Electronic Supplementary Information

Expeditious synthesis of CF_3-phenantridones through a base-mediated cross-conjugated vinylogous benzannulation (VBA)

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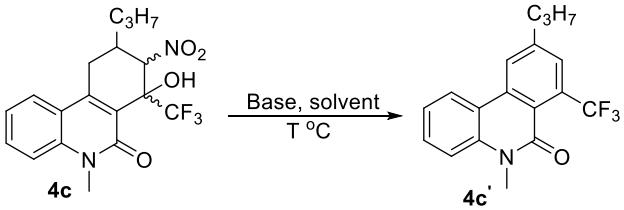
Table of contents

1 General Information.

All the reactions were performed in oven-dried glass apparatus, and the air- and moisture-sensitive reactions were carried out under an inert atmosphere (nitrogen) using freshly distilled solvents. General reactions were conducted in reagent-grade solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography (TLC) carried out on silica plates using UV light and anisaldehyde for visualization. The ^{1}H NMR spectra, the ^{13}C{1H} NMR spectra, and the ^{19}F NMR spectra were recorded on (500, 400, and 300 MHz), (125, 100, and 75 MHz), and (377 and 471 MHz) spectrometers, respectively. 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), and so forth. δ 7.26 and δ 1.56 correspond to $CDCl_3$ and moisture, respectively, and δ 2.5 and δ 3.3 correspond to DMSO-d_6 and moisture, respectively, in ^{1}H NMR. δ 77.16 is related to $CDCl_3$, and δ 39.5 is related to DMSO-d_6 residual solvent peaks in ^{13}C{1H} NMR. High-resolution mass spectra (HRMS) were obtained with an ESI resource by using either a TOF or a double-focusing spectrometer. Column chromatography was performed on silica gel (200−300 mesh) using hexanes and ethyl acetate as eluents. Commercially available chemicals were obtained from Aldrich Chemical Co., Alfa Aesar, TCI and used as received unless otherwise stated.

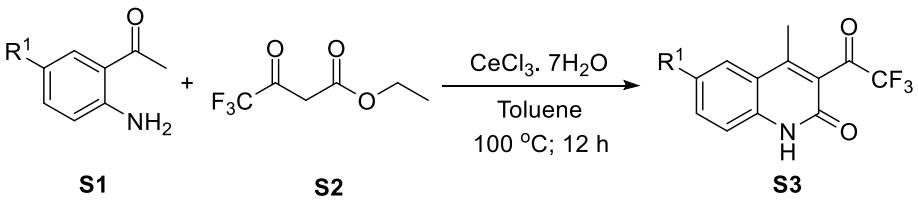
2. Table S1: Attempts for the synthesis of 5-methyl-9-propyl-7-(trifluoromethyl)phenanthridin-6(5*H*)-one from compound 4c



S. No	Base	Solvent	T °C	Yield (4c')
1	KO^{t}Bu (3 equiv.)	THF	rt	-
2	KO^{t}Bu (5 equiv.)	THF	80 °C	-
3	DBU (2 equiv.)	THF	80 °C	-
4	DABCO (2 equiv.)	THF	80 °C	-
5	TEA(1.1 equiv.) PPh_3(1.2equiv.)	CCl_4	80 °C	-
6	$Sc(OTf)_3$ (20 mol%)	Toluene	100 °C	-
[a]Experiments were carried out using **4c** (0.1 mmol) in 2 mL of solvent for 24 hours.				

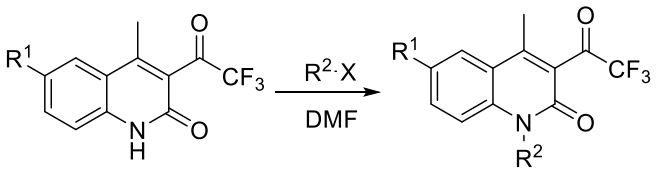
3. General procedure for the synthesis of substituted 4-methyl quinolones (1) (Method A)

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 %, 0.4 equiv) were taken in toluene (5 mL). The reaction was heated at 100 °C (oil bath temperature) for 12 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*-hexanes/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.[1]



S1 **S2** **S3**

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 °C. 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 hexanes/ethyl acetate solvent system) to afford the pure product **1**.

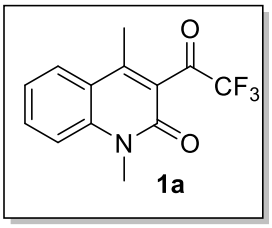


S3 **1**

The characterization data of new compounds **1a, 1b, 1c, 1d, 1f, 1g, 1i,** and **1j,** are summarized below and compounds**1e**, **1h**, **1k**, **1l** and **1m**, are synthesised from reported literature.[2,3]

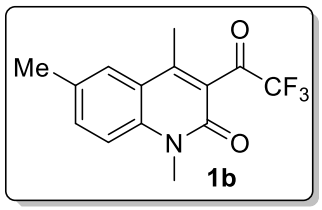
Nitro styrenes (**2**) were prepared following reported literature procedures [4-6]

1,4-Dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1a)



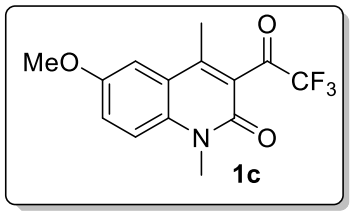
Following the general method A, 4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3a** (102.02 mg, 0.40 mmol), NaH (19.20 mg, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1a,** was a white solid, yield 93% (100.09 mg), mp: 124-126 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.1, 1.4 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.32 (m, 1H), 3.73 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.9 (q, J = 38.0 Hz), 159.3, 147.9, 140.0, 132.7, 126.5, 126.4, 123.0, 120.3, 115.4 (q, J = 291.1 Hz), 114.9, 29.1, 15.7; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.27 (S, 3F); **HRMS (ESI)**: calcd for $C_{13}H_{11}F_3NO_2$ $[M + H]^+$: 270.0742, found: 270.0739.

1,4,6-Trimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1b)



Following the general method A, 4,6-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1H)-one **S3b** (107.62 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 to afford the compound **1b** as a white solid, yield 93% (105.30 mg), mp: 132-134 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, J = 0.7 Hz, 1H), 7.51 (dd, J = 8.6, 1.7 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 3.71 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 182.3 (q, J = 38.0 Hz), 154.5, 142.9, 133.3, 129.2, 127.8, 121.5, 121.1, 120.8, 115.5, 110.6 (q, J = 291.3 Hz), 110.0, 24.4, 16.2, 11.0; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.25 (S, 3F); **HRMS (ESI)**: calcd for $C_{14}H_{13}F_3NO_2$ $[M + H]^+$: 284.0898, found: 284.0916.

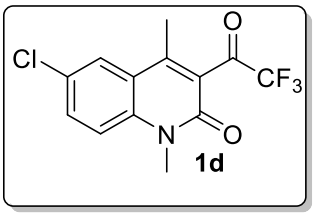
6-Methoxy-1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1c)



Following the general method A, 6-methoxy-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3c** (114.02 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 to afford the compound **1c** as a white solid, yield 94% (112.45 mg), mp: 135-137 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 9.2 Hz, 1H), 7.30 (dd, J = 9.2, 2.8 Hz, 1H), 7.22 (d, J = 2.7 Hz, 1H), 3.90 (s, 3H), 3.70 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.0 (q, J = 38.4 Hz), 158.9, 155.2, 147.0, 134.5, 126.8, 121.1, 120.9, 116.1, 115.4 (q, J = 291.3 Hz), 108.8, 55.8, 29.2, 15.9; **^{19}F**

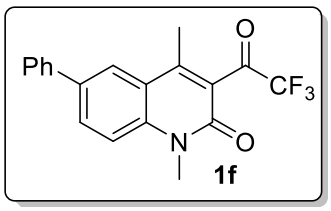
NMR (377 MHz, $CDCl_3$) δ –76.25 (S, 3F); **HRMS (ESI)**: calcd for $C_{14}H_{13}F_3NO_3$ $[M + H]^+$: 300.0847, found: 300.0848.

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



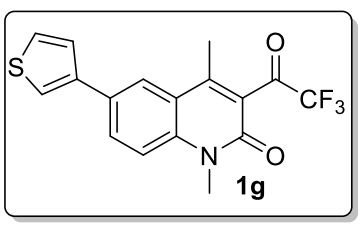
Following the general method A, 6-chloro-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3d** (115.60 mg, 0.40 mmol), NaH (19.20 gm, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1d** as a white solid, yield 79% (95.75 mg), mp: 162-165 ℃; **^{1}H 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), 159.0, 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 –76.32 (s, 3F); **HRMS (ESI)**: calcd for $C_{13}H_{10}ClF_3NO_2$ $[M + H]^+$: 304.0352, found: 304.03481.

1,4-Dimethyl-6-phenyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1f)



Following the general method A, 4-methyl-6-phenyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3f** (132.43 mg, 0.40 mmol), NaH (19.20 gm, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1f** as a white solid, yield 91% (125.61 mg), mp: 166-168 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 1.9 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.62 (dd, J = 8.3, 1.1 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.44 – 7.38 (m, 1H), 3.77 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.9 (q, J = 37.8 Hz), 159.4, 147.9, 139.6, 139.3, 136.3, 131.8, 129.3, 128.0, 127.2, 126.9, 124.8, 120.7, 115.5, 29.4, 15.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –76.25 (S, 3F); **HRMS (ESI)**: calcd for $C_{19}H_{15}F_3NO_2$ $[M + H]^+$: 346.1055, found: 346.1050.

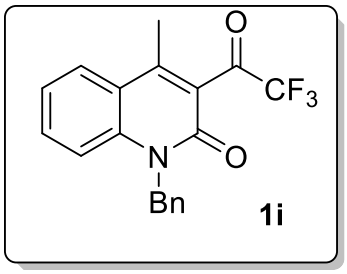
1,4-Dimethyl-6-(thiophen-3-yl)-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1g)



Following the general method A, 4-methyl-6-(thiophen-3-yl)-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3g** (134.81 mg, 0.40 mmol), NaH (19.20 gm, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1g** as a white solid, yield 88% (123.57 mg), mp:

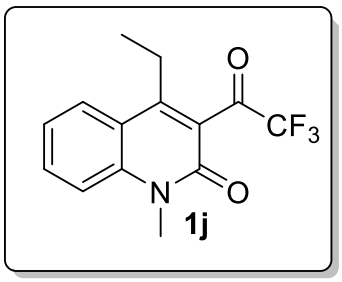
170-172 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 2.0 Hz, 1H), 7.91 (dd, J = 8.8, 2.1 Hz, 1H), 7.52 (dd, J = 2.9, 1.4 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.42 (dd, J = 5.0, 1.4 Hz, 1H), 3.75 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.9 (q, J = 38.1 Hz), 159.3, 147.8, 140.7, 139.1, 131.2, 131.1, 127.2, 126.9, 126.2, 123.9, 121.0, 120.7, 115.5 (q, J = 291.4 Hz), 115.5, 29.4, 15.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –76.25 (S, 3F); **HRMS (ESI)**: calcd for $C_{17}H_{13}F_3NO_2S$ $[M + H]^+$: 352.0619, found: 352.0614.

1-Benzyl-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1i)



Following the general method A, 4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3a** (102.02 mg, 0.40 mmol), NaH (19.20 mg, 0.48 mmol), benzyl bromide (102.62 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1i** as a white solid, yield 94% (129.76 mg), mp: 146-148 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.1, 1.3 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.20 (m, 3H), 5.55 (s, 2H), 2.50 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.9 (q, J = 38.2 Hz), 159.7, 148.7, 139.5, 135.7, 132.8, 129.0, 127.7, 126.7, 126.3, 123.1, 120.6, 115.8, 115.5 (q, J = 291.2 Hz), 45.7, 15.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –76.14 (S, 3F); **HRMS (ESI)**: calcd for $C_{19}H_{15}F_3NO_2$ $[M + H]^+$: 346.1055, found: 346.1042.

4-Ethyl-1-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one (1j)

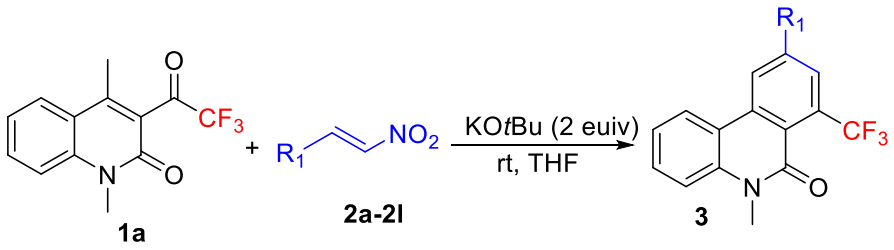


Following the general method A, 4-ethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **S3j** (107.60 mg, 0.40 mmol), NaH (19.20 gm, 0.48 mmol), methyl iodide (85.16 mg, 0.6 mmol) and 3 mL DMF were used to afford the compound **1j** as a white solid, yield 86% (97.35 mg), mp: 166-168 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.2, 1.3 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.47 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 3.73 (s, 3H), 2.82 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.0 (q, J = 37.8 Hz), 159.6, 153.8, 140.5, 132.6, 126.5, 125.5, 122.9, 119.1, 115.3 (q, J = 291.1 Hz), 115.1, 29.2, 22.9, 15.0; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.03; **HRMS (ESI)**: calcd for $C_{14}H_{13}F_3NO_2$ $[M + H]^+$: 284.0898, found: 284.8693.

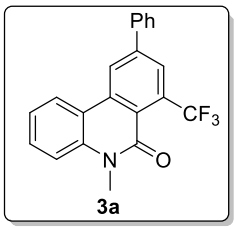
4. Synthesis of 7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3a-3t):

General procedure B:

In a reaction viol 3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1** (0.1 mmol) corresponding nitro olefin **2** (0.15 mmol) were dissolved in 2 mL dry THF, was added slowly pre-sublimised KO*t*Bu (2 equiv) in an argon-filled glove box, upon which the reaction mixture colour turned to deep red colour was stirred another 15 to 30 min at room temperature. The progress of the reaction was monitored by TLC, and upon completion of the reaction, the mixture was poured into 10 mL water and extracted with ethyl acetate (2x 15 mL) dried over anhydrous sodium sulphate, the solvent was evaporated in a vacuum, the crude was purified by column chromatography.

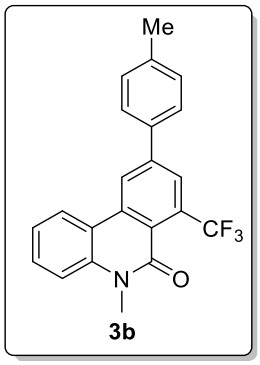


5-Methyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3a):



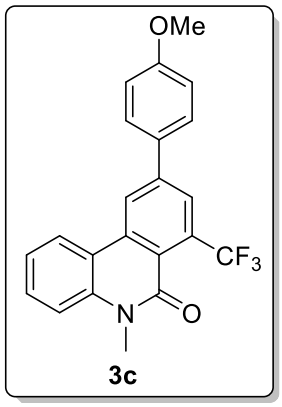
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene (**2a**) (23 mg, 0.15 mmol) were used to afford the compound **3a**, yield 85% (30 mg), white solid, mp 213 °C; **^{1}HNMR** (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.6 Hz, 1H,), 8.38 (dd, J = 8.2, 1.2 Hz, 1H), 8.25 (d, J = 0.8 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.62 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.59 – 7.42 (m, 4H), 7.35 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 144.3, 138.9, 138.5, 136.7, 131.4 (q, J = 33.1 Hz), 130.7, 129.3, 129.0, 127.3 (q, J = 7.7 Hz), 127.5, 124.1, 124.01 (q, J = 273.9 Hz), 123.8, 122.6, 122.2, 118.2 (s), 114.9, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –57.71 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{15}F_3NO$: 354.1106, found: 354.1120.

5-Methyl-9-(p-tolyl)-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3b):



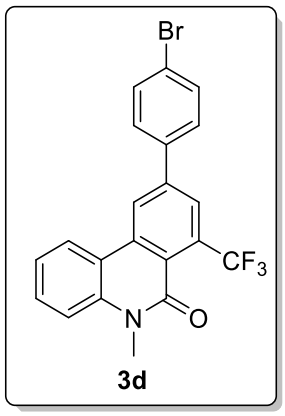
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (**2b**) (24 mg, 0.015 mmol) were used to afford the compound **3b**, yield 84% (31 mg), white solid, mp 218 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, J = 1.4 Hz, 1H), 8.34 (dd, J = 8.2, 0.9 Hz, 1H), 8.22 (s, 1H), 7.66 – 7.56 (m, 3H), 7.41 (d, J = 7.9 Hz, 1H), 7.37 – 7.31 (m, 3H), 3.80 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 144.1, 139.1, 138.5, 136.7, 135.9, 131.3 (q, J = 32.0 Hz), 130.6, 130.0, 127.3, 127.08 (q, J = 7.7 Hz), 124.1 (q, J = 273.4 Hz), 123.7, 123.6, 122.5, 121.9, 118.3, 114.9, 30.3, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.67 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{17}F_3NO$: 368.1262, found: 368.1257.

9-(4-Methoxyphenyl)-5-N-methylphenanthridin-6(5*H*)-one (3c):



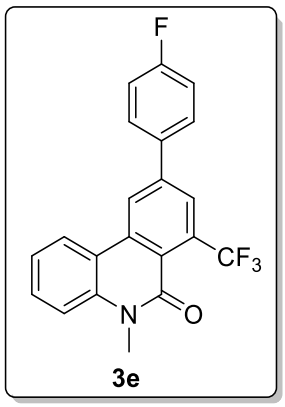
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (**2c**) (27 mg, 0.15 mmol) were used to afford the compound **3c**, yield 75% (29 mg), White solid, mp 203 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, J = 1.5 Hz, 1H), 8.33 (dd, J = 8.2, 1.1 Hz, 1H), 8.19 (s, 1H), 7.70 – 7.63 (m, 2H), 7.62 – 7.56 (m, 1H), 7.35 – 7.30 (m, 1H), 7.08 – 7.03 (m, 2H), 3.90 (s, 3H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 158.8, 143.7, 138.5, 136.7, 131.3 (q, J = 32.0 Hz) 131.2, 130.6, 128.6, 126.8 (q, J = 7.6 Hz), 124.1 (q, J = 273.4 Hz), 123.7, 123.2, 122.5, 121.5, 118.3, 114.9, 114.7, 55.5, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –57.70 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{17}F_3NO_2$: 384.1211, found: 384.1208.

9-(4-Bromophenyl)-5-N-methyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3d):



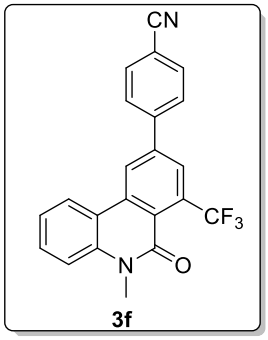
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-bromo-4-(2-nitrovinyl)benzene (**2d**) (34 mg, 0.15 mmol) were used to afford the compound **3d**, yield 79% (34 mg), white solid, mp 237 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.34 (d, *J* = 8.1 Hz, 1H), 8.18 (s, 1H), 7.67 (t, *J* = 8.3 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 143.0, 138.5, 137.8, 136.9, 132.5, 131.6 (q, *J* = 32.3 Hz), 130.8, 129.0, 126.9 (q, *J* = 7.6 Hz), 123.9 (q, J = 272.7 Hz), 123.9, 123.7, 123.6, 122.6, 122.4, 118.0, 115.0, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –57.76 (s, 3F); **HRMS** (ESI) m/z [M + H]+ calcd for $C_{21}H_{14}BrF_3NO$: 432.0211, found: 432.0215.

9-(4-Fluorophenyl)-5-N-methylphenanthridin-6(5*H*)-one (3e):



Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-fluoro-4-(2-nitrovinyl)benzene(**2e**) (25 mg, 0.015 mmol) were used to afford the compound **3e**, yield 83% (31 mg), mp 226 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.4 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.16 (s, 1H), 7.72 – 7.65 (m, 2H), 7.63 – 7.57 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.27 – 7.24 (m, 1H), 7.22 – 7.18 (m, 1H), 3.78 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.4, 162.4, 158.7, 143.1, 138.5, 136.8, 135.0, 131.4 (q, J = 32.1 Hz), 130.8, 129.2 (d, *J* = 8.3 Hz), 127.0 (q, *J* = 7.6 Hz), 123.9 (q, *J* = 273.4 Hz), 123.8 (d, *J* = 13.0 Hz), 122.6, 122.1, 118.0, 116.3 (d, *J* = 21.7 Hz), 115.0, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –57.72 (s, 3F), –112.59 (s, 1F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{14}F_4NO$: 372.1012, found: 372.1007.

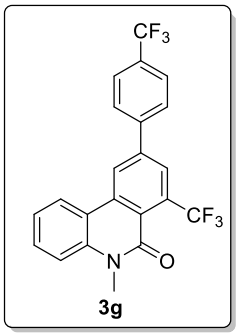
4-(5-Methyl-6-oxo-7-(trifluoromethyl)-5, 6-dihydrophenanthridin-9-yl) benzonitrile (3f):



Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-4-(2-nitrovinyl)benzonitrile (**2f**) (26 mg, 0.15 mmol) were used to afford the compound **3f**, yield 86% (32 mg), white solid, mp 226 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 1.2 Hz, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 8.21 (s, 1H), 7.85 (s, 4H), 7.67 – 7.61 (m, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.33 (m, 1H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5,

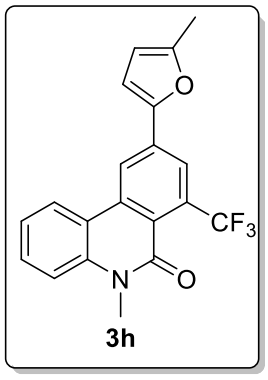
143.3, 142.1, 138.6, 137.0, 133.0, 131.9 (q, *J* = 32.1 Hz), 131.1, 129.8, 128.2, 126.9 (q, *J* = 7.6 Hz), 124.5, 123.8 (q, *J* = 273.3 Hz), 123.1, 122.7, 118.4, 117.8, 115.1, 112.8, 30.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ – 57.80 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{14}F_3N_2O$: 379.1058, found: 379.1054.

5-Methyl-7-(trifluoromethyl)-9-(4-(trifluoromethyl) phenyl) phenanthridin-6(5*H*)-one (3g):



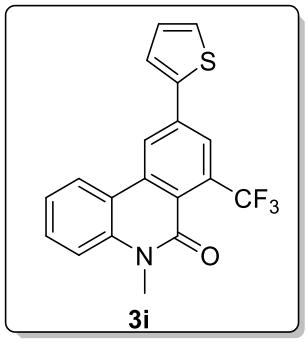
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (E)-1-(2-nitrovinyl)-4-(trifluoromethyl)benzene (**2g**) (33 mg, 0.15 mmol) were used to afford the compound **3g**, white solid, yield 80% (34 mg), mp 237 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.70 (d, *J* = 1.5 Hz, 1H), 8.36 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.23 (d, *J* = 0.7 Hz, 1H), 7.83 (q, *J* = 8.5 Hz, 4H), 7.67 – 7.60 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.33 (m, 1H), 3.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 158.6, 142.8, 142.6 (q, *J* = 9.4 Hz), 142.5, 138.6, 136.9, 131.5 (q, *J* = 90.0 Hz), 131.0 (q, *J* = 88.7 Hz), 131.0, 127.9, 127.1 (q, J = 7.6 Hz), 126.3, 126.2, 124.5, 124.0 (q, *J* = 272.7 Hz), 123.9 (q, *J* = 273.2 Hz), 123.7, 122.9, 122.7, 118.0, 115.1, 30.4; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –57.78 (s, 3F), – 62.63 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{14}F_6NO_2$: 422.0980, found: 422.0972.

5-Methyl-9-(5-methylfuran-2-yl)-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3h)



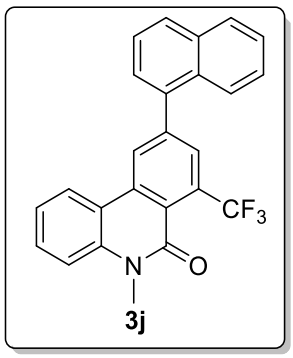
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-2-methyl-5-(2-nitrovinyl)furan (**2h**) (23 mg, 0.15 mmol) were used to afford the compound **3h**, Gray colour solid, yield 76% (27 mg), mp 232 °C; IR (KBr): υ 1657, 1252 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.54 (d, *J* = 1.3 Hz, 1H), 8.26 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.10 (d, *J* = 0.4 Hz, 1H), 7.62 – 7.47 (m, 1H), 7.38 – 7.27 (m, 2H), 6.79 (d, *J* = 3.3 Hz, 1H), 6.22 – 6.08 (m, 1H), 3.72 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 158.6, 154.5, 150.0, 138.4, 136.8, 133.4, 131.2 (q, *J* = 32.0 Hz), 130.5, 124.0 (q, *J* = 273.5 Hz), 123.8, 123.2 (q, *J* = 7.9 Hz), 122.4, 121.0, 118.8, 118.1, 114.8, 109.9, 108.7, 30.2, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* –57.86 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{15}F_3NO_2$: 358.1055, found: 358.1050.

5-Methyl-9-(thiophen-2-yl)-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3i)



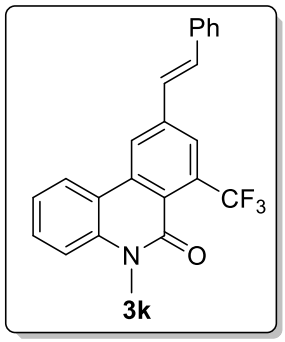
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-2-(2-nitrovinyl)thiophene (**2i**) (23 mg, 0.15 mmol) were used to afford the compound **3i**, Pale yellow solid, yield 78% (28 mg), mp 202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, J = 1.5 Hz, 1H), 8.29 (d, J = 7.2 Hz, 1H), 8.21 (s, 1H), 7.63 – 7.54 (m, 2H), 7.47 (dd, J = 5.1, 1.0 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.19 (dd, J = 5.1, 3.7 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 141.7, 138.5, 137.3, 136.9, 131.5 (q, J = 32.2 Hz), 130.8, 128.7, 127.4, 125.7, 125.6 (q, J = 7.6 Hz), 123.8 (q, J = 273.6 Hz), 123.7, 122.6, 122.0, 121.9, 117.9, 114.9, 30.3; **^{19}F NMR** (377 MHz, CDCl3) δ –57.91 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{13}F_3NOS$: 360.0670, found: 360.0684.

5-Methyl-9-(naphthalen-1-yl)-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3j)



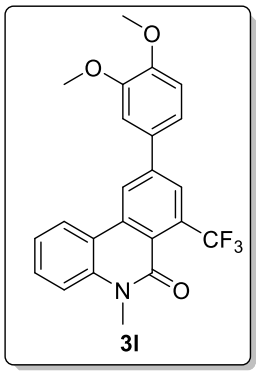
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-2-(2-nitrovinyl)naphthalene (**2j**) (30 mg, 0.15 mmol) were used to afford the compound **3j**, Pale grey colour solid, yield 79% (32 mg), mp 205 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, J = 1.4 Hz, 1H), 8.26 (dd, J = 8.2, 1.2 Hz, 1H), 8.19 (s, 1H), 8.03 – 7.95 (m, 2H), 7.84 – 7.75 (m, 1H), 7.64 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.52 – 7.48 (m, 1H), 7.45 (dd, J = 8.5, 0.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 3.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 144.3, 138.5, 137.8, 136.5, 133.9, 131.1, 131.1, 130.7, 130.0 (q, J = 7.7 Hz), 129.1, 128.7, 127.4, 127.3, 127.0, 126.4, 125.4, 125.1, 125.1 (q, J = 293.4 Hz), 123.9, 122.6, 122.4, 118.2, 115.0, 30.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.59 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{17}F_3NO$: 404.1262, found: 404.1255.

(E)-5-Methyl-9-styryl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3k)



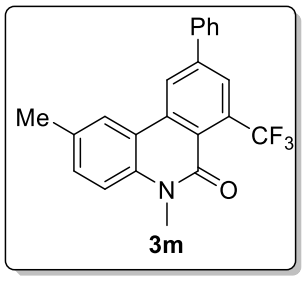
Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and ((1*E*,3*E*)-4-nitrobuta-1,3-dien-1-yl)benzene (**2k**) (27 mg, 0.15 mmol) were used to afford the compound **3k**, Pale grey solid, yield 77% (29 mg), mp 201 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 8.20 (s, 1H), 7.65 – 7.58 (m, 3H), 7.47 – 7.32 (m, 6H), 7.27 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.6, 140.1, 138.4, 136.7, 136.1, 133.0, 131.1 (q, *J* = 31.7 Hz), 130.6, 128.9, 128.9, 127.1, 126.2, 125.6 (q, *J* = 6.9 Hz), 124.0 (q, J = 273.4 Hz), 123.7, 123.5, 122.5, 122.0, 118.0, 114.9, 30.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.78 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{17}F_3NO$: 380.1262, found: 380.1260.

9-(3,4-Dimethoxyphenyl)-5-methyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3l)



Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene (**2l**) (31 mg, 0.15 mmol) were used to afford the compound **3l**, Pale yellow solid, yield 82% (34 mg), mp 197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.5 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.13 (s, 1H), 7.59 – 7.49 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.24 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.8, 150.0, 149.6, 144.0, 138.5, 136.7, 131.7, 131.2 (q, *J* = 32.4 Hz), 127.0 (q, *J* = 7.6 Hz), 124.0 (q, *J* = 273.5 Hz), 123.7, 123.4, 122.5, 121.6, 120.2, 118.2, 114.9, 111.7, 110.4, 56.2, 56.1, 30.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.66 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{19}F_3NO_3$: 414.1317, found: 414.1304.

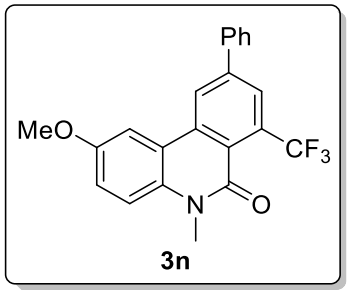
2, 5-Dimethyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3m):



Following the general method B, 1,4,6-trimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1b** (28 mg, 0.1 mmol) and (E)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3m**, White solid, yield 81% (30 mg), mp 218 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.4 Hz, 1H), 8.20 (s, 1H), 8.09 (s, 1H), 7.75 – 7.70 (m, 2H), 7.57 – 7.52 (m, 2H), 7.51 – 7.46 (m, 1H), 7.39 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 2.49 (s, 3H); **^{13}C**

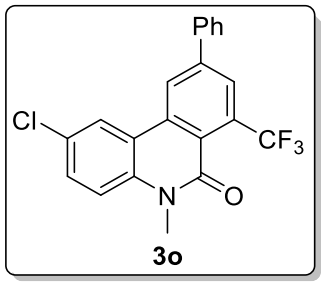
NMR (101 MHz, $CDCl_3$) δ 158.6, 144.0, 139.0, 136.6, 136.4, 132.0, 131.7, 131.3 (q, J = 31.9 Hz), 129.3, 129.0, 127.5, 127.1 (q, J = 7.5 Hz), 124.1 (q, J = 273.6 Hz), 124.0, 123.8, 122.2, 118.0, 114.9, 30.3, 21.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.61(s, 3F); **HRMS** (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{17}F_3NO$: 368.1262, found: 368.1259.

2-Methoxy-5-methyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3n):



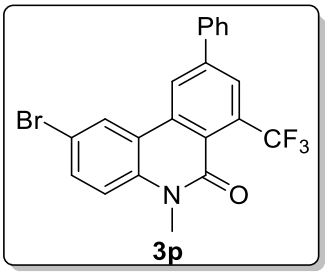
Following the general method B, 6-methoxy-1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1c** (30 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3n**, White solid, yield 79% (30 mg), mp 211 °C; IR (KBr): υ 1659, 1256 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, J = 1.4 Hz, 1H), 8.23 (s, 1H), 7.78 (d, J = 2.7 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.59 – 7.53 (m, 2H), 7.52 – 7.47 (m, 1H), 7.34 (d, J = 9.1 Hz, 1H), 7.20 (dd, J = 9.1, 2.7 Hz, 1H), 3.94 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 155.1, 144.1, 139.0, 136.3, 132.8, 131.4 (q, J = 32.2 Hz), 129.3, 129.0, 127.5, 127.4 (q, J = 7.9 Hz), 124.1, 124.0 (q, J = 272.5 Hz), 122.5, 119.1, 117.4, 116.1, 107.9, 55.9, 30.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.58 (s, 3F); **HRMS** (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{17}F_3NO_2$: 384.1211, found: 384.1208.

2-Chloro-5-methyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3o)



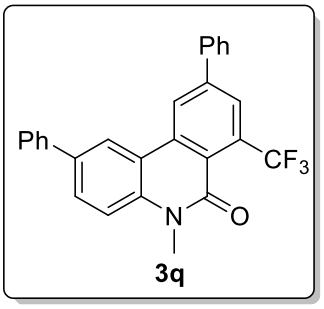
Following the general method B, 6-chloro-1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1d** (30 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3o**, White solid, yield 72% (28 mg), mp 229 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, J = 1.3 Hz, 1H), 8.26 – 8.13 (m, 2H), 7.72 – 7.60 (m, 2H), 7.54 – 7.40 (m, 4H), 7.28 (d, J = 9.0 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.4, 144.6, 138.6, 137.0, 135.5, 131.5 (q, J = 32.0 Hz), 130.5, 129.4, 129.2, 128.3, 127.9 (q, J = 7.8 Hz), 127.5, 124.0, 123.8 (q, J = 273.5 Hz), 123.5, 122.3, 119.5, 116.4, 30.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.80 (s, 3F); **HRMS** (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{14}ClF_3NO$: 388.0716, found: 388.0710.

2-Bromo-5-methyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3p):



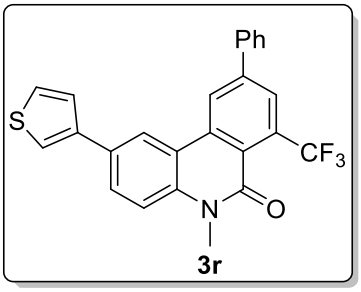
Following the general method B, 6-bromo-1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1e** (35 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3p**, Pale yellow solid, yield 70% (30 mg), mp 251 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, J = 1.4 Hz, 1H), 8.42 (d, J = 2.1 Hz, 1H), 8.27 (s, 1H), 7.77 – 7.71 (m, 2H), 7.67 (dd, J = 8.9, 2.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.28 (d, J = 9.0 Hz, 1H), 3.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 144.7, 138.6, 137.5, 135.4, 133.3, 131.5 (q, J = 32.2 Hz), 129.4, 129.2, 127.9 (q, J = 7.4 Hz), 127.5, 126.4, 124.0, 123.8 (q, J = 273.2 Hz), 122.3, 119.9, 116.6, 115.7, 30.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.80 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{14}BrF_3NO$: 432.0211, found: 432.0205.

5-Methyl-2, 9-diphenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3q):



Following the general method B, 1,4-dimethyl-6-phenyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1f** (35 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3q**, Gray solid, yield 80% (34 mg), mp 221 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, J = 1.1 Hz, 1H), 8.44 (d, J = 1.7 Hz, 1H), 8.22 (s, 1H), 7.77 (dd, J = 8.7, 1.8 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.67 – 7.63 (m, 2H), 7.57 – 7.48 (m, 5H), 7.45 – 7.39 (m, 2H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 144.3, 140.1, 138.9, 137.7, 136.7, 135.7, 131.4 (q, J = 32.2 Hz), 129.6, 129.3, 129.1, 128.9, 127.6, 127.5, 127.4 (q, J = 7.3 Hz), 127.1, 124.0, 124.0 (q, J = 273.2 Hz), 122.2, 118.4, 115.4, 30.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.61 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{19}F_3NO$: 430.1419, found: 430.1418.

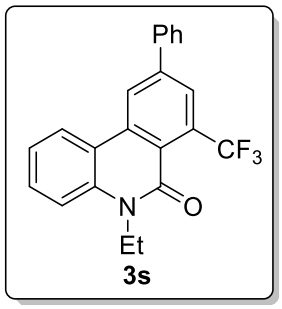
5-Methyl-9-phenyl-2-(thiophen-3-yl)-7-(trifluoromethyl)phenanthridin-6(5*H*)-one (3r)



Following the general method B, 1,4-dimethyl-6-(thiophen-3-yl)-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1g** (35 mg, 0.1 mmol) and (E)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3r**, White solid, yield 71% (31 mg), mp 212 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, J = 1.5 Hz, 1H), 8.42 (d, J = 1.9 Hz, 1H), 8.18 (s, 1H), 7.74 (dd, J = 8.7, 1.9 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.54 – 7.42 (m, 4H), 7.41 – 7.35 (m, 3H), 3.75 (s, 3H);**^{13}CNMR** (151 MHz, $CDCl_3$) δ 158.7, 144.4, 141.3, 139.0, 137.6, 136.6, 131.5 (q, J = 32.7

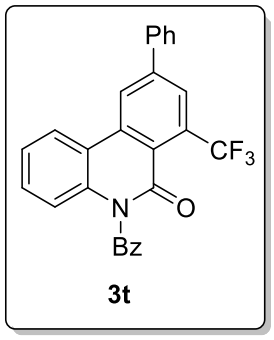
Hz), 130.6, 129.3, 129.1, 129.1, 127.6, 127.5 (q, *J* = 8.0 Hz), 126.8, 126.3, 124.1, 124.0 (q, *J* = 273.8 Hz), 122.4, 121.5, 120.6, 118.5, 115.5, 30.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.71 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{17}F_3NOS$: 436.0983, found: 436.0975.

5-Ethyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3s):



Following the general method B, 1-ethyl-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1h** (28 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **3s**, White solid, yield 73% (27 mg), mp 224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.3 Hz, 1H), 8.32 (d, *J* = 7.3 Hz, 1H), 8.17 (s, 1H), 7.72 – 7.63 (m, 2H), 7.58 – 7.45 (m, 3H), 7.45 – 7.34 (m, 2H), 7.30 – 7.22 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3, 144.2, 139.0, 137.4, 136.7, 131.3 (q, *J* = 31.8 Hz), 131.2, 130.7, 129.3, 129.0, 127.5, 127.2 (q, *J* = 8.0 Hz), 124.0 (q, *J* = 273.2 Hz), 124.0, 122.3, 122.3, 118.5, 114.9, 38.2, 12.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.72 9 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{17}F_3NO$: 368.1262, found: 368.1208.

5-Benzyl-9-phenyl-7-(trifluoromethyl) phenanthridin-6(5*H*)-one (3t):



Following the general method A, 1-benzyl-4-methyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1i** (34 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.015 mmol) were used to afford the compound **3t**, White solid, yield 79% (34 mg), mp 230 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.27 (s, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.47 – 7.40 (m, 1H), 7.34 – 7.19 (m, 7H), 5.65 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 144.5, 138.9, 137.9, 137.0, 136.3, 131.6 (q, *J* = 32.0 Hz), 130.6, 129.3, 129.1, 129.0, 128.9, 127.8 (q, *J* = 278.4 Hz), 127.5, 127.4, 127.3, 126.6, 125.4, 124.1, 123.8, 122.7, 122.0, 118.4, 115.9, 46.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –57.69 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{19}F_3NO$: 430.1419, found: 430.1415.

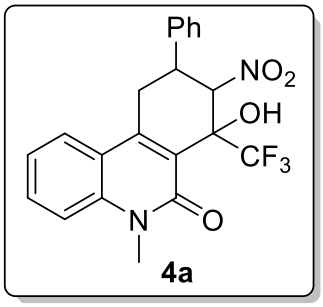
5. Synthesis of 7-hydroxy-8-nitro-7-(trifluoromethyl)-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (4):

General procedure C:

The synthesis of compounds **4** were carried out according to the modified procedure B, with the variation being the quantity of base used and temperature.

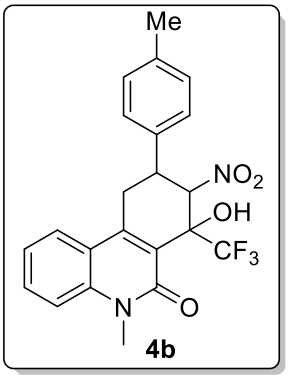
In a reaction viol 3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1**(0.1 mmol) corresponding nitro olefin **2**(0.15 mmol) were dissolved in 2 mL dry THF, was added slowly pre-sublimised KO*t*Bu (1 equiv) in an argon filled glove box, was stirred another 15 to 20 min at 0 ℃. The progress of reaction was monitored by TLC, and upon completion of the reaction, mixture was poured in 10 mL water and extracted with ethyl acetate (2x 15 mL) dried over anhydrous sodium sulphate, solvent was evaporated in vacuum, the crude was purified by column chromatography.

7-Hydroxy-5-methyl-8-nitro-9-phenyl-7-(trifluoromethyl)-7,8,9,10-tetrahydrophenanthri din-6(5*H*)-one (4a)



Following the general method C, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-(2-nitrovinyl)benzene **2a** (23 mg, 0.15 mmol) were used to afford the compound **4a**, white solid, yield 34% (14 mg), mp 205 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.82 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.26 – 7.20 (m, 2H), 5.33 (d, *J* = 4.0 Hz, 1H), 3.82 – 3.76 (m, 1H), 3.70 (s, 3H), 3.58 (ddd, *J* = 26.1, 18.5, 9.1 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.5, 148.5, 139.0, 136.9, 132.2, 129.5, 128.9, 127.4, 125.3, 124.8 (q, *J* = 290.8 Hz), 123.5, 119.5, 116.4, 115.2, 88.4, 76.2 (q, *J* = 29.3 Hz), 38.2, 29.9, 28.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –74.89 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{18}F_3N_2O_4$: 419.12132, found: 419.12099.

