Supporting Information

One pot synthesis of 3-trifluoromethylbenzo[*b*][1,4]oxazines from CF_3-imidoyl sulfoxonium ylides with 2-bromophenols

Mingshi Pan, Yixin Tong, Xiaodong Qiu, Xiaobao Zeng and Biao Xiong*

School of Pharmacy, Nantong University, 19 Qixiu Road, Nantong, Jiangsu Province 226001, China.

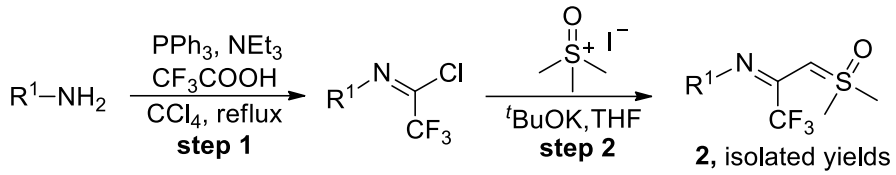
Table of contents

General information	S2
Preparation of CF_3-imidoyl sulfoxonium ylides	S3-S6
Screening of reaction conditions	S6-S9
Typical procedure for the synthesis of **3aa**	S9
Substrates employed for synthesis	S10
References	S10
GC-MS spectrums of control experiments	S11-S12
Gram-scale reaction and derivatization of **3aa**	S13-S15
Single crystal X-ray diffraction of **3ga**	S16-S17
Analytical data of the obtained compounds	S18-S32
NMR spectra of obtained compounds	S33-S90

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and high-resolution mass spectrum (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; high-resolution mass spectra were recorded on a FTLA2000 spectrometer. ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were obtained on Bruker-400, and the chemical shifts of deuterated chloroform are 7.26 ppm and 77 ppm in ^{1}H-NMR and ^{13}C-NMR with TMS as internal standard (0 ppm), respectively. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (J&KChemic, TCI, Bidepharm, Aladdin, SCRC), used without further purification.

Table S1. Preparation of CF_3-imidoyl sulfoxonium ylides (2a-2o)



Entry	R^1	**2**[ref.], Yield
1	C_6H_5	**2a**[3], 90%
2	4-MeC_6H_4	**2b**[3], 92%
3	3-MeC_6H_4	**2c**[3], 91%
4	2-MeC_6H_4	**2d**[3], 86%
5	4-OMeC_6H_4	**2e**[3], 90%
6	4-ClC_6H_4	**2f**[3], 88%
7	4-BrC_6H_4	**2g**[3], 84%
8	4-$CF_3C_6H_4$	**2h**[3], 84%
9	4-CNC_6H_4	**2i**[3],87%
10	3-$NO_2C_6H_4$	**2j**, 86%
11	3,4-OMeC_6H_3	**2k**, 91%
12	benzo[*d*][1,3]dioxol-5-yl	**2l**, 89%
13	pyridin-3-yl	**2m**, 83%
14	α-naphthyl	**2n**, 85%
15	n-hexyl	**2o**, 82%

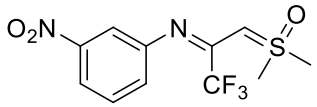
The preparation of ylides **2** was similar to the literature procedures.[1-3]

Step 1: To a solution of triphenylphosphine (21.48 g, 82 mmol) and triethylamine (3.25g, 32.2 mmol) in CCl_4 (100 mL), trifluoroacetic acid (3.13 g, 27.4 mmol) were added dropwise at 0 °C. After stirring for 10~15 min at 0 °C, the amine (27.4 mmol) was added by syringe. The mixture was refluxed for 4 hours and then cooled at room temperature, and filtered under reduced pressure. The filtrate was concentrated under vacuum, and the resulting residue was purified by flash chromatography on silica gel with petroleum ether.

Step 2: To a suspension of trimethylsulfoxonium iodide (6.60 g, 30 mmol) in THF (150 mL), ^{t}BuOK (3.36 g, 30 mmol) were added in portion and the mixture was stirred at room temperature for 2 hours under N_2 atmosphere. Then, fluorinated acetimidoyl chloride (10 mmol) was added by syringe. The mixture was stirred at room temperature for 3 hours and then filtered through celite before all volatiles were removed by reduced pressure distillation. Purification by flash chromatography (DCM/MeOH = 100: 1) afforded products.

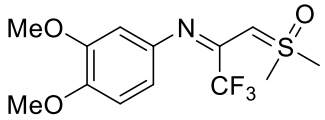
Analytical data of synthesized unknown CF_3-imidoyl sulfoxonium ylides

(*E*)-*N*-(3-nitrophenyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoropropan-2-imine (2j)



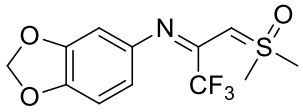
Yellow solid (2.65 g, 86% yield); m.p: 96-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.63 (s, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 4.28 (s, 1H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.55, 148.51, 131.20, 129.15, 127.46, 117.05, 115.84, 61.76, 41.35. HRMS (ESI): Calcd. for $C_{11}H_{11}F_3N_2O_3S$ $[M+H]^+$: 309.0515; found: 309.0514.

(*E*)-*N*-(3,4-dimethoxyphenyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoro-propan-2-imine (2k)



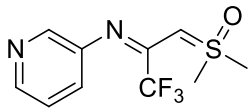
Yellow solid (2.93 g, 91% yield); m.p: 88-89 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (d, *J* = 8.8 Hz, 1H), 6.44 (s, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 4.12 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.96, 144.67, 144.00, 111.55, 111.35, 105.27, 59.45, 56.08, 55.79, 40.99 HRMS (ESI): Calcd. for $C_{13}H_{16}F_3NO_3S$ $[M+H]^+$: 324.0876; found: 324.0874.

(*E*)-*N*-(benzo[*d*][1,3]dioxol-5-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoropropan-2-imine (2l)



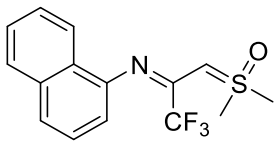
Yellow solid (2.73 g, 89% yield); m.p: 112-113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (d, *J* = 8.0 Hz, 1H), 6.37 (m, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 4.14 (s, 1H), 3.46 (s, 4.5H) 3.24 (s, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.51, 144.96, 142.81, 112.64, 107.78, 102.65, 100.90, 59.51, 41.26. HRMS (ESI): Calcd. for $C_{12}H_{12}F_3NO_3S$ $[M+H]^+$: 308.0563; found: 308.0559.

(*E*)-*N*-(pyridin-3-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoropropan-2-imine (2m)



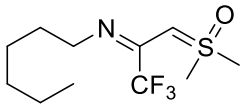
Yellow solid (2.19 g, 83% yield); m.p: 147-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 4.4 Hz, 1H), 8.11 (s, 1H), 7.22-7.07 (m, 2H), 4.25 (s, 1H), 3.49 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.51, 143.49, 142.45, 127.79, 123.19, 61.21, 41.24. HRMS (ESI): Calcd. for $C_{10}H_{11}F_3N_2OS$ $[M+H]^+$: 265.0617; found: 265.0613.

(*E*)-*N*-(naphthalen-1-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoropropan-2-imine (2n)



Reddish brown solid (2.66 g, 85% yield); m.p: 50-51 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.63 (m, 2H), 7.48-7.22 (m, 4H), 6.68 (s, 1H), 4.16 (s, 1H), 3.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.98, 134.14, 127.92, 125.97, 125.21, 124.02, 122.51, 114.57, 60.39, 41.72. HRMS (ESI): Calcd. for $C_{15}H_{14}F_3NOS$ $[M+H]^+$: 314.0821; found: 314.0819.

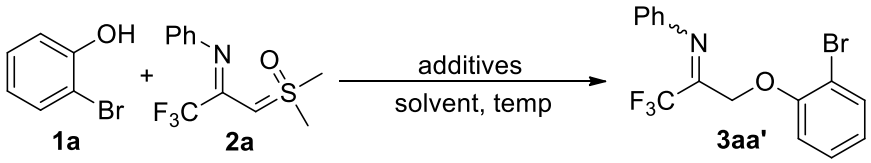
(*E*)-*N*-(*n*-hexyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-1,1,1-trifluoropropan-2-imine (2o)



Yellow oil (2.22 g, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 1H), 3.40 (s, 6H), 1.58 (t, *J* = 6.8 Hz, 2H), 1.41-1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 56.12, 50.48, 41.42, 31.70, 29.66, 27.24, 22.65, 14.06. HRMS (ESI): Calcd. for $C_{11}H_{20}F_3NOS$ $[M+H]^+$: 272.1290; found: 272.1287.

Screening of reaction conditions

Table S2. **Screening of the reaction conditions of ylide insertion**[a]



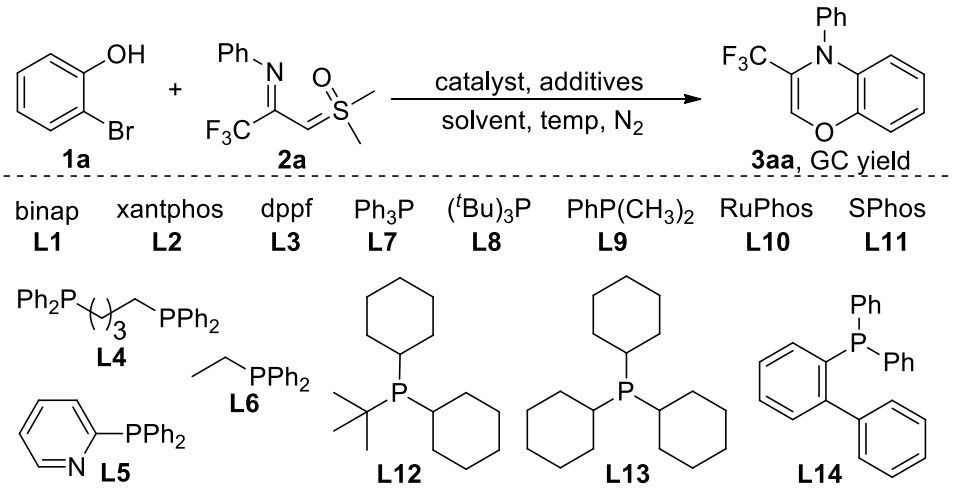
Entry	Solvent	Additive	Temp (^{o}C)	Yield of **3aa'** (%)[b]
1	MeCN	LiBr	80	95
2	DMF	LiBr	80	77
3	Toluene	LiBr	80	26
4	1,4-Dioxane	LiBr	80	26
5	THF	LiBr	80	35
6	MeCN	LiBr	70	85
7	MeCN	LiBr	90	95
8	MeCN	LiCl	80	Trace
9	MeCN	KBr	80	Trace
10	MeCN	$ZnBr_2$	80	0
11	MeCN	$TiCl_4$	80	0
12	MeCN	LiBr	80	(37, 95)[c]

[a] Unless otherwise stated, the reaction was performed with **1a** (0.3 mmol), **2a** (0.3 mmol), additive (100 mmol%) in solvent (1.0 mL) at 80 ^{o}C for 2 hours under N_2. [b] GC yield. [c] Yields are with respect to use 50 mmol% and 150 mmol% of LiBr, respectively.

In the step of O-H insertion of CF_3-imidoyl sulfoxonium ylides, by performing the reaction at 80℃ in the presence of LiBr under N_2 condition, we tested the effect of different solvents, respectively (Table S2, entries 1-5). Gratifyingly, MeCN exhibits good result to give **3aa'** in 95% yield. The screening of temperature reveals that MeCN heated to 80°C is sufficient (entry 6-7). Then, other four Lewis acids showed to be invalid for the transformation as compared to LiBr (entry 8-11). Finally, screening the amount of LiBr reveals that 100 mmol% is optimal (entry 13).

In the step of Buchwald–Hartwig reaction, by performing the reaction in toluene at 110℃ in the presence of NaOH under N_2 condition, we tested the effect of different ligands with $Pd(OAc)_2$, respectively (Table S3, entries 1-14). To our delight, $(^tBu)_3P$ exhibited good effect to give **3aa** in 91% yield (entry 8). Next, four different catalysts were employed into the protocol to examine the catalyst system, and the results show that $Pd(OAc)_2$ remains the most suitable catalyst (entries 15-18). Then, several solvents such as dioxane, DMF, THF, MeCN, and *p*-Xylene were investigated (entries 19–23). However, all these solvents decreased the yield in different degrees relative to toluene. Then, other eight bases showed to be less effective for the transformation as compared to NaOH (entry 24-31). Finally, the screening of temperature reveals that toluene heated to 100 °C is suitable (entry 32).

Table S3. **Screening of the reaction conditions**[a]



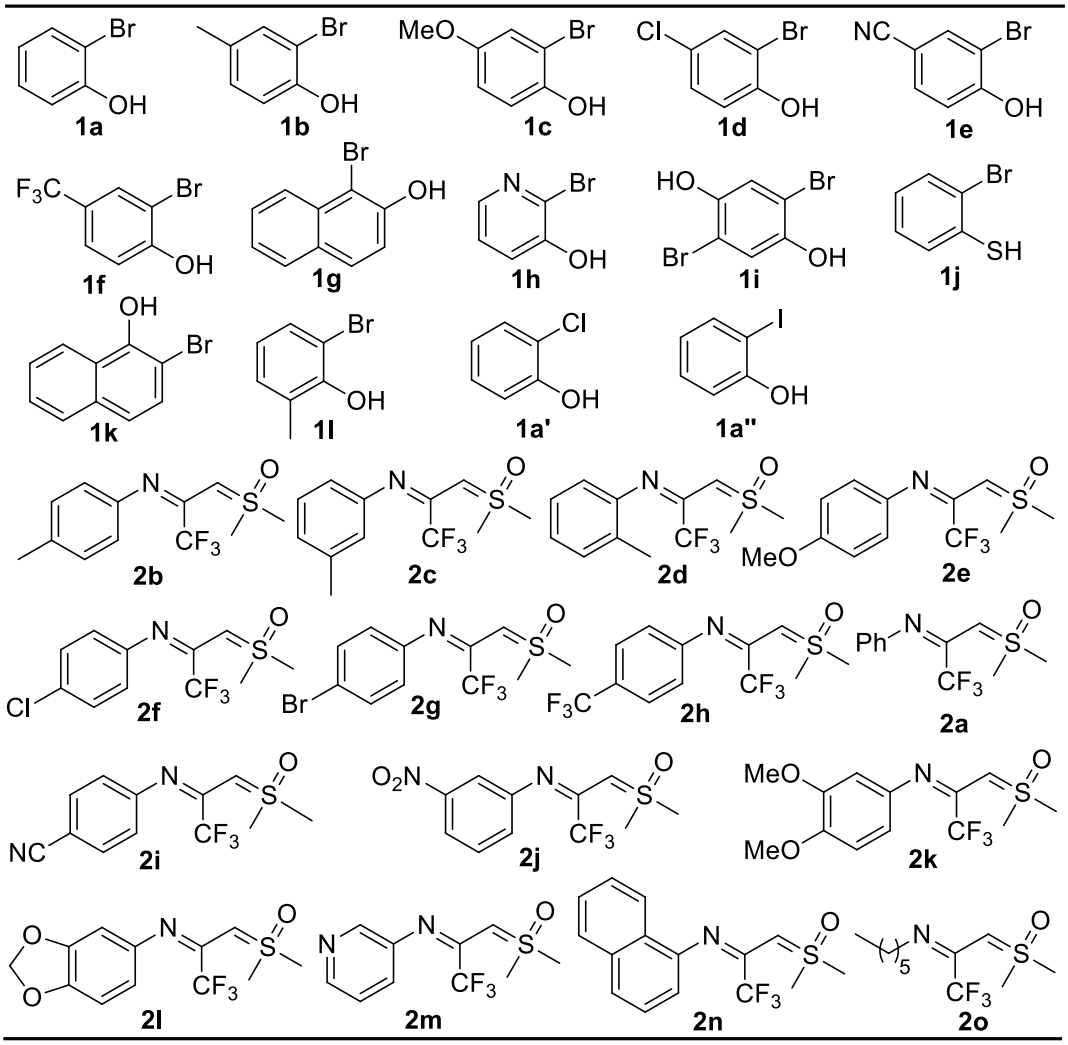
Entry	Catalyst	Ligand	Solvent	Base	Yield (%)[b]
1	$Pd(OAc)_2$	**L1**	Toluene	NaOH	53
2	$Pd(OAc)_2$	**L2**	Toluene	NaOH	45
3	$Pd(OAc)_2$	**L3**	Toluene	NaOH	18
4	$Pd(OAc)_2$	**L4**	Toluene	NaOH	10
5	$Pd(OAc)_2$	**L5**	Toluene	NaOH	31
6	$Pd(OAc)_2$	**L6**	Toluene	NaOH	22
7	$Pd(OAc)_2$	**L7**	Toluene	NaOH	17
8	$Pd(OAc)_2$	**L8**	Toluene	NaOH	91
9	$Pd(OAc)_2$	**L9**	Toluene	NaOH	19
10	$Pd(OAc)_2$	**L10**	Toluene	NaOH	70
11	$Pd(OAc)_2$	**L11**	Toluene	NaOH	72
12	$Pd(OAc)_2$	**L12**	Toluene	NaOH	74
13	$Pd(OAc)_2$	**L13**	Toluene	NaOH	30
14	$Pd(OAc)_2$	**L14**	Toluene	NaOH	28
15	$Pd(PPh_3)_4$	**L8**	Toluene	NaOH	24
16	$Pd(PPh_3)_2Cl_2$	**L8**	Toluene	NaOH	78
17	$PdCl_2$	**L8**	Toluene	NaOH	81
18	$Pd(OH)_2$	**L8**	Toluene	NaOH	28
19	$Pd(OAc)_2$	**L8**	1,4-Dioxane	NaOH	78
20	$Pd(OAc)_2$	**L8**	DMF	NaOH	80
21	$Pd(OAc)_2$	**L8**	THF	NaOH	75
22	$Pd(OAc)_2$	**L8**	MeCN	NaOH	72
23	$Pd(OAc)_2$	**L8**	*p*-Xylene	NaOH	84
24	$Pd(OAc)_2$	**L8**	Toluene	^{t}BuOK	22
25	$Pd(OAc)_2$	**L8**	Toluene	^{t}BuONa	55
26	$Pd(OAc)_2$	**L8**	Toluene	K_2CO_3	32
27	$Pd(OAc)_2$	**L8**	Toluene	Cs_2CO_3	28
28	$Pd(OAc)_2$	**L8**	Toluene	K_3PO_4	68
29	$Pd(OAc)_2$	**L8**	Toluene	CsOH	66

30	$Pd(OAc)_2$	**L8**	Toluene	KOH	54
31	$Pd(OAc)_2$	**L8**	Toluene	LiOH	26
32	$Pd(OAc)_2$	**L8**	Toluene	NaOH	(55, 91, 89)[c]

[a] Unless otherwise stated, all the reaction were performed using **1a** (0.3 mmol), **2a** (0.3 mmol) and LiBr (0.3 mmol) in dry MeCN (1.0 mL) at 80 °C for 2 h under N_2. Then, catalyst (5 mol %), ligand (10 mol %), base (150 mmol %) and solvent (1.5 mL) were added after removing the MeCN under vacuum, and the resulting mixture was stirred at 110 °C for 10 h under N_2. [b] GC yield. [c] Yields are with respect to the temperature at 90 °C, 100 °C and 120 °C respectively.

Typical procedure for the synthesis of 3aa

Under N_2 atmosphere, 2-bromophenol **1a** (51.6 mg, 0.3 mmol), (*E*)-3-(dimethyl(oxo)-λ6-sulfanylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine **2a** (78.9 mg, 0.3 mmol), LiBr (25.8 mg, 100 mol %), and MeCN (1.0 mL) were added in a 25 mL Schlenk tube. Then the mixture was stirred at 80 °C for 2 hours and cooled down to room temperature. After removing the solvent under vacuum, $Pd(OAc)_2$ (3.4 mg, 5 mol %), tri-tert-butylphosphine (6.0 mg, 10 mol %), NaOH (18 mg, 150 mol %) and toluene (1.5 mL) were added successively. Then, the resulting mixture was stirred at 100 °C for 10 h under N_2. After cooled to room temperature, the mixture was concentrated and the residue was purified by flash chromatography (petroleum ether) to give 4-phenyl-3-(trifluoromethyl)-*4H*-benzo[*b*][1,4]oxazine **3aa** as light yellow oil.



Scheme S1. Substrates employed for synthesizing *4H*-benzo[*b*][1,4]oxazine

Reference

[1] (a) Wang, Z.; Li, T.; Zhao, J.; Shi, X.; Jiao, D.; Zheng, H.; Chen, C.; Zhu, B. *Org. Lett*., **2018**, *20*, 6640-6645; (b) Wang, L.-C.; Du, S.; Chen, Z.; Wu, X.-F. *Org. Lett.*, **20 20**, *22*, 5567-5571.

[2] (a) Dias, R. M. P.; Burtoloso, A. C. B. *Org. Lett.*, **2016**, *18*, 3034-3037; (b) Phelps, A. M.; Chan, V. S.; Napolitano, J. G.; Krabbe, S. W.; Schomaker, J. M.; Shekhar, S. *J. Org. Chem.*, **2016**, *81*, 4158-4169; (c) Barday, M.; Janot, C.; Halcovitch, N. R.; Muir, J.; Aissa, C. *Angew. Chem., Int. Ed*., **2017**, *56*, 13117-13121.

[3] Wen S, Tian Q, Chen Y, Zhang Y, Cheng G. *Org Lett.*, **2021**, *23*, 7407-7411.

GC-MS spectrums of control experiments

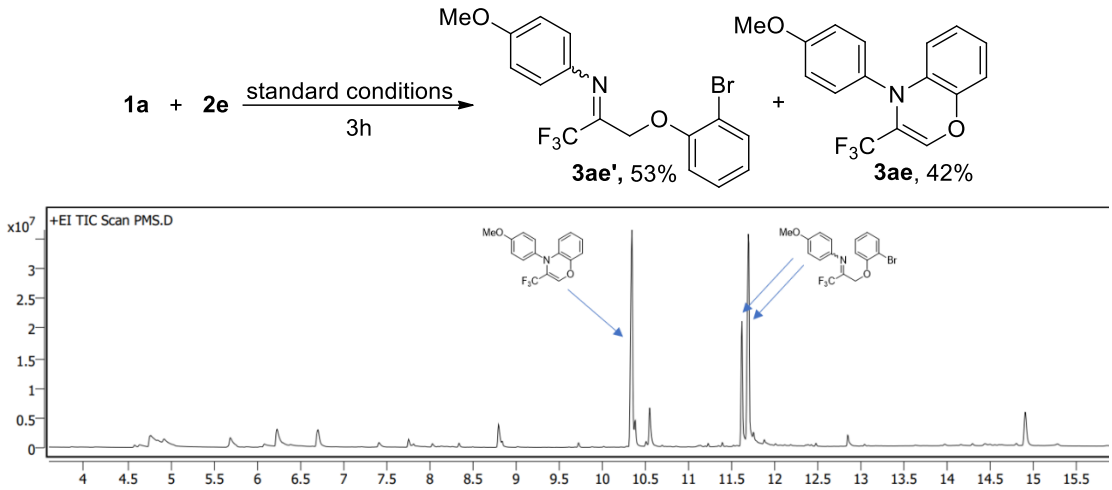


Figure S1 GC-MS of the reaction of **1a** and **2e** after 3 hours.

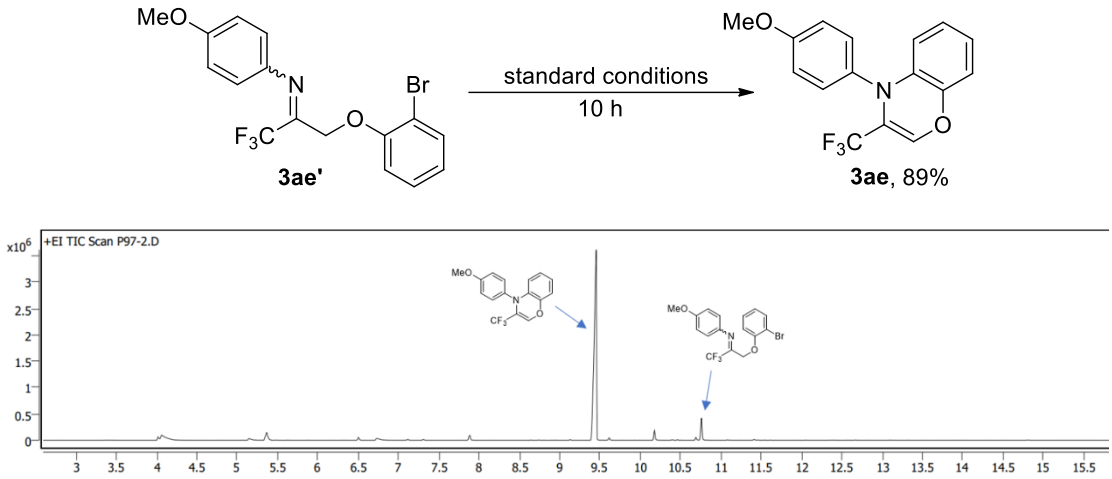


Figure S2 GC-MS of the reaction from **3ae'** after 10 hours.

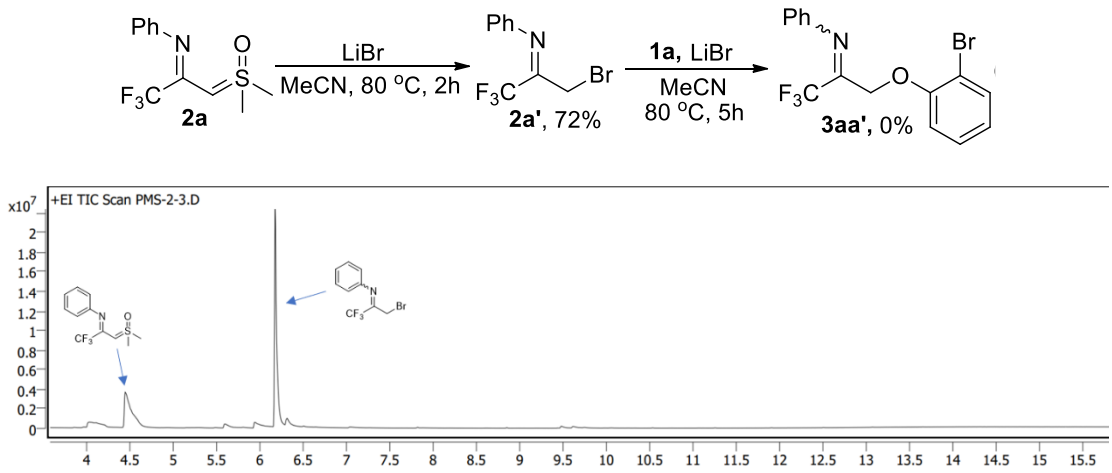


Figure S3 GC-MS of the reaction of **2a** and LiBr

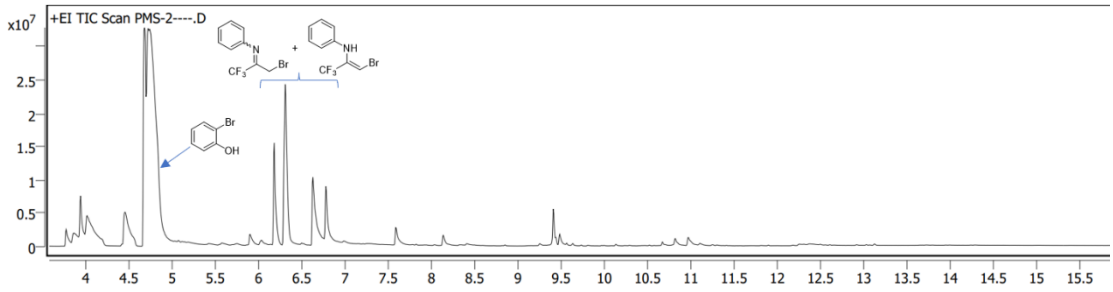
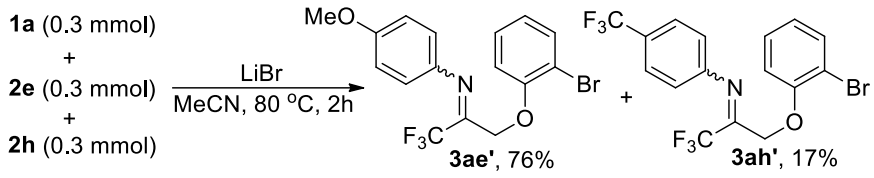


Figure S4 GC-MS of the reaction of **1a** and **2a'**



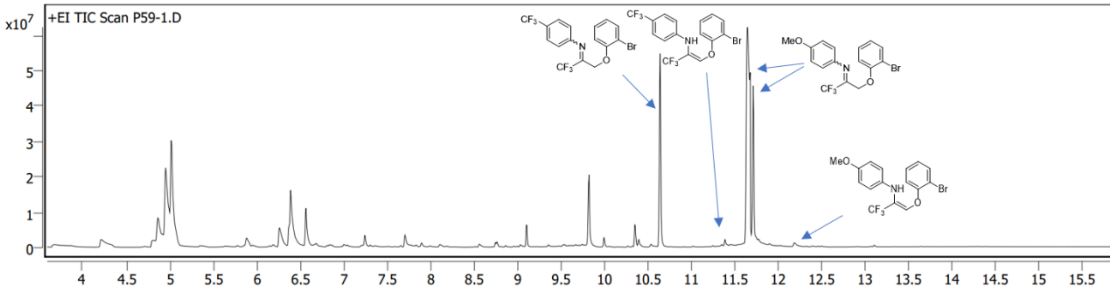
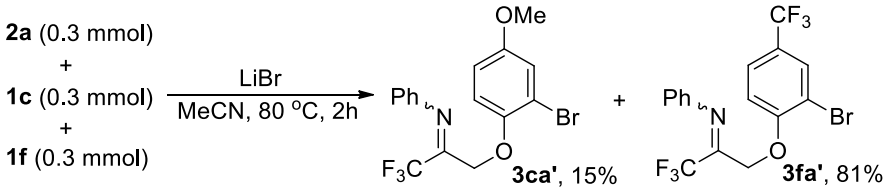


Figure S5 GC-MS of the competition reaction of **2e** and **2h**.



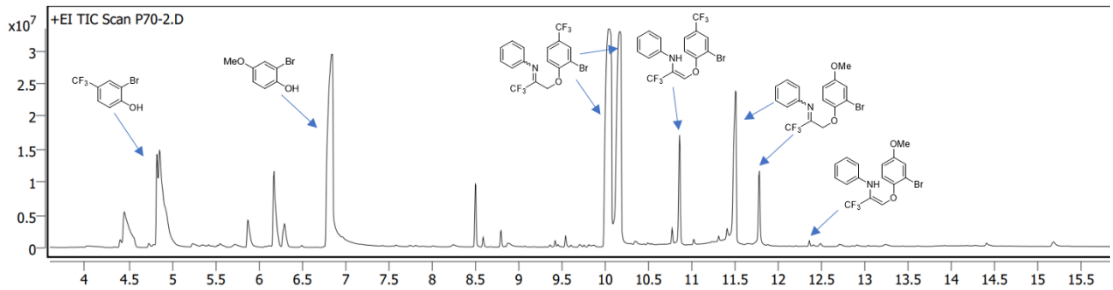
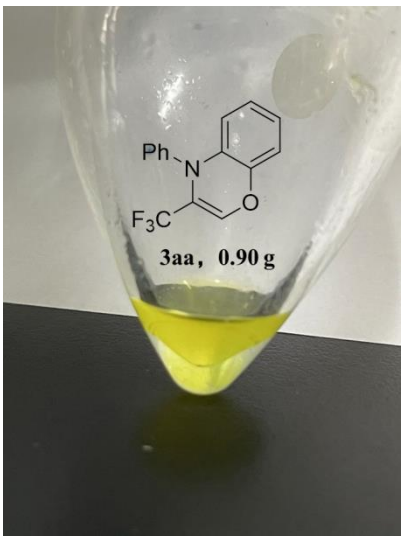


Figure S6 GC-MS of the competition reaction of **1c** and **1f**.

Gram-scale reaction and derivatization of 3aa

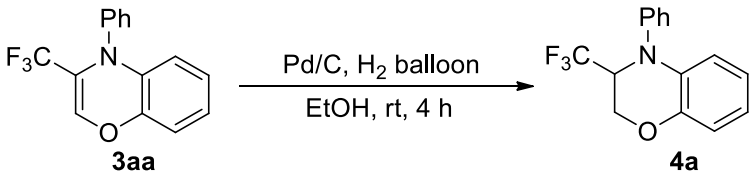
Details of the gram reaction

Under N_2 atmosphere, 2-bromophenol **1a** (0.86 g, 5.0 mmol), (*E*)-3-(dimethyl(oxo)-λ6-sulfanylidene)-1,1,1-trifluoro-*N*-phenylpropan-2-imine **2a** (1.32 g, 5.0 mmol), LiBr (0.43 g, 100 mol %), and dry MeCN (20.0 mL) were added in a 100 mL Schlenk tube. Then the mixture was stirred at 80 °C for 3 hours and cooled down to room temperature. After removing the solvent under vacuum, $Pd(OAc)_2$ (33.6 mg, 3 mol %), tri-*tert*-butylphosphine (60.0 mg, 6 mol %), NaOH (200.0 mg, 100 mol %) and toluene (20 mL) were added successively. Then, the resulting mixture was stirred at 100 °C for 20 h under N_2. After cooled to room temperature, the mixture was concentrated and the residue was purified by flash chromatography (petroleum ether) to give 4-phenyl-3-(trifluoromethyl)-*4H*-benzo[*b*][1,4]oxazine **3aa** (0.90 g, 65% yield) as light yellow oil.



Derivatization of 3aa

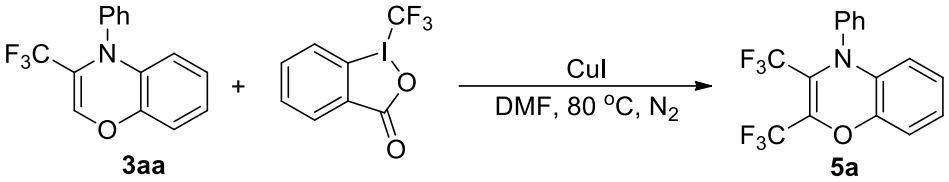
1. Synthesis of 4a



3aa (55.4 mg, 0.2 mmol), Pd/C (60 % wet; 10 wt %, 10 mg) and EtOH (3 mL) were

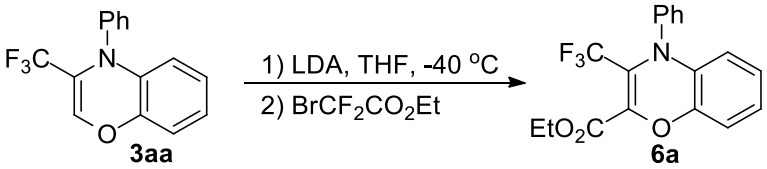
added in a flask (25 mL) which was equipped with a hydrogen balloon and stirred for 4 hours under room temperature. Then, the mixture was filtered under reduced pressure. The filtrate was concentrated under vacuum, and the resulting residue was purified by layer chromatography on silica gel with petroleum ether to give the oil product **4a** (51.9 mg, 93%).

2. Synthesis of 5a



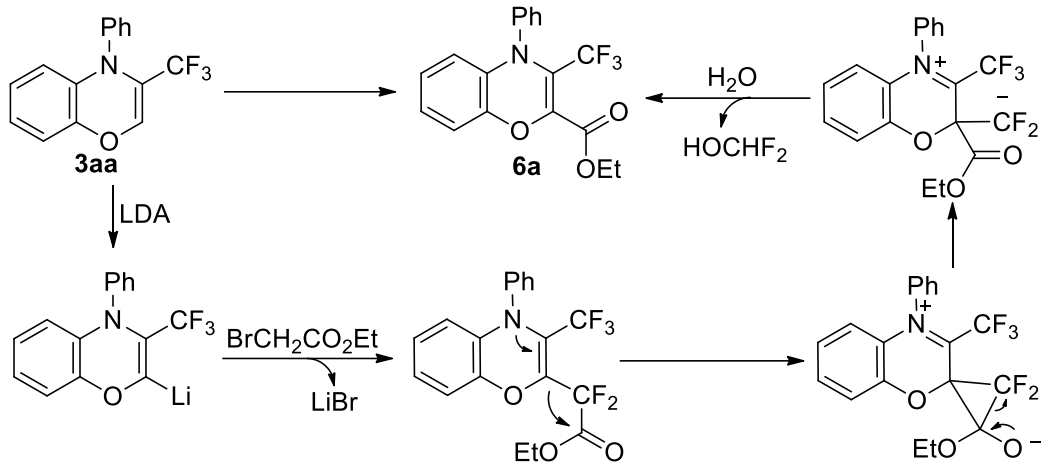
Under N_2 atmosphere, CuI (0.02 mmol, 3.8 mg), anhydrous DMF (1.5 mL), Togni reagent (0.3 mmol, 94.8 mg), **3aa** (0.2 mmol, 55.4 mg) were added in a Schlenk tube (25 mL). Then, the Schlenk tube was closed and stirred for 20 h under 80 °C until the disappearance of substrate **3aa** as indicated by TLC. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified with silica gel chromatography (petroleum ether) to give the colorless oil **5a** (46.9 mg, 68%).

3. Synthesis of 6a



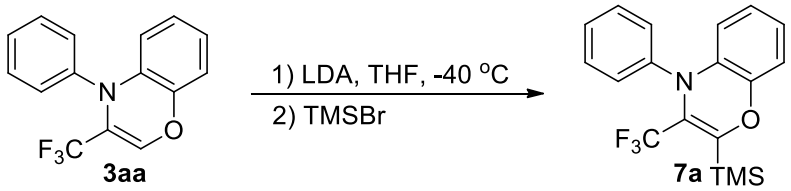
Under N_2 atmosphere, to a cold (-40 ℃) solution of **3aa** (0.2 mmol, 55.4 mg) in dry THF (2 mL) was added a solution of LDA 2 M in heptane/THF (0.4 mmol, 0.2 mL) in a Schlenk tube (25 mL). The reaction solution was stirred at -40 ℃ for 35 min and ethyl bromodifluoroacetate (0.3 mmol, 60.6 mg) were added. After 20 hours, the resulting mixture was treated with a solution of saturated ammonium chloride solution, and allowed to warm to room temperature, which was extracted with EtOAc. The

organic layer was dried over $MgSO_4$ and concentrated. The residue was purified with silica gel chromatography (petroleum ether/EtOAc = 20: 1) to give the colorless oil compound **6a** (37.0 mg, 53%).



