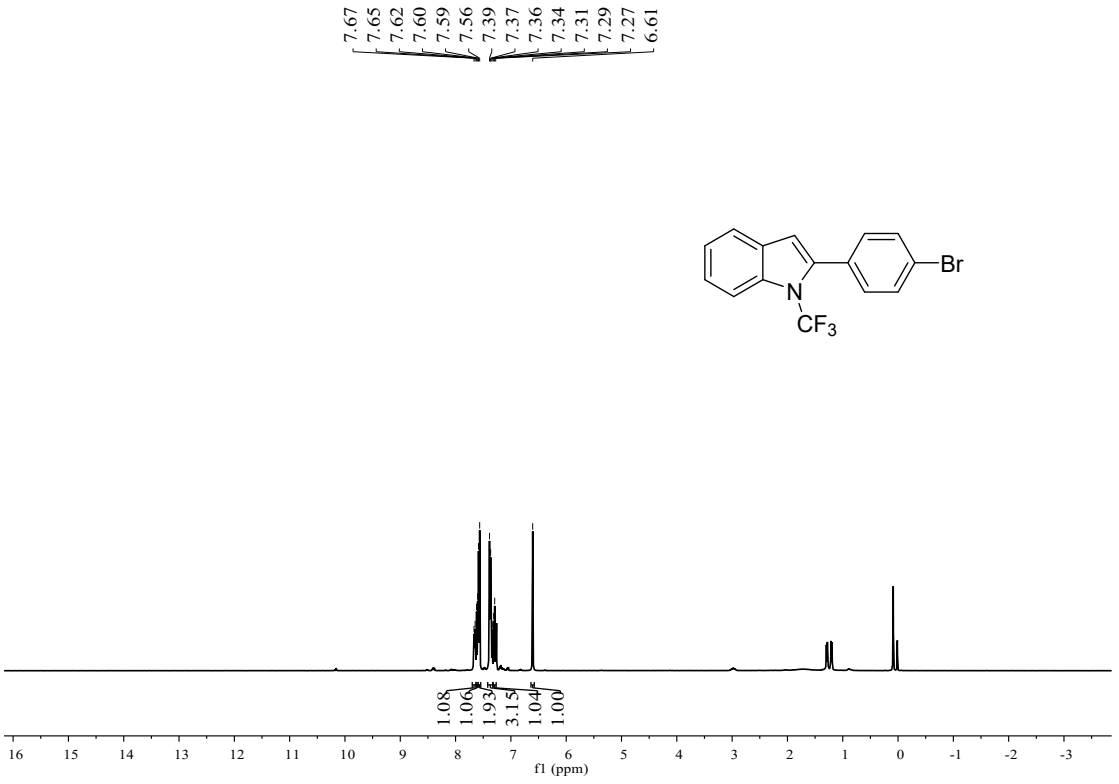
^{19}F NMR Spectrum of **3ao** (376 MHz, $CDCl_3$)



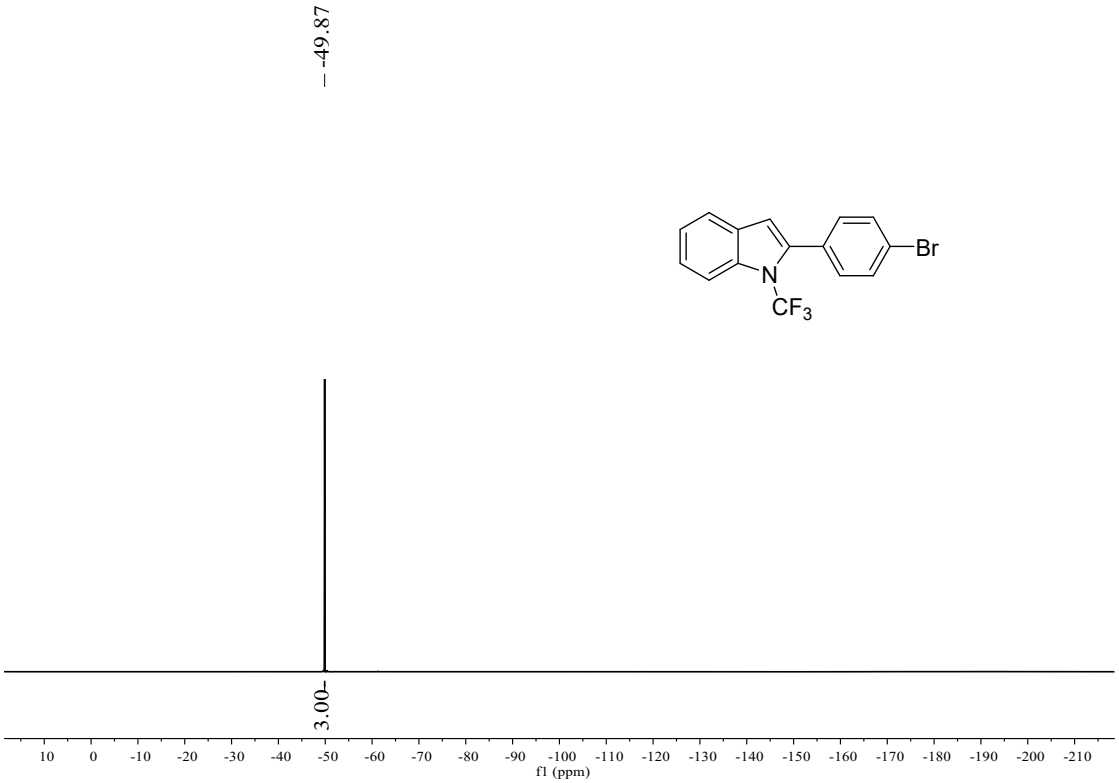
^{13}C NMR Spectrum of **3ao** (101 MHz, $CDCl_3$)



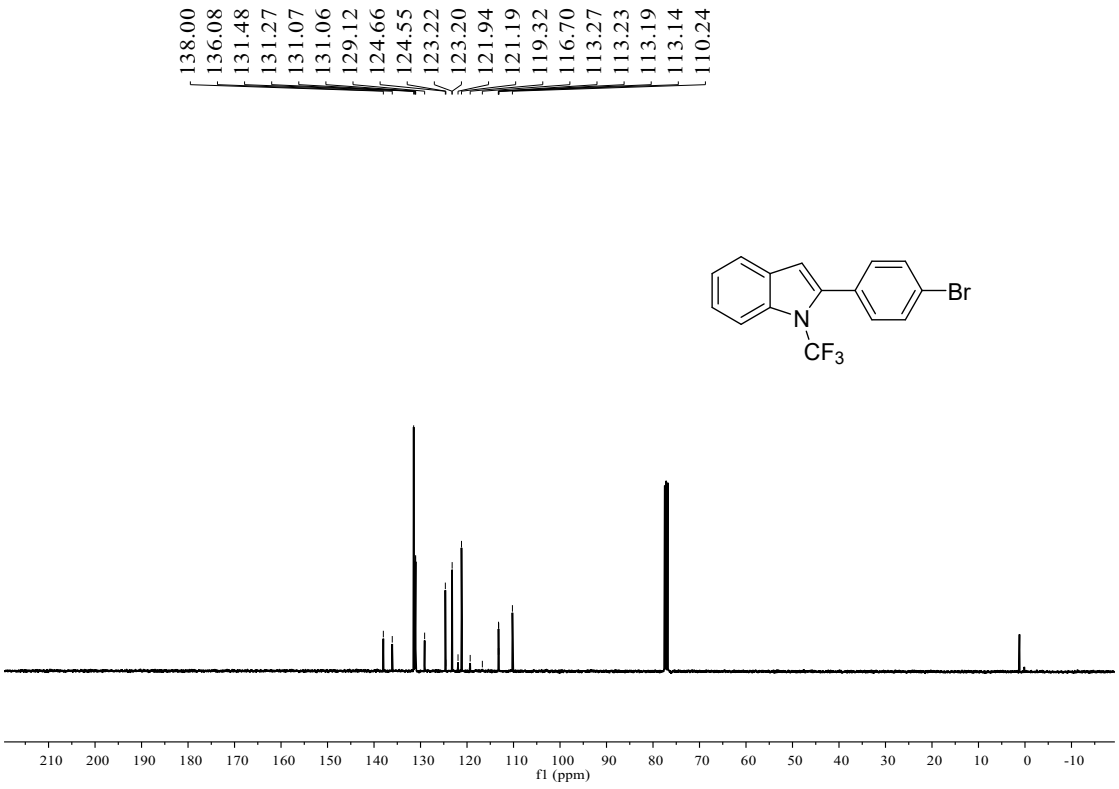
^{1}H NMR Spectrum of **3ap** (400 MHz, $CDCl_3$)



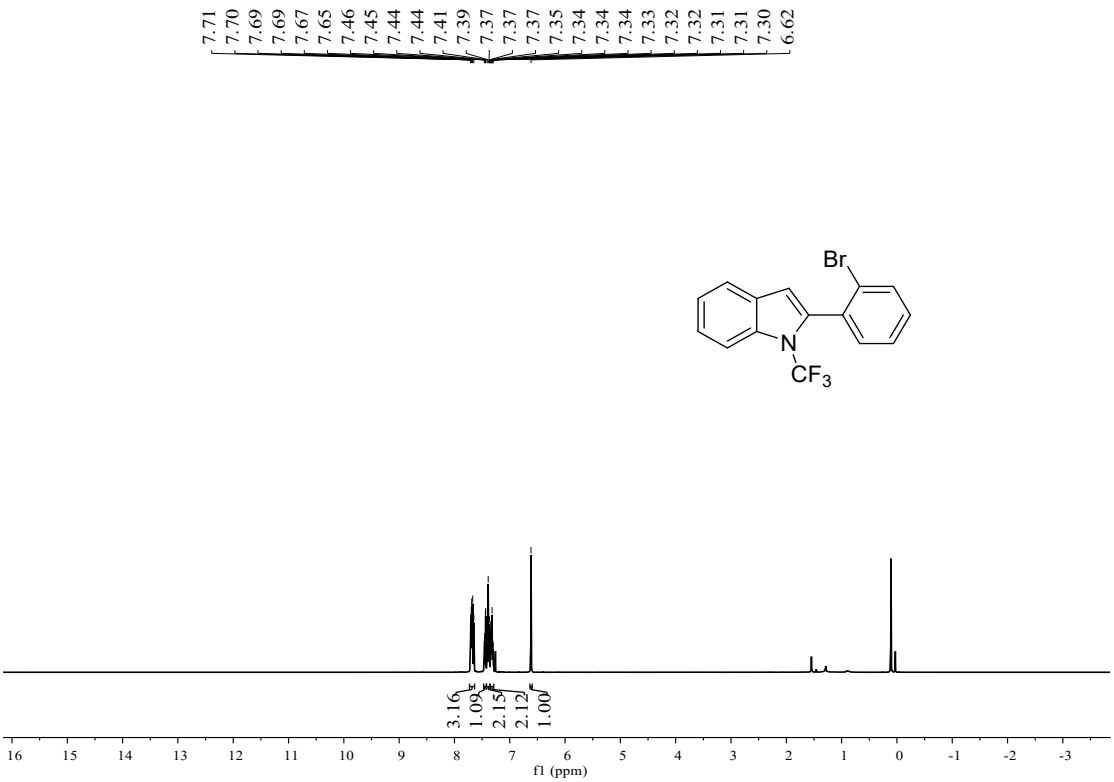
^{19}F NMR Spectrum of **3ap** (376 MHz, $CDCl_3$)



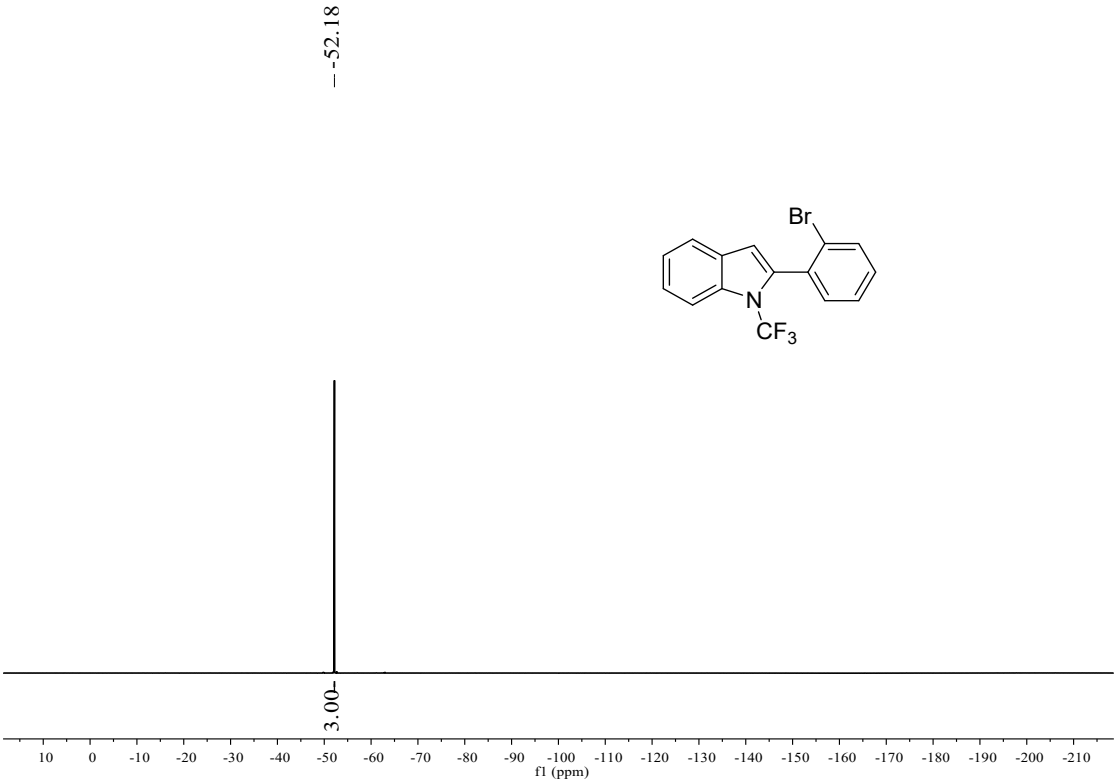
^{13}C NMR Spectrum of **3ap** (101 MHz, $CDCl_3$)



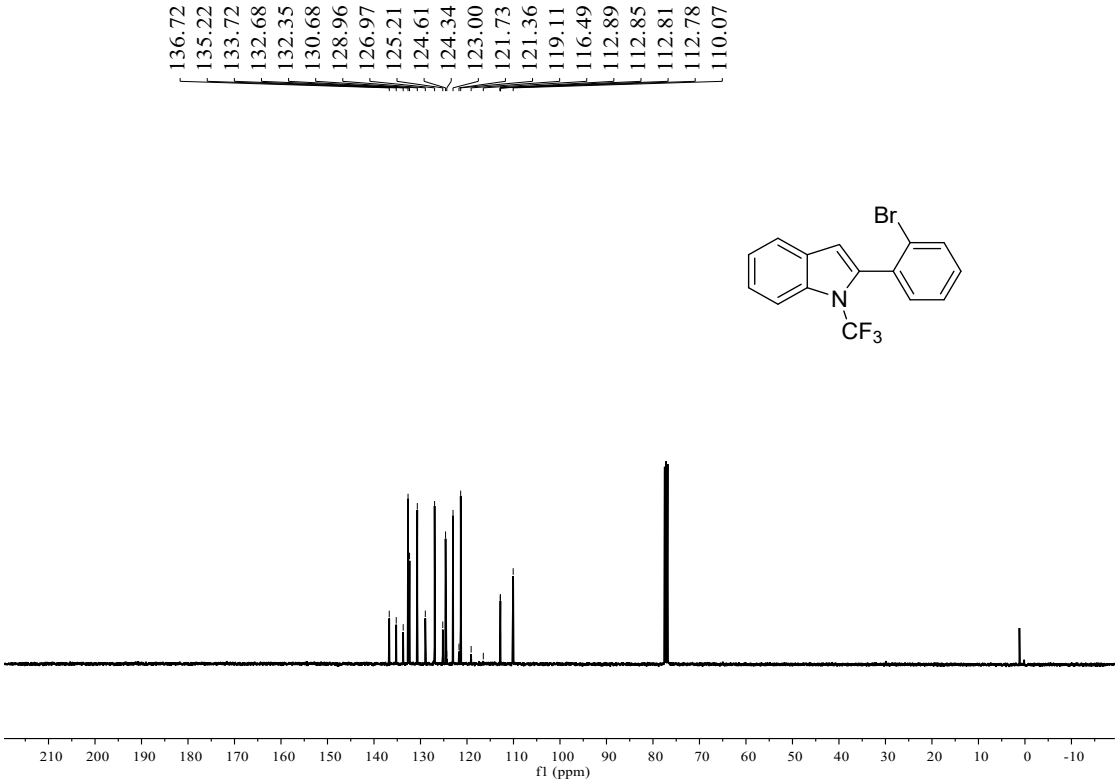
^{1}H NMR Spectrum of **3aq** (400 MHz, $CDCl_3$)



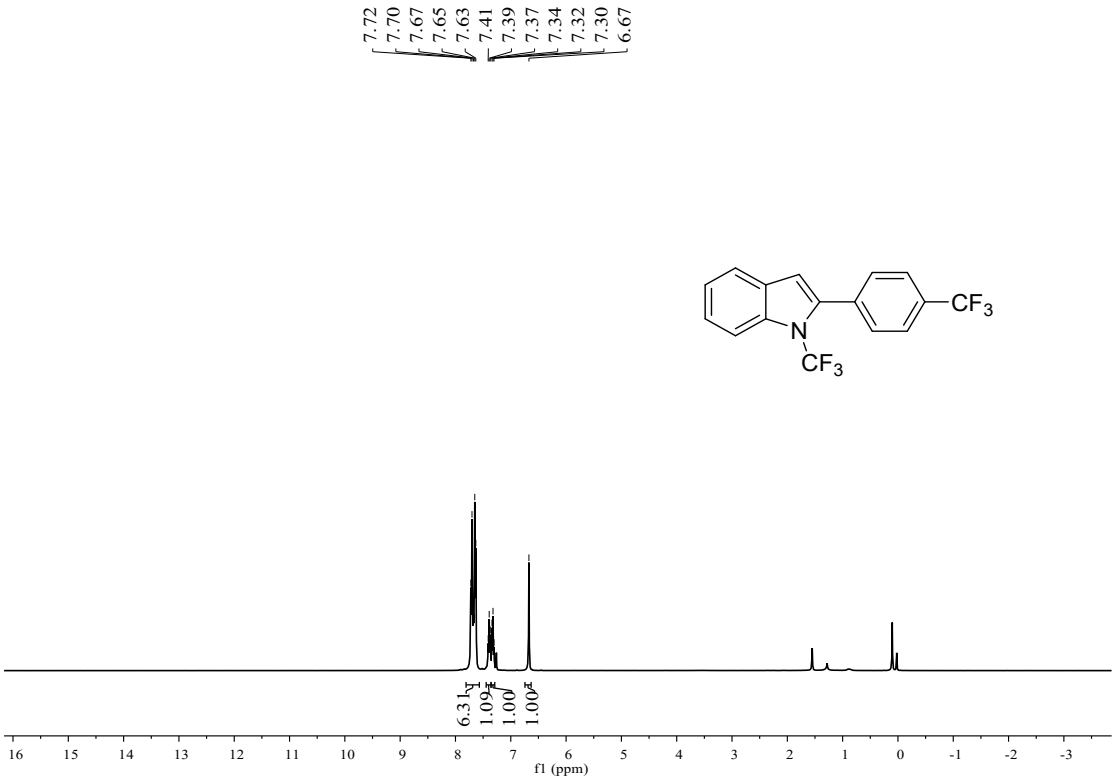
^{19}F NMR Spectrum of **3aq** (376 MHz, $CDCl_3$)



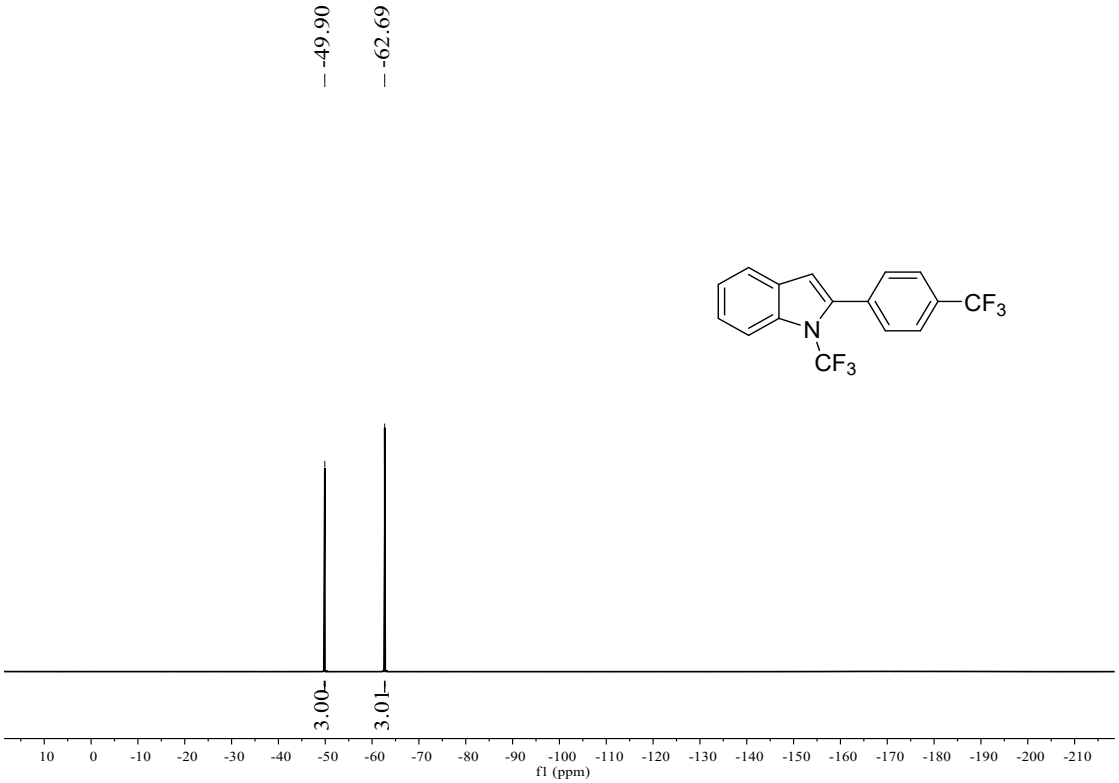
^{13}C NMR Spectrum of **3aq** (101 MHz, $CDCl_3$)



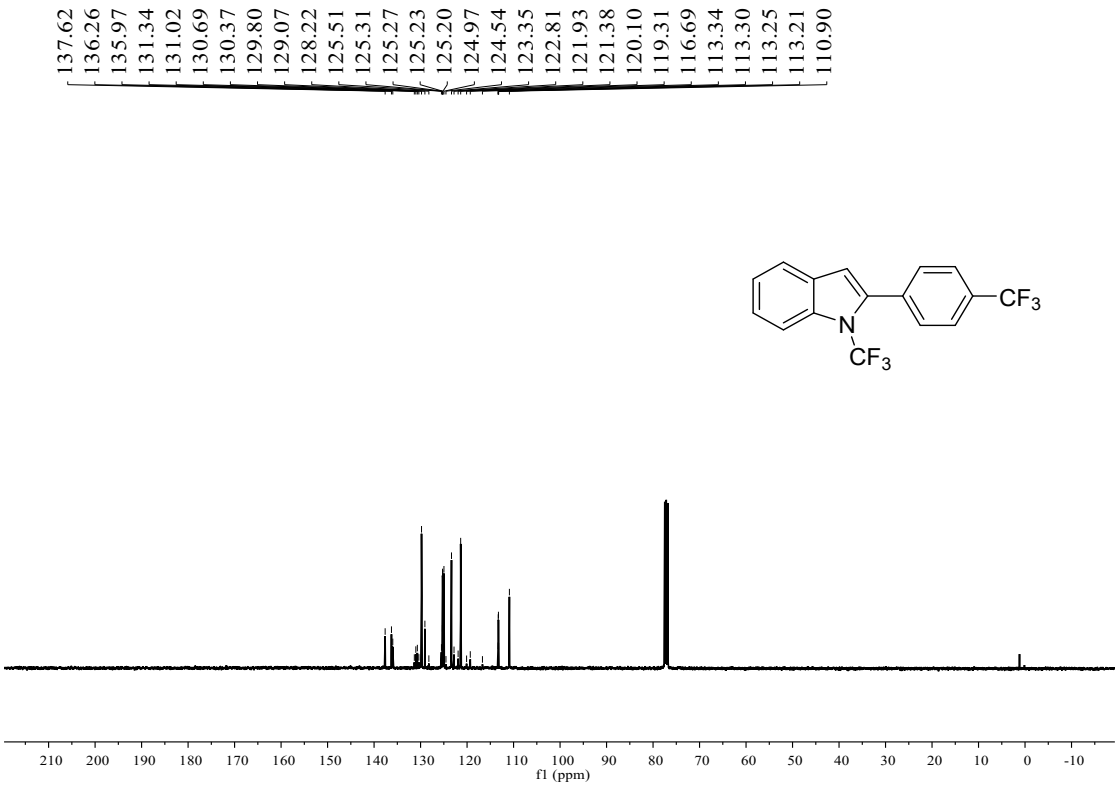
^{1}H NMR Spectrum of **3ar** (400 MHz, $CDCl_3$)



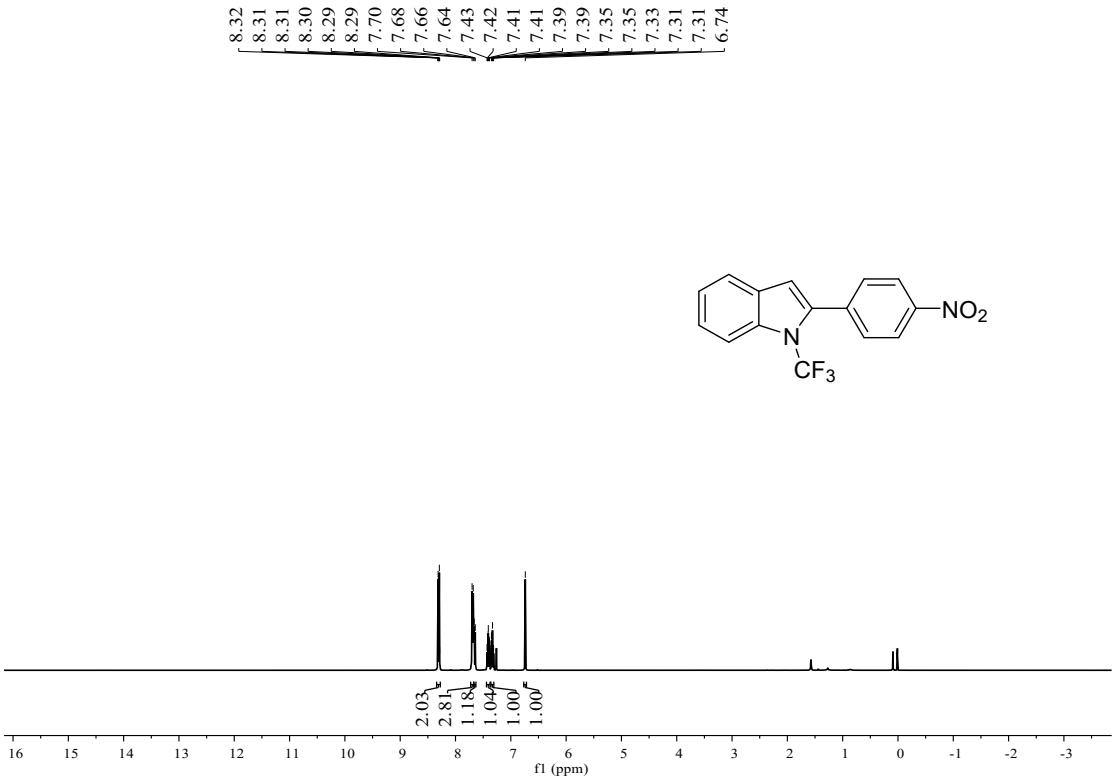
^{19}F NMR Spectrum of **3ar** (376 MHz, $CDCl_3$)



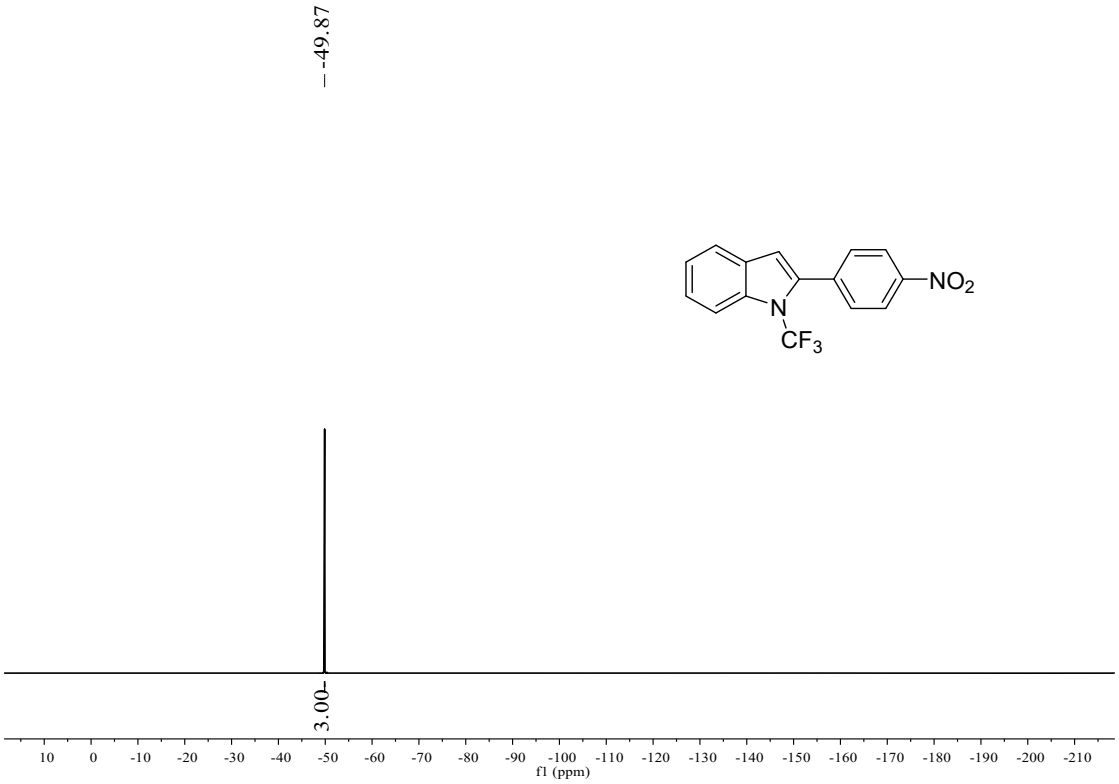
^{13}C NMR Spectrum of **3ar** (101 MHz, $CDCl_3$)



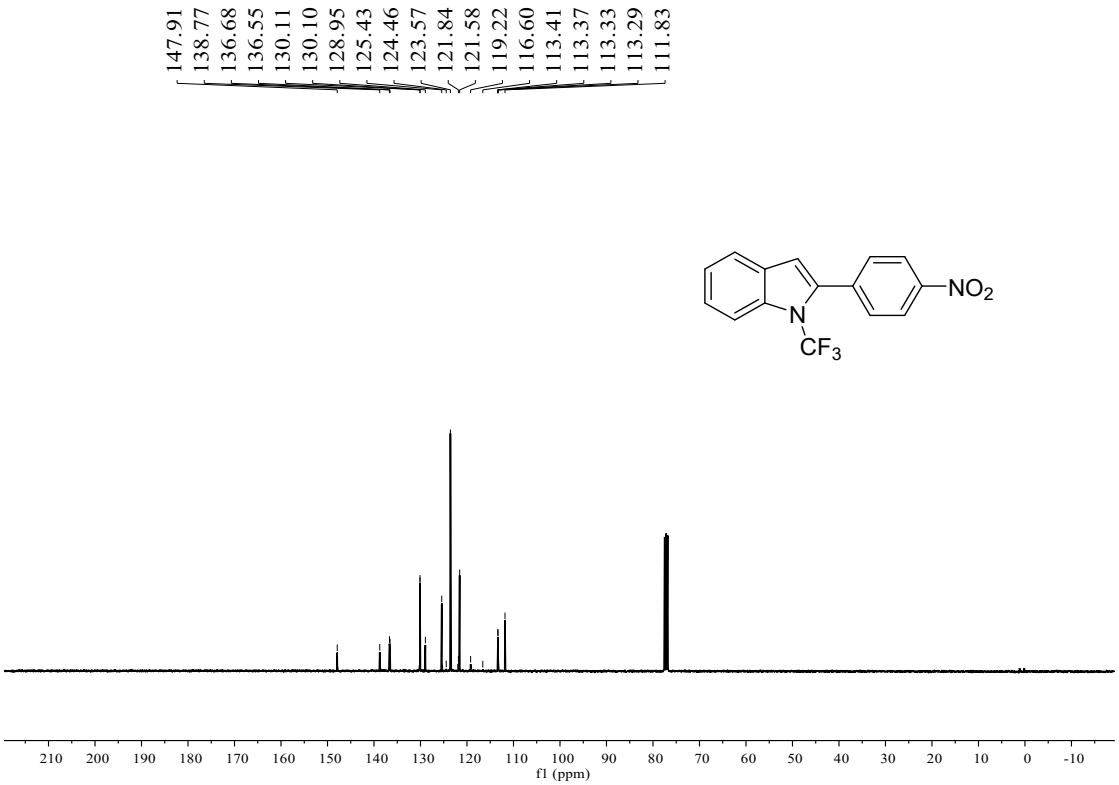
^{1}H NMR Spectrum of **3as** (400 MHz, $CDCl_3$)



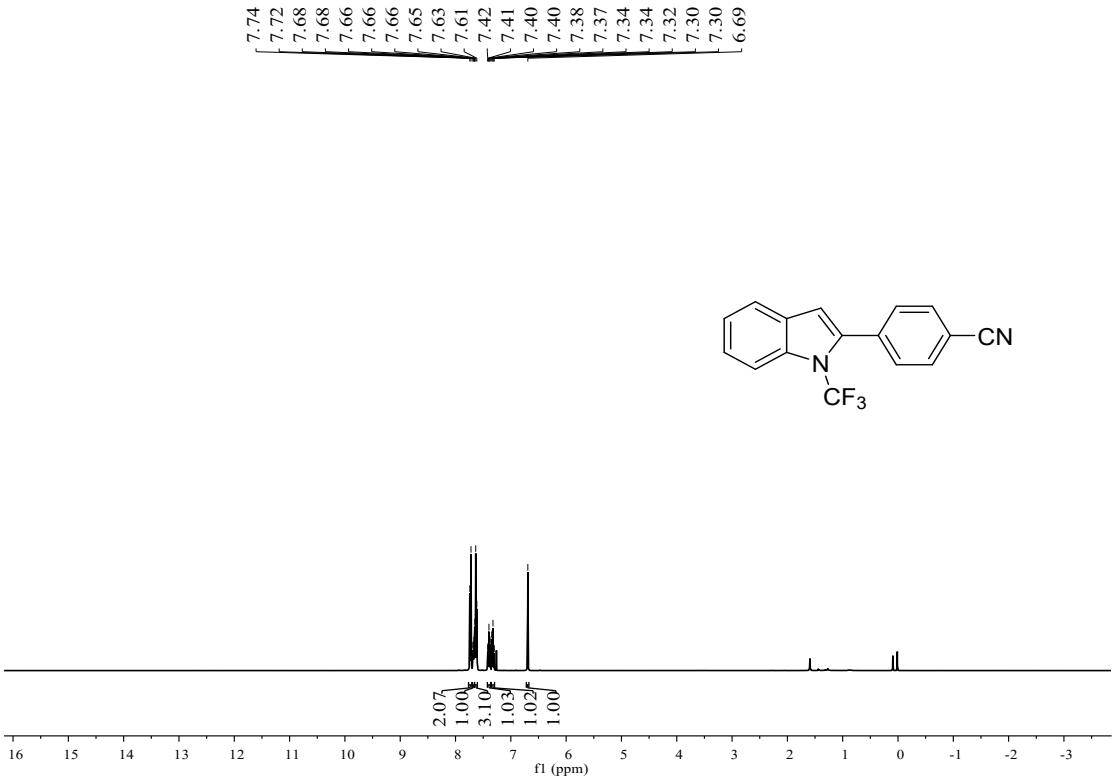
^{19}F NMR Spectrum of **3as** (376 MHz, $CDCl_3$)



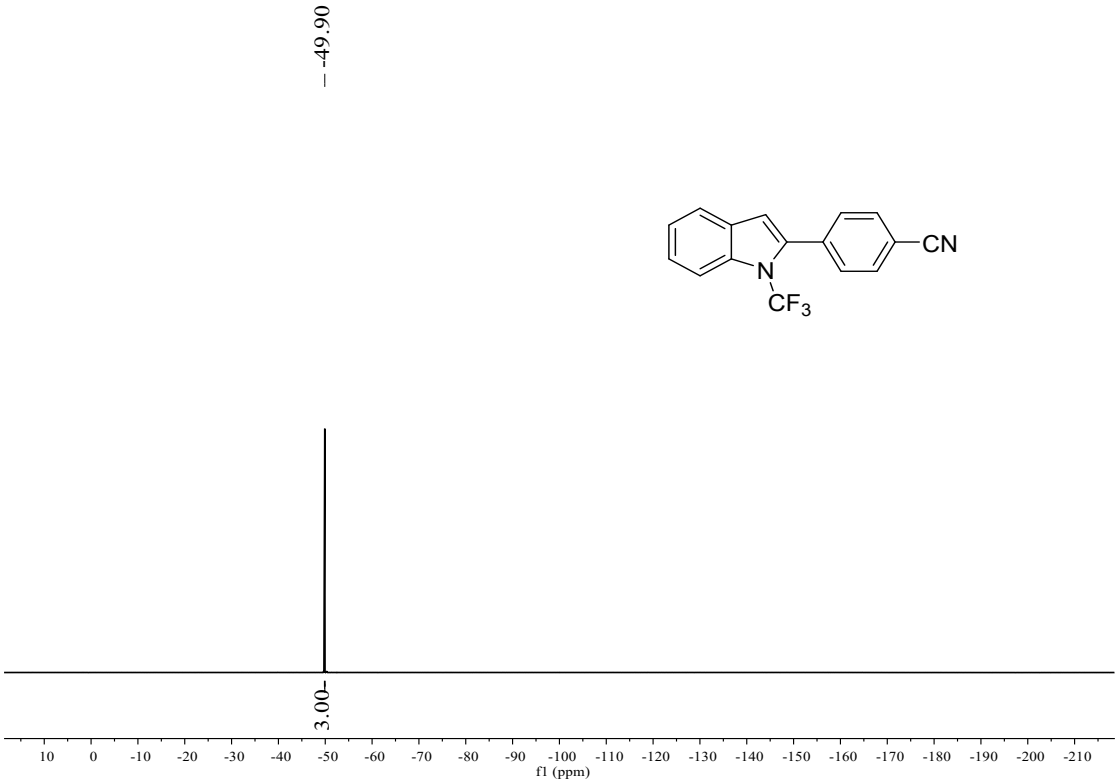
^{13}C NMR Spectrum of **3as** (101 MHz, $CDCl_3$)



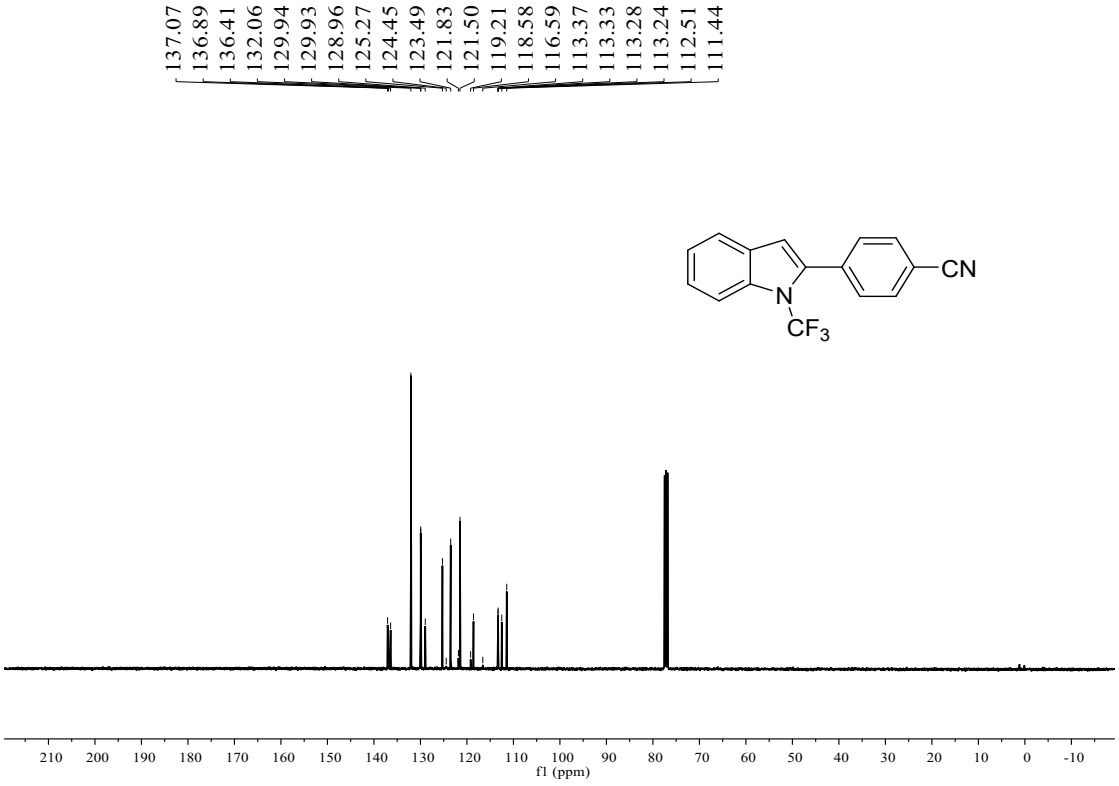
^{1}H NMR Spectrum of **3at** (400 MHz, $CDCl_3$)



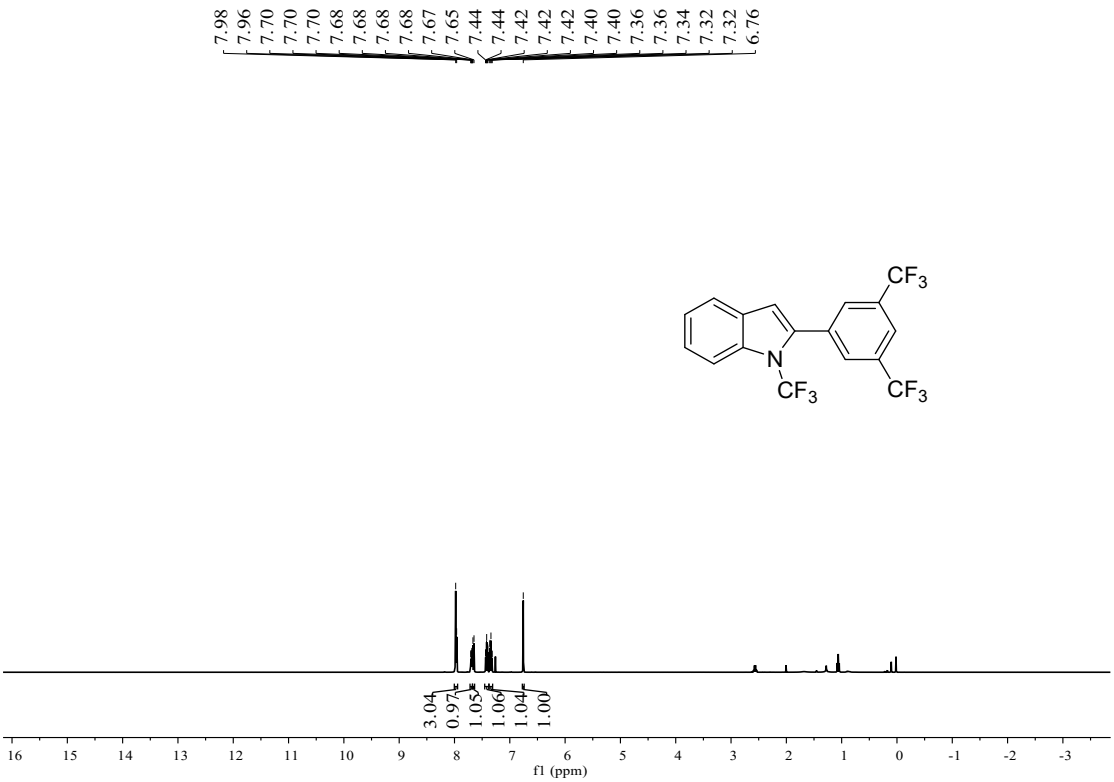
^{19}F NMR Spectrum of **3at** (376 MHz, $CDCl_3$)



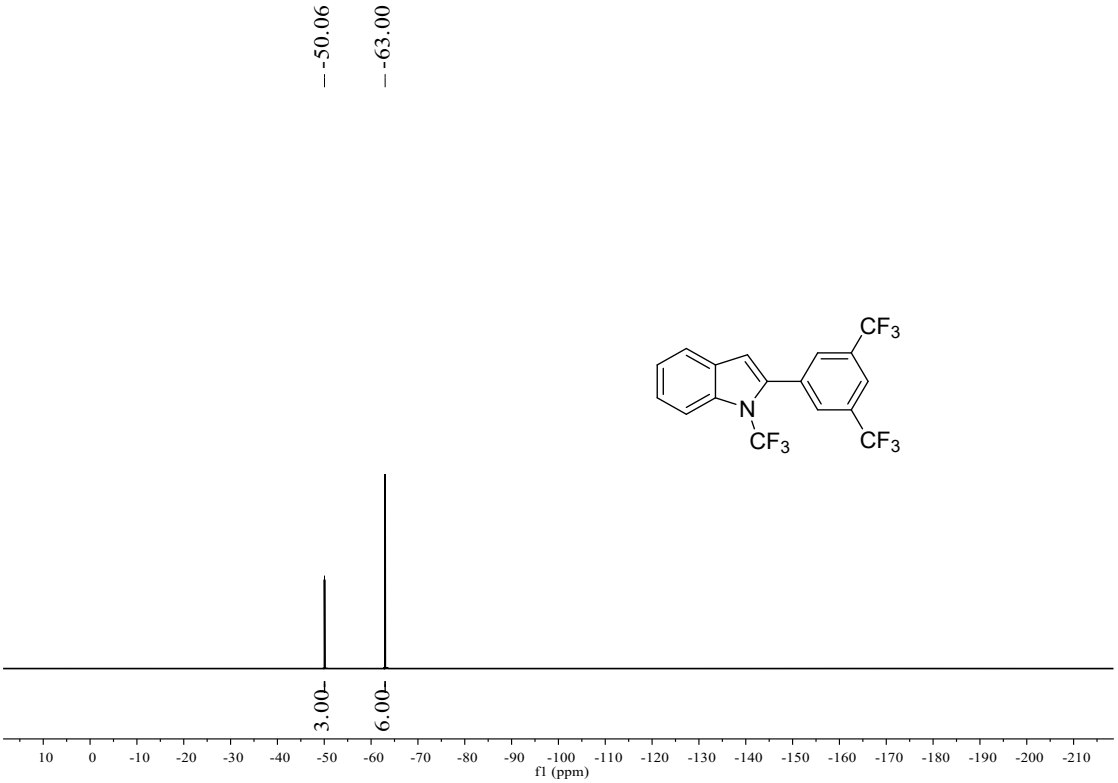
^{13}C NMR Spectrum of **3at** (101 MHz, $CDCl_3$)



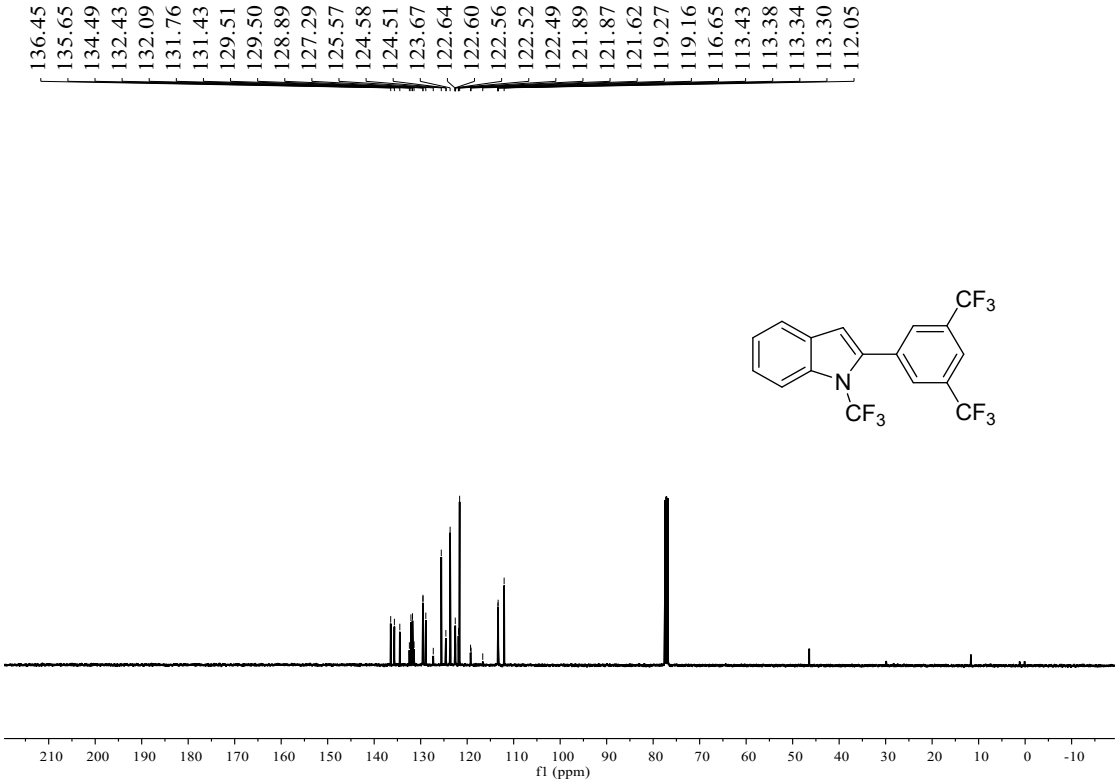
^{1}H NMR Spectrum of **3au** (400 MHz, $CDCl_3$)



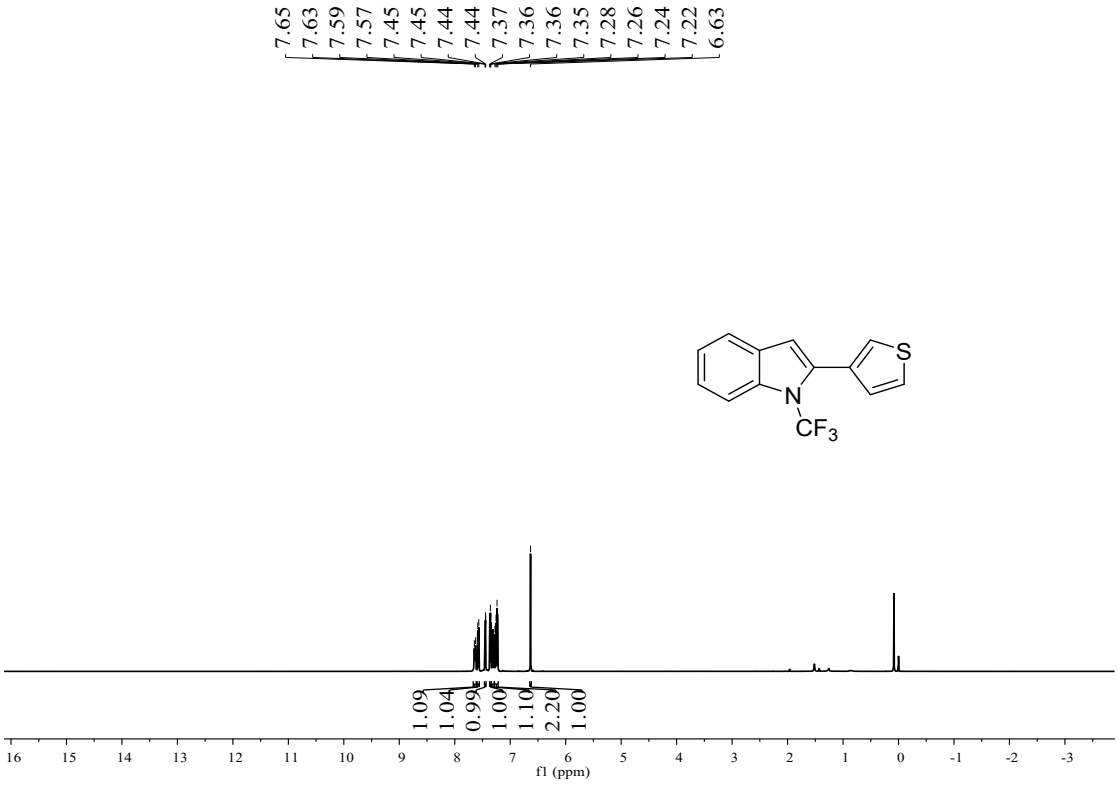
^{19}F NMR Spectrum of **3au** (376 MHz, $CDCl_3$)



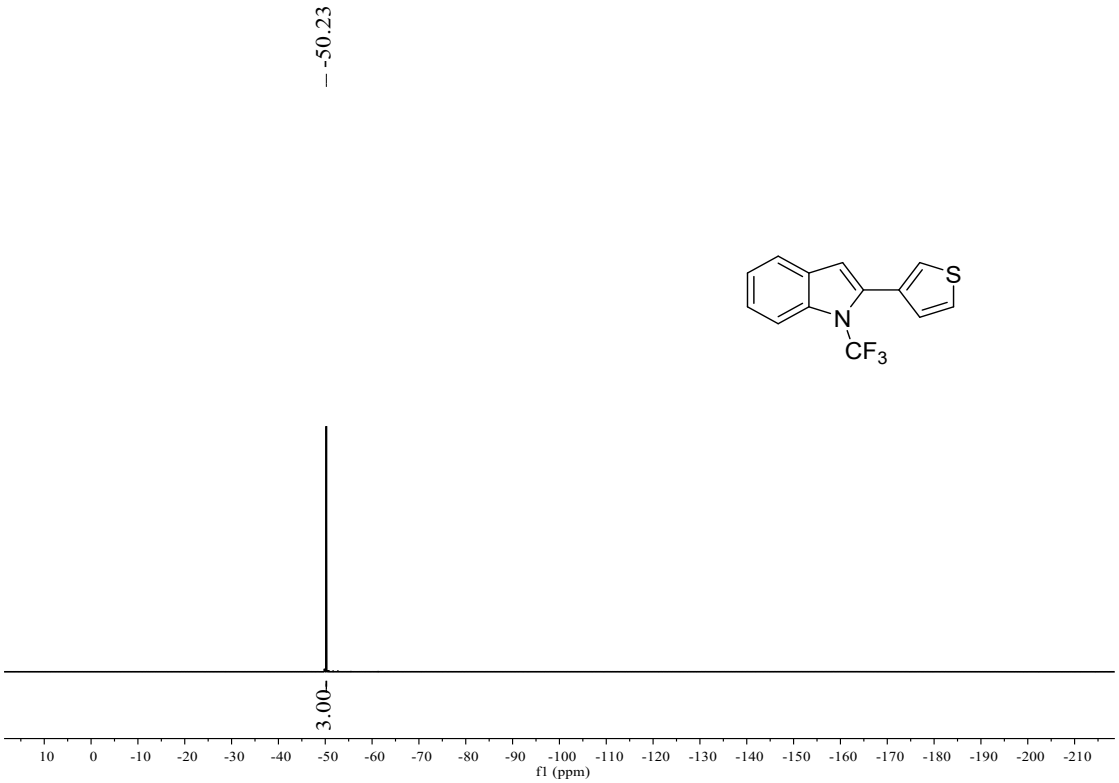
^{13}C NMR Spectrum of **3au** (101 MHz, $CDCl_3$)