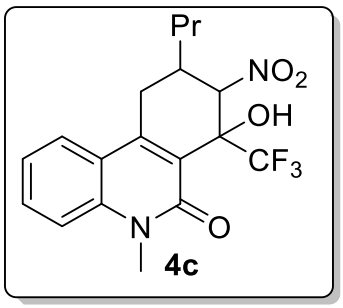
7-Hydroxy-5-methyl-8-nitro-9-(p-tolyl)-7-(trifluoromethyl)-7,8,9,10-tetrahydro phenanthridin-6(5*H*)-one (4b)



Following the general method C, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (**2b**) (24 mg, 0.015 mmol) were used to afford the compound **4b**, white solid, yield 35% (15 mg), mp 199 °C; **^{1}H NMR** (500 MHz, CDCl3) δ 9.86 (s, 1H), 7.86 – 7.80 (m, 1H), 7.77 – 7.70 (m, J = 8.6, 7.2, 1.3 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.20 (s, 4H), 5.48 (d, J = 11.7 Hz, 1H), 3.81 (s, 3H), 3.68 (td, J = 13.1, 4.0 Hz, 1H), 3.47 (dd, J = 16.6, 4.0 Hz, 1H), 3.03 – 2.91 (m, J = 16.4, 13.6

Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 150.2, 139.0, 138.4, 135.6, 132.7, 130.1, 127.3, 125.5, 123.7, 122.9 (q, J = 291.3 Hz), 119.2, 117.8, 115.3, 91.6, 74.3 (q, J = 30.0 Hz), 42.8, 30.0, 29.7, 21.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –80.98 (s, 3F); **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{20}F_3N_2O_4$: 433.1375, found: 433.1301.

7-Hydroxy-5-methyl-8-nitro-9-propyl-7-(trifluoromethyl)-7,8,9,10-tetrahydrophenanthri din-6(5*H*)-one (4c)



Following the general method B, 1,4-dimethyl-3-(2,2,2-trifluoroacetyl)quinolin-2(1*H*)-one **1a** (27 mg, 0.1 mmol) and (*E*)-1-nitropent-1-ene **2m** (17 mg, 0.15 mmol) were used to afford the compound **4c**, yield 51% (22 mg), mp 195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.79 (dd, J = 8.2, 1.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.35 – 7.27 (m, 1H), 5.27 (d, J = 4.1 Hz, 1H), 3.70 (s, 3H), 3.33 (dd, J = 18.8, 7.5 Hz, 1H), 2.83 (dd, J = 18.8, 9.9 Hz, 1H), 2.57 – 2.44 (m, 1H), 1.57 – 1.43 (m, 4H), 0.99 – 0.92 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.44, 148.41, 138.89, 132.03, 125.21, 123.35, 119.48, 116.63, 115.08, 86.90, 75.73 (q, J = 28.9 Hz), 35.04, 31.32, 29.78, 29.49, 19.62, 13.84; **^{19}F NMR** (377 MHz, CDCl3) δ –75.52. **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{20}F_3N_2O_4$ 385.1375, found 385.8213.

6. References

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4 Taniguchi T, Fujii T, Ishibashi H. Iron-Mediated Radical Halo-Nitration of Alkenes. *J Org Chem*. 2010;75(23):8126-8132. doi:10.1021/jo101769d

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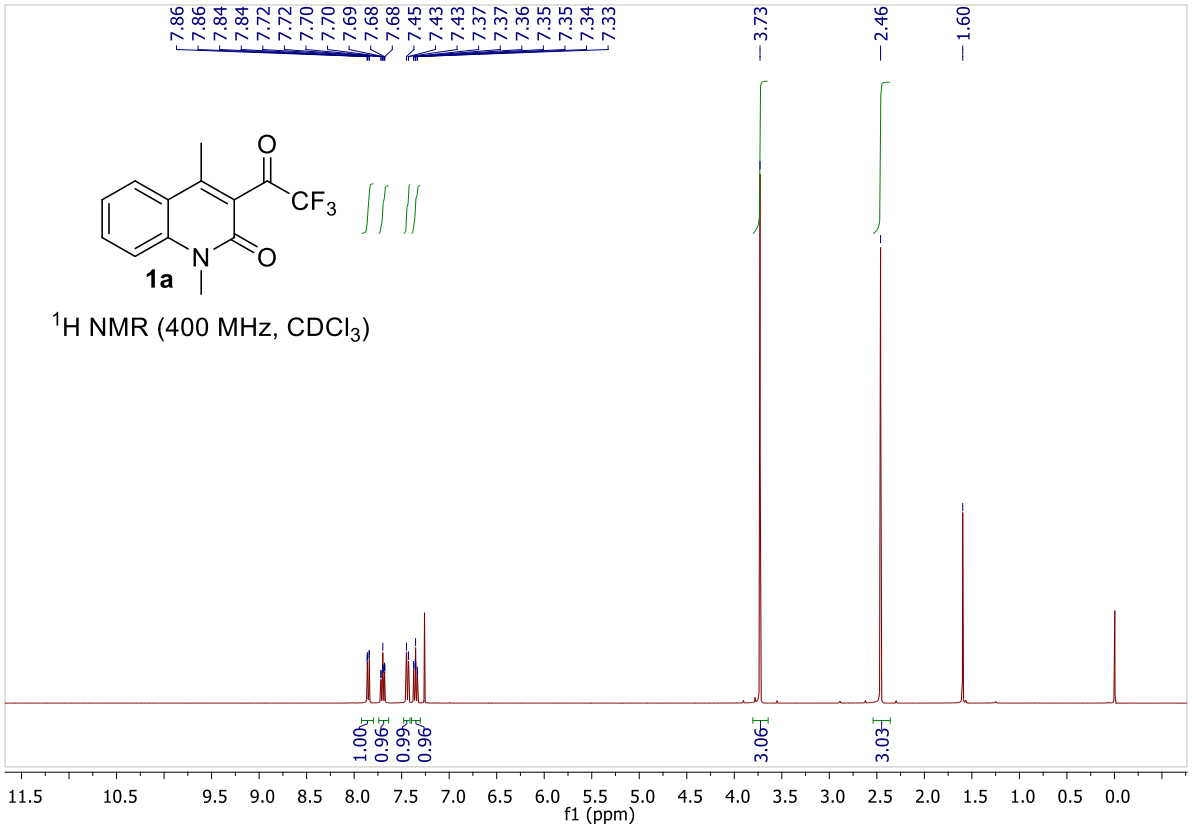
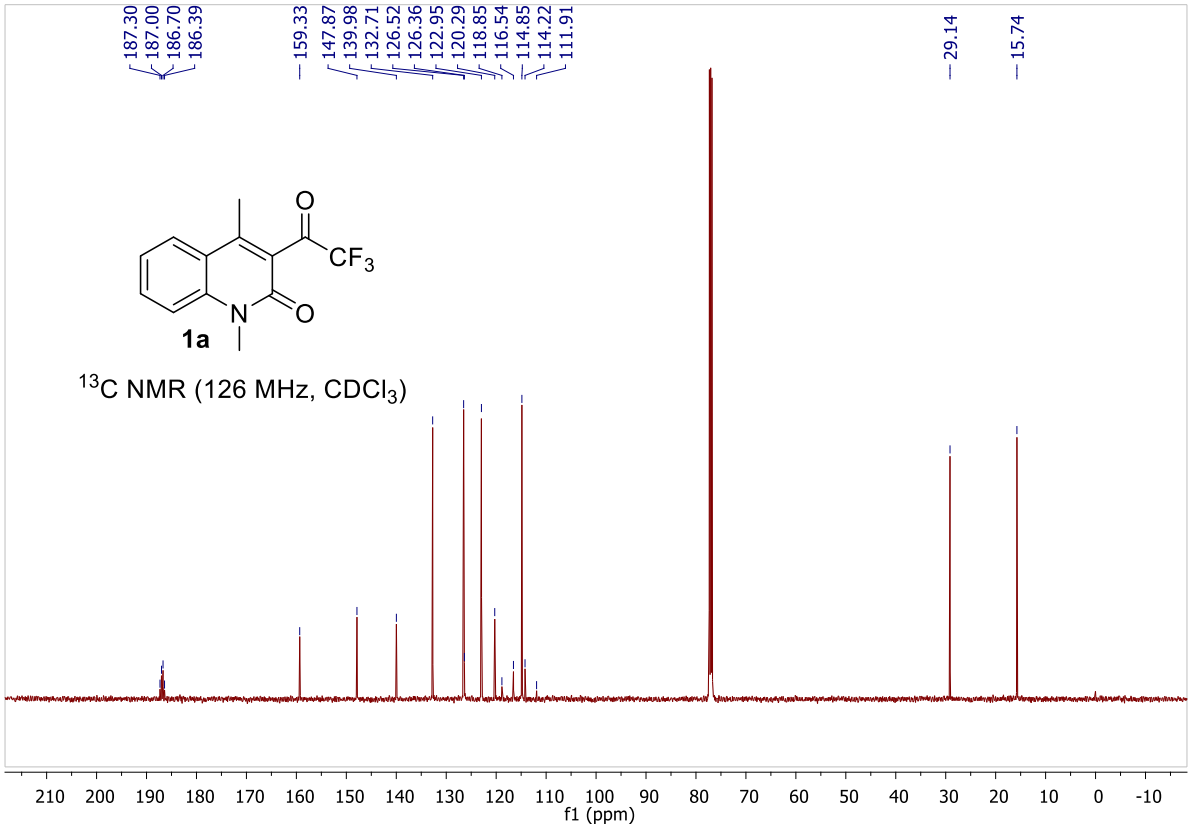
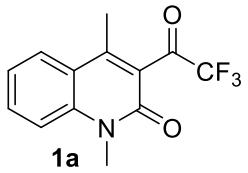
7. NMR-Spectra

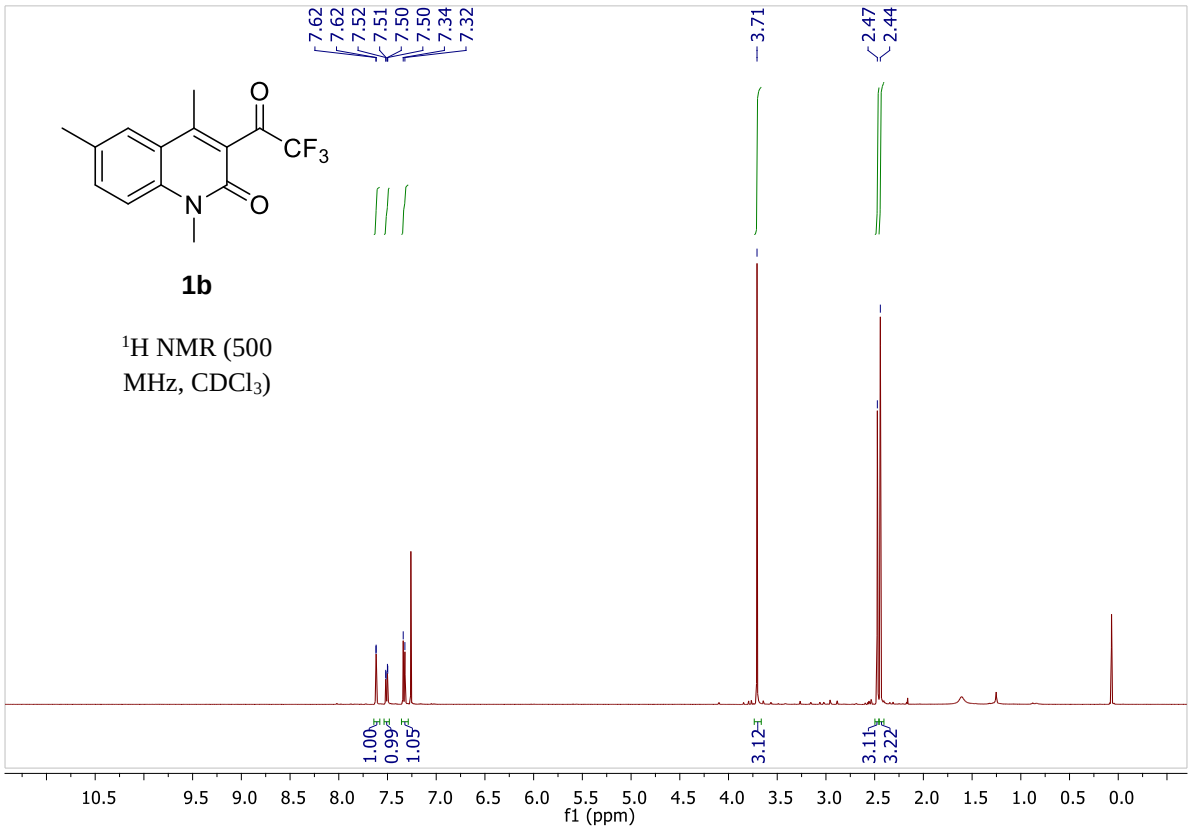






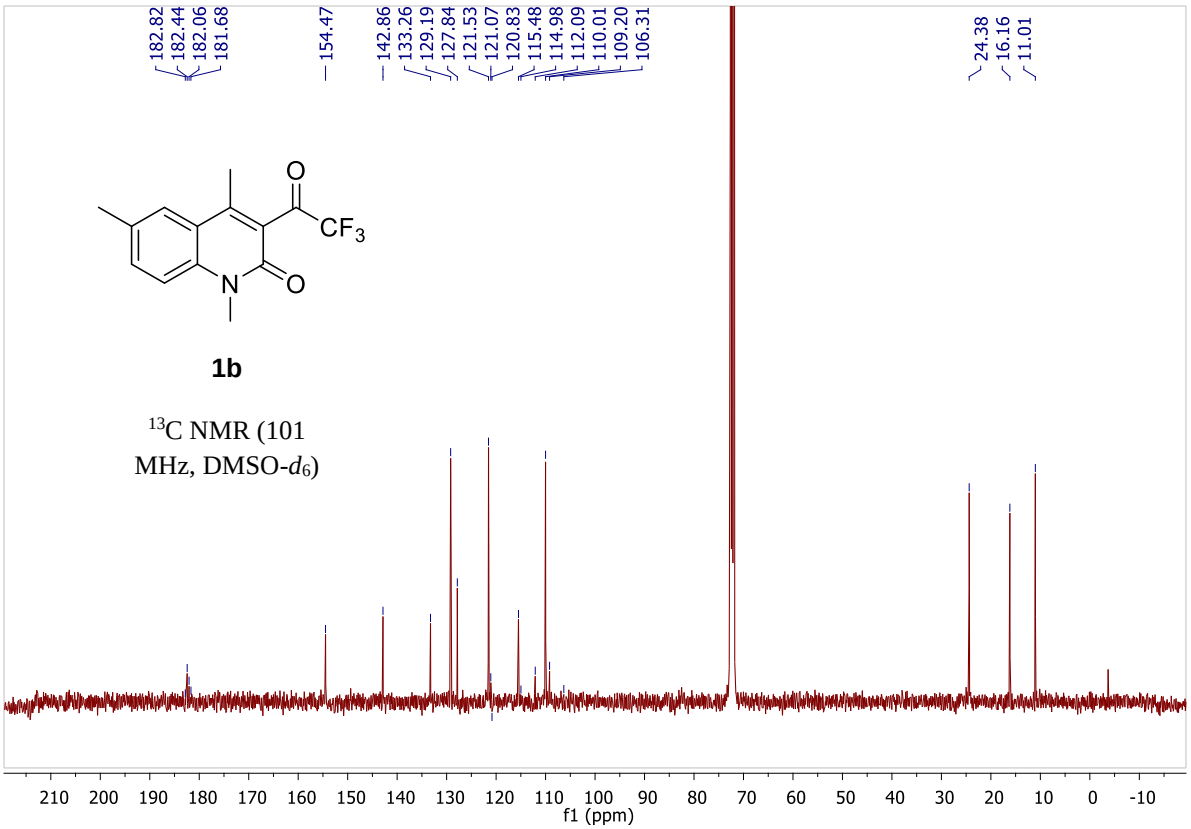
1a

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



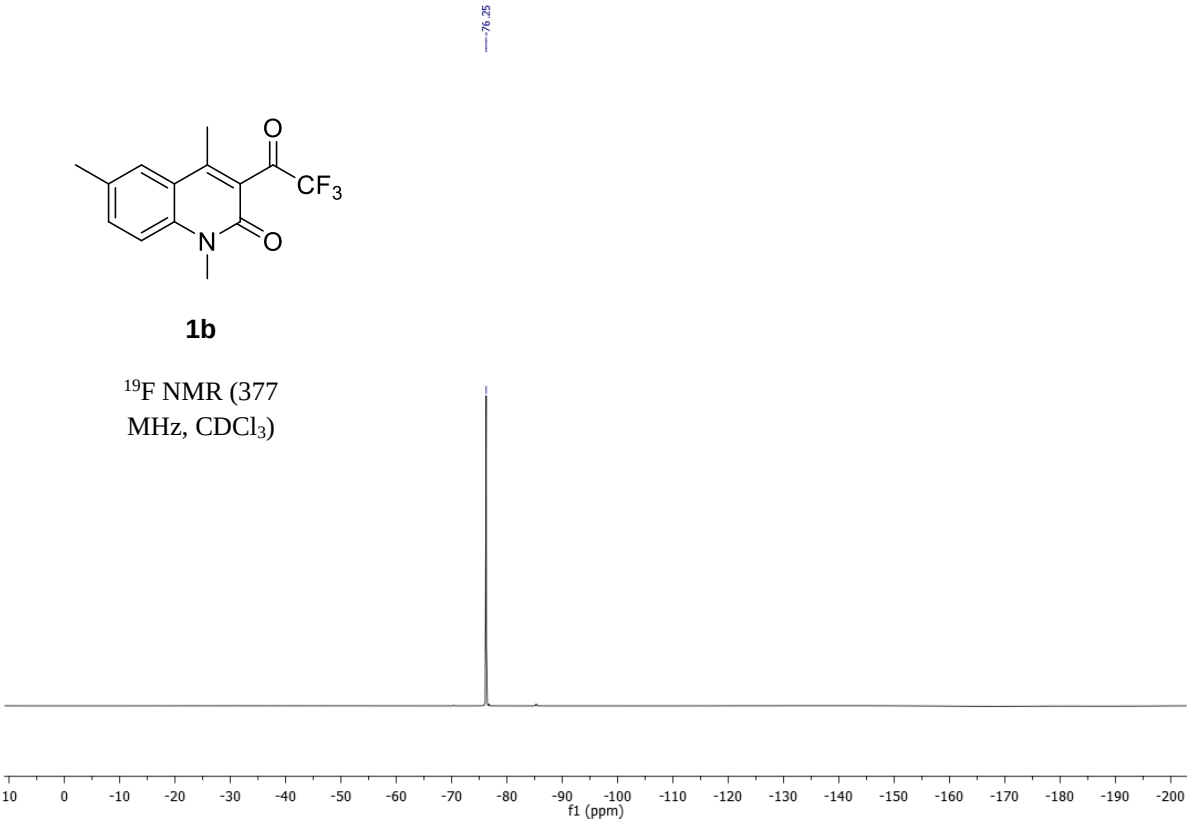
1b

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



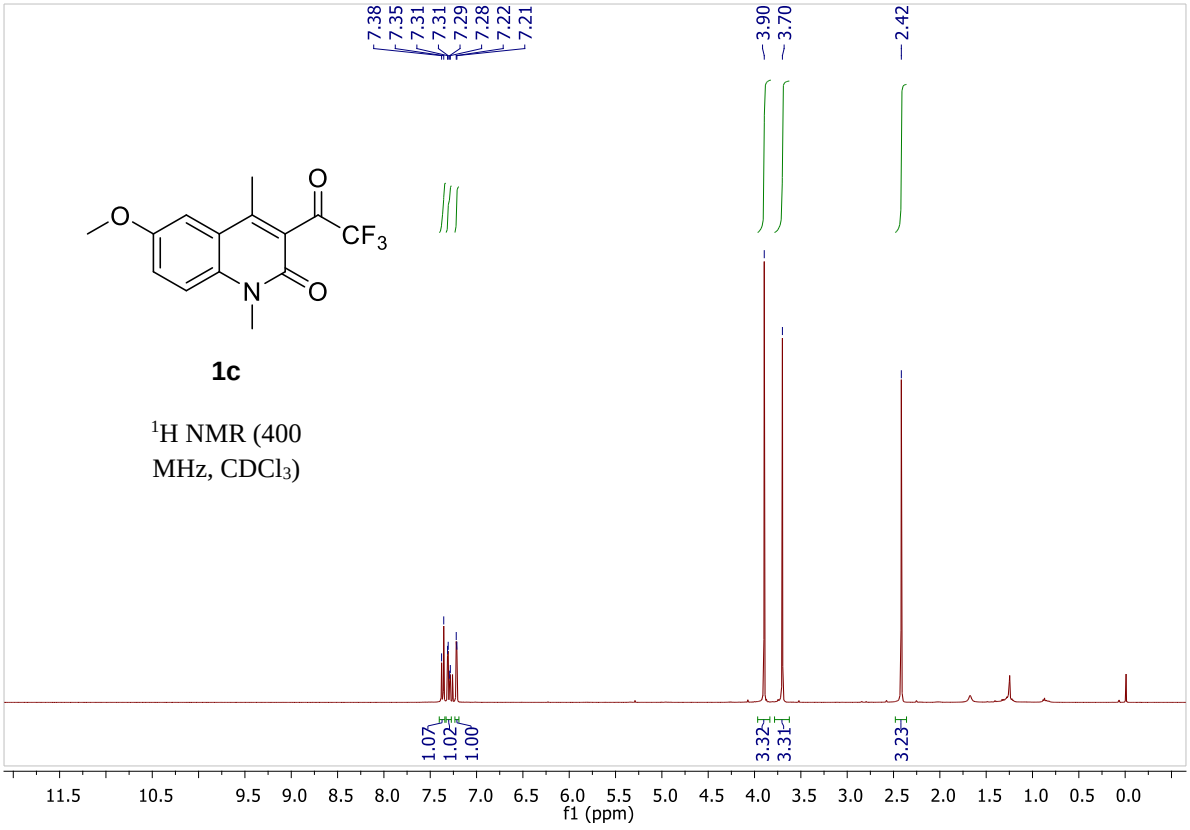
1b

^{13}C NMR (101 MHz, DMSO-d_6)



