Electronic Supplementary Information

Palladium-catalyzed ortho-vinylation of *β*-naphthols with *α*-trifluoromethyl allyl carbonates: One-pot access to naphtho[2,1-*b*]furans

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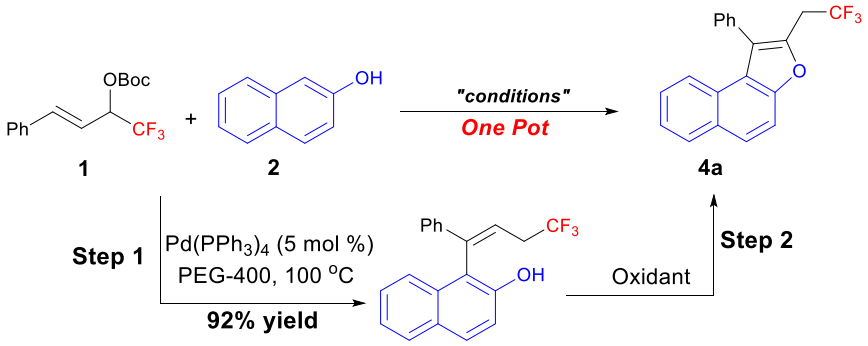
1. General information:

All the reactions were performed in oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under 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 carried out 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 $CDCl_3$ and DMSO-d_6 on 500 MHz, 400 MHz and 300 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 ^1H 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^+, ESI^-, EI^+] were obtained by using either a TOF or a double focusing spectrometer.

2. Table S_1: Optimization of reaction condition for one pot synthesis of naphtho[2,1-*b*]furan[a]

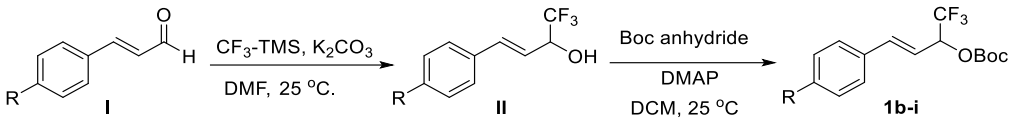


Entry	Reaction condition for Step-2		Yield (%)
	Oxidant (1 equiv)	Catalyst	4a
1	oxone	–	10
2	$Na_2S_2O_8$	–	41
3	$(NH_4)_2S_2O_8$	–	28
4	$K_2S_2O_8$	–	74
5	$K_2S_2O_8$	10 mol% Ag_2CO_3	36
6	$K_2S_2O_8$	10 mol% $AgNO_3$	25
7	Ag_2O	–	52
8[b]	$K_2S_2O_8$	–	–
9[c]	$K_2S_2O_8$	–	–

[a]Reaction conditions unless otherwise stated; **Step 1**: All the reactions were performed using 0.24 mmol of **1a** with 0.2 mmol of **2a** in 1 mL of PEG-400 with $Pd(PPh_3)_4$ (5 mol %) at 100 °C (oil bath temperature) for 10 h. **Step 2**: after confirming the formation of compound **3a** by TLC, reaction mixture was cooled to room temperature, then, oxidant and catalyst was added, and stirred at 80 °C. [b]Reaction at 40 °C. [c]Reaction at room temperature.

3. Experimental procedures and characterization data of Starting materials:

3.1. General procedure for synthesis of CF_3 allyl carbonates 1 (Method A):

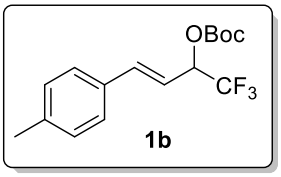


According to the literature procedure,[1] in a flame dried 100 mL round bottom flask, aldehyde **I** (10 mmol, 1.0 equiv) and $TMSCF_3$ (20 mmol, 2.0 equiv) was suspended in anhydrous DMF (20 mL). To this solution dry K_2CO_3 (10 mol %, 0.1 equiv) was added and the mixture was stirred vigorously at room temperature under N_2 atmosphere. Completion of the reaction was monitored by TLC. To this reaction mixture, aqueous HCl solution (2 M, 4 mL) was added and stirred for 3 h at room temperature. The reaction mixture was then extracted with ethyl acetate (3 × 30 mL). Combined organic layers were finally washed with brine solution, dried over anhydrous Na_2SO_4, and then solvent was removed under reduced pressure. The crude product **II** was further utilized without column chromatography.

To the stirred solution of crude alcohol **II** (10 mmol, 1 equiv) in DCM (10 mL) were added Boc-anhydride (12 mmol, 1.2 equiv) and DMAP (0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the pure CF_3-allyl carbonates (**1b -1i)**. The characterization data of **1** are summarized below.

Starting materials **1a** and **1j** were reported in previous articles.[2]

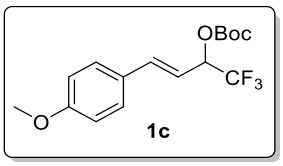
(*E*)-Tert-butyl (1,1,1-trifluoro-4-(p-tolyl) but-3-en-2-yl) carbonate(1b):



Following the general procedure **A**, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-ol (2.2 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and

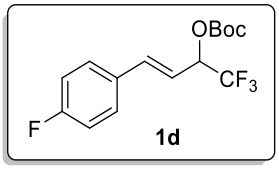
stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the (*E*)-Tert-butyl (1,1,1-trifluoro-4-(*p*-tolyl) but-3-en-2-yl) carbonate **1b**, pale yellow solid, 2.53 g, 80% yield, R_f = 0.5 (hexane/ethyl acetate = 9.5:0.5); mp: 57–59 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 7.9 Hz, 1H), 5.57 (m, 1H), 2.35 (s, 3H), 1.51 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 139.3, 138.9, 132.4, 129.6, 127.2, 123.2 (q, *J* = 280.6 Hz), 116.2, 84.1, 74.2 (q, *J* = 33.6 Hz), 27.8, 21.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.68 (s, 3F); **IR(KBr)**: νmax = 2965, 1660, 1130 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{16}H_{19}O_3F_3$ $(M)^+$: 316.12863, found: 316.12736.

(*E*)-Tert-butyl (1,1,1-trifluoro-4-(4-methoxyphenyl) but-3-en-2-yl) carbonate (1c):



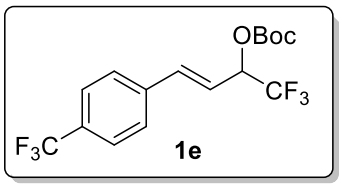
Following the general procedure **A**, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ol (2.3 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the (*E*)-tert-butyl (1,1,1-trifluoro-4-(4-methoxyphenyl) but-3-en-2-yl) carbonate **1c**, white solid, 2.72 g, 82% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 67–69 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.78 (m, 3H), 6.00 (dd, *J* = 15 .9, 8.1 Hz, 1H), 5.57 (m, 1H), 3.80 (s, 3H), 1.49 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 151.9, 138.6, 128.6, 127.9, 123.3 (q, *J* = 280.6 Hz), 114.8, 114.2, 84.0, 74.3 (q, *J* = 33.5 Hz), 55.4, 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.71 (s, 3F); **IR (KBr)**: νmax = 2970, 1665, 1143 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{16}H_{19}O_4F_3$ $(M)^+$: 332.12354, found: 332.12505.

(*E*)-Tert-butyl (1,1,1-trifluoro-4-(4-fluorophenyl) but-3-en-2-yl) carbonate (1d):



Following the general procedure, A, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-ol (2.2 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the (*E*)-tert-butyl (1,1,1-trifluoro-4-(4-fluorophenyl) but-3-en-2-yl) carbonate **1d**, white solid, 2.74 g, 85% yield, R_f = 0.5 (hexane/ethyl acetate = 9.5:0.5); mp: 55–57 ^{o}C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.63 – 5.52 (m, 1H), 1.51 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 249.1 Hz), 151.9, 137.6, 131.3, 128.9 (d, *J* = 21.8 Hz), 123.7 (q, *J* = 280.6 Hz), 117.1, 115.9 (d, *J* = 8.3 Hz), 84.2, 73.9 (q, *J* = 33.6 Hz), 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.65 (s, 3F), –111.94 (s, F). **IR (KBr)**: νmax = 2968, 1670, 1150 cm^{-1}; **HRMS (EI)$^{+}$**: *m/z* calcd for $C_{11}H_8O_3F_4$ $(M–56)^{+}$: 264.04096, found: 264.03985.

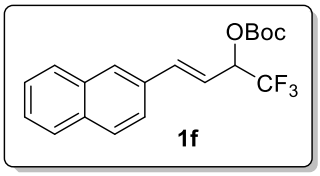
(*E*)-Tert-butyl (1,1,1-trifluoro-4-(4-(trifluoromethyl) phenyl) but-3-en-2yl carbonate (1e):



Following the general procedure **A**, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-ol (2.7 gm, 10 mmol, 1equiv) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the (*E*)-tert-butyl (1,1,1-trifluoro-4-(4-(trifluoromethyl) phenyl) but-3-en-2yl carbonate **1e**, off-white solid, 2.82 g, 76% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 74–76 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 7.4 Hz, 1H), 5.62 (m, 1H), 1.52 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ151.8, 138.6, 137.0, 130.9 (q, *J* = 32.5 Hz), 127.4, 125.9, 124.08 (q, *J* = 271.9 Hz), 123.04 (q, *J* = 280.9 Hz), 120.1, 84.5, 73.54 (q, *J* = 33.7 Hz), 27.8; **^{19}F NMR**

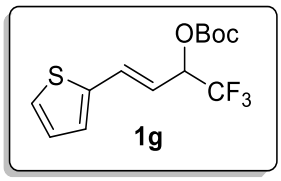
(377 MHz, $CDCl_3$) δ –76.16 (s, 3F), –76.59 (s, 3F). **IR (KBr)**: νmax = 2970, 1650, 1155 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{12}H_8O_3F_6$ $(M–56)^+$: 314.03776, found: 314.03825.

(*E*)-Tert-butyl (1,1,1-trifluoro-4-(naphthalen-2-yl) but-3-en-2-yl) carbonate (1f):



Following the general procedure **A**, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-en-2-ol (2.5 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent to afford the (*E*)-tert-butyl (1,1,1-trifluoro-4-(naphthalen-2-yl) but-3-en-2-yl) carbonate **1f**, Pale yellow liquid, 2.82 g, 79% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.67 (d, *J* = 15.7 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.48 – 7.44 (m, 1H), 6.19 (dd, *J* = 15.7, 7.6 Hz, 1H), 5.75 – 5.68 (m, 1H), 1.54 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 136.4, 133.7, 132.9, 131.2, 129.4, 128.8, 126.7, 126.2, 125.6, 124.7, 123.6,123.2 (q, *J* = 280.9 Hz), 120.5, 84.3, 74.0 (q, *J* = 33.6 Hz), 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.50 (s, 3F); **IR (neat)**: νmax = 2972, 1653, 1158 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{19}H_{19}O_3F_3$ $(M)^+$: 352.12863, found: 352.13015.

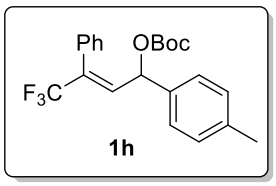
(*E*)-Tert-butyl (1,1,1-trifluoro-4-(thiophen-2-yl) but-3-en-2-yl) carbonate (1g):



Following the general procedure **A**, To the stirred solution of (*E*)-1,1,1-trifluoro-4-(thiophen-2-yl)but-3-en-2-ol (2.1 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified

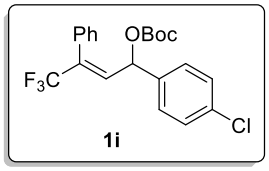
by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford (*E*)-tert-butyl (1,1,1-trifluoro-4-(thiophen-2-yl) but-3-en-2-yl) carbonate **1g**, colorless oil, 2.51 g, 83% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 7.01 (m, 2H), 5.95 (dd, *J* = 15.7, 7.8 Hz, 1H), 5.55 (m, 1H), 1.51 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 139.9, 131.8, 128.3, 127.7, 126.4, 123.1 (q, *J* = 280.7 Hz), 116.3, 84.2, 73.8 (q, *J* = 33.8 Hz), 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –76.65 (s, 3F). **IR (neat)**: νmax = 2971, 1648, 1152 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_9H_7O_3F_3S$ $(M–56)^+$: 252.00680, found: 252.00567.

(*E*)-Tert-butyl (4,4,4-trifluoro-3-phenyl-1-(p-tolyl) but-2-en-1-yl) carbonate (1h):



Following the general procedure **A**, To the stirred solution of (*E*)-4,4,4-trifluoro-3-phenyl-1-(p-tolyl)but-2-en-1-ol[3] (2.9 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the (*E*)-Tert-butyl (4,4,4-trifluoro-3-phenyl-1-(p-tolyl) but-2-en-1-yl) carbonate **1h**, colorless oil, 2.90 g, 83% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 3H), 7.25 – 7.21 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.65 (dd, *J* = 9.1, 1.5 Hz, 1H), 5.87 (d, *J* = 9.1 Hz, 1H), 2.33 (s, 3H), 1.43 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 138.7, 135.2, 133.5 (q, *J* = 5.2 Hz), 133.1 (q, *J* = 30.4 Hz), 131.1, 129.7, 129.6, 129.3, 128.7, 126.9, 123.1 (q, *J* = 273.5 Hz), 82.8, 74.9, 27.9, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –68.64 (s, 3F); **IR (neat):** νmax = 3063, 1648, 1168 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{18}H_{15}O_3F_3$ $(M–56)^+$: 336.09733, found: 336.09627**.**

(*E*)-Tert-butyl (1-(4-chlorophenyl) -4,4,4-trifluoro-3-phenylbut-2-en-1-yl) carbonate (1i):

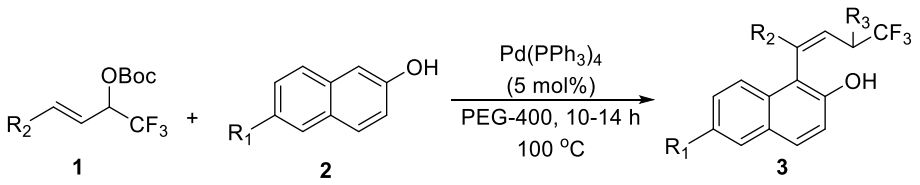


Following the general procedure **A**, To the stirred solution of (*E*)-1-(4-chlorophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol[3] (3.1 gm, 10 mmol) in DCM (10 mL) were added Boc-anhydride (2.6 gm, 12 mmol) and DMAP (122 mg, 0.1 equiv) at 0 °C, and the solution was warmed to room temperature and stirred for until completion of starting material monitored by TLC. Then, the reaction mixture was concentrated under reduced pressure and obtained residue was purified by using column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the (*E*)-Tert-butyl (1-(4-chlorophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-yl) carbonate **1i**, colorless oil, 3.21 g, 80% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.32 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 7.13 – 7.10 (m, 2H), 6.63 – 6.60 (m, 1H), 5.88 (d, *J* = 8.9 Hz, 1H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.1, 136.7, 134.8, 133.8 (q, *J* = 30.6 Hz), 132.9, 130.9, 129.5, 129.4, 129.2, 128.8, 128.4, 122.9 (q, *J* = 273.6 Hz), 83.2, 74.2, 27.7; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –68.52 (s, 3F); **IR (neat)**: νmax = 3068, 1647, 1166 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{17}H_{12}O_3F_3Cl$ $(M–56)^+$: 356.04271, found: 356.04413**.**

4. Experimental procedures and characterization data of compounds:

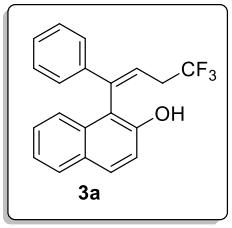
4.1 General procedure for synthesis of CF_3-(*Z*)-propenylnaphthols 3 (Method B):

General reaction:



To a stirred solution of CF_3-allyl carbonate **1** (0.24 mmol) in 1 mL of PEG-400 was added *β*-naphthol **2** (0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10–14 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 CF_3-propenyl *β*-naphthols **3**. The characterization data of **3** are summarized below.

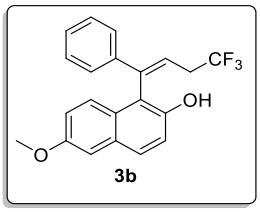
(*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3a):



3a

Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3a**, off-white solid, 72 mg, 92% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 99–101 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.50 – 7.46 (m, 1H), 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 3H), 7.25 (d, *J* = 4.3 Hz, 1H), 6.68 (t, *J* = 7.1 Hz, 1H), 5.22 (s, 1H), 2.81 – 2.69 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 139.8, 138.3, 132.3, 130.4, 129.1, 128.9, 128.7, 128.3, 127.1, 126.3,125.9 (q, *J* = 276.9 Hz), 124.1, 123.8, 121.5, 117.5, 116.5, 34.9 (q, *J* = 29.8 Hz,); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.55 (s, 3F**)**; **IR (KBr)**: νmax = 3546, 3022, 2401, 1214, 751 cm^{-1}; **HRMS (ESI)$^+$**: *m/z* calcd for $C_{20}H_{16}OF_3$ $(M+H)^+$: 329.1156, found: 329.1151.

(*Z*)-6-Methoxy-1-(4,4,4-trirfluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3b):

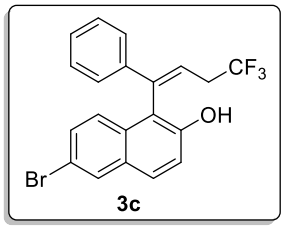


3b

Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2b** (34.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) as added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 11 h. 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 hexane/ethyl acetate is an eluant to obtain (*Z*)-6-Methoxy-1-(4,4,4-trirfluoro-

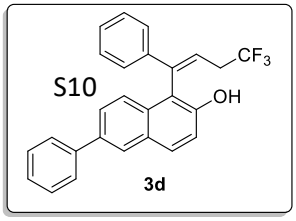
1-phenylbut-1-en-1-yl) naphthalen-2-ol **3b**, pale yellow oil, 76 mg, 89% yield; R_f = 0.4 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.30 – 7.27 (m, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 7.04 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.66 (t, *J* = 7.1 Hz, 1H), 5.03 (s, 1H), 3.89 (s, 3H), 2.80 – 2.67 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 148.7, 140.1, 138.5, 130.2, 129.1, 129.0, 128.9, 127.6, 126.4, 126.1 (q, *J* = 276.9 Hz), 125.8, 121.4, 119.7, 118.0, 116.9, 106.9, 55.5, 35.1 (q, *J* = 29.9 Hz); **^{19}FNMR** (376 MHz, $CDCl_3$) δ –65.44 (s, 3F); **IR (neat)**: νmax =3542, 3021, 2403, 1214, 750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{21}H_{16}O_2F_3$ $(M–H)^-$: 357.1102, found: 357.1102.

(*Z*)-6-Bromo-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3c):



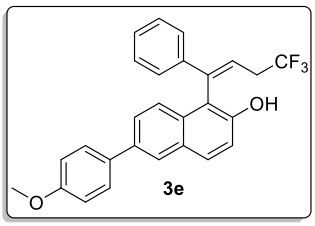
Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2c** (44.4 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. After 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 hexane/ethyl acetate is an eluant to obtain the **(***Z*)-6-Bromo-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3c**, brown oil, 81 mg, 83% yield, R_f = 0.6 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.41 (m, 1H), 7.36 – 7.33 (m, 1H), 7.31 – 7.27 (m, 6H), 6.68 (t, *J* = 7.1 Hz, 1H), 5.25 (s, 1H), 2.78 – 2.71 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 139.4, 138.0, 130.9, 130.4, 130.3, 129.5, 129.0, 128.9, 126.9, 126.3, 126.0, 125.9 (q, *J* = 277.0 Hz), 121.7, 118.7, 117.6, 116.0, 34.9 (q, *J* = 29.9 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.36 (s, 3F); **IR (neat)**: νmax =3542, 3021, 2403, 1214, 750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{20}H_{13}BrOF_3$$(M–H)^-$: 405.0102, found: 405.0106**.**

(*Z*)-6-phenyl-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3d):



Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2d** (44 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-6-phenyl-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3d**, colorless oil, 82 mg, 85% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.1, 1.0 Hz, 2H), 7.54 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.38 (t, *J* = 10.4, 4.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.24 – 7.16 (m, 4H), 6.63 (t, *J* = 7.1 Hz, 1H), 5.17 (s, 1H), 2.77 – 2.64 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 140.9, 139.9, 138.4, 136.7, 131.6, 130.8, 129.6, 129.1, 128.9, 128.9, 127.3, 126.9, 126.5, 126.3, 126.1 (q, *J* = 277.0 Hz), 124.8, 121.7, 121.7, 118.1, 116.6,35.1 (q, *J* = 30.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –65.41 (s, 3F); **IR (neat)**: νmax =3542, 3021, 2403, 1214, 750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{26}H_{18}OF_3$ $(M–H)^-$: 403.1312, found: 403.1316.

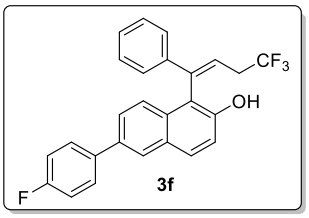
(*Z*)-6-(4-Methoxyphenyl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3e):



Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2e** (50 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C(oil bath temperature) for 14 h. 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

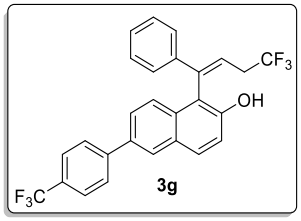
chromatography hexane/ethyl acetate is an eluant to obtain the (*Z*)-6-(4-Methoxyphenyl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3e**, pale-yellow oil, 83 mg, 80% yield, R_f = 0.4 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.29 (td, *J* = 6.0, 2.2 Hz, 4H), 7.02 – 6.97 (m, 2H), 6.70 (t, *J* = 7.1 Hz, 1H), 5.21 (s, 1H), 3.86 (s, 3H), 2.85 – 2.71 (m, 2H); **^{13}C NMR**(101 MHz, $CDCl_3$) δ 159.2, 150.1, 139.9, 138.4, 136.2, 133.4, 131.2, 130.5, 129.5, 128.9, 128.8, 128.2, 126.7, 126.4, 125.5, 124.8 (q, *J* = 273.9 Hz), 124.7, 121.5, 117.9, 116.4, 114.3, 55.4, 34.9 (q ,*J* = 30.1Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.40 (s, 3F); **IR (neat)**: νmax =3542, 3021, 2403, 1214, 750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{27}H_{20}O_2F_3$ $(M–H)^-$: 433.1415, found: 433.1414.

(*Z*)-6-(4-Fluorophenyl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3f):



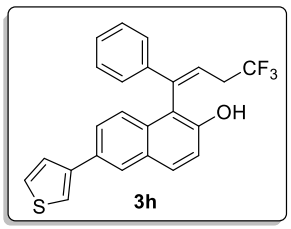
Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2f** (47.6 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. After 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 hexane/ethyl acetate is an eluant to obtain (*Z*)-6-(4-Fluorophenyl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3f,** brown oil, 79 mg, 78% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.54 (d, *J* = 9.6 Hz, 2H), 7.35 (s, 2H), 7.32 – 7.28 (m, 4H), 7.14 (t, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.0 Hz, 1H), 5.25 (s, 1H), 2.85 – 2.72 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (d, *J*= 246.3 Hz),150.5, 139.9, 138.4, 137.1, 135.7, 131.6, 130.7, 129.5, 129.1, 128.9 (d, *J* = 5.0 Hz),128.8, 126.8, 126.5, 126.18, 126.1 (q, *J* = 277.1 Hz), 124.9, 121.7, 118.2, 116.6,115.9 (d, *J* = 21.4 Hz), 35.1 (q, *J* = 29.9 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.38 (s, 3F), –115.78 (s, 1F); **IR (neat)**: νmax =3544, 3021, 2402, 1216, 746 cm^{-1} ; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{26}H_{17}OF_4$ $(M–H)^-$: 421.1216, found: 421.1223.

(*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl)-6-(4-(trifluoromethyl)phenyl)napthalen-2-ol (3g):



Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2g** (57.6 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. 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 hexane/ethyl acetate is an eluent to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl)-6-(4-(trifluoromethyl)phenyl)napthalen-2-ol **3g,** brown oil, 82 mg, 72% yield, R_f = 0.4 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.21 (m, 3H), 7.21 – 7.15 (m, 1H), 6.63 (t, *J* = 7.1 Hz, 1H), 5.24 (s, 1H), 2.78 – 2.63 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 144.5, 139.8, 138.4, 135.2, 132.1, 130.9, 129.5, 129.4, 129.1, 129.0, 127.6, 126.9, 126.6, 126.5,126.1 (q, *J* = 277.2 Hz), 125.9, 125.2,124.5 (q, *J* = 272.5 Hz), 121.8, 118.4, 116.7, 35.1 (q, *J* = 29.8 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.36 (s, 3F), –65.38 (s, 3F); **IR (KBr)**: νmax =3541, 3019, 2401, 1212, 743 cm^{-1}; **HRMS(ESI)$^-$**: *m/z* calcd for $C_{27}H_{17}OF_6$ $(M–H)^-$: 471.11936, found: 471.11781.

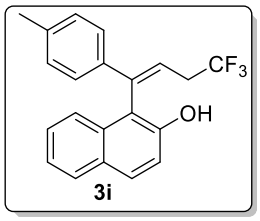
(*Z*)-6-(Thiophen-3yl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) napthalen-2-ol (3h):



Following the general procedure **B**, To a stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2h** (45.2 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for

11 h. 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 hexane/ethyl acetate is an eluant to obtain (Z)-6-(Thiophen-3yl)-1-(4,4,4-trifluoro-1-phenylbut-1-en-1-yl) napthalen-2-ol **3h**, brown oil , 70 mg, 71% yield, R_f= 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.5 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.62 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.41 (m, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.29 (m, 3H), 7.27 (d, *J* = 11.8 Hz, 1H), 6.70 (t, *J* = 7.1 Hz, 1H), 5.21 (s, 1H), 2.85 – 2.73 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 142.1, 139.9, 138.4, 136.4, 131.5, 131.5, 130.6, 129.5, 129.1, 128.9, 127.0, 126.5, 126.1 (q, *J* = 276.9 Hz), 125.4, 124.9, 121.6,120.8, 120.4, 118.1, 116.7, 35.1 (q, *J* = 29.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –65.39 (s, 3F); **IR (neat)**: νmax =3542, 3021, 2403, 1214, 750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{24}H_{16}OF_3S$ $(M–H)^-$: 409.0874, found: 409.0880.

(*Z*)-1-(4,4,4-Trifluoro-1-(p-tolyl)but-1-en-1-yl)naphthalen-2-ol (3i):

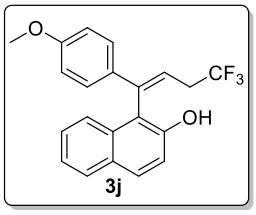


3i

Following the general procedure **B**, To a stirred solution of **1b** (75.9 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 hexane/ethyl acetate is an eluant to obtain (*Z*)-1-(4,4,4-Trifluoro-1-(p-tolyl)but-1-en-1-yl)naphthalen-2-ol **3i,** yellow oil, 67 mg, 82% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.64 (t, *J* = 7.1 Hz, 1H), 5.23 (s, 1H), 2.77 – 2.67 (m, 2H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 139.7, 138.9, 135.6, 132.4, 130.4, 129.7, 129.2, 128.4, 127.3, 126.1 (q, *J* = 276.8 Hz), 126.3, 124.3, 123.8, 120.5, 117.6, 116.7, 21.3, 34.9 (q, *J* = 29.7 Hz); **^{19}F NMR** (377

MHz, $CDCl_3$) δ –65.46 (s, 3F); **IR (neat)**: νmax =3540, 2927, 1908, 1256, 756cm^{-1}; **HRMS (ESI)**$^{-}$: *m/z* calcd for $C_{21}H_{16}OF_3$ $(M–H)^-$: 341.1147, found: 341.1165.

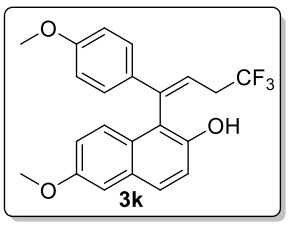
(*Z*)-1-(4,4,4-Trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol (3j):



3j

Following the general procedure **B**, To a stirred solution of **1c** (79.7 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) as added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol **3j**, off-white solid, 71 mg, 83% yield, R_f = 0.4 (hexane/ethyl acetate = 9:1); mp: 97–99 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.49 – 7.46 (m, 1H), 7.37 – 7.31 (m, 2H), 7.27 (d, *J* = 3.6 Hz, 2H), 7.25 – 7.24 (m, 1H), 6.83 – 6.77 (m, 2H), 6.57 (t, *J* = 7.1 Hz, 1H), 5.20 (s, 1H), 3.77 (s, 3H), 2.76 – 2.67 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 150.2, 139.2, 132.4, 130.9, 130.4, 129.3, 128.4, 127.7, 127.2,126.1 (q, *J* = 276.9 Hz), 124.3, 123.9, 119.3, 117.6, 114.4, 109.6, 55.4, 34.9 (q, *J* = 29.8 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.53 (s, 3F); **IR (KBr)**: νmax =3542, 3021, 2403, 1214, 750cm^{-1}; **HRMS (ESI)**$^{-}$: *m/z* calcd for $C_{21}H_{16}O_2F_3$ $(M–H)^-$: 357.1102, found: 357.1107.

(*Z*)-6-Methoxy-1-(4,4,4-trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol (3k):

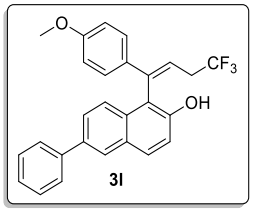


3k

Following the general procedure **B**, To a stirred solution of **1c** (79.7 mg, 0.24 mmol) in 1mL of PEG-400 was added **2b** (34.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for

11 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-6-Methoxy-1-(4,4,4-trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol **3k**, brown oil, 75 mg, 81% yield, R_f = 0.3 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.24 (m, 3H), 7.14 (d, *J* = 2.6 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.54 (t, *J* = 7.1 Hz, 1H), 5.06 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.74 – 2.68 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 156.3, 148.6, 139.3, 130.9, 130.2, 129.0, 127.7, 127.6, 126.2 (q, *J* = 277.1 Hz), 125.9, 119.6, 119.1, 118.0, 117.1, 114.3, 106.8, 55.5, 55.4, 34.9 (q, *J* = 29.7 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.52 (s, 3F); **IR (neat)**: νmax =3687, 3021, 2402, 1215, 742 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{22}H_{18}O_3F_3$ $(M–H)^-$: 387.1208, found: 387.1212.

(*Z*)-6-Phenyl-1-(4,4,4-trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol (3l):

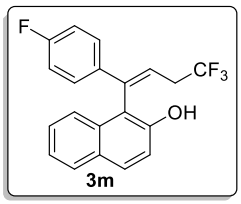


3l

Following the general procedure **B**, To a stirred solution of **1c** (79.7 mg, 0.24 mmol) in 1mL of PEG-400 was added **2d** (44 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10–12 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-6-Phenyl-1-(4,4,4-trifluoro-1-(4-methoxy phenyl) but-1-en-1-yl) naphthalen-2-ol **3l**, brown oil, 81 mg, 78% yield, R_f = 0.4 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.66 (m, 2H), 7.62 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.27 (m, 3H), 6.83 – 6.80 (m, 2H), 6.59 (t, *J* = 7.1 Hz, 1H), 5.25 (s, 1H), 3.77 (s, 3H), 2.75 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 150.4, 141.0, 139.2, 136.7, 131.6, 130.8, 130.7, 129.5, 128.9, 127.5, 127.3, 126.9, 126.3, 126.2 (q, *J* = 276.7 Hz), 124.9, 119.4, 119.3, 118.0, 116.7, 114.4, 55.4, 35.0 (q, *J* = 29.8 Hz,); **^{19}F NMR**

(377 MHz, $CDCl_3$) δ –65.47 (s, 3F); **IR (neat)**: νmax =3689, 3022, 2404, 121, 743 cm^{-1}; **HRMS (ESI)**$^-$: *m/z* calcd for $C_{27}H_{20}O_2F_3$ $(M–H)^-$: 433.1413, found: 433.1419.

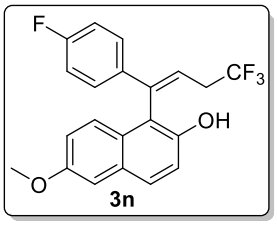
(*Z*)-1-(4,4,4-Trifluoro-1-(4-fluoro phenyl) but-1-en-1-yl) naphthalen-2-ol (3m):



3m

Following the general procedure **B**, To a stirred solution of **1d** (76.8 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-(4-fluoro phenyl) but-1-en-1-yl) naphthalen-2-ol **3m,** off-white solid, 65 mg, 79% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 83–85 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 3H), 7.46 – 7.43 (m, 1H), 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.01 – 6.95 (m, 2H), 6.62 (t, *J* = 7.1 Hz, 1H), 5.16 (s, 1H), 2.80 – 2.67 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.13 (d, *J* = 248.9 Hz), 150.2, 139.0, 134.6, 132.3, 130.7, 129.3, 128.5, 128.2, 128.1, 127.4,126.1 (q, *J* = 276.6 Hz), 124.1 (d, *J* = 12.5 Hz), 121.2, 117.6, 116.4, 115.9 (d, *J* = 21.7 Hz), 35.0 (q, *J* = 29.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –65.48 (S, 3F), –112.88 (s, 1F); **IR (KBr)**: νmax = 3687, 3021, 2402, 1216, 746 cm^{-1}; **HRMS (ESI)**$^-$: *m/z* calcd for $C_{20}H_{13}OF_4$ $(M–H)^-$: 345.08988, found: 345.08970.

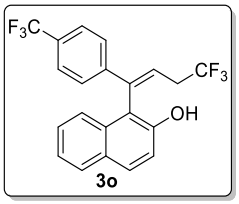
(*Z*)-6-Methoxy-1-(4,4,4-trifluoro-1-(4-fluoro phenyl) but-1-en-1-yl) naphthalen-2-ol (3n):



3n

Following the general procedure **B**, To a stirred solution of **1d** (76.8 mg, 0.24 mmol) in 1mL of PEG-400 was added **2b** (34.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 14 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-6-Methoxy-1-(4,4,4-trifluoro-1-(4-fluoro phenyl) but-1-en-1-yl) naphthalen-2-ol **3n**, pale-yellow oil, 70 mg, 78% yield%, R_f = 0.4 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, DMSO) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 9.1 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 7.04 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.58 (t, *J* = 7.1 Hz, 1H), 5.04 (s, 1H), 3.89 (s, 3H), 2.80 – 2.66 (m, 2H); **^{13}C NMR** (101 MHz, DMSO) δ 163.12 (d, *J* = 248.8 Hz), 156.4, 148.6, 139.2, 134.8, 130.3, 129.3, 128.2 (d, *J* = 8.2 Hz), 127.5, 125.7,123.3 (q, *J* = 277.6 Hz), 121.0, 119.8, 118.1, 116.7,115.9 (d, *J* = 21.7 Hz), 106.9, 55.5, 35.0 (q, *J* = 30.0 Hz); **^{19}F NMR** (376 MHz, DMSO) δ –70.18 (s, 3F), –117.67 (s, 1F); **IR (neat)**: νmax = 3686, 3021, 2403,1214,750 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{21}H_{15}O_2F_4$ $(M–H)^-$: 375.10027, found: 375.10187.

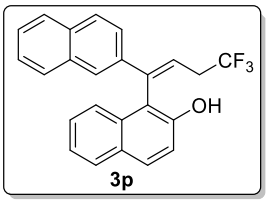
(*Z*)-1-(4,4,4-Trifluoro-1-(4-(trifluoromethyl) phenyl) but-1-en-1-yl) naphthalen-2-ol (3o):



Following the general procedure **B**, to a stirred solution of **1e** (88.8 mg, 0.24mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-(4-(trifluoromethyl) phenyl) but-1-en-1-yl) naphthalen-2-ol **3o**, brown oil, 68 mg, 72% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.41 (m, 3H), 7.39 – 7.34 (m, 2H), 7.27

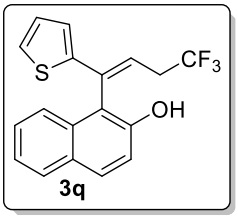
(d, *J* = 9.7 Hz, 1H), 6.76 (t, *J* = 7.1 Hz, 1H), 5.16 (s, 1H), 2.86 – 2.73 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 142.1, 139.2, 132.3, 130.9, 129.3, 128.6, 127.6, 126.8, 126.0, 125.9(q, *J* = 276.7 Hz,), 125.9, 124.1, 124.1 (q, *J* = 272.2 Hz), 123.9, 123.7, 117.7, 115.9, 35.2 (q, *J* = 30.1 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.71 (s, 3F), –65.31 (s, 3F); **IR(neat)**: νmax = 3553, 3025, 2403,1135,760 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{21}H_{13}OF_6$ $(M–H)^-$: 395.08651, found: 395.08703.

(*Z*)-1-(4,4,4-Trifluoro-1-(naphthalen-2-yl) but-1-en-1-yl) naphthalen-2-ol (3p):



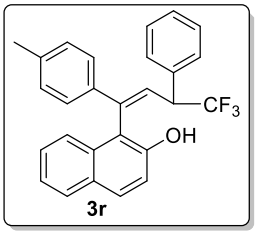
Following the general procedure **B**, To a stirred solution of **1f** (84.5 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-(naphthalen-2-yl) but-1-en-1-yl) naphthalen-2-ol **3p**, pale yellow solid, 68 mg, 75% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 111-113 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (m, 1H), 7.60 (m, 1H), 7.53 (m, 1H), 7.36 – 7.30 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.22 (m, 2H), 6.51 (t, *J* = 7.1 Hz, 1H), 5.47 (s, 1H), 2.93 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 138.7, 137.9, 134.6, 132.6, 131.0, 130.5, 130.3, 129.4, 129.2, 128.9, 128.5, 127.4, 127.2, 126.5, 126.2 (q, *J* = 277.0 Hz), 126.1, 125.3, 124.7, 124.3, 123.9, 118.9, 117.7, 35.3 (q, *J* = 29.9 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.25 (s, 3F); **IR (KBr)**: νmax =3688, 3059, 2398, 1259, 756 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{24}H_{16}OF_3$ $(M–H)^-$: 377.1153, found: 377.1147.

(*E*)-1-(4,4,4-Trifluoro-1-(thiophen-2-yl)but-1-en-1-yl)naphthalen-2-ol (3q):



Following the general procedure **B**, To a stirred solution of **1g** (73.9 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 11 h. 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 hexane/ethyl acetate is an eluant to obtain the (*E*)-1-(4,4,4-Trifluoro-1-(thiophen-2-yl)but-1-en-1-yl)naphthalen-2-ol **3q**, colorless oil, 56 mg, 70% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.26 (d, *J* = 8.9 Hz, 1H), 7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.61 – 6.56 (m, 2H), 5.23 (s, 1H), 2.70 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 142.9, 134.2, 132.3, 130.8, 129.2, 128.4, 127.9, 127.4, 126.9, 126.1, 125.9 (q, *J* = 276.9 Hz) 124.15, 123.9, 119.6, 117.7, 115.9, 34.7 (q, *J* = 30.1 Hz); **^{19}FNMR** (377 MHz, $CDCl_3$) δ –65.39 (s, 3F); **IR (neat)**: νmax = 3539, 3064, 2495,1252,752 cm^{-1}; **HRMS(ESI)$^-$**: *m/z* calcd for $C_{18}H_{12}OF_3S(M–H)^-$: 333.0555, found: 333.0572.

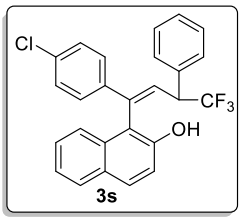
(*Z*)-1-(4,4,4-trifluoro-3-phenyl-1-(p-tolyl) but-1-en-1-yl) naphthalen-2-ol (3r):



Following the general procedure **B**, To a stirred solution of **1h** (94.1 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 using hexane/ethyl acetate to obtain the (*Z*)-1-(4,4,4-trifluoro-3-phenyl-1-(p-tolyl) but-1-en-1-yl) naphthalen-2-ol **3r,** pale yellow oil, 87 mg, 87% yield , R_f = 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.17 (m, 4H), 7.16 – 7.10 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.05 – 6.94 (m, 3H), 6.89 (d, *J* = 7.5 Hz, 2H), 5.29 (s, 1H), 3.80 (p, *J* = 9.5 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 139.1, 138.9, 135.5, 134.2, 132.3, 130.4, 129.7, 129.1, 128.9, 128.6, 128.1, 128.1, 126.7, 126.4, 125.7, 124.6, 123.9, 123.7, 117.7, 116.8, 50.8 (q, *J* = 26.4 Hz), 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –68.64 (s, 3F); **IR (neat)**: νmax = 3623, 2986, 2256,1236,732 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{27}H_{20}OF_3$ $(M–H)^-$: 417.1466, found: 417.1471.

(*Z*)-1-(1-(4-Chlorophenyl)-4,4,4-trifluoro-3-phenylbut-1-en-1-yl) naphthalen-2-ol (3s):

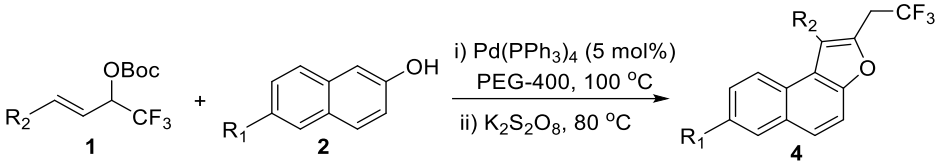


3s

Following the general procedure **B**, to a stirred solution of **1i** (98.9 mg, 0.24 mmol) in 1mL of PEG-400 was added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(1-(4-Chlorophenyl)-4,4,4-trifluoro-3-phenylbut-1-en-1-yl) naphthalen-2-ol **3s**, off-white solid, 88 mg, 84% yield, R_f = 0.5 (hexane/ethyl acetate = 9:1); mp: 133–135 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.27 (t, *J* = 2.0 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.24 – 7.18 (m, 3H), 7.16 – 7.11 (m, 2H), 7.03 (m, 1H), 6.99 (d, *J* = 10.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 2H), 5.26 (s, 1H), 3.81 (p, *J* = 9.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 138.2, 136.8, 134.9, 133.8, 132.1, 130.7, 129.1, 128.8, 128.7, 128.2, 127.8, 127.4, 126.9, 126.8, 126.12 (q, *J* = 280.3 Hz), 124.3, 123.9, 117.8, 117.5, 116.2, 50.9 (q, *J* = 28.2 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –68.52 (s, 3F); **IR (KBr)**: νmax = 3685, 3022, 2405, 1132, 748 cm^{-1}; **HRMS (ESI)$^-$**: *m/z* calcd for $C_{26}H_{17}OClF_3$ $(M–H)^-$: 437.0920, found: 437.0918.

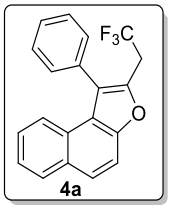
4.2 General procedure for the synthesis of CF_3-naphtho[2,1-b]furans 4 (Method C):

General reaction:



To a stirred solution of CF_3-allyl carbonate **1** (0.24 mmol) in 1 mL of PEG-400 was added *β*-naphthol **2** (0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10–14 h. The reaction progress was monitored by TLC. After completion of the *β*-naphthol **2**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C and stirred for until completion of compound **3**. 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 using flash column chromatography (using 9.5:0.5 hexane/ethyl acetate) to obtain the pure product CF_3-naphtho[2,1-*b*]furans **4**. The characterization data of **4** are summarized below.

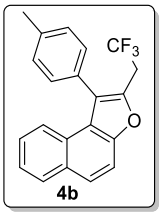
1-Phenyl-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4a):



By using the method **C**, To the stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. The reaction progress was monitored by TLC. After completion of the **2a**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 1 h. 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 using flash column chromatography using hexane as a eluant to obtain the 1-

Phenyl-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4a,** colorless oil, 58 mg, 74% yield, R_f = 0.5 (hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.66 – 7.63 (m, 1H), 7.57 – 7.49 (m, 5H), 7.41 (m, 1H), 7.30 (m, 1H), 3.53 (q, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 143.1, 132.7, 130.9, 130.6, 130.5, 129.1, 128.5, 128.2, 126.5, 126.3,124.8 (q, *J* = 278.1 Hz), 124.6, 124.1, 123.1, 121.9, 112.4, 32.2(q, *J* = 32.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.38 (s, 3F); **IR (neat)**: νmax = 3634, 2926, 1259, 1144, 776 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{20}H_{13}OF_3$ $(M)^+$: 326.0918, found: 326.0908**.**

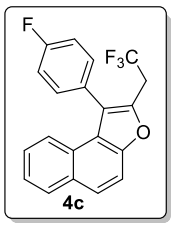
1-(P-tolyl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4b):



4b

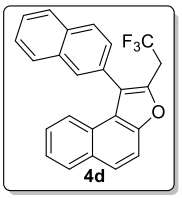
By using the method **C**, To the stirred solution of **1b** (75.9 mg, 0.24 mmol) in 1 mL of PEG-400 added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 11 h. The reaction progress was monitored by TLC. After completion of the **2a**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 3 h. 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 using flash column chromatography hexane as a eluant to obtain 1-(P-tolyl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4b**, pale yellow oil, 57 mg, 70% yield, R_f = 0.6 (hexane); **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.69 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.36 (m, 5H), 7.30 (m, 1H), 3.53 (q, *J* = 10.0 Hz, 2H), 2.49 (s, 3H); **^{13}CNMR** (101 MHz, $CDCl_3$) δ 152.4, 143.1, 138.3, 130.9, 130.3, 129.8, 129.6, 129.0, 128.2, 126.3, 126.3, 124.8 (q, *J* = 278.3 Hz), 124.5, 124.0, 123.2, 121.9, 112.4, 32.2 (q, *J* = 32.2 Hz), 21.5; **^{19}F NMR**(377 MHz, $CDCl_3$) δ –64.38 (s, 3F); **IR (neat)**: νmax = 3654,3051,1258,1142,808 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{21}H_{15}OF_3$ $(M)^+$: 340.1075, found: 340.1087.

1-(4-Fluorophenyl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4c):



By using the method **C**, To the stirred solution of **1d** (76.8 mg, 0.24 mmol) in 1 mL of PEG-400 added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 11 h. The reaction progress was monitored by TLC. After completion of the **2a**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 4 h. 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 using flash column chromatography hexane as a eluant to obtain the 1-(4-Fluorophenyl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4c,** colorless oil, 57 mg, 69% yield, R_f = 0.5 (hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.61 – 7.58 (m, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.39 (m, 1H), 7.31 (m, 1H), 7.27 – 7.21 (m, 2H), 3.51 (q, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.01 (d, *J* = 247.8 Hz), 152.4, 143.3, 132.2, 132.1, 130.9, 129.1, 128.6, 128.1, 126.5 (d, *J* = 17.1 Hz), 124.7 (q, *J* = 278.0 Hz), 124.7, 123.0, 122.9, 121.8, 116.2 (d, *J* = 21.5 Hz), 112.4, 32.2 (q, *J* = 32.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.39 (s, 3F), –113.26 (s, 1F); **IR (neat)**: νmax = 3678,3019,1215,1144,749 cm^{-1}**; HRMS(EI)$^+$**: *m/z* calcd for $C_{20}H_{12}OF_4$ $(M)^+$: 344.08243, found: 344.08362.

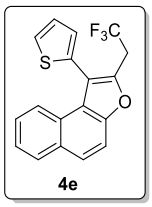
1-(Naphthalen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4d):



By using the method **C**, To the stirred solution of **1f** (84.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2a** (28.2mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. The reaction progress was monitored by TLC. After completion of the **2a**, reaction mixture was

cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 2 h. 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 using flash column chromatography hexane as a eluant to obtain 1-(Naphthalen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4d**, colorless oil, 47 mg, 52% yield, R_f = 0.5 (hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.64 (m, 1H), 7.61 – 7.56 (m, 2H), 7.51 (m, 1.1 Hz, 1H), 7.32 (m, 2H),7.10 – 7.01 (m, 2H), 3.54 (m, 1H), 3.40 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 143.9, 133.9, 132.9, 131.9, 130.9, 129.9, 129.3, 128.8, 128.7, 128.5, 128.0, 126.9, 126.6, 126.4, 125.9, 125.8, 124.7 (q, *J* = 278.2 Hz), 124.6, 123.1, 122.9, 121.8, 112.5, 32.3 (q, *J* = 32.2 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.28 (s, 3F); **IR (KBr)**: νmax = 3610, 3010, 1250, 1140, 760 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{24}H_{15}OF_3$ $(M)^+$: 376.1075, found: 376.1090.

1-(Thiophen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4e):

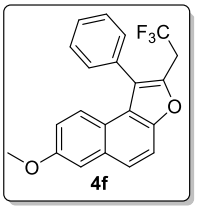


4e

By using the method **C**, To the stirred solution of **1g** (73.9 mg, 0.24 mmol) in 1 mL of PEG-400 added **2a** (28.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) as added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. The reaction progress was monitored by TLC. After completion of the **2a**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 5 h. 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 using flash column chromatography hexane as a eluant to obtain the 1-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4e**, brown oil, 47 mg, 59% yield, R_f = 0.6 (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 5.0 Hz, 1H), 7.43 (m, 1H), 7.36 (m, 1H), 7.23 (m, 2H), 3.60 (q, *J* = 10.0, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 145.0, 132.4, 131.0, 129.5, 129.0,

127.9, 127.9, 127.7, 126.7, 126.5, 124.8, 124.6 (q, J = 278.2 Hz), 123.0, 122.2, 116.7, 112.3, 32.3 (q, J = 32.4 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.33 (s, 3F); **IR (neat)**: νmax = 3695, 3055, 1217, 1140, 753 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{18}H_{11}OF_3S$ $(M)^+$: 332.04827, found: 332.04696.

