Supporting Information

Selective Defluorinative [4+3] Annulation to Access Fluorinated Oxazepines and Thiazepines

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1. General information

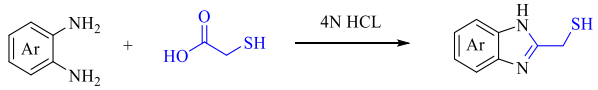
All reagents and solvents were used as received from Adamas without additional purification. Workup procedures were performed in the air. Thin-layer chromatography (TLC) utilized glass plates with 0.25 mm silica gel. Products were separated by column chromatography using silica gel with a mesh size of 200-400. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded with a Bruker spectrometer (600 MHz). ^{1}H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublets of triplets, td = triplet of doublets, qd = quartet of doublets, brs = broad singlet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ at 77.16 ppm. HRMS analysis was performed on a UPLC G2-XS mass spectrometer, with all signals reported as the *m/z* ratio. Melting points were measured using a Büchi M-560 at a heating rate of 20°C and are uncorrected.

All commercially available reagents were purchased and used without additional purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualization method. Flash column chromatography was carried out using silica gel (200–300 mesh) with the specified solvent system. All reactions were conducted in oven-dried Schlenk tubes.

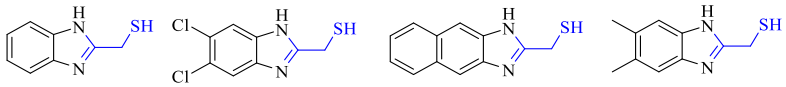
2. Experimental procedures.

2.1 General procedure for the Synthesis of (1H-benzo[d]imidazol-2-yl)methanethiol **(1a-1d)**

In a round-bottom flask, the aromatic diamine (5.0 mmol, 540 mg, 1.0 equiv) and thioglycolic acid (20.0 mmol, 1.84 g, 2.8 mL, 4.0 equiv) were refluxed in an aqueous 4N HCl solution (10 mL) for 3-4 hours. Upon cooling the reaction mixture to room temperature, saturated NaOH solution was added dropwise to achieve a pH of approximately 7-8. The product precipitated as an off-white solid, which was filtered, washed with ice-cold water, and dried under vacuum to obtain the derivatives of pure (1H-benzo[d]imidazol-2-yl)methanethiol **1a-1d**.[1]



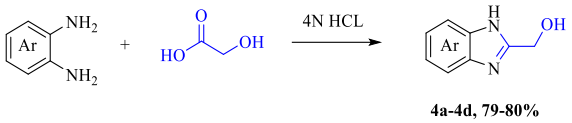
1a-1d, 85-90%



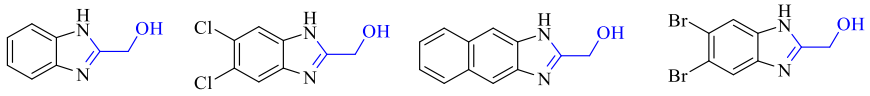
1a **1b** **1c** **1d**

2.2 General procedure for the Synthesis of (1H-benzo[d]imidazol-2-yl)methanol **(4a-4d).**

For the synthesis of substrates **4a-4d**[2], different substituted aromatic diamines (5.0 mmol, 540 mg, 1.0 equiv) were added to glyoxylic acid (20.0 mmol, 1.52 g, 4.0 equiv) in an aqueous 4N HCl solution (10 mL). Then, the mixture was refluxed in a round-bottom flask for 4 hours, and product formation was monitored with TLC. The reaction mixture was cooled to 0 °C. Saturated NaOH solution was added dropwise to neutralize the mixture. The product precipitated as a white solid. The precipitate was filtered, washed with ice-cold water, and dried under vacuum to obtain the pure products.



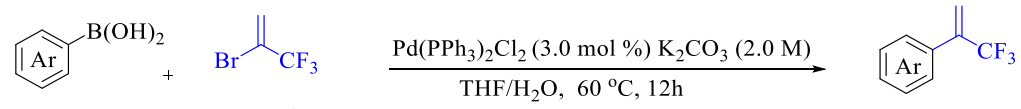
4a-4d, 79-80%



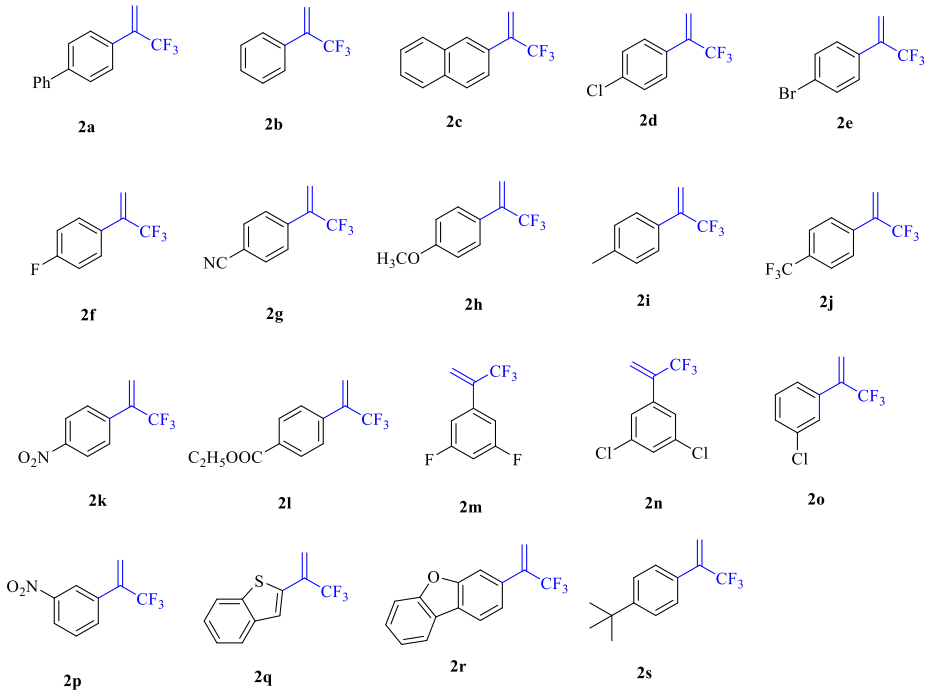
4a **4b** **4c** **4d**

2.3 General procedure for the synthesis of α- (trifluoromethyl) styrene **(2a-2s):**

In a 50 mL dried round-bottom flask equipped with a magnetic stir bar and septum, arylboronic acid (1 equiv.) and $Pd(PPh_3)_2Cl_2$ (3 mol%) were added, after which the flask was evacuated and filled with nitrogen gas. Then, THF (0.3 M) and an aqueous K_2CO_3 solution (2.0 M, 4.0 equiv.) were added, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (1.5 equiv.). The reaction mixture was heated to 60°C under stirring in an oil bath for 12 hours. The progress of the reaction was monitored by TLC. Upon completion, the mixture was cooled to room temperature and extracted three times with ethyl acetate (15.0 mL each). The organic layer was washed with brine (20.0 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Silica gel column chromatography (petroleum ether/ethyl acetate = 200/1) was performed to obtain the desired product (α- (trifluoromethyl) styrene), compounds **2a-2s**.[3-4]



1.0 equiv 1.2 equiv **2a-2s**



3. Experimental procedures for the synthesis of final compounds:

3.1 Synthesis of compounds **3a-3s:**

To a 10 mL oven-dried glass vial equipped with a stir bar, (1H-benzo[d]imidazol-2-yl)methanethiol **1a-1d** (0.2 mmol), α-(trifluoromethyl) styrene **2** (0.2 mmol), K_2CO_3 (3.5 equivalents), and DMSO (1 mL) were vigorously stirred at 65°C for 12 hours. After the reaction was completed and monitored by TLC, water was added, resulting in the precipitation of the product, which was then extracted with EtOAc (three times, 10 mL each). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and the solvents were evaporated under reduced pressure. Finally, the compounds were purified by flash chromatography (eluting with petroleum ether/ethyl acetate) to afford the corresponding products **3a-3s**.

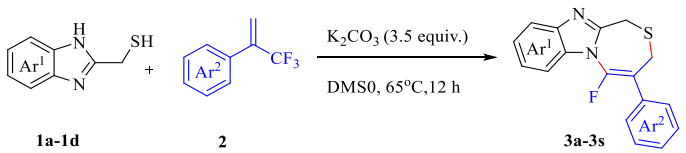
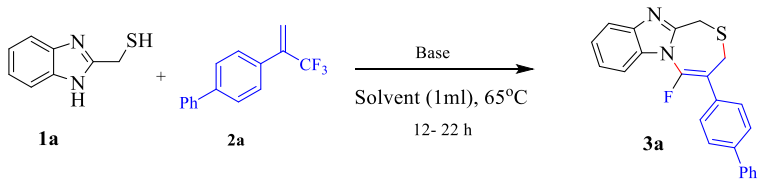


Table 1 Optimization of reaction conditions

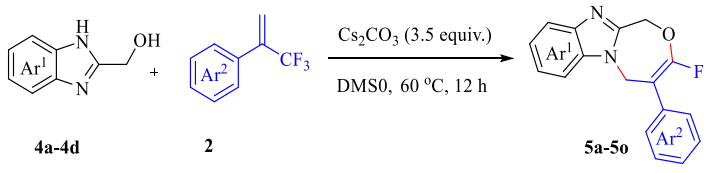


entry	base (3.5 equiv.)	solvent	temp. (°C)	time (h)	[b]yield (%)
1	Na_2CO_3	DMF	r.t	12	trace
2	Cs_2CO_3	DMF	r.t	12	0
3	K_3PO_4	DMF	r.t	12	0
4	K_2CO_3	DMF	r.t	12	22
5	K_2CO_3	DMSO	r.t	12	42
6[c]	K_2CO_3	DMSO	45	12	45
7[d]	K_2CO_3	DMSO	50	12	54
8	**K_2CO_3**	**DMSO**	**65**	**12**	**77**
9[e]	K_2CO_3	DMSO	80	12	77
10[f]	K_2CO_3 (2 equiv.)	DMSO	65	12	59
11[g]	K_2CO_3 (2.5 equiv.)	DMSO	65	12	62
12[h]	K_2CO_3 (3 equiv.)	DMSO	65	12	64
13	DABCO	DMSO	65	12	trace
14	Et_3N	DMSO	65	12	trace
15	DBU	DMSO	65	12	trace
16	K_2CO_3	C_2H_5OH	65	12	0
17	K_2CO_3	CH_3CN	65	12	trace
18	K_2CO_3	1,4 dioxane	65	12	0
19	K_2CO_3	THF	65	12	trace
20	----	DMSO	65	12	0

[a] General Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), base (0.7mmol), solvent (1 mL), 65 °C, 12 h. [b] Isolated yield. [c]Temperature at 45 °C. [d] Temperature at 50 °C. [e] Temperature at 80°C. [f] with (2 equiv) of K_2CO_3, [g]with (2.5 equiv) of K_2CO_3, [h] with (3 equiv) of K_2CO_3.

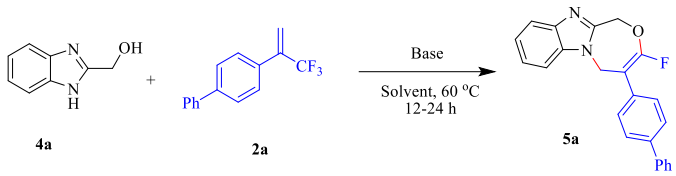
3.2 Synthesis of compounds **5a-5o:**

To a 10 mL oven-dried glass vial equipped with a stir bar, (1H-benzo[d]imidazol-2-yl)methanol **4a-4d** (0.2 mmol), α- (trifluoromethyl) styrene 2 (0.2 mmol), Cs_2CO_3 (3.5 equiv), and DMSO (1 mL) were vigorously stirred at 60°C for 12 hours. After the reaction was complete, as monitored by TLC, water was added to cause the product to precipitate, and it was then extracted with EtOAc (3×10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and all volatiles were evaporated under reduced pressure. Finally, the compounds were purified by flash chromatography (eluting with petroleum ether/ethyl acetate), yielding the corresponding products **5a-5o**.



4a-4d **2** **5a-5o**

Table 2. Optimization of reaction conditions



4a 2a 5a

entry	base (3.5 equiv.)	solvent	temp (°C)	time (h)	yield (%)
1	NaOH	DMF	r.t	12	trace
2	Na_2CO_3	DMF	r.t	12	trace
3	$Na_2 CO_3$	DMSO	r.t	12	trace
4	K_2CO_3	DMF	r.t	12	trace
5	K_2CO_3	DMSO	r.t	12	trace
6	Cs_2CO_3	DMF	r.t	12	41
7	Cs_2CO_3	DMSO	r.t	12	44
8[c]	Cs_2CO_3	DMSO	45	12	49
9	**Cs_2CO_3**	**DMSO**	**60**	**12**	**88**
10[d]	Cs_2CO_3(2 equiv.)	DMSO	60	12	52
11[e]	Cs_2CO_3(2.5 equiv.)	DMSO	60	12	60
12[f]	Cs_2CO_3 (3 equiv.)	DMSO	60	12	73
13	DBU	DMSO	60	12	trace
14	DABCO	DMSO	60	12	0
15	Et_3N	DMSO	60	12	0
16	Cs_2CO_3	EtOH	60	12	0
17	Cs_2CO_3	MeOH	60	12	0
18	Cs_2CO_3	Acetone	60	12	0
19	Cs_2CO_3	THF	60	12	0
20	----	DMSO	60	12	0

[a]General Reaction conditions: **4a** (0.2 mmol), **2a** (0.2 mmol), base (0.7mmol), solvent (1 mL), 60 °C, 12 h. [b] Isolated yield. [c]temperature at 45 °C. [d] with (2 equiv.) of Cs_2CO_3. [e] with (2.5 equiv) of Cs_2CO_3. [f] with (3 equiv.) of Cs_2CO_3.

3.3 Synthesis of compounds **7a-7k:**

To a 10 mL oven-dried glass vial equipped with a stir bar, (1H-indol-2-yl)methanol 6 (0.2 mmol), α-(trifluoromethyl)styrene **2** (0.2 mmol), t-BuOK (3.5 equivalents), and CH3CN (1 mL) were vigorously stirred at 80 °C for 12 hours. After monitoring the reaction by TLC and completion, water

was added, resulting in the precipitation of the product. The precipitate was then extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and all volatiles were evaporated under reduced pressure. Finally, the compounds were purified by flash chromatography (eluting with petroleum ether/ethyl acetate), yielding the corresponding products **7a-7k**.

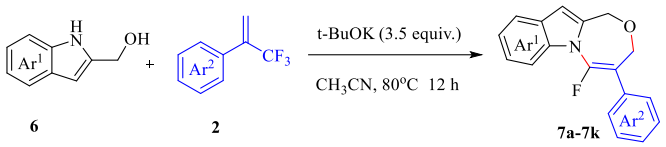
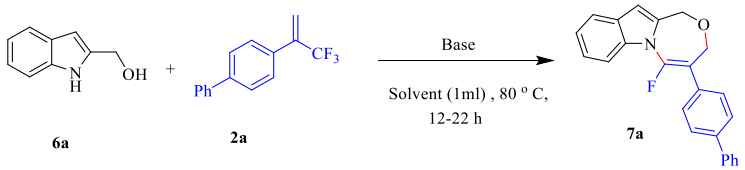


Table 3. Optimization of reaction conditions



entry	base (3.5 equiv.)	solvent	temp (°C)	time (h)	[b]yield (%)
1	Cs_2CO_3	DMF	r.t	12	trace
2	Cs_2CO_3	DMSO	r.t	12	trace
3	K_2CO_3	DMF	r.t	12	trace
4	K_2CO_3	DMSO	r.t	12	trace
5	K_2CO_3	CH_3CN	r.t	12	0
6	*t*-BuONa	CH_3CN	r.t	12	26
7	*t*-BuOK	CH_3CN	r.t	12	31
8[c]	*t*-BuOK	CH_3CN	40	12	37
9[d]	*t*-BuOK	CH_3CN	55	12	39
10[e]	*t*-BuOK	CH_3CN	65	12	42
11	*t*-BuOK	CH_3CN	80	12	78
12[f]	*t*-BuOK (2 equiv.)	CH_3CN	80	12	49
13[g]	*t*-BuOK (2.5 equiv.)	CH_3CN	80	12	55
14[h]	*t*-BuOK (3 equiv.)	CH_3CN	80	12	63
15	DBU	CH_3CN	80	12	trace
16	DABCO	CH_3CN	80	12	0
17	Et_3N	CH_3CN	80	12	0
18	*t*-BuOK	EtOH	80	12	0
19	*t*-BuOK	MeOH	80	12	0
18	*t*-BuOK	toluene	60	12	0

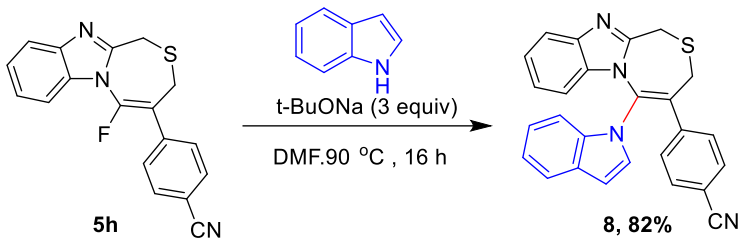
19	*t*-BuOK	THF	60	12	0
20	----	CH_3CN	60	12	0

4. [a] General Reaction conditions: **6a** (0.2 mmol), **2a** (0.2 mmol), base (0.7mmol), solvent (1 mL), 80 °C, 12 h. [b] Isolated yield. [c]Temperature at 40 °C. [d]Temperature at 55 °C. [e]Temperature at 65. [f] with (2 equiv) of K_2CO_3, [g] with (2.5equiv) of K_2CO_3. [h]with (3 equiv) of K_2CO_3.

5. Transformation of 5h

5.1 General procedure for the synthesis of compound **5h**

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **5h** (0.2 mmol), indole (0.4 mmol), *t*-BuONa (0.6 mmol), and DMF (1 mL) was vigorously stirred at 90 °C for 16 hours. Then, the mixture was stopped, water (15 mL) was added, and it was extracted with EtOAc (15 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) yielded the defluorination product **8** with an isolated yield of 82%.



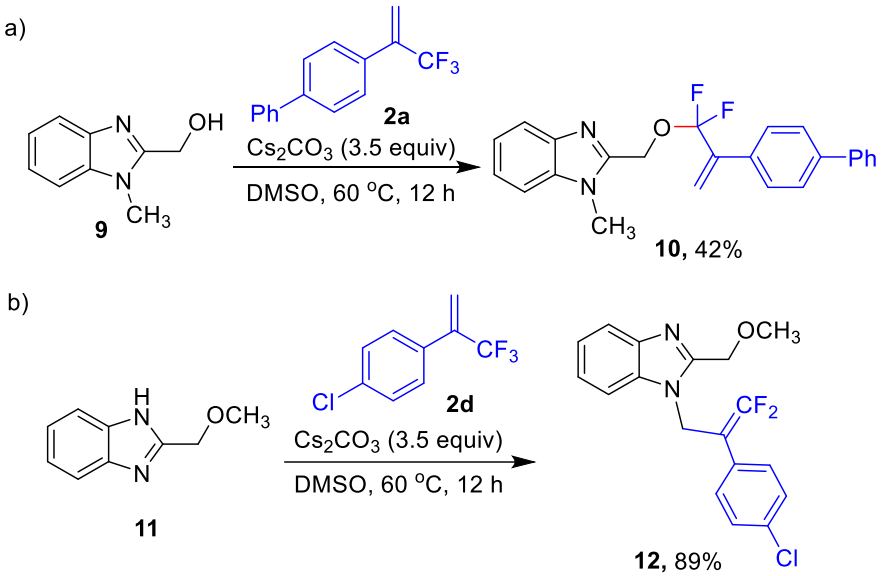
6. Mechanistic Studies

6.1 Control experiments

We carried out two control experiments to gain further insights into the mechanism. **a**) To a 10 mL oven-dried glass vial equipped with a stir bar, *N*-Protected (1-methyl-1H-benzo[d]imidazol-2-yl)methanol (0.2 mmol) **9**, α- (trifluoromethyl) styrene **2a** (0.2 mmol), Cs_2CO_3 (3.5 equivalents), and DMSO (1 mL) were vigorously stirred at 60 °C for 12 hours. After the reaction was complete, monitored by TLC, water was added to precipitate the product, which was then extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all volatiles were evaporated under reduced pressure. Finally, the *gem*-difluoroalkylated product **10** was obtained and purified by flash chromatography (eluting with petroleum ether/ethyl acetate).

b) The second control experiment was also conducted under the same standard reaction conditions, where *O*-protected 2-(methoxymethyl)-1H-benzo[d]imidazole (0.2 mmol) **11**, α-(trifluoromethyl) styrene **2d** (0.2 mmol), Cs_2CO_3 (3.5 equivalents), and DMSO (1 mL) were vigorously stirred at 60 °C for 12 hours. After the reaction was monitored by TLC and shown to be complete, water was added,

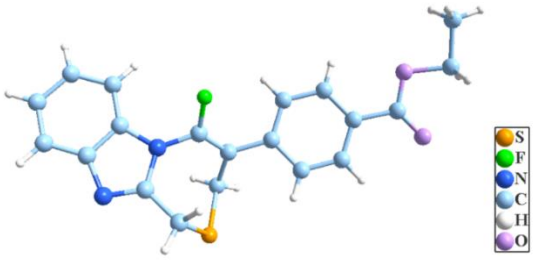
precipitating the product, which was then extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and all volatiles were evaporated under reduced pressure. Finally, flash chromatography (eluting with petroleum ether/ethyl acetate) was used to obtain the desired compound **12** in 89% yield. The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of the new compound indicate that the reaction mechanism involves a unique sequential *ipso*-/*γ*-selective defluorinative cyclization.



7. X-ray Crystallographic Data of compounds 3k, 5o and 7g.

7.1 The preparation of a crystal of compound **3k (CCDC 2451045).**

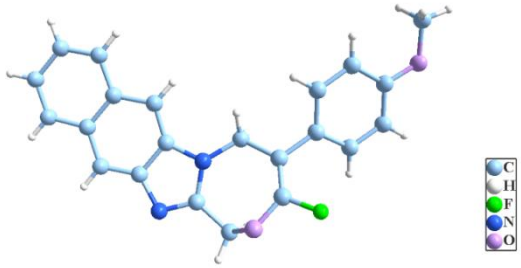
The obtained compound **3k** (55 mg,79% yield) was dissolved in an appropriate amount of dichloromethane (CH_2Cl_2) in a 5 ml glass vial to form a saturated solution at room temperature. Then the petroleum ether (10 ml) was added to form the two-phase mixture. Slow evaporation of a two-phase mixture led to odorless, colorless crystals. Thermal ellipsoids of the crystal structure of compound **3k** were set at 50% occupancy, and the crystal data have been deposited in the CCDC under the number **2451045.**



Identification code	CCDC 2451045
Empirical formula	$C_{20}H_{17}FN_2O_2S$
Formula weight	368.41
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	14.458(3)
b/Å	7.3920(19)
c/Å	33.338(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3563.0(16)
Z	8
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	0.208
F(000)	1536.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.636 to 50.104
Index ranges	$-17 \leq h \leq 17$, $-8 \leq k \leq 8$, $-39 \leq l \leq 38$
Reflections collected	45643
Independent reflections	6259 [R_{int} = 0.0788, R_{sigma} = 0.0592]
Data/restraints/parameters	6259/119/511
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1026
Final R indexes [all data]	R_1 = 0.0990, wR_2 = 0.1275
Largest diff. peak/hole / e Å^{-3}	0.20/-0.23
Flack parameter	0.35(4)

7.2 The preparation of a crystal of compound **5o (CCDC 2451045).**

The obtained compound **5o** (47 mg,76% yield) was dissolved in an appropriate amount of methanol (CH_3OH) in a 5 ml glass vial to form a saturated solution at room temperature. Then ethyl acetate (5ml) and petroleum ether (5ml) were added to form the three-phase mixture. The vial was then sealed with parafilm. Slow evaporation of the three-phase mixture resulted in odorless light green crystals. Thermal ellipsoids of the crystal structure of **5o** were set at 50% and the crystal data have been deposited to CCDC number **2451045**.

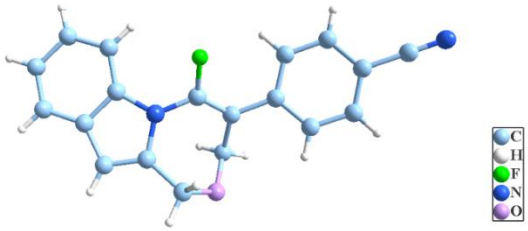


Identification code	2470562
Empirical formula	$C_{22}H_{17}FN_2O_2$
Formula weight	360.37
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	14.974
b/Å	7.741
c/Å	29.954
α/°	90
β/°	91.40
γ/°	90
Volume/Å^3	3471.1
Z	8
ρ_{calc}g/cm^3	1.379
μ/mm^{-1}	0.793
F(000)	1504.0
Crystal size/mm^3	0.12 × 0.1 × 0.08

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.902 to 134.41
Index ranges	$-17 \leq h \leq 17$, $-9 \leq k \leq 9$, $0 \leq l \leq 35$
Reflections collected	5853
Independent reflections	3085 [R_{int} = 0.1120, R_{sigma} = 0.0924]
Data/restraints/parameters	3085/0/245
Goodness-of-fit on F^2	0.936
Final R indexes [I>=2σ (I)]	R_1 = 0.0724, wR_2 = 0.1988
Final R indexes [all data]	R_1 = 0.1104, wR_2 = 0.2317
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.26

7.3 The preparation of a crystal of compound **7g (CCDC 2470561).**

The obtained compound **7g** (55 mg, 91% yield) was dissolved in an appropriate amount of dichloromethane (CH_2Cl_2) in a 5 ml glass vial to form a saturated solution at room temperature. Then the petroleum ether (10 ml) was added to form the two-phase mixture. Slow evaporation of the two-phase mixture yielded odorless red crystals weighing **7g**. Thermal ellipsoids of the crystal structure were set at 50%, and the crystal data have been deposited in the CCDC under the number 2470561.

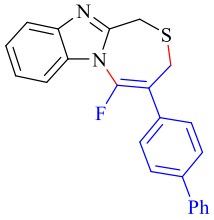


Identification code	2470561
Empirical formula	$C_{19}H_{13}FN_2O$
Formula weight	304.31
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.149
b/Å	12.237
c/Å	11.005

α/°	90
β/°	97.90
γ/°	90
Volume/Å^3	1487.1
Z	4
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	0.771
F(000)	632.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.006 to 133.348
Reflections collected	2595
Independent reflections	2595 [R_{int} = 0, R_{sigma} = 0.0394]
Data/restraints/parameters	2595/0/208
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1615
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1693
Largest diff. peak/hole / e Å^{-3}	0.16/-0.26

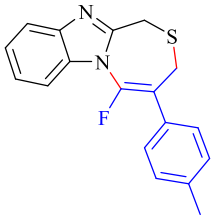
8. Analytical and characterization data

4-([1,1'-biphenyl]-4-yl)-5-fluoro-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3a)**



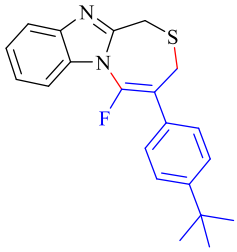
Compound **3a** was isolated as a white solid after flash chromatography (petroleum ether/EtOAc = 10:4), 57 mg, 77 % yield, m.p.: 198–202 ˚C, R_f = 0.42.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84–7.81 (m, 1H), 7.80–7.78 (m, 2H), 7.73–7.70 (m, 2H), 7.67–7.64 (m, 2H), 7.58–7.55 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42–7.37 (m, 4H), 4.17 (s, 2H), 3.47 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2 (d, *J* = 264.6 Hz), 135.1, 134.9 (d, *J* = 4.3 Hz), 132.9, 131.3, 130.4, 127.7, 127.6, 127.6, 126.7 (d, *J* = 2.3 Hz), 125.6, 125.1, 124.4, 124.2, 122.8, 121.2, 120.3, 111.7 (d, *J* = 7.6 Hz), 104.2 (d, *J* = 2.0 Hz), 102.4 (d, *J* = 18.5 Hz), 67.4 (d, *J* = 4.4 Hz), 61.1.^{19}F NMR (565 MHz, $CDCl_3$) δ -97.34. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}FN_2S$ 373.1175, found 373.1181.

5-fluoro-4-(p-tolyl)-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]thiazepine (**3b)**



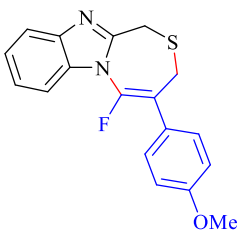
Compound (**3b)** was isolated as light-yellow crystals after flash chromatography(petroleum ether/EtOAc = 10:4), 20 mg, 32% yield, m.p.: 156–158 ˚C, R_f = 0.45. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.80 (m, 1H), 7.61–7.58 (m, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.39–7.35 (m, 2H), 7.30–7.28 (m, 2H), 4.15 (s, 2H), 3.42 (d, *J* = 1.6 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 143.7, 141.9, 138.7, 133.3, 130.4 (d, *J* = 4.9 Hz), 129.5, 127.9 (d, *J* = 4.7 Hz), 124.4, 124.2, 120.3, 111.2 (d, *J* = 2.2 Hz),30.8 (d, *J* = 2.4 Hz), 25.2, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.90. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}FN_2S$ 311.1018, found 311.1014.

4-(4-(*tert*-butyl)phenyl)-5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3c)**



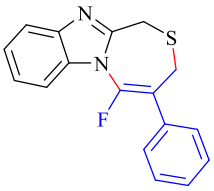
Compound **(3c)** was isolated as a light orange solid after flash chromatography (petroleum ether/EtOAc = 10:3), 49 mg, 71% yield, m.p.: 146–148 ˚C, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.67–7.63 (m, 2H), 7.54 (m, *J* = 6.1, 2.1 Hz, 1H), 7.52–7.48 (m, 2H), 7.39–7.35 (m, 2H), 4.14 (s, 2H), 3.43 (d, *J* = 1.5 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 150.9 (d, *J* = 2.1 Hz), 143.9, 142.7, 142.1, 133.5 (d, *J* = 4.5 Hz), 130.5 (d, *J* = 5.0 Hz), 127.9 (d, *J* = 4.9 Hz), 125.9, 124.5, 124.2, 120.45, 111.3 (d, *J* = 2.4 Hz), 111.2, 111.1, 34.9, 31.4, 30.8 (d, *J* = 2.5 Hz), 25.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -94.10. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}FN_2S$ 353.1488, found 353.1491.

5-fluoro-4-(4-methoxyphenyl)-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3d)**



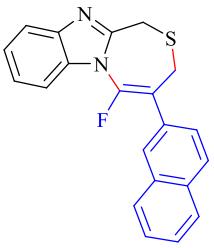
Compound **(3d)** was isolated as light colorless crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 24 mg, 36% yield, m.p.: 98–100˚C, R_f = 0.41. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.80 (m, 1H), 7.66–7.63 (m, 2H), 7.54 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.40–7.35 (m, 3H), 7.02–6.99 (m, 2H), 4.15 (s, 2H), 3.87 (s, 3H), 3.41 (d, *J* = 1.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 150.8, 141.3, 129.4 (d, *J* = 5.0 Hz), 125.4 (d, *J* = 5.0 Hz), 124.4, 124.1, 120.2, 114.2, 111.1, 55.3, 30.7, 25.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ -94.72. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}FN_2OS$ 327.0967, found 327.0962.

5-fluoro-4-phenyl-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3e)**



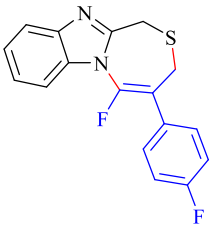
Compound **(3e)** was isolated as a colorless solid. after flash chromatography (petroleum ether/EtOAc = 10:3), 82 mg, 52% yield, m.p.: 149–150 ˚C, R_f = 0.46. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.71 (m, *J* = 8.2, 1.2 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.42–7.37 (m, 3H), 4.16 (s, 2H), 3.44 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 143.9, 142.6, 142.2, 133.4 (d, *J* = 4.9 Hz), 133.2, 128.7, 128.5, 128.0 (d, *J* = 4.6 Hz), 124.3, 124.1, 120.3, 111.1, 111.1 (d, *J* = 2.4 Hz), 111.0, 30.8 (d, *J* = 2.2 Hz), 25.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -92.51. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}FN_2S$ 297.0862, found 297.0853.

5-fluoro-4-(naphthalen-1-yl)-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3f)**



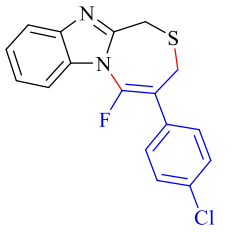
Compound **(3f)** was isolated as a yellow-orange solid after flash chromatography (petroleum ether/EtOAc = 10:4), 52 mg, 75% yield, m.p.: 162–164 ˚C, R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.93 (m, 3H), 7.87–7.83 (m, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.62–7.54 (m, 4H), 7.43–7.35 (m, 2H), 4.23 (d, J = 75.5 Hz, 2H), 3.49 (d, J = 113.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 145.8, 143.1 (d, *J* = 4.0 Hz), 134.4, 133.9 (d, *J* = 4.6 Hz), 131.7 (d, *J* = 2.2 Hz), 129.8, 129.3, 127.7 (d, *J* = 2.3 Hz), 127.3, 126.8, 125.9, 125.2, 124.9, 124.7, 120.9, 111.7 (d, *J* = 2.5 Hz), 111.1, 110.9, 32.4 (d, *J* = 2.3 Hz), 26.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.75. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{16}FN_2S$ 347.1018, found 347.1024.

5-fluoro-4-(4-fluorophenyl)-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3g)**



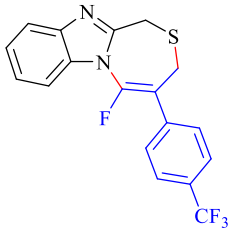
Compound **(3g)** was isolated as yellow crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 24 mg, 38% yield, m.p.: 224–226˚C, R_f = 0.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83–7.79 (m, 1H), 7.72–7.67 (m, 2H), 7.56–7.51 (m, 1H), 7.40–7.36 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 4.15 (s, 2H), 3.41 (d, *J* = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 151.2, 130.5 (dd, *J* = 8.2, 4.9 Hz), 129.8, 125.1, 124.9, 120.7, 116.5, 116.2, 111.6 (d, *J* = 2.3 Hz), 111.1, 110.9, 31.3 (d, *J* = 2.3 Hz), 25.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -98.50, -111.96. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}F_2N_2S$ 315.0786, found 315.0778.

4-(4-chlorophenyl)-5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4] thiazepine **(3h)**



Compound **(3h)** was isolated as a yellow-orange solid after flash chromatography (petroleum ether/EtOAc = 10:3), 52 mg, 78% yield, m.p.: 237–239 ˚C, R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.79 (m, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.55–7.51 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.39–7.36 (m, 2H), 4.14 (s, 2H), 3.40 (d, J = 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 144.6, 142.5, 141.9, 134.4, 133.1 (d, *J* = 4.9 Hz), 131.7 (d, *J* = 4.9 Hz), 129.2 (d, *J* = 5.1 Hz), 128.8, 124.3, 124.1, 120.3, 110.9 (d, *J* = 2.4 Hz), 109.9, 109.8, 30.5 (d, *J* = 2.1 Hz), 25.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -97.29. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClFN_2S$ 331.0477, found 331.0484.

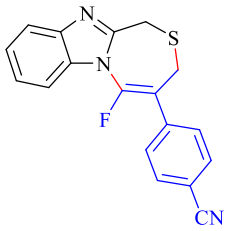
5-fluoro-4-(4-(trifluoromethyl) phenyl)-1*H*,3*H*-benzo [4,5] imidazo[2,1-c] [1,4] thiazepine **(3i)**



Compound **(3i)** was isolated as light-yellow crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 56 mg, 78% yield, m.p.: 179–181 ˚C, R_f = 0.54. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85–7.80 (m, 3H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.55 (dd, *J* = 6.3, 3.1 Hz, 1H), 7.41–7.37 (m, 2H), 4.17 (s, 2H), 3.44 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8 (d, *J* = 2.0 Hz), 145.4, 143.6, 142.9, 137.5, 133.6 (d, *J* = 4.5 Hz), 131.0, 130.8, 128.8 (d, *J* = 4.9 Hz), 126.1 (q, *J* = 3.8 Hz), 125.1, 124.9, 124.7, 120.8, 111.5 (d, *J* = 2.4 Hz), 110.3 (d, *J* = 16.5 Hz), 31.0 (d, *J* = 2.1 Hz), 25.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -93.42, -126.79. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}F_4N_2S$ 365.0736, found 365.0741.

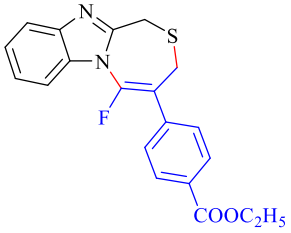
.

4-(5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepin-4-yl)benzonitrile **(3j)**



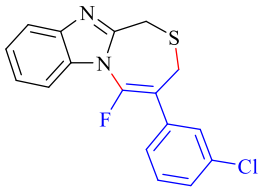
Compound **(3j)** was isolated as a dark brown solid after flash chromatography (petroleum ether/EtOAc = 10:3), 52 mg, 81% yield, m.p.: 249–251 ˚C, R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 3H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.56–7.52 (m, 1H), 7.41–7.37 (m, 2H), 4.16 (s, 2H), 3.44 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8 (d, *J* = 2.1 Hz), 146.3, 143.6, 142.9, 138.7 (d, *J* = 5.2 Hz), 133.6 (d, *J* = 4.5 Hz), 132.9, 129.2 (d, *J* = 5.3 Hz), 125.2, 124.9, 120.9, 118.8, 112.7, 111.6 (d, *J* = 2.5 Hz), 110.1, 109.9, 30.9 (d, *J* = 2.0 Hz), 25.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.68. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}FN_3S$ 322.0814, found 322.0813.

ethyl 4-(5-fluoro-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]thiazepin-4-yl)benzoate **(3k)**



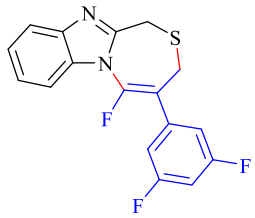
Compound **(3k)** was isolated as a dark brown solid after flash chromatography (petroleum ether/EtOAc = 10:3), 57 mg, 79% yield, m.p.: 272–274 ˚C, R_f = 0.41. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H), 7.71–7.66 (m, 3H), 7.45–7.43 (m, 1H), 7.29–7.27 (m, 2H), 4.32 (d, J = 7.2 Hz, 2H), 4.06 (s, 2H), 3.34 (d, J = 1.5 Hz, 2H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 150.4 (d, J = 2.1 Hz), 145.2, 142.4, 137.8 (d, J = 5.1 Hz), 133.1 (d, J = 4.6 Hz), 130.2, 129.7, 127.9 (d, J = 5.0 Hz), 124.4, 124.1, 120.3, 110.9 (d, J = 2.3 Hz), 110.1 (d, J = 16.3 Hz), 61.0, 30.4 (d, J = 2.2 Hz), 25.1, 14.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.99. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{18}FN_2O_2S$ 369.1073, found 369.1064.

4-(3-chlorophenyl)-5-fluoro-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3l)**



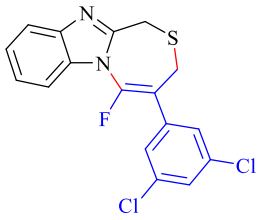
Compound **(3l)** was isolated as Light green crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 44 mg, 66% yield, m.p.: 254–256˚C, R_f = 0.52. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.80 (m, 1H), 7.71–7.70 (m, 1H), 7.59 (dd, J = 7.4, 1.4 Hz, 1H), 7.54 (d, J = 7.0 Hz, 1H), 7.43–7.36 (m, 4H), 4.15 (s, 2H), 3.41 (d, J = 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5 (d, J = 2.0 Hz), 144.6, 142.8, 142.5,135.2 (d, J = 4.8 Hz), 134.6, 133.2 (d, J = 4.7 Hz), 129.9, 128.6, 128.1 (d, J = 5.0 Hz), 1126.2 (d, J = 4.5 Hz), 124.5, 124.2, 120.4, 111.1 (d, J = 2.5 Hz), 109.9 (d, J = 16.4 Hz), 30.6 (d, J = 2.1 Hz), 25.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -95.50. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClFN_2S$ 331.0472, found 331.0477.

4-(3,5-difluorophenyl)-5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3m)**



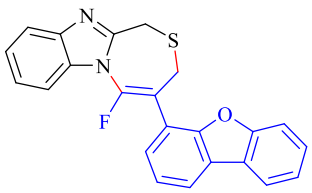
Compound **(3m)** was isolated as light colorless crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 28 mg, 42% yield, m.p.: 200–202 ˚C, R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.77 (m, 1H), 7.53 (dd, J = 4.6, 2.6 Hz, 1H), 7.40–7.36 (m, 2H), 7.26 (m, J = 5.5, 2.1 Hz, 2H), 6.86 (s, 1H), 4.14 (s, 2H), 3.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (dd, J = 249.0,13.1 Hz), 150.8 (d, J = 1.9 Hz), 143.0, 133.7, 125.2, 124.9, 120.9, 111.9, 111.8, 111.6, 111.6, 111.5, 104.6 (t, J = 25.2 Hz), 30.9 (d, J = 2.0 Hz), 25.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.88, -108.65. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{12}F_3N_2S$ 333.0672, found 333.0674.

4-(3,5-dichlorophenyl)-5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3n)**



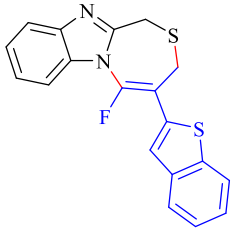
Compound **(3n)** was isolated as a dark yellow solid after flash chromatography (petroleum ether/EtOAc = 10:4), 49 mg, 66 % yield, m.p.: 202–204 °C, R_f = 0.47. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.79 (m, 1H), 7.59 (d, *J* = 1.8 Hz, 2H), 7.52 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.41–7.36 (m, 3H), 4.14 (s, 2H), 3.38 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 145.6, 143.8, 143.0, 136.7 (d, *J* = 4.9 Hz), 135.8, 133.5 (d, *J* = 4.6 Hz), 128.9, 126.9 (d, *J* = 5.2 Hz), 125.0, 124.7, 120.9, 111.4 (d , *J* = 2.5 Hz), 109.2 (d, *J* = 16.4 Hz), 30.8 (d, *J* = 2.1 Hz), 25.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -93.08. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{12}Cl_2FN_2S$, 365.0082 found 365.0085.

4-(dibenzo[b,d]furan-4-yl)-5-fluoro-1H,3H-benzo [4,5] imidazo[2,1-c] [1,4] thiazepine **(3o)**



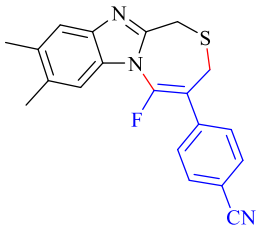
Compound **3o** was isolated as a light-yellow solid after flash chromatography (petroleum ether/EtOAc = 10:3), 59 mg, 70% yield, m.p.: 192–194 °C. R_f = 0.39. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04–7.99 (m, 2H), 7.85–7.83 (m, 1H), 7.64 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.61 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.55 (s, 1H), 7.53–7.43 (m, 2H), 7.42–7.35 (m, 3H), 4.30 (s, 2H), 3.66 (d, *J* = 1.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 153.8, 151.5, 145.5, 143.6, 142.9, 133.5 (d, *J* = 4.4 Hz), 128.0, 127.5 (d, *J* = 3.2 Hz), 125.4, 124.8, 124.5, 124.3, 123.5 (d, *J* = 5.9 Hz), 121.6, 121.2, 120.7, 117.9 (d, *J* = 3.3 Hz), 112.2, 111.7 (d, *J* = 2.6 Hz), 107.3 (d, *J* = 19.7 Hz), 31.2 (d, *J* = 2.6 Hz), 25.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.63. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{16}FN_2S$ 387.0967, found 387.0971.

4-(benzo[b]thiophen-2-yl)-5-fluoro-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepine **(3p)**



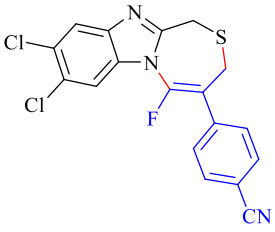
Compound **3p** was isolated as an orange solid after flash chromatography (eluting with petroleum ether/EtOAc = 10:4),46 mg, 65% yield, m.p.: 243–245 °C, R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 1H), 7.82 (m, J = 6.6, 3.9 Hz, 2H), 7.61 (s, 1H), 7.59–7.55 (m, 1H), 7.40 (m, J = 5.0, 4.5, 2.1 Hz, 4H), 4.13 (s, 2H), 3.58 (d, J = 1.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6 (d, *J* = 2.5 Hz), 142.8, 140.2 (d, *J* = 7.0 Hz), 139.4, 134.5 (d, *J* = 9.3 Hz), 133.5 (d, *J* = 4.8 Hz), 125.5, 124.9, 124.8, 124.5, 124.1, 123.9, 123.9, 122.2, 120.6, 111.4 (d, *J* = 2.4 Hz), 106.8 (d, *J* = 16.8 Hz), 29.9 (d, *J* = 2.7 Hz), 25.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -91.60. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{14}FN_2S_2$ 353.0582, found 353.0589.

4-(5-fluoro-8,9-dimethyl-1*H*,3*H*-benzo[4,5]imidazo[2,1-c][1,4]thiazepin-4-yl)benzonitrile **(3q)**



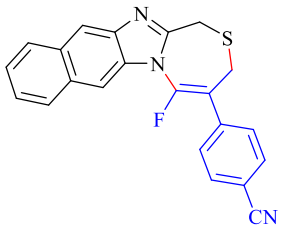
Compound **3q** was isolated as a dark brown solid after flash chromatography (petroleum ether/EtOAc = 10:3), 62 mg, 89% yield, m.p.: 233-235 ˚C, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.54 (s, 1H), 7.30 (s, 1H), 4.12 (s, 2H), 3.41 (s, 2H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (d, *J* = 1.9 Hz), 146.3, 143.6, 141.2, 138.6 (d, *J* = 5.2 Hz), 134.2, 133.6, 132.6, 131.8 (d, *J* = 4.7 Hz), 128.9 (d, *J* = 5.2 Hz), 120.6, 118.6, 112.1, 111.5 (d, *J* = 2.4 Hz), 109.3, 109.1, 30.6 (d, *J* = 2.1 Hz), 25.4, 20.5 (d, *J* = 19.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.34. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{17}FN_3S$ 350.1127, found 350.1131.

4-(8,9-dichloro-5-fluoro-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]thiazepin-4-yl)benzonitrile **(3r)**



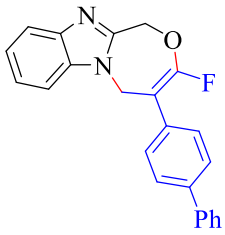
Compound **(3r)** was isolated as yellow crystals after flash chromatography (petroleum ether/EtOAc = 10:3), 61 mg, 73% yield, m.p.: 269–271 ˚C, R_f = 0.34. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66(d, *J* = 1.5 Hz, 1H), 4.13 (s, 2H), 3.43 (d, *J* = 1.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 144.4, 142.6, 141.9, 137.7 (d, *J* = 5.4 Hz), 132.5, 132.1 (d, *J* = 4.5 Hz), 128.9, 128.8, 128.7 (d, *J* = 5.2 Hz), 121.7, 118.2, 112.6 (d, *J* = 2.5 Hz), 112.5, 110.4, 110.3, 30.3, 25.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.58. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{11}Cl_2FN_3S$ 390.0035, found 390.0037.

4-(5-fluoro-1*H*,3*H*-naphtho[2',3':4,5]imidazo[2,1-c][1,4]thiazepin-4-yl)benzonitrile **(3s)**



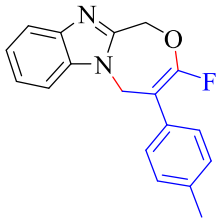
Compound **(3s)** was isolated as a dark orange solid after flash chromatography (petroleum ether/EtOAc = 10:3), 68 mg, 92 % yield, m.p.: 239–241 ˚C, R_f = 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.05–8.02 (m, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.80–7.77 (m, 2H), 7.50 (td, *J* = 7.2, 1.5 Hz, 2H), 4.21 (s, 2H), 3.49 (d, *J* = 1.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7 (d, *J* = 2.1 Hz), 144.0, 142.6, 142.2, 141.3, 140.2, 133.3 (d, *J* = 4.5 Hz), 132.2 (d, *J* = 5.2 Hz), 128.8, 128.4 (d, *J* = 4.9 Hz), 127.7, 127.3, 127.0, 124.3, 124.1, 120.3, 111.1 (d, *J* = 2.3 Hz), 110.7 (d, *J* = 16.4 Hz), 30.6 (d, *J* = 2.4 Hz), 25.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -95.50. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}FN_3S$ 372.0971, found 372.0967.

4-([1,1'-biphenyl]-4-yl)-3-fluoro-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5a)**



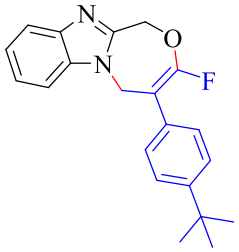
Compound **(5a)** was isolated as colorless crystals after flash chromatography (petroleum ether/EtOAc = 1:1), 62 mg, 88% yield, m.p.: 136–138˚C, R_f = 0.55. **^{1}H** NMR (600 MHz, $CDCl_3$) δ 7.84–7.81 (m, 1H), 7.66–7.60 (m, 4H), 7.48–7.42 (m, 5H), 7.39–7.32 (m, 3H), 5.56 (s, 2H), 5.09 (d, J = 4.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 157.0, 148.6 (d, J = 2.3 Hz), 142.1, 140.8, 140.6, 135.2, 133.7 (d, J = 2.8 Hz), 129.2, 129.0 (d, J = 3.2 Hz), 127.9, 127.7, 127.3, 123.8, 123.1, 120.6, 109.4, 93.3 (d, J = 28.4 Hz), 67.5, 44.1 (d, J = 3.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.99. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}FN_2O$ 357.1403, found 357.1407.

3-fluoro-4-(p-tolyl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5b)**



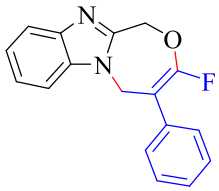
Compound **(5b)** was isolated as a yellow solid after flash chromatography (petroleum ether/EtOAc = 1:1), 33 mg, 56% yield, m.p.: 102–104 ˚C, R_f = 0.42. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.6, 1.4 Hz, 1H), 7.41–7.39 (m, 1H), 7.37–7.31 (m, 2H), 7.25–7.24 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 5.55 (s, 2H), 5.05 (d, J = 4.2 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 148.4, 141.6, 137.7, 134.9, 131.4 (d, J = 2.8 Hz), 129.5, 128.2 (d, J = 3.2 Hz), 123.5, 122.9, 120.2, 109.1, 93.3 (d, J = 28.9 Hz), 67.2, 44.1 (d, J = 3.4 Hz), 21.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.34. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}FN_2O$ 295.1247, found 294.1250.

4-(4-(tert-butyl)phenyl)-3-fluoro-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5c)**



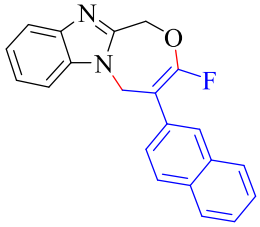
Compound **(5c)** was isolated as off-white crystals after flash chromatography (petroleum ether/EtOAc = 1:1), 41 mg, 61% yield, m.p.: 133–135 ˚C, R_f = 0.54. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.78 (m, 1H), 7.45–7.40 (m, 3H), 7.38–7.28 (m, 4H), 5.56 (s, 2H), 5.08 (d, J = 4.1 Hz, 2H), 1.34 (d, J = 1.3 Hz, 9H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5 (d, J = 269.7 Hz), 150.8, 148.3, 141.3, 134.8, 131.2 (d, J = 2.8 Hz), 127.9 (d, J = 3.2 Hz), 125.7, 123.5, 122.9, 120.0, 109.0, 93.5 (d, J = 28.7 Hz), 67.2, 43.9 (d, J = 3.4 Hz), 34.6, 31.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -76.05. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}FN_2O$ 337.1750, found 337.1754.

3-fluoro-4-phenyl-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5d)**



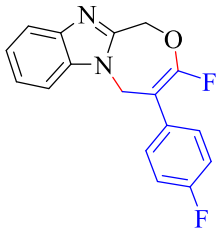
Compound **(5d)** was isolated as a dark brown solid after flash chromatography (petroleum ether/EtOAc = 1:1), 34 mg, 60% yield, m.p.: 122–124 ˚C, R_f = 0.59. H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.43–7.38 (m, 3H), 7.36 (m, 3H), 7.32 (m,2H), 5.54 (s, 2H), 5.07 (d, J = 4.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, J = 268.5 Hz), 148.6 (d, J = 2.5 Hz), 141.9, 135.2, 134.8 (d, J = 2.7 Hz), 129.4, 129.1, 128.7 (d, J = 3.0 Hz), 128.1, 123.9, 123.2, 120.5, 109.4, 93.6 (d, J = 28.5 Hz), 67.4, 44.3 (d, J = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -79.88. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}FN_2O$ 281.1090, found 281.1089.

3-fluoro-4-(naphthalen-2-yl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepane **(5e)**



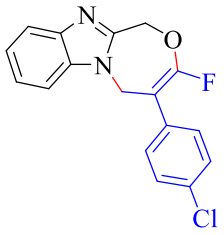
Compound **(5e)** was isolated as an orange solid after flash chromatography (petroleum ether/EtOAc = 1:1), 49 mg, 74% yield, m.p.: 157–159 ˚C, R_f = 0.46. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.87–7.84 (m, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.52 (m, J = 7.8, 5.7, 4.1 Hz, 2H), 7.49–7.44 (m, 2H), 7.36–7.30 (m, 2H), 7.25 (d, J = 1.8 Hz, 1H), 5.73–5.61 (m, 2H), 5.09–4.97 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4 (d, J = 257.2 Hz), 148.3, 141.8, 135.0, 134.0, 131.9, 131.2, 128.8 (d, J = 6.9 Hz), 127.9, 126.9, 126.2, 125.6, 124.3, 123.7, 122.9, 120.4, 109.1, 88.5 (d, J = 32.9 Hz), 66.3, 44.1 (d, J = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -75.99. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{16}FN_2O$ 331.1247, found 331.1253.

3-fluoro-4-(4-fluorophenyl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5f)**



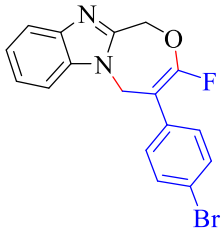
Compound **(5f)** was isolated as a white solid after flash chromatography (petroleum ether/EtOAc = 1:1), 35 mg, 55% yield, m.p.: 167–169 ˚C, R_f = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.9, 1.8 Hz, 1H), 7.41–7.30 (m, 6H), 7.13–7.07 (m, 2H), 5.54 (s, 2H), 5.03 (d, J = 4.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.6, 158.7, 156.1, 147.9, 141.6, 134.7, 130.3, 129.9 (dd, J = 8.2, 3.0 Hz), 123.4, 122.7, 120.2, 115.6 (d, J = 21.7 Hz), 108.8, 91.9 (d, J = 28.8 Hz), 66.9, 43.8 (d, J = 3.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -79.58, -113.69. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}F_2N_2O$ 299.0996, found 299.0997.

4-(4-chlorophenyl)-3-fluoro-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5g)**



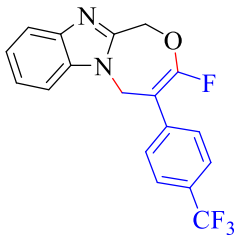
Compound **(5g)** was isolated as light-yellow crystals after flash chromatography (petroleum ether/EtOAc = 1:1), 52 mg, 83% yield, m.p.: 150–152˚C, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.36 (dt, *J* = 6.9, 2.2 Hz, 4H), 7.32 (dd, *J* = 7.2, 2.3 Hz, 1H), 7.28 (s, 1H), 5.53 (s, 2H), 5.01 (d, *J* = 4.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 156.7, 148.5 (d, *J* = 2.1 Hz), 142.2, 135.3, 134.0, 133.4 (d, *J* = 2.6 Hz), 130.1 (d, *J* = 3.2 Hz), 129.4, 124.0, 123.3, 120.8, 109.4, 92.4 (d, *J* = 28.5 Hz), 67.5, 44.1 (d, *J* = 3.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.76. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{13}ClFN_2O$ 315.0700, found 315.0707.

4-(4-bromophenyl)-3-fluoro-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5h)**



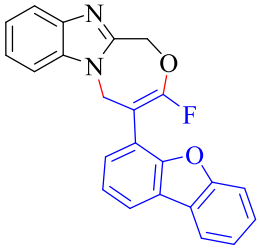
Compound **(5h)** was isolated as a light-yellow solid after flash chromatography (petroleum ether/EtOAc = 1:1), 55 mg, 77% yield, m.p.: 132–134 ˚C, R_f = 0.31. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81–7.79 (m, 1H), 7.55–7.52 (m, 2H), 7.40–7.31 (m, 3H), 7.23 (dd, *J* = 8.6, 1.2 Hz, 2H), 5.56 (s, 2H), 5.04 (d, *J* = 4.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 156.6, 147.9 (d, *J* = 2.2 Hz), 141.7, 134.8, 133.4 (d, *J* = 2.6 Hz), 131.9, 129.9 (d, *J* = 3.2 Hz), 123.5, 122.8, 121.6, 120.3, 108.9, 91.9 (d, *J* = 28.4 Hz), 66.9, 43.6 (d, *J* = 3.3 Hz). ^{19}F NMR (565 MHz, CDCl3) δ -78.62. HRMS (ESI-TOF) m/z $[M+H]+$ calcd for $C_{17}H_{13}BrFN_2O$ 359.0195, found 359.0197.

