Supporting Information

Electrochemical Synthesis of PhSe/CF_3-containing Dibenzazepines via Radical Cascade Cyclization of Alkynes

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1. General Information

All commercially available reagents were used as supplied without further purification unless stated otherwise. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica gel plates (GF 254) using UV light as a visualizing agent. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2. Graphite, reticulated vitreous carbon (RVC), glassy carbon (GC) and Pt electrodes were purchased from taobao. Graphite electrodes could be used several times by renewing the top surface of the graphite.

^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 in Chloroform-*d*. For ^{1}H NMR, Chloroform-*d* (δ = 7.26 ppm) tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; for ^{13}C NMR, Chloroform-*d* (δ = 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, h = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration.

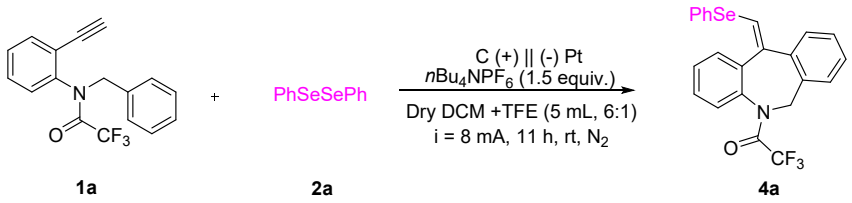
The electrochemical reactions were performed on a DJS-292B potentiostat (made in China) in constant current mode. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using Time-of-Flight (TOF) MS and electrospray ionization. The cyclic voltammetry measurements were detected by using a CHI 760E electrochemical workstation.

The procedures for the synthesis of substrates are according to the reported method.[1]

2. General Procedures

Materials used for set-up: 25 mL three-necked flask, carbon rod (ϕ = 4 mm) anode, platinum wire (10×15×0.2 mm) cathode, DJS-292B potentiostat.

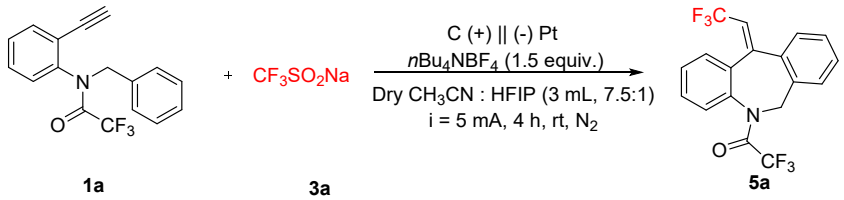
To a three-necked flask equipped with a stir bar, a carbon rod anode, and a platinum wire cathode was added the substrate **1a** (0.2 mmol, 60.6 mg) and **2a** (0.2 mmol, 1.0 equiv.) and electrolyte nBu$_4$NPF$_6$ (1.5 equiv.), 5.0 mL solvent (DCM: TFE = 6:1). The distance of electrodes was approximately 1.0 cm. The constant current (8 mA) electrolysis was then performed at room temperature under nitrogen atmosphere with stirring for the indicated time as monitored by TLC or NMR analysis. After completion of the reaction, the resulting mixture was purified by column chromatography on silica gel (eluted with PE/EA) to afford the desired products **4a**.



1a **2a** **4a**

Scheme S1. Reaction formula

To a three-necked flask equipped with a stir bar, a carbon rod anode, and a platinum wire cathode was added the substrate **1a** (0.2 mmol, 60.6 mg) and **3a** (0.4 mmol, 2.0 equiv.) and electrolyte nBu$_4$NBF$_4$ (1.5 equiv.), 3.0 mL solvent (CH$_3$CN: HFIP = 7.5:1). The distance of electrodes was approximately 1.0 cm. The constant current (5 mA) electrolysis was then performed at room temperature under nitrogen atmosphere with stirring for the indicated time as monitored by TLC or NMR analysis. After completion of the reaction, the resulting mixture was purified by column chromatography on silica gel (eluted with PE/EA) to afford the desired products **5a**.



1a **3a** **5a**

Scheme S2. Reaction formula

3. Reaction Optimizations

3.1 Optimization of reaction conditions for synthesis of PhSe-containing dibenzazepines

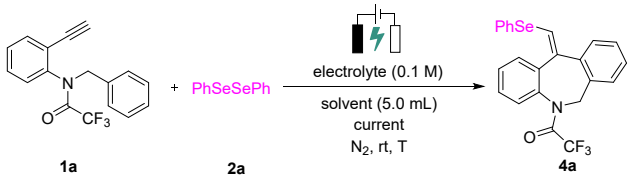


Table S1. The solvent experiments of selenylation reaction

entry	solvent	yield
1	dry CH_3CN	30%
2	dry DCM	50%
3	dry DMF	n.d.
4	dry DMSO	n.d.
5	dry DMA	n.d.
6	dry THF	n.d.

Table S2. The electrolyte experiments of selenylation reaction

entry	electrolyte	yield
1	nBu$_4$NPF$_6$	50%
2	nBu$_4$NBF$_4$	35%
3	nBu$_4$NOAc	n.d.
4	nBu$_4$NClO$_4$	n.d.
5	nBu$_4$NI	n.d.
6	nBu$_4$NCl	n.d.
7	nBu$_4$NBr	n.d.
8	KPF_6	n.d.

Table S3. The electrode experiments of selenylation reaction

entry	electrode	yield
1	C (+) || (-) Pt	70%
2	C (+) || (-) C	37%
3	Pt (+) || (-) Pt	42%
4	C (+) || (-)Ni	45%
5	RVC (+) || (-) Pt	n.d.

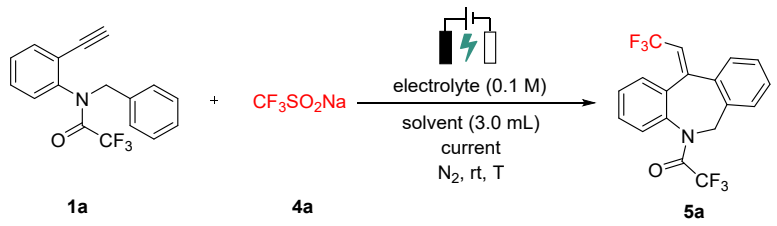
Table S4. The current experiments of selenylation reaction

entry	current	time	yield
1	5 mA	5 h	50%
2	5 mA	12 h	54%
3	8 mA	8 h	64%
5	8 mA	11h	70%

Table S5. The solvent experiments of selenylation reaction

entry	solvent (5 mL)	yield
1	dry DCM: CH_3OH (20:l)	n.d.
2	dry DCM: HFIP (20:1)	20%
3	dry DCM: AcOH (20:1)	30%
4	dry DCM: H_2O (20:1)	trace
5	dry DCM: TFE (20:1)	50%
6	dry DCM: TFE (10:1)	54%
7	dry DCM: TFE (8:1)	60%
8	dry DCM: TFE (6:1)	68%
9	dry DCM: TFE (4:1)	63%
10	TFE	30%

3.2 Optimization of reaction conditions for synthesis of CF_3-containing dibenzazepines



1a **4a** **5a**

Table S6. The solvent experiments of trifluoromethyl reaction

entry	solvent (3.0 mL)	yield
1	DCM	trace
2	CH_3CN	30%
3	DMF	n.d
4	DMA	trace
5	DMSO	n.d
6	THF	n.d
7	CH_3CN+CH_3OH (15:1)	n.d
8	CH_3CN+TFE (15:1)	45%
9	CH_3CN+AcOH (15:1)	30%
10	CH_3CN+HFIP (15:1)	45%
11	CH_3CN+HFIP (10:1)	56%
12	CH_3CN+HFIP (7.5:1)	77%
13	CH_3CN+HFIP (5:1)	60%

Table S7. The electrolyte experiments of trifluoromethyl reaction

entry	electrolyte	yield
1	nBu$_4$NPF$_6$	58%
2	nBu$_4$NBF$_4$	45%
3	nBu$_4$NOAc	77%
4	nBu$_4$NClO$_4$	48%
5	nBu$_4$NI	n.d
6	nBu$_4$NCl	n.d
7	nBu$_4$NBr	50%

Table S8. The electrode experiments of trifluoromethyl reaction

entry	electrode	yield
1	C (+) || (-) Pt	77%
2	C (+) || (-) C	50%
3	Pt (+) || (-) Pt	40%
4	C (+) || (-) Ni	50%
5	C felt (+) || (-) Pt	58%

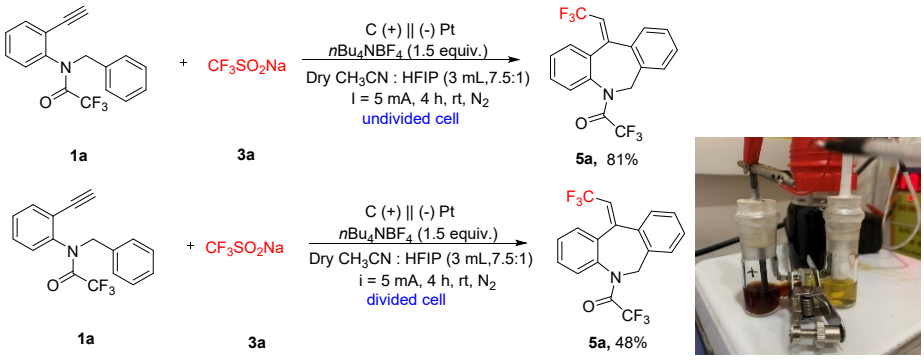
Table S9. The current experiments of trifluoromethyl reaction

entry	current	time	yield
1	4 mA	5 h	49%
2	5 mA	5 h	77%
3	6 mA	5 h	45%
5	5 mA	4 h	81%

4. Mechanistic Studies

4.1 Comparison of standard conditions with conditions in divided cell

The reaction vessel is an H-type divided electrolytic cell (10 mL+ 10 mL) separated by a hydrogen ion permeable membranel (Dupont N-117). The Part of the anode was added the substrate **1a** (0.2 mmol, 60.6 mg), CF_3SO_2Na (**3a**, 0.4 mmol, 2.0 equiv.), and electrolyte nBu$_4$NBF$_4$ (1.5 equiv.), CH_3CN and HFIP (3 mL, 7.5:1), and a magnetic stirrer bar. The part of the cathode was added electrolyte nBu$_4$NBF$_4$ (1.5 equiv.), CH_3CN and HFIP (3 mL, 7.5:1) and a magnetic stirrer bar. Subsequently, the flask was equipped with a graphite rod anode and a platinum plate cathode, the distance between which was approximately 3.0 cm. The constant current (5 mA) electrolysis was then performed at room temperature under nitrogen atmosphere (sealed tube) with vigorous stirring for 5 h. The resulting mixture was monitored by TLC, only trace desired product was detected. These results suggest that all of the steps occur in the vicinity of the anode.



Scheme S3. Reaction formula

4.2 Cyclic Voltammetry Studies

Substrate redox potentials were determined using CV with the following method in Figure S1-S3. Cyclic voltammetry experiments were performed on a CHI 760E potentiostat using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference. Samples were prepared with 0.1 mmol of substrate in 10 mL of 0.1 M tetrabutylammonium tetrafluoroborate (nBu$_4$NBF$_4$) in dry, degassed MeCN. The scan rate is 0.1 V/s. Potentials are reported by using half-peak potentials against SCE. The measured values are basically consistent with the literature. [2]

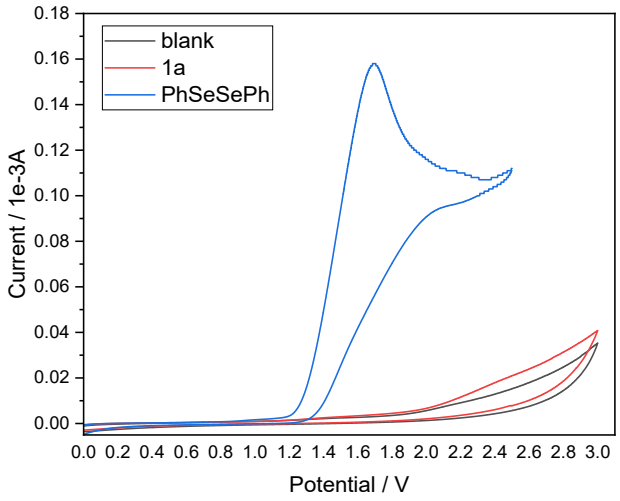


Figure S1. Cyclic voltammogram of PhSeSePh(**2a**) in MeCN shows an irreversible oxidation event, half peaks at 1.47V vs. SCE (IUPAC convention)

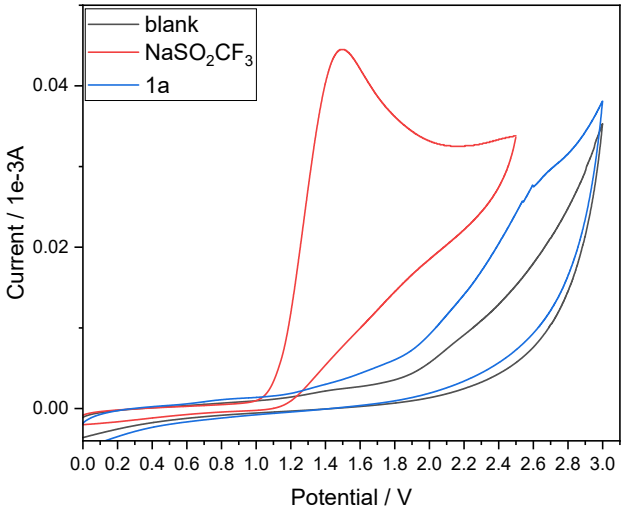


Figure S2. Cyclic voltammogram of $NaSO_2CF_3$(**3a**) in MeCN shows an irreversible oxidation event, half peaks at 1.28V vs. SCE (IUPAC convention)

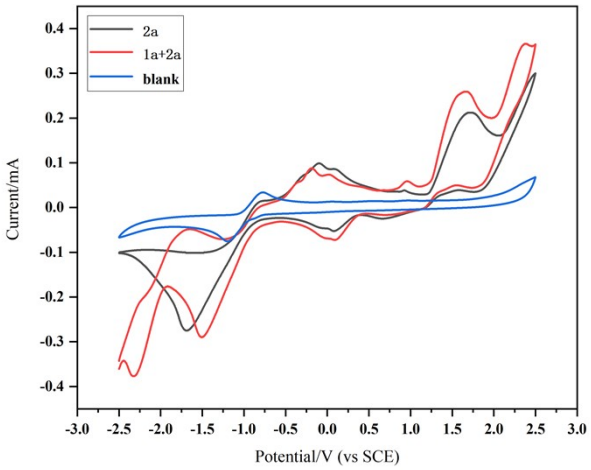
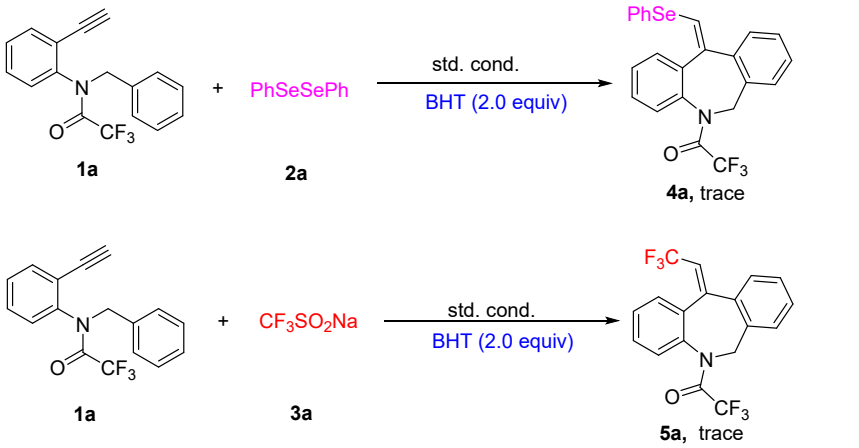


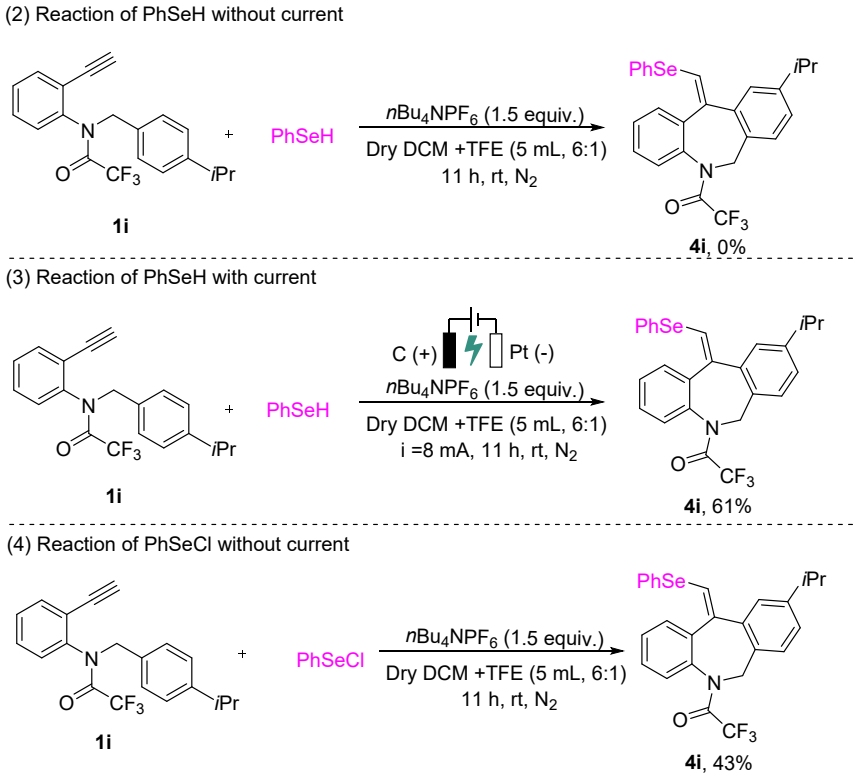
Figure S3. Cyclic voltammogram of **2a,** mixture of substrates **1a** with **2a** vs. SCE

4.3 Control experiments.

To judging from the reaction process, we selected BHT (7, 2,4-di-tert-butyl-4-methylphenol) as a radical trapping agent. Because its oxidation occurred at lower potential than for the substrate **1a**, but at a indicating a direct oxidation of the **2a** and **3a** are easier to be anodized than **1**. This electrochemistry cyclization reaction was fully suppressed under the standard condition in presence of BHT with a trace of products **4a** and **5a** formed (Scheme S4.1), proving this transformation involved a free radical process. To further illustrate the point, the reaction of **1i** with **PhSeH** was investigated under both current and noncurrent conditions. It was found that the reaction could not be carried out without current, and that it was possible to isolate 61% of the product **4i** under current conditions, which indicated that a phenylselenyl radical might be involved in this electrochemical reaction. Meanwhile desired product **4i** could be obtained in 43% yield when **1i** was reacted with PhSeCl under the conditions without current,suggeting the ionic pathwaycould not be excluded.

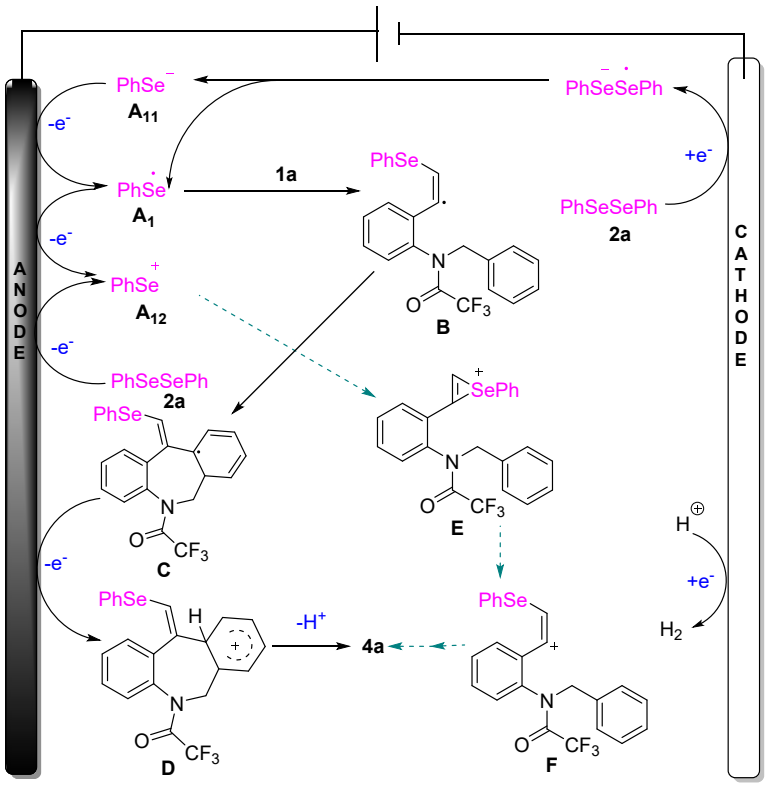
(1). Radical inhibition experiment





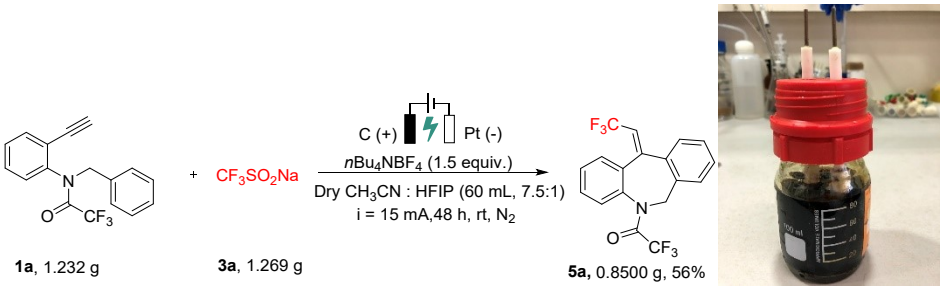
Scheme S4. Control experiments.

4.4 Proposed mechanism.



Scheme S5. Proposed mechanism

5. Large-Scale Reaction



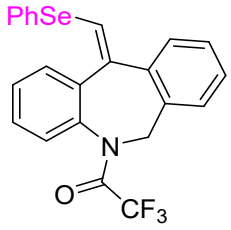
The large scale reaction was carried out using an oven-dried 100-mL beaker, the anode graphite plate (20×20×3 mm) and cathode platinum plate (30×30×0.2 mm). To an oven-dried 100-mL beaker equipped with a stir bar, a graphite plate anode, and a platinum plate cathode was added **1a** (4 mmol, 1.232 g), **3a** (8 mmol, 2.0 equiv., 1.269 g), and *n*Bu_4NBF_4 (0.1 M, 1.97 g), followed by sequential addition via syringe of CH_3CN and HFIP (60 mL, 7.5:1). The reaction mixture was stirred at room temperature under nitrogen atmosphere, and at a constant current of 15.0 mA for 48 h. The resulting mixture was purified by column chromatography on silica gel (eluted with PE/EA) to afford the desired condensation product.

6. Reference

1. P. Xiong, H.-H. Xu, J. Song, H.-C. Xu, *J. Am. Chem. Soc. 2018*, **140**, 246.

2. (a) S. Chen, Q. Yan, J. Fan, Y. Gao, X. Yang, L. Li, Z. Liu, Z. Li, *Green Chem. 2022*, **24**, 4742; (b) V. A. Vil', V. M. Merkulova, A. I. Ilovaisky, S. A. Paveliev, G. I. Nikishin, A. O. Terent'ev, *Org. Lett. 2021*, **23**, 5107.

7. Characterization Data



(*Z*)-2,2,2-trifluoro-1-(11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4a)

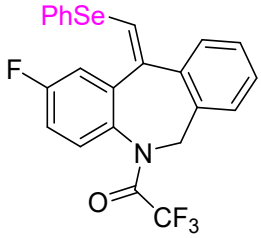
Yellow oil, 62.4 mg; purified by flash chromatography eluted with PE/EA = 50:1, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.54 – 7.44 (m, 5H), 7.43 – 7.38 (m, 2H), 7.29 – 7.28 (m, 3H), 7.25 – 7.21 (m, 2H), 7.17 (s, 1H), 7.14 – 7.10 (m, 1H), 5.85 (d, J = 16.7 Hz, 1H), 4.34 (d, J = 16.6 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.19.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$ = 36.4 Hz), 139.1, 138.6, 137.0, 136.3, 132.8, 132.3, 129.5, 129.4, 129.2, 129.0, 128.1, 127.9, 127.8, 126.9, 116.6 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.6.

HRMS (ESI) calculated for $C_{23}H_{17}F_3NOSe^+$ m/z $[M+H]^+$: 460.0422, found: 460.0427.



(*Z*)-2,2,2-trifluoro-1-(2-fluoro-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4b)

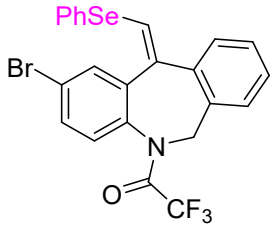
White solid, 64.9 mg; purified by flash chromatography eluted with PE/EA = 50:1, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.52 - 7.50 (m, 2H), 7.42 - 7.34 (m, 2H), 7.33 - 7.28 (m, 3H), 7.27 - 7.23 (m, 3H), 7.19 (s, 1H), 7.15 - 7.08 (m, 2H), 5.83 (d, J = 16.7 Hz, 1H), 4.31 (d, J = 16.7 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.16 (s, 3F), -110.42 (q, J = 7.5 Hz, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 251.5 Hz), 156.6 (q, $J_{C\text{-}F}$ = 36.4 Hz), 141.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 137.4, 135.8, 133.0, 132.9, 132.2, 130.3, 130.0, 129.5, 129.3, 128.8 (d, $J_{C\text{-}F}$ = 9.1 Hz), 128.3, 128.0, 127.9, 127.8, 116.5 (q, $J_{C\text{-}F}$ = 24.2 Hz), 116.3 (q, $J_{C\text{-}F}$ = 290.9 Hz), 116.0 (q, $J_{C\text{-}F}$ = 22.2 Hz), 51.6.

HRMS (ESI) calculated for $C_{23}H_{16}F_4NOSe^+$ m/z $[M+H]^+$: 478.0328, found: 478.0323.



(*Z*)-1-(2-bromo-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4c)

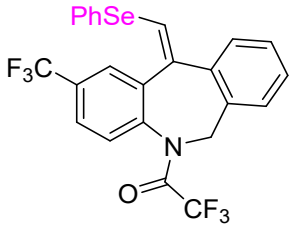
Yellow solid, 53.7 mg; purified by flash chromatography eluted with PE/EA = 50:1, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.69 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 (dd, *J* = 6.2, 2.9 Hz, 2H), 7.42 - 7.35 (m, 1H), 7.30 - 7.26 (m, 4H), 7.24 (t, *J* = 5.2 Hz, 2H), 7.19 (s, 1H), 7.12 - 7.10 (m, 1H), 5.82 (d, *J* = 16.6 Hz, 1H), 4.30 (d, *J* = 16.6 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.17.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (q, $J_{C\text{-}F}$ = 36.4 Hz), 141.0, 137.1, 136.0, 135.8, 132.9, 132.3, 132.1, 130.3, 130.1, 129.5, 129.3, 128.5, 128.3, 128.0, 123.3, 116.3 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.4.

HRMS (ESI) calculated for $C_{23}H_{16}BrF_3NOSe^+$ m/z $[M+H]^+$: 537.9527, found: 537.9528.



(*Z*)-2,2,2-trifluoro-1-(11-((phenylselanyl)methylene)-2-(trifluoromethyl)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4d)

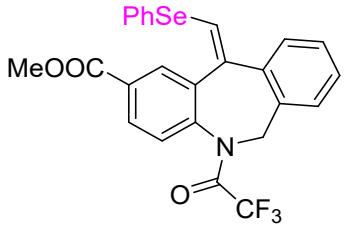
Yellow oil, 45.3 mg; purified by flash chromatography eluted with PE/EA = 50:1, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.84 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.56 - 7.47 (m, 3H), 7.42 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.33 - 7.29 (m, 3H), 7.26 - 7.25 (m, 3H), 7.14 - 7.12 (m, 1H), 5.87 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 15.7 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (d, *J* = 7.5 Hz, 3F), -67.20 (s, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (q, $J_{C\text{-}F}$ = 36.4 Hz), 140.1, 140.0, 137.0, 135.6, 133.0, 131.9, 130.6, 130.1, 129.6, 129.2, 128.4, 128.1, 128.0, 127.9, 127.7, 126.8 (q, $J_{C\text{-}F}$ =3.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 3.0 Hz), 126.3 (q, $J_{C\text{-}F}$ = 3.0 Hz), 116.2 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.4.

HRMS (ESI) calculated for $C_{24}H_{16}F_6NOSe^+$ m/z $[M+H]^+$: 528.0296, found: 528.0294.



Methyl (*Z*)-11-((phenylselanyl)methylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5H-dibenzo[b,e]azepine-2-carboxylate (4e)

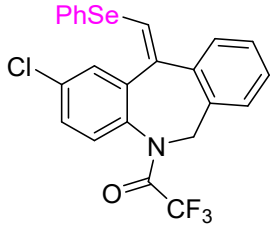
Yellow oil, 67.2 mg; purified by flash chromatography eluted with PE/EA = 50:1, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 8.23 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.53 - 7.45 (m, 3H), 7.44 - 7.39 (m, 1H), 7.31 - 7.26 (m, 3H), 7.25 - 7.23 (m, 3H), 7.11 - 7.09 (m, 1H), 5.86 (d, J = 15.6 Hz, 1H), 4.32 (d, J = 15.8 Hz, 1H), 3.96 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.19.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 156.3 (q, $J_{C\text{-}F}$ = 36.4 Hz), 140.8, 139.4, 137.6, 135.9, 132.9 , 131.9, 131.2, 130.7, 130.6, 130.4, 130.0, 129.5, 129.2, 128.3, 128.0, 127.9, 127.1, 116.3 (q, $J_{C\text{-}F}$ = 289.9 Hz), 52.7, 51.4.

HRMS (ESI) calculated for $C_{25}H_{19}F_3NO_3Se^+$ m/z $[M+H]^+$: 518.0477, found: 518.0475.



(*Z*)-1-(2-chloro-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4f)

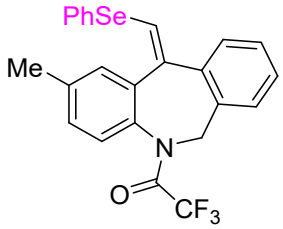
White solid, 58.2 mg; purified by flash chromatography eluted with PE/EA = 50:1, 59% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.55 - 7.48 (m, 3H), 7.44 - 7.37 (m, 2H), 7.33 (d, J = 8.9 Hz, 1H), 7.32 - 7.28 (m, 3H), 7.26 - 7.21 (m, 2H), 7.19 (s, 1H), 7.11 (d, J = 7.1 Hz, 1H), 5.83 (d, J = 16.6 Hz, 1H), 4.30 (d, J = 16.6 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.17.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4 (q, $J_{C\text{-}F}$ = 36.4 Hz), 140.8, 137.2, 135.8, 135.5, 135.3, 132.9, 132.1, 130.3, 130.0, 129.5, 129.4, 129.3, 129.2, 128.3, 128.0, 127.9, 116.3 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.5.

HRMS (ESI) calculated for $C_{23}H_{16}ClF_3NOSe^+$ m/z $[M+H]^+$: 494.0032, found: 494.0031



(*Z*)-2,2,2-trifluoro-1-(2-methyl-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4g)

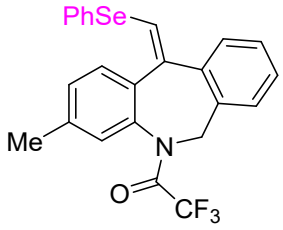
Yellow oil, 71.9 mg; purified by flash chromatography eluted with PE/EA = 50:1, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.57 - 7.50 (m, 2H), 7.41 - 7.39 (m, 1H), 7.33 (s, 1H), 7.30 - 7.25 (m, 4H), 7.23 - 7.21 (m, 3H), 7.16 - 7.14 (m, 1H), 7.12 - 7.07 (m, 1H), 5.84 (d, J = 16.6 Hz, 1H), 4.31 (d, J = 16.6 Hz, 1H), 2.43 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.14.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, $J_{C\text{-}F}$ = 36.4 Hz), 139.6, 138.9, 138.8, 136.5, 134.3, 132.8 , 132.4, 130.8, 129.9, 129.8, 129.5, 129.2, 128.6, 128.1, 128.0, 127.8, 126.6, 116.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.7, 21.4.

HRMS (ESI) calculated for $C_{24}H_{19}F_3NOSe^+$ m/z $[M+H]^+$: 474.0578, found: 474.0574.



(*Z*)-2,2,2-trifluoro-1-(3-methyl-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one) (4h)

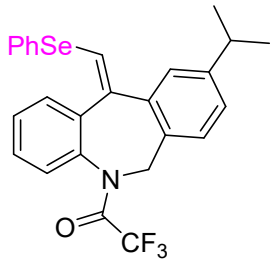
Yellow oil, 64.3 mg; purified by flash chromatography eluted with PE/EA = 50:1, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.49 (dd, J = 6.1, 2.7 Hz, 2H), 7.40 (dd, J = 6.9, 3.6 Hz, 2H), 7.29 - 7.24 (m, 4H), 7.23 - 7.17 (m, 3H), 7.14 (s, 1H), 7.12 - 7.08 (m, 1H), 5.82 (d, J = 16.6 Hz, 1H), 4.31 (d, J = 16.6 Hz, 1H), 2.41 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.13.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$ = 36.4 Hz), 139.7, 138.7, 136.8, 136.5, 136.0, 132.8, 132.4, 130.8, 130.0, 129.4, 129.2, 129.1, 128.6, 128.0, 127.9, 127.8, 127.7, 127.3, 116.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.7, 21.3.

HRMS (ESI) calculated for $C_{24}H_{19}F_3NOSe^+$ m/z $[M+H]^+$: 474.0578, found: 474.0574.



(*Z*)-2,2,2-trifluoro-1-(9-isopropyl-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4i)

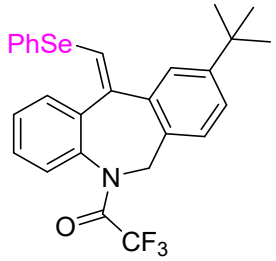
Yellow solid, 72.2 mg; purified by flash chromatography eluted with PE/EA = 50:1, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.54 - 7.47 (m, 4H), 7.45 - 7.40 (m, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.32 - 7.26 (m, 3H), 7.25 (s, 1H), 7.16 (s, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 5.83 (d, *J* = 16.6 Hz, 1H), 4.30 (d, *J* = 16.5 Hz, 1H), 2.87 (p, *J* = 6.9 Hz, 1H), 1.23 (s, 3H), 1.21 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.14.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$ = 36.4 Hz), 148.6, 139.3, 139.2, 136.9, 136.1, 132.7 , 130.8, 129.8, 129.5, 129.4, 129.3, 129.2, 128.2, 128.0, 127.7, 127.4, 126.8, 126.3, 116.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.4, 33.9, 24.2, 23.9.

HRMS (ESI) calculated for $C_{26}H_{23}F_3NOSe^+$ m/z $[M+H]^+$: 502.0891, found: 502.0889.



(*Z*)-1-(9-(tert-butyl)-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4j)

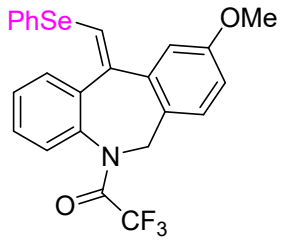
White solid, 70.1 mg; purified by flash chromatography eluted with PE/EA = 50:1, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.53 - 7.46 (m, 3H), 7.46 - 7.35 (m, 4H), 7.29 - 7.27 (m, 4H), 7.15 (d, *J* = 1.2 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 5.84 (d, *J* = 16.5 Hz, 1H), 4.30 (d, *J* = 16.5 Hz, 1H), 1.30 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.12.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$ = 36.4 Hz), 150.9, 139.8, 139.3, 136.9, 135.9, 132.5, 130.9, 129.5, 129.4, 129.3, 129.3, 127.9, 127.7, 127.7, 126.8, 125.9, 125.6, 116.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.3, 34.6, 31.4.

HRMS (ESI) calculated for $C_{27}H_{25}F_3NOSe^+$ m/z $[M+H]^+$: 515.1048, found: 515.1052.



(*Z*)-2,2,2-trifluoro-1-(9-methoxy-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (4k)

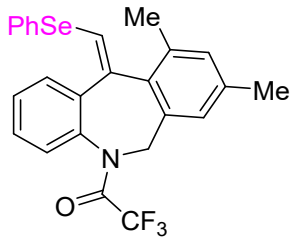
Yellow oil, 65.5 mg; purified by flash chromatography eluted with PE/EA = 50:1, 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.47 (m, 3H), 7.47 – 7.40 (m, 2H), 7.39 – 7.33 (m, 2H), 7.28 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.05 (s, 1H), 6.77 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 5.79 (d, *J* = 16.6 Hz, 1H), 4.30 (d, *J* = 16.6 Hz, 1H), 3.77 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.26.

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 156.6 (q, $J_{C\text{-}F}$ = 35.8 Hz), 139.5, 138.4, 136.9, 133.7, 132.9, 132.7, 131.0, 130.6, 129.5, 129.4, 129.3, 127.7, 126.9, 116.4 (q, $J_{C\text{-}F}$ = 287.4 Hz),, 113.8, 112.7, 55.5, 51.83.

HRMS (ESI) calculated for $C_{24}H_{20}F_3NO_2Se^+$ m/z $[M+H]^+$: 490.0528, found: 490.0524.



(*Z*)-1-(8,10-dimethyl-11-((phenylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4l)

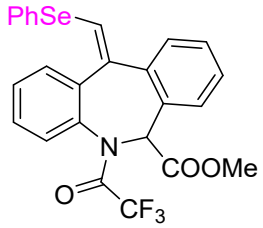
Yellow oil, 87.7 mg; purified by flash chromatography eluted with PE/EA = 50:1, 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.50 - 7.31 (m, 6H), 7.25 - 7.23 (m, 3H), 6.95 (s, 1H), 6.80 (s, 1H), 6.76 (s, 1H), 5.93 (d, *J* = 16.8 Hz, 1H), 4.25 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 2.23 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.15.

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 140.7, 137.1, 136.2, 135.9, 135.0, 133.3, 132.8, 132.6, 131.2, 130.8, 129.4, 129.0, 128.8, 128.4, 127.6, 126.8, 126.1, 116.5 (q, $J_{C\text{-}F}$ = 289.9 Hz), 51.0, 22.2, 20.9.

HRMS (ESI) calculated for $C_{25}H_{21}F_3NOSe^+$ m/z $[M+H]^+$: 488.0735, found: 488.0732.



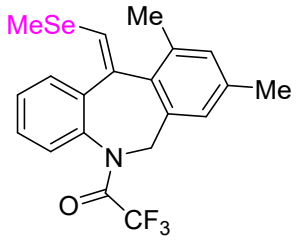
Methyl (*Z*)-11-((phenylselanyl)methylene)-5-(2,2,2-trifluoroacetyl)-6,11-dihydro-5H-dibenzo[b,e]azepine-6-carboxylate (4q)

Yellow oil, 65.1 mg; purified by flash chromatography eluted with PE/EA = 50:1, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.55 - 7.43 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.31 - 7.24 (m, 5H), 7.19 - 7.12 (m, 2H), 6.80 (s, 1H), 3.60 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.60.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 156.9 (q, $J_{C\text{-}F}$ = 36.4 Hz), 139.5, 138.1, 136.5, 133.4, 132.9, 130.6, 130.5, 130.0, 129.9, 129. 6, 129.5, 129.4, 129.1, 128.8, 128.7, 127.9, 127.8, 116.4 (q, $J_{C\text{-}F}$ = 289.9 Hz), 61.8, 52.9.



(*Z*)-1-(8,10-dimethyl-11-((methylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4r)

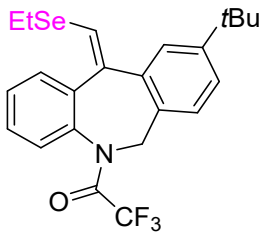
Yellow oil, 73.1 mg; purified by flash chromatography eluted with PE/EA = 30:1, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.97 (s, 1H), 6.75 (s, 1H), 6.62 (s, 1H), 5.88 (d, *J* = 16.9 Hz, 1H), 4.24 (d, *J* = 16.9 Hz, 1H), 2.46 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.31.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7 (q, *J* = 35.6 Hz), 140.936, 136.871, 136.199, 135.874, 133.690, 132.661, 131.162, 129.332, 129.205, 128.768, 128.443, 126.735, 126.049, 120.789, 116.5 (q, *J* = 287.0 Hz), 51.1 22.0, 20.9, 7.1.

HRMS (ESI) calculated for $C_{20}H_{18}F_3NOSe^+$ m/z $[M+H]^+$: 426.0578, found: 426.0576.



(*Z*)-1-(9-(tert-butyl)-11-((ethylselanyl)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4s)

Yellow solid, 67.3 mg; purified by flash chromatography eluted with PE/EA = 50:1, 72% yield.

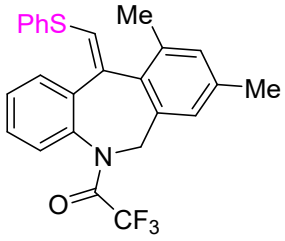
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.43 – 7.38 (m, 3H), 7.37 – 7.32 (m, 1H), 7.28 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 7.01 (s, 1H), 5.81 (d, *J* = 16.5 Hz, 1H), 4.27 (d, *J* = 16.5 Hz, 1H), 2.77 (p, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.5 Hz, 3H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.11.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, *J* = 36.0 Hz), 150.8, 139.7, 138.9, 137.0, 136.3, 129.6, 129.2, 129.1, 129.0, 127.7, 127.4, 126.7, 126.0, 125.2, 116.4 (q, *J* = 287.0 Hz), 51.4, 34.7, 31.5, 21.1, 16.1.

HRMS (ESI) calculated for $C_{23}H_{24}F_3NOSe^+$ m/z $[M+H]^+$: 468.1048, found: 468.1043.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 303.44, 303.29, 303.14.



(*Z*)-1-(8,10-dimethyl-11-((phenylthio)methylene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (4t)

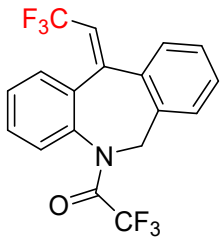
Yellow oil, 42.2 mg; purified by flash chromatography eluted with PE/EA = 40:1, 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.37 (t, *J* = 9.3 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 4H), 7.21 (t, *J* = 6.6 Hz, 1H), 6.98 (s, 1H), 6.78 (s, 1H), 6.54 (s, 1H), 5.94 (d, *J* = 17.0 Hz, 1H), 4.28 (d, *J* = 16.9 Hz, 1H), 2.50 (s, 3H), 2.25 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.58.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.2, 136.0, 135.7, 133.7, 133.1, 132.9, 131.2, 130.9, 130.3, 129.7, 129.4, 129.3, 129.0, 127.1, 126.8, 126.1, 51.0, 22.2, 20.9.

HRMS (ESI) calculated for $C_{25}H_{21}F_3NOS^+$ m/z $[M+H]^+$: 440.1290, found: 440.1293.



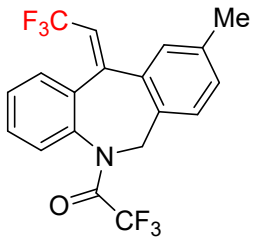
(*Z*)-2,2,2-trifluoro-1-(11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5a)

Yellow solid, 60.1 mg; purified by flash chromatography eluted with PE/EA = 75:1, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.46 - 7.39 (m, 4H), 7.36 (d, J = 7.1 Hz, 1H), 7.33 (d, J = 7.0 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.11 (q, J = 8.0 Hz, 1H), 5.97 (d, J = 17.1 Hz, 1H), 4.33 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.13 (m, 3F), -67.86 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156. 9 (q, $J_{C\text{-}F}$ = 36.4 Hz), 148.7 (q, $J_{C\text{-}F}$ = 6.1 Hz), 136.3, 135.9, 134.8, 133.7, 130.1, 129.9, 129.4, 129.3, 128.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 128.1, 128.0, 126.7 (d, $J_{C\text{-}F}$ = 1.0 Hz), 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.2 (q, $J_{C\text{-}F}$ = 35.3 Hz), 116. 2 (q, $J_{C\text{-}F}$ = 289.9 Hz), 50.68.



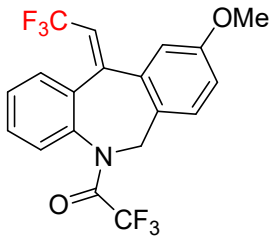
(*Z*)-2,2,2-trifluoro-1-(9-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5b)

Yellow oil, 50.8 mg; purified by flash chromatography eluted with PE/EA = 75:1, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.47 - 7.38 (m, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.21 (s, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.03 (d, J = 7.9 Hz, 1H), 6.11 (q, J = 8.1 Hz, 1H), 5.93 (d, J = 16.9 Hz, 1H), 4.28 (d, J = 17.0 Hz, 1H), 2.36 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.11(m, 3F), -67.88 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (q, $J_{C\text{-}F}$ = 36.4 Hz), 148.7 (q, $J_{C\text{-}F}$ = 6.1 Hz), 137.8, 136.4, 135.9, 134.6, 130.7, 130.6, 130.0, 129.7, 129.4, 128.8 (q, $J_{C\text{-}F}$ = 3.0 Hz), 128.0, 126.7(d, $J_{C\text{-}F}$ = 1.0 Hz), 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 119.9 (q, $J_{C\text{-}F}$ = 35.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 289.9 Hz), 50.5, 20.9.



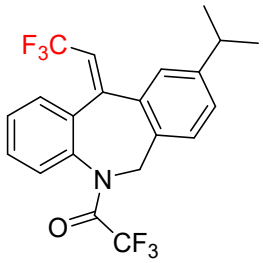
(*Z*)-2,2,2-trifluoro-1-(9-methoxy-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5c)

Yellow solid, 34.5 mg; purified by flash chromatography eluted with PE/EA = 75:1, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm =7.49 - 7.38 (m, 3H), 7.36 (d, J = 6.0 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 6.96 - 6.86 (m, 2H), 6.13 (q, J = 7.8, 6.9 Hz, 1H), 5.90 (d, J = 16.6 Hz, 1H), 4.26 (d, J = 16.5 Hz, 1H), 3.83 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.16 (m, 3F), -67.87 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 156.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 148.6 (q, $J_{C\text{-}F}$ = 6.1 Hz), 136.1, 135.9, 135.7, 130.1, 129.4, 129.3, 128.8, 126.7, 125.4, 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.2 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 115.6, 114.3, 55.6, 50.2.



(*Z*)-2,2,2-trifluoro-1-(9-isopropyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5d)

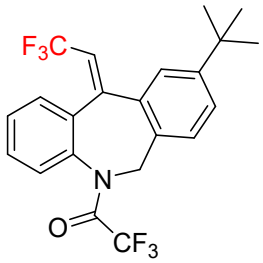
Yellow oil, 52.9 mg; purified by flash chromatography eluted with PE/EA = 75:1, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.44 (m, 3H), 7.35 (d, J = 7.3 Hz, 1H), 7.23 - 7.22 (m, 2H), 7.07 (d, J = 4.3 Hz, 1H), 6.12 (q, J = 8.1 Hz, 1H), 5.94 (d, J = 16.9 Hz, 1H), 4.29 (d, J = 16.9 Hz, 1H), 2.92 (m, 1H), 1.27 (s, 3H), 1.25 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.02 (m, 3F), -67.87 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 149.0 (q, $J_{C\text{-}F}$ = 6.1 Hz), 148.9, 136.4, 135.9, 134.6, 131.1, 130.0, 129.4, 128.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 128.2, 128.1, 127.3, 126.7 (d, $J_{C\text{-}F}$ = 1.0 Hz), 122.3 (q, $J_{C\text{-}F}$ =271.7 Hz), 120.0 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.2 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.6, 33.9, 24.0, 23.9.

HRMS (ESI) calculated for $C_{21}H_{18}F_6NO^+$ m/z $[M+H]^+$: 414.1287, found: 414.1290.



(*Z*)-1-(9-(*tert*-butyl)-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5e)

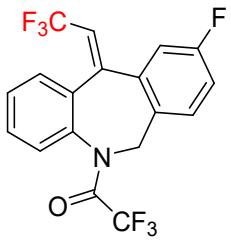
Yellow oil, 57.2 mg; purified by flash chromatography eluted with PE/EA = 75:1, 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.44 (m, 3H), 7.41 - 7.33 (m, 3H), 7.09 (d, J = 8.0 Hz, 1H), 6.11 (q, J = 8.1 Hz, 1H), 5.94 (d, J = 17.0 Hz, 1H), 4.30 (d, J = 17.0 Hz, 1H), 1.34 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.95 (m, 3F), -67.86 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 151.2, 149.2 (q, $J_{C\text{-}F}$ = 6.1 Hz), 136.5, 135.9, 134.3, 130.7, 130.0, 129.3, 128.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 127.9, 127.2, 126.7, 125.9, 122.3 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.0 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.2 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.5, 34.7, 31.3.

HRMS (ESI) calculated for $C_{22}H_{20}F_6NO^+$ m/z $[M+H]^+$: 428.1444, found: 428.1448.



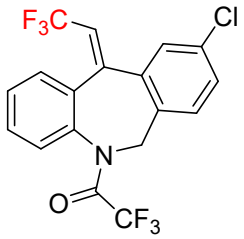
(*Z*)-2,2,2-trifluoro-1-(9-fluoro-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5f)

Yellow solid, 44.4 mg; purified by flash chromatography eluted with PE/EA = 75:1, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.51 - 7.43 (m, 2H), 7.41 (d, J = 7.1 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.16 - 7.11 (m, 2H), 7.06 (td, J = 8.2, 2.5 Hz, 1H), 6.13 (q, J = 7.9 Hz, 1H), 5.94 (d, J = 17.0 Hz, 1H), 4.28 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.34 (m, 3F), -67.93 (q, J = 7.5 Hz, 3F), -114.07 (q, J = 7.5 Hz, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (q, $J_{C\text{-}F}$, J = 249.5 Hz), 156.8 (q, $J_{C\text{-}F}$ = 37.4 Hz), 147.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 136.4 (d, $J_{C\text{-}F}$ = 7.0 Hz), 135.9, 135.6, 130.4, 129.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.6, 129.4 (d, $J_{C\text{-}F}$, J = 3 Hz), 128.9 (q, $J_{C\text{-}F}$ = 2.0 Hz), 126.8 (q, $J_{C\text{-}F}$ = 1.0 Hz), 122.0 (q, $J_{C\text{-}F}$ = 270.7 Hz), 121.1 (q, $J_{C\text{-}F}$ = 35.4 Hz), 117.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 115.9 (d, $J_{C\text{-}F}$ = 23.2 Hz), 50.16.