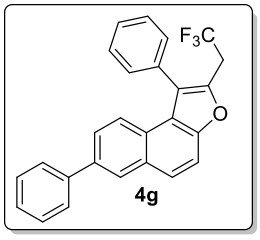
7-Methoxy-1-phenyl-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4f):



4f

By using the method **C**, To the stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2b** (34.8 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. The reaction progress was monitored by TLC. After completion of the **2b**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 1 h. 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 using flash column chromatography hexane as a eluant to obtain the 7-Methoxy-1-phenyl-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4f**, colorless oil, 61 mg, 72% yield, R_f = 0.4 (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.3 Hz, 2H), 7.55 (d, J = 3.4 Hz, 1H), 7.53 (dd, J = 4.3, 1.7 Hz, 2H), 7.51 (d, J = 4.0 Hz, 1H), 7.48 (dd, J = 7.5, 1.9 Hz, 2H), 7.28 – 7.21 (m, 1H), 6.97 (dd, J= 9.1, 2.7 Hz, 1H), 3.89 (s, 3H), 3.52 (q, J = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 151.3, 143.1, 132.7, 132.2, 130.5, 129.1, 128.5, 127.5 (q, J = 278.2 Hz), 125.3, 124.5, 123.8, 123.0, 122.1, 118.1, 112.7, 108.0, 55.4, 32.2 (q, J = 32.1 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.36 (s, 3F); **IR (neat)**: νmax = 3610, 3020, 1234, 1130, 750 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{21}H_{15}O_2F_3$ $(M)^+$: 356.1024, found: 356.1037.

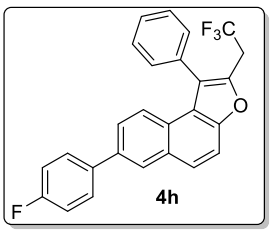
1,7-Diphenyl-2-(2,2,2-trifluoroethyl) naphtho [2,1-b]furan (4g):



4g

By using the method **C**, To the stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2d** (44 mg, 0.2 mmol) at room temperature. Then, 5 mol % of $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. The reaction progress was monitored by TLC. After completion of the **2d**, reaction mixture was cooled to room temperature and added $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 3 h. 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 using flash column chromatography hexane as a eluant to obtain the 1,7-Diphenyl-2-(2,2,2-trifluoroethyl) naphtho [2,1-b] furan **4g**, brown oil, 60 mg, 62% yield, R_f = 0.5 (hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.66 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.52 – 7.51 (m, 1H), 7.45 (dd, *J* = 10.5, 4.9 Hz, 2H), 7.37 – 7.33 (m, 1H), 3.54 (q, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 143.2, 141.1, 137.3, 132.6, 131.3, 130.3, 129.1, 128.9, 128.6, 127.4, 127.2, 126.9, 126.7, 125.8, 124.8 (q, *J* = 278.2 Hz), 124.0, 123.6, 121.9, 120.6, 112.8, 32.3 (q, *J* = 32.1 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.33 (s,3F); **IR (neat)**: νmax = 3622, 3025, 1260, 1145, 763 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{26}H_{17}OF_3$ $(M)^+$: 402.1231, found: 402.1213.

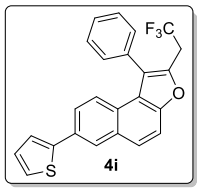
7-(4-Fluorophenyl)-1-phenyl-2-(2,2,2-trifluoroethyl)naphtho[2,1-b]furan (4h):



By using the method **C**, To the stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2f** (47.6 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 11 h. The reaction progress was monitored by TLC. After completion of the **2f**, reaction mixture was cooled to room temperature and added the $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 2 h. 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 using flash column chromatography hexane as a eluant to obtain 7-(4-

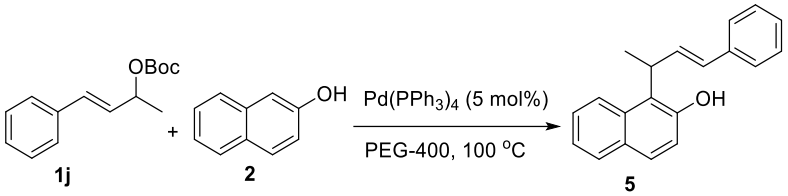
Fluorophenyl)-1-phenyl-2-(2,2,2-trifluoroethyl)naphtho[2,1-b]furan **4h**, pale yellow oil, 60 mg, 60% yield R_f = 0.5 (hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.64 – 7.59 (m, 2H), 7.57 (m, 3H), 7.54 – 7.49 (m, 3H), 7.17 – 7.11 (m, 2H), 3.55 (q, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.60 (d, *J* = 246.3 Hz), 152.5, 143.3, 137.2, 136.4, 132.6, 131.2, 130.5, 129.1, 128.9 (d, *J* = 8.0 Hz), 128.6, 127.2, 126.7 (d, *J* = 16.4 Hz), 125.7, 124.7 (q, *J* = 278.1 Hz), 124.0, 123.7, 122.8, 121.9, 115.9 (d, *J* = 21.4 Hz), 112.9, 32.3 (q, *J* = 32.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.34 (s, 3F), –115.79 (s, 1F); **IR (KBr)**: νmax = 3649, 2926, 1259, 1145, 825 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{26}H_{16}OF_4$ $(M)^+$: 420.1137, found: 420.1155.

1-Phenyl-7-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan (4i):



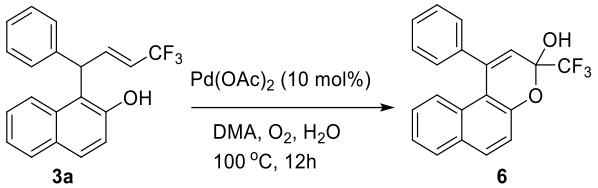
By using the method **C**, To the stirred solution of **1a** (72.5 mg, 0.24 mmol) in 1 mL of PEG-400 added **2h** (45.2 mg, 0.2 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 12 h. The reaction progress was monitored by TLC. After completion of the **2h**, reaction mixture was cooled to room temperature and added $K_2S_2O_8$ (54.1 mg, 0.2 mmol). Then the temperature of reaction mixture was raised to 80 °C for 5 h. 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 using flash column chromatography hexane as a eluant to obtain 1-Phenyl-7-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl) naphtho[2,1-b]furan **4i**, off-white solid, 51 mg, 52% yield, R_f = 0.5 (hexane); **mp**: 152-154 °C**; ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 6.6, 2.1 Hz, 3H), 7.54 – 7.50 (m, 3H), 7.48 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.41 (dd, *J* = 5.0, 2.9 Hz, 1H), 3.54 (q, *J* = 10.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 143.2, 142.3, 132.6, 132.1, 131.3, 130.5, 129.1, 128.6, 127.2, 126.6, 126.5, 126.5, 126.0, 125.3, 124.7 (q, *J* = 278.1 Hz)**,** 123.9, 123.6, 121.9, 120.4, 112.9, 32.3 (q, *J*= 32.4 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.35(s, 3F); **IR (KBr)**: νmax = 3694, 2928, 1257, 1142, 866 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{24}H_{15}OF_3S$ $(M)^+$: 408.0795, found: 408.0814.

Prpepration of (*E*)-1-(4-Phenylbut-3-en-2-yl) naphthalen-2-ol (5):



Following the general procedure **B**, to the solution of (*E*)-tert-butyl (4-phenylbut-3-en-2-yl) carbonate **1j** (59.5 mg, 0.24 mmol) and naphthalen-2-ol **2a** (28.8 mg, 0.2 mmol) in 1 mL of PEG-400 in a reaction vial was added at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added and stirred at 100 °C (oil bath temperature) for 11 h. The crude product was purified by column chromatography on silica gel by using Ethyl acetate/ hexanes as an eluent to afford the corresponding product (*E*)-1-(4-phenylbut-3-en-2-yl)naphthalen-2-ol **5**, 43 mg, 65% yield, yellow oil, R_f= 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.49 (t, *J* = 8.3, 7.1 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.34 (m, 3H), 7.26 – 7.22 (m, 1H), 7.07 (d, *J* = 8.8, 2.9 Hz, 1H), 6.76 (s, 2H), 5.89 (s, 1H), 4.64 (q, *J* = 7.0 Hz, 1H), 1.64 (d, *J* = 7.1, 3.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 136.8, 133.7, 132.6, 130.6, 129.8, 129.1, 128.9, 128.8, 127.9, 126.7, 126.5, 123.2, 122.5, 121.4, 119.4, 33.6, 17.4; **IR (neat)**: νmax = 3350, 1704, 1260, 1214, 753 cm^{-1}; **HRMS (EI)$^+$**: *m/z* calcd for $C_{20}H_{18}O$ $(M)^+$: 274.1357, found: 274.1344.

Synthesis of 1-phenyl-3-(trifluoromethyl)-3*H*-benzo[*f*]chromen-3-ol (6):

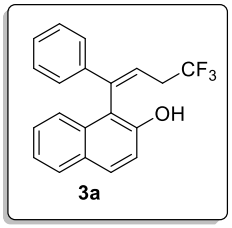


To the stirred solution of (*E*)-1-(4,4,4-trifluoro-1-phenylbut-2-en-1-yl) naphthalen-2-ol **3a** (78.7 mg, 0.24 mmol) in 1 mL of DMA and H_2O mixture (8:2), was added $Pd(OAc)_2$ (22.45 mg, 10 mol%) at room temperature under oxygen atmosphere and stirred at 100 °C (oil bath temperature) for 12 h. After completion of the reaction (monitored by TLC) the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel by using Ethyl acetate/ hexanes as an eluent to afford the corresponding product 1-phenyl-3-(trifluoromethyl)-3*H*-benzo[f]chromen-3-ol **6**, 52 mg, 63%

yield, colorless oil; R_f= 0.5 (hexane/ethyl acetate = 9:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 (s, 2H), 7.30 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.11 – 7.07 (m, 1H), 5.99 (s, 1H), 3.49 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 141.9, 140.1, 132.2, 131.0, 129.8, 128.9, 128.8, 128.6, 126.5, 126.4 (q, *J* = 258.0 Hz), 125.9, 124.3, 123.6, 118.3, 115.4, 114.1, 93.1 (q, *J* = 33.9 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –83.84 (s, 3F); **IR (KBr)**: νmax = 3713, 2930, 1715, 1191, 765 cm^{-1}; **HRMS (ESI)$^-$** : *m/z* calcd for $C_{20}H_{12}O_2F_3$ $(M–H)^-$: 341.0783, found: 341.0799.

5) Gram scale reaction of 3a:

(*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol (3a):



Following the general procedure **B**, To a stirred solution of **1a** (1 g, 3.31 mmol) in 10 mL of PEG-400 was added **2a** (395 mg, 2.74 mmol) at room temperature. Then, $Pd(PPh_3)_4$ (11.5 mg, 5 mol%) was added to the reaction mixture and stirred at 100 °C (oil bath temperature) for 10 h. After completion of the reaction, mixture was diluted with 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 hexane/ethyl acetate is an eluant to obtain the (*Z*)-1-(4,4,4-Trifluoro-1-phenylbut-1-en-1-yl) naphthalen-2-ol **3a**, off-white solid, 966 mg, 89% yield.

6) X-ray analysis data of 3j:

X-ray Crystallography:

X-ray data for the compound **3j** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[4] The structure was solved using intrinsic phasing method and further refined with the SHELXL[5] program and expanded using Fourier techniques. Anisotropic

displacement parameters were included for all non-hydrogen atoms. The O bound H atoms were located in difference Fourier density map and their position and thermal parameters were refined isotropically. 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 $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms].

Crystal structure determination of 3j:

Crystal Data for $C_{21}H_{17}O_2F_3$ (M =358.35 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.3698(4) Å, b = 12.1098(5) Å, c = 29.2861(12) Å, β = 92.224(2)°, V = 3674.9(3) Å^3, Z = 8, T = 294.15 K, μ(MoKα) = 0.103 mm^{-1}, *Dcalc* = 1.295 g/cm^3, 22819 reflections measured (4.366° ≤ 2Θ ≤ 49.998°), 6454 unique (R_{int} = 0.0484, R_{sigma} = 0.0541) which were used in all calculations. The final R_1 was 0.0671 (I > 2σ(I)) and wR_2 was 0.2111 (all data). CCDC 2088167 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

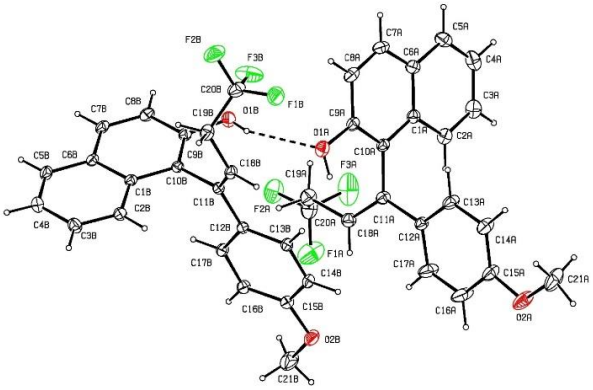


Fig.1. A view of **3j**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii. Hydrogen bond is shown as dashed lines. The asymmetric unit contains two crystallographically independent molecules.

7) References:

1) (a) Zhou, M.; Zhang, J.; Zhang, X. G.; Zhang, X. Ni-Catalyzed Defluorination for the Synthesis of gem-Difluoro-1,3-dienes and Their [4 + 2] Cycloaddition Reaction. *Org. Lett*. **2019**, *21*, 671-674. (b) Ortega, A.; Manzano, R.; Uria, U.; Carrillo, L.; Reyes, E.; Tejero, T.; Merino, P.; Vicario, J. L. Catalytic Enantioselective Cloke−Wilson Rearrangement. *Angew. Chem., Int. Ed.* **2018**, *57*, 8225−8229.

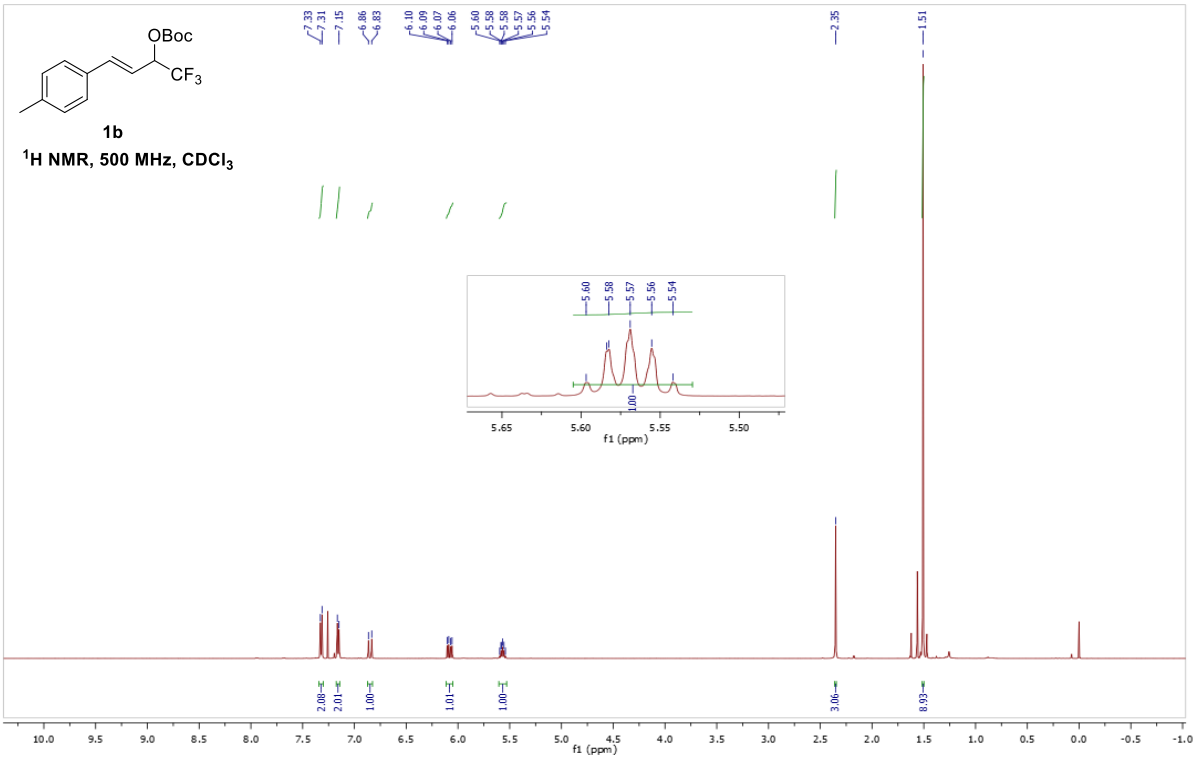
2) (a) Li, C.; Xing, J.; Zhao, J.; Huynh, P.; Zhang, W.; Jiang, P.; Zhang, Y. J. Pd-catalyzed regioselective and stereospecific SuzukiMiyaura coupling of allylic carbonates with arylboronic acids. *Org. Lett.* **2012**, *14*, 390−393. (b) Hirakawa, T.; Ikeda, K.; Ikeda, D.; Tanaka, T.; Ogasa, H.; Kawatsura, M.; Itoh, T. Regioselective synthesis of trifluoromethyl group containing allylic amines by palladium-catalyzed allylic amination and sequential isomerization. *Tetrahedron* **2011**, *67*, 8238

3) Wu, M.; Kong, L. Y.; Wang, K. W.; Jin, R. H.; Cheng, T. Y.; Liu, G. H. Enantioselective 1,2-reductions of β-trifluoromethylated-α,βunsaturated ketones to chiral allylic alcohols over organorutheniumfunctionalized mesoporous silica nanospheres. *Catal. Sci. Technol*. **2015**, 5, 1750– 1757.

4) Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

5) Sheldrick G. M. (2015**)** Acta Crystallography C71: 3-8.

8) ^{1}H NMR and ^{13}C NMR and^{19} F spectral copies of compounds: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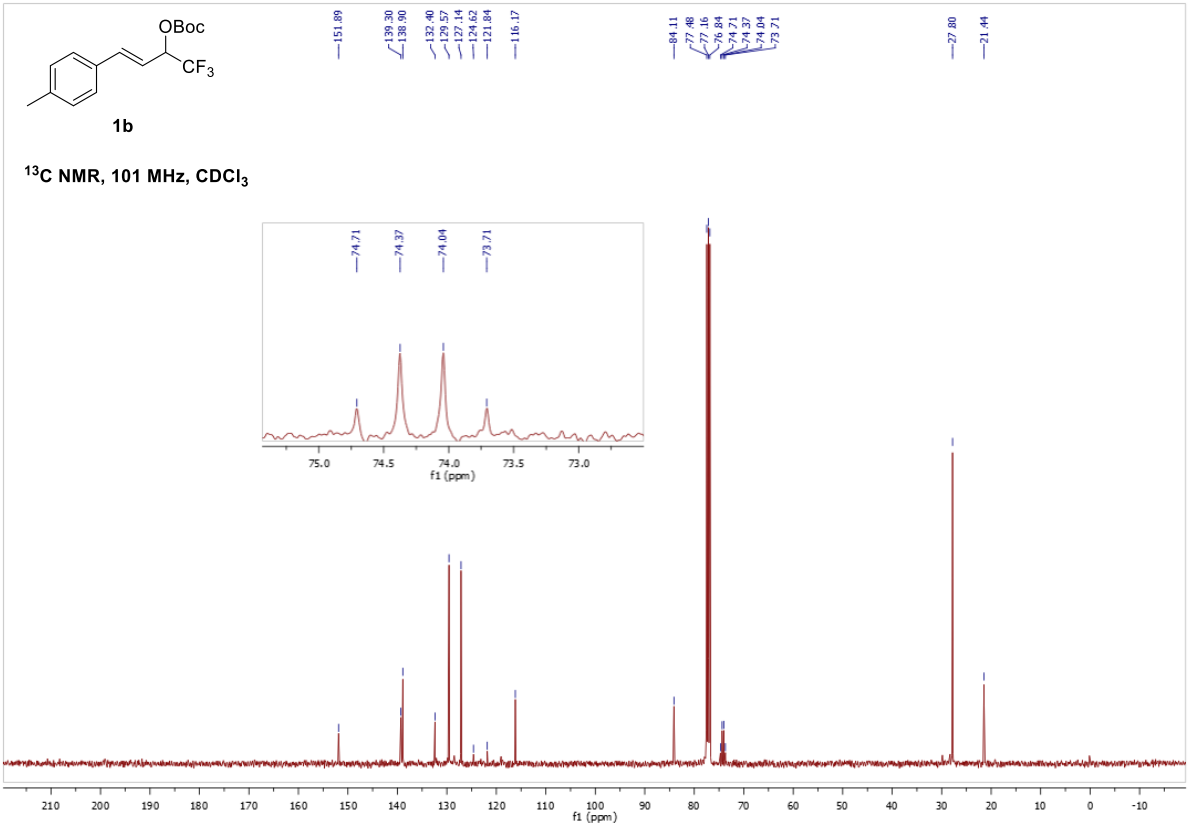
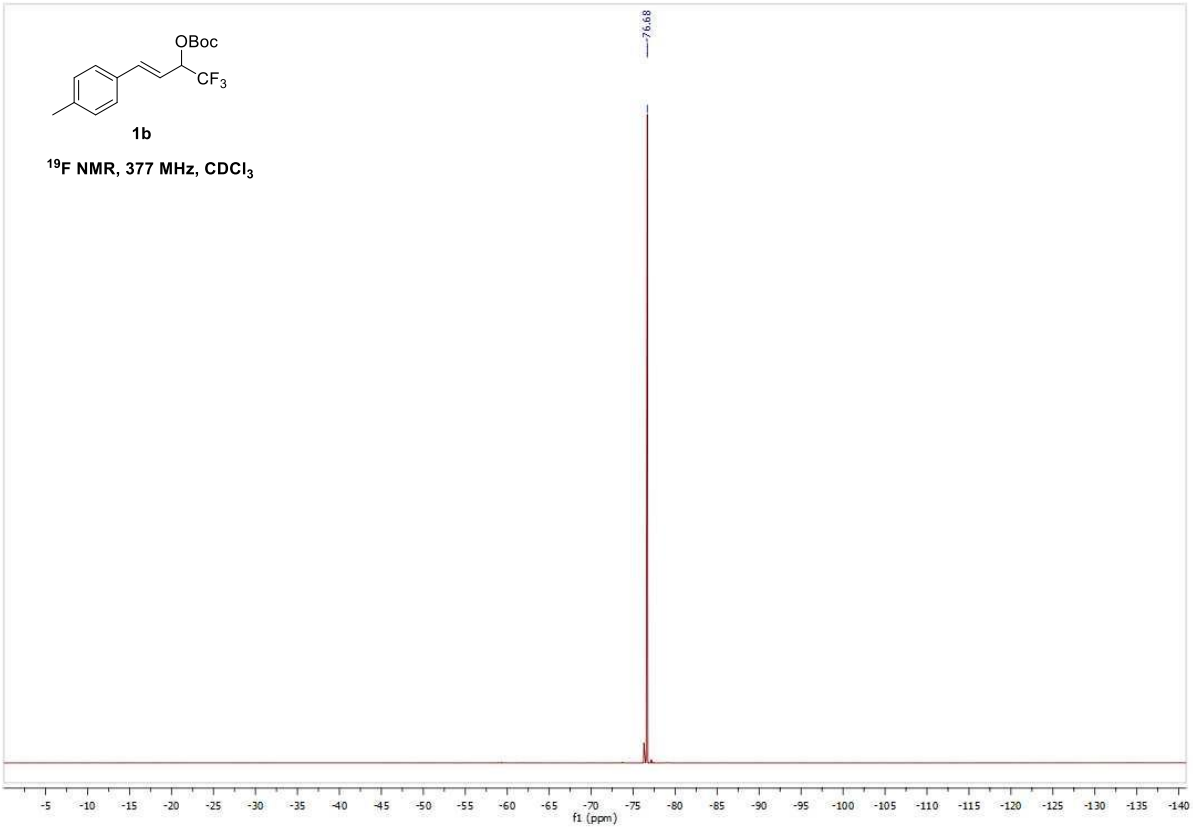
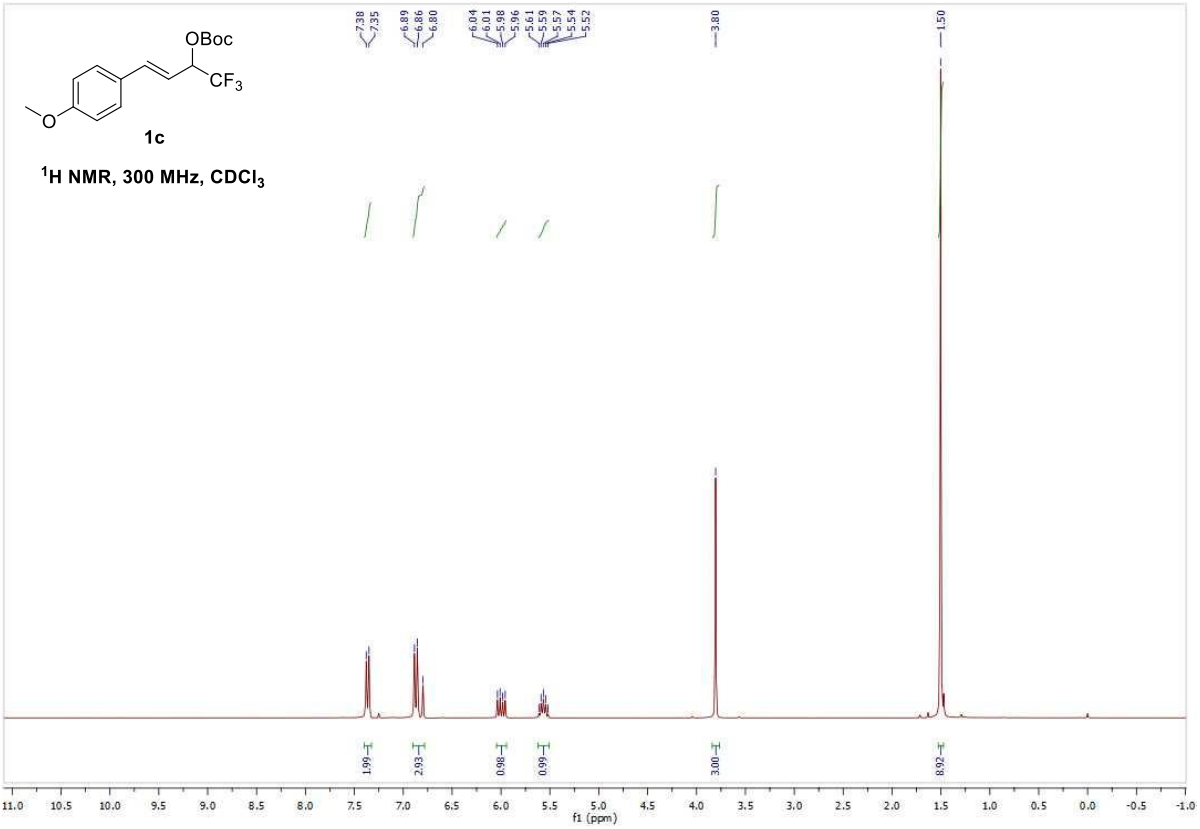
1H NMR, 500 MHz, CDCl3
f1 (ppm)


OBoc
CF3
1b
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OBoc
CF3
1b
19F NMR, 377 MHz, CDCl3
-76.68
f1 (ppm)


OBoc
CF3
O
1c
1H NMR, 300 MHz, CDCl3
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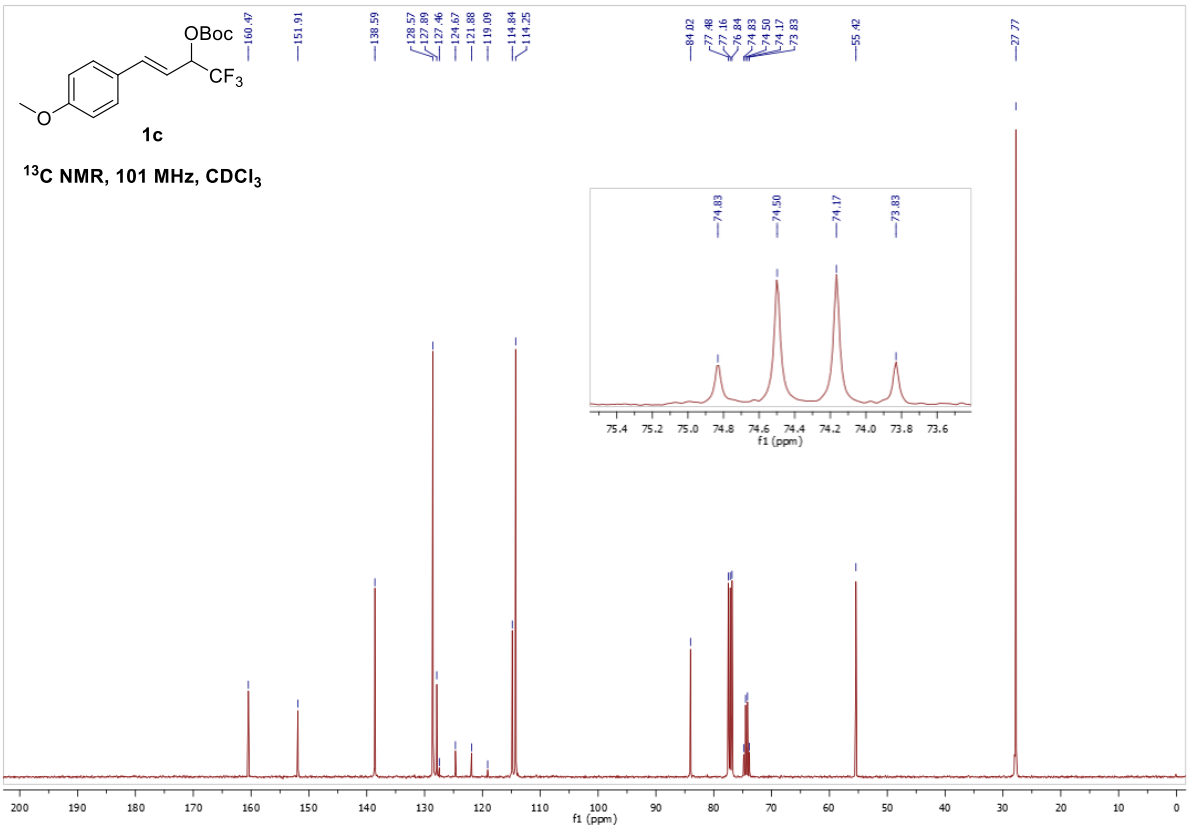
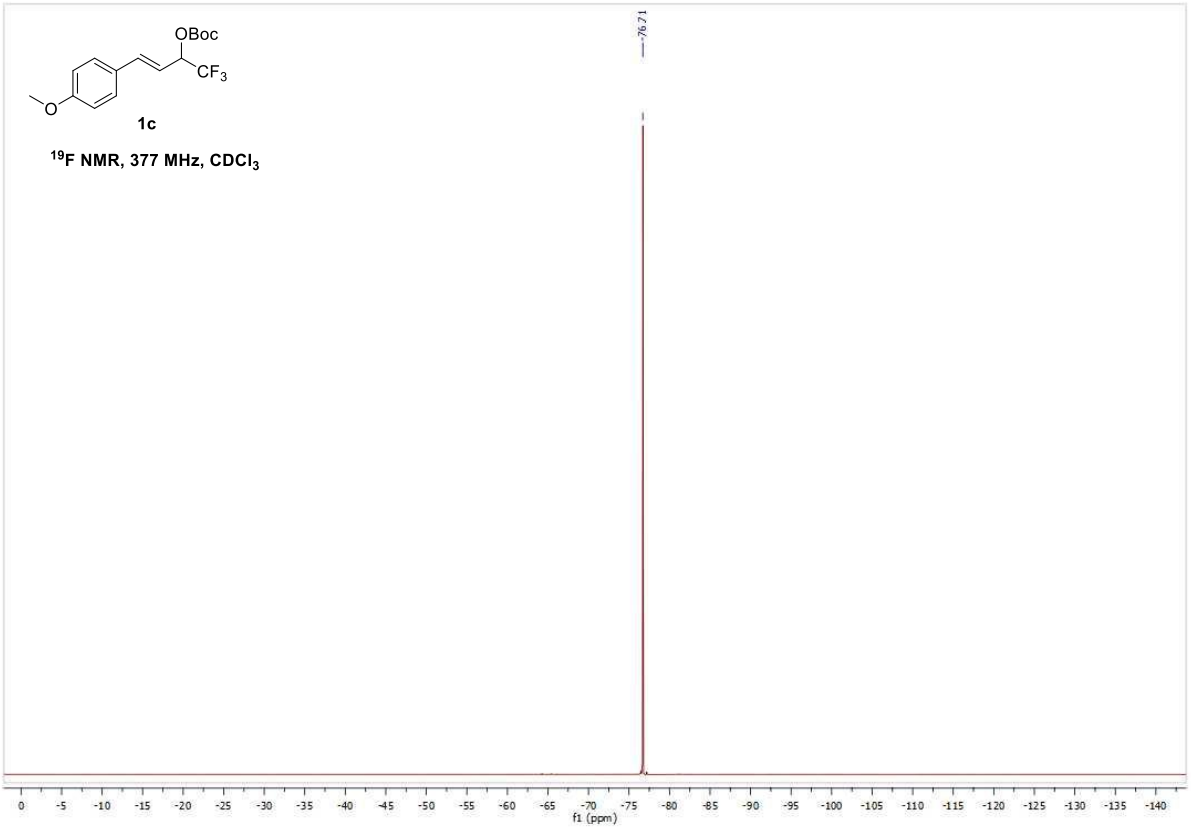
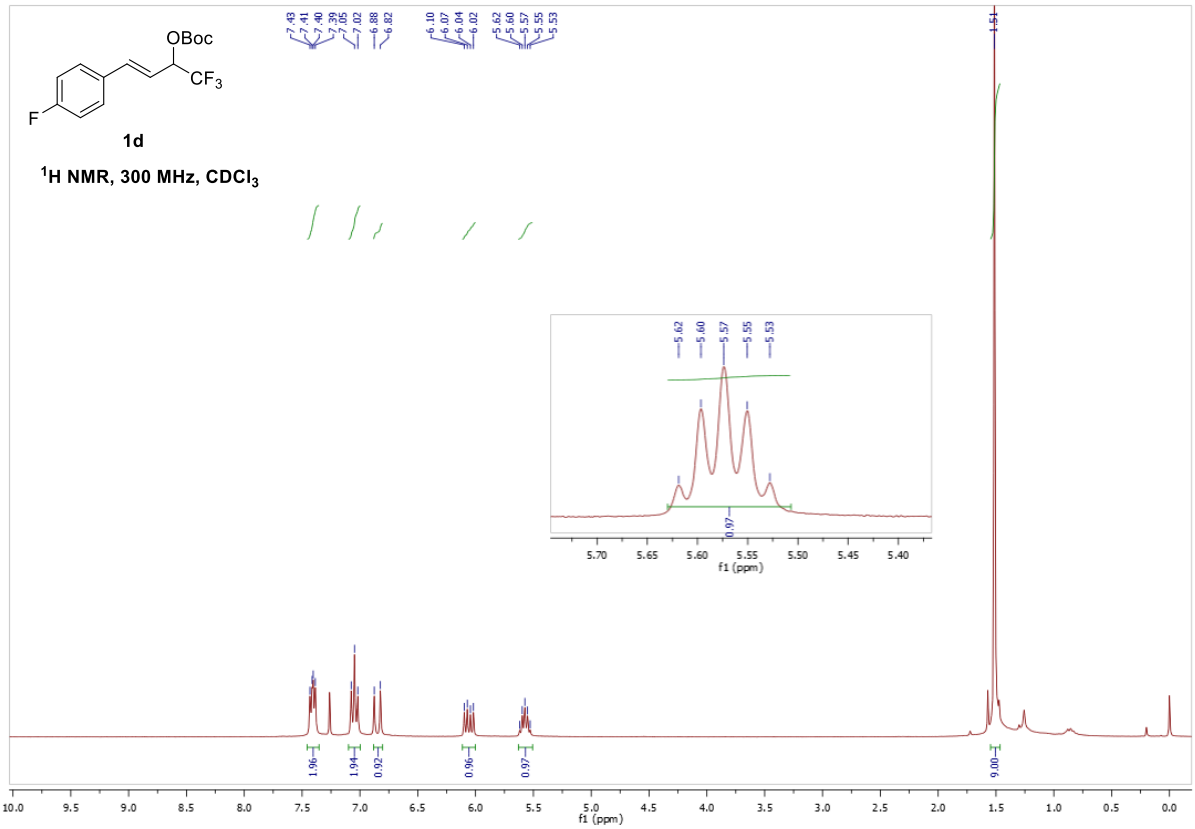
7.35
6.89
6.86
6.80
6.04
6.01
5.98
5.96
5.61
5.59
5.57
5.54
5.52
3.80
1.50
1.99
2.93
0.98
0.99
3.00
8.92
f1 (ppm)

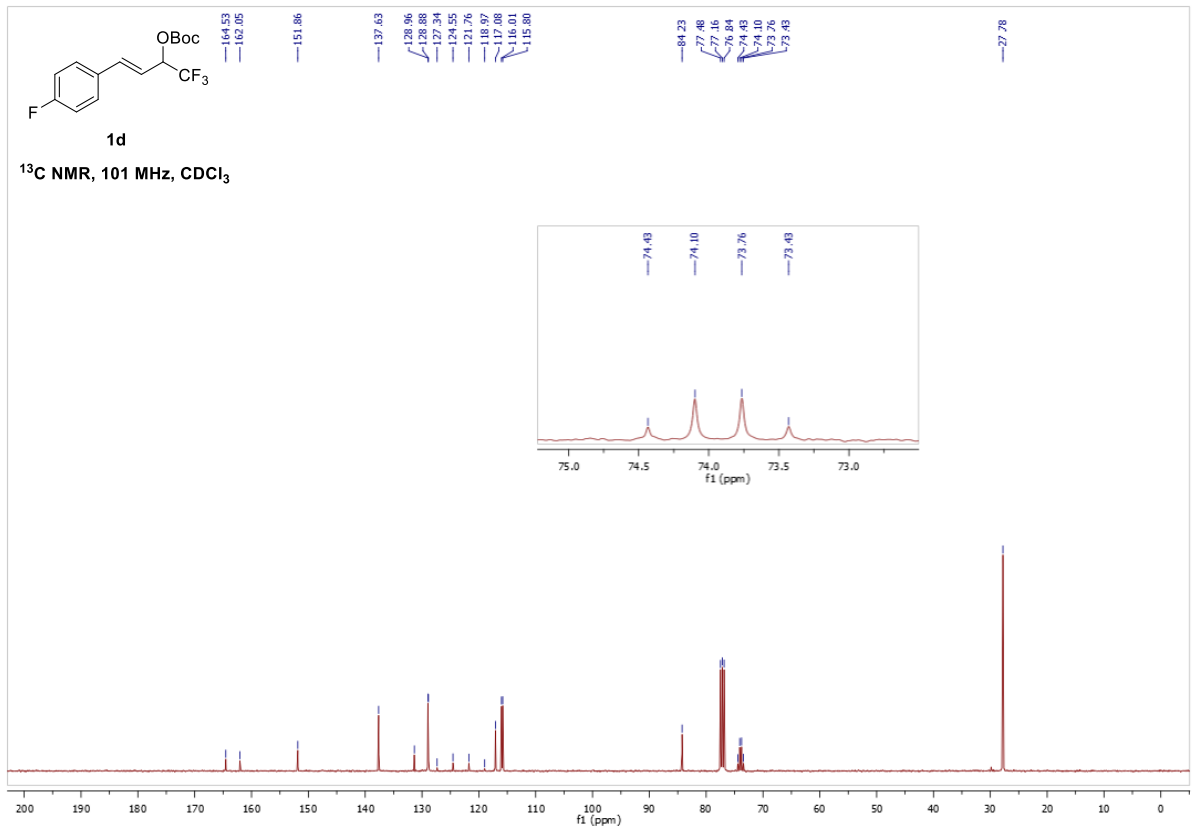


^{13}C NMR, 101 MHz, $CDCl_3$



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


OBoc
CF3
F
1d
1H NMR, 300 MHz, CDCl3
f1 (ppm)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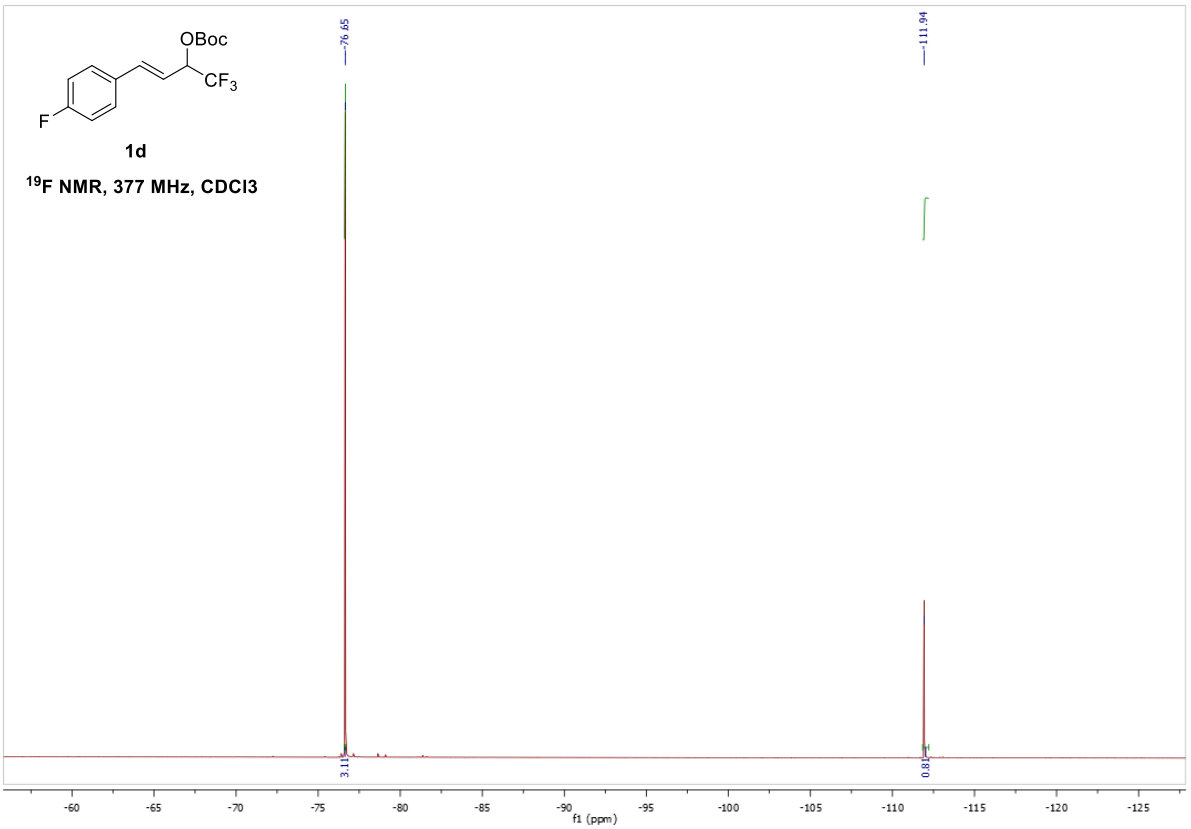
CF3
F
1d
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OBoc
CF3
F
1d
19F NMR, 377 MHz, CDCl3
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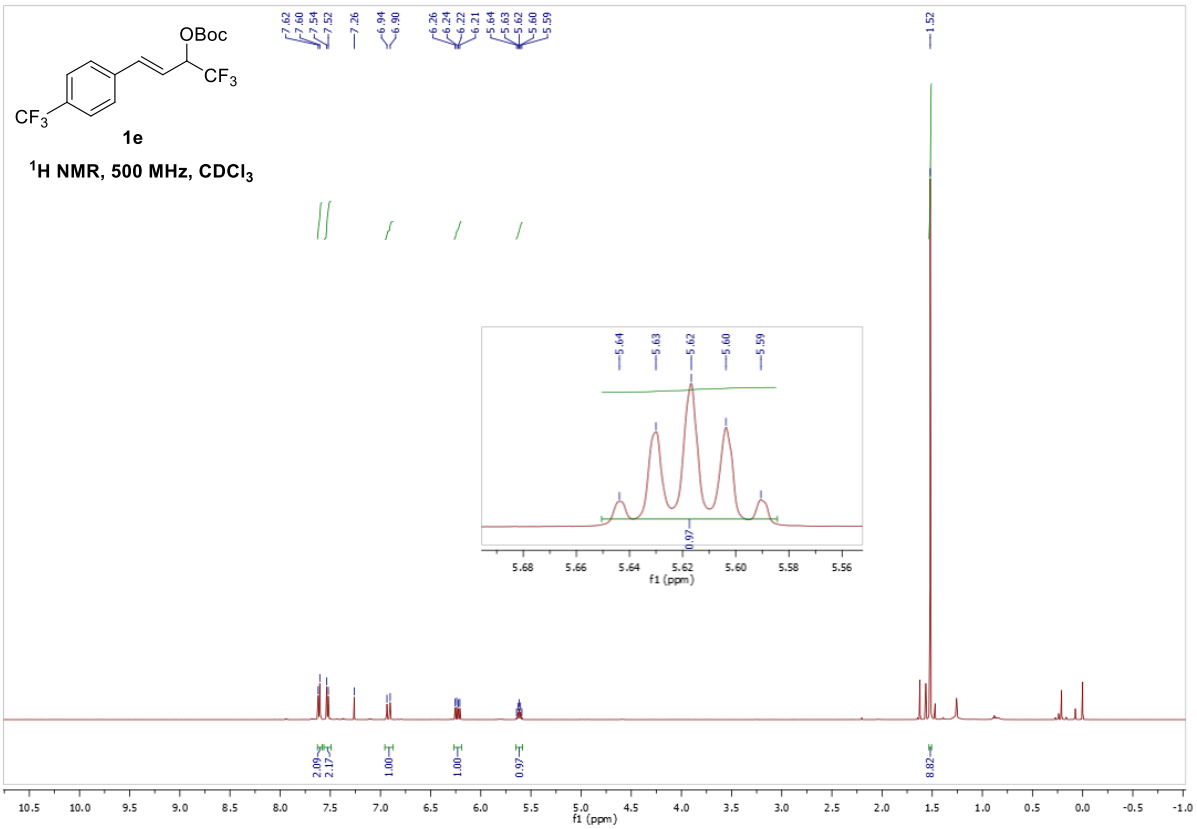
-111.94
3.11
0.81
f1 (ppm)


OBoc
CF3
CF3
1e
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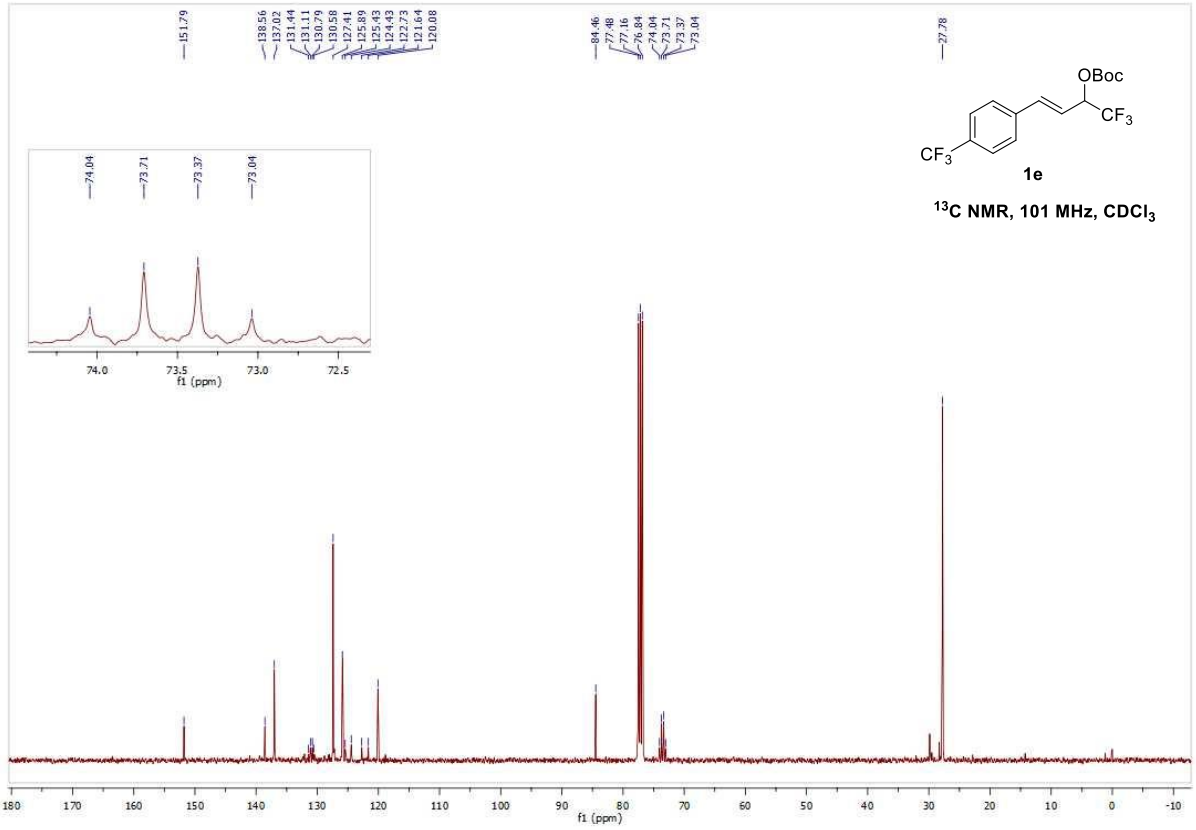
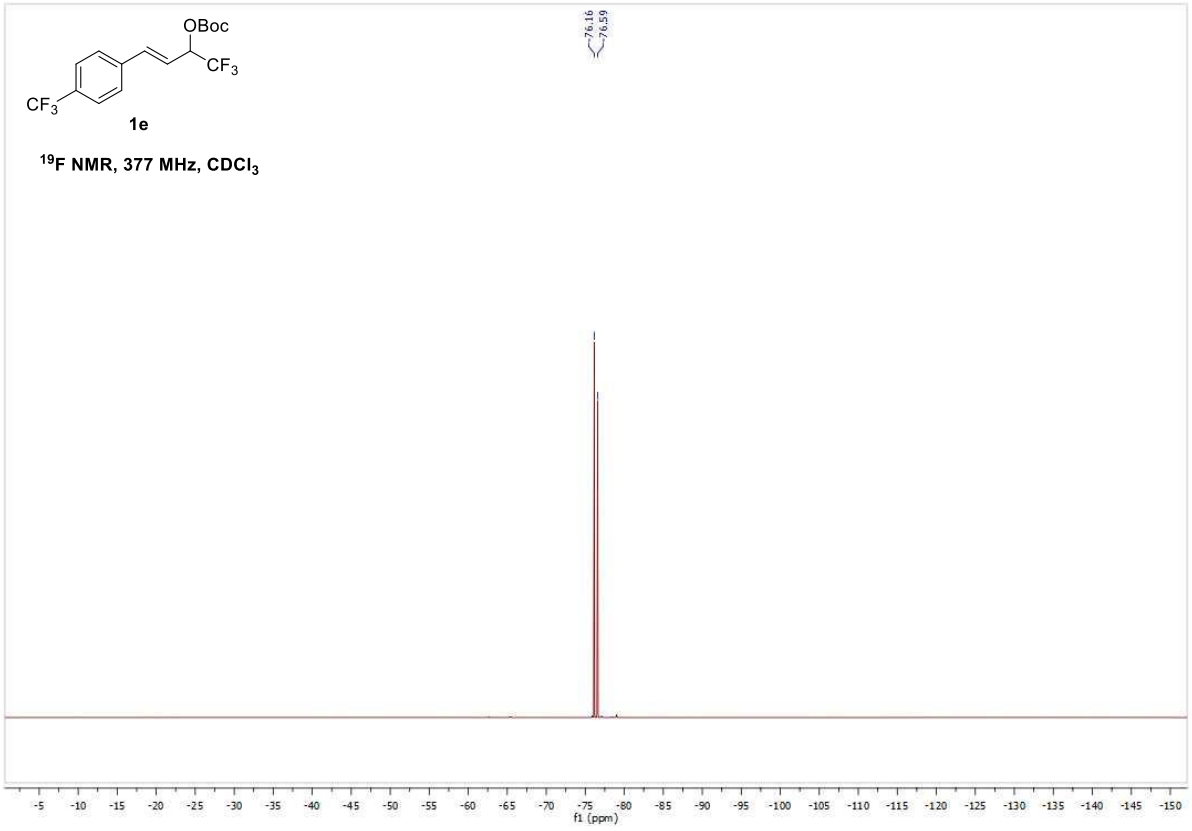
7.60
7.54
7.52
7.26
6.94
6.90
6.26
6.24
6.22
6.21
5.64
5.63
5.62
5.60
5.59
1.52
0.97
2.09
2.17
1.00
1.00
0.97
8.82
f1 (ppm)