Scheme S2. Possible mechanism of the synthesis of **6a** from **3aa**

4. Synthesis of 7a



Under N_2 atmosphere, to a cold (-40 ℃) solution of **3aa** (0.2 mmol, 1.0 equiv) in dry THF (2 mL) was added a solution of LDA 2 M in heptane/THF (0.4 mmol, 0.2 mL) in a Schlenk tube (25 mL). The reaction solution was stirred at -40 ℃ for 35 min and bromotrimethylsilane (0.3 mmol, 45.9 mg) were added. After 20 hours, the resulting mixture was treated with a solution of saturated ammonium chloride solution, and allowed to warm to room temperature, which was extracted with EtOAc. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified with silica gel chromatography (Petroleum ether) to give the yellow oil product **7a** (62.1 mg, 89%).

Single crystal X-ray diffraction of 3ga

Colorless and transparent block-like single crystals of **3ga** were grown by layering a dichlormethane solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on an Agilent Gemini E diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 293 K, using the ω - and φ - scans to a maximum θ value of 27.48°. The data were refined by full-matrix least-squares techniques on F^2 with OLEX-2. And the structures were solved by direct methods OLEX-2. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.

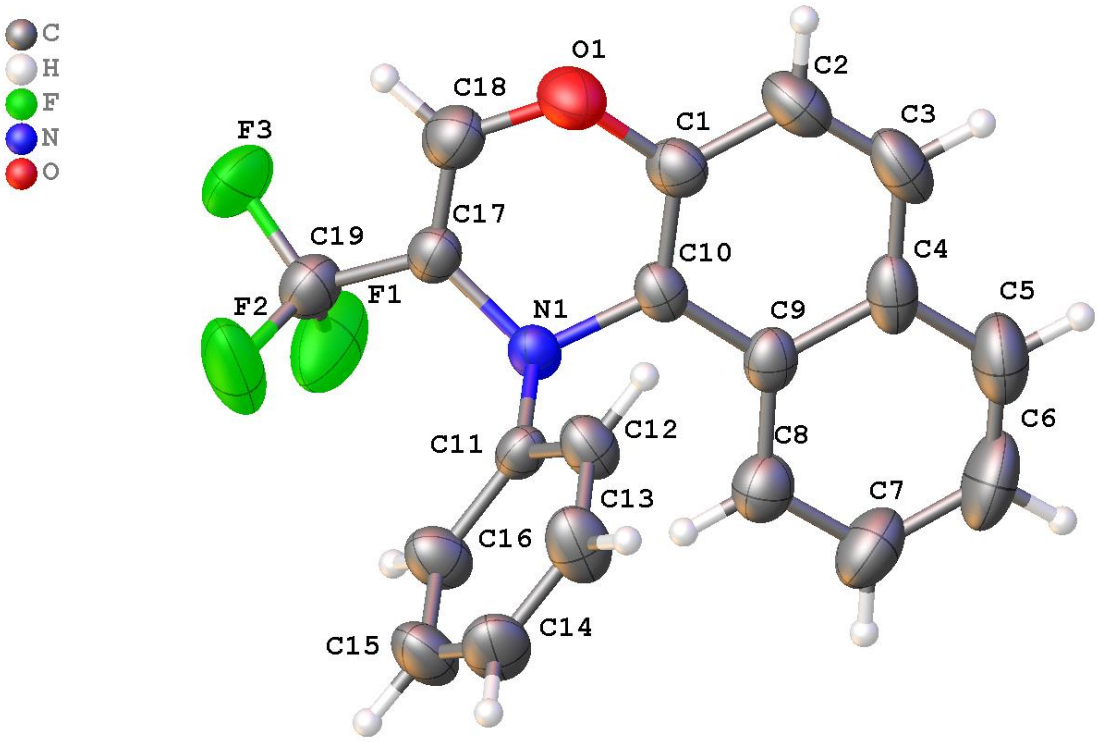


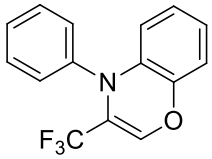
Figure S7. ORTEP drawing of **3ga** (CCDC 2193498) obtained by single-crystal X-ray diffraction studies with the ellipsoid contour at 30% probability levels.

Table S4. Crystal data and structure refinement for 3ga.

Identification code	**3ga**
Empirical formula	$C_{19}H_{12}F_3NO$
Formula weight	327.30
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P $2_1/n$
a/Å	7.2901(13)
b/Å	7.7946(13)
c/Å	26.574(4)
α/°	90
β/°	95.936(15)
γ/°	90
Volume/Å^3	1501.9(4)
Z	4
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	0.115
F(000)	672.0
Crystal size/mm^3	0.2 × 0.19 × 0.18
Radiation	Mo Kα (λ = 0.71073 Å)
2θ range for data collection/°	5.448 to 58.572
Index ranges	$-7 \leq h \leq 10$, $-9 \leq k \leq 9$, $-36 \leq l \leq 26$
Reflections collected	8471
Independent reflections	3506 [R_{int} = 0.0595, R_{sigma} = 0.1097]
Data/restraints/parameters	3506/0/217
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0776, wR_2 = 0.1367
Final R indexes [all data]	R_1 = 0.1837, wR_2 = 0.1780
Largest diff. peak/hole / e Å^{-3}	0.19/-0.23

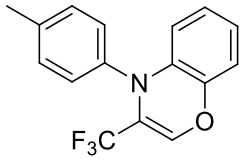
Analytic data of the obtained compounds

(1) 4-phenyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3aa)



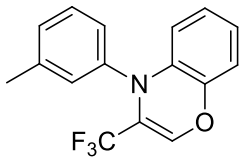
Yellow oil (71.4 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.77-6.68 (m, 2H), 6.66-6.61 (m, 1H), 6.59 (s, 1H), 6.30 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.78, 144.98, 135.44, 134.30 (q, J_{C-F} = 7.1 Hz), 130.05, 129.81, 127.92, 124.85, 124.03, 121.26 (q, J_{C-F} = 272.7 Hz), 119.53 (q, J_{C-F} = 32.3 Hz), 119.40, 115.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.35; MS (EI, m/z): 277 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{10}F_3NO$ $[M+H]^+$: 278.0787; found: 278.0786.

(2) 4-(p-tolyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ab)



Yellow solid (71.6 mg, 82% yield); m.p: 36-37 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.74-6.66 (m, 2H), 6.60 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.54 (s, 1H), 6.26 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.61, 142.06, 137.81, 135.63, 133.73 (q, J_{C-F} = 7.1 Hz), 130.41, 129.85, 124.76, 123.77, 121.24 (q, J_{C-F} = 272.7 Hz), 119.59 (q, J_{C-F} = 32.3 Hz), 119.02, 115.85, 21.17. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.34; MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO$ $[M+H]^+$: 292.0944; found: 292.0940.

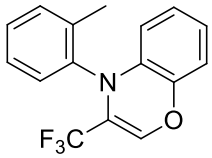
(3) 4-(m-tolyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ac)



Yellow solid (66.3 mg, 76% yield); m.p: 55-56 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.76-6.67 (m, 2H), 6.62 (dd, *J* = 7.2 Hz,

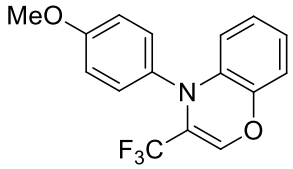
2.0 Hz, 1H), 6.58 (q, *J* = 1.2 Hz, 1H), 6.31 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ145.83, 144.96, 139.80, 135.52, 134.27 (q, J_{C-F} = 7.1 Hz), 130.43, 129.45, 128.67, 126.96, 124.80, 123.92, 121.25 (q, J_{C-F} = 272.7 Hz), 119.64 (q, J_{C-F} = 32.3 Hz), 119.44, 115.92, 21.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.40; MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO$ $[M+H]^+$: 292.0944; found: 292.0940.

(4) 4-(o-tolyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ad)



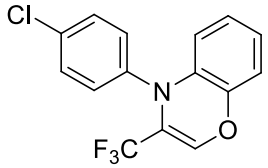
Yellow oil (69.8 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 1H), 7.31-7.25 (m, 3H), 6.68-6.59 (m, 2H), 6.54 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.37 (s, 1H), 5.92 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.67, 140.20, 139.06, 134.88, 131.82 (q, J_{C-F} = 7.1 Hz), 131.80, 131.62, 128.62, 127.32, 124.79, 123.25, 121.07 (q, J_{C-F} = 272.7 Hz), 118.88 (q, J_{C-F} = 32.3 Hz), 116.33, 115.69, 17.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.95; MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO$ $[M+H]^+$: 292.0944; found: 292.0940.

(5) 4-(4-methoxyphenyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ae)



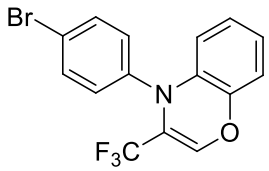
Yellow solid (79.2 mg, 86% yield); m.p: 42-43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.74-6.65 (m, 2H), 6.58 (dd, *J* = 7.2 Hz, 2.0 Hz, 1H), 6.49 (s, 1H), 6.20 (dd, *J* = 7.2 Hz, 2.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.96, 145.35, 136.91, 135.79, 133.13 (q, J_{C-F} = 7.1 Hz), 131.39, 124.73, 123.62, 121.22 (q, J_{C-F} = 272.7 Hz), 119.58 (q, J_{C-F} = 32.3 Hz), 118.60, 115.81, 114.87, 55.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.33; MS (EI, m/z): 307 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO_2$ $[M+H]^+$: 308.0893; found: 308.0891.

(6) 4-(4-chlorophenyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3af)



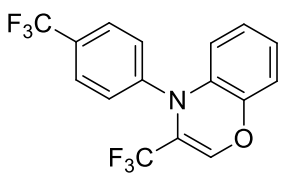
Colourless oil (71.8 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.34 (m, 4H), 6.83-6.70 (m, 2H), 6.65 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.62 (s, 1H), 6.29 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.84, 143.72, 134.98, 134.80 (q, J_{C-F} = 7.1 Hz), 133.67, 131.30, 130.04, 124.94, 124.37, 121.15 (q, J_{C-F} = 272.7 Hz), 119.50, 119.25 (q, J_{C-F} = 32.3 Hz), 116.14. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.38; MS (EI, m/z): 311 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_9ClF_3NO$ $[M+H]^+$: 312.0398; found: 312.0393.

(7) 4-(4-bromophenyl)-3-(trifluoromethyl)-4H-benzo[b][1,4]oxazine (3ag)



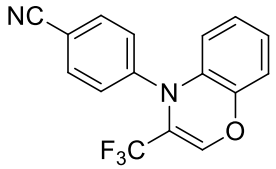
Colourless oil (72.4 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.36-7.32 (m, 2H), 6.80-6.72 (m, 2H), 6.65 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.63 (s, 1H), 6.30 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.84, 143.28, 133.89 (q, J_{C-F} = 7.1 Hz), 131.99, 130.55, 128.71, 123.90, 123.36, 120.64, 120.10 (q, J_{C-F} = 272.7 Hz), 118.53, 118.31 (q, J_{C-F} = 32.3 Hz), 115.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.37; MS (EI, m/z): 355 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_9BrF_3NO$ $[M+H]^+$: 355.9892; found: 355.9884.

(8) 3-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-*4H*-benzo[b][1,4]oxazine (3ah)



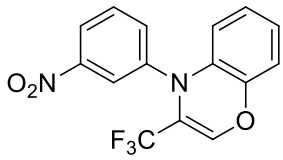
Colourless oil (75.5 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.88-6.74 (m, 3H), 6.72 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.44 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.05, 146.62, 136.60 (q, J_{C-F} = 7.1 Hz), 134.53, 129.61 (q, J_{C-F} = 32.3 Hz), 129.46, 126.94 (q, J_{C-F} = 4.0 Hz), 125.08, 124.94, 123.84 (q, J_{C-F} = 272.7 Hz), 120.41, 119.19 (q, J_{C-F} = 32.3 Hz), 116.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47, -65.37; MS (EI, m/z): 345 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_9F_6NO$ $[M+H]^+$: 346.0661; found: 346.0659.

(9) 4-(3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazin-4-yl)benzonitrile (3ai)



Yellow oil (52.5 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.96-6.83 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.46, 147.50, 138.59 (q, J_{C-F} = 7.1 Hz), 133.99, 133.72, 128.59, 125.55, 125.23, 121.26, 121.10 (q, J_{C-F} = 272.7 Hz), 119.02 (q, J_{C-F} = 32.3 Hz), 118.26, 116.66, 110.80. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.23; MS (EI, m/z): 302 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_9F_3N_2O$ $[M+H]^+$: 303.0740; found: 303.0736.

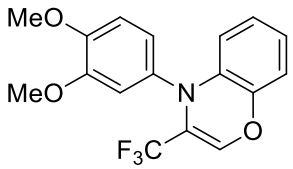
(10) 4-(3-nitrophenyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3aj)



Red brown oil (69.5 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (t, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 2.4Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 6.92-6.80 (m, 3H), 6.76 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.47 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.16, 146.34, 145.61, 136.17 (q, J_{C-F} = 7.1 Hz), 134.46, 133.08, 129.53, 124.29, 124.21, 123.23, 121.53, 120.06 (q, J_{C-F} = 272.7 Hz), 119.55, 117.79 (q, J_{C-F} = 33.3 Hz), 115.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -

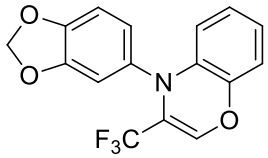
65.40; MS (EI, m/z): 322 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_9F_3N_2O_3$ $[M+H]^+$: 323.0638; found: 323.0632.

(11) 4-(3,4-dimethoxyphenyl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ak)



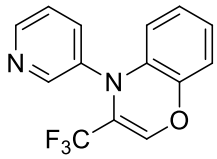
Yellow solid (81.9 mg, 81% yield); m.p: 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.75-6.66 (m, 2H), 6.59 (dd, *J* = 7.2 Hz, 2.4 Hz, 1H), 6.50 (s, 1H), 6.25 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.75, 148.71, 145.25, 136.97, 135.61, 133.17 (q, J_{C-F} = 7.1 Hz), 124.77, 123.70, 122.69, 121.23 (q, J_{C-F} = 272.7 Hz), 119.51 (q, J_{C-F} = 32.3 Hz), 118.56, 115.84, 113.01, 111.25, 56.05, 55.93. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.35; MS (EI, m/z): 337 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{14}F_3NO_3$ $[M+H]^+$: 338.0999; found: 338.0994.

(12) 4-(benzo[d][1,3]dioxol-5-yl)-3-(trifluoromethyl)-4H-benzo[b][1,4]oxazine (3al)



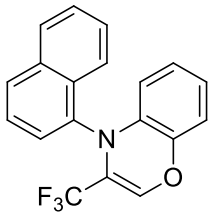
Yellow oil (75.1 mg, 78% yield); m.p: 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.90 (m, 2H), 6.83-6.78 (m, 1H), 6.77-6.68 (m, 2H), 6.64-6.57 (m, 1H), 6.53 (s, 1H), 6.34-6.27 (m, 1H), 5.99 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.50, 147.19, 145.48, 138.63, 135.46, 133.77 (q, J_{C-F} = 7.1 Hz), 124.81, 123.94, 123.91, 121.79 (q, J_{C-F} = 272.7 Hz), 119.45 (q, J_{C-F} = 32.3 Hz), 119.11, 115.93, 110.68, 108.57, 101.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.43; MS (EI, m/z): 321 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{10}F_3NO_3$ $[M+H]^+$: 322.0686; found: 322.0683.

(13) 4-(pyridin-3-yl)-3-(trifluoromethyl)-4H-benzo[b][1,4]oxazine (3am)



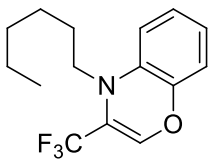
Yellow oil (38.4 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.59 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 6.87-6.74 (m, 2H), 6.74-6.65 (m, 2H), 6.33 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.37, 148.67, 146.11, 141.77, 137.34, 135.66 (q, $J_{C\text{-}F}$ = 7.1 Hz), 134.54, 125.13, 124.81, 124.46, 121.07 (q, $J_{C\text{-}F}$ = 272.7 Hz), 119.66, 118.94 (q, $J_{C\text{-}F}$ = 32.3 Hz), 116.36. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.36; MS (EI, m/z): 278 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_9F_3N_2O$ $[M+H]^+$: 279.0740; found: 279.0736.

(14) 4-(naphthalen-1-yl)-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3an)



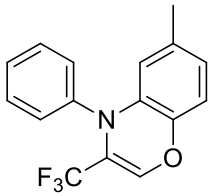
Yellow oil (63.7 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 9.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.60-7.48 (m, 3H), 6.72-6.60 (m, 2H), 6.58-6.48 (m, 2H), 6.01 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.01, 139.45, 135.70, 134.95, 132.96 (q, $J_{C\text{-}F}$ = 7.1 Hz), 132.71, 129.18, 128.96, 128.47, 127.20, 126.52, 126.03, 124.87, 123.70, 123.36, 121.15 (q, $J_{C\text{-}F}$ = 272.7 Hz), 119.97 (q, $J_{C\text{-}F}$ = 32.3 Hz), 117.33, 115.91. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.62; MS (EI, m/z): 327 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{12}F_3NO$ $[M+H]^+$: 328.0944; found: 328.0940.

(15) 4-hexyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ao)



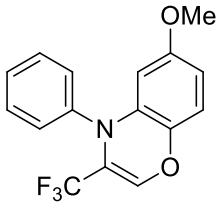
Colourless oil (60.7 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.85 (m, 1H), 6.79-6.74 (m, 1H), 6.68 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 6.61-6.52 (m, 2H), 3.24 (t, *J* = 8.0 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 2H), 1.31-1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.02, 136.23 (q, J_{C-F} = 7.1 Hz), 134.92, 124.99, 123.65, 121.75 (q, J_{C-F} = 272.7 Hz), 118.97 (q, J_{C-F} = 32.3 Hz), 118.49, 115.81, 52.20, 31.49, 26.45, 26.33, 22.58, 13.96. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.95; MS (EI, m/z): 285 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{18}F_3NO$ $[M+H]^+$: 286.1413; found: 286.1409.

(16) 6-methyl-4-phenyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ba)



Yellow solid (70.7 mg, 81% yield), m.p: 141-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.38 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.61 (s, 1H), 6.58-6.51 (m, 2H), 6.13 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 143.69, 134.93, 134.60 (q, J_{C-F} = 7.1 Hz), 134.55, 129.96, 129.73, 127.79, 124.33, 121.34 (q, J_{C-F} = 272.7 Hz), 120.13, 119.37 (q, J_{C-F} = 32.3 Hz), 115.65, 20.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.33; MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO$ $[M+H]^+$: 292.0944; found: 292.0939.

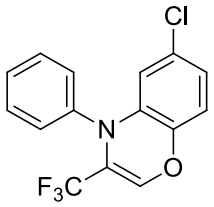
(17) 6-methoxy-4-phenyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3ca)



Yellow oil (76.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 4H), 7.36-7.30 (m, 1H), 6.59-6.53 (m, 2H), 6.25 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 5.84 (d, *J* = 2.8 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.62, 144.37, 139.45, 136.11, 134.13 (q, J_{C-F} = 7.1 Hz), 130.03, 129.78, 128.00, 121.33 (q, J_{C-F} = 272.7 Hz), 118.49 (q, J_{C-F} = 32.3 Hz), 116.04, 107.08, 106.05, 55.45. ^{19}F NMR (376 MHz, $CDCl_3$)

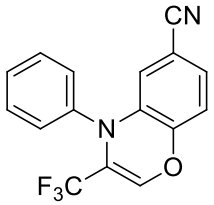
δ -65.11; MS (EI, m/z): 307 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO_2$ $[M+H]^+$: 308.0893; found: 308.0889.

(18) 6-chloro-4-phenyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3da)



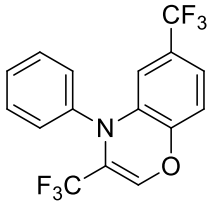
White solid (72.8, 78% yield) m.p: 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.36 (s, 5H), 6.72-6.65 (m, 1H), 6.56-6.49 (m, 2H), 6.23-6.13 (m, 1H), 6.80 (t, *J* = 2.8 Hz, 1H), 6.75 (t, *J* = 2.8 Hz, 1H), 6.38 (dd, *J* = 3.5, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.08, 143.42, 136.57, 133.56 (q, J_{C-F} = 7.1 Hz), 130.15, 130.08, 129.63, 128.47, 123.43, 121.01 (q, J_{C-F} = 272.7 Hz), 119.17 (q, J_{C-F} = 32.3 Hz), 118.59, 116.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.22; MS (EI, m/z): 311 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_9ClF_3NO$ $[M+H]^+$: 312.0398; found: 312.0395.

(19) 4-phenyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine-6-carbonitrile (3ea)



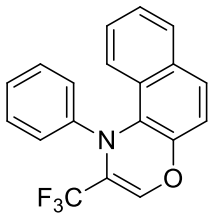
Yellow solid, 62% yield, m.p: 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.45-7.38 (m, 3H), 7.00 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 6.30 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.81, 141.89, 136.80, 132.23 (q, J_{C-F} = 7.1 Hz), 130.41, 130.24, 129.02, 128.51, 120.58, 120.57 (q, J_{C-F} = 272.7 Hz), 119.79 (q, J_{C-F} = 32.3 Hz), 118.18, 116.61, 108.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.31; MS (EI, m/z): 302 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_9F_3N_2O$ $[M+H]^+$: 303.0740; found: 303.0736.

(20) 4-phenyl-3,6-bis(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3fa)



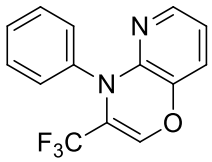
Yellow oil (77.6 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 4H), 7.42-7.36 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 6.39 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.06, 143.09, 136.20, 133.24 (q, $J_{C\text{-}F}$ = 7.1 Hz), 130.17, 130.11, 128.62, 127.23 (q, $J_{C\text{-}F}$ = 32.3 Hz), 123.43 (q, $J_{C\text{-}F}$ = 272.7 Hz), 120.81 (q, $J_{C\text{-}F}$ = 272.7 Hz), 121.16 (q, $J_{C\text{-}F}$ = 1.6 Hz), 119.81 (q, $J_{C\text{-}F}$ = 32.3 Hz), 116.11, 115.34 (q, $J_{C\text{-}F}$ = 1.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81, -65.39; MS (EI, m/z): 345 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_9F_6NO$ $[M+H]^+$: 346.0661; found: 346.0657.

(21) 1-phenyl-2-(trifluoromethyl)-*1H*-naphtho[2,1-b][1,4]oxazine (3ga)



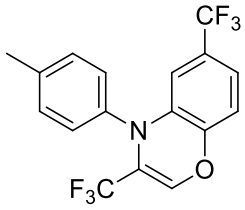
Yellow solid (70.6 mg, 72% yield) m.p: 115-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39-7.31 (m, 2H), 7.29-7.23 (m, 3H), 7.19-7.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.11, 148.89, 143.56 (q, $J_{C\text{-}F}$ = 6.1 Hz), 132.15, 129.31, 128.73, 128.04, 127.99, 127.05, 126.82, 126.49, 126.07, 125.21, 122.84, 122.76 (q, $J_{C\text{-}F}$ = 34.3 Hz), 121.94 (q, $J_{C\text{-}F}$ = 272.7 Hz), 116.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.49; MS (EI, m/z): 327 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{12}F_3NO$ $[M+H]^+$: 328.0944; found: 328.0940.

(22) 4-phenyl-3-(trifluoromethyl)-*4H*-pyrido[3,2-b][1,4]oxazine (3ha)



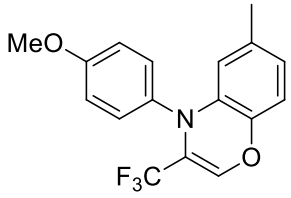
Yellow oil (58.4 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 5.2 Hz, 2.0 Hz, 1H), 7.40-7.33 (m, 4H), 7.30-7.24 (m, 1H), 6.69 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.52 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 6.37-6.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.81, 142.11, 140.49, 139.37, 131.47 (q, J_{C-F} = 7.1 Hz), 129.24, 128.28, 127.07, 121.07, 119.66 (q, J_{C-F} = 272.7 Hz), 118.81 (q, J_{C-F} = 32.3 Hz), 118.06. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.43; MS (EI, m/z): 278 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_9F_3N_2O$ $[M+H]^+$: 279.0740; found: 279.0737.

(23) 4-(p-tolyl)-3,6-bis(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3fb)



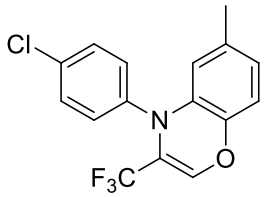
Colourless oil (81.8 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.46 (s, 1H), 6.35 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.92, 140.08, 138.62, 136.40, 132.74 (q, J_{C-F} = 7.1 Hz), 130.82, 129.89, 127.14 (q, J_{C-F} = 33.3 Hz), 123.47 (q, J_{C-F} = 272.7 Hz), 120.93 (q, J_{C-F} = 4.0 Hz), 120.82 (q, J_{C-F} = 272.7 Hz), 119.83 (q, J_{C-F} = 32.3 Hz), 115.99, 114.97 (q, J_{C-F} = 4.0 Hz), 21.23. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80, -65.33; MS (EI, m/z): 359 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{11}F_6NO$ $[M+H]^+$: 360.0818; found: 360.0814.

(24) 4-(4-methoxyphenyl)-6-methyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3be)



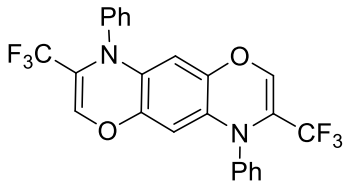
Yellow oil (80.9 mg, 84% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.56-6.45 (m, 3H), 6.03 (s, 1H), 3.81 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.91, 143.22, 137.19, 135.28, 134.46, 133.40 (q, J_{C-F} = 7.1 Hz), 131.37, 123.93, 121.36 (q, J_{C-F} = 272.7 Hz), 119.38, 119.35 (q, J_{C-F} = 32.3 Hz), 115.52, 114.84, 55.39, 20.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.26; MS (EI, m/z): 321 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{14}F_3NO_2$ $[M+H]^+$: 322.1049; found: 322.1048.

(25) 4-(4-chlorophenyl)-6-methyl-3-(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (3bf)



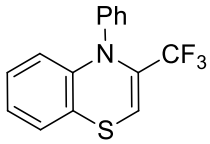
Yellow oil (74.1 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4H), 6.63 (d, *J* = 1.2 Hz, 1H), 6.60-6.53 (m, 2H), 6.11 (d, *J* = 1.2 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.99, 143.67, 135.03 (q, J_{C-F} = 7.1 Hz), 134.72, 133.55, 131.29, 130.01, 124.67, 121.25 (q, J_{C-F} = 272.7 Hz), 120.21, 119.01 (q, J_{C-F} = 32.3 Hz), 115.82, 20.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.32; MS (EI, m/z): 325 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{17}ClF_3NO$ $[M+H]^+$: 326.0554; found: 326.0552.

(26) 4,9-diphenyl-3,8-bis(trifluoromethyl)-4,9-dihydrobenzo[1,2-b:4,5-b']bis([1,4] oxazine) (3ia)



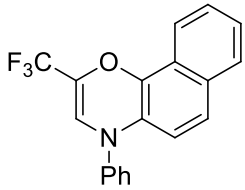
Yellow solid (98.5 mg, 69% yield); m.p: 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.37 (m, 8H), 7.36-7.32 (m, 2H), 6.47 (s, 2H), 5.70 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.79, 141.95, 133.95 (q, J_{C-F} = 7.1 Hz), 130.88, 129.86, 129.60, 128.07, 120.97 (q, J_{C-F} = 272.7 Hz), 118.71 (q, J_{C-F} = 32.3 Hz), 107.48. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.43; HRMS (ESI): Calcd. for $C_{24}H_{14}F_6N_2O_2$ $[M+H]^+$: 477.1032; found: 477.1032.

(27) 1-phenyl-2-(trifluoromethyl)-*1H*-benzo[b][1,4]thiazine (3ja)



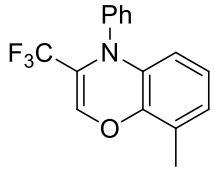
Yellow oil (59.6 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 4H), 7.22-7.17 (m, 1H), 7.15-7.11 (m, 1H), 7.09-7.05 (m, 1H), 7.05-6.97 (m, 2H), 6.77 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.65, 143.38, 132.62 (q, J_{C-F} = 33.3 Hz), 129.38, 128.20, 127.90, 127.28, 125.78, 125.44, 125.15, 124.11, 120.08 (q, J_{C-F} = 275.7 Hz), 119.13 (q, J_{C-F} = 4.04 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.86; MS (EI, m/z): 293 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{10}F_3NS$ $[M+H]^+$: 294.0559; found: 294.0556. The compound was purified by preparative TLC on silica, eluting with mixed solvent (petroleum ether: ethyl acetate = 10: 1) to give the desired product.

(28) 4-phenyl-2-(trifluoromethyl)-4H-naphtho[1,2-b][1,4]oxazine (3ka)



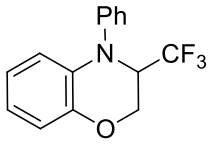
Yellow solid (73.6 mg, 75% yield); m.p: 54-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.59-7.52 (m, 2H), 7.47-7.38 (m, 3H), 7.37-7.26 (m, 3H), 6.91 (d, *J* = 1.2 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.05, 140.11, 136.60 (q, J_{C-F} = 7.1 Hz), 131.18, 130.42, 129.81, 129.78, 127.74, 127.51, 126.66, 125.44, 124.40, 123.67, 121.42 (q, J_{C-F} = 273.7 Hz), 120.51 (q, J_{C-F} = 32.3 Hz), 120.37, 120.28. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.82; MS (EI, m/z): 327 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{12}F_3NO$ $[M+H]^+$: 328.0944; found: 328.0938.

(29) 8-methyl-4-phenyl-3-(trifluoromethyl)-4H-benzo[*b*][1,4]oxazine (3la)



White solid (58.5 mg, 67% yield); m.p: 33-34 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.37 (m, 4H), 7.36-7.28 (m, 1H), 6.67 (s, 1H), 6.65-6.56 (m, 2H), 6.26-6.11 (m, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.55, 144.23, 135.15, 134.70 (q, J_{C-F} = 7.1 Hz), 129.80, 129.66, 127.66, 125.89, 125.56, 123.94, 121.30 (q, J_{C-F} = 273.7 Hz), 119.55 (q, J_{C-F} = 32.3 Hz), 117.41, 15.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.49; MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3NO$ $[M+H]^+$: 292.0944; found: 282.0938.

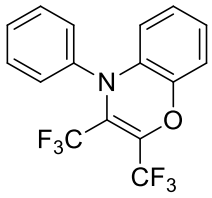
(30) 1-phenyl-2-(trifluoromethyl)-2,3-dihydro-*1H*-benzo[b][1,4]oxazine (4a)



Yellow oil (51.9 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.35-7.28 (m, 2H), 7.23-7.17 (m, 1H), 6.97-6.90 (m, 1H), 6.85-6.73 (m, 3H), 4.68-4.61 (m, 1H), 4.11-4.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.60, 143.18, 129.37, 128.86, 124.50, 124.18, 123.72 (q, J_{C-F} = 284.8 Hz), 120.63, 119.86, 117.80,

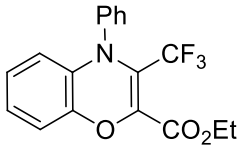
116.23, 59.43 (q, J_{C-F} = 3.0 Hz), 59.19 (q, J_{C-F} = 30.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.42; MS (EI, m/z): 279 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{12}F_3NO$ $[M+H]^+$: 280.0944; found: 280.0942.

(31) 4-phenyl-2,3-bis(trifluoromethyl)-*4H*-benzo[b][1,4]oxazine (5a)



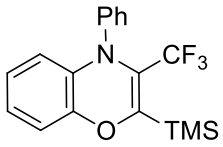
Yellow oil (46.9 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 6.98-6.81 (m, 4H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.74, 144.87, 138.32 (qq, J_{C-F} = 39.4 Hz, 2.0 Hz), 133.02, 128.74, 126.58, 126.50, 124.67, 122.23 (qq, J_{C-F} = 37.4 Hz, 2.0 Hz), 120.28, 118.96 (q, J_{C-F} = 275.7 Hz), 117.65 (q, J_{C-F} = 273.7 Hz), 115.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.13, -66.13; MS (EI, m/z): 345 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_9F_6NO$ $[M+e]^-$: 345.0594; found: 345.0590.

(32) ethyl 1-phenyl-2-(trifluoromethyl)-*1H*-benzo[b][1,4]oxazine-3-carboxylate (6a)



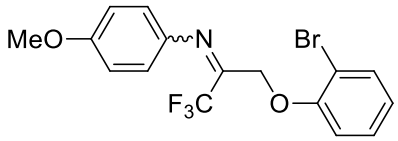
Colorless oil (37.0 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.28 (m, 1H), 6.90-6.81 (m, 3H), 6.76-6.69 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.77, 148.02, 145.87, 139.99 (q, J_{C-F} = 3.0 Hz), 134.33, 129.97, 129.70, 128.22, 127.54, 125.16, 122.90 (q, J_{C-F} = 35.4 Hz), 120.60 (q, J_{C-F} = 274.7 Hz), 120.57, 116.34, 62.51, 13.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.70; MS (EI, m/z): 349 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{14}F_3NO_3$ $[M+H]^+$: 350.0999; found: 350.0992.

(33) 1-phenyl-2-(trifluoromethyl)-3-(trimethylsilyl)-*1H*-benzo[b][1,4]oxazine (7a)



Colorless oil (62.1 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 6.88-6.78 (m, 2H), 6.77-6.68 (m, 2H), 0.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54 (q, $J_{C\text{-}F}$ = 4.7 Hz), 150.66, 148.28, 137.11, 130.57, 129.18 (q, $J_{C\text{-}F}$ = 35.4 Hz), 128.37, 127.61, 125.78, 125.34, 123.21 (q, $J_{C\text{-}F}$ = 274.7 Hz), 122.25, 116.98, 0.02. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.10; MS (EI, m/z): 349 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{18}F_3NOSi$ $[M+H]^+$: 350.1183; found: 350.1177.

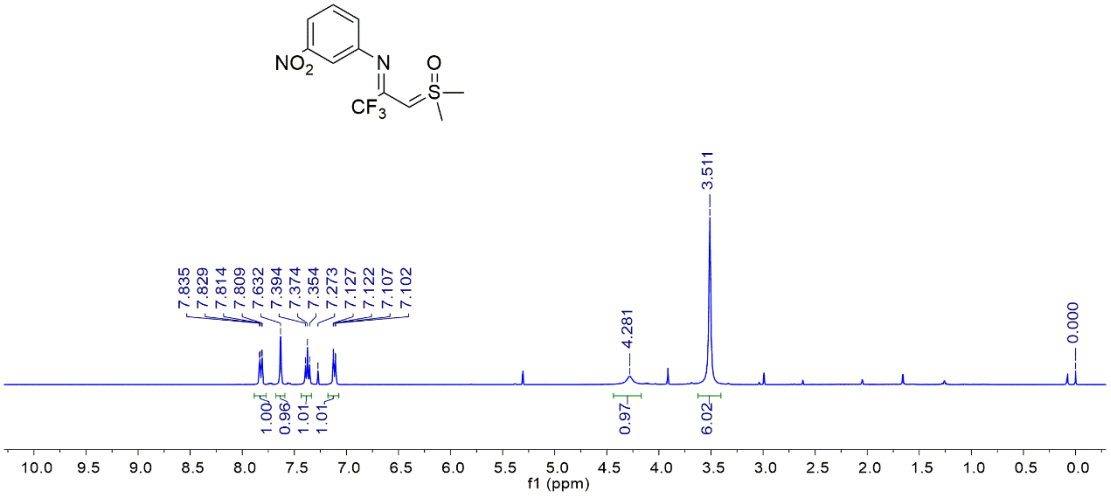
(34) *N*-(3-(2-bromophenoxy)-1,1,1-trifluoropropan-2-ylidene)-4-methoxy aniline (3ae')



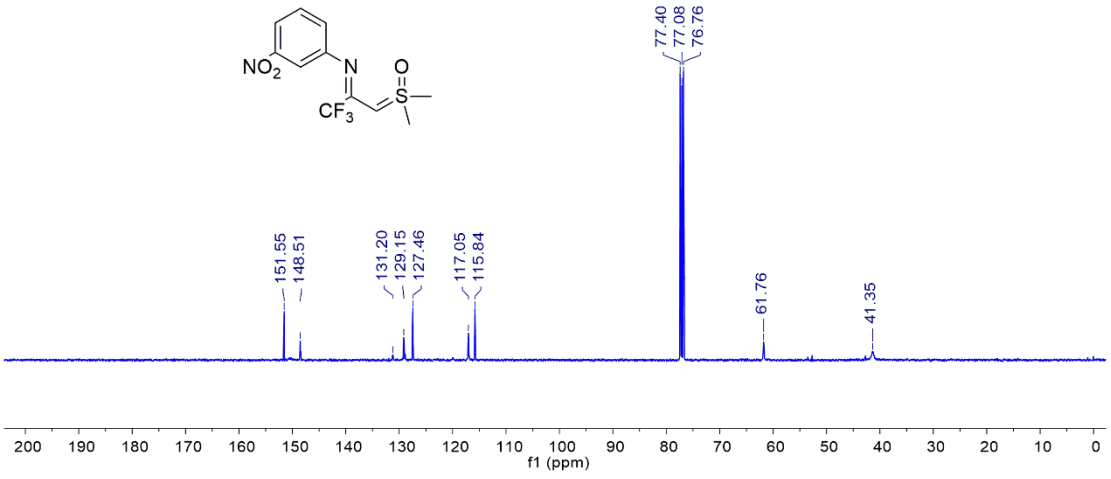
Yellow oil (95.2 mg, 82% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.25-7.18 (m, 1H), 7.05-6.97 (m, 2H), 6.94-6.86 (m, 3H), 6.72 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 4.70 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.58, 154.08, 152.52 (q, $J_{C\text{-}F}$ = 33.3 Hz), 138.94, 133.82, 128.50, 123.42, 122.05, 119.61 (q, $J_{C\text{-}F}$ = 274.7 Hz), 114.44, 113.54, 112.56, 61.78, 55.49. MS (EI, m/z): 387 $[M]^+$.

