Electronic Supplementary Information

Access to benzo-fused nine-membered heterocyclic alkenes with a trifluoromethyl carbinol moiety via a double decarboxylative formal ring-expansion process under palladium catalysis

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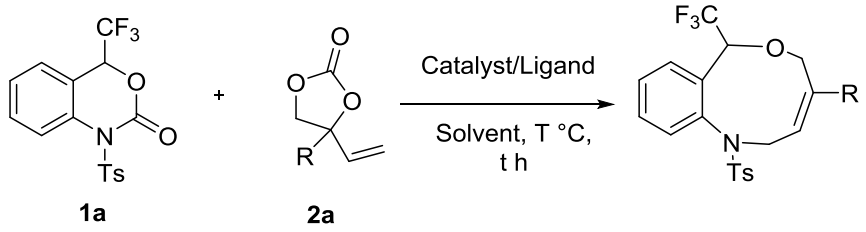
Table of Contents:

1. Optimization Data of Double Decarboxylative (DDC) reaction

Table S1: Preliminary Investigation:[a]

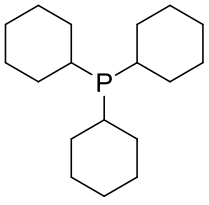


1a 2a

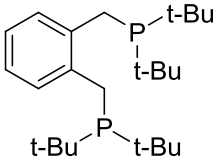
Entry	Catalyst	Ligand	Solvent	T (°C)	t (h)	Yield[b]
1[c]	10 mol % $Pd_2(dba)_3{\cdot}CHCl_3$	-	DCM	rt	24	-
2[d]	5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$	-	THF	40	24	-
3	5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$	10 mol % PCy_3	THF	40	24	-
4	5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$	10 mol % dtbpmb	THF	40	24	-
5	5 mol % $Pd(PPh_3)_4$	-	Tol	50	24	47 (42)
6	**5 mol % $Pd(PPh_3)_4$**	**-**	**Tol**	**50**	**36**	**68 (66)**
7	5 mol % $Pd(PPh_3)_4$	-	Tol	80	12	55 (45)
8	5 mol % $Pd(PPh_3)_4$	-	Tol	100	12	16 (10)

[a] Experiments were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) in 1mL solvent. [b] ^{19}F NMR yields with reference $PhCF_3$ and isolated yields are given in the parenthesis. [c,d] **2a** (0.12 mmol) was used.

PCy_3: Tricyclohexyl phosphine; dtbpmb: 1,2-Bis(di-^{t}butyl phosphinomethyl)benzene;



PCy_3



dtbpmb

Table S2: Solvent screening[a]

Entry	Catalyst	Solvent	T (°C)	t (h)	Yield[b]
1	5 mol % $Pd(PPh_3)_4$	Tol	50	36	68 (66)
2	5 mol % $Pd(PPh_3)_4$	THF	50	7	75 (70)
3	**5 mol % $Pd(PPh_3)_4$**	**DCE**	**50**	**12**	**83 (79)**
4	5 mol % $Pd(PPh_3)_4$	1,4-Dioxane	50	20	67 (62)
5	5 mol % $Pd(PPh_3)_4$	Xylene	50	24	78 (74)
6	5 mol % $Pd(PPh_3)_4$	Benzene	50	20	68 (64)
7	5 mol % $Pd(PPh_3)_4$	Acetonitrile	50	15	81 (74)

[a] Experiments were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) in 1mL solvent [b] ^{19}F NMR yields with reference $PhCF_3$ and isolated yields are given in the parenthesis.

Table S3: Temperature screening[a]

Entry	Catalyst	Solvent	T (°C)	t (h)	Yield[b]
1	5 mol % $Pd(PPh_3)_4$	DCE	50	12	83 (79)
2	**5 mol % $Pd(PPh_3)_4$**	**DCE**	**80**	**12**	**91 (89)**
3	5 mol % $Pd(PPh_3)_4$	DCE	Reflux	12	40 (34)

[a] Experiments were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) in 1mL DCE [b] ^{19}F NMR yields with reference $PhCF_3$ and isolated yields are given in the parenthesis.

Table S4: Catalyst and Additive screening[a]

Entry	Catalyst	Additive	Solvent	T (°C)	t (h)	Yield[b]
1	2 mol % $Pd(PPh_3)_4$	Et_3N (0.5 equiv)	DCE	50	12	34 (27)
2	2 mol % $Pd(PPh_3)_4$	K_2CO_3 (1.0 equiv)	DCE	50	12	75 (72)
3	2 mol % $Pd(PPh_3)_4$	Cs_2CO_3 (1.0 equiv)	DCE	50	12	72 (68)
4	2 mol % $Pd(PPh_3)_4$	K_2HPO_4 (1.0 equiv)	DCE	50	12	81 (79)
5	2 mol % $Pd(PPh_3)_4$	K_2HPO_4 (1.0 equiv)	DCE	40	12	68 (63)
6	2 mol % $Pd(PPh_3)_4$	K_2HPO_4 (1.0 equiv)	DCE	60	12	75 (71)
7	2 mol % $Pd(PPh_3)_4$	K_2HPO_4 (1.0 equiv)	DCE	reflux	12	44 (36)

[a] Experiments were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) in 1mL DCE. [b] ^{19}F NMR yields with reference $PhCF_3$ and isolated yields are given in the parenthesis.

Table S5: Amount of catalyst screening[a]

Entry	Catalyst	Solvent	T (°C)	t (h)	Yield[b]
1	2.5 mol % $Pd(PPh_3)_4$	DCE	80	12	64 (59)
2	**5 mol % $Pd(PPh_3)_4$**	**DCE**	**80**	**12**	**91 (89)**
3	10 mol % $Pd(PPh_3)_4$	DCE	80	12	11

[a] Experiments were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) in 1mL DCE [b] ^{19}F NMR yields with reference $PhCF_3$ and isolated yields are given in the parenthesis.

2. Density functional theory (DFT) calculation[1]

In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Spartan' 14 software. Geometry optimization was carried out by B3LYP/6-311+G** level of theory. The chemical reactivity descriptors calculated using DFT are: total energy (E), chemical hardness (η), electronic chemical potential (μ) and electrophilicity (ω).
Chemical hardness (η) measures the resistance to change in the electron distribution or charge transfer and it associates with the stability and reactivity of a chemical system. On the basis of frontier molecular orbitals, chemical hardness corresponds to the gap between the HOMO and LUMO. Chemical hardness is approximated using equation 1

$$\eta = (E_{LUMO} - E_{HOMO})/2 \qquad (1)$$

where E_{LUMO} and E_{HOMO} are the LUMO and HOMO energies.
Electronic chemical potential (μ) is defined as the negative of electronegativity of a molecule and calculated using equation 2.

$$\mu = (E_{LUMO} + E_{HOMO})/2 \qquad (2)$$

Physically, μ describes the escaping tendency of electrons from an equilibrium system.
Global electrophilicity index (ω), is calculated using the electronic chemical potential and chemical hardness as shown in equation 3.

$$\omega = \mu^2/2\eta \qquad (3)$$

This index measures the propensity or capacity of a species to accept electrons. It is a measure of the stabilization in energy after a system accepts additional amount of electronic charge from the environment.

3. Structural and electronic properties

DFT calculations were performed for benzoxazinanone **1** derivatives. The contour plots of the frontier orbitals for the ground state are shown in Figure S1 including the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

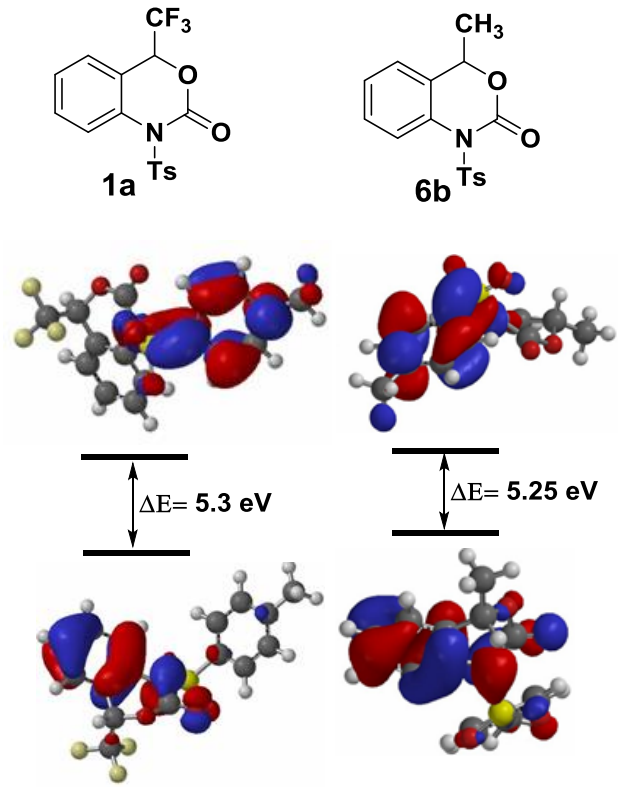


Figure S1. Frontier molecular orbitals of benzoxazinanone **1** derivatives.

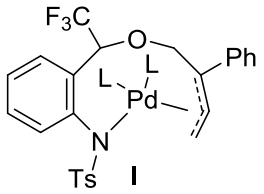
Table S6 contains the computed global chemical reactivity indices for compounds **1a** and **6b**. The electrophilicity (ω) values for the derivatives **1a** and **6b** are 3.67 eV and 3.33 eV respectively. Among the derivatives, derivative **1a** is the strongest electrophilic compared to **6b**.

Table S6. Comparative studies of global chemical reactivity indices of benzoxazinanone **1** derivatives.

	1a; R=CF_3	**6b; R=CH_3**
Total Energy, E (au)	-1670.62	-1372.81
E_{HOMO} (eV)	-7.06	-6.81
E_{LUMO} (eV)	-1.76	-1.56
Dipole moment (debye)	6.83	4.54
Energy gap (Δ) (eV)	5.30	5.25
Chemical hardness, η(eV)	2.65	2.63
Electronic chemical potential, μ(eV)	- 4.41	- 4.18
Global electrophilicity index, ω(eV)	3.67	3.33

4. LC-MS analysis of Pd-π-allyl complex I

LC-MS analysis confirmed that the Pd-π-allyl complex **I** was formed during the progress of the reaction. LC-MS (ESI, m/z): $[M]^+$ 1103.85 (isotopic pattern) (Figure S2)



m/z= 1103.85
(LC-MS)

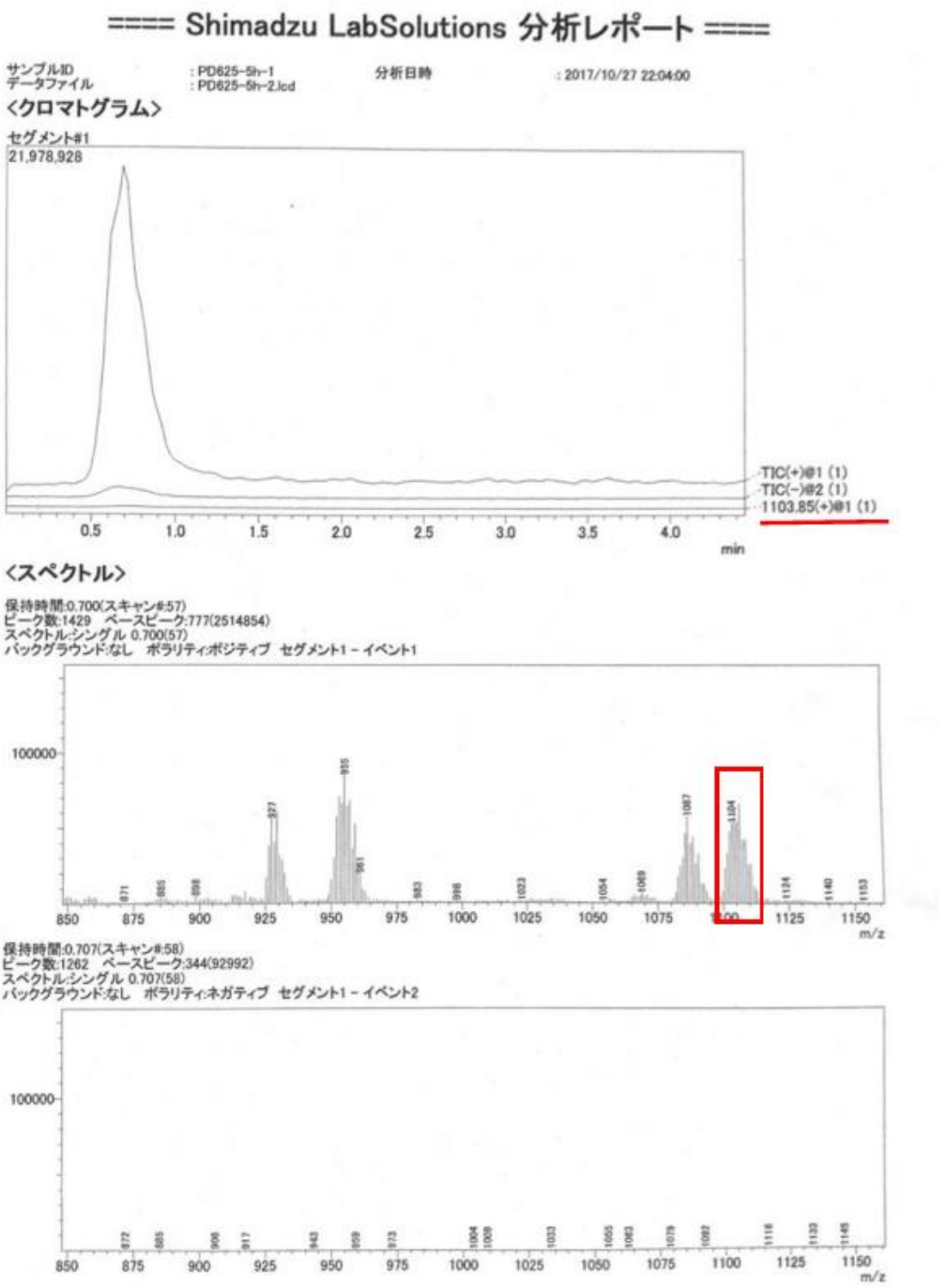


Figure S2. LC-MS spectra of Pd-π-allyl complex **I.**

5. ^{19}F NMR studies to observe the progress of the DDC reaction

To an oven dried NMR tube **1a** (0.03 mmol, 0.011 g, 1.0 equiv) was transferred inside the glove box. To it 0.5 mL DCE-d_4 was added and recorded the ^{19}F NMR [Figure S3 a)]. To the above solution, $Pd(PPh_3)_4$ (0.009 mmol, 0.0104 g, 0.3 equiv) was added and stirred at room temperature and recorded the NMR spectra after 4 h [Figure S3 b)]. **2a** was added to the above reaction mixture inside the glove box and recorded the crude ^{19}F NMR spectra after 10 min, 1 h, 12 h and 18 h [Figure S3 c)-f)] respectively. After 10 min of addition of **2a**, progress of the reaction was observed through the NMR spectra. After 18 h, i.e. completion of the reaction, we had added D_2O to the above reaction mixture and stirred vigorously to ensure complete mixing and recorded the NMR spectra [Figure S3 g)].

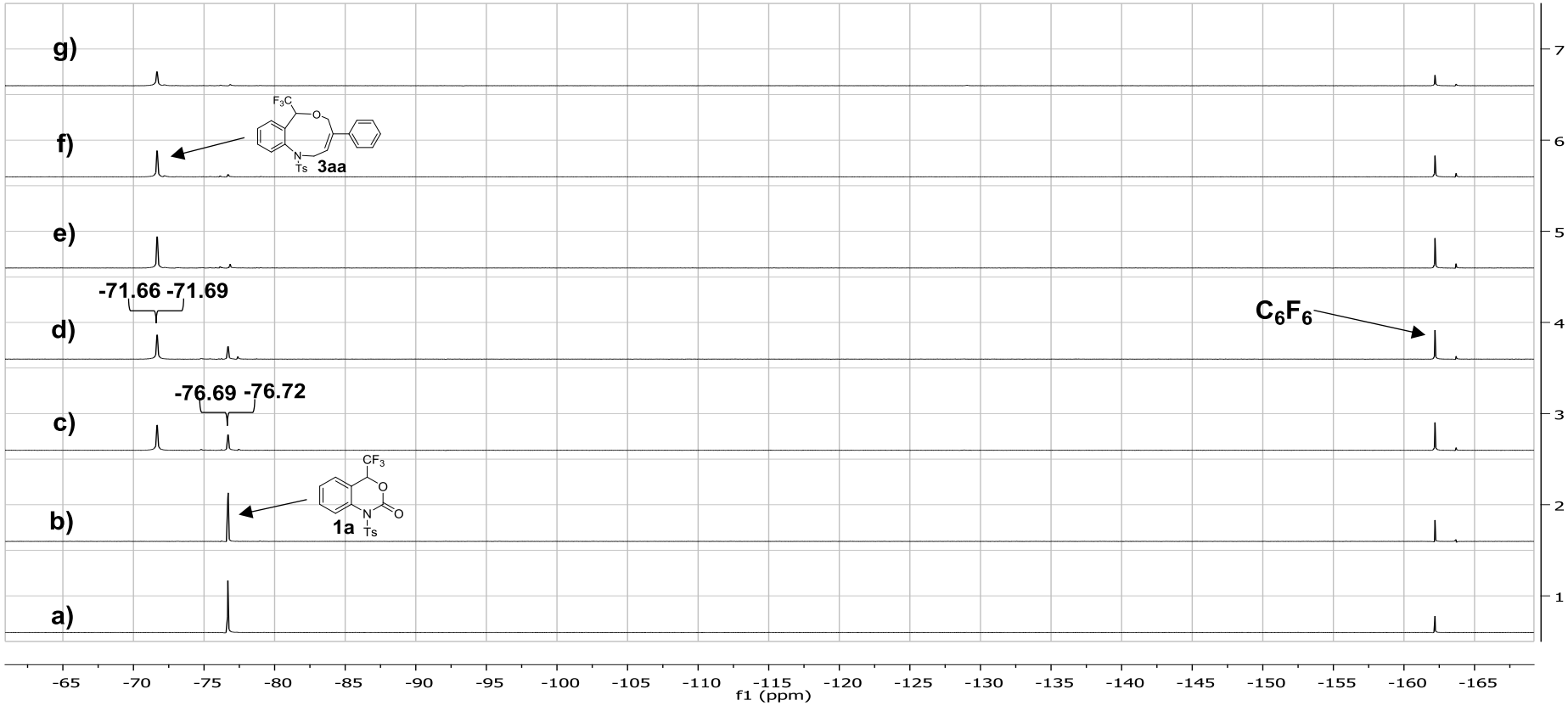


Figure S3. ^{19}F NMR investigation in between the reaction of 1a and 2a in DCE-*d*$_4$.

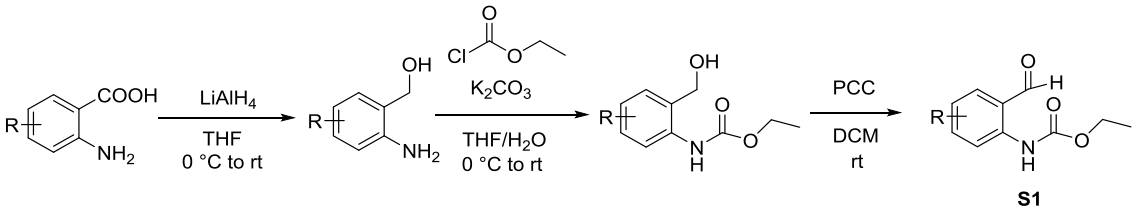
6. General information

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen or argon. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All solvents were dried by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat or *p*-anisaldehyde solution/heat. All of the reaction products were purified by column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 mm. The ^{1}H NMR (300 MHz, 400 MHz and 500 MHz) and ^{19}F NMR (282 MHz) spectra (with Hexafluorobenzene (δ ppm −162.2) as an internal standard) as for solution in $CDCl_3$ were recorded on a Varian Mercury 300. ^{13}C NMR (126 MHz) spectra for solution in $CDCl_3$ was recorded on a BRUKER 500 UltraShieldTR . Chemical shifts (δ) are expressed in ppm downfield from internal TMS or C_6F_6. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020(ESI-MS). Infrared spectra were recorded on JASCO FT/IR-200 or a JASCO FT/IR-4100 spectrometer. Melting points were measured on Buchi M-565 device.

Commercially available chemicals were obtained from Aldrich Chemical Co., Alfa Aesar, TCI, Ark Farm and used as received unless otherwise stated. The residual solvent signals were used as references (TMS: δH = 0.00 ppm, δC =77.16 ppm; and C_6F_6: δF = −162.2

ppm). High resolution mass spectrometry (HRMS) was carried out on an electron impact ionization mass spectrometer with a micro-TOF analyzer.

7. General experimental procedure for the preparation of substituted ethyl (2-formylphenyl)carbamate S1 (method A)



The substituted ethyl (2-formylphenyl)carbamate S**1** were prepared according to literature procedures[2,3,4] in three steps starting from substituted 2-aminobenzoic acid.

To a solution of substituted 2-amino-benzoic acid (20 mmol) in dry THF (30 mL) was added dropwise a solution of $LiAlH_4$ in THF (1M, 30 mL) while the temperature was maintained at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then hydrolyzed by dropwise addition of water (5 mL) and 5% NaOH (7 mL). The resulting suspension was filtered and the precipitate was washed with ethyl acetate. Then the combined organic phase was evaporated. The residue was recrystallized from ethyl acetate and petroleum ether, affording the corresponding alcohols quantitatively as a fine white or pale yellow solid.

To a solution of substituted 2-amino benzyl alcohol in saturated K_2CO_3 aq. and THF (v:v= 2:1, 45 mL) was added ethyl chloroformate (25 mmol). The mixture was stirred at room temperature for 3 h and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to afford the desired substituted *N*-protected 2-aminobenzyl alcohol without purification.

In a flame dried 200 mL two neck round bottom flask, pyridinium chlorochromate (4.85 g, 22.5 mmol, 1.5 equiv) was suspended in anhydrous DCM (60 mL) fitted with a 100-mL addition funnel. A solution of substituted *N*-protected 2-aminobenzyl alcohol (3.13 g, 15 mmol, 1.0 equiv) in anhydrous DCM (60 mL) was placed in the addition funnel and dropwise added to the flask. As the addition progressed, the reaction became black and opaque. The reaction was stirred for 2.5 h at ambient temperature. Upon completion, the black solution was decanted from the black precipitate and filtered through a short pad of silica gel. The precipitate was washed with DCM (15 mL × 3) to ensure complete transfer.

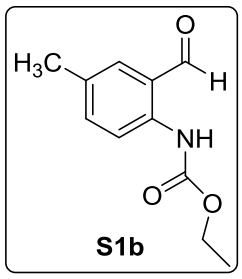
The DCM was removed *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (using 8:2 hexane/ethyl acetate).

Starting materials **S1a** was reported in previous articles.[5]

Stabilized vinylethylene carbonates **2** were prepared according to the known procedure.[6]

Ethyl (2-formyl-4-methylphenyl)carbamate (S1b)

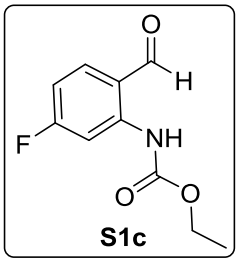
Cream colored solid, 90% yield, mp. 39.7-42.2 °C. Using the general method A, in a flame dried 200 mL two neck round bottom flask, pyridinium chlorochromate (4.85 g, 22.5 mmol, 1.5 equiv) was suspended in anhydrous DCM (60 mL) fitted with a 100-mL addition funnel. A solution of substituted *N*-protected 2-amino-5-methylbenzyl alcohol (3.13 g, 15 mmol, 1.0 equiv) in anhydrous DCM (60 mL) was placed in the addition funnel and added dropwise to the flask. The reaction was stirred for 2.5 h at ambient temperature. After completion of the reaction DCM was removed *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (using 8:2 hexane/ethyl acetate) to obtain the pure product.



^{1}H NMR (300 MHz, $CDCl_3$) δ 10.46 (s, 1H, -CHO), 9.86 (s, 1H, -NH), 8.45 – 8.26 (m, 2H, ArH), 7.42 (s, 1H, ArH), 4.24 (q, *J* = 7.1 Hz, 2H, -O-CH_2), 2.37 (s, 3H, Ar-CH_3), 1.33 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.28, 153.92, 139.11, 136.98, 136.23, 131.49, 121.36, 118.43, 61.42, 20.46, 14.62. **IR** (KBr): 2975, 2927, 2873, 1737, 1660, 1590, 1529, 1396, 1319, 1058, 887, 767. cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{13}NO_3Na$ $[M+Na]^+$ 230.0793, found 230.0790.

Ethyl (5-fluoro-2-formylphenyl)carbamate (S1c)

Cream colored solid, 67% yield, mp 30.6-36.8 °C. Using the general method A, in a flame dried 200 mL two neck round bottom flask, pyridinium chlorochromate (3.23 g, 15 mmol, 1.5 equiv) was suspended in anhydrous DCM (50 mL) fitted with a 100-mL addition funnel. A solution of substituted *N*-protected 2-amino-4-fluorobenzyl alcohol (2.1 g, 10 mmol, 1.0 equiv) in anhydrous DCM (50 mL) was placed in the addition funnel and added dropwise to the flask. The reaction was stirred for 2.5 h at ambient temperature. After completion of the reaction, DCM was removed *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (using 8:2 hexane/ethyl acetate) to obtain the pure product.

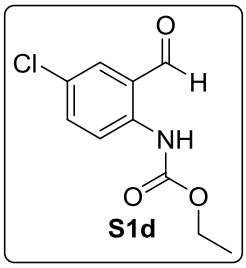


^{1}H NMR (300 MHz, $CDCl_3$) δ 10.75 (s, 1H,-CHO), 9.84 (s, 1H, NH), 8.23 (d, *J* = 12.0 Hz, 1H, ArH), 7.74 – 7.53 (m, 1H, ArH), 6.95 – 6.72 (m, 1H, ArH), 4.24 (q, *J* = 7.1 Hz, 2H, -OCH_2), 1.33 (t, *J*

= 7.1 Hz, 3H,CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.70, 167.53 (d, *J* = 256.2 Hz), 153.66, 144.05 (d, *J* = 13.7 Hz), 138.71 (d, *J* = 12.0 Hz), 118.30 (d, *J* = 1.8 Hz), 109.59 (d, *J* = 23.4 Hz), 105.93 (d, *J* = 28.8 Hz), 61.85, 14.56. **IR** (KBr): 3250, 3117, 2991, 1737, 1678, 1536, 1401, 1324, 1198, 1114, 872, 770, 725 cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_9FNO_3$ $[M-H]^-$ 210.0566, found 210.0558.

Ethyl (4-chloro-2-formylphenyl)carbamate (S1d)

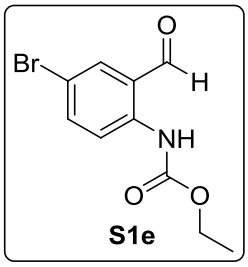
Cream colored solid, 84% yield, mp. 73.4-75.1 °C. Using the general method A, in a flame dried 200 mL two neck round bottom flask, pyridinium chlorochromate (3.6 g, 16.5 mmol, 1.5 equiv) was suspended in anhydrous DCM (40 mL) fitted with a 100-mL addition funnel. A solution of substituted *N*-protected 2-amino-5-chlorobenzyl alcohol



(2.52 g, 11 mmol, 1.0 equiv) in anhydrous DCM (40 mL) was placed in the addition funnel and added dropwise to the flask. The reaction was stirred for 2.5 h at ambient temperature. After completion of the reaction DCM was removed *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (using 8:2 hexane/ethyl acetate) to obtain the pure product. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.47 (s, 1H, CHO), 9.85 (s, 1H, NH), 8.46 (d, *J* = 9.0 Hz, 1H, ArH), 7.61 (d, *J* = 2.5 Hz, 1H, ArH), 7.53 (dd, *J* = 9.0, 2.5 Hz, 1H, ArH), 4.25 (q, *J* = 7.1 Hz, 2H, -OCH_2), 1.34 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.97, 153.67, 140.02, 135.96, 135.06, 127.00, 122.29, 120.14, 61.77, 14.56. **IR** (KBr): 2985, 2911, 2871, 2765, 1727, 1590, 1309, 1093, 728, 651 cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_9ClNO_3$ $[M-H]^-$ 226.0271, found 226.0269.

Ethyl (4-bromo-2-formylphenyl)carbamate (S1e)

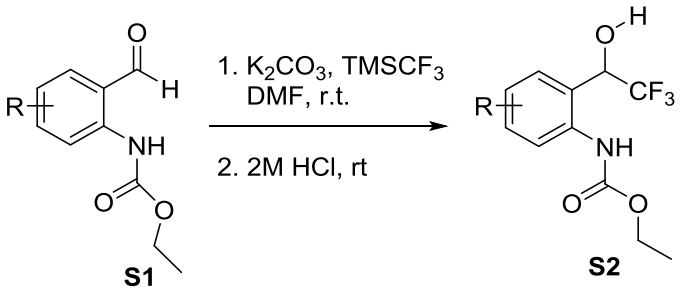
White powder, 91% yield, mp. 90.5-91.5 °C. Using the general method A, in a flame dried 200 mL two neck round bottom flask, pyridinium chlorochromate (3.4 g, 15.9 mmol, 1.5 equiv) was suspended in anhydrous DCM (40 mL) fitted with a 100-mL addition funnel.



A solution of substituted *N*-protected 2-amino-5-bromobenzyl alcohol (2.9 g, 10.6 mmol, 1.0 equiv) in anhydrous DCM (40 mL) was placed in the addition funnel and added dropwise to the flask. The reaction was stirred for 2.5 h at ambient temperature. After completion of the reaction DCM was removed *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (using 8:2 hexane/ethyl acetate) to obtain the pure product. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.47 (s, 1H, -CHO), 9.84 (s, 1H, NH), 8.40 (d, *J* = 9.0 Hz,

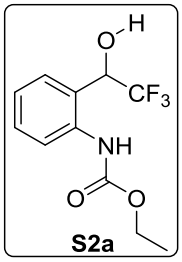
1H, ArH), 7.75 (d, *J* = 2.4 Hz, 1H, ArH), 7.69 – 7.65 (m, 1H, ArH), 4.25 (q, *J* = 7.1 Hz, 2H, -OCH_2), 1.34 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.91, 153.64, 140.49, 138.80, 138.10, 122.69, 120.42, 114.00, 61.80, 14.56. **IR** (KBr): 2983, 2867, 1729, 1585, 1386, 1309, 1058, 885, 808, 767, 715 cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_9BrNO_3$ $[M-H]^-$ 269.9766, found 269.9768.

8. General experimental procedure for the synthesis of CF_3 substituted alcohol S2 (method B)[7]



In a flame dried 100 mL round bottom flask, aldehyde **S1a** (10 mmol, 1.932 g, 1.0 equiv) and $TMSCF_3$ (neat, 20 mmol, 3 mL, 2.0 equiv) was suspended in anhydrous DMF (20 mL). To this solution dry K_2CO_3 (10 mol %, 0.138 g, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. Completion of the reaction was monitored by TLC. To this reaction mixture, 2M HCl solution (4 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3×30 mL). Combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4, and then solvent was removed under reduced pressure. The crude product was further purified by column chromatography (using 8:2 hexane/ethyl acetate) to afford pure product **S2a**. The characterization data of **S2a** are summarized below.

Ethyl (2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)carbamate (S2a)

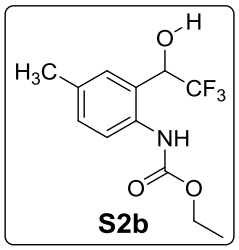


White solid, 62% yield, mp. 104.2-106.9 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 25.1 Hz, 1H, ArH), 7.40 – 7.28 (m, 1H, ArH), 7.24 (d, *J* = 7.7 Hz, 1H, ArH), 7.10 (t-like, *J* = 7.5 Hz, 1H, ArH), 5.08 – 5.01 (m, 1H, CH-CF_3), 4.42 (d-like, *J* = 4.6 Hz, 1H, -OH), 4.16 (q, *J* = 7.1 Hz, 2H, -OCH_2), 1.28 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.93, 137.23, 130.26, 129.64, 124.58 (q, *J* = 282.8 Hz), 124.31, 123.71, 123.04, 72.64 (q, *J* = 33.6 Hz), 61.79, 14.52. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.69 (d, *J* = 7.0 Hz, 3F). **IR** (KBr): 3334, 2991, 1702, 1594, 1452, 1357, 1261, 1170, 1068, 838,

754 cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{12}F_3NO_3Na$ $[M+Na]^+$ 286.0667, found 286.0673.

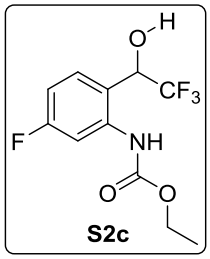
Ethyl (4-methyl-2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)carbamate (S2b)

Light yellow solid, 61% yield, mp. 131.5-133.0 °C. Using the general method B, in a flame dried 100 mL round bottom flask, aldehyde **S1b** (5 mmol, 1.03 g, 1.0 equiv) and $TMSCF_3$ (neat, 10 mmol, 1.5 mL, 2.0 equiv) was suspended in anhydrous DMF (15 mL). To this solution dry K_2CO_3 (10 mol %, 0.07 g, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. After completion of the reaction, 2M HCl solution (2 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3 × 30 mL) and purified by column chromatography (using 8:2 hexane/ethyl acetate) to afford pure product **S2b**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 1.9 Hz, 1H, ArH), 7.17 (d, *J* = 1.5 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 5.14 – 5.06 (m, 1H, -CH-CF_3), 4.19 (q, *J* = 7.1 Hz, 2H, -OCH_2), 3.62 (d-like, *J* = 4.6 Hz, 1H, OH), 2.33 (s, 3H, Ph-CH_3), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.99, 134.65, 134.34, 131.02, 129.73, 124.62, 124.61 (q, *J* = 282.5 Hz), 123.86, 71.88 (q, *J* = 28.5 Hz), 61.72, 20.94, 14.63. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.46. **IR** (KBr): 3307, 2992, 2744, 1693, 1602, 1531, 1348, 1261, 1166, 1068, 840, 775 cm^{-1}. **HRMS** (ESI) calculated for $C_{12}H_{14}F_3NO_3Na$ $[M+Na]^+$ 300.0823, found 300.0825.



Ethyl (5-fluoro-2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)carbamate (S2c)

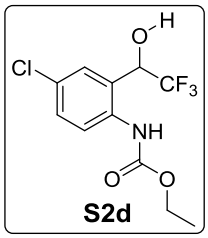
White solid, 77% yield, mp. 115.7-117.5 °C. Using the general method B, in a flame dried 100 mL round bottom flask, aldehyde **S1c** (3.8 mmol, 0.8 g, 1.0 equiv) and $TMSCF_3$ (neat, 5.3 mmol, 0.8 mL, 1.4 equiv) was suspended in anhydrous DMF (10 mL). To this solution dry K_2CO_3 (10 mol %, 0.05 g, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. After completion of the reaction, 2M HCl solution (1 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3 × 30 mL) and purified by column chromatography (using 8:2 hexane/ethyl acetate) to afford pure product **S2c**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (br s, 1H, -NH), 7.79 (d, *J* = 8.7 Hz, 1H, ArH), 7.23 – 7.13 (m, 1H, ArH), 6.79 – 6.75 (m, 1H, ArH), 5.18 – 4.99 (m, 1H,-CH-CF_3), 4.21 (q, *J* = 7.1 Hz, 2H, -CH_2), 3.72 (br s, 1H, -OH), 1.31 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.59 (d, *J* = 247.8 Hz), 153.98, 139.49 (d, *J* = 11.5 Hz), 131.16



(d, *J* = 10.0 Hz), 124.26 (q, *J* = 282.7 Hz), 117.36, 110.40 (d, *J* = 22.0 Hz), 109.24 (d, *J* = 27.1 Hz), 73.07 (q, *J* = 33.0 Hz), 61.74, 14.41. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.92 (d, *J* = 7.0 Hz, 3F), -109.93 (s, 1F). **IR** (KBr): 3322, 1700, 1544, 1444, 1270, 1171, 1125, 1063, 811 cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{11}F_4NO_3Na$ $[M+Na]^+$ 304.0573, found 304.0578.

Ethyl (4-chloro-2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)carbamate (S2d)

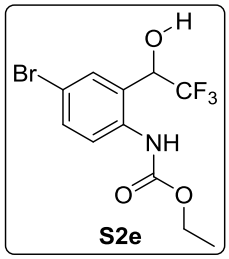
White solid, 62% yield, mp. 95.2-98.7 °C. Using the general method B, in a flame dried 100 mL round bottom flask, aldehyde **S1d** (9 mmol, 2.0 g, 1.0 equiv) and $TMSCF_3$ (neat, 18 mmol, 2.66 mL, 2.0 equiv) was suspended in anhydrous DMF (20 mL). To this solution dry K_2CO_3 (10 mol %, 0.12 g, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. After completion of the reaction, 2M HCl solution (2 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3 × 30 mL) and purified by column chromatography (using 8:2 hexane/ethyl acetate) to afford pure product **S2d**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.33 (d, *J* = 8.8 Hz, 1H, ArH), 5.11 – 5.00 (m, 1H, -CH-CF_3), 4.19 (q, *J* = 7.0 Hz, 2H, -CH_2), 1.30 (t, *J* = 7.4 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.59, 135.83, 130.34, 129.63, 129.41, 125.22, 124.48, 124.28 (q, *J* = 283.0 Hz), 72.08 (q, *J* = 33.1 Hz), 61.99, 14.55. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.78 (d, *J* = 7.4 Hz, 3F). **IR** (KBr): 3289, 2992, 1693, 1589, 1529, 1407, 1303, 1174, 910, 840, 746 cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{11}ClF_3NO_3Na$ $[M+Na]^+$ 320.0277, found 320.0273.



S2d

Ethyl (4-bromo-2-(2,2,2-trifluoro-1-hydroxyethyl)phenyl)carbamate (S2e)

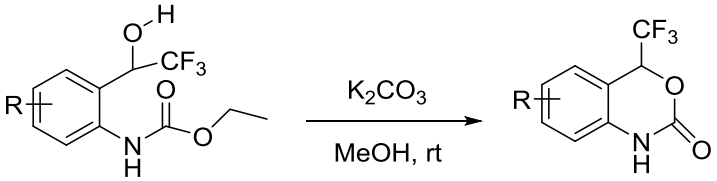
White solid, 79% yield, mp. 86.0-89.2 °C. Using the general method B, in a flame dried 100 mL round bottom flask, aldehyde **S1e** (9.5 mmol, 2.58 g, 1.0 equiv) and $TMSCF_3$ (neat, 19 mmol, 2.81 mL, 2.0 equiv) was suspended in anhydrous DMF (25 mL). To this solution dry K_2CO_3 (10 mol %, 0.131 g, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. After completion of the reaction, 2M HCl solution (2 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3 × 30 mL) and purified by column chromatography (using 8:2 hexane/ethyl acetate) to afford pure product **S2e**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (br s, 1H, NH), 7.75 (s, 1H, ArH), 7.47 (d, *J* = 2.3 Hz, 1H, ArH), 7.40 (d, *J* = 1.9 Hz, 1H, ArH), 5.07 – 5.00 (m, 1H,



S2e

-CH-CF_3), 4.37 (br d, *J* = 4.5 Hz, 1H, -OH), 4.18 (q, *J* = 7.1 Hz, 2H, -CH_2), 1.30 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.58, 138.90, 138.20, 136.42, 133.25, 132.36, 124.55, 123.17 (q, *J* = 283.5 Hz), 72.19 (q, *J* = 32.5 Hz), 62.01, 14.53. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -71.94 (d, *J* = 7.9 Hz, 3F). **IR** (KBr): 3340, 2992, 1708, 1587, 1513, 1398, 1178, 885, 838, 728 cm^{-1}. **HRMS** (ESI) calculated for $C_{11}H_{10}BrF_3NO_3$ $[M-H]^-$ 339.9796, found 339.9790.

9. General experimental procedure for the synthesis of substituted 4-(trifluoromethyl)-1,4-dihydro-benzoxazin-2-one S3 (method C)

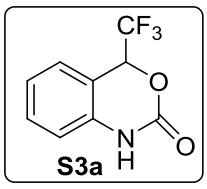


S2 **S3**

In a flame dried 100 mL round bottom flask, compound **S2a** (5 mmol, 1.316 g, 1.0 equiv) was suspended in anhydrous MeOH (30 mL). To this solution dry K_2CO_3 (1 mmol, 1.037 g, 1.5 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The reaction mixture was then extracted with ethyl acetate (3× 30 mL). Combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4, and then solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **S3a.** The characterization data of **S3a** are summarized below.

4-(Trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3a)

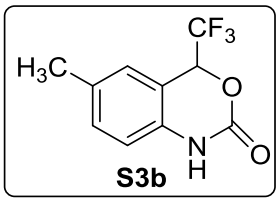
White solid, 98% yield, mp. 179.9-182.1 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 1H, ArH), 7.27 (d, *J* = 0.8 Hz, 1H, ArH), 7.20 – 7.11 (m, 1H, ArH), 6.92 (d, *J* = 8.0 Hz, 1H, ArH), 5.66 (q, *J* = 6.5 Hz, 1H, -CH-CF_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.83, 135.36, 131.44, 127.07, 124.04, 122.82 (q, *J* = 284.3 Hz), 115.00, 110.89, 76.61 (q, *J* = 34.4 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.56 (d, *J* = 6.5 Hz, 3F). **IR** (KBr):3170, 3114, 3004, 2944, 1995, 1725, 1608, 1502, 1384, 1274, 1186, 1081, 854, 755 cm^{-1}. **HRMS** (ESI) calculated for $C_9H_6F_3NO_2Na$ $[M+Na]^+$ 240.0248, found 240.0238.



S3a

6-Methyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3b)

Dirty white solid, 78% yield, mp. 207.9-210.2 °C. Using the general method C, in a flame dried 100 mL round bottom flask, compound **S2b** (2.85 mmol, 0.79 g, 1.0 equiv) was suspended in anhydrous MeOH (25 mL). To this solution dry K_2CO_3 (2.85 mmol, 0.4 g, 1.0 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated, extracted with ethyl acetate and the crude product was purified by flash column chromatography (using 6:4 hexane/ethyl acetate) to obtain the pure product **S3b**.

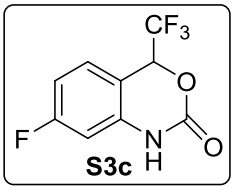


S3b

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (br s, 1H, NH), 7.19 (d, *J* = 8.1 Hz, 1H, ArH), 7.04 (s, 1H, ArH), 6.79 (d, *J* = 8.1 Hz, 1H, ArH), 5.58 (q, *J* = 6.5 Hz, 1H, -CH-CF_3), 2.34 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.73, 133.85, 132.93, 132.01, 127.36, 122.86 (q, *J* = 284.76 Hz), 114.79, 110.78, 76.48 (q, *J* = 34.02 Hz), 20.91. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.42 (d, *J* = 6.5 Hz, 3F). **IR** (KBr): 2950, 2346, 1724, 1621, 1425, 1299, 1187, 1135, 931, 734 cm^{-1}. **HRMS** (ESI) calculated for $C_{10}H_8F_3NO_2Na$ $[M+Na]^+$ 254.0405, found 254.0405.

7-Fluoro-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3c)

White solid, 74% yield, mp. 170.5-174.5 °C. Using the general method C, in a flame dried 100 mL round bottom flask, compound **S2c** (2.85 mmol, 0.8 g, 1.0 equiv) was suspended in anhydrous EtOH (15 mL). To this solution dry K_2CO_3 (2.85 mmol, 0.39 g, 1.0 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated, extracted with ethyl acetate and the crude product was purified by flash column chromatography (using 6:4 hexane/ethyl acetate) to obtain the pure product **S3c**.

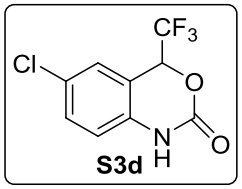


S3c

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (br s, 1H, NH), 7.22 (d, *J* = 6.5 Hz, 1H, ArH), 6.95 – 6.77 (m, 1H, ArH), 6.67 (dd, *J* = 8.8, 2.1 Hz, 1H, ArH), 5.63 (q, *J* = 6.4 Hz, 1H, -CH-CF_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.39 (d, *J* = 250.8 Hz), 149.38, 137.17 (d, *J* = 11.3 Hz), 128.99 (d, *J* = 10.0 Hz), 122.68 (q, *J* = 283.9 Hz), 111.31 (d, *J* = 22.6 Hz), 106.71, 102.75 (d, *J* = 26.5 Hz), 76.29 (q, *J* = 34.8 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.75 (d, *J* = 6.4 Hz, 3F), -108.16 – -108.28 (m, 1F). **IR** (KBr): 3114, 3089, 2924, 1618, 1522, 1499, 1421, 1378, 1266, 1199, 1137, 1113, 858, 736 cm^{-1}. **HRMS** (ESI) calculated for $C_9H_4F_4NO_2$ $[M-H]^-$ 234.0178, found 234.0162.

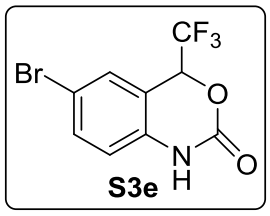
6-Chloro-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3d)

Cream color solid, 82% yield, mp. 216.8-220.4 °C. Using the general method C, in a flame dried 100 mL round bottom flask, compound **S2d** (5.4 mmol, 1.61 g, 1.0 equiv) was suspended in anhydrous MeOH (50 mL). To this solution dry K_2CO_3 (6.5 mmol, 0.89 g, 1.2 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated, extracted with ethyl acetate and the crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **S3d**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (br s, 1H, NH), 7.38 (d, *J* = 8.3 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 6.85 (d, *J* = 8.5 Hz, 1H, ArH), 5.60 (q, *J* = 6.3 Hz, 1H, -CH-CF_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.99, 134.04, 131.62, 129.33, 127.14, 122.57 (q, *J* = 284.3 Hz), 116.20, 112.44, 76.10 (q, *J* = 34.6 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.30 (d, *J* = 6.3 Hz, 3F). **IR** (KBr): 2977, 1727, 1600, 1423, 1367, 1270, 1189, 1083, 854, 767 cm^{-1}. **HRMS** (ESI) calculated for $C_9H_4ClF_3NO_2$ $[M-H]^-$ 249.9883, found 249.9892.



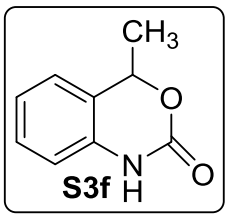
6-Bromo-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3e)

Brown color solid, 68% yield, mp. 213.8-215.6 °C. Using the general method C, in a flame dried 100 mL round bottom flask, compound **S2e** (7.2 mmol, 2.45 g, 1.0 equiv) was suspended in anhydrous MeOH (50 mL). To this solution dry K_2CO_3 (8.64 mmol, 1.2 g, 1.2 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated, extracted with ethyl acetate and the crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **S3e**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (br s, 1H, NH), 7.53 – 7.50 (m, 1H, ArH), 7.40 (s, 1H, ArH), 6.79 (d, *J* = 8.5 Hz, 1H, ArH), 5.60 (q, *J* = 6.6 Hz, 1H, -CH-CF_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.93, 134.51, 134.49, 129.97, 122.56 (q, *J* = 285.6 Hz), 116.48, 116.39, 112.81, 75.98 (q, *J* = 34.8 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -71.94 (d, *J* = 6.6 Hz, 3F). **IR** (KBr): 3151, 2003, 1710, 1600, 1417, 1365, 1272, 1191, 1139, 1081, 854, 767 cm^{-1}. **HRMS** (ESI) calculated for $C_9H_4BrF_3NO_2$ $[M-H]^-$ 293.9378. found 293.9403.



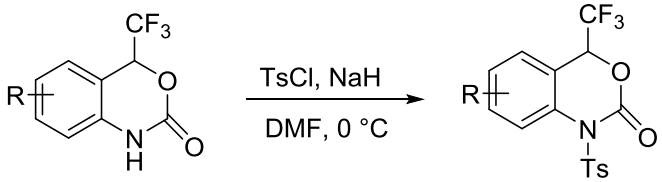
4-Methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (S3f)

White solid, 80% yield, mp. 100.6-104.8 °C. Using the general method B, in a flame dried 100 flame dried 100 mL round bottom flask, aldehyde **S1a** (2.59 mmol, 0.5 g, 1.0 equiv) and CH_3MgBr in THF solution (3.0 M, 1 mL) was suspended in anhydrous THF (10 mL) at 0 °C and the mixture was stirred vigorously at room temperature under N_2 atmosphere. After completion of the reaction, mixture was concentrated on reduced pressure and re-dissolve in EtOH (15 mL). To this solution dry K_2CO_3 (2.59 mmol, 0.357 g, 1.0 equiv) was added and the mixture was stirred overnight at room temperature under Ar atmosphere. After completion of the reaction, the reaction mixture was concentrated, extracted with ethyl acetate and the crude product was purified by flash column chromatography (using 6:4 hexane/ethyl acetate) to obtain the pure product **S3f**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (br s, 1H, NH), 7.28 – 7.24 (m, 1H, ArH), 7.16 – 6.99 (m, 2H, ArH), 6.87 (d, *J* = 7.8 Hz, 1H, ArH), 5.53 (q, *J* = 6.6 Hz, 1H, CH-CH_3), 1.72 (d, *J* = 6.6 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.46, 134.85, 129.09, 123.75, 123.43, 122.57, 114.31, 75.88, 20.29. **IR** (KBr): 3162, 3102, 2990, 2934, 1600, 1495, 1453, 1431, 1397, 1261, 1073, 1046, 761 cm^{-1}. **HRMS** (ESI) calculated for $C_9H_9NO_2Na$ $[M+Na]^+$ 186.0531, found 186.0525.



S3f

10. General experimental procedure for the synthesis of substituted 4-trifluoromethyl benzoxazinanone 1 (method D)



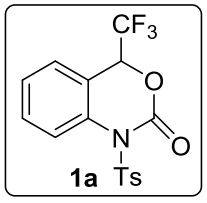
S3 **1**

In a flame dried 100 mL round bottom flask, compound **S3a** (3.1 mmol, 0.673 g, 1.0 equiv) was suspended in dry DMF (30 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 4.65 mmol, 0.112 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (3.41 mmol, 0.648 g, 1.1 equiv) in dry DMF (3 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC. After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate (3 × 30 mL). Combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4 and then solvent was removed under reduced

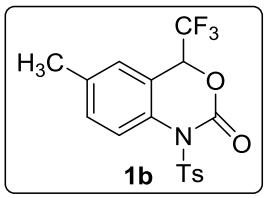
pressure. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **1a**. The characterization data of **1a** are summarized below.

1-Tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1a)

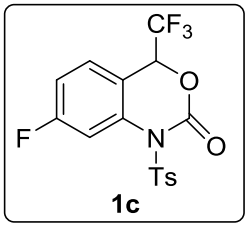
White solid, 48% yield, mp.162.1-165.9 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H, ArH), 7.78 (d, *J* = 8.4 Hz, 1H, ArH), 7.56 – 7.51 (m, 1H, ArH), 7.39 (d, *J* = 8.1 Hz, 2H, ArH), 7.35 – 7.30 (m, 2H, ArH), 5.42 (q, *J* = 7.0 Hz, 1H, -$CHCF_3$), 2.47 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.65, 146.30, 134.90, 134.37, 131.03, 129.81, 129.55, 127.38, 126.34, 122.19 (q, *J* = 284.3 Hz), 121.14, 117.22, 75.91 (q, *J* = 35.3 Hz), 21.90. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.27 (d, *J* = 7.0 Hz,3F). **IR** (KBr): 3118, 1756, 1594, 1496, 1465, 1367, 1299, 1191, 1016, 971, 958, 840, 815, 769 cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{12}F_3NO_4SNa$ $[M+Na]^+$ 394.0337, found 394.0333.



6-Methyl-1-tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1b) Dirty white solid, 67% yield, mp. 144.6-148.9 °C. Using the general method D, in a flame dried 100 mL round bottom flask, compound **S3b** (2.0 mmol, 0.462 g, 1.0 equiv) was suspended in dry DMF (18 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 3.0 mmol, 0.072 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (2.2 mmol, 0.42 g, 1.1 equiv) in dry DMF (2 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 6:4 hexane/ethyl acetate) to obtain the pure product **1b**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H, ArH), 7.66 (d, *J* = 8.5 Hz, 1H, ArH), 7.38 (dd, *J* = 8.6, 0.6 Hz, 2H, ArH), 7.32 (dd, *J* = 8.5, 1.6 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 5.36 (q, *J* = 6.8 Hz, 1H, -$CHCF_3$), 2.47 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.74, 146.19, 136.53, 134.97, 131.90, 131.67, 129.76, 129.53, 127.66, 122.21 (q, *J* = 284.3 Hz), 121.00, 117.05, 75.97 (q, *J* = 35.2 Hz), 21.90, 20.86. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.30 (d, *J* = 6.8 Hz, 3F). **IR** (KBr): 2931, 1762, 1594, 1500, 1454, 1371, 1295, 1265, 1238, 1170, 1083, 970, 912, 833, 744 cm^{-1}. **HRMS** (ESI) calculated for $C_{17}H_{14}F_3NO_4SNa$ $[M+Na]^+$ 408.0493, found 408.0490.

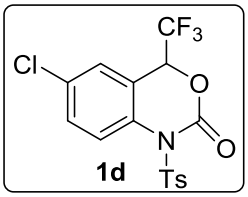


7-Fluoro-1-tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1c) White solid, 61% yield, mp. 178.4-182.6 °C. Using the general method D, in a flame dried 100 mL round bottom flask, compound **S3c** (1.5 mmol, 0.35 g, 1.0 equiv) was suspended in dry DMF (10 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 2.2 mmol, 0.0536 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (1.8 mmol, 0.342 g, 1.2 equiv) in dry DMF (2 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **1c**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H, ArH), 7.58 (dd, *J* = 10.2, 2.4 Hz, 1H, ArH), 7.40 (d, *J* = 8.1 Hz, 2H, ArH), 7.29 (dd, *J* = 8.5, 5.6 Hz, 1H, ArH), 7.08 – 7.02 (m, 1H, ArH), 5.40 (q, *J* = 6.8 Hz, 1H, -$CHCF_3$), 2.48 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.65 (d, *J* = 251.2 Hz), 146.64, 146.12, 135.86 (d, *J* = 11.6 Hz), 134.50, 129.92, 129.63, 128.92 (d, *J* = 9.9 Hz), 122.07 (q, *J* = 284.3 Hz), 113.64 (d, *J* = 22.6 Hz), 112.89 (d, *J* = 3.1 Hz), 109.37 (d, *J* = 28.3 Hz), 75.52 (q, *J* = 35.5 Hz), 21.95. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.61 (d, *J* = 6.8 Hz, 3F), -106.78 – -106.92 (m, 1F). **IR** (KBr):3110, 3084, 1777, 1509, 1379, 1326, 1294, 1187, 1113, 1019, 877, 736 cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{11}F_4NO_4SNa$ $[M+Na]^+$ 412.0228, found 412.0243.