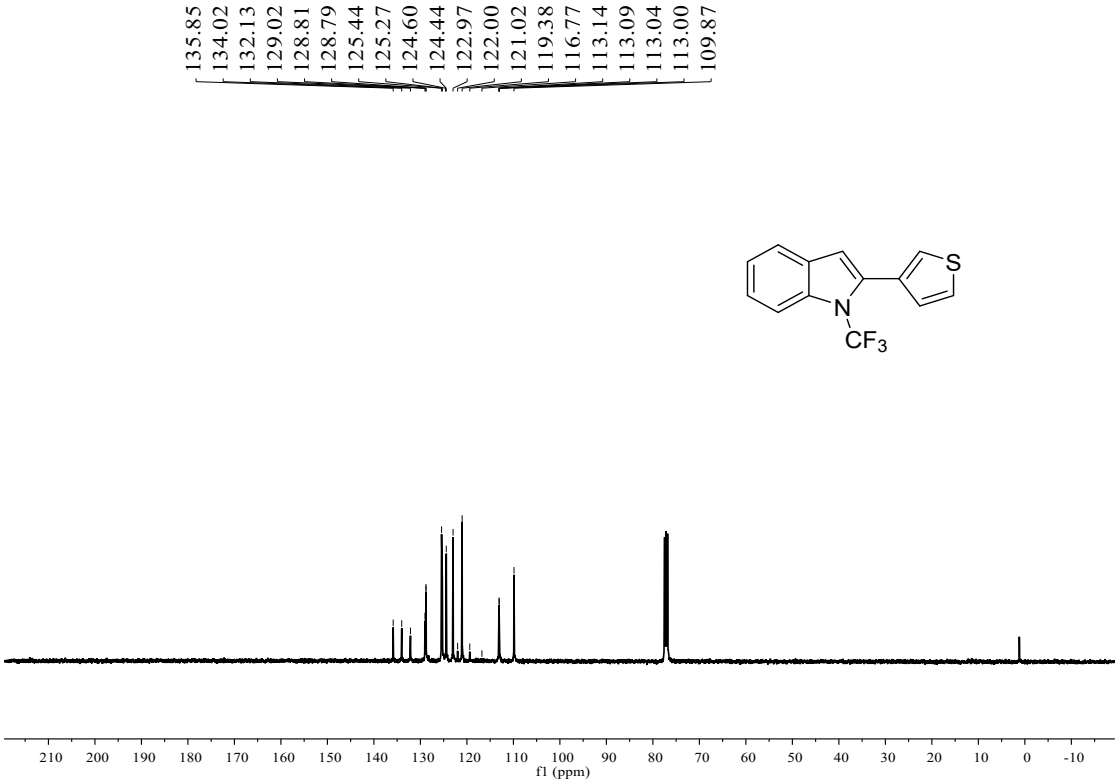
^{1}H NMR Spectrum of **3av** (400 MHz, $CDCl_3$)



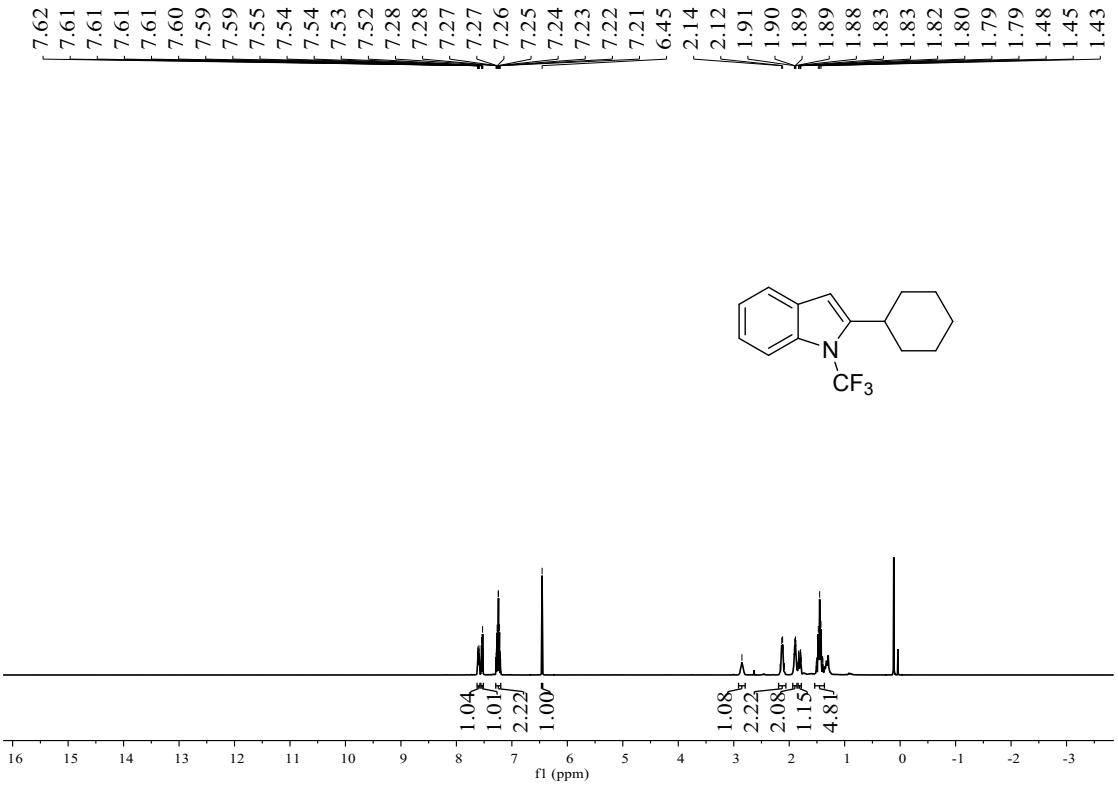
^{19}F NMR Spectrum of **3av** (376 MHz, $CDCl_3$)



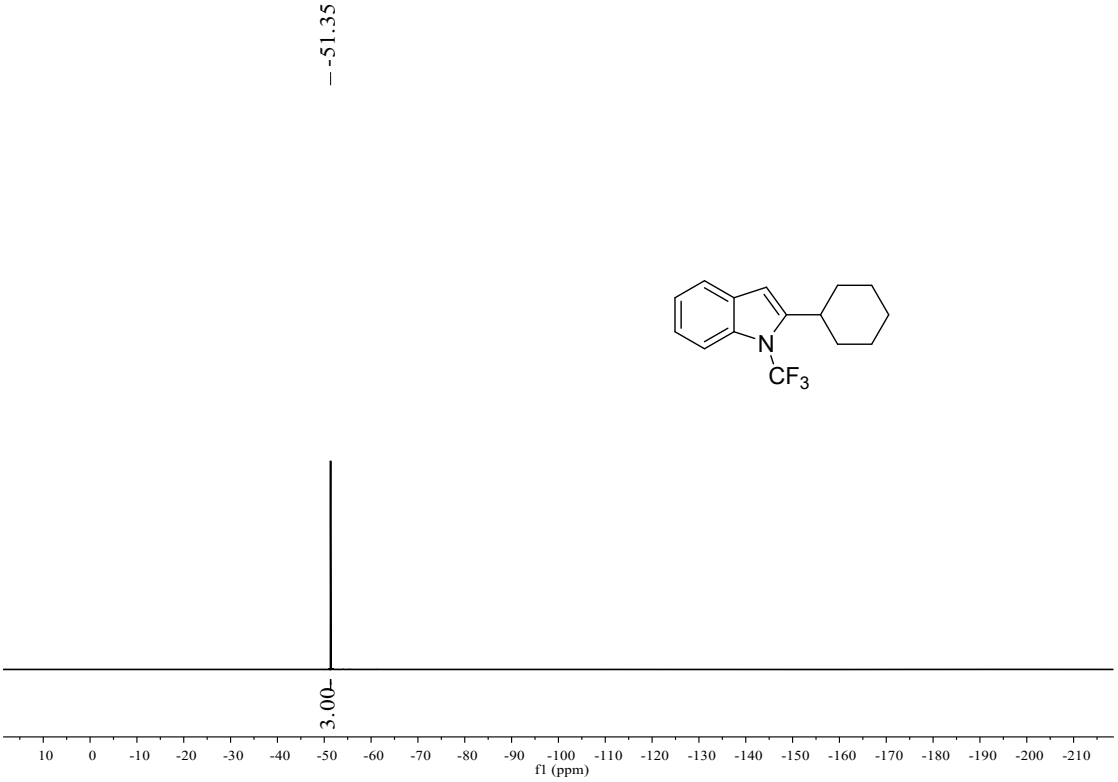
^{13}C NMR Spectrum of **3av** (101 MHz, $CDCl_3$)



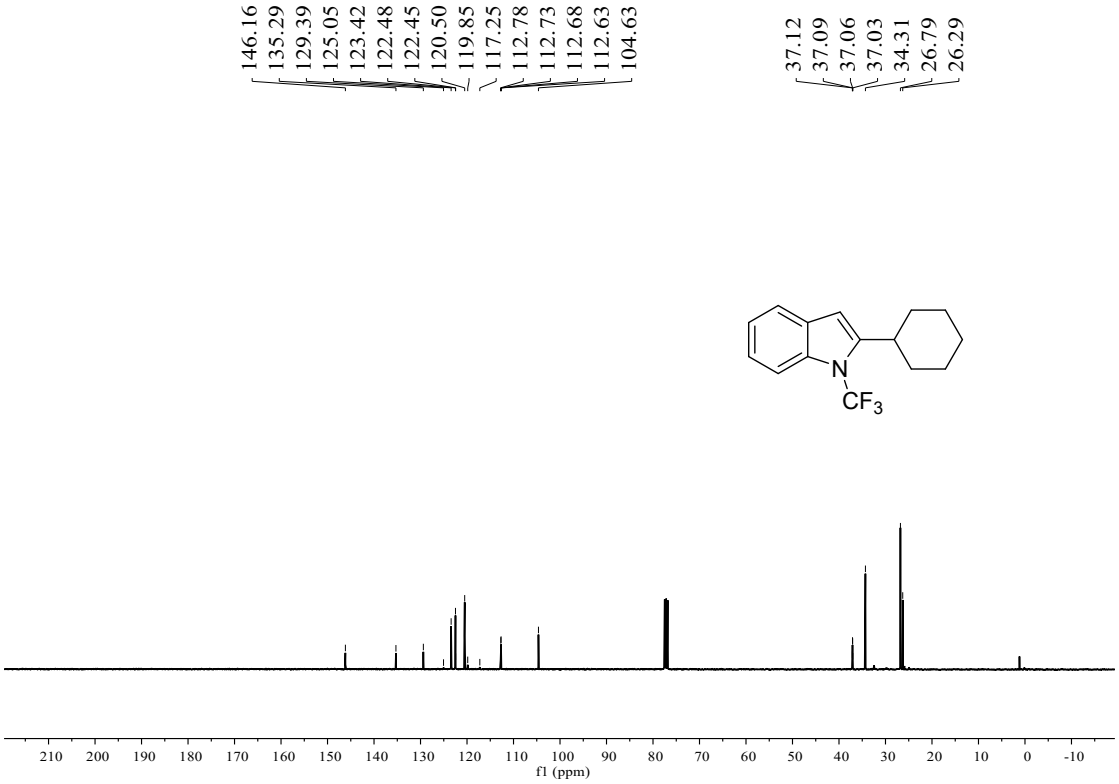
^{1}H NMR Spectrum of **3aw** (400 MHz, $CDCl_3$)



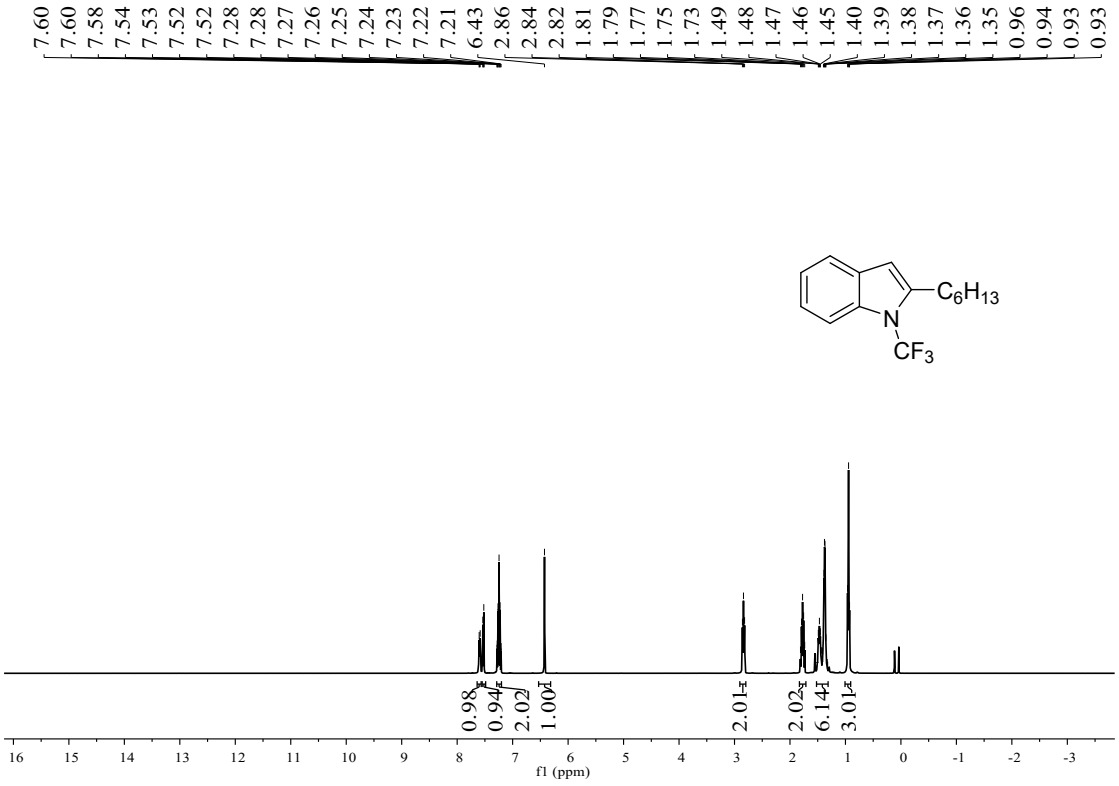
^{19}F NMR Spectrum of **3aw** (376 MHz, $CDCl_3$)



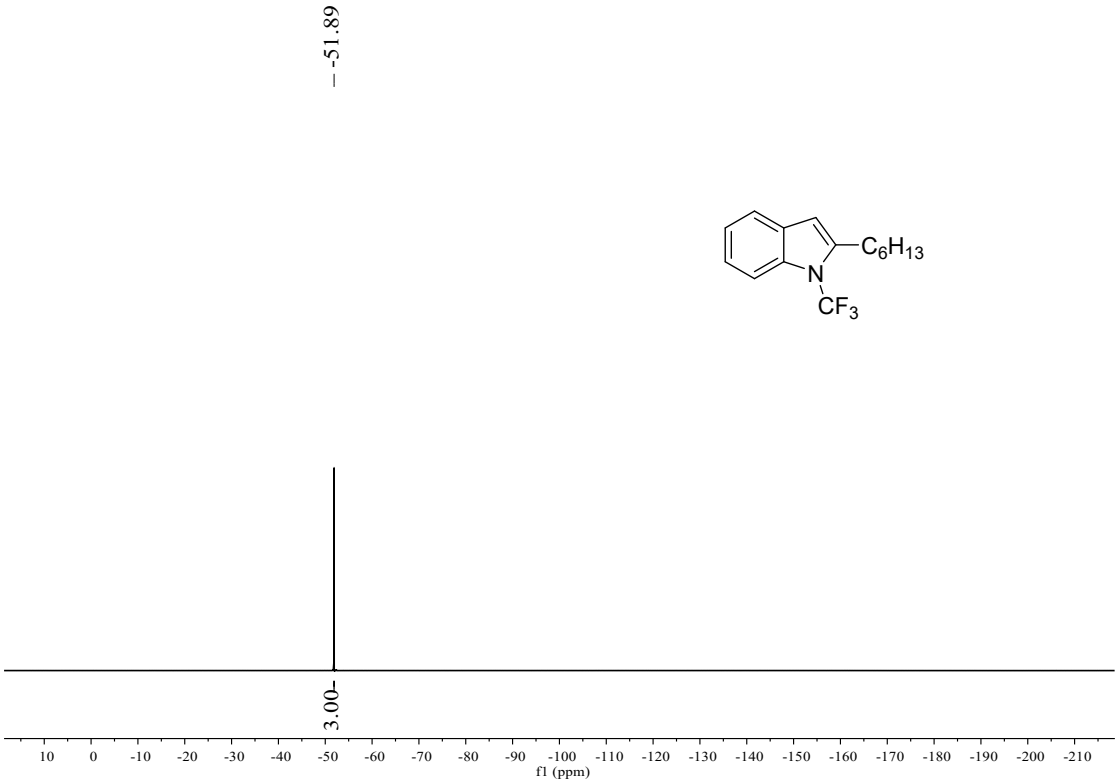
^{13}C NMR Spectrum of **3aw** (101 MHz, $CDCl_3$)



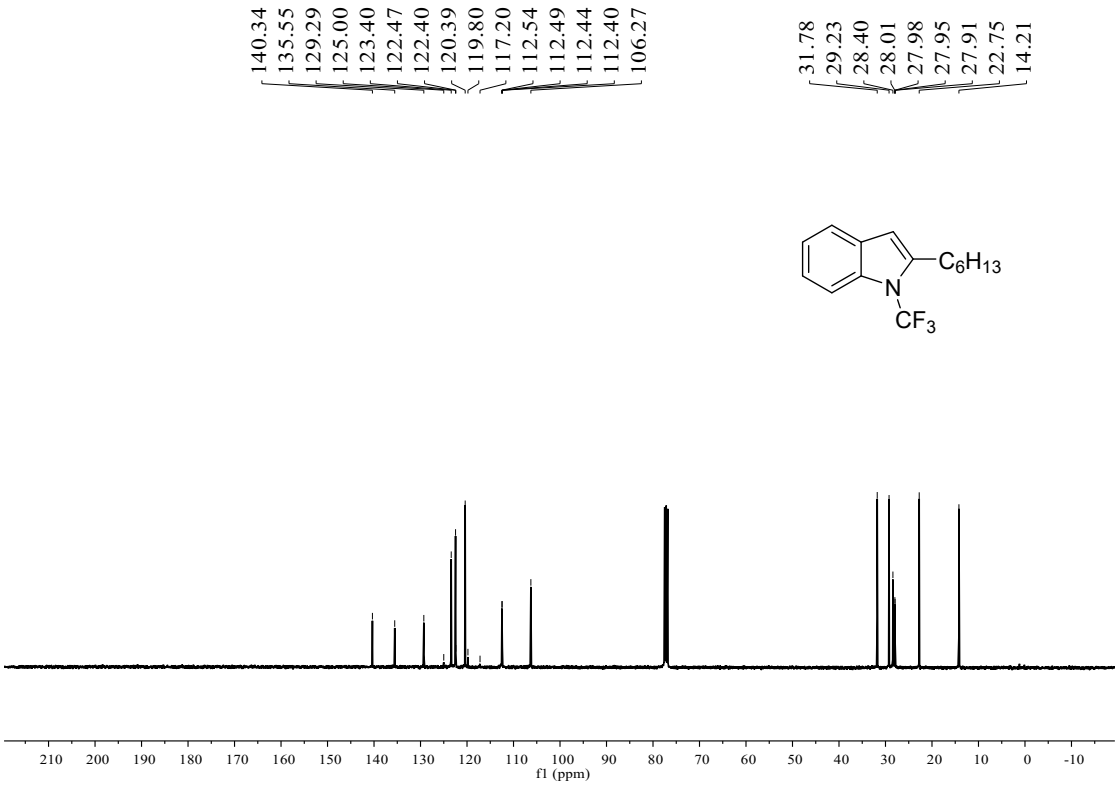
^{1}H NMR Spectrum of **3ax** (400 MHz, $CDCl_3$)



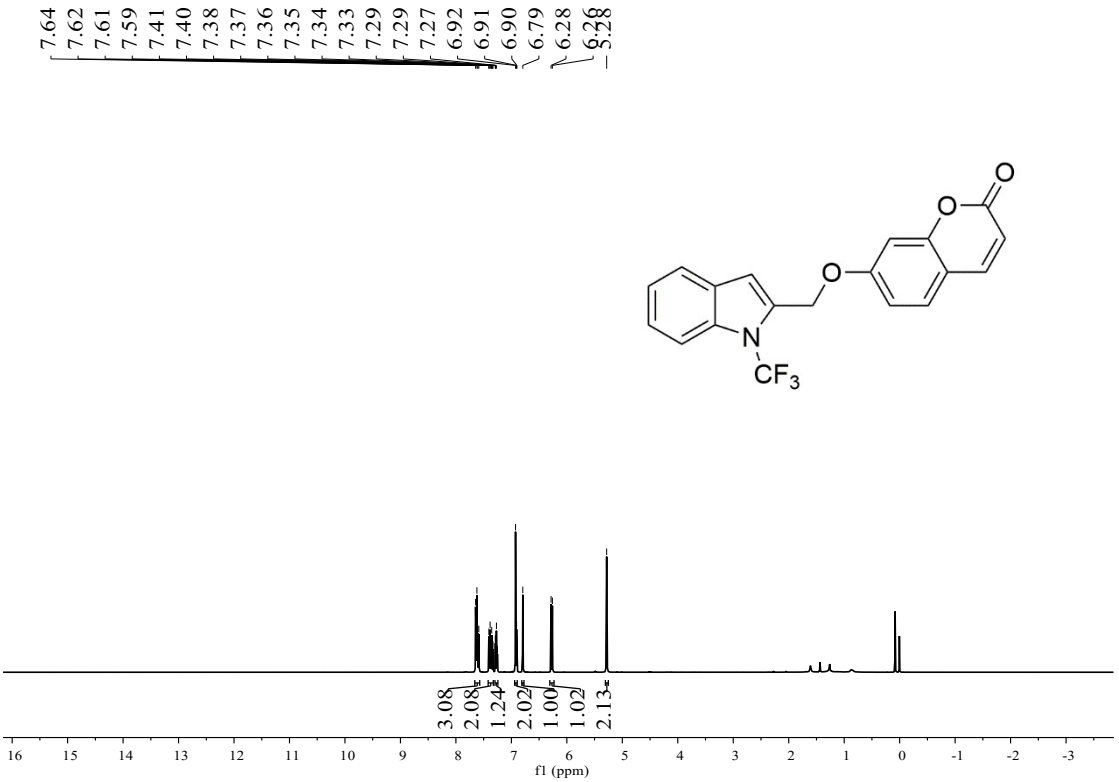
^{19}F NMR Spectrum of **3ax** (376 MHz, $CDCl_3$)



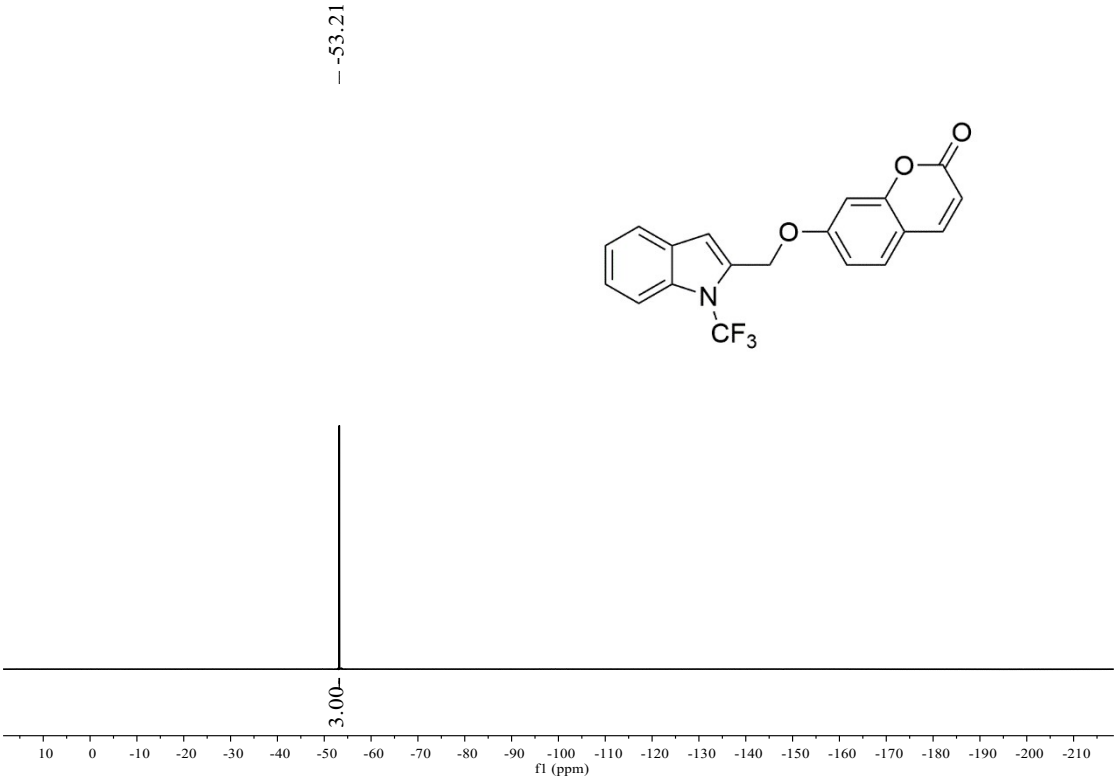
^{13}C NMR Spectrum of **3ax** (101 MHz, $CDCl_3$)



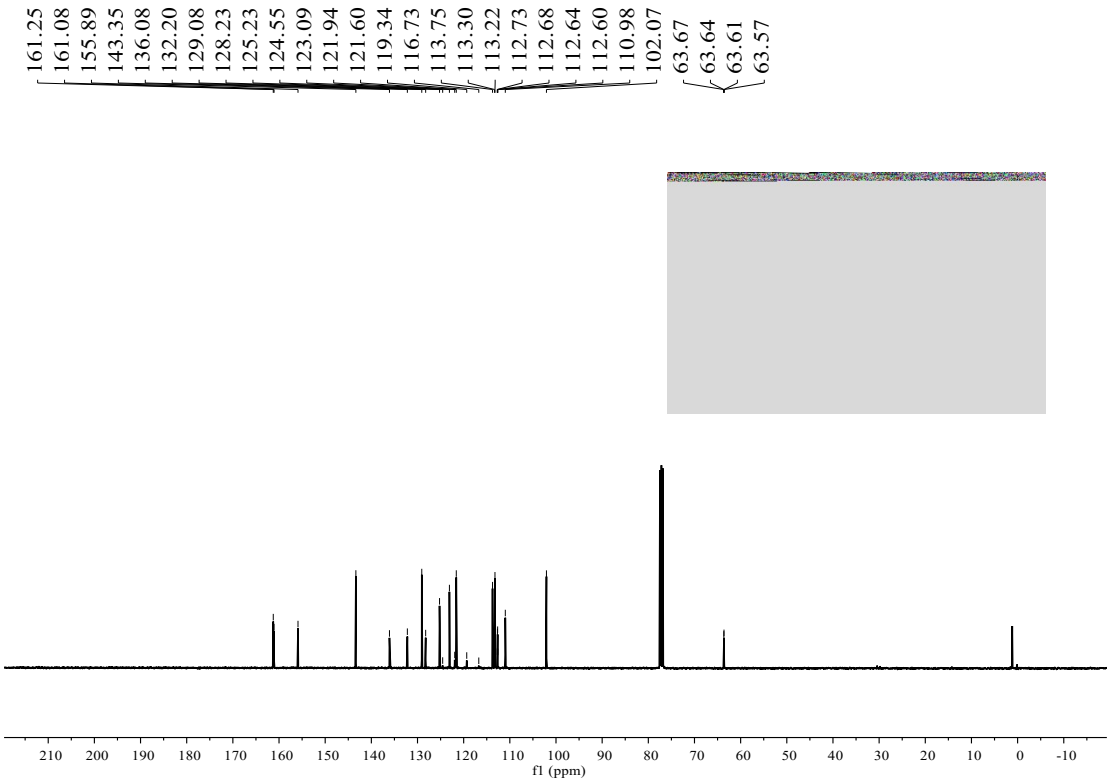
^{1}H NMR Spectrum of **3ay** (400 MHz, $CDCl_3$)



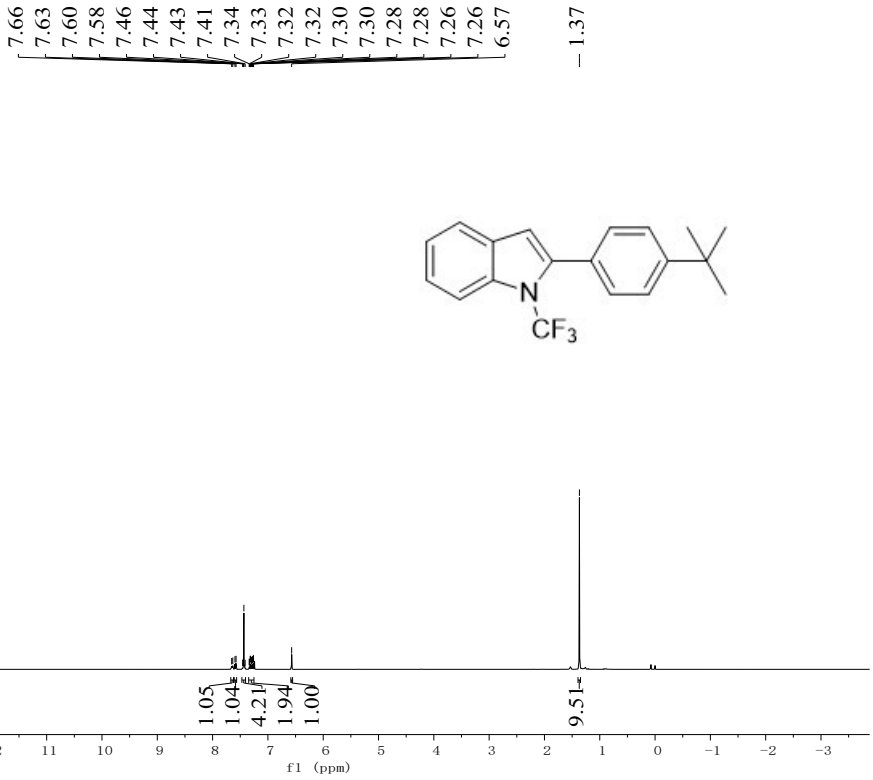
^{19}F NMR Spectrum of **3ay** (376 MHz, $CDCl_3$)



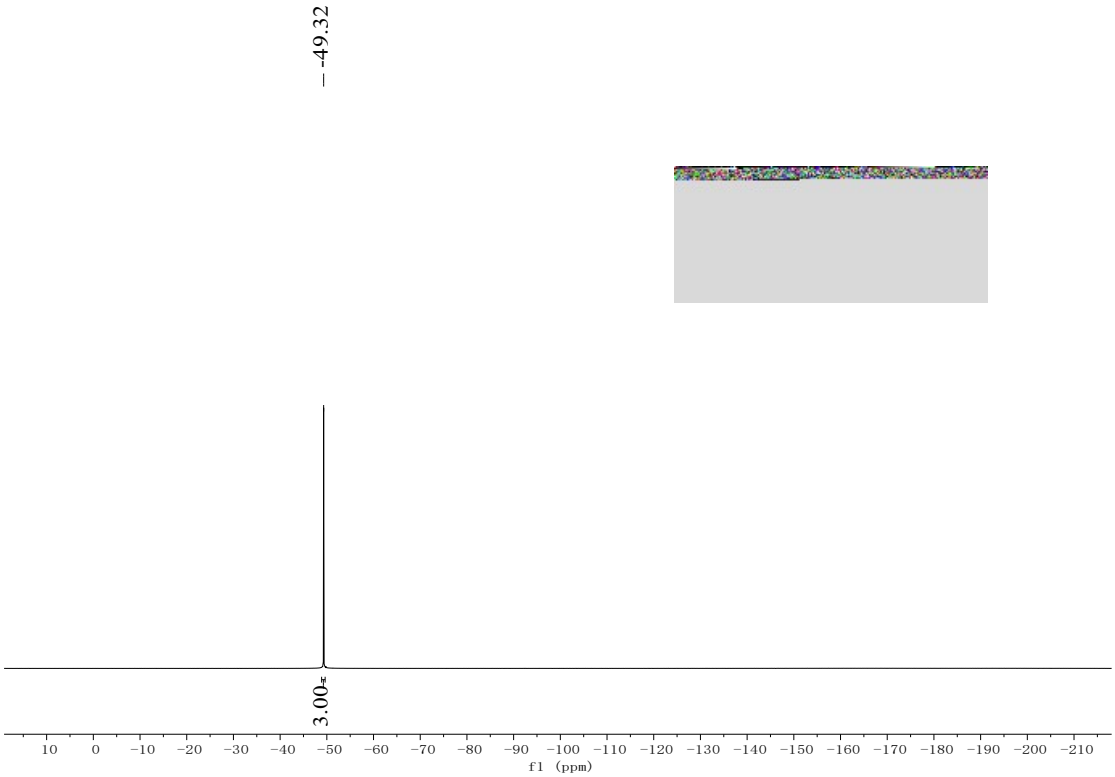
^{13}C NMR Spectrum of **3ay** (101 MHz, $CDCl_3$)



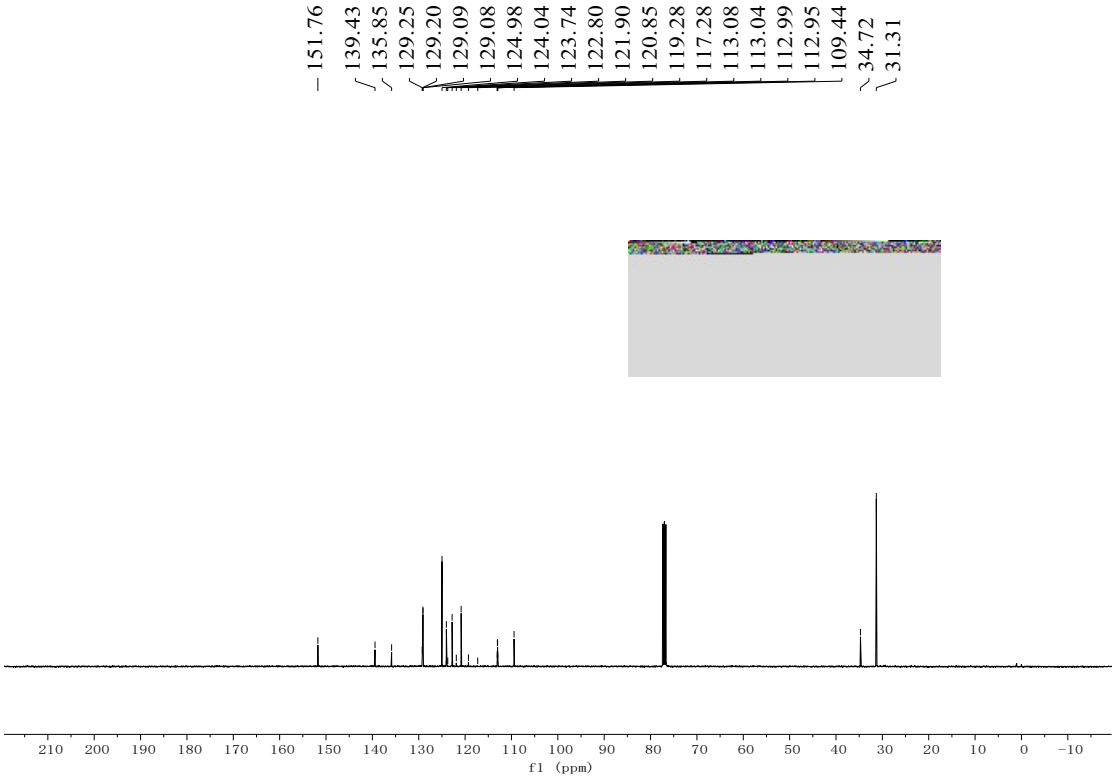
^{1}H NMR Spectrum of **3az** (400 MHz, $CDCl_3$)



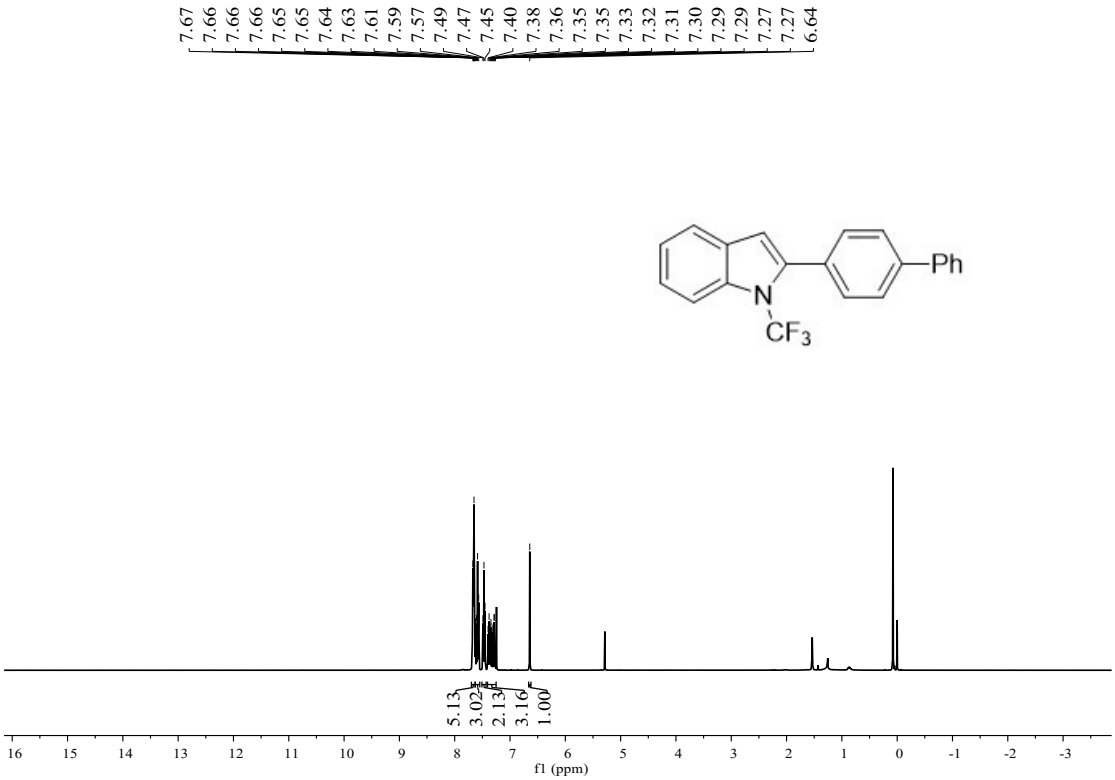
^{19}F NMR Spectrum of **3az** (376 MHz, $CDCl_3$)



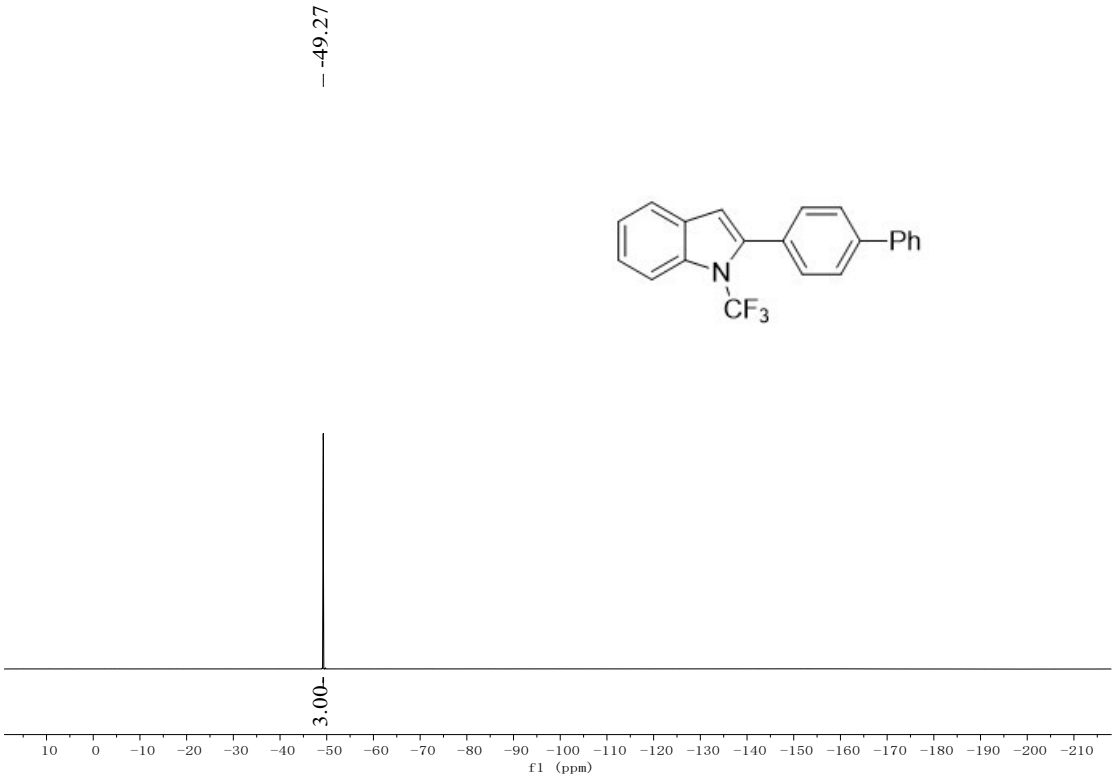
^{13}C NMR Spectrum of **3az** (101 MHz, $CDCl_3$)



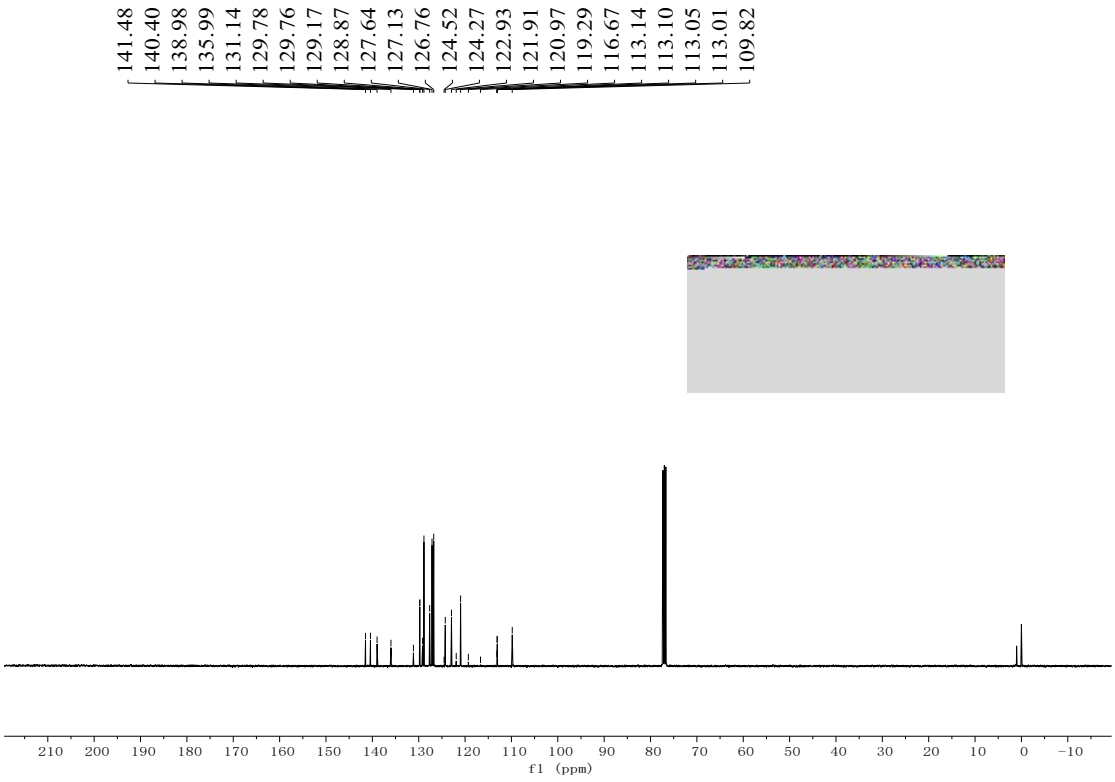
^{1}H NMR Spectrum of **3aa′** (400 MHz, $CDCl_3$)



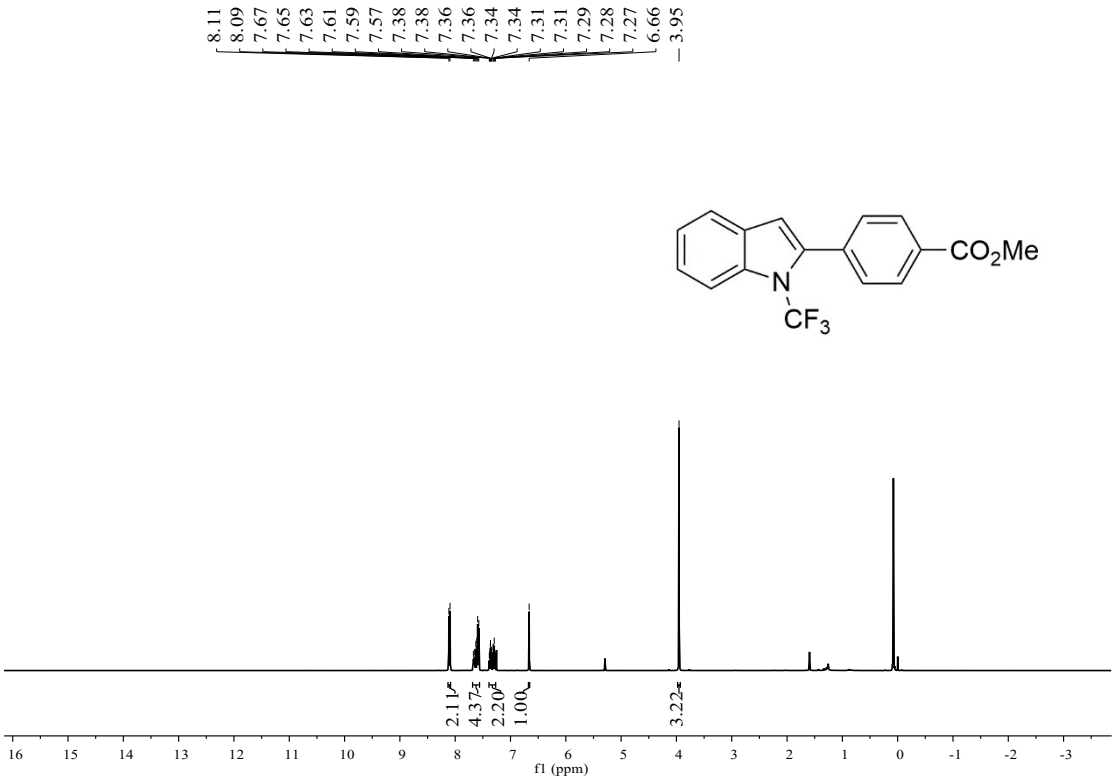
^{19}F NMR Spectrum of **3aa′** (376 MHz, $CDCl_3$)



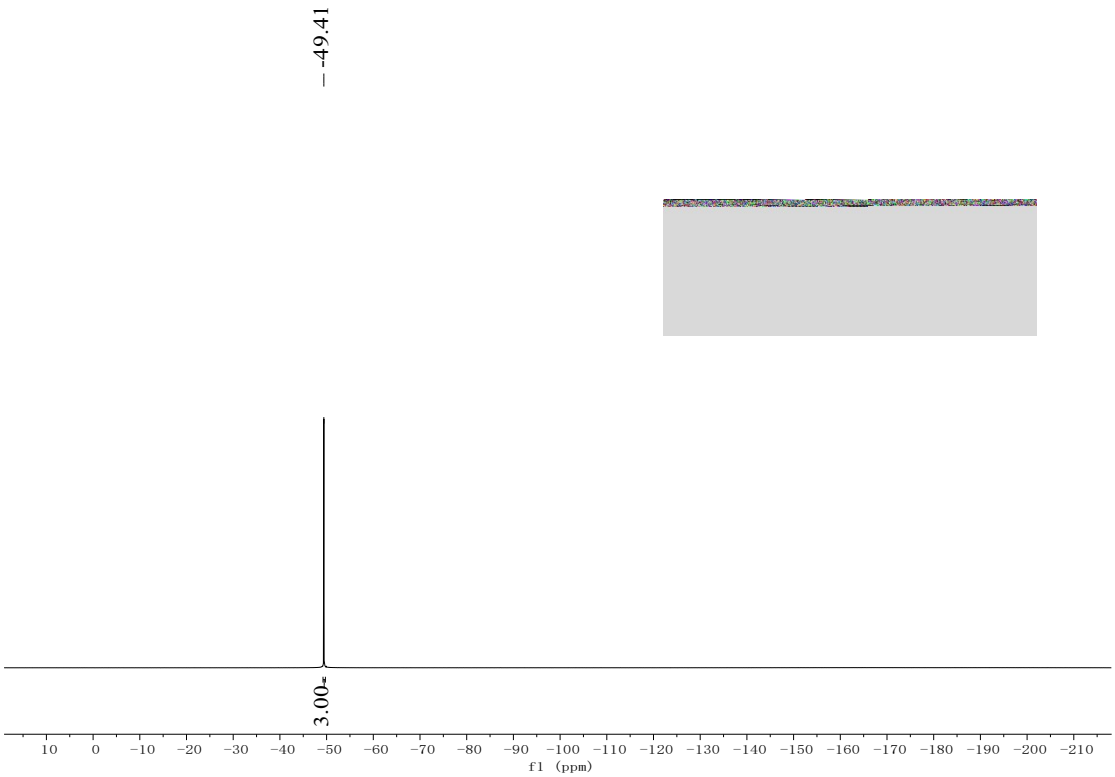
^{13}C NMR Spectrum of **3aa′** (101 MHz, $CDCl_3$)



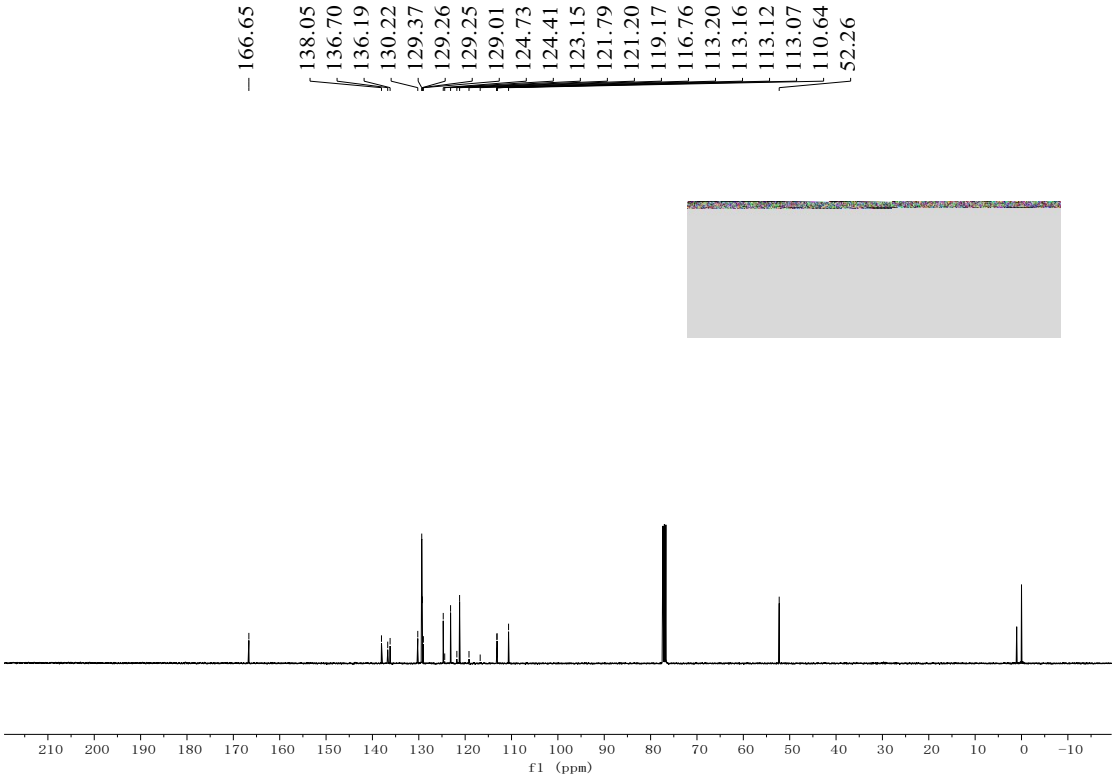
^{1}H NMR Spectrum of **3ab′** (400 MHz, $CDCl_3$)



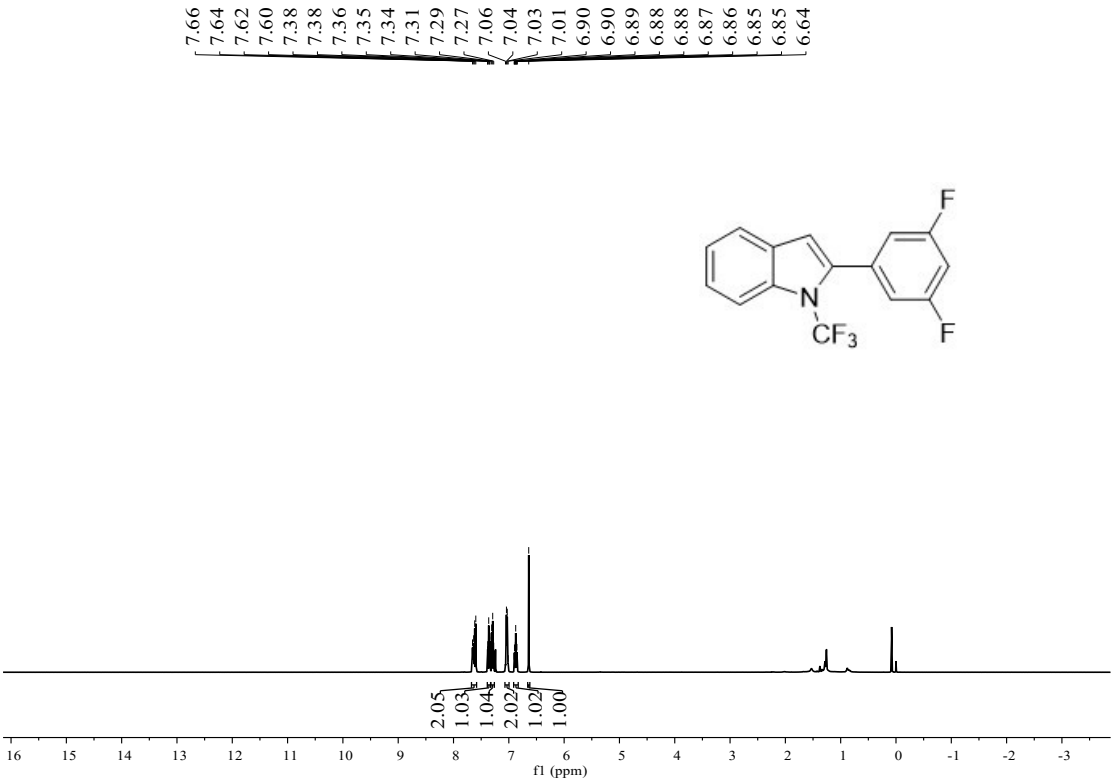
^{19}F NMR Spectrum of **3ab′** (376 MHz, $CDCl_3$)