3-fluoro-4-(4-(trifluoromethyl)phenyl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5i)**



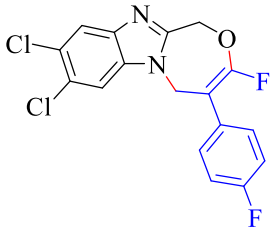
Compound **(5i)** was isolated as a colorless solid after flash chromatography (petroleum ether/EtOAc = 1:1), 48 mg, 61% yield, m.p.: 158–159 ˚C, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.40–7.30 (m, 3H), 5.57 (d, *J* = 1.7 Hz, 2H), 5.07 (dd, *J* = 4.2, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 157.1, 147.9 (d, *J* = 2.1 Hz), 141.9, 138.6, 134.9, 129.9 (d, *J* = 32.7 Hz), 128.9 (d, *J* = 3.3 Hz), 125.9 (q, *J* = 3.8 Hz), 124.9, 123.8, 123.2, 123.1, 120.6, 109.1, 91.7 (d, *J* = 28.2 Hz), 67.0, 43.6 (d, *J* = 3.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -93.08, 78.94. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}F_4N_2O$ 349.0964, found 349.0969.

4-(dibenzo[b,d]furan-4-yl)-3-fluoro-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5j)**



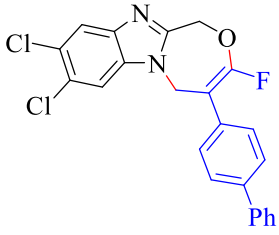
Compound **(5j)** was isolated as an off-white solid after flash chromatography (petroleum ether/EtOAc = 1:1), 33 mg, 45% yield, m.p.:169–170 ˚C, R_f = 0.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.52–7.35 (m, 9H), 5.68 (s, 2H), 5.30 (d, J = 4.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9 (d, J = 266.1 Hz), 155.8, 153.3, 148.1, 141.4, 135.0, 128.0 (d, J = 3.7 Hz), 127.5, 124.8, 123.9, 123.4, 123.1, 122.9, 122.8, 120.8, 120.4, 120.2, 118.6 (d, J = 2.1 Hz), 111.7, 109.6, 66.6, 42.6 (d, J = 3.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -77.91. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{16}FN_2O_2$ 371.1196, found 371.1192.

8,9-dichloro-3-fluoro-4-(4-fluorophenyl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5k)**



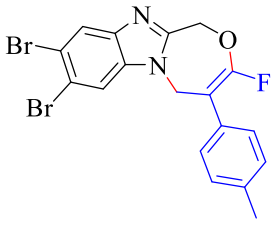
Compound **(5k)** was isolated as a colorless solid after flash chromatography (petroleum ether/EtOAc = 1:1), 46 mg, 63% yield, m.p.: 175–177˚C, R_f = 0.47. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.50 (s, 1H), 7.32–7.29 (m, 2H), 7.11 (t, J = 8.6 Hz, 2H), 5.52 (s, 2H), 4.97 (d, J = 4.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 161.2, 158.4, 156.6, 150.1 (d, J = 2.3 Hz), 140.9, 133.9, 129.9 (dd, J = 8.2, 3.1 Hz), 129.8 (t, J = 3.2 Hz), 127.7, 127.0, 121.4, 115.9, 115.8, 110.5, 92.4 (d, J = 29.0 Hz), 66.9, 44.4 (d, J = 3.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -79.38, -113.19. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{11}Cl_2F_2N_2O$ 367.0216, found 367.0220.

4-([1,1'-biphenyl]-4-yl)-8,9-dichloro-5-fluoro-1H,3H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine**(5l)**



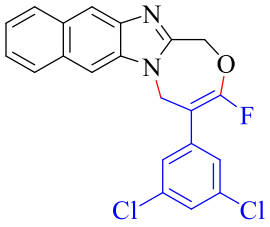
Compound **5l** was isolated as a brown solid after flash chromatography (petroleum ether/EtOAc = 1:1), 39 mg, 46% yield, m.p.: 210–212 ˚C, R_f = 0.56. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.66–7.64 (m, 2H), 7.62–7.59 (m, 2H), 7.54 (s, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.43–7.41 (m, 2H), 7.38 (d, J = 7.4 Hz, 1H), 5.55 (s, 2H), 5.05 (d, J = 4.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 156.8, 140.8, 140.8, 140.2, 134.0, 132.7 (d, J = 3.2 Hz), 128.8, 128.7, 128.5 (d, J = 3.5 Hz), 127.8, 127.6, 127.5, 127.1, 126.9, 126.8, 126.8, 126.7, 121.3, 110.6, 93.5 (d, J = 28.6 Hz), 67.1, 44.3 (d, J = 3.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.90. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{16}Cl_2FN_2O$ 425.0624, found 425.0627.

8,9-dibromo-3-fluoro-4-(p-tolyl)-1H,5H-benzo[4,5]imidazo[2,1-c][1,4]oxazepine **(5m)**



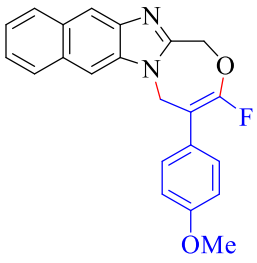
Compound **5m** was isolated as an off-white solid after flash chromatography (eluting with petroleum ether/EtOAc = 1:1), 52 mg, 58% yield, m.p.: 176–178˚C, R_f = 0.50. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.68 (s, 1H), 7.23 (s, 4H), 5.50 (s, 2H), 4.98 (d, J = 4.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 156.6, 150.3 (d, J = 2.2 Hz), 142.1, 137.9, 135.1, 130.8 (d, J = 3.2 Hz), 129.6, 128.1 (d, J = 3.2 Hz), 124.7, 118.9, 118.1, 113.8, 93.7 (d, J = 28.9 Hz), 67.2, 44.5 (d, J = 3.3 Hz), 21.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -81.53. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}Br_2FN_2O$ 452.9436, found 452.9429.

4-(3,5-dichlorophenyl)-3-fluoro-1H,5H-naphtho[2',3':4,5]imidazo[2,1-c][1,4]oxazepine **(5n)**



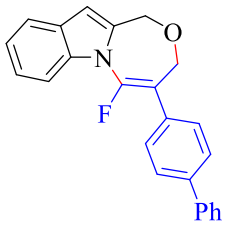
Compound **(5n)** was isolated as a light brown solid after flash chromatography (petroleum ether/EtOAc = 1:1),31 mg, 39 % yield, m.p.: 138–140˚C, R_f = 0.49. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.01 (dd, J = 11.4, 8.3 Hz, 2H), 7.87 (s, 1H), 7.81 (dd, J = 21.0, 7.8 Hz, 2H), 7.48 (dd, J = 8.3, 1.4 Hz, 1H), 7.45 (dd, J = 8.2, 1.4 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 5.64 (s, 2H), 5.31 (d, J = 3.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 142.0, 139.8 (d, J = 14.6 Hz), 135.9, 131.1 (d, J = 22.1 Hz), 129.1, 127.9, 125.5, 125.2, 124.5, 123.9, 122.4, 122.1 (d, J = 4.8 Hz), 117.9, 105.5, 68.3, 43.6 (d, J = 3.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.05. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{14}Cl_2FN_2O$ 399.0462, found 399.0463.

3-fluoro-4-(4-methoxyphenyl)-1H,5H-naphtho[2',3':4,5]imidazo[2,1-c][1,4]oxazepine **(5o)**



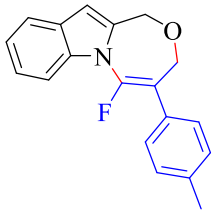
Compound **(5o)** was isolated as a light brown solid after flash chromatography (petroleum ether/EtOAc = 1:1), 52 mg, 76% yield, m.p.: 148–150 ˚C, R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.03–7.99 (m, 1H), 7.97–7.93 (m, 1H), 7.76 (s, 1H), 7.44 (m, J = 7.2, 1.5 Hz, 2H), 7.35–7.29 (m, 2H), 6.98–6.93 (m, 2H), 5.57 (s, 2H), 5.09 (d, J = 4.1 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 158.7, 155.9, 152.3 (d, J = 2.5 Hz), 141.5, 135.3, 130.4, 130.3, 129.3 (d, J = 3.3 Hz), 128.4, 127.3, 126.1 (d, J = 3.2 Hz), 124.7, 123.7, 116.9, 114.1, 104.7, 93.9 (d, J = 28.7 Hz), 67.6, 55.2, 44.2 (d, J = 3.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.43. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{18}FN_2O_2$ 361.1352, found 361.1350.

4-([1,1'-biphenyl]-4-yl)-5-fluoro-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7a)**



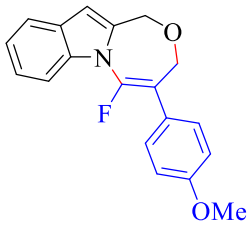
Compound **(7a)** was isolated as brown crystals after flash chromatography (petroleum ether/EtOAc = 10:1), 31 mg, 43% yield, m.p.: 118–120 ˚C, R_f=0.42. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.64 (m, 9H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.40–7.34 (m, 2H), 6.68 (s, 1H), 4.90 (s, 2H), 4.42 (d, *J* = 2.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8 (d, *J* = 272.7 Hz), 140.9, 140.72, 136.6, 136.1 (d, *J* = 4.3 Hz), 133.9 (d, *J* = 4.7 Hz), 129.2, 129.0, 128.7 (d, *J* = 4.9 Hz), 127.9, 127.6, 127.4, 124.2, 122.7, 121.8, 112.8 (d, *J* = 5.8 Hz), 105.4 (d, *J* = 2.3 Hz), 104.5 (d, *J* = 13.9 Hz), 67.6 (d, *J* = 5.4 Hz), 61.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -92.13. . HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}FNO$ 356.1451, found 356.1456.

5-fluoro-4-(p-tolyl)-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7b)**



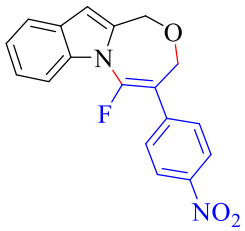
Compound **(7b)** was isolated as a yellow solid after flash chromatography (petroleum ether/EtOAc = 10:1), 27 mg, 46% yield, m.p.: 102–104 ˚C, R_f=0.59. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (m, J = 8.3, 3.4, 0.9 Hz, 1H), 7.64 (dt, J = 7.8, 1.0 Hz, 1H), 7.53–7.50 (m, 2H), 7.33 (m, J = 8.3, 7.1, 1.2 Hz, 1H), 7.27 (d, J = 1.3 Hz, 1H), 7.26–7.24 (m, 2H), 6.65 (d, J = 1.0 Hz, 1H), 4.87 (s, 2H), 4.36 (d, J = 2.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) 147.9 (d, *J* = 272.1 Hz) 137.5, 136.3, 135.8 (d, *J* = 4.1 Hz), 131.7 (d, *J* = 4.7 Hz), 129.3, 128.6, 127.8 (d, *J* = 4.5 Hz), 123.7, 122.2, 121.4, 112.5 (d, *J* = 5.6 Hz), 104.8 (d, *J* = 2.2 Hz), 104.5 (d, *J* = 14.1 Hz), 67.4 (d, *J* = 5.4 Hz), 61.4, 21.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -88.14. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{17}FNO$ 294.1294, found 294.1296.

5-fluoro-4-(4-methoxyphenyl)-1*H,3H*-[1,4]oxazepino[4,3-a]indole **(7c)**



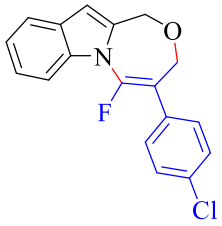
Compound **(7c)** was isolated as a yellow solid after flash chromatography (petroleum ether/EtOAc = 10:1), 32 mg, 52% yield, m.p.: 97–99 ˚C, R_f=0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (m, J = 8.2, 3.4, 1.0 Hz, 1H), 7.65 (dd, J = 7.8, 1.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.33 (m, J = 8.3, 7.1, 1.2 Hz, 1H), 7.00–6.97 (m, 3H), 6.65 (s, 1H), 4.87–4.87 (m, 2H), 4.35 (d, J = 2.4 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 147.5 (d, *J* = 271.2 Hz), 136.2, 135.7 (d, *J* = 4.4 Hz), 129.1 (d, *J* = 4.6 Hz), 128.5, 126.9 (d, *J* = 4.5 Hz), 123.6, 122.1, 121.3, 113.9, 112.4 (d, *J* = 5.7 Hz), 104.7 (d, *J* = 2.0 Hz), 104.2 (d, *J* = 14.2 Hz), 67.3 (d, *J* = 5.4 Hz), 61.3, 55.3.^{19}F NMR (565 MHz, $CDCl_3$) δ-99.47. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{17}FNO_2$ 310.1243, found 310.1240.

5-fluoro-4-(4-nitrophenyl)-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7d)**



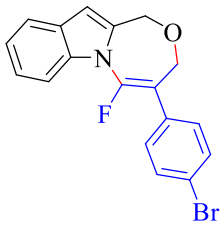
Compound **(7d)** was isolated as dark orange crystals after flash chromatography (petroleum ether/EtOAc = 10:1), 57 mg, 89% yield, m.p.: 141–143˚C, R_f=0.34. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32–8.27 (m, 2H), 7.80–7.76 (m, 2H), 7.70 (dd, J = 8.3, 3.4 Hz, 1H), 7.66 (dd, J = 7.9, 1.1 Hz, 1H), 7.37 (m, J = 8.3, 7.1, 1.2 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 6.71 (s, 1H), 4.89 (s, 2H), 4.41 (d, J = 2.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 149.1, 146.7, 141.7 (d, J = 5.3 Hz), 135.9, 135.8 (d, J = 4.4 Hz), 128.8, 128.6, 128.56, 124.3, 123.9, 122.9, 112.5 (d, J = 6.0 Hz), 112.5, 106.3 (d, J = 2.1 Hz), 102.6 (d, J = 13.0 Hz), 66.7 (d, J = 5.4 Hz), 61.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -95.83. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}FN_2O_3$ 325.0988, found 325.0984.

4-(4-chlorophenyl)-5-fluoro-1H,3H-[1,4]oxazepino[4,3-a]indole **(7e)**



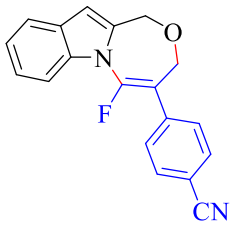
Compound **(7e)** was isolated as a brown solid after flash chromatography (petroleum ether/EtOAc = 10:1), 56 mg, 90 % yield, m.p.: 104–106 ˚C, R_f=0.50. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68–7.66 (m, 1H), 7.64 (dt, J = 7.9, 0.9 Hz, 1H), 7.55–7.53 (m, 2H), 7.41–7.39 (m, 2H), 7.33 (m, J = 8.3, 7.1, 1.2 Hz, 1H), 7.28–7.24 (m, 1H), 6.65 (s, 1H), 4.85 (s, 2H), 4.33 (d, J = 2.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.3, 147.5, 136.0, 135.7 (d, J = 4.4 Hz), 133.3, 133.1 (d, J = 4.6 Hz), 129.2 (d, J = 4.8 Hz), 128.7, 128.6, 123.9, 122.4, 121.4, 112.4 (d, J = 5.9 Hz), 105.2 (d, J = 2.1 Hz), 103.4 (d, J = 14.1 Hz), 67.1 (d, J = 5.2 Hz), 61.4. ^{19}FNMR (565 MHz, $CDCl_3$) δ -95.83. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}ClFNO$ 314.0748, found 314.0751.

4-(4-bromophenyl)-5-fluoro-1*H*,3*H*-[1,4]oxazepino[4,3-a] indole **(7f)**



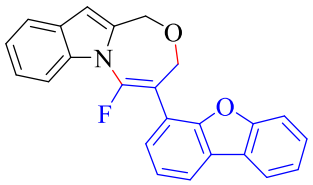
Compound **(7f)** was isolated as a white solid after flash chromatography (petroleum ether/EtOAc = 10:1), 60 mg, 84% yield, m.p.: 101–102 ˚C, R_f =0.52.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (m, J = 8.2, 3.4, 1.0 Hz, 1H), 7.65 (dt, J = 7.8, 1.0 Hz, 1H), 7.58–7.56 (m, 2H), 7.50–7.48 (m, 2H), 7.34 (m, J = 8.3, 7.2, 1.3 Hz, 1H), 7.29–7.27 (m, 1H), 6.67 (d, J = 0.9 Hz, 1H), 4.87 (s, 2H), 4.34 (d, J = 2.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0 (d, J = 2.1 Hz), 145.9, 144.2, 142.4, 138.6 (d, J = 5.4 Hz), 133.3, 133.3 (d, J = 4.3 Hz), 132.6, 131.6, 129.2–129.0 (m) 127.9, 127.1, 126.0, 125.2, 118.8, 118.3, 112.5, 109.6 (d, J = 16.7 Hz), 107.97 (d, J = 2.6 Hz), 30.9 (d, J = 2.0 Hz), 25.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.78. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}BrFNO$ 358.0243, found 358.0239.

4-(5-fluoro-1H,3H-[1,4]oxazepino[4,3-a] indol-4-yl) benzonitrile **(7g)**



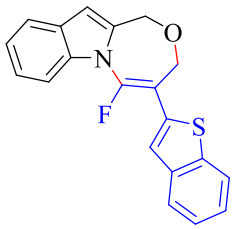
Compound **(7g)** was isolated as red crystals after flash chromatography (petroleum ether/EtOAc = 10:1), 55 mg, 91% yield, m.p.: 151–153 ˚C, R_f =0.49.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.65 (dd, *J* = 8.2, 3.4 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.33 (m, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.27–7.22 (m, 1H), 6.66 (s, 1H), 4.84 (s, 2H), 4.34 (d, *J* = 2.2 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4 (d, *J* = 275.1 Hz), 139.5 (d, *J* = 5.1 Hz), 135.8, 135.6 (d, *J* = 4.4 Hz), 132.2, 128.6, 128.3 (d, *J* = 5.2 Hz), 124.1, 122.7, 121.5, 118.6, 112.4 (d, *J* = 6.0 Hz), 110.8, 105.9 (d, *J* = 2.0 Hz), 102.7 (d, *J* = 13.1 Hz), 66.7 (d, *J* = 5.4 Hz), 61.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -93.16. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{14}FN_2O$ 305.1090, found 305.1097.

4-(dibenzo[b,d]furan-4-yl)-5-fluoro-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7h)**



Compound **(7h)** was isolated as dark yellow liquid after flash chromatography (petroleum ether/EtOAc = 10:1), 60 mg, 82% yield, R_f =0.34.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89–7.84 (m, 2H), 7.61–7.57 (m, 1H), 7.56 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.49 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.43 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.37 (m, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (td, *J* = 7.5, 1.0 Hz, 1H), 7.24–7.20 (m, 1H), 7.18–7.13 (m, 1H), 6.60 (d, *J* = 1.0 Hz, 1H), 4.90 (s, 2H), 4.49 (d, *J* = 2.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 153.9, 150.2, 148.4, 136.9, 136.0 (d, *J* = 4.2 Hz), 129.0, 127.8 (d, *J* = 4.3 Hz), 125.1, 124.5, 124.2, 123.3 (d, *J* = 6.1 Hz), 122.7, 121.7, 121.1, 120.7, 119.5 (d, *J* = 2.3 Hz), 113.1 (d, *J* = 6.9 Hz), 112.2, 105.7 (d, *J* = 2.0 Hz), 100.2 (d, *J* = 17.3 Hz), 67.7 (d, *J* = 5.2 Hz), 62.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ -94.56. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{17}FNO_2$ 370.1243, found 370.1247.

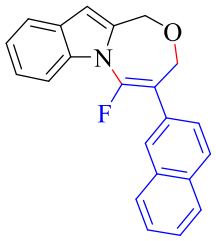
4-(benzo[b]thiophen-2-yl)-5-fluoro-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7i)**



Compound **(7i)** was isolated as brown crystals after flash chromatography (petroleum ether/EtOAc = 10:1), 51 mg, 76% yield, m.p.: 125–127 ˚C, R_f =0.41.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.76 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.70 (dd, *J* = 8.2, 3.5 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.51 (s, 1H), 7.33 (td, *J* = 6.9, 1.6 Hz, 3H), 7.29–7.22 (m, 1H), 6.66 (s, 1H), 4.83 (s, 2H), 4.50 (d, *J* = 2.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 147.5, 139.6 (d, *J* = 7.0 Hz), 139.4, 136.4 (d, *J* = 8.5 Hz), 135.8, 135.7 (d, *J* = 4.4 Hz), 128.6, 124.6 (d, *J* = 5.7 Hz), 124.0, 123.4, 122.6, 121.9, 121.8 (d, *J* = 5.4 Hz), 121.4, 112.6 (d, *J* = 6.0 Hz), 105.8 (d, *J* = 2.0 Hz), 99.9 (d,

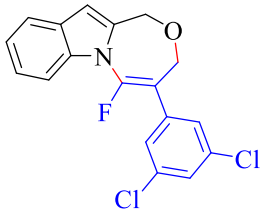
J = 13.9 Hz), 66.1 (d, *J* = 5.5 Hz), 61.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -92.34. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{15}FNOS$ 336.0858, found 336.0855.

5-fluoro-4-(naphthalen-2-yl)-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7j)**



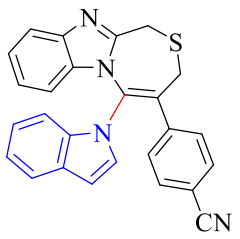
Compound **(7j)** was isolated as a brown liquid after flash chromatography (petroleum ether/EtOAc = 10:1), 51 mg, 78% yield. R_f =0.47. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03–7.99 (m, 1H), 7.88–7.82 (m, 2H), 7.65–7.59 (m, 2H), 7.53–7.46 (m, 4H), 7.28–7.23 (m, 1H), 7.22–7.18 (m, 1H), 6.65 (s, 1H), 5.01 (s, 2H), 4.39 (d, *J* = 3.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.3, 147.5, 136.0, 135.7 (d, *J* = 4.5 Hz), 133.6 (d, *J* = 4.8 Hz), 131.9, 131.7, 129.5 (d, *J* = 4.8 Hz), 128.6 (d, *J* = 7.7 Hz), 126.9, 123.9, 122.4, 121.4 (d, *J* = 1.8 Hz), 121.4, 112.4 (d, *J* = 5.8 Hz), 105.3 (d, *J* = 2.1 Hz), 103.4 (d, *J* = 13.9 Hz), 67.1 (d, *J* = 5.2 Hz), 61.4.^{19}F NMR (565 MHz, $CDCl_3$) δ -93.79. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{17}FNO$ 330.1294, found 330.1287.

4-(3,5-dichlorophenyl)-5-fluoro-1*H*,3*H*-[1,4]oxazepino[4,3-a]indole **(7k)**



Compound **(7k)** was isolated as White solid after flash chromatography (petroleum ether/EtOAc = 10:1), 44 mg, 64% yield, m.p.: 143–145˚C, R_f=0.63. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H), 7.51 (dd, *J* = 1.8, 0.7 Hz, 2H), 7.37–7.32 (m, 2H), 7.28 (m, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.68 (t, *J* = 0.9 Hz, 1H), 4.87 (d, *J* = 0.6 Hz, 2H), 4.33 (d, *J* = 2.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4 (d, *J* = 275.1 Hz), 137.8 (d, *J* = 4.8 Hz), 136.1, 135.7 (d, *J* = 4.4 Hz), 135.3, 128.9, 127.6, 126.2 (d, *J* = 5.0 Hz), 124.3, 122.8, 121.7, 112.4 (d, *J* = 6.0 Hz), 105.8 (d, *J* = 2.1 Hz), 102.1 (d, *J* = 13.5 Hz), 66.8 (d, *J* = 5.3 Hz), 61.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -94.30. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}Cl_2FNO$ 348.0358, found 348.0355.

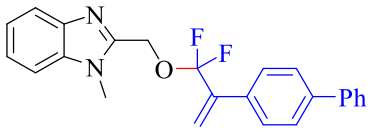
4-(5-(1H-indol-1-yl)-1,11a-dihydro-3H-11λ^2-benzo[4,5]imidazo[2,3-c][1,4]thiazepin-4-yl)benzonitrile **(8)**



Compound **(8)** was isolated as an orange solid after flash chromatography (petroleum ether/EtOAc = 5:1), 68 mg, 82% yield, m.p.: 289–291, R_f=0.54. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.27–7.24 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.57 (d, *J* = 3.5 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 1H), 4.36 (s, 2H), 3.94–3.44 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 141.8 (d, *J* = 347.8 Hz), 133.6, 133.0, 129.5, 128.9, 124.8, 124.3, 124.2, 122.4,

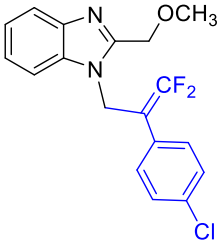
121.9, 121.8, 120.7, 118.6, 112.3, 111.1, 110.6, 32.7, 26.1. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{19}N_4S$ 419.1130, found 419.1336

2-(((2-([1,1'-biphenyl]-4-yl)-1,1-difluoroallyl)oxy)methyl)-1-methyl-1H-benzo[d]imidazole **(10)**



Compound **(10)** was isolated as a light brown solid after flash chromatography (petroleum ether/EtOAc = 1:1), 33 mg, 42% yield, yellow liquid. R_f =0.61.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.60–7.57 (m, 2H), 7.56–7.51 (m, 5H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.38–7.33 (m, 3H), 5.95 (s, 1H), 5.71 (d, *J* = 1.7 Hz, 1H), 5.34 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 140.6, 140.3, 133.9, 128.8, 128.0, 127.5, 126.9 (d, *J* = 11.6 Hz), 123.6, 122.7, 122.3, 120.1, 119.5, 109.5, 58.5, 30.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ -74.97. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{21}F_2N_2O$ 391.1622, found 391.1628.

1,1'-(2-([1,1'-biphenyl]-4-yl)-1-fluoroprop-2-ene-1,1-diyl)bis(2-(methoxymethyl)-1H-benzo[d]imidazole) **(12)**



Compound **(12)** was isolated as yellow liquid after flash chromatography (petroleum ether/EtOAc = 10:5), 94 mg, 89% yield, R_f =0.32. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.28 – 7.24 (m, 4H), 7.14 – 7.12 (m, 1H), 7.10 – 7.08 (m, 2H), 4.83 (dd, *J* = 14.9, 4.5 Hz, 1H), 4.68 (dd, *J* = 14.9, 9.2 Hz, 1H), 4.47 (d, *J* = 13.0 Hz, 1H), 4.19 (d, *J* = 13.0 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 142.1, 135.2, 134.9, 130.8, 123.0 (d, *J* = 130.9 Hz), 126.5, 124.7, 123.4, 122.6, 120.3, 109.1, 67.2, 58.3, 49.7 (d, *J* = 26.8 Hz), 49.7 (d, *J* = 26.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -145.57. HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{18}H_{16}ClF_2N_2O_2$ 349.0919, found 349.0916.

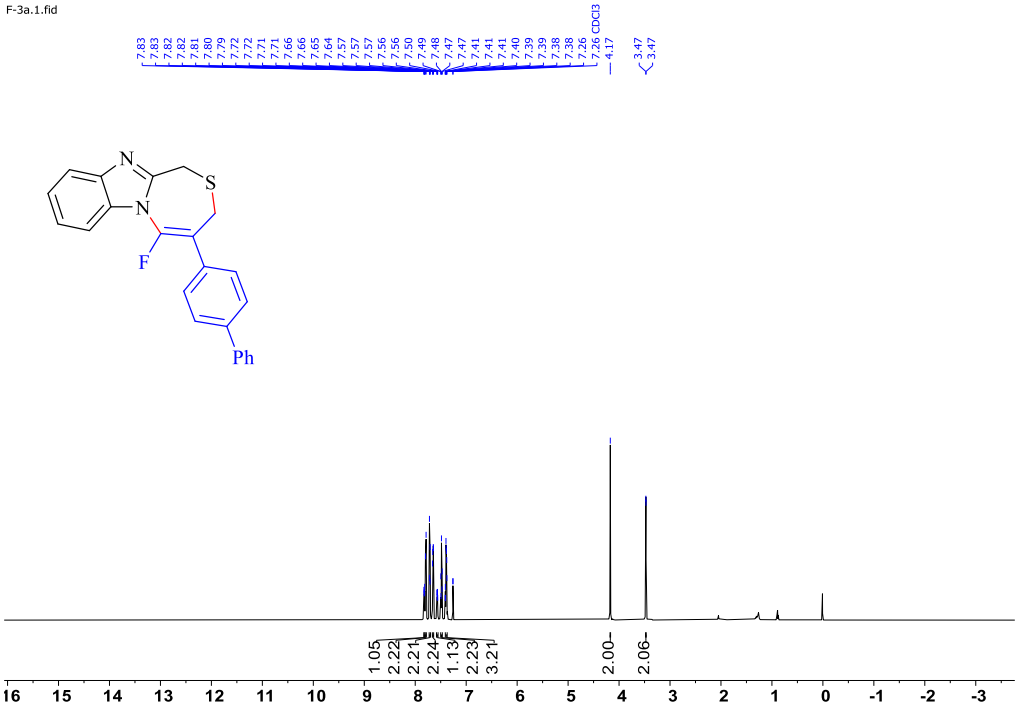
9. References:

1. H. Qin, Y. Miao, J. Xu and Q. Bi, A Facile and Efficient [4+2] Annulation Reaction of Sulfur Ylides: Access to N-Fused Benzimidazoles, *Org. Chem. Front.,* 2019, **2**, 205-208.
2. L.S. Cui, J.U. Kim, H. Nomura, H. Nakanotani and C. Adachi, Benzimidazobenzothiazole-Based Bipolar Hosts to Harvest Nearly All of the Excitons from Blue Delayed Fluorescence and Phosphorescent Organic Light-Emitting Diodes. *Angew. Chem. Int. Ed.,* 2016, ***55***, 6864.
3. P.J. Xia, Z. Ye, Y. Hu, D. Song, H.Y. Xiang, X. Chen and H. Yang, Photocatalytic Phosphoranyl Radical-Mediated N–O Cleavage of Strained Cycloketone Oximes. *Org. Lett.* 2019, **8**, 2658-2662.

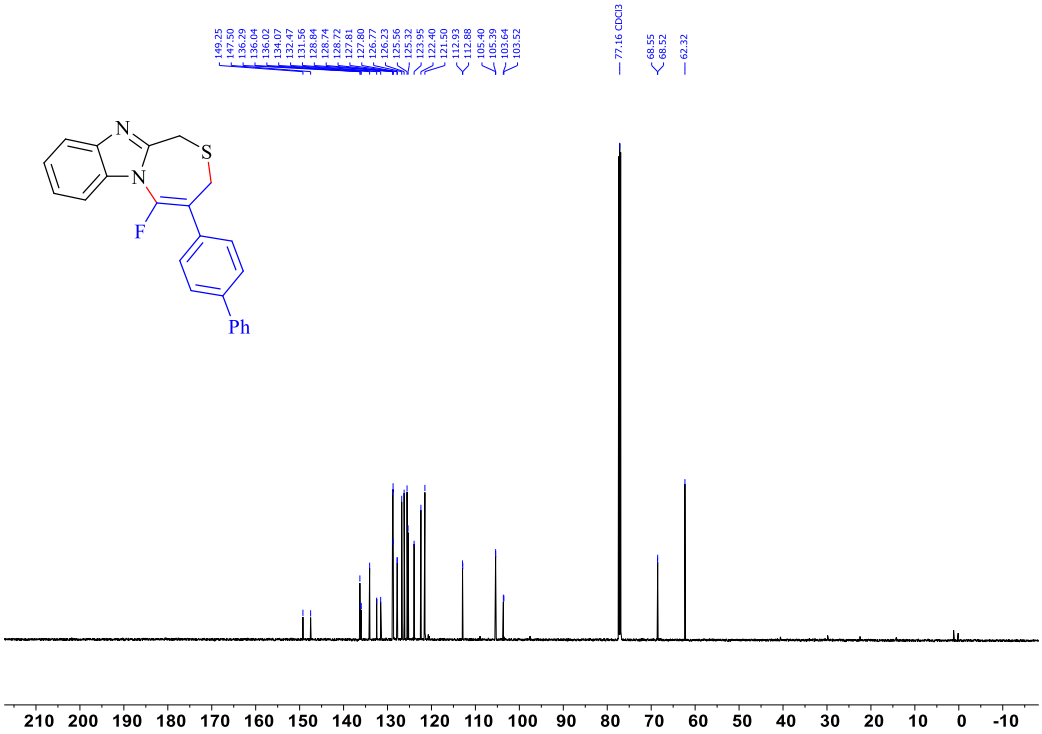
4. Y. Guo, Y. Cao, H. Song, Y. Liu and Q. Wang, Photoredox Relay-Catalyzed Gem-Difluoroallylation of Alkyl Iodides, *Chem. Comm.,* 2021, **76**, 9768-9771.

10. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of all products

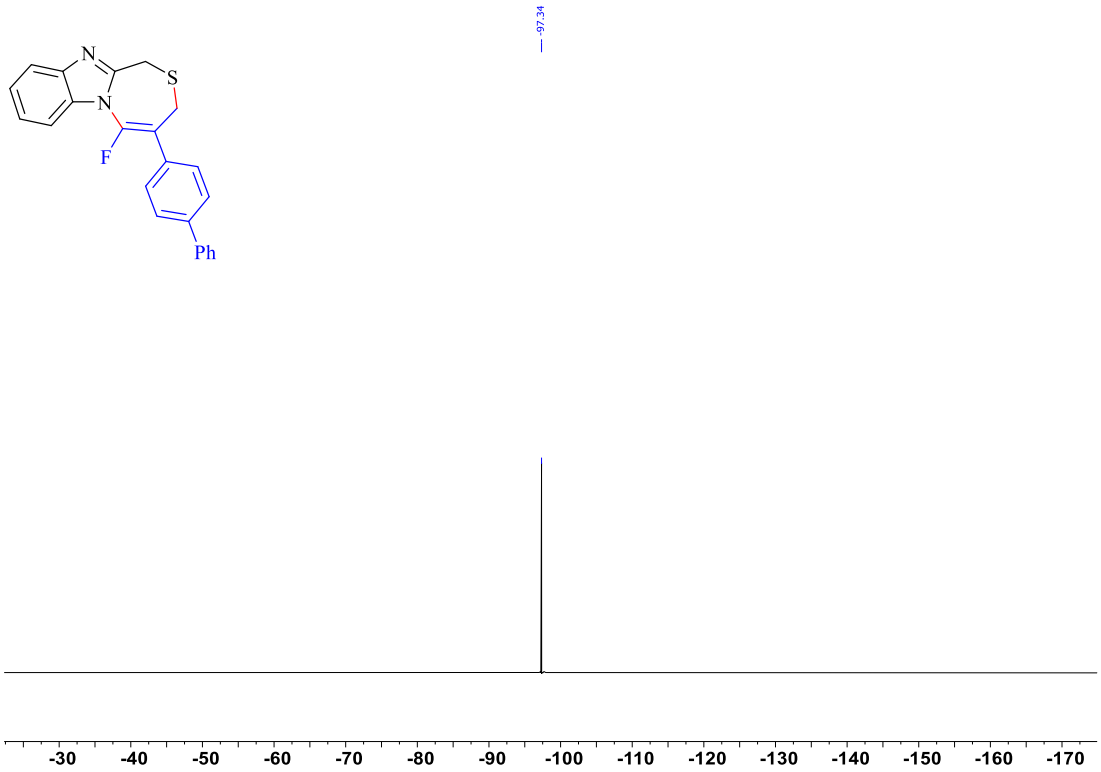
^{1}H NMR spectrum of product **3a** in $CDCl_3$ (600 MHz)



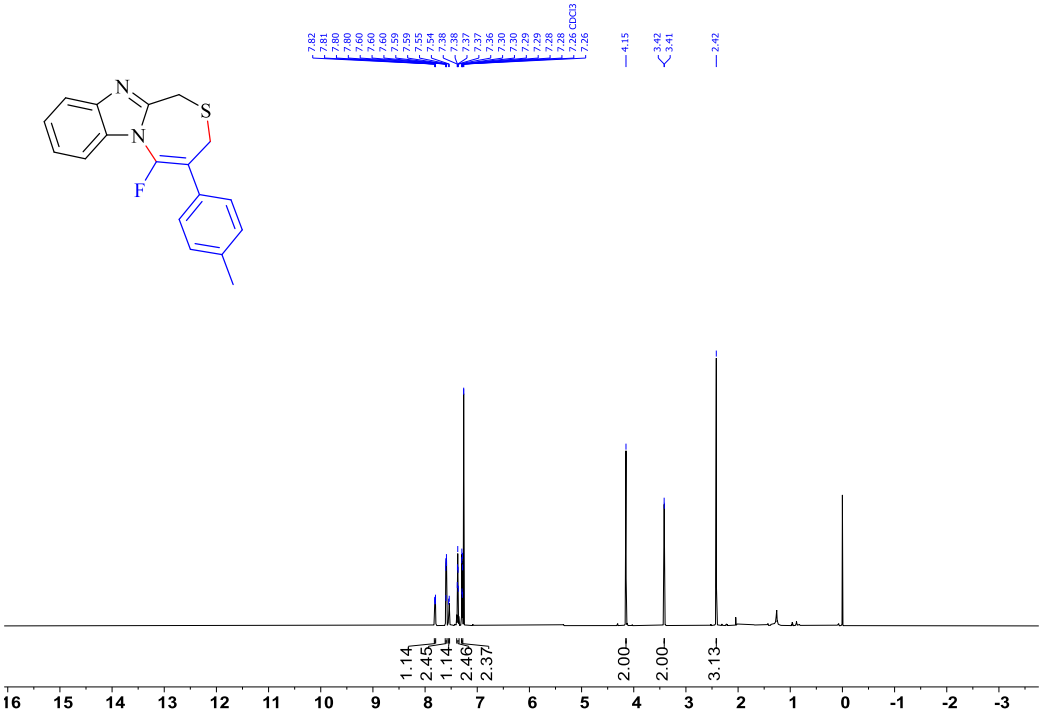
^{13}C NMR spectrum of product **3a** in $CDCl_3$ (151 MHz)



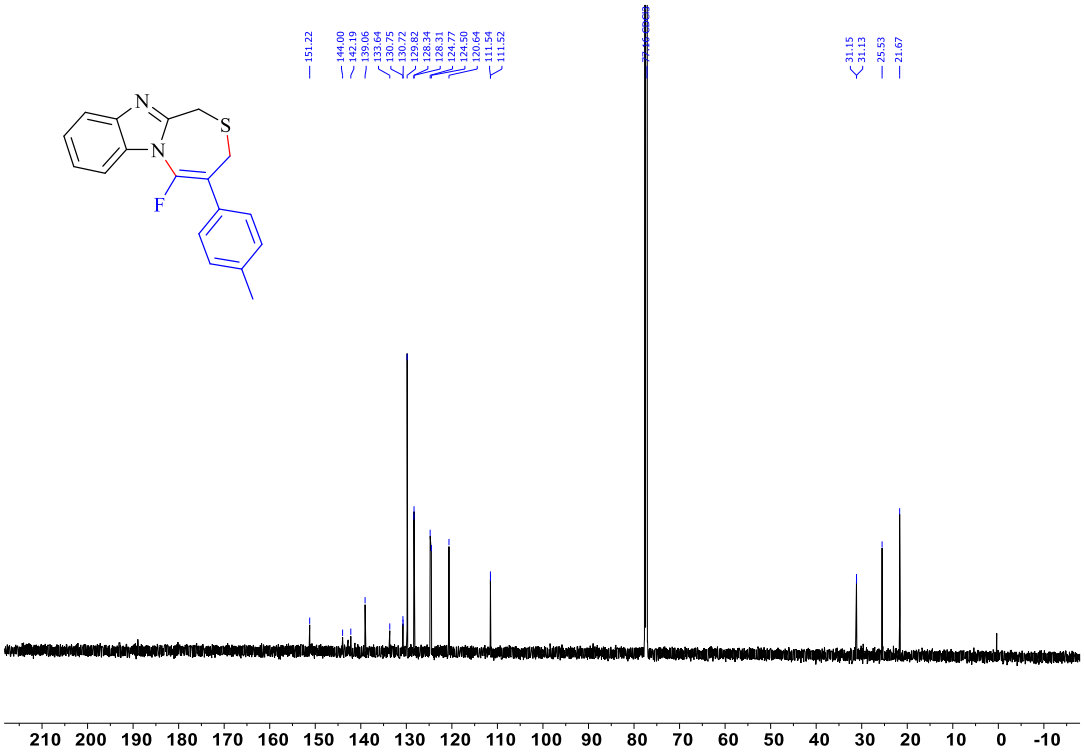
^{19}F-NMR spectrum of product **3a** in $CDCl_3$ (565 MHz)



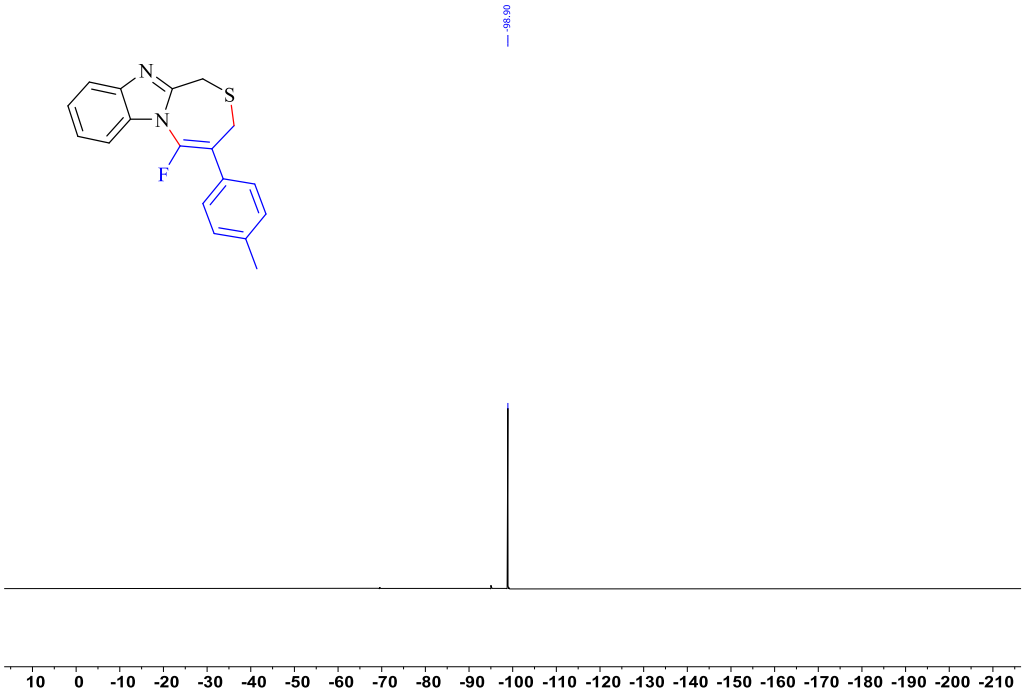
^{1}H NMR spectrum of product **3b** in $CDCl_3$ (600 MHz)



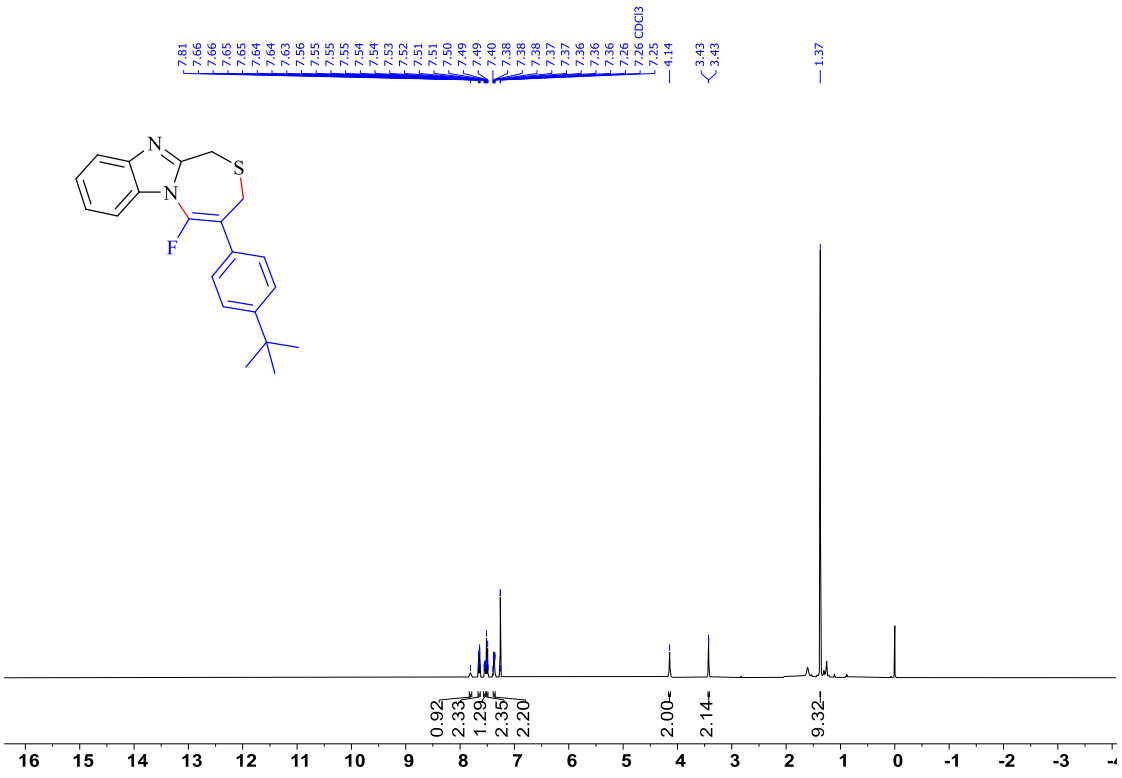
^{13}C NMR spectrum of product **3b** in $CDCl_3$ (151 MHz)



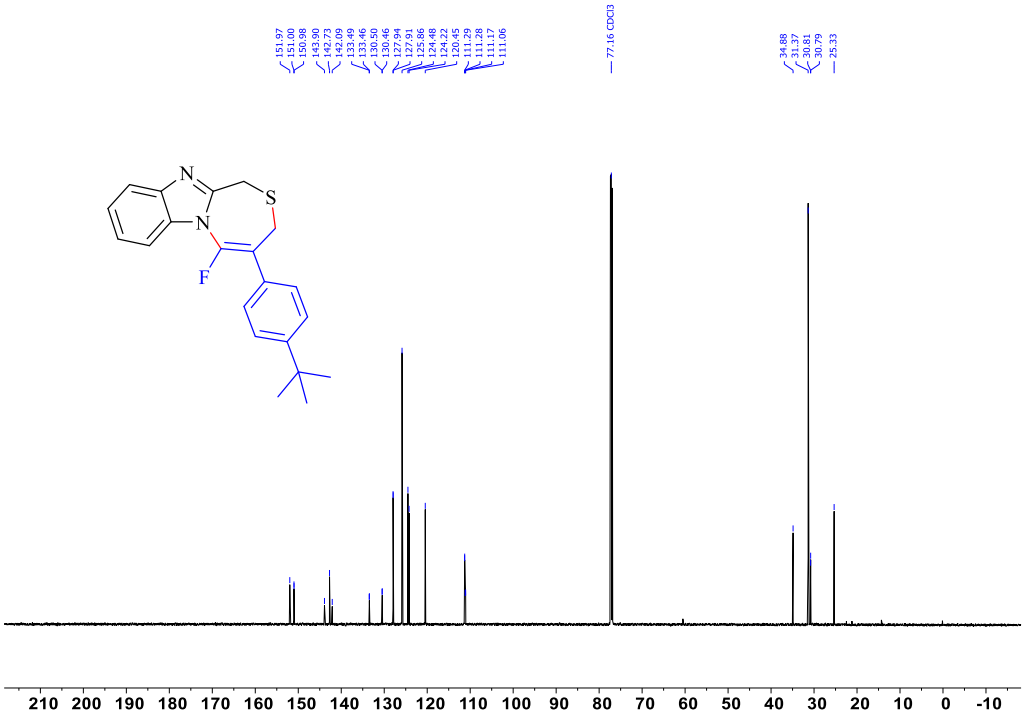
^{19}F-NMR spectrum of product **3b** in $CDCl_3$ (565 MHz)



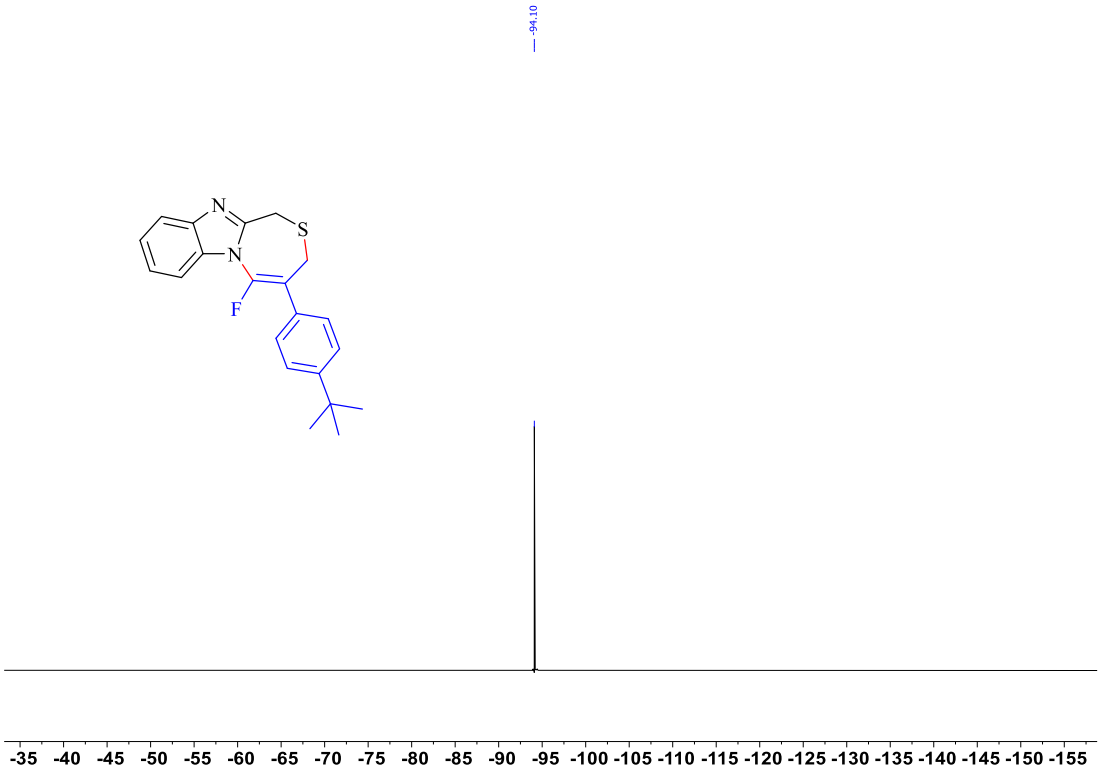
^{1}H NMR spectrum of product **3c** in $CDCl_3$ (400 MHz)



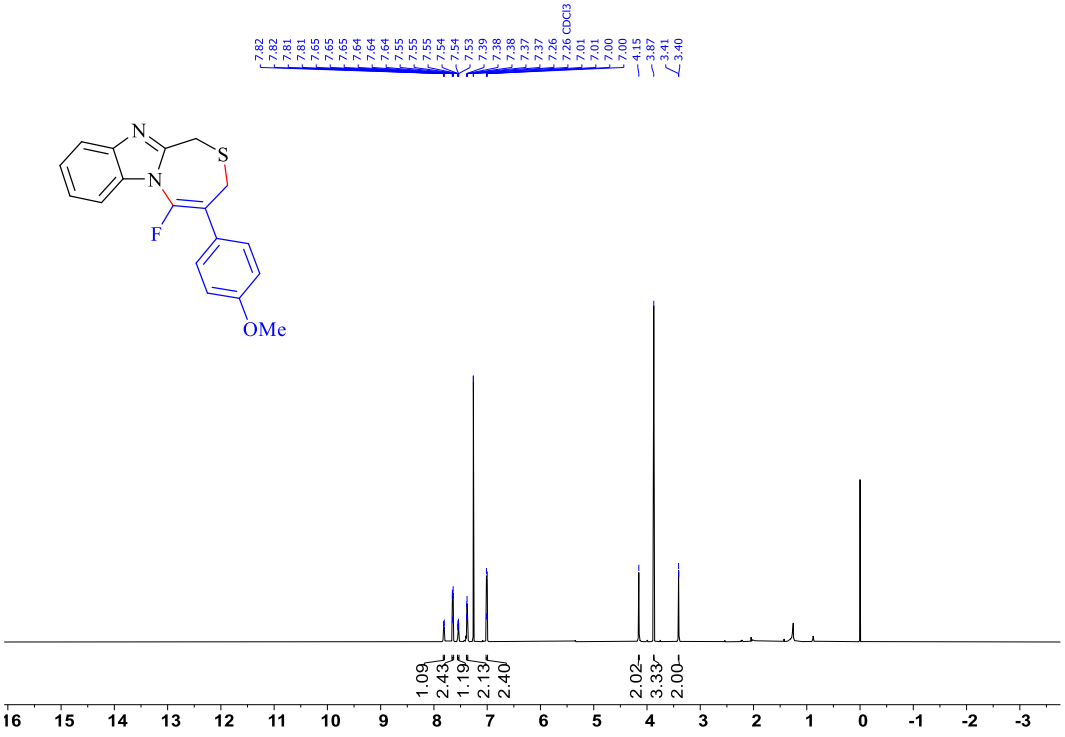
^{13}C NMR spectrum of product **3c** in $CDCl_3$ (151 MHz)



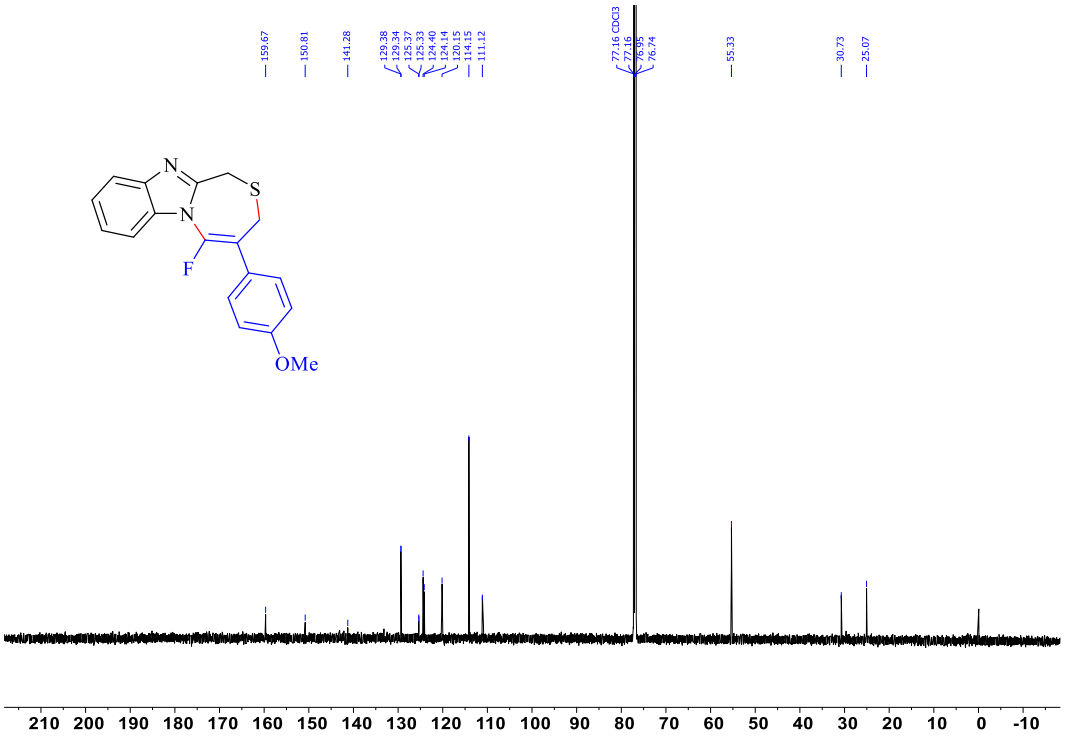
^{19}F-NMR spectrum of product **3c** in $CDCl_3$ (565 MHz)



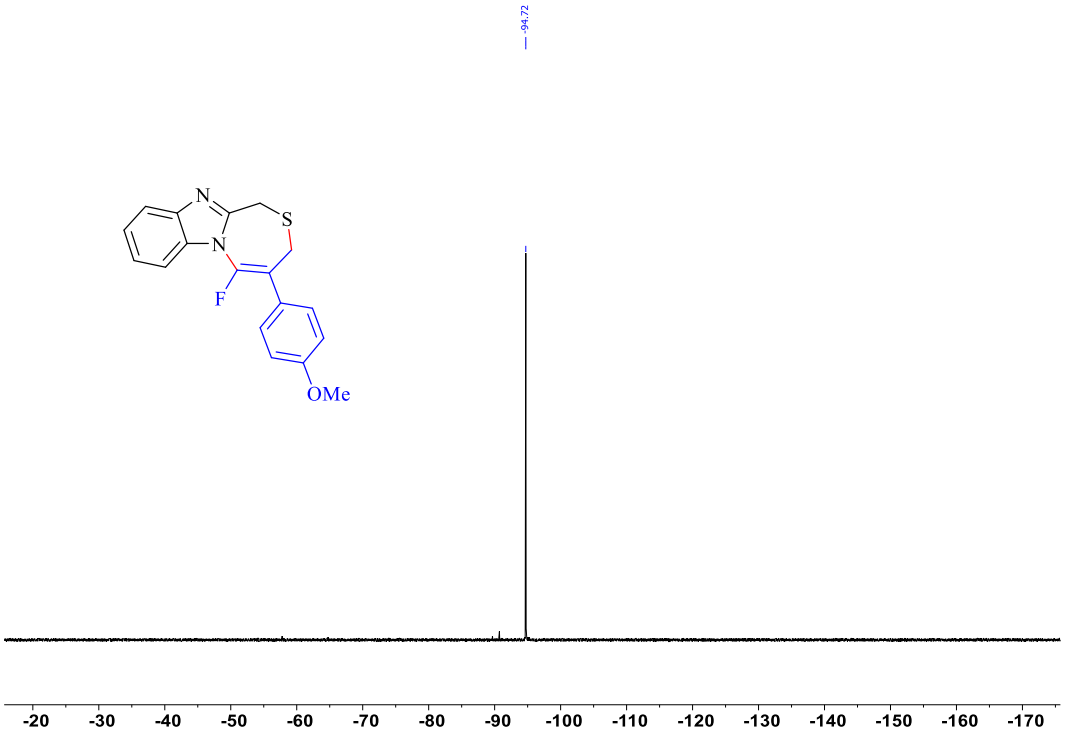
^{1}H NMR spectrum of product **3d** in $CDCl_3$ (600 MHz)