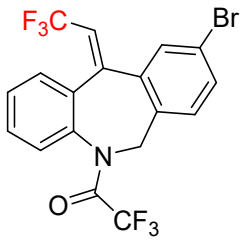
(*Z*)-1-(9-chloro-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5g)

Yellow solid, 42.2 mg; purified by flash chromatography eluted with PE/EA = 75:1, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.50 - 7.39 (m, 4H), 7.37 (d, J = 7.4 Hz, 1H), 7.32 (dd, J = 8.3, 2.0 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H), 6.14 (q, J = 7.9 Hz, 1H), 5.94 (d, J = 17.2 Hz, 1H), 4.28 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ-57.36 (m, 3F), -67.93 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (q, $J_{C\text{-}F}$ = 37.4 Hz), 147.3 (q, $J_{C\text{-}F}$ = 6.0 Hz), 136.3, 135.8, 135.7, 133.6, 132.3, 130.4, 129.8, 129.6, 129.5, 129.1, 128.9(d, $J_{C\text{-}F}$ = 2.0 Hz), 126.8, 121.9 (q, $J_{C\text{-}F}$ = 271.7 Hz), 121.1 (q, $J_{C\text{-}F}$ = 35.4 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.2.



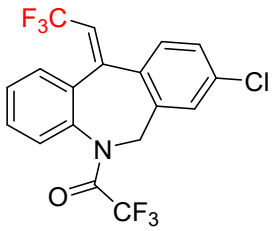
(*Z*)-1-(9-bromo-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5h)

Yellow solid, 50.3 mg; purified by flash chromatography eluted with PE/EA = 75:1, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.57 (d, J = 1.9 Hz, 1H), 7.46 (m, 3H), 7.40 (d, J = 7.2 Hz, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.13 (q, J = 7.9 Hz, 1H), 5.92 (d, J = 17.2 Hz, 1H), 4.25 (d, J = 17.2 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.36 (m, 3F), -67.93 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 (q, $J_{C\text{-}F}$ = 37.4 Hz), 147.2 (q, $J_{C\text{-}F}$ = 3.0 Hz), 136.5, 135.8, 135.6, 132.7, 132.7, 131.9, 130.4, 129.7, 129.6, 128.9, 126.8, 121.9 (q, $J_{C\text{-}F}$ = 271.7 Hz), 121.4 (q, $J_{C\text{-}F}$ = 2.0 Hz), 121.1 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.2.



(*Z*)-1-(8-chloro-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5i)

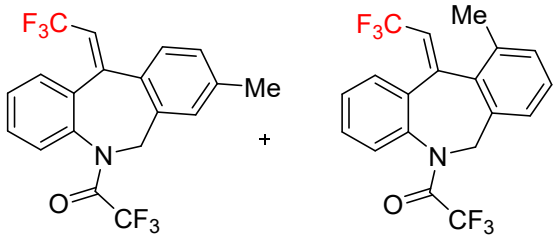
Yellow solid, 42.9 mg; purified by flash chromatography eluted with PE/EA = 75:1, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.51 - 7.43 (m, 2H), 7.44 - 7.40 (m, 1H), 7.39 - 7.33 (m, 2H), 7.31 - 7.25 (m, 2H), 7.16 (s, 1H), 5.93 (d, J = 17.5 Hz, 1H), 4.29 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.28 (q, J = 7.6 Hz), -67.98 (q, J = 7.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (q, $J_{C\text{-}F}$ = 36.7 Hz), 147.6 (q, $J_{C\text{-}F}$ = 37.4 Hz), 136.0, 135.8, 135.6, 133.4, 130.8, 130.4, 129.7, 129.0 (q, $J_{C\text{-}F}$ = 2.7 Hz), 128.3, 128.1, 126.9, 126.9, 122.1 (q, $J_{C\text{-}F}$ = 269.6 Hz), 120.7 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 286.3 Hz), 50.5.

HRMS (ESI) calculated for $C_{18}H_{11}ClF_6NO^+$ m/z $[M+H]^+$: 406.0428, found: 406.0427.



(*Z*)-2,2,2-trifluoro-1-(8-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one; (*Z*)-2,2,2-trifluoro-1-(10-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (2:1) (5j)

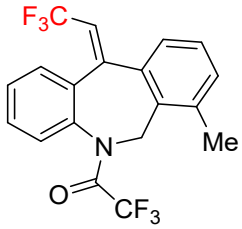
Yellow solid, 40.0 mg; purified by flash chromatography eluted with PE/EA = 75:1, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.48 - 7.32 (m, 7H), 7.31 (s, 1H), 7.17 (d, J = 4.8 Hz, 1H), 7.09 (dd, J = 7.9, 1.7 Hz, 1H), 6.96 (d, J = 3.4 Hz, 2H), 6.08 (q, J = 8.1 Hz, 1H), 6.03 - 5.87 (m, 2H), 4.30 (t, J = 19.3 Hz, 2H), 2.48 (s, 2H), 2.32 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.97 (m, 3F), -58.45 (m, 3F), -67.35 (q, J = 7.5 Hz, 3F), -67.89 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 37.4 Hz), 148.5 (q, $J_{C\text{-}F}$ = 6.1 Hz), 140.2, 138.1, 136.5, 135.9, 135.0, 134.9, 134.4, 133.5, 132.9, 132.0, 130.4, 130.0, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.7, 127.1, 126.9, 126.9, 126.7, 125.9, 122.3 (q, $J_{C\text{-}F}$ = 272.7 Hz), 122.1 (q, $J_{C\text{-}F}$ = 271.7 Hz), 122.0 (q, $J_{C\text{-}F}$ = 34.3 Hz), 121.88 , 120.04 , 119.5 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.2 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.7, 50.5, 21.2, 21.0.

HRMS (ESI) calculated for $C_{19}H_{14}F_6NO^+$ m/z $[M+H]^+$: 386.0974, found: 386.0976.



(*Z*)-2,2,2-trifluoro-1-(7-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5k)

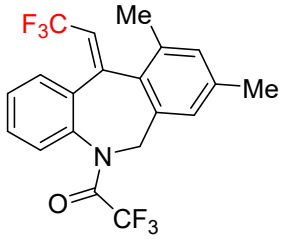
Yellow solid, 46.2 mg; purified by flash chromatography eluted with PE/EA = 75:1, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.47 - 7.40 (m, 2H), 7.39 - 7.36 (m, 2H), 7.25 - 7.22 (m, 1H), 7.20 - 7.176 (m, 2H), 6.10 (q, *J* = 8.1 Hz, 1H), 5.94 (d, *J* = 17.0 Hz, 1H), 4.11 (d, *J* = 17.3 Hz, 1H), 2.26 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.38 (q, *J* = 8.3 Hz, 3F), -67.86 (q, *J* = 7.6 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (q, $J_{C\text{-}F}$ = 36.1 Hz), 149.1 (q, $J_{C\text{-}F}$ = 5.5 Hz), 137.0, 136.5, 135.7, 135.2, 132.0, 131.8, 130.0, 129.5, 128.4 (q, $J_{C\text{-}F}$ = 2.4 Hz), 127.7, 127.6, 126.6, 122.3 (q, $J_{C\text{-}F}$ = 269.4 Hz), 119.7 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 286.2 Hz), 49.3, 19.6.

HRMS (ESI) calculated for $C_{19}H_{14}F_6NO^+$ m/z $[M+H]^+$: 386.0974, found: 386.0972.



(*Z*)-1-(8,10-dimethyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5l)

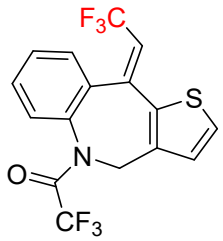
Yellow solid, 51.9 mg; purified by flash chromatography eluted with PE/EA = 75:1, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.40 - 7.37 (m, 2H), 7.35 - 7.32 (m, 2H), 6.99 (s, 1H), 6.78 (s, 1H), 5.95 (d, *J* = 17.2 Hz, 1H), 5.87 (q, *J* = 7.9 Hz, 1H), 4.28 (d, *J* = 17.2 Hz, 1H), 2.45 (s, 3H), 2.25 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.48 (m, 3F), -67.56 (q, *J* = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (q, $J_{C\text{-}F}$ = 36.4 Hz), 144.5 (q, $J_{C\text{-}F}$ = 6.1 Hz), 138.6, 138.3, 134.9, 134.5, 132.9, 132.1, 131.2, 129.4, 129.3, 127.1 (q, $J_{C\text{-}F}$ = 1.0 Hz), 126.8, 126.5, 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 121.8 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 289.9 Hz), 50.6, 21.2, 20.9.

HRMS (ESI) calculated for $C_{20}H_{16}F_6NO^+$ m/z $[M+H]^+$: 400.1131, found: 400.1130.



(*E*)-2,2,2-trifluoro-1-(10-(2,2,2-trifluoroethylidene)-4,10-dihydro-5H-benzo[b]thieno[2,3-e]azepin-5-yl)ethan-1-one (5m)

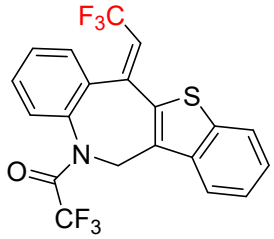
White solid, 41.5 mg; purified by flash chromatography eluted with PE/EA = 75:1, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.48 (m, 3H), 7.39 (t, J = 8.6 Hz, 1H), 7.22 (d, J = 5.2 Hz, 1H), 7.03 (d, J = 5.2 Hz, 1H), 6.13 (q, J = 8.2 Hz, 1H), 5.97 (d, J = 16.8 Hz, 1H), 4.28 (d, J = 16.8 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.20 (m, 3F), -67.93(q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4 (q, $J_{C\text{-}F}$ = 36.4 Hz), 142.8 (q, $J_{C\text{-}F}$ = 6.0 Hz), 136.2, 135.9, 134.1, 130.3, 129.7 (q, $J_{C\text{-}F}$ = 3.0 Hz), 129.6, 127.6, 127.4, 124.3, 122.4 (q, $J_{C\text{-}F}$ = 271.7 Hz), 119.0 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 47. 5.

HRMS (ESI) calculated for $C_{16}H_{10}F_6NOS^+$ m/z $[M+H]^+$:378.0382, found: 378.0378.



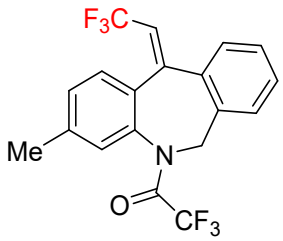
(*E*)-2,2,2-trifluoro-1-(6-(2,2,2-trifluoroethylidene)-6,12-dihydro-11H-benzo[b]benzo[4,5]thieno[2,3-e]azepin-11-yl)ethan-1-one (5n)

White solid, 40.1 mg; purified by flash chromatography eluted with PE/EA = 75:1, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.93 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 6.8 Hz, 3H), 7.42 - 7.36 (m, 2H), 6.31 (q, J = 8.0 Hz, 1H), 6.18 (d, J = 17.4 Hz, 1H), 4.38 (d, J = 17.4 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.67 (m, 3F), -67.75 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (q, $J_{C\text{-}F}$ = 37.4 Hz), 140.7 (q, $J_{C\text{-}F}$ = 6.1 Hz), 138.7, 137.4, 137.3, 136.9, 135.3, 130.1, 129.6, 128.8 (q, $J_{C\text{-}F}$ = 3.0 Hz), 128.2, 127.6, 125.3, 125.3, 122.7, 122.5 (q, $J_{C\text{-}F}$ = 270.7 Hz), 122.2, 121.2 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.1 (q, $J_{C\text{-}F}$ = 288.9 Hz), 47.4.



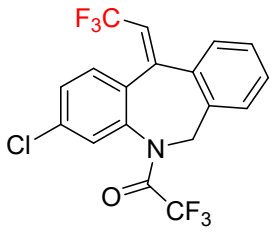
(*Z*)-2,2,2-trifluoro-1-(3-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5o)

Yellow solid, 40.8 mg; purified by flash chromatography eluted with PE/EA = 75:1, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.40 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H), 7.31 - 7.26 (m, 2H), 7.23 (d, J = 6.5 Hz, 1H), 7.19 - 7.11 (m, 2H), 6.10 (m, 1H), 5.95 (d, J = 16.9 Hz, 1H), 4.32 (d, J = 16.9 Hz, 1H), 2.41 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.11 (m, 3F), -67.86 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (q, $J_{C\text{-}F}$ = 36.4 Hz), 148.7 (q, $J_{C\text{-}F}$ = 6.1 Hz), 140.6, 135.8, 135.0, 133.7, 133.2, 130.1, 129.7, 129.3, 128.6 (q, $J_{C\text{-}F}$ = 3.0 Hz), 128.1, 127.9, 127.1, 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.1 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.2 (q, $J_{C\text{-}F}$ =288.9 Hz), 50.7, 21.2.



(*Z*)-1-(3-chloro-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5p)

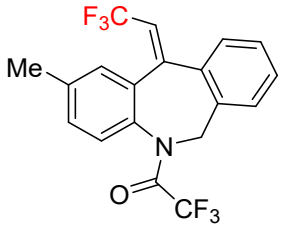
Yellow solid, 49.4 mg; purified by flash chromatography eluted with PE/EA = 75:1, 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.62 - 7.52 (m, 2H), 7.42 - 7.34 (m, 2H), 7.34 - 7.28 (m, 1H), 7.26 - 7.24 (m, 1H), 7.15 (d, J = 6.6 Hz, 1H), 6.13 (q, J = 6.0 Hz, 1H), 5.96 (d, J = 17.1 Hz, 1H), 4.31 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.32 (m,3F), -67.88 (d, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7(q, $J_{C\text{-}F}$ = 37.4 Hz), 147.1 (q, $J_{C\text{-}F}$ = 6.1 Hz), 138.2, 134.9, 134.2, 133.5, 133.2, 131.8 (q, $J_{C\text{-}F}$ = 3.0 Hz), 130.2, 129.4, 128.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.2, 128.1, 123.3,122.0 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.8 (q, $J_{C\text{-}F}$ = 35.4 Hz), 116.0 (q, $J_{C\text{-}F}$ = 288.9Hz), 50.5.

HRMS (ESI) calculated for $C_{18}H_{11}ClF_6NO^+$ m/z $[M+H]^+$: 406.0428, found: 400.0430.



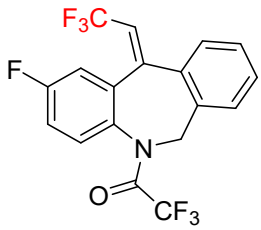
(*Z*)-2,2,2-trifluoro-1-(2-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5q)

Yellow soilid, 53.1 mg; purified by flash chromatography eluted with PE/EA = 75:1, 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.39 (dd, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.4, 1.5 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.23 (s, 2H), 7.20 (s, 1H), 7.13 (d, J = 7.6 Hz, 1H), 6.09 (q, J = 8.1 Hz, 1H), 5.95 (d, J = 17.1 Hz, 1H), 4.30 (d, J = 17.1 Hz, 1H), 2.38 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.19 (m, 3F), -67.87 (q, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (q, $J_{C\text{-}F}$ = 37.4 Hz), 148.8 (q, $J_{C\text{-}F}$ = 6.1 Hz), 148. 8, 139.7, 136.1, 135.0, 133.8, 133.2, 130.6, 129.8, 129.3, 129.2, 128.1, 127.9, 126.5, 122.2 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.0 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.2 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.7, 21.2.



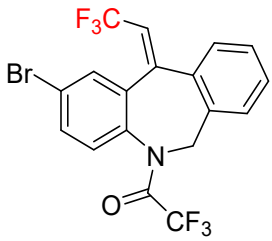
(*Z*)-2,2,2-trifluoro-1-(2-fluoro-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5r)

Yellow solid, 46.7 mg; purified by flash chromatography eluted with PE/EA = 75:1, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.40 - 7.35 (m, 3H), 7.32 - 7.29 (m, 1H), 7.16 - 7.12 (m, 3H), 6.13 (q, J = 8.0 Hz, 1H), 5.96 (d, J = 17.1 Hz, 1H), 4.31 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.31 (m, 3F), -67.91 (q, J = 7.5 Hz, 3F), -110.41 (q, J = 7.5 Hz, 1F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 252.5 Hz), 156.8 (q, $J_{C\text{-}F}$ = 36.4 Hz), 147.4 (q, $J_{C\text{-}F}$ = 6.1 Hz), 138.5 (d, $J_{C\text{-}F}$ = 9.1 Hz), 134.2, 133.6, 131.9, 130.2, 129.5, 128.8 (d, $J_{C\text{-}F}$ = 10.1 Hz), 128.1, 128.0, 122.0 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.7 (q, $J_{C\text{-}F}$ = 35.4 Hz), , 116.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 116.3 (q, $J_{C\text{-}F}$ = 289.9 Hz), 116.1 (d, $J_{C\text{-}F}$ = 24.2 Hz), 50.7 .



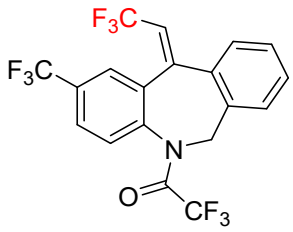
(*Z*)-1-(2-bromo-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)-2,2,2-trifluoroethan-1-one (5s)

Yellow solid, 56.6 mg; purified by flash chromatography eluted with PE/EA = 75:1, 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.42 - 7.38 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 6.13 (q, J = 8.0 Hz, 1H), 5.95 (d, J = 17.1 Hz, 1H), 4.33 (d, J = 17.1 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.19 (m, 3F), -67.90 (d, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, $J_{C\text{-}F}$ = 37.4 Hz), 147.5 (q, $J_{C\text{-}F}$ = 6.1 Hz), 136.9, 135.4, 134.9, 134.3, 133.4, 130.1, 129.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 129.8, 129.4, 128.1 (s, 2C), 127.2 (d, $J_{C\text{-}F}$ = 1.0 Hz), 122.1 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.7 (q, $J_{C\text{-}F}$ = 35.4 Hz), 116.0 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.6.



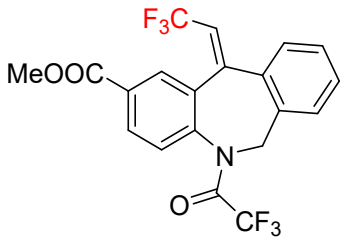
(*Z*)-2,2,2-trifluoro-1-(11-(2,2,2-trifluoroethylidene)-2-(trifluoromethyl)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5t)

White solid, 50.9 mg; purified by flash chromatography eluted with PE/EA = 75:1, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.74 (d, J = 8.1 Hz, 1H), 7.69 (s, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.40 -7.31 (m, 2H), 7.17 (d, J = 7.3 Hz, 1H), 6.18 (q, J = 7.9 Hz, 1H), 6.00 (d, J = 16.8 Hz, 1H), 4.33 (d, J = 16.5 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.36 (m, 3F), -62.90 (s, 3F), -67.92 (d, J = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$ = 37.4 Hz),147.2 (q, $J_{C\text{-}F}$ = 5.0 Hz), 139.1, 137.2, 133.9, 133.3, 131.8 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.3, 129.4, 128.3, 128.1, 127.5, 127.2 (q, $J_{C\text{-}F}$ = 3.0 Hz), 126.2, 123.2(q, $J_{C\text{-}F}$ = 274.2 Hz), 121.9 (q, $J_{C\text{-}F}$ = 271.7 Hz), 121.2 (q, $J_{C\text{-}F}$ = 35.4 Hz), 116.0 (q, $J_{C\text{-}F}$ = 288.9 Hz), 50.4.



Methyl (*Z*)-5-(2,2,2-trifluoroacetyl)-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepine-2-carboxylate (5u)

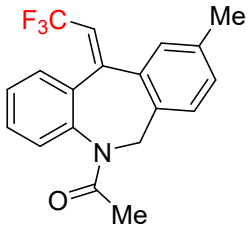
Yellow oil, 54.9 mg; purified by flash chromatography eluted with PE/EA = 75:1, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$)) δ ppm = 8.14 (d, *J* = 8.2 Hz, 1H), 8.09 (s, 1H), 7.49 - 7.40 (m, 2H), 7.34 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.16 (q, *J* = 7.6 Hz, 1H), 6.00 (d, *J* = 16.9 Hz, 1H), 4.33 (d, *J* = 16.5 Hz, 1H), 3.93 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.31 (m, 3F), -67.91 (d, *J* = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 156.5 (q, $J_{C\text{-}F}$ = 37.4 Hz), 147.6 (q, $J_{C\text{-}F}$ = 5.0 Hz), 139.7, 136.6, 134.3, 133.3, 131.4, 131.3, 130.1, 129.3, 128.2, 128.1, 127.0, 122.0 (q, $J_{C\text{-}F}$ = 272.7 Hz), 120.8 (q, $J_{C\text{-}F}$ = 34.3 Hz), 116.0 (q, $J_{C\text{-}F}$ = 288.9 Hz), 52.7, 50.4.

HRMS (ESI) calculated for $C_{20}H_{14}F_6NO_3^+$ m/z $[M+H]^+$: 430.0872, found: 430.0873.



(*Z*)-1-(9-methyl-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepin-5-yl)ethan-1-one (5v)

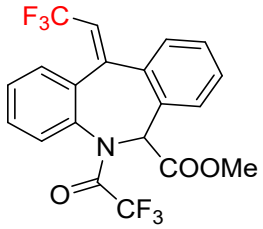
Yellow solid, 34.4 mg; purified by flash chromatography eluted with PE/EA = 75:1, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.47 - 7.41 (m, 1H), 7.39 (s, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.10-6.03 (m, 2H), 4.11 (d, *J* = 16.2 Hz, 1H), 2.34 (s, 3H), 1.92 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -55.61 (d, *J* = 7.5 Hz, 3F).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 151.1 (q, $J_{C\text{-}F}$ = 6.1 Hz), 138.9, 137.3, 137.0, 135.0, 132.7, 130.3, 130.2, 129.3, 128.6, 128.48 (q, $J_{C\text{-}F}$ = 2.0 Hz), 128.0, 127.1, 122.6 (q, $J_{C\text{-}F}$ = 272.7 Hz), 119.1 (q, $J_{C\text{-}F}$ = 34.3 Hz), 47.9, 21.5, 20.9.

HRMS (ESI) called. for $C_{19}H_{17}F_3NO^+$ m/z $[M+H]^+$:332.1257, found: 332.1254.



Methyl (*Z*)-5-(2,2,2-trifluoroacetyl)-11-(2,2,2-trifluoroethylidene)-6,11-dihydro-5H-dibenzo[b,e]azepine-6-carboxylate (5w)

Yellow solid, 71.2 mg; purified by flash chromatography eluted with PE/EA = 75:1, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 7.47 (d, *J* = 6.1 Hz, 1H), 7.40 (d, *J* = 13.2 Hz, 5H), 7.31 (s, 1H), 7.22 (d, *J* = 6.7 Hz, 1H), 6.85 (s, 1H), 6.17 – 6.05 (m, 1H), 3.65 (s, 3H).

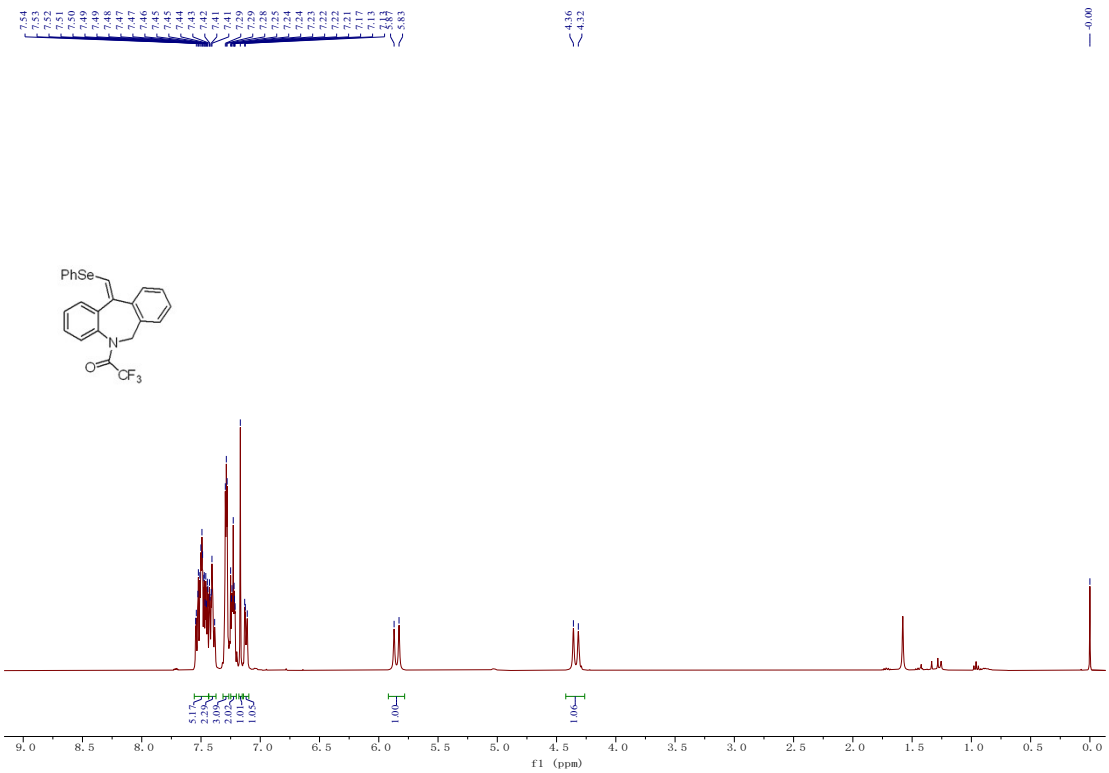
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.00 (m, 3F), -67.38 (d, *J* = 7.5 Hz, 3F).

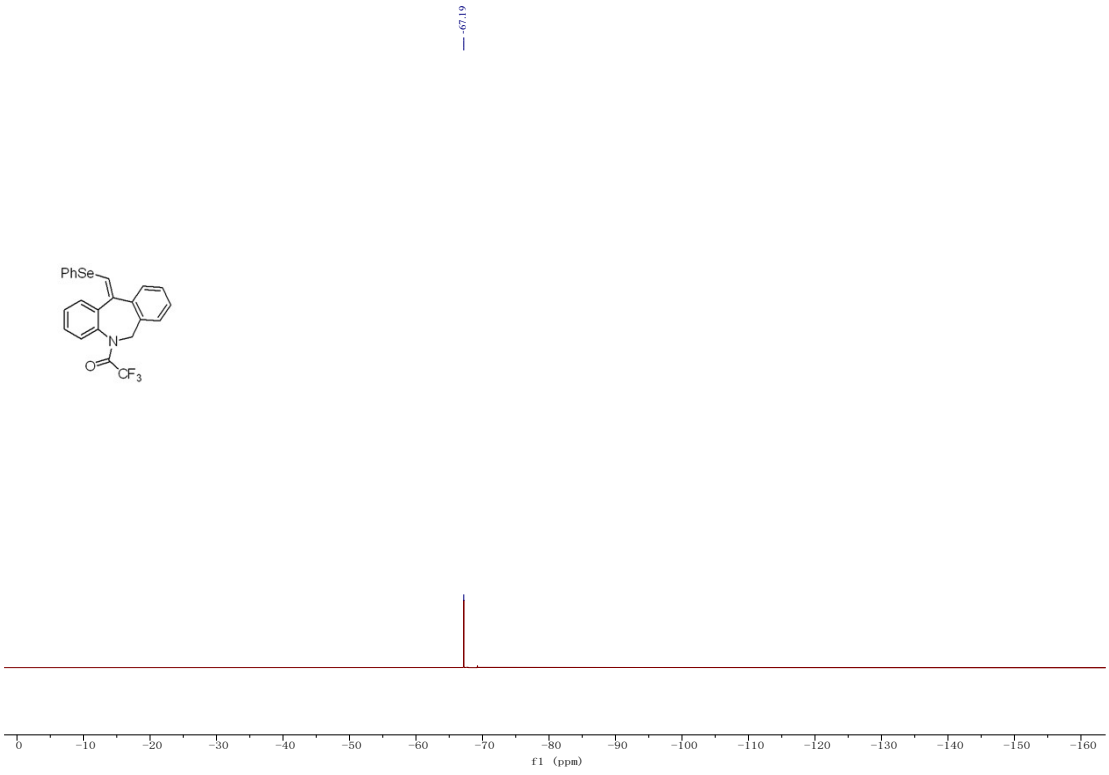
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 157.3 (q, $J_{C\text{-}F}$ = 37.4 Hz), 148.3 (q, $J_{C\text{-}F}$ = 6.1 Hz), 136.3, 134.8, 132.8, 130.9, 130.8, 129.9, 129.6, 129.2, 129.0, 128.3 (q, $J_{C\text{-}F}$ = 1.0 Hz), 122.1 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.8 (q, $J_{C\text{-}F}$ = 35.4 Hz), 116.1 (q, $J_{C\text{-}F}$ = 289.9 Hz), 60.9, 53.0.

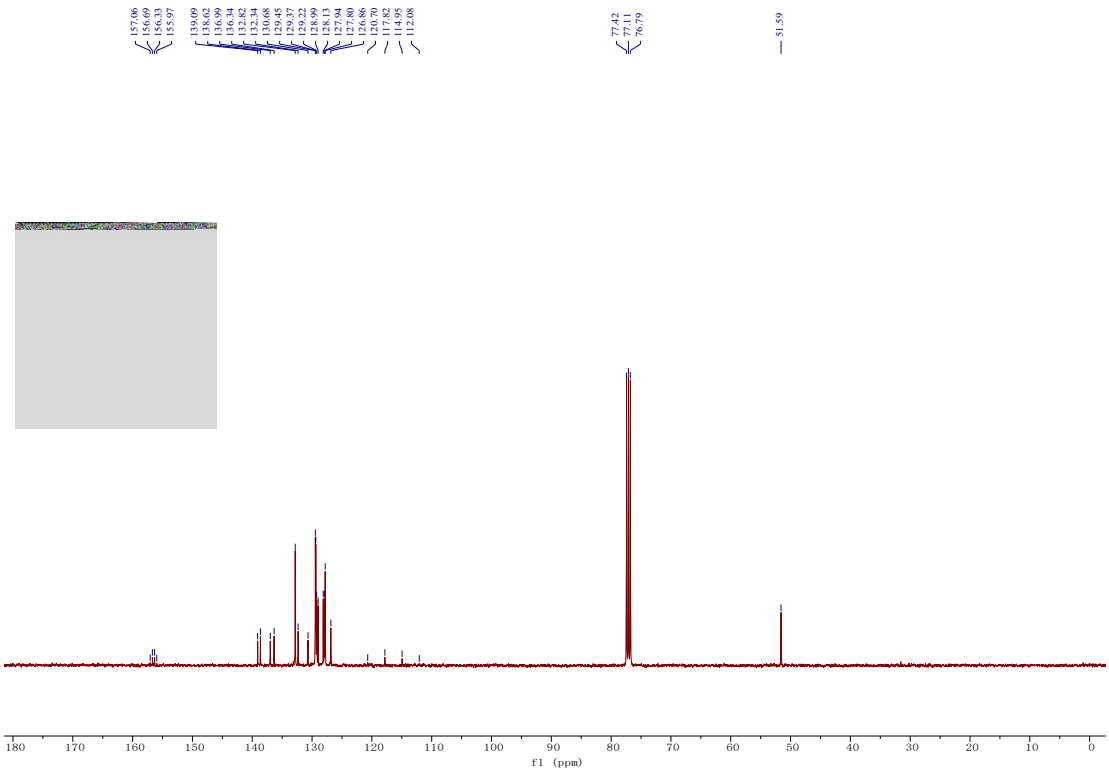
HRMS (ESI) calculated for $C_{20}H_{14}F_6NO_3^+$ m/z $[M+H]^+$:430.0872, found: 430.0873.

8. NMR Spectra

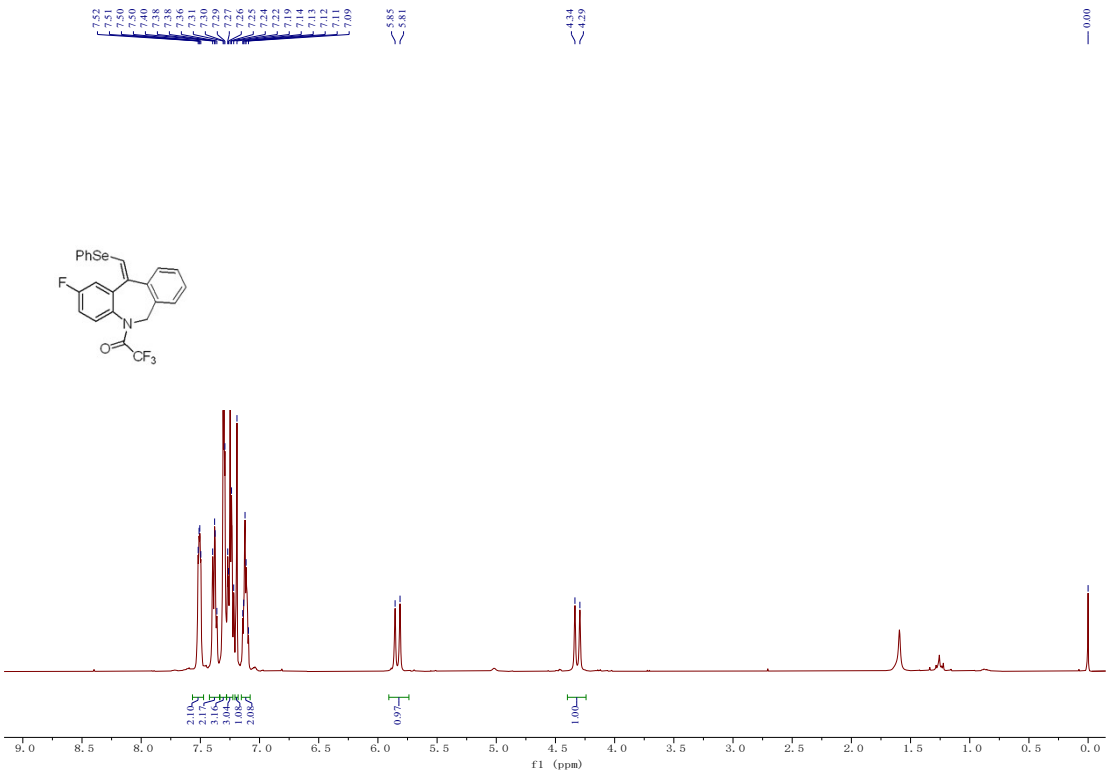
4a ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

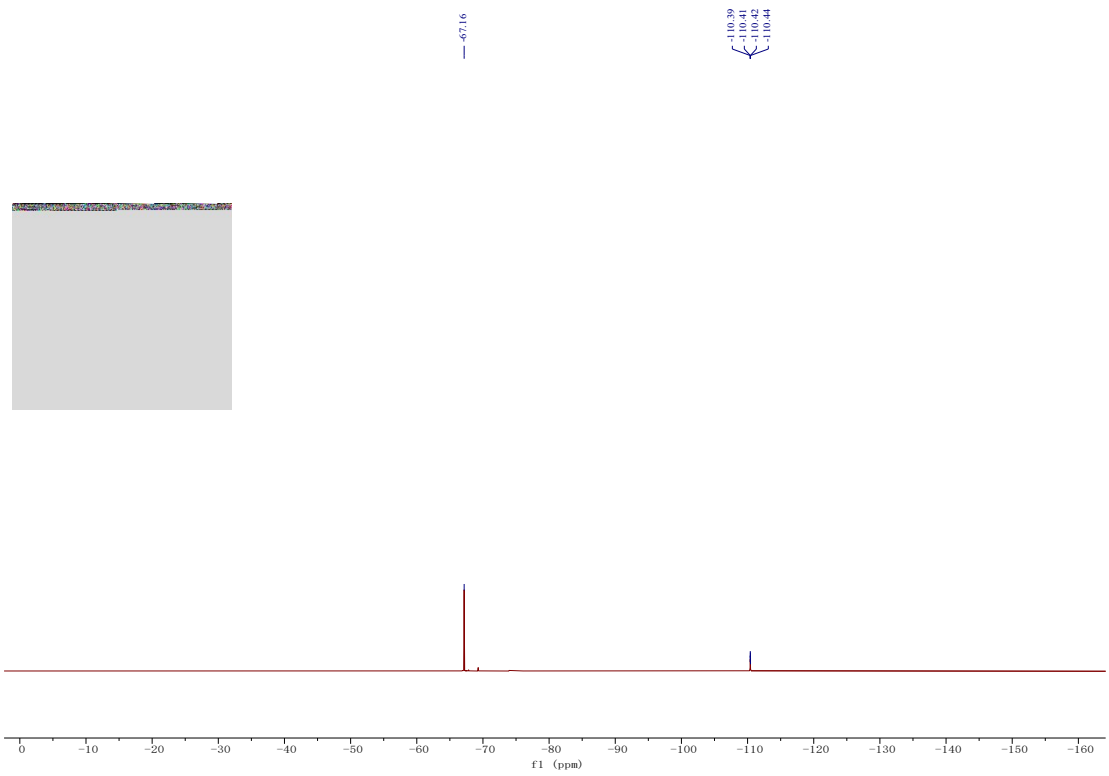






4b ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

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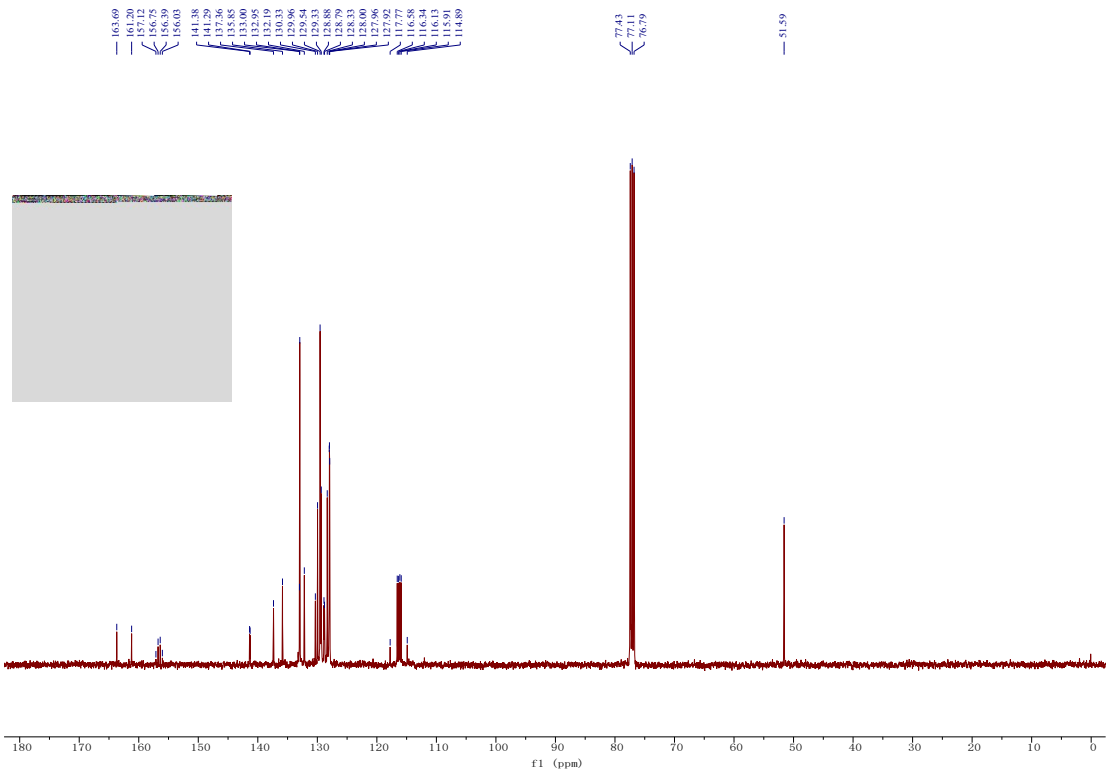
-120
-130
-140
-150
-160
f1 (ppm)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132.95
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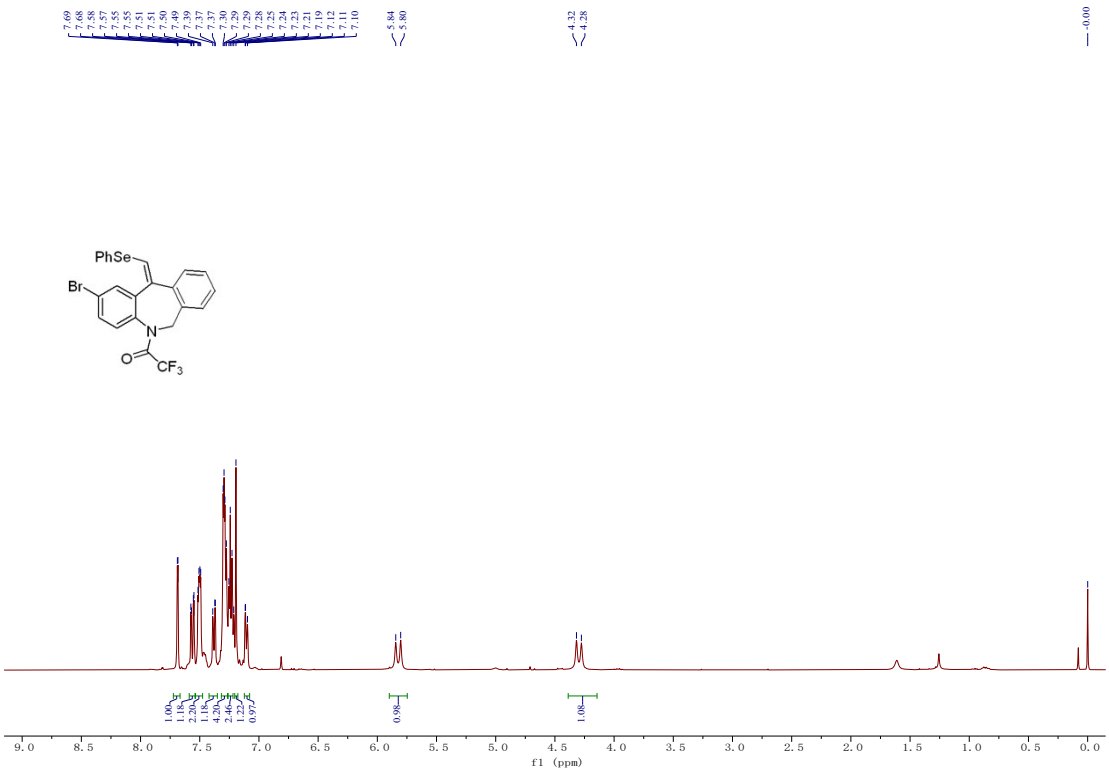
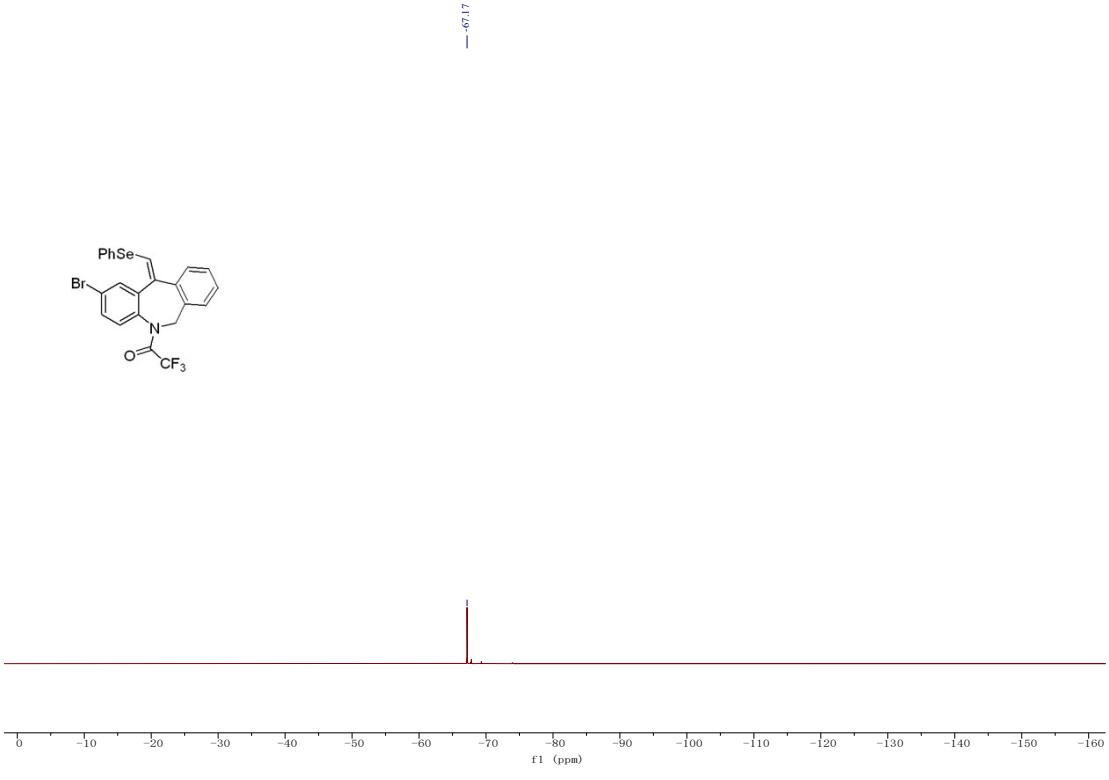
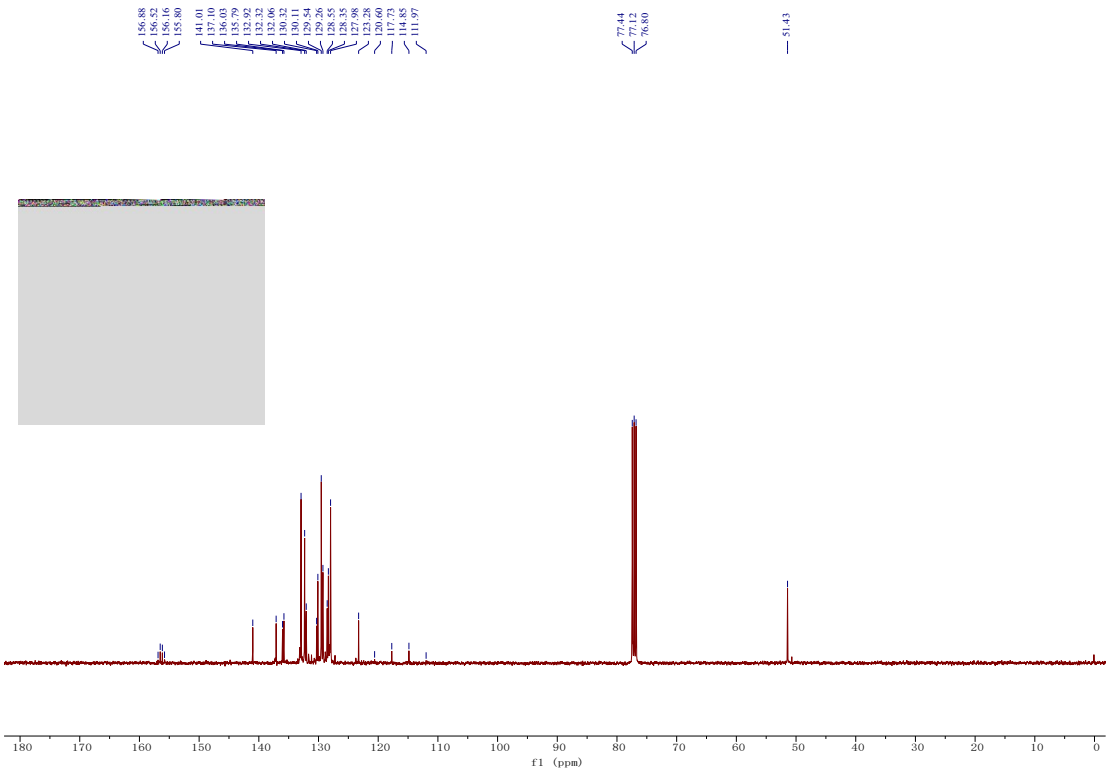
76.79
51.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

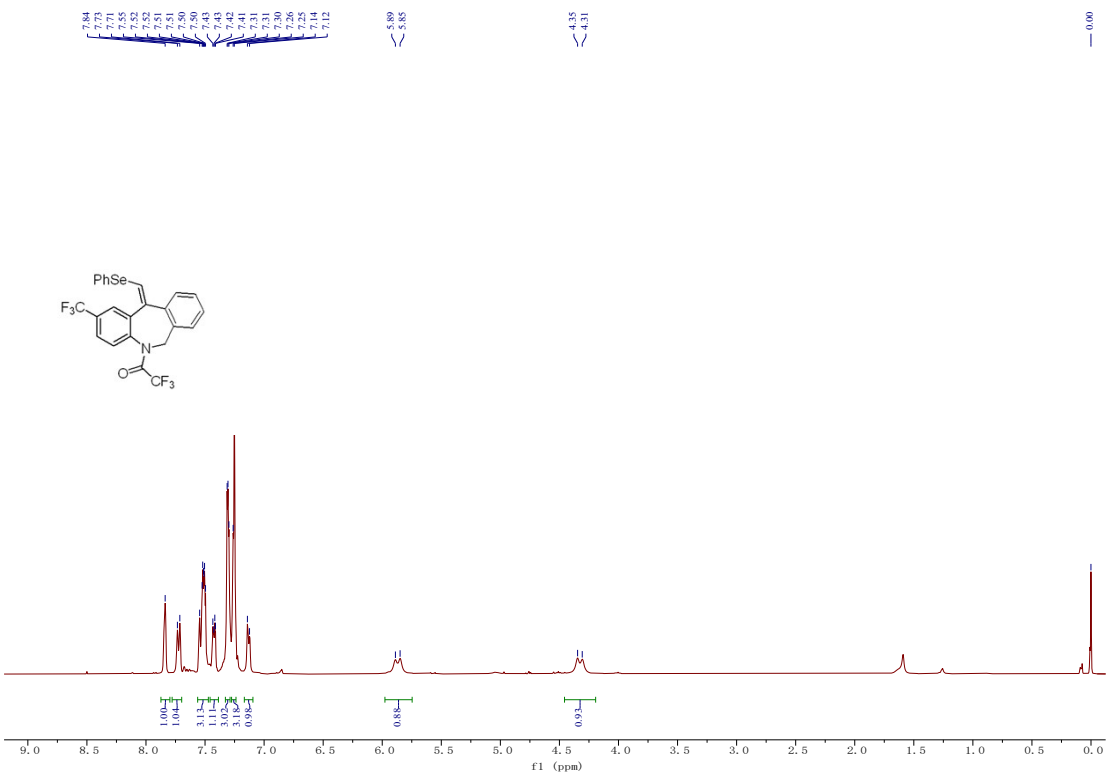
4c ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