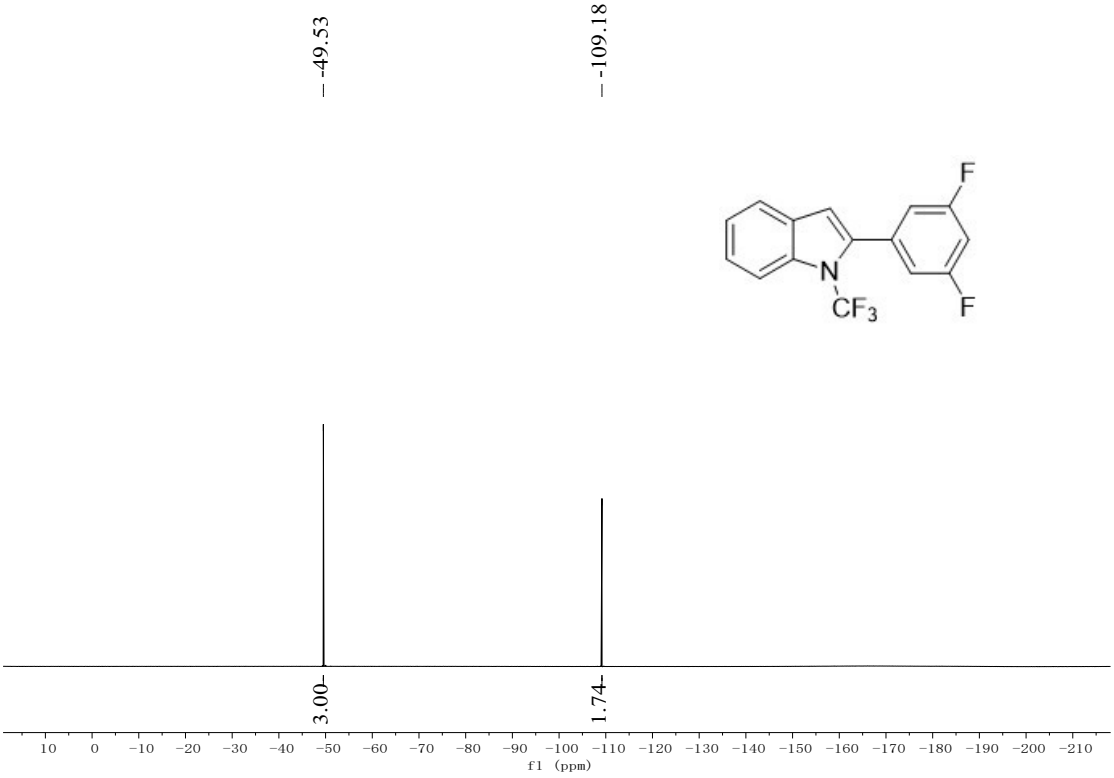
^{13}C NMR Spectrum of **3ab′** (101 MHz, $CDCl_3$)



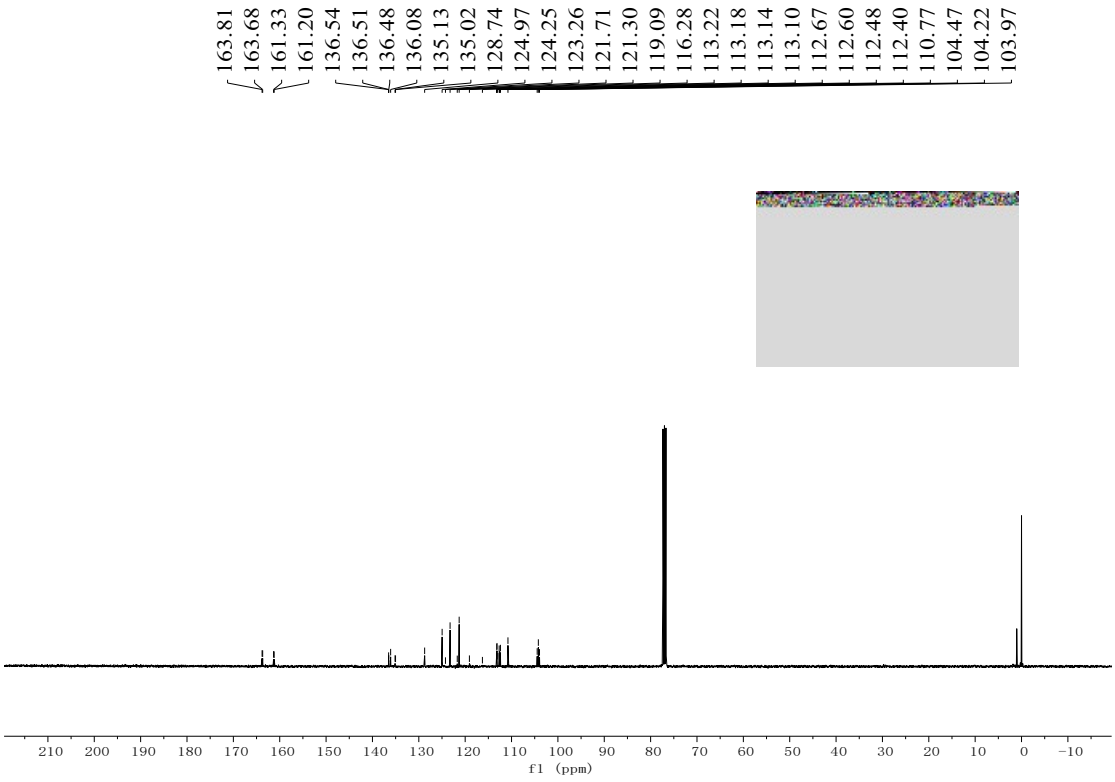
^{1}H NMR Spectrum of **3ac′** (400 MHz, $CDCl_3$)



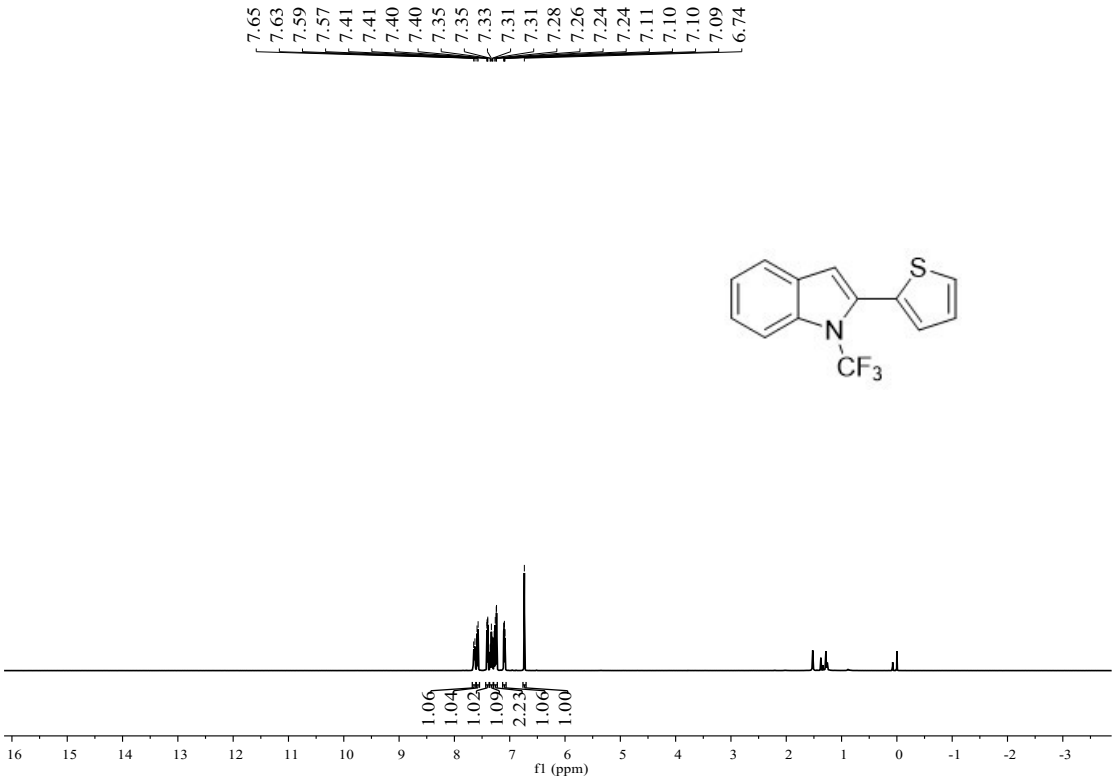
^{19}F NMR Spectrum of **3ac′** (376 MHz, $CDCl_3$)



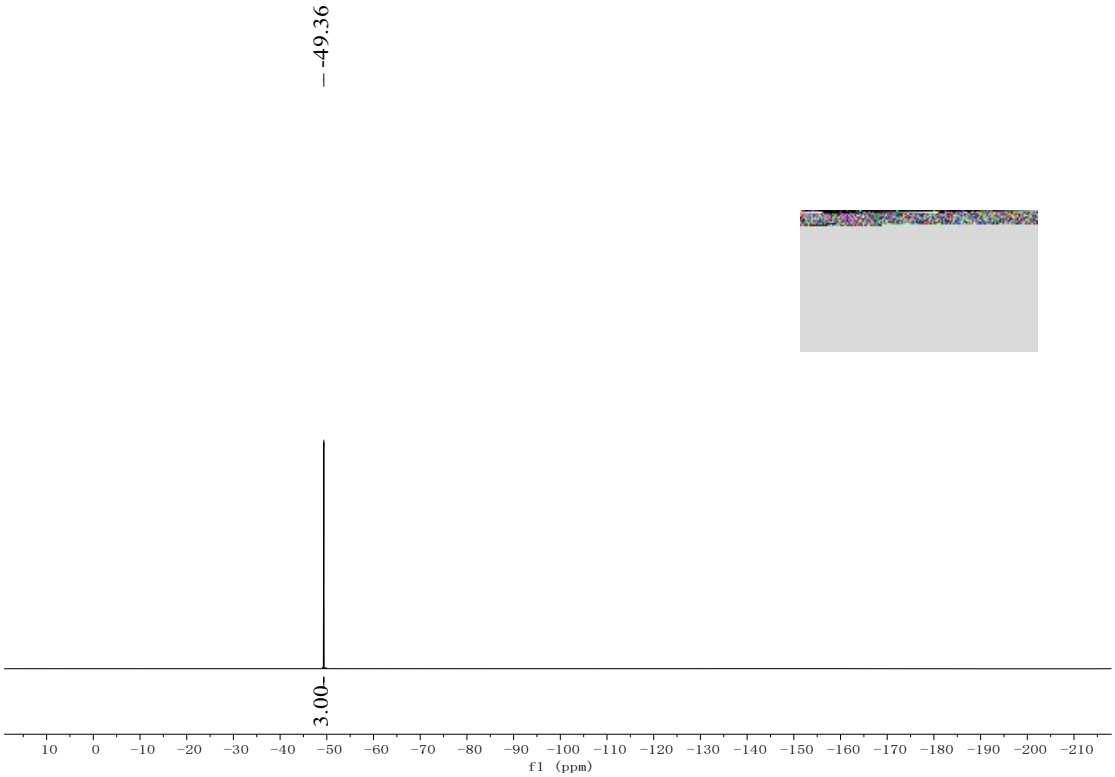
^{13}C NMR Spectrum of **3ac′** (101 MHz, $CDCl_3$)



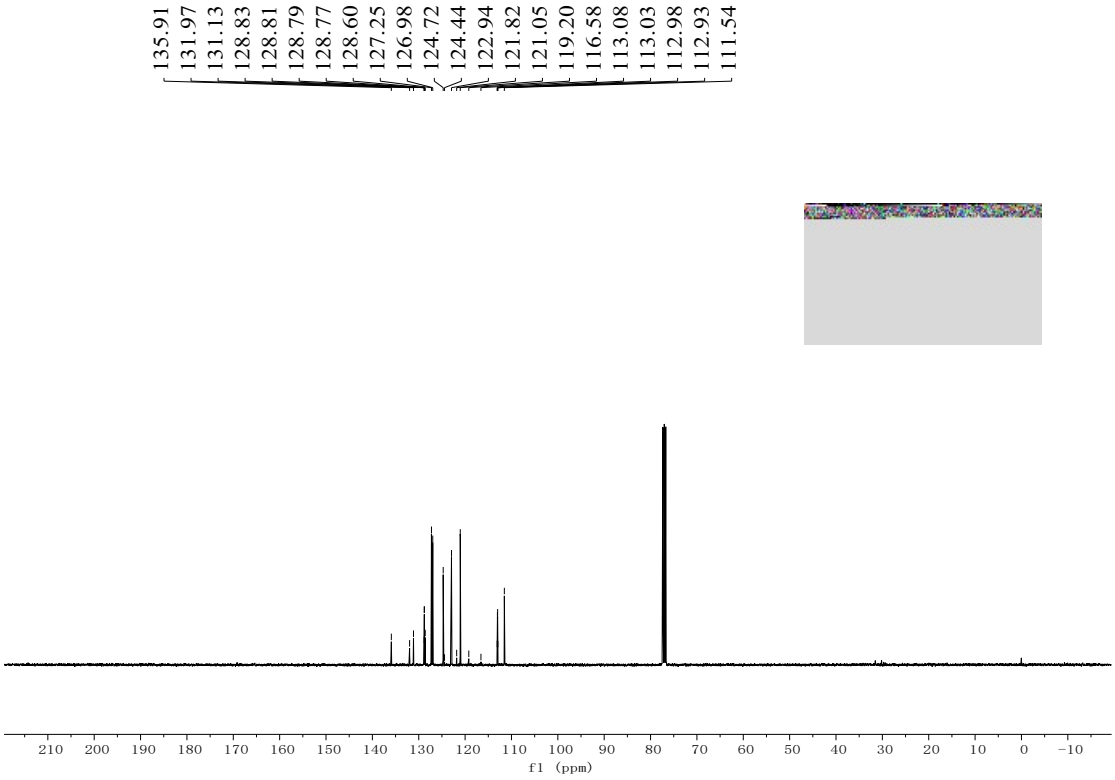
^{1}H NMR Spectrum of **3ad′** (400 MHz, $CDCl_3$)



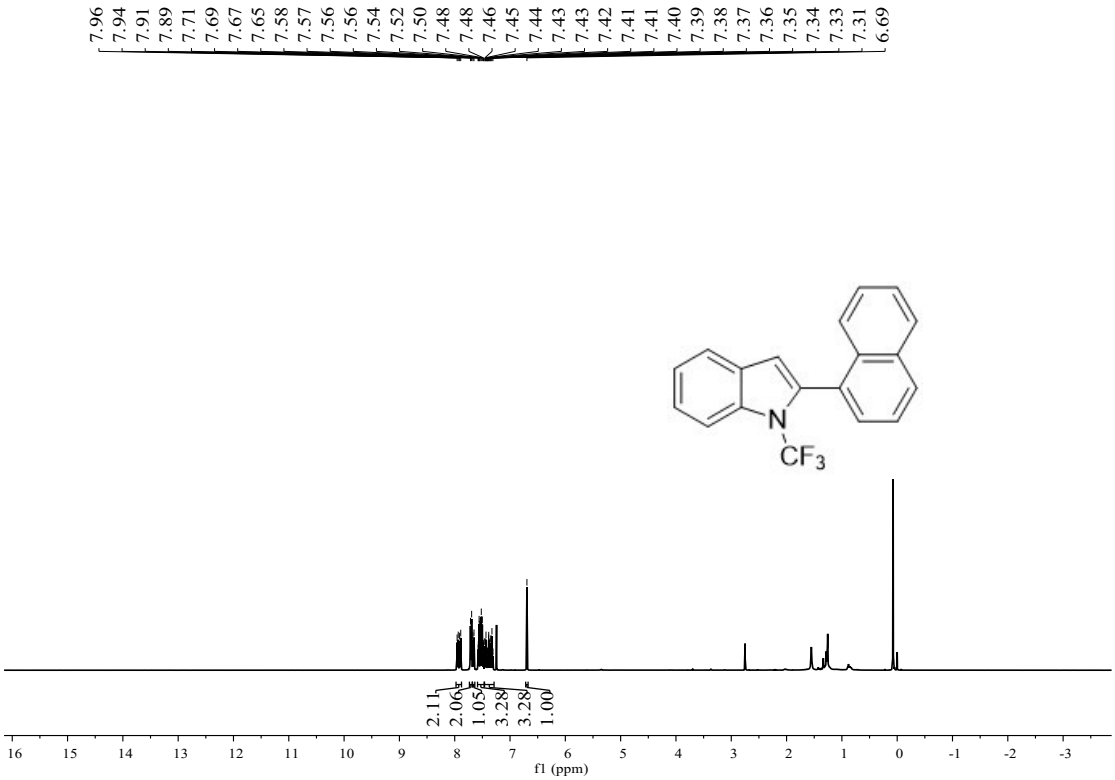
^{19}F NMR Spectrum of **3ad′** (376 MHz, $CDCl_3$)



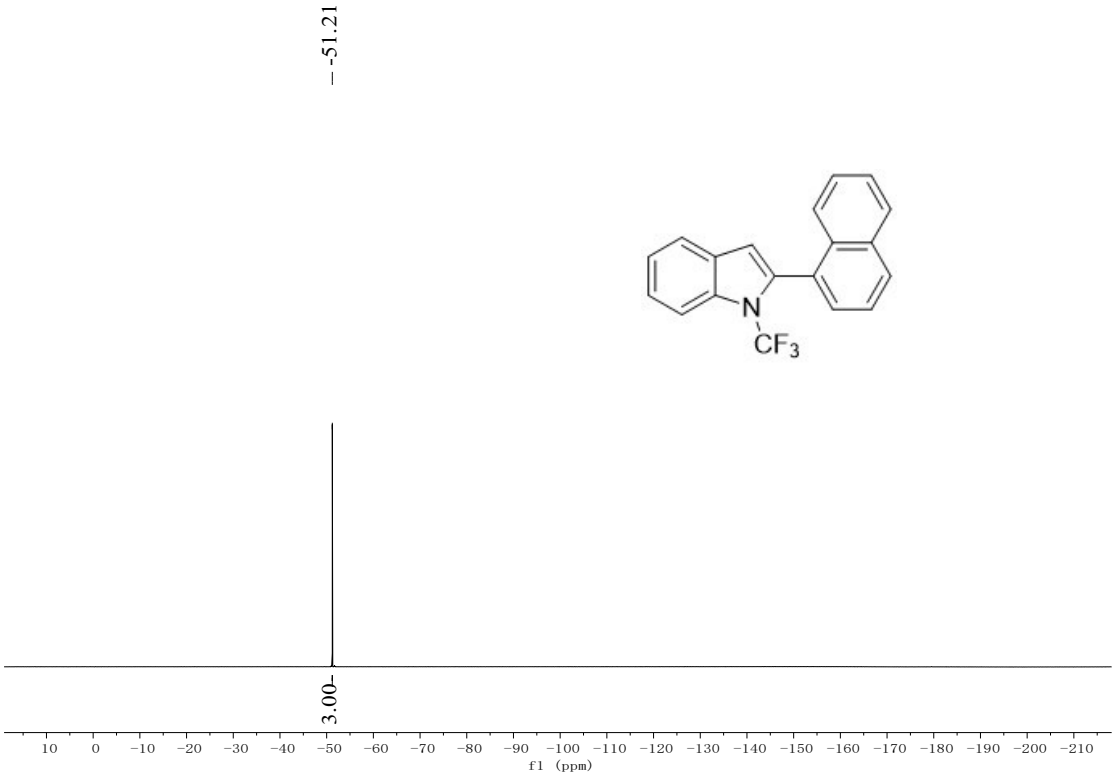
^{13}C NMR Spectrum of **3ad′** (101 MHz, $CDCl_3$)



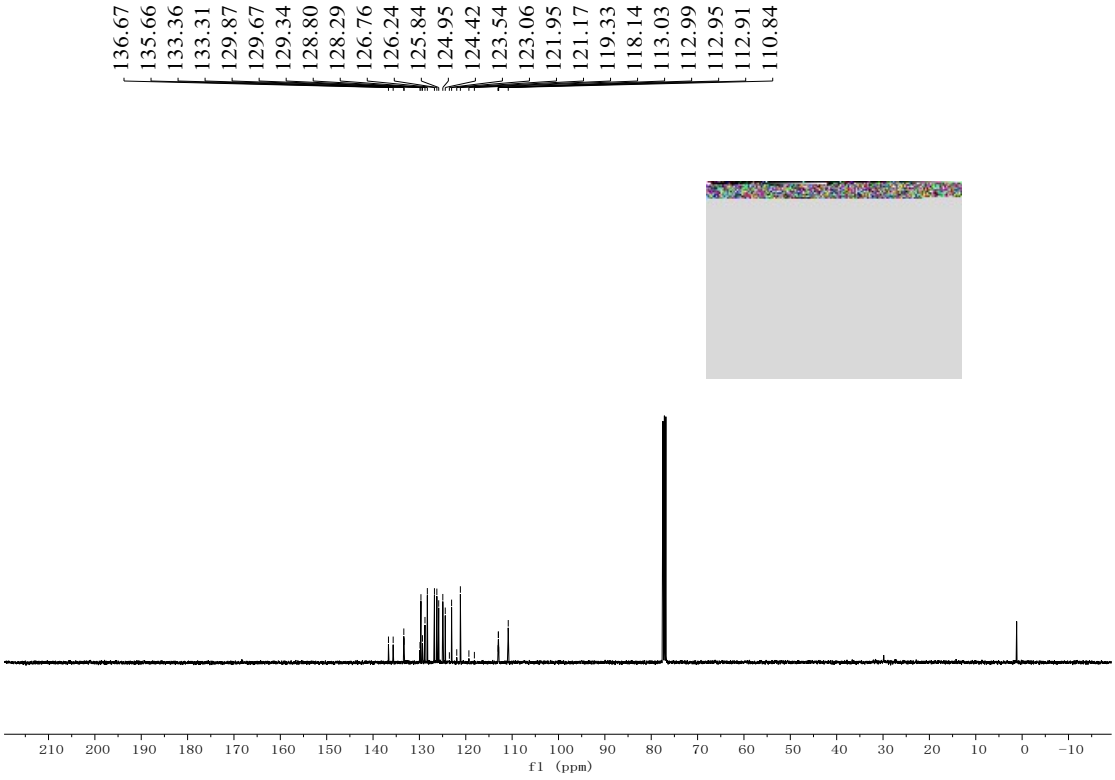
^{1}H NMR Spectrum of **3ae′** (400 MHz, $CDCl_3$)



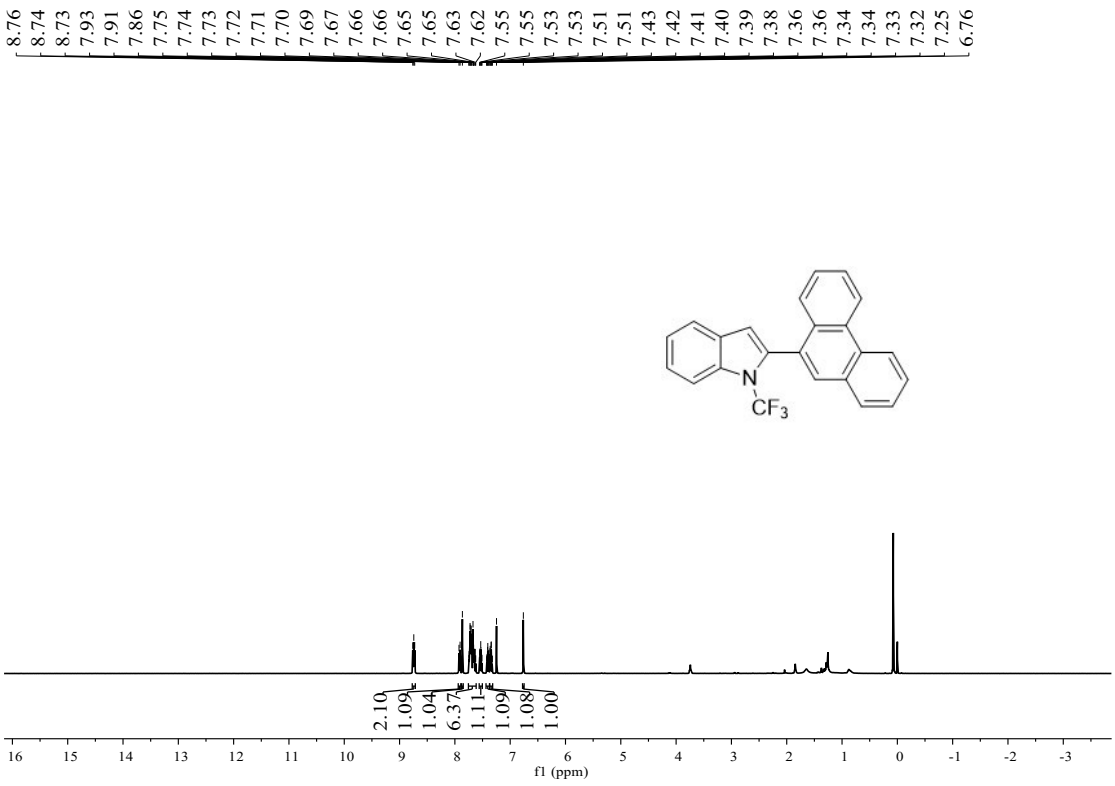
^{19}F NMR Spectrum of **3ae′** (376 MHz, $CDCl_3$)



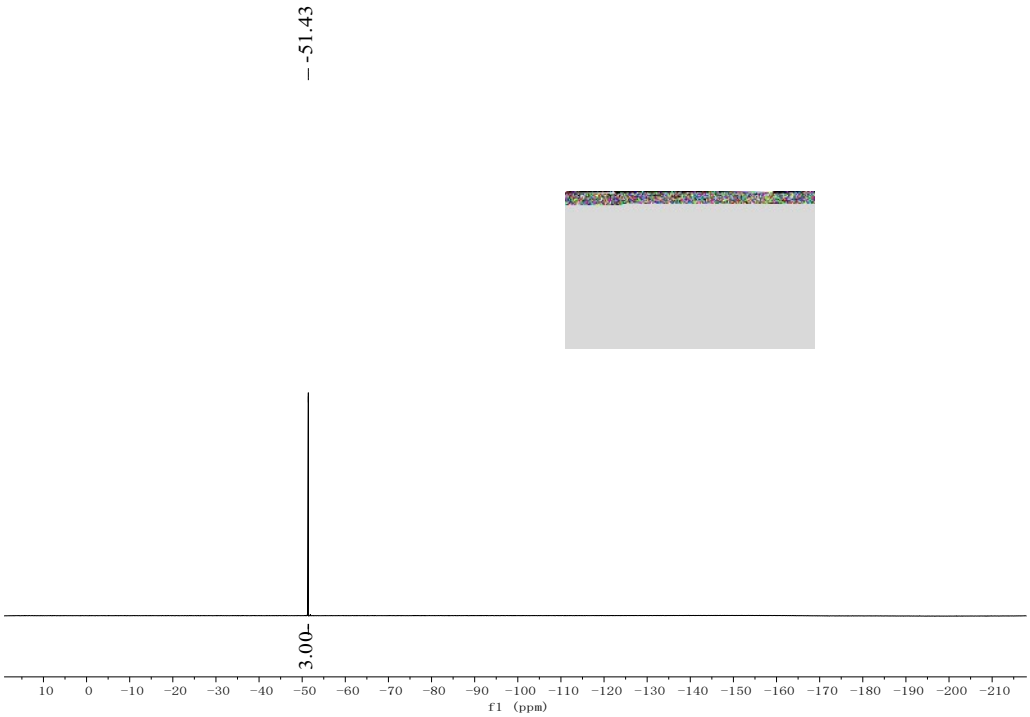
^{13}C NMR Spectrum of **3ae′** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3af′** (400 MHz, $CDCl_3$)

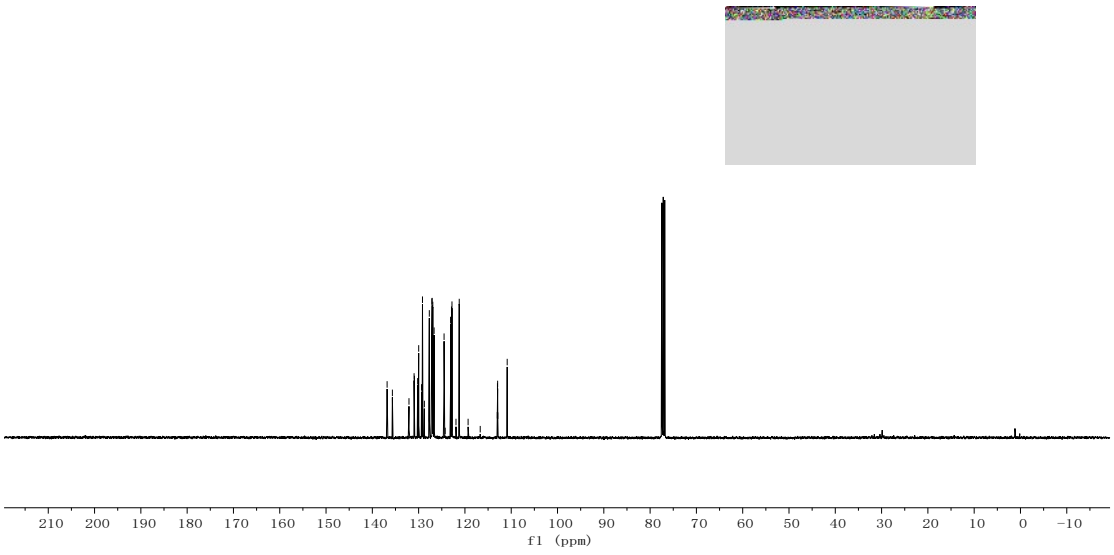


^{19}F NMR Spectrum of **3af′** (376 MHz, $CDCl_3$)

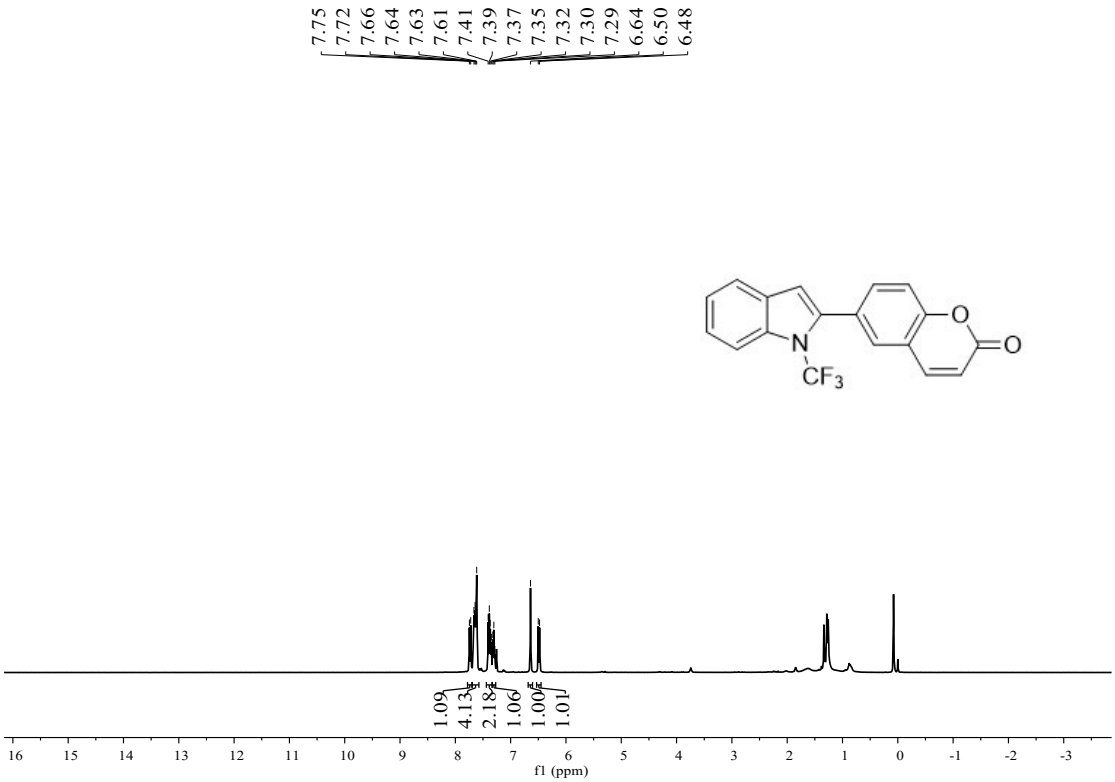


^{13}C NMR Spectrum of **3af′** (101 MHz, $CDCl_3$)

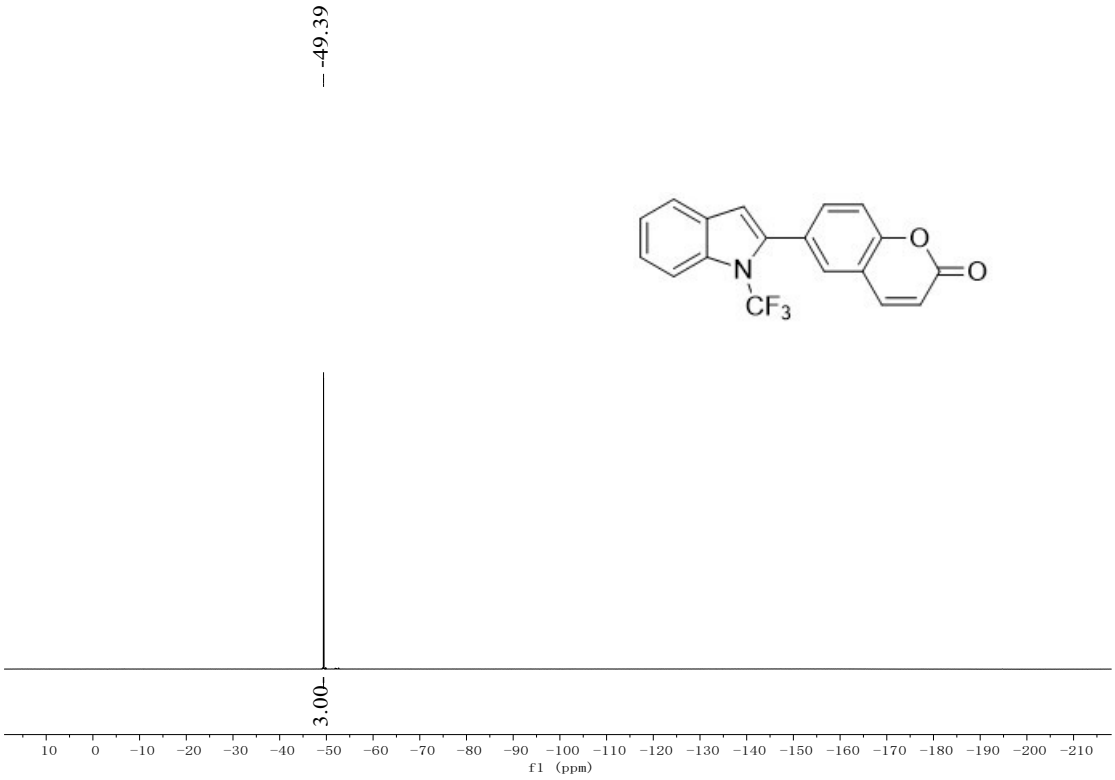
136.81
135.67
132.09
130.98
130.90
130.21
129.99
129.37
129.17
128.76
127.69
127.15
127.08
126.94
126.66
124.50
124.26
123.10
122.90
122.80
121.93
121.23
119.31
116.70
113.01
112.97
112.93
112.90
110.87



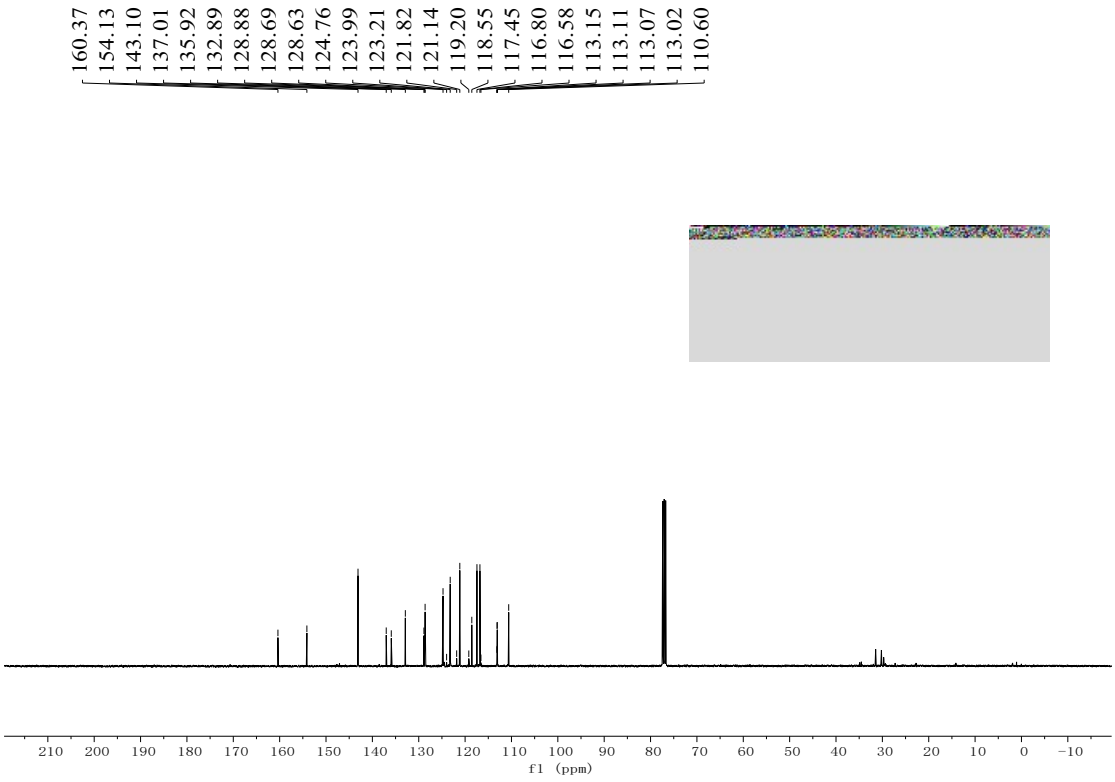
^{1}H NMR Spectrum of **3ag′** (400 MHz, $CDCl_3$)



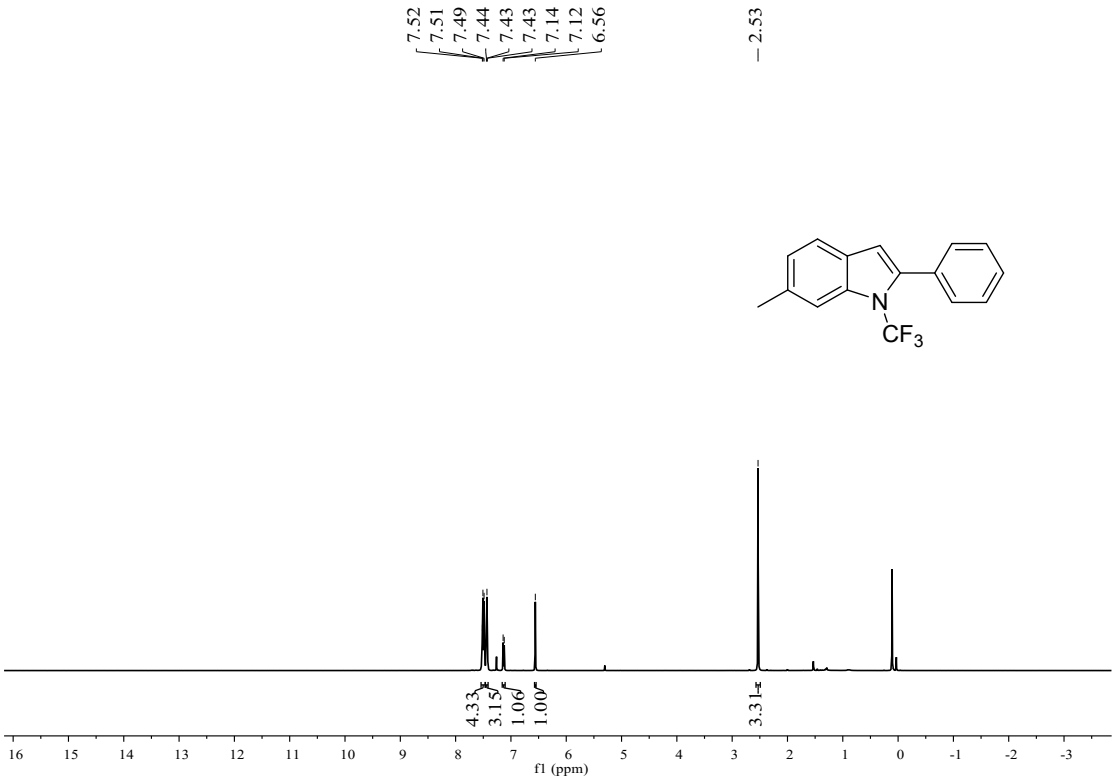
^{19}F NMR Spectrum of **3ag′** (376 MHz, $CDCl_3$)



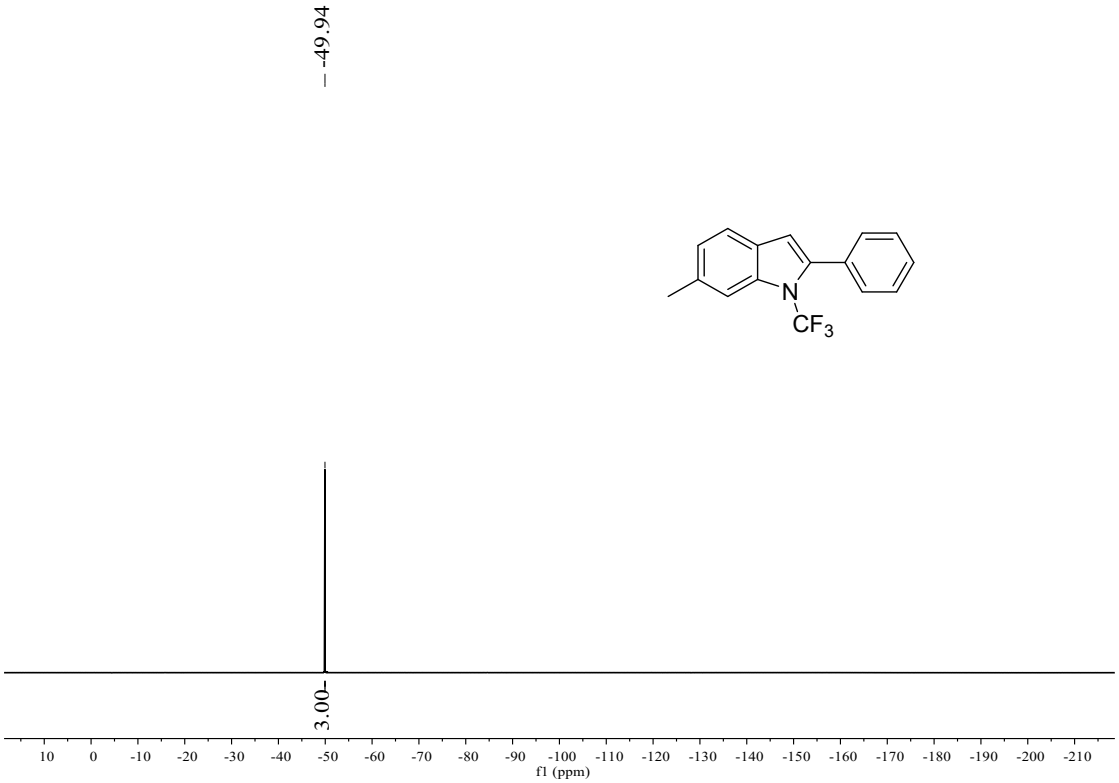
^{13}C NMR Spectrum of **3ag′** (101 MHz, $CDCl_3$)



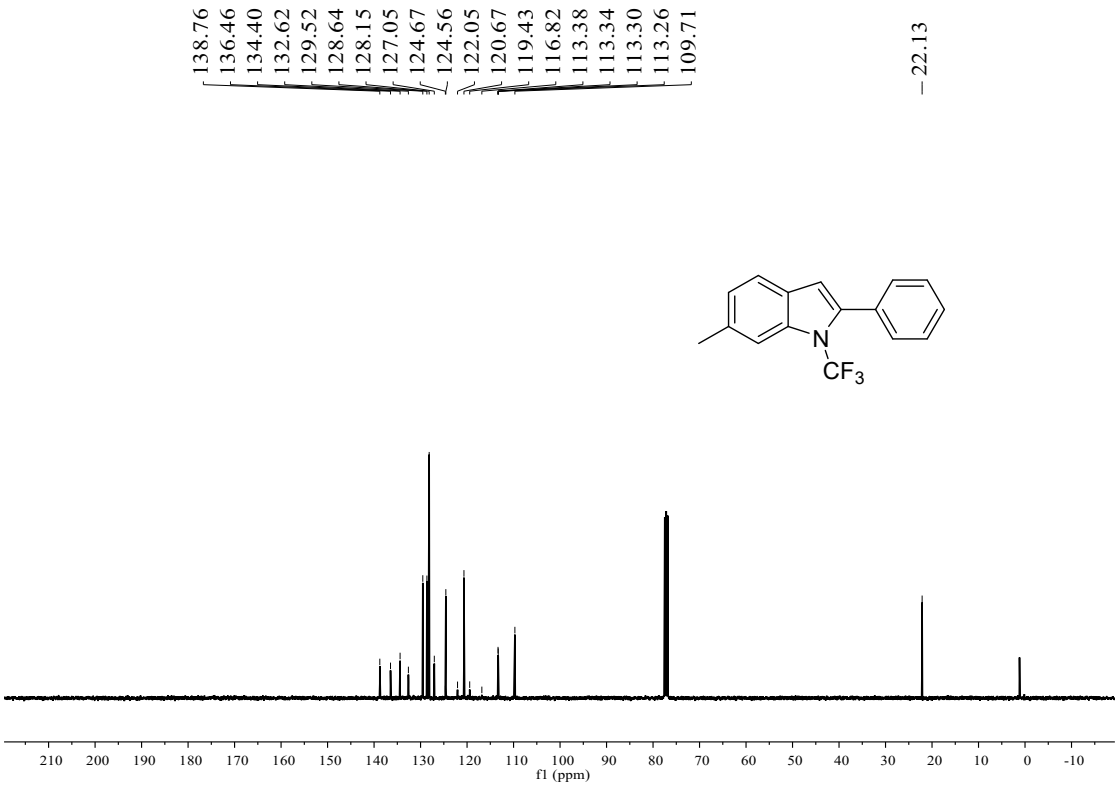
^{1}H NMR Spectrum of **3ba** (400 MHz, $CDCl_3$)



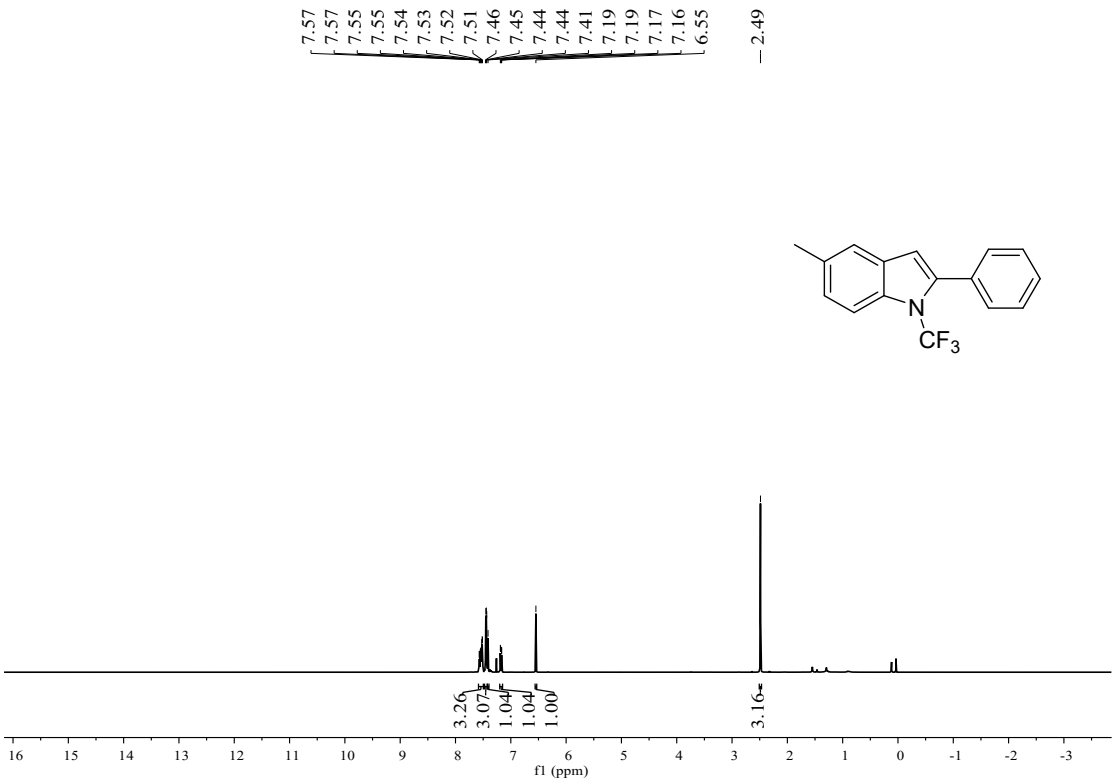
^{19}F NMR Spectrum of **3ba** (376 MHz, $CDCl_3$)



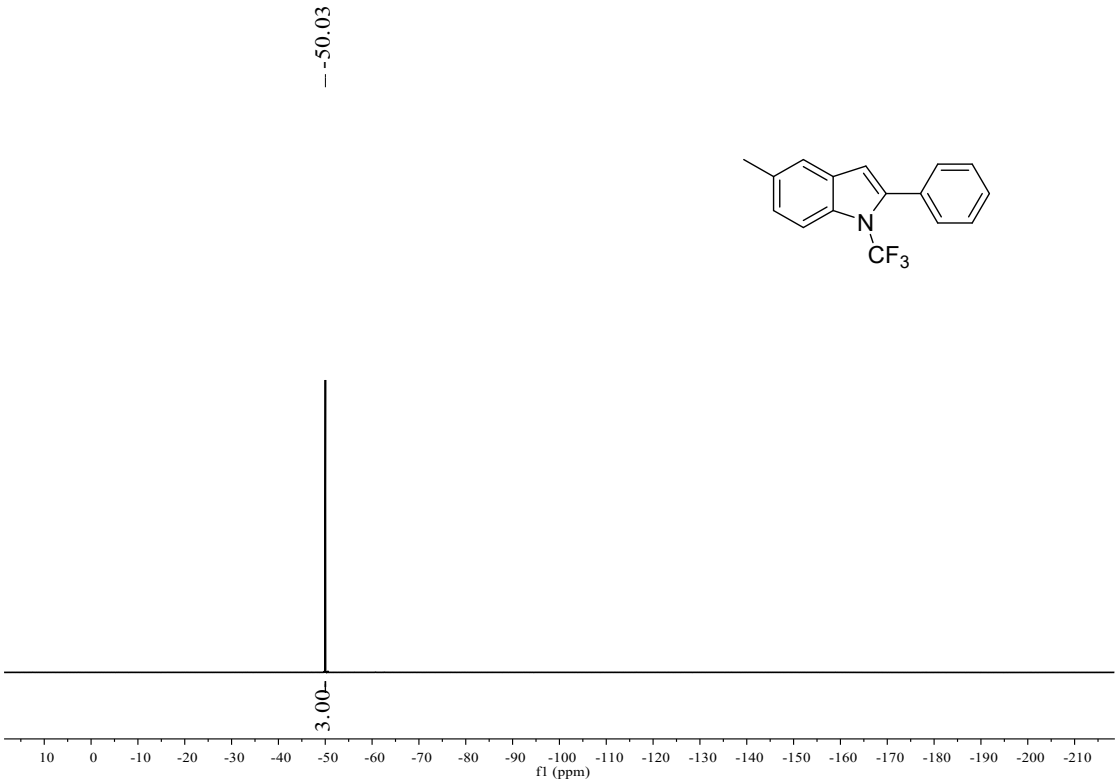
^{13}C NMR Spectrum of **3ba** (101 MHz, $CDCl_3$)



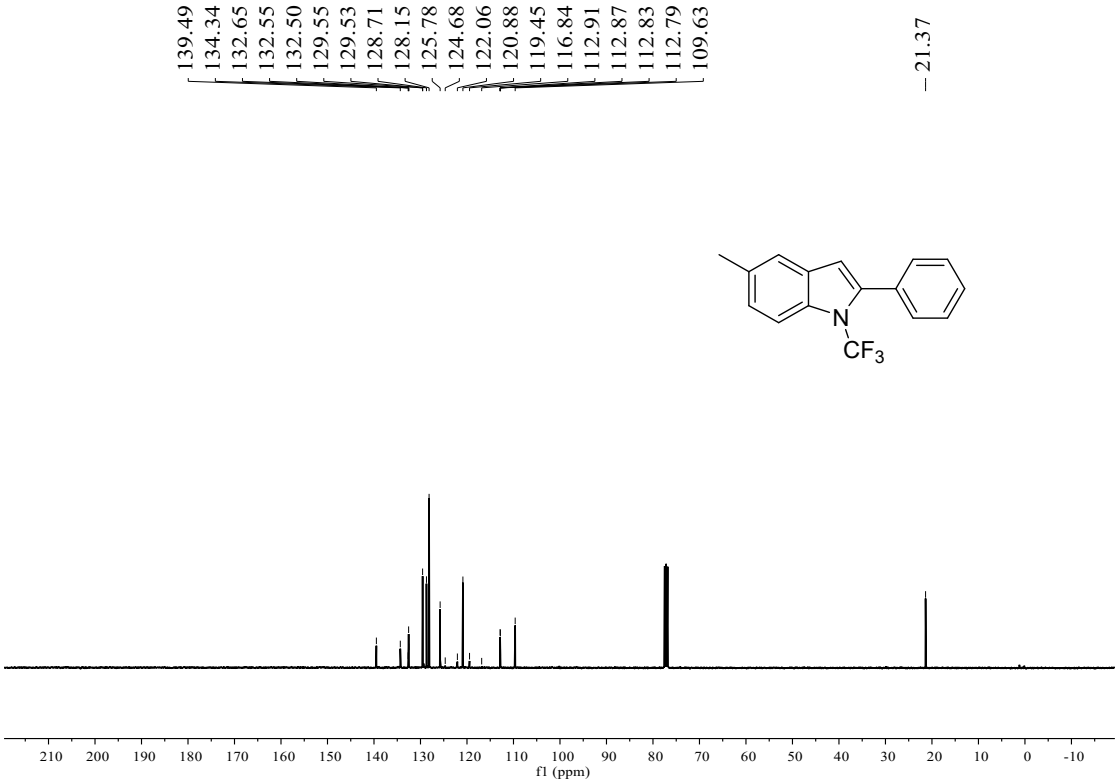
^{1}H NMR Spectrum of **3bb** (400 MHz, $CDCl_3$)



