Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Electrochemical tandem trifluoromethylation of allylamines/formal (3+2)-cycloaddition for the rapid access to CF_3-containing imidazolines and oxazolidines

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1. General informations

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification.

Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator; spots were visualized by UV light (254 nm) and/or by staining with a $KMnO_4$ solution. Flash column chromatographies were performed on kieselgel 35-70 μm particle sized silica gel (200-400 mesh).

^{1}H, ^{13}C and ^{19}F NMR analyses were recorded on a Bruker Avance 300 or 500 spectrometer in $CDCl_3$. The chemical shifts (δ) are reported in parts per million (ppm) and were referenced to the residual isotopomer solvent signals ($CHCl_3$: δ = 7.26 ppm, CD_3CN: δ = 1.94 ppm) for ^{1}H NMR spectra, to the solvent signal ($CDCl_3$: δ = 77.16 ppm, CD_3CN: δ = 118.26 ppm) for ^{13}C NMR spectra. Coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

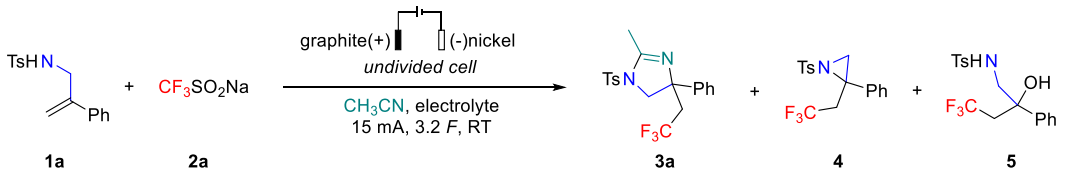
HRMS were determined on a Waters XevoQTof spectrometer using an electrospray ionization coupled with a time of flight analyzer (ESI-TOF) after dissolving the analyte in CH_3CN. Melting points were measured with a Stuart Scientific melting point apparatus SMP1.

Infrared spectra were recorded on an IR spectrometer (Perkin Elmer BX FT-IR), and absorption frequencies were reported in reciprocal centimeters (cm^{-1}).

Melting points were measured in capillary tubes on a Büchi B-540 apparatus and were uncorrected.

Electrochemical reactions and cyclic voltammetry experiments were carried out with an IKA ElectraSyn 2.0 Pro apparatus.

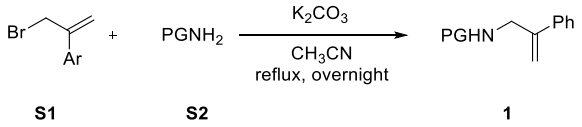
2. Optimization of reaction conditions



entry[a]	solvent	electrolyte	additive	**3a**[b]	**4**[b]	**5**[b]
1	CH_3CN/DCM (1:1)	$LiClO_4$	-	40%	33%	13%
2	CH_3CN	$LiClO_4$	-	54%	20%	24%
3	CH_3CN	Et_4NBF_4	-	nd[c] (43%)	nd[c]	nd[c]
4	CH_3CN	*n*-Bu_4NBF_4	-	nd[c] (37%)	nd[c]	nd[c]
5	CH_3CN	*n*-Bu_4HSO_4	-	nd[c] (11%)	nd[c]	nd[c]
6	CH_3CN	$LiClO_4$	K_2CO_3 (1 equiv)	49%	21%	7%
7[d]	CH_3CN	$LiClO_4$	-	36%	34%	17%
8	CH_3CN	$LiClO_4$	CH_3COOH (1 equiv)	22%	22%	8%
9	CH_3CN	$LiClO_4$	CF_3COOH (1 equiv)	45%	27%	19%
10	CH_3CN	$LiClO_4$	$Bi(OTf)_3$ (0.2 equiv)	45%	19%	20%
11	CH_3CN	$LiClO_4$	$Bi(OTf)_3$ (1 equiv)	48%	0%	22%
12	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (0.5 equiv)	48%	0%	22%
13	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (1 equiv)	64% (62%)	0%	16%
14	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (1 equiv) + MS 3Å (300 mg)	38%	18%	0%
15	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (1 equiv) + $MgSO_4$ (600 mg)	54%	11%	20%
16[e]	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (1 equiv)	63%	0%	8%
17[f]	CH_3CN	$LiClO_4$	$BF_3.OEt_2$ (1 equiv)	0%	0%	0%

[a]Unless otherwise noted, the reaction conditions were: undivided cell, **1a** (0.25 mmol), **2** (0.5 mmol), solvent (2.5 mL), $LiClO_4$ (0.2 M), CCE (15 mA), 3.2 F.mol^{-1}, RT. [b]NMR yields were determined by ^{1}H NMR analysis of the crude material and using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield is written between brackets. [c]nd: not determined (due to the presence of the electrolyte in the crude material which hampers the analysis of the spectrum). [d]2.2 F.mol^{-1} instead of 3.2 F.mol^{-1}. [e]Graphite (-) instead of nickel (-). [f]No electricity.

3. Preparation of the starting materials



To a stirred solution of **S1** (1 equiv.) in CH_3CN (0.125 M) at room temperature was added **S2** (3 equiv.) and K_2CO_3 (1 equiv.) as solids. The reaction was stirred overnight under reflux. Full consumption of the starting material was monitored by TLC (DCM: 100%). Distilled water was added and the phases were separated. The aqueous phase was extracted with EtOAc (x3). The combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated under vacuum. Purification by flash column chromatography (DCM:100%) afforded **1** as a white solid.

Analytical data were in agreement with those previously reported in the literature. **1a**, **1c**-**1g**: Liu, Y.; Che, C.-M. *Chem. Eur. J.* **2010**, *16*, 10494. **1b**, **1h**: Kiyokawa, K.; Kojima, T.; Hishikawa, Y.; Minakata, S. *Chem. Eur. J.* **2015**, *21*, 15548.

1i: Wei, Y.; Liang, F.; Zhang, X. *Org. Lett.* **2013**, *15*, 5186.

4. Electrochemical synthesis of CF_3 and CF_2H-containing imidazolines 3

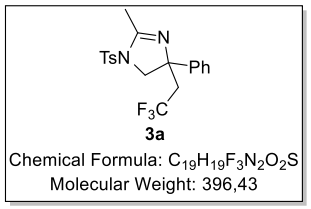
4.1. General procedure A

An oven-dried, undivided electrochemical cell was charged with a magnetic stir bar, allylamine **1** (0.25 mmol, 1.0 equiv.) and sodium sulfinate **2** (0.5 mmol, 2.0 equiv). The vial was closed with a rubber septum and flushed under argon for 2 min. A 0.2 M solution of $LiClO_4$ in CH_3CN (predried over MS 3Å, 2.5 mL) was added and the mixture was stirred for 1 min. $BF_3.OEt_2$ (31 µL, 0.25 mmol, 1.0 equiv) was added. The rubber septum was replaced by a cap holding the electrodes (a Graphite SK-50 anode and a Nickel cathode). The electrolysis was carried out at room temperature under constant current (15 mA) and was stopped after 1 h 25 min (electricity = 3.2 $F.mol^{-1}$). The reaction mixture was further stirred for 30 min at room temperature. EtOAc (10 mL) and a saturated aqueous $NaHCO_3$ solution (10 mL) were added. The phases were separated and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 100:0 to 80:20) to yield the desired product **3**.

Reaction conducted on 1 mmol scale: Following the general procedure A using allylamine **1a** (287 mg, 1 mmol, 1.0 equiv.), CF_3SO_2Na **2a** (312 mg, 2 mmol, 2.0 equiv.) and $BF_3.OEt_2$ (123 µL, 1 mmol, 1.0 equiv.) in a 0.2M solution of $LiClO_4$ in CH_3CN (10 mL), **3a** was obtained as a yellow oil (252 mg, 0.636 mmol, 64%).

4.2. Characterization of imidazolines **3**

2-methyl-4-phenyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1*H*-imidazole (**3a**)

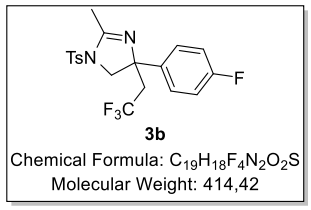


3a
Chemical Formula: $C_{19}H_{19}F_3N_2O_2S$
Molecular Weight: 396,43

Following the general procedure A using allylamine **1a** (71.8 mg), CF_3SO_2Na (78 mg), **3a** was obtained as a yellow oil (61.4 mg, 0.154 mmol, 62%).

IR: ν 703, 734, 1123, 1168, 1265, 1367, 1733 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.83 – 7.64 (m, 2H), 7.47 – 7.20 (m, 7H), 4.23 (d, *J* = 10.2 Hz, 1H), 4.01 (d, *J* = 10.1 Hz, 1H), 2.71 – 2.54 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 155.8, 144.9, 143.8, 135.2, 130.1, 128.7, 127.6, 127.1, 125.3, 125.1 (q, $^1J_{C-F}$ = 275.3 Hz), 69.3, 58.1, 45.0 (q, $^2J_{C-F}$ = 26.2 Hz), 21.6, 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.18 (t, *J* = 11.3 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{19}H_{20}F_3N_2O_2S]^+$ ($[M+H]^+$): 397.1198, found: 397.1193.

4-(4-fluorophenyl)-2-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3b**)

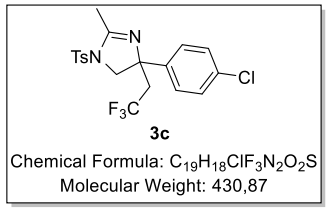


3b
Chemical Formula: $C_{19}H_{18}F_4N_2O_2S$
Molecular Weight: 414,42

Following the general procedure A using allylamine **1b** (72.8 mg), CF_3SO_2Na (78 mg), **3b** was obtained as a yellow oil (58.1 mg, 0.140 mmol, 56%).

IR: ν 703.3, 732.7, 896.0, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.24 (m, 4H), 7.07 – 6.93 (m, 2H), 4.19 (d, *J* = 10.2 Hz, 1H), 3.98 (d, *J* = 10.2 Hz, 1H), 2.56 (qd, *J* = 10.5, 7.0 Hz, 2H), 2.45 (s, 3H), 2.37 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): 162.0 (d, $^1J_{C-F}$= 245.2 Hz), 156, 1, 145.0, 139.4, 135.1, 130.1, 127.2 (d, $^3J_{C-F}$= 8.2 Hz), 127.1, 125.0 (q, $^1J_{C-F}$ = 276.8 Hz), 115.6 (d, $^2J_{C-F}$ = 21.7 Hz), 68.9, 58.2, 45.2 (q, $^2J_{C-F}$= 26.2 Hz), 29.7, 21.6, 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.20 (t, *J* = 11.2 Hz, 3F), -114.59 (s, 1F); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{19}H_{19}F_4N_2O_2S]^+$ ($[M+H]^+$): 415.1103, found: 415.1094.

4-(4-chlorophenyl)-2-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3c**)

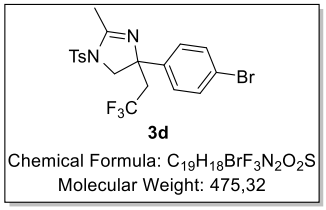


3c
Chemical Formula: $C_{19}H_{18}ClF_3N_2O_2S$
Molecular Weight: 430,87

Following the general procedure A using allylamine **1c** (80.5 mg), CF_3SO_2Na (78 mg), **3c** was obtained as a colorless oil (47.7 mg, 0.111 mmol, 44%).

IR: ν 704.3, 733.6, 896.0, 1264.4, 1422.0 cm^{-1}; **^{1}H {^{13}C} NMR** (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.17 (m, 6H), 4.17 (d, *J* = 10.2 Hz, 1H), 3.94 (d, *J* = 10.3 Hz, 1H), 2.55 (tq, *J* = 10.5, 5.4 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$): 156.3, 145.2, 142.3, 135.2, 133.7, 130.2, 128.9, 127.3, 127.0, 124.9 (q, $^1J_{C-F}$ = 277.2 Hz), 69.0, 58.3, 45.1 (q, $^2J_{C-F}$= 26.2 Hz), 21.7, 16.8; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.13 (t, *J* = 10.1 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{19}H_{19}ClF_3N_2O_2S]^+$ ($[M+H]^+$): 431.0808, found: 431.0824.

4-(4-bromophenyl)-2-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3d**)

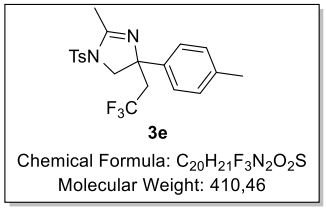


3d
Chemical Formula: $C_{19}H_{18}BrF_3N_2O_2S$
Molecular Weight: 475,32

Following the general procedure A using allylamine **1d** (91.6 mg), CF_3SO_2Na (78 mg), **3c** was obtained as an orange gum (56.3 mg, 0.119 mmol, 47%).

IR: ν 704.0, 733.0, 896.0, 1264.5, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.03 (d, *J* = 10.3 Hz, 1H), 3.79 (d, *J* = 10.3 Hz, 1H), 2.41 (qd, *J* = 10.5, 4.9 Hz, 2H), 2.29 (s, 3H), 2.22 (s, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$): 156.3, 145.1, 142.8, 135.1, 132.1, 131.7, 127.2, 127.1, 126.7 (q, $^1J_{C\text{-}F}$ = 277.1 Hz), 121.7, 69.0, 58.1, 44.9, (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 21.5, 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.11 (t, *J* = 10.0 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{19}H_{19}BrF_3N_2O_2S]^+$ ($[M+H]^+$): 475.0303, found: 475.0302.

2-methyl-4-(*p*-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3e**)

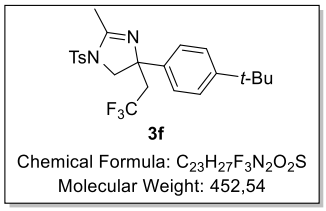


3e
Chemical Formula: $C_{20}H_{21}F_3N_2O_2S$
Molecular Weight: 410,46

Following the general procedure A using allylamine **1d** (75.3 mg), CF_3SO_2Na (78 mg), **3c** was obtained as a yellow oil (43.8 mg, 0.108 mmol, 43%).

IR: ν 704.1, 733.2, 896.0, 1264.4, 1421.9 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.00 (m, 4H), 4.18 (d, *J* = 10.1 Hz, 1H), 3.98 (d, *J* = 10.1 Hz, 1H), 2.70 – 2.45 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): 155.7, 144.9, 140.8, 137.4, 135.3, 130.1, 129.3, 127.2, 125.2, 125.1 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 69.1, 58.1, 44.8 (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 21.6, 21.0, 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.19 (t, *J* = 10.2 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{20}H_{22}F_3N_2O_2S]^+$ ($[M+H]^+$): 411.1354, found: 411.1348.

4-(4-(*tert*-butyl)phenyl)-2-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3f**)

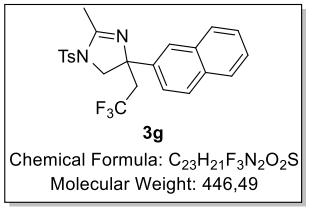


3f
Chemical Formula: $C_{23}H_{27}F_3N_2O_2S$
Molecular Weight: 452,54

Following the general procedure A using allylamine **1f** (85.9 mg), CF_3SO_2Na (78 mg), **3f** was obtained as a yellow oil (50.9 mg, 0.112 mmol, 45%).

IR: ν 704.0, 732.7, 896.0, 1264.4, 1421.7 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.77 – 7.71 (m, 2H), 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 2H), 4.23 (d, *J* = 10.1 Hz, 1H), 4.05 (d, *J* = 10.1 Hz, 1H), 2.60 (qd, *J* = 10.6, 4.4 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H), 1.32 (s, 9H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): 155.7, 150.6, 144.8, 140.8, 135.3, 130.1, 127.2, 125.6, 125.2 (q, $^1J_{C\text{-}F}$= 276.8 Hz), 124.9, 69.1, 57.8, 45.1 (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 34.4, 31.2, 21.6, 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.21 (t, *J* = 10.3 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{23}H_{28}F_3N_2O_2S]^+$ ($[M+H]^+$): 453.1824, found: 453.1821.

2-methyl-4-(naphthalen-2-yl)-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3g**)

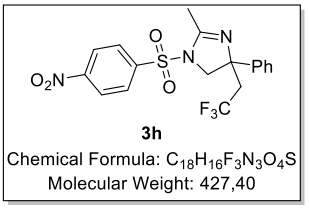


3g
Chemical Formula: $C_{23}H_{21}F_3N_2O_2S$
Molecular Weight: 446,49

Following the general procedure A using allylamine **1g** (84.4 mg), CF_3SO_2Na (78 mg), **3f** was obtained as a yellow oil (39.4 mg, 0.087 mmol, 35%).

IR: ν 704.2, 733.4, 896.0, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.88 – 7.62 (m, 6H), 7.55 – 7.46 (m, 2H), 7.42 – 7.33 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.30 (d, *J* = 10.3 Hz, 1H), 4.12 (d, *J* = 10.3 Hz, 1H), 2.72 (qd, $^2J_{C\text{-}F}$ = 10.5, 6.5 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): 155.9, 144.9, 141.02, 140.96, 133.0, 132.6, 130.0, 128.7, 128.2, 127.5, 127.1, 126.5, 126.4, 125.1 (q, $^1J_{C\text{-}F}$= 276.8 Hz), 124.2, 123.2, 69.5, 58.2, 44.7 (q, $^2J_{C\text{-}F}$= 26.2 Hz), 21.5, 16.7; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.15 (t, *J* = 10.0 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{23}H_{22}F_3N_2O_2S]^+$ ($[M+H]^+$): 447.1354, found: 447.1353.