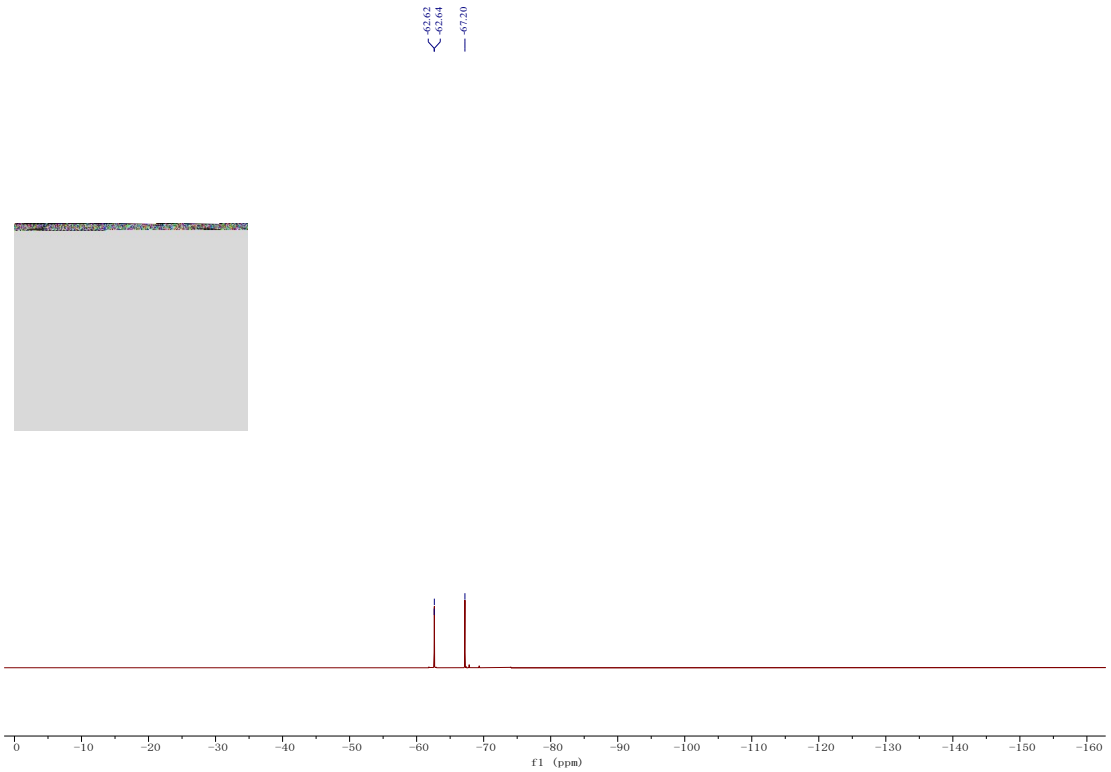






4d ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

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-67.20
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−10
−20
−30
−40
−50
−60
−70
−80
−90
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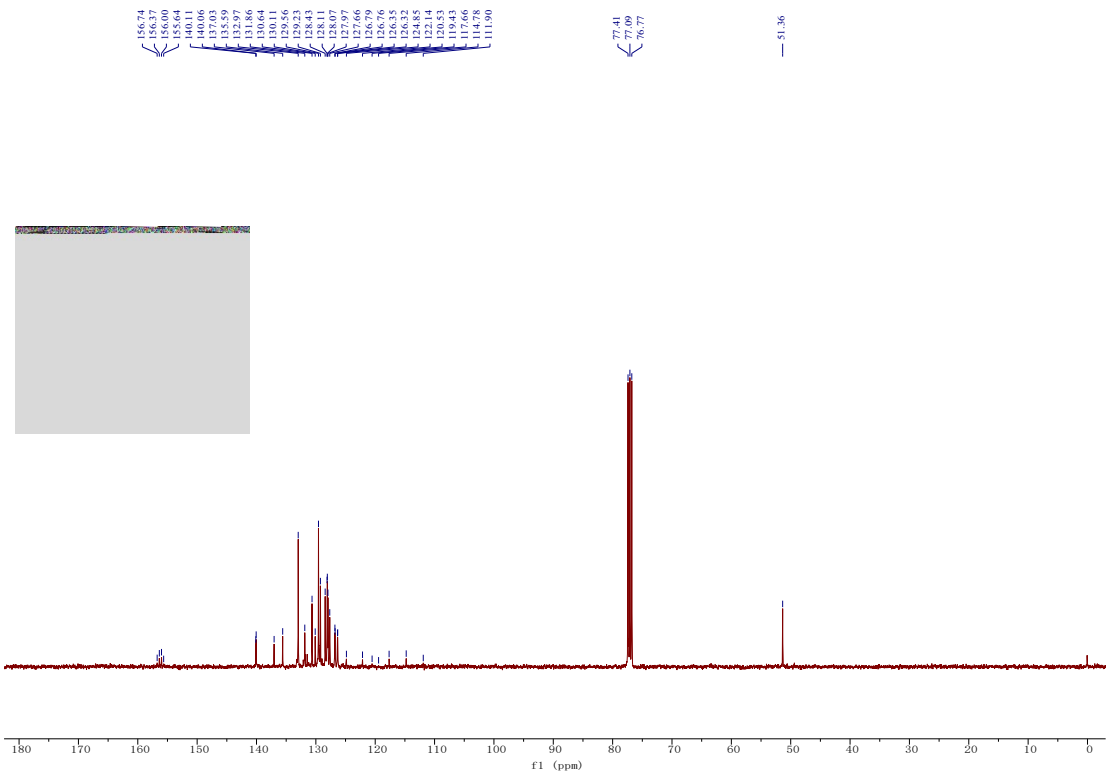
−110
−120
−130
−140
−150
−160
f1 (ppm)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51.36
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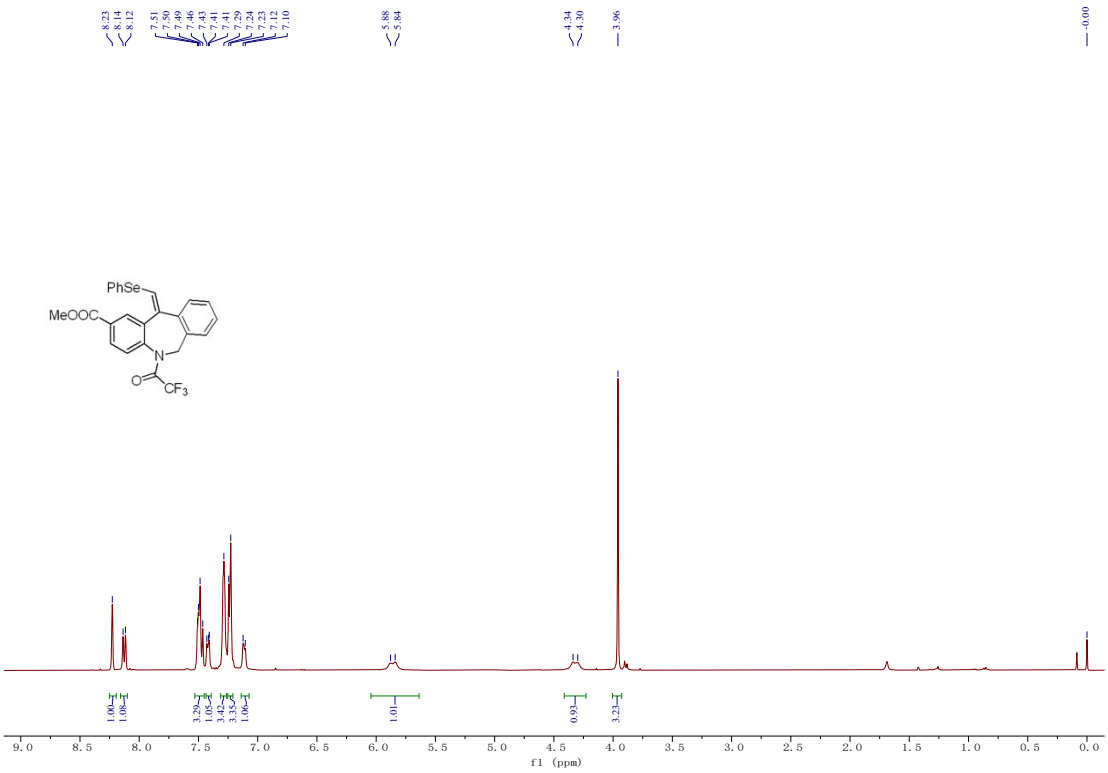
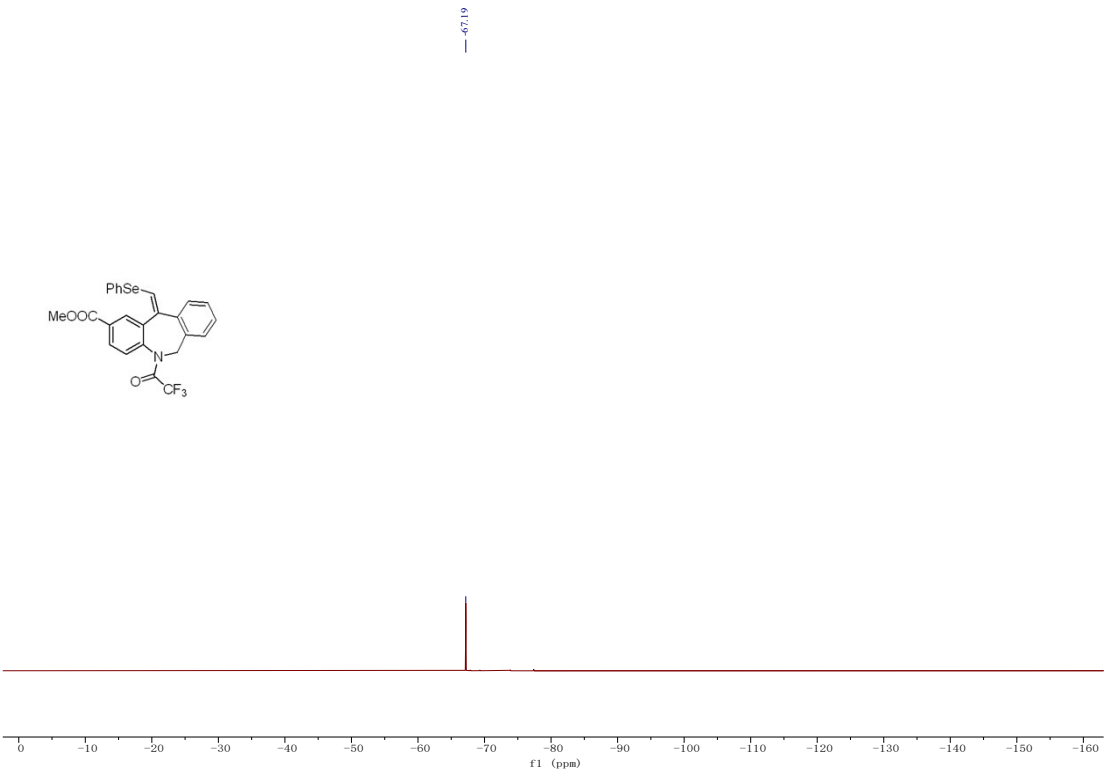
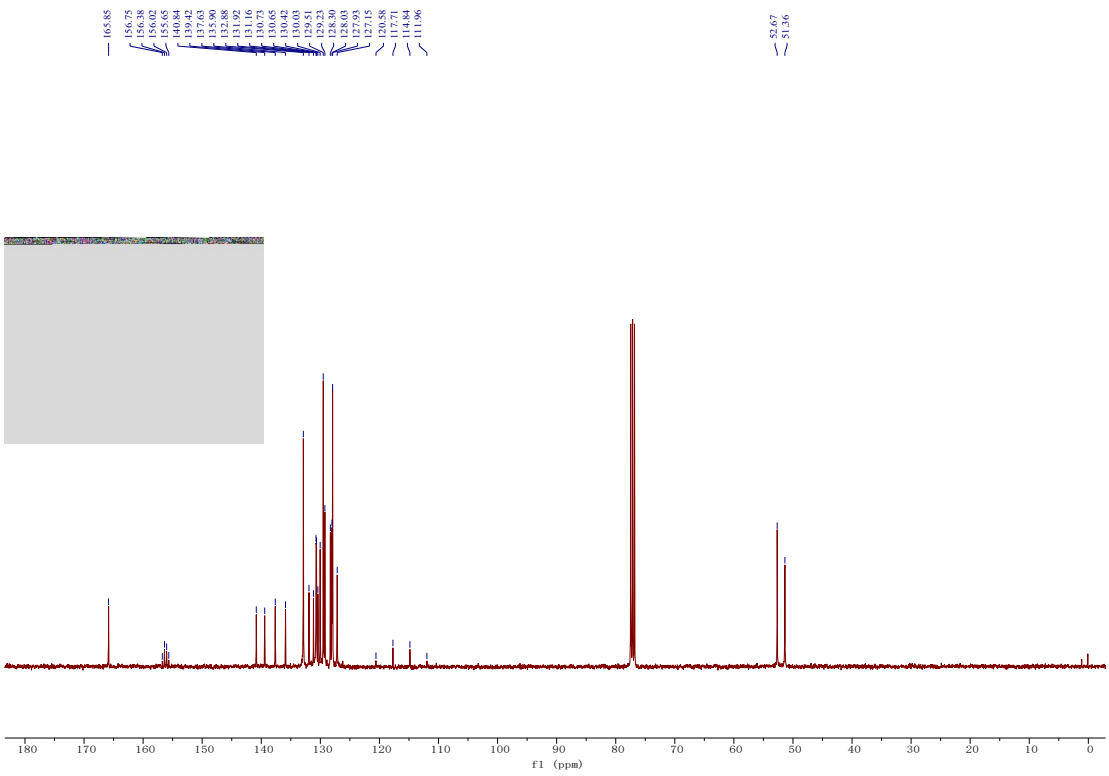
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

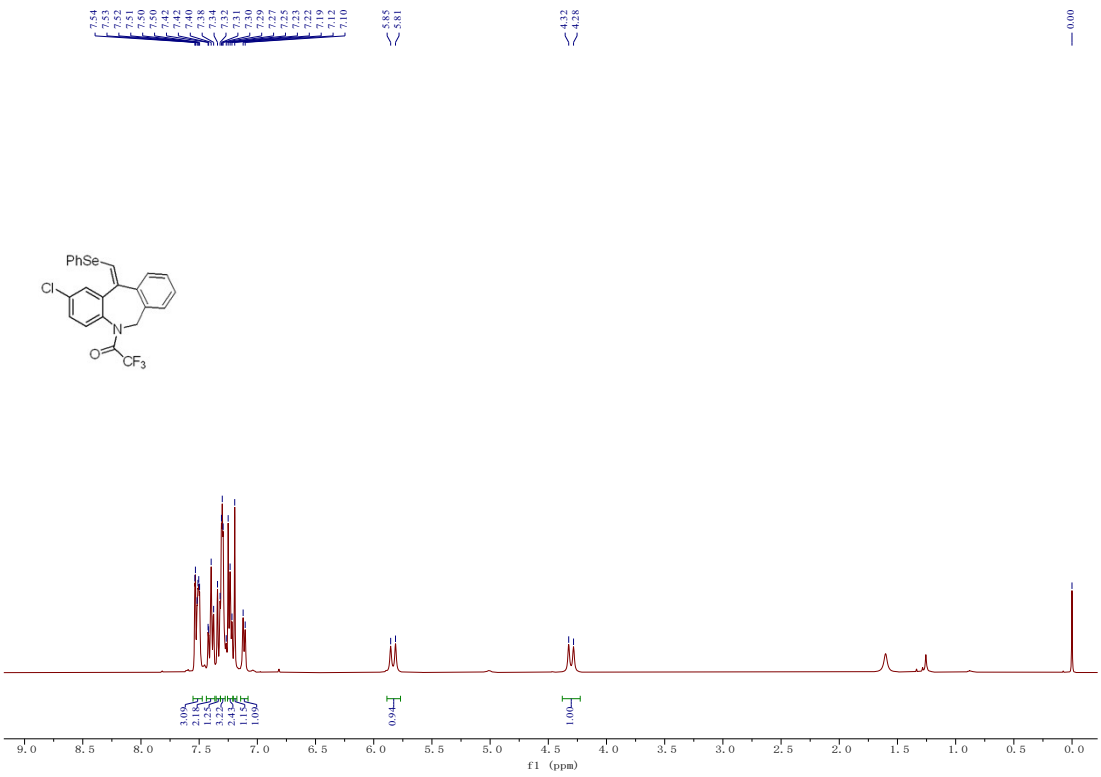
4e ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

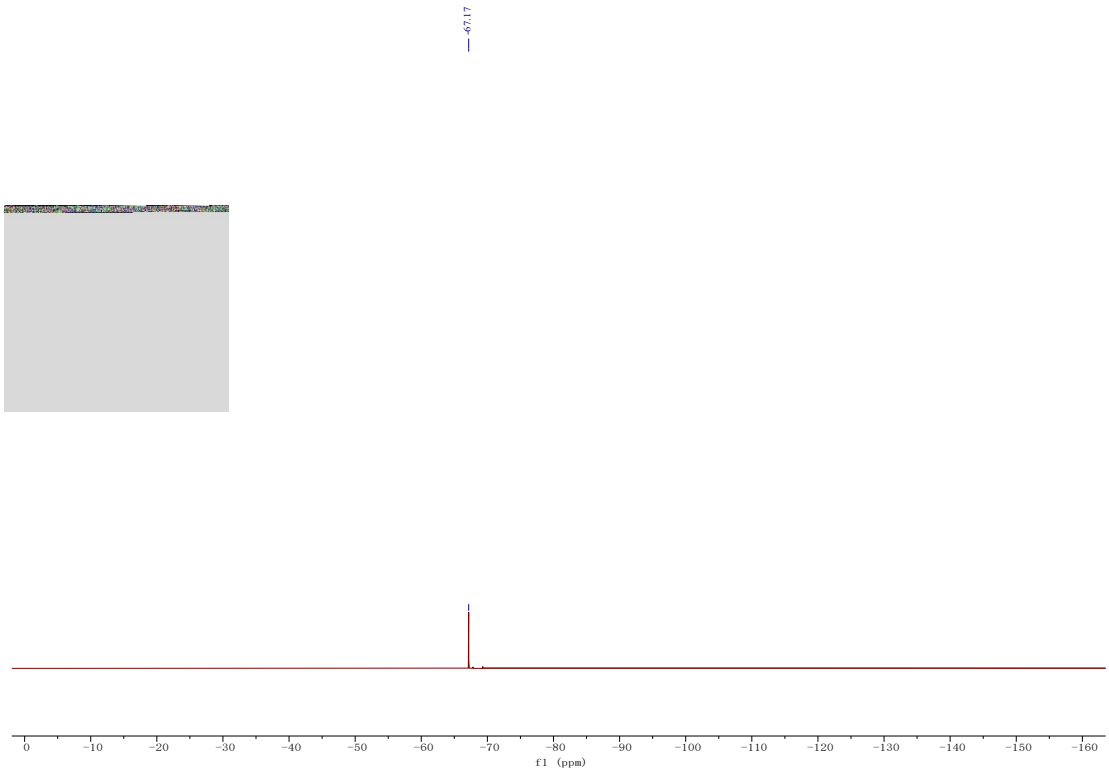


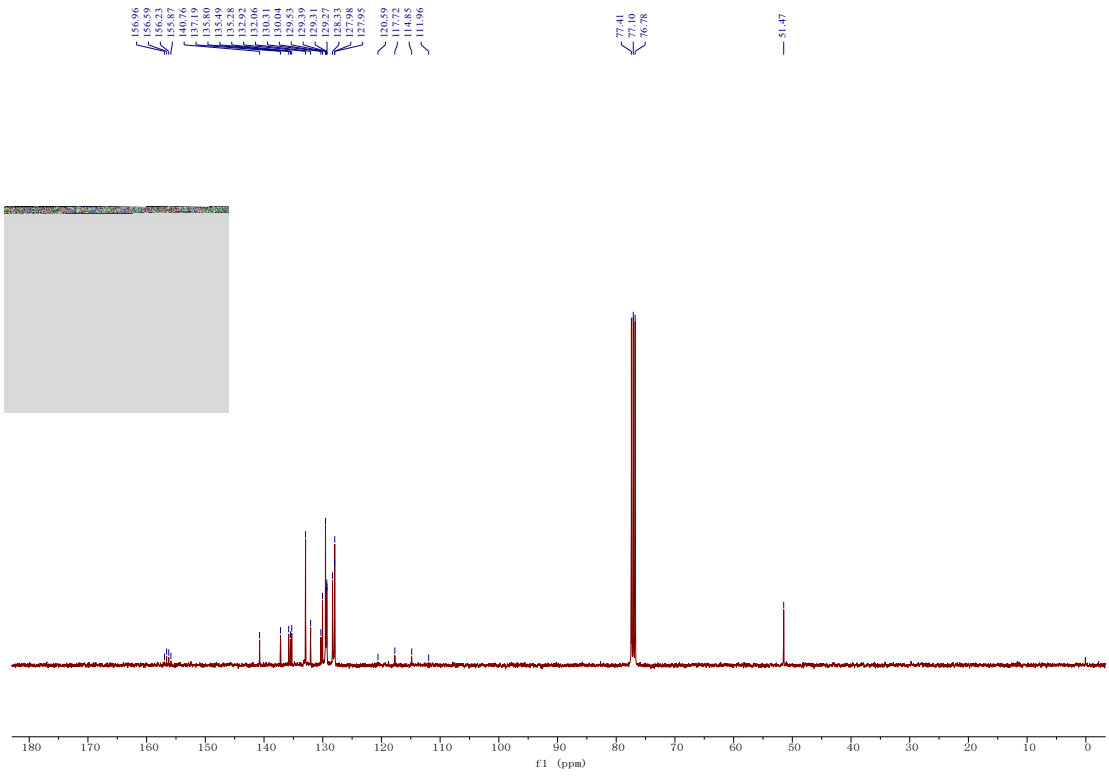




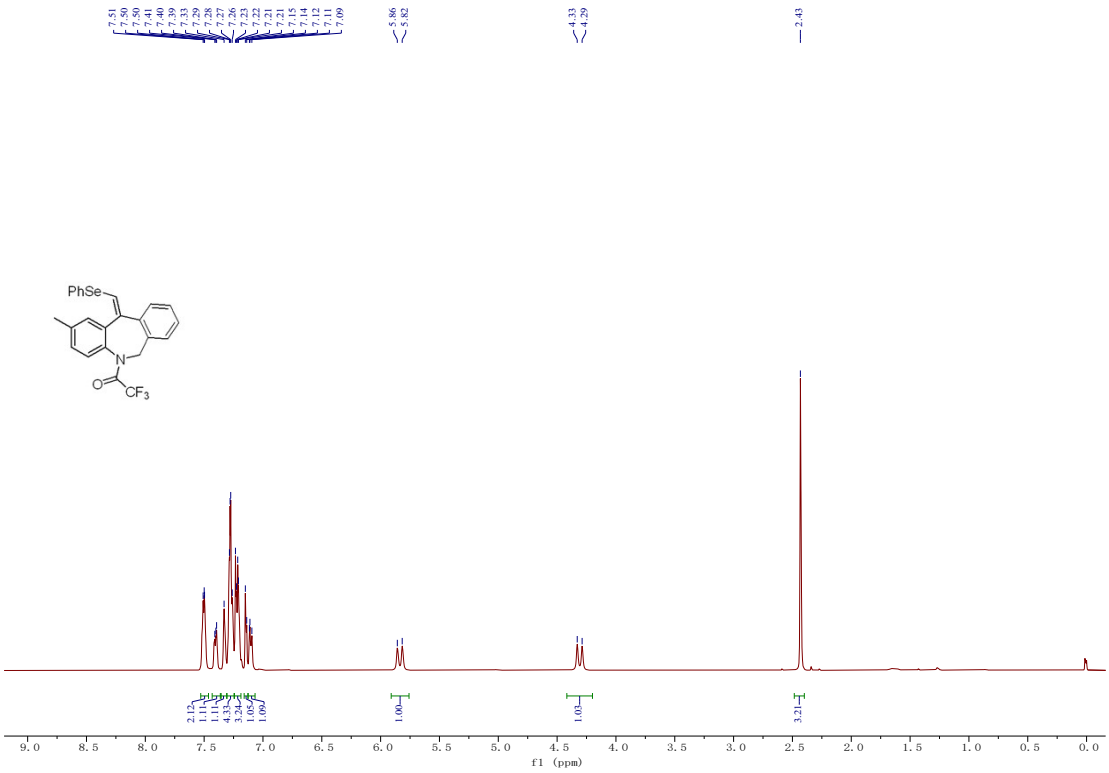
4f ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

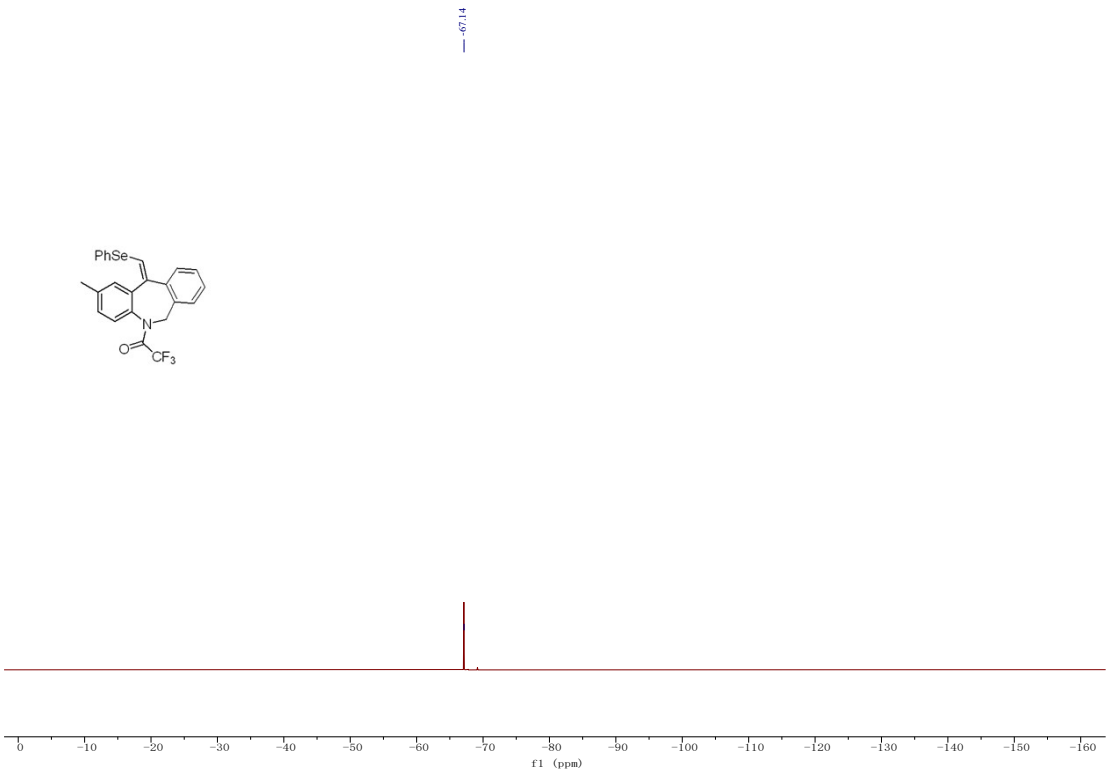


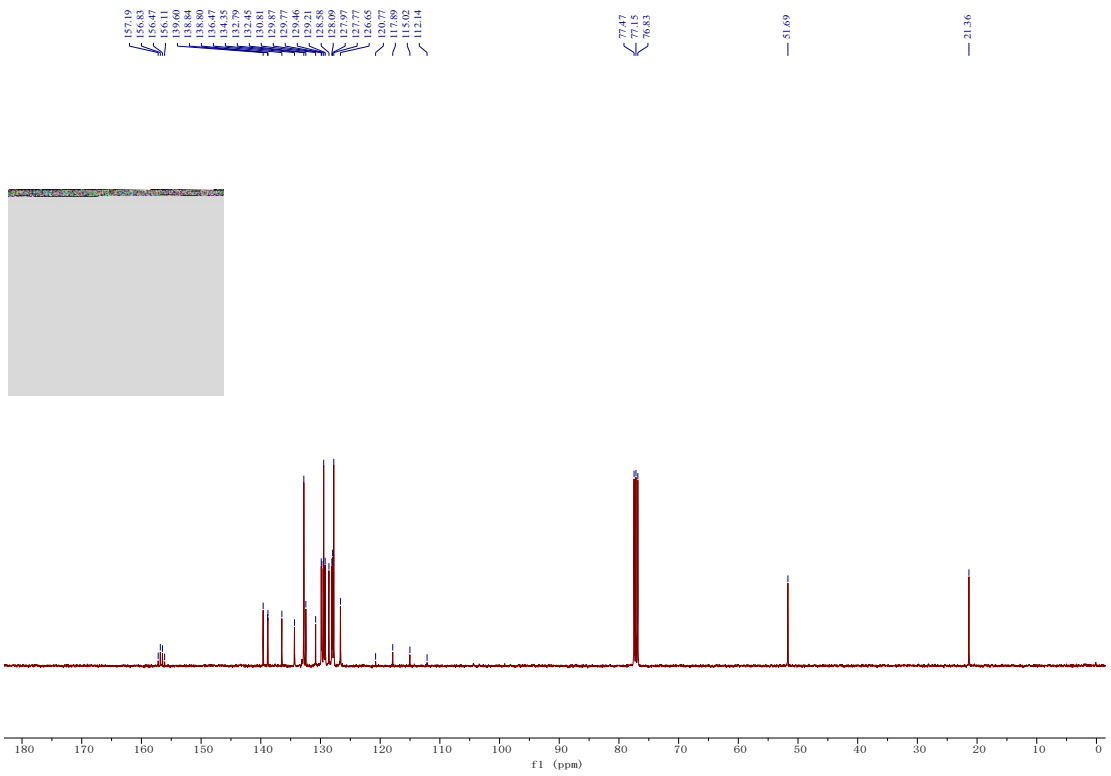

-67.17
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


156.96
156.59
156.23
155.87
140.76
137.19
135.80
135.49
135.28
132.92
132.66
130.31
130.04
129.53
129.39
129.31
129.27
129.13
127.98
127.95
120.59
117.72
114.85
111.96
77.41
77.10
76.78
51.47
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

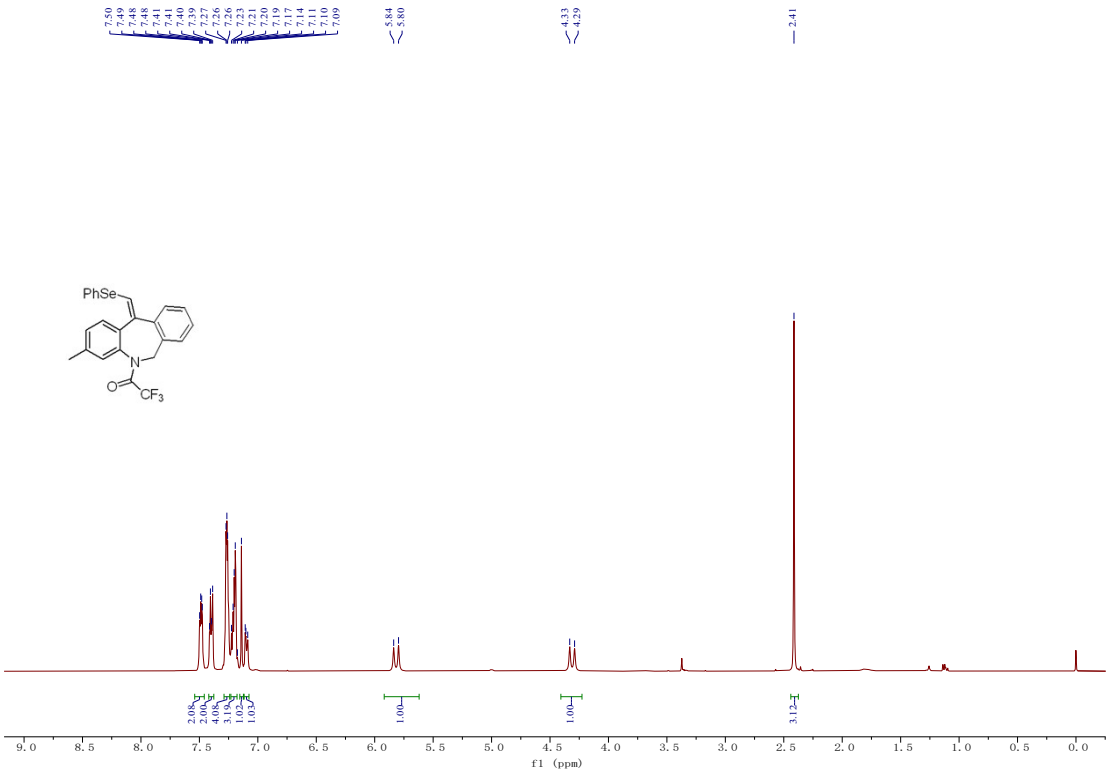
4g ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

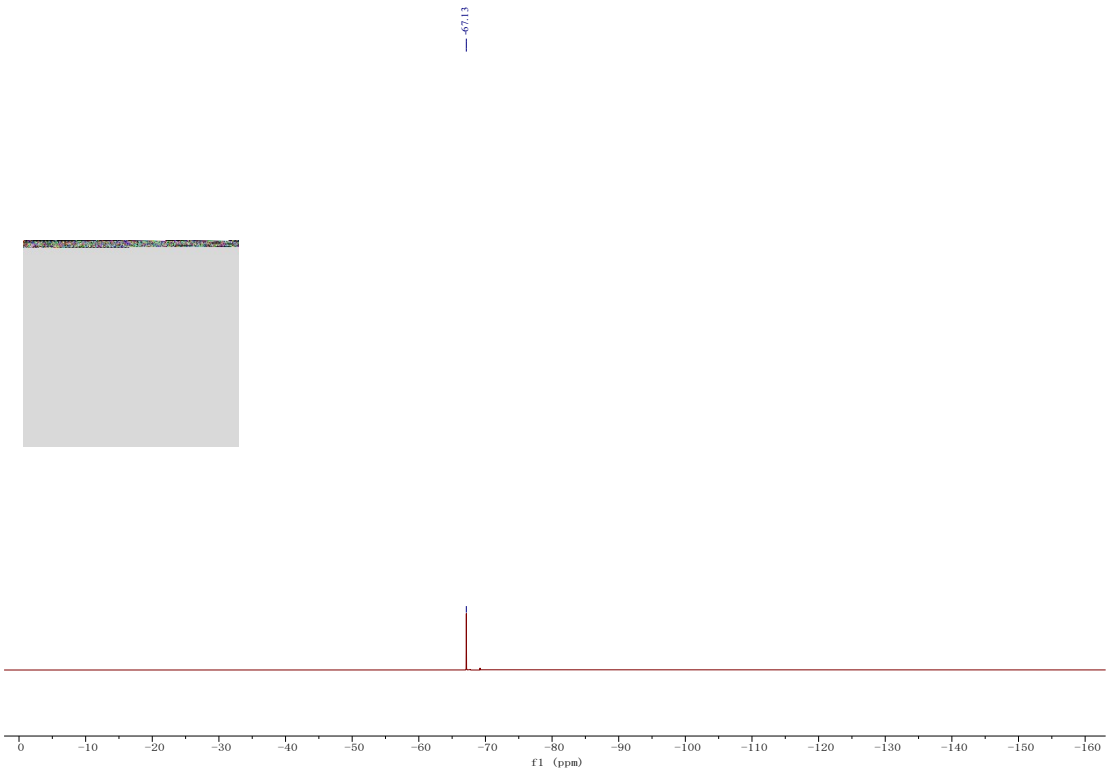


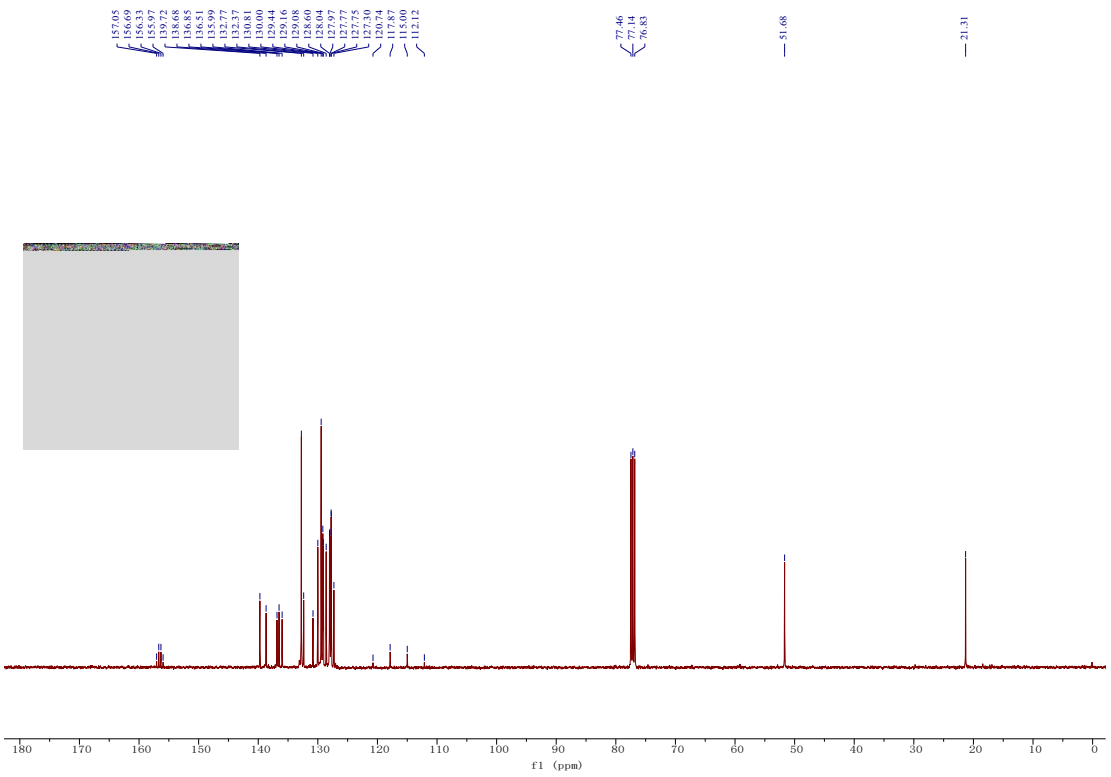




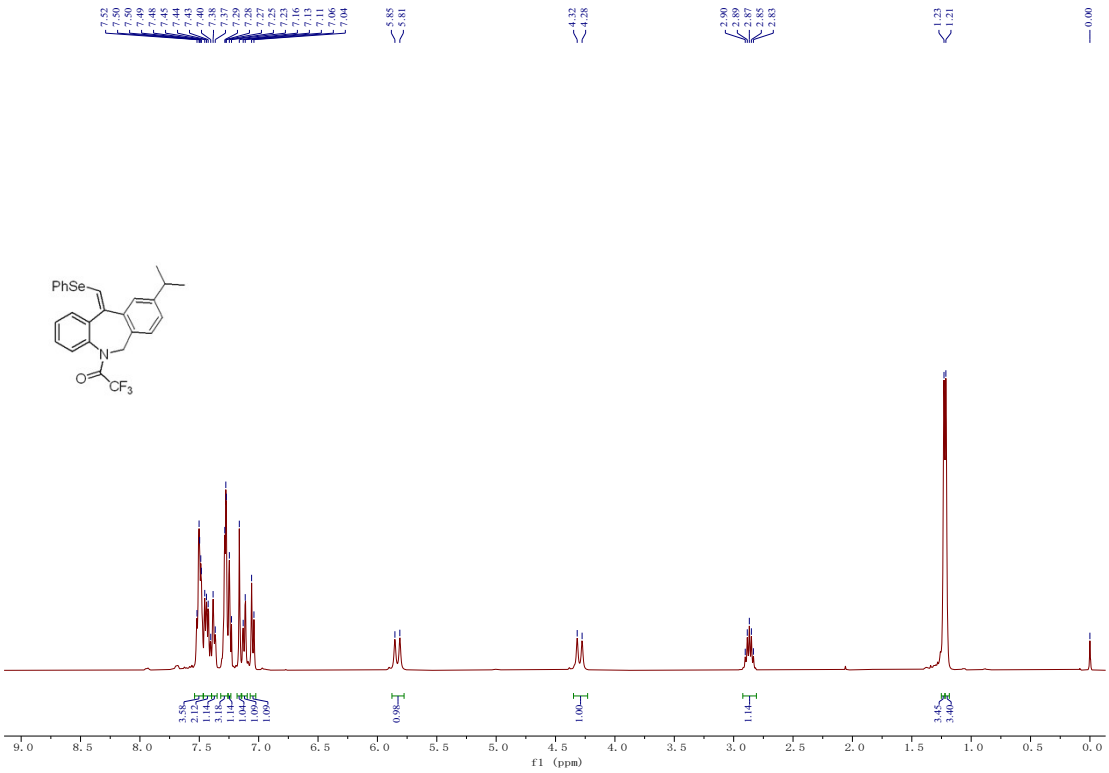
4h ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

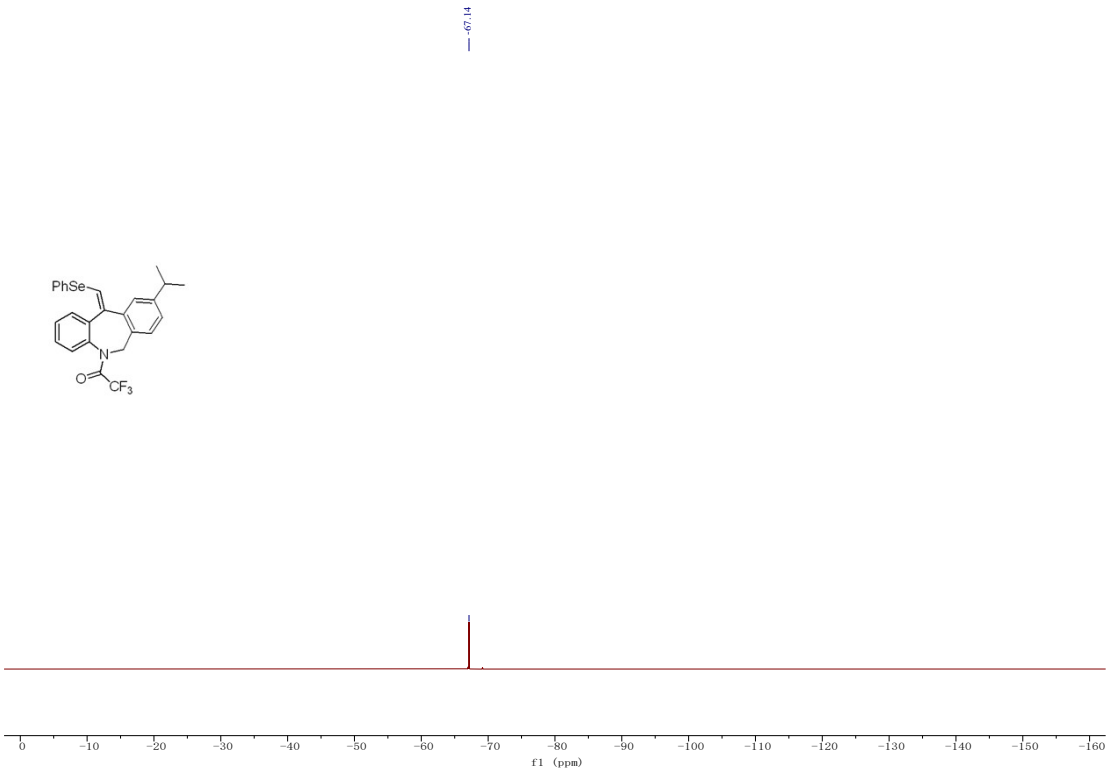


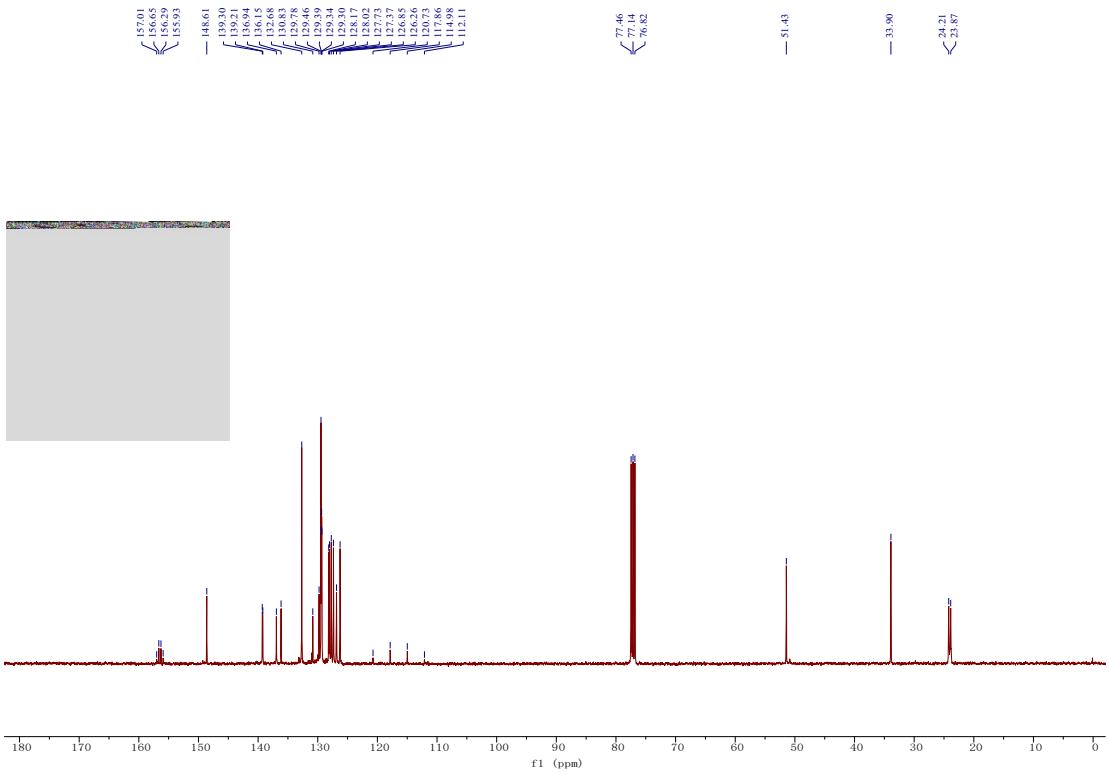

-67.13
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


157.05
154.69
156.33
155.97
139.72
138.68
136.85
136.51
135.99
132.77
132.37
130.81
130.00
129.44
129.16
129.08
128.60
128.04
127.97
127.77
127.75
127.30
120.74
117.87
115.00
112.12
77.46
77.14
76.83
51.68
21.31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

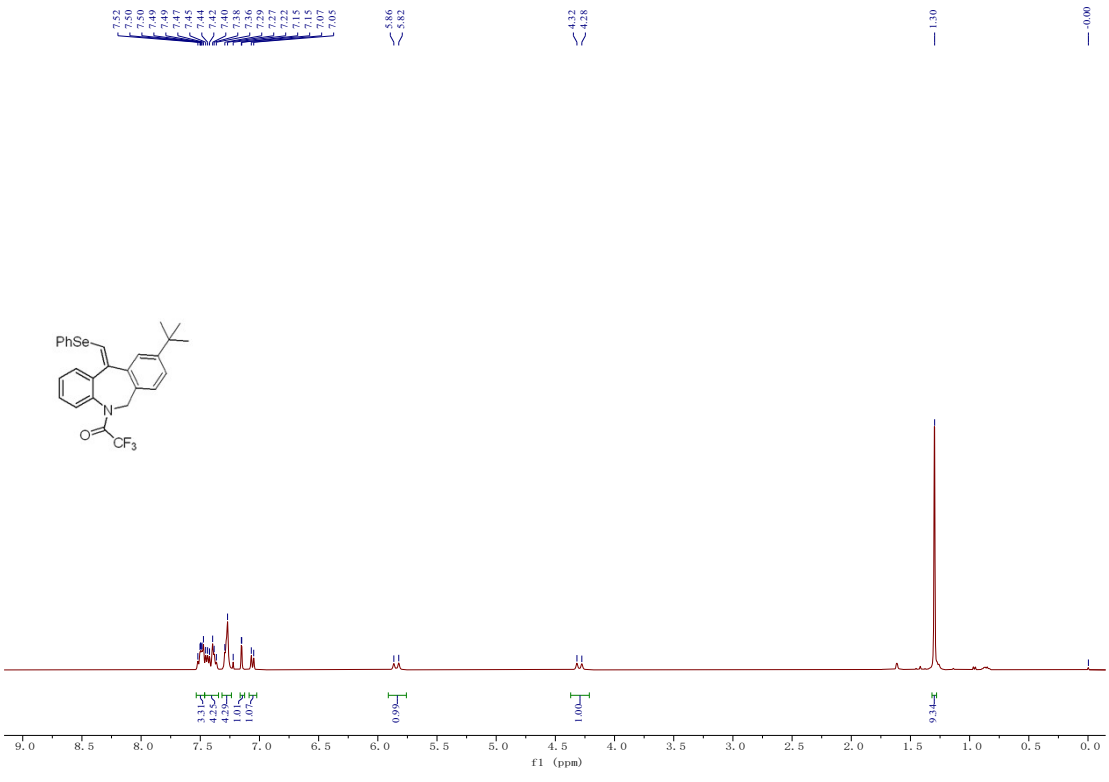
4i ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

