Electronic Supplementary Information

Cross-conjugated vinylogous annulation of π-CF_3-allyl Pd-complexes with 4-methyl-3-trifluoroacetyl-quinolones

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1. General information:

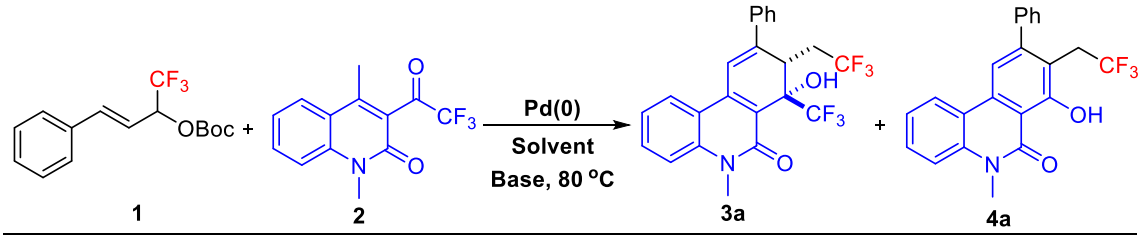
All the reactions were performed in an oven-dried glass apparatus, the air and moisture-sensitive reactions were carried out under an inert atmosphere (nitrogen) using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100-200 mesh) using hexanes and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$ on 500 MHz and 400 MHz,^{13}C NMR was recorded on 125 MHz, 100 MHz and 75 MHz and ^{19}F NMR was recorded on 377 MHz. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and *J* values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. δ 7.26 and δ 1.56 are corresponding to $CDCl_3$ and moisture respectively in ^{1}H NMR, δ 77.16 is related to $CDCl_3$ in ^{13}C NMR. FT-IR spectra were recorded on Alpha (Bruker) Infrared Spectrophotometer. High resolution mass spectra (HRMS) [ESI^+] were obtained using a TOF or a double-focusing spectrometer.

2. Methods and Instrumentation

Both differential pulse and cyclic voltammetric measurements were performed by using CHI instruments model CHI 620C potentiostat as detailed in our previous reports. UV-visible spectra were recorded with a Shimadzu spectrophotometer (Model UV-3600). Concentration of the samples used for these measurements ranged from about 5 x 10^{-5} M. Steady-state fluorescence spectra were measured by using Fluorolog-3 spectrofluorometer (Fluoro Log3 model, JobinYvon) as detailed in our previous reports. Fluorescence lifetime measurements were carried on a picosecond time-correlated single photon counting (TCSPC) setup (Fluoro Log3-Triple Illuminator, IBH Horiba JobinYvon) employing a picosecond light emitting diode laser (NanoLED, λex = 370 nm) as the excitation source.

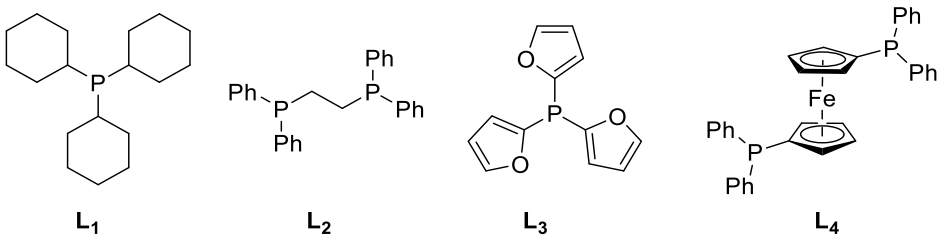
We have adopted Gaussian 09 quantum chemical software on personal computer for full geometry optimization of all sensitizers. For further calculations we have used B3LYP hybrid functional and 6−31 G (d,p) basis set as input. Ground state properties such as optimized energy structures, frontier molecular orbitals (FMO) were performed by Density Functional Theory (DFT) in the gas phase.Time Dependent Density Functional Theory (TD-DFT) were used for calculating the excited state properties like percentage of molecular contribution, oscillatory strength, singlet transition energy in the tetrahydrofuran solvent.[1-4]

3. Table S1: Optimization of the reaction conditions.[a]



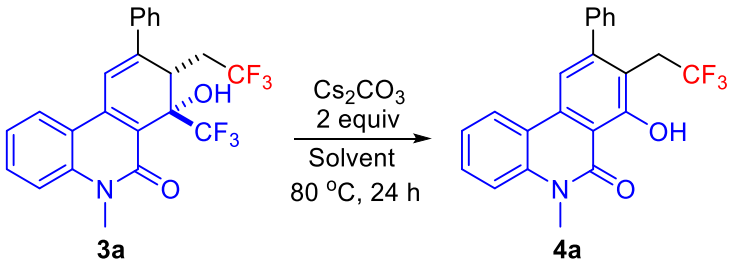
Entry	Pd-Source	Base	Solvent	3a/4a (%)	dr of **3a**
1	$PdCl_2$	Cs_2CO_3	CH_3CN	55/4	> 20:1
2	$Pd(OAc)_2$	Cs_2CO_3	CH_3CN	50/8	> 20:1
3	**$Pd(PPh_3)_4$**	**Cs_2CO_3**	**CH_3CN**	**83/10**	**> 20:1**
4	$Pd_2(dba)_3.CHCl_3/L_1$	Cs_2CO_3	CH_3CN	29/3	> 20:1
5	$Pd_2(dba)_3.CHCl_3/L_2$	Cs_2CO_3	CH_3CN	44/6	> 20:1
6	$Pd_2(dba)_3.CHCl_3/L_3$	Cs_2CO_3	CH_3CN	18/0	> 20:1
7	$Pd_2(dba)_3.CHCl_3/L_4$	Cs_2CO_3	CH_3CN	33/5	> 20:1
8	$Pd(PPh_3)_4$	DBU	CH_3CN	-	-
9	$Pd(PPh_3)_4$	K_2CO_3	CH_3CN	43/0	> 20:1
10	$Pd(PPh_3)_4$	NaOEt	CH_3CN	11/0	> 20:1
11	$Pd(PPh_3)_4$	Cs_2CO_3	DCE	31/0	> 20:1
12	$Pd(PPh_3)_4$	Cs_2CO_3	PEG-400	-	-
13	$Pd(PPh_3)_4$	Cs_2CO_3	THF	15/0	> 20:1
14	**$Pd(PPh_3)_4$**	**Cs_2CO_3**	**DMF**	**9/82**	**> 20:1**
15	$Pd(PPh_3)_4$	Cs_2CO_3	Toulene	-	-
16[b]	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN	24/0	> 20:1
17[c]	$Pd(PPh_3)_4$	Cs_2CO_3	CH_3CN	-	-

[a]Experiments were carried out using **1a** (0.24 mmol), **2a** (0.2 mmol), base (2 equiv) and the Pd source (5 mol %) and the ligand (10 mol%) in 1.0 mL of solvent at 80 °C. isolated yields. [b] Reaction at 40 °C. [c]Reaction at RT



L_1 L_2 L_3 L_4

3.1 Table S2: Study of solvent effect:



S.No	Solvent	Yield of compound 4a (%)
1	CH_3CN	21
2*	DMF	95
3	THF	47

* Reaction completed in 4 h

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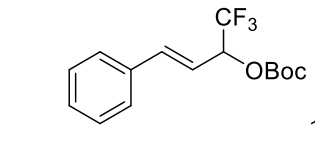
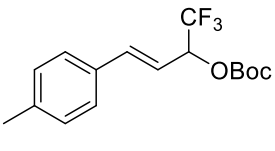
To know the solvent effect in the conversion of compound **3a** to compound **4a**, several reactions have been attempted in different solvents in the presence of 2 equiv Cs_2CO_3. Here, the reaction in the presence of acetonitrile furnishes desired aromatized product **4** in 21% yield, whereas DMF is giving excellent yield (95%). Next, the reaction in the THF solvent afforded the corresponding product in 47% yield. All these results indicate that the slightly acidic nature of acetonitrile is the reason for low conversion to get the desired product and previous literature supports that the trifluoromethyl group could be eliminated easily in DMF solvent.[5,6]

Starting materials CF_3-allylcarbonates and 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-ones were reported in previousarticles:[7,8,9,10]



1a



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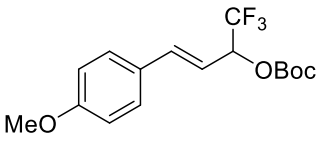

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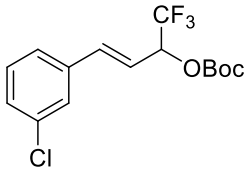

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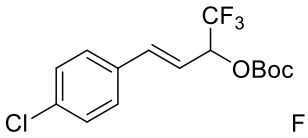

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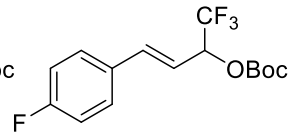

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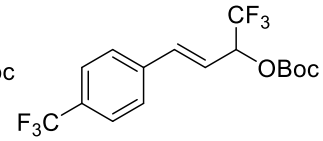

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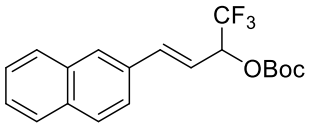

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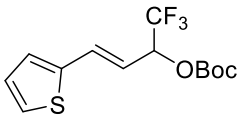

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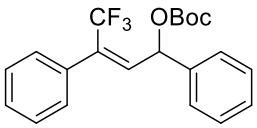

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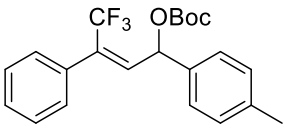

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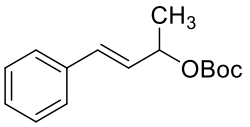

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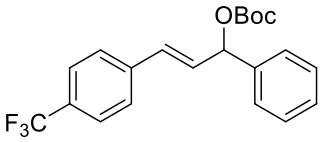

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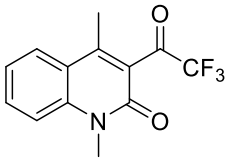
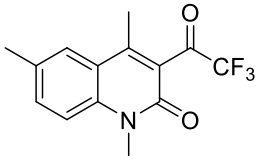
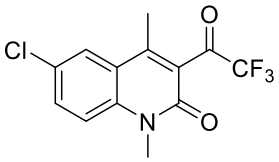


2a



2b



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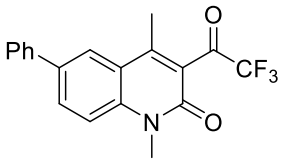

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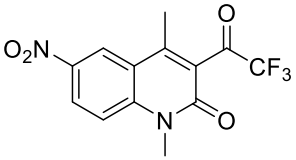

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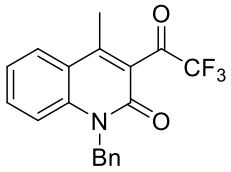

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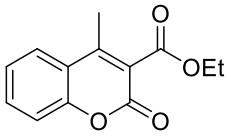
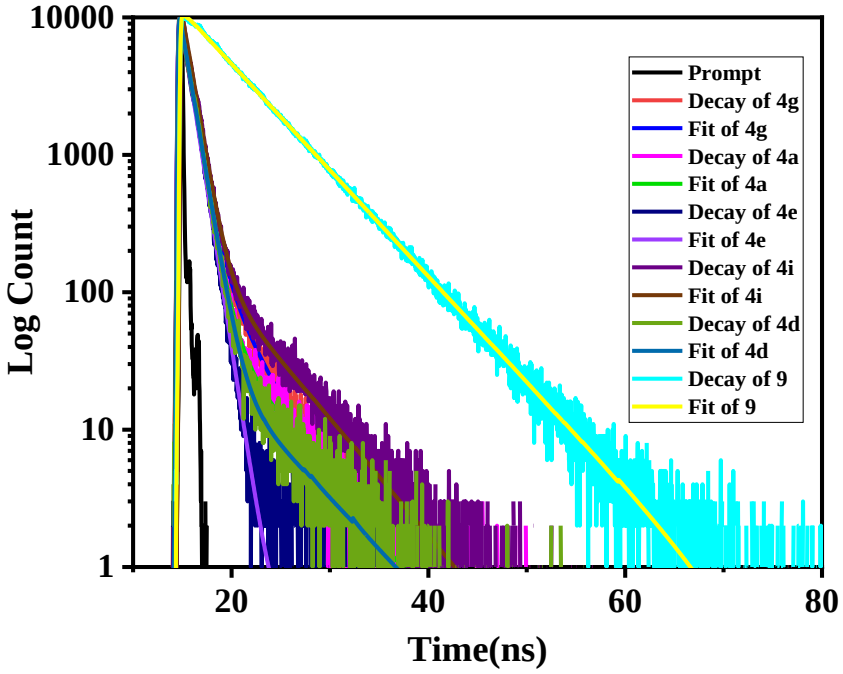
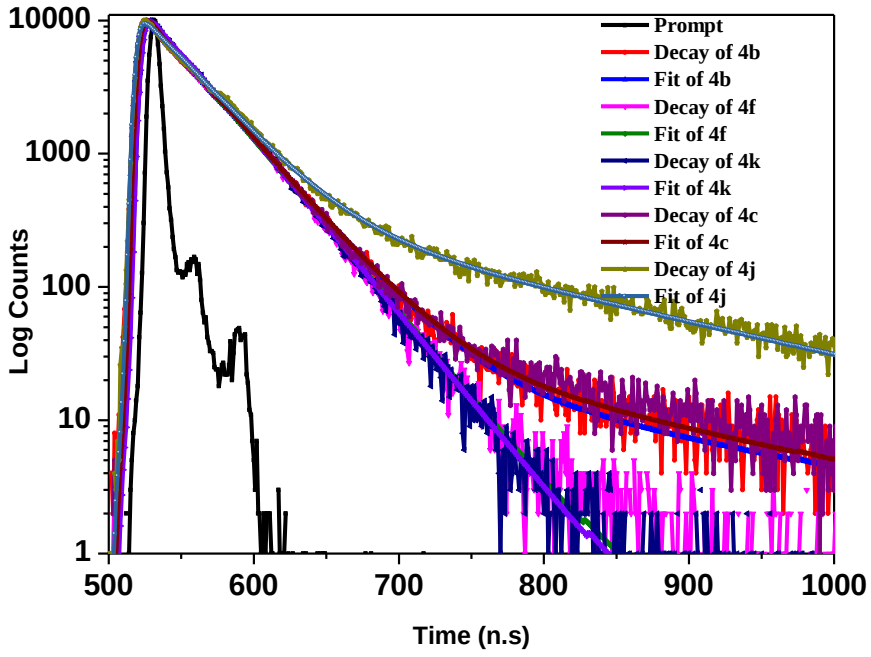


2g

4. Figure S1: Fluorescence decay curves of investigated compounds in dichloromethane solvent.



5. Figure S2: Fluorescence decay curves of investigated compounds in dichloromethane solvent.

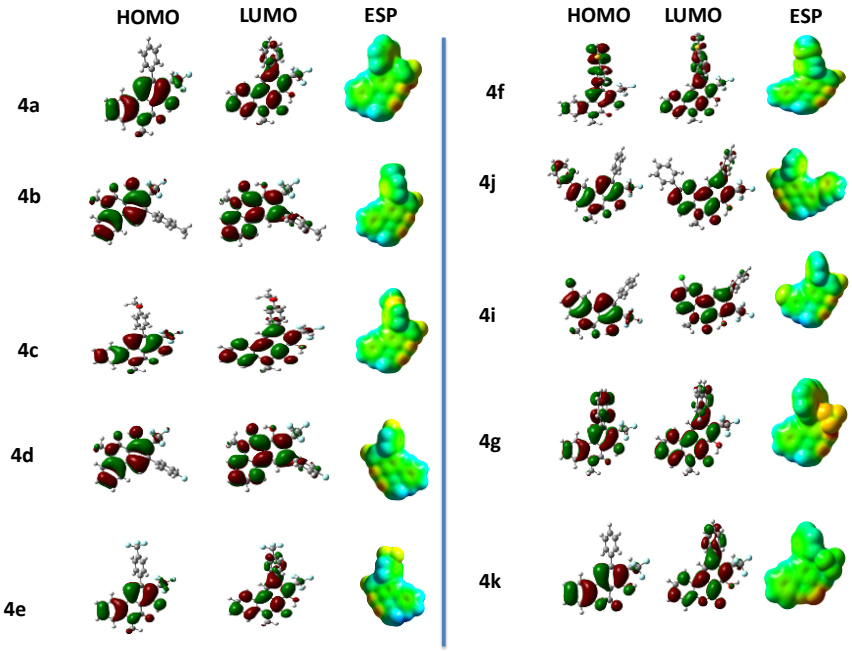


6. Table S3. Optical and emission properties of phenanthridone derivatives **4**.

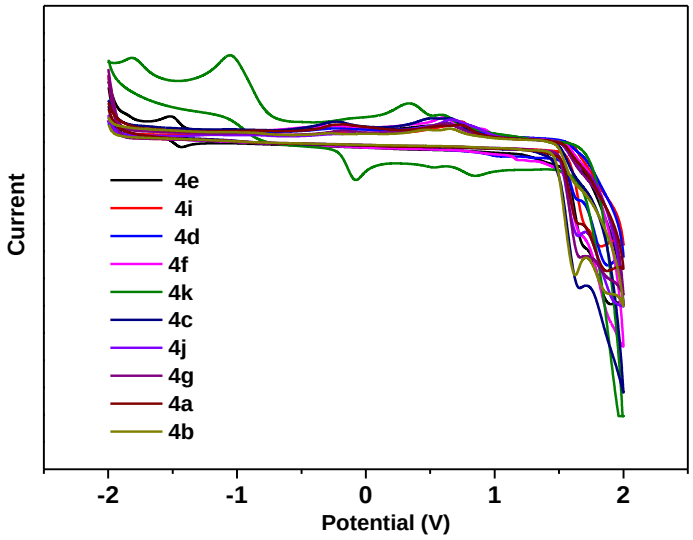
Entry	λmax nm (logε, M−1cm−1)[a]	λmax nm (emission)[b]	τ, ns[c]	Quantum Yield [d]
4a	344 (4.10) 361 (4.11)	405 462	0.92 (95.88) 4.68 (4.12)	0.52
4b	345 (4.31) 361 (4.32)	405 462	0.15 (3.52) 0.97 (94.40) 5.84 (2.08)	0.62
4c	344 (4.12) 361 (4.09)	406 460	0.14 (3.70) 0.95 (93.61) 5.32 (2.69)	0.60
4d	344 (4.39) 361 (4.80)	405 463	0.15 (3.52) 0.97 (94.41) 5.84 (2.08)	0.63
4e	345 (4.22) 361 (4.24)	405 463	0.93 (100)	0.57
4f	344 (4.38) 361 (4.39)	404 463	0.94 (100)	0.63
4g	349 (4.20) 365 (4.22)	404 465	0.93 (89.90) 3.34 (10.10)	0.46
4h	340 (4.07) 354 (4.11)	405 432	0.11 (3.20) 0.92 (96.80)	0.40
4i	349 (4.27) 366 (4.30)	405 465	0.94 (91.06) 5.18 (8.94)	0.59
4j	349 (4.43) 365 (4.44)	404 460	0.93 (83.22) 4.97 (16.78)	0.74

[a]Solvent: DCM, Error limits: λ_{max}, ±1 nm, ε ±10%. [b]Error limits: λ_{em}, ±1 nm. [c]Error limits τ ~10%. [d]ϕ, ±0.01%.

7. Figure S3: Isodensity (0.02) plots of FMOs using the B3LYP method 6-31G(d,p), and molecular electrostatic potential maps (ESP).



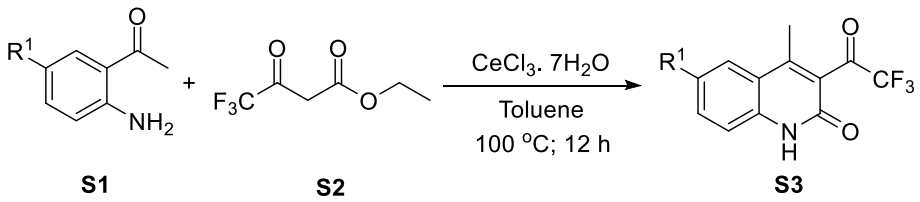
8. Figure S4: Cyclic voltammogrammes of investigated compounds in dichloromethane solvent using 0.1 M TBAP.



9. Experimental procedures and characterization data of compounds:

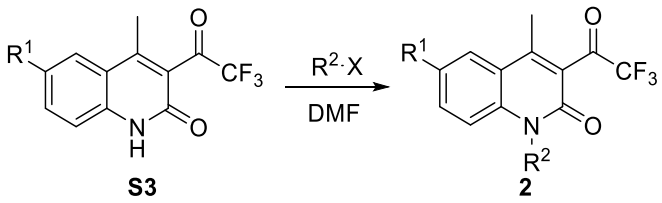
9.1 General procedure for the synthesis of substituted 4-methyl quinolones (method A):

In an oven-dried round bottom flask, 2-amino acetophenones **S1**(10.0 mmol, 1.0 equiv), ethyl 4,4,4-trifluoromethyl-acetoacetate **S2** (13.0 mmol 1.3 equiv), and $CeCl_3 \cdot 7H_2O$ (40 mol %, 0.4equiv) were taken in toluene (5 mL). The reaction was heated at 120 ^oC (oil bath temperature) for 24 h, under a nitrogen atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure, the obtained solid was washed with *n*-hexane, followed by ice-cold water (20 mL), and filtered. The separated solid product was dried and purified by column chromatography using n-hexane/ethyl acetate as an eluent to afford 3-(2,2,2-trifluoroacetyl) quinolin-2(1*H*)-ones. The data of compound **S3** were reported in previous literature.[8]

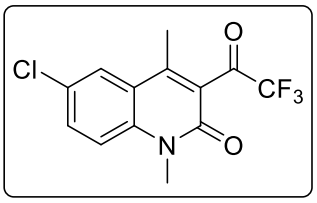


To the stirred solution of compound **S3** (0.40 mmol) in 10 ml DMF was added NaH (60% in mineral oil, 0.48 mmol) portion-wise at 0 ^oC. To this reaction mixture, alkyl halide (0.60 mmol)

was added dropwise, and then warmed to room temperature. The progress of the reaction was monitored by TLC, after completion of the starting material, the reaction mixture was quenched with saturated NH_4Cl solution and the organic layer was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was further purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system) to afford the pure product **2**.[8]

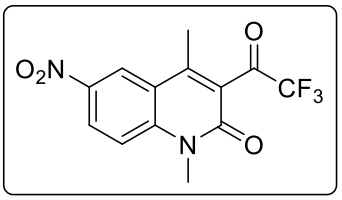


6-Chloro-1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (2c)



Following the general method (6-chloro-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3c** (115.60 mg, 0.40 mmol), NaH (19.20 mg, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used. compound **2c** was obtained as a white solid, yield 92% (111.51 mg), mp: 150-152 ℃;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.4 Hz, 1H), 7.63 (dd, J = 9.0, 2.4 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 3.70 (s, 3H), 2.42 (s, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.4 (q, J = 38.6 Hz), 158.9, 146.7, 138.5, 132.6, 128.8, 127.4, 125.9, 121.4, 116.3, 115.3 (q, J = 291.1 Hz), 29.4, 15.8;**^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.27 (s, 3F);**HRMS** (ESI) m/z $[M + H]^+$calcd for $C_{13}H_{10}ClF_3NO_2$, 304.0352, found 304.03481.

1,4-Dimethyl-6-nitro-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (2e)

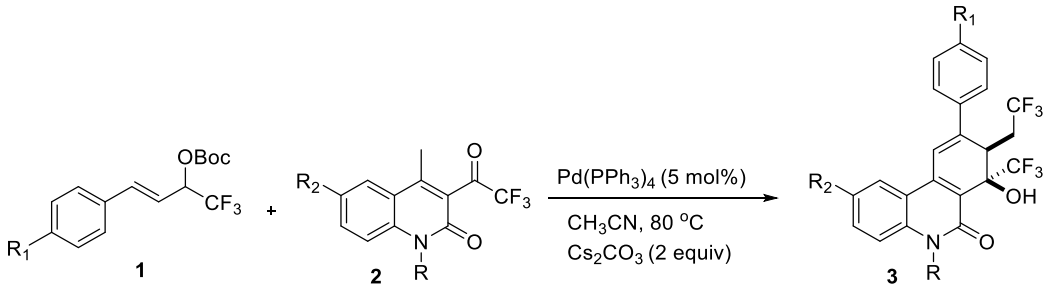


Following the general method (4-methyl-6-nitro-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3e** (60 mg, 0.20 mmol), NaH (19.20 gm, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used) compound **2e** was obtained as a white solid, yield 82% (51.5 mg),

mp: 136-138 °C;**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, J = 2.5 Hz, 1H), 8.53 (dd, J = 9.3, 2.5 Hz, 1H), 7.55 (d, J = 9.3 Hz, 1H), 3.78 (s, 3H), 2.54 (s, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.7 (q, J = 39.1 Hz), 159.1, 147.5, 143.8, 142.7, 128.2, 127.0, 122.6, 120.1, 115.7, 115.2 (q, J = 291.0 Hz), 29.9, 15.9; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.25 (s, 3F); **HRMS** (ESI) m/z [M + H]$^{+}$calcd for $C_{13}H_{10}F_3N_2O_4$, 315.0593, found 315.05892.

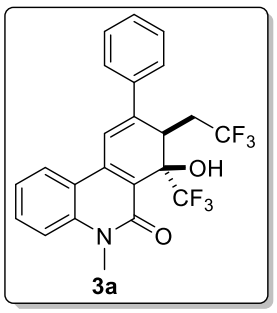
9.2 General procedure for synthesis of CF_3-7, 8-dihydrophenanthridin-6(5*H*)-one (method B):

General reaction:



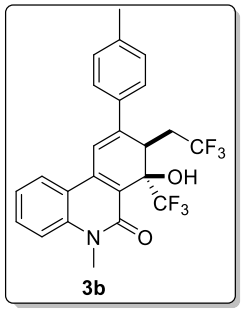
To a stirred solution of CF_3-allyl carbonate **1** (0.24 mmol) in 1 mL of acetonitrile was added 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **2** (0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ and Cs_2CO_3 (0.4 mmol) were added to the reaction mixture and stirred at 80 °C (oil bath temperature) for 3-6 h. The reaction progress was monitored by TLC. After completion of the reaction, mixture was diluted with water and extracted with ethyl acetate (3 X 15 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product 7-hydroxy-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one **3**. The characterization data of **3** are summarized below.

7-Hydroxy-5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3a)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3a** was obtained as off-white solid, yield 83% (75.2 mg);mp: 168-170 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.33 (s, 1H), 8.09 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.74 (m, 1H), 7.62 – 7.57 (m, 2H), 7.52 (d, *J*= 8.0 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.20 (s, 1H), 3.81 (s, 3H), 3.75 (dd, *J* = 9.7, 3.3 Hz, 1H), 3.18 (m, 1H), 2.24 – 2.09 (m, 1H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.1, 149.7, 142.9, 140.1, 138.5, 132.4, 129.7, 128.9, 128.9 (q, *J* = 274.6 Hz), 126.8, 126.6 (q, *J* = 260.0 Hz), 125.4, 123.5, 117.9, 117.4, 115.4, 113.4, 76.68 (q, *J* = 28.4 Hz), 35.9, 33.9 (q, *J* = 29.4 Hz), 29.9;**^{19}F NMR (377 MHz, $CDCl_3$)** δ –61.94 (s, 3F), –79.92 (s, 3F);**IR (KBr)**: 3051, 1632, 1589, 751 cm^{-1};**HRMS(ESI)**: calcd for $C_{23}H_{18}F_6NO_2$ $[M + H]^+$: 454.1236, found: 454.1230.

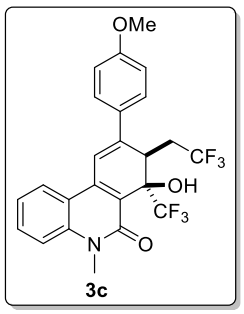
7-Hydroxy-5-methyl-9-(*p*-tolyl)-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3b)



3b

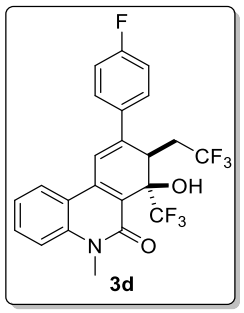
Following the general procedure **B**, **1b** (75.9 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3b** was obtained as off-white solid, yield 81% (75.67 mg); mp: 223-225 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.32 (s, 1H), 8.09 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.52 – 7.48 (m, 3H), 7.42 (m, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 7.18 (s, 1H), 3.81 (s, 3H), 3.73 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.25 – 3.10 (m, 1H), 2.42 (s, 3H), 2.15 (m, 1H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.1, 149.7, 143.1, 140.1, 140.0, 135.6, 132.4, 129.7, 128.8 (q, *J* = 250.1 Hz), 126.7, 126.6 (q, *J* = 255.4 Hz), 125.4, 123.4, 118.0, 116.5, 115.3, 113.2, 76.5 (q, *J* = 27.7 Hz), 35.9, 33.9(q, *J* = 29.4 Hz), 29.9, 21.5;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –61.89 (s, 3F), –79.93 (s, 3F); **IR (KBr):** 3050, 1630, 1582, 752 cm^{-1};**HRMS (ESI)**: calcd for $C_{24}H_{20}F_6NO_2$ $[M + H]^+$: 468.1393, found: 468.1395

7-Hydroxy-9-(4-methoxyphenyl)-5-methyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3c)



Following the general procedure **B**, **1c** (79.7 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3c** was obtained as off-white solid, yield 82% (79.23 mg);mp: 218-216 ^oC;**^{1}H NMR(400 MHz, $CDCl_3$)** δ 9.33 (s, 1H), 8.09 (dd, J = 8.2, 1.2 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.56 (d, J = 8.9 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.42 (m, 1H), 7.14 (s, 1H), 6.99 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.72 (dd, J = 9.6, 3.3 Hz, 1H), 3.18 (m, 1H), 2.19 – 2.07 (m, 1H);**^{13}C NMR(101 MHz, $CDCl_3$)** δ 163.1, 161.0, 149.3, 143.2, 140.1, 132.3, 130.8, 129.2 (q, J = 251.9 Hz), 128.2, 127.8 (q, J = 274.7 Hz), 125.4, 123.4, 118.0, 115.4, 115.3, 114.4, 112.9, 77.5 (q, J = 32.4 Hz), 55.5, 35.9, 34.1 (q, J = 29.3 Hz), 29.9;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –61.87 (s, 3F), –79.93 (s, 3F);**IR (KBr):** 3053, 1631, 1580, 753 cm^{-1}; **HRMS (ESI)**: calcd for $C_{24}H_{20}F_6NO_3$ $[M + H]^+$: 484.1342, found: 484.1336

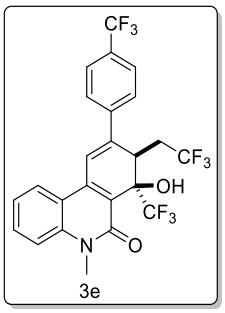
9-(4-Fluorophenyl)-7-hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3d)



Following the general procedure **B**, **1f** (76.8 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3d** was obtained as off-white solid, yield 76% (71.6 mg); mp: 208-210 ^oC;**^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.32 (s, 1H), 8.07 (dd, J = 8.2, 1.0 Hz, 1H), 7.74 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.18 – 7.14 (m, 3H), 3.81 (s, 3H), 3.68 (dd, J = 9.9, 3.2 Hz, 1H), 3.19 (m, 1H), 2.21 – 2.08 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.7 (d, J = 250.3 Hz), 163.0, 148.6, 142.7, 140.1, 134.8, 132.5,129.3

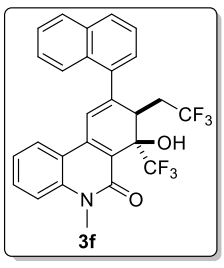
(q, *J* = 291.7 Hz), 128.6 (d, *J* = 8.3 Hz), 126.4 (q, *J* = 291.1 Hz), 125.3, 123.5, 117.9, 117.3, 116.1 (d, *J* = 21.8 Hz), 115.4, 113.4, 76.4 (q, *J* = 28.1 Hz), 36.2, 33.9 (q, *J* = 29.3 Hz), 29.9;**^{19}F NMR (377 MHz, $CDCl_3$)** δ –61.91 (s, 3F), –79.87 (s, 3F), –111.34 (s, F);**IR (KBr):** 3052, 1629, 1579, 754 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{17}F_7NO_2$ $[M + H]^+$: 472.1142, found: 472.1134

7-Hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-9-(4-(trifluoromethyl)phenyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3e)



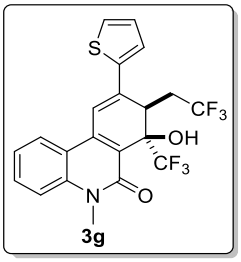
Following the general procedure **B**, **1g** (88.8 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3e** was obtained as off-white solid, yield 71% (74.0 mg);mp: 208-210 ^oC;**^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.31 (s, 1H), 8.08 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.74 – 7.68 (m, 4H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.24 (s, 1H), 3.82 (s, 3H), 3.71 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.20 (m, 1H), 2.18 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 148.1, 142.3, 142.1, 140.1, 131.3 (q, *J* = 32.8 Hz), 132.7, 127.0, 126.6 (q, *J* = 261.6 Hz), 126.4 (q, *J* = 291.6 Hz), 125.9 (q, *J* = 3.4 Hz), 125.3, 124.0 (q, *J* = 271.9 Hz), 123.6, 119.4, 117.8, 115.5, 113.9, 76.6 (q, *J* = 28.6 Hz), 35.9, 33.9 (q, *J* = 29.3 Hz), 30.0;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –61.90 (s, 3F), –62.72 (s, 3F), –79.79 (s, 3F); **IR (KBr):** 3051, 1632, 1581, 752 cm^{-1};**HRMS (ESI)**: calcd for $C_{24}H_{17}F_9NO_2$ $[M + H]^+$: 522.1110, found: 522.1110

7-Hydroxy-5-methyl-9-(naphthalen-1-yl)-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3f)



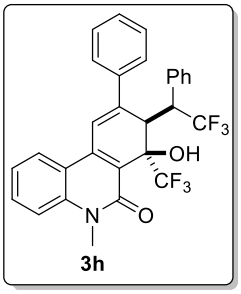
Following the general procedure **B**, **1h** (84.5 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3f** was obtained as off-white solid, yield 70% (70.4 mg);mp: 258-260 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.45 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.99 – 7.88 (m, 3H), 7.74 (m, 1H), 7.62 – 7.52 (m, 5H), 7.41 (t, J = 7.6 Hz, 1H), 7.24 (s, 1H), 3.84 (s, 3H), 3.76 (dd, J = 8.6, 3.0 Hz, 1H), 3.26 (m, 1H), 2.43 – 2.18 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 147.3, 142.4, 140.2, 137.2, 134.4, 132.4, 131.0, 130.2 (q, J = 255.5 Hz), 129.5, 129.0, 126.9,126.54 (q, J = 276.4 Hz), 126.2, 126.1, 125.4, 125.3, 125.1, 123.6, 121.5, 118.1, 115.4, 113.1, 76.5 (q, J = 28.2 Hz), 38.9, 33.3 (q, J = 29.9 Hz), 29.9;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –62.83 (s, 3F), –80.01 (s, 3F);**IR (KBr):** 3055, 1639, 1575, 755 cm^{-1};**HRMS (ESI)**: calcd for $C_{27}H_{20}F_6NO_2$ $[M + H]^+$: 504.1393, found: 504.1389

7-Hydroxy-5-methyl-9-(thiophen-2-yl)-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3g)



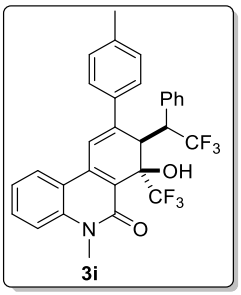
Following the general procedure **B**, **1i** (73.9 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3g** was obtained as off-white solid, yield 72% (66.1 mg);mp: 180-182 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.37 (s, 1H), 8.04 (dd, J = 8.2, 1.2 Hz, 1H), 7.73 (m, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 (d, J = 3.6 Hz, 1H), 7.24 (s, 1H), 7.13 (dd, J = 5.1, 3.8 Hz, 1H), 3.80 (s, 3H), 3.67 (dd, J = 9.3, 3.4 Hz, 1H), 3.24 (m, 1H), 2.29 – 2.13 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 142.9, 142.6, 142.0, 140.0, 132.5, 131.8 (q, J = 251.5 Hz), 128.5, 128.1, 127.5, 125.4, 123.5, 123.4 (q, J = 291.5 Hz), 117.8, 115.3, 114.4, 112.9, 76.3 (q, J = 28.1 Hz), 36.7, 34.1 (q, J = 29.6 Hz), 29.9;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –61.81 (s, 3F), –80.10 (s, 3F);**IR (KBr):** 3042, 1638, 1575, 750 cm^{-1};**HRMS (ESI)**: calcd for $C_{21}H_{16}F_6NO_2S$ $[M + H]^+$: 460.0800, found: 460.0799

7-Hydroxy-5-methyl-9-phenyl-8-(2,2,2-trifluoro-1-phenylethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3h)



Following the general procedure **B**, **1j** (90.75 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3h** was obtained as off-white solid, yield 55% (58.2 mg);mp: 204-206 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.67 (s, 1H), 7.70 – 7.65 (m, 3H), 7.61 – 7.56 (m, 1H), 7.54 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 3.7 Hz, 3H), 6.72 (t, *J* = 7.7 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 1H), 4.81 (qd, *J* = 11.6, 2.2 Hz, 1H), 4.18 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.3, 144.4, 142.8, 139.5, 139.4, 131.9, 131.8, 130.3, 129.4, 129.3 (q, *J* = 280.7 Hz),129.1, 127.2, 127.0, 126.8, 126.4 (q, *J* = 251.1 Hz), 124.8, 122.9, 122.2, 117.4, 114.8, 113.8, 76.4 (q, *J* = 28.2 Hz), 47.4 (q, *J* = 27.6 Hz), 39.7, 29.6;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –64.12 (s, 3F), –80.37 (s, 3F); **IR (KBr):** 3053, 1640, 1583, 749 cm^{-1}**; HRMS (ESI)**: calcd for $C_{29}H_{22}F_6NO_2$ $[M + H]^+$: 530.1549, found: 530.1548

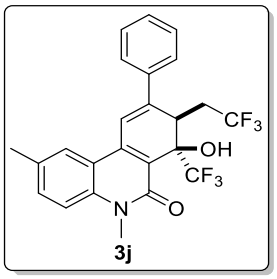
7-Hydroxy-5-methyl-9-(*p*-tolyl)-8-(2,2,2-trifluoro-1-phenylethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3i)



Following the general procedure **B**, **1k** (94.1 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3i** was obtained as off-white solid, yield 50% (54.3 mg);mp: 196-198 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.67 (s, 1H), 7.67 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.3, 2.3 Hz, 3H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.08 (s, 1H), 6.72 (m, 2H), 6.59 – 6.54 (m, 1H), 4.80 (qd, *J* = 11.7, 2.2 Hz, 1H), 4.17

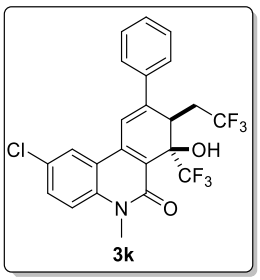
(d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 2.45 (s, 3H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.3, 144.4, 142.9, 139.7, 139.4, 136.7, 131.9, 131.7, 130.3, 129.8, 128.54 (q, *J* = 292.2 Hz), 127.2, 127.0, 126.7, 126.60 (q, *J* = 279.7 Hz), 124.8, 122.8, 121.3, 117.51, 114.7, 113.6, 76.2 (q, *J* = 27.8 Hz), 47.4 (q, *J* = 27.2 Hz), 39.7, 29.6, 21.5;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –64.05 (s, 3F), –80.36 (s, 3F); **IR (KBr):** 3047, 1638, 1582, 748 cm^{-1};**HRMS (ESI)**: calcd for $C_{30}H_{24}F_6NO_2$ $[M + H]^+$: 544.1706, found: 544.1709

7-Hydroxy-2,5-dimethyl-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3j)



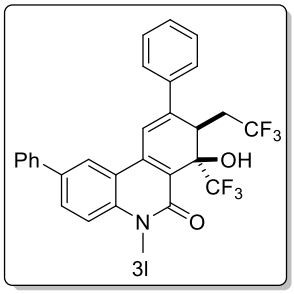
Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2b** (56.6 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3j** was obtained as off-white solid, yield 83% (77.5 mg); mp: 191-193 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.41 (s, 1H), 7.84 (s, 1H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.55 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.19 (s, 1H), 3.77 (s, 3H), 3.73 (dd, *J* = 9.7, 3.2 Hz, 1H), 3.26 – 3.09 (m, 1H), 2.53 (s, 3H), 2.16 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 149.5, 142.6, 138.6, 138.2, 133.7, 133.2, 129.6, 129.5 (q, *J* = 277.9 Hz), 128.9, 126.8, 126.6 (q, *J* = 264.1 Hz), 125.0, 117.9, 117.5, 115.3, 113.3, 77.5 (q, *J* = 31.5 Hz), 35.9, 33.9 (q, *J* = 29.4 Hz), 29.9, 21.2;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –61.95 (3F, s), –79.88 (3F, s);**IR (KBr)**: 3053, 1642, 1584, 753 cm^{-1};**HRMS (ESI)**: calcd for $C_{24}H_{20}F_6NO_2$ $[M + H]^+$: 468.1393, found: 468.1387

2-Chloro-7-hydroxy-5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3k)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2c** (60.6 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3k** was obtained as off-white solid, yield 69% (67.2 mg);mp: 222-224 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.16 (s, 1H), 8.02 (d, J = 2.3 Hz, 1H), 7.67 (dd, J = 9.1, 2.3 Hz, 1H), 7.60 (dd, J = 8.0, 1.5 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.08 (s, 1H), 3.79 (s, 3H), 3.75 (dd, J = 9.5, 3.3 Hz, 1H), 3.15 (m, 1H), 2.16 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.7, 150.3, 141.9, 138.6, 138.2, 132.4, 129.9, 129.3 (q, J = 276.9 Hz), 129.3, 129.1, 128.7, 126.8, 126.5 (q, J = 261.5 Hz), 124.8, 119.0, 116.8, 114.6, 77.5 (q, J = 35.0 Hz), 35.9, 33.9 (q, J = 29.5 Hz), 30.1;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –61.93 (3F, s), –79.94 (3F, s);**IR (KBr):** 3047, 1645, 1575, 747 cm^{-1}; **HRMS (ESI)**: calcd for $C_{23}H_{17}ClF_6NO_2$ $[M + H]^+$: 488.0847, found: 488.0853

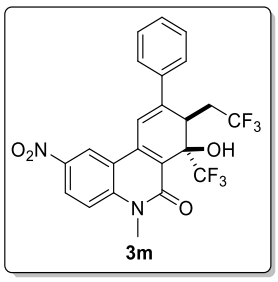
7-Hydroxy-5-methyl-2,9-diphenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3l)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2d** (69.0 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3l** was obtained as yellow solid, yield 71% (75.1 mg);mp: 194-196 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.32 (s, 1H), 8.21 (d, J = 2.0 Hz, 1H), 7.95 (dd, J = 8.8, 2.0 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.60 (ddd, J = 8.7, 5.2, 3.5 Hz, 3H), 7.56 – 7.52 (m, 2H), 7.51 – 7.42 (m, 4H), 7.26 (s, 1H), 3.85 (s, 3H), 3.76 (dd, J = 9.6, 3.3 Hz, 1H), 3.19 (m, 1H), 2.20 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 149.9, 142.9, 139.8, 139.3, 138.5, 136.8, 131.6, 129.7, 129.3, 129.0, 128.1, 127.4, 126.8, 126.40 (q, J = 274.3 Hz), 126.6 (q, J = 264.8 Hz), 123.5, 118.2, 117.3, 115.9, 113.8, 76.45 (d, J = 26.8 Hz), 36.0, 33.9 (q, J = 29.6 Hz), 30.0;**^{19}F NMR (376**

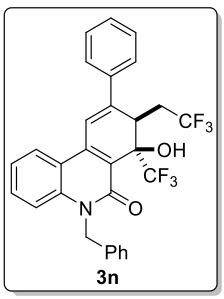
MHz, $CDCl_3$) δ –61.93 (s, 3F), –79.89 (s, 3F);**IR (KBr):** 3054, 1643, 1578, 750 cm^{-1}; **HRMS (ESI)**: calcd for $C_{29}H_{22}F_6NO_2$ $[M + H]^+$: 530.1549, found: 530.1549.

7-Hydroxy-5-methyl-2-nitro-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3m)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2e** (62.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3m** was obtained as off-white solid, yield 51% (50.8 mg);mp: 122-124 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.98 (d, J = 2.4 Hz, 1H), 8.75 (s, 1H), 8.55 (dd, J = 9.3, 2.5 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.52 (m, 3H), 7.18 (s, 1H), 3.86 (s, 3H), 3.80 (dd, J = 9.2, 3.5 Hz, 1H), 3.13 (m, 1H), 2.20 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.1, 151.5, 143.8, 143.3, 142.9, 137.8, 132.4, 130.3, 129.2, 129.2 (q, J = 275.7 Hz), 128.0 (q, J = 270.5 Hz), 126.9, 126.6, 121.6, 117.6, 116.2, 115.5, 76.8 (q, J = 33.1 Hz), 36.0, 33.8 (q, J = 29.5 Hz), 30.6;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –61.88 (s, 3F), –80.04 (s, 3F);**IR (KBr)**: 3053, 1648, 1584, 752 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{17}F_6N_2O_4$ $[M + H]^+$: 499.1087, found: 499.1088

5-Benzyl-7-hydroxy-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-7,8-dihydrophenanthridin-6(5*H*)-one (3n)

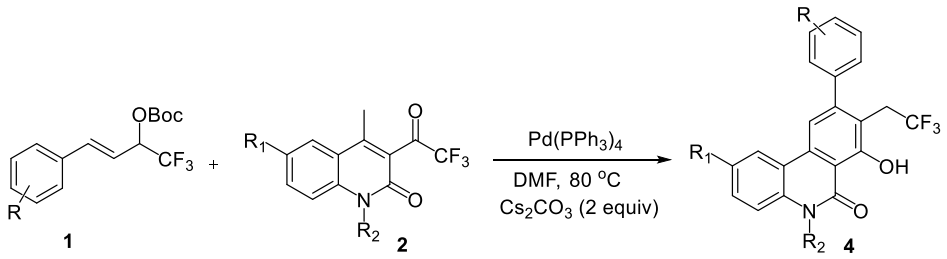


Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2f** (69.0 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **3n** was obtained as off-white solid, yield 73% (77.2 mg); mp: 188-190 ^oC;**^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.32 (s, 1H), 8.09 (d, J = 7.3 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.59 – 7.56

(m, 1H), 7.48 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.23 (m, 3H), 5.63 (d, *J* = 41.4 Hz, 2H), 3.78 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.29 – 3.11 (m, 1H), 2.34 – 2.12 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.7, 161.9, 150.7, 140.7, 136.9, 135.9, 134.1, 130.3, 129.1, 128.9, 128.7 (q, *J* = 275.9 Hz), 128.6, 128.0, 127.6, 126.5, 126.1 (q, *J* = 278.4 Hz), 124.1, 123.7, 119.8, 116.4, 113.6, 109.1, 77.5 (q, *J* = 33.4 Hz), 46.0, 30.7 (q, *J* = 30.9 Hz);**^{19}F NMR (471 MHz, $CDCl_3$)** δ –61.86 (s, 3F), –80.08 (s, 3F);**IR (KBr):** 3047, 1647, 1585, 751 cm^{-1};**HRMS (ESI)**: calcd for $C_{29}H_{22}F_6NO_2$ $[M + H]^+$: 530.1549, found: 530.1549

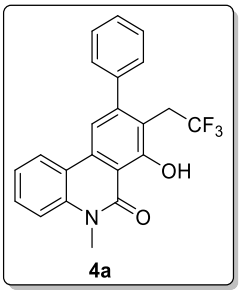
9.3 General procedure for synthesis of CF_3-7-hydroxy-phenanthridin-6(5*H*)-one (method C):

General reaction:



To a stirred solution of CF_3-allyl carbonate **1** (0.24 mmol) in 1 mL of *N*,*N*-dimethylformamide was added 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **2** (0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ and Cs_2CO_3 (0.4 mmol) were added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 4-6 h. The reaction progress was monitored by TLC. After completion of the reaction, mixture was diluted with cold water and extracted with ethyl acetate (3 X 15 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product 7-hydroxy-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one **4**. The characterization data of **4** are summarized below.