1c

6-Chloro-1-tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (1d): White powder, 60% yield, mp. 142.5-145.8 °C. Using the general method D, in a flame dried 100 mL round bottom flask, compound **S3d** (4.5 mmol, 1.13 g, 1.0 equiv) was suspended in dry DMF (40 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 6.75 mmol, 0.162 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (4.95 mmol, 0.941 g, 1.1 equiv) in dry DMF (4 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **1d**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H, ArH), 7.75 (d, *J* = 8.9 Hz, 1H, ArH), 7.50 (dd, *J* = 8.9, 2.4 Hz, 1H, ArH), 7.39 (d, *J* = 8.1 Hz, 2H, ArH), 7.31 (d, *J* = 2.2 Hz, 1H,

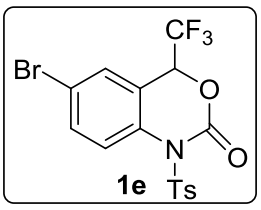


1d

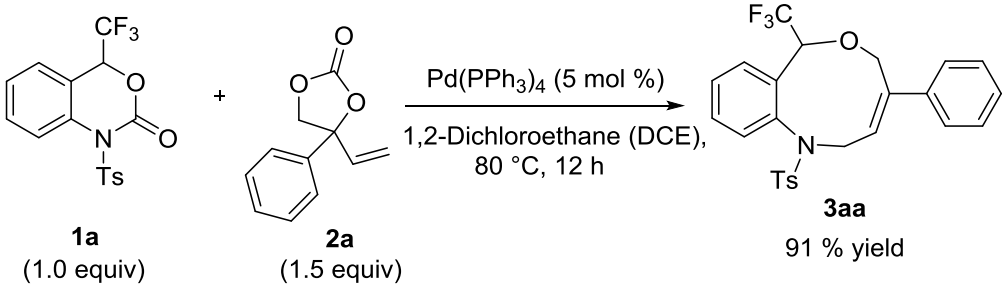
ArH), 5.38 (q, J = 6.5 Hz, 1H, -$CHCF_3$), 2.47 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.61, 146.12, 134.46, 132.92, 132.11, 131.16, 129.87, 129.63, 127.23, 122.61, 121.92 (q, J = 284.4 Hz), 118.81, 75.31 (q, J = 35.5 Hz), 21.92. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.23 (d, J = 6.5 Hz, 3F). **IR** (KBr): 3122, 2969, 1764, 1594, 1486, 1428, 1369, 1290, 1267, 1172, 1085, 970, 842, 750 cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{11}ClF_3NO_4SNa$ $[M+Na]^+$ 427.9947, found 427.9946.

6-bromo-1-tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one(1e)

Light yellow solid, 48% yield, mp. 127.7-131.8 °C. Using the general method D, in a flame dried 50 mL round bottom flask, compound **S3e** (2.35 mmol, 0.695 g, 1.0 equiv) was suspended in dry DMF (20 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 3.53 mmol, 0.085 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (2.6 mmol, 0.494 g, 1.1 equiv) in dry DMF (2 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **1e**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H, ArH), 7.72 – 7.63 (m, 2H, ArH), 7.45 (d, J = 1.6 Hz, 1H, ArH), 7.39 (d, J = 8.1 Hz, 2H, ArH), 5.38 (q, J = 7.6 Hz, 1H, CF_3-CH) , 2.47 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.64, 146.10, 134.46, 134.13, 133.49, 130.15, 129.89, 129.67, 122.85, 121.95 (q, J = 284.6 Hz), 119.58, 119.08, 75.23 (q, J = 35.7 Hz), 21.96. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -77.24 (d, J = 7.6 Hz, 3F). **IR** (KBr): 2987, 1764, 1594, 1486, 1427, 1367, 1292, 1186, 1085, 970, 842, 692 cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{11}BrF_3NO_4SNa$ $[M+Na]^+$ 471.9442, found 471.9425.



11. Typical procedure for the preparation of DDC products 3 (method E)

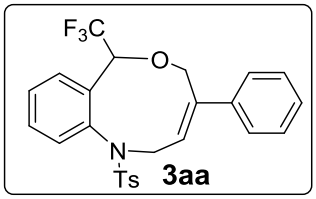


In a flame dried Schlenk tube 1 mL DCE was taken. The solvent was degassed by using

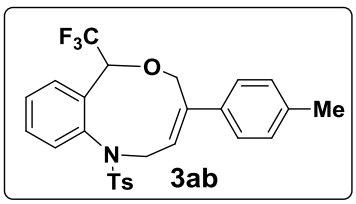
standard “freeze-pump-thaw” method. The process was repeated for three times and finally the Schlenk tube was filled with argon gas. After that, $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken in the schlenk tube inside the glove box and allowed to stir for few minutes. To the above mixture 1-tosyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and 4-phenyl-4-vinyl-1,3-dioxolan-2-one **2a** (0.15 mmol, 0.029 g, 1.5 equiv) were added and the mixture was allowed to stir at 80 °C until complete conversion of **1a** (reaction time 12 h for the formation of **3aa**) under Ar atmosphere. Completion of the reaction was monitored by TLC. After completion, crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3aa** in 89% isolated yield as light yellow solid. The characterization data of **3aa** are summarized below.

12. Characterization Data of Products 3

4-Phenyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5]oxazonine (3aa) Light yellow solid, mp. 150.0-152.4 °C, 89% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 1H, ArH), 7.65 (d, *J* = 12 Hz, 2H, ArH), 7.51 – 7.48 (m, 2H, ArH), 7.47 – 7.39 (m, 2H, ArH), 7.39 – 7.31 (m, 3H, ArH), 7.29-7.26 (m, 2H, ArH), 7.00 (dd, *J* = 7.6, 1.6 Hz, 1H, ArH), 6.58 (dd, *J* = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.15 (q, *J* = 6.8 Hz, 1H, CF_3-CH), 4.76 (dd, *J* = 15.2, 7.2 Hz, 1H, -N-CH-), 4.50, 3.94 (J_{AB} = 12.6, 2H, -O-CH_2-), 3.65 (dd, *J* = 15.2, 8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.21, 142.28, 140.37, 140.06, 136.61, 133.52, 131.33, 129.99, 129.95, 129.92, 129.37, 129.19, 128.64, 128.23, 127.82, 126.57, 124.42 (q, *J* = 281.40 Hz), 71.04 (q, *J* = 32.3 Hz), 65.19, 49.15, 21.69. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.36 (d, *J* = 6.8 Hz, 3F). **IR** (KBr): 3060, 2940, 1590, 1344, 1280, 1168, 1128, 1060, 862, 765, 709 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{22}F_3NO_3SNa$ $[M+Na]^+$ 496.1170, found 496.1175.

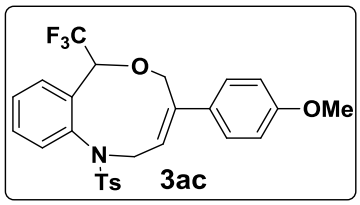


4-(p-Tolyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5]oxazonine (3ab) White solid, 83% isolated yield, mp. 155.9-163.3 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2b** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2



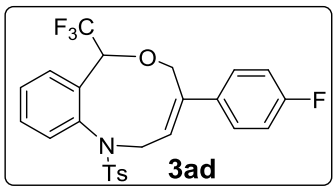
hexane/ethyl acetate) to obtain the pure product **3ab**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 1H, ArH), 7.65 (d, *J* = 8.0 Hz, 2H, ArH), 7.47 – 7.41 (m, 2H, ArH), 7.39 (d, *J* = 8.4 Hz, 2H, ArH), 7.27 (d, *J* = 8.8 Hz, 2H, ArH), 7.16 (d, *J* = 7.9 Hz, 2H, ArH), 7.01 (dd, *J* = 7.8, 1.4 Hz, 1H, ArH), 6.56 (dd, *J* = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.12 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.75 (dd, *J* = 15.0, 7.2 Hz, 1H, -N-CH-), 4.48, 3.92 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.64 (dd, *J* = 15.0, 8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.17, 142.28, 139.87, 138.14, 137.41, 136.66, 133.53, 131.30, 129.95, 129.91, 129.45, 129.35, 129.21, 129.05, 127.82, 126.43, 127.64 – 120.91 (q, *J* = 281.93 Hz), 70.98 (q, *J* = 32.6 Hz), 65.15, 49.21, 21.70, 21.31. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.43 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3045, 2944, 1587, 1336, 1272, 1164, 873, 825, 723 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{24}F_3NO_3SNa$ $[M+Na]^+$ 510.1327, found 510.1318.

4-(4-Metoxypheny1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ac) White solid, 78% isolated yield, mp. 153.6-166.3 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2c** (0.15 mmol, 0.033 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ac**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 1H, ArH), 7.65 (d, *J* = 8.3 Hz, 2H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.44 – 7.36 (m, 2H, ArH), 7.33 – 7.24 (m, 2H, ArH), 6.99 (dd, *J* = 7.7, 1.5 Hz, 1H, ArH), 6.92 – 6.85 (m, 2H, ArH), 6.54 (t, *J* = 8.0 Hz, 1H, -CH-alkene), 5.14 (q, *J* = 7.2 Hz, 1H, CF_3-CH), 4.74 (dd, *J* = 15.1, 7.3 Hz, 1H, -N-CH), 4.47, 3.90 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.83 (s, 3H, OCH_3), 3.63 (dd, *J* = 15.0, 8.6 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.71, 144.14, 142.27, 139.33, 136.66, 133.52, 132.72, 131.30, 129.94, 129.89, 129.41, 128.25, 127.79, 127.75, 126.67, 124.41 (q, *J* = 279.3 Hz), 113.96, 70.92 (q, *J* = 32.2 Hz), 65.08, 55.43, 49.27, 21.68. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.41 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3068, 2937, 1602, 1348, 1280, 1164, 1128, 1022, 865, 775, 701 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{24}F_3NO_4SNa$ $[M+Na]^+$ 526.1276, found 526.1276.



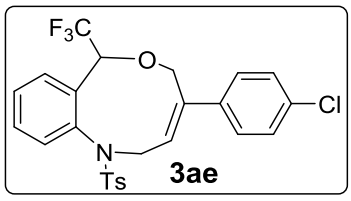
4-(4-Fluorophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ad) Light yellow solid, 69% isolated yield, mp. 142.5-144.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol,

0.037 g, 1.0 equiv) and **2d** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 14 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ad**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H, ArH), 7.65 (d, *J* = 8.4 Hz, 2H, ArH), 7.50 – 7.46 (m, 2H, ArH), 7.46 – 7.42 (m, 1H, ArH), 7.42 – 7.38 (m, 1H, ArH), 7.28 (d, *J* = 7.9 Hz, 2H, ArH), 7.07 – 7.00 (m, 2H, ArH), 6.97 (dd, *J* = 7.9, 1.3 Hz, 1H, ArH), 6.55 (dd, *J* = 8.4, 7.4 Hz, 1H, -CH-alkene), 5.15 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.74 (dd, *J* = 15.2, 7.4 Hz, 1H, - N-CH-), 4.45, 3.91 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.63 (dd, *J* = 15.2, 8.4 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.87 (d, *J* = 247.6 Hz), 144.26, 142.26, 139.05, 136.48 (d, *J* = 18.0 Hz), 136.44., 133.45, 131.39, 130.02 (d, *J* = 9.5 Hz), 129.93, 129.31, 129.22 (d, *J* = 2.3 Hz), 128.34, 128.28, 127.82, 124.41 (q, *J* = 277.1 Hz), 115.53 (d, *J* = 21.4 Hz), 71.03 (q, *J* = 32.7 Hz), 65.11, 49.12, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.43 (d, *J* = 7.1 Hz, 3F), -113.86 – -115.46 (m, 1F). **IR** (KBr): 3060, 2944, 1594, 1355, 1160, 877, 765, 730 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}F_4NO_3SNa$ $[M+Na]^+$ 514.1076, found 514.1080.



3ad

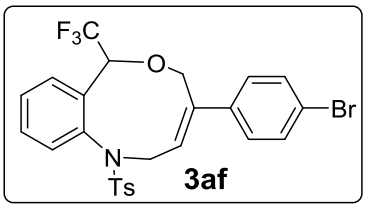
4-(4-Chlorophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ae) Light yellow solid, 86% isolated yield, mp. 125.4-130.9 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2e** (0.15 mmol, 0.034 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ae**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.65 (d, *J* = 8.3 Hz, 2H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.43 – 7.37 (m, 2H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.31 – 7.28 (m, 1H, ArH), 7.29 – 7.27 (m, 1H, ArH), 6.96 (dd, *J* = 7.9, 1.3 Hz, 1H, ArH), 6.58 (dd, *J* = 8.4, 7.4 Hz, 1H, -CH-alkene), 5.14 (q, *J* = 6.8 Hz, 1H, CF_3-CH), 4.74 (dd, *J* = 15.0, 7.4 Hz, 1H, - N-CH-), 4.45, 3.91 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.63 (dd, *J* = 15.0, 8.4 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.30, 142.23, 138.94, 138.74, 136.49, 134.23, 133.42, 131.42, 130.47, 130.08, 129.94, 129.27, 129.21, 128.80, 127.88, 127.81, 124.37 (q, *J* = 281.2 Hz), 71.06 (q, *J* = 32.4 Hz), 64.94, 49.06, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.41 (d, *J* = 6.8 Hz, 3F). **IR** (KBr): 3056, 2956, 1587, 1344, 1276, 1157, 1097, 1068, 873, 765, 719 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}ClF_3NO_3SNa$ $[M+Na]^+$



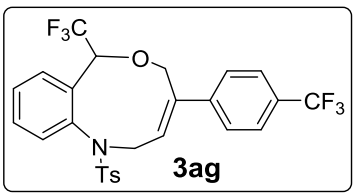
3ae

530.0780, found 530.0780.

4-(4-Bromophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3af) White solid, 91% isolated yield, mp. 153.3-154.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2f** (0.15 mmol, 0.0404 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3af**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 1H, ArH), 7.65 (d, J = 8.4 Hz, 2H, ArH), 7.49 – 7.46 (m, 2H, ArH), 7.46 – 7.39 (m, 2H, ArH), 7.38 – 7.36 (m, 2H, ArH), 7.29 – 7.26 (m, 2H, ArH), 6.95 (dd, J = 7.9, 1.3 Hz, 1H, ArH), 6.58 (dd, J = 8.4, 7.4 Hz, 1H, -CH-alkene), 5.14 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.73 (dd, J = 15.0, 7.4 Hz, 1H, -N-CH-), 4.44, 3.91 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.63 (dd, J = 15.0, 8.4 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.30, 142.22, 139.20, 138.99, 136.47, 133.40, 131.76, 131.42, 130.52, 130.08, 129.94, 129.25, 129.18, 128.18, 127.80, 124.36 (q, J = 281.4 Hz), 122.46, 71.07 (q, J = 32.5 Hz), 64.90, 49.05, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.40 (d, J = 7.1 Hz, 3F). **IR** (KBr): 3052, 2952, 1590, 1344, 1276, 1157, 1086, 1068, 877, 723 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}BrF_3NO_3SNa$ $[M+Na]^+$ 574.0275, found 574.0292.

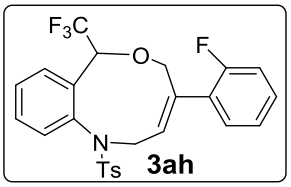


1-Tosyl-7-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1,2,5,7-tetrahydrobenzo [*c*][1,5]oxazonine (3ag) Light yellow solid, 56% isolated yield, mp. 142.0-151.7 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2g** (0.15 mmol, 0.0387 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ag**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.7 Hz, 1H, ArH), 7.66 (d, J = 8.4 Hz, 2H, ArH), 7.65 – 7.61 (m, 4H, ArH), 7.49 – 7.38 (m, 2H, ArH), 7.30 – 7.26 (m, 2H, ArH), 6.96 (dd, J = 7.9, 1.3 Hz, 1H, ArH), 6.65 (dd, J = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.18 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.76 (dd, J = 15.2, 7.2 Hz, 1H, -N-CH-), 4.48, 3.95 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.66 (dd, J = 15.2, 8.4 Hz, 1H,-N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.38, 143.85, 142.23, 139.00, 136.39, 133.40, 131.94, 131.48, 130.34, 130.16, 130.08, 129.98, 129.22, 127.84, 126.90, 125.63 (q, J = 4.1 Hz), 124.36 (q, J = 281.2 Hz),

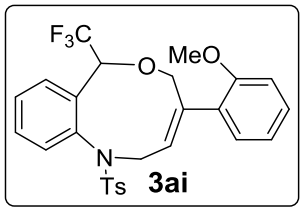


124.25(q, J = 272.7 Hz), 71.19 (q, J = 32.4 Hz), 64.94, 48.97, 21.71. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -63.07 (s, 3F), -72.37 (d, J = 7.1 Hz, 3F). **IR** (KBr): 2960, 1542, 1332, 1276, 1157, 1120, 1060, 873, 738, 715 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{21}F_6NO_3SNa$ $[M+Na]^+$ 564.1044, found 564.1059.

4-(2-Fluorophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ah) White solid, 84% isolated yield, mp. 166.1-168.0 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2h** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 13 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ah**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.4 Hz, 1H, ArH), 7.69 (d, J = 8.3 Hz, 2H, ArH), 7.47 – 7.39 (m, 2H, ArH), 7.34 – 7.29 (m, 2H, ArH), 7.29 – 7.24 (m, 1H, ArH), 7.21 – 7.17 (m, 1H, ArH), 7.13 – 7.08 (m, 1H, ArH), 7.07 – 7.02 (m, 1H, ArH), 7.01 – 6.98 (m, 1H, ArH), 6.40 (br t, J = 7.8 Hz, 1H, -CH-alkene), 5.20 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.71 (dd, J = 15.0, 7.2 Hz, 1H, -N-CH-), 4.47, 3.94 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.72 (dd, J = 15.0, 8.4 Hz, 1H, -N-CH-), 2.45 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.74 (d, J = 247.7 Hz), 144.29, 142.25, 136.53, 136.26, 133.45 (d, J = 3.3 Hz), 131.35, 130.57 (d, J = 3.4 Hz), 130.00, 129.97, 129.73 (d, J = 8.3 Hz), 129.70, 129.34, 129.11, 128.31 (d, J = 13.5 Hz), 127.84, 124.41 (d, J = 3.6 Hz), 124.40 (q, J = 281.7 Hz), 115.85 (d, J = 22.6 Hz), 71.47 (q, J = 32.3 Hz), 65.70, 48.71, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.32 (d, J = 7.1 Hz, 3F), -116.65 (d, J = 4.5 Hz, 1F). **IR** (KBr): 3060, 2948, 1587, 1340, 1284, 1160, 873, 761, 715 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}F_4NO_3SNa$ $[M+Na]^+$ 514.1076, found 514.1082.

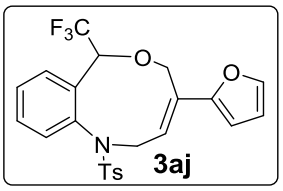


4-(2-Methoxyphenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ai) White solid, 88% isolated yield, mp. 197.3-199.4 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2i** (0.15 mmol, 0.033 g, 1.5 equiv) were added. After being stirred at 80 °C for 13 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ai**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 1.0 Hz, 1H, ArH), 7.71 (d, J = 8.3 Hz, 2H, ArH), 7.47 – 7.43 (m, 1H, ArH), 7.43 – 7.39 (m, 1H, ArH), 7.33 (dd, J = 8.5, 0.6 Hz, 2H, ArH), 7.30 – 7.26 (m, 1H, ArH), 7.05 – 7.02 (m, 1H,



ArH), 6.91 – 6.87 (m, 1H, ArH), 6.84 (dd, J = 8.3, 0.7 Hz, 1H, ArH), 6.80 (dd, J = 7.4, 1.8 Hz, 1H, ArH), 6.17 (dd, J = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.16 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.68 (dd, J = 15.2, 7.2 Hz, 1H, -N-CH-), 4.58, 3.95 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.76 (s, 3H, OCH_3), 3.79 – 3.72 (dd, J = 15.2, 8.4 Hz, 1H, -N-CH-), 2.46 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.34, 144.15, 142.27, 140.64, 136.87, 133.66, 131.39, 131.18, 130.69, 129.96, 129.83, 129.61, 129.60, 129.44, 129.07, 127.83, 124.40 (q, J = 271.4 Hz), 120.78, 110.52, 71.59 (q, J = 32.1 Hz), 65.28, 55.31, 48.70, 21.71. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.27 (d, J = 7.1 Hz, 3F). **IR** (KBr): 3048, 2937, 1606, 1359, 1272, 1172, 1128, 1064, 881, 782, 746, 646 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{24}F_3NO_4SNa$ $[M+Na]^+$ 526.1276, found 526.1290.

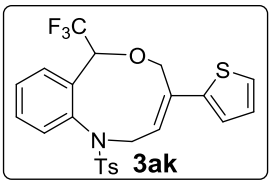
4-(Furan-2-yl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3aj) White solid, 76% isolated yield, mp. 97.6-106.8 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2j** (0.2 mmol, 0.036 g, 2.0 equiv) were added. After being stirred at 80 °C for 16 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3aj**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.66 (d, J = 8.3 Hz, 2H, ArH), 7.46 – 7.42 (m, 1H, ArH), 7.40 – 7.35 (m, 2H, ArH), 7.29 – 7.26 (m, 2H, ArH), 6.93 (dd, J = 7.8, 1.6 Hz, 1H, furyl-H), 6.77 (dd, J = 8.6, 7.4 Hz, 1H, -CH-alkene), 6.52 (br d, J = 3.6 Hz, 1H, furyl-H), 6.42 (dd, J = 3.4, 1.6 Hz, 1H, furyl-H), 5.09 (q, J = 7.2 Hz, 1H, CF_3-CH), 4.77 (dd, J = 15.2, 7.4 Hz, 1H, -N-CH-), 4.47, 3.84 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.66 (dd, J = 15.2, 8.6 Hz, 1H, -N-CH-), 2.42 (s, 3H,CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.83, 144.20, 142.80, 142.29, 136.51, 133.57, 131.33, 130.05, 130.02, 129.90, 129.38, 129.14, 127.85, 125.48, 124.29 (q, J = 281.5 Hz), 111.76, 108.59, 71.44 (q, J = 31.9 Hz), 62.97, 48.92, 21.69. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.48 (d, J = 7.2 Hz, 3F). **IR** (KBr): 3100, 2948, 1594, 1348, 1276, 1168, 869, 769, 715, 651 cm^{-1}. **HRMS** (ESI) calculated for $C_{23}H_{20}F_3NO_4SNa$ $[M+Na]^+$486.0963, found 486.0970.



3aj

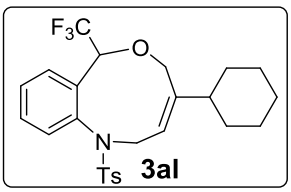
4-(Thiophen-2-yl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ak) Light yellow solid, 79% isolated yield, mp. 167.3-175.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2k** (0.2 mmol, 0.0392 g, 2.0 equiv) were added. After being stirred at 80 °C for 16 h, the mixture was dried in vacuo. The crude product was purified by flash

column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ak**.



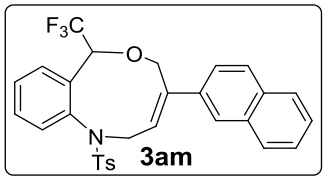
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 1H, ArH), 7.65 (d, *J* = 8.3 Hz, 2H, ArH), 7.48 – 7.42 (m, 1H, ArH), 7.42 – 7.38 (m, 1H, ArH), 7.28 (br d, *J* = 0.5 Hz, 1H, thienyl-H), 7.26 (d, *J* = 1.0 Hz, 1H, ArH), 7.24 – 7.21 (m, 2H, ArH), 7.02 (dd, *J* = 5.2, 3.6 Hz, 1H, thienyl-H), 6.99 (dd, *J* = 7.8, 1.4 Hz, 1H, thienyl-H), 6.63 (dd, *J* = 8.6, 7.6 Hz, 1H, -CH-alkene), 5.07 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.74 (dd, *J* = 15.2, 7.6 Hz, 1H, -N-CH-), 4.51, 3.90 (J_{AB} = 12.8 Hz, 2H, -O-CH_2-), 3.64 (dd, *J* = 15.2, 8.6 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.24, 143.27, 142.25, 136.53, 134.35, 133.39, 131.40, 130.07, 129.94, 129.53, 129.20, 129.18, 127.92, 127.80, 125.67, 125.35, 122.05 (q, *J* = 280.0 Hz), 71.24 (q, *J* = 32.6 Hz), 64.67, 49.17, 21.69. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.38 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3031, 2964, 2908, 1733, 1631, 1598, 1392, 1336, 1268, 1153, 1132, 1068, 865, 765, 719 cm^{-1}. **HRMS** (ESI) calculated for $C_{23}H_{20}F_3NO_3S_2Na$ $[M+Na]^+$ 502.0734, found 502.0737.

4-Cyclohexyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5]oxazonine (3al) White solid, 53% isolated yield, mp. 125.3-130.1 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2l** (0.15 mmol, 0.0294 g, 1.5 equiv) were added. After being stirred at 80 °C for 16 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3al**. **^{1}H NMR**

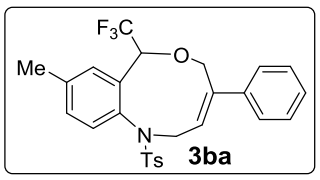


(300 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H, ArH), 7.65 (d, *J* = 8.3 Hz, 2H, ArH), 7.46 – 7.36 (m, 2H, ArH), 7.29 (d, *J* = 8.2 Hz, 2H, ArH), 7.07 – 7.00 (m, 1H, ArH), 5.97 (br t, *J* = 7.9 Hz, 1H, -CH-alkene), 4.89 (q, *J* = 7.2 Hz, 1H, CF_3-CH), 4.58 (dd, *J* = 15.0, 7.3 Hz, 1H, -N-CH-), 4.07, 3.59 (J_{AB} = 12.4 Hz, 2H, -O-CH_2-), 3.56 – 3.47 (m, 1H, -N-CH-), 2.43 (s, 3H, CH_3), 2.08 – 1.95 (m, 1H, cyclohex-H), 1.83 – 1.74 (m, 2H, cyclohex-H), 1.72 – 1.59 (m, 3H, cyclohex-H), 1.36 – 1.02 (m, 5H, cyclohex-H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.66, 144.05, 142.29, 136.93, 133.45, 131.17, 129.86, 129.77, 129.70, 128.96, 127.77, 126.04, 124.50 (q, *J* = 281.6 Hz), 71.08 (q, *J* = 31.9 Hz), 64.62, 48.74, 44.33, 32.62, 32.10, 26.82, 26.72, 26.23, 21.67. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.17 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3108, 2929, 2852, 1598, 1392, 1351, 1268, 1160, 1056, 869, 719 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{28}F_3NO_3SNa$ $[M+Na]^+$ 502.1640, found 502.1638.

4-(Naphthalen-2-yl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3am) White solid, 65% isolated yield, mp. 128.9-136.2 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1a** (0.1 mmol, 0.037 g, 1.0 equiv) and **2m** (0.15 mmol, 0.036 g, 1.5 equiv) were added. After being stirred at 80 °C for 15 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3am**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.3 Hz, 1H, ArH), 7.88 – 7.83 (m, 2H, ArH), 7.83 – 7.79 (m, 2H, ArH), 7.69 – 7.63 (m, 2H, ArH), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H, ArH), 7.50 – 7.47 (m, 3H, ArH), 7.45 – 7.38 (m, 2H, ArH), 7.28 (d, *J* = 0.5 Hz, 1H, ArH), 7.05 (dd, *J* = 7.8, 1.5 Hz, 1H, ArH), 6.73 (dd, *J* = 8.6, 7.2 Hz, 1H, -CH-alkene), 5.18 (q, *J* = 7.9 Hz, 1H, CF_3-CH), 4.82 (dd, *J* = 15.2, 7.2 Hz, 1H, -N-CH-), 4.63, 4.03 (J_{AB} =12.6 Hz, 2H, -O-CH_2-), 3.72 (dd, *J* = 15.2, 8.6 Hz, 1H, -N-CH-), 2.41 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.23, 142.28, 139.95, 137.47, 136.59, 133.50, 133.46, 133.11, 131.37, 130.28, 130.02, 129.94, 129.49, 129.23, 128.59, 128.24, 127.81, 127.67, 126.44, 126.41, 125.86, 124.37, 124.36 (q, *J* = 276.0 Hz), 71.11 (q, *J* = 32.3 Hz), 65.15, 49.22, 21.69. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.35 (d, *J* = 7.9 Hz, 3F). **IR** (KBr): 3060, 2948, 1598, 1351, 1265, 1160, 1089, 1033, 869, 786, 734, 694 cm^{-1}. **HRMS** (ESI) calculated for $C_{29}H_{24}F_3NO_3SNa$ $[M+Na]^+$ 546.1327, found 546.1327.

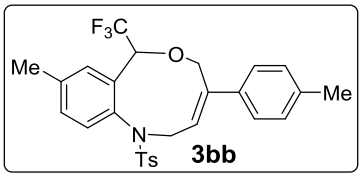


9-Methyl-4-phenyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ba) White solid, 81% isolated yield, mp. 153.0-156.9 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1b** (0.1 mmol, 0.0385 g, 1.0 equiv) and **2a** (0.15 mmol, 0.029 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ba**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.53 – 7.48 (m, 2H, ArH), 7.39 – 7.34 (m, 2H, ArH), 7.34 – 7.30 (m, 1H, ArH), 7.28 (d, *J* = 0.6 Hz, 2H, ArH), 7.22 – 7.17 (m, 1H, ArH), 6.87 (d, *J* = 8.1 Hz, 1H, ArH), 6.61 (dd, *J* = 8.4, 7.4 Hz, 1H, -CH-alkene), 5.10 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.74 (dd, *J* = 15.0, 7.2 Hz, 1H, -N-CH-), 4.48, 3.92 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.62 (dd, *J* = 15.0, 8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.08, 140.42, 140.20, 139.88, 139.75, 136.75, 133.01, 132.14, 130.29, 129.87, 129.54, 128.99, 128.62, 128.18, 127.79, 126.56, 124.45 (q, *J* = 280.3 Hz), 70.88 (q, *J* = 32.6 Hz),

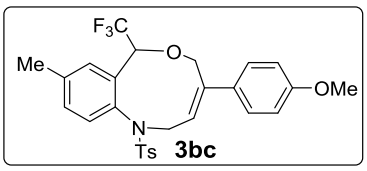


65.01, 49.25, 21.67, 21.53. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.25 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3083, 3052, 2933, 1590, 1336, 1276, 1157, 1060, 962, 873, 769, 686 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{24}F_3NO_3SNa$ $[M+Na]^+$ 510.1327, found 510.1330.

9-Methyl-4-(p-tolyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3bb) White solid, 84% isolated yield, mp. 181.9-187.2 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1b** (0.1 mmol, 0.0385 g, 1.0 equiv) and **2b** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3bb**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H, ArH), 7.54 (s, 1H, ArH), 7.43 – 7.38 (m, 2H, ArH), 7.24 (dd, *J* = 7.5, 1.1 Hz, 2H, ArH), 7.21 – 7.18 (m, 1H, ArH), 7.16 (d, *J* = 7.9 Hz, 2H, ArH), 6.87 (d, *J* = 8.1 Hz, 1H, ArH), 6.58 (dd, *J* = 8.4, 7.4 Hz, 1H, -CH-alkene), 5.08 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.73 (dd, *J* = 15.2, 7.4 Hz, 1H, -N-CH-), 4.46, 3.90 (J_{AB} = 12.4 Hz, 2H, -O-CH_2-), 3.60 (dd, *J* = 15.2, 8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.04, 140.15, 139.75, 139.68, 138.07, 137.46, 136.79, 133.02, 132.11, 129.85, 129.54, 129.38, 129.32, 129.04, 127.78, 126.42, 124.46 (q, *J* = 282.9 Hz), 70.83 (q, *J* = 32.2 Hz), 64.98, 49.30, 21.67, 21.53, 21.29. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.32 (d, *J* = 7.1 Hz, 3F). **IR** (KBr): 3072, 3052, 2929, 1594, 1388, 1344, 1280, 1149, 1068, 877, 809, 701 cm^{-1}. **HRMS** (ESI) calculated for $C_{27}H_{26}F_3NO_3SNa$ $[M+Na]^+$ 524.1483, found 524.1496.

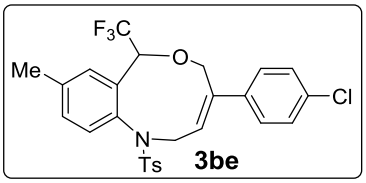


4-(4-Methoxyphenyl)-9-methyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo [*c*][1,5]oxazonine (3bc) Light yellow solid, 81% isolated yield, mp. 165.2-170.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.0058 g) was taken. To it **1b** (0.1 mmol, 0.0385 g, 1.0 equiv) and **2c** (0.15 mmol, 0.033 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3bc**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H, ArH), 7.54 (s, 1H, ArH), 7.49 – 7.43 (m, 2H, ArH), 7.28 – 7.25 (m, 2H, ArH), 7.20 – 7.18 (m, 1H, ArH), 6.91 – 6.87 (m, 3H, ArH), 6.55 (dd, *J* = 8.4, 7.6 Hz, 1H, -CH-alkene), 5.08 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.73 (dd, *J* = 15.0, 7.6 Hz, 1H, -N-CH-), 4.45, 3.89 (J_{AB} = 12.4 Hz, 2H,- O-CH_2-), 3.83 (s, 3H, OCH_3), 3.59 (dd, *J* = 15.0,

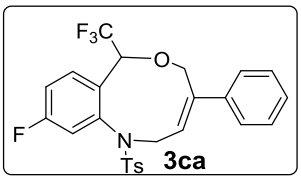


8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.70, 144.03, 140.16, 139.76, 139.19, 136.82, 133.02, 132.80, 132.77, 132.11, 129.85, 129.54, 129.07, 128.57, 127.77, 123.34 (q, J = 271.7 Hz), 113.97, 70.77 (q, J = 32.7 Hz), 64.94, 55.44, 49.38, 21.65, 21.54. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.32 (d, J = 7.1 Hz, 3F). **IR** (KBr): 3031, 2929, 1602, 1344, 1280, 1247, 1105, 1060, 917, 873, 817, 671 cm^{-1}. **HRMS** (ESI) calculated for $C_{27}H_{26}F_3NO_4SNa$ $[M+Na]^+$ 540.1432, found 540.1436.

4-(4-Chlorophenyl)-9-methyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo [*c*][1,5]oxazonine (3be) Light yellow solid, 79% isolated yield, mp. 205.6-212.5 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1b** (0.1 mmol, 0.0385 g, 1.0 equiv) and **2e** (0.15 mmol, 0.034 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3be**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H, ArH), 7.55 (s, 1H, ArH), 7.48 – 7.43 (m, 2H, ArH), 7.35 – 7.30 (m, 2H, ArH), 7.30 – 7.25 (m, 2H, ArH), 7.21 – 7.18 (m, 1H, ArH), 6.83 (d, J = 8.1 Hz, 1H, ArH), 6.61 (dd, J = 8.4, 7.2 Hz, 1H,-CH-alkene), 5.09 (q, J = 7.2 Hz, 1H, CF_3-CH), 4.72 (dd, J = 15.2, 7.2 Hz, 1H, -N-CH-), 4.43, 3.90 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.60 (dd, J = 15.2, 8.4 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3), 2.39 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.17, 140.33, 139.72, 138.80, 136.65, 134.21, 132.91, 132.22, 130.78, 129.90, 129.58, 129.57, 128.95, 128.81, 127.89, 127.80, 124.41 (q, J = 281.5 Hz), 70.93 (q, J = 32.3 Hz), 64.79, 49.18, 21.70, 21.56. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.32 (d, J = 7.2 Hz, 3F). **IR** (KBr): 3060, 2956, 2921, 1594, 1355, 1284, 1149, 1060, 881, 813, 715 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{23}ClF_3NO_3SNa$ $[M+Na]^+$ 544.0937, found 544.0941.

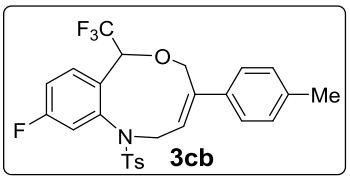


10-Fluoro-4-phenyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ca) Light yellow solid, 69% isolated yield, mp. 169.5-172.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1c** (0.1 mmol, 0.039 g, 1.0 equiv) and **2a** (0.15 mmol, 0.029 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ca**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.8, 6.2 Hz, 1H, ArH), 7.69 – 7.66 (m, 1H, ArH), 7.66 – 7.64 (m, 1H, ArH),



7.50 – 7.48 (m, 1H, ArH), 7.47 (dd, J = 2.0, 1.3 Hz, 1H, ArH), 7.39 – 7.35 (m, 1H, ArH), 7.35 – 7.32 (m, 2H, ArH), 7.31 (d, J = 0.6 Hz, 1H, ArH), 7.29 (d, J = 0.6 Hz, 1H, ArH), 7.19 – 7.15 (m, 1H, ArH), 6.77 (dd, J = 9.1, 2.7 Hz, 1H, ArH), 6.57 (dd, J = 8.8, 7.2 Hz, 1H,-CH-alkene), 5.07 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.74 (dd, J = 15.2, 7.2 Hz, 1H, -N-CH-), 4.51, 3.95 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.65 (dd, J = 15.2, 8.8 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.55 (d, J = 253.6 Hz), 144.59, 143.73 (d, J = 9.5 Hz), 140.23 (d, J = 9.1 Hz), 136.15, 130.73 (d, J = 7.1 Hz), 130.08, 129.68, 129.66, 129.57, 128.69, 128.35, 127.80, 126.53, 124.26 (q, J = 281.5 Hz), 117.49 (d, J = 21.3 Hz), 116.54 (d, J = 21.4 Hz), 70.67 (q, J = 32.5 Hz), 65.20, 48.98, 21.71. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.60 (d, J = 7.1 Hz, 3F), -108.41 (dd, J = 15.0, 7.8 Hz, 1F). **IR** (KBr): 3068, 2960, 2925, 1594, 1351, 1276, 1160, 1135, 1097, 1056, 842, 757, 694 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}F_4NO_3SNa$ $[M+Na]^+$ 514.1076, found 514.1082.

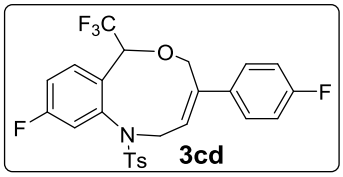
10-Fluoro-4-(p-tolyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3cb) Light yellow solid, 72% isolated yield, mp. 152.7-160.6 °C. By using



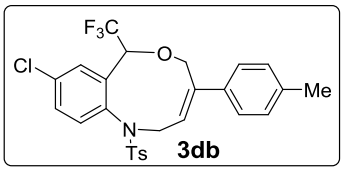
3cb

method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1c** (0.1 mmol, 0.039 g, 1.0 equiv) and **2b** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 14 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3cb**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.8, 6.2 Hz, 1H, ArH), 7.67 (d, J = 1.7 Hz, 1H, ArH), 7.66 – 7.63 (m, 1H, ArH), 7.38 (d, J = 1.7 Hz, 1H, ArH), 7.38 – 7.35 (m, 1H, ArH), 7.31 – 7.27 (m, 2H, ArH), 7.19 – 7.13 (m, 3H, ArH), 6.78 (dd, J = 9.1, 2.7 Hz, 1H, ArH), 6.54 (dd, J = 8.8, 7.2 Hz, 1H, -CH-alkene), 5.05 (q, J = 7.2 Hz, 1H, CF_3-CH), 4.73 (dd, J = 15.0, 7.2 Hz, 1H, -N-CH-), 4.49, 3.93 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.64 (dd, J = 15.0, 8.8 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.52 (d, J = 253.2 Hz), 144.55, 143.71 (d, J = 9.7 Hz), 140.06, 138.25, 137.24, 136.18, 130.69 (d, J = 7.1 Hz), 130.05, 129.68 (d, J = 3.6 Hz), 129.37, 128.66, 127.78, 126.38, 124.26 (q, J = 281.6 Hz), 117.44 (d, J = 21.1 Hz), 116.56 (d, J = 21.4 Hz), 70.62 (q, J = 32.5 Hz), 65.16, 49.02, 21.69, 21.28. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.63 (d, J = 7.2 Hz, 3F), -108.49 (dd, J = 14.8, 7.8 Hz, 1F). **IR** (KBr): 3031, 2948, 1594, 1375, 1355, 1284, 1164, 1060, 892, 809, 686 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{23}F_4NO_3SNa$ $[M+Na]^+$ 528.1232, found 528.1229.

10-Fluoro-4-(4-fluorophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo [*c*][1,5]oxazonine (3cd) White solid, 33% isolated yield, mp. 159.2-166.6 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1c** (0.1 mmol, 0.039 g, 1.0 equiv) and **2d** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 14 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3cd**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.8, 6.2 Hz, 1H, ArH), 7.67 (d, *J* = 1.7 Hz, 1H, ArH), 7.65 (d, *J* = 1.7 Hz, 1H, ArH), 7.50 – 7.44 (m, 2H, ArH), 7.30 (d, *J* = 7.9 Hz, 2H, ArH), 7.20 – 7.16 (m, 1H, ArH), 7.08 – 7.01 (m, 2H, ArH), 6.74 (dd, *J* = 9.0, 2.7 Hz, 1H, ArH), 6.53 (dd, *J* = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.08 (q, *J* = 7.0 Hz, 1H, CF_3-CH), 4.72 (dd, *J* = 15.0, 7.2 Hz, 1H, -N-CH-), 4.46, 3.92 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.63 (dd, *J* = 15.0, 8.4 Hz, 1H,-N-CH-), 2.44 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.57 (d, *J* = 253.9 Hz), 162.91 (d, *J* = 248.5 Hz), 144.64, 143.72 (d, *J* = 9.8 Hz), 139.22, 136.26 (d, *J* = 3.3 Hz), 136.09, 130.76 (d, *J* = 9.9 Hz), 130.09, 129.63, 129.57, 128.28 (d, *J* = 8.3 Hz), 127.79, 124.23 (q, *J* = 281.4 Hz), 117.56 (d, *J* = 21.2 Hz), 116.48 (d, *J* = 21.6 Hz), 115.58 (d, *J* = 21.3 Hz), 70.64 (q, *J* = 32.5 Hz), 65.10, 48.94, 21.72. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.63 (d, *J* = 7.0 Hz, 3F), -108.25 (dd, *J* = 15.0, 7.6 Hz, 1F), -114.30 (dd, *J* = 8.9, 3.8 Hz, 1F). **IR** (KBr): 3060, 2948, 2308, 1598, 1355, 1276, 1160, 1097, 1056, 892, 817, 690 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{20}F_5NO_3SNa$ $[M+Na]^+$ 532.0982, found 532.0998.

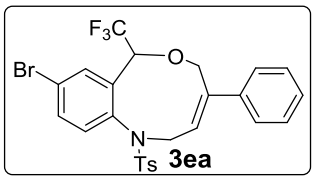


9-Chloro-4-(p-tolyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*] [1,5]oxazonine (3db) Light yellow solid, 40% isolated yield, mp. 61.2-79.9 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1d** (0.1 mmol, 0.041 g, 1.0 equiv) and **2b** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 15 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3db**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.4 Hz, 1H, ArH), 7.63 (d, *J* = 8.4 Hz, 2H, ArH), 7.39 (d, *J* = 1.0 Hz, 1H, ArH), 7.36 (dd, *J* = 3.6, 2.1 Hz, 2H, ArH), 7.29 (d, *J* = 0.6 Hz, 1H, ArH), 7.26 (d, *J* = 3.0 Hz, 1H, ArH), 7.18 (d, *J* = 0.5 Hz, 1H, ArH), 7.16 (s, 1H, ArH), 6.97 (d, *J* = 8.6 Hz, 1H, ArH), 6.55 (dd, *J* = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.05 (q, *J* = 7.1 Hz, 1H, CF_3-CH), 4.75 (dd, *J* = 15.0, 7.2 Hz, 1H, -N-CH-), 4.51, 3.93 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.61 (dd, *J* = 15.0, 8.4 Hz, 1H, -N-CH-), 2.42 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.44, 140.65,

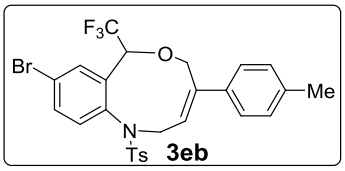


139.87, 138.29, 137.16, 136.30, 135.83, 135.34, 131.56, 130.81, 130.02, 129.40, 128.88, 127.98, 127.77, 126.37, 124.07 (q, J = 281.7 Hz), 70.80 (q, J = 32.5 Hz), 65.36, 49.18, 21.70, 21.30. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.53 (d, J = 7.1 Hz, 3F). **IR** (KBr): 3100, 3027, 2929, 1695, 1511, 1344, 1276, 1176, 1068, 813, 734 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{23}ClF_3NO_3SNa$ $[M+Na]^+$ 544.0937, found 544.0953.

9-Bromo-4-phenyl-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3ea) Light yellow solid, 78% isolated yield, mp. 132.3-140.4 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1e** (0.1 mmol, 0.045 g, 1.0 equiv) and **2a** (0.15 mmol, 0.029 g, 1.5 equiv) were added. After being stirred at 80 °C for 12 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ea**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89 (d, J = 2.1 Hz, 1H, ArH), 7.64 (d, J = 8.3 Hz, 2H, ArH), 7.53 (dd, J = 8.6, 2.3 Hz, 1H, ArH), 7.51 – 7.46 (m, 2H, ArH), 7.41 – 7.35 (m, 2H, ArH), 7.35 – 7.32 (m, 1H, ArH), 7.28 (d, J = 8.2 Hz, 1H, ArH), 7.27 (d, J = 3.5 Hz, 1H, ArH), 6.88 (d, J = 8.5 Hz, 1H, ArH), 6.59 (t, J = 7.9 Hz, 1H, -CH-alkene), 5.08 (q, J = 7.0 Hz, 1H, CF_3-CH), 4.75 (dd, J = 15.1, 7.3 Hz, 1H, -N-CH-), 4.52, 3.94 (J_{AB} = 12.7 Hz, 2H, -O-CH_2), 3.62 (dd, J = 15.0, 8.6 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.49, 141.20, 140.11, 140.05, 136.26, 135.60, 134.60, 132.39, 131.00, 130.04, 129.81, 128.70, 128.37, 127.77, 126.52, 124.08 (q, J = 281.3 Hz), 123.96, 70.78 (q, J = 32.6 Hz), 65.39, 49.09, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.46 (d, J = 7.0 Hz, 3F). **IR** (KBr): 3079, 2956, 1805, 1602, 1348, 1280, 1164, 1060, 885, 769, 734 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{21}BrF_3NO_3SNa$ $[M+Na]^+$ 574.0275, found 574.0281.

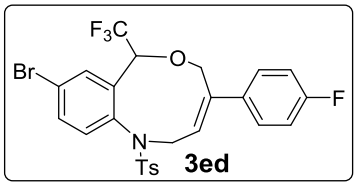


9-Bromo-4-(p-tolyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*][1,5] oxazonine (3eb) Light yellow solid, 61% isolated yield, mp. 122.0-129.2 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1e** (0.1 mmol, 0.045 g, 1.0 equiv) and **2b** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 15 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3eb**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.88 (d, J = 2.1 Hz, 1H, ArH), 7.63 (d, J = 8.3 Hz, 2H, ArH), 7.53 (dd, J = 8.5, 2.3 Hz, 1H, ArH), 7.39 (d, J = 8.2 Hz, 2H, ArH), 7.29 (s, 1H, ArH), 7.25 (d, J = 6.4 Hz, 1H, ArH), 7.18 (d, J = 8.0 Hz, 2H, ArH),



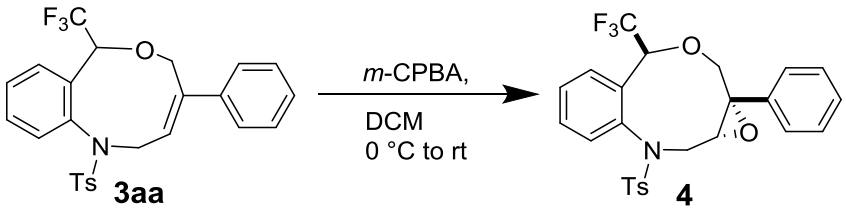
6.90 (d, J = 8.5 Hz, 1H, ArH), 6.57 (dd, J = 8.4, 7.5 Hz, 1H, -CH-alkene), 5.05 (q, J = 7.0 Hz, 1H, CF_3-CH), 4.75 (dd, J = 15.1, 7.3 Hz, 1H, -N-CH-), 4.51, 3.92 (J_{AB} = 12.6 Hz, 2H, -O-CH_2), 3.61 (dd, J = 15.0, 8.6 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.45, 141.20, 139.87, 138.31, 137.16, 136.30, 135.61, 134.57, 132.39, 131.08, 130.03, 129.40, 128.88, 127.77, 126.38, 124.06 (q, J = 281.2 Hz), 123.92, 70.73 (q, J = 32.6 Hz), 65.37, 49.15, 21.71, 21.31. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.48 (d, J = 6.8 Hz, 3F). **IR** (KBr): 3019, 2967, 1508, 1367, 1340, 1276, 1168, 1052, 877, 809, 734, 698 cm^{-1}. **HRMS** (ESI) calculated for $C_{26}H_{23}BrF_3NO_3SNa$ $[M+Na]^+$ 588.0432, found 588.0432.

9-Bromo-4-(4-fluorophenyl)-1-tosyl-7-(trifluoromethyl)-1,2,5,7-tetrahydrobenzo[*c*] [1,5]oxazonine (3ed) Light yellow solid, 77% isolated yield, mp. 150.1-156.7 °C. By using method E, in DCE solution $Pd(PPh_3)_4$ (5 mol %; 0.006 g) was taken. To it **1e** (0.1 mmol, 0.045 g, 1.0 equiv) and **2d** (0.15 mmol, 0.031 g, 1.5 equiv) were added. After being stirred at 80 °C for 15 h, the mixture was dried in vacuo. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **3ed**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 2.2 Hz, 1H, ArH), 7.63 (d, J = 8.0 Hz, 2H, ArH), 7.52 (dd, J = 8.5, 2.3 Hz, 1H, ArH), 7.49 – 7.44 (m, 2H, ArH), 7.29 (d, J = 7.9 Hz, 2H, ArH), 7.08 – 7.01 (m, 2H, ArH), 6.84 (d, J = 8.5 Hz, 1H, ArH), 6.55 (dd, J = 8.4, 7.2 Hz, 1H, -CH-alkene), 5.08 (q, J = 7.1 Hz, 1H, CF_3-CH), 4.73 (dd, J = 15.2, 7.2 Hz, 1H, -N-CH-), 4.47, 3.91 (J_{AB} = 12.6 Hz, 2H, -O-CH_2-), 3.60 (dd, J = 15.2, 8.4 Hz, 1H, -N-CH-), 2.43 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.92 (d, J = 247.8 Hz), 144.55, 141.19, 141.19, 139.00, 139.00, 136.18 (d, J = 3.4 Hz), 135.53, 134.66, 132.40, 130.92, 130.05, 128.28 (d, J = 8.1 Hz), 127.76, 124.06 (q, J = 281.6 Hz), 124.03, 115.59 (d, J = 21.2 Hz), 70.76 (q, J = 32.7 Hz), 65.29, 49.06, 21.70. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.48 (d, J = 7.1 Hz, 3F), -114.21 (d, J = 4.5 Hz, 1F). **IR** (KBr): 3045, 2944, 1594, 1344, 1280, 1164, 1060, 958, 838, 723 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{20}BrF_4NO_3SNa$ $[M+Na]^+$ 592.0181, found 592.0181.



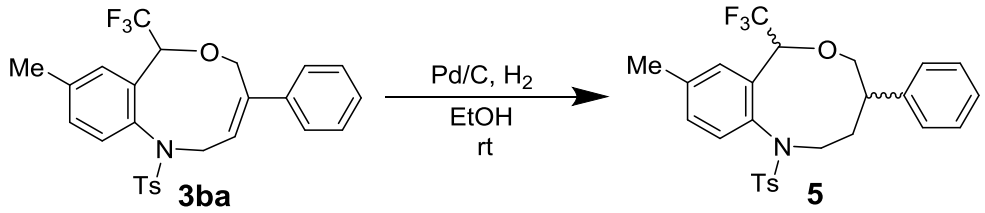
13. Application of CF_3-benzoxazonine 3aa

General procedure for the preparation of 1a-Phenyl-9-tosyl-4-(trifluoromethyl)-1a,2,4,9,10,10a-hexahydrobenzo[*c*]oxireno[2,3-*g*][1,5]oxazonine (4)



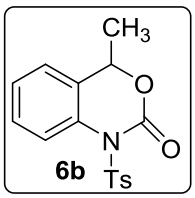
To a solution of nine-membered heterocycle **3aa** (0.10 mmol, 0.0473 g, 1.0 equiv) in DCM (2 mL) was added the DCM solution (2 mL) of *m*-CPBA (0.30 mmol, 0.0518 g, 3.0 equiv, 70 % wt/wt in water) dropwise at 0 °C under nitrogen. The reaction mixture was sealed under nitrogen and allowed to warm to room temperature and stirred for 11 h. The reaction was then quenched with saturated $NaHCO_3$ aq. solution and extracted with DCM. The combined organic phase was collected and dried with Na_2SO_4. After filtration and evaporation, the residue was purified by flash column chromatography (eluted with 8:2 hexane/ethyl acetate) to obtain the pure product **4** (32 mg, 67% yield) as white solid. This compound was observed as a mixture of two diastereoisomers in the NMR and the major diastereoisomer was isolated. Mp. 164.1-168.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H, ArH), 7.73 – 7.71 (m, 1H, ArH), 7.59 – 7.57 (m, 1H, ArH), 7.57 – 7.55 (m, 1H, ArH), 7.49 – 7.44 (m, 1H, ArH), 7.43 – 7.40 (m, 1H, ArH), 7.39 (dd, *J* = 3.6, 1.7 Hz, 2H, ArH), 7.38 – 7.36 (m, 2H, ArH), 7.34 (d, *J* = 0.6 Hz, 1H, ArH), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 5.75 (q, *J* = 6.8 Hz, 1H, CF_3-CH), 4.70 (dd, *J* = 15.6, 5.2 Hz, 1H, -N-CH-), 4.31, 2.99 (J_{AB} = 13.0 Hz, 2H, -O-CH_2-), 3.96 (ddd, *J* = 8.8, 5.2, 1.0 Hz, 1H, -CH-epoxide), 2.83 (dd, *J* = 15.6, 8.8 Hz, 1H, -N-CH-), 2.47 (s, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.72, 143.41, 137.40, 135.92, 132.46, 131.64, 130.34, 130.14, 129.26, 128.91, 128.63, 128.38, 128.03, 127.42, 124.12 (q, *J* = 281.7 Hz), 71.44 (q, *J* = 32.4 Hz), 66.83, 61.48, 60.37, 53.44, 21.76. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.61 (d, *J* = 6.8 Hz, 3F). **IR** (KBr): 3064, 2940, 1598, 1388, 1355, 1284, 1164, 1097, 966, 873, 817, 761, 727 cm^{-1}. **HRMS** (ESI) calculated for $C_{25}H_{22}F_3NO_4SNa$ $[M+Na]^+$ 512.1119, found 512.1122.

General procedure[9] for the preparation of 9-methyl-4-phenyl-1-tosyl-7-(trifluoromethyl)-1,2,3,4,5,7-hexahydrobenzo[*c*][1,5]oxazonine (5)

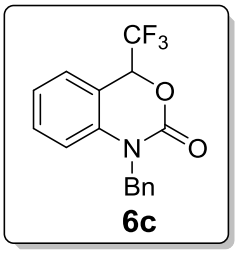


To a solution of nine-membered heterocycle **3ba** (0.03 mmol, 0.014g, 1.0 equiv.) in dry ethanol (2 mL). This mixture was degassed of dissolved air and purged with an argon atmosphere. To it 10% Pd/C (10 mol %, 0.0003g) was carefully added. The above reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 2 h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and concentrated under reduced pressure and purified by flash column chromatography. (using 9:1 hexane/ethyl acetate) to obtain the pure product **5** as white solid 74% yield. This compound was observed as a mixture of two diastereoisomers in the NMR and the major diastereoisomer was isolated. mp. 73.1-76.5 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H, ArH), 7.42 – 7.33 (m, 4H, ArH), 7.36 – 7.29 (m, 2H, ArH), 7.29 – 7.24 (m, 2H, ArH), 7.02 (d, *J* = 8.0 Hz, 1H, ArH), 6.35 (d, *J* = 8.0 Hz, 1H, ArH), 5.67 (q, *J* = 7.3 Hz, 1H, CF_3-CH), 4.68 (dd, *J* = 12.5, 10.6 Hz, 1H, -O-CH-), 4.50 (dd, *J* = 10.2, 5.4 Hz, 1H, -NCH-), 4.28 – 4.18 (m, 1H, -O-CH-), 3.25 – 3.13 (m, 1H, PhCH), 2.92 (ddd, *J* = 12.9, 5.4, 1.5 Hz, 1H, -NCH-), 2.46 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 1.97 – 1.83 (m, 1H, -CH-CPh), 1.64 – 1.55 (m, 1H, -CH-CPh). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.26, 140.63, 139.33, 137.41, 137.36, 134.11, 130.03, 129.73, 128.94, 128.61, 128.51, 127.45, 127.10, 126.74, 125.08 (q, *J* = 271.0 Hz), 80.32 (q, *J* = 31.5 Hz), 78.26, 48.50, 44.70, 29.43, 21.77, 21.68. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -72.83 (d, *J* = 7.3 Hz, 3F). **IR** (KBr): 3054, 2912, 1590, 1448, 1336, 1272, 1168, 1128, 1093, 898, 831, 765, 707 cm^{-1}. LC-MS (ESI, m/z): $[M+Na]^+$ 512.10.