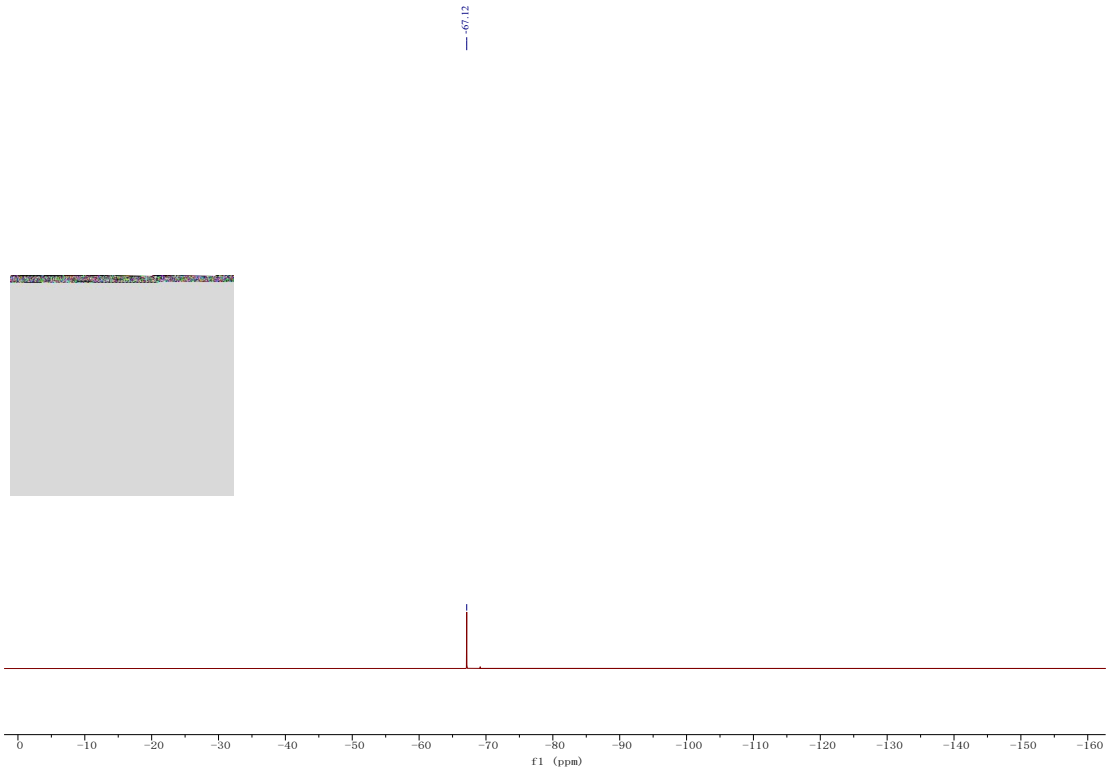


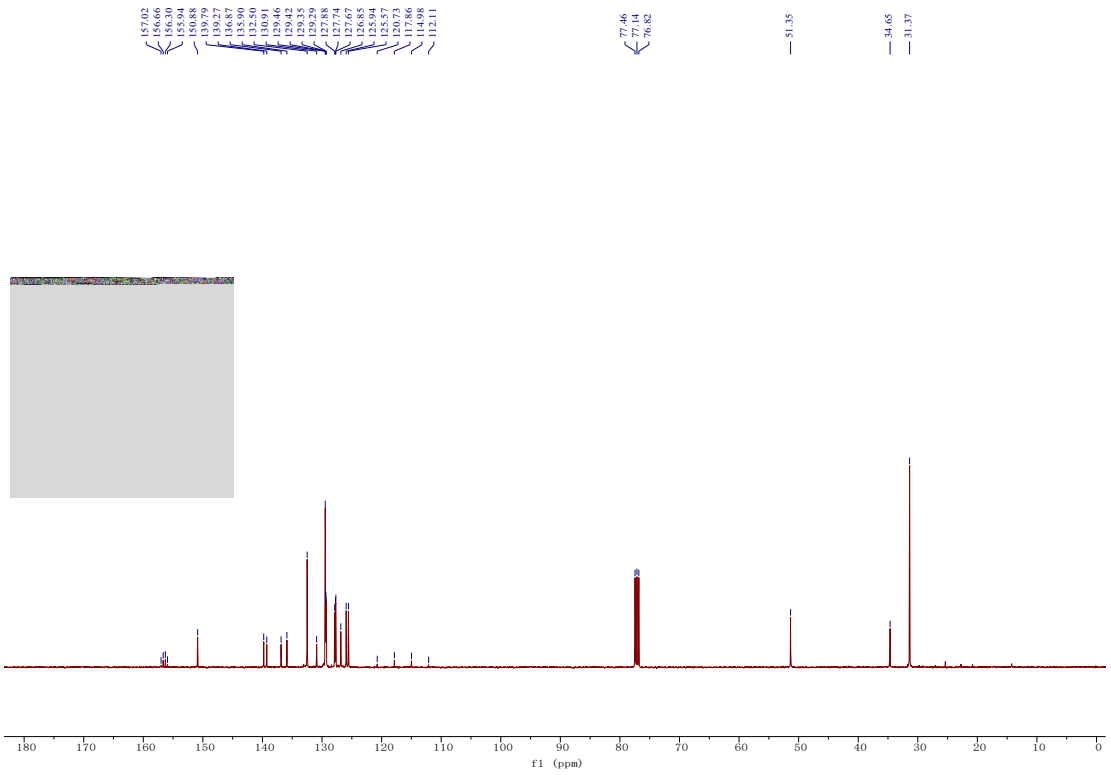




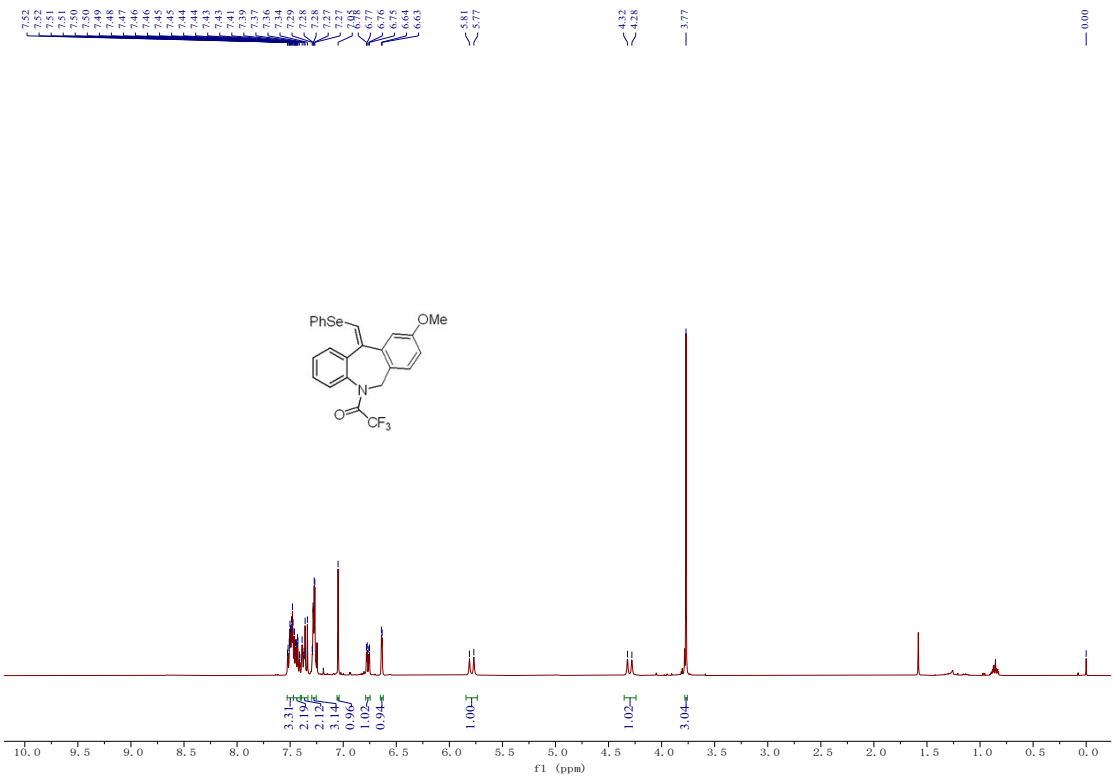
4j ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

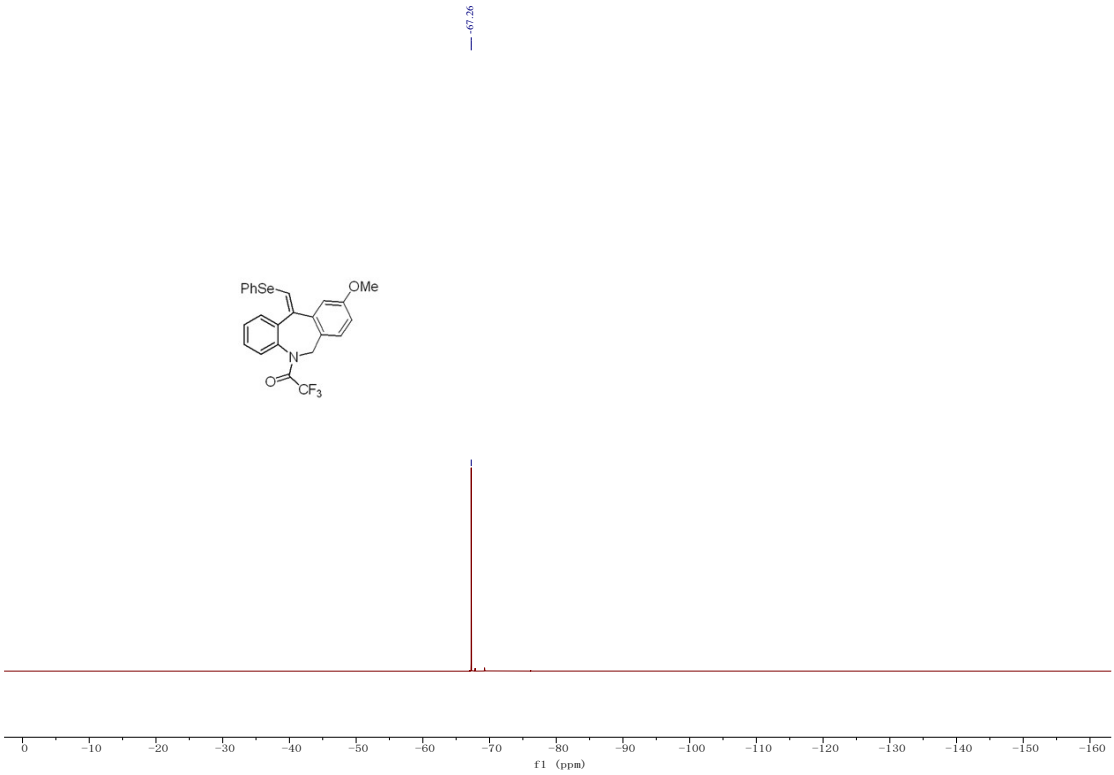


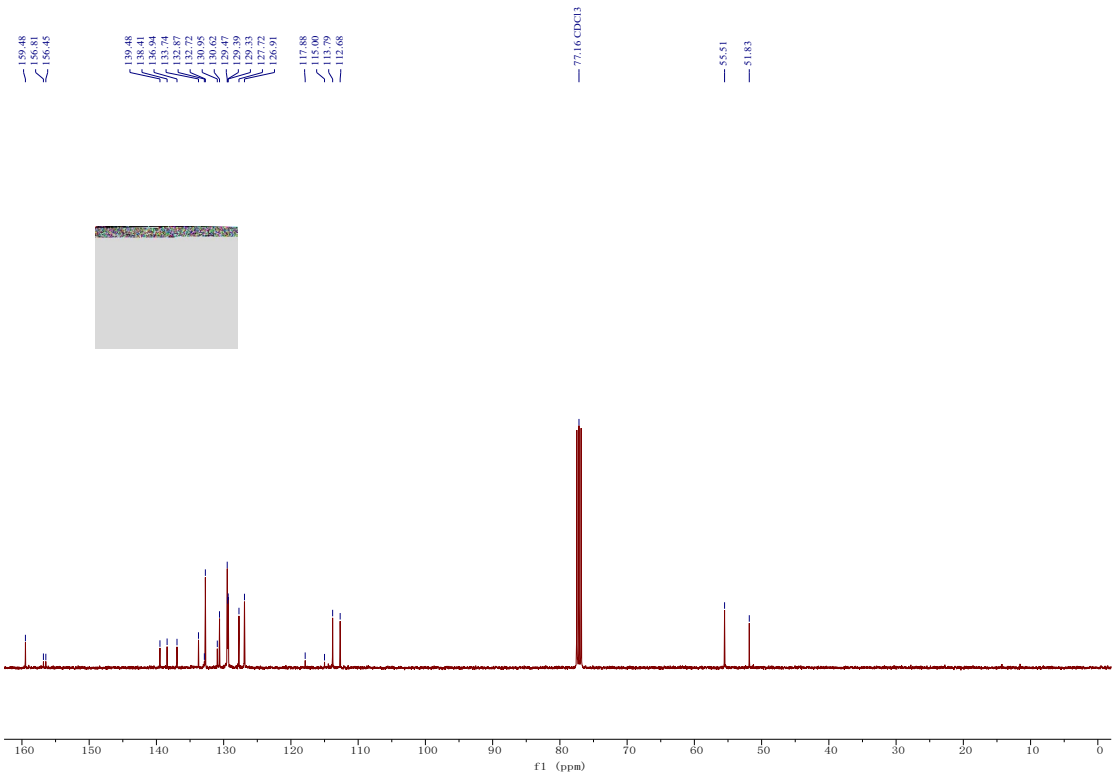




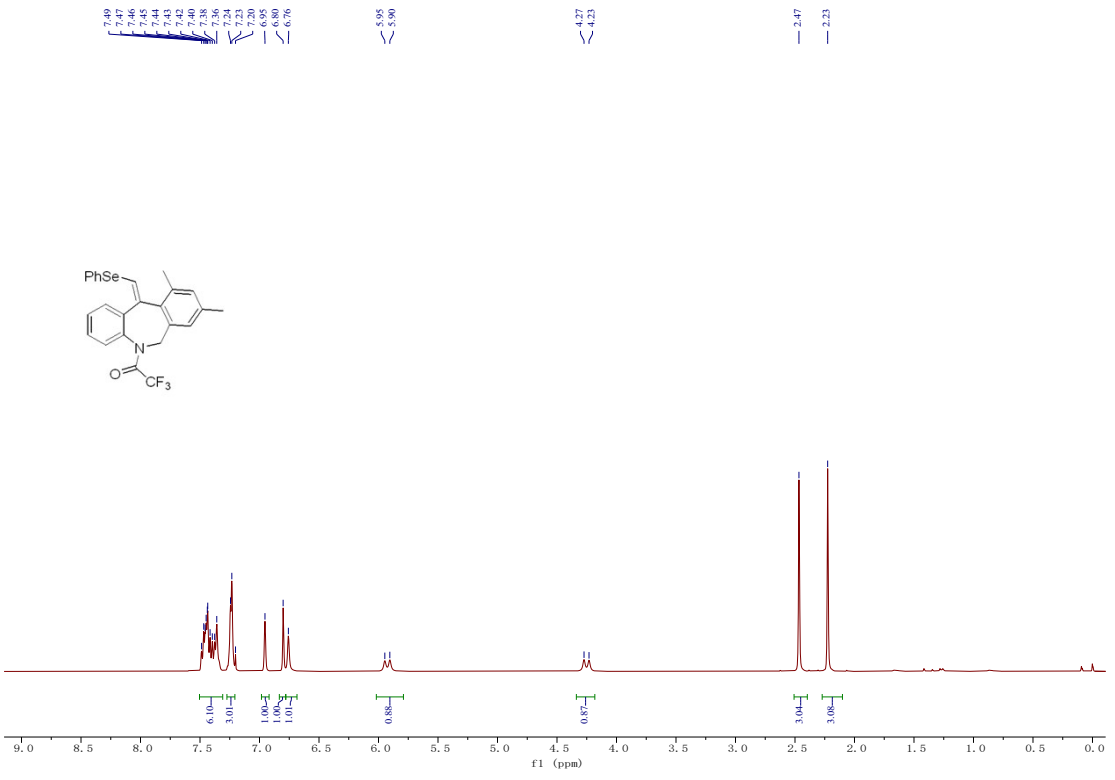
4k ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

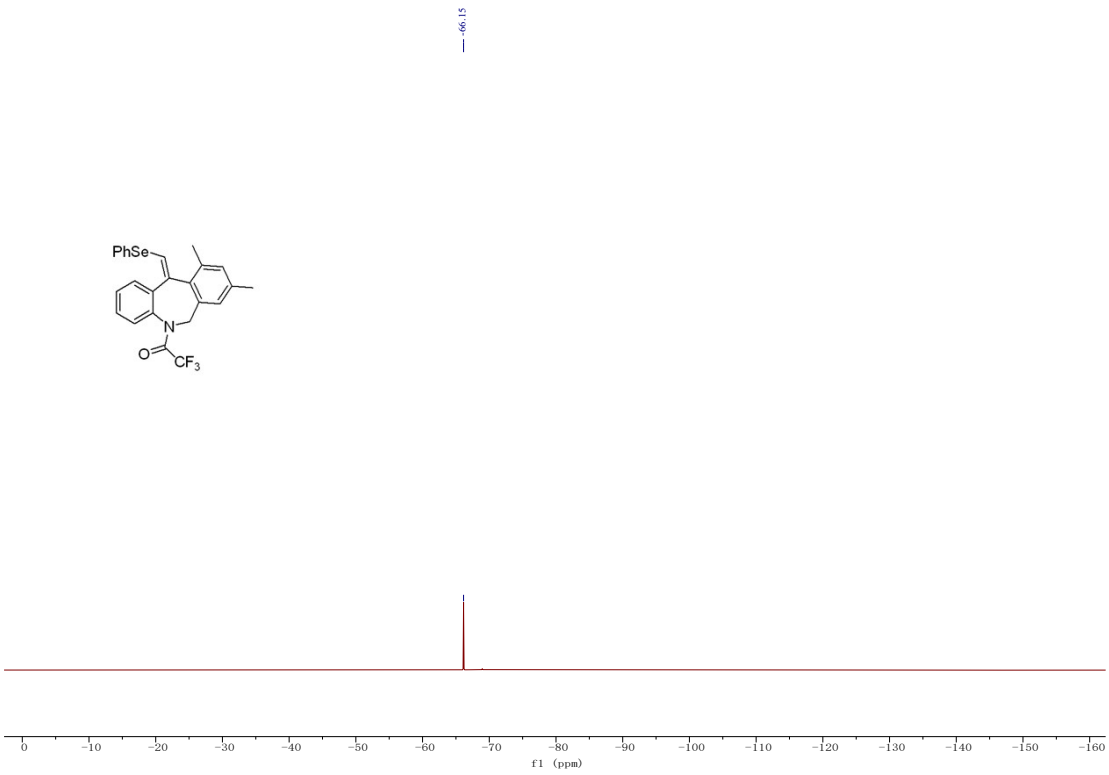

7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.41
7.39
7.37
7.36
7.34
7.29
7.28
7.28
7.27
7.27
6.78
6.77
6.76
6.75
6.64
6.63
5.81
5.77
4.32
4.28
3.77
0.00
PhSe
OMe
N
O
CF3
3.31
2.19
2.12
3.14
0.96
1.02
0.94
1.00
1.02
3.04
f1 (ppm)

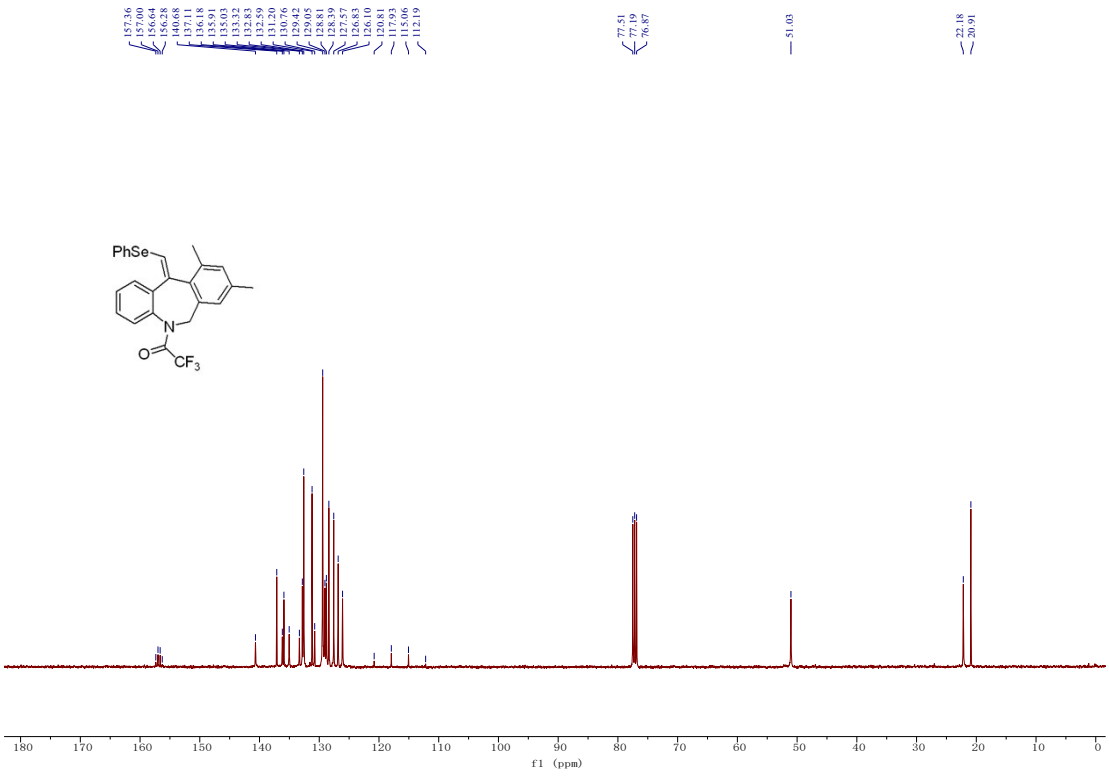

-67.26
PhSe
OMe
N
O
CF3
f1 (ppm)



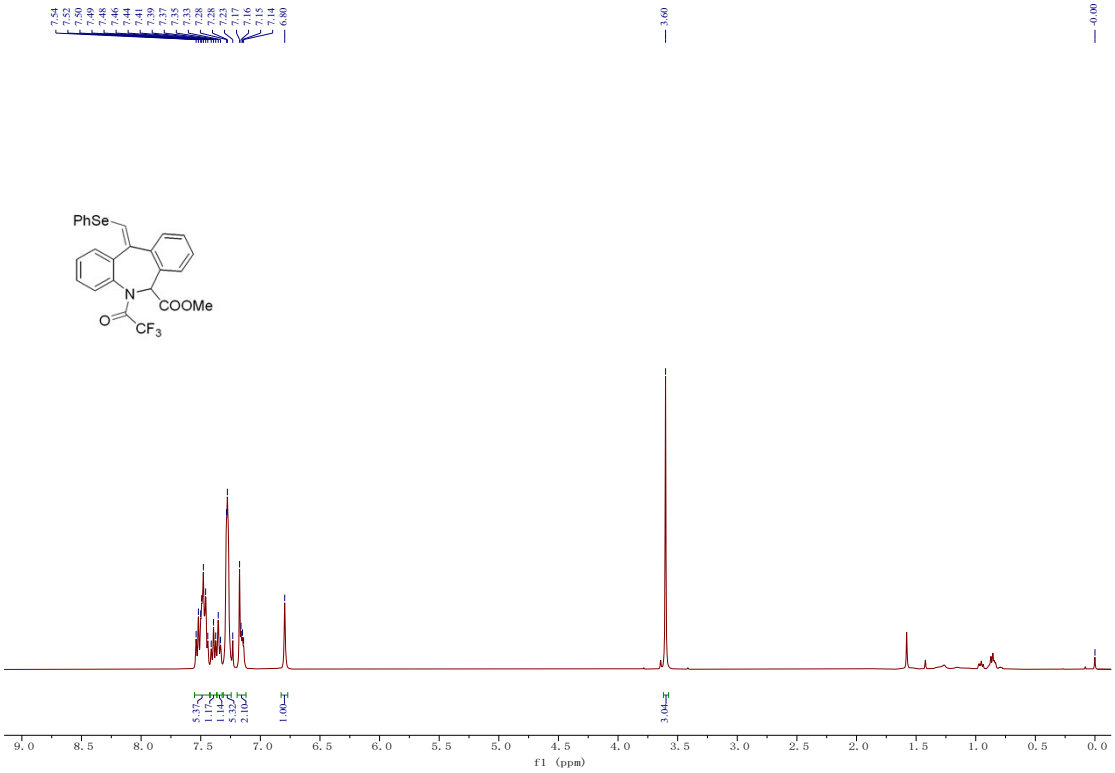
4l ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

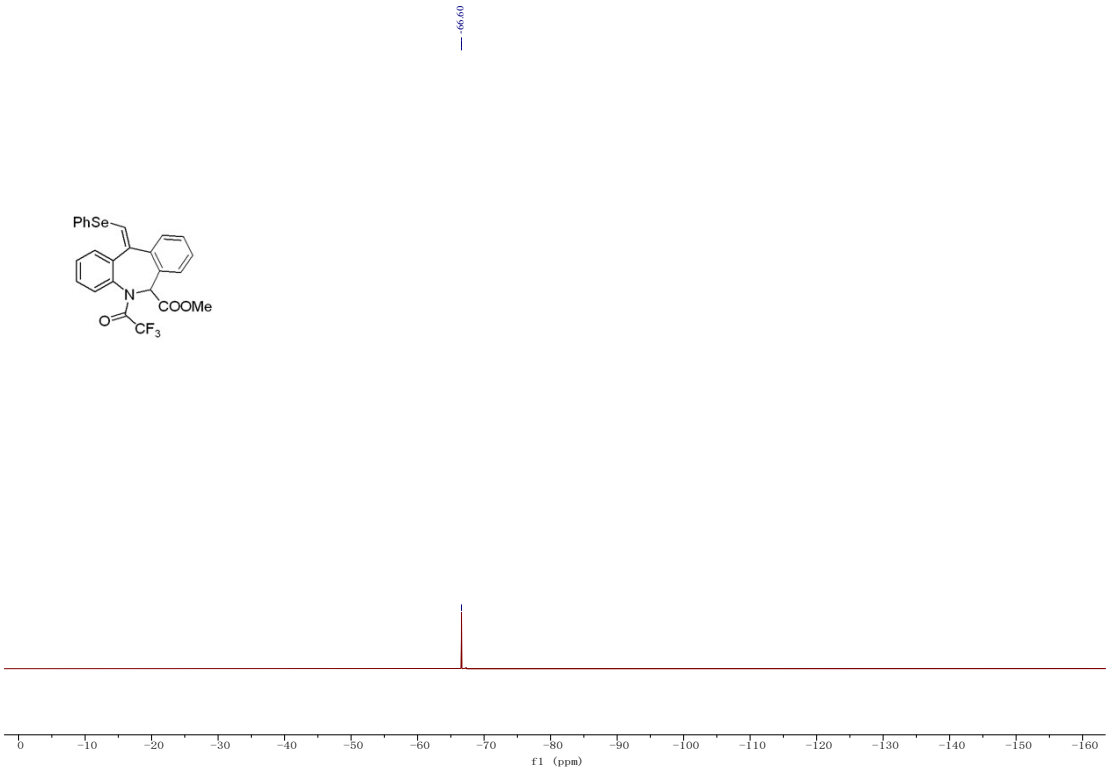


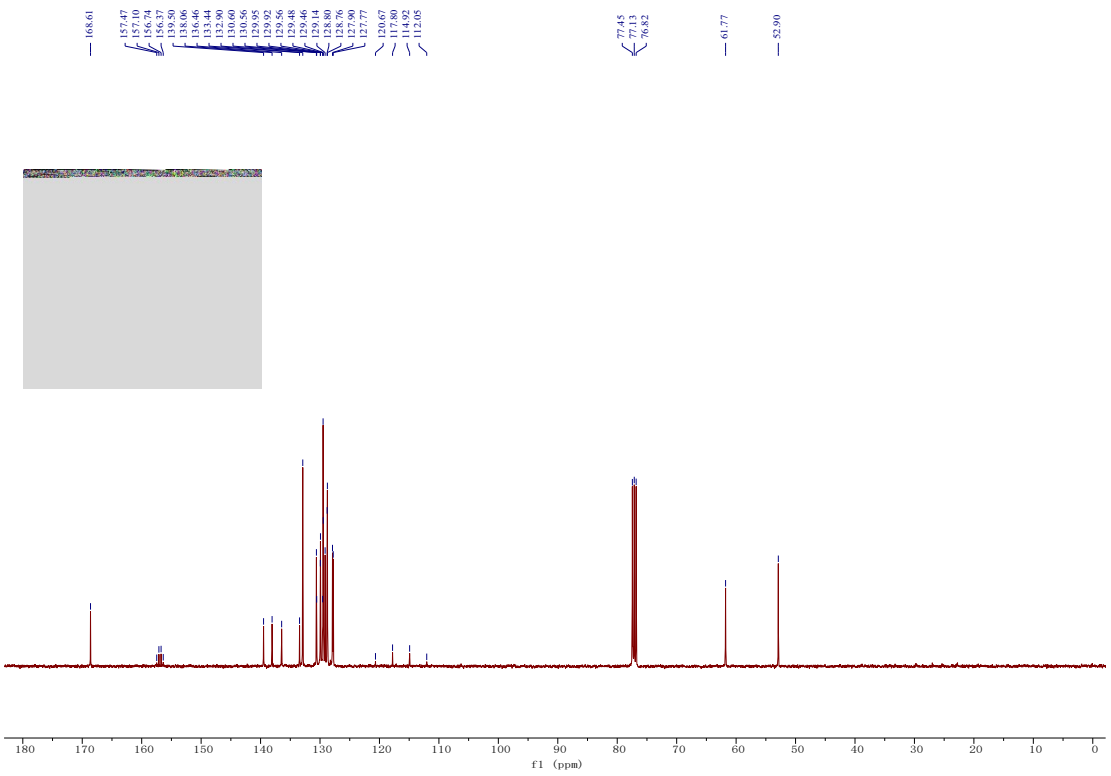




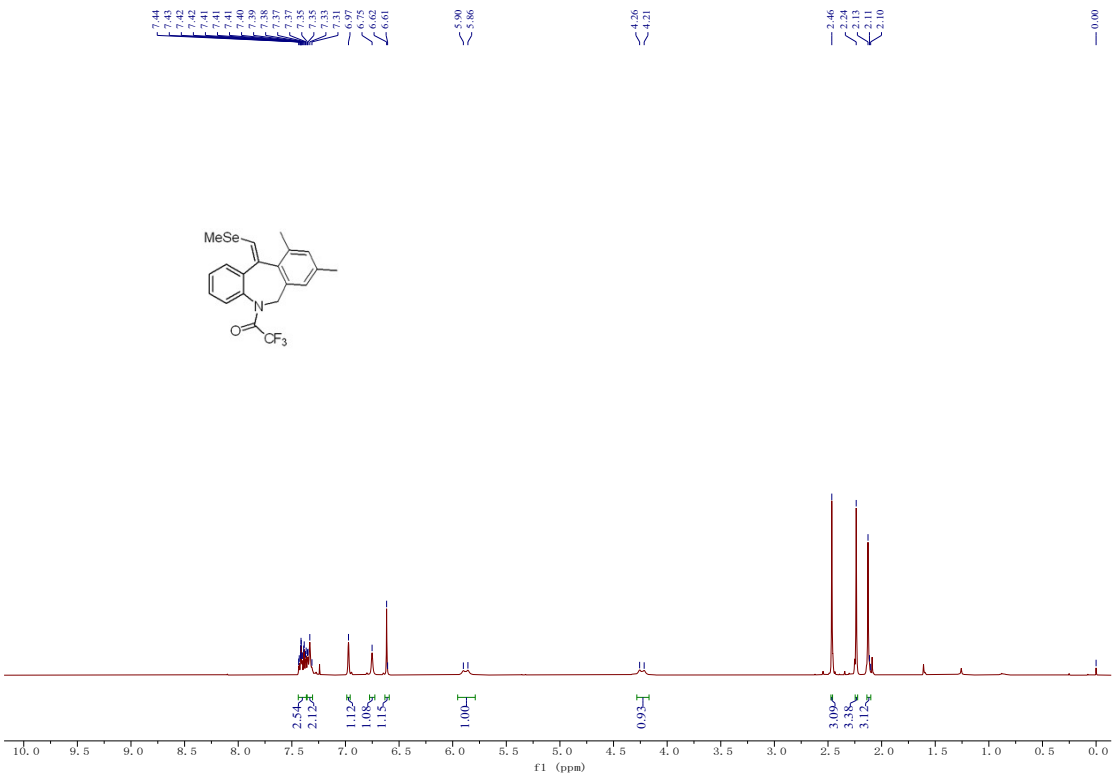
4q ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

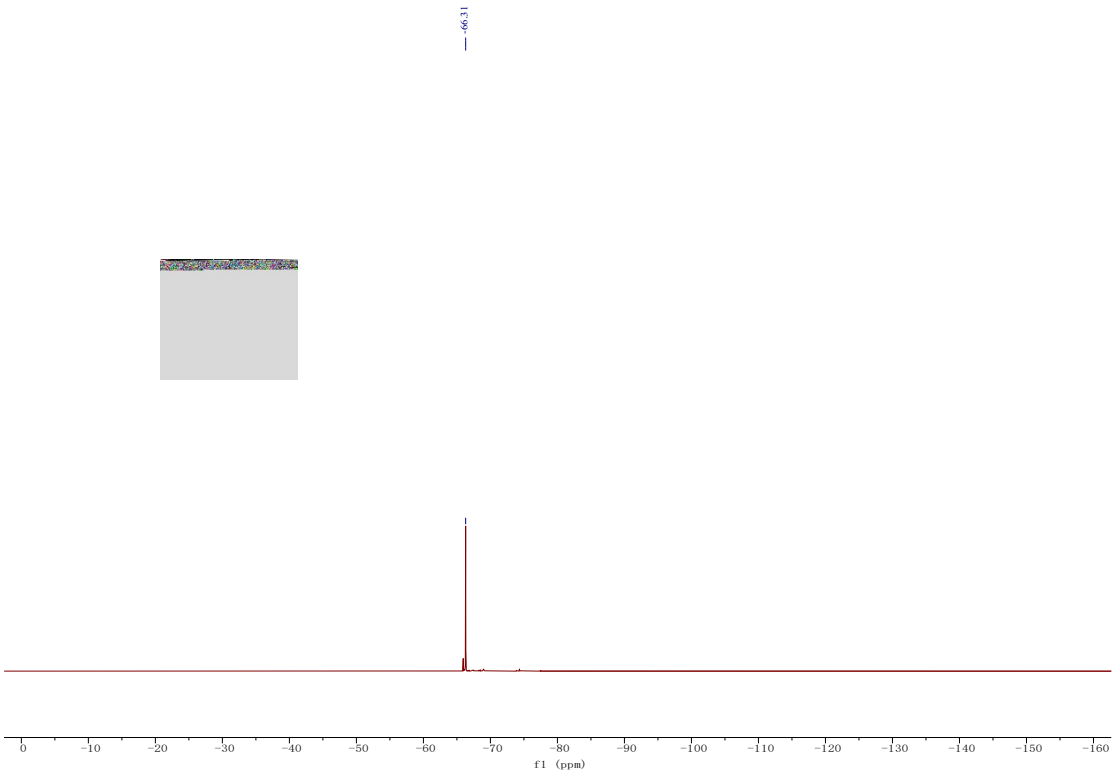

7.54
7.52
7.50
7.49
7.48
7.46
7.44
7.41
7.39
7.37
7.35
7.33
7.28
7.28
7.23
7.17
7.16
7.15
7.14
6.80
3.60
0.00
PhSe
N
COOMe
O
CF3
5.37
1.17
1.14
5.32
2.10
1.00
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

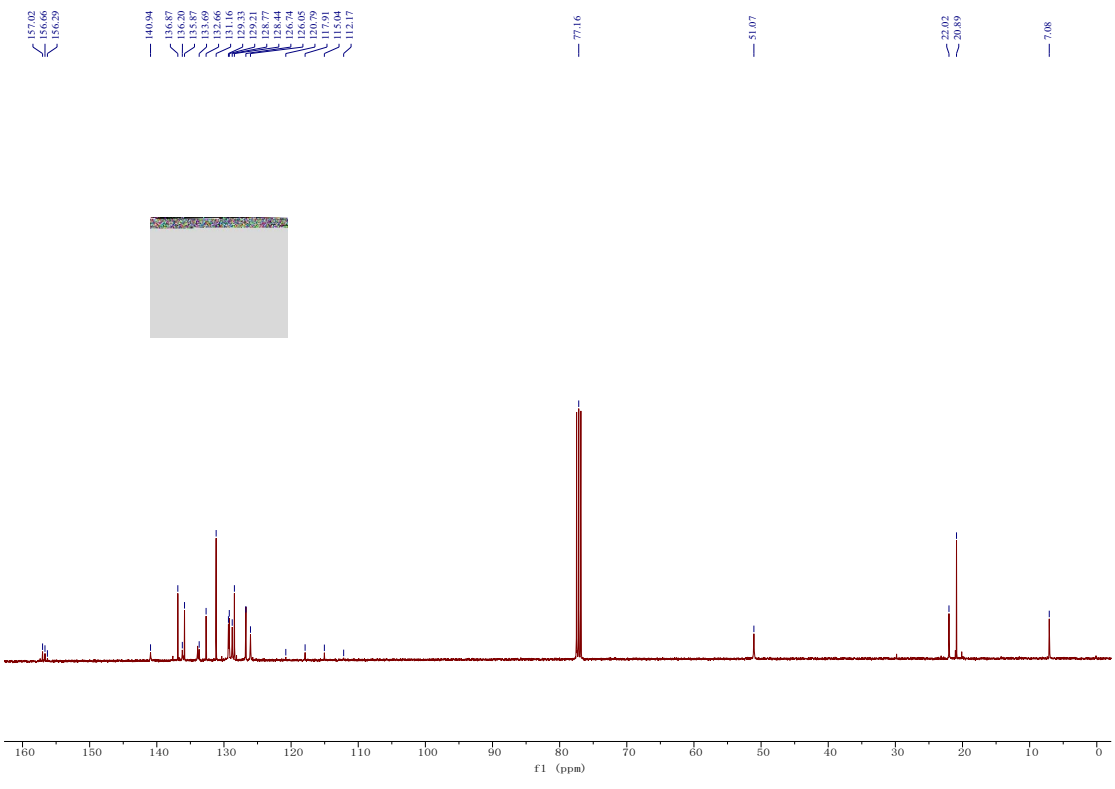

-66.60
PhSe
N
COOMe
O
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)



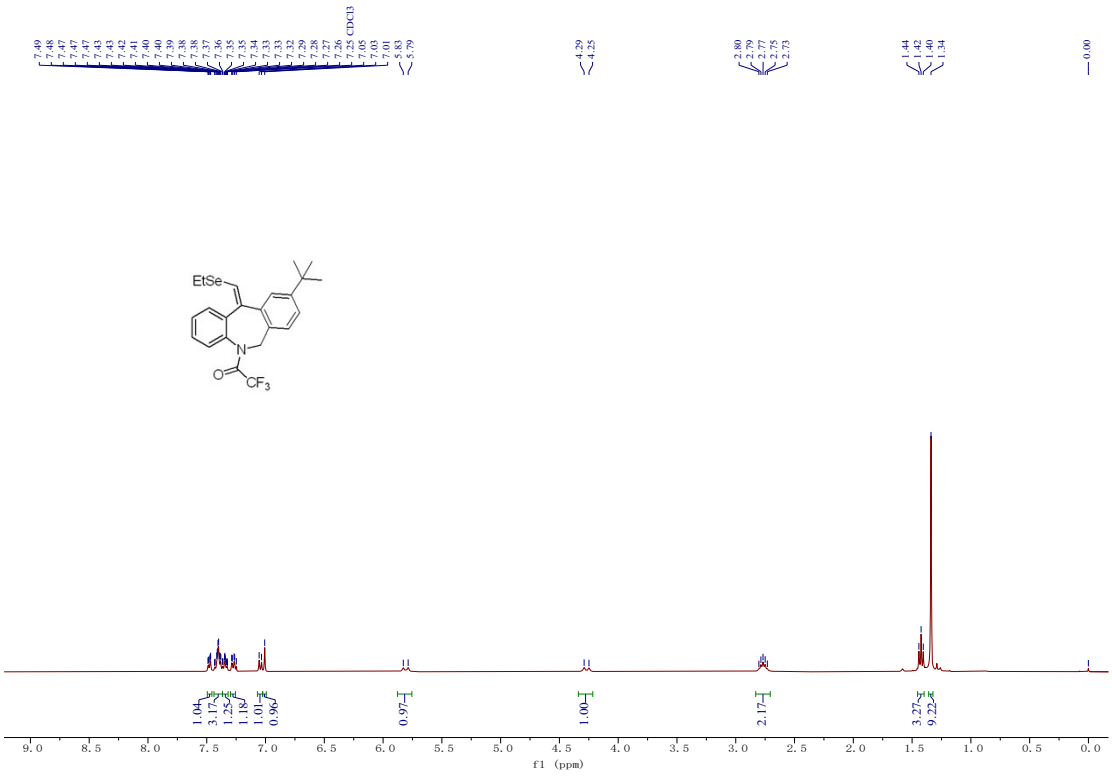
4r ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

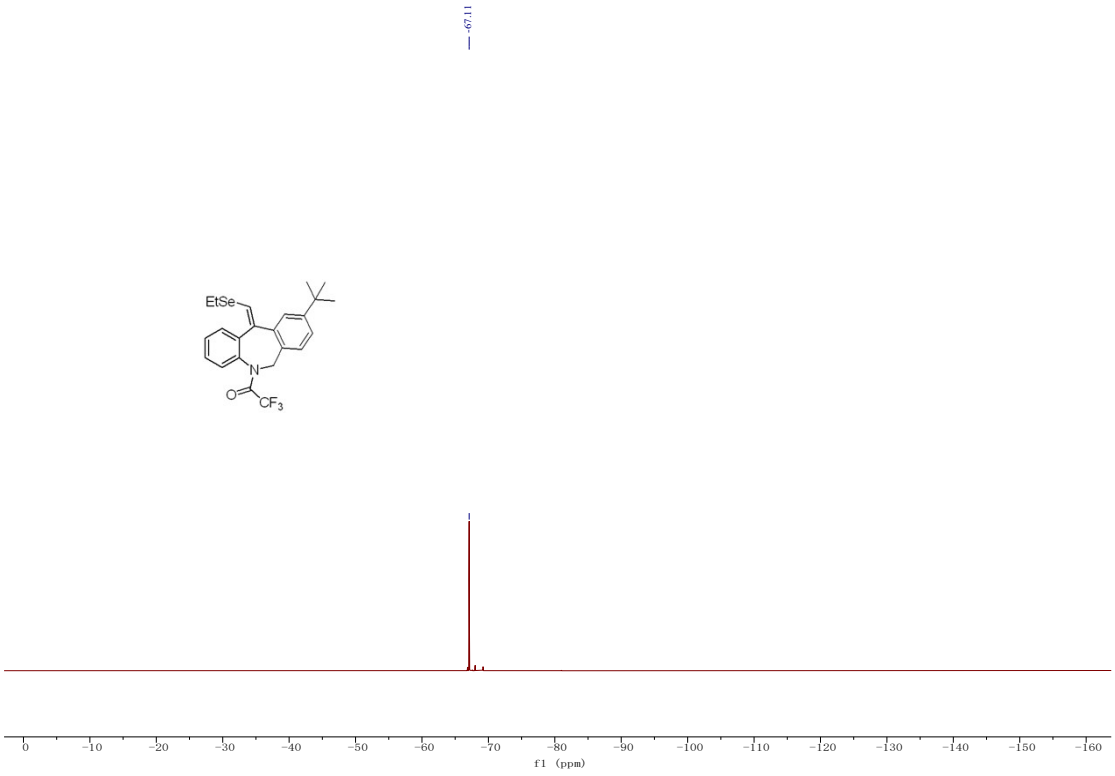


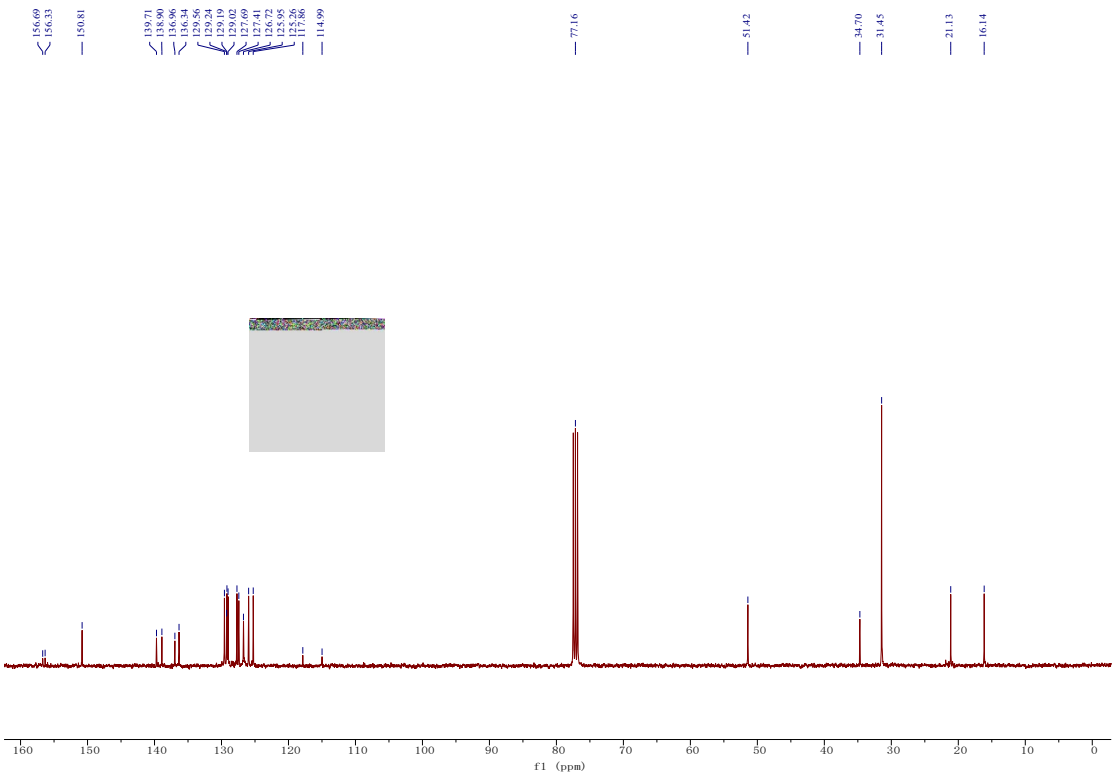

-66.31
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

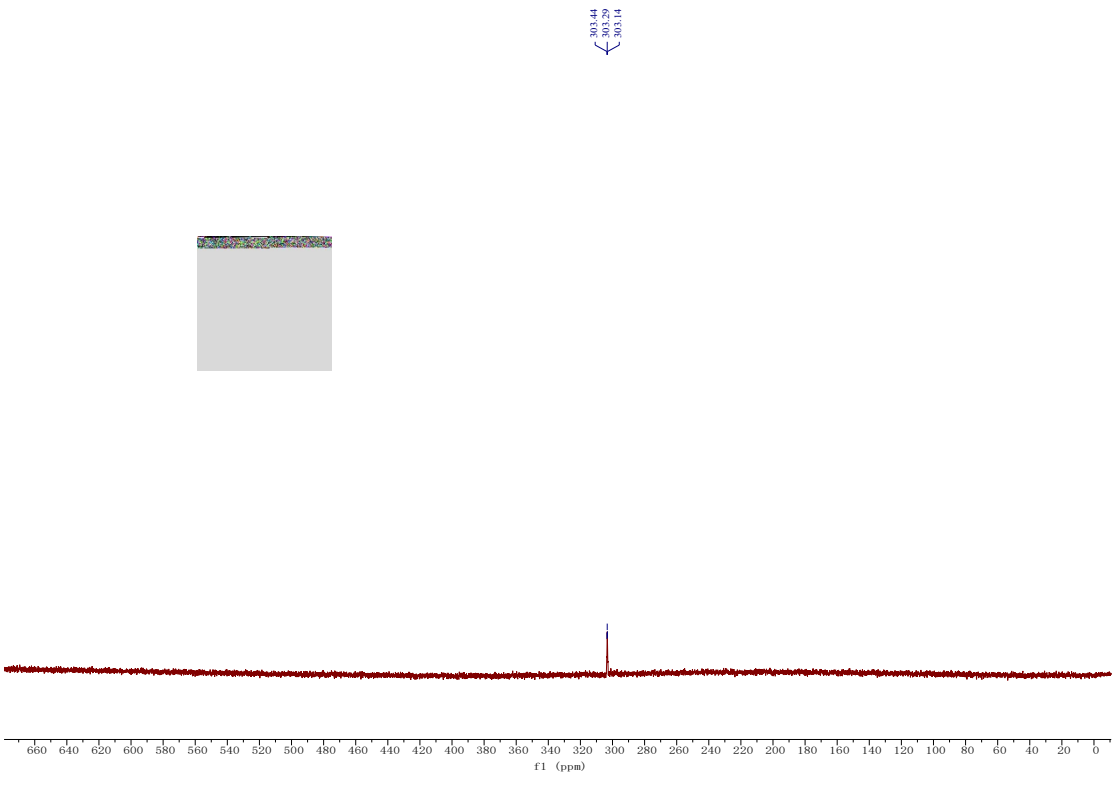

157.02
156.66
156.29
140.94
136.87
136.20
135.87
133.69
132.66
131.16
129.33
129.21
128.77
128.44
126.74
126.05
120.79
117.91
115.64
112.17
77.16
51.07
22.02
20.89
7.08
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4s ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), ^{13}C NMR (101 MHz) and ^{77}Se (76 MHz MHz)