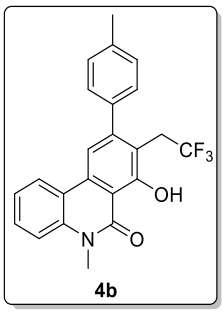
7-Hydroxy-5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4a)



4a

Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4a** was obtained as white solid, yield 82% (62.8mg); mp: 214-216 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 13.98 (s, 1H), 8.24 – 8.15 (m, 1H), 7.60 (s, 1H), 7.57 (m, 1H), 7.51 – 7.41 (m, 4H), 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 3.80 (s, 3H), 3.63 (q, J = 10.5 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.5, 161.6, 150.3, 140.7, 137.5, 133.9, 130.3, 128.9, 128.5, 127.9, 126.1 (q, J = 279.2 Hz), 124.1, 123.6, 119.6, 115.4, 114.8, 113.5, 109.3, 30.7 (q, J = 30.7 Hz), 29.5;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.69 (s, 3F); **IR (KBr):** 3095, 1630, 1582, 750 cm^{-1};**HRMS (ESI)**: calcd for $C_{22}H_{17}F_3NO_2$ $[M + H]^+$: 384.1206, found: 384.1197

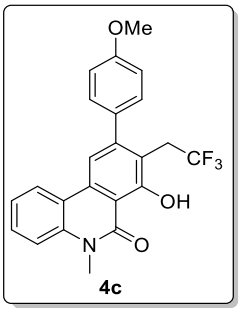
7-Hydroxy-5-methyl-9-(p-tolyl)-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4b)



4b

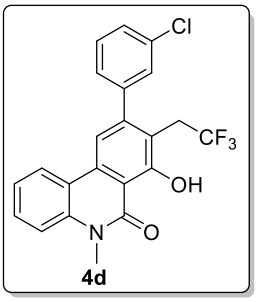
Following the general procedure **B**, **1b** (75.9 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4b** was obtained as off-white solid, yield 81 % (64.3 mg); mp: 206-208 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ 13.96 (s, 1H), 8.20 (dd, J = 8.1, 1.3 Hz, 1H), 7.59 (s, 1H), 7.59 – 7.54 (m, 1H), 7.44 (dd, J = 8.5, 0.8 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.25 – 7.22 (m, 2H), 3.81 (s, 3H), 3.64 (q, J = 10.5 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 161.7, 150.2, 140.9, 135.5, 133.9, 133.2, 131.3, 128.9, 128.5, 126.1 (q, J = 280.0 Hz), 124.8, 124.2, 119.5, 115.3, 114.7, 113.4, 109.4, 30.7 (q, J = 31.0 Hz), 29.5, 21.1;**^{19}F NMR (471 MHz, $CDCl_3$)** δ –63.65 (s, 3F); **IR (KBr):** 3098, 1635, 1583, 752 cm^{-1}; **HRMS (ESI)**: calcd for $C_{23}H_{19}F_3NO_2$ $[M + H]^+$: 398.1362, found: 398.1360

7-Hydroxy-9-(4-methoxyphenyl)-5-methyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4c)



Following the general procedure **B**, **1c** (79.7 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4c** was obtained as white solid, yield 83% (68.6 mg);mp: 200-202 ^oC**;^{1}H NMR (500 MHz, $CDCl_3$)** δ 13.96 (s, 1H), 8.21 (dd, J = 8.1, 1.3 Hz, 1H), 7.59 (s, 1H), 7.57 (m, 1H), 7.46 – 7.43 (m, 1H), 7.34 – 7.30 (m, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.02 – 6.99 (m, 2H), 3.89 (s, 3H), 3.81 (s, 3H), 3.64 (q, J = 10.5 Hz, 2H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.5, 161.6, 159.4, 150.1, 137.5, 133.8, 133.1, 130.2, 130.1, 126.2 (q, J = 278.9 Hz), 124.1, 123.6, 119.7, 115.4, 115.1, 113.9, 113.7, 109.2, 55.5, 30.8 (q, J = 30.5 Hz), 29.5;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.62 (3F, s);**IR(KBr):** 3096, 1645, 1581, 754 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{19}F_3NO_3$ $[M + H]^+$: 414.1312, found: 414.1308

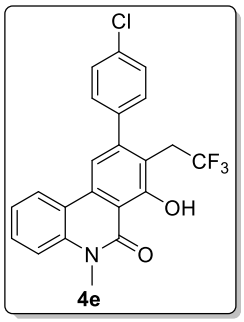
9-(3-Chlorophenyl)-7-hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4d)



Following the general procedure **B**, **1d** (80.6 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4d** was obtained as white solid, yield 79% (65.9 mg); mp: 222-224 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ14.02 (s, 1H), 8.24 – 8.09 (m, 1H), 7.59 – 7.53 (m, 2H), 7.44 – 7.39 (m, 3H), 7.36 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 3.78 (s, 3H), 3.61 (q, J = 10.4 Hz, 2H);**^{13}C**

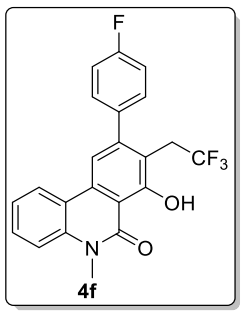
NMR (126 MHz, $CDCl_3$) δ 165.3, 161.7, 148.6, 142.4, 137.5, 134.4, 134.0, 130.4, 129.8, 129.1, 128.2, 127.2, 126.0 (q, J = 279.1 Hz), 124.0, 123.6, 119.4, 115.4, 114.6, 113.2, 109.5, 30.7 (q, J = 30.7 Hz), 29.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.71 (3F, s);**IR (KBr):** 3093, 1640, 1582, 753 cm^{-1}; **HRMS (ESI)**: calcd for $C_{22}H_{16}ClF_3NO_2$ $[M + H]^+$: 418.0816, found: 418.0811

9-(4-Chlorophenyl)-7-hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4e)



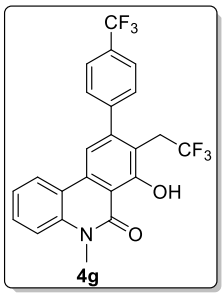
Following the general procedure **B**, **1e** (80.6 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4e** was obtained as white solid, yield 77% (64.2 mg); mp: 211-213 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.01 (s, 1H), 8.19 (d, J = 7.3 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.41 (m, 3H), 7.36 – 7.31 (m, 1H), 7.28 (m, 2H), 3.80 (s, 3H), 3.60 (q, J = 10.4 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 161.7, 149.0, 139.1, 137.5, 134.1, 134.0, 130.4, 130.3, 128.8, 126.0 (q, J = 279.3 Hz), 124.0, 123.7, 119.5, 115.5, 114.7, 113.3, 109.5, 30.7 (q, J = 31.1 Hz), 29.6;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.71 (3F, s);**IR (KBr):** 3092, 1643, 1579, 749 cm^{-1};**HRMS (ESI)**: calcd for $C_{22}H_{16}ClF_3NO_2$ $[M + H]^+$: 418.0806, found: 418.0800

9-(4-Fluorophenyl)-7-hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4f)



Following the general procedure **B**, **1f** (76.8 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4f** was obtained as white solid, yield 76% (60.9 mg);mp: 201-203 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.00 (s, 1H), 8.21 (dd, J = 8.1, 1.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.20 – 7.14 (m, 2H), 3.81 (s, 3H), 3.60 (q, J = 10.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 162.6 (d, J = 247.3 Hz), 161.6, 149.2, 137.4, 136.6, 133.8, 130.7 (d, J = 8.0 Hz), 130.3, 126.1 (q, J = 279.0 Hz), 123.9, 123.6, 119.4, 115.6, 115.4, 115.3, 114.9, 113.4, 109.3, 30.7 (q, J = 30.9 Hz), 29.5;**^{19}F NMR (377 MHz, $CDCl_3$)** δ –69.31 (3F, s), –119.18 (1F, s); **IR (KBr):** 3097, 1640, 1585, 755 cm^{-1}**; HRMS (ESI)**: calcd for $C_{22}H_{16}F_4NO_2$ $[M + H]^+$: 402.1112, found: 402.1114

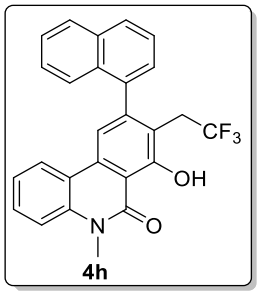
7-Hydroxy-5-methyl-8-(2,2,2-trifluoroethyl)-9-(4-(trifluoromethyl)phenyl)-phenanthridin-6(5*H*)-one (4g)



4g

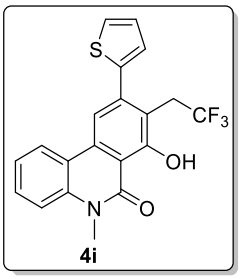
Following the general procedure **B**, **1g** (88.8 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4g** was obtained as white solid, yield 75% (67.7 mg);mp: 226-228 ^oC**;^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.06 (s, 1H), 8.20 (dd, J = 8.2, 1.2 Hz, 1H), 7.76 (s, 1H), 7.74 (s, 1H), 7.60 (m, 1H), 7.56 (s, 1H), 7.48 (m, 3H), 7.37 – 7.32 (m, 1H), 3.82 (s, 3H), 3.59 (q, J = 10.4 Hz, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.4, 161.8, 148.7, 144.4, 137.6, 134.1, 131.9 (q, J = 32.1 Hz), 130.5, 129.4, 129.1 (q, J = 278.3 Hz), 125.8 (q, J = 251.2 Hz), 125.6, 124.1, 123.7, 119.4, 115.5, 114.5, 113.1, 109.7, 31.0 (q, J = 31.1 Hz), 29.6;**^{19}F NMR (377 MHz, $CDCl_3$)** δ –62.71 (s, 3F), –65.31 (s, 3F);**IR (KBr):** 3092, 1642, 1587, 747 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{16}F_6NO_2$ $[M + H]^+$: 452.1080, found: 452.1093.

7-Hydroxy-5-methyl-9-(naphthalen-1-yl)-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4h)



Following the general procedure **B**, **1h** (84.5 mg, 0.24 mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4h** was obtained as white solid, yield 72% (62.4 mg);mp: 240-242 ^oC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.06 (s, 1H), 8.15 (dd, J = 8.2, 1.3 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.68 (s, 1H), 7.61 – 7.55 (m, 2H), 7.53 – 7.49 (m, 1H), 7.49 – 7.45 (m, 2H), 7.39 (m, 2H), 7.32 – 7.27 (m, 1H), 3.84 (s, 3H), 3.72 (m, 1H), 3.11 (m, 1H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.5, 161.7, 148.5, 137.6, 134.1, 133.6, 131.6, 130.3, 129.6, 128.6, 128.5, 127.5, 126.7, 126.2, 125.9 (q, J = 279.2 Hz), 125.5, 125.4, 124.2, 123.6, 119.6, 116.3, 115.4, 114.3, 109.6, 31.2 (q, J = 31.1 Hz), 29.6;**^{19}F NMR (377 MHz, $CDCl_3$)** δ –64.38 (s, 3F);**IR (KBr):** 3093, 1637, 1584, 749 cm^{-1};**HRMS (ESI)**: calcd for $C_{26}H_{18}F_3NO_2$ $[M + H]^+$: 434.1362, found: 434.1356

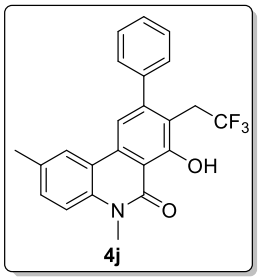
7-Hydroxy-5-methyl-9-(thiophen-2-yl)-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4i)



Following the general procedure **B**, **1i** (73.9 mg, 0.24mmol), **2a** (53.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4i** was obtained as white solid, yield 78% (60.7 mg); mp: 228-230 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.00 (s, 1H), 8.23 (dd, J = 8.1, 1.1 Hz, 1H), 7.76 (s, 1H), 7.62 – 7.55 (m, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.31 (m, 1H), 7.17 (ddd, J = 8.5, 4.2, 2.4 Hz, 2H), 3.83 – 3.74 (m, 5H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.3, 161.9, 142.4, 141.2, 137.5, 133.8, 130.4, 127.8, 127.6, 126.7, 126.2 (q, J = 278.9 Hz), 124.1, 123.7, 119.4, 115.6, 115.4, 114.6, 109.6, 31.1 (q, J = 30.9 Hz), 29.5**;^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.25 (3F, s); **IR (KBr):** 3092,

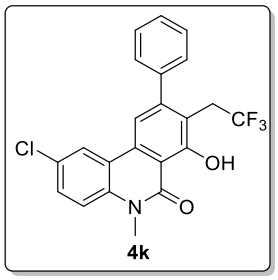
1675, 1577, 752 cm^{-1}**; HRMS (ESI)**: calcd for $C_{20}H_{15}F_3NO_2S$ $[M + H]^+$: 390.0770, found: 390.0774

7-Hydroxy-2,5-dimethyl-9-phenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4j)



Following the general procedure **B**, **1a** (72.5 mg, 0.24mmol), **2b** (56.62 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL CH_3CN were used. Compound **4j** was obtained as off-white solid, yield 65 % (51.6 mg);mp: 220-222 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.06 (s, 1H), 7.99 (s, 1H), 7.58 (s, 1H), 7.51 – 7.43 (m, 3H), 7.40 – 7.31 (m, 4H), 3.79 (s, 3H), 3.63 (q, J = 10.5 Hz, 2H), 2.44 (s, 3H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 161.7, 150.2, 140.8, 135.4, 133.8, 133.2, 131.3, 128.9, 128.5, 127.9, 126.1 (q, J = 278.9 Hz), 124.1, 119.5, 115.3, 114.6, 113.4, 109.4, 30.7 (q, J = 30.6 Hz), 29.5, 21.1;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.70 (s, 3F);**IR (KBr):** 3089, 1631, 1580, 751 cm^{-1}; **HRMS (ESI)**: calcd for $C_{23}H_{19}F_3NO_2$ $[M + H]^+$:398.1362 , found: 398.1358

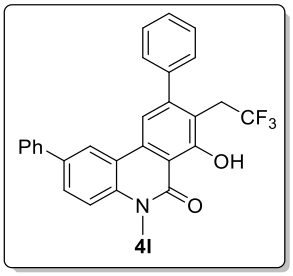
2-Chloro-7-hydroxy-5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4k)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2c** (60.61 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4k** was obtained as off-white solid, yield 72 % (72.1 mg);mp: 248-250 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 13.88 (s, 1H), 8.15 (d, J = 2.3 Hz, 1H), 7.52 (s, 1H), 7.51 – 7.44 (m, 4H), 7.38 – 7.32 (m, 3H), 3.78 (s, 3H), 3.64 (q, J = 10.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 161.6, 148.9, 139.0, 137.4, 134.0, 133.9, 130.3, 130.2, 126.0 (q, J = 279.9 Hz), 123.9,

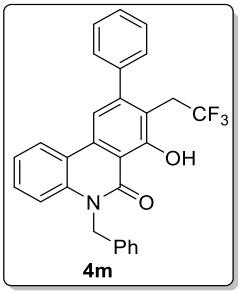
123.6, 121.7, 119.4, 115.4, 114.6, 113.2, 109.4, 30.8 (q, *J* = 30.6 Hz), 29.46;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.63 (s, 3F);**IR (KBr):** 3093, 1633, 1582, 756 cm^{-1};**HRMS (ESI)**: calcd for $C_{22}H_{16}ClF_3NO_2$ $[M + H]^+$:418.0816 , found: 418.0825.

7-Hydroxy-5-methyl-2,9-diphenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4l)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2d** (69.02 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4l** was obtained as yellow solid, yield 63 % (57.8 mg); mp: 238-240 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 14.00 (s, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.66 (s, 1H), 7.65 – 7.61 (m, 2H), 7.52 – 7.49 (m, 1H), 7.50 – 7.45 (m, 4H), 7.44 (m, 1H), 7.40 – 7.34 (m, 3H), 3.83 (s, 3H), 3.64 (q, *J* = 10.5 Hz, 2H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.5, 161.7, 148.5, 137.6, 134.1, 133.6, 131.6, 130.3, 128.7, 128.6, 127.5, 126.7, 126.2, 125.93 (q, *J* = 279.2 Hz), 125.5, 125.4, 124.2, 123.6, 119.6, 115.4, 114.3, 109.6, 31.2 (q, *J* = 31.1 Hz), 29.6;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.64 (s, 3F);**IR (KBr):** 3089, 1631, 1580, 751 cm^{-1};**HRMS (ESI)**: calcd for $C_{28}H_{21}F_3NO_2$ $[M + H]^+$: 460.1519 , found: 460.1518

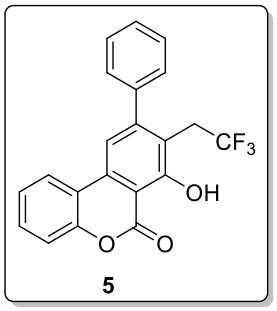
5-Benzyl-7-hydroxy-9-phenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (4m)



Following the general procedure **B**, **1a** (72.5 mg, 0.24 mmol), **2e** (69.02 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), Cs_2CO_3 (130 mg, 0.4 mmol) and 1 mL DMF were used. Compound **4m** was obtained as off-white solid, yield 68% (62.4 mg);mp: 216-218 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 13.94 (s, 1H), 8.22 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.64 (s, 1H), 7.52 – 7.48 (m, 1H), 7.48 – 7.44 (m, 2H), 7.43 – 7.40 (m, 1H), 7.37 (m, 1H), 7.36 – 7.33 (m, 3H), 7.32 (m,

1H), 7.30 – 7.26 (m, 4H), 5.65 (s, 2H), 3.66 (q, *J* = 10.5 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.7, 161.9, 150.7, 140.7, 136.9, 135.9, 134.1, 130.3, 129.1, 128.9, 128.7, 128.0, 127.6, 126.5, 126.1 (q, *J* = 278.4 Hz), 124.1, 123.7, 119.9, 116.4, 114.9, 113.6, 109.1, 46.1, 30.7 (q, *J* = 30.9 Hz);**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.64 (s, 3F);**IR (KBr):** 3094, 1638, 1586, 753 cm^{-1};**HRMS (ESI)**: calcd for $C_{28}H_{21}F_3NO_2$ $[M + H]^+$: 460.1519, found: 460.1522

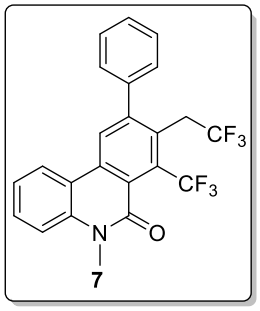
7-hydroxy-9-phenyl-8-(2,2,2-trifluoroethyl)-6*H*-benzo[*c*]chromen-6-one (5)



5

Following the general procedure **A**, **1a** (72.5 mg, 0.24 mmol), **2g** (46.4 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) and 1 mL CH_3CN were used. Compound **5** was obtained as white solid, yield 26% (23.09 mg);mp: 195-197 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.98 (s, 1H), 8.00 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 – 7.46 (m, 5H), 7.41 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.37 – 7.31 (m, 3H), 3.62 (q, *J* = 10.3 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.6, 161.9, 153.2, 150.9, 139.9, 134.5, 131.1, 128.7, 128.6, 128.4, 125.8 (q, *J* = 278.9 Hz), 125.4, 123.5, 118.1, 117.9, 116.5, 114.3, 105.1, 30.8 (q, *J* = 31.1 Hz);**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.64 (s, 3F);**IR (KBr):** 3093,1693, 1584, 752 cm^{-1};**HRMS (ESI)**: calcd for $C_{21}H_{14}F_3O_3$ $[M + H]^+$: 371.0890, found: 371.0901.

9.4 General procedure for the synthesis of5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)phenanthridin-6(5*H*)-one (7)

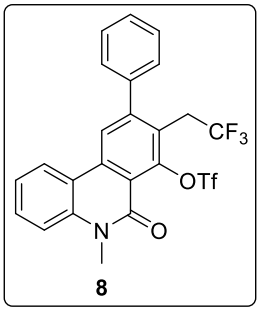


7

To a stirred solution of **3a** (100 mg, 0.22 mmol) in 1 mL of dichloromethane was added triflic acid (99.36 mg, 3 equiv) at 0 ^oC and allowed to stirrer in room temperature 24 h. The reaction

progress was monitored by TLC. After completion of the reaction, reaction mixture was quenched with aq. $NaHCO_3$ and extracted with ethyl acetate (3 X 15 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product **8** white in color with yield 51% (48.8 mg);mp: 192-194 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 8.18 – 8.14 (m, 1H), 7.62 – 7.56 (m, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.41 (d, *J*= 8.3 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 3.98 (q, *J* = 10.0 Hz, 2H), 3.80 (s, 3H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 148.9, 140.0, 138.9, 134.8, 130.9 (d, *J* = 260.7 Hz), 130.9, 129.3, 129.0, 128.9, 128.6, 128.5, 127.3, 125.2 (q, *J* = 270.2 Hz), 124.9 (q, *J* = 278.5 Hz), 123.9, 122.7, 117.7, 115.1, 30.6, 35.6 (q, *J* = 31.4 Hz);**^{19}F NMR (377 MHz, $CDCl_3$)** δ –62.36 (s, 3F), –65.38 (s, 3F); **IR (KBr):** 1671, 1570, 756 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{16}F_6NO$ $[M + H]^+$: 436.1131, found: 436.1127

9.5 General procedure for the synthesis of 5-methyl-6-oxo-9-phenyl-8-(2,2,2-trifluoroethyl)-5,6-dihydrophenanthridin-7-yl trifluoromethanesulfonate (8)

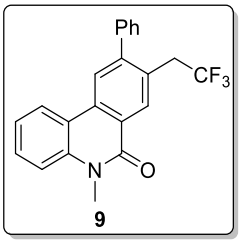


8

To a stirred solution of **4a** (100 mg, 0.22 mmol) in 1mL of dichloromethane was added pyridine (3 equiv) and triflic anhydride (99.36 mg, 1.5 equiv) at 0 ^oC and allowed to stirrer in room temperature for 6 h. The reaction progress was monitored by TLC. After completion of the reaction, reaction mixture was quenched with cold water and extracted with ethyl acetate (3 X 15 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product which is white solid with yield 60% (68.0 mg);mp: 200-202 ^oC;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 8.21 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.56 – 7.48 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 3.83 (s, 3H), 3.72 (q, *J* = 9.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.5, 161.6, 150.3, 140.7, 137.5, 133.9, 130.3, 128.9, 128.5, 127.9, 126.1 (q,

J = 278.7 Hz), 124.1, 123.6, 120.5, 119.6, 115.4, 114.9, 113.5, 109.3, 30.7 (q, *J* = 31.0 Hz), 29.5;**^{19}F NMR (376 MHz, $CDCl_3$)** δ –64.09 (s, 3F), –73.39 (s, 3F); **IR (KBr)**: 1642, 1573, 761 cm^{-1};**HRMS (ESI)**: calcd for $C_{23}H_{16}F_6NO_4S$ $[M + H]^+$:516.0699 , found: 516.0698

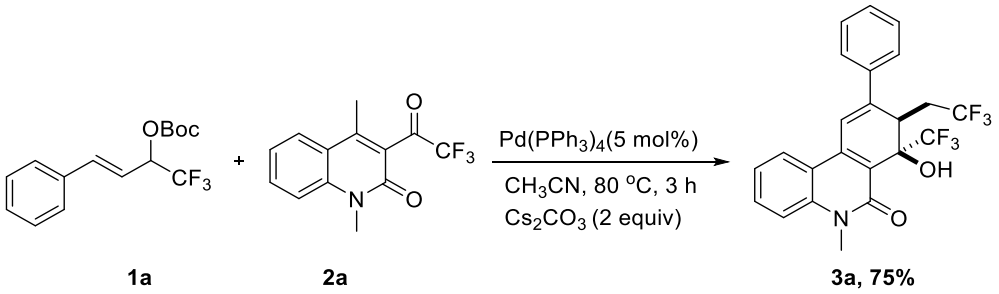
9.6 General procedure for the synthesis of 5-methyl-9-phenyl-8-(2,2,2-trifluoroethyl)phenanthridin-6(5*H*)-one (9)



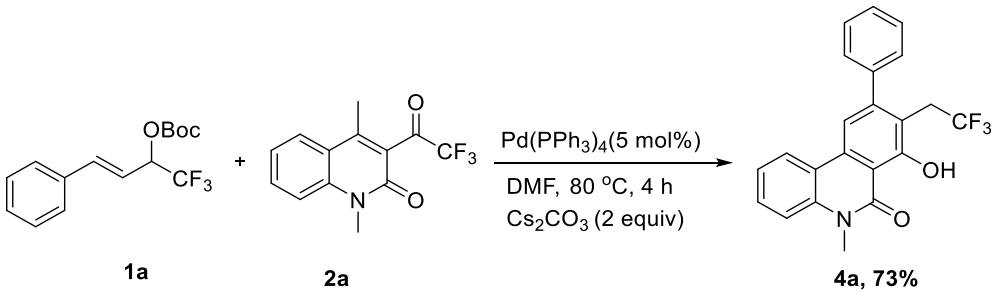
9

To a stirred solution of **9** (51 mg, 0.1 mmol) in 1mL of ethanol:water (4:1) was added sodiumcarbonate (20.58 mg, 2equiv) at room temperature. Then, $Pd(PPh_3)_4$ (5.72mg, 5 mol%) was added to the reaction mixture and stirred at 80 °C (oil bath temperature) for 8h. The reaction progress was monitored by TLC. After completion of the reaction, reaction mixture was extracted with ethyl acetate (3 X 15 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product which is white solid with yield 85% (31.2 mg);mp: 170-172 ^oC;**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.65 (s, 1H), 8.23 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.17 (s, 1H), 7.56 (m, 1H), 7.53 – 7.46 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 3.84 (s, 3H), 3.53 (q, *J* = 10.6 Hz, 2H);**^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.3, 147.8, 140.2, 138.5, 133.1, 131.5, 130.1, 129.2, 128.7, 128.3, 128.1, 125.8 (q, *J* = 277.3 Hz), 124.9, 124.0, 123.6, 122.7, 118.9, 115.3, 36.8 (q, *J* = 29.5 Hz), 30.2;**^{19}F NMR (376 MHz, CDCl3)** δ –69.33 (s, 3F);**IR (KBr):**1689, 1570, 737 cm^{-1};**HRMS (ESI)**: calcd for $C_{22}H_{17}F_3NO$ $[M + H]^+$: 368.1257, found: 368.1248.

10. Gram scale reaction of 3a & 4a.



To a stirred solution of compound **1a** (1.4 gm, 4.5 mmol) in 10 mL CH_3CN, were added **2a** (1 gm, 3.7 mmol), $Pd(PPh_3)_4$ (214.7 mg, 5 mol%) and Cs_2CO_3 (2.4 gm, 7.4 mmol) at room temperature and raised the temperature to 80 ^oC (oil bath). The reaction progress was monitored by TLC. After completion of the reaction, mixture was diluted with cold water and extracted with ethyl acetate (3 X 25 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product **3a** (yield 75%, 1.3 gm).



To a stirred solution of compound **1a** (1.4 gm, 4.5 mmol) in 10 mL DMF, were added **2a** (1 gm, 3.7 mmol), $Pd(PPh_3)_4$ (214.7 mg, 5 mol%) and Cs_2CO_3 (2.4 gm, 7.4 mmol)at room temperature and raised the temperature to 80 ^oC (oil bath). The reaction progress was monitored by TLC. After completion of the reaction, mixture was diluted with cold water and extracted with ethyl acetate (3 X 25 mL). Combined organic layers were dried over sodium sulphate and concentrated on rotary evaporation. The obtained crude product was purified by flash column chromatography on silica gel 100-200 mesh using (hexane/ethyl acetate) to obtain the pure product **4a** (yield 73%, 1.03 gm).

11. X-ray analysis data of 3a

X-ray Crystallography.

X-ray data for the compound **3a** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[11] The structure was solved using intrinsic phasing method and further refined with the SHELXL[12] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The O-H atoms were located in the difference Fourier map and its positions and isotropic displacement parameters were refined. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3a:

Crystal Data for $C_{23}H_{17}NO_2F_6$ (*M* =453.38 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 11.4138(11) Å, *b* = 11.2940(11) Å, *c* = 15.5406(13) Å, *β* = 97.968(3)°, *V* = 1984.0(3) $Å^3$, *Z* = 4, *T* = 294.15 K, μ(MoKα) = 0.135 mm^{-1}, *Dcalc* = 1.518 g/cm^3, 21908 reflections measured (4.474° ≤ 2Θ ≤ 56.628°), 4904 unique (R_{int} = 0.0515, R_{sigma} = 0.0489) which were used in all calculations. The final R_1 was 0.0546 (I > 2σ(I)) and wR_2 was 0.1442 (all data). **CCDC** 2360628 deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

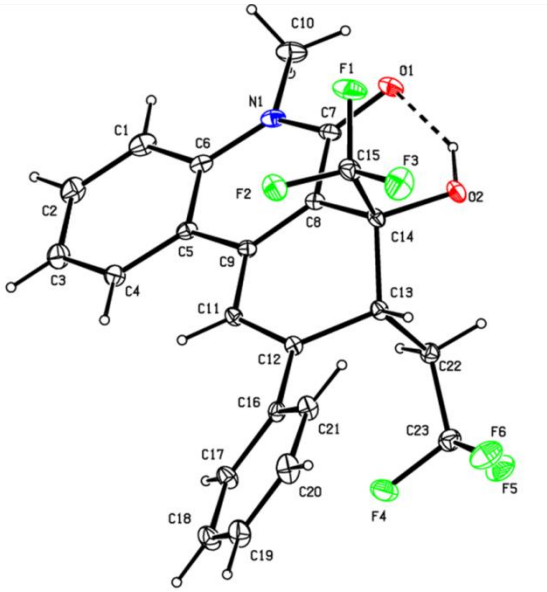


Figure caption: ORTEP diagram of KA1169 compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

12. References:

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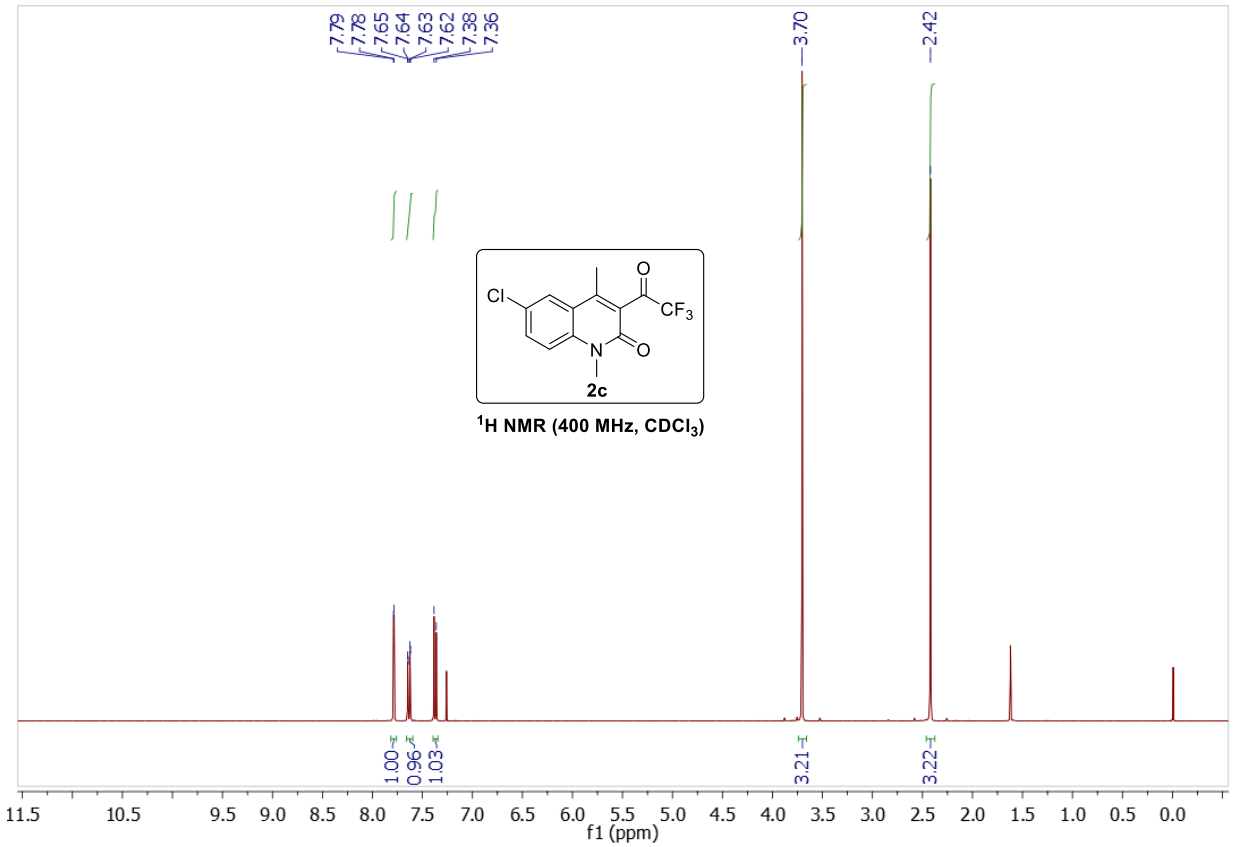
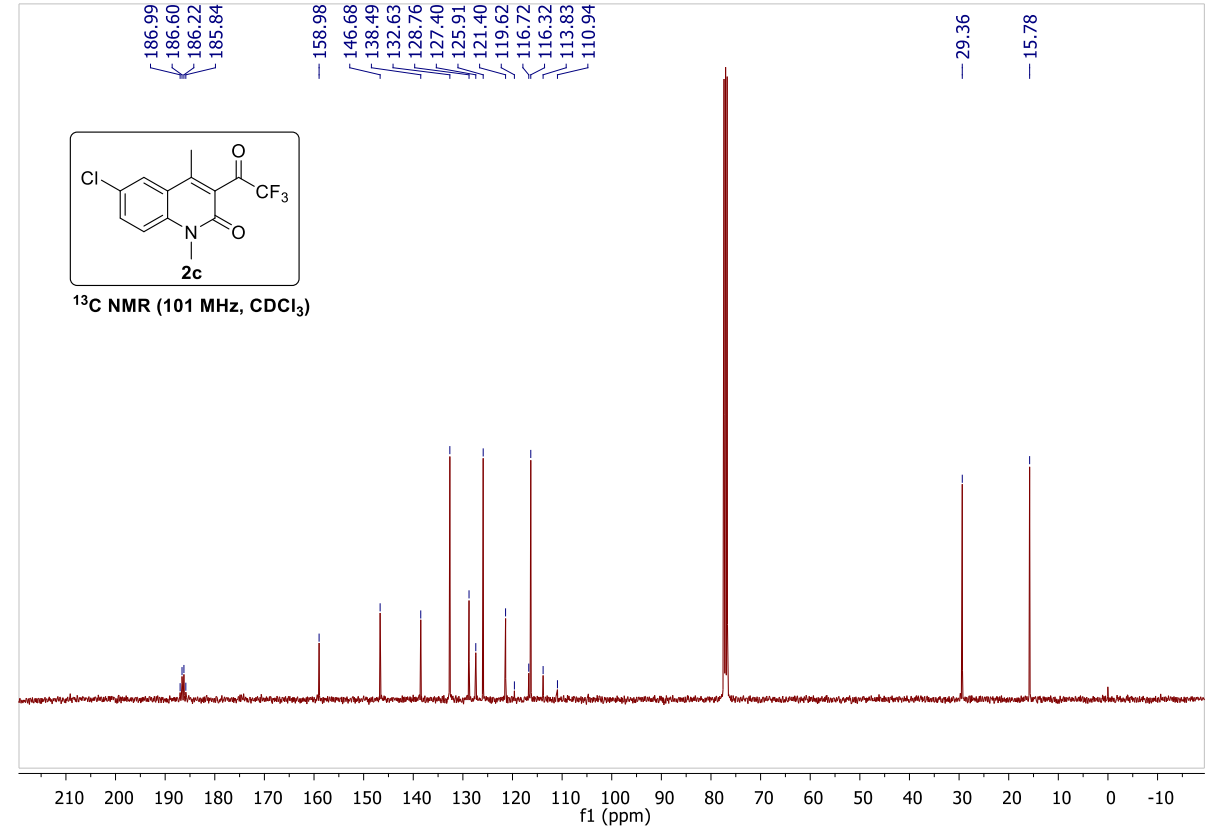
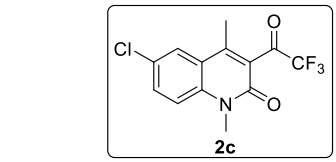
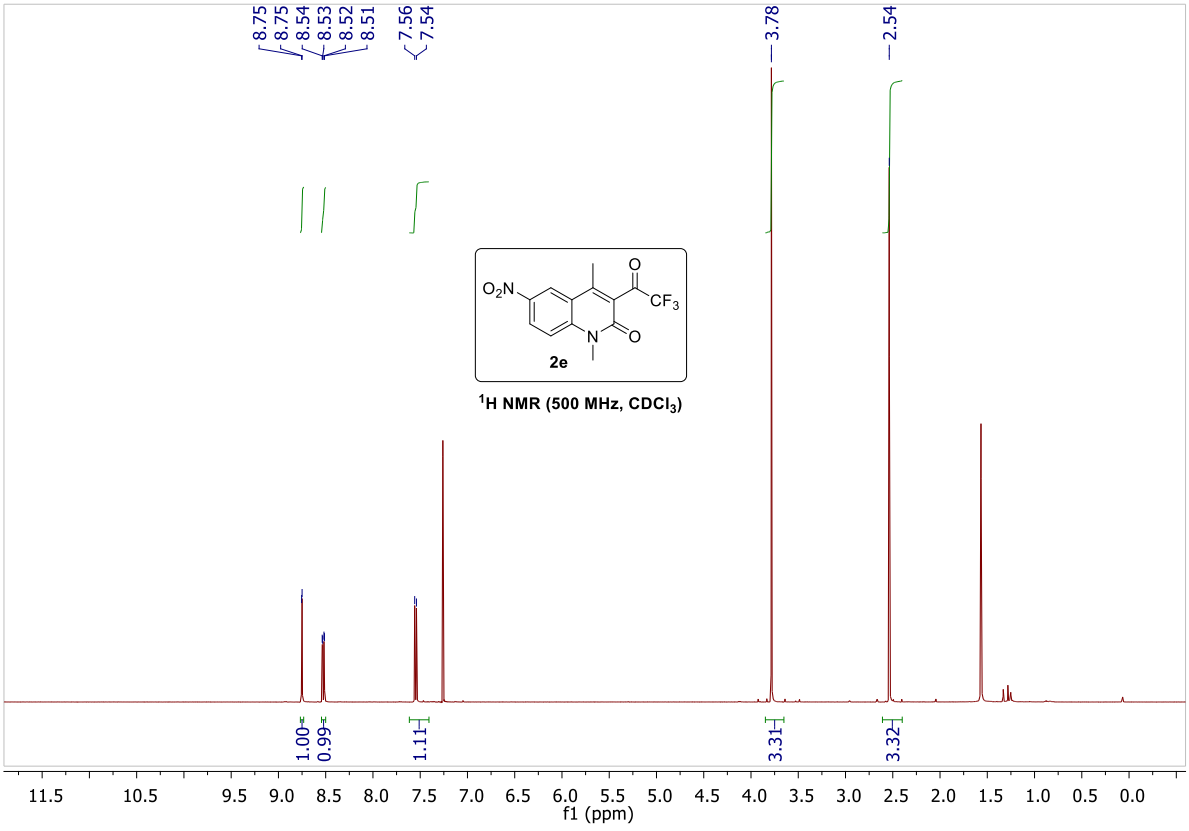
13. ^{1}H NMR, ^{13}C NMR and ^{19}F spectral copies of compound


7.79
7.78
7.65
7.64
7.63
7.62
7.38
7.36
3.70
2.42
Cl
O
CF3
N
O
2c
1H NMR (400 MHz, CDCl3)
1.00
0.96
1.03
3.21
3.22
11.5
10.5
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)

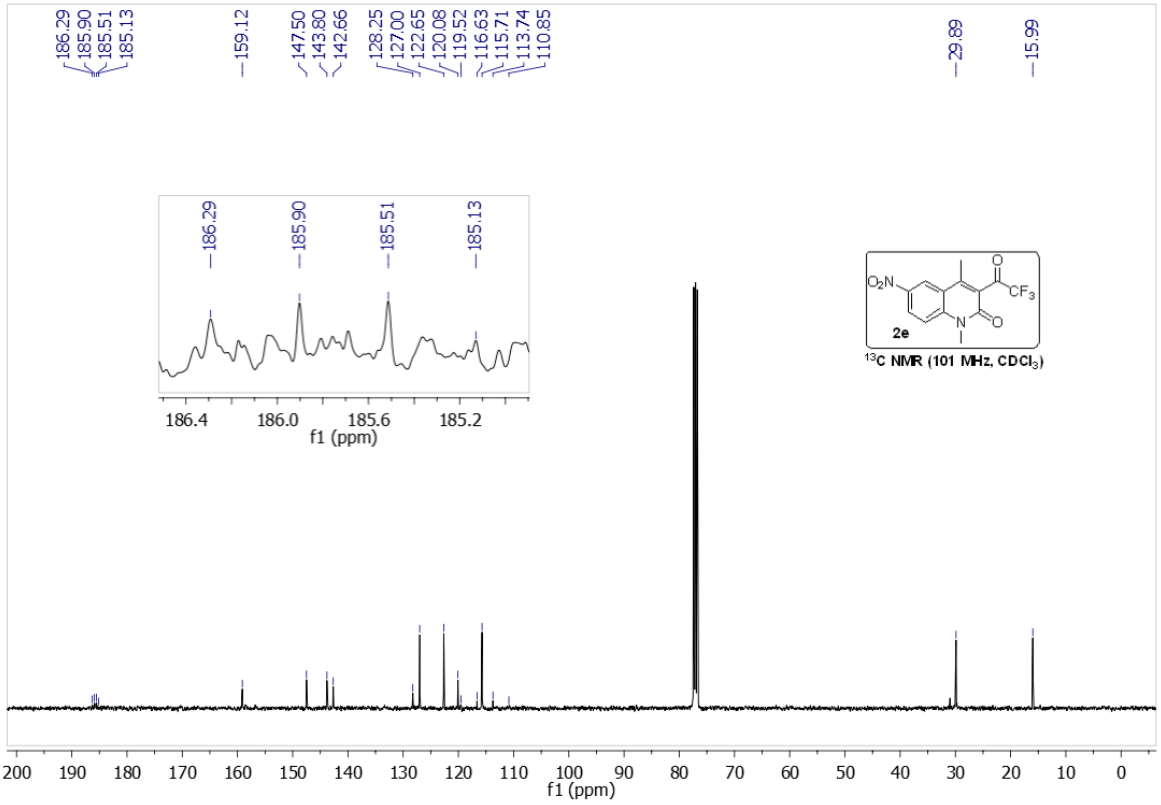

186.99
186.60
186.22
185.84
158.98
146.68
138.49
132.63
128.76
127.40
125.91
121.40
119.62
116.72
116.32
113.83
110.94
29.36
15.78
Cl
O
CF3
N
O
2c
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

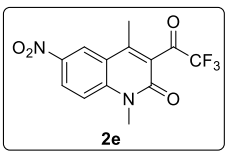


^{19}F NMR, 377 MHz, $CDCl_3$

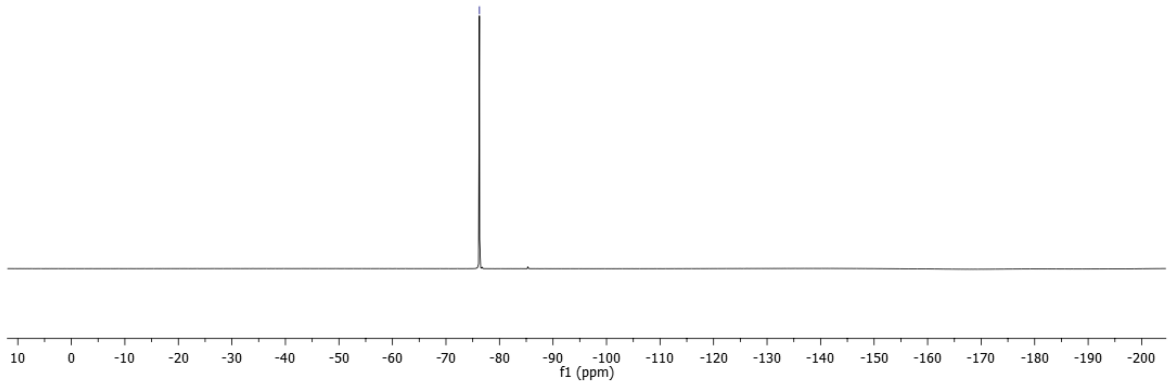


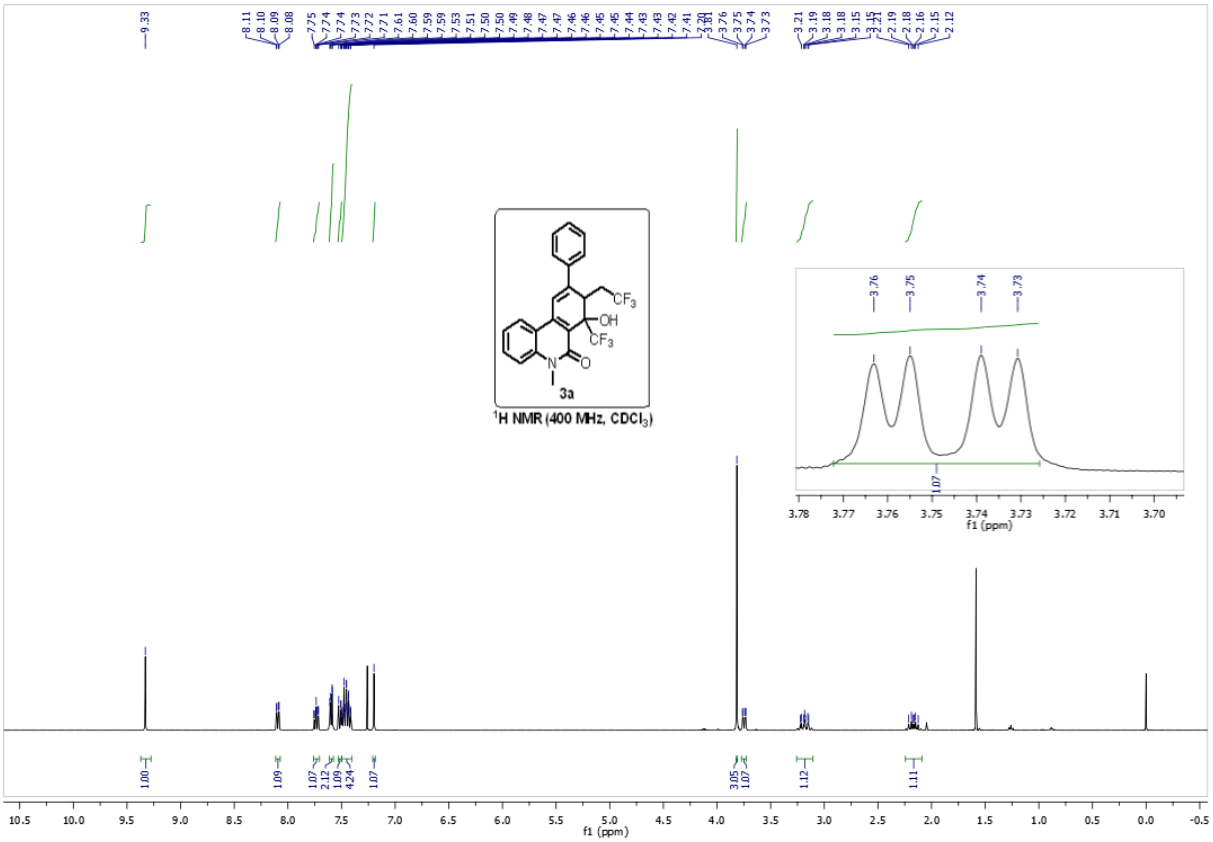
^{1}H NMR (500 MHz, $CDCl_3$)