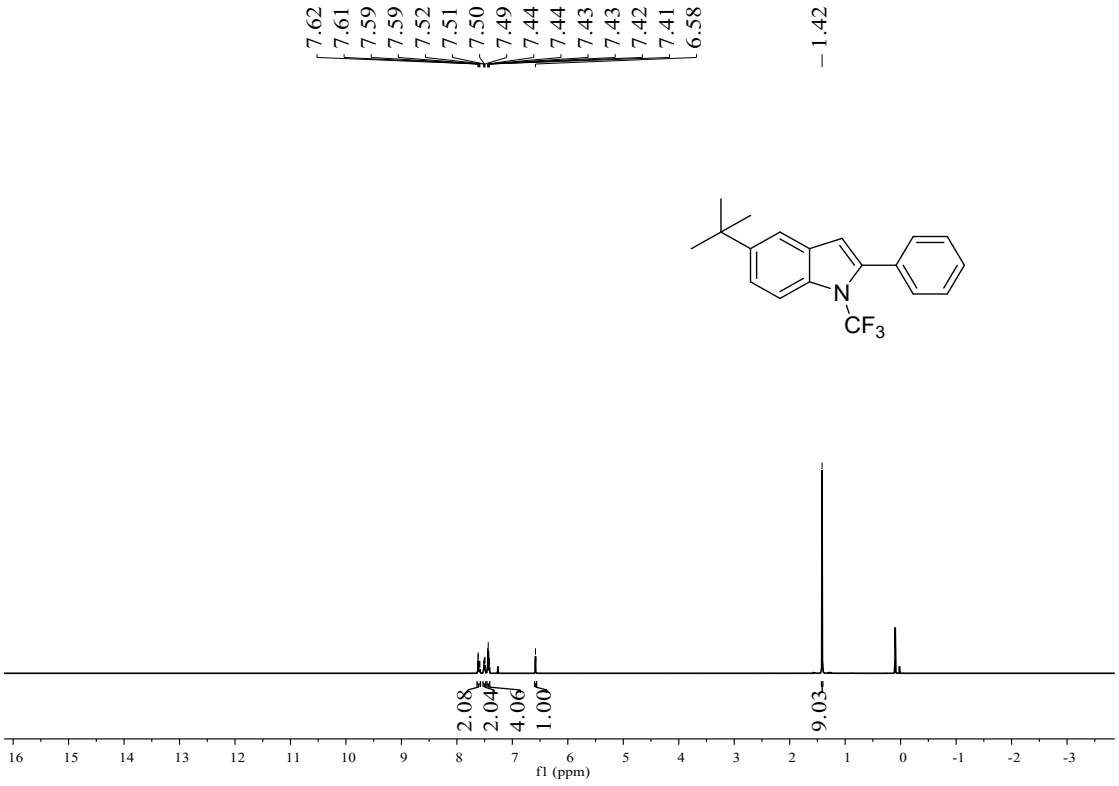
^{19}F NMR Spectrum of **3bb** (376 MHz, $CDCl_3$)



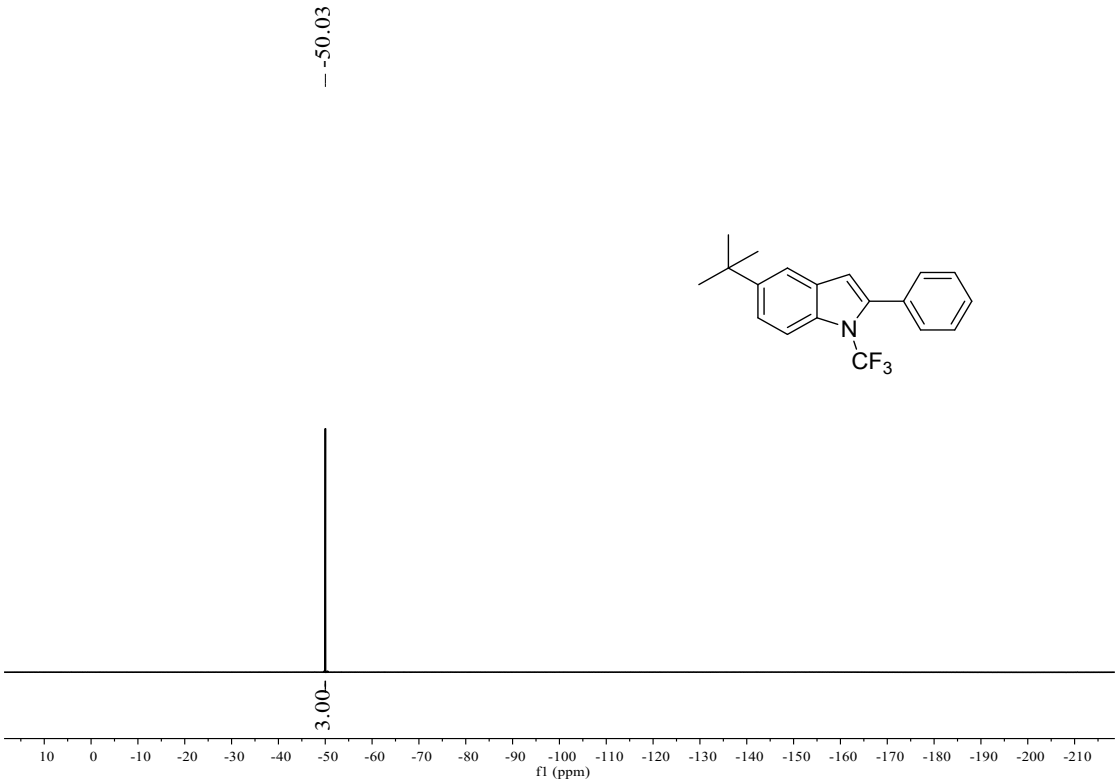
^{13}C NMR Spectrum of **3bb** (101 MHz, $CDCl_3$)



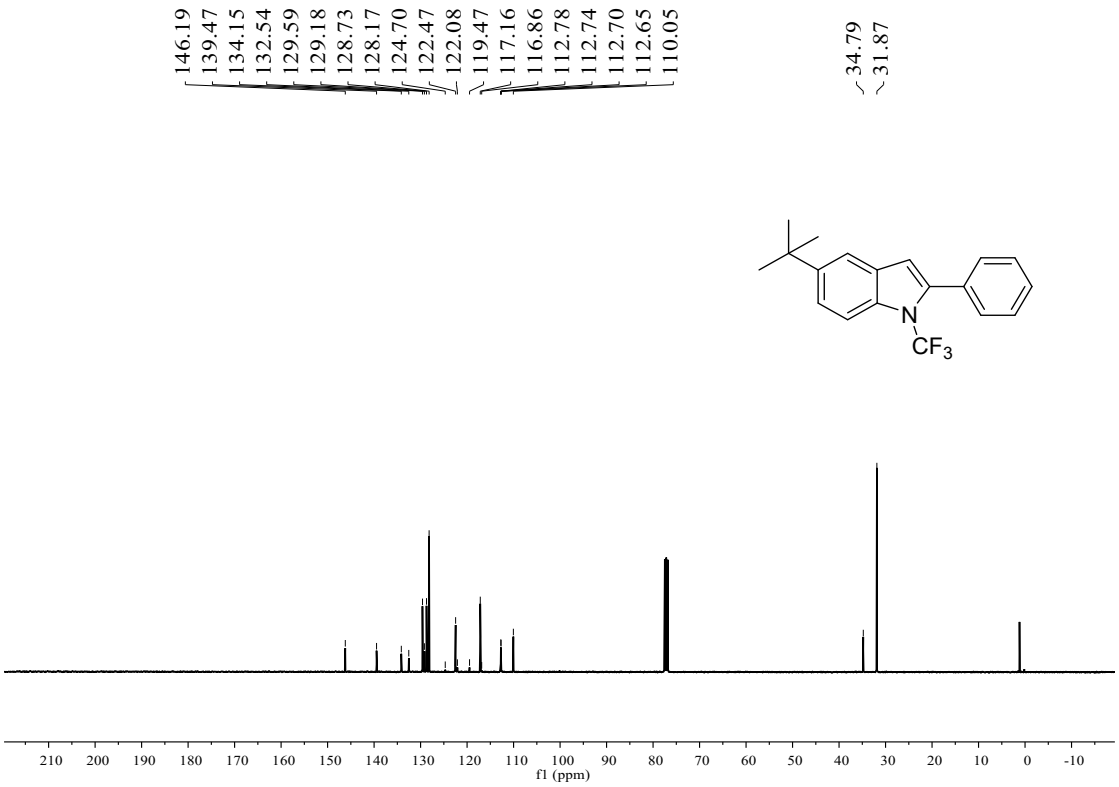
^{1}H NMR Spectrum of **3bc** (400 MHz, $CDCl_3$)



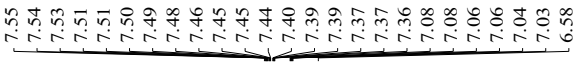
^{19}F NMR Spectrum of **3bc** (376 MHz, $CDCl_3$)

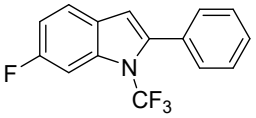


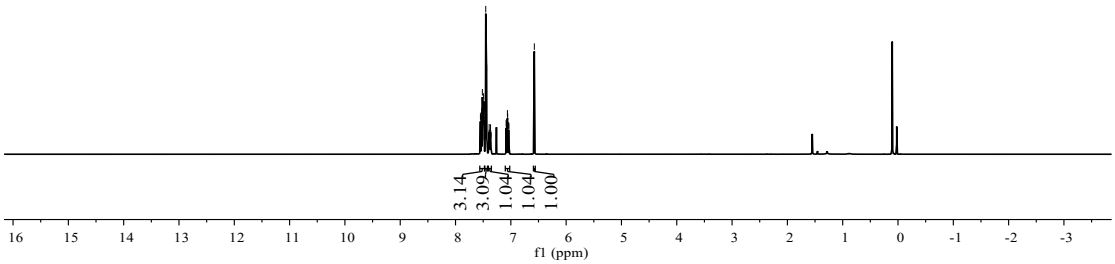
^{13}C NMR Spectrum of **3bc** (101 MHz, $CDCl_3$)



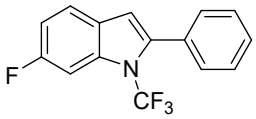
^{1}H NMR Spectrum of **3bd** (400 MHz, $CDCl_3$)

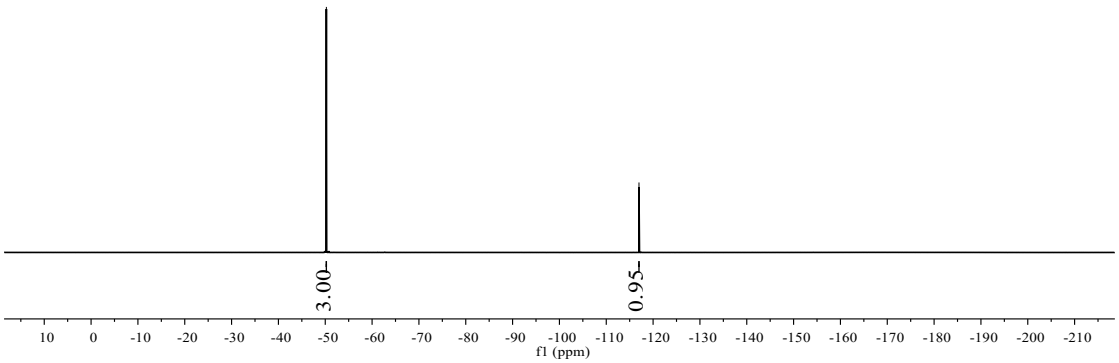




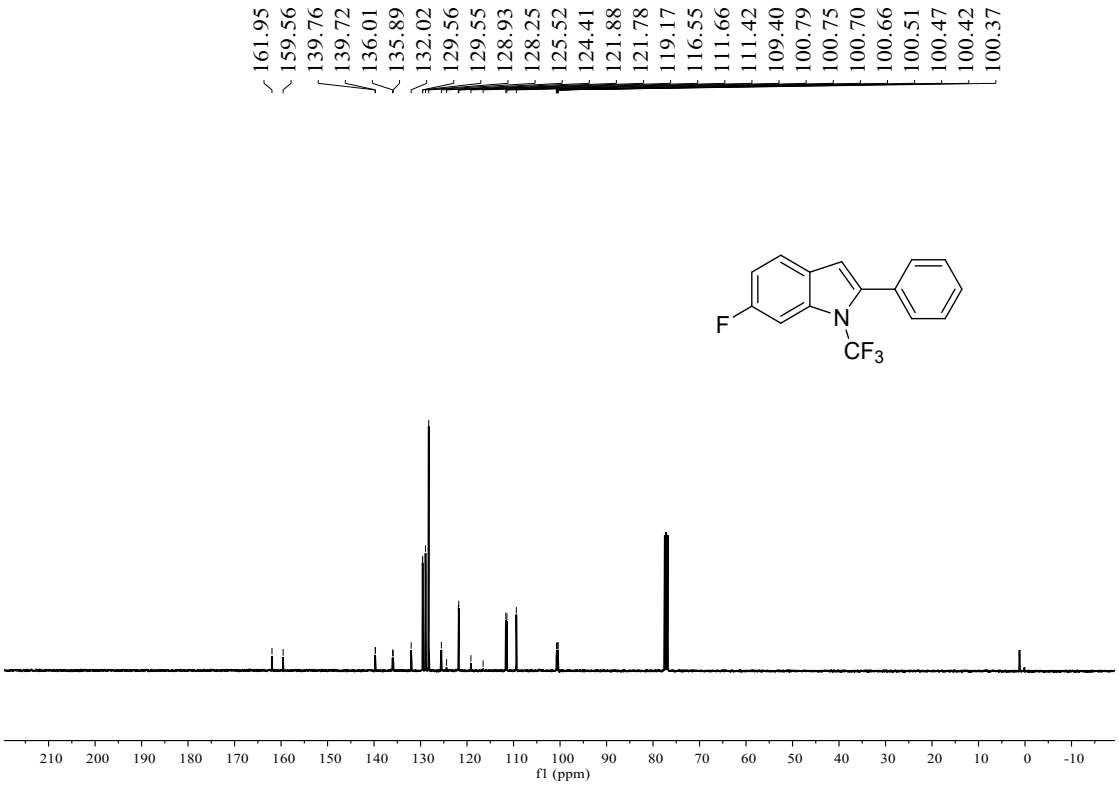


^{19}F NMR Spectrum of **3bd** (376 MHz, $CDCl_3$)

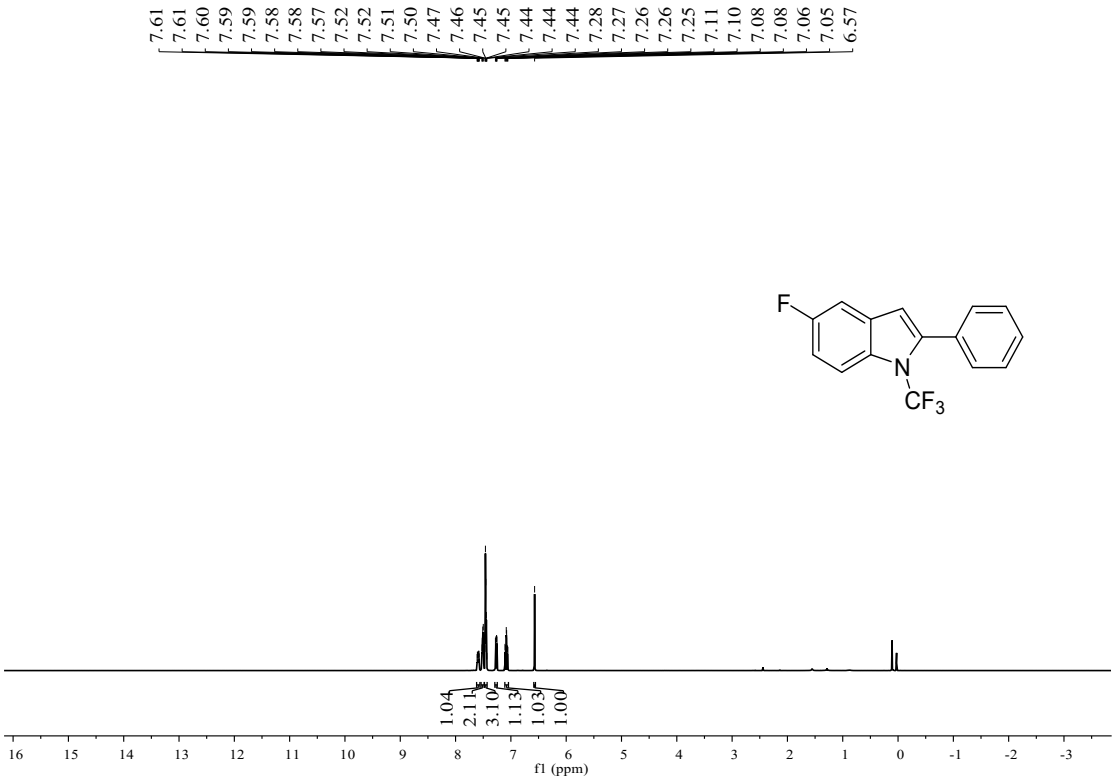




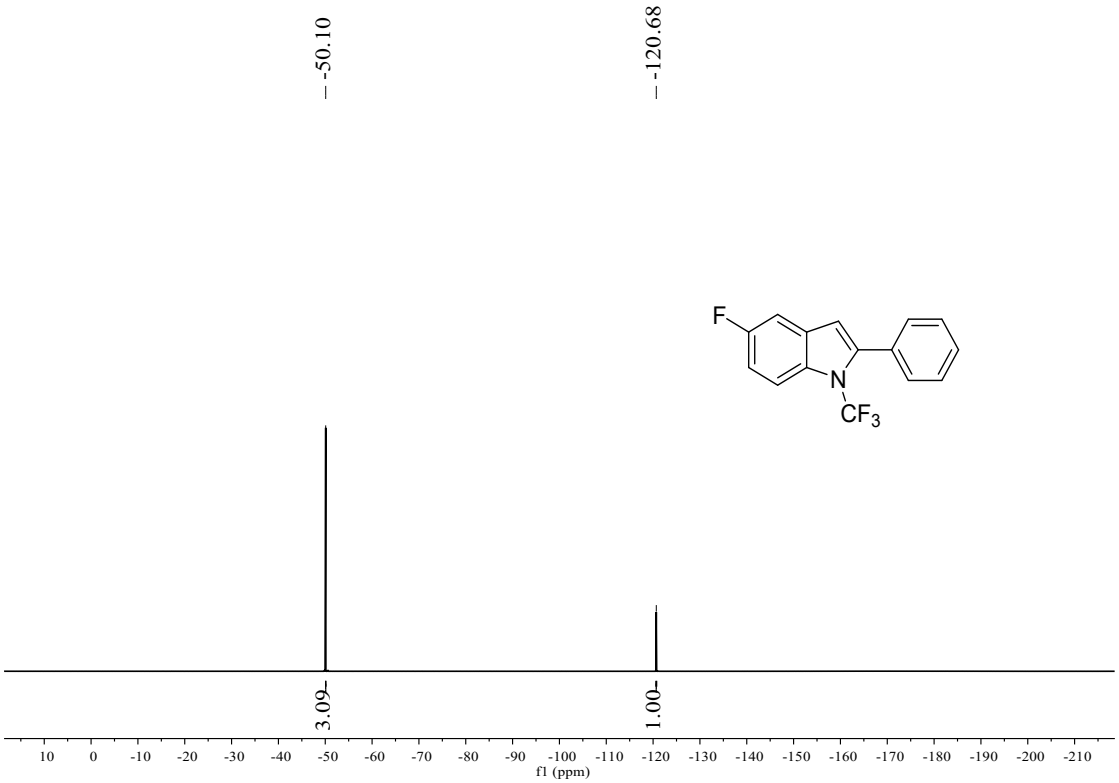
^{13}C NMR Spectrum of **3bd** (101 MHz, $CDCl_3$)



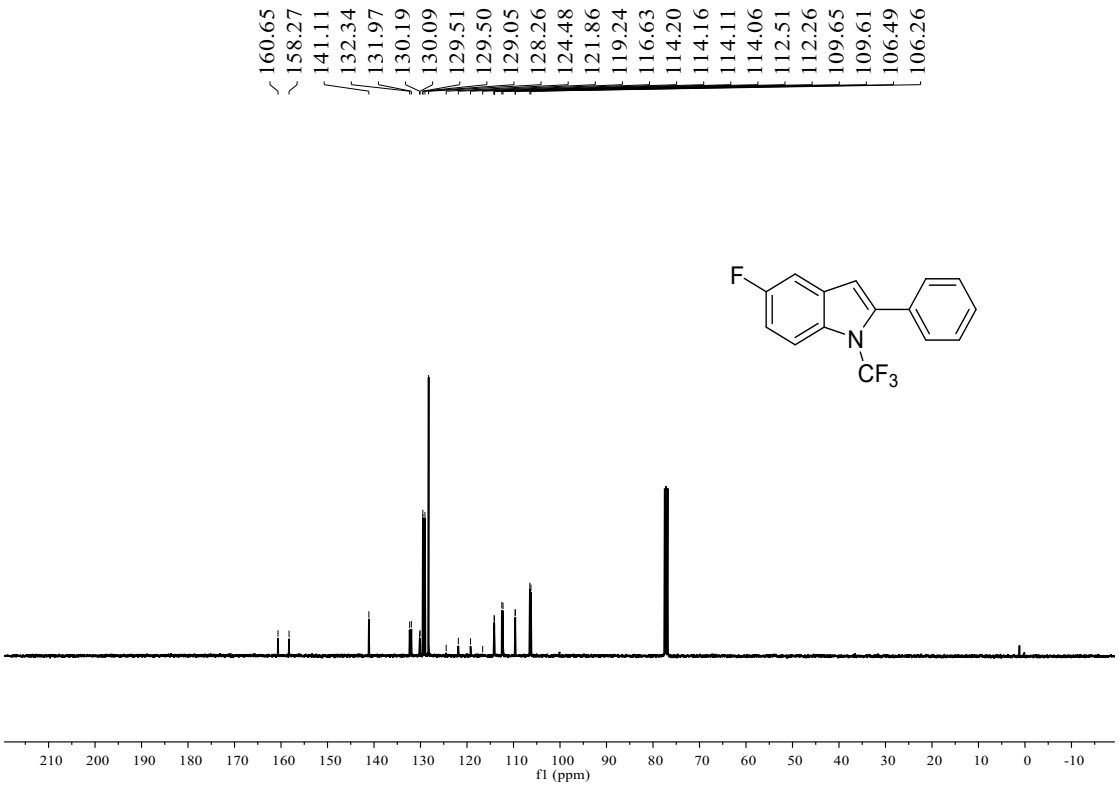
^{1}H NMR Spectrum of **3be** (400 MHz, $CDCl_3$)



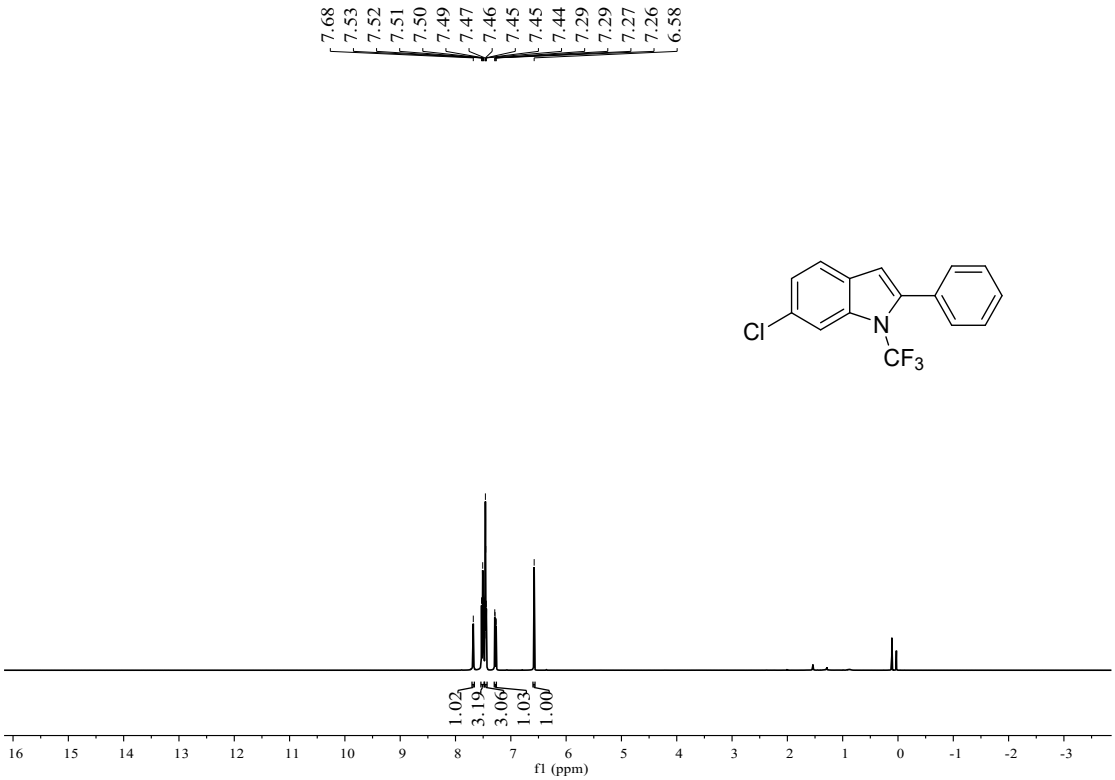
^{19}F NMR Spectrum of **3be** (376 MHz, $CDCl_3$)



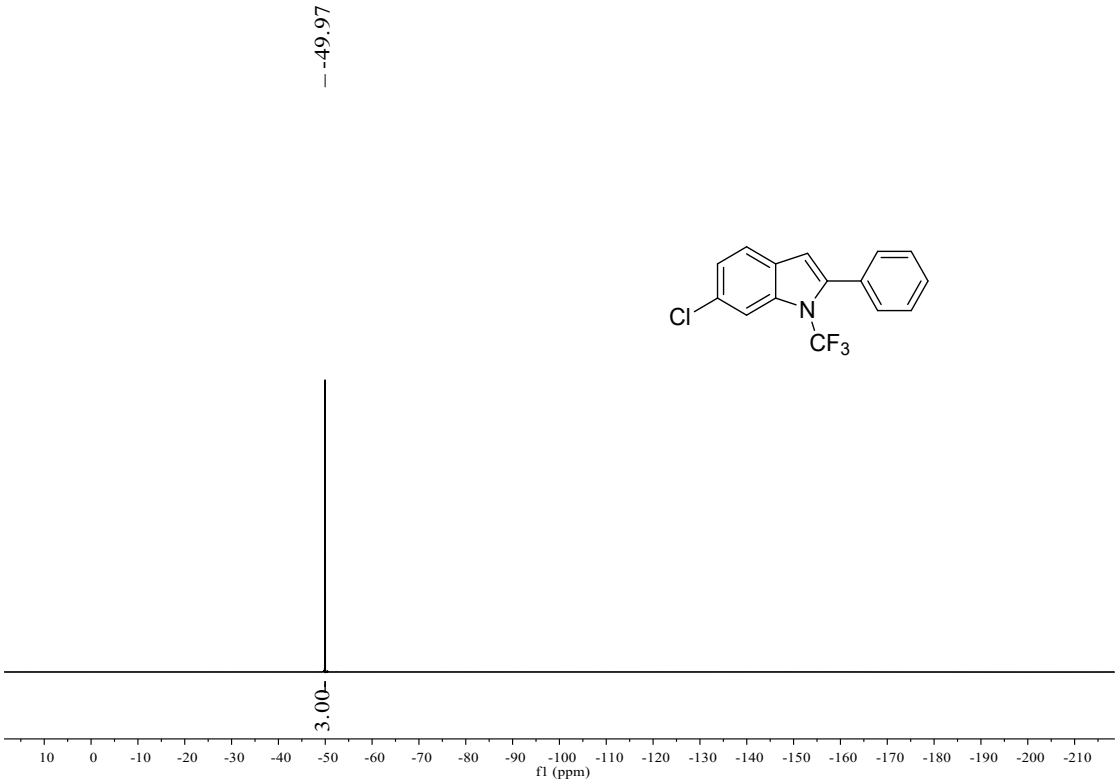
^{13}C NMR Spectrum of **3be** (101 MHz, $CDCl_3$)



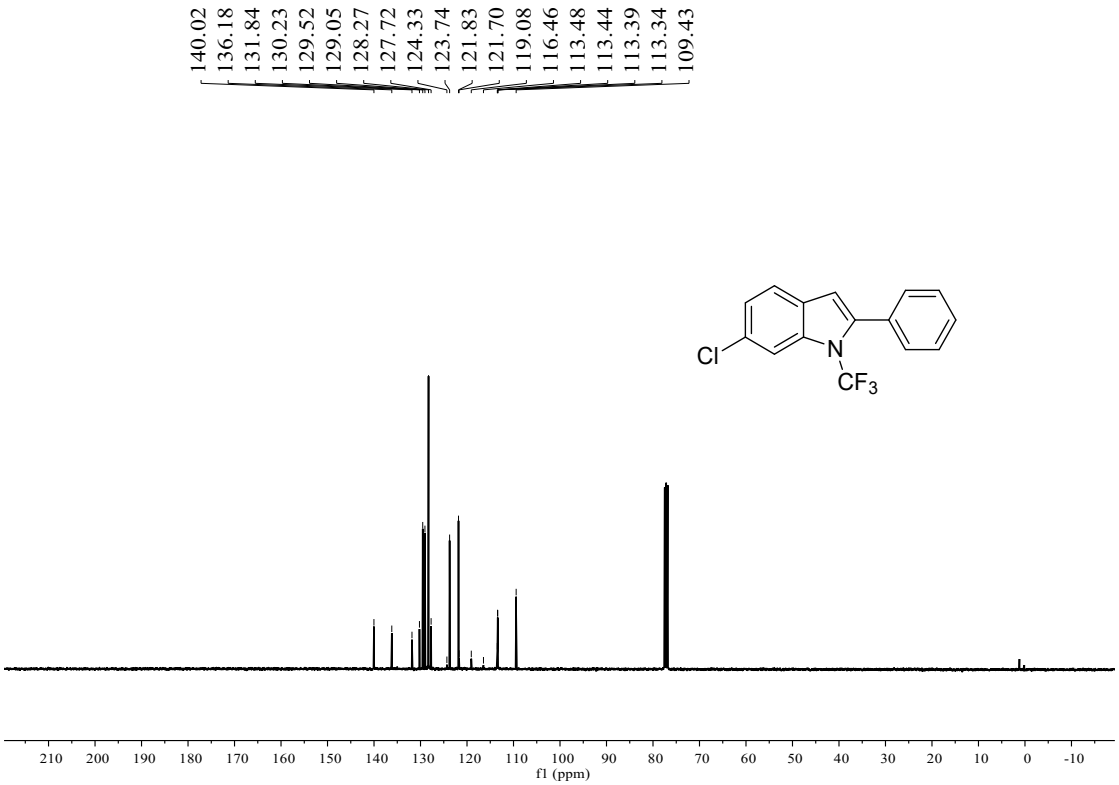
^{1}H NMR Spectrum of **3bf** (400 MHz, $CDCl_3$)



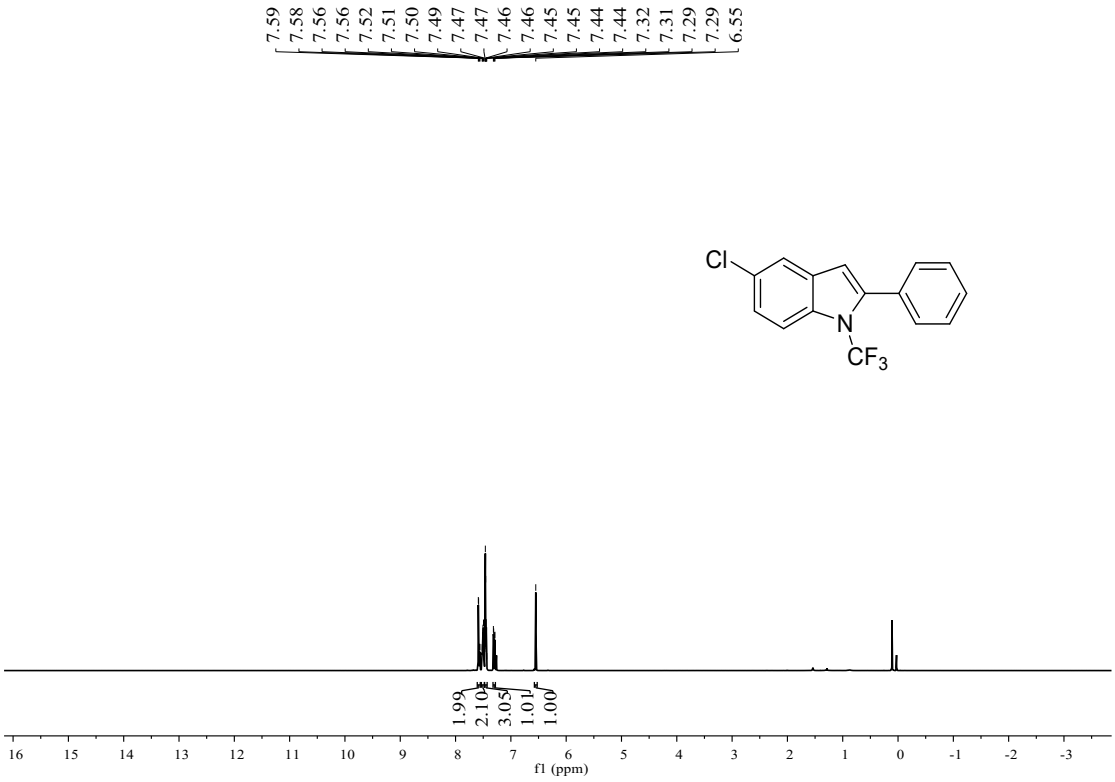
^{19}F NMR Spectrum of **3bf** (376 MHz, $CDCl_3$)



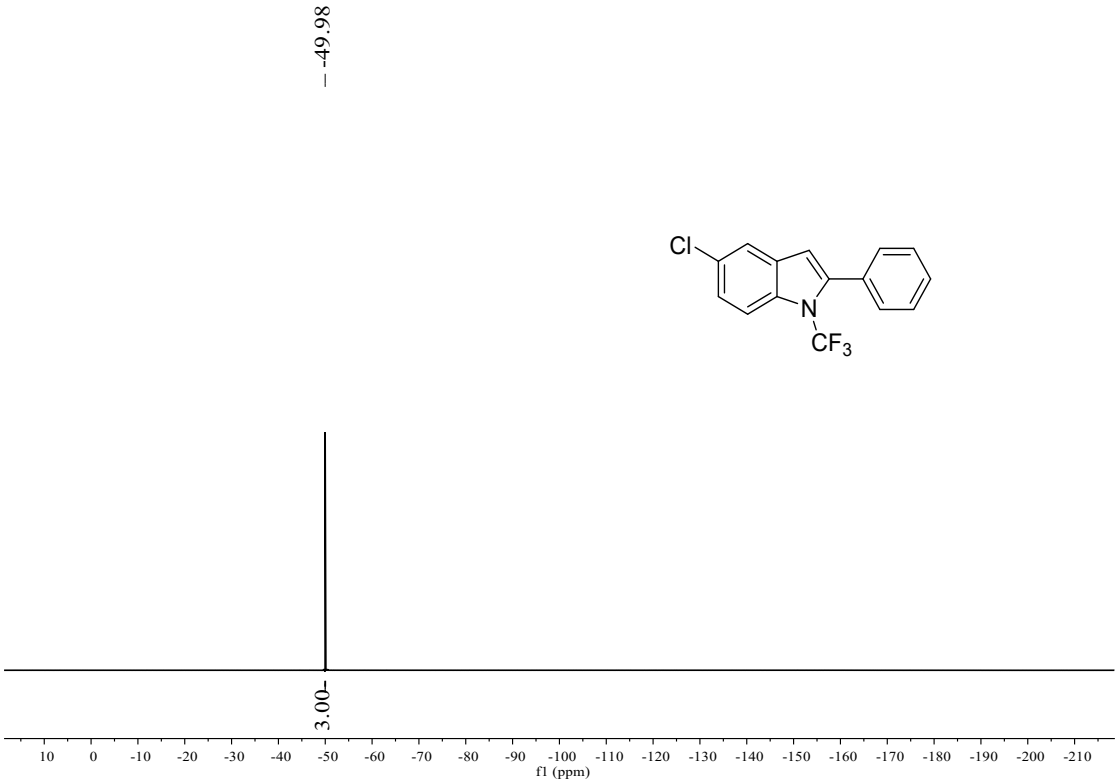
^{13}C NMR Spectrum of **3bf** (101 MHz, $CDCl_3$)



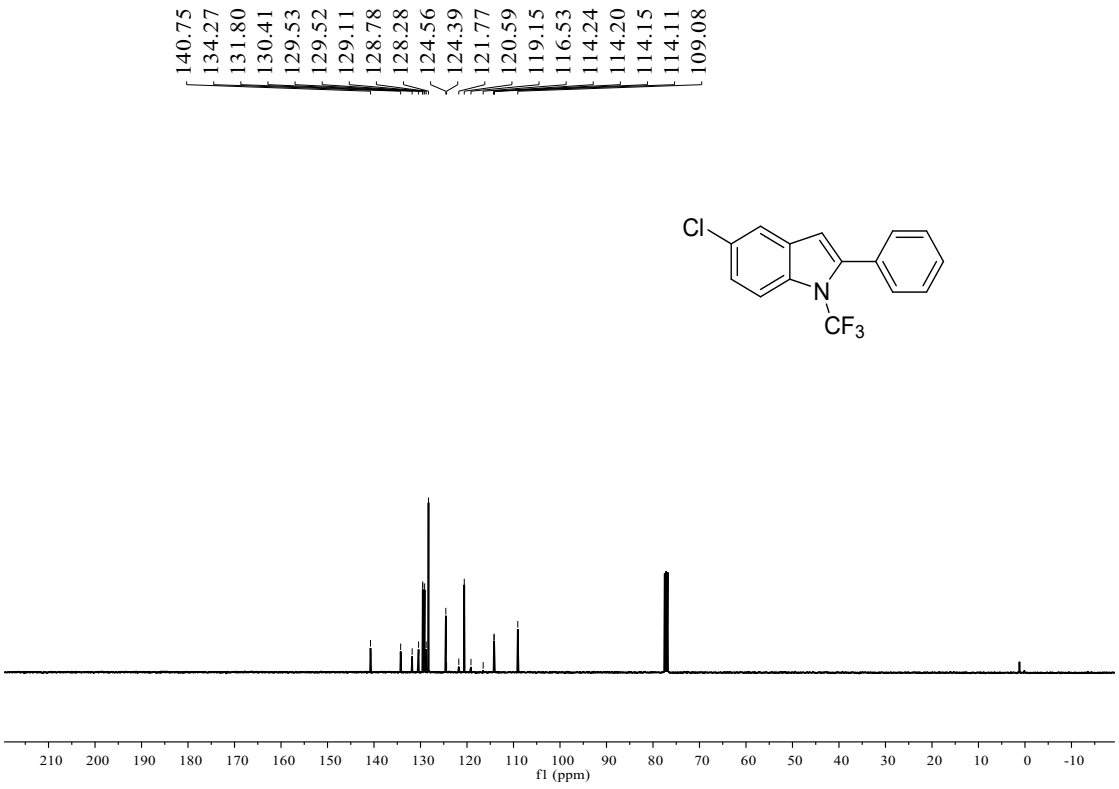
^{1}H NMR Spectrum of **3bg** (400 MHz, $CDCl_3$)



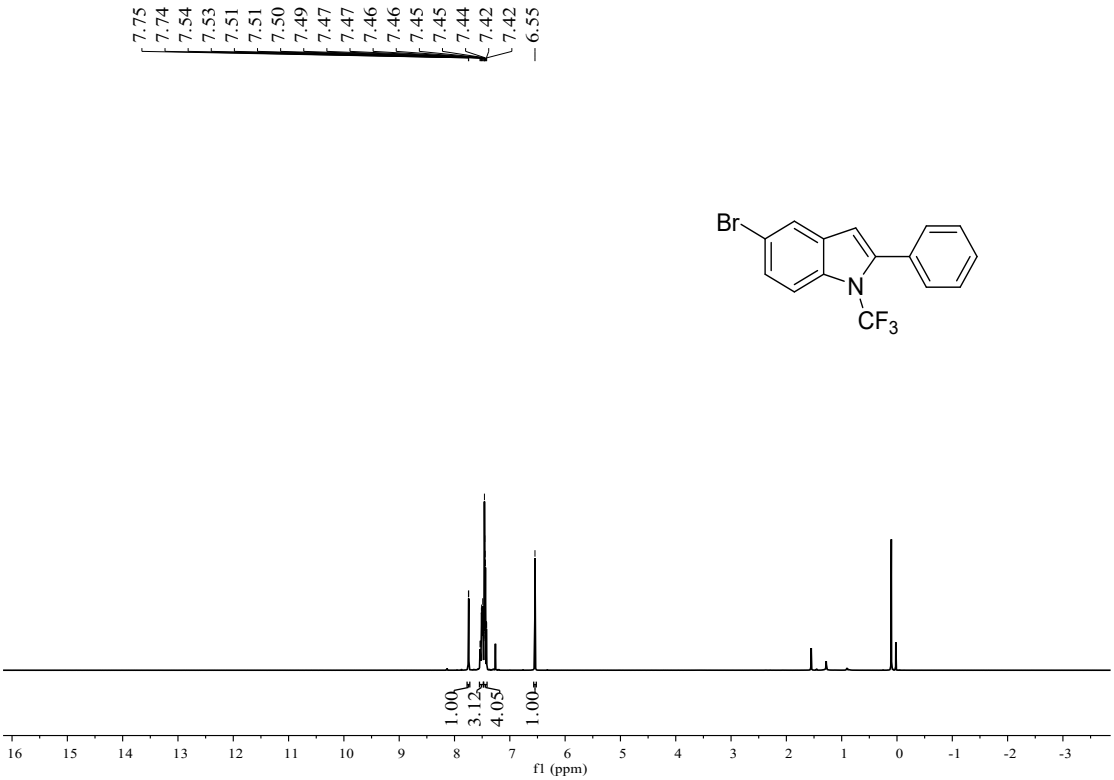
^{19}F NMR Spectrum of **3bg** (376 MHz, $CDCl_3$)



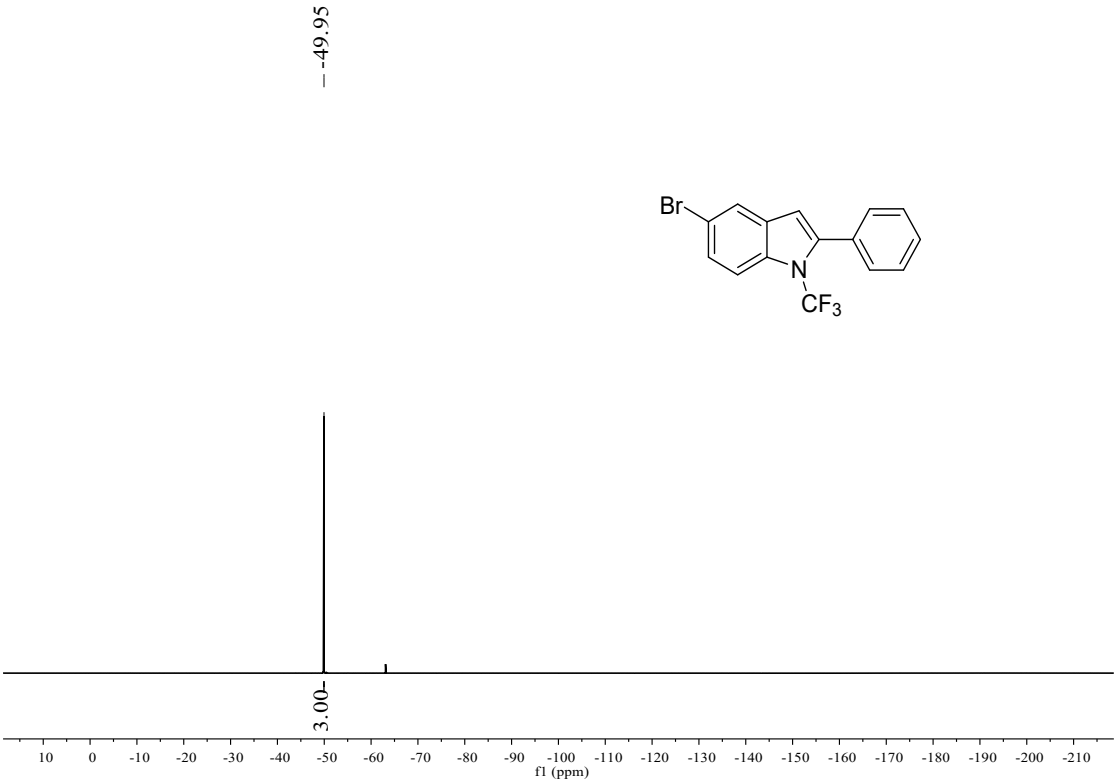
^{13}C NMR Spectrum of **3bg** (101 MHz, $CDCl_3$)



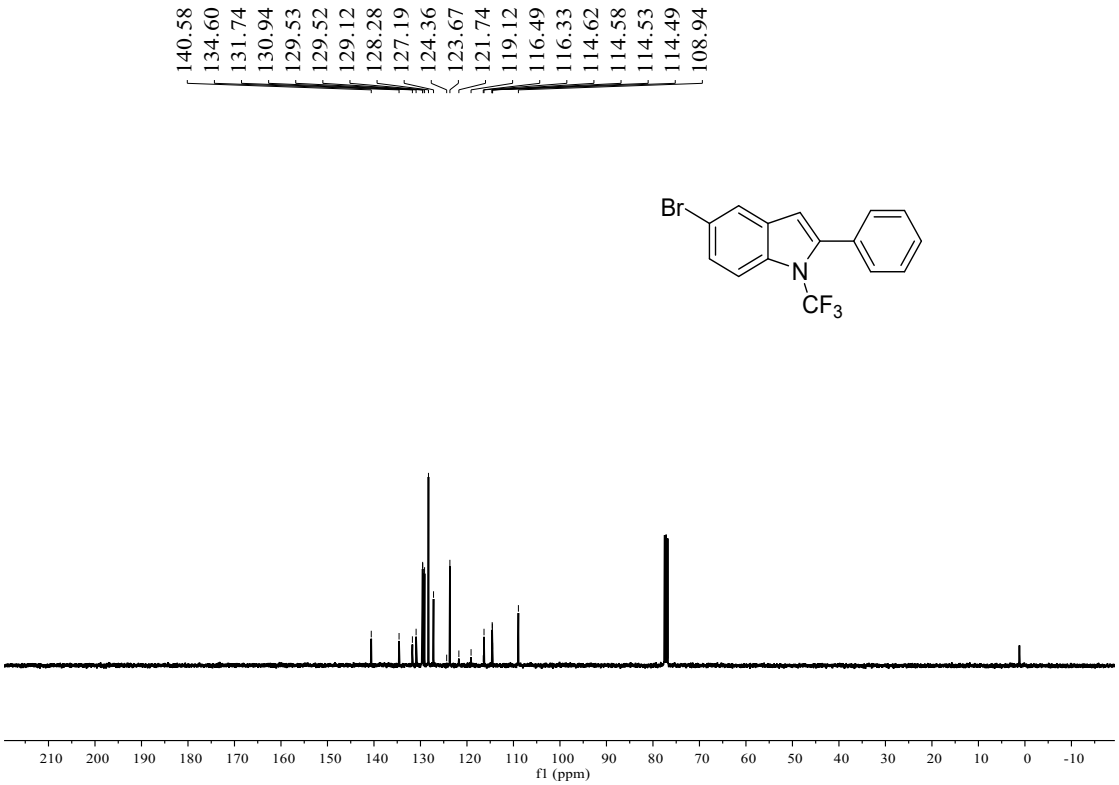
^{1}H NMR Spectrum of **3bh** (400 MHz, $CDCl_3$)



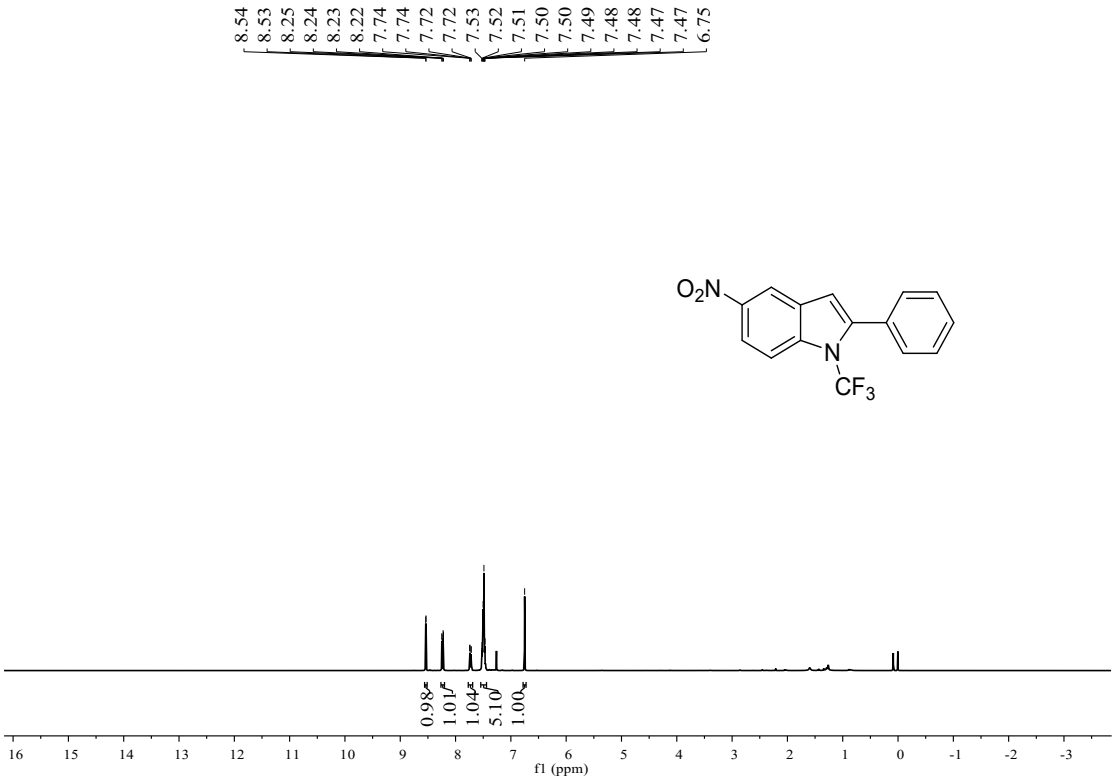
^{19}F NMR Spectrum of **3bh** (376 MHz, $CDCl_3$)



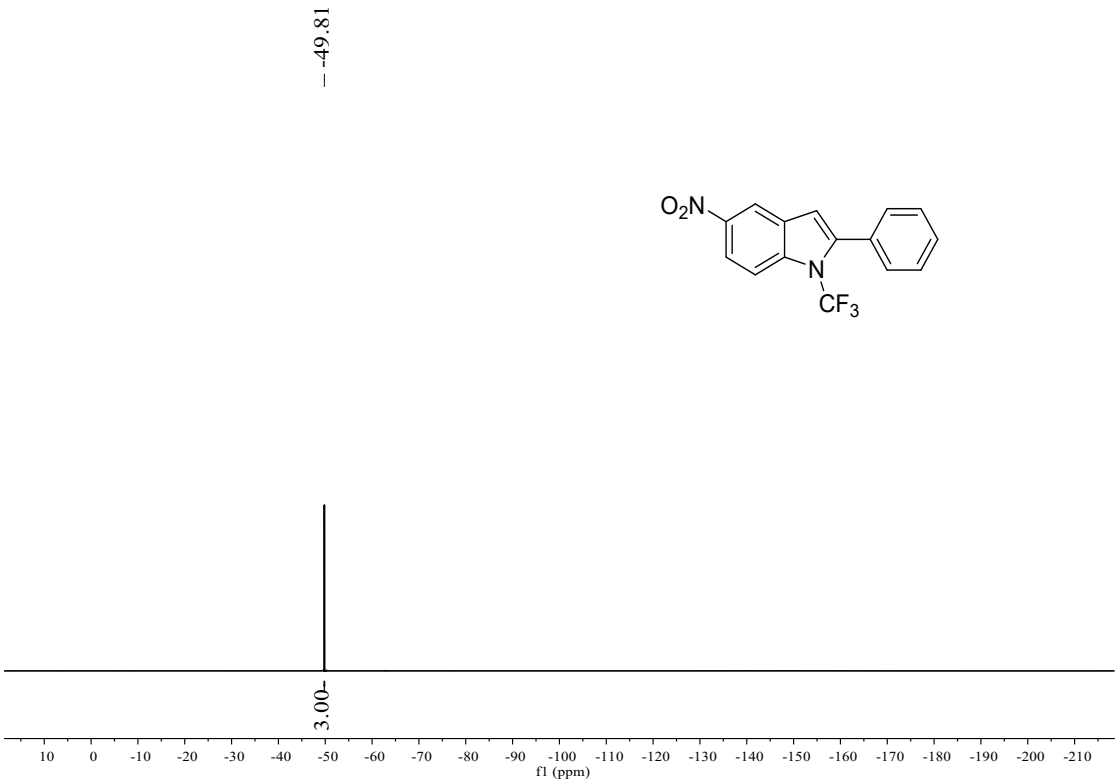
^{13}C NMR Spectrum of **3bh** (101 MHz, $CDCl_3$)



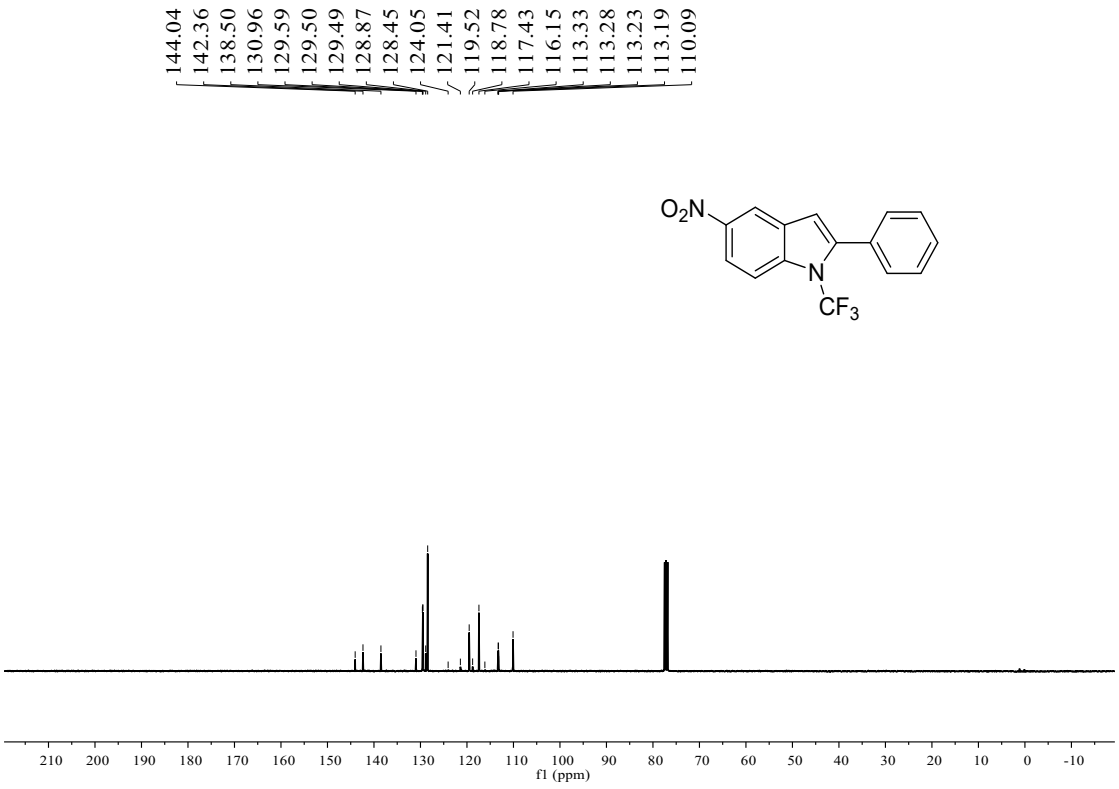
^{1}H NMR Spectrum of **3bi** (400 MHz, $CDCl_3$)