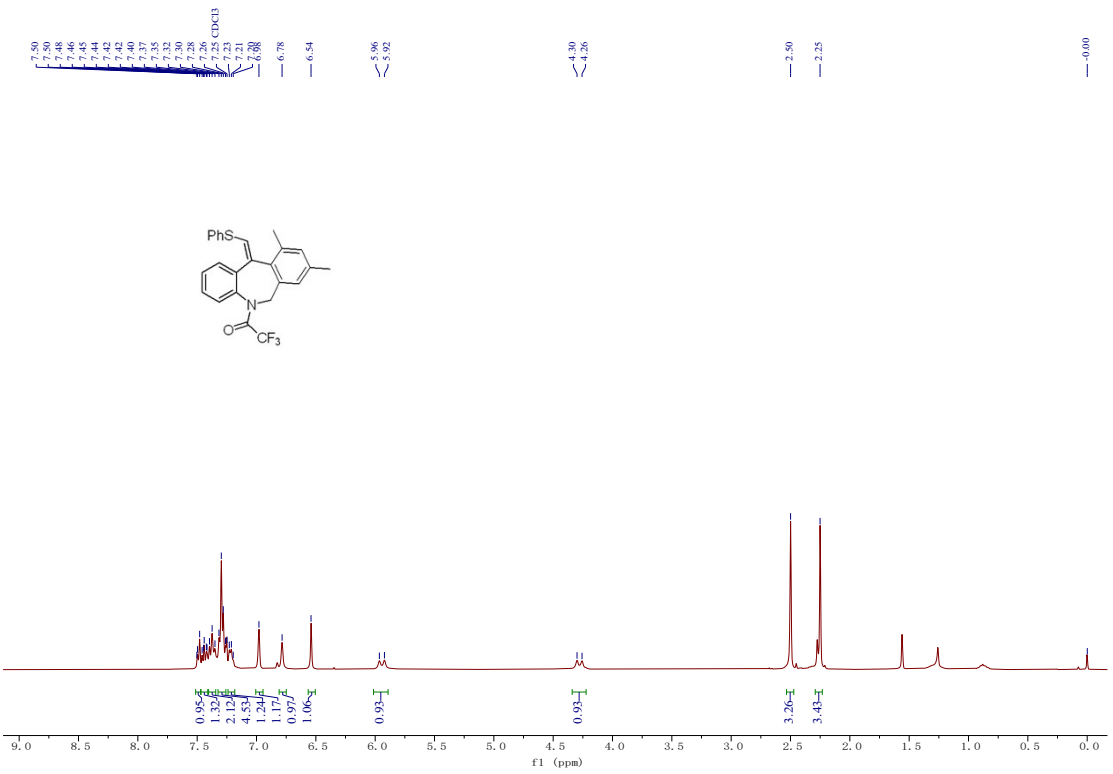


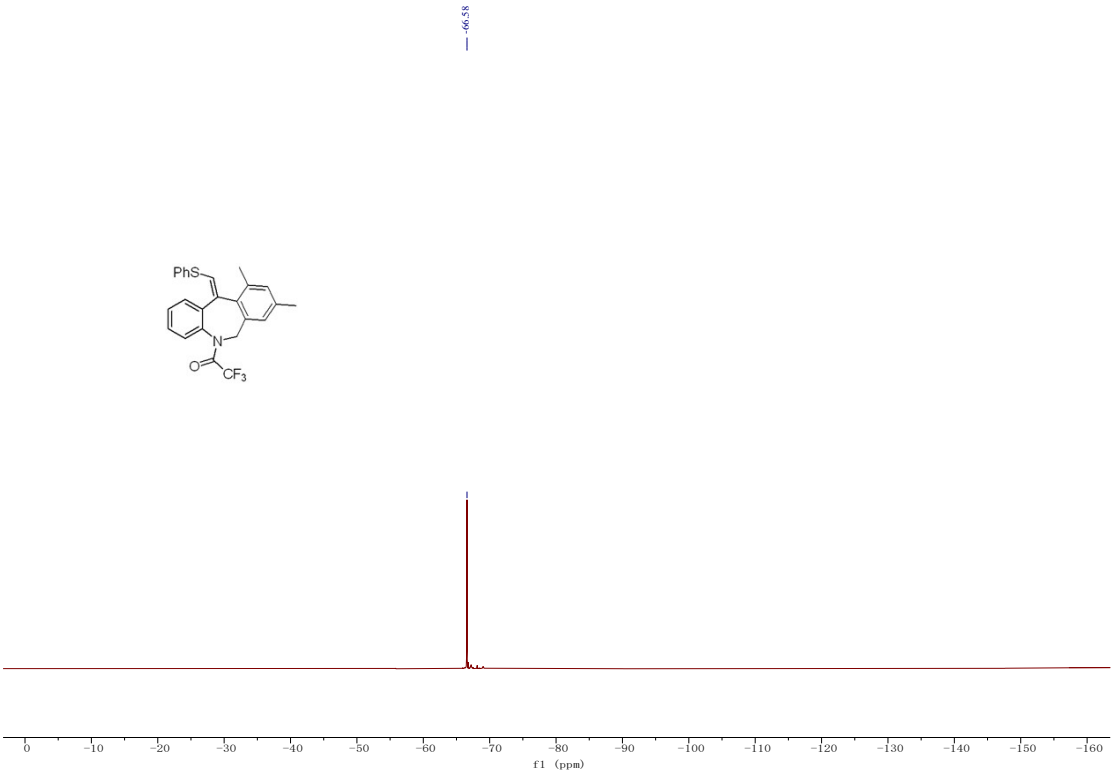


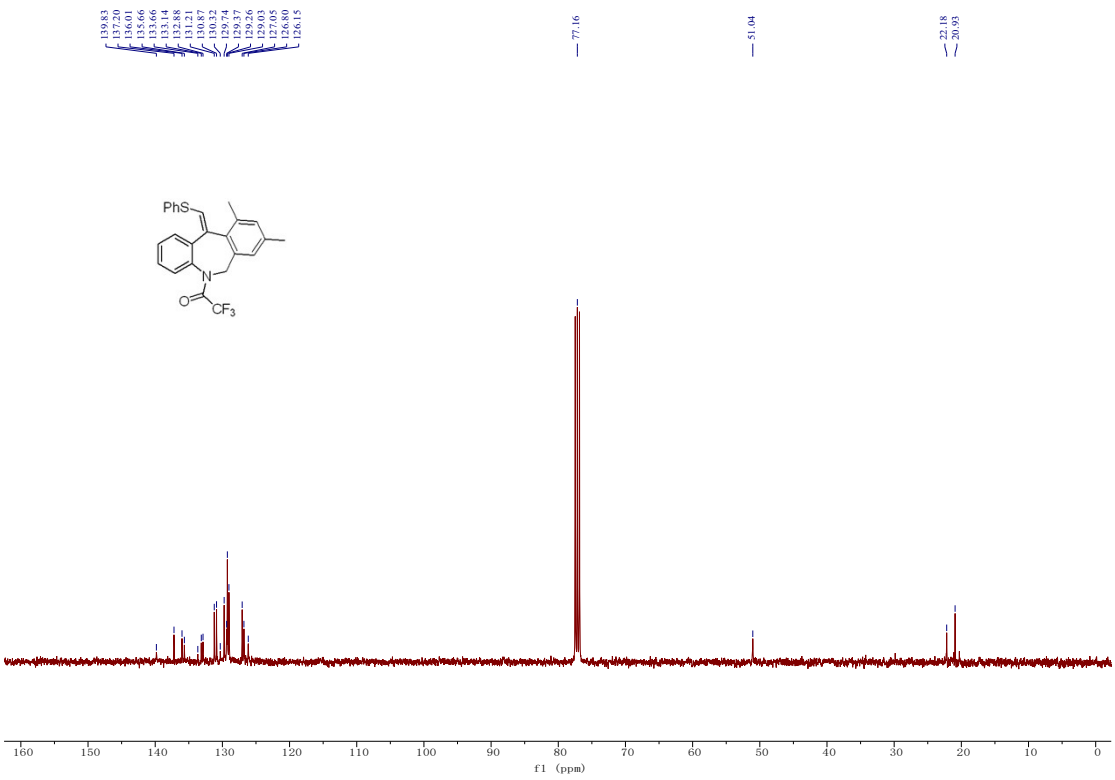

156.69
156.33
150.81
139.71
138.90
136.96
136.34
129.56
129.24
129.19
129.02
127.69
127.41
126.72
125.95
125.26
117.86
114.99
77.16
51.42
34.70
31.45
21.13
16.14
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


303.44
303.29
303.14
660 640 620 600 580 560 540 520 500 480 460 440 420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

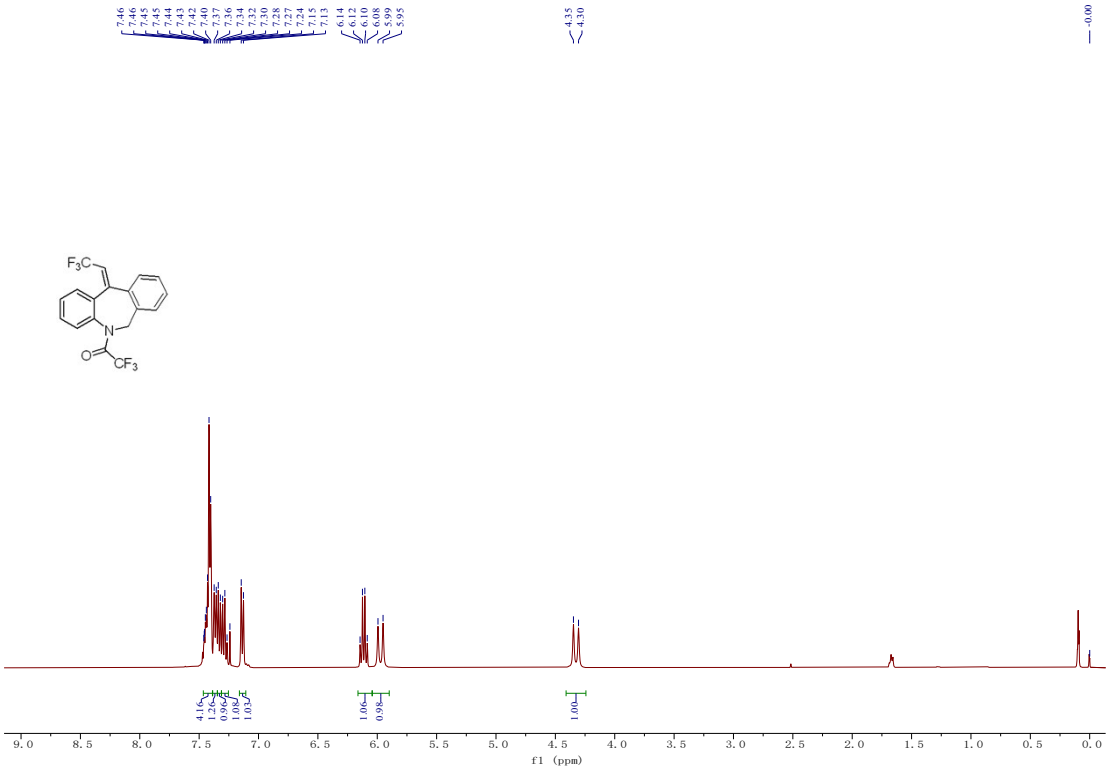
4t ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

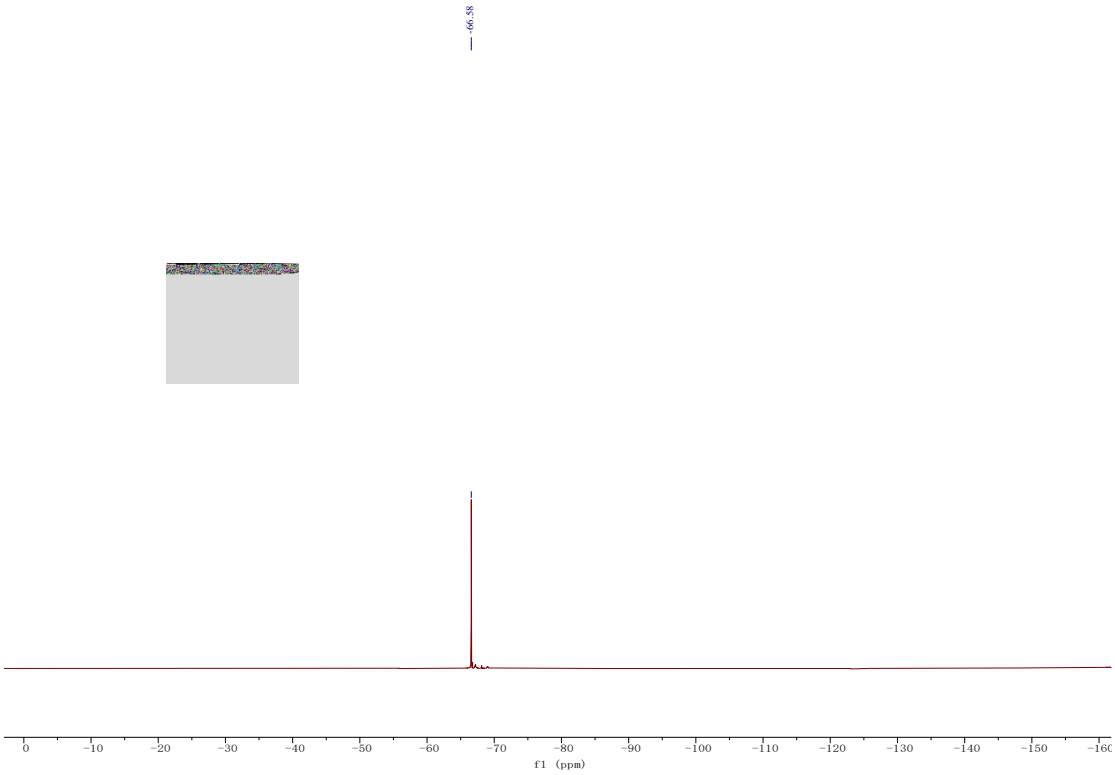


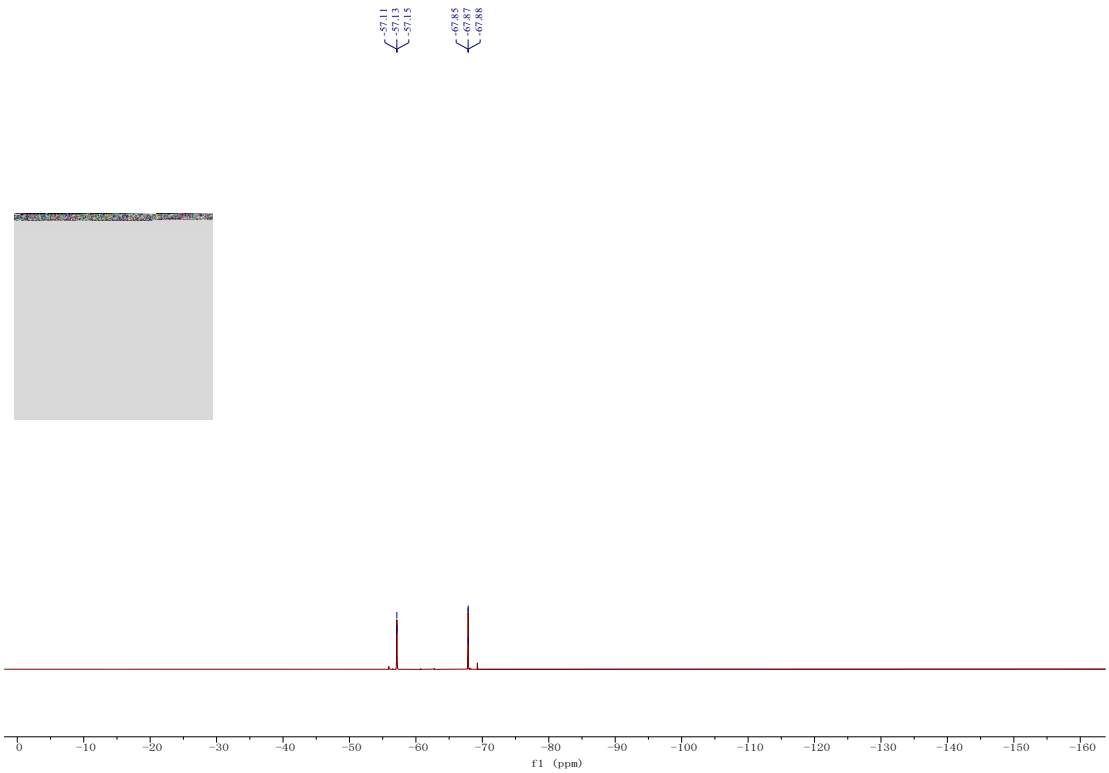


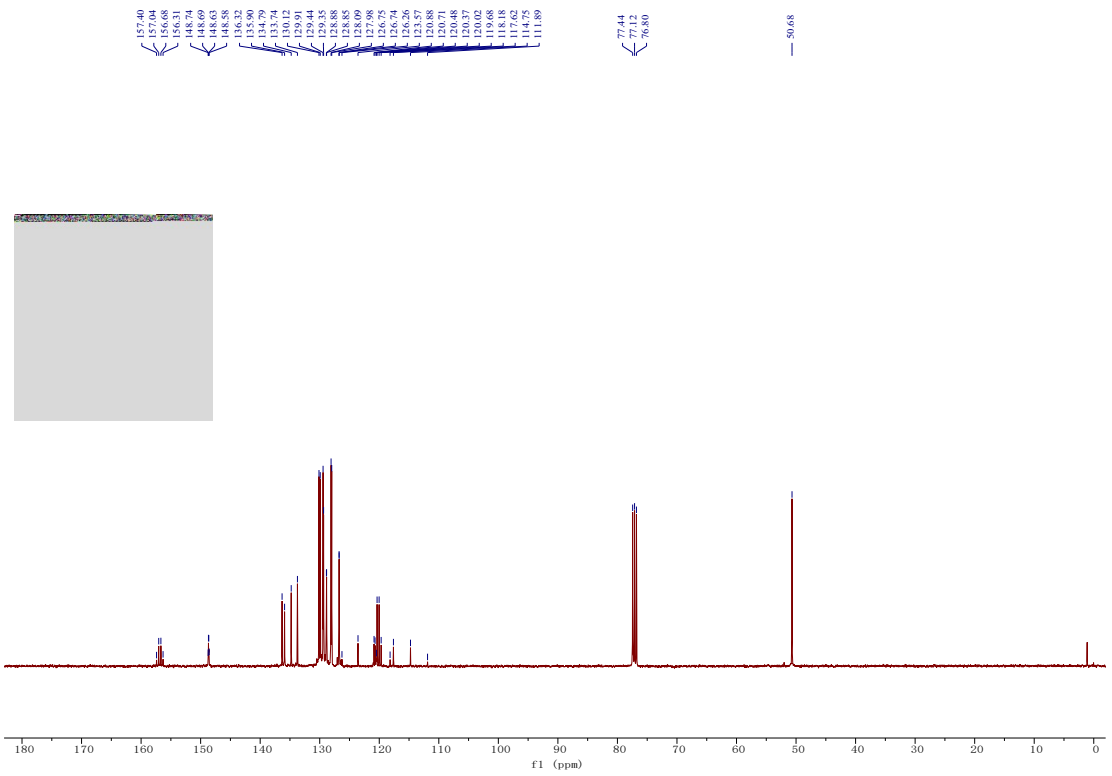


5a ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

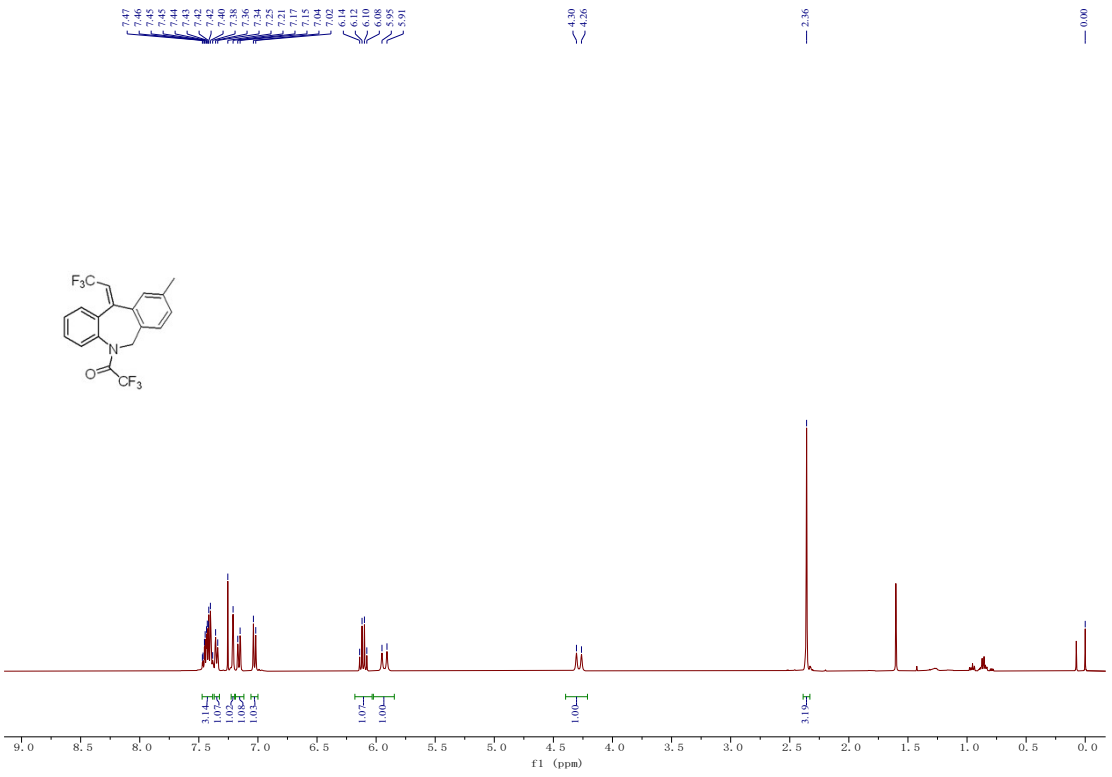


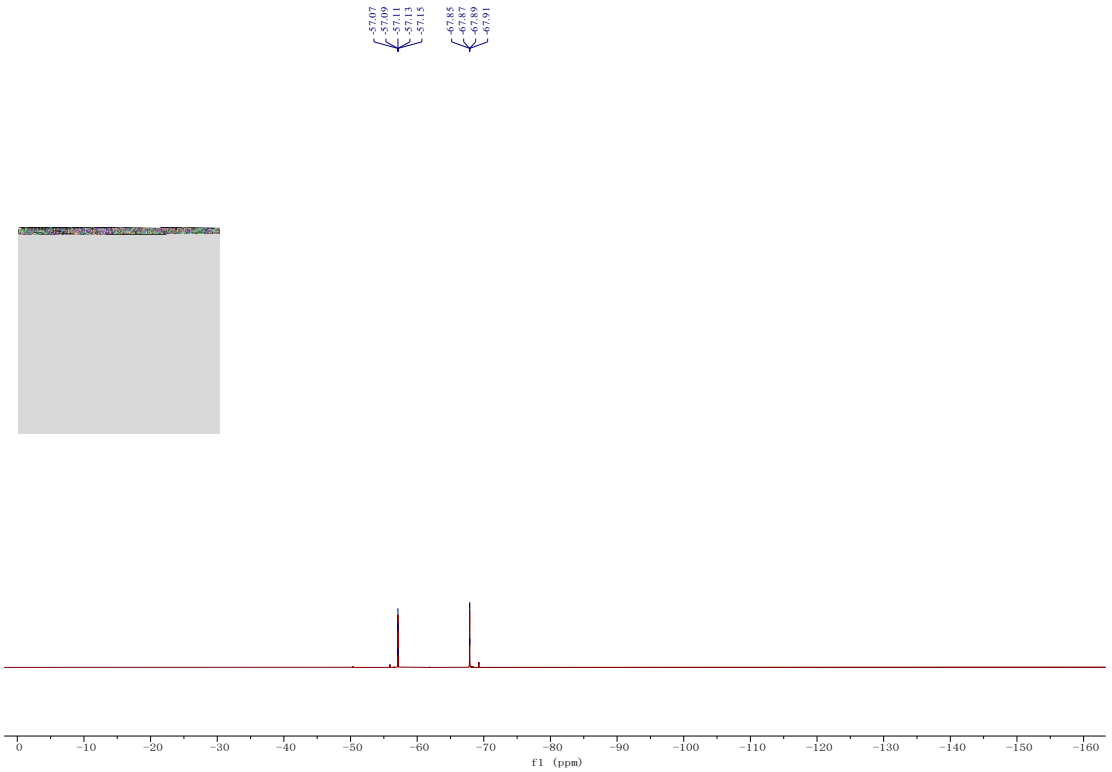

-66.58
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

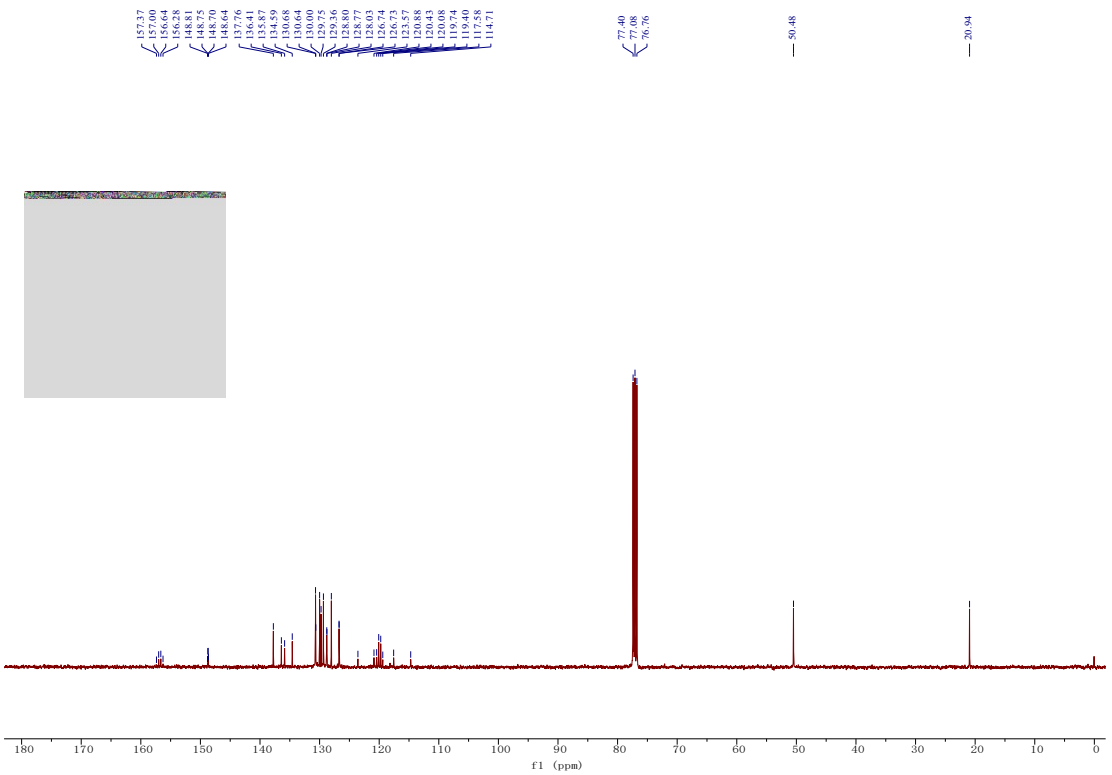

-57.11
-57.13
-57.15
-67.85
-67.87
-67.88
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)



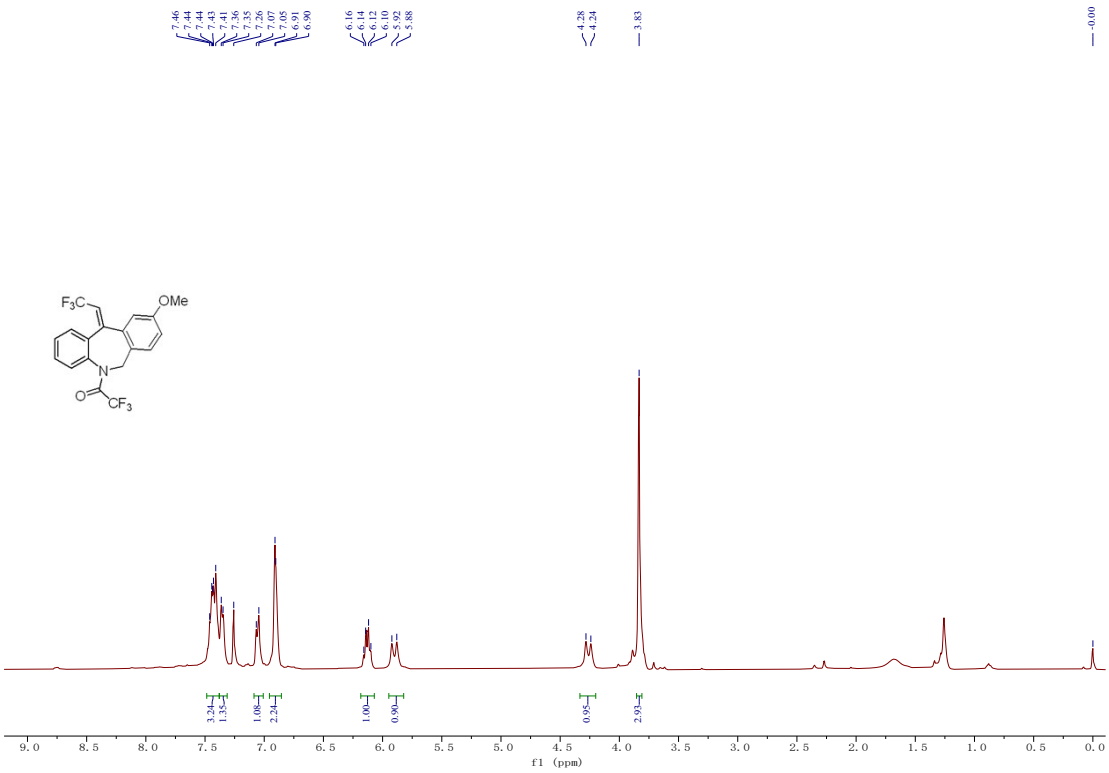
5b ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

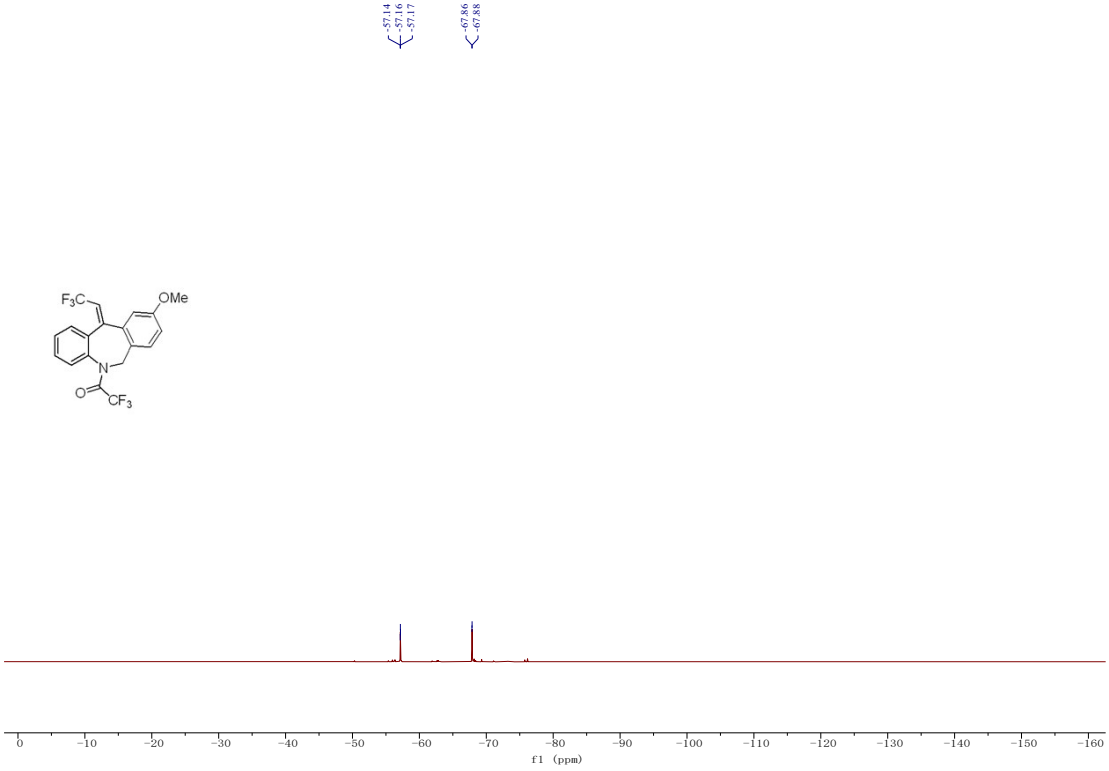


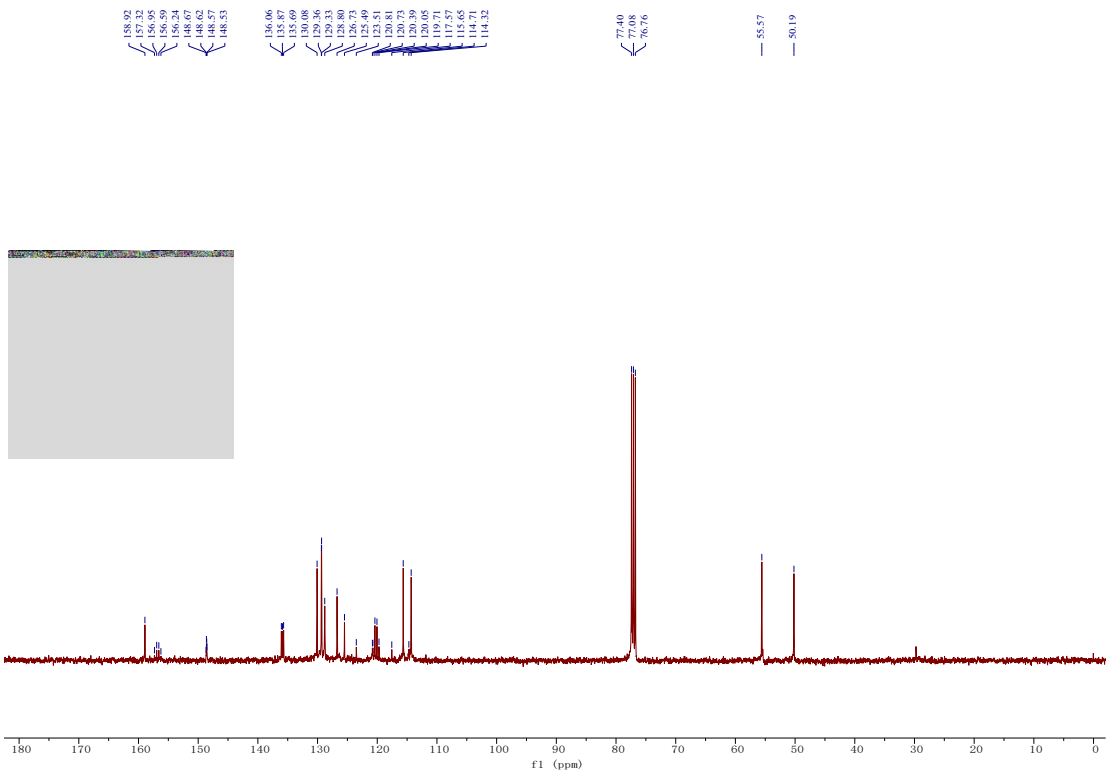

-57.07
-57.09
-57.11
-57.13
-57.15
-67.85
-67.87
-67.89
-67.91
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)


157.37
157.00
156.64
156.28
148.81
148.75
148.70
148.64
137.76
136.41
135.87
134.59
130.68
130.64
130.00
129.75
129.36
128.80
128.77
128.03
126.74
126.73
123.57
120.88
120.43
120.08
119.74
119.40
117.58
114.71
77.40
77.08
76.76
50.48
20.94
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

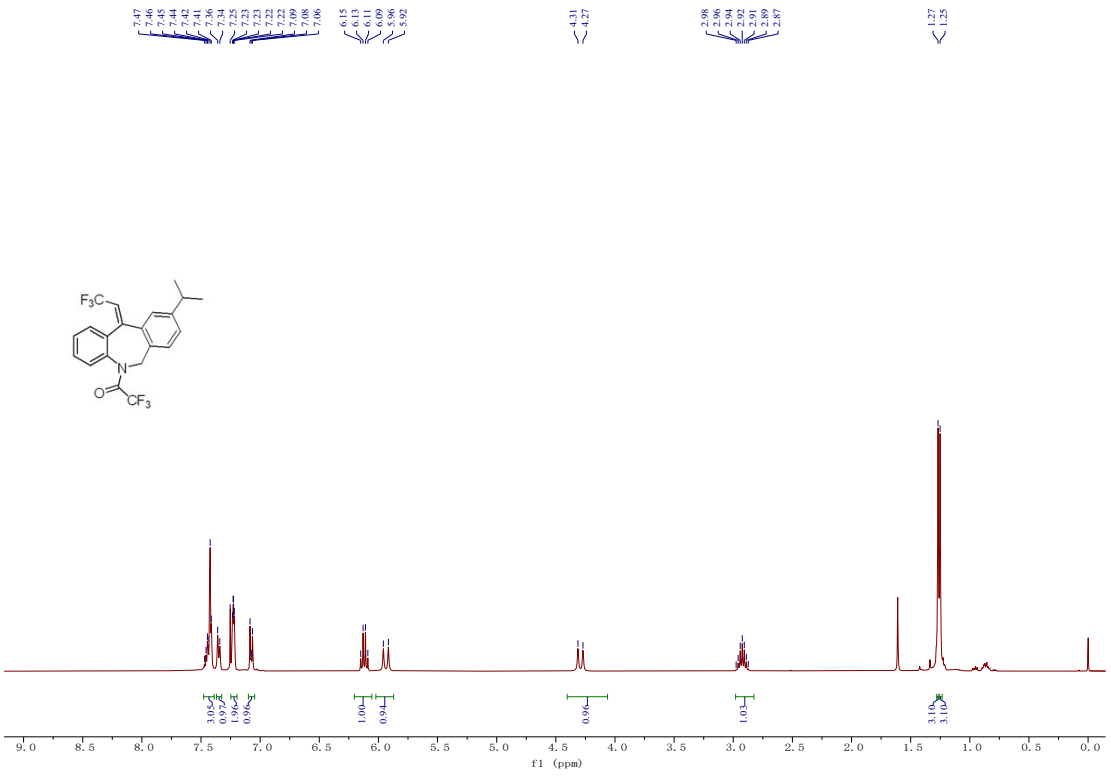
5c ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

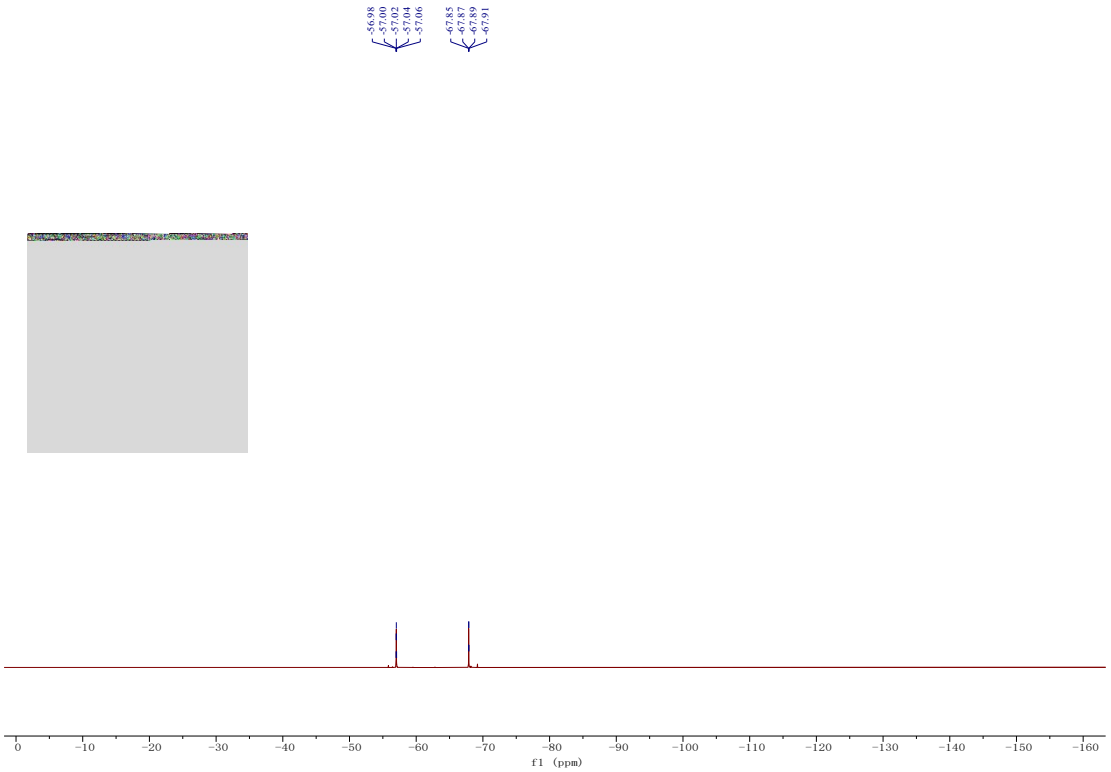


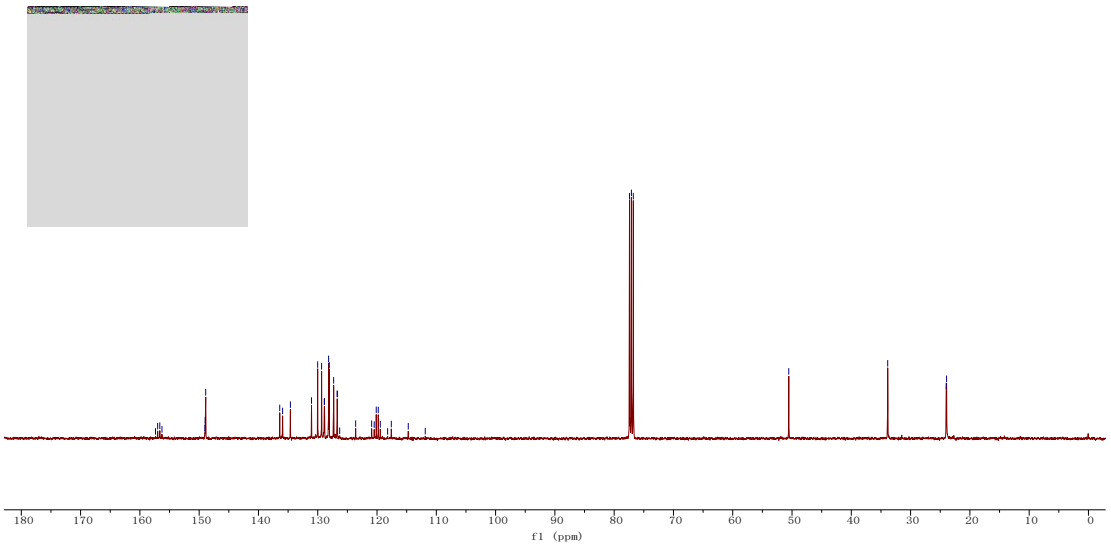




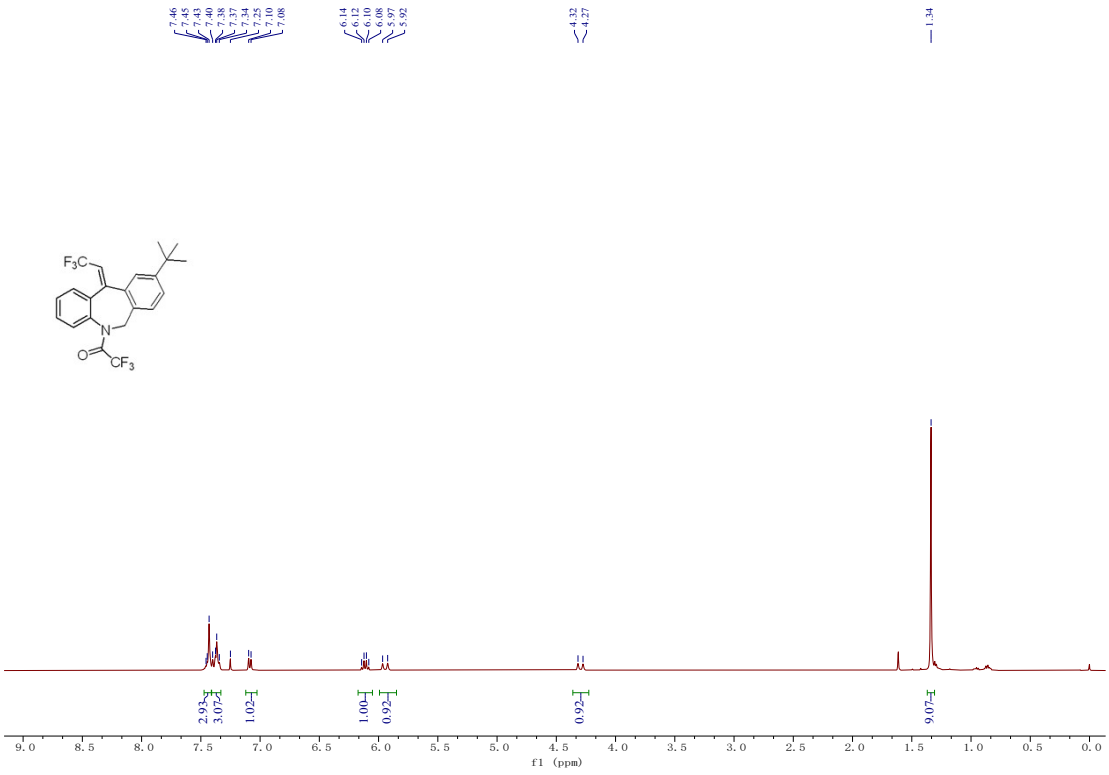
5d ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

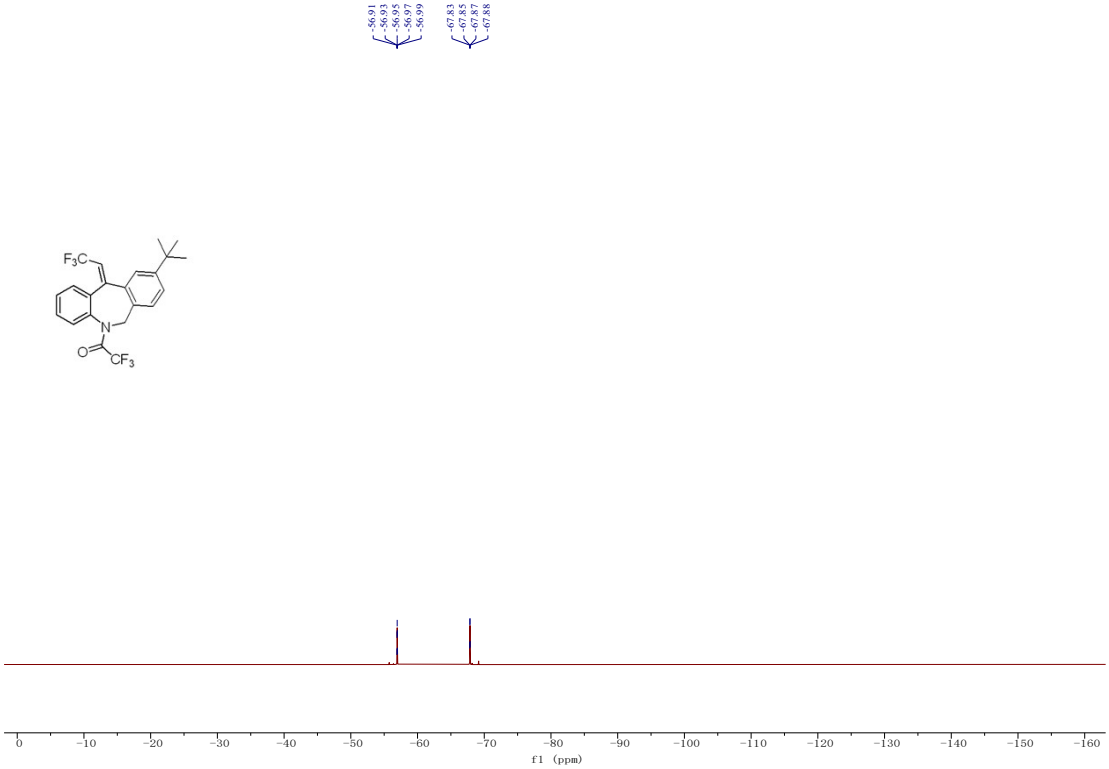


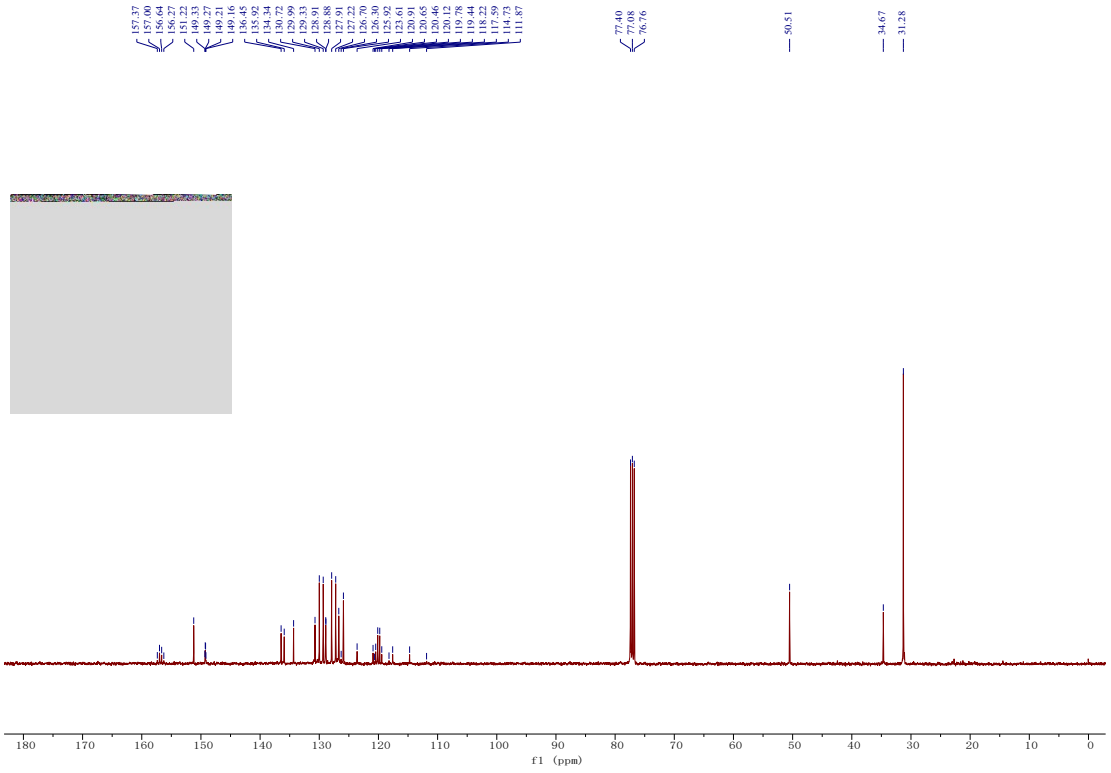

-56.98
-57.00
-57.02
-57.04
-57.06
-67.85
-67.87
-67.89
-67.91
f1 (ppm)