2-methyl-1-((4-nitrophenyl)sulfonyl)-4-phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3h**)

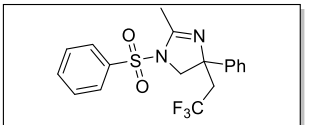


3h
Chemical Formula: $C_{18}H_{16}F_3N_3O_4S$
Molecular Weight: 427,40

Following the general procedure A using allylamine **1h** (79.6 mg), CF_3SO_2Na (78 mg), **3a** was obtained as an orange gum (57.2 mg, 0.134 mmol, 54%).

IR: ν 704.4, 733.6, 896.0, 1264.4, 1421.7, 3055.0 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 8.36 – 8.29 (m, 2H), 8.02 – 7.96 (m, 2H), 7.38 – 7.23 (m, 5H), 4.27 (d, *J* = 10.3 Hz, 1H), 4.05 (d, *J* = 10.3 Hz, 1H), 2.65 (q, *J* = 10.5 Hz, 2H), 2.42 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 154.9, 150.7, 143.9, 143.7, 128.8, 128.3, 127.9, 125.1, 125.0 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 124.6, 69.8, 58.1, 45.2 (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 29.7; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.28 (t, *J* = 11.3 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{18}H_{17}F_3N_3O_4S]^+$ ($[M+H]^+$): 428.0892, found: 428.0900.

2-methyl-4-phenyl-1-(phenylsulfonyl)-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3i**)

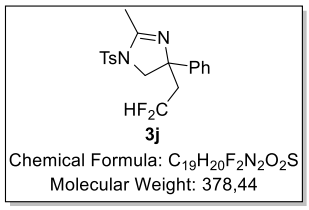


3i
Chemical Formula: $C_{18}H_{17}F_3N_2O_2S$
Molecular Weight: 382,40

Following the general procedure A using allylamine **1i** (68.3 mg), CF_3SO_2Na (78 mg), **3a** was obtained as a white gum (66.1 mg, 0.173 mmol, 69%).

IR: ν 704.1, 733.4, 896.0, 1172.2, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.90 – 7.80 (m, 2H), 7.68 – 7.47 (m, 3H), 7.33 (d, *J* = 3.8 Hz, 5H), 4.25 (d, *J* = 10.1 Hz, 1H), 4.04 (d, *J* = 10.2 Hz, 1H), 2.61 (qd, *J* = 10.6, 3.7 Hz, 2H), 2.39 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 155.7, 143.8, 138.2, 133.8, 129.5, 128.7, 127.7, 127.1, 125.3, 125.1 (q, $^1J_{C\text{-}F}$= 276.9 Hz), 69.4, 58.0, 44.8 (q, $^2J_{C\text{-}F}$ = 25.5 Hz), 16.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.24 (t, *J* = 10.2 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{18}H_{18}F_3N_2O_2S]^+$ ($[M+H]^+$): 383.1041, found: 383.1028.

4-(2,2-difluoroethyl)-2-methyl-4-phenyl-1-tosyl-4,5-dihydro-1H-imidazole (**3j**)

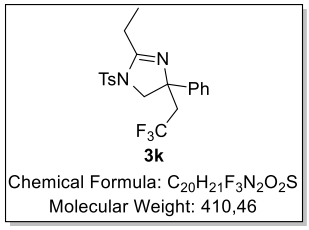


3j
Chemical Formula: $C_{19}H_{20}F_2N_2O_2S$
Molecular Weight: 378,44

Following the general procedure A using allylamine **1a** (71.8 mg), CF_2HSO_2Na (69 mg), **3j** was obtained as a yellow oil (29.1 mg, 0.077 mmol, 31%).

IR: ν 703.9, 732.9, 896.0, 1067.3, 1168.7, 1264.5, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.24 (m, 7H), 5.64 (tt, *J* = 56.1, 4.7 Hz, 1H), 4.11 (d, *J* = 12Hz, 1H), 3.92 (d, *J* = 12Hz, 1H), 2.44 (s, 3H), 2.39 (s, 3H), 2.30 (tdd, *J* = 16.0, 4.7, 2.6 Hz, 2H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 155.9, 144.9, 144.1, 130.1, 130.0, 128.8, 127.5, 127.1, 125.2, 115.5 (t, $^1J_{C\text{-}F}$ = 237.8 Hz), 69.5, 59.2, 45.9 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 21.6, 16.7; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -113.62 (dt, *J* = 56.0, 15.5 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{19}H_{21}F_2N_2O_2S]^+$ ($[M+H]^+$): 379.1292, found: 379.1275.

2-ethyl-4-phenyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3k**)

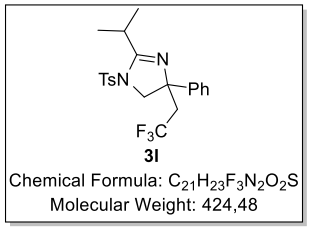


3k
Chemical Formula: $C_{20}H_{21}F_3N_2O_2S$
Molecular Weight: 410,46

Following a modified general procedure A using allylamine **1a** (71.8 mg), CF_3SO_2Na (78 mg) and propionitrile as solvent (instead of acetonitrile), **3k** was obtained as a colorless oil (35.1 mg, 0.086 mmol, 34%).

IR: ν 704.2, 733.5, 896.0, 1165.6, 1264.4, 1421.8, 3054.9 cm^{-1}; **^{1}H {^{13}C} NMR** (500 MHz, CD_3CN): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.21 (m, 5H), 4.16 (d, *J* = 10.5 Hz, 1H), 3.79 (d, *J* = 10.5 Hz, 1H), 2.89 – 2.58 (m, 4H), 2.38 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H); **^{13}C {^{1}H} NMR** (126 MHz, CD_3CN): δ 161.0, 146.2, 145.6, 135.8, 131.1, 129.4, 128.2, 128.1, 126.7 (q, $^1J_{C\text{-}F}$ = 278.8 Hz), 126.3, 70.2, 60.4, 44.7 (q, $^2J_{C\text{-}F}$ = 26.1 Hz), 24.1, 21.5, 11.2; **^{19}F NMR** (282 MHz, CD_3CN): δ -60.43 (t, *J* = 10.3 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $C_{20}H_{22}F_3N_2O_2S$ ($[M+H]^+$): 411.1354, found: 411.1365.

2-isopropyl-4-phenyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-imidazole (**3l**)



3l
Chemical Formula: $C_{21}H_{23}F_3N_2O_2S$
Molecular Weight: 424,48

Following a modified general procedure A using allylamine **1a** (71.8 mg), CF_3SO_2Na (78 mg) and *iso*-butyronitrile as solvent (instead of acetonitrile), **3l** was obtained as a yellow oil (39.7 mg, 0.094 mmol, 39%).

IR: ν 703.9, 733.1, 895.9, 1166.8, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.24 (m, 7H), 4.21 (d, *J* = 10.4 Hz), 3.96 (d, *J* = 10.4 Hz), 3.36 (hept, *J* = 6.6 Hz, 1H), 2.58 (q, *J* = 10.6 Hz, 2H), 2.42 (s, 3H), 1.31 – 1.26 (m, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 164.5, 144.9, 144.7, 135.3, 129.9, 128.6, 127.4, 127.0, 125.1 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 125.2, 69.1, 58.7, 44.9 (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 28.4, 21.5, 21.02, 20.97; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -59.86 (t, *J* = 10.0 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{21}H_{24}F_3N_2O_2S]^+$ ($[M+H]^+$): 425.1511, found: 425.1511.

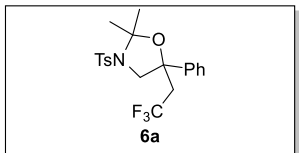
5. Electrochemical synthesis of CF_3 and CF_2H-containing oxazolidines 6

5.1. General procedure B

An oven-dried, undivided electrochemical cell was charged with MS 3 Å (300 mg). The vial was flame-dried under high vacuum during 1 min and put under argon. A magnetic stir bar, allylamine **1** (0.25 mmol, 1.0 equiv.), sodium sulfinate **2** (0.5 mmol, 2.0 equiv) and $LiClO_4$ (0.2 M, 53 mg) were quickly added. The vial was closed with a rubber septum and flushed under argon for 2 min. Acetone (2.5 mL) was added and the mixture was stirred for 1 min. The rubber septum was replaced by a cap holding the electrodes (a Graphite SK-50 anode and a Nickel cathode). The electrolysis was carried out at room temperature under constant current (15 mA) and was stopped after 1 h 25 min (electricity = 3.2 $F.mol^{-1}$). The reaction mixture was further stirred for 30 min at room temperature. The reaction mixture was filtered over a pad of celite (rinsed with EtOAc, 15 mL). The filtrate was transferred in a separatory funnel containing a saturated aqueous $NaHCO_3$ solution (10 mL). The phases were separated and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 100:0 to 90:10) to yield the desired product **6**.

5.2. Characterization of oxazolidines **6**

2-methyl-4-phenyl-1-tosyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1*H*-imidazole (**6a**)

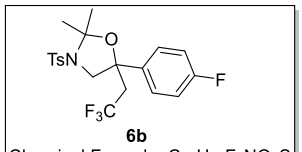


6a
Chemical Formula: $C_{20}H_{22}F_3NO_3S$
Molecular Weight: 413,46

Following the general procedure B using allylamine **1a** (71.8 mg), CF_3SO_2Na (78 mg), **6a** was obtained as a colorless oil (62 mg, 0.150 mmol, 60%).

IR: ν 703, 734, 1123, 1168, 1265, 1367, 1733 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.22 (m, 7H), 3.79 (s, 2H), 2.69 (dtt, *J* = 25.7, 15.3, 10.7 Hz, 2H), 2.42 (s, 3H), 1.74 (s, 3H), 1.40 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 143.8, 141.6, 136.7, 129.6, 128.4, 127.9, 127.5, 126.6 (q, $^1J_{C\text{-}F}$= 276.7 Hz), 125.0, 97.8, 79.7, 56.1, 44.7 (q, $^2J_{C\text{-}F}$ = 26.2 Hz), 28.4, 27.2, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.18 (m); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{22}H_{25}F_3N_2NaO_3S]^+$ ($[M+CH_3CN+Na]^+$): 477.1436, found: 477.1440.

5-(4-fluorophenyl)-2,2-dimethyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6b**)



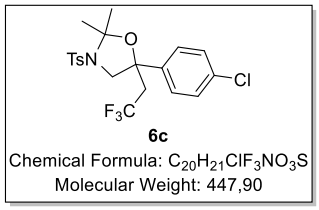
6b
Chemical Formula: $C_{20}H_{21}F_4NO_3S$
Molecular Weight: 431,45

Following the general procedure B using allylamine **1b** (72.8 mg), CF_3SO_2Na (78 mg), **6b** was obtained as a colorless oil (72.4 mg, 0.168 mmol, 67%).

IR: ν 704.3, 733.6, 896.0, 1264.4, 1422.0 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.17 (m, 4H), 7.02 – 6.87 (m, 2H), 3.74 (s, 2H), 2.73 – 2.52 (m, 2H), 2.40 (s, 3H), 1.68 (s, 3H), 1.37 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 143.9, 137.3, 136.7, 129.7, 127.4, 126.9 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 124.6 (q, $^1J_{C\text{-}F}$ = 276.8 Hz), 115.2 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 97.8, 69.3, 56.1, 44.7 (q, $^2J_{C\text{-}F}$= 26.2 Hz),

28.3, 27.3, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.28 (t, *J* = 11.3 Hz, 3F), -114.29 (s, 1F); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{20}H_{22}F_4NO_3S]^+$ ($[M+H]^+$): 432.1257, found: 432.1256.

5-(4-chlorophenyl)-2,2-dimethyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6c**)

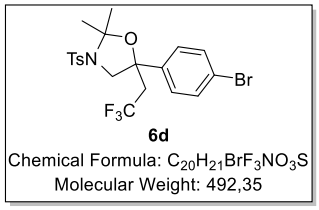


6c
Chemical Formula: $C_{20}H_{21}ClF_3NO_3S$
Molecular Weight: 447,90

Following the general procedure B using allylamine **1c** (80.5 mg), CF_3SO_2Na (78 mg), **6c** was obtained as a colorless oil (50.4 mg, 0.113 mmol, 45%).

IR: ν 704.3, 733.7, 896.0, 1010.2, 1264.4, 1421.9 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.10 (m, 6H), 3.69 (s, 2H), 2.68 – 2.47 (m, 2H), 2.35 (s, 3H), 1.64 (s, 3H), 1.32 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 144.0, 140.1, 136.6, 133.9, 129.7, 128.5, 127.4, 126.6, 124.6 (q, $^1J_{C\text{-}F}$= 277.5 Hz), 97.9, 79.3, 56.0, 44.5 (q, $^2J_{C\text{-}F}$ = 27Hz), 28.3, 27.2, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.18 (t, *J* = 10.0 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{20}H_{22}ClF_3NO_3S]^+$ ($[M+H]^+$): 448.0961, found: 448.0952.

5-(4-bromophenyl)-2,2-dimethyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6d**)

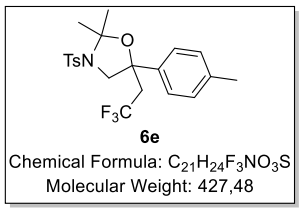


6d
Chemical Formula: $C_{20}H_{21}BrF_3NO_3S$
Molecular Weight: 492,35

Following the general procedure B using allylamine **1d** (91.6 mg), CF_3SO_2Na (78 mg), **6d** was obtained as a colorless oil (73.2 mg, 0.149 mmol, 59%).

IR: ν 704.3, 733.5, 896.0, 1264.4, 1422.0 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 2H), 2.61 (m, 2H), 2.39 (s, 3H), 1.67 (s, 3H), 1.36 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 143.9, 140.7, 136.6, 131.5, 129.7, 127.4, 126.9, 124.6 (q, $^1J_{C\text{-}F}$= 276.0 Hz), 122.0, 97.9, 79.3, 56.0, 44.6 (q, $^2J_{C\text{-}F}$ = 27.0 Hz), 28.3, 27.2, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.16 (t, *J* = 10.0 Hz) ; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{20}H_{22}BrF_3NO_3S]^+$ ($[M+H]^+$): 492.0456, found: 492.0451.

5-(4-bromophenyl)-2,2-dimethyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6e**)

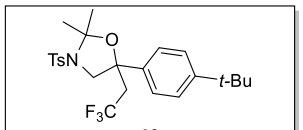


6e
Chemical Formula: $C_{21}H_{24}F_3NO_3S$
Molecular Weight: 427,48

Following the general procedure B using allylamine **1e** (75.3 mg), CF_3SO_2Na (78 mg), **6e** was obtained as a yellow oil (65.8 mg, 0.154 mmol, 62%).

IR: ν 704.2, 733.3, 896.0, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.21 – 7.05 (m, 4H), 3.79 (s, 2H), 2.84 – 2.56 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.74 (s, 3H), 1.40 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 143.8, 138.7, 137.6, 136.7, 129.6, 129.0, 127.5, 124.8 (q, $^1J_{C\text{-}F}$= 276.0 Hz), 124.9, 97.7, 79.6, 56.1, 44.5 (q, $^2J_{C\text{-}F}$= 26.2 Hz), 28.4, 27.2, 21.5, 21.0; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.16 (t, *J* = 11.3 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{23}H_{27}F_3N_2NaO_3S]^+$ ($[M+CH_3CN+Na]^+$): 491.1592, found: 491.1611.

5-(4-(*tert*-butyl)phenyl)-2,2-dimethyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6f**)

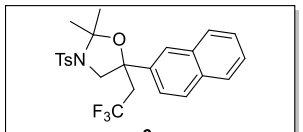


6f
Chemical Formula: $C_{24}H_{30}F_3NO_3S$
Molecular Weight: 469,56

Following the general procedure B using allylamine **1f** (85.9 mg), CF_3SO_2Na (78 mg), **6e** was obtained as a yellow oil (81.7 mg, 0.174 mmol, 70%).

IR: ν 704.0, 732.8, 896.0, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.08 (m, 6H), 3.74 (s, 2H), 2.71 – 2.50 (m, 2H), 2.36 (s, 3H), 1.68 (s, 3H), 1.34 (s, 3H), 1.25 (s, 9H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 150.8, 143.7, 138.6, 136.9, 129.6, 127.5, 125.2, 124.8 (q, $^1J_{C\text{-}F}$= 276.8 Hz), 124.7, 97.7, 79.7, 56.0, 44.6 (q, $^2J_{C\text{-}F}$ = 27Hz), 34.5, 31.3, 28.4, 27.2, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.14 (t, *J* = 10.9 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{24}H_{31}F_3NO_3S]^+$ ($[M+H]^+$): 470.1977, found: 470.1981.

2,2-dimethyl-5-(naphthalen-2-yl)-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6g**)

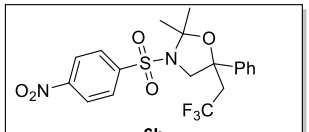


6g
Chemical Formula: $C_{24}H_{24}F_3NO_3S$
Molecular Weight: 463,52

Following the general procedure B using allylamine **1g** (84.4 mg), CF_3SO_2Na (78 mg), **6g** was obtained as a yellow gum (62.7 mg, 0.135 mmol, 54%).