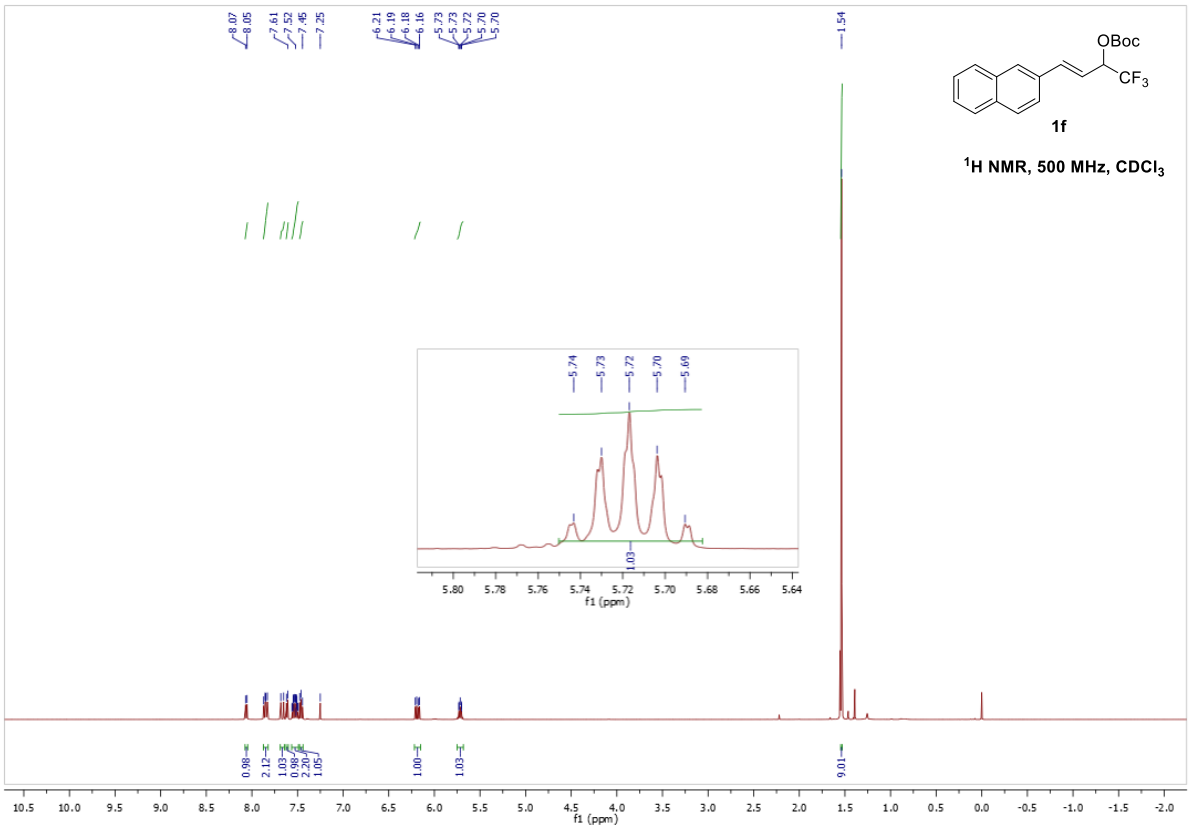
1e

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



1e

^{19}F NMR, 377 MHz, $CDCl_3$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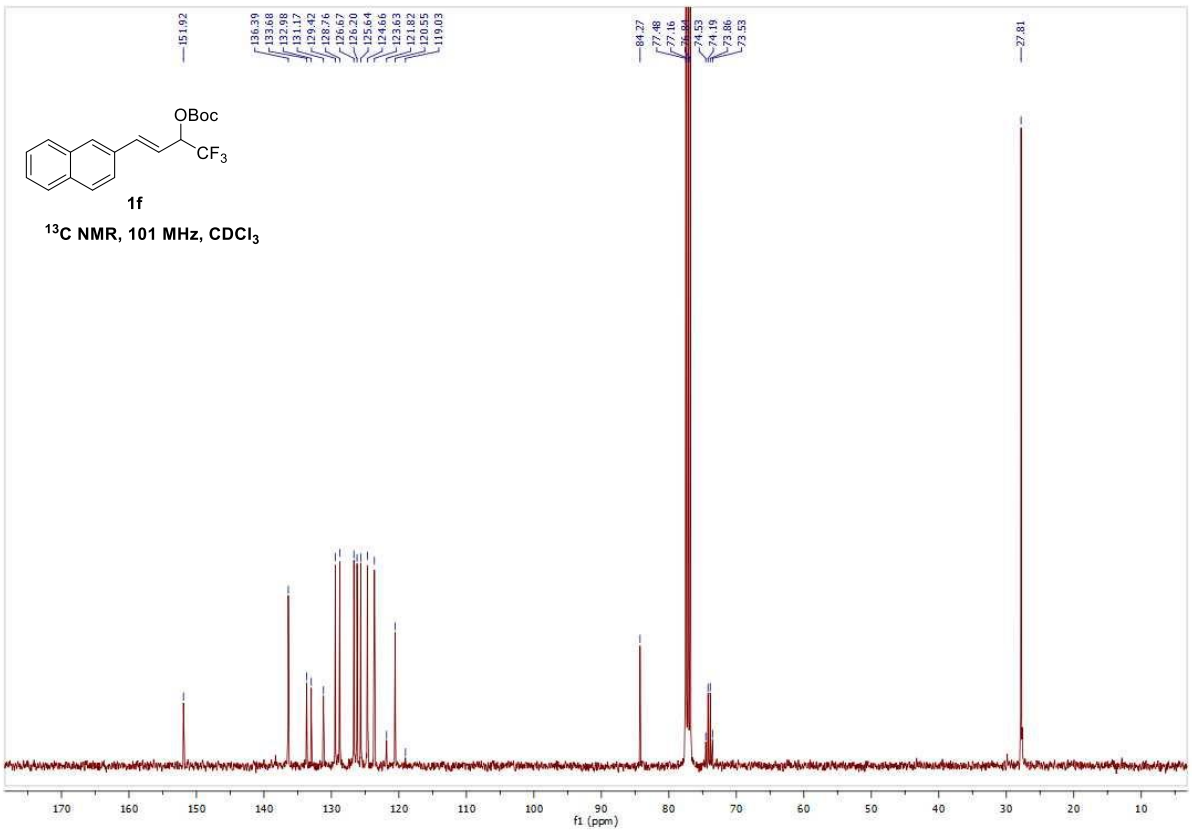
CF3
1f
1H NMR, 500 MHz, CDCl3
f1 (ppm)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CF3
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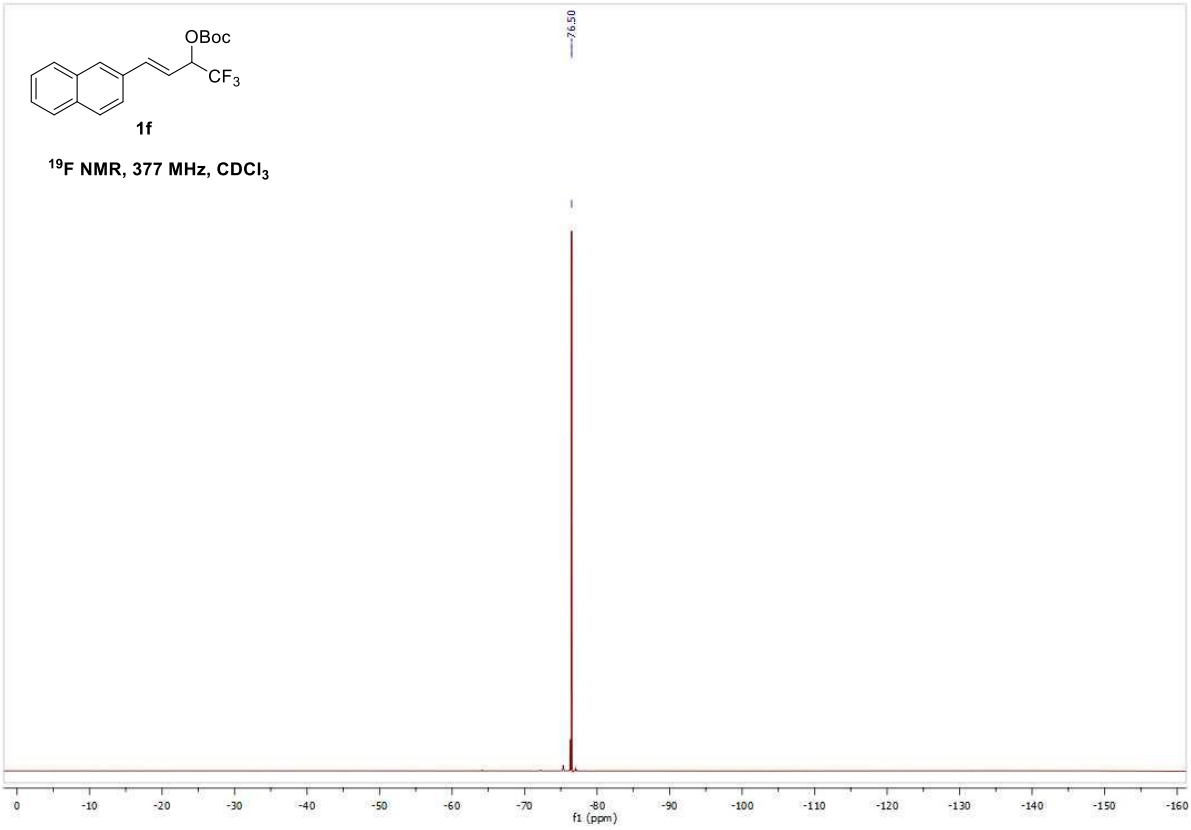
13C NMR, 101 MHz, CDCl3
f1 (ppm)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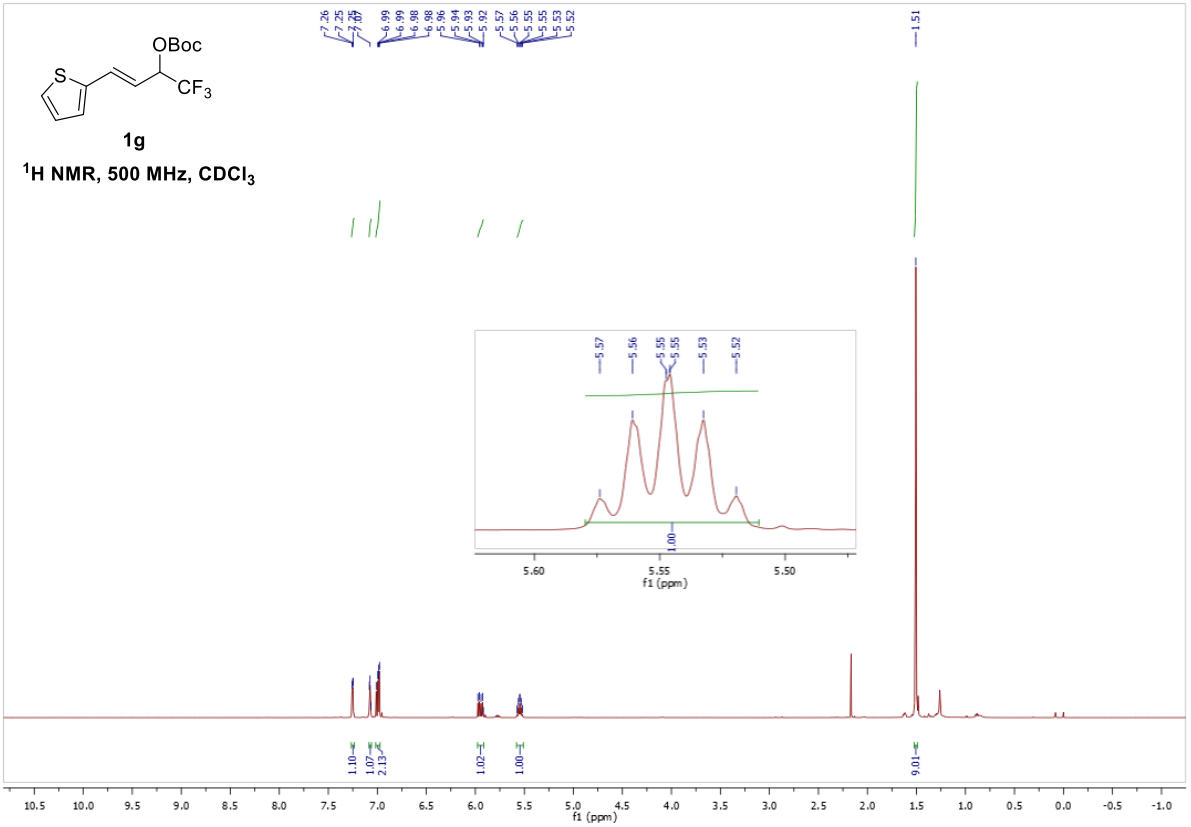
CF3
1f
19F NMR, 377 MHz, CDCl3
-76.50
f1 (ppm)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S
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1g
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7.23
6.99
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5.92
5.57
5.56
5.55
5.55
5.53
5.52
1.51
5.57
5.56
5.55
5.55
5.53
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f1 (ppm)
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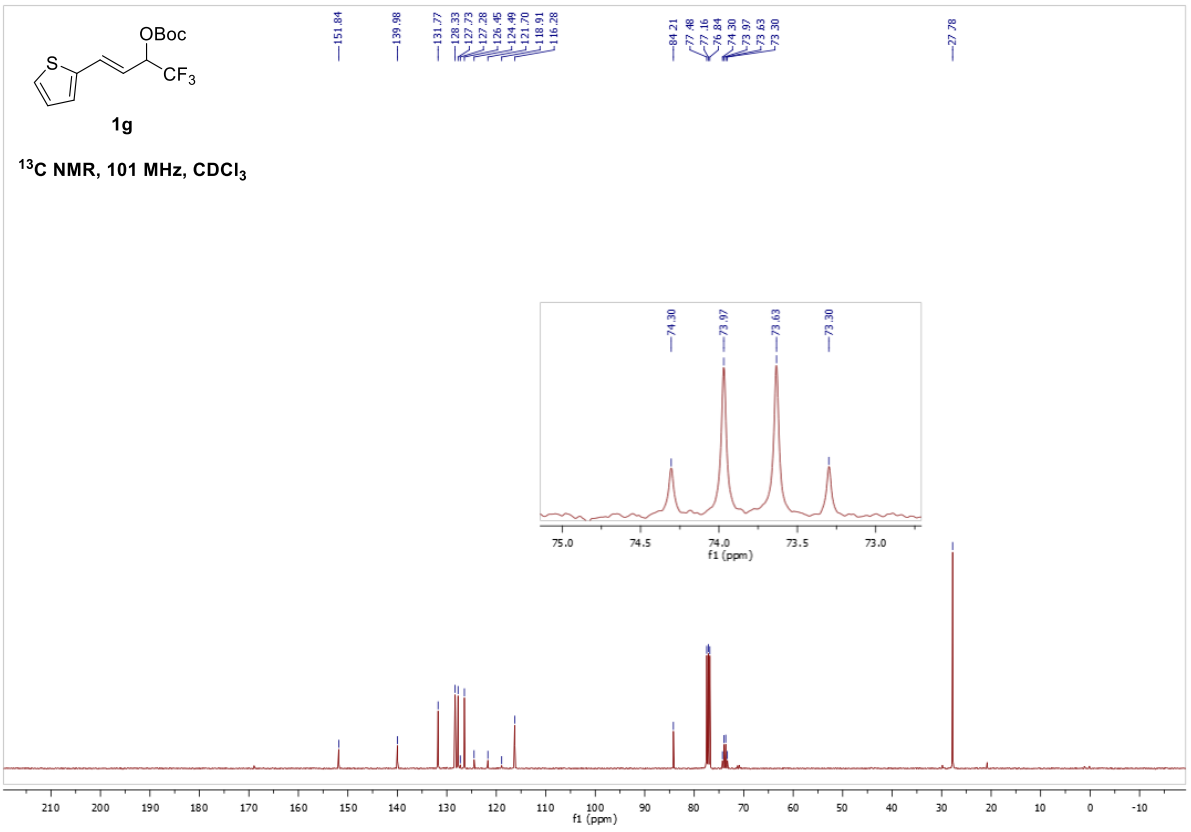
1.02
1.00
9.01
f1 (ppm)



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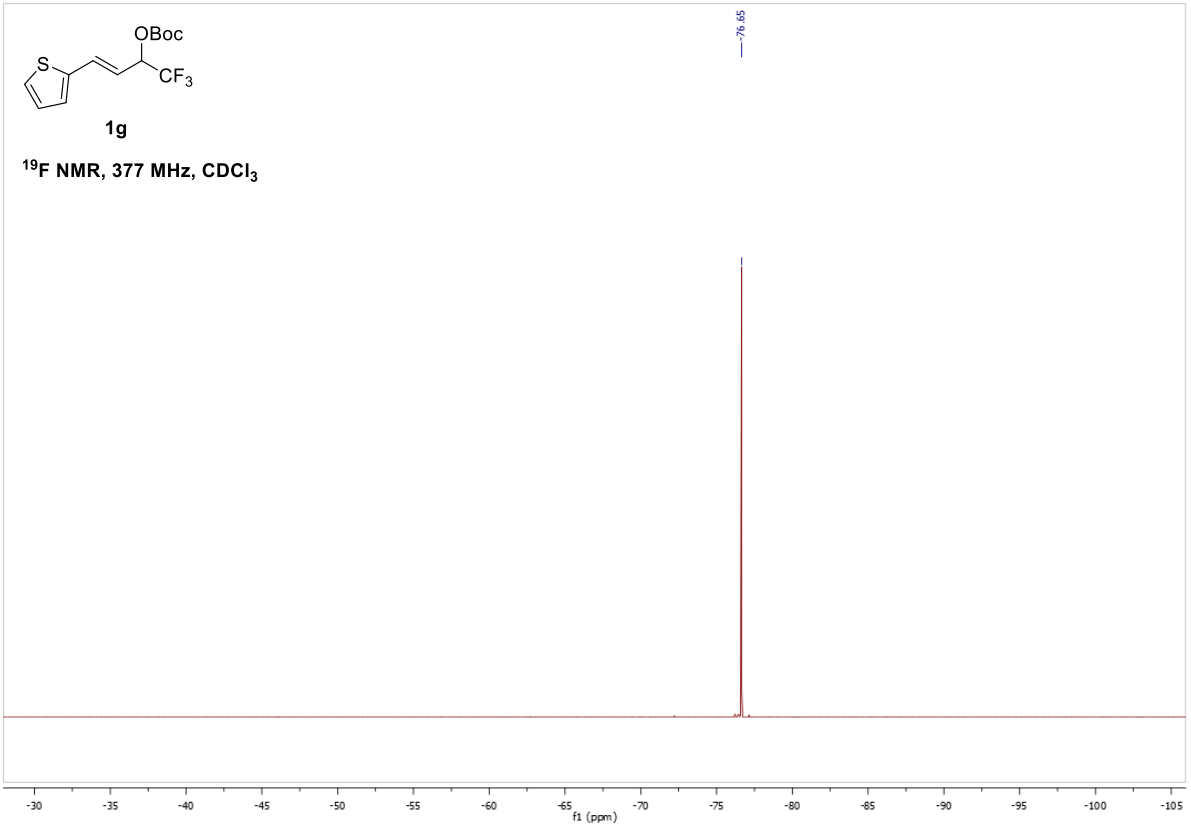
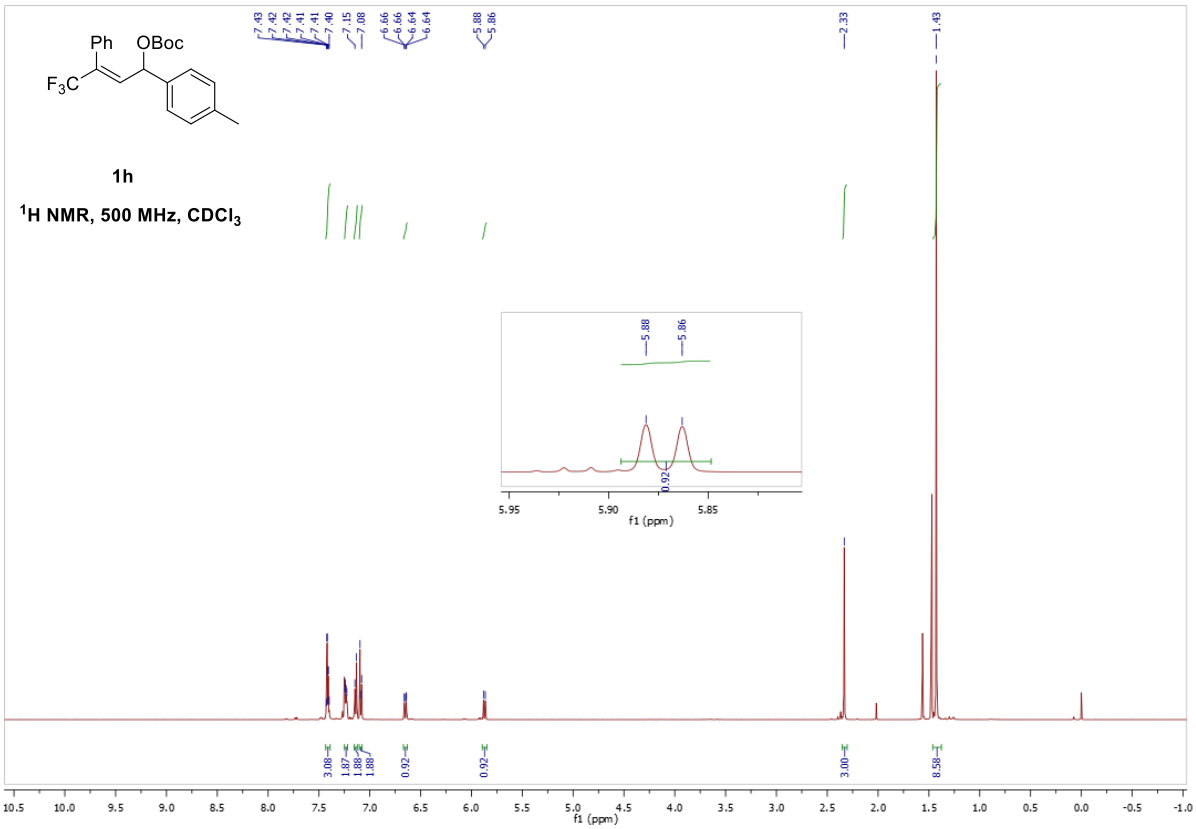


^{19}F NMR, 377 MHz, $CDCl_3$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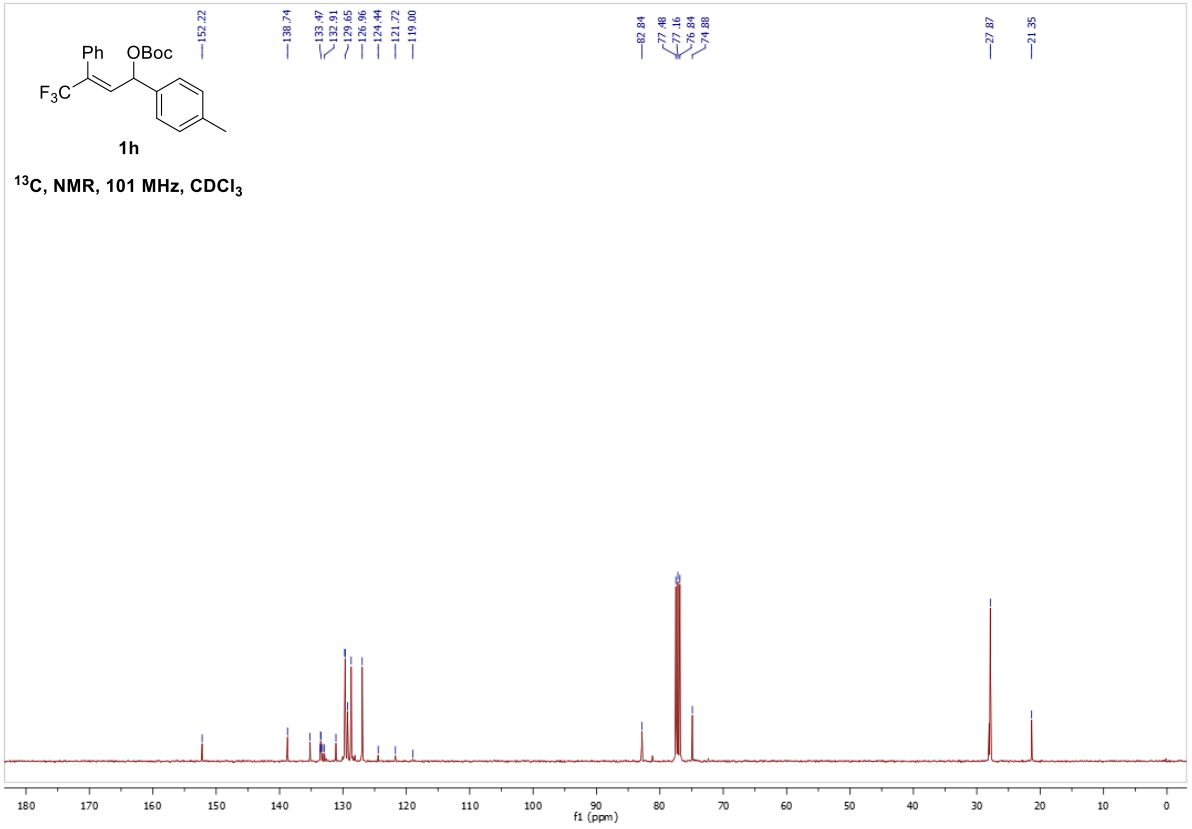
F3C
1h
1H NMR, 500 MHz, CDCl3
f1 (ppm)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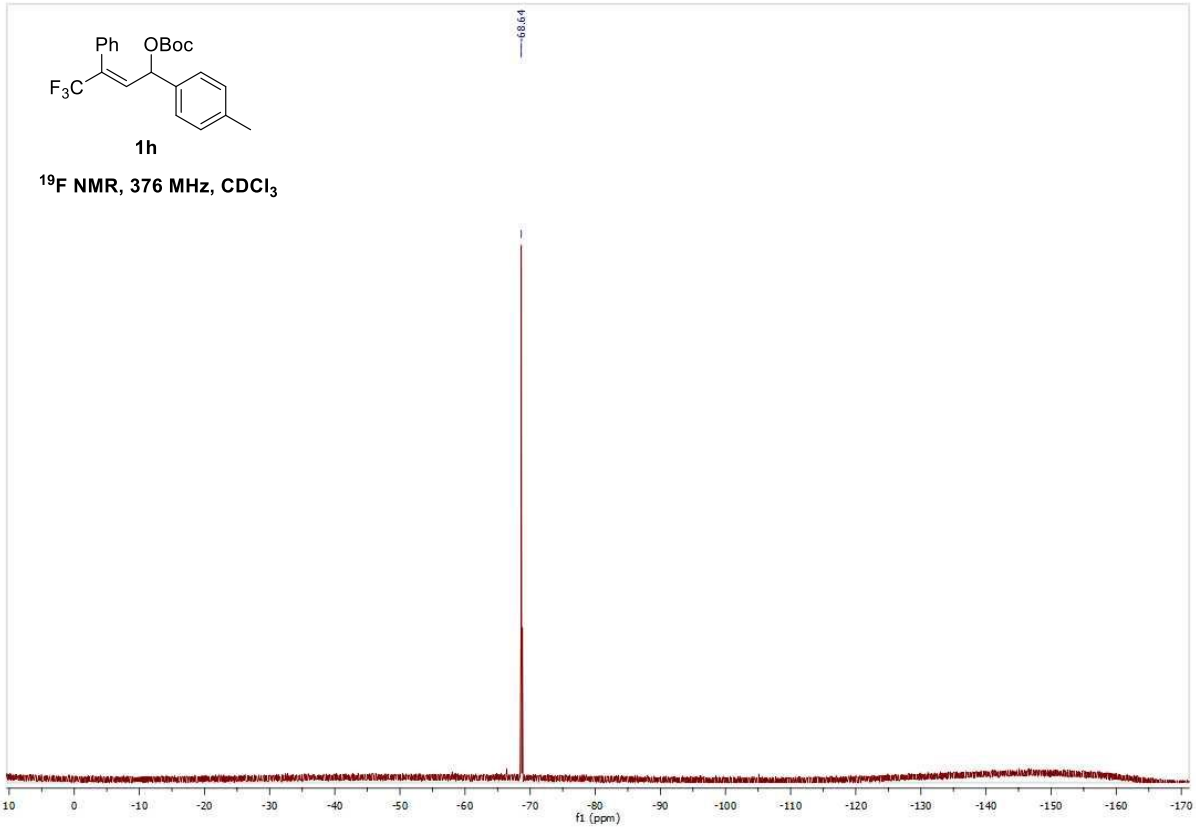
F3C
1h
13C, NMR, 101 MHz, CDCl3
f1 (ppm)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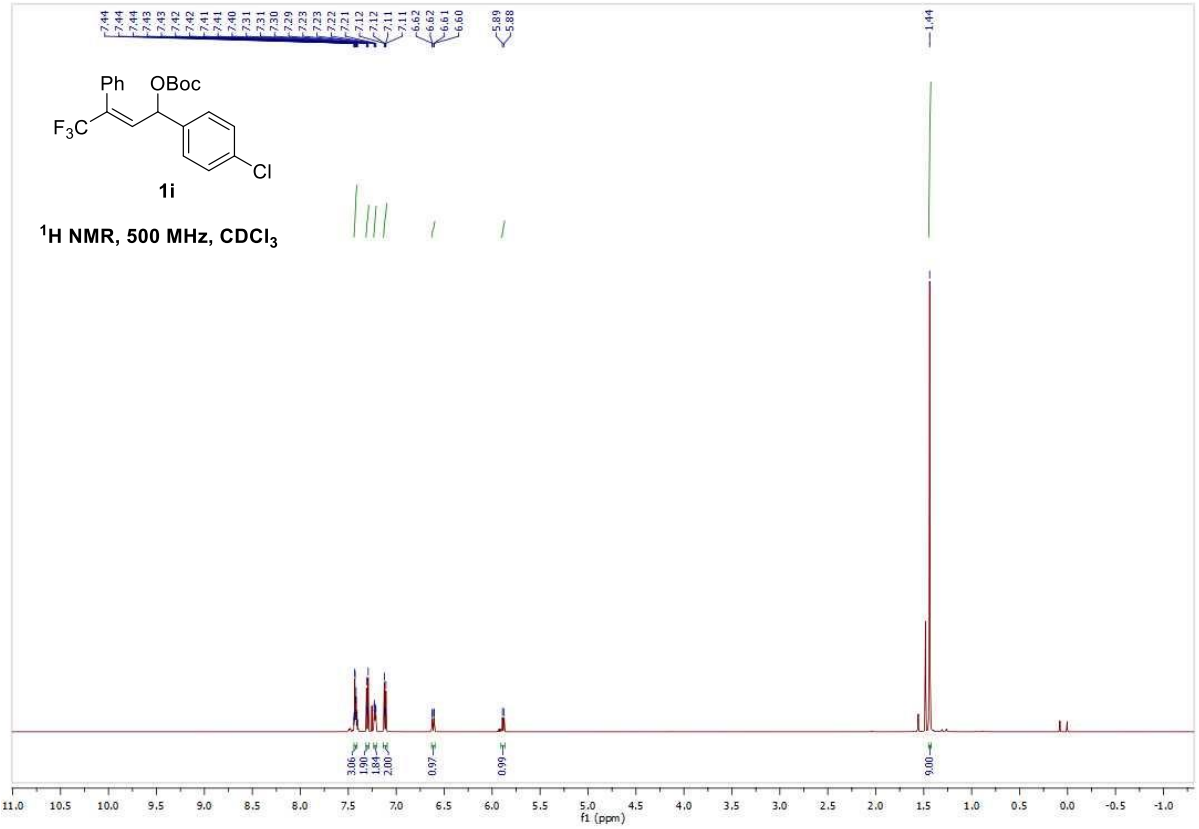
OBoc
F3C
1h
19F NMR, 376 MHz, CDCl3
-68.64
f1 (ppm)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OBoc
F3C
Cl
1i
1H NMR, 500 MHz, CDCl3
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7.43
7.43
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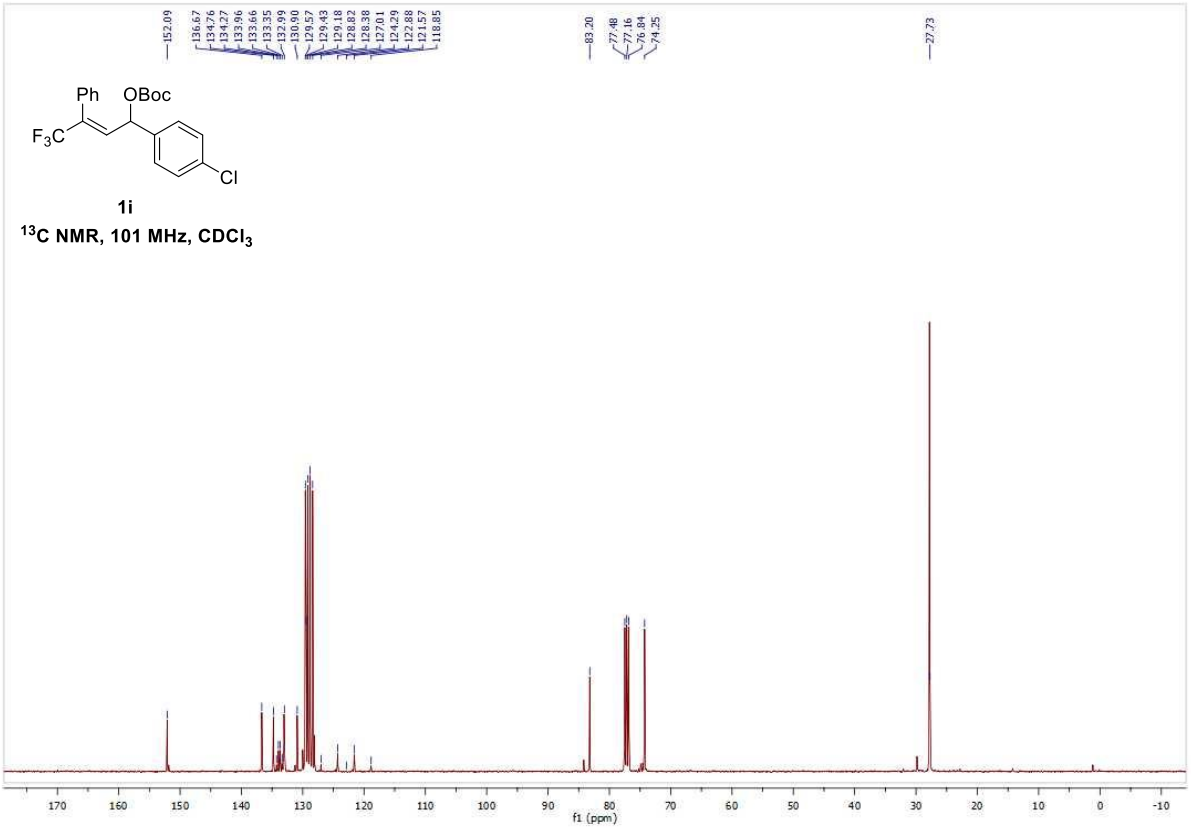
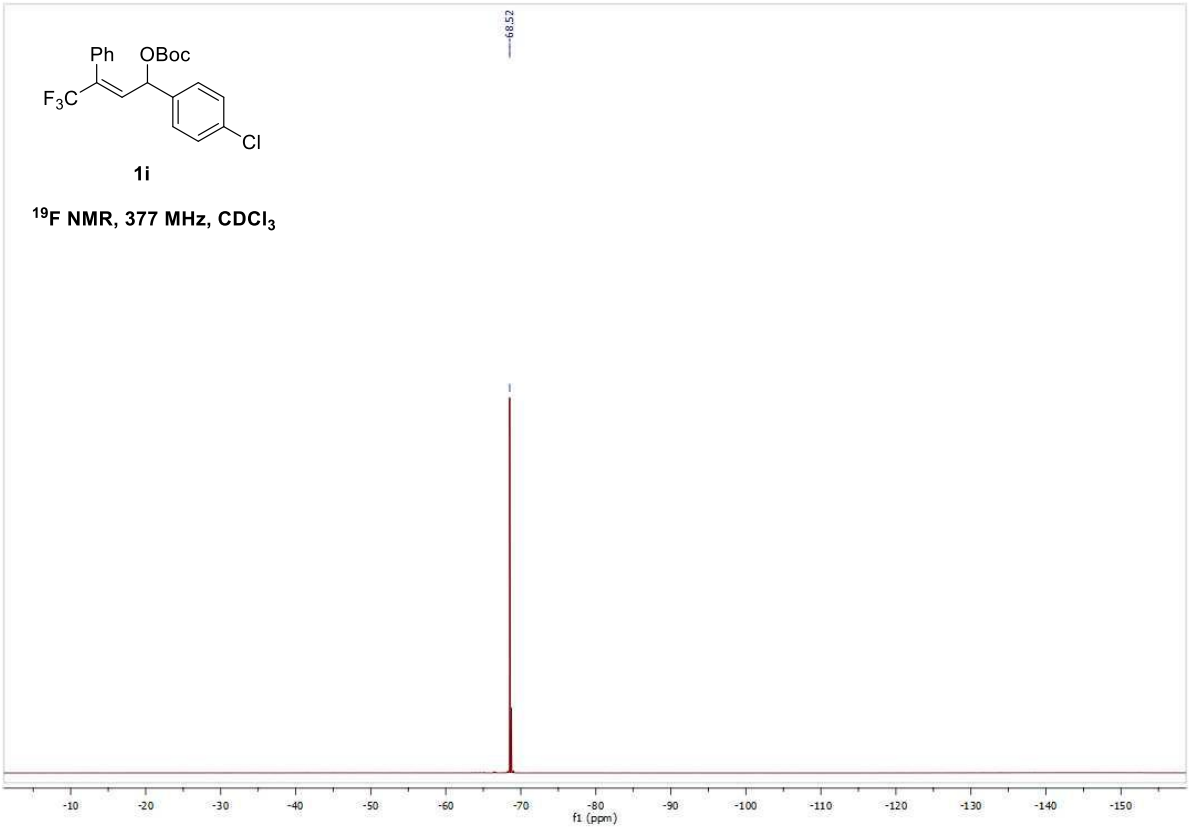
7.42
7.41
7.41
7.40
7.31
7.31
7.30
7.29
7.23
7.23
7.22
7.21
7.12
7.11
6.62
6.62
6.61
6.60
5.89
5.88
1.44
3.06
1.90
1.84
2.00
0.97
0.99
9.00
f1 (ppm)