157.37
157.00
156.64
156.27
149.03
148.97
148.89
136.41
134.93
134.61
131.05
130.01
129.35
128.89
128.86
128.16
128.06
127.32
126.71
126.70
126.30
123.60
120.91
120.47
120.13
119.79
119.45
118.21
117.59
114.73
111.87
77.41
77.09
76.77
50.55
33.86
24.00
23.93
f1 (ppm)

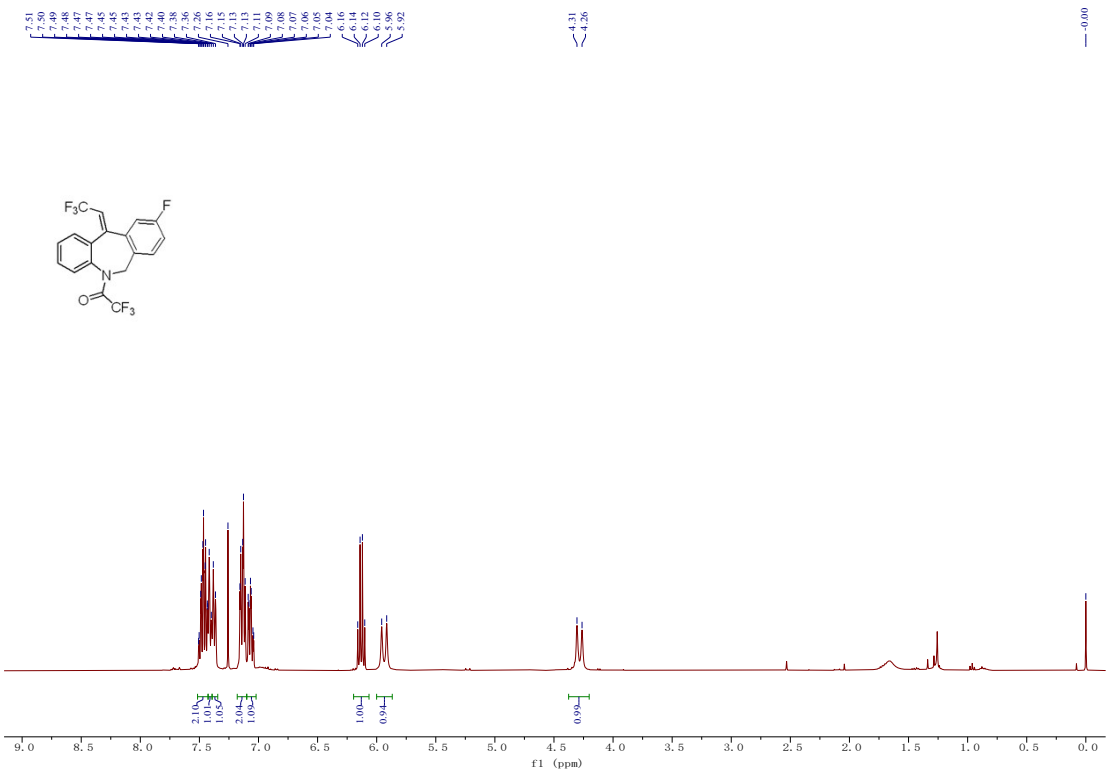
5e ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

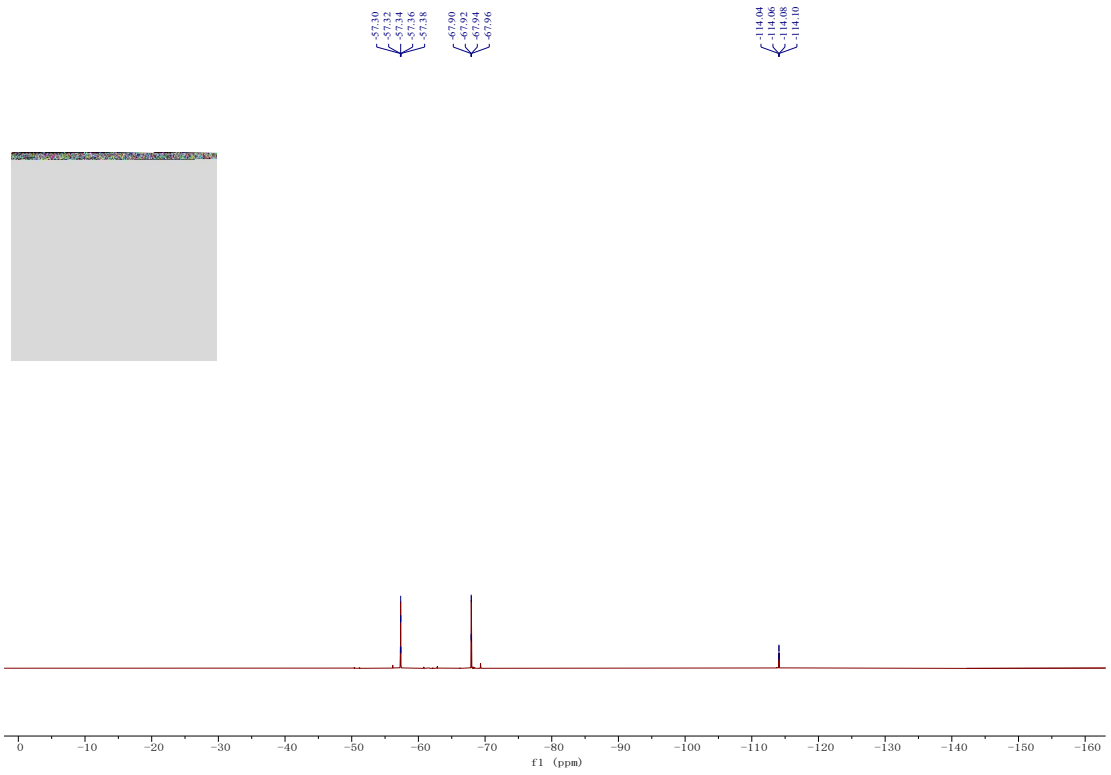


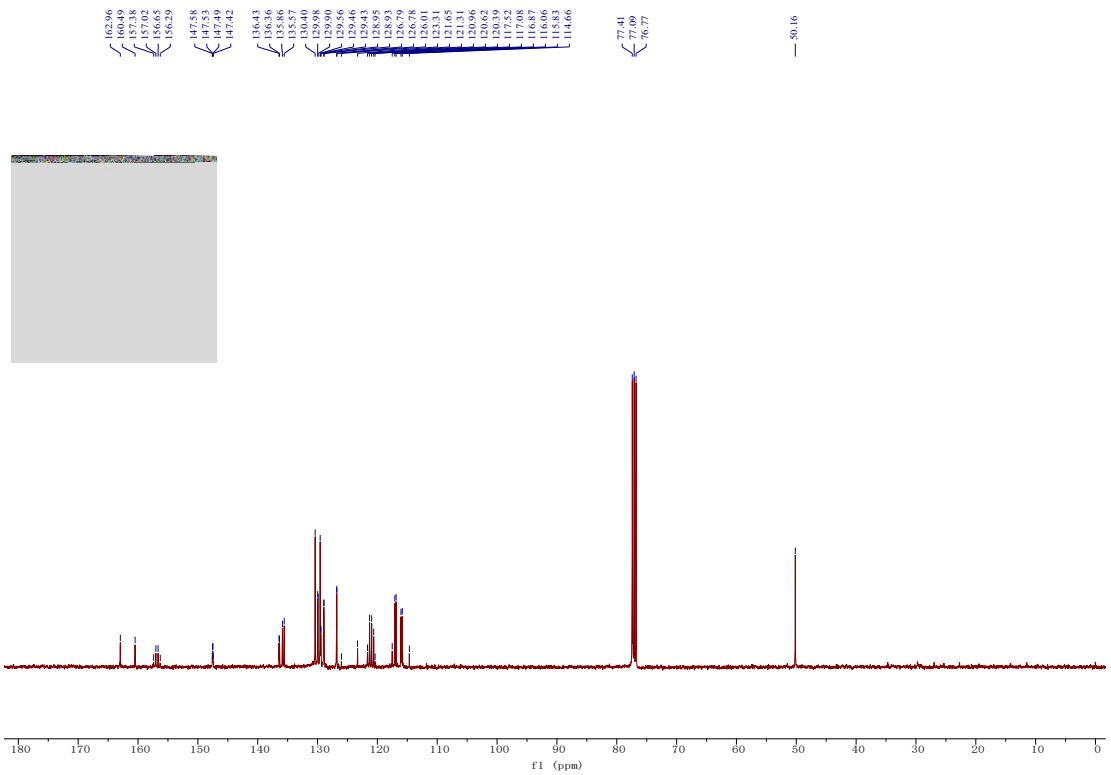




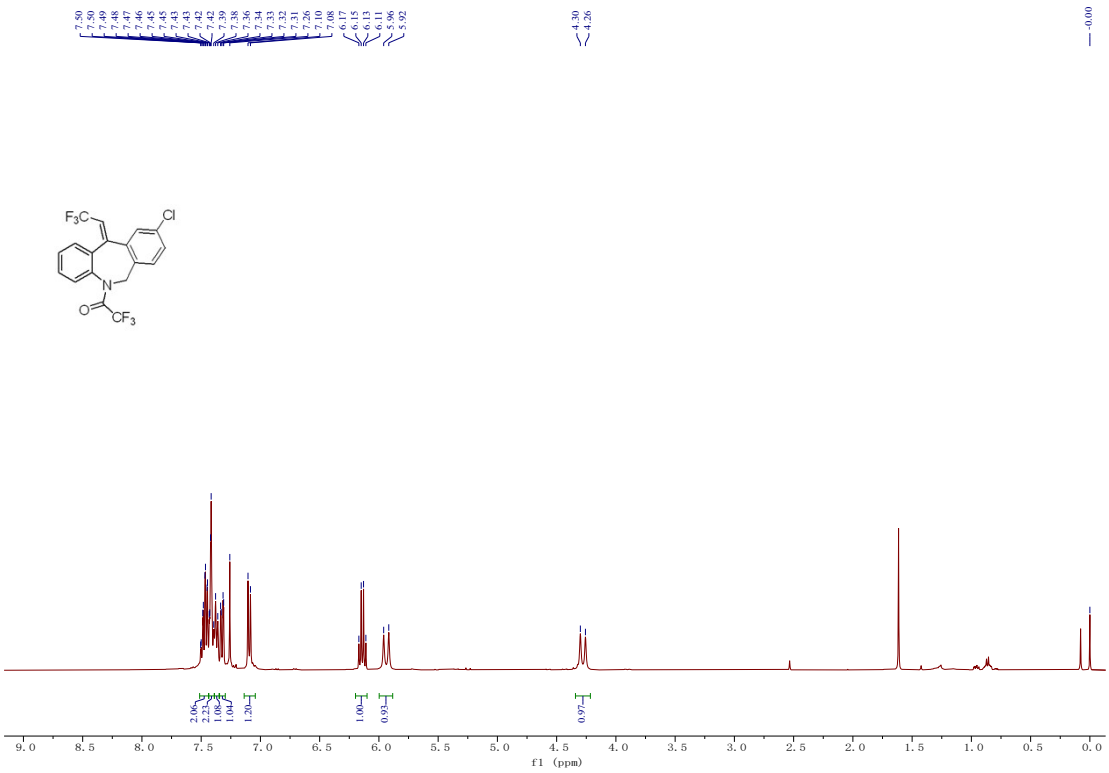
5f ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

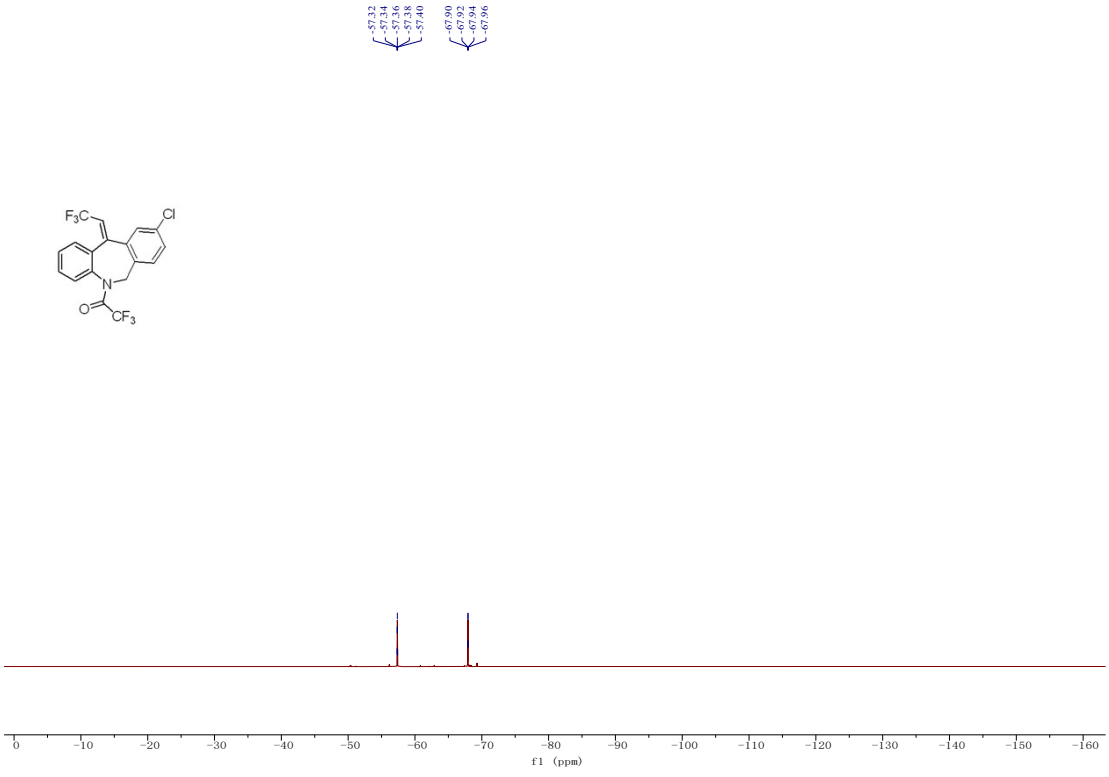


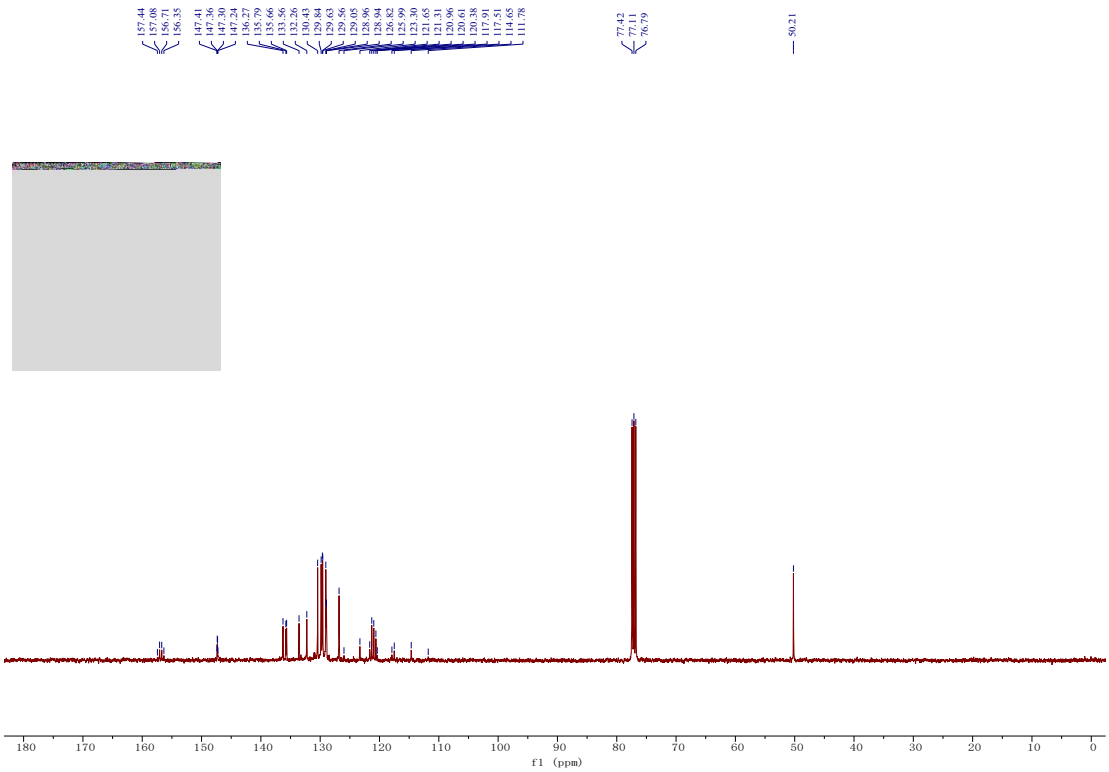

-57.30
-57.32
-57.34
-57.36
-57.38
-67.90
-67.92
-67.94
-67.96
-114.04
-114.06
-114.08
-114.10
f1 (ppm)


162.96
160.49
157.38
157.02
156.65
156.29
147.58
147.53
147.49
147.42
136.43
135.86
135.57
130.40
129.98
129.90
129.56
129.46
129.41
128.95
128.93
126.79
126.78
126.01
123.11
121.65
121.31
120.96
120.62
120.39
117.52
117.08
116.87
116.06
115.83
114.66
77.41
77.09
76.77
50.16
f1 (ppm)

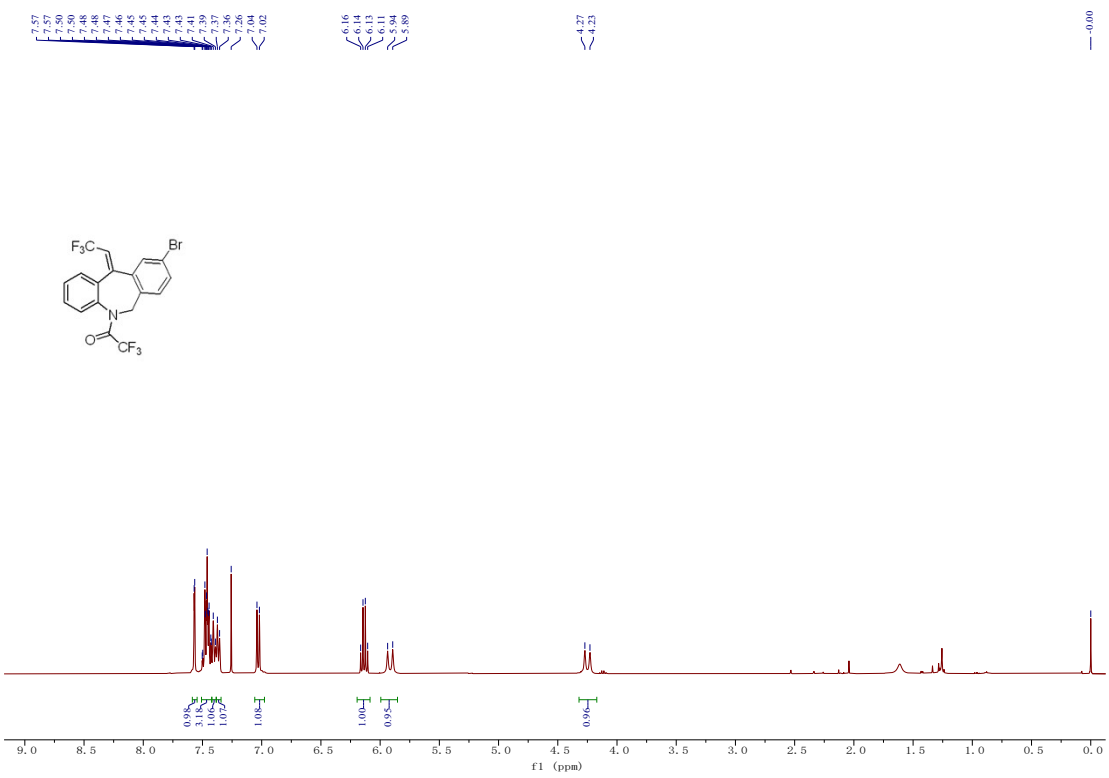
5g ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

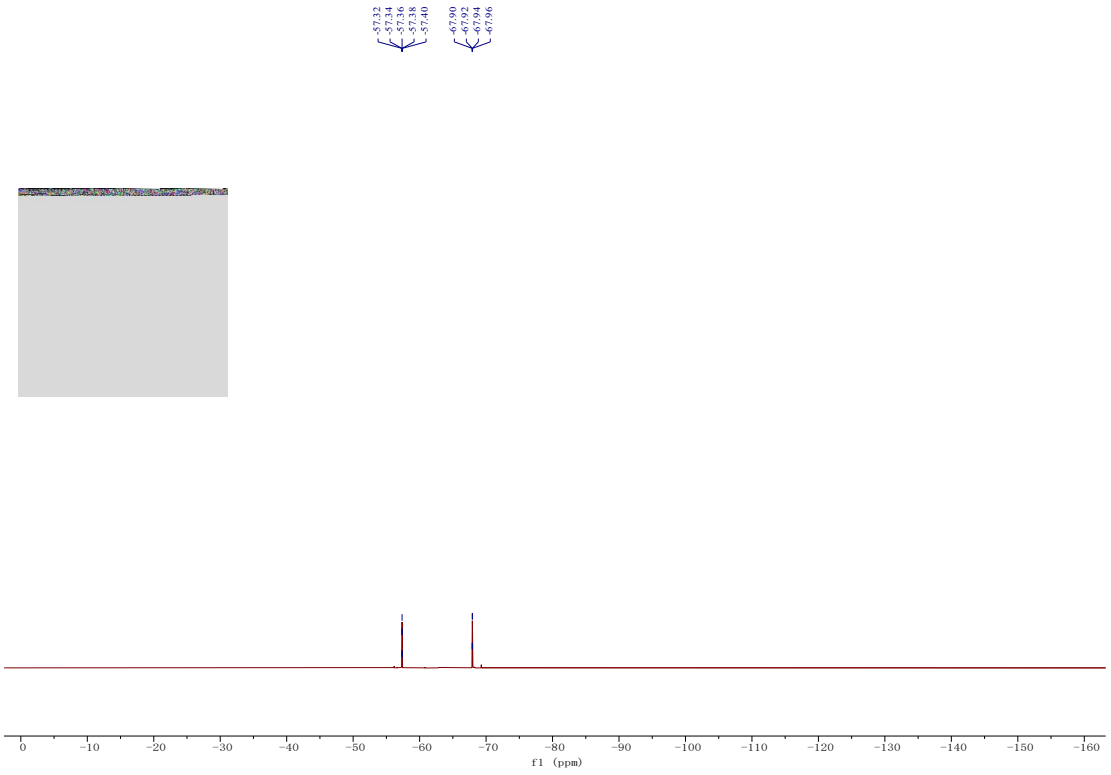


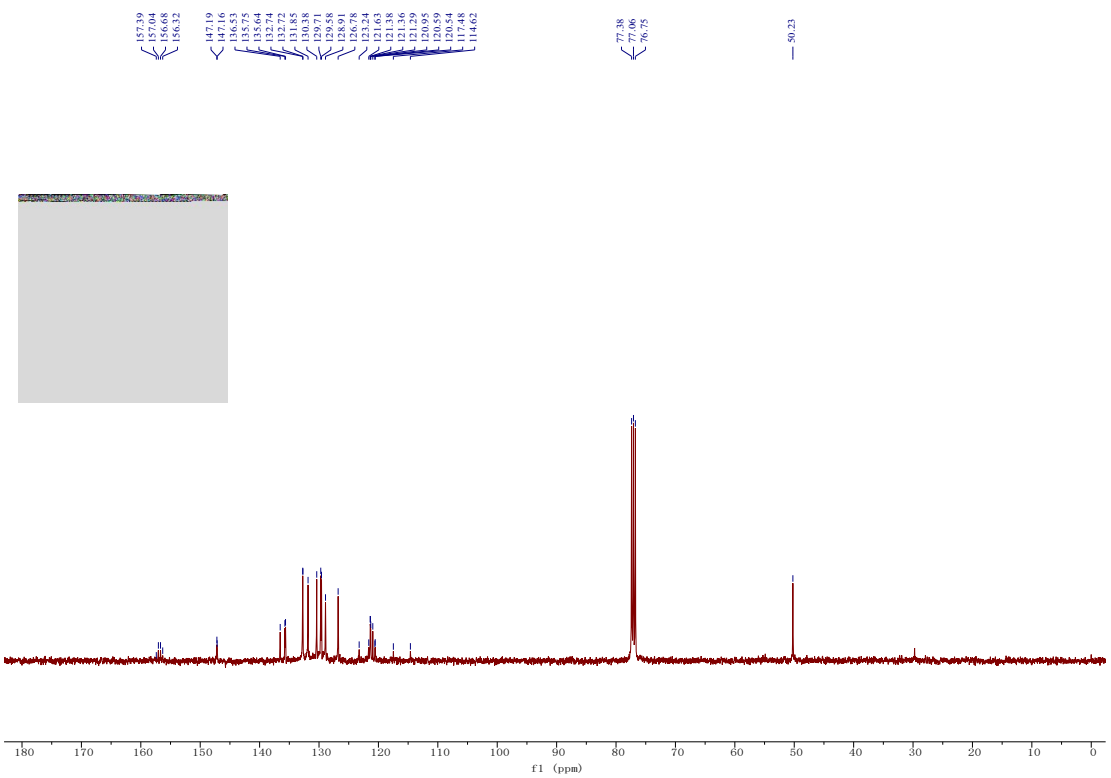




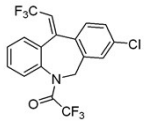
5h ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

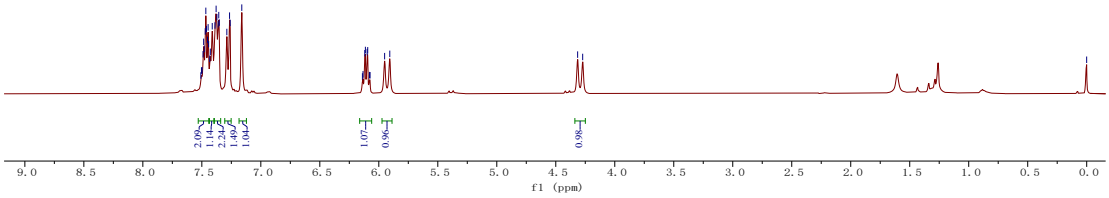


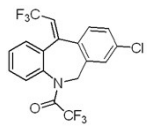

-57.32
-57.34
-57.36
-57.38
-57.40
-67.90
-67.92
-67.94
-67.96
f1 (ppm)

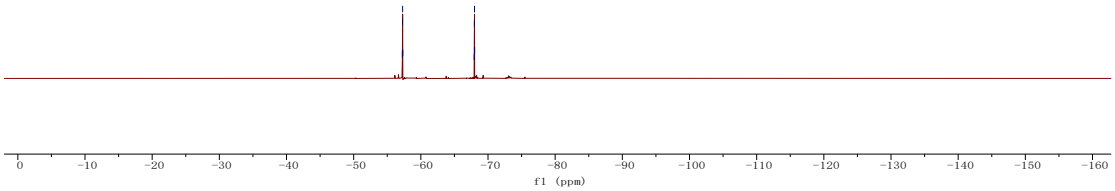

157.39
157.04
156.68
156.32
147.19
147.16
136.53
135.75
135.64
132.74
132.72
131.65
130.38
129.71
129.58
128.91
126.78
124.34
121.63
121.38
121.36
121.29
120.95
120.59
120.54
117.48
114.62
77.38
77.06
76.75
50.23
f1 (ppm)

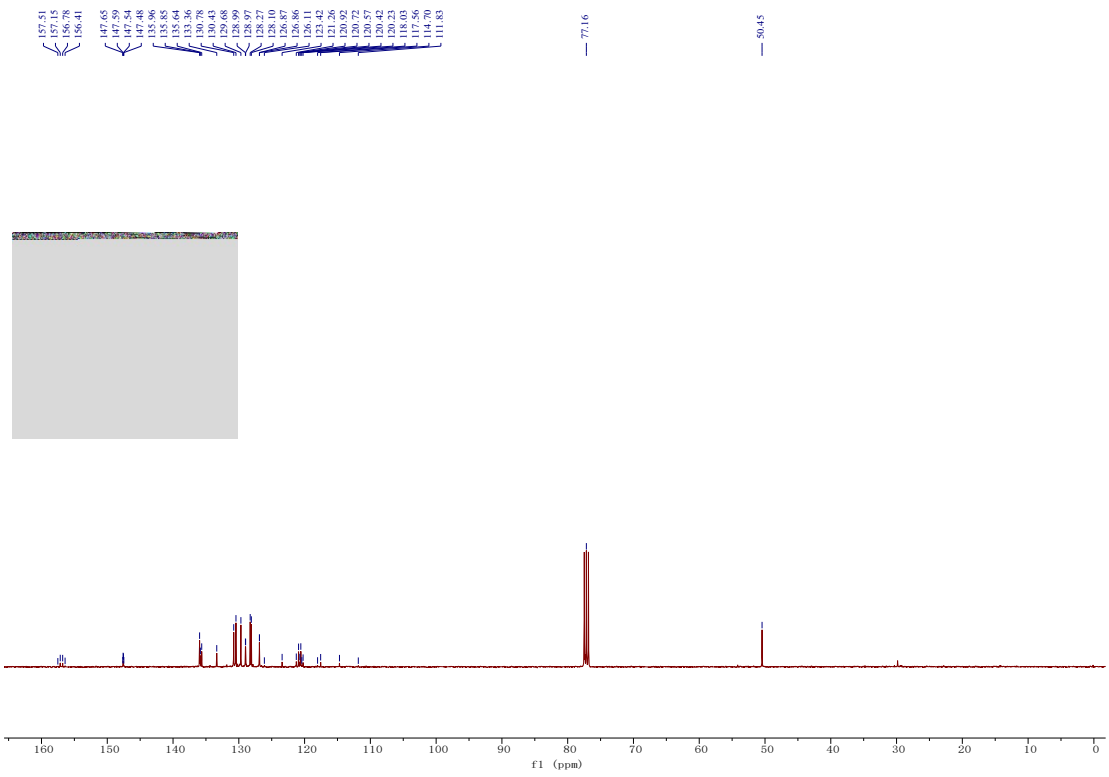
5i ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)



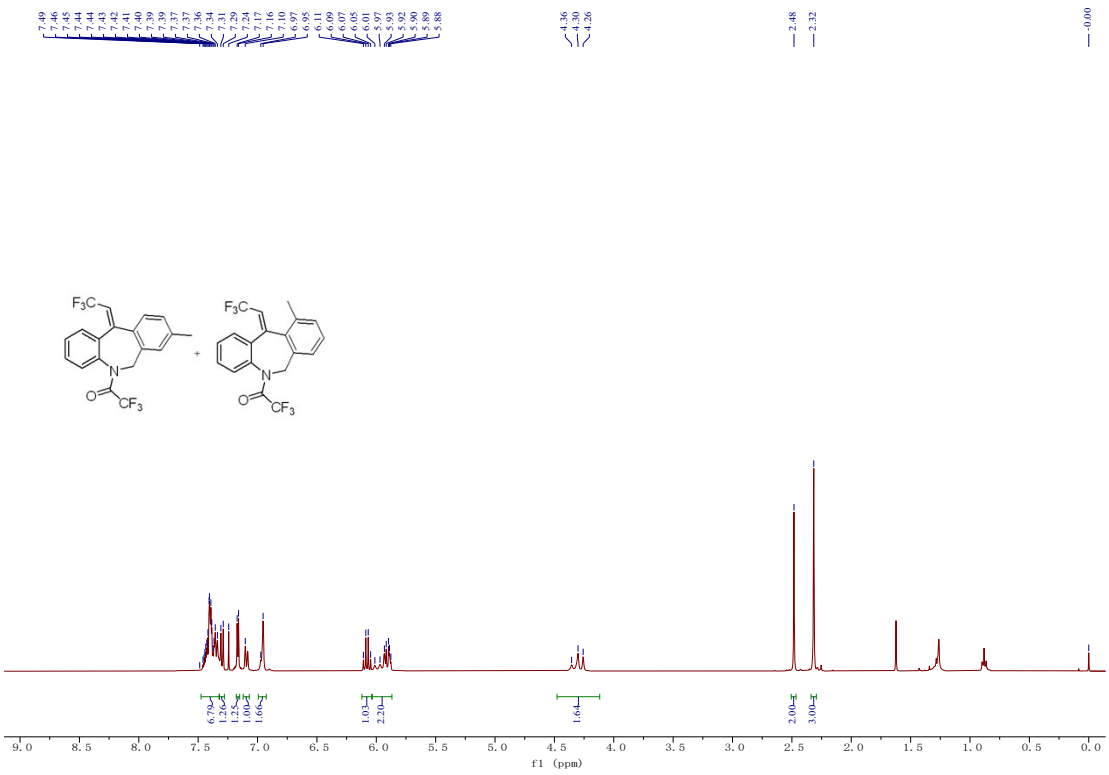


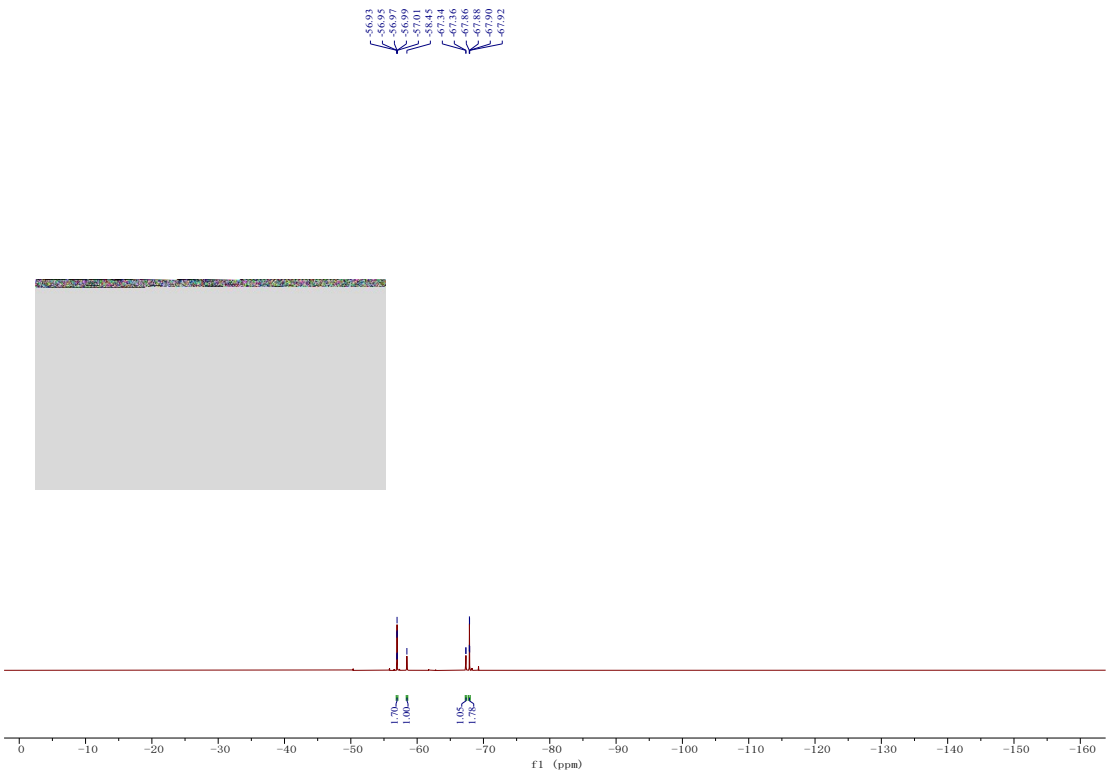


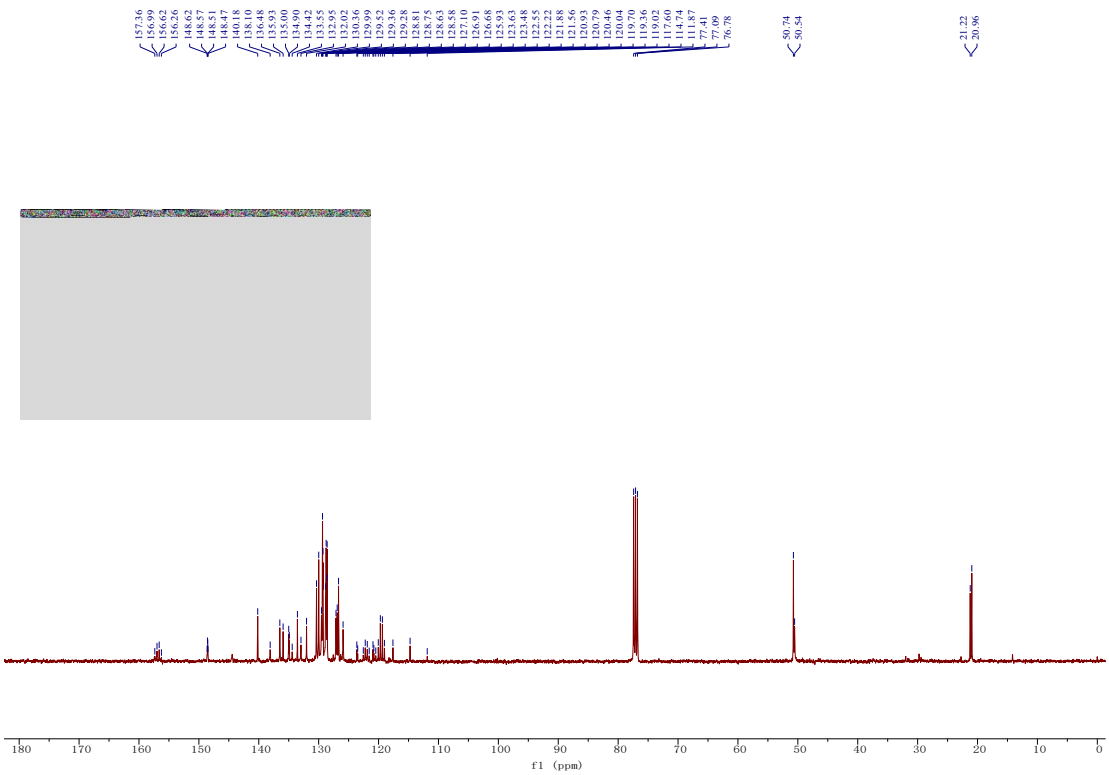




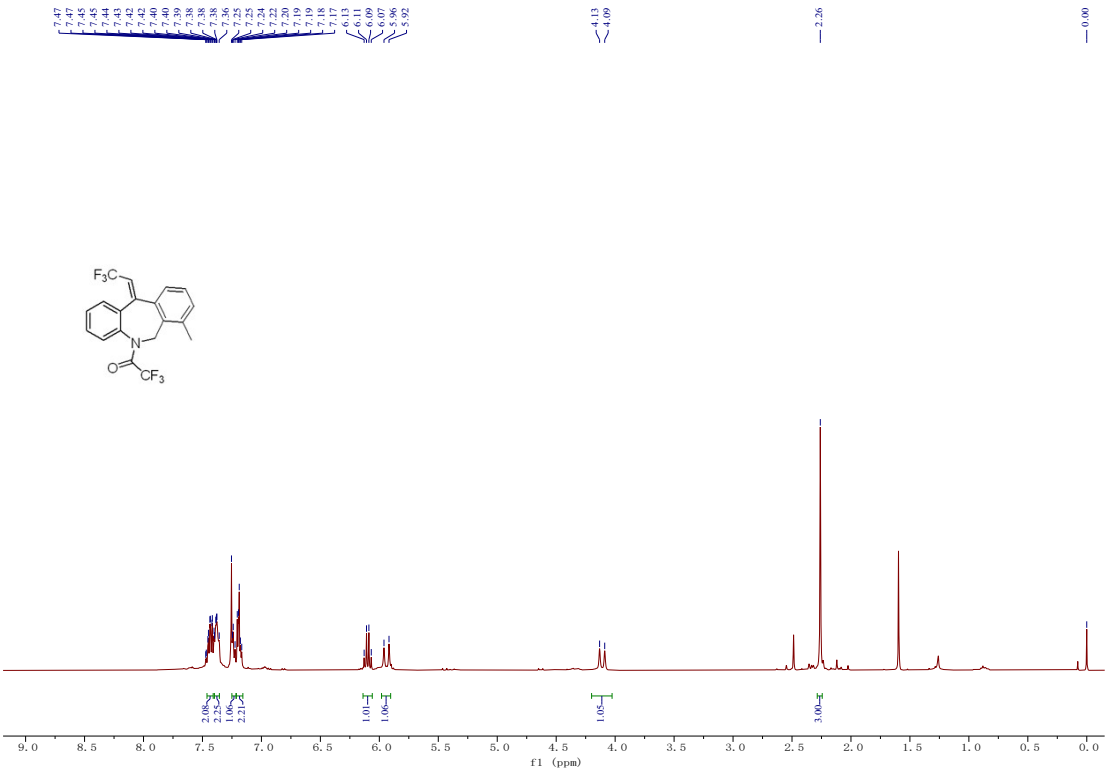
5j ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

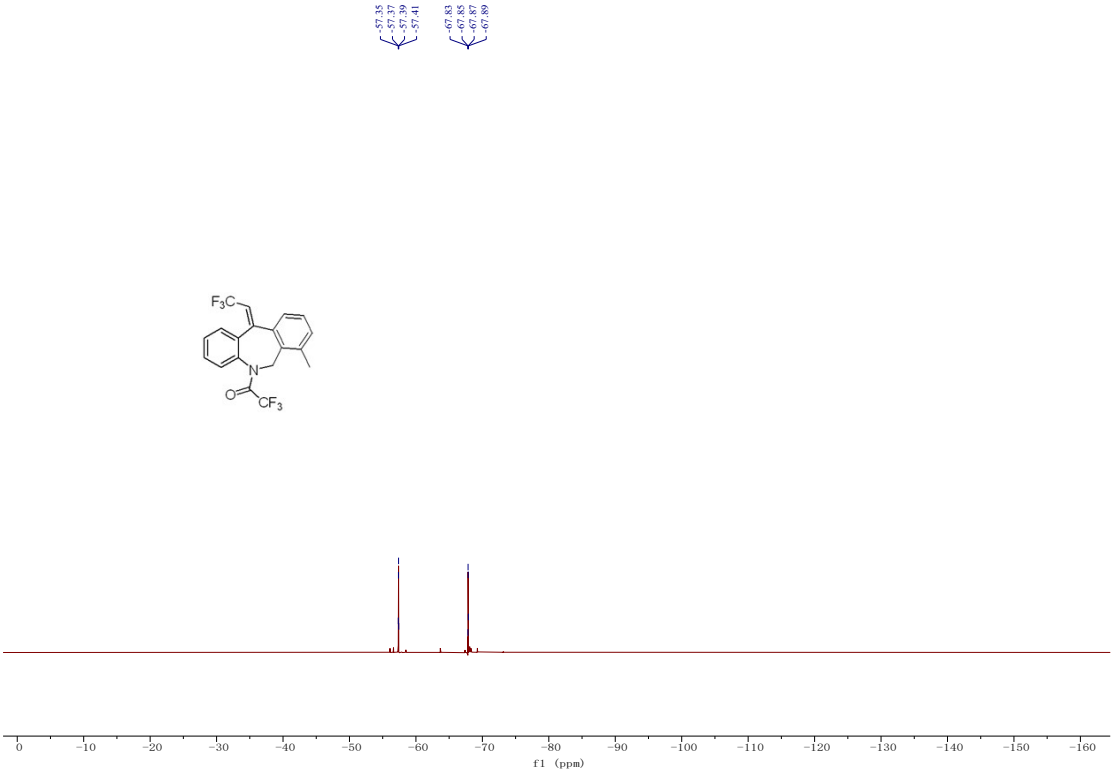


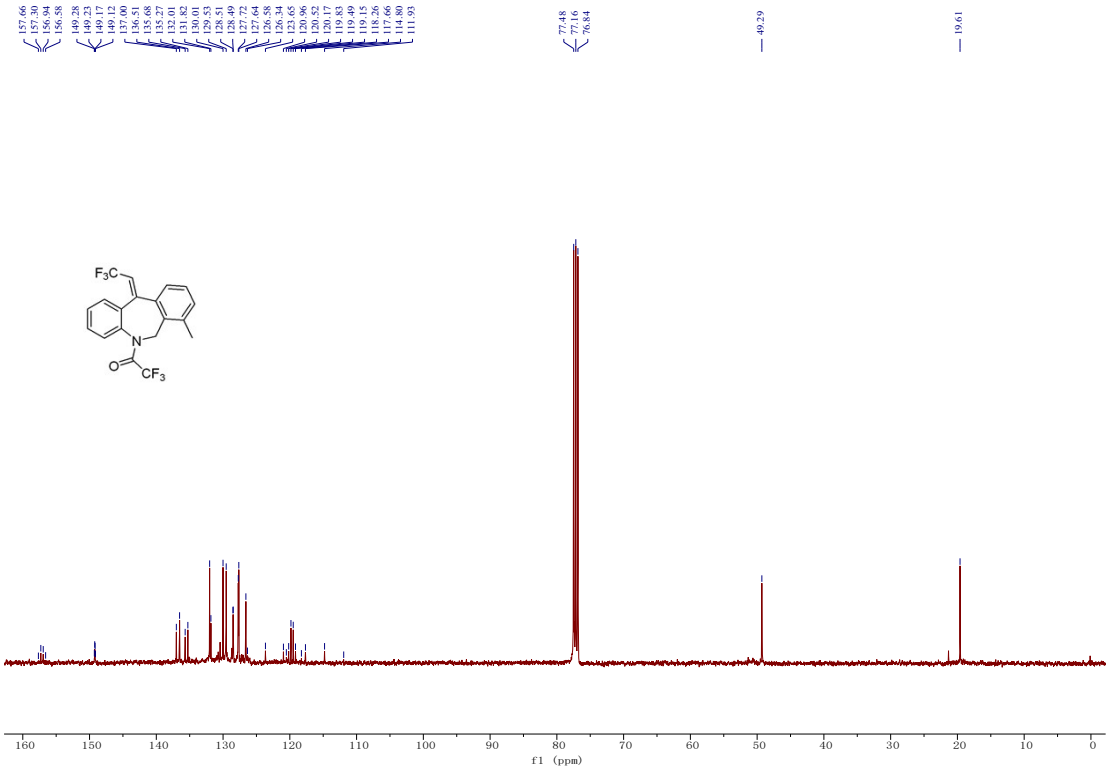

-56.93
-56.95
-56.97
-56.99
-57.01
-58.45
-67.34
-67.36
-67.86
-67.88
-67.90
-67.92
1.70
1.00
1.05
1.78
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)


157.36
156.99
156.62
156.26
148.62
148.57
148.51
148.47
140.18
138.10
136.48
135.93
135.00
134.90
134.42
133.55
132.95
132.02
130.36
129.99
129.53
129.36
129.28
128.81
128.75
128.63
128.58
127.10
126.91
126.68
125.93
123.63
123.48
122.55
122.22
121.88
121.56
120.93
120.79
120.46
120.04
119.79
119.36
119.02
117.60
114.74
111.87
77.41
77.09
76.78
50.74
50.54
21.22
20.96
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

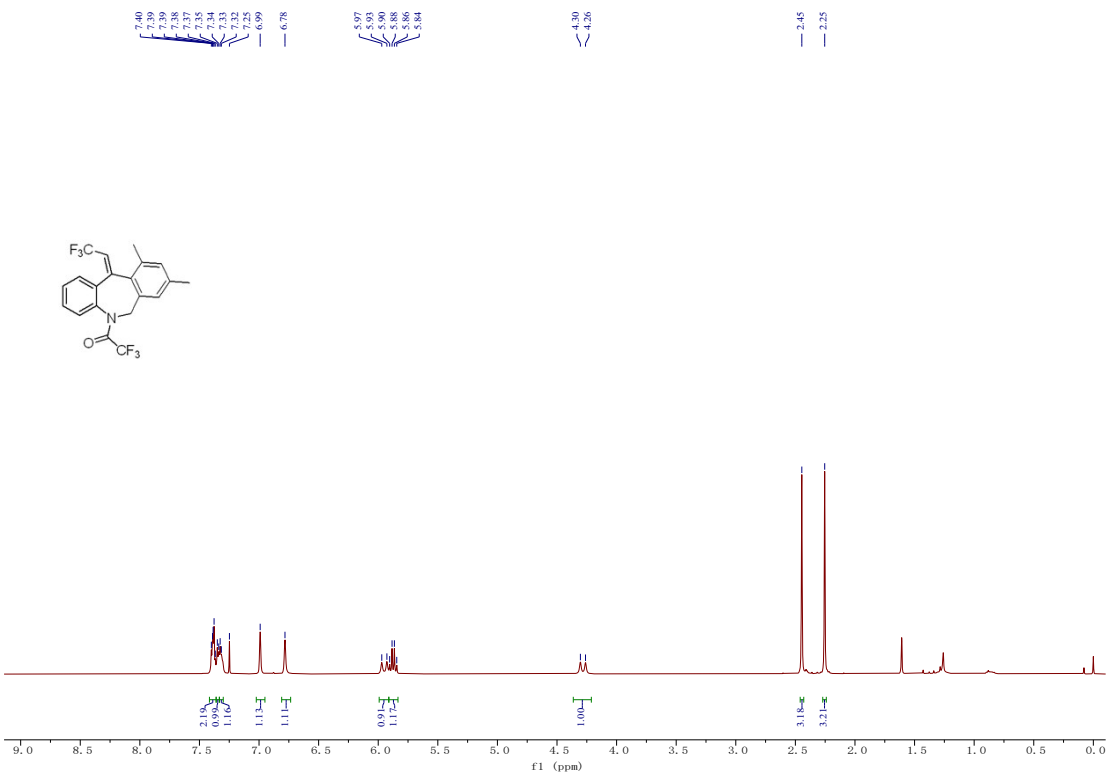
5k ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