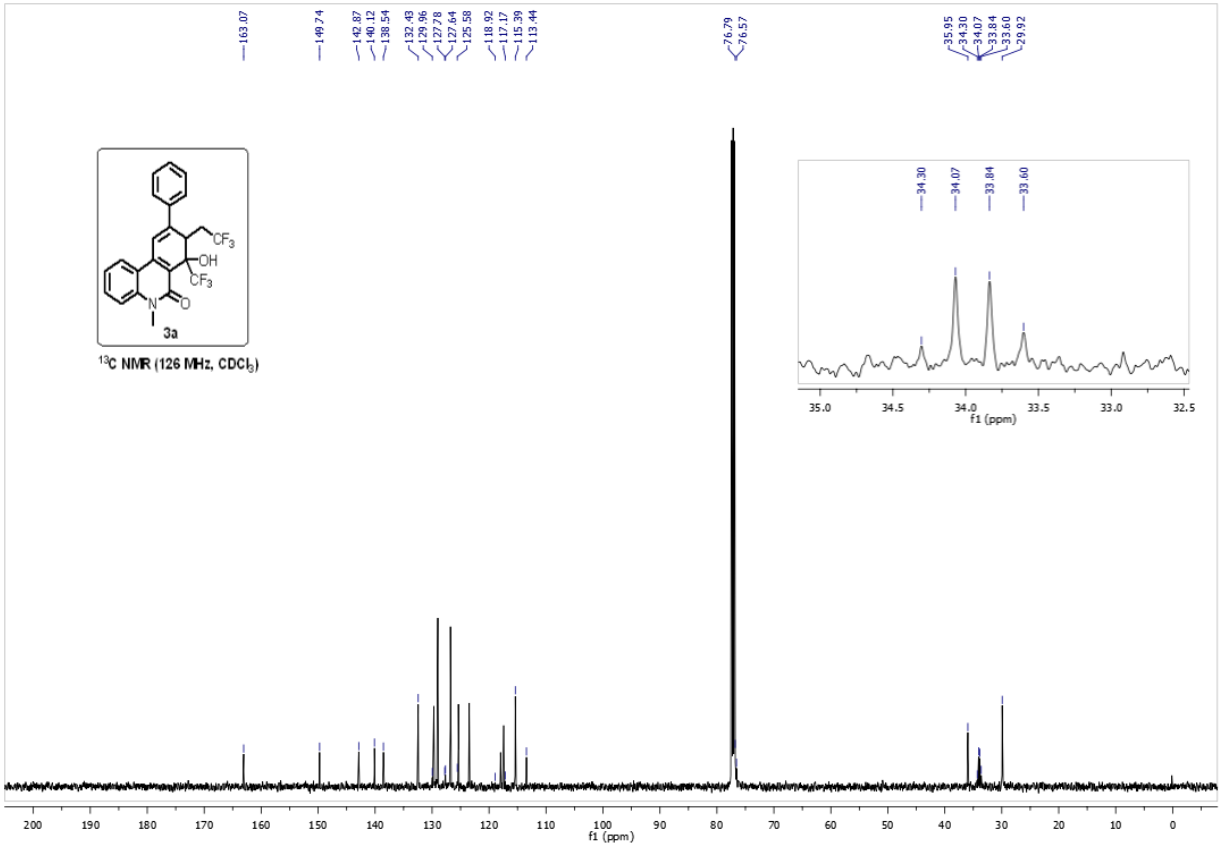


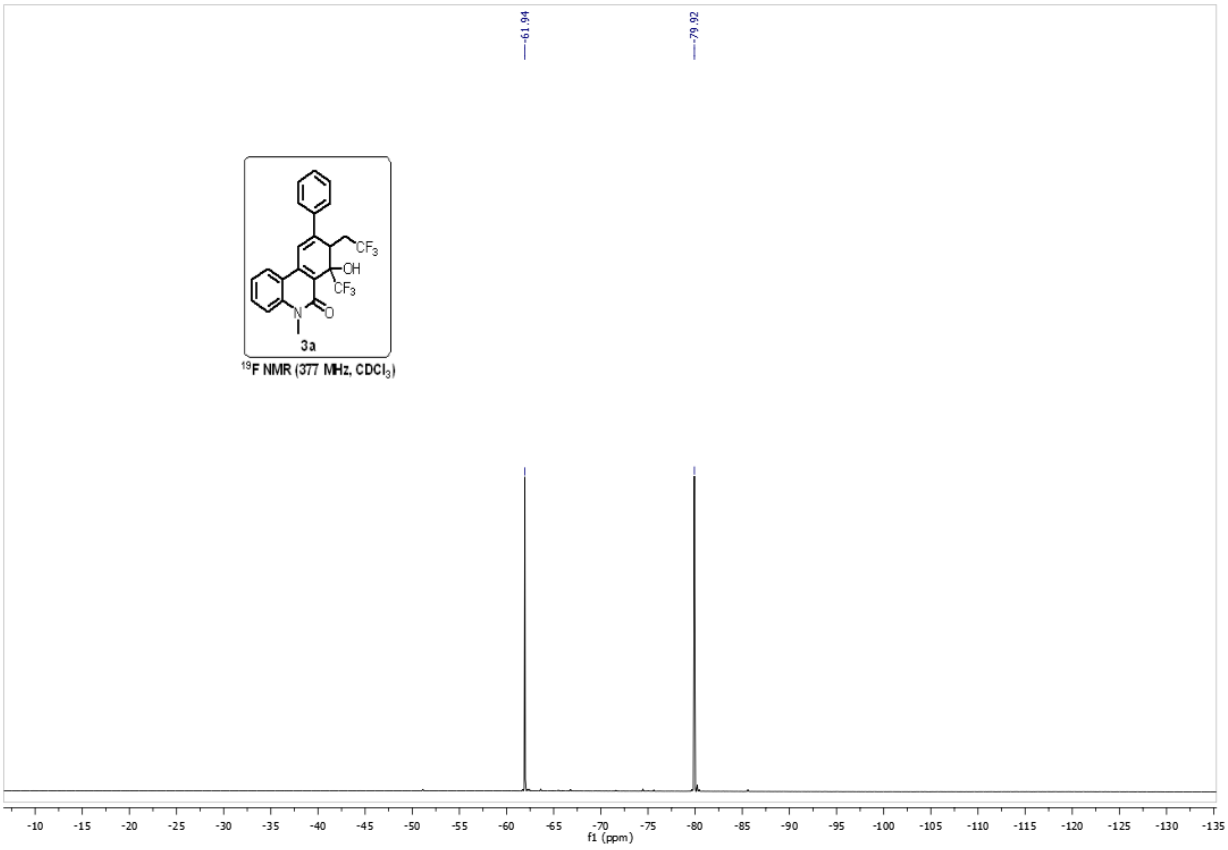


^{19}F NMR, 377 MHz, $CDCl_3$




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


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


-61.94
-79.92
3a
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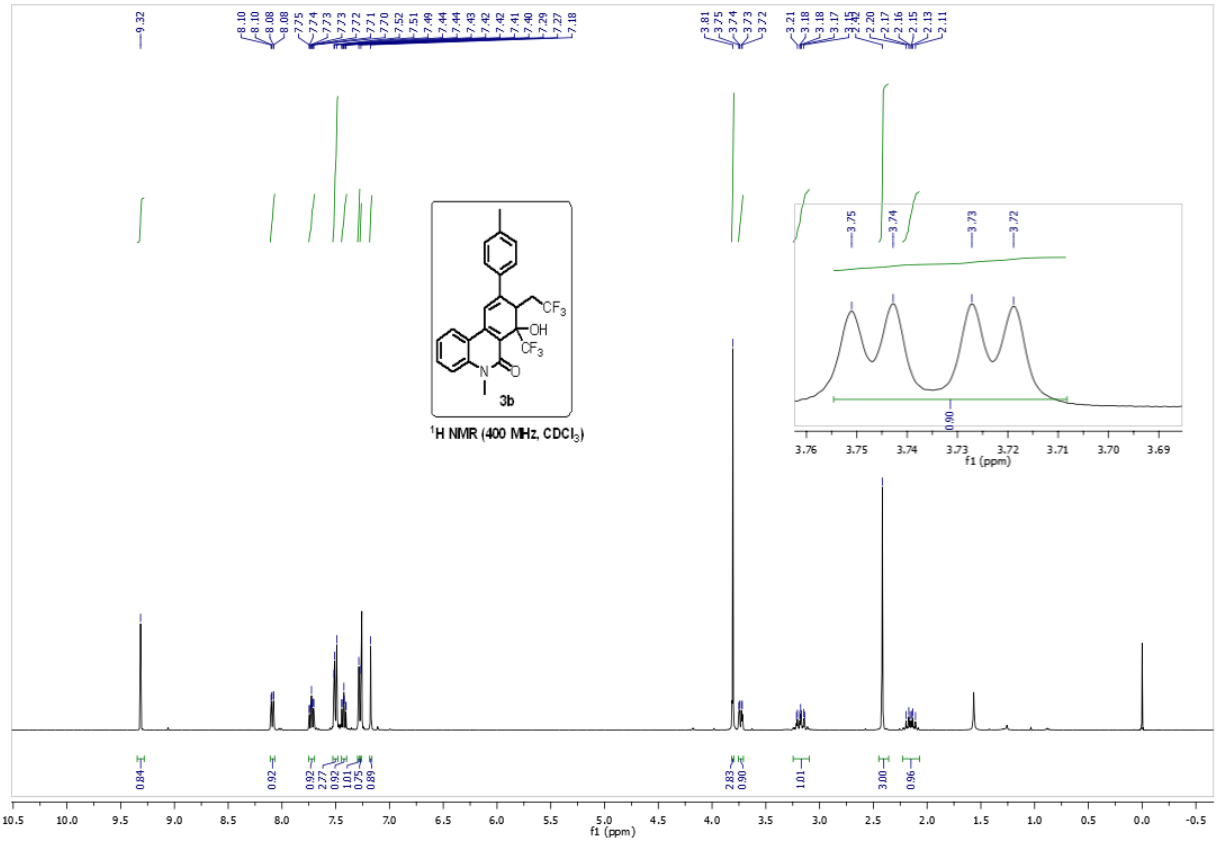
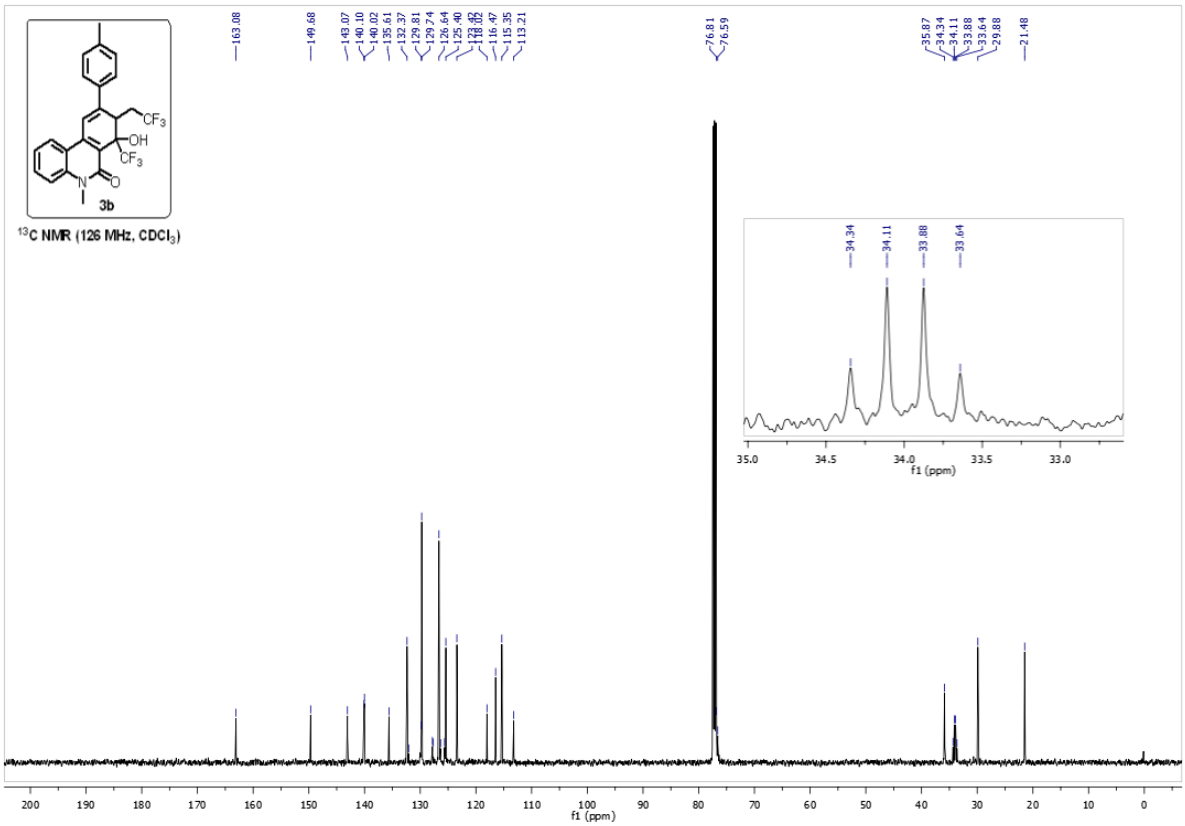
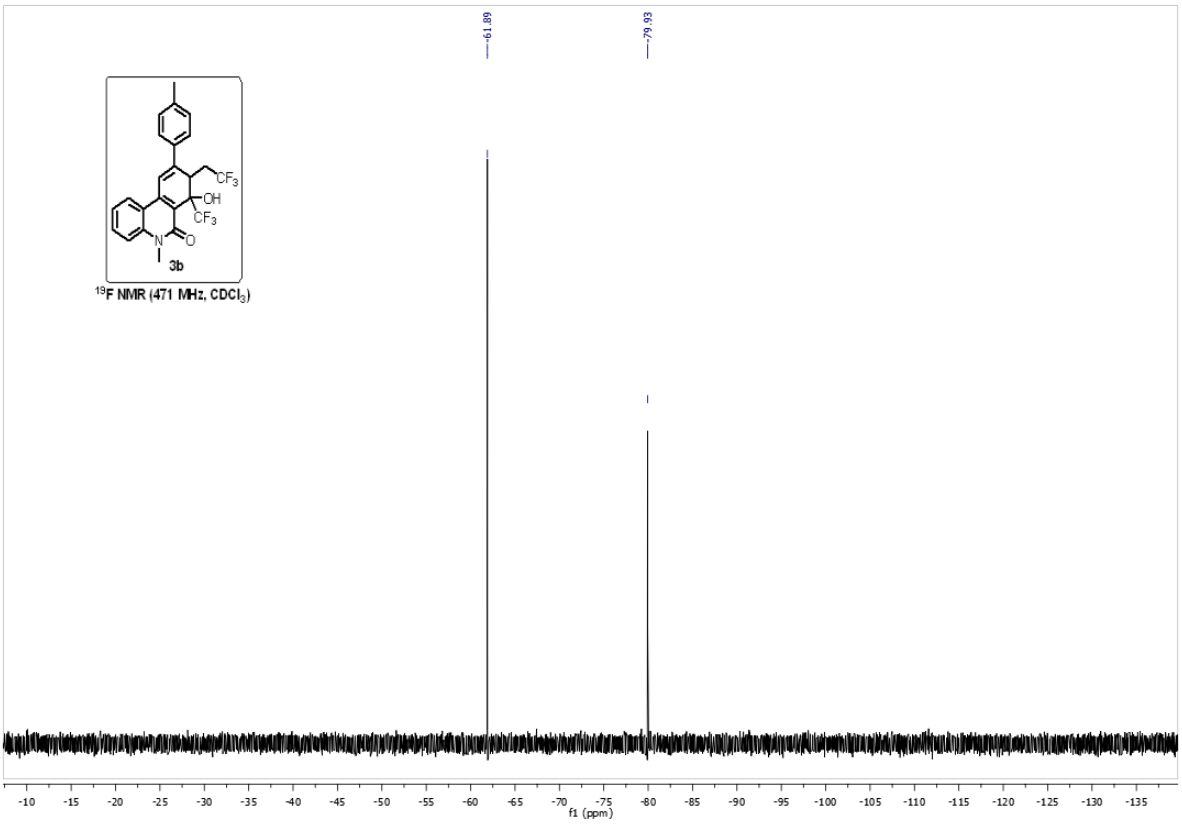
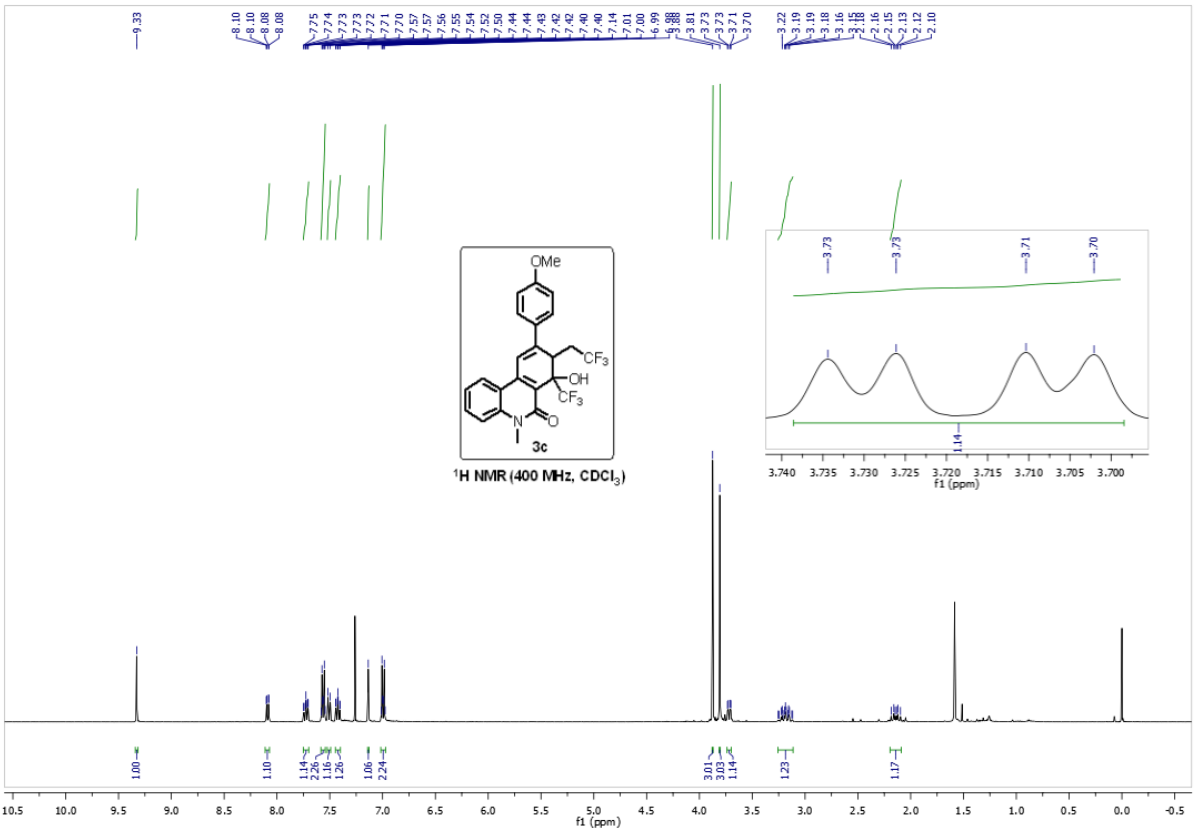
f1 (ppm)


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


3b
^{13}C NMR (126 MHz, $CDCl_3$)
163.08
149.68
143.07
140.10
140.02
135.61
132.37
129.81
129.74
126.64
125.40
116.47
115.35
113.21
76.81
76.59
35.87
34.34
34.11
33.88
33.64
29.88
21.48
f1 (ppm)


3b
^{19}F NMR (471 MHz, $CDCl_3$)
-61.89
-79.93
f1 (ppm)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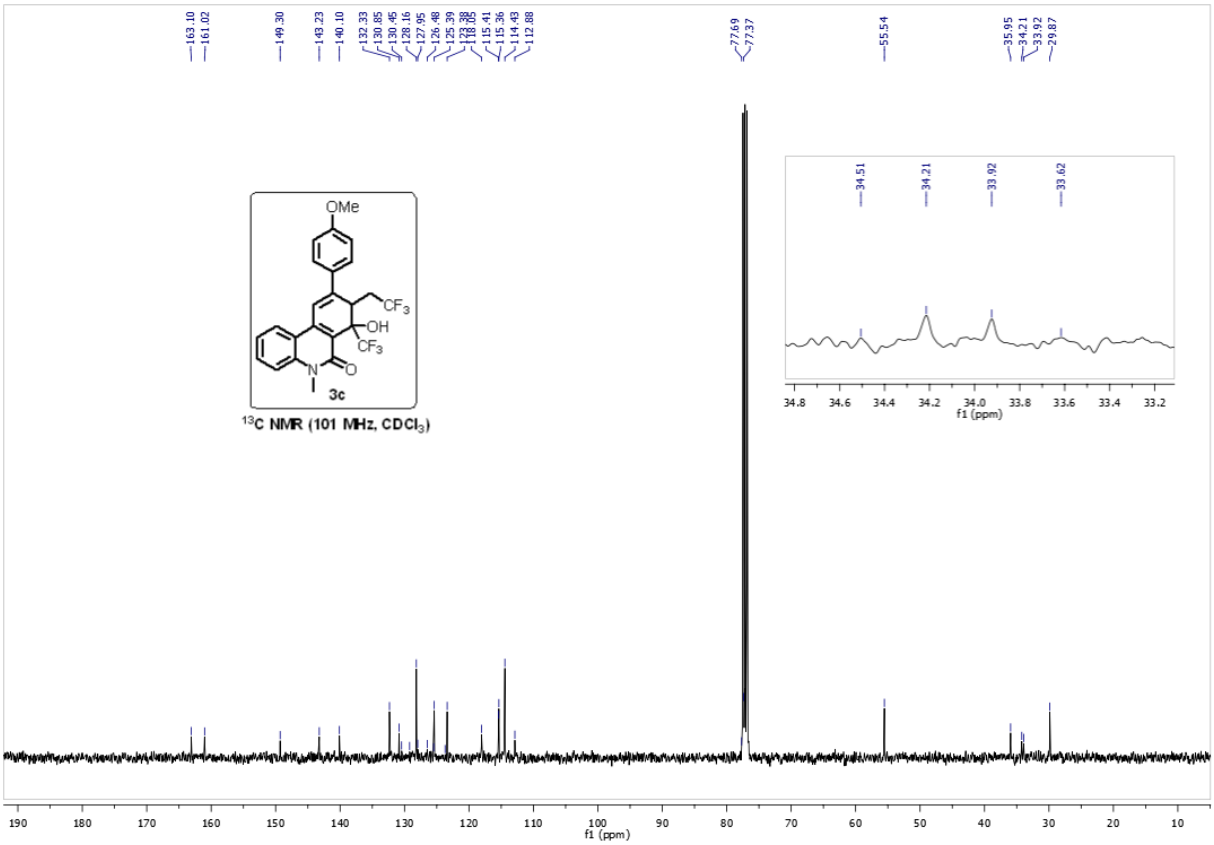
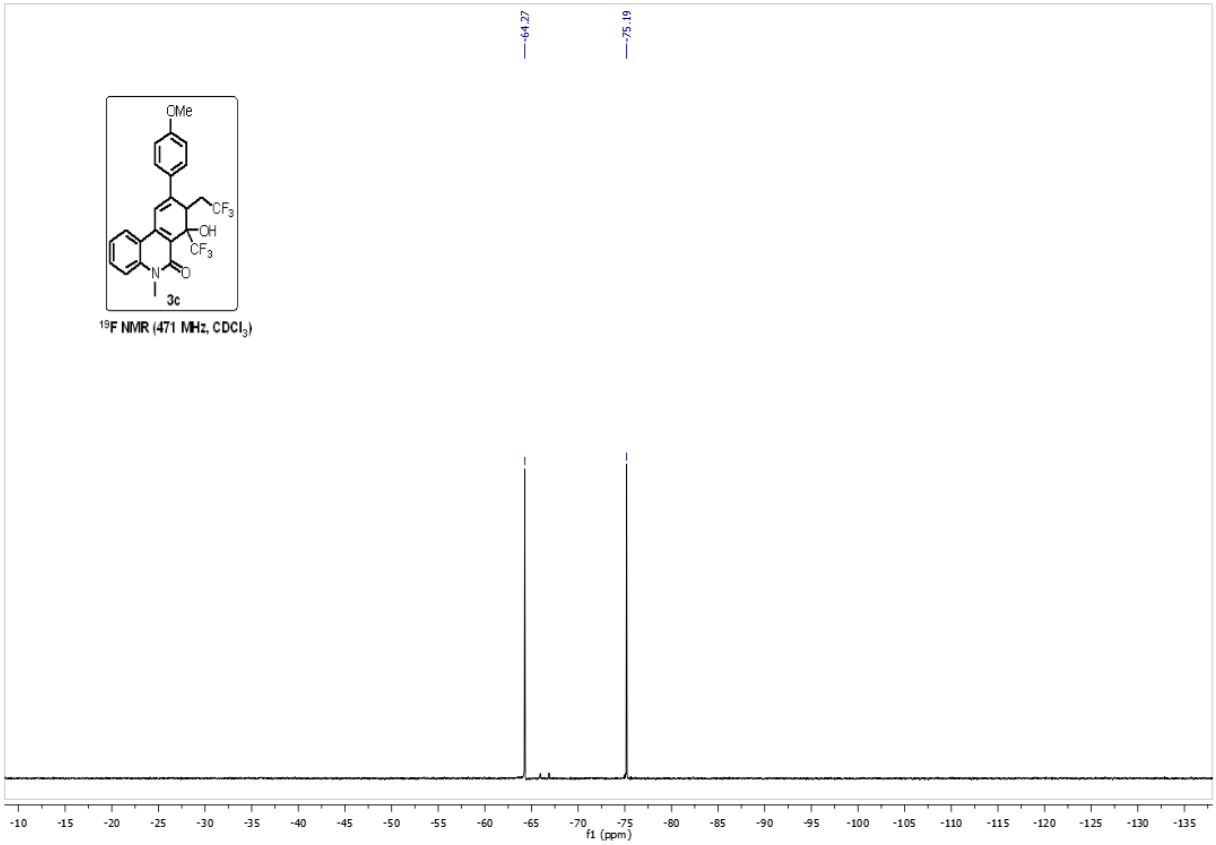
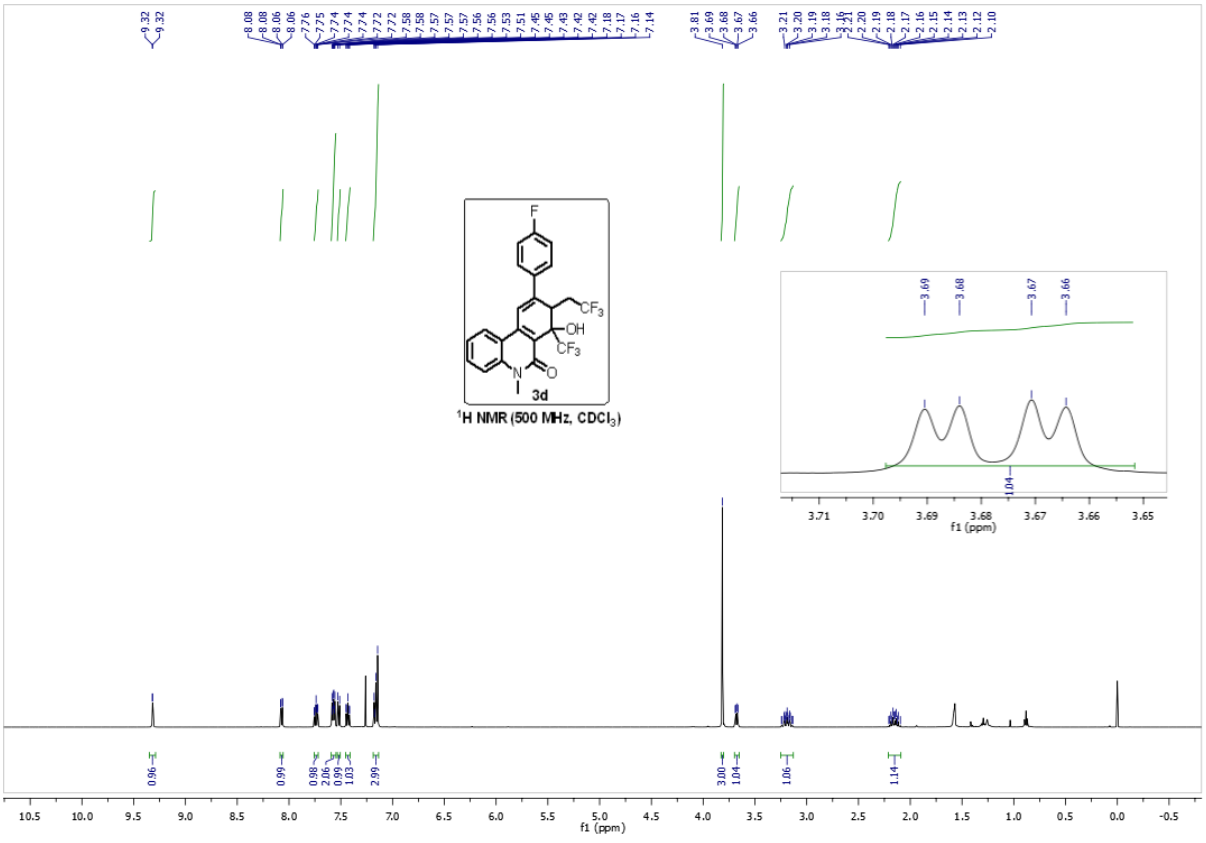
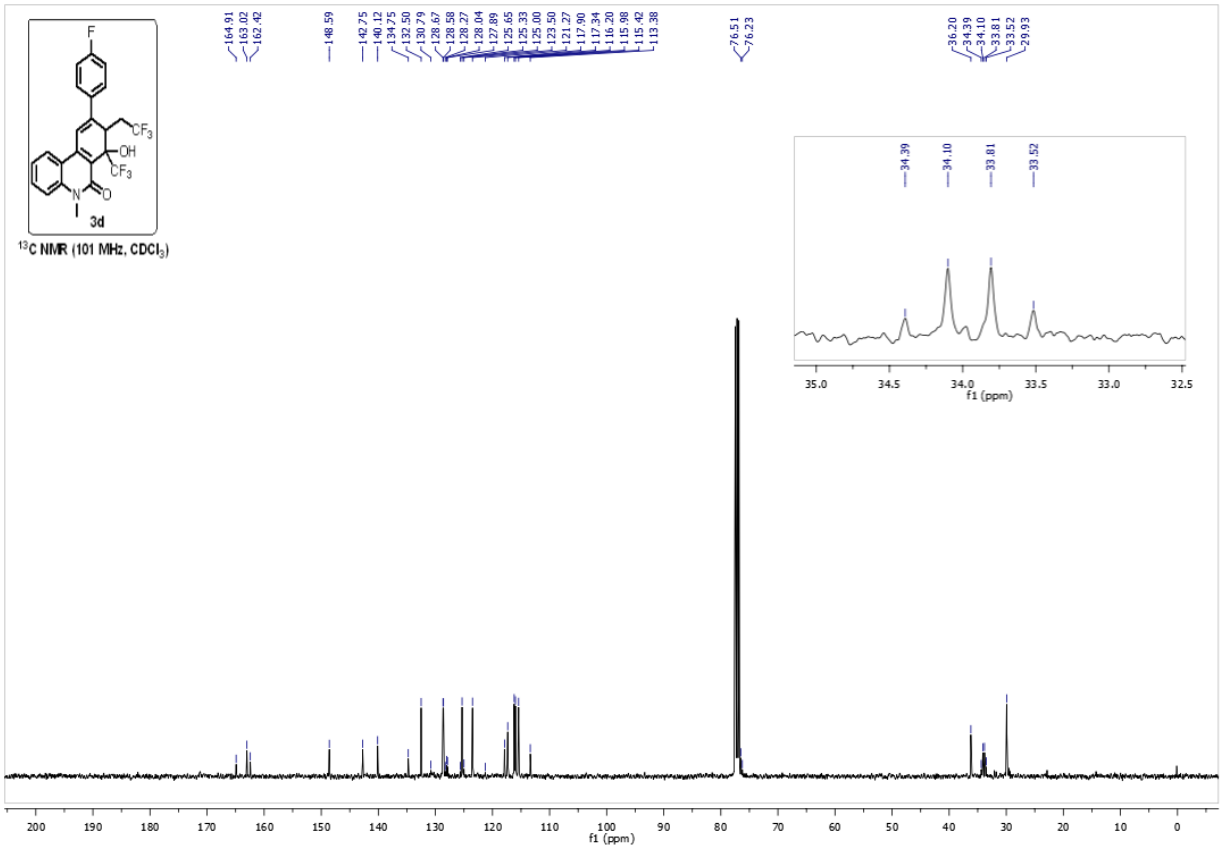
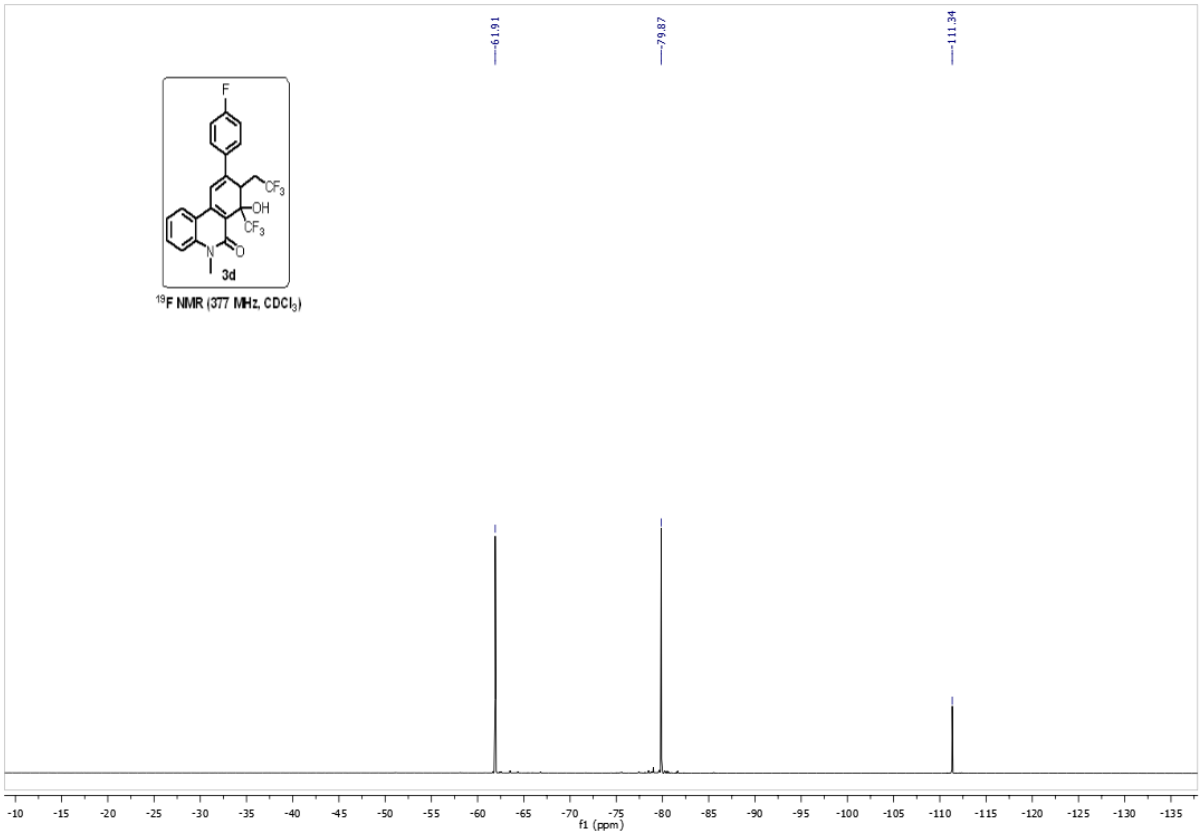
CF3
OH
CF3
N
O
3c
1H NMR (400 MHz, CDCl3)
f1 (ppm)

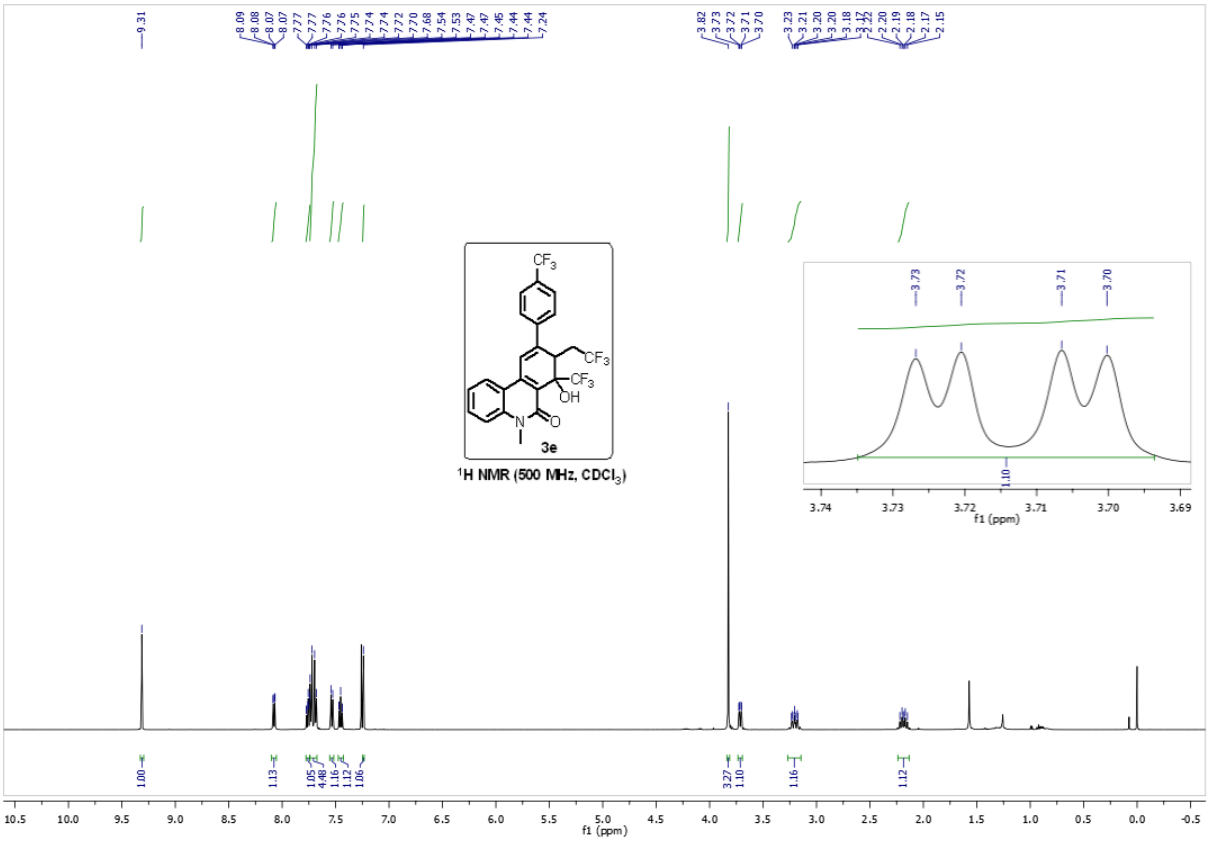

OMe
CF3
OH
CF3
N
O
3c
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-64.27
-75.19
OMe
CF3
OH
CF3
N
O
3c
19F NMR (471 MHz, CDCl3)
f1 (ppm)


F
CF3
OH
CF3
N
O
3d
1H NMR (500 MHz, CDCl3)
3.69
3.68
3.67
3.66
1.04
f1 (ppm)


3d
^{13}C NMR (101 MHz, CDCl$_3$)
164.91
163.02
162.42
148.59
142.75
140.12
134.75
132.50
130.79
128.67
128.58
128.27
128.04
127.89
125.65
125.33
125.00
123.50
121.27
117.90
117.34
116.20
115.98
115.42
113.38
76.51
76.23
36.20
34.39
34.10
33.81
33.52
29.93
f1 (ppm)


3d
^{19}F NMR (377 MHz, CDCl$_3$)
-61.91
-79.87
-111.34
f1 (ppm)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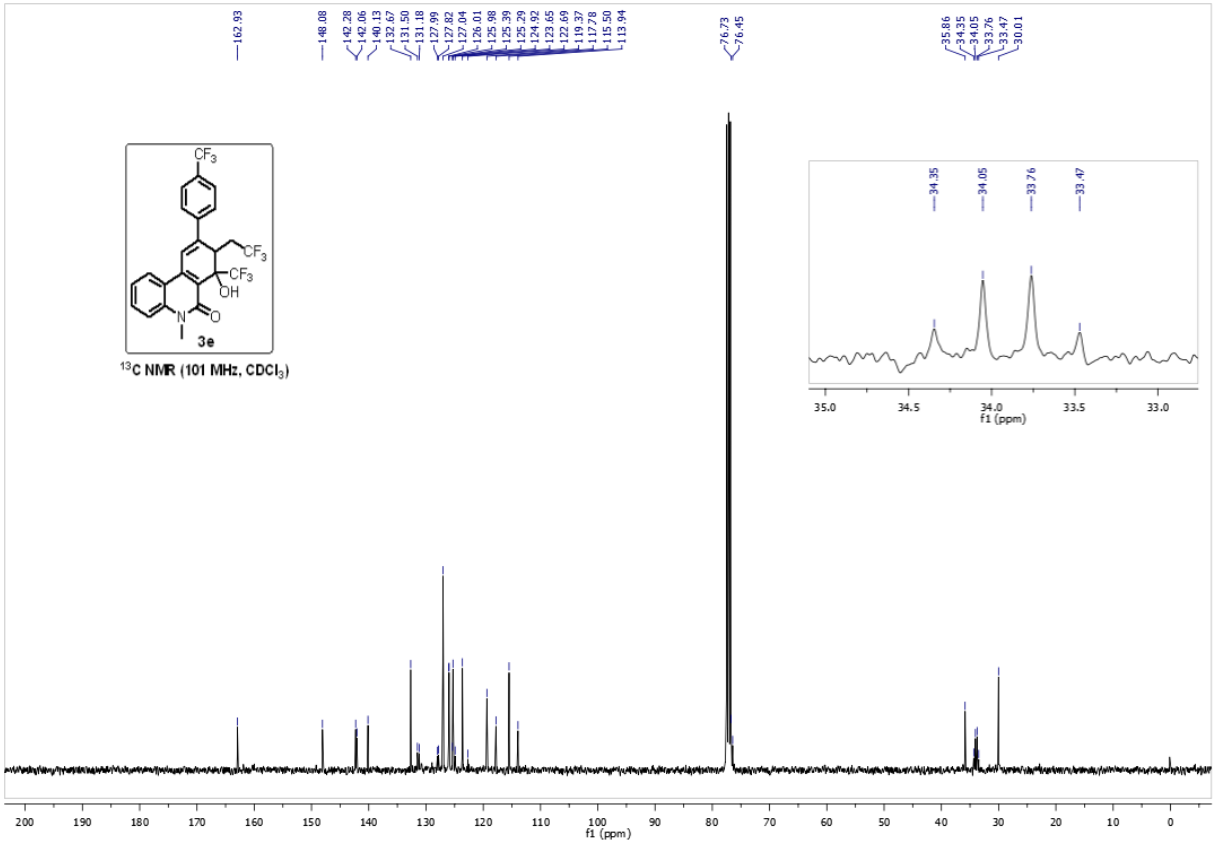
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)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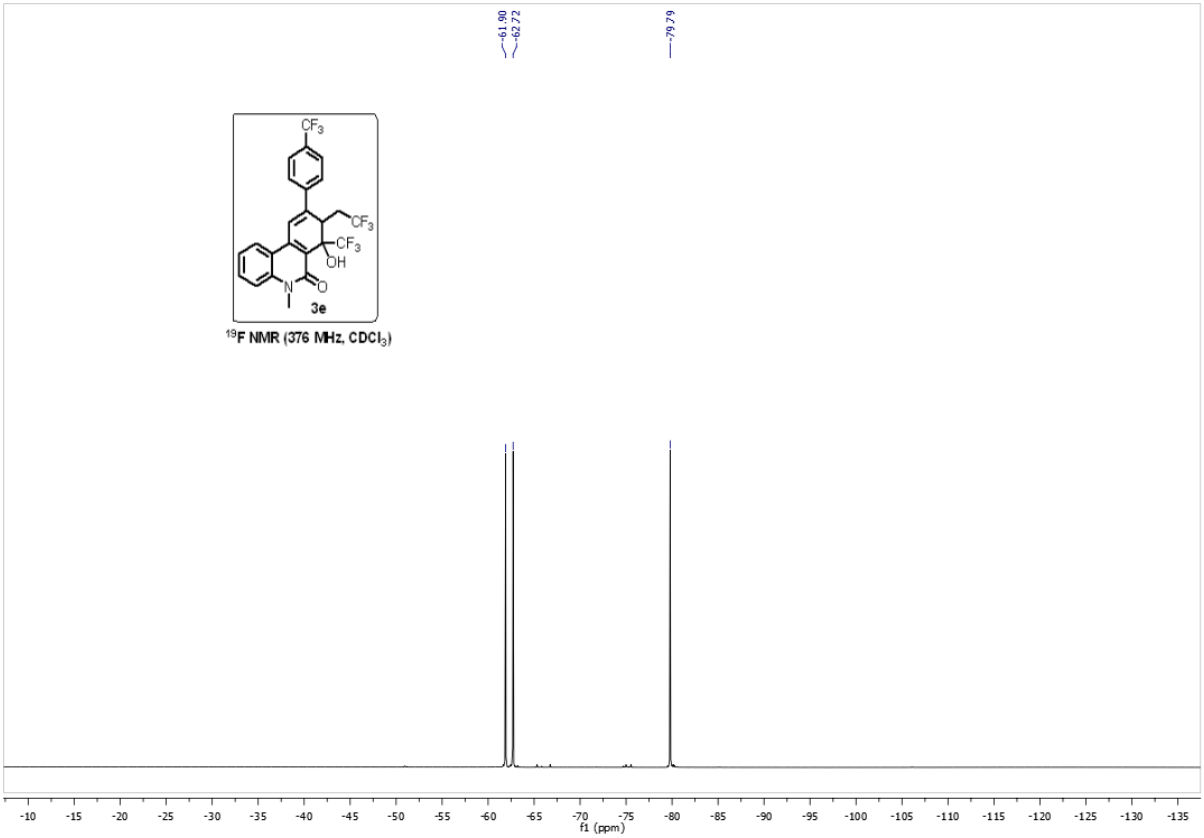
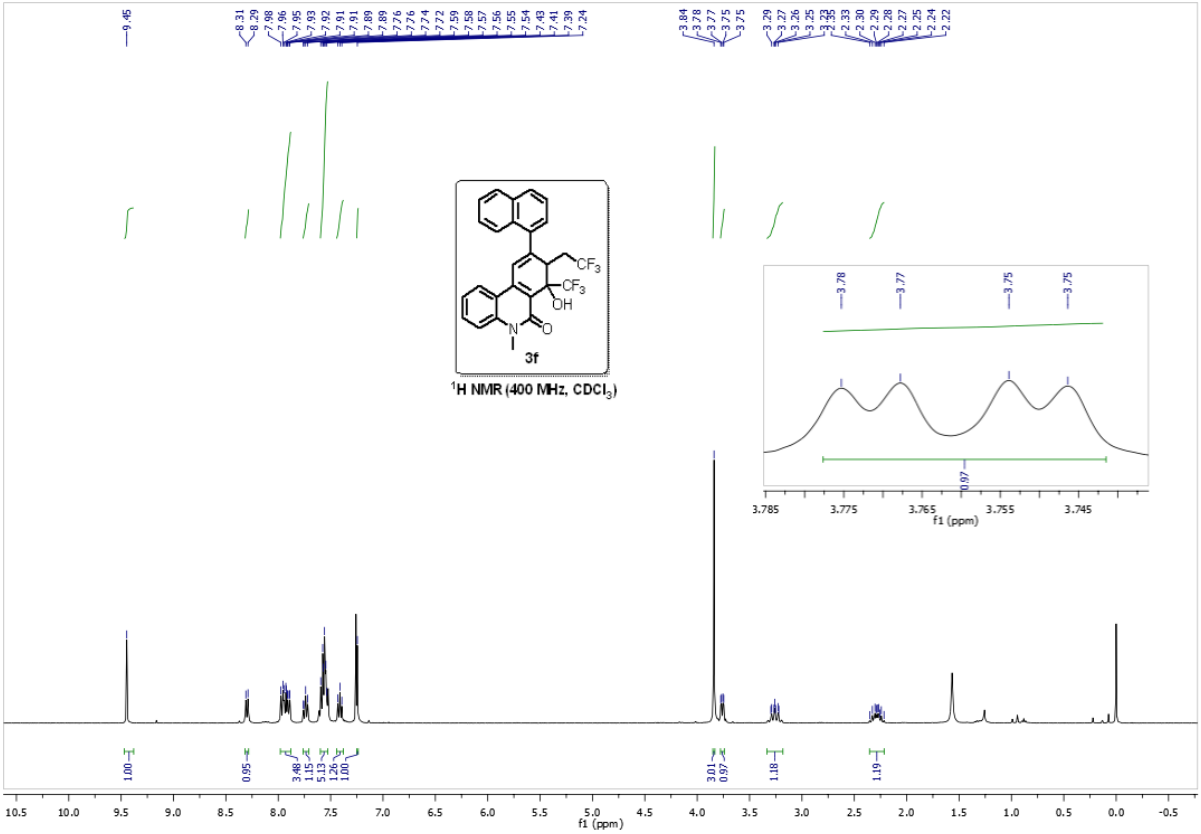
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


-61.90
-62.72
-79.79
3e
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)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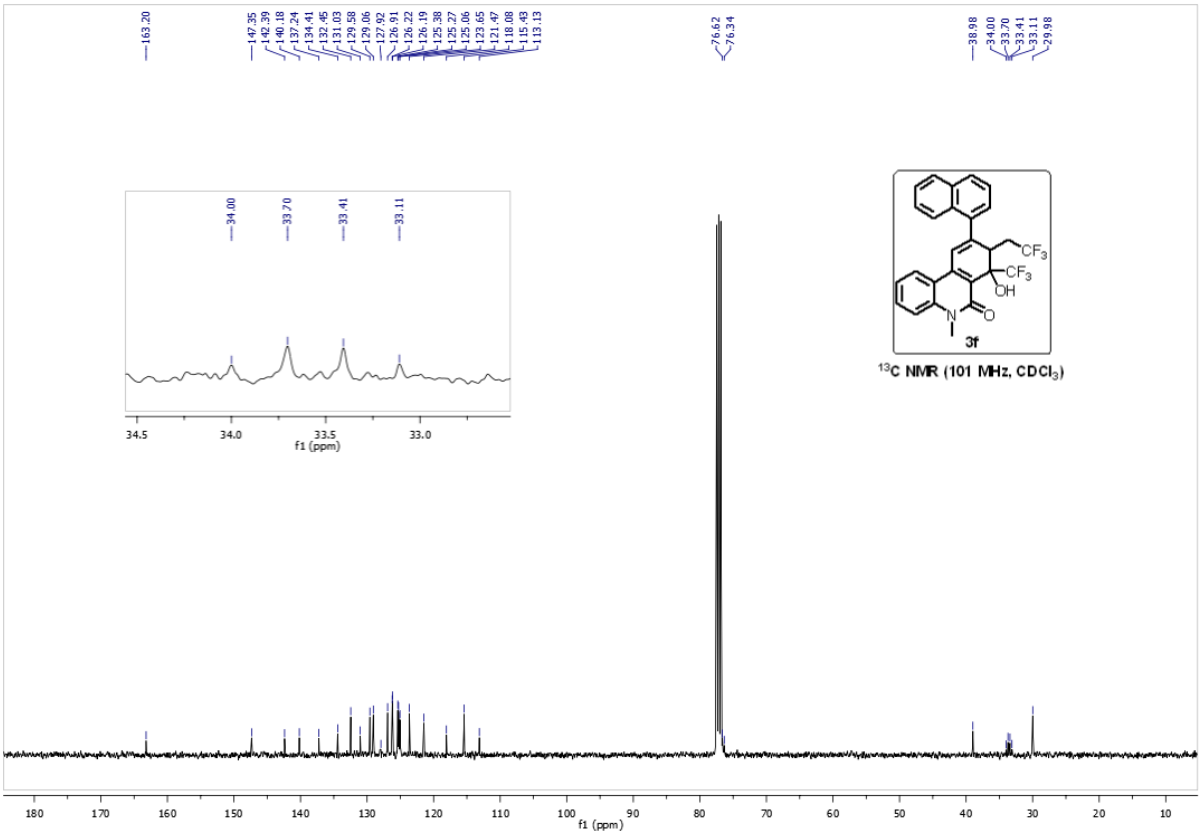
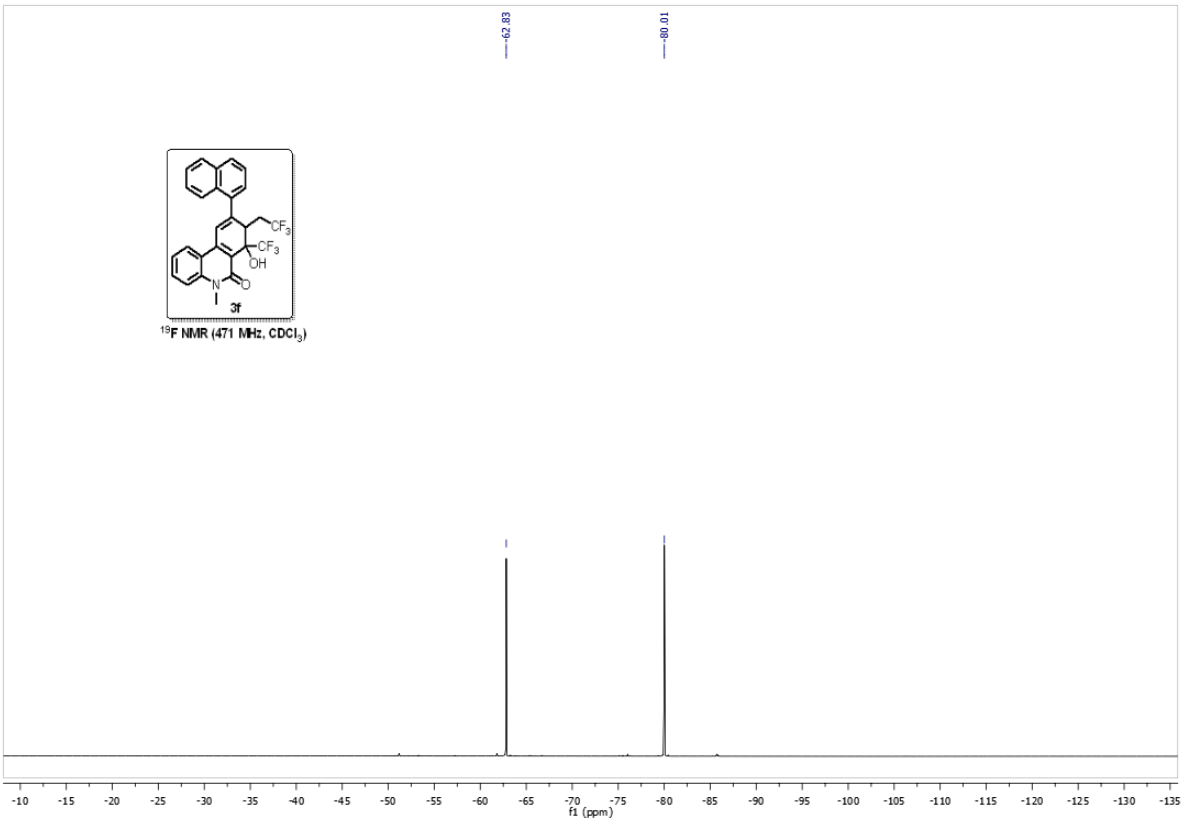
f1 (ppm)