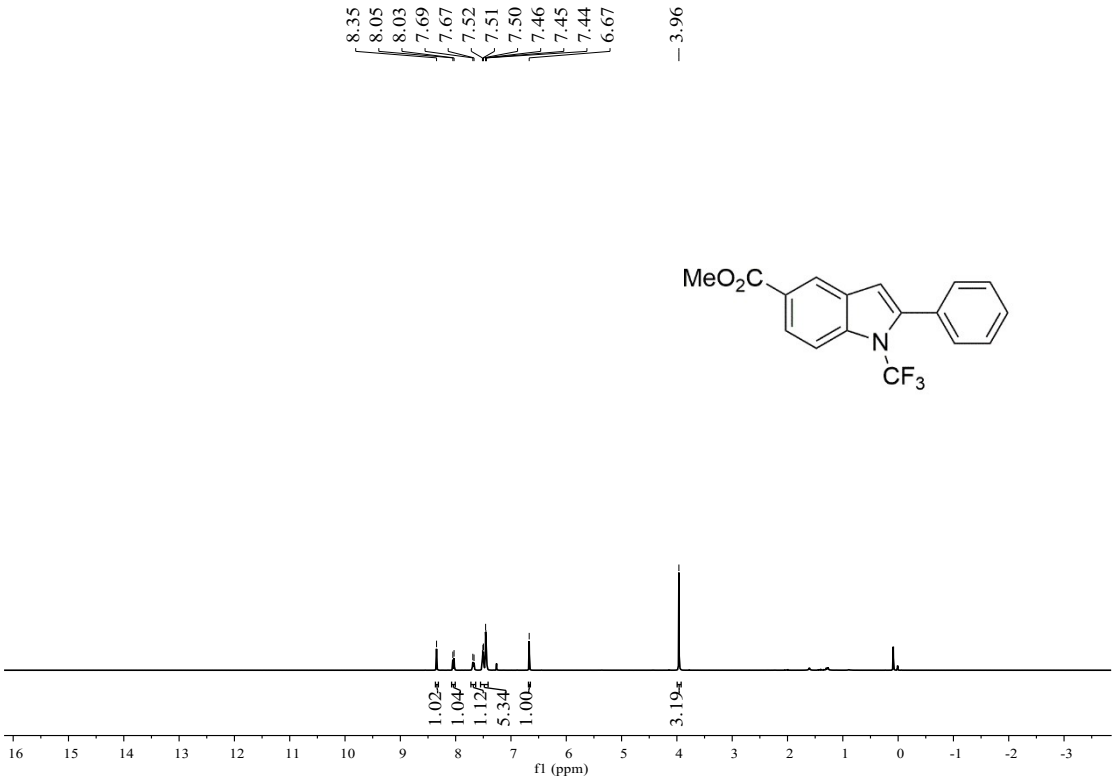
^{19}F NMR Spectrum of **3bi** (376 MHz, $CDCl_3$)



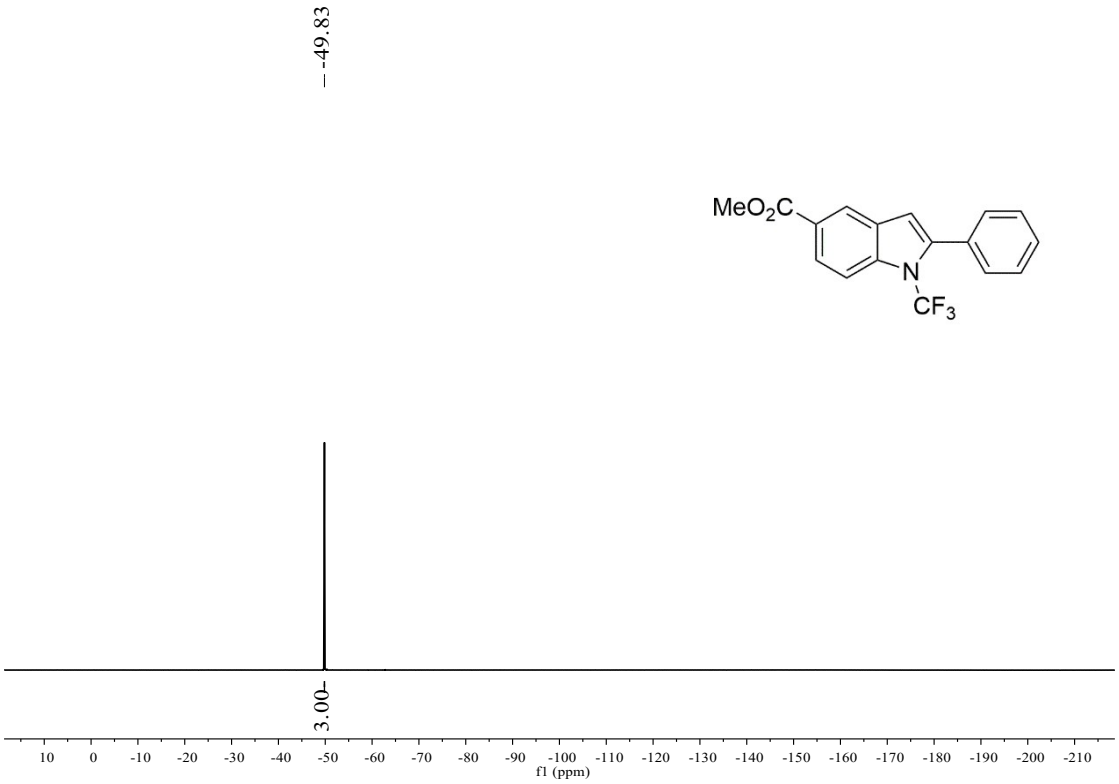
^{13}C NMR Spectrum of **3bi** (101 MHz, $CDCl_3$)



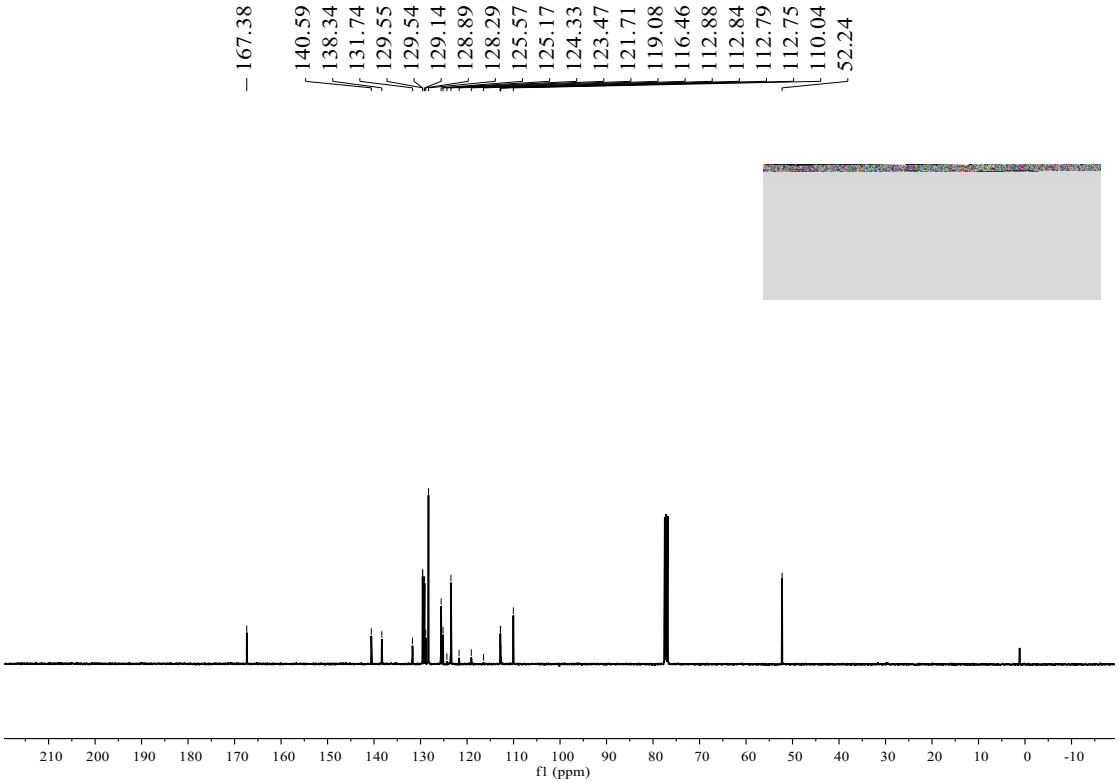
^{1}H NMR Spectrum of **3bj** (400 MHz, $CDCl_3$)



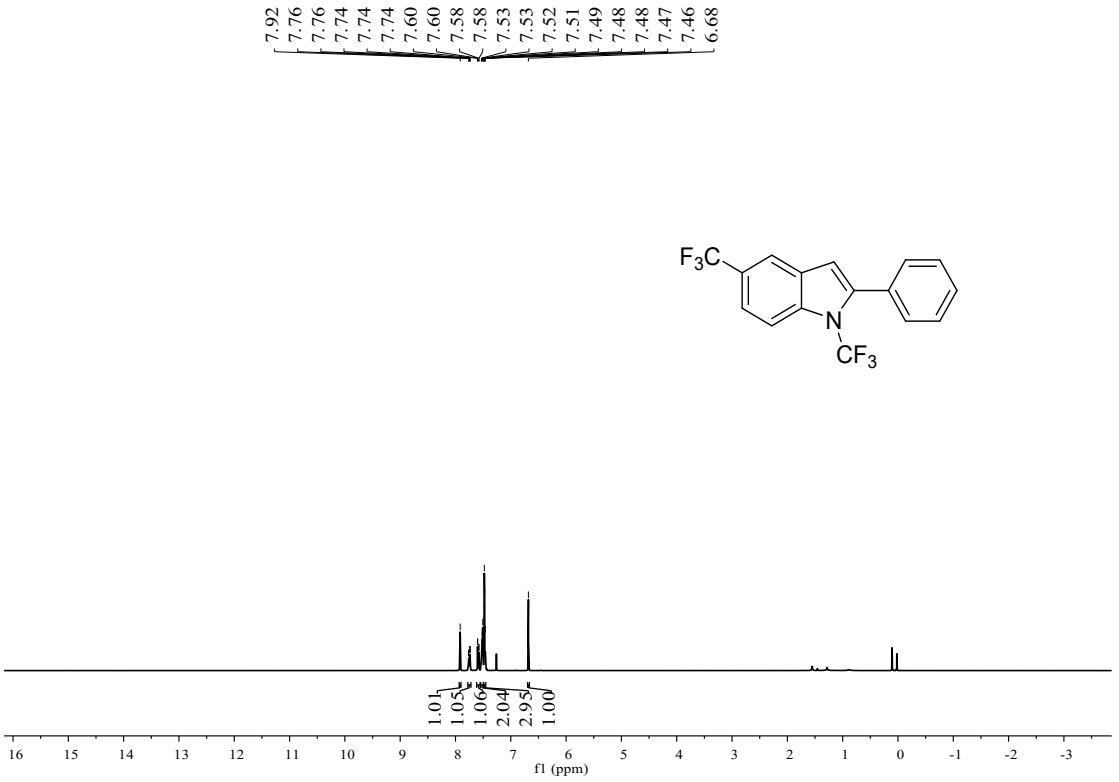
^{19}F NMR Spectrum of **3bj** (376 MHz, $CDCl_3$)



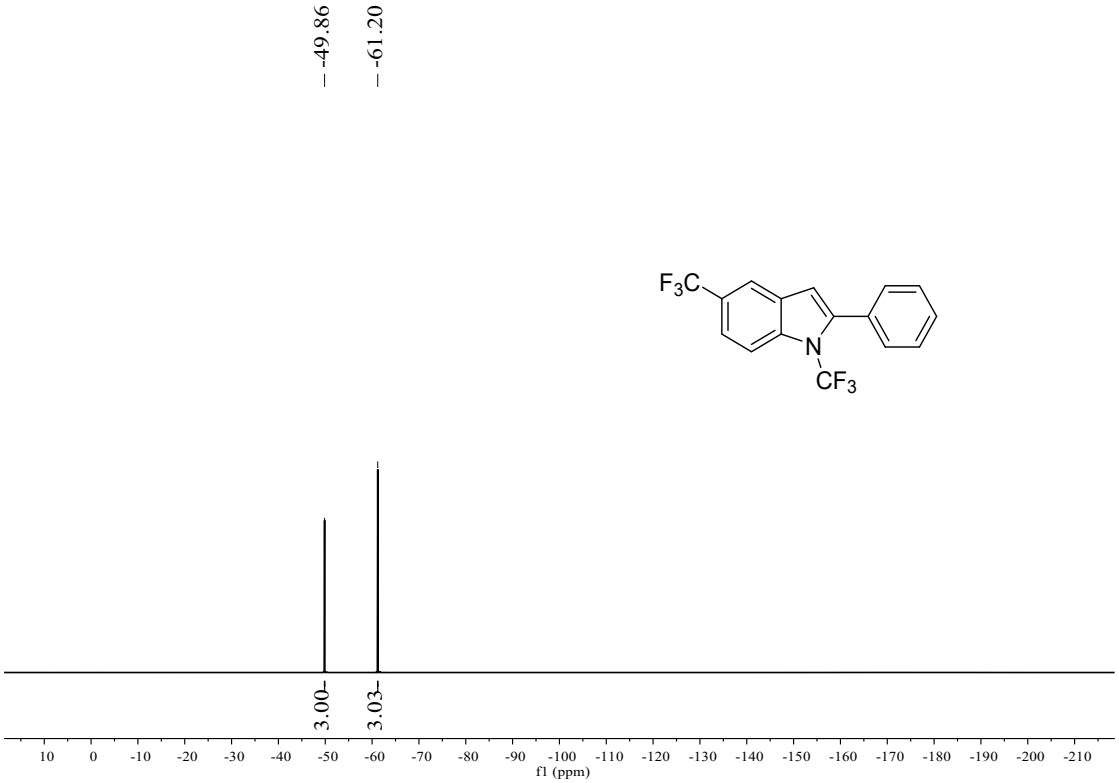
^{13}C NMR Spectrum of **3bj** (101 MHz, $CDCl_3$)



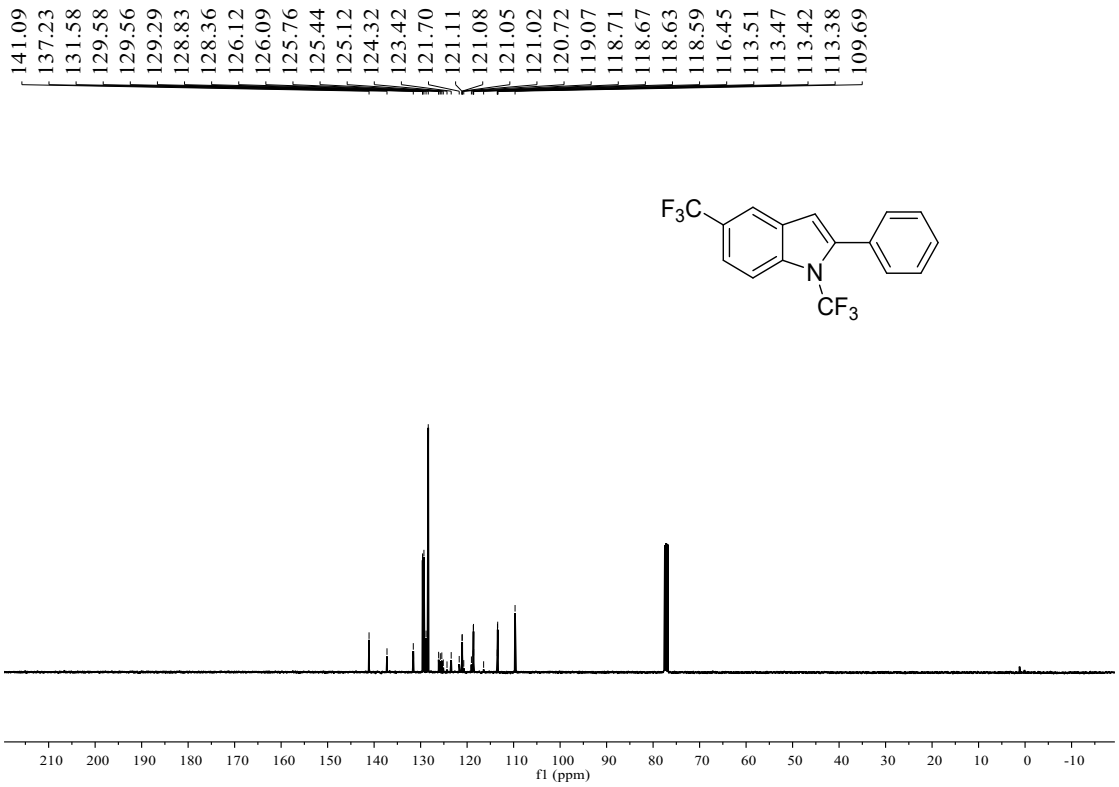
^{1}H NMR Spectrum of **3bk** (400 MHz, $CDCl_3$)



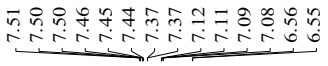
^{19}F NMR Spectrum of **3bk** (376 MHz, $CDCl_3$)

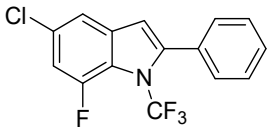


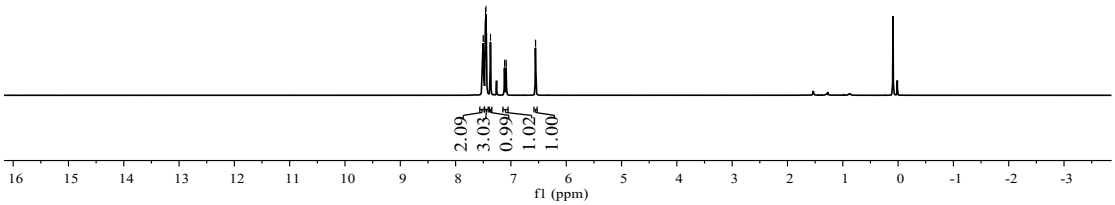
^{13}C NMR Spectrum of **3bk** (101 MHz, $CDCl_3$)



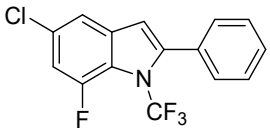
^{1}H NMR Spectrum of **3bl** (400 MHz, $CDCl_3$)

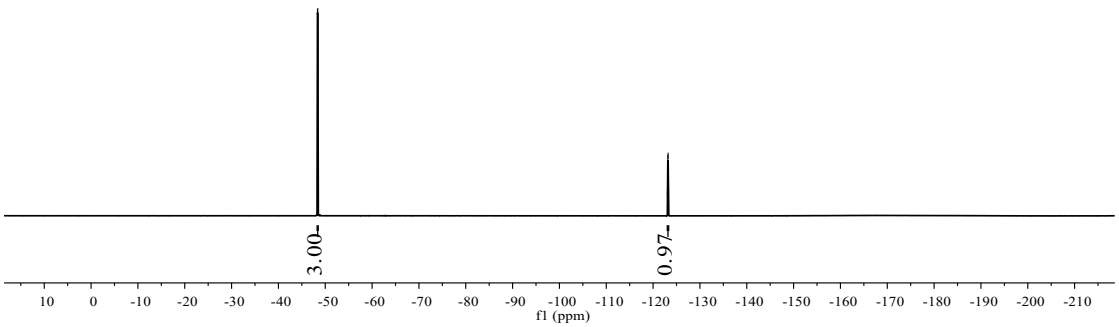




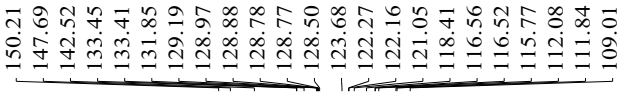


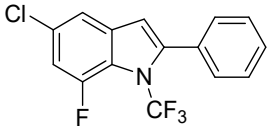
^{19}F NMR Spectrum of **3bl** (376 MHz, $CDCl_3$)

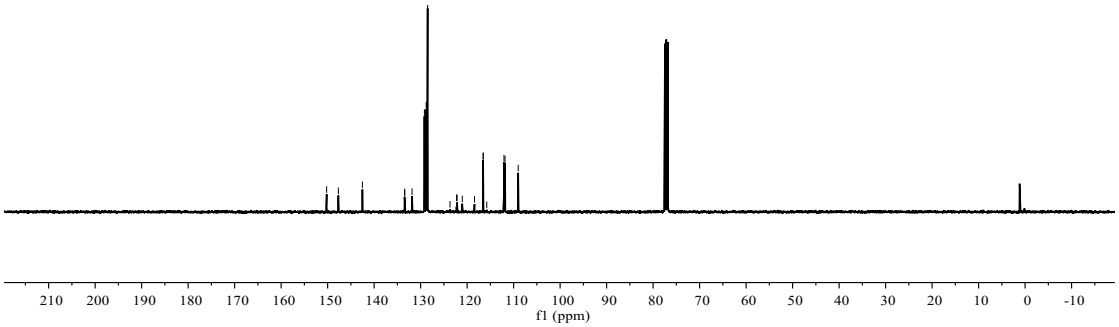




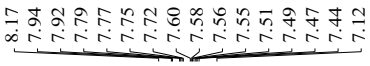
^{13}C NMR Spectrum of **3bl** (101 MHz, $CDCl_3$)

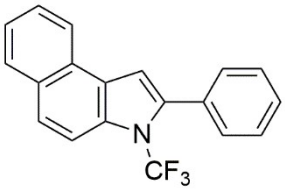


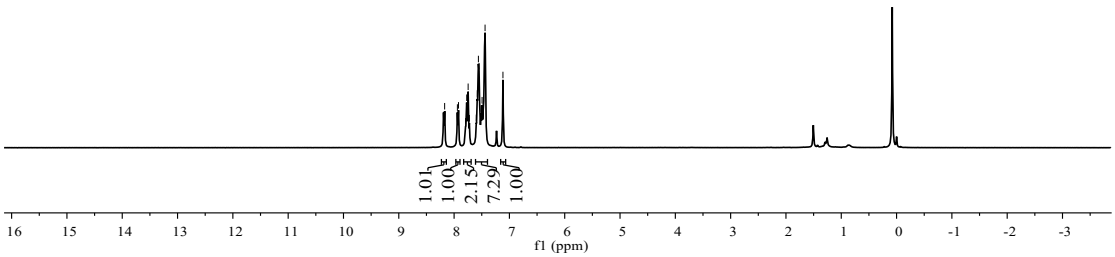




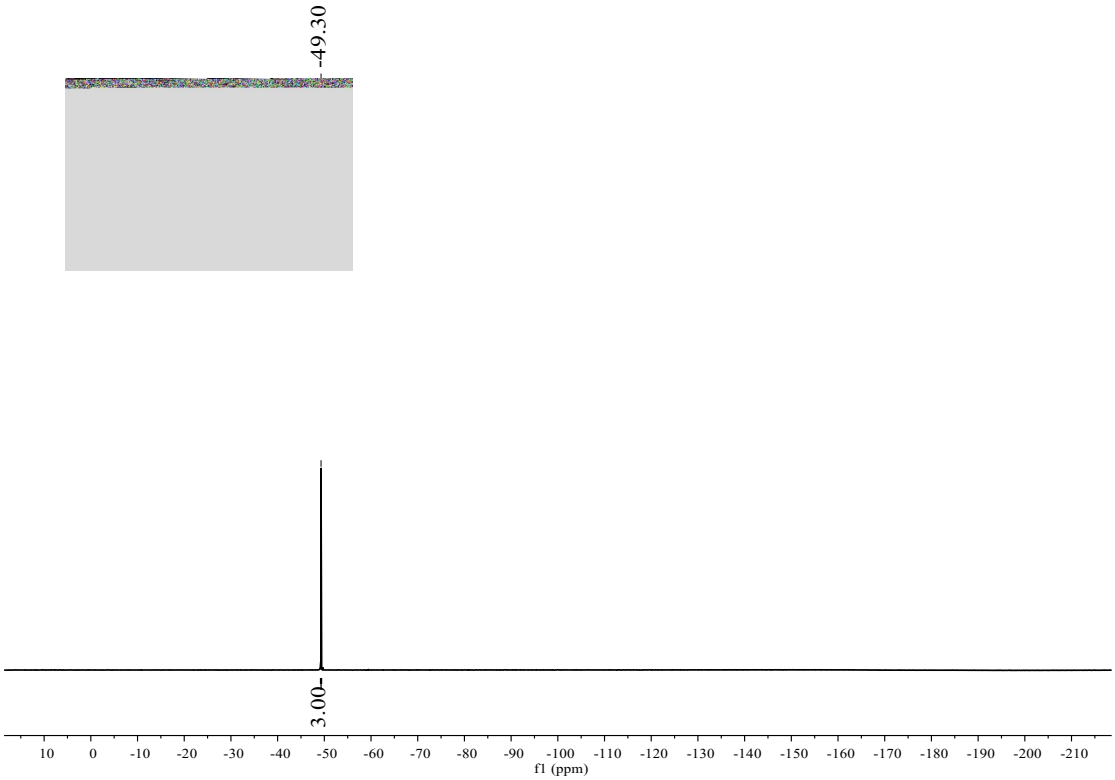
^{1}H NMR Spectrum of **3bm** (400 MHz, $CDCl_3$)



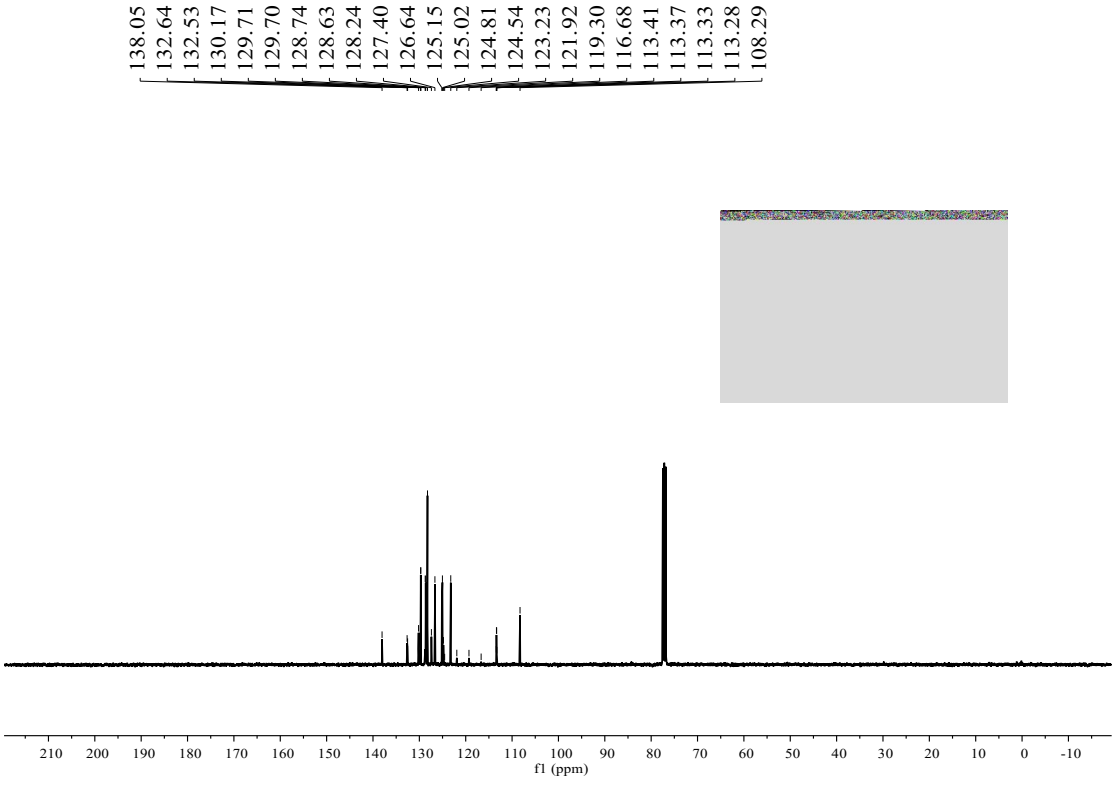




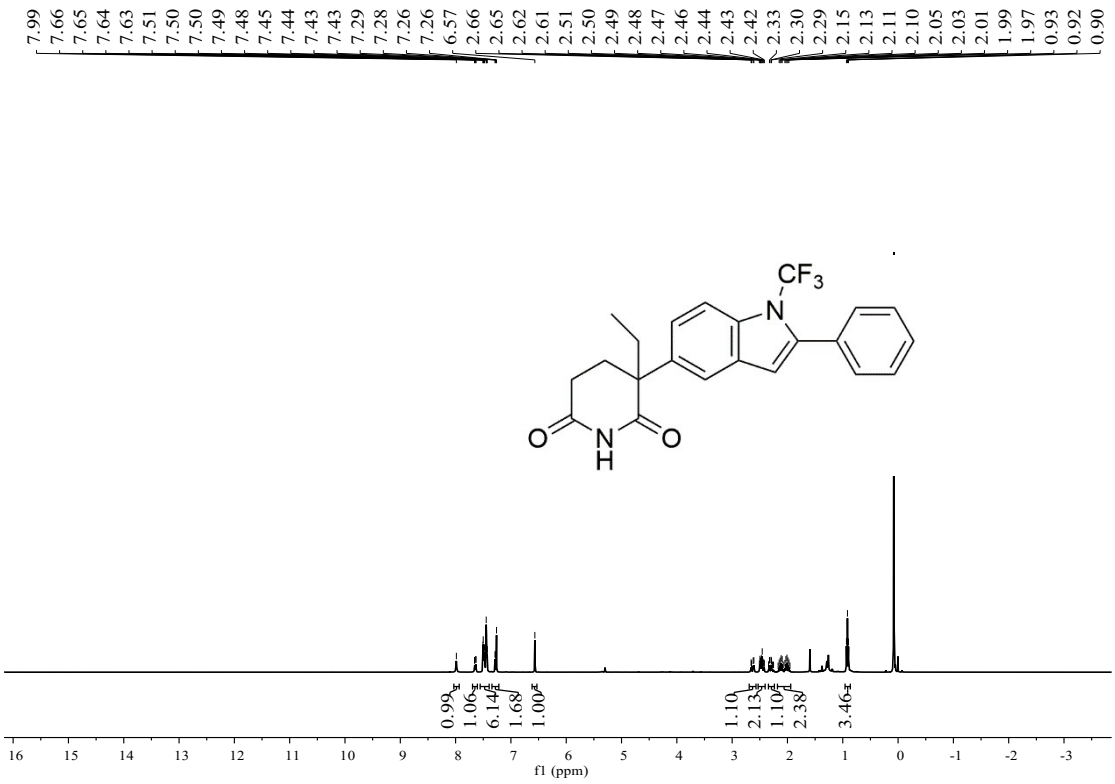
^{19}F NMR Spectrum of **3bm** (376 MHz, $CDCl_3$)



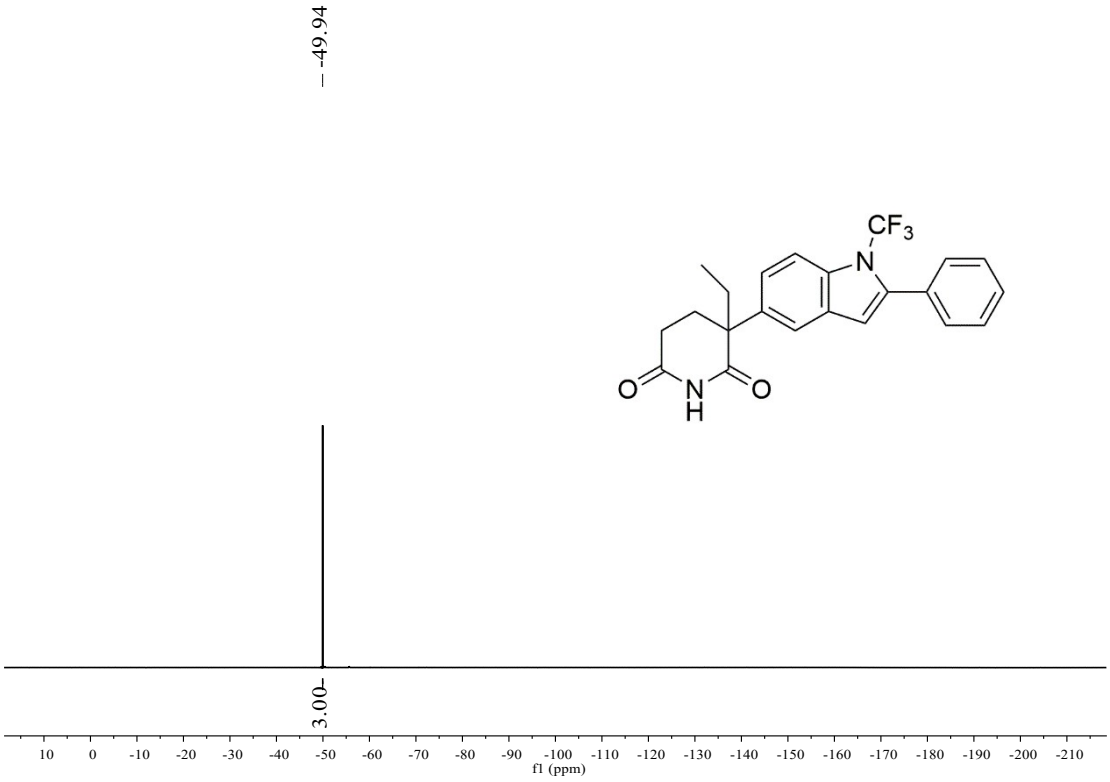
^{13}C NMR Spectrum of **3bm** (101 MHz, $CDCl_3$)



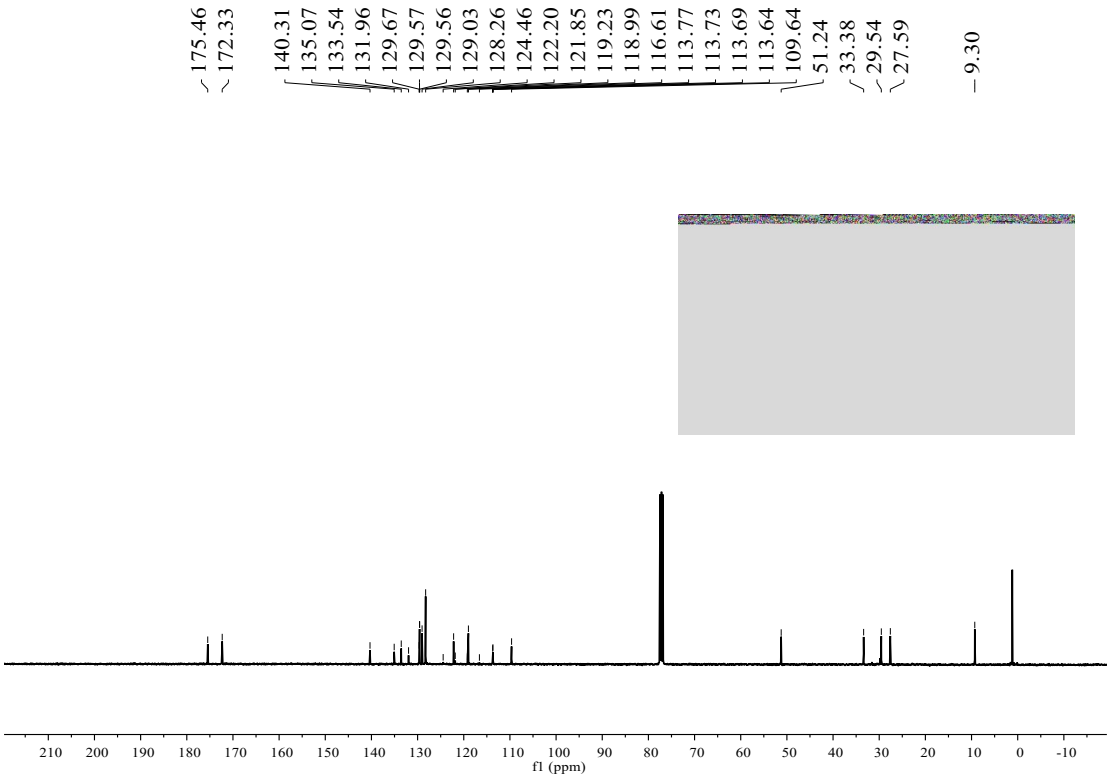
^{1}H NMR Spectrum of **3bn** (400 MHz, $CDCl_3$)



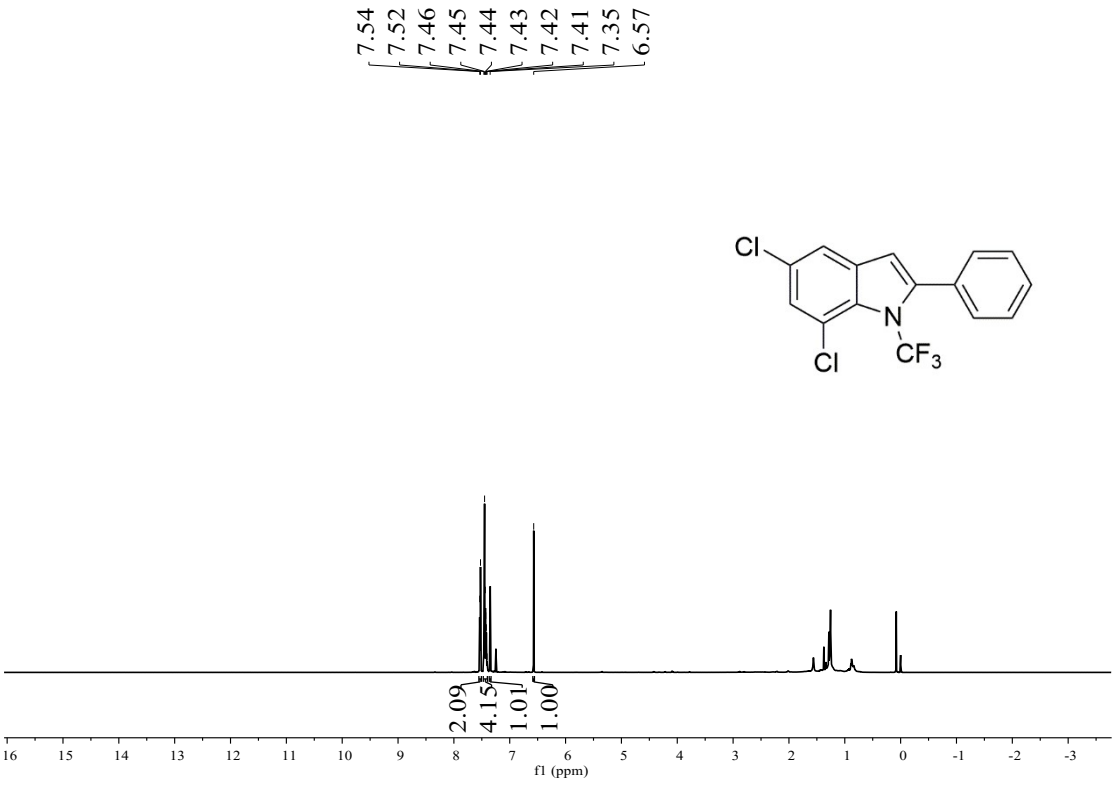
^{19}F NMR Spectrum of **3bn** (376 MHz, $CDCl_3$)



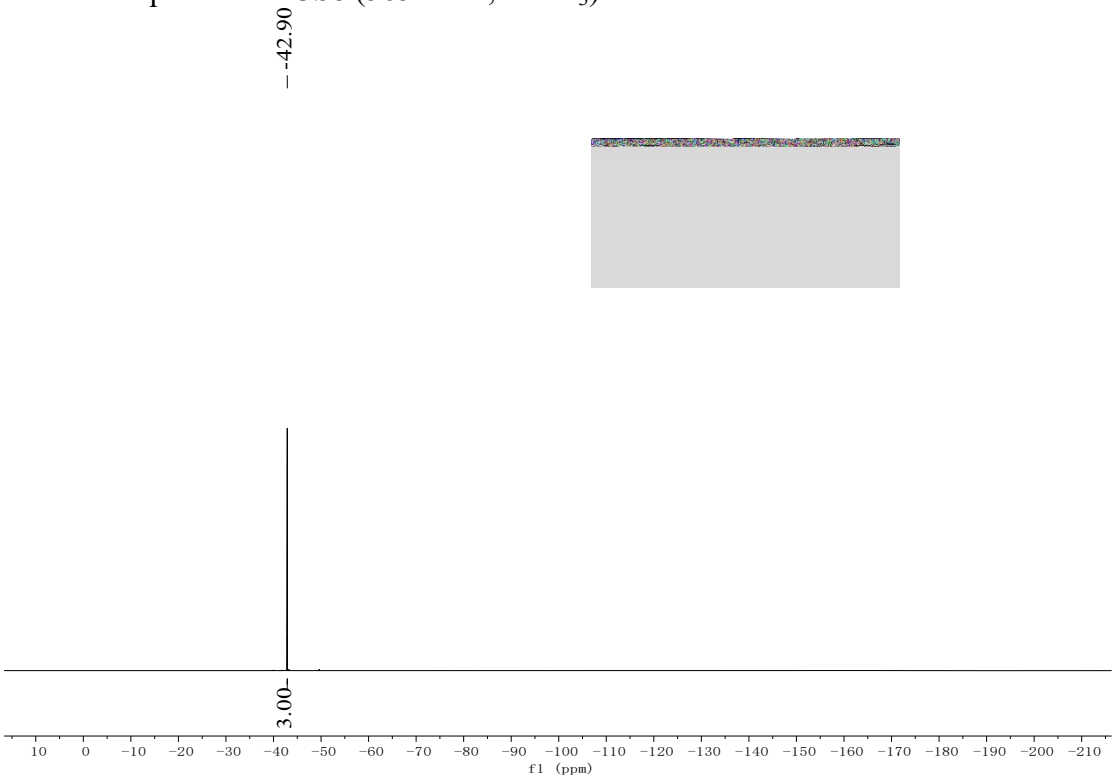
^{13}C NMR Spectrum of **3bn** (101 MHz, $CDCl_3$)



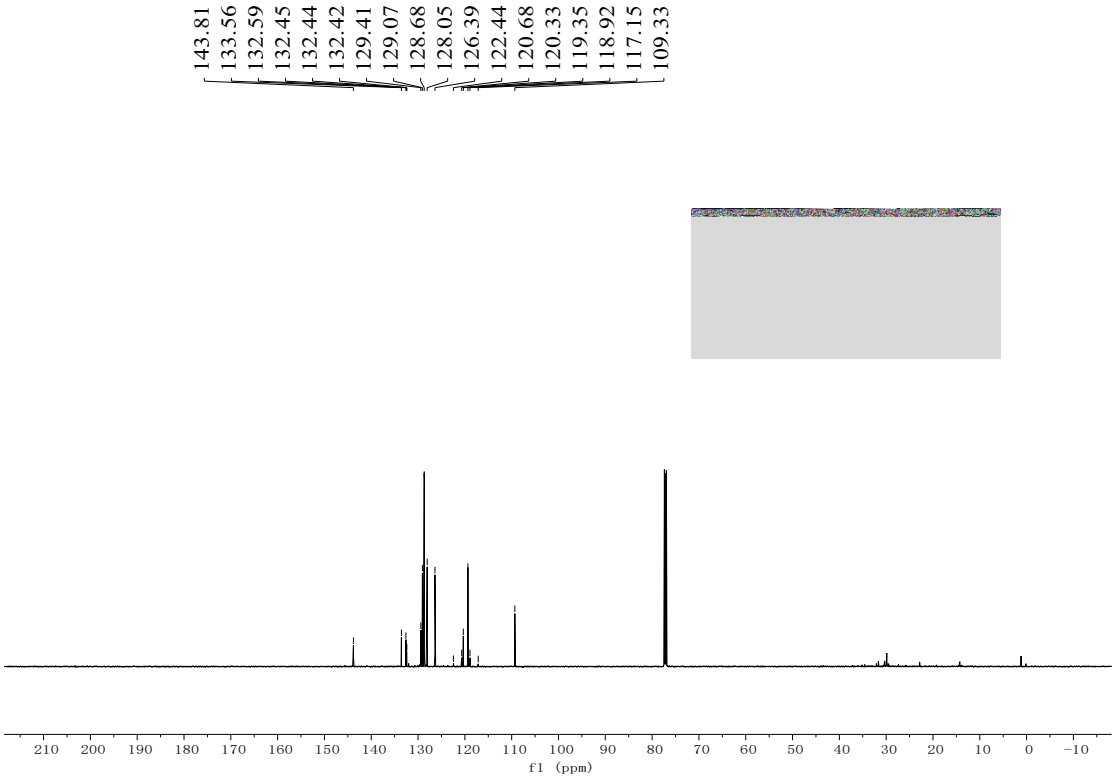
^{1}H NMR Spectrum of **3bo** (600 MHz, $CDCl_3$)



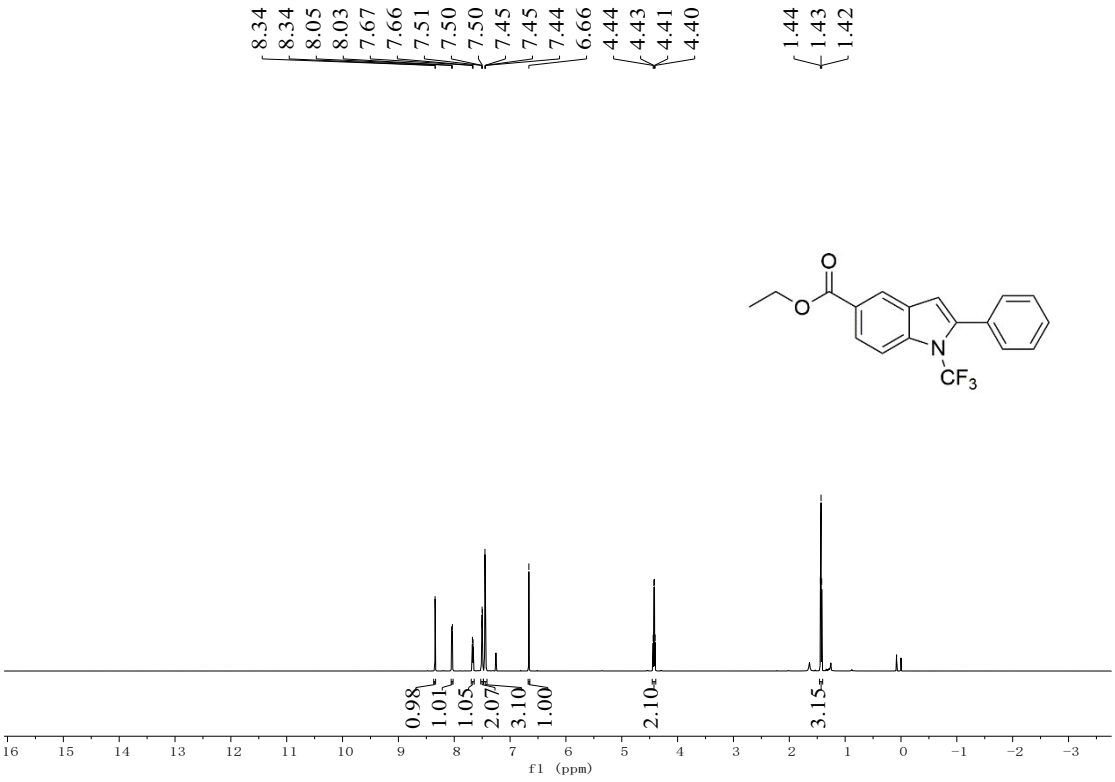
^{19}F NMR Spectrum of **3bo** (565 MHz, $CDCl_3$)



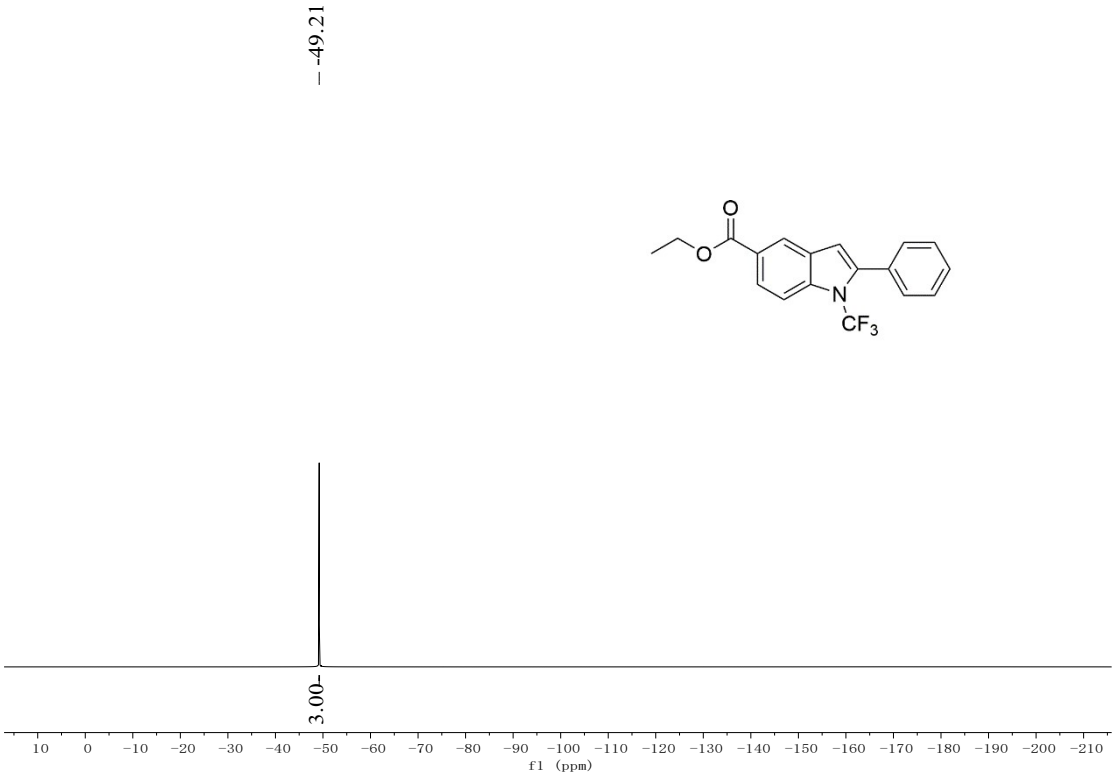
^{13}C NMR Spectrum of **3bo** (151 MHz, $CDCl_3$)



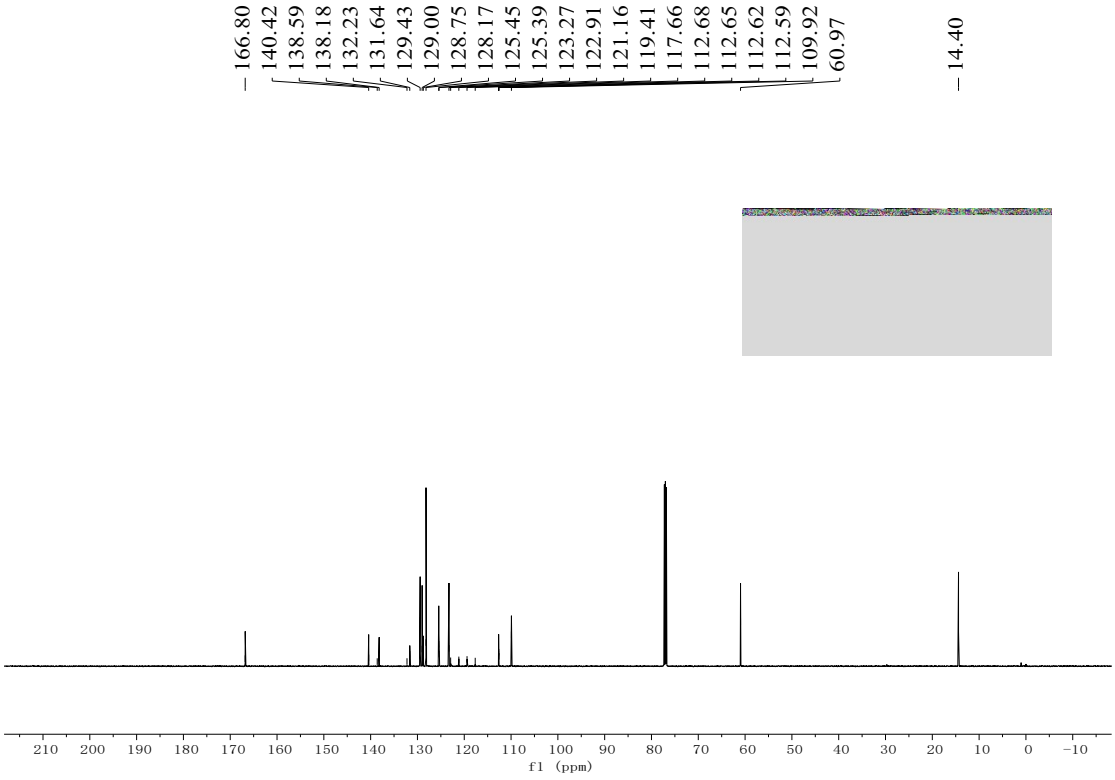
^{1}H NMR Spectrum of **3bp** (600 MHz, $CDCl_3$)



^{19}F NMR Spectrum of **3bp** (565 MHz, $CDCl_3$)