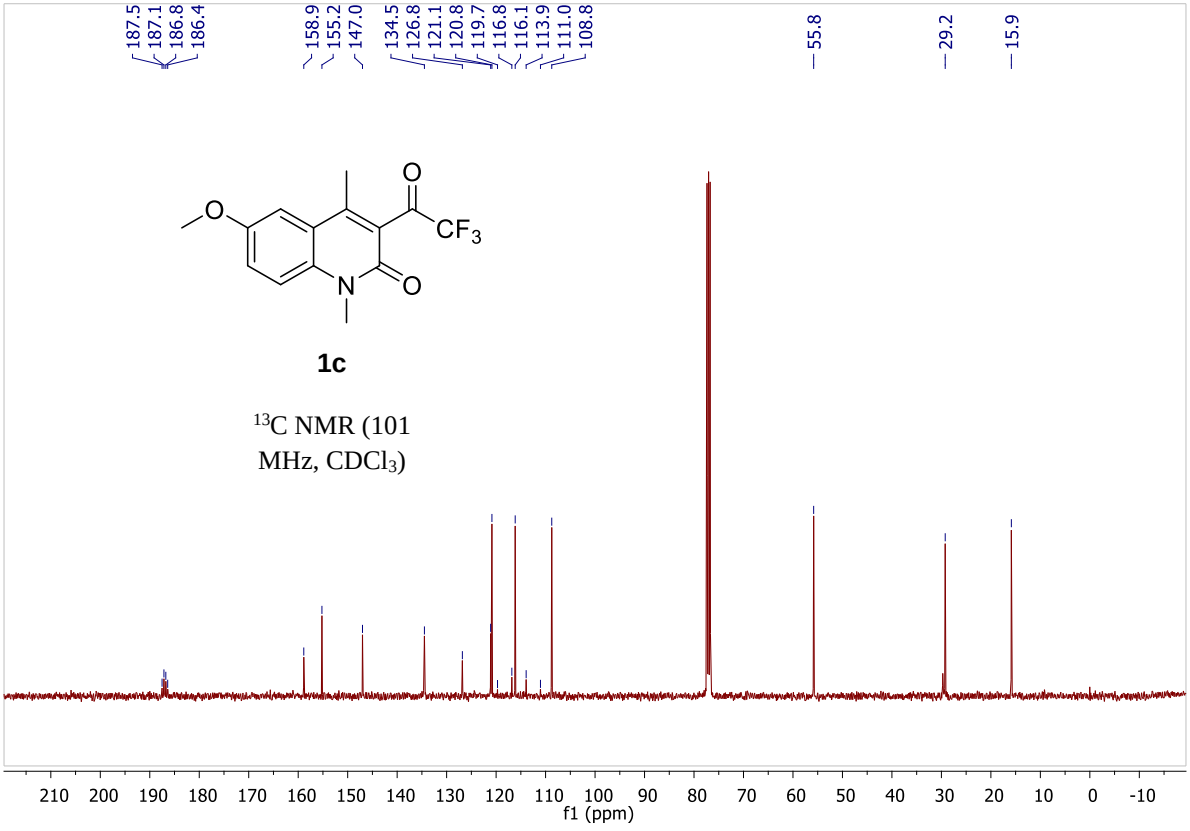
1b

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



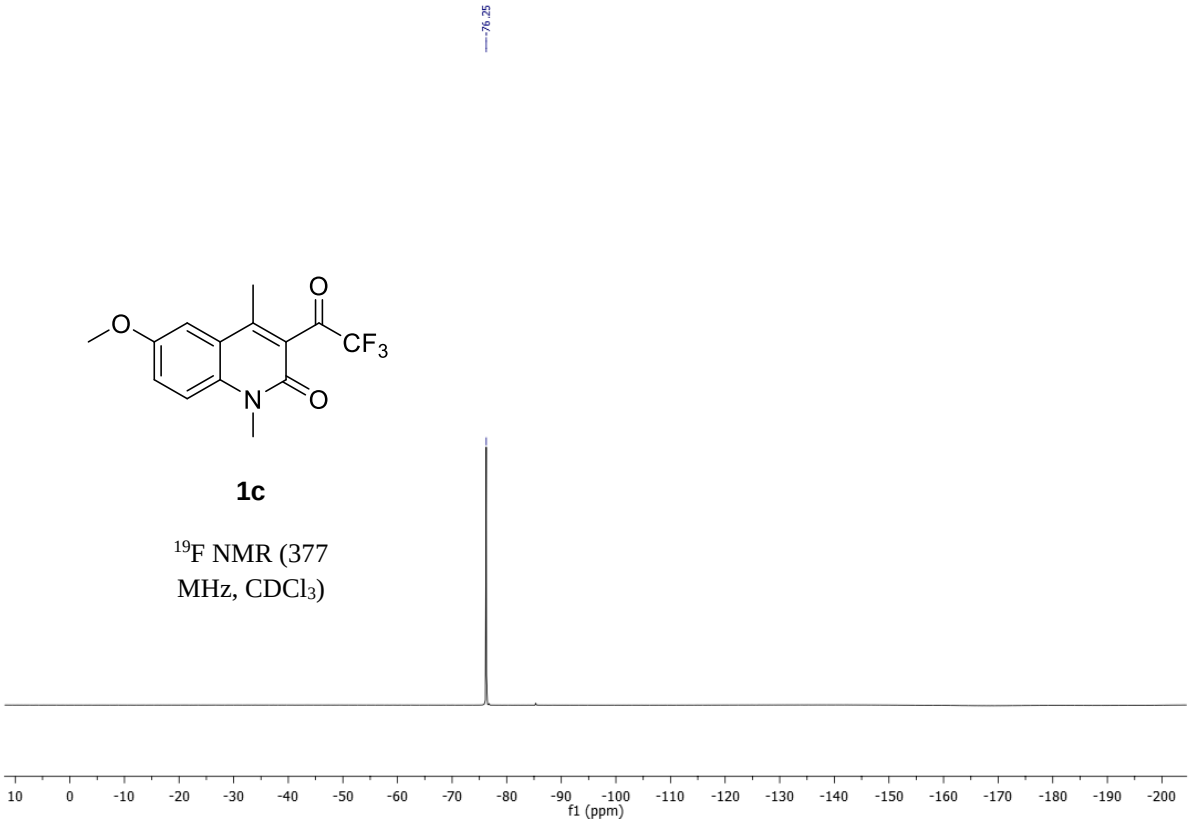
1c

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



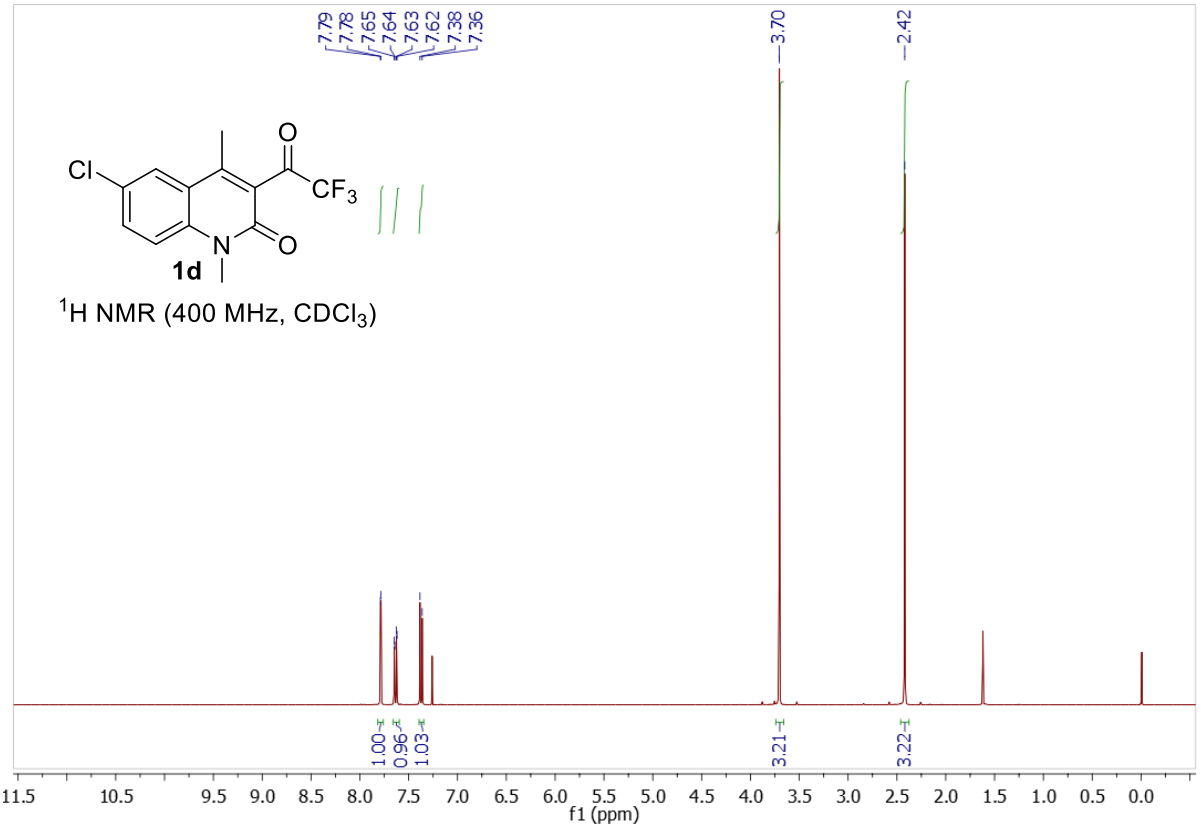
1c

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



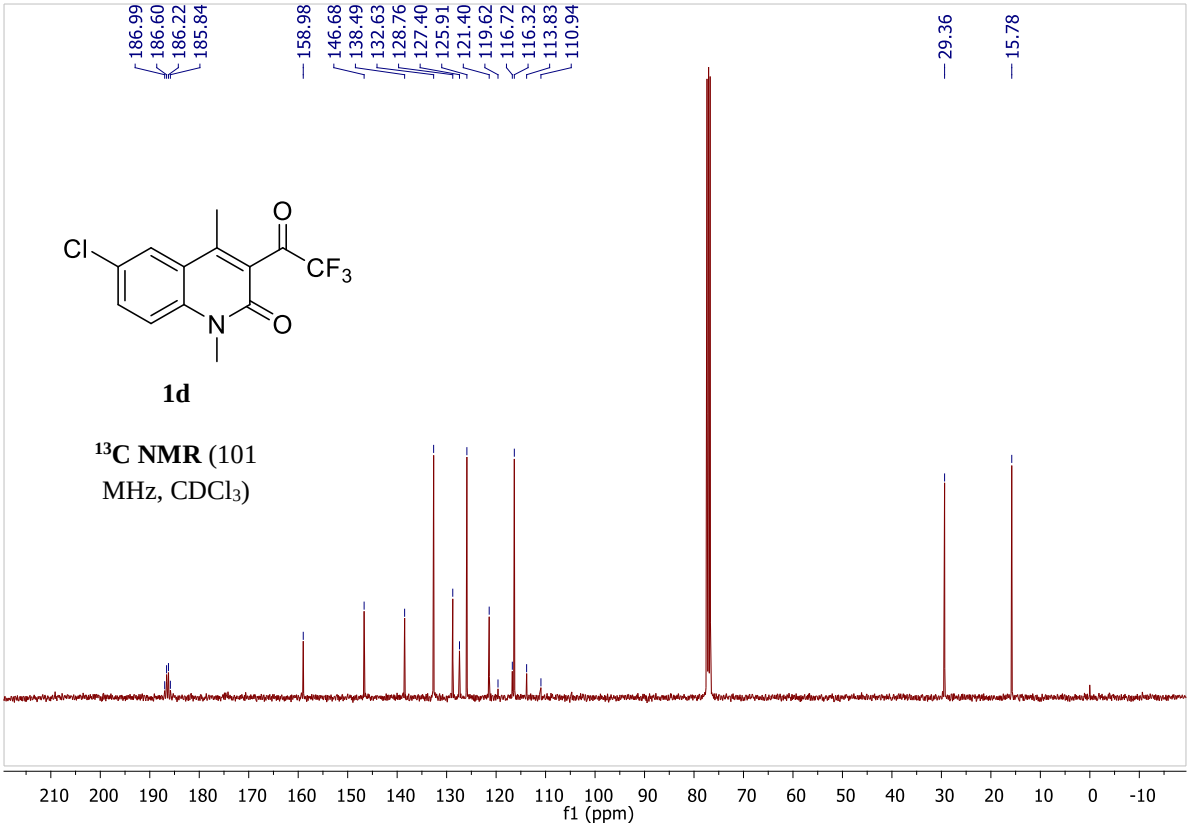
1c

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



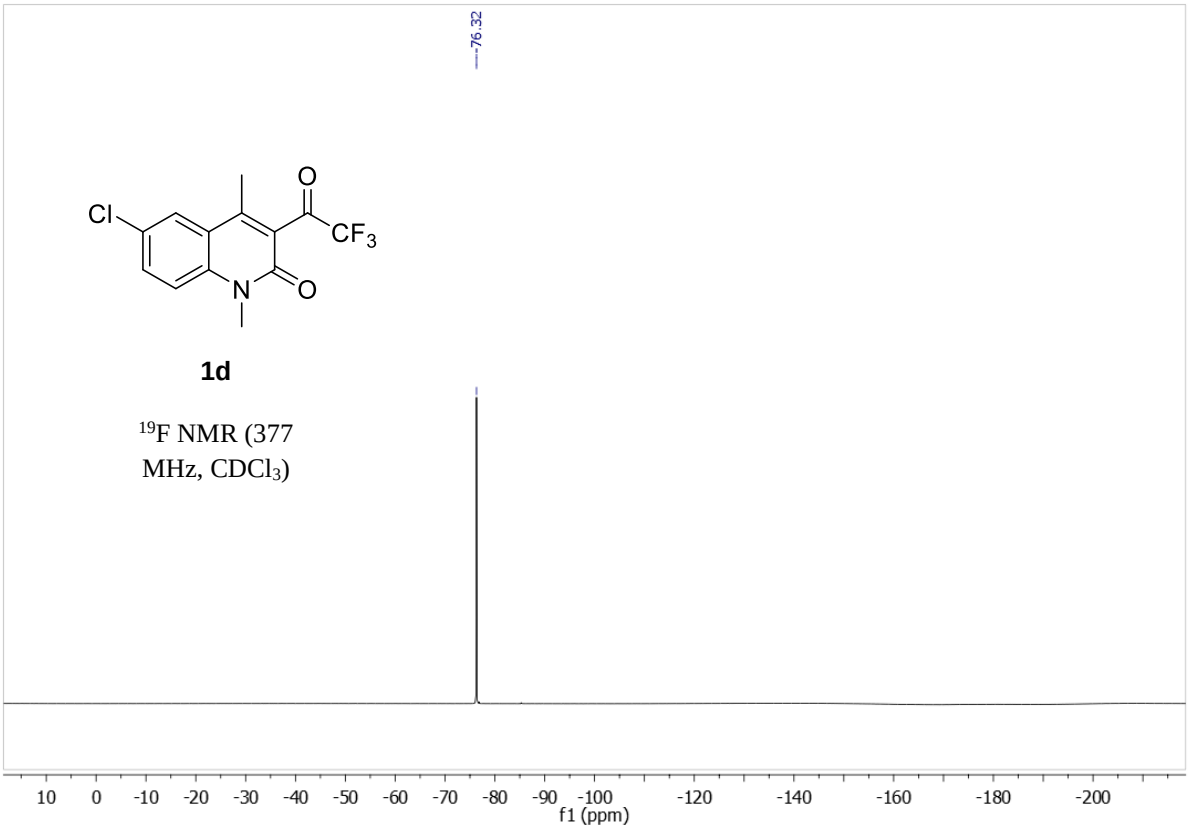
1d

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



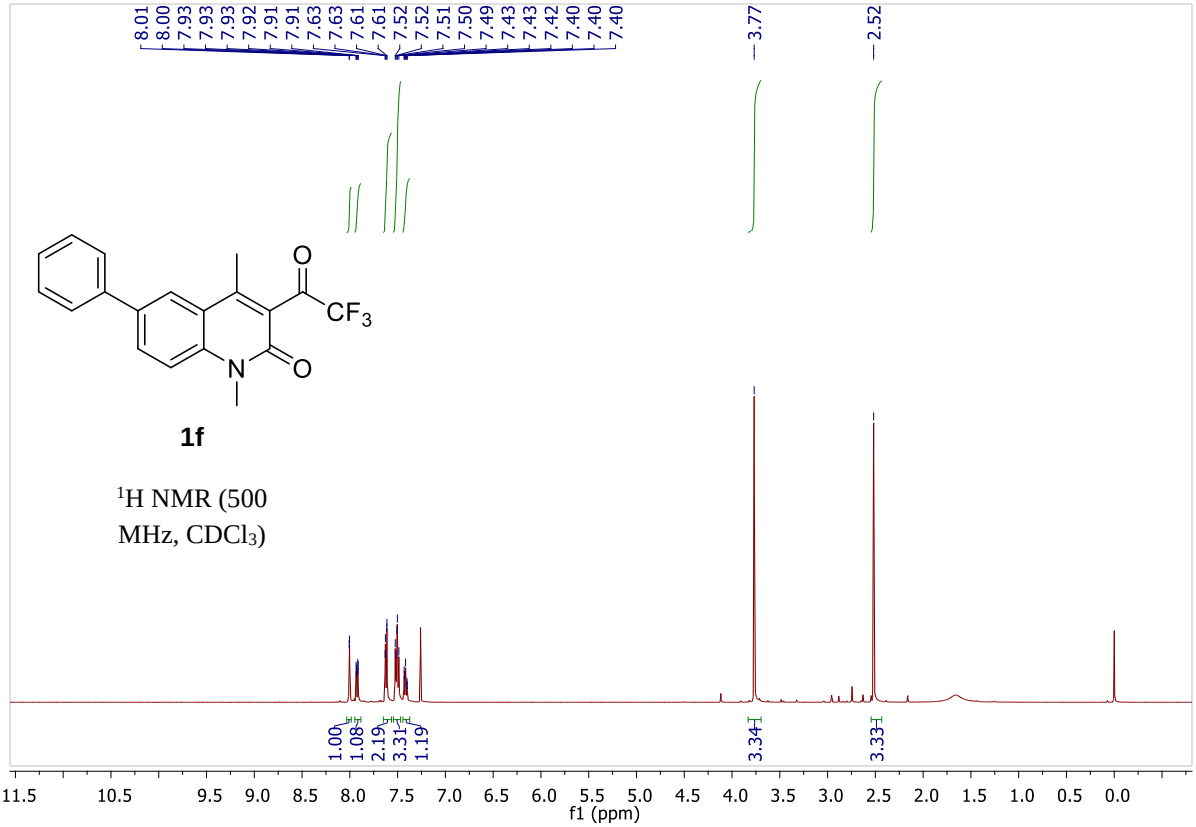
1d

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



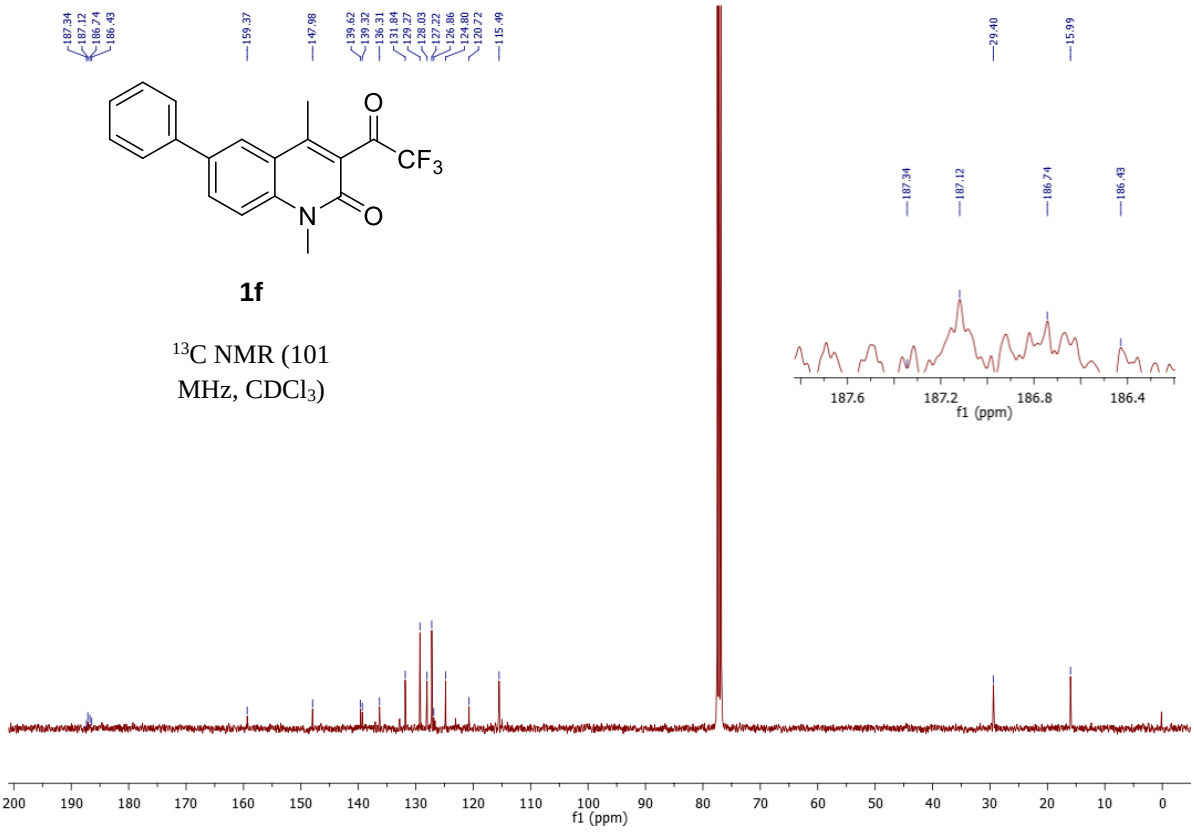
1d

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



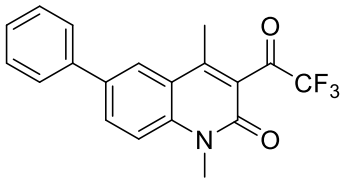
1f

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



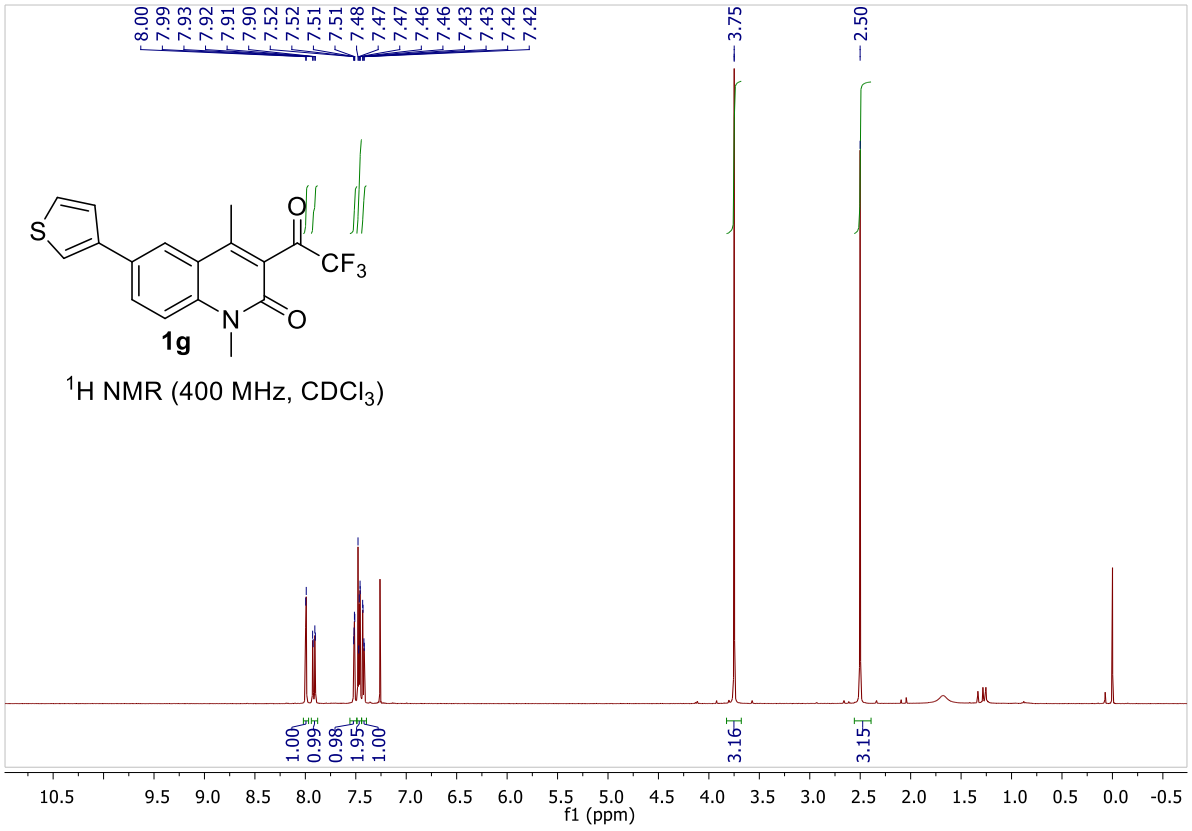
1f

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

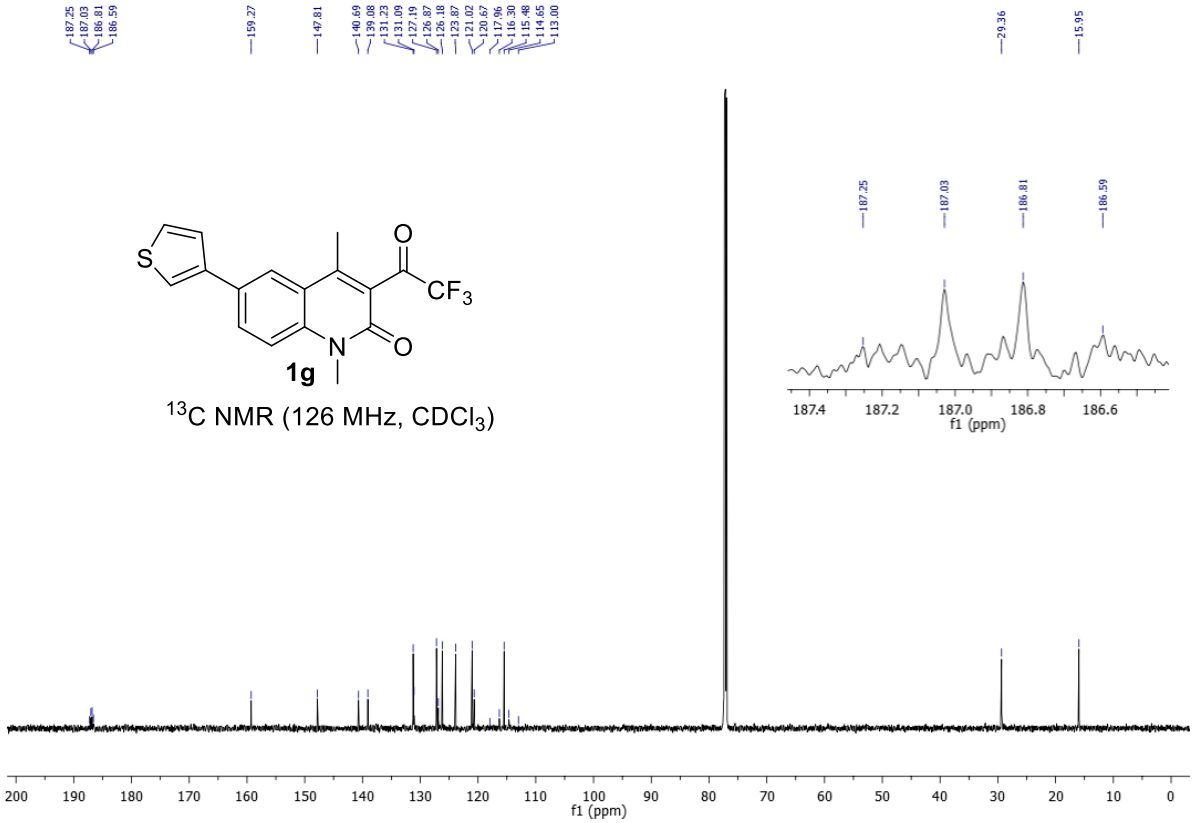


1f

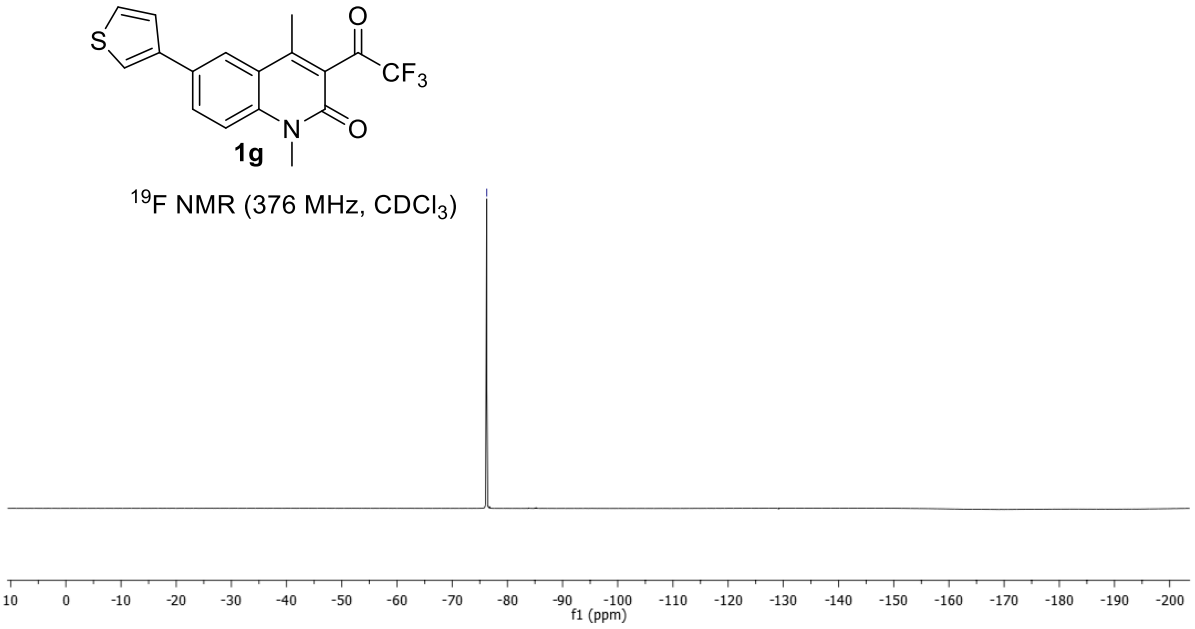
^{19}F NMR (376 MHz, $CDCl_3$)



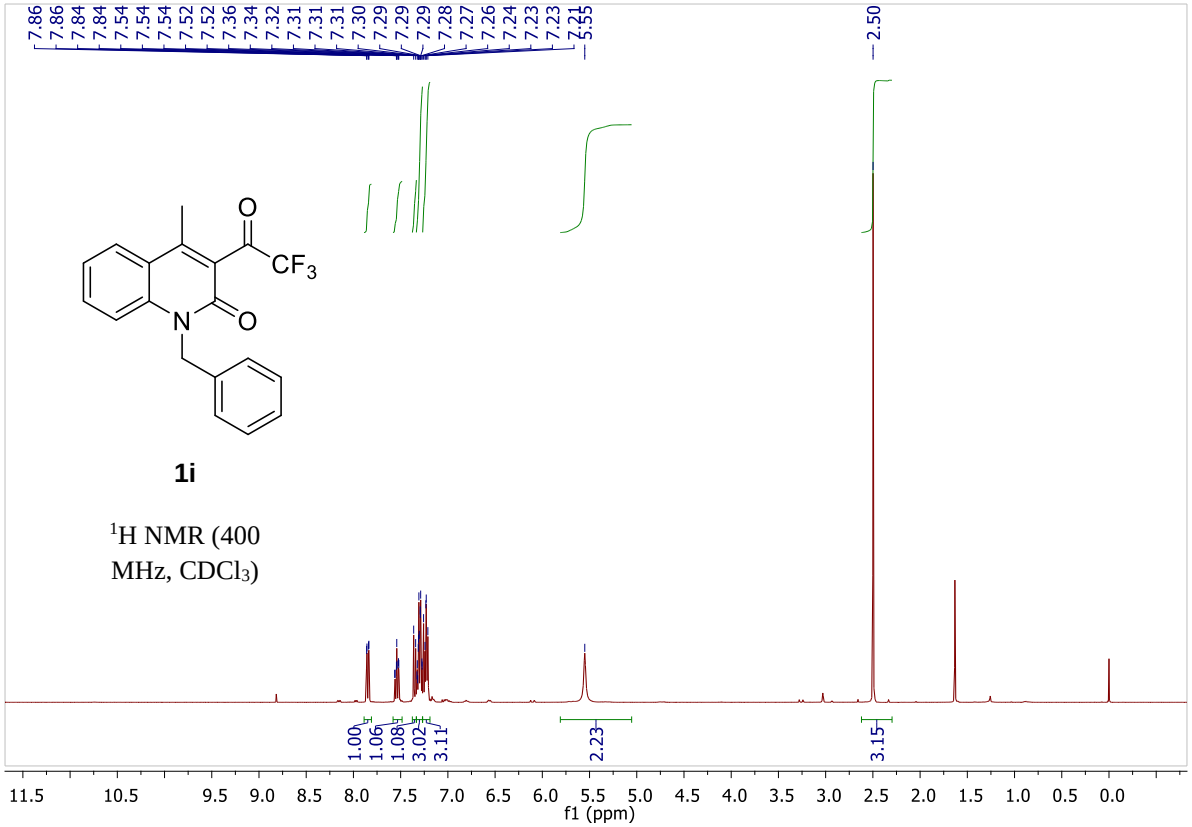
^{1}H NMR (400 MHz, $CDCl_3$)



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

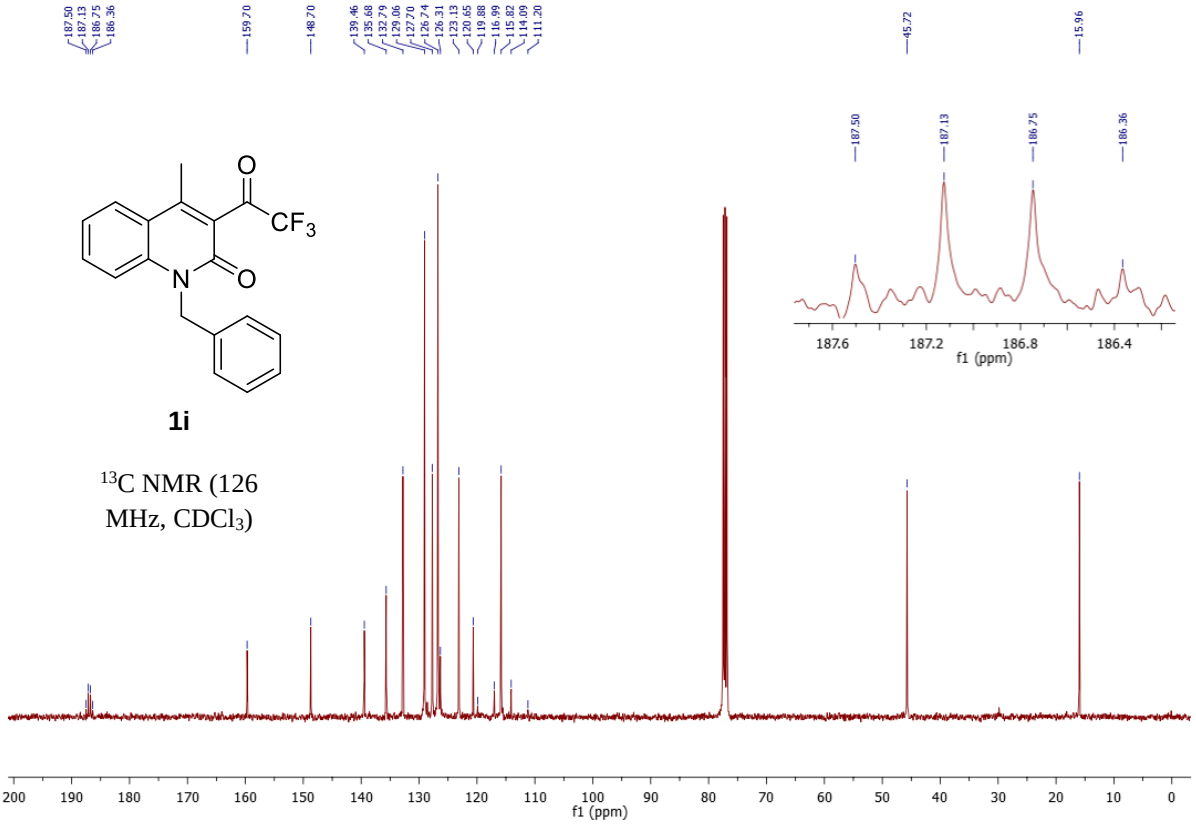


^{19}F NMR (376 MHz, $CDCl_3$)



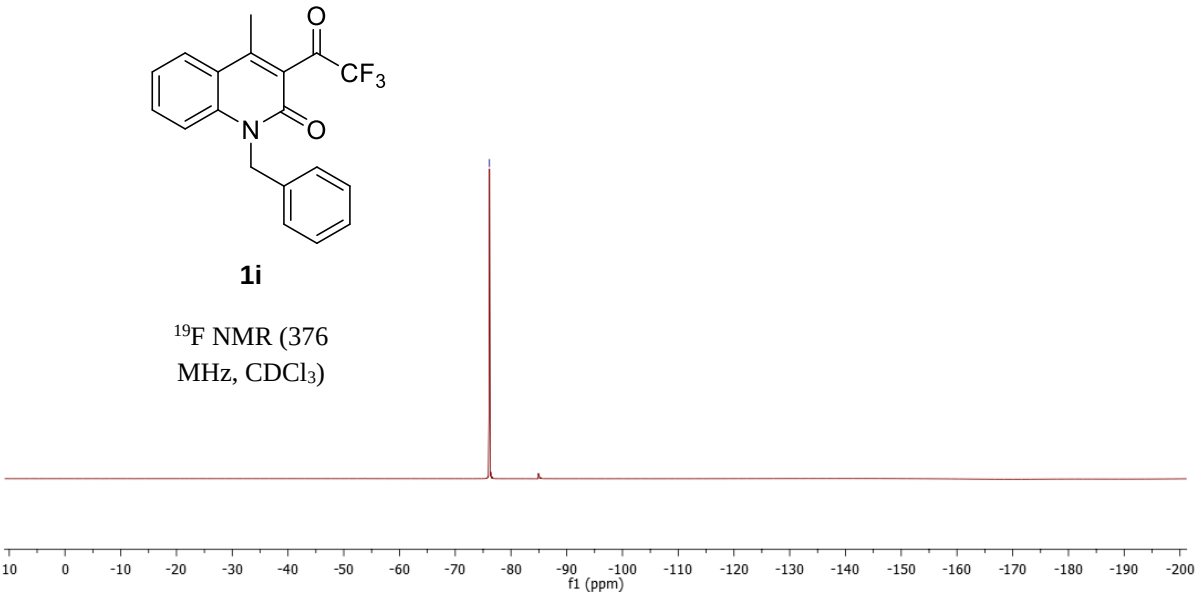
1i

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



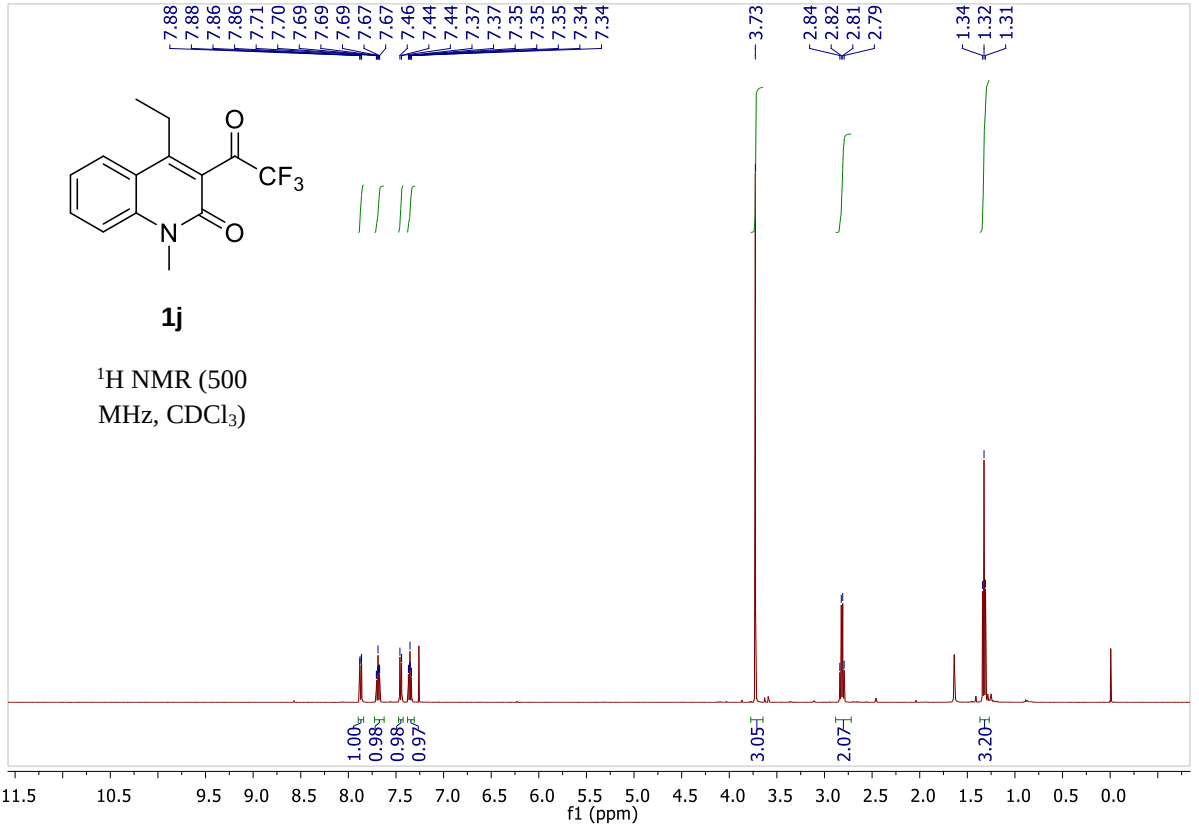
1i

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



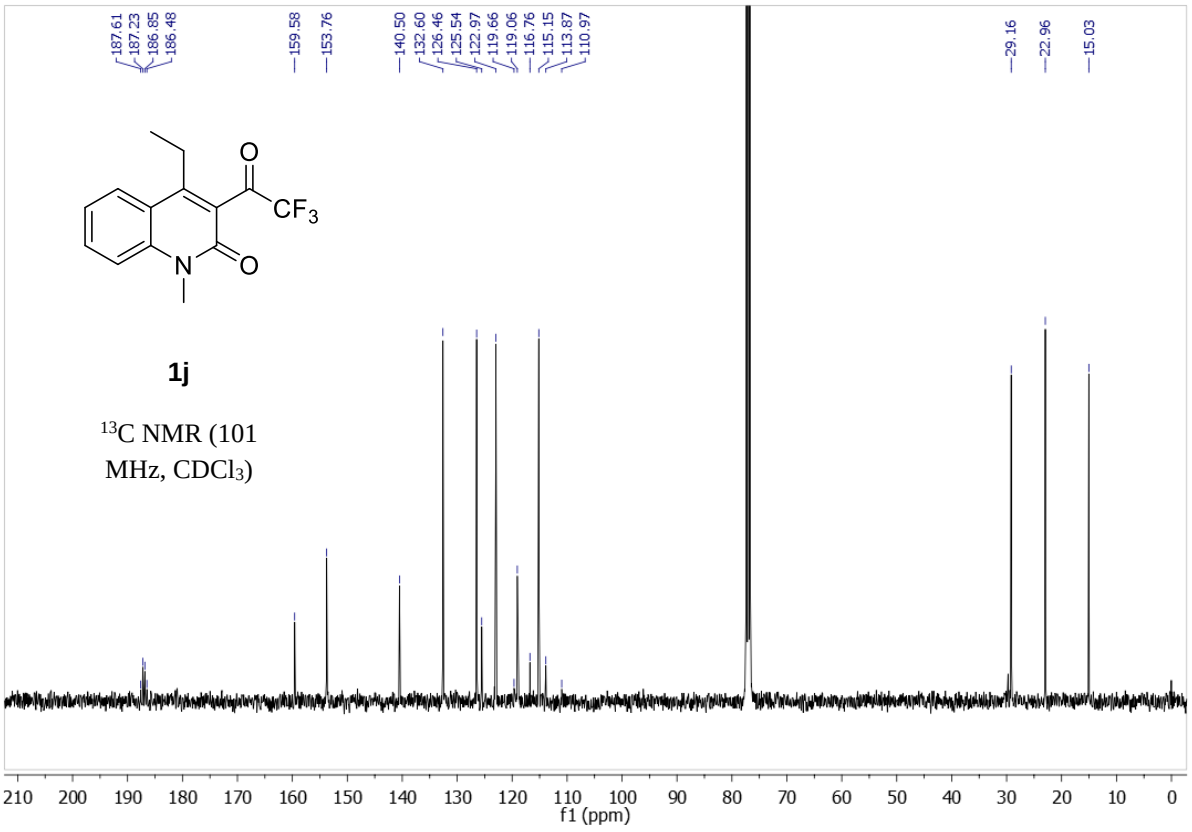
1i

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



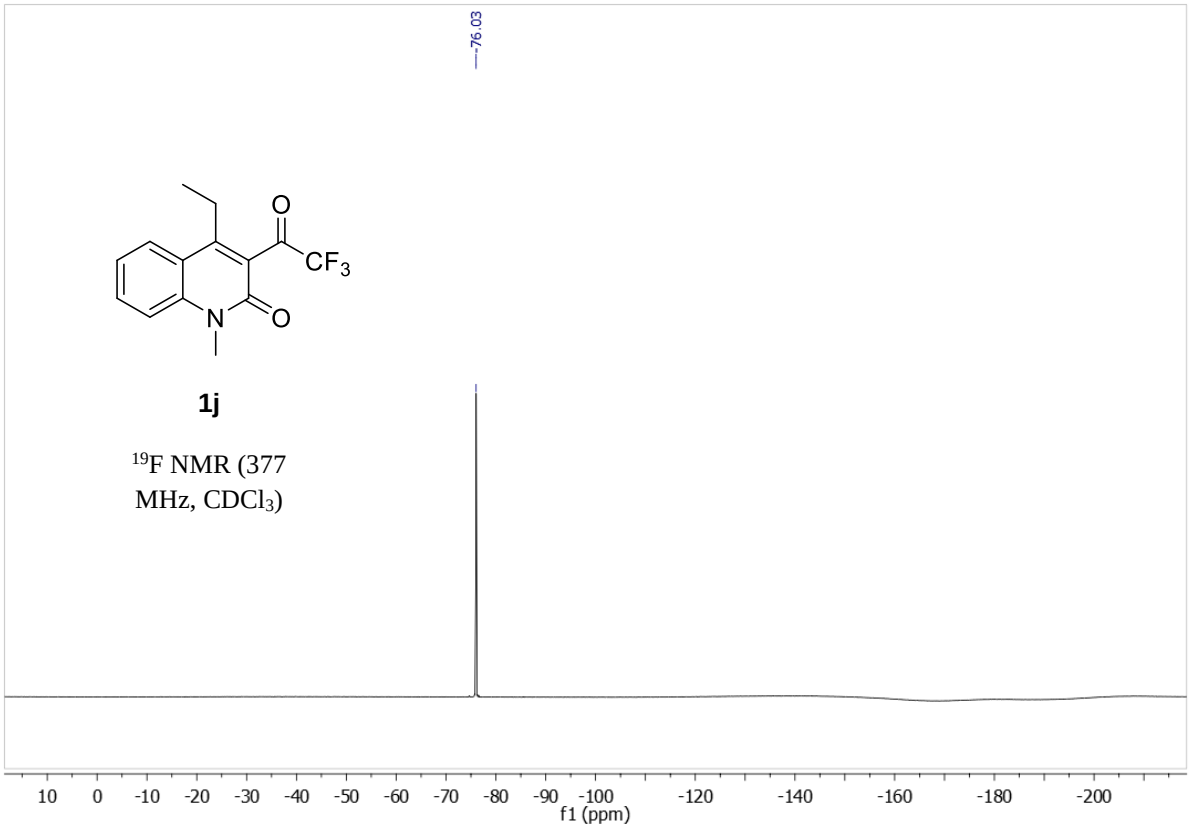
1j

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



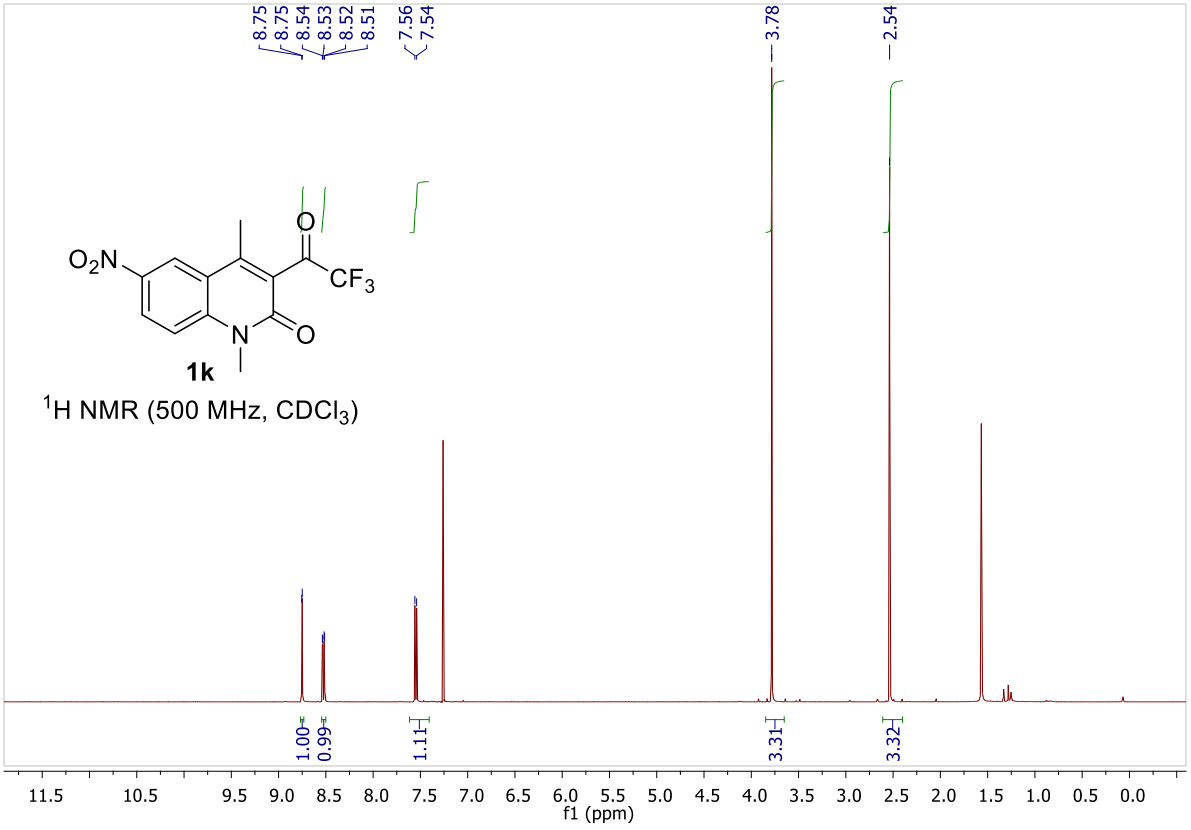
1j

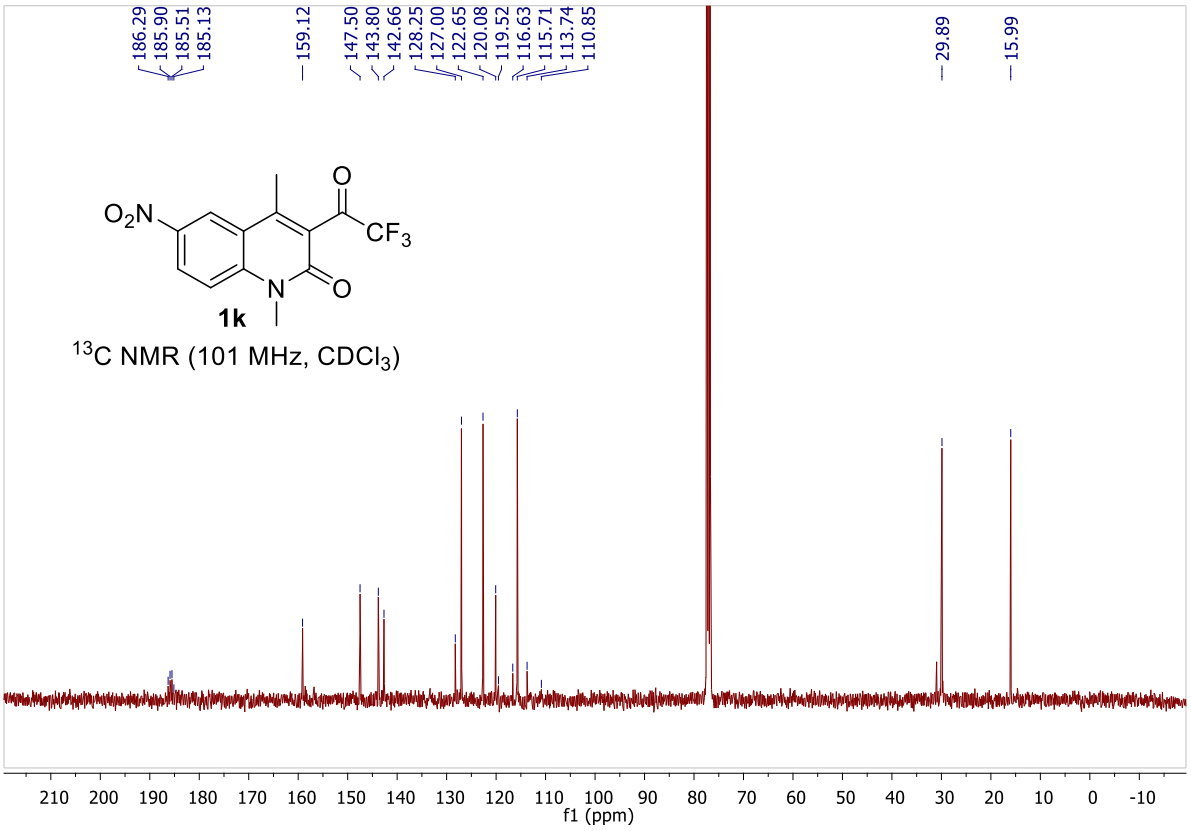
^{13}C NMR (101 MHz, $CDCl_3$)

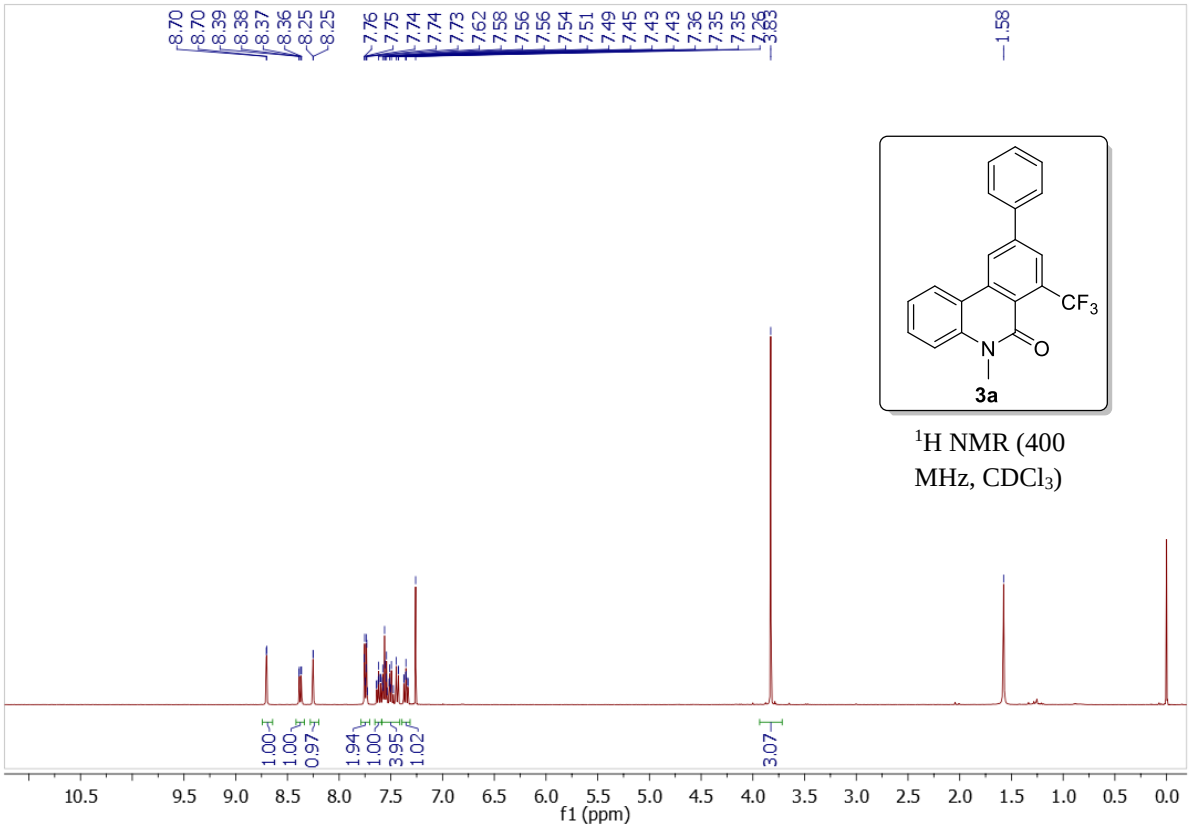


1j

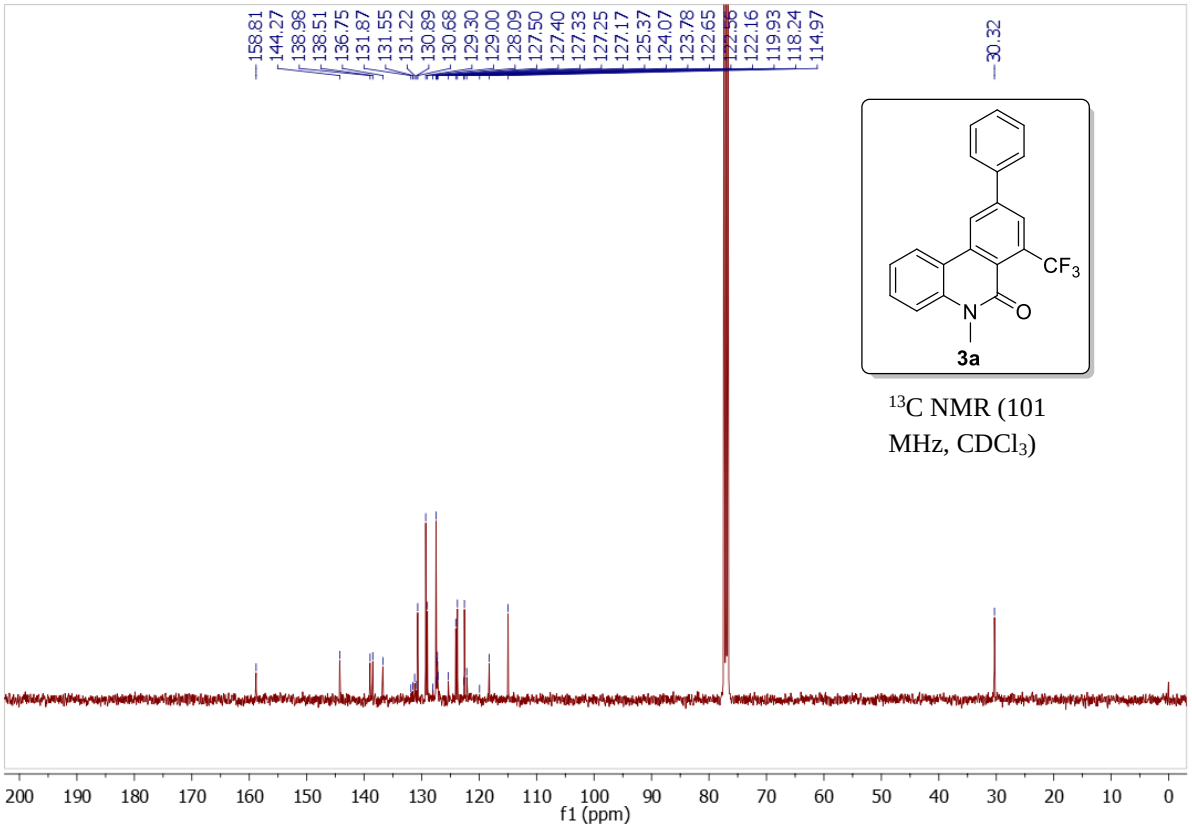
^{19}F NMR (377 MHz, $CDCl_3$)


8.75
8.75
8.54
8.53
8.52
8.51
7.56
7.54
3.78
2.54
O2N
O
CF3
N
O
1k
1H NMR (500 MHz, CDCl3)
1.00
0.99
1.11
3.31
3.32
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)