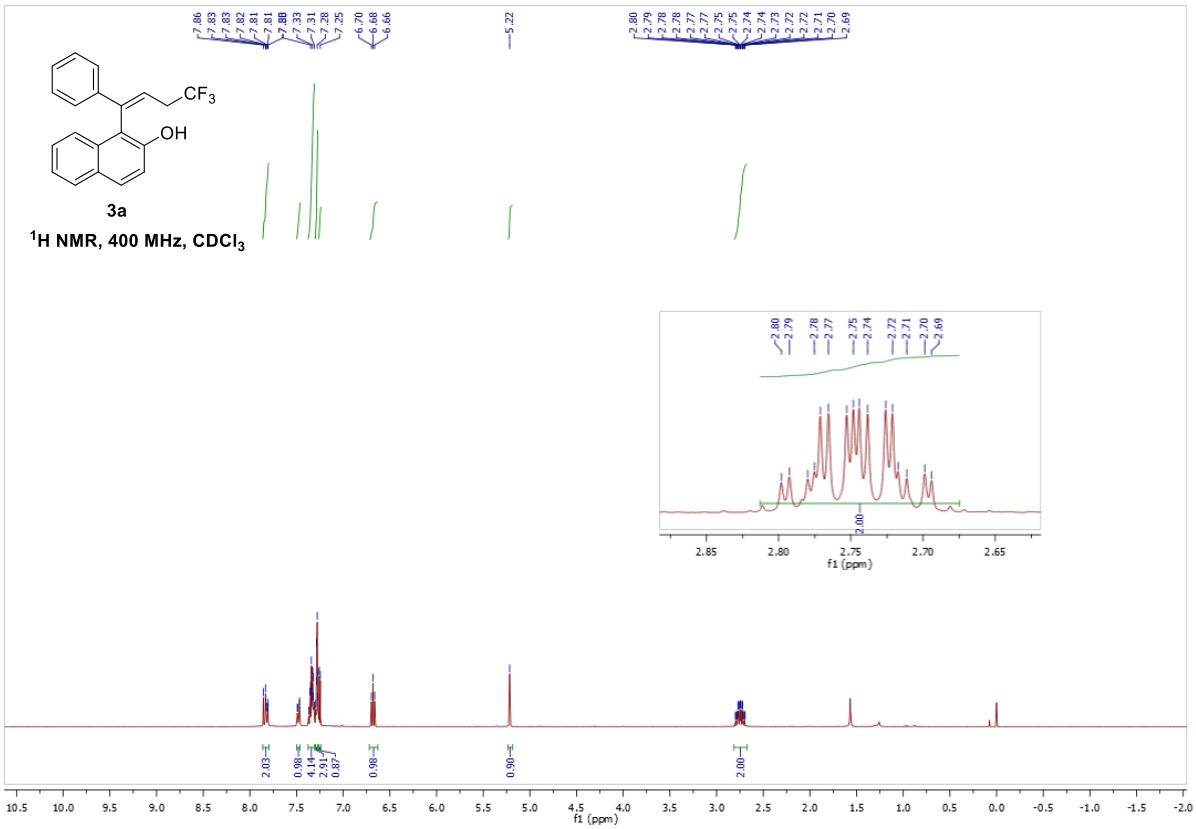
1i

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



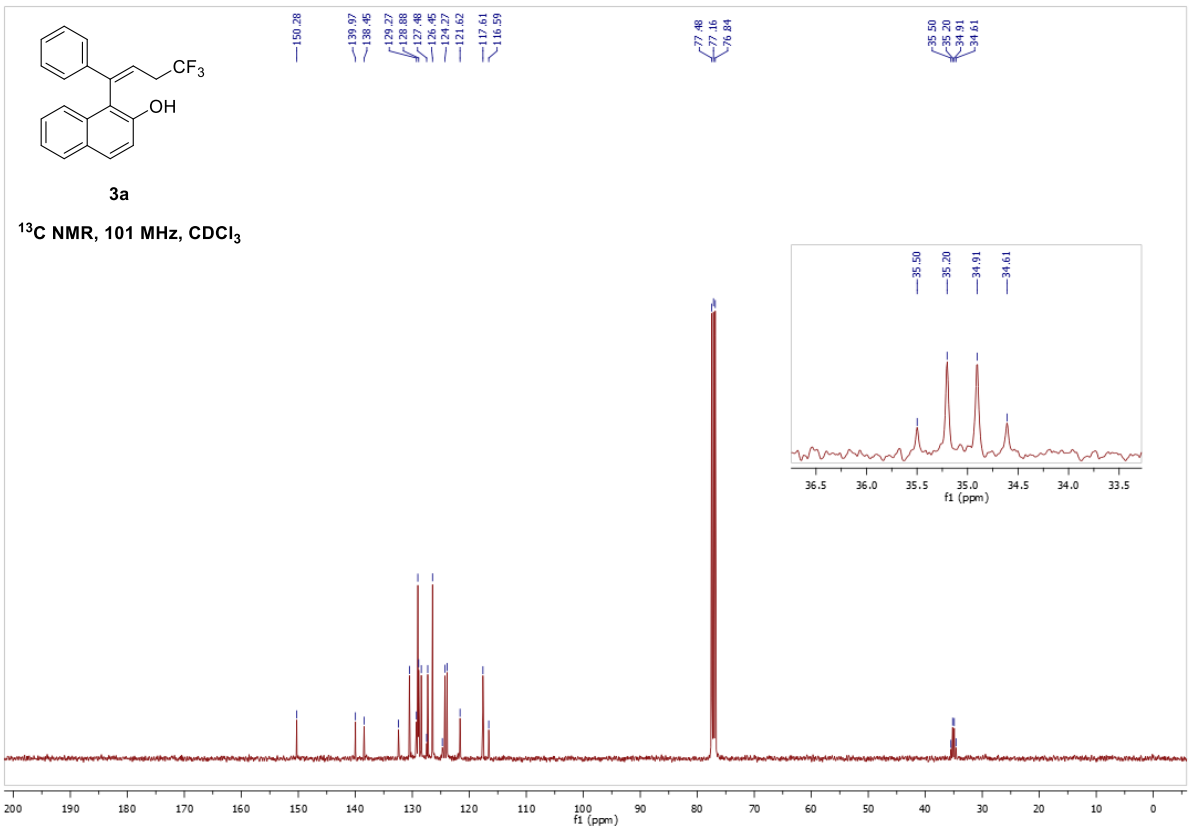
1i

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



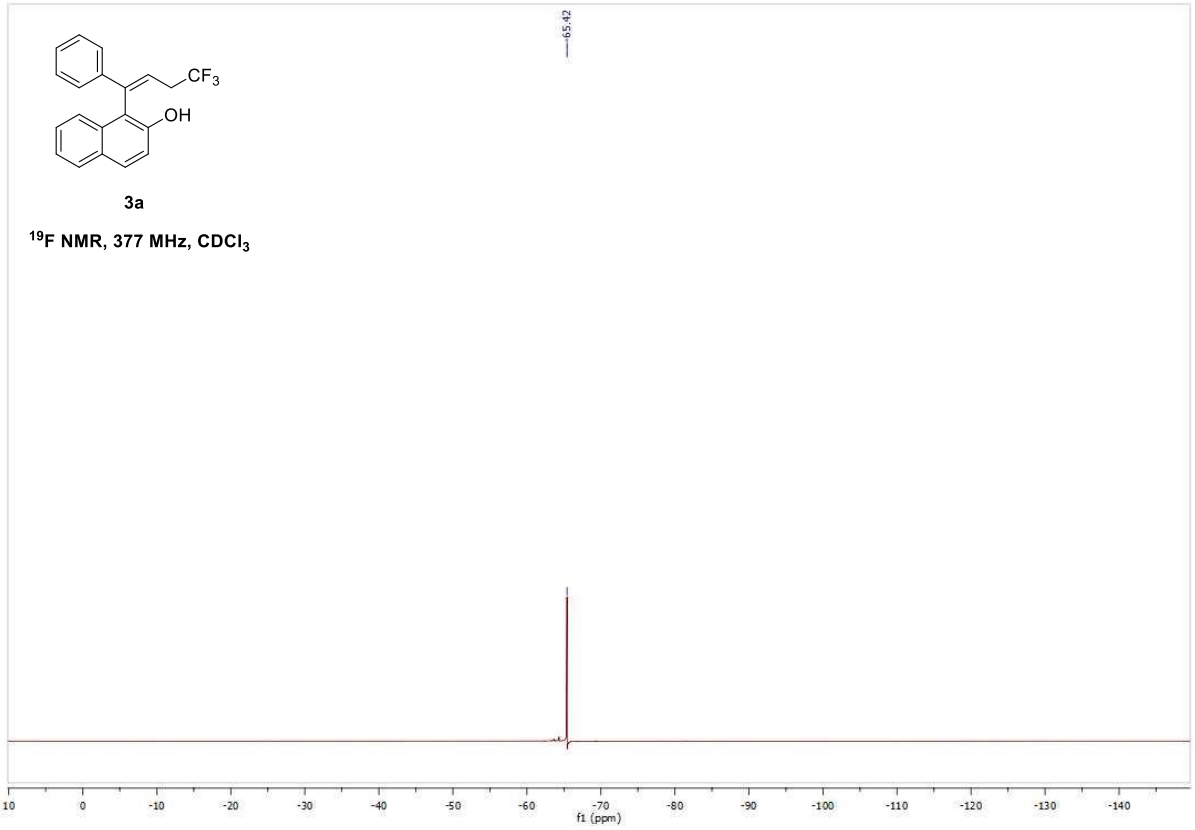
3a

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



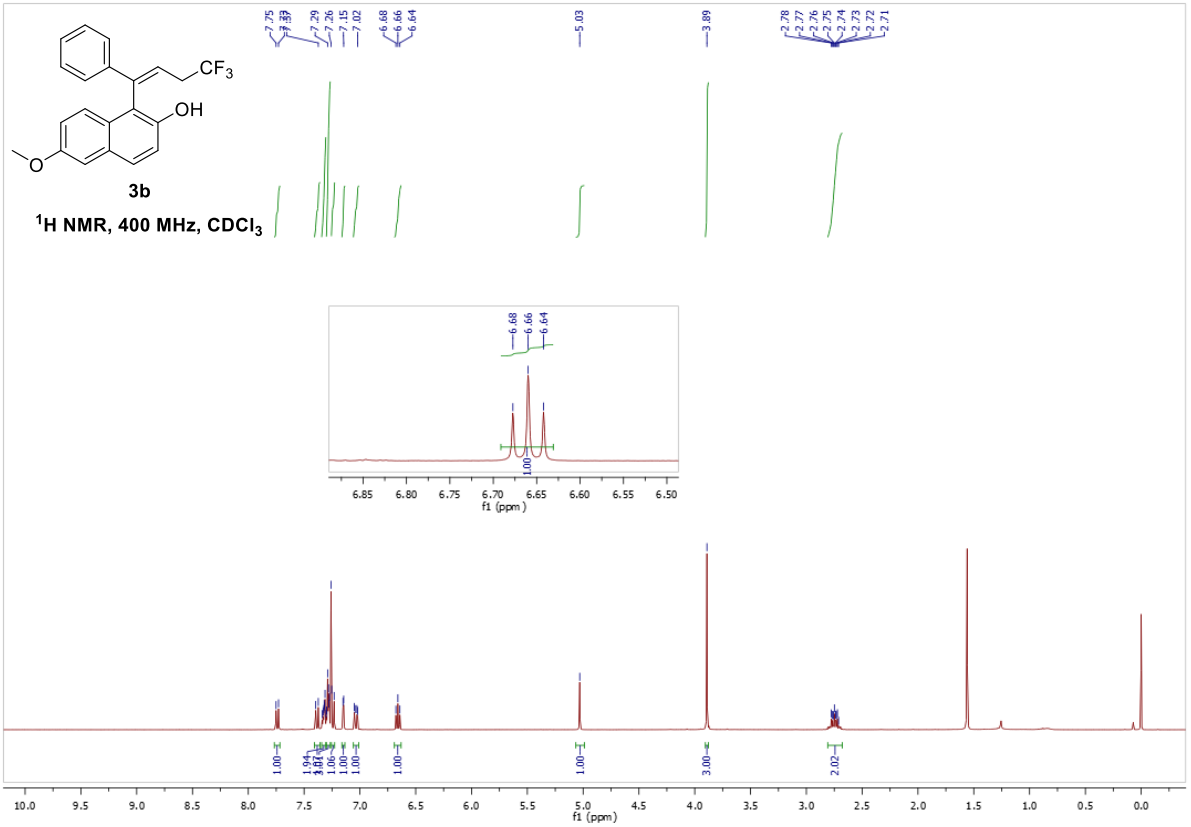
3a

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



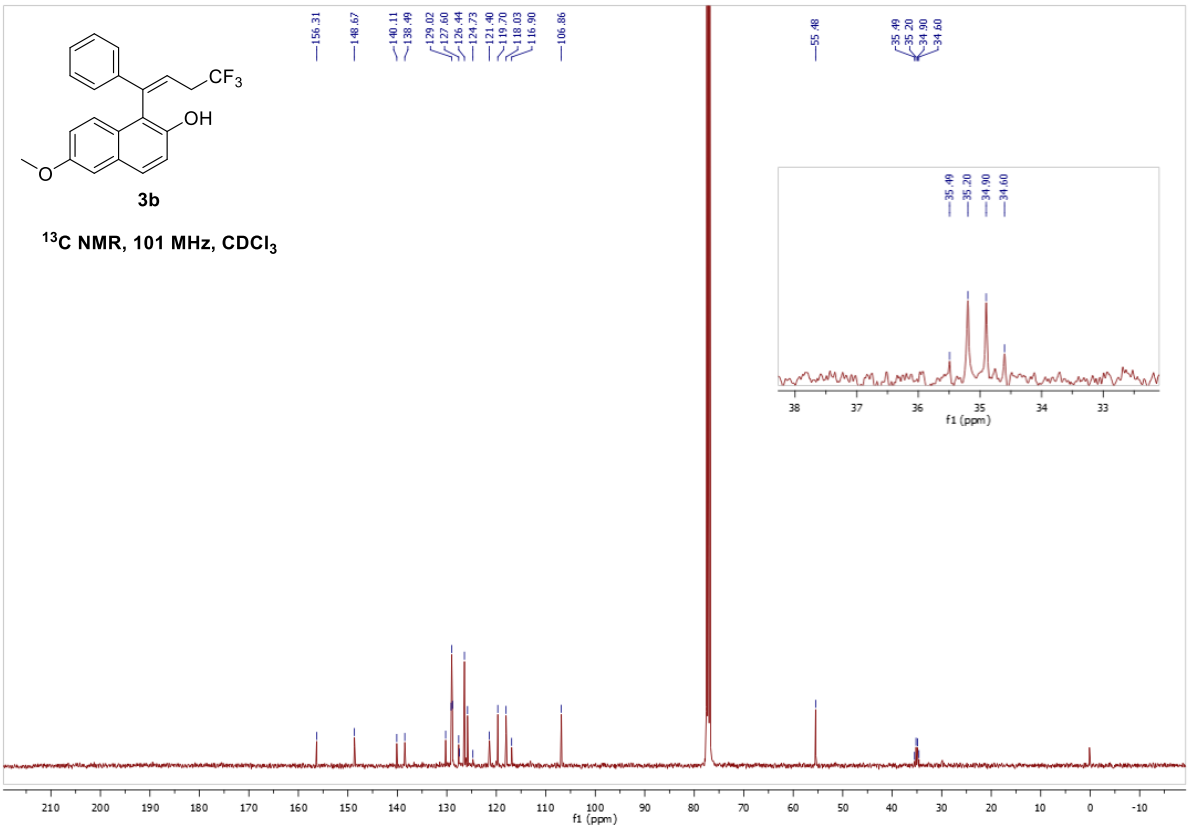
3a

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

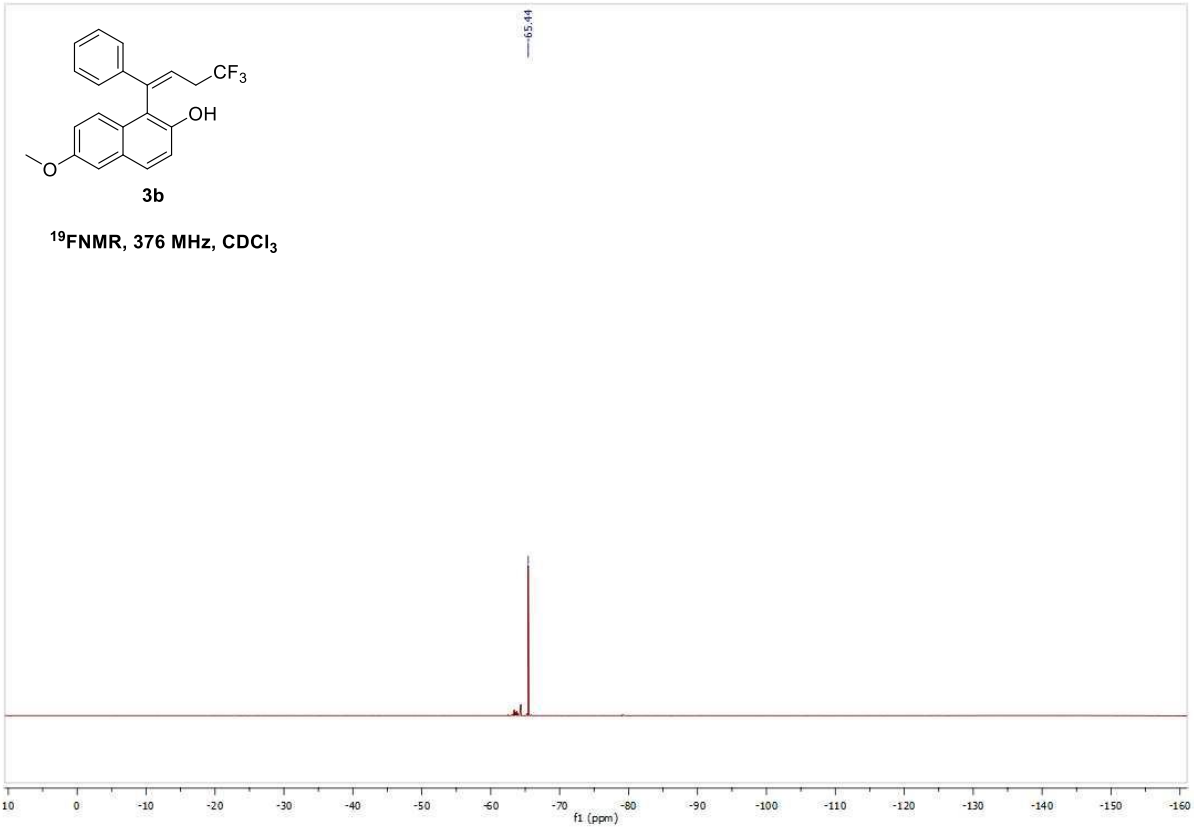


3b

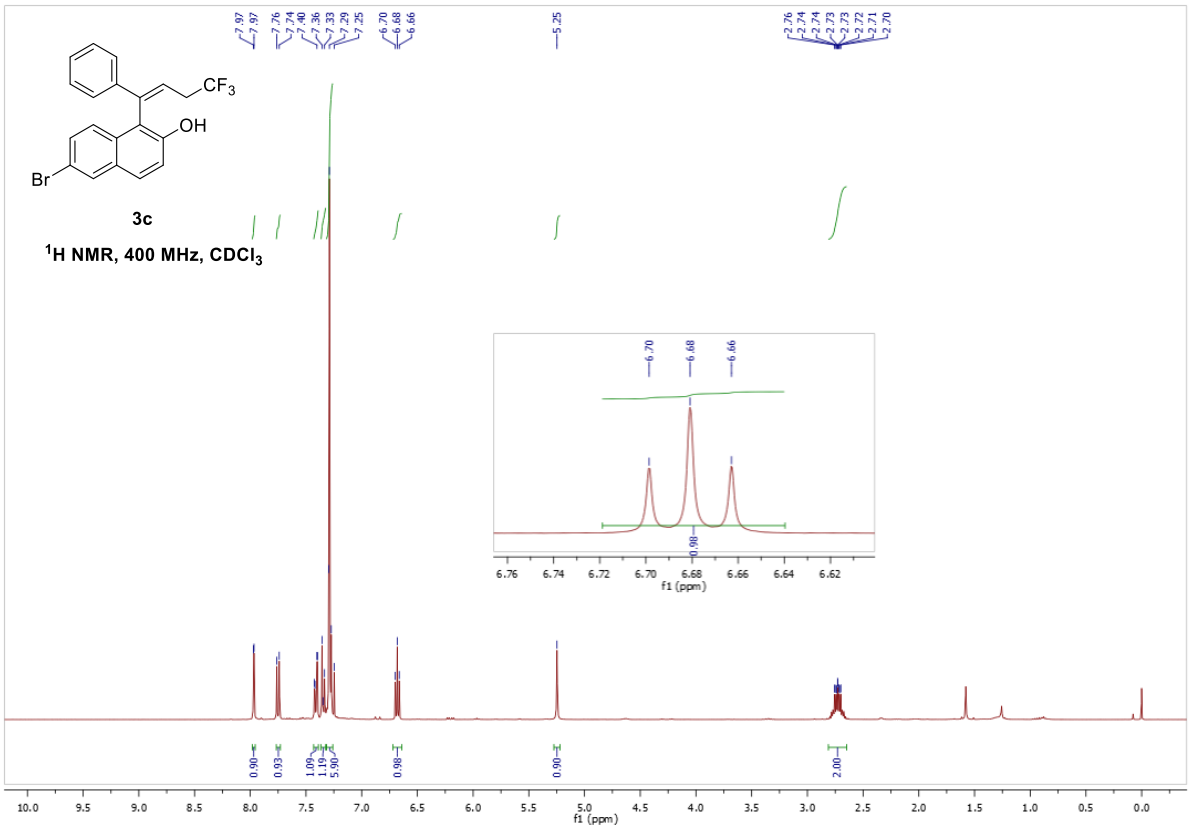
^{1}H NMR, 400 MHz, $CDCl_3$

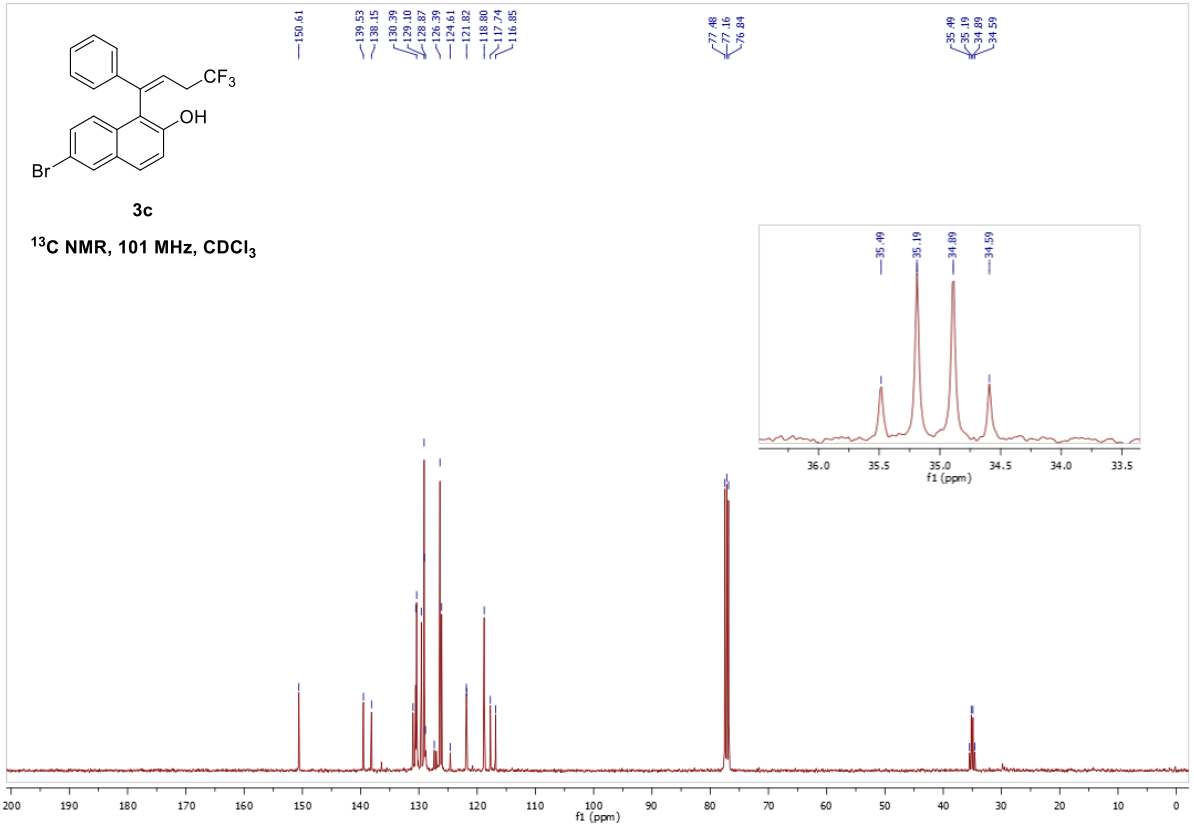


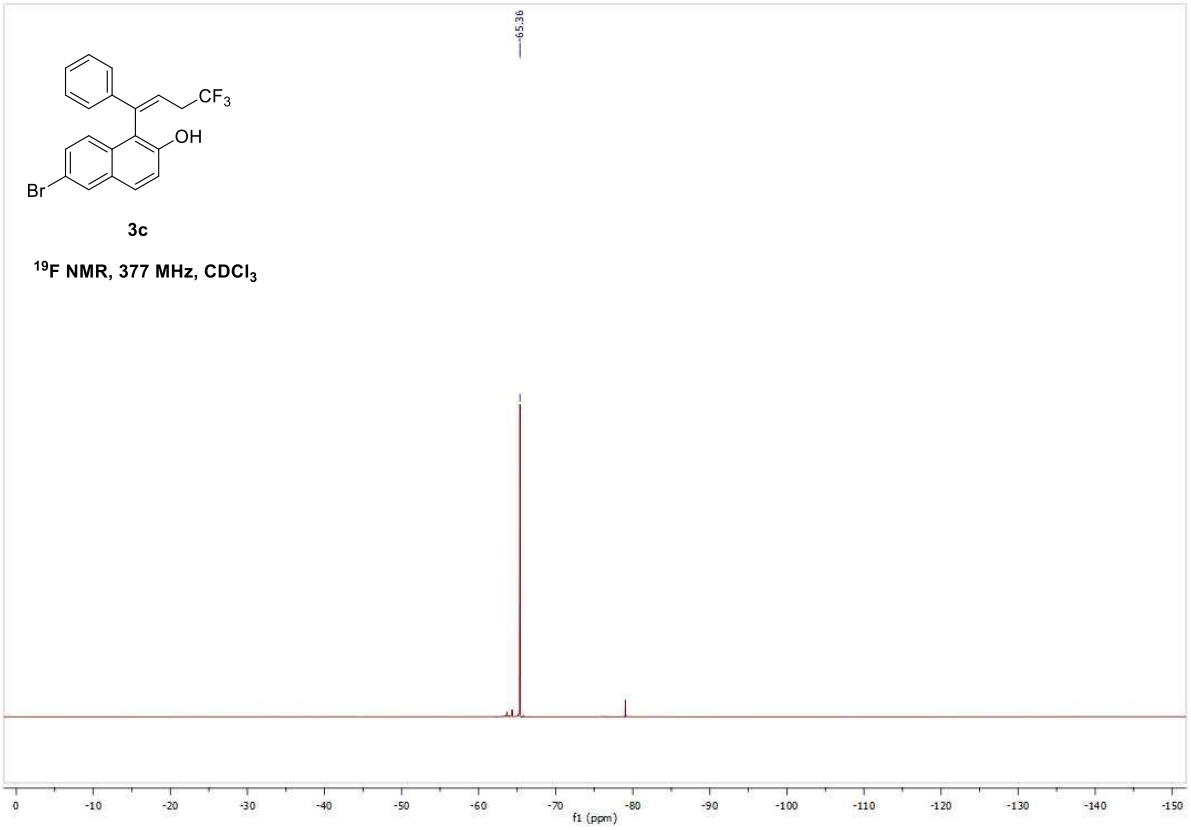
^{13}C NMR, 101 MHz, $CDCl_3$



^{19}FNMR, 376 MHz, $CDCl_3$

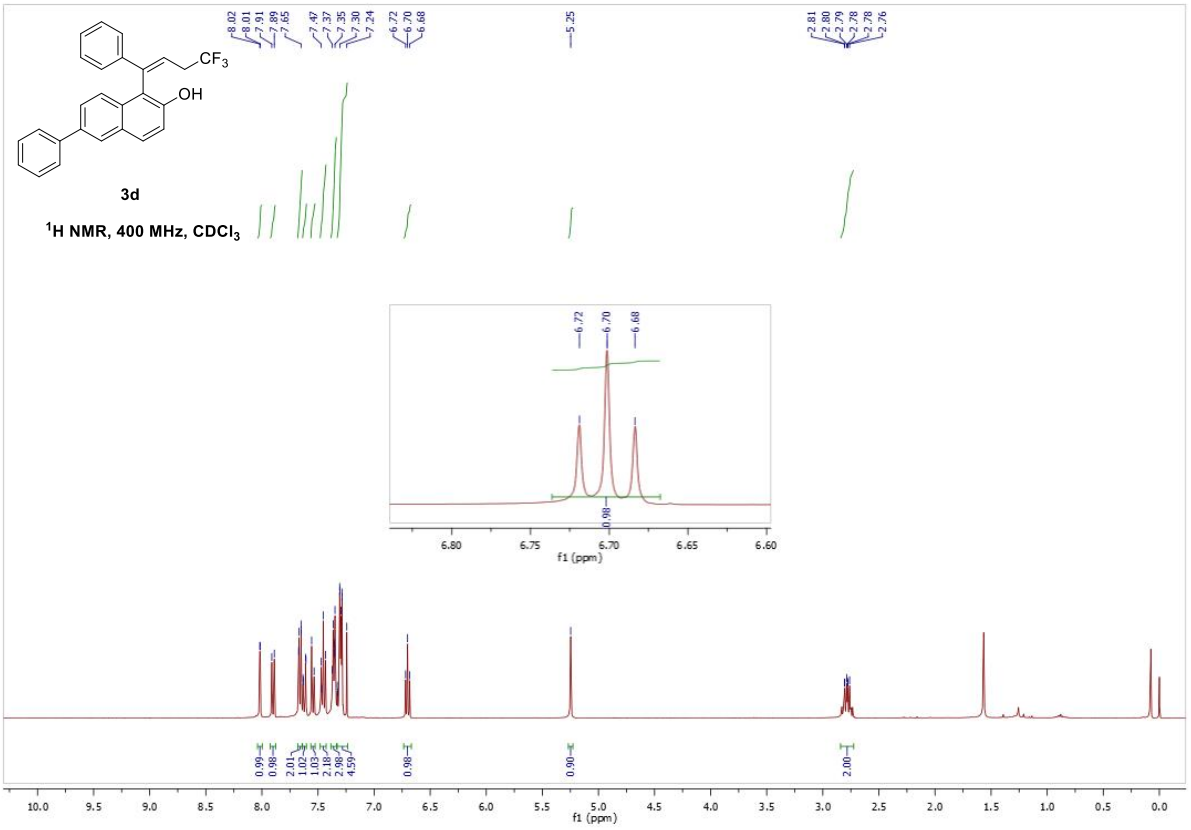

CF3
OH
Br
3c
1H NMR, 400 MHz, CDCl3
f1 (ppm)


CF3
OH
Br
3c
13C NMR, 101 MHz, CDCl3
f1 (ppm)



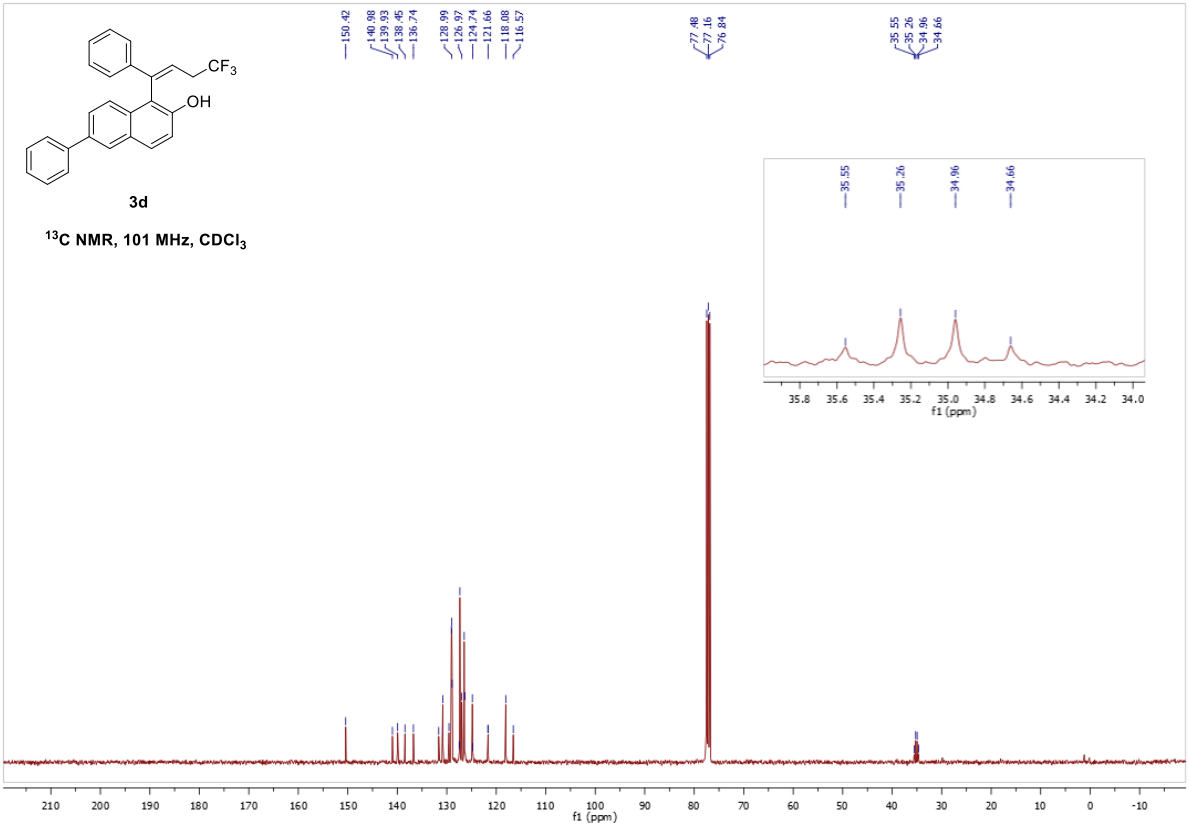
3c

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



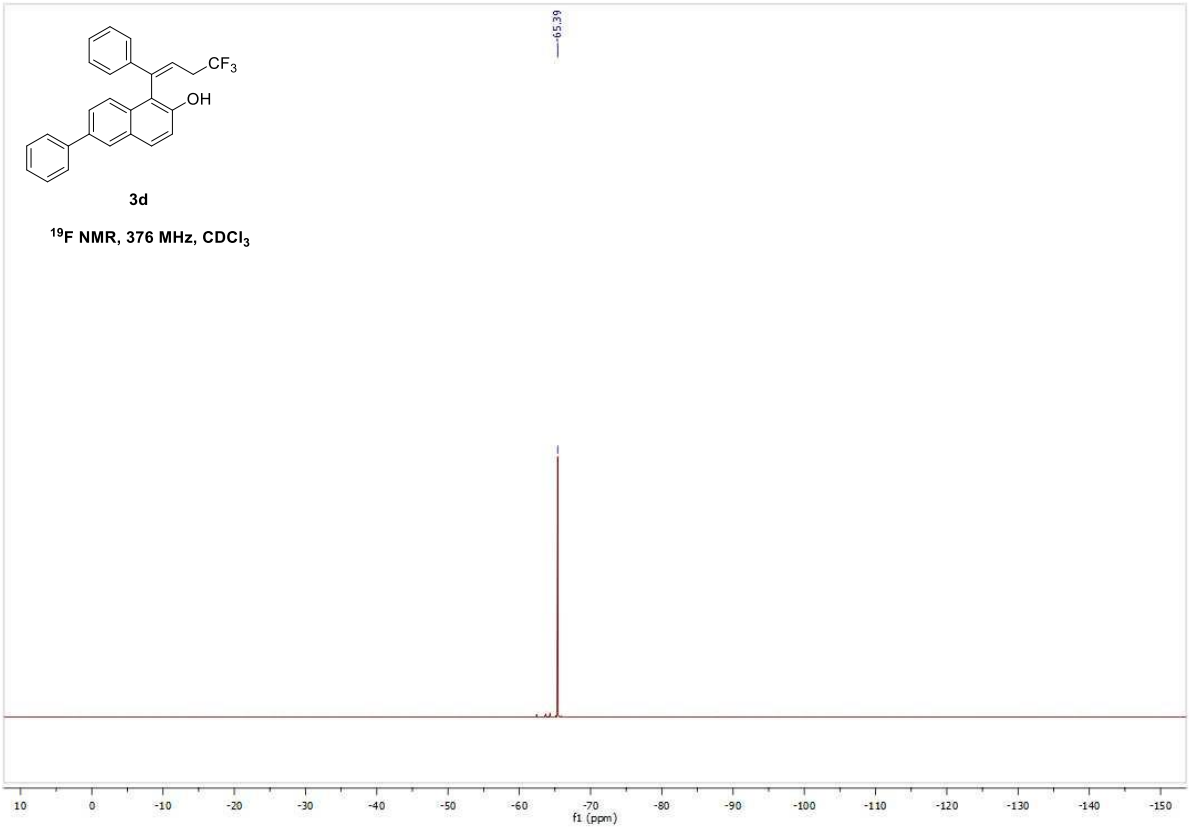
3d

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



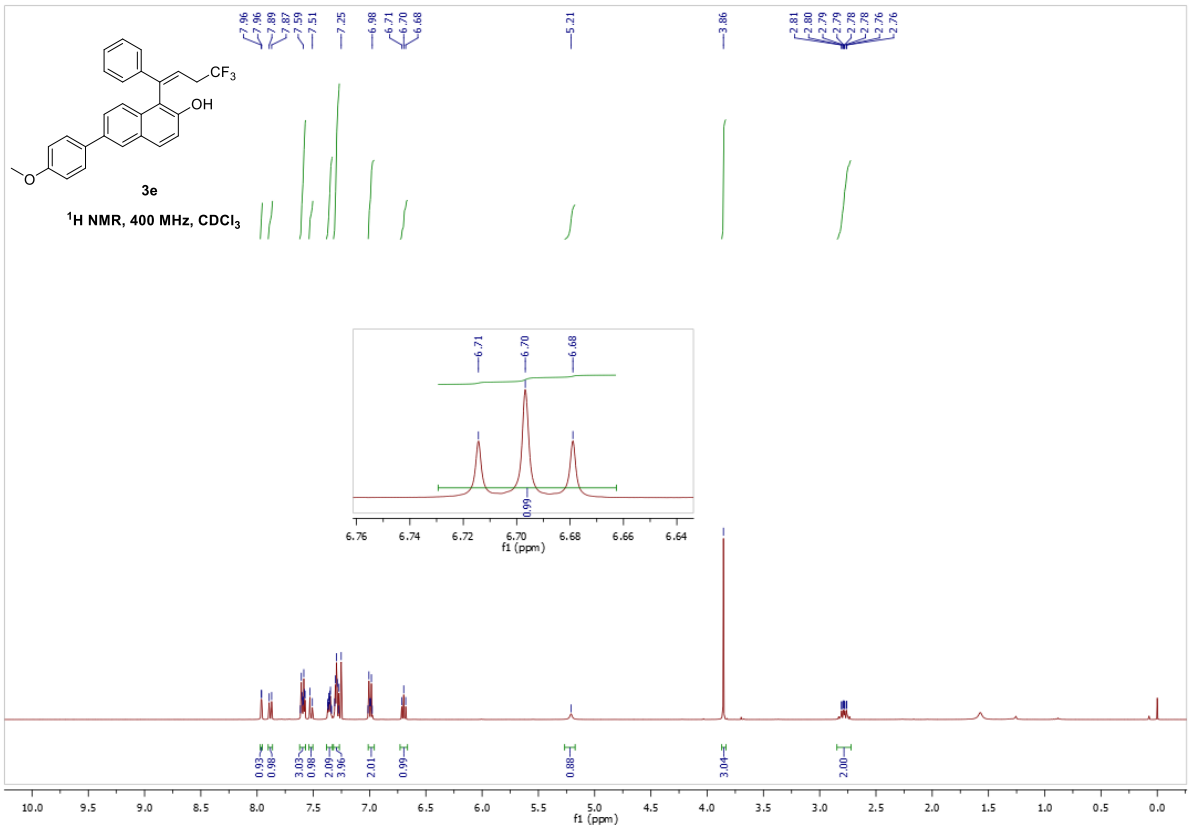
3d

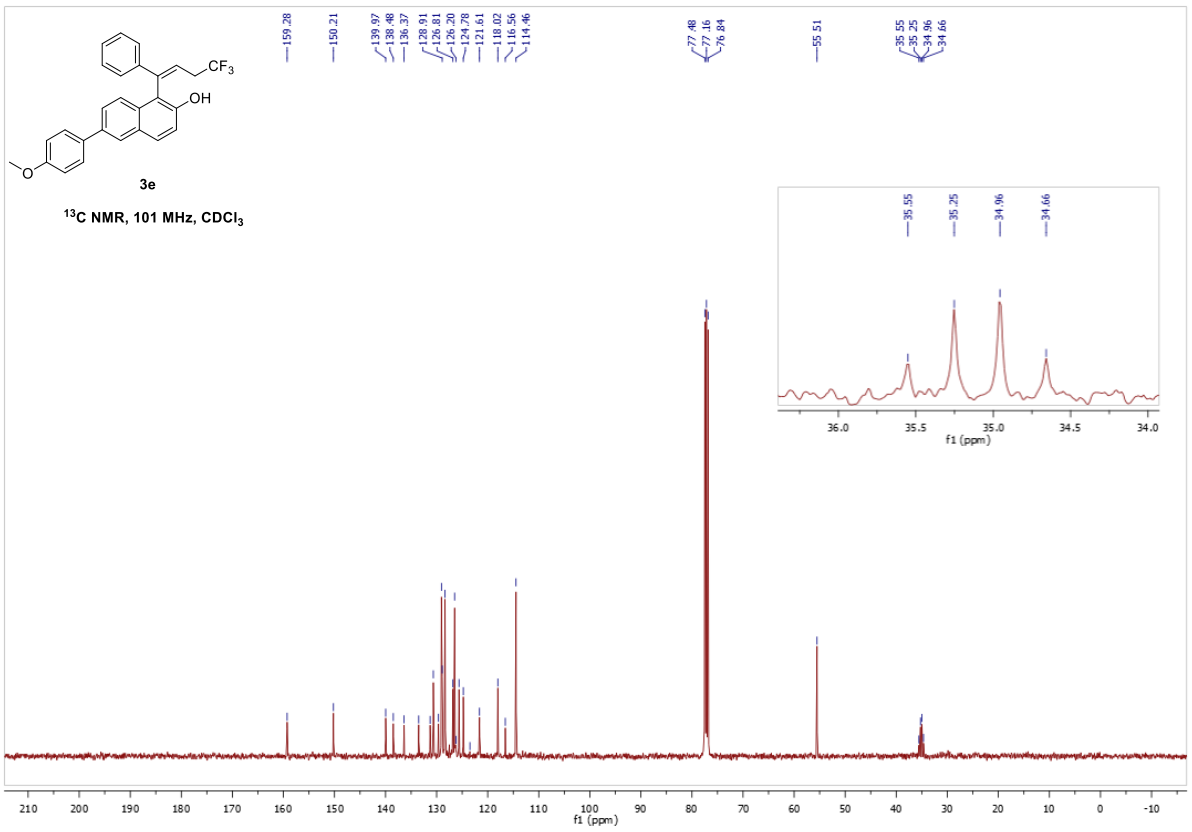
^{13}C NMR, 101 MHz, $CDCl_3$

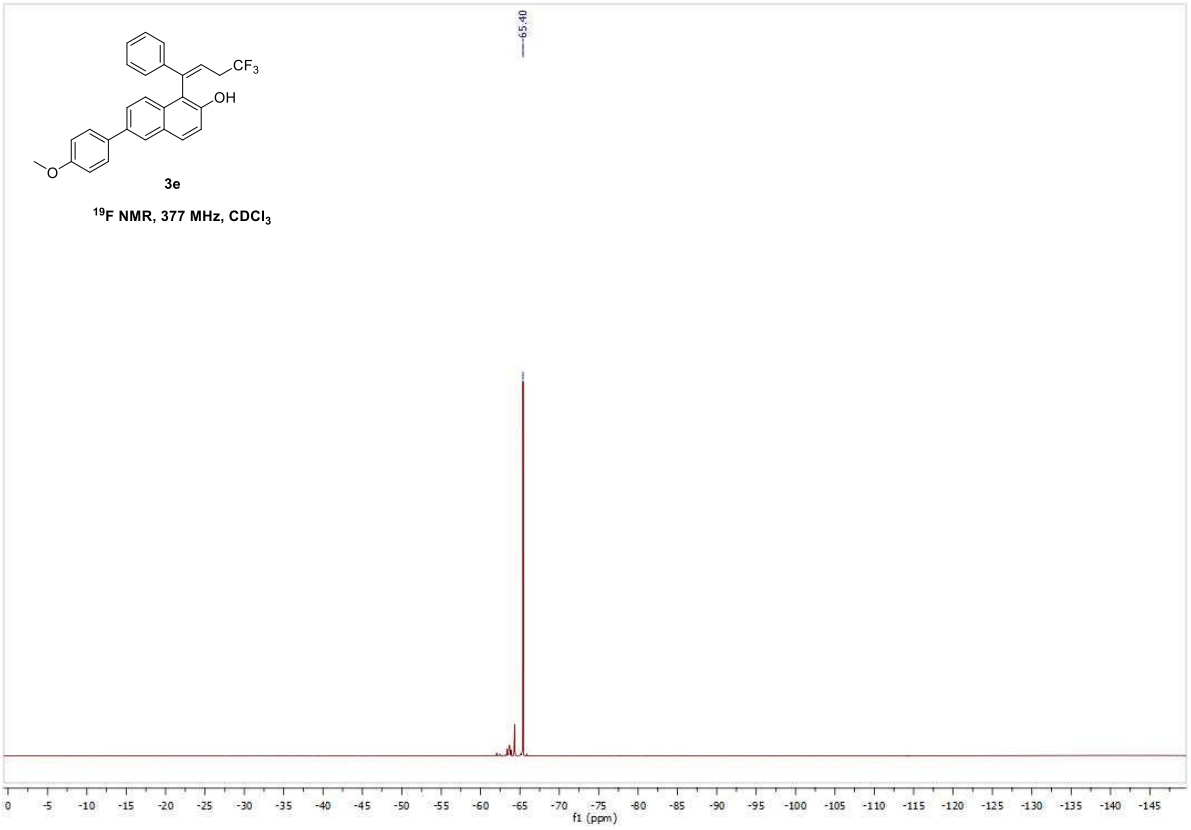


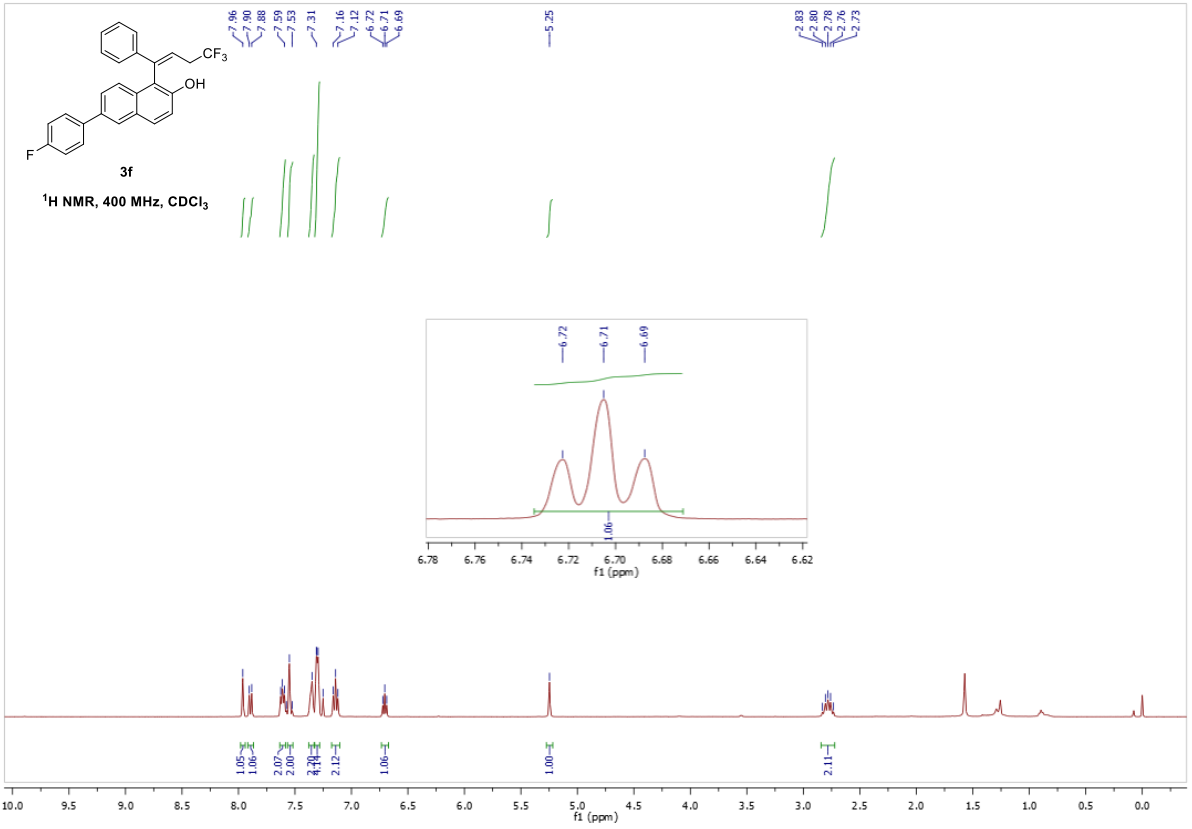
3d

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


3e
^{1}H NMR, 400 MHz, CDCl$_3$


3e
^{13}C NMR, 101 MHz, CDCl$_3$


CF3
OH
O
3e
19F NMR, 377 MHz, CDCl3
-65.40
f1 (ppm)


CF3
OH
F
3f
1H NMR, 400 MHz, CDCl3
7.96
7.90
7.88
7.59
7.53
7.31
7.16
7.12
6.72
6.71
6.69
5.25
2.83
2.80
2.78
2.76
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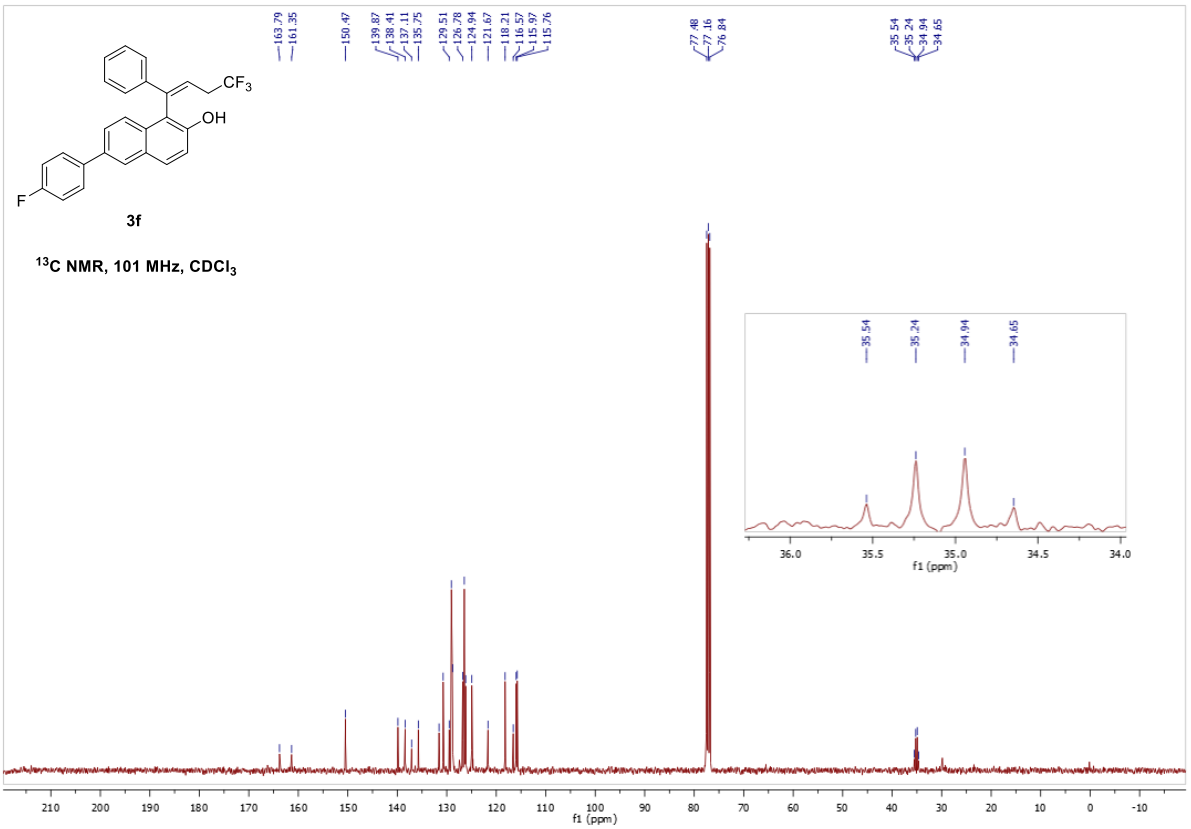
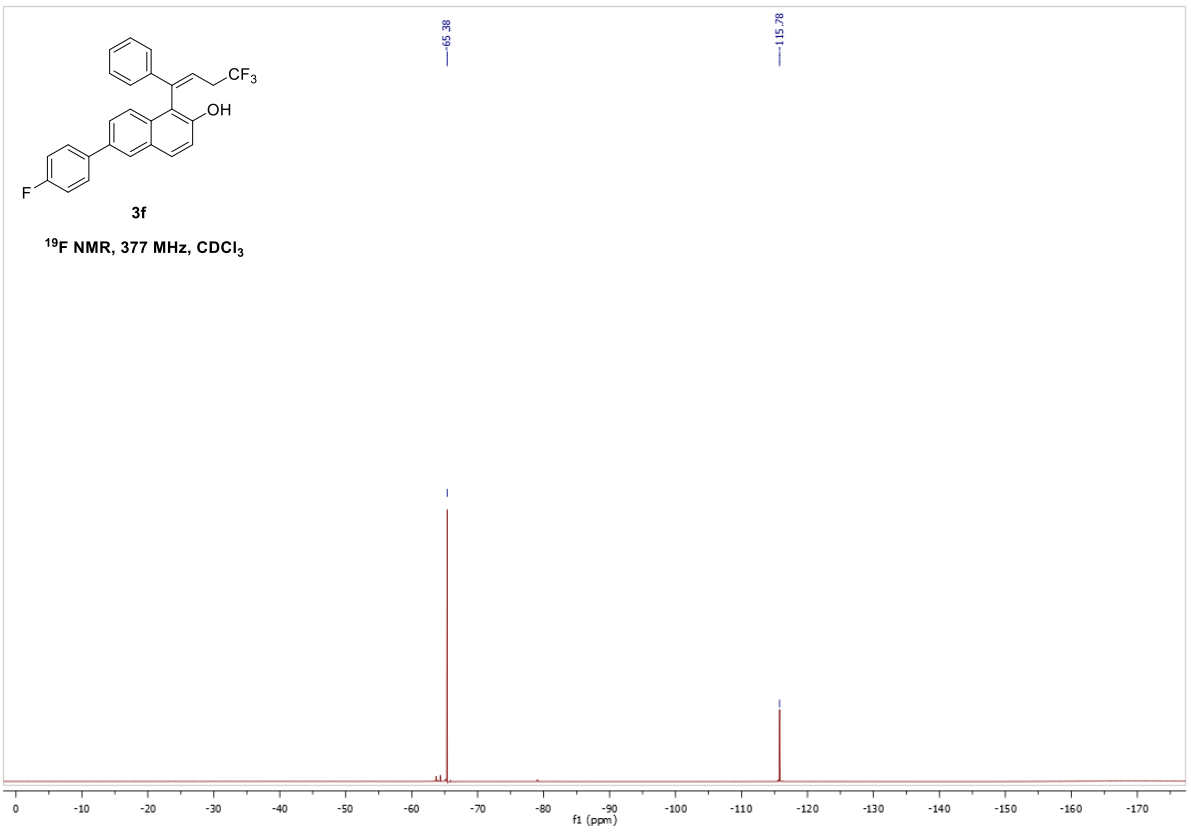
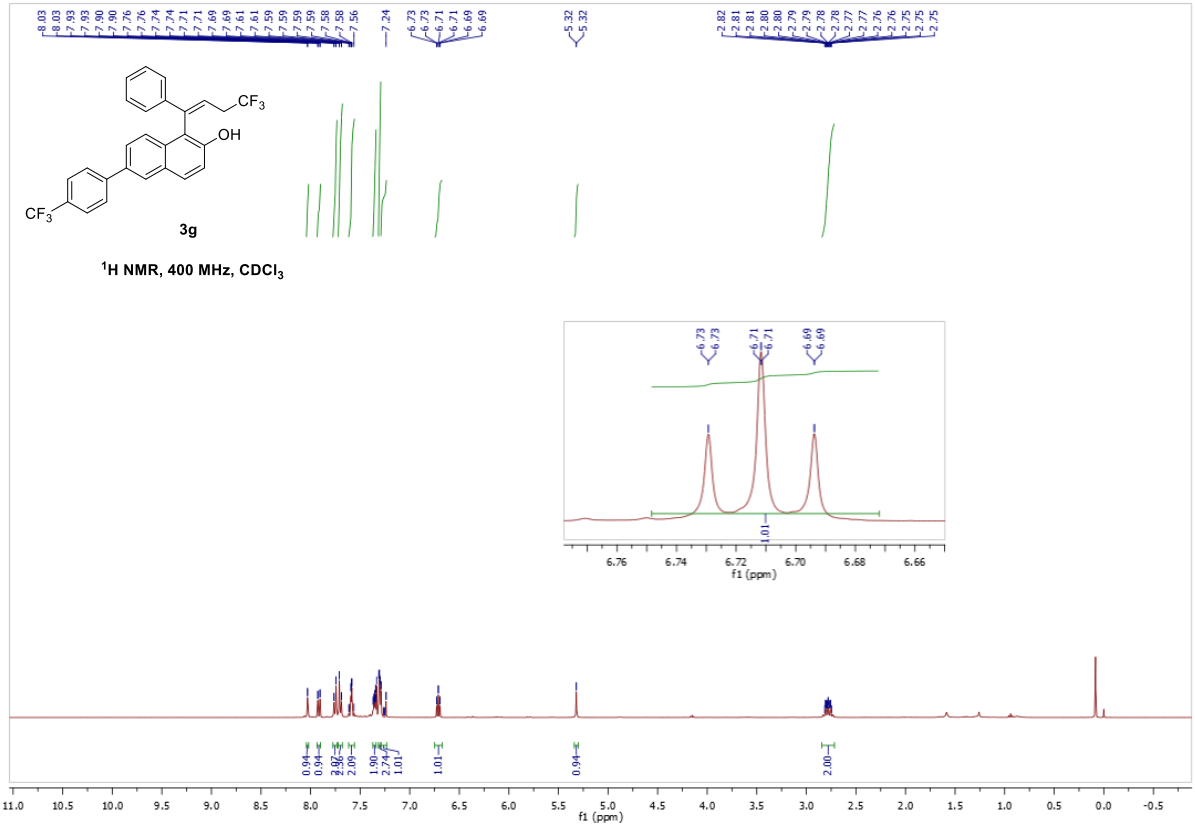
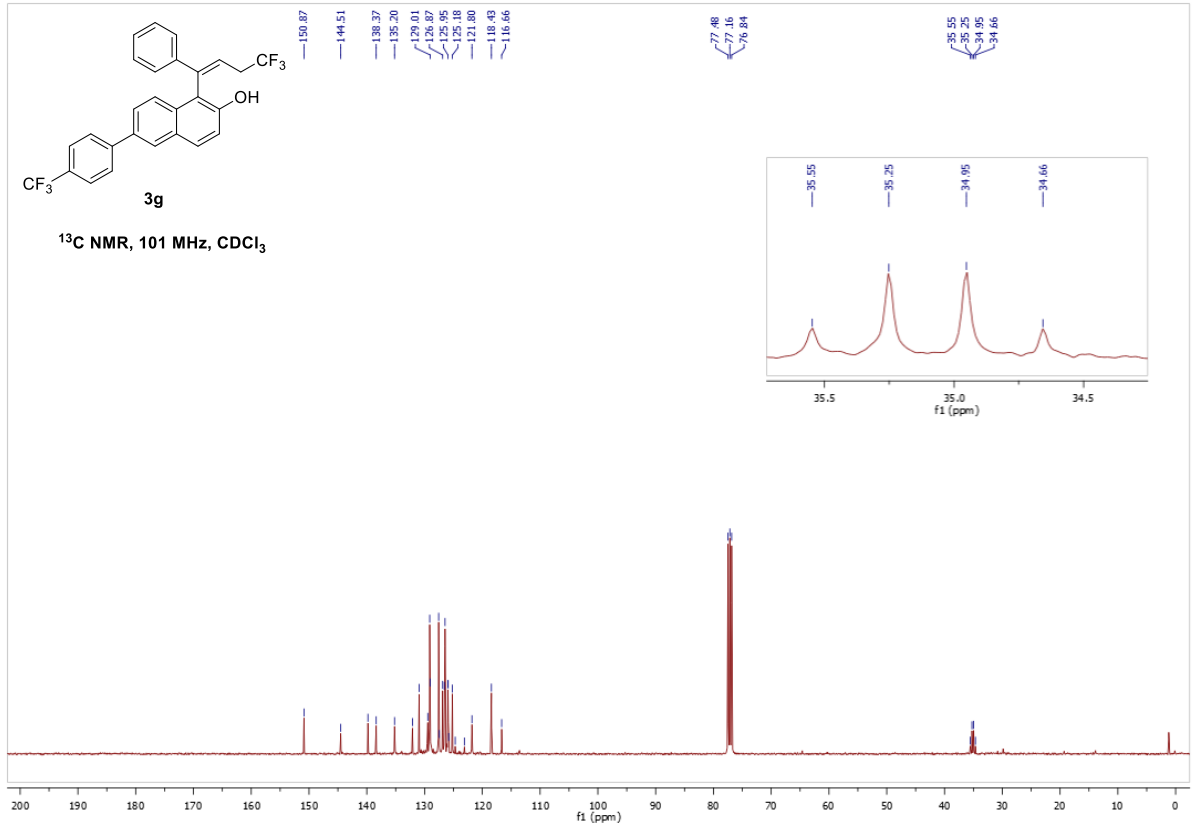
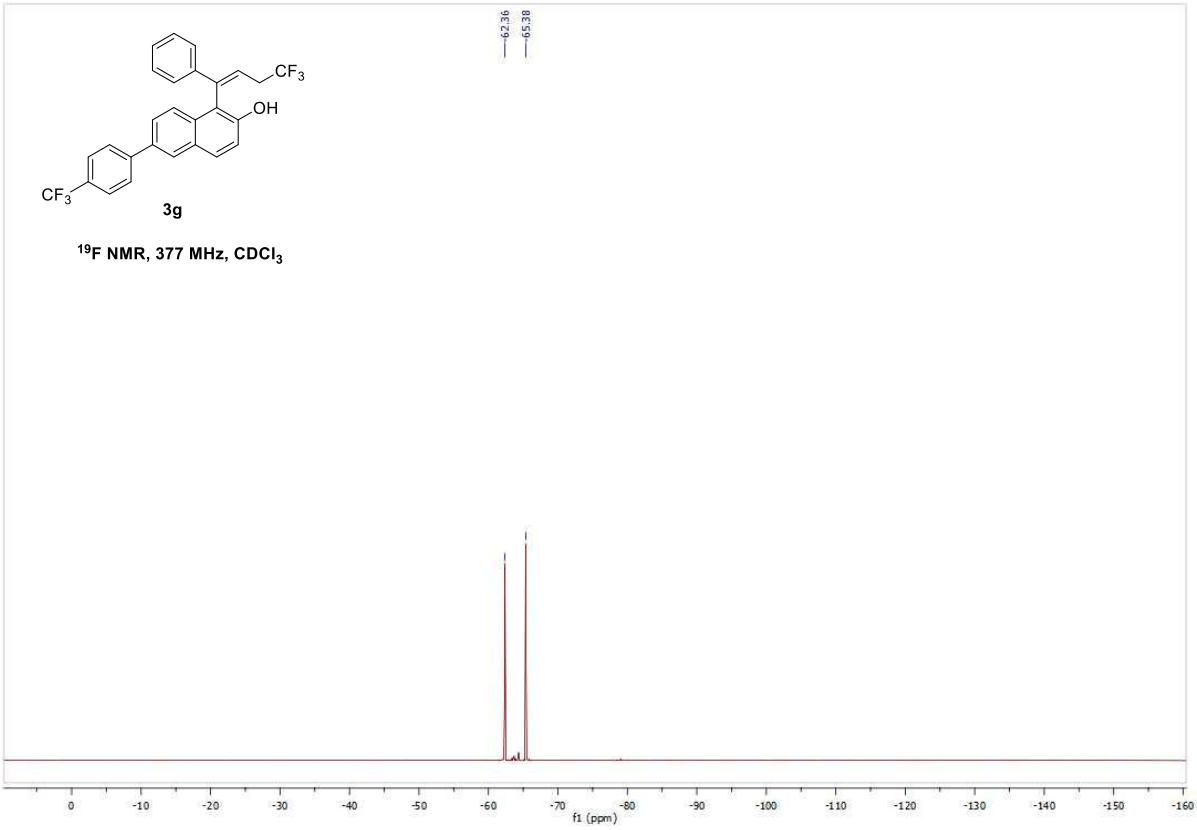
1.05
1.06
2.07
2.00
2.12
1.06
1.00
2.11
f1 (ppm)