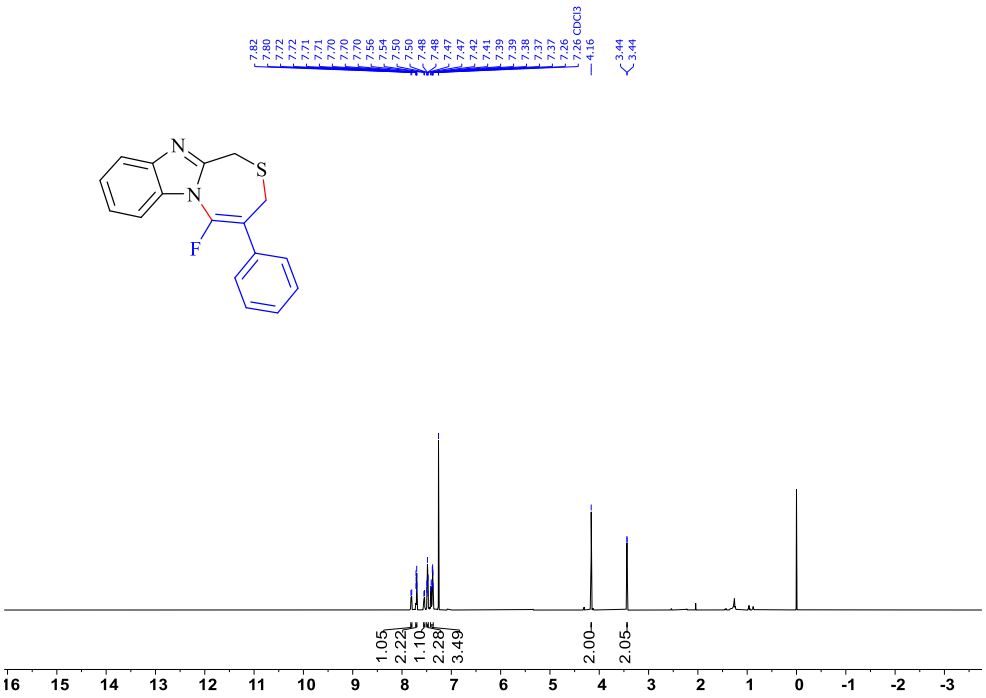
^{13}C NMR spectrum of product **3d** in $CDCl_3$ (151 MHz)



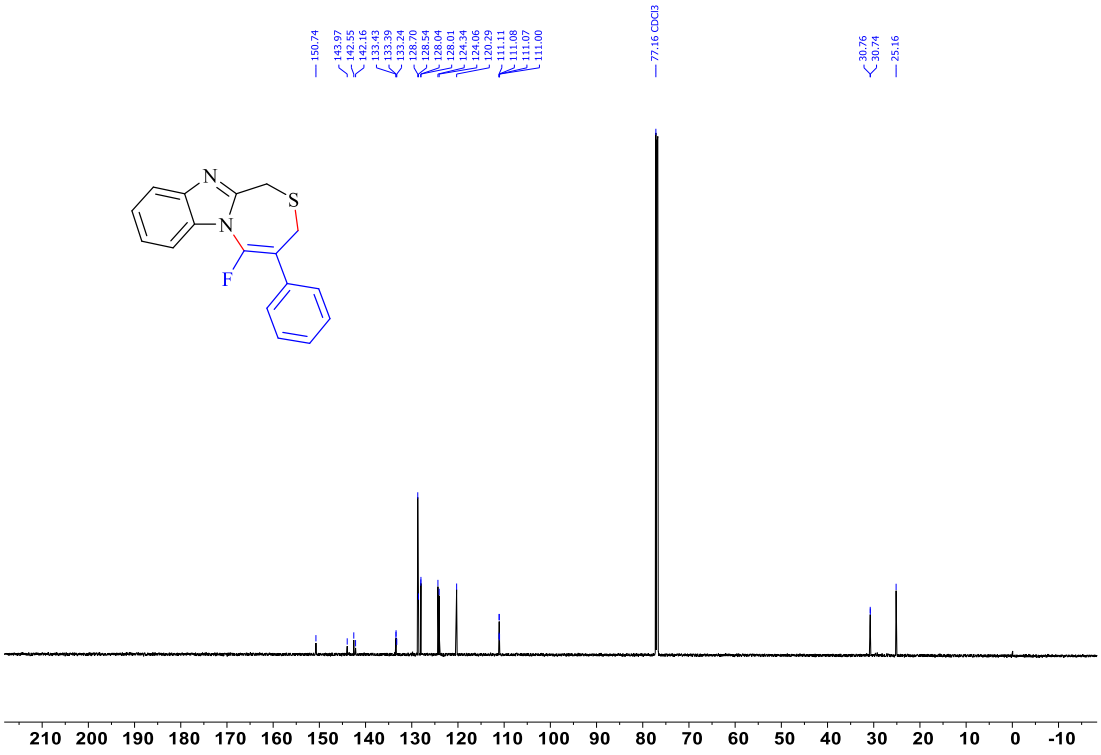
^{19}F-NMR spectrum of product **3d** in $CDCl_3$ (565 MHz)



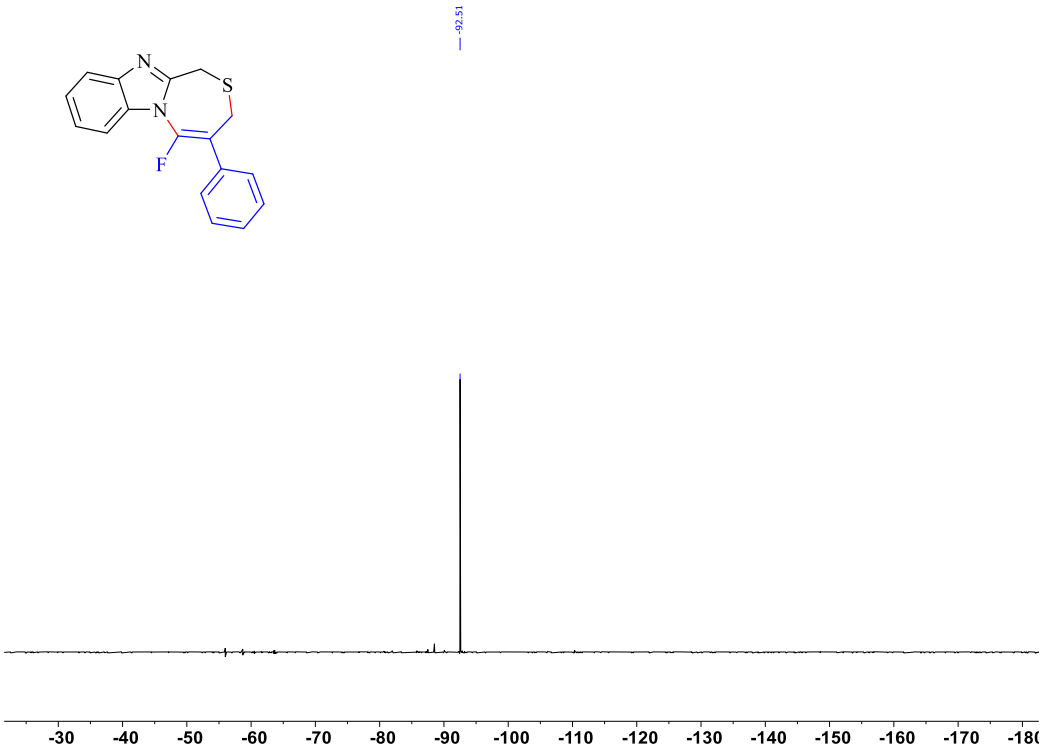
^{1}H NMR spectrum of product **3e** in $CDCl_3$ (600 MHz)



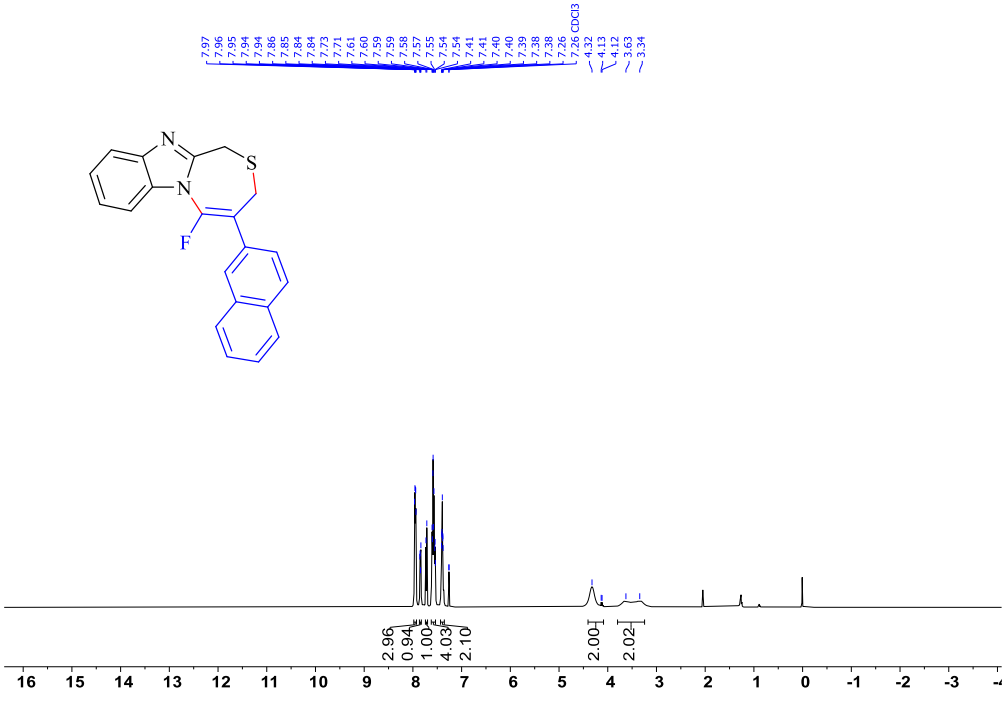
^{13}C NMR spectrum of product **3e** in $CDCl_3$ (151 MHz)



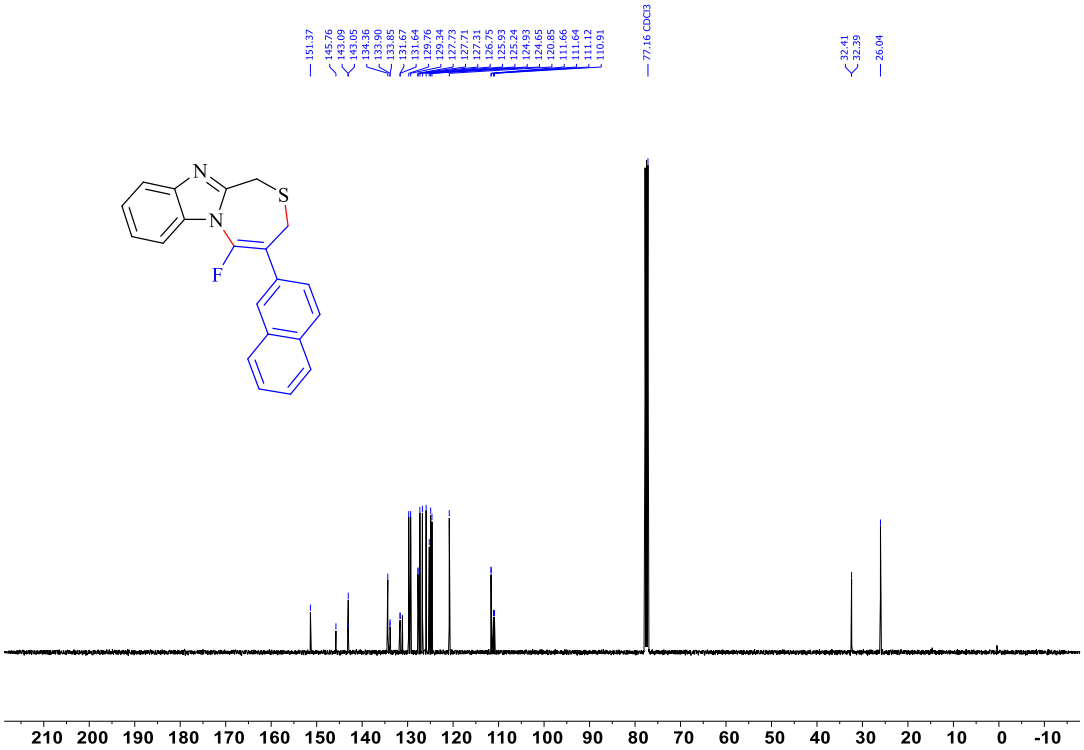
^{19}F-NMR spectrum of product **3e** in $CDCl_3$ (565 MHz)



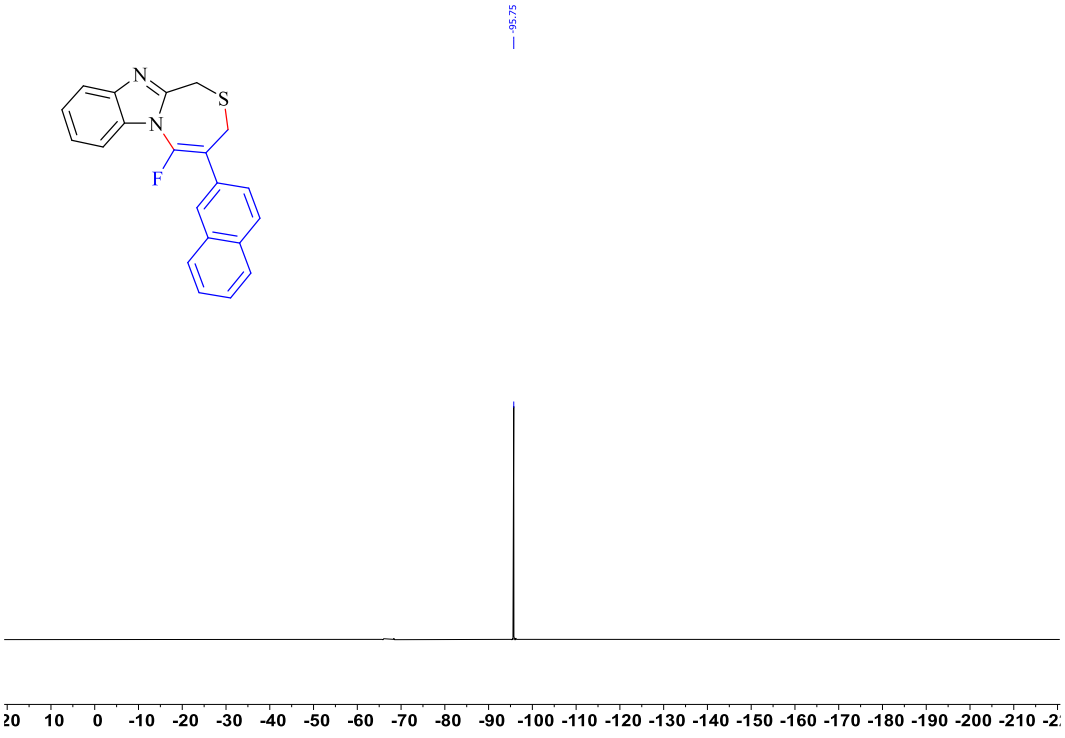
^{1}H NMR spectrum of product **3f** in $CDCl_3$ (400 MHz)



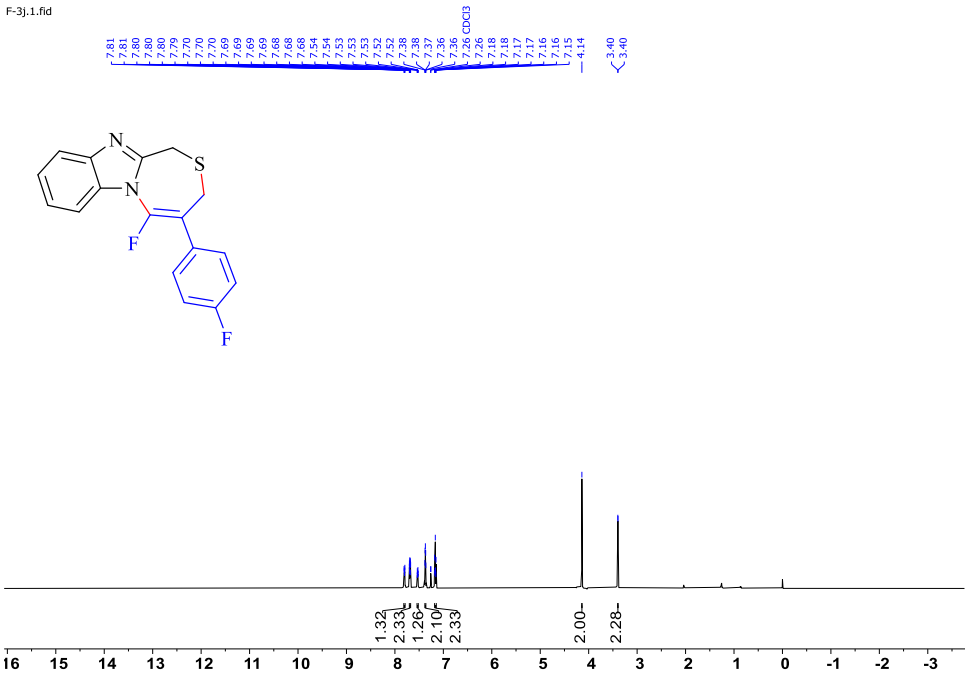
^{13}C NMR spectrum of product **3f** in $CDCl_3$ (101 MHz)



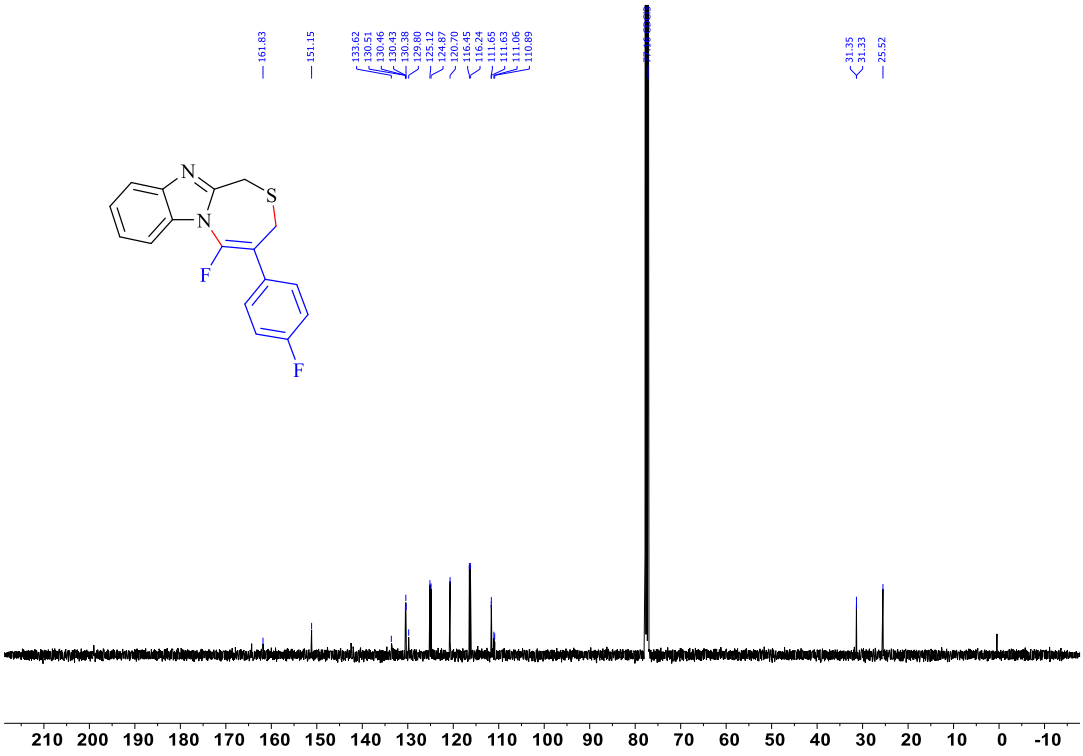
^{19}F-NMR spectrum of product **3f** in $CDCl_3$ (377 MHz)



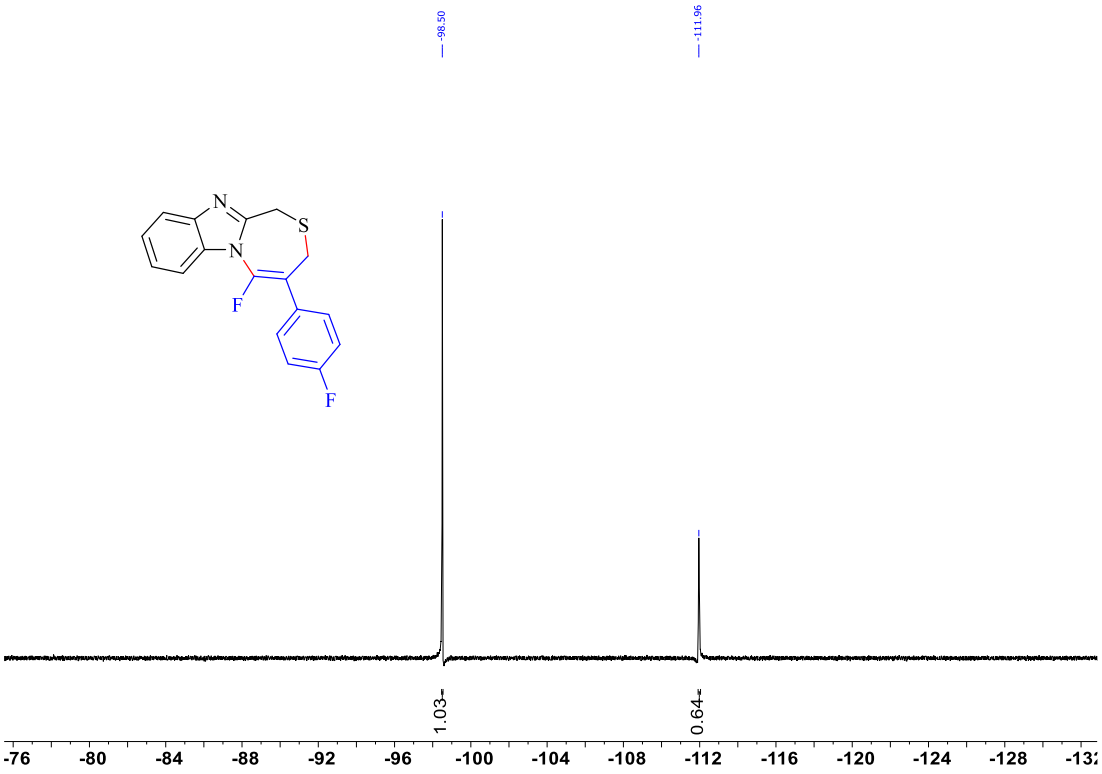
^{1}H NMR spectrum of product **3g** in $CDCl_3$ (600 MHz)



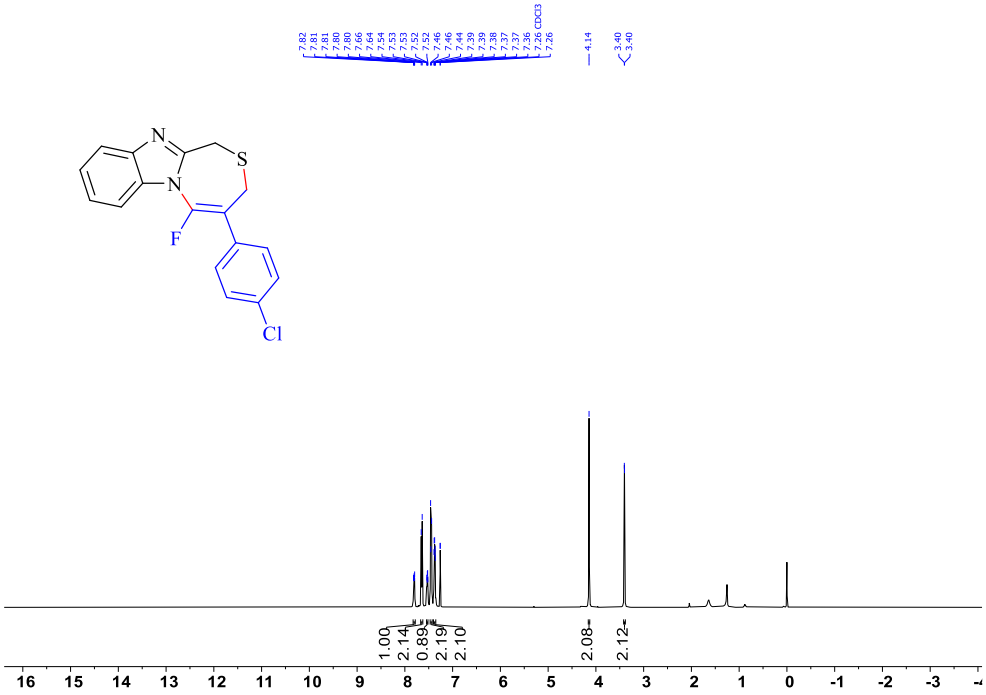
^{13}C NMR spectrum of product **3g** in $CDCl_3$ (101 MHz)



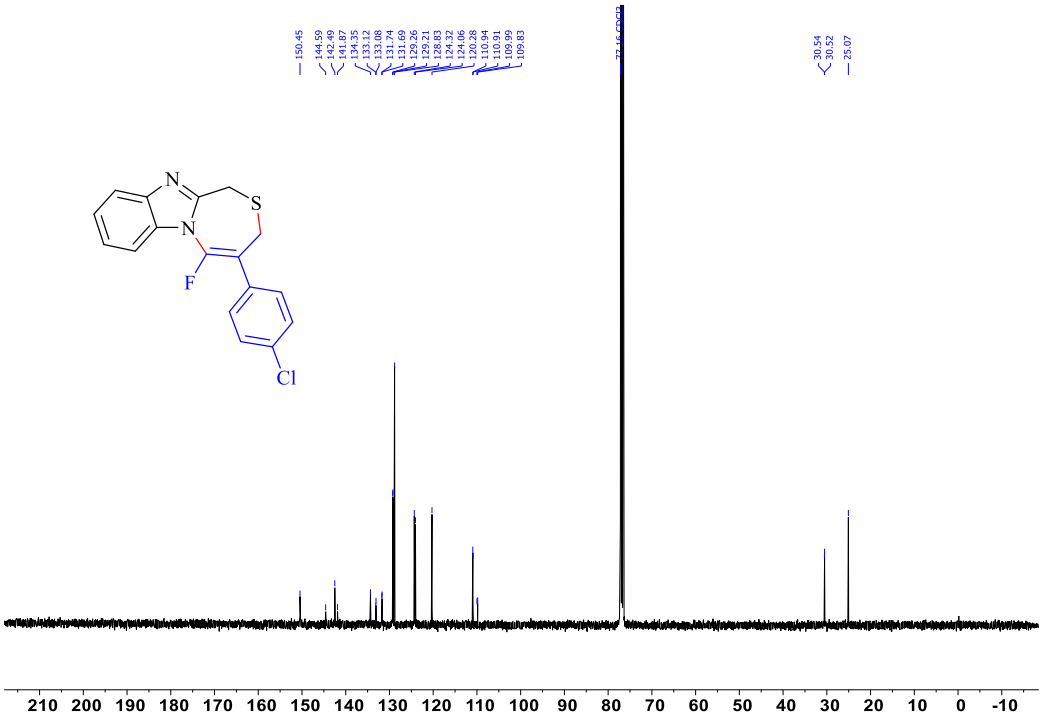
^{19}F-NMR spectrum of product **3g** in $CDCl_3$ (377 MHz)



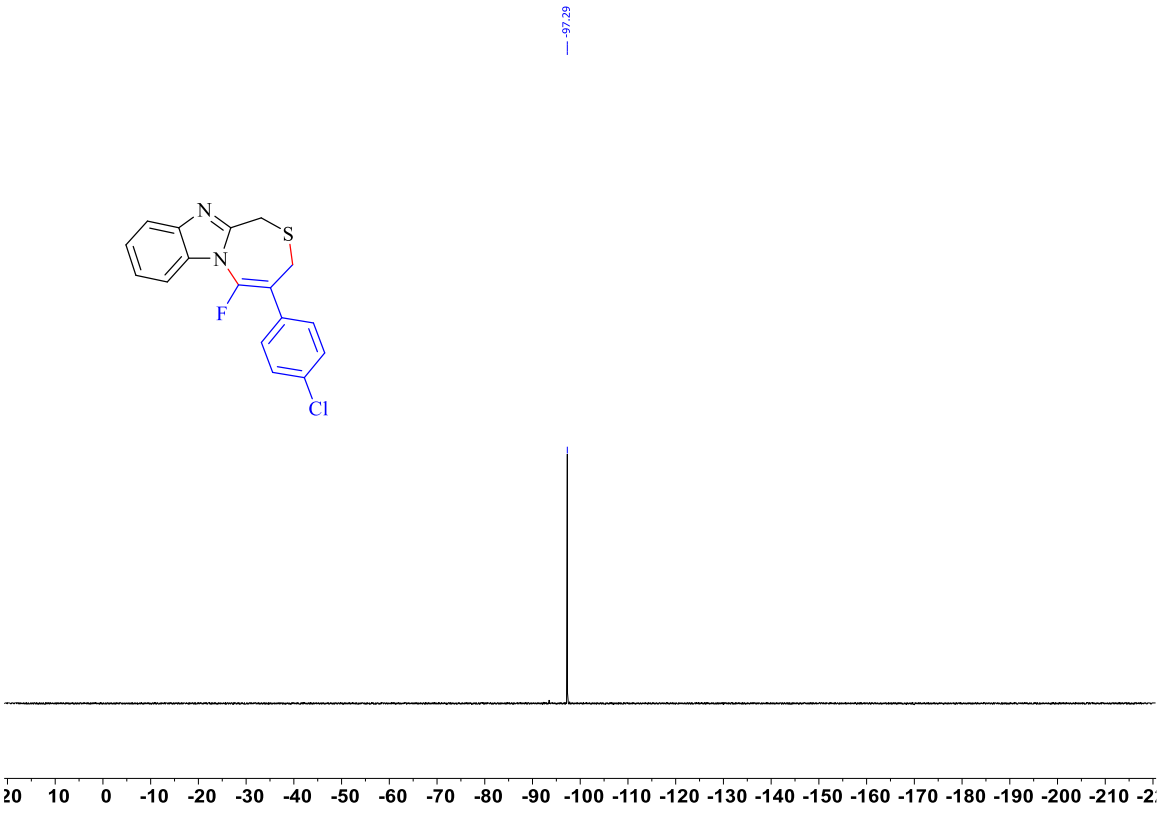
^{1}H NMR spectrum of product **3h** in $CDCl_3$ (400 MHz)



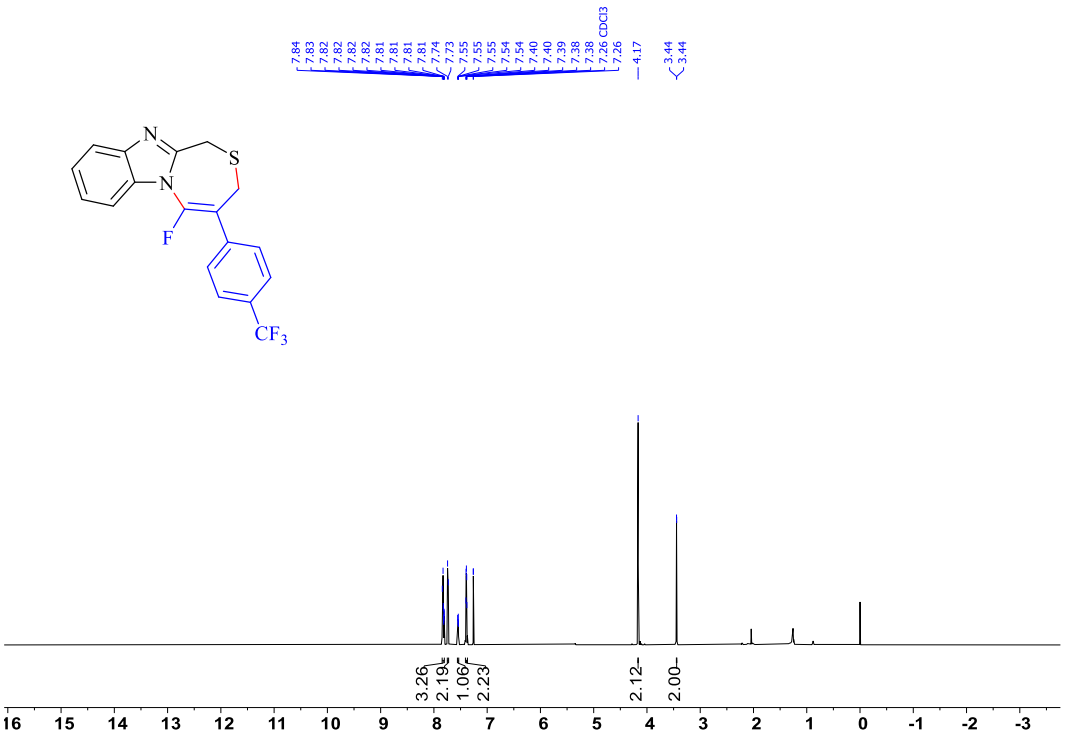
^{13}C NMR spectrum of product **3h** in $CDCl_3$ (101 MHz)



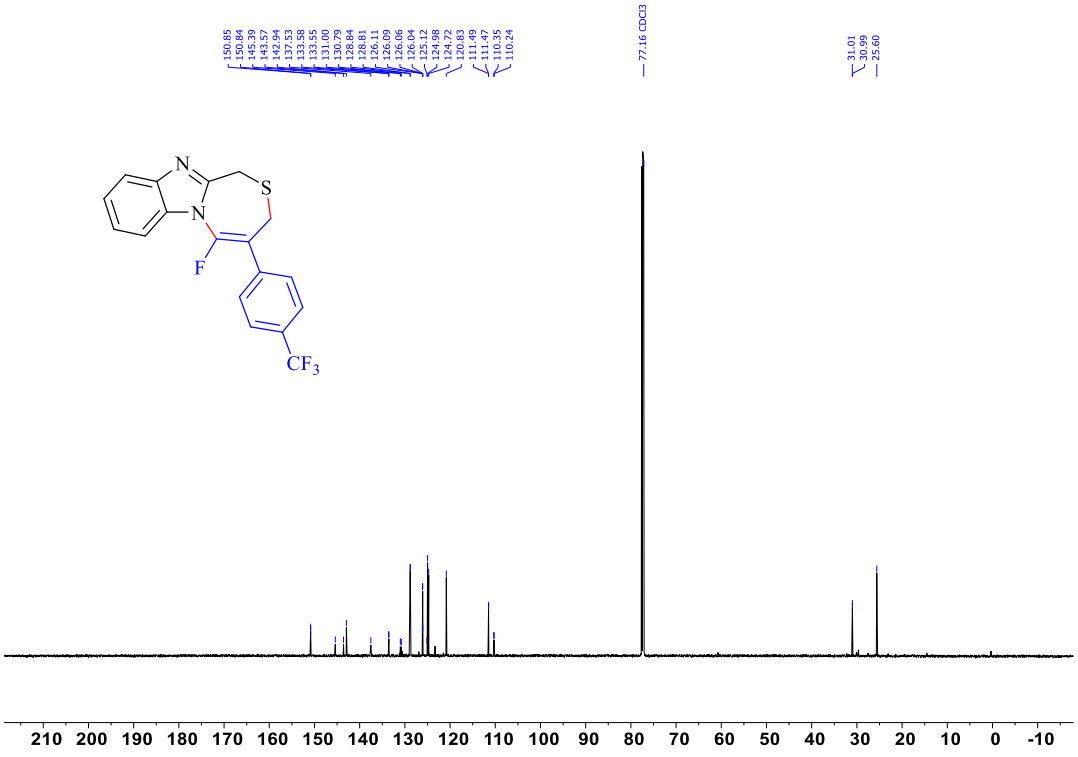
^{19}F-NMR spectrum of product **3h** in $CDCl_3$ (377 MHz)



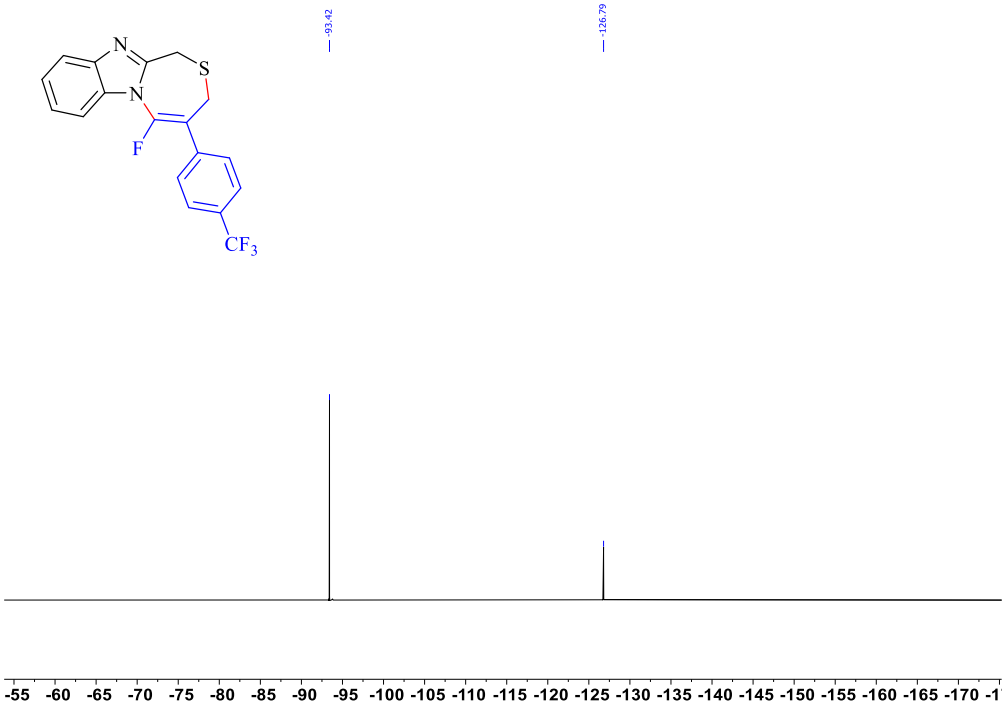
^{1}H NMR spectrum of product **3i** in $CDCl_3$ (600 MHz)



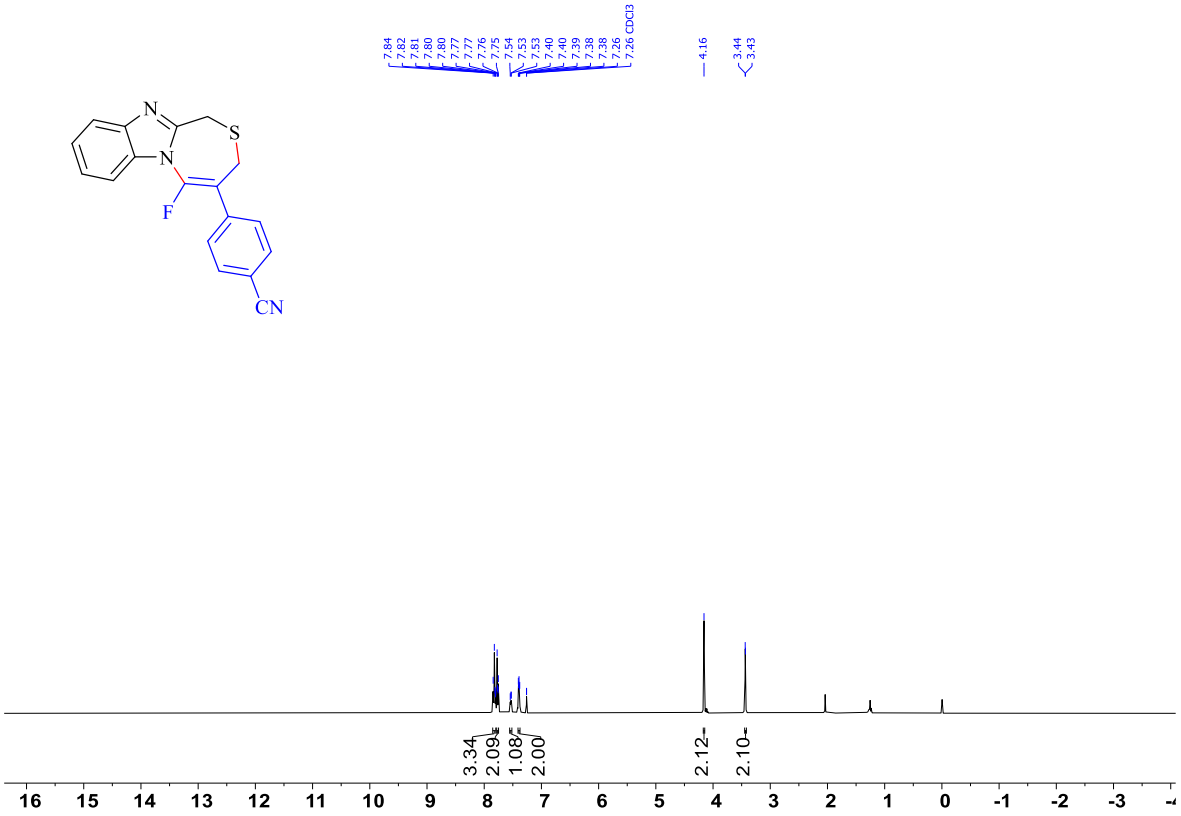
^{13}C NMR spectrum of product **3i** in $CDCl_3$ (151 MHz)



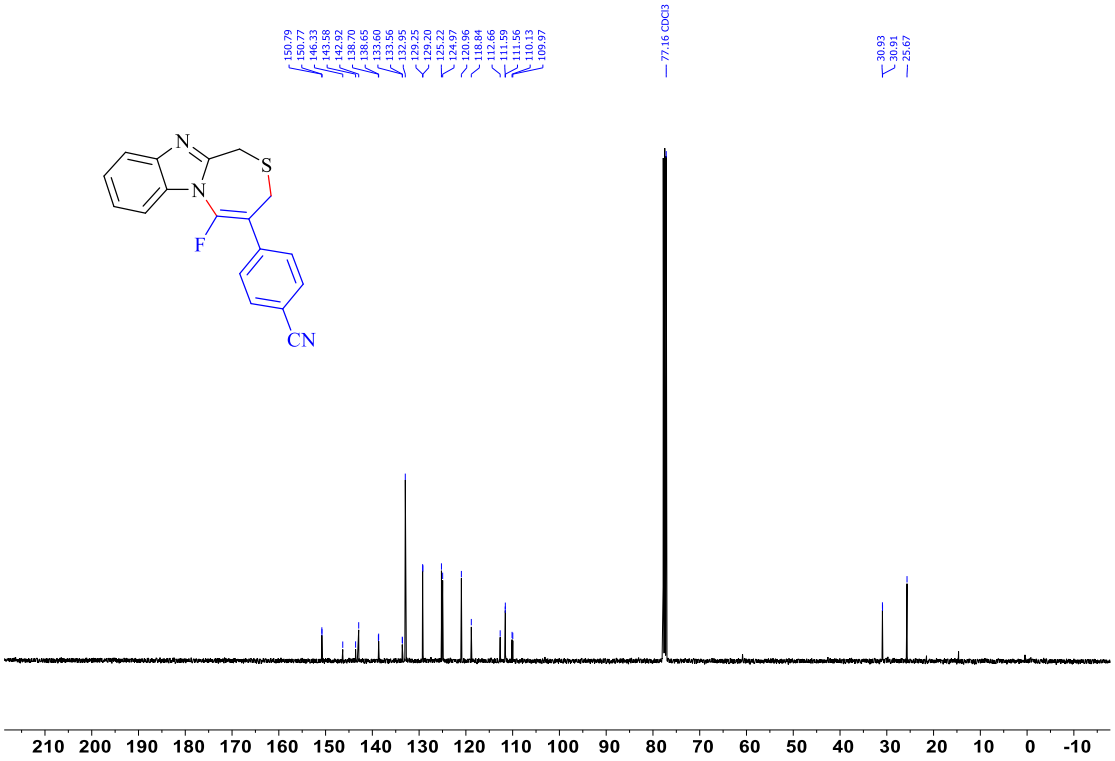
^{19}F-NMR spectrum of product **3i** in $CDCl_3$ (565 MHz)



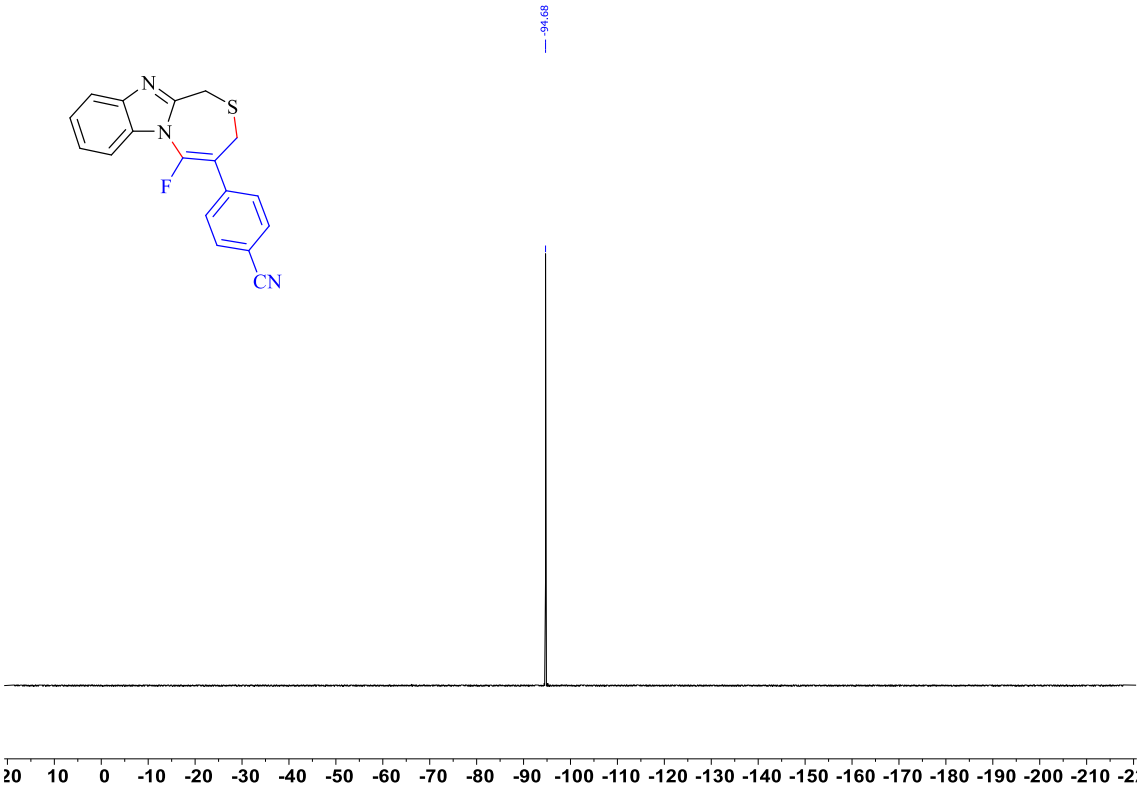
^{1}H NMR spectrum of product **3j** in $CDCl_3$ (400 MHz)



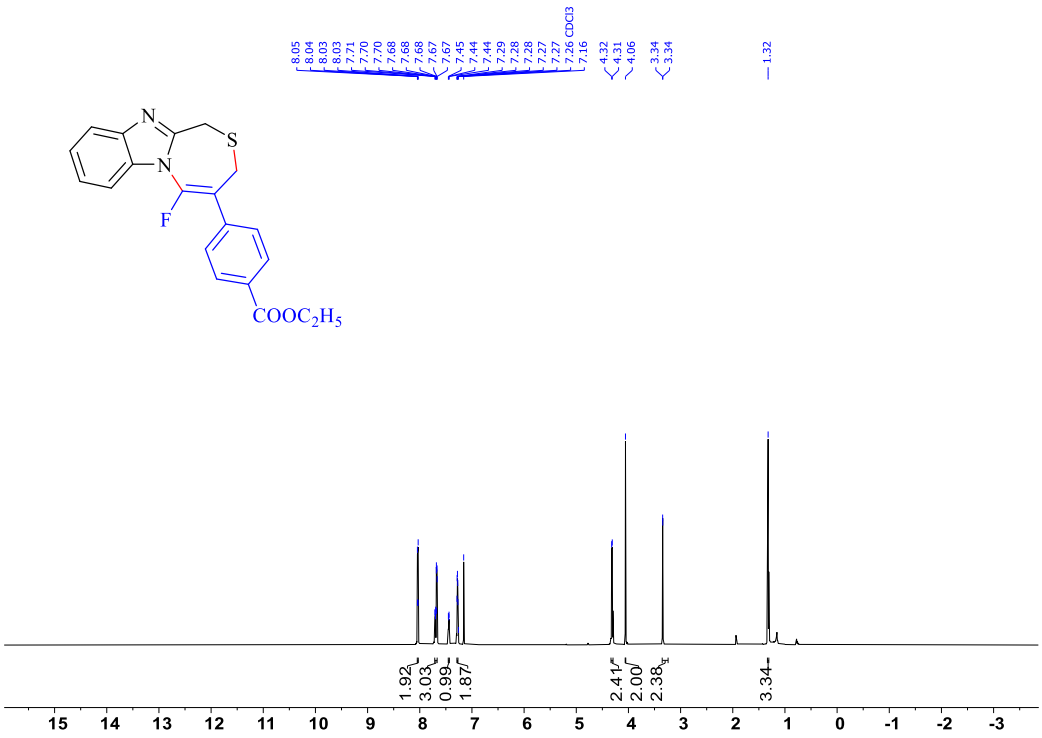
^{13}C NMR spectrum of product **3j** in $CDCl_3$ (101 MHz)



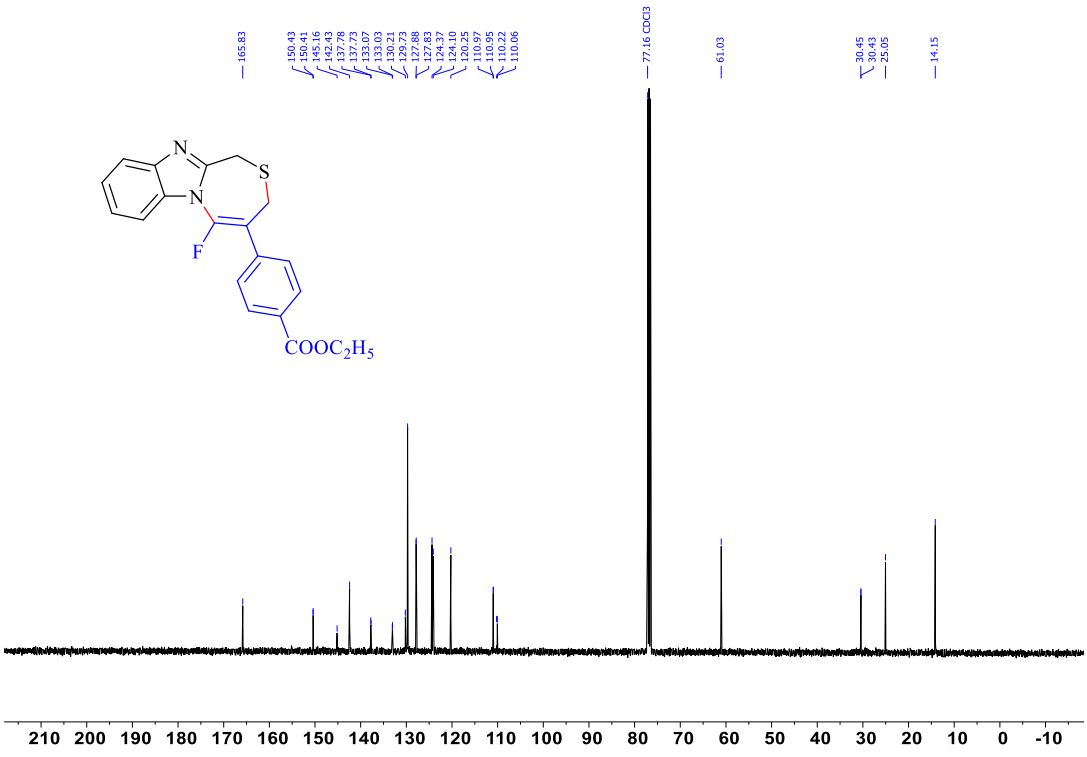
^{19}F-NMR spectrum of product **3j** in $CDCl_3$ (377 MHz)



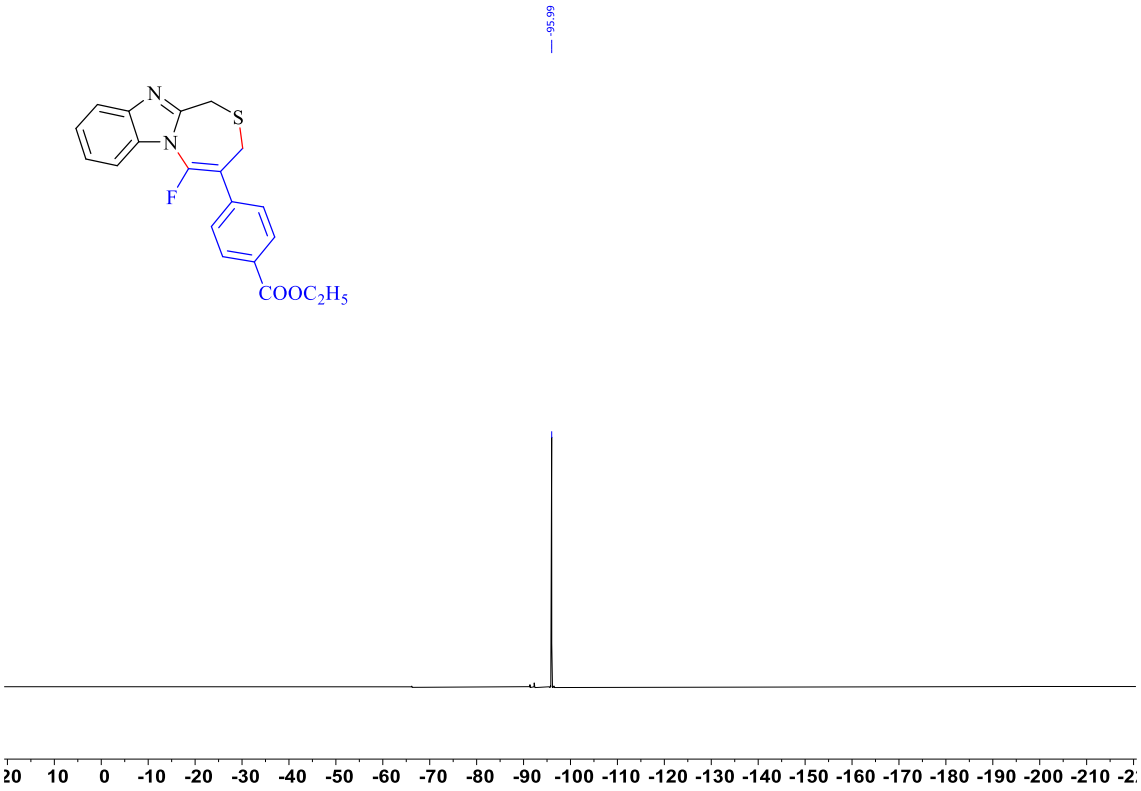
^{1}H NMR spectrum of product **3k** in $CDCl_3$ (600 MHz)



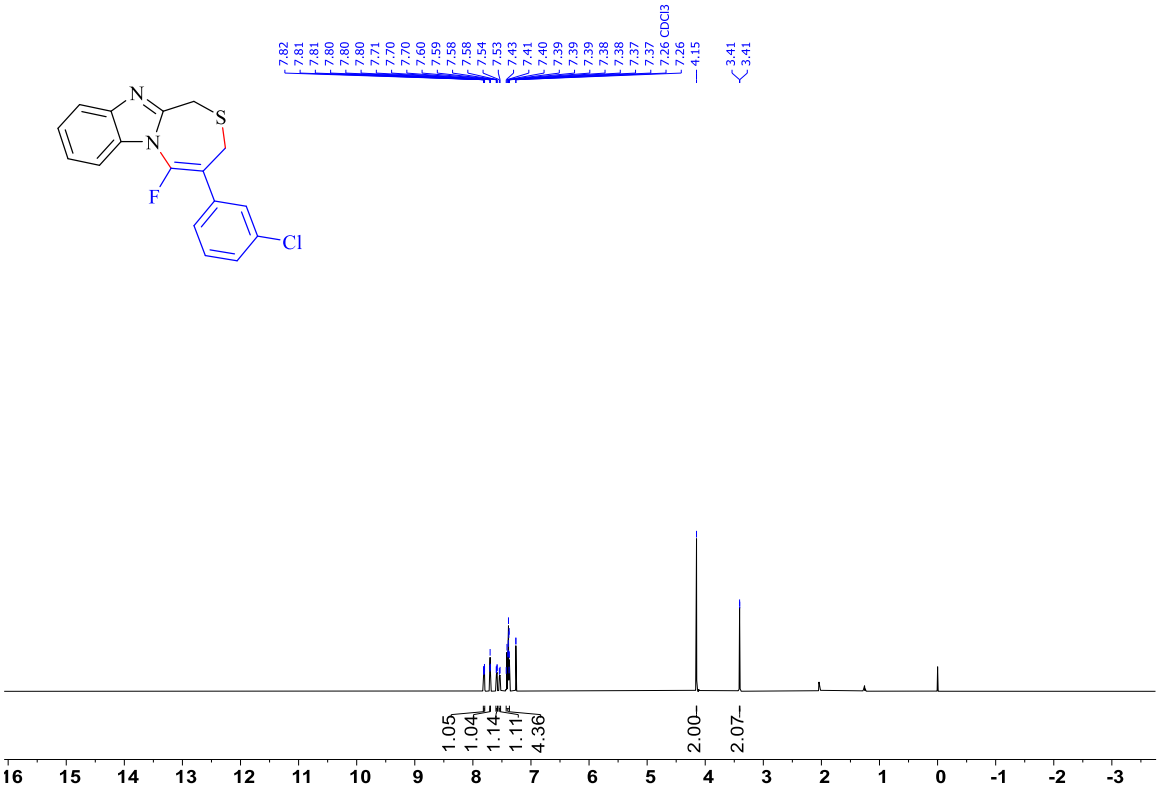
^{13}C NMR spectrum of product **3k** in $CDCl_3$ (101 MHz)