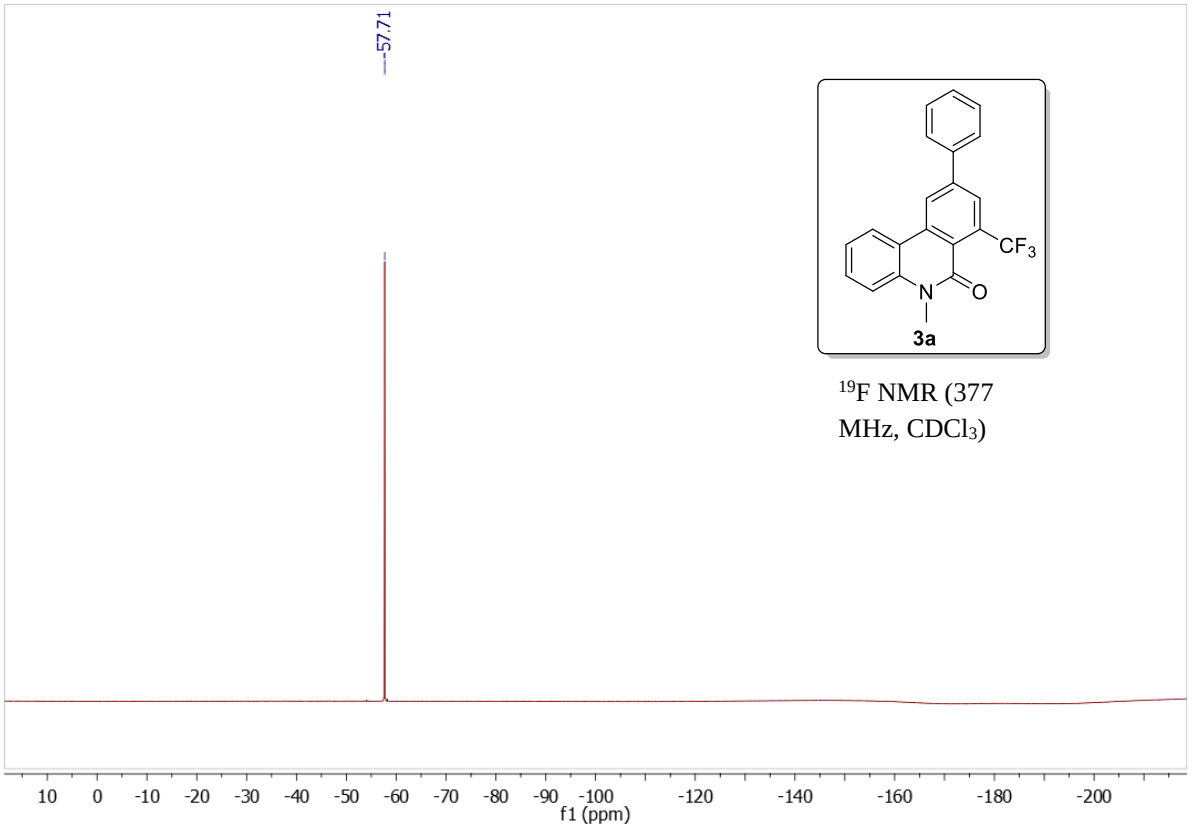

186.29
185.90
185.51
185.13
159.12
147.50
143.80
142.66
128.25
127.00
122.65
120.08
119.52
116.63
115.71
113.74
110.85
29.89
15.99
O2N
O
CF3
N
O
1k
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



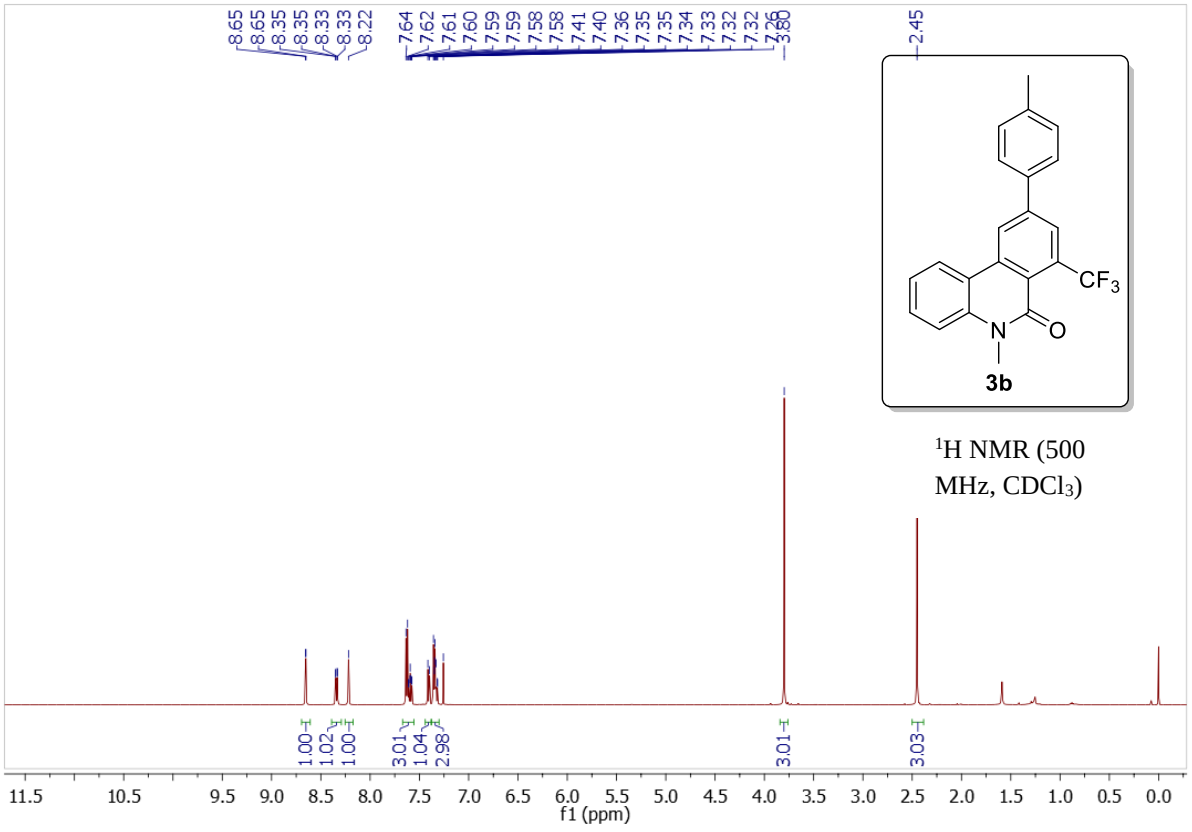
^{1}H NMR (400 MHz, $CDCl_3$)



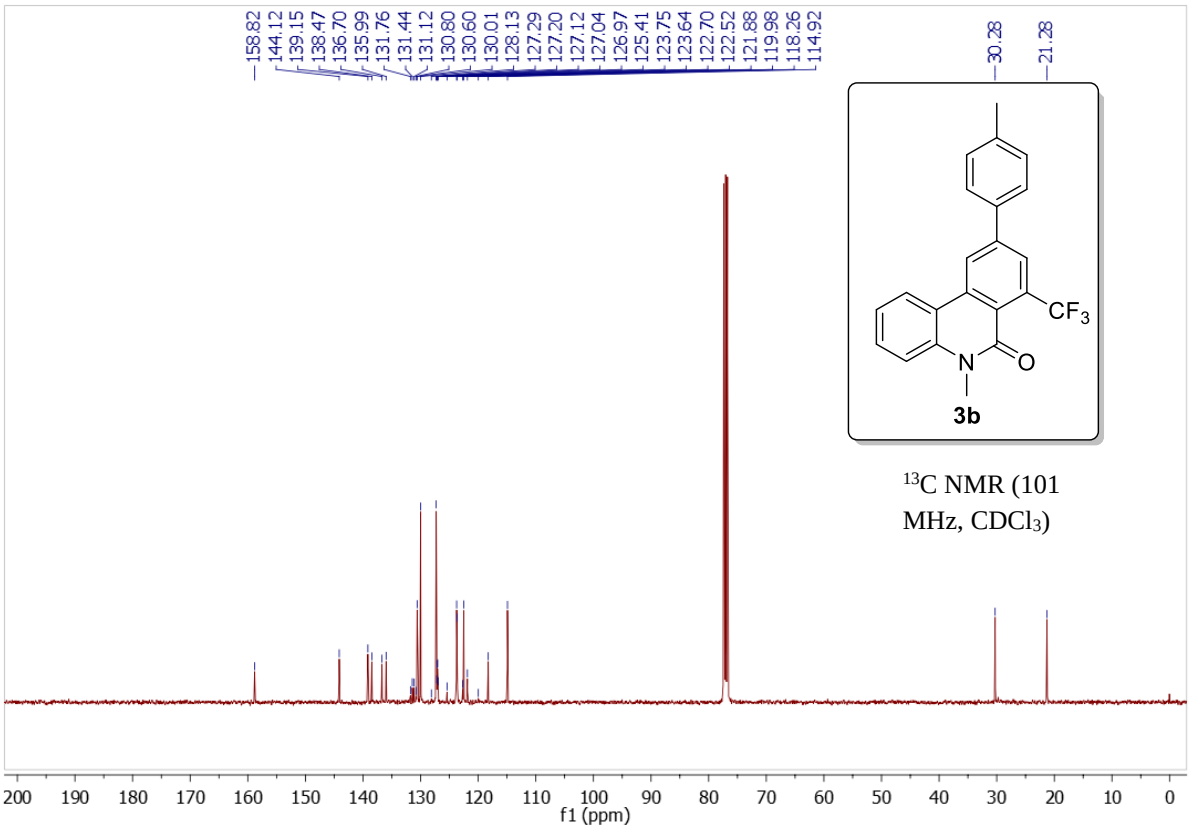
^{13}C NMR (101 MHz, $CDCl_3$)



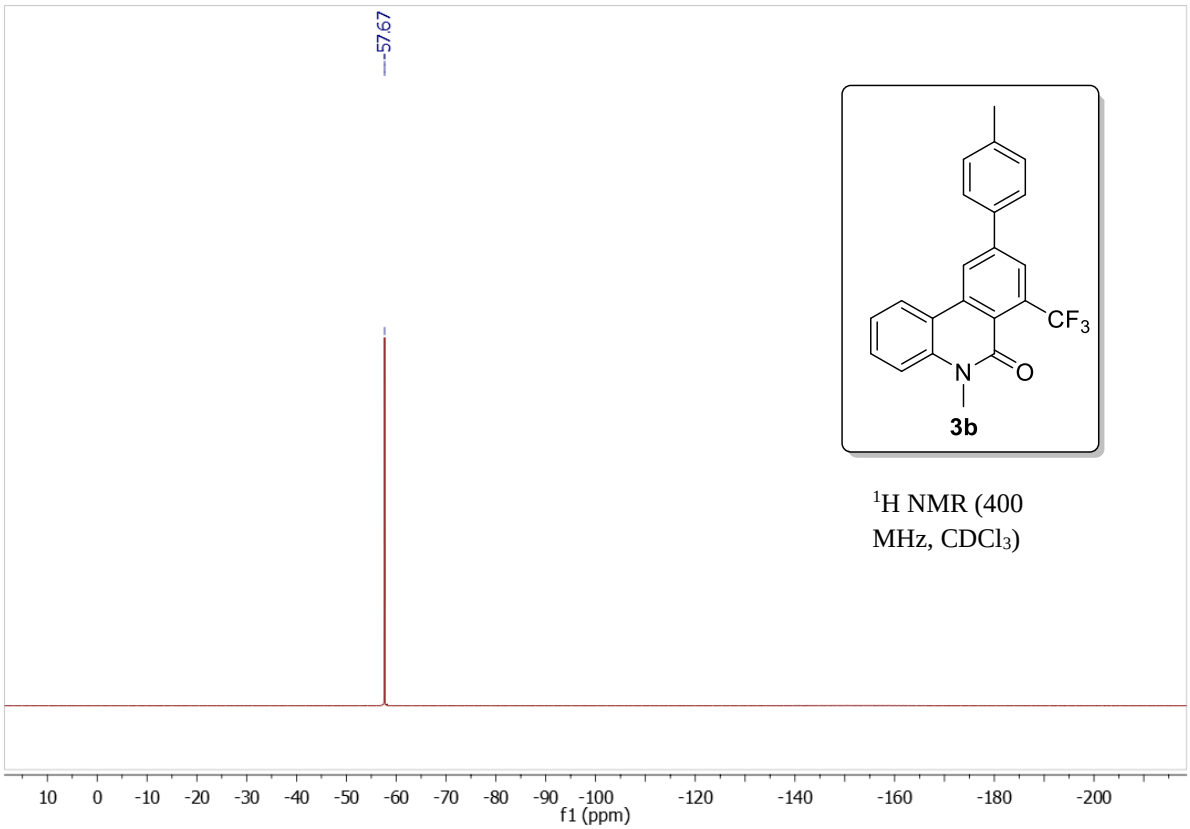
^{19}F NMR (377 MHz, $CDCl_3$)



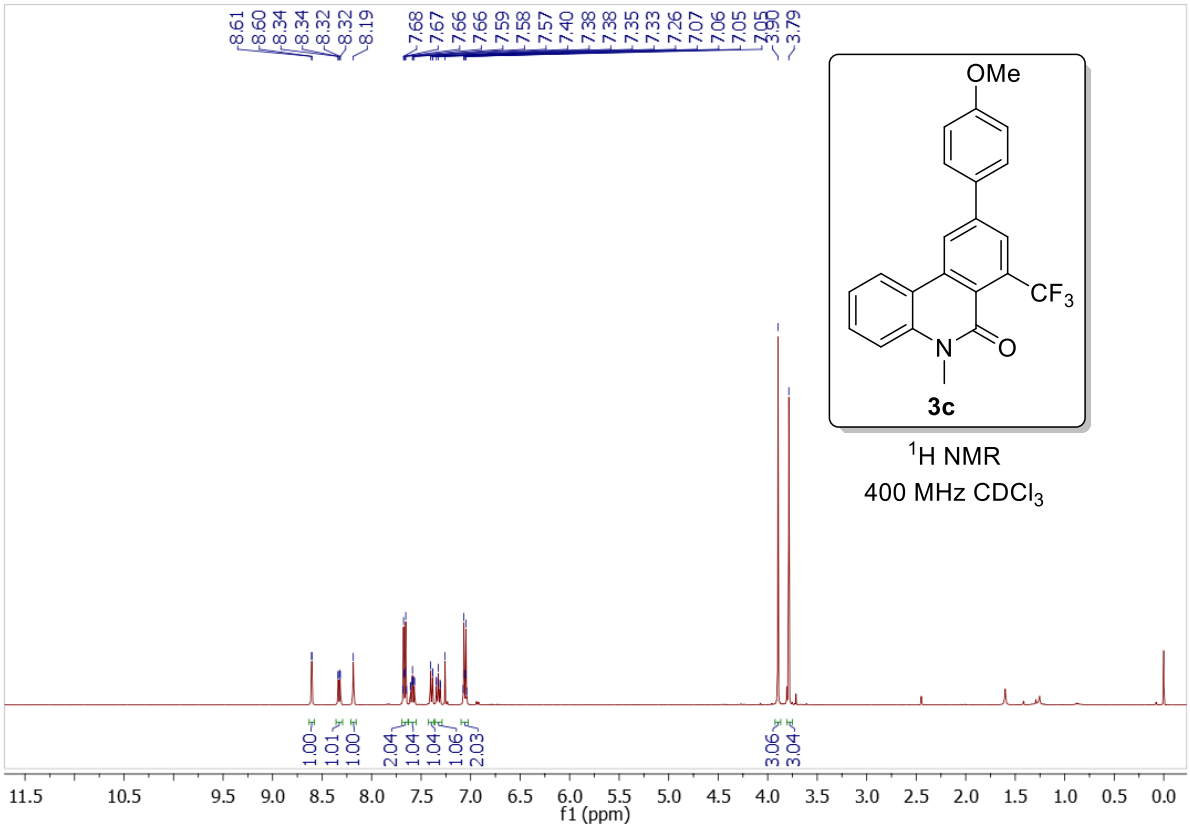
^{1}H NMR (500 MHz, $CDCl_3$)



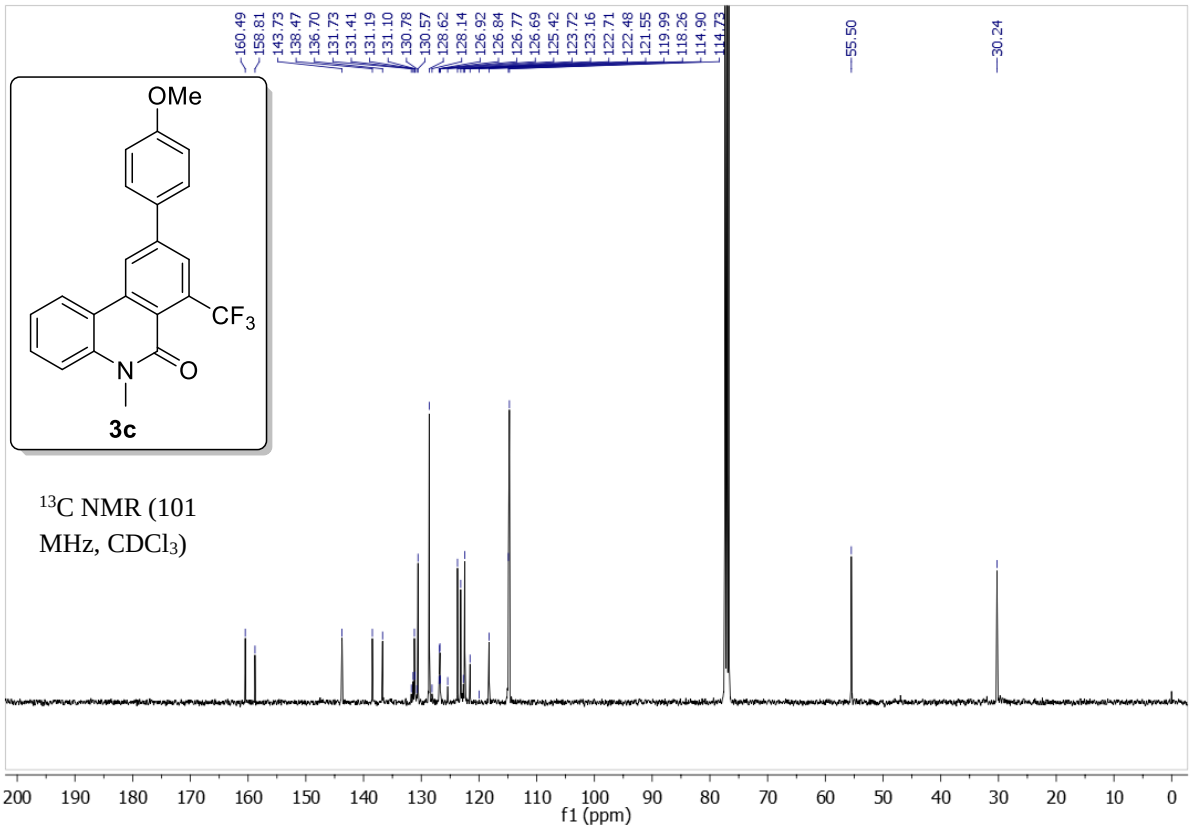
^{13}C NMR (101 MHz, $CDCl_3$)



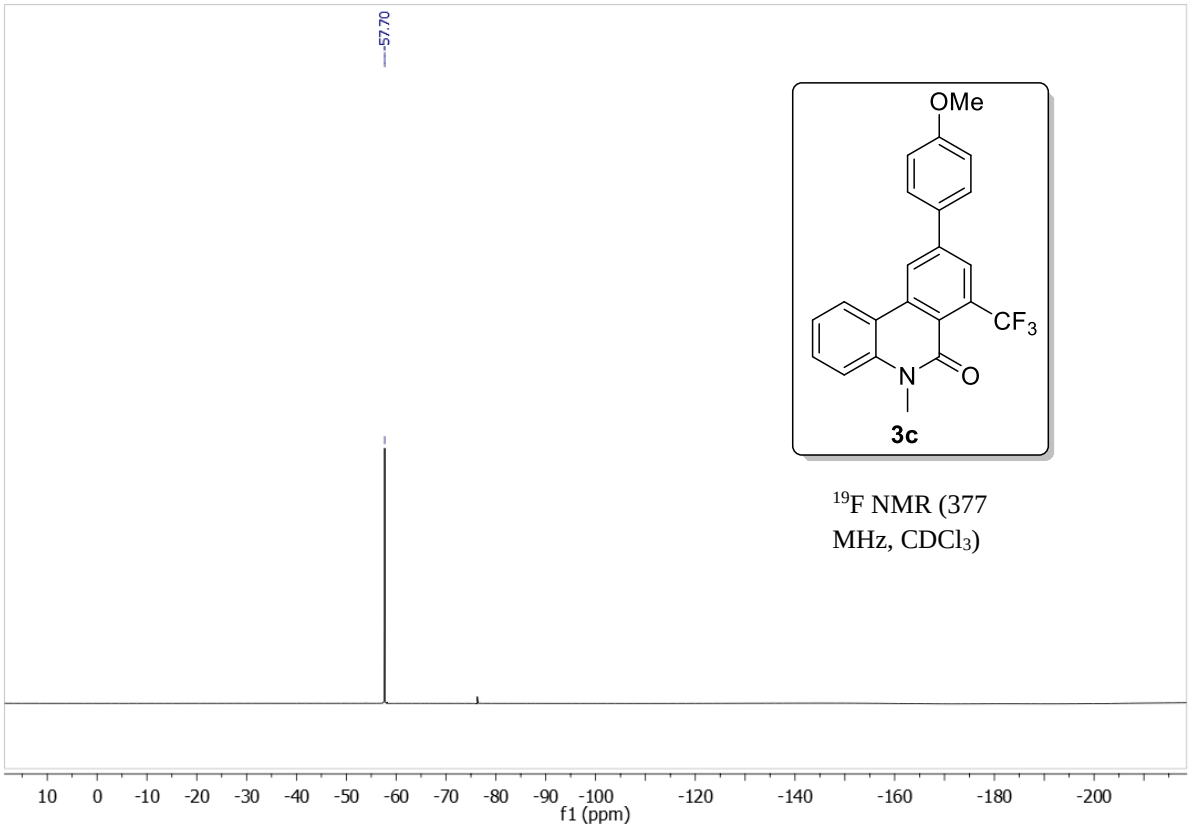
^{1}H NMR (400 MHz, $CDCl_3$)



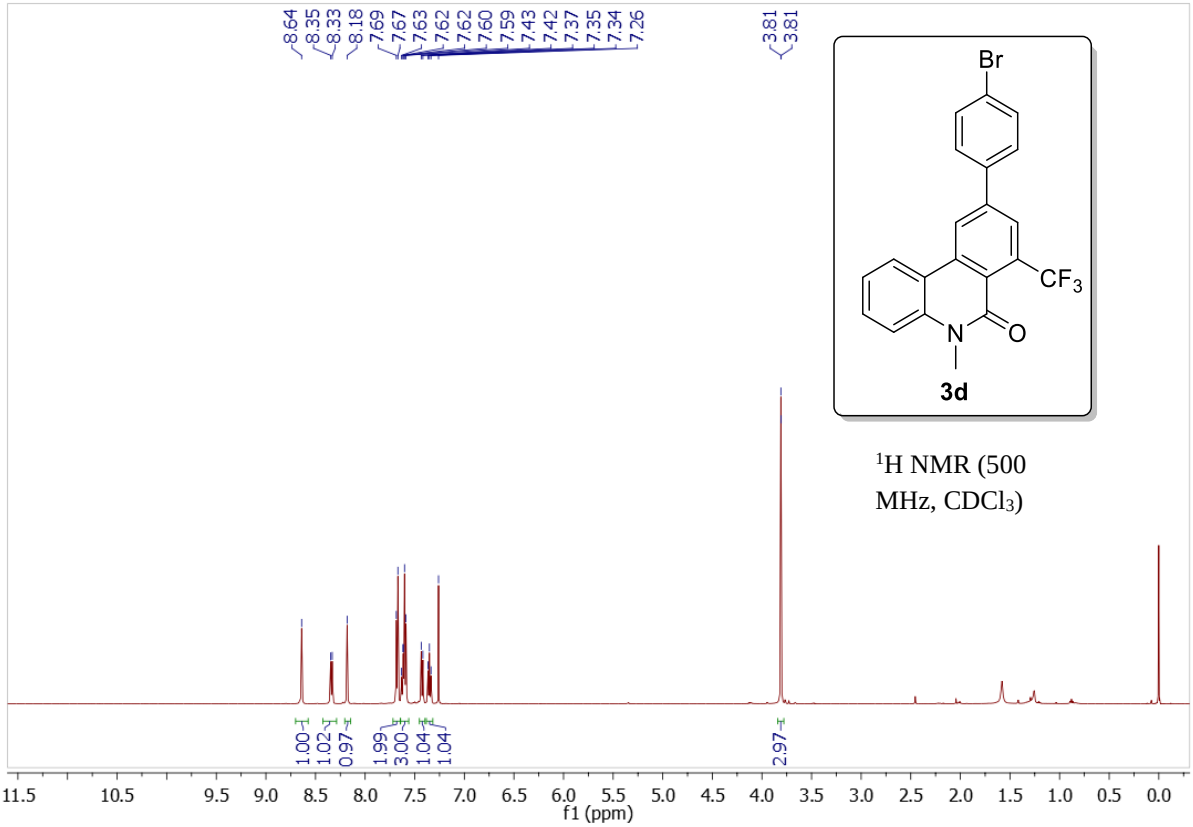
^{1}H NMR
400 MHz $CDCl_3$



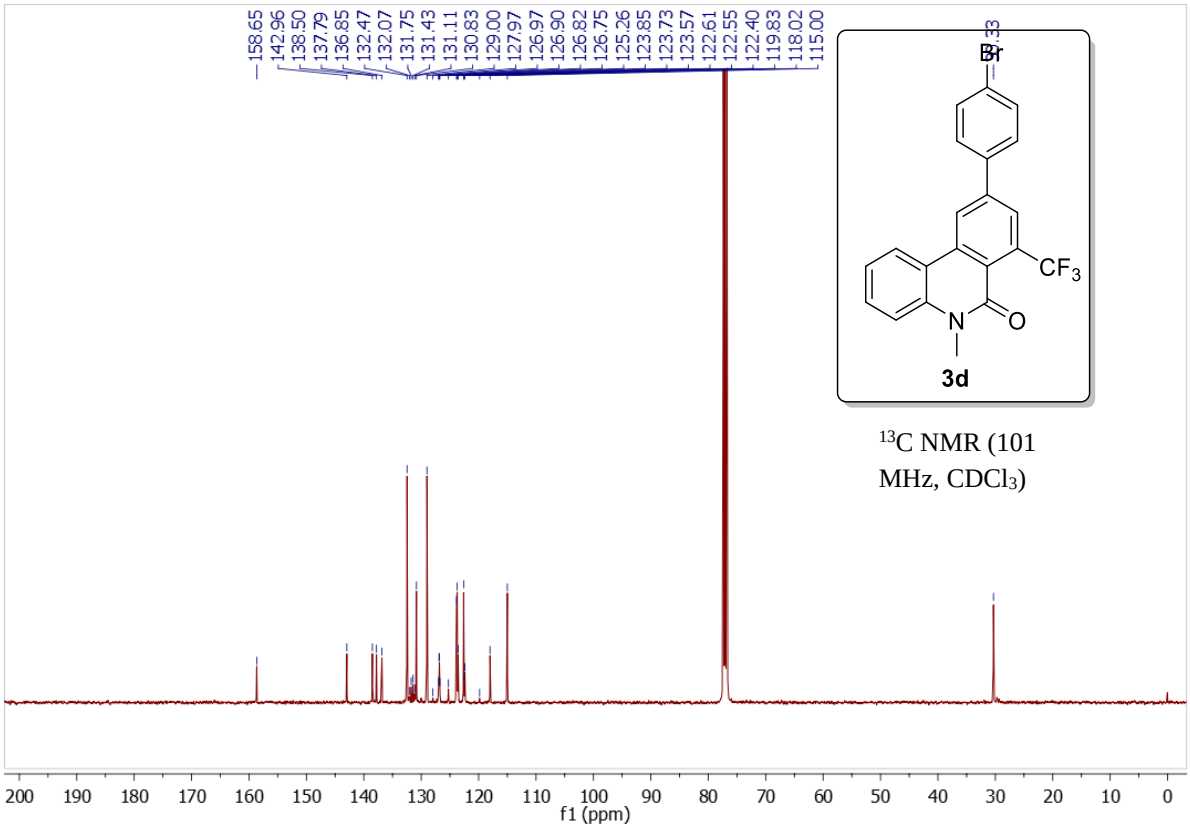
^{13}C NMR (101 MHz, $CDCl_3$)



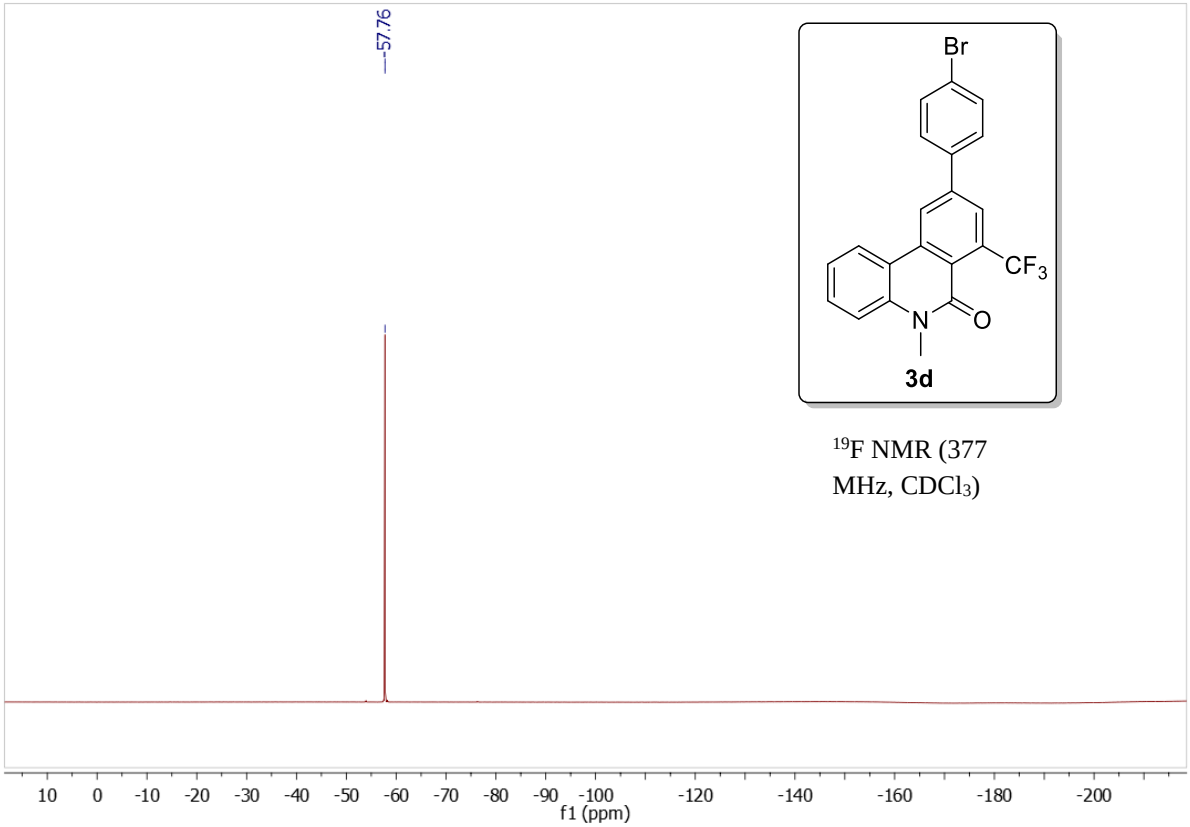
^{19}F NMR (377 MHz, $CDCl_3$)



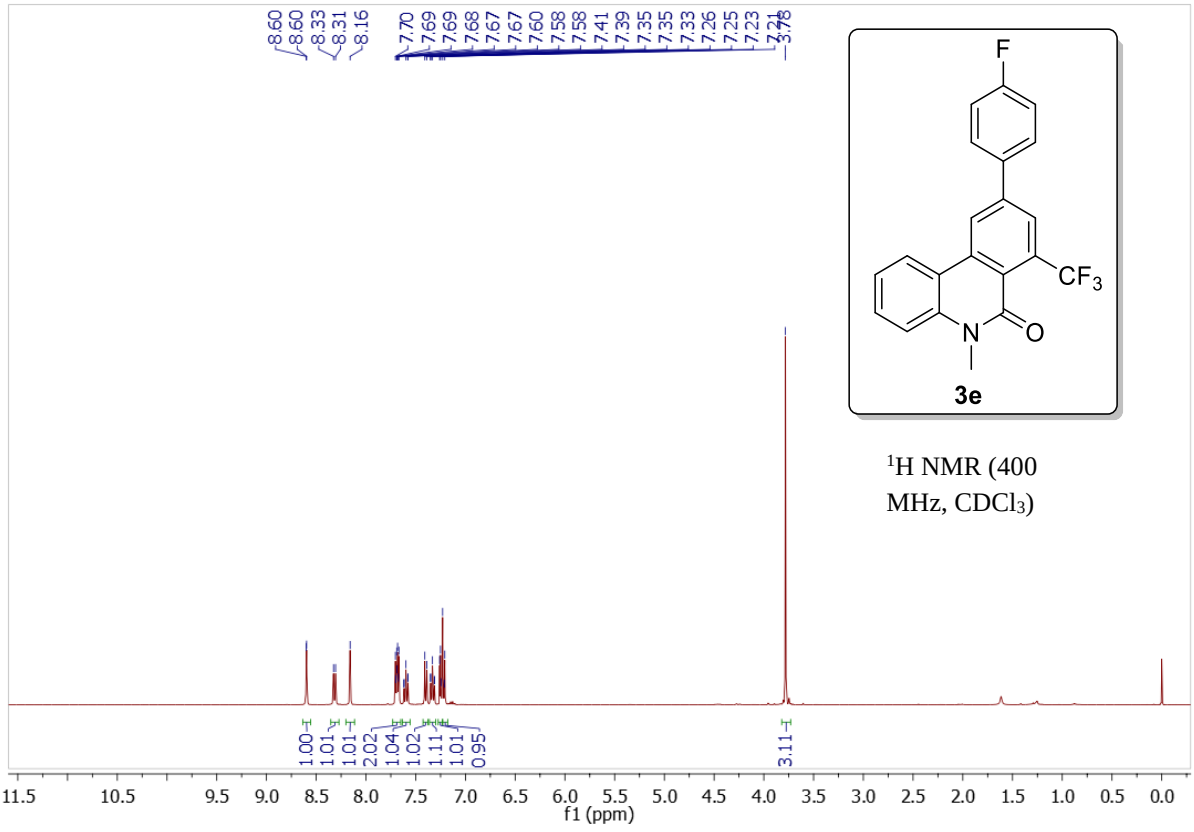
^{1}H NMR (500 MHz, $CDCl_3$)



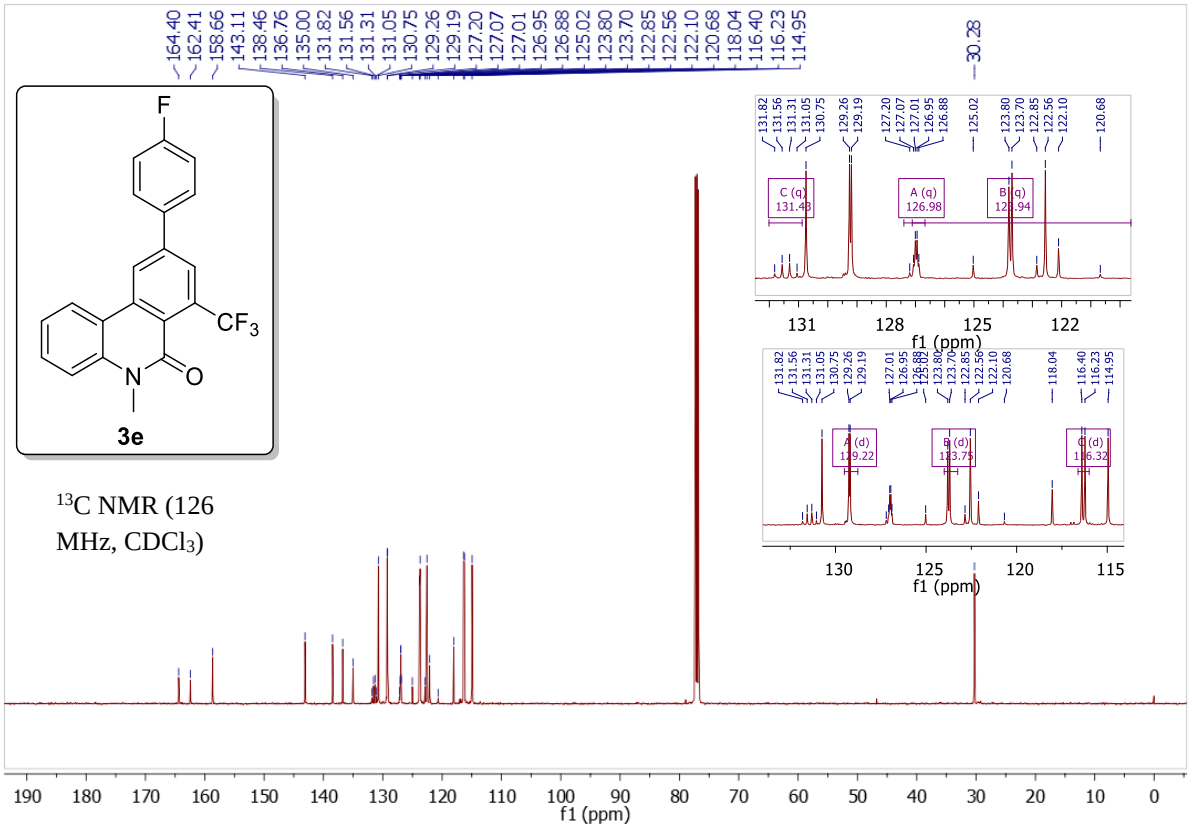
^{13}C NMR (101 MHz, $CDCl_3$)



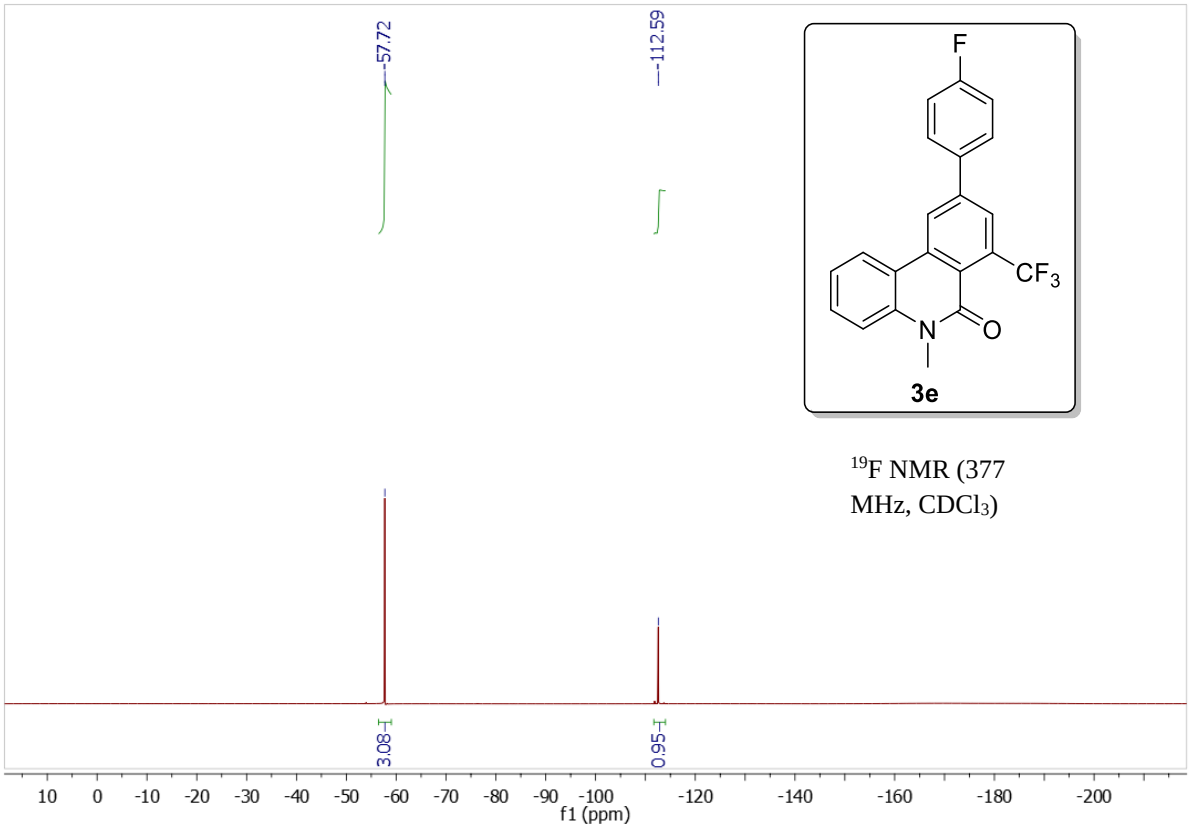
^{19}F NMR (377 MHz, $CDCl_3$)



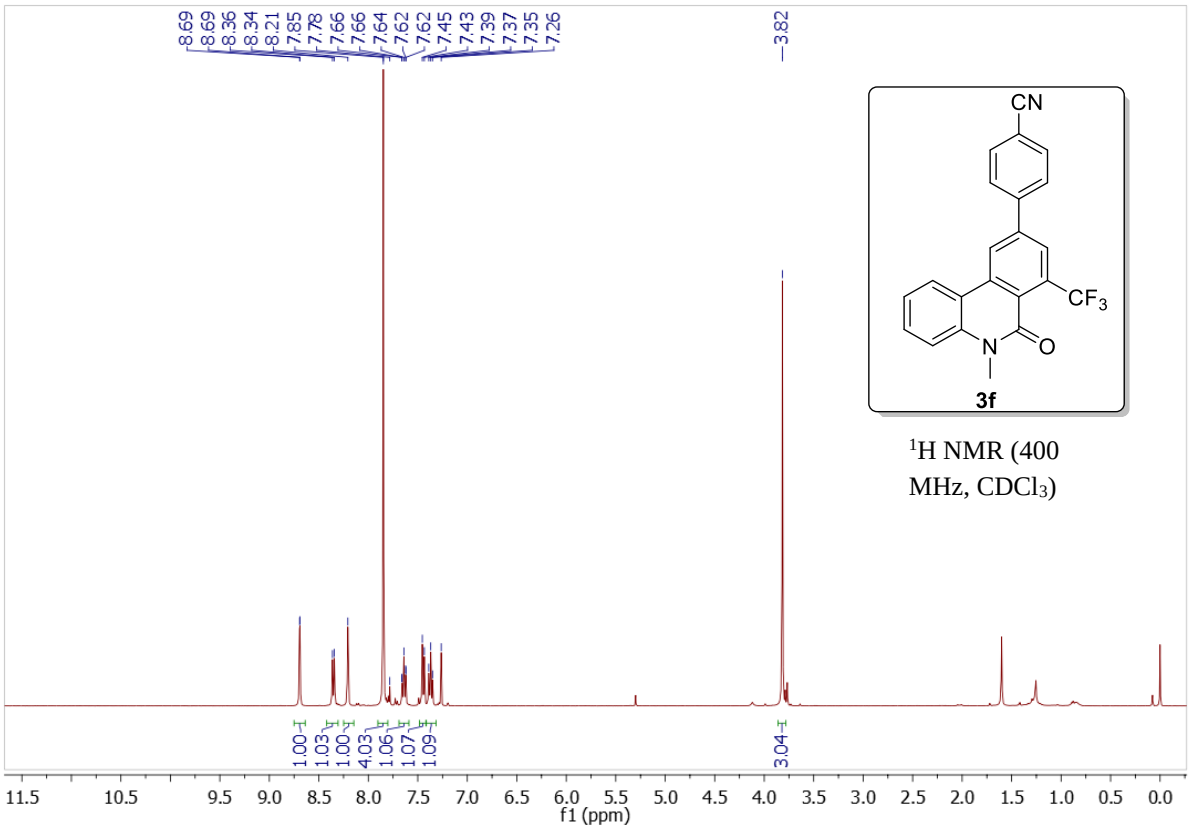
^{1}H NMR (400 MHz, $CDCl_3$)