14. Preparation of 4-Methyl-1-tosyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (6b) Cream colored solid, 64% yield, mp. 107.4-111.4 °C. Using the general method D, in a flame dried 100 mL round bottom flask, compound **S3f** (2.1 mmol, 0.34 g, 1.0 equiv) was suspended in dry DMF (8 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 3.1 mmol, 0.075 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of *p*-toluenesulfonyl chloride (2.7 mmol, 0.515 g, 1.3 equiv) in dry DMF (2 mL) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 6:2 hexane/ethyl acetate) to obtain the pure product **6b**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H, ArH), 7.59 (d, *J* = 8.2 Hz, 1H, ArH), 7.41 (dd, *J* = 11.4, 4.7 Hz, 2H, ArH), 7.31 – 7.18 (m, 3H, ArH), 5.36 (q, *J* = 6.8 Hz, 1H, CH_3-CH), 2.47 (s, 3H, Ts-CH_3), 1.72 (d, *J* = 6.8 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.91, 145.73, 136.03, 134.42, 129.95, 129.14, 129.11, 129.06, 126.20, 123.88, 120.65, 75.21, 21.89, 18.23. **IR** (KBr): 1752, 1595, 1374, 1335, 1222, 1173, 1085, 1056, 761 cm^{-1}. **HRMS** (ESI) calculated for $C_{16}H_{15}NO_4SNa$ $[M+Na]^+$ 340.0619, found 340.0638.

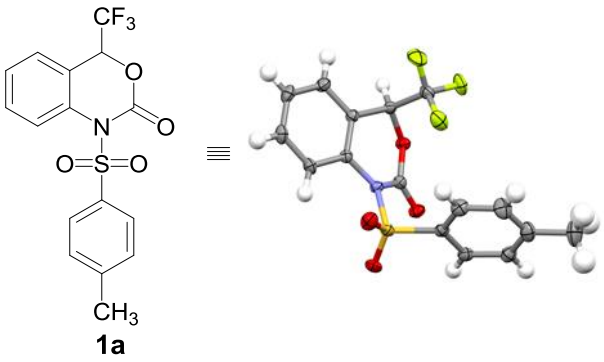


Preparation of 1-benzyl-4-(trifluoromethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (6c) White solid, 63% yield, mp. 133-134°C. Using the general method D, in a flame dried 20 mL round bottom flask, compound **S3a** (1.0 mmol, 0.217 g, 1.0 equiv) was suspended in dry DMF (5 mL) and allowed to cool to 0 °C. To this solution NaH (60% dispersion in mineral oil, 1.5 mmol, 0.036 g, 1.5 equiv) was added and the mixture was allowed to stir for 1 h under Ar atmosphere. After 1 h, a solution of benzyl bromide (1.1 mmol, 0.13 mL, 1.1 equiv) was added dropwise to the reaction mixture. Completion of the reaction was monitored by TLC After completion, the reaction mixture was poured into crushed ice followed by extraction with ethyl acetate. The crude product was purified by flash column chromatography (using 8:2 hexane/ethyl acetate) to obtain the pure product **6c**. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 3H, ArH), 7.29 – 7.21 (m, 4H, ArH), 7.16 – 7.08 (m, 1H, ArH), 6.89 (d, *J* = 8.3 Hz, 1H, ArH), 5.60 (q, *J* = 6.8 Hz, 1H, CF_3-CH), 5.18 (s, 2H, CH_2). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.88, 137.21, 135.51, 131.27, 129.07, 127.76, 127.34, 126.57, 123.61, 122.93 (q, *J* = 284.3 Hz), 114.85, 113.13, 75.57



(q, J = 34.1 Hz), 48.37. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -79.29 (d, J = 6.7 Hz, 3F). **IR** (KBr): 3073, 2965, 1724, 1606, 1455, 1390, 1139, 1095, 914 cm^{-1}. LCMS (ESI^+) m/z: 308.25 $[M+H]^+$

15. X-Ray crystallographic structures are shown below



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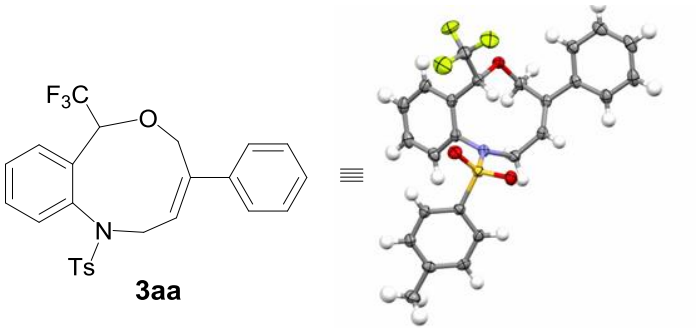

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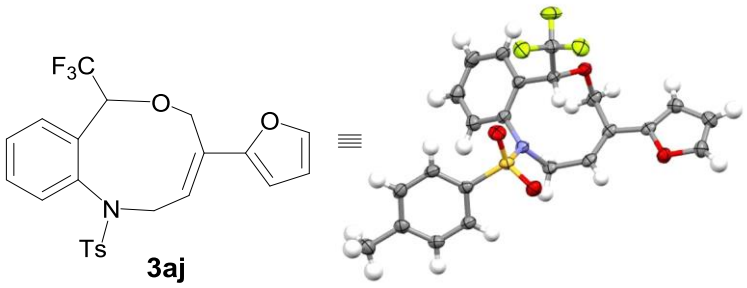

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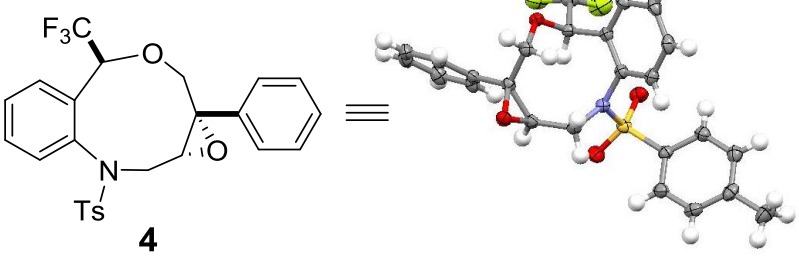

4

16.References

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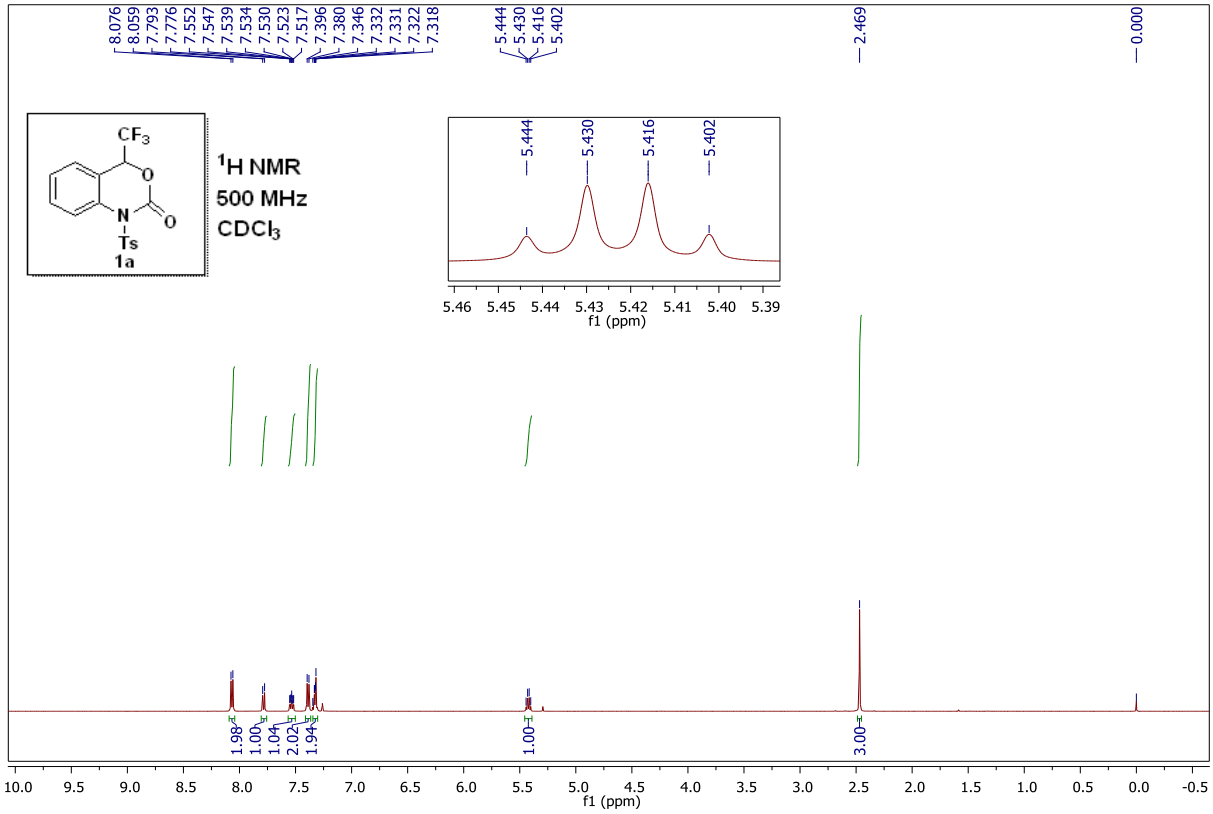
17. NMR Data
(^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR)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7.331
7.322
7.318
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5.430
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5.402
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CF3
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N
O
Ts
1a
1H NMR
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5.402
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1.04
2.02
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1.00
3.00
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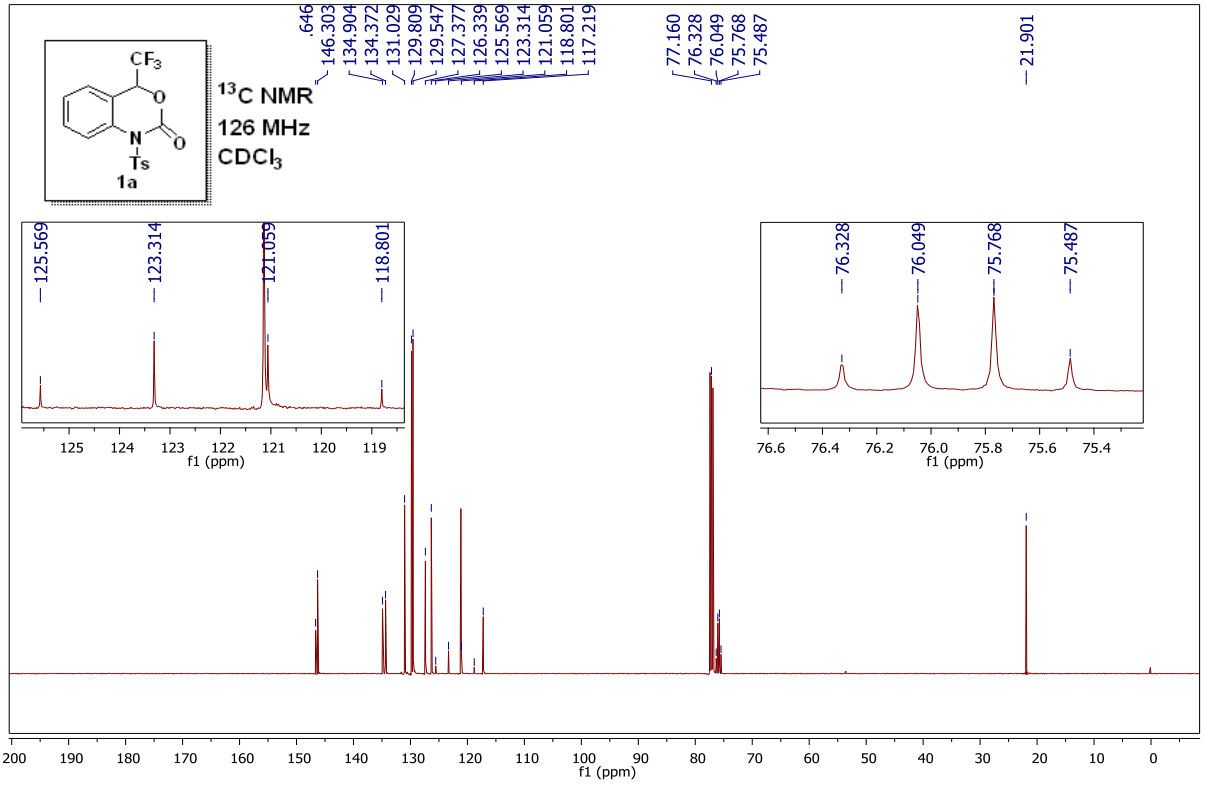
f1 (ppm)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117.219
77.160
76.328
76.049
75.768
75.487
21.901
CF3
O
N
O
Ts
1a
13C NMR
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CDCl3
125.569
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121.059
118.801
125 124 123 122 121 120 119
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76.049
75.768
75.487
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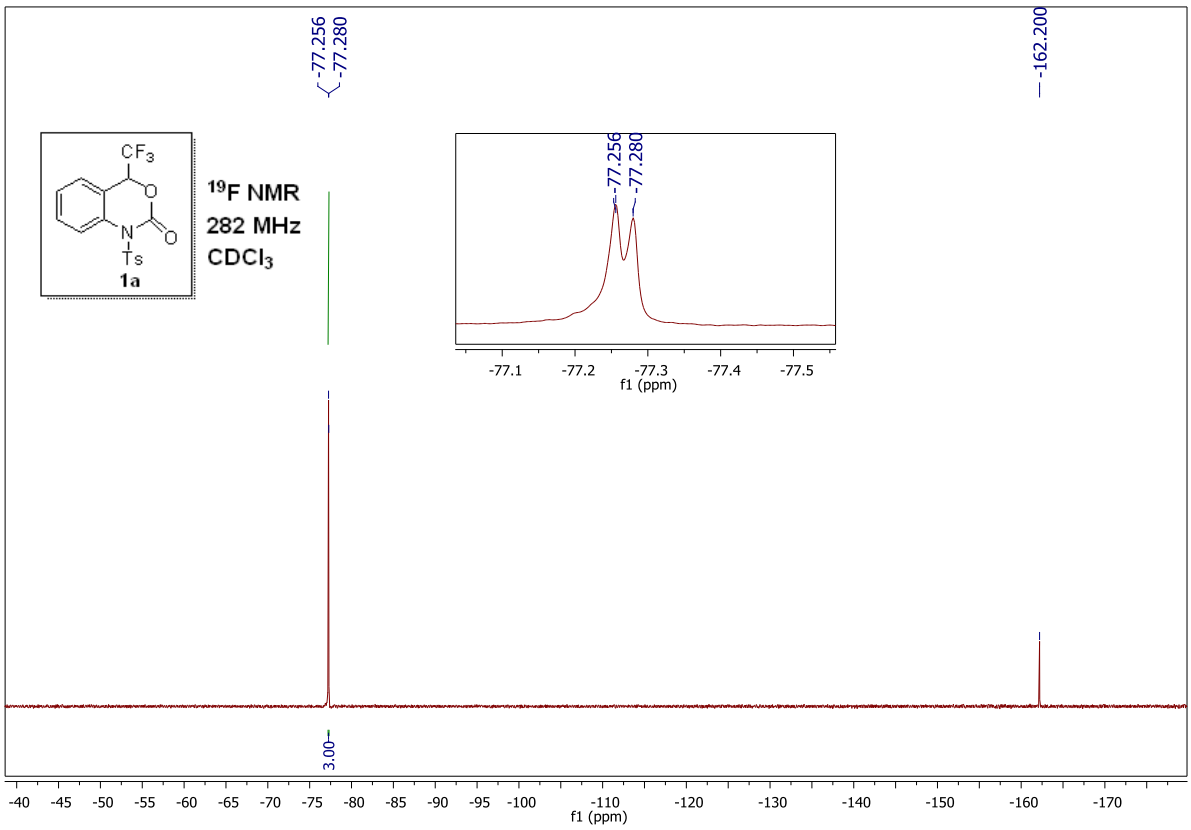
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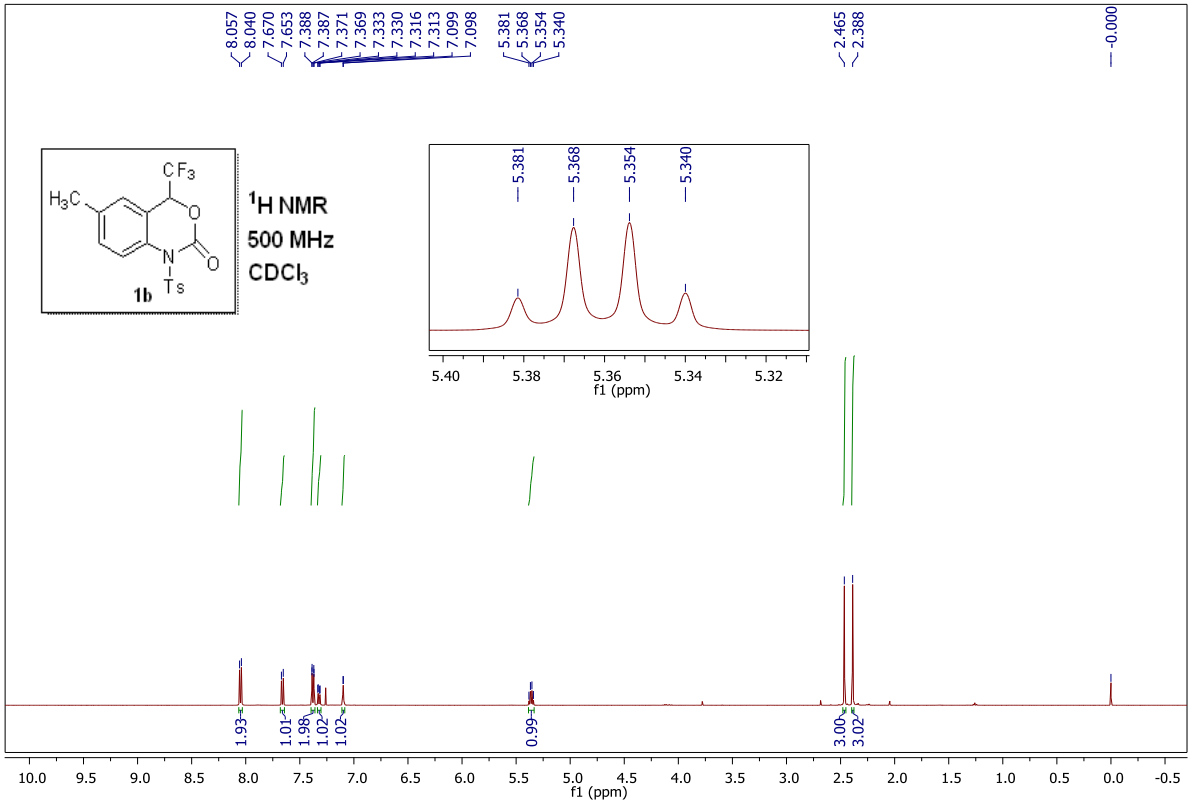
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Ts
1b
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5.340
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f1 (ppm)
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1.02
1.02
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3.02
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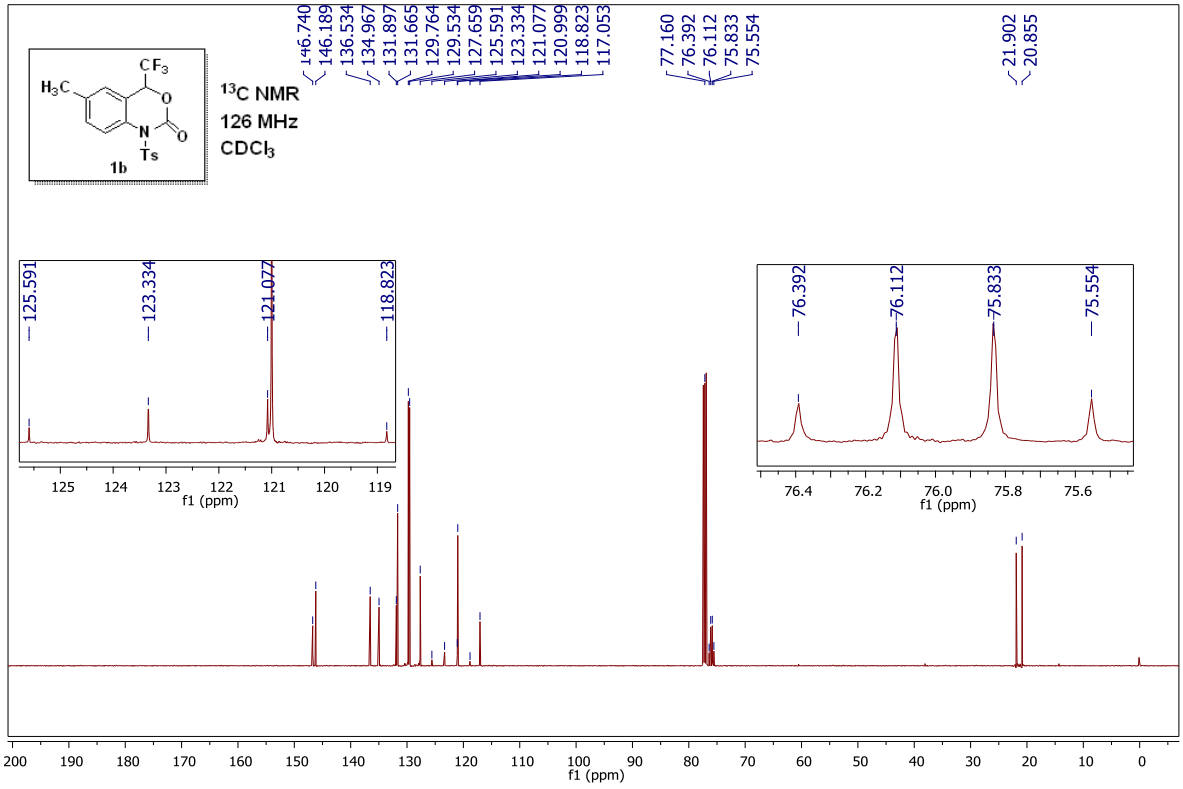
f1 (ppm)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75.554
21.902
20.855
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126 MHz
CDCl3
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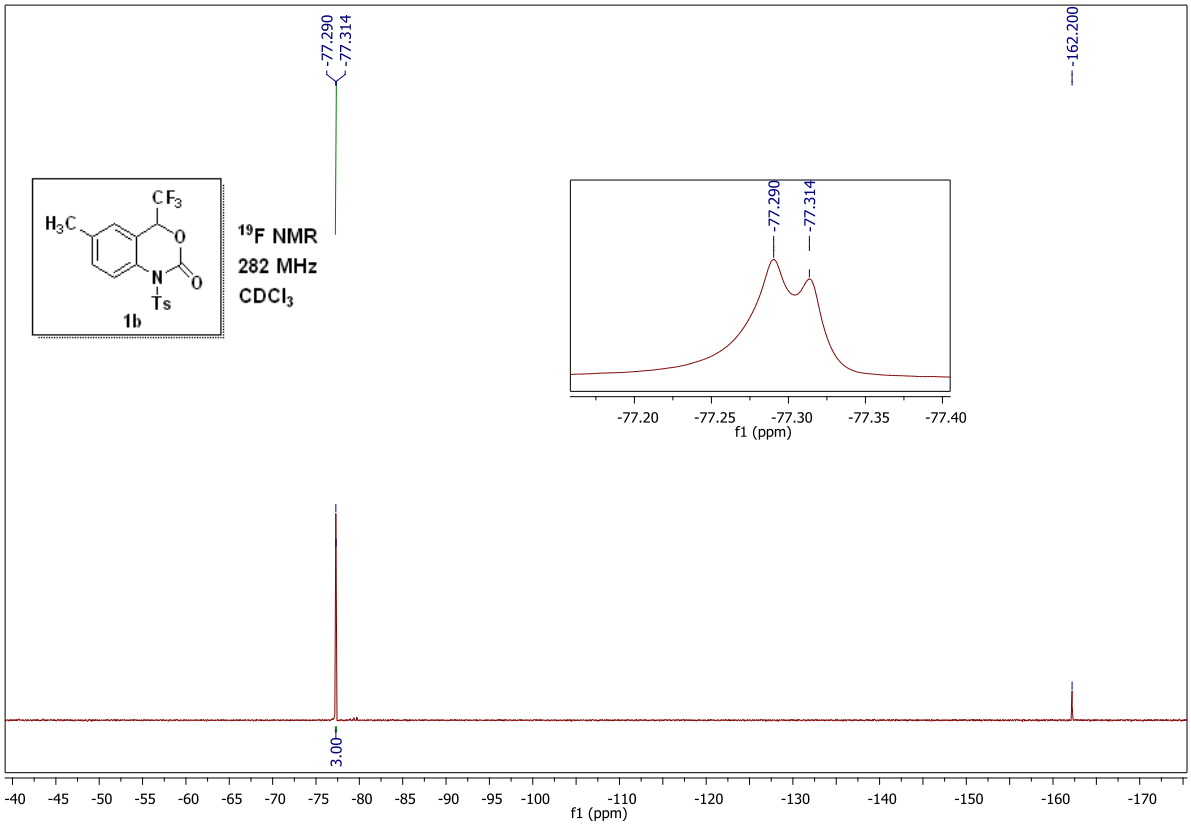
f1 (ppm)
f1 (ppm)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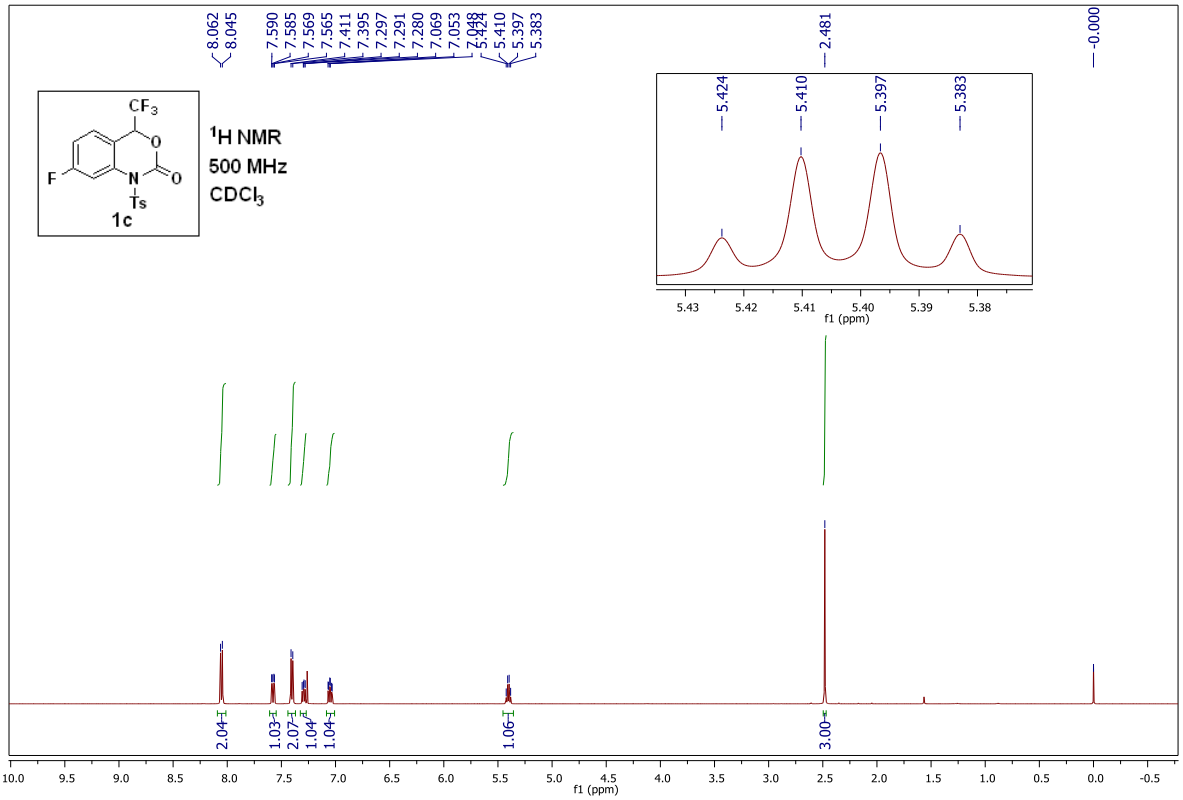
f1 (ppm)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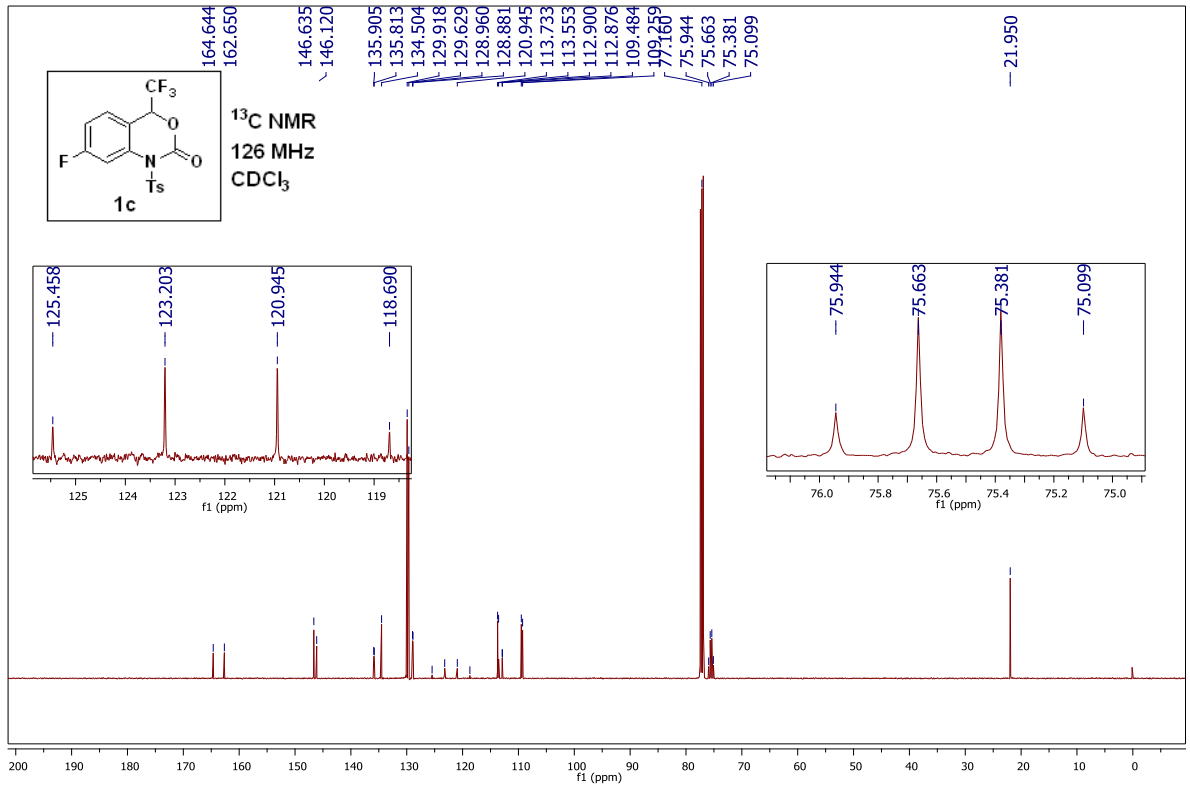
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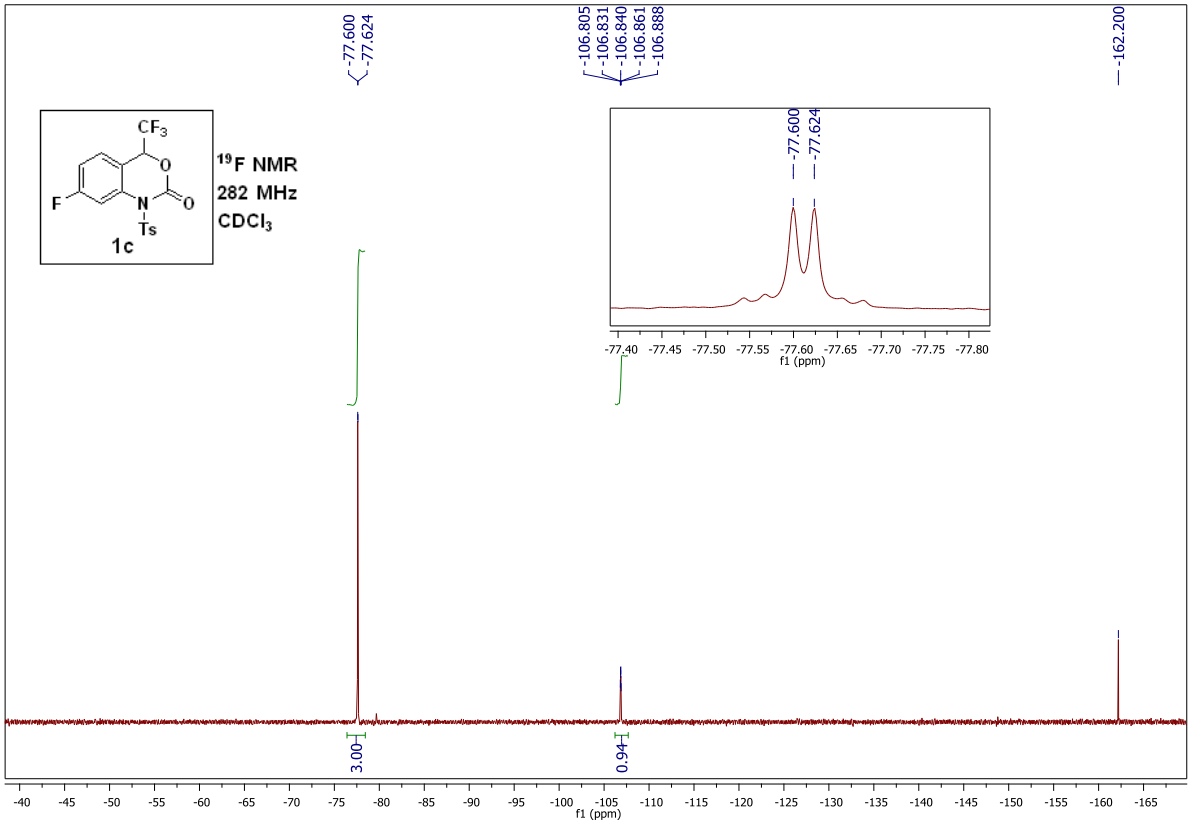
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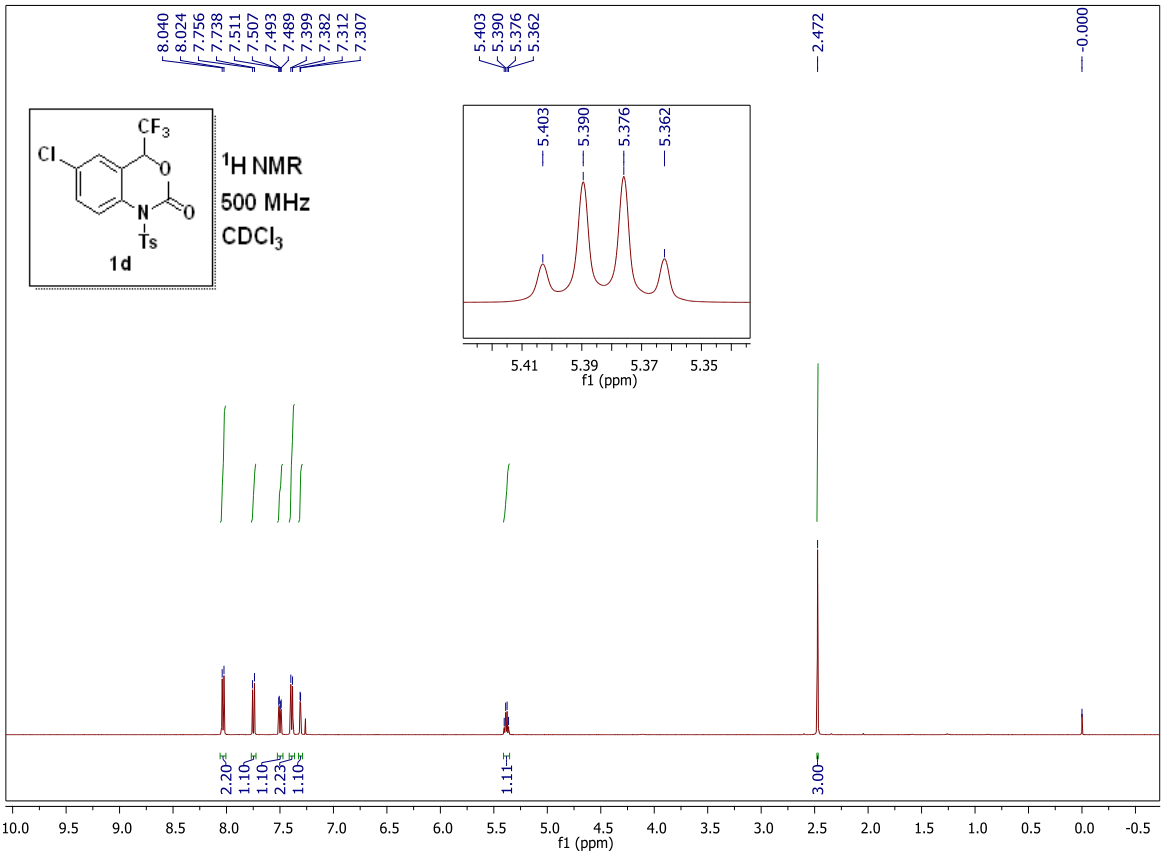
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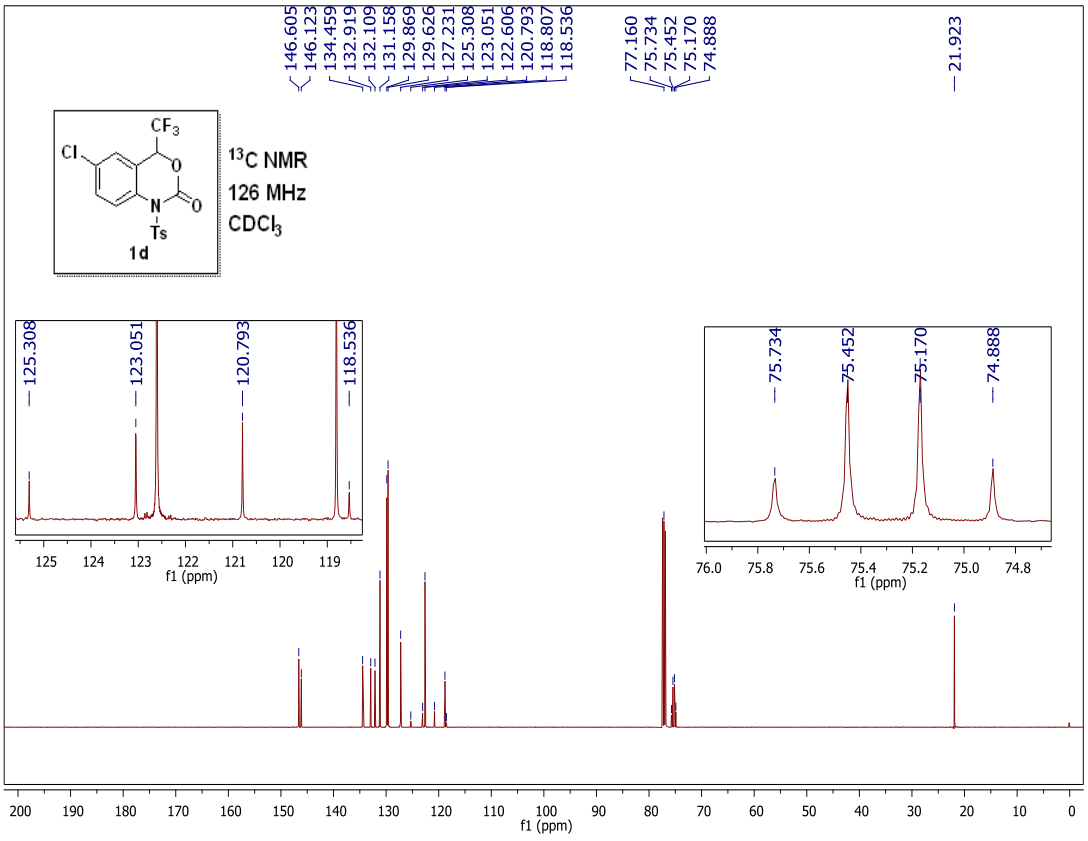
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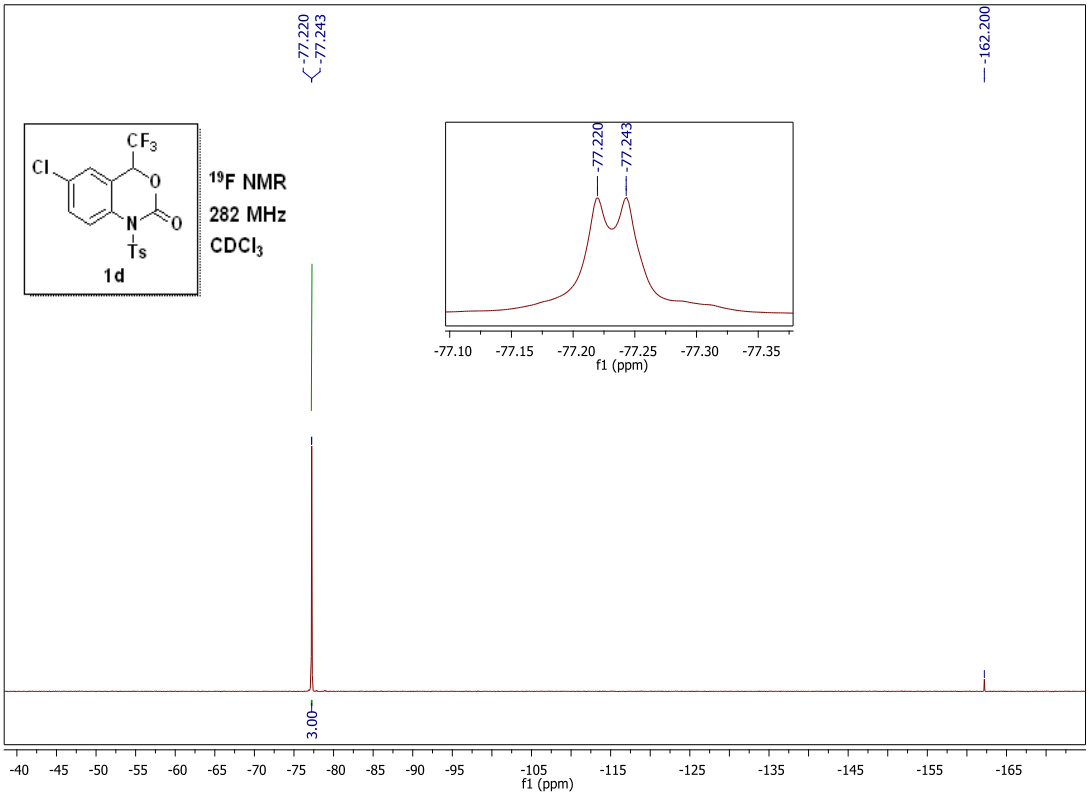
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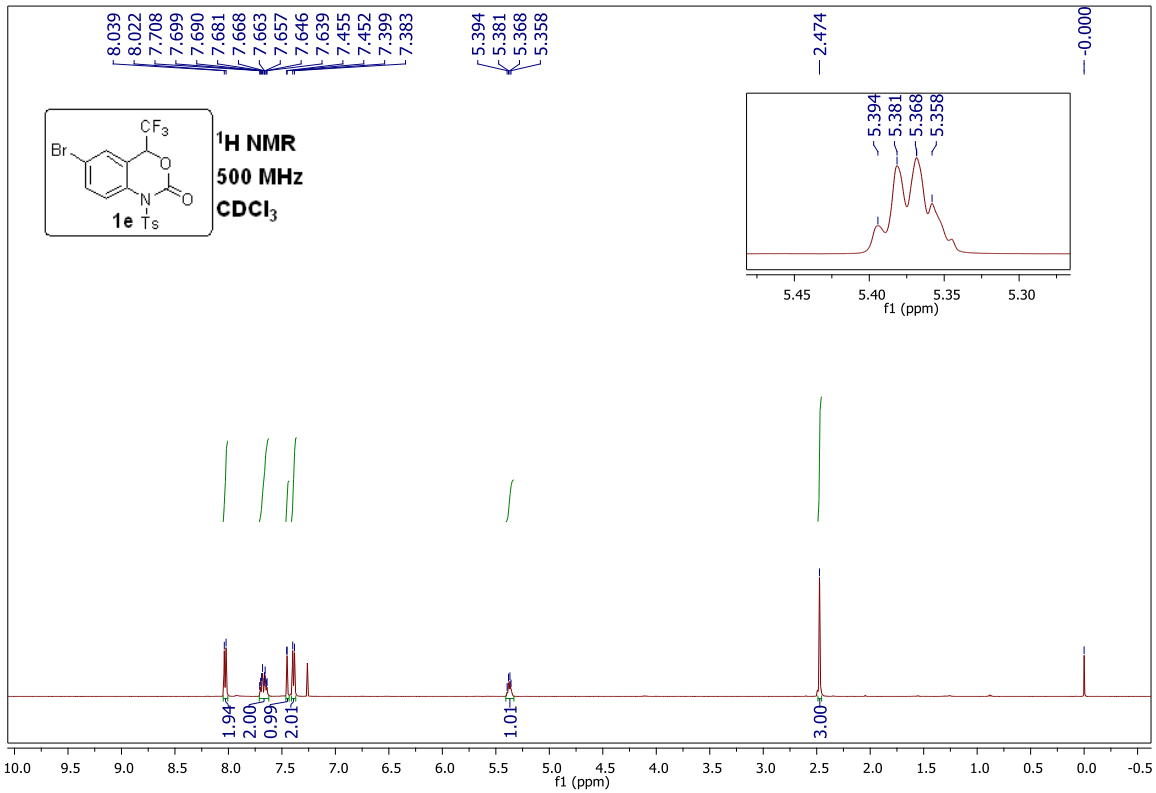
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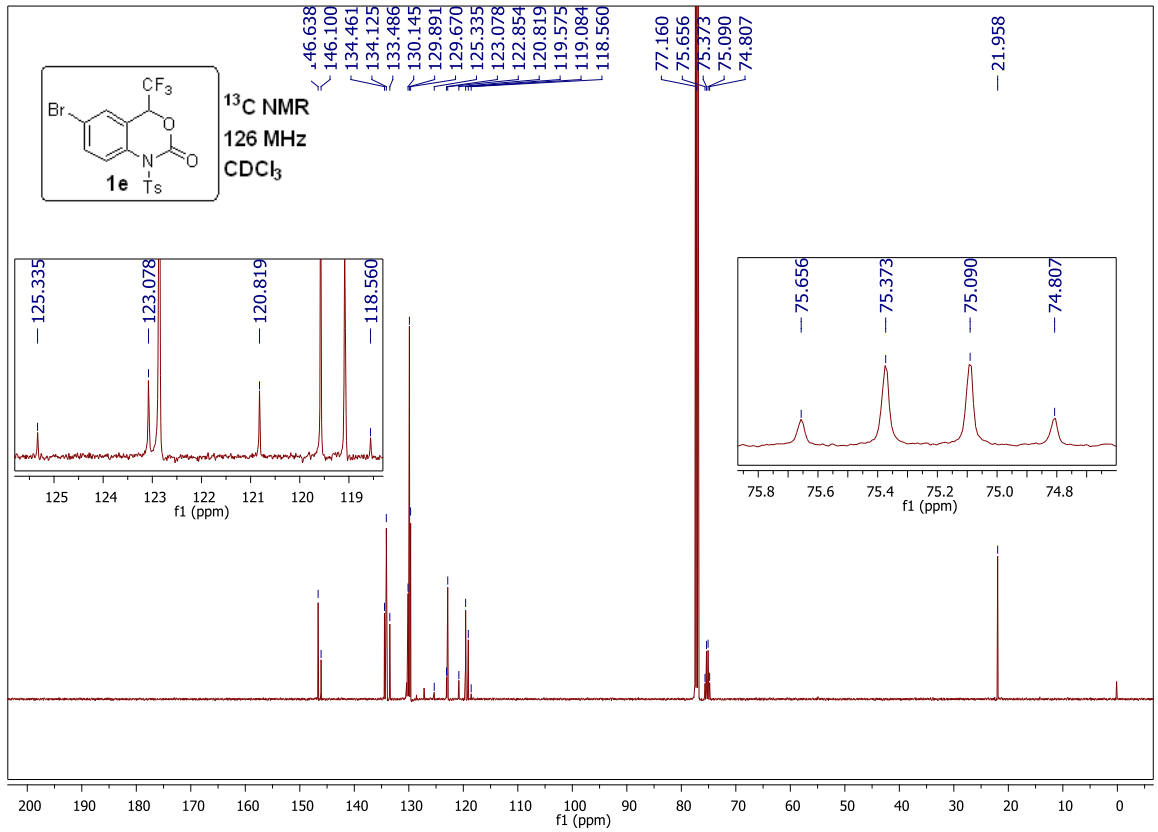
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CDCl3
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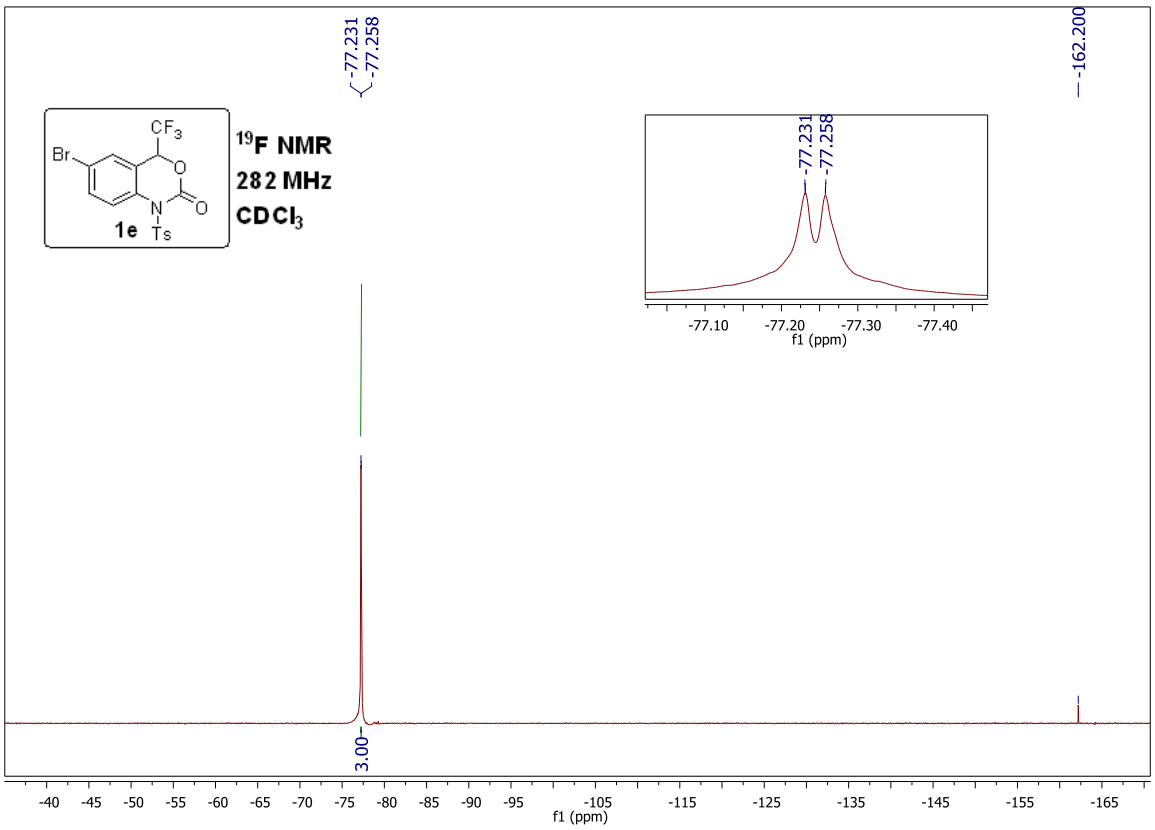
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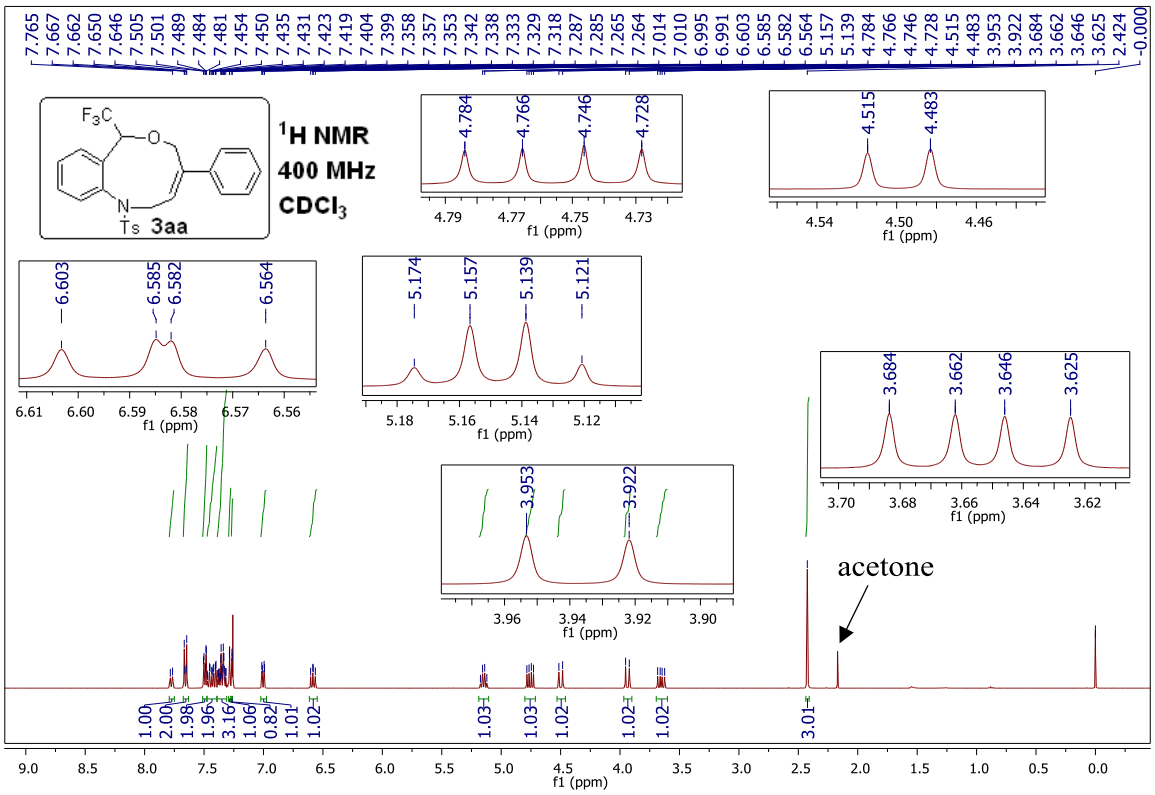
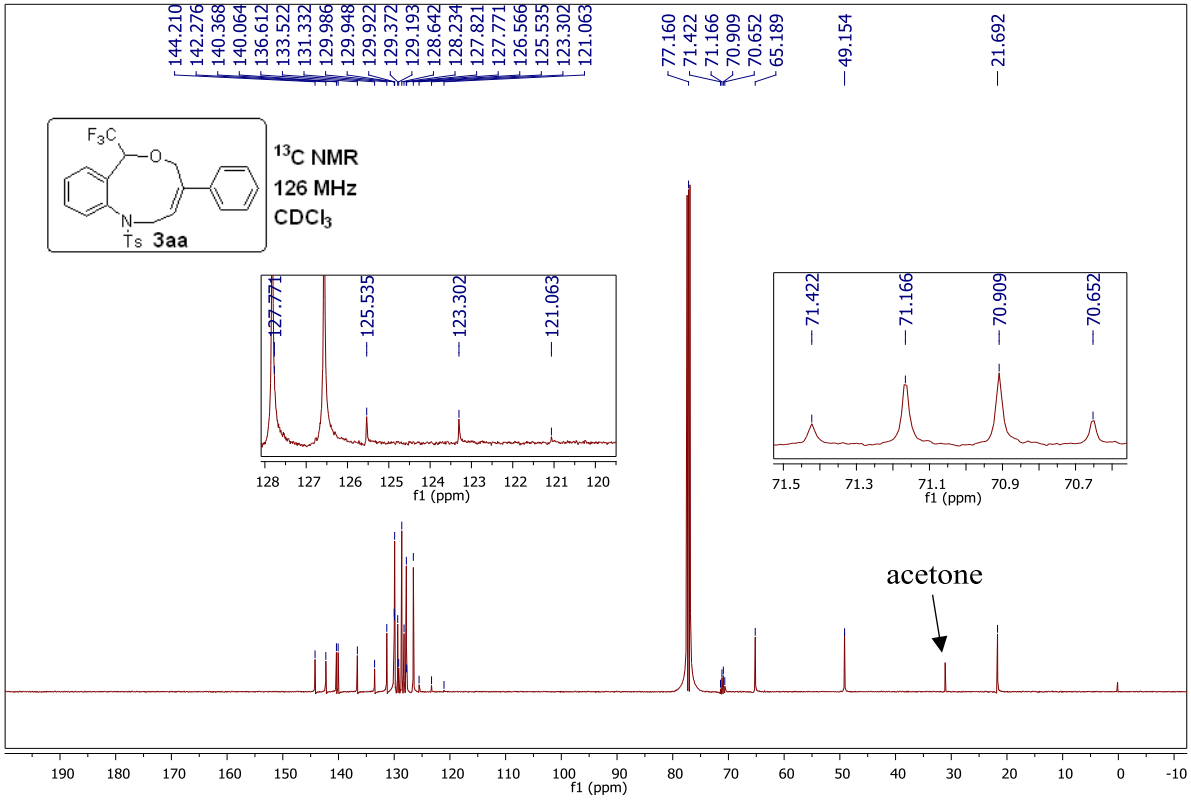
3.00
f1 (ppm)