NMR spectra of the obtained compounds

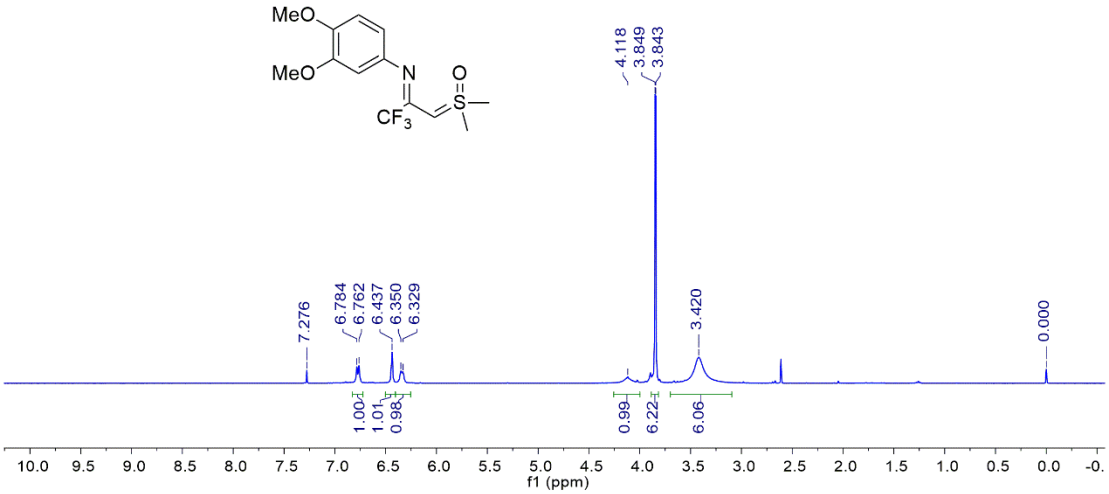
^{1}H-NMR spectrum of 2j



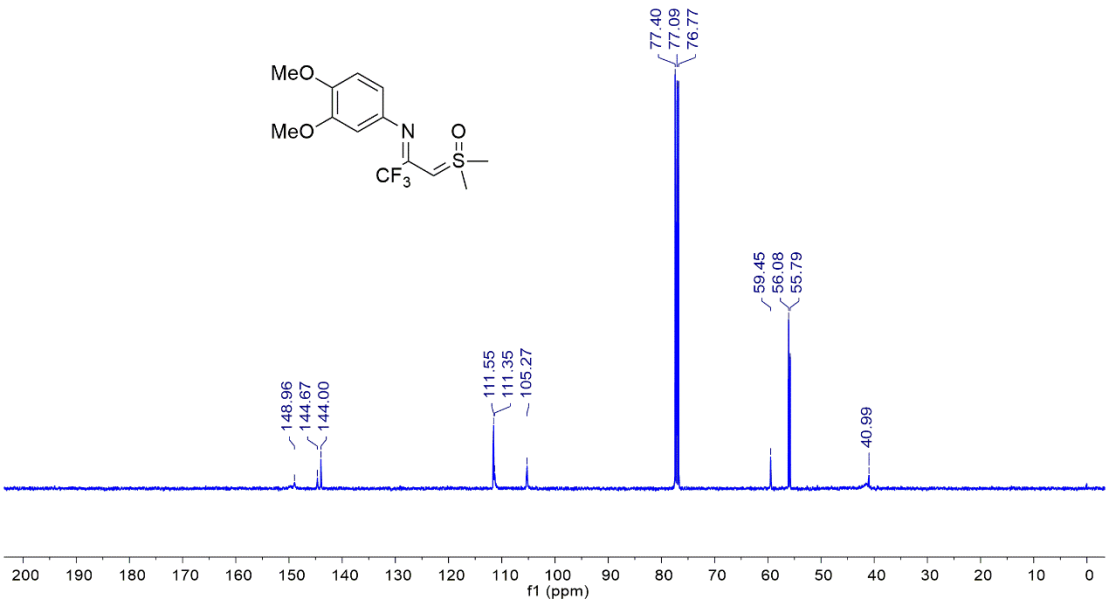
^{13}C-NMR spectrum of 2j



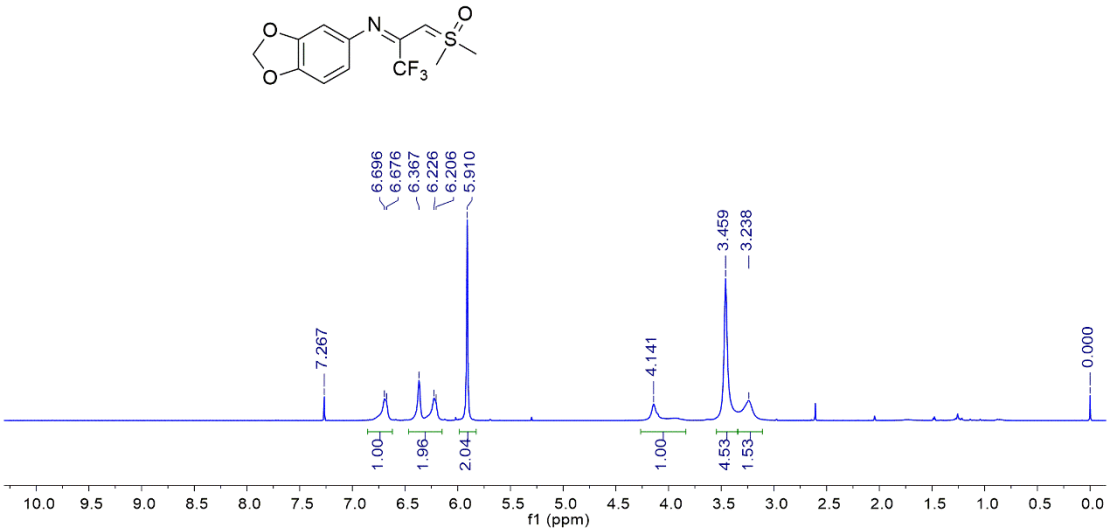
^{1}H-NMR spectrum of 2k



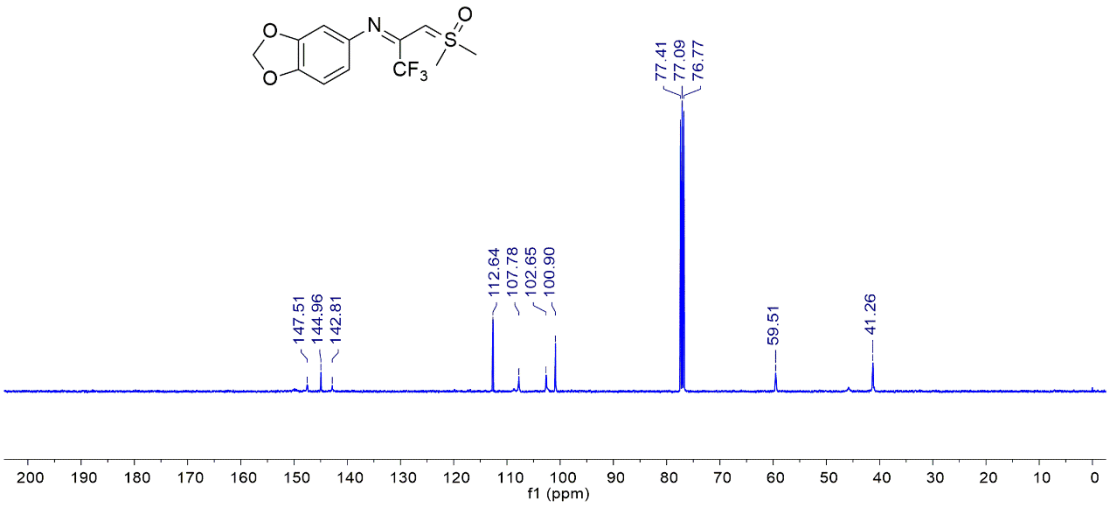
^{13}C-NMR spectrum of 2k



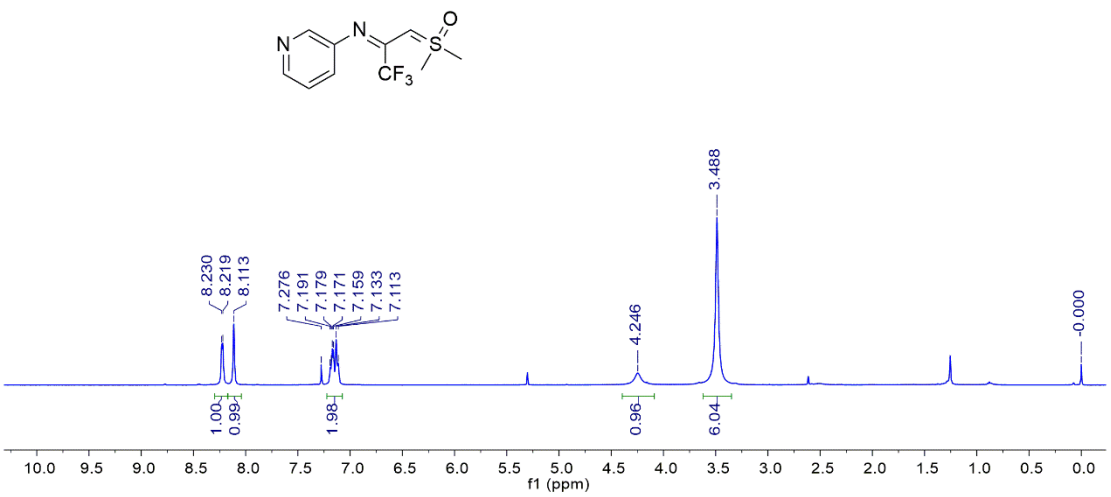
^{1}H-NMR spectrum of 2l



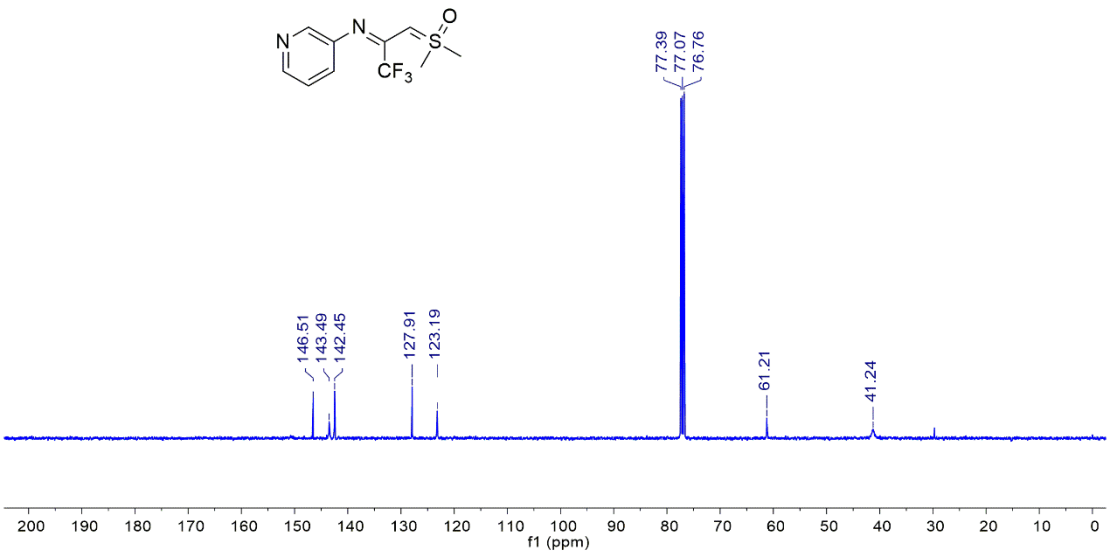
^{13}C-NMR spectrum of 2l



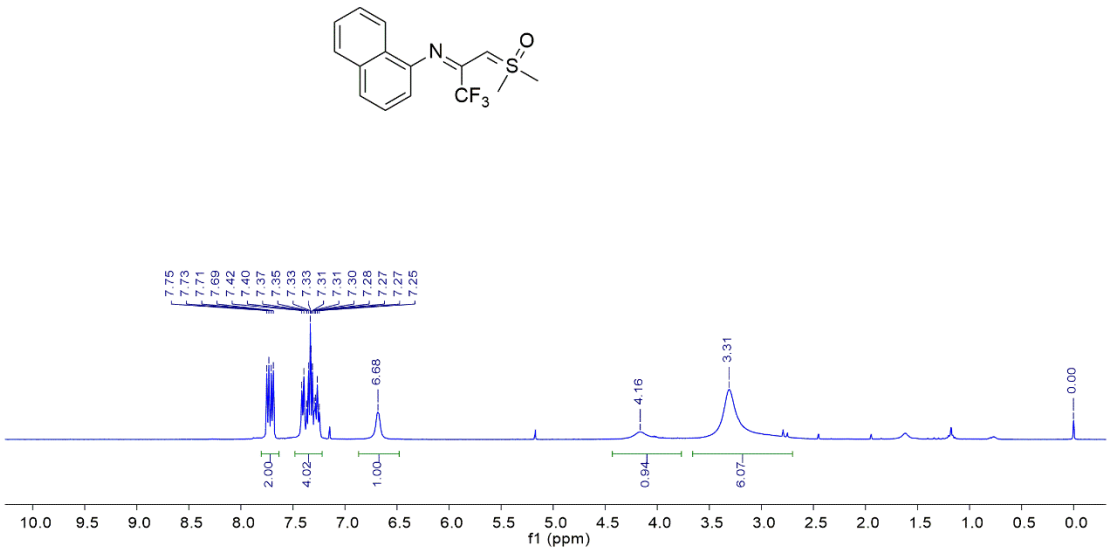
^{1}H-NMR spectrum of 2m



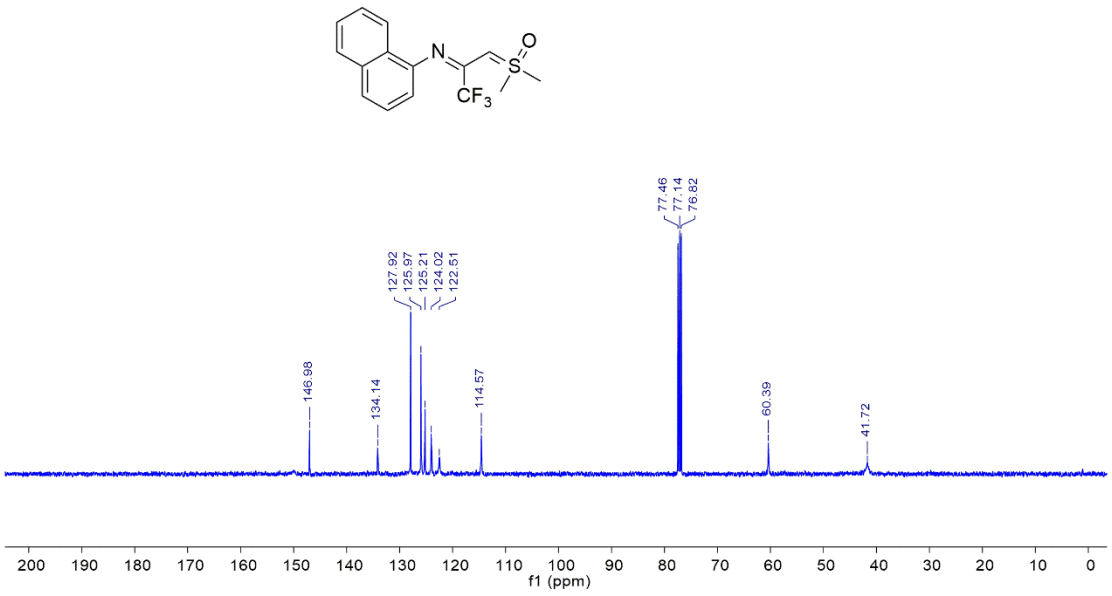
^{13}C-NMR spectrum of 2m



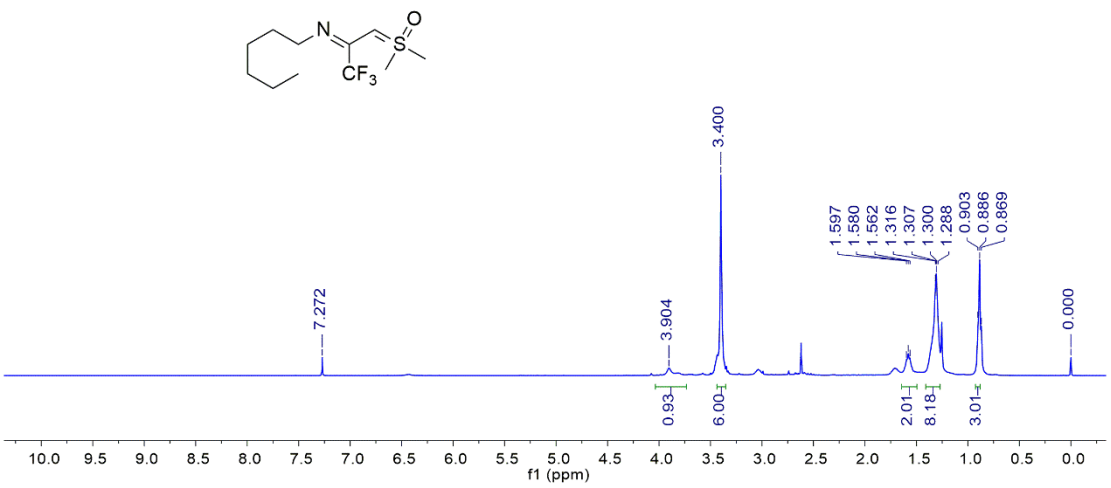
^{1}H-NMR spectrum of 2n



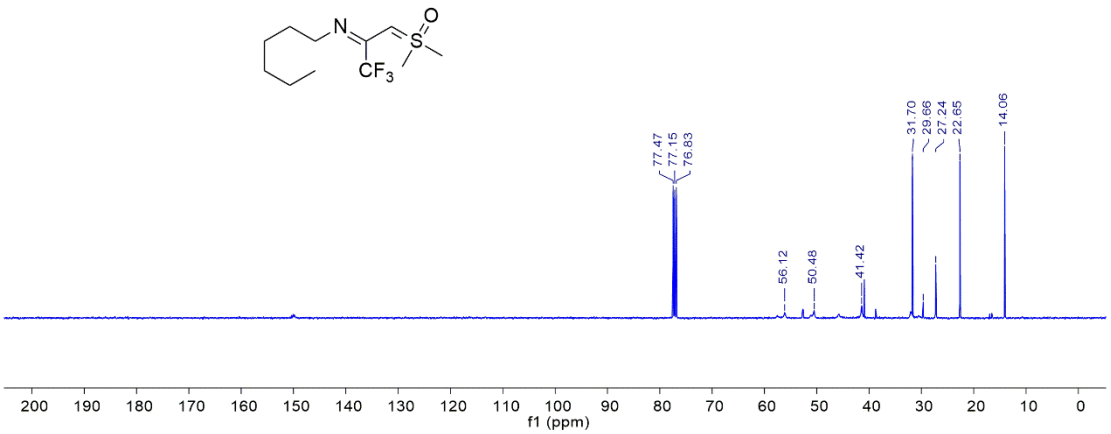
^{13}C-NMR spectrum of 2n



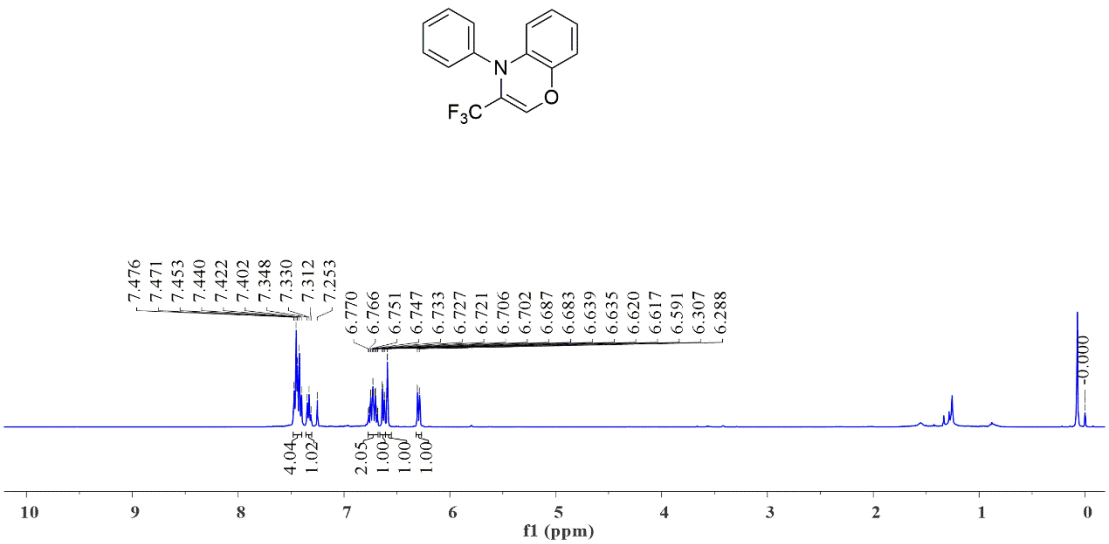
^{1}H-NMR spectrum of 2o



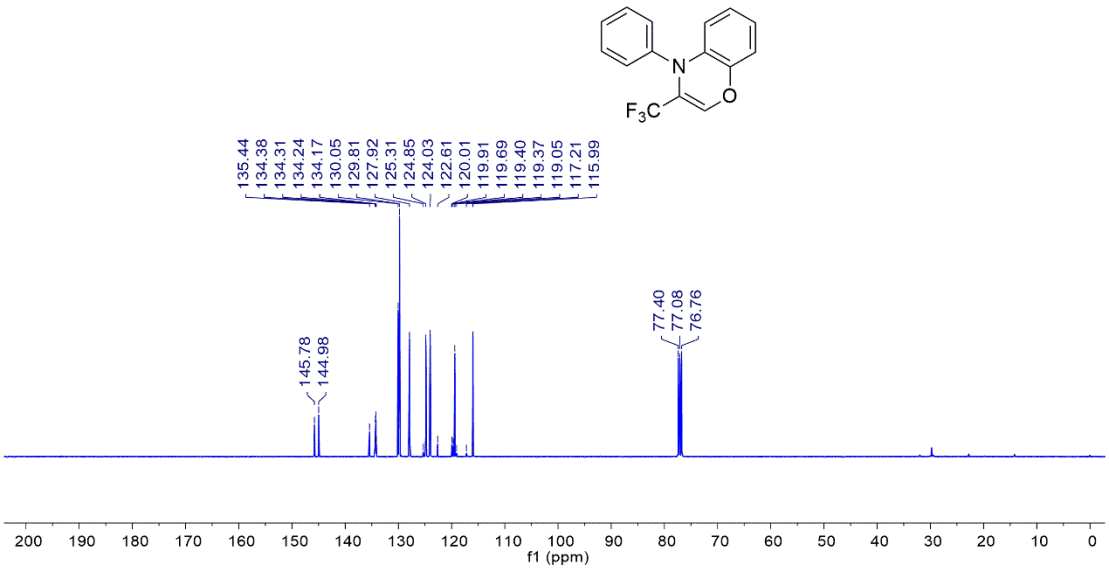
^{13}C-NMR spectrum of 2o



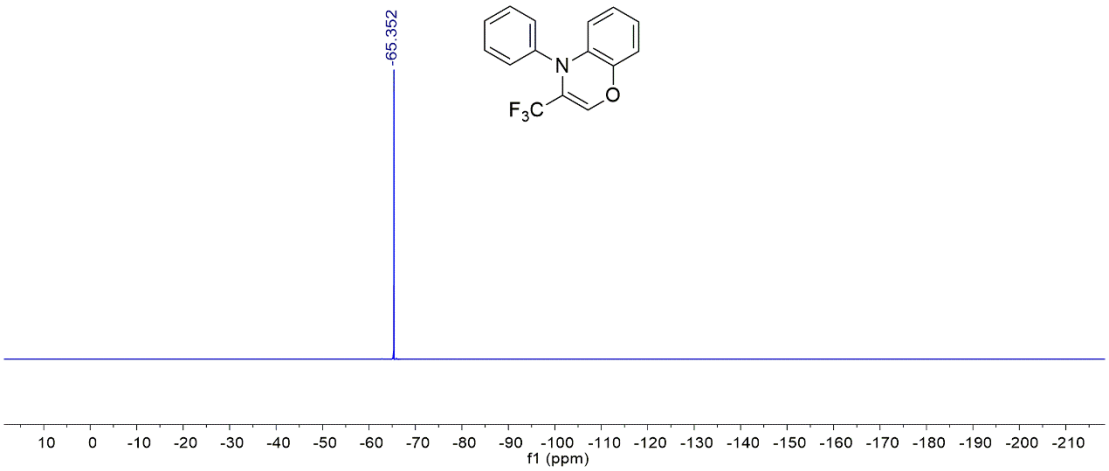
^{1}H-NMR spectrum of 3aa



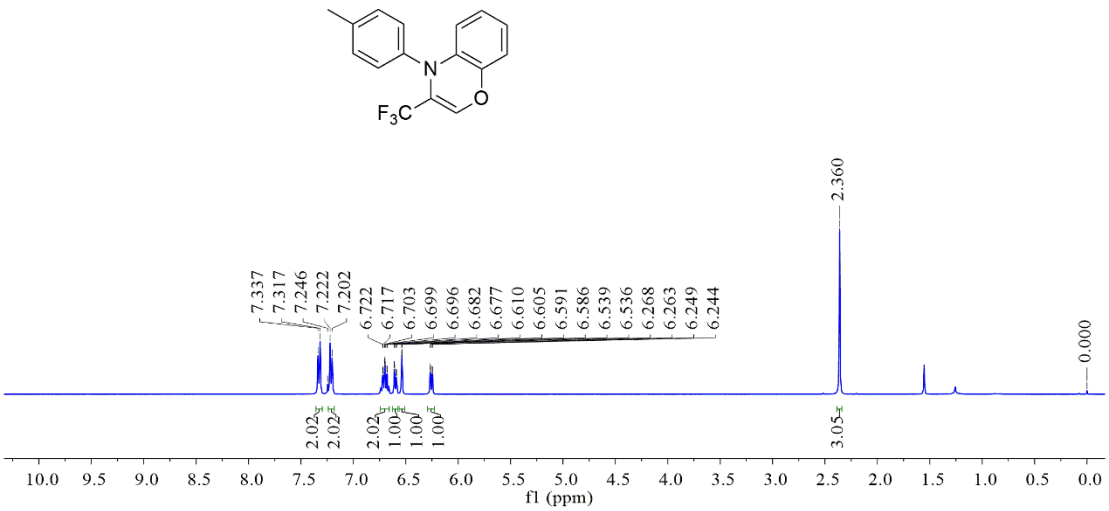
^{13}C-NMR spectrum of 3aa



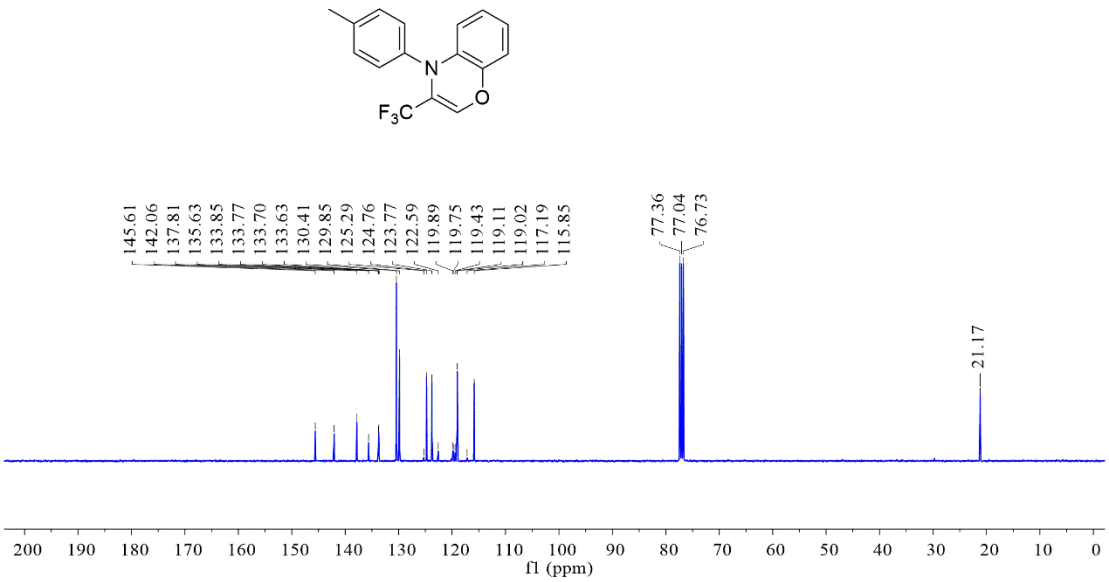
^{19}F-NMR spectrum of 3aa



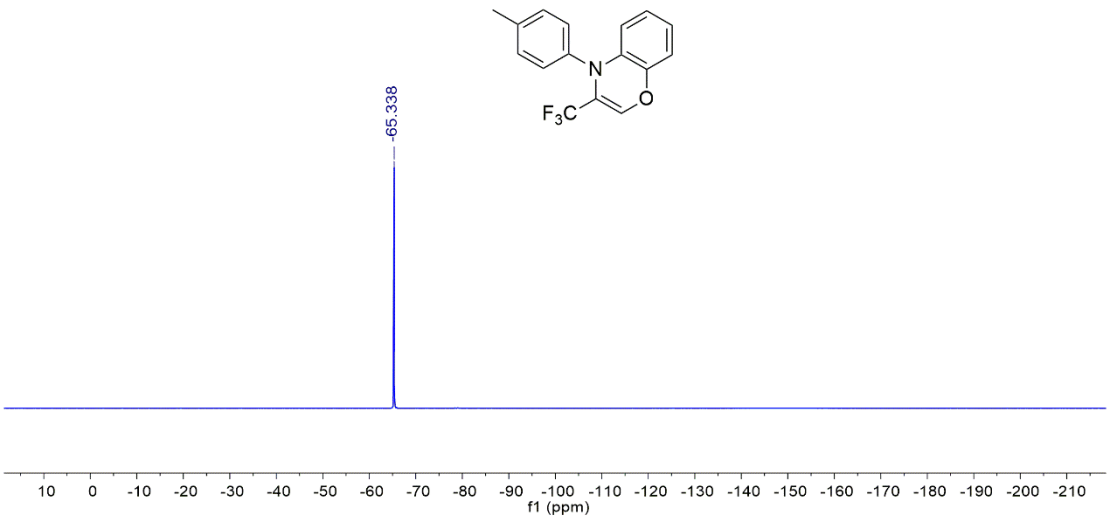
^{1}H-NMR spectrum of 3ab



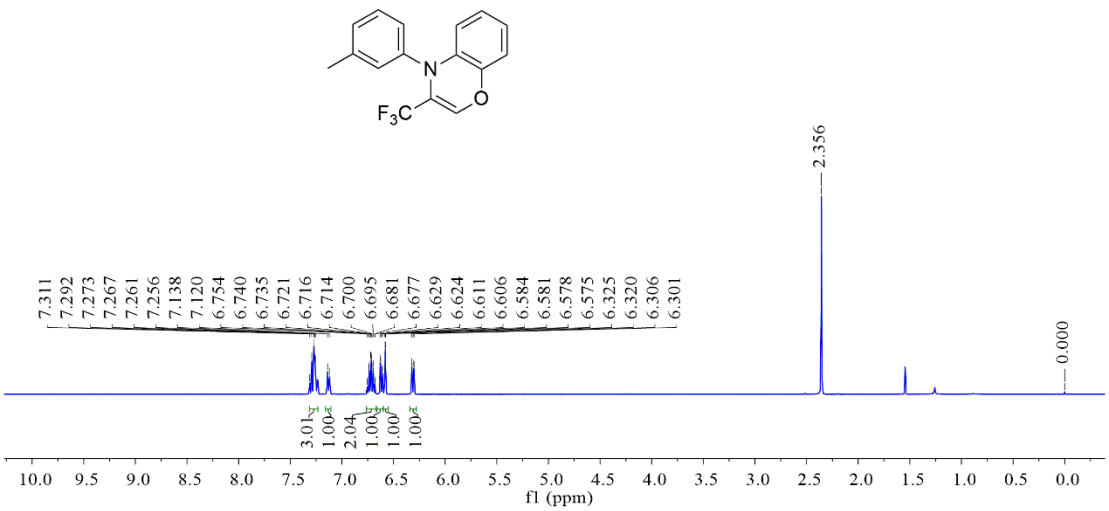
^{13}C-NMR spectrum of 3ab



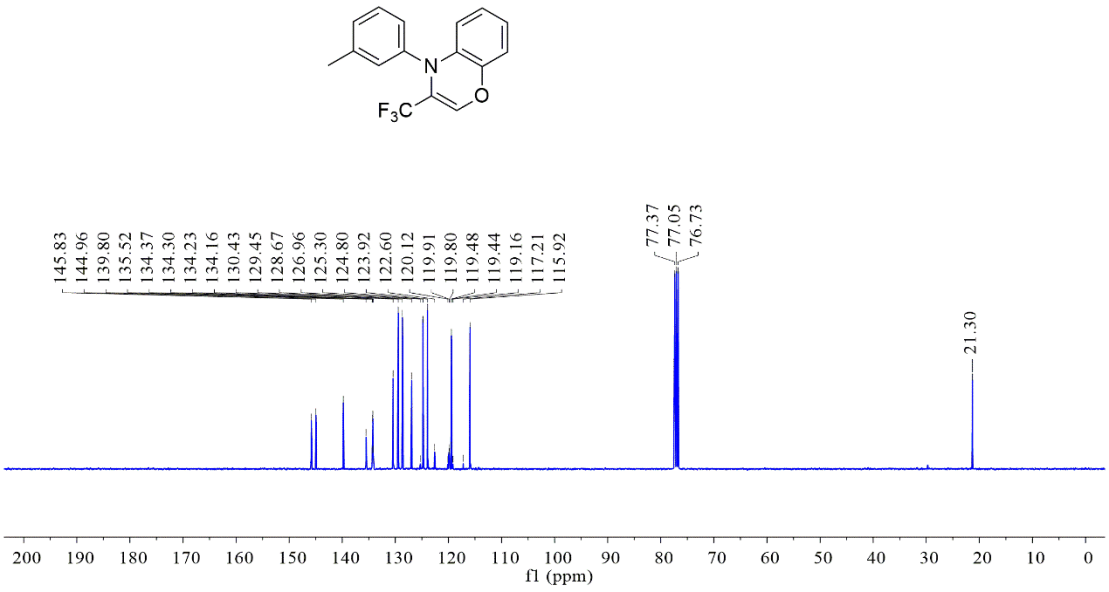
^{19}F-NMR spectrum of 3ab



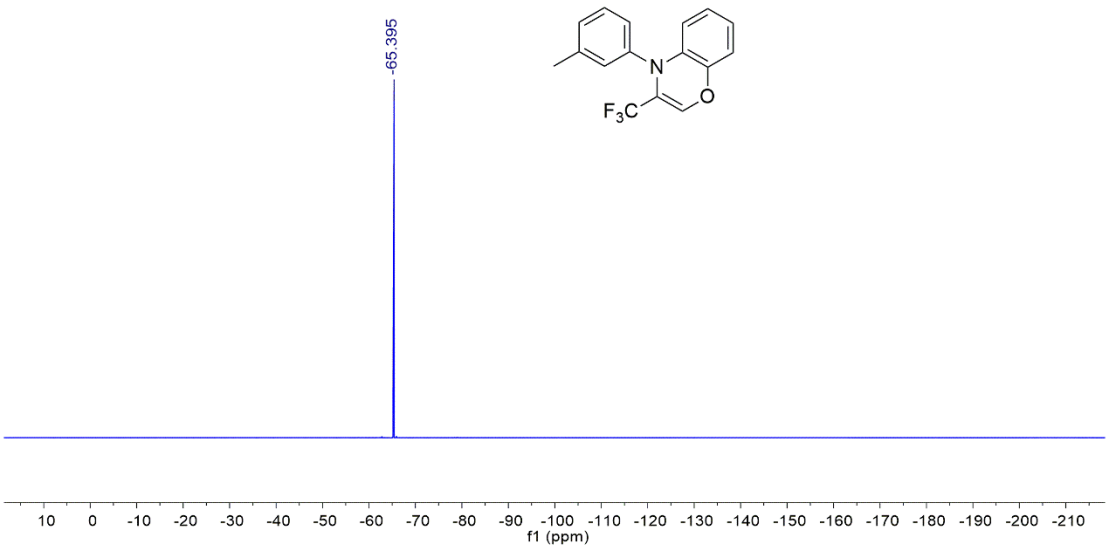
^{1}H-NMR spectrum of 3ac