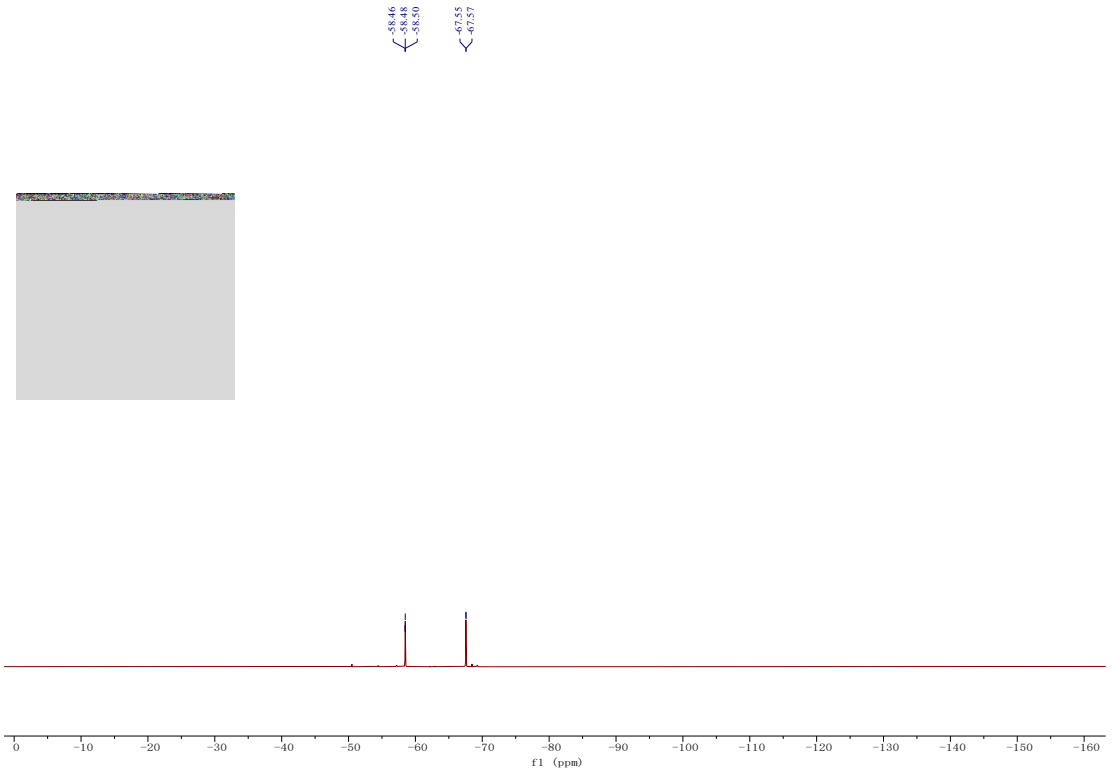


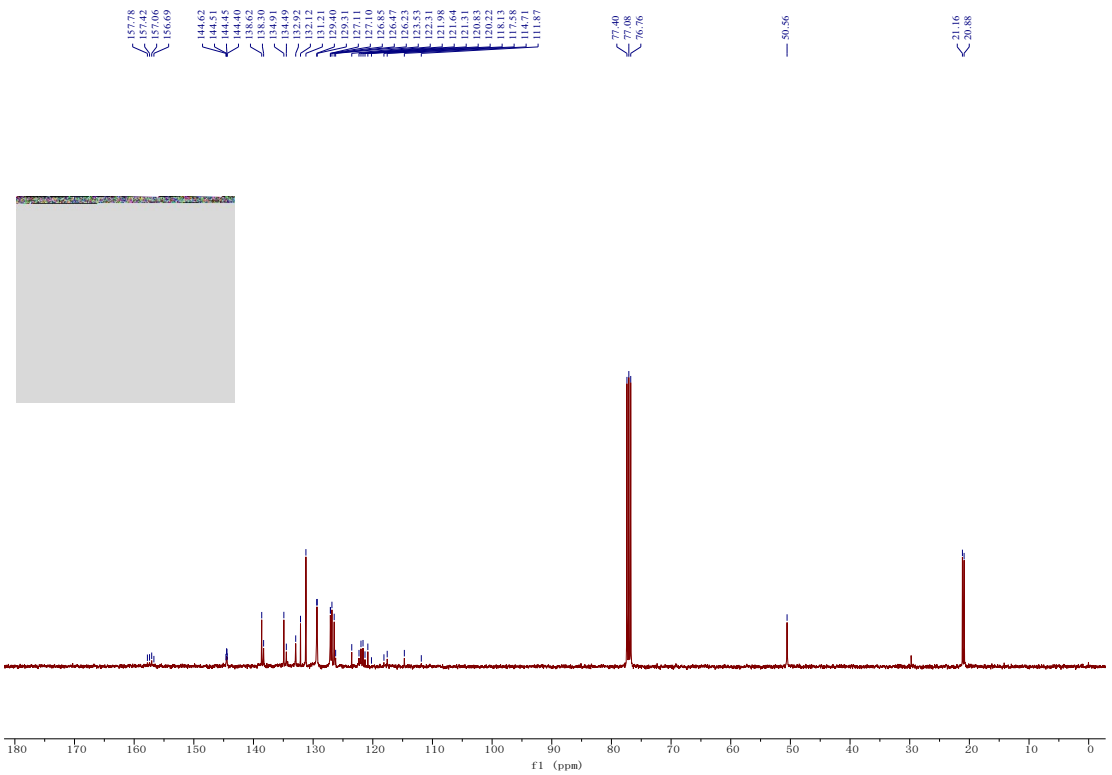




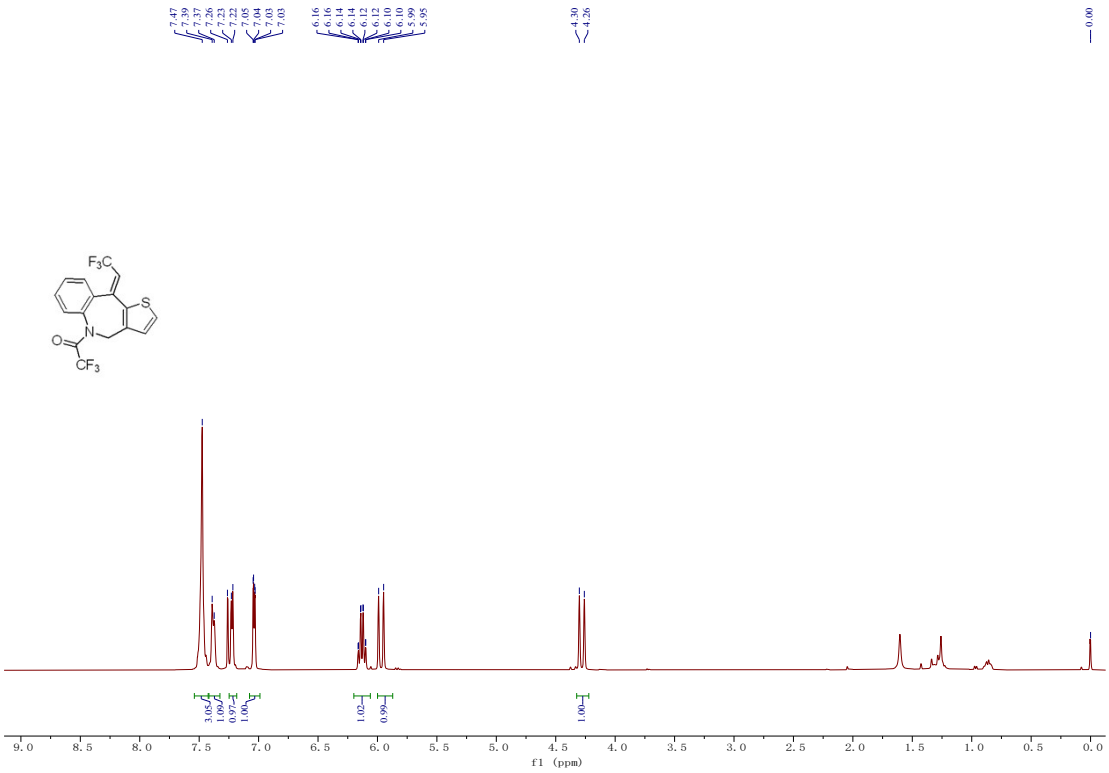
5l ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

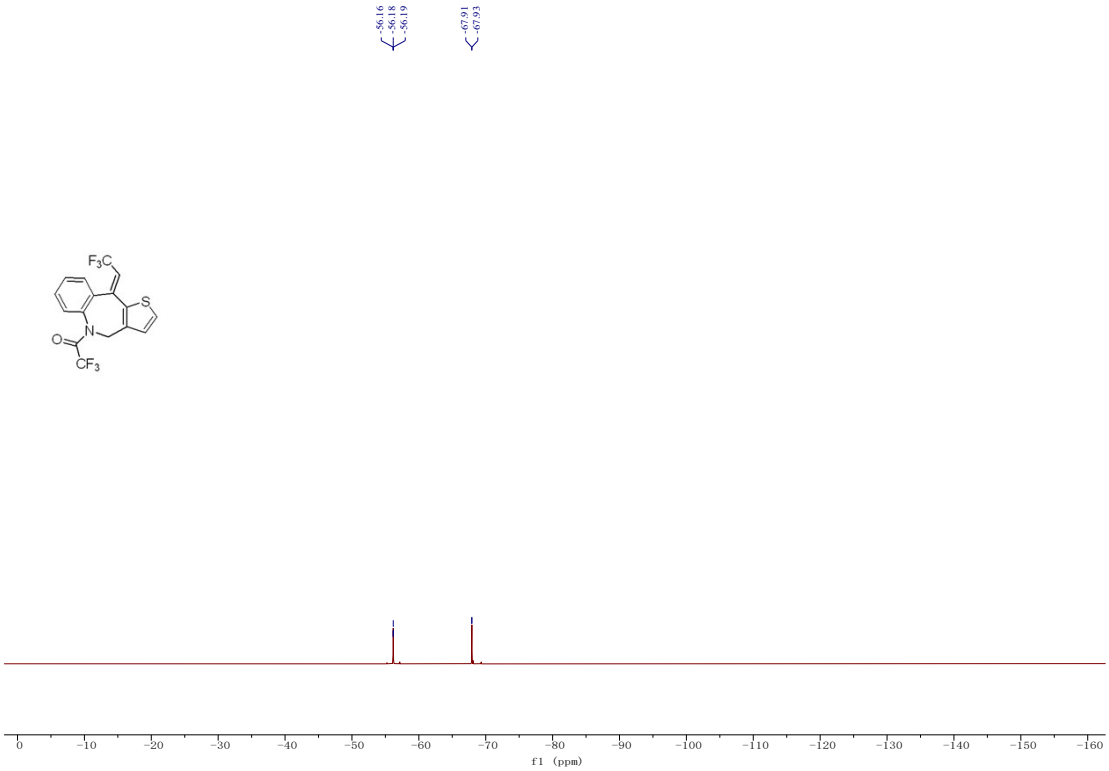


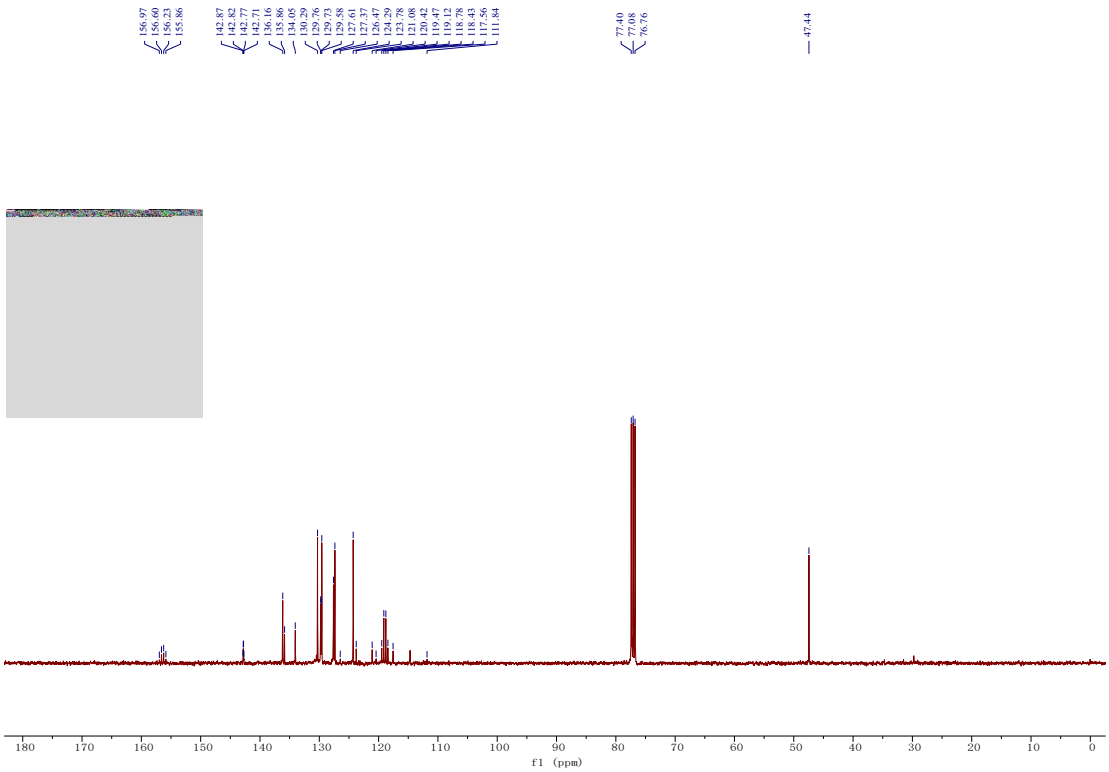

-58.46
-58.48
-58.50
-67.55
-67.57
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)


157.78
157.42
157.06
156.69
144.62
144.51
144.45
144.40
138.62
138.30
134.91
134.49
132.92
132.12
131.21
129.40
129.31
127.11
127.10
126.65
126.47
126.23
123.53
122.31
121.98
121.64
121.31
120.85
120.22
118.13
117.58
114.71
111.87
77.40
77.08
76.76
50.56
21.16
20.88
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

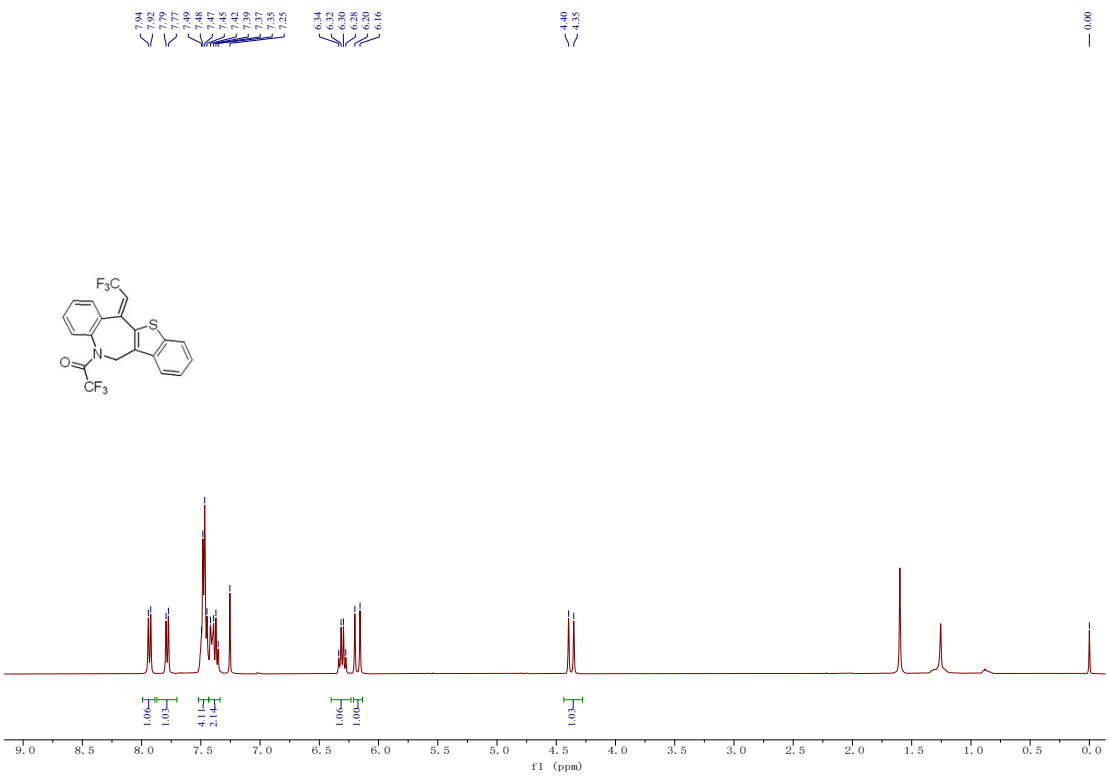
5m ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

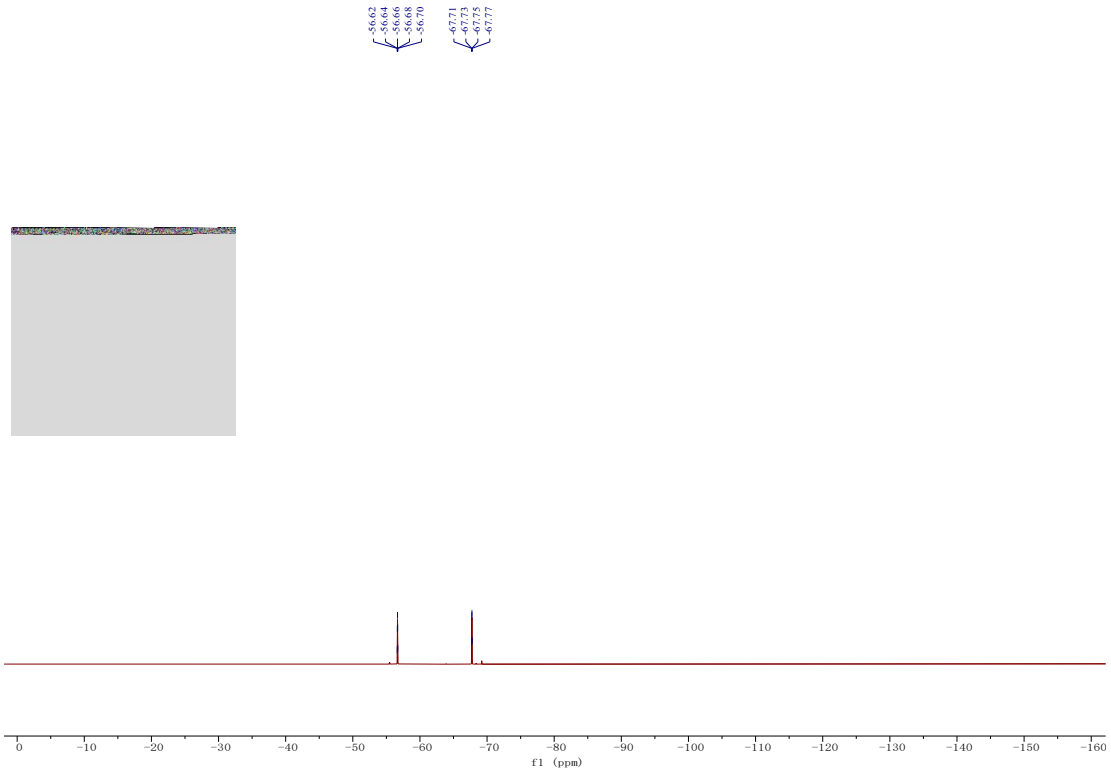


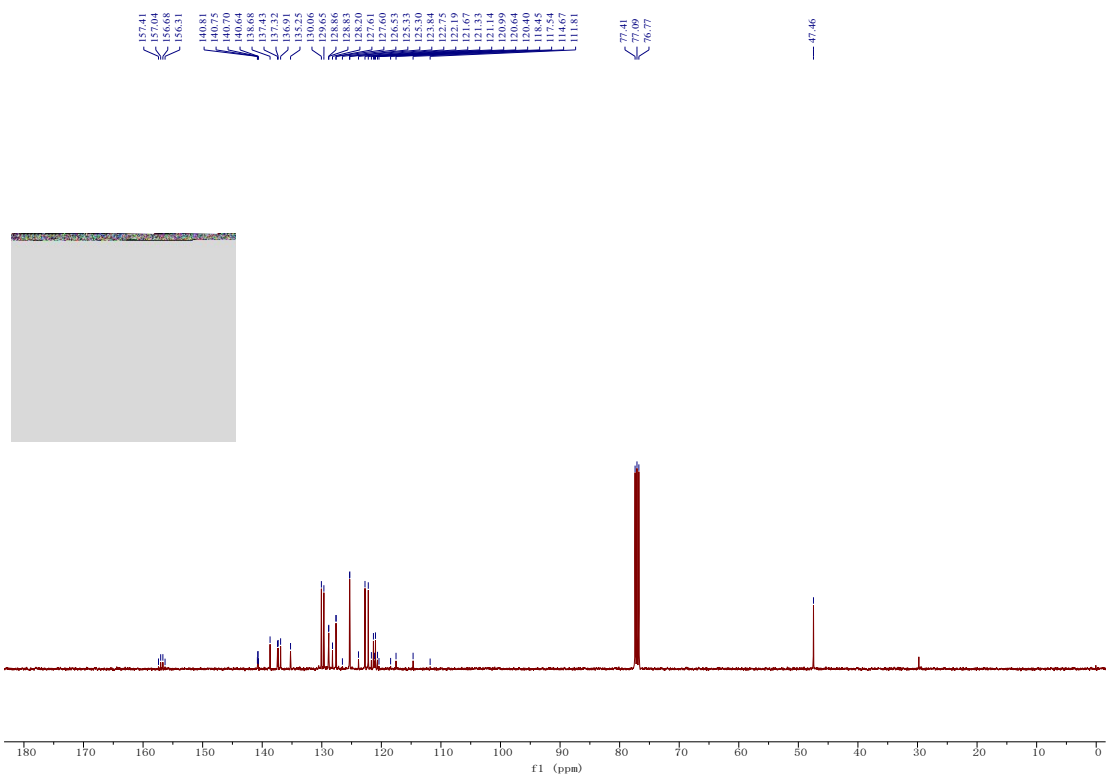




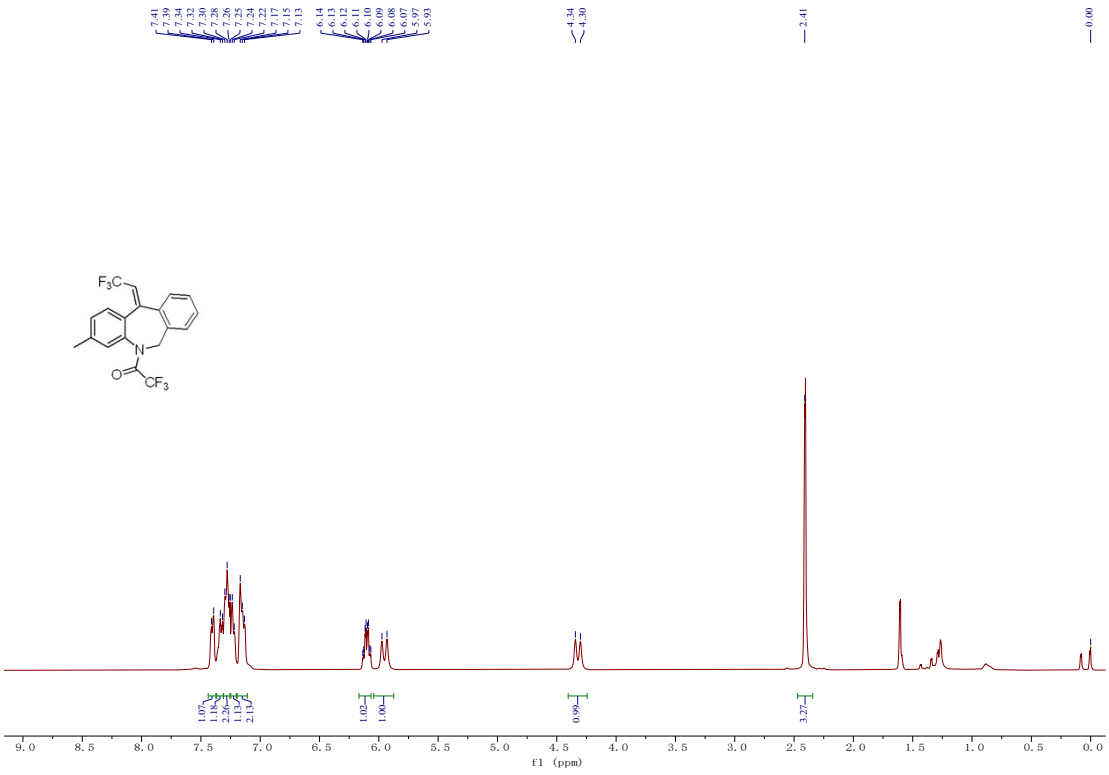
5n ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

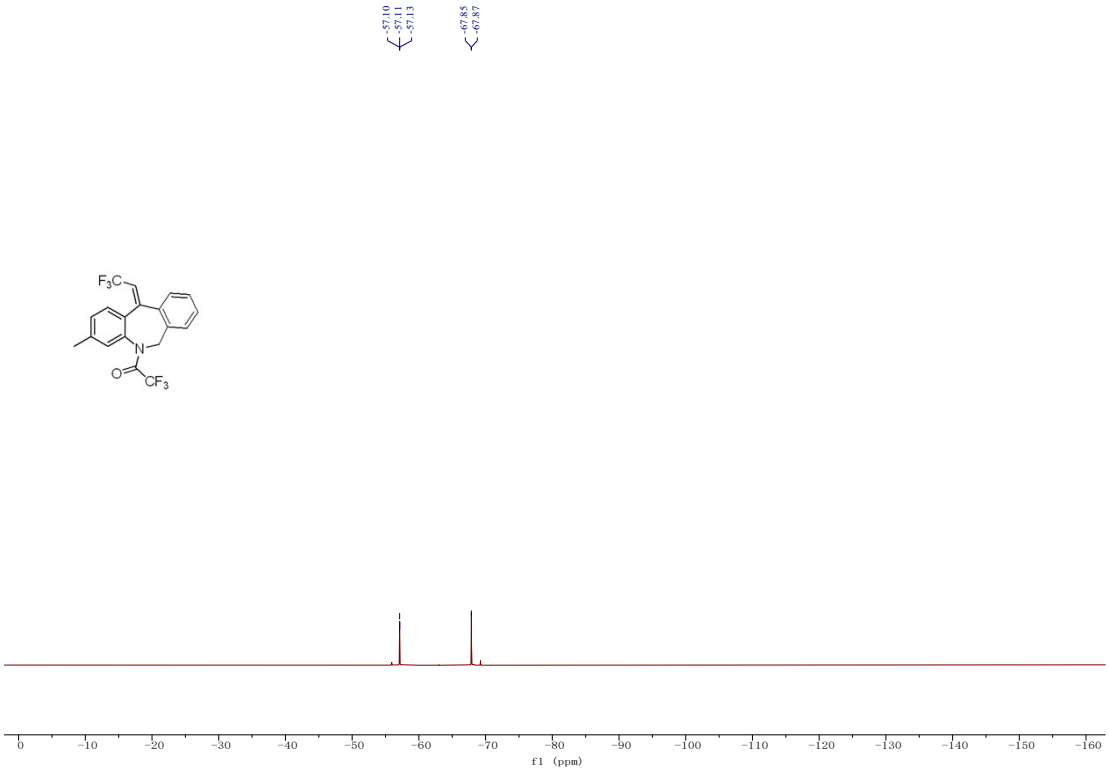


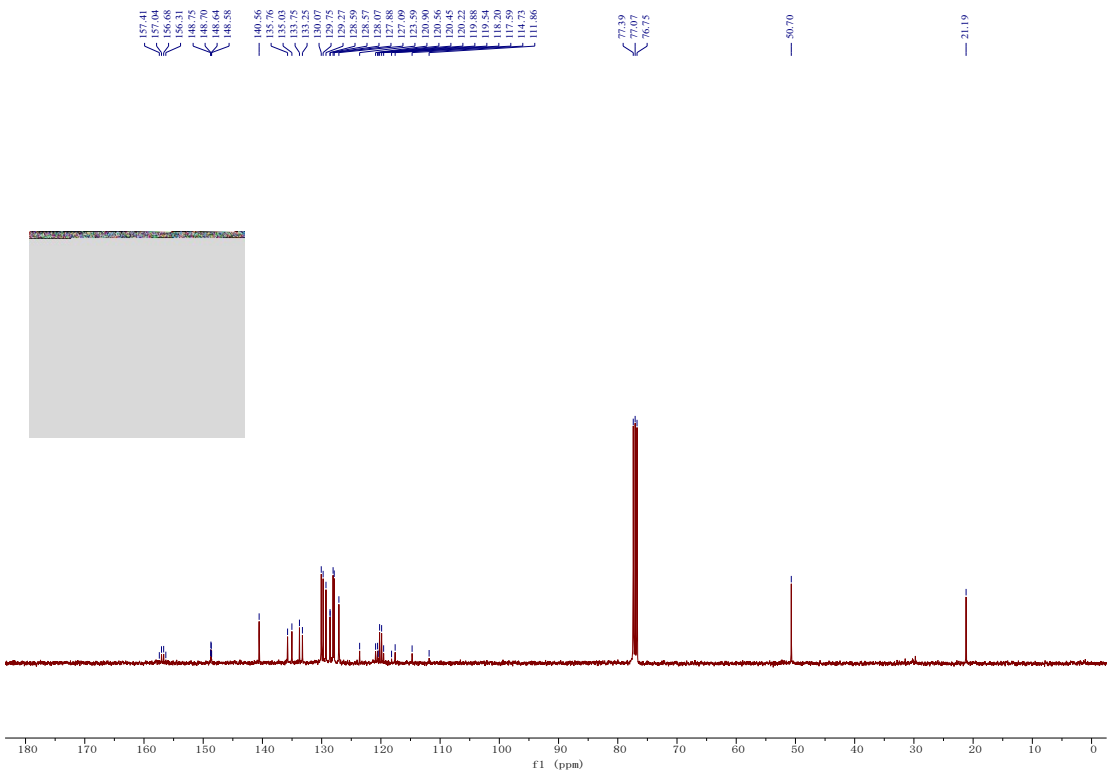

-56.62
-56.64
-56.66
-56.68
-56.70
-67.71
-67.73
-67.75
-67.77
f1 (ppm)


157.41
157.04
156.68
156.31
140.81
140.75
140.70
140.64
138.68
137.43
137.32
136.91
135.25
130.06
129.65
128.86
128.83
128.20
127.61
127.60
126.53
126.33
125.30
123.84
122.75
122.19
121.67
121.33
121.14
120.99
120.64
120.40
118.45
117.54
114.67
111.61
77.41
77.09
76.77
47.46
f1 (ppm)

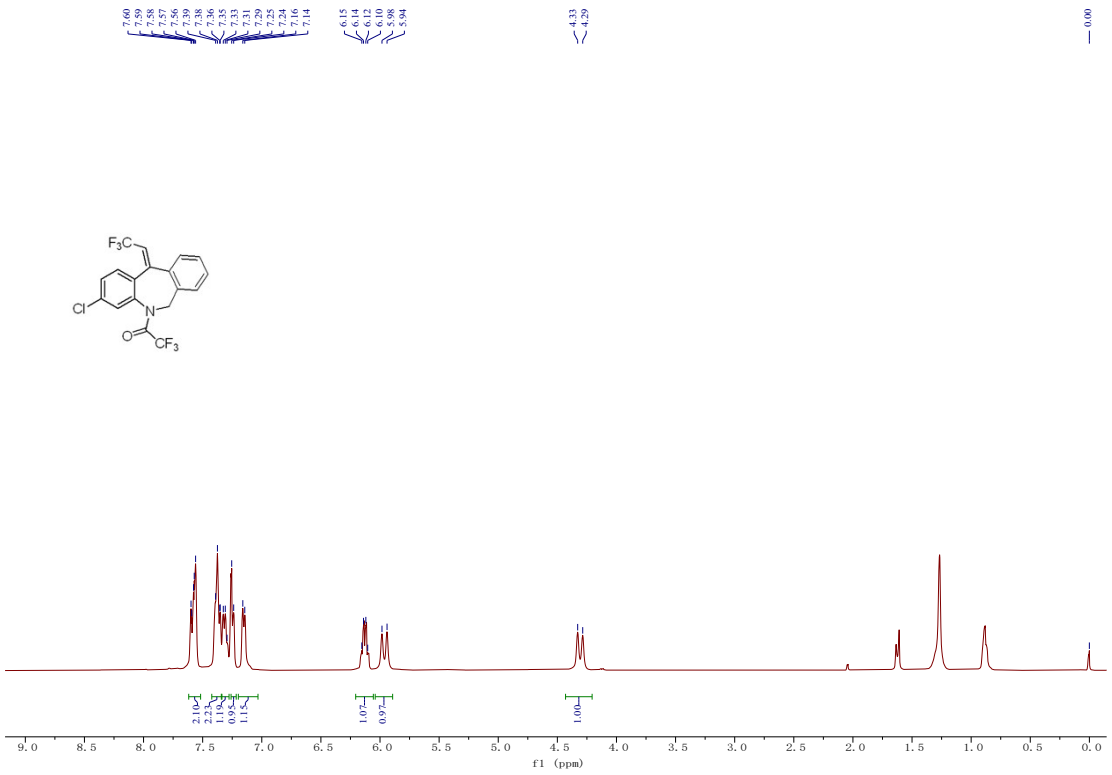
5o ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

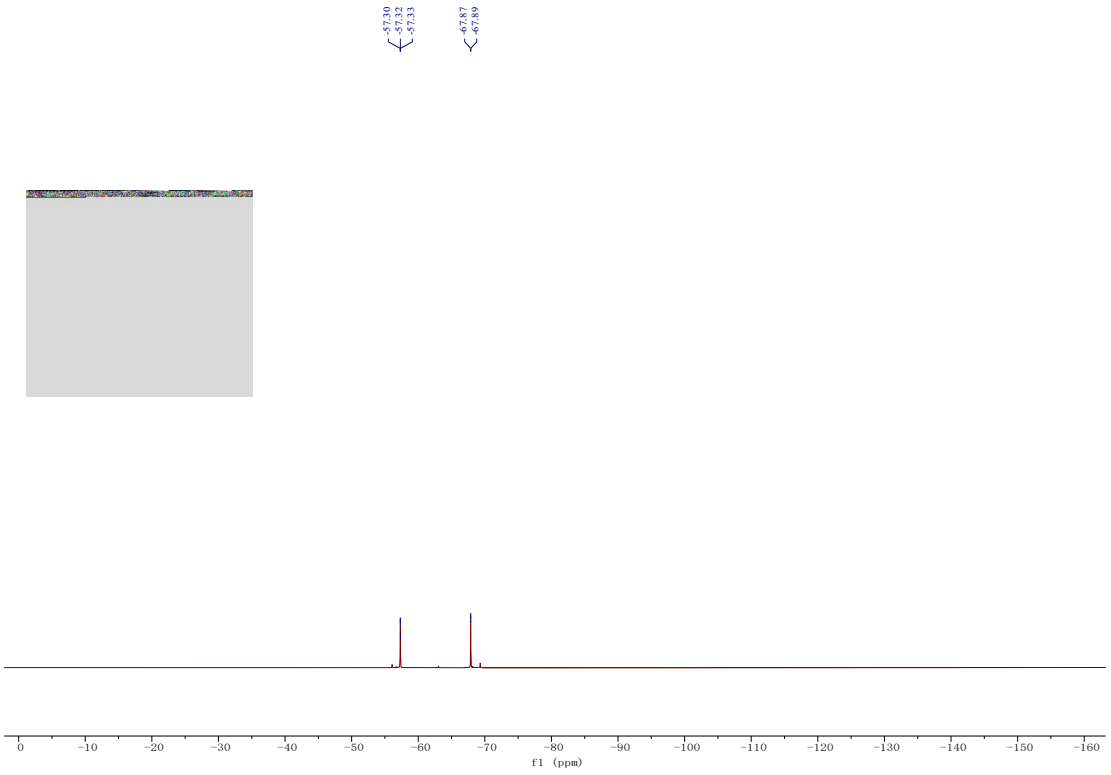


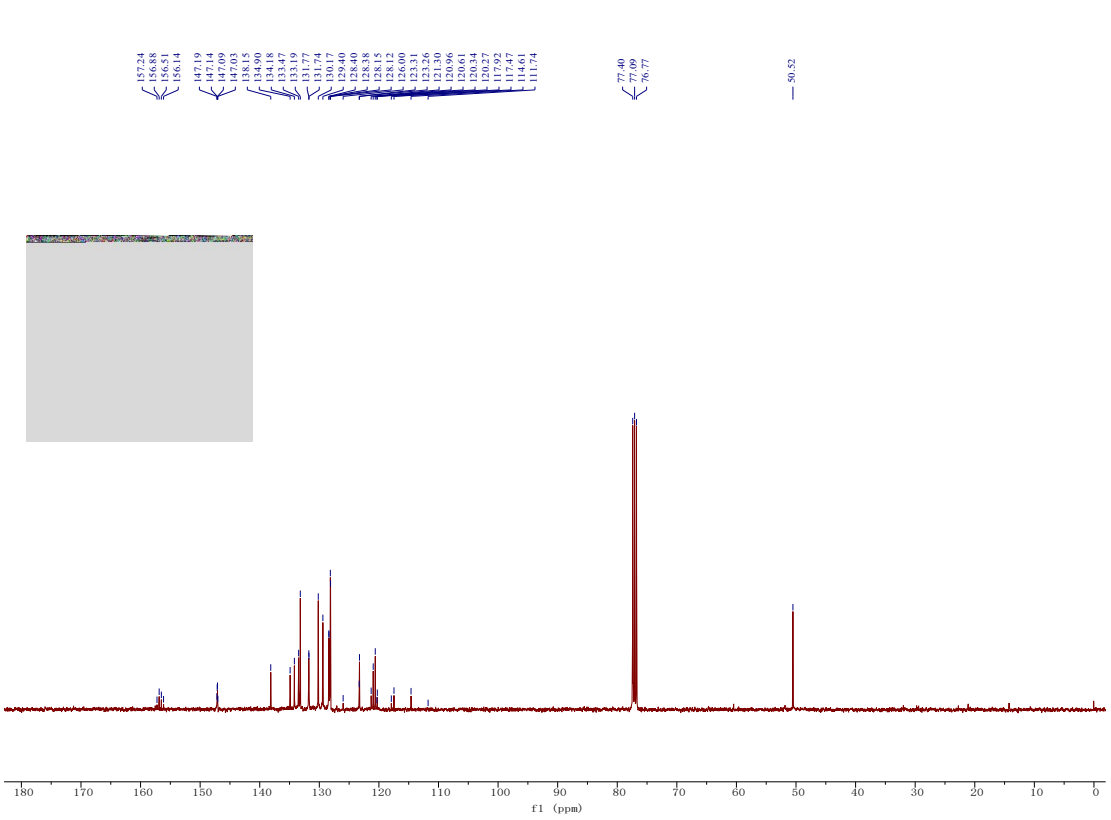




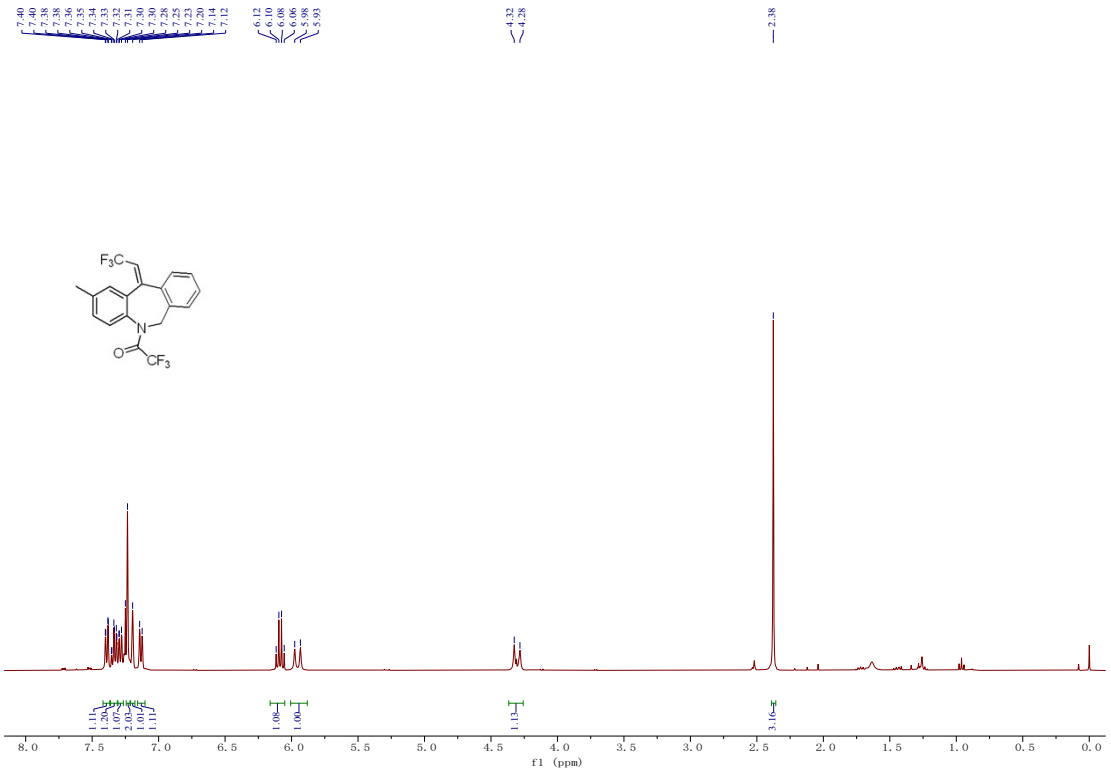
5p ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

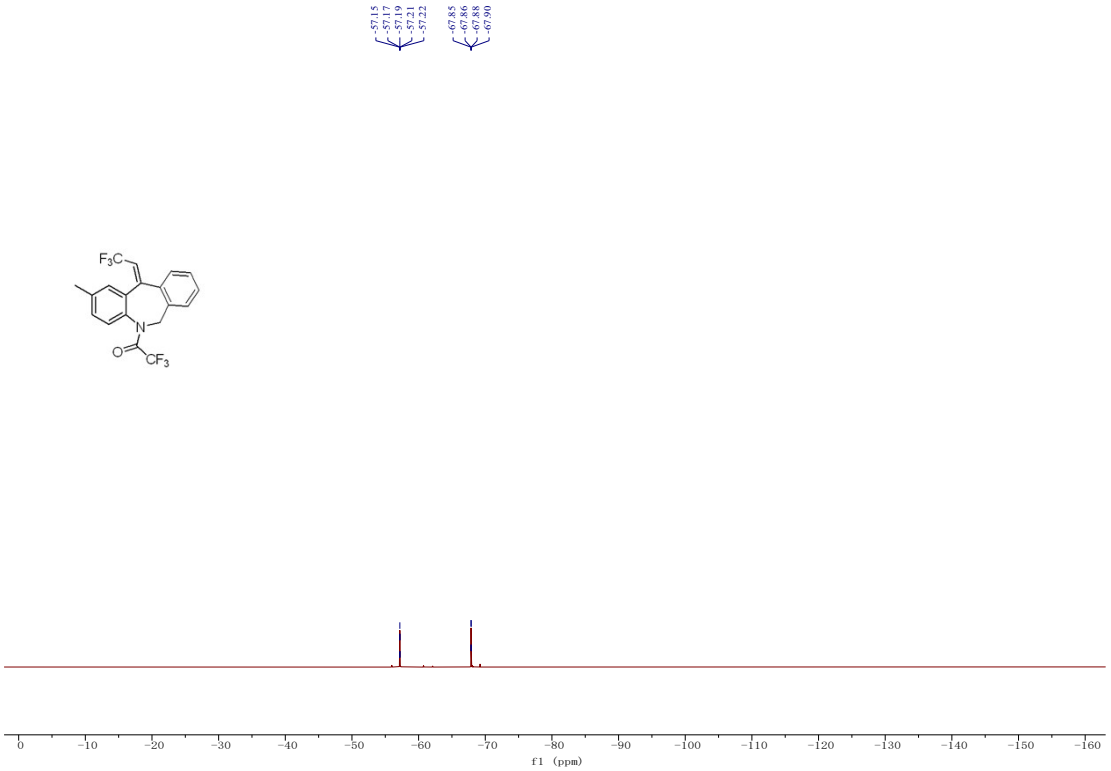


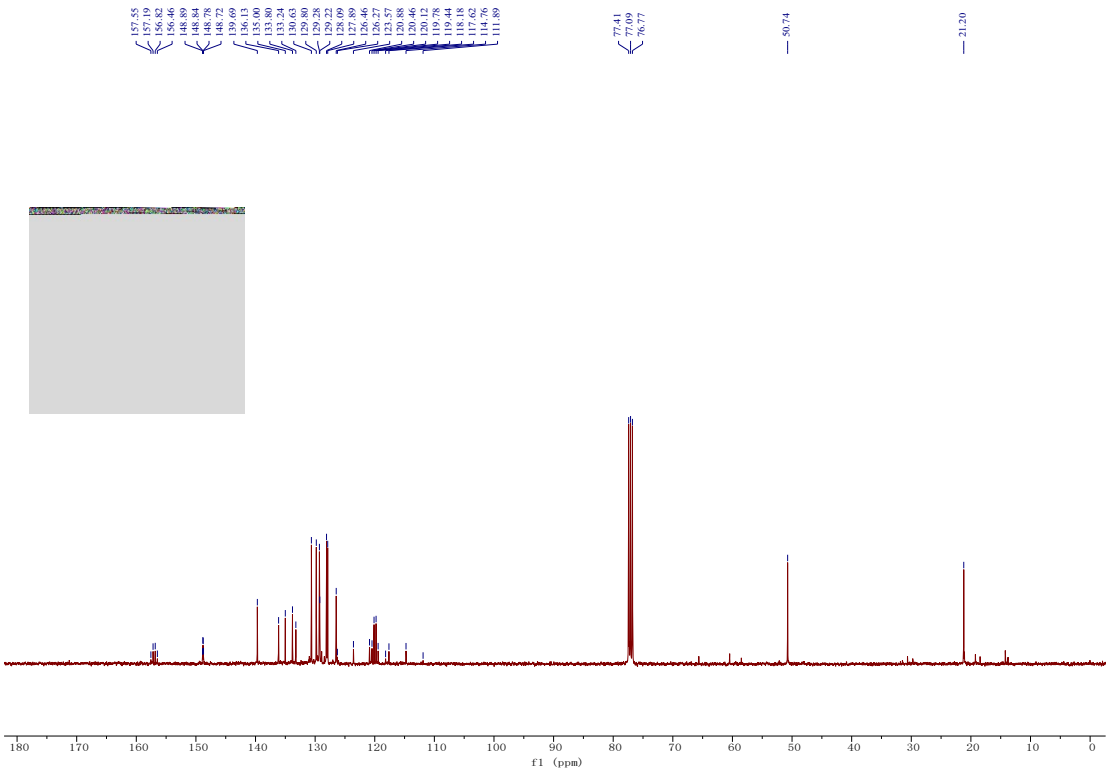

-57.30
-57.32
-57.33
-67.87
-67.89
f1 (ppm)


157.24
156.68
156.51
156.14
147.19
147.14
147.09
147.03
138.15
134.90
134.18
133.47
133.19
131.77
131.74
130.17
129.40
128.40
128.38
128.15
128.12
126.00
123.31
123.26
121.30
120.96
120.61
120.34
120.27
117.92
117.47
114.61
111.74
77.40
77.09
76.77
50.52
f1 (ppm)

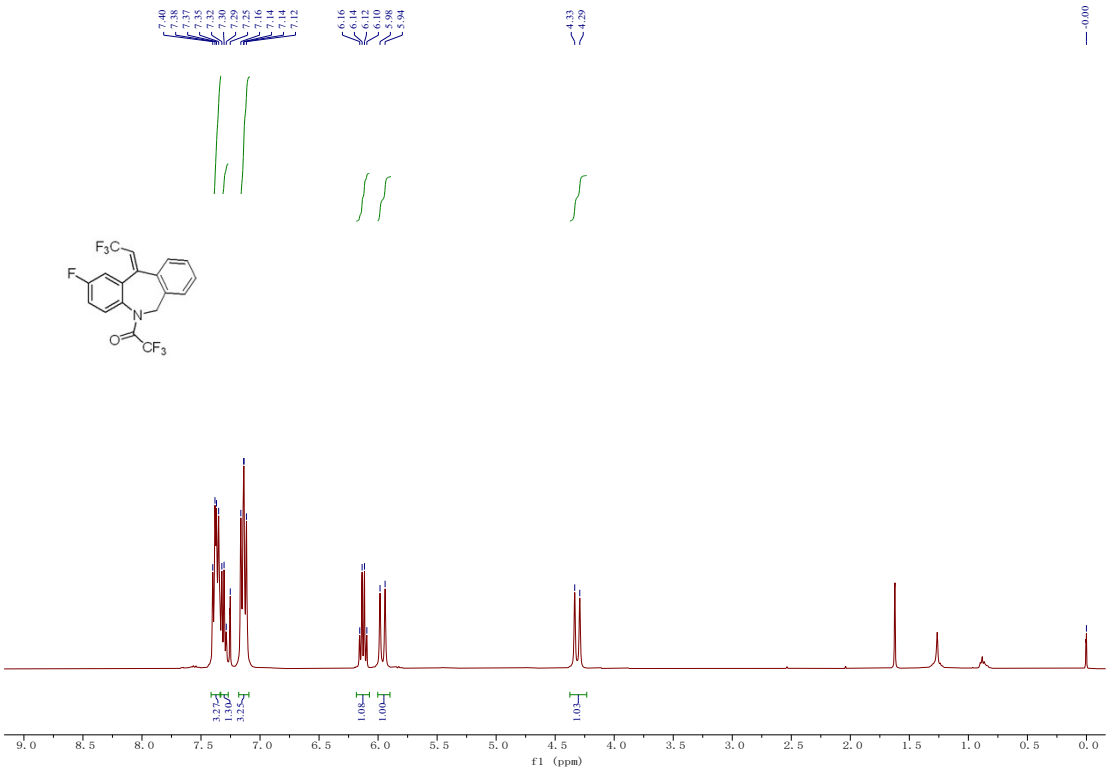
5q ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