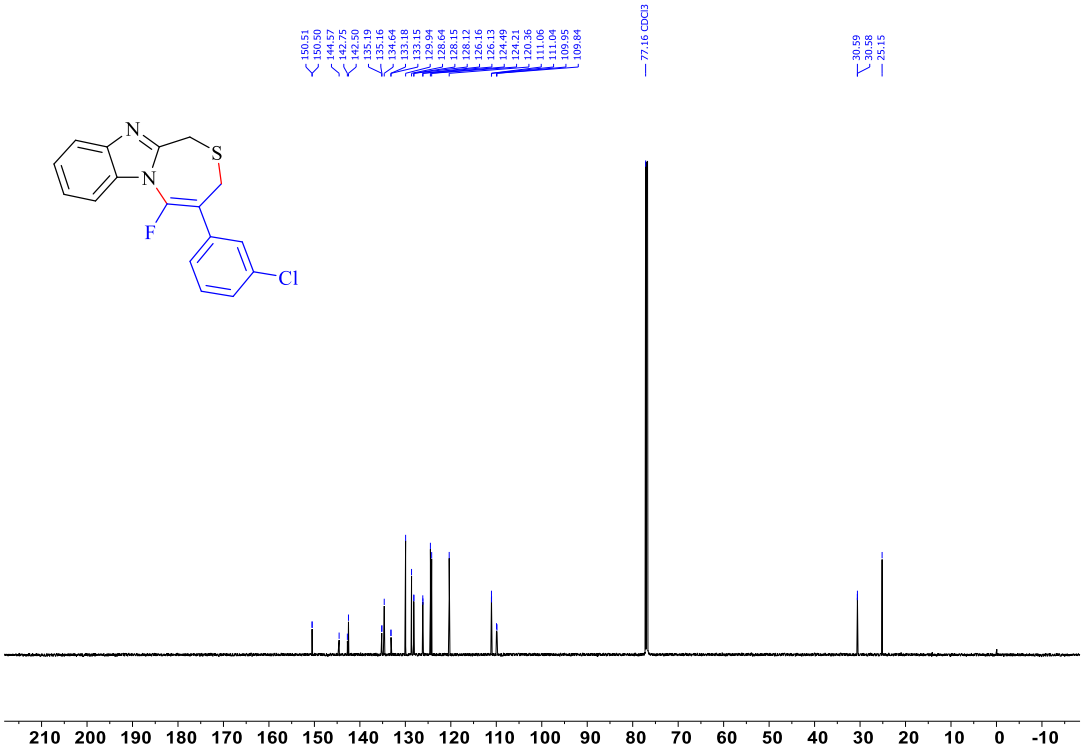
^{19}F-NMR spectrum of product **3k** in $CDCl_3$ (377 MHz)



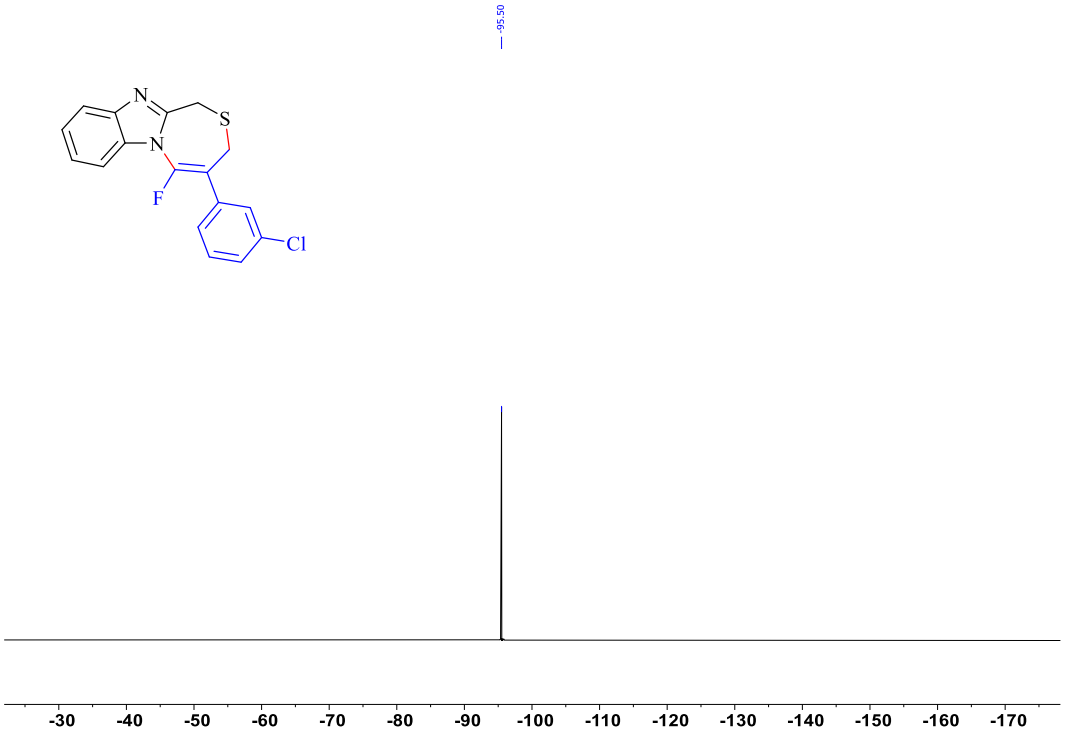
^{1}H NMR spectrum of product **3l** in $CDCl_3$ (600 MHz)



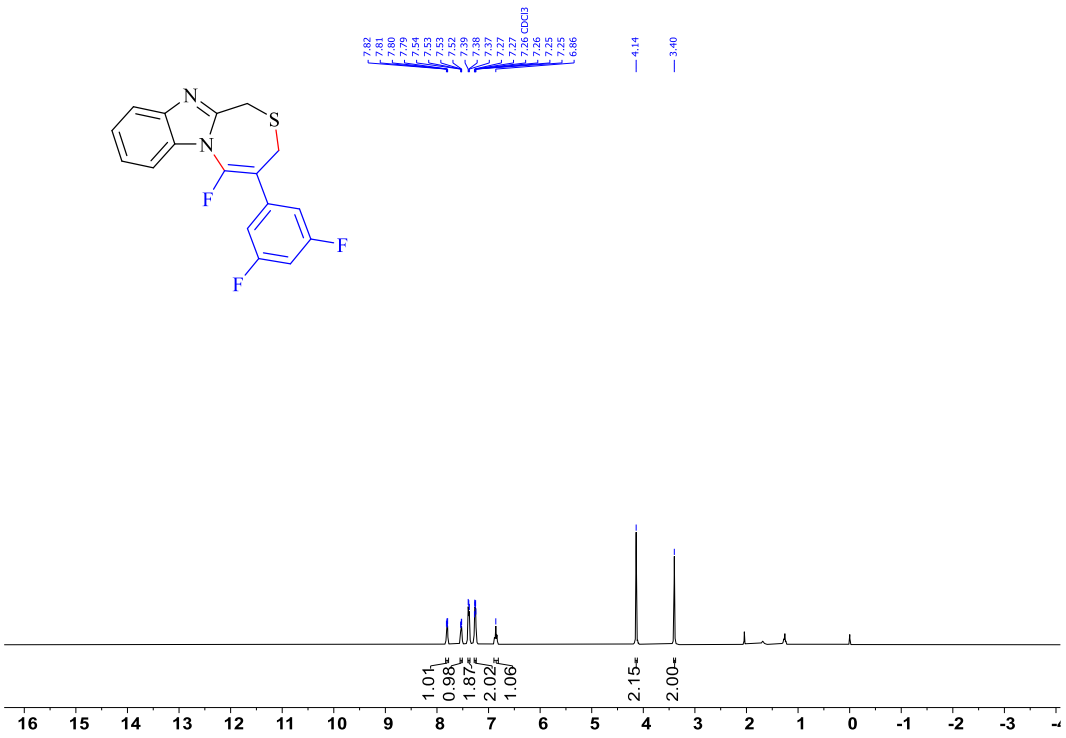
^{13}C NMR spectrum of product **3l** in $CDCl_3$ (151 MHz)



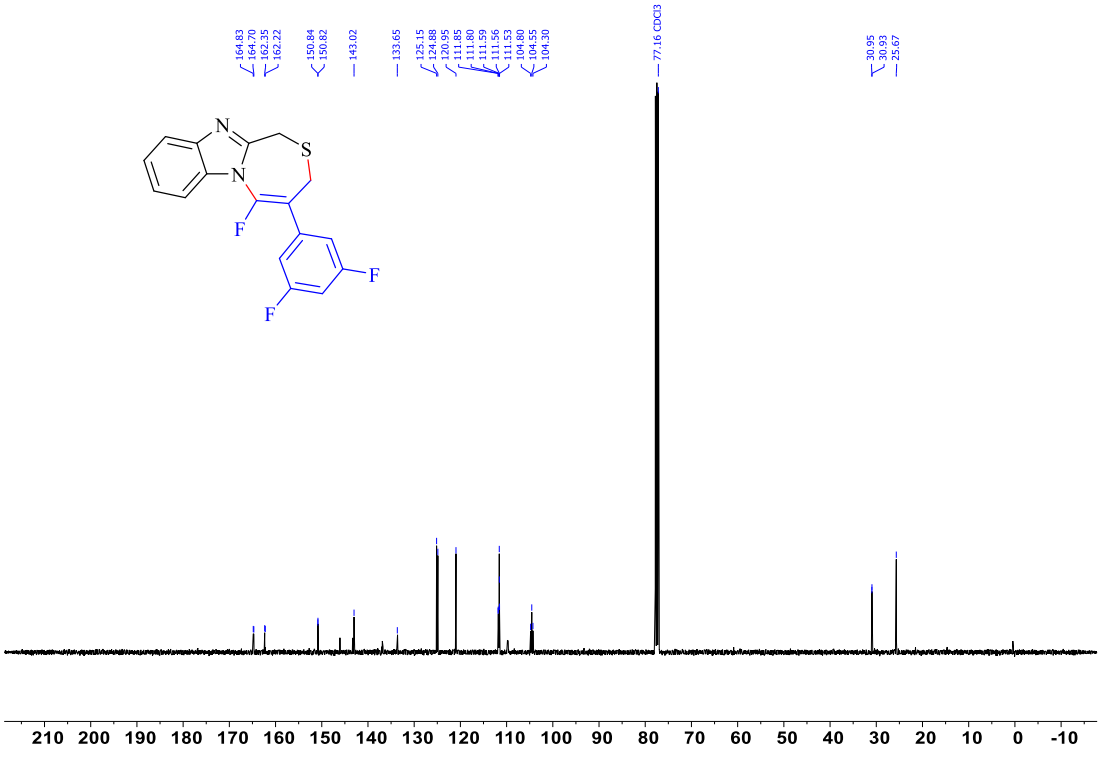
^{19}F-NMR spectrum of product **3l** in $CDCl_3$ (565 MHz)



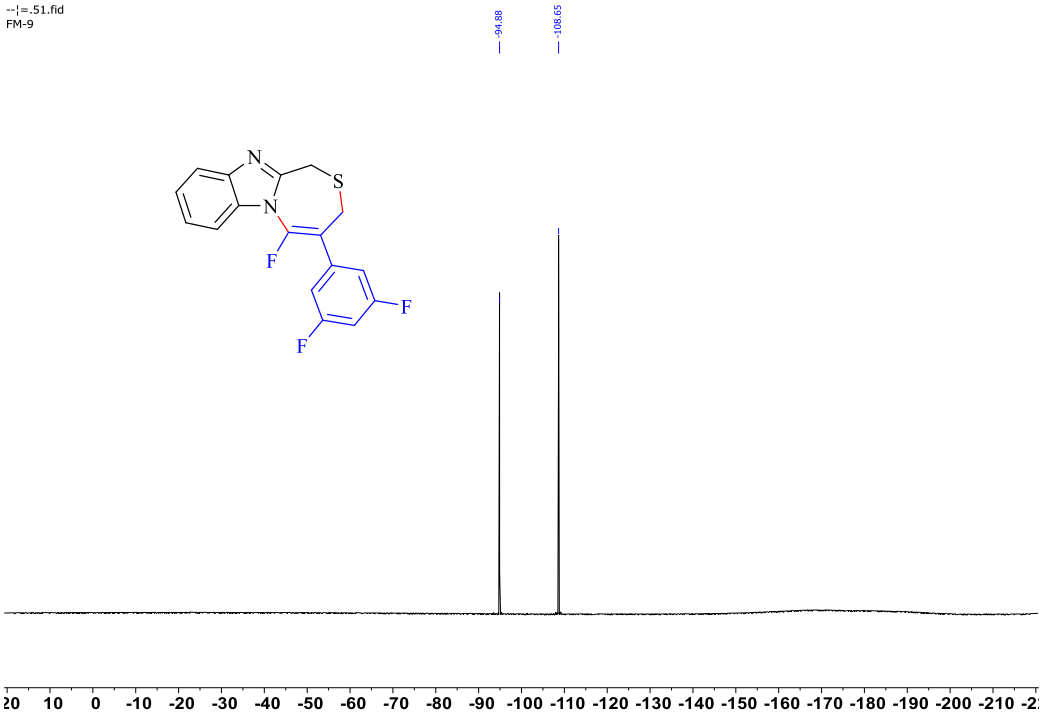
^{1}H NMR spectrum of product **3m** in $CDCl_3$ (400 MHz)



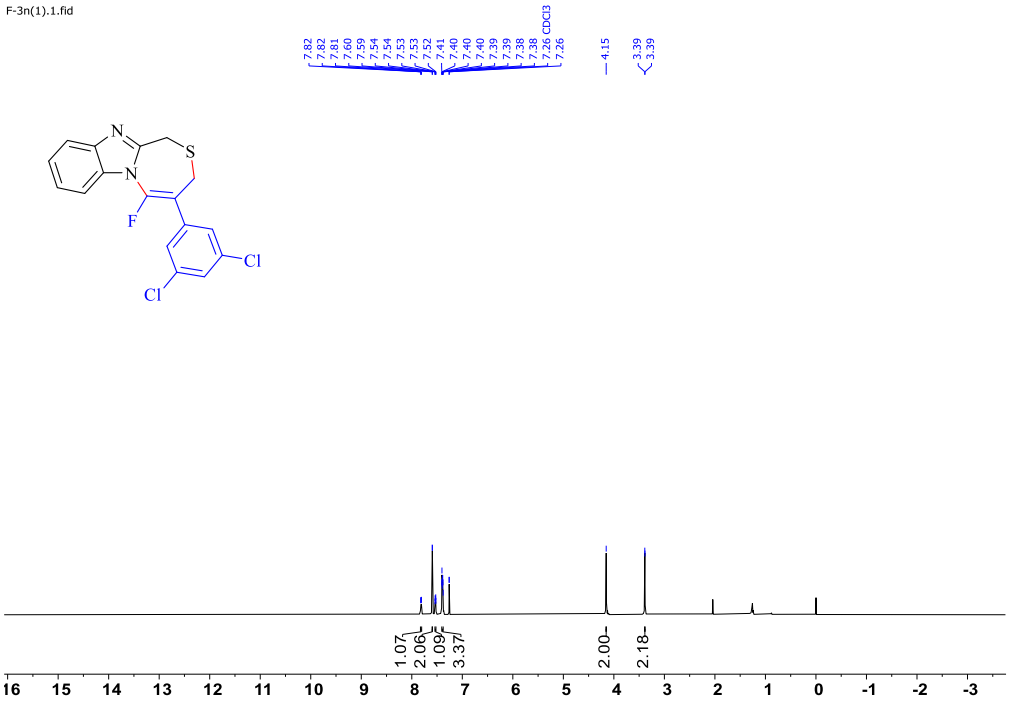
^{13}C NMR spectrum of product **3m** in $CDCl_3$ (101 MHz)



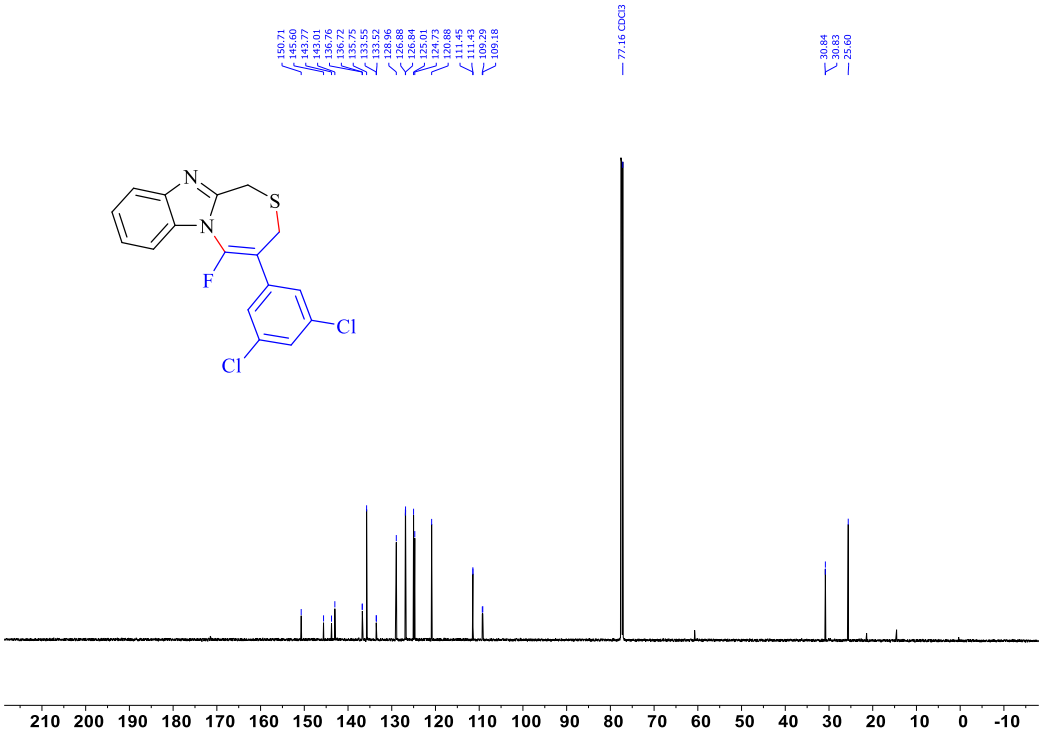
^{19}F-NMR spectrum of product **3m** in $CDCl_3$ (377 MHz)



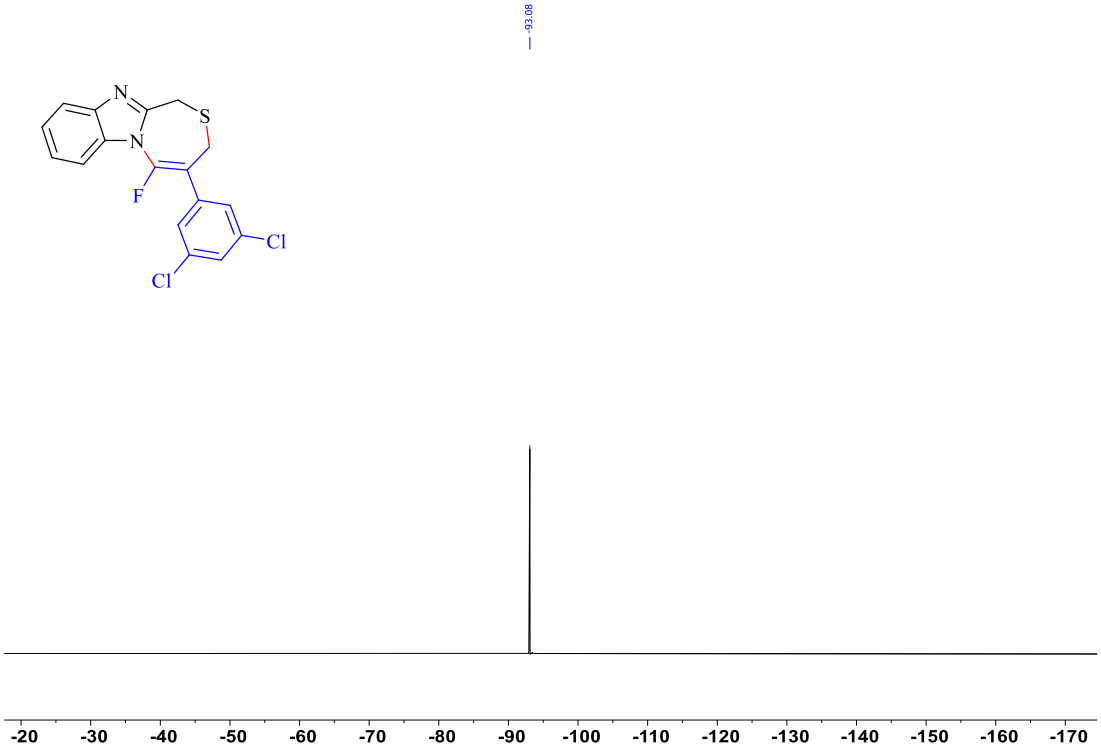
^{1}H NMR spectrum of product **3n** in $CDCl_3$ (600 MHz)



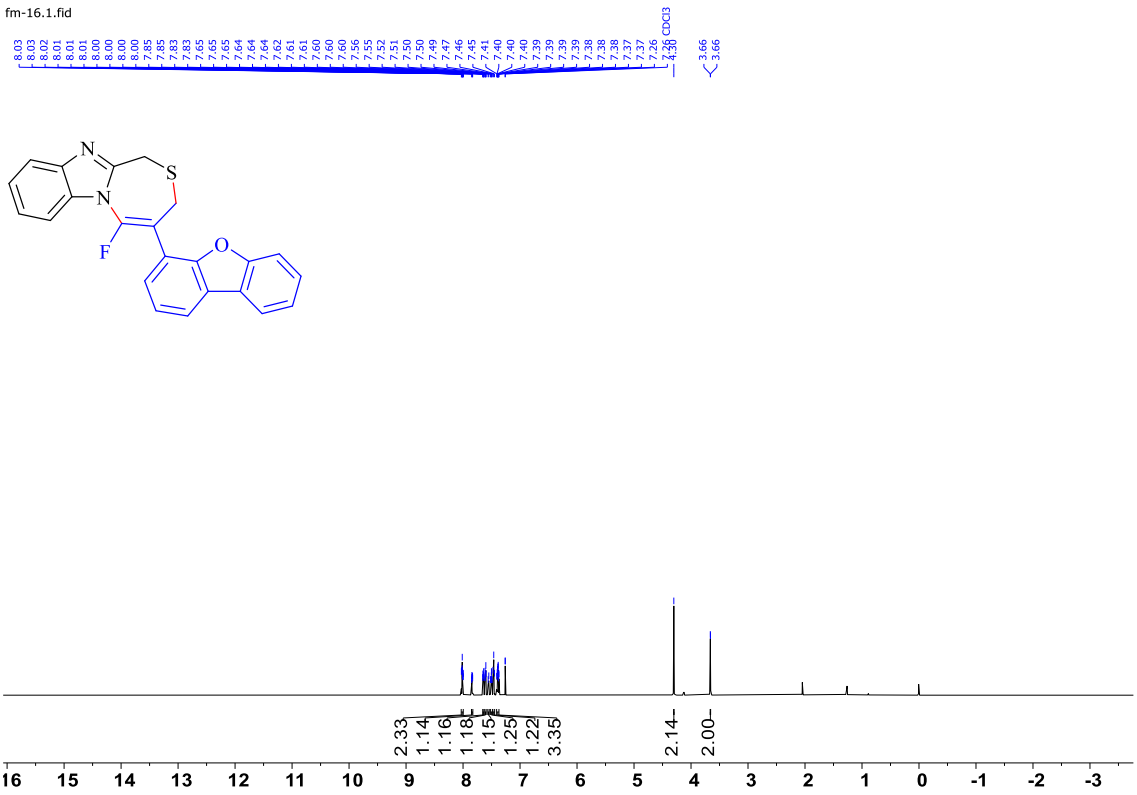
^{13}C NMR spectrum of product **3n** in $CDCl_3$ (151 MHz)



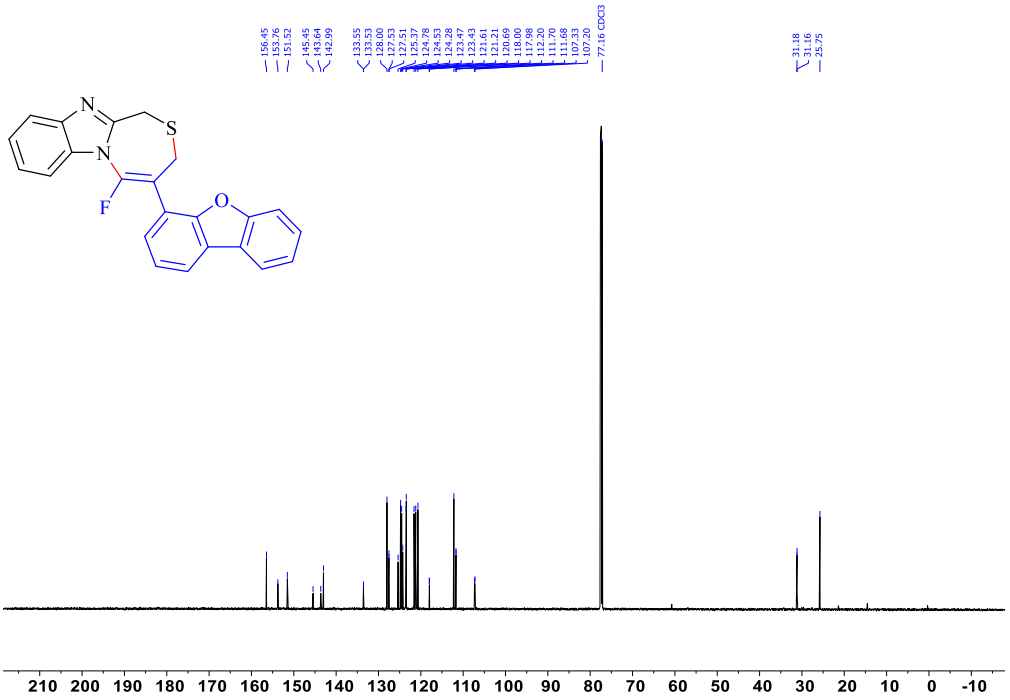
^{19}F-NMR spectrum of product **3n** in $CDCl_3$ (565 MHz)



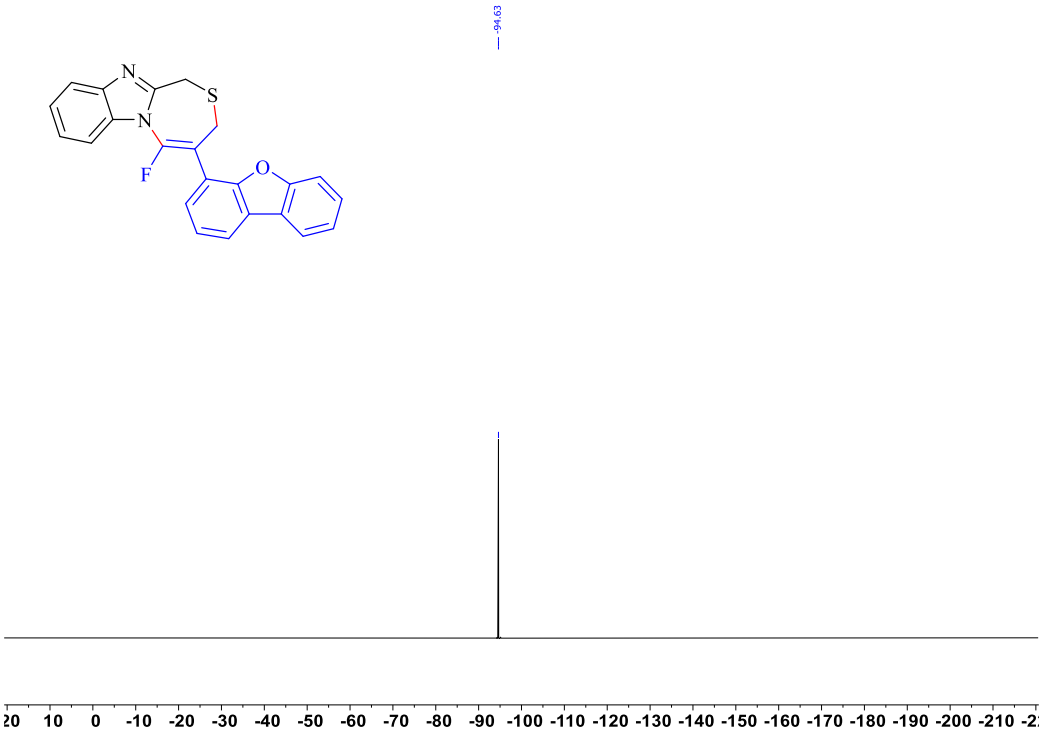
^{1}H NMR spectrum of product **3o** in $CDCl_3$ (600 MHz)



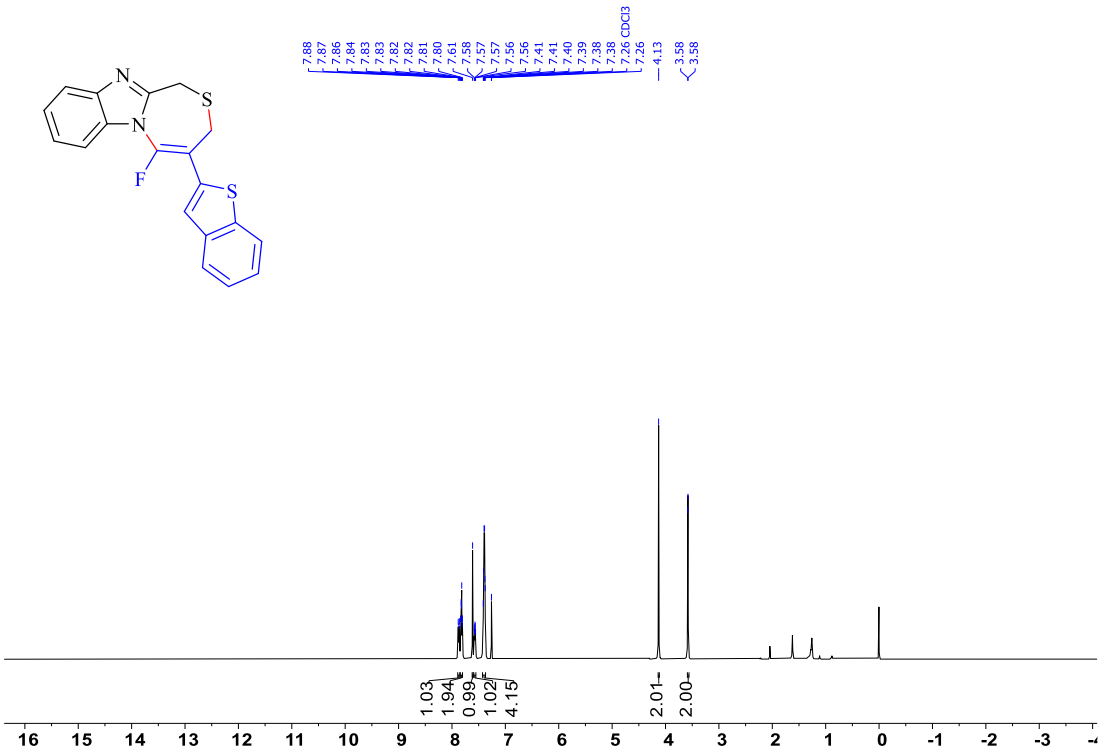
^{13}C NMR spectrum of product **3o** in $CDCl_3$ (151 MHz)



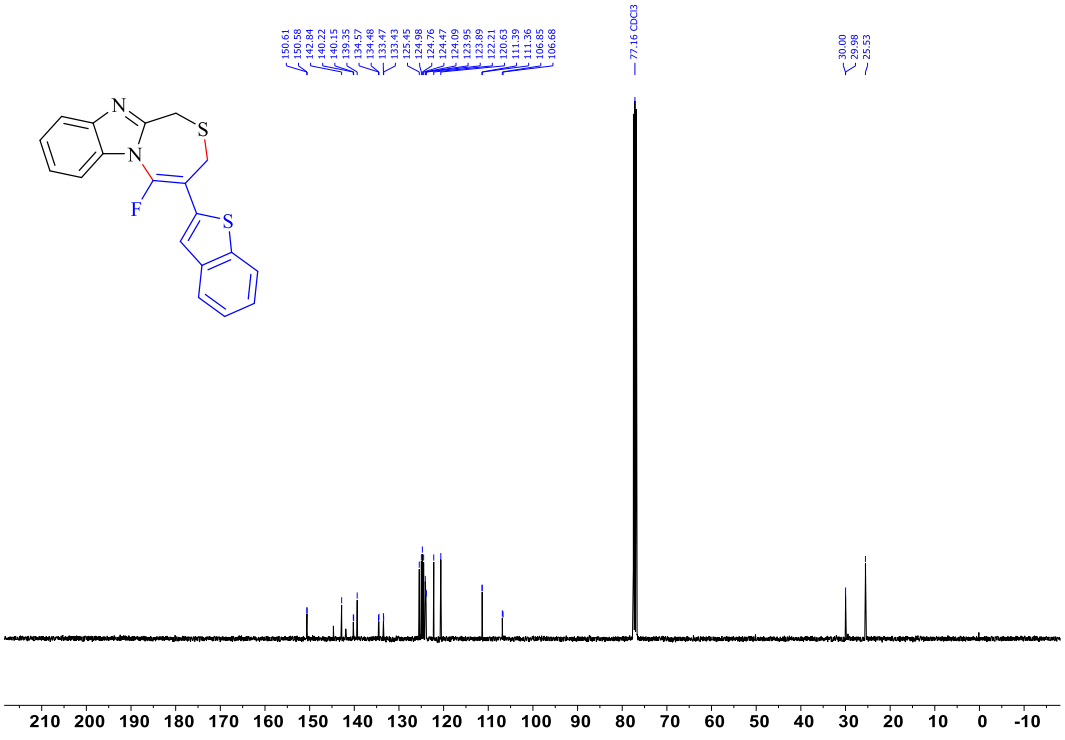
^{19}F-NMR spectrum of product **3o** in $CDCl_3$ (377 MHz)



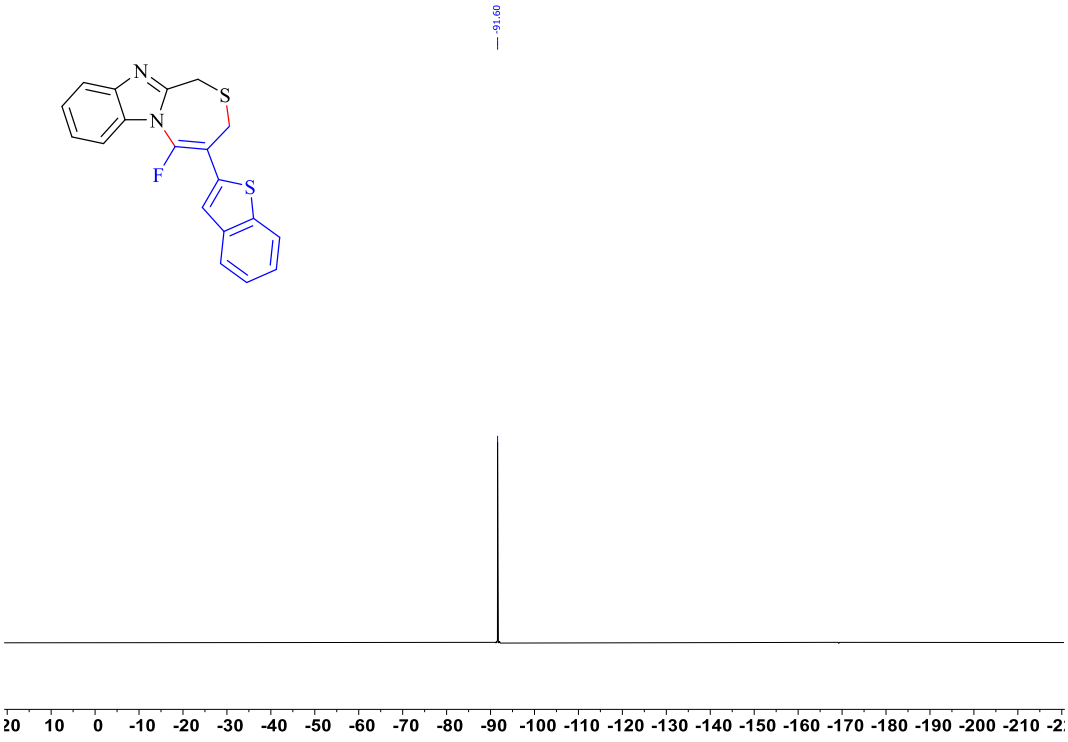
^{1}H NMR spectrum of product **3p** in $CDCl_3$ (400 MHz)



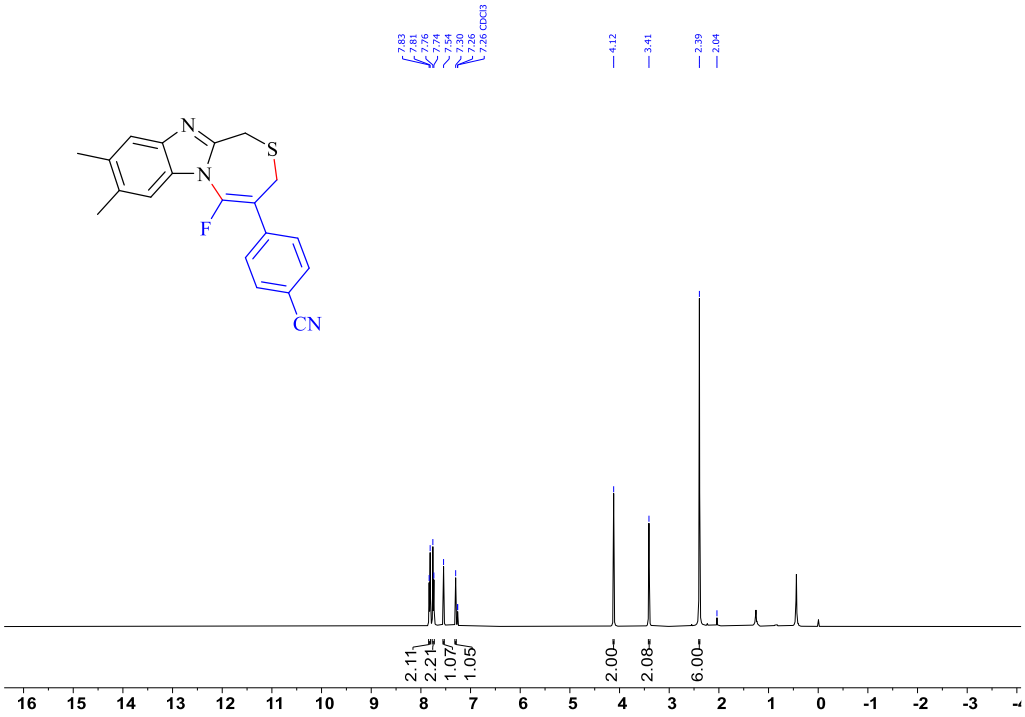
^{13}C NMR spectrum of product **3p** in $CDCl_3$ (101 MHz)



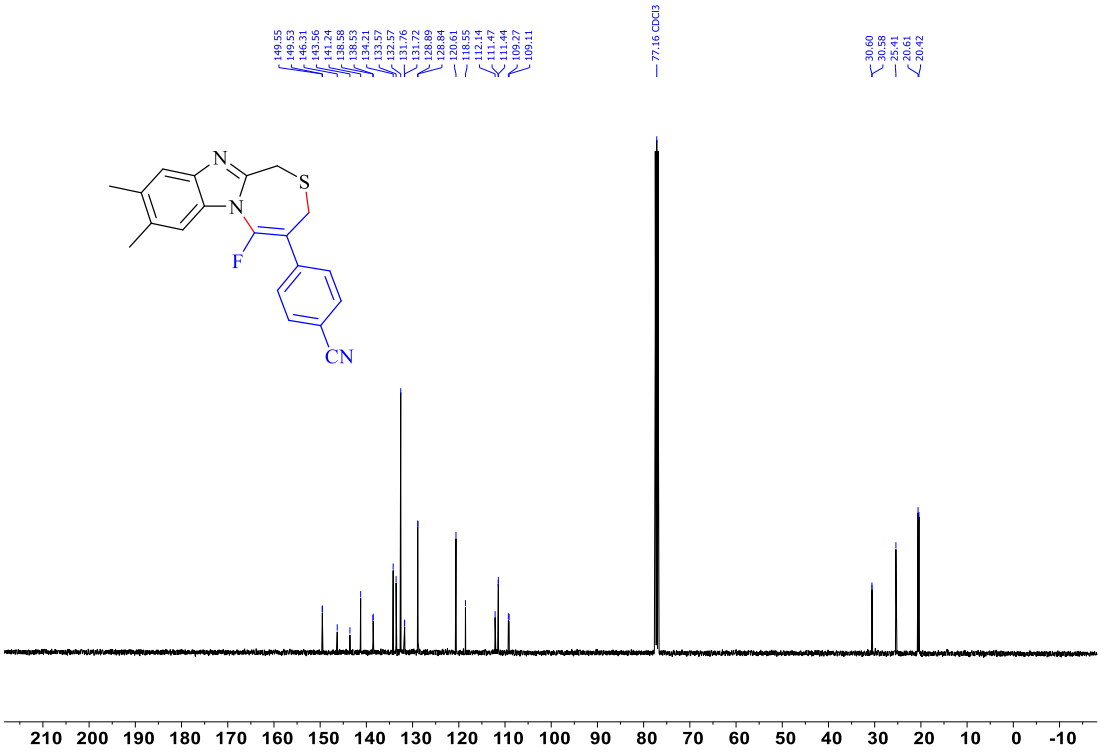
^{19}F-NMR spectrum of product **3p** in $CDCl_3$ (377 MHz)



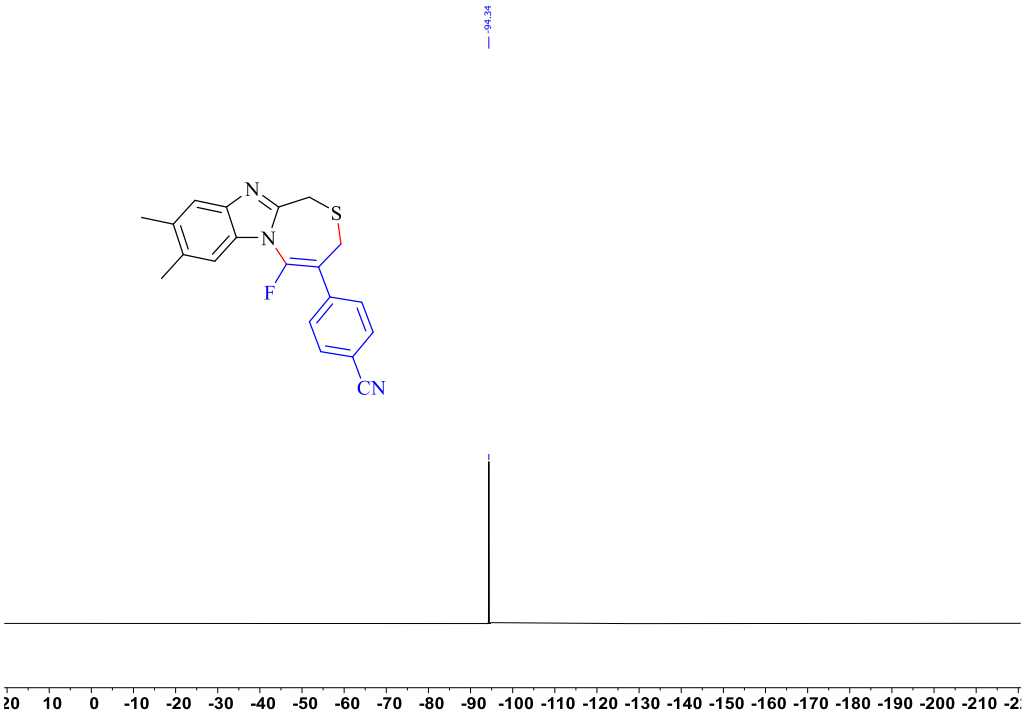
^{1}H NMR spectrum of product **3q** in $CDCl_3$ (400 MHz)



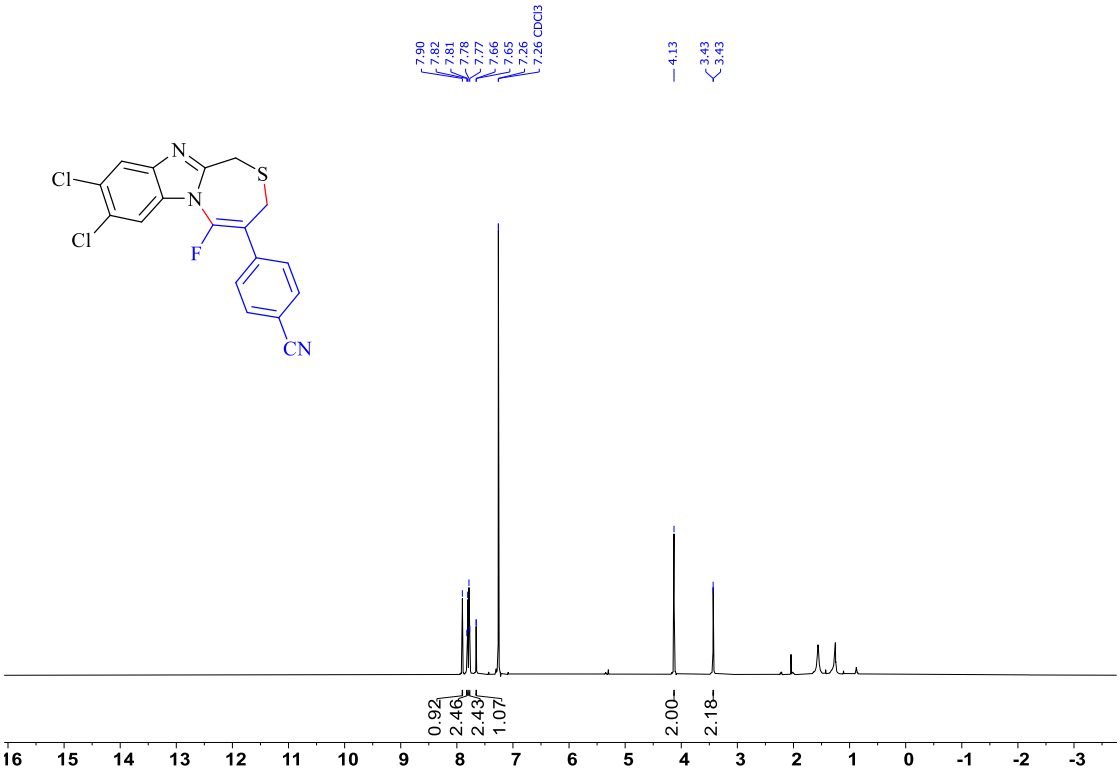
^{13}C NMR spectrum of product **3q** in $CDCl_3$ (101 MHz)



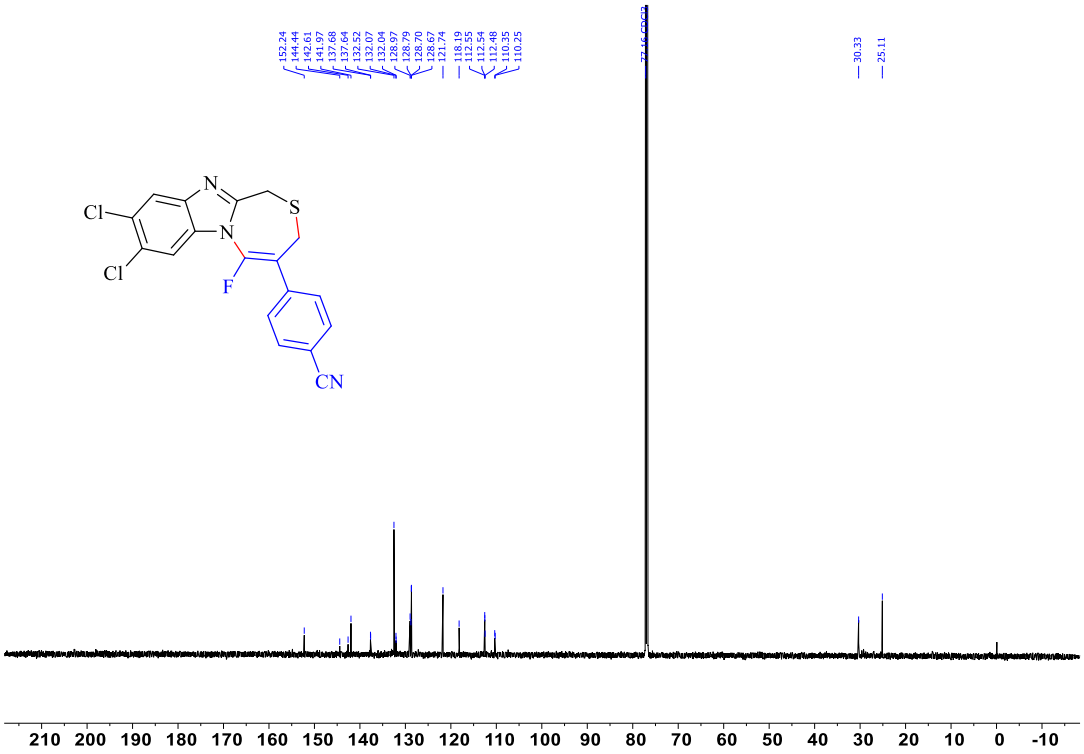
^{19}F-NMR spectrum of product **3q** in $CDCl_3$ (377 MHz)



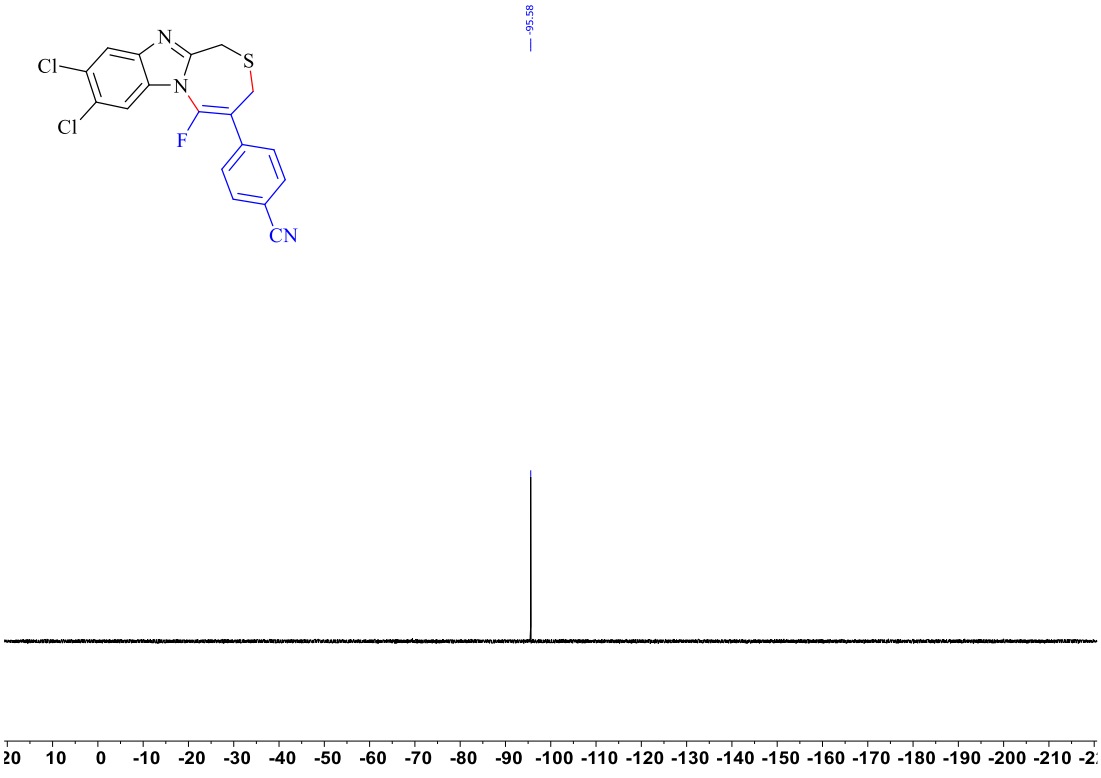
^{1}H NMR spectrum of product **3r** in $CDCl_3$ (600 MHz)



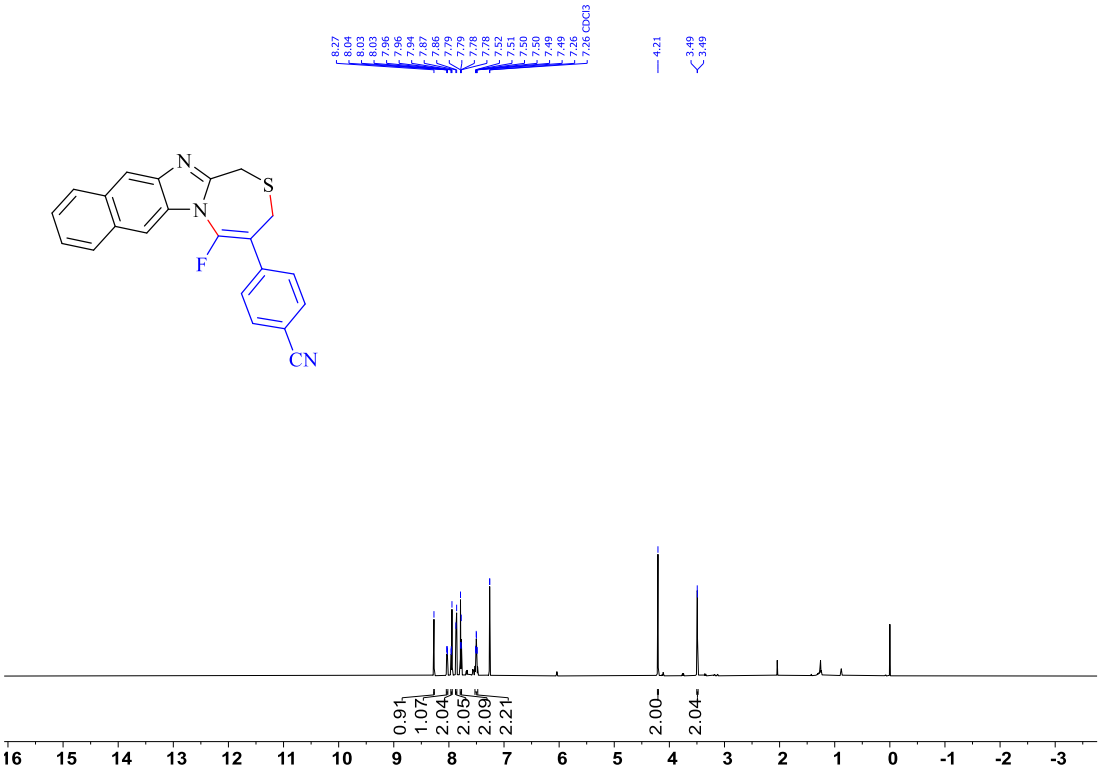
^{13}C NMR spectrum of product **3r** in $CDCl_3$ (151 MHz)



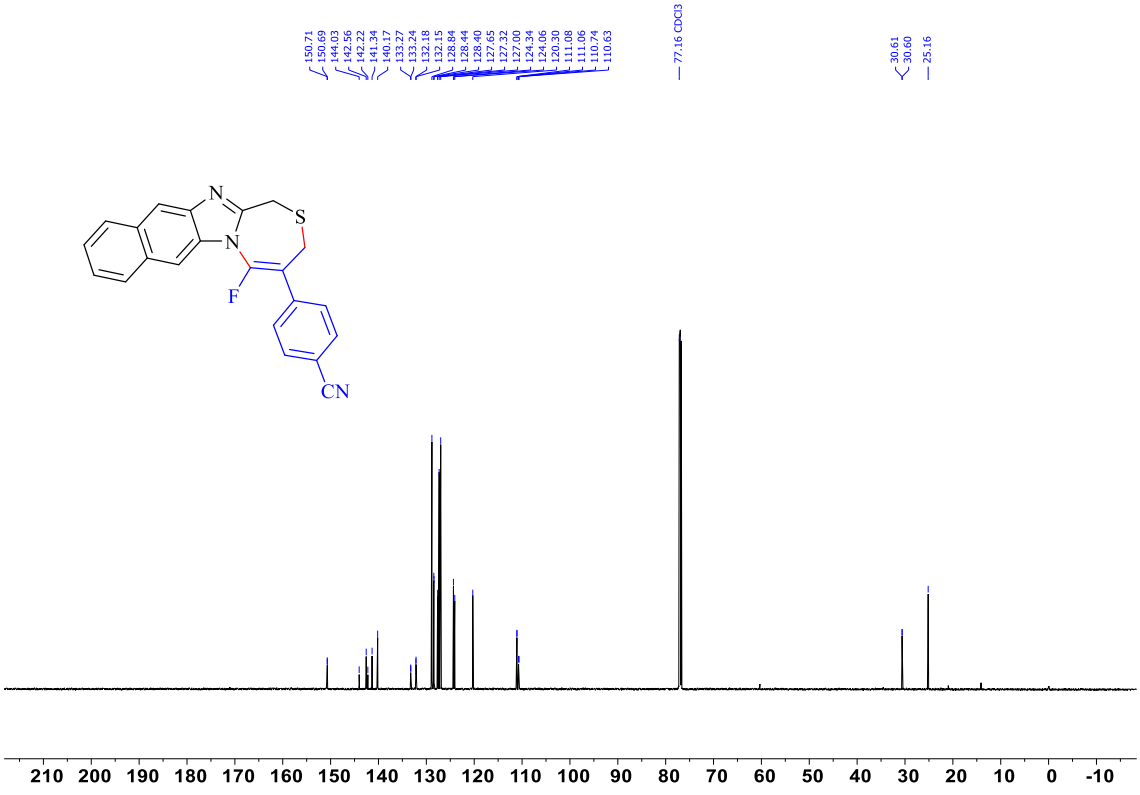
^{19}F-NMR spectrum of product **3r** in $CDCl_3$ (377 MHz)