CF3
OH
F
3f
13C NMR, 101 MHz, CDCl3
163.79
161.35
150.47
139.87
138.41
137.11
135.75
129.51
126.78
124.94
121.67
118.21
116.57
115.97
115.76
77.48
77.16
76.84
35.54
35.24
34.94
34.65
f1 (ppm)


CF3
OH
F
3f
19F NMR, 377 MHz, CDCl3
-65.38
-115.78
f1 (ppm)

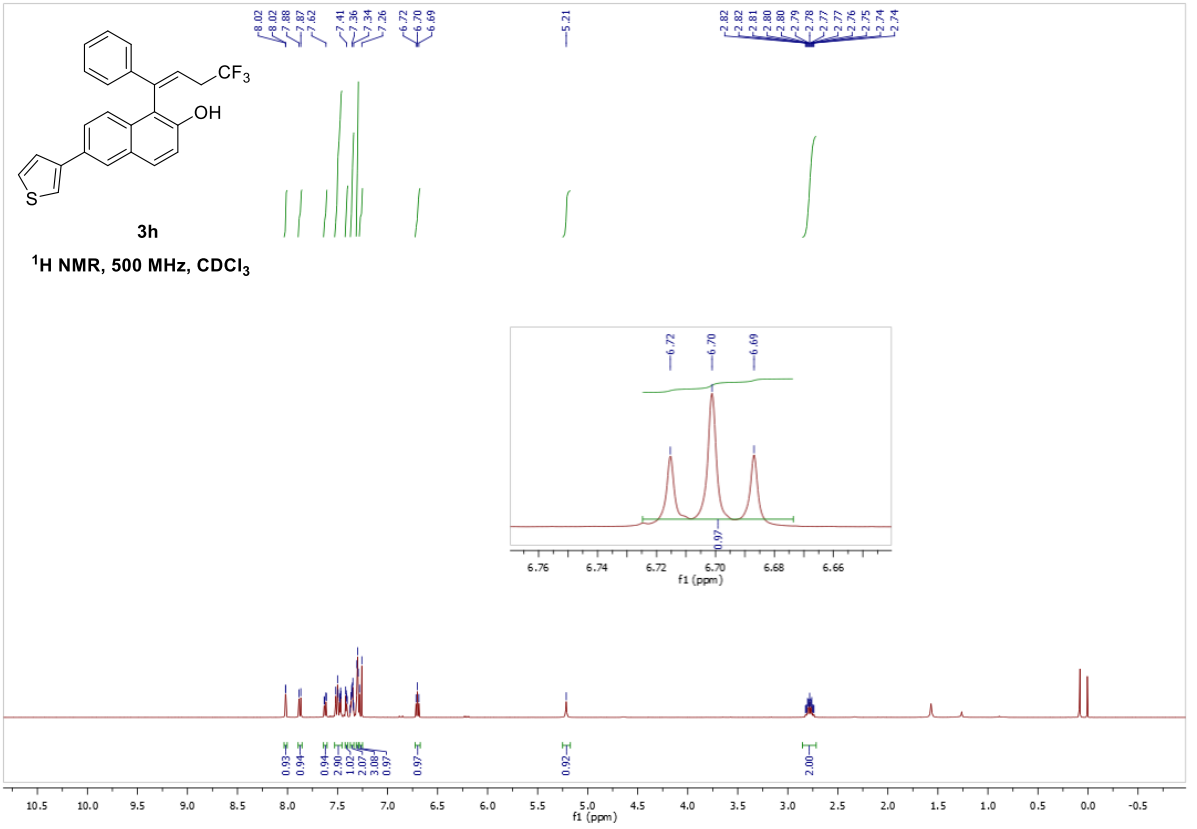

CF3
OH
CF3
3g
1H NMR, 400 MHz, CDCl3
f1 (ppm)


CF3
OH
CF3
3g
13C NMR, 101 MHz, CDCl3
f1 (ppm)



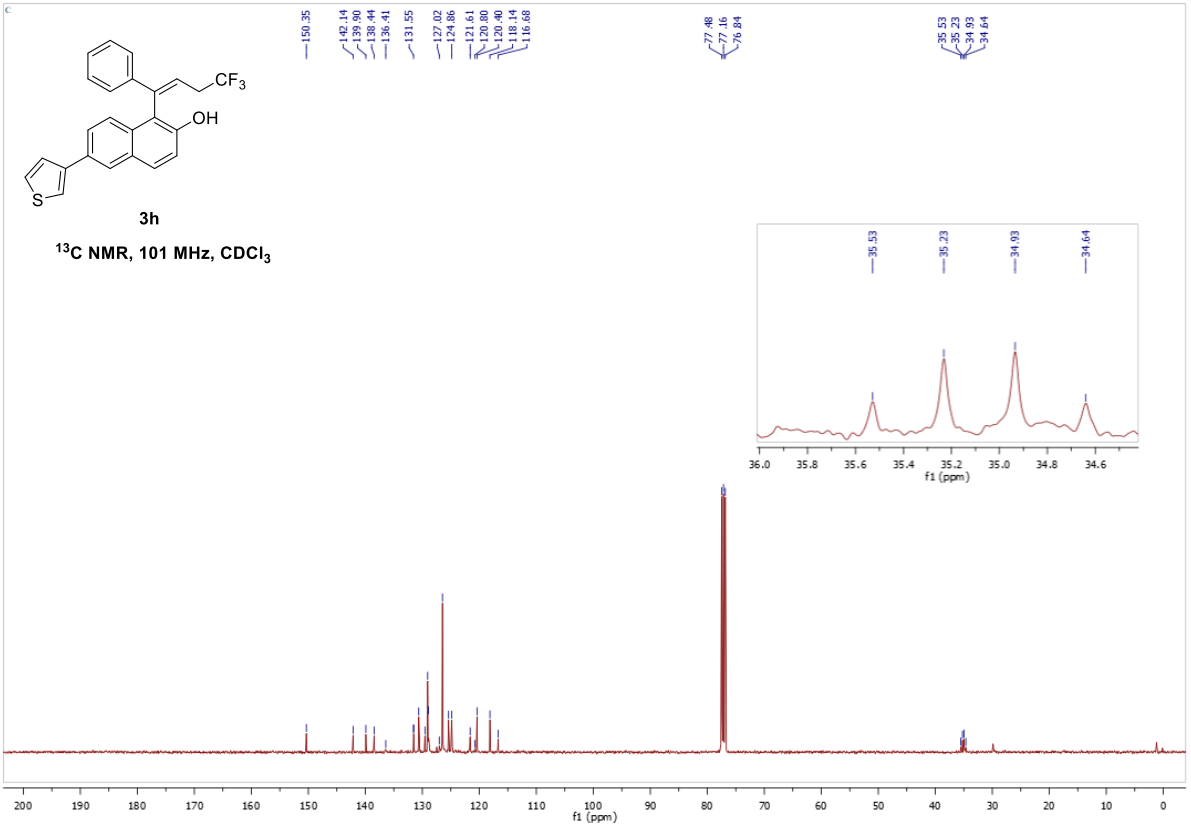
3g

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



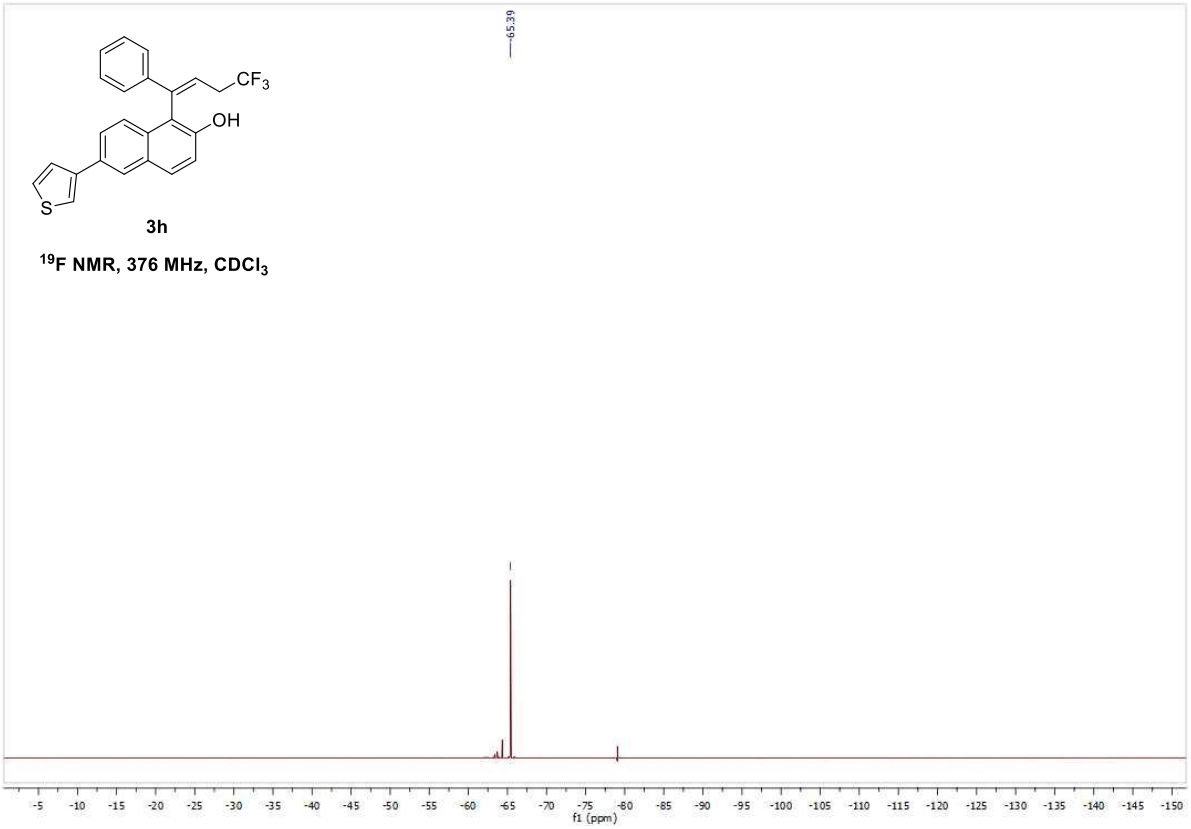
3h

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



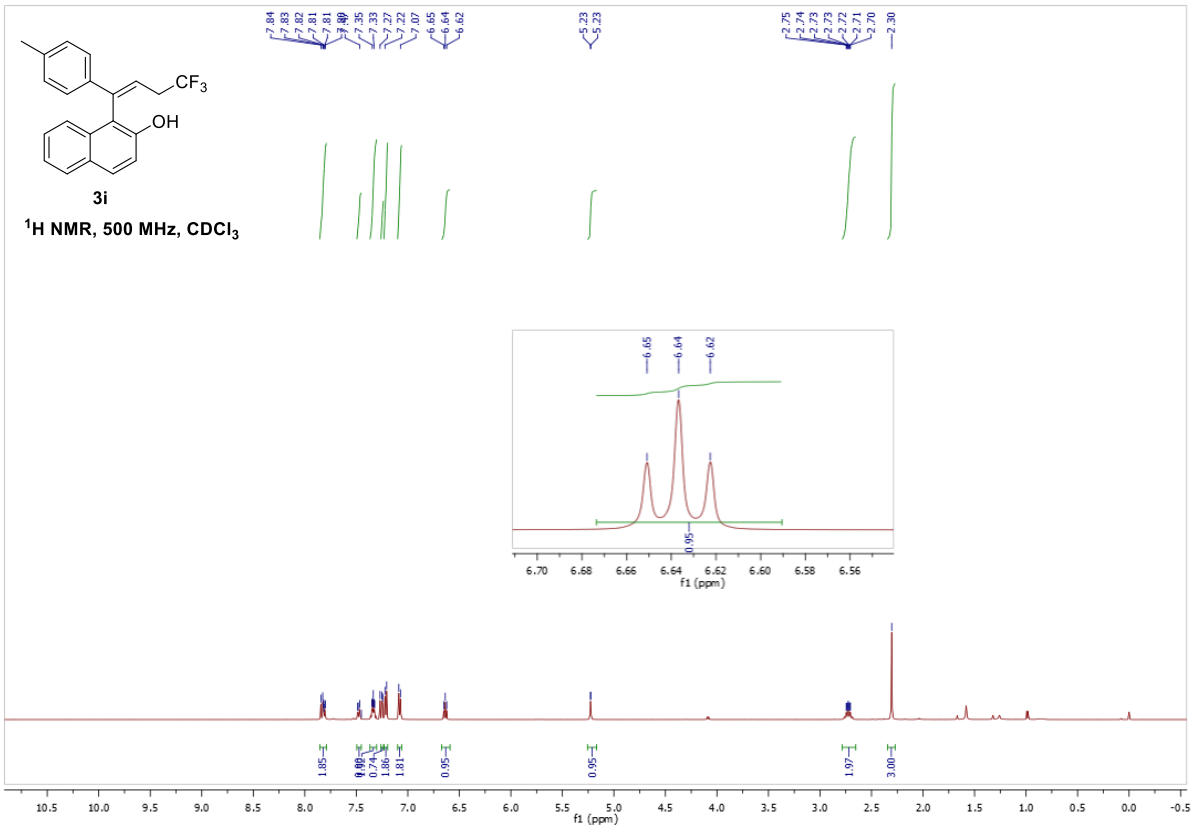
3h

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



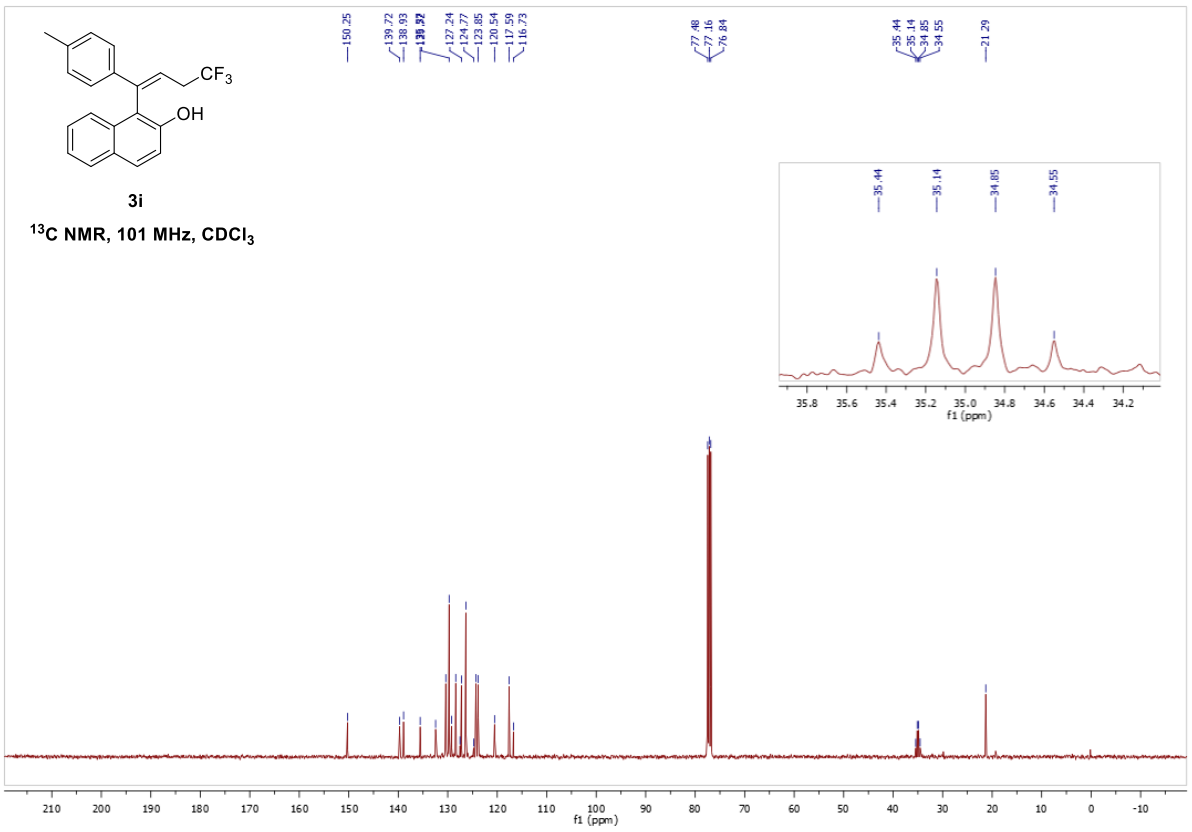
3h

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



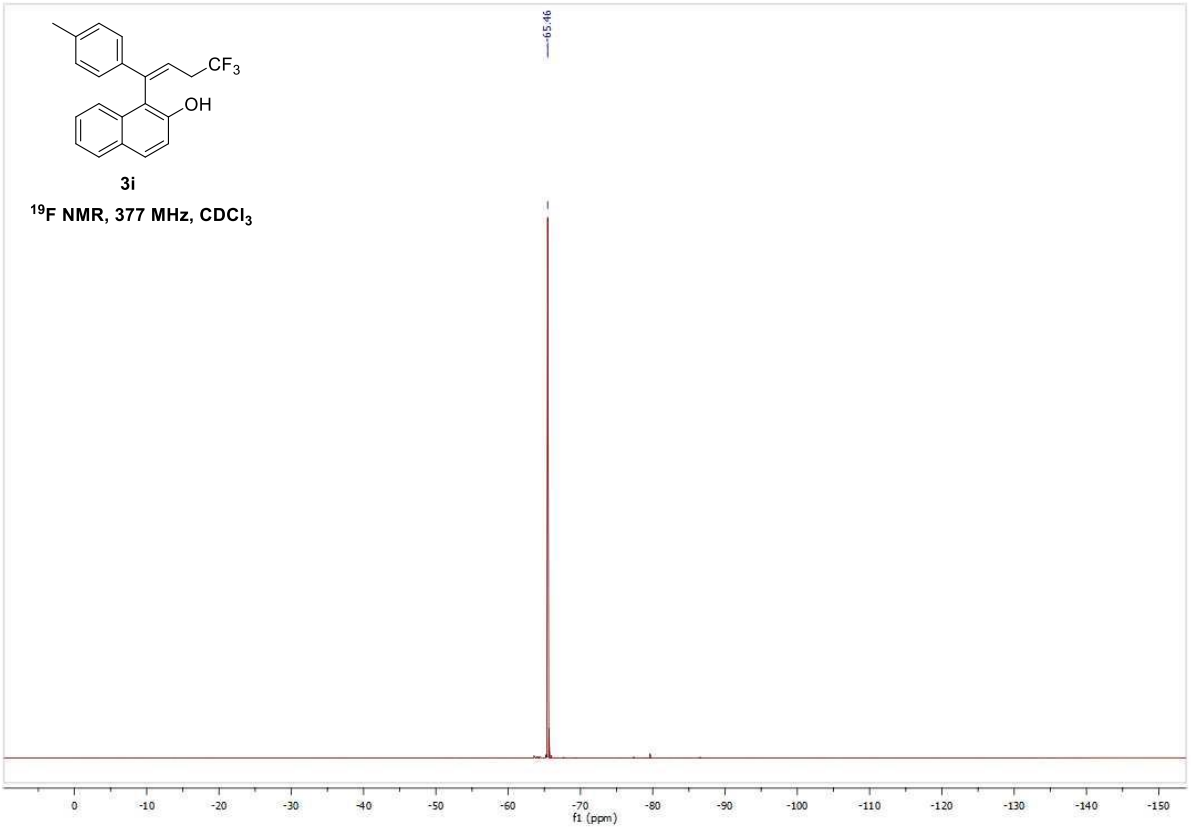
3i

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



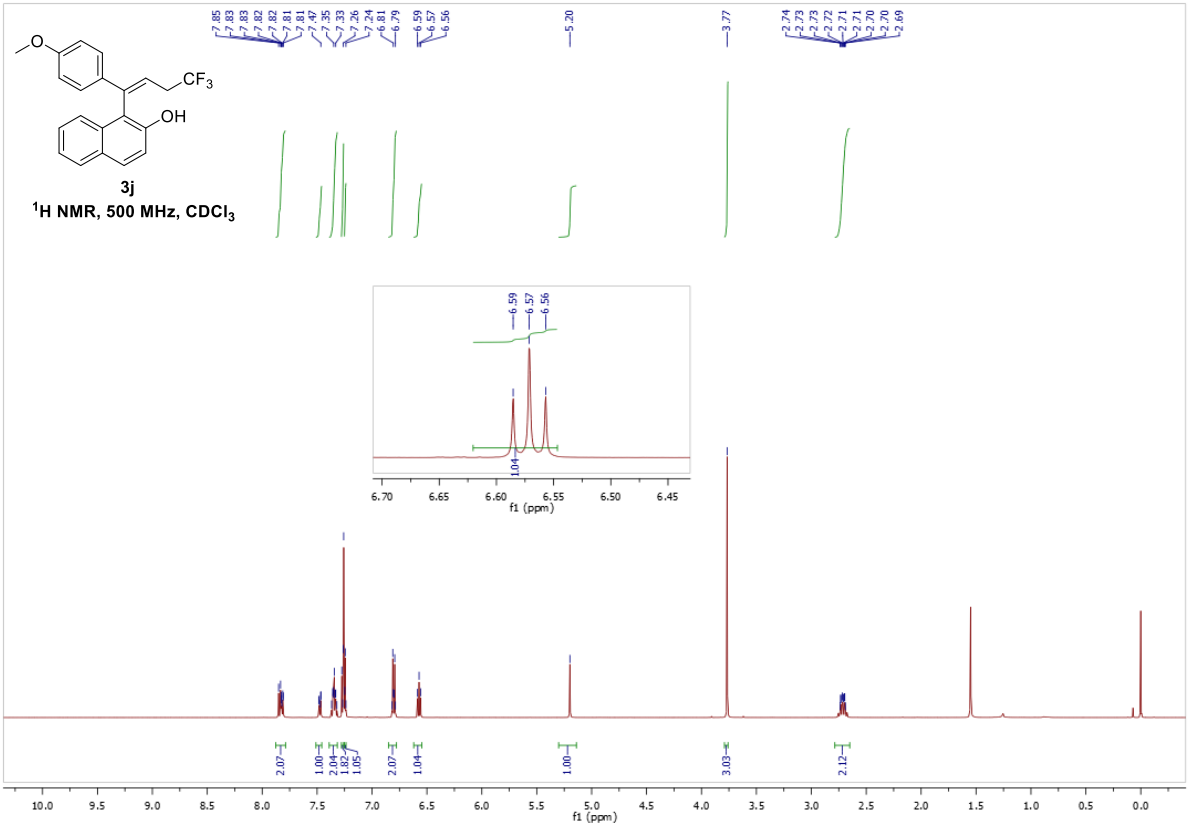
3i

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



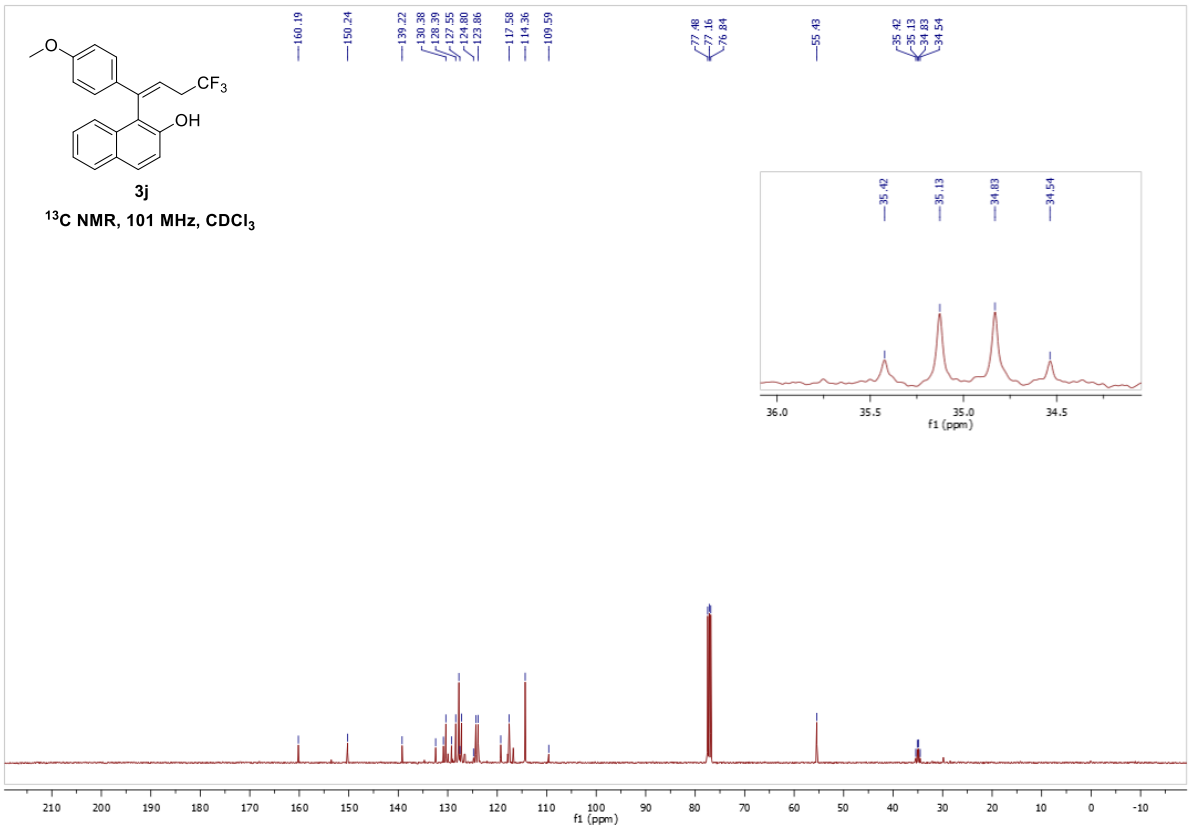
3i

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



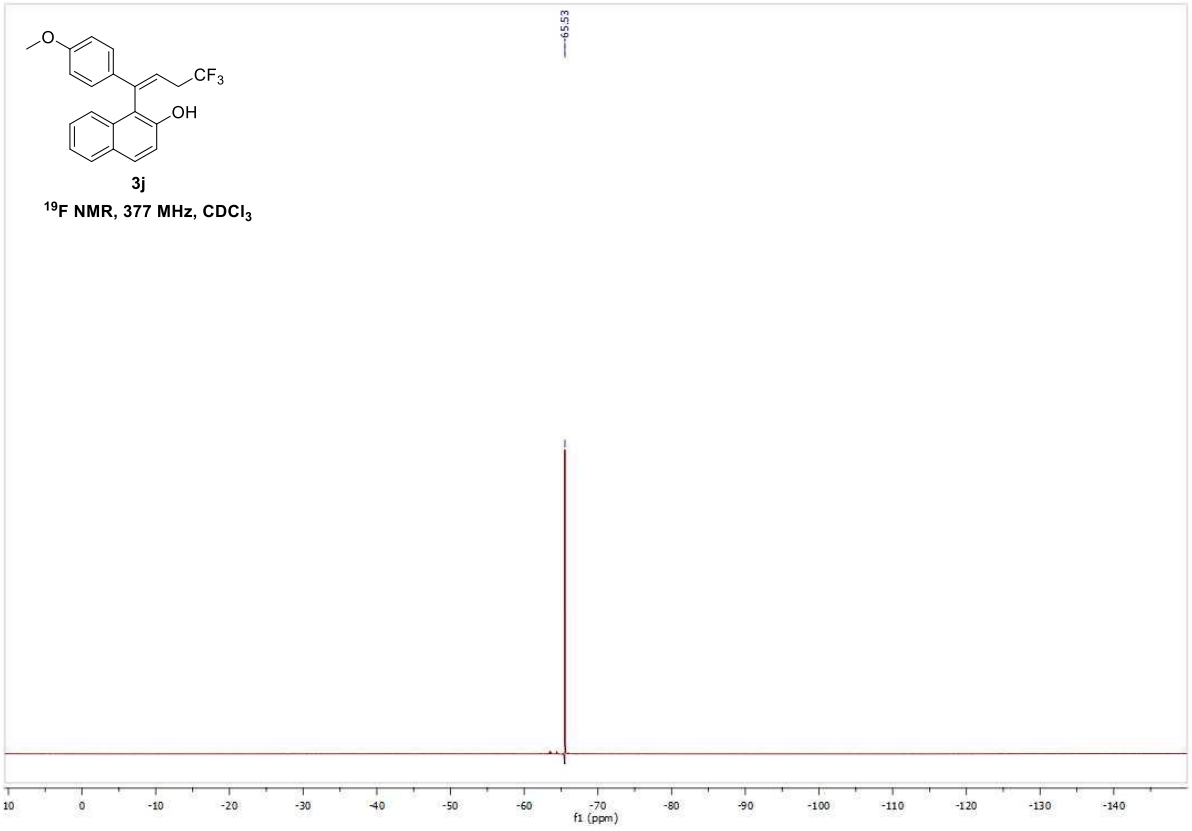
3j

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



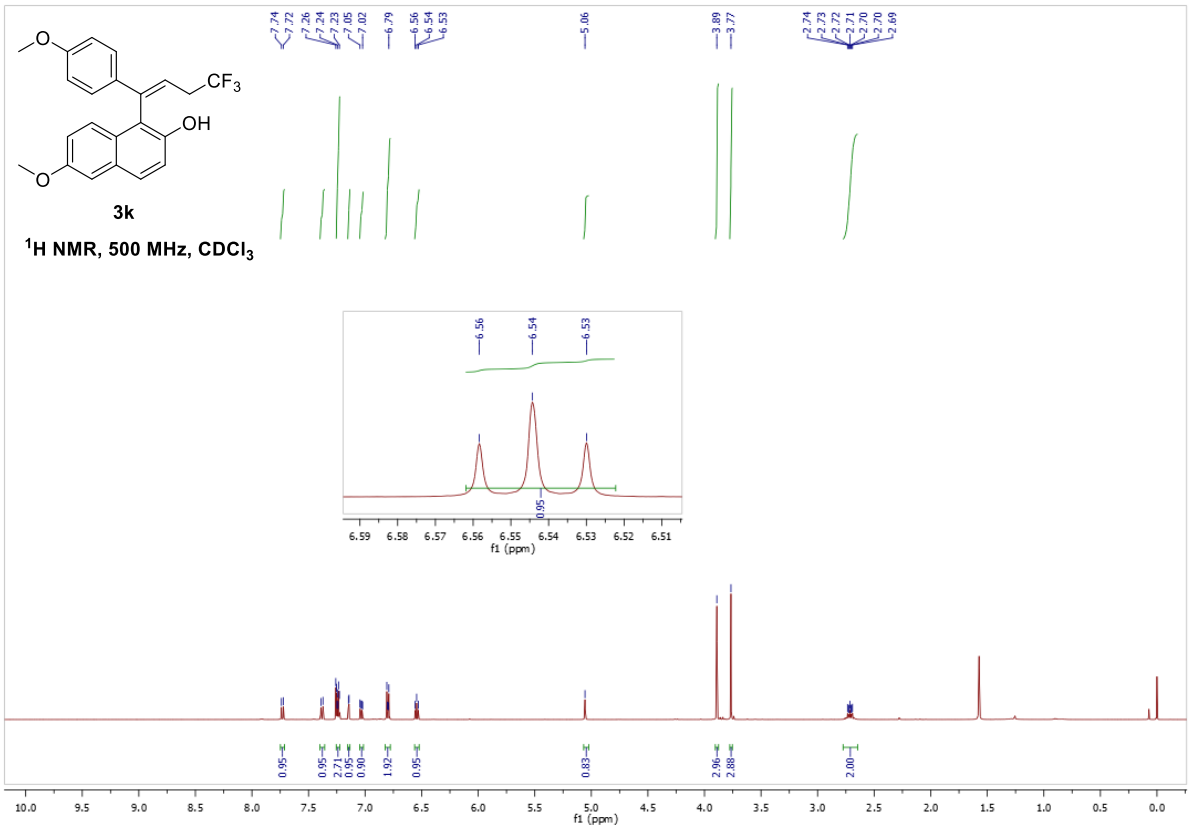
3j

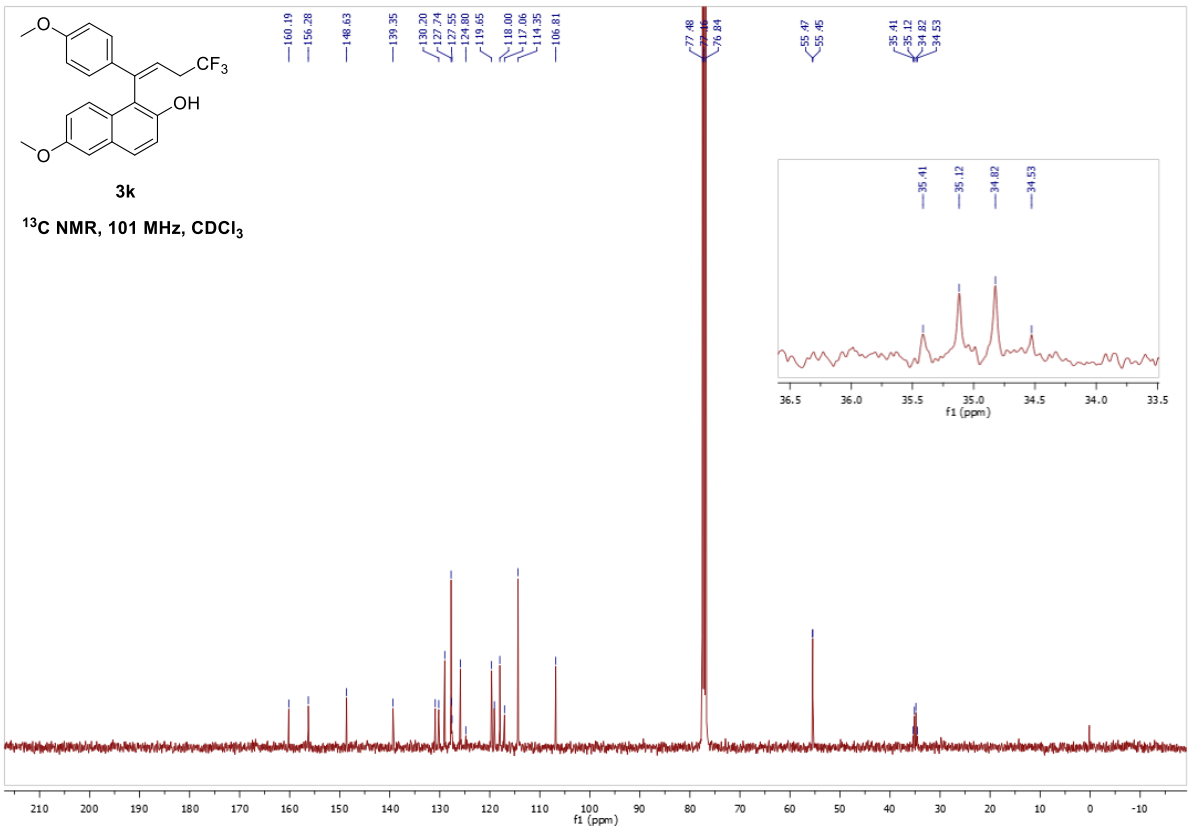
^{13}C NMR, 101 MHz, $CDCl_3$

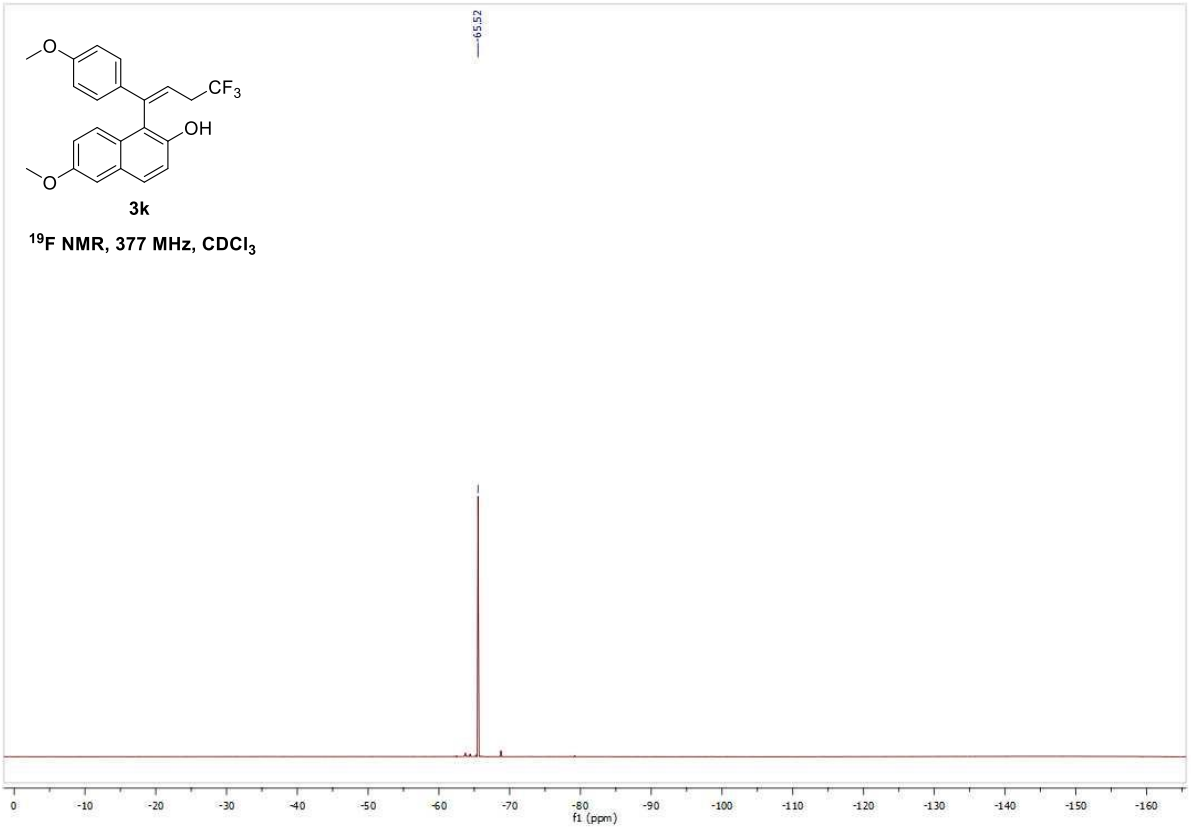


3j

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

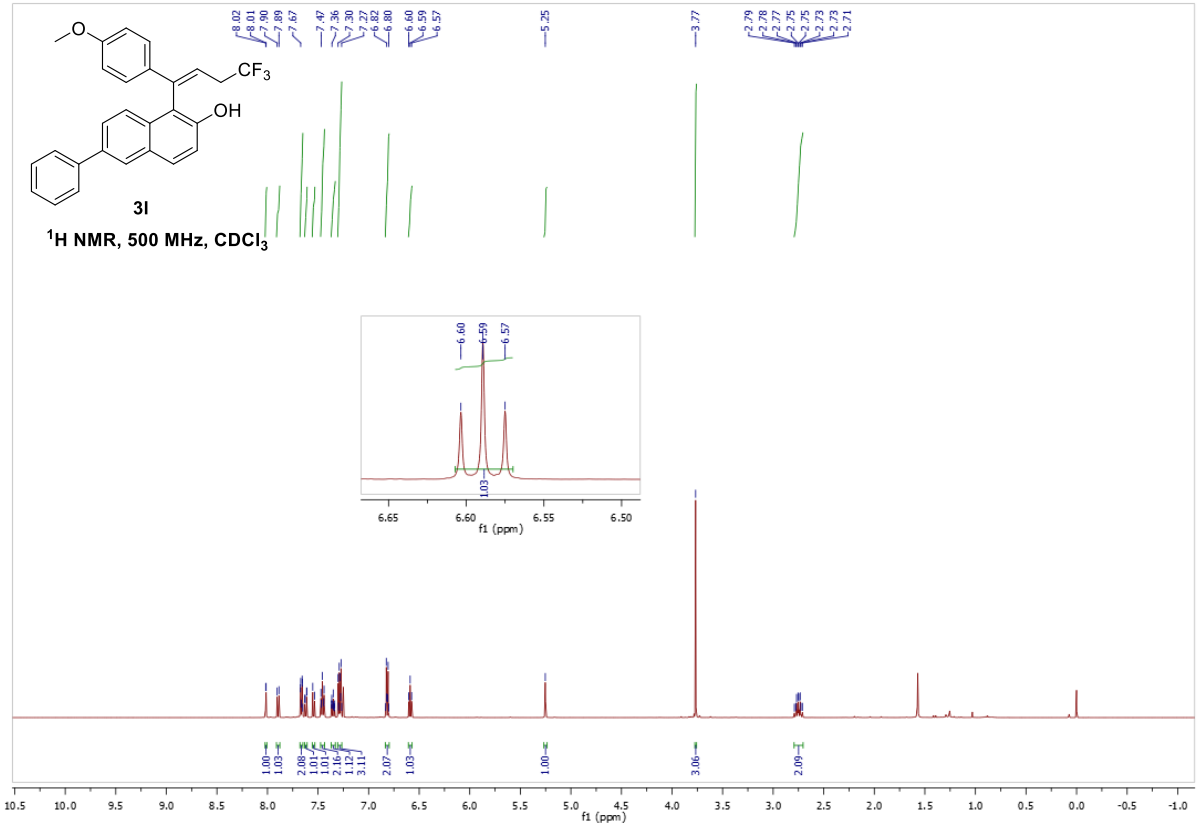

CF3
OH
O
O
3k
1H NMR, 500 MHz, CDCl3
7.74
7.72
7.26
7.24
7.23
7.05
7.02
6.79
6.56
6.54
6.53
5.06
3.89
3.77
2.74
2.73
2.72
2.71
2.70
2.70
2.69
0.95
0.95
2.71
0.95
0.90
1.92
0.95
0.83
2.96
2.88
2.00
f1 (ppm)


CF3
OH
O
O
3k
13C NMR, 101 MHz, CDCl3
160.19
156.28
148.63
139.35
130.20
127.74
127.55
124.80
119.65
118.00
117.06
114.35
106.81
77.48
77.16
76.84
55.47
55.45
35.41
35.12
34.82
34.53
f1 (ppm)