^{13}C NMR (101 MHz, $CDCl_3$)



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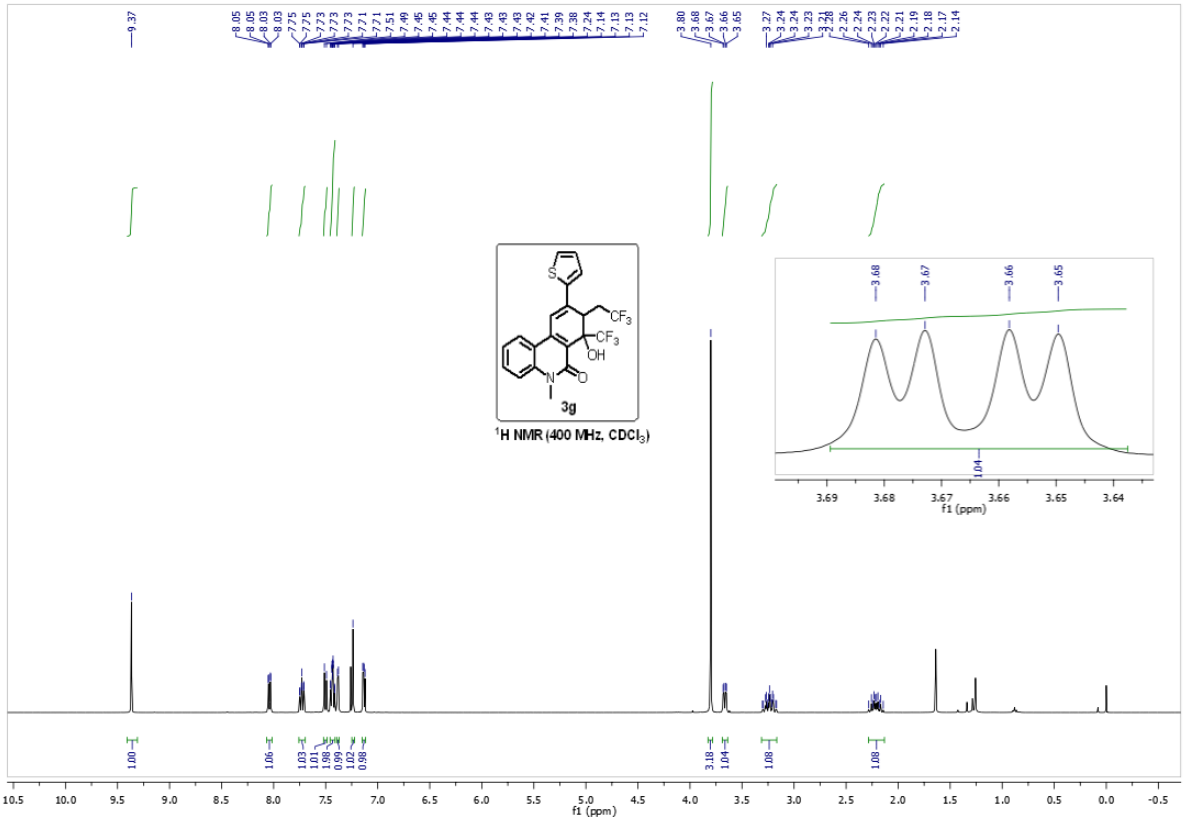
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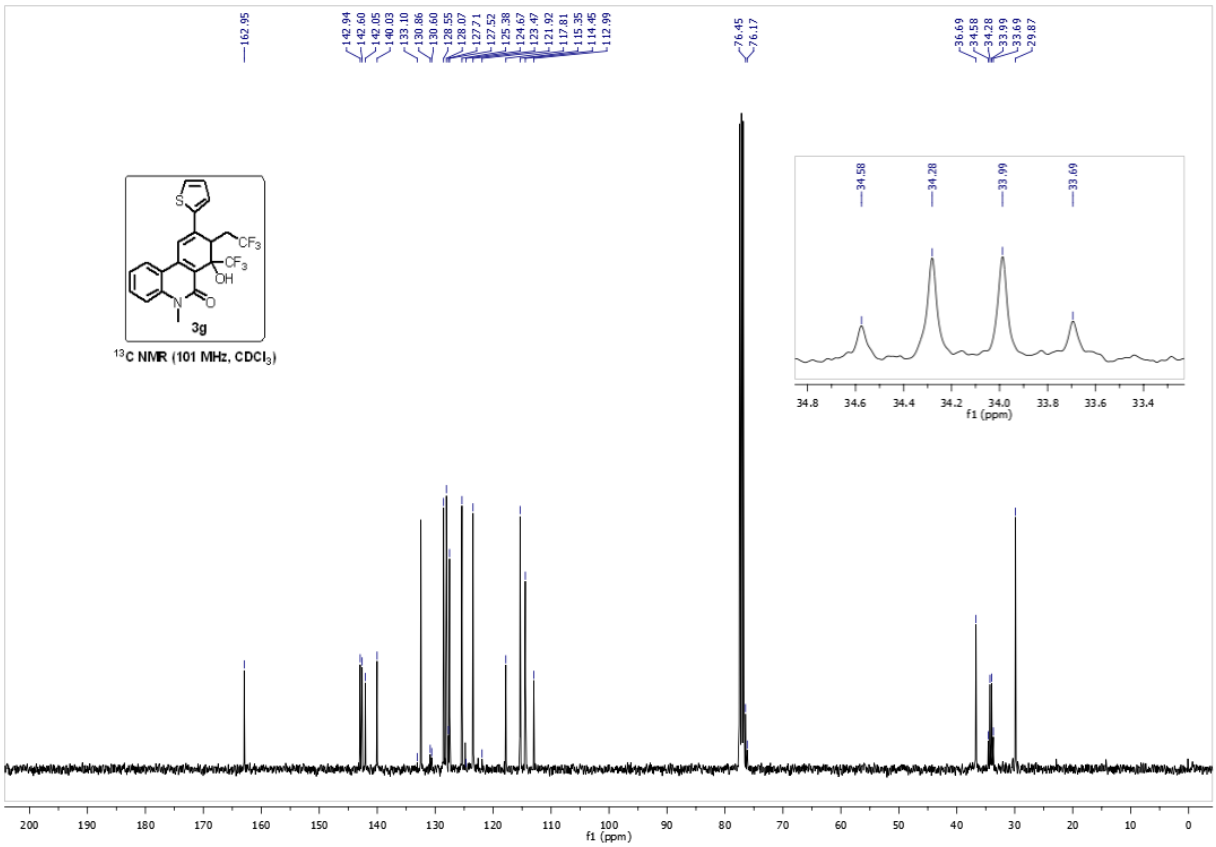
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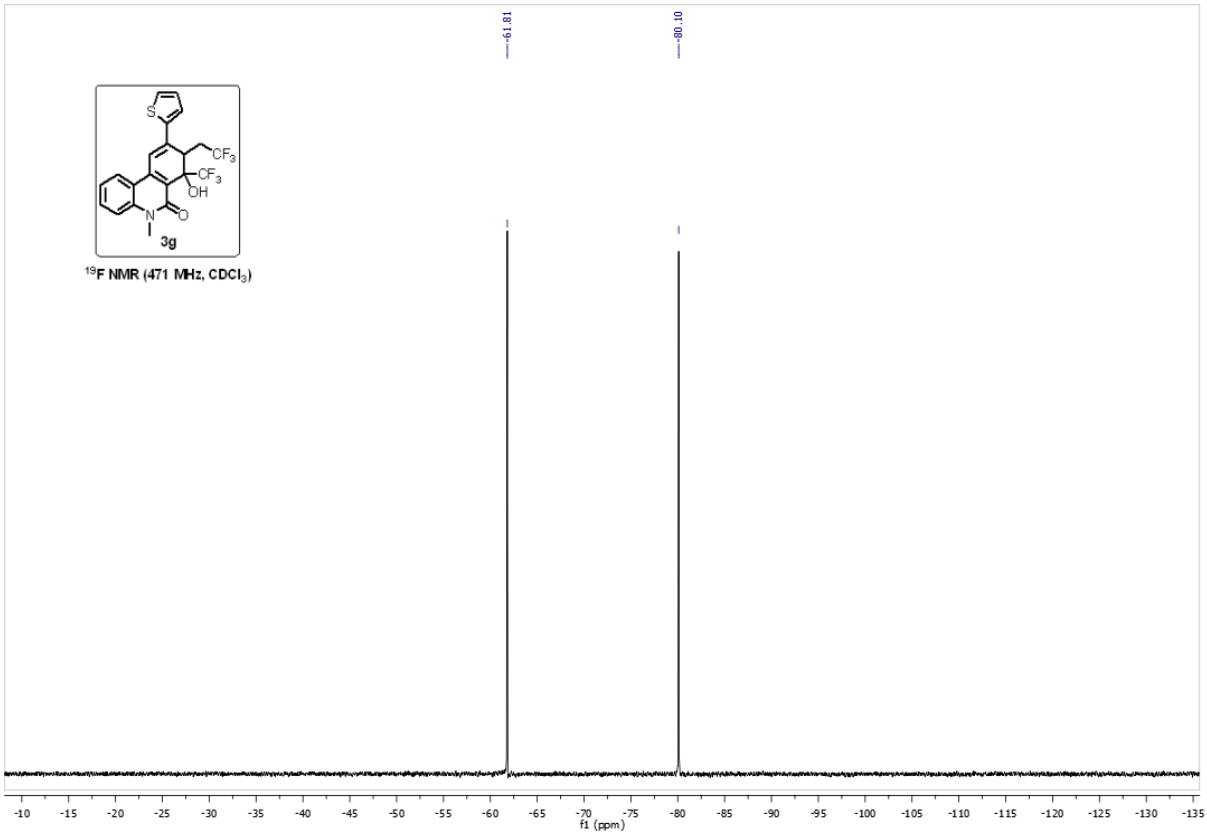
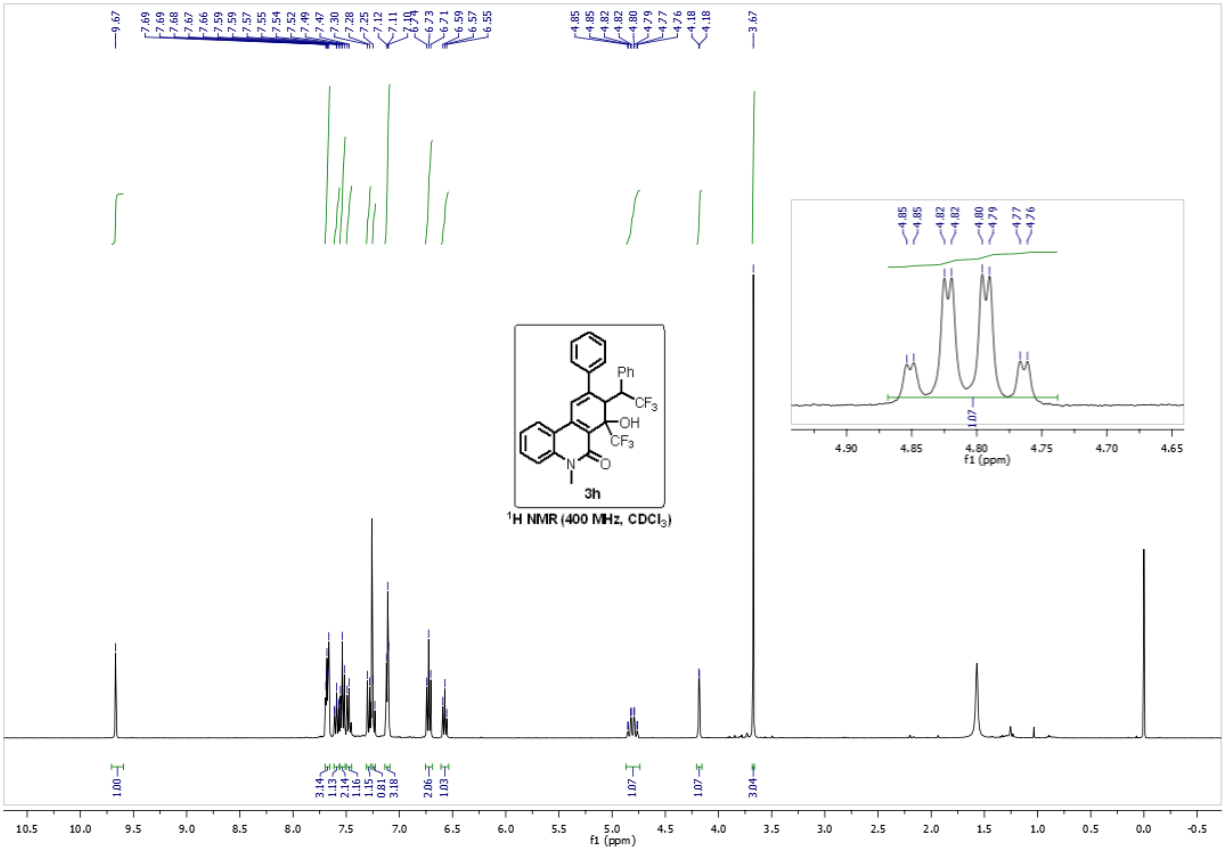

-61.81
-80.10
3g
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)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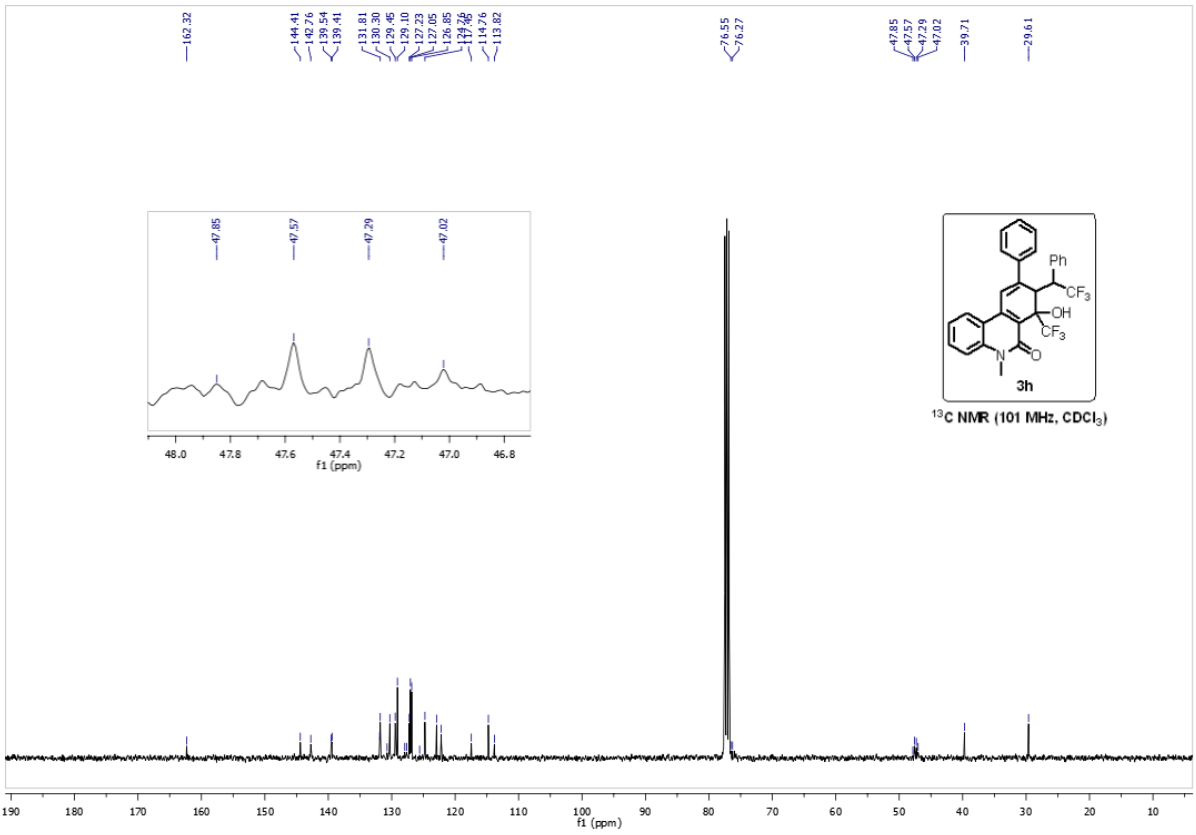
f1 (ppm)



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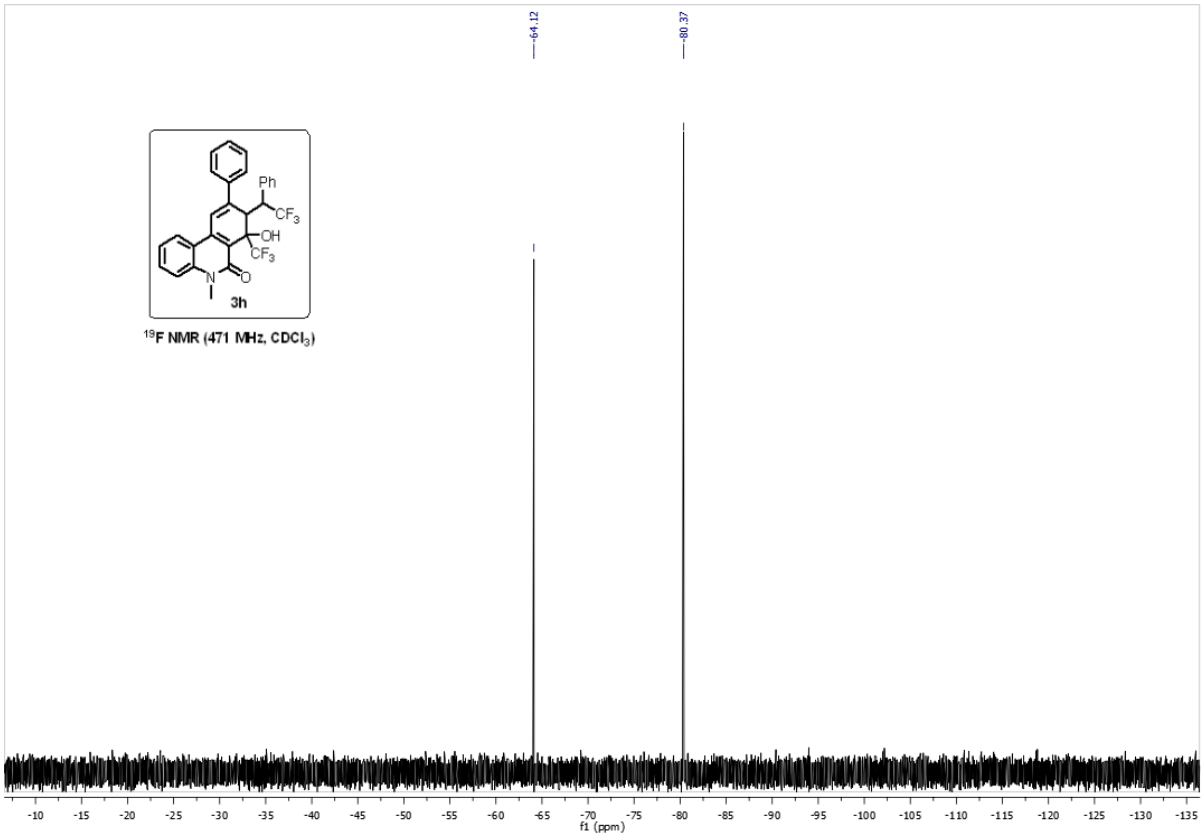
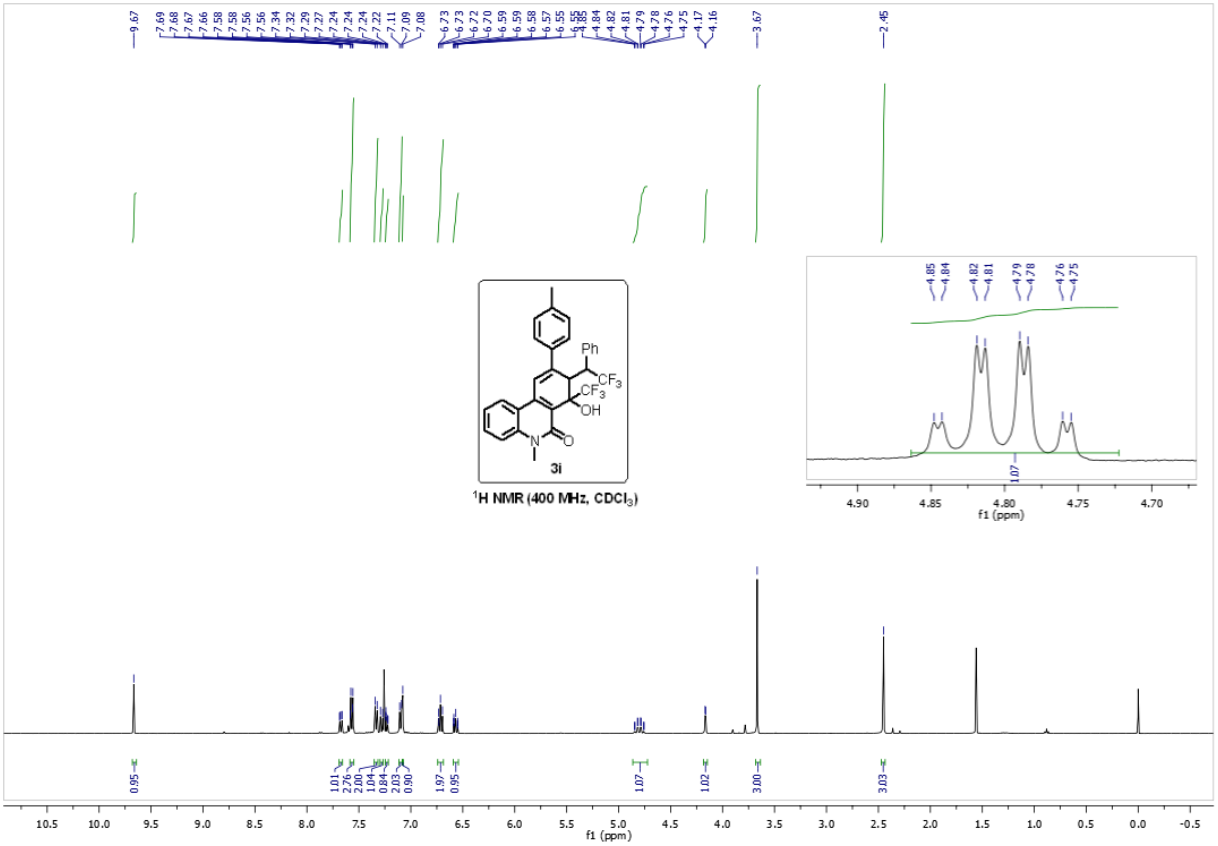


^{19}F NMR (471 MHz, $CDCl_3$)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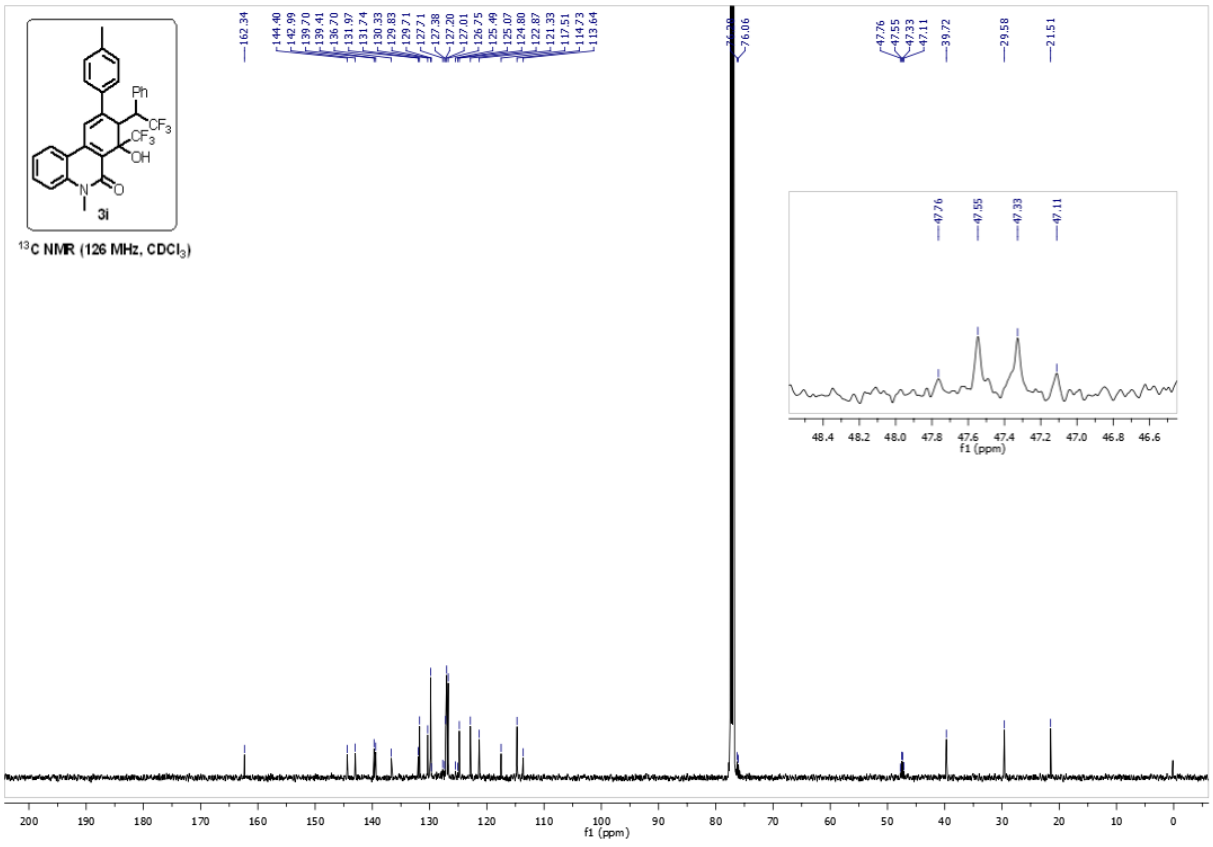
f1 (ppm)


3i
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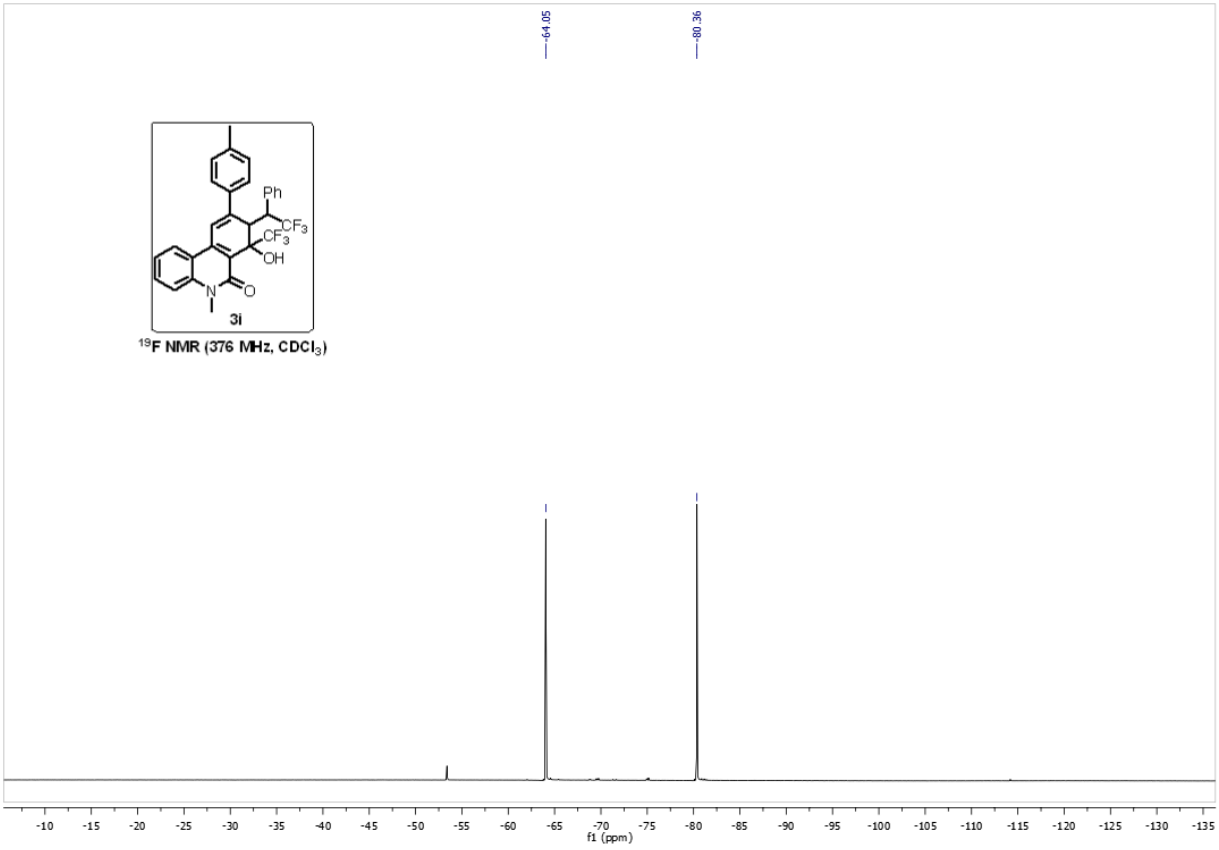
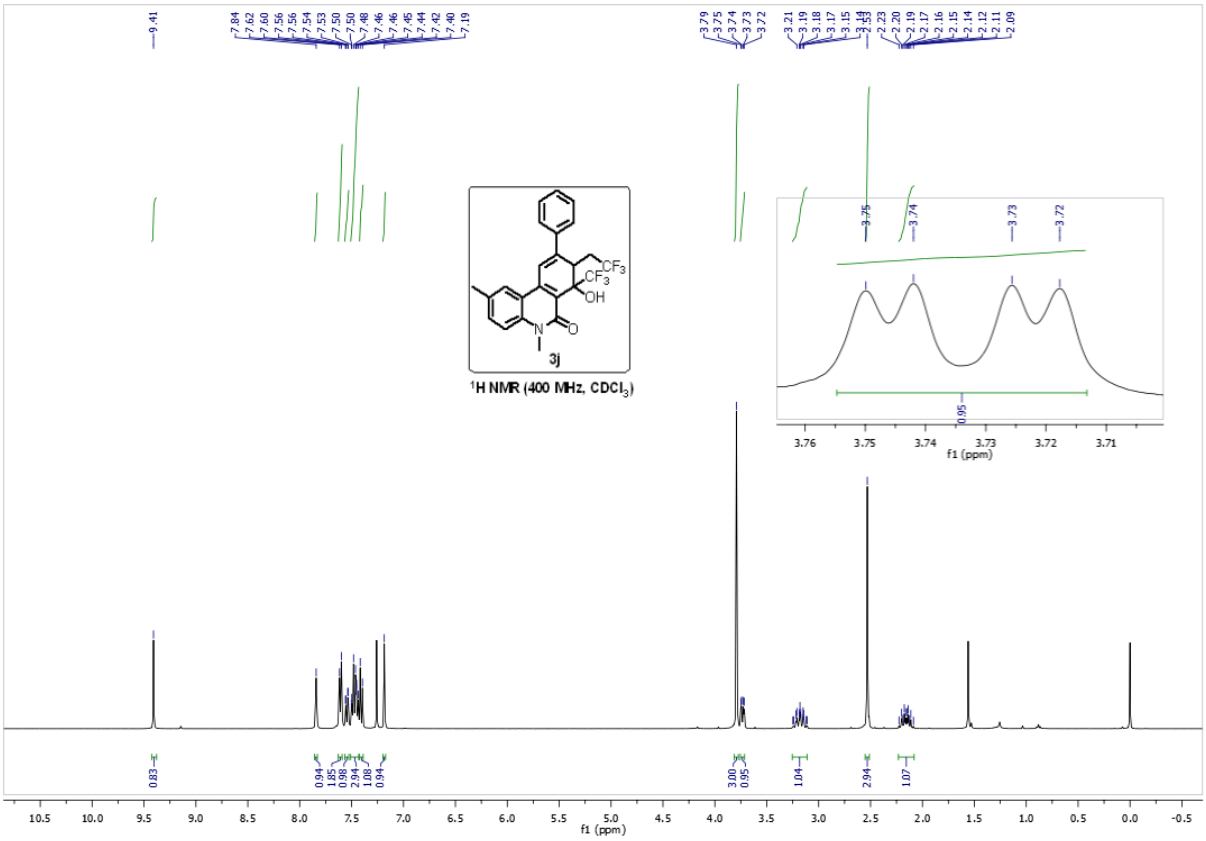
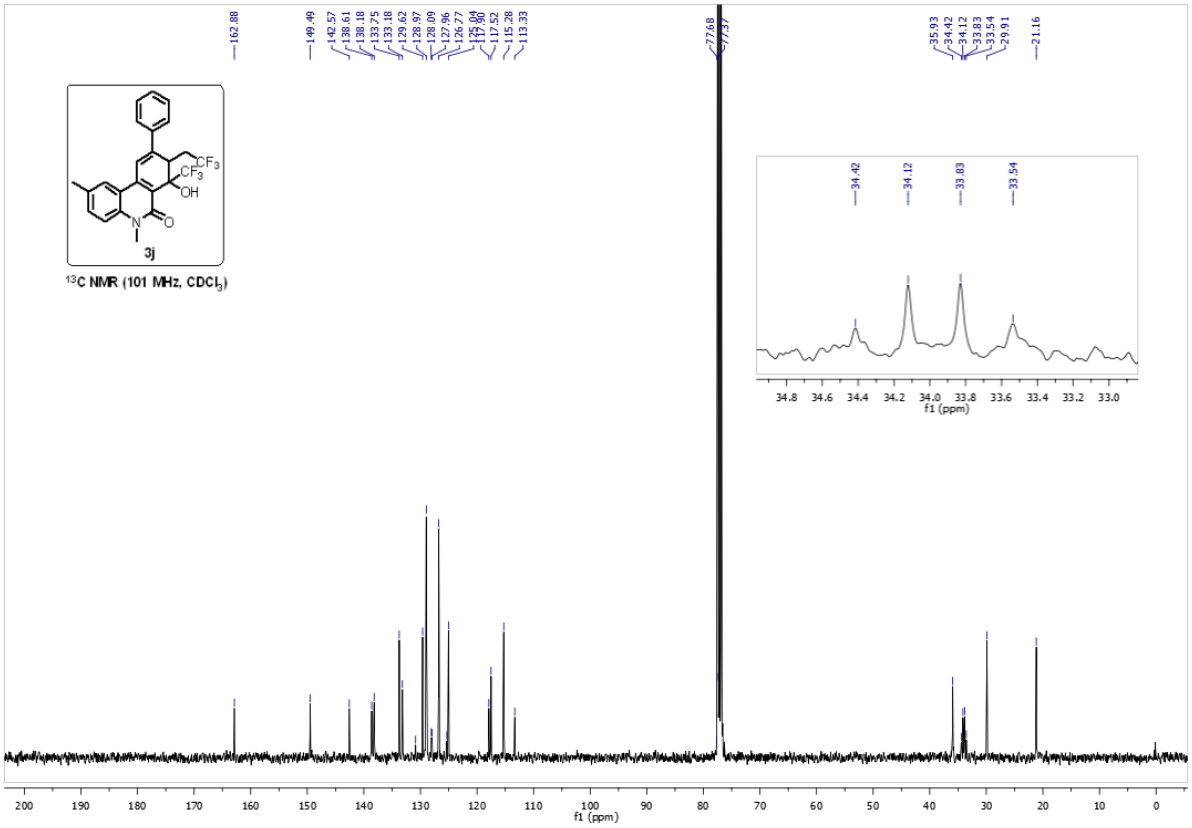
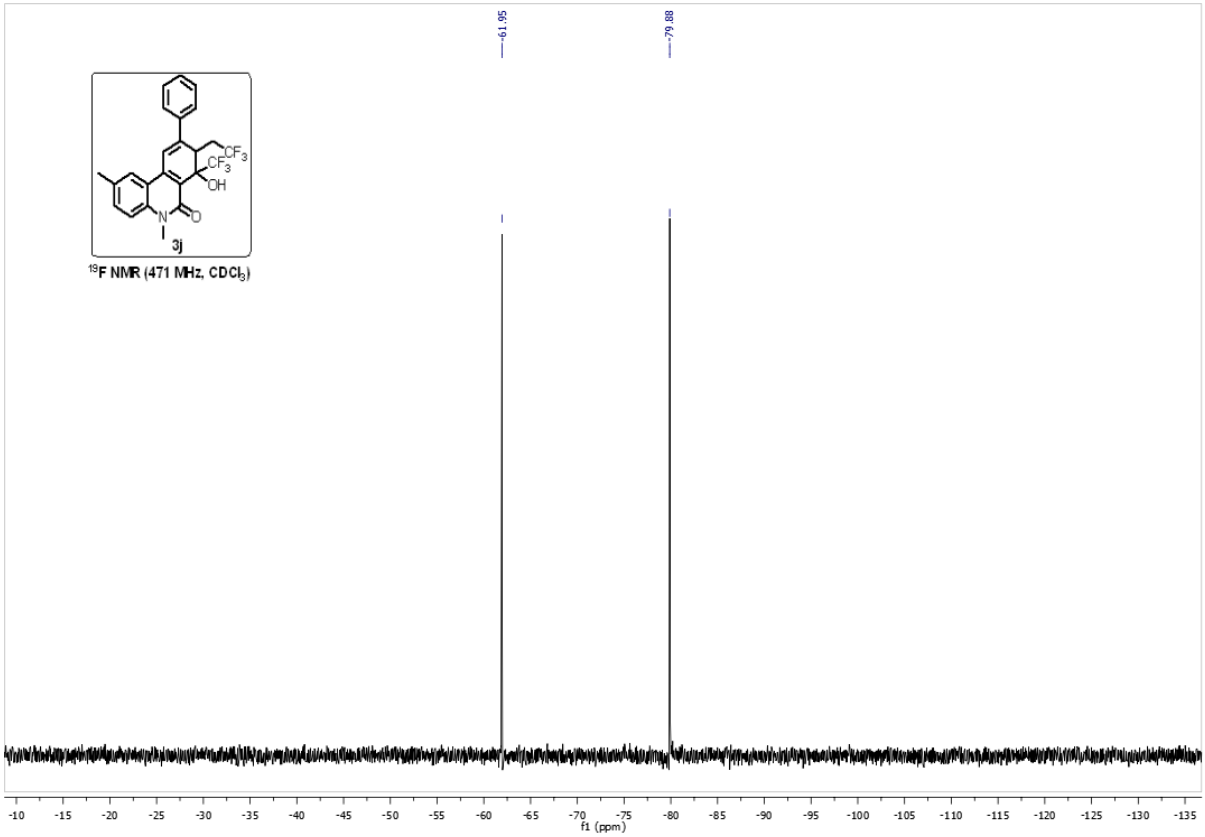
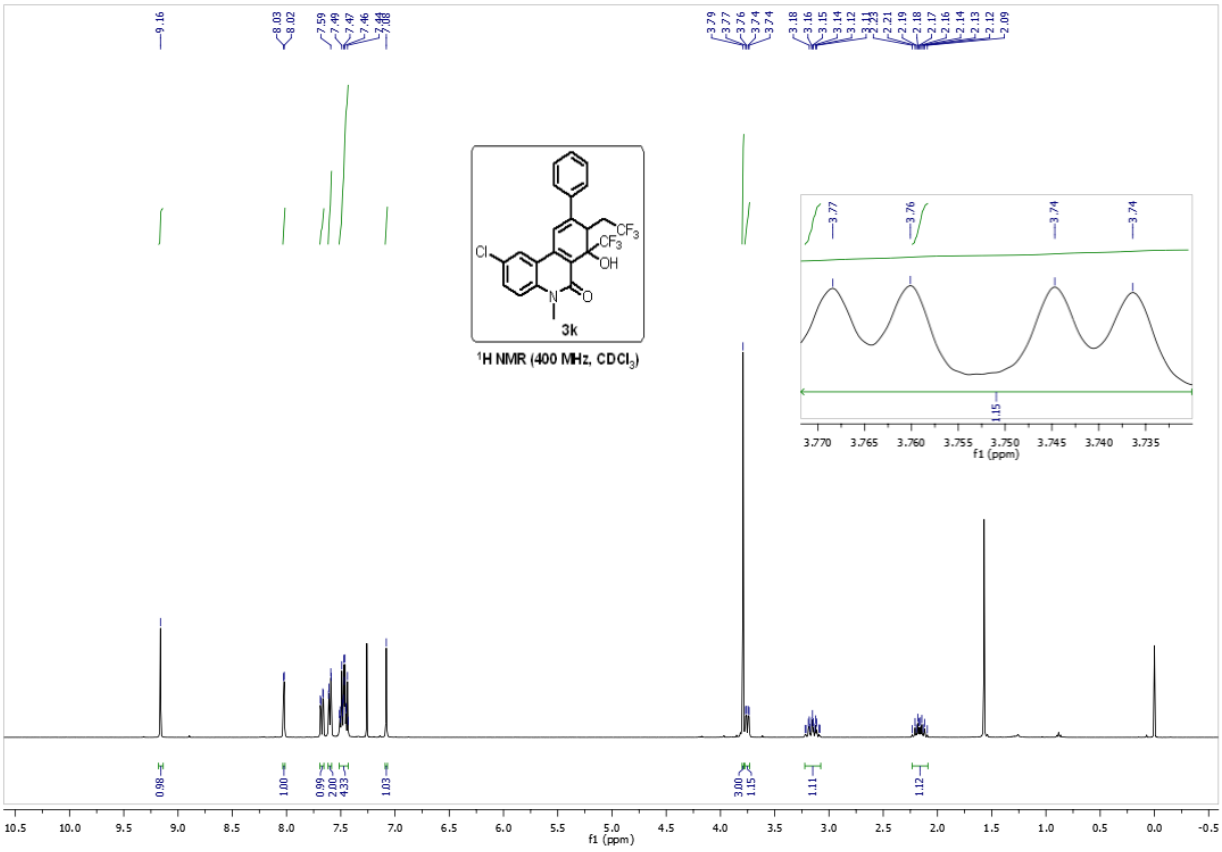
f1 (ppm)

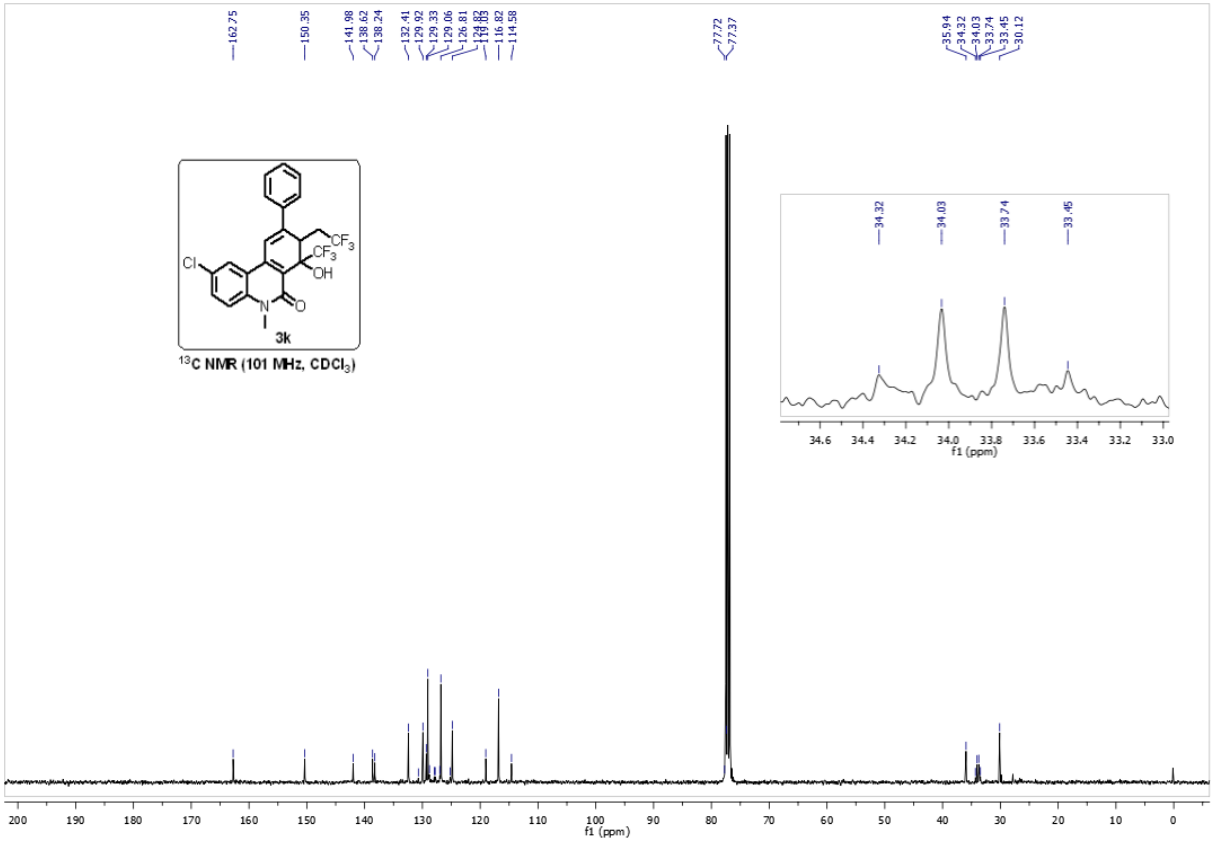

-64.05
-80.36
Ph
CF3
CF3
OH
N
O
3i
19F NMR (376 MHz, CDCl3)
f1 (ppm)