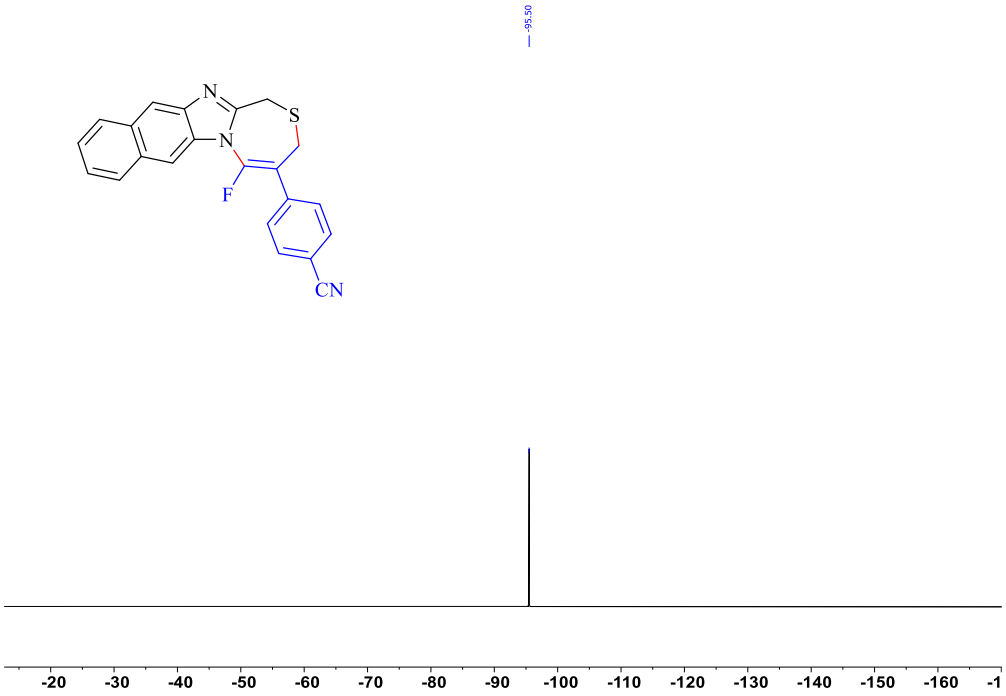
^{1}H NMR spectrum of product **3s** in $CDCl_3$ (600 MHz)



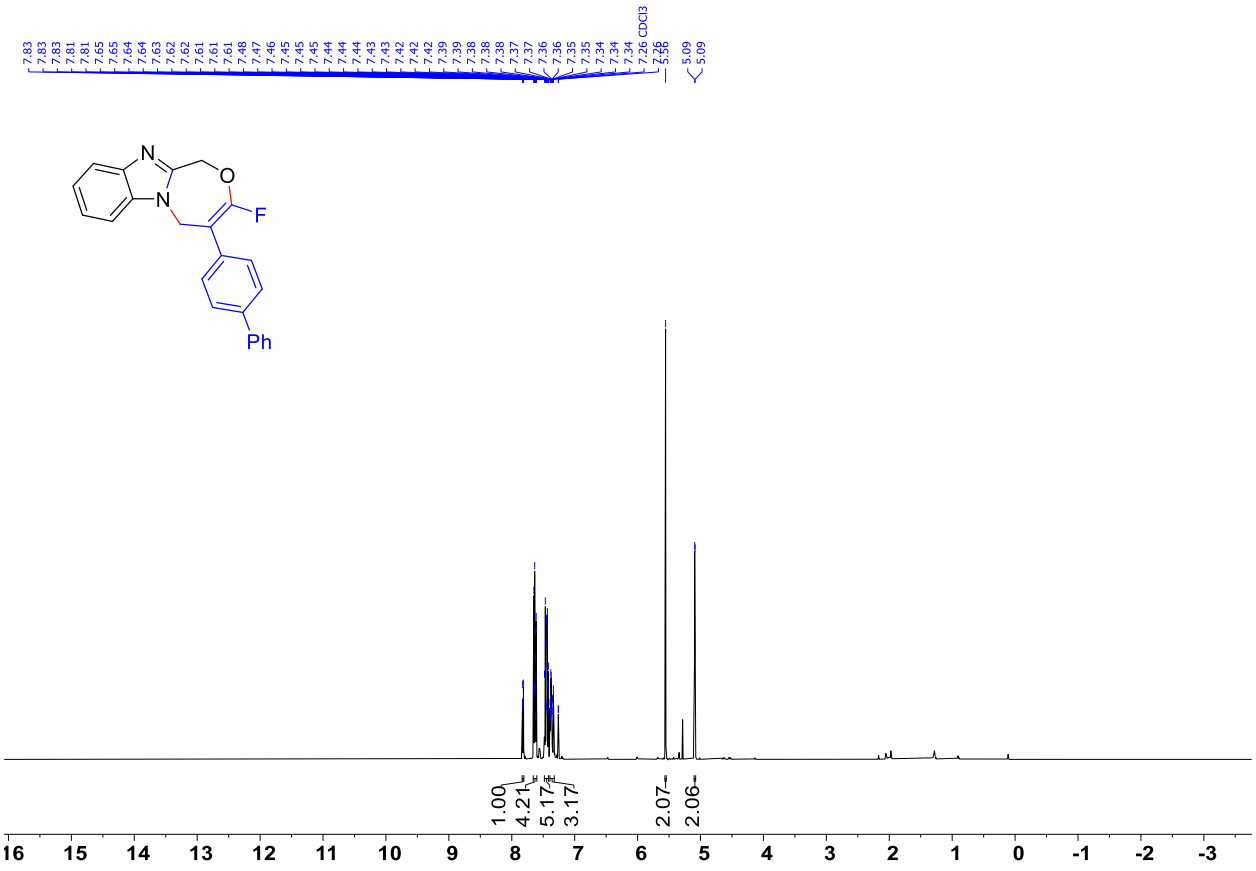
^{13}C NMR spectrum of product **3s** in $CDCl_3$ (151 MHz)



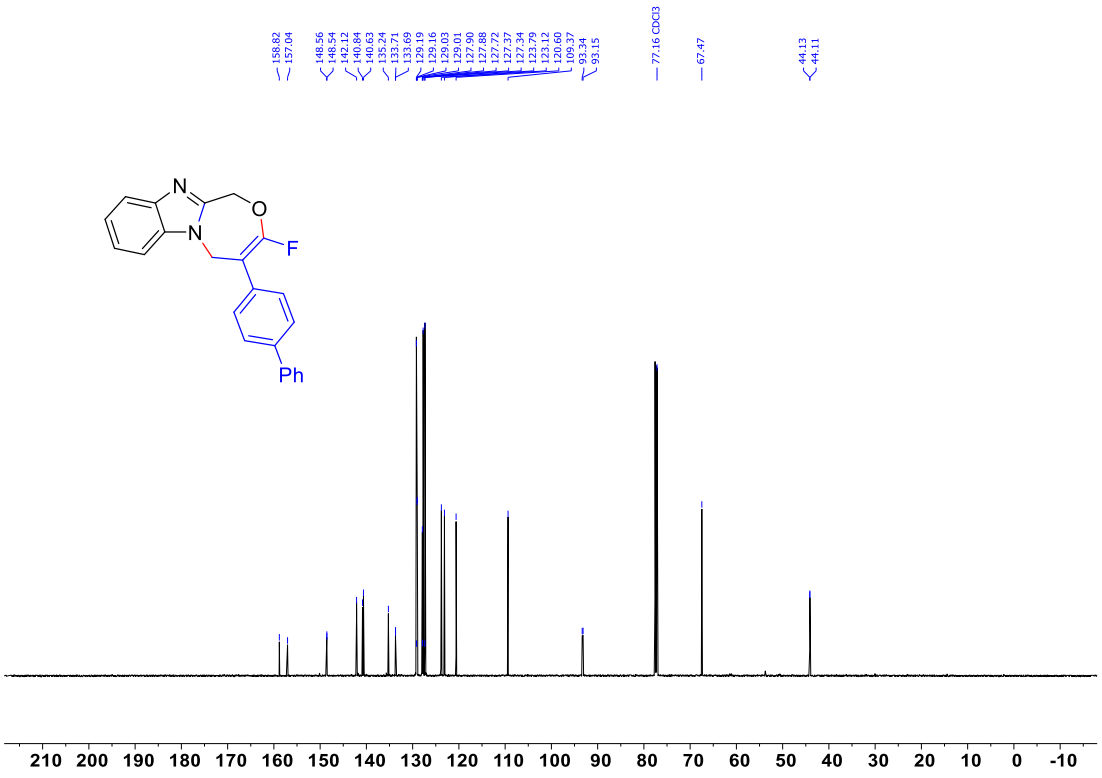
^{19}F-NMR spectrum of product **3s** in $CDCl_3$ (565 MHz)



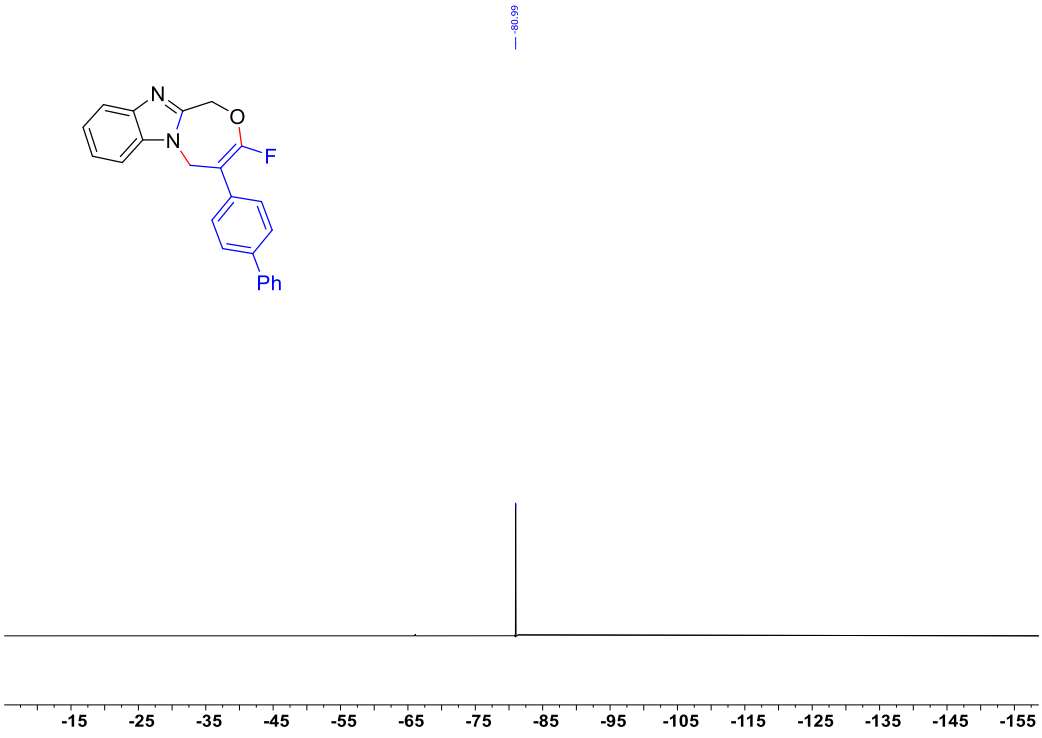
^{1}H NMR spectrum of product **5a** in $CDCl_3$ (600 MHz)



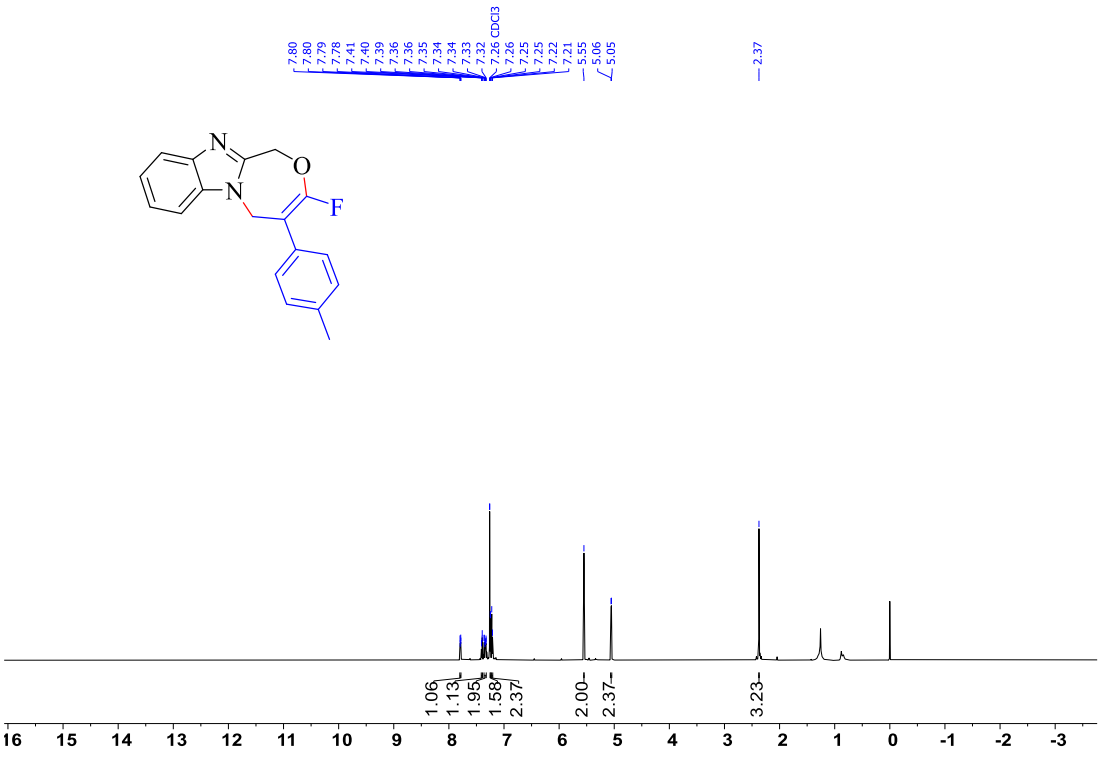
^{13}C NMR spectrum of product **5a** in $CDCl_3$ (151 MHz)



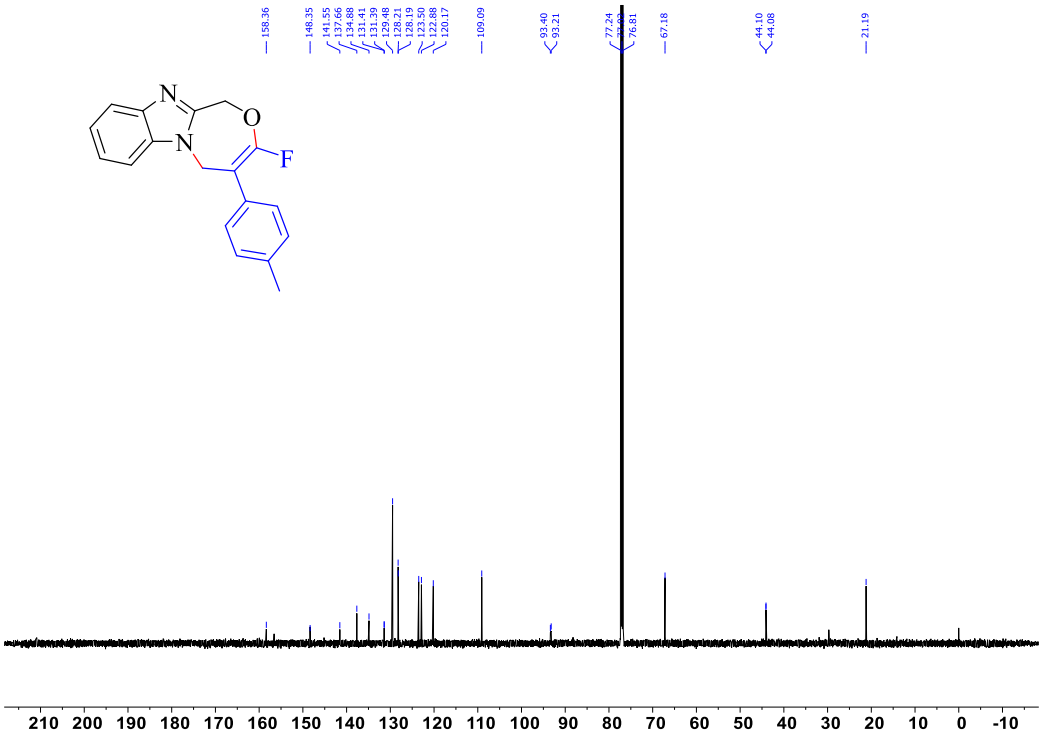
^{19}F-NMR spectrum of product **5a** in $CDCl_3$ (565 MHz)



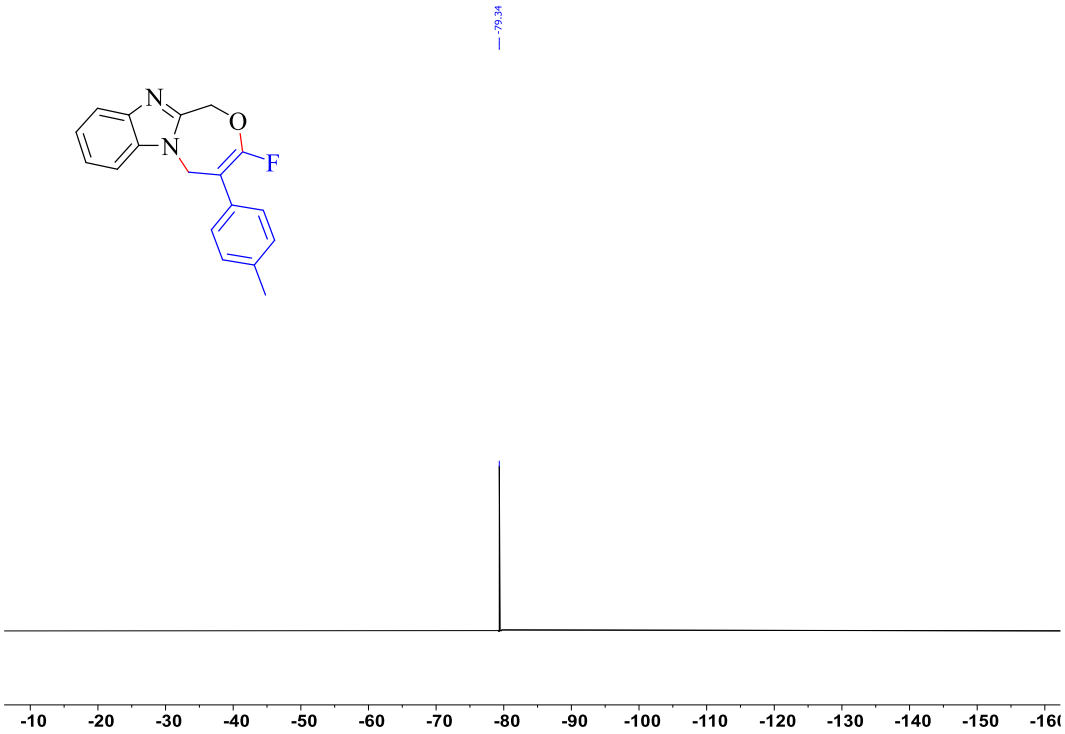
^{1}H NMR spectrum of product **5b** in $CDCl_3$ (600 MHz)



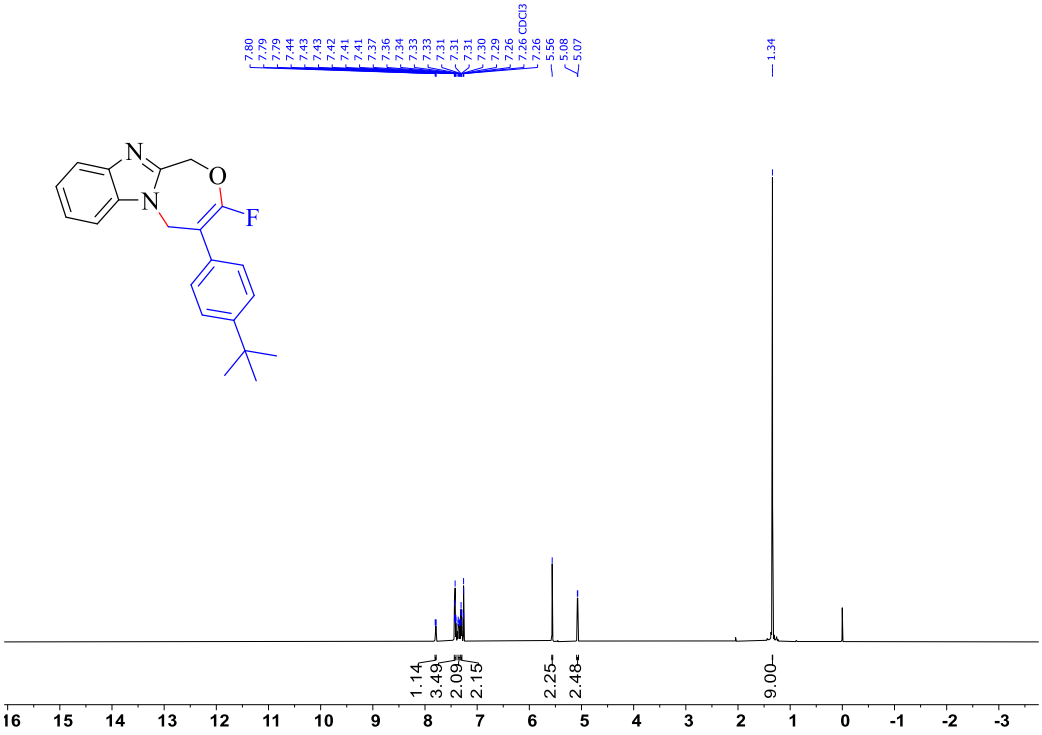
^{13}C NMR spectrum of product **5b** in $CDCl_3$ (151 MHz)



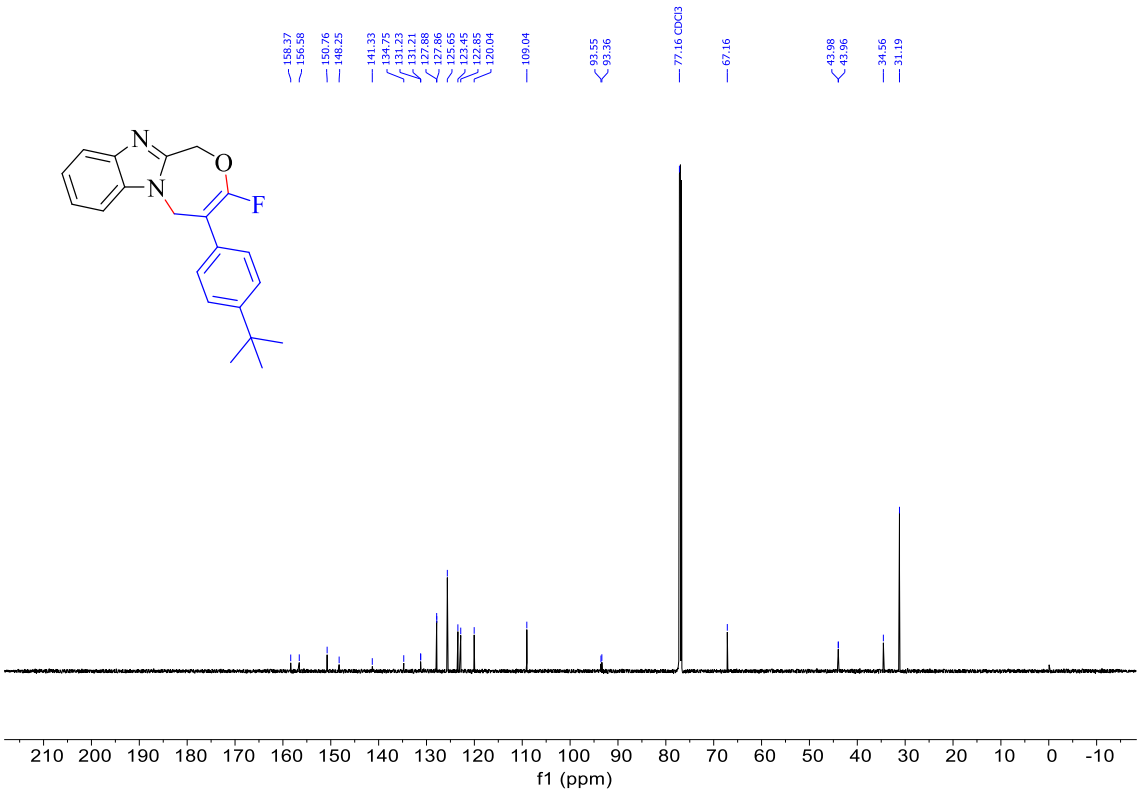
^{19}F-NMR spectrum of product **5b** in $CDCl_3$ (565 MHz)



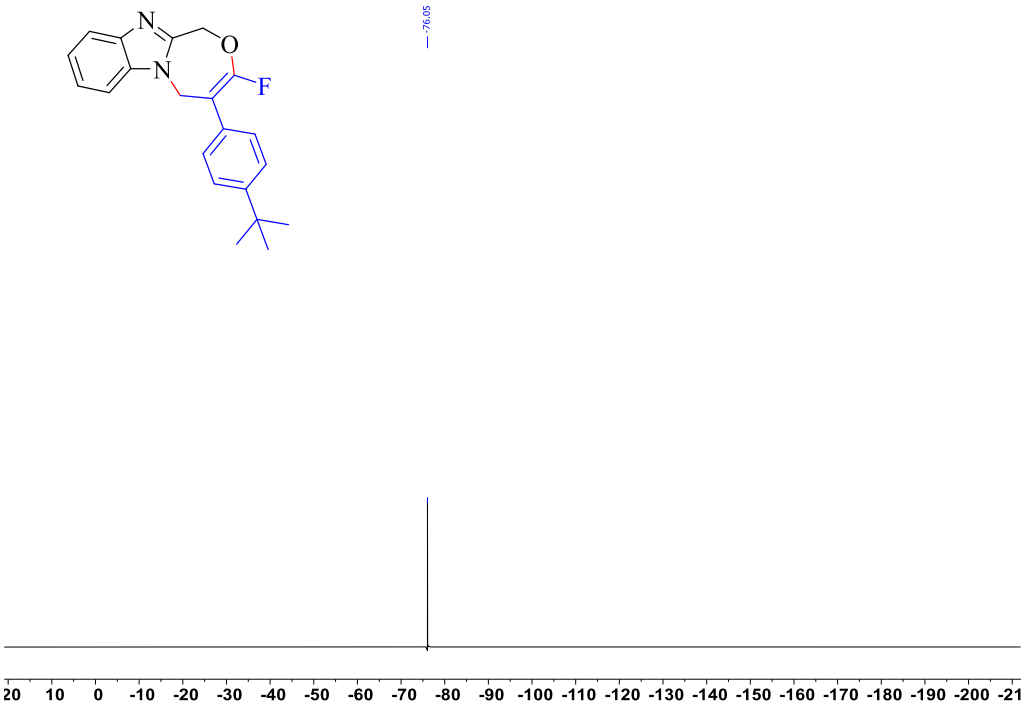
^{1}H NMR spectrum of product **5c** in $CDCl_3$ (600 MHz)



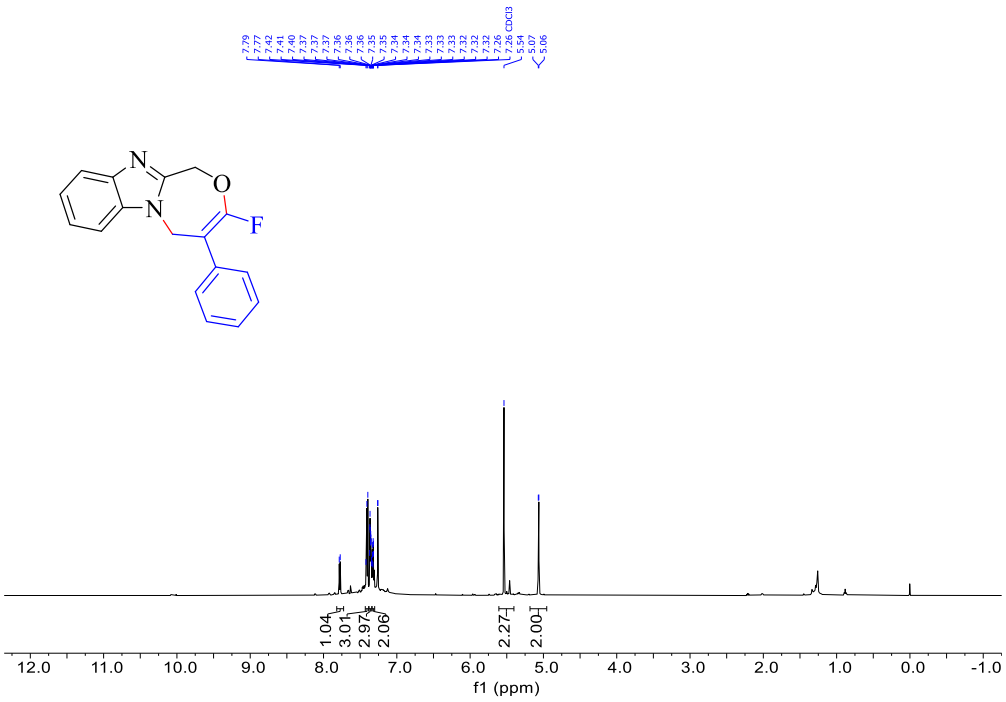
^{13}C NMR spectrum of product **5c** in $CDCl_3$ (151 MHz)



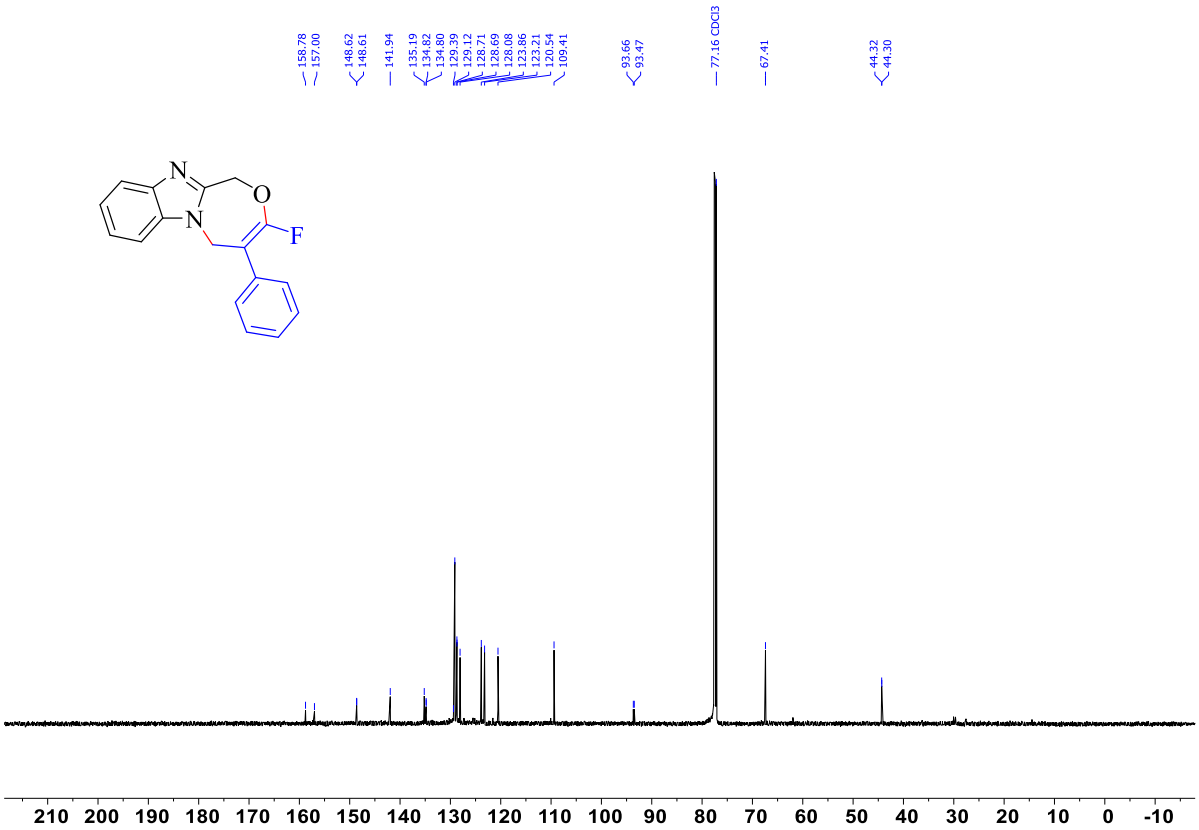
^{19}F-NMR spectrum of product **5c** in $CDCl_3$ (565 MHz)



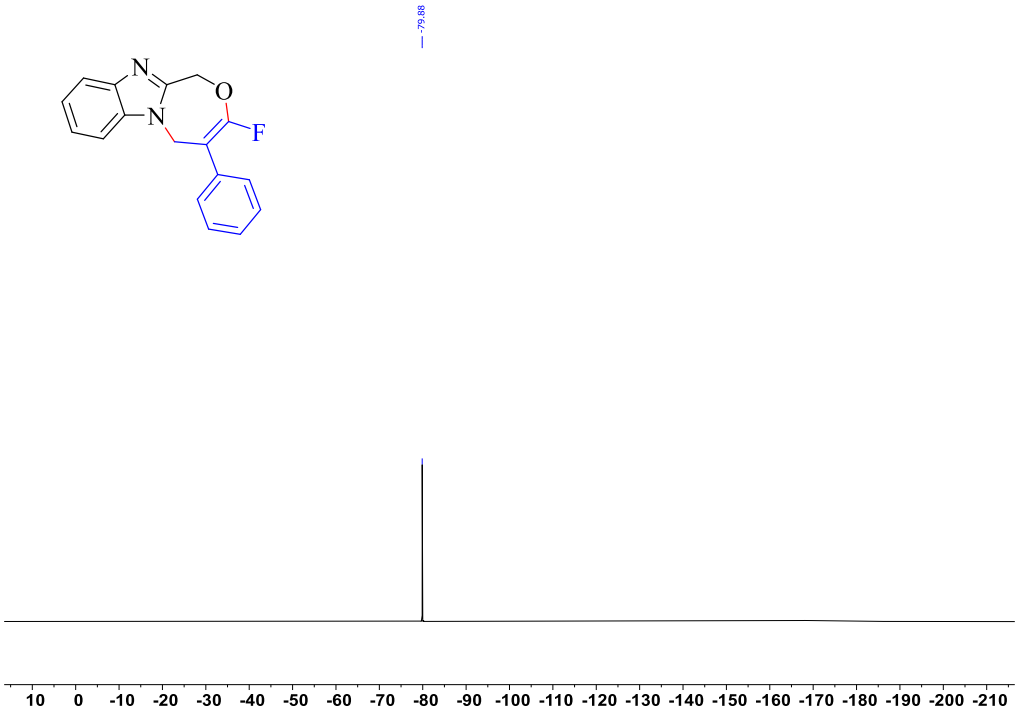
^{1}H NMR spectrum of product **5d** in $CDCl_3$ (600 MHz)



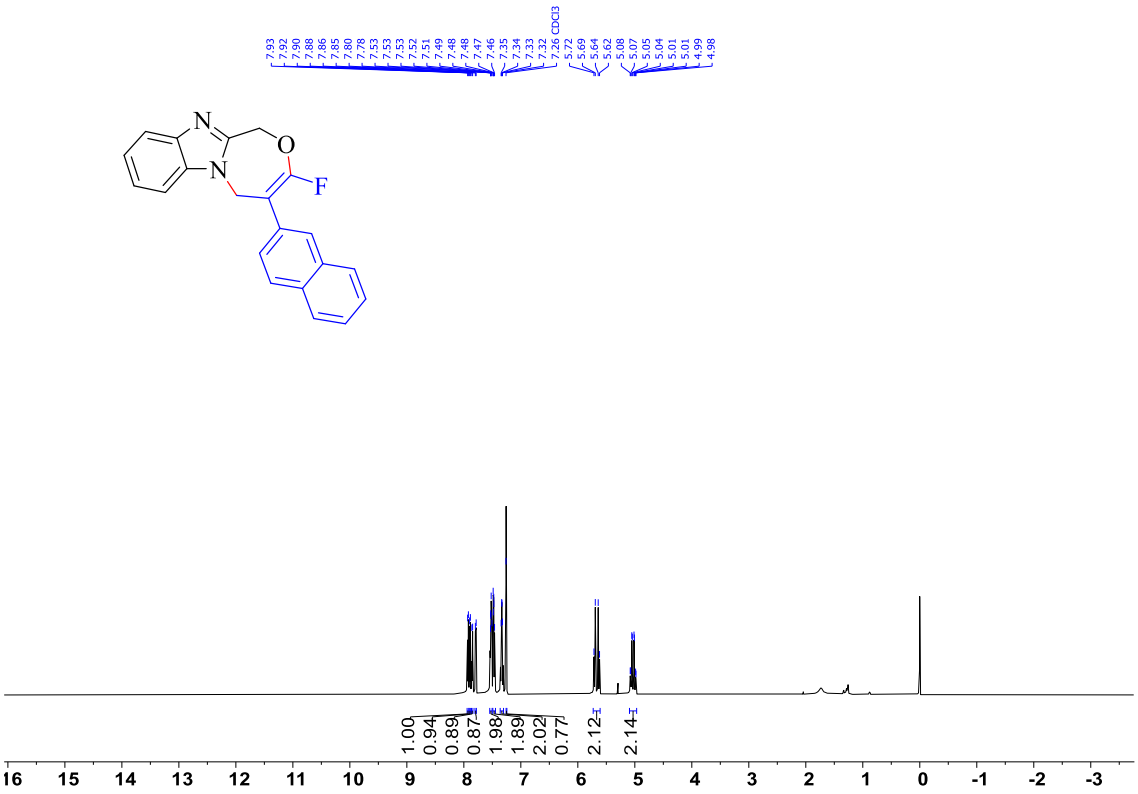
^{13}C NMR spectrum of product **5d** in $CDCl_3$ (151 MHz)



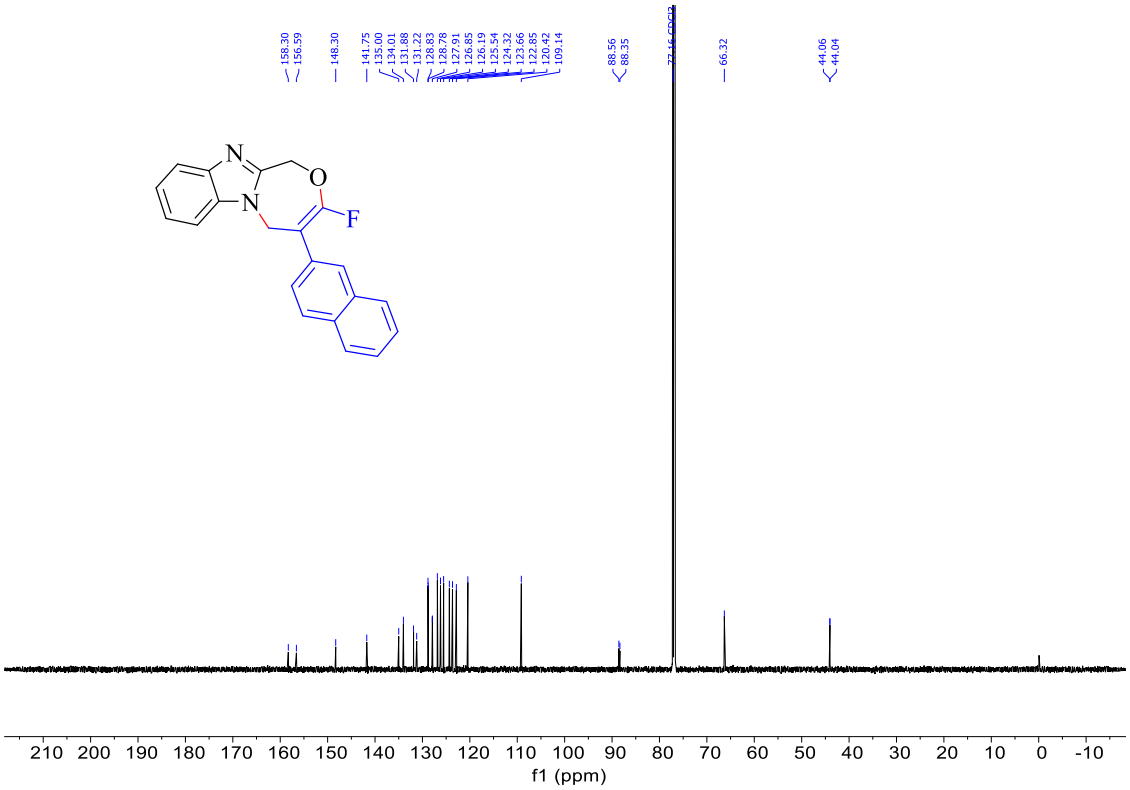
^{19}F-NMR spectrum of product **5d** in $CDCl_3$ (565 MHz)



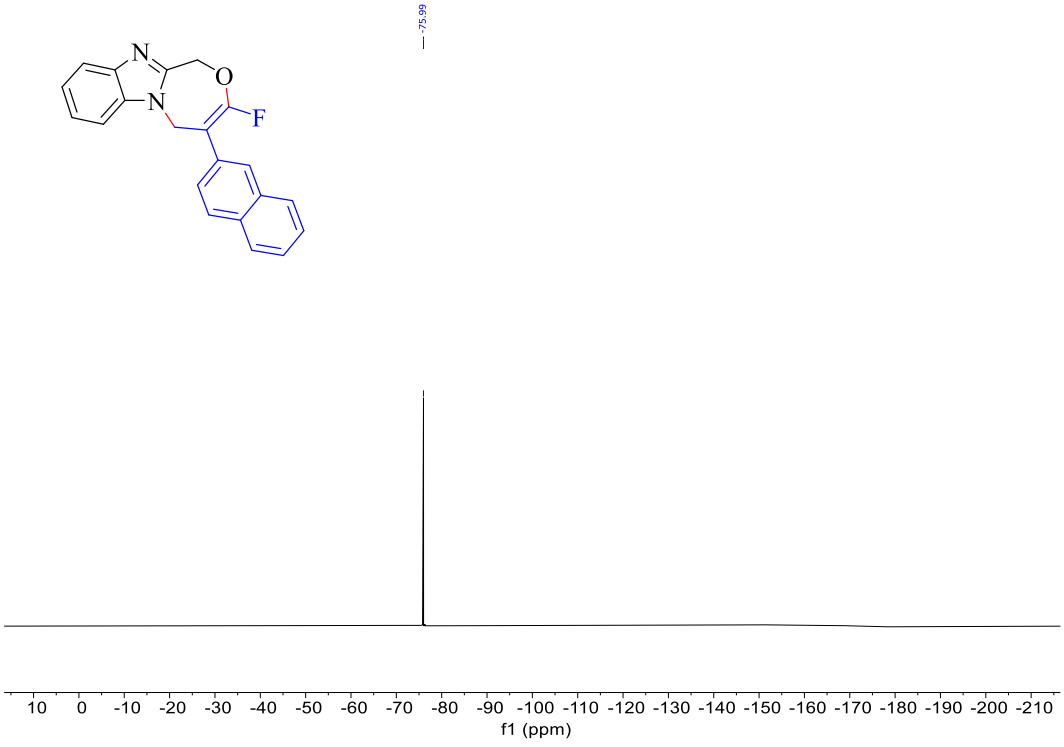
^{1}H NMR spectrum of product **5e** in $CDCl_3$ (600 MHz)



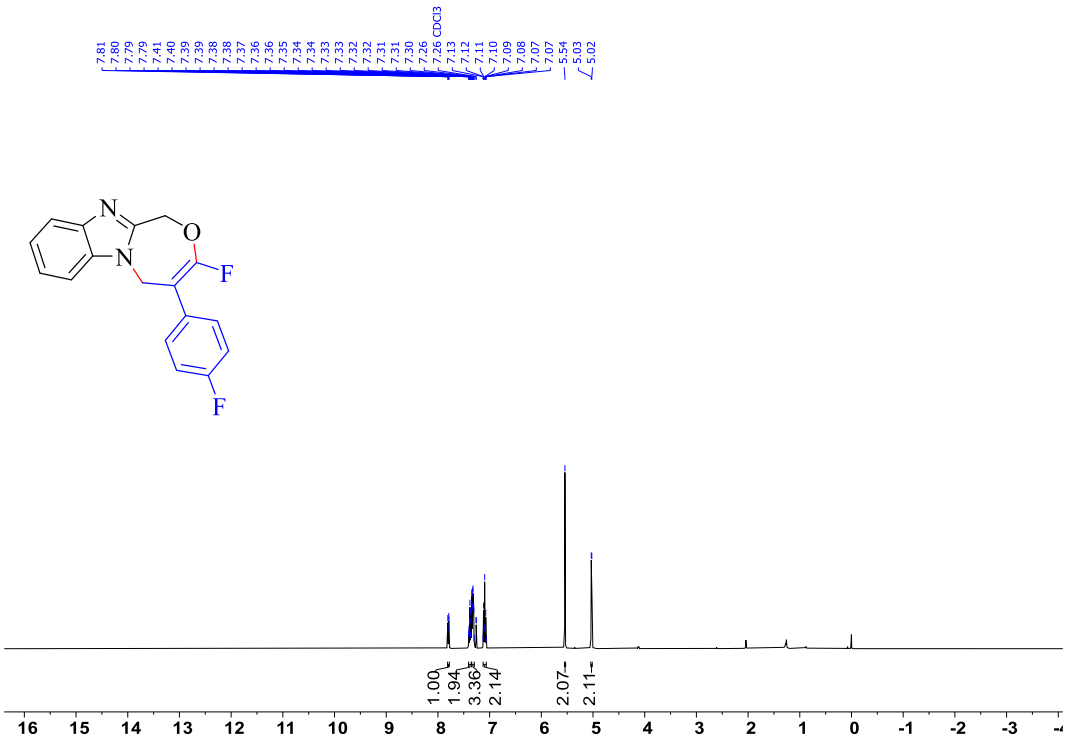
^{13}C NMR spectrum of product **5e** in $CDCl_3$ (151 MHz)



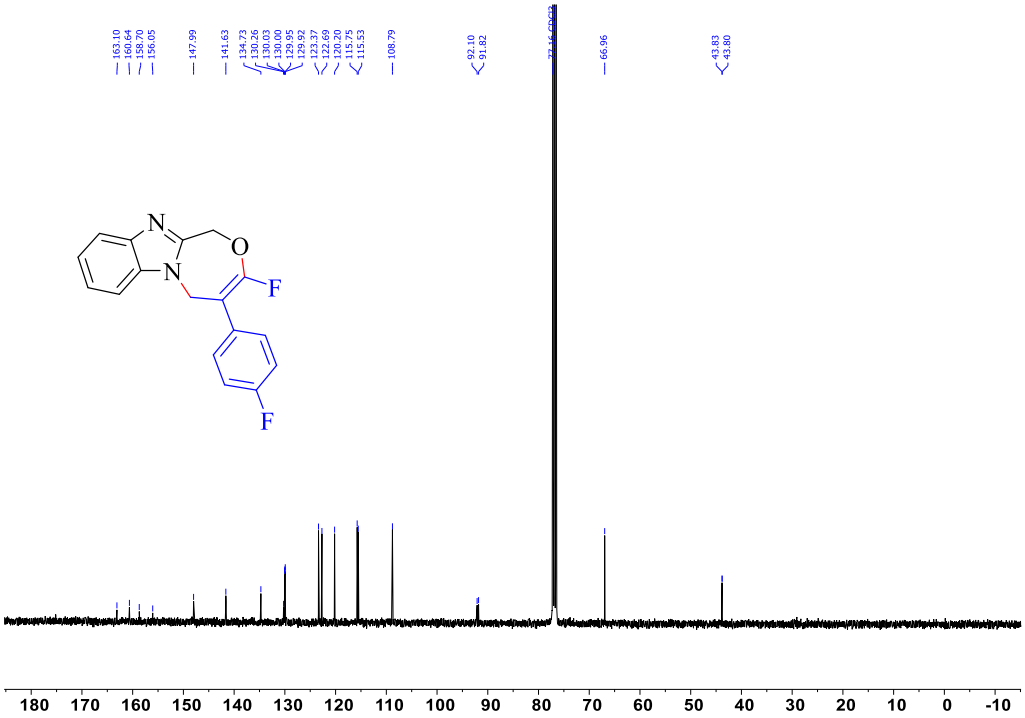
^{19}F-NMR spectrum of product **5e** in $CDCl_3$ (565 MHz)



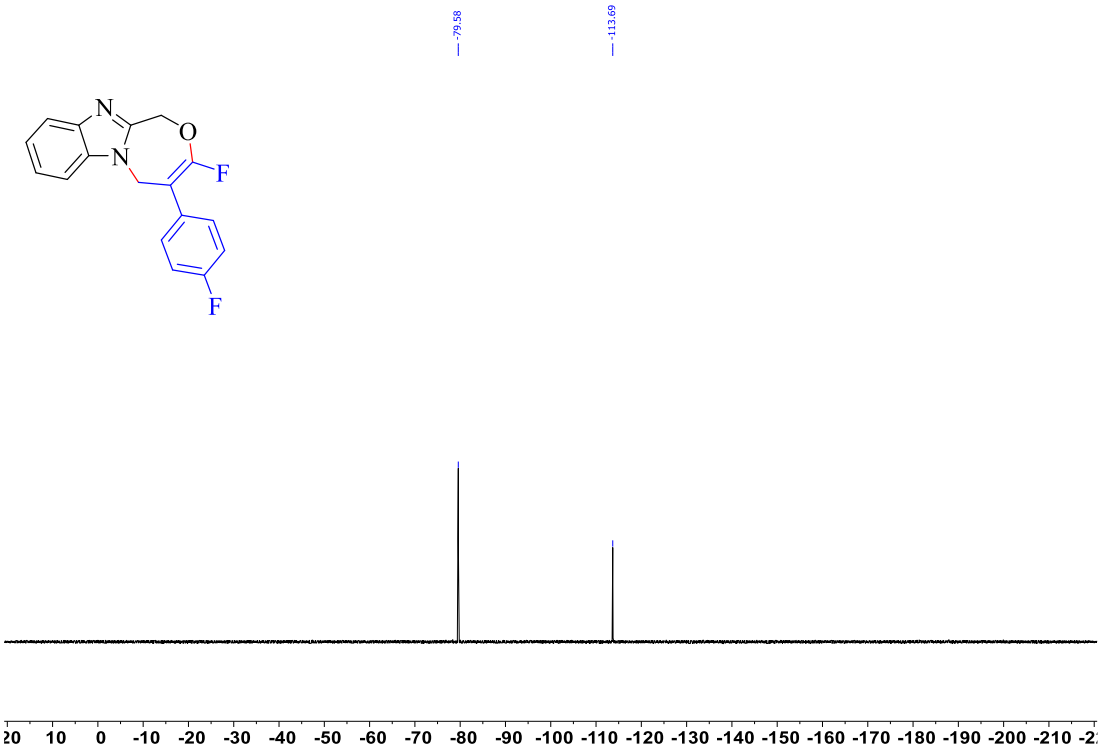
^{1}H NMR spectrum of product **5f** in $CDCl_3$ (400 MHz)



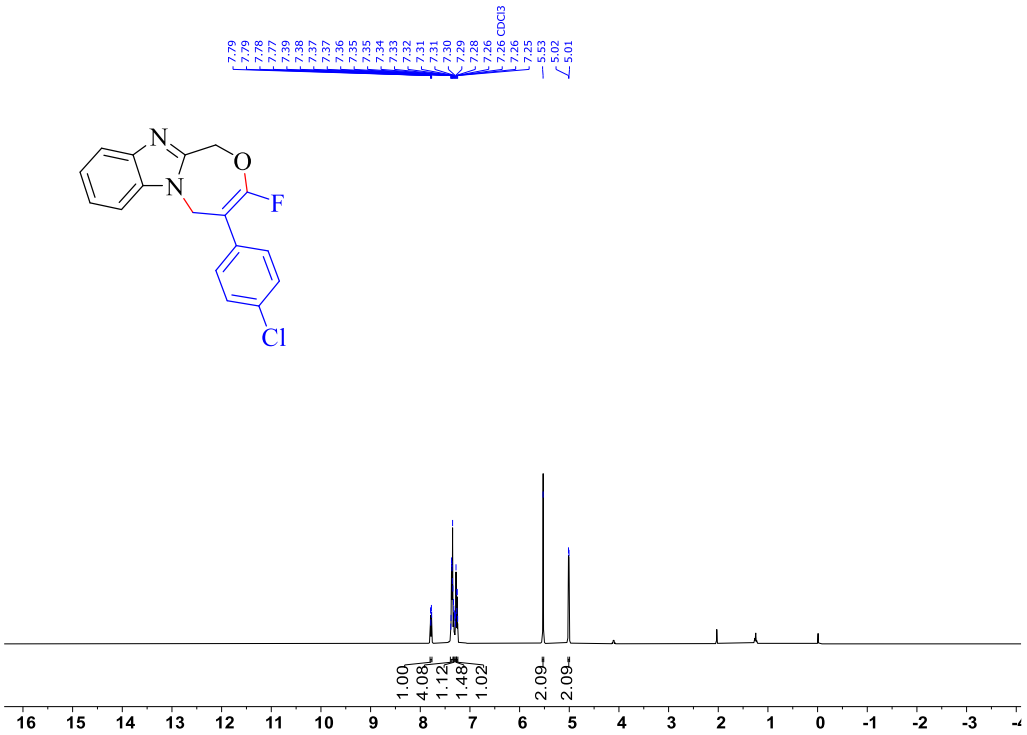
^{13}C NMR spectrum of product **5f** in $CDCl_3$ (101 MHz)



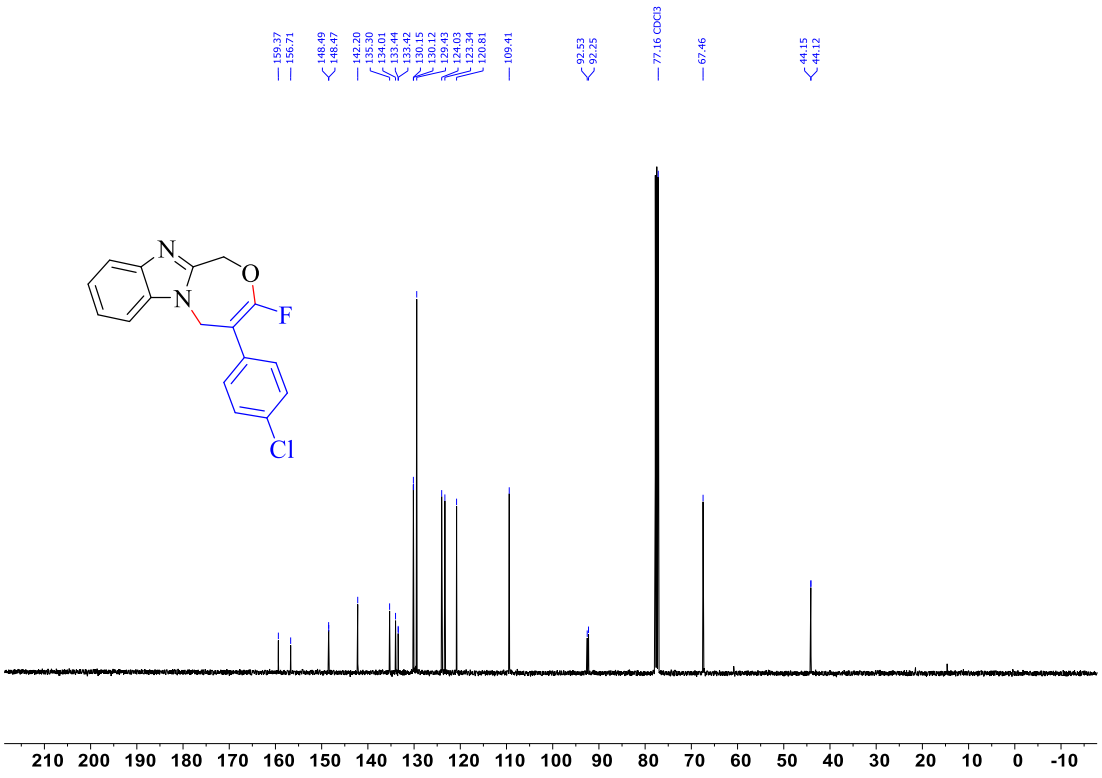
^{19}F-NMR spectrum of product **5f** in $CDCl_3$ (377 MHz)