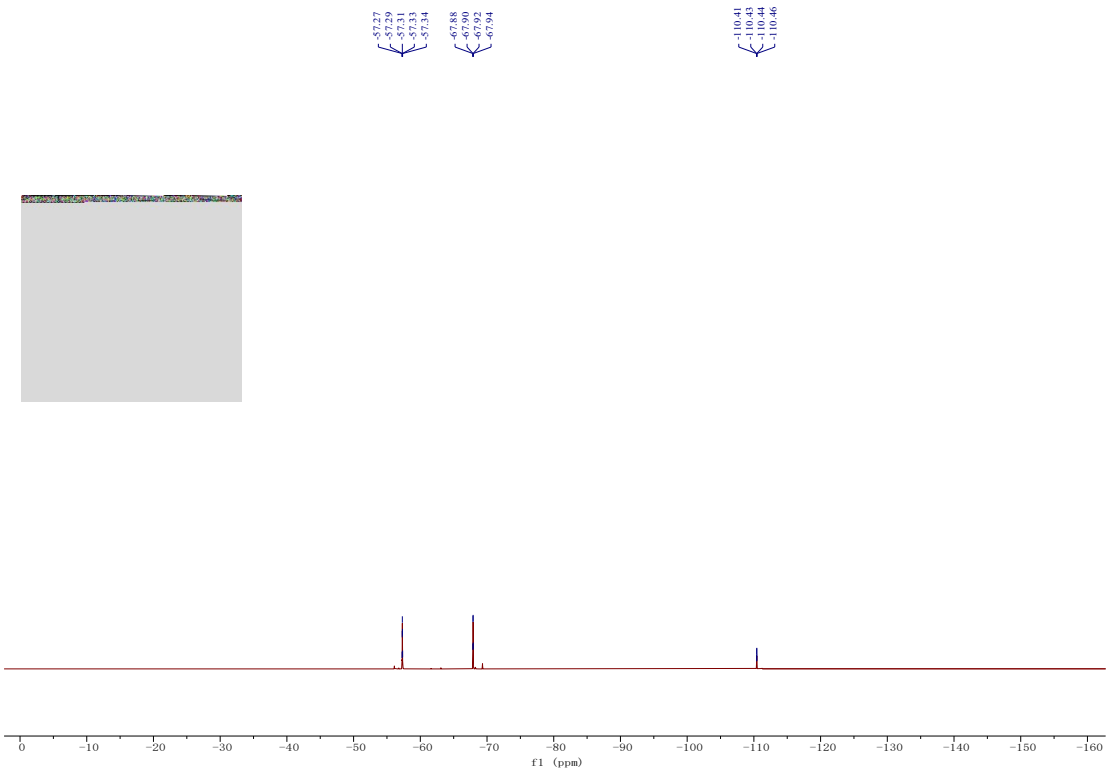


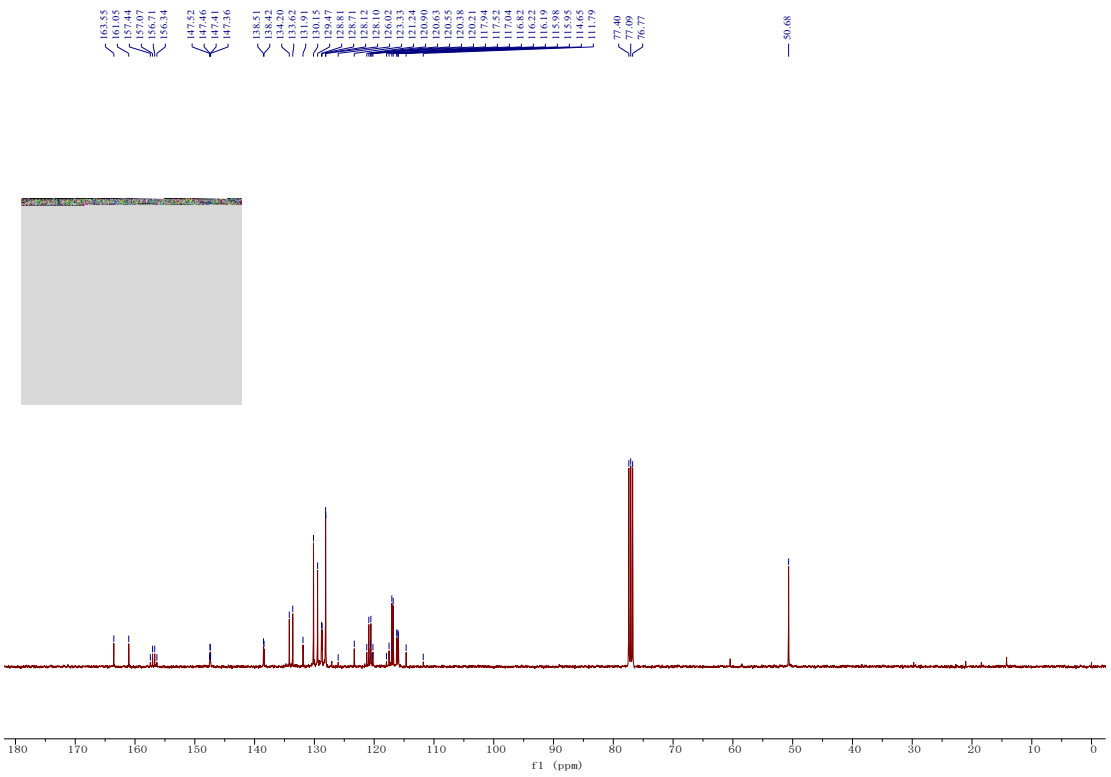




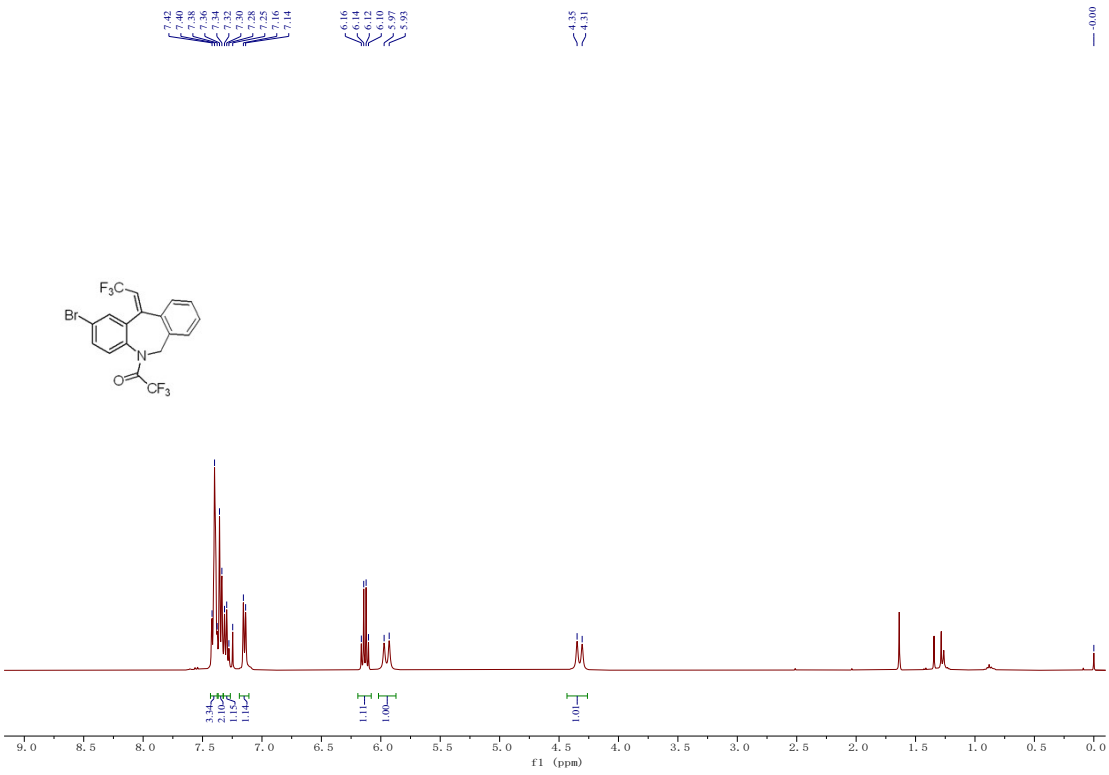
5r ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

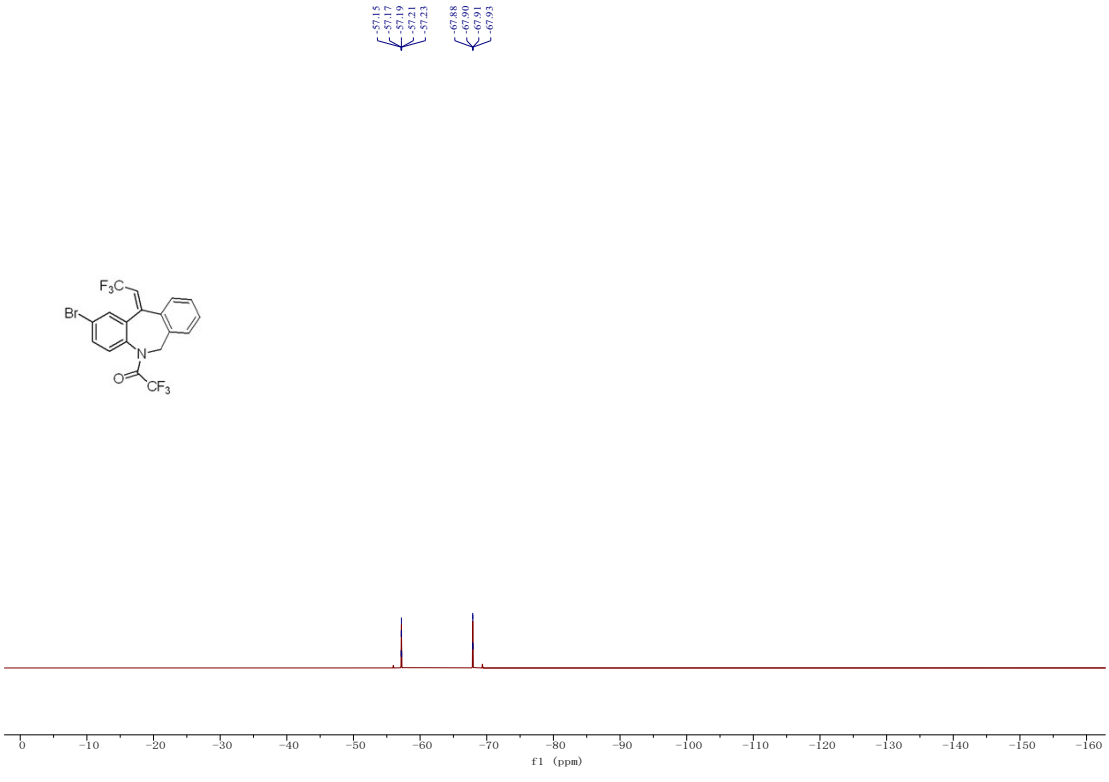


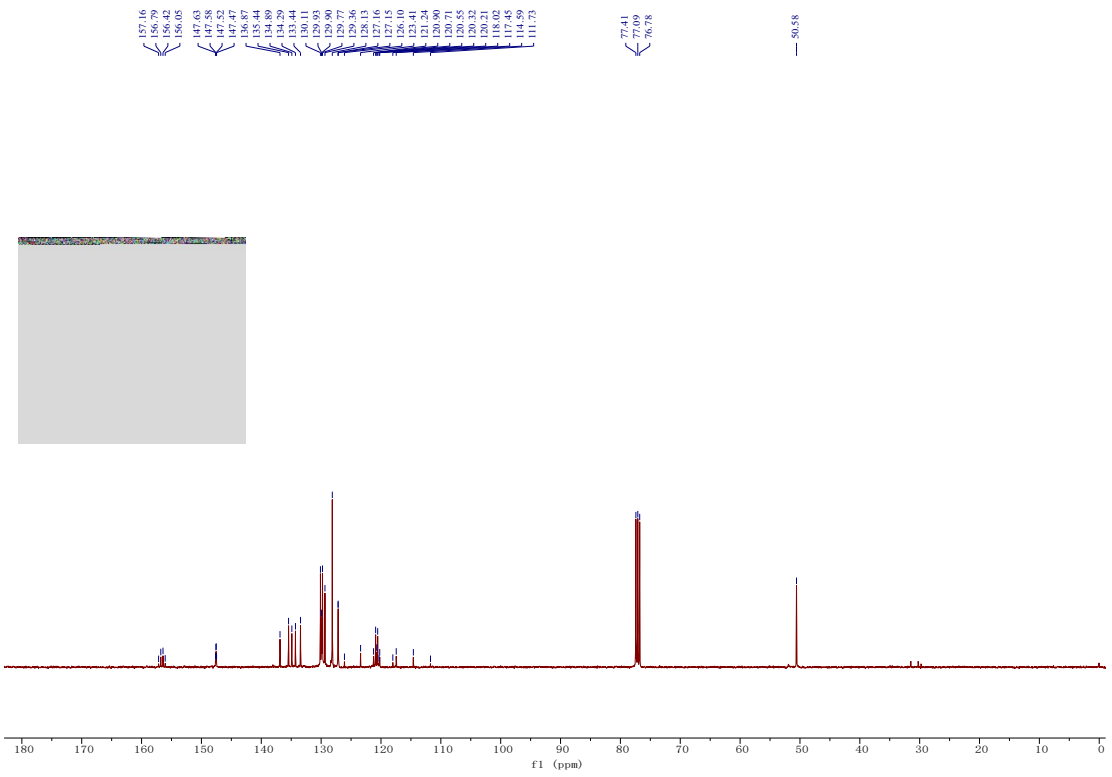

-57.27
-57.29
-57.31
-57.33
-57.34
-67.88
-67.90
-67.92
-67.94
-110.41
-110.43
-110.44
-110.46
f1 (ppm)


163.55
161.05
157.44
157.07
156.71
156.34
147.52
147.46
147.41
147.36
138.51
134.42
134.20
133.62
131.91
130.15
129.47
128.81
128.71
128.12
128.10
126.02
123.33
121.24
120.90
120.63
120.55
120.38
120.21
117.94
117.52
117.04
116.82
116.22
116.19
115.98
115.95
114.65
111.79
77.40
77.09
76.77
50.68
f1 (ppm)

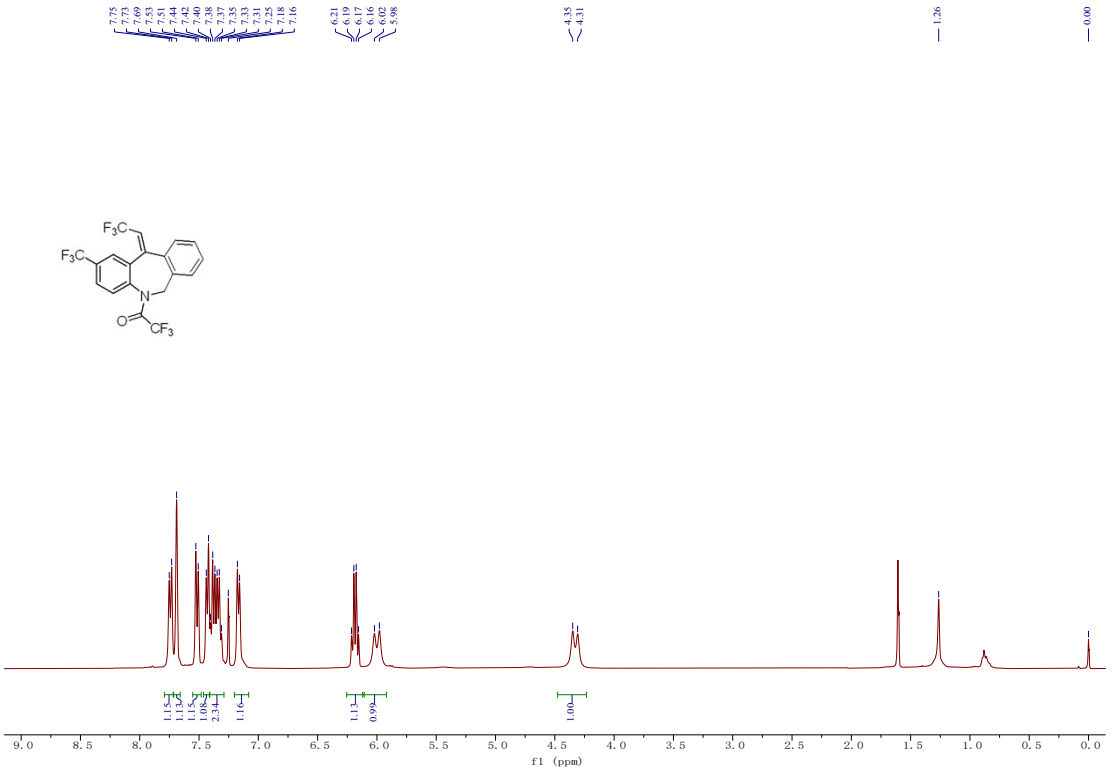
5s ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

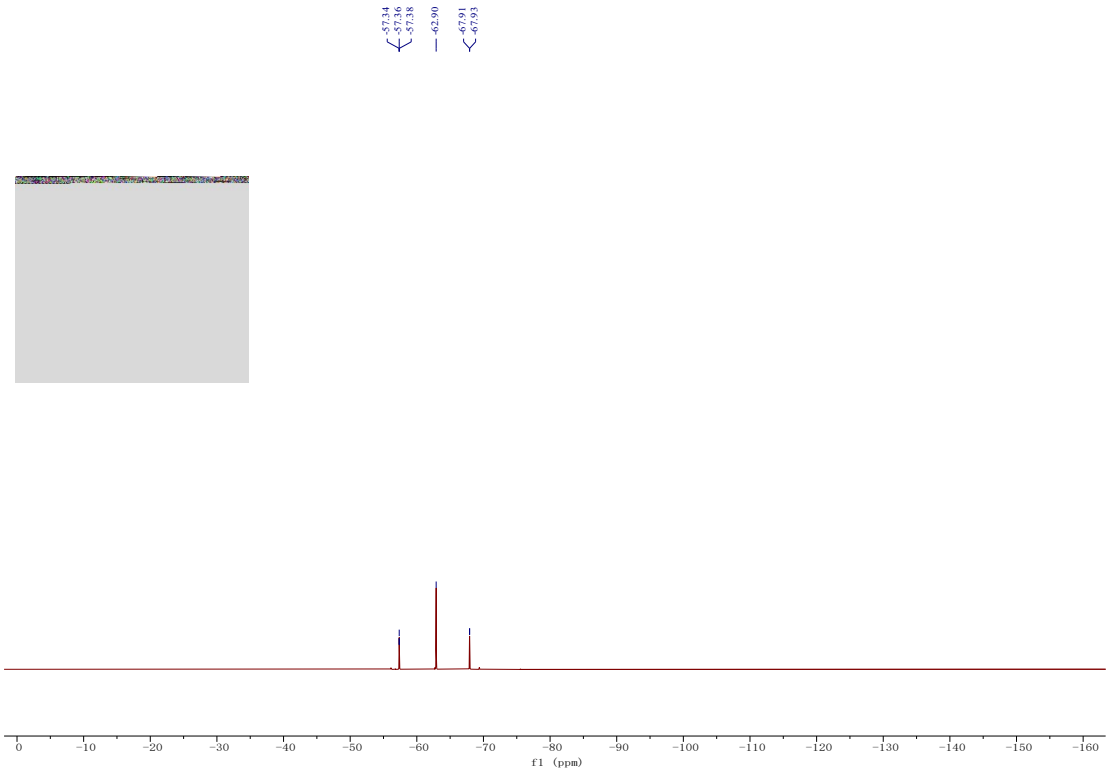


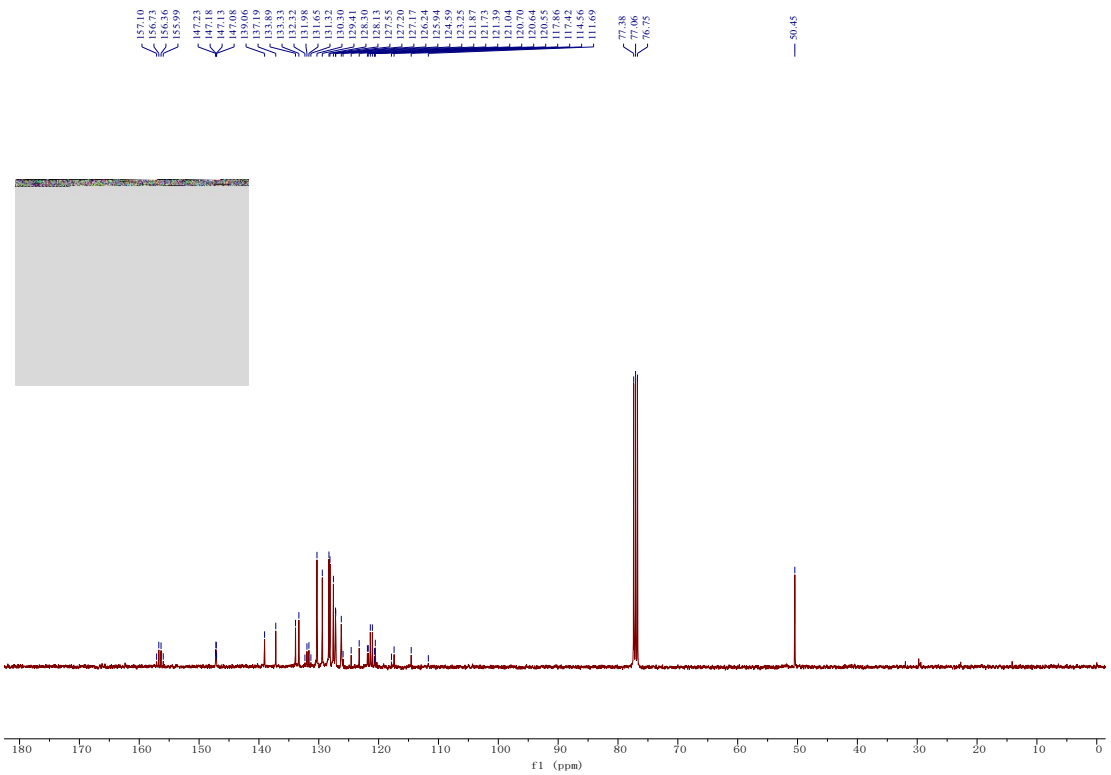




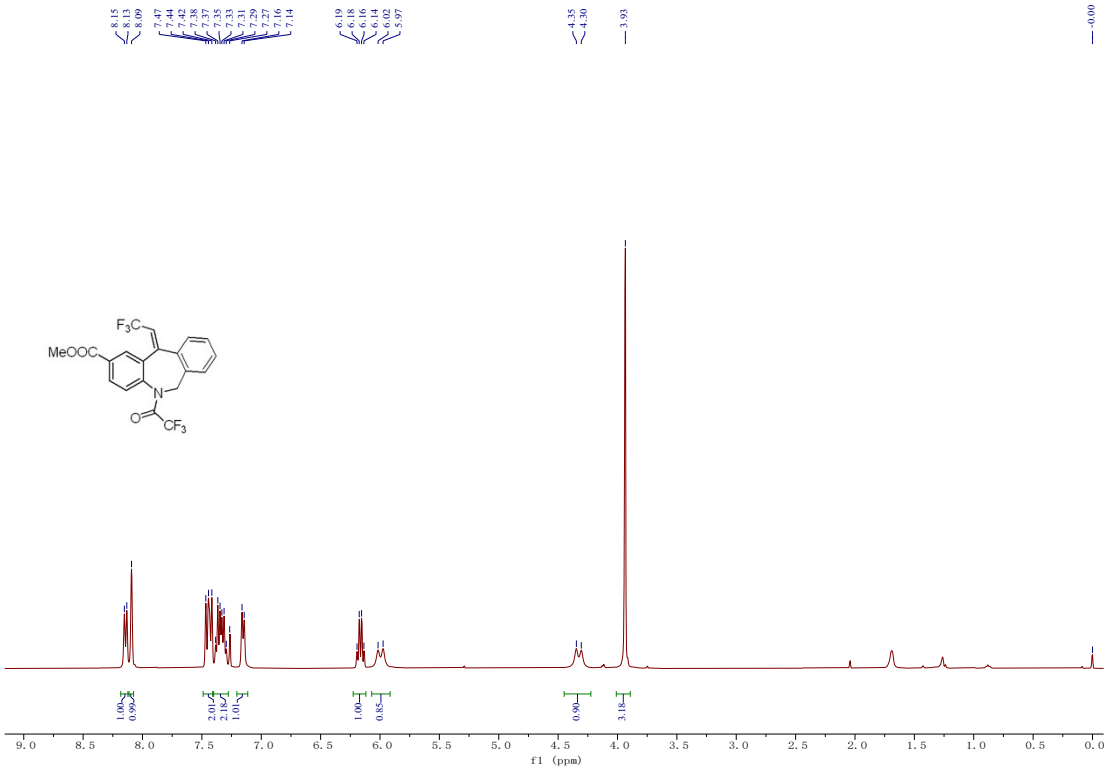
5t ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

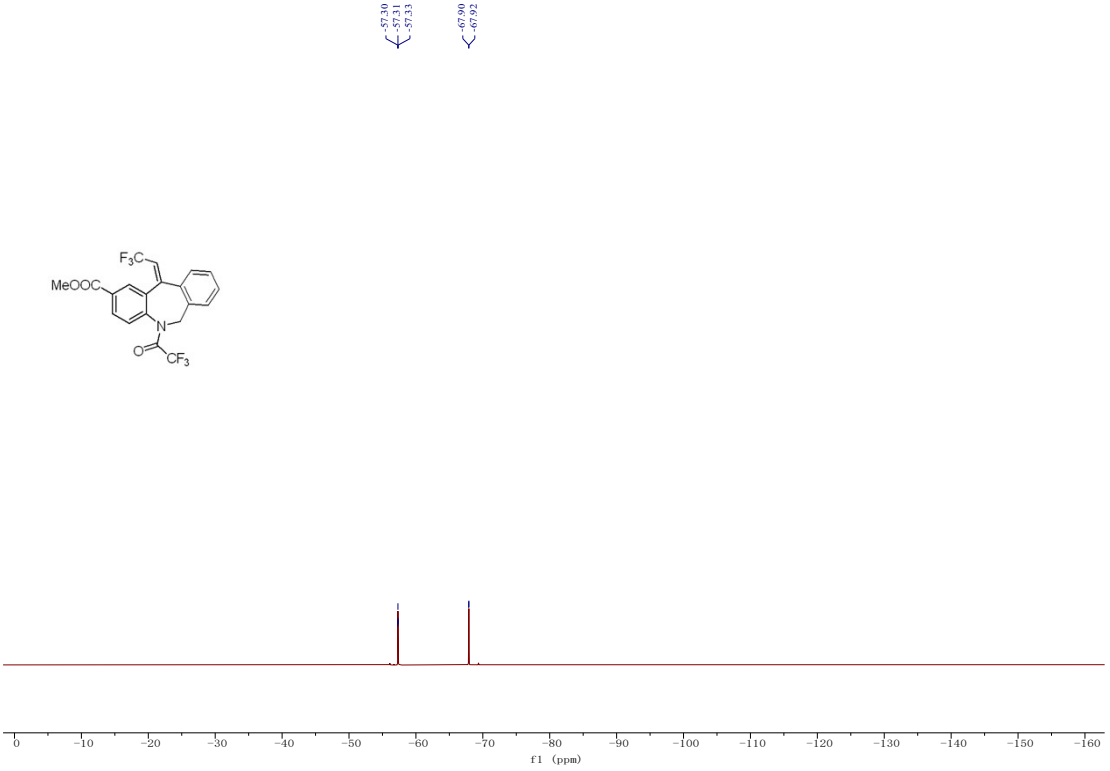


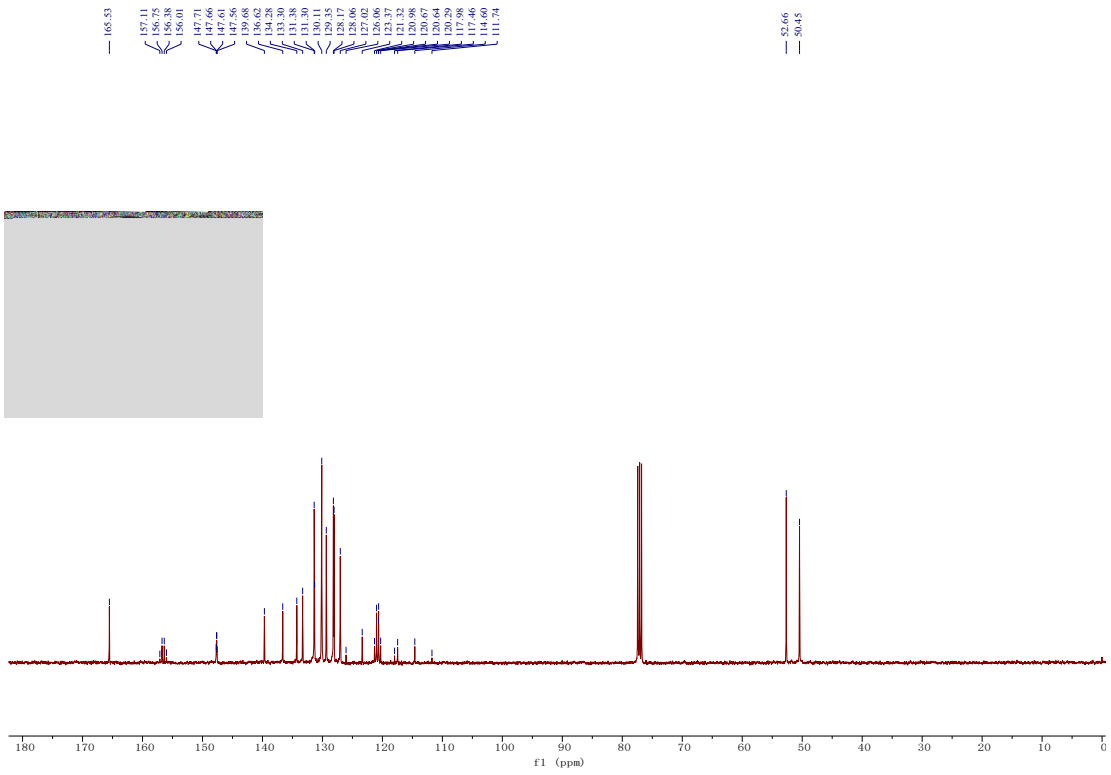

-57.34
-57.36
-57.38
-62.90
-67.91
-67.93
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160
f1 (ppm)


157.10
156.73
156.36
155.99
147.23
147.18
147.13
147.08
139.06
137.19
133.89
133.53
132.32
131.98
131.65
131.32
130.30
129.41
128.90
128.13
127.55
127.20
127.17
126.24
125.54
124.99
123.25
121.87
121.73
121.39
121.04
120.79
120.64
120.55
117.86
117.42
114.56
111.69
77.38
77.06
76.75
50.45
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

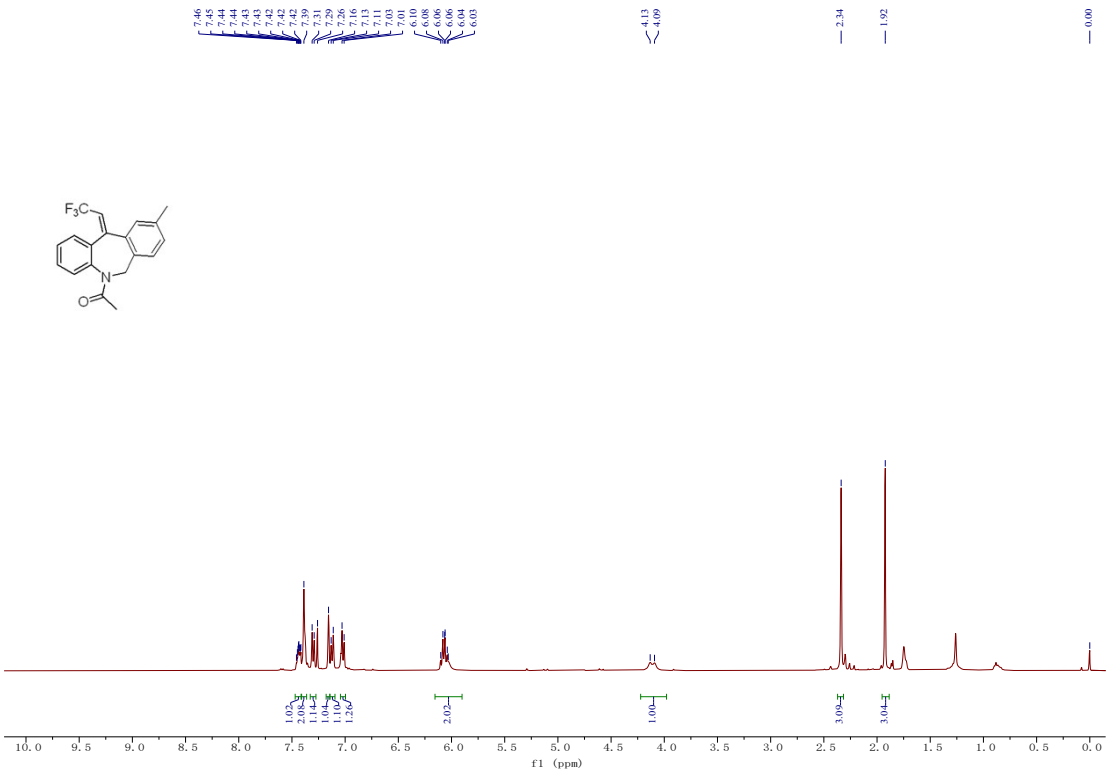
5u ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

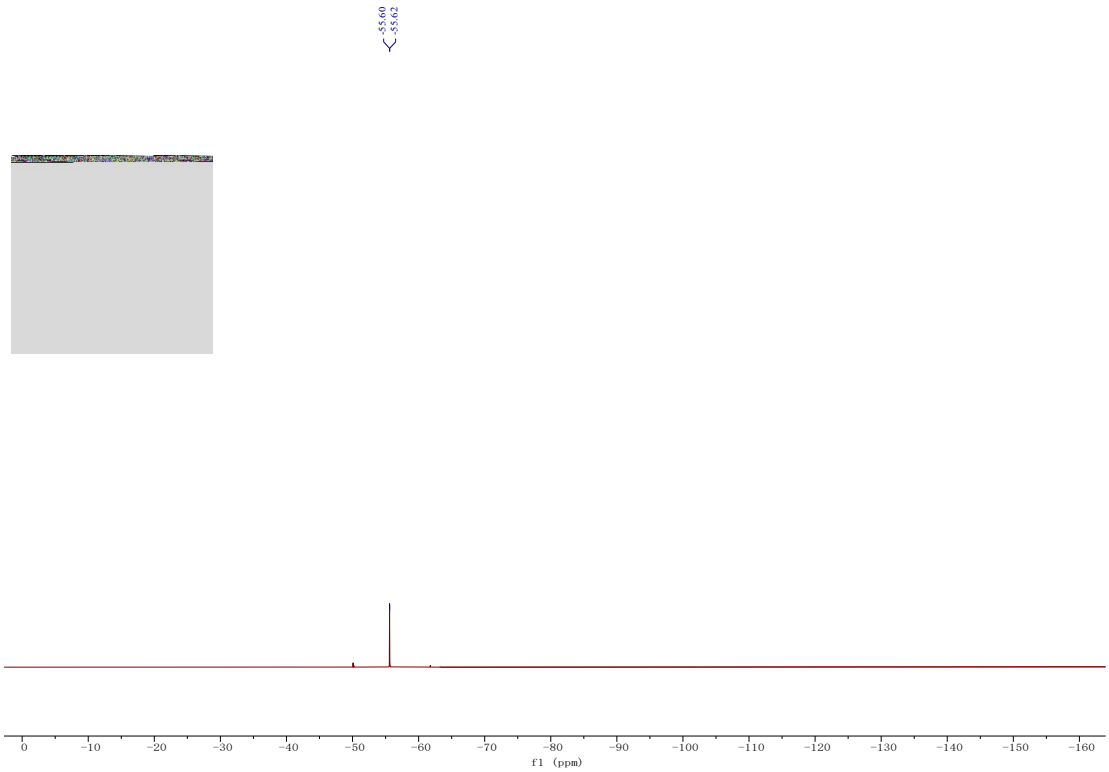


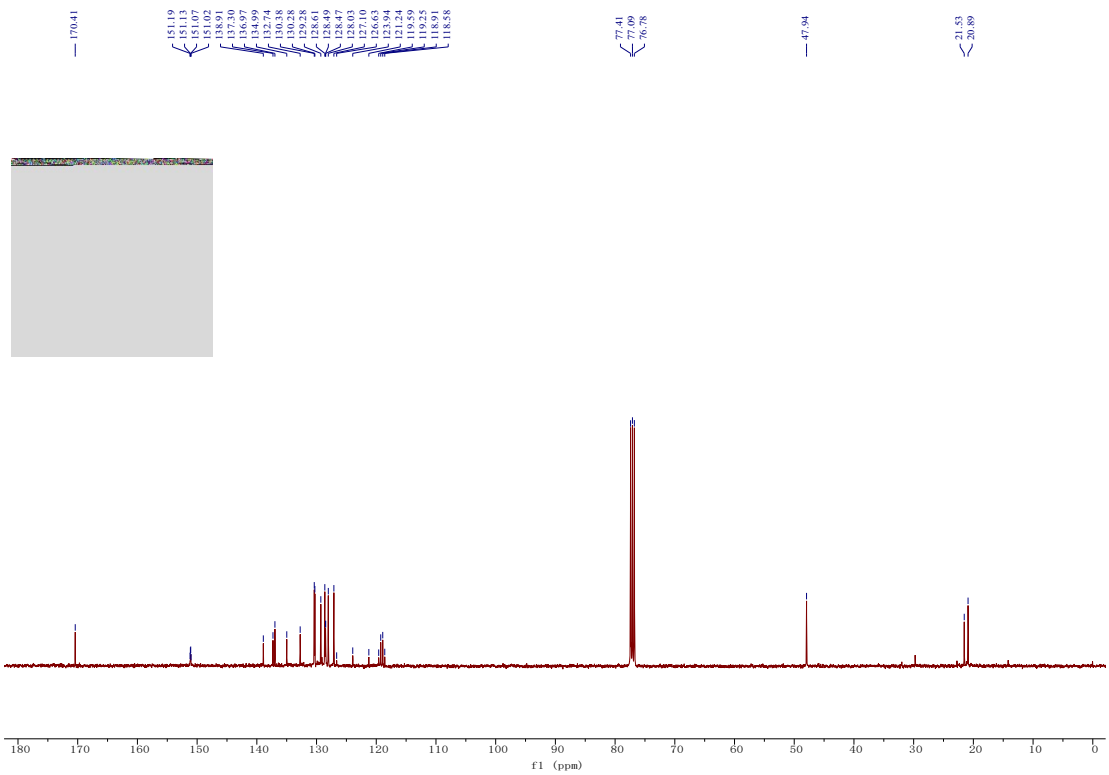




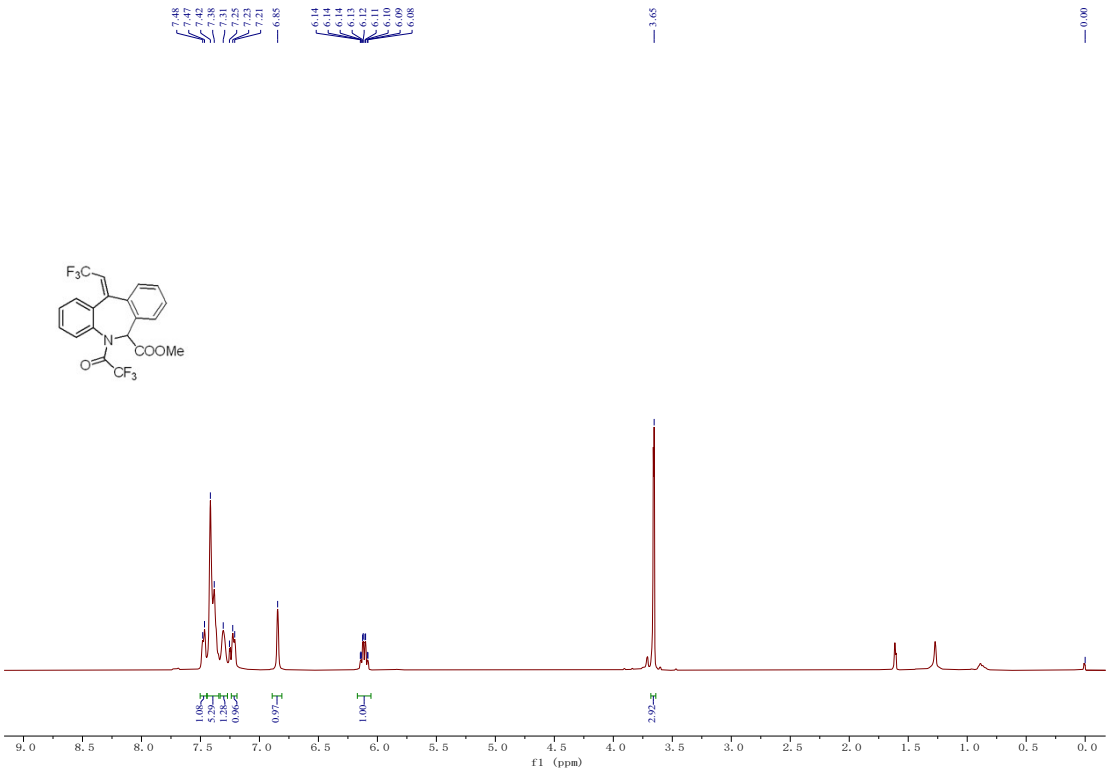
5v ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)

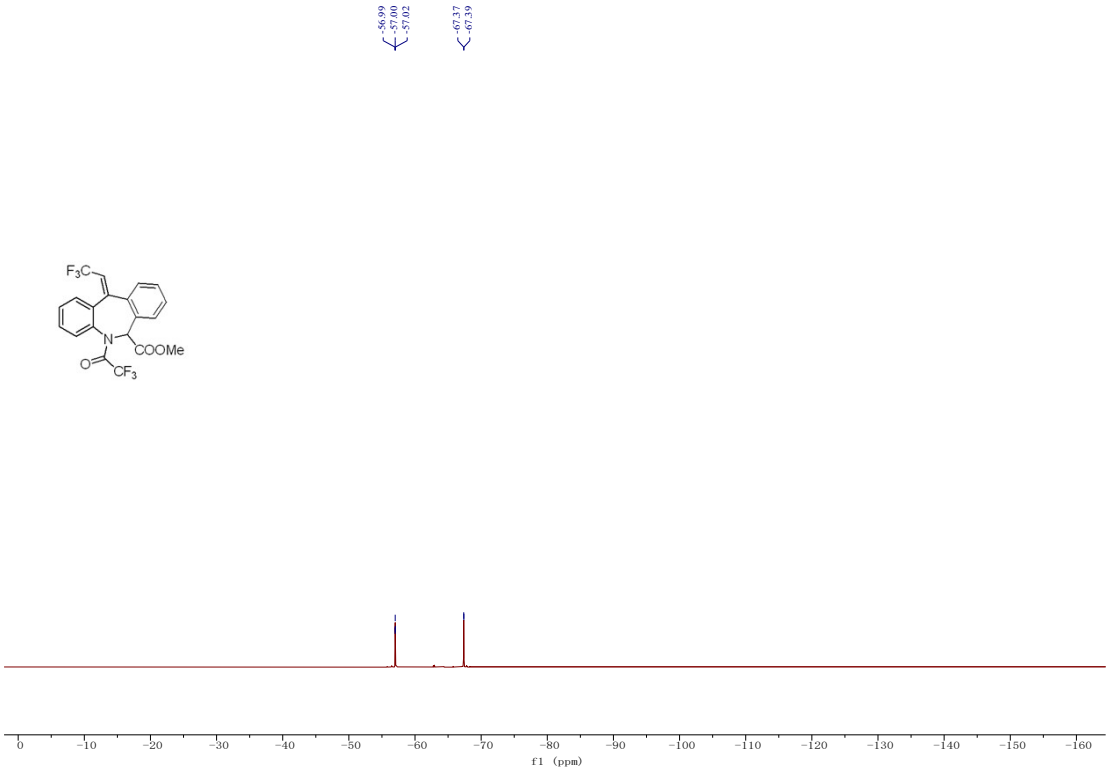


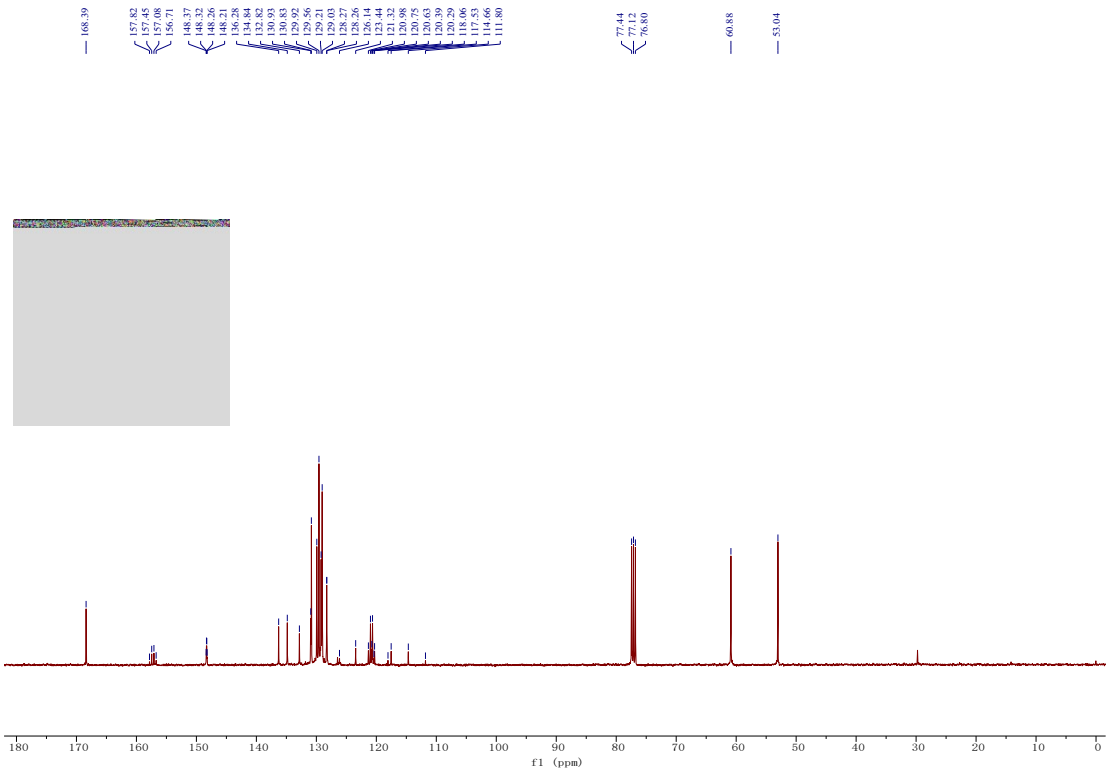

-55.60
-55.62
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
f1 (ppm)


170.41
151.19
151.13
151.07
151.02
138.91
137.30
136.97
134.99
132.74
130.38
130.28
129.28
128.61
128.49
128.47
128.03
127.10
126.63
123.94
121.24
119.59
119.25
118.91
118.58
77.41
77.09
76.78
47.94
21.53
20.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

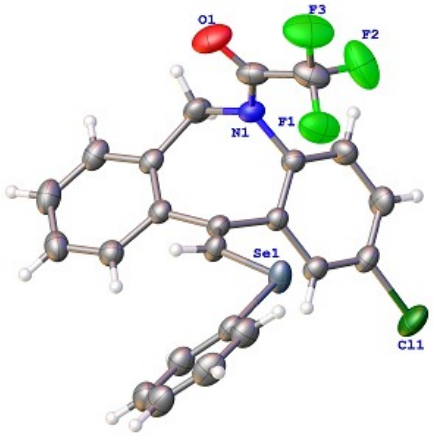
5w ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz)






168.39
157.82
157.45
157.08
156.71
148.37
148.32
148.26
148.21
136.28
134.84
132.82
130.93
130.63
129.92
129.56
129.21
129.03
128.27
128.26
126.14
123.44
121.32
120.98
120.75
120.63
120.39
120.29
118.66
117.53
114.66
111.80
77.44
77.12
76.80
60.88
53.04
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9. Crystal data and structure refinement



The X-ray crystallographic structure for **4f**. Crystal data have been deposited to CCDC, number 2212147.

Identification code	**4f**
Empirical formula	$C_{23}H_{15}ClF_3NOSe$
Formula weight	492.77
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.11240(10)
b/Å	16.3595(2)
c/Å	12.41890(10)
α/°	90
β/°	98.7950(10)
γ/°	90
Volume/Å^3	2030.35(4)
Z	4
ρ_{calc}g/cm^3	1.612
μ/mm^{-1}	4.096
F(000)	984.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.008 to 153.64
Index ranges	$-12 \le h \le 11$, $-19 \le k \le 19$, $-15 \le l \le 15$
Reflections collected	13217

Independent reflections	3942 [R_{int} = 0.0285, R_{sigma} = 0.0243]
Data/restraints/parameters	3942/0/271
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0385, wR_2 = 0.0983
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.57