IR: ν 704.0, 733.1, 896.1, 1160.3, 1264.4, 1421.9 cm^{-1}; **^{1}H {^{13}C} NMR** (500 MHz, $CDCl_3$): δ 7.84 (m, 2H), 7.80 – 7.58 (m, 4H), 7.52 (m, 2H), 7.42 (m, 1H), 7.20 (m, 2H), 3.95 (s, 2H), 2.95 – 2.65 (m, 2H), 2.39 (s, 3H), 1.82 (s, 3H), 1.45 (s, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$): δ 143.9, 138.9, 136.8, 132.9, 129.7, 128.5, 128.4, 127.7, 127.5, 126.6, 126.5, 124.9 (q, $^1J_{C\text{-}F}$= 276.0 Hz), 124.0, 123.2, 98.0, 80.0, 56.0, 44.8 (q, $^2J_{C\text{-}F}$ = 27Hz), 28.6, 27.3, 21.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.18 (t, *J* = 9.9 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{26}H_{27}F_3N_2NaO_3S]^+$ ($[M+CH_3CN+Na]^+$): 527.1592, found: 527.1610.

2,2-dimethyl-3-((4-nitrophenyl)sulfonyl)-5-phenyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6h**)

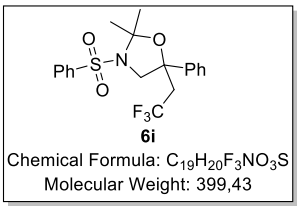


6h
Chemical Formula: $C_{19}H_{19}F_3N_2O_5S$
Molecular Weight: 444,43

Following the general procedure B using allylamine **1h** (79.6 mg), CF_3SO_2Na (78 mg), **6h** was obtained as a yellow oil (69 mg, 0.155 mmol, 62%).

IR: ν 704.3, 733.5, 896.0, 1264.4, 1421.9 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.26 (m, 5H), 4.02 (d, *J* = 10.2 Hz, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 2.70 (tq, *J* = 10.4, 5.6 Hz, 2H), 1.76 (s, 3H), 1.46 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 150.4, 146.0, 141.8, 128.8, 128.7, 128.6, 125.4, 124.9 (q, $^1J_{C\text{-}F}$= 276.8 Hz), 124.6, 98.4, 80.4, 56.3, 45.2 (q, $^2J_{C\text{-}F}$= 27.0 Hz), 28.8, 27.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.31 (t, ^1J= 8.5 Hz); **HRMS (ESI$^-$)**: *m/z* calcd for $[C_{19}H_{19}ClF_3N_2O_5S]^-$ ($[M+Cl]^-$): 479.0655, found: 479.0647.

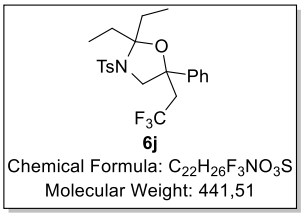
2,2-dimethyl-5-phenyl-3-(phenylsulfonyl)-5-(2,2,2-trifluoroethyl)oxazolidine (**6i**)



6i
Chemical Formula: $C_{19}H_{20}F_3NO_3S$
Molecular Weight: 399,43

Following the general procedure B using allylamine **1h** (68.3 mg), CF_3SO_2Na (78 mg), **6i** was obtained as a yellow oil (60.5 mg, 0.151 mmol, 61%).

IR: ν 704.1, 733.5, 896.0, 1164.5, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.89 – 7.74 (m, 2H), 7.63 – 7.56 (m, 1H), 7.53 – 7.45 (m, 2H), 7.36 – 7.28 (m, 5H), 3.85 (s, 2H), 2.70 (m, 2H), 1.77 (s, 3H), 1.43 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 141.6, 139.7, 132.9, 129.0, 128.4, 128.0, 127.4, 125.0, 124.7 (q, $^1J_{C\text{-}F}$ = 276.2 Hz), 97.8, 79.7, 56.0, 44.6 (q, $^2J_{C\text{-}F}$ = 27.0 Hz), 28.3, 27.2; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.23 (t, *J* = 8.5 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{21}H_{23}F_3NaN_2O_3S]^+$ ($[M+CH_3CN+Na]^+$): 463.1279, found: 463.1253.



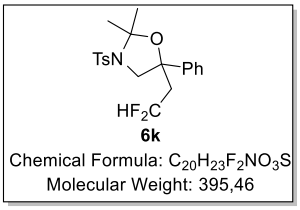
6j
Chemical Formula: $C_{22}H_{26}F_3NO_3S$
Molecular Weight: 441,51

2,2-diethyl-5-phenyl-3-tosyl-5-(2,2,2-trifluoroethyl)oxazolidine (**6j**)

Following a modified procedure using allylamine **1a** (71.8 mg), CF_3SO_2Na (2.5 equiv., 97.5 mg), $LiClO_4$ (0.4 M, 106 mg), pentan-3-one (2.5 mL) under constant current electrolysis at 15 mA at 35 °C. At the end of the electrolysis (2.8 $F.mol^{-1}$ were consumed)*, $BF_3.OEt_2$ (31 µL, 0.25 mmol, 1 equiv.) was added and the reaction mixture was further stirred overnight at room temperature. The same work-up than in procedure B afforded **6j** as a colorless oil (62.4 mg, 0.143 mmol, 57%).

IR: ν 707.6, 943.4, 1006.3, 1093.1, 1142.0, 1150.1, 1262.6, 1339.0, 1462.5, 2920.3 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.18 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.13 (dd, *J* = 6.6, 3.1 Hz, 2H), 3.86 (d, *J* = 9.9 Hz, 1H), 3.66 (d, *J* = 9.9 Hz, 1H), 2.78 – 2.62 (m, 1H), 2.62 – 2.48 (m, 1H), 2.37 (s, 3H), 2.07 (dt, *J* = 14.5, 7.3 Hz, 1H), 1.98 – 1.82 (m, 2H), 1.26 (dd, *J* = 14.2, 7.3 Hz, 1H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.68 (t, *J* = 7.3 Hz, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 143.7, 141.1, 137.3, 129.7, 128.2, 128.0, 127.3, 125.2, 124.7 (q, $^1J_{C\text{-}F}$ = 276.7 Hz), 103.7, 79.7, 56.3, 45.3 (q, $^2J_{C\text{-}F}$ = 27.0 Hz), 31.3, 30.8, 21.5, 8.60 8.2; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -60.53 (t, *J* = 9.8 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{22}H_{27}F_3NO_3S]^+$ ($[M+H]^+$): 442.1664, found: 442.1663.

5-(2,2-difluoroethyl)-2,2-dimethyl-5-phenyl-3-tosyloxazolidine (**6k**)



6k
Chemical Formula: $C_{20}H_{23}F_2NO_3S$
Molecular Weight: 395,46

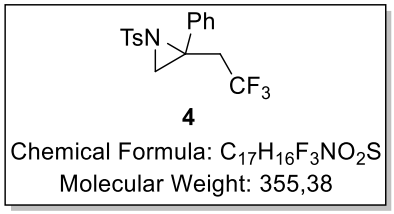
Following the general procedure B using allylamine **1a** (71.8 mg), CF_2HSO_2Na (69 mg), **6k** was obtained as a yellow gum (40.3 mg, 0.102 mmol, 41%).

IR: ν 704.0, 733.3, 896.0, 1038.0, 1264.4, 1421.8 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.72 – 7.66 (m, 2H), 7.38 – 7.28 (m, 6H), 7.27 (s, 1H), 5.62 (tt, *J* = 56.1, 4.7 Hz, 1H), 3.78 (s, 2H), 2.44 (s, 3H), 2.42 – 2.28 (m, 2H), 1.75 (s, 3H), 1.45 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 143.7, 142.2, 136.9, 129.6, 128.6, 127.9, 127.4, 124.8, 115.2 (t, $^1J_{C\text{-}F}$= 237.7 Hz), 97.6, 80.3, 56.2, 45.6 (t, $^2J_{C\text{-}F}$= 21.0 Hz), 28.4, 27.2, 21.5; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -113.74 (app. dq, *J* = 55.9, 14.7 Hz); **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{22}H_{26}F_2NaN_2O_3S]^+$ ($[M+CH_3CN+Na]^+$): 459.1530, found: 459.1537.

* In pentan-3-one, it was not possible to maintain 15 mA and to reach 3.2 $F.mol^{-1}$ probably due to the low conductivity of this solvent.

6. Characterization of side products 4 and 5

2-phenyl-1-tosyl-2-(2,2,2-trifluoroethyl)aziridine (**4**)



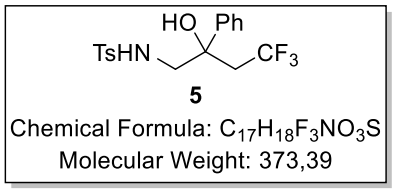
4

Chemical Formula: $C_{17}H_{16}F_3NO_2S$
Molecular Weight: 355,38

colorless oil.

IR: ν 739.2, 878.3, 1057.0, 1278.4, 1419.7 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.48 – 7.27 (m, 7H), 3.35 (dqd, *J* = 15.1, 9.7, 1.6 Hz, 1H), 3.12 – 2.97 (m, 3H), 2.45 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 144.7, 136.8, 136.7, 129.8, 128.8, 128.6 (*two overlapping peaks*), 127.9, 125.4 (q, $^{1}J_{C\text{-}F}$= 276.0 Hz), 49.9, 40.5 (q, $^{2}J_{C\text{-}F}$= 28.5 Hz), 38.8, 21.7; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -62.05 (t, *J* = 8.5 Hz); **HRMS (ESI^{+})**: *m/z* calcd for $[C_{17}H_{17}F_3NO_2S]^{+}$ ($[M+H]^{+}$): 356.0932, found: 356.0936.

2-phenyl-1-tosyl-2-(2,2,2-trifluoroethyl)aziridine (**5**)



5

Chemical Formula: $C_{17}H_{18}F_3NO_3S$
Molecular Weight: 373,39

colorless oil.

IR: ν 705, 734, 1264, 3055 cm^{-1}; **^{1}H {^{13}C} NMR** (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.20 (m, 7H), 4.80 – 4.77 (m, 1H), 3.33 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.20 (s, 1H), 3.11 (dd, *J* = 13.3, 4.7 Hz, 1H), 2.90 – 2.70 (m, 2H), 2.42 (s, 3H); **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$): δ 144.1, 141.4, 136.5, 130.1, 128.9, 128.2, 127.0, 125.7 (q, $^{1}J_{C\text{-}F}$ = 276.7 Hz), 125.0, 73.7, 53.1, 42.7 (q, $^{1}J_{C\text{-}F}$ = 26.2 Hz), 21.6; **^{19}F NMR** (282 MHz, $CDCl_3$): δ -59.04 (m); **HRMS (ESI^{+})**: *m/z* calcd for $[C_{17}H_{19}F_3NO_3S]^{+}$ ($[M+H]^{+}$): 374.1038, found: 374.1040.

7. Cyclic voltammetry analyses

Cyclic voltammetry analyses were carried out in a 10 mL IKA ElectraSyn vial.
Working electrode: GC; Counter electrode: Pt; Reference electrode: Ag/AgCl (3M aq. KCl). Sweep rate: 200 $mV.s^{-1}$. 0.005 M analyte and 0.1 M $LiClO_4$ in CH_3CN (5 mL).

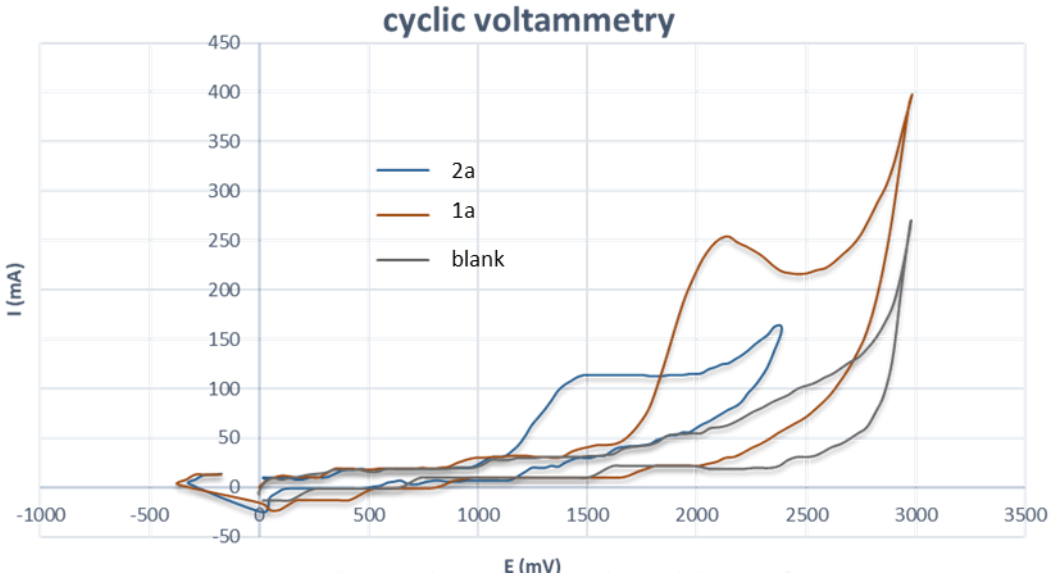


Figure S1: Cyclic voltammograms of 0.1 M $LiClO_4$ solutions in CH_3CN: none (grey line); **1a** 0.005 M (brown line); CF_3SO_2Na **2a** 0.005 M (blue line).

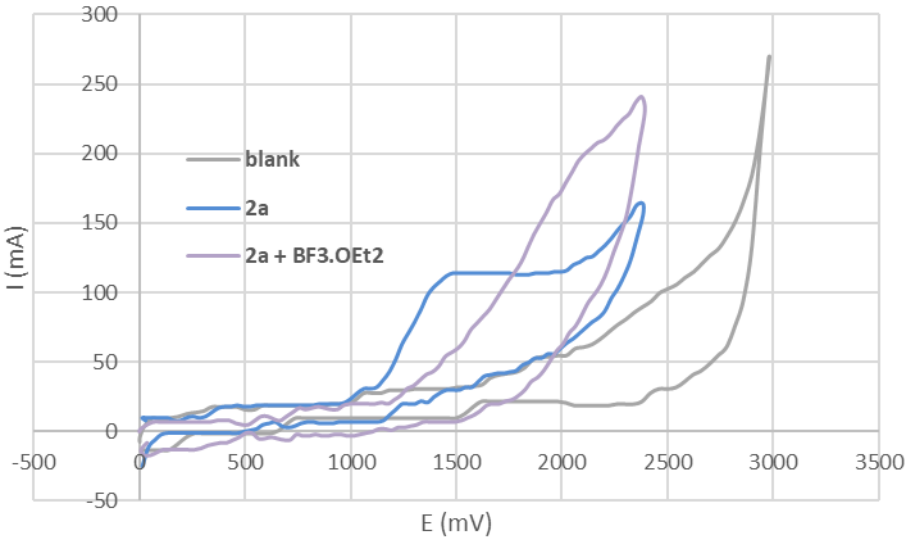
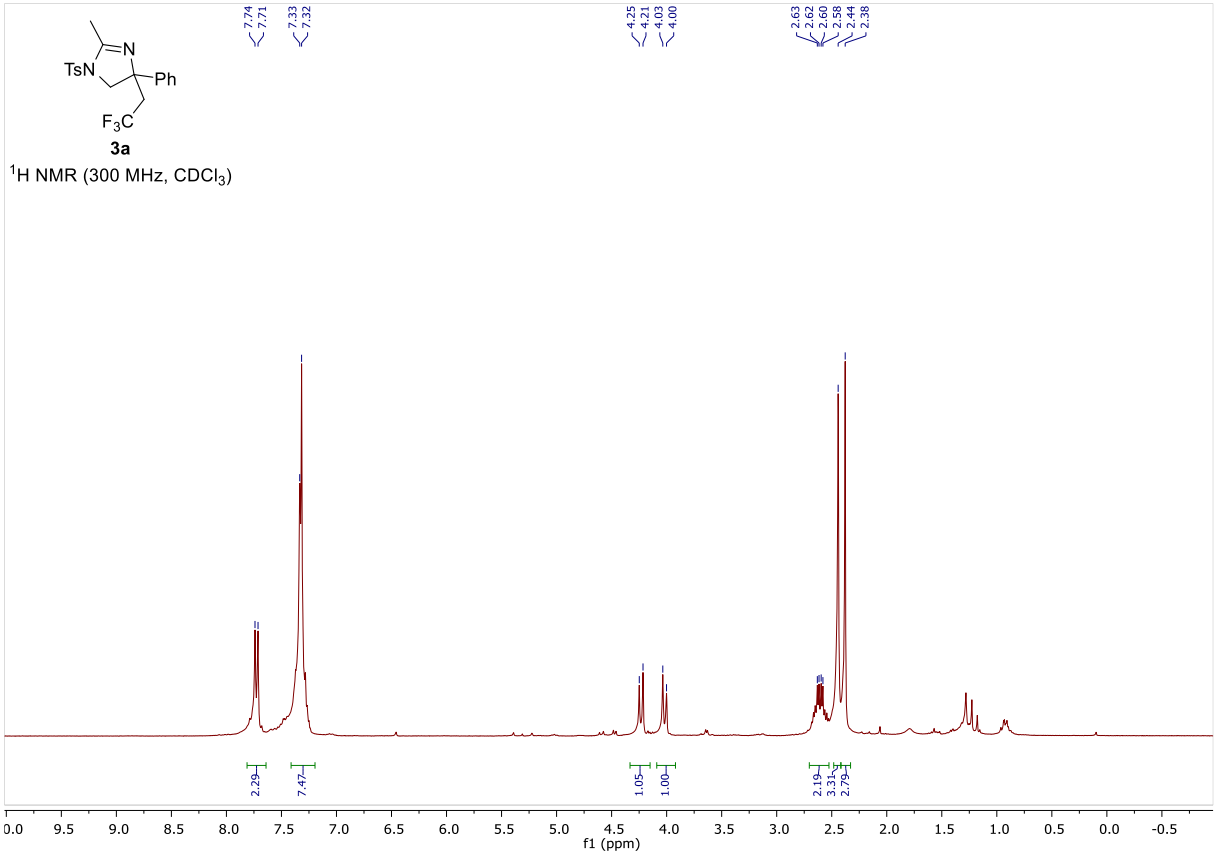
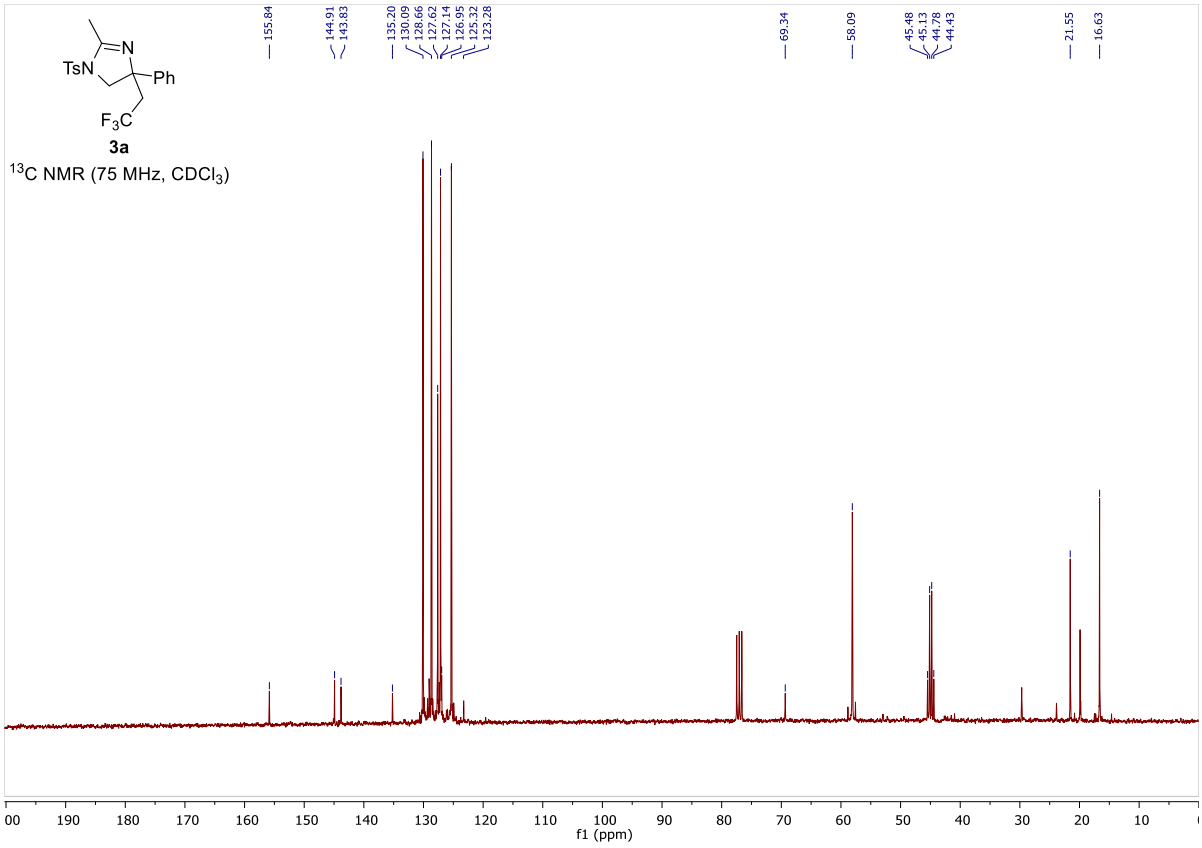