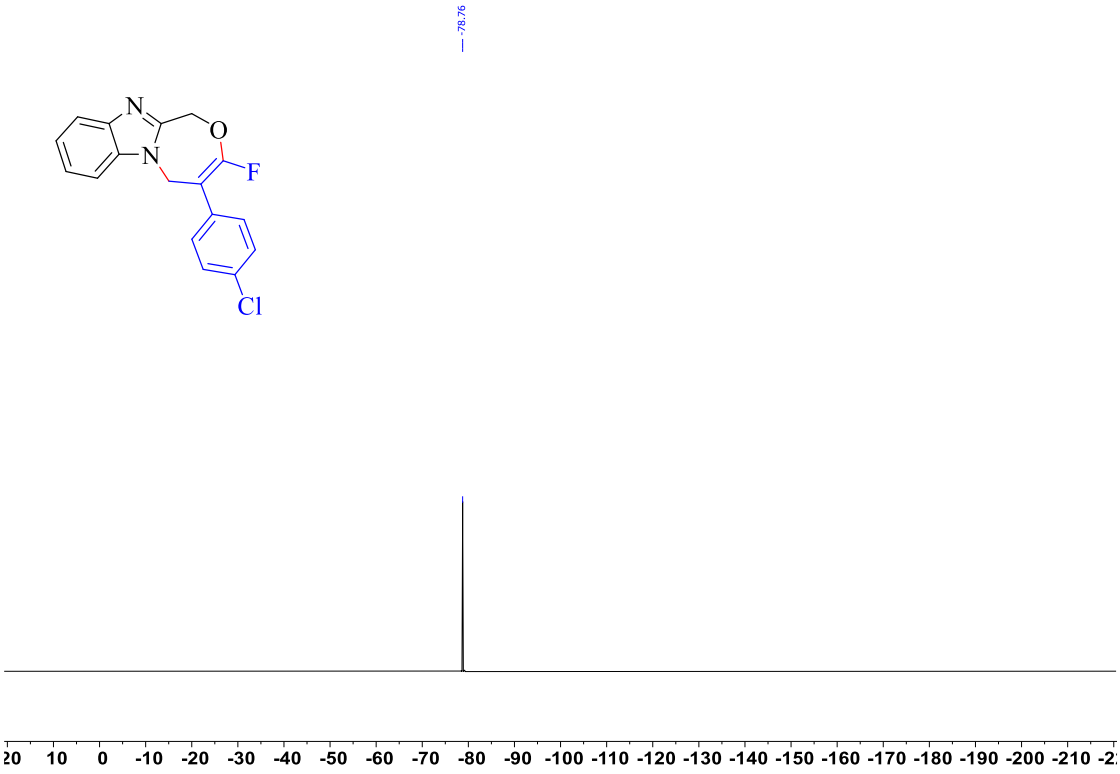
^{1}H NMR spectrum of product **5g** in $CDCl_3$ (400 MHz)



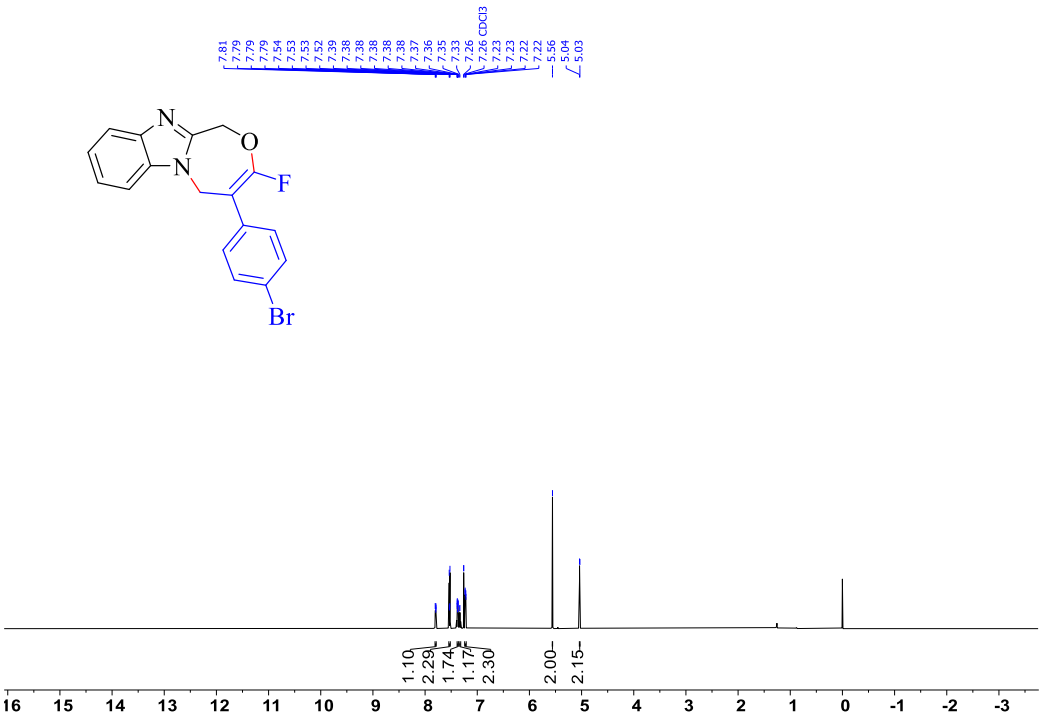
^{13}C NMR spectrum of product **5g** in $CDCl_3$ (101 MHz)



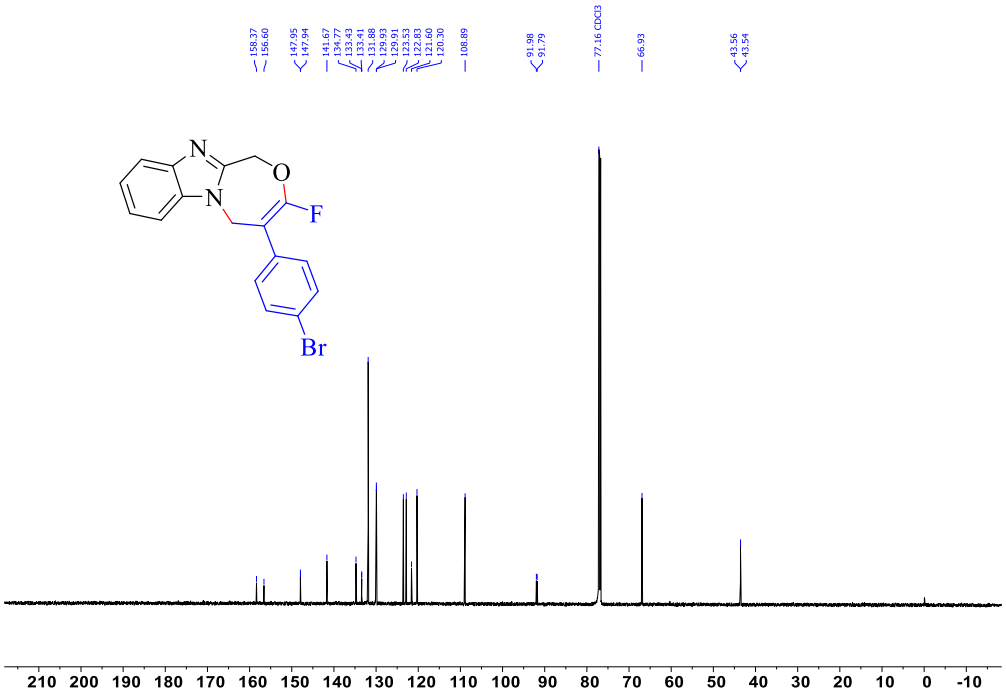
^{19}F-NMR spectrum of product **5g** in $CDCl_3$ (377 MHz)



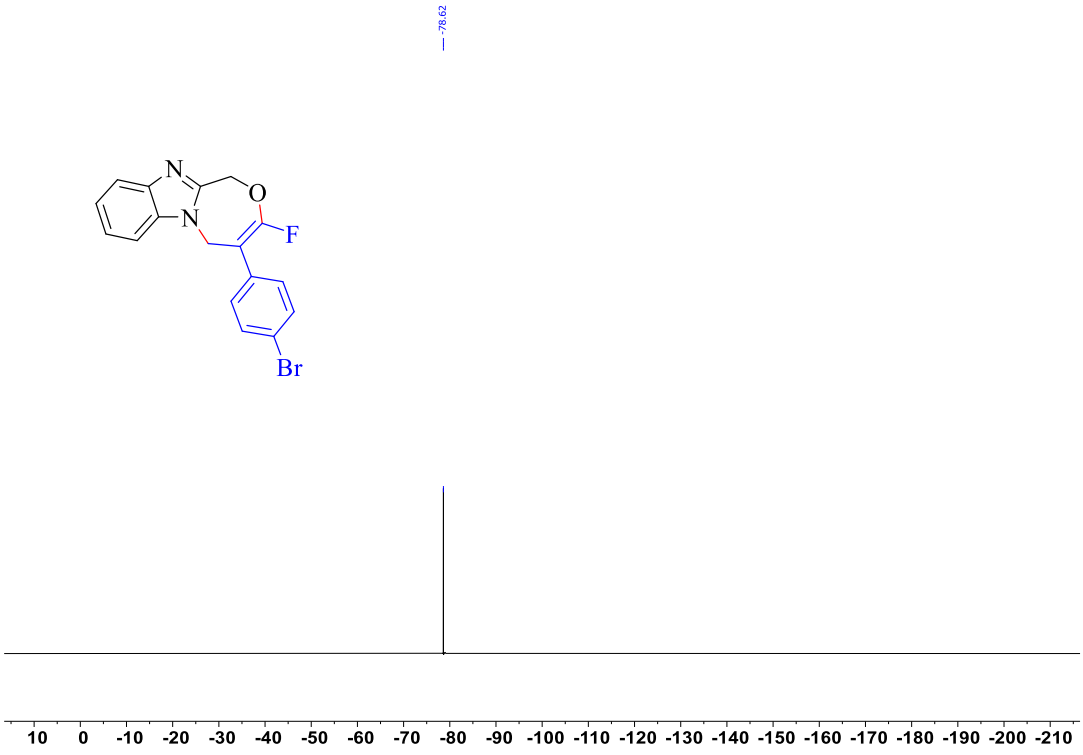
^{1}H NMR spectrum of product **5h** in $CDCl_3$ (600 MHz)



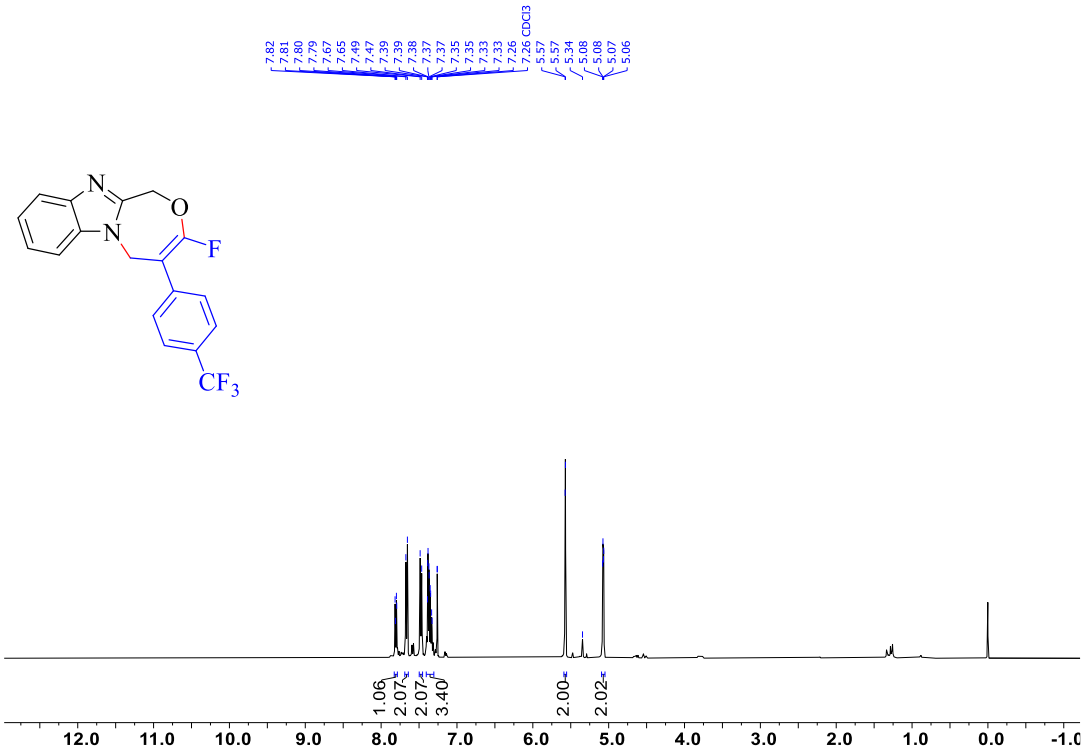
^{13}C NMR spectrum of product **5h** in $CDCl_3$ (151 MHz)



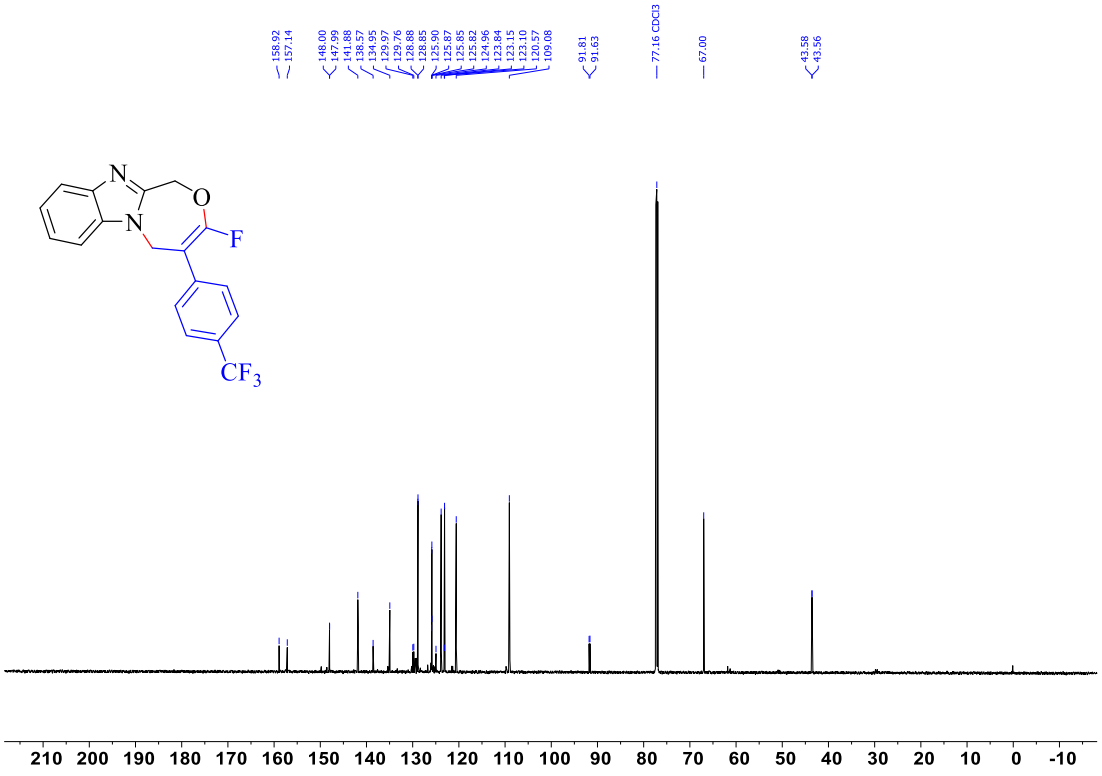
^{19}F-NMR spectrum of product **5h** in $CDCl_3$ (565 MHz)



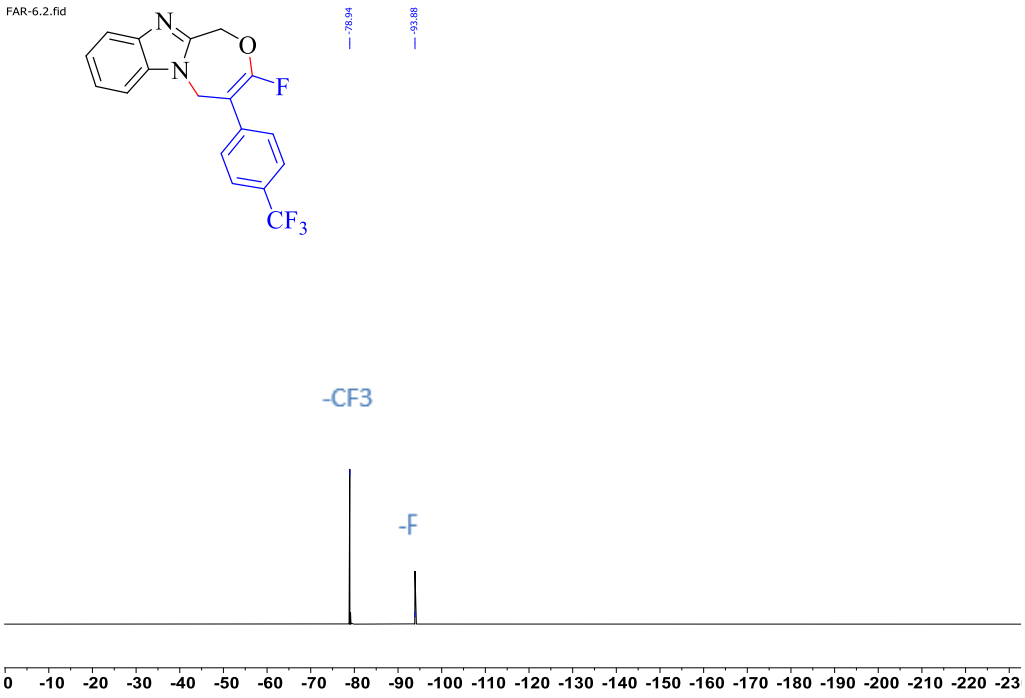
^{1}H NMR spectrum of product **5i** in $CDCl_3$ (400 MHz)



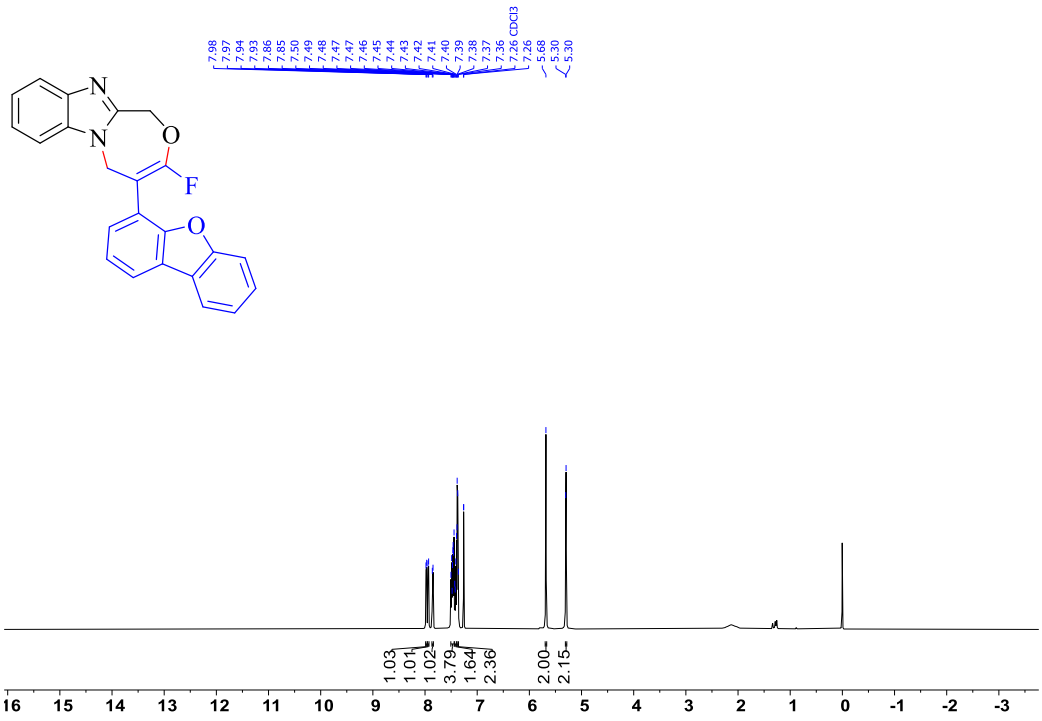
^{13}C NMR spectrum of product **5i** in $CDCl_3$ (151 MHz)



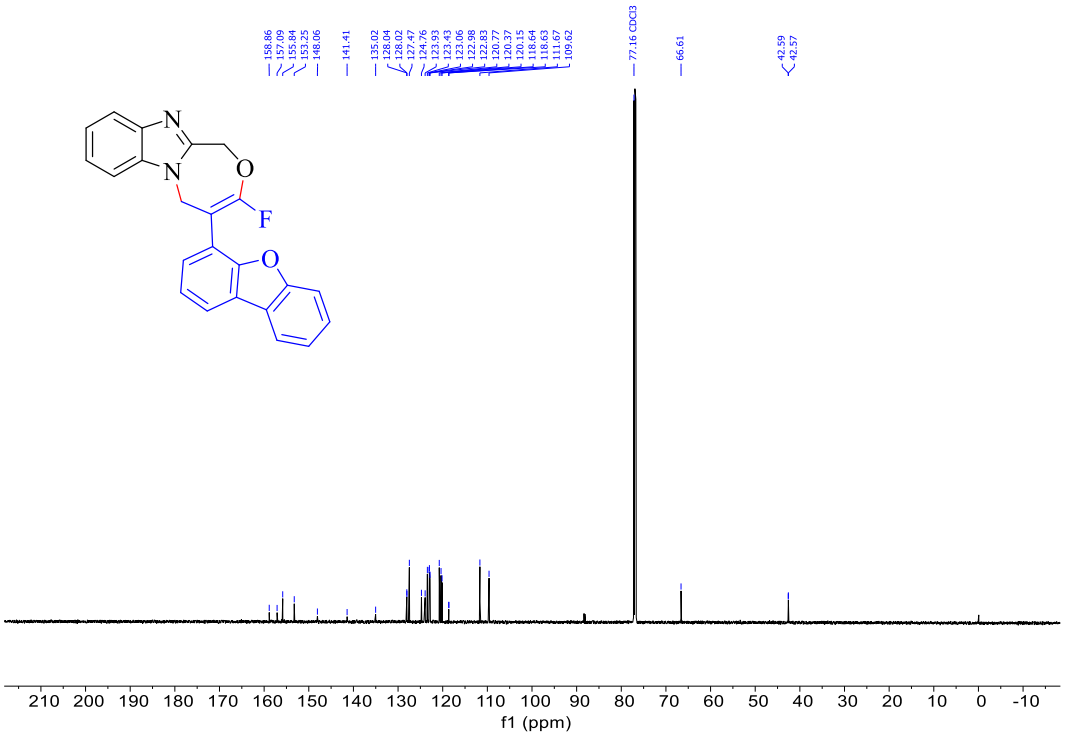
^{19}F-NMR spectrum of product **5i** in $CDCl_3$ (565 MHz)



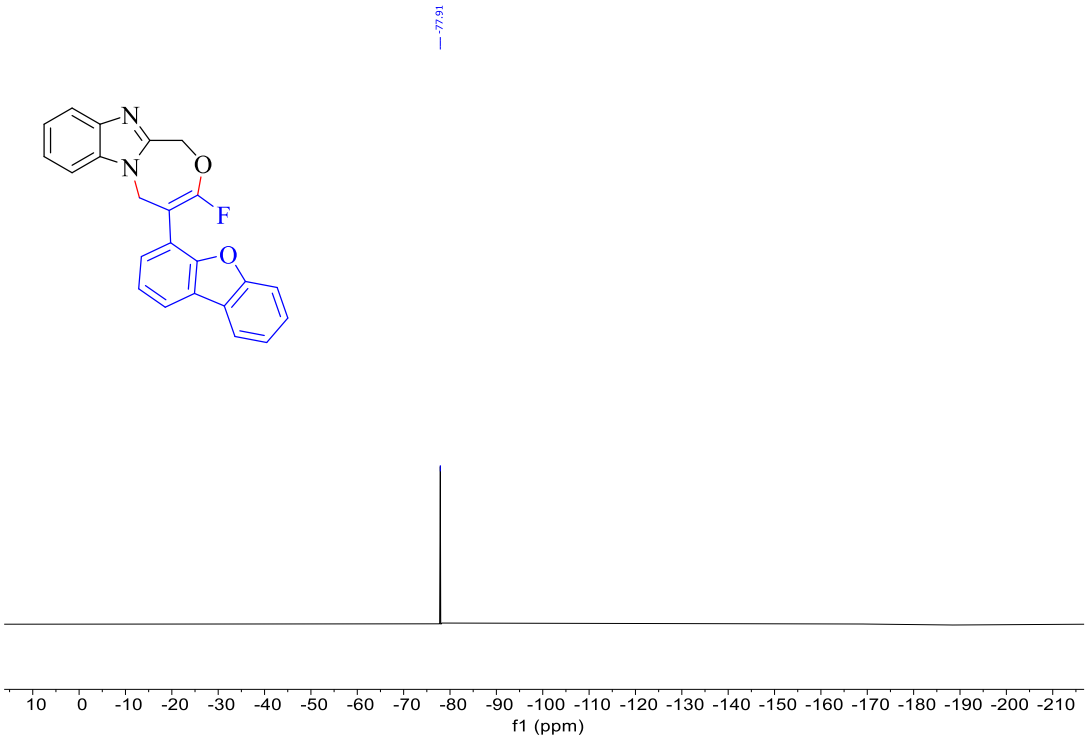
^{1}H NMR spectrum of product **5j** in $CDCl_3$ (600 MHz)



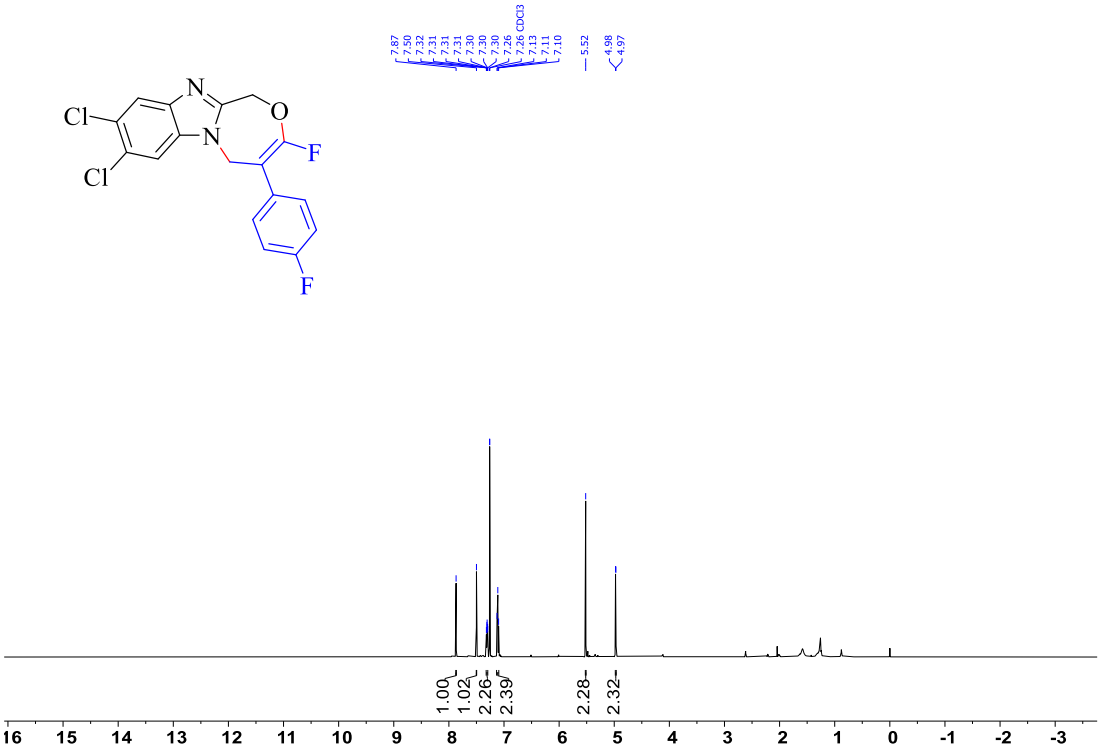
^{13}C NMR spectrum of product **5j** in $CDCl_3$ (151 MHz)



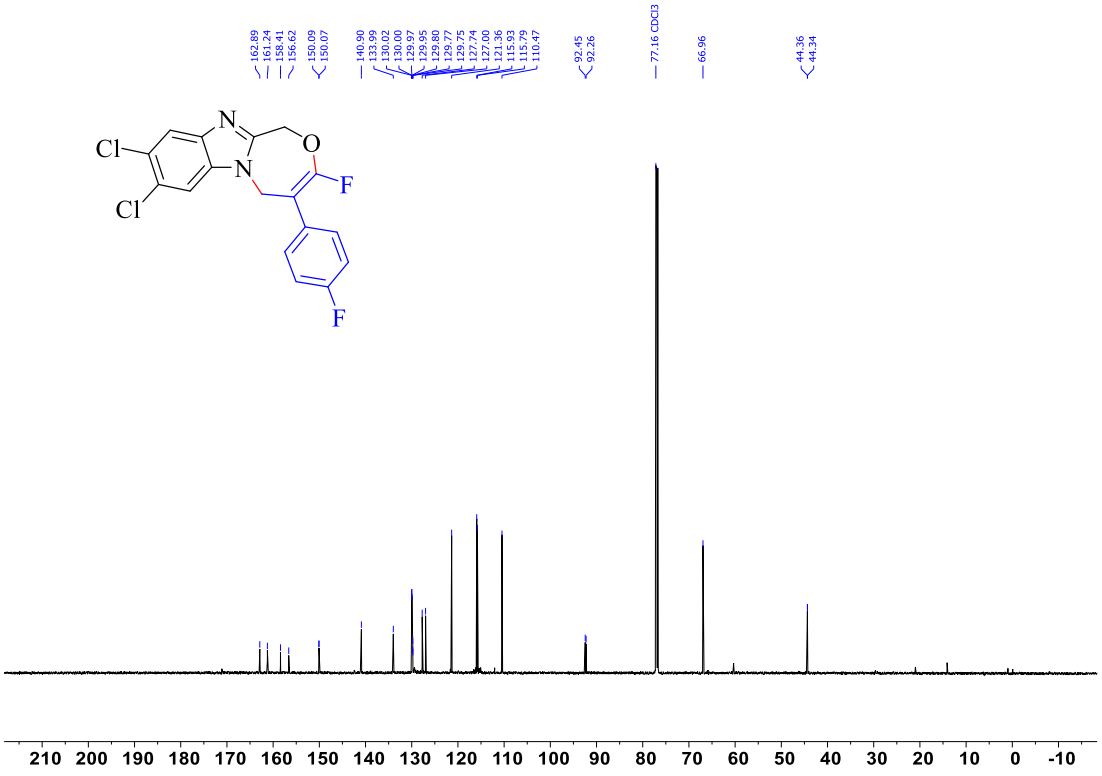
^{19}F-NMR spectrum of product **5j** in $CDCl_3$ (565 MHz)



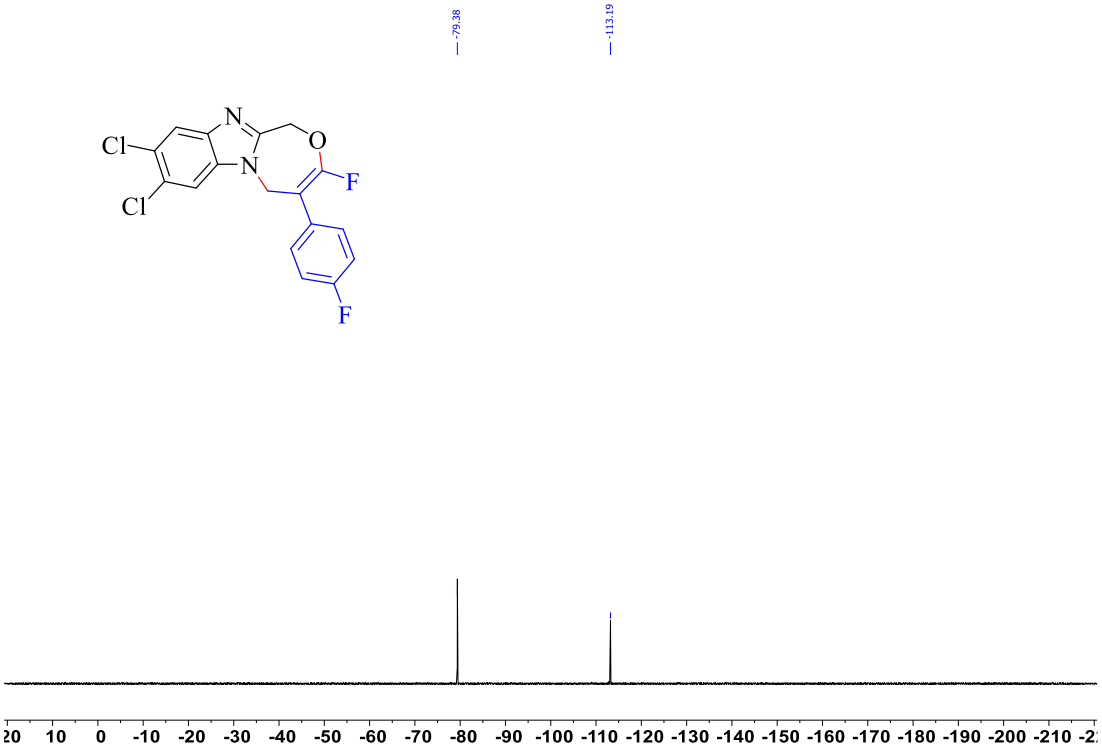
^{1}H NMR spectrum of product **5k** in $CDCl_3$ (600 MHz)



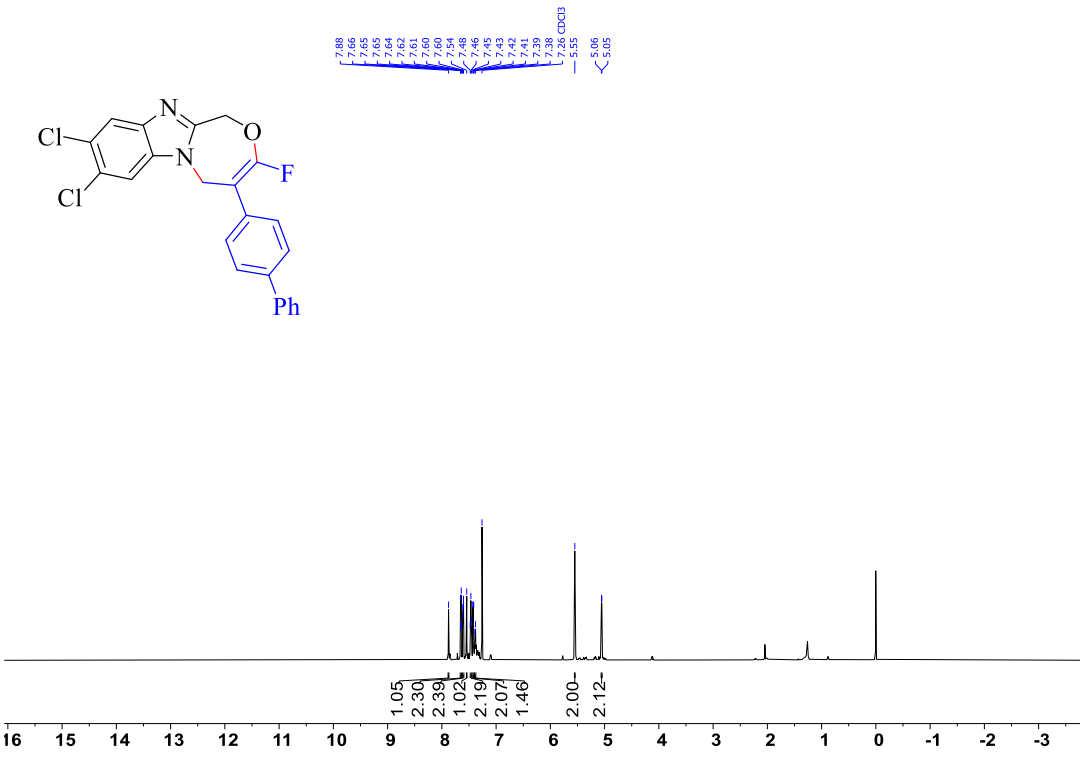
^{13}C NMR spectrum of product **5k** in $CDCl_3$ (151 MHz)



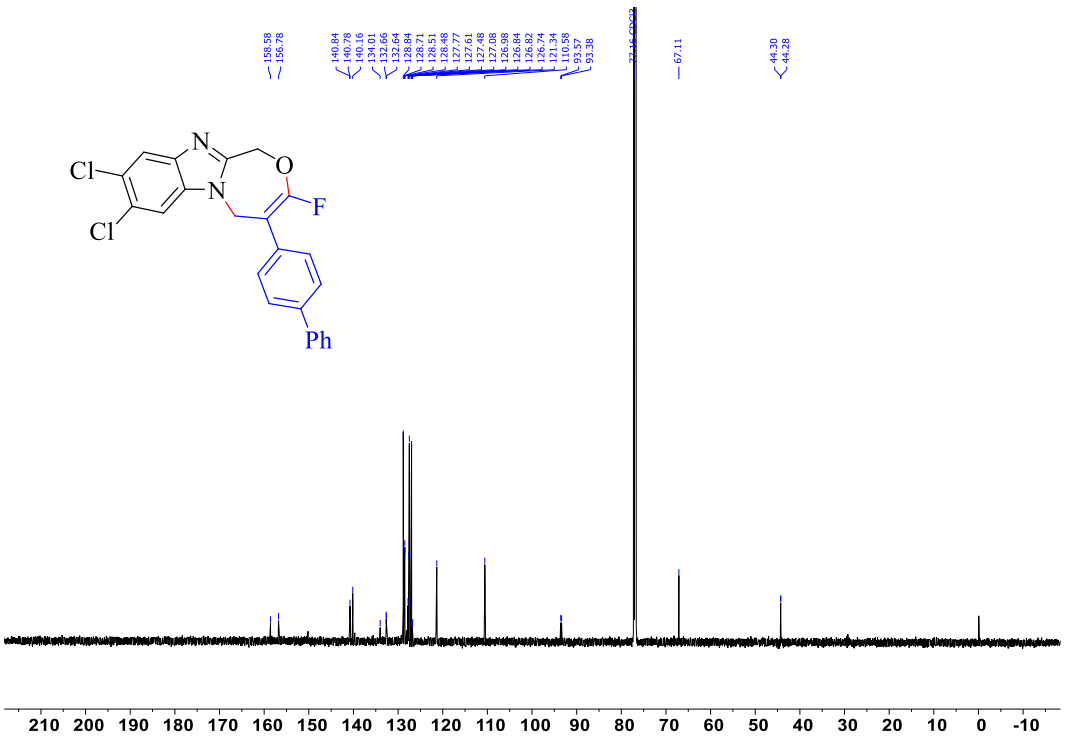
^{19}F-NMR spectrum of product **5k** in $CDCl_3$ (377 MHz)



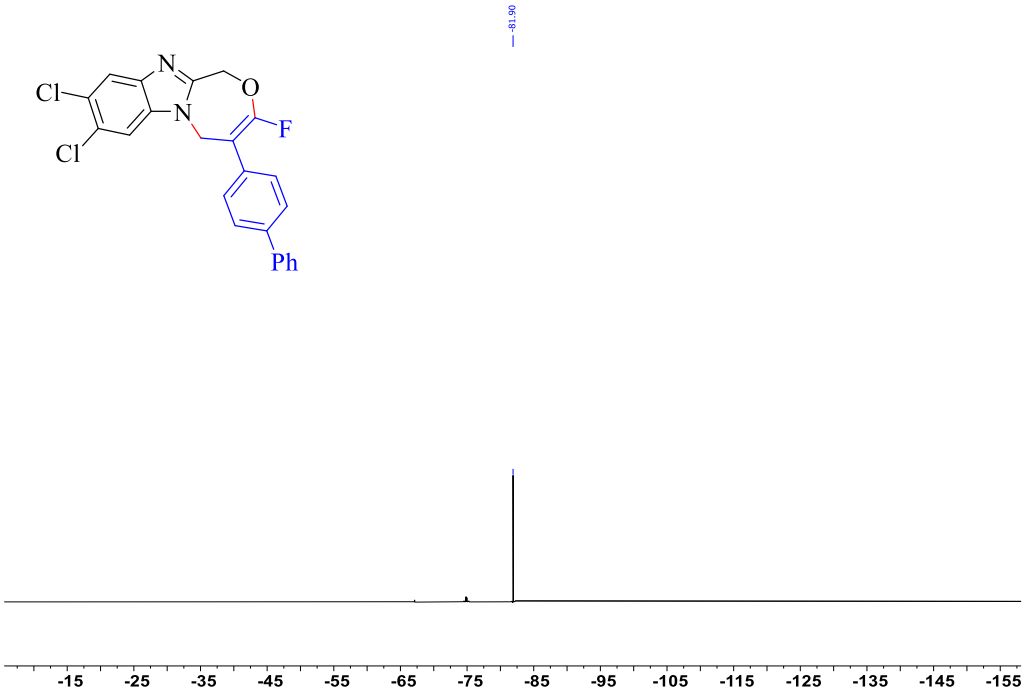
^{1}H NMR spectrum of product **5l** in $CDCl_3$ (600 MHz)



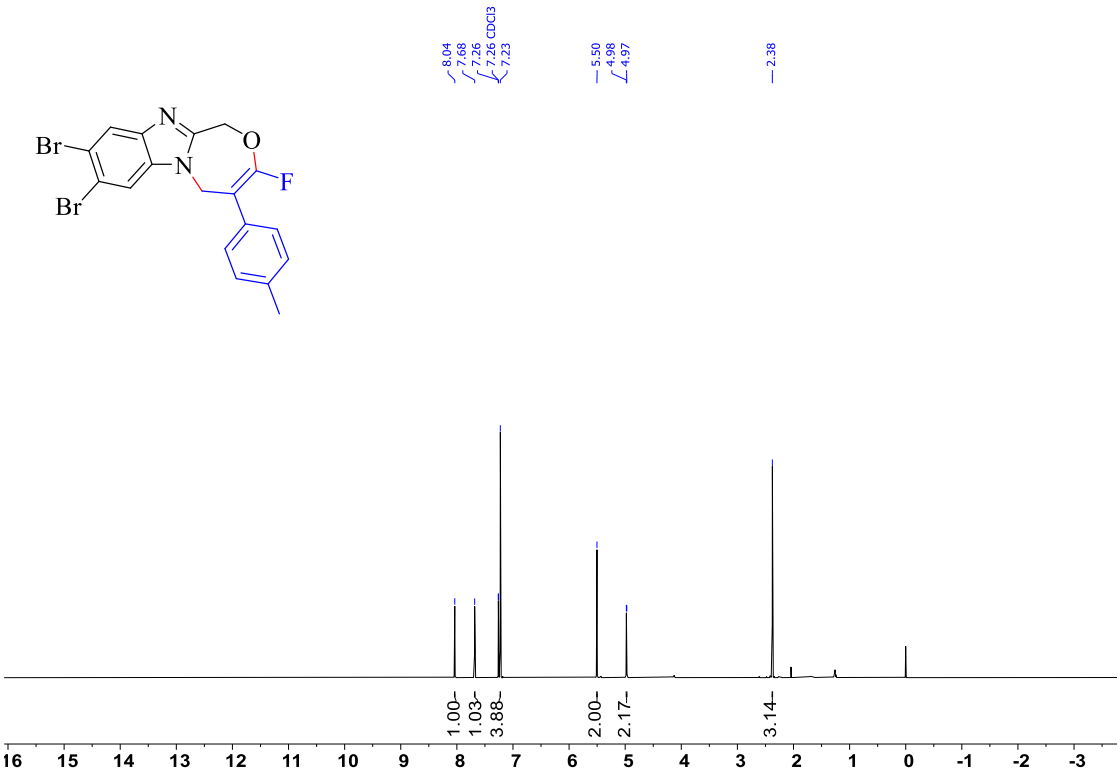
^{13}C NMR spectrum of product **5l** in $CDCl_3$ (151 MHz)



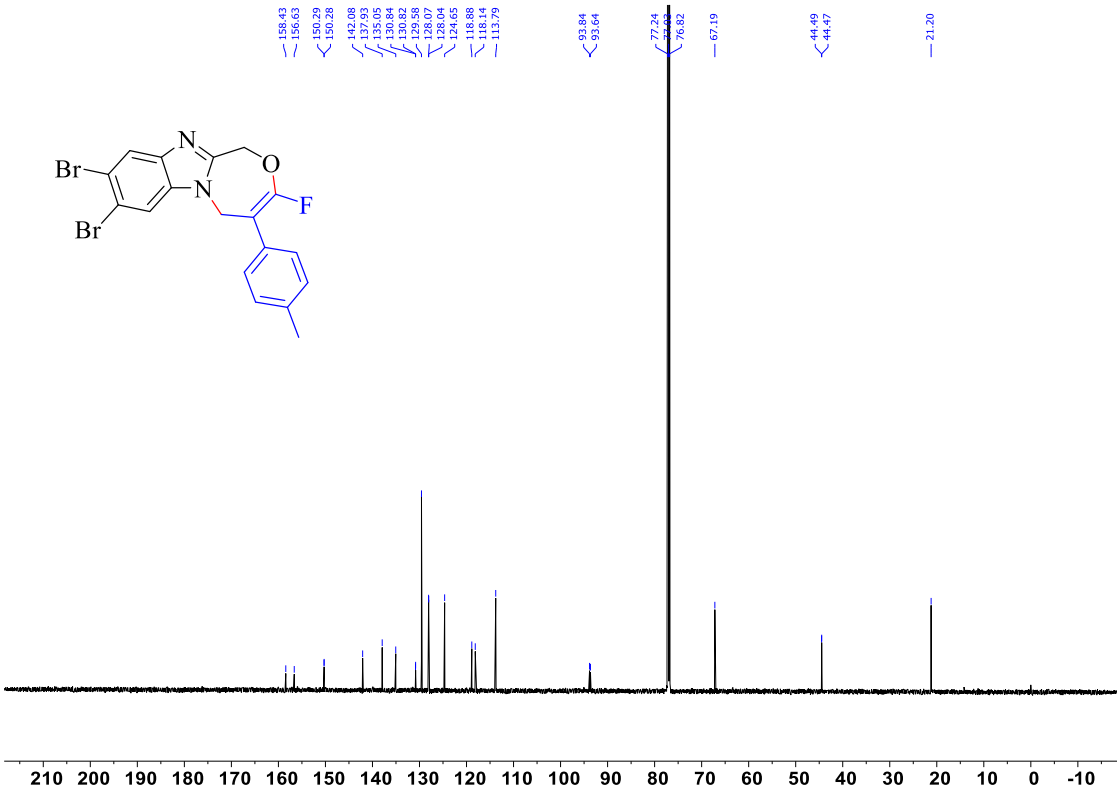
^{19}F-NMR spectrum of product **5l** in $CDCl_3$ (565 MHz)



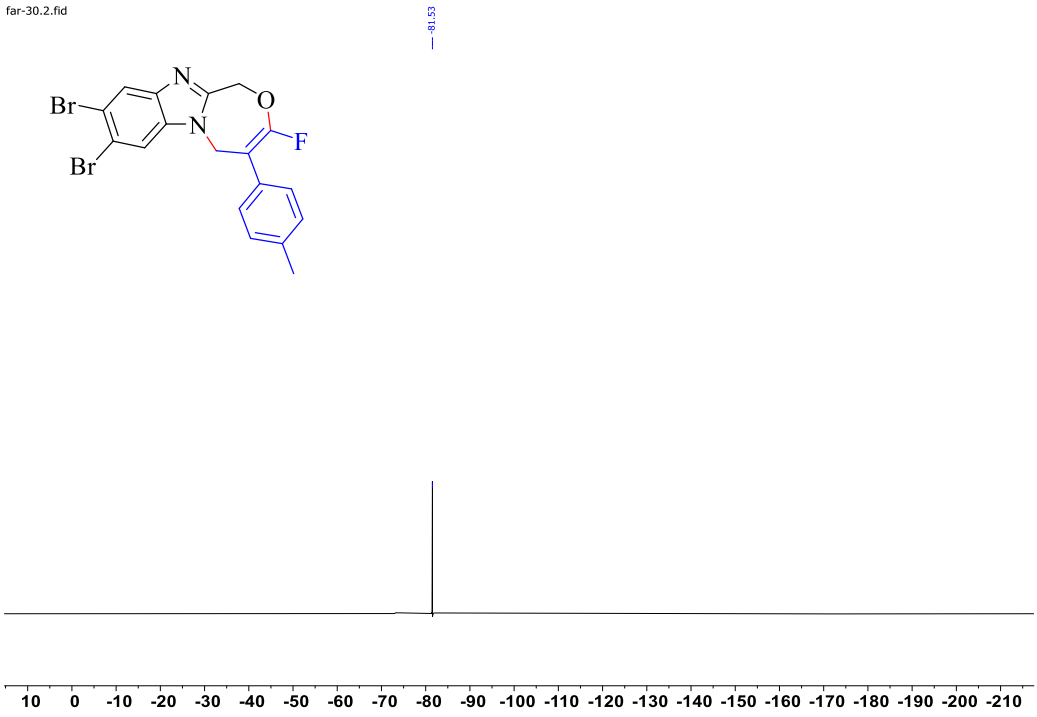
^{1}H NMR spectrum of product **5m** in $CDCl_3$ (600 MHz)



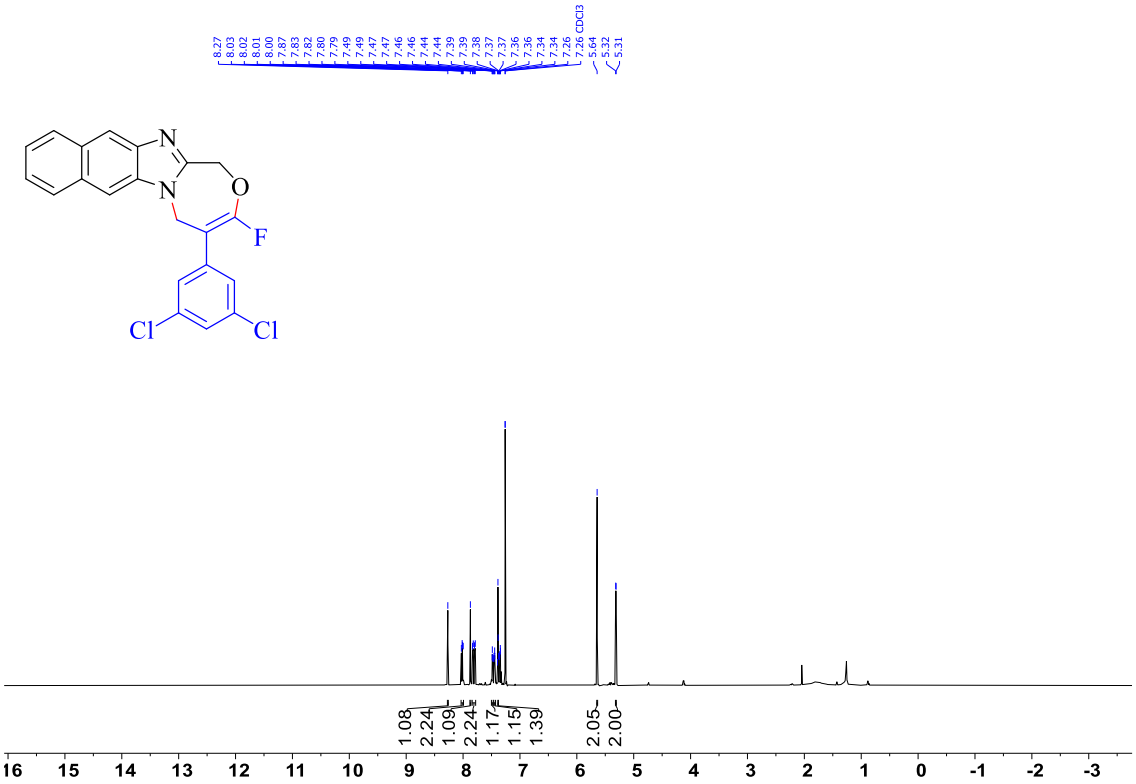
^{13}C NMR spectrum of product **5m** in $CDCl_3$ (151 MHz)



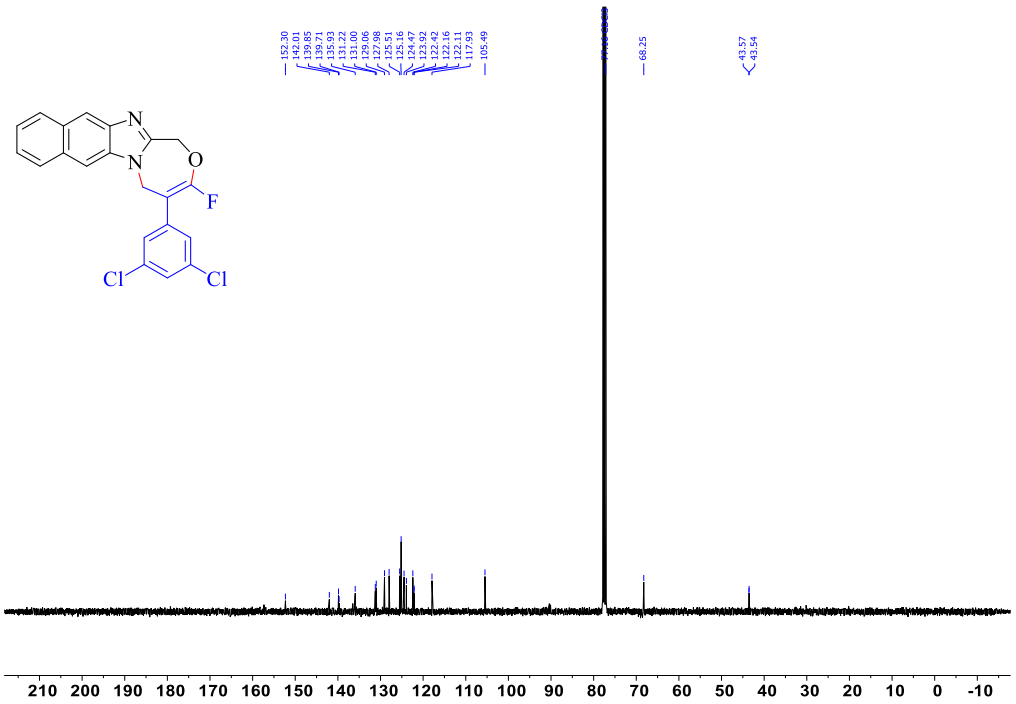
^{19}F-NMR spectrum of product **5m** in $CDCl_3$ (565 MHz)



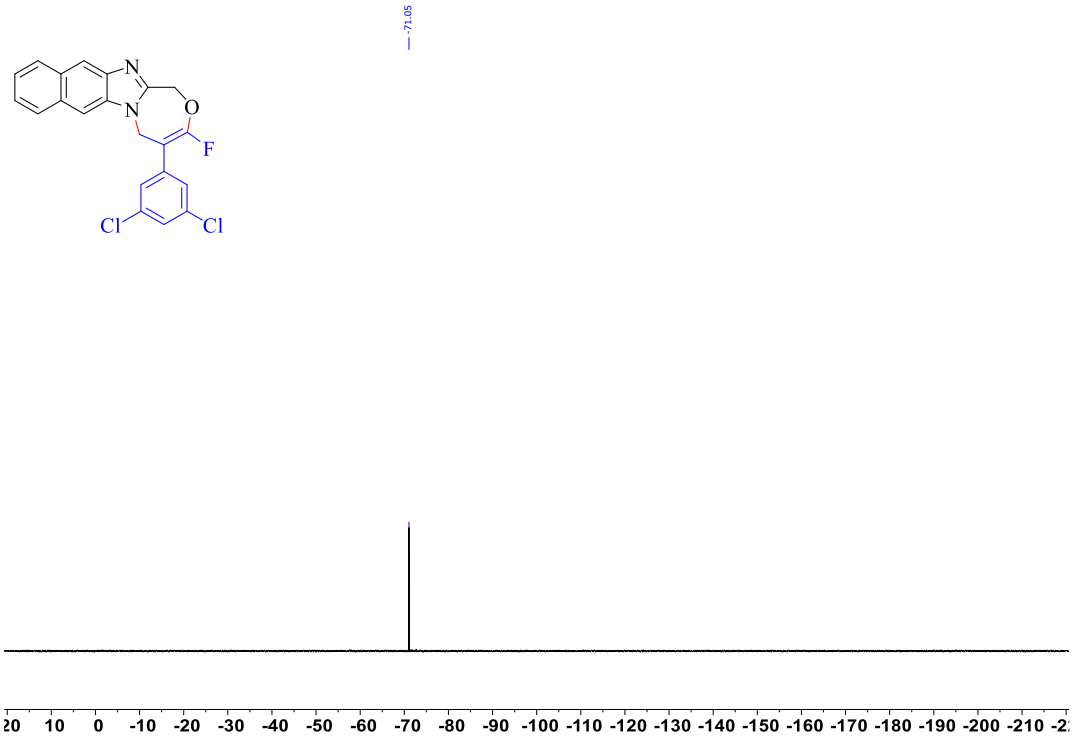
^{1}H NMR spectrum of product **5n** in $CDCl_3$ (600 MHz)