1H NMR
400 MHz
CDCl3
3aa Ts
acetone
f1 (ppm)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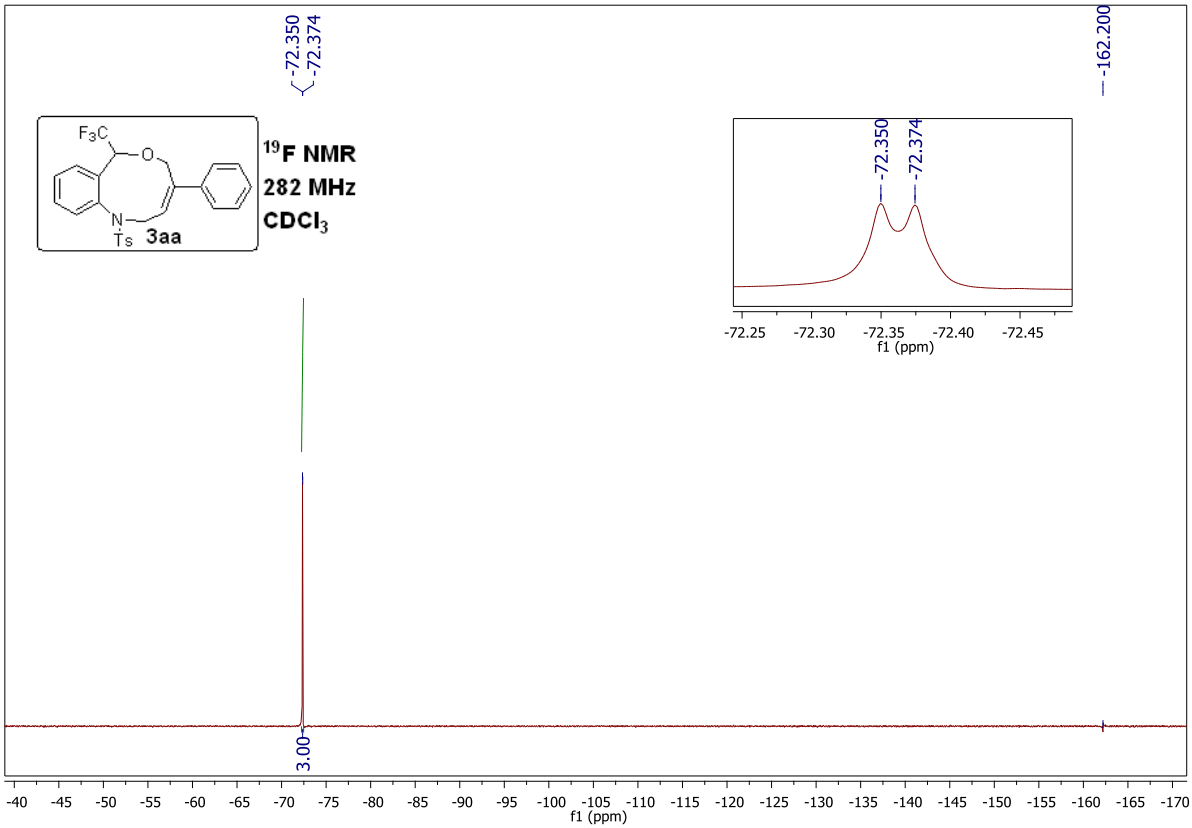
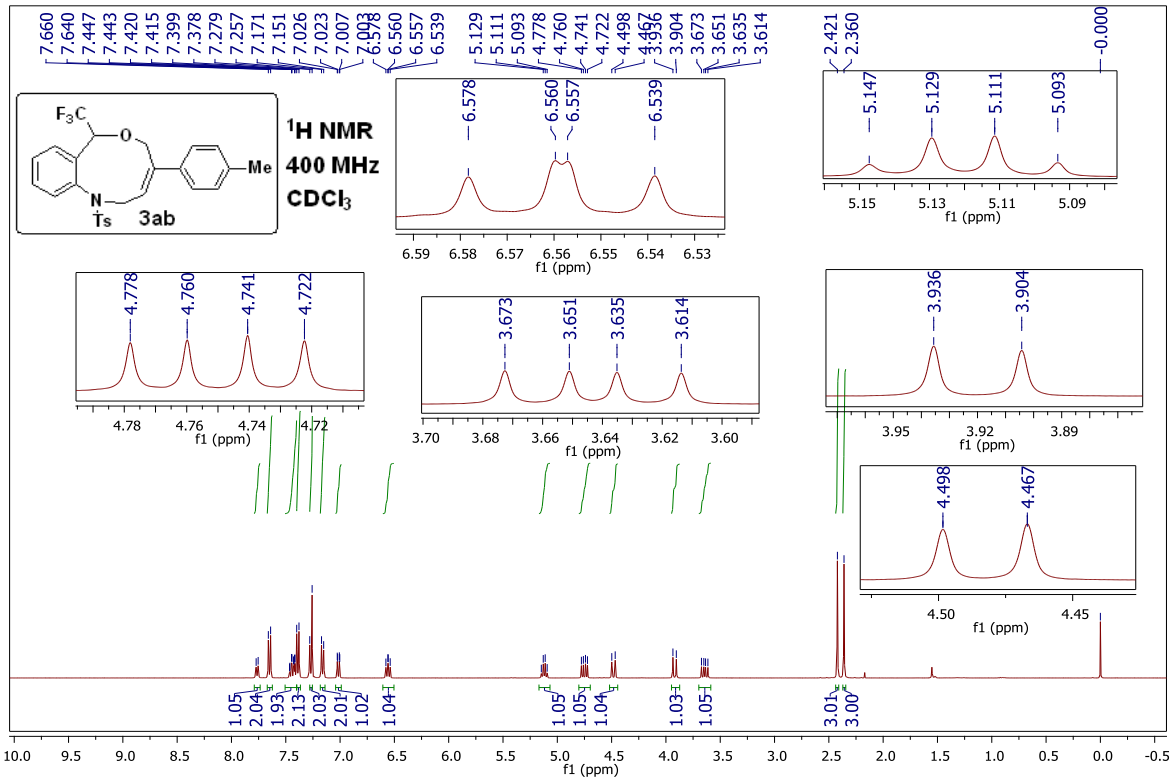
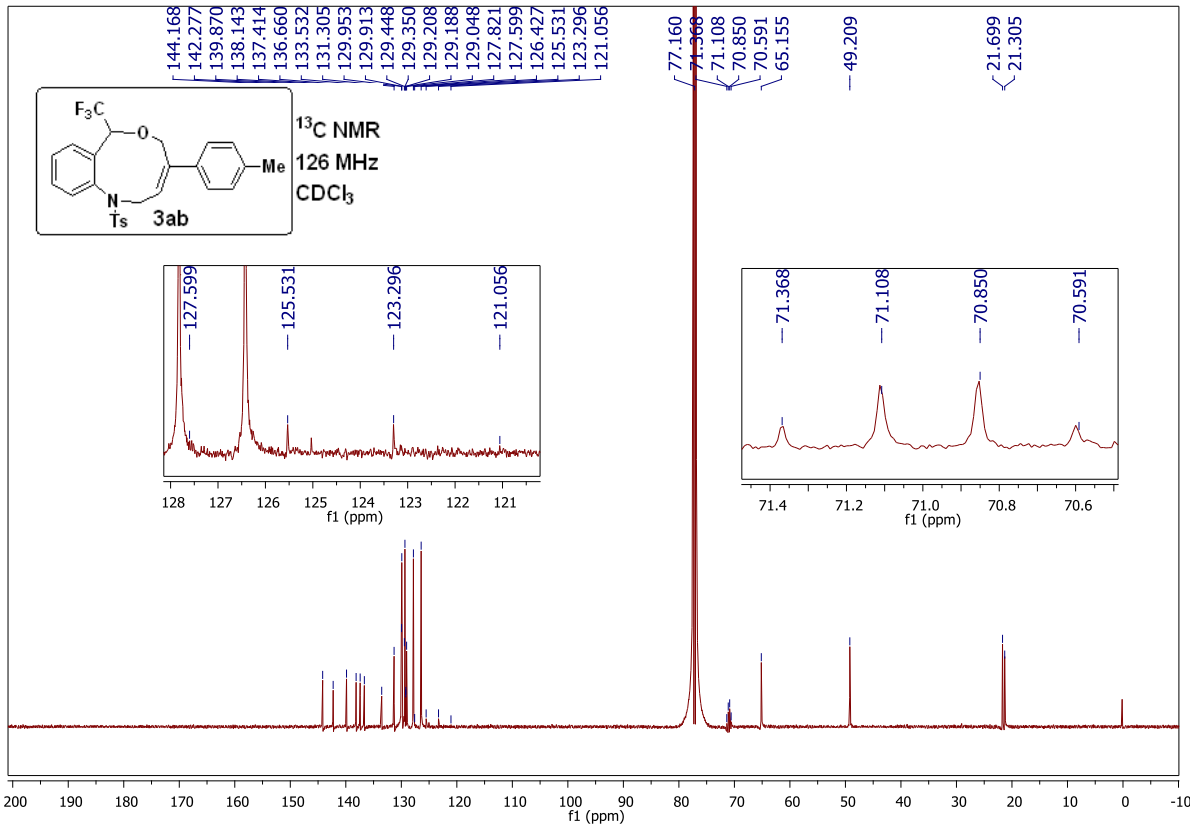
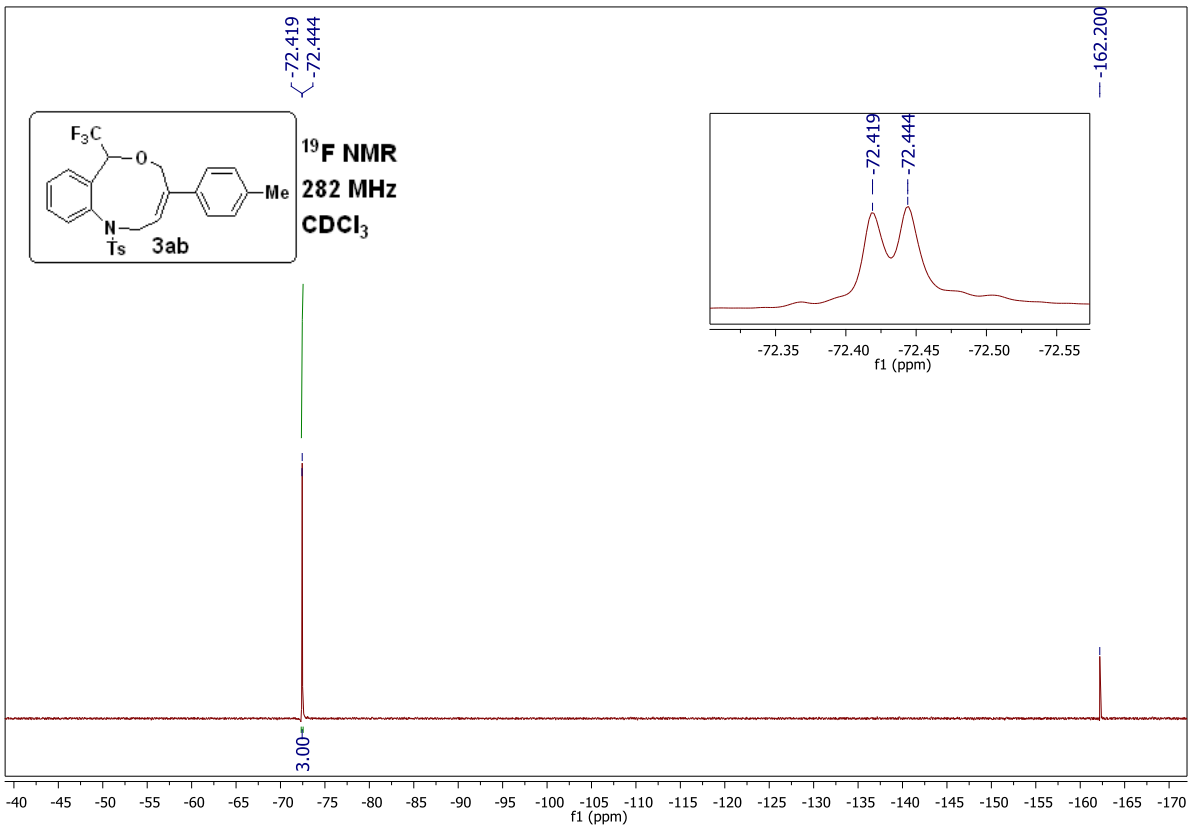
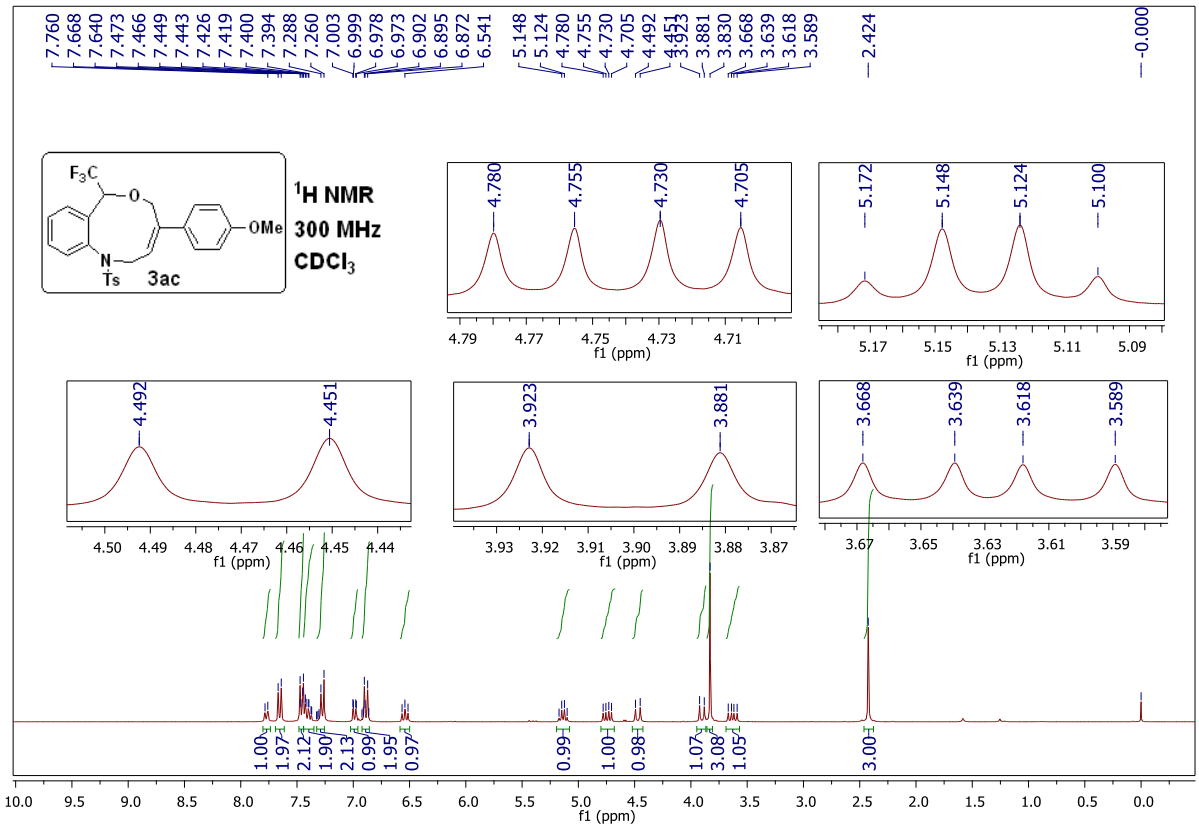
142.276
140.368
140.064
136.612
133.522
131.332
129.986
129.948
129.922
129.372
129.193
128.642
128.234
127.821
127.771
126.566
125.535
123.302
121.063
77.160
71.422
71.166
70.909
70.652
65.189
49.154
21.692
F3C
O
N
Ts 3aa
13C NMR
126 MHz
CDCl3
127.771
125.535
123.302
121.063
128 127 126 125 124 123 122 121 120
f1 (ppm)
71.422
71.166
70.909
70.652
71.5 71.3 71.1 70.9 70.7
f1 (ppm)
acetone
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

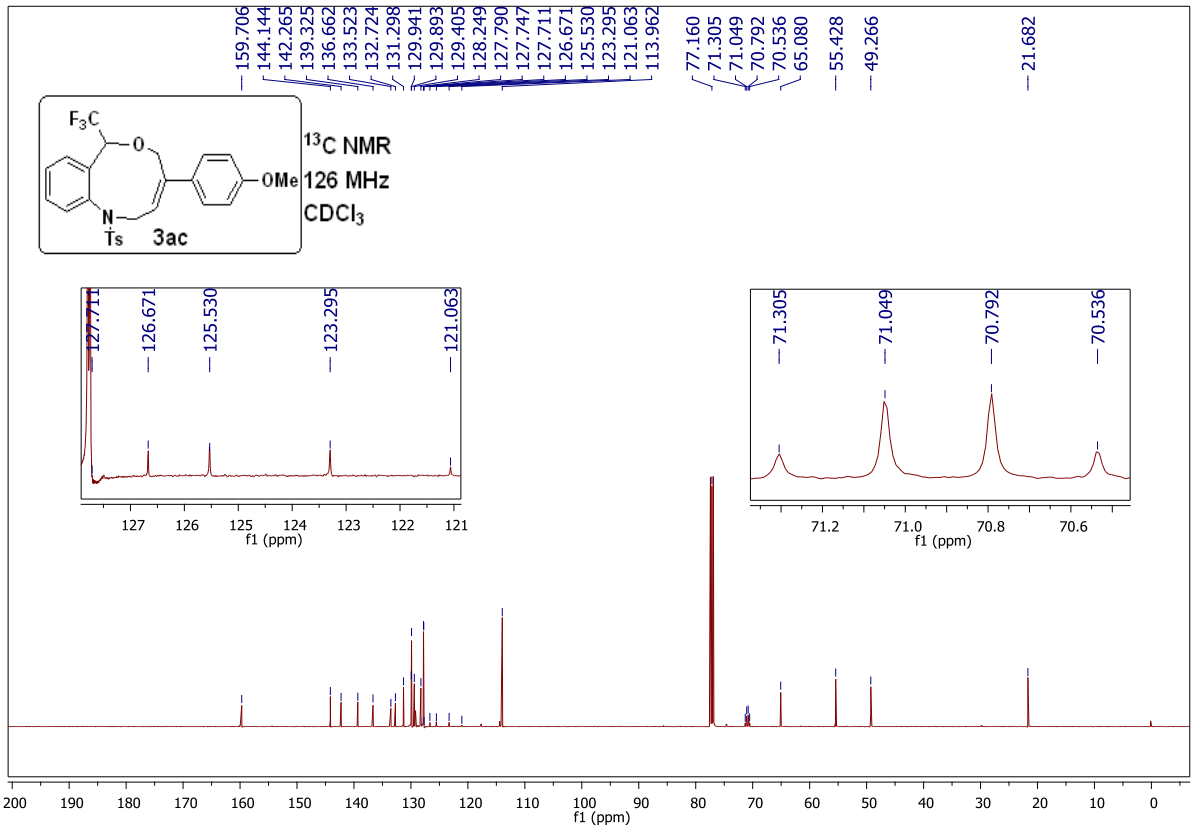

-72.350
-72.374
-162.200
F3C
O
N
Ts 3aa
19F NMR
282 MHz
CDCl3
-72.350
-72.374
-72.25 -72.30 -72.35 -72.40 -72.45
f1 (ppm)
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

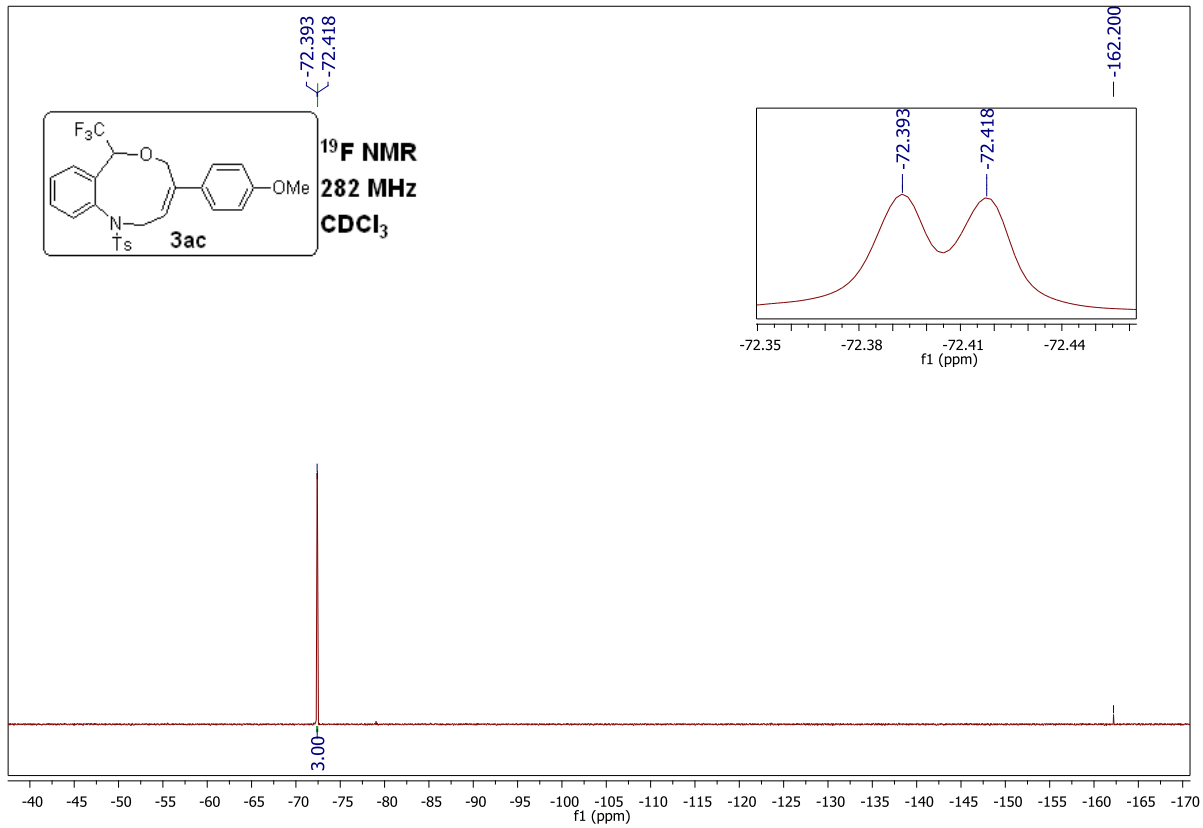

^{1}H NMR
400 MHz
CDCl$_3$
3ab
f1 (ppm)

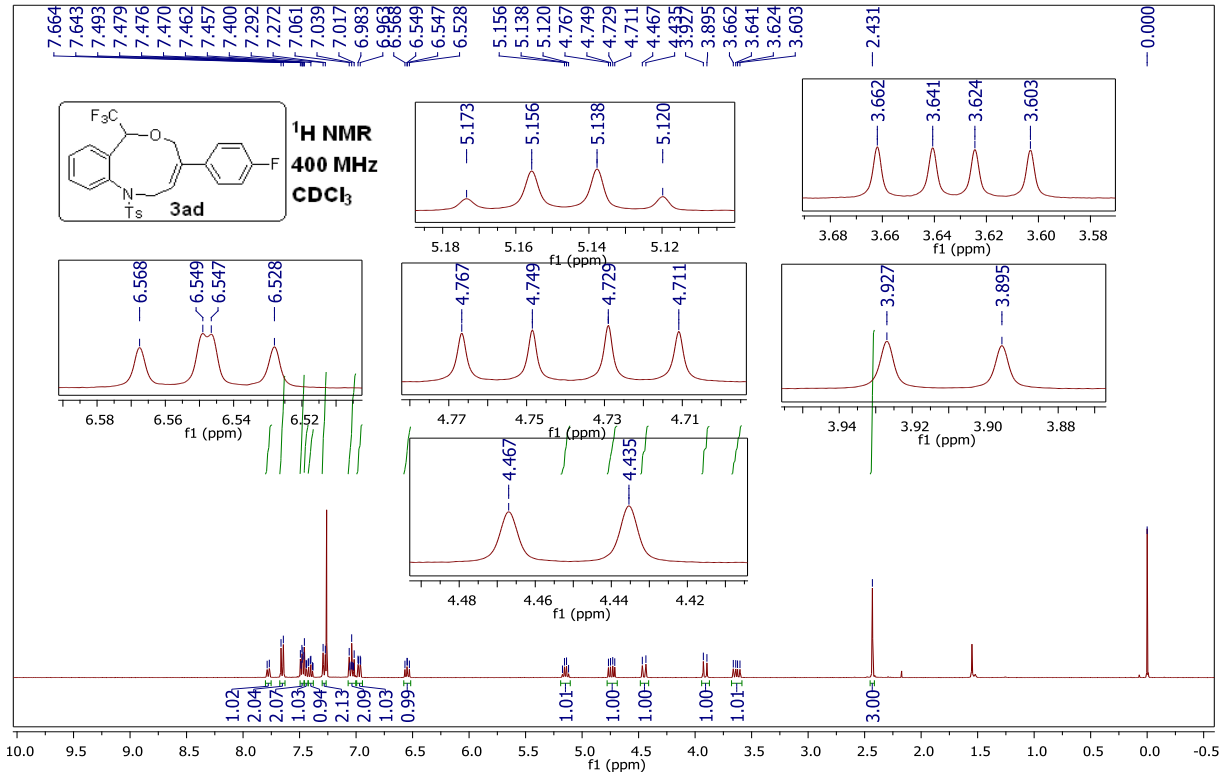

^{13}C NMR
126 MHz
CDCl$_3$
3ab
f1 (ppm)

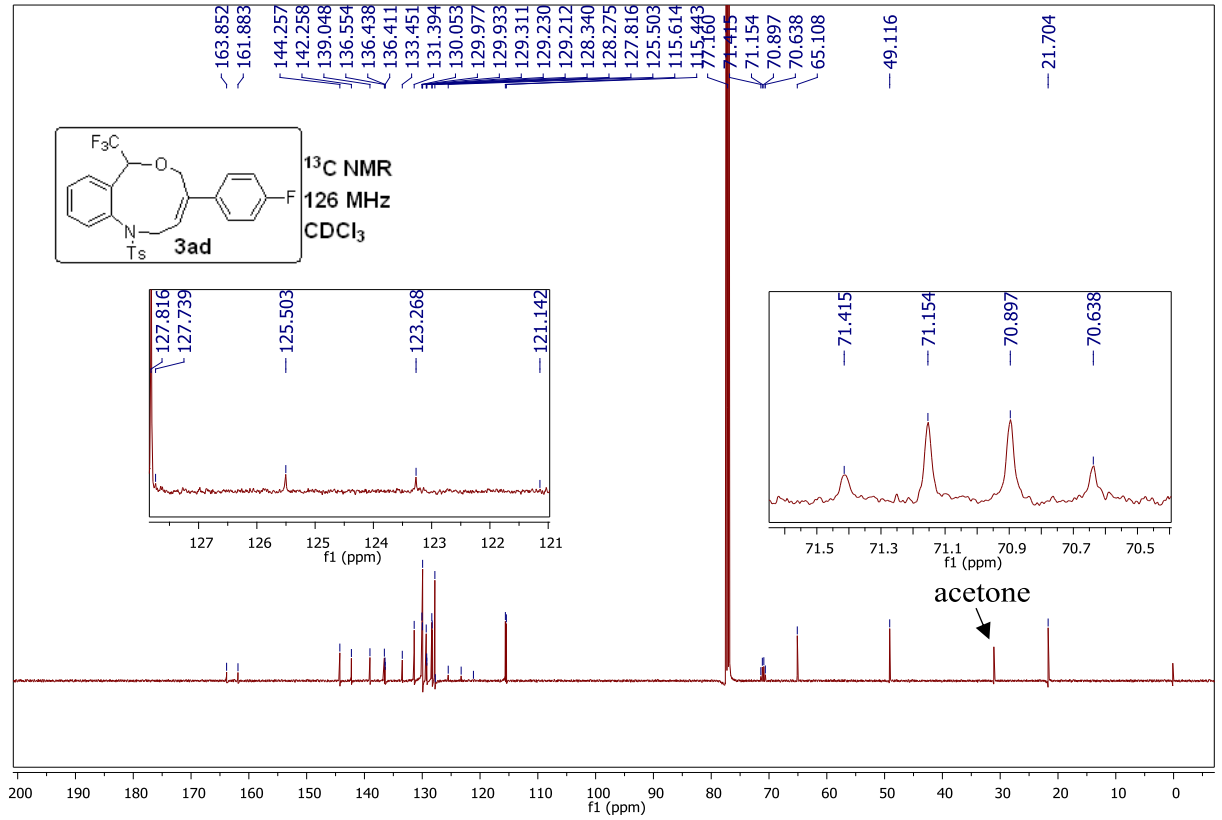

-72.419
-72.444
-162.200
F3C
O
Me
N
Ts
3ab
19F NMR
282 MHz
CDCl3
-72.419
-72.444
-72.35
-72.40
-72.45
-72.50
-72.55
f1 (ppm)
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

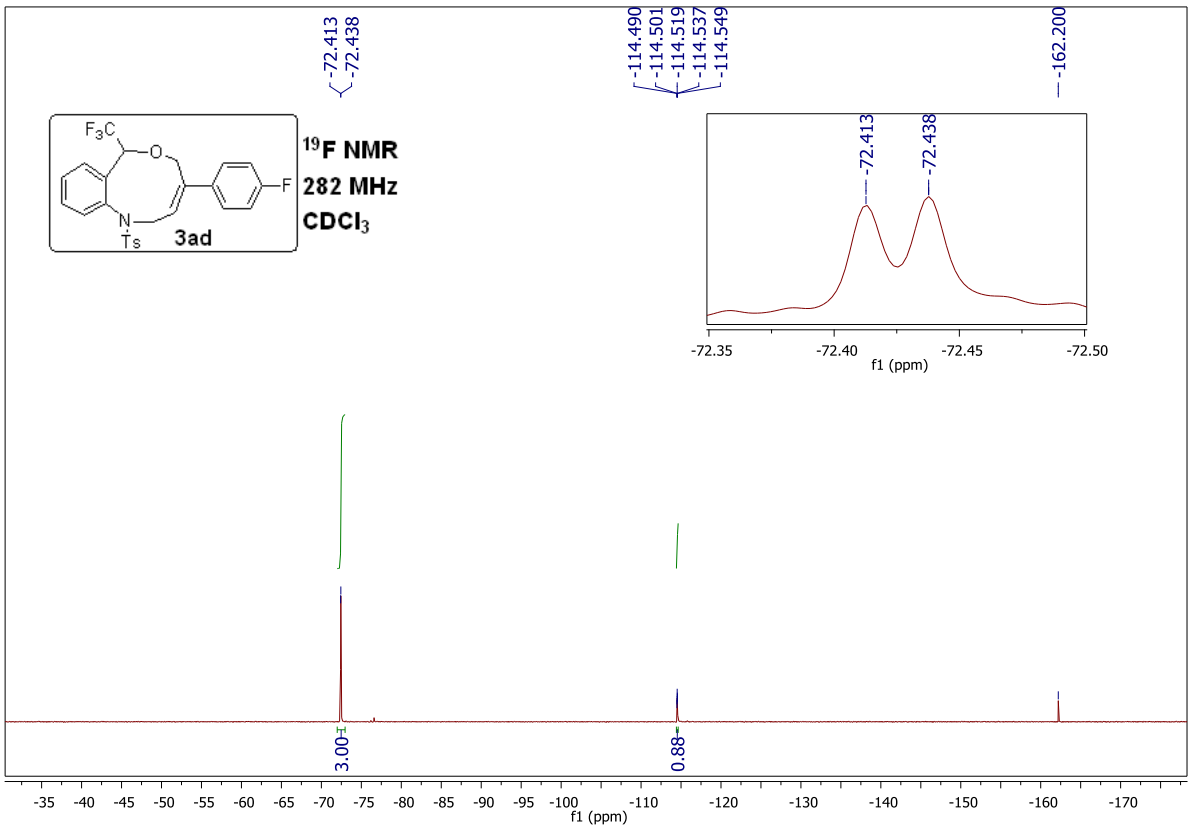

7.760
7.668
7.640
7.473
7.466
7.449
7.443
7.426
7.419
7.400
7.394
7.288
7.260
7.003
6.999
6.978
6.973
6.902
6.895
6.872
6.541
5.148
5.124
4.780
4.755
4.730
4.705
4.492
4.451
3.923
3.881
3.830
3.668
3.639
3.618
3.589
2.424
-0.000
F3C
O
OMe
N
Ts
3ac
1H NMR
300 MHz
CDCl3
4.780
4.755
4.730
4.705
4.79 4.77 4.75 4.73 4.71
f1 (ppm)
5.172
5.148
5.124
5.100
5.17 5.15 5.13 5.11 5.09
f1 (ppm)
4.492
4.451
4.50 4.49 4.48 4.47 4.46 4.45 4.44
f1 (ppm)
3.923
3.881
3.93 3.92 3.91 3.90 3.89 3.88 3.87
f1 (ppm)
3.668
3.639
3.618
3.589
3.67 3.65 3.63 3.61 3.59
f1 (ppm)
1.00
1.97
2.12
1.90
2.13
0.99
1.95
0.97
0.99
1.00
0.98
1.07
3.08
1.05
3.00
10.0 9.5 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)

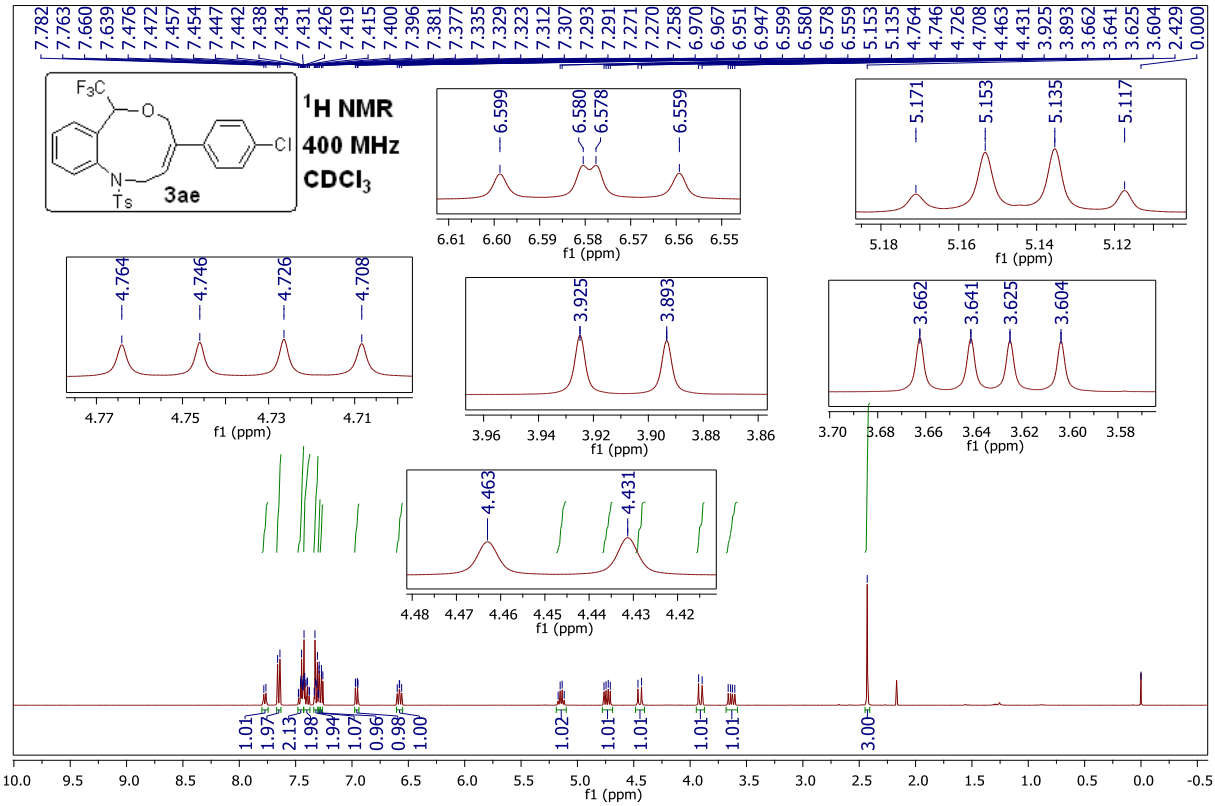

159.706
144.144
142.265
139.325
136.662
133.523
132.724
131.298
129.941
129.893
129.405
128.249
127.790
127.747
127.711
126.671
125.530
123.295
121.063
113.962
77.160
71.305
71.049
70.792
70.536
65.080
55.428
49.266
21.682
F3C
O
OMe
N
Ts
3ac
13C NMR
126 MHz
CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)

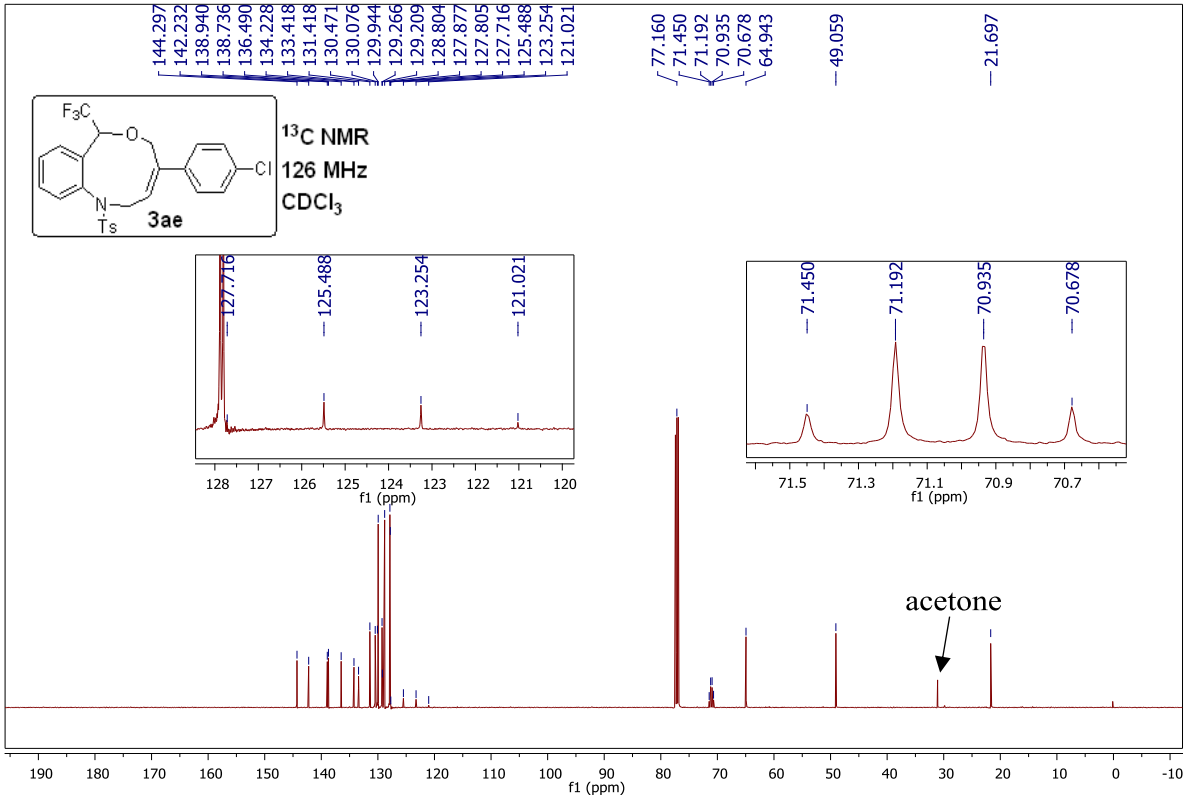

-72.393
-72.418
-162.200
F3C
O
OMe
N
Ts
3ac
19F NMR
282 MHz
CDCl3
3.00
f1 (ppm)
f1 (ppm)
f1 (ppm)

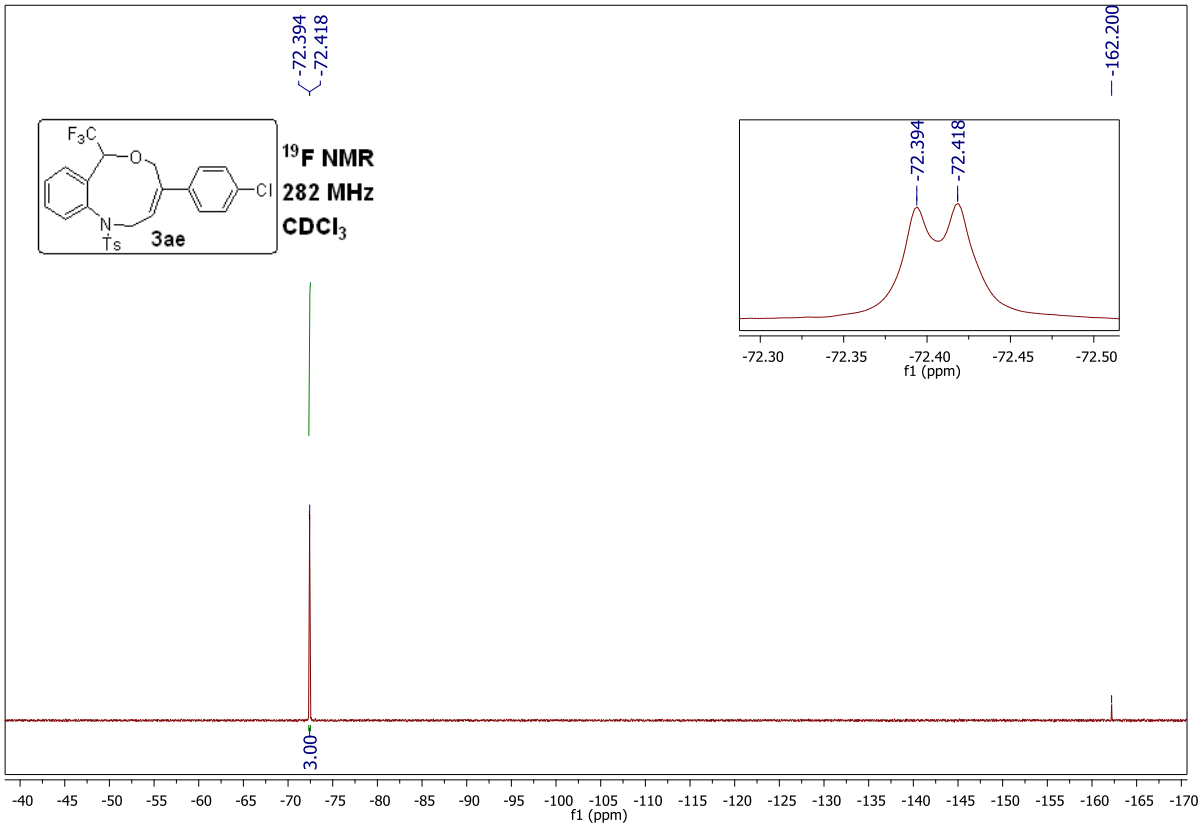

7.664 7.643 7.493 7.479 7.476 7.470 7.462 7.457 7.400 7.292 7.272 7.061 7.039 7.017 6.983 6.963 6.568 6.549 6.547 6.528 5.156 5.138 5.120 4.767 4.749 4.729 4.711 4.467 4.435 3.927 3.895 3.662 3.641 3.624 3.603 2.431 0.000
^{1}H NMR
400 MHz
CDCl$_3$
3ad
1.02 2.04 2.07 1.03 0.94 2.13 2.09 1.03 0.99 1.01 1.00 1.00 1.00 1.01 3.00
f1 (ppm)

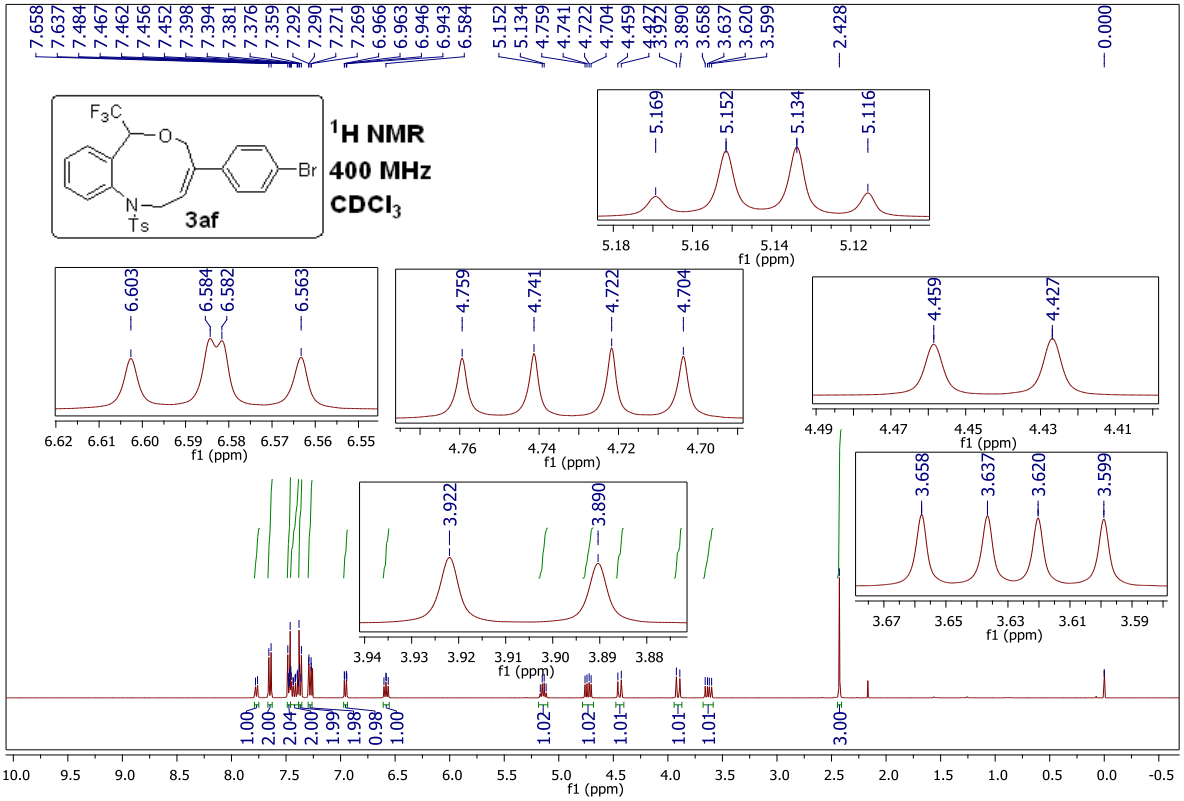

163.852 161.883 144.257 142.258 139.048 136.554 136.438 136.411 133.451 131.394 130.053 129.977 129.933 129.311 129.230 129.212 128.340 128.275 127.816 125.503 115.614 115.443 77.160 71.415 71.154 70.897 70.638 65.108 49.116 21.704
^{13}C NMR
126 MHz
CDCl$_3$
3ad
acetone
f1 (ppm)


-72.413
-72.438
-114.490
-114.501
-114.519
-114.537
-114.549
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3ad
f1 (ppm)
3.00
0.88


^{1}H NMR
400 MHz
CDCl$_3$
3ae
f1 (ppm)