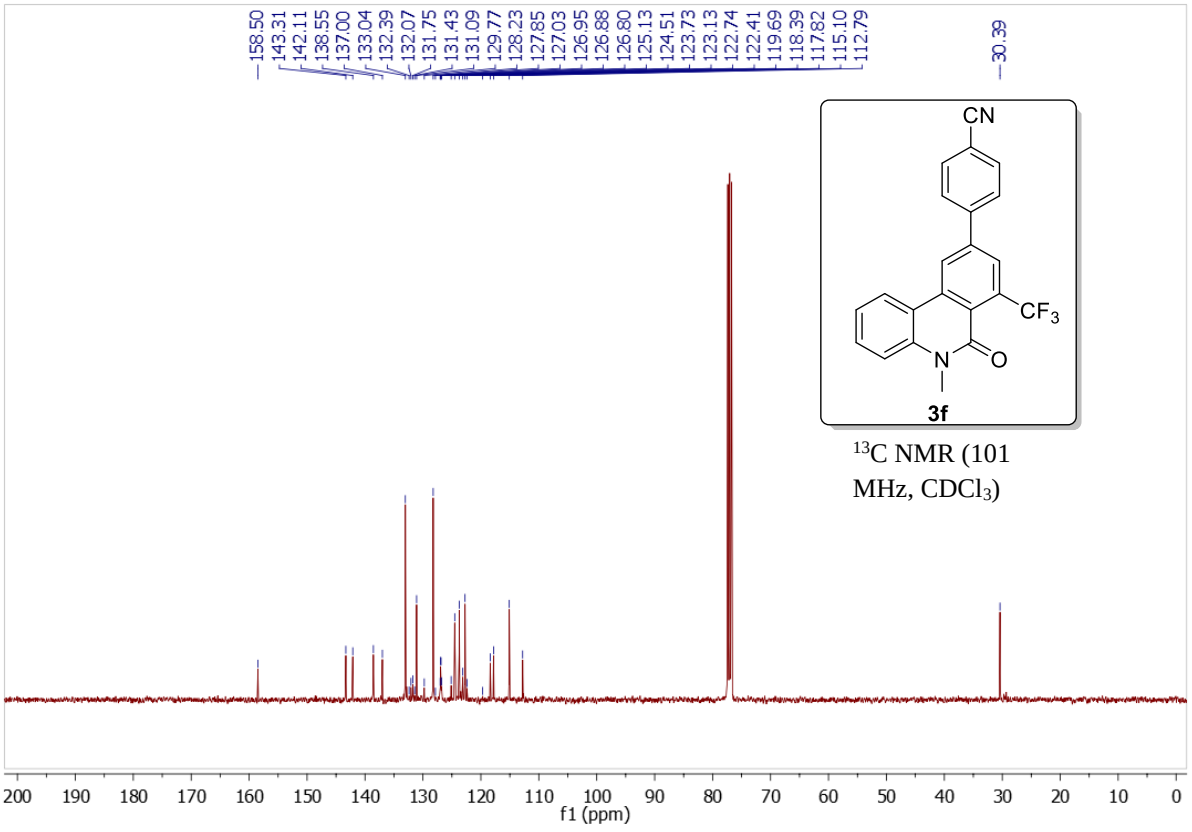
^{13}C NMR (126 MHz, $CDCl_3$)



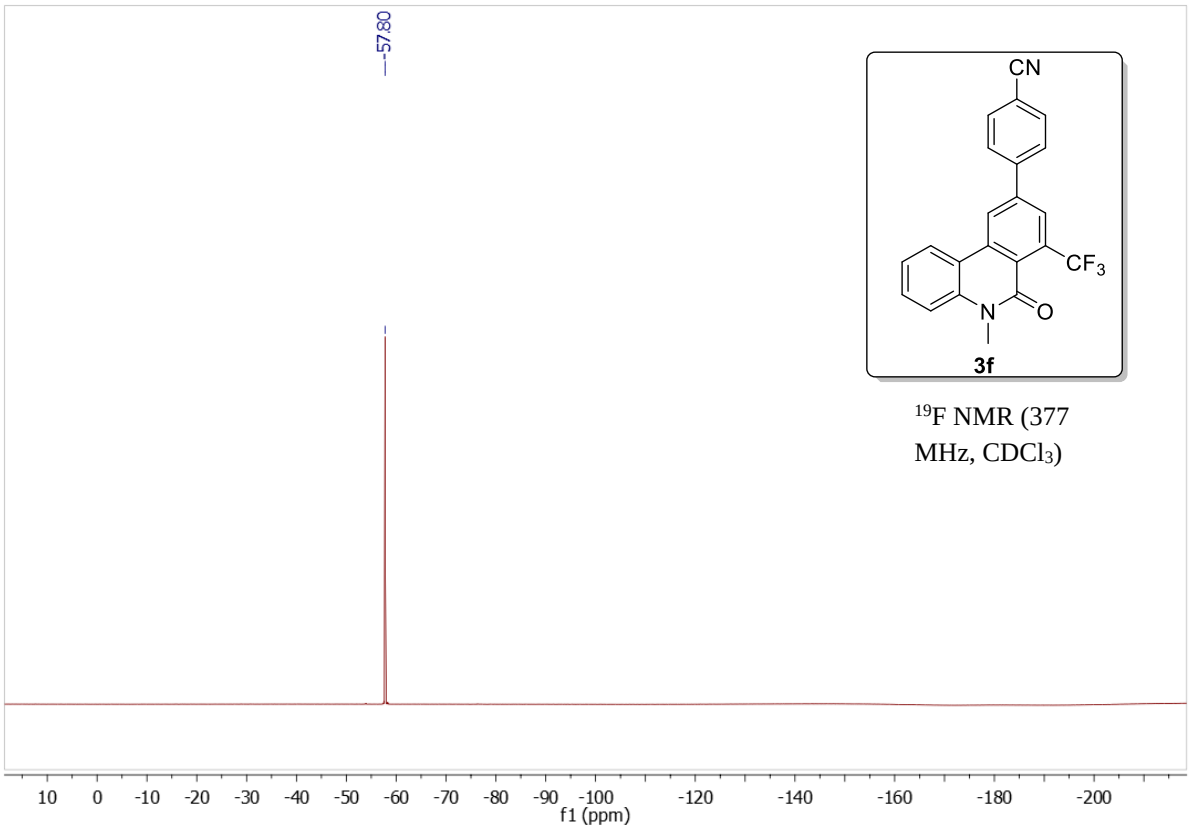
^{19}F NMR (377 MHz, $CDCl_3$)



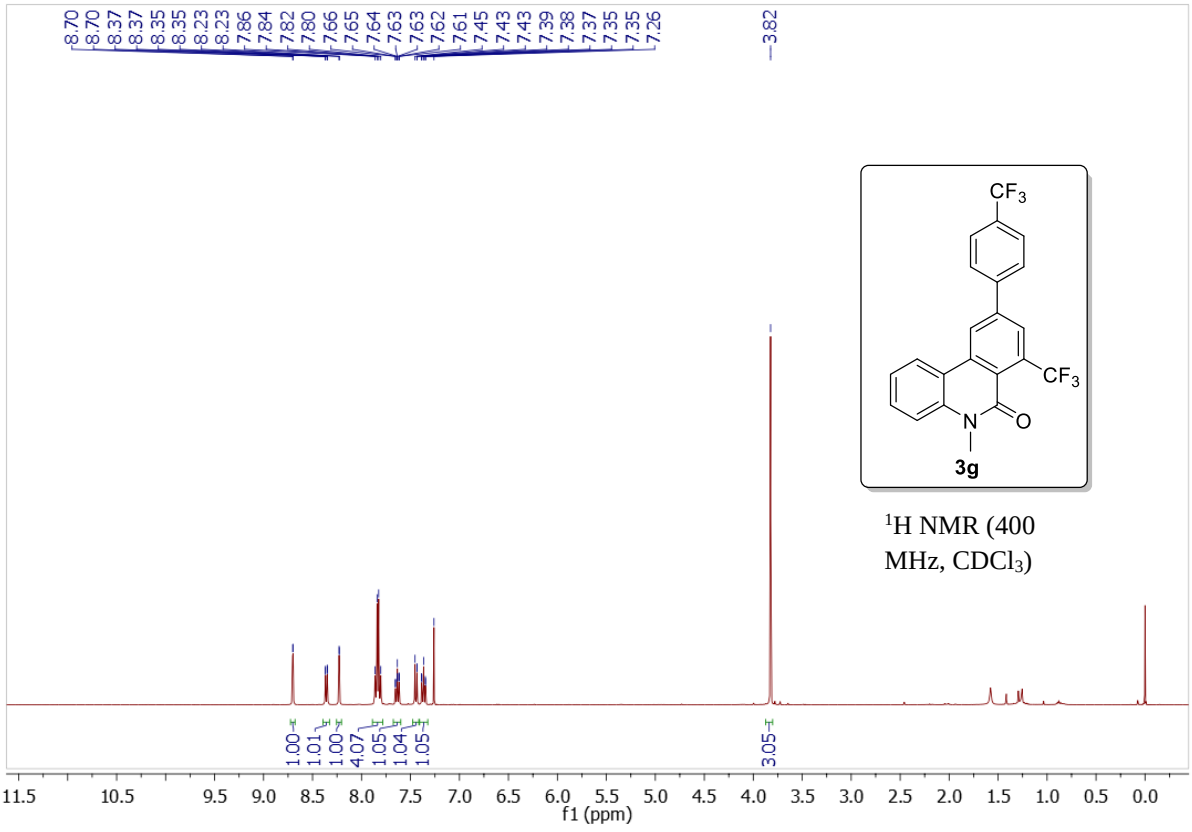
^{1}H NMR (400 MHz, $CDCl_3$)



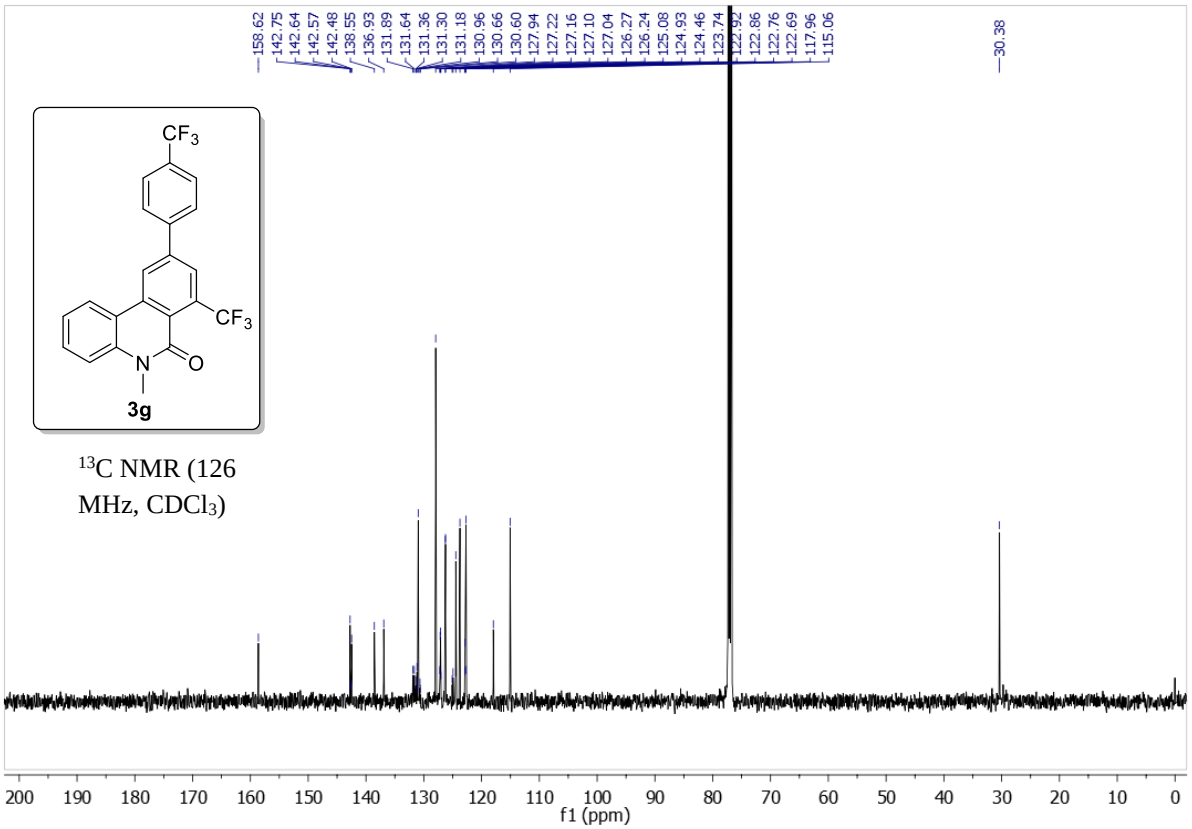
^{13}C NMR (101 MHz, $CDCl_3$)



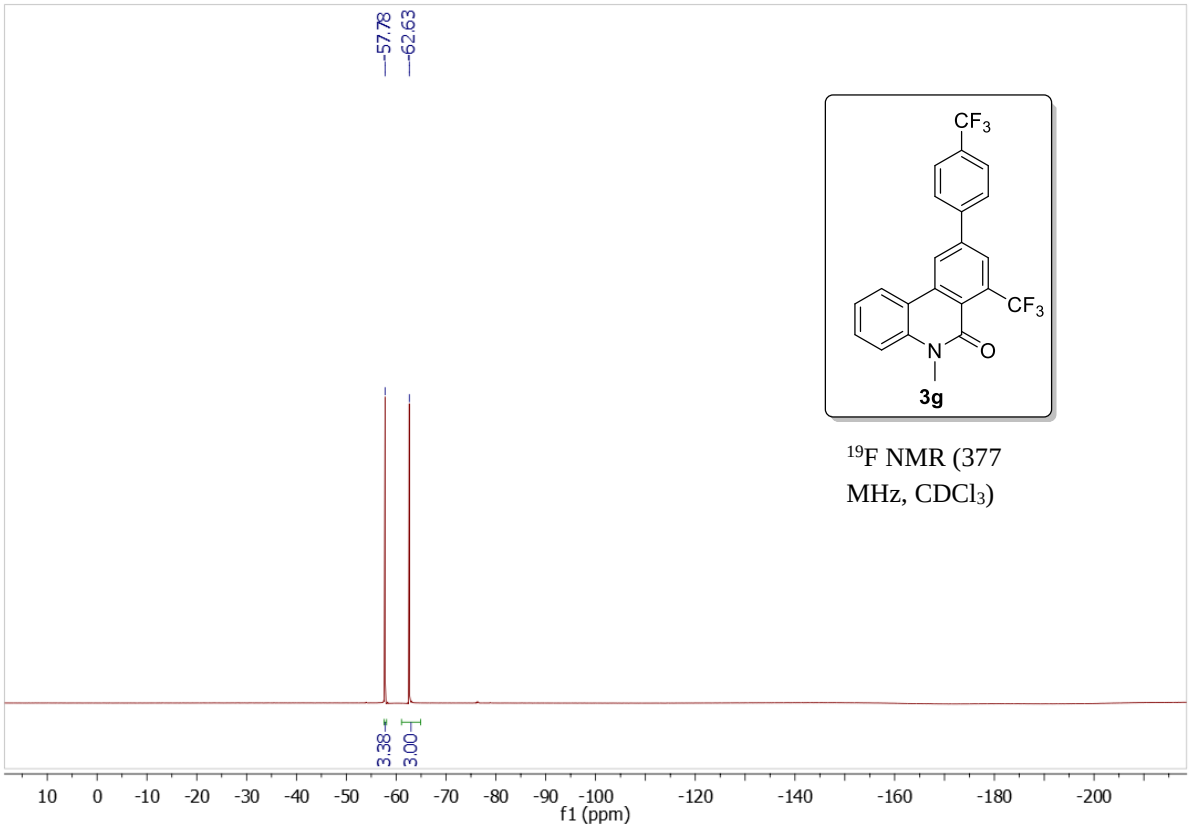
^{19}F NMR (377 MHz, $CDCl_3$)



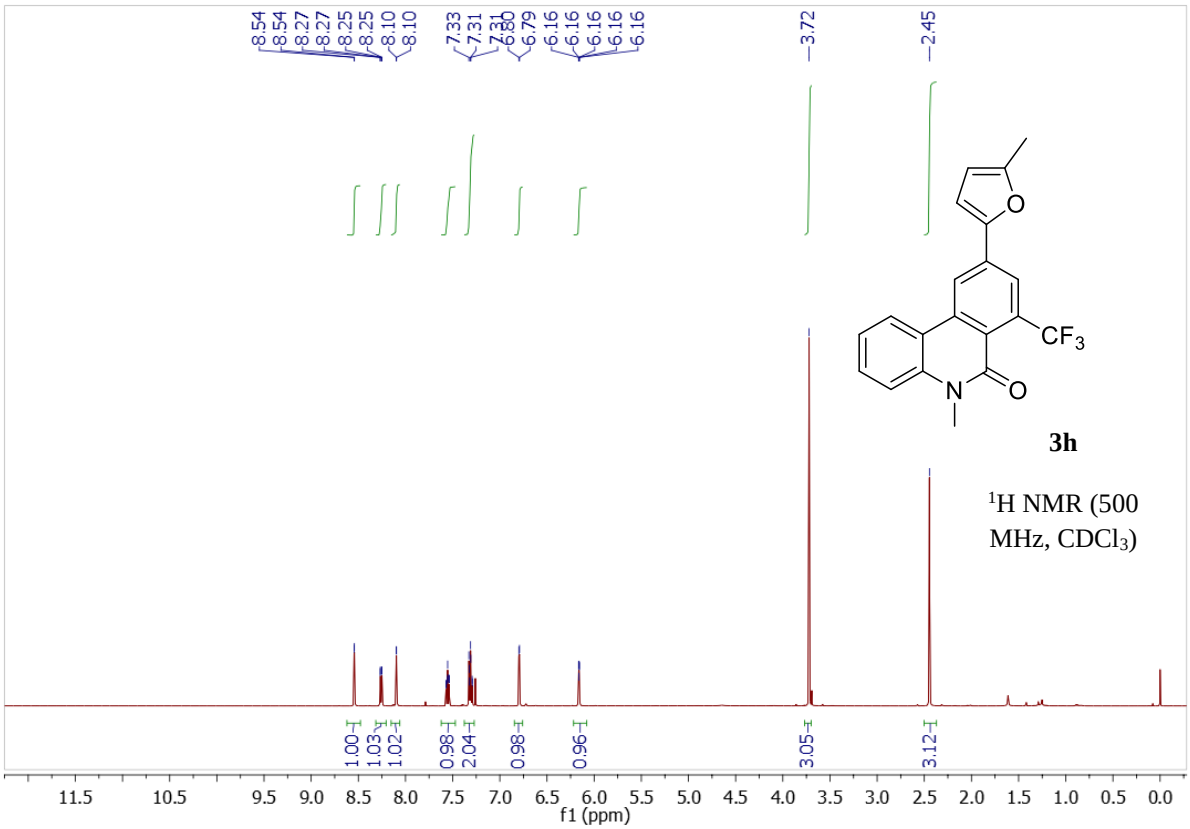
^{1}H NMR (400 MHz, $CDCl_3$)



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

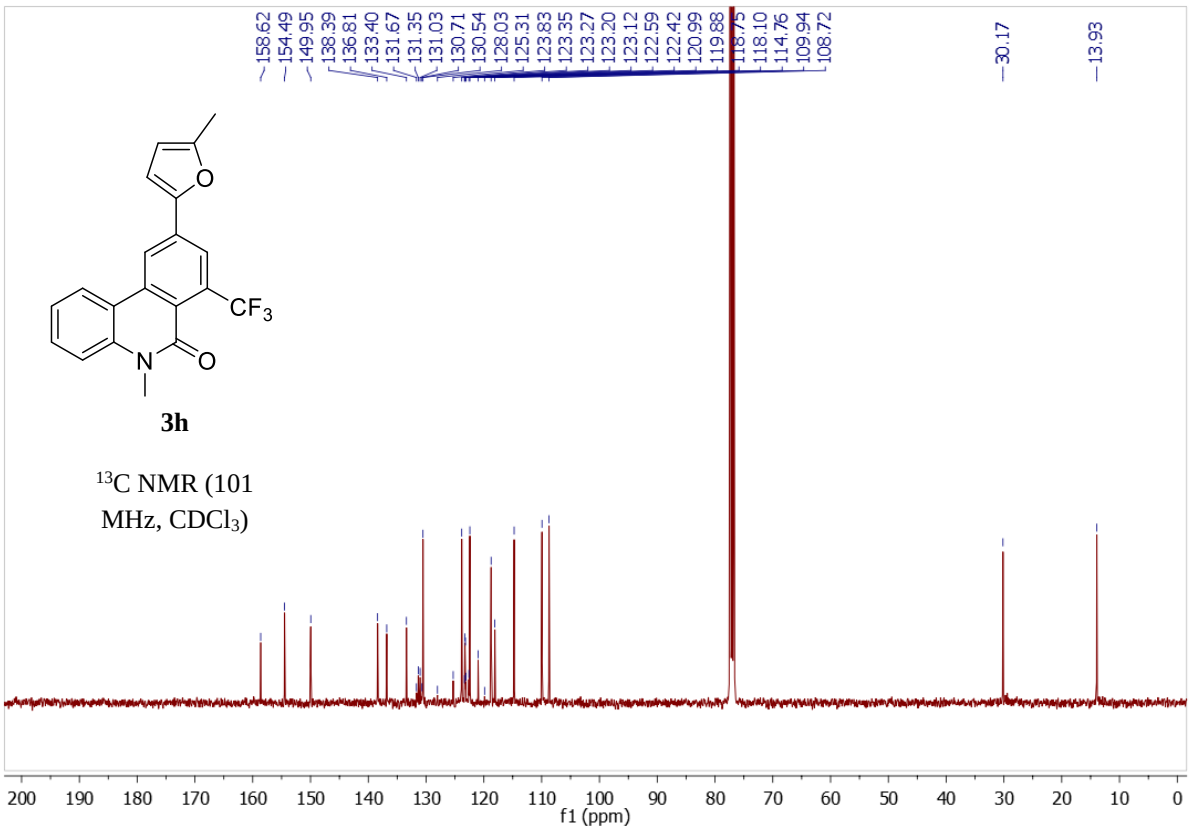


^{19}F NMR (377 MHz, $CDCl_3$)



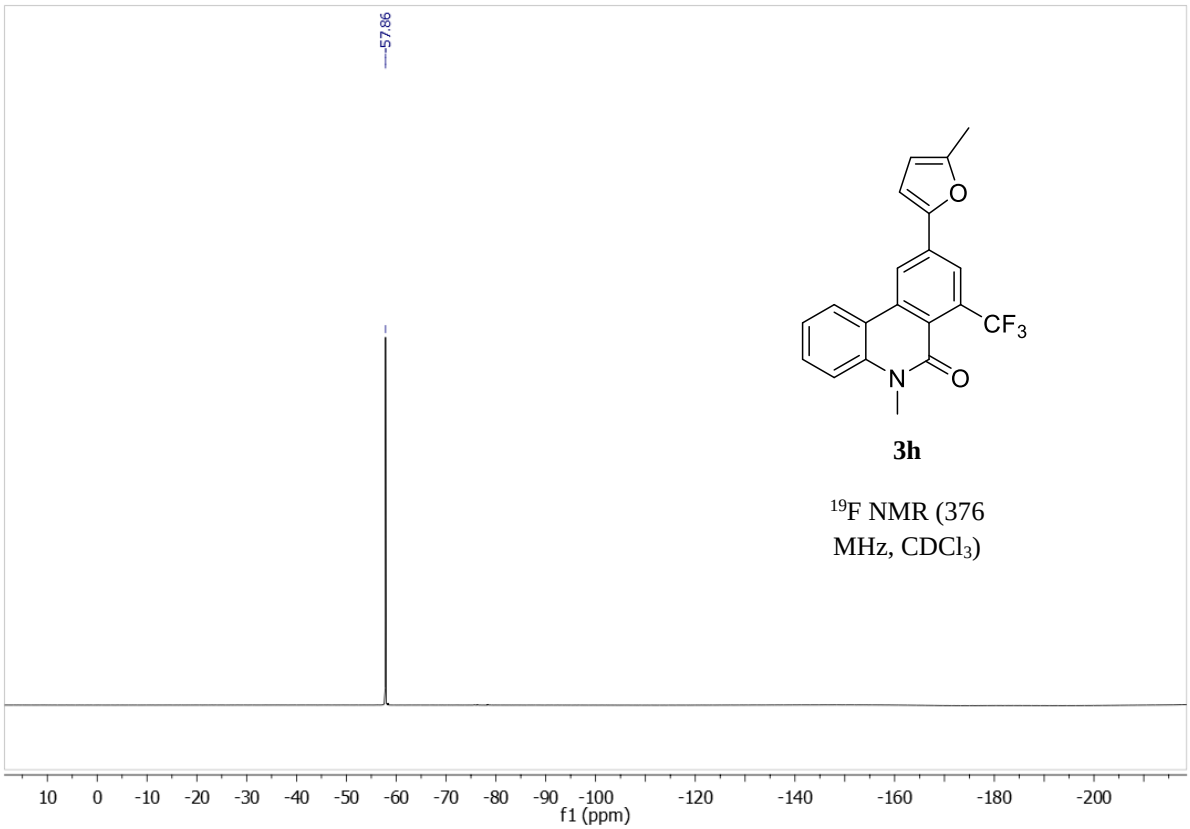
3h

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



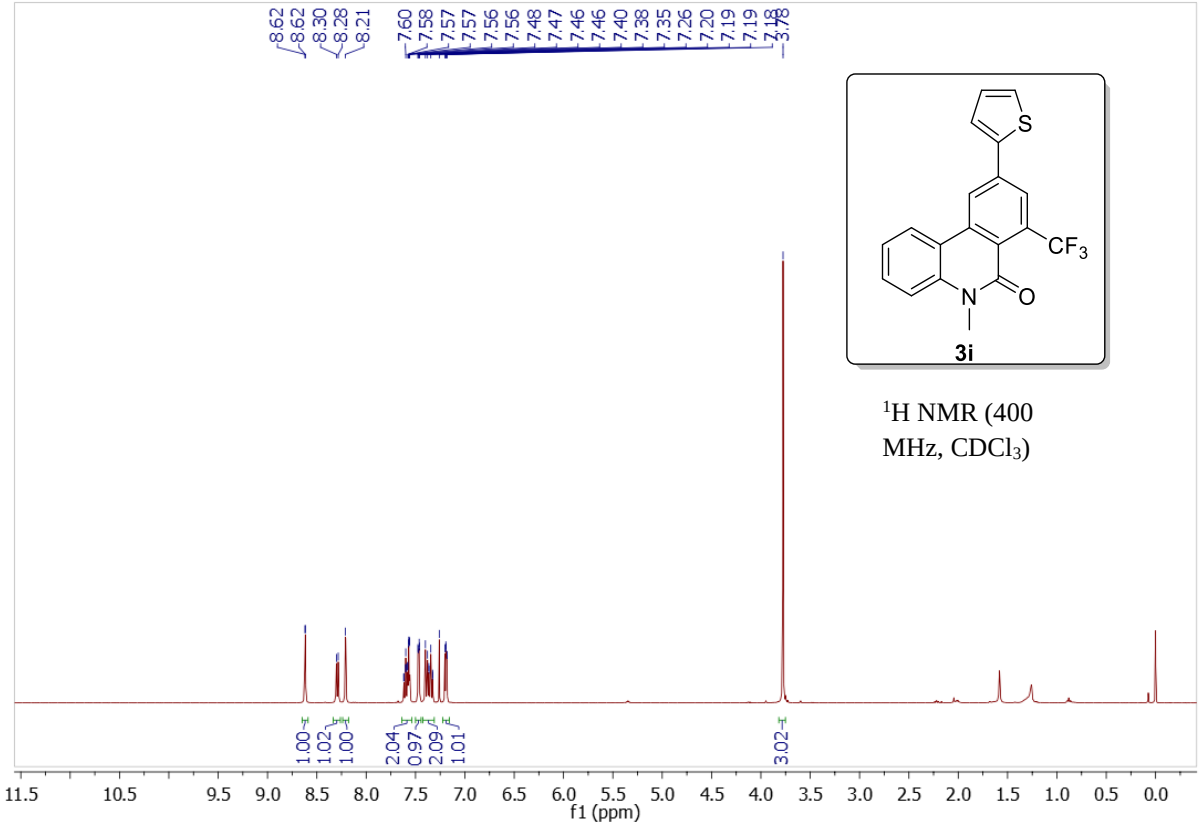
3h

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



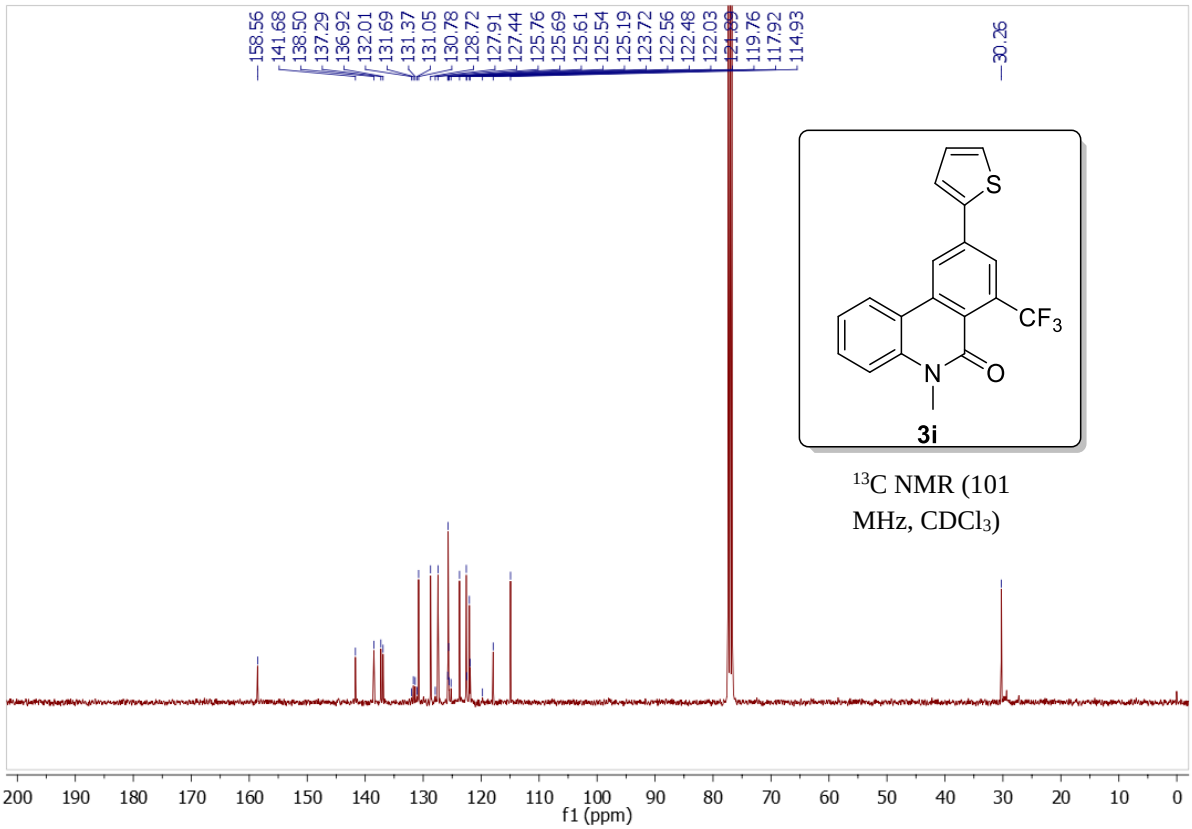
3h

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

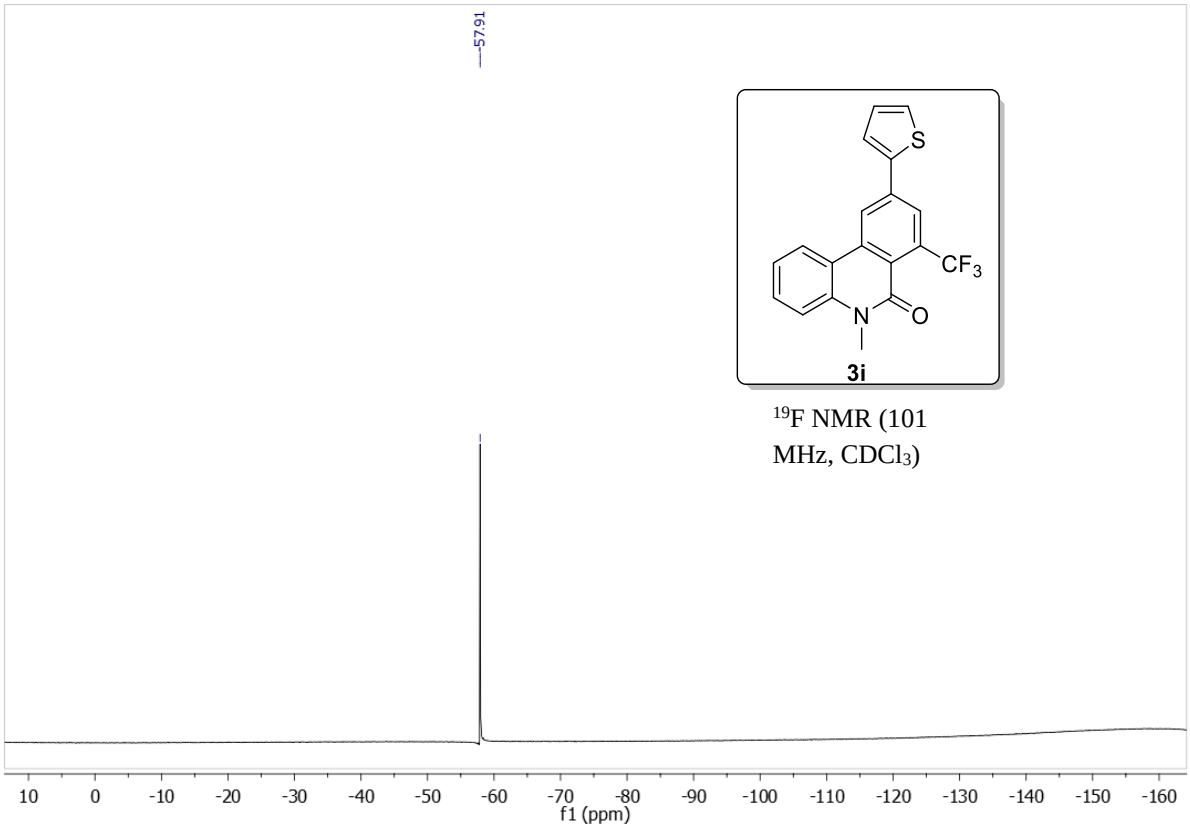


3i

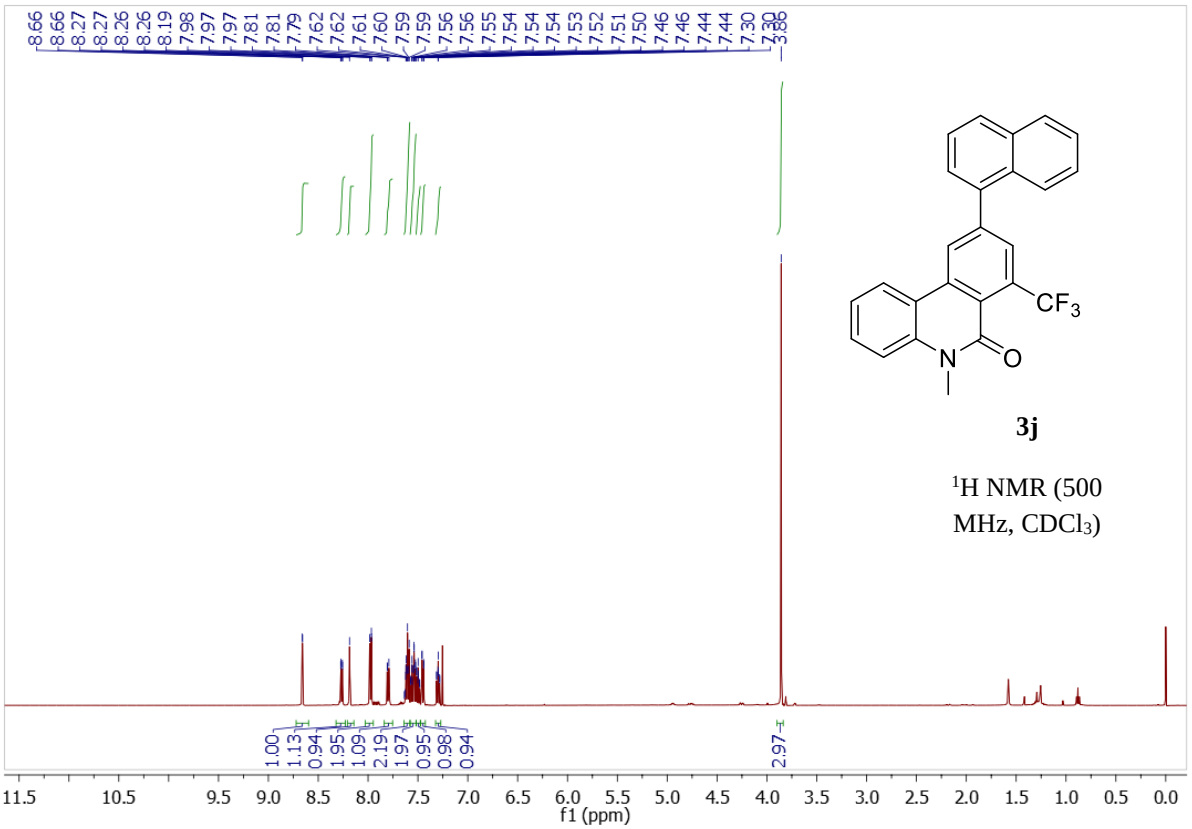
^{1}H NMR (400 MHz, $CDCl_3$)



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

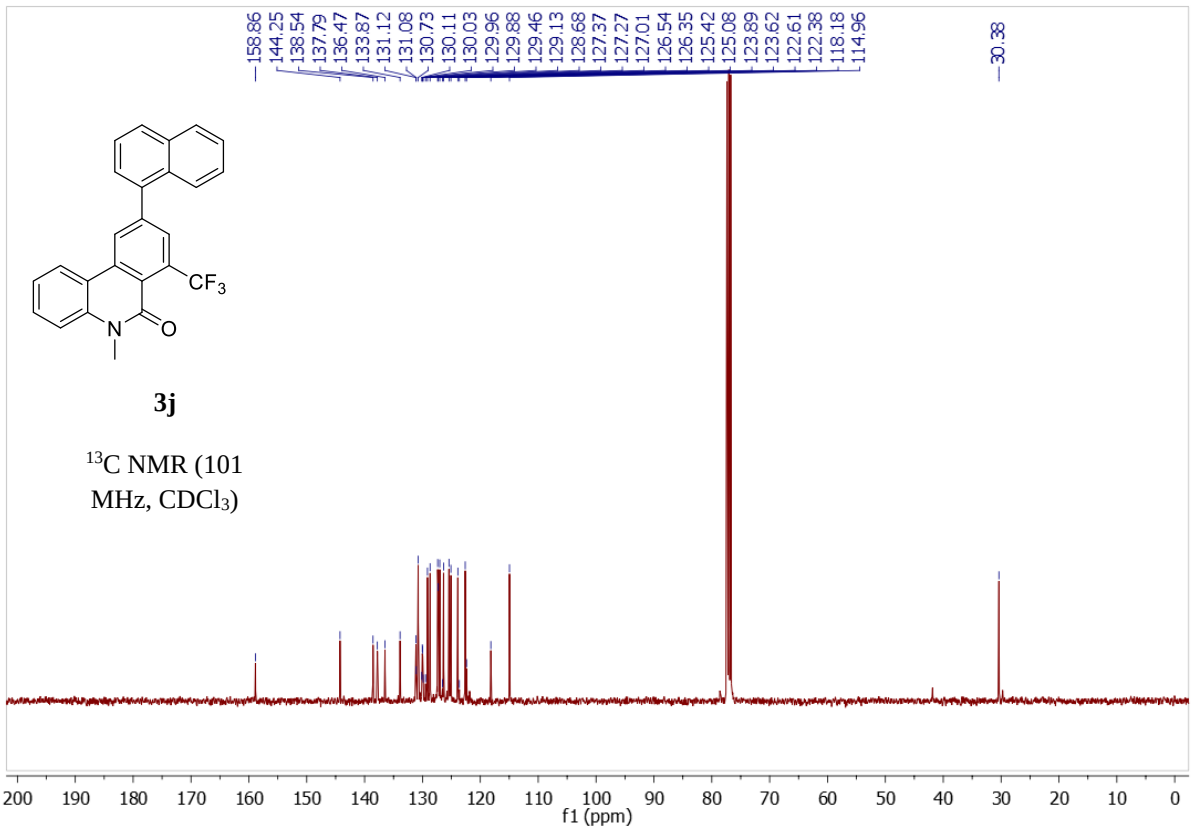


^{19}F NMR (101 MHz, $CDCl_3$)