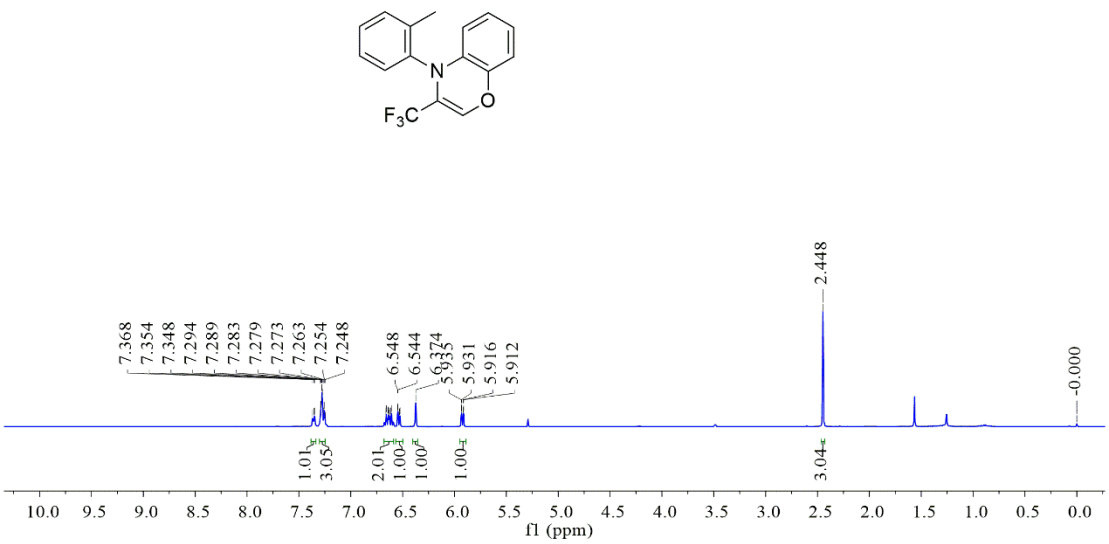
^{13}C-NMR spectrum of 3ac



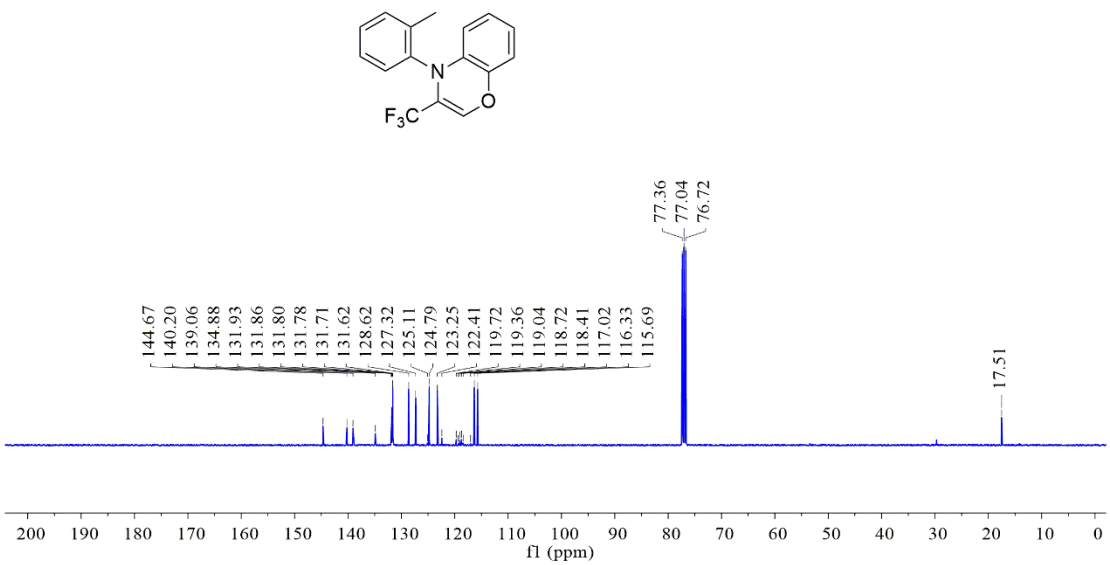
^{19}F-NMR spectrum of 3ac



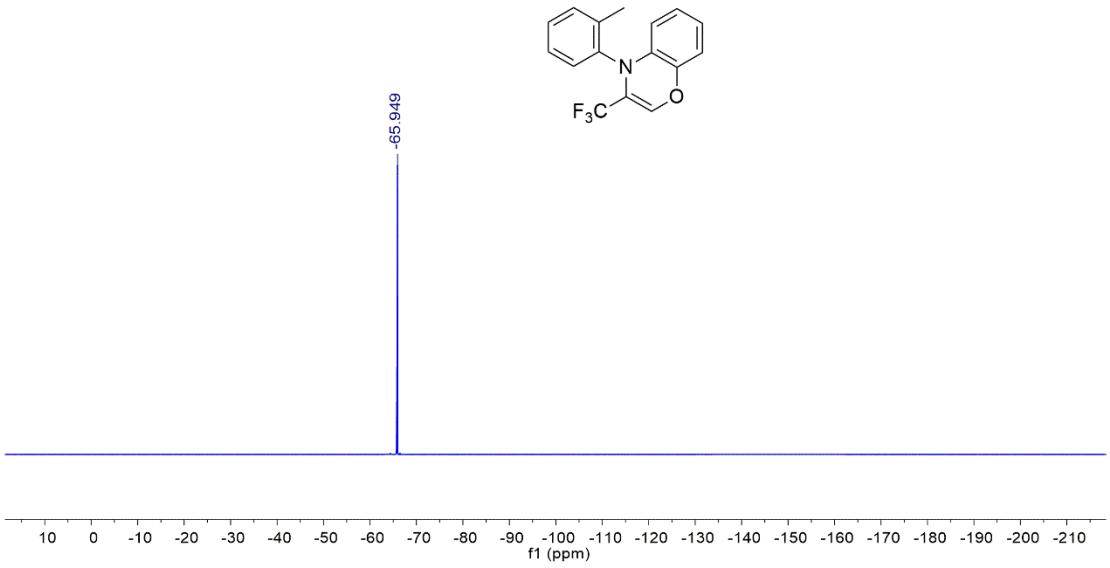
^{1}H-NMR spectrum of 3ad



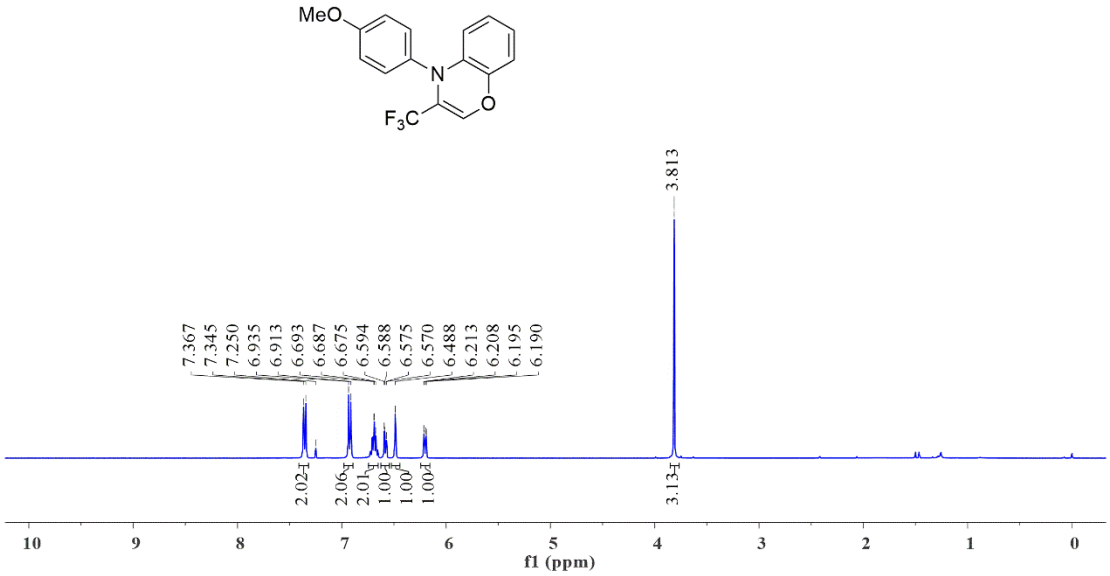
^{13}C-NMR spectrum of 3ad



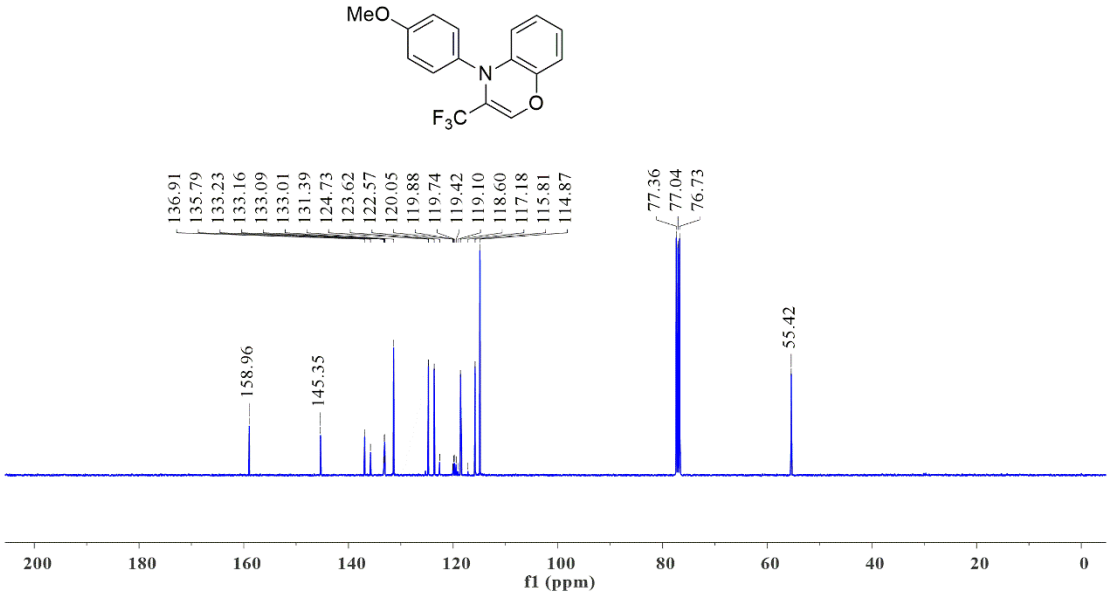
^{19}F-NMR spectrum of 3ad



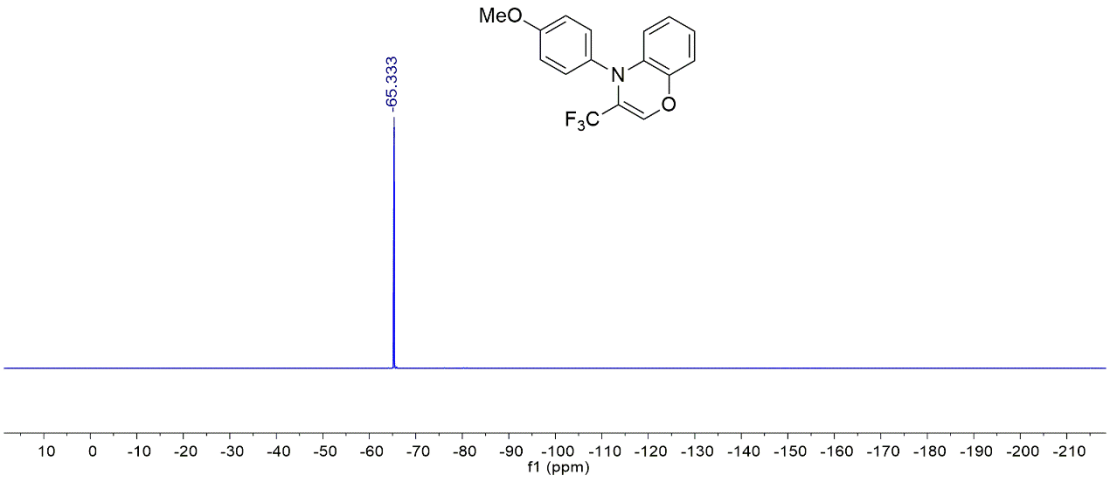
^{1}H-NMR spectrum of 3ae



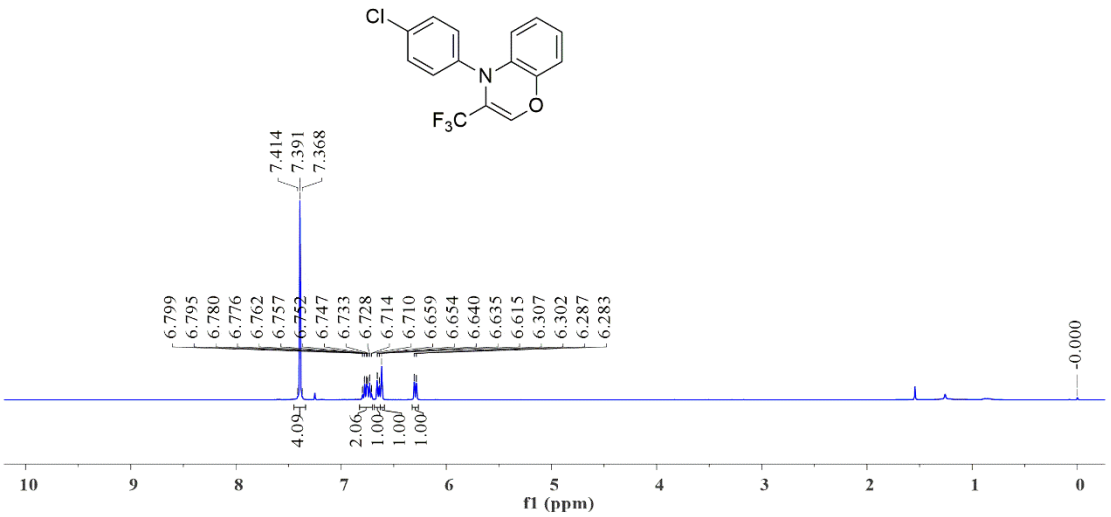
^{13}C-NMR spectrum of 3ae



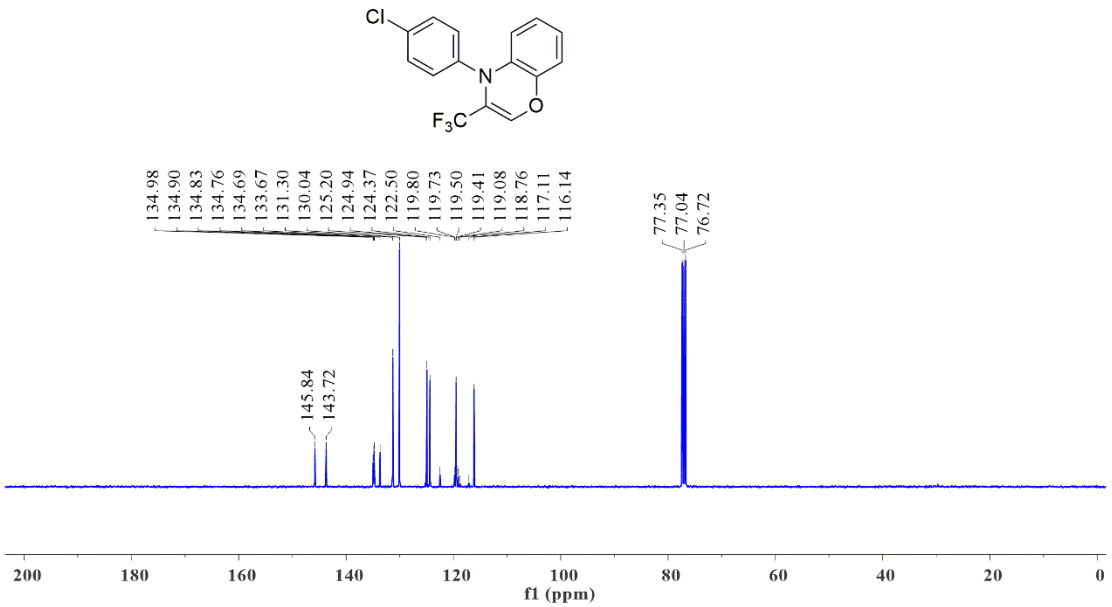
^{19}F-NMR spectrum of 3ae



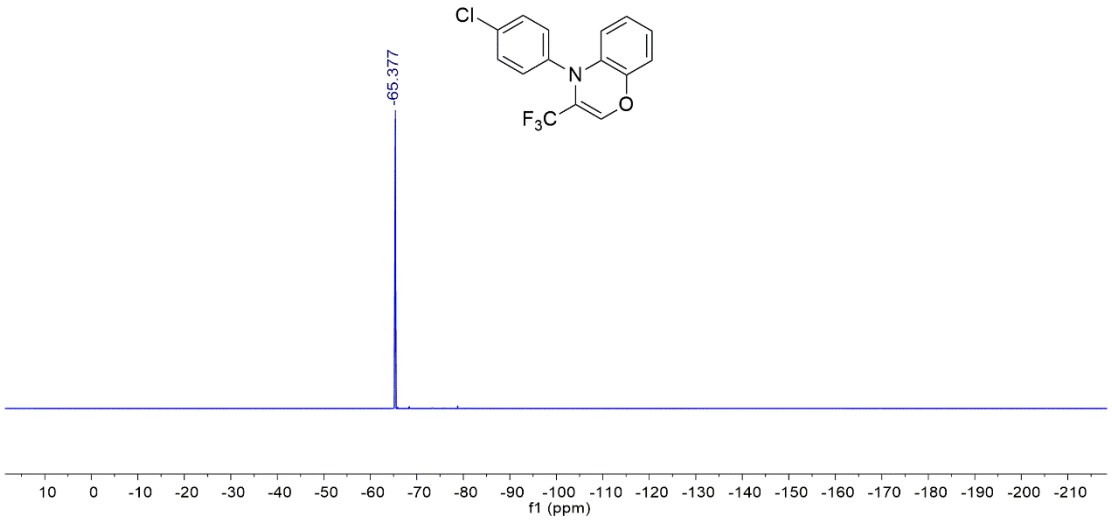
^{1}H-NMR spectrum of 3af



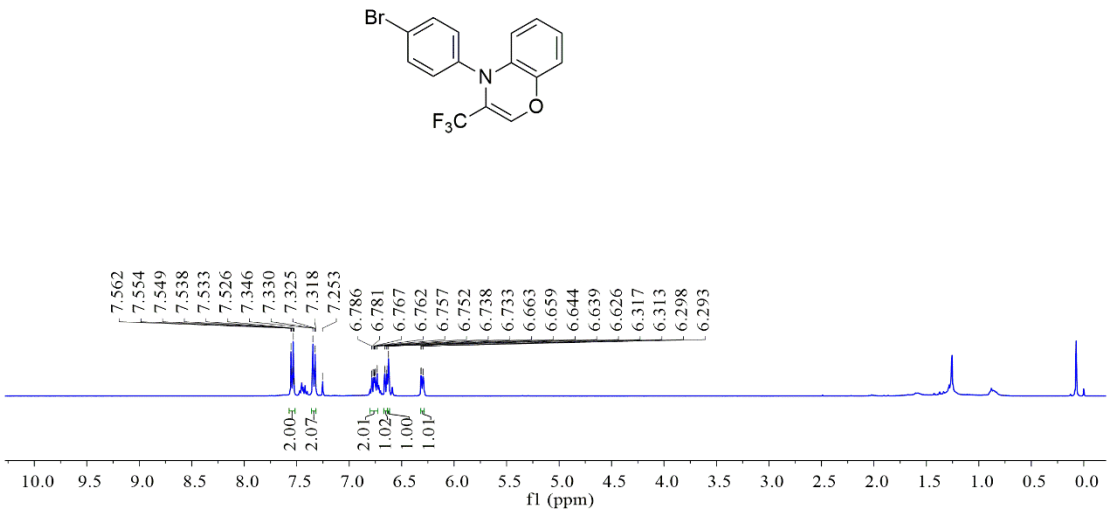
^{13}C-NMR spectrum of 3af



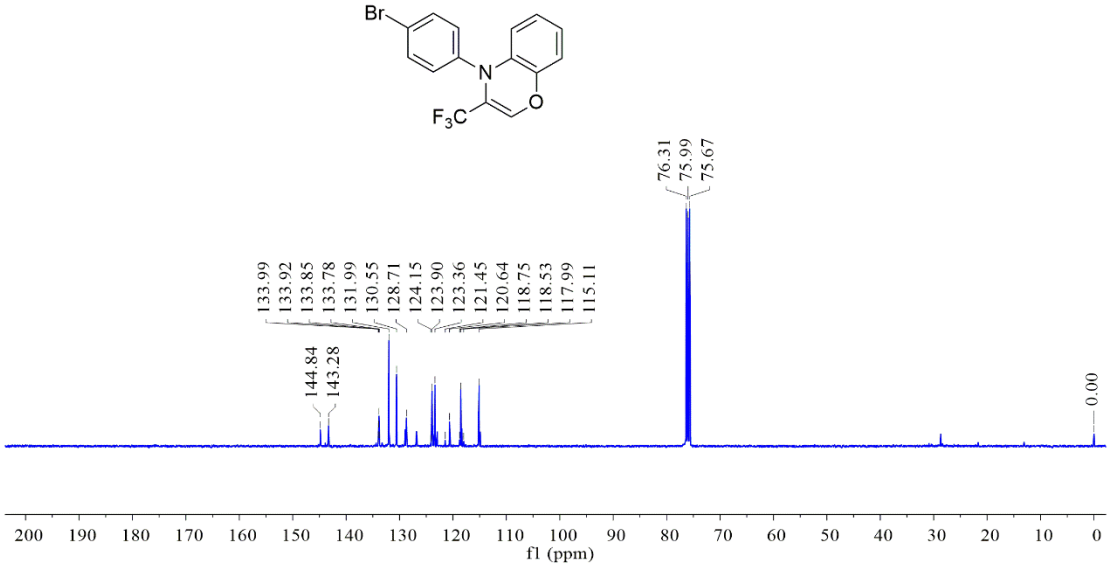
^{19}F-NMR spectrum of 3af



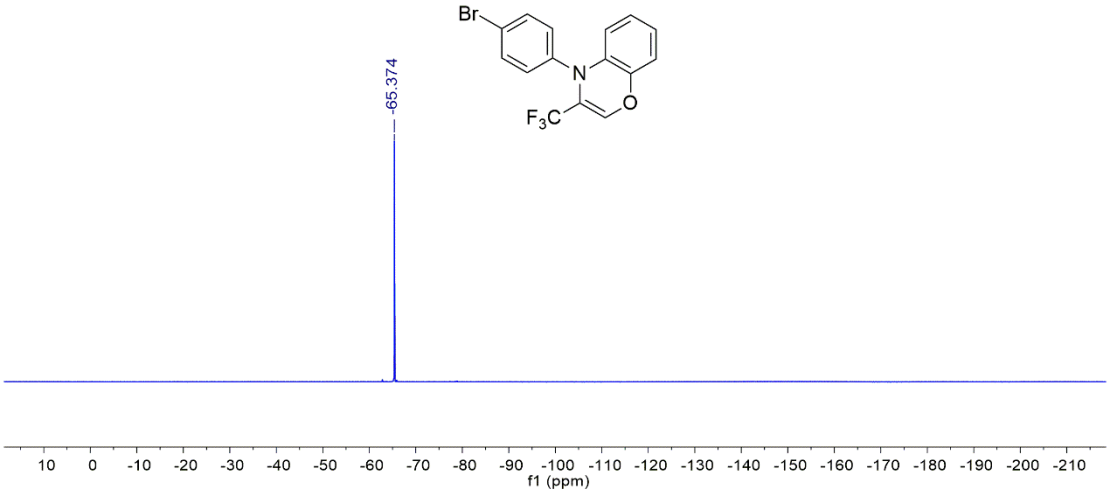
^{1}H-NMR spectrum of 3ag



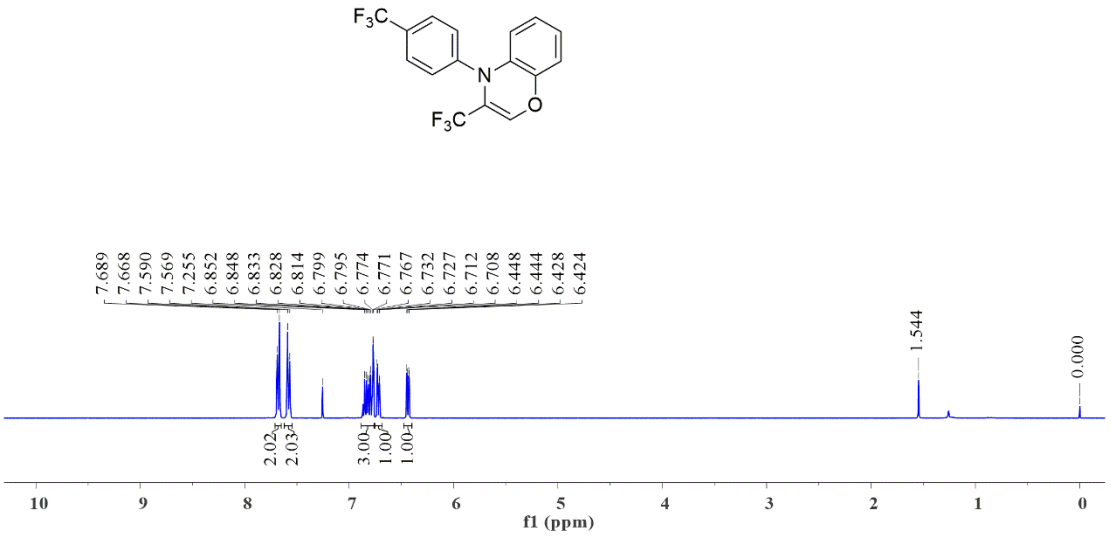
^{13}C-NMR spectrum of 3ag



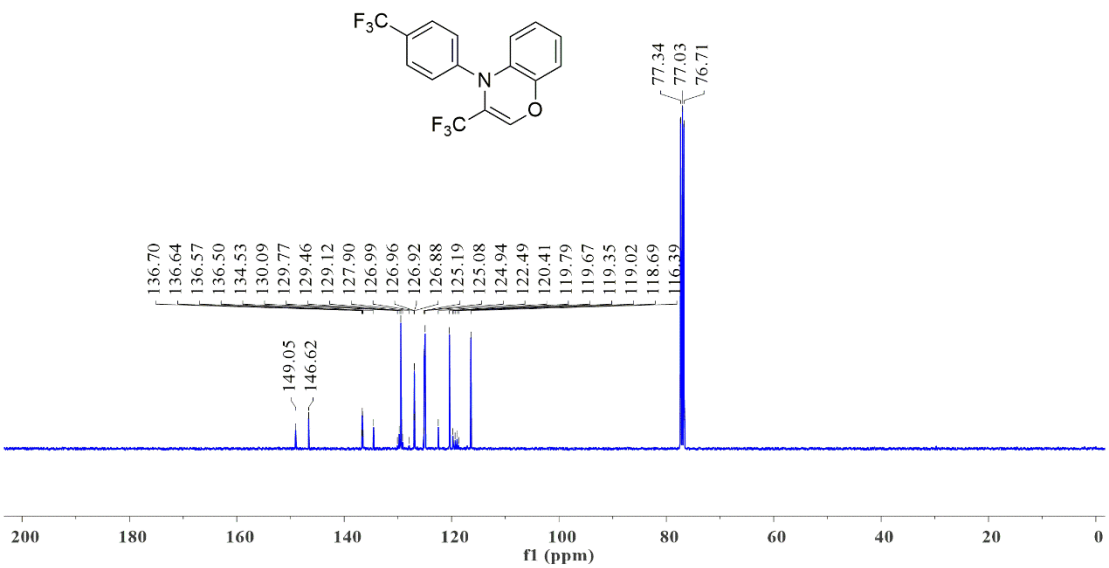
^{19}F-NMR spectrum of 3ag



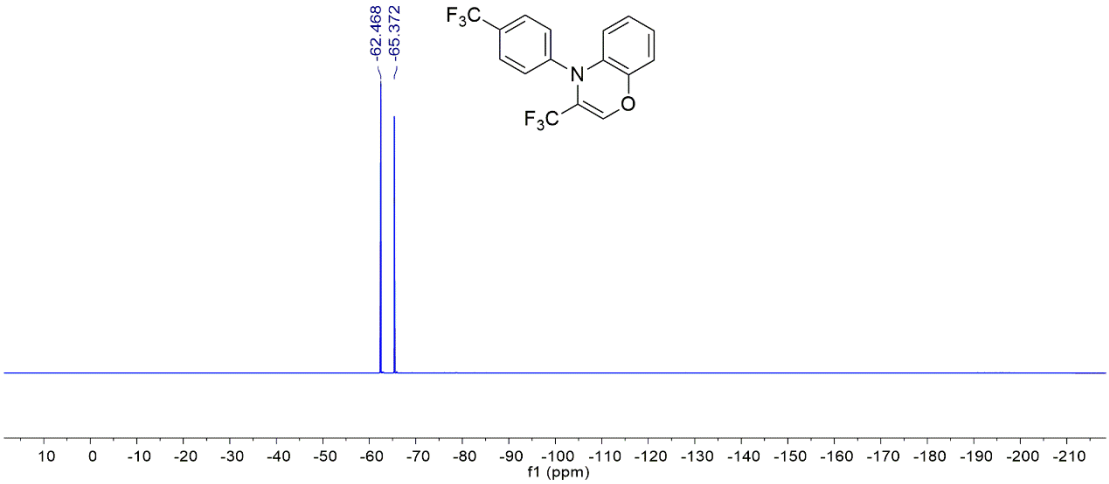
^{1}H-NMR spectrum of 3ah



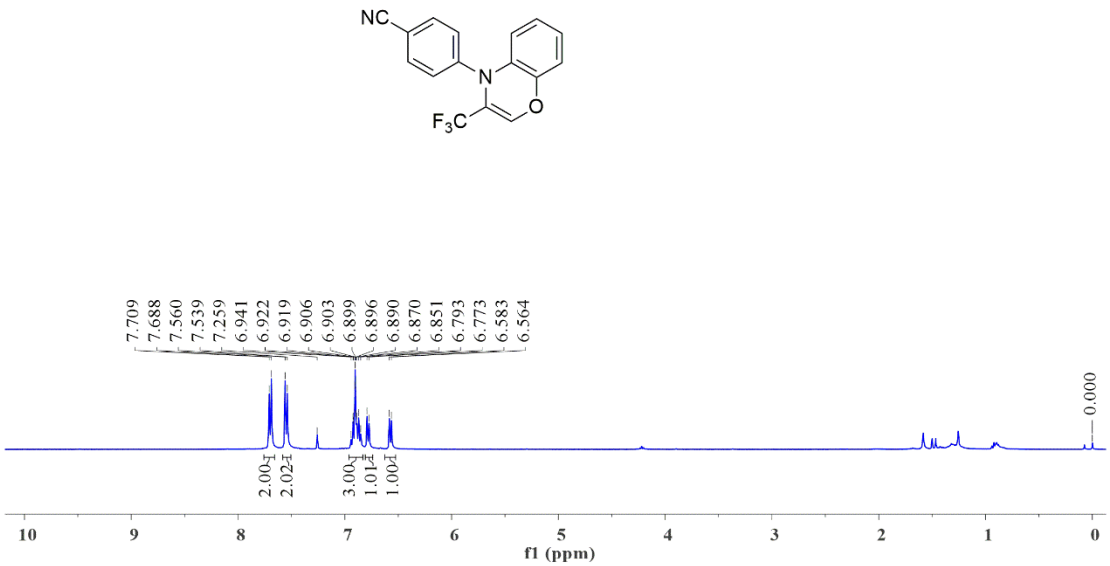
^{13}C-NMR spectrum of 3ah



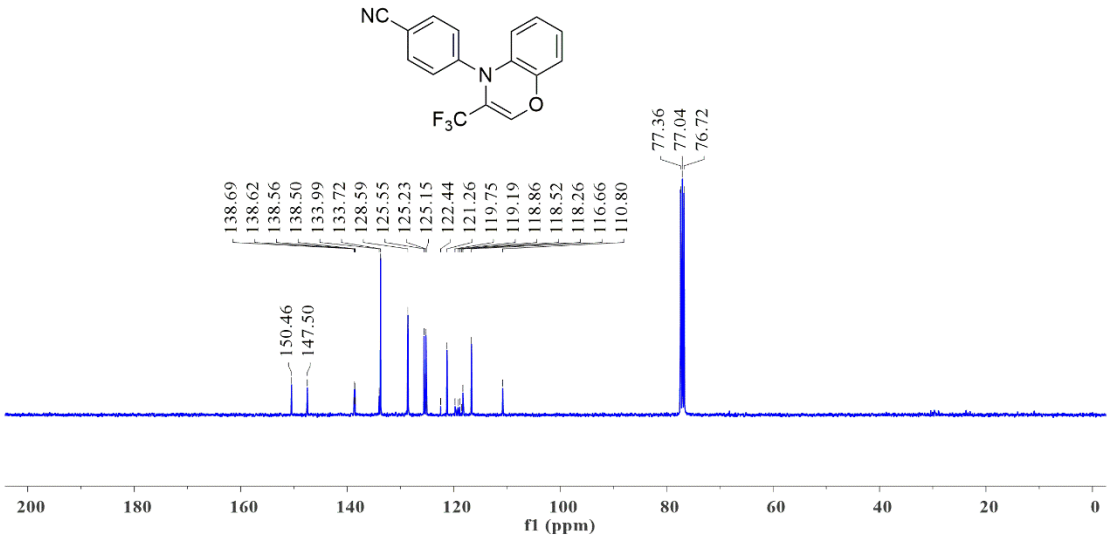
^{19}F-NMR spectrum of 3ah



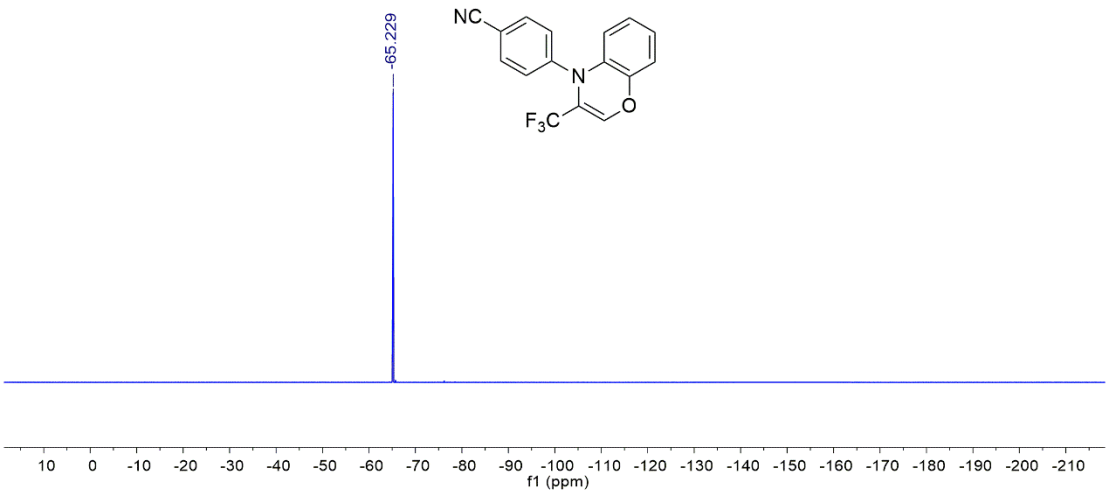
^{1}H-NMR spectrum of 3ai



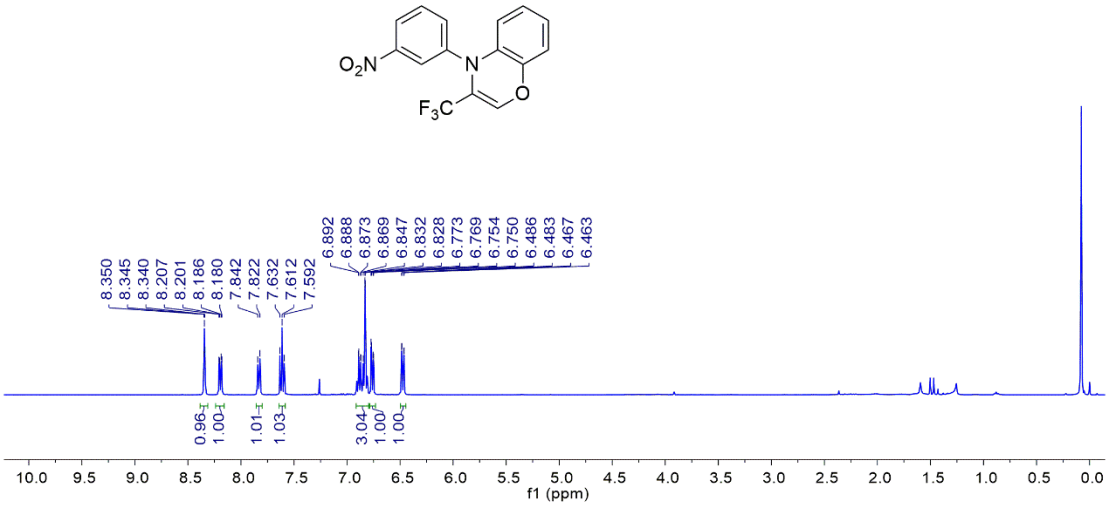
^{13}C-NMR spectrum of 3ai