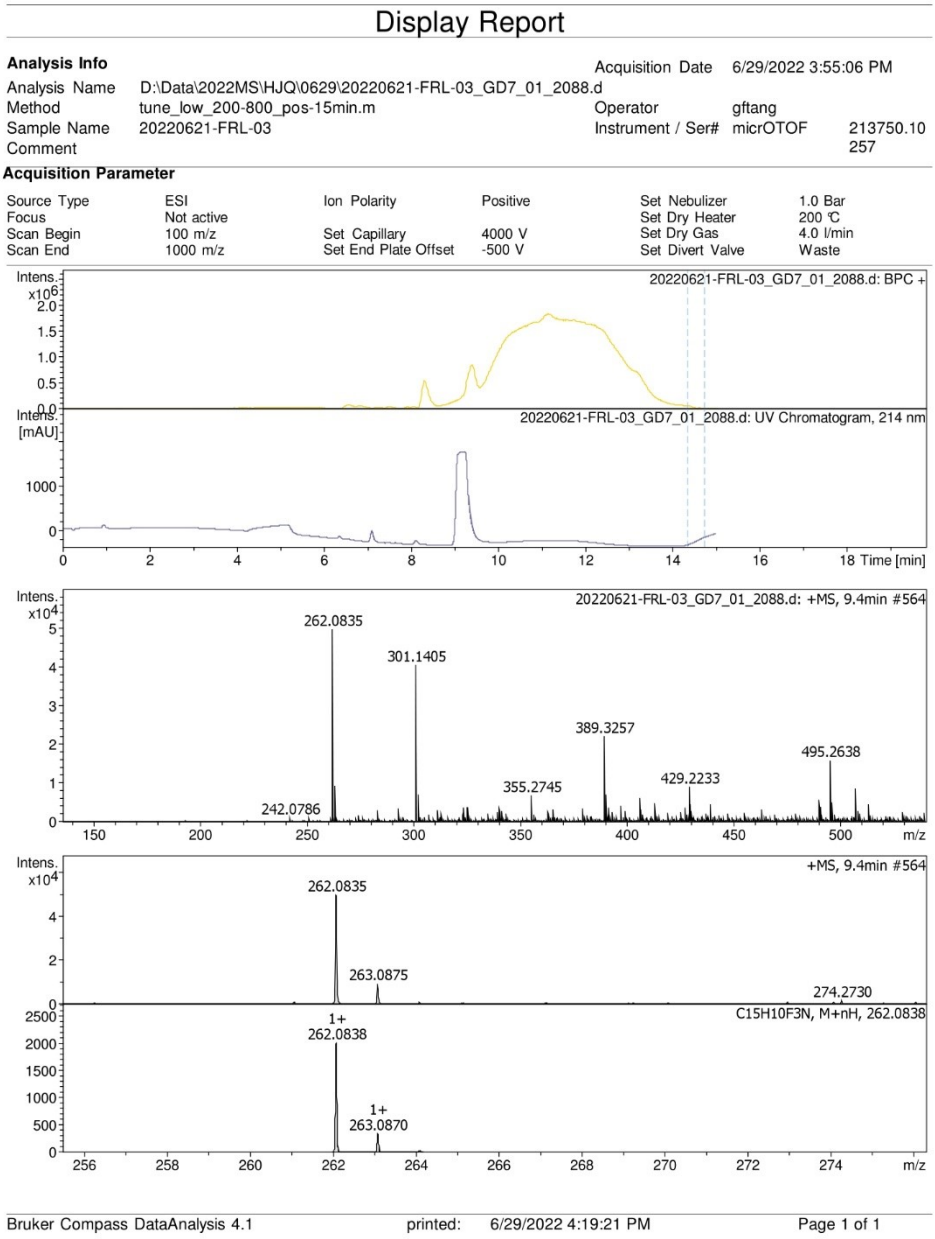


^{13}C NMR Spectrum of **3bp** (151 MHz, $CDCl_3$)

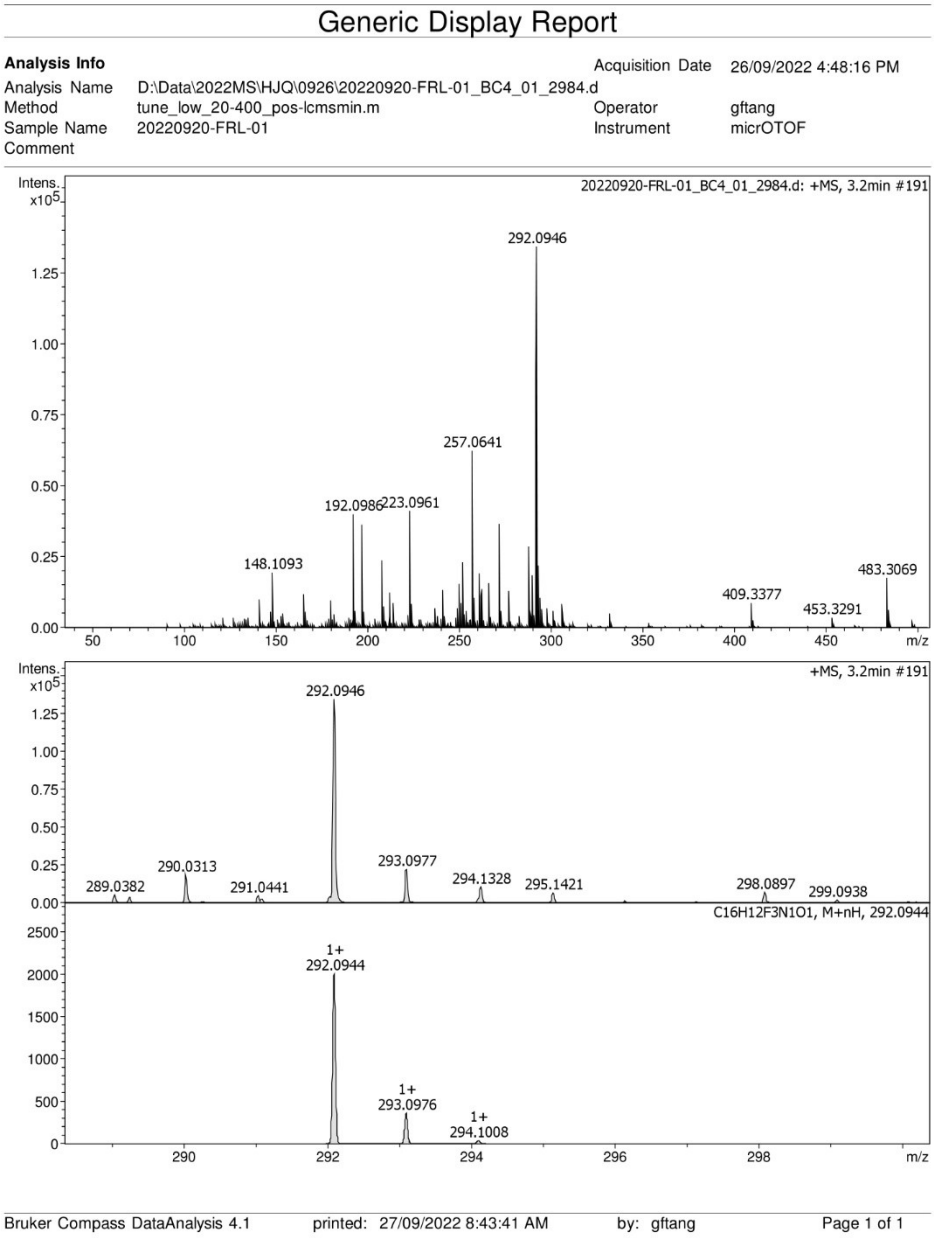


10. HRMS analysis reports for the new compounds

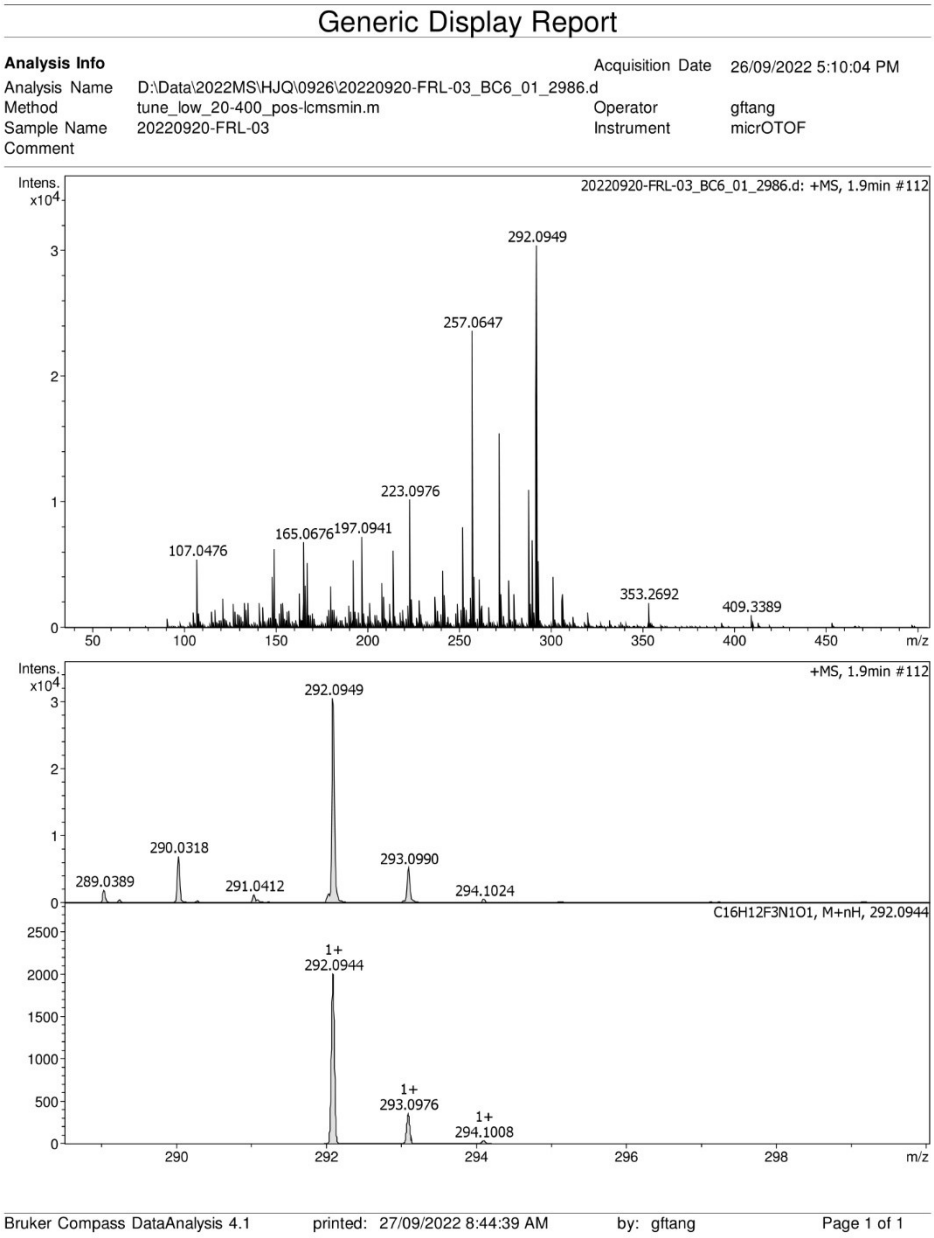
HRMS (ESI) spectra of **3aa**



HRMS (ESI) spectra of **3ab**



HRMS (ESI) spectra of **3ac**



HRMS (ESI) spectra of **3ad**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-02_BC5_01_2985.d	Acquisition Date	26/09/2022 4:59:10 PM
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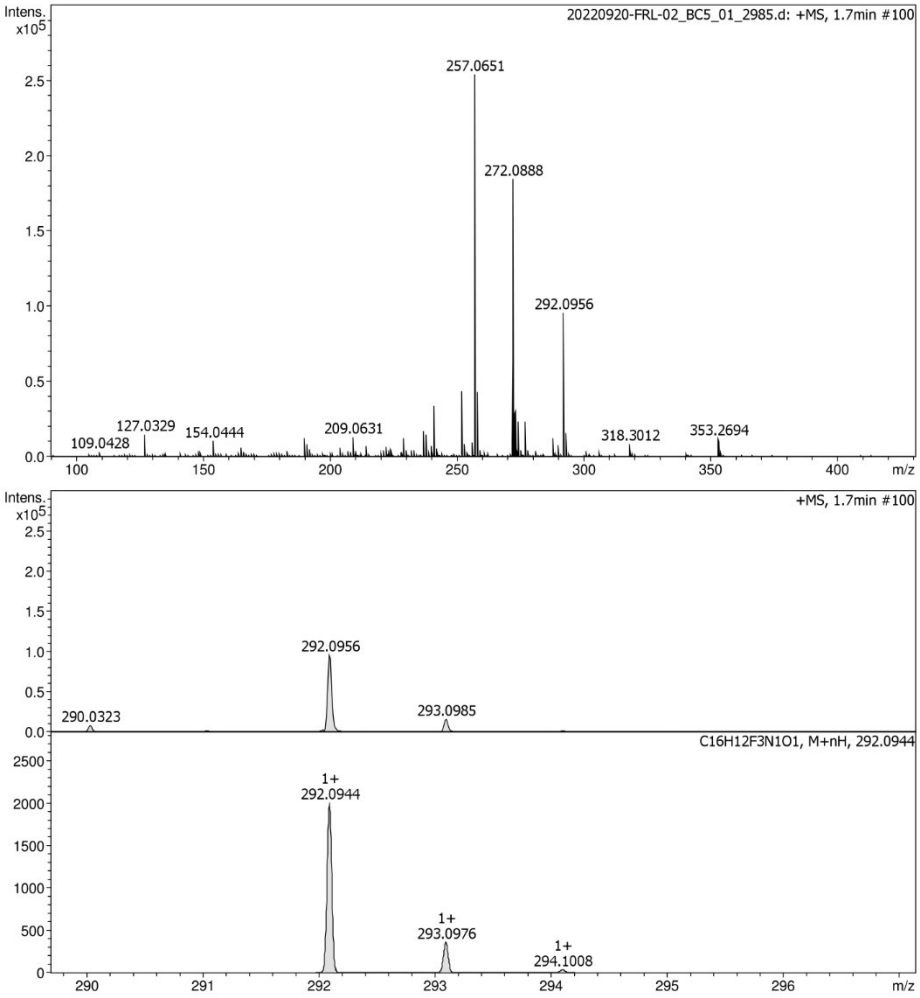
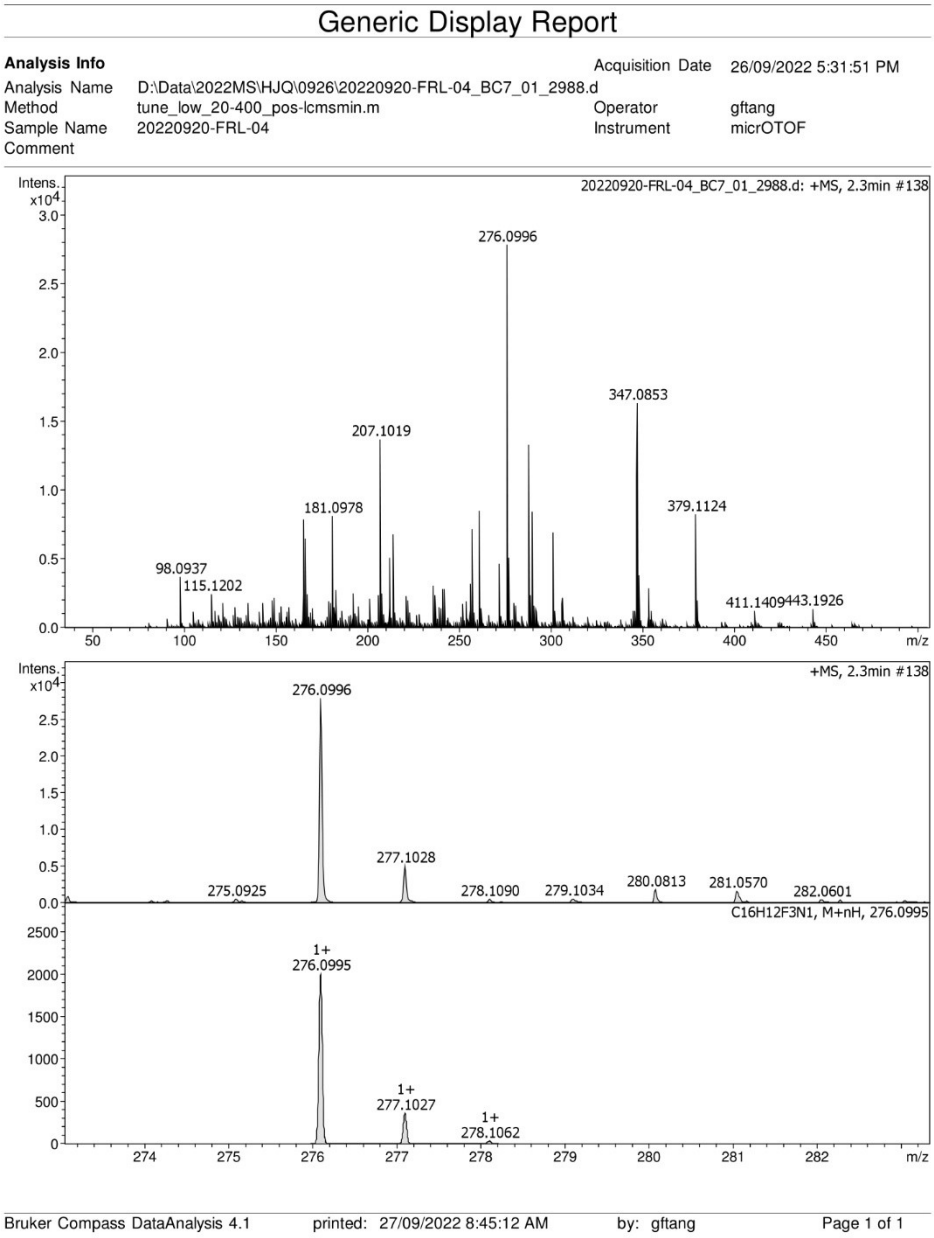
Sample Name	20220920-FRL-02	Instrument	micrOTOF
Comment			



Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 8:44:15 AM by: gftang Page 1 of 1

HRMS (ESI) spectra of **3ae**



HRMS (ESI) spectra of **3af**

Generic Display Report

Analysis Info

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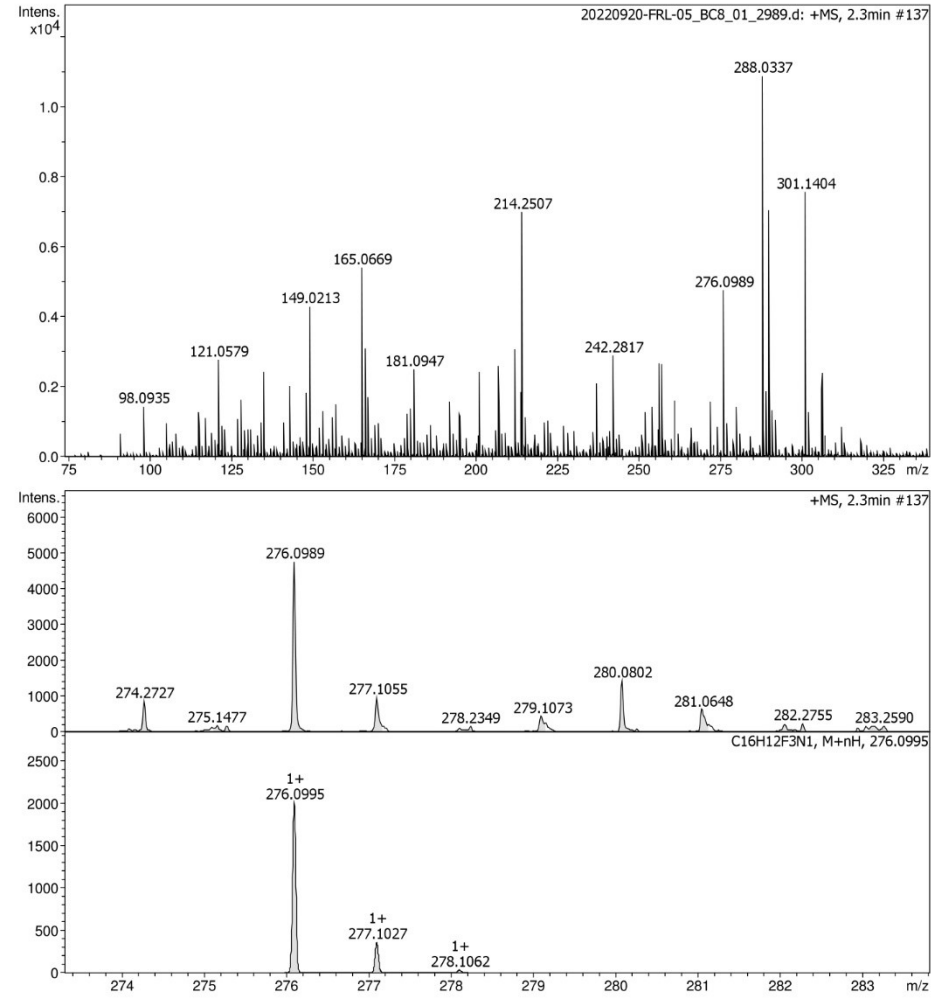

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HRMS (ESI) spectra of **3ag**

Generic Display Report

Analysis Info

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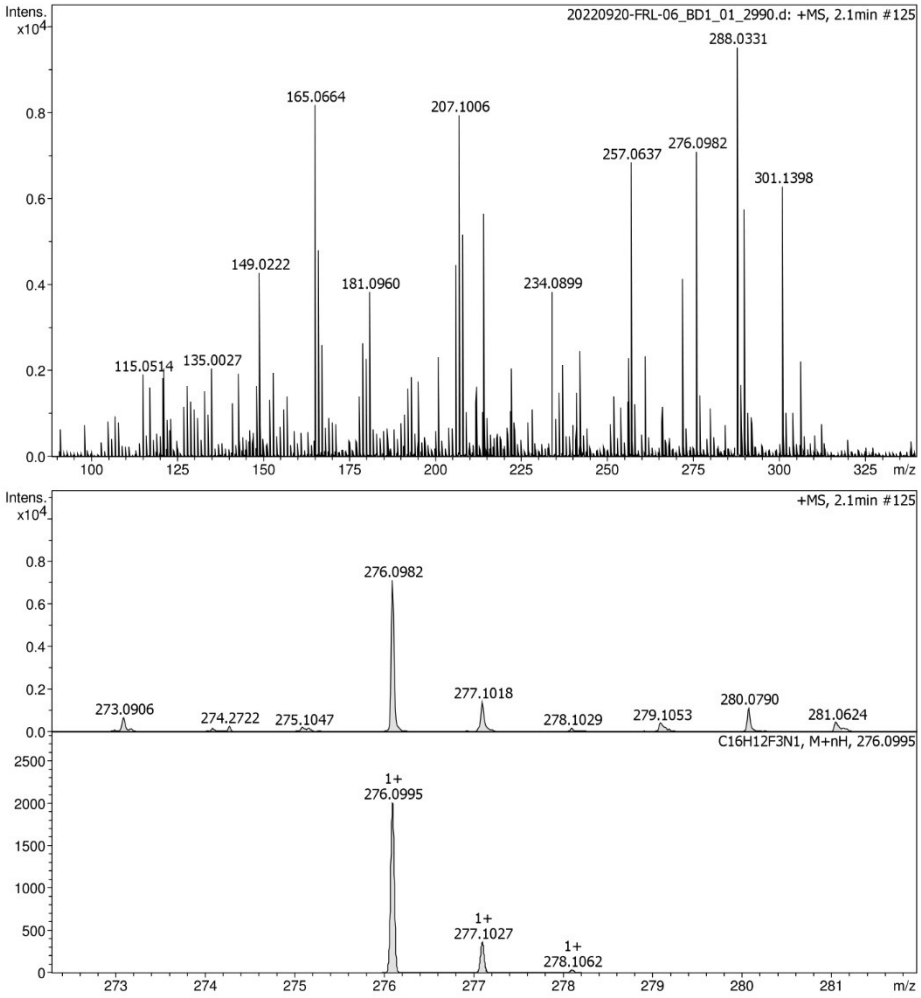
Comment			



Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 8:46:56 AM by: gftang Page 1 of 1

HRMS (ESI) spectra of **3ah**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-18_BE5_01_3002.d	Acquisition Date	26/09/2022 8:04:29 PM
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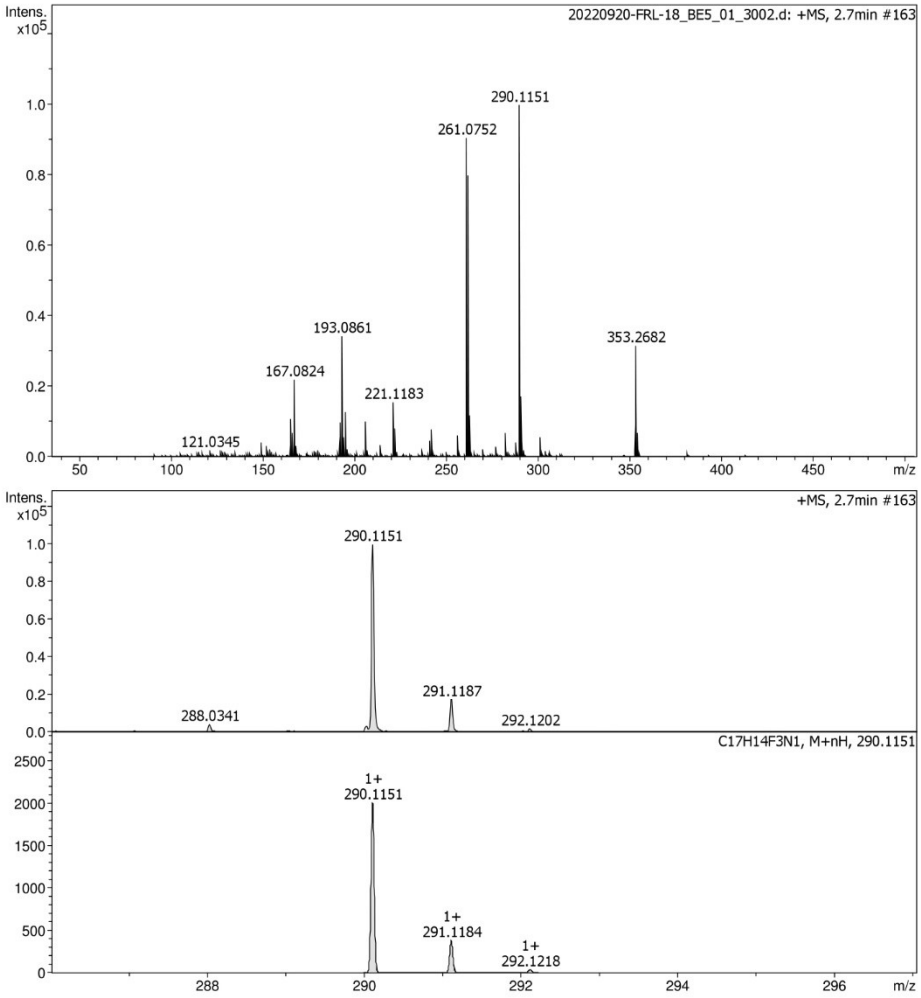
Comment			



Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 8:55:24 AM by: gftang Page 1 of 1

HRMS (ESI) spectra of **3ai**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-19_BE6_01_3003.d	Acquisition Date	26/09/2022 8:15:23 PM
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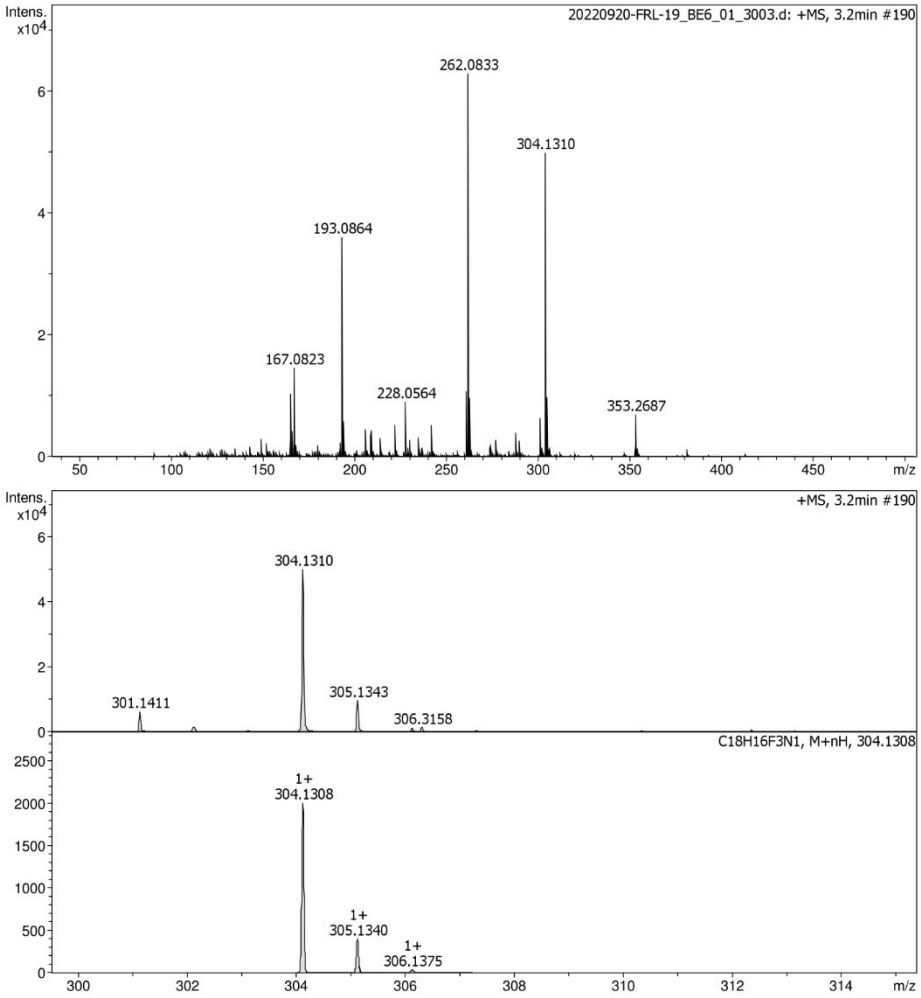

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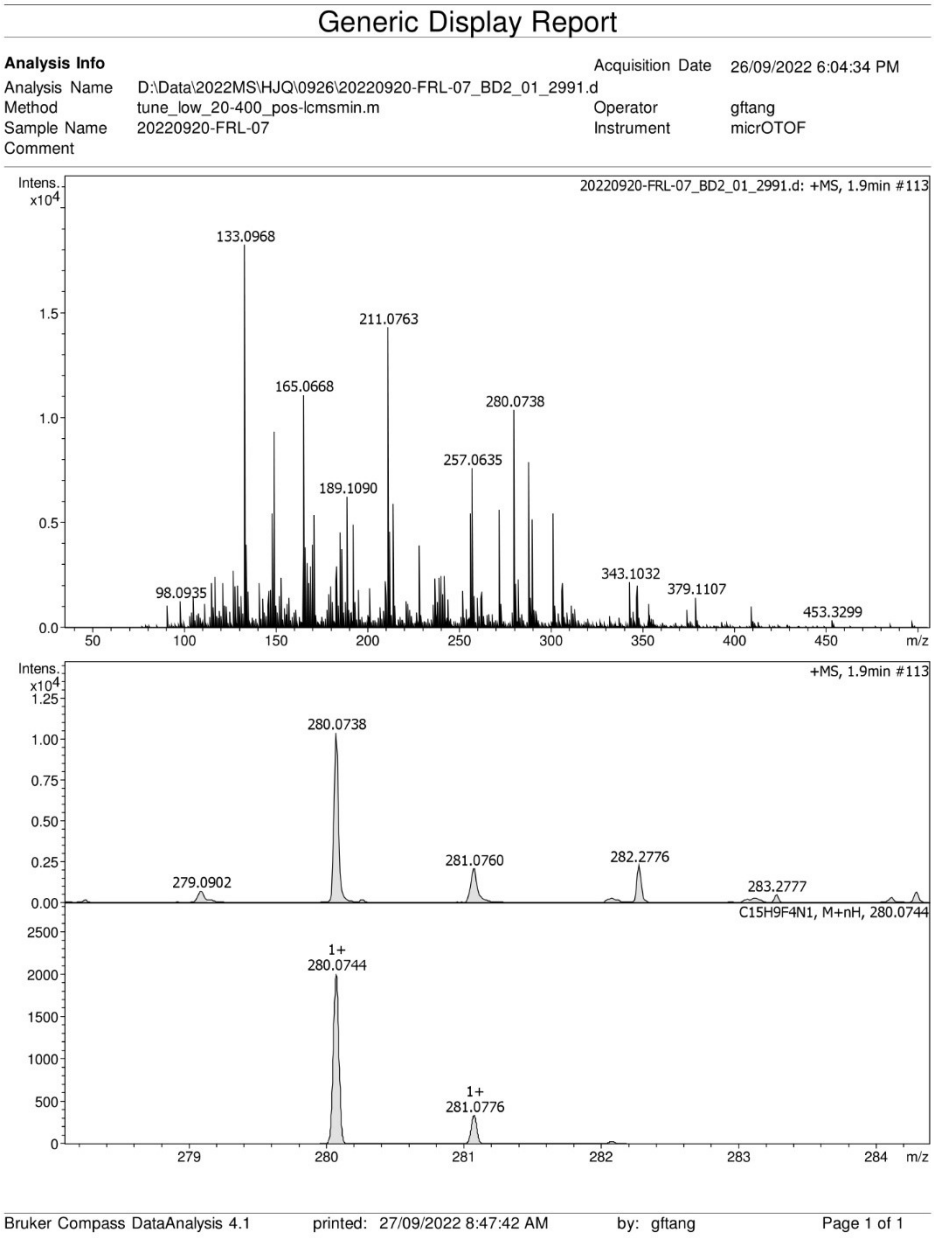
HRMS (ESI) spectra of **3aj**



HRMS (ESI) spectra of **3ak**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-08_BD3_01_2992.d	Acquisition Date	26/09/2022 6:15:27 PM
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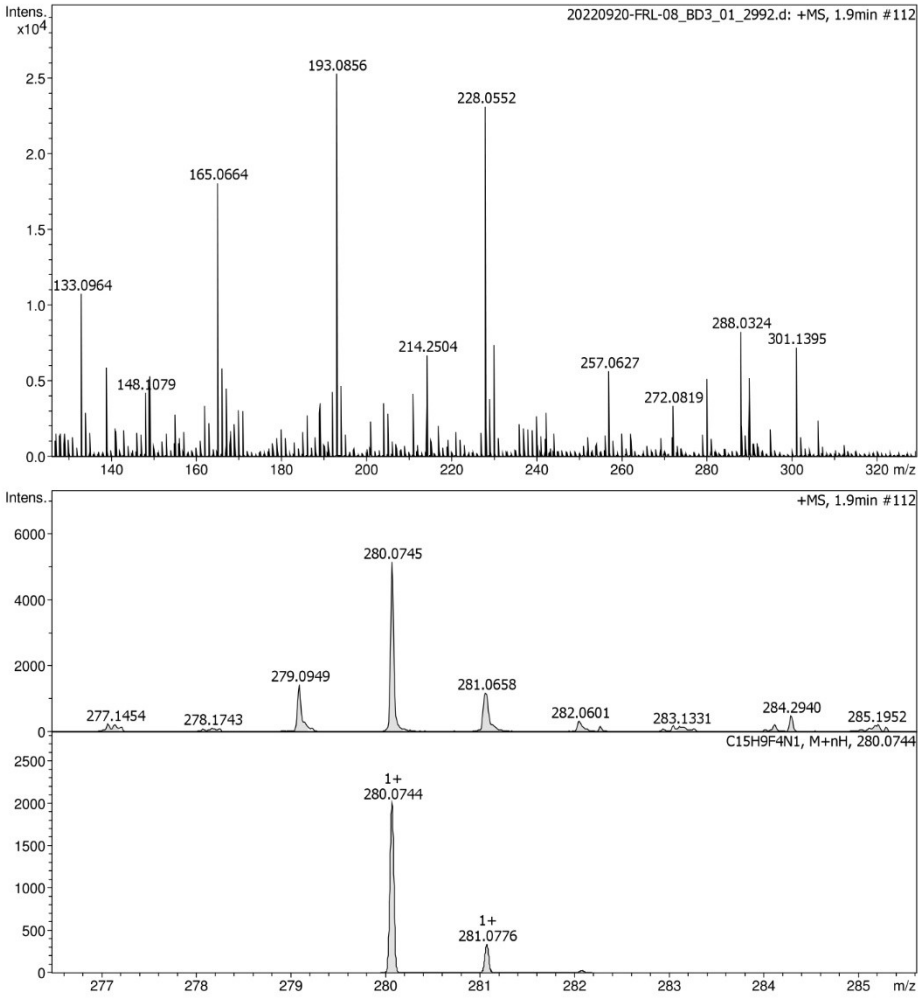
Comment			



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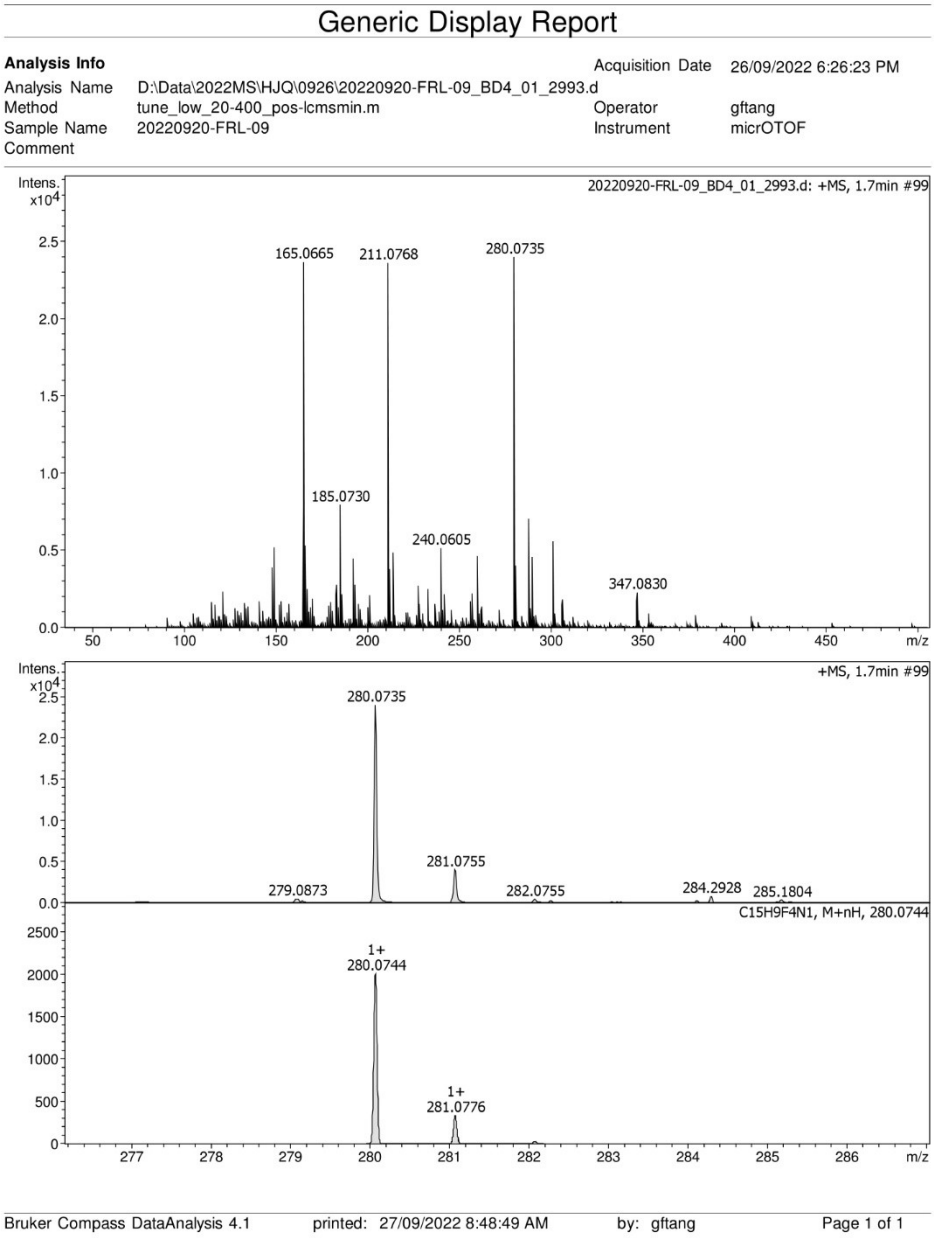
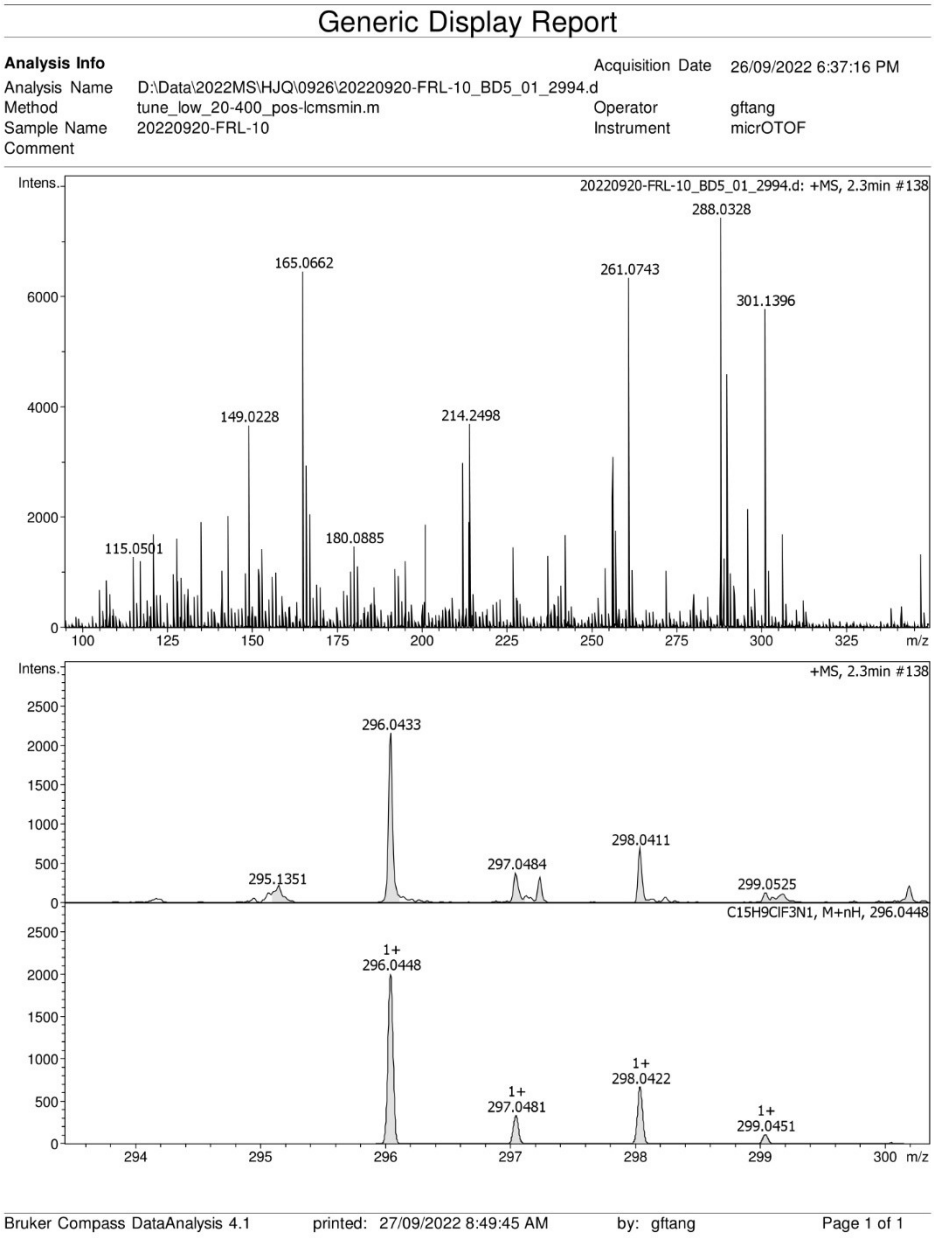
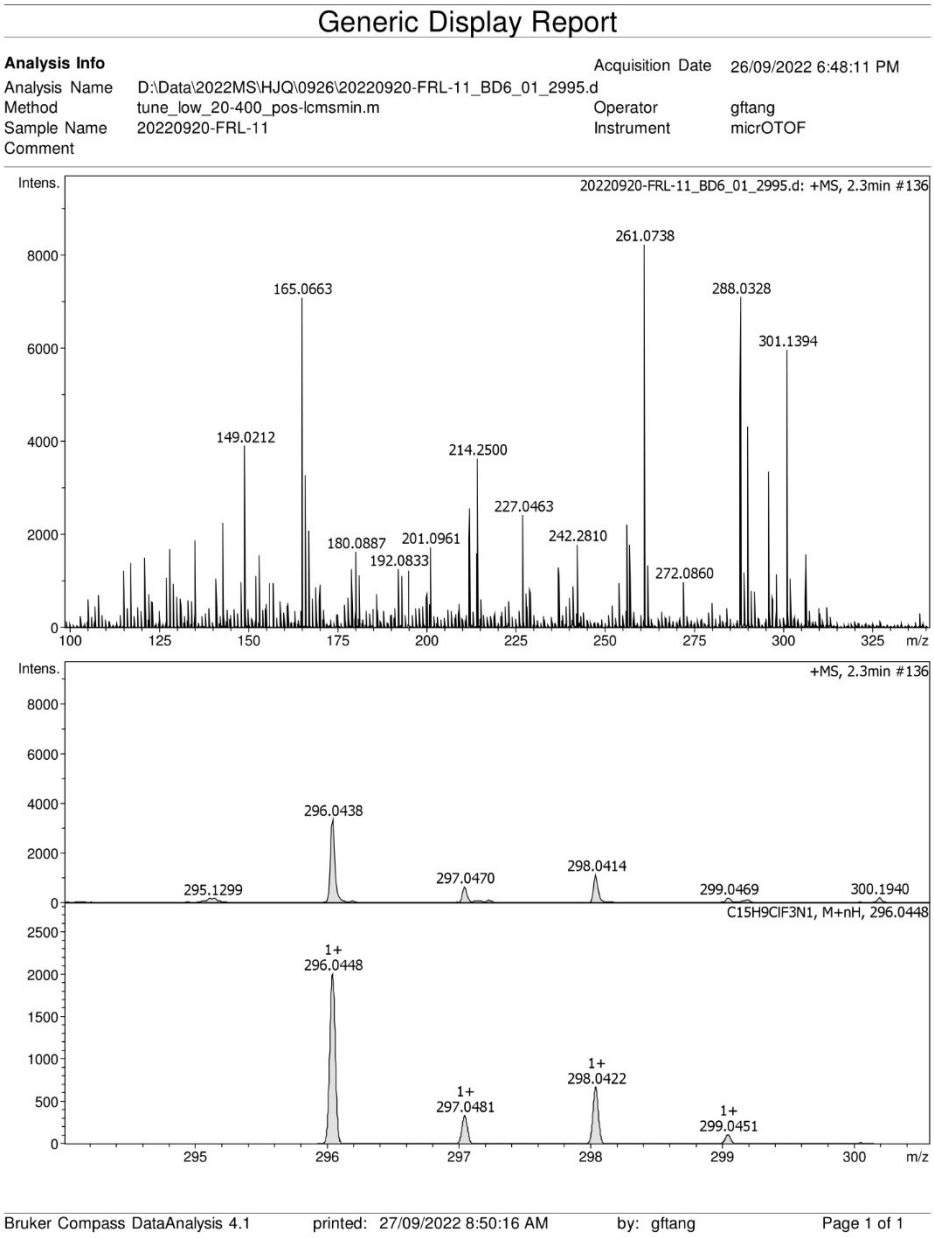
HRMS (ESI) spectra of **3al**



HRMS (ESI) spectra of **3am**



HRMS (ESI) spectra of **3an**



HRMS (ESI) spectra of **3ao**

Generic Display Report

Analysis Info

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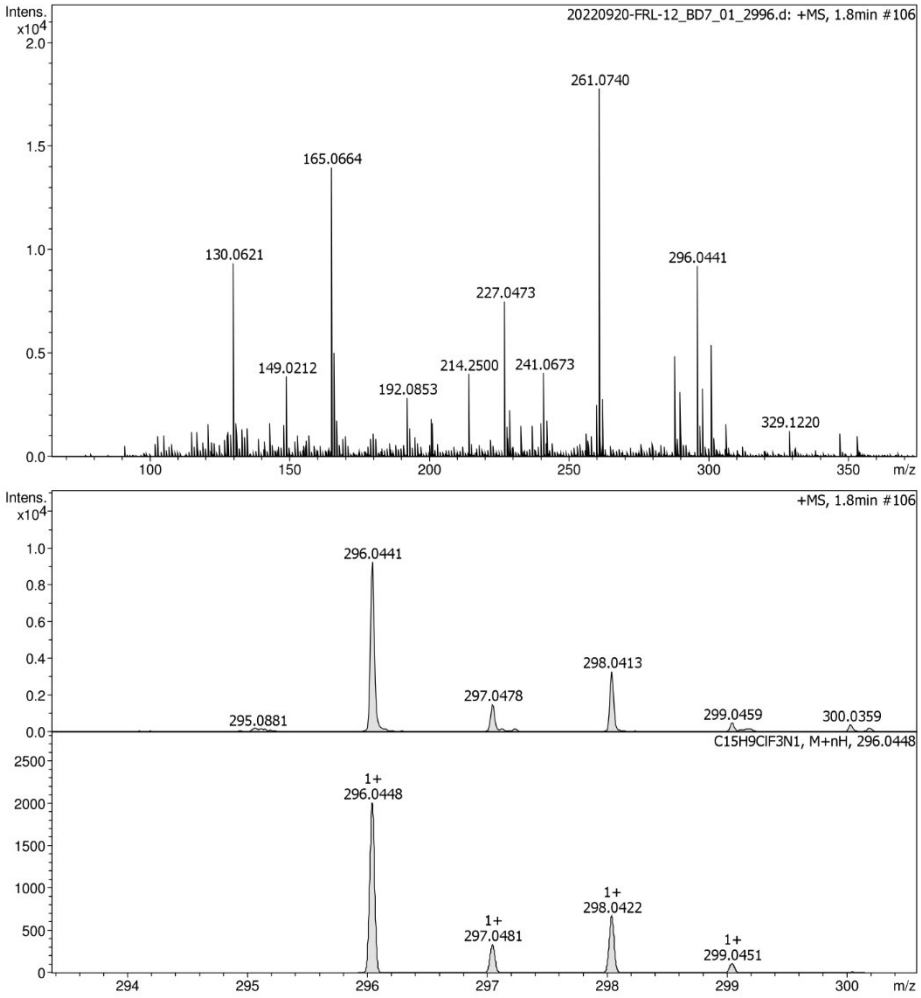
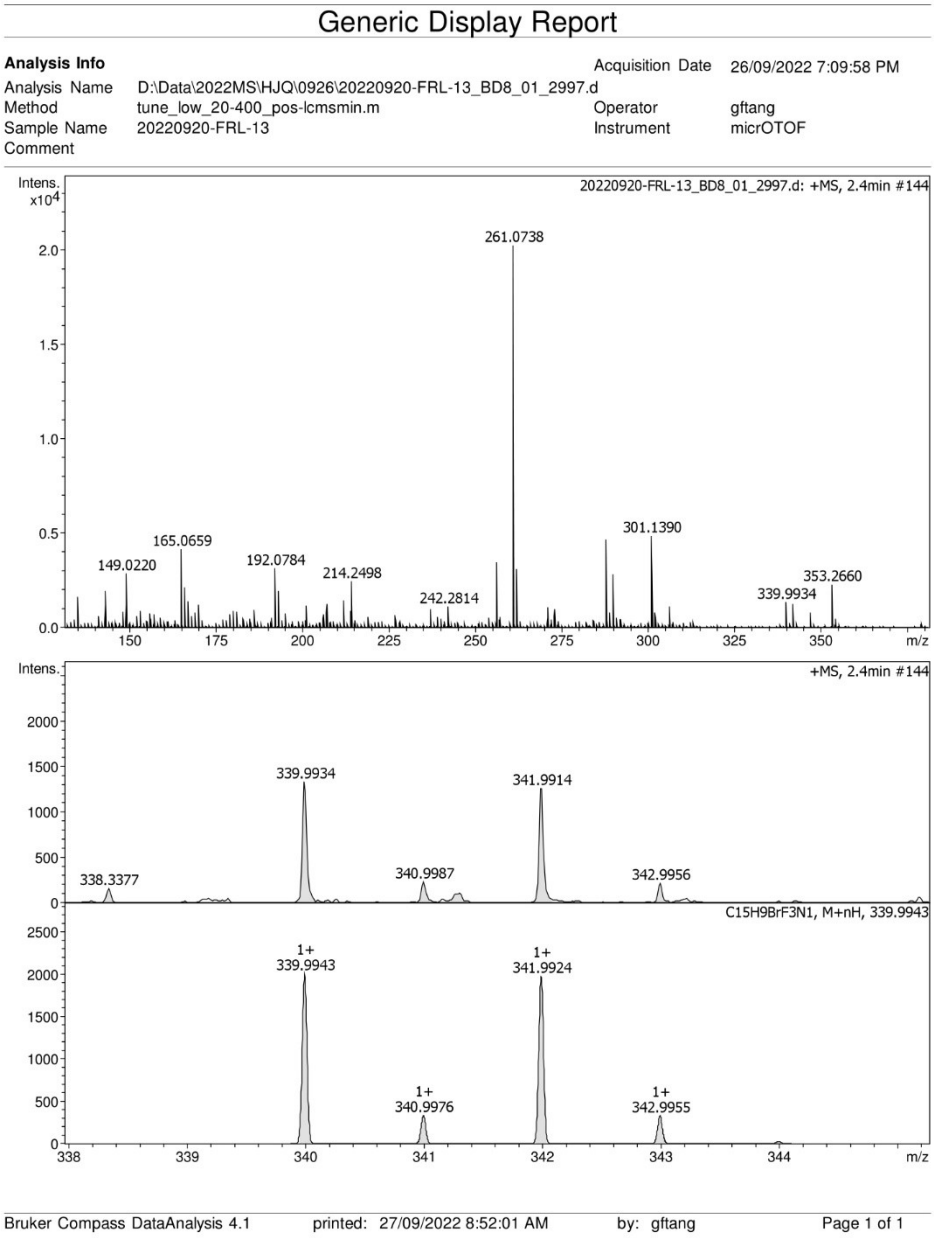
Comment			

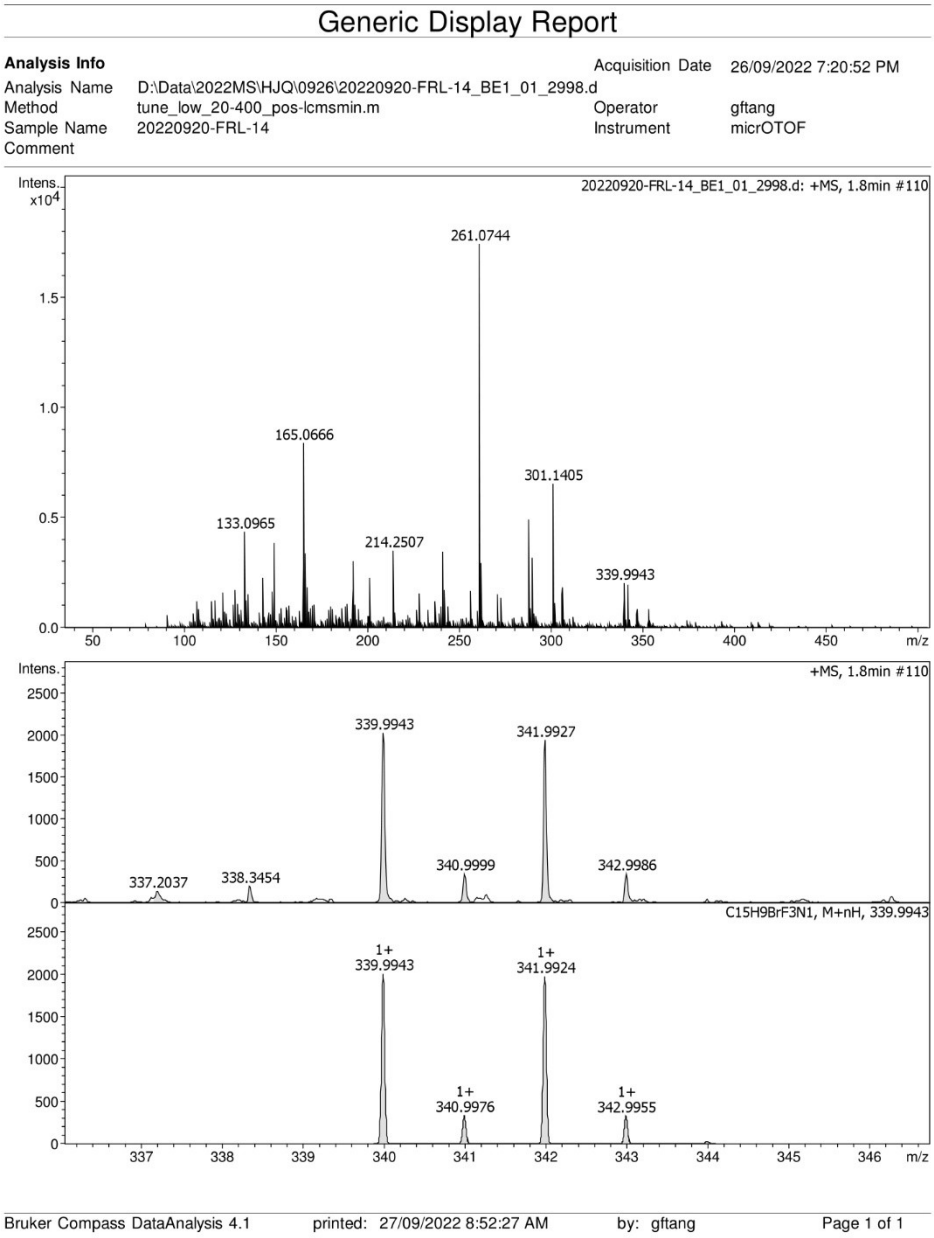


Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 8:51:01 AM by: gftang Page 1 of 1