144.297
142.232
138.940
138.736
136.490
134.228
133.418
131.418
130.471
130.076
129.944
129.266
129.209
128.804
127.877
127.805
127.716
125.488
123.254
121.021
77.160
71.450
71.192
70.935
70.678
64.943
49.059
21.697
F3C
O
Cl
N
Ts
3ae
13C NMR
126 MHz
CDCl3
127.716
125.488
123.254
121.021
128 127 126 125 124 123 122 121 120
f1 (ppm)
71.450
71.192
70.935
70.678
71.5 71.3 71.1 70.9 70.7
f1 (ppm)
acetone
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-72.394
-72.418
-162.200
F3C
O
Cl
N
Ts
3ae
19F NMR
282 MHz
CDCl3
-72.394
-72.418
-72.30 -72.35 -72.40 -72.45 -72.50
f1 (ppm)
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)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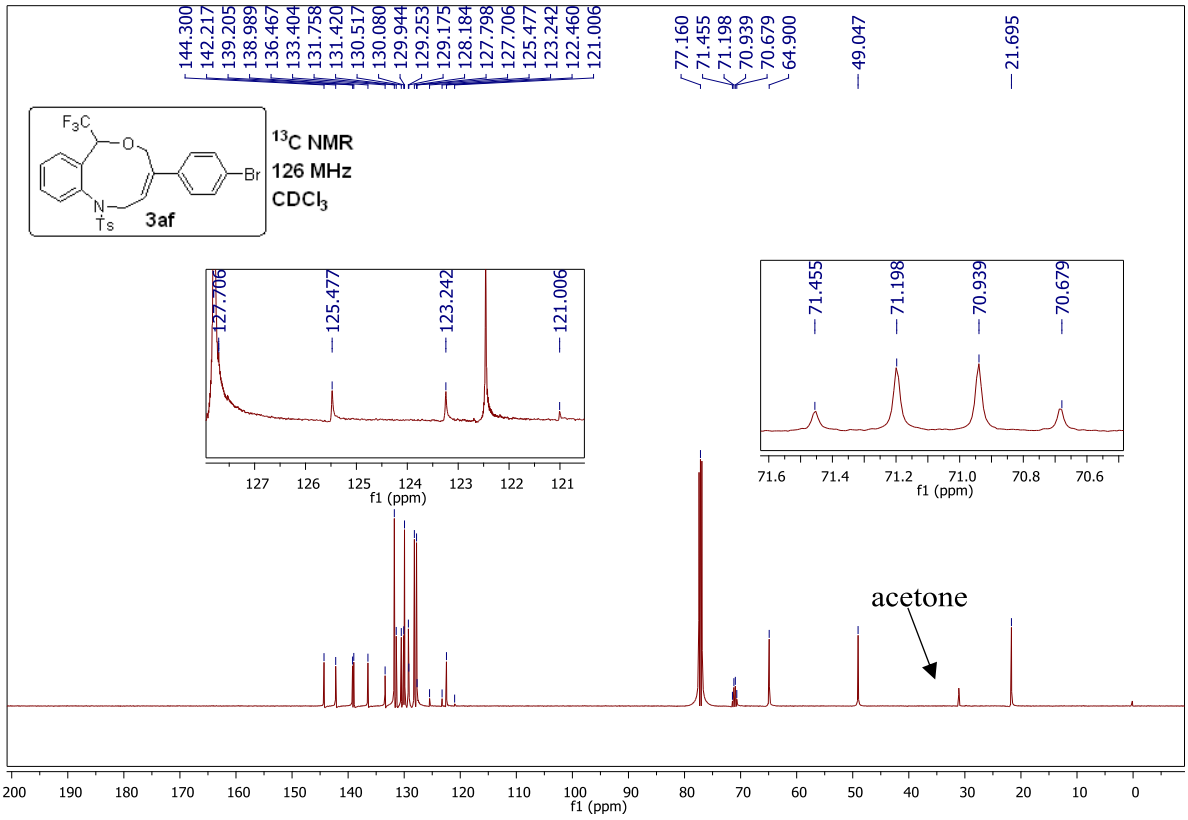
7.637
7.484
7.467
7.462
7.456
7.452
7.398
7.394
7.381
7.376
7.359
7.292
7.290
7.271
7.269
6.966
6.963
6.946
6.943
6.584
5.152
5.134
4.759
4.741
4.722
4.704
4.459
4.427
3.922
3.890
3.658
3.637
3.620
3.599
2.428
0.000
F3C
O
Br
N
Ts
3af
1H NMR
400 MHz
CDCl3
5.169
5.152
5.134
5.116
6.603
6.584
6.582
6.563
4.759
4.741
4.722
4.704
4.459
4.427
3.922
3.890
3.658
3.637
3.620
3.599
1.00
2.00
2.04
2.00
1.99
0.98
1.00
1.02
1.02
1.01
1.01
1.01
3.00
f1 (ppm)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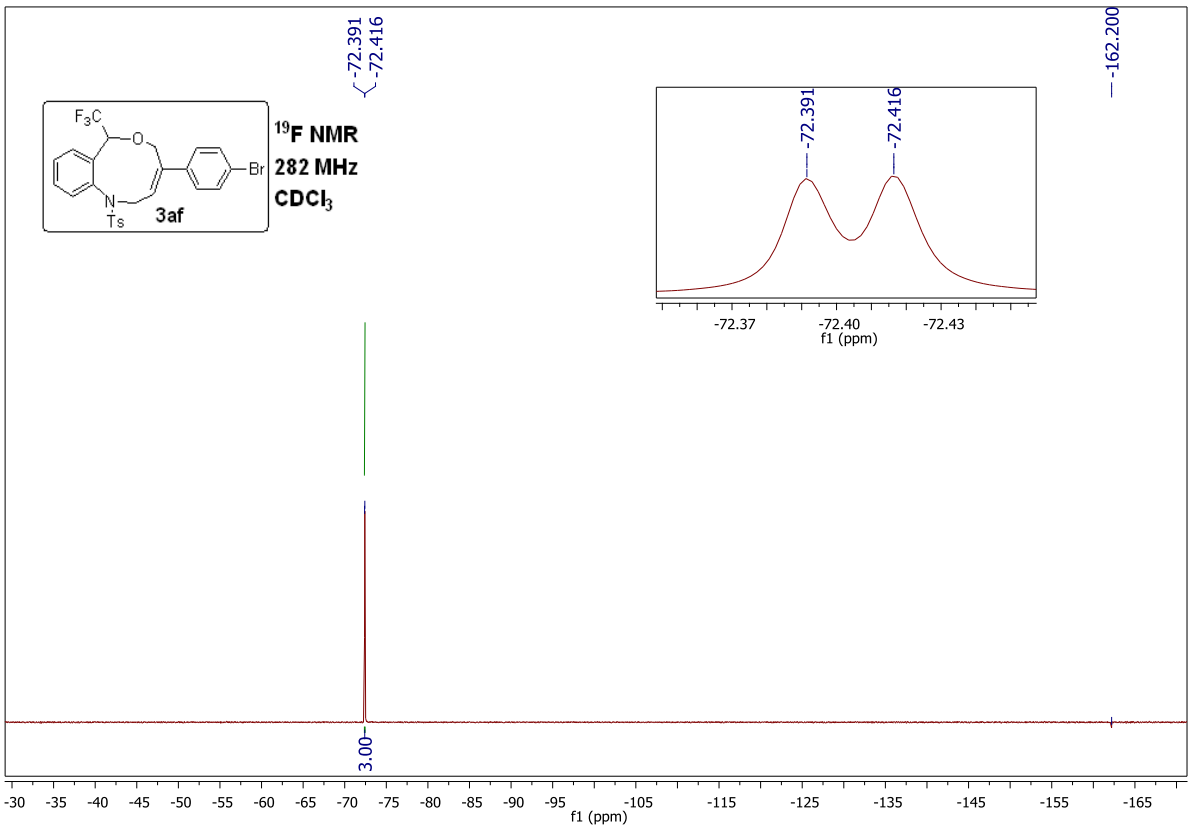
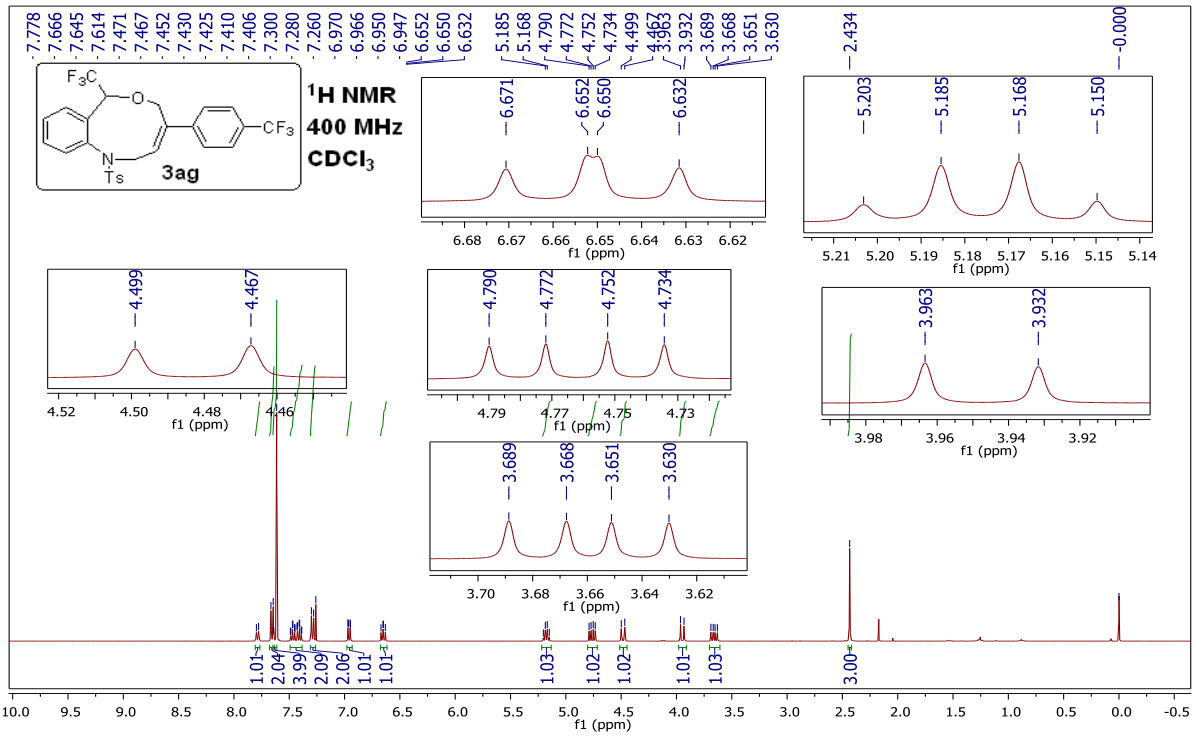
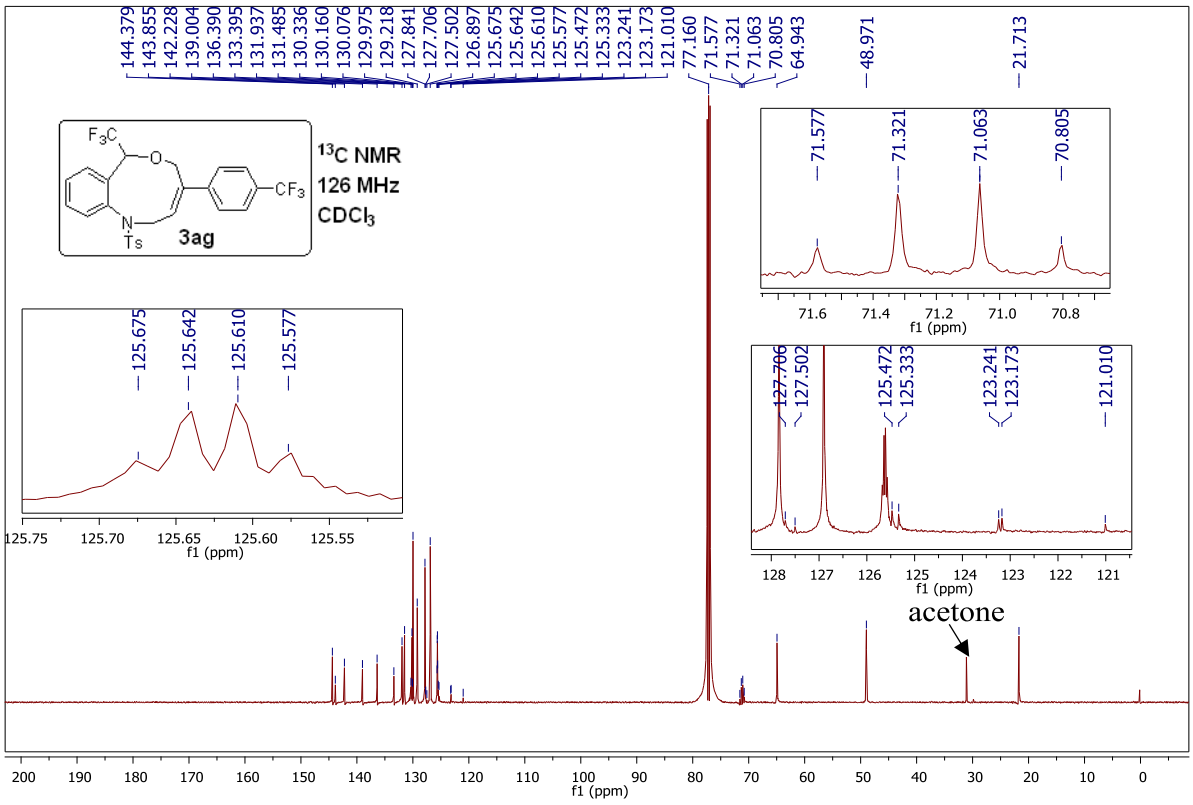
142.217
139.205
138.989
136.467
133.404
131.758
131.420
130.517
130.080
129.944
129.253
129.175
128.184
127.798
127.706
125.477
123.242
122.460
121.006
77.160
71.455
71.198
70.939
70.679
64.900
49.047
21.695
F3C
O
Br
N
Ts
3af
13C NMR
126 MHz
CDCl3
127.706
125.477
123.242
121.006
71.455
71.198
70.939
70.679
acetone
f1 (ppm)


-72.391
-72.416
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3af
3.00
f1 (ppm)


^{1}H NMR
400 MHz
CDCl$_3$
3ag
f1 (ppm)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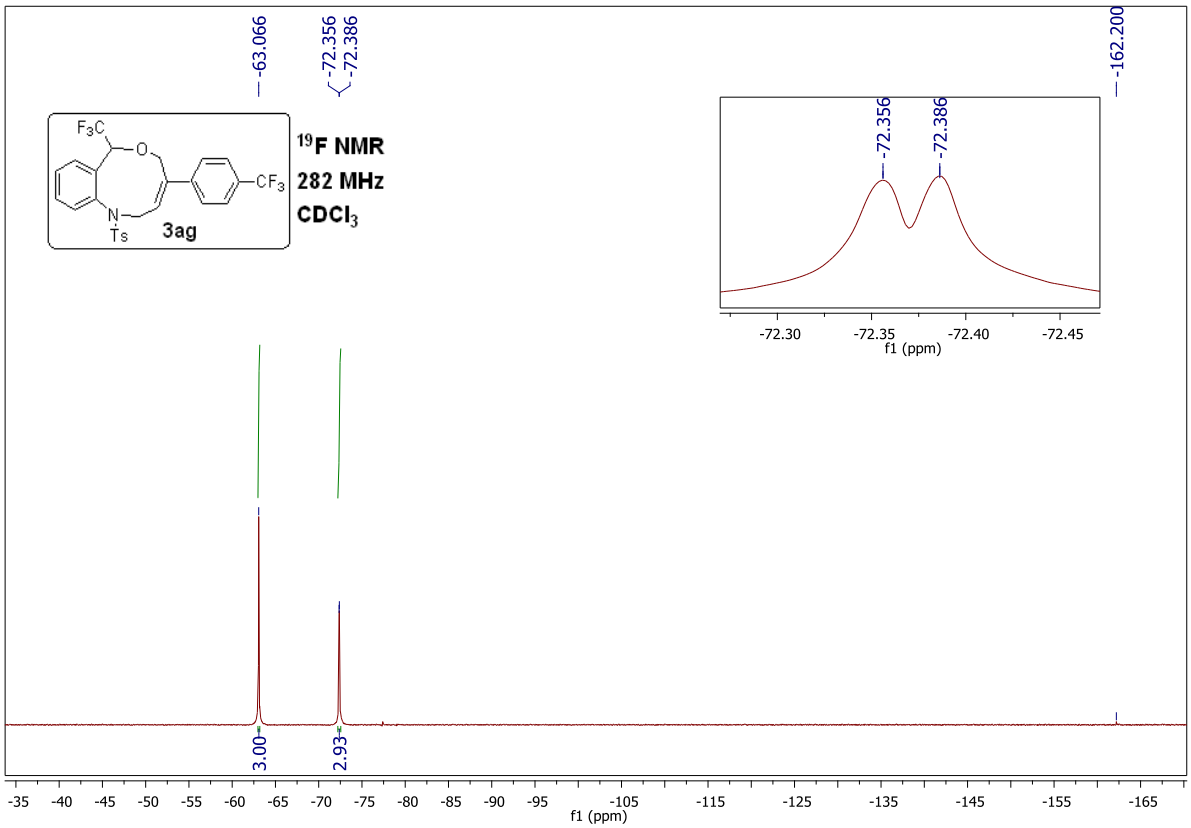
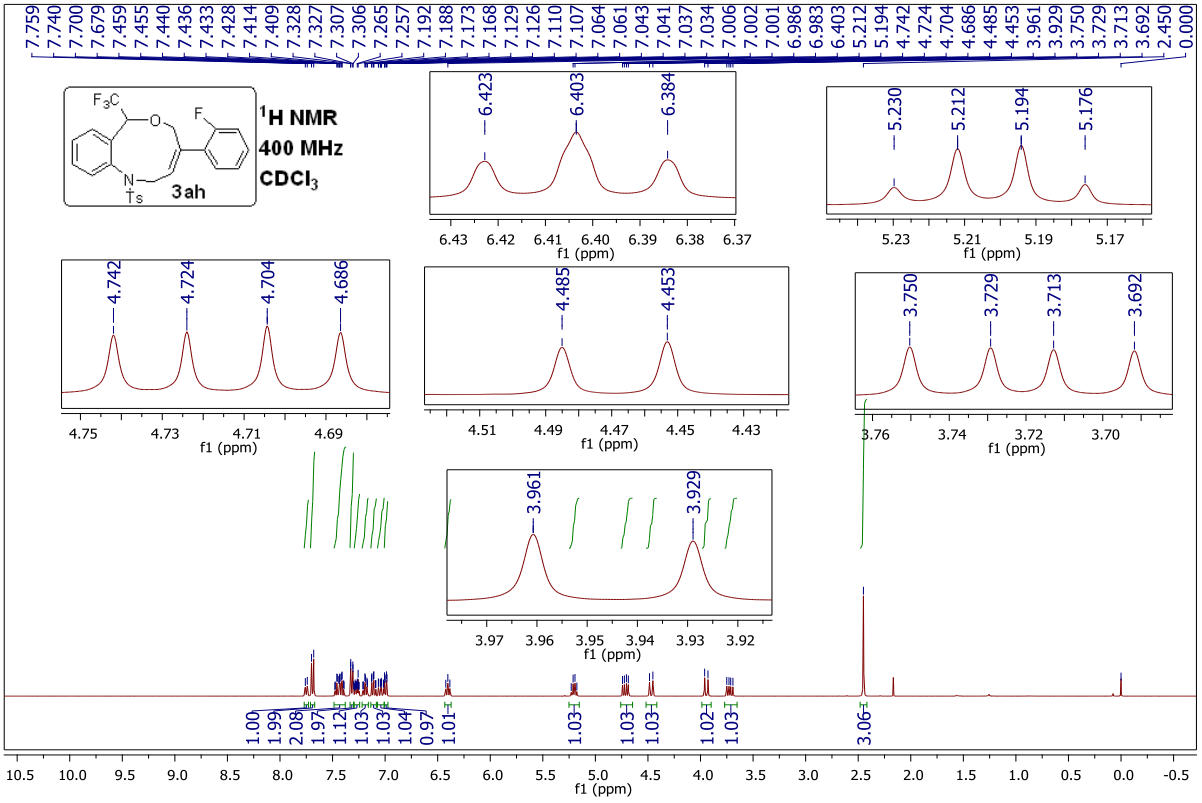
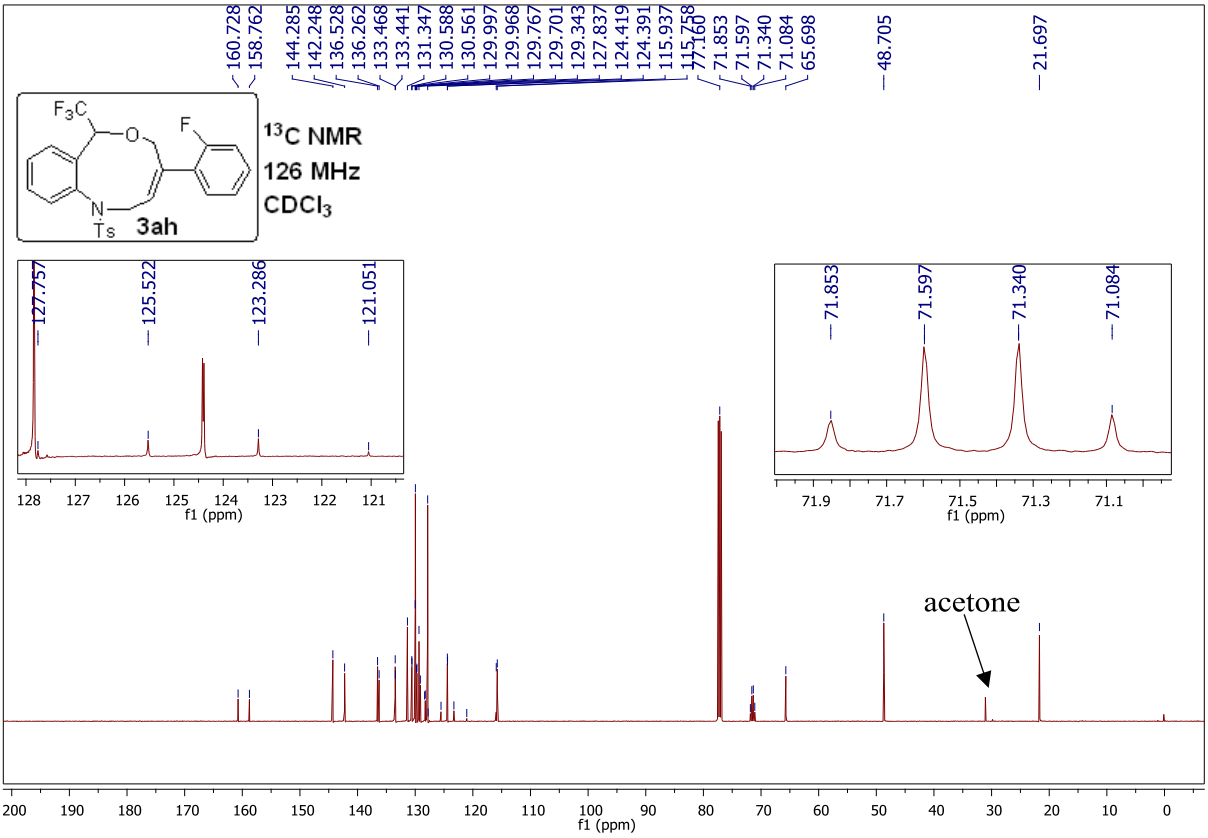
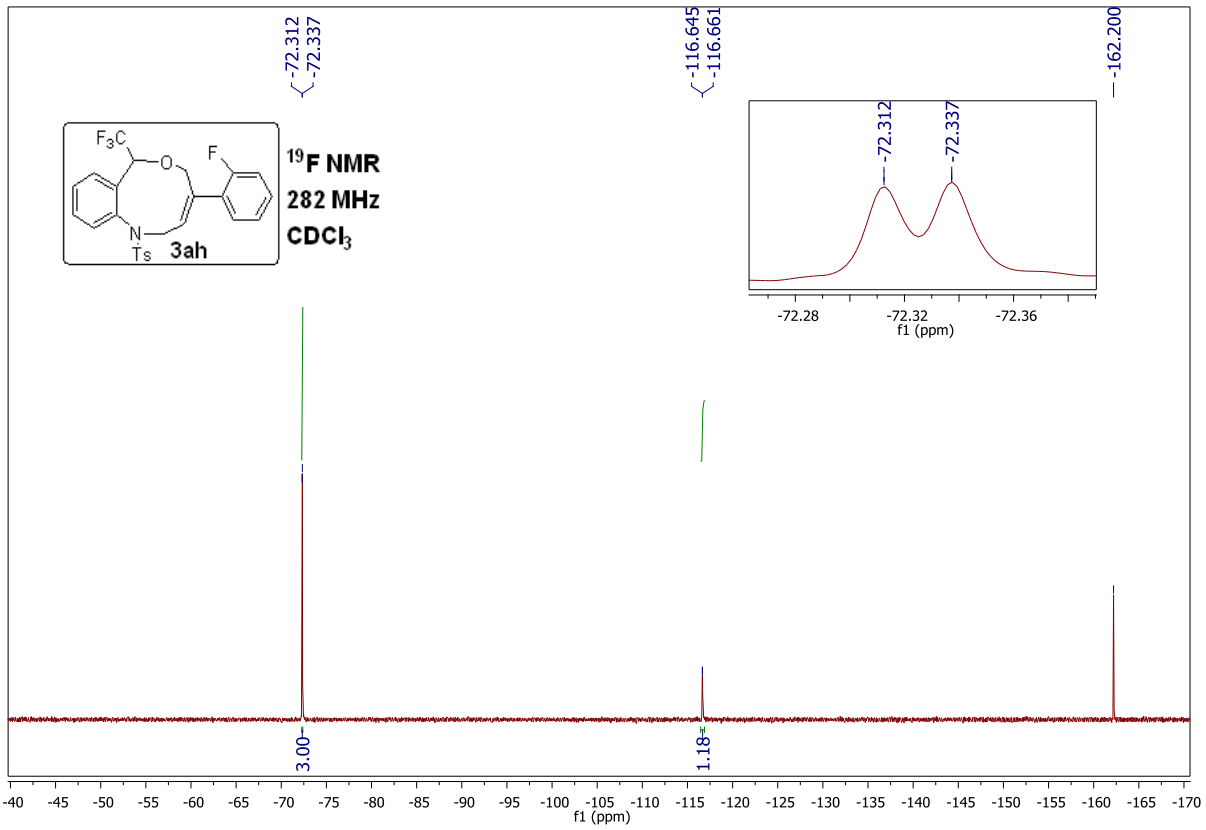
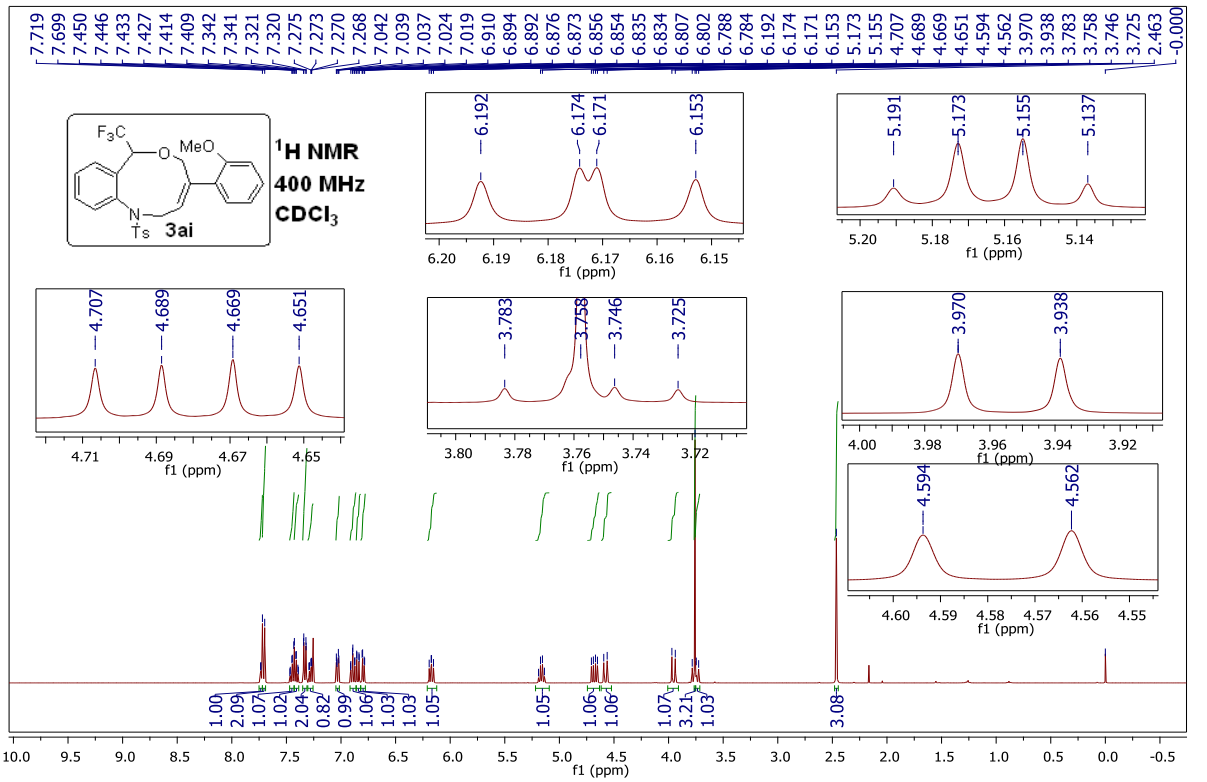
143.855
142.228
139.004
136.390
133.395
131.937
131.485
130.336
130.160
130.076
129.975
129.218
127.841
127.706
127.502
126.897
125.675
125.642
125.610
125.577
125.472
125.333
123.241
123.173
121.010
77.160
71.577
71.321
71.063
70.805
64.943
48.971
21.713
3ag
13C NMR
126 MHz
CDCl3
71.577
71.321
71.063
70.805
71.6
71.4
71.2
71.0
70.8
f1 (ppm)
125.675
125.642
125.610
125.577
125.75
125.70
125.65
125.60
125.55
f1 (ppm)
127.706
127.502
125.472
125.333
123.241
123.173
121.010
128
127
126
125
124
123
122
121
f1 (ppm)
acetone
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

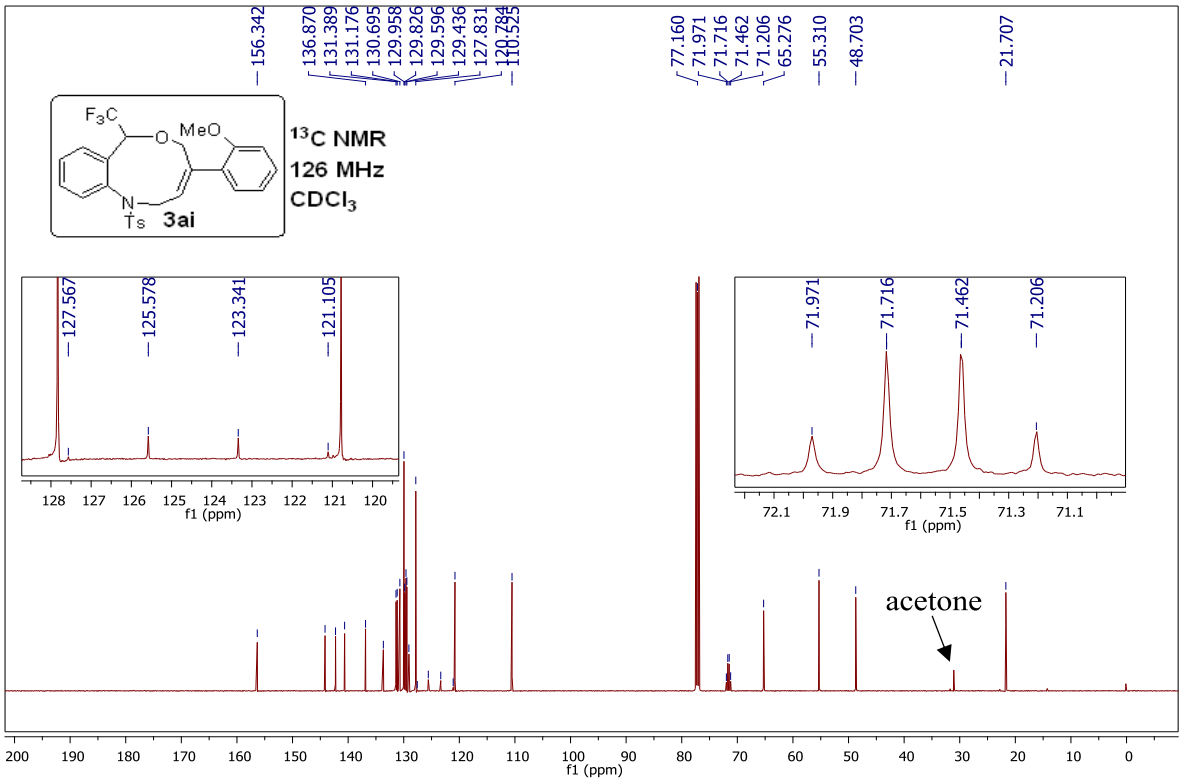

-63.066
-72.356
-72.386
-162.200
3ag
19F NMR
282 MHz
CDCl3
-72.356
-72.386
-72.30
-72.35
-72.40
-72.45
f1 (ppm)
3.00
2.93
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
-165
f1 (ppm)

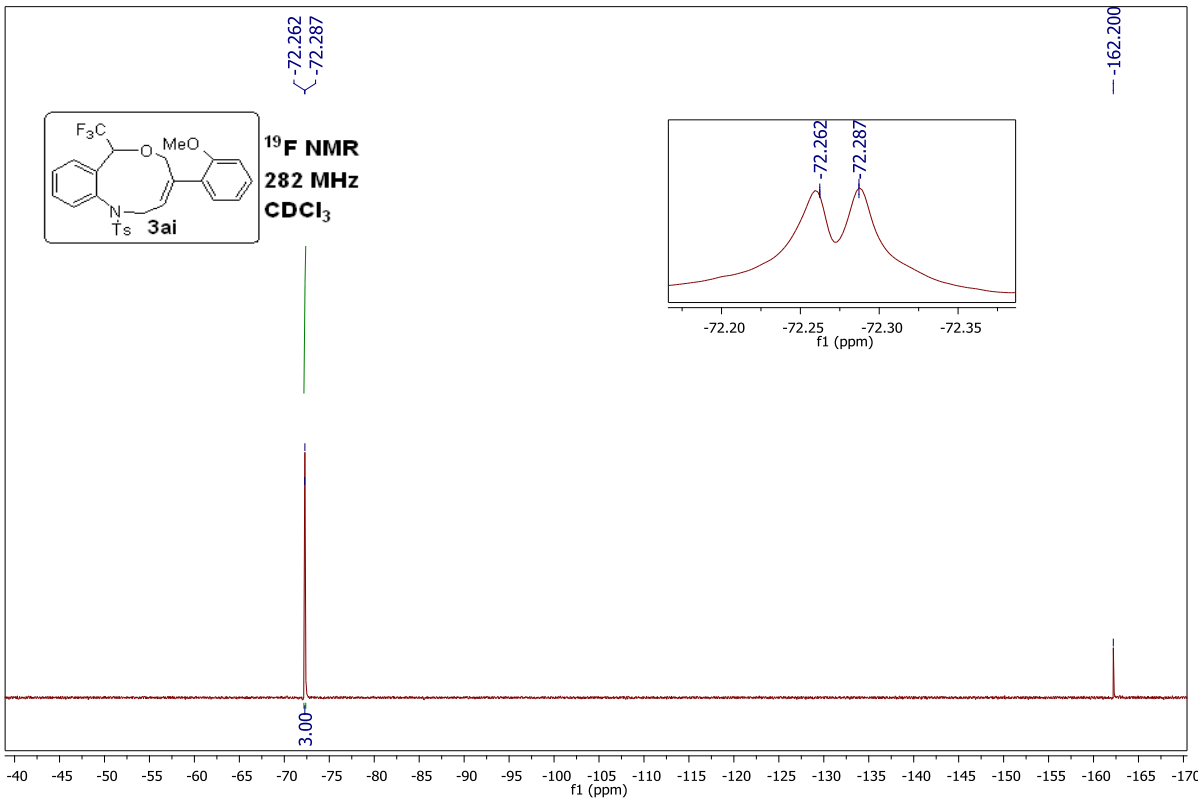

1H NMR
400 MHz
CDCl3
3ah

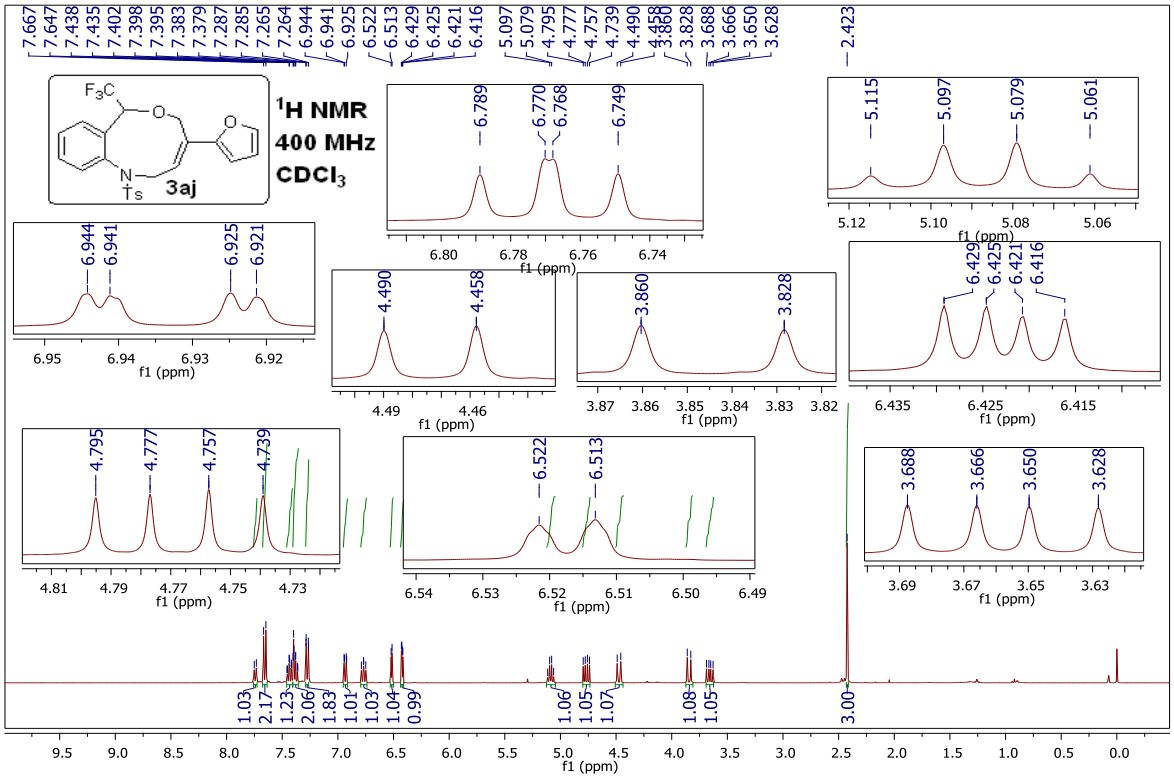

13C NMR
126 MHz
CDCl3
3ah
acetone

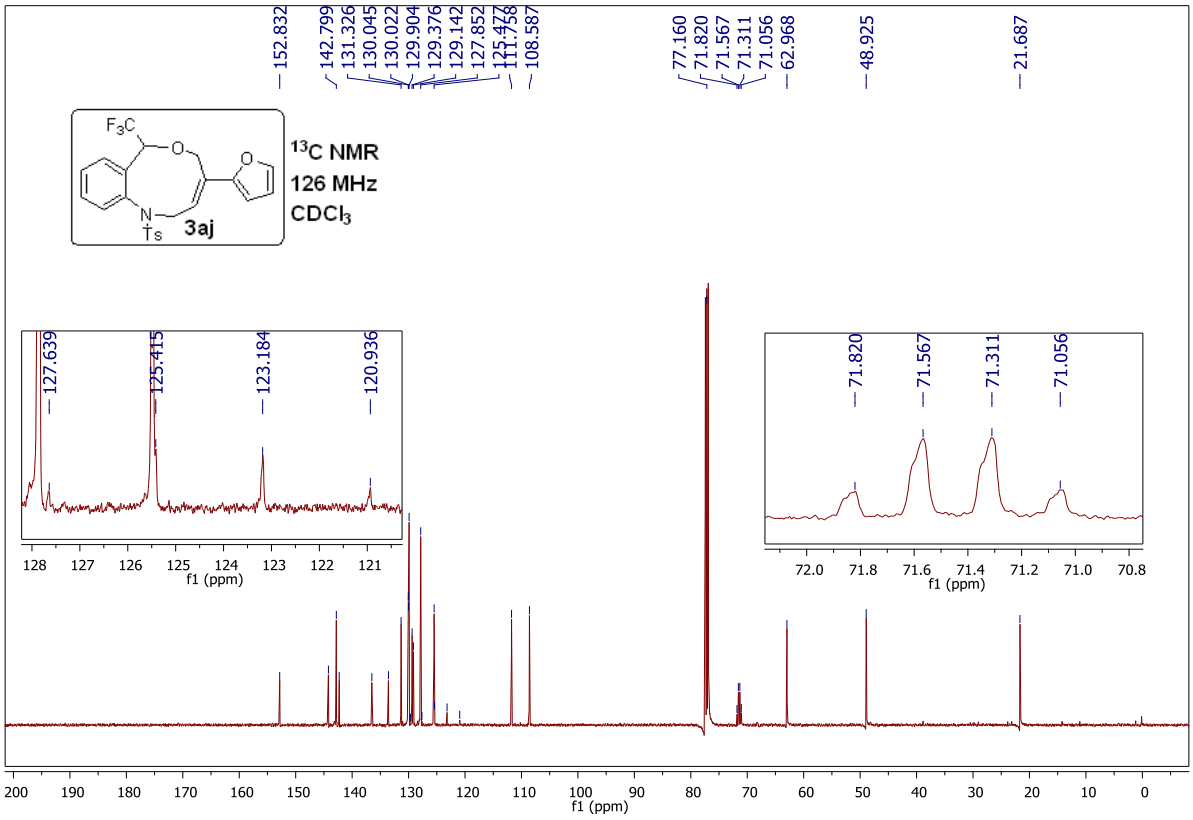

-72.312
-72.337
-116.645
-116.661
-162.200
F3C
O
F
N
Ts
3ah
19F NMR
282 MHz
CDCl3
-72.28
-72.32
-72.36
f1 (ppm)
3.00
1.18
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

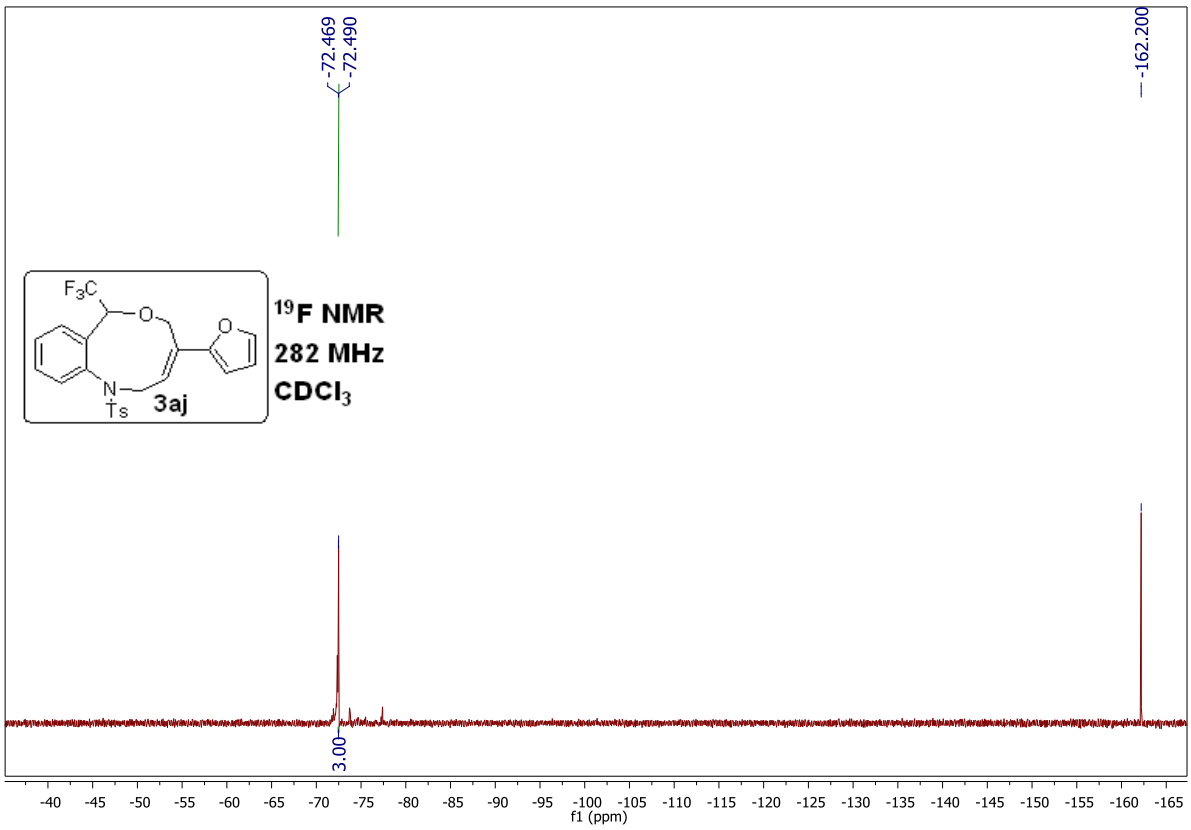

7.719 7.699 7.450 7.446 7.433 7.427 7.414 7.409 7.342 7.341 7.321 7.320 7.275 7.273 7.270 7.268 7.042 7.039 7.037 7.024 7.019 6.910 6.894 6.892 6.876 6.873 6.856 6.854 6.835 6.834 6.807 6.802 6.788 6.784 6.192 6.174 6.171 6.153 5.173 5.155 4.707 4.689 4.669 4.651 4.594 4.562 3.970 3.938 3.783 3.758 3.746 3.725 2.463 -0.000
F3C
O
MeO
N
Ts
3ai
1H NMR
400 MHz
CDCl3
6.192
6.174
6.171
6.153
6.20 6.19 6.18 6.17 6.16 6.15
f1 (ppm)
5.191
5.173
5.155
5.137
5.20 5.18 5.16 5.14
f1 (ppm)
4.707
4.689
4.669
4.651
4.71 4.69 4.67 4.65
f1 (ppm)
3.783
3.758
3.746
3.725
3.80 3.78 3.76 3.74 3.72
f1 (ppm)
3.970
3.938
4.00 3.98 3.96 3.94 3.92
f1 (ppm)
4.594
4.562
4.60 4.59 4.58 4.57 4.56 4.55
f1 (ppm)
1.00 2.09 1.07 1.02 2.04 0.82 0.99 1.06 1.03 1.03 1.05 1.05 1.06 1.06 1.07 3.21 1.03 3.08
10.0 9.5 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 -0.5
f1 (ppm)

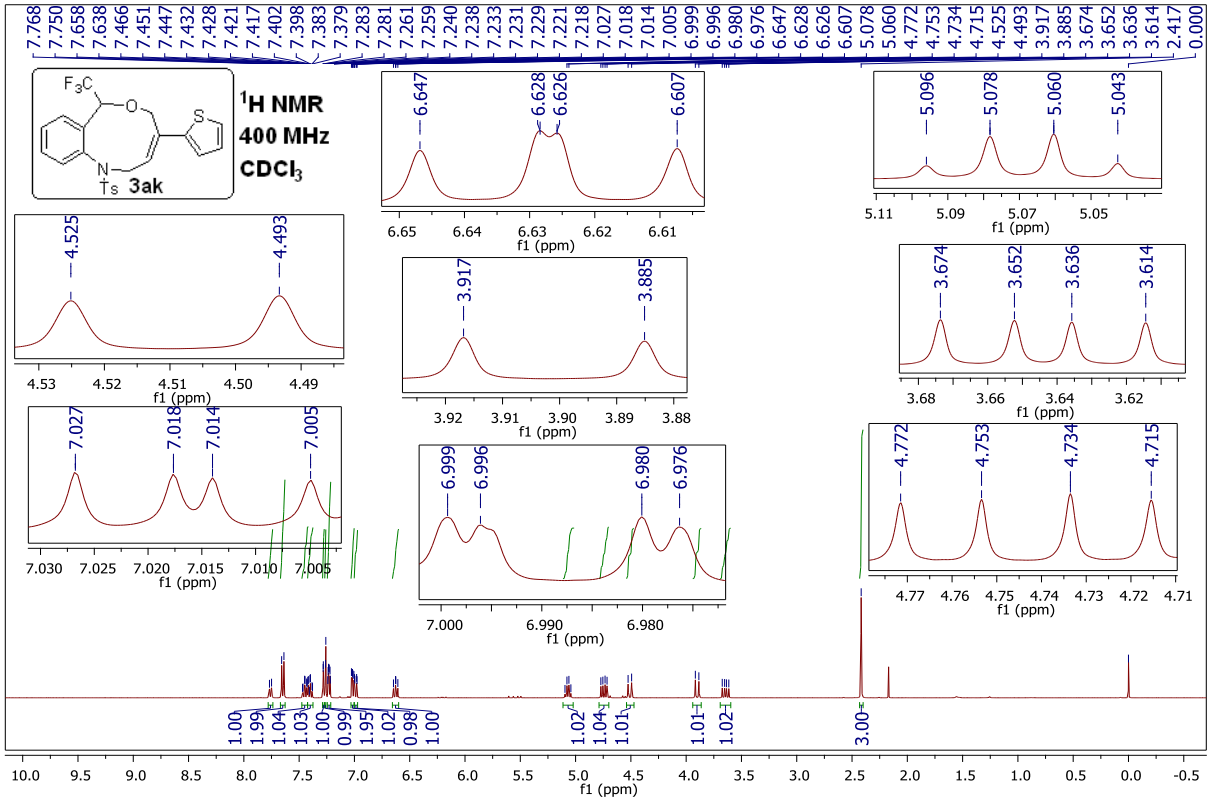

156.342
136.870
131.389
131.176
130.695
129.958
129.826
129.596
129.436
127.831
110.525
77.160
71.971
71.716
71.462
71.206
65.276
55.310
48.703
21.707
F3C
MeO
N
Ts
3ai
13C NMR
126 MHz
CDCl3
127.567
125.578
123.341
121.105
71.971
71.716
71.462
71.206
acetone
f1 (ppm)

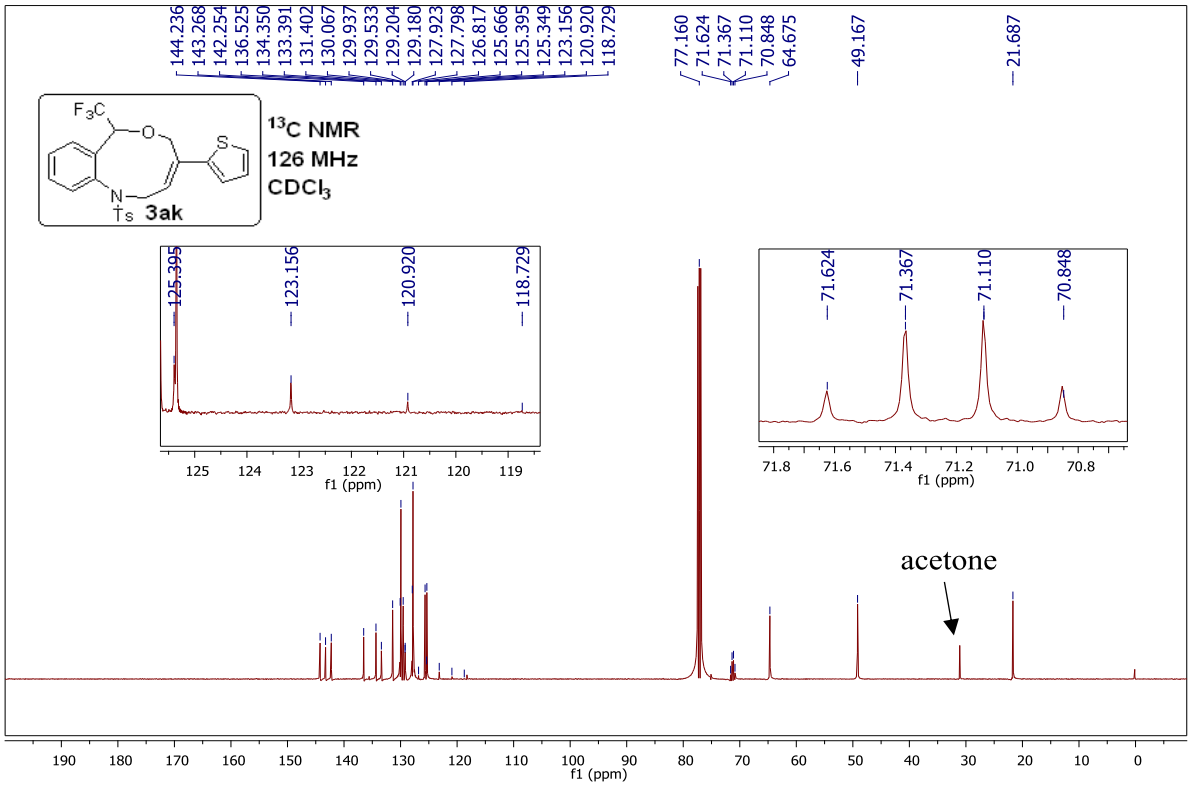

-72.262
-72.287
-162.200
F3C
MeO
N
Ts
3ai
19F NMR
282 MHz
CDCl3
3.00
f1 (ppm)

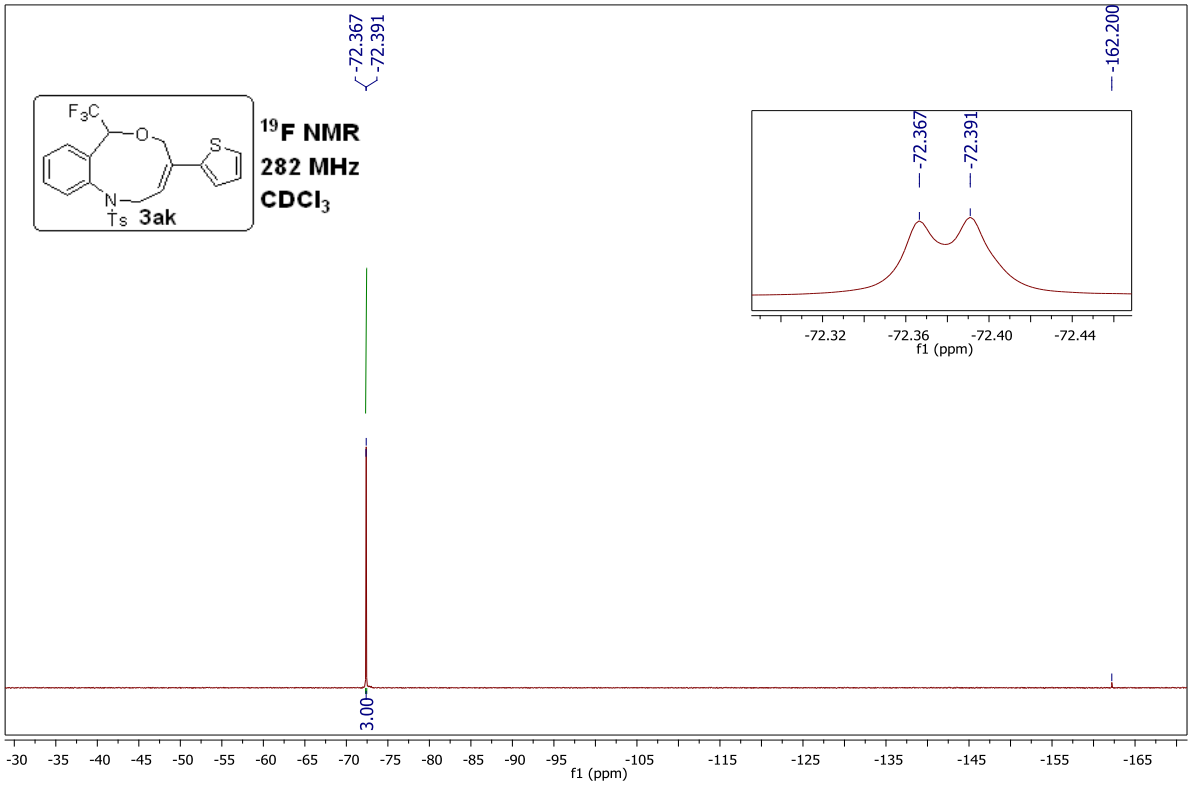

^{1}H NMR
400 MHz
CDCl$_3$
3aj
f1 (ppm)

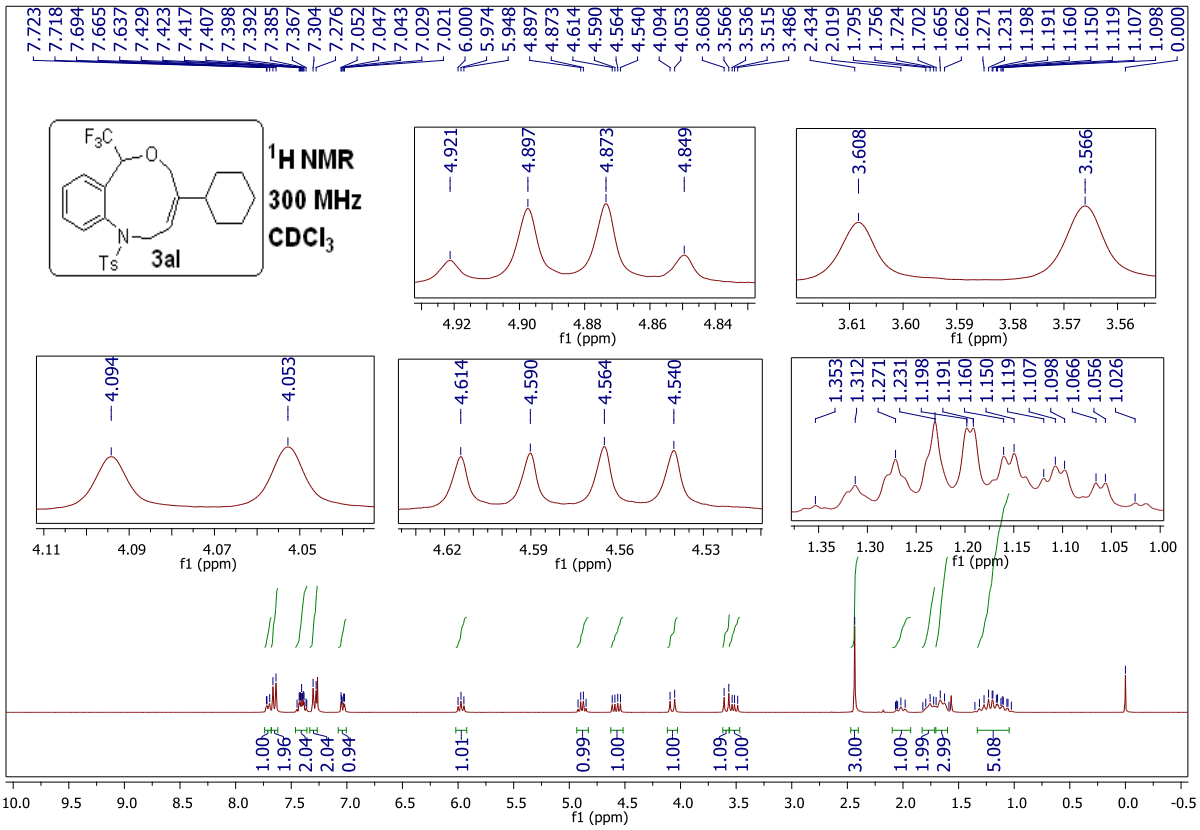

^{13}C NMR
126 MHz
CDCl$_3$
3aj
f1 (ppm)

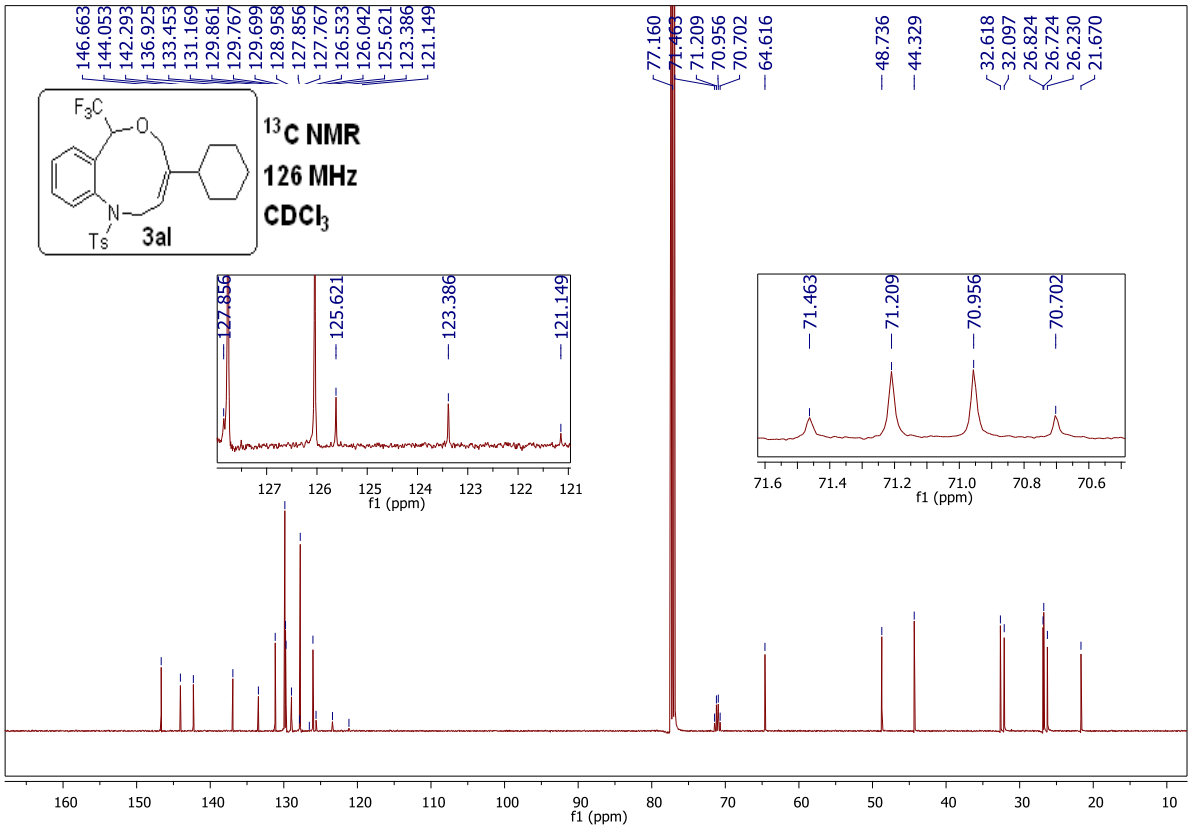

-72.469
-72.490
-162.200
F3C
O
O
N
Ts
3aj
19F NMR
282 MHz
CDCl3
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)