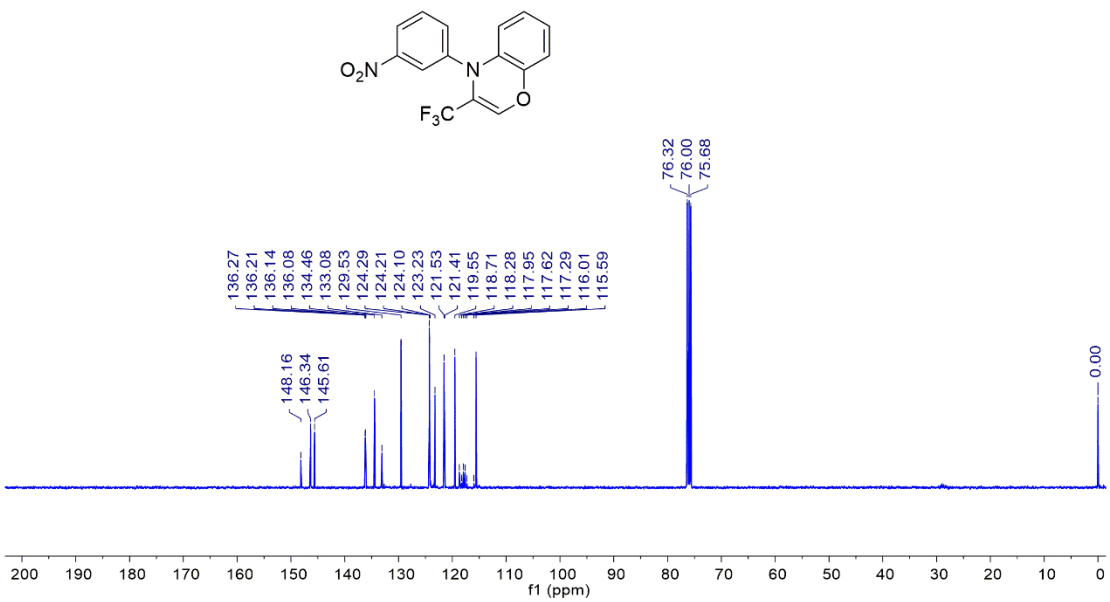
^{19}F-NMR spectrum of 3ai



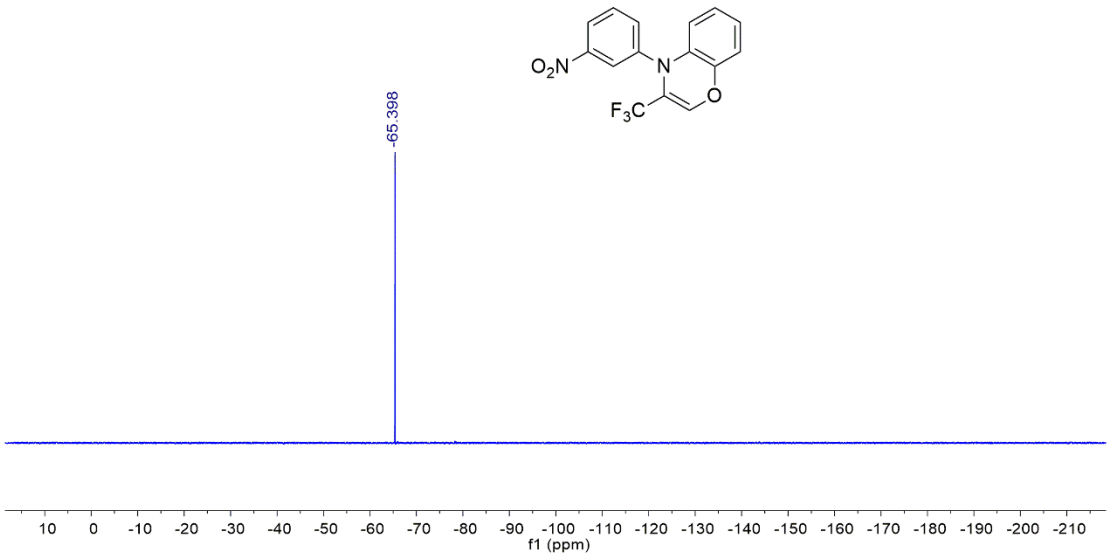
^{1}H-NMR spectrum of 3aj



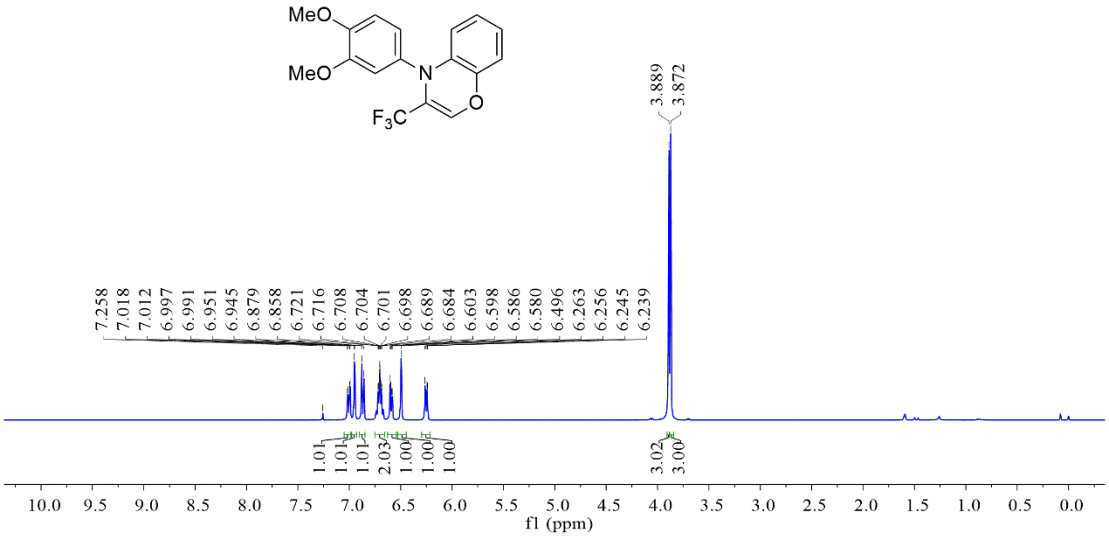
^{13}C-NMR spectrum of 3aj



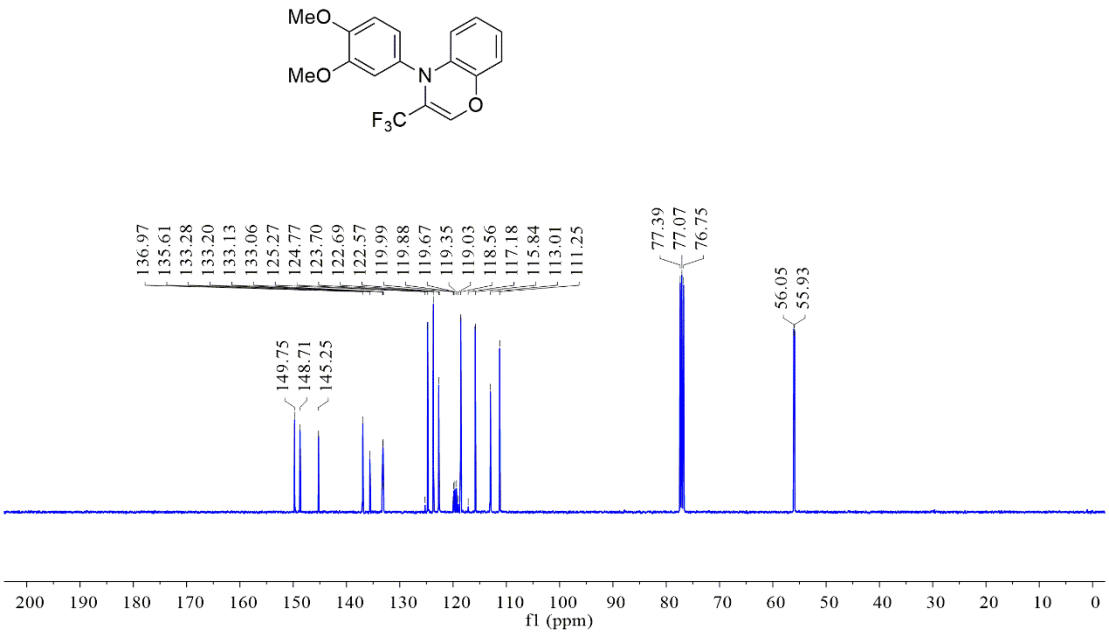
^{19}F-NMR spectrum of 3aj



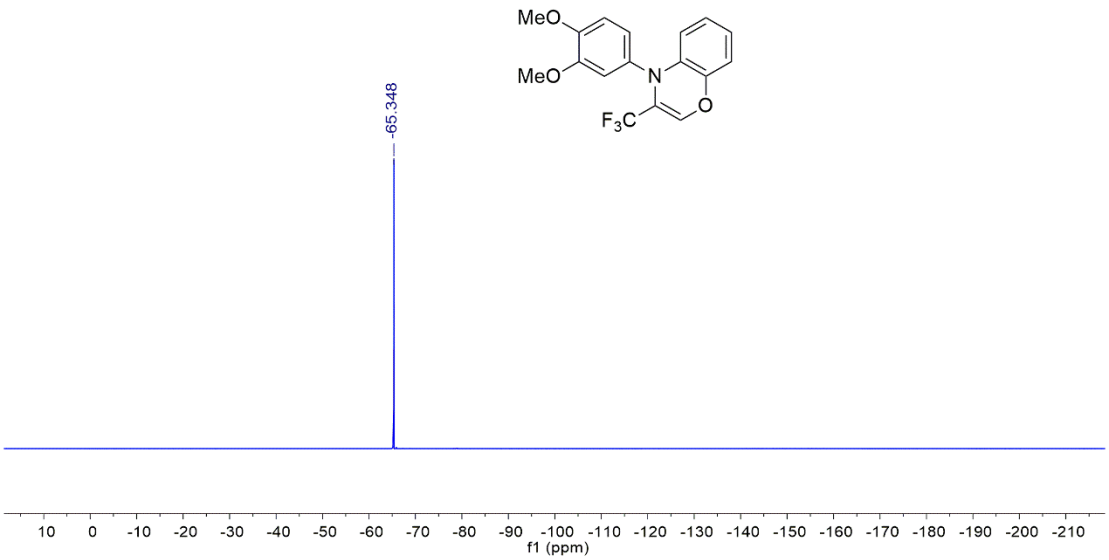
^{1}H-NMR spectrum of 3ak



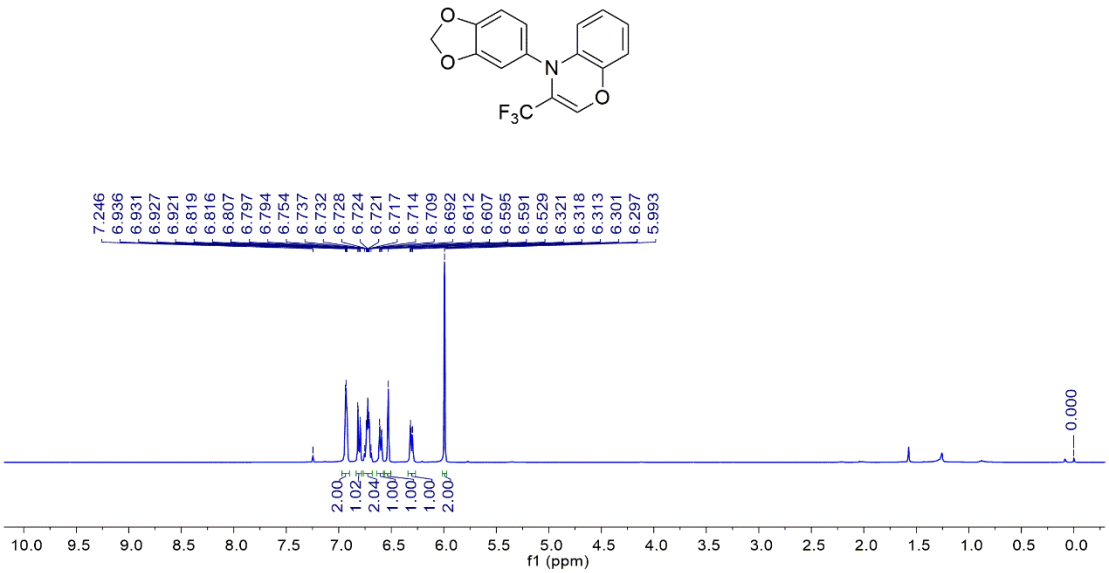
^{13}C-NMR spectrum of 3ak



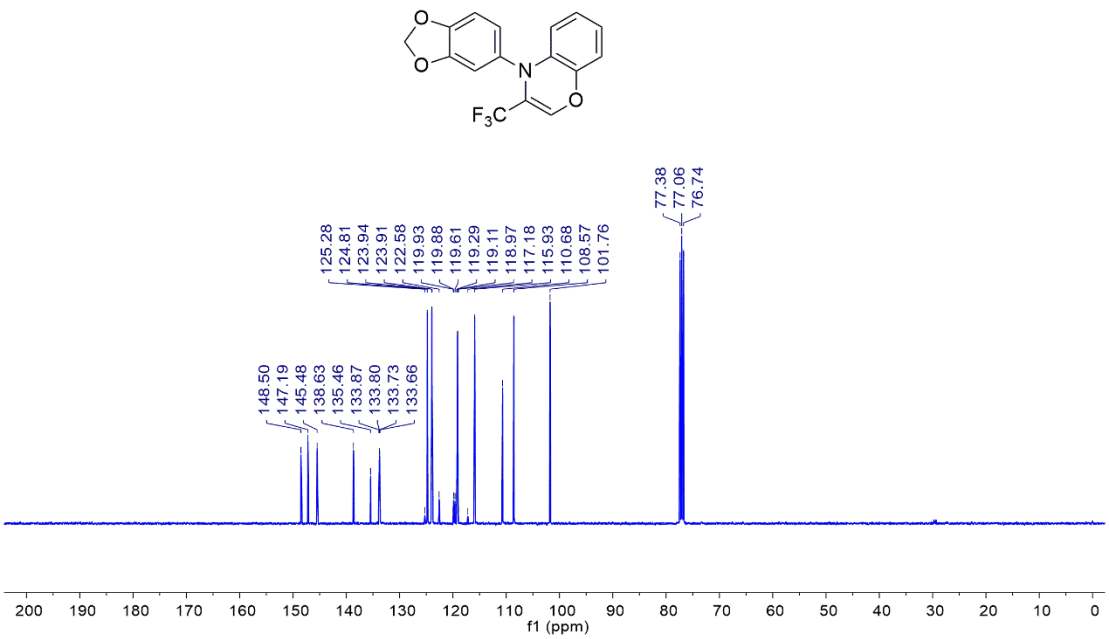
^{19}F-NMR spectrum of 3ak



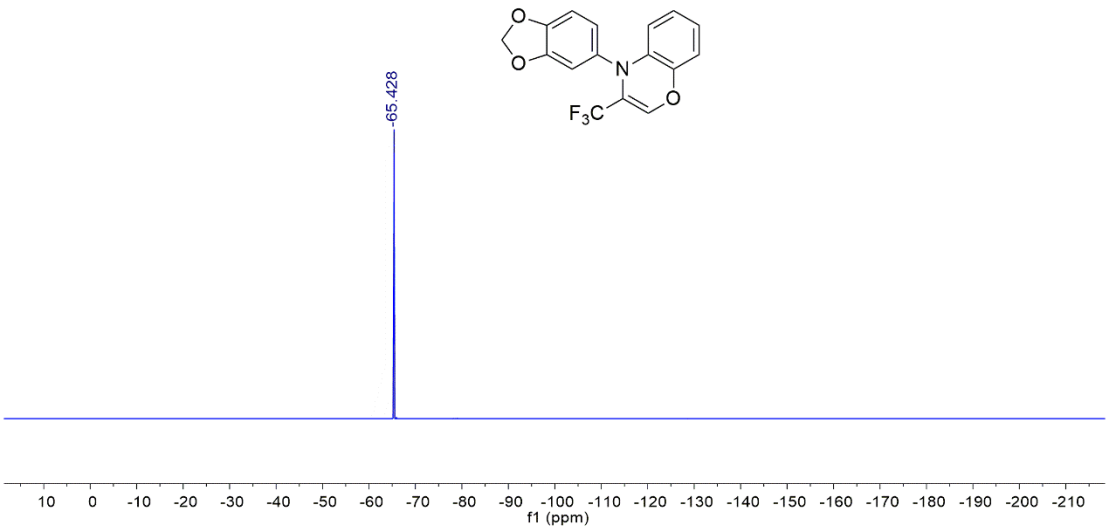
^{1}H-NMR spectrum of 3al



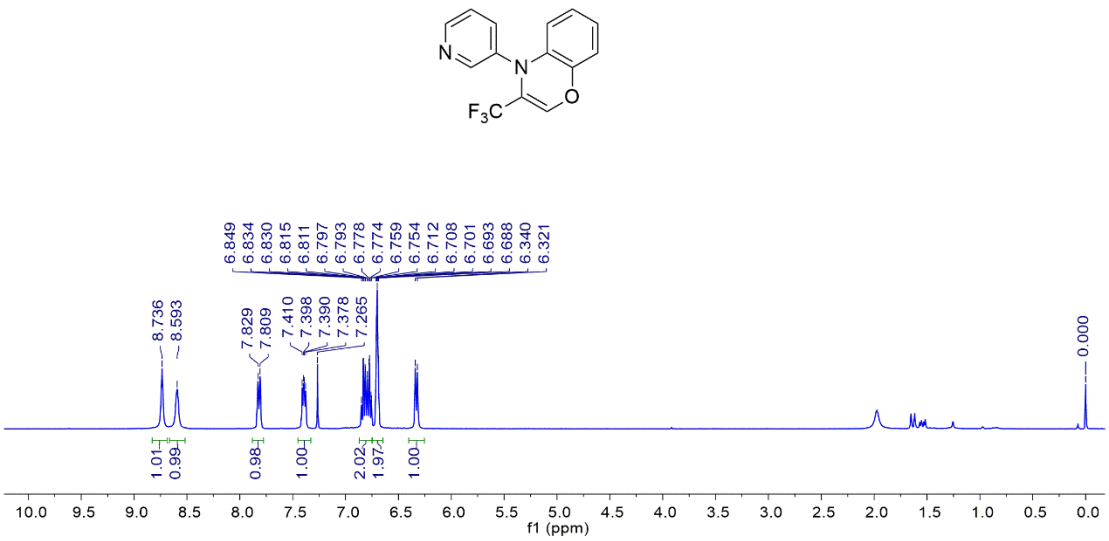
^{13}C-NMR spectrum of 3al



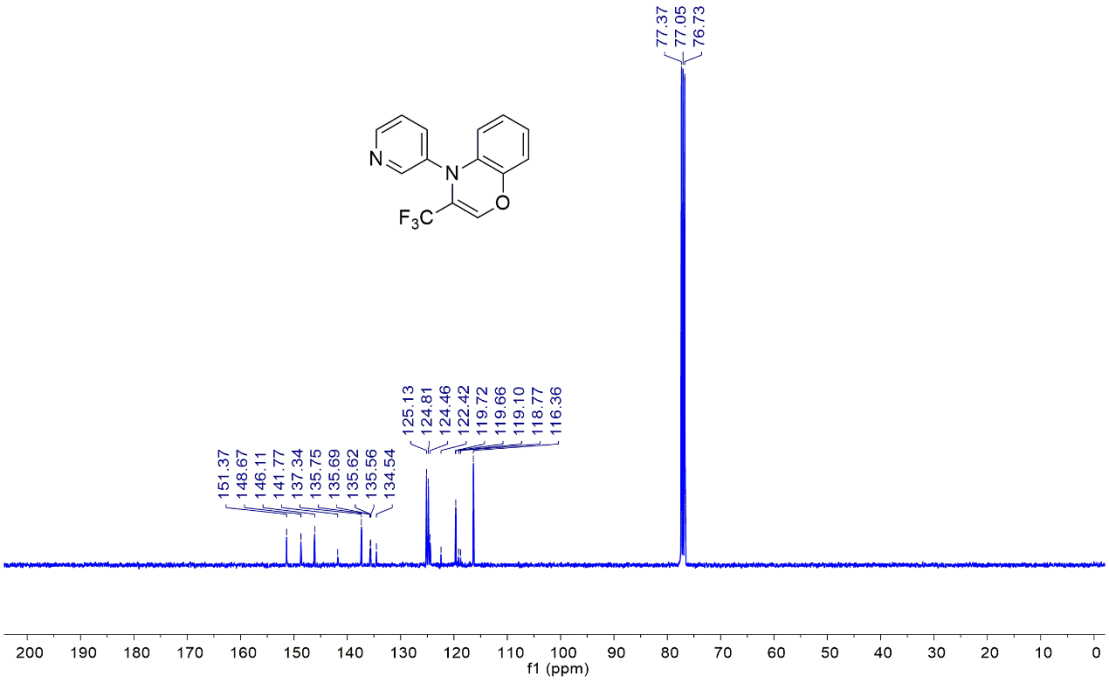
^{19}F-NMR spectrum of 3al



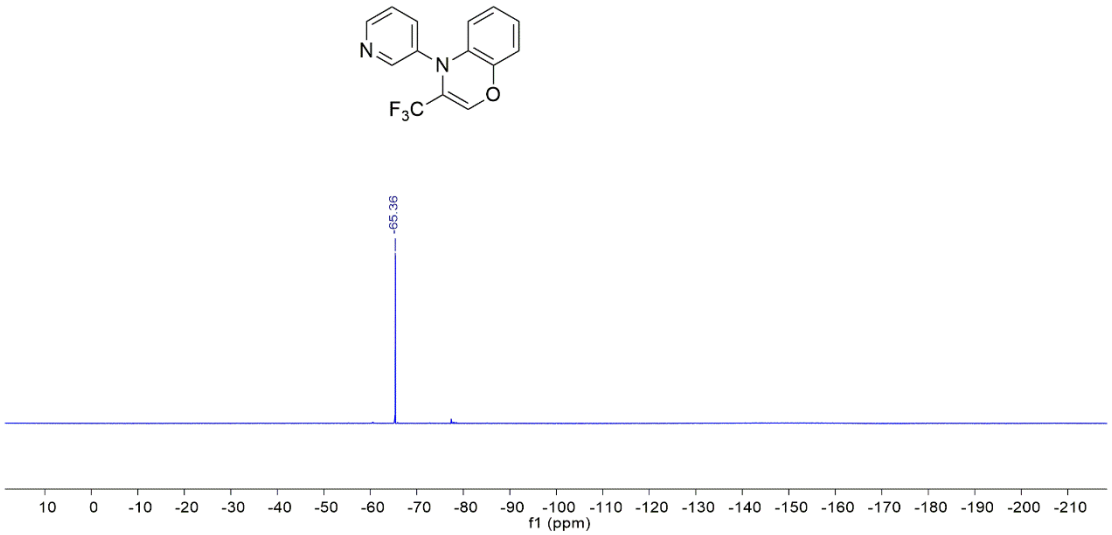
^{1}H-NMR spectrum of 3am



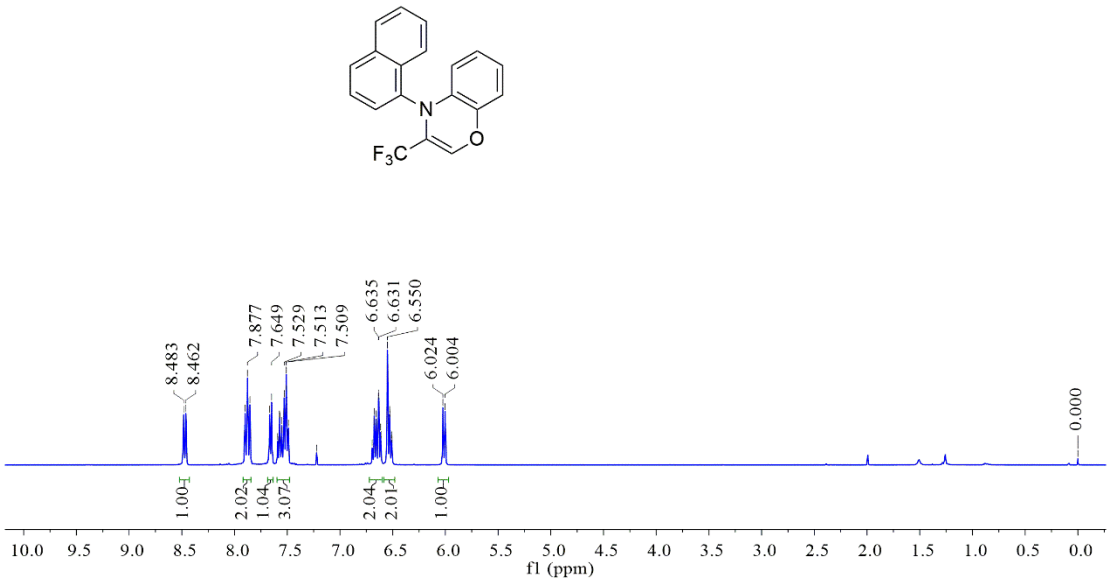
^{13}C-NMR spectrum of 3am



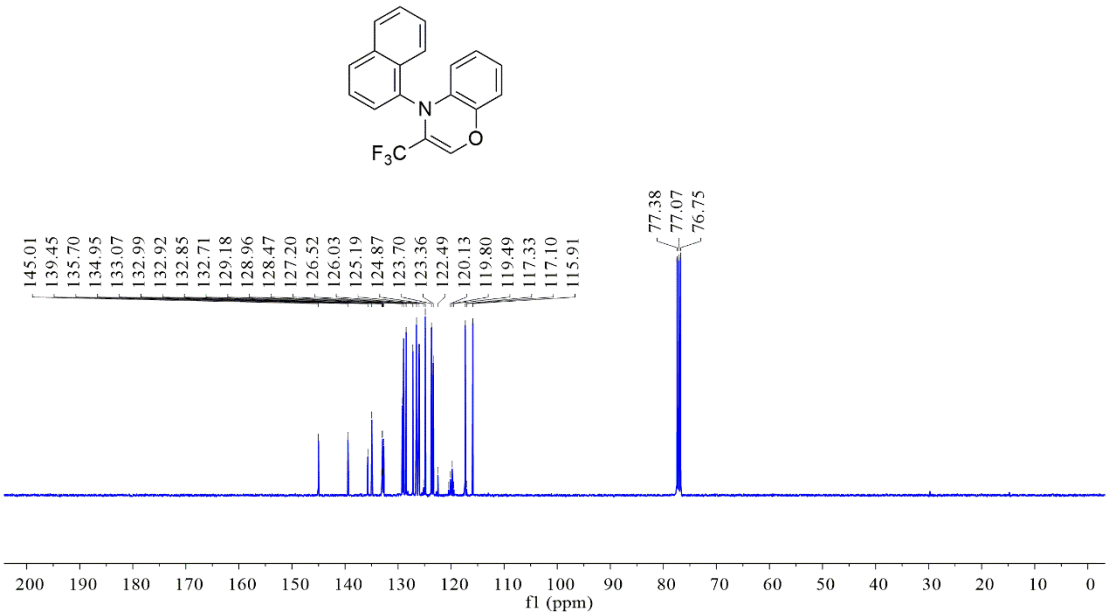
^{19}F-NMR spectrum of 3am



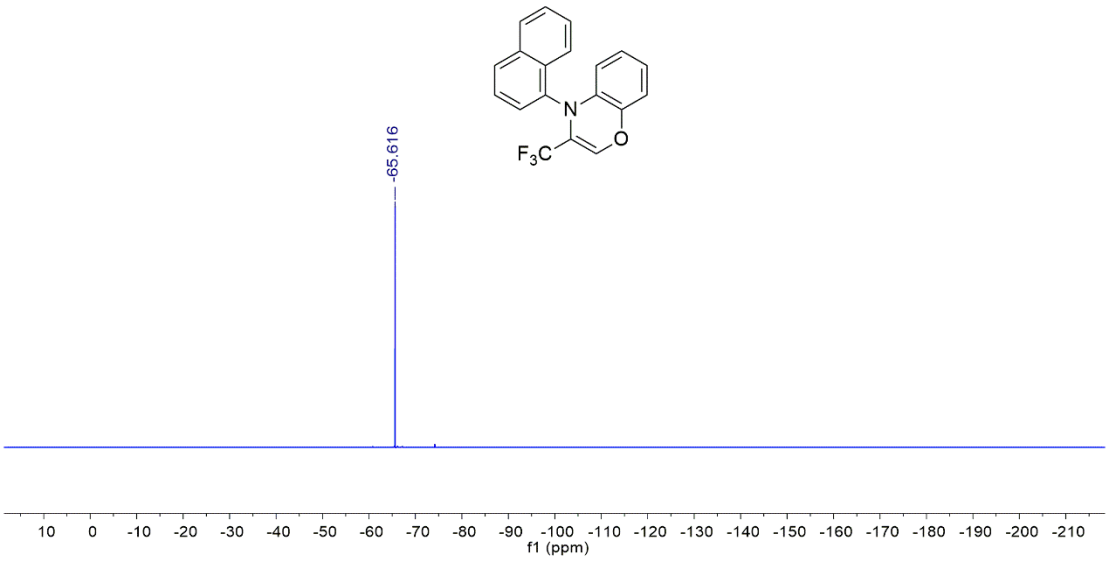
^{1}H-NMR spectrum of 3an



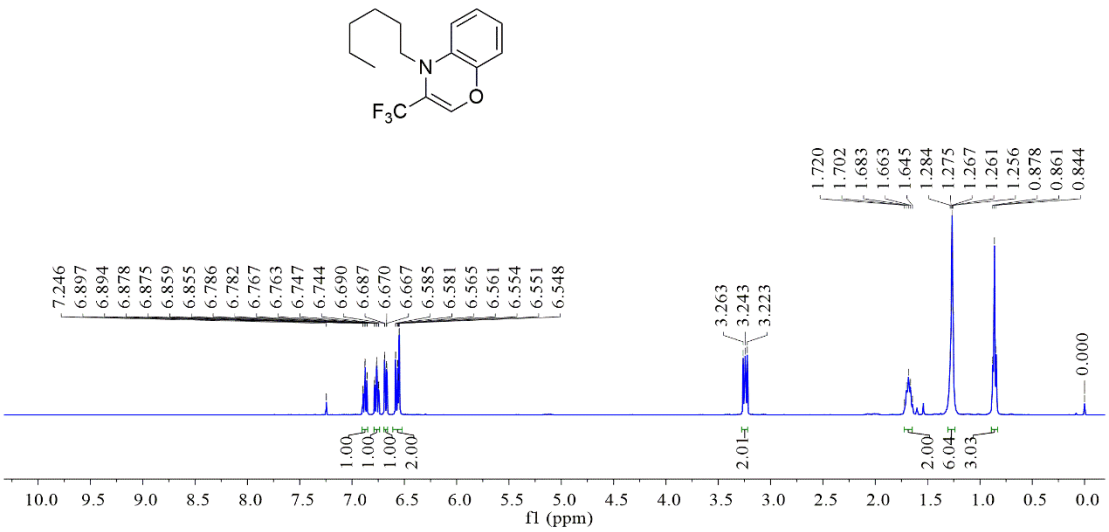
^{13}C-NMR spectrum of 3an



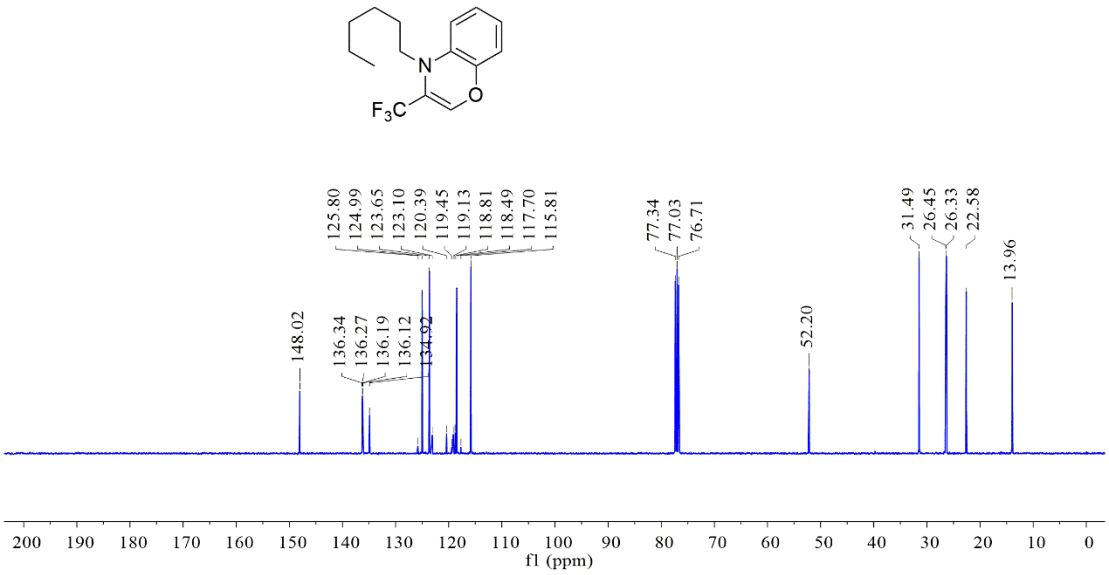
^{19}F-NMR spectrum of 3an



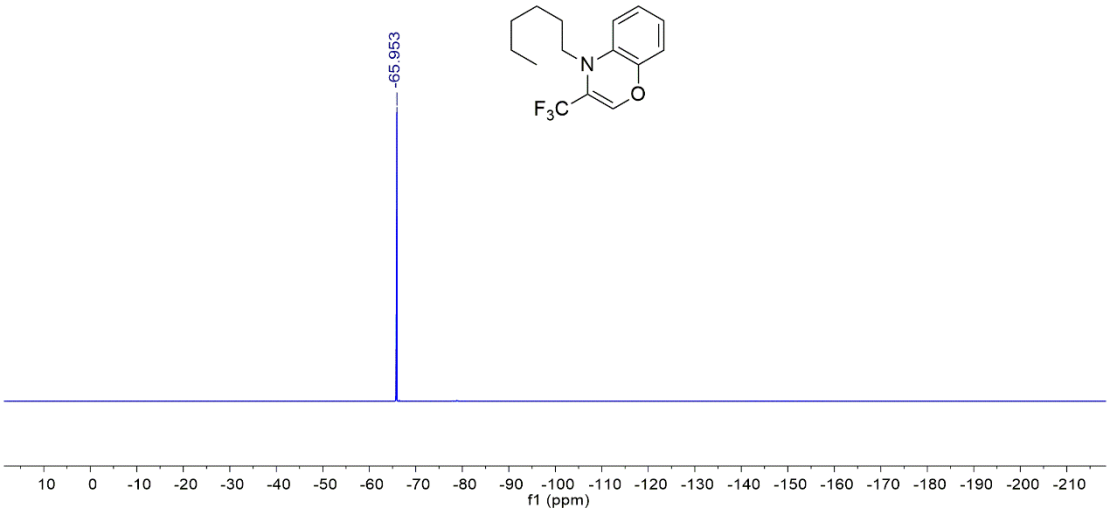
^{1}H-NMR spectrum of 3ao



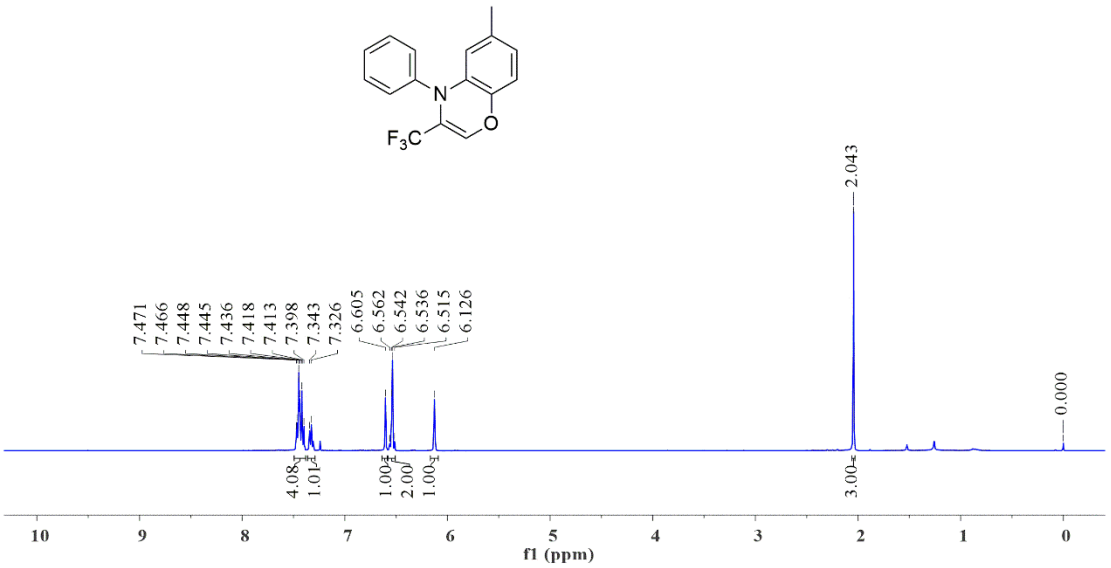
^{13}C-NMR spectrum of 3ao



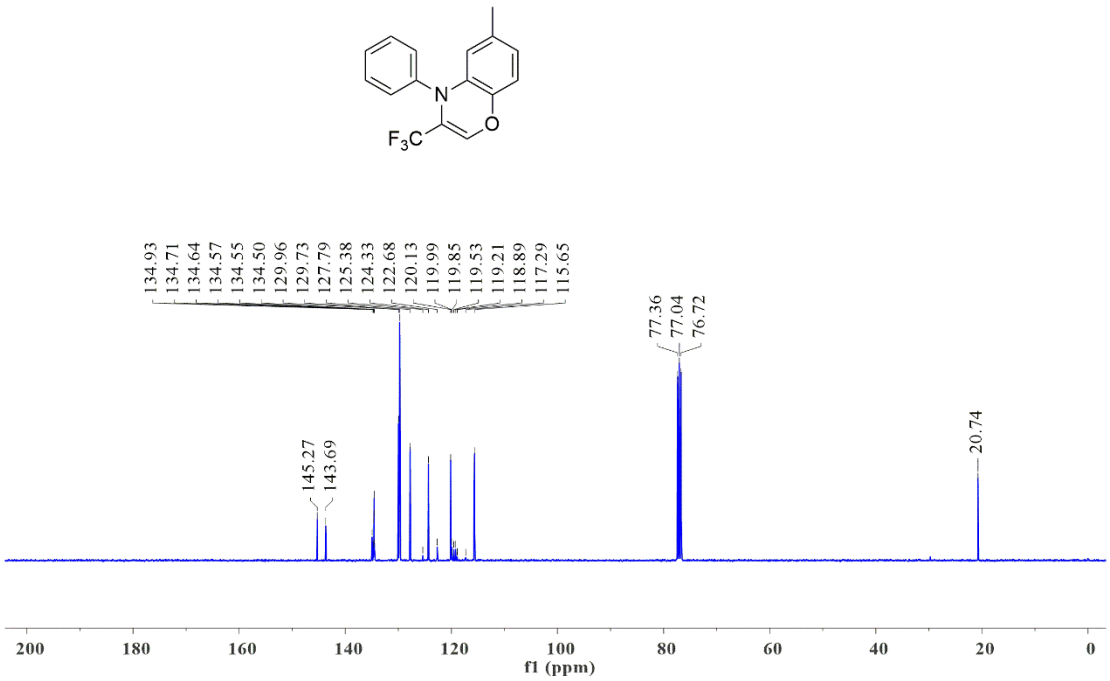
^{19}F-NMR spectrum of 3ao