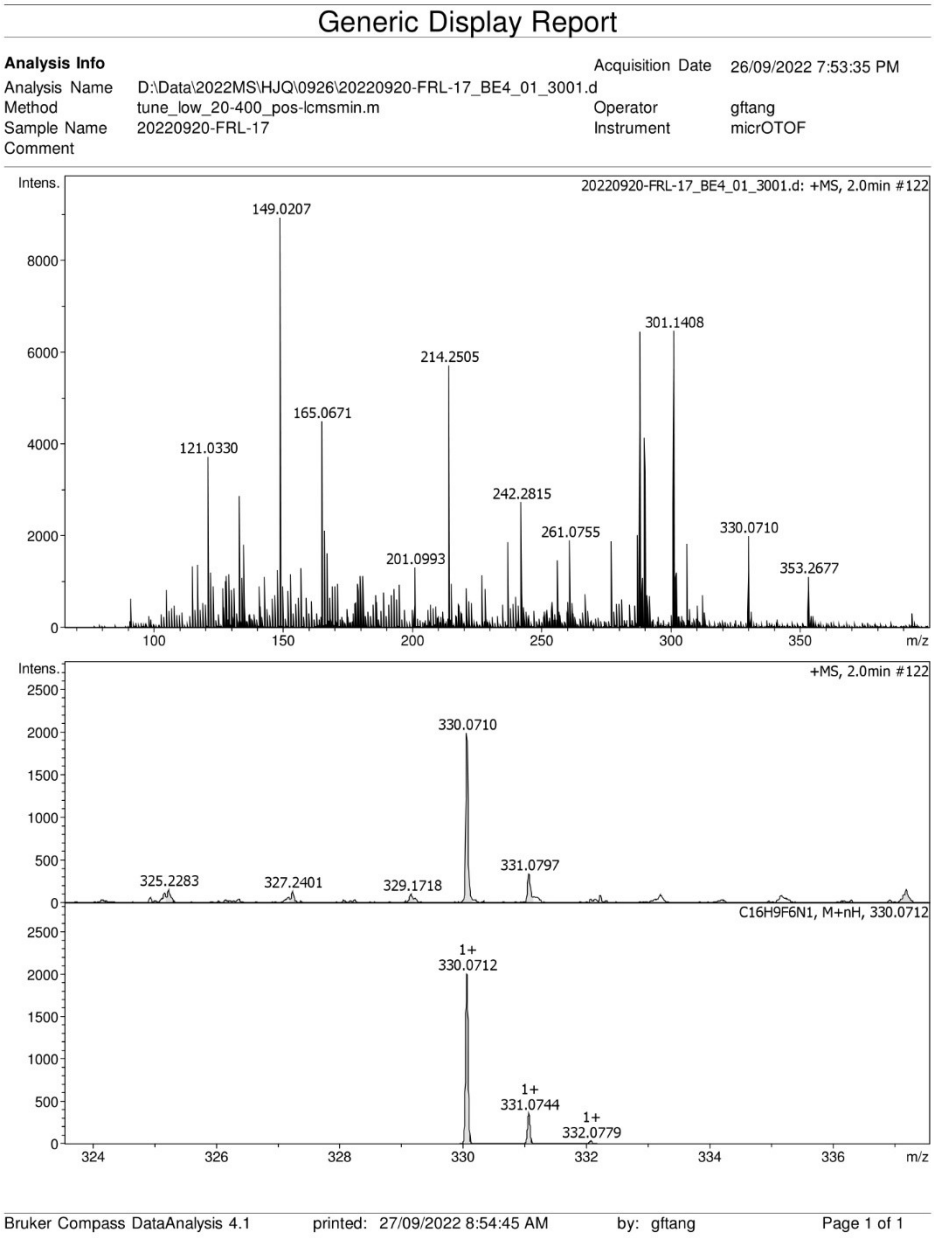
HRMS (ESI) spectra of **3ap**



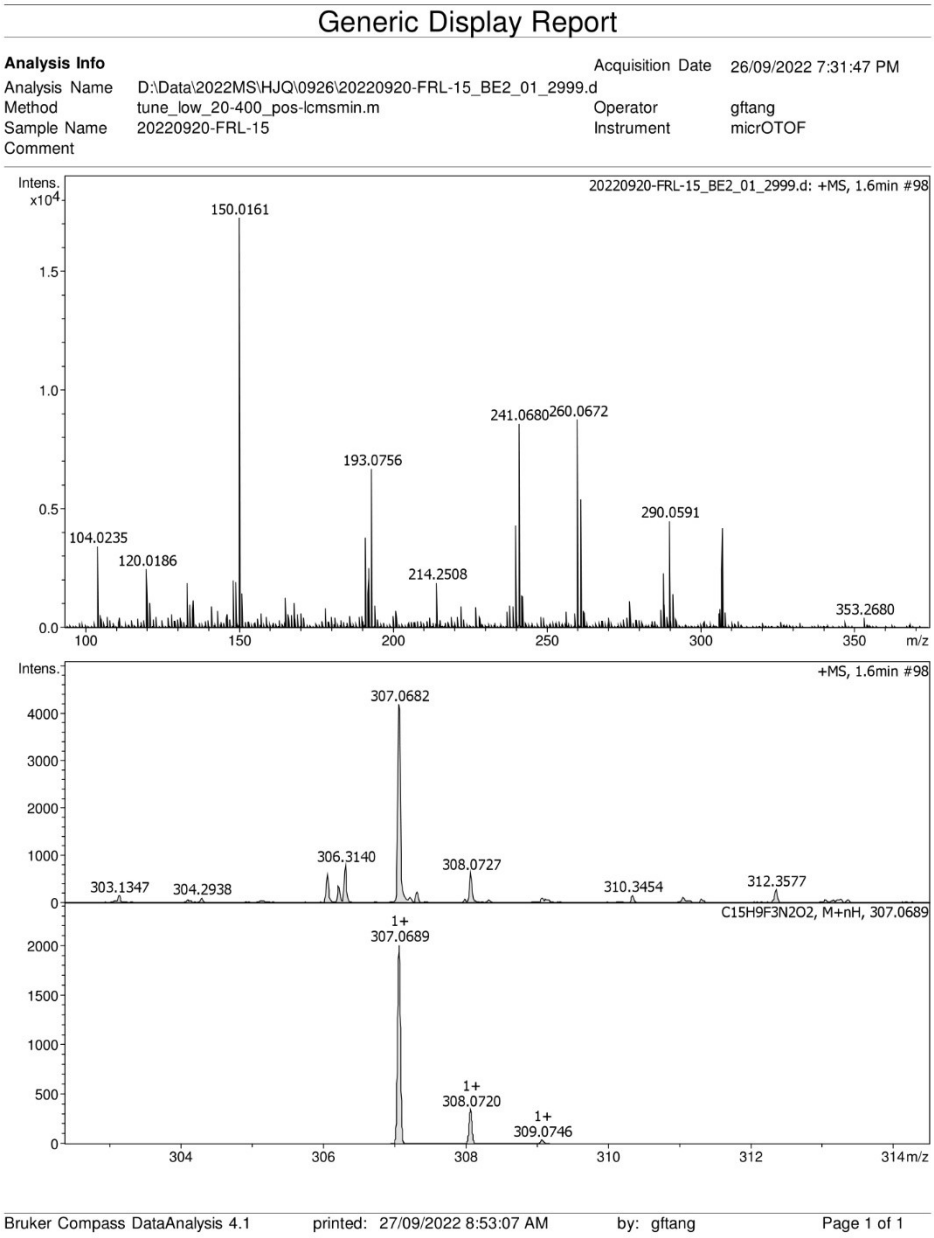
HRMS (ESI) spectra of **3aq**



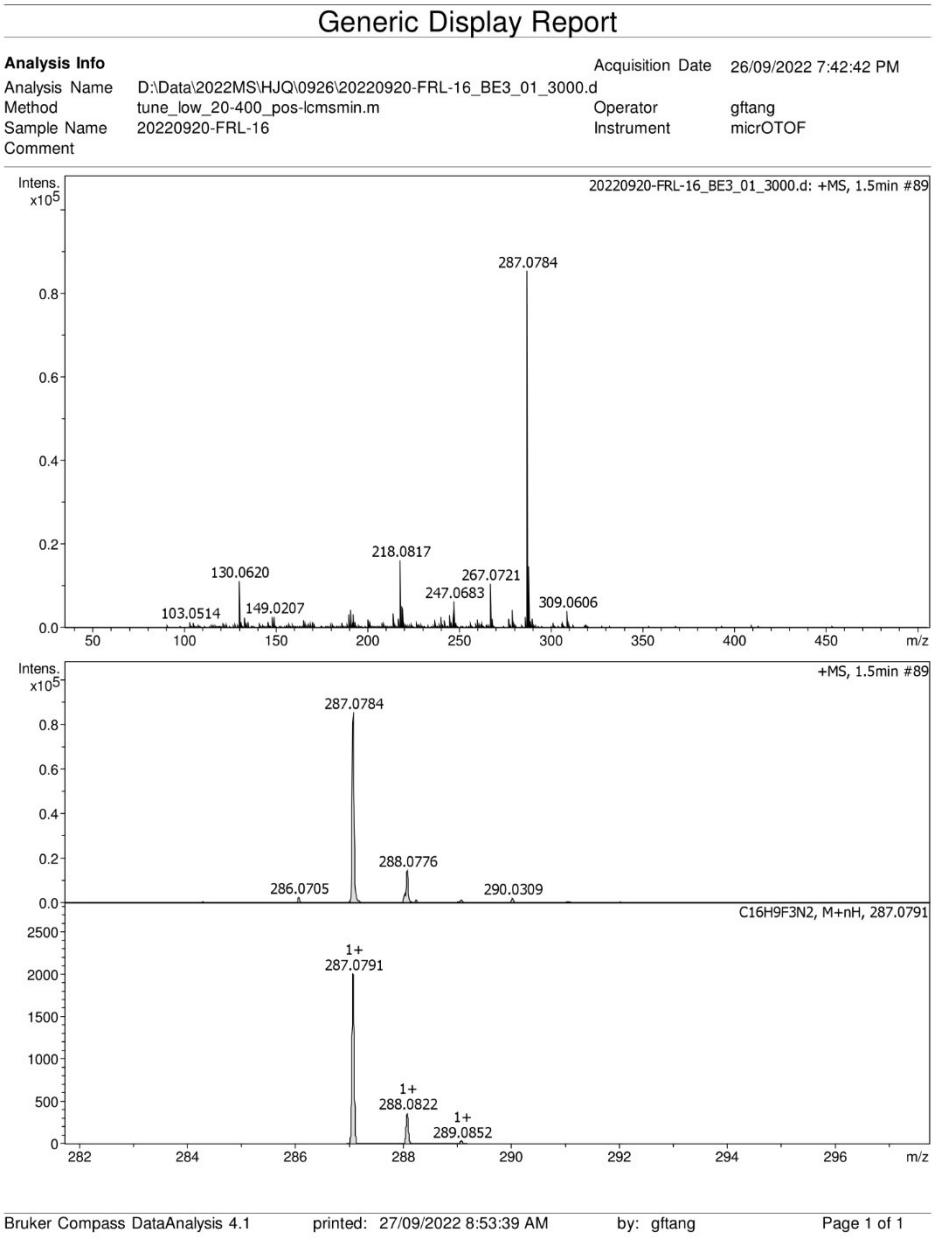
HRMS (ESI) spectra of **3ar**



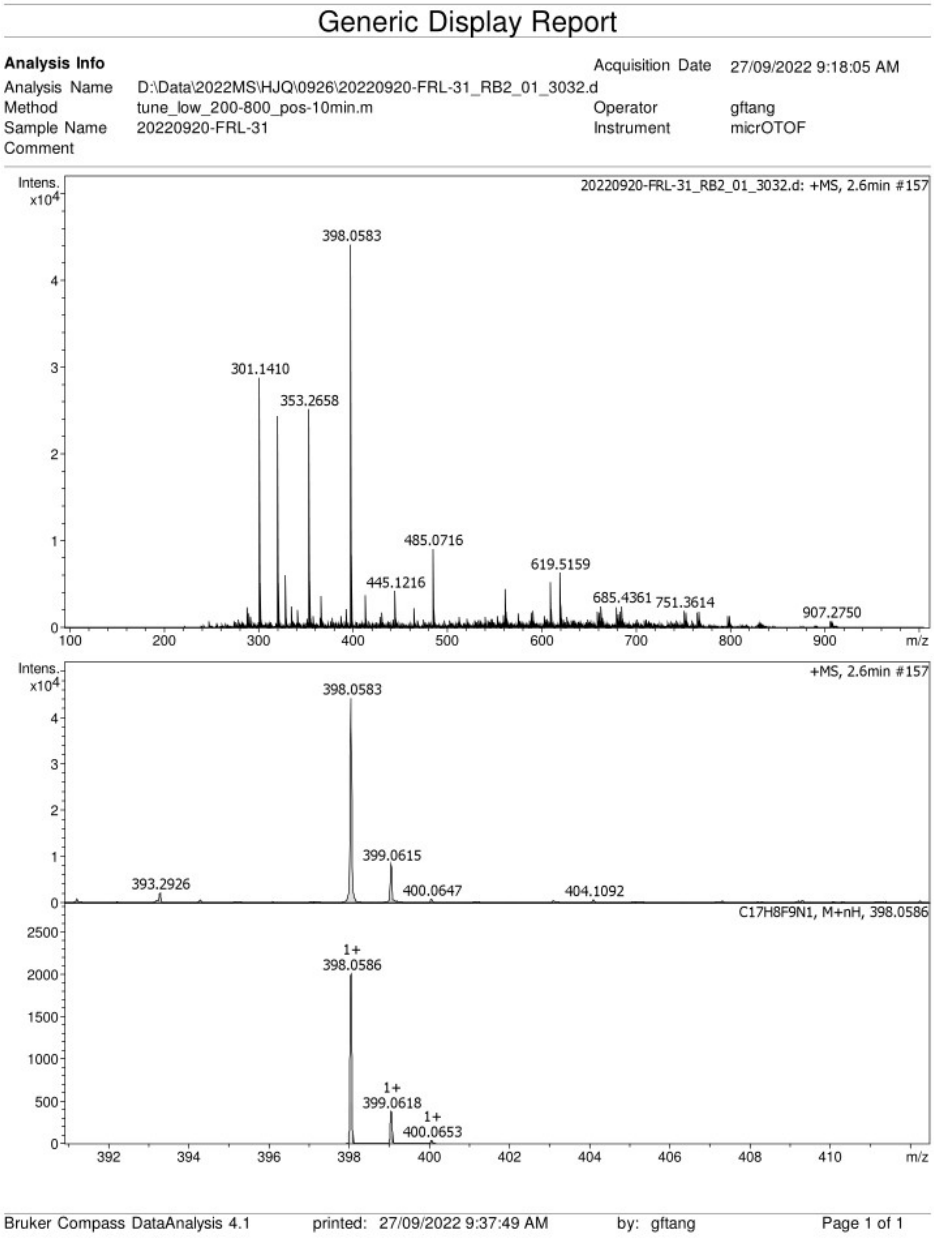
HRMS (ESI) spectra of **3as**



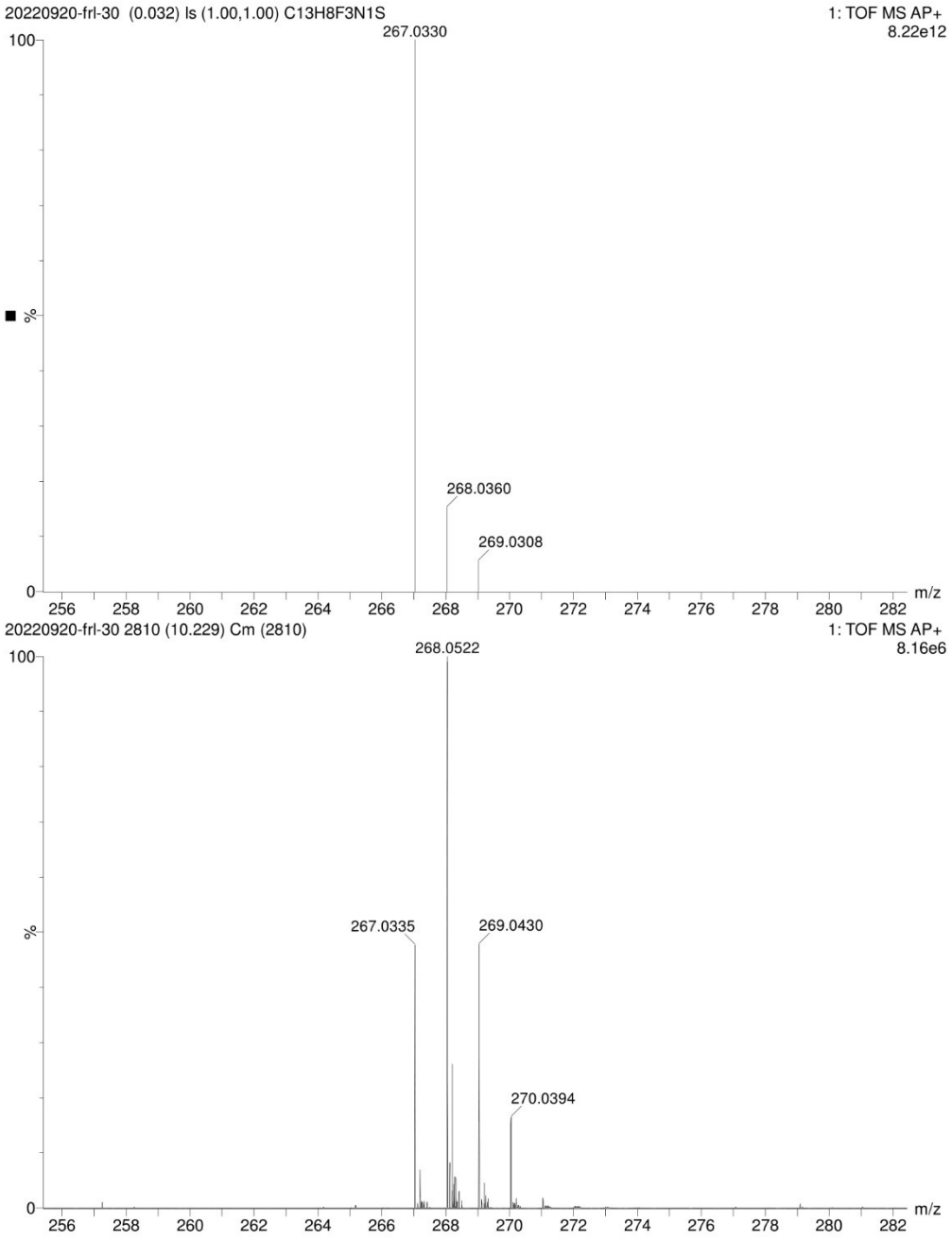
HRMS (ESI) spectra of **3at**



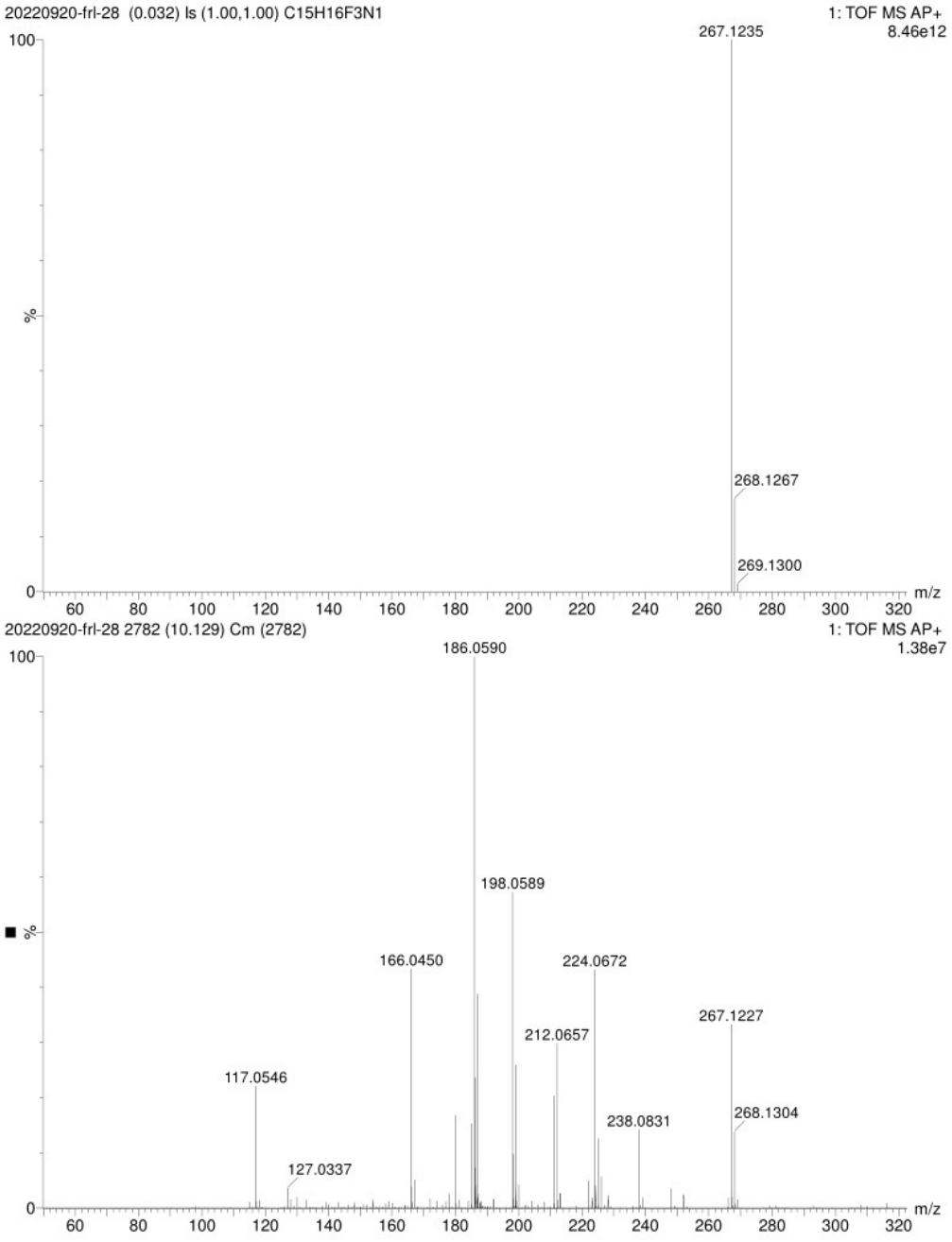
HRMS (ESI) spectra of **3au**



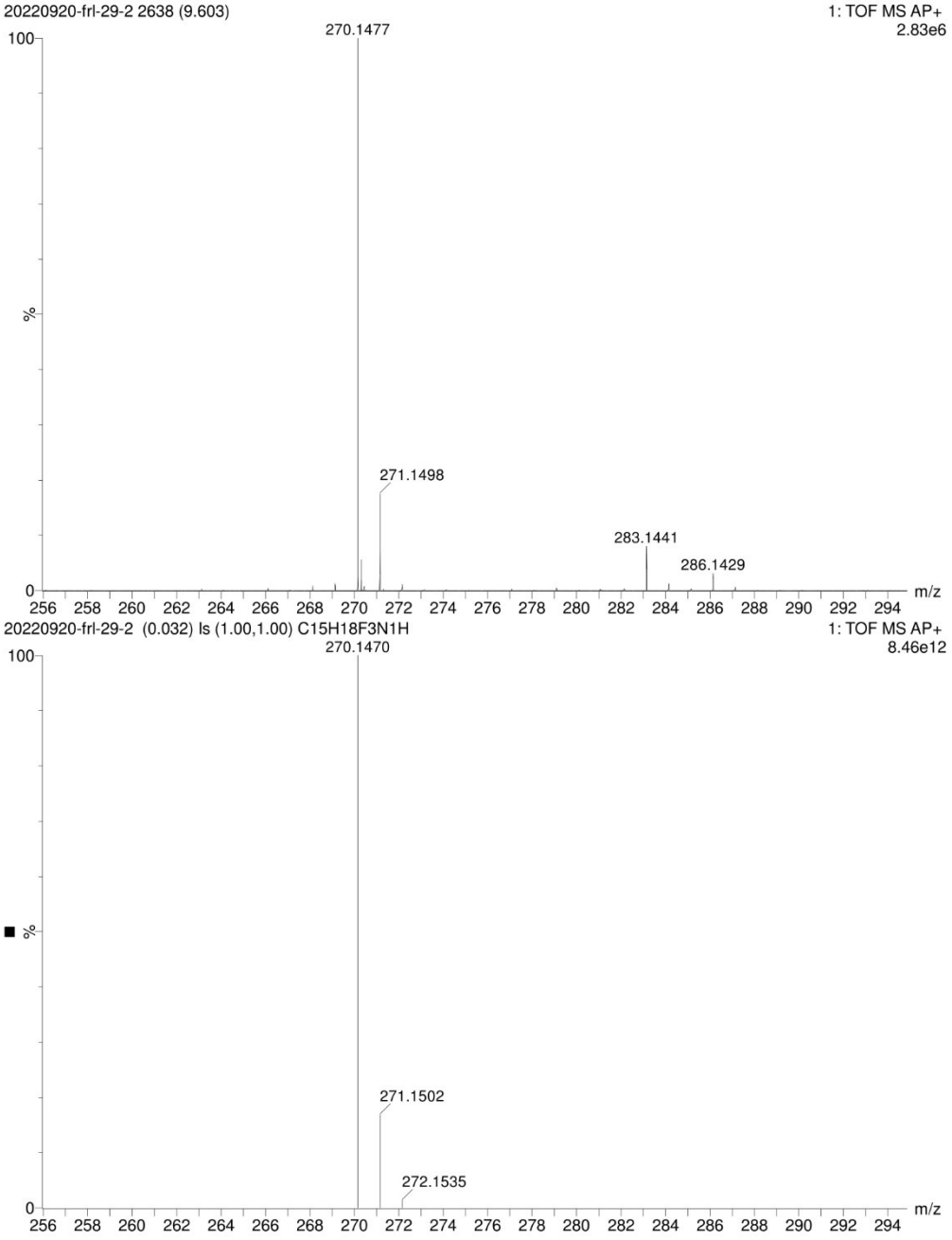
HRMS (AP) spectra of **3av**



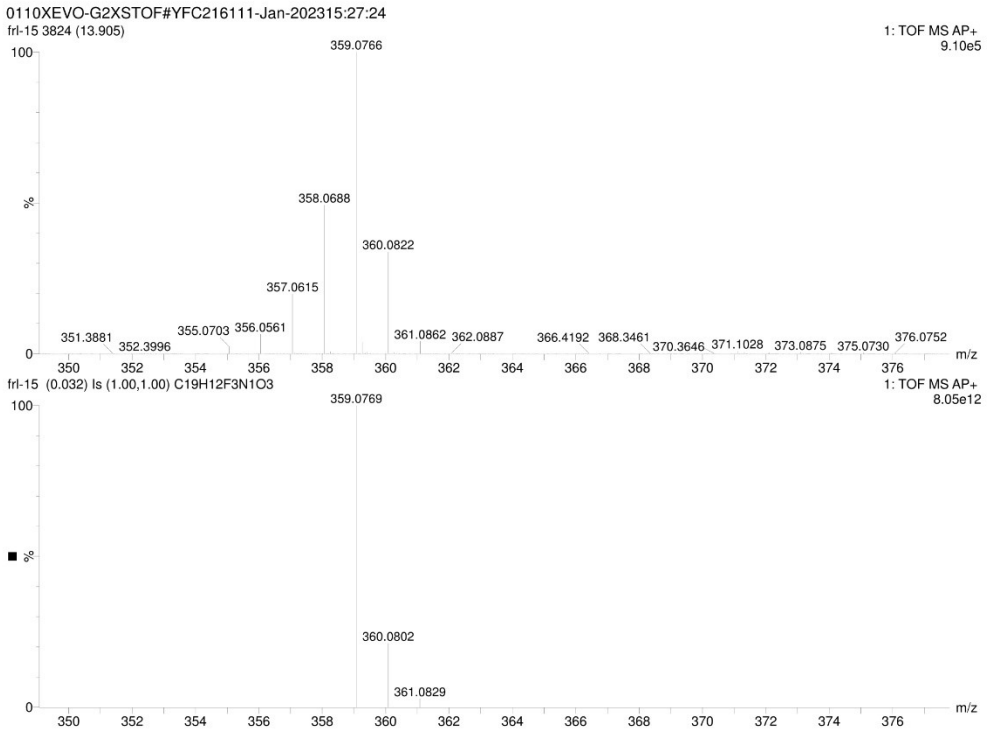
HRMS (AP) spectra of **3aw**



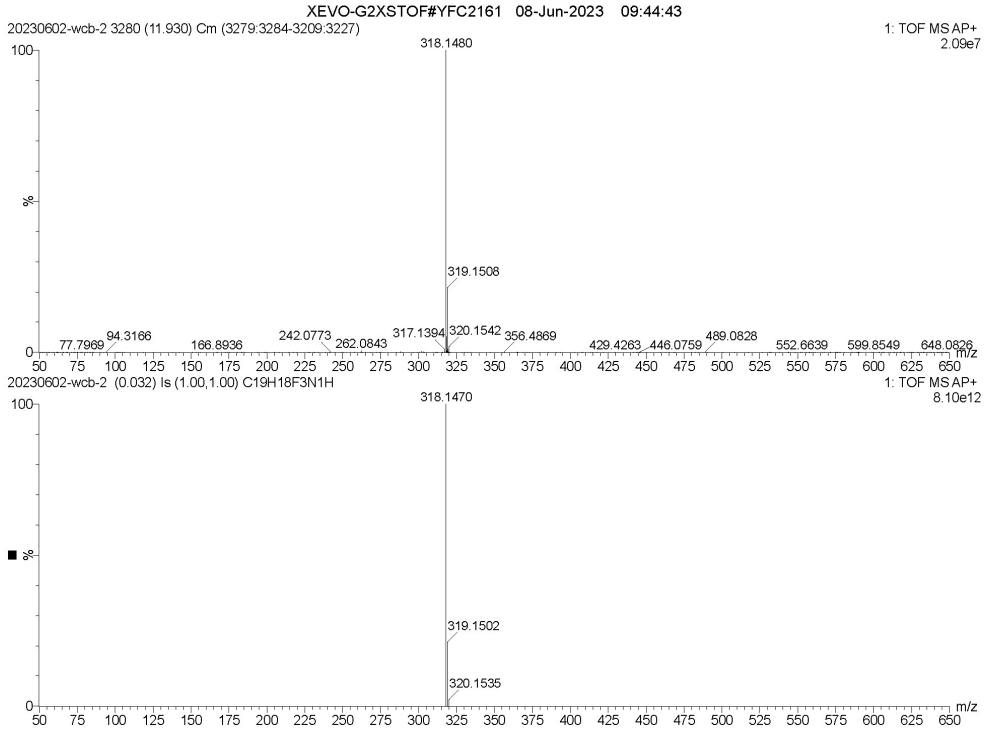
HRMS (AP) spectra of **3ax**



HRMS (AP) spectra of **3ay**



HRMS (AP) spectra of **3az**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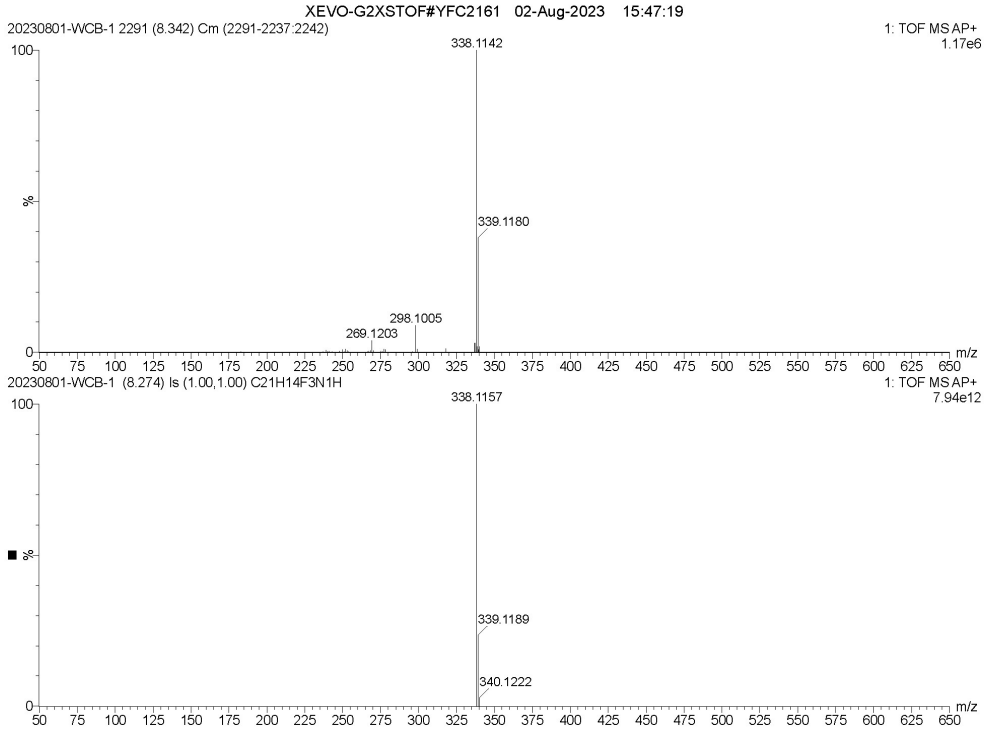
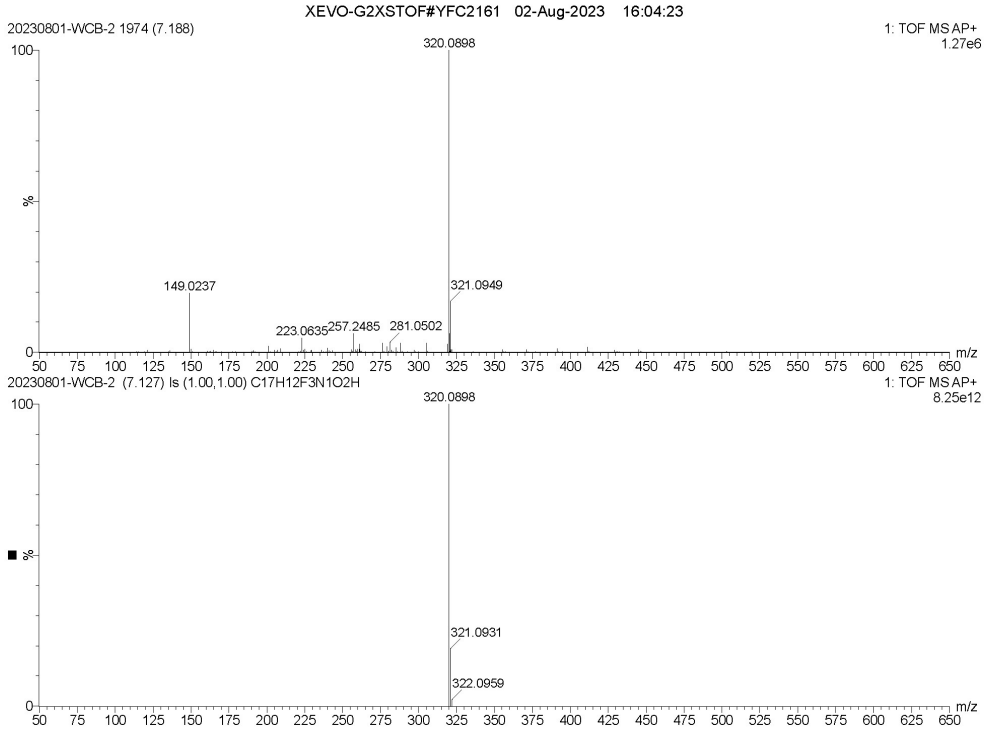
318.1470
319.1502
320.1535

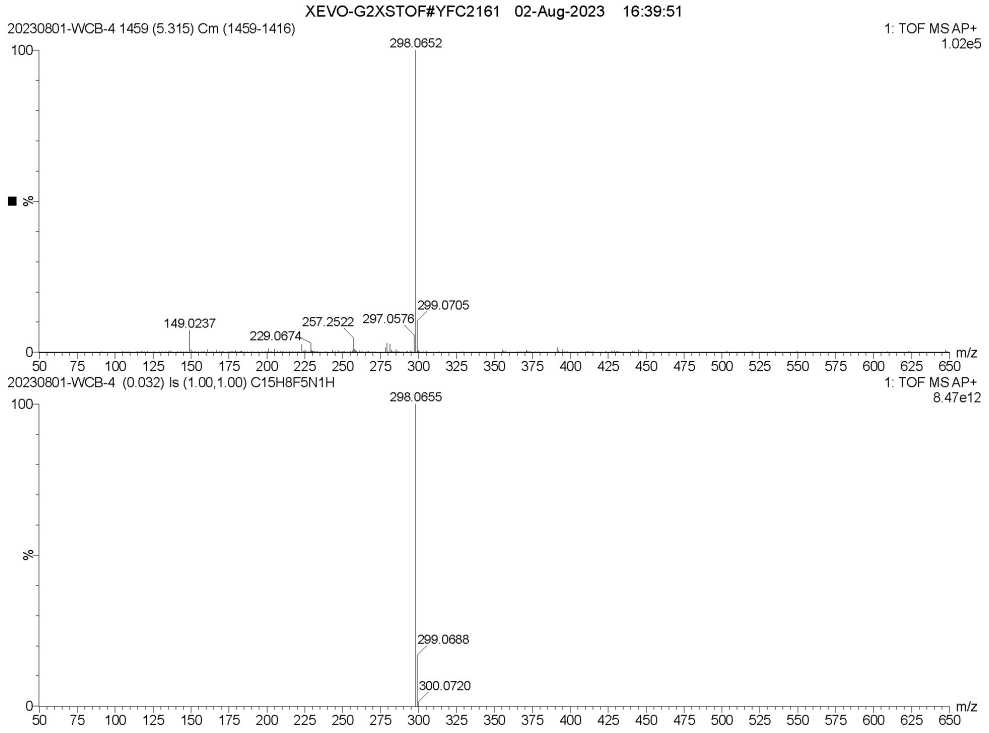
RMS (AP) spectra of **3aa′**



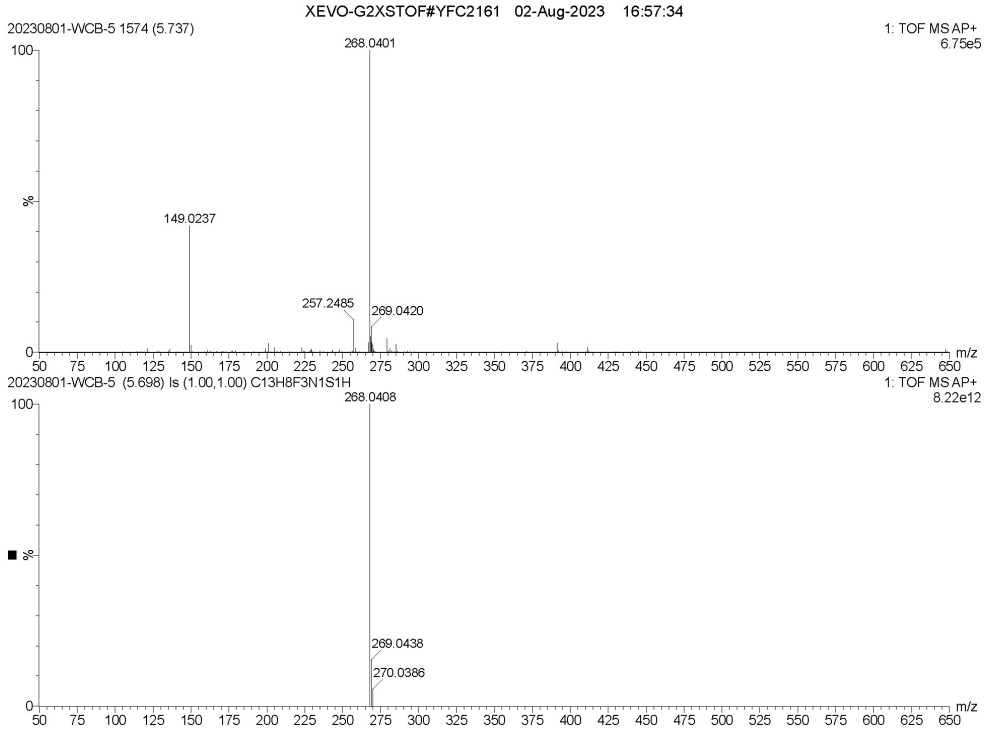
HRMS (AP) spectra of **3ab′**


XEVO-G2XSTOF#YFC2161 02-Aug-2023 16:04:23
20230801-WCB-2 1974 (7.188)
1: TOF MS AP+
1.27e6
320.0898
149.0237
321.0949
223.0635
257.2485
281.0502
m/z
20230801-WCB-2 (7.127) Is (1.00,1.00) C17H12F3N1O2H
1: TOF MS AP+
8.25e12
320.0898
321.0931
322.0959
m/z

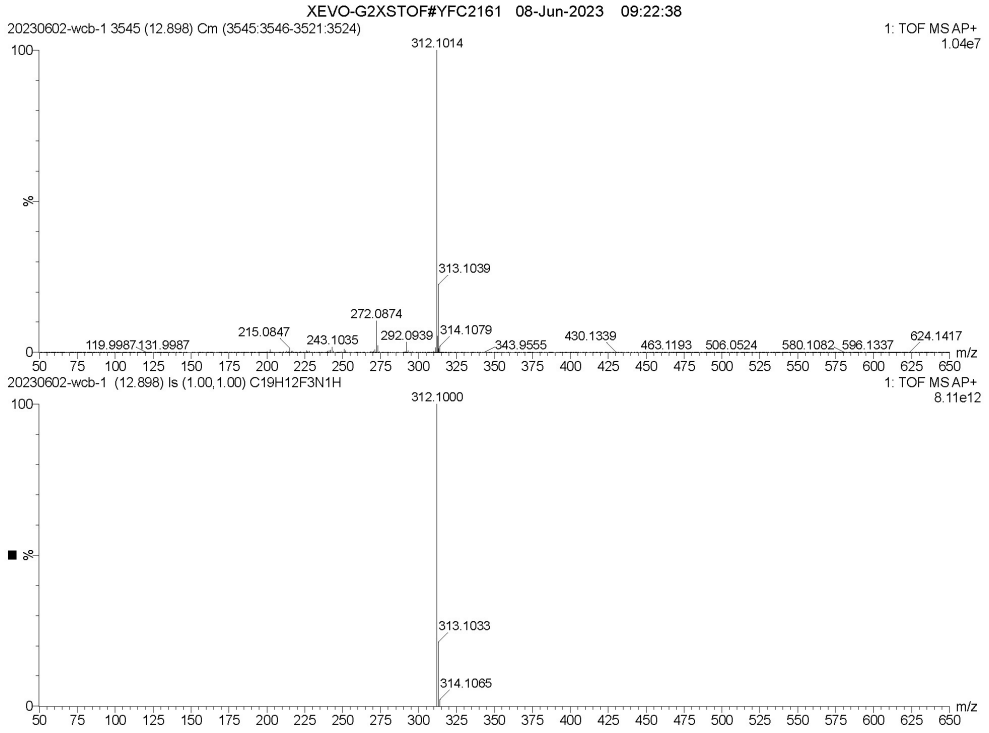
HRMS (AP) spectra of **3ac′**



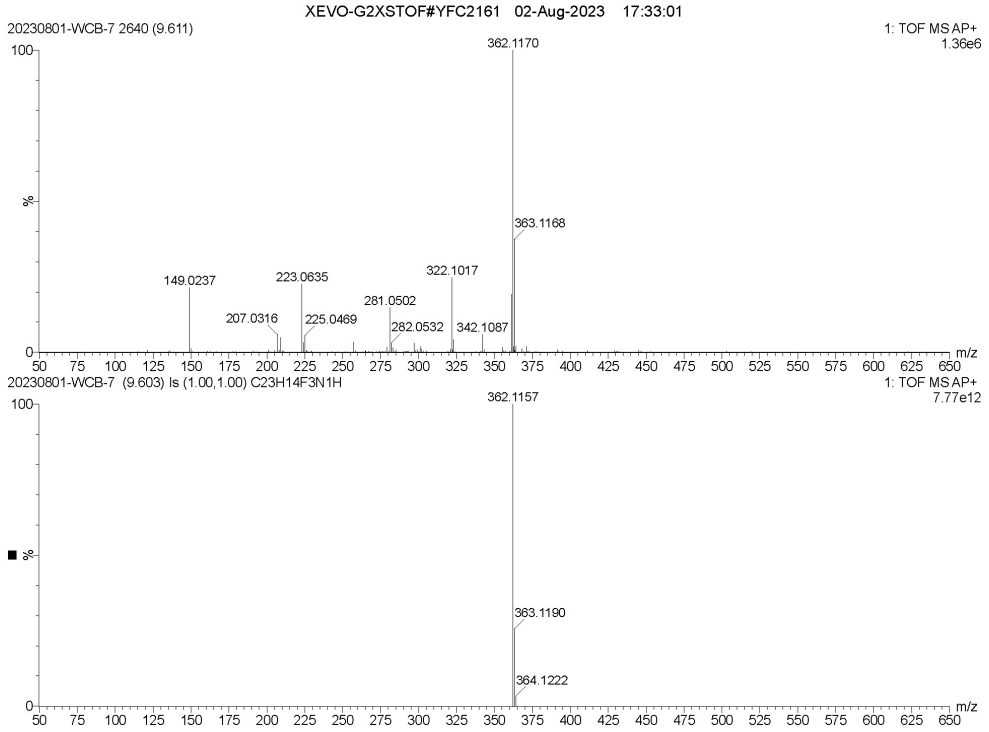
HRMS (AP) spectra of **3ad′**


XEVO-G2XSTOF#YFC2161 02-Aug-2023 16:57:34
20230801-WCB-5 1574 (5.737)
1: TOF MS AP+
6.75e5
268.0401
149.0237
257.2485
269.0420
20230801-WCB-5 (5.698) Is (1.00,1.00) C13H8F3N1S1H
1: TOF MS AP+
8.22e12
268.0408
269.0438
270.0386
%
m/z

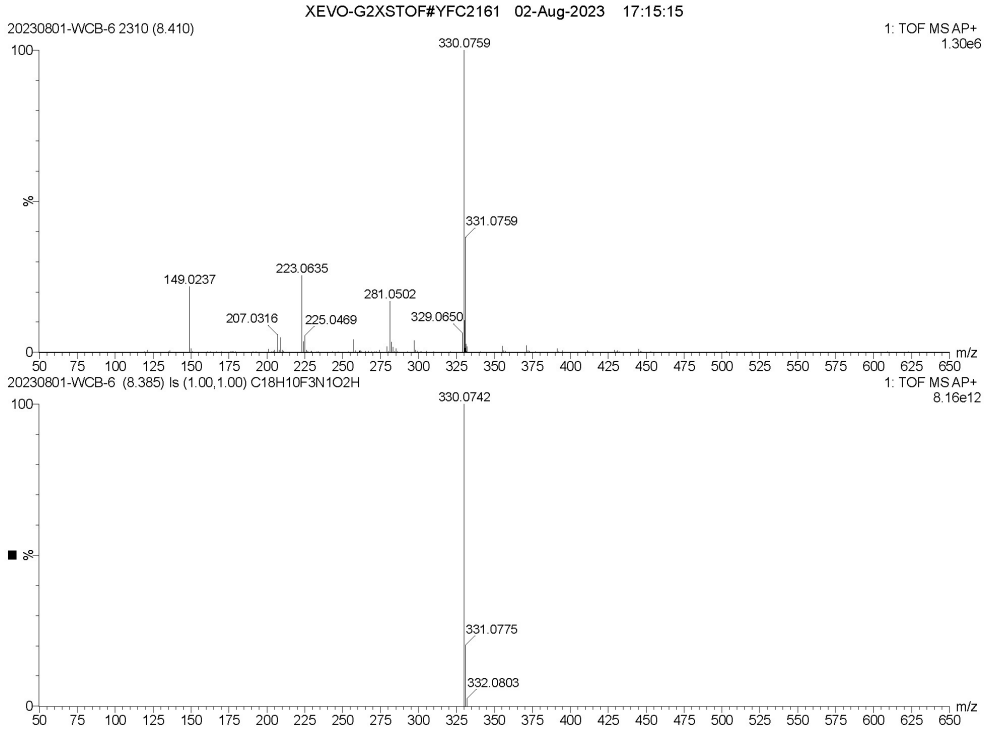
HRMS (AP) spectra of **3ae′**



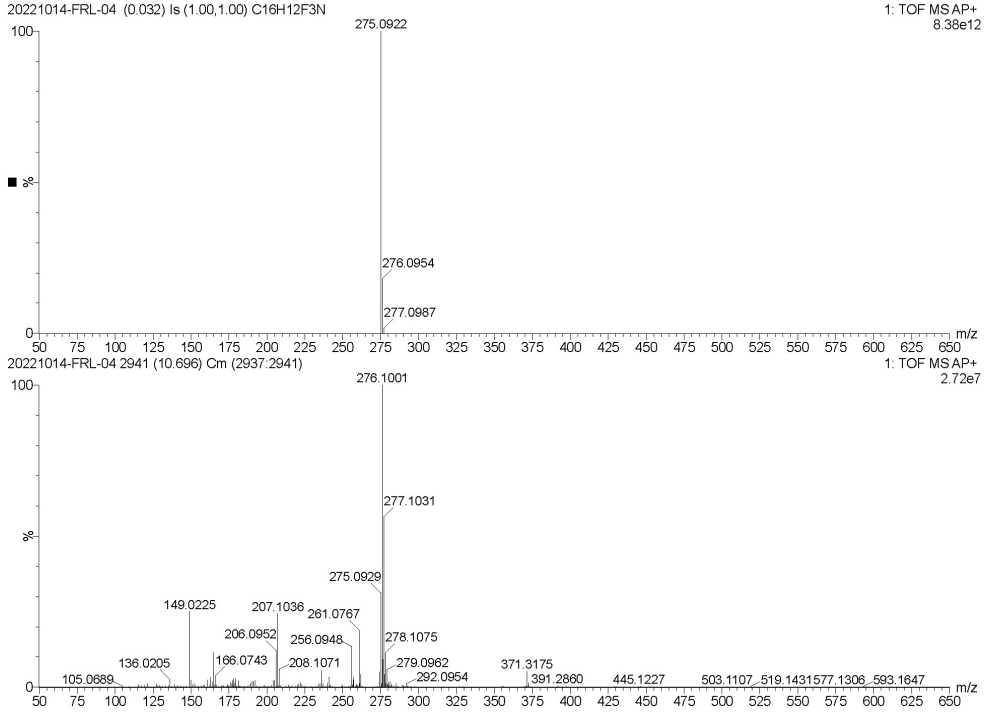
HRMS (AP) spectra of **3af′**


XEVO-G2XSTOF#YFC2161 02-Aug-2023 17:33:01
20230801-WCB-7 2640 (9.611)
1: TOF MS AP+
1.36e6
362.1170
363.1168
322.1017
149.0237
223.0635
281.0502
207.0316
225.0469
282.0532
342.1087
20230801-WCB-7 (9.603) Is (1.00,1.00) C23H14F3N1H
1: TOF MS AP+
7.77e12
362.1157
363.1190
364.1222
%
m/z

HRMS (AP) spectra of **3ag′**



HRMS (AP) spectra of **3ba**

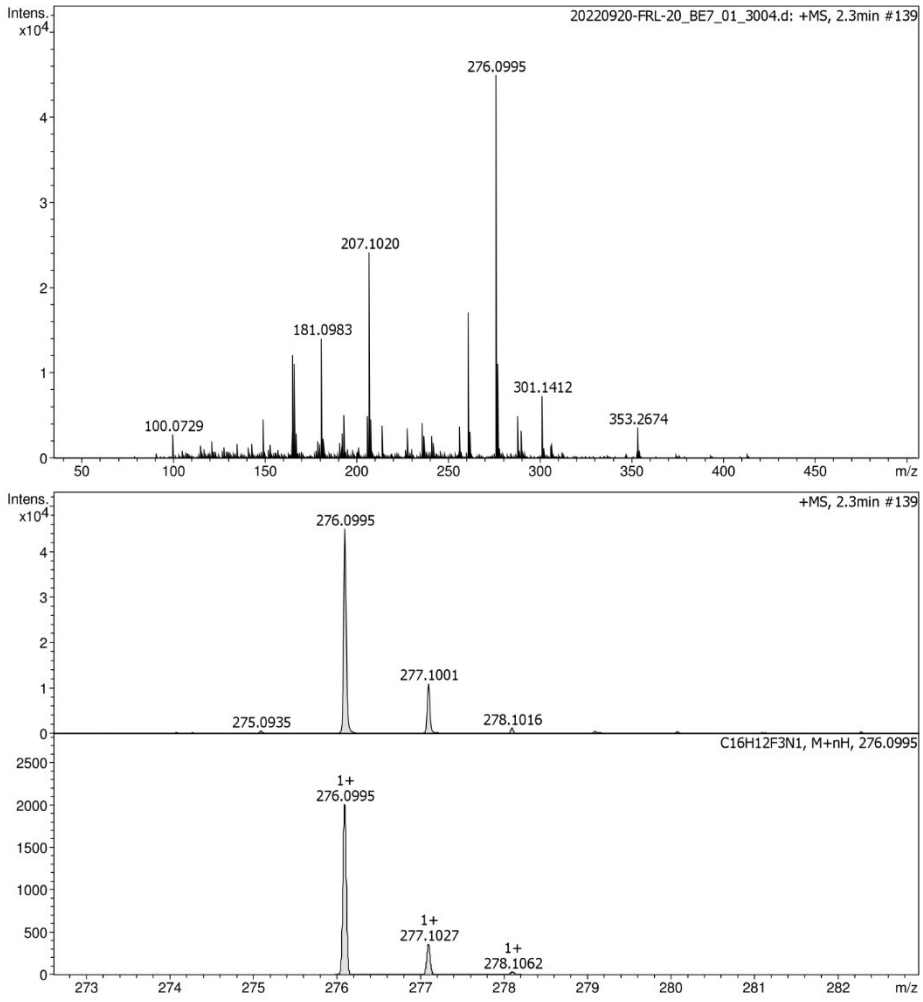


HRMS (ESI) spectra of **3bb**

Generic Display Report

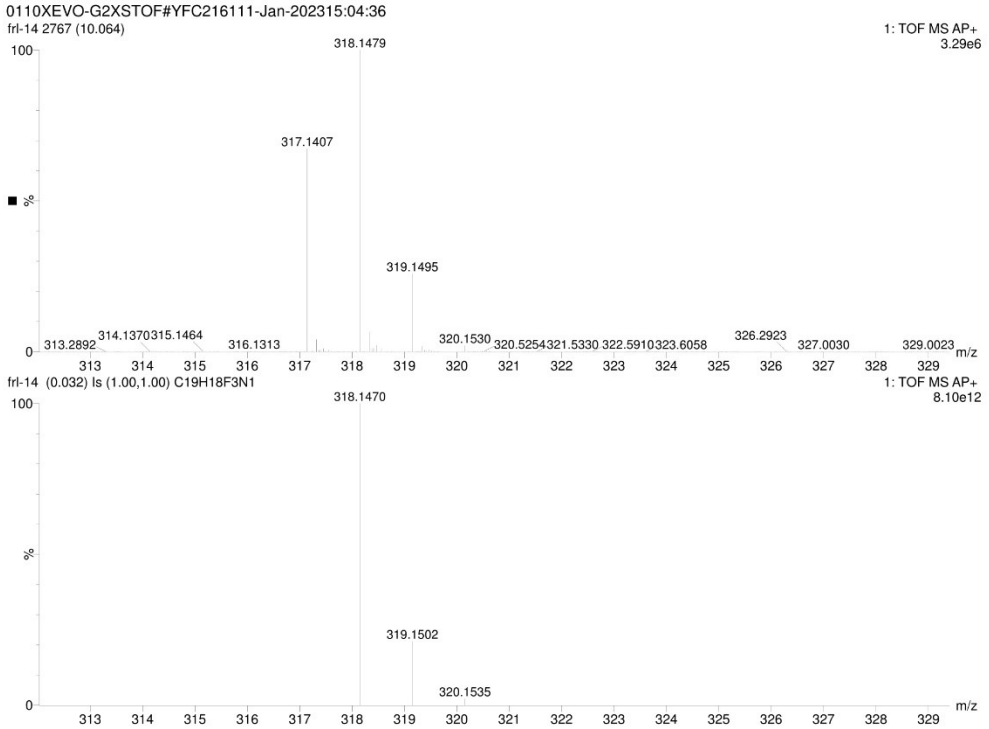
Analysis Info

Acquisition Date	26/09/2022 8:26:17 PM		
Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-20_BE7_01_3004.d		
Method	tune_low_20-400_pos-lcmsmin.m	Operator	gftang
Sample Name	20220920-FRL-20	Instrument	micrOTOF
Comment			