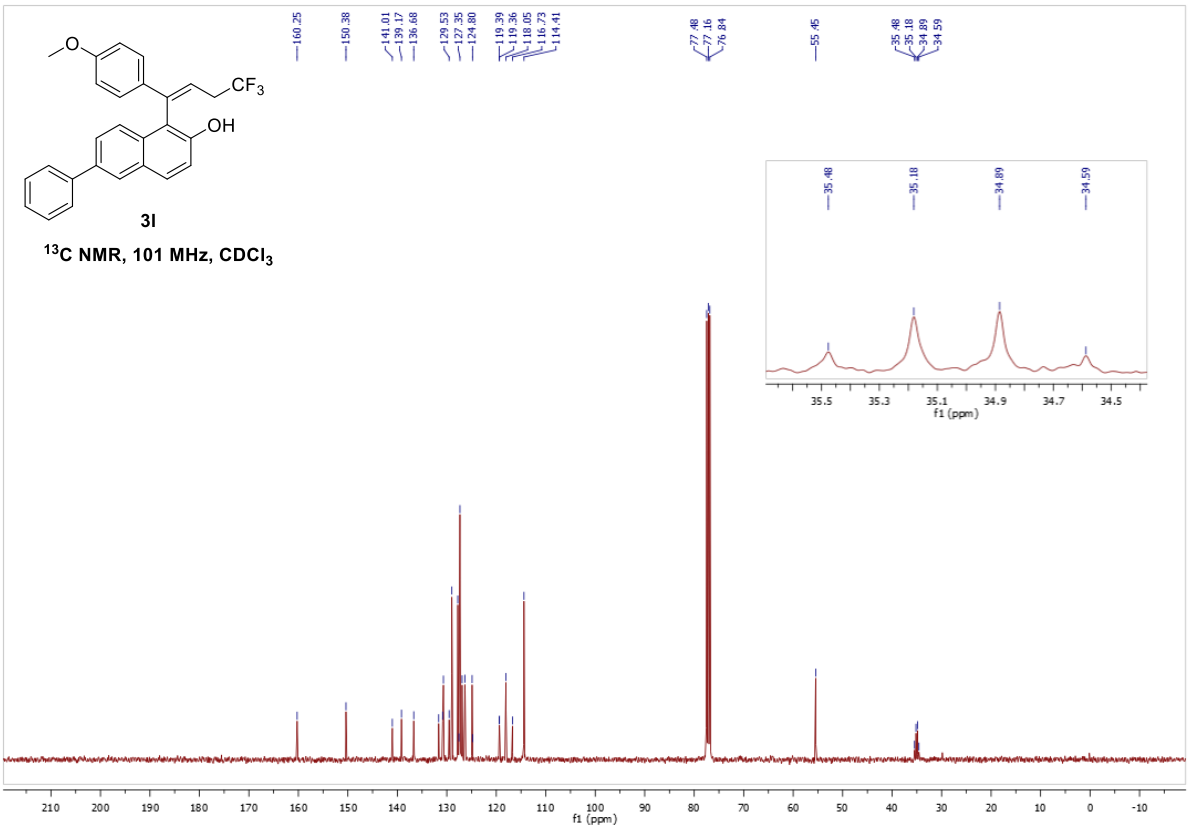
3k

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



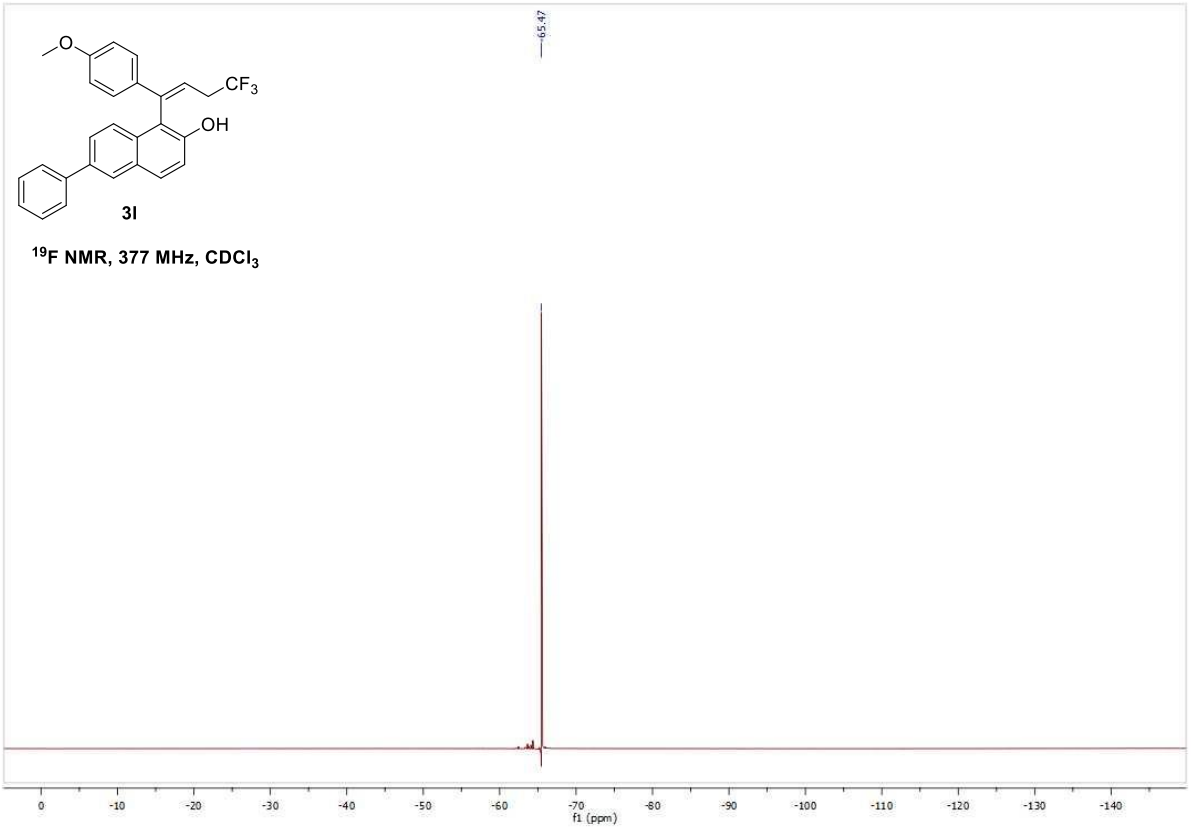
3l

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



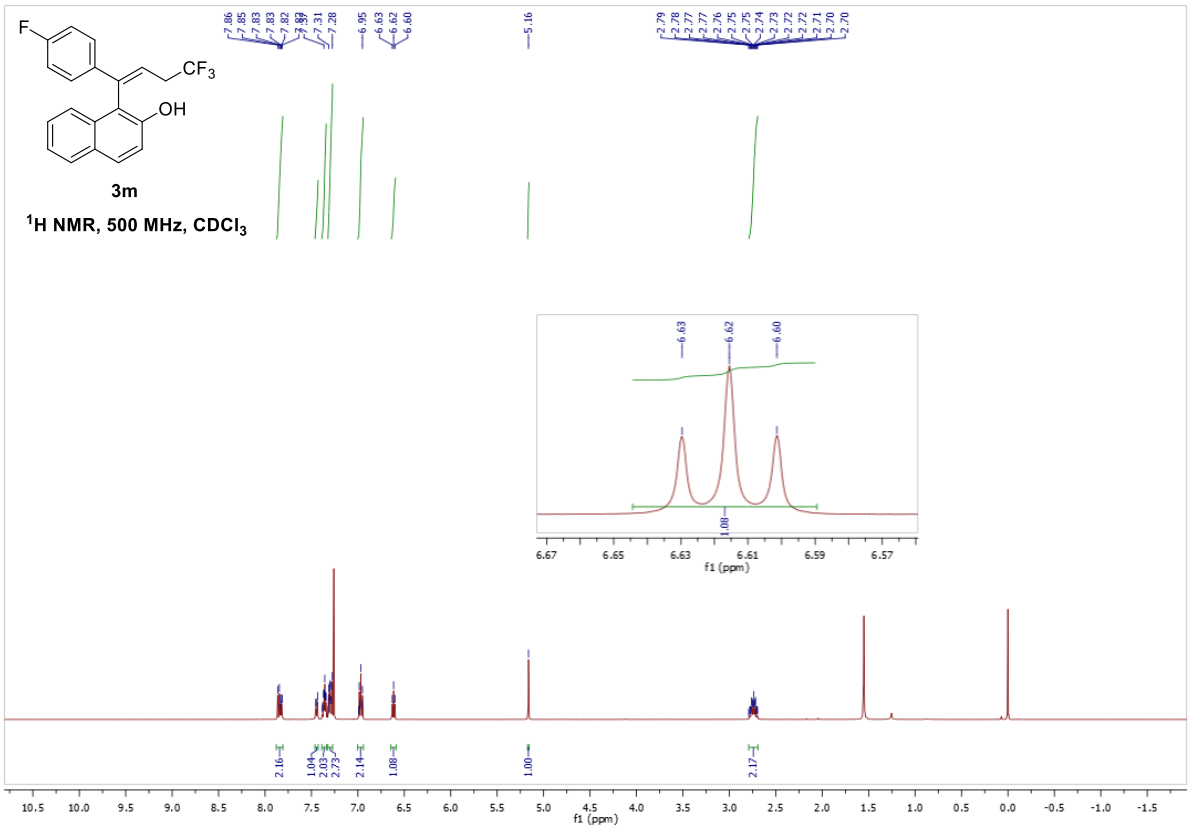
3l

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



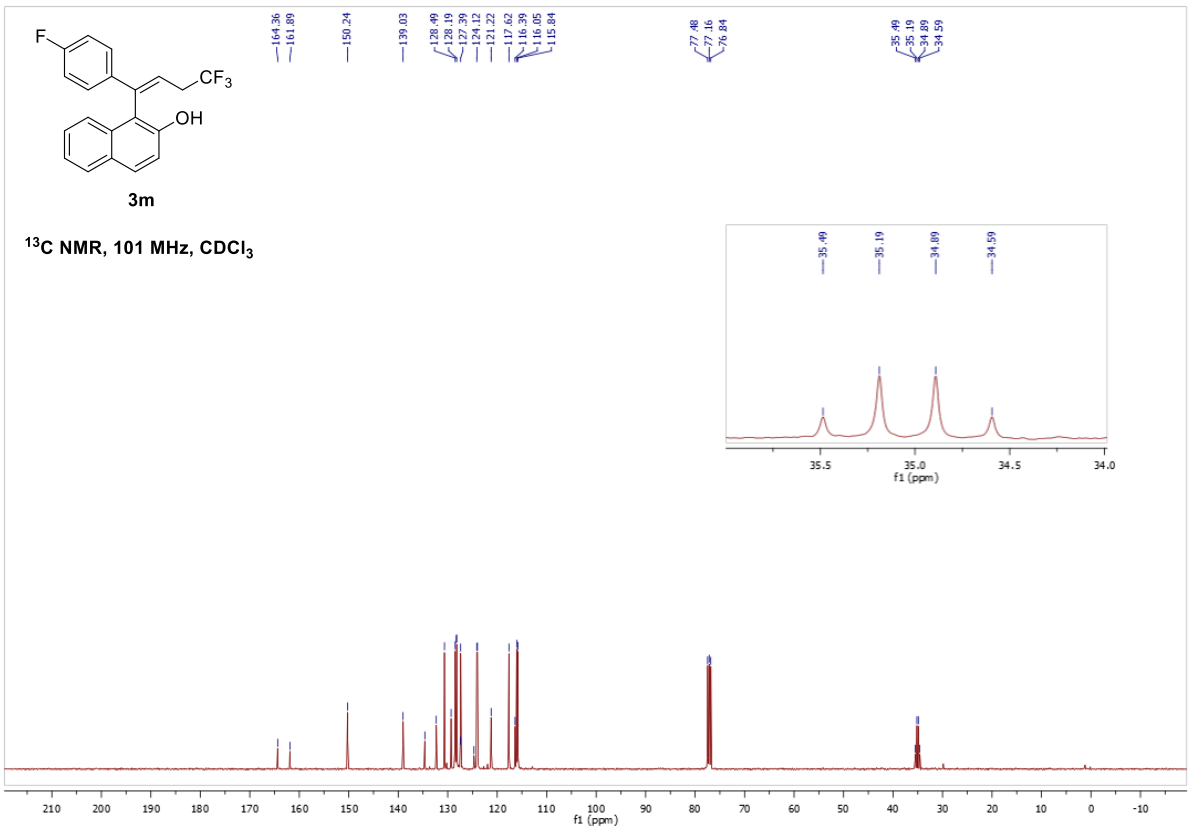
3l

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



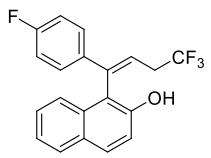
3m

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



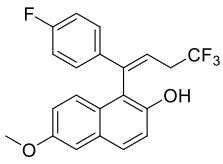
3m

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



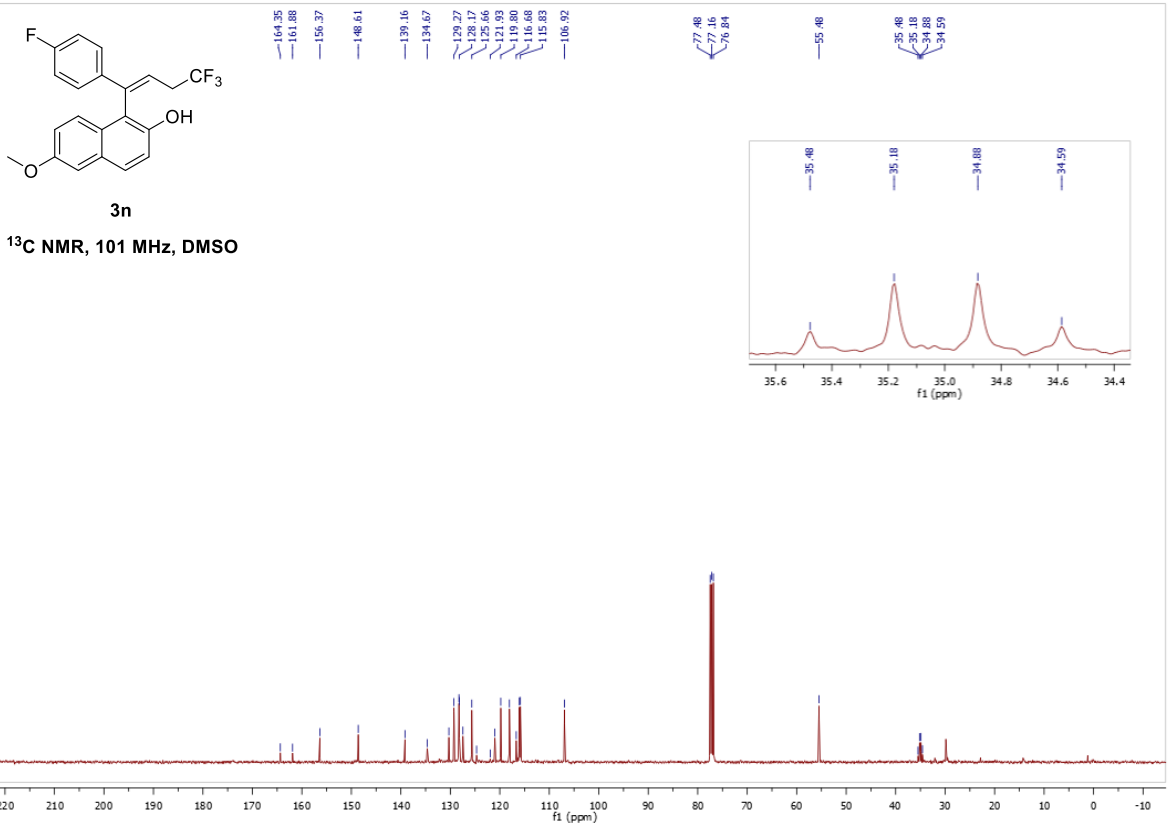
3m

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



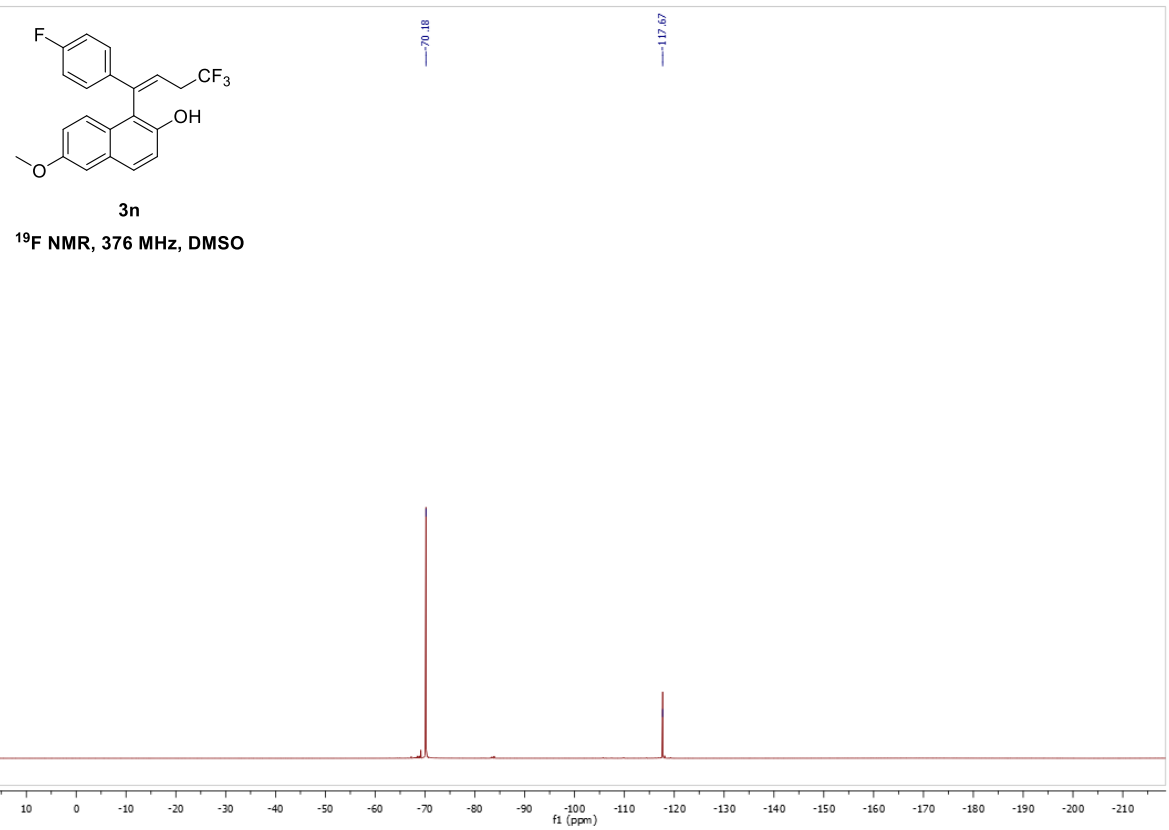
3n

^{1}H NMR, 400 MHz, DMSO



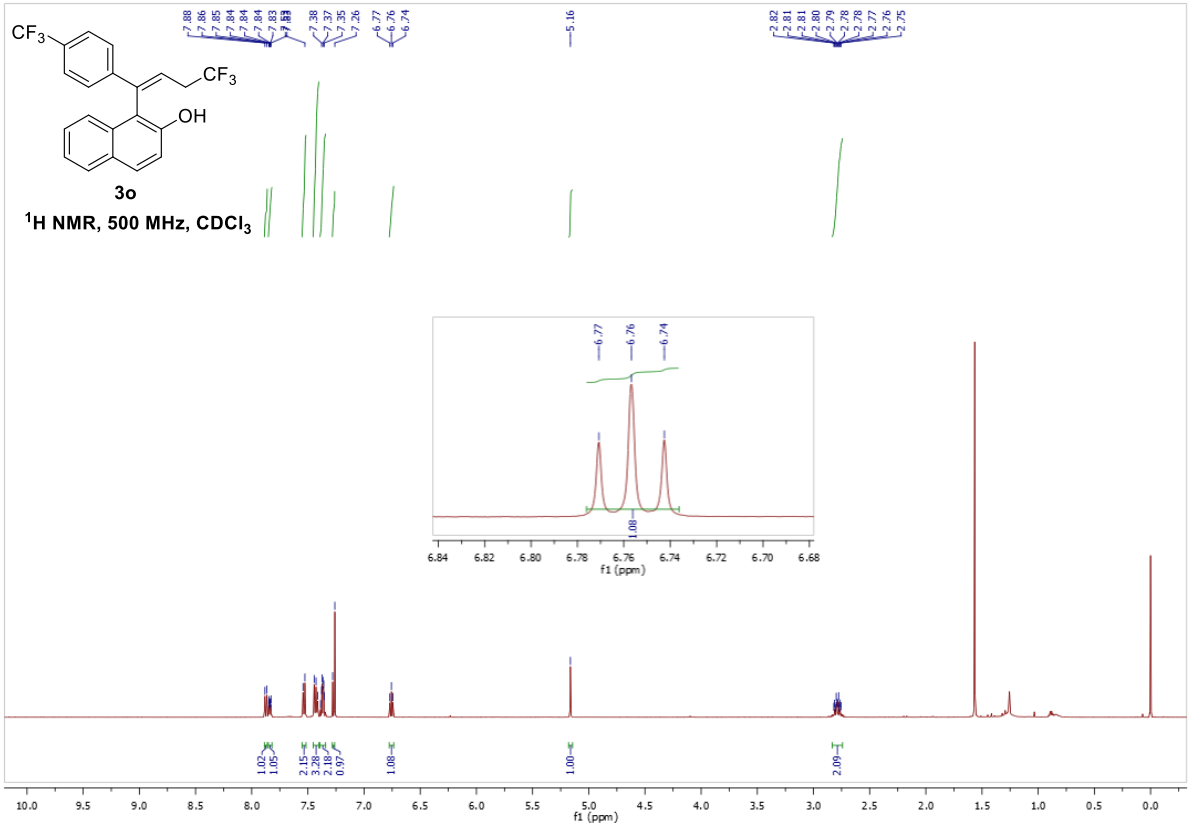
3n

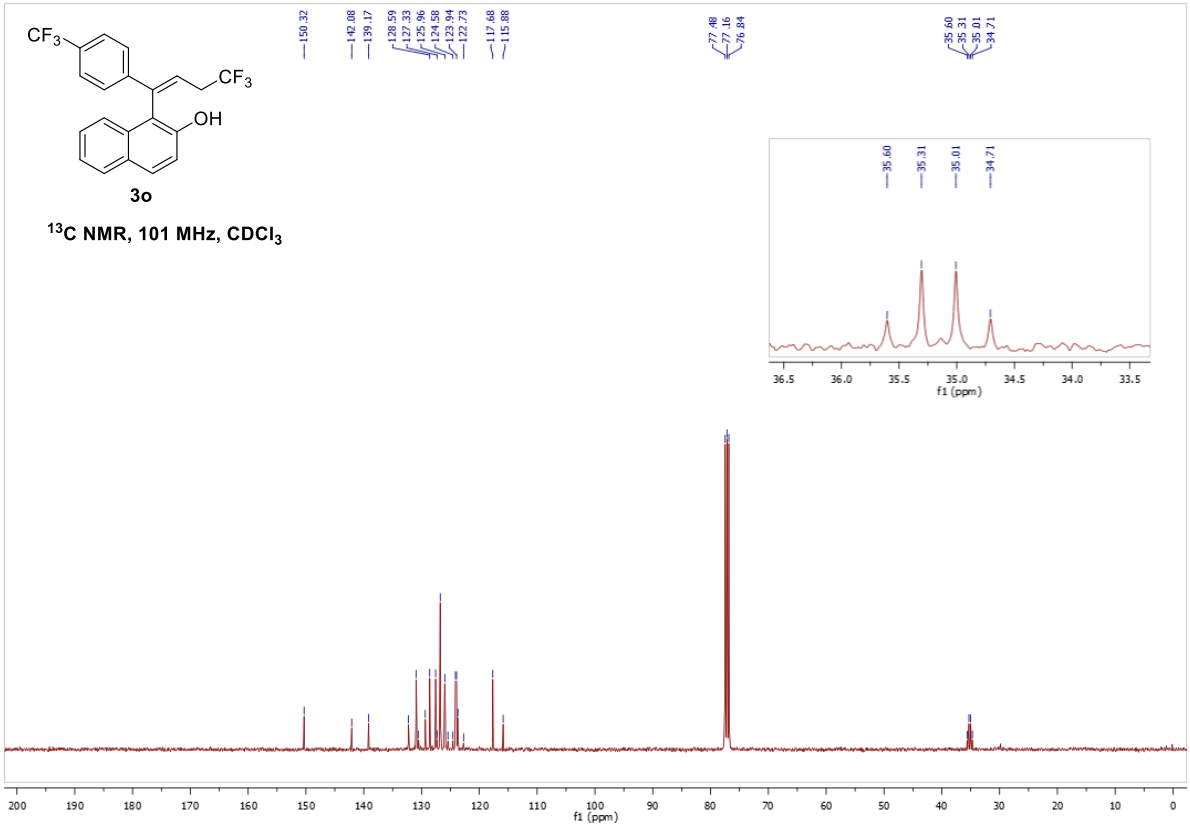
^{13}C NMR, 101 MHz, DMSO

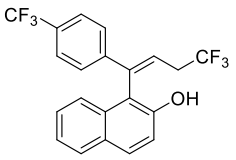


3n

^{19}F NMR, 376 MHz, DMSO

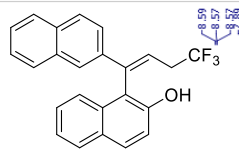

CF3
CF3
OH
3o
1H NMR, 500 MHz, CDCl3


CF3
CF3
OH
3o
13C NMR, 101 MHz, CDCl3



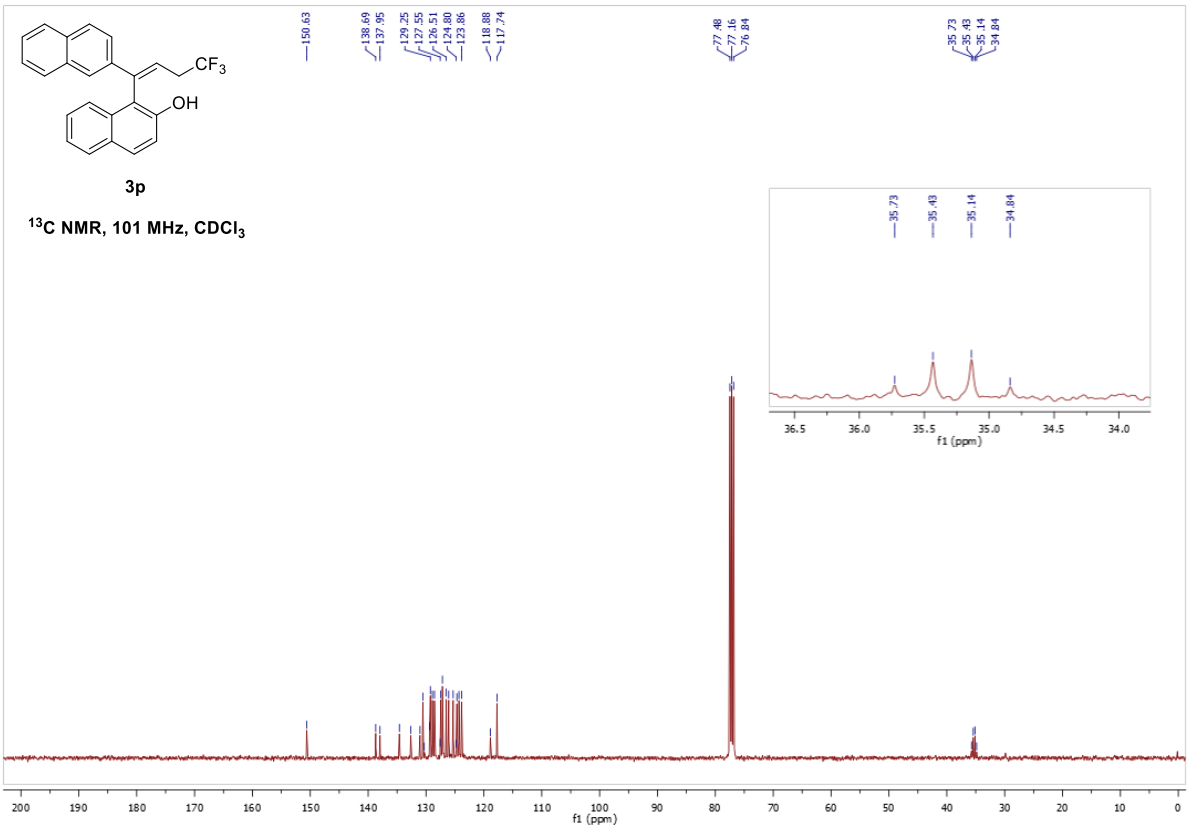
3o

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



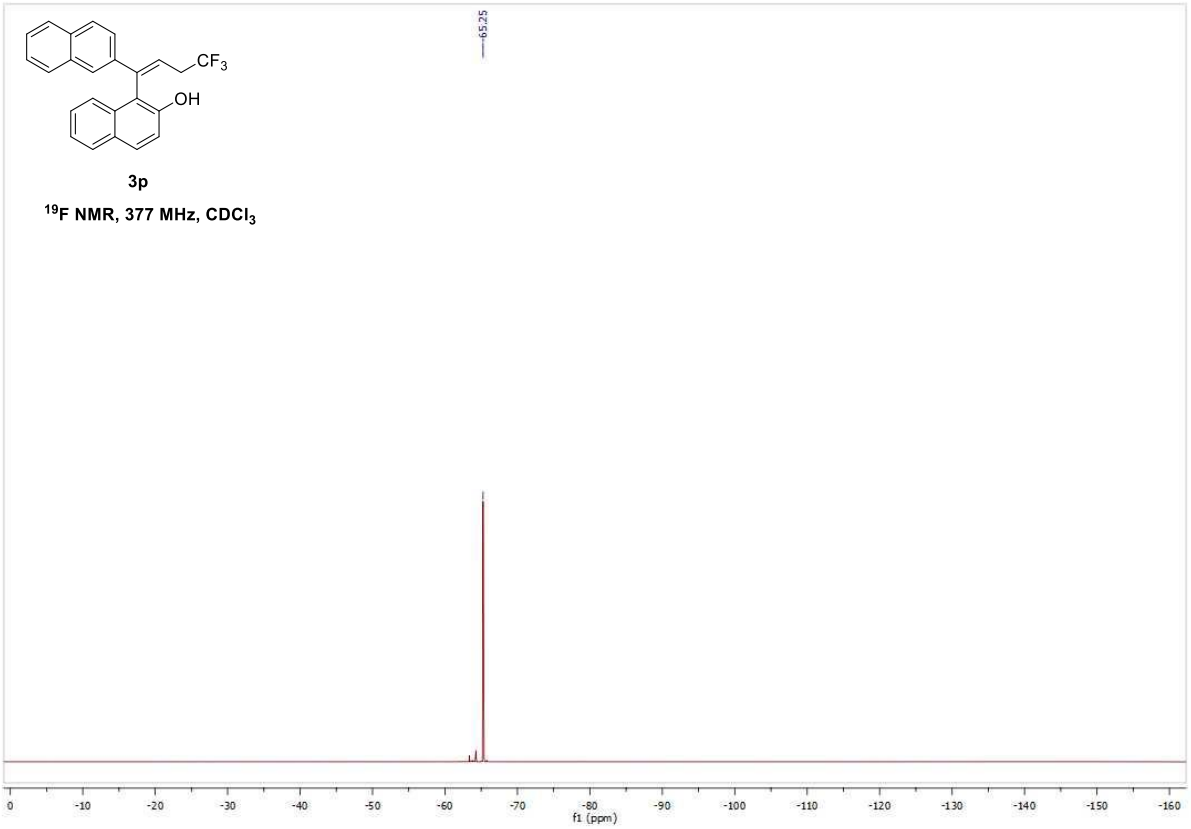
3p

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



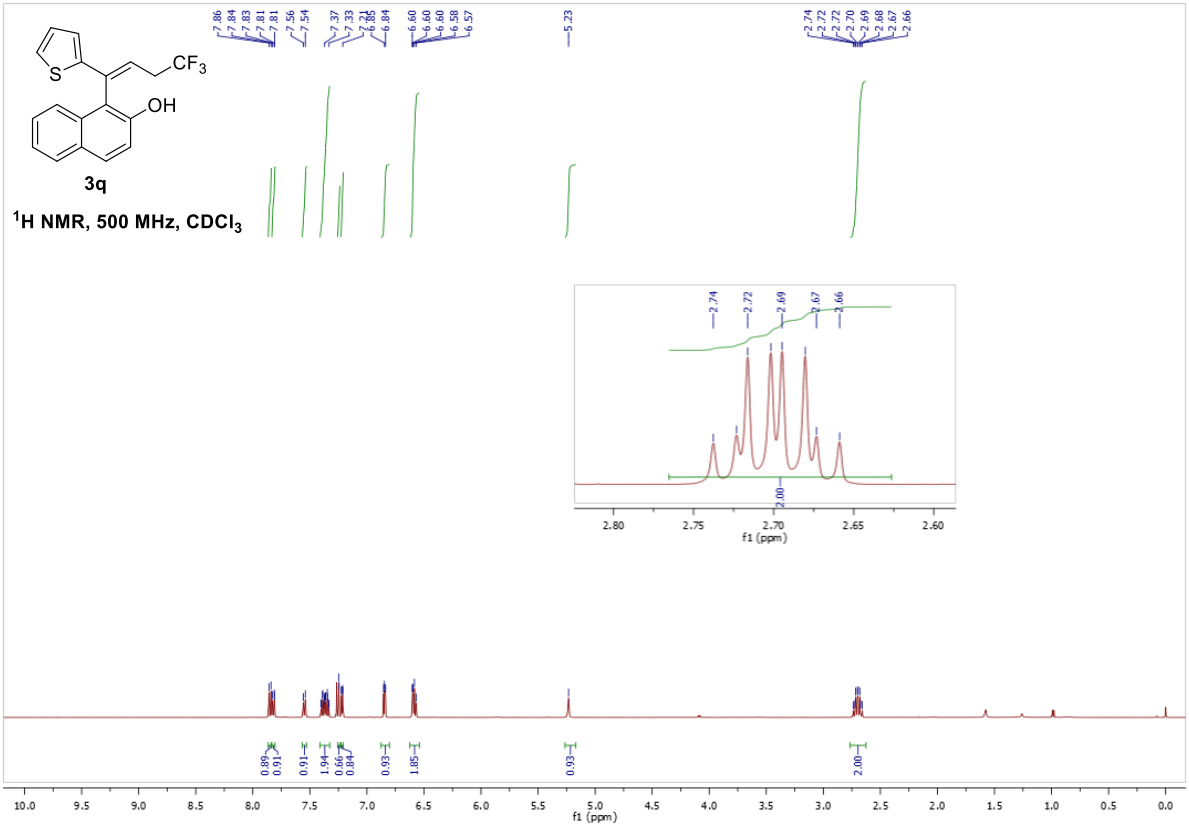
3p

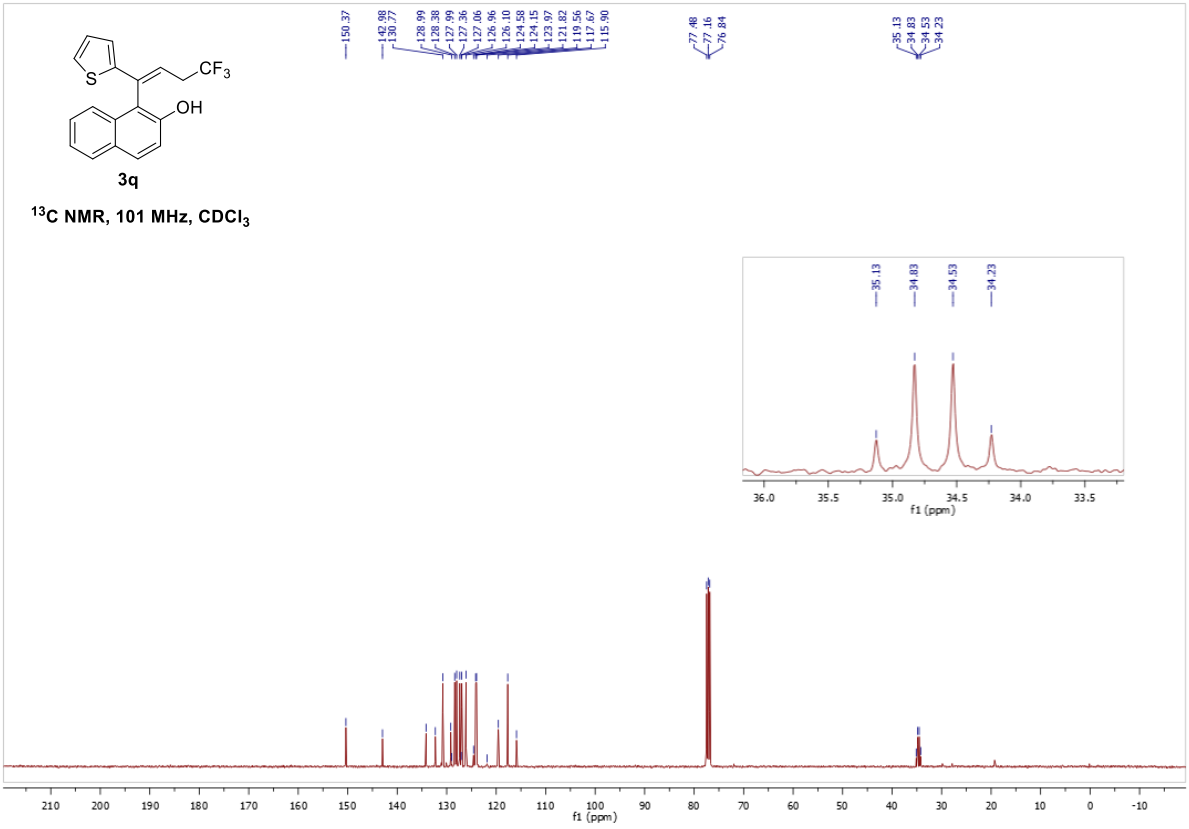
^{13}C NMR, 101 MHz, $CDCl_3$

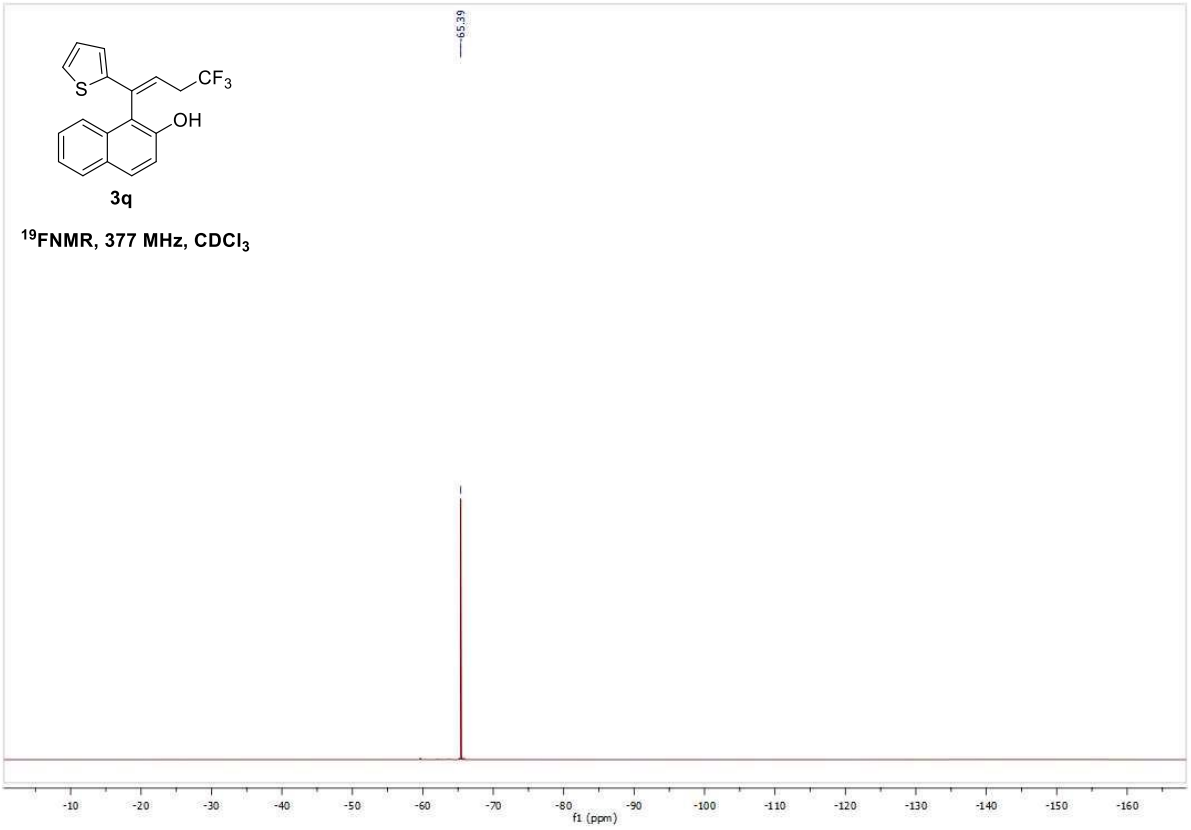


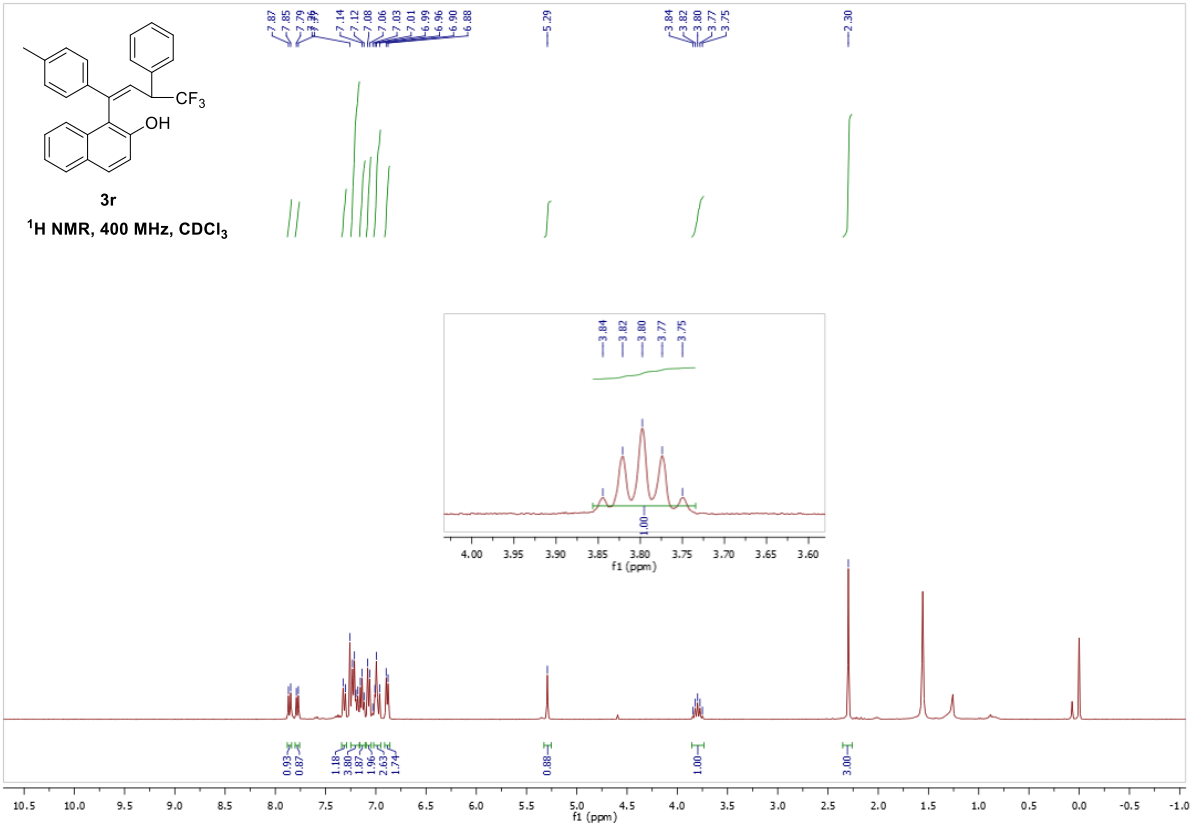
3p

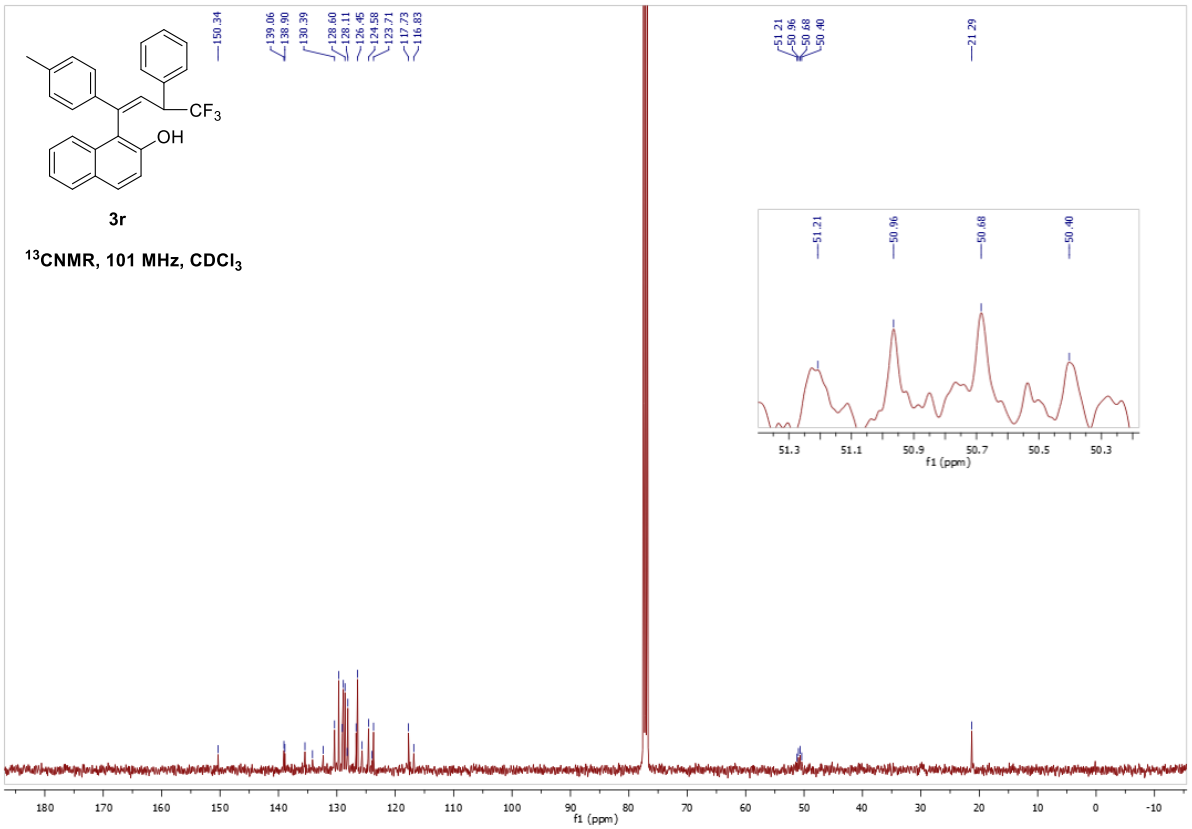
^{19}F NMR, 377 MHz, $CDCl_3$


CF3
S
OH
3q
1H NMR, 500 MHz, CDCl3
f1 (ppm)


CF3
S
OH
3q
13C NMR, 101 MHz, CDCl3
f1 (ppm)

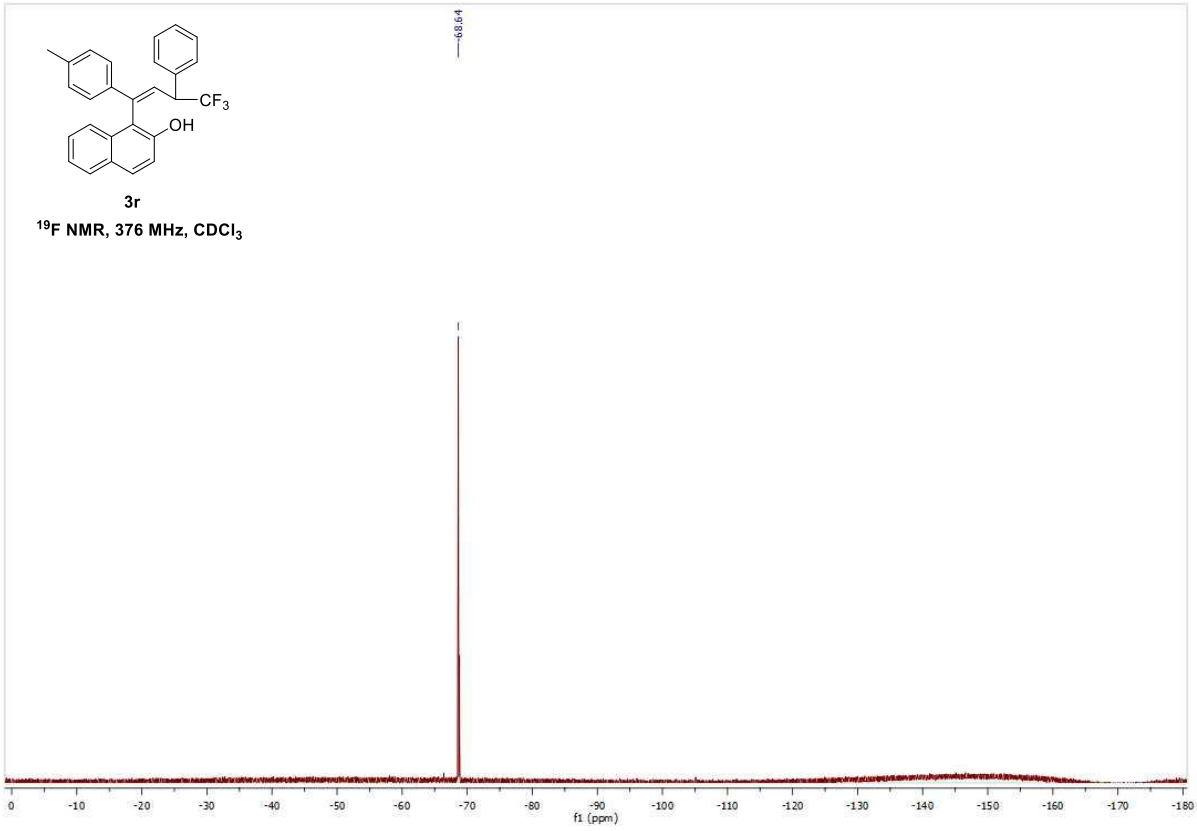

S
CF3
OH
3q
19FNMR, 377 MHz, CDCl3
-65.39
f1 (ppm)


CF3
OH
3r
1H NMR, 400 MHz, CDCl3
7.87
7.85
7.79
7.14
7.12
7.08
7.06
7.03
7.01
6.99
6.96
6.90
6.88
5.29
3.84
3.82
3.80
3.77
3.75
2.30
1.00
f1 (ppm)