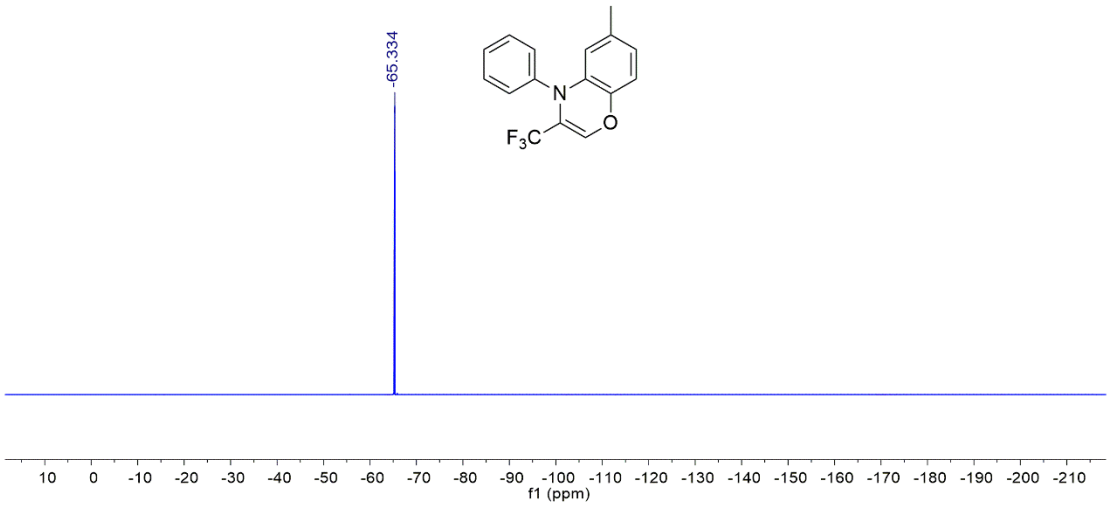
^{1}H-NMR spectrum of 3ba



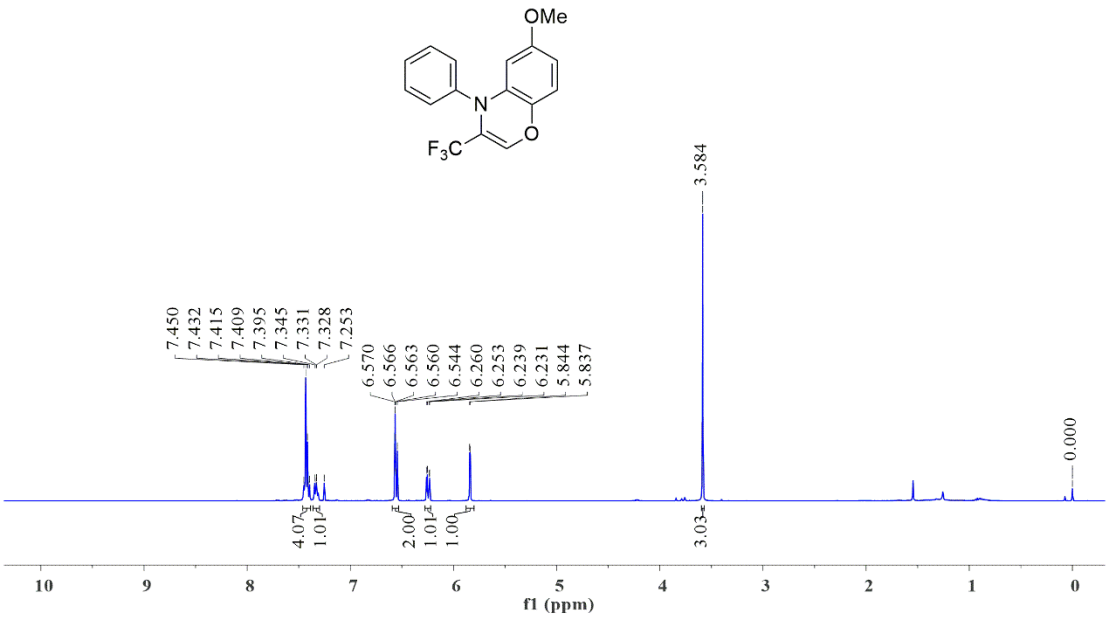
^{13}C-NMR spectrum of 3ba



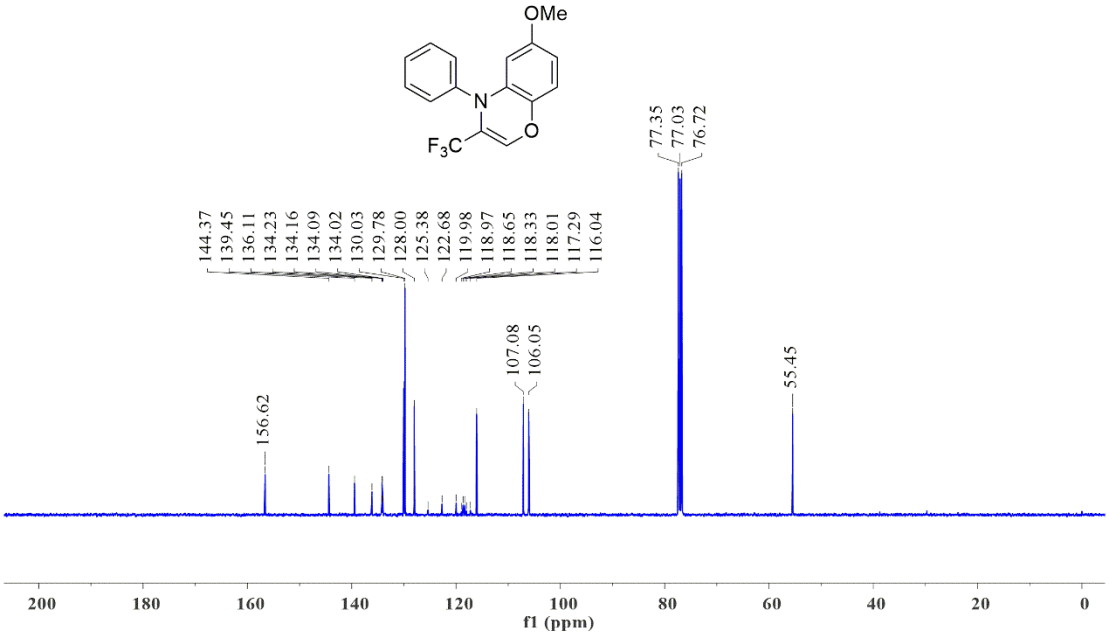
^{19}F-NMR spectrum of 3ba



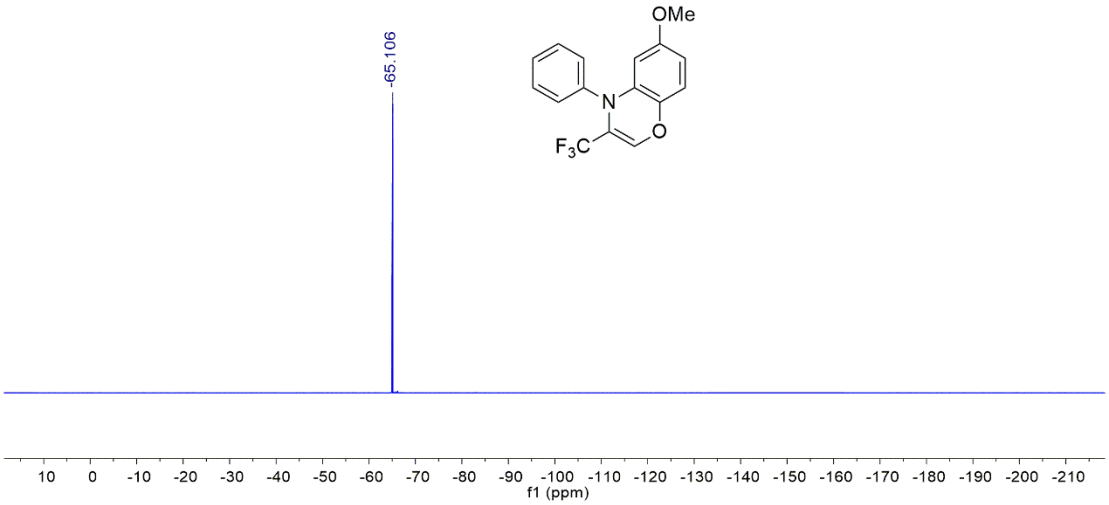
^{1}H-NMR spectrum of 3ca



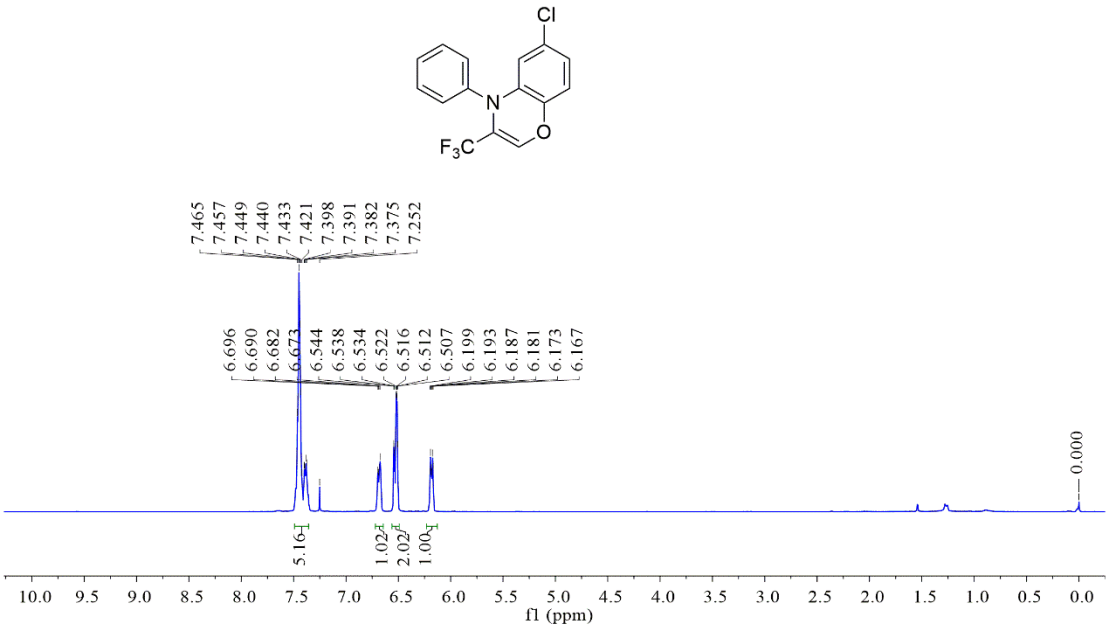
^{13}C-NMR spectrum of 3ca



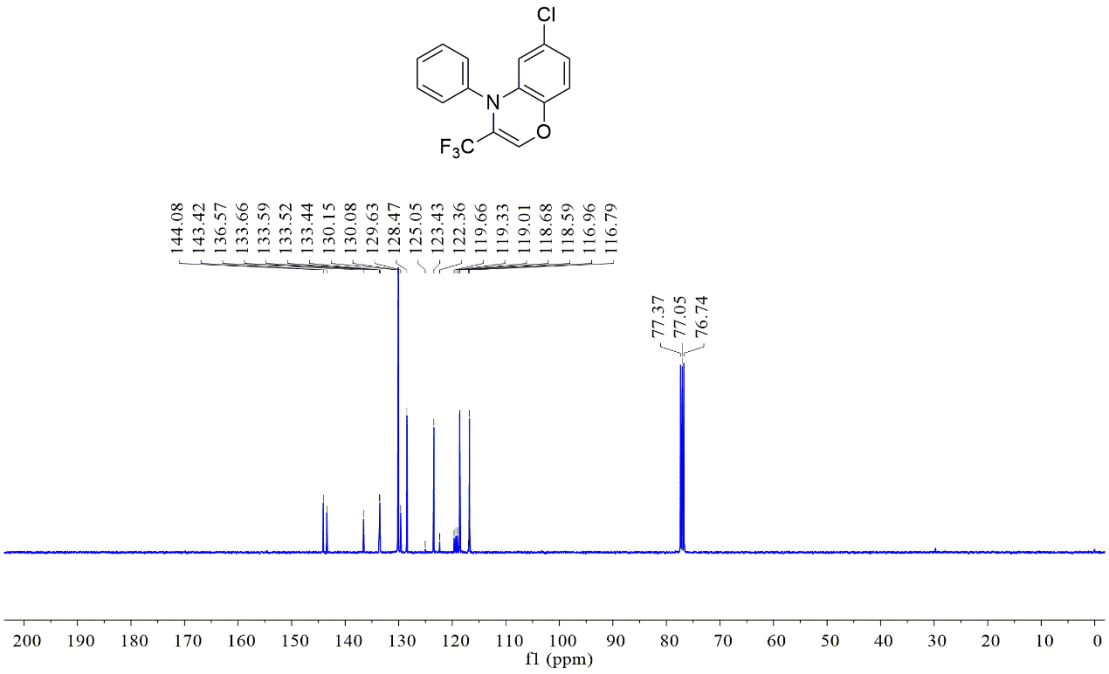
^{19}F-NMR spectrum of 3ca



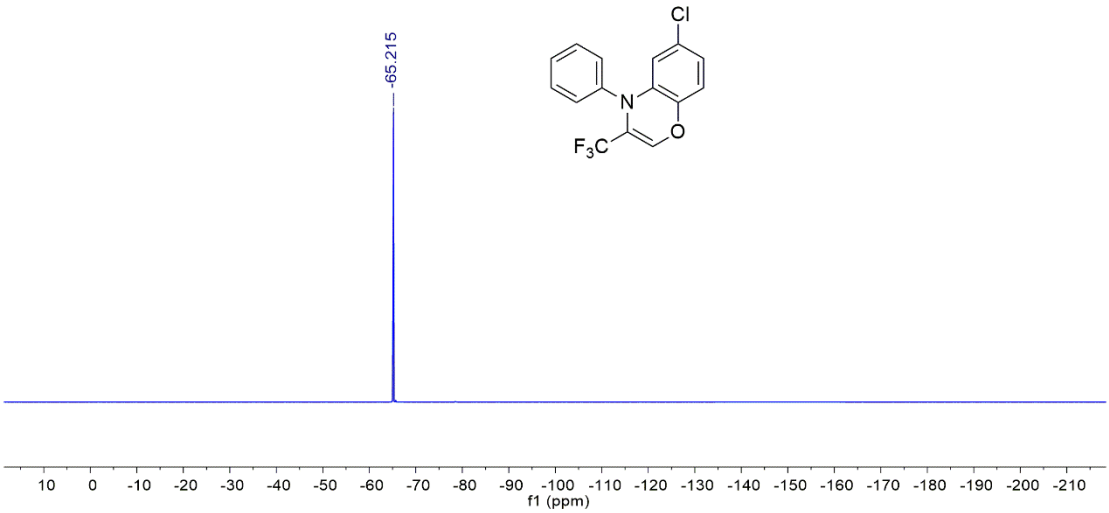
^{1}H-NMR spectrum of 3da



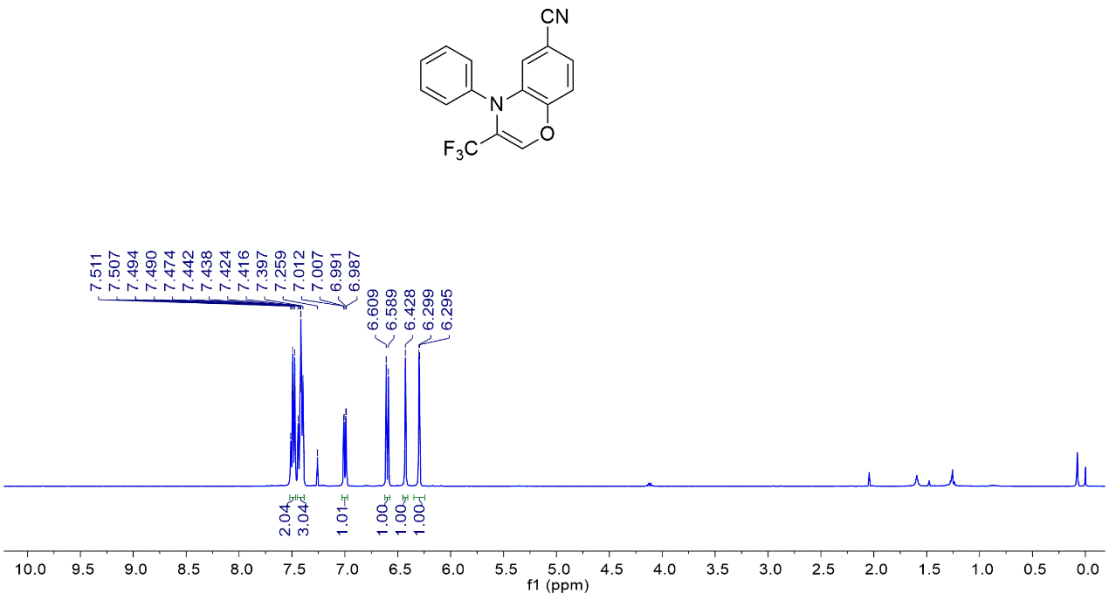
^{13}C-NMR spectrum of 3da



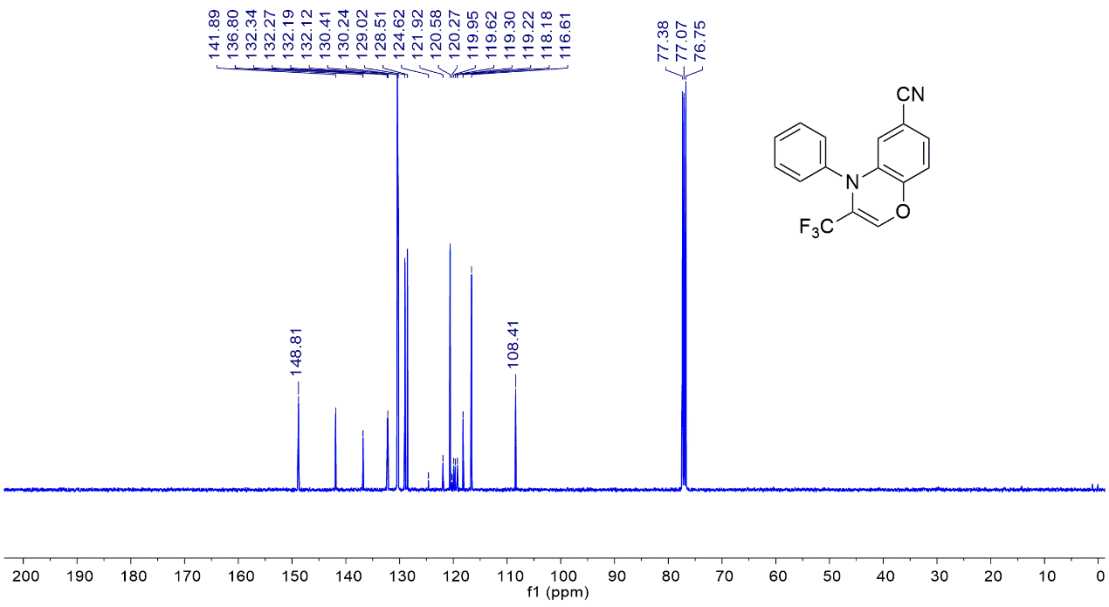
^{19}F-NMR spectrum of 3da



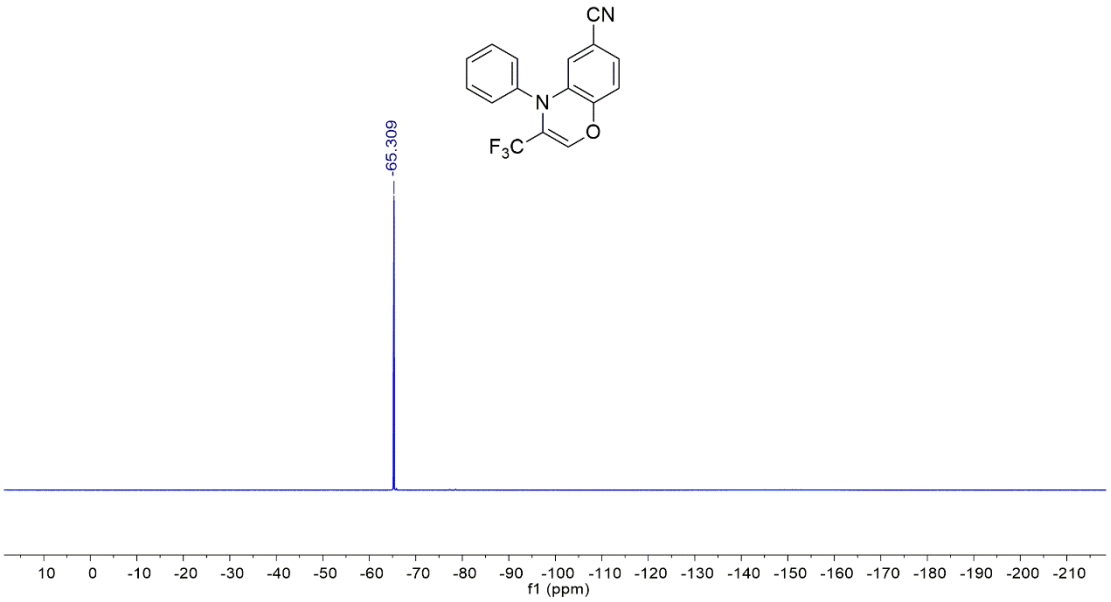
^{1}H-NMR spectrum of 3ea



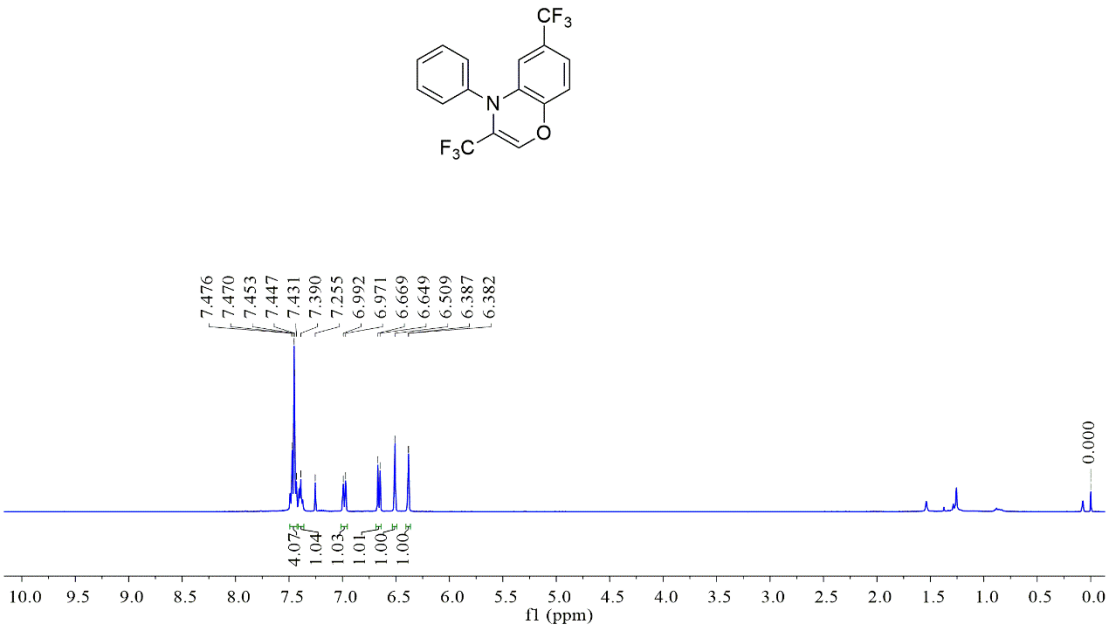
^{13}C-NMR spectrum of 3ea



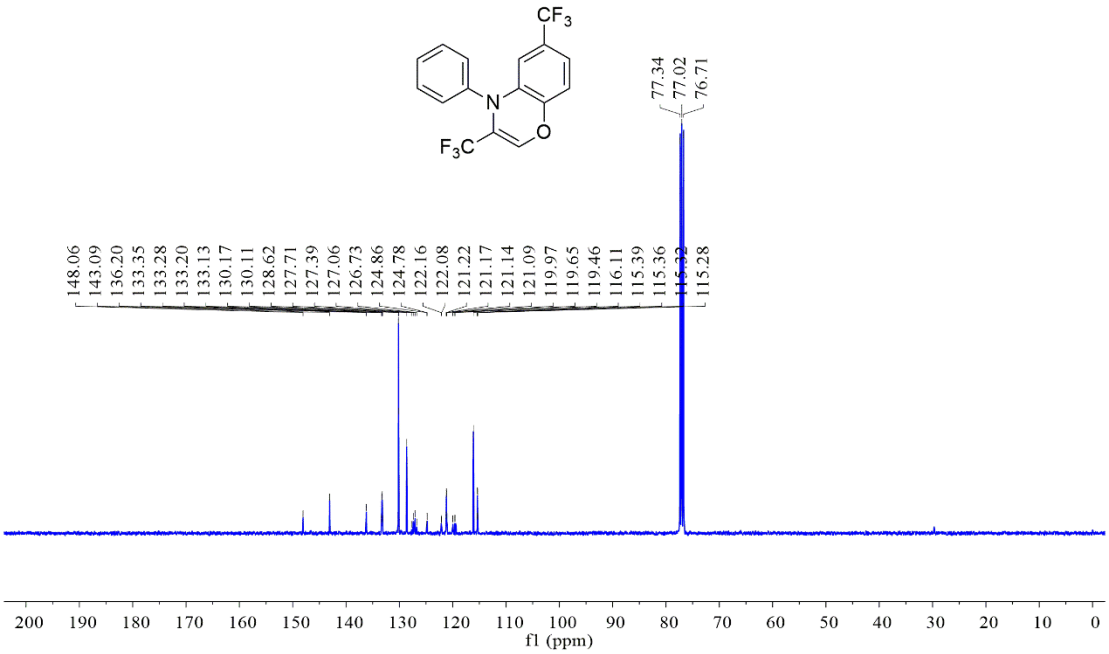
^{19}F-NMR spectrum of 3ea



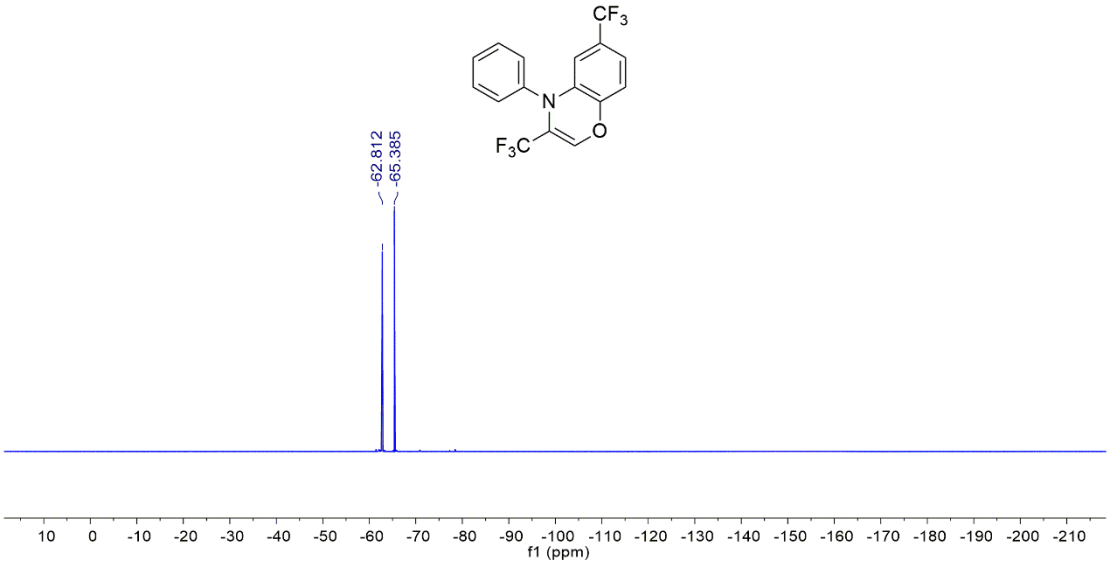
^{1}H-NMR spectrum of 3fa



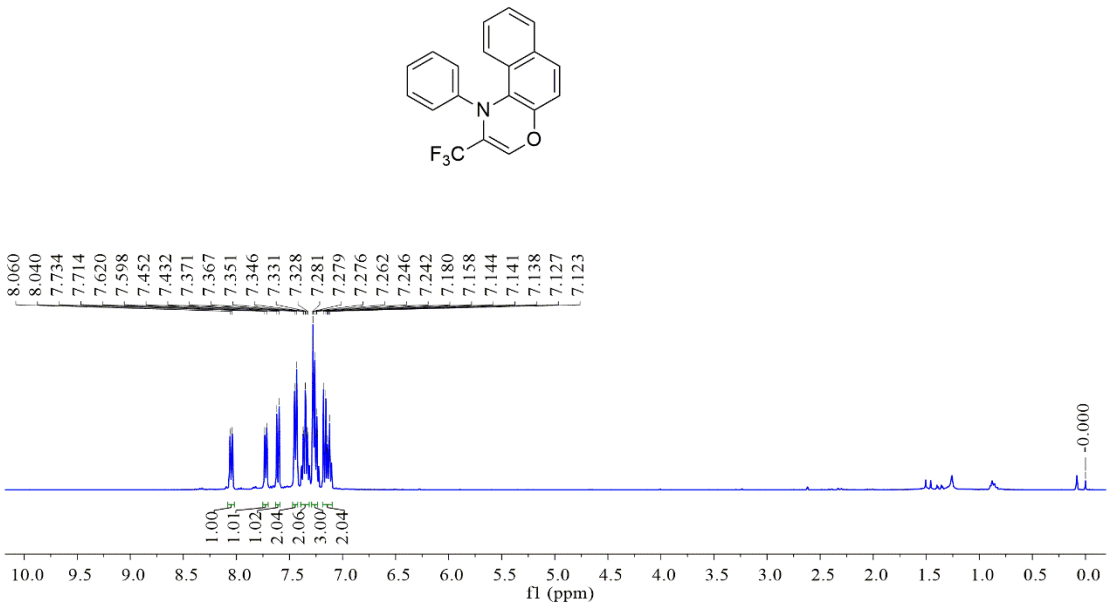
^{13}C-NMR spectrum of 3fa



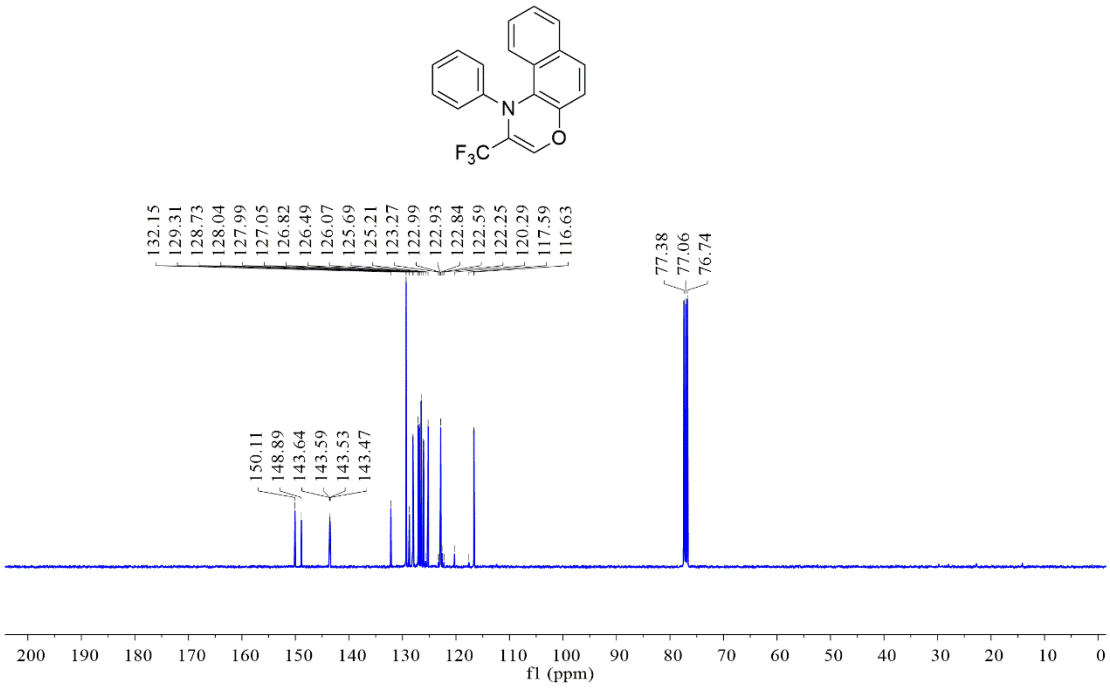
^{19}F-NMR spectrum of 3fa



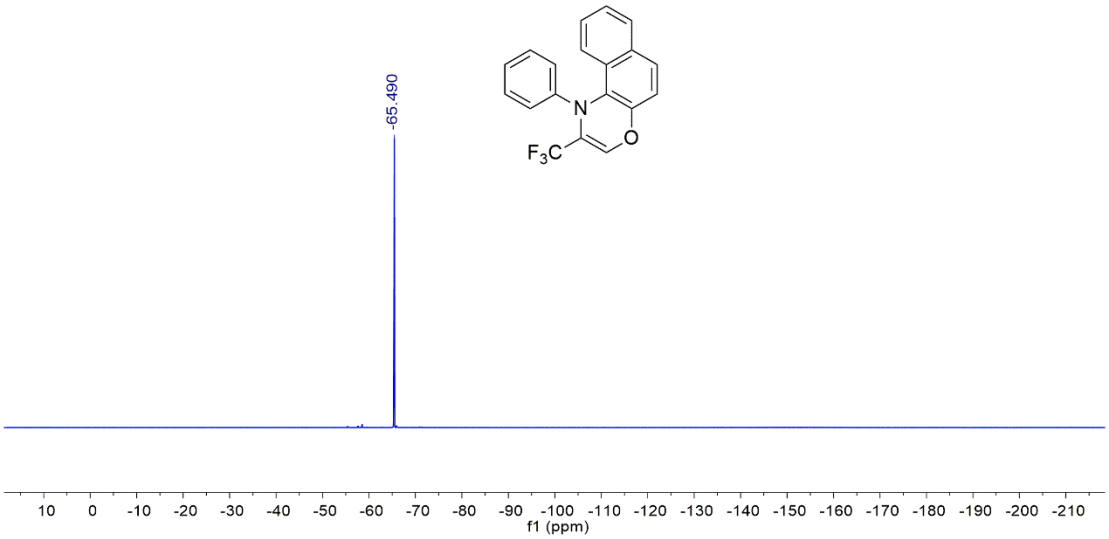
^{1}H-NMR spectrum of 3ga



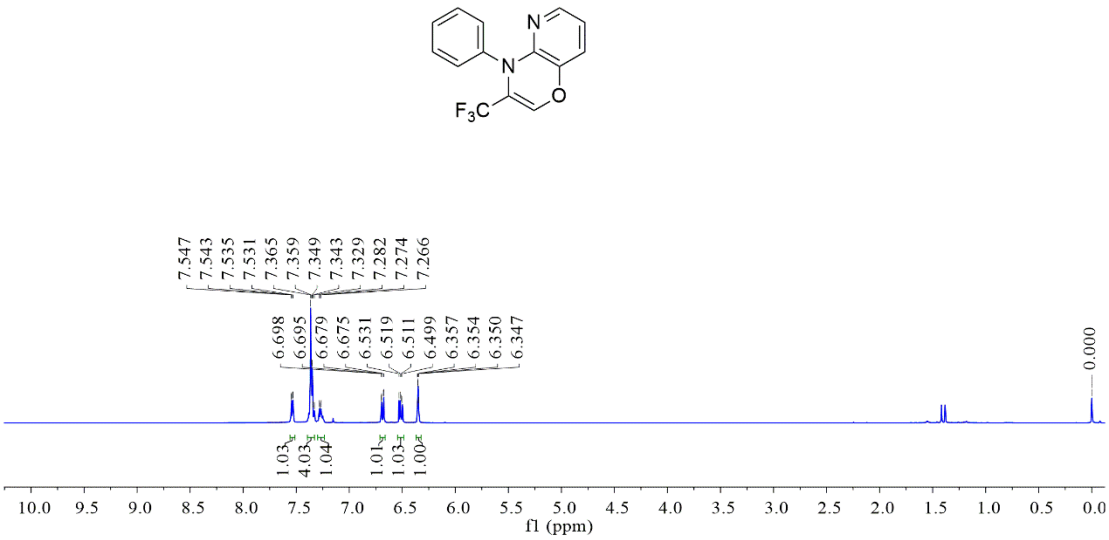
^{13}C-NMR spectrum of 3ga



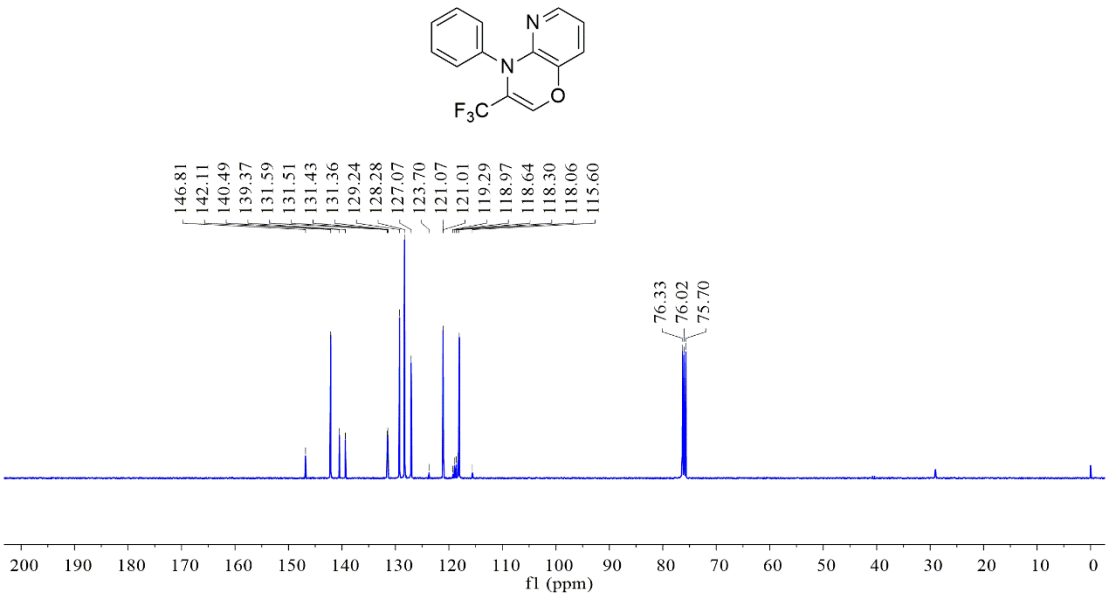
^{19}F-NMR spectrum of 3ga



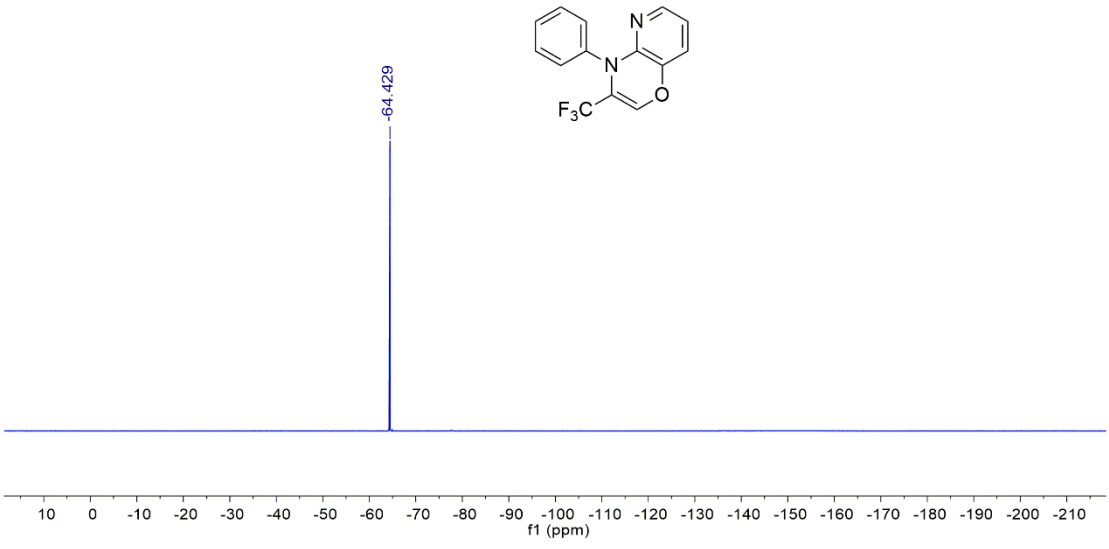
^{1}H-NMR spectrum of 3ha



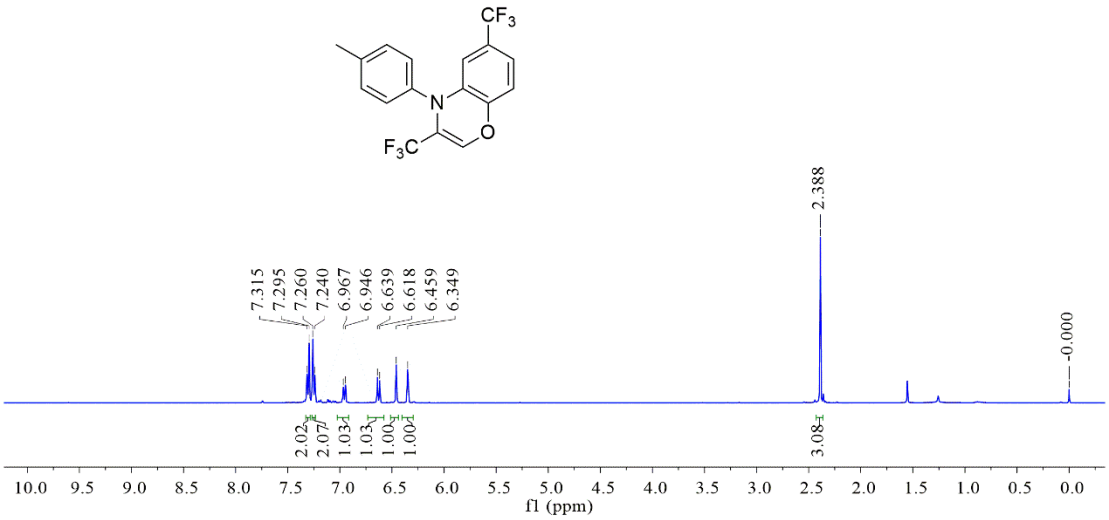