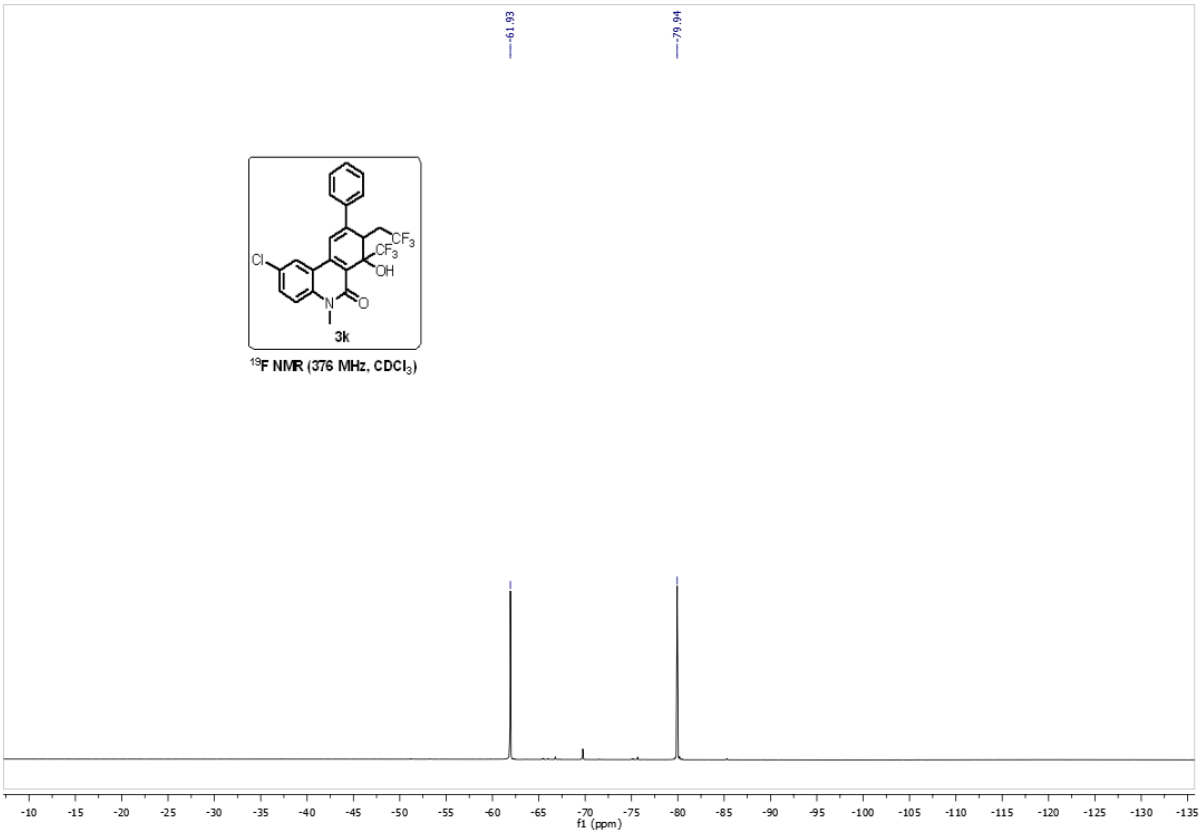

9.41
7.84
7.62
7.60
7.56
7.56
7.54
7.53
7.50
7.50
7.48
7.46
7.45
7.44
7.42
7.40
7.19
3.79
3.75
3.74
3.73
3.72
3.21
3.19
3.18
3.17
3.15
2.23
2.20
2.19
2.17
2.16
2.15
2.14
2.12
2.11
2.09
CF3
CF3
OH
N
O
3j
1H NMR (400 MHz, CDCl3)
3.75
3.74
3.73
3.72
0.95
f1 (ppm)
0.83
0.94
1.85
0.98
2.94
1.08
0.94
3.00
0.95
1.04
2.94
1.07
f1 (ppm)

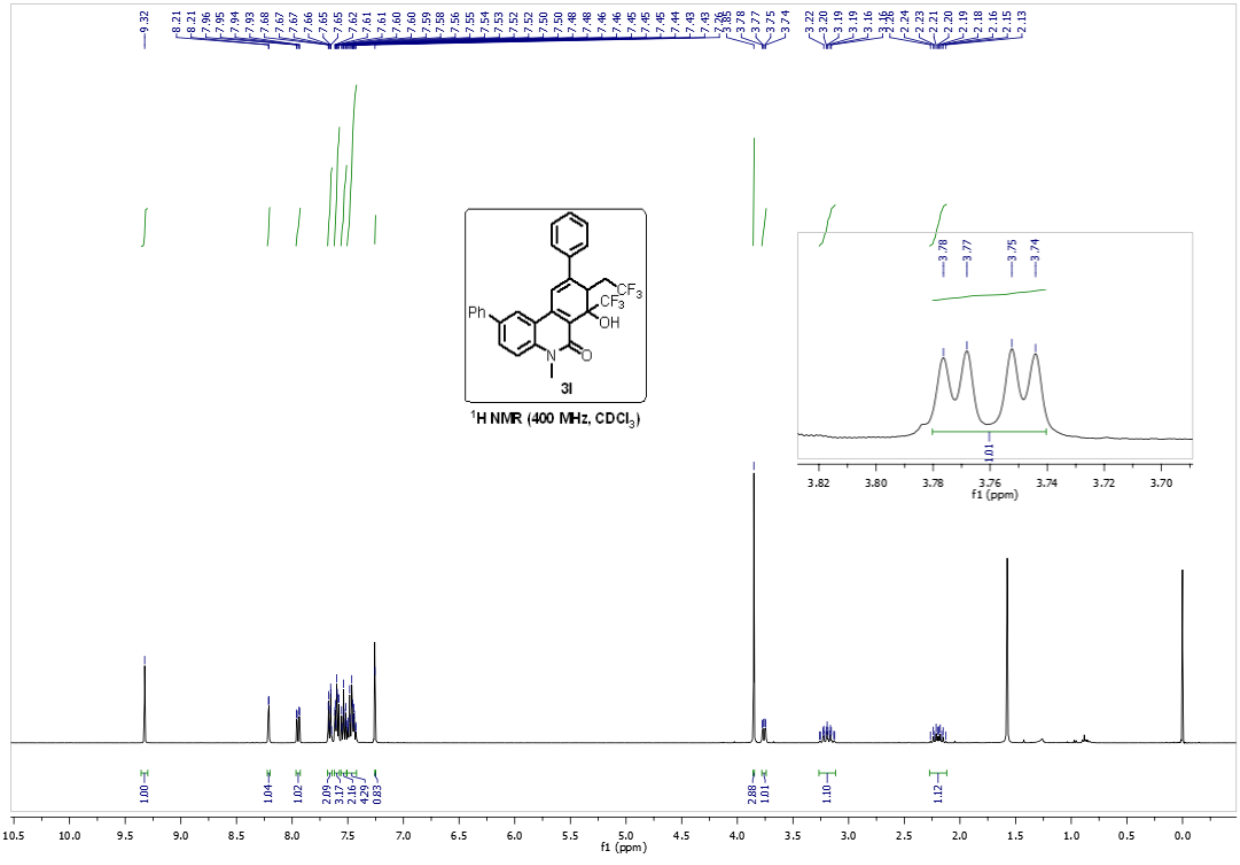

3j
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

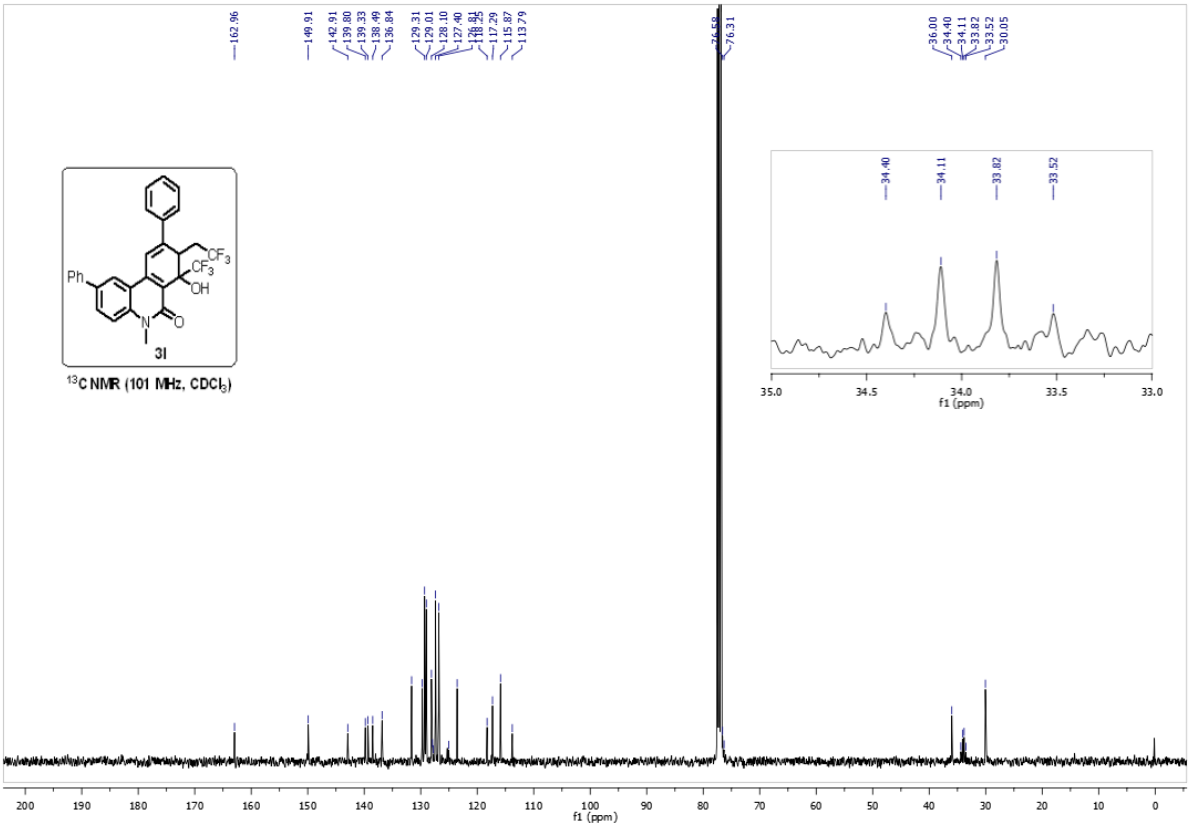

3j
^{19}F NMR (471 MHz, CDCl$_3$)
f1 (ppm)


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

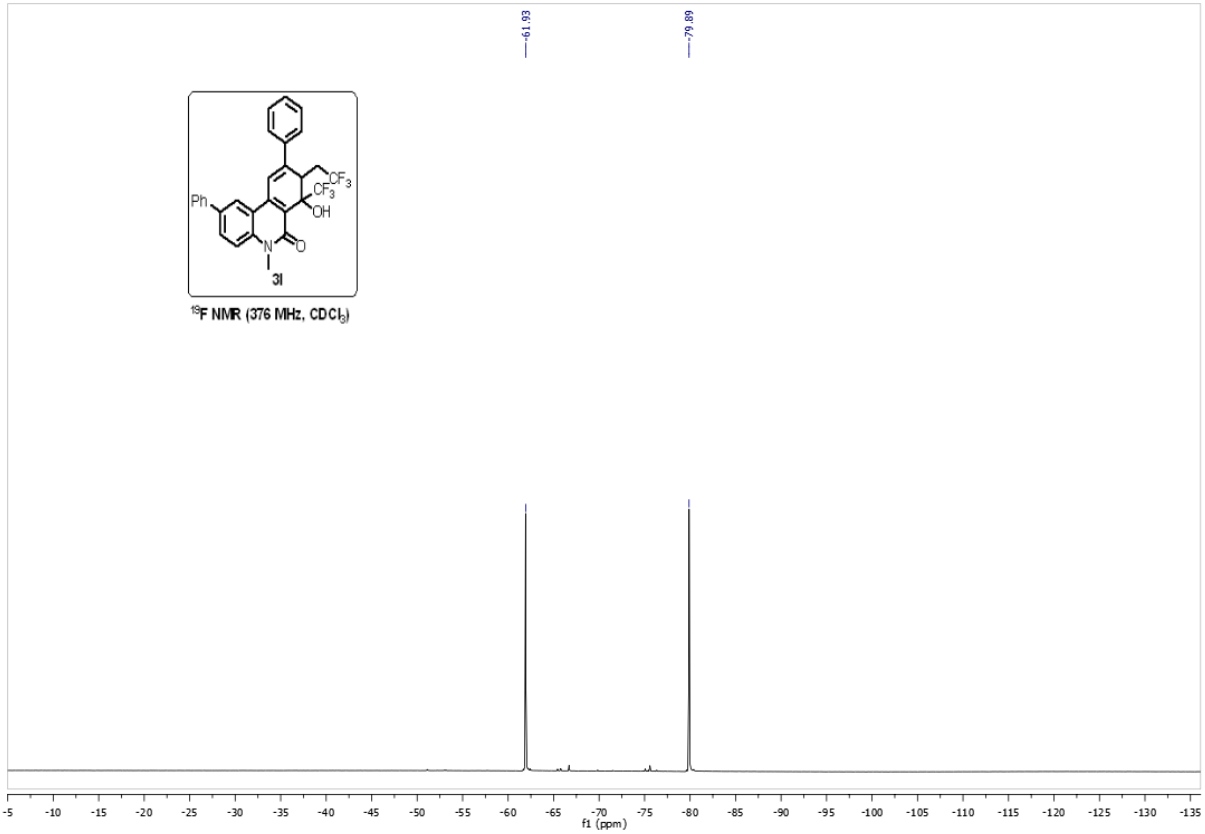

3k
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


-61.93
-79.94
3k
^{19}F NMR (376 MHz, $CDCl_3$)
f1 (ppm)

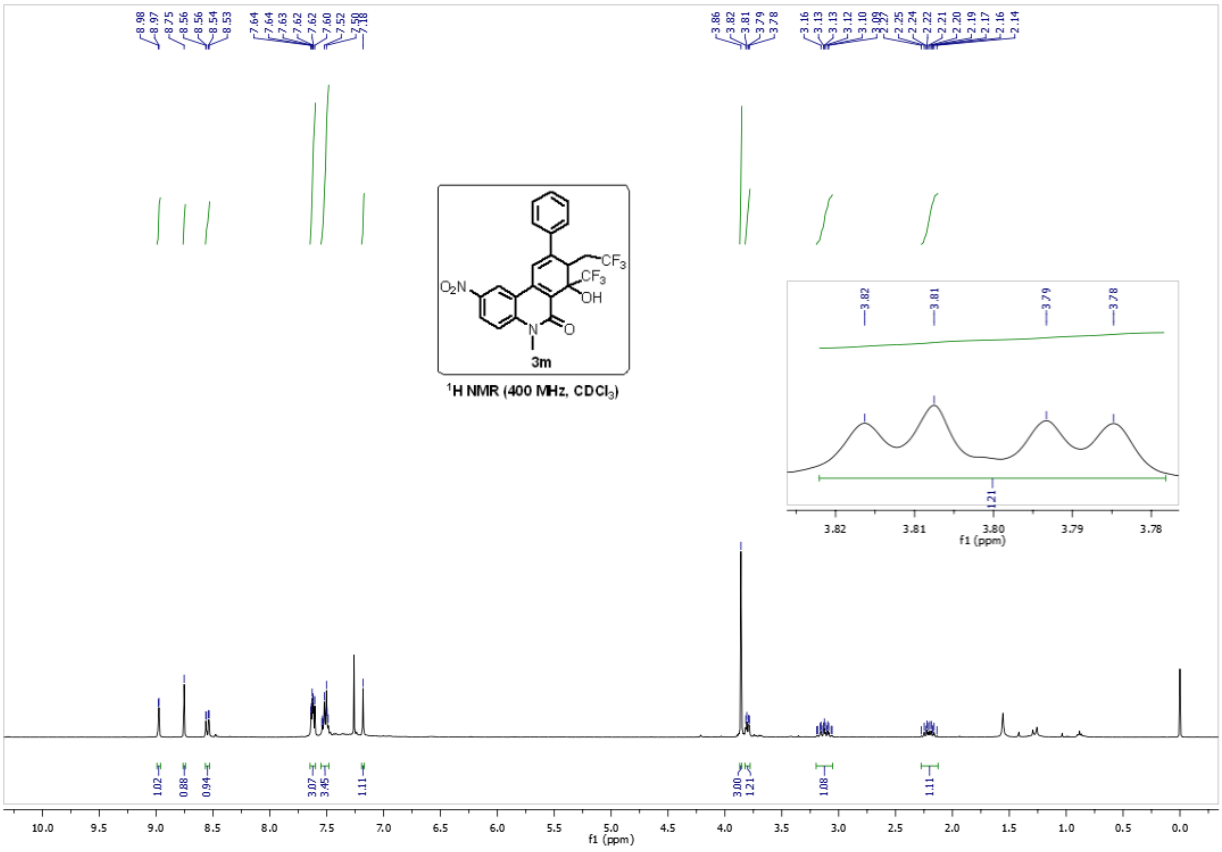

3l
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

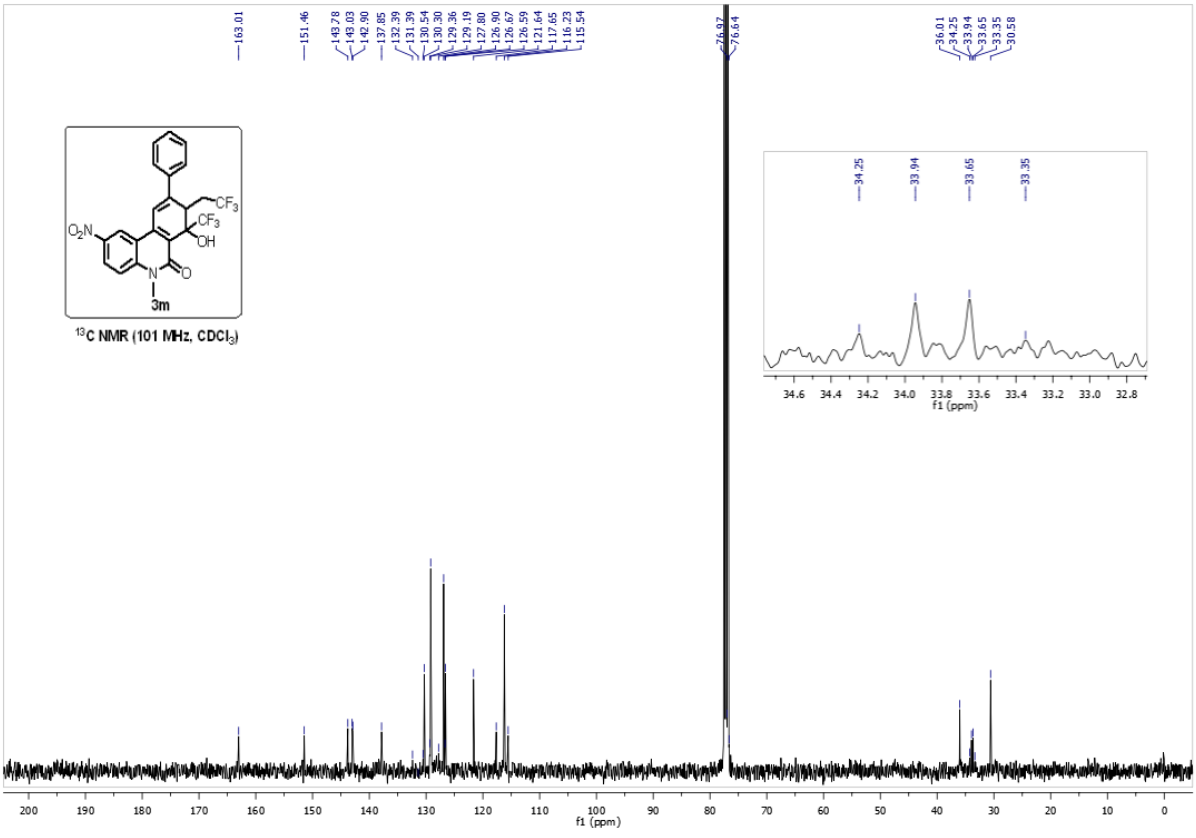


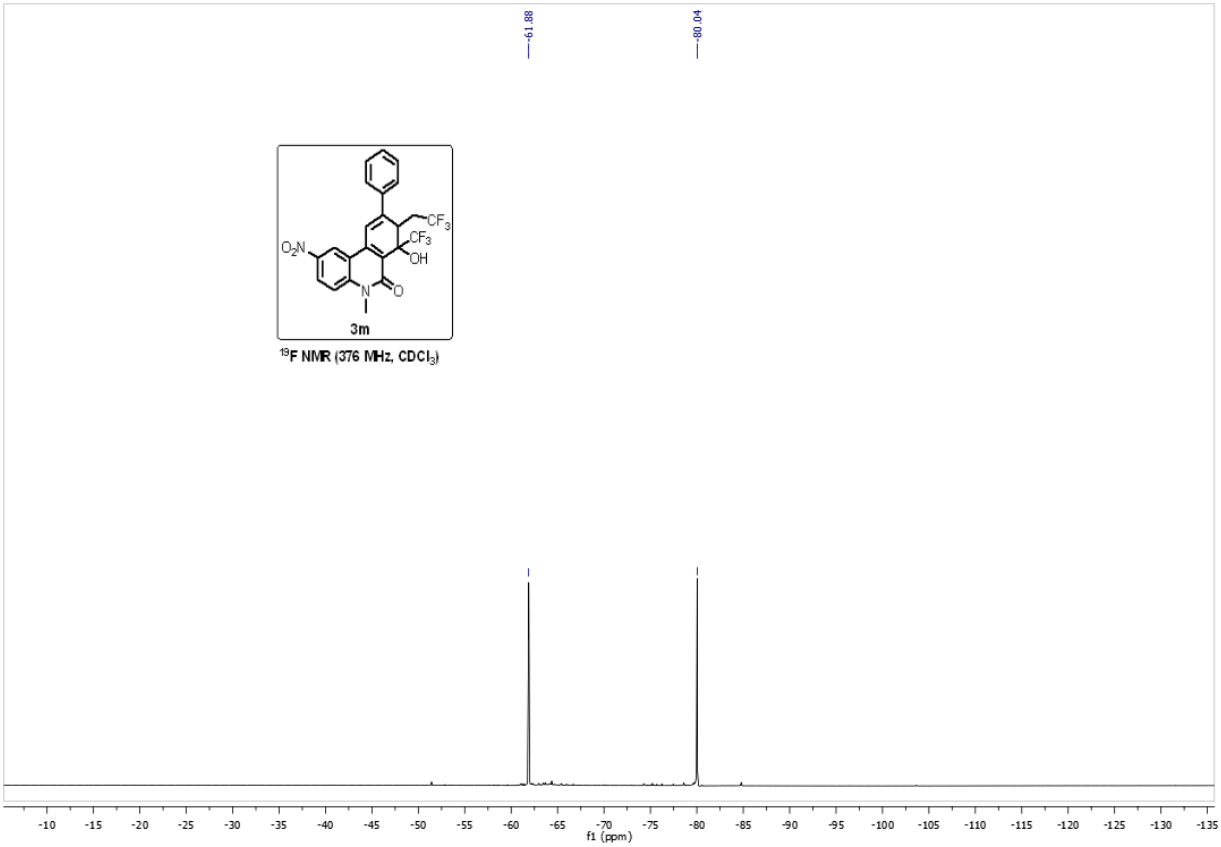
^{13}C NMR (101 MHz, $CDCl_3$)

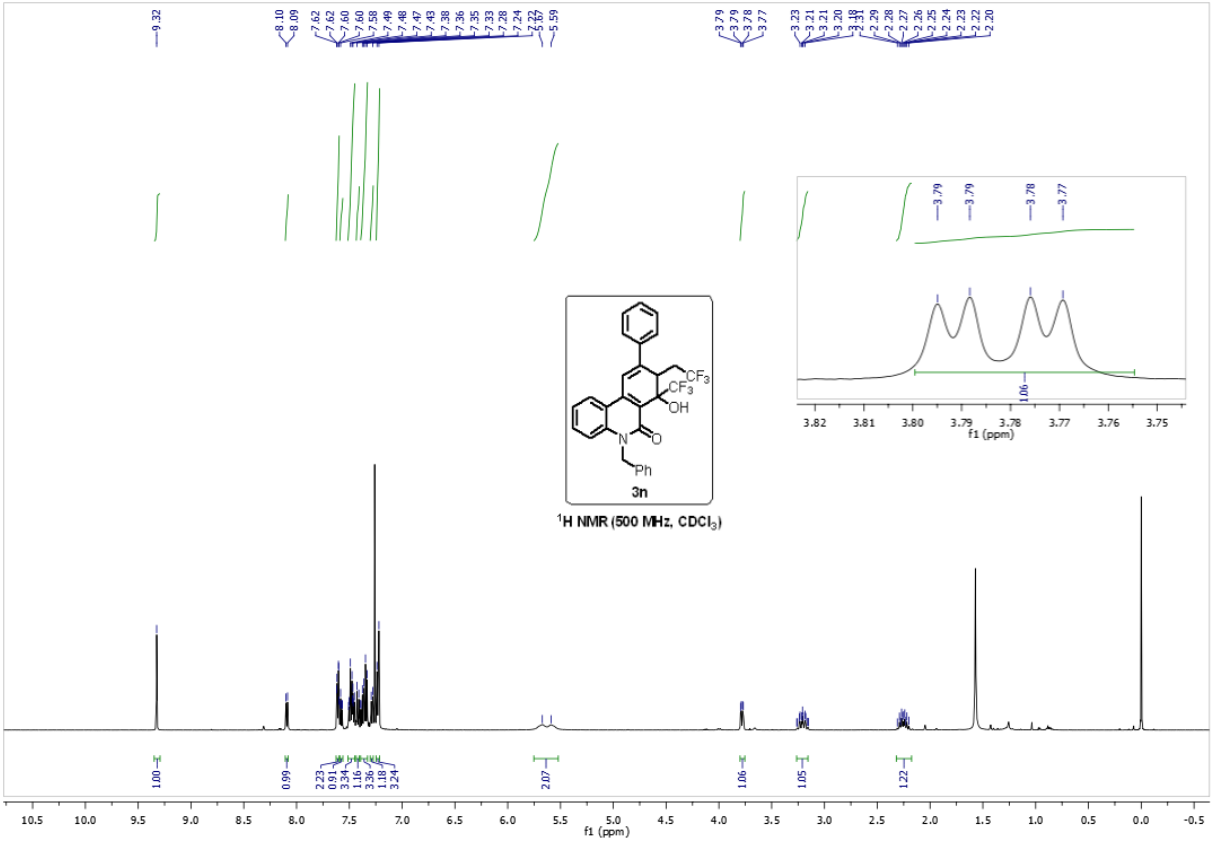


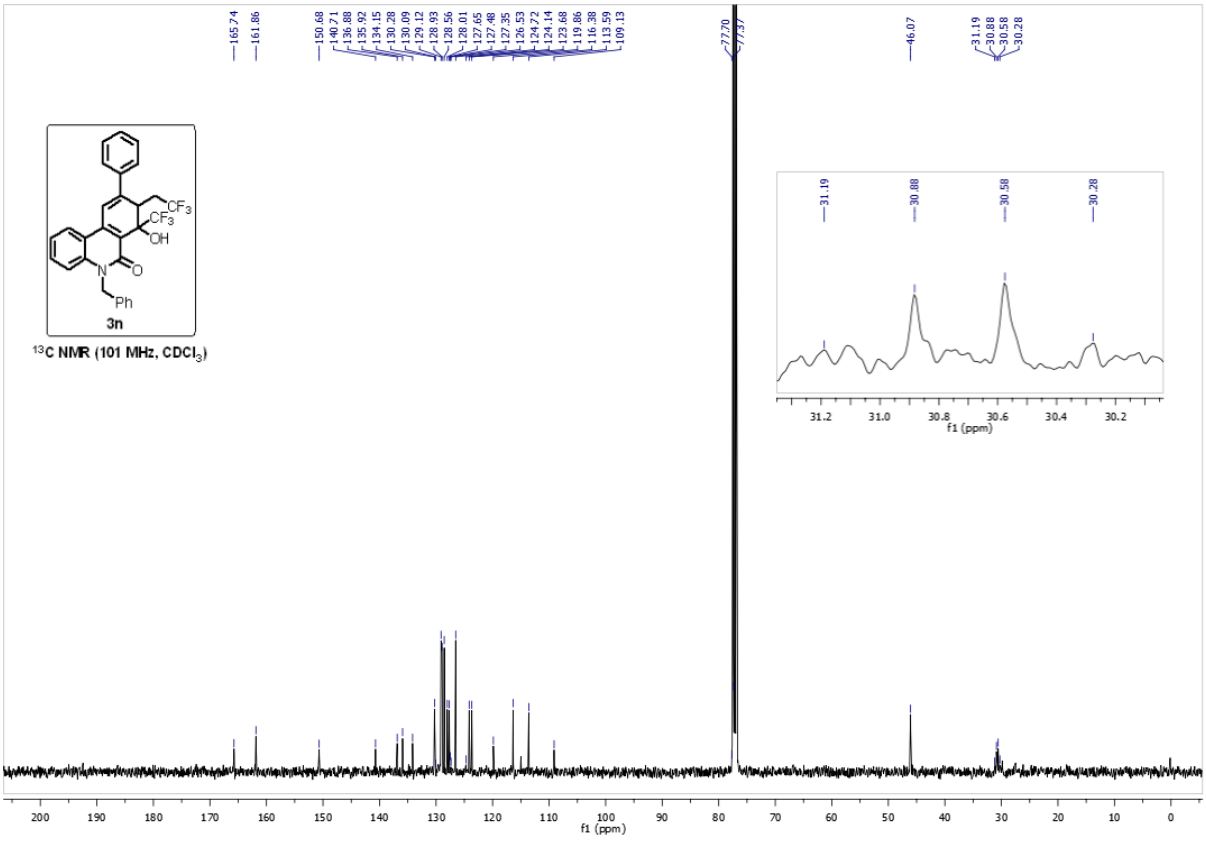
^{19}F NMR (376 MHz, $CDCl_3$)

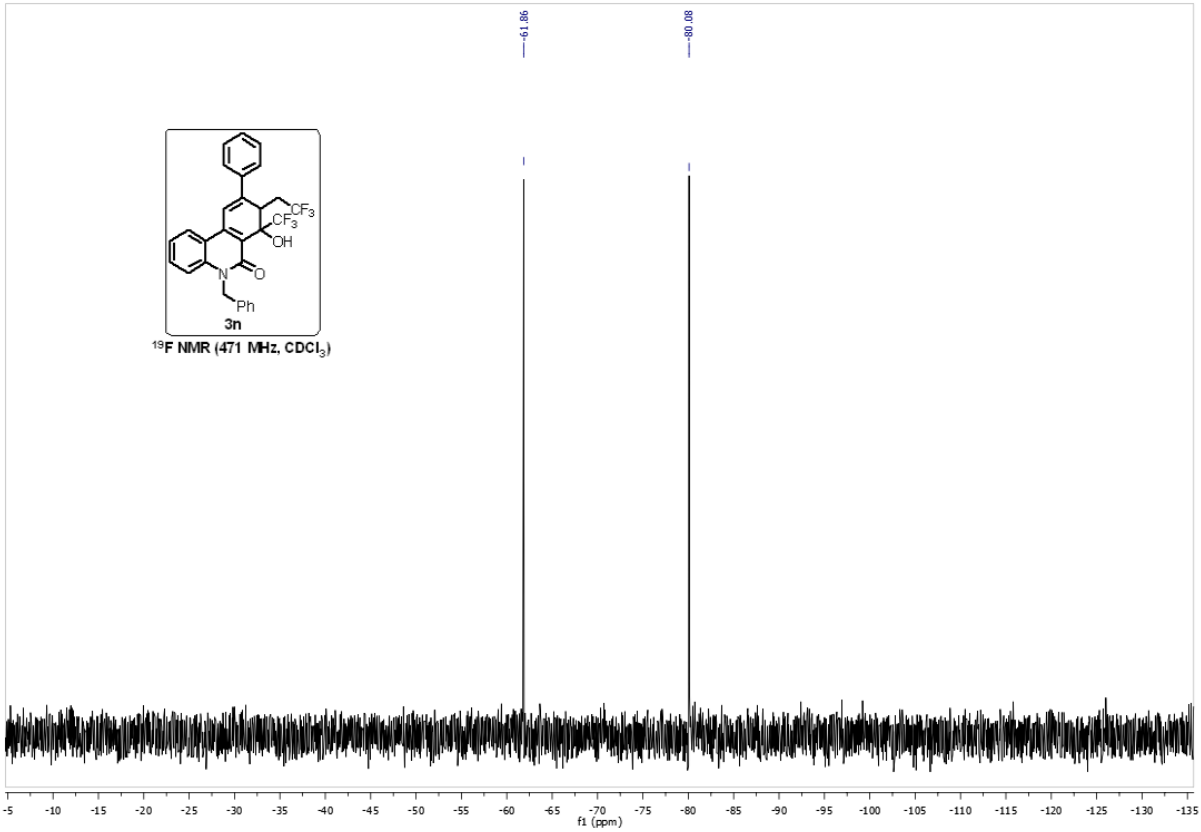

3m
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

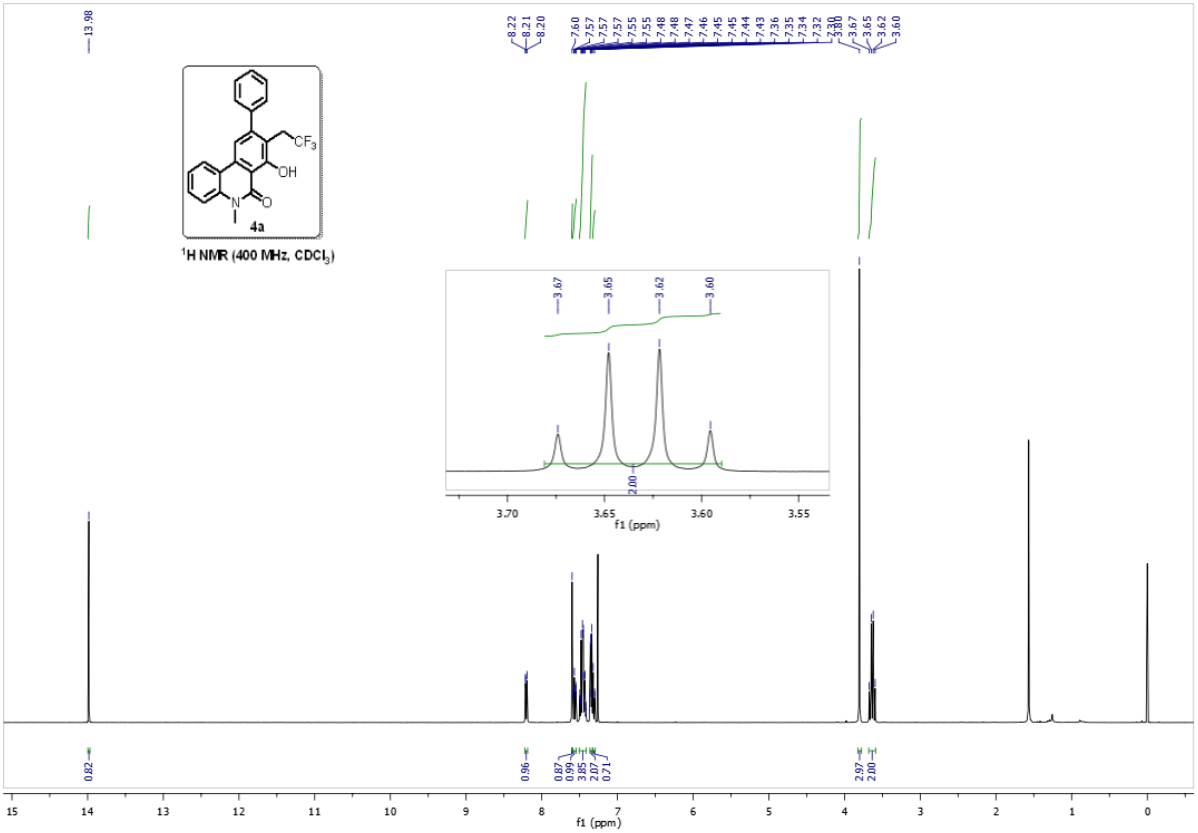

3m
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

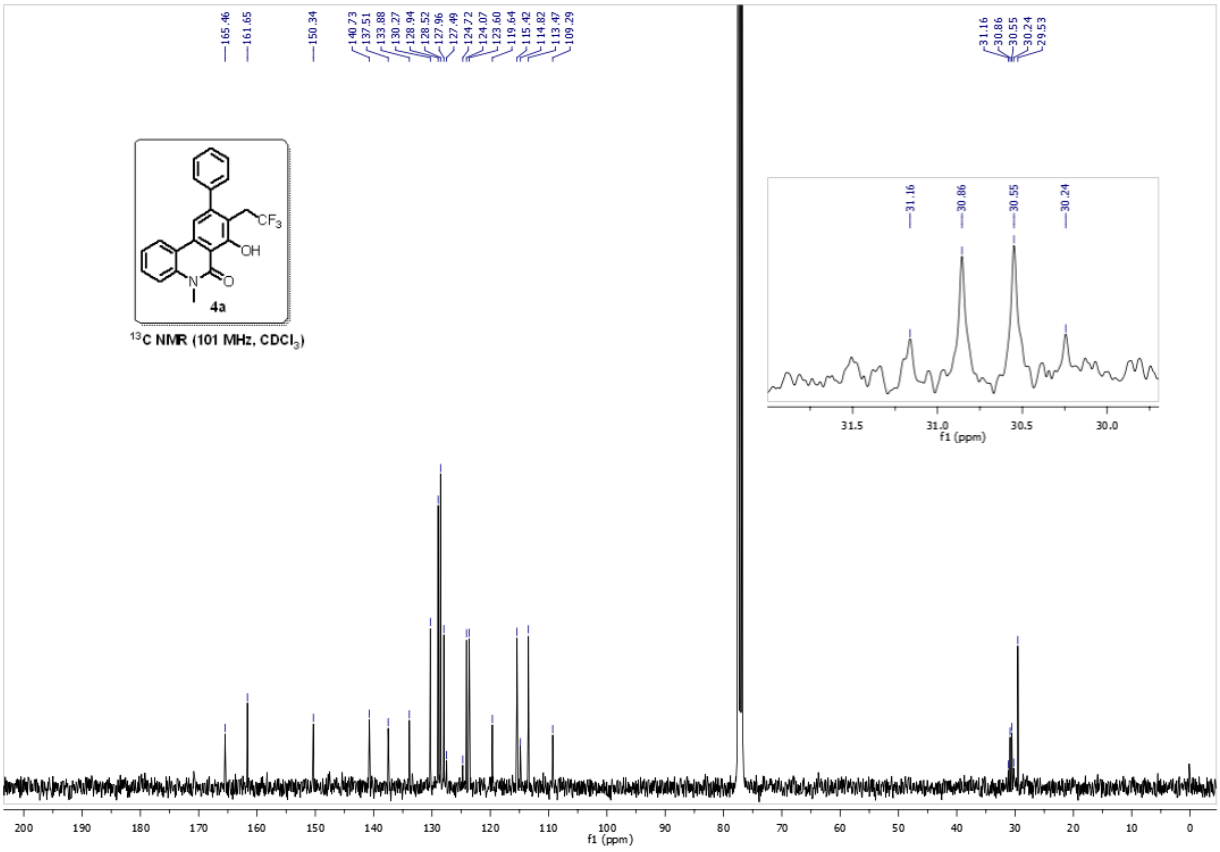

-61.88
-80.04
3m
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)

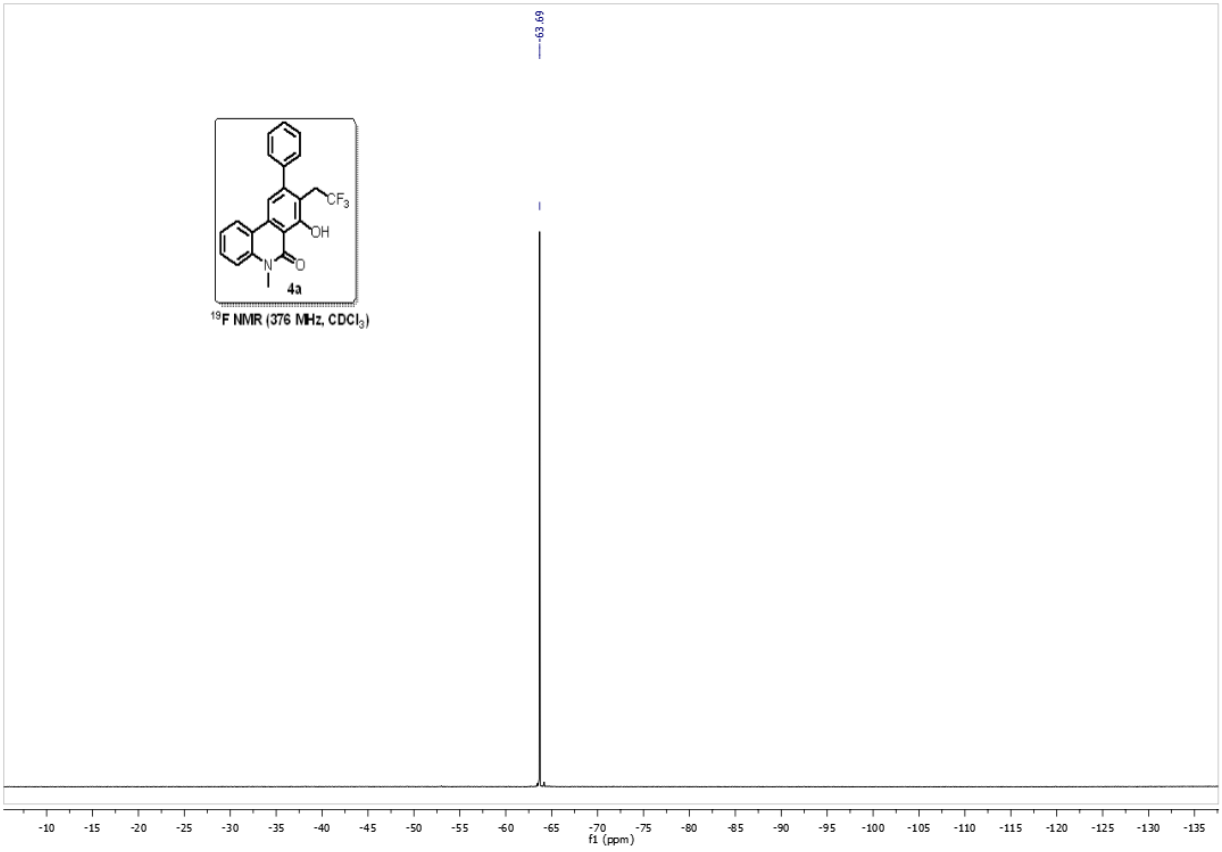

3n
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

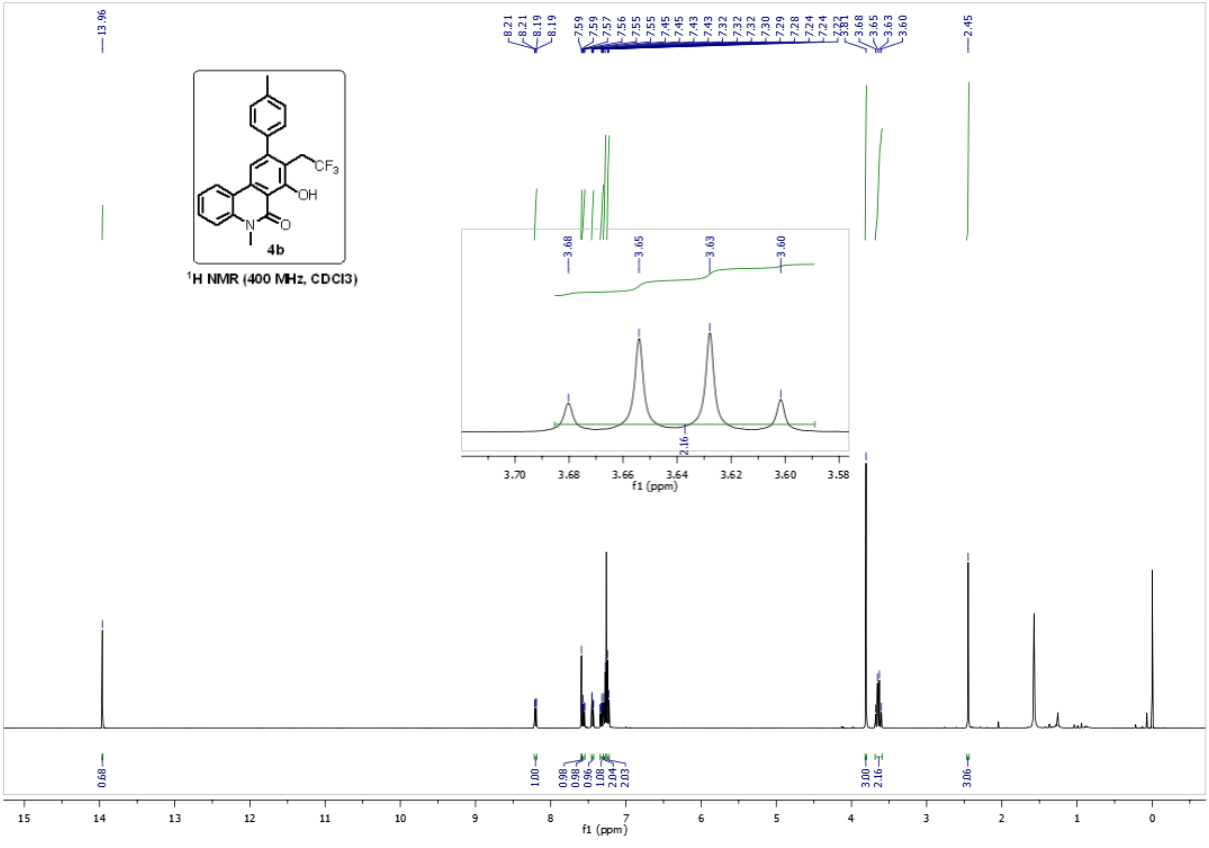

165.74
161.86
150.68
140.71
136.88
135.92
134.15
130.28
130.09
129.12
128.93
128.56
128.01
127.65
127.48
127.35
126.53
124.72
124.14
123.68
119.86
116.38
113.59
109.13
77.70
77.37
46.07
31.19
30.88
30.58
30.28
CF3
CF3
OH
N
O
Ph
3n
13C NMR (101 MHz, CDCl3)
f1 (ppm)

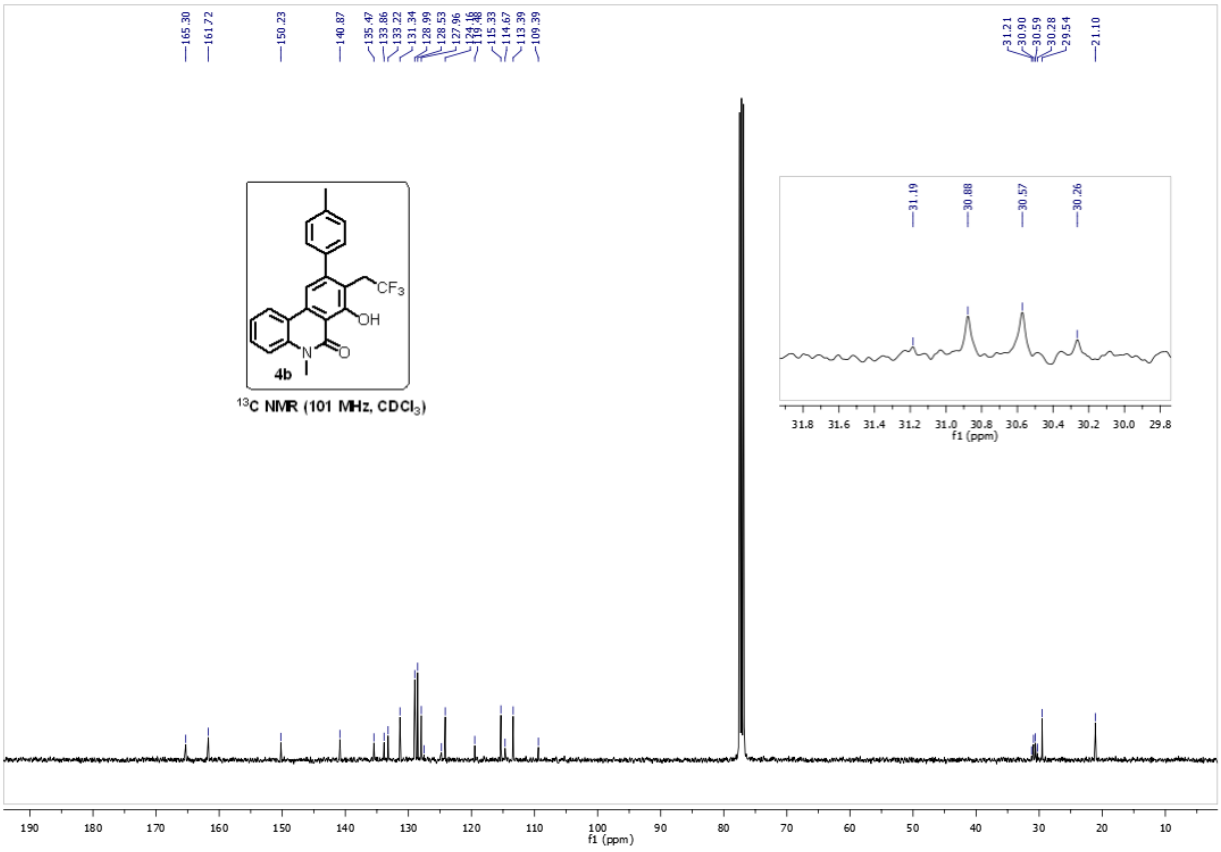

-61.86
-80.08
CF3
CF3
OH
N
O
Ph
3n
19F NMR (471 MHz, CDCl3)
f1 (ppm)