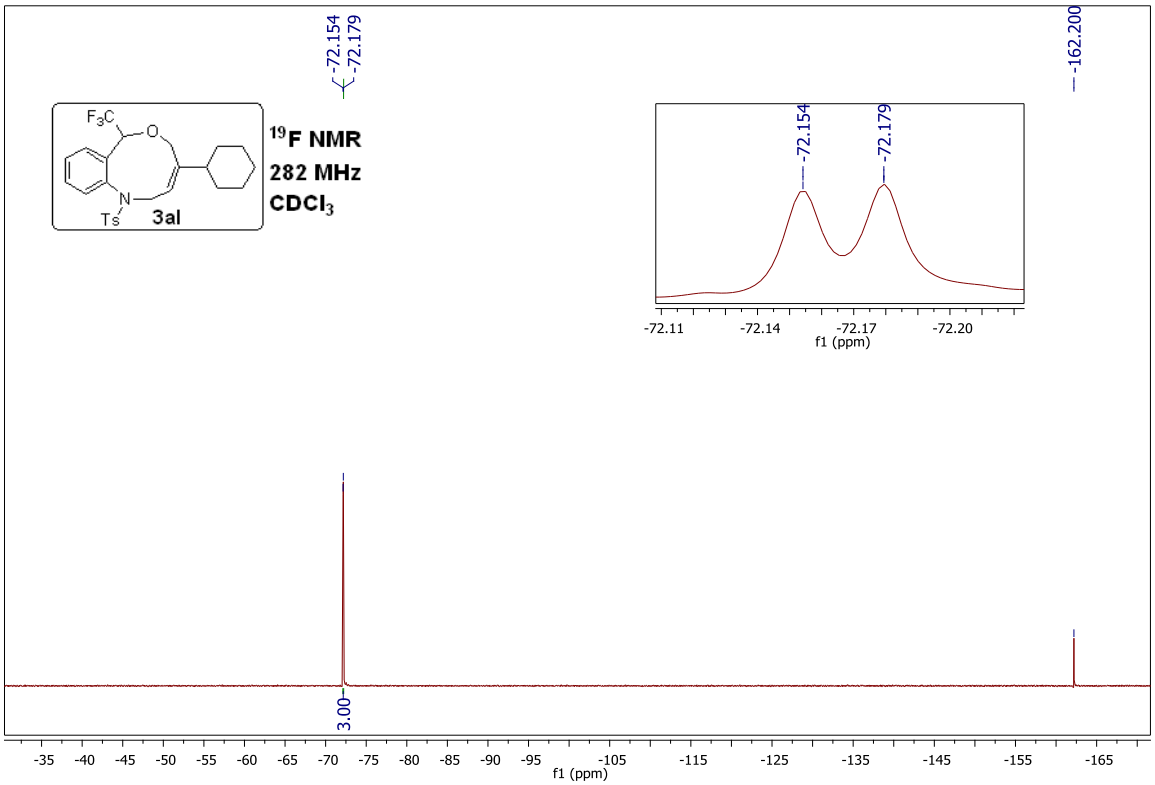

7.768 7.750 7.658 7.638 7.466 7.451 7.447 7.432 7.428 7.421 7.417 7.402 7.398 7.383 7.379 7.283 7.281 7.261 7.259 7.240 7.238 7.233 7.231 7.229 7.221 7.218 7.027 7.018 7.014 7.005 6.999 6.996 6.980 6.976 6.647 6.628 6.626 6.607 5.078 5.060 4.772 4.753 4.734 4.715 4.525 4.493 3.917 3.885 3.674 3.652 3.636 3.614 2.417 0.000
F3C
O
S
N
Ts
3ak
1H NMR
400 MHz
CDCl3
6.647
6.628
6.626
6.607
6.65 6.64 6.63 6.62 6.61
f1 (ppm)
5.096
5.078
5.060
5.043
5.11 5.09 5.07 5.05
f1 (ppm)
4.525
4.493
4.53 4.52 4.51 4.50 4.49
f1 (ppm)
3.917
3.885
3.92 3.91 3.90 3.89 3.88
f1 (ppm)
3.674
3.652
3.636
3.614
3.68 3.66 3.64 3.62
f1 (ppm)
7.027
7.018
7.014
7.005
7.030 7.025 7.020 7.015 7.010 7.005
f1 (ppm)
6.999
6.996
6.980
6.976
7.000 6.990 6.980
f1 (ppm)
4.772
4.753
4.734
4.715
4.77 4.76 4.75 4.74 4.73 4.72 4.71
f1 (ppm)
1.00 1.99 1.04 1.03 1.00 0.99 1.95 1.02 0.98 1.00
1.02 1.04 1.01
1.01 1.02
3.00
10.0 9.5 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 -0.5
f1 (ppm)

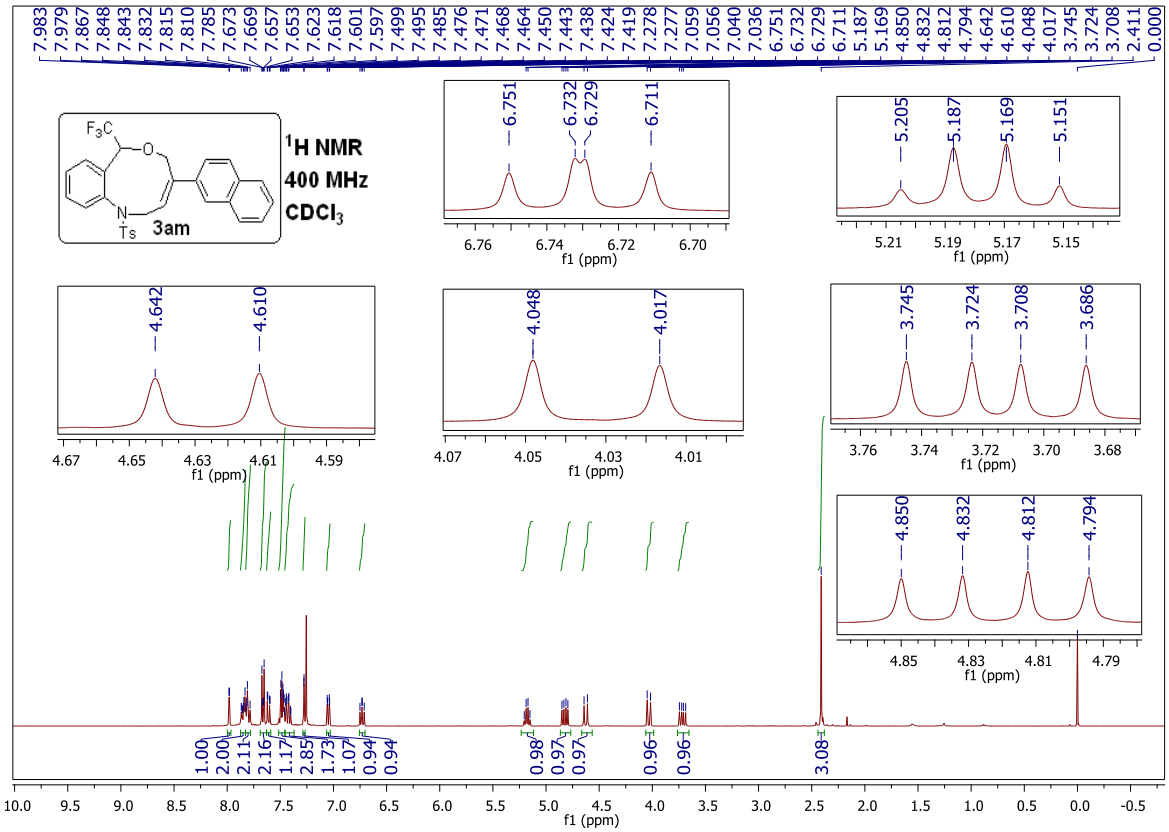

144.236
143.268
142.254
136.525
134.350
133.391
131.402
130.067
129.937
129.533
129.204
129.180
127.923
127.798
126.817
125.666
125.395
125.349
123.156
120.920
118.729
77.160
71.624
71.367
71.110
70.848
64.675
49.167
21.687
F3C
O
S
N
Ts
3ak
13C NMR
126 MHz
CDCl3
125.395
123.156
120.920
118.729
71.624
71.367
71.110
70.848
acetone
f1 (ppm)

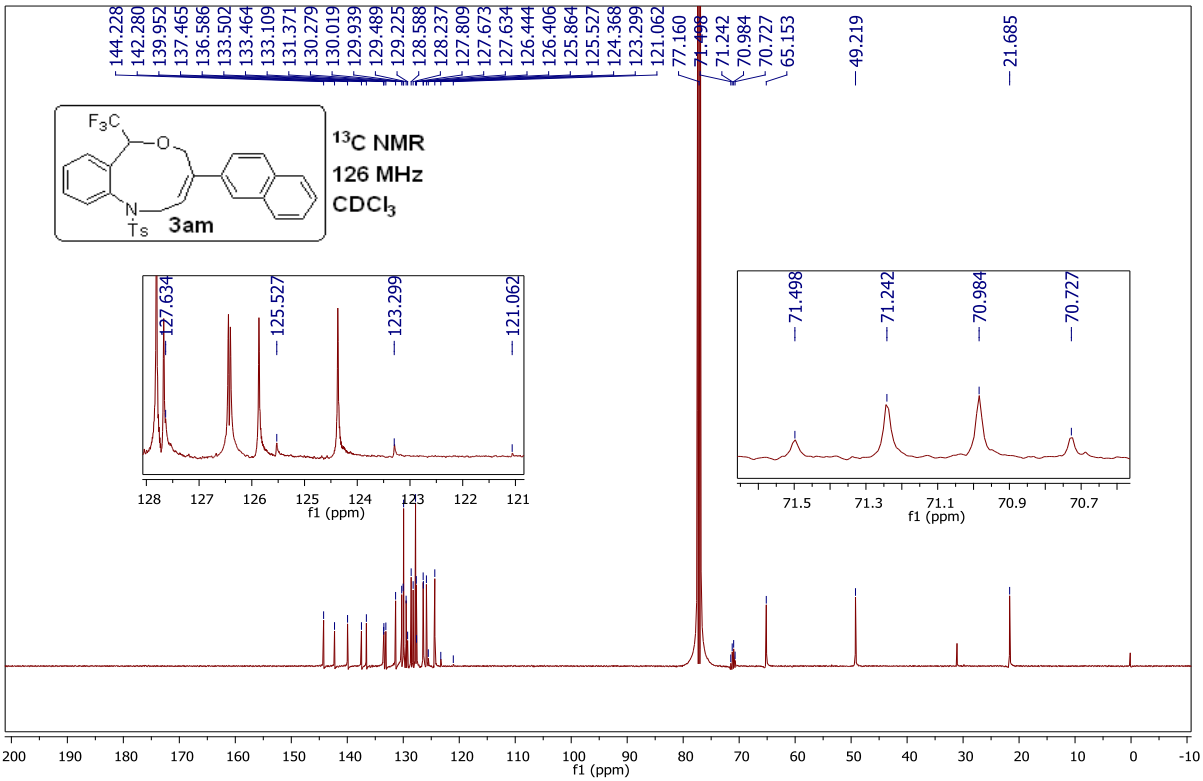

-72.367
-72.391
-162.200
F3C
O
S
N
Ts
3ak
19F NMR
282 MHz
CDCl3
3.00
f1 (ppm)

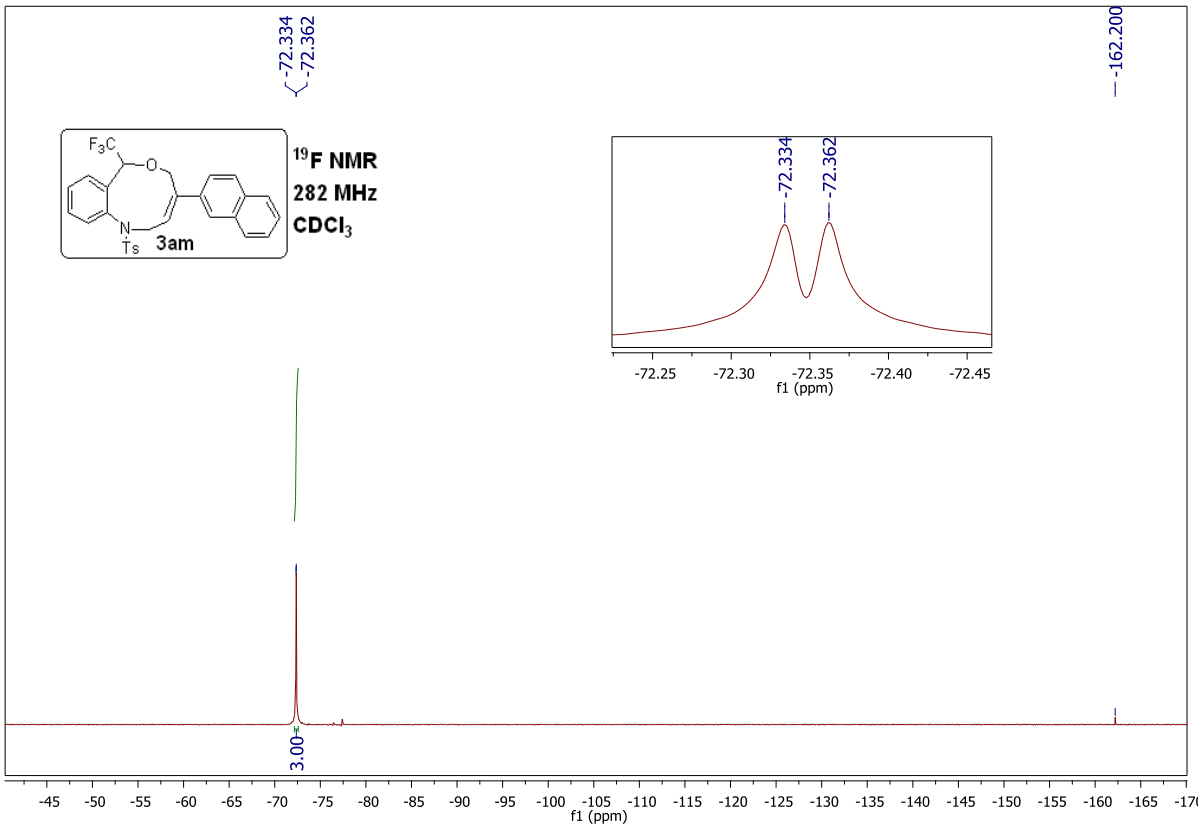

3al
^{1}H NMR
300 MHz
$CDCl_3$
f1 (ppm)

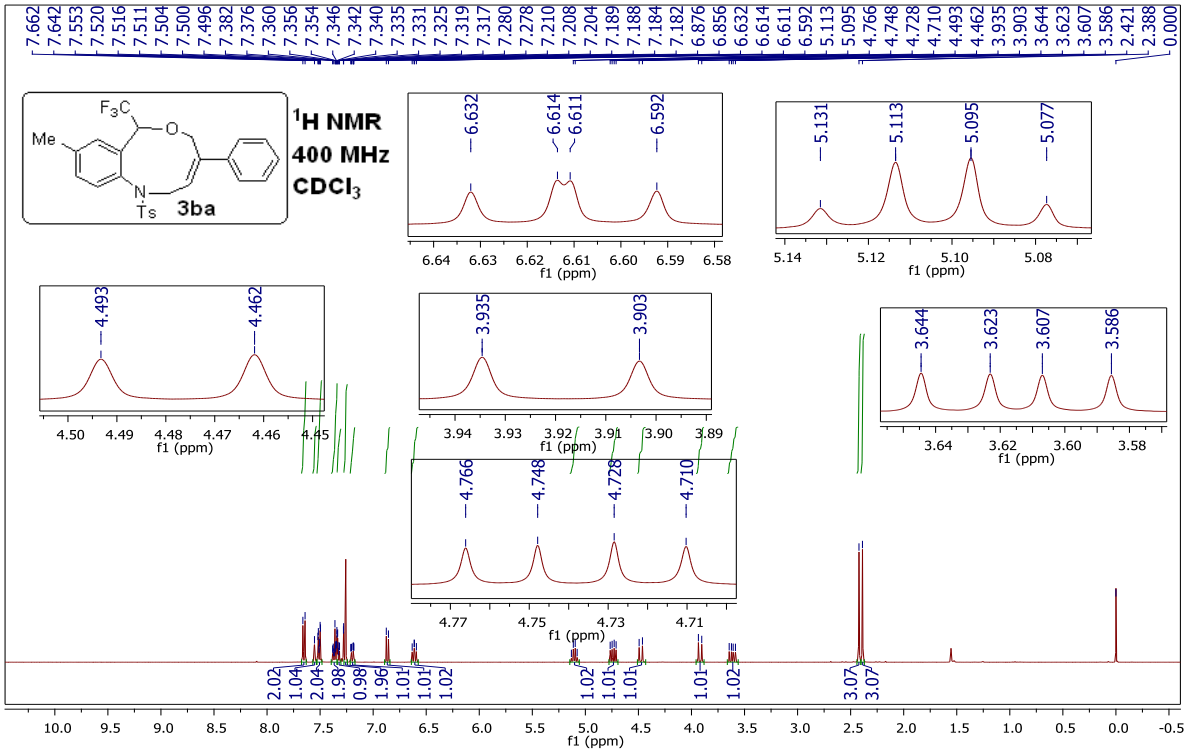

3al
^{13}C NMR
126 MHz
$CDCl_3$
f1 (ppm)

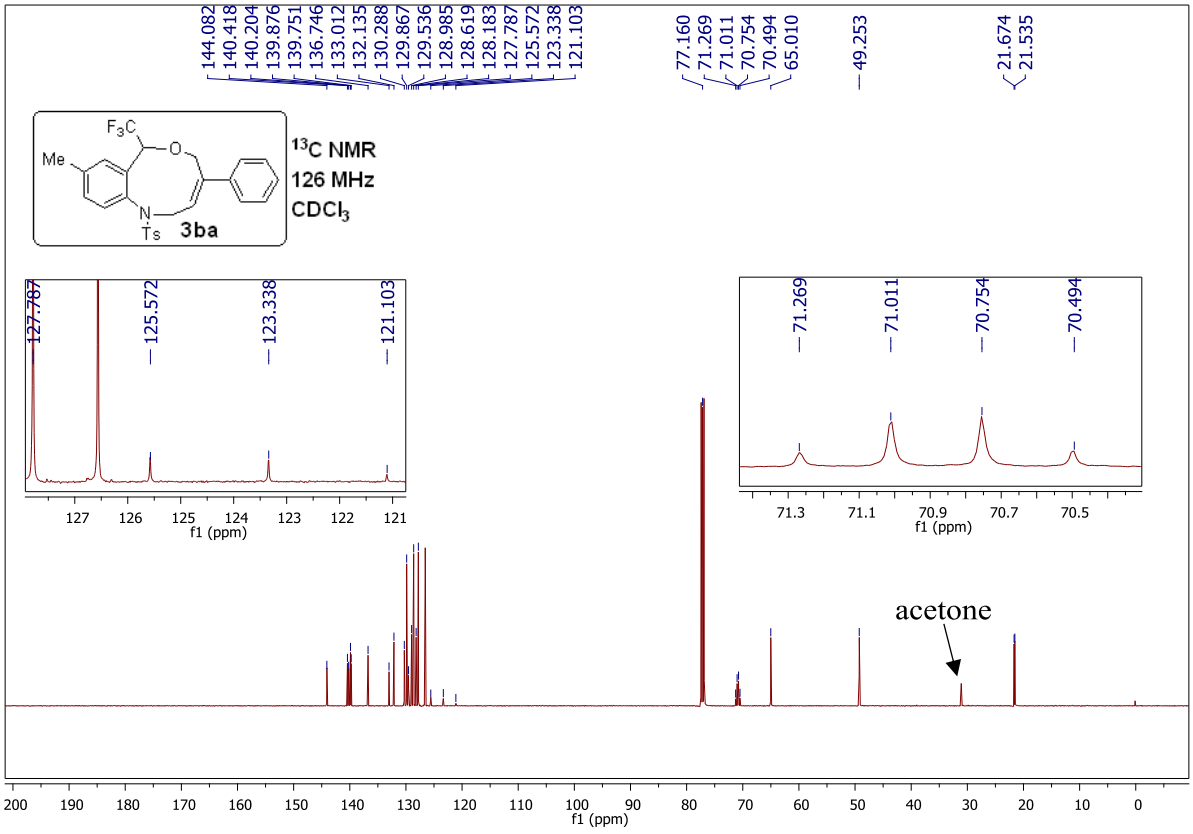

-72.154
-72.179
-162.200
3al
19F NMR
282 MHz
CDCl3
-72.154
-72.179
-72.11
-72.14
-72.17
-72.20
f1 (ppm)
3.00
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165
f1 (ppm)

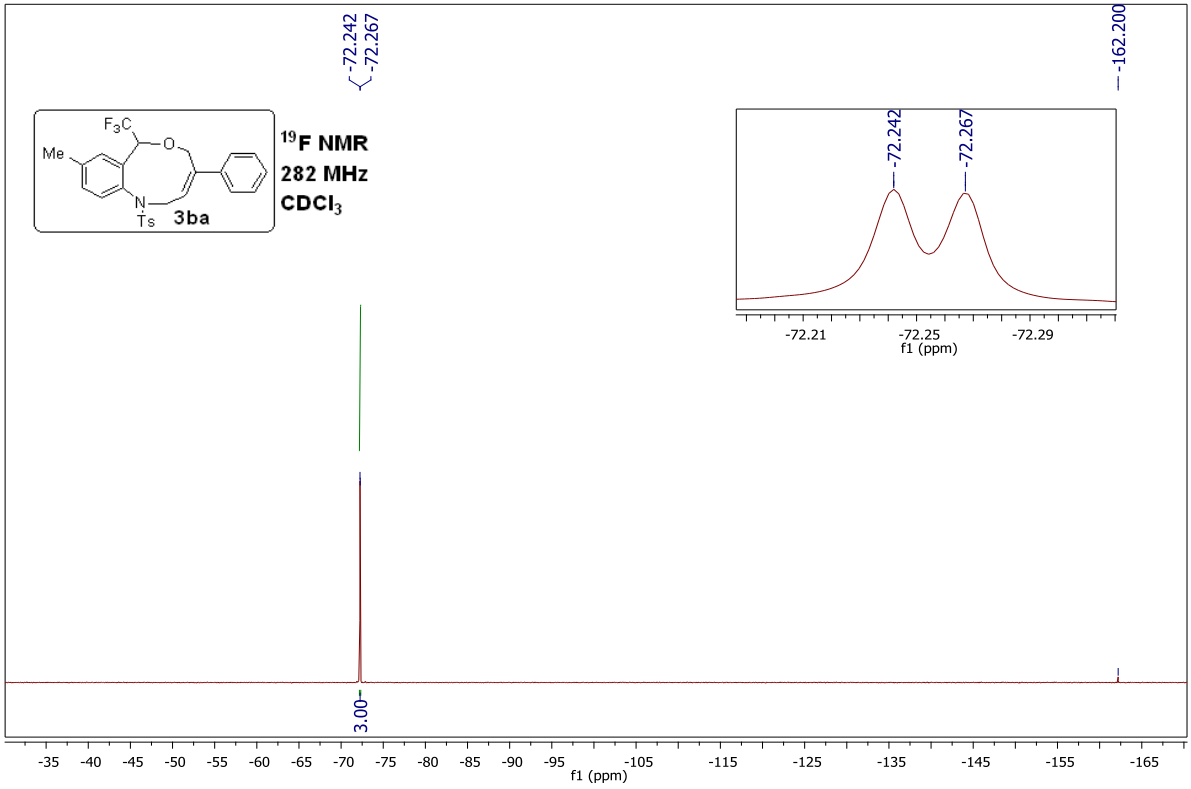

7.983 7.979 7.867 7.848 7.843 7.832 7.815 7.810 7.785 7.673 7.669 7.657 7.653 7.623 7.618 7.601 7.597 7.499 7.495 7.485 7.476 7.471 7.468 7.464 7.450 7.443 7.438 7.424 7.419 7.278 7.277 7.059 7.056 7.040 7.036 6.751 6.732 6.729 6.711 5.187 5.169 4.850 4.832 4.812 4.794 4.642 4.610 4.048 4.017 3.745 3.724 3.708 2.411 0.000
3am
1H NMR
400 MHz
CDCl3
6.751
6.732
6.729
6.711
6.76 6.74 6.72 6.70
f1 (ppm)
5.205
5.187
5.169
5.151
5.21 5.19 5.17 5.15
f1 (ppm)
4.642
4.610
4.67 4.65 4.63 4.61 4.59
f1 (ppm)
4.048
4.017
4.07 4.05 4.03 4.01
f1 (ppm)
3.745
3.724
3.708
3.686
3.76 3.74 3.72 3.70 3.68
f1 (ppm)
4.850
4.832
4.812
4.794
4.85 4.83 4.81 4.79
f1 (ppm)
1.00 2.00 2.11 2.16 1.17 2.85 1.73 1.07 0.94 0.94
0.98 0.97 0.97
0.96 0.96
3.08
10.0 9.5 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 -0.5
f1 (ppm)

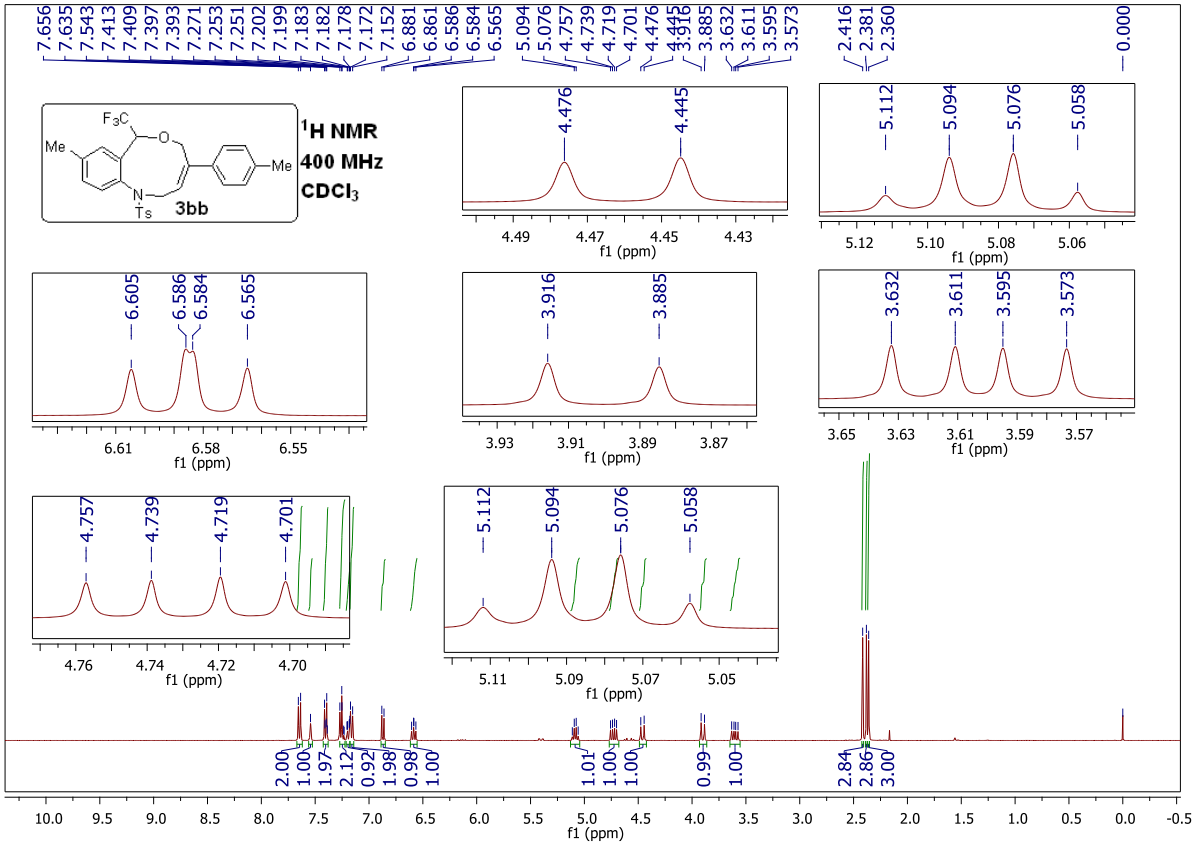

144.228
142.280
139.952
137.465
136.586
133.502
133.464
133.109
131.371
130.279
130.019
129.939
129.489
129.225
128.588
128.237
127.809
127.673
127.634
126.444
126.406
125.864
125.527
124.368
123.299
121.062
77.160
71.498
71.242
70.984
70.727
65.153
49.219
21.685
^{13}C NMR
126 MHz
CDCl$_3$
3am
f1 (ppm)

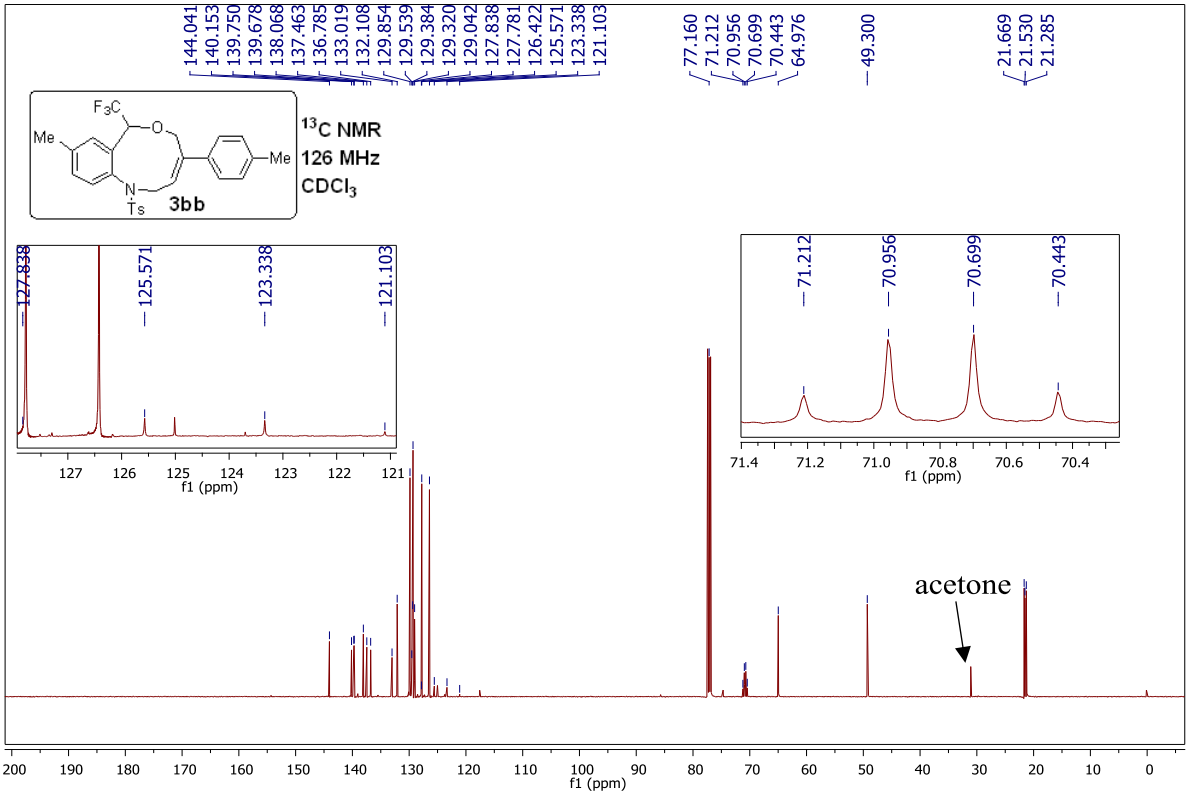

-72.334
-72.362
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3am
3.00
f1 (ppm)

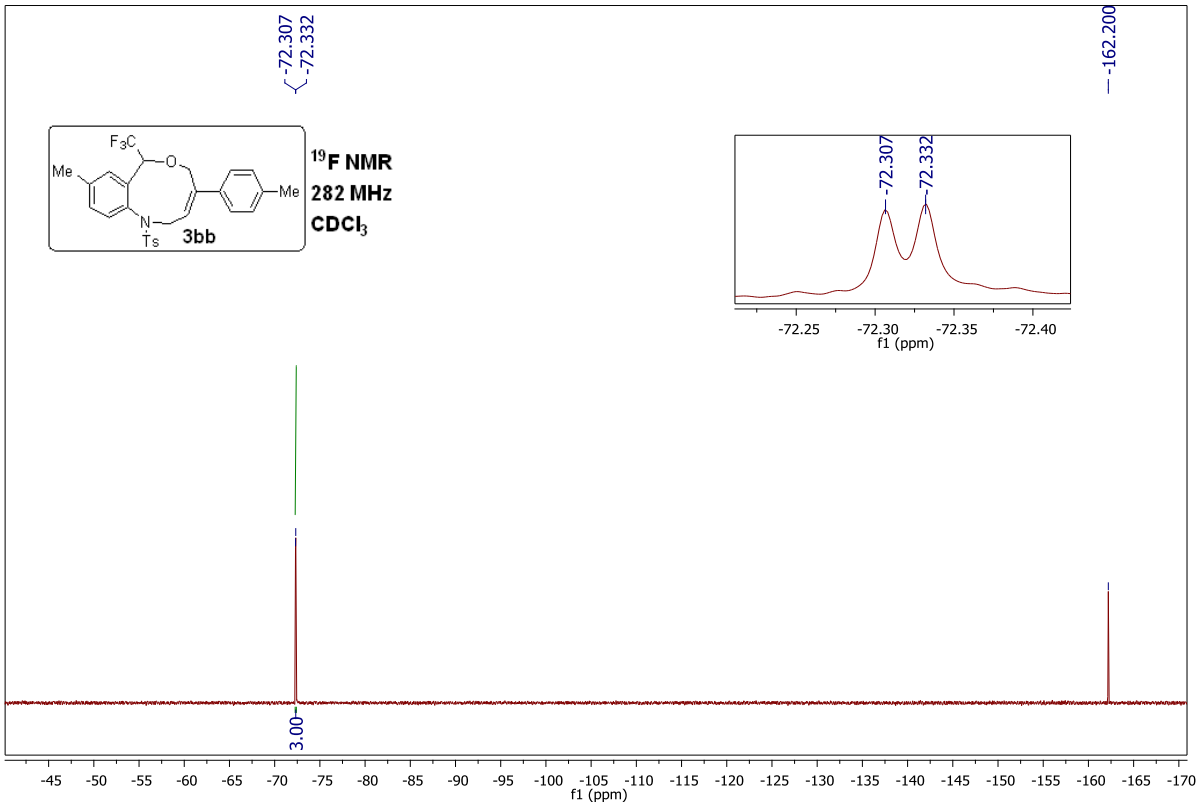

3ba
^{1}H NMR
400 MHz
$CDCl_3$
f1 (ppm)

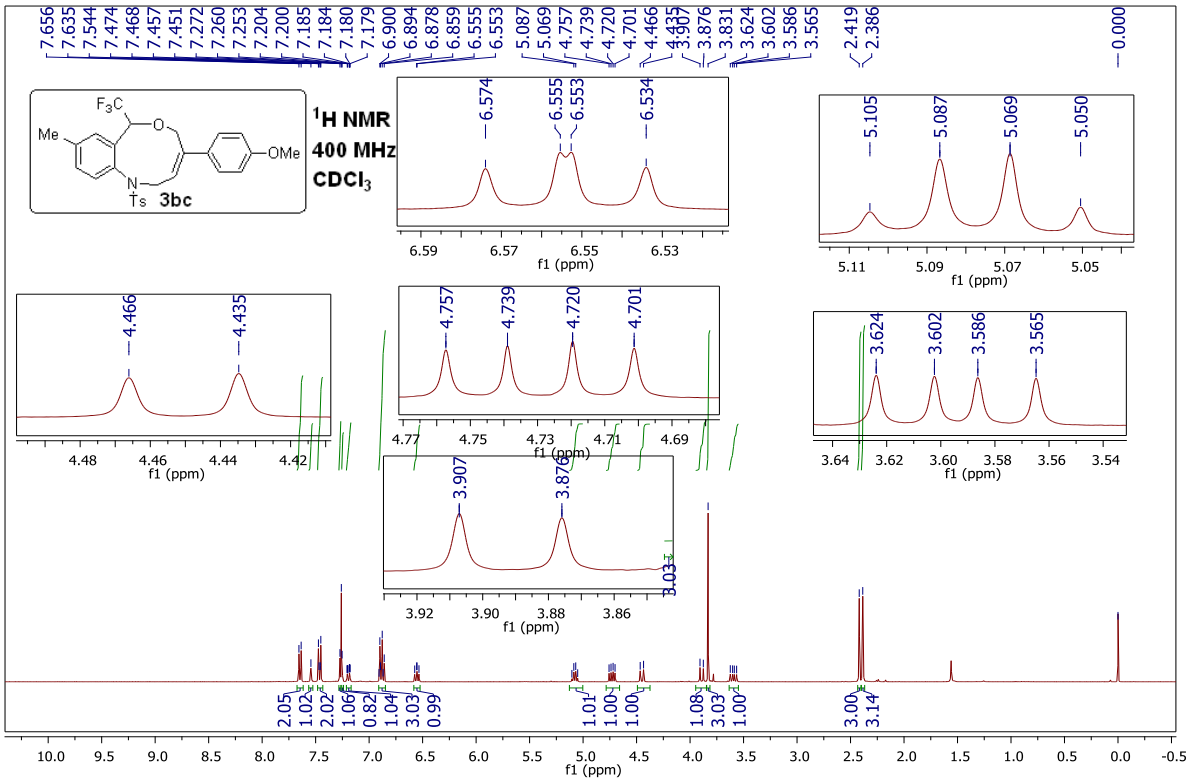

3ba
^{13}C NMR
126 MHz
$CDCl_3$
acetone
f1 (ppm)

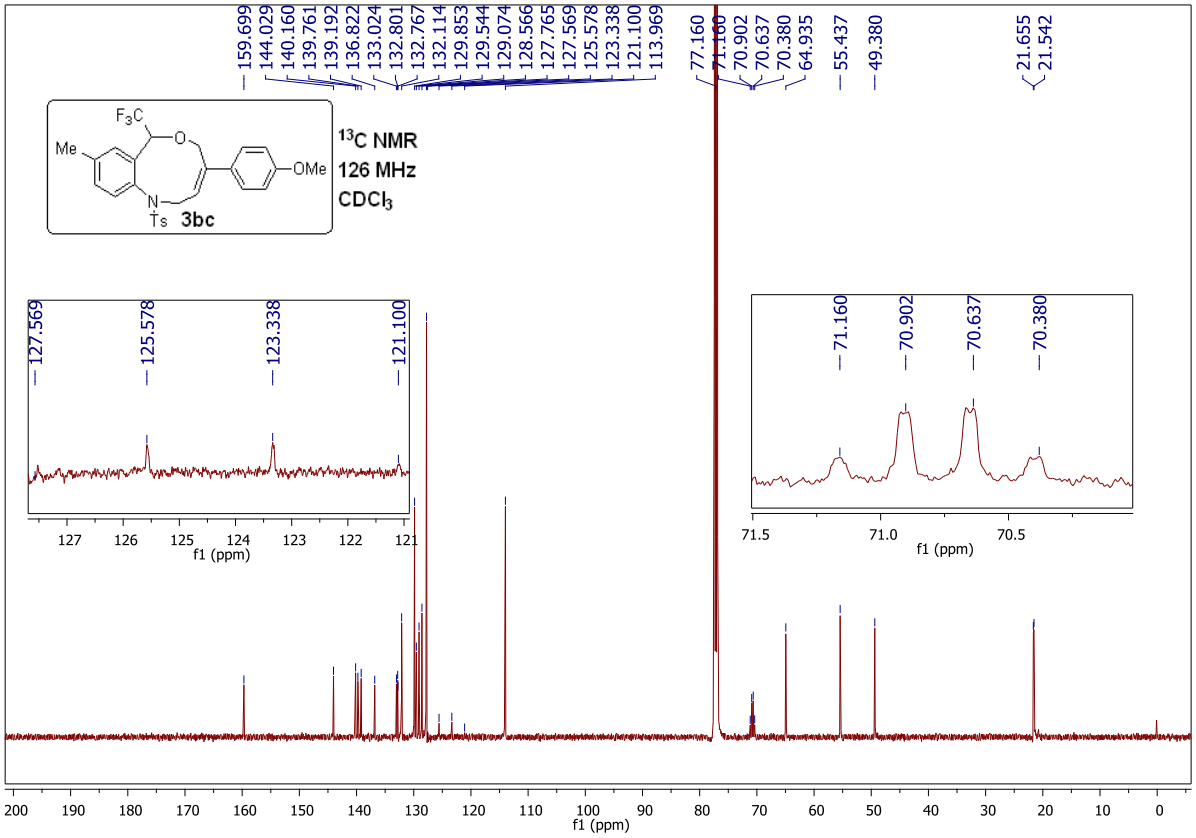

-72.242
-72.267
-162.200
F3C
O
Me
N
Ts
3ba
19F NMR
282 MHz
CDCl3
-72.242
-72.267
-72.21
-72.25
-72.29
f1 (ppm)
3.00
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165
f1 (ppm)

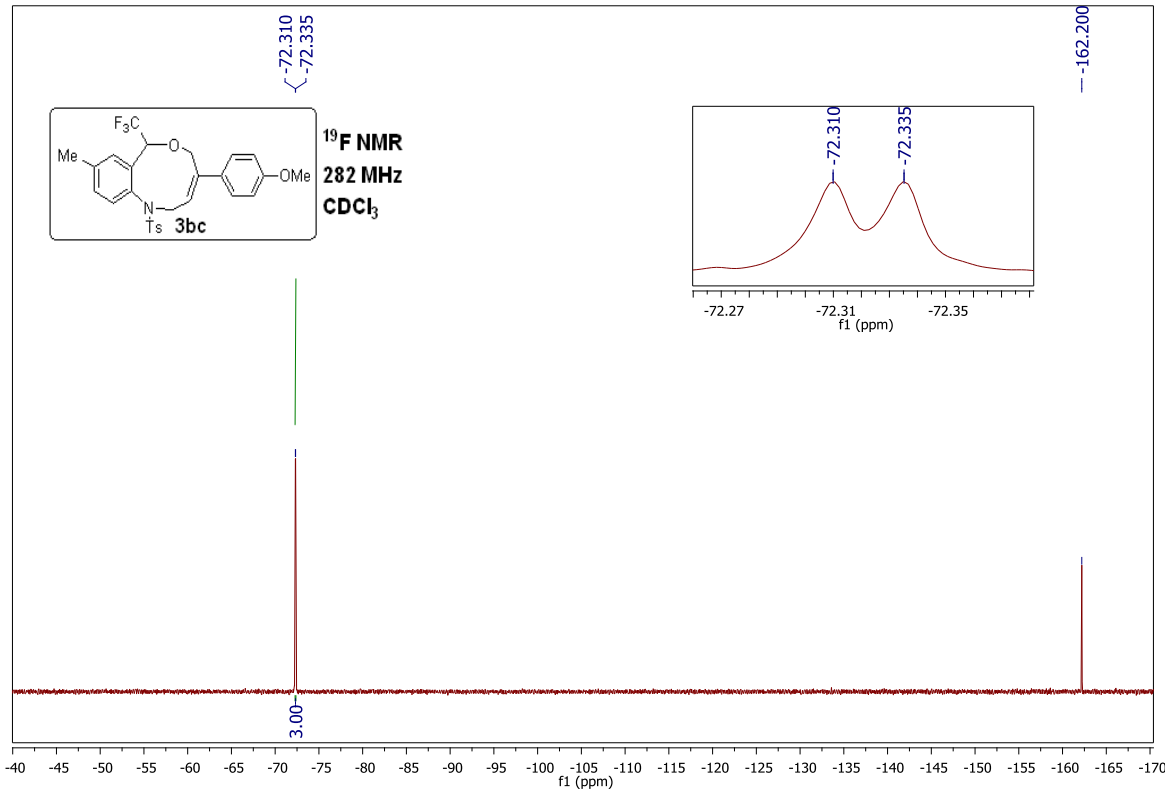

7.656 7.635 7.543 7.413 7.409 7.397 7.393 7.271 7.253 7.251 7.202 7.199 7.183 7.182 7.178 7.172 7.152 6.881 6.861 6.586 6.584 6.565
5.094 5.076 4.757 4.739 4.719 4.701 4.476 4.445 3.916 3.885 3.632 3.611 3.595 3.573
2.416 2.381 2.360
0.000
F3C
O
Me
Me
N
Ts
3bb
1H NMR
400 MHz
CDCl3
4.476
4.445
4.49 4.47 4.45 4.43
f1 (ppm)
5.112
5.094
5.076
5.058
5.12 5.10 5.08 5.06
f1 (ppm)
6.605
6.586
6.584
6.565
6.61 6.58 6.55
f1 (ppm)
3.916
3.885
3.93 3.91 3.89 3.87
f1 (ppm)
3.632
3.611
3.595
3.573
3.65 3.63 3.61 3.59 3.57
f1 (ppm)
4.757
4.739
4.719
4.701
4.76 4.74 4.72 4.70
f1 (ppm)
5.112
5.094
5.076
5.058
5.11 5.09 5.07 5.05
f1 (ppm)
2.00 1.00 1.97 2.12 0.92 1.98 0.98 1.00
1.01 1.00 1.00
0.99 1.00
2.84 2.86 3.00
10.0 9.5 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 -0.5
f1 (ppm)

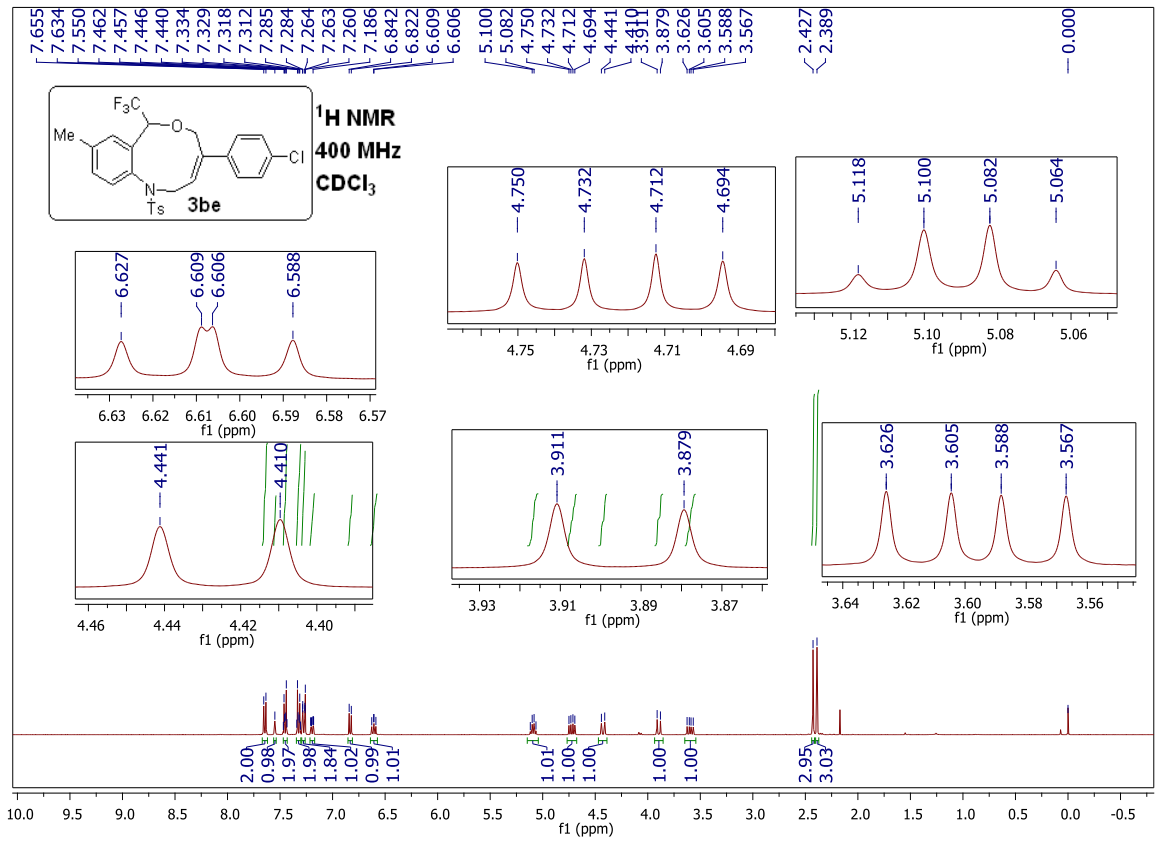

144.041
140.153
139.750
139.678
138.068
137.463
136.785
133.019
132.108
129.854
129.539
129.384
129.320
129.042
127.838
127.781
126.422
125.571
123.338
121.103
77.160
71.212
70.956
70.699
70.443
64.976
49.300
21.669
21.530
21.285
13C NMR
126 MHz
CDCl3
3bb
127.838
125.571
123.338
121.103
f1 (ppm)
71.212
70.956
70.699
70.443
f1 (ppm)
acetone
f1 (ppm)


-72.307
-72.332
-162.200
19F NMR
282 MHz
CDCl3
3bb
-72.307
-72.332
f1 (ppm)
3.00
f1 (ppm)


7.656 7.635 7.544 7.474 7.468 7.457 7.451 7.272 7.260 7.253 7.204 7.200 7.185 7.184 7.180 7.179 6.900 6.894 6.878 6.859 6.555 6.553 5.087 5.069 4.757 4.739 4.720 4.701 4.466 4.435 3.907 3.876 3.831 3.624 3.602 3.586 3.565 2.419 2.386 0.000
F3C
Me
OMe
N
Ts 3bc
1H NMR
400 MHz
CDCl3
6.574 6.555 6.553 6.534
5.105 5.087 5.069 5.050
4.466 4.435
4.757 4.739 4.720 4.701
3.624 3.602 3.586 3.565
3.907 3.876
3.03
2.05 1.02 2.02 1.06 0.82 1.04 3.03 0.99 1.01 1.00 1.00 1.08 3.03 1.00 3.00 3.14
f1 (ppm)


159.699 144.029 140.160 139.761 139.192 136.822 133.024 132.801 132.767 132.114 129.853 129.544 129.074 128.566 127.765 127.569 125.578 123.338 121.100 113.969 77.160 71.160 70.902 70.637 70.380 64.935 55.437 49.380 21.655 21.542
F3C
Me
OMe
N
Ts 3bc
13C NMR
126 MHz
CDCl3
127.569 125.578 123.338 121.100
71.160 70.902 70.637 70.380
f1 (ppm)