^{13}C-NMR spectrum of 3ha



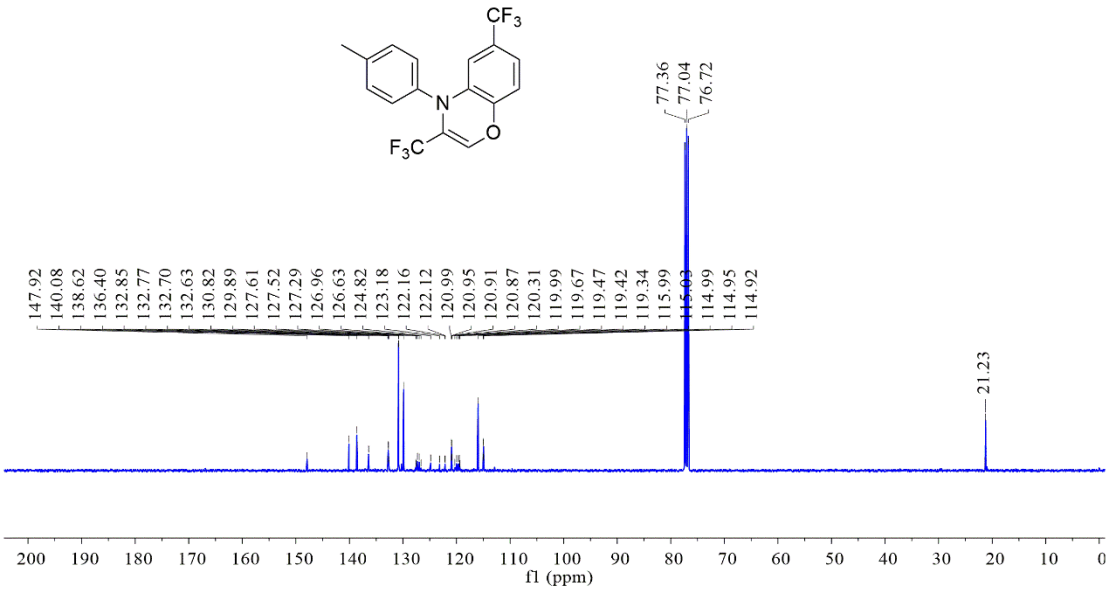
^{19}F-NMR spectrum of 3ha



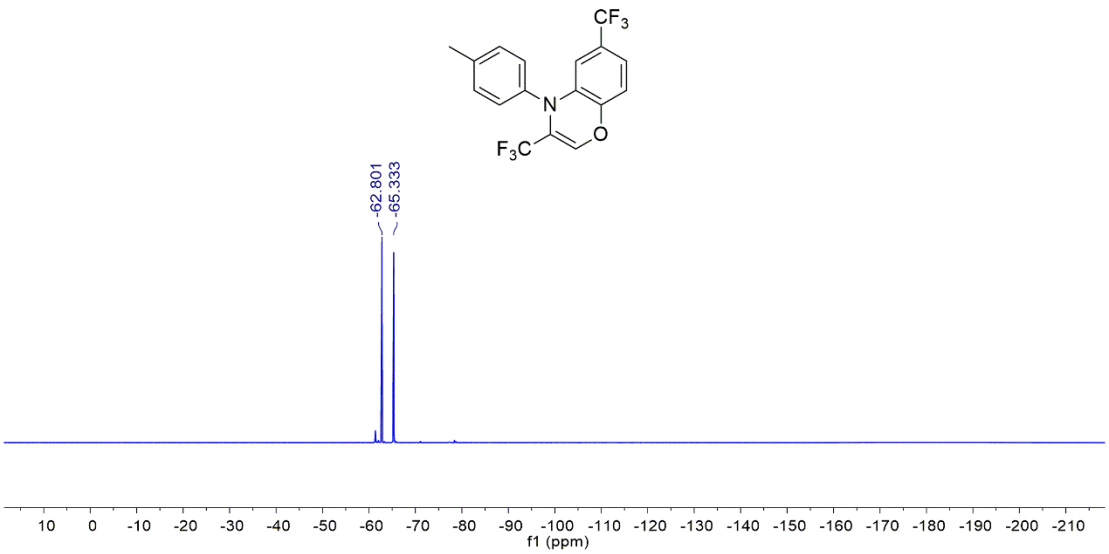
^{1}H-NMR spectrum of 3fb



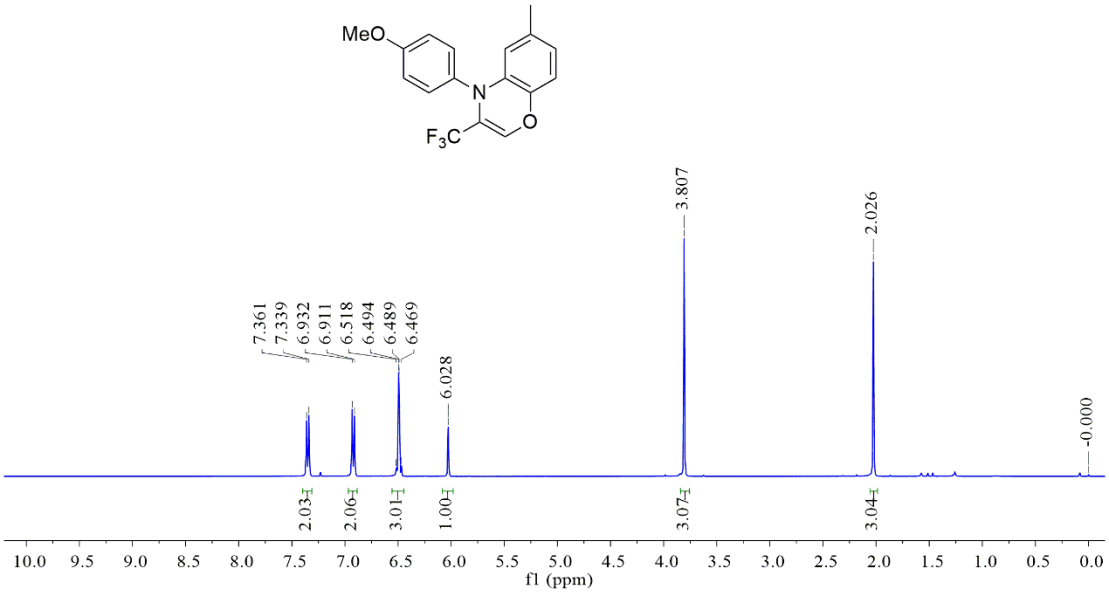
^{13}C-NMR spectrum of 3fb



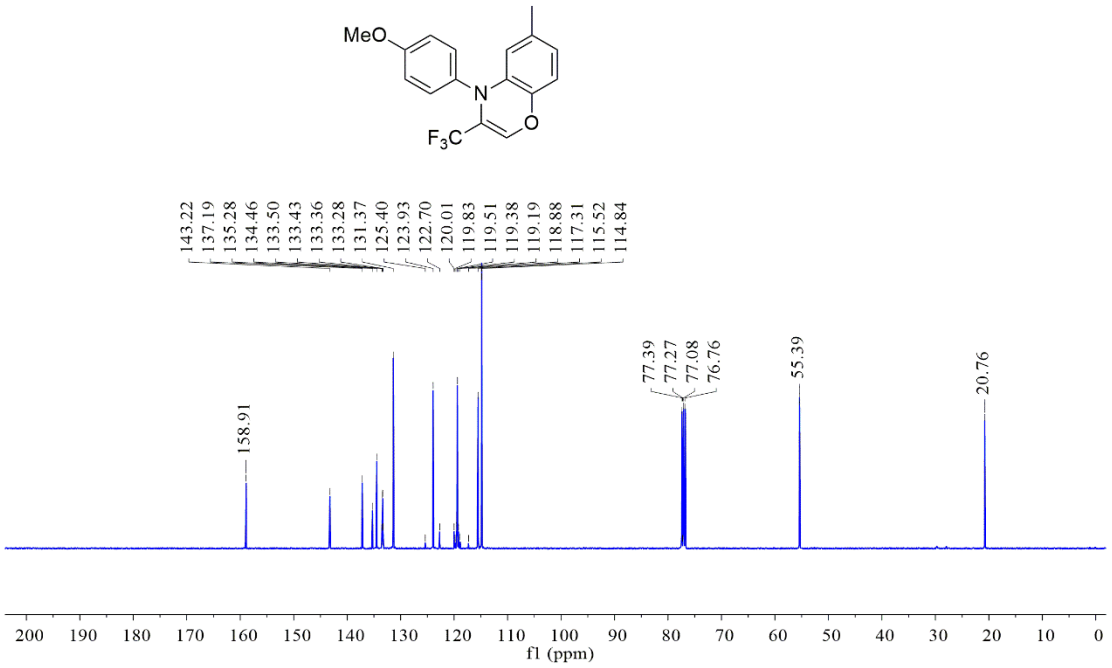
^{19}F-NMR spectrum of 3fb



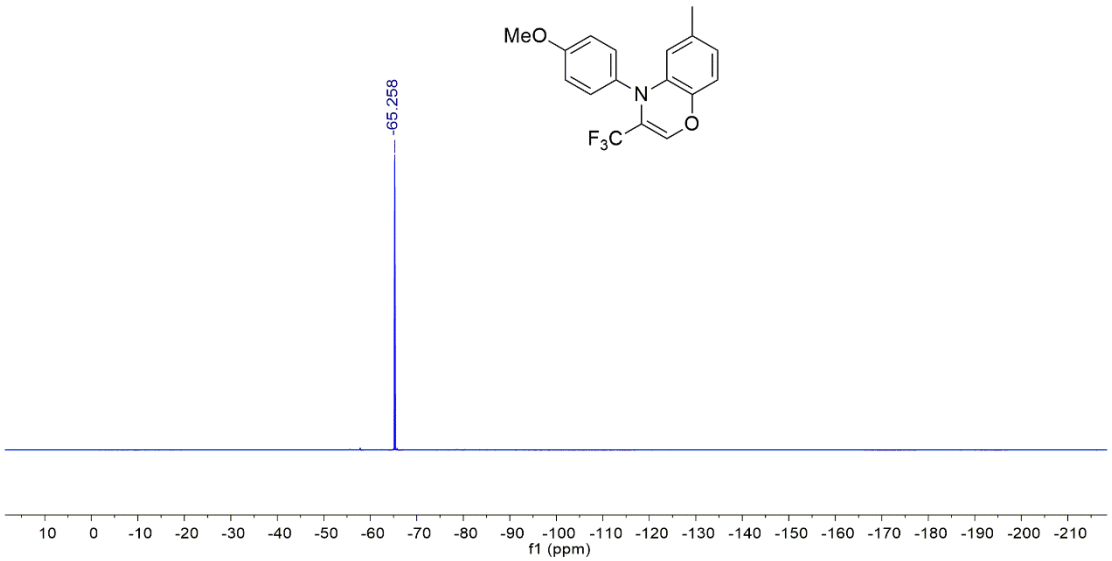
^{1}H-NMR spectrum of 3be



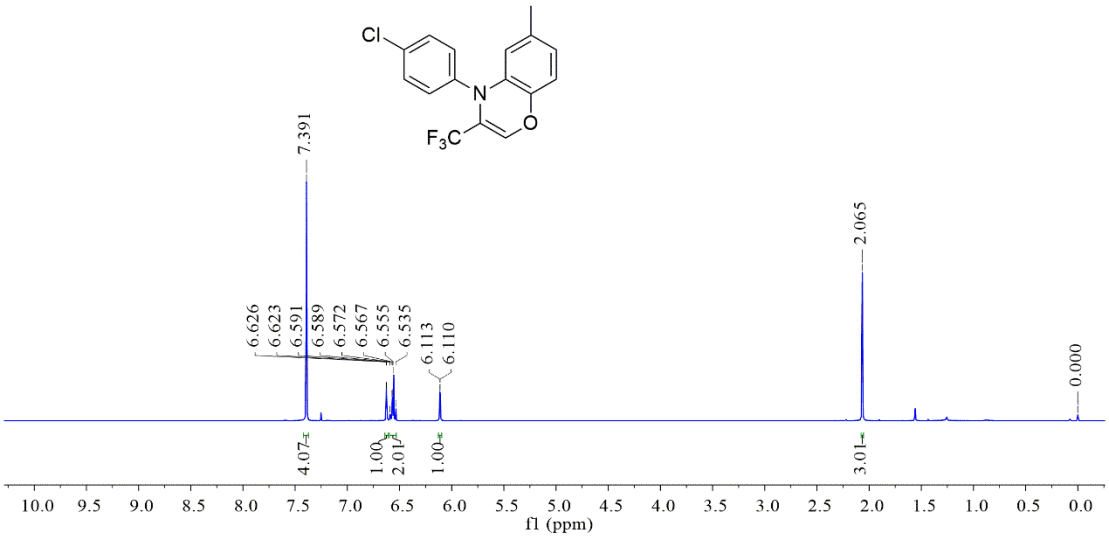
^{13}C-NMR spectrum of 3be



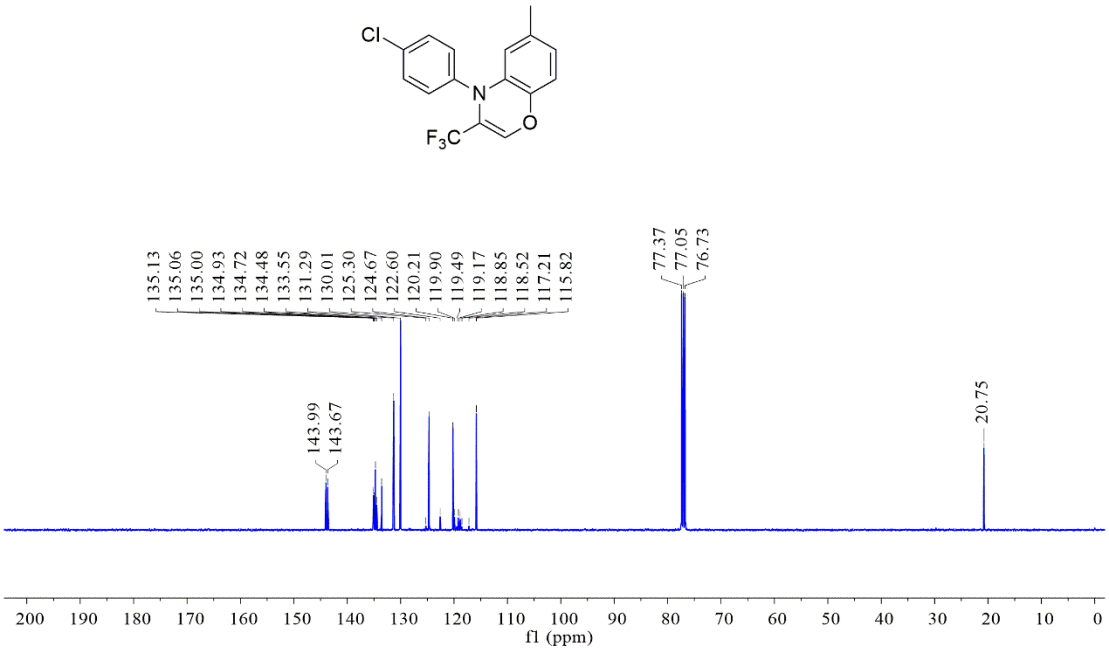
^{19}F-NMR spectrum of 3be



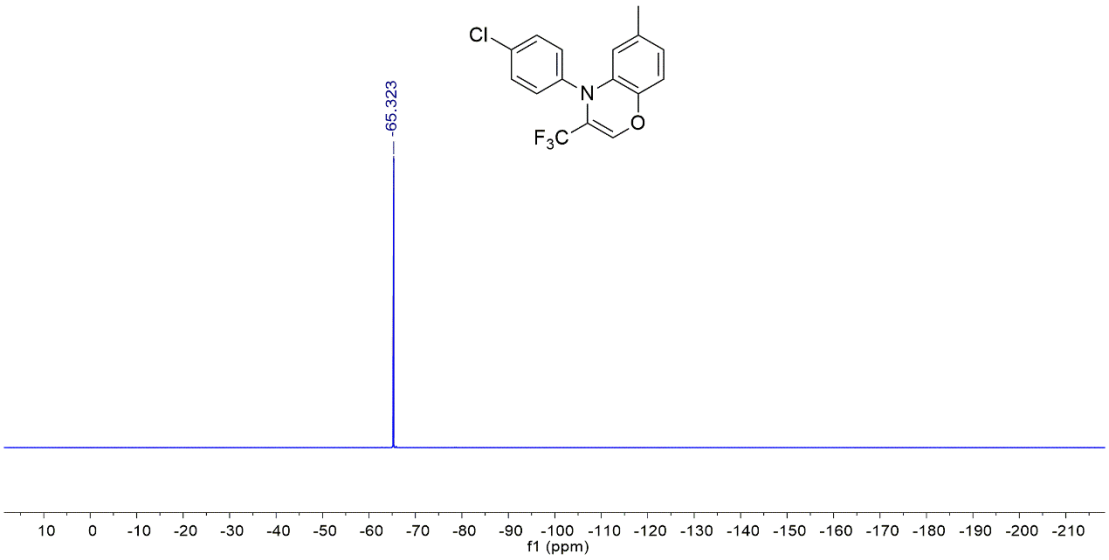
^{1}H-NMR spectrum of 3bf



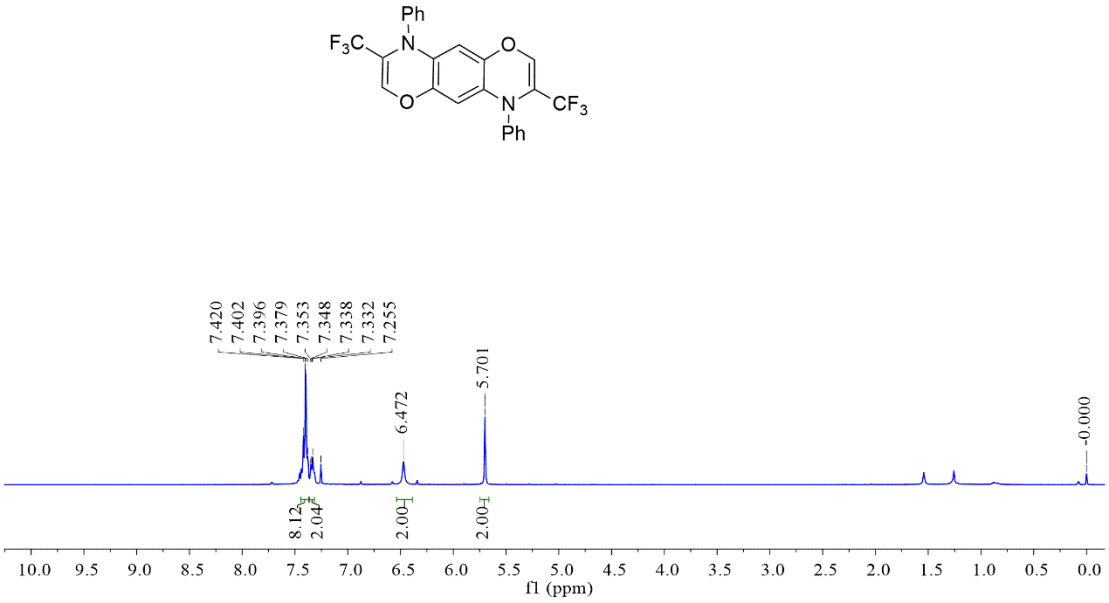
^{13}C-NMR spectrum of 3bf



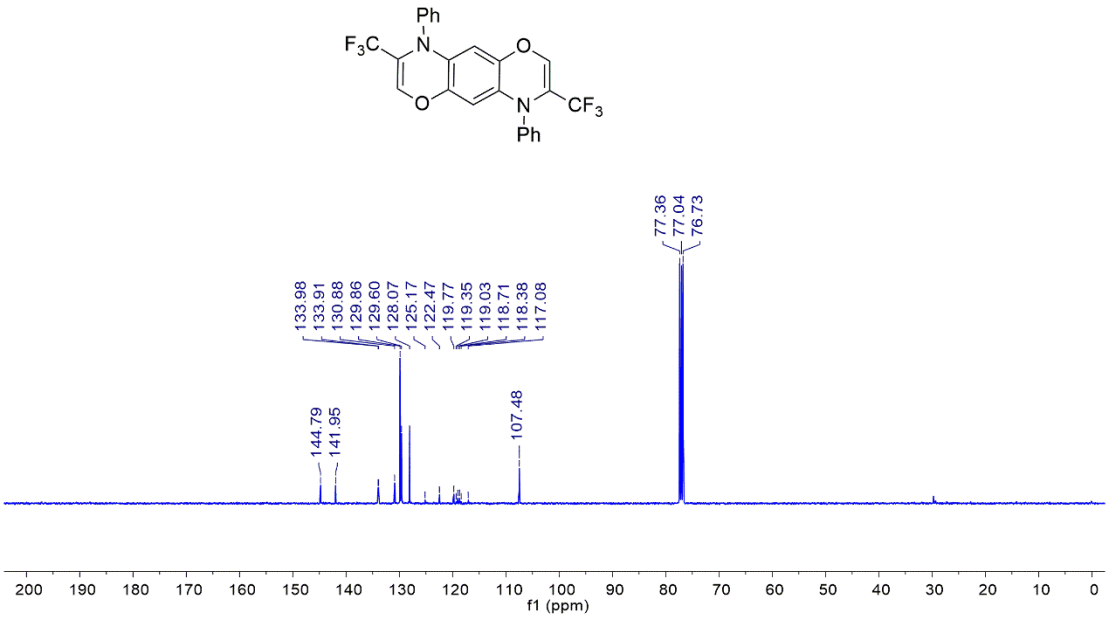
^{19}F-NMR spectrum of 3bf



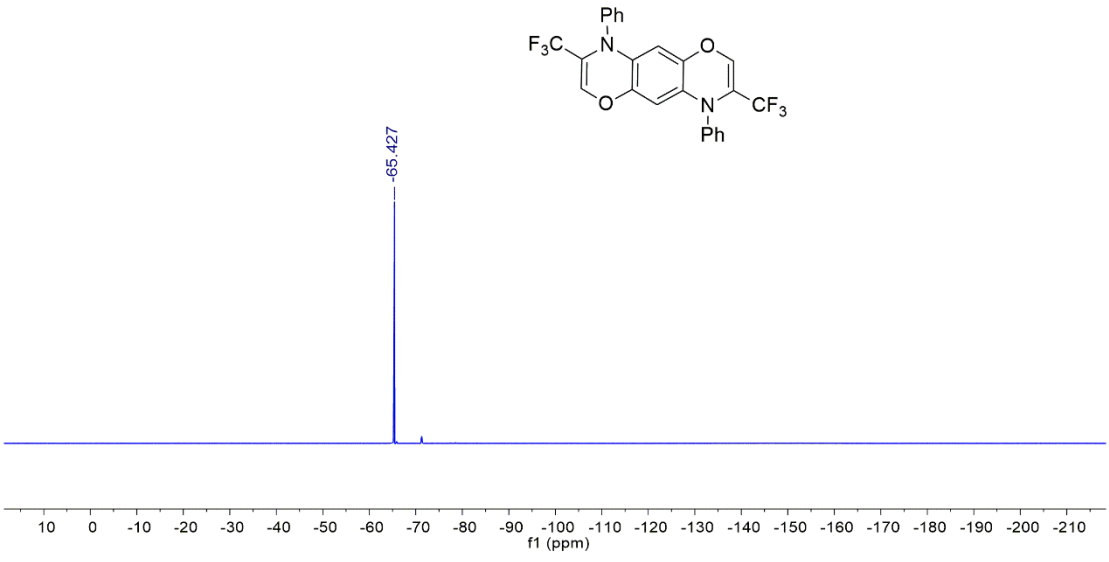
^{1}H-NMR spectrum of 3ia



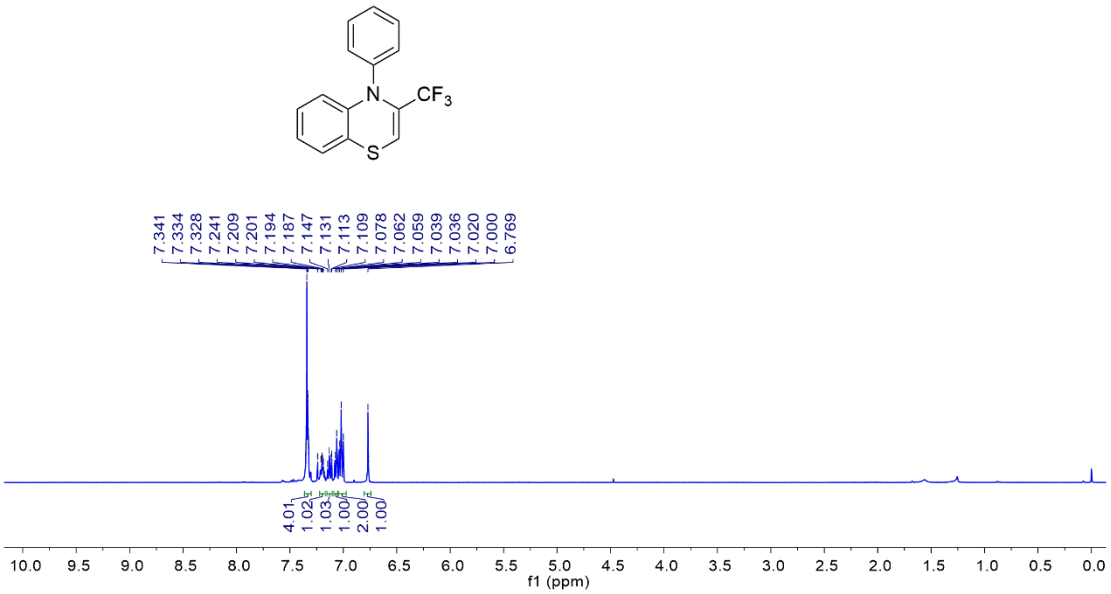
^{13}C-NMR spectrum of 3ia



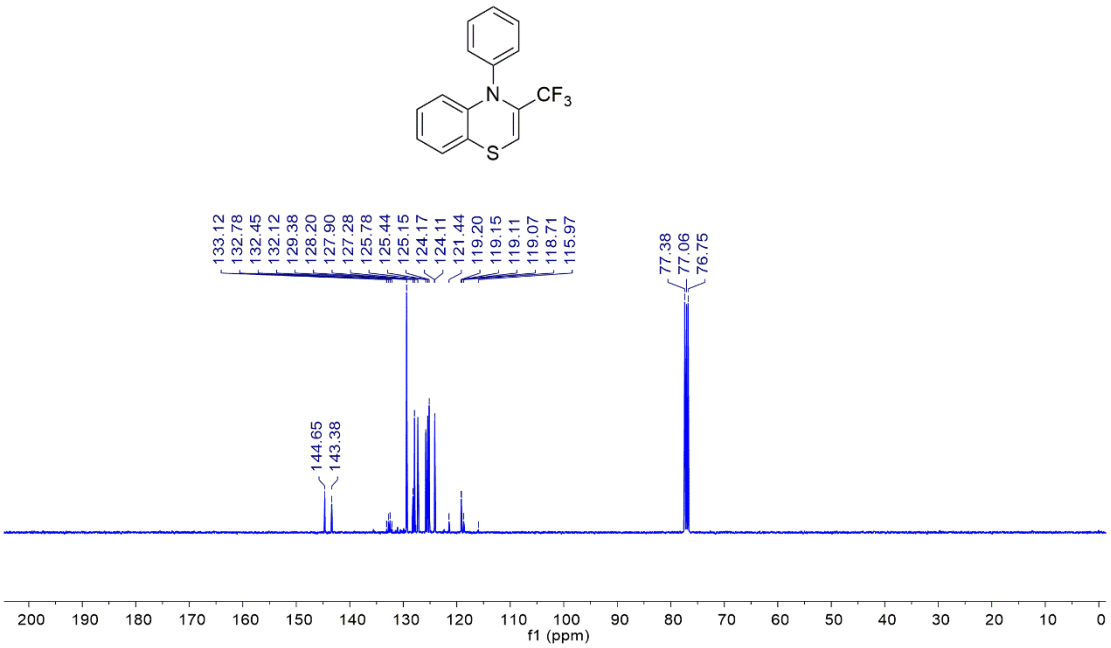
^{19}F-NMR spectrum of 3ia



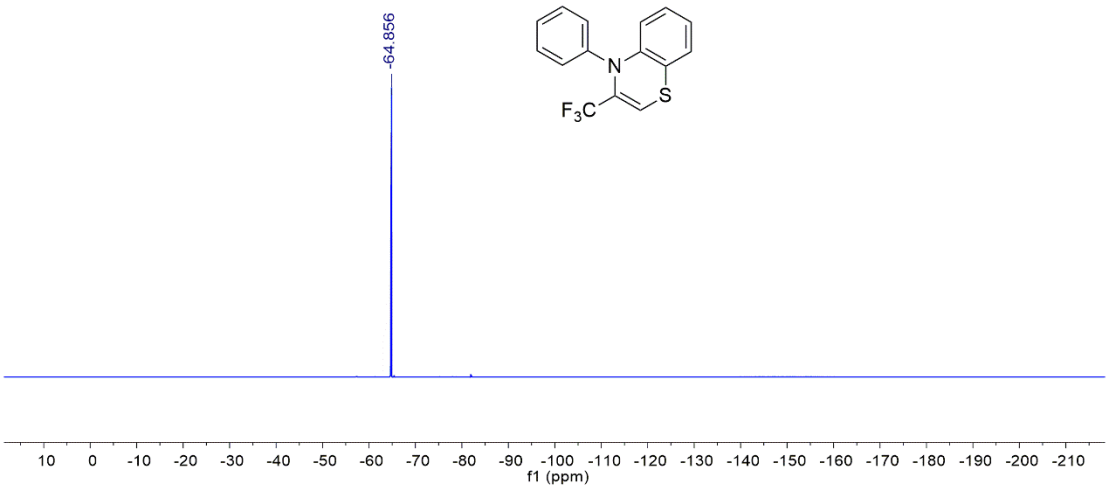
^{1}H-NMR spectrum of 3ja



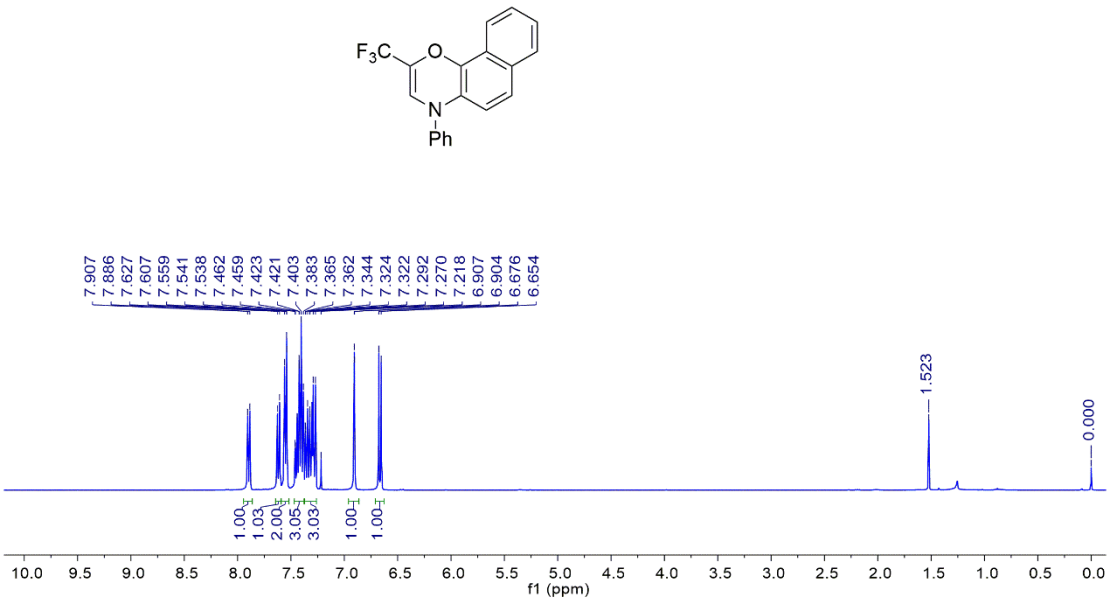
^{13}C-NMR spectrum of 3ja



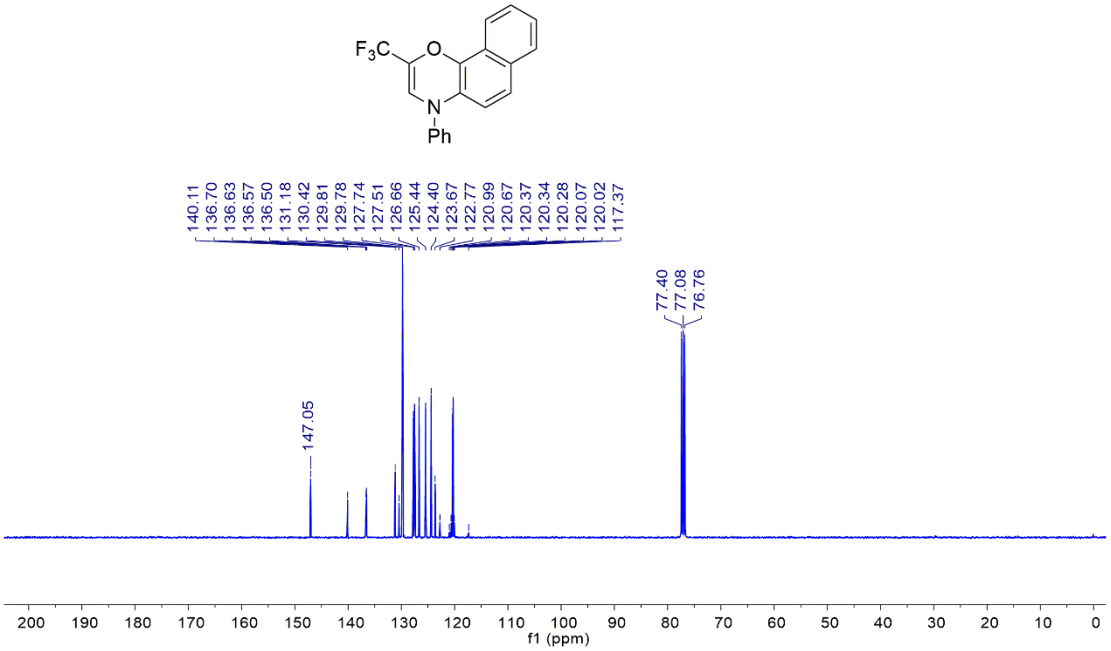
^{19}F-NMR spectrum of 3ja



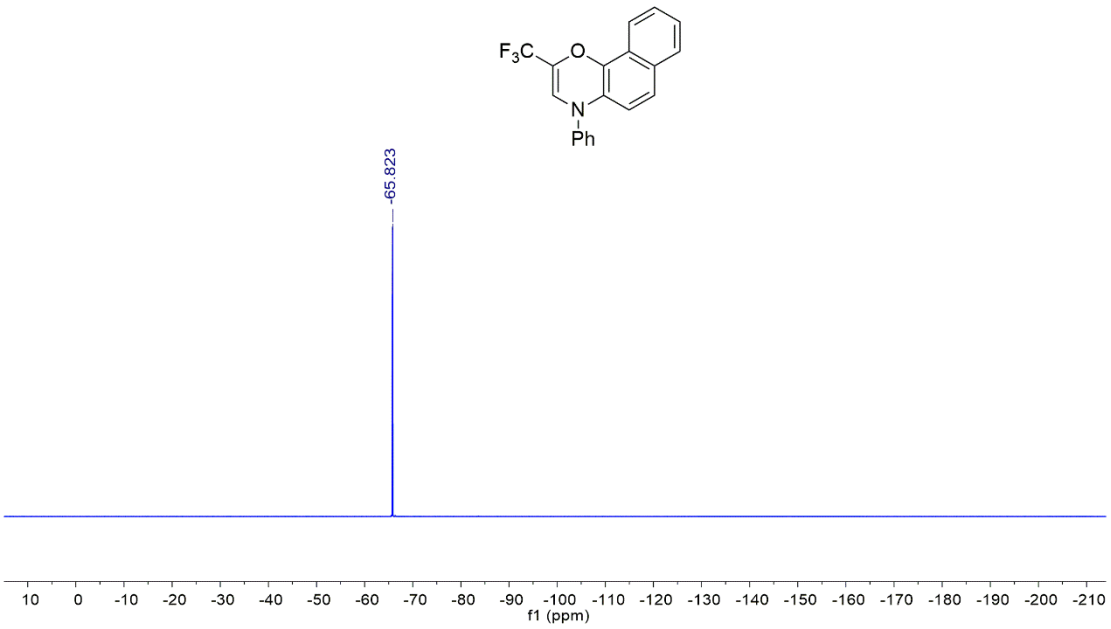
^{1}H-NMR spectrum of 3ka



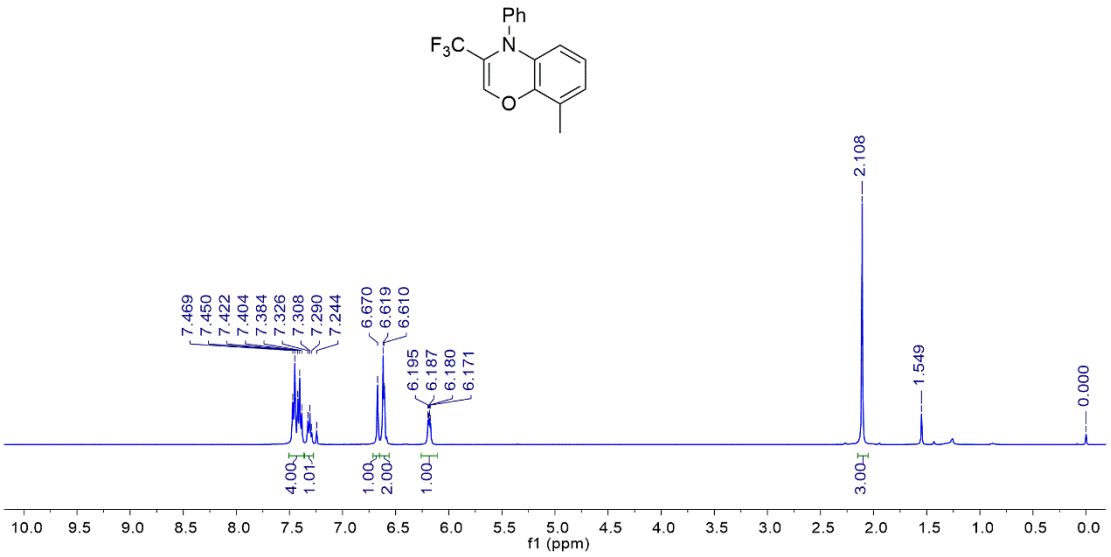
^{13}C-NMR spectrum of 3ka



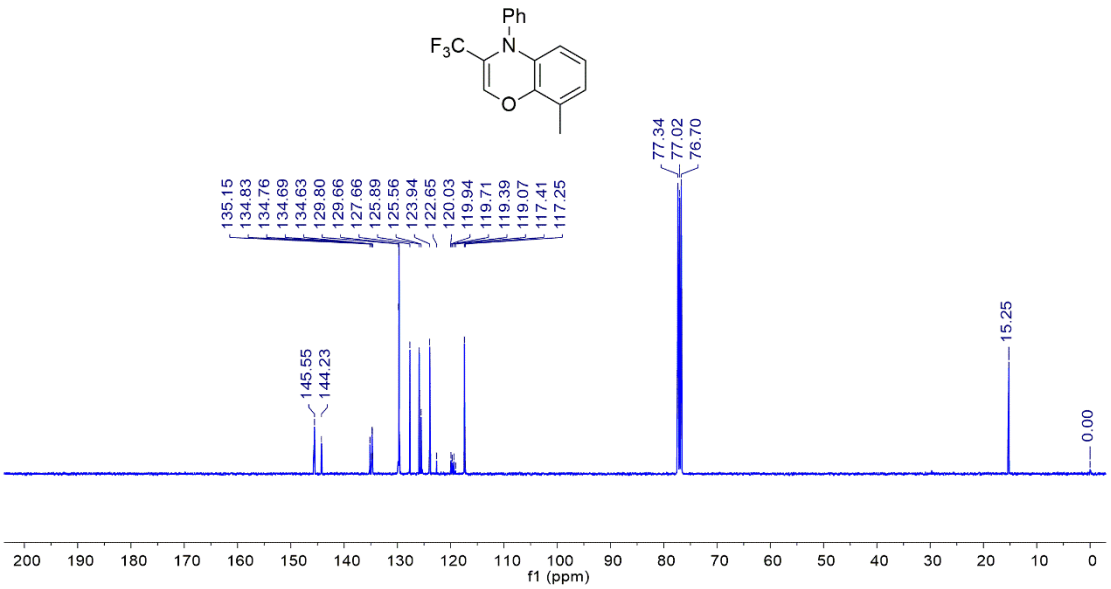