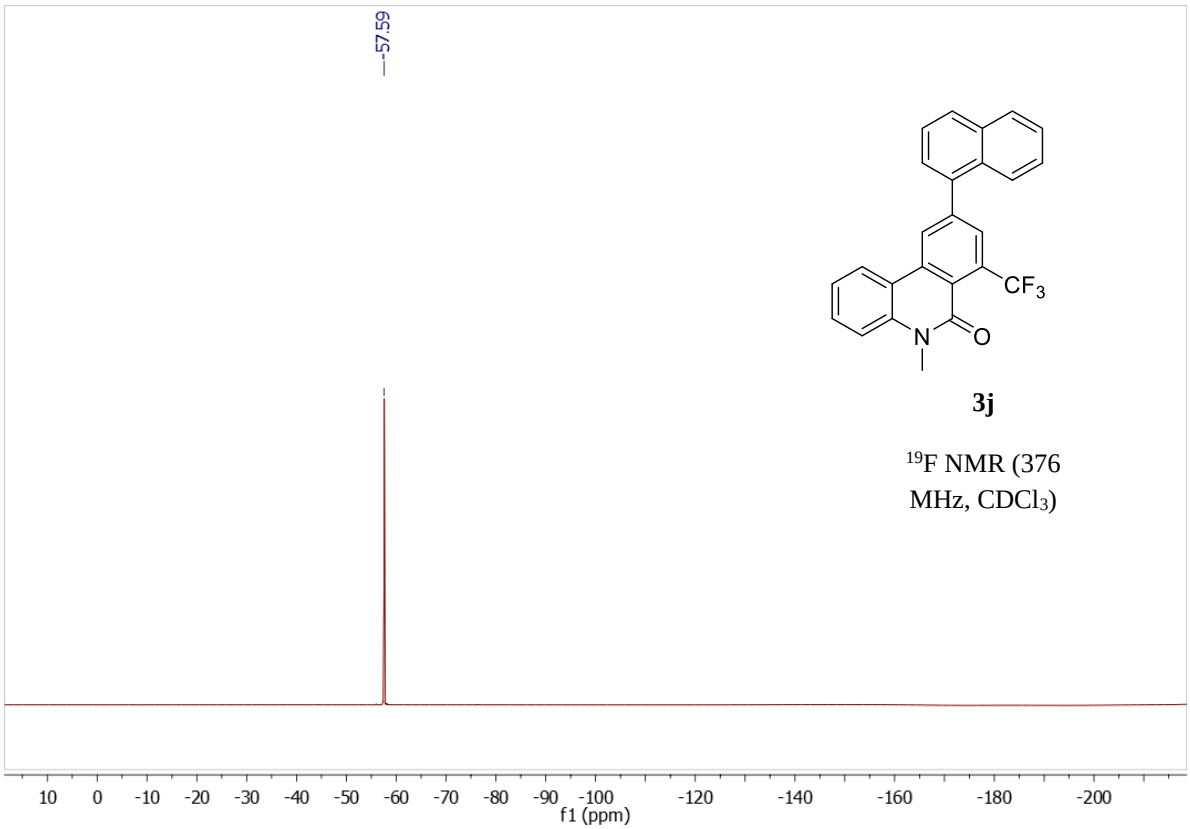
3j

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



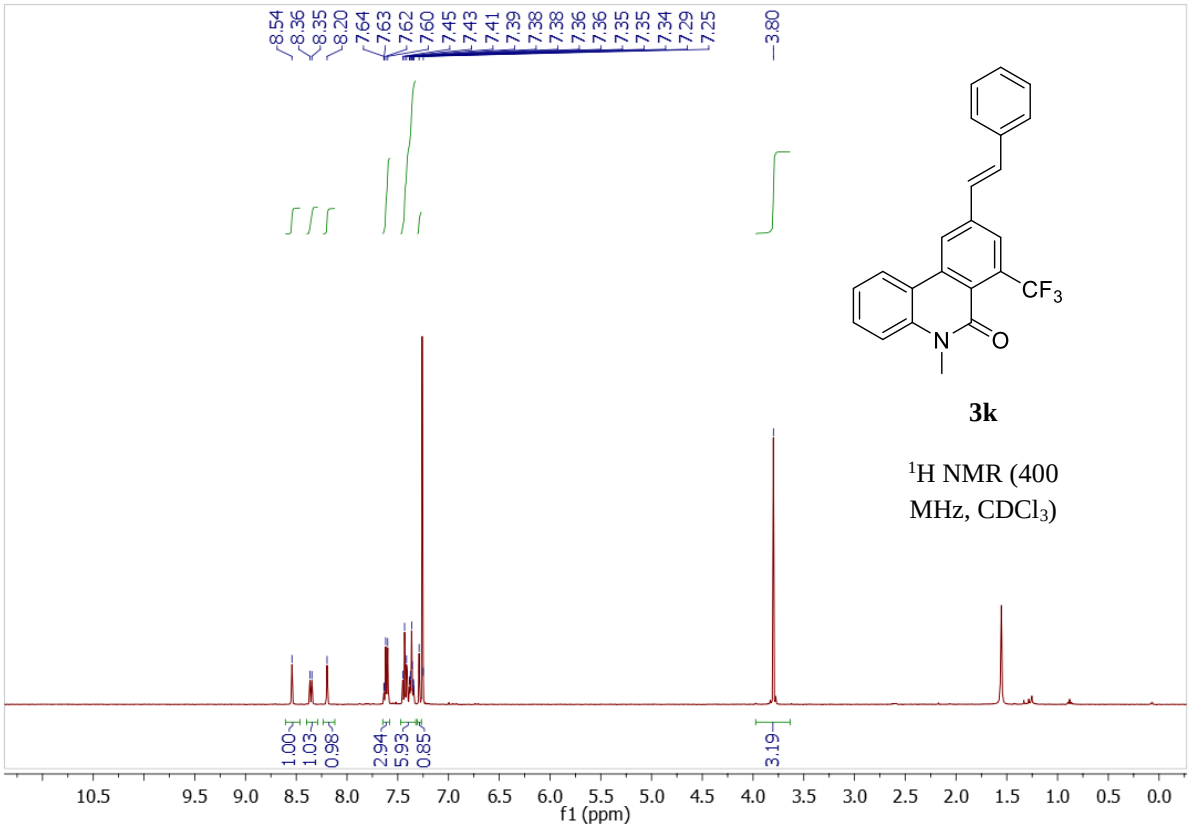
3j

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



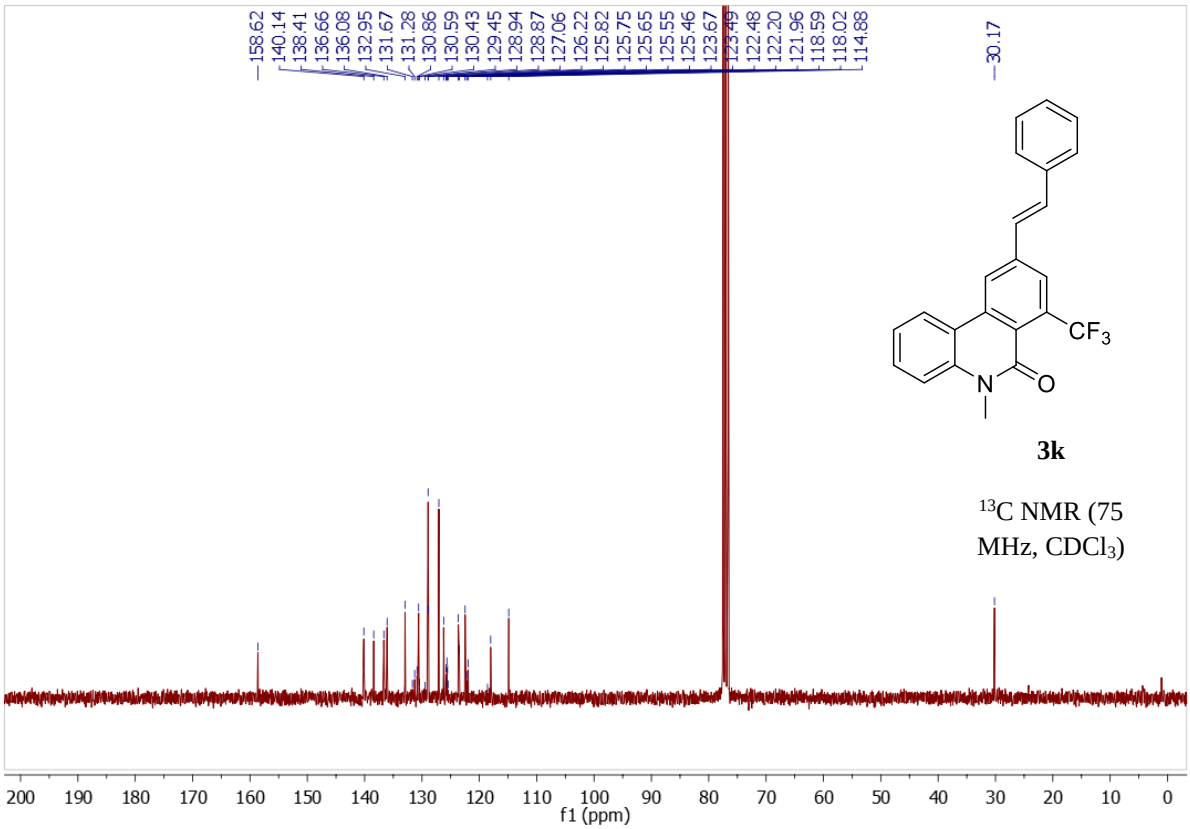
3j

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



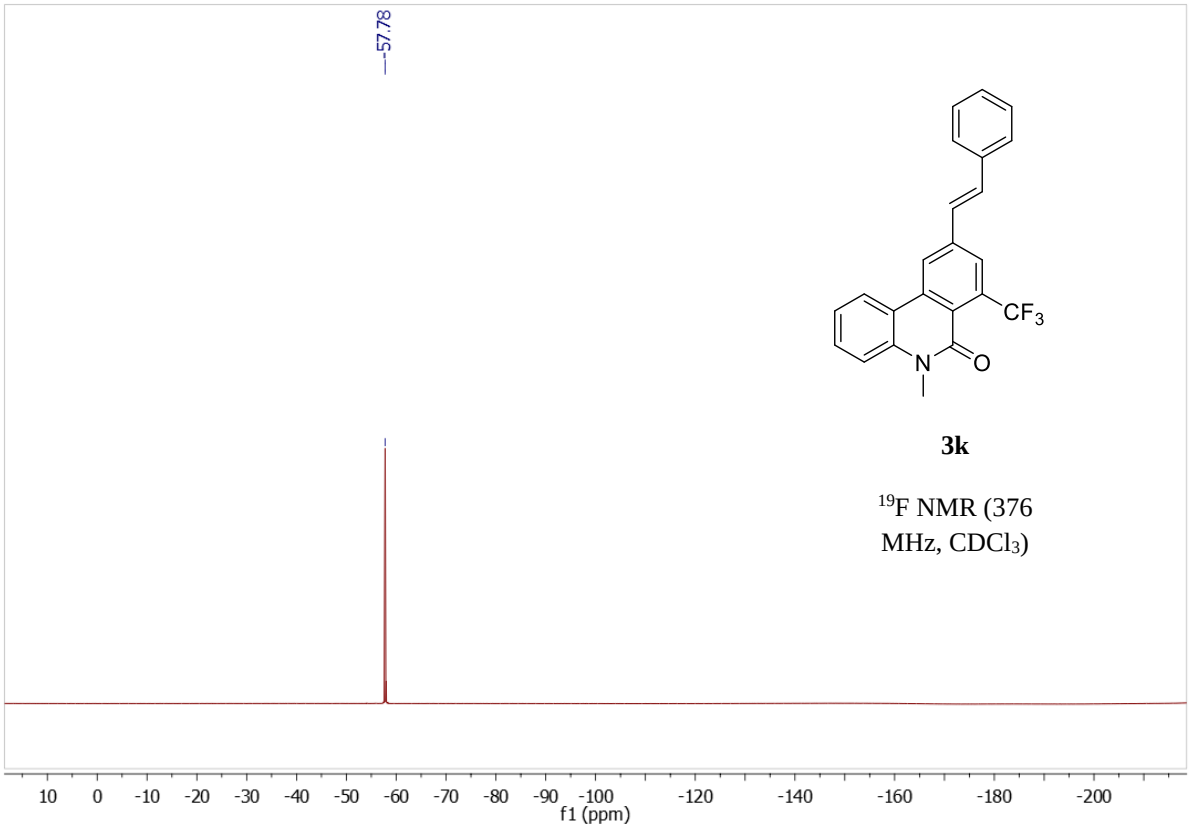
3k

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



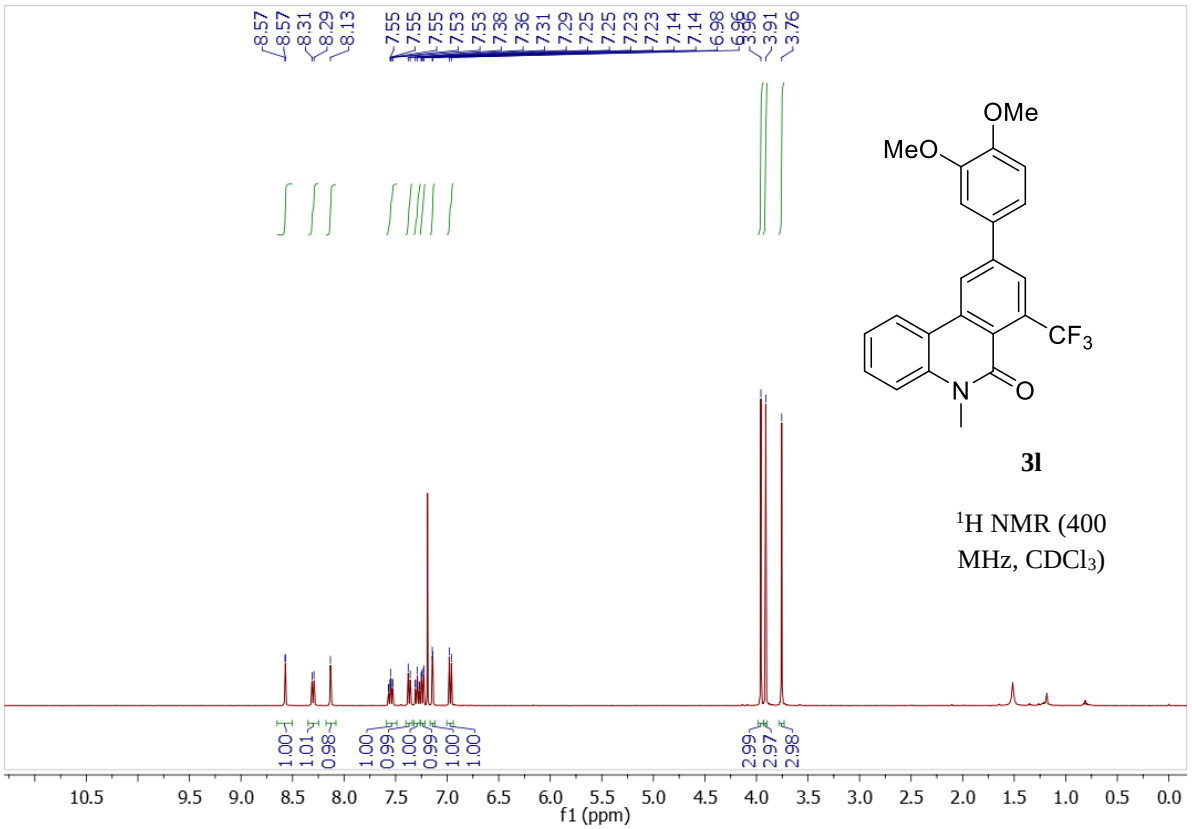
3k

^{13}C NMR (75 MHz, $CDCl_3$)



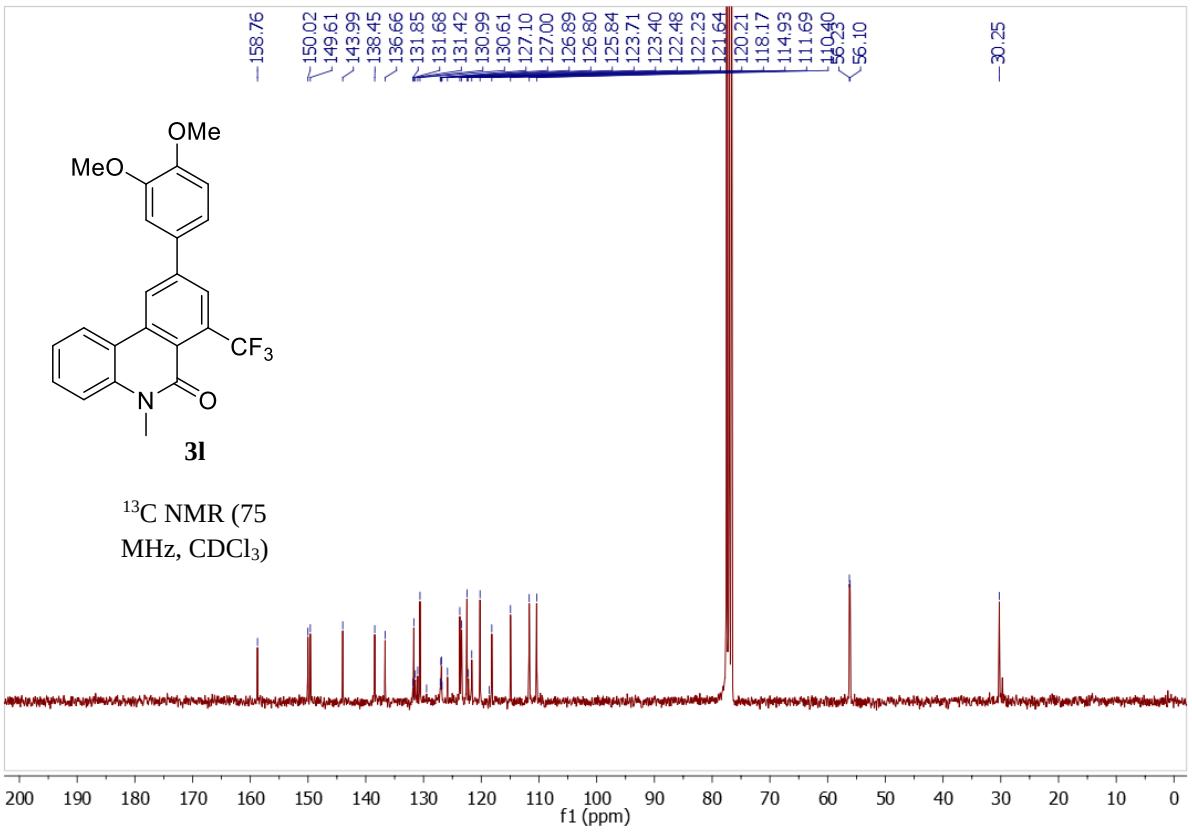
3k

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



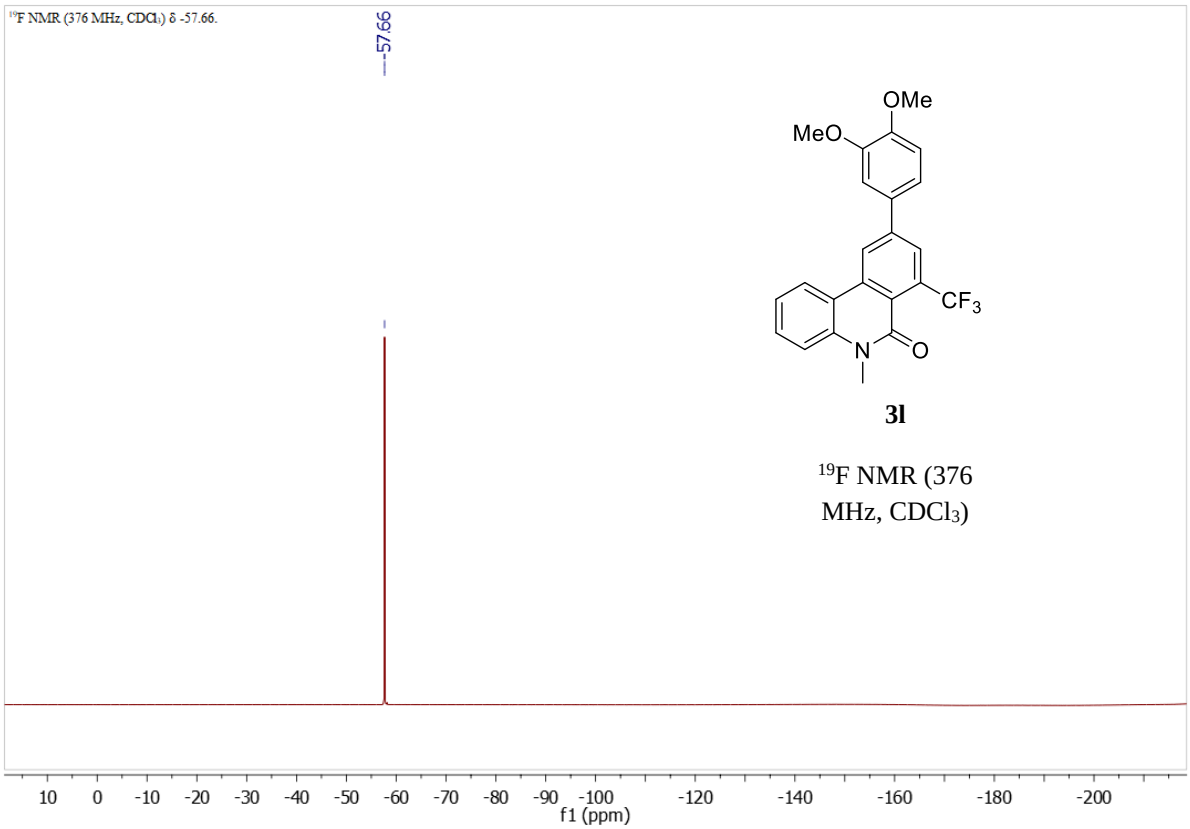
3l

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



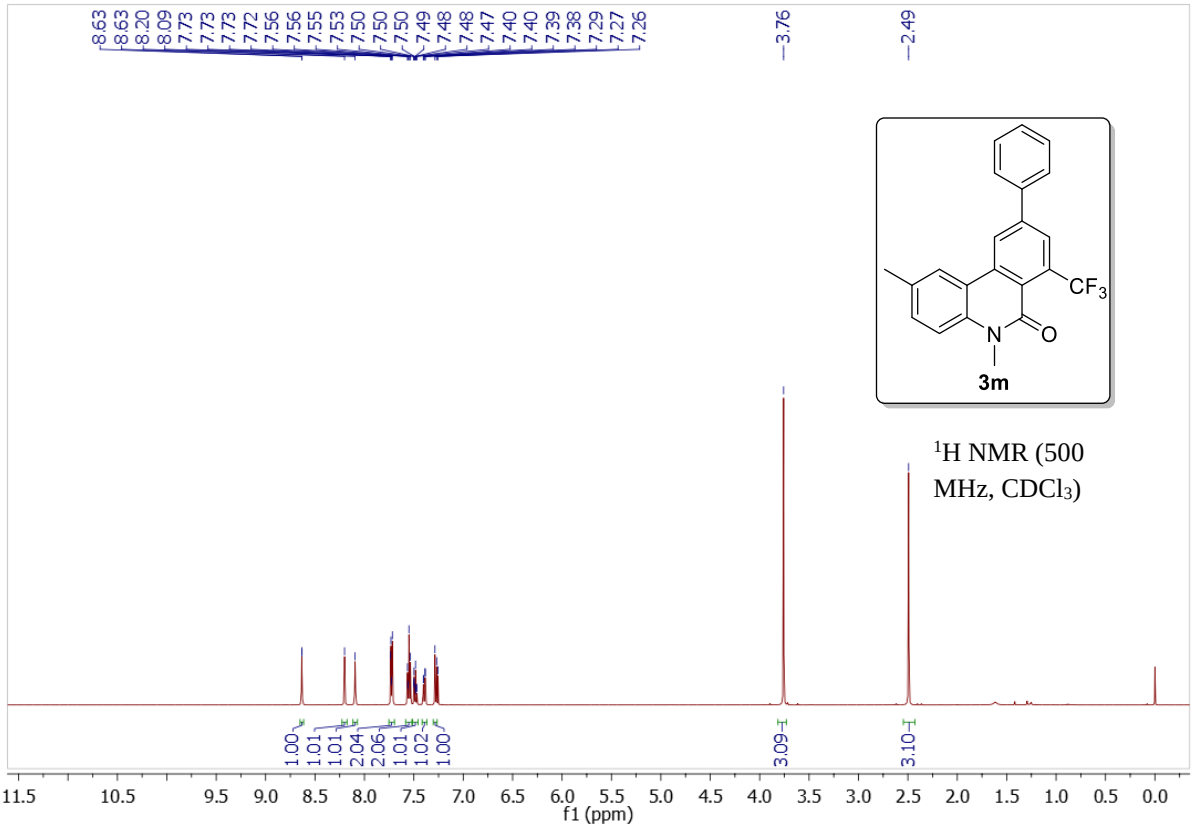
3l

^{13}C NMR (75 MHz, $CDCl_3$)

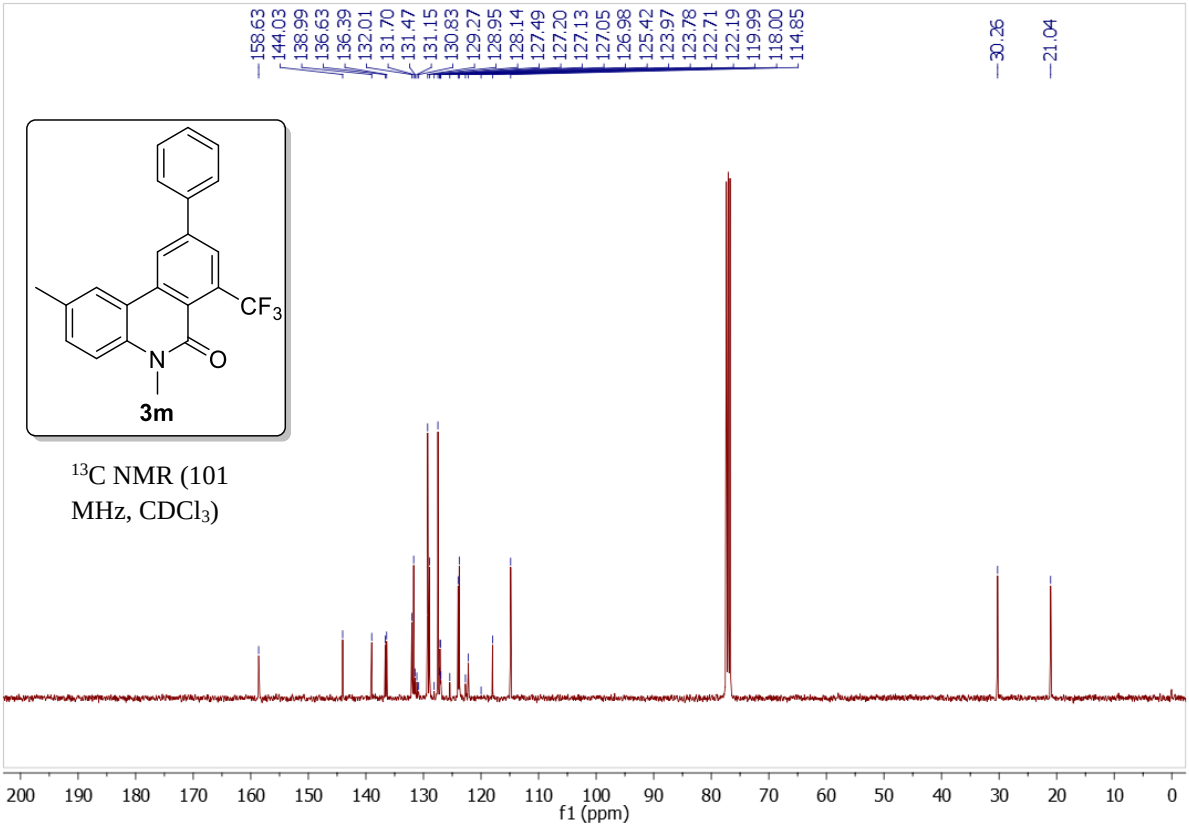


3l

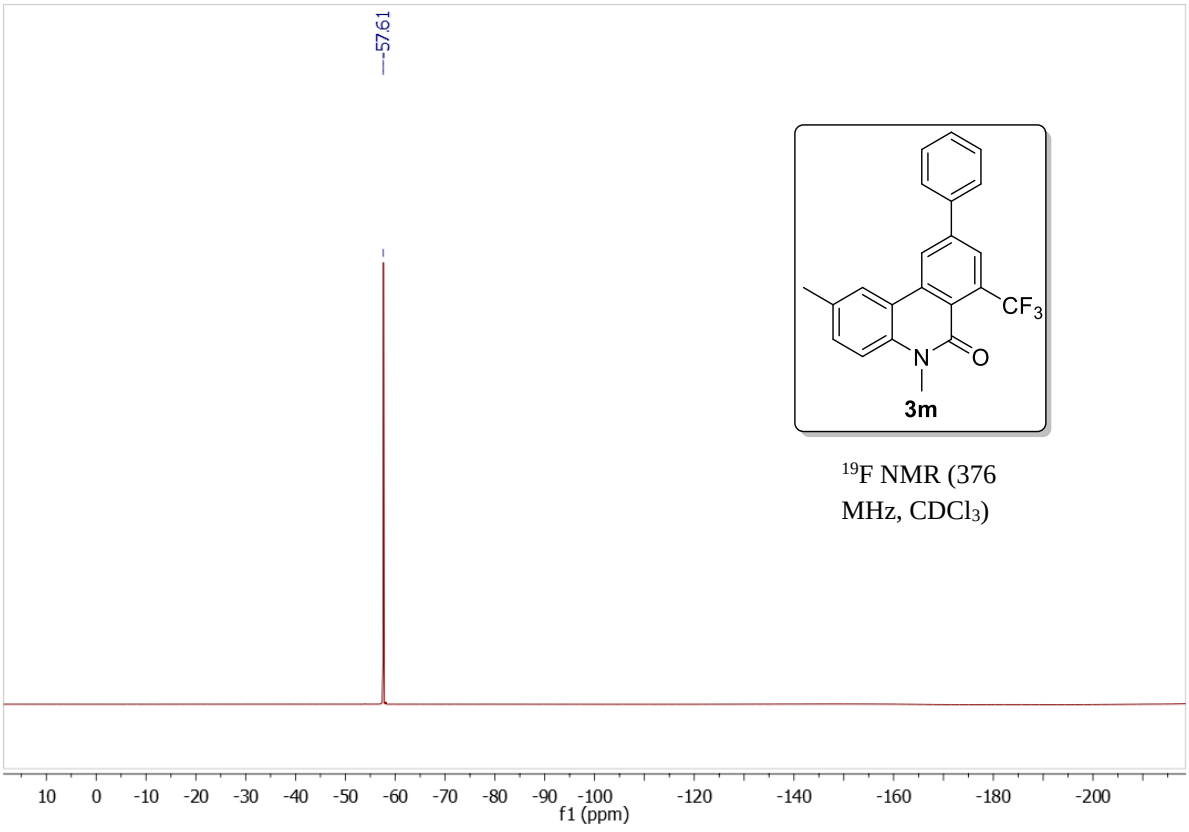
^{19}F NMR (376 MHz, $CDCl_3$)



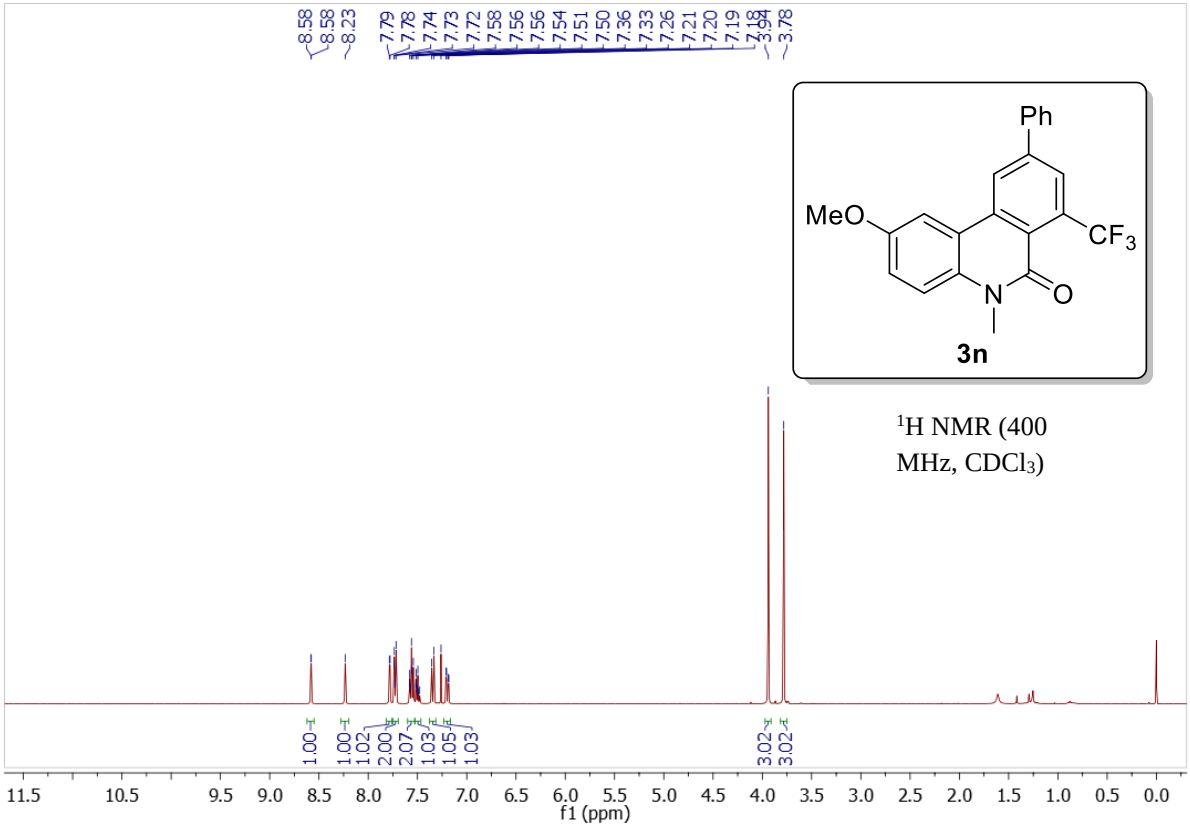
^{1}H NMR (500 MHz, $CDCl_3$)



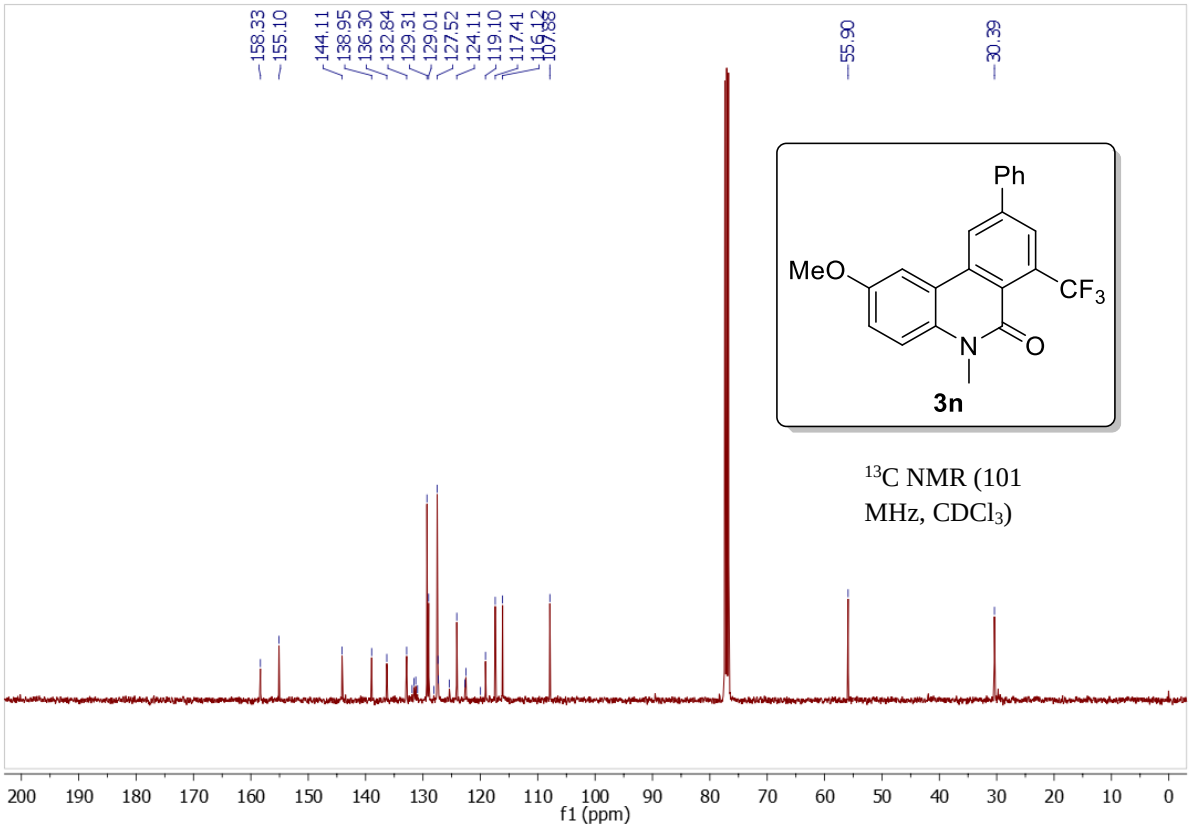
^{13}C NMR (101 MHz, $CDCl_3$)



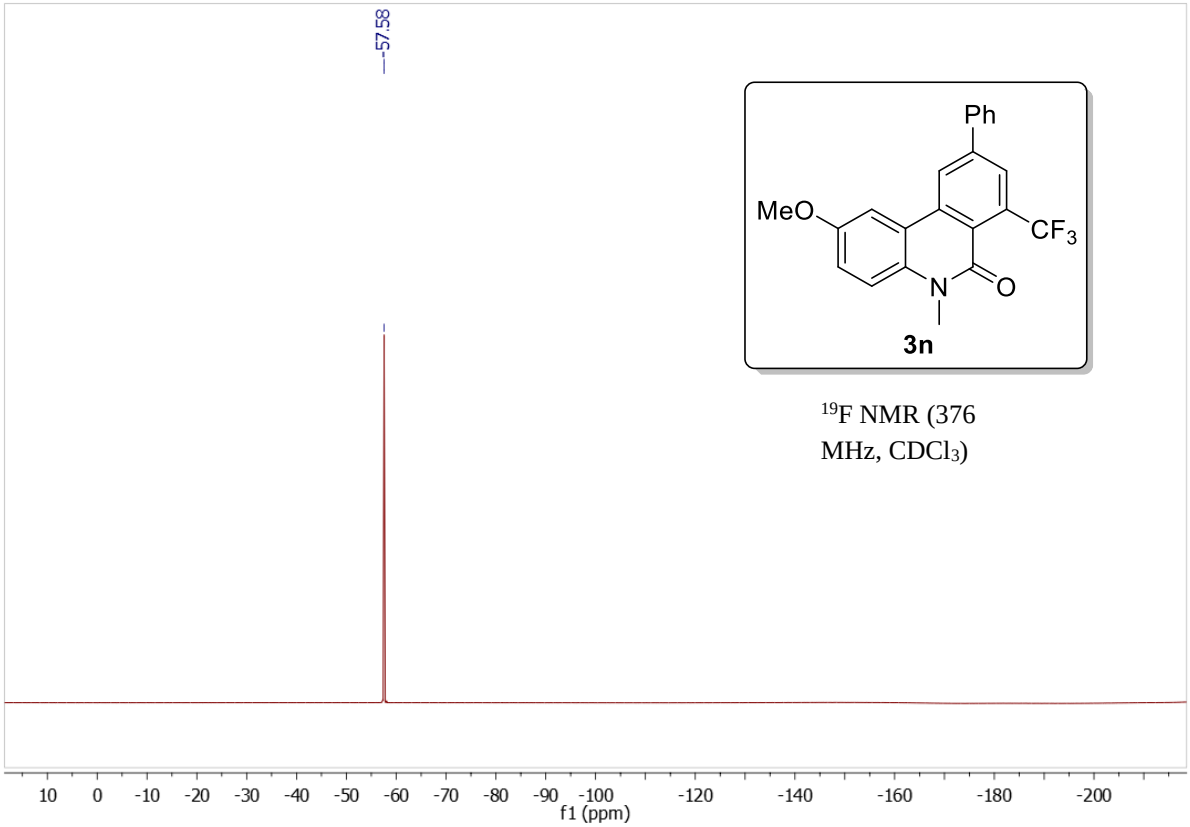
^{19}F NMR (376 MHz, $CDCl_3$)