-72.310
-72.335
-162.200
F3C
Me
O
OMe
N
Ts
3bc
19F NMR
282 MHz
CDCl3
-72.27
-72.31
-72.35
f1 (ppm)
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)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7.457
7.446
7.440
7.334
7.329
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7.312
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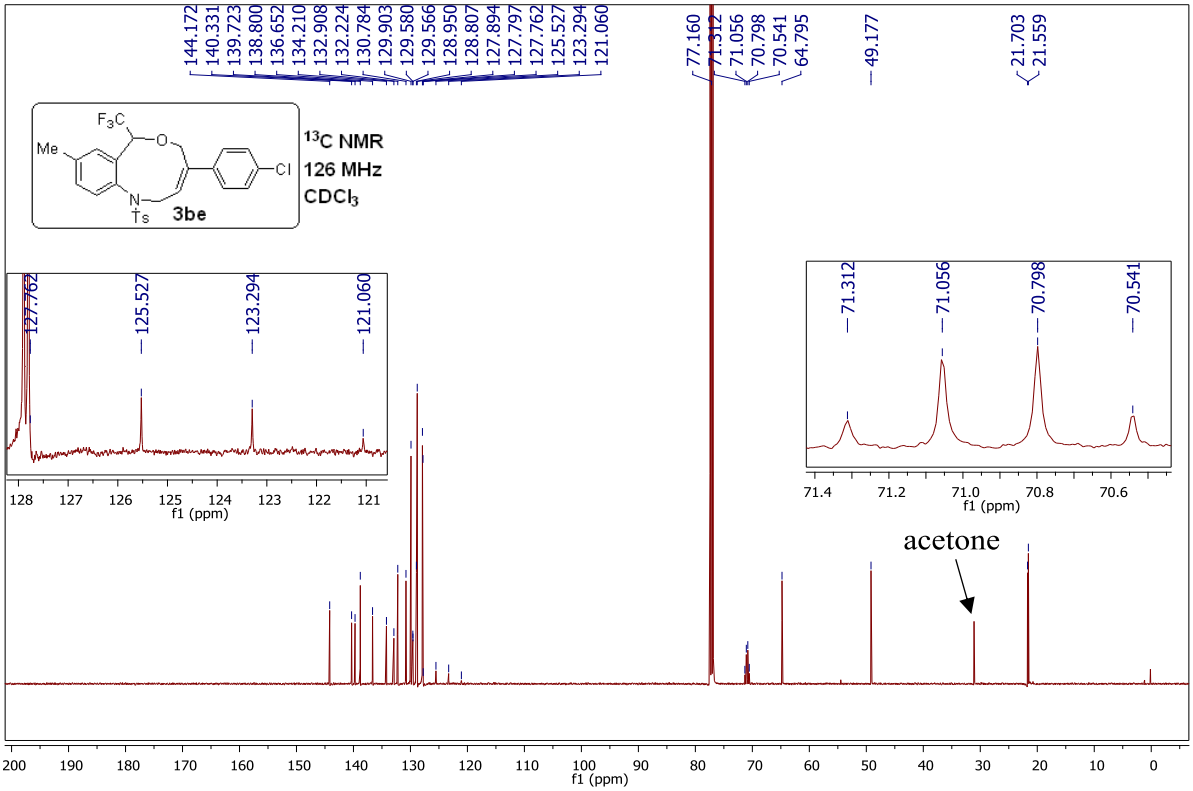
7.284
7.264
7.263
7.260
7.186
6.842
6.822
6.609
6.606
5.100
5.082
4.750
4.732
4.712
4.694
4.441
4.410
3.911
3.879
3.626
3.605
3.588
3.567
2.427
2.389
0.000
F3C
Me
O
Cl
N
Ts
3be
1H NMR
400 MHz
CDCl3
6.627
6.609
6.606
6.588
6.63 6.62 6.61 6.60 6.59 6.58 6.57
f1 (ppm)
4.750
4.732
4.712
4.694
4.75 4.73 4.71 4.69
f1 (ppm)
5.118
5.100
5.082
5.064
5.12 5.10 5.08 5.06
f1 (ppm)
4.441
4.410
4.46 4.44 4.42 4.40
f1 (ppm)
3.911
3.879
3.93 3.91 3.89 3.87
f1 (ppm)
3.626
3.605
3.588
3.567
3.64 3.62 3.60 3.58 3.56
f1 (ppm)
2.00
0.98
1.97
1.98
1.84
1.02
0.99
1.01
1.01
1.00
1.00
1.00
2.95
3.03
10.0 9.5 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 -0.5
f1 (ppm)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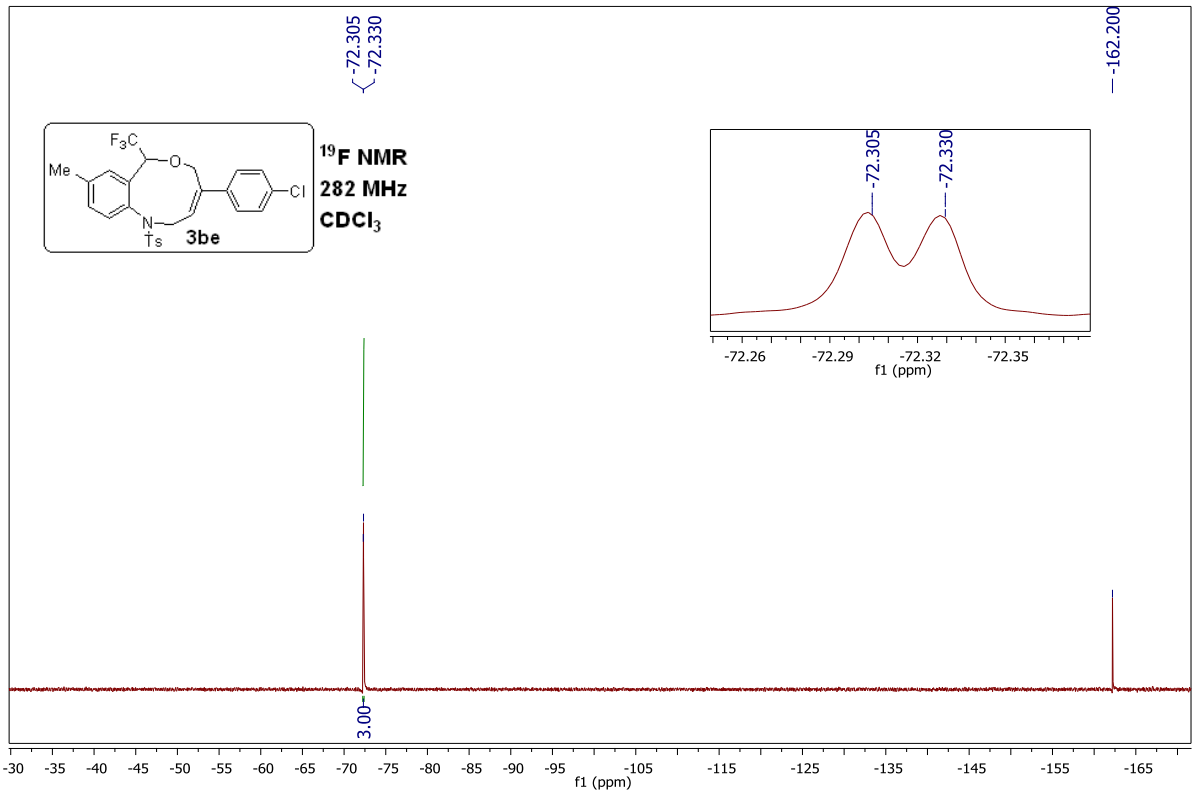
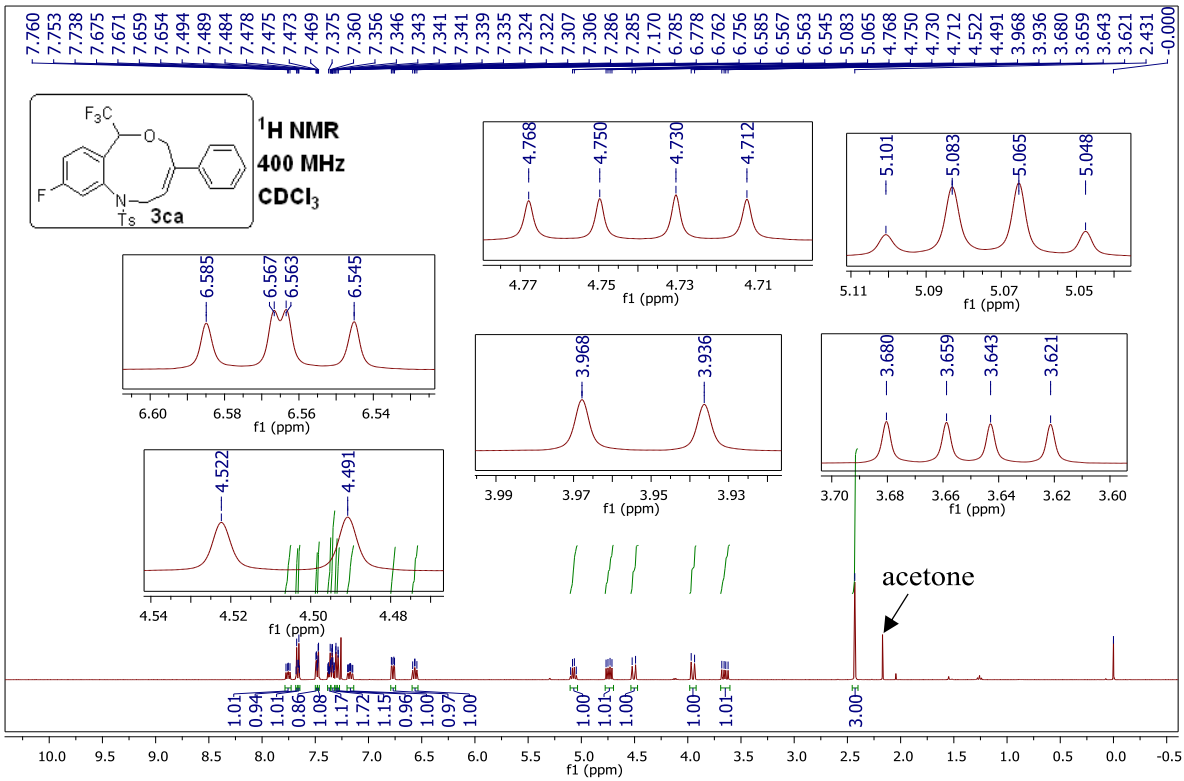
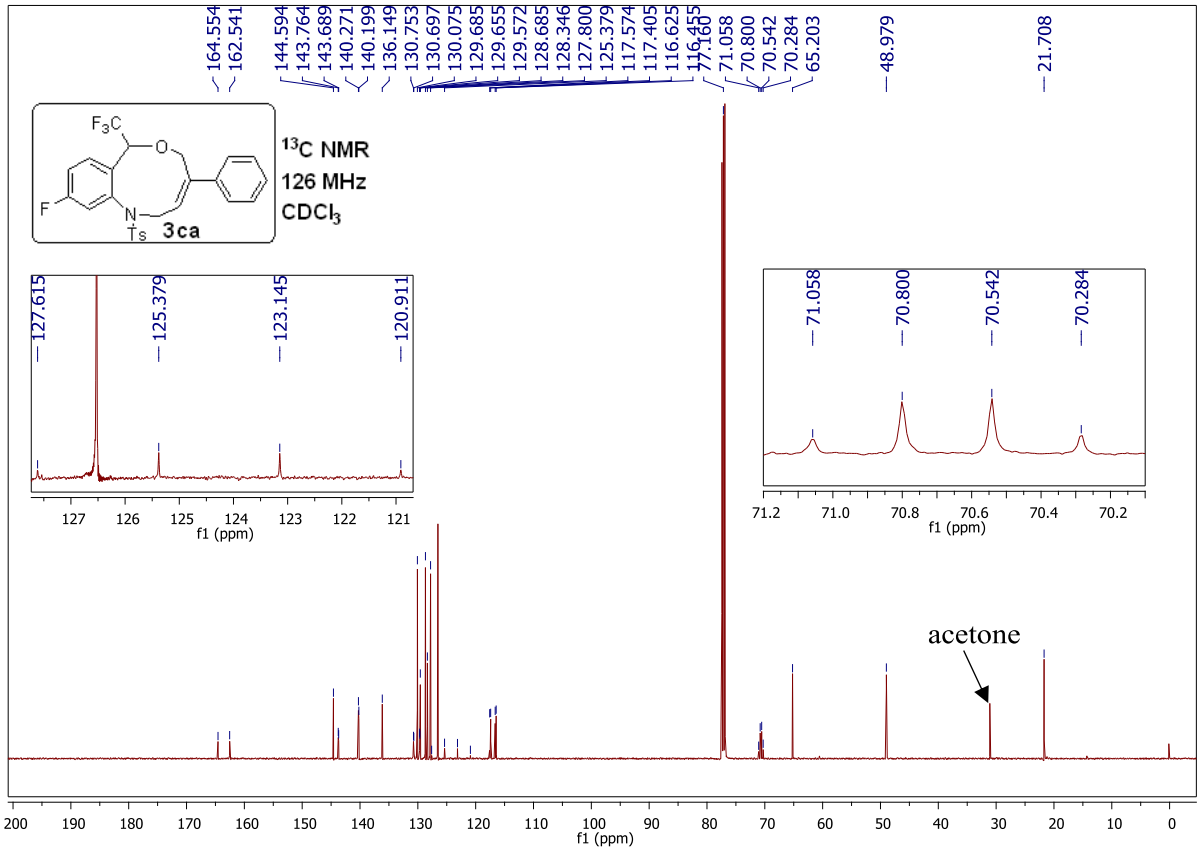
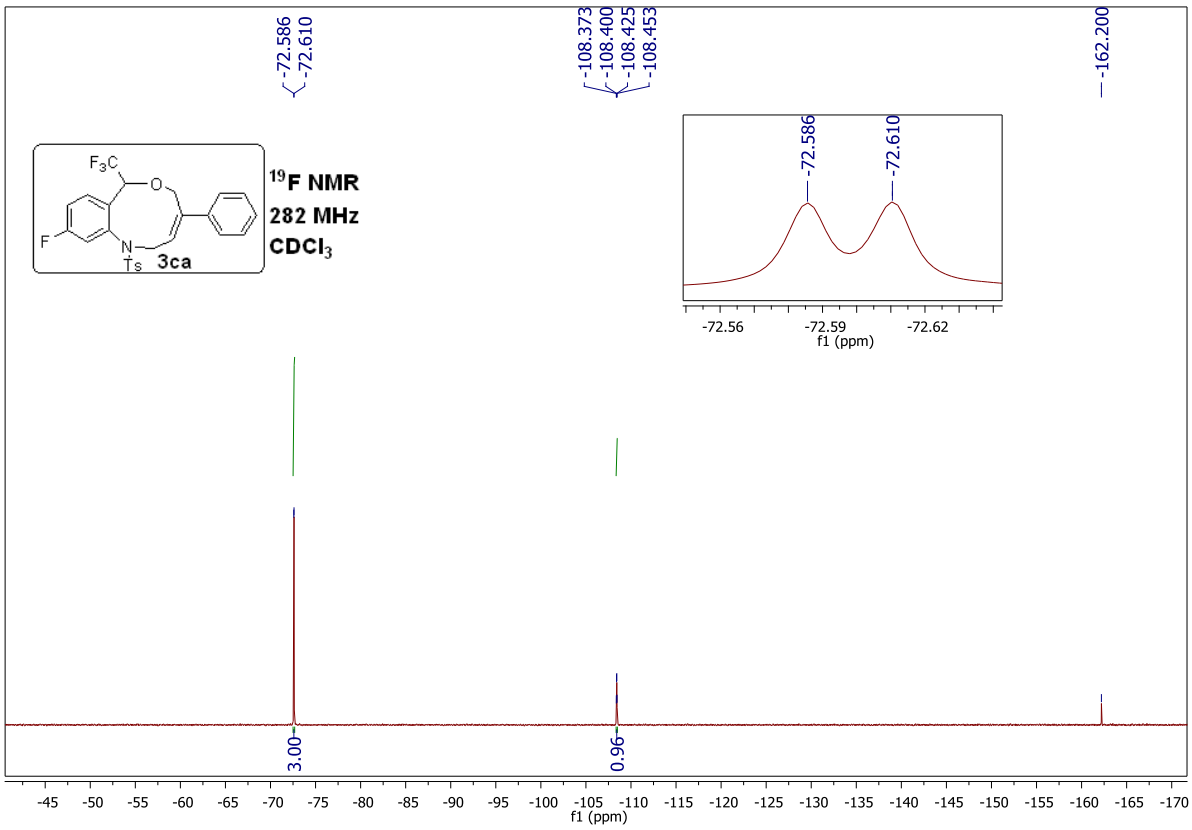
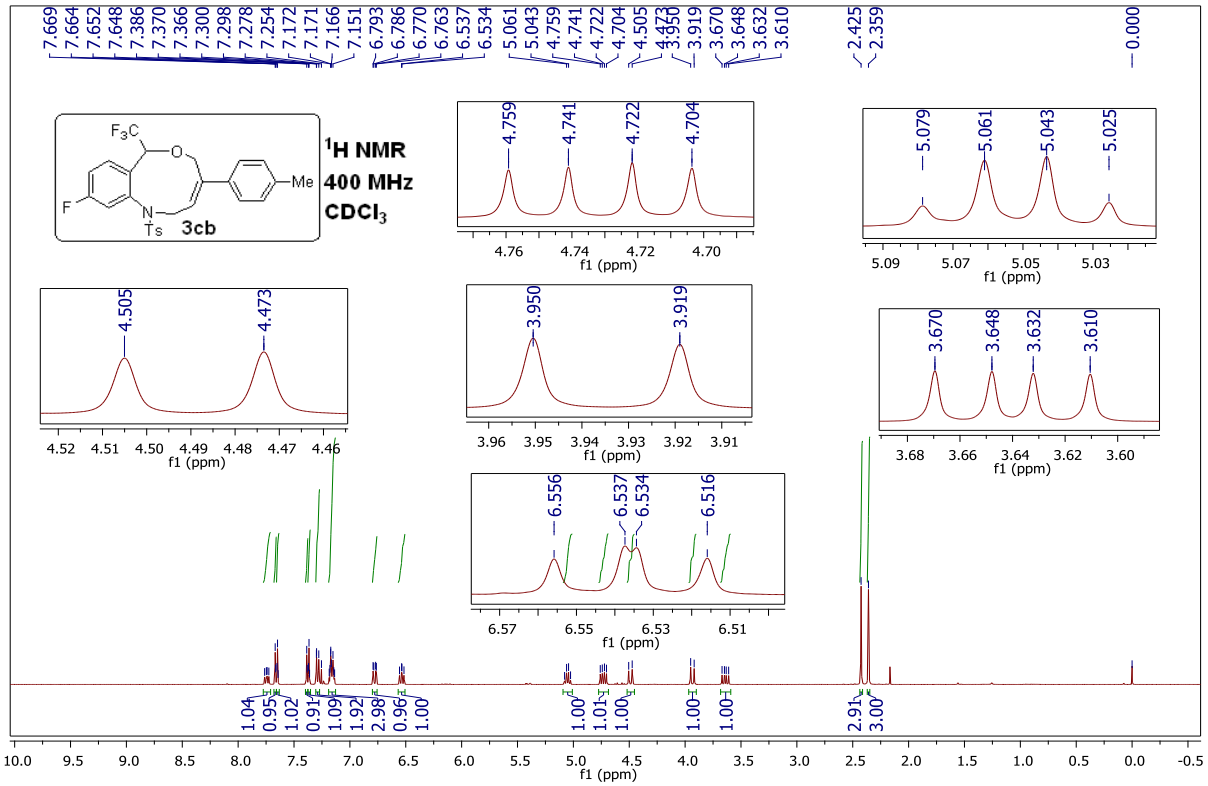
140.331
139.723
138.800
136.652
134.210
132.908
132.224
130.784
129.903
129.580
129.566
128.950
128.807
127.894
127.797
127.762
125.527
123.294
121.060
77.160
71.312
71.056
70.798
70.541
64.795
49.177
21.703
21.559
13C NMR
126 MHz
CDCl3
3be
acetone
f1 (ppm)

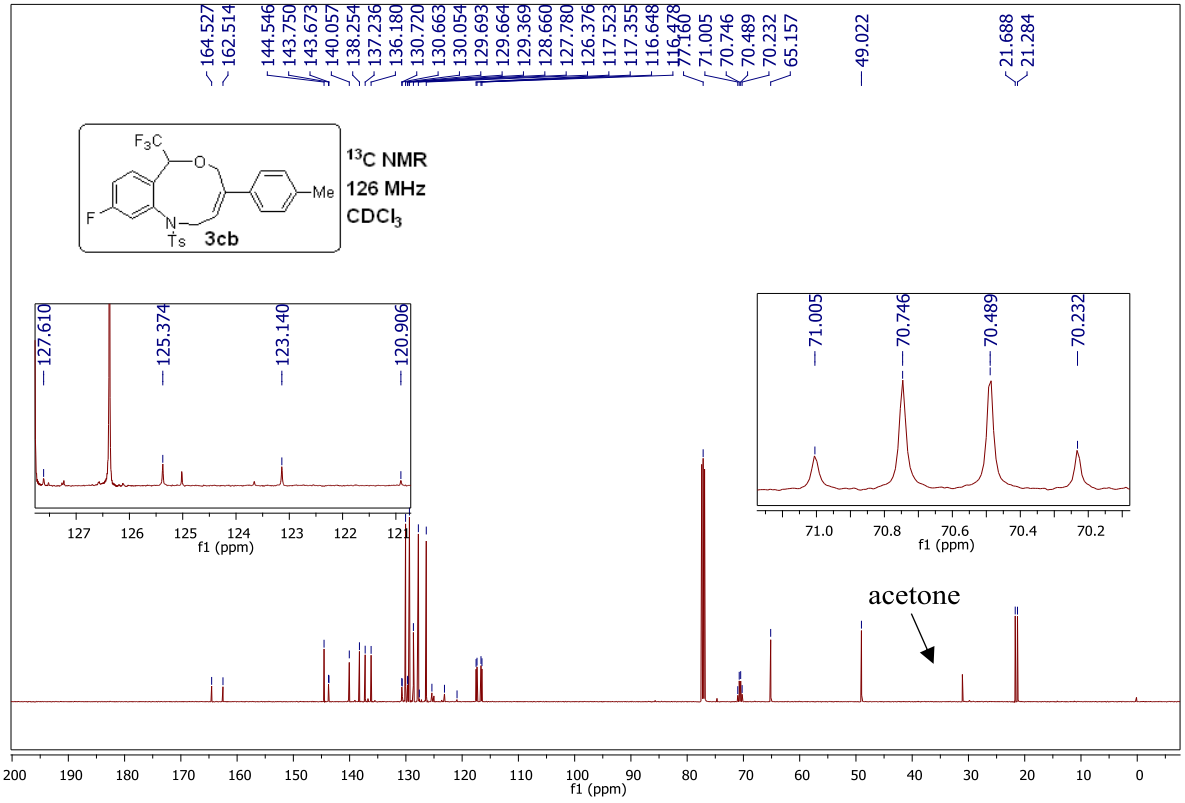

-72.305
-72.330
-162.200
19F NMR
282 MHz
CDCl3
3be
3.00
f1 (ppm)

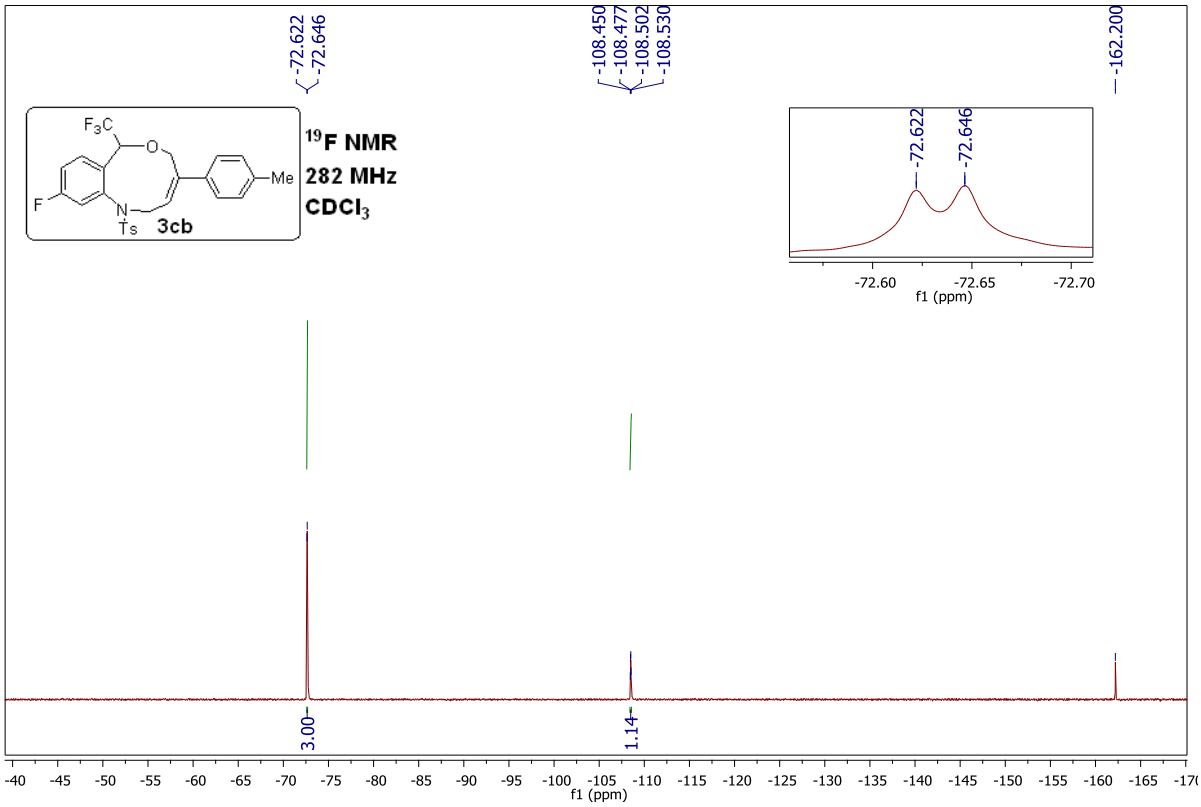

^{1}H NMR
400 MHz
CDCl$_3$
3ca
acetone
f1 (ppm)

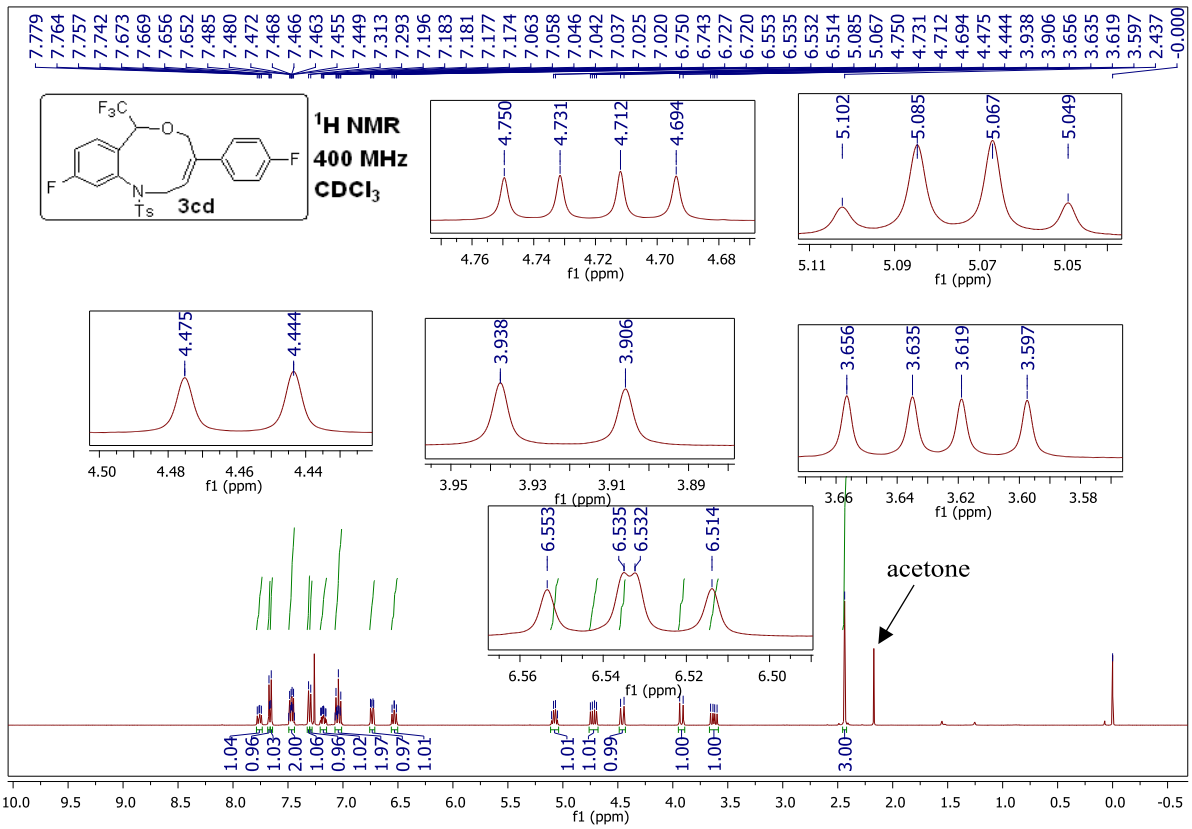

^{13}C NMR
126 MHz
CDCl$_3$
3ca
acetone
f1 (ppm)

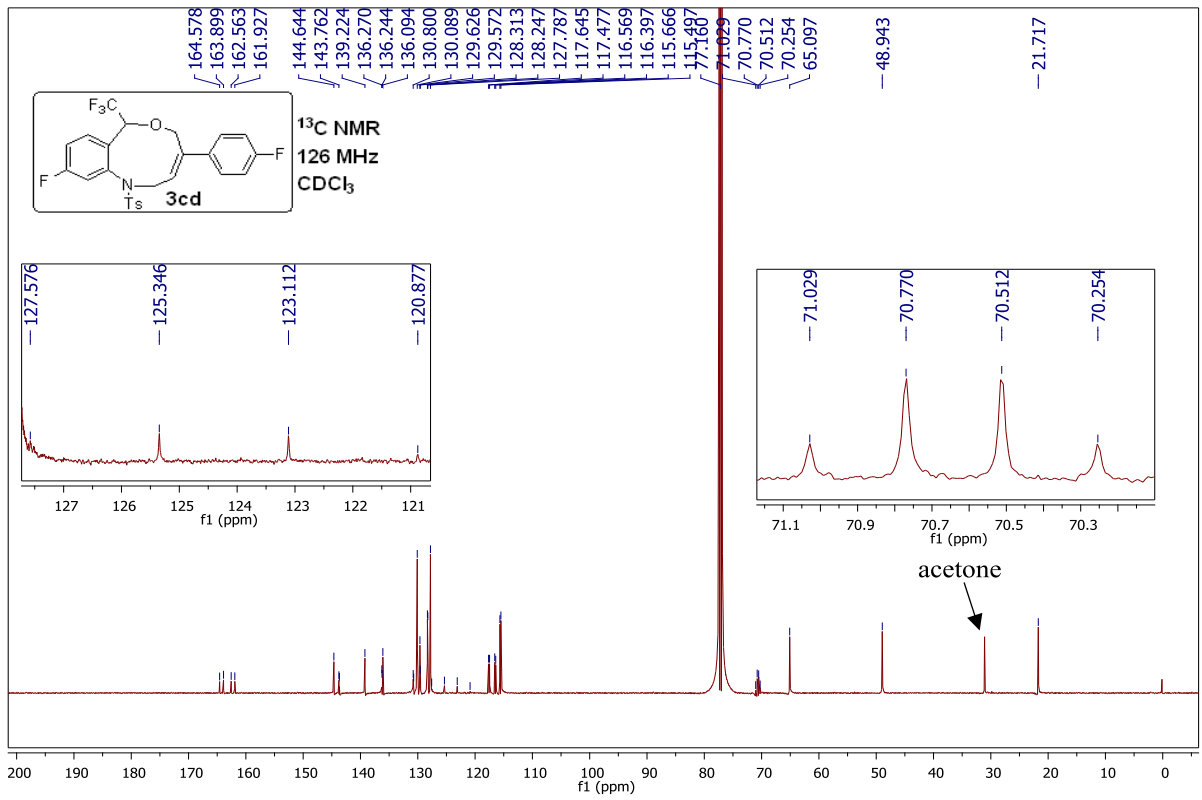

-72.586
-72.610
-108.373
-108.400
-108.425
-108.453
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3ca
3.00
0.96
f1 (ppm)

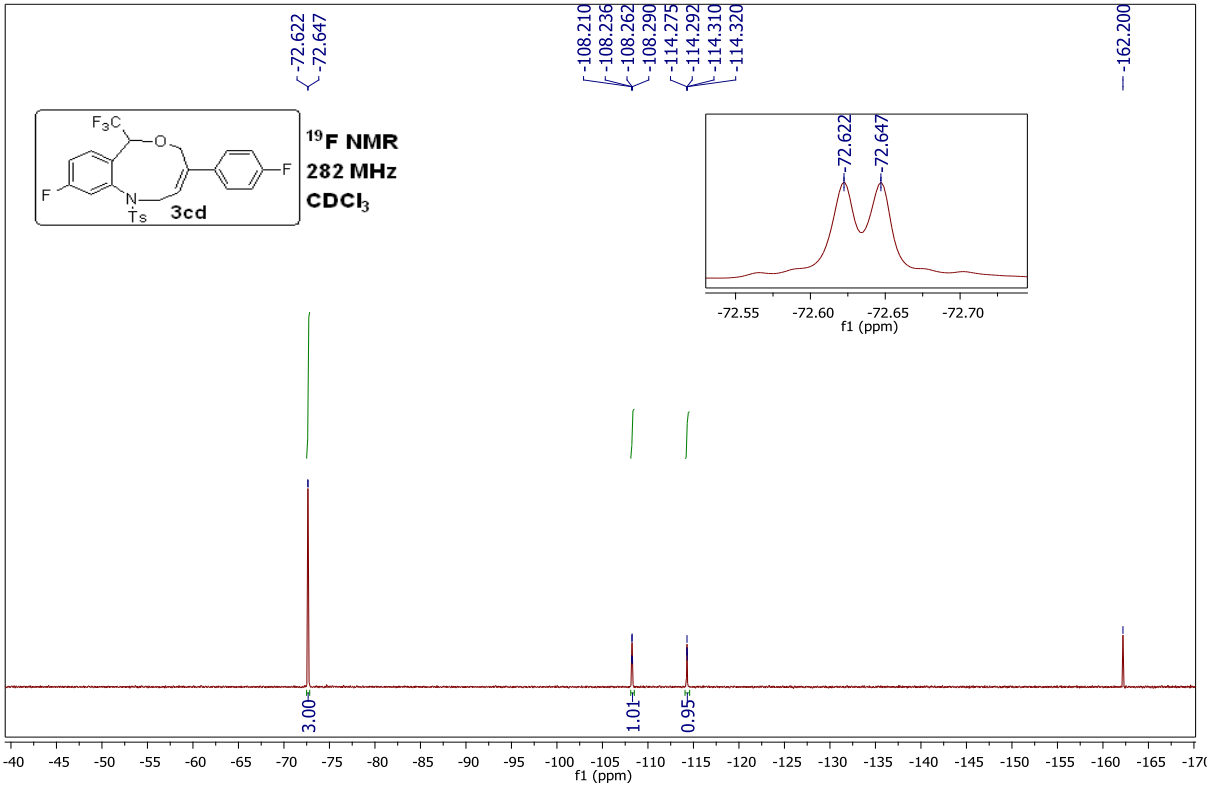

^{1}H NMR
400 MHz
CDCl$_3$
3cb
f1 (ppm)

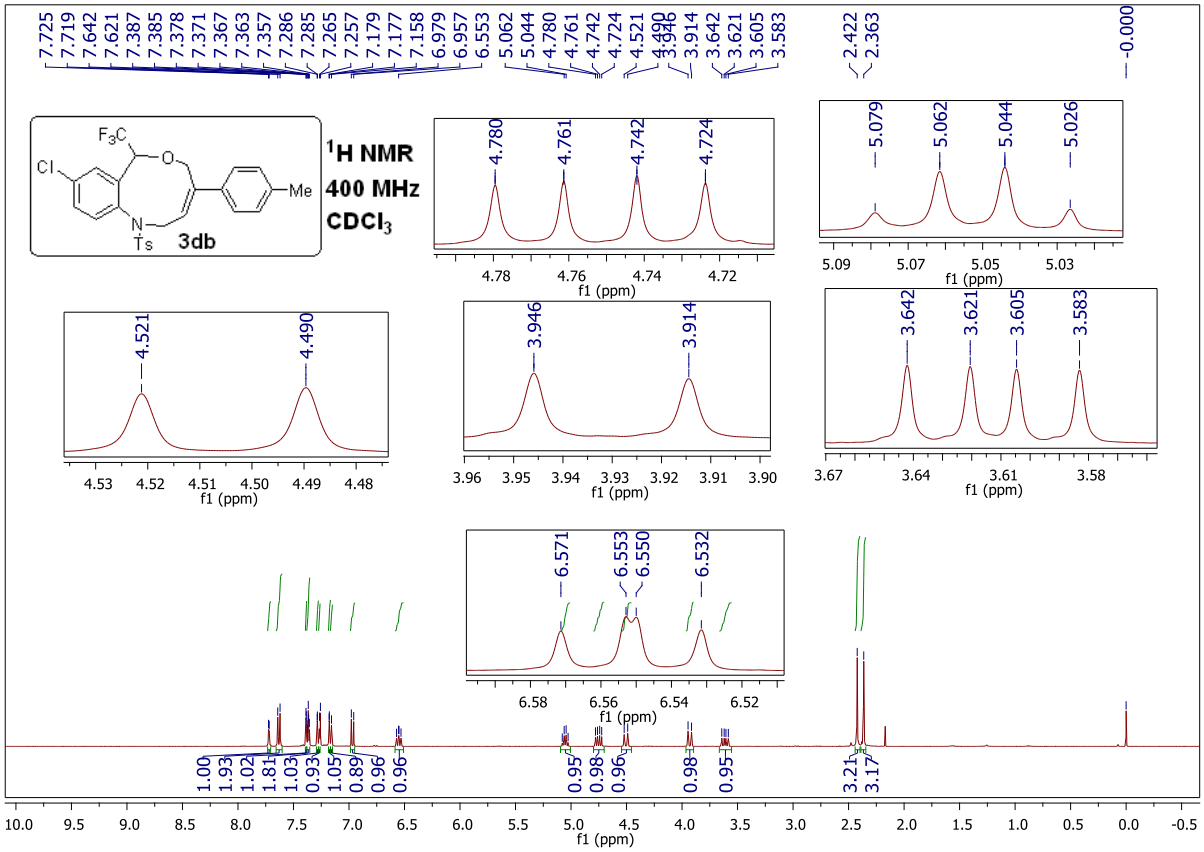

164.527
162.514
144.546
143.750
143.673
140.057
138.254
137.236
136.180
130.720
130.663
130.054
129.693
129.664
129.369
128.660
127.780
126.376
117.523
117.355
116.648
116.478
77.160
71.005
70.746
70.489
70.232
65.157
49.022
21.688
21.284
13C NMR
126 MHz
CDCl3
3cb
127.610
125.374
123.140
120.906
f1 (ppm)
71.005
70.746
70.489
70.232
f1 (ppm)
acetone
f1 (ppm)

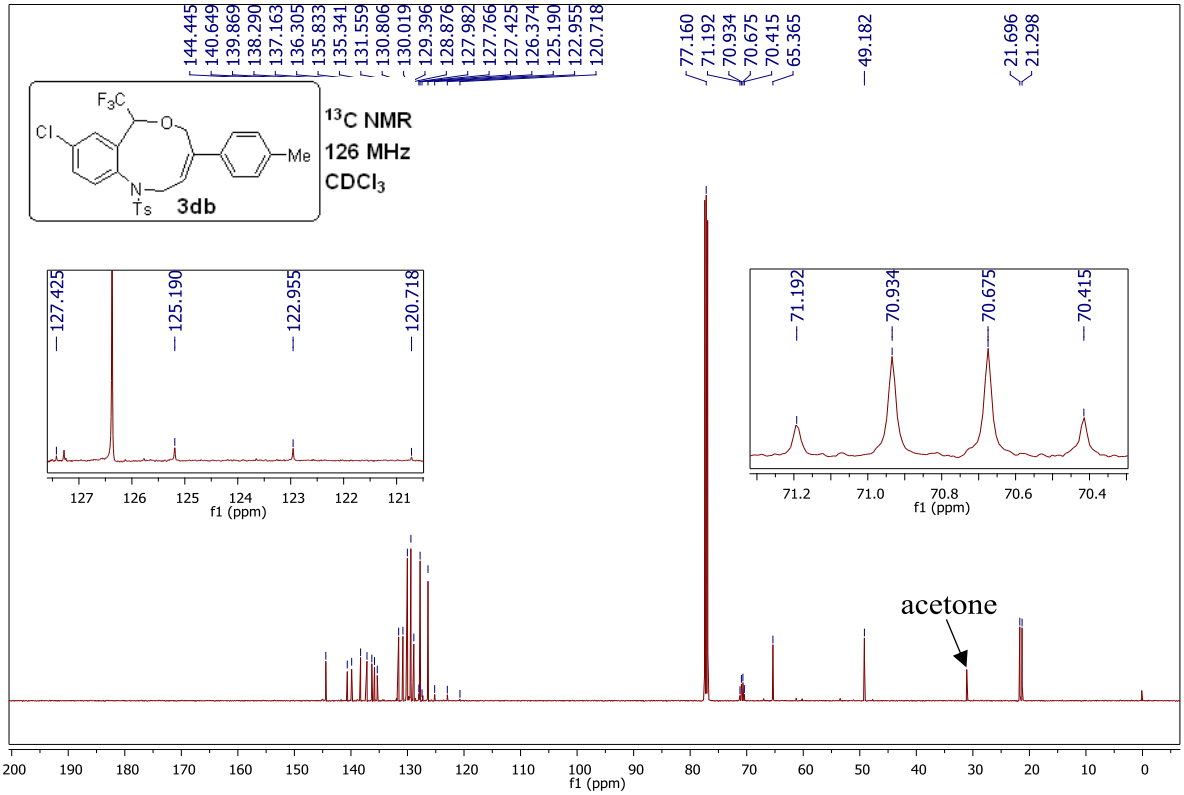

-72.622
-72.646
-108.450
-108.477
-108.502
-108.530
-162.200
19F NMR
282 MHz
CDCl3
3cb
-72.622
-72.646
f1 (ppm)
3.00
1.14
f1 (ppm)

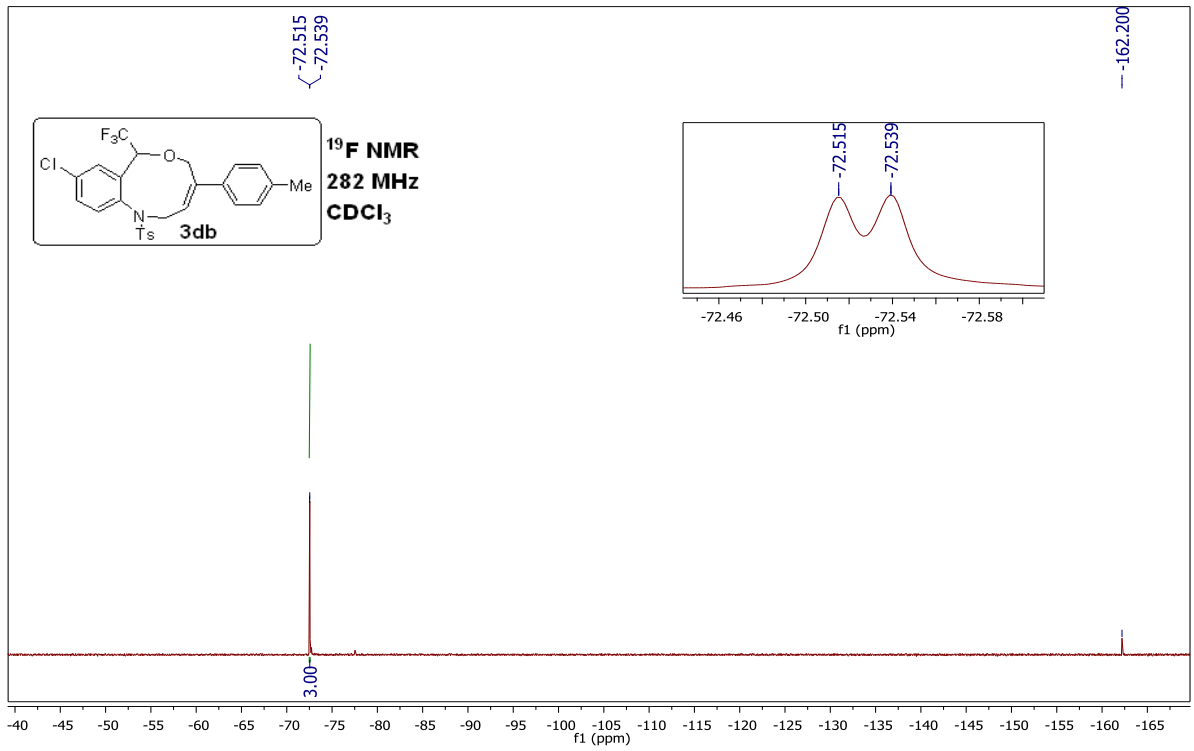

7.779 7.764 7.757 7.742 7.673 7.669 7.656 7.652 7.485 7.480 7.472 7.468 7.466 7.463 7.455 7.449 7.313 7.293 7.196 7.183 7.181 7.177 7.174 7.063 7.058 7.046 7.042 7.037 7.025 7.020 6.750 6.743 6.727 6.720 6.553 6.535 6.532 6.514 5.085 5.067 4.750 4.731 4.712 4.694 4.475 4.444 3.938 3.906 3.656 3.635 3.619 3.597 2.437 -0.000
F3C
O
F
F
N
Ts
3cd
1H NMR
400 MHz
CDCl3
4.750
4.731
4.712
4.694
5.102
5.085
5.067
5.049
4.475
4.444
3.938
3.906
3.656
3.635
3.619
3.597
6.553
6.535
6.532
6.514
acetone
f1 (ppm)
1.04 0.96 1.03 2.00 1.06 0.96 1.02 1.97 0.97 1.01 1.01 1.01 0.99 1.00 1.00 3.00

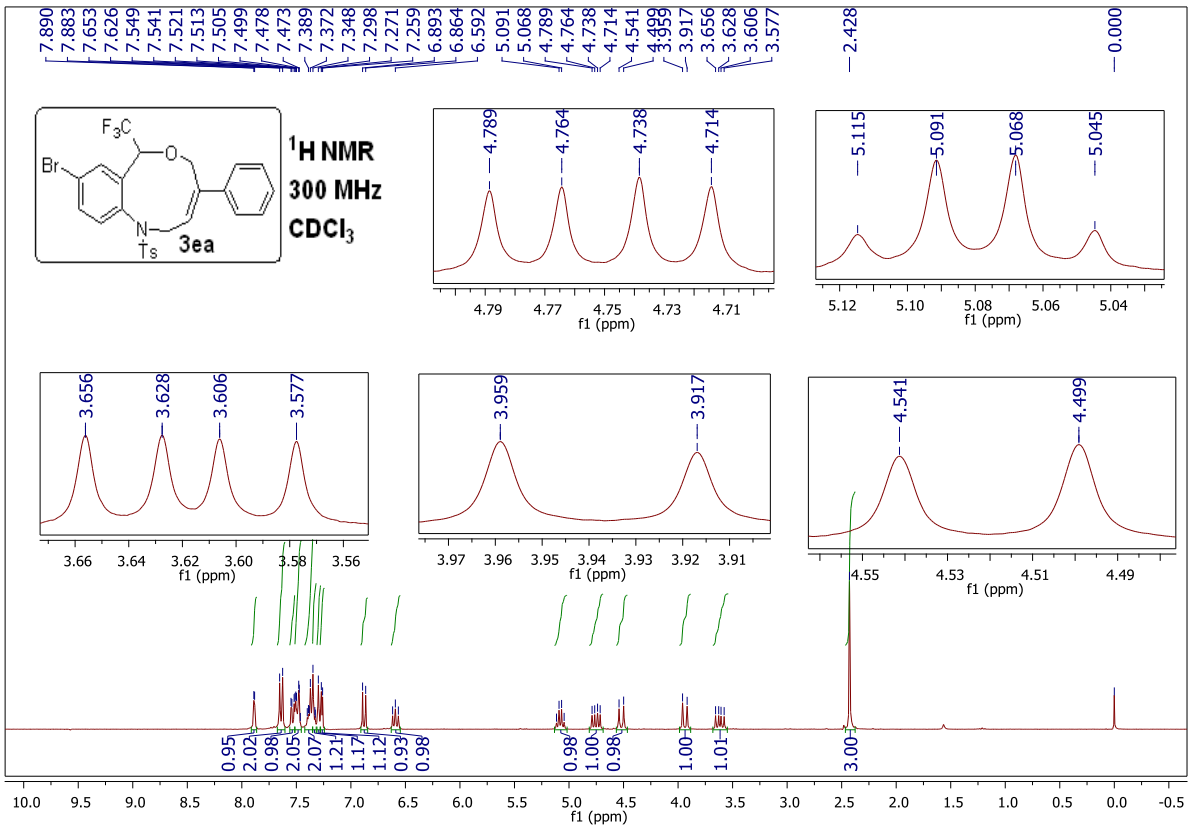

164.578 163.899 162.563 161.927 144.644 143.762 139.224 136.270 136.244 136.094 130.800 130.089 129.626 129.572 128.313 128.247 127.787 117.645 117.477 116.569 116.397 115.666 115.497 77.160 71.029 70.770 70.512 70.254 65.097 48.943 21.717
F3C
O
F
F
N
Ts
3cd
13C NMR
126 MHz
CDCl3
127.576
125.346
123.112
120.877
71.029
70.770
70.512
70.254
acetone
f1 (ppm)

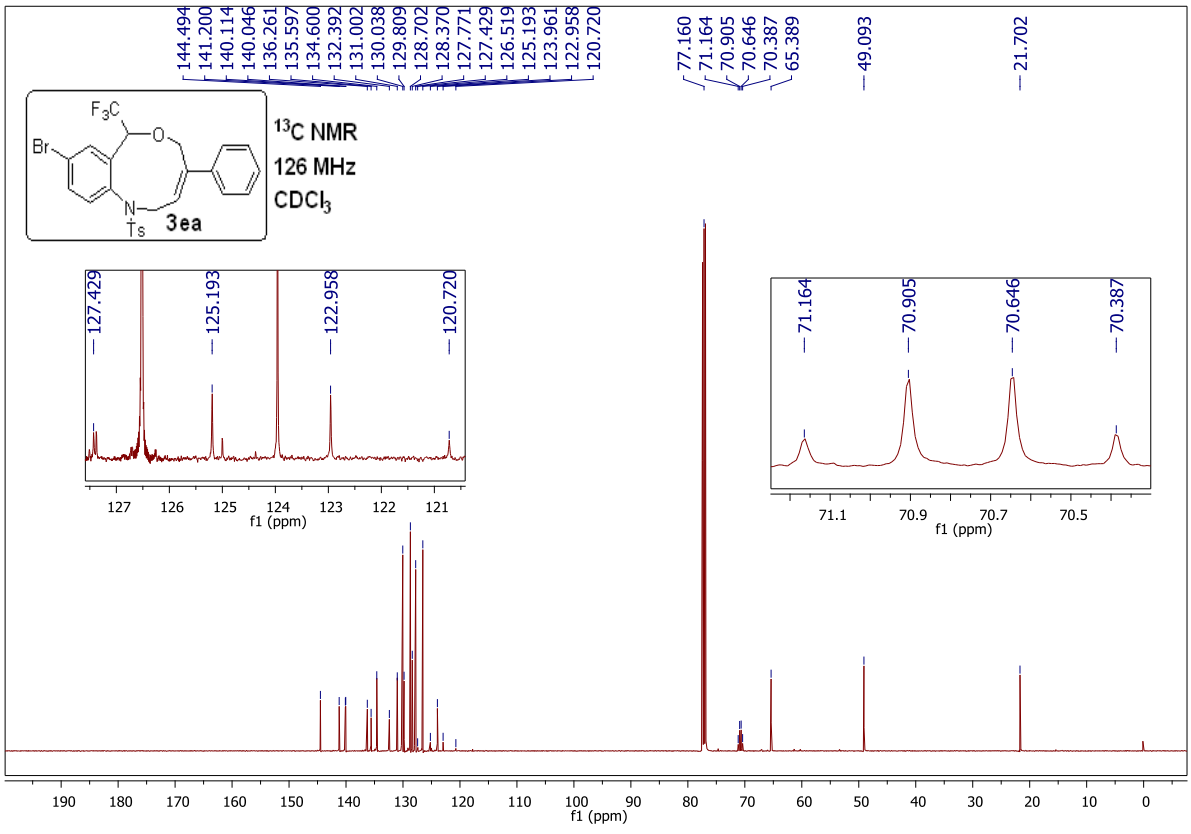

-72.622
-72.647
-108.210
-108.236
-108.262
-108.290
-114.275
-114.292
-114.310
-114.320
-162.200
F3C
O
F
F
N
Ts
3cd
19F NMR
282 MHz
CDCl3
-72.622
-72.647
-72.55
-72.60
-72.65
-72.70
f1 (ppm)
3.00
1.01
0.95
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

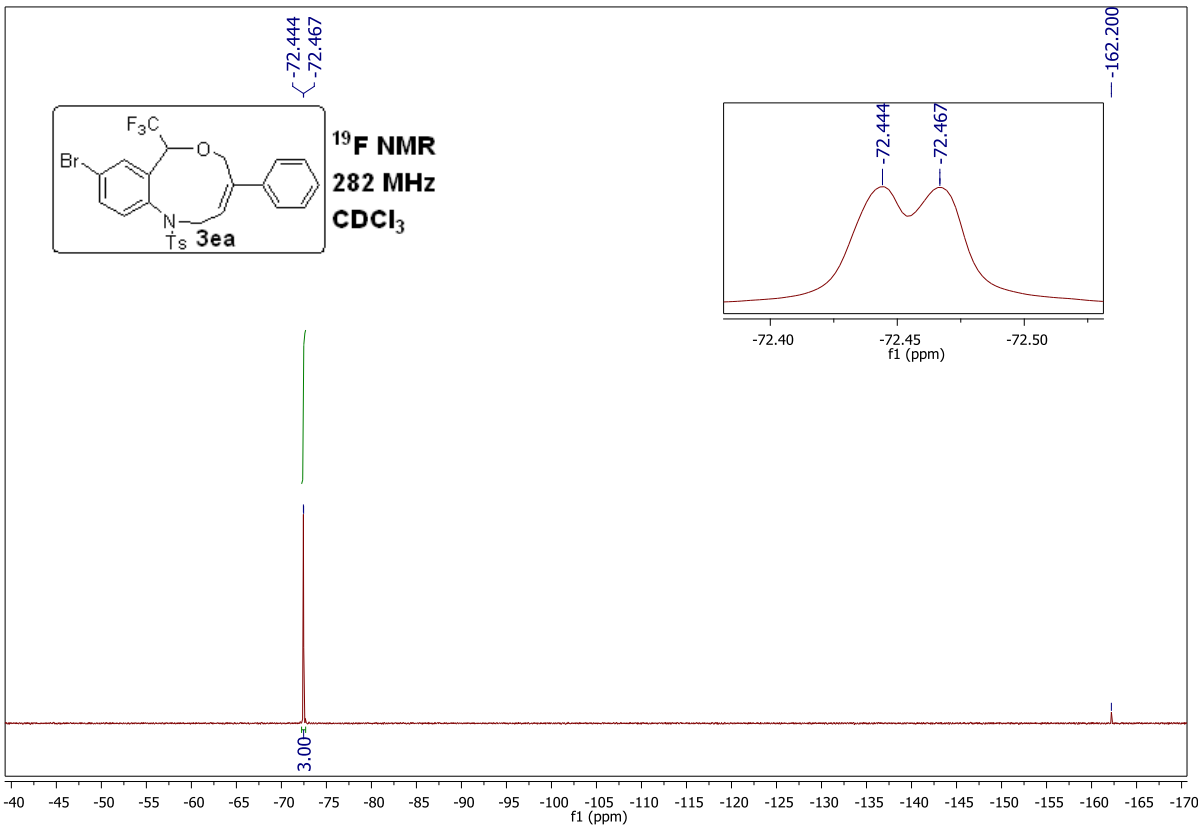

7.725
7.719
7.642
7.621
7.387
7.385
7.378
7.371
7.367
7.363
7.357
7.286
7.285
7.265
7.257
7.179
7.177
7.158
6.979
6.957
6.553
5.062
5.044
4.780
4.761
4.742
4.724
4.521
4.490
3.946
3.914
3.642
3.621
3.605
3.583
2.422
2.363
-0.000
F3C
O
Cl
Me
N
Ts
3db
1H NMR
400 MHz
CDCl3
4.780
4.761
4.742
4.724
4.78 4.76 4.74 4.72
f1 (ppm)
5.079
5.062
5.044
5.026
5.09 5.07 5.05 5.03
f1 (ppm)
4.521
4.490
4.53 4.52 4.51 4.50 4.49 4.48
f1 (ppm)
3.946
3.914
3.96 3.95 3.94 3.93 3.92 3.91 3.90
f1 (ppm)
3.642
3.621
3.605
3.583
3.67 3.64 3.61 3.58
f1 (ppm)
6.571
6.553
6.550
6.532
6.58 6.56 6.54 6.52
f1 (ppm)
1.00 1.93 1.02 1.81 1.03 0.93 1.05 0.89 0.96 0.96
0.95 0.98 0.96 0.98 0.95
3.21 3.17
10.0 9.5 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 -0.5
f1 (ppm)

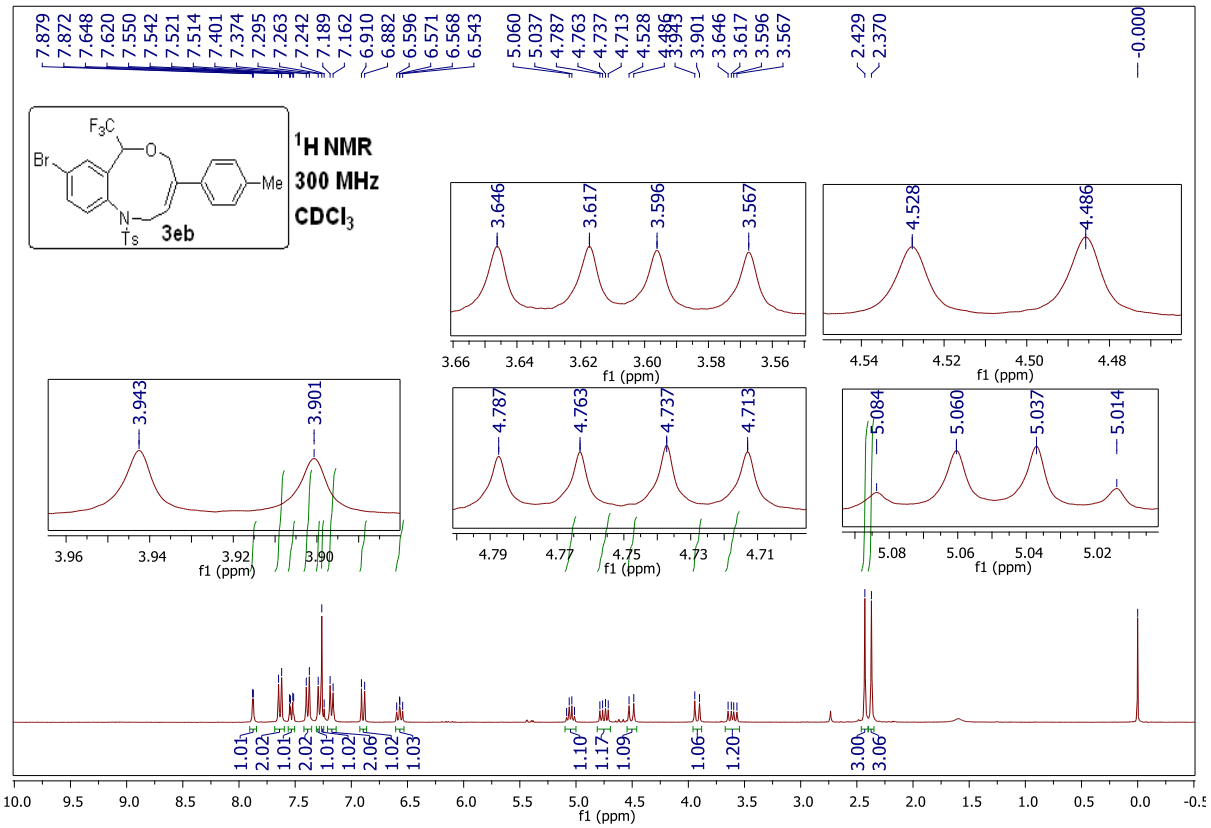

144.445
140.649
139.869
138.290
137.163
136.305
135.833
135.341
131.559
130.806
130.019
129.396
128.876
127.982
127.766
127.425
126.374
125.190
122.955
120.718
77.160
71.192
70.934
70.675
70.415
65.365
49.182
21.696
21.298
^{13}C NMR
126 MHz
CDCl$_3$
3db
acetone
f1 (ppm)