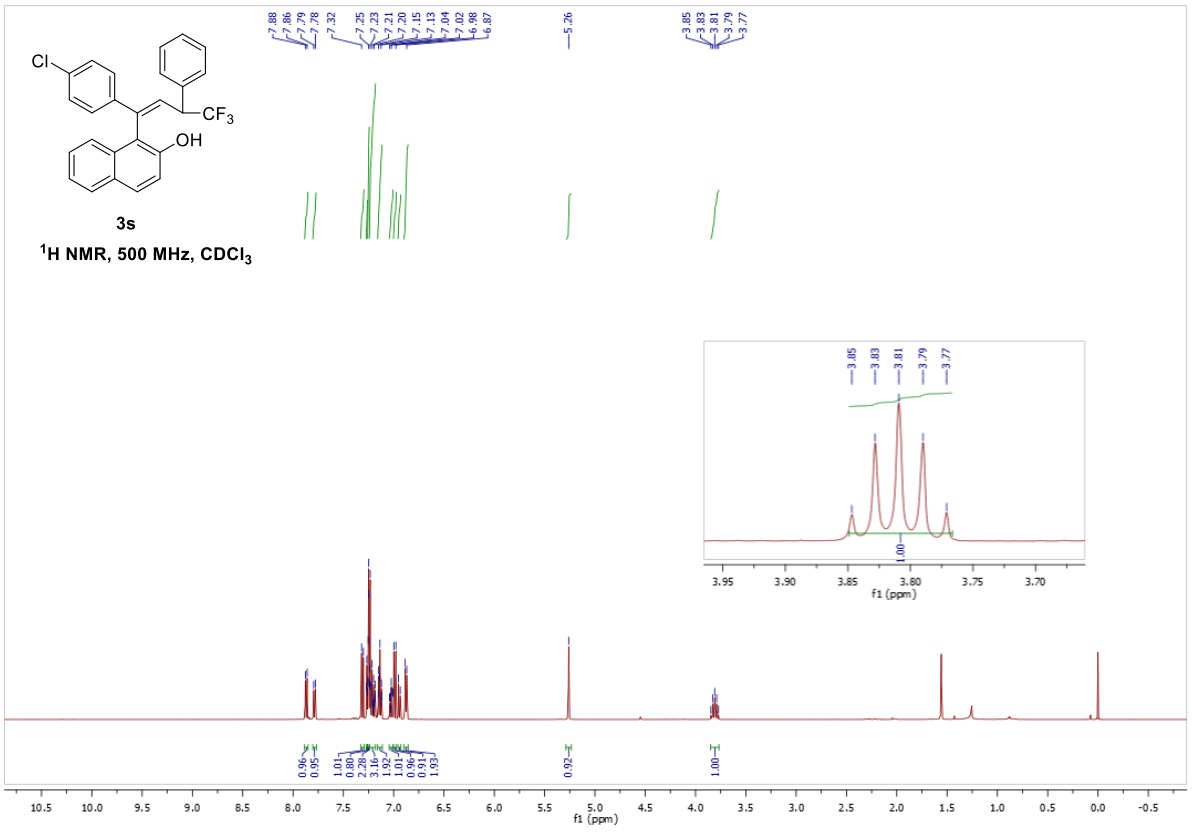
3r

^{13}CNMR, 101 MHz, $CDCl_3$



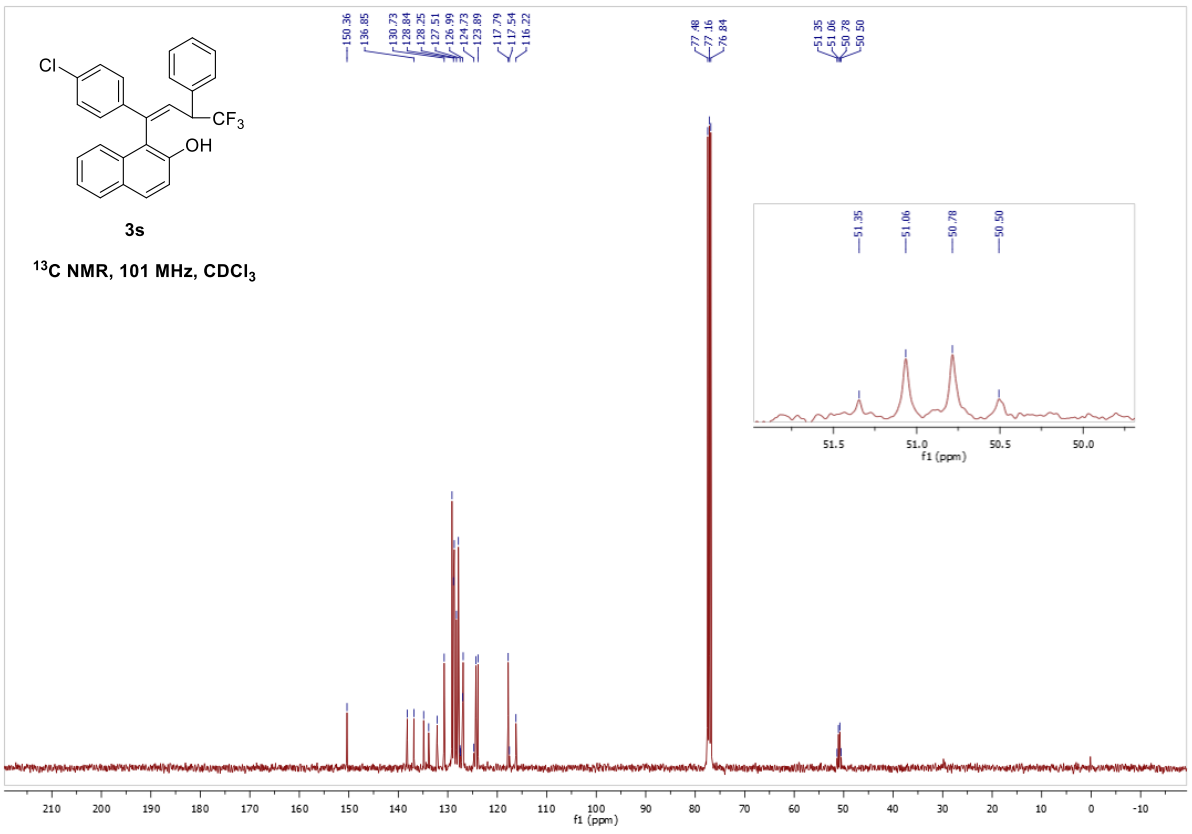
3r

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



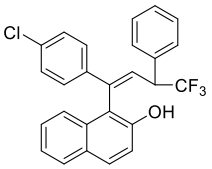
3s

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



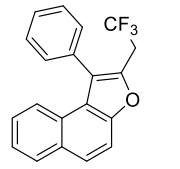
3s

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



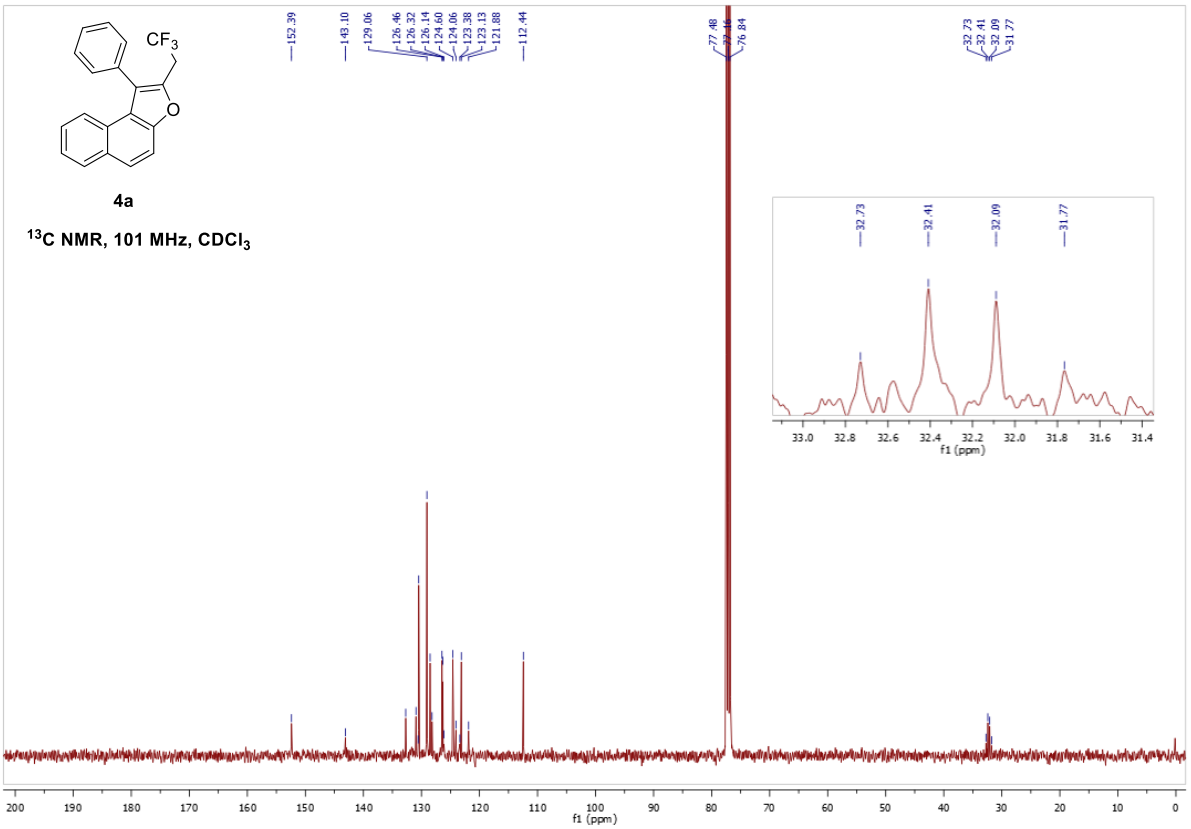
3s

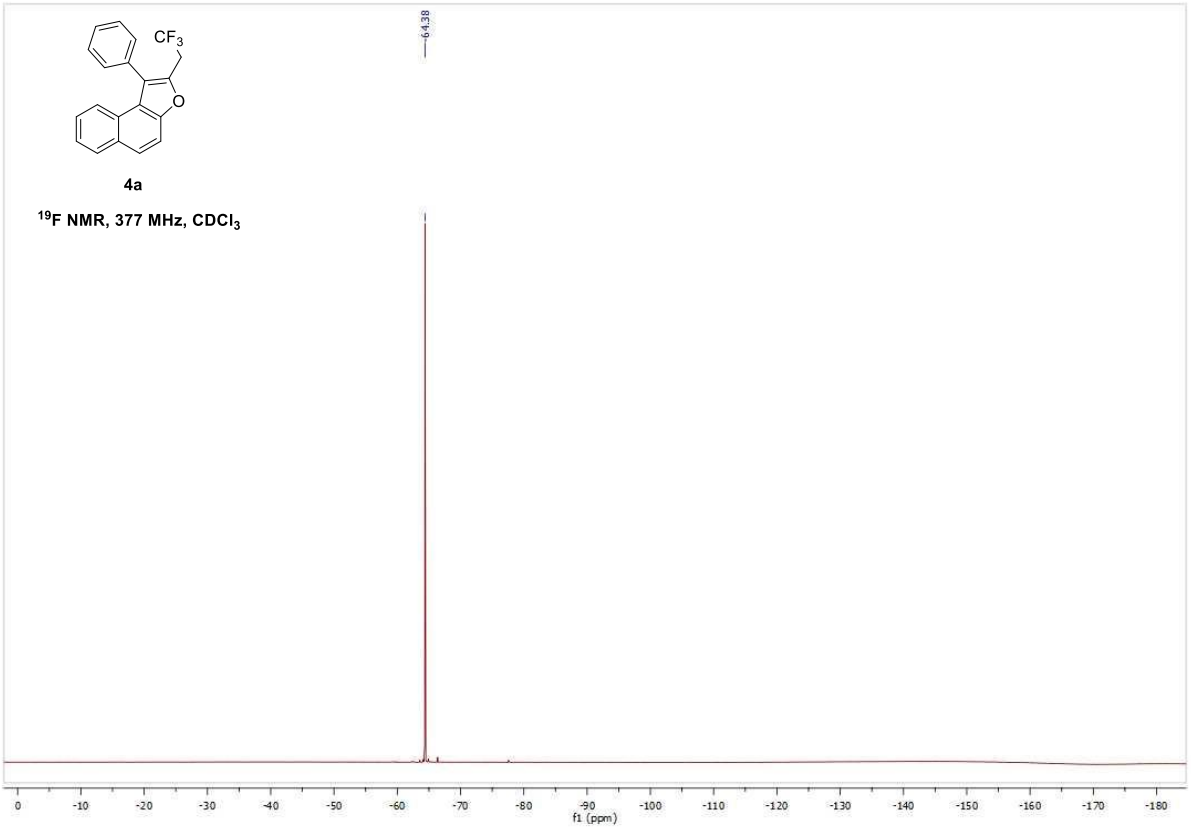
^{19}F NMR, 377 MHz, $CDCl_3$

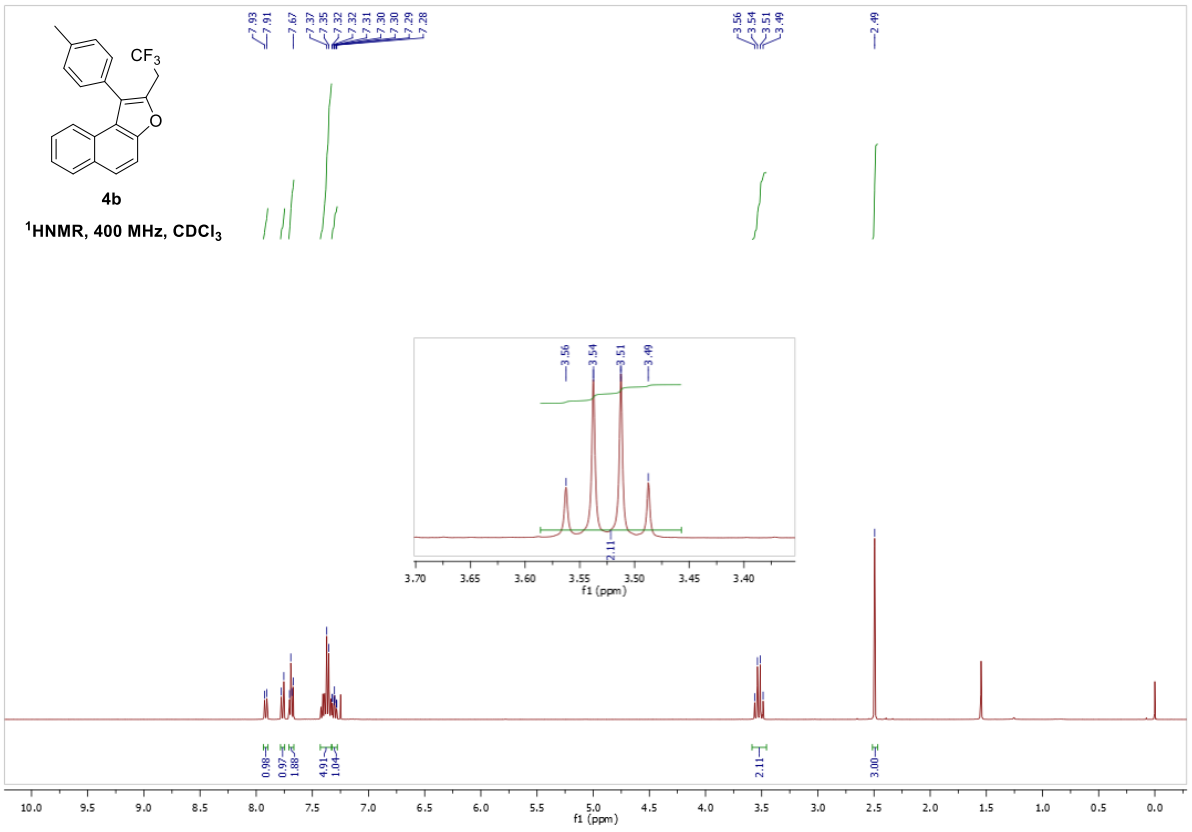


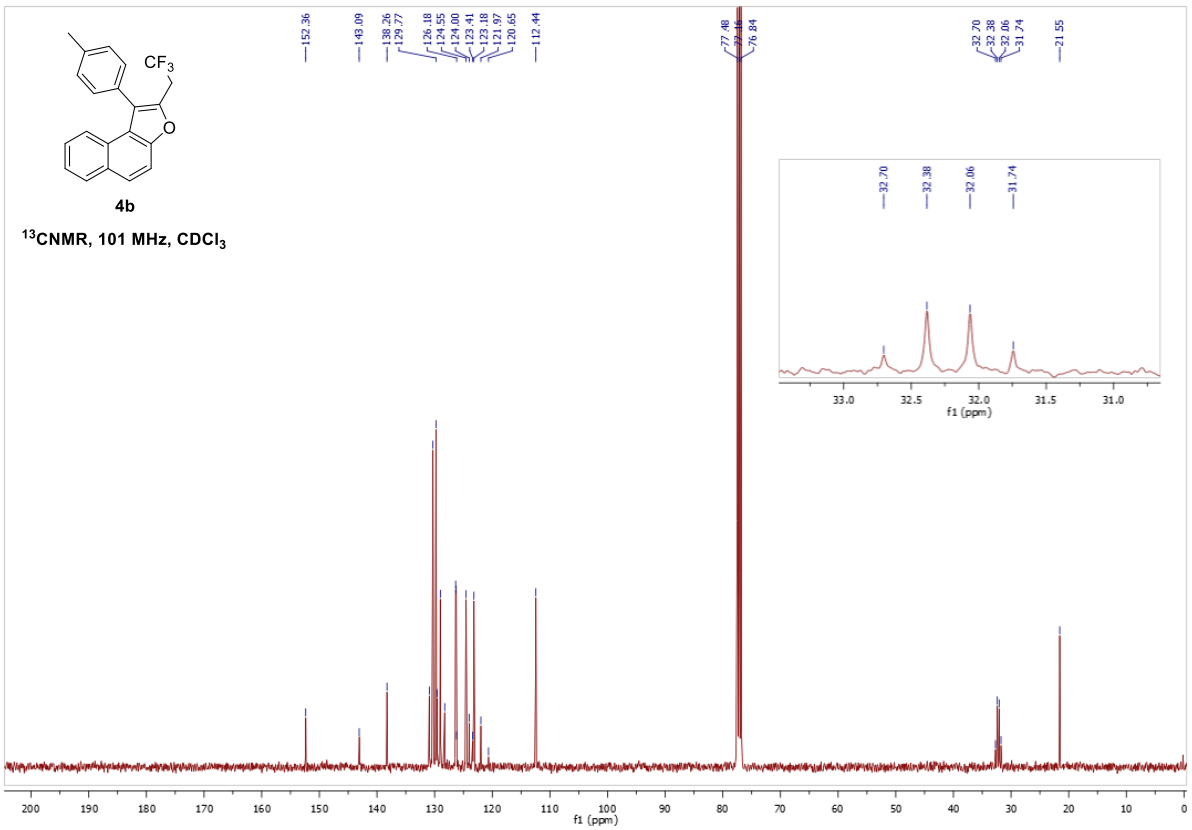
4a

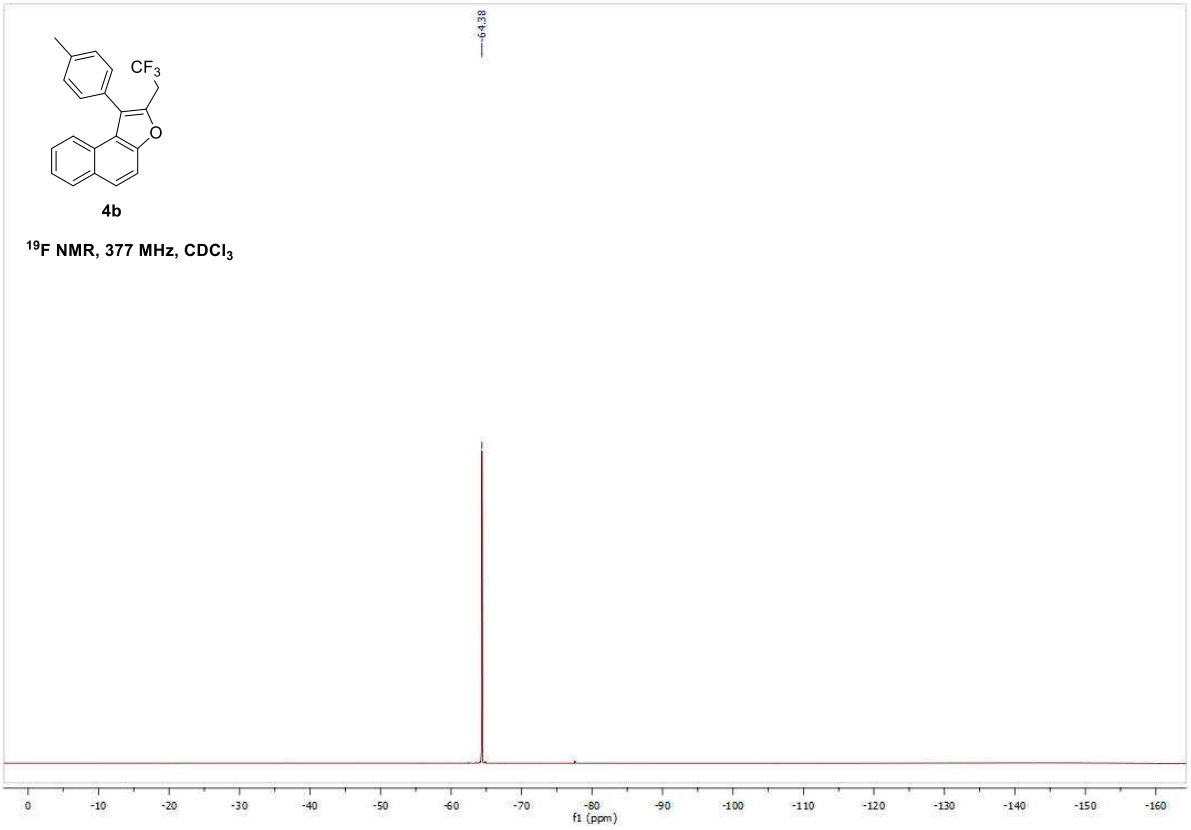
^{1}H NMR, 500 MHz, $CDCl_3$


CF3
O
4a
13C NMR, 101 MHz, CDCl3
152.39
143.10
129.06
126.46
126.32
126.14
124.60
124.06
123.38
123.13
121.88
112.44
77.48
77.16
76.84
32.73
32.41
32.09
31.77
f1 (ppm)


CF3
O
4a
19F NMR, 377 MHz, CDCl3
-64.38
f1 (ppm)

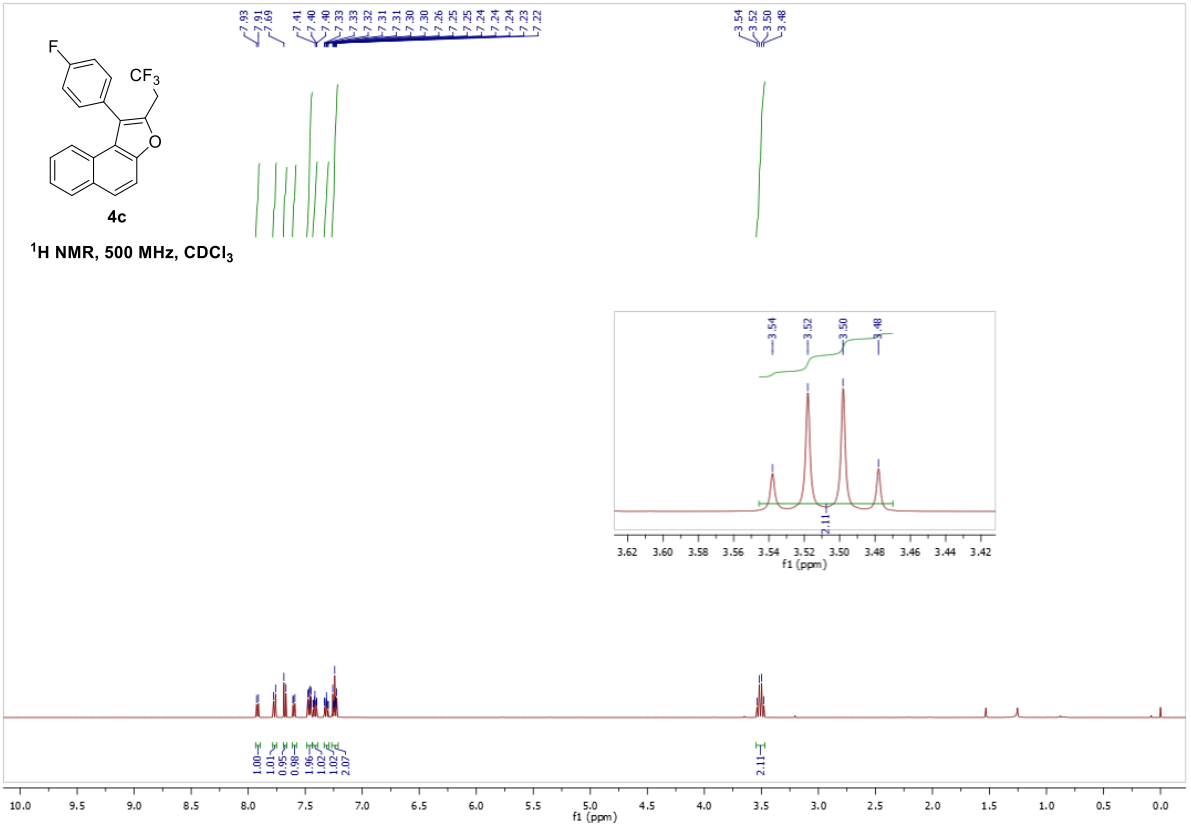

CF3
O
4b
1HNMR, 400 MHz, CDCl3
7.93
7.91
7.67
7.37
7.35
7.32
7.32
7.31
7.30
7.30
7.29
7.28
3.56
3.54
3.51
3.49
2.49
0.98
0.97
1.88
4.91
1.04
2.11
3.00
f1 (ppm)


CF3
O
4b
13CNMR, 101 MHz, CDCl3
152.36
143.09
138.26
129.77
126.18
124.55
124.00
123.41
123.18
121.97
120.65
112.44
77.48
77.16
76.84
32.70
32.38
32.06
31.74
21.55
f1 (ppm)