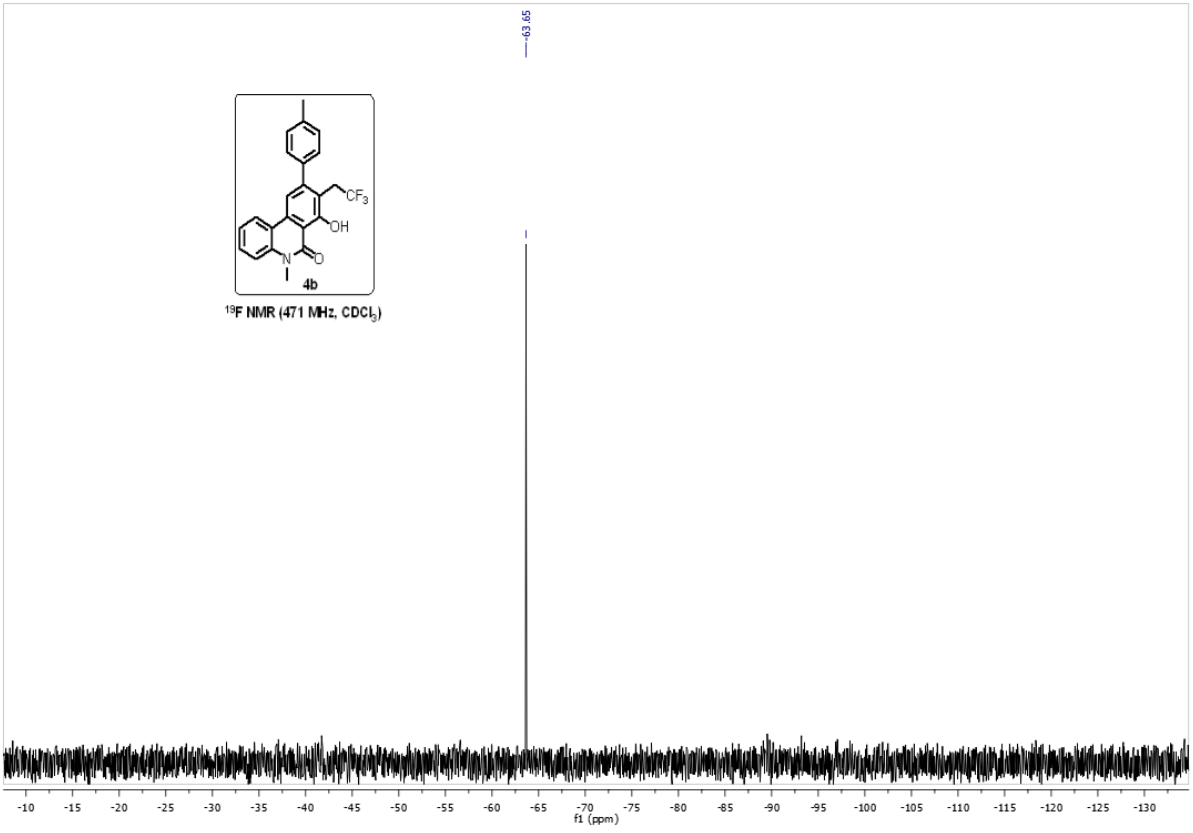

4a
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

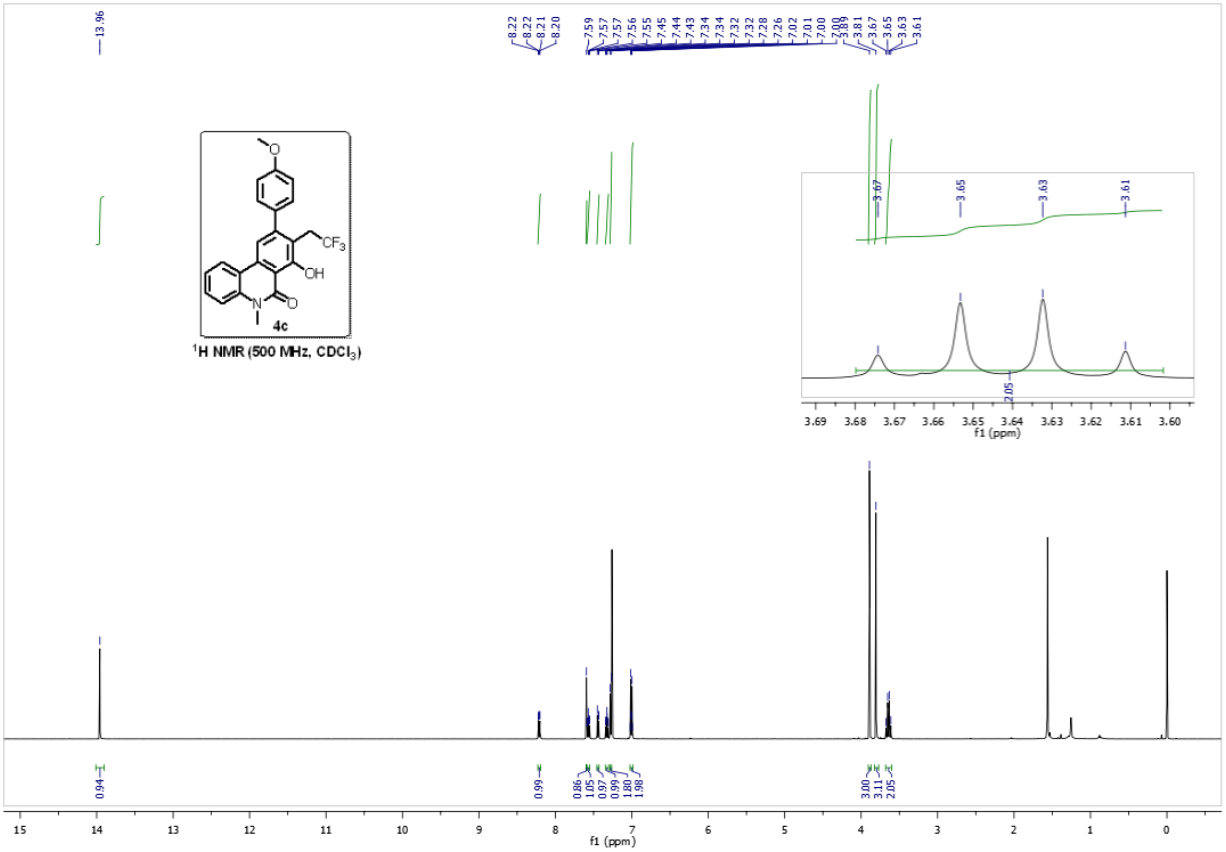

4a
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

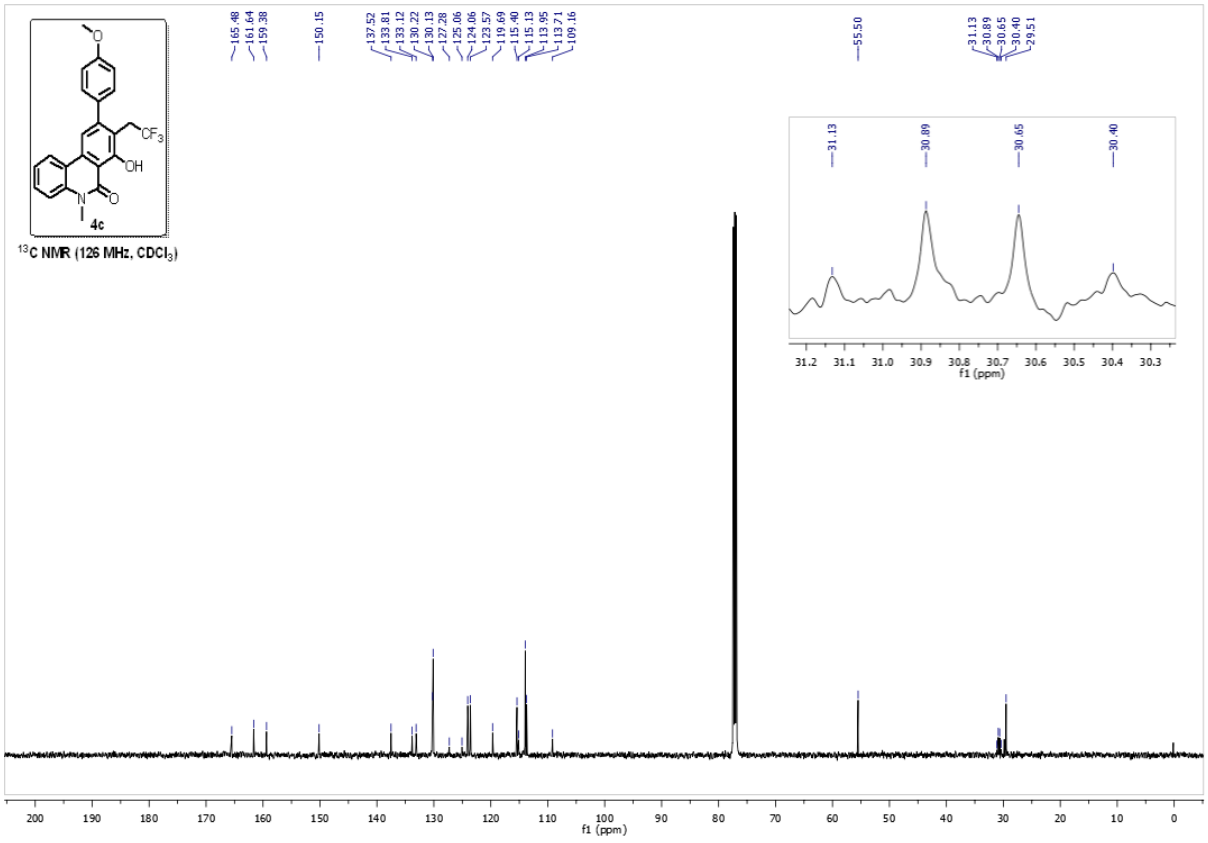

-63.69
CF3
OH
O
N
4a
19F NMR (376 MHz, CDCl3)
f1 (ppm)

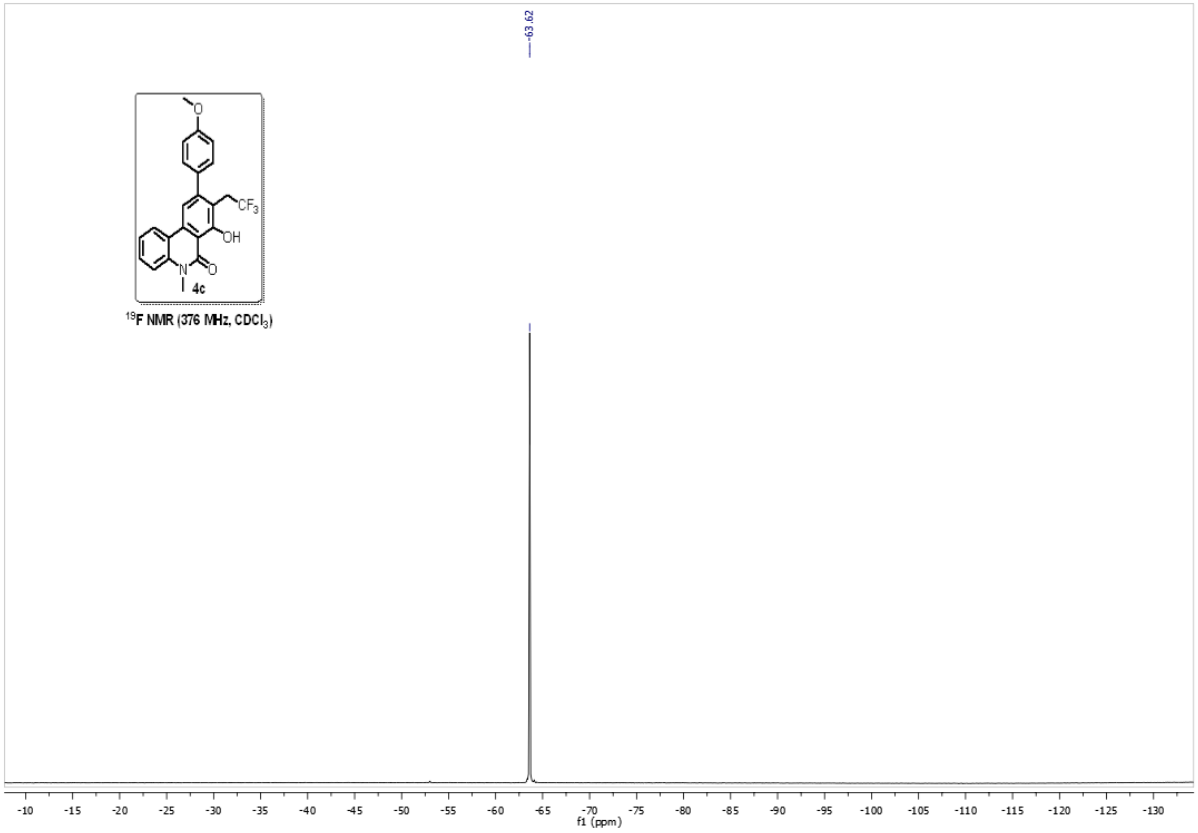

13.96
8.21
8.19
7.59
7.57
7.56
7.55
7.45
7.43
7.32
7.30
7.29
7.28
7.24
3.68
3.65
3.63
3.60
2.45
CF3
OH
O
N
4b
1H NMR (400 MHz, CDCl3)
2.16
f1 (ppm)
0.68
1.00
0.98
0.98
0.96
1.08
1.04
2.03
3.00
2.16
3.06
f1 (ppm)

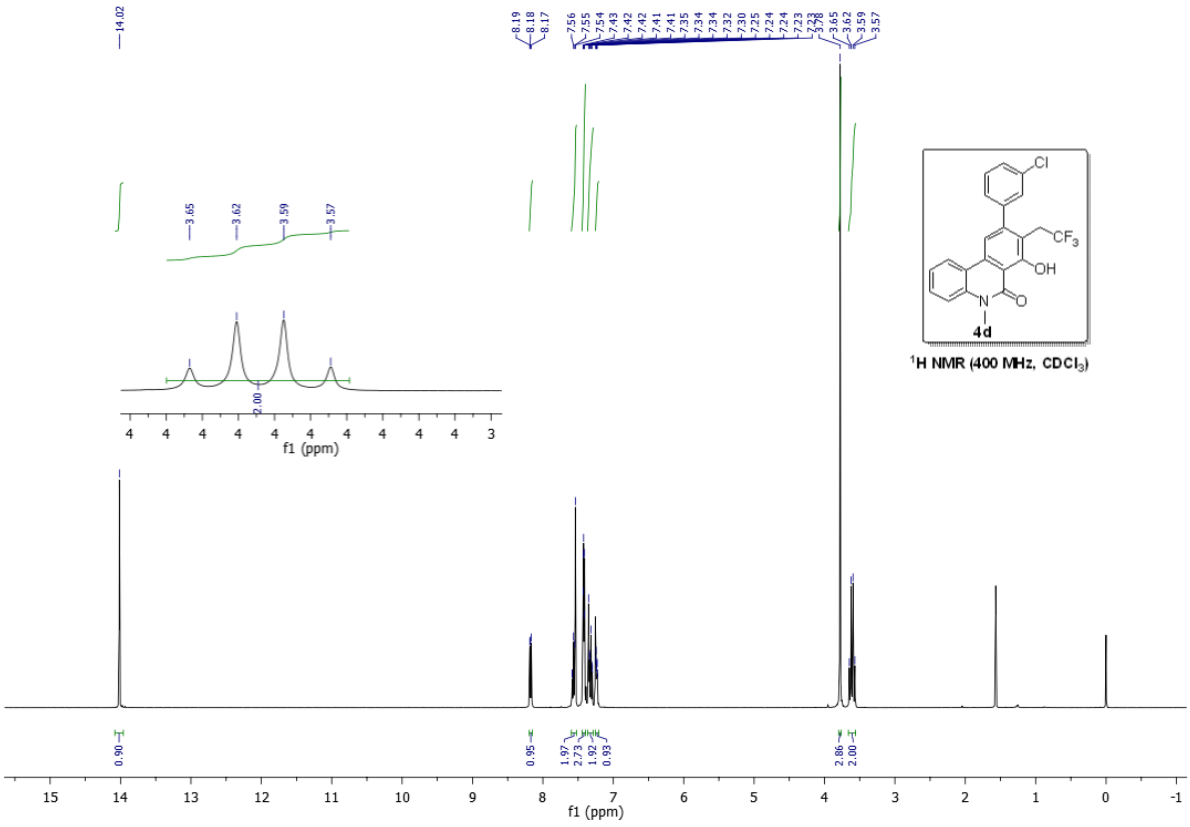

165.30
161.72
150.23
140.87
135.47
133.86
133.22
131.34
128.99
128.53
127.96
124.16
119.48
115.33
114.67
113.39
109.39
31.21
30.90
30.59
30.28
29.54
21.10
31.19
30.88
30.57
30.26
CF3
OH
N
O
4b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

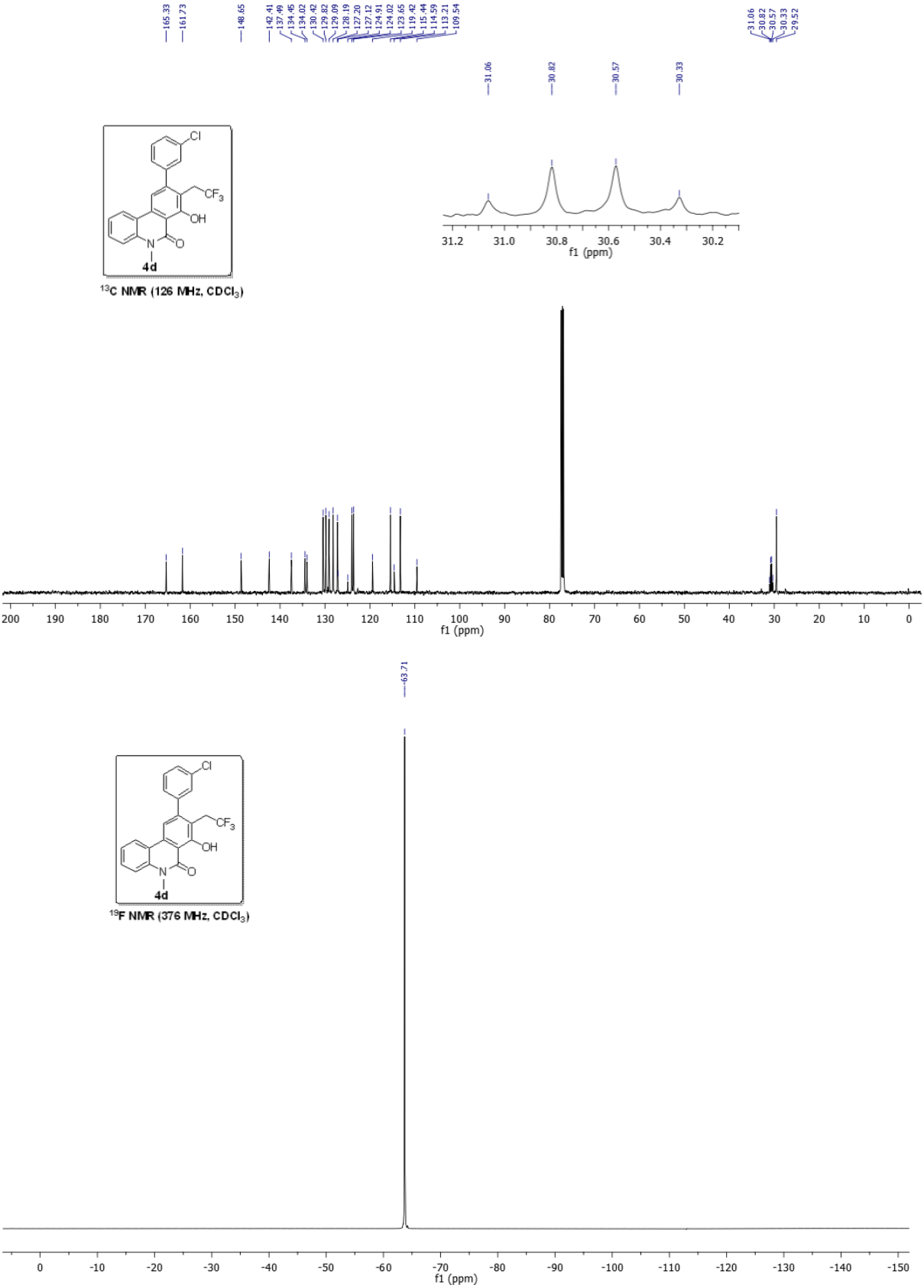

63.65
CF3
OH
N
O
4b
19F NMR (471 MHz, CDCl3)
f1 (ppm)


4c
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)


4c
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

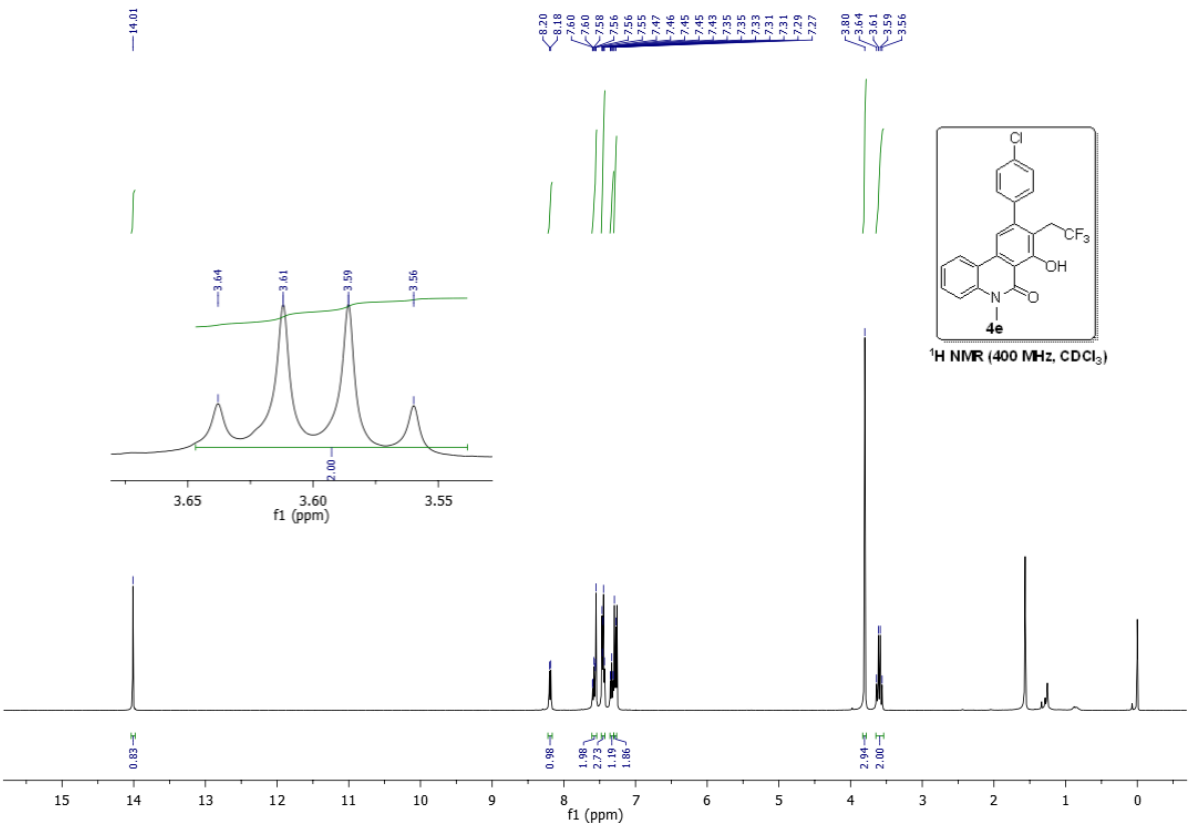

-63.62
4c
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)

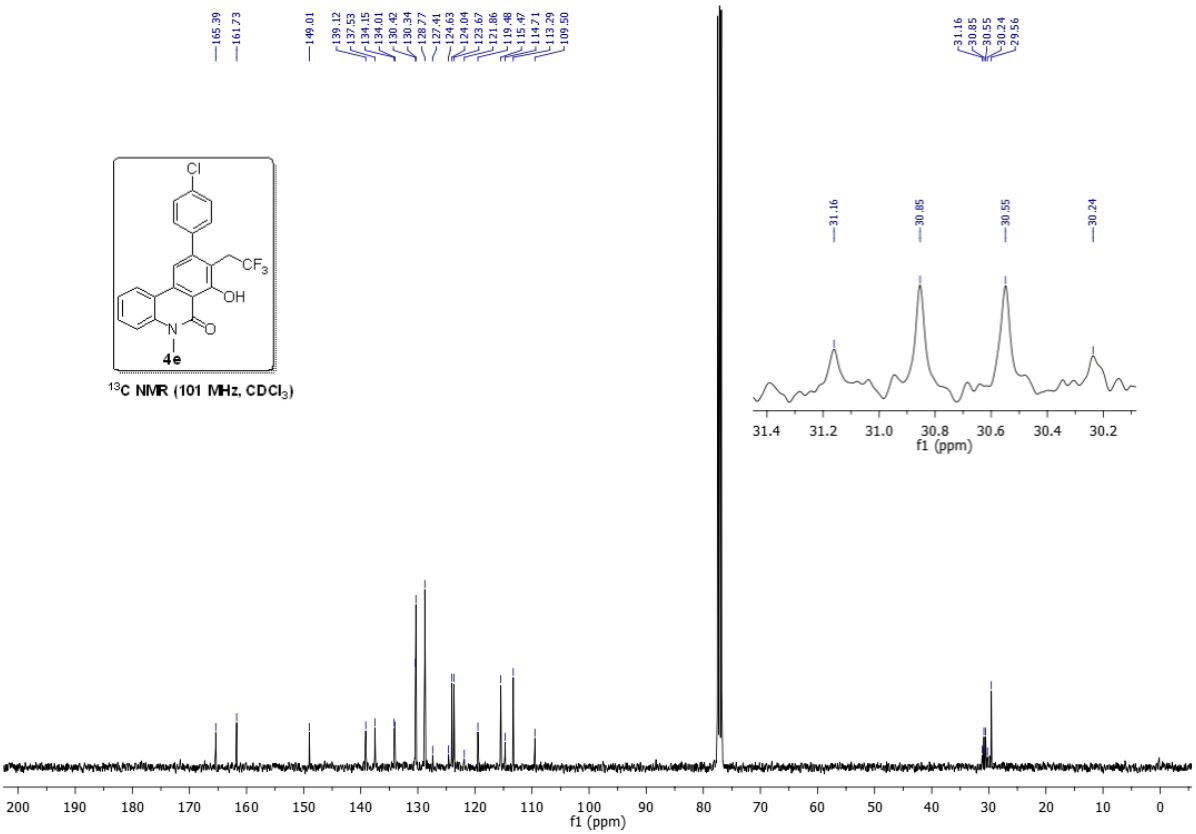

14.02
8.19
8.18
8.17
7.56
7.55
7.54
7.43
7.42
7.42
7.41
7.41
7.35
7.34
7.34
7.32
7.30
7.25
7.24
7.24
7.23
3.65
3.62
3.59
3.57
2.00
4d
^{1}H NMR (400 MHz, CDCl$_3$)
0.90
0.95
1.97
2.73
1.92
0.93
2.86
2.00
f1 (ppm)

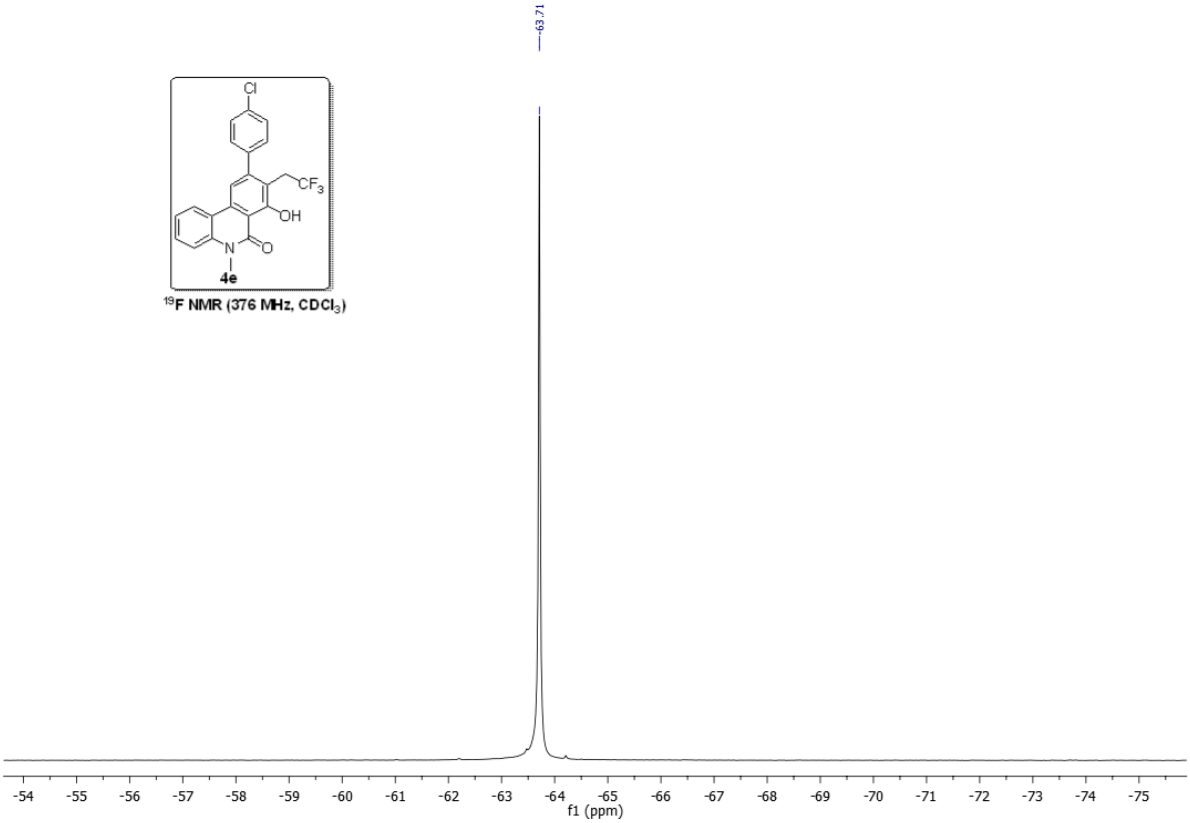


^{13}C NMR (126 MHz, $CDCl_3$)

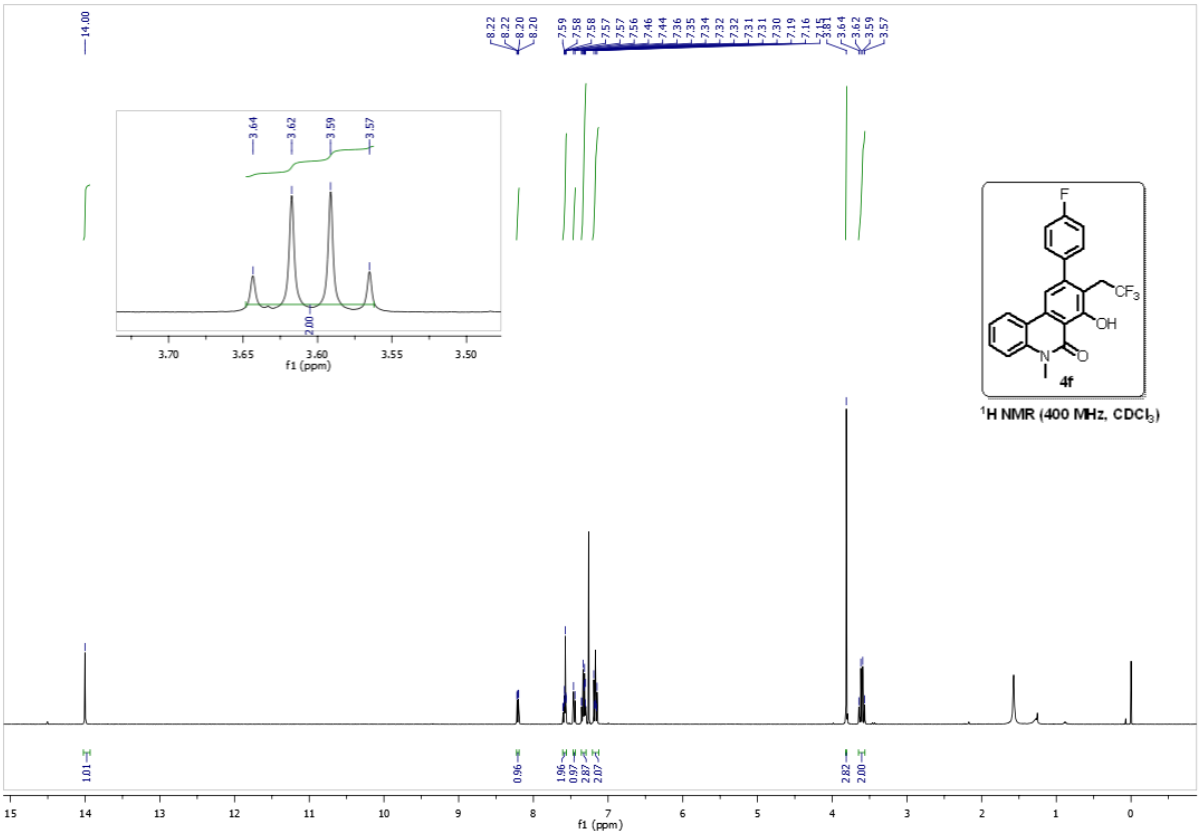
^{19}F NMR (376 MHz, $CDCl_3$)


14.01
8.20
8.18
7.60
7.58
7.56
7.55
7.47
7.46
7.45
7.43
7.35
7.33
7.31
7.29
7.27
3.80
3.64
3.61
3.59
3.56
Cl
CF3
OH
N
O
4e
1H NMR (400 MHz, CDCl3)
3.64
3.61
3.59
3.56
2.00
3.65
3.60
3.55
f1 (ppm)
0.83
0.98
1.98
2.73
1.19
1.86
2.94
2.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

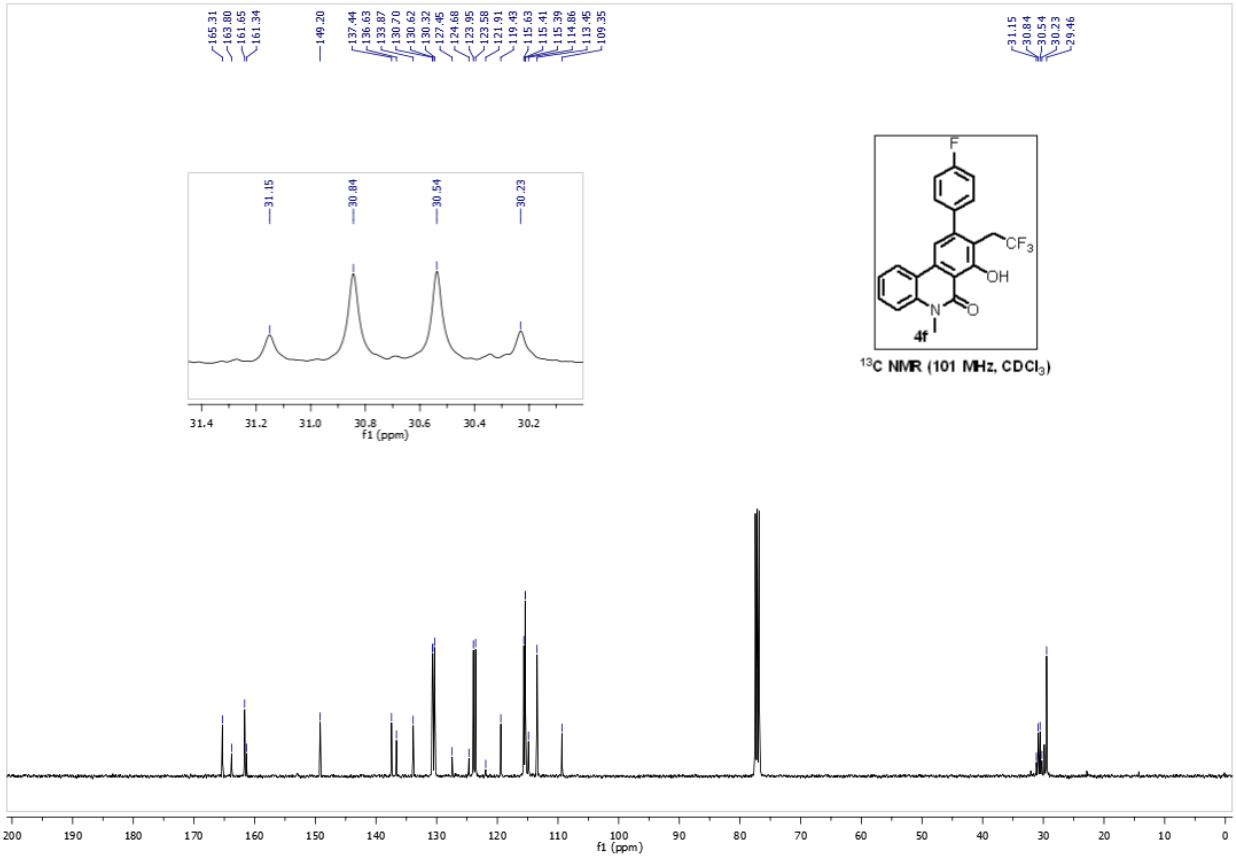

165.39
161.73
149.01
139.12
137.53
134.15
134.01
130.42
130.34
128.77
127.41
124.63
124.04
123.67
121.86
119.48
115.47
114.71
113.29
109.50
31.16
30.85
30.55
30.24
29.56
Cl
CF3
OH
N
O
4e
13C NMR (101 MHz, CDCl3)
31.16
30.85
30.55
30.24
31.4
31.2
31.0
30.8
30.6
30.4
30.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

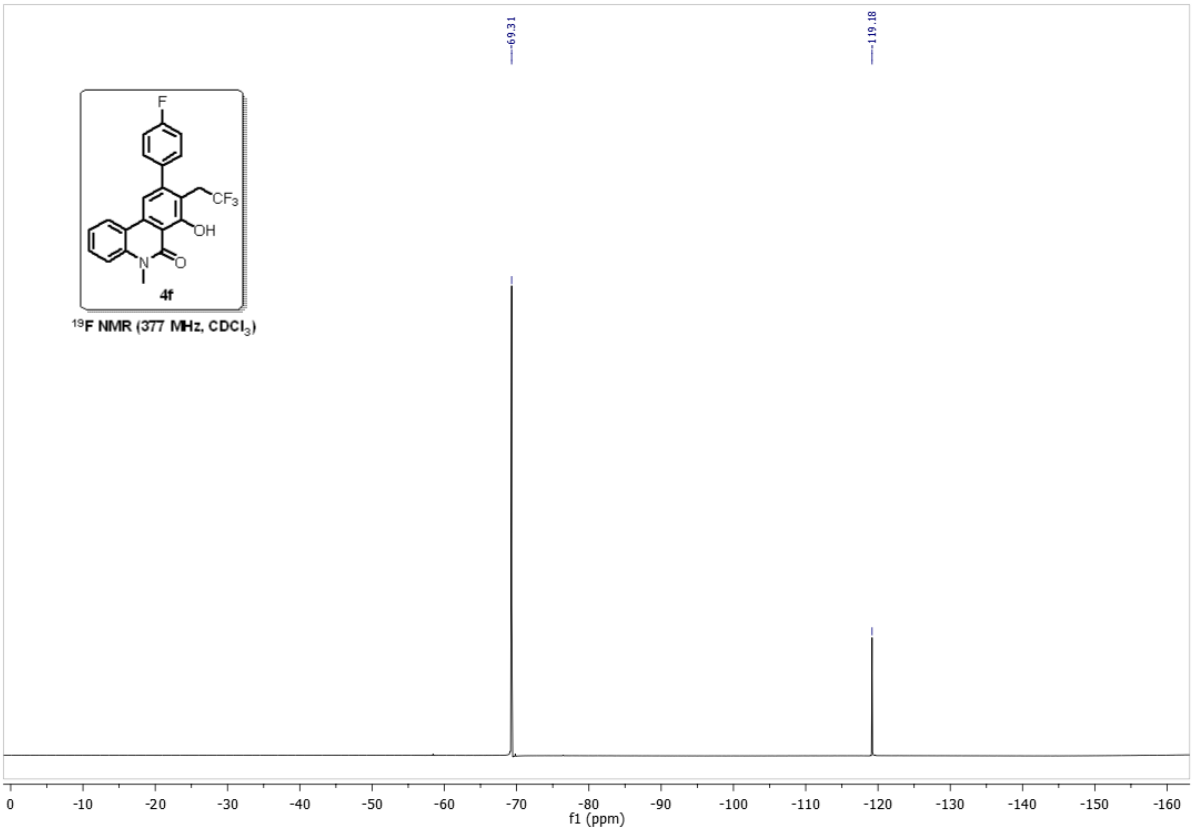


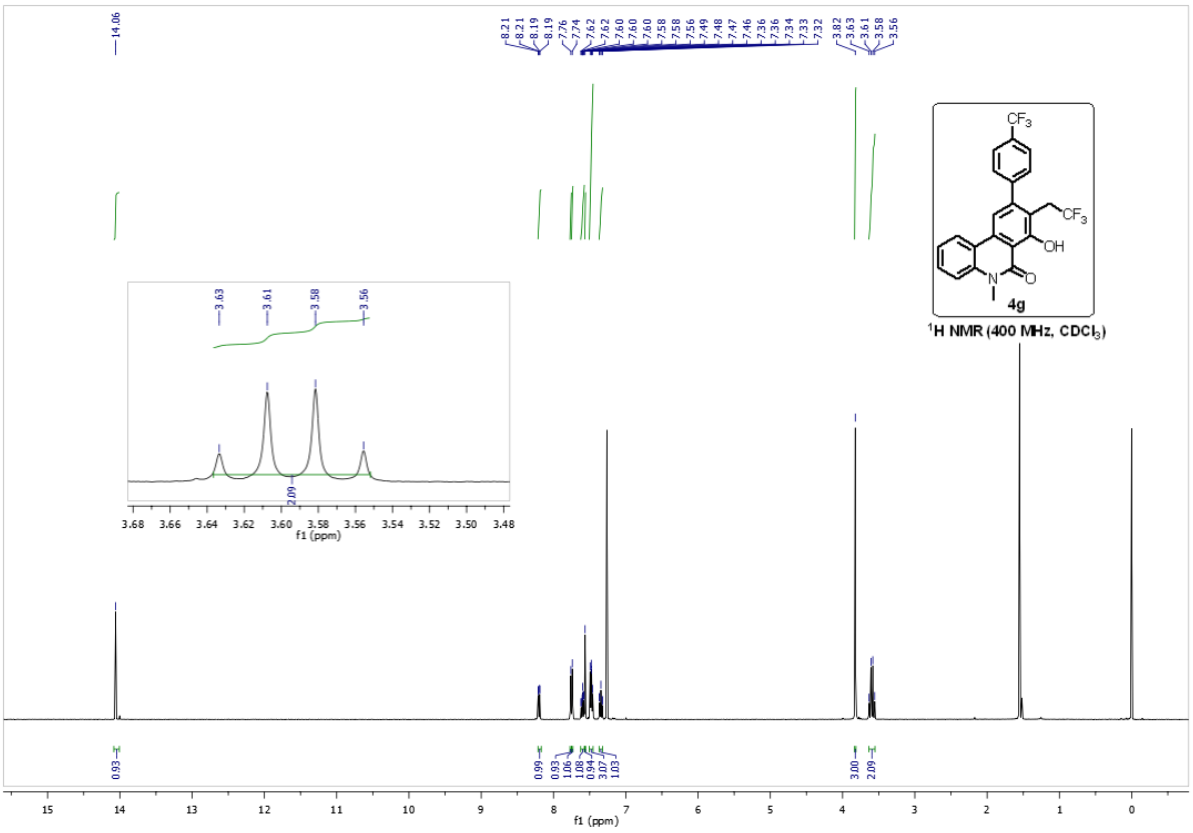
^{19}F NMR (376 MHz, $CDCl_3$)

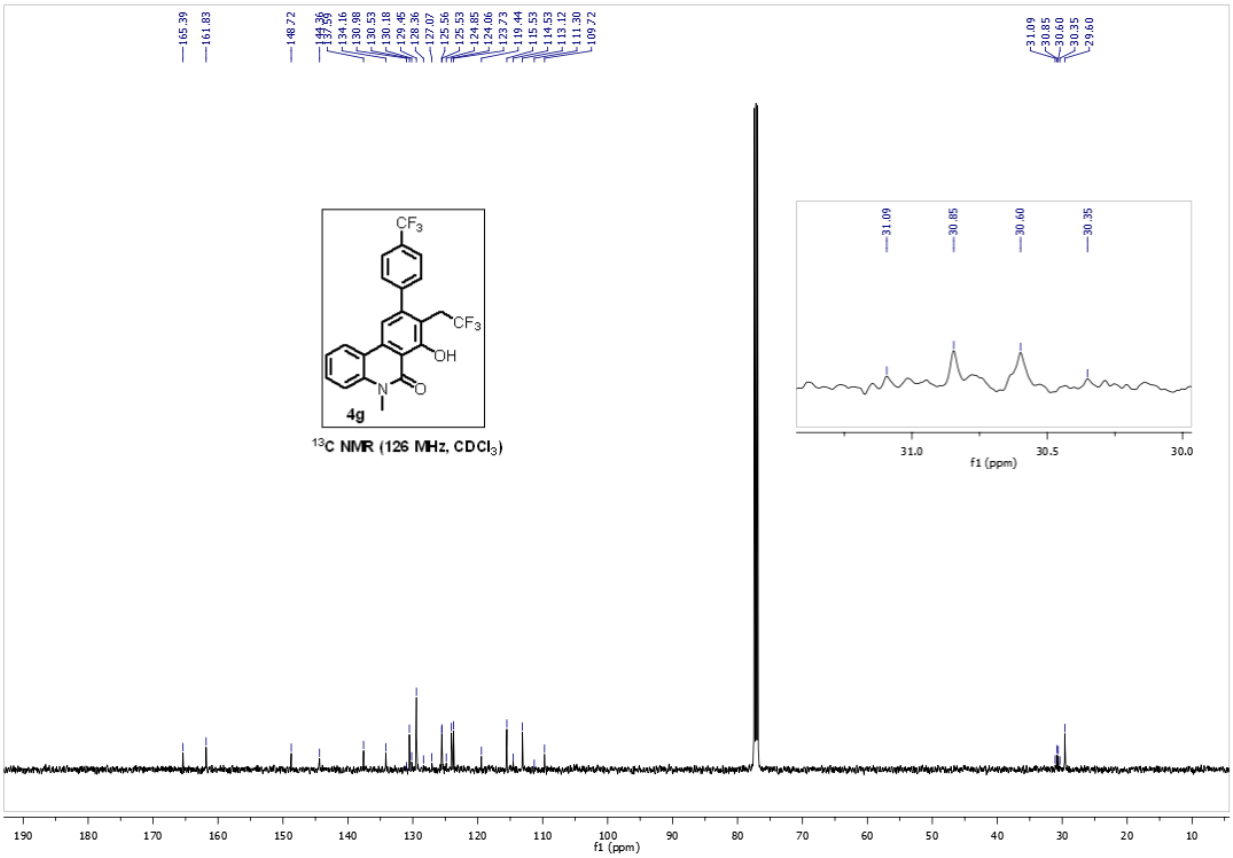


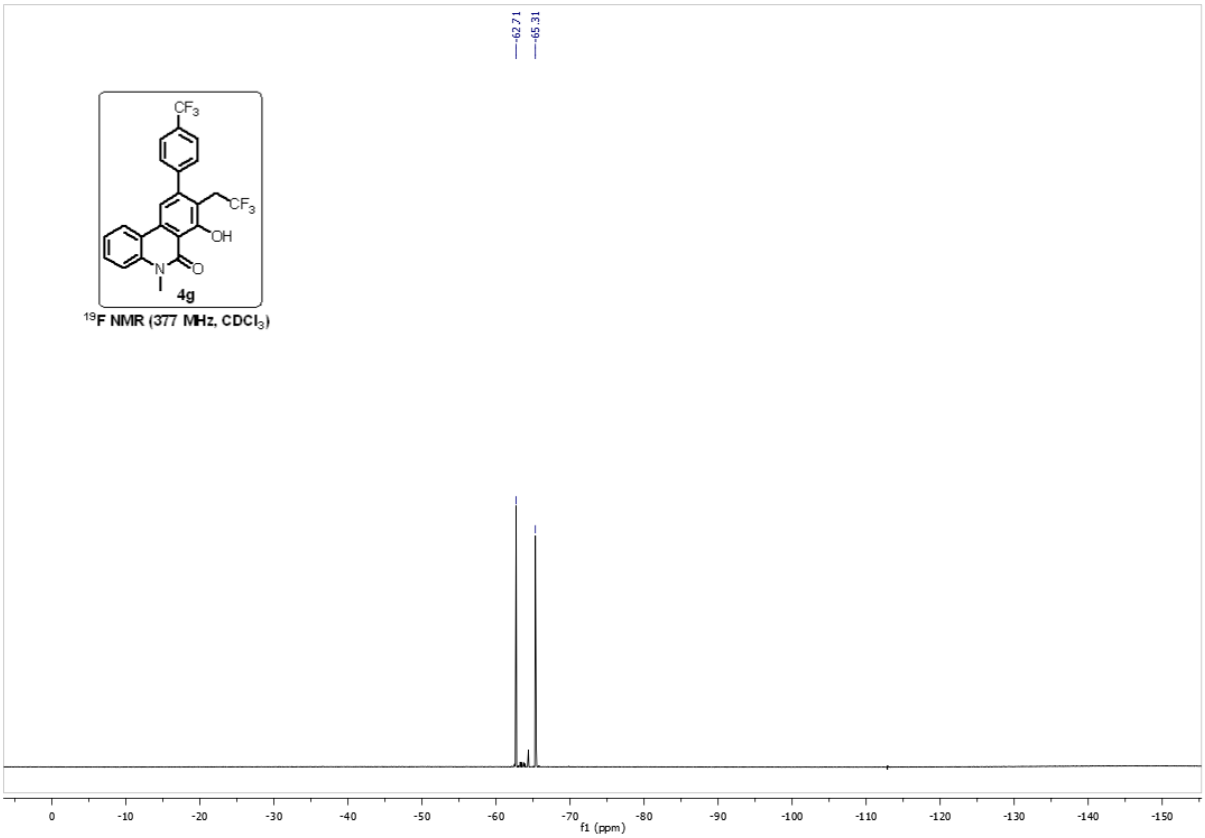
^{1}H NMR (400 MHz, $CDCl_3$)

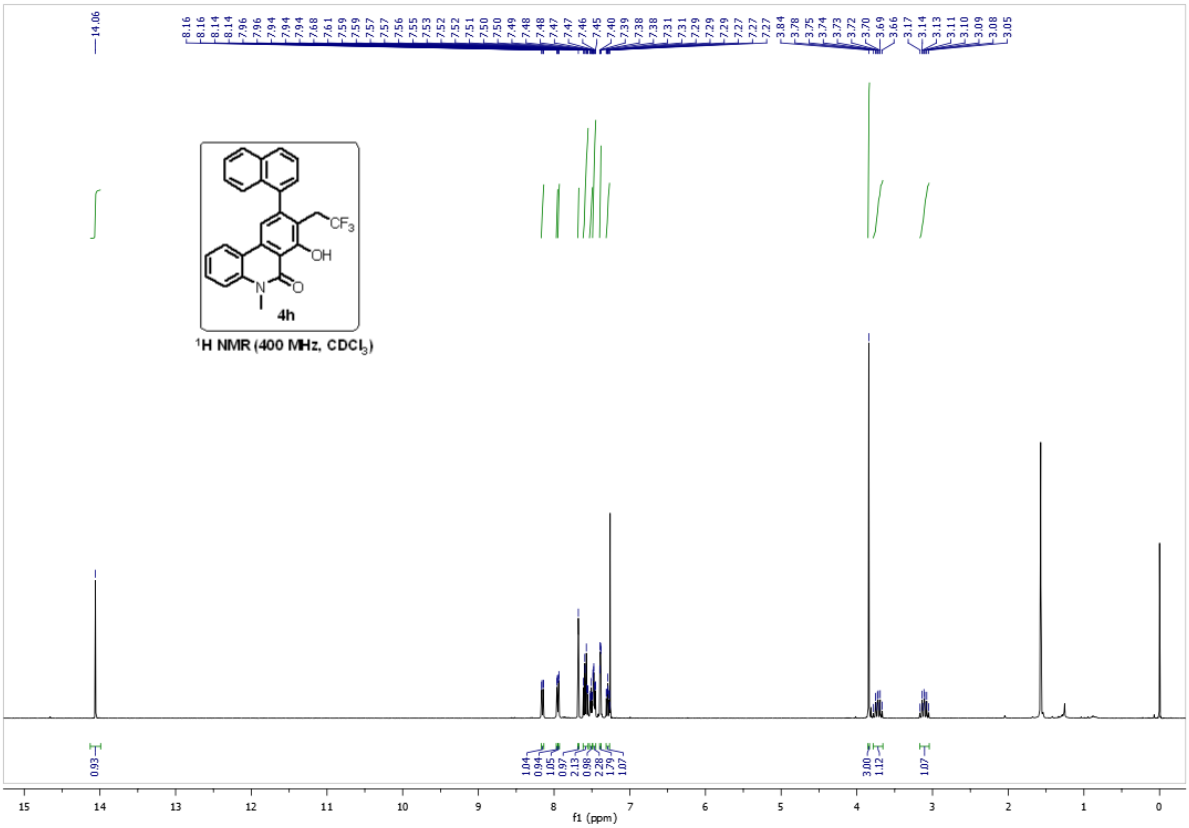

165.31
163.80
161.65
161.34
149.20
137.44
136.63
133.87
130.70
130.62
130.32
127.45
124.68
123.95
123.58
121.91
119.43
115.63
115.41
115.39
114.86
113.45
109.35
31.15
30.84
30.54
30.23
29.46
31.15
30.84
30.54
30.23
31.4
31.2
31.0
30.8
30.6
30.4
30.2
f1 (ppm)
F
CF3
OH
N
O
4f
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

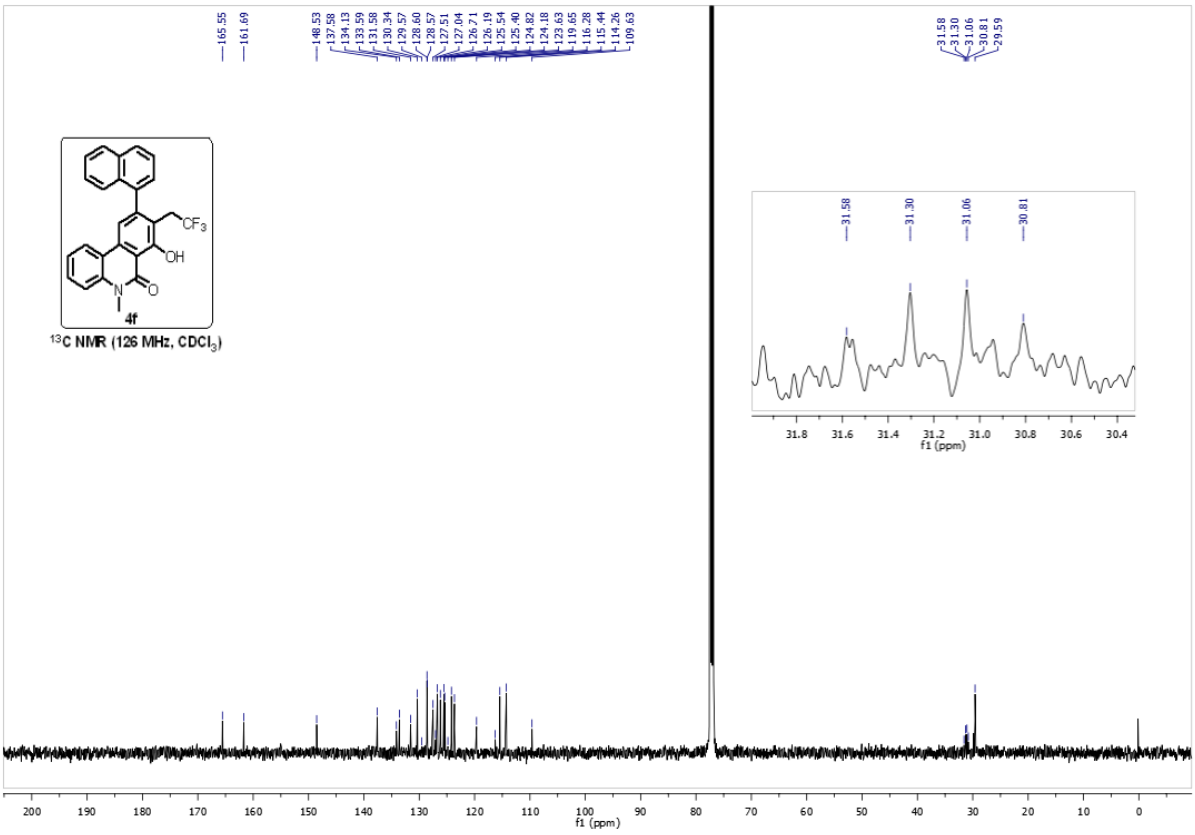

-69.31
-119.18
F
CF3
OH
N
O
4f
19F NMR (377 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

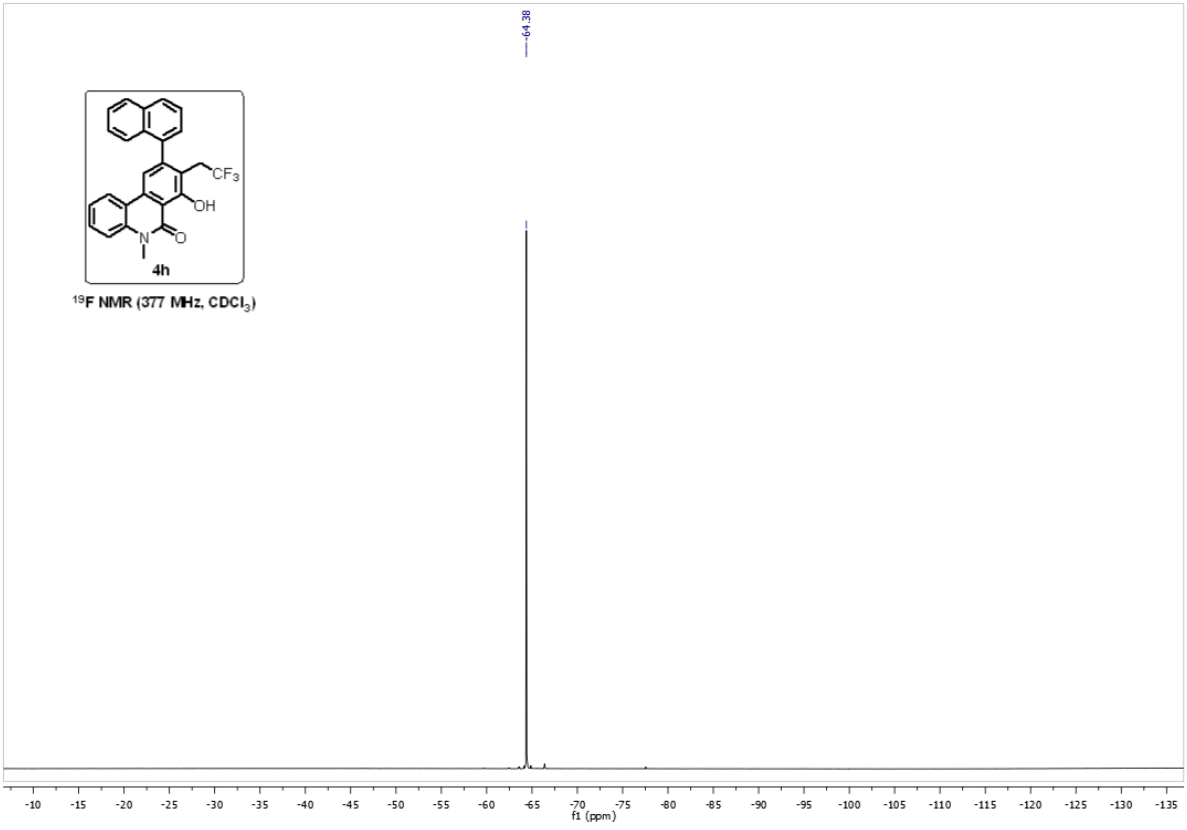

4g
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

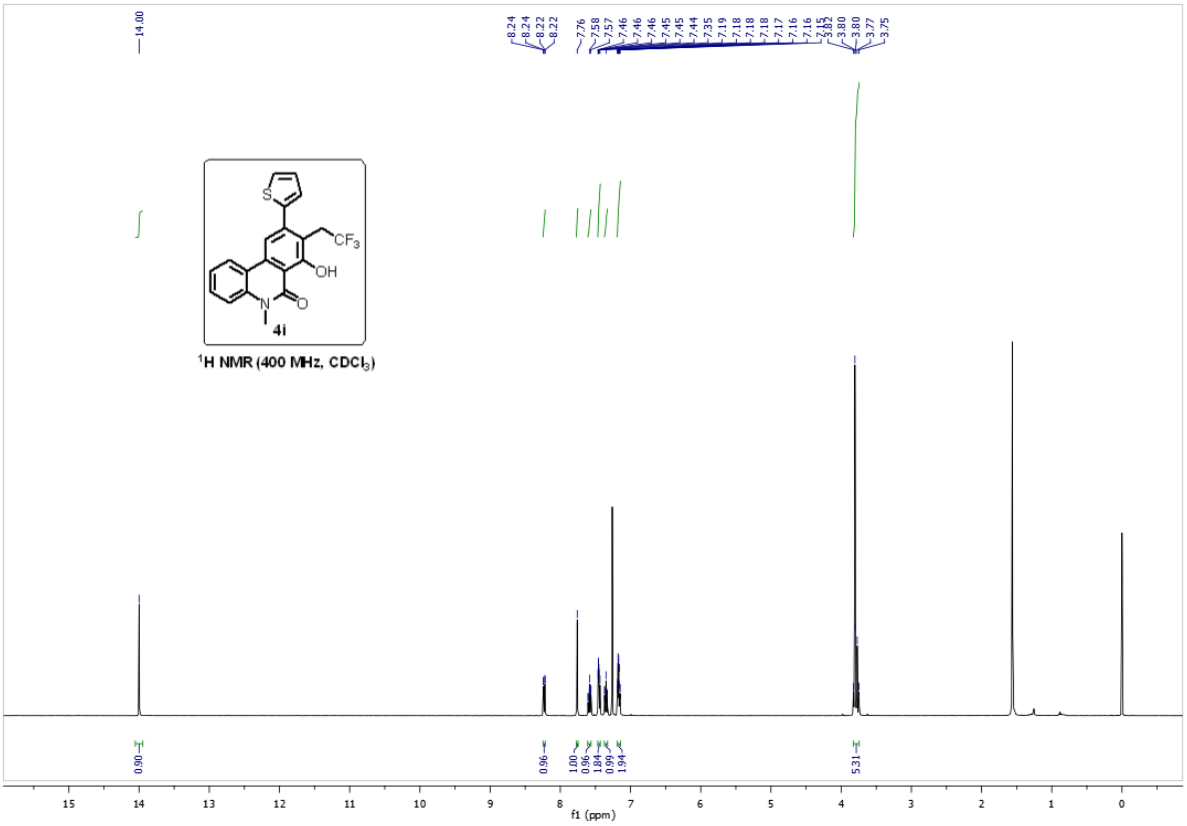

4g
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)


-62.71
-65.31
CF3
CF3
OH
N
O
4g
19F NMR (377 MHz, CDCl3)
f1 (ppm)

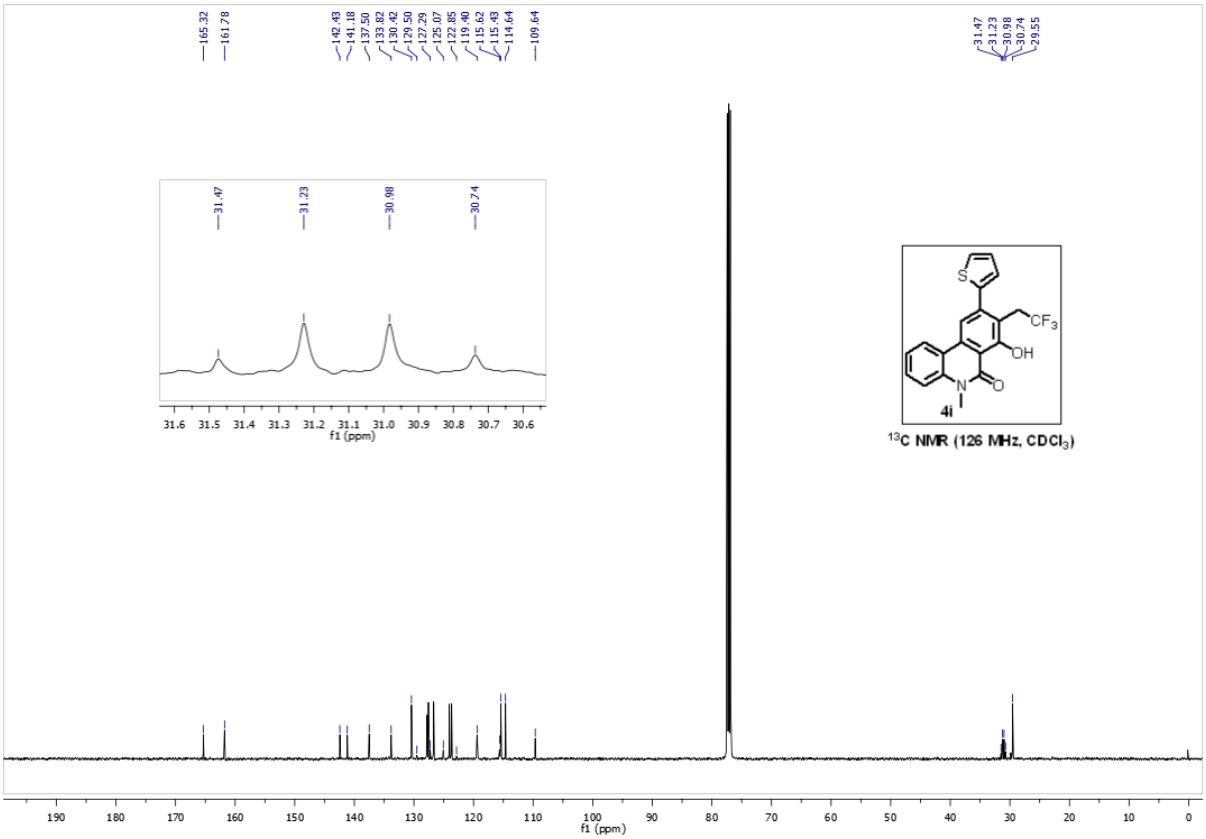

14.06
CF3
OH
N
O
4h
1H NMR (400 MHz, CDCl3)
f1 (ppm)


165.55
161.69
148.53
137.58
134.13
133.59
131.58
130.34
129.57
128.60
128.57
127.51
127.04
126.71
126.19
125.54
125.40
124.82
124.18
123.63
119.65
116.28
115.44
114.26
109.63
31.58
31.30
31.06
30.81
29.59
CF3
OH
N
O
4f
13C NMR (126 MHz, CDCl3)
f1 (ppm)

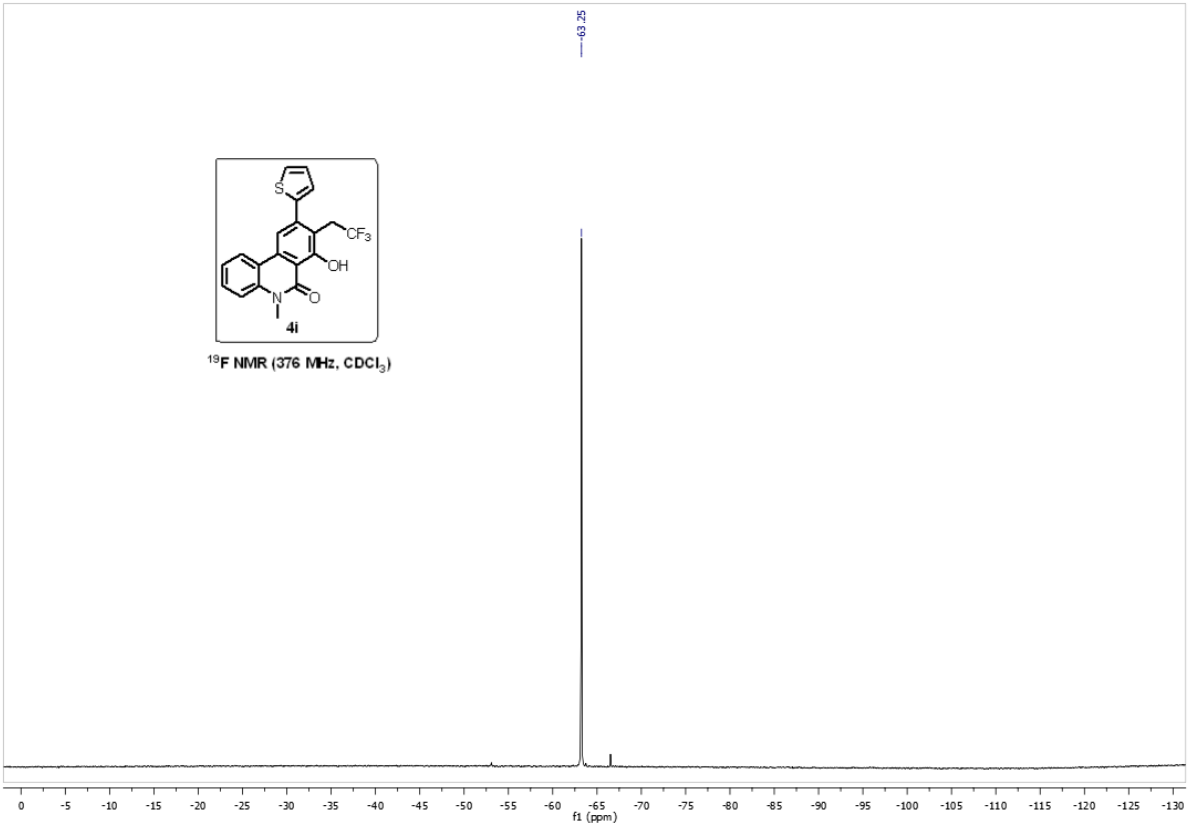

64.38
CF3
OH
N
O
4h
19F NMR (377 MHz, CDCl3)
f1 (ppm)

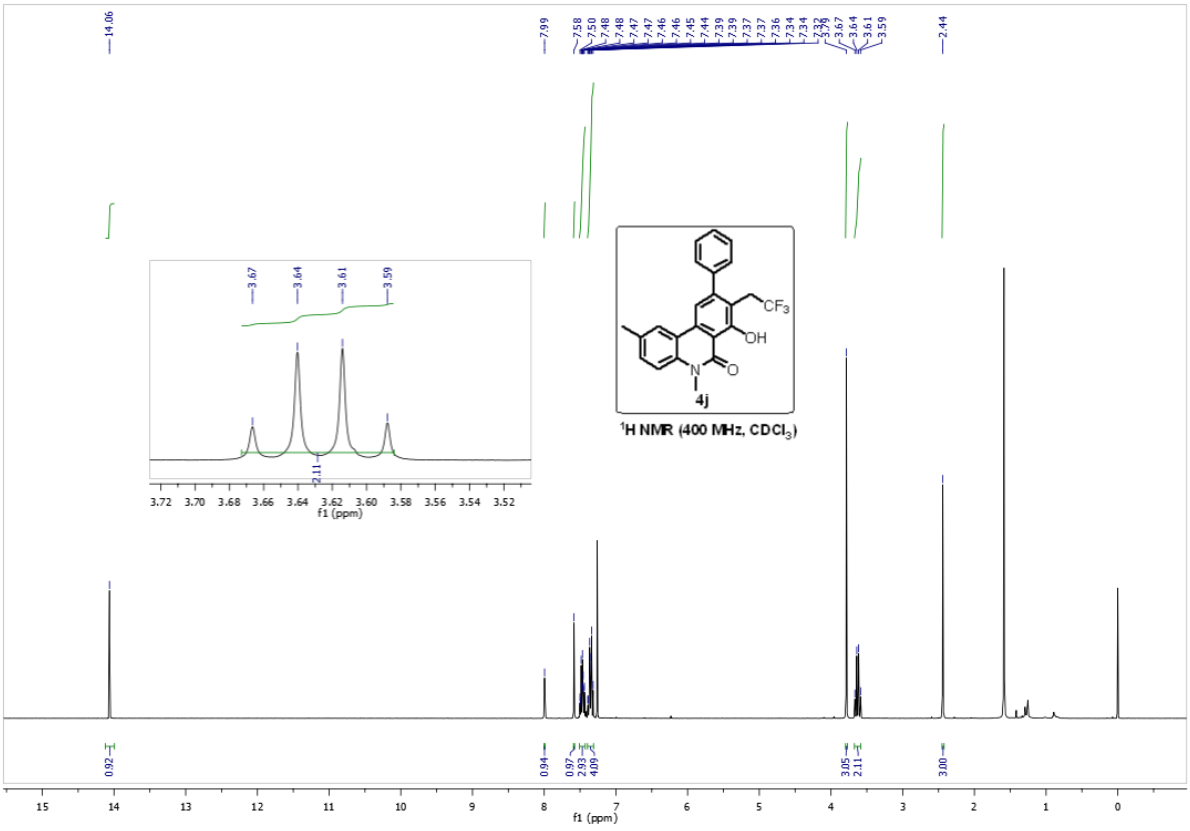


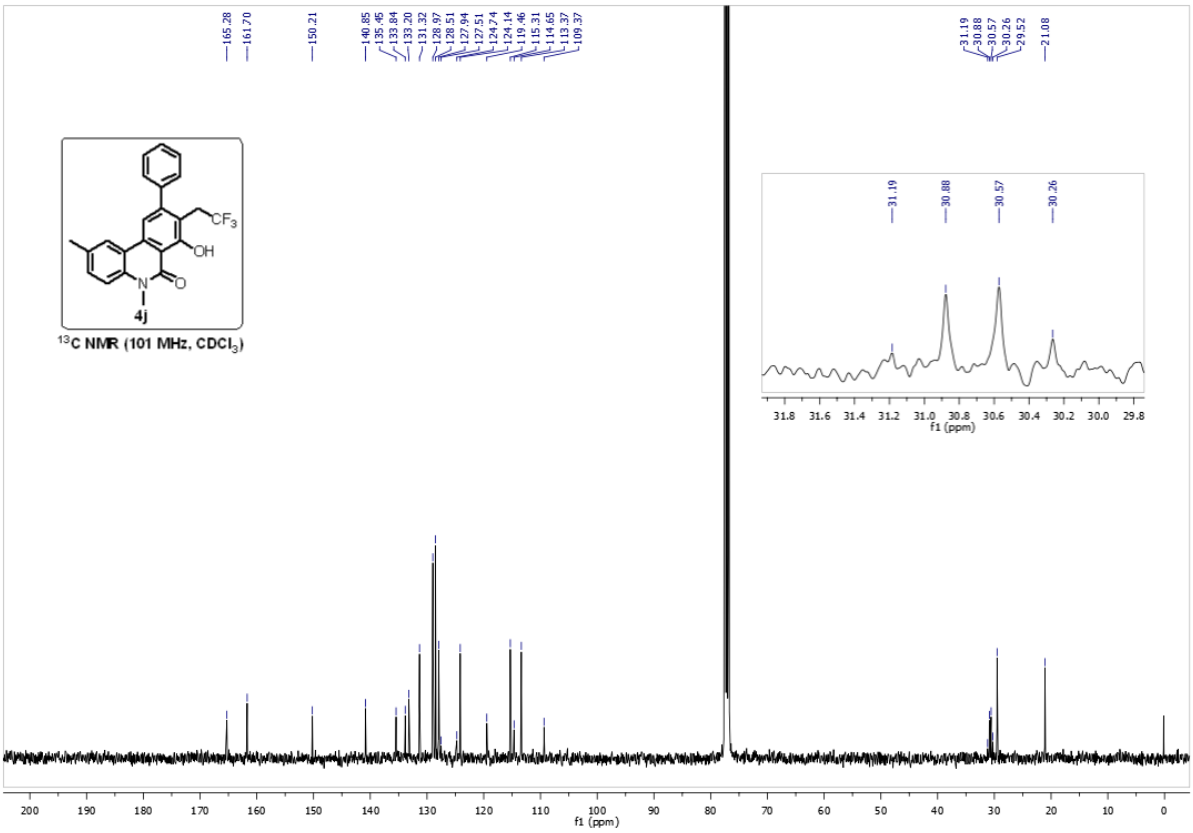
^{1}H NMR (400 MHz, $CDCl_3$)



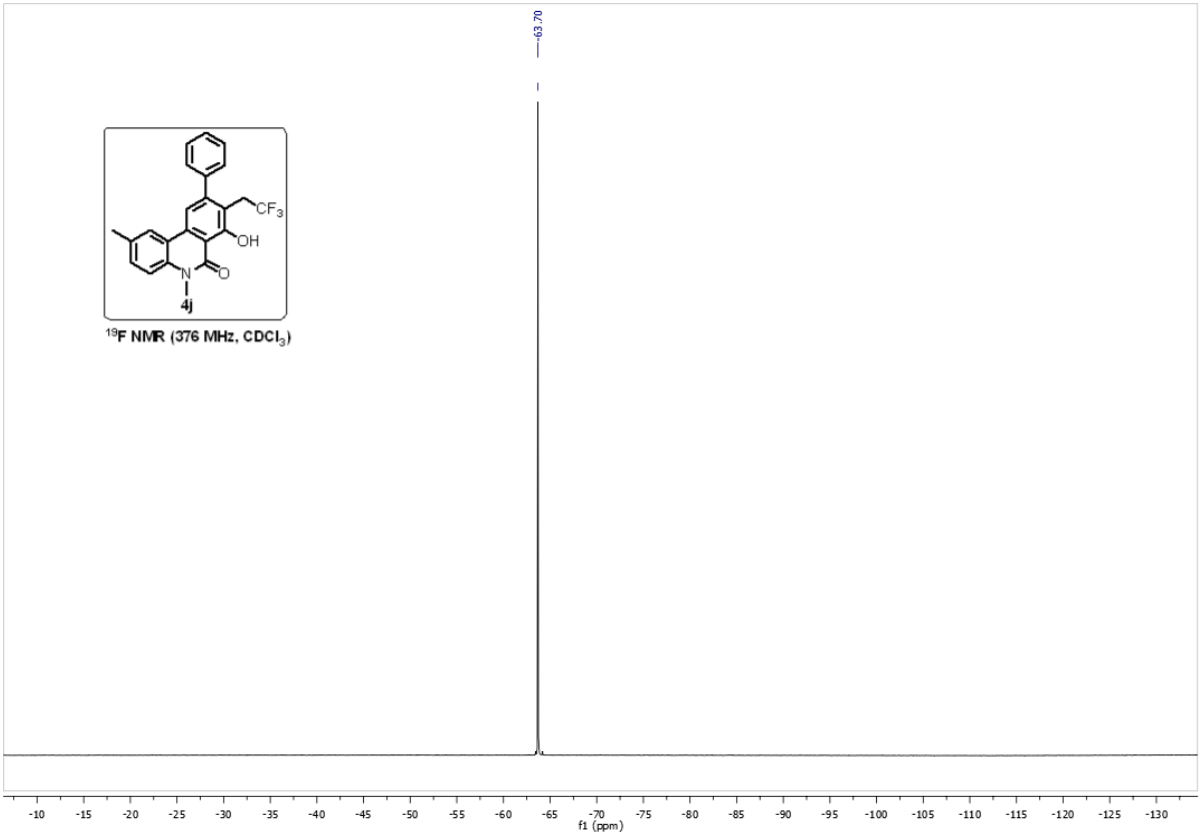
^{13}C NMR (126 MHz, $CDCl_3$)


-63.25
4i
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)

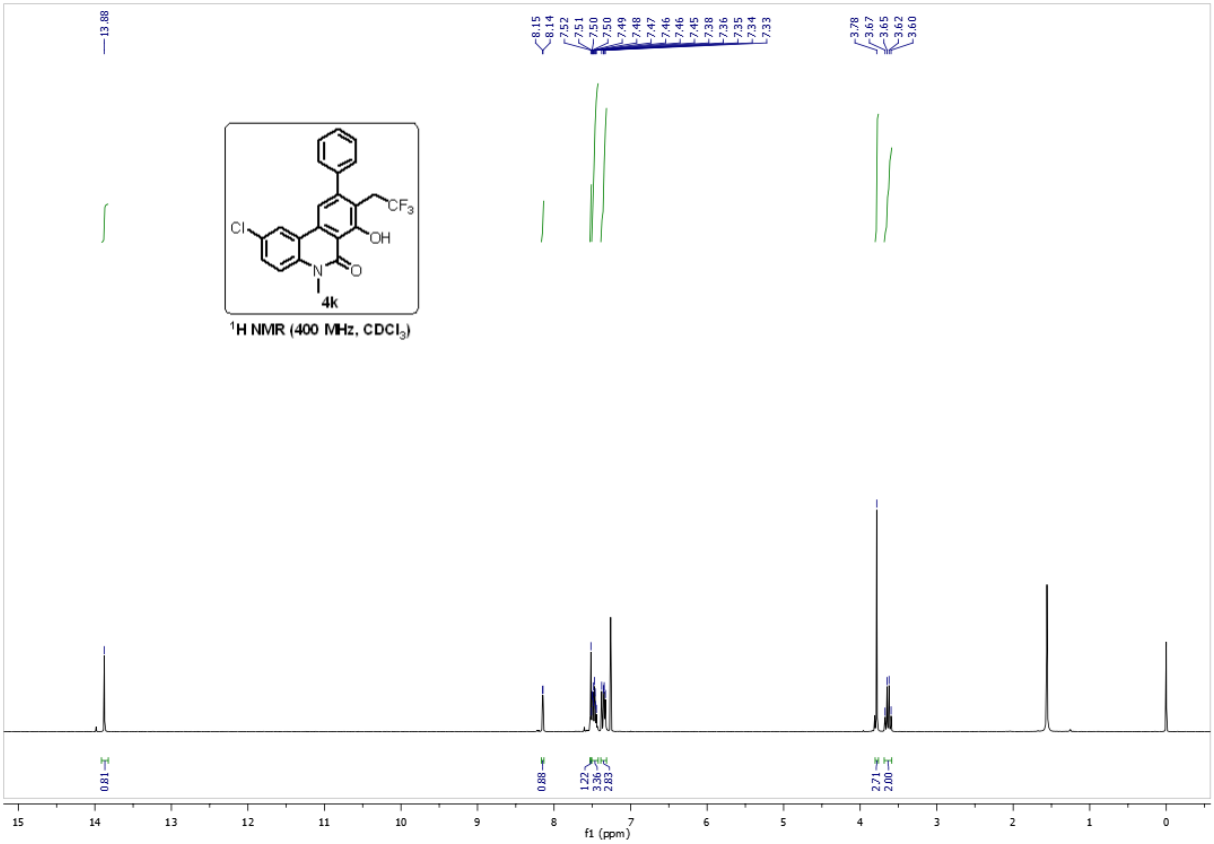

14.06
7.99
7.58
7.50
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.39
7.39
7.37
7.37
7.36
7.34
7.34
7.32
3.67
3.64
3.61
3.59
2.44
4j
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)



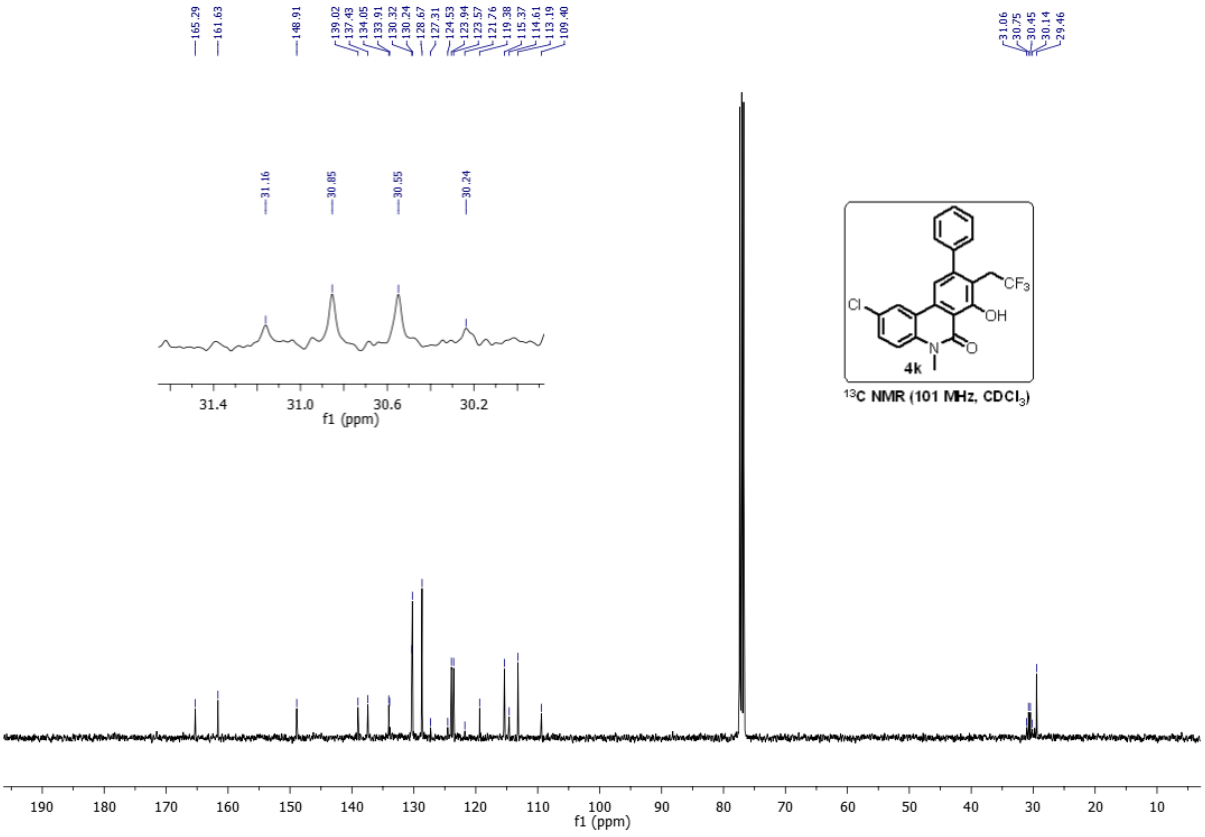
^{13}C NMR (101 MHz, $CDCl_3$)



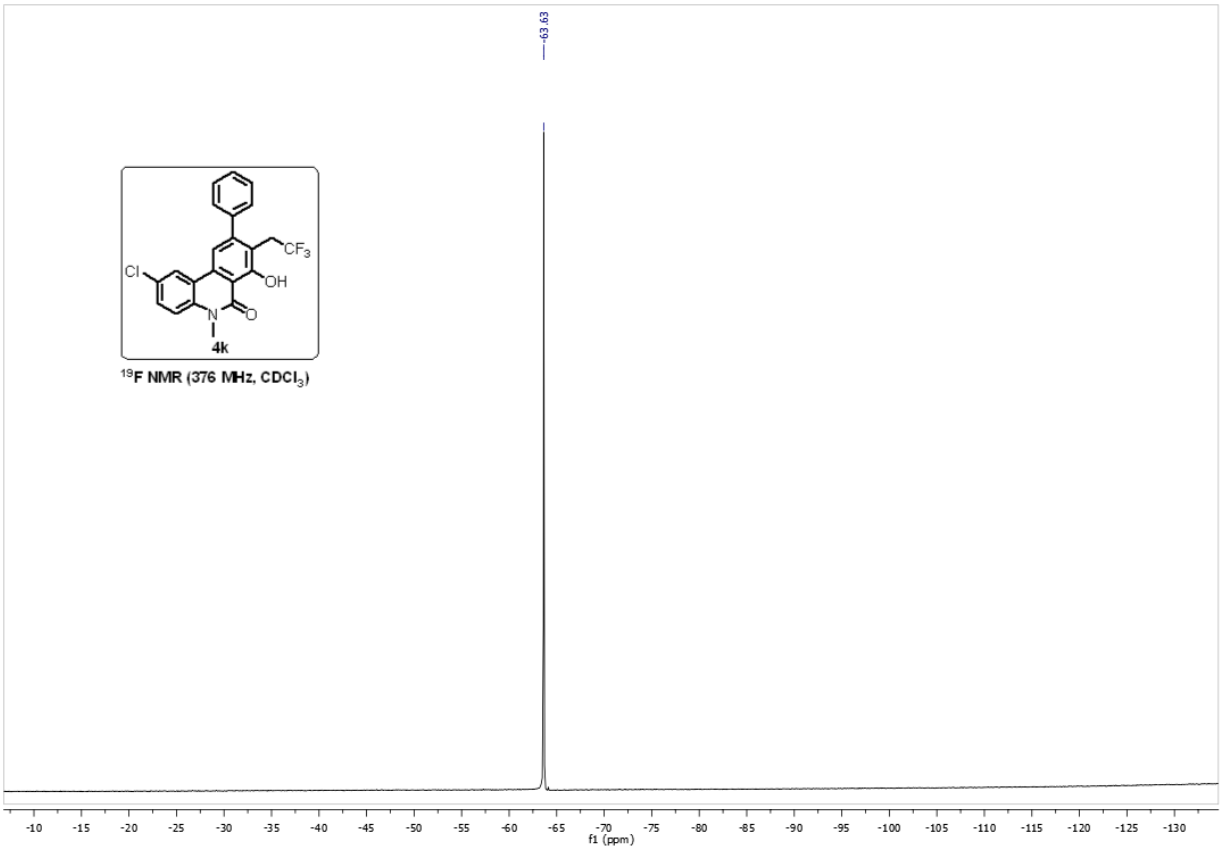
^{19}F NMR (376 MHz, $CDCl_3$)

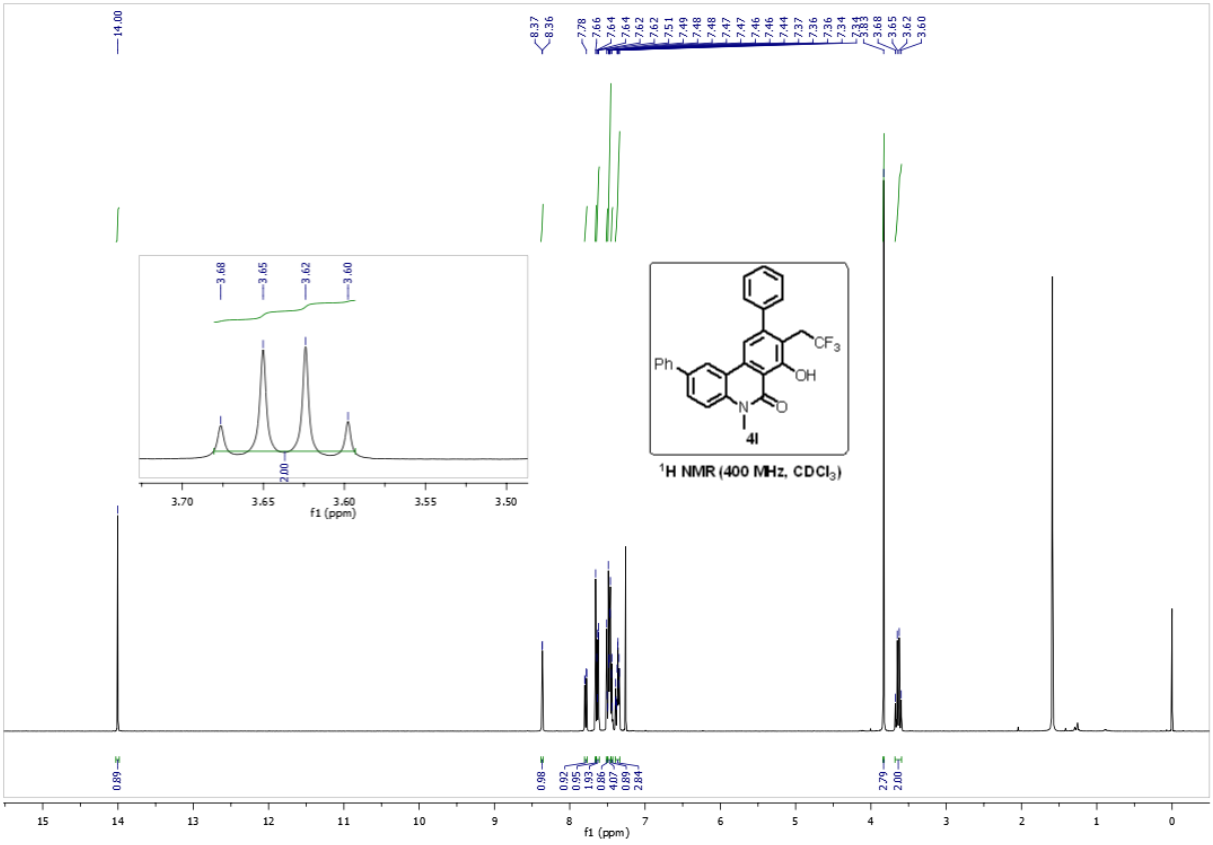


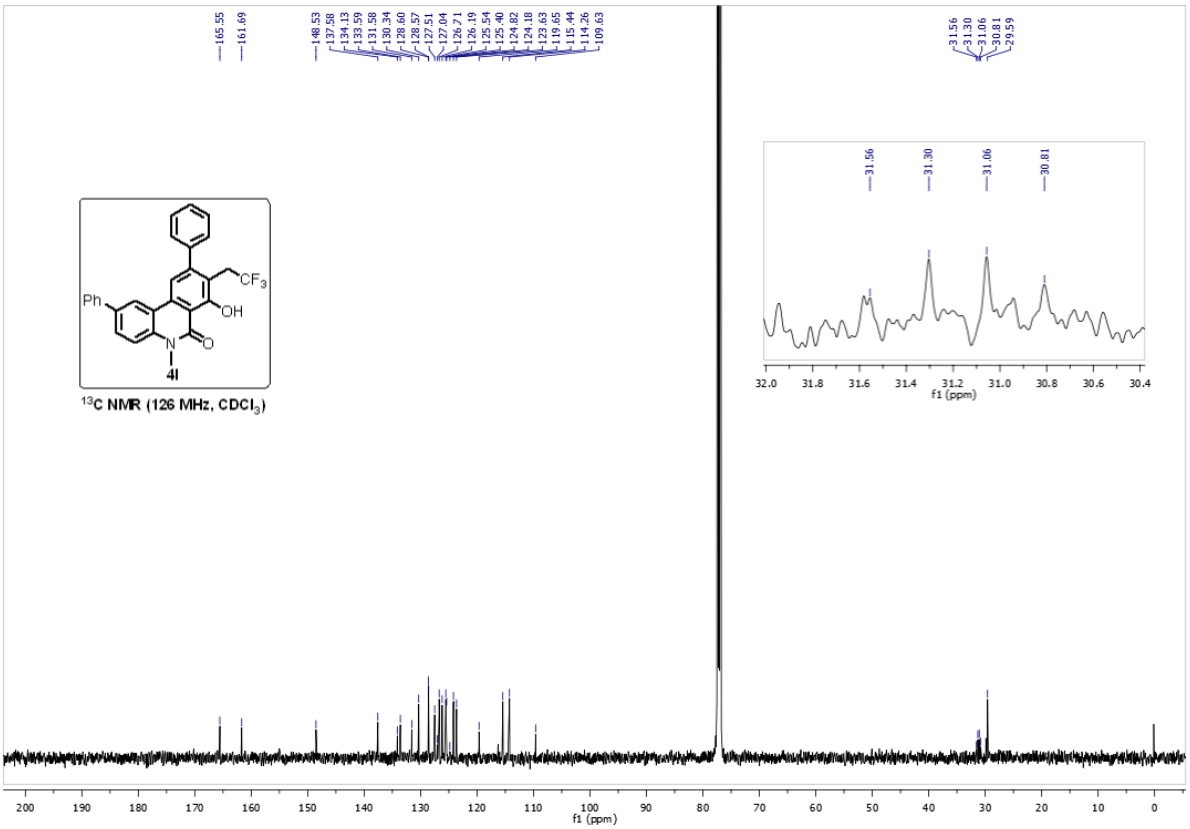
^{1}H NMR (400 MHz, $CDCl_3$)

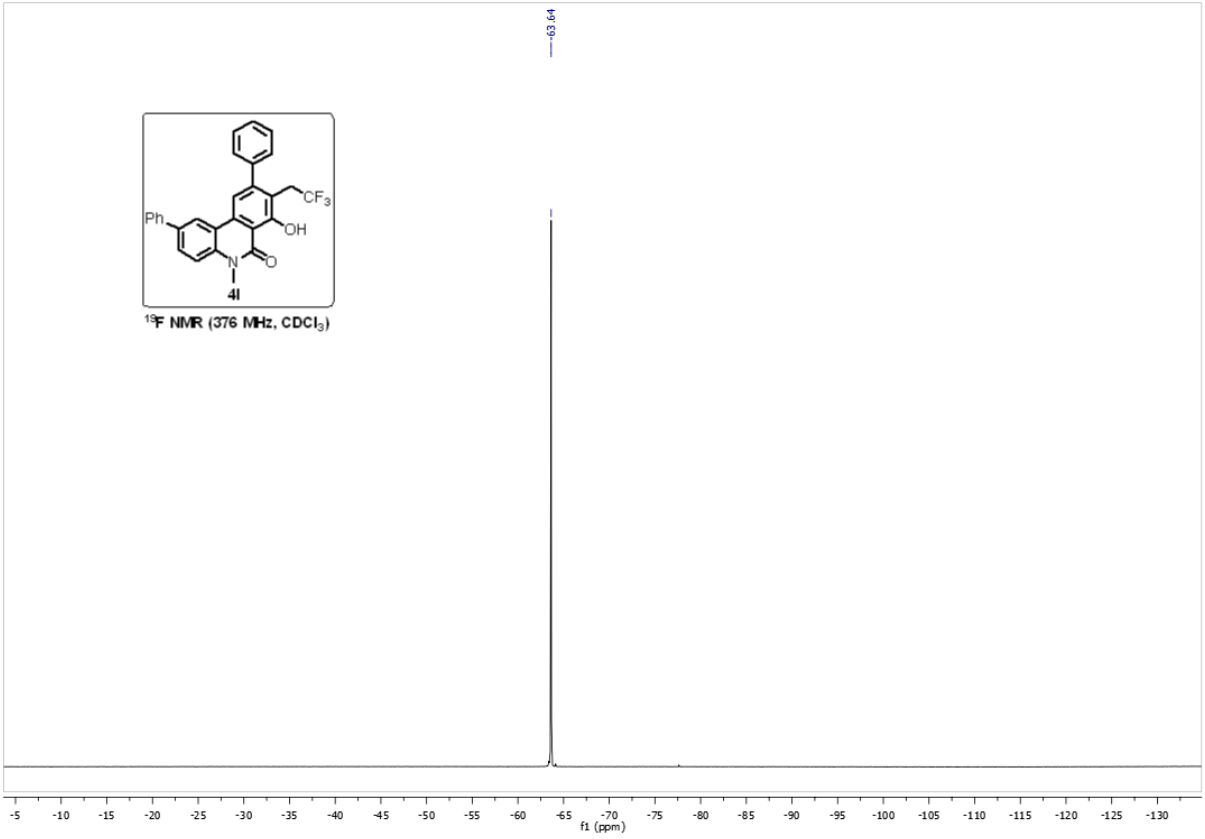


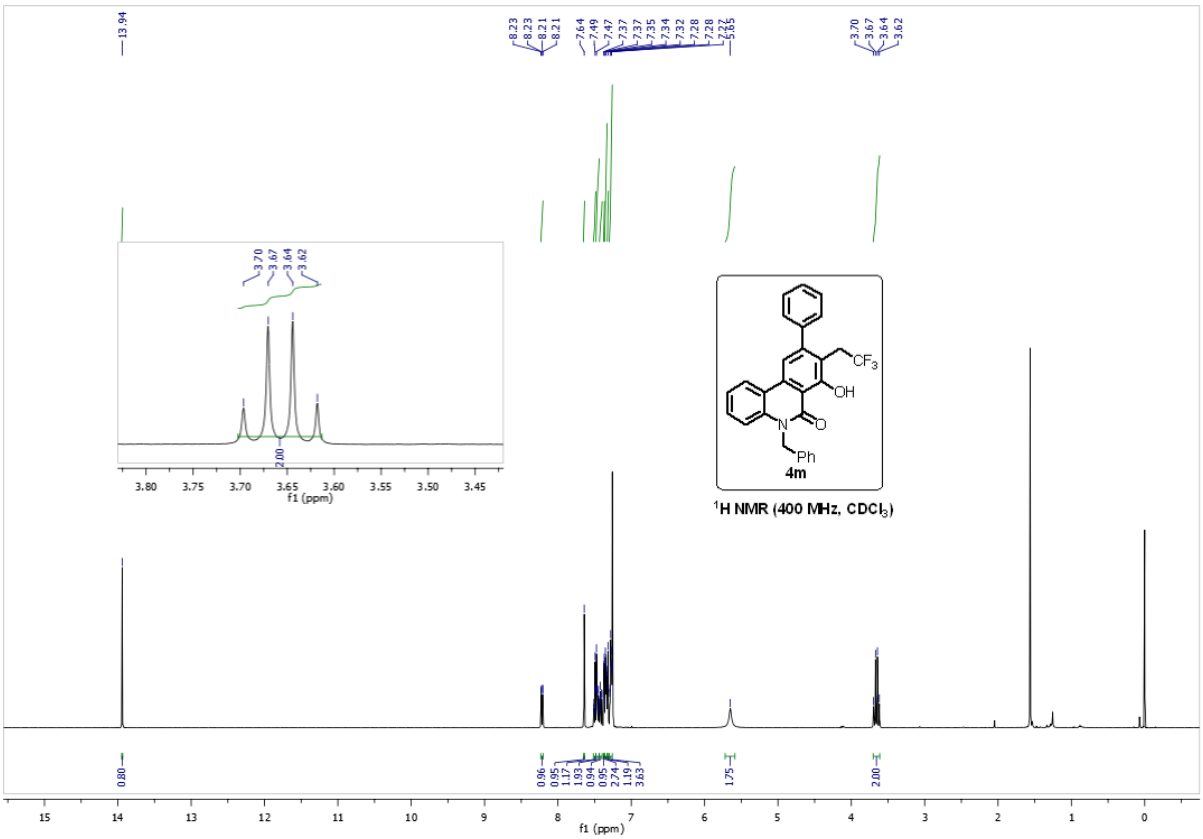
^{13}C NMR (101 MHz, $CDCl_3$)