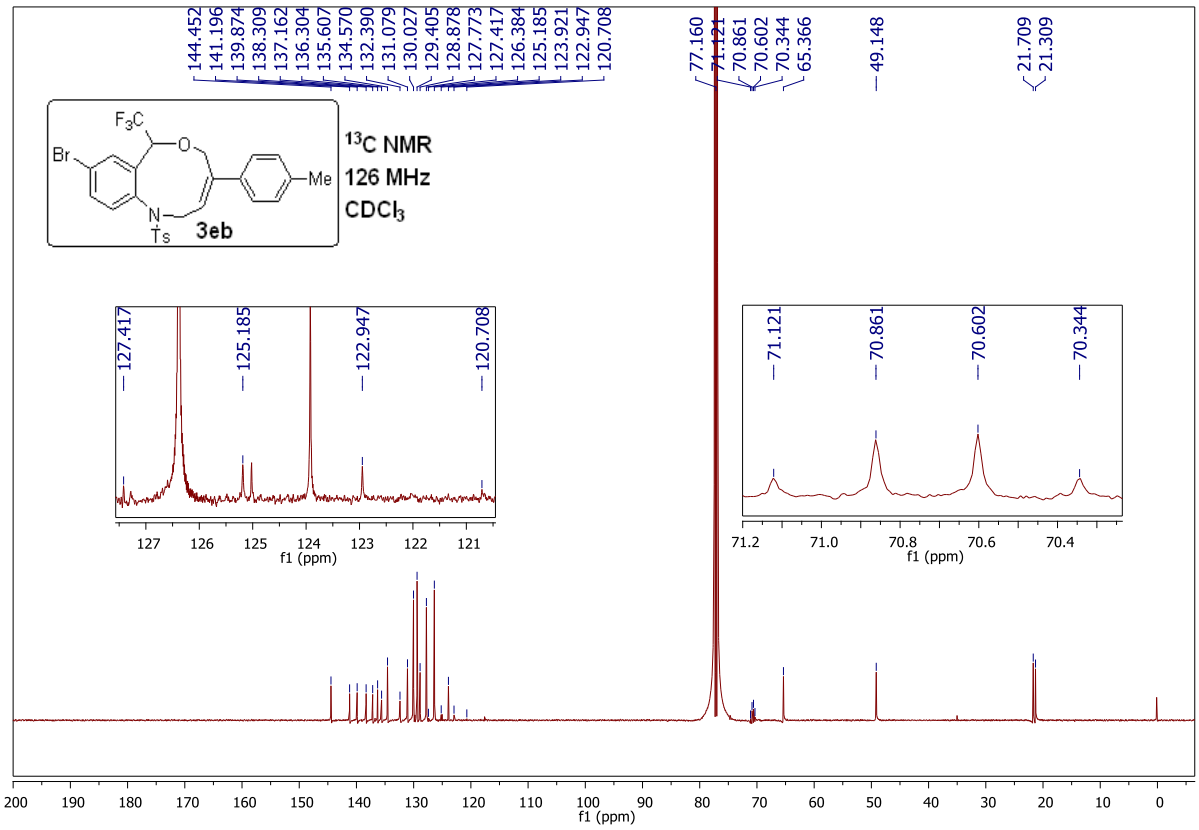

-72.515
-72.539
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3db
3.00
f1 (ppm)

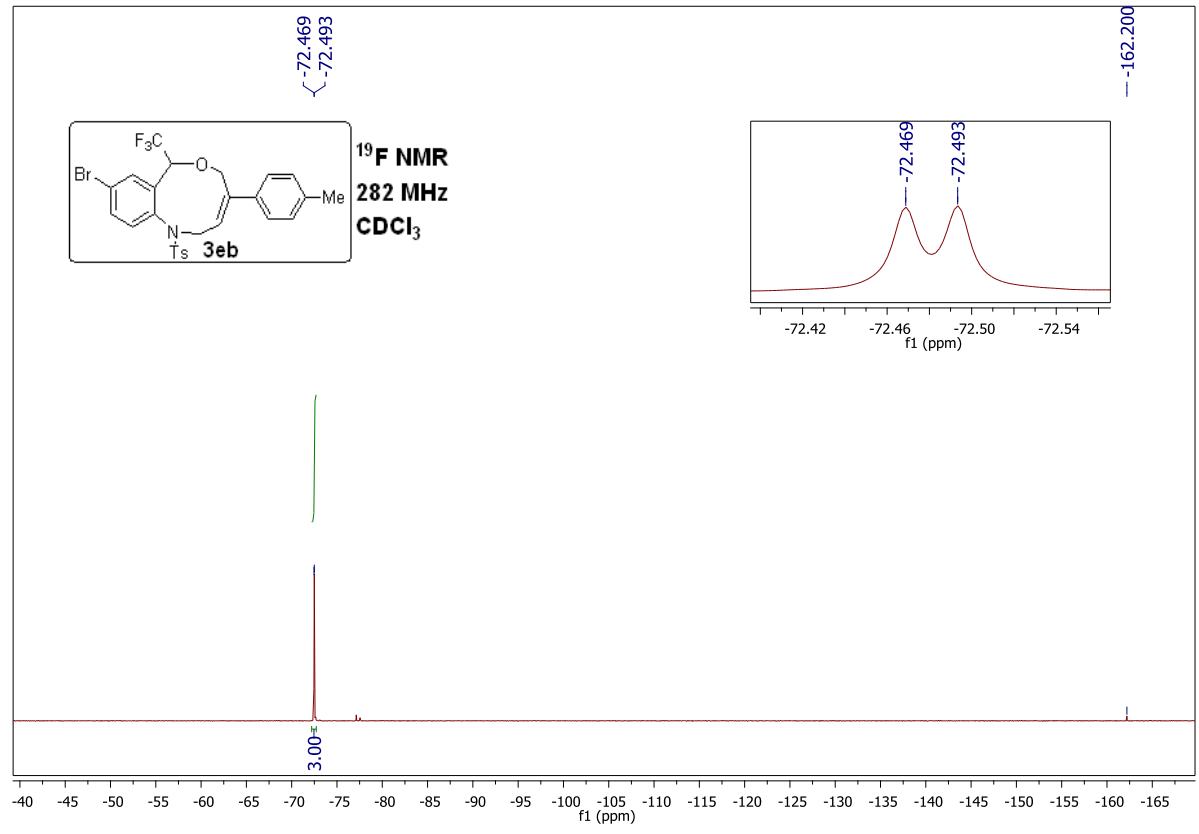

7.890 7.883 7.653 7.626 7.549 7.541 7.521 7.513 7.505 7.499 7.478 7.473 7.389 7.372 7.348 7.298 7.271 7.259 6.893 6.864 6.592 5.091 5.068 4.789 4.764 4.738 4.714 4.541 4.499 3.959 3.917 3.656 3.628 3.606 3.577 2.428 0.000
^{1}H NMR
300 MHz
CDCl$_3$
3ea
f1 (ppm)

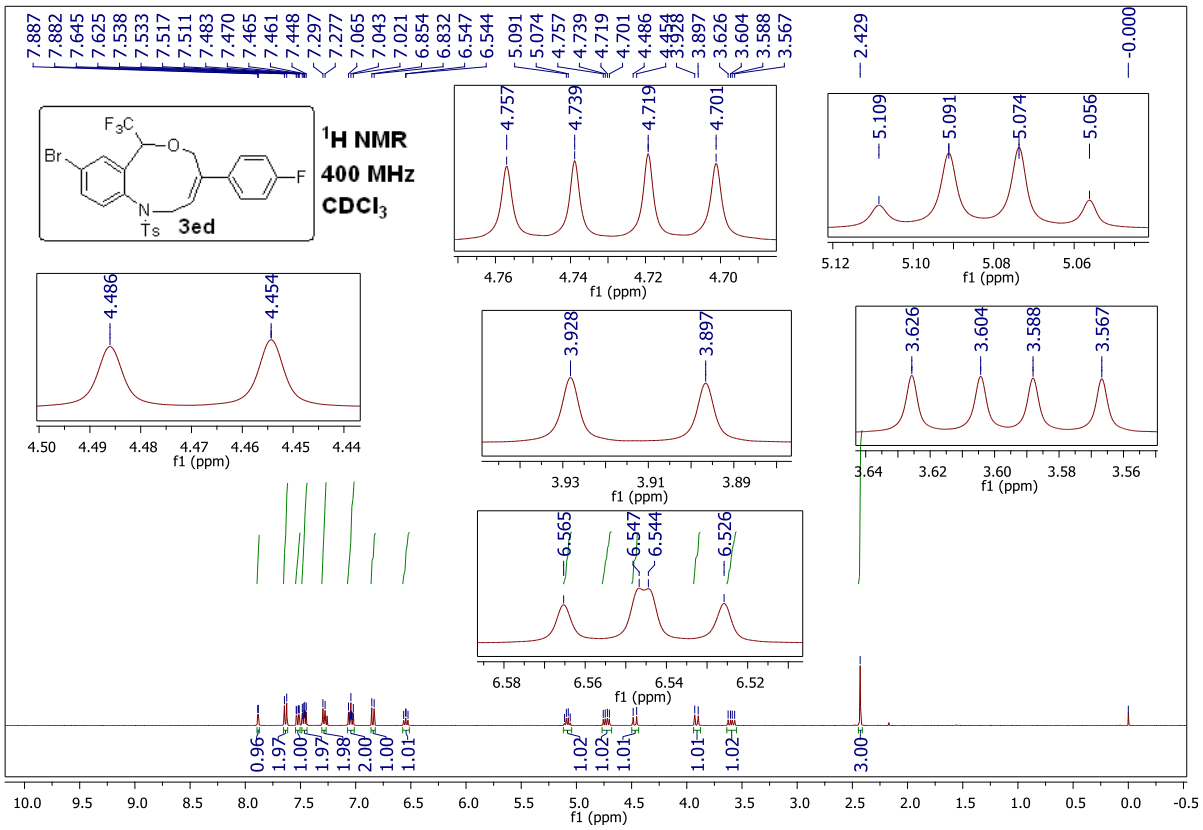

144.494 141.200 140.114 140.046 136.261 135.597 134.600 132.392 131.002 130.038 129.809 128.702 128.370 127.771 127.429 126.519 125.193 123.961 122.958 120.720 77.160 71.164 70.905 70.646 70.387 65.389 49.093 21.702
^{13}C NMR
126 MHz
CDCl$_3$
3ea
f1 (ppm)

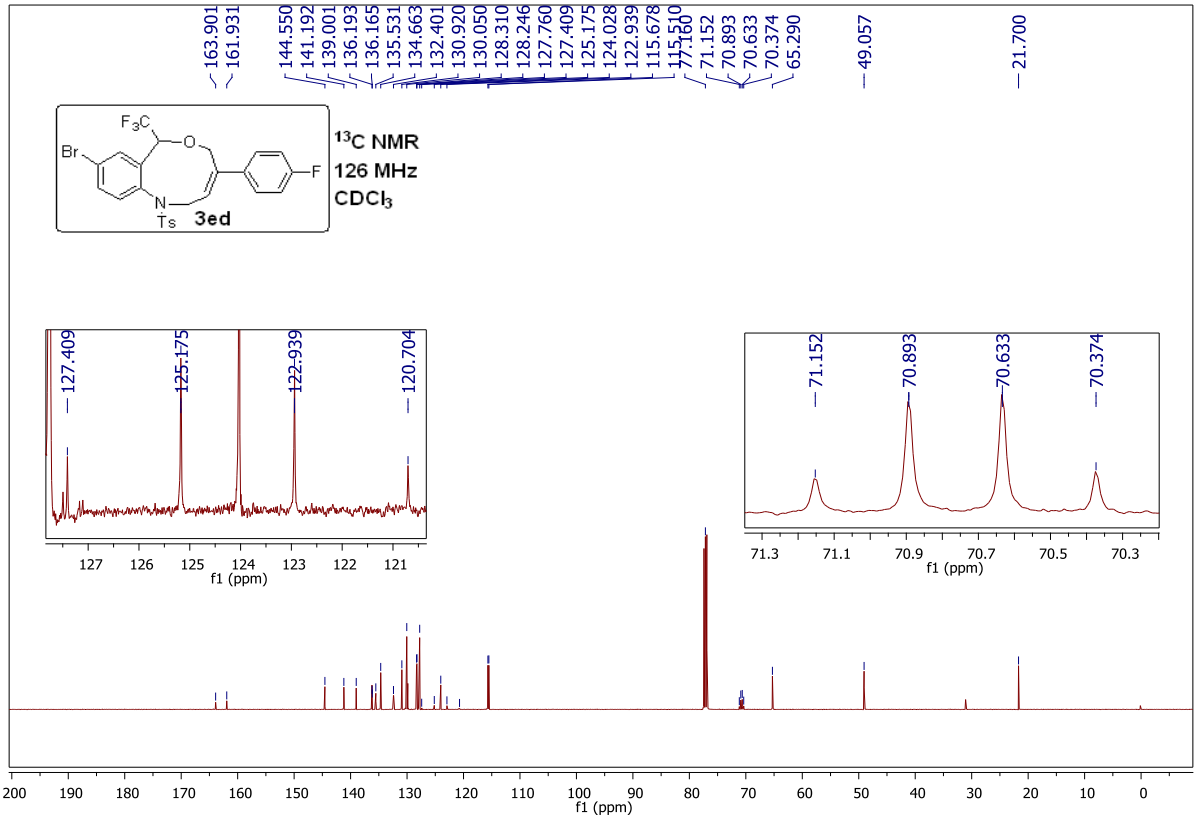

-72.444
-72.467
-162.200
19F NMR
282 MHz
CDCl3
3ea
3.00
f1 (ppm)

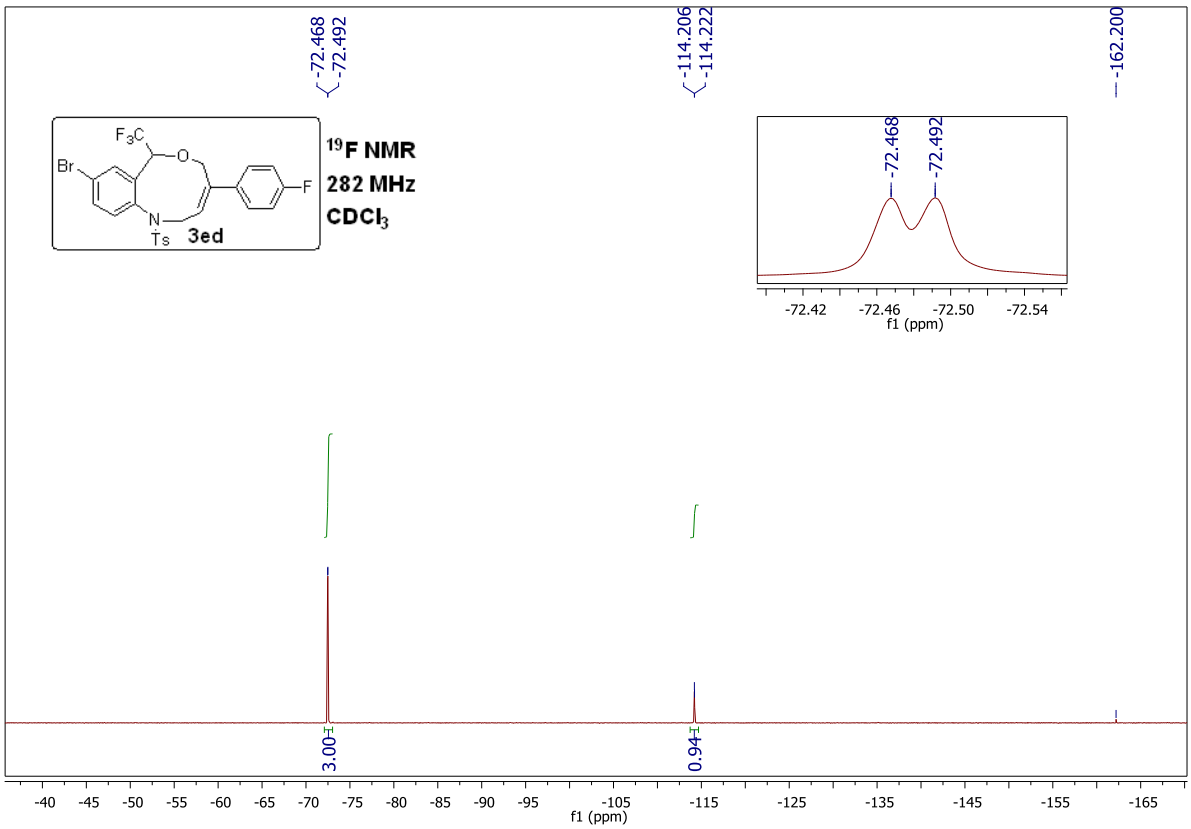

1H NMR
300 MHz
CDCl3
3eb
-0.000
f1 (ppm)

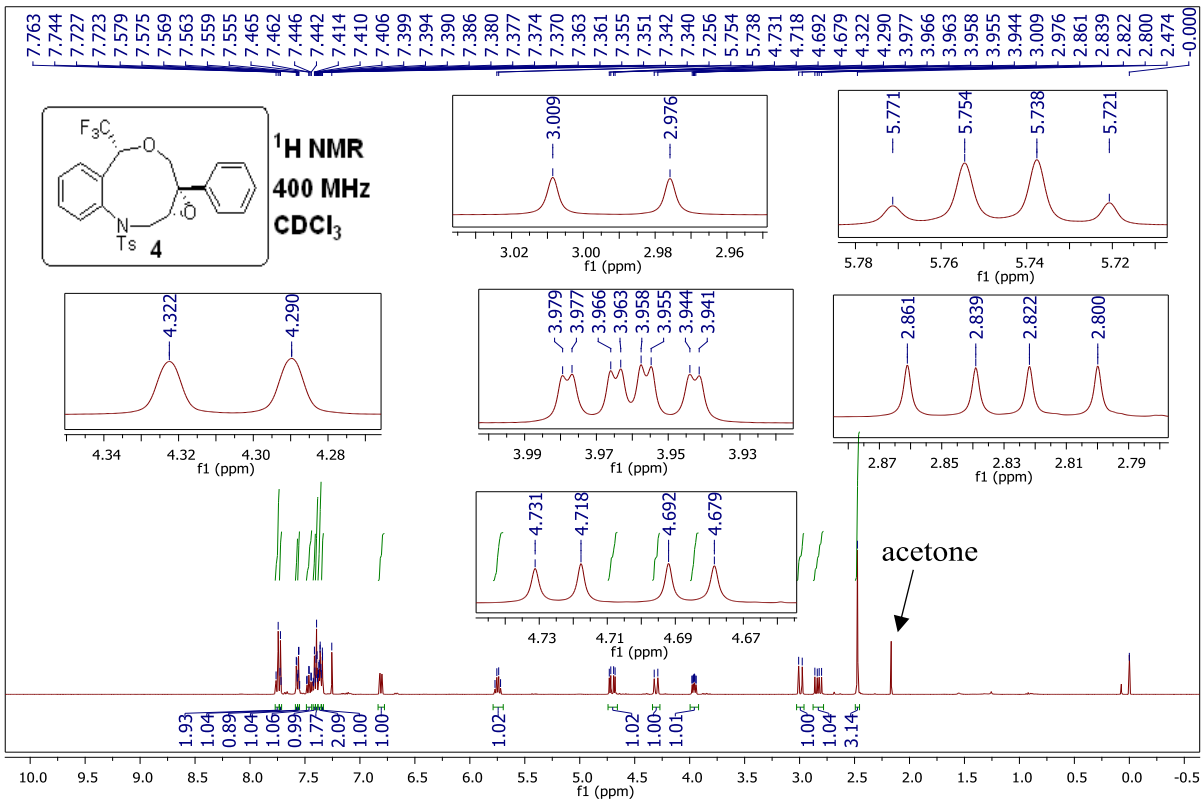

144.452
141.196
139.874
138.309
137.162
136.304
135.607
134.570
132.390
131.079
130.027
129.405
128.878
127.773
127.417
126.384
125.185
123.921
122.947
120.708
77.160
71.121
70.861
70.602
70.344
65.366
49.148
21.709
21.309
^{13}C NMR
126 MHz
CDCl$_3$
3eb
127.417
125.185
122.947
120.708
71.121
70.861
70.602
70.344
f1 (ppm)

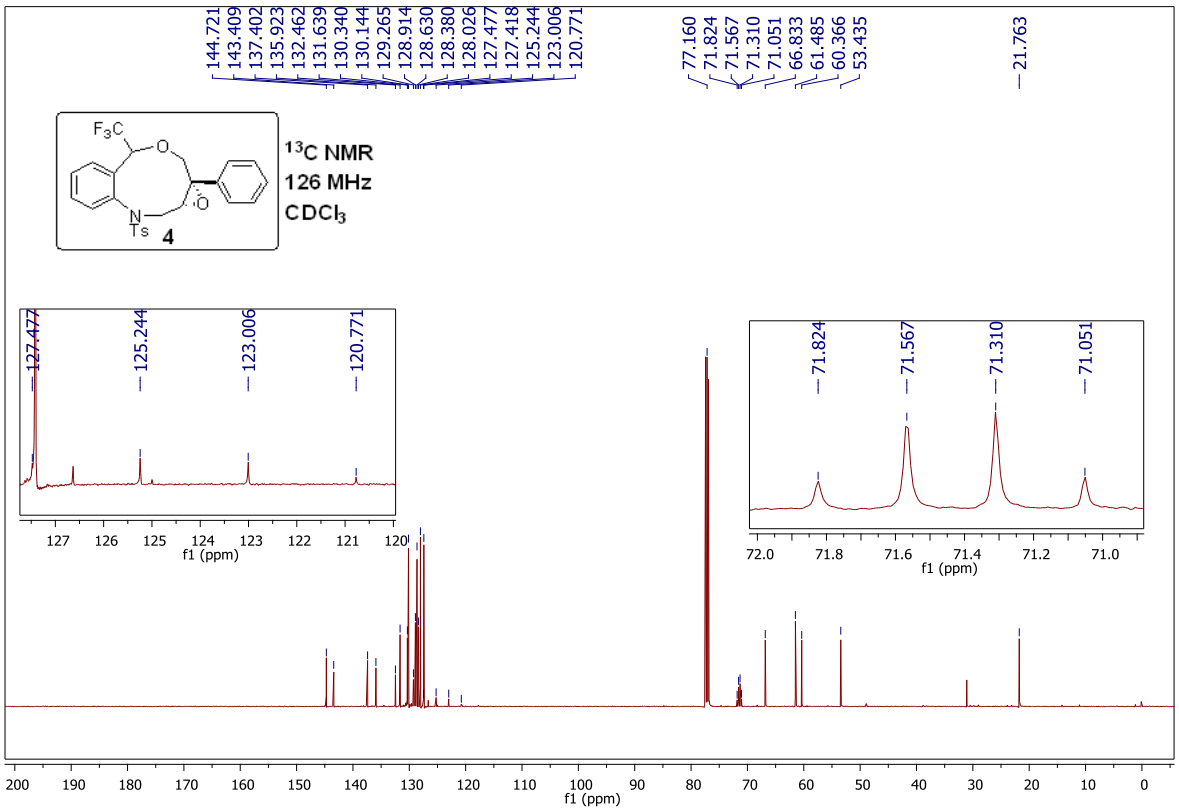

-72.469
-72.493
-162.200
^{19}F NMR
282 MHz
CDCl$_3$
3eb
3.00
f1 (ppm)

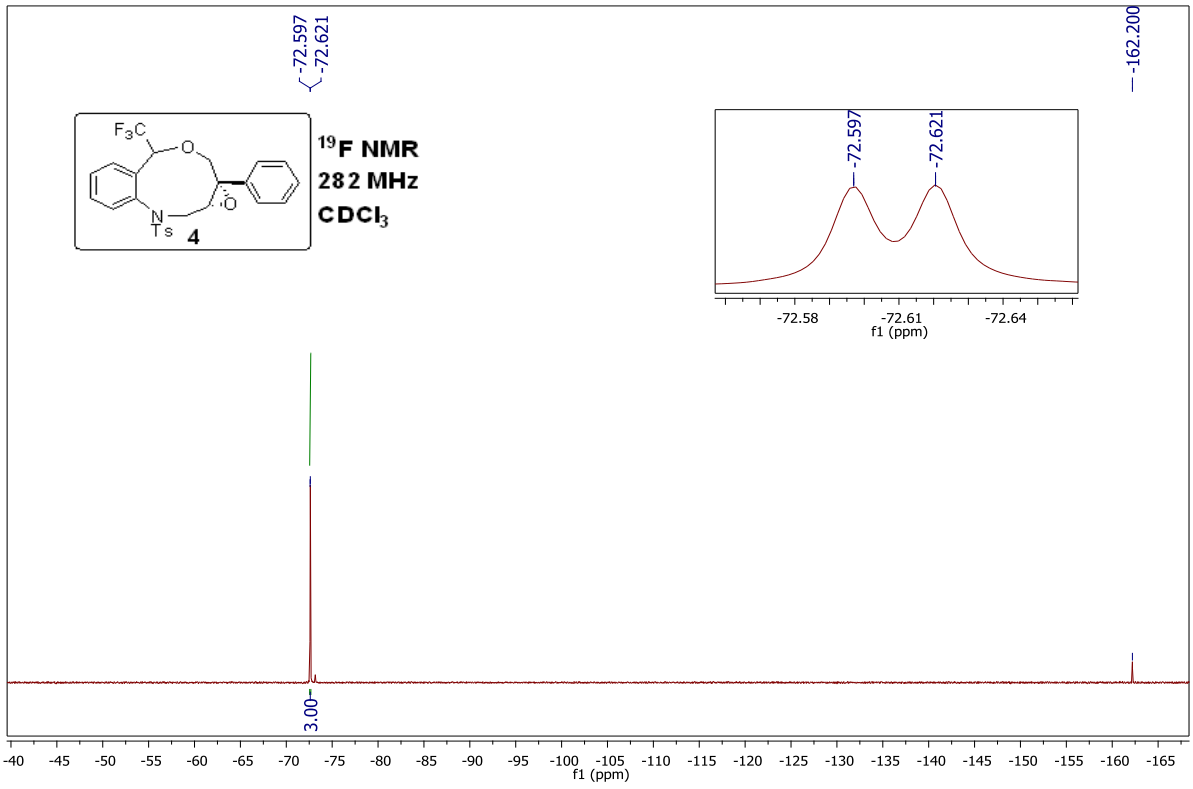

7.887 7.882 7.645 7.625 7.538 7.533 7.517 7.511 7.483 7.470 7.465 7.461 7.448 7.297 7.277 7.065 7.043 7.021 6.854 6.832 6.547 6.544 5.091 5.074 4.757 4.739 4.719 4.701 4.486 4.454 3.928 3.897 3.626 3.604 3.588 3.567 2.429 -0.000
F3C
Br
O
F
N
Ts
3ed
1H NMR
400 MHz
CDCl3
4.757 4.739 4.719 4.701
4.76 4.74 4.72 4.70
f1 (ppm)
5.109 5.091 5.074 5.056
5.12 5.10 5.08 5.06
f1 (ppm)
4.486 4.454
4.50 4.49 4.48 4.47 4.46 4.45 4.44
f1 (ppm)
3.928 3.897
3.93 3.91 3.89
f1 (ppm)
3.626 3.604 3.588 3.567
3.64 3.62 3.60 3.58 3.56
f1 (ppm)
6.565 6.547 6.544 6.526
6.58 6.56 6.54 6.52
f1 (ppm)
0.96 1.97 1.00 1.97 1.98 2.00 1.00 1.01 1.02 1.02 1.01 1.01 1.02 3.00
10.0 9.5 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 -0.5
f1 (ppm)

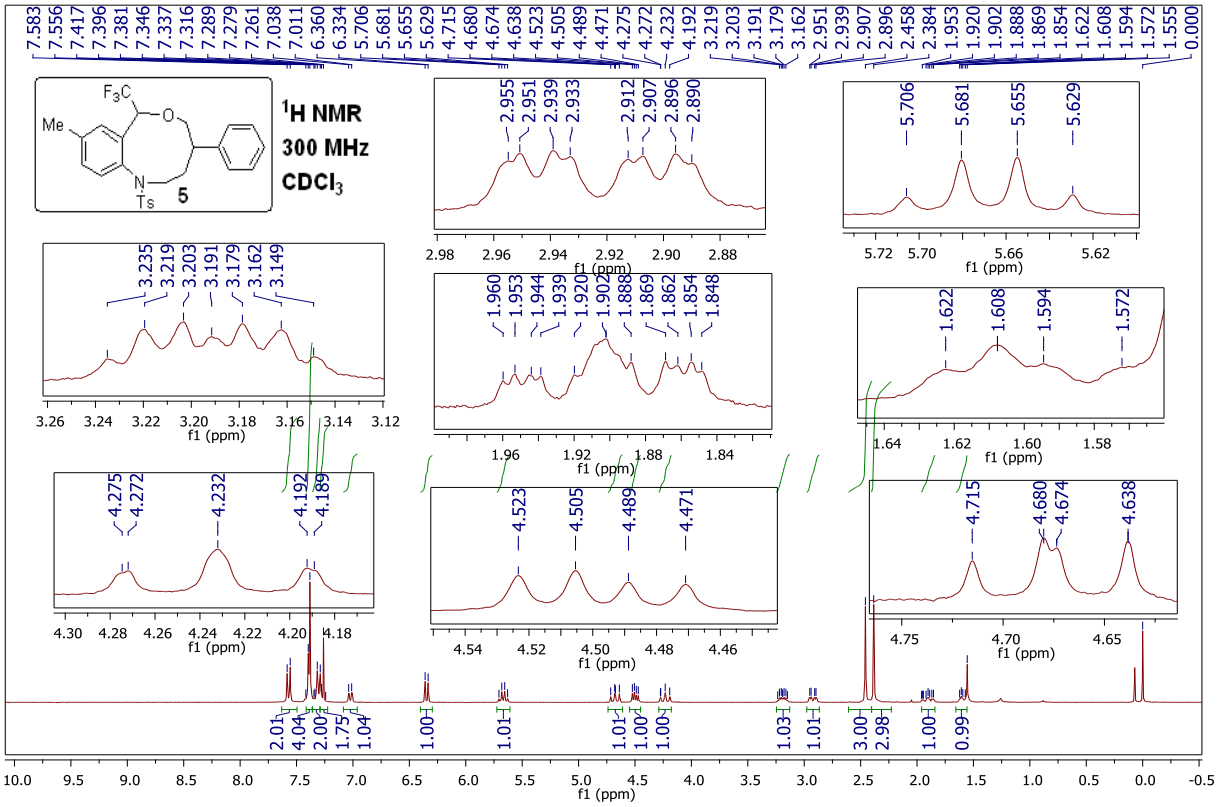

163.901 161.931 144.550 141.192 139.001 136.193 136.165 135.531 134.663 132.401 130.920 130.050 128.310 128.246 127.760 127.409 125.175 124.028 122.939 115.678 115.510 77.160 71.152 70.893 70.633 70.374 65.290 49.057 21.700
F3C
Br
O
F
N
Ts
3ed
13C NMR
126 MHz
CDCl3
127.409 125.175 122.939 120.704
127 126 125 124 123 122 121
f1 (ppm)
71.152 70.893 70.633 70.374
71.3 71.1 70.9 70.7 70.5 70.3
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

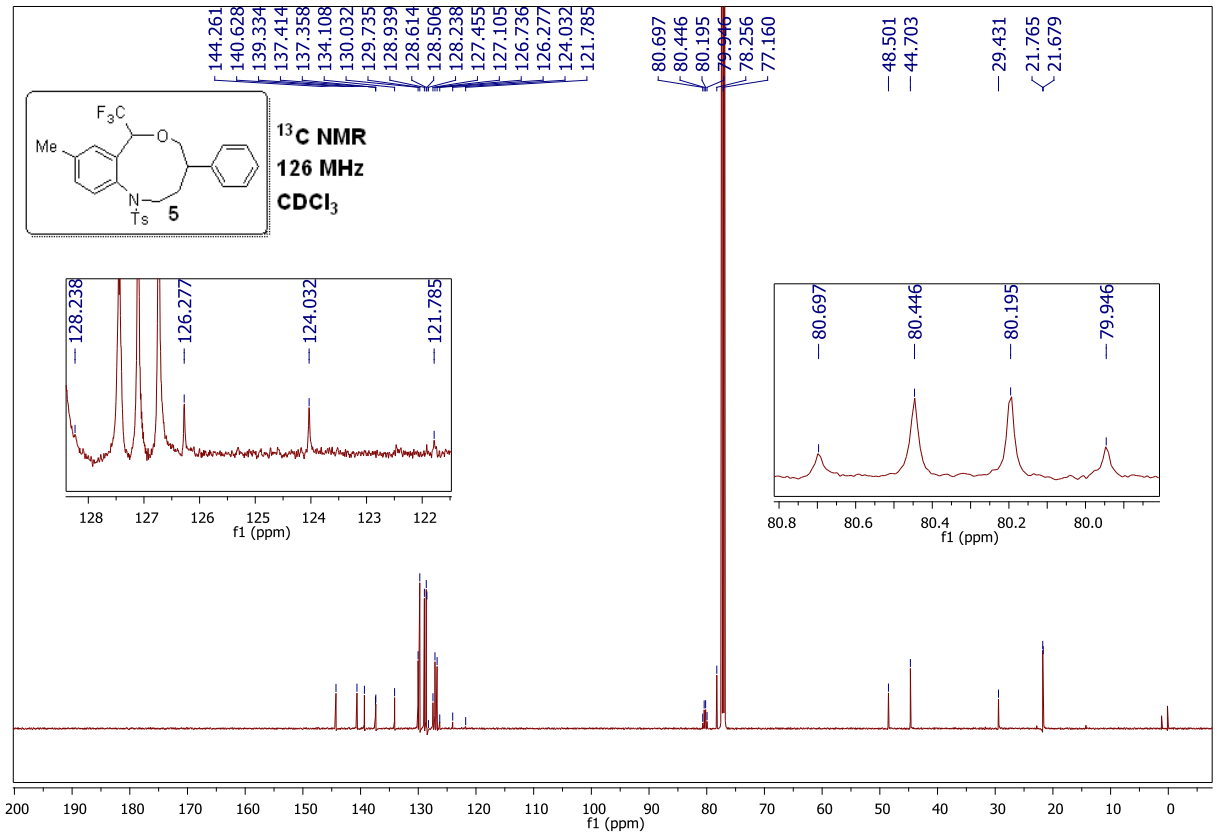

-72.468
-72.492
-114.206
-114.222
-162.200
19F NMR
282 MHz
CDCl3
3ed
3.00
0.94
f1 (ppm)

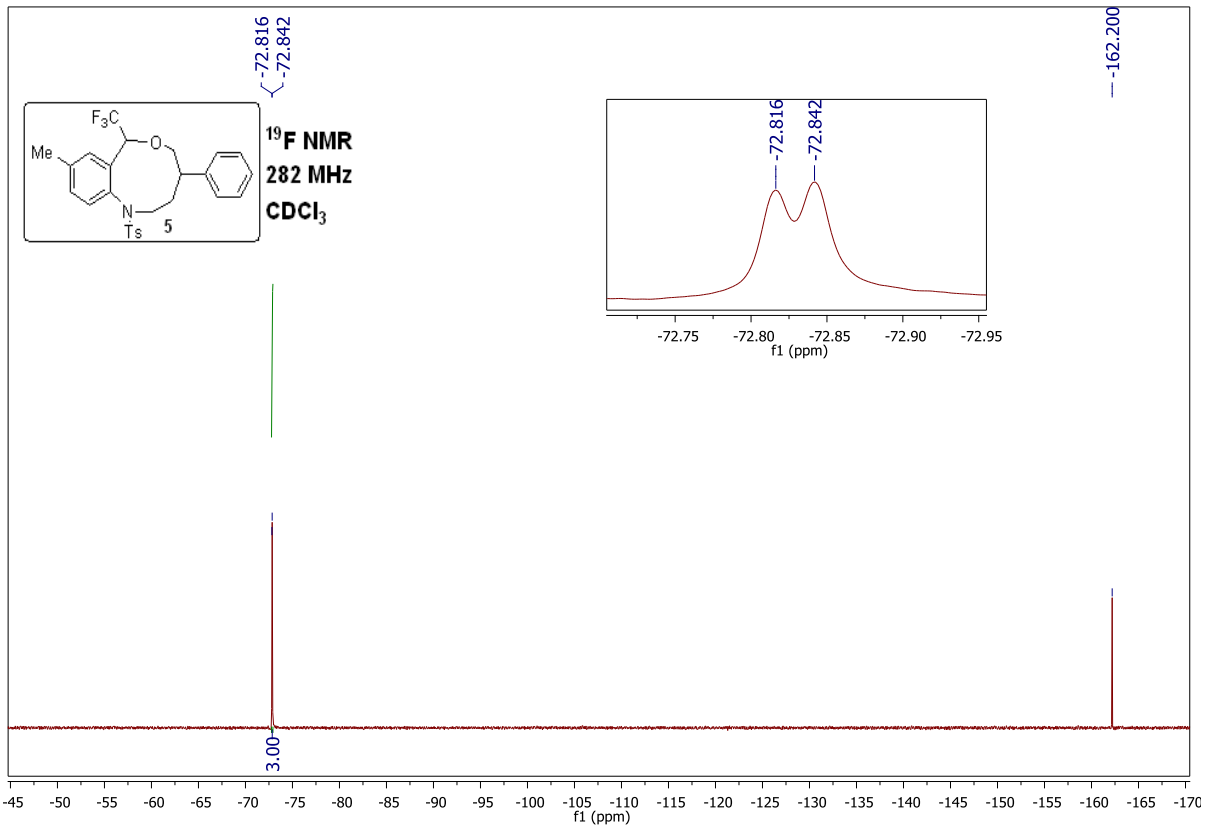

1H NMR
400 MHz
CDCl3
4
acetone
f1 (ppm)

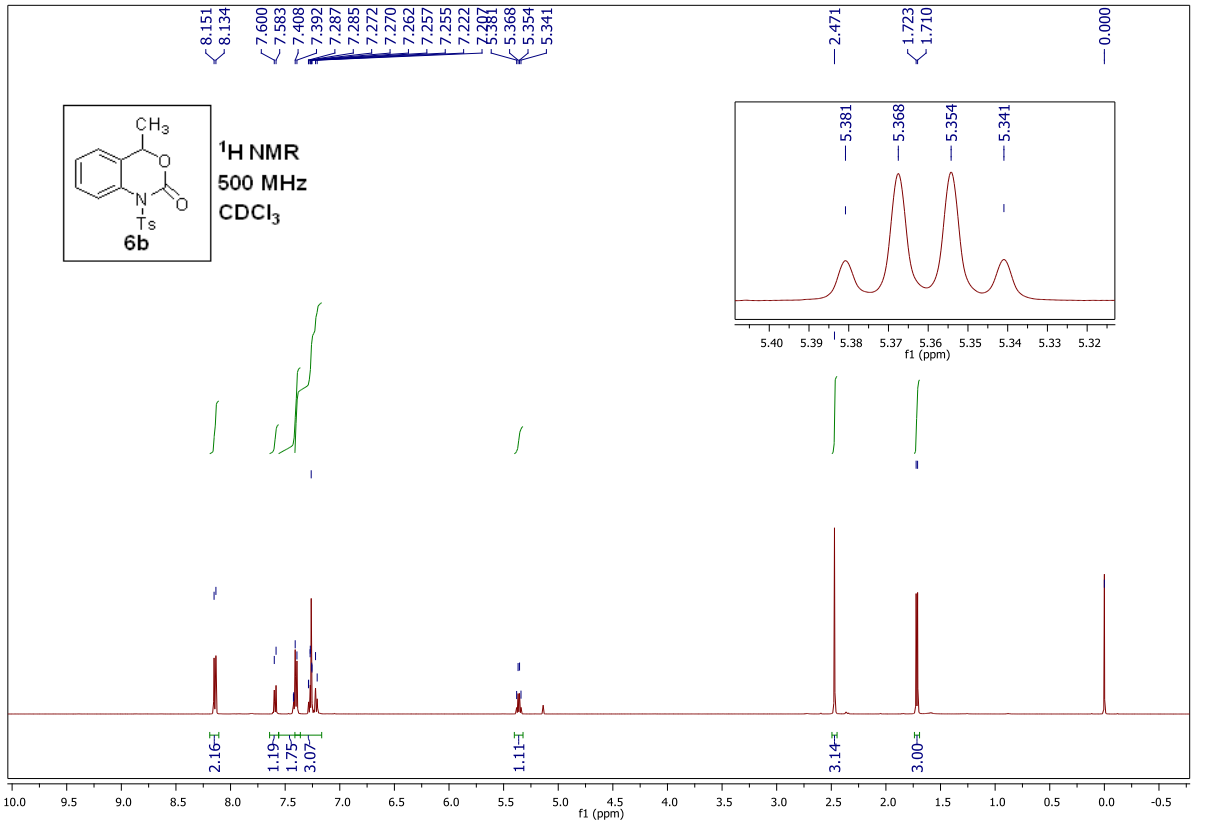

144.721
143.409
137.402
135.923
132.462
131.639
130.340
130.144
129.265
128.914
128.630
128.380
128.026
127.477
127.418
125.244
123.006
120.771
77.160
71.824
71.567
71.310
71.051
66.833
61.485
60.366
53.435
21.763
13C NMR
126 MHz
CDCl3
4
f1 (ppm)

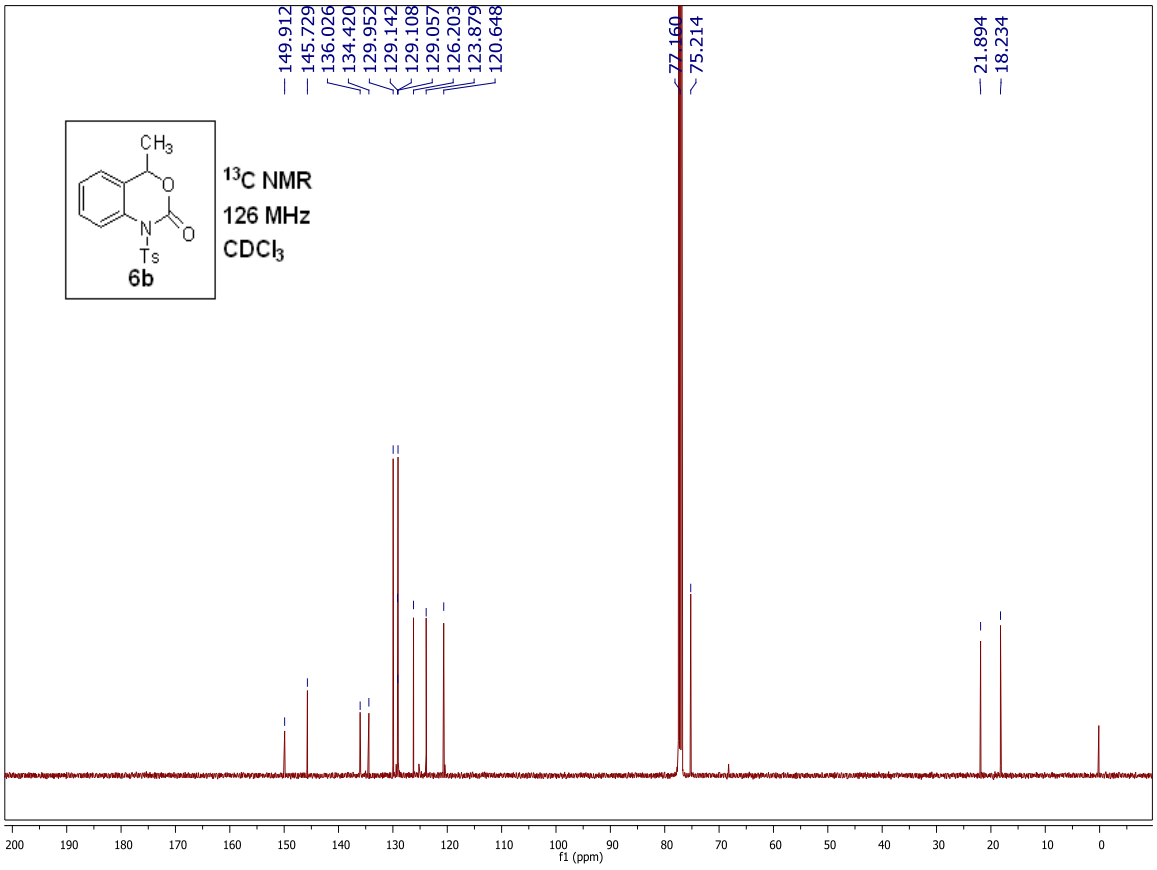

-72.597
-72.621
-162.200
19F NMR
282 MHz
CDCl3
4
3.00
f1 (ppm)

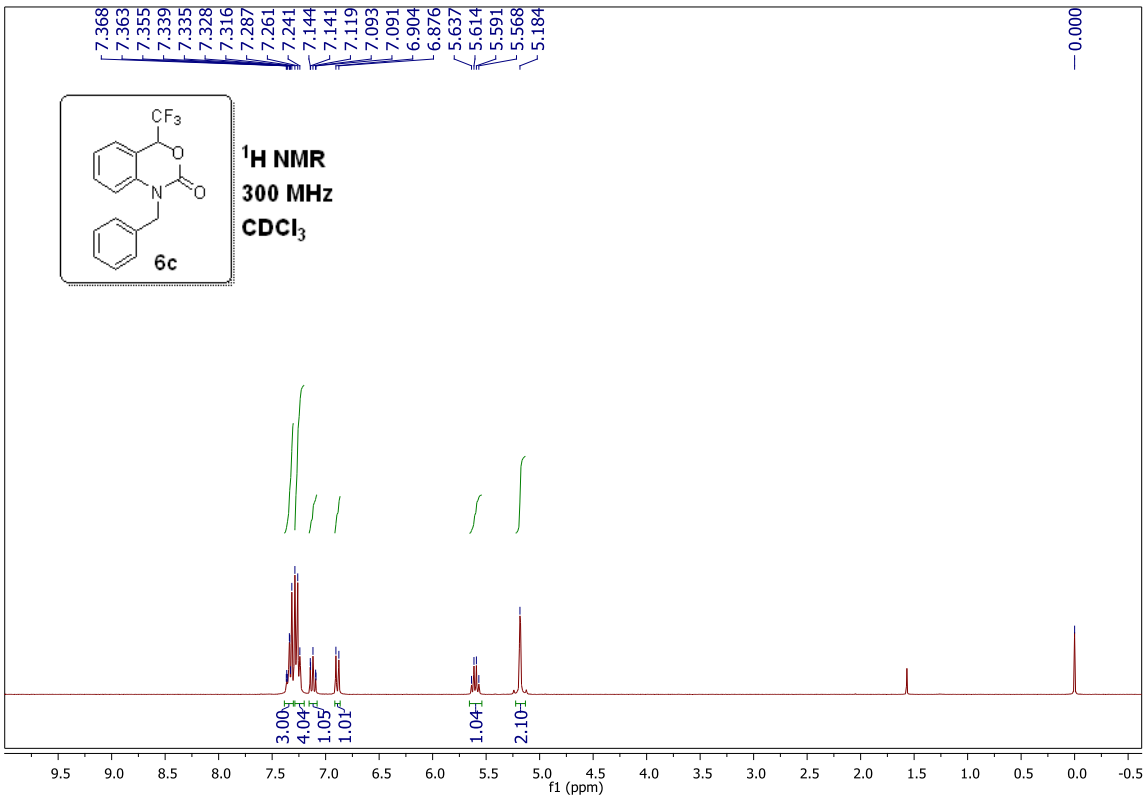

^{1}H NMR
300 MHz
CDCl$_3$
5

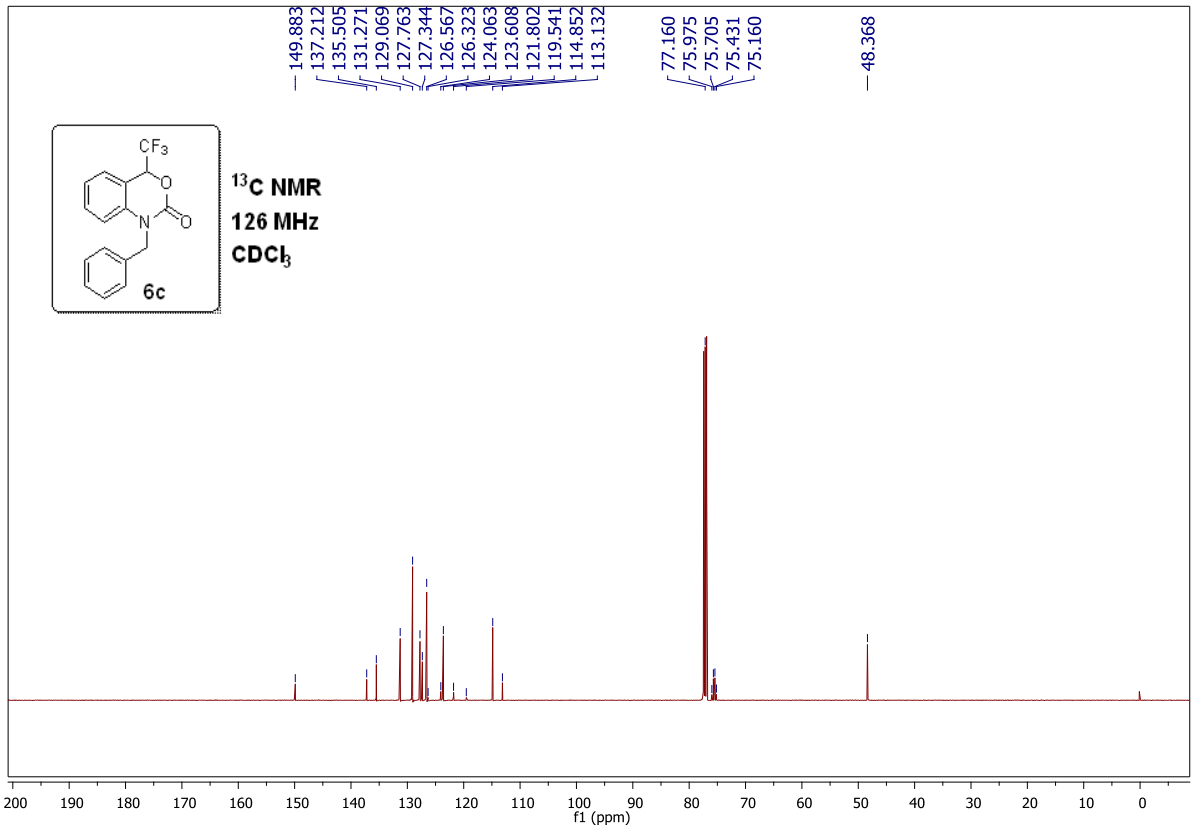

^{13}C NMR
126 MHz
CDCl$_3$
5

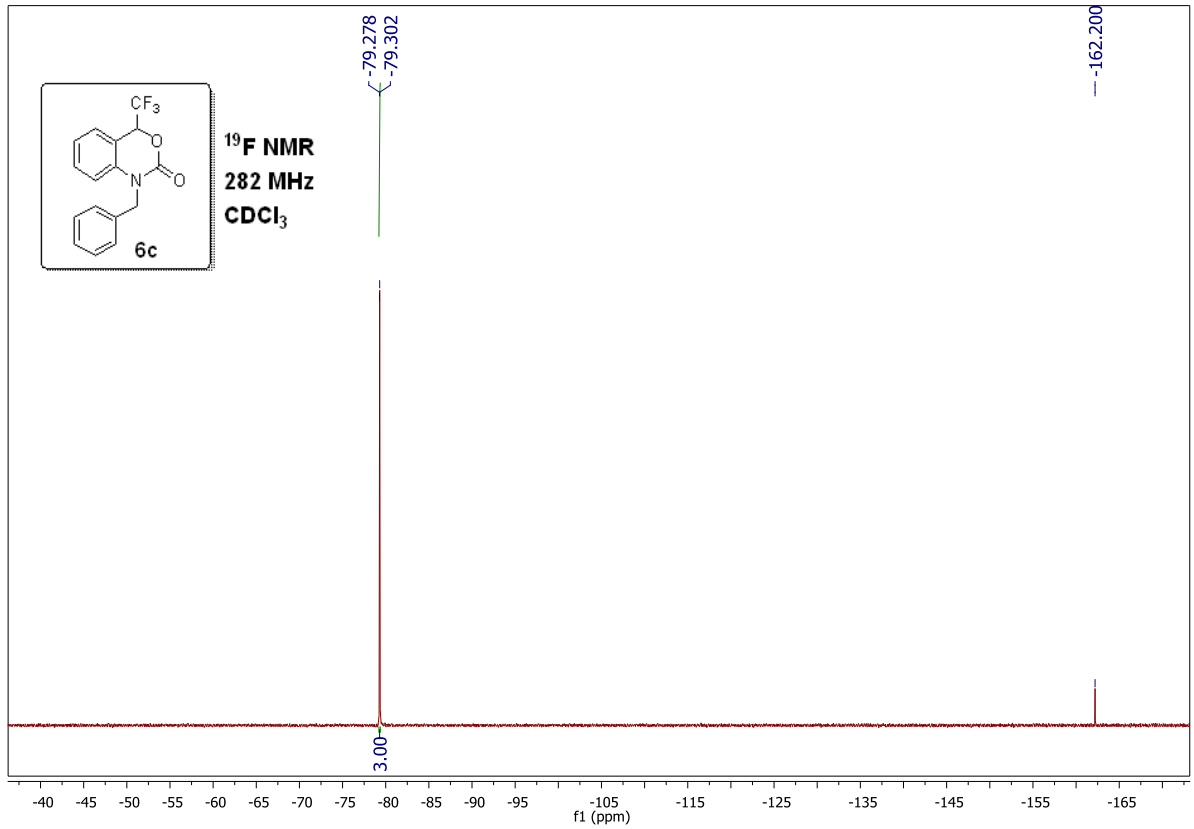

-72.816
-72.842
-162.200
F3C
Me
O
N
Ts
5
19F NMR
282 MHz
CDCl3
-72.816
-72.842
-72.75
-72.80
-72.85
-72.90
-72.95
f1 (ppm)
3.00
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)


8.151
8.134
7.600
7.583
7.408
7.392
7.287
7.285
7.272
7.270
7.262
7.257
7.255
7.222
7.207
5.381
5.368
5.354
5.341
2.471
1.723
1.710
0.000
CH3
O
N
O
Ts
6b
1H NMR
500 MHz
CDCl3
5.381
5.368
5.354
5.341
5.40 5.39 5.38 5.37 5.36 5.35 5.34 5.33 5.32
f1 (ppm)
2.16
1.19
1.75
3.07
1.11
3.14
3.00
10.0 9.5 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 -0.5
f1 (ppm)


149.912
145.729
136.026
134.420
129.952
129.142
129.108
129.057
126.203
123.879
120.648
77.160
75.214
21.894
18.234
CH3
O
N
O
Ts
6b
13C NMR
126 MHz
CDCl3
f1 (ppm)


7.368
7.363
7.355
7.339
7.335
7.328
7.316
7.287
7.261
7.241
7.144
7.141
7.119
7.093
7.091
6.904
6.876
5.637
5.614
5.591
5.568
5.184
0.000
CF3
O
N
O
6c
1H NMR
300 MHz
CDCl3
3.00
4.04
1.05
1.01
1.04
2.10
f1 (ppm)


149.883
137.212
135.505
131.271
129.069
127.763
127.344
126.567
126.323
124.063
123.608
121.802
119.541
114.852
113.132
77.160
75.975
75.705
75.431
75.160
48.368
CF3
O
N
O
6c
13C NMR
126 MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-79.278
-79.302
-162.200
CF3
O
N
O
6c
19F NMR
282 MHz
CDCl3
3.00
-40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155 -165
f1 (ppm)