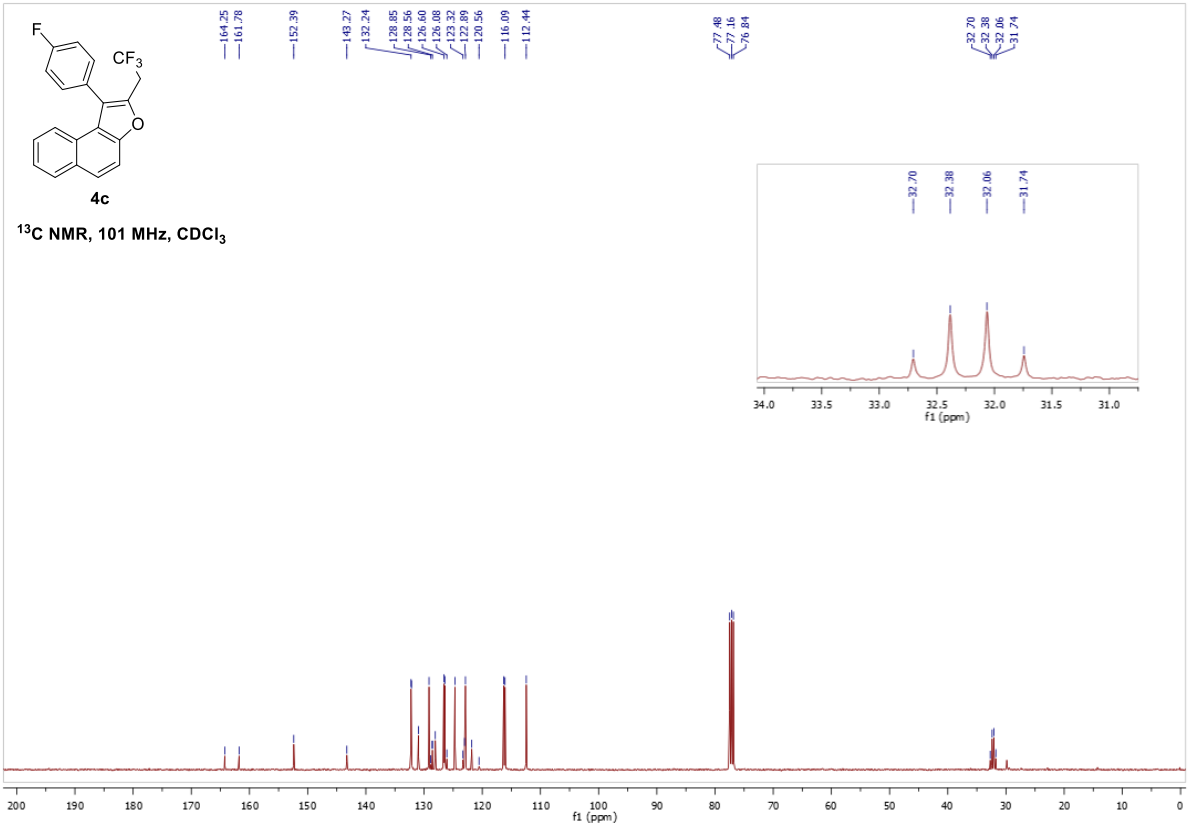
4b

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



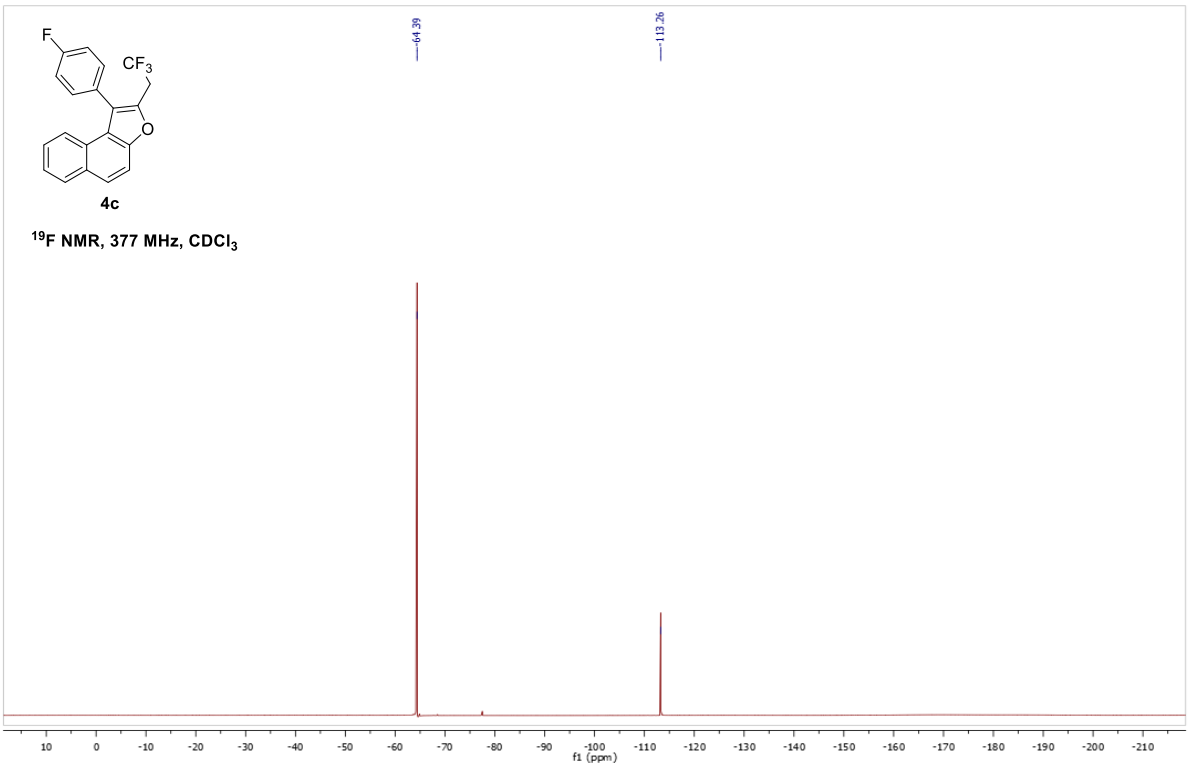
4c

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



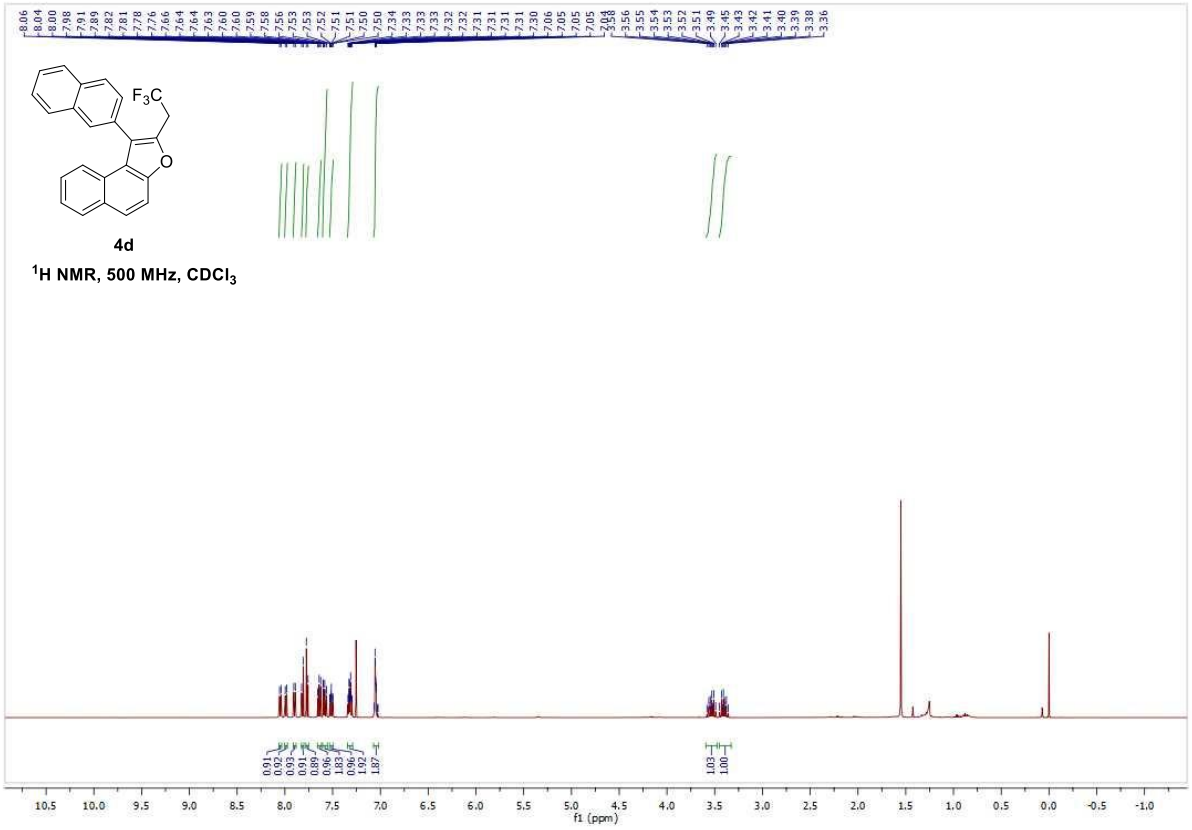
4c

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



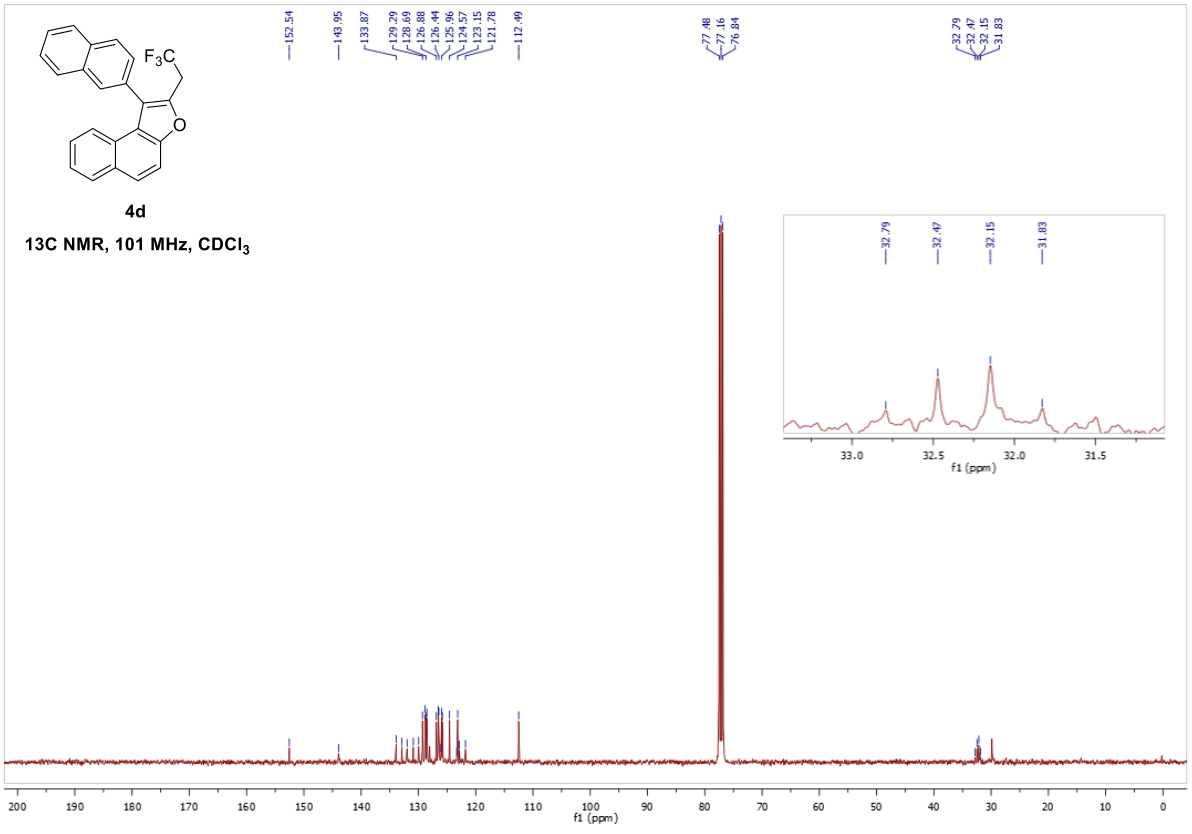
4c

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



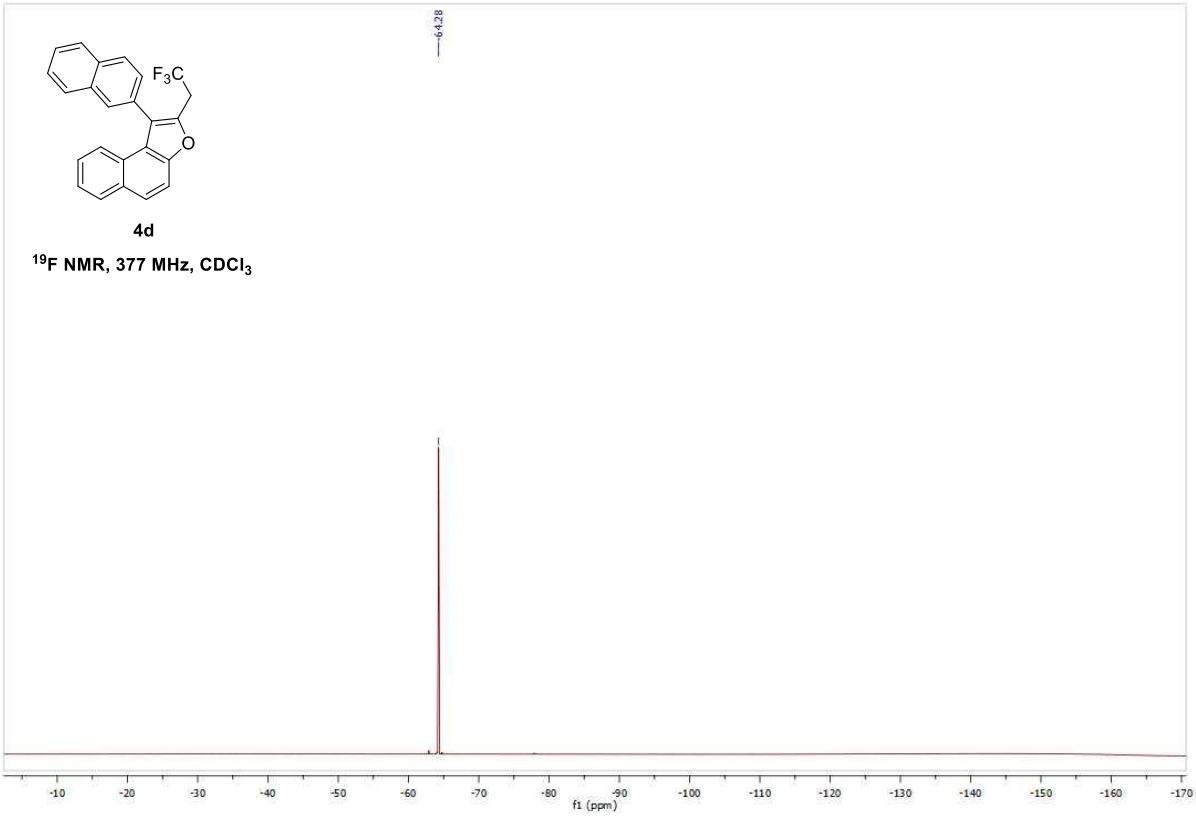
4d

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



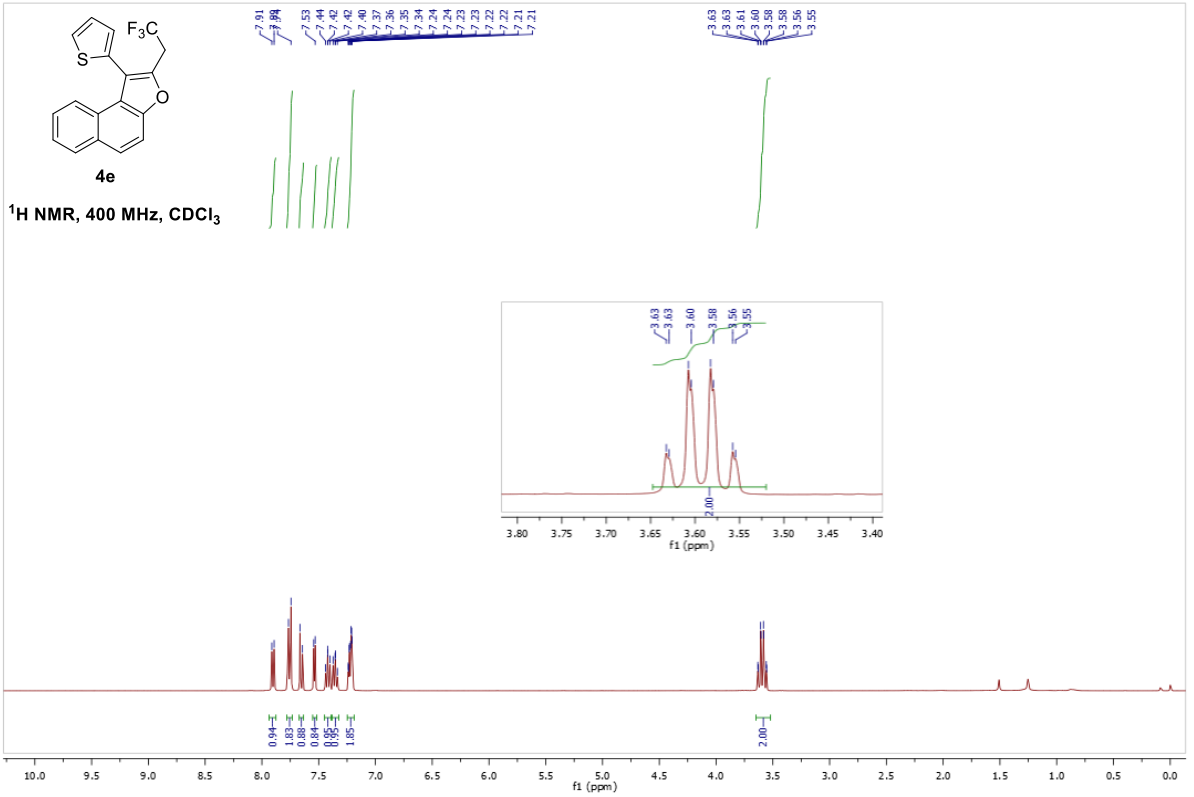
4d

13C NMR, 101 MHz, $CDCl_3$



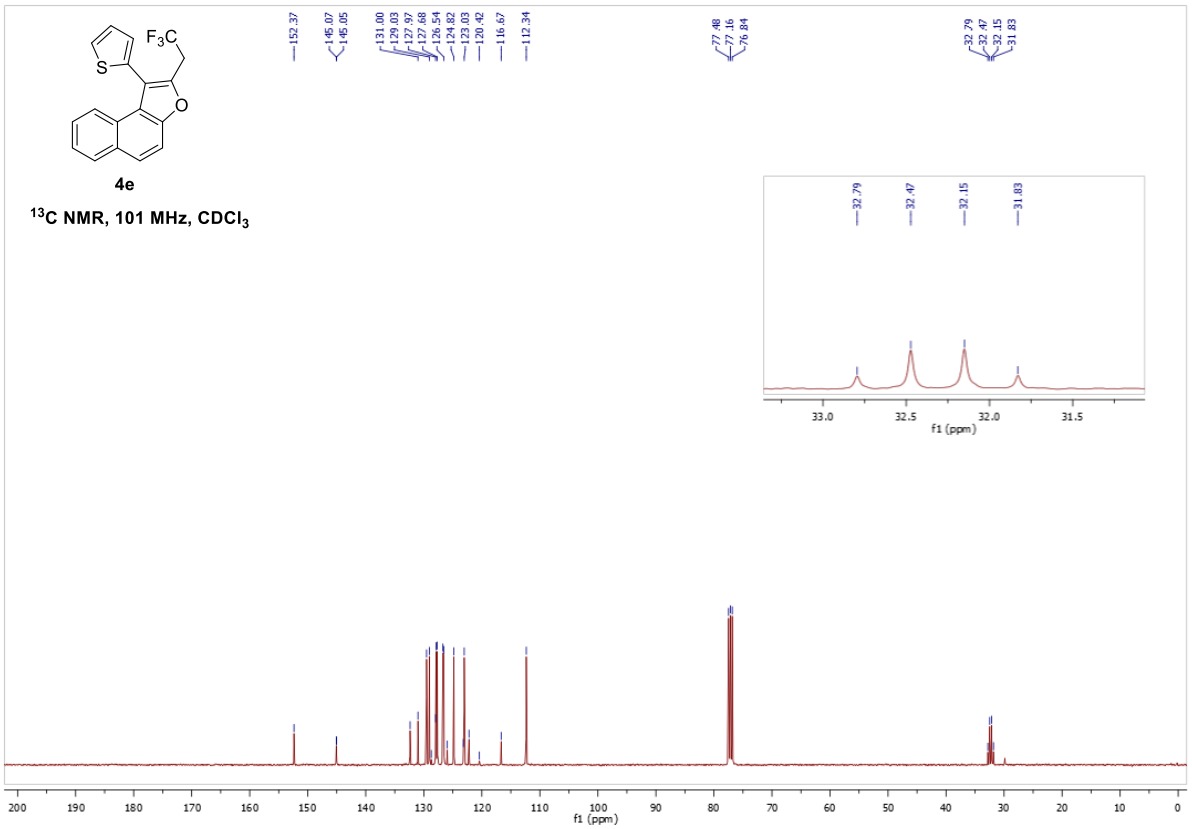
4d

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



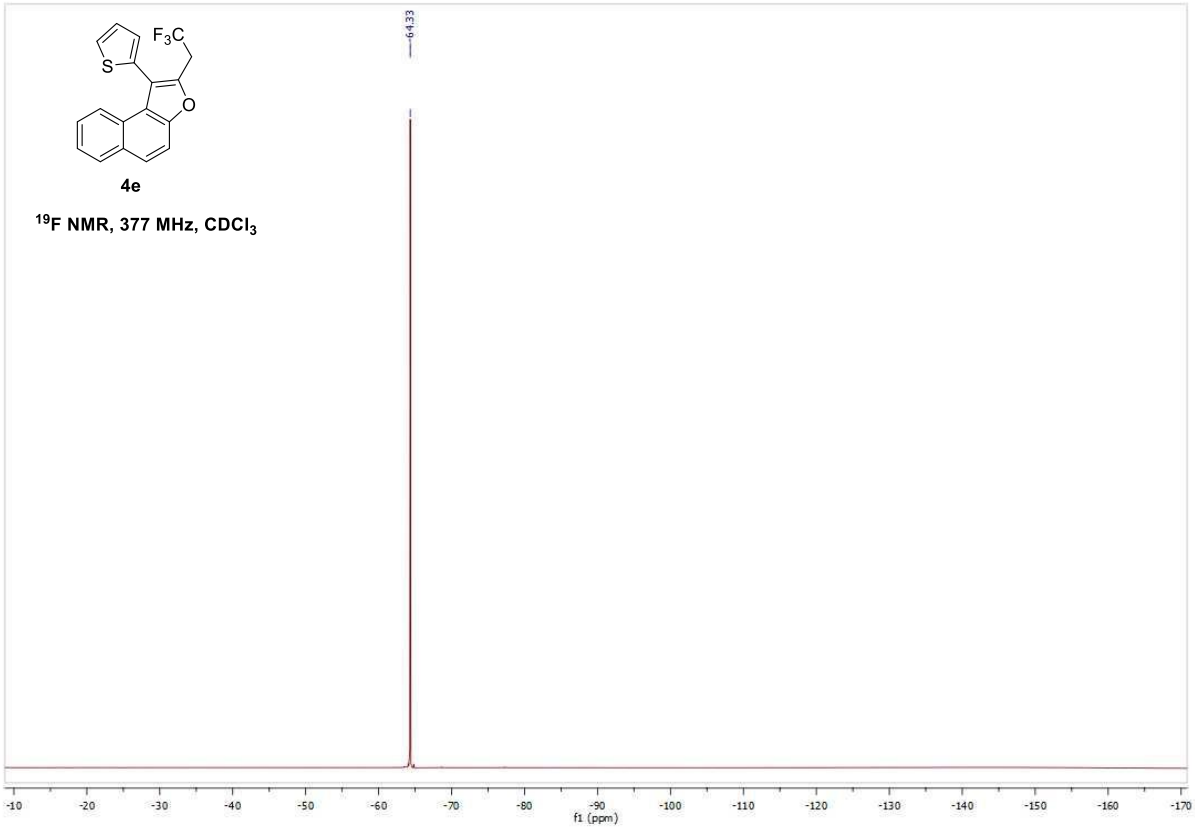
4e

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



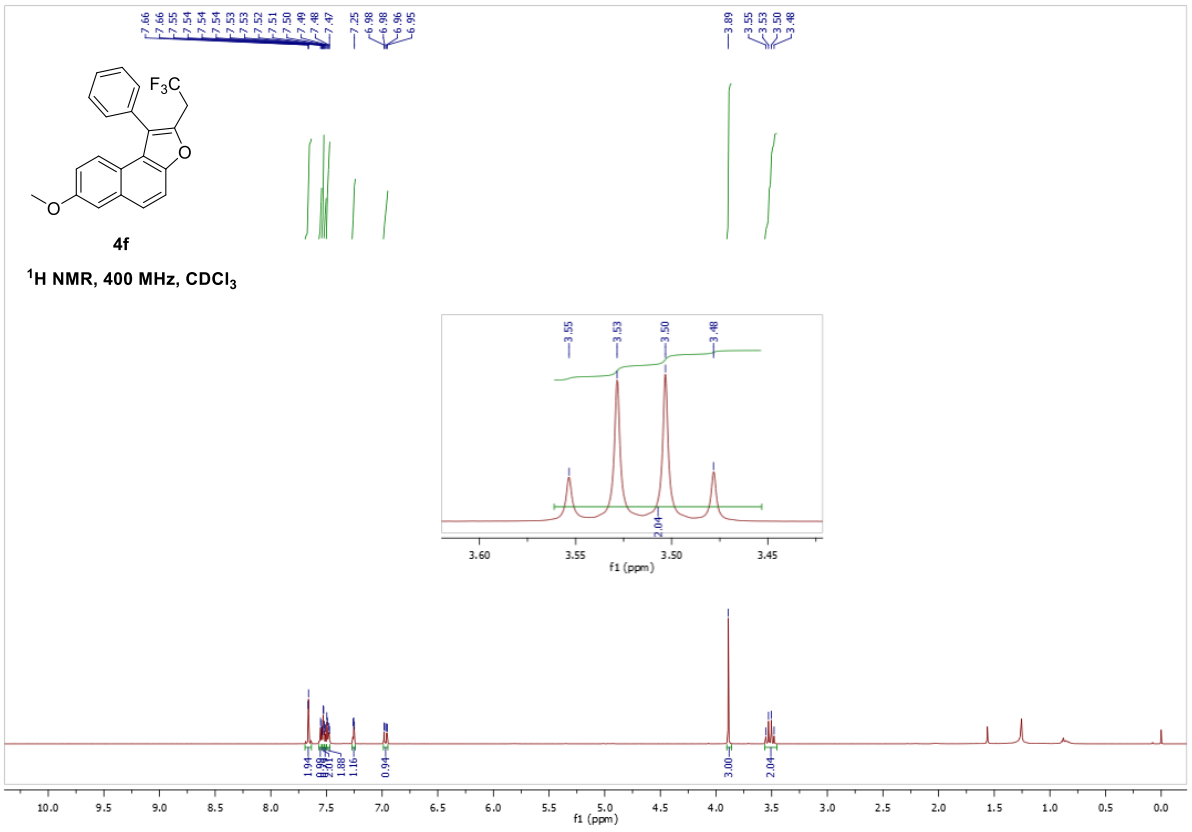
4e

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



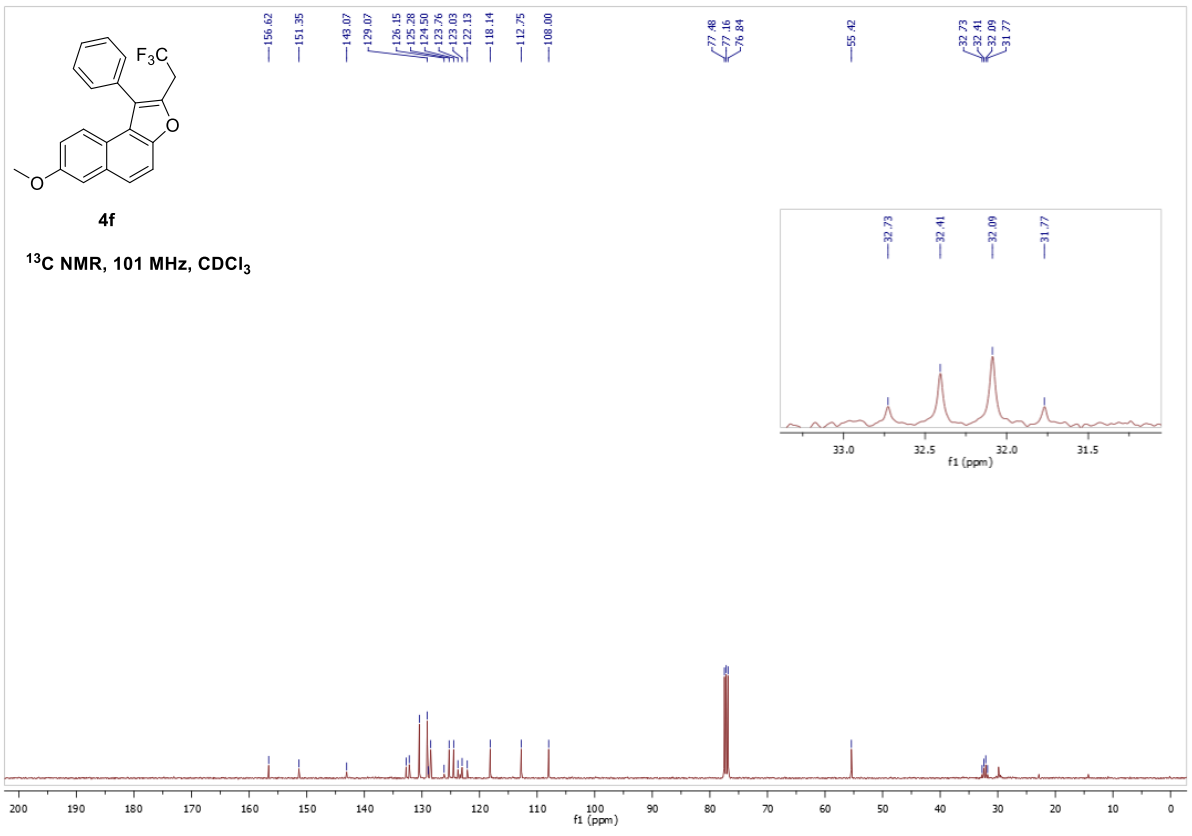
4e

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



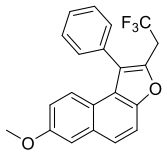
4f

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



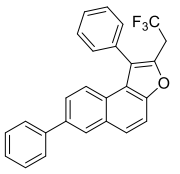
4f

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



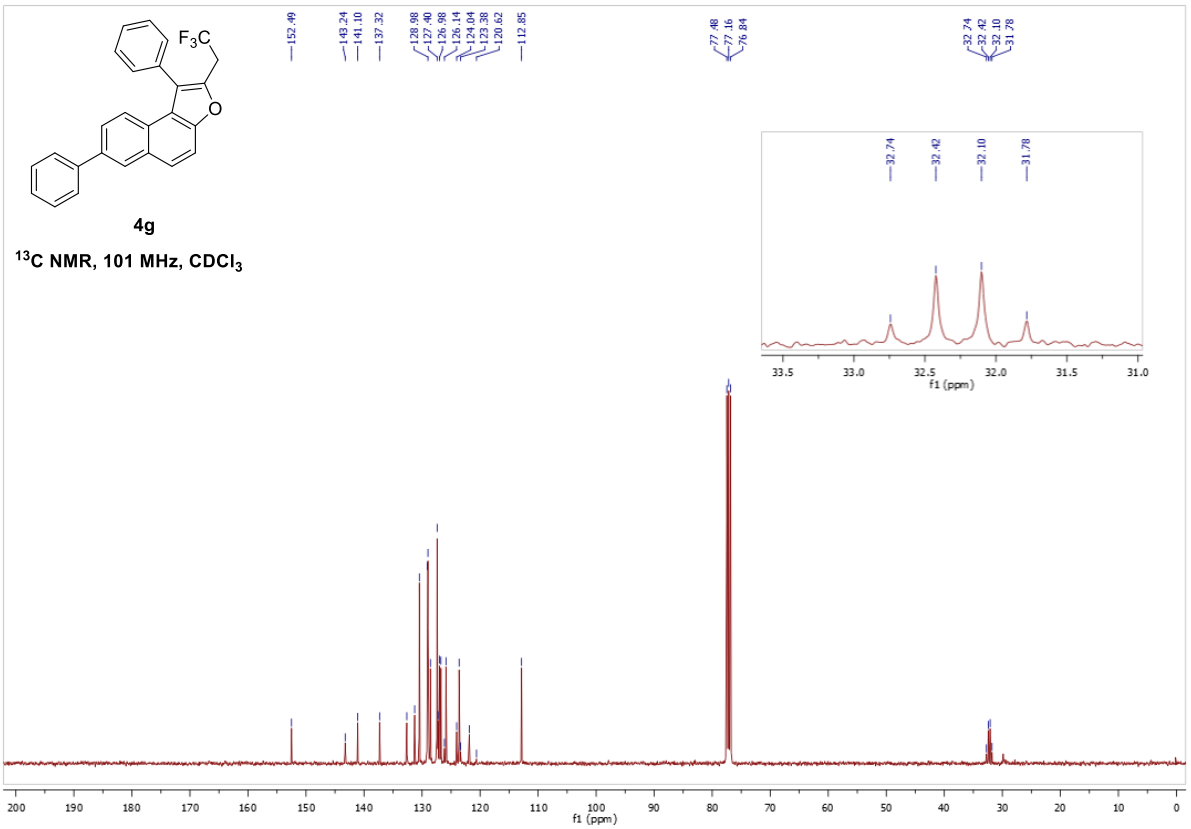
4f

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



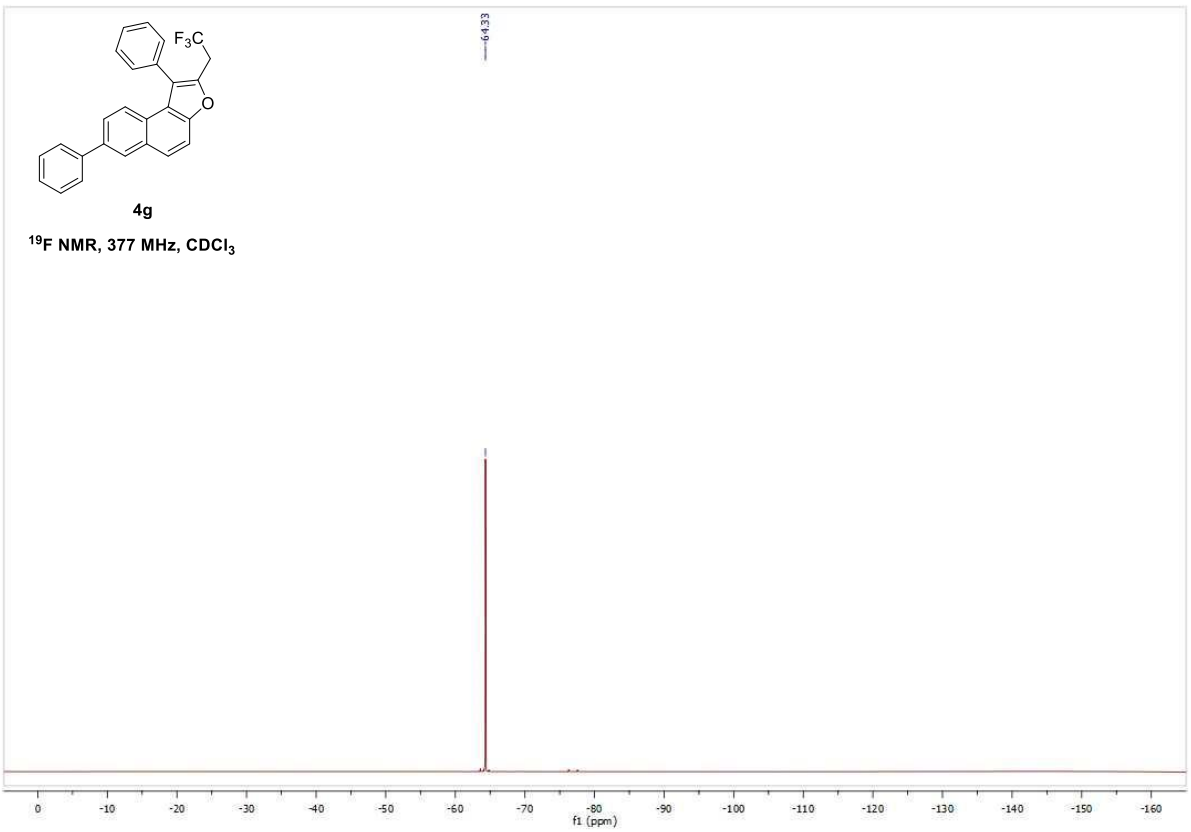
4g

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



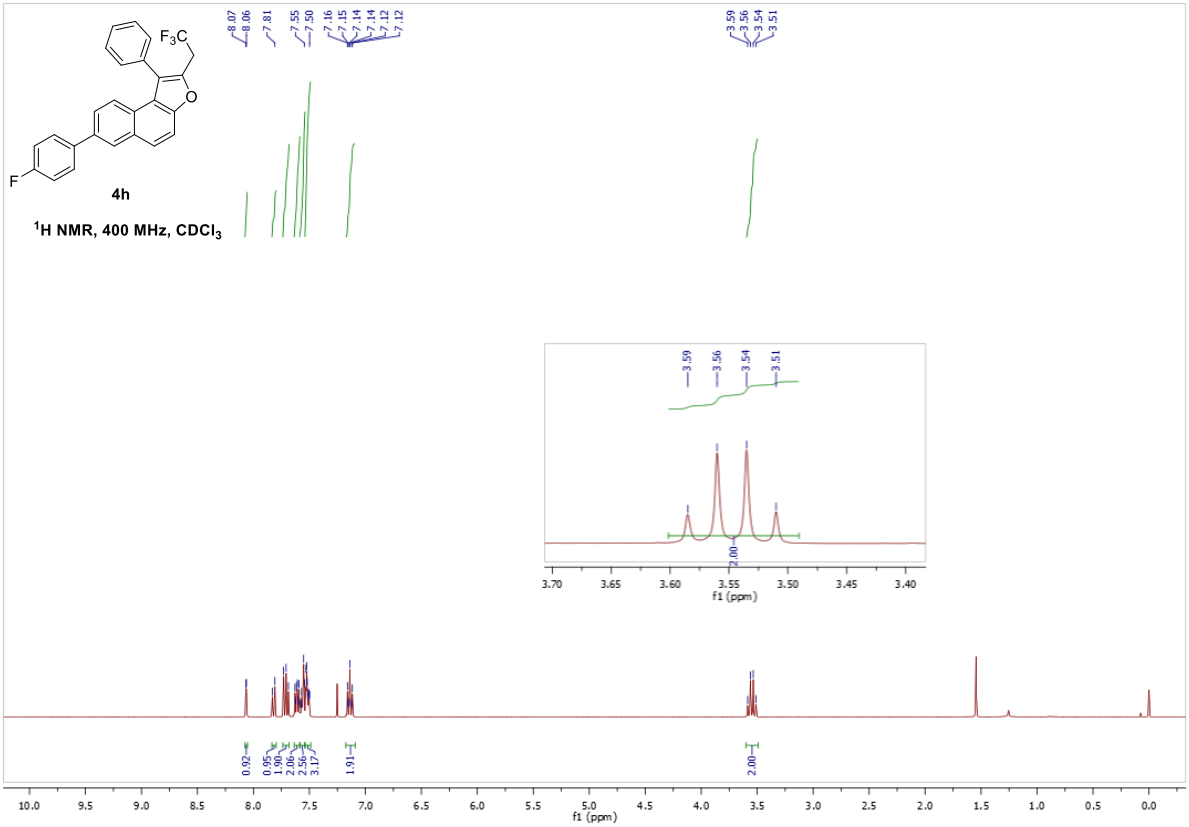
4g

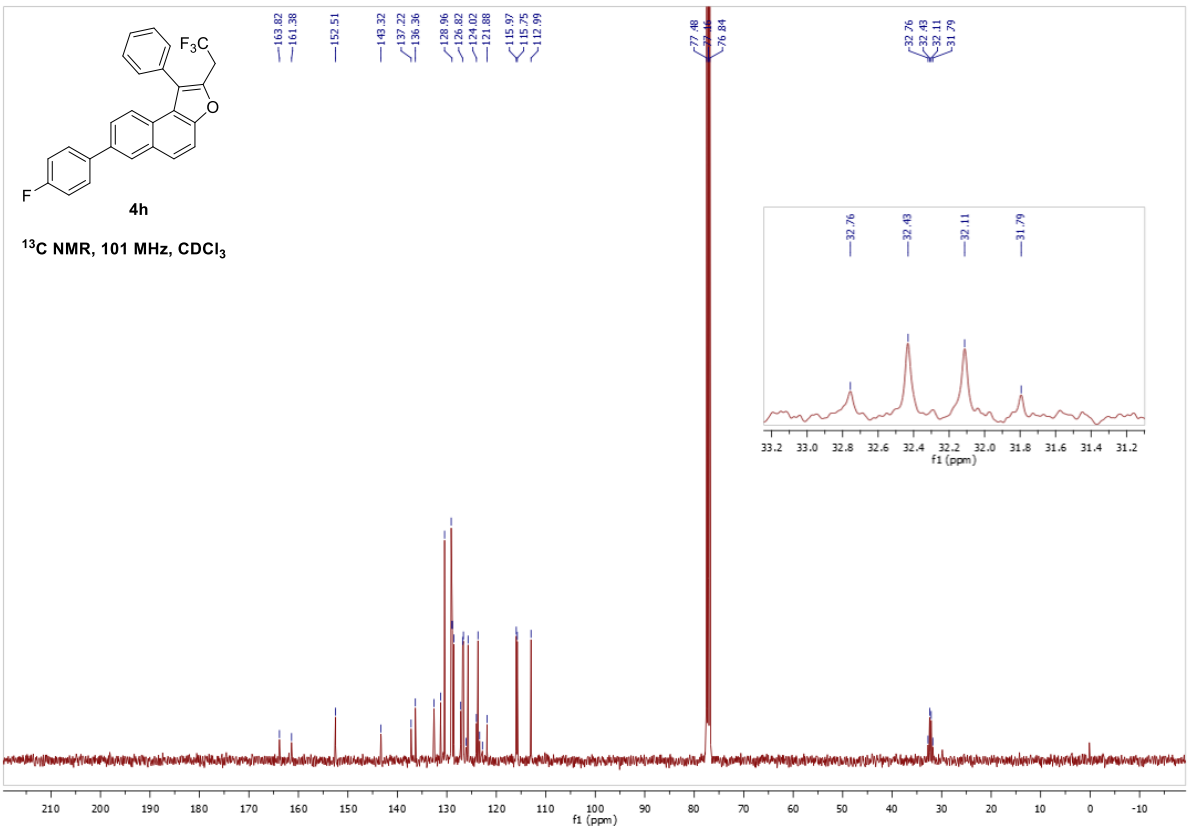
^{13}C NMR, 101 MHz, $CDCl_3$

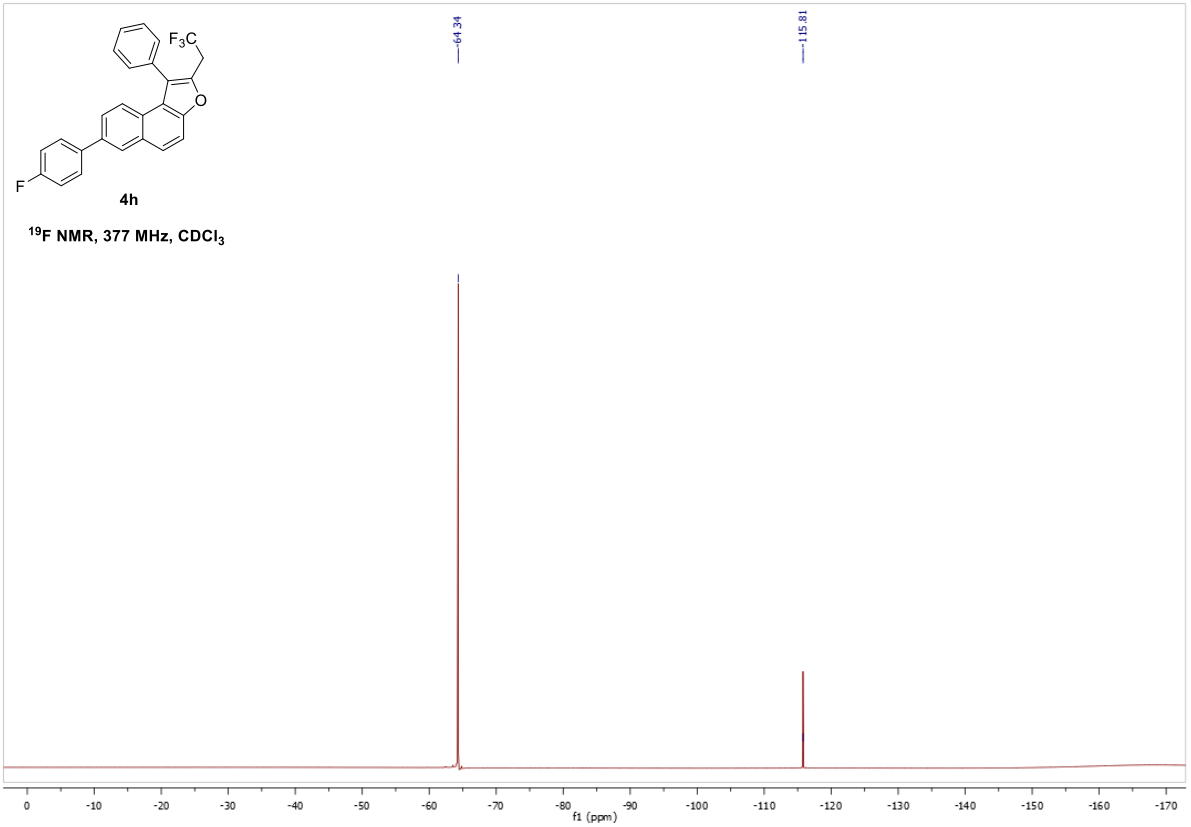


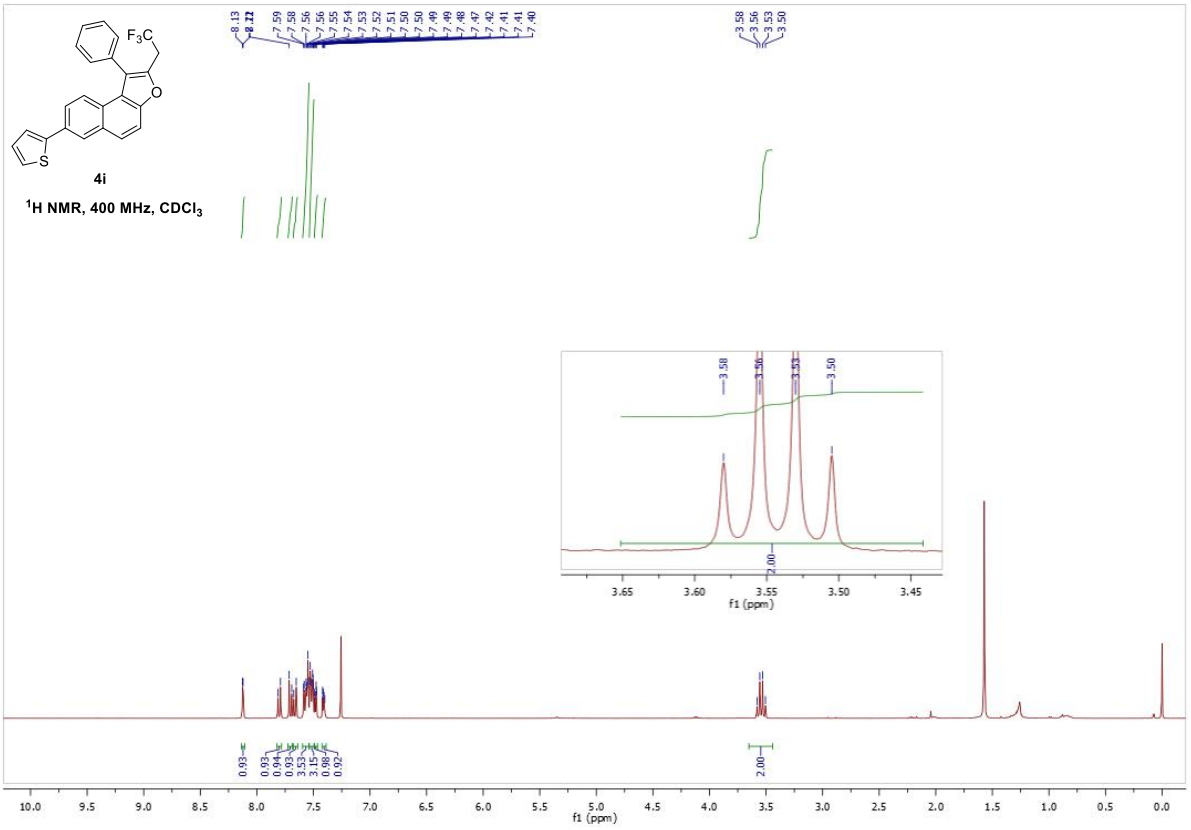
4g

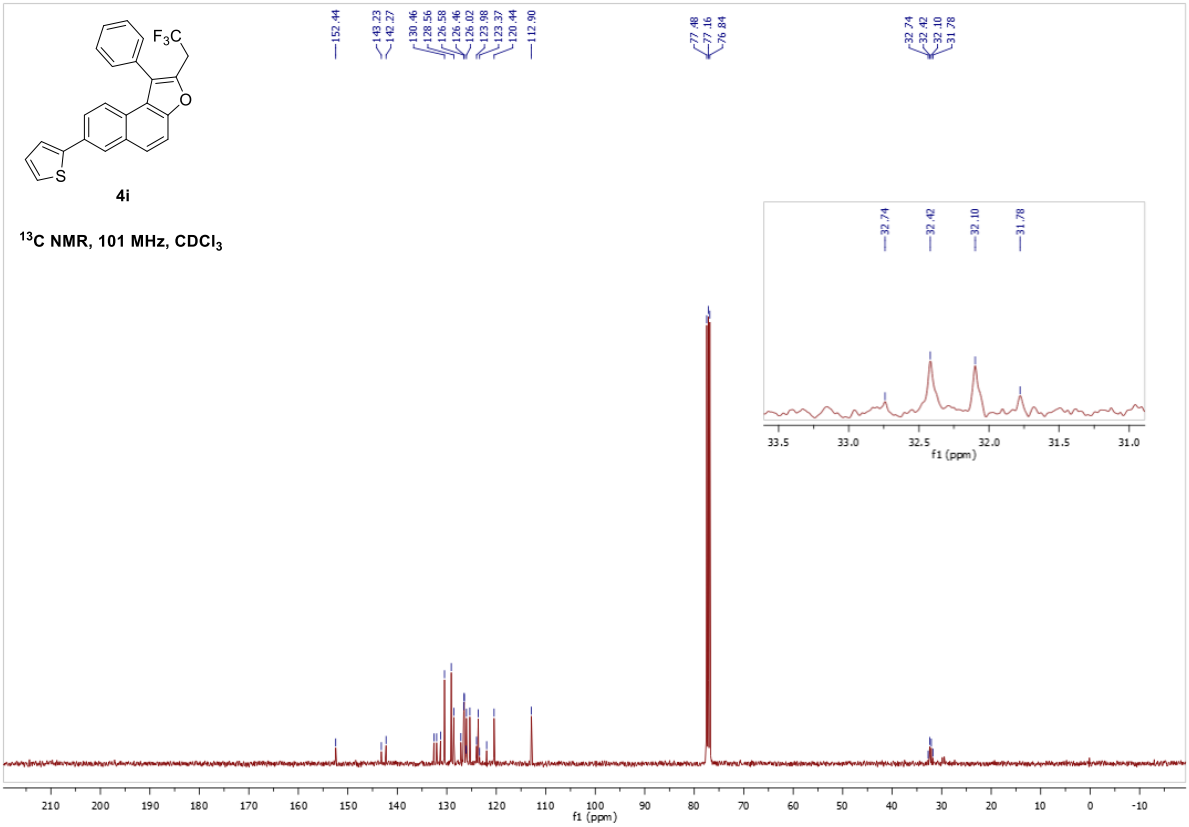
^{19}F NMR, 377 MHz, $CDCl_3$

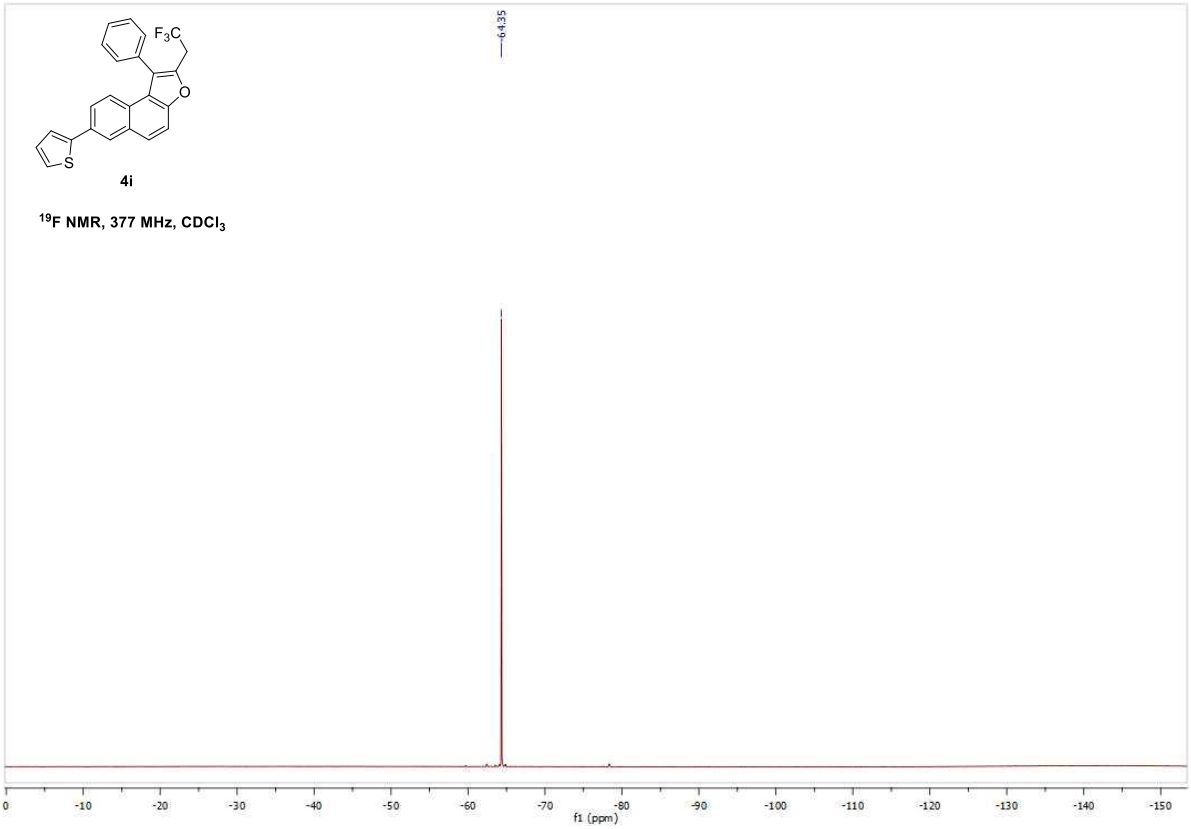

F3C
O
F
4h
1H NMR, 400 MHz, CDCl3
8.07
8.06
7.81
7.55
7.50
7.16
7.15
7.14
7.14
7.12
7.12
3.59
3.56
3.54
3.51
2.00
0.92
0.95
1.00
1.06
2.56
3.17
1.91
2.00
f1 (ppm)

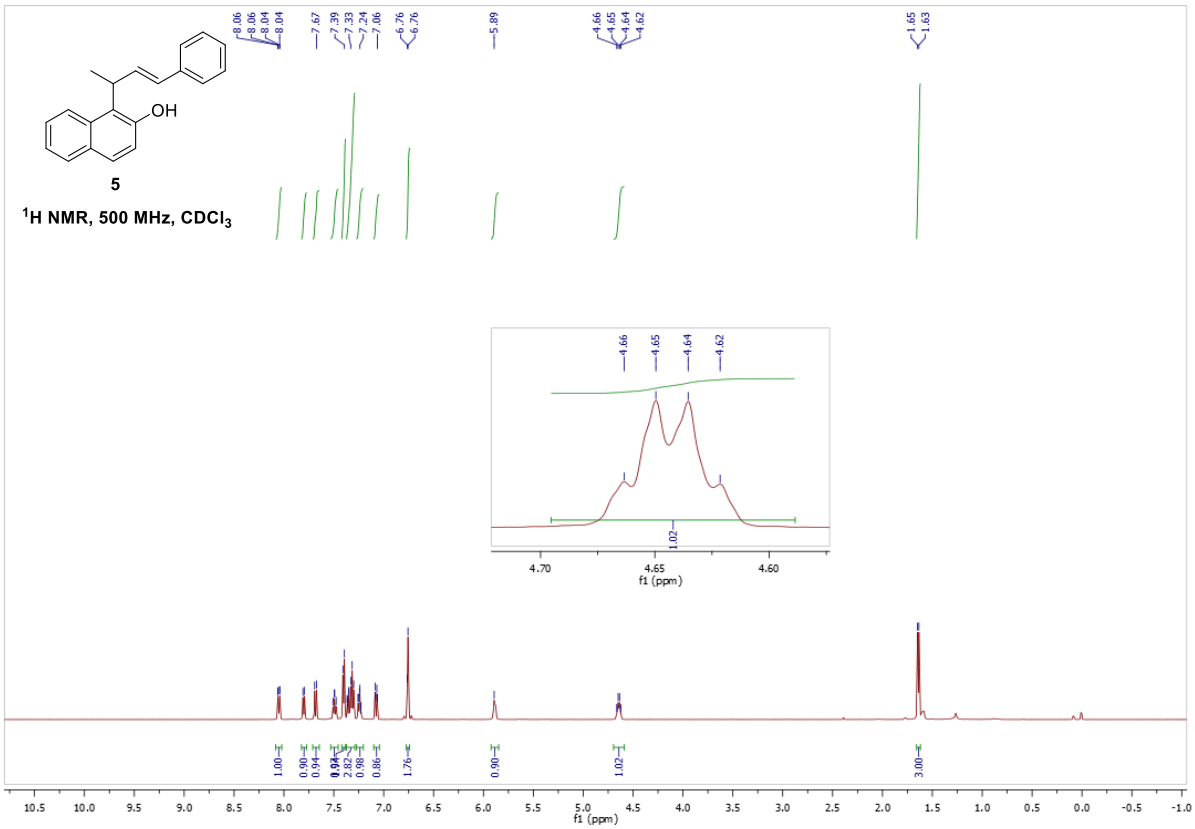

F3C
O
F
4h
13C NMR, 101 MHz, CDCl3
163.82
161.38
152.51
143.32
137.22
136.36
128.96
126.82
124.02
121.88
115.97
115.75
112.99
77.48
77.16
76.84
32.76
32.43
32.11
31.79
f1 (ppm)

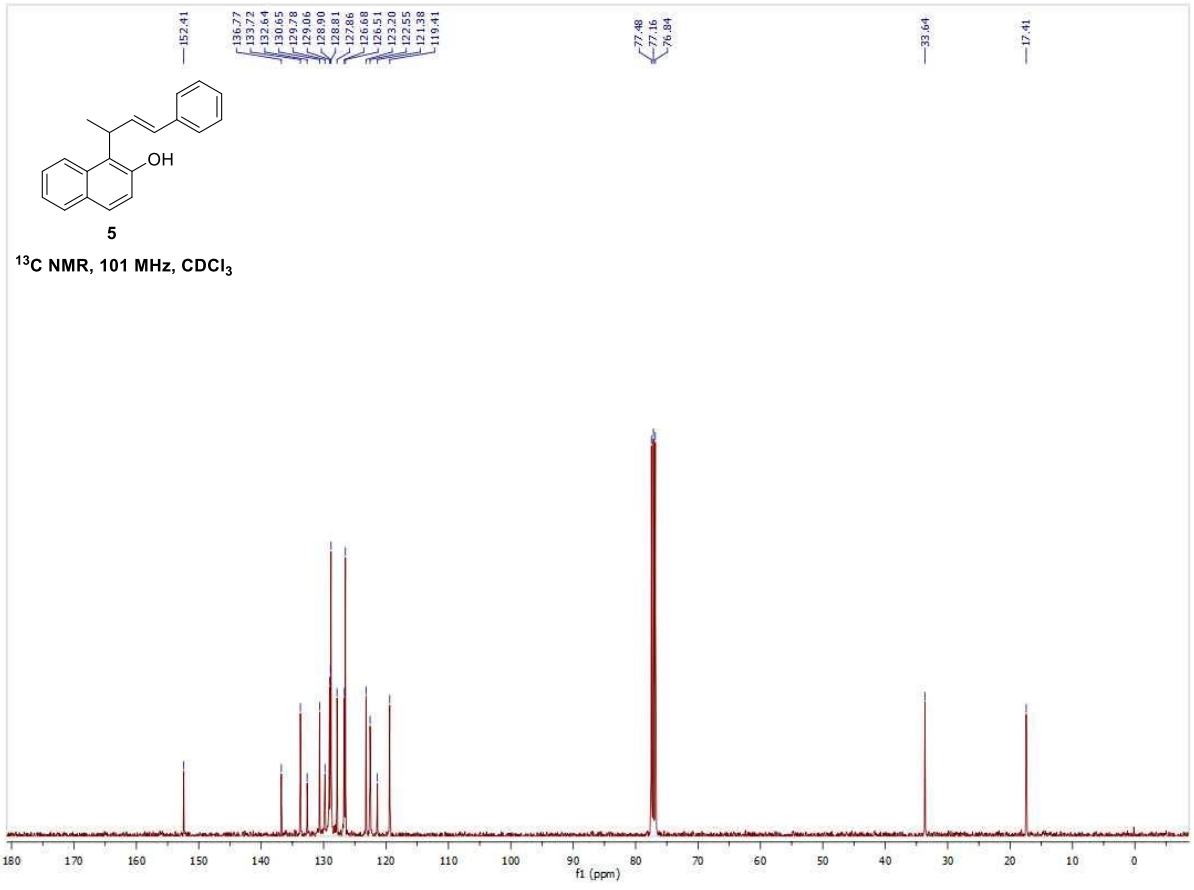

F3C
O
F
4h
19F NMR, 377 MHz, CDCl3
-64.34
-115.81
f1 (ppm)

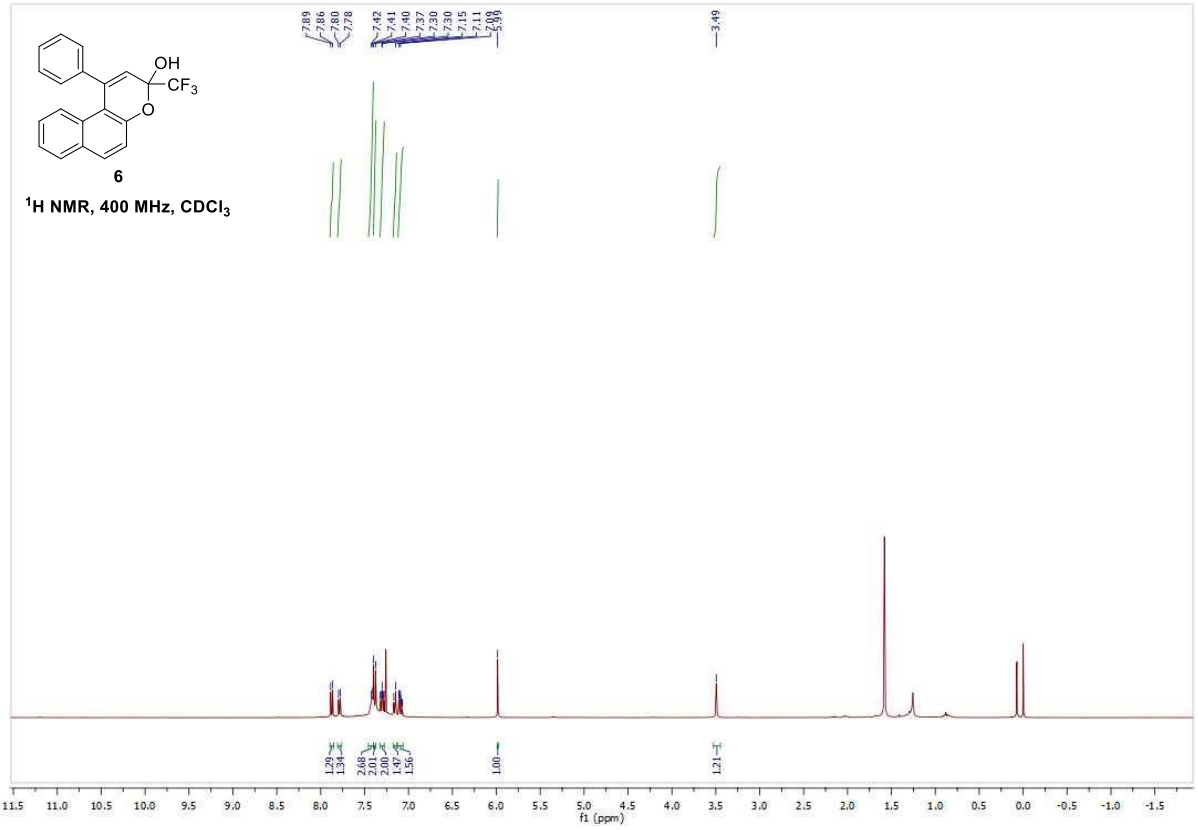

F3C
O
S
4i
1H NMR, 400 MHz, CDCl3
f1 (ppm)

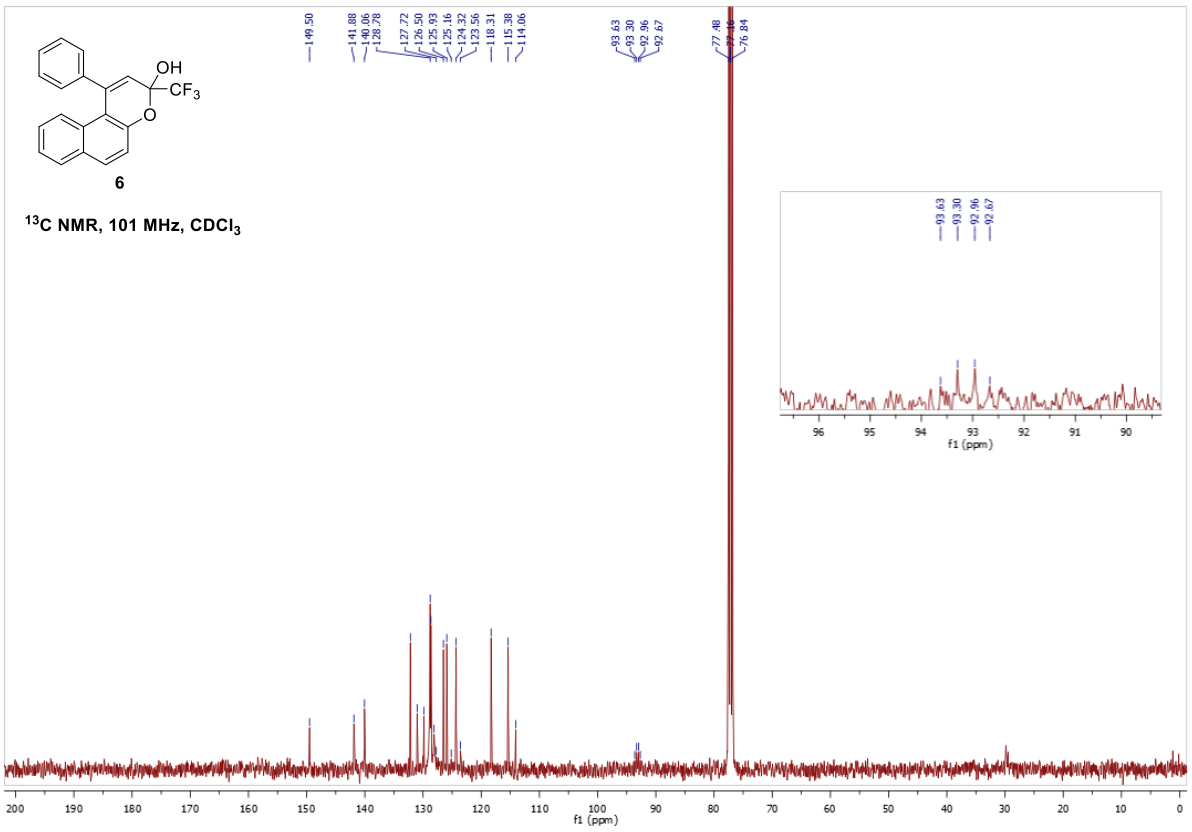

F3C
O
S
4i
13C NMR, 101 MHz, CDCl3
152.44
143.23
142.27
130.46
128.56
126.58
126.46
126.02
123.98
123.37
120.44
112.90
77.48
77.16
76.84
32.74
32.42
32.10
31.78
f1 (ppm)

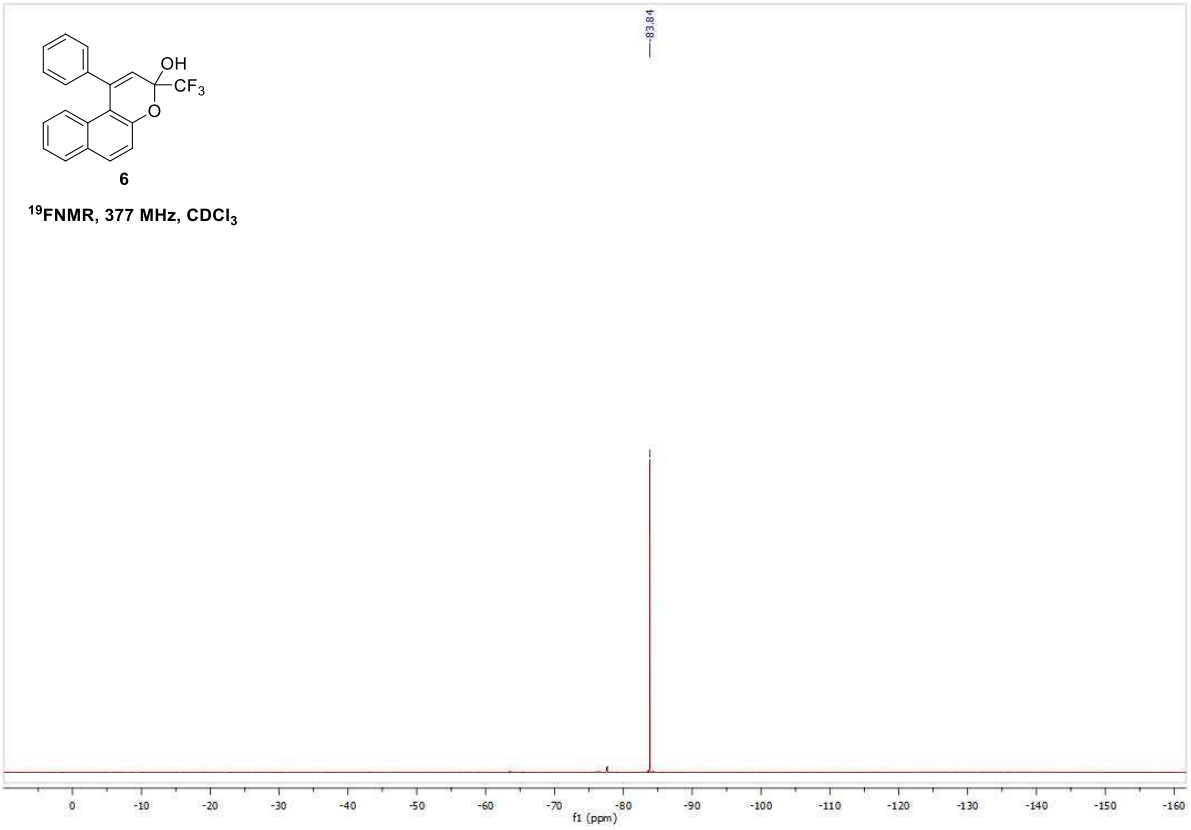

F3C
O
S
4i
19F NMR, 377 MHz, CDCl3
-64.35
f1 (ppm)


OH
5
1H NMR, 500 MHz, CDCl3
f1 (ppm)


OH
5
13C NMR, 101 MHz, CDCl3
f1 (ppm)


OH
CF3
O
6
1H NMR, 400 MHz, CDCl3
7.89
7.86
7.80
7.78
7.42
7.41
7.40
7.37
7.30
7.30
7.15
7.11
7.09
5.99
3.49
1.29
1.34
2.68
2.01
2.00
1.47
1.56
1.00
1.21
f1 (ppm)


OH
CF3
O
6
13C NMR, 101 MHz, CDCl3
149.50
141.88
140.06
128.78
127.72
126.50
125.93
125.16
124.32
123.56
118.31
115.38
114.06
93.63
93.30
92.96
92.67
77.48
77.16
76.84
f1 (ppm)


OH
CF3
O
6
19FNMR, 377 MHz, CDCl3
-83.84
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)