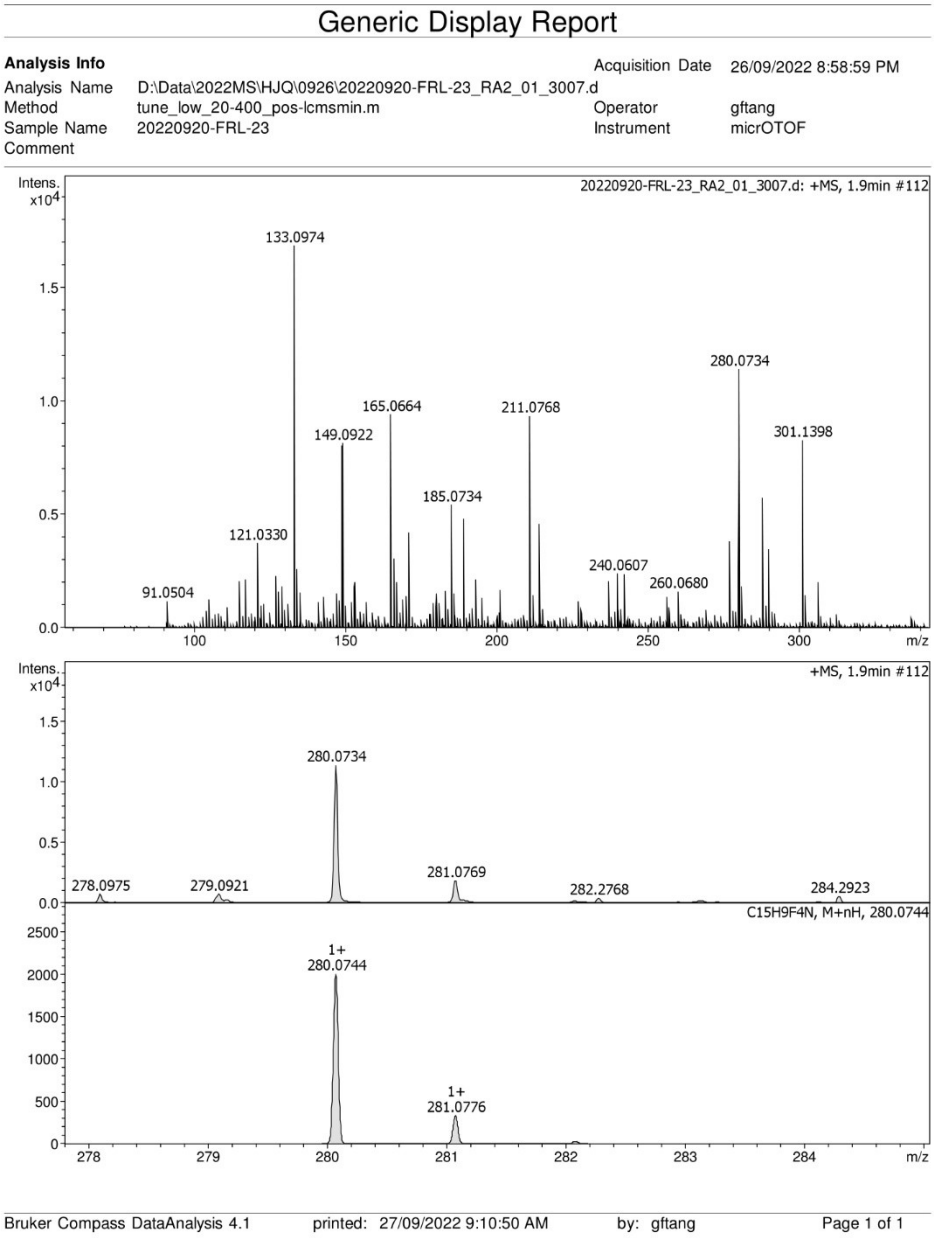


Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 8:56:32 AM by: gftang Page 1 of 1

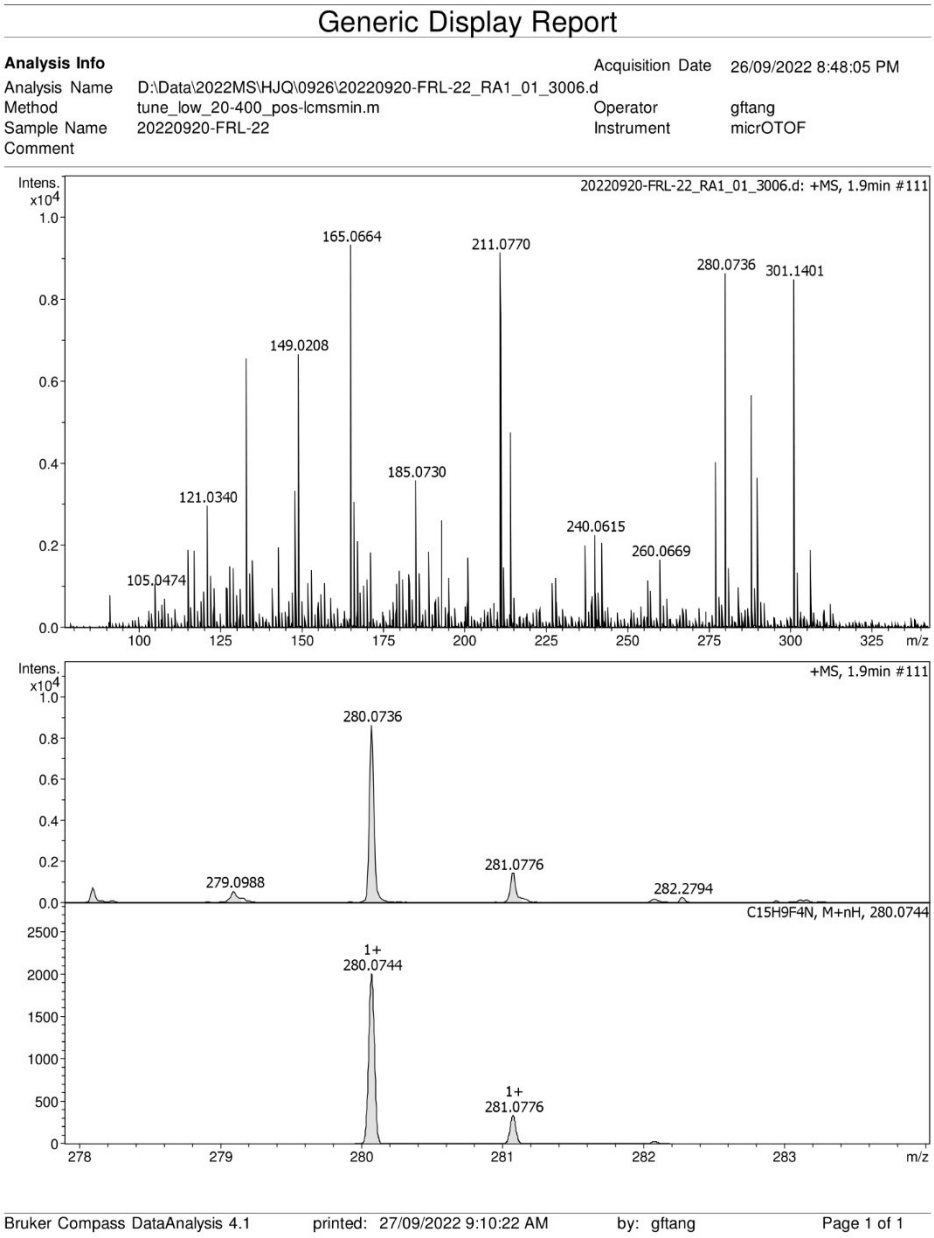
HRMS (AP) spectra of **3bc**



HRMS (ESI) spectra of **3bd**



HRMS (ESI) spectra of **3be**

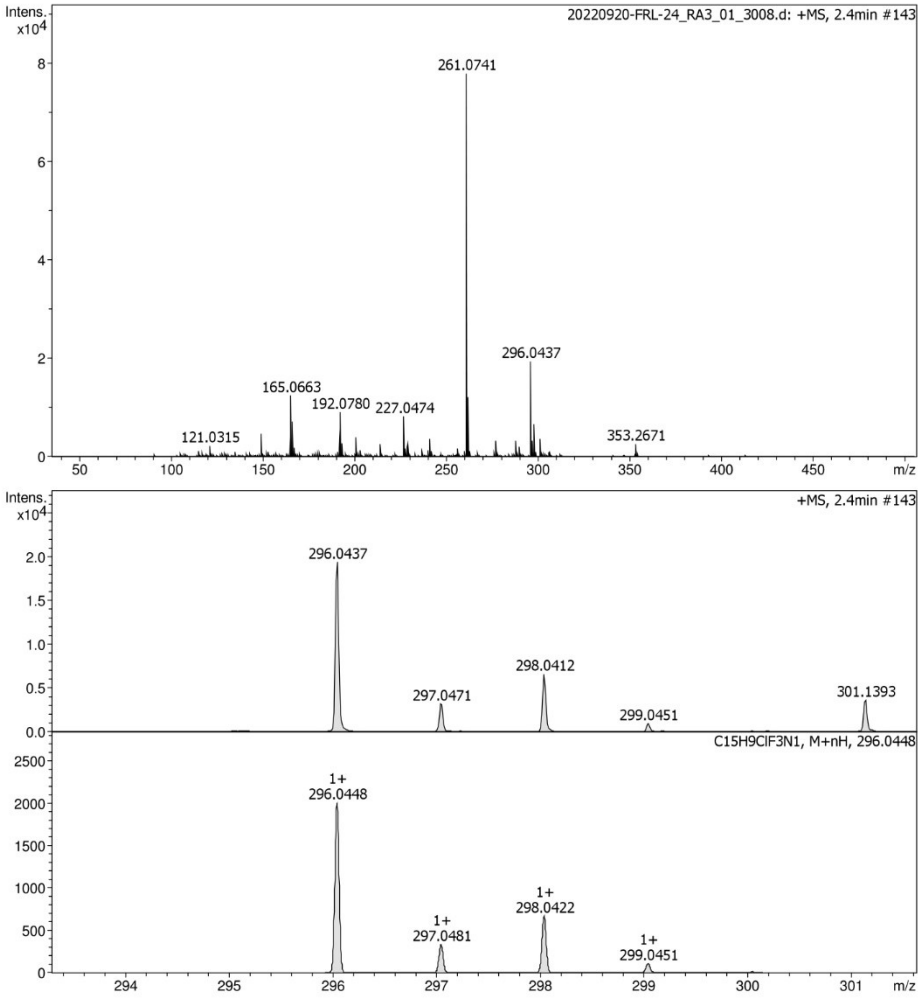


HRMS (ESI) spectra of **3bf**

Generic Display Report

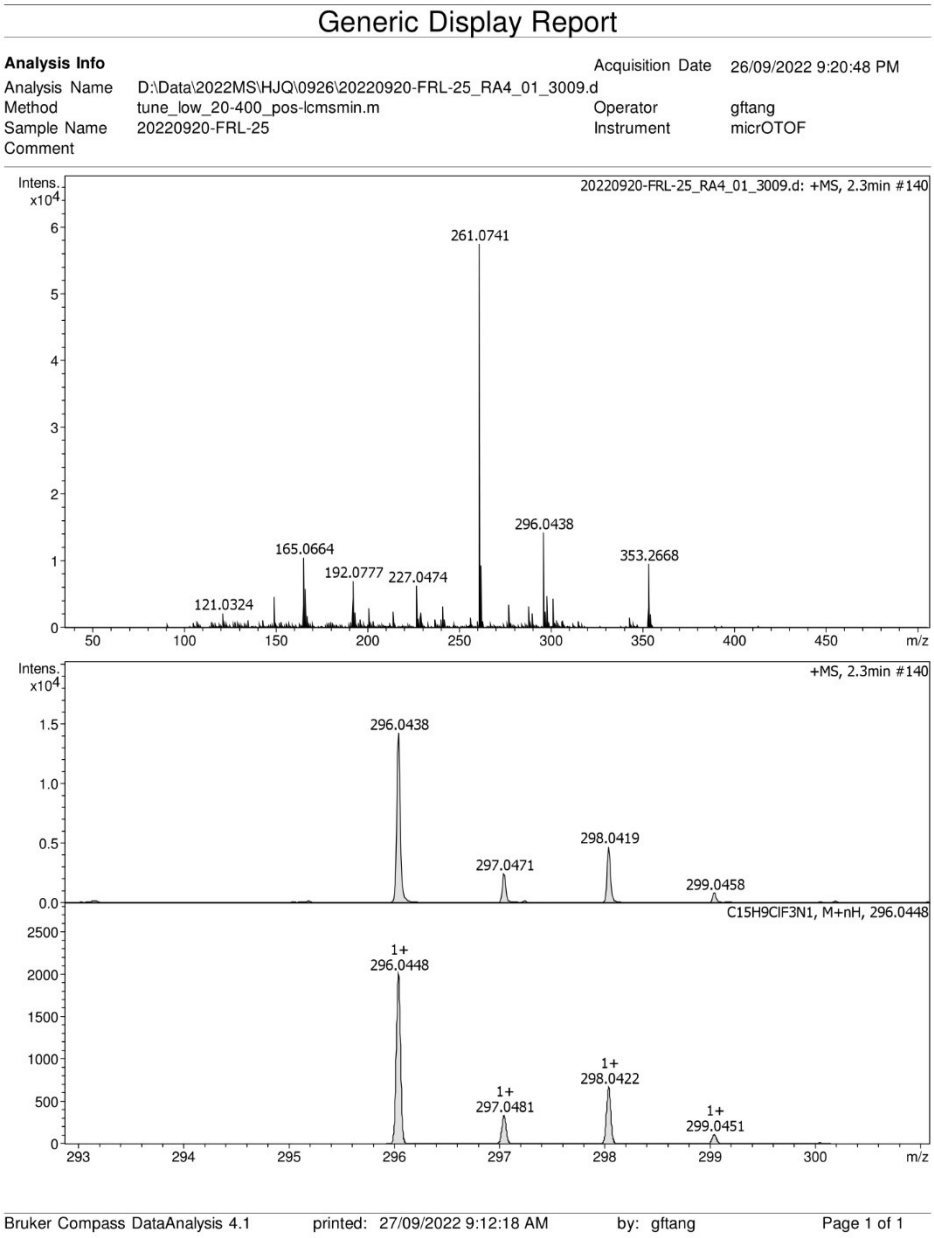
Analysis Info

Acquisition Date	26/09/2022 9:09:54 PM		
Analysis Name	D:\Data\2022MS\HJQ\0926\20220920-FRL-24_RA3_01_3008.d		
Method	tune_low_20-400_pos-lcmsmin.m	Operator	gftang
Sample Name	20220920-FRL-24	Instrument	micrOTOF
Comment			

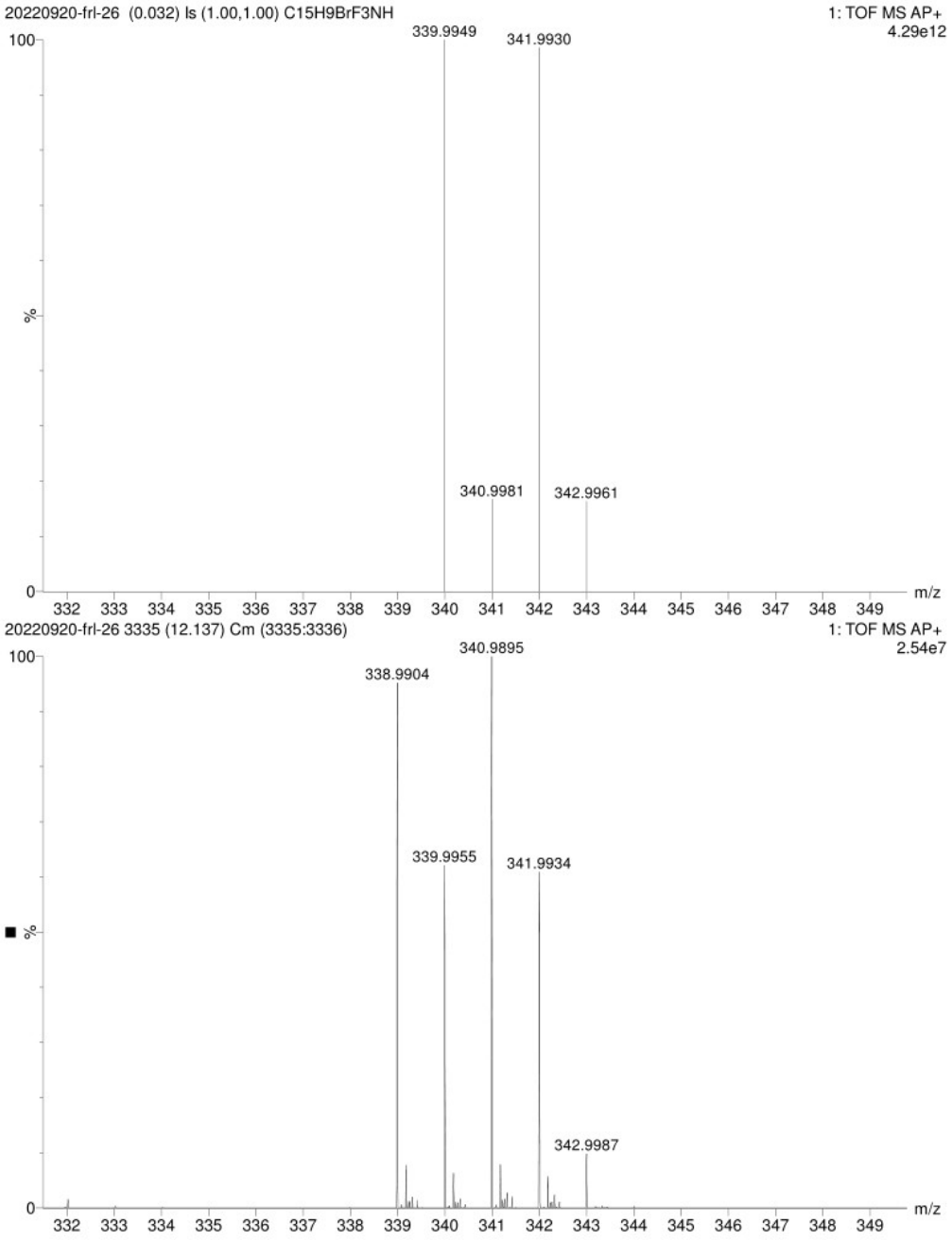


Bruker Compass DataAnalysis 4.1 printed: 27/09/2022 9:11:33 AM by: gftang Page 1 of 1

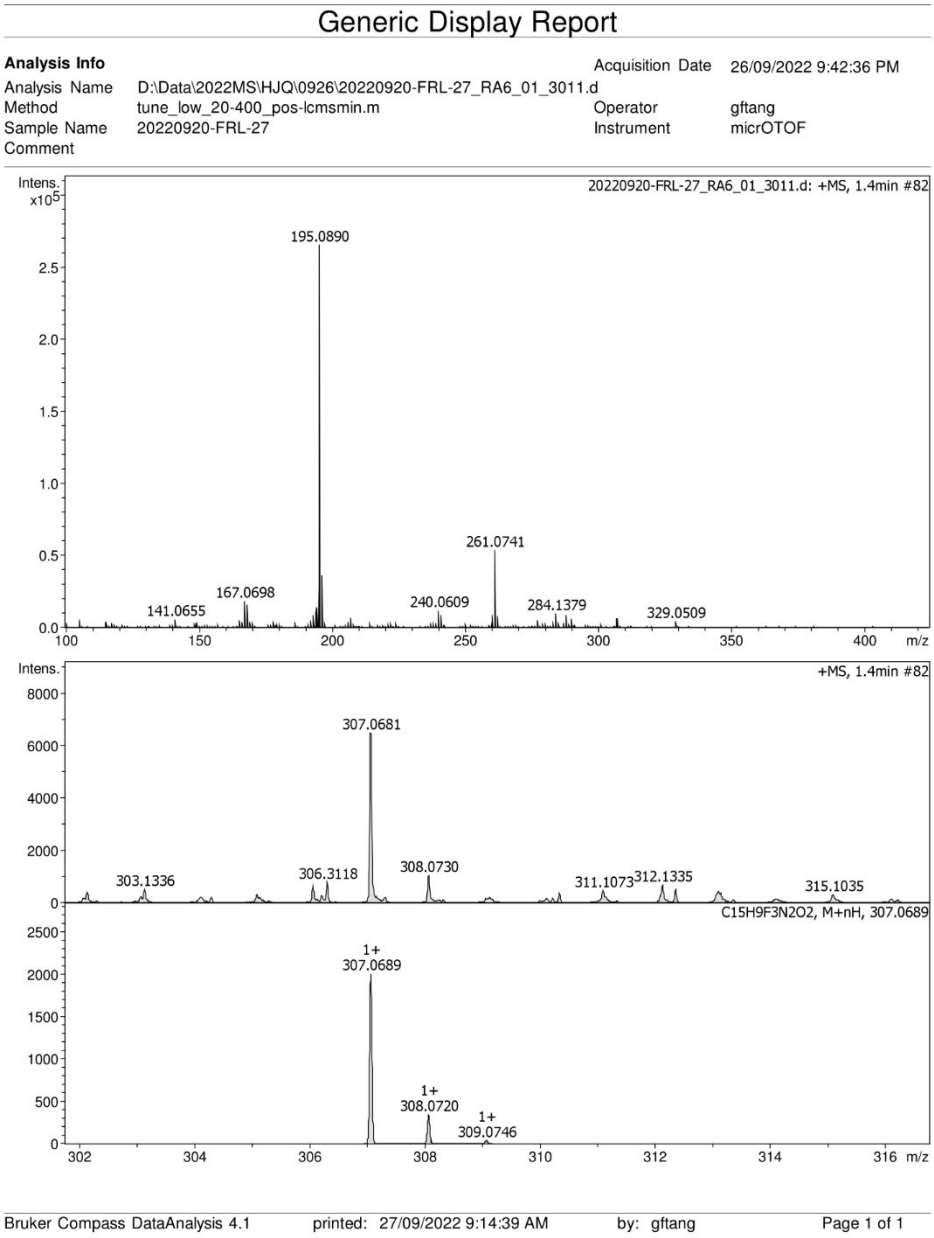
HRMS (ESI) spectra of **3bg**



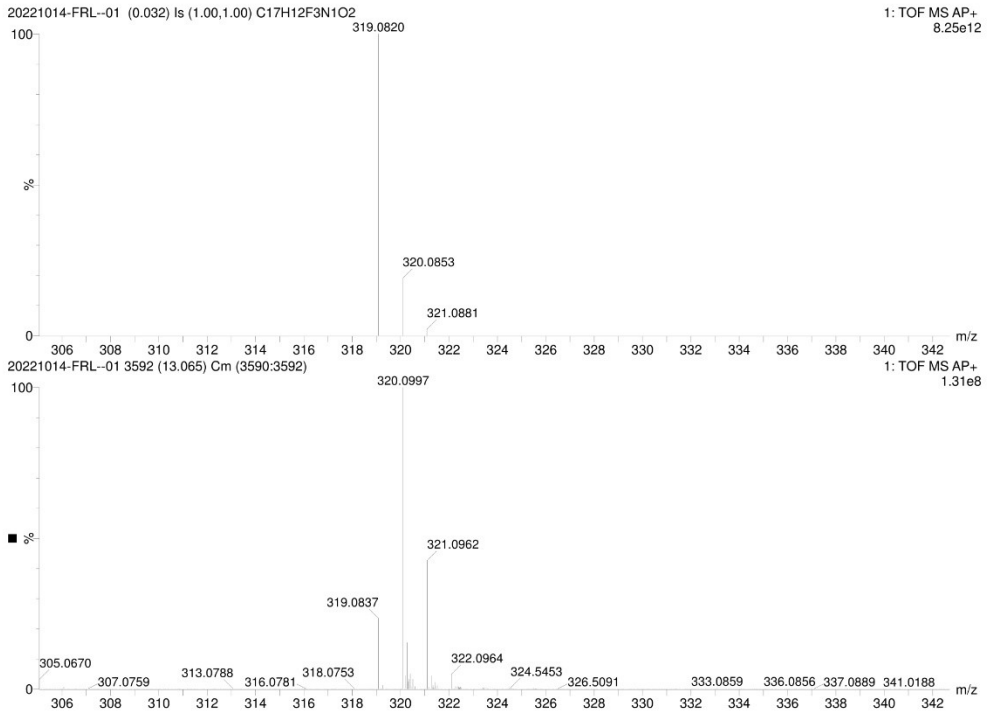
HRMS (AP) spectra of **3bh**



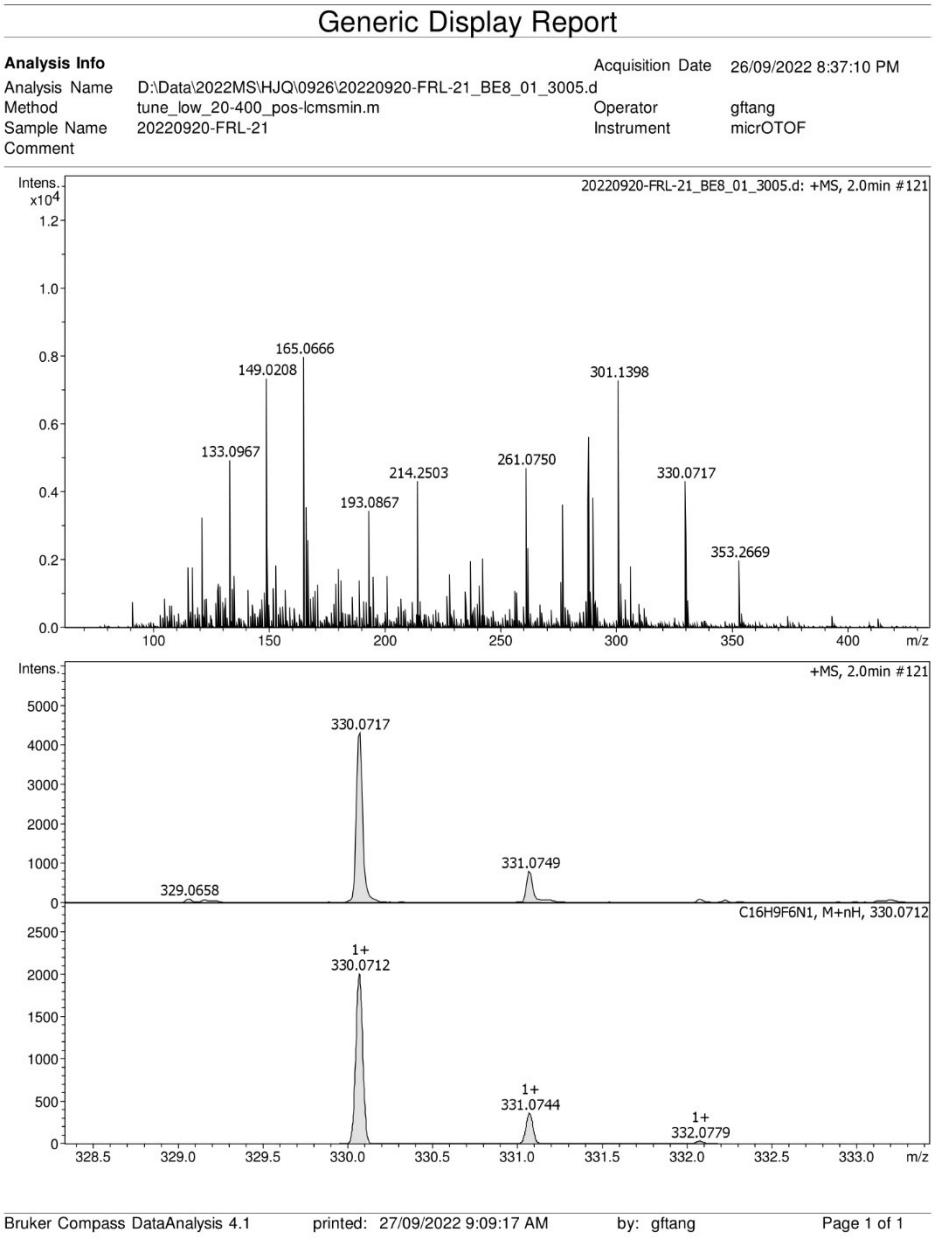
HRMS (ESI) spectra of **3bi**



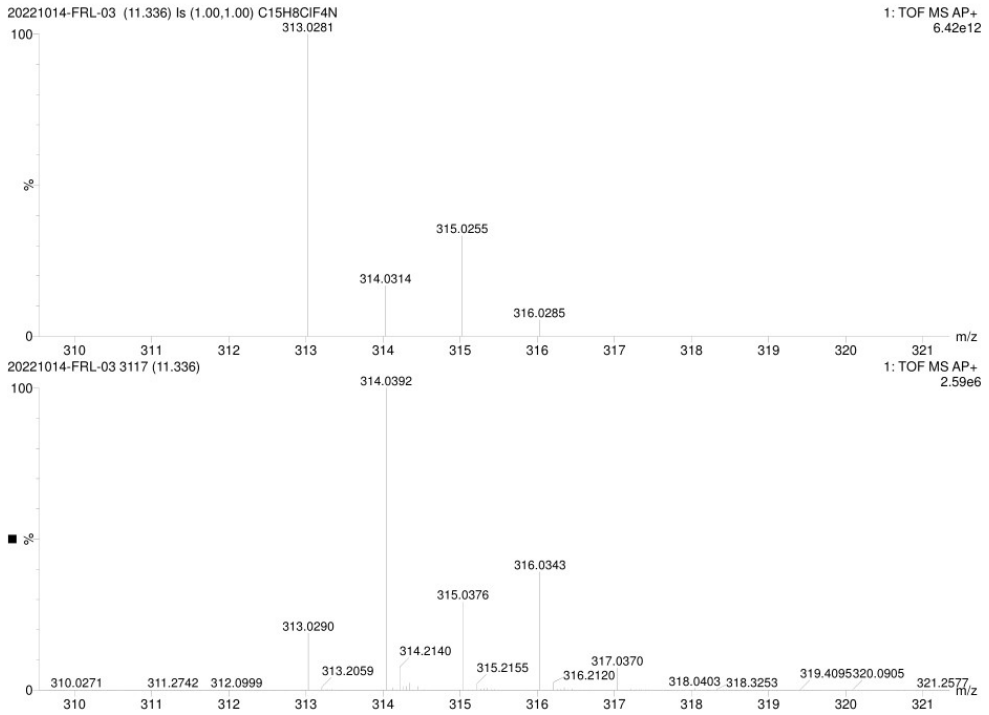
HRMS (AP) spectra of **3bj**



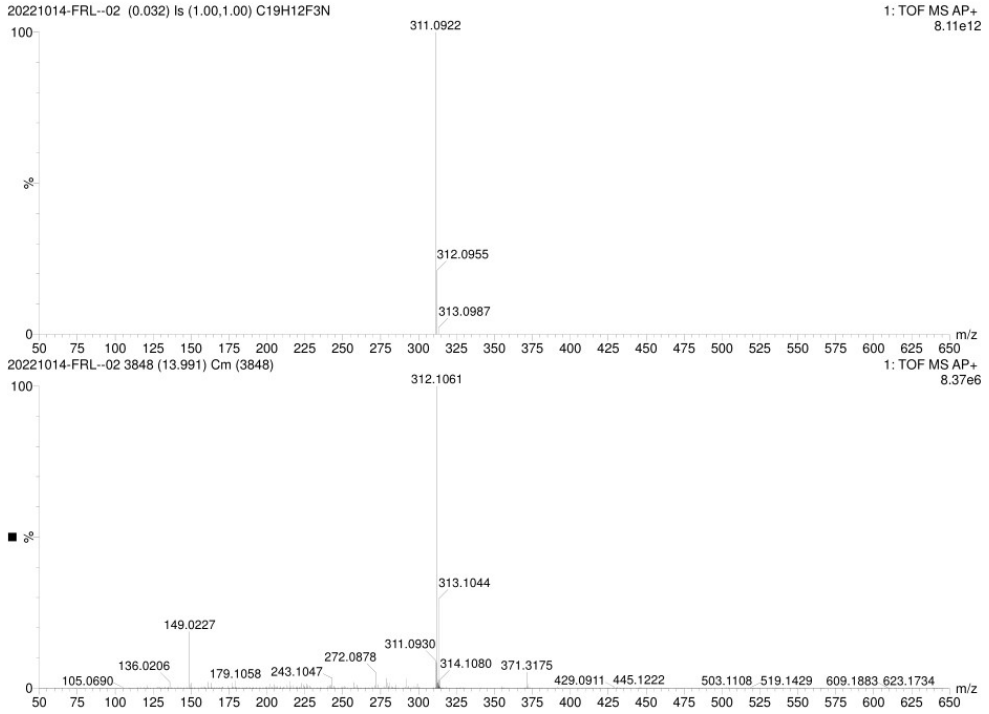
HRMS (ESI) spectra of **3bk**



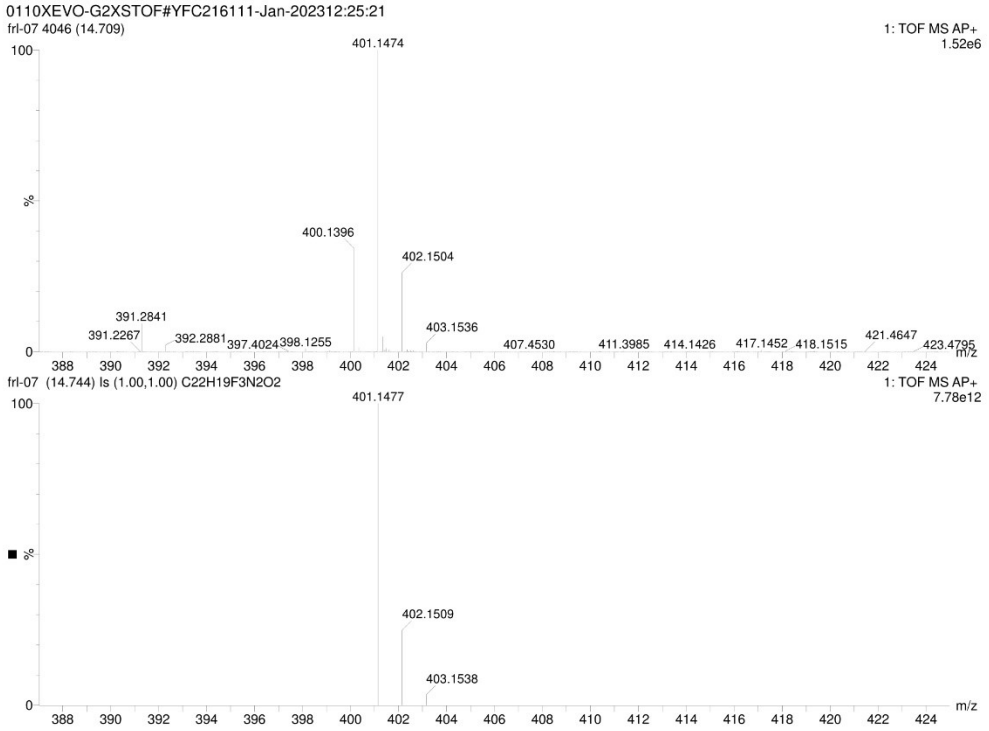
HRMS (AP) spectra of **3bl**



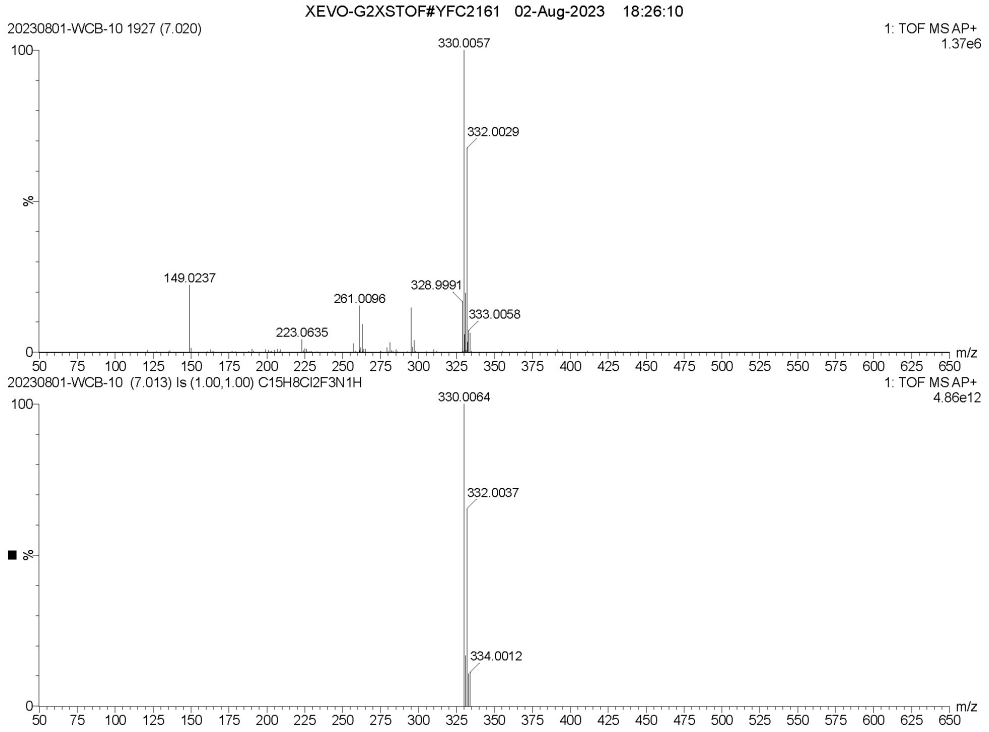
HRMS (AP) spectra of **3bm**


20221014-FRL--02 (0.032) Is (1.00,1.00) C19H12F3N
1: TOF MS AP+
8.11e12
311.0922
312.0955
313.0987
20221014-FRL--02 3848 (13.991) Cm (3848)
1: TOF MS AP+
8.37e6
312.1061
313.1044
149.0227
311.0930
272.0878
136.0206
314.1080
371.3175
105.0690
179.1058
243.1047
429.0911
445.1222
503.1108
519.1429
609.1883
623.1734
%
m/z

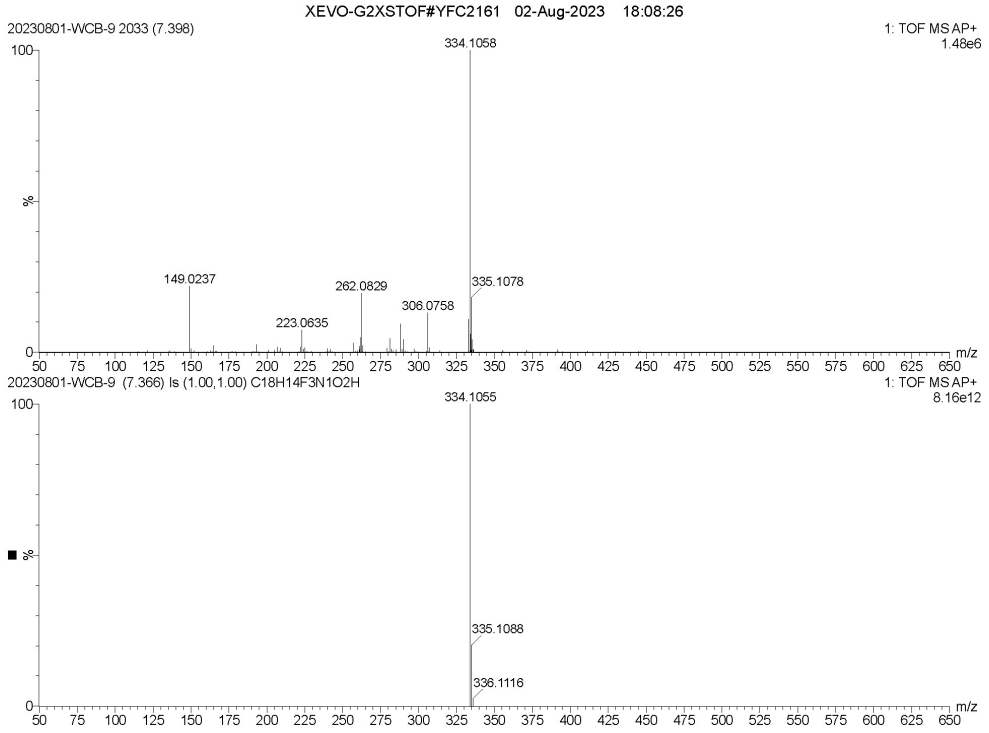
HRMS (AP) spectra of **3bn**



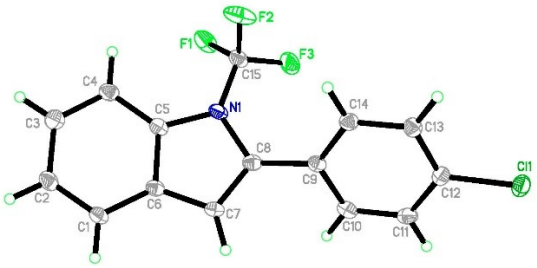
HRMS (AP) spectra of **3bo**


XEVO-G2XSTOF#YFC2161 02-Aug-2023 18:26:10
20230801-WCB-10 1927 (7.020)
1: TOF MS AP+
1.37e6
330.0057
332.0029
149.0237
328.9991
261.0096
333.0058
223.0635
%
m/z
20230801-WCB-10 (7.013) Is (1.00,1.00) C15H8Cl2F3N1H
1: TOF MS AP+
4.86e12
330.0064
332.0037
334.0012

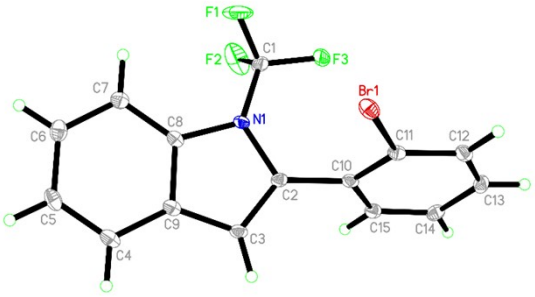
HRMS (AP) spectra of **3bp**



11. Crystal data and structure refinement for the products

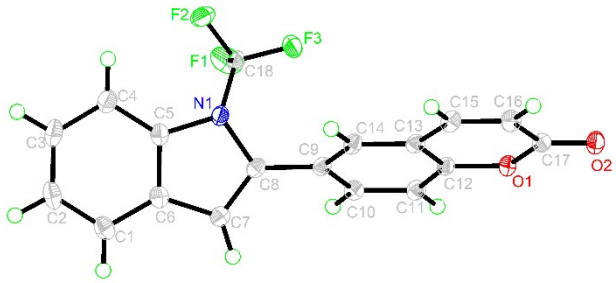


Identification code	3am	
Empirical formula	C15 H9 Cl F3 N	
Formula weight	295.68	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 5.9221(4) Å	α= 90°.
	b = 21.7851(16) Å	β= 100.563(4)°.
	c = 10.0601(8) Å	γ = 90°.
Volume	1275.89(16) $Å^3$	
Z	4	
Density (calculated)	1.539 Mg/m^3	
Absorption coefficient	2.903 mm^{-1}	
F(000)	600	
Crystal size	0.15 x 0.20 x 0.25 mm^3	
Theta range for data collection	4.058 to 68.245°.	
Index ranges	-7<=h<=5, -26<=k<=25, -12<=l<=11	
Reflections collected	6340	
Independent reflections	1822 [R(int) = 0.0526]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Multi-Scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1822 / 2 / 181	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0859	
R indices (all data)	R1 = 0.0407, wR2 = 0.0891	
Absolute structure parameter	0.037(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.269 and -0.207 $e.Å^{-3}$	



Identification code	3aq	
Empirical formula	C15 H9 Br F3 N	
Formula weight	340.14	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1764(6) Å	α= 86.542(2)°
	b = 10.5249(7) Å	β= 88.533(2)°
	c = 15.2713(10) Å	γ = 89.967(2)°
Volume	1311.36(16) $Å^3$	
Z	4	
Density (calculated)	1.723 Mg/m^3	
Absorption coefficient	4.521 mm^{-1}	
F(000)	672	
Crystal size	0.15 x 0.20 x 0.25 mm^3	
Theta range for data collection	2.900 to 68.317°	
Index ranges	-9<=h<=9, -12<=k<=12, -18<=l<=18	
Reflections collected	17835	
Independent reflections	4791 [R(int) = 0.0430]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Multi-Scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4791 / 24 / 361	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0831	

R indices (all data)	R1 = 0.0333, wR2 = 0.0844
Extinction coefficient	n/a
Largest diff. peak and hole	0.807 and -0.546 e.Å^{-3}



Identification code	3ag′	
Empirical formula	C18 H10 F3 N O2	
Formula weight	329.27	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.6165(5) Å	α= 96.542(3)°
	b = 10.3211(8) Å	β= 96.293(3)°
	c = 10.9424(8) Å	γ = 102.766(3)°
Volume	716.99(9) Å^3	
Z	2	
Density (calculated)	1.525 Mg/m^3	
Absorption coefficient	1.088 mm^{-1}	
F(000)	336	
Crystal size	0.028 x 0.097 x 0.26 mm^3	
Theta range for data collection	4.106 to 68.360°	
Index ranges	-7<=h<=7, -12<=k<=12, -13<=l<=13	
Reflections collected	8757	
Independent reflections	2627 [R(int) = 0.0553]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Multi-Scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2627 / 0 / 217	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1258	
R indices (all data)	R1 = 0.0525, wR2 = 0.1303	
Extinction coefficient	n/a	

Largest diff. peak and hole 0.456 and -0.323 e.Å^{-3}

12. Checkcif report for the products

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3am

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3am

```
Bond precision:   C-C = 0.0051 A          Wavelength=1.54178

Cell:             a=5.9221(4)     b=21.7851(16)       c=10.0601(8)
                  alpha=90        beta=100.563(4)     gamma=90
Temperature:      100 K

                 Calculated                Reported
Volume           1275.90(16)               1275.90(16)
Space group      C c                       C 1 c 1
Hall group       C -2yc                    C -2yc
Moiety formula   C15 H9 Cl F3 N            C15 H9 Cl F3 N
Sum formula      C15 H9 Cl F3 N            C15 H9 Cl F3 N
Mr               295.68                    295.68
Dx,g cm-3        1.539                     1.539
Z                4                         4
Mu (mm-1)        2.903                     2.903
F000             600.0                     600.0
F000'            603.47
h,k,lmax         7,26,12                   7,26,12
Nref             2333[ 1173]               1822
Tmin,Tmax        0.523,0.647               0.533,0.753
Tmin'            0.461

Correction method= # Reported T Limits: Tmin=0.533 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.55/0.78        Theta(max)= 68.250

R(reflections)= 0.0358( 1699)                    wR2(reflections)=
                                                 0.0829( 1822)
S = 1.101                 Npar= 181
```

```
The following ALERTS were generated. Each ALERT has the format
        test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.48 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00513 Ang.
```

Alert level G

```
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C15 Check
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT915_ALERT_3_G No Flack x Check Done: Low Friedel Pair Coverage         56 %
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT089_3am
;
PROBLEM: Poor Data / Parameter Ratio (Zmax < 18) ........       6.48 Note
RESPONSE: ...
;
_vrf_PLAT340_3am ;

PROBLEM: Low Bond Precision on  C-C Bonds ..............    0.00513 Ang.
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

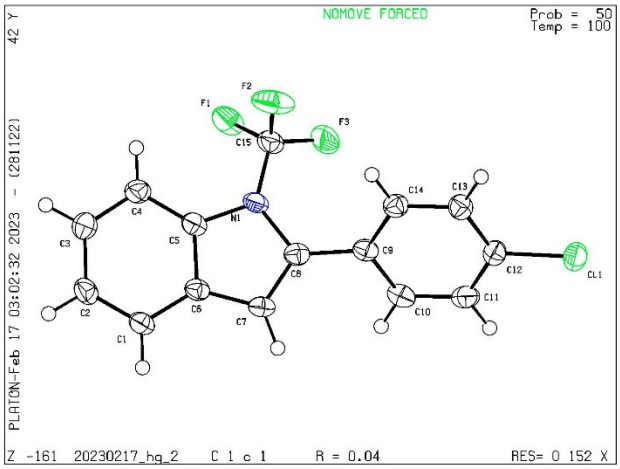
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock: 3aq - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3aq

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3aq

Bond precision: C-C = 0.0035 A Wavelength=1.54178

Cell: a=8.1764(6) b=10.5249(7) c=15.2713(10)
alpha=86.542(2) beta=88.533(2) gamma=89.967(2)
Temperature: 100 K

	Calculated	Reported
Volume	1311.36(16)	1311.36(16)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H9 Br F3 N	C15 H9 Br F3 N
Sum formula	C15 H9 Br F3 N	C15 H9 Br F3 N
Mr	340.13	340.14
Dx,g cm-3	1.723	1.723
Z	4	4
Mu (mm-1)	4.521	4.521
F000	672.0	672.0
F000'	671.30	
h,k,lmax	9,12,18	9,12,18
Nref	4804	4791
Tmin,Tmax	0.389,0.508	0.533,0.753
Tmin'	0.281	

Correction method= # Reported T Limits: Tmin=0.533 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 68.320

R(reflections)= 0.0317(4551) wR2(reflections)= 0.0810(4791)

S = 1.056 Npar= 361

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT213_ALERT_2_C Atom F1              has ADP max/min Ratio .....        3.5 prolat
PLAT213_ALERT_2_C Atom F4              has ADP max/min Ratio .....        3.6 prolat
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C30 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C29 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          6 Report
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          4 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0200 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0200 Report
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        24 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          7 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.7 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT213_3aq
;
PROBLEM: Atom F1              has ADP max/min Ratio .....        3.5 prolat
RESPONSE: ...
;
_vrf_PLAT242_3aq
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of        C30 Check
RESPONSE: ...
;
_vrf_PLAT911_3aq


;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600          6 Report
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

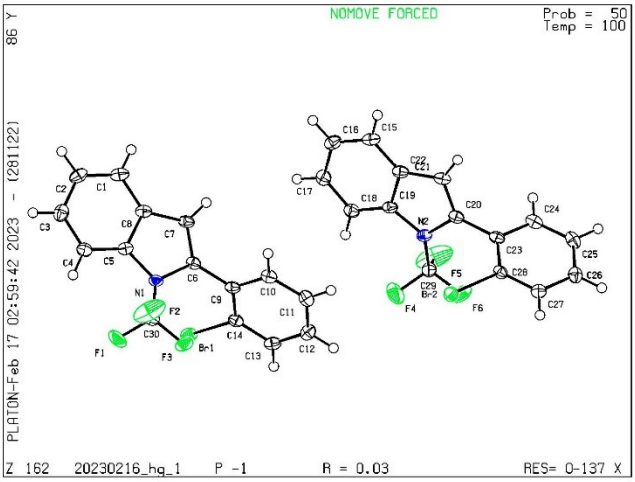
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022

Datablock 3aq- ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3ag'

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3ag'

```
Bond precision:   C-C = 0.0022 A           Wavelength=1.54178

Cell:           a=6.6165(5)       b=10.3211(8)      c=10.9424(8)
                alpha=96.542(3)   beta=96.293(3)    gamma=102.766(3)
Temperature:    100 K

                 Calculated                Reported
Volume           717.00(9)                 716.99(9)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C18 H10 F3 N O2           C18 H10 F3 N O2
Sum formula      C18 H10 F3 N O2           C18 H10 F3 N O2
Mr               329.27                    329.27
Dx,g cm-3        1.525                     1.525
Z                2                         2
Mu (mm-1)        1.088                     1.088
F000             336.0                     336.0
F000'            337.30
h,k,lmax         7,12,13                   7,12,13
Nref             2633                      2627
Tmin,Tmax        0.881,0.970               0.667,0.753
Tmin'            0.754

Correction method= # Reported T Limits: Tmin=0.667 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.998           Theta(max)= 68.360

R(reflections)= 0.0483( 2361)                  wR2(reflections)=
                                               0.1303( 2627)
S = 1.063                  Npar= 217
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 5 Report

Alert level G

PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.003 Degree
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 2 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 3.3 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 3 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by 2 Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT911_3ag'
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600          5 Report
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

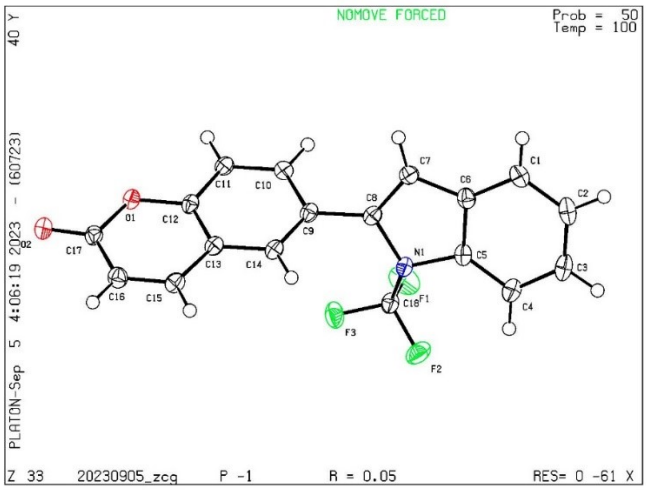
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 06/07/2023; check.def file version of 30/06/2023

Datablock 3ag' - ellipsoid plot



13. References

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