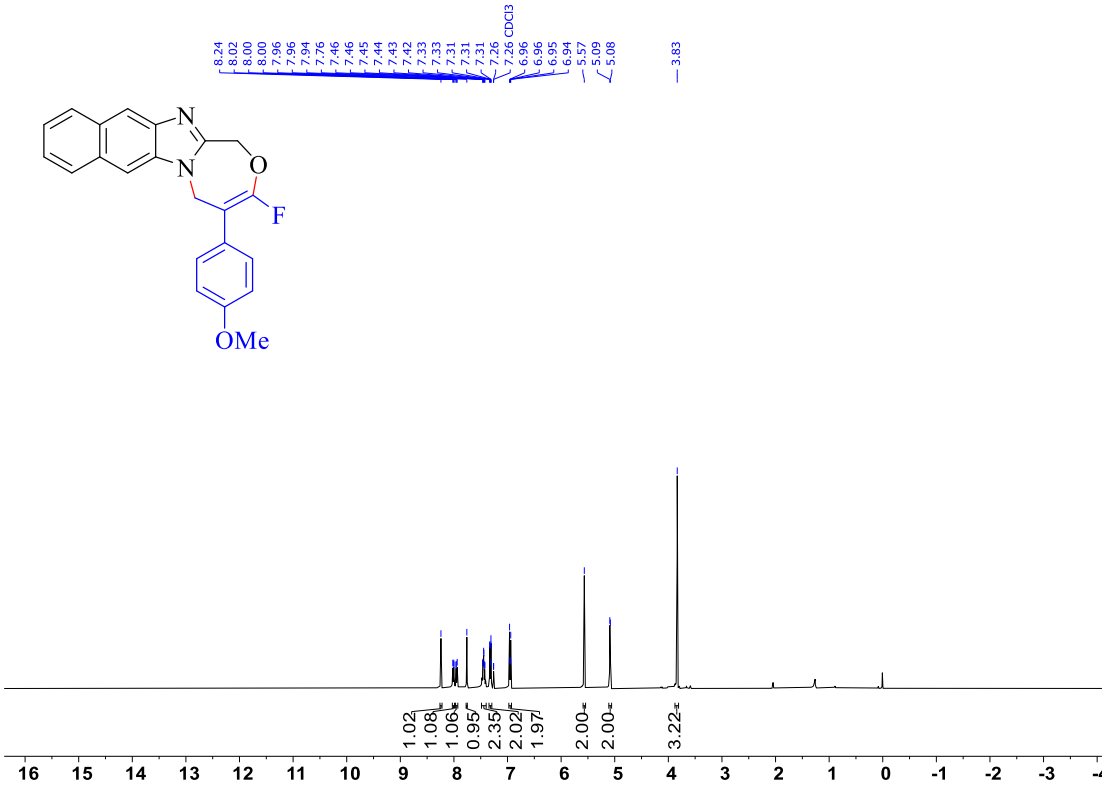
^{13}C NMR spectrum of product **5n** in $CDCl_3$ (101 MHz)



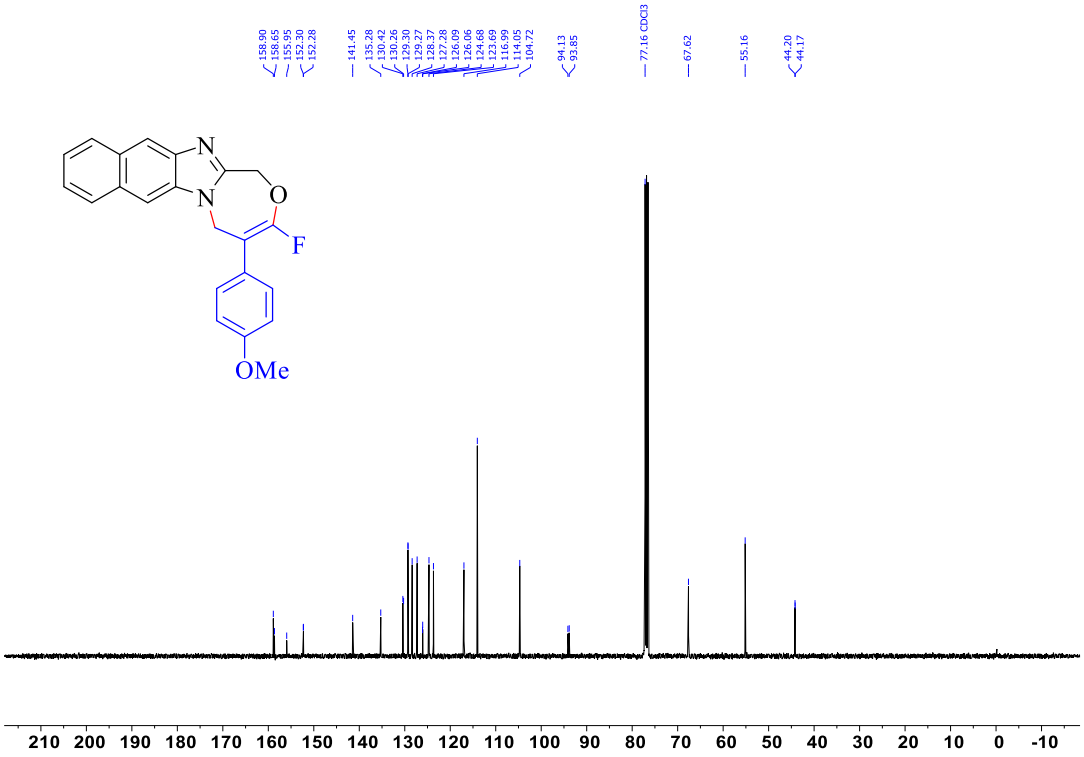
^{19}F-NMR spectrum of product **5n** in $CDCl_3$ (377 MHz)



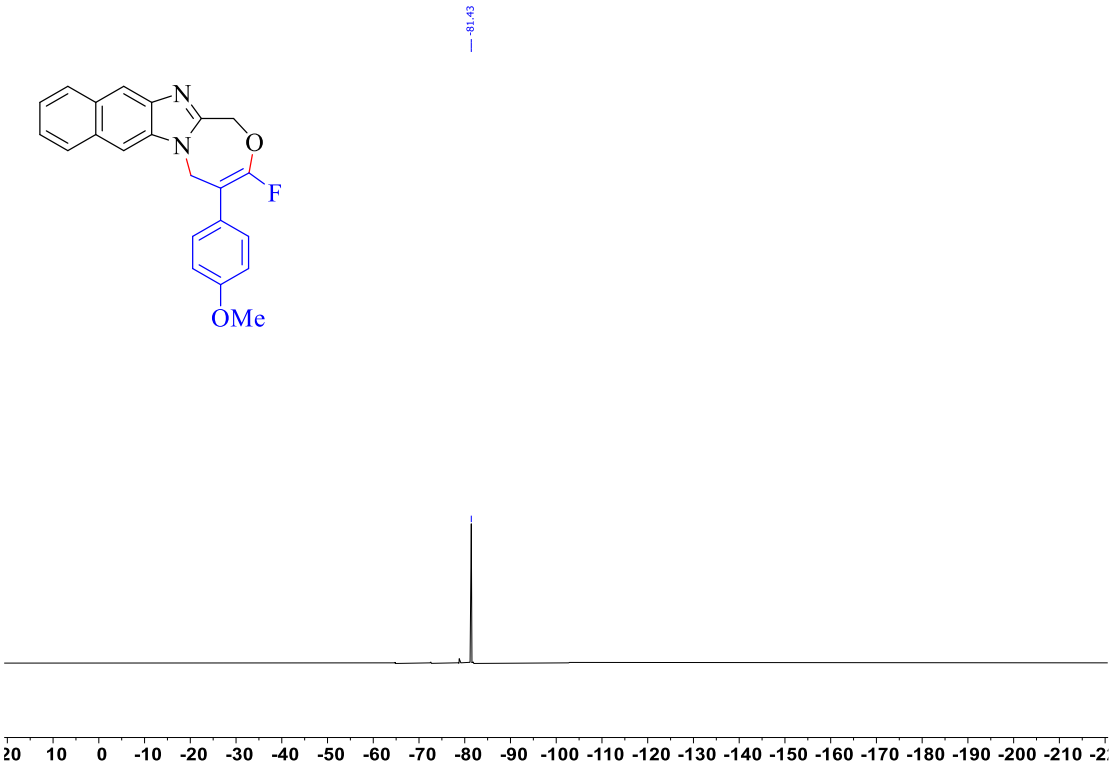
^{1}H NMR spectrum of product **5o** in $CDCl_3$ (400 MHz)



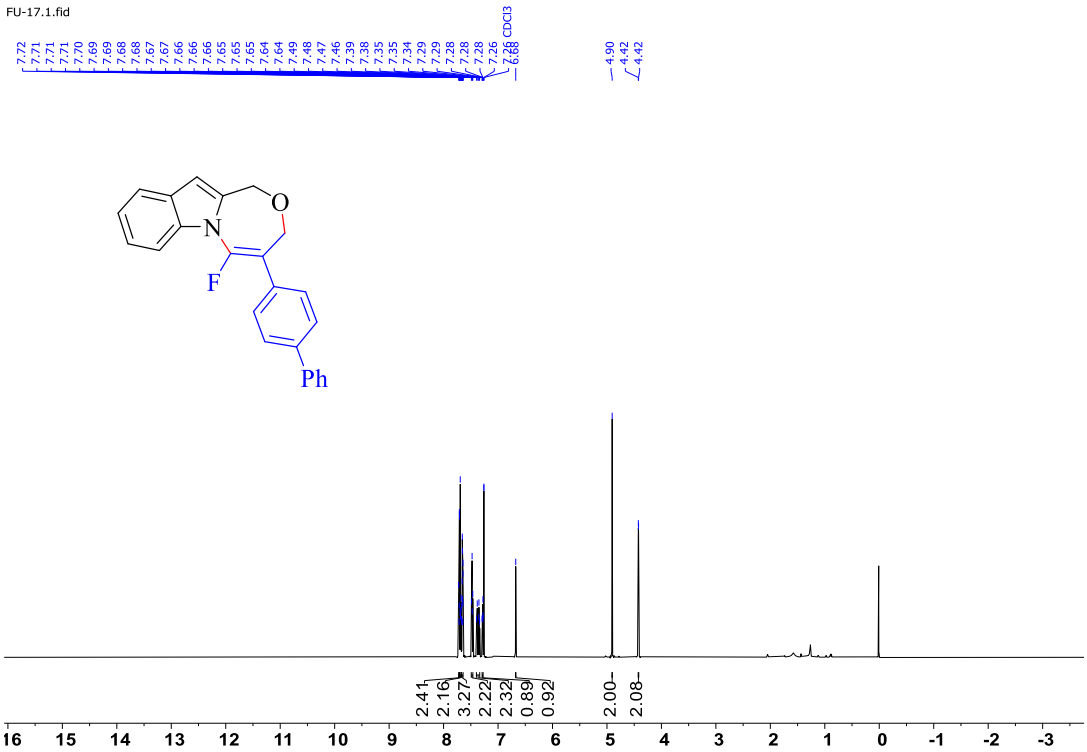
^{13}C NMR spectrum of product **5o** in $CDCl_3$ (101 MHz)



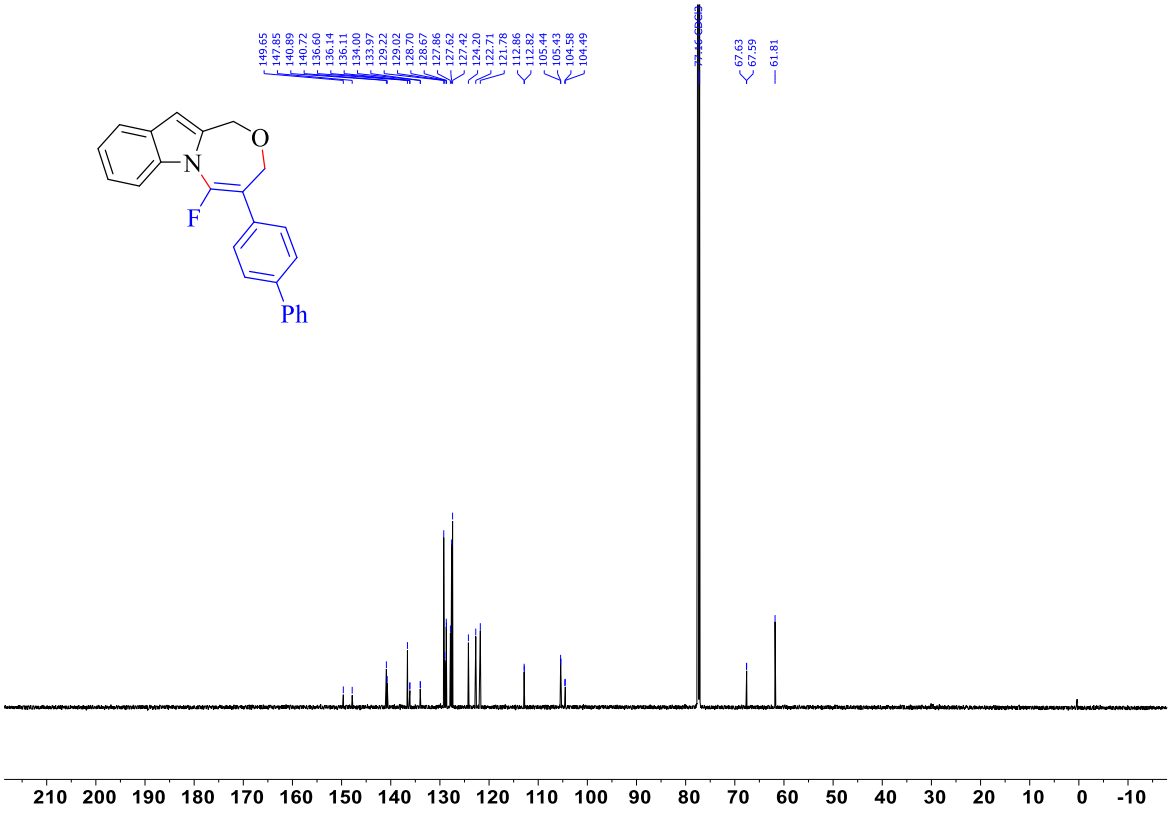
^{19}F-NMR spectrum of product **5o** in $CDCl_3$ (377 MHz)



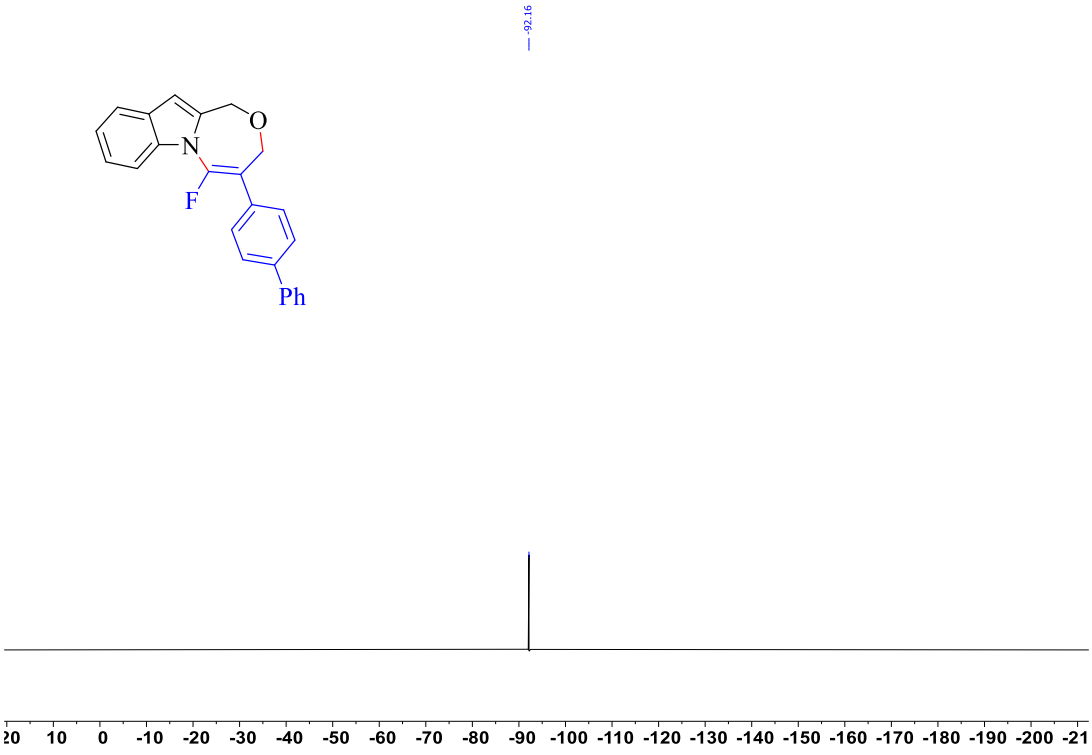
^{1}H NMR spectrum of product **7a** in $CDCl_3$ (600 MHz)



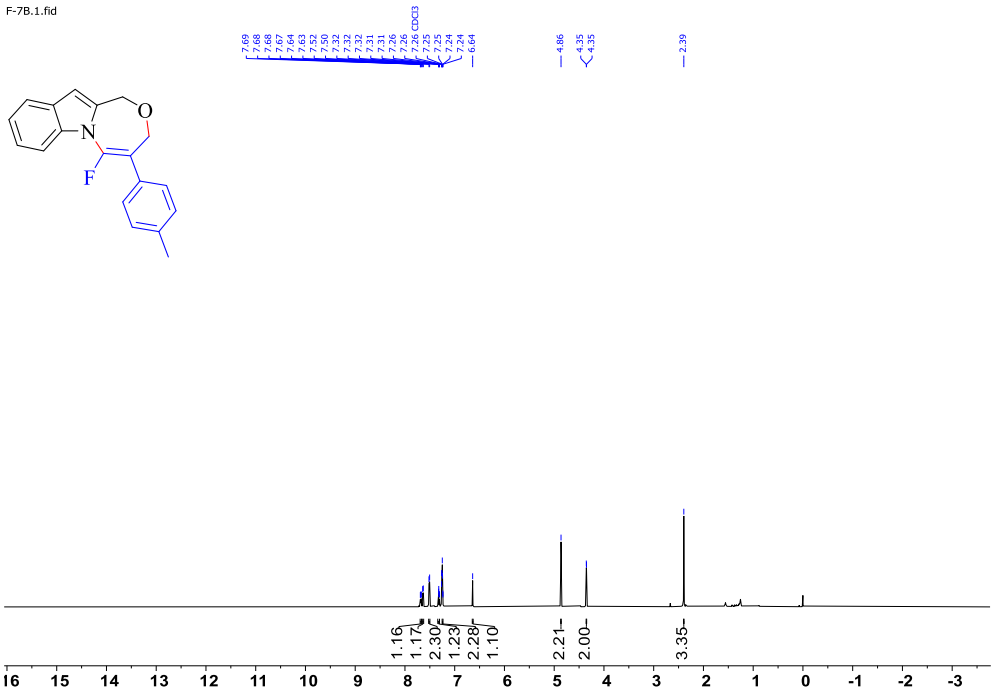
^{13}C NMR spectrum of product **7a** in $CDCl_3$ (151 MHz)



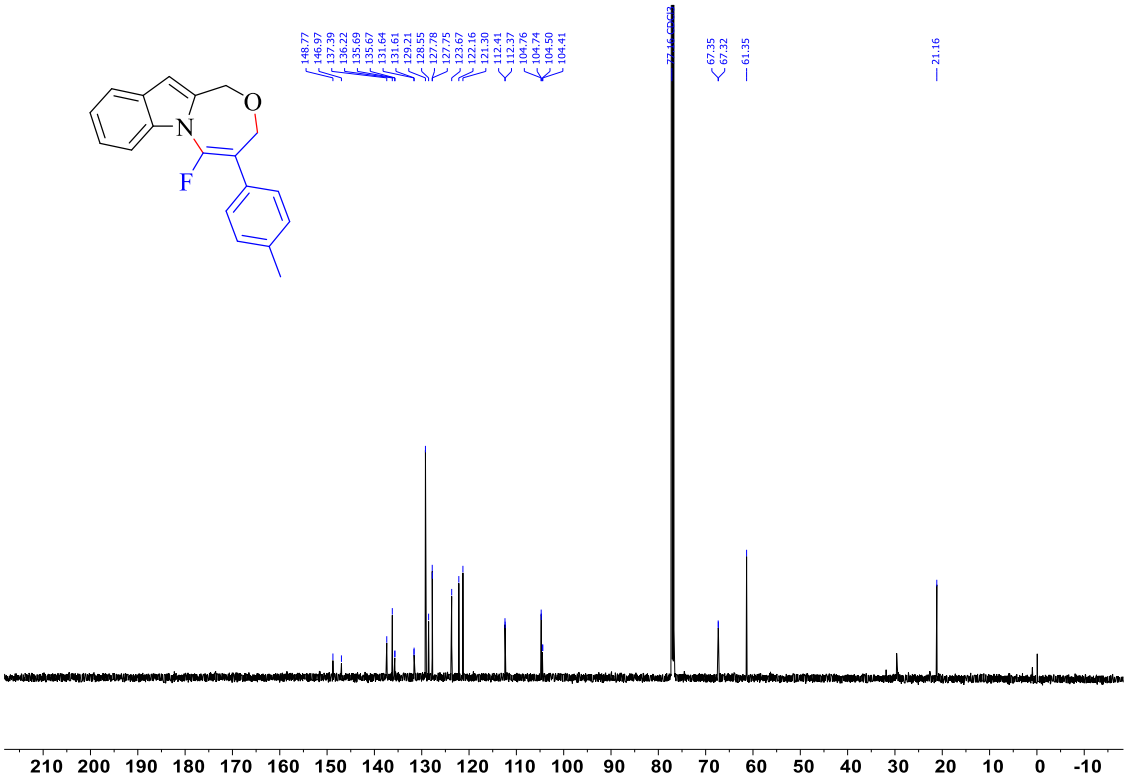
^{19}F-NMR spectrum of product **7a** in $CDCl_3$ (565 MHz)



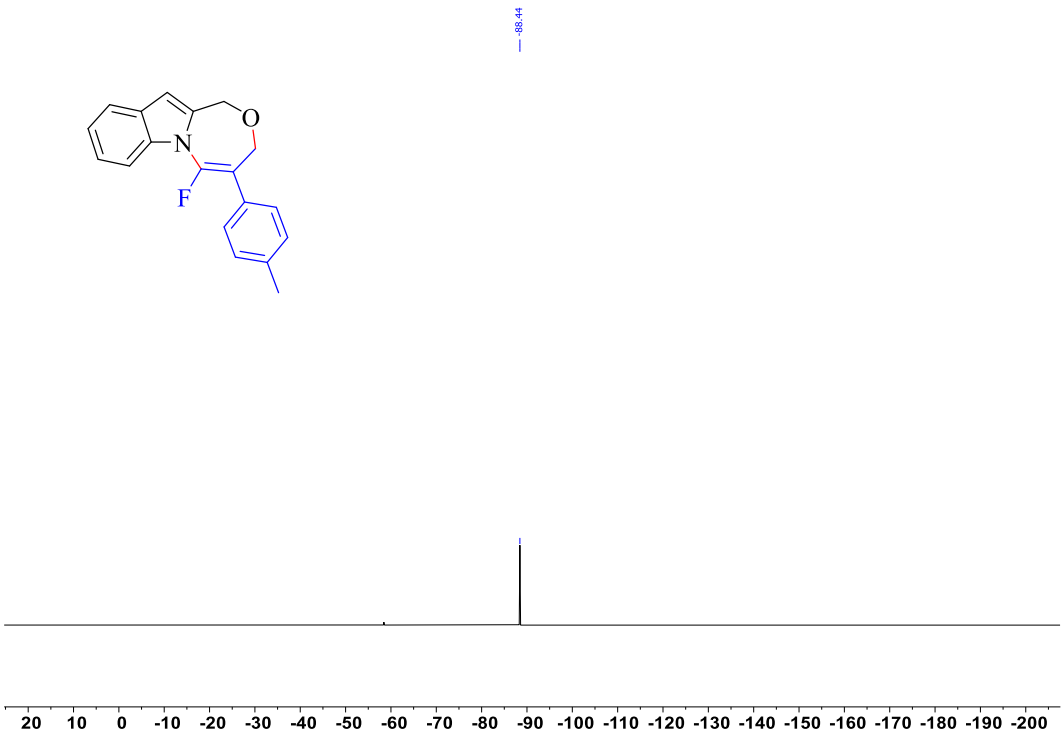
^{1}H NMR spectrum of product **7b** in $CDCl_3$ (600 MHz)



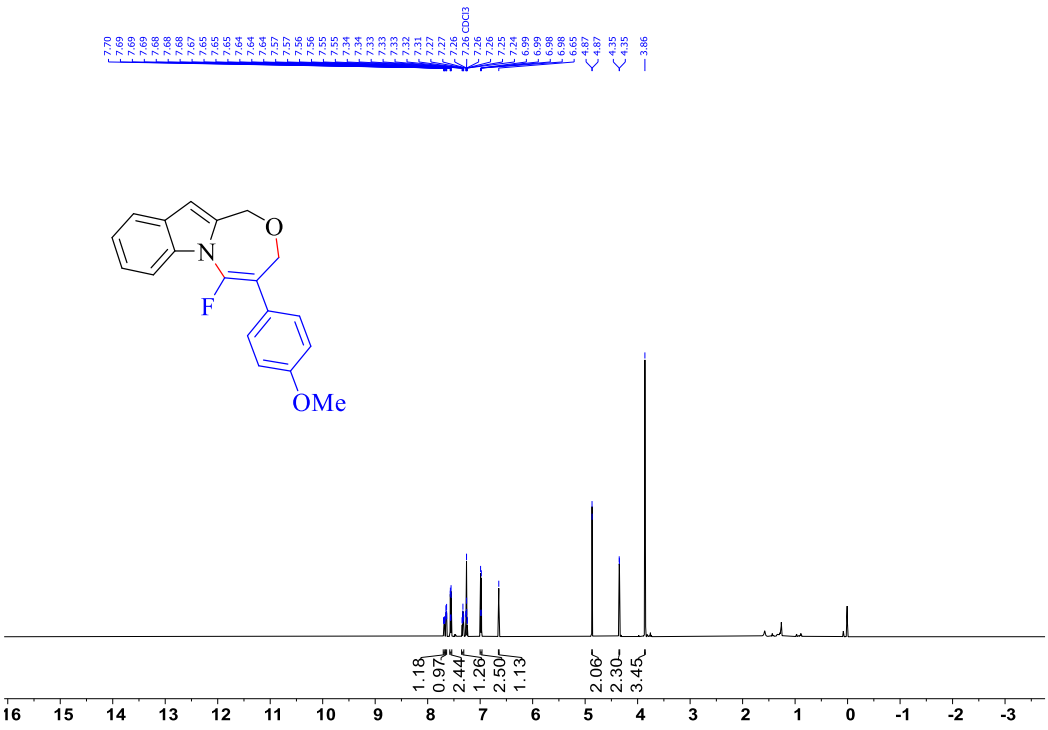
^{13}C NMR spectrum of product **7b** in $CDCl_3$ (151 MHz)



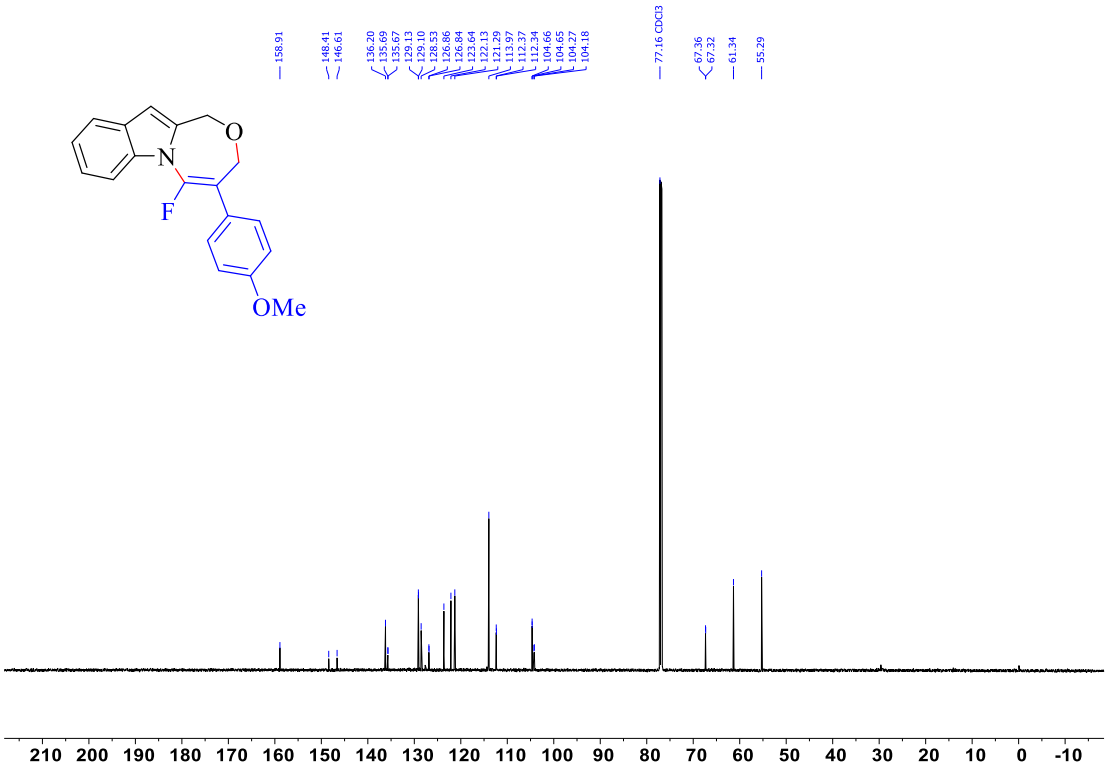
^{19}F-NMR spectrum of product **7b** in $CDCl_3$ (565 MHz)



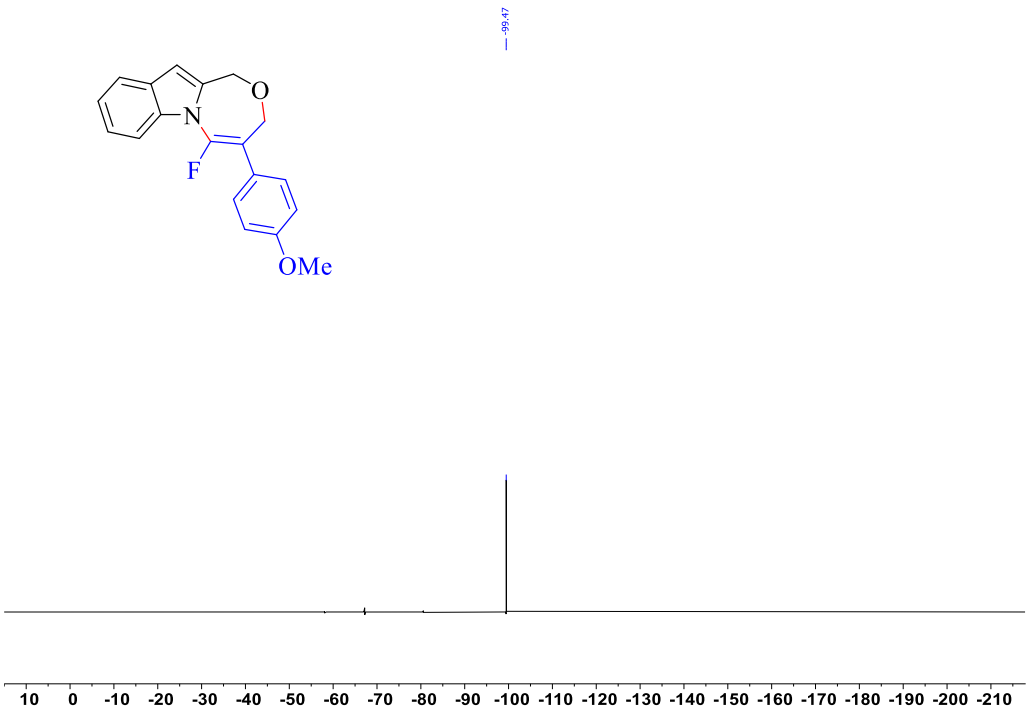
^{1}H NMR spectrum of product **7c** in $CDCl_3$ (600 MHz)



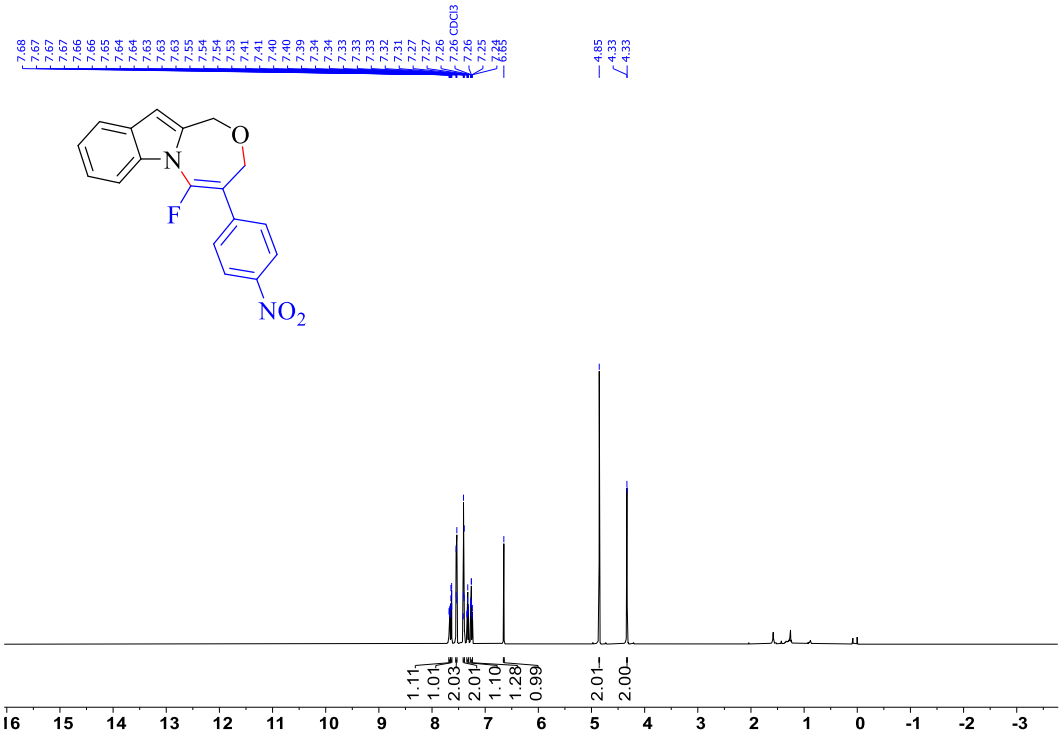
^{13}C NMR spectrum of product **7c** in $CDCl_3$ (151 MHz)



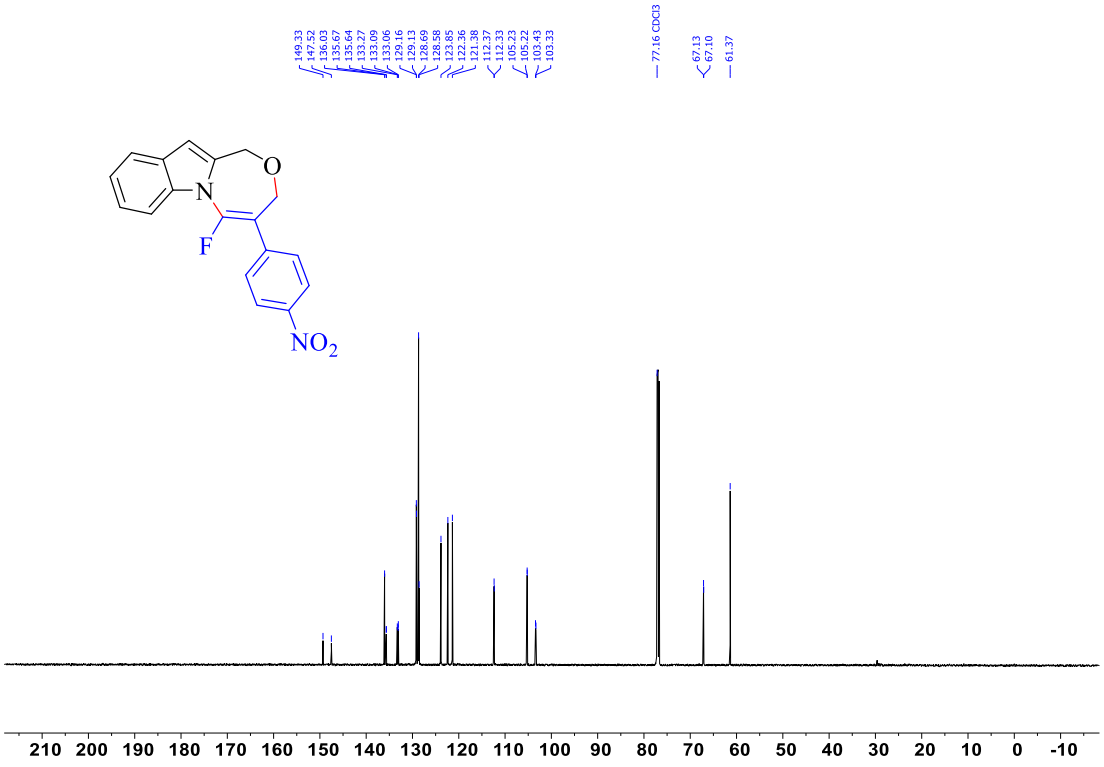
^{19}F-NMR spectrum of product **7c** in $CDCl_3$ (565 MHz)



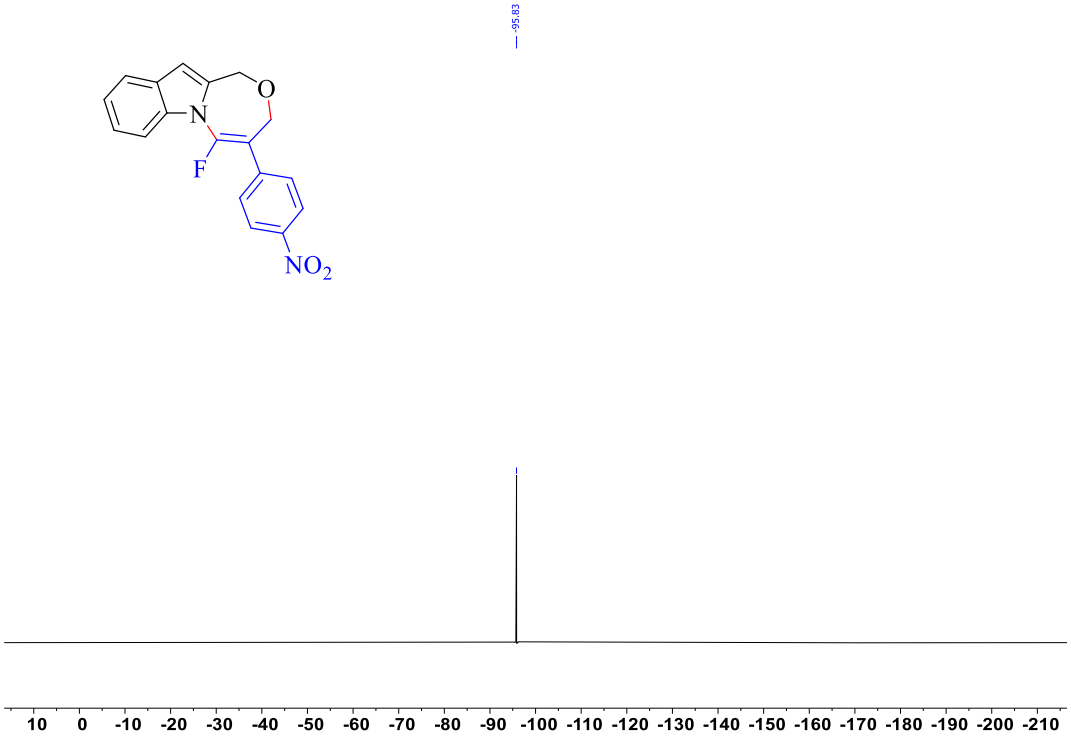
^{1}H NMR spectrum of product **7d** in $CDCl_3$ (600 MHz)



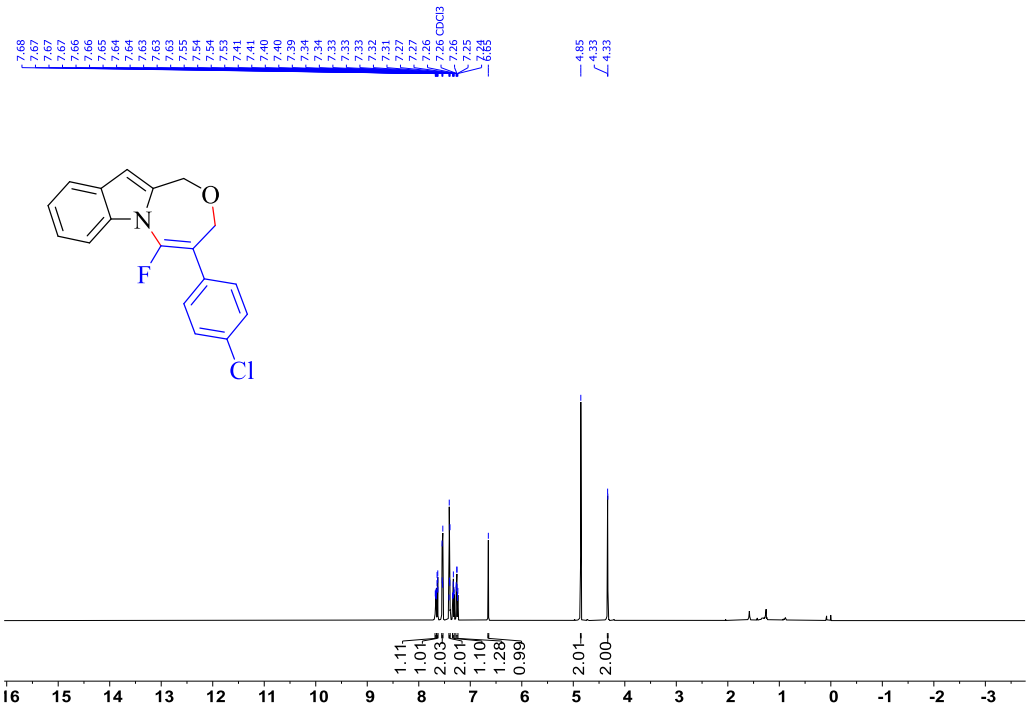
^{13}C NMR spectrum of product **7d** in $CDCl_3$ (151 MHz)



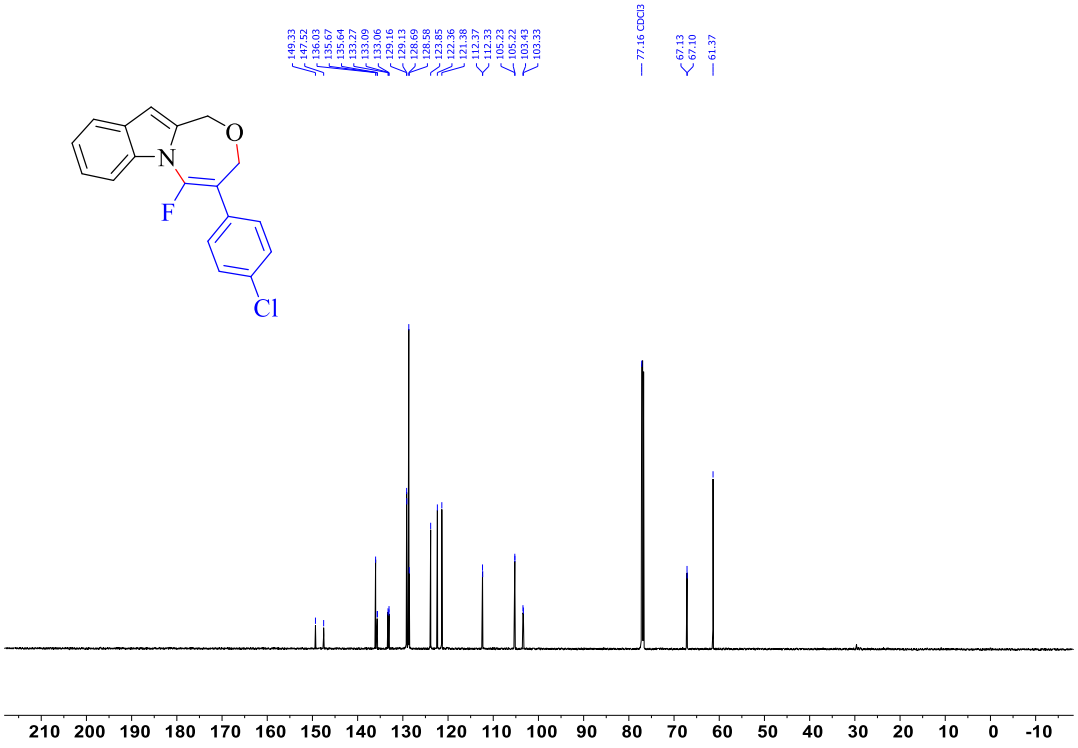
^{19}F-NMR spectrum of product **7d** in $CDCl_3$ (565 MHz)



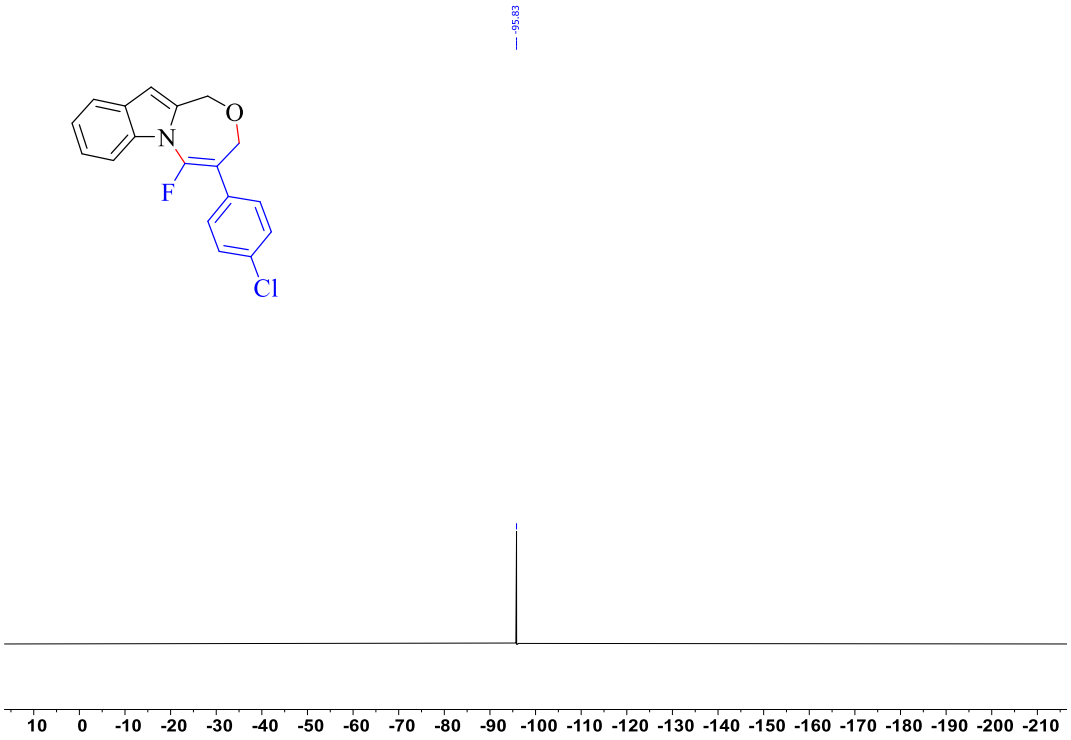
^{1}H NMR spectrum of product **7e** in $CDCl_3$ (600 MHz)



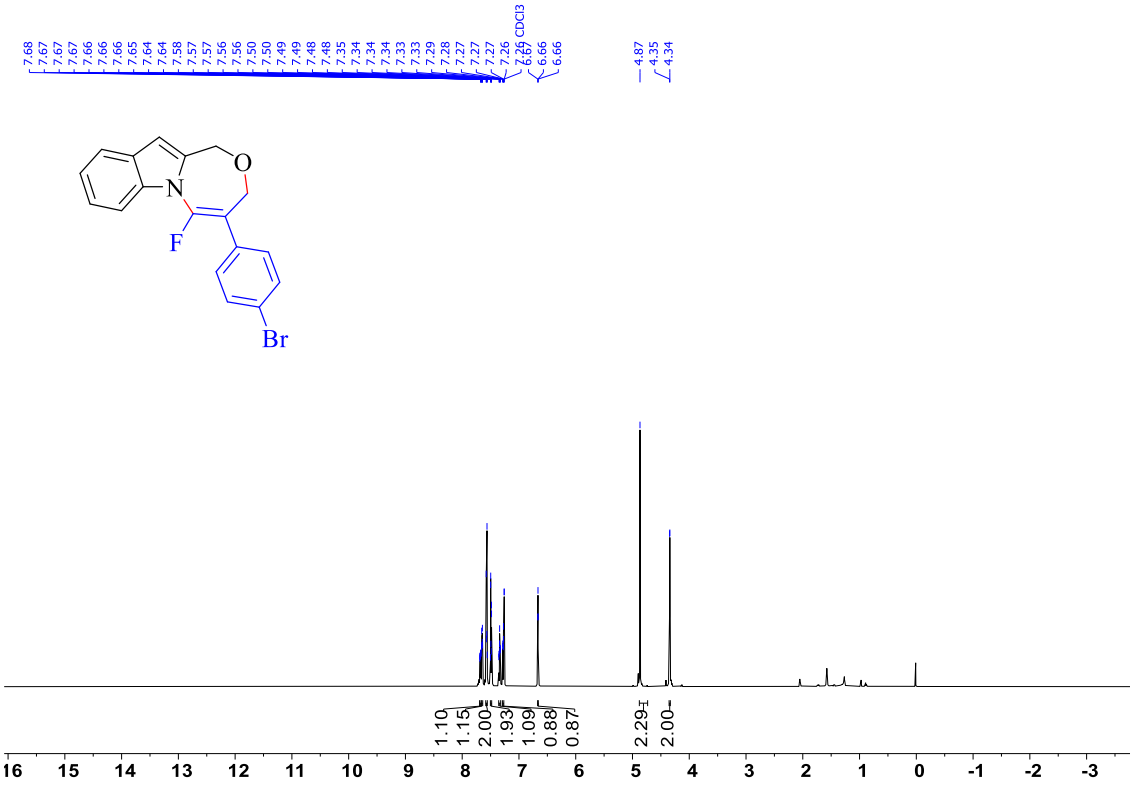
^{13}C NMR spectrum of product **7e** in $CDCl_3$ (151 MHz)



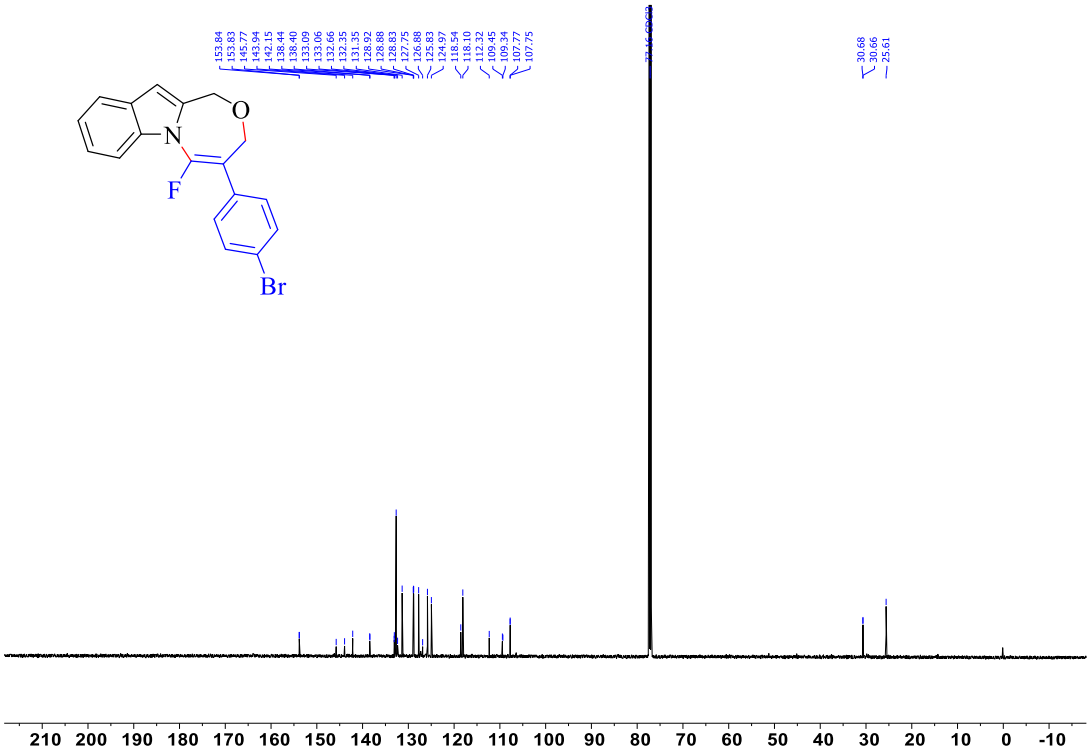
^{19}F-NMR spectrum of product **7e** in $CDCl_3$ (565 MHz)



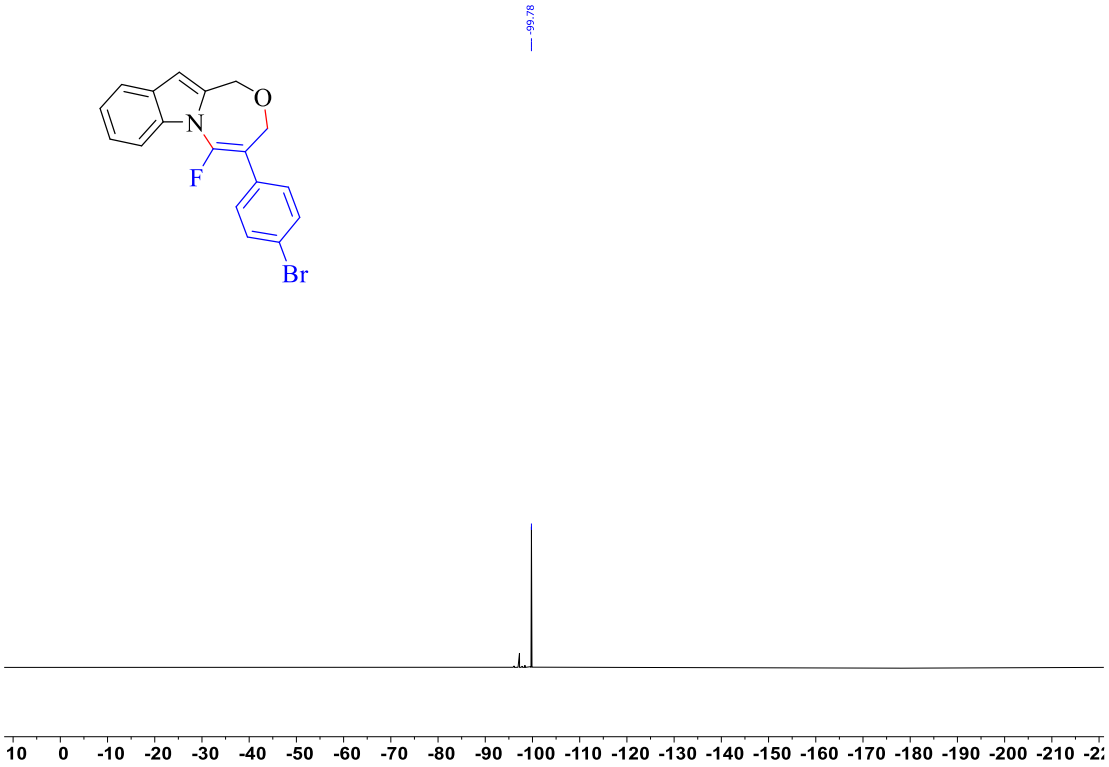
^{1}H NMR spectrum of product **7f** in $CDCl_3$ (600 MHz)



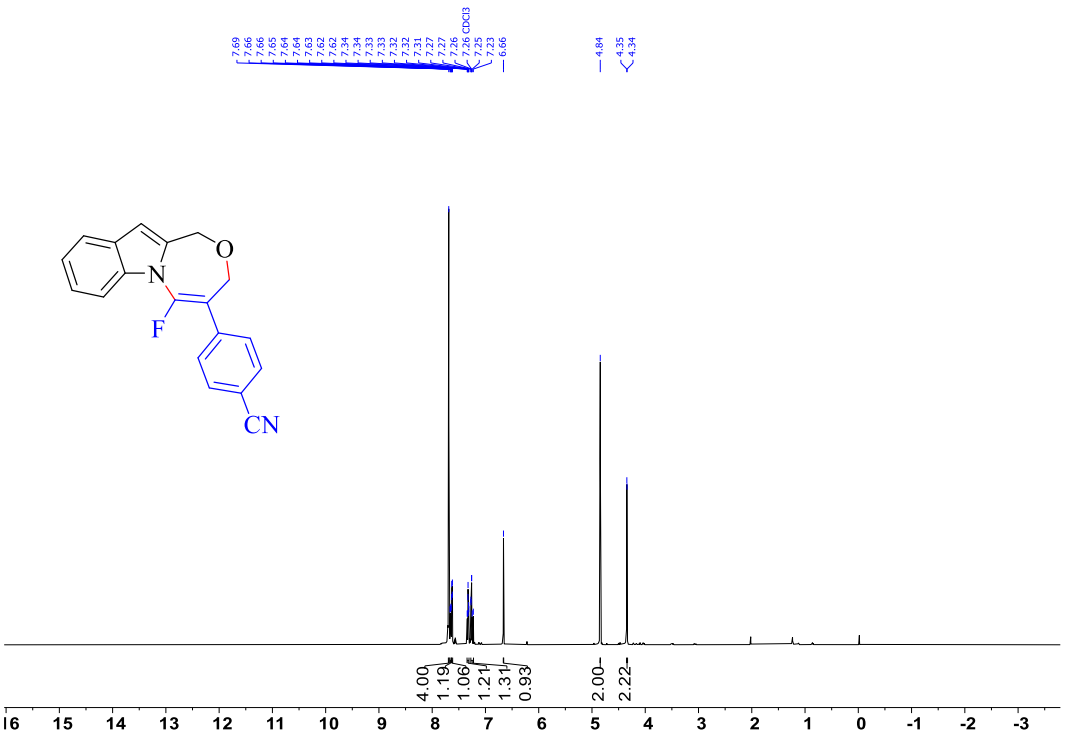
^{13}C NMR spectrum of product **7f** in $CDCl_3$ (151 MHz)