^{19}F-NMR spectrum of 3ka



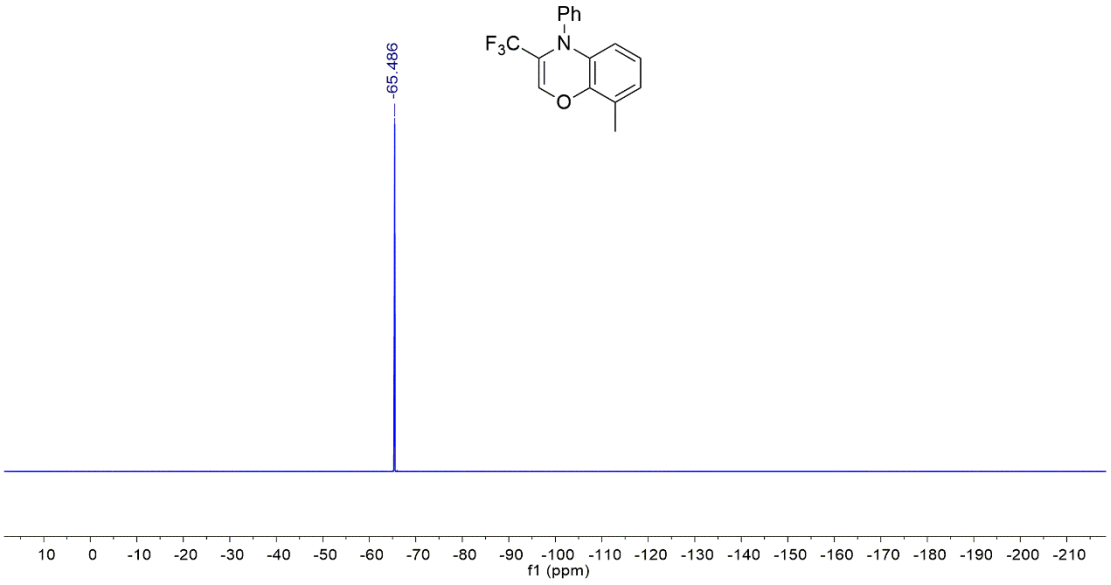
^{1}H-NMR spectrum of 3la



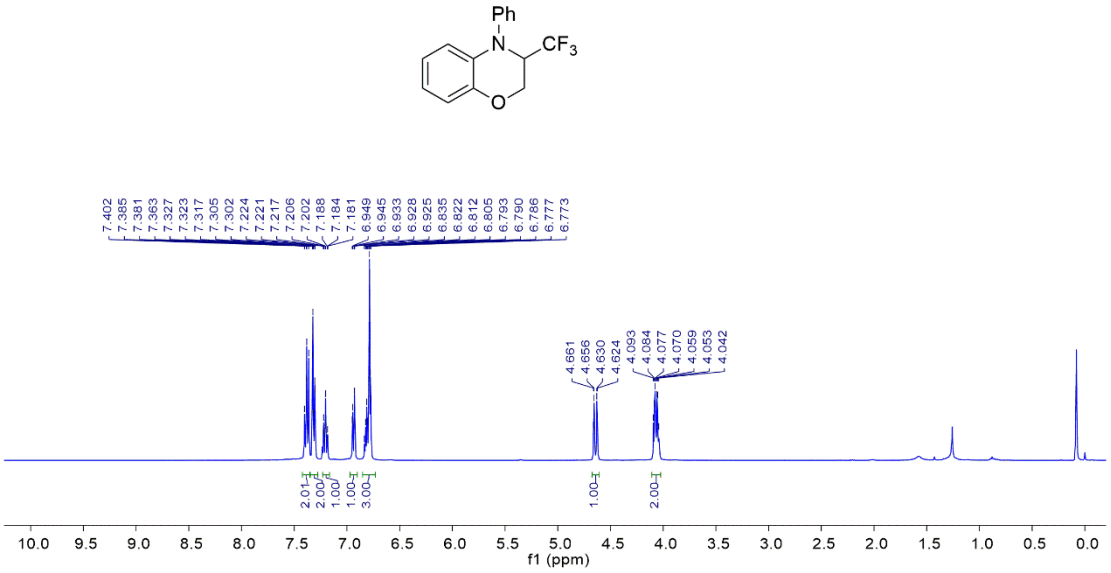
^{13}C-NMR spectrum of 3la



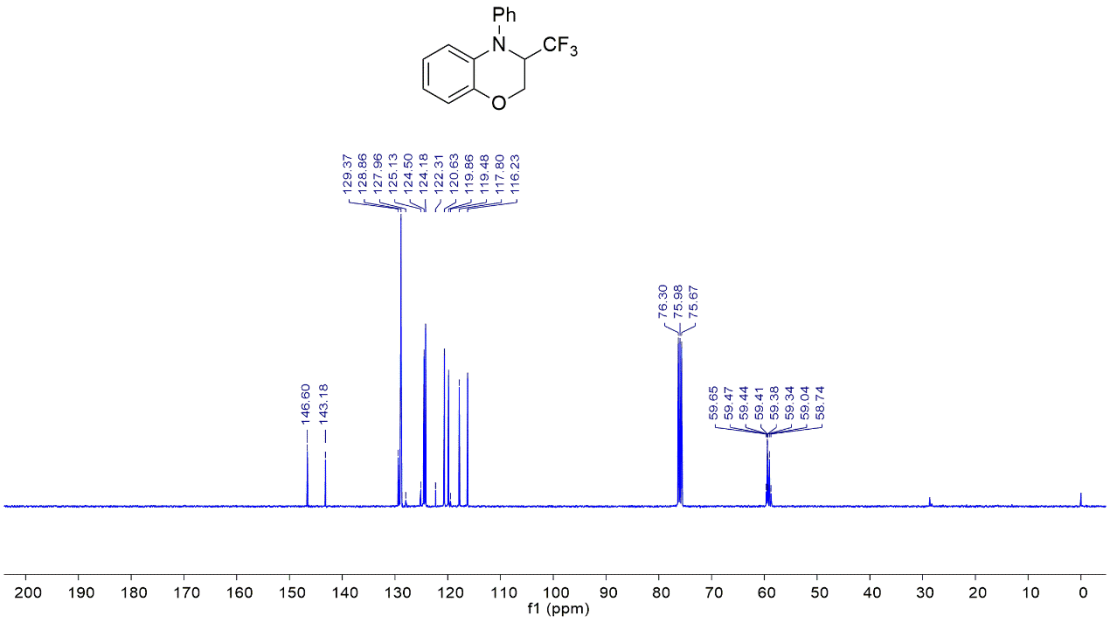
^{19}F-NMR spectrum of 3la



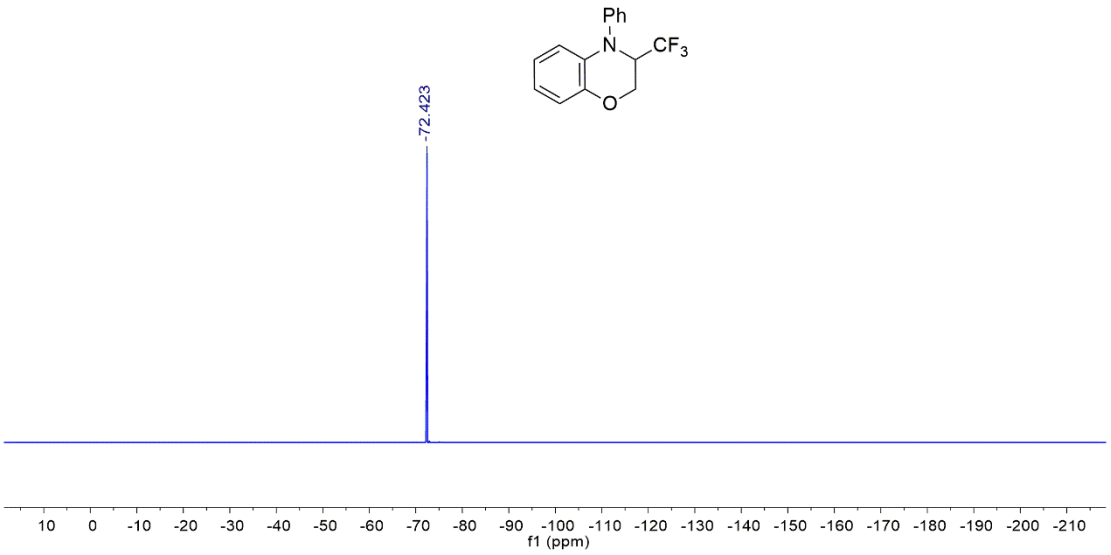
^{1}H-NMR spectrum of 4a



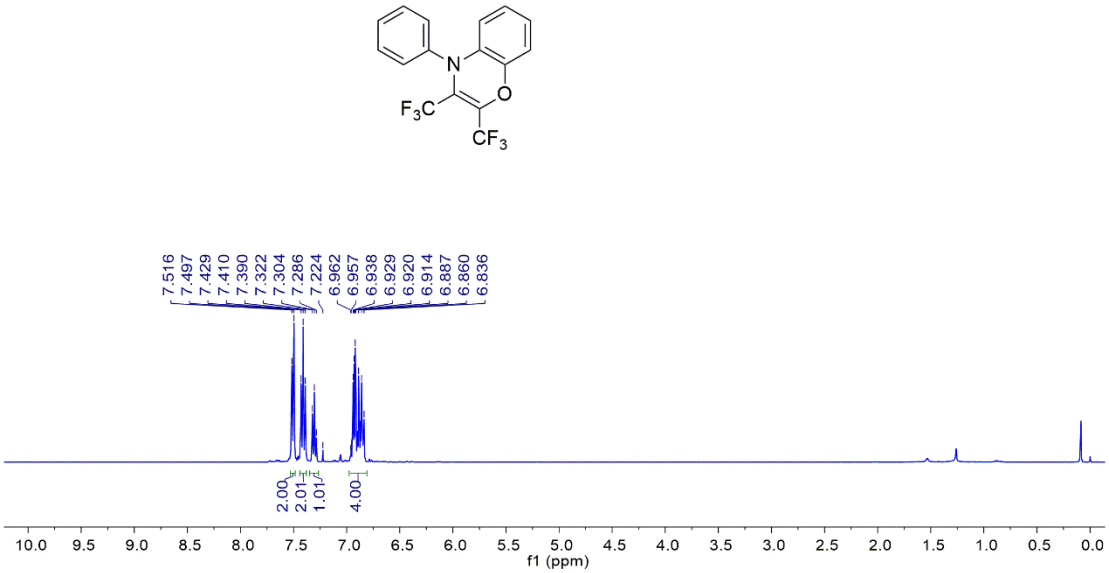
^{13}C-NMR spectrum of 4a



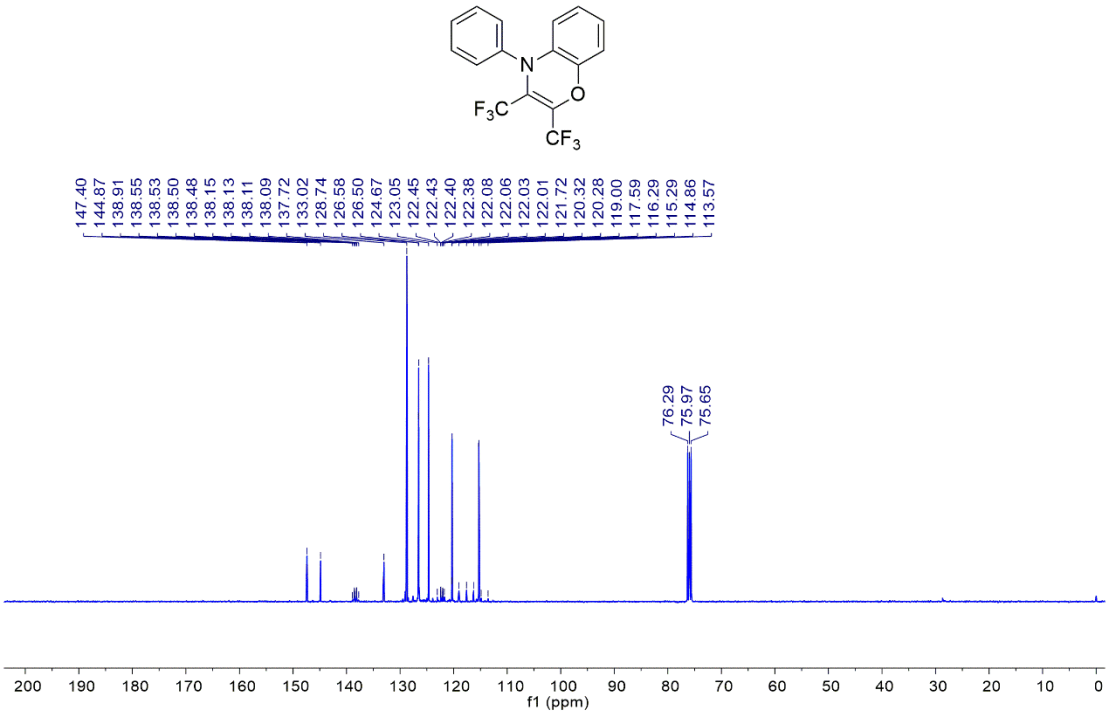
^{19}F-NMR spectrum of 4a



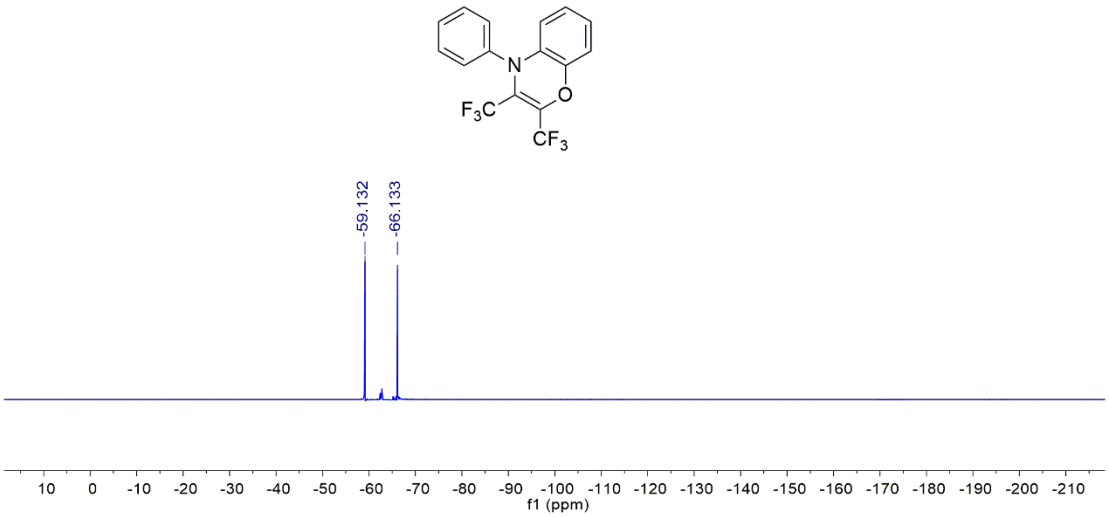
^{1}H-NMR spectrum of 5a



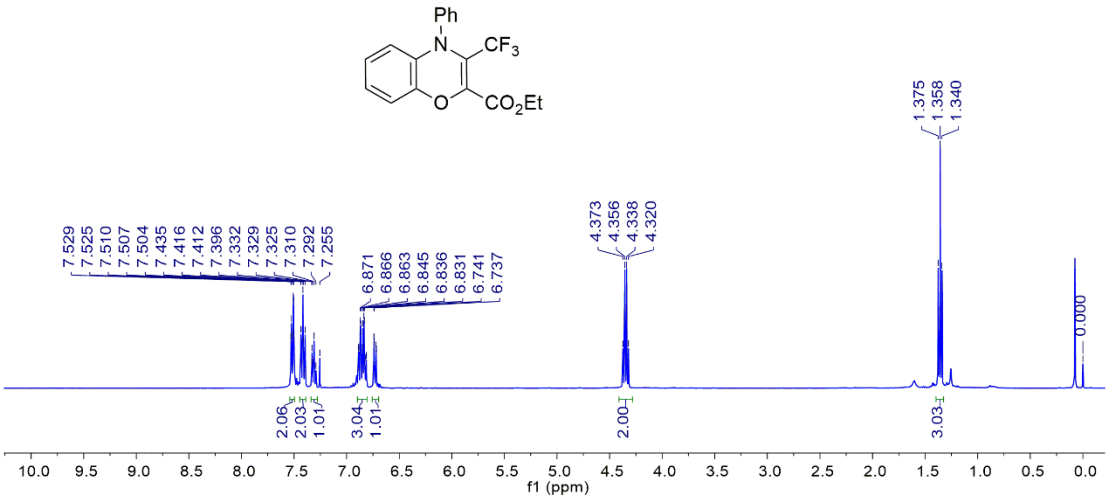
^{13}C-NMR spectrum of 5a



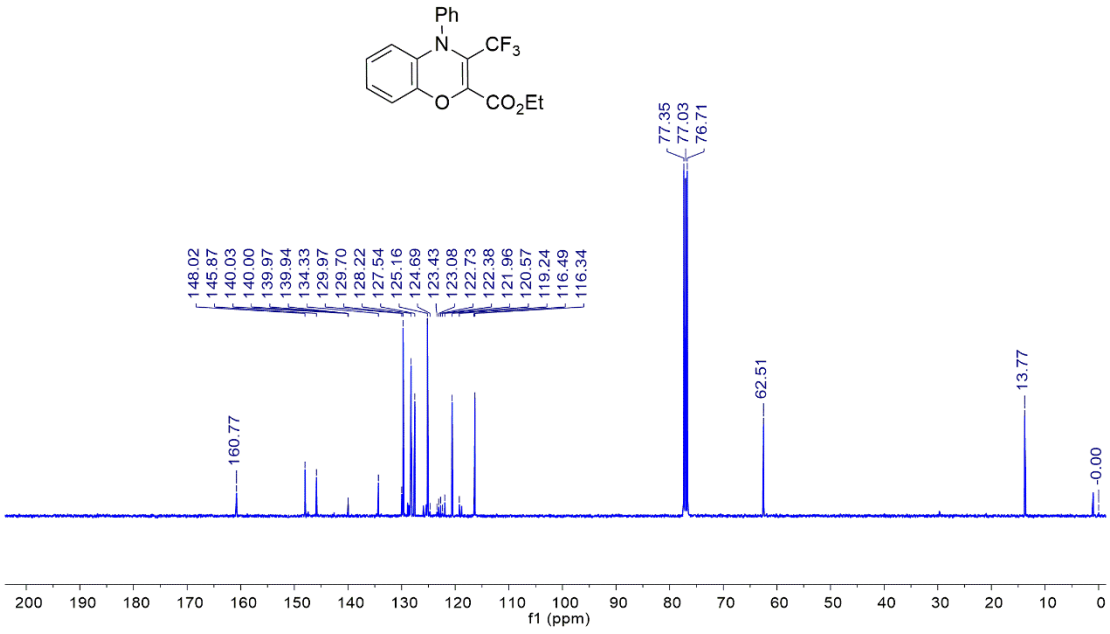
^{19}F-NMR spectrum of 5a



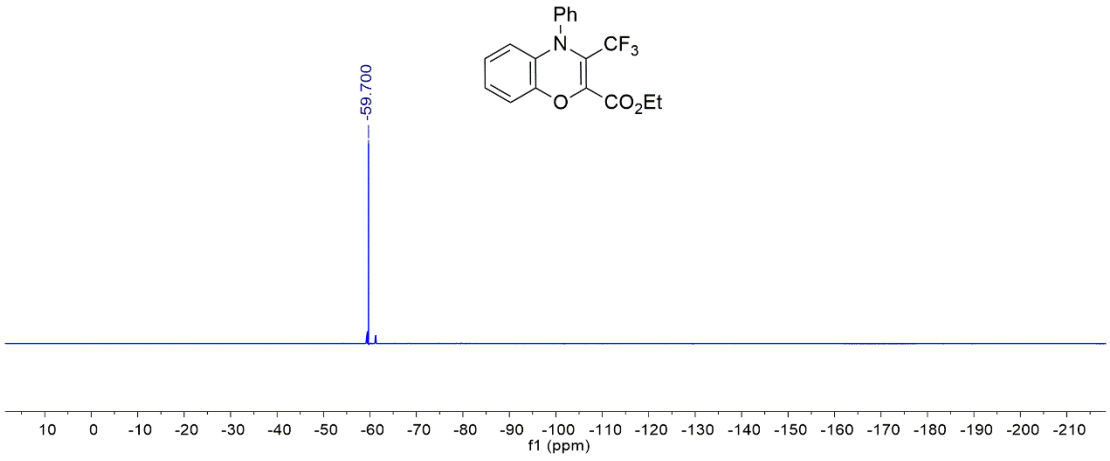
^{1}H-NMR spectrum of 6a



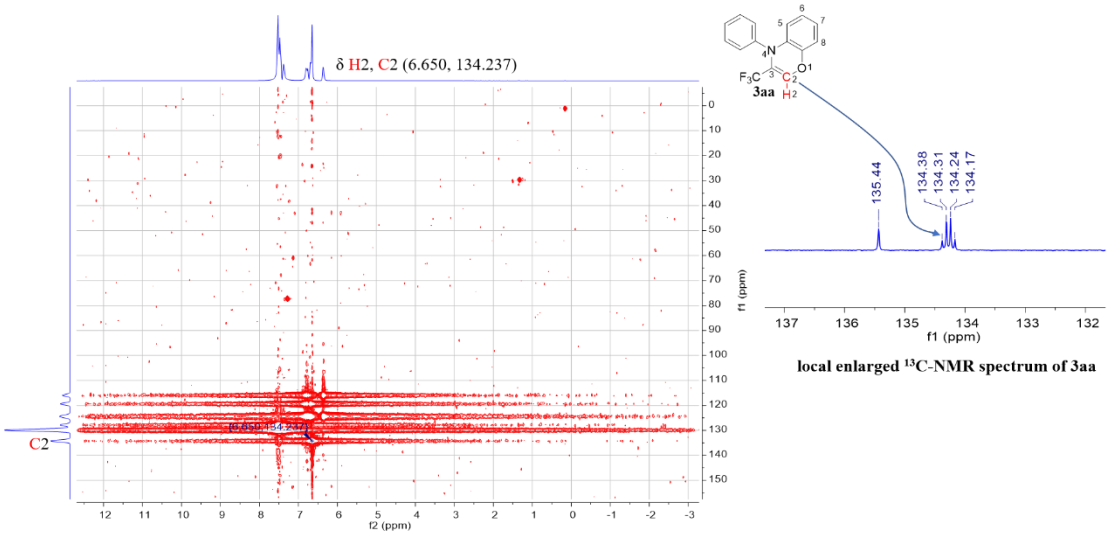
^{13}C-NMR spectrum of 6a



^{19}F-NMR spectrum of 6a



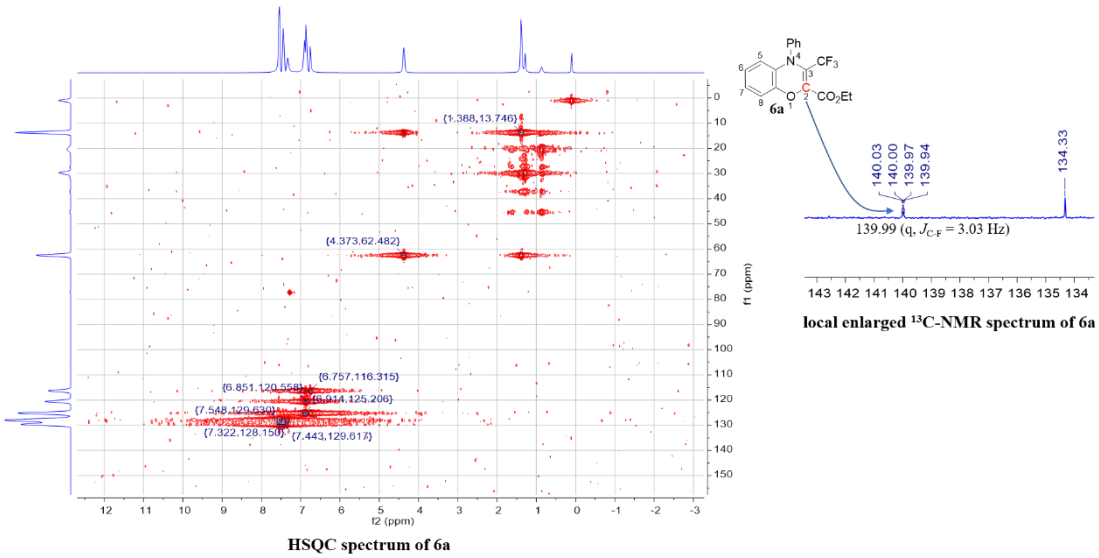
HSQC spectrum of 3aa



HSQC spectrum of 3aa

local enlarged ^{13}C-NMR spectrum of 3aa

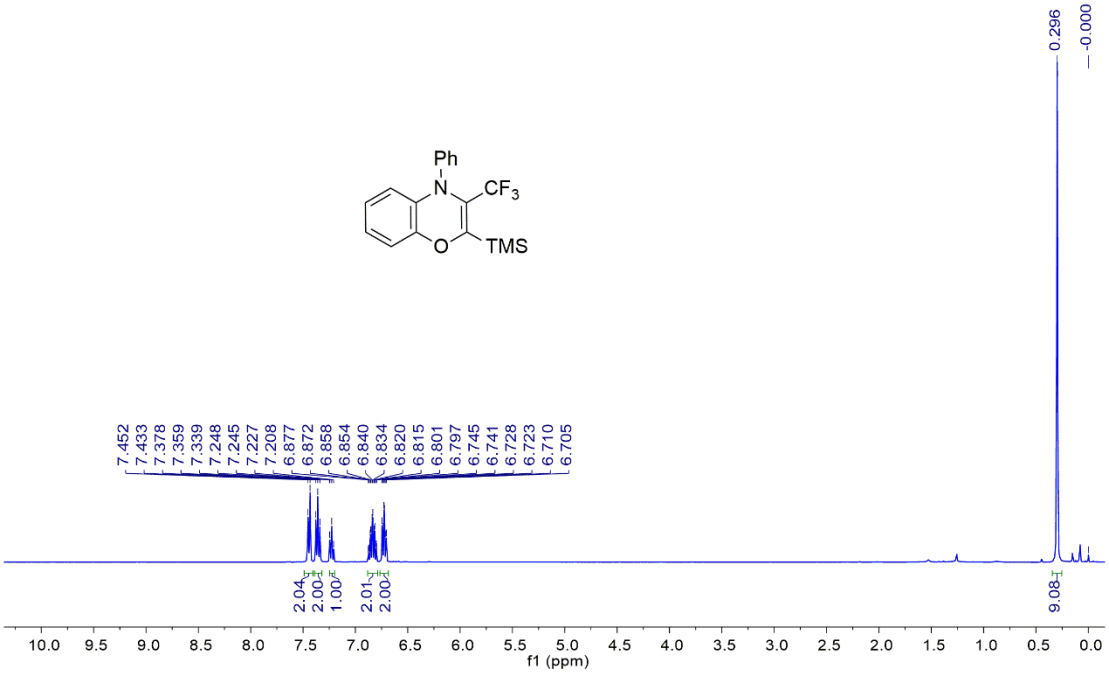
HSQC spectrum of 6a



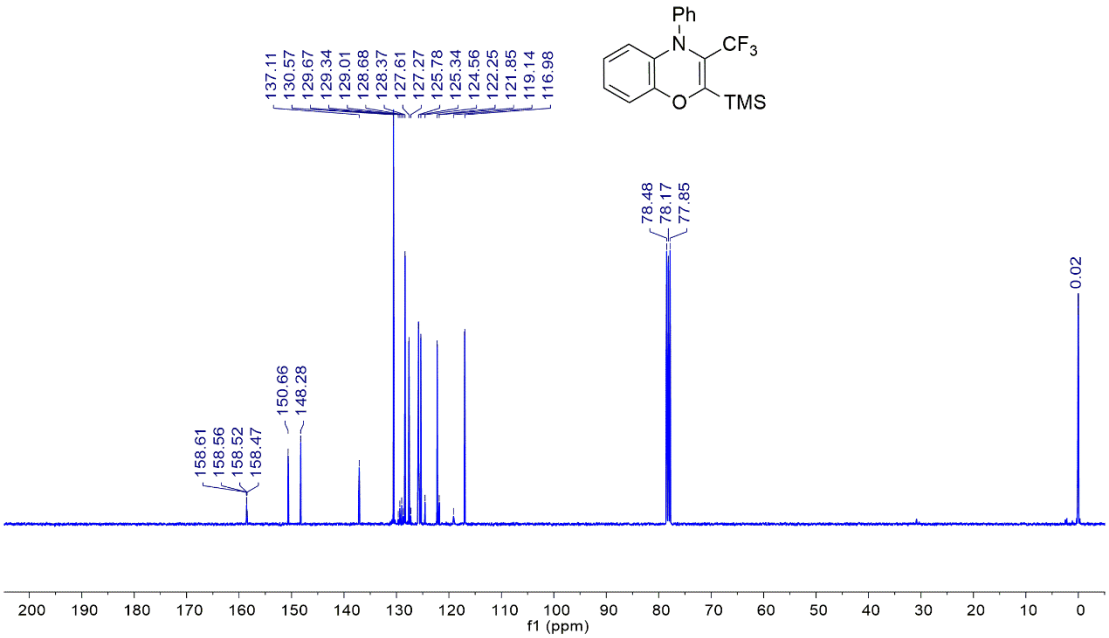
HSQC spectrum of 6a

local enlarged ^{13}C-NMR spectrum of 6a

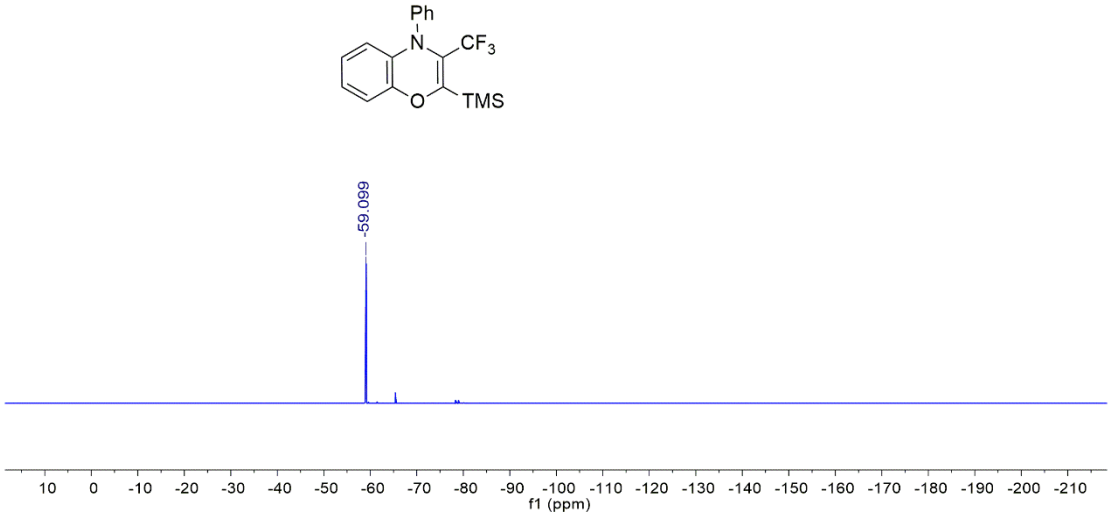
^{1}H-NMR spectrum of 7a



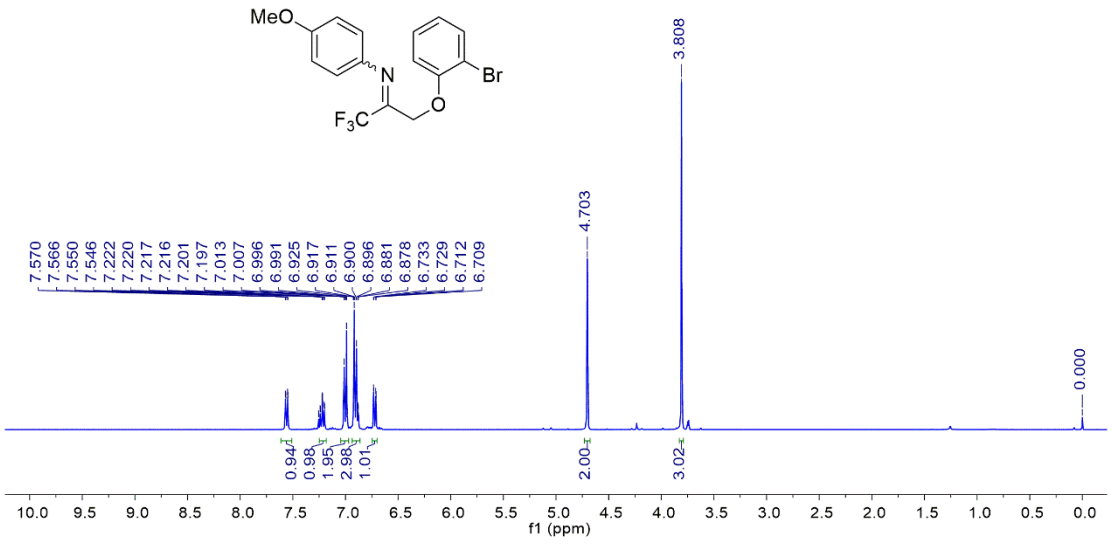
^{13}C-NMR spectrum of 7a



^{19}F-NMR spectrum of 7a



^{1}H-NMR spectrum of 3ae’



^{13}C-NMR spectrum of 3ae’