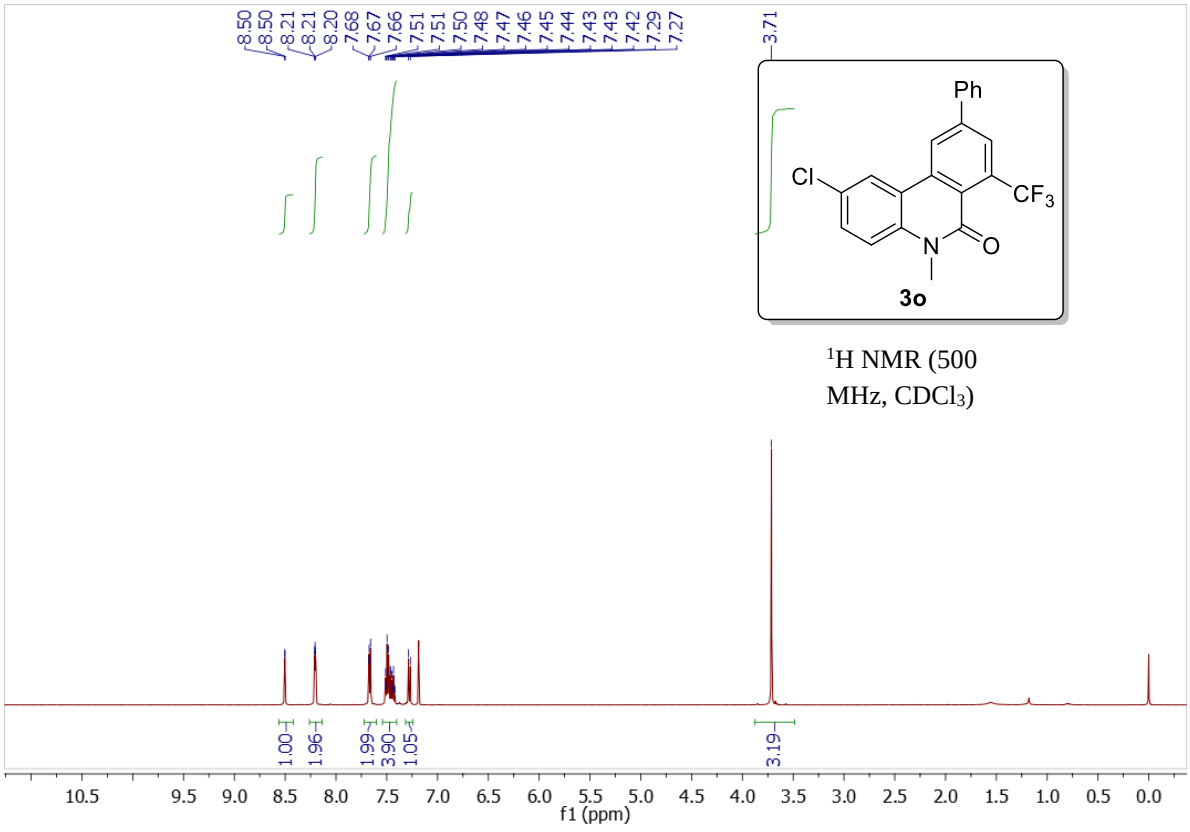
^{1}H NMR (400 MHz, $CDCl_3$)



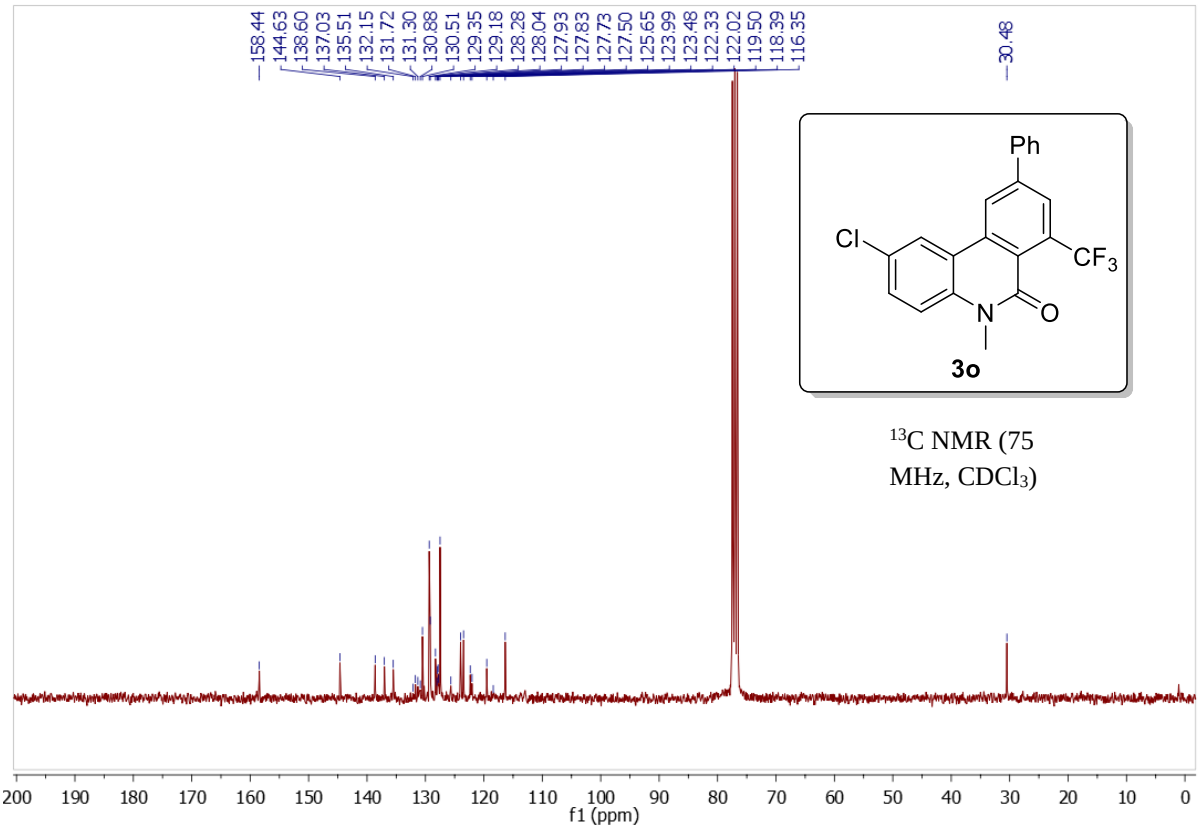
^{13}C NMR (101 MHz, $CDCl_3$)



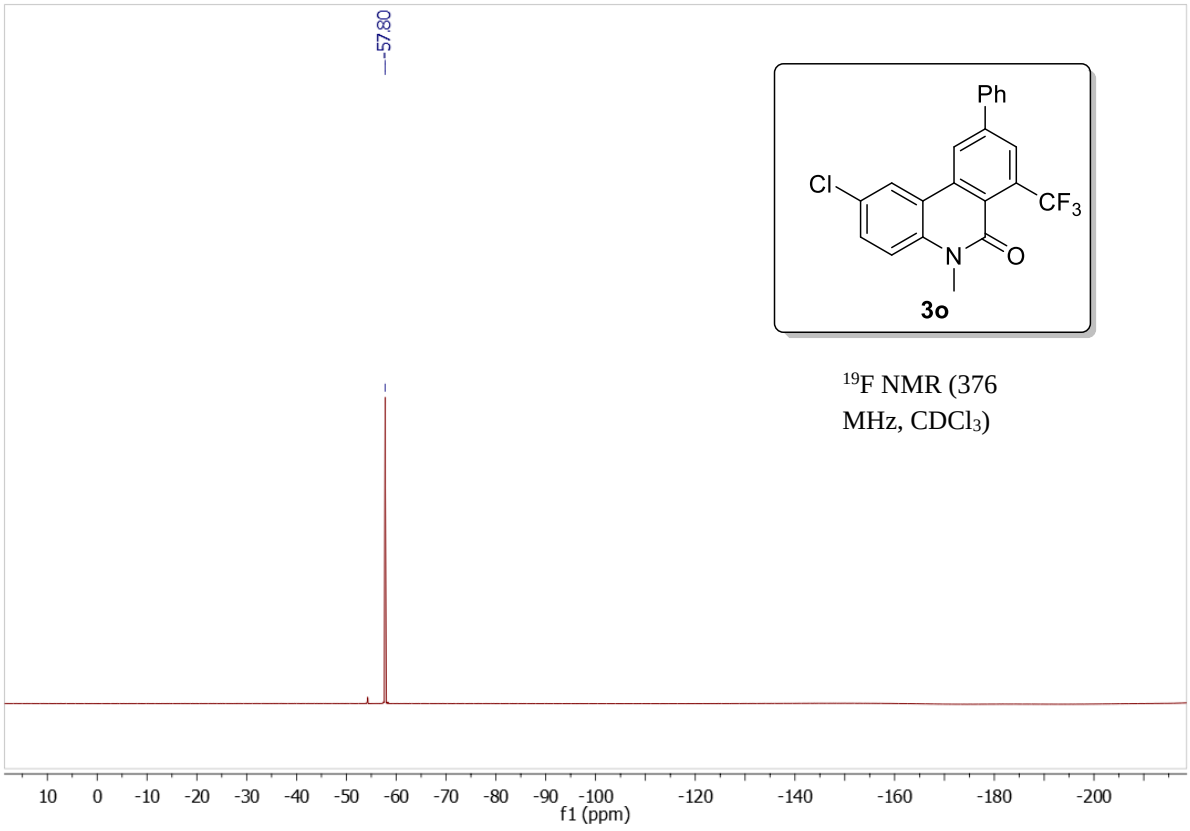
^{19}F NMR (376 MHz, $CDCl_3$)



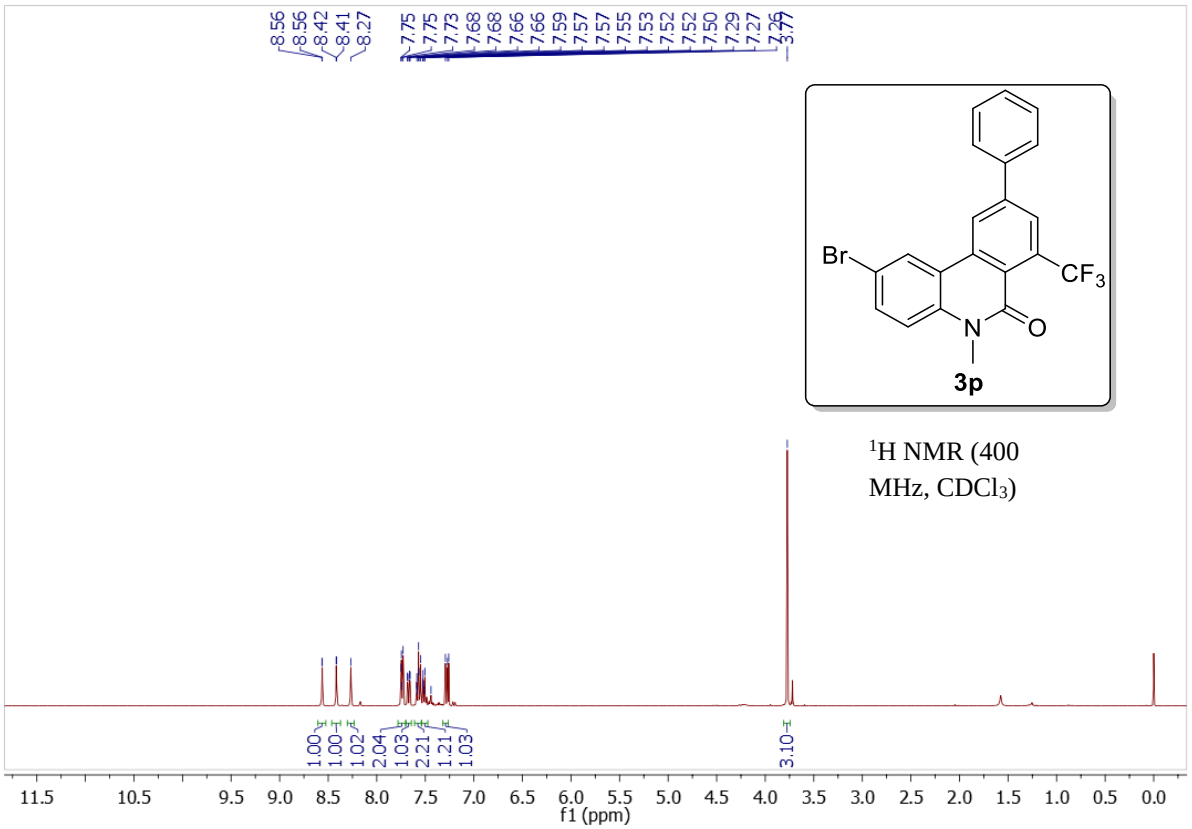
^{1}H NMR (500 MHz, $CDCl_3$)



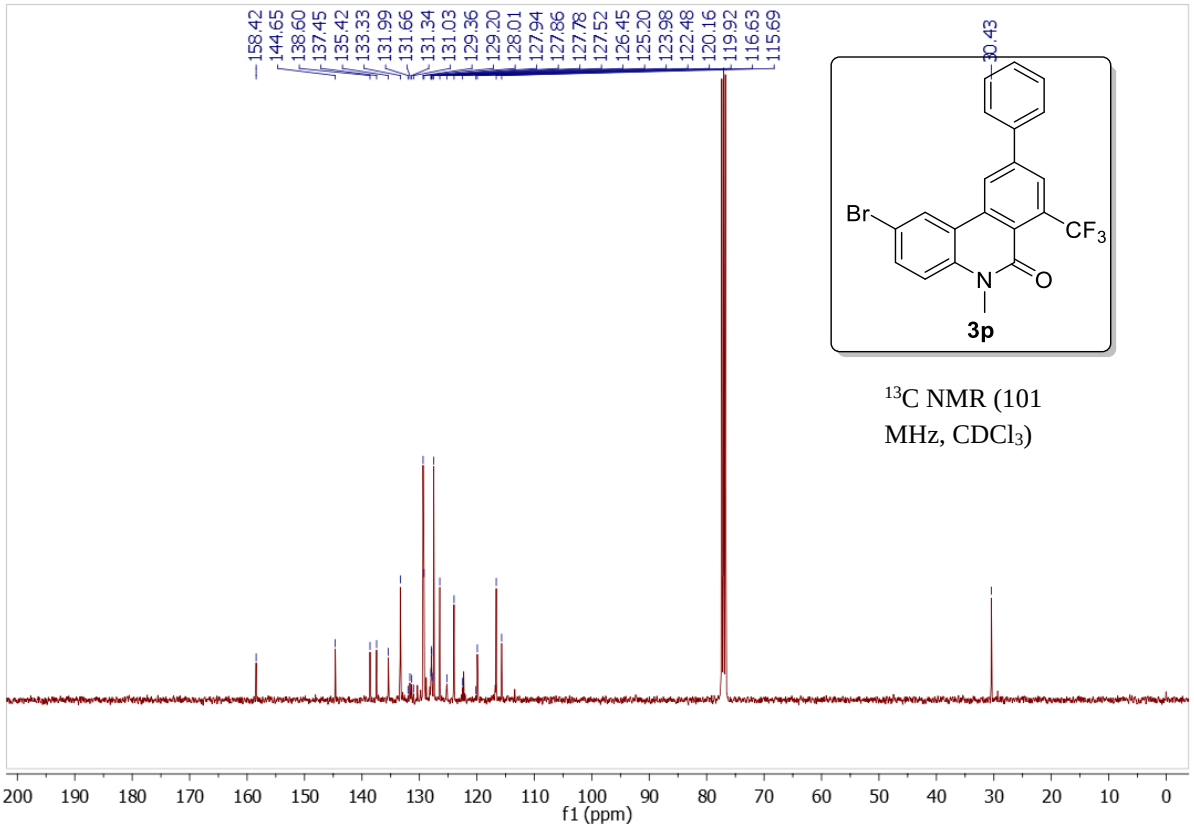
^{13}C NMR (75 MHz, $CDCl_3$)



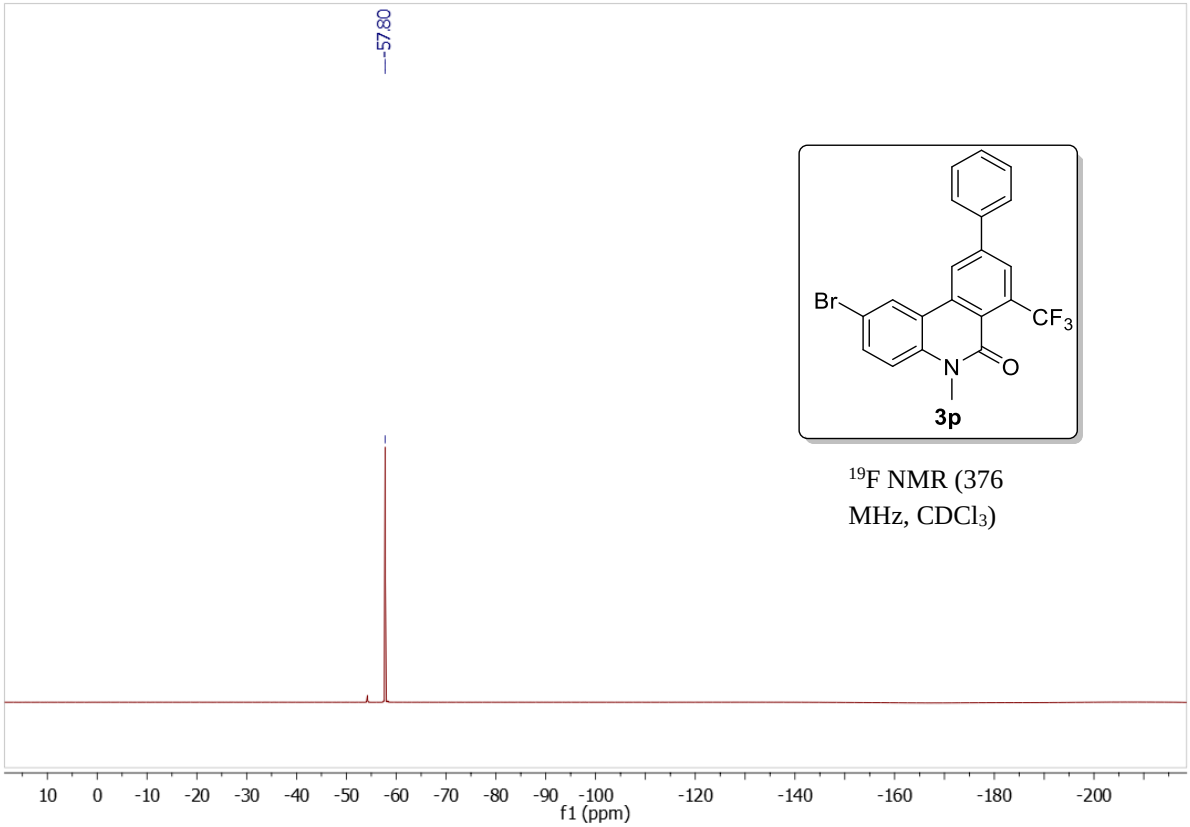
^{19}F NMR (376 MHz, $CDCl_3$)



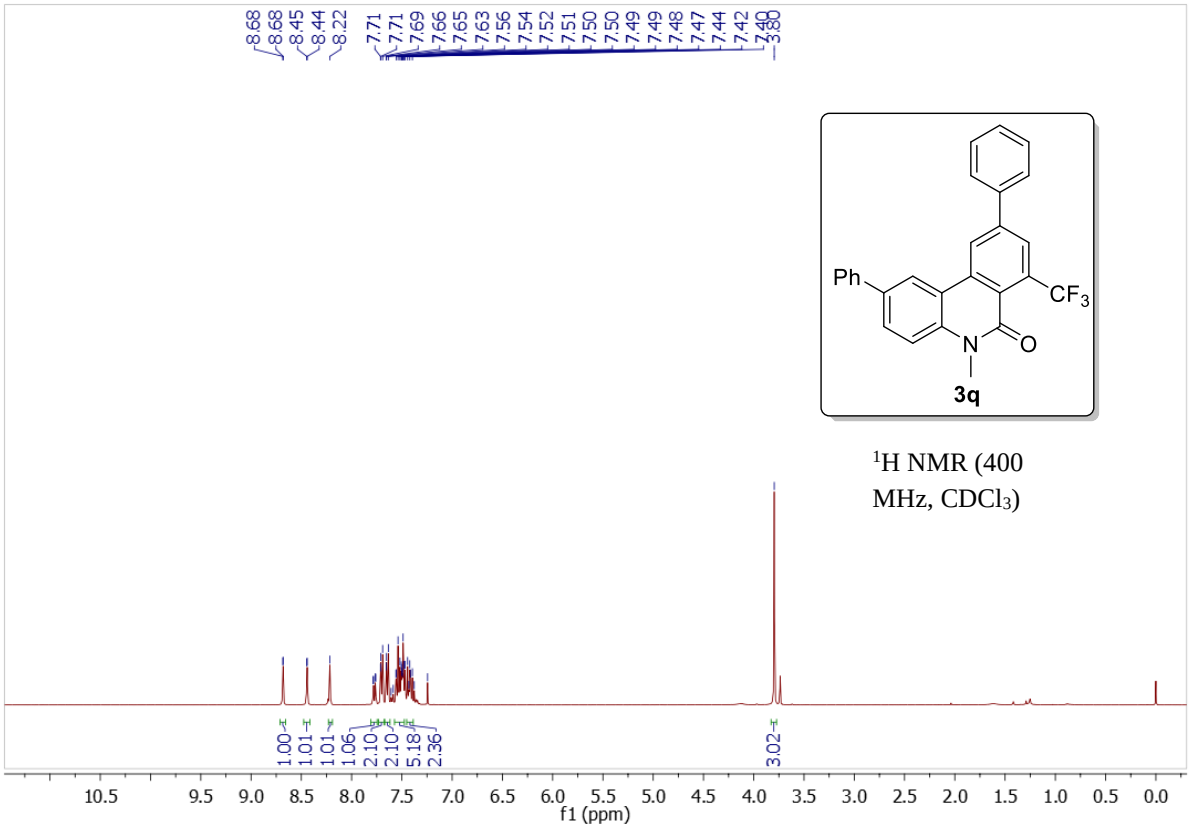
^{1}H NMR (400 MHz, $CDCl_3$)



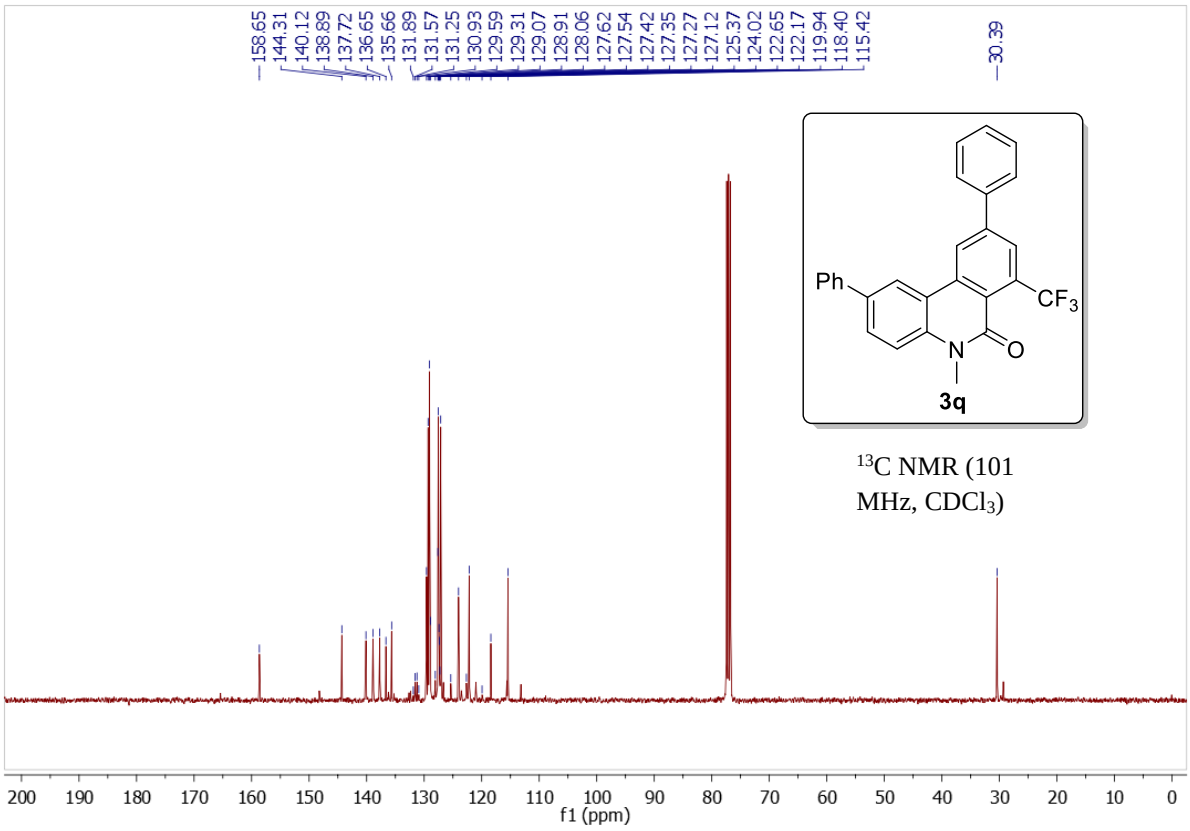
^{13}C NMR (101 MHz, $CDCl_3$)



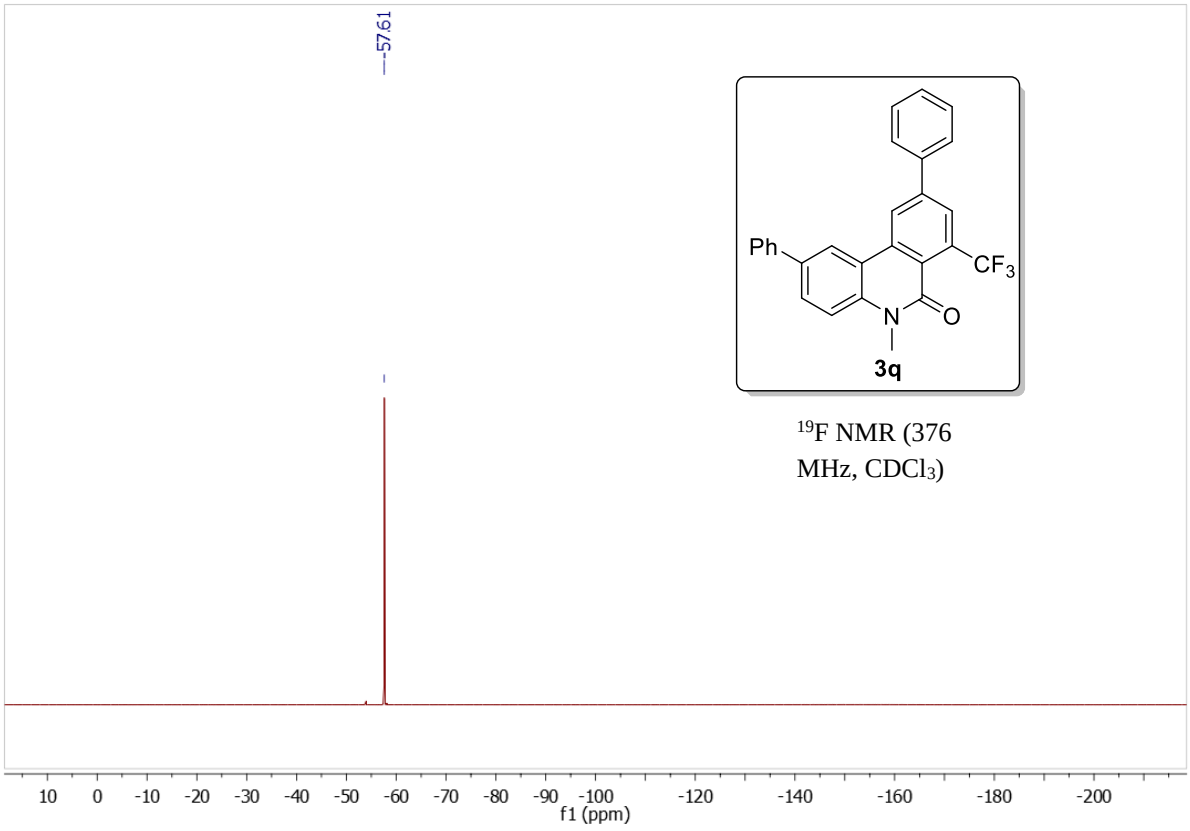
^{19}F NMR (376 MHz, $CDCl_3$)



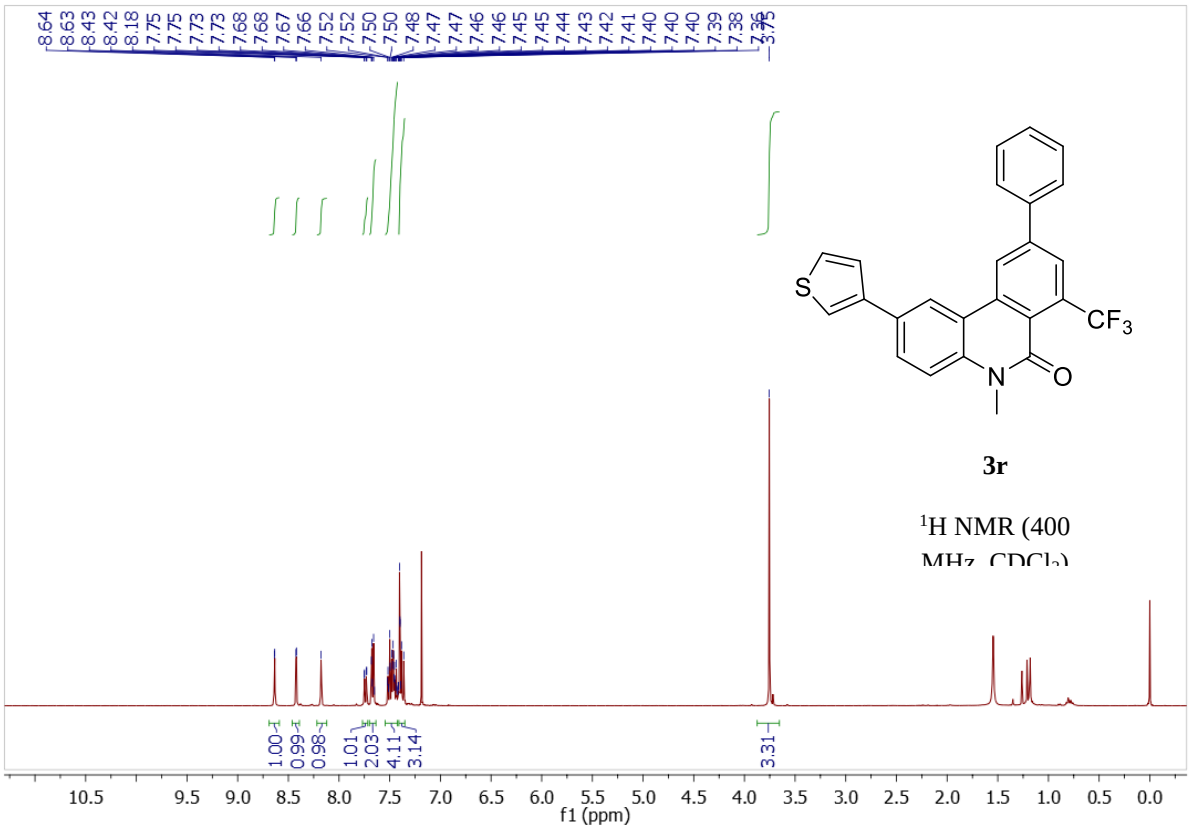
^{1}H NMR (400 MHz, $CDCl_3$)



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

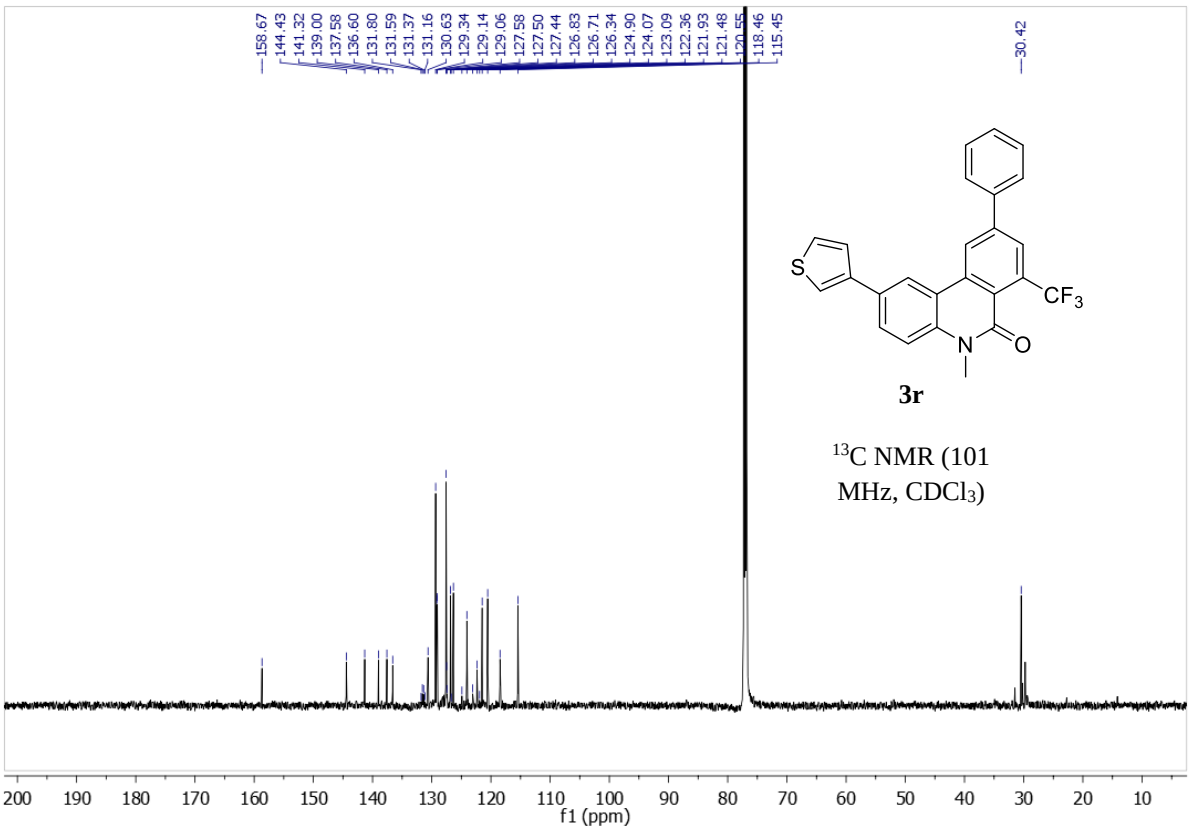


^{19}F NMR (376 MHz, $CDCl_3$)