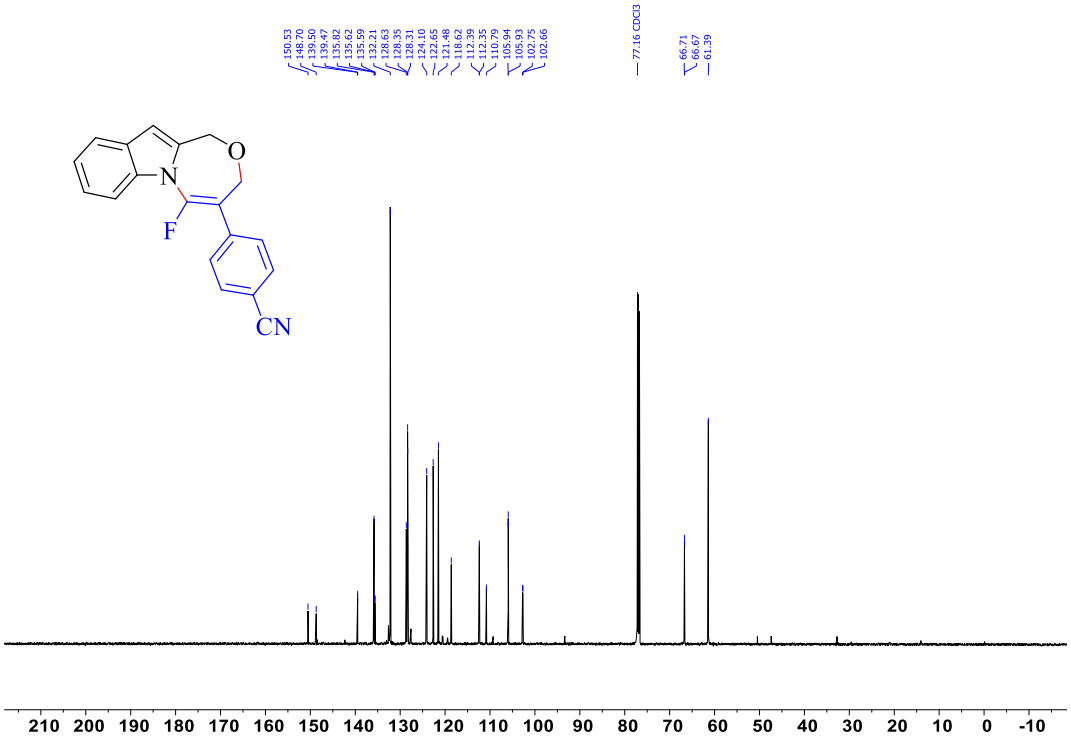
^{19}F-NMR spectrum of product **7f** in $CDCl_3$ (565 MHz)



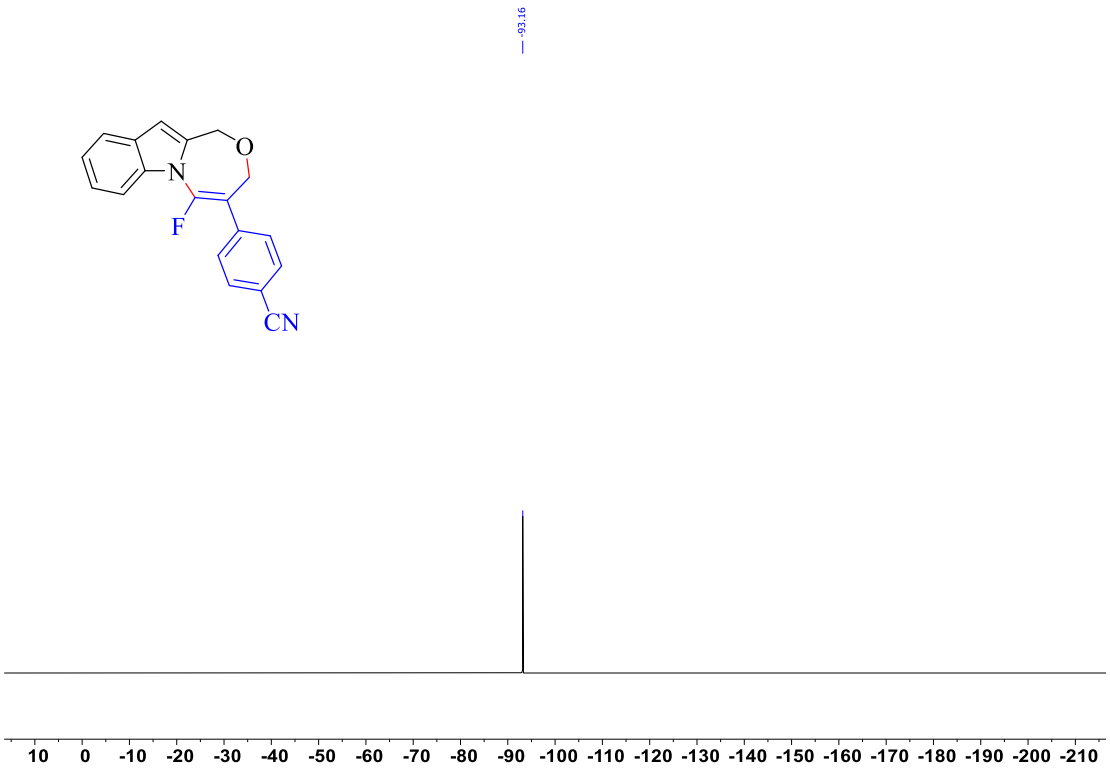
^{1}H NMR spectrum of product **7g** in $CDCl_3$ (600 MHz)



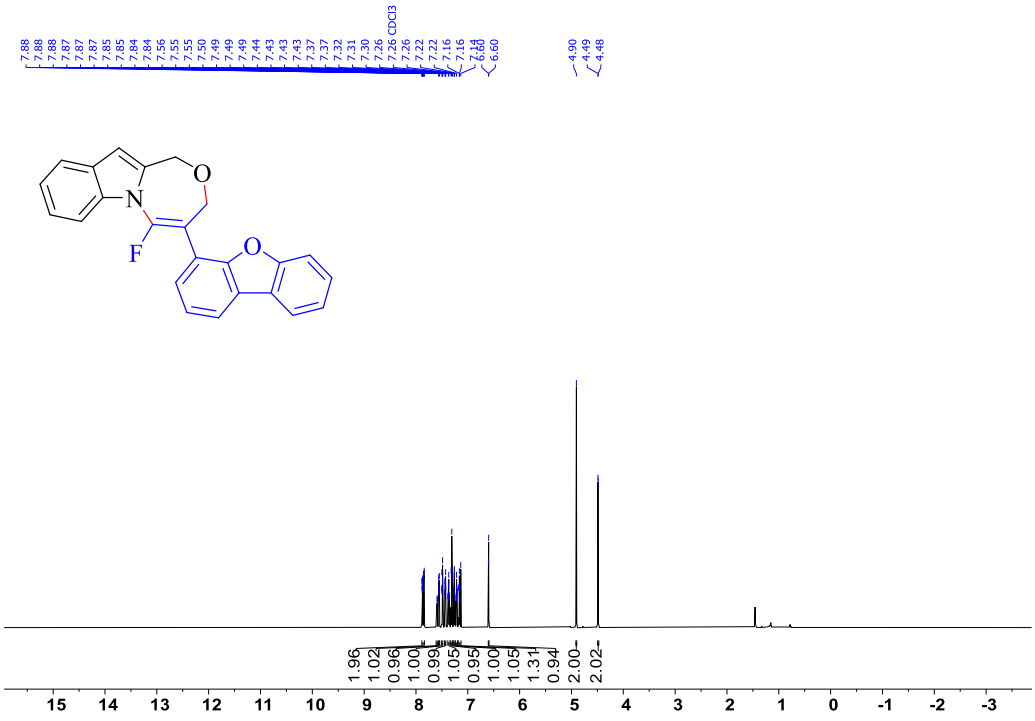
^{13}C NMR spectrum of product **7g** in $CDCl_3$ (151 MHz)



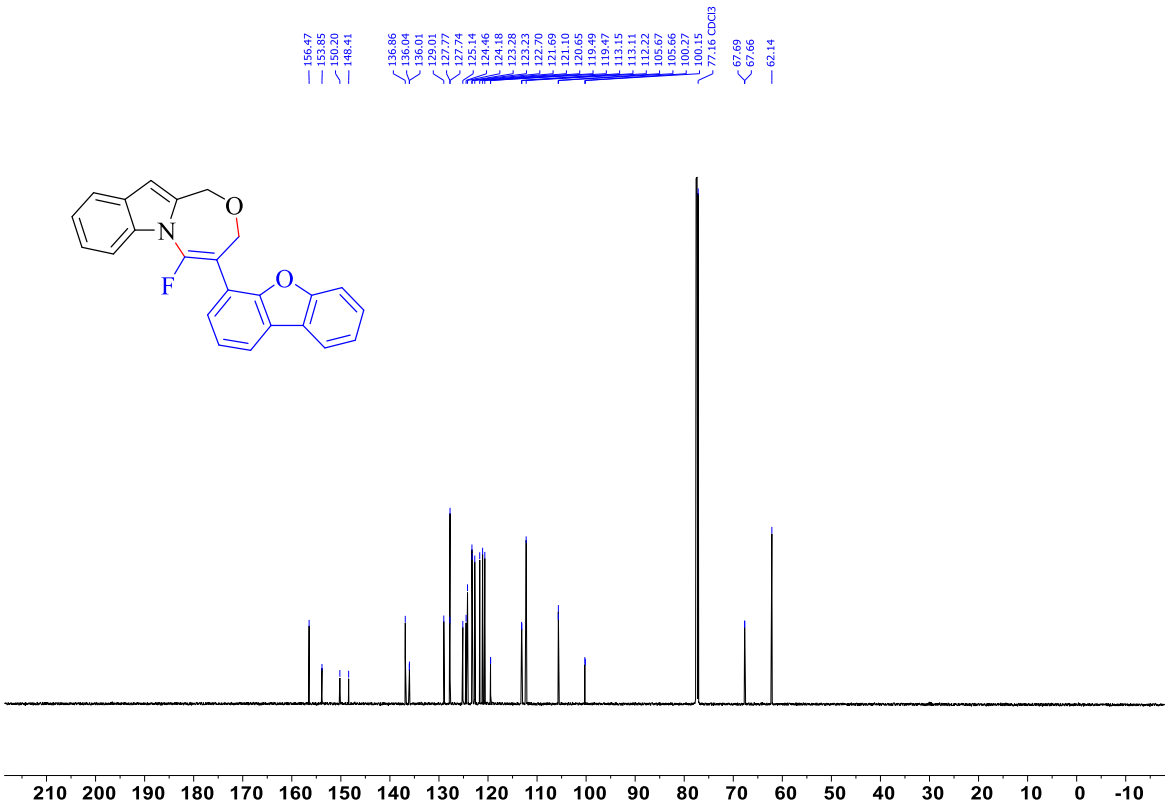
^{19}F-NMR spectrum of product **7g** in $CDCl_3$ (565 MHz)



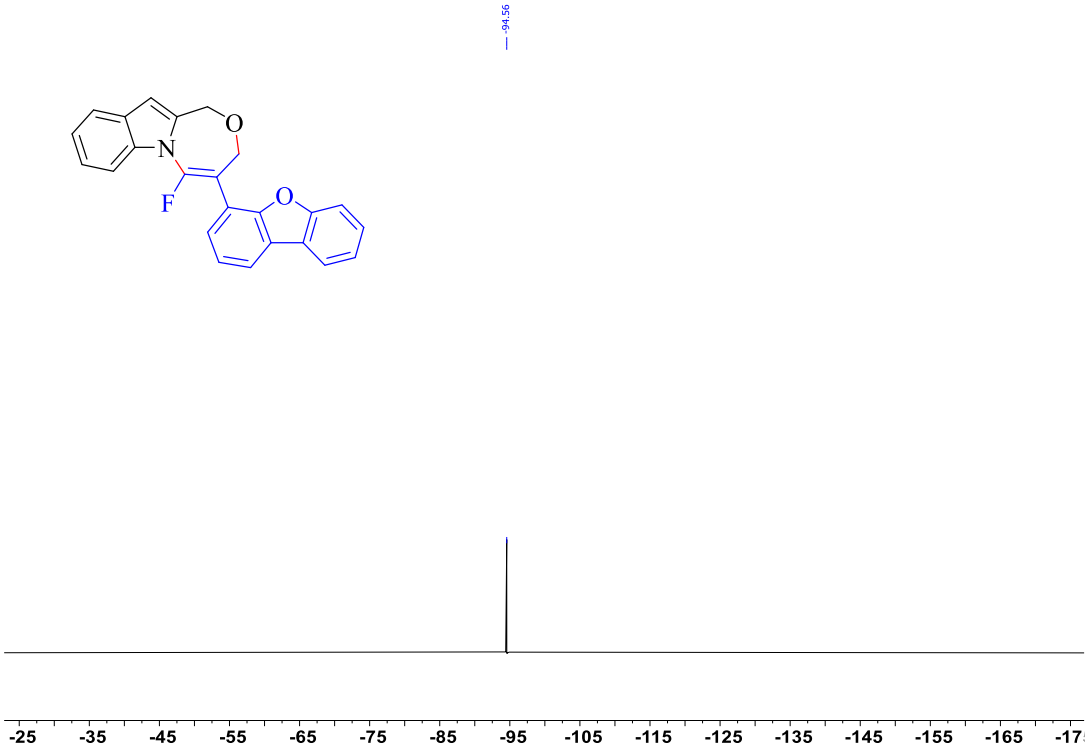
^{1}H NMR spectrum of product **7h** in $CDCl_3$ (600 MHz)



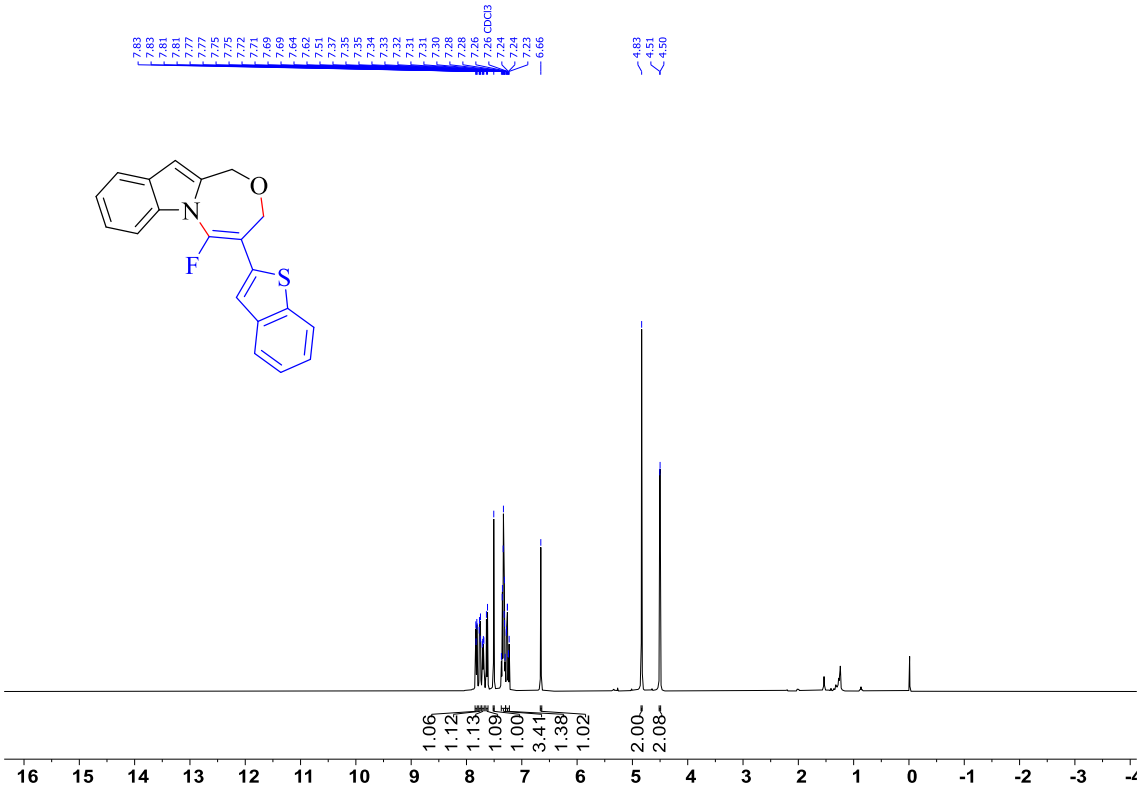
^{13}C NMR spectrum of product **7h** in $CDCl_3$ (151 MHz)



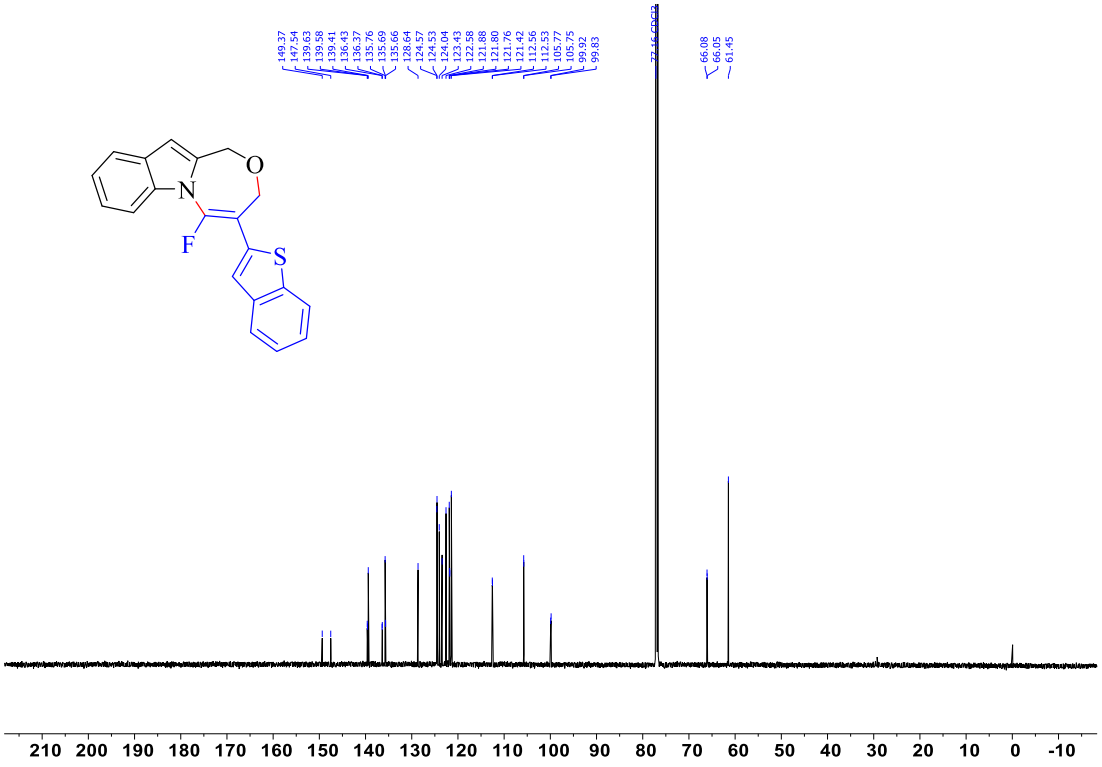
^{19}F-NMR spectrum of product **7h** in $CDCl_3$ (565 MHz)



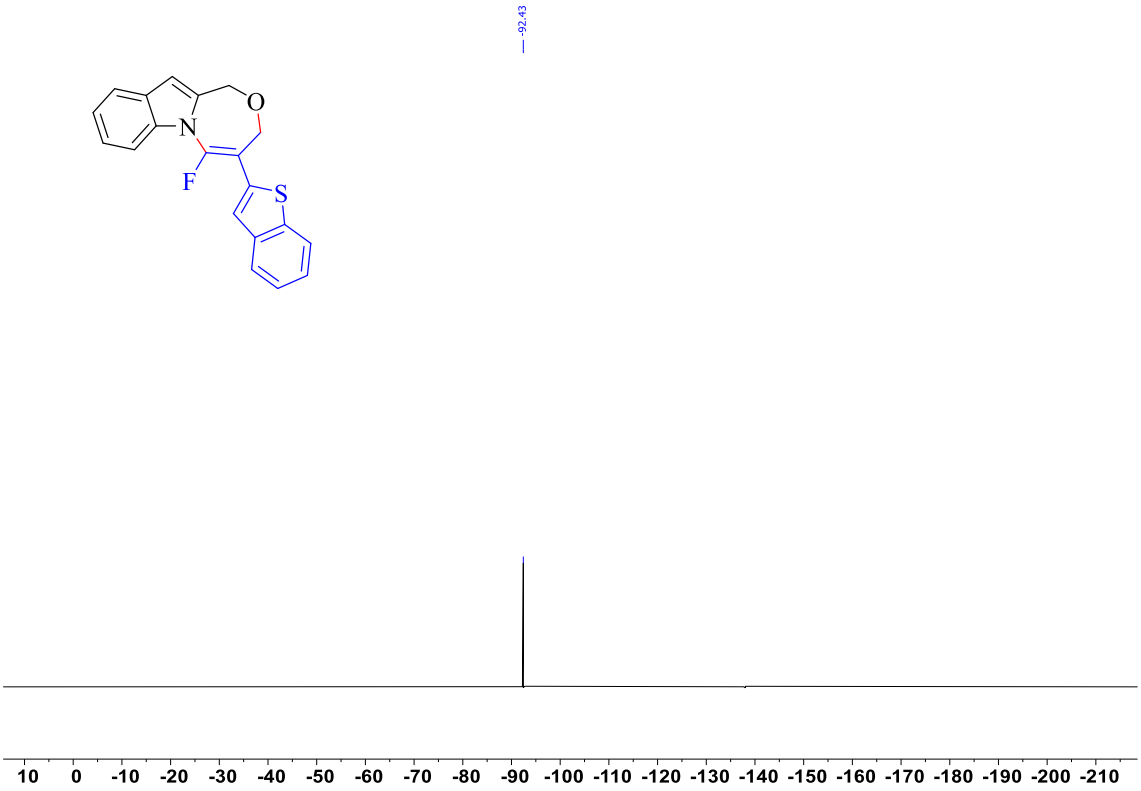
^{1}H NMR spectrum of product **7i** in $CDCl_3$ (400 MHz)



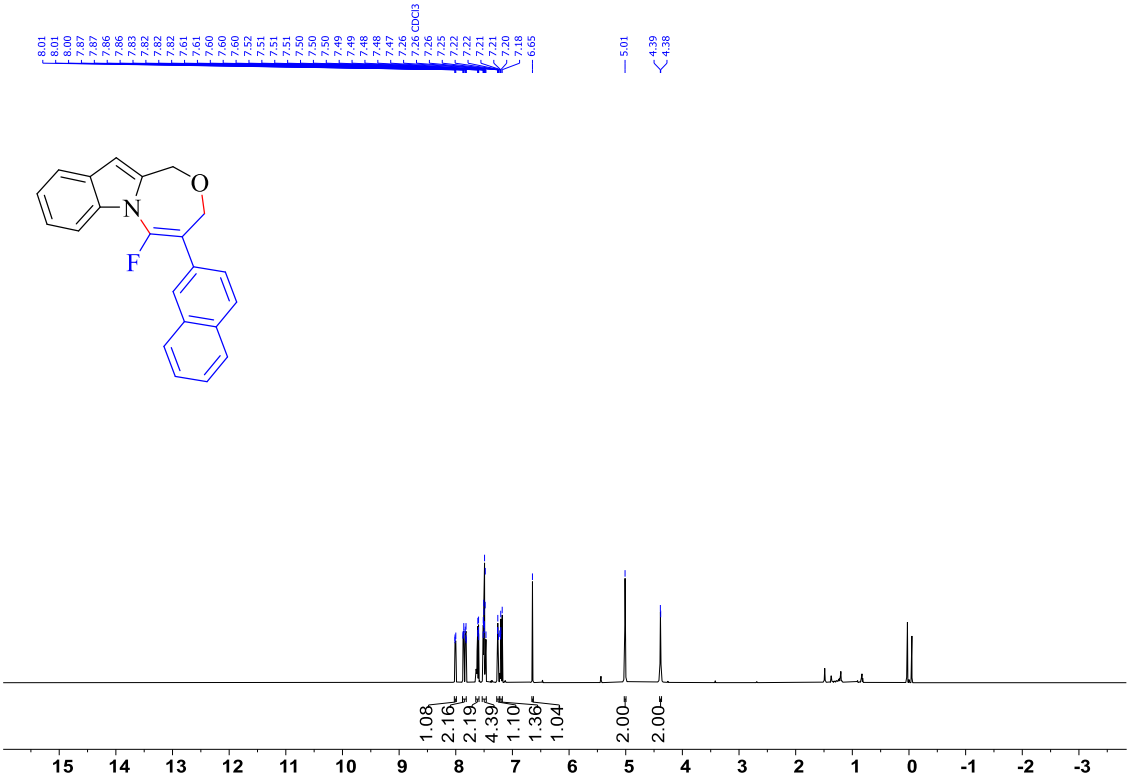
^{13}C NMR spectrum of product **7i** in $CDCl_3$ (151 MHz)



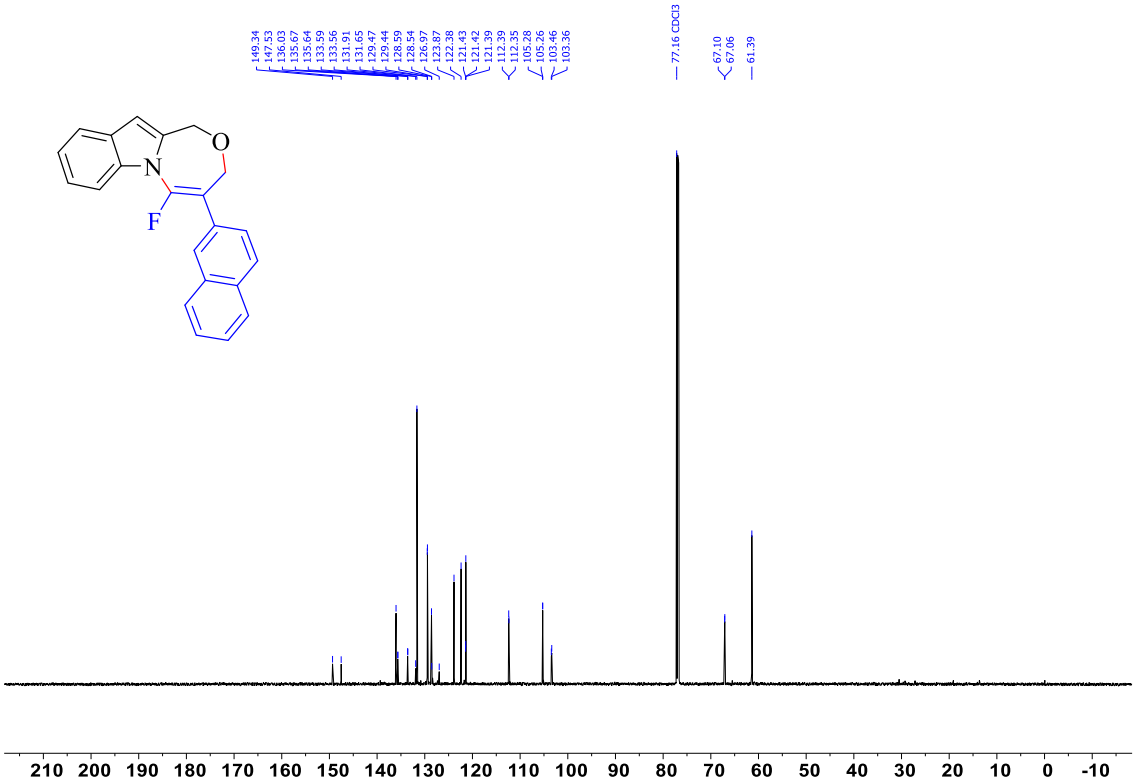
^{19}F-NMR spectrum of product **7i** in $CDCl_3$ (565 MHz)



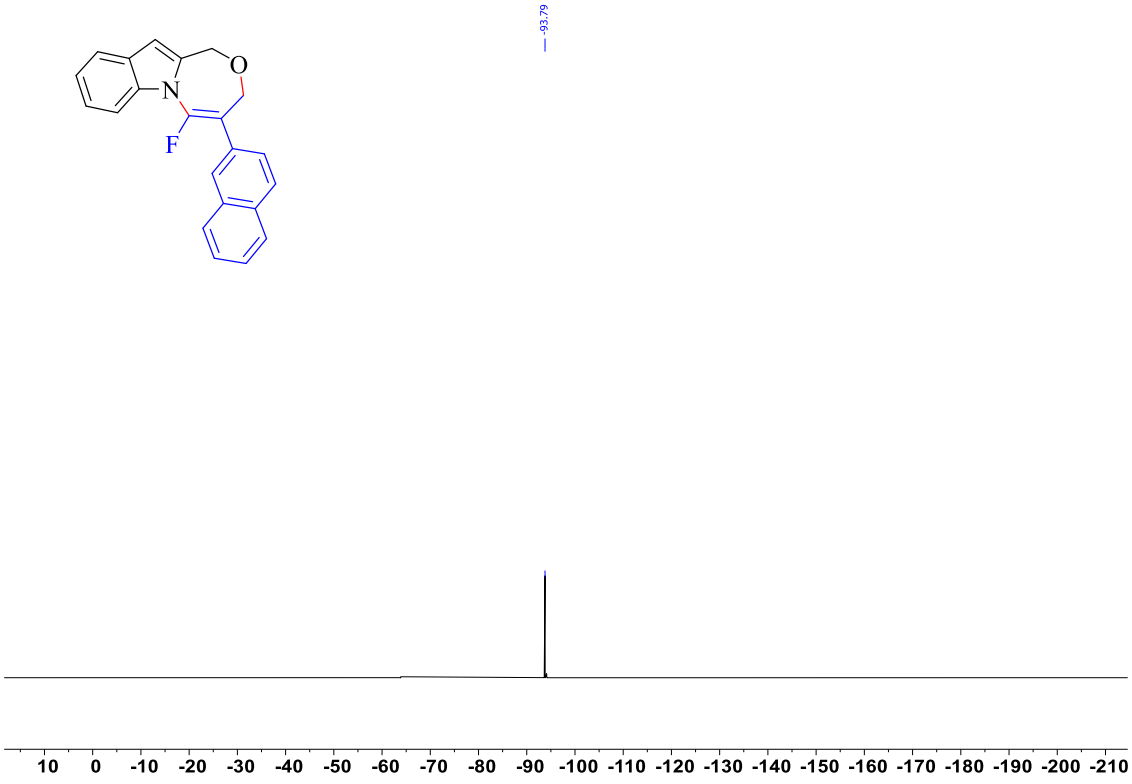
^{1}H NMR spectrum of product **7j** in $CDCl_3$ (600 MHz)



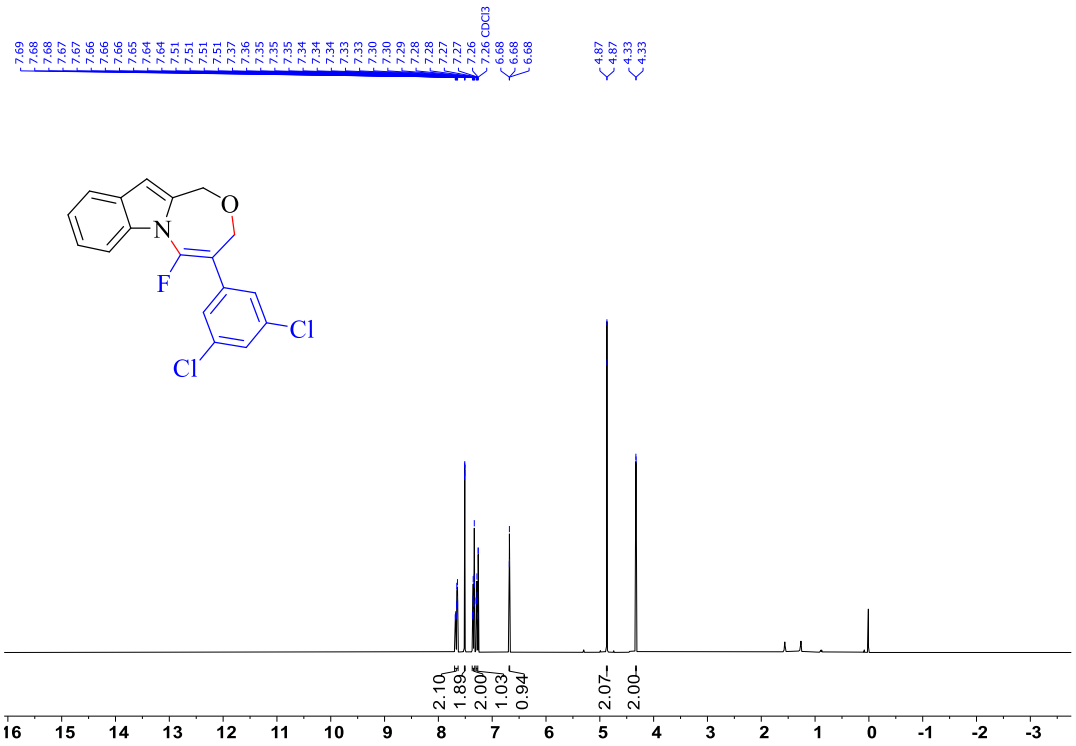
^{13}C NMR spectrum of product **7j** in $CDCl_3$ (151 MHz)



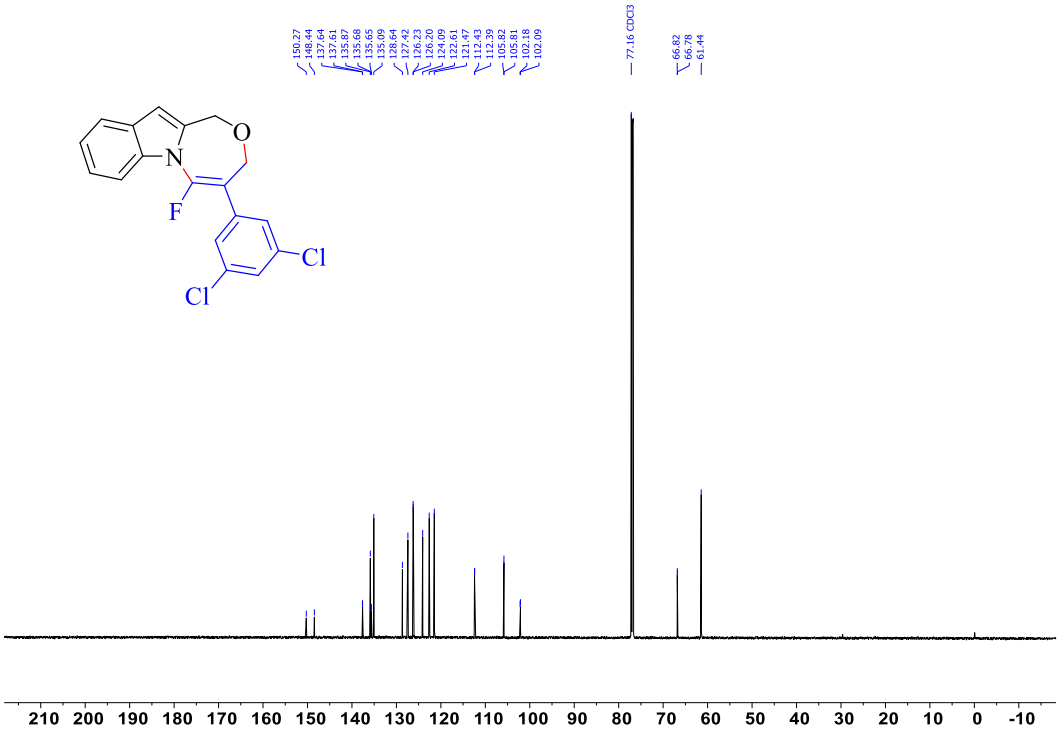
^{19}F-NMR spectrum of product **7j** in $CDCl_3$ (565 MHz)



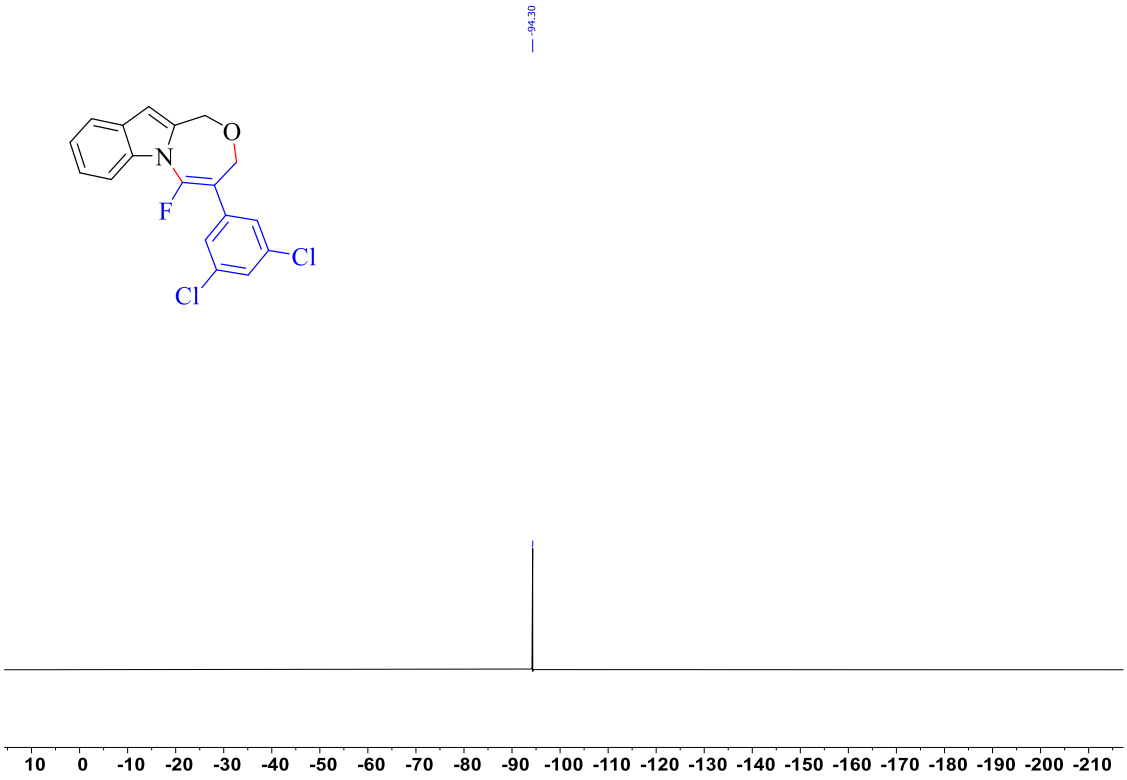
^{1}H NMR spectrum of product **7k** in $CDCl_3$ (600 MHz)



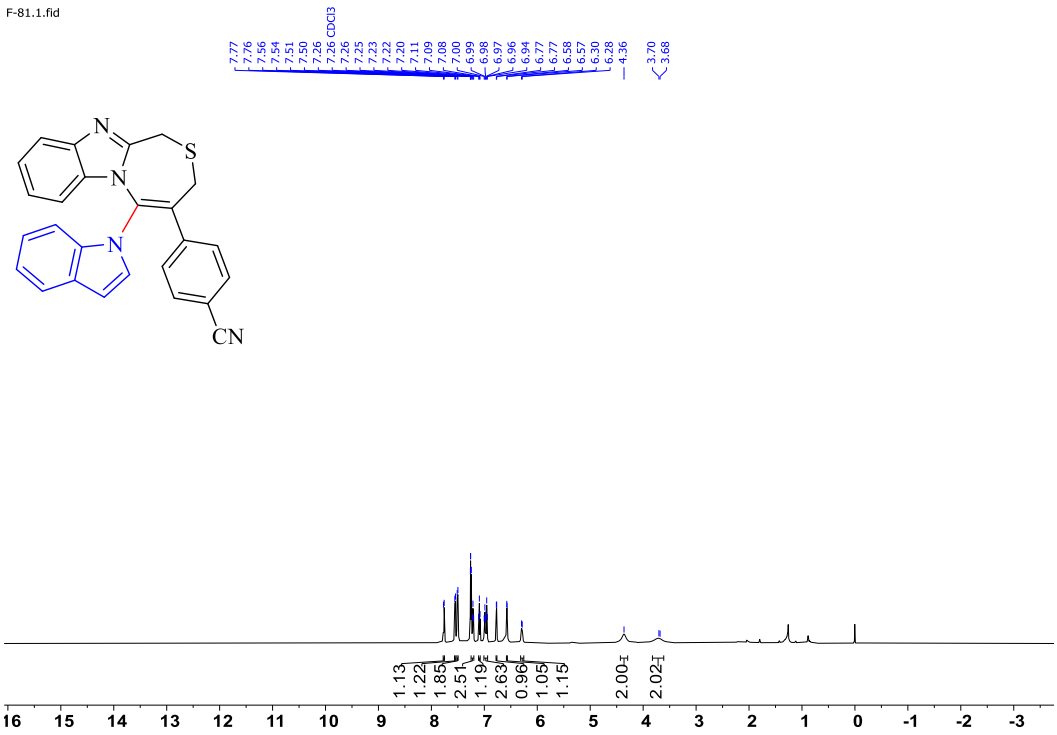
^{13}C NMR spectrum of product **7k** in $CDCl_3$ (151 MHz)



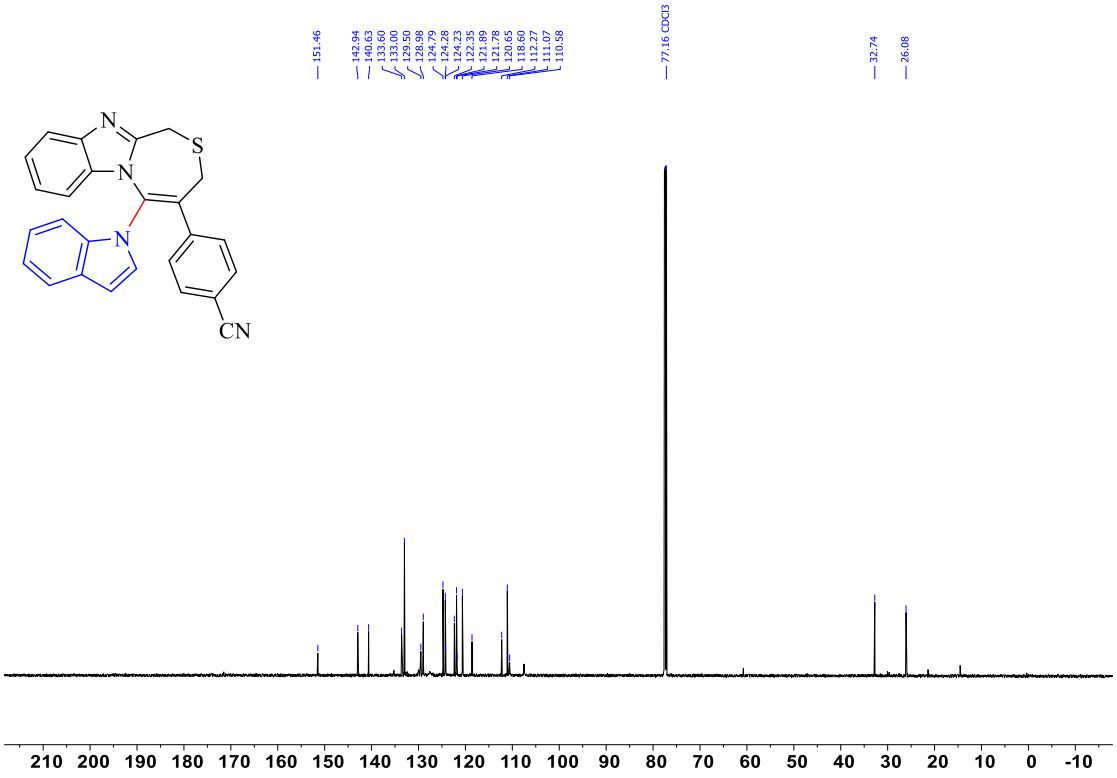
^{19}F-NMR spectrum of product **7k** in $CDCl_3$ (565 MHz)



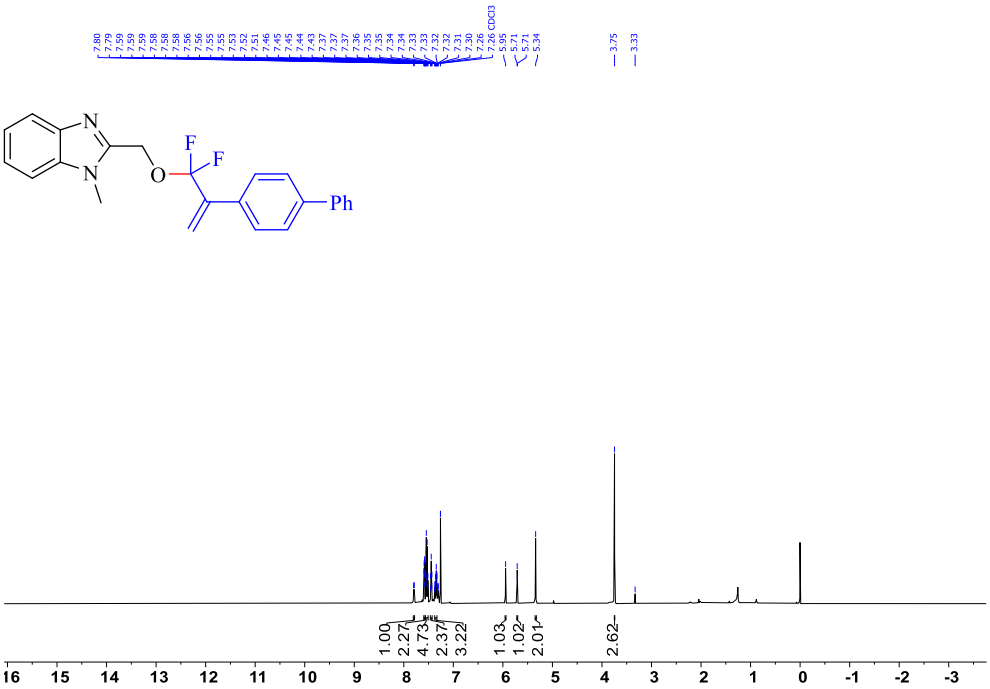
^{1}H NMR spectrum of product **8** in $CDCl_3$ (600 MHz)



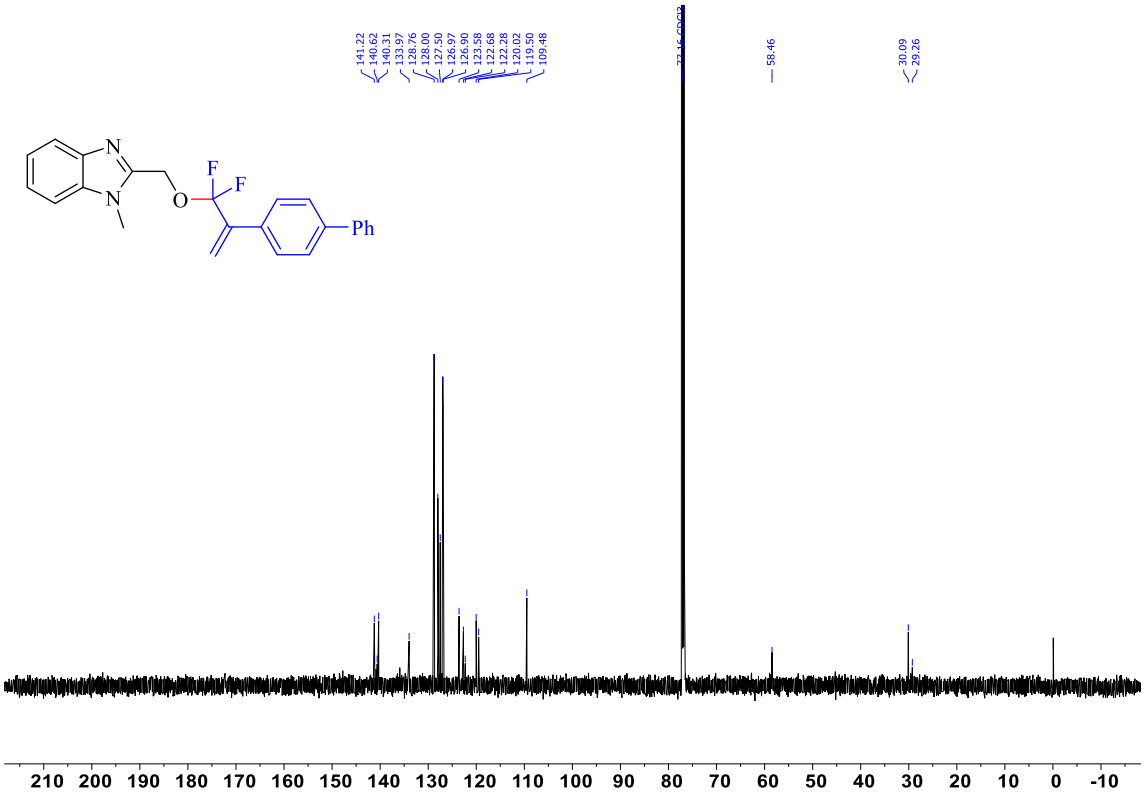
^{13}C NMR spectrum of product **8** in $CDCl_3$ (151 MHz)



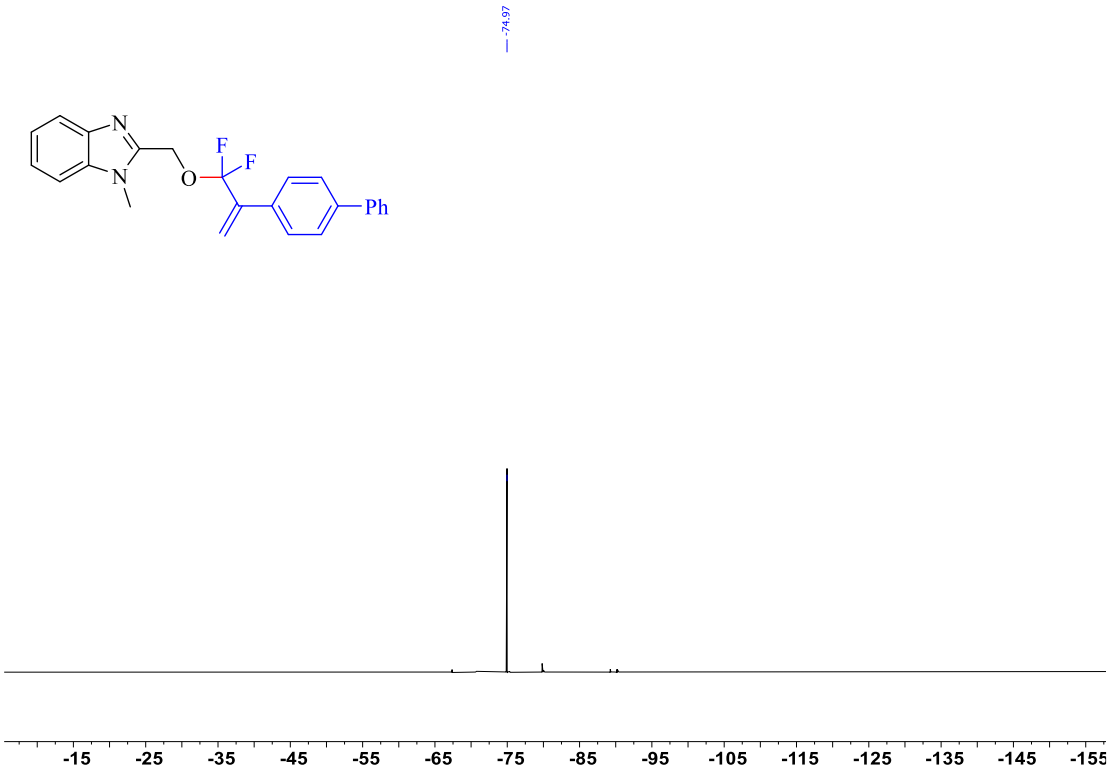
^{1}H NMR spectrum of product **10** in $CDCl_3$ (600 MHz)



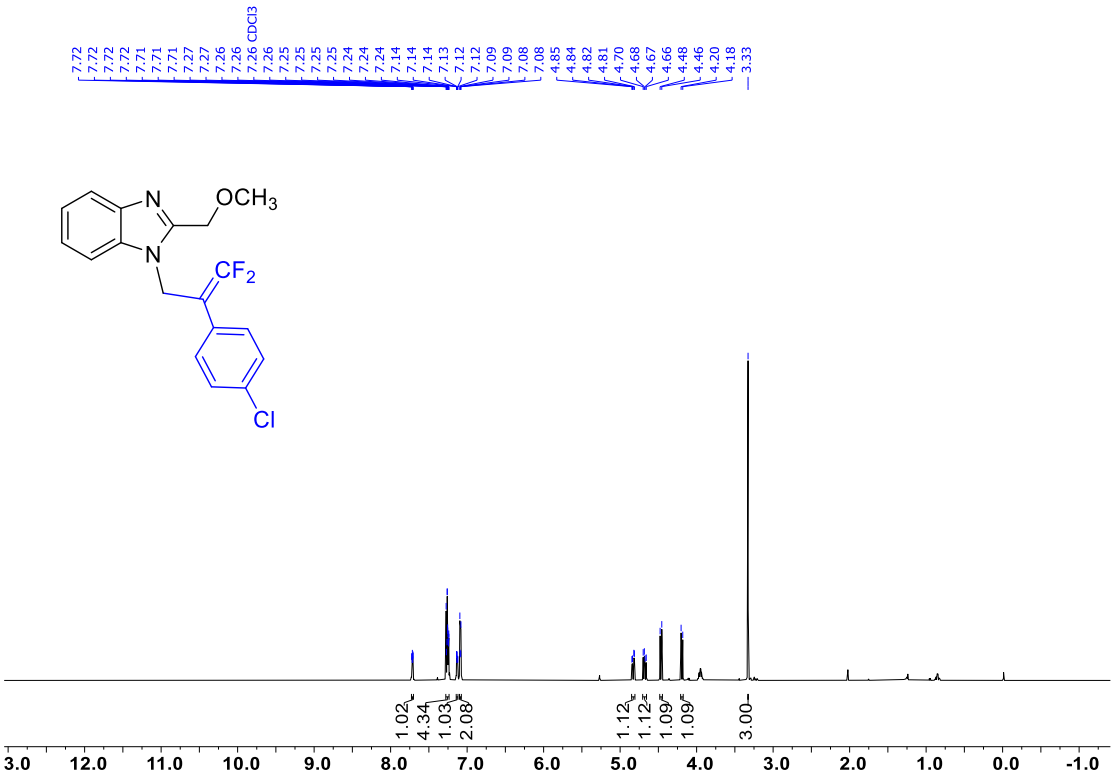
^{13}C NMR spectrum of product **10** in $CDCl_3$ (151 MHz)



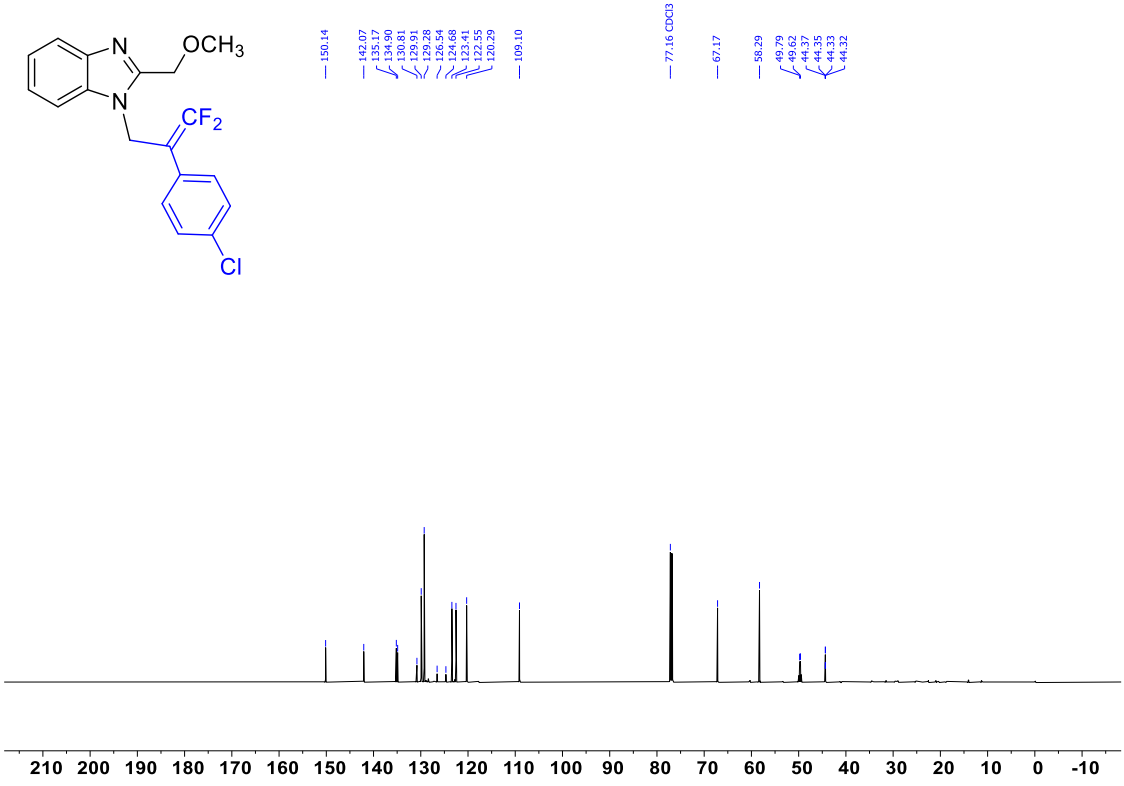
^{19}F-NMR spectrum of product **10** in $CDCl_3$ (565 MHz)



^{1}H NMR spectrum of product **12** in $CDCl_3$ (600 MHz)



^{13}C NMR spectrum of product **12** in $CDCl_3$ (101 MHz)



^{19}F-NMR spectrum of product **12** in $CDCl_3$ (565 MHz)