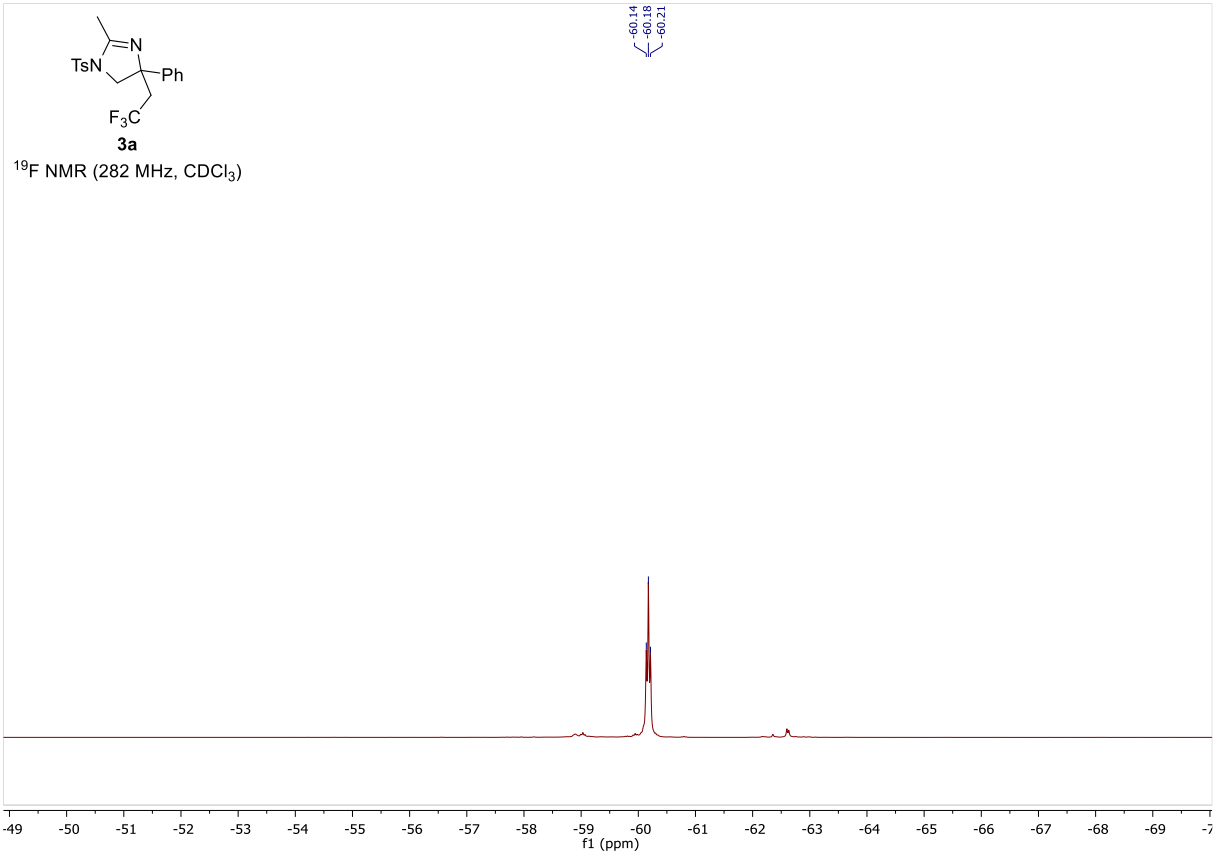
Figure S2: Cyclic voltammograms of 0.1 M $LiClO_4$ solutions in CH_3CN: none (grey line); CF_3SO_2Na **2a** 0.005 M (blue line); CF_3SO_2Na **2a** 0.005 M + $BF_3.OEt_2$ 0.005 M (purple line).

*The comparison of the cyclic voltammetry profiles of CF_3SO_2Na and CF_3SO_2Na in the presence of $BF_3.OEt_2$ reveals an onset of oxidation little bit superior in the presence of the Lewis acid. E_{onset} (CF_3SO_2Na) = 0.97 V; E_{onset} (CF_3SO_2Na+$BF_3.OEt_2$) = 1.18 V. In both cases, these oxidations occur before the oxidation of allylamine **1a**; E_{onset} (**1a**) = 1.67 V.*

8. NMR spectra

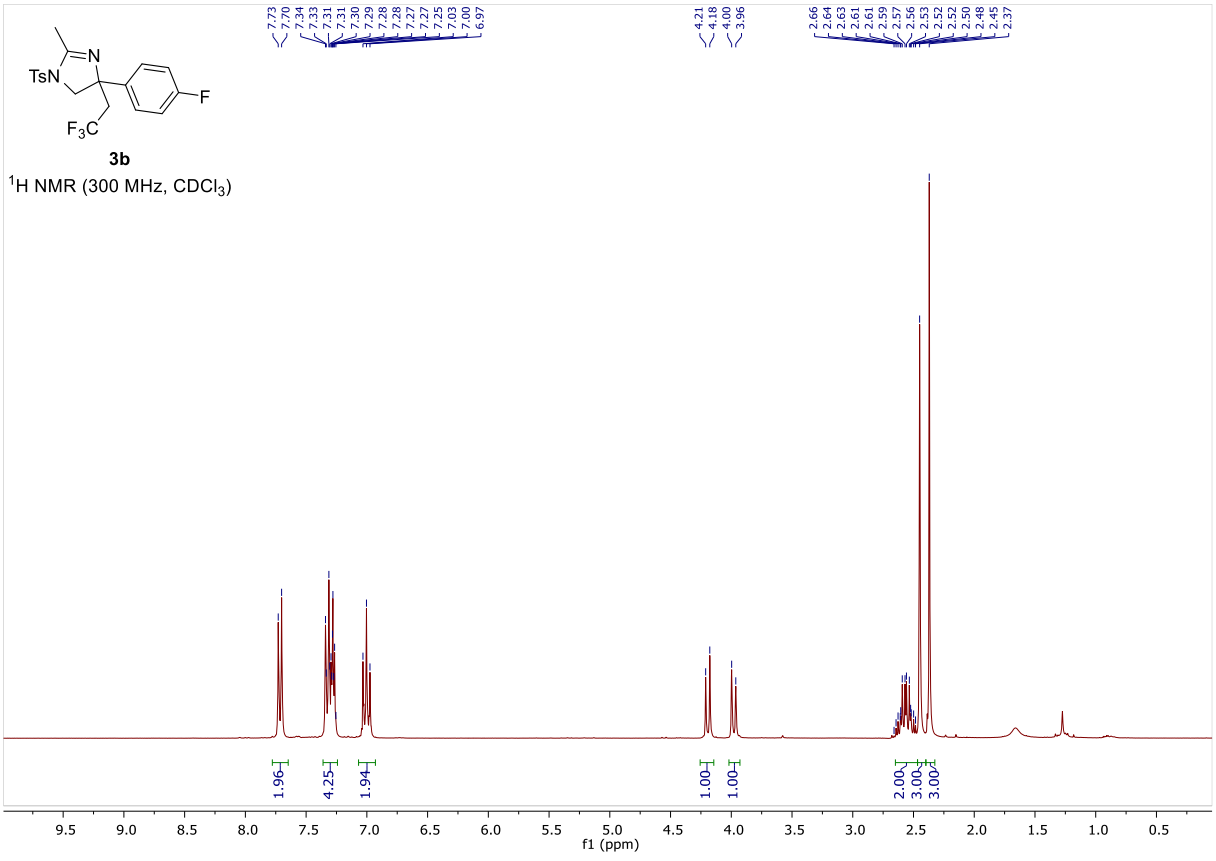

7.74
7.71
7.33
7.32
4.25
4.21
4.03
4.00
2.63
2.62
2.60
2.58
2.44
2.38
TsN
N
Ph
F3C
3a
1H NMR (300 MHz, CDCl3)
2.29
7.47
1.05
1.00
2.19
3.31
2.79
f1 (ppm)


155.84
144.91
143.83
135.20
130.09
128.66
127.62
127.14
126.95
125.32
123.28
69.34
58.09
45.48
45.13
44.78
44.43
21.55
16.63
TsN
N
Ph
F3C
3a
13C NMR (75 MHz, CDCl3)
f1 (ppm)



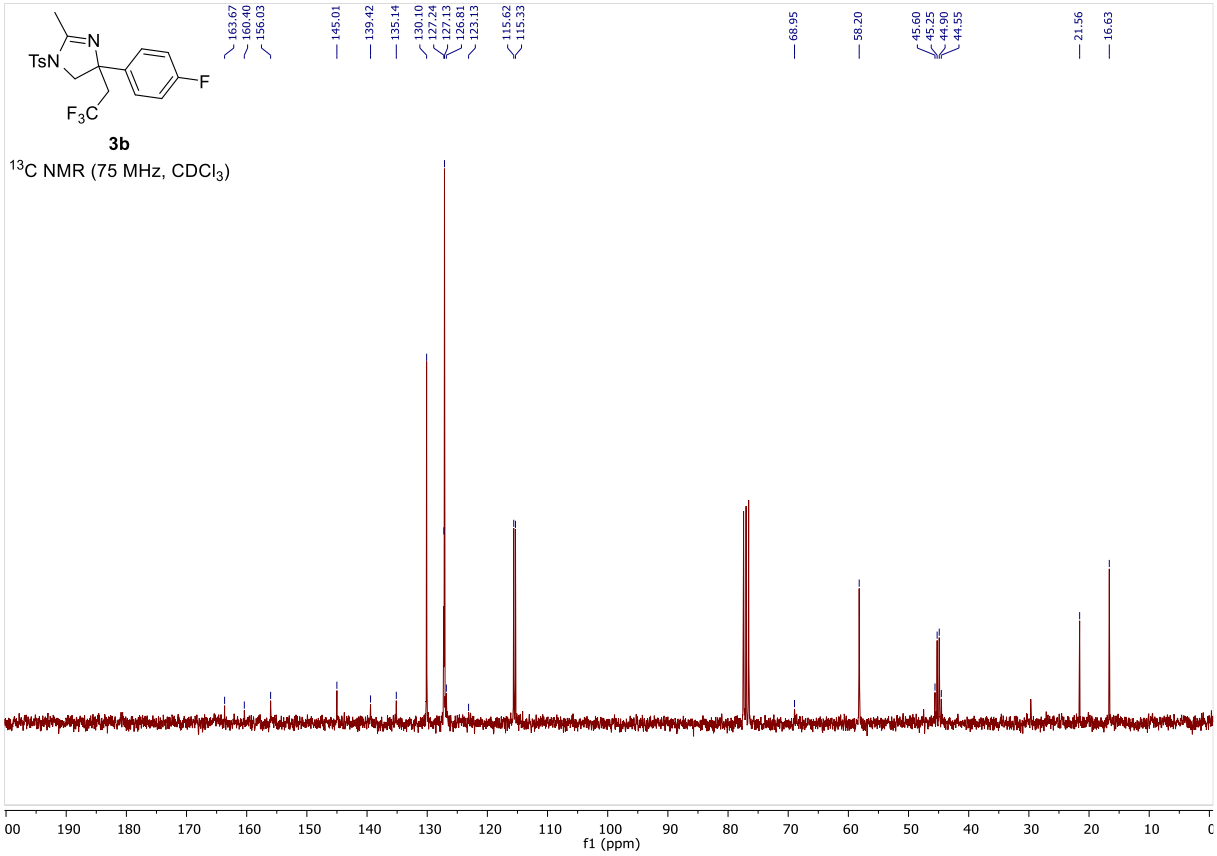
3a

^{19}F NMR (282 MHz, $CDCl_3$)



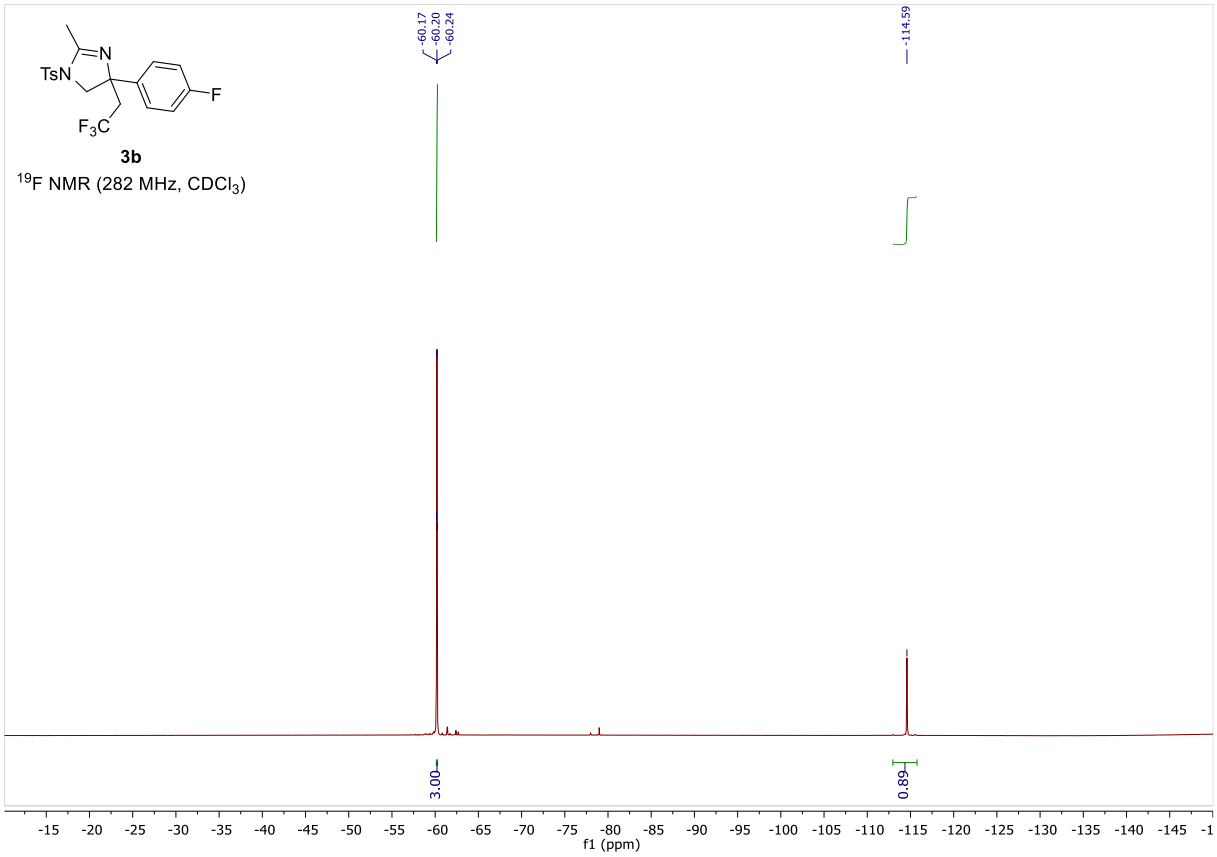
3b

^{1}H NMR (300 MHz, $CDCl_3$)



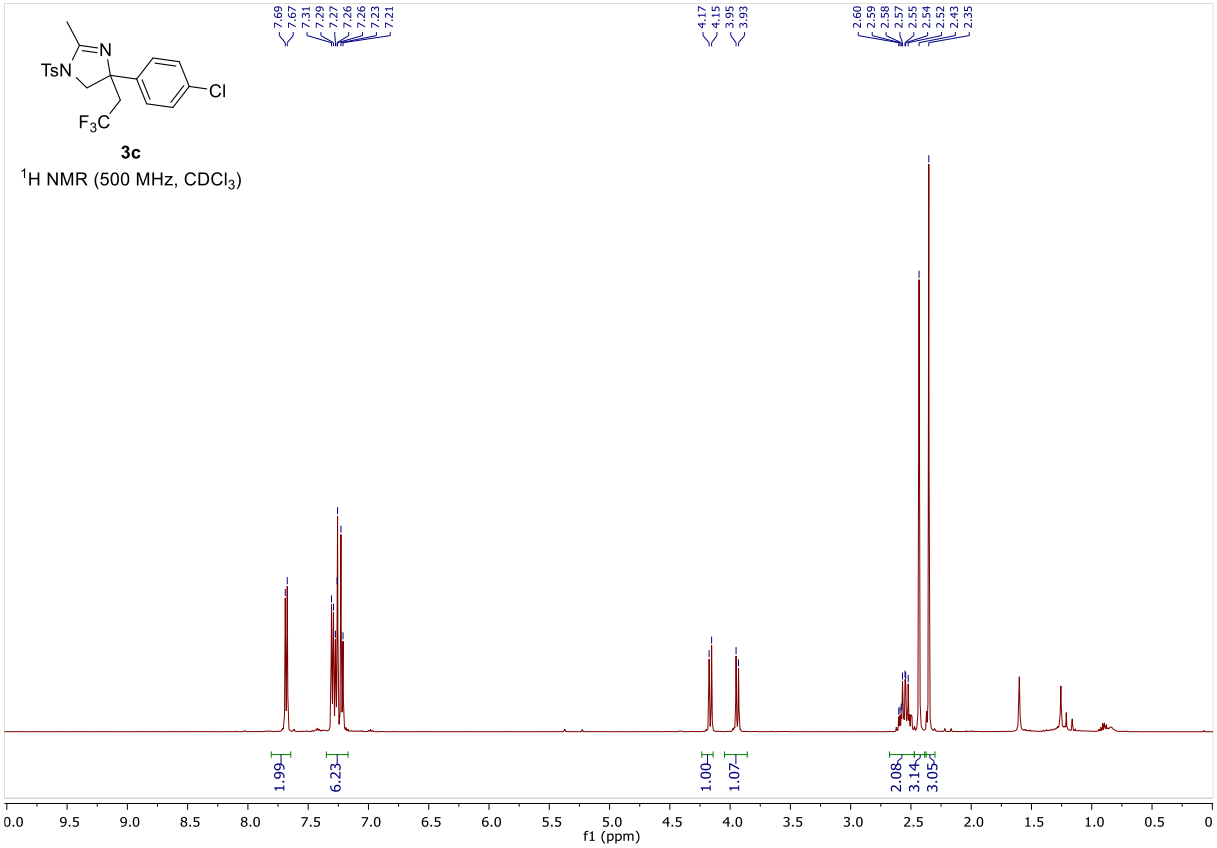
3b

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



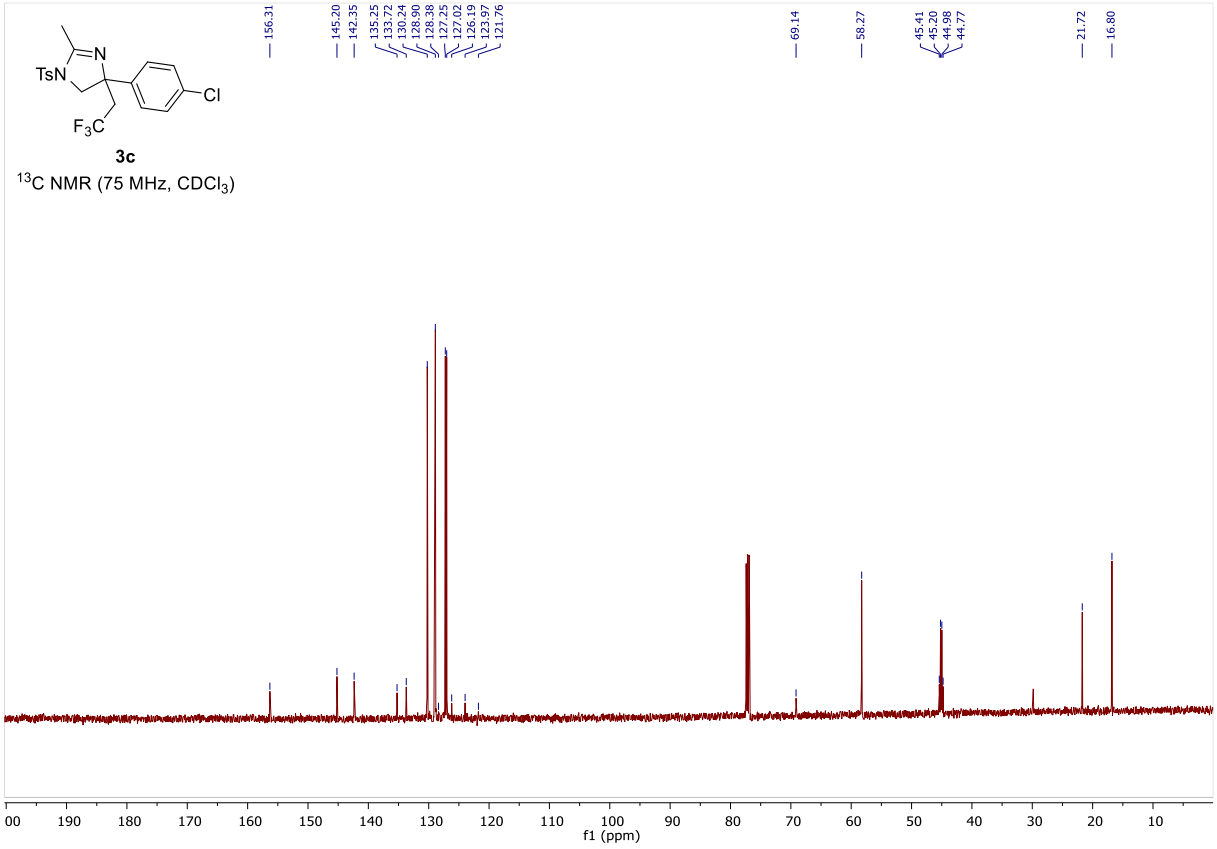
3b

^{19}F NMR (282 MHz, $CDCl_3$)



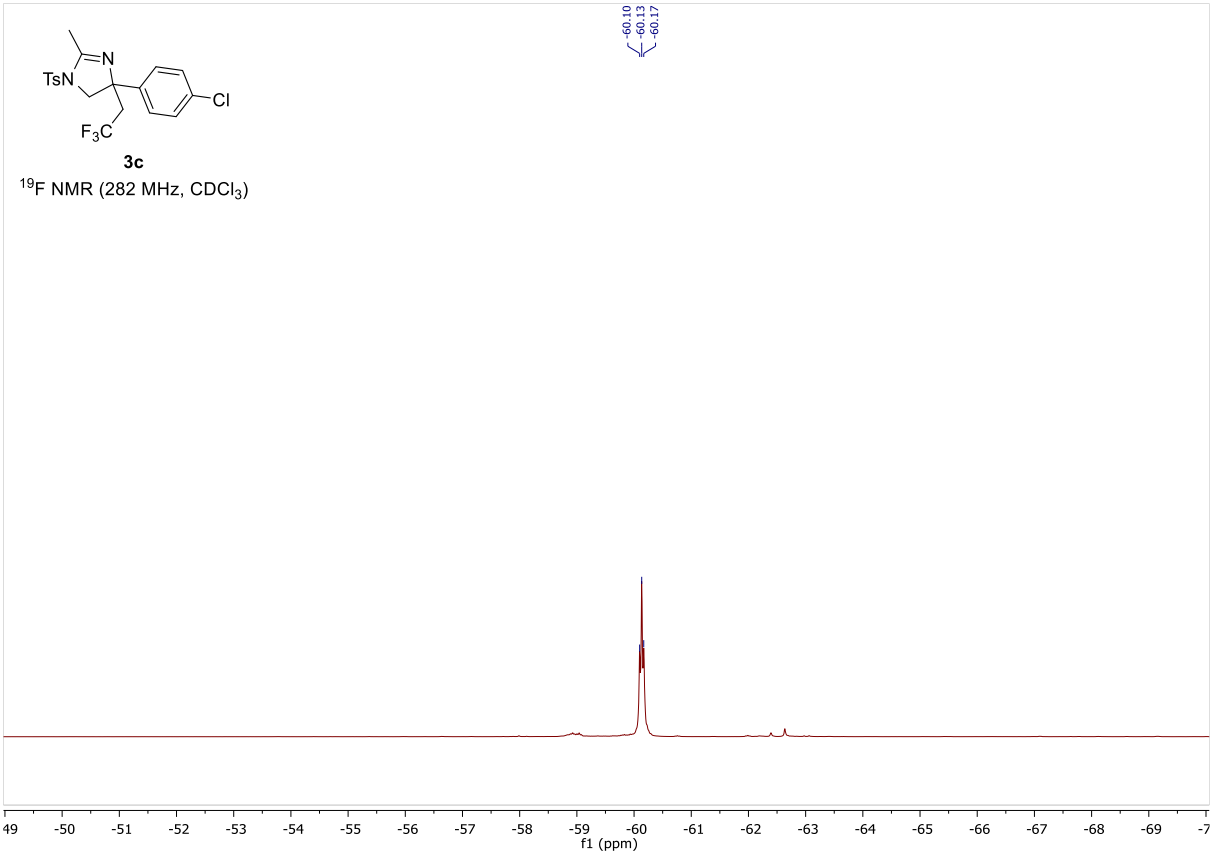
3c

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



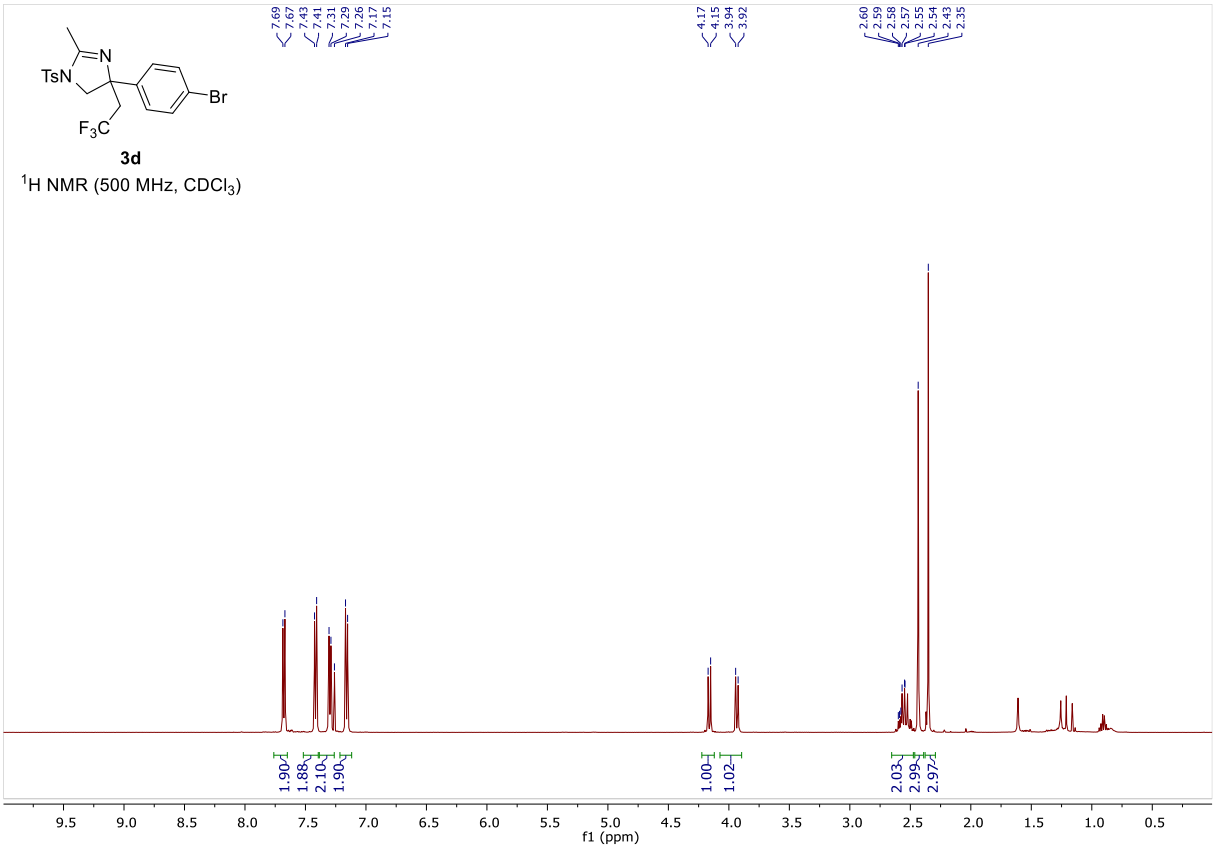
3c

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



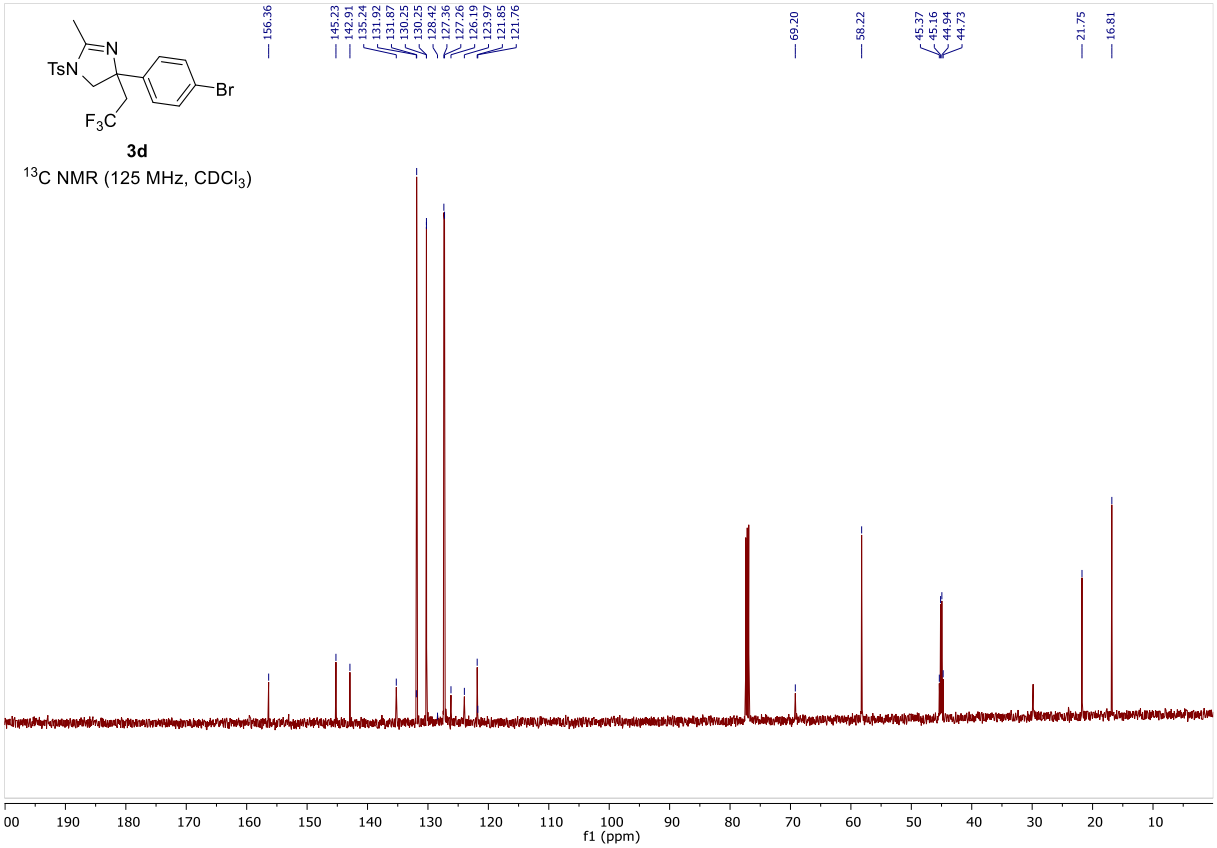
3c

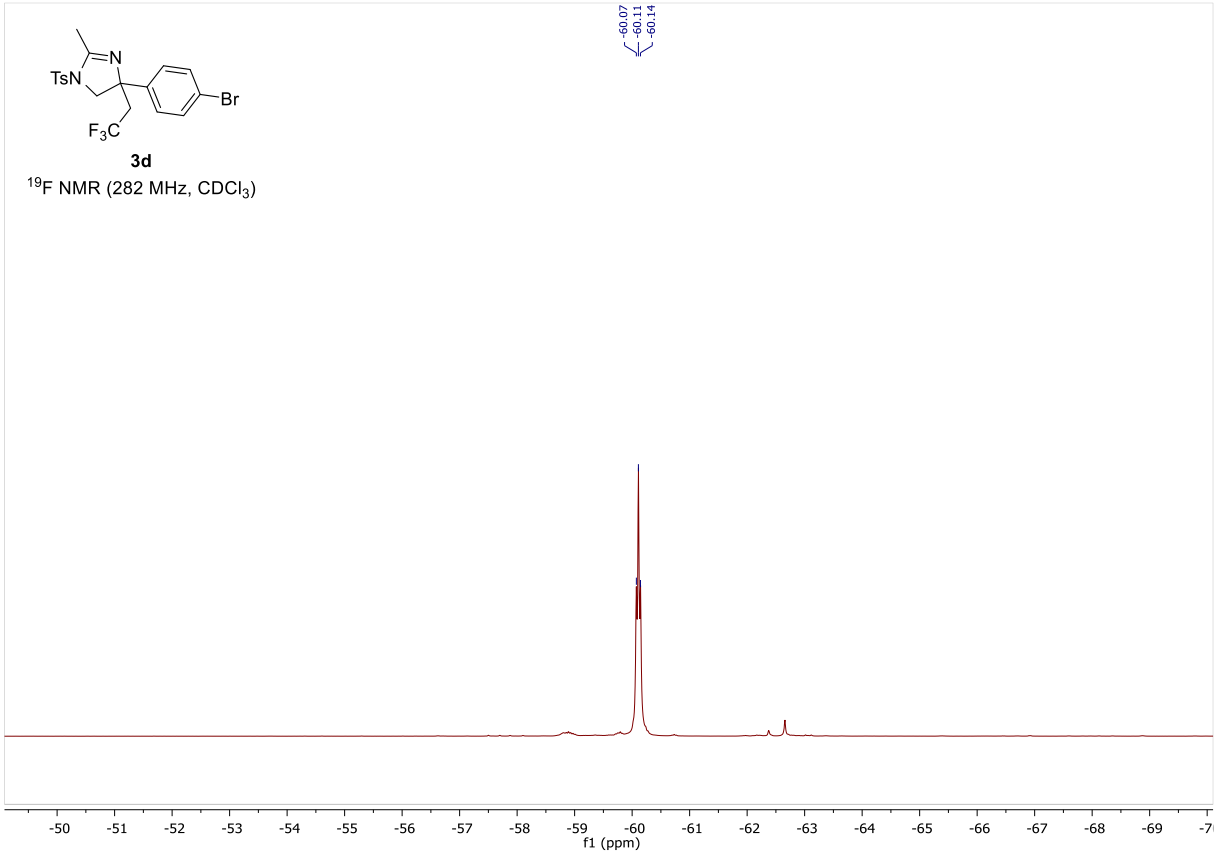
^{19}F NMR (282 MHz, $CDCl_3$)

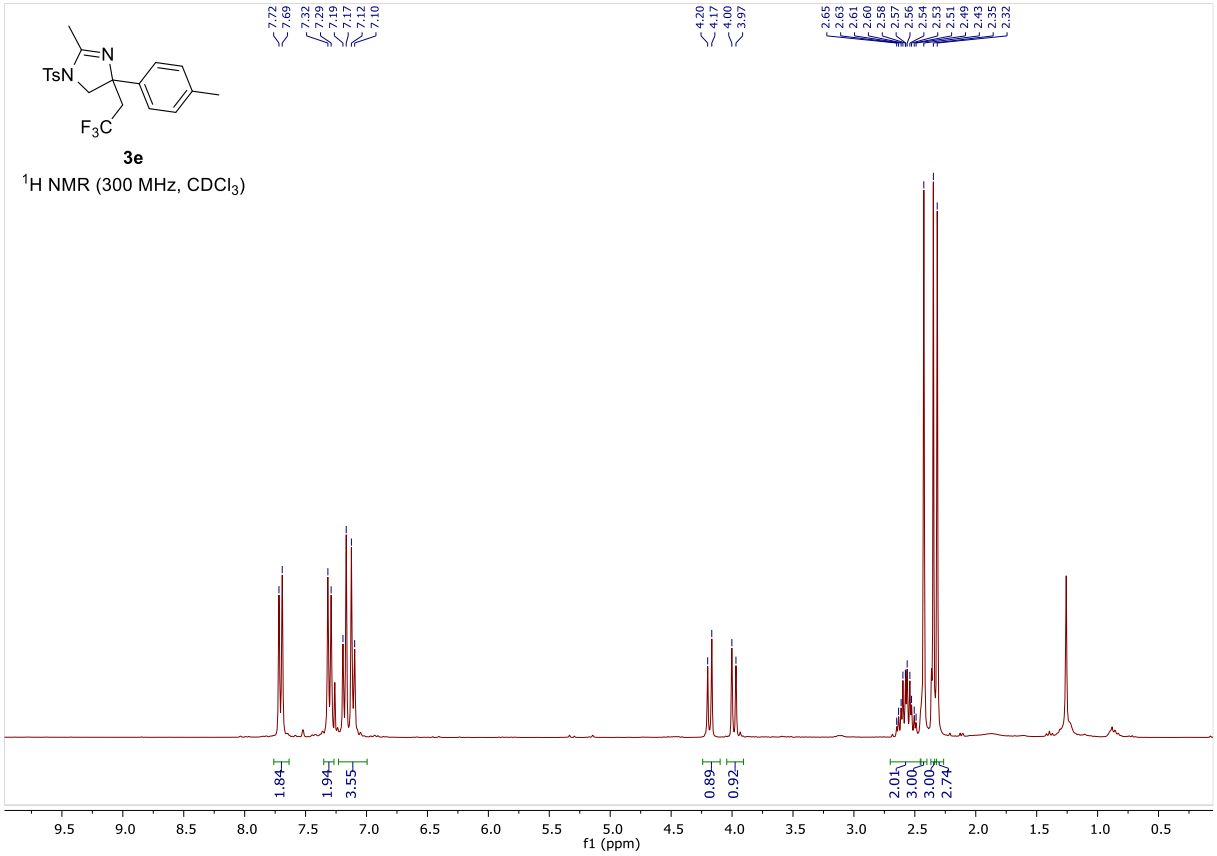


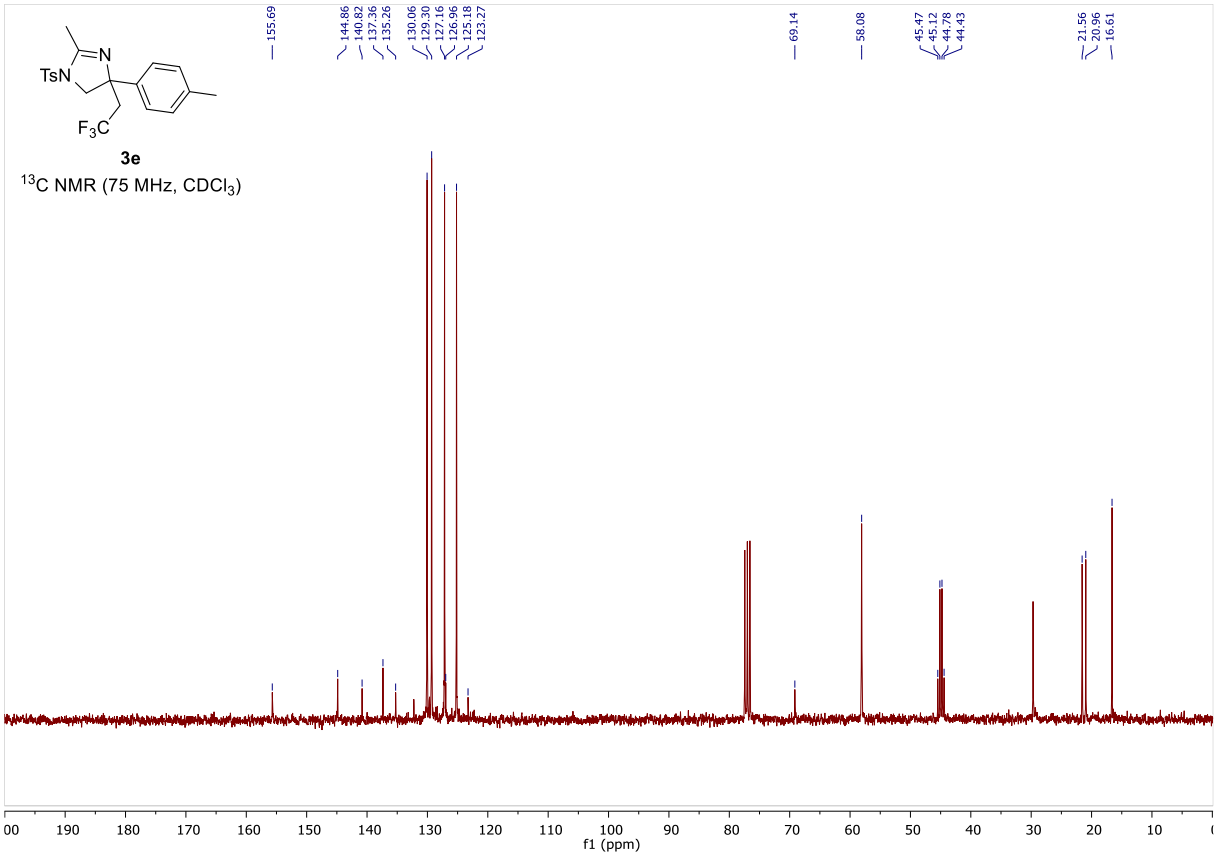
3d

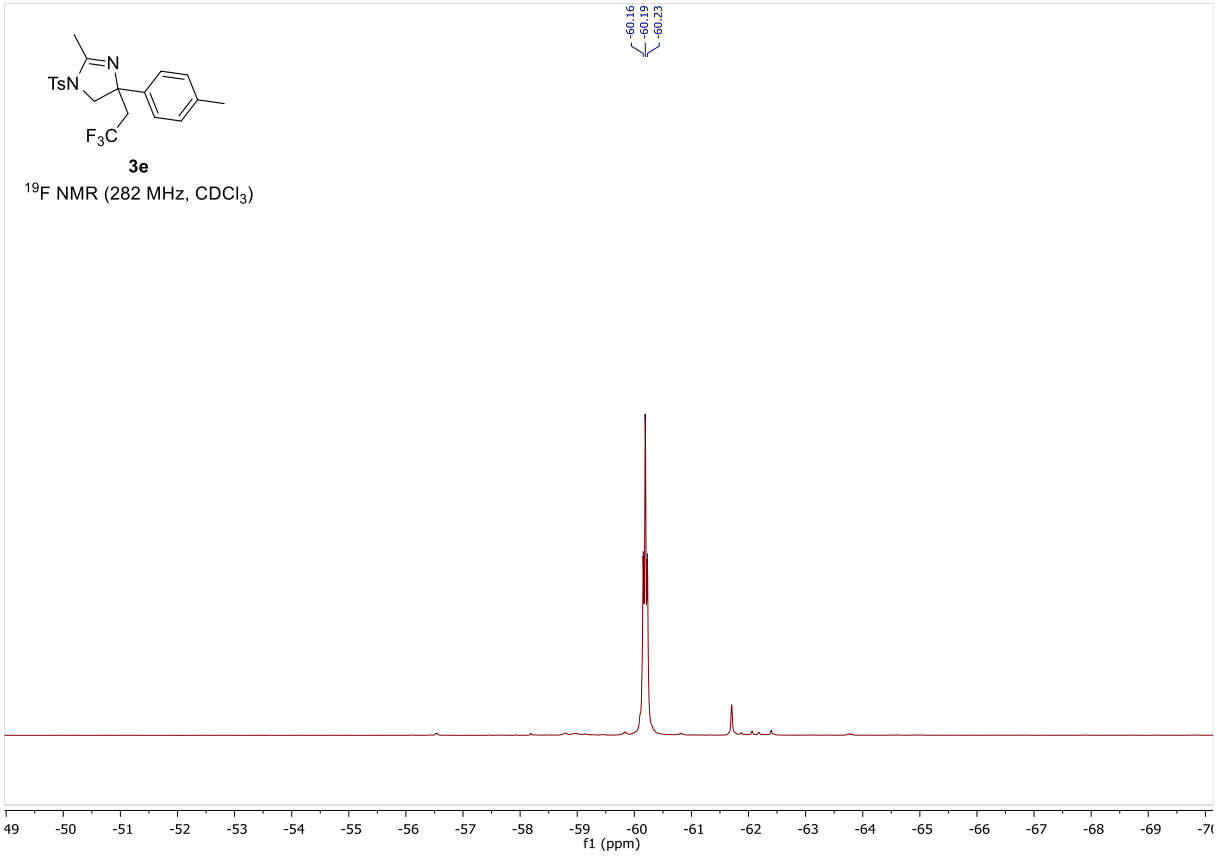
^{1}H NMR (500 MHz, $CDCl_3$)


TsN
N
Br
F3C
3d
13C NMR (125 MHz, CDCl3)
156.36
145.23
142.91
135.24
131.92
131.87
130.25
130.25
128.42
127.36
127.26
126.19
123.97
121.85
121.76
69.20
58.22
45.37
45.16
44.94
44.73
21.75
16.81
f1 (ppm)


TsN
N
Br
F3C
3d
19F NMR (282 MHz, CDCl3)
-60.07
-60.11
-60.14
f1 (ppm)

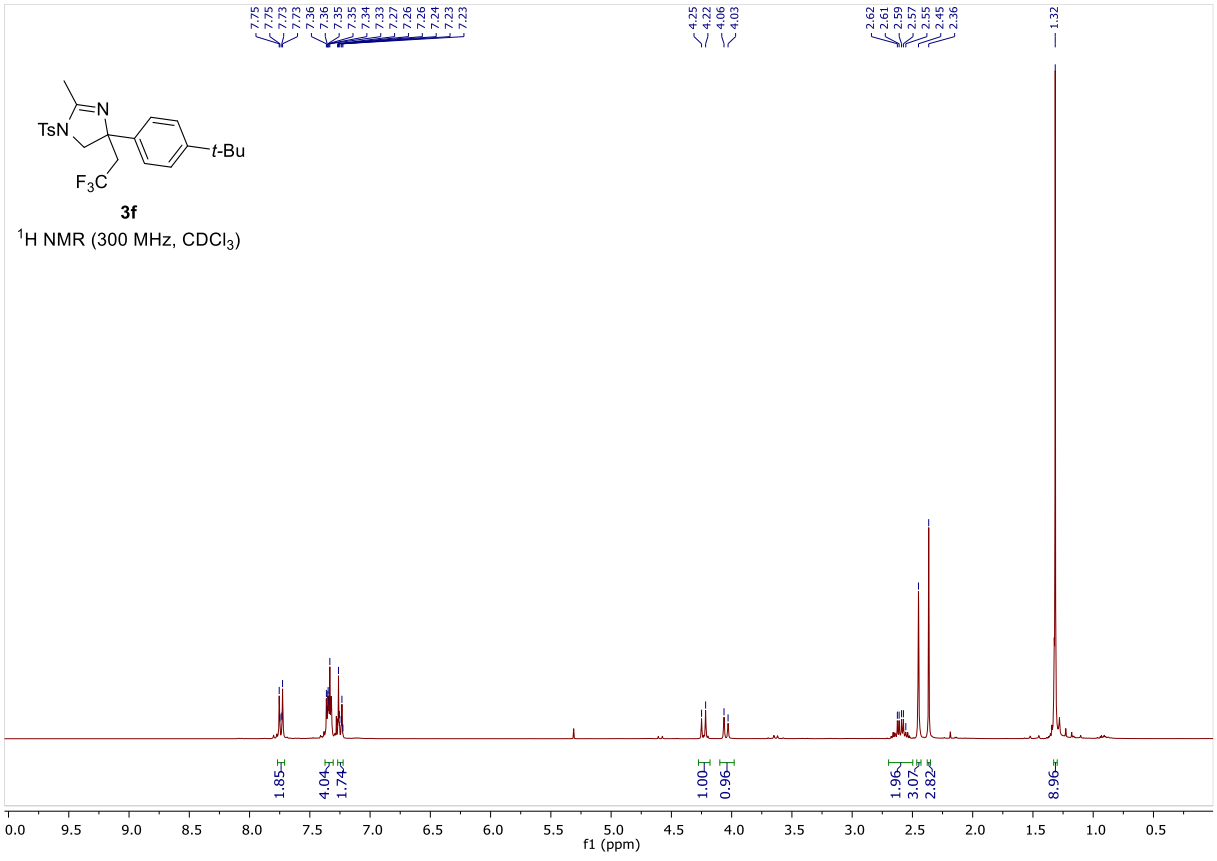

TsN
F3C
3e
1H NMR (300 MHz, CDCl3)
7.72
7.69
7.32
7.29
7.19
7.17
7.12
7.10
4.20
4.17
4.00
3.97
2.65
2.63
2.61
2.60
2.58
2.57
2.56
2.54
2.53
2.51
2.49
2.43
2.35
2.32
1.84
1.94
3.55
0.89
0.92
2.01
3.00
3.00
2.74
f1 (ppm)


TsN
F3C
3e
13C NMR (75 MHz, CDCl3)
155.69
144.86
140.82
137.36
135.26
130.06
129.30
127.16
126.96
125.18
123.27
69.14
58.08
45.47
45.12
44.78
44.43
21.56
20.96
16.61
f1 (ppm)



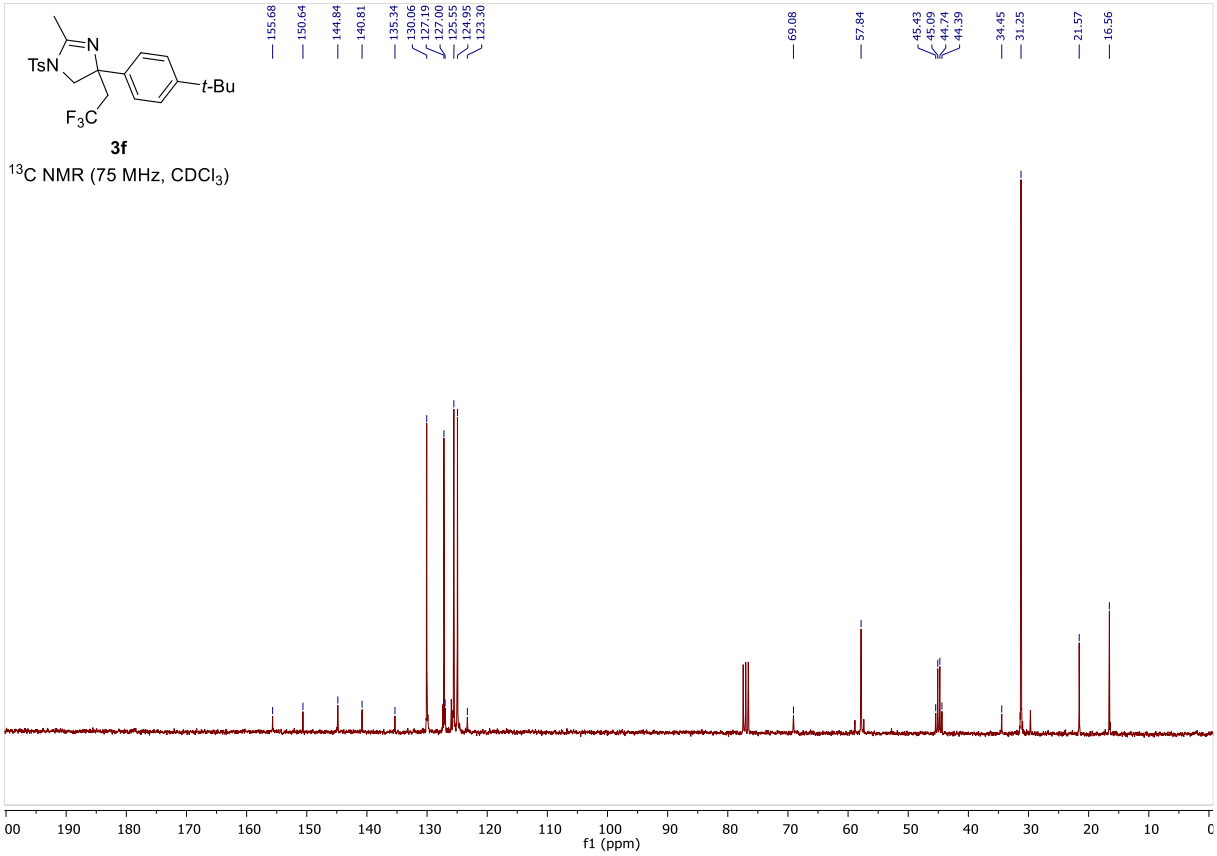
3e

^{19}F NMR (282 MHz, $CDCl_3$)



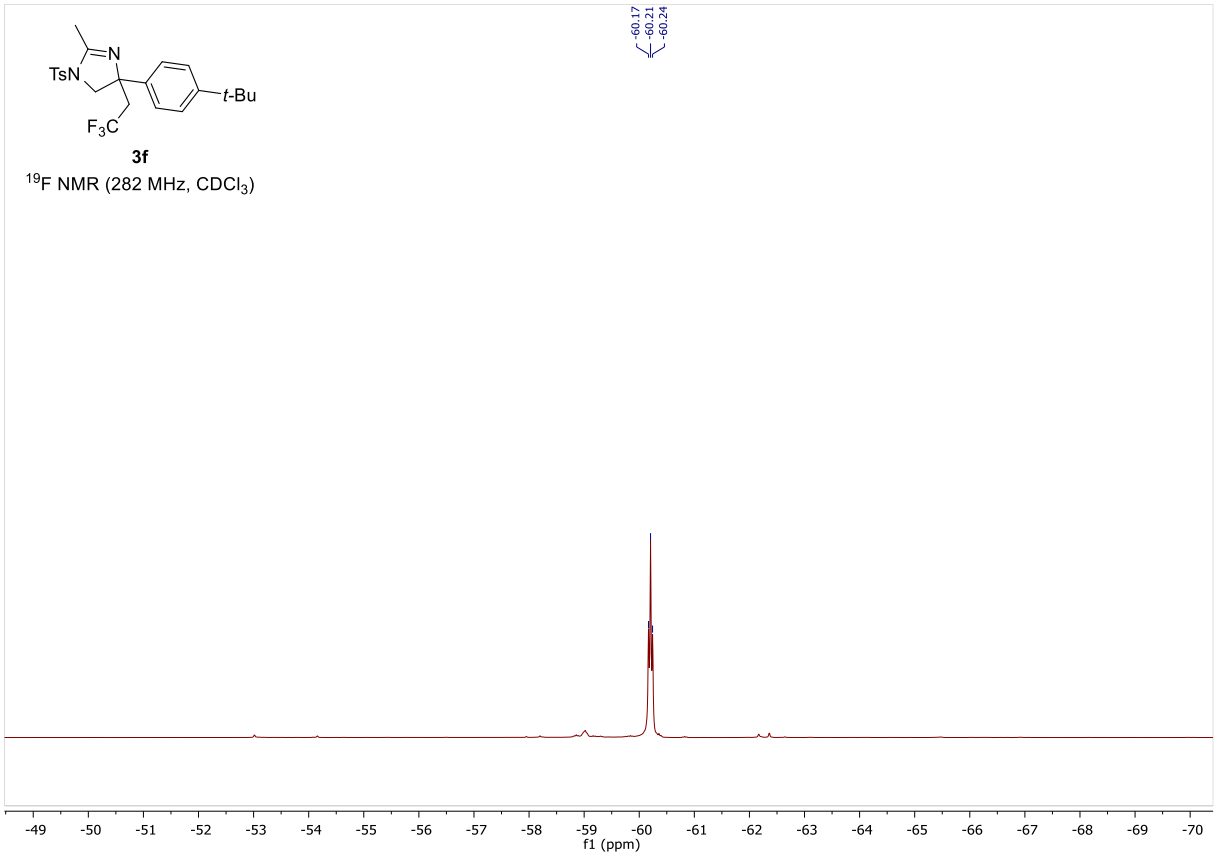
3f

^{1}H NMR (300 MHz, $CDCl_3$)



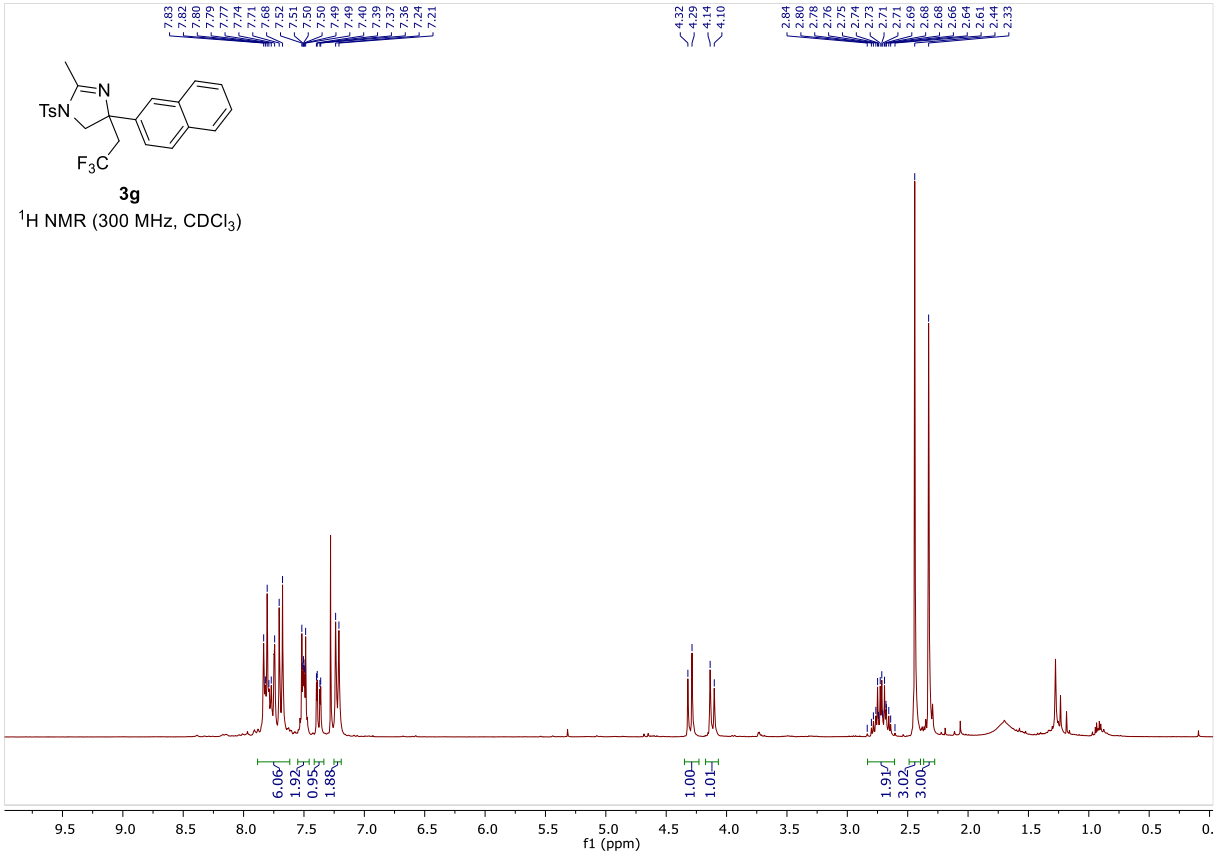
3f

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



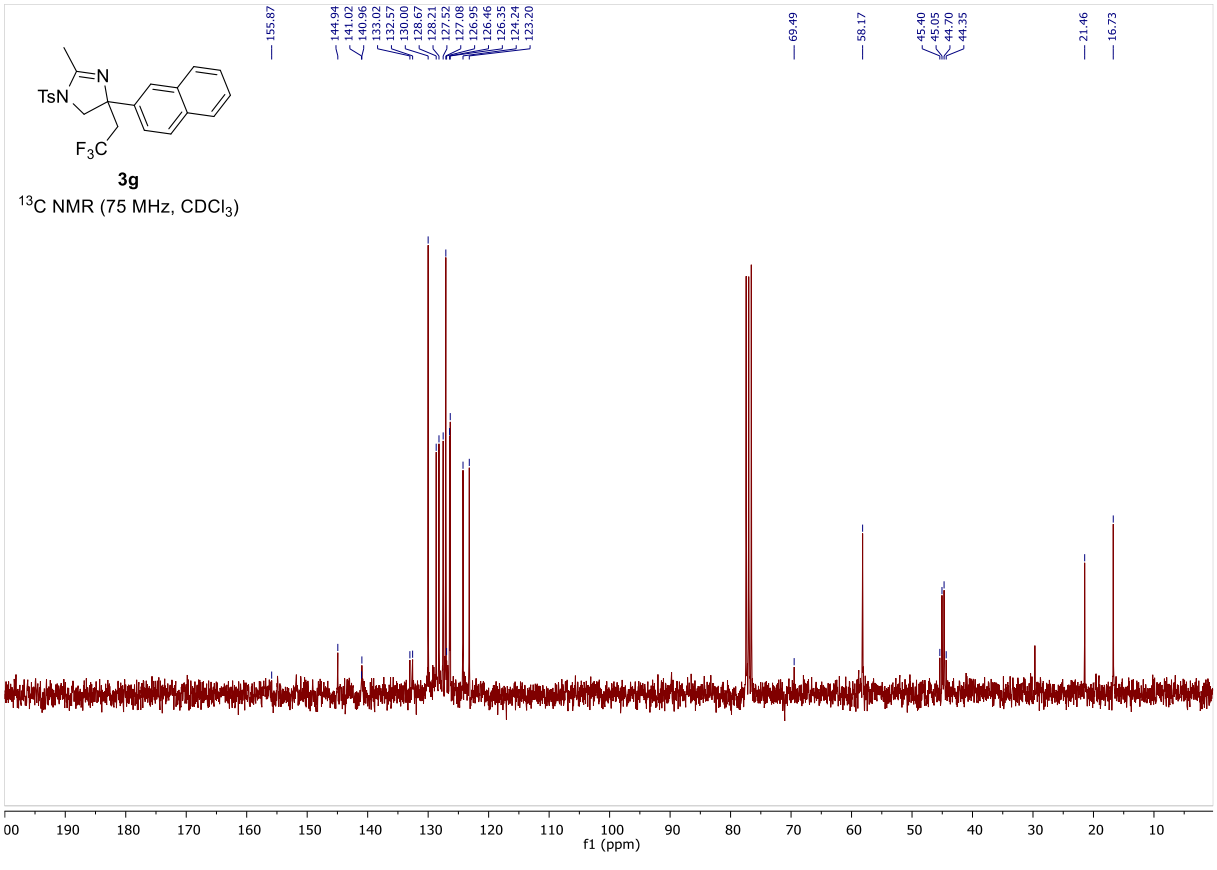
3f

^{19}F NMR (282 MHz, $CDCl_3$)



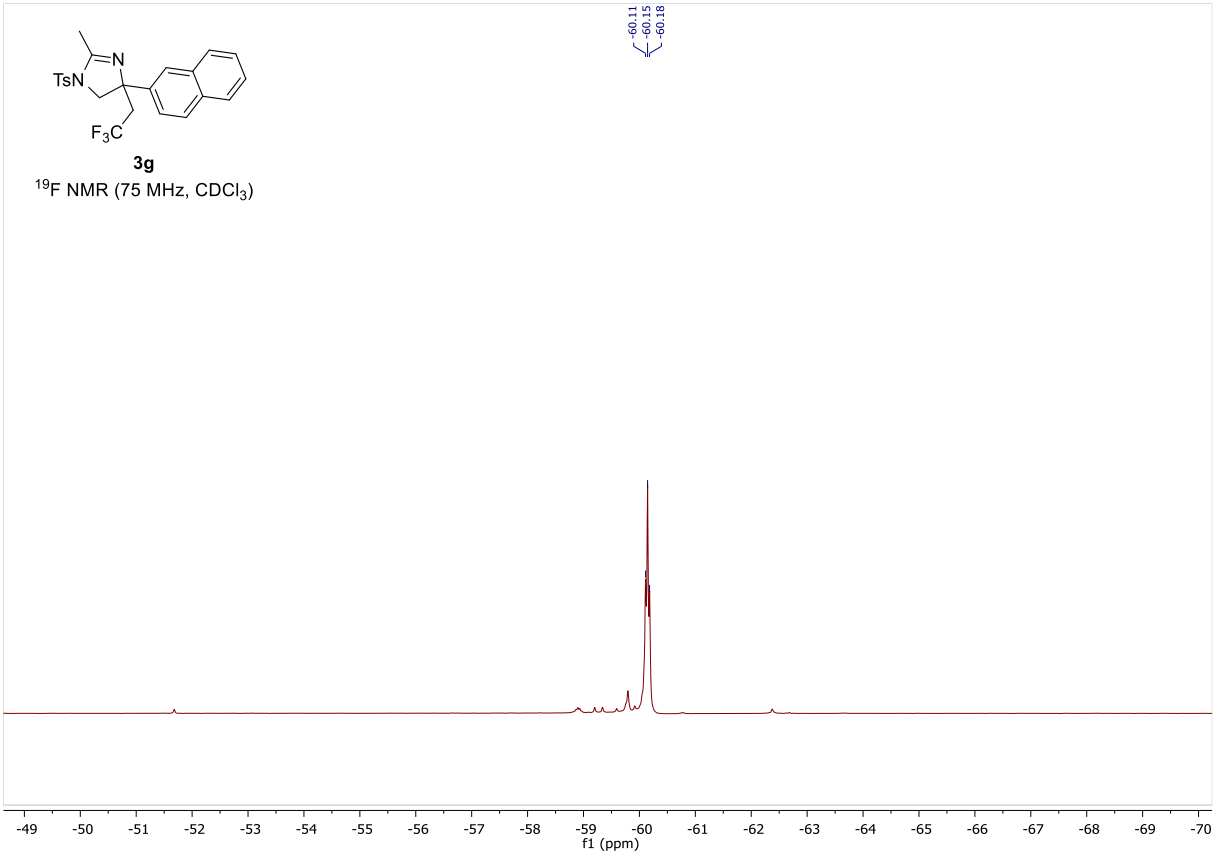
3g

^{1}H NMR (300 MHz, $CDCl_3$)



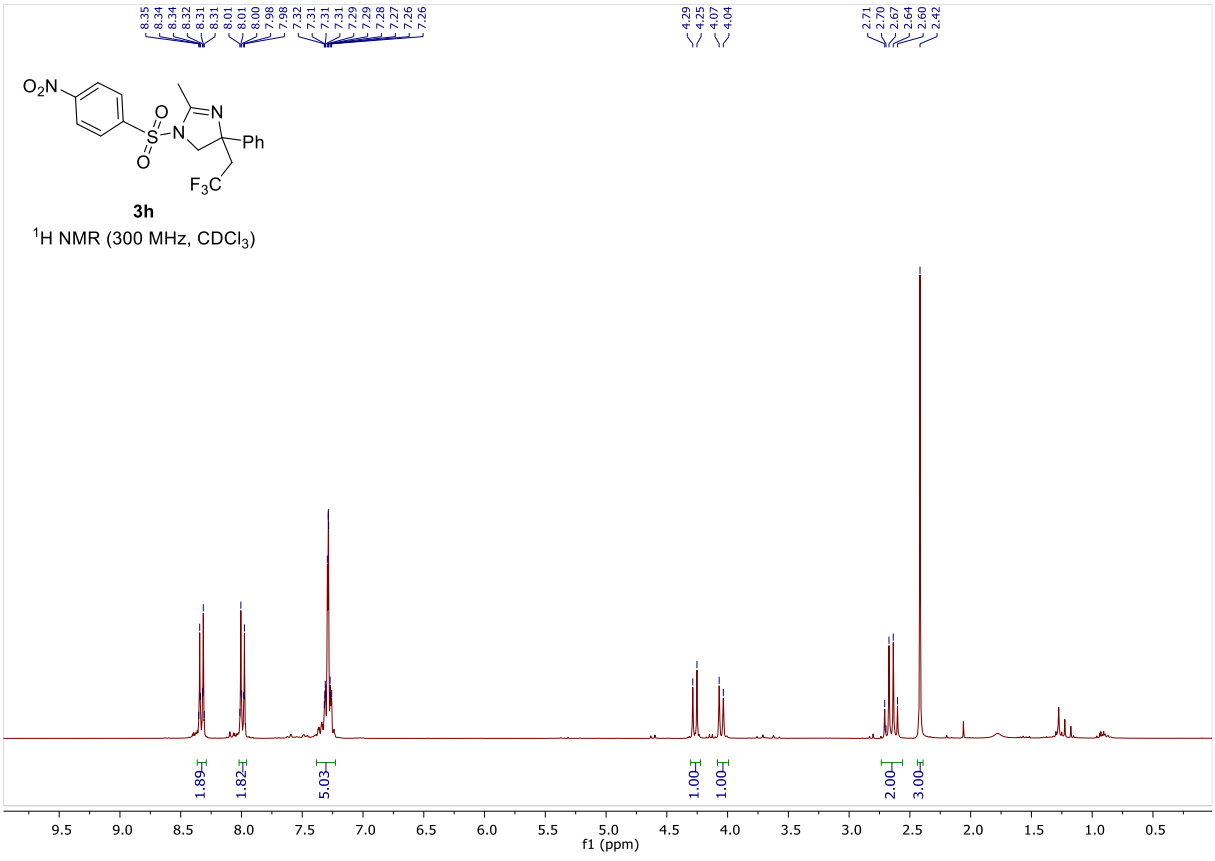
3g

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



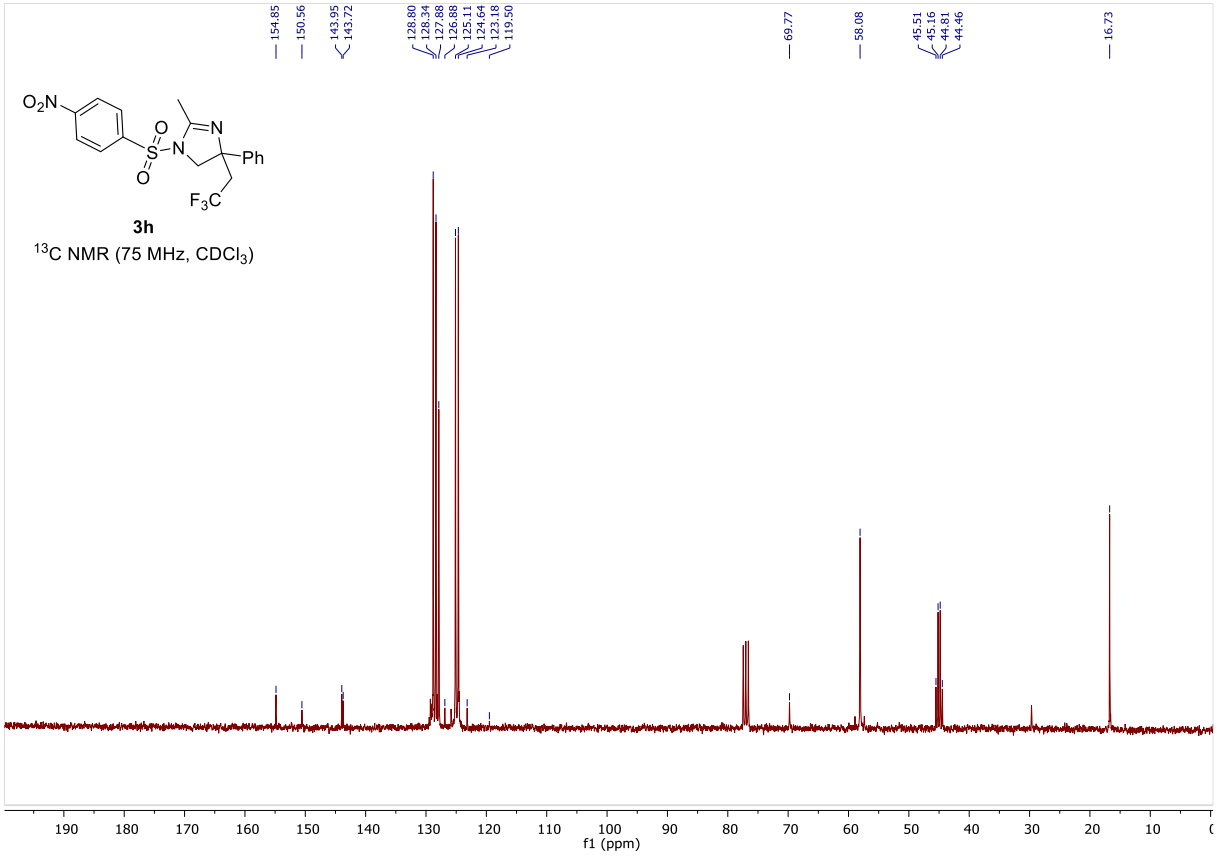
3g

^{19}F NMR (75 MHz, $CDCl_3$)



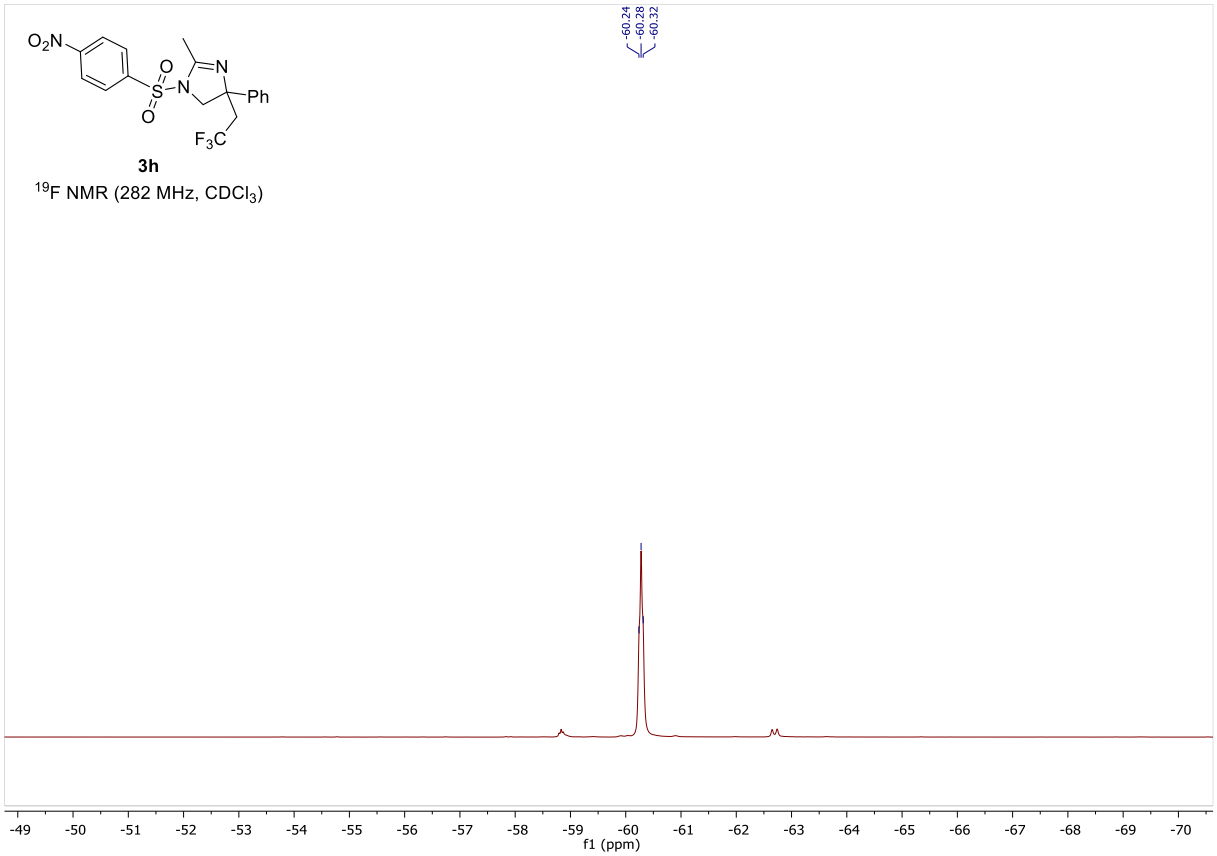
3h

^{1}H NMR (300 MHz, $CDCl_3$)



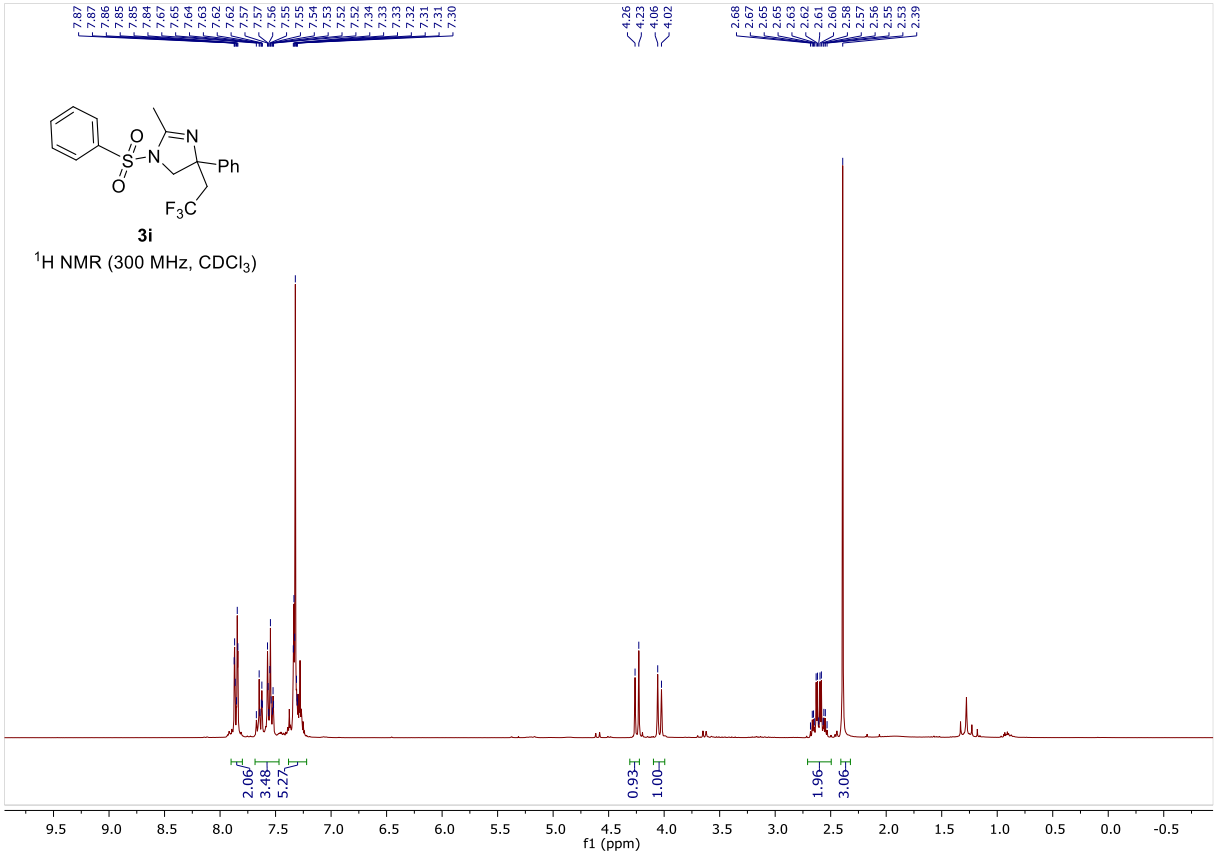
3h

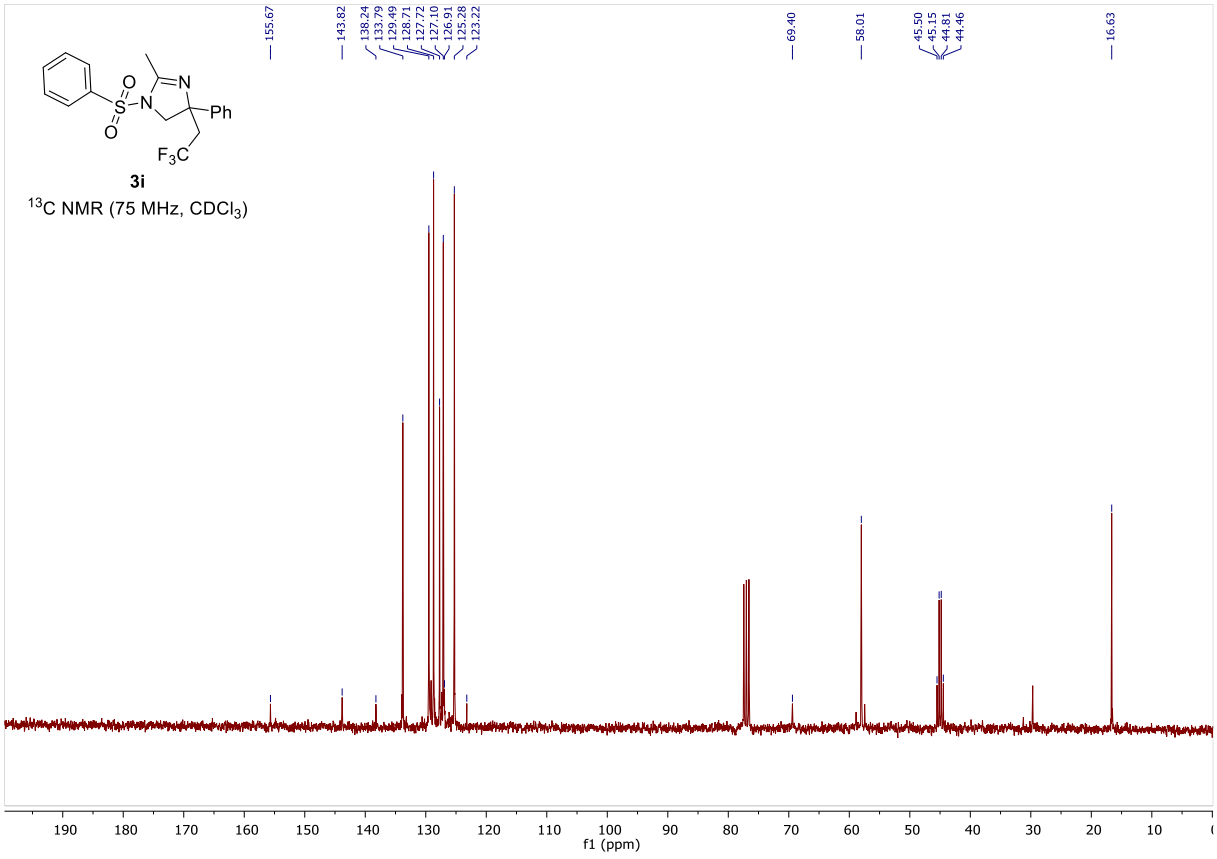
^{13}C NMR (75 MHz, $CDCl_3$)