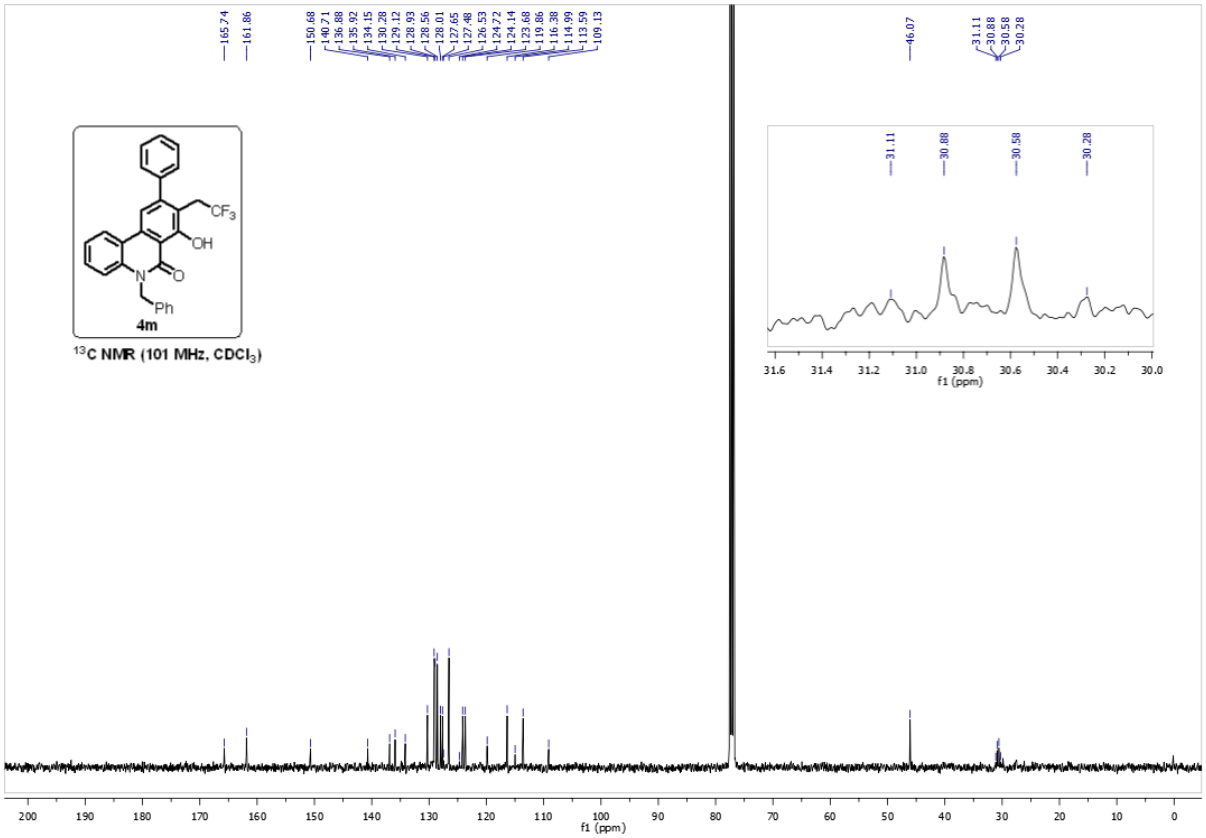

-63.63
Cl
CF3
OH
N
O
4k
19F NMR (376 MHz, CDCl3)
f1 (ppm)

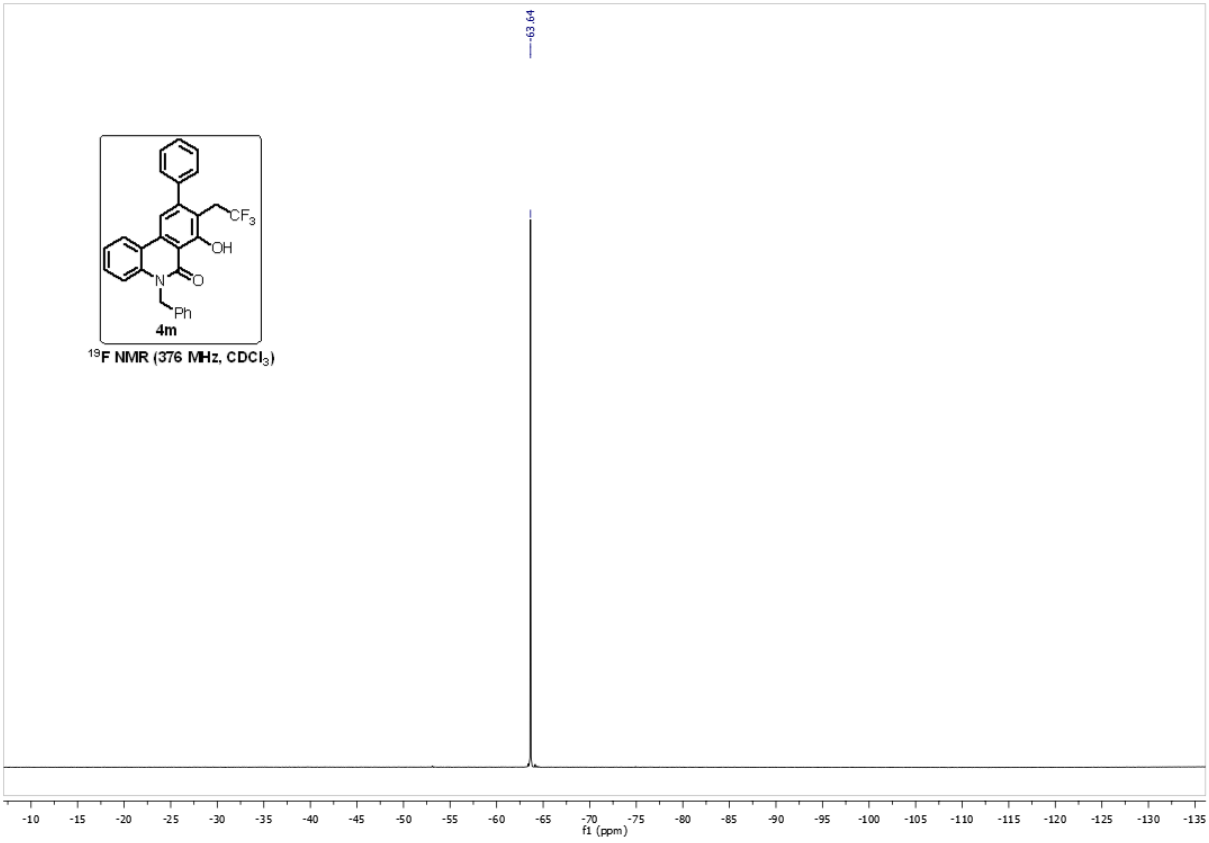

14.00
8.37
8.36
7.78
7.66
7.64
7.64
7.62
7.62
7.51
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.44
7.37
7.36
7.36
7.34
3.68
3.65
3.62
3.60
3.68
3.65
3.62
3.60
2.00
3.70
3.65
3.60
3.55
3.50
f1 (ppm)
Ph
CF3
OH
N
O
4l
1H NMR (400 MHz, CDCl3)
0.89
0.88
0.92
0.95
1.93
0.86
4.07
0.89
2.84
2.79
2.00
f1 (ppm)

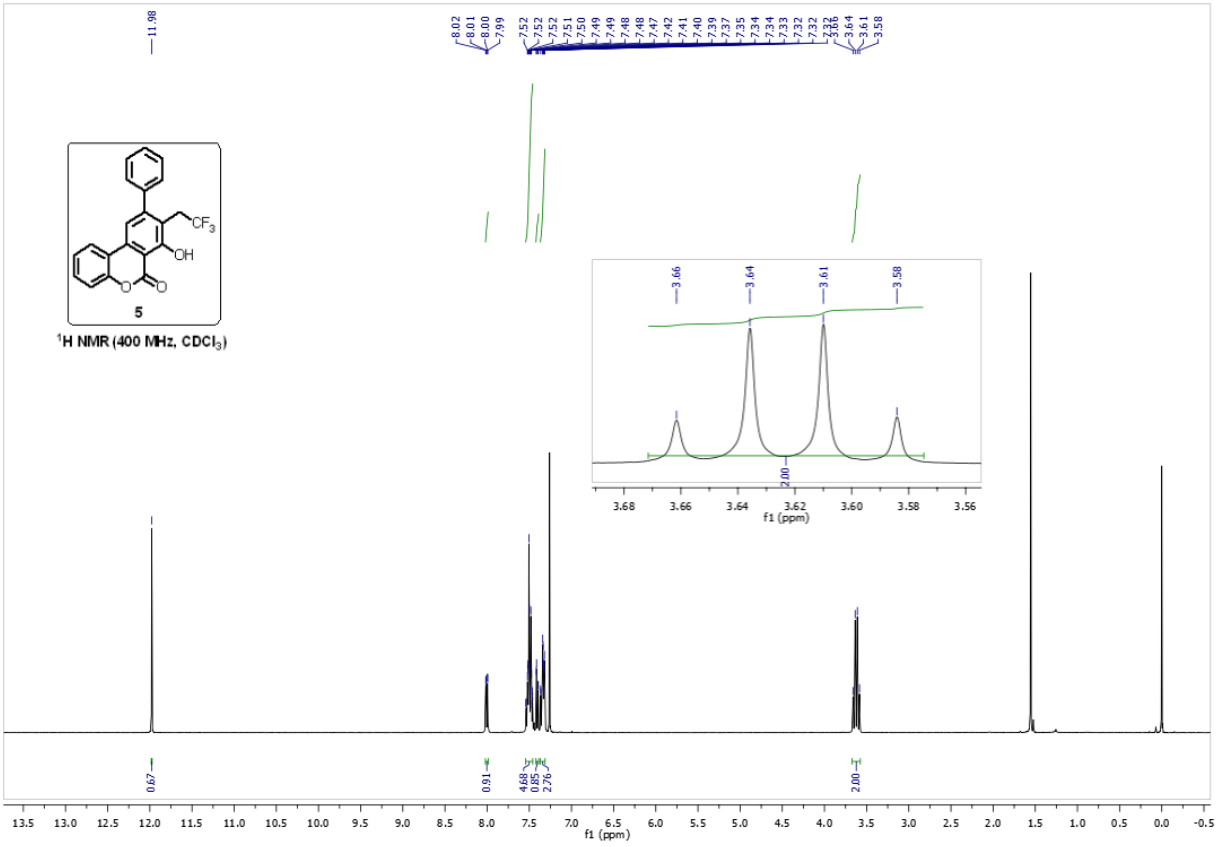

165.55
161.69
148.53
137.58
134.13
133.59
131.58
130.34
128.60
128.57
127.51
127.04
126.71
126.19
125.54
125.40
124.82
124.18
123.63
119.65
115.44
114.26
109.63
31.56
31.30
31.06
30.81
29.59
Ph
CF3
OH
N
O
4l
13C NMR (126 MHz, CDCl3)
f1 (ppm)

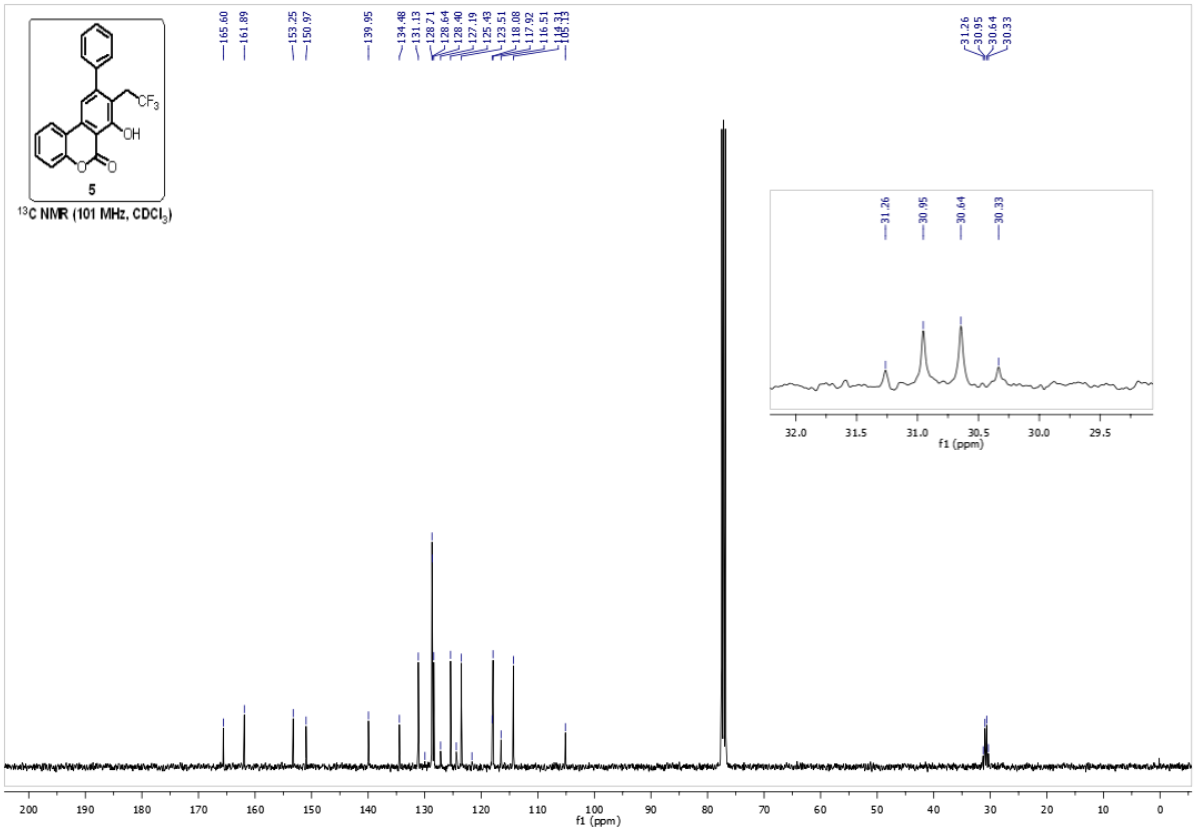

63.64
Ph
CF3
OH
N
O
4l
19F NMR (376 MHz, CDCl3)
f1 (ppm)

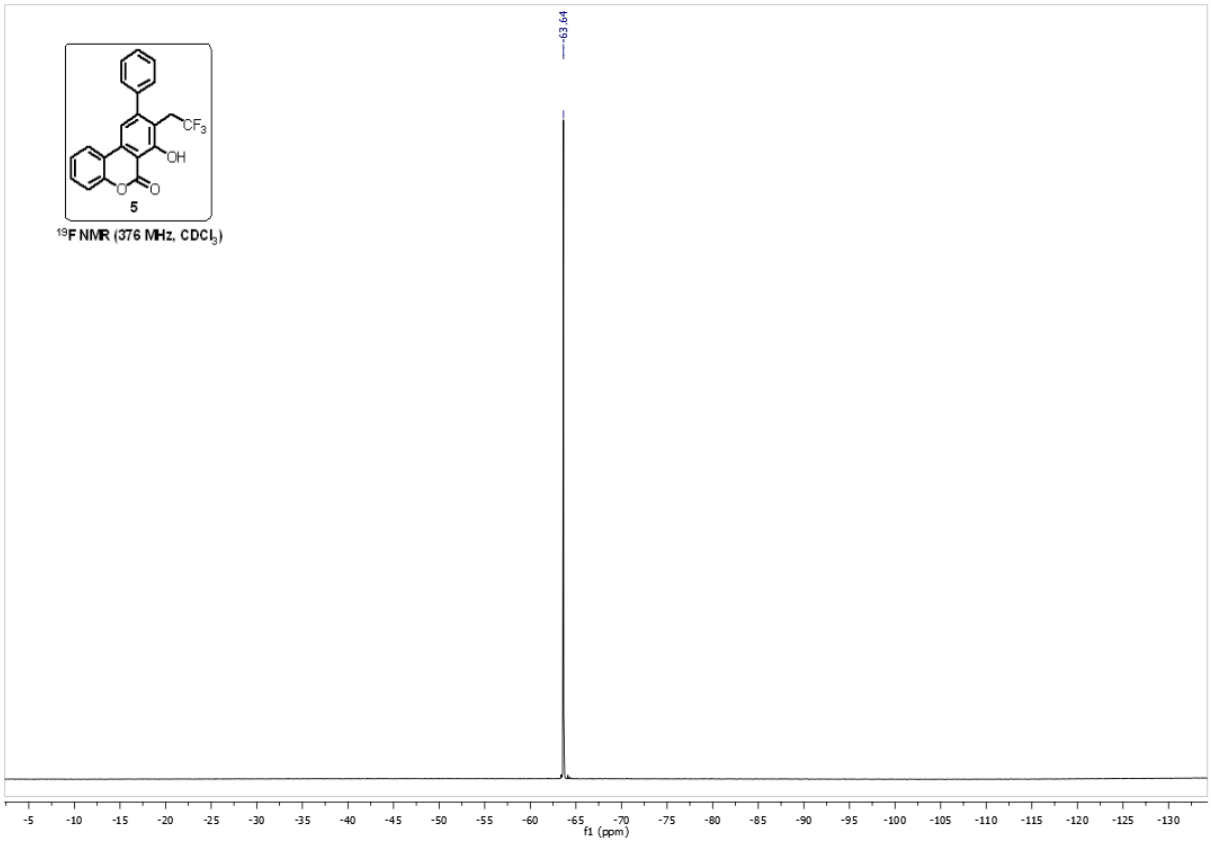

4m
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

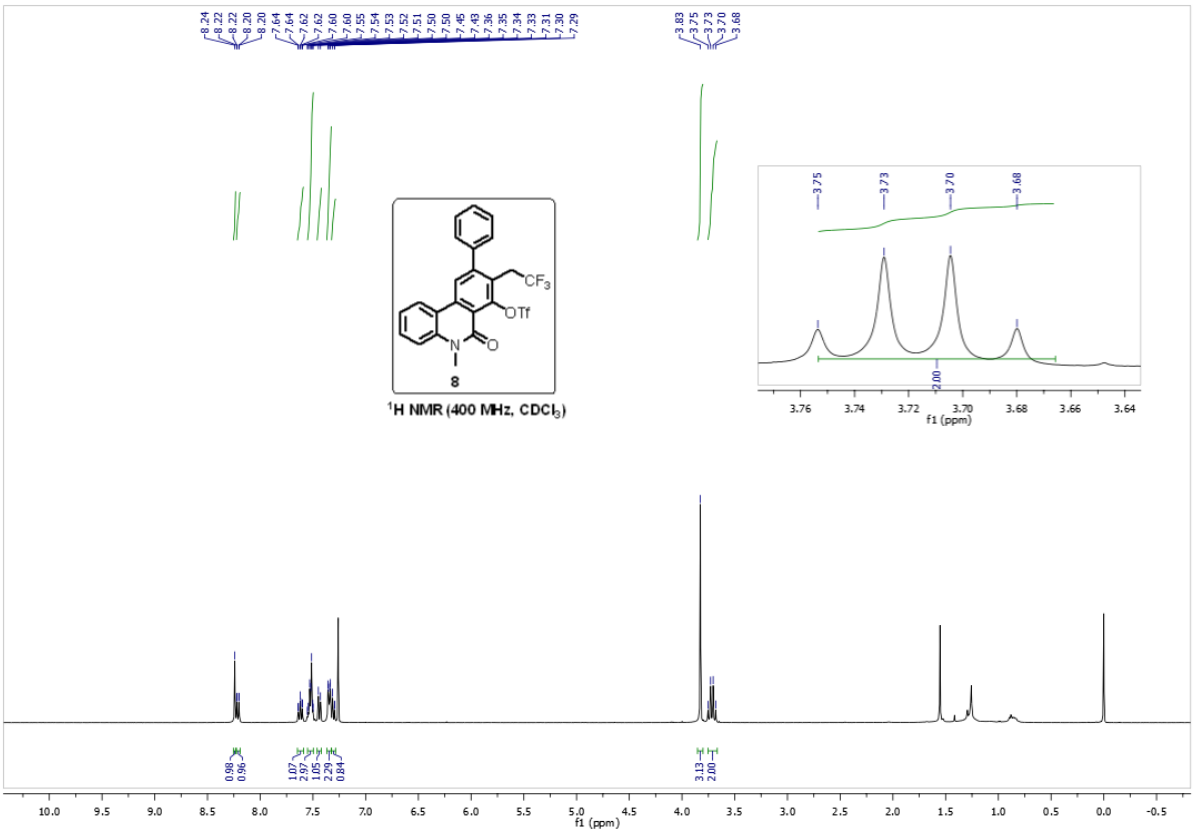

4m
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

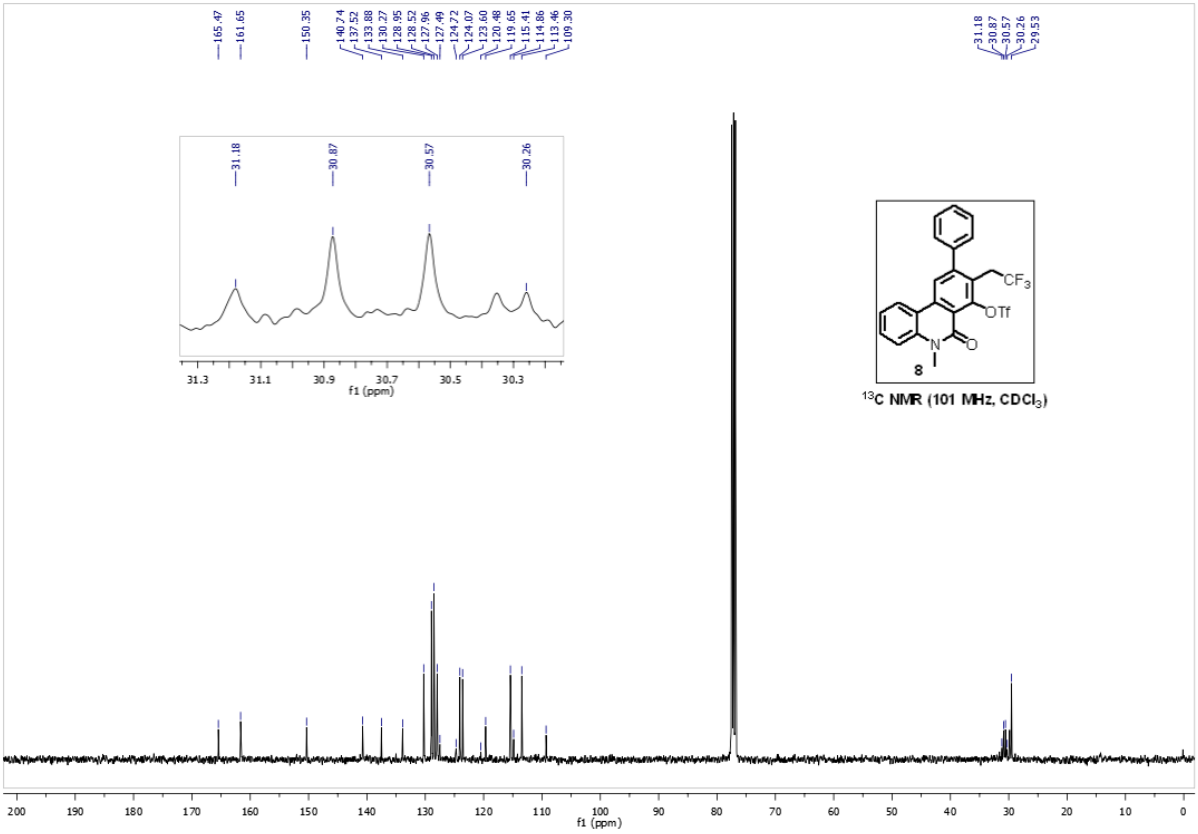

-63.64
CF3
OH
N
O
Ph
4m
19F NMR (376 MHz, CDCl3)
f1 (ppm)

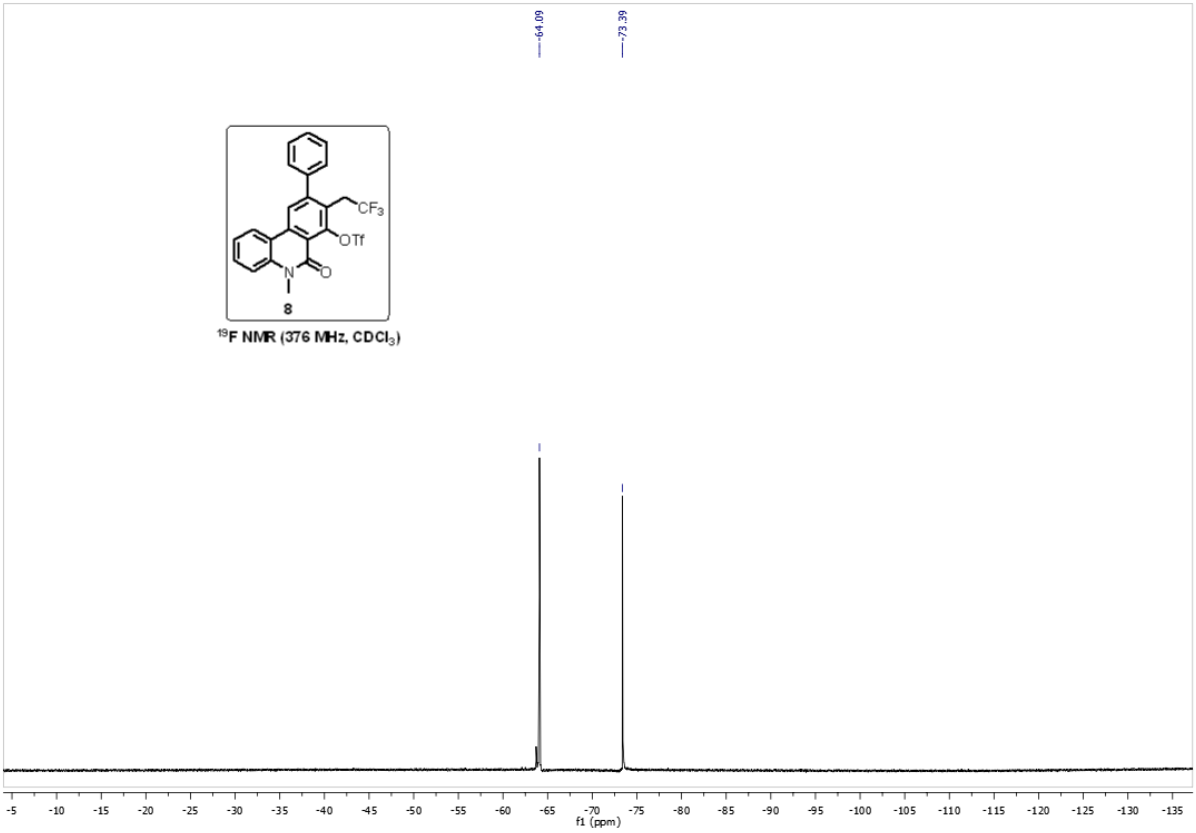

11.98
8.02
8.01
8.00
7.99
7.52
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.42
7.41
7.40
7.39
7.37
7.35
7.34
7.34
7.33
7.32
7.32
3.66
3.64
3.61
3.58
CF3
OH
O
O
5
1H NMR (400 MHz, CDCl3)
2.00
f1 (ppm)
0.67
0.91
4.68
0.85
2.76
2.00
f1 (ppm)


5
^{13}C NMR (101 MHz, $CDCl_3$)
165.60
161.89
153.25
150.97
139.95
134.48
131.13
128.71
128.64
128.40
127.19
125.43
123.51
118.08
117.92
116.51
31.26
30.95
30.64
30.33
f1 (ppm)

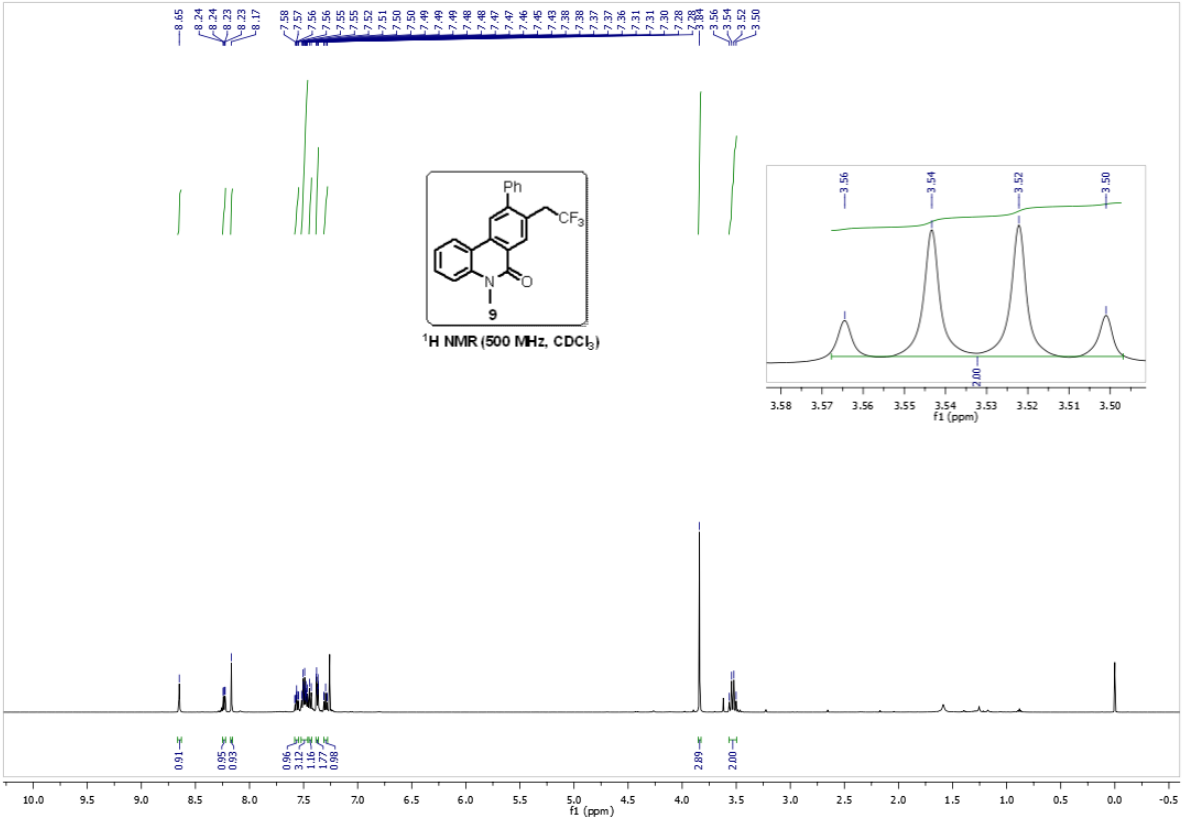

5
^{19}F NMR (376 MHz, $CDCl_3$)
-63.64
f1 (ppm)


8.24
8.22
8.22
8.20
8.20
7.64
7.64
7.62
7.62
7.60
7.60
7.55
7.54
7.53
7.52
7.51
7.50
7.50
7.45
7.43
7.36
7.35
7.34
7.33
7.31
7.30
7.29
3.83
3.75
3.73
3.70
3.68
CF3
OTf
N
O
8
1H NMR (400 MHz, CDCl3)
0.98
0.96
1.07
2.97
1.05
2.29
0.84
3.13
2.00
f1 (ppm)

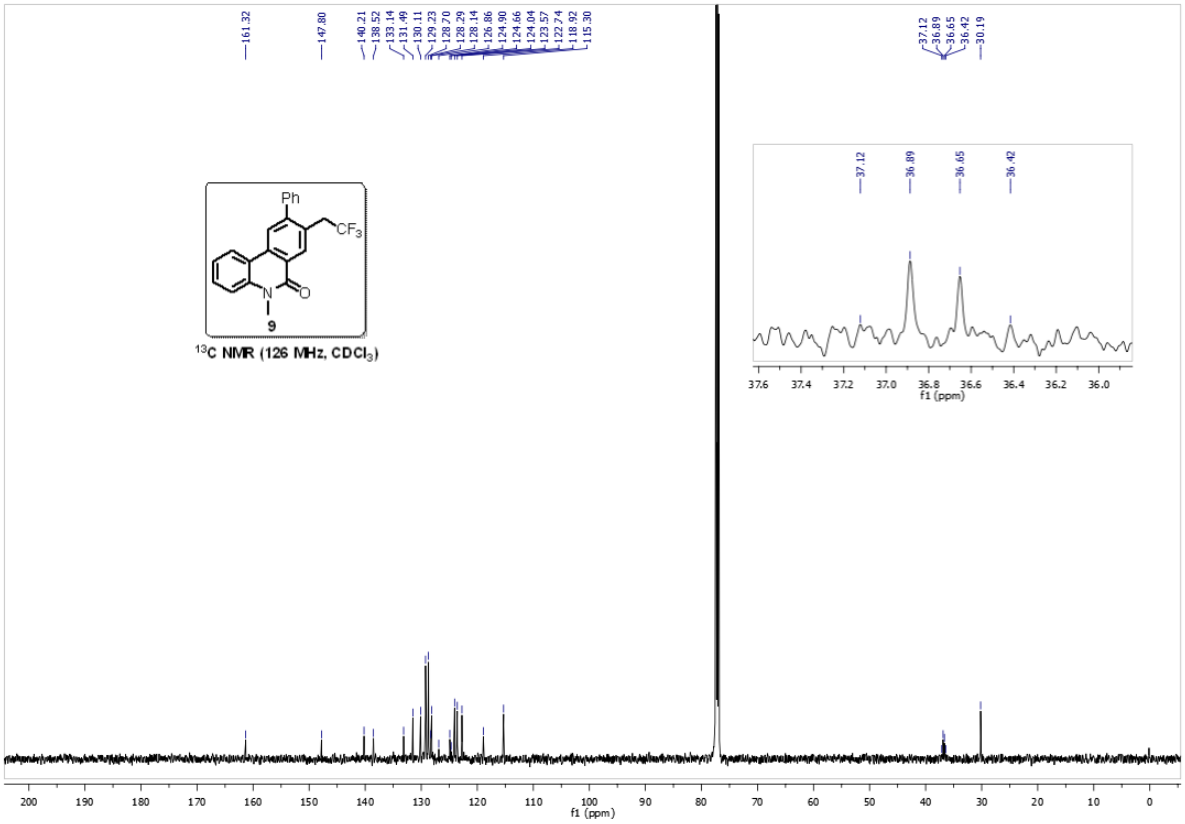

165.47
161.65
150.35
140.74
137.52
133.88
130.27
128.95
128.52
127.96
127.49
124.72
124.07
123.60
120.48
119.65
115.41
114.86
113.46
109.30
31.18
30.87
30.57
30.26
29.53
CF3
OTf
N
O
8
13C NMR (101 MHz, CDCl3)
f1 (ppm)



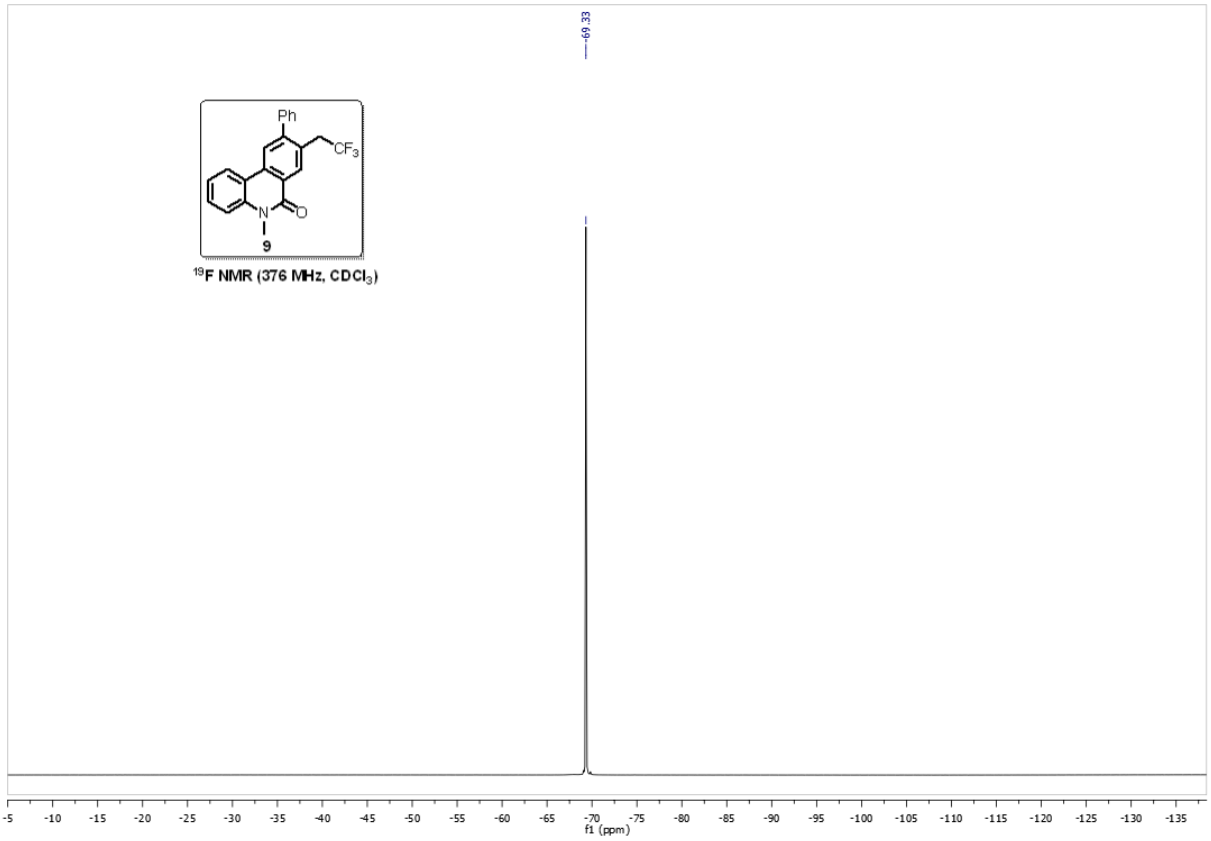
^{19}F NMR (376 MHz, $CDCl_3$)



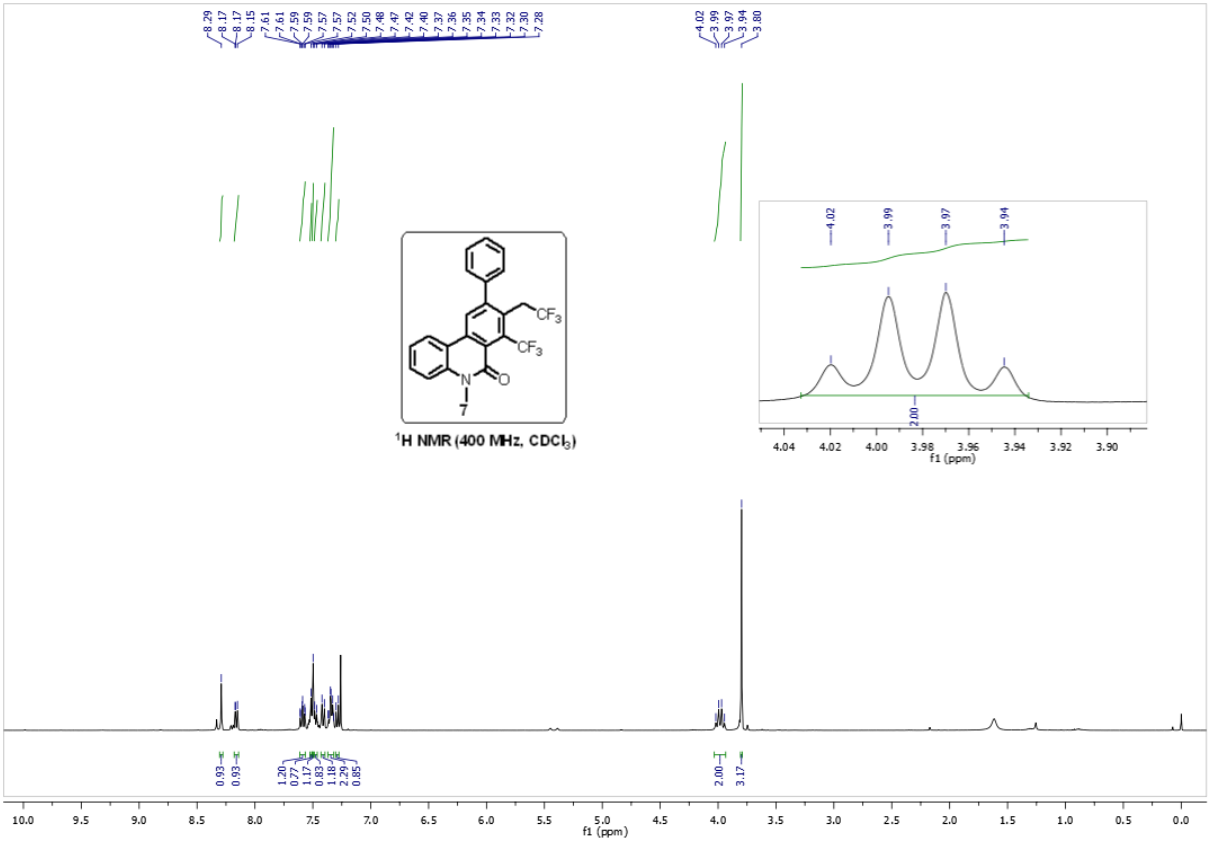
^{1}H NMR (500 MHz, $CDCl_3$)



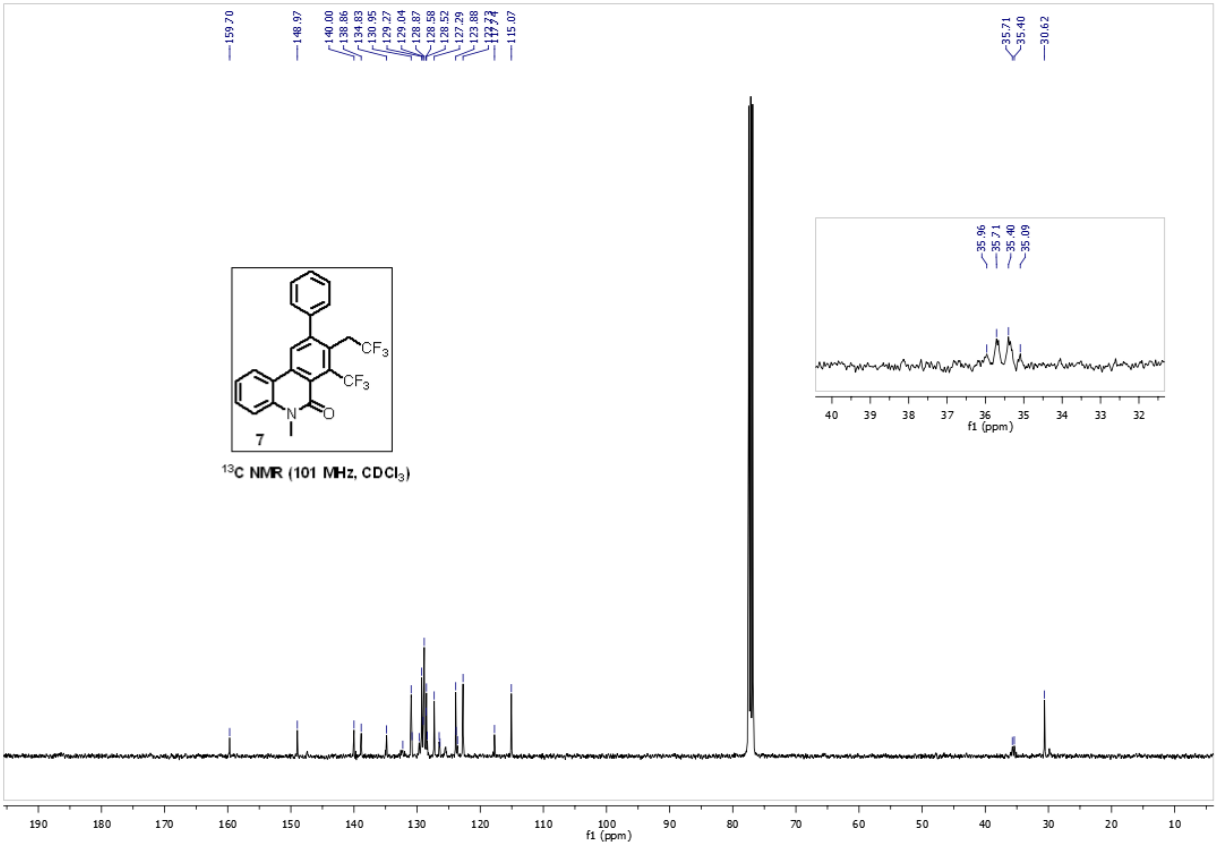
^{13}C NMR (126 MHz, $CDCl_3$)



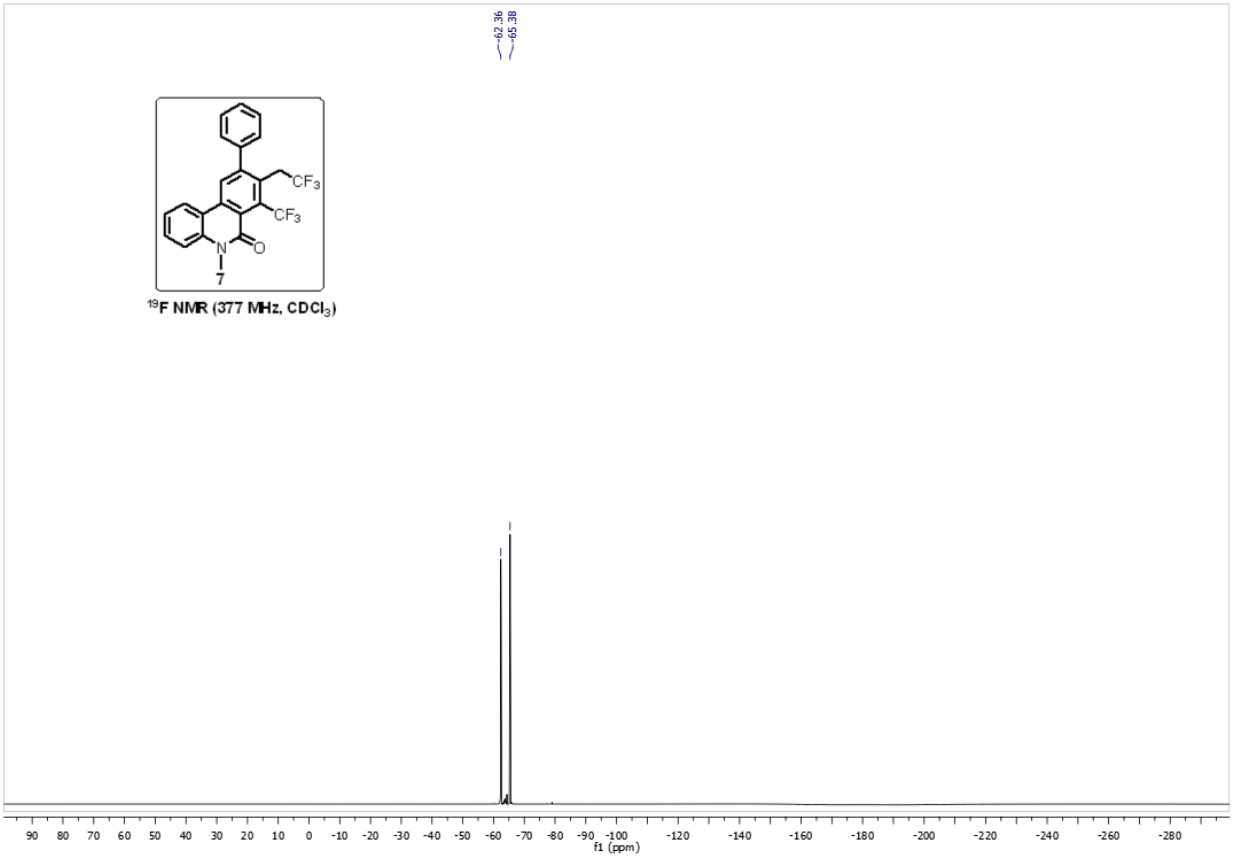
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)