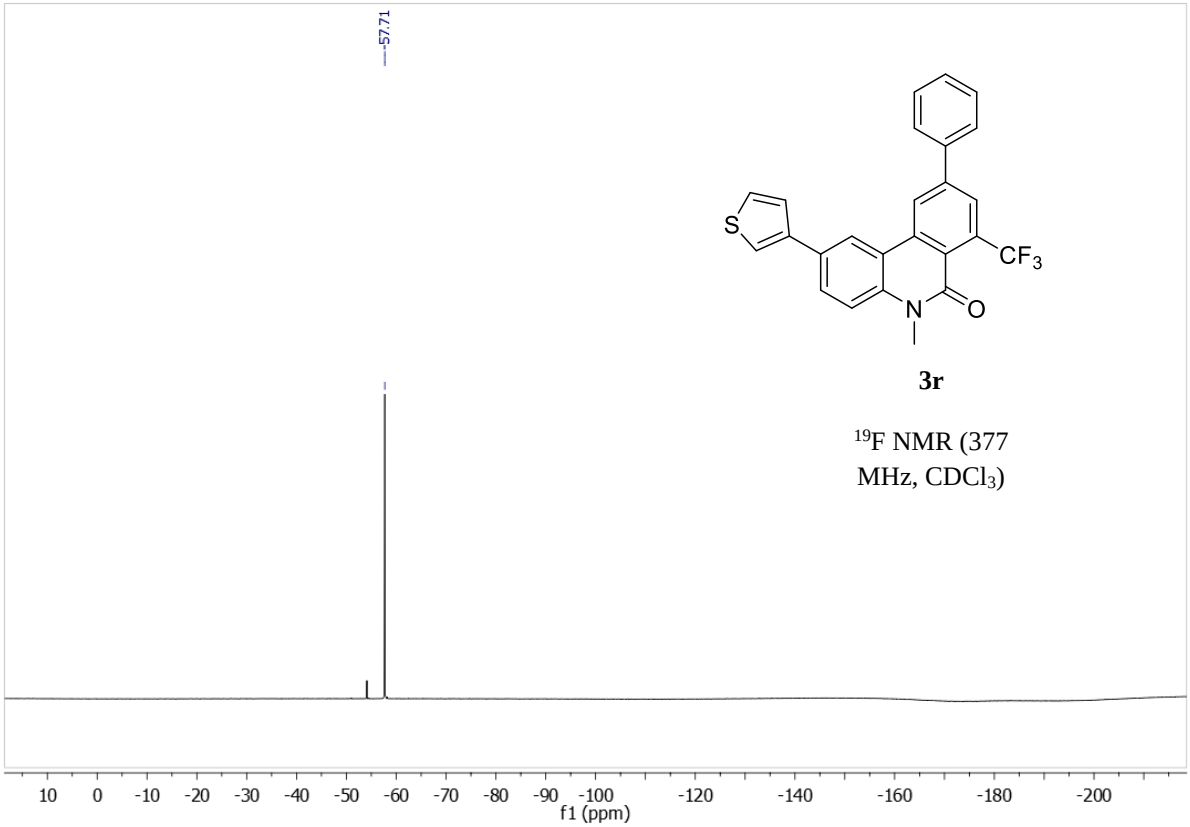
3r

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



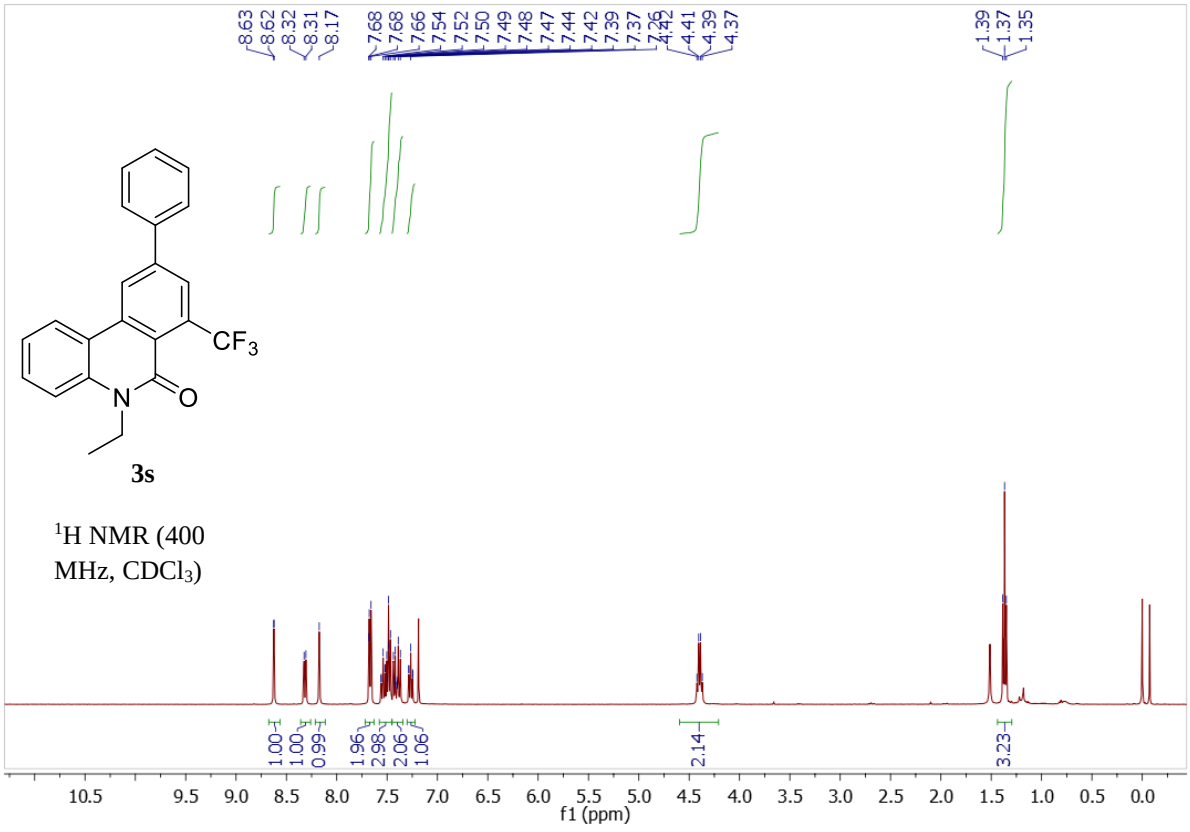
3r

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



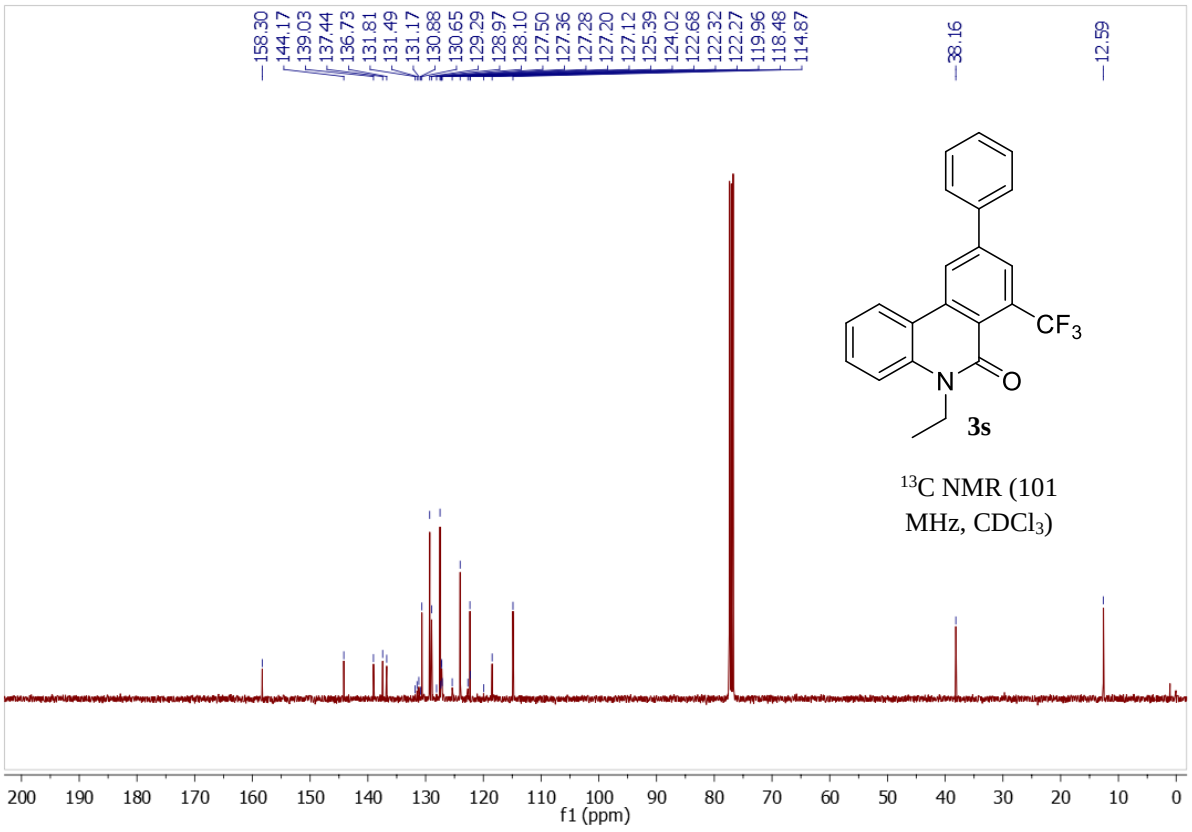
3r

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



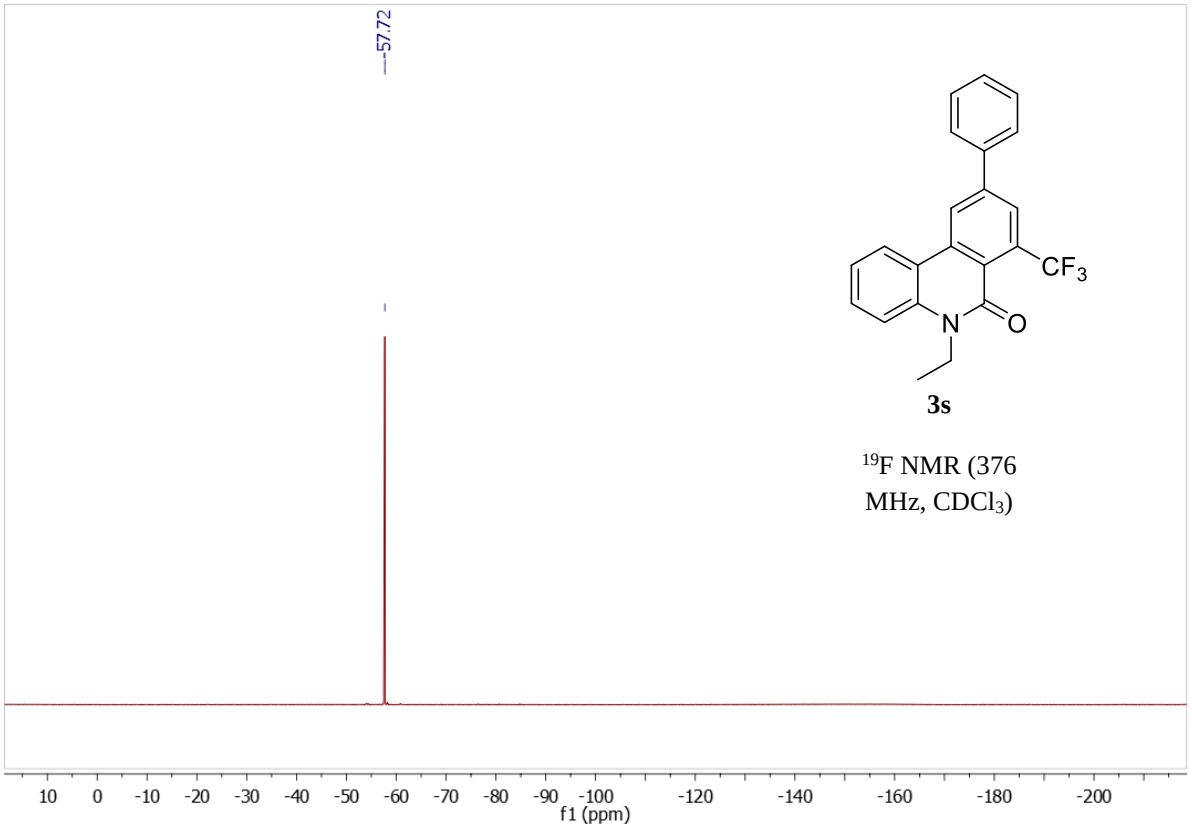
3s

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



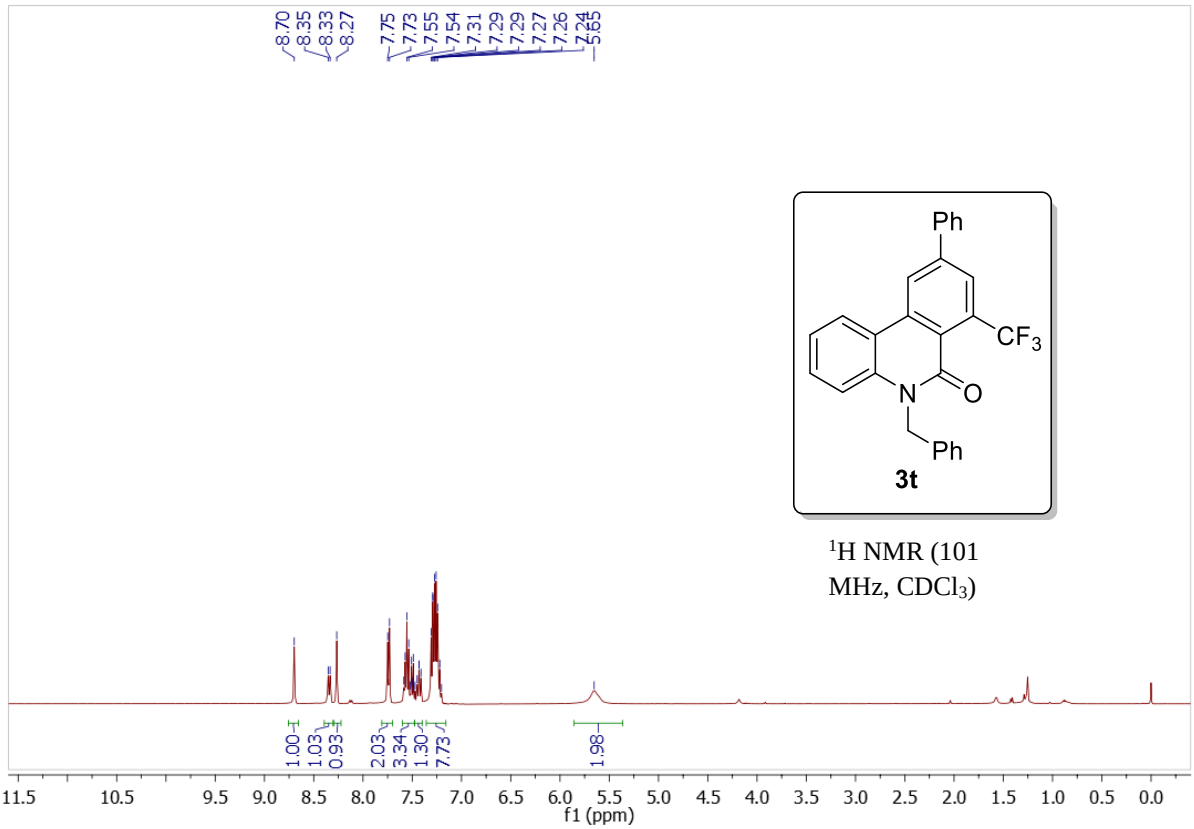
3s

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

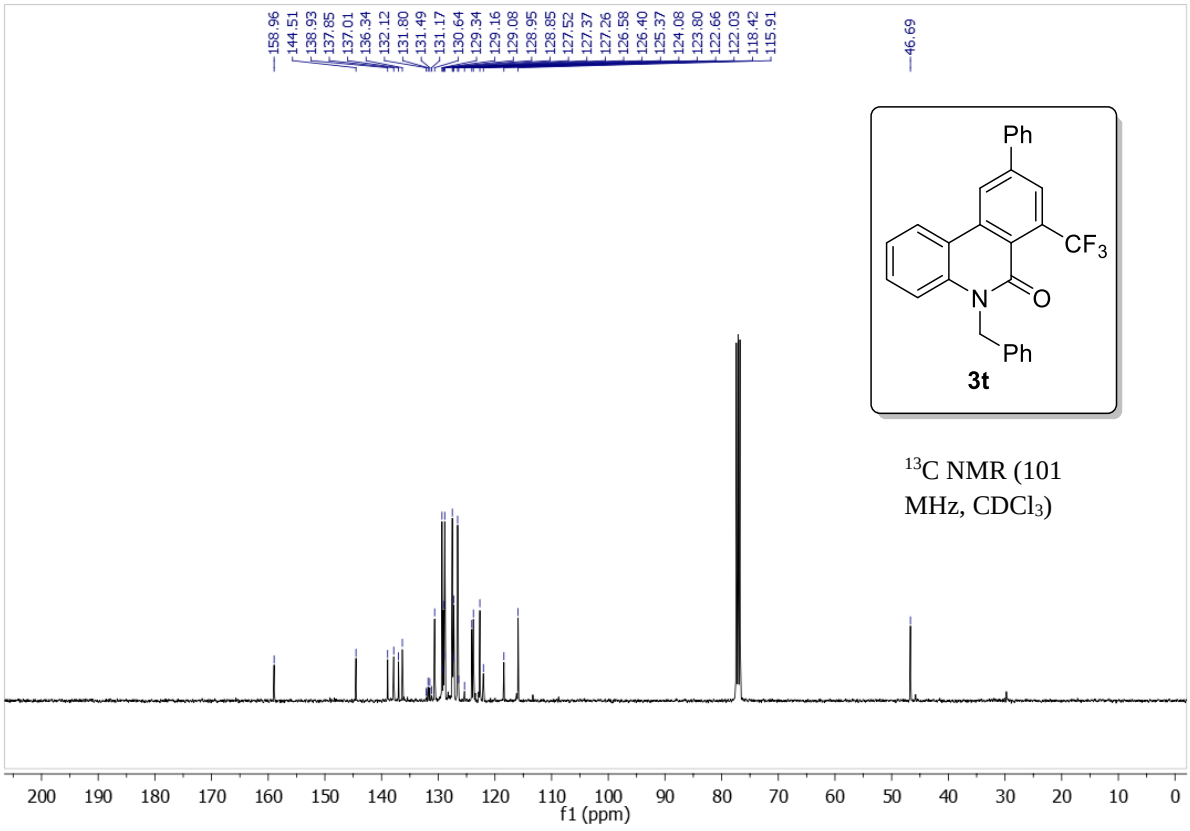


3s

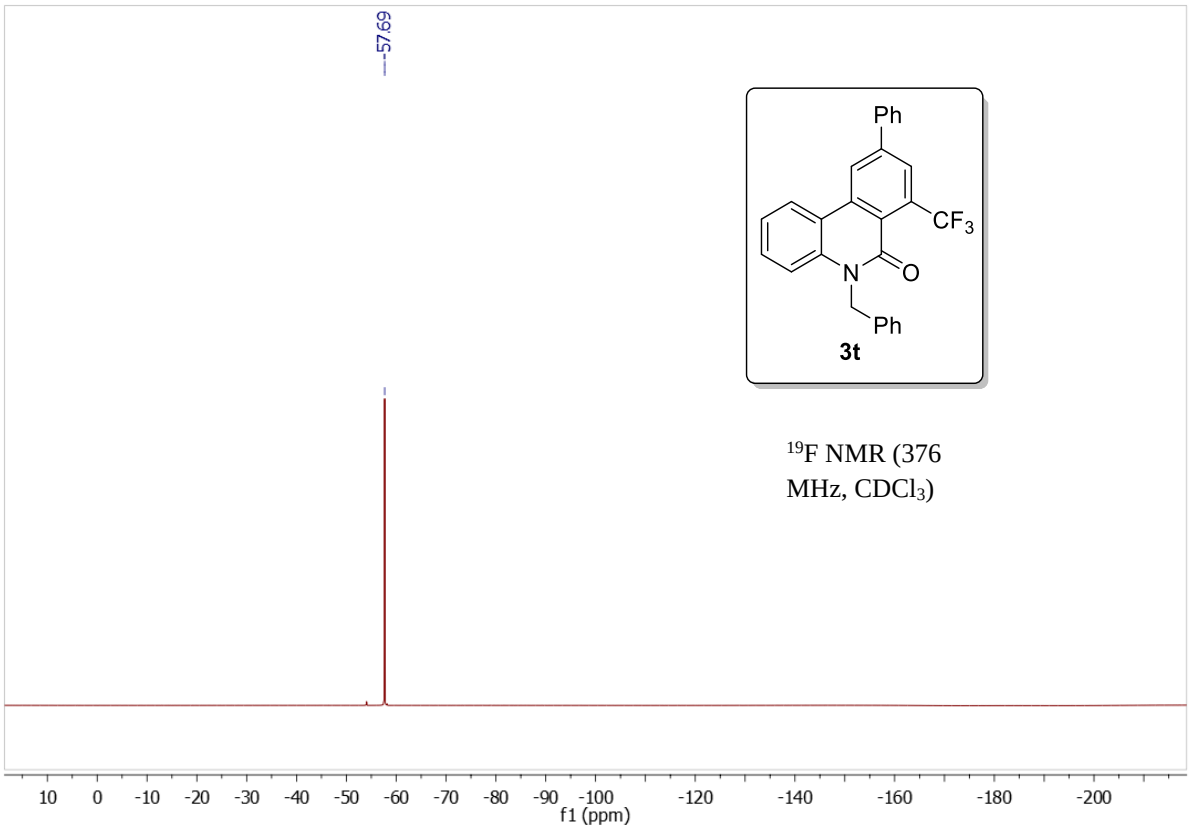
^{19}F NMR (376 MHz, $CDCl_3$)



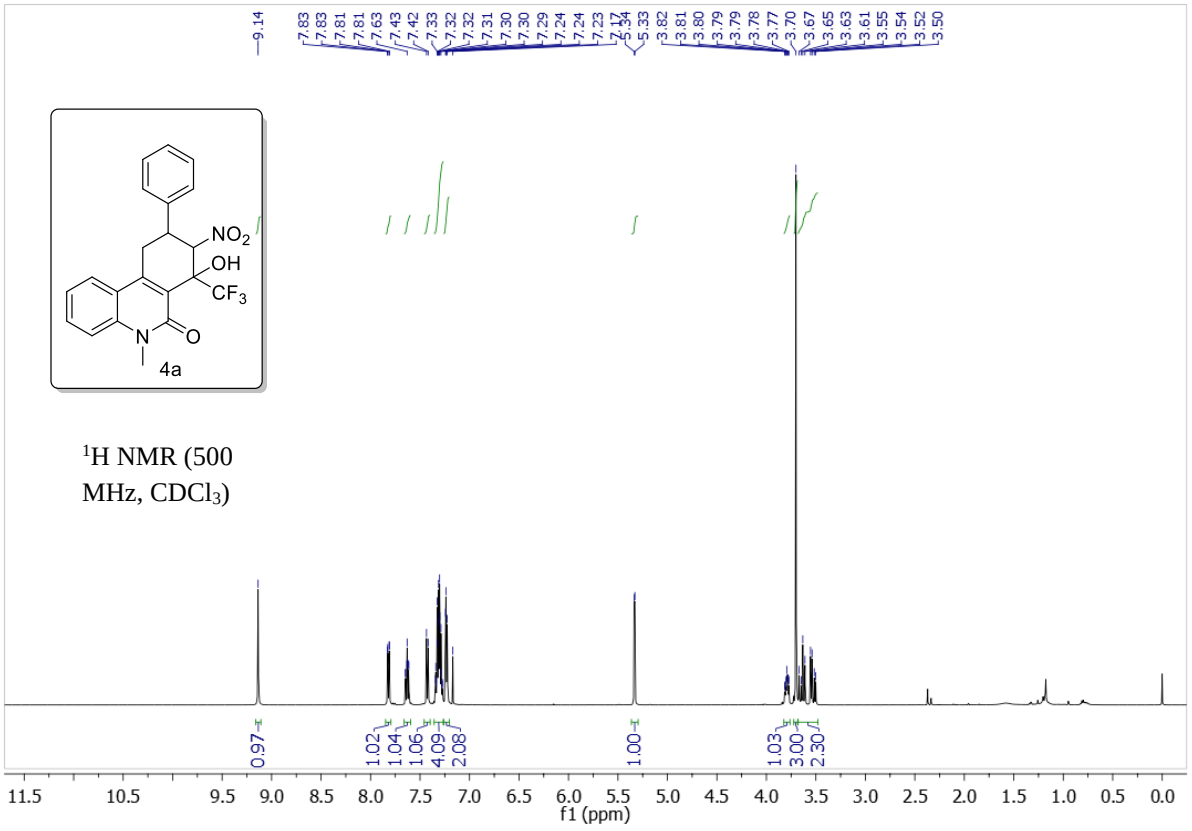
^{1}H NMR (101 MHz, $CDCl_3$)



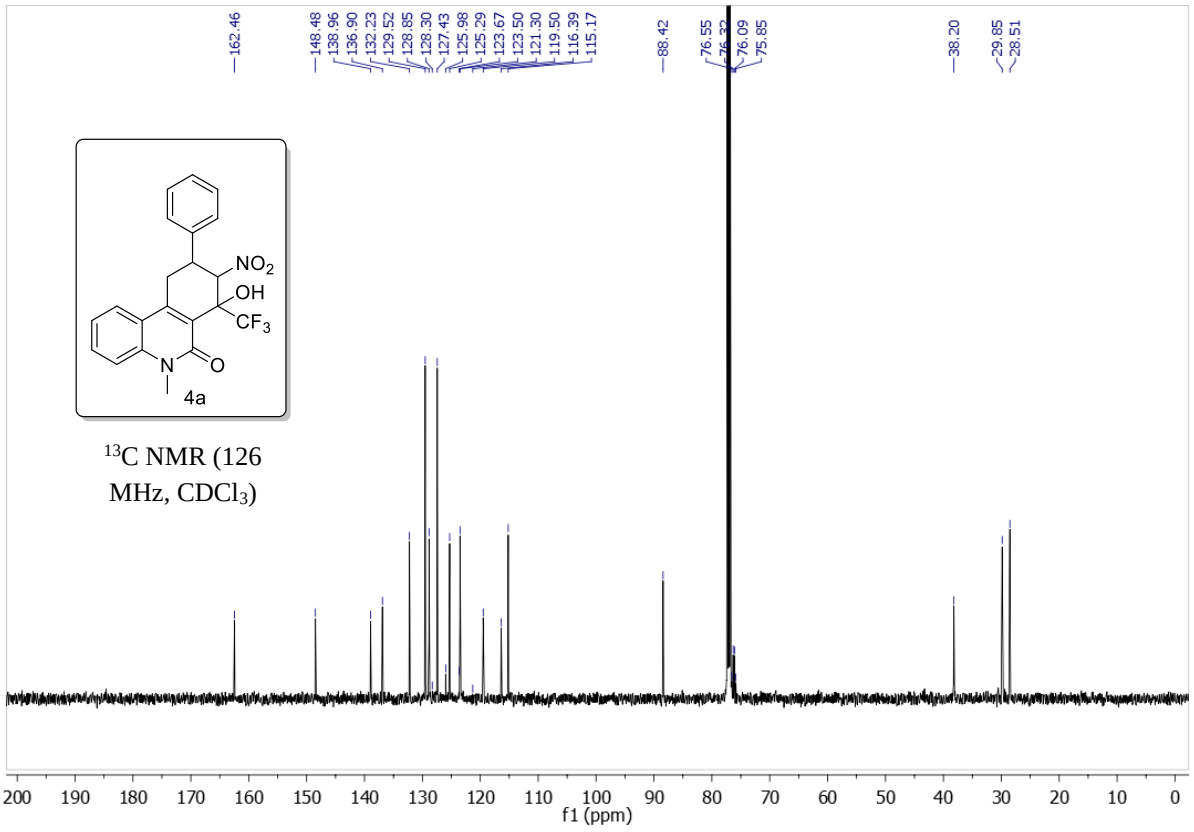
^{13}C NMR (101 MHz, $CDCl_3$)



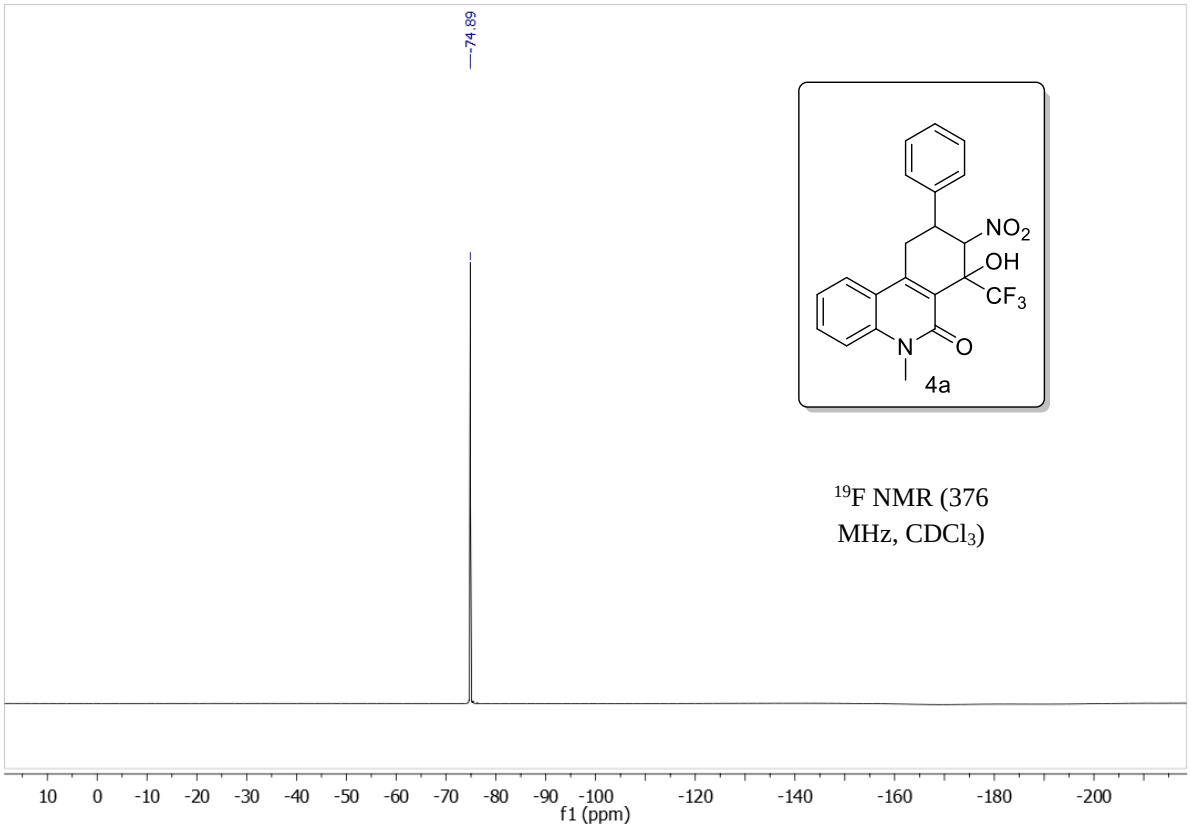
^{19}F NMR (376 MHz, $CDCl_3$)



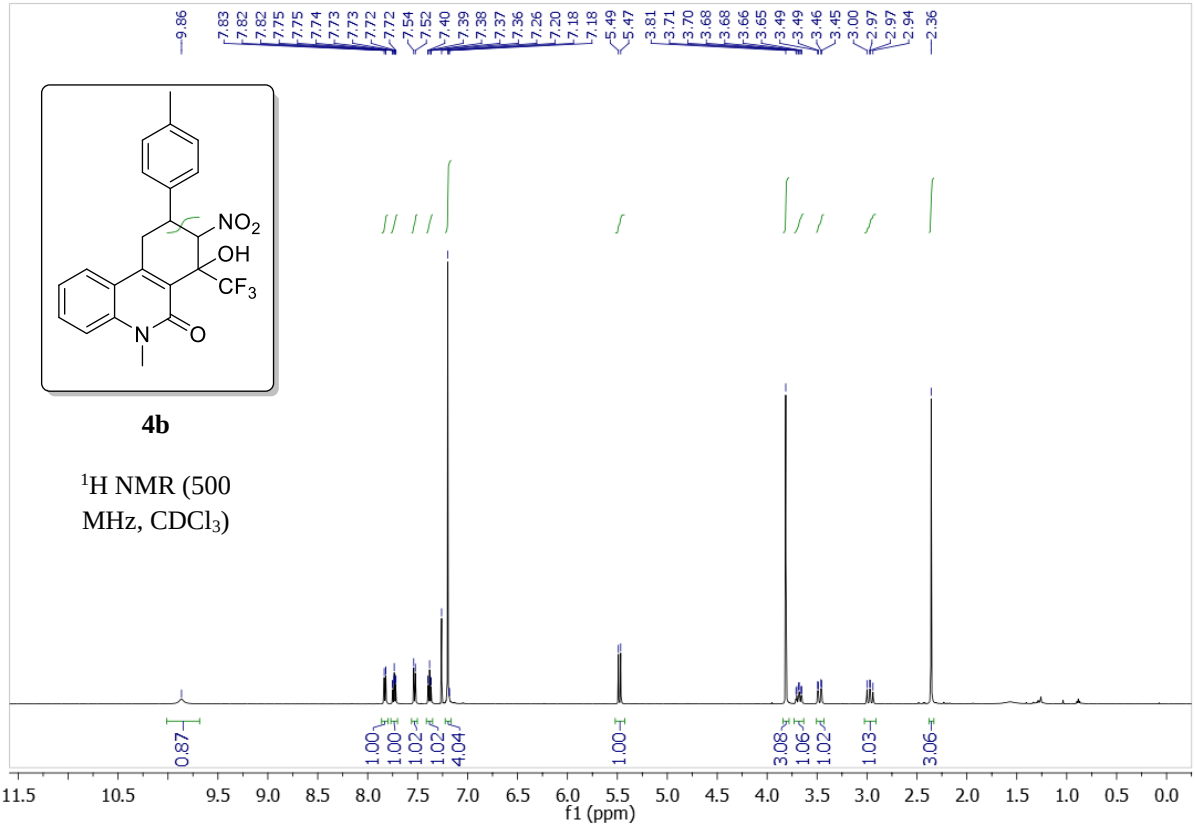
^{1}H NMR (500 MHz, $CDCl_3$)



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

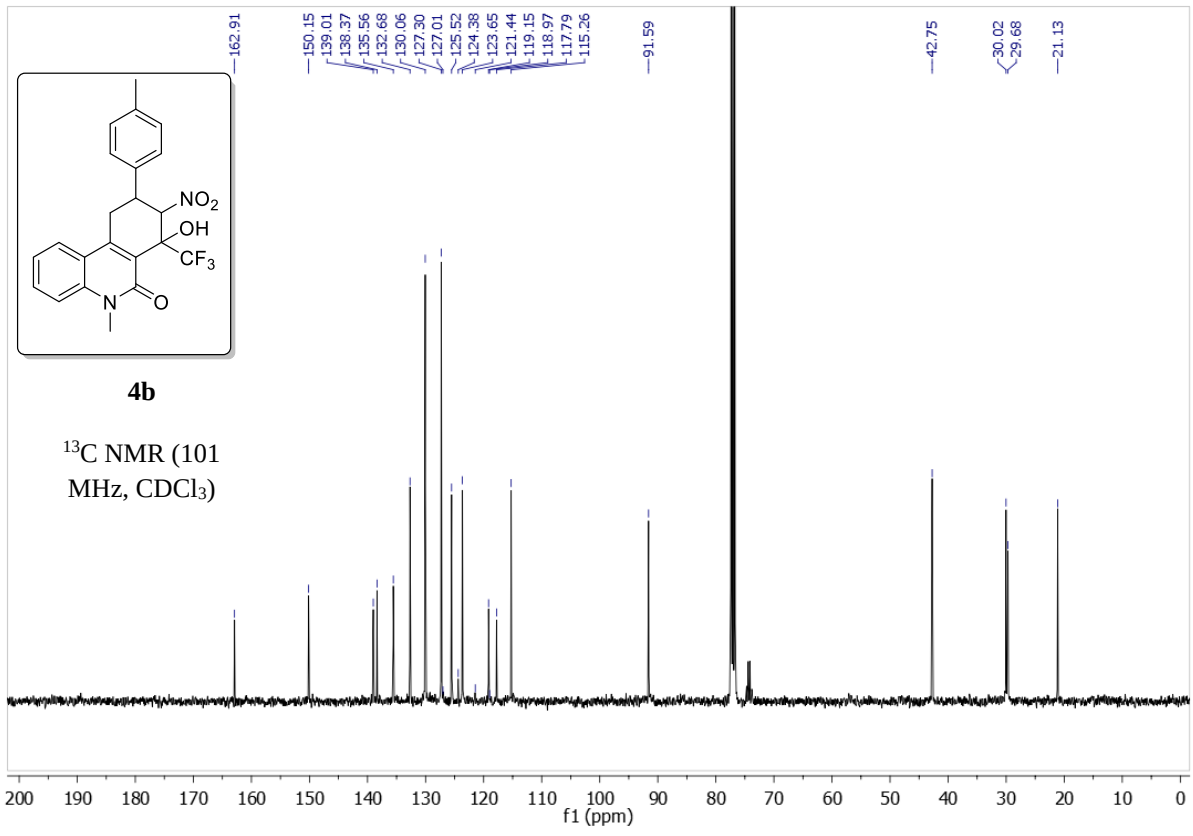


^{19}F NMR (376 MHz, $CDCl_3$)



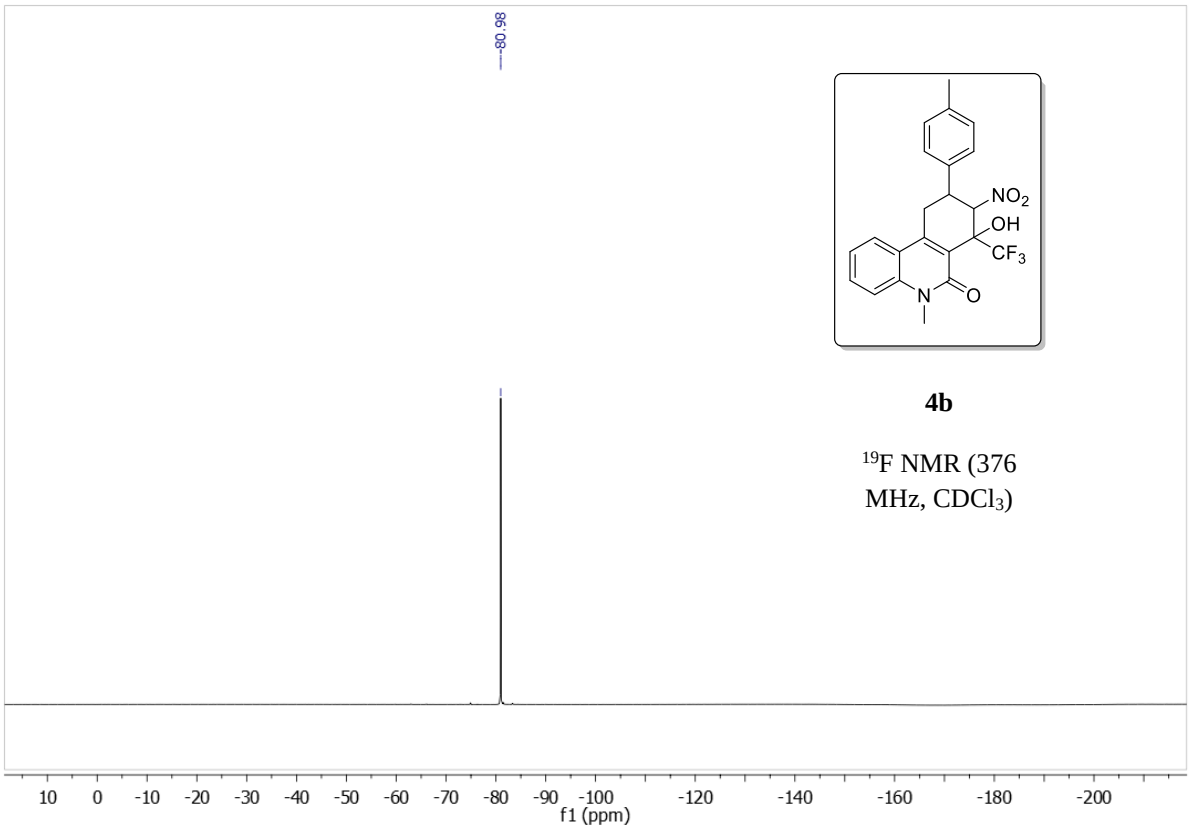
4b

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



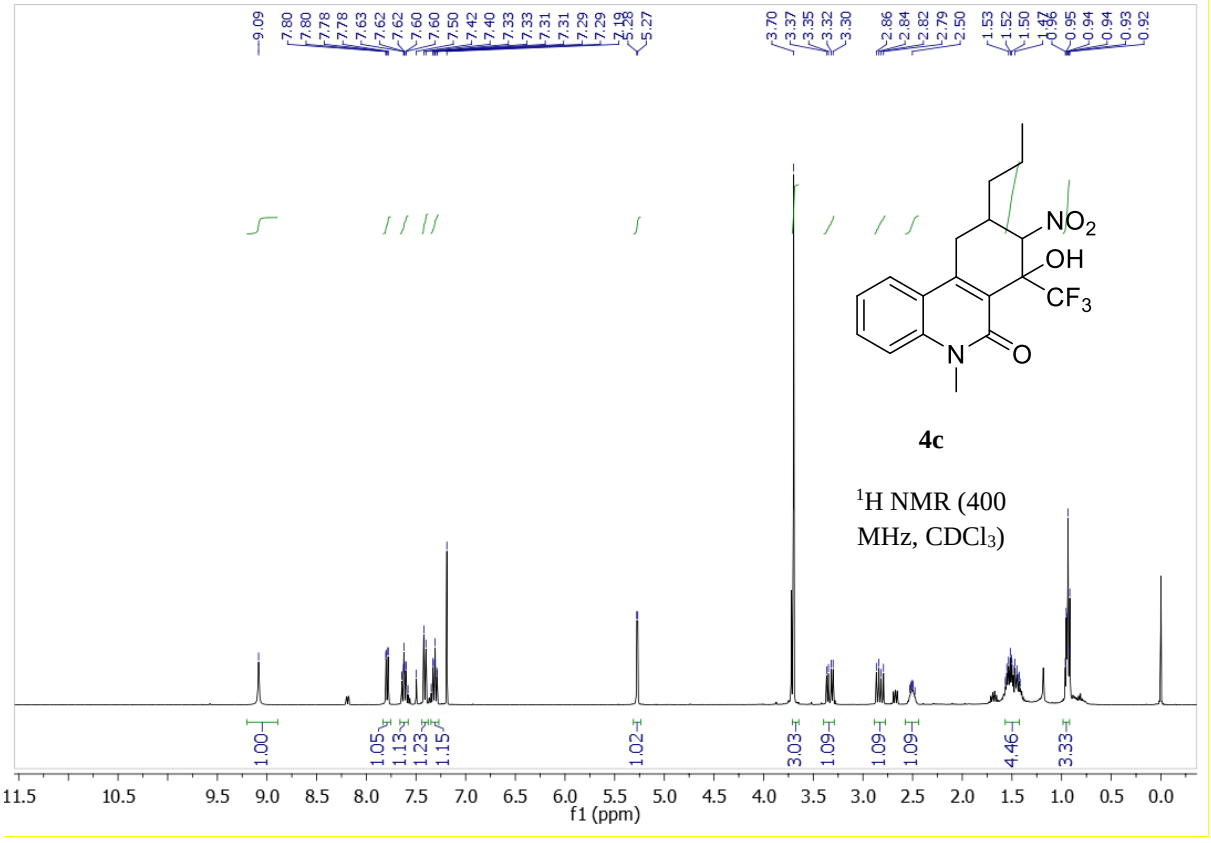
4b

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



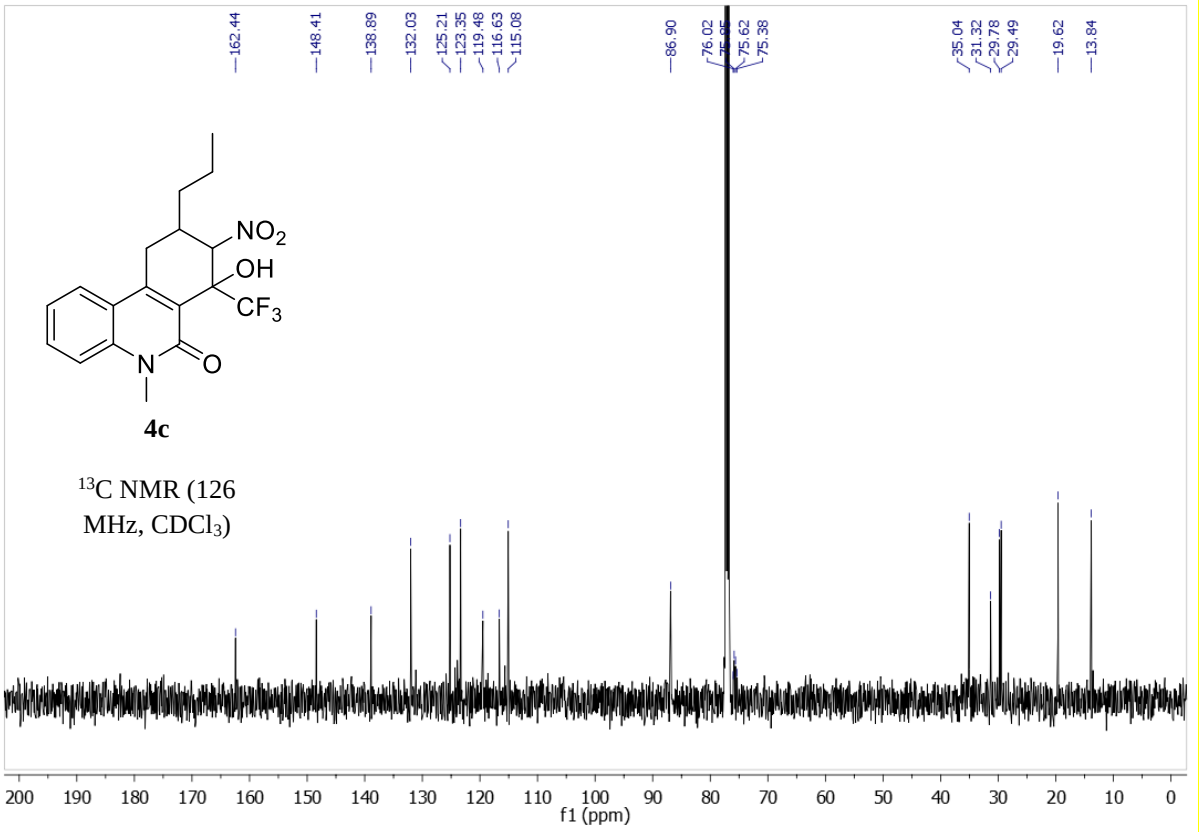
4b

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



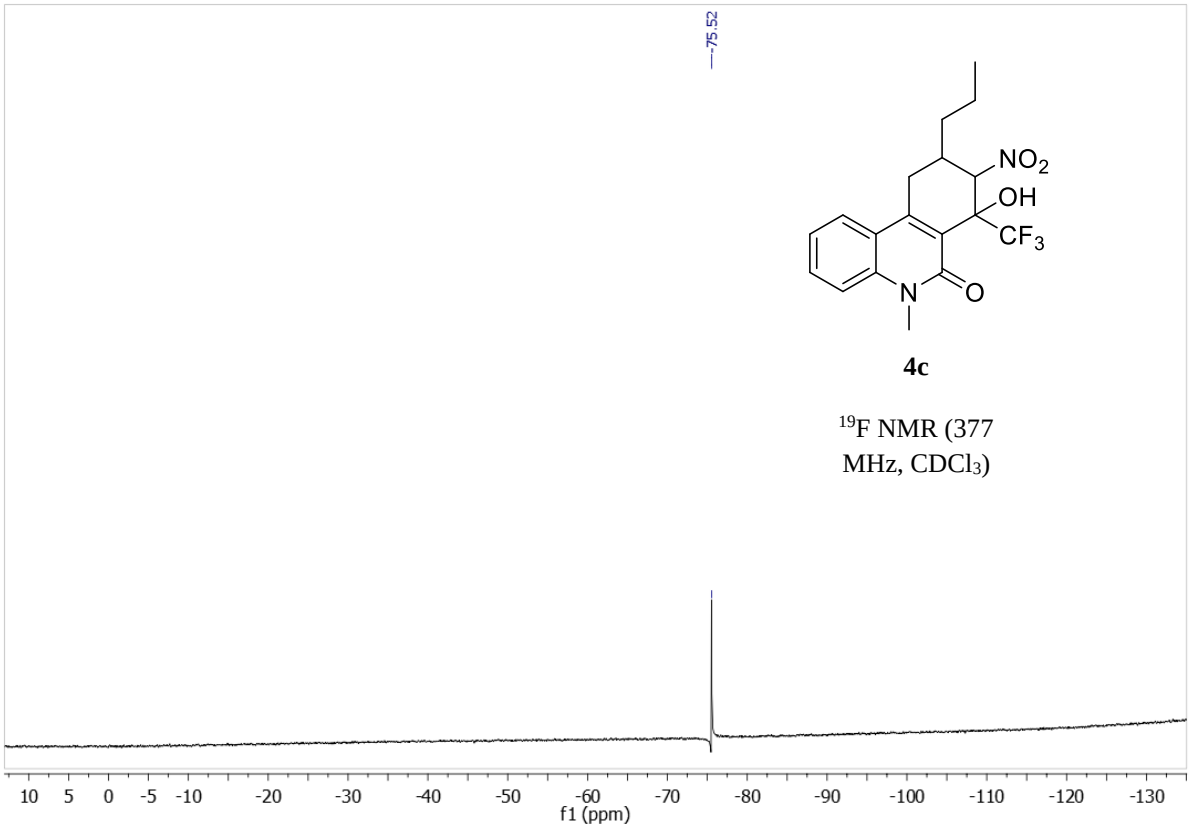
4c

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



4c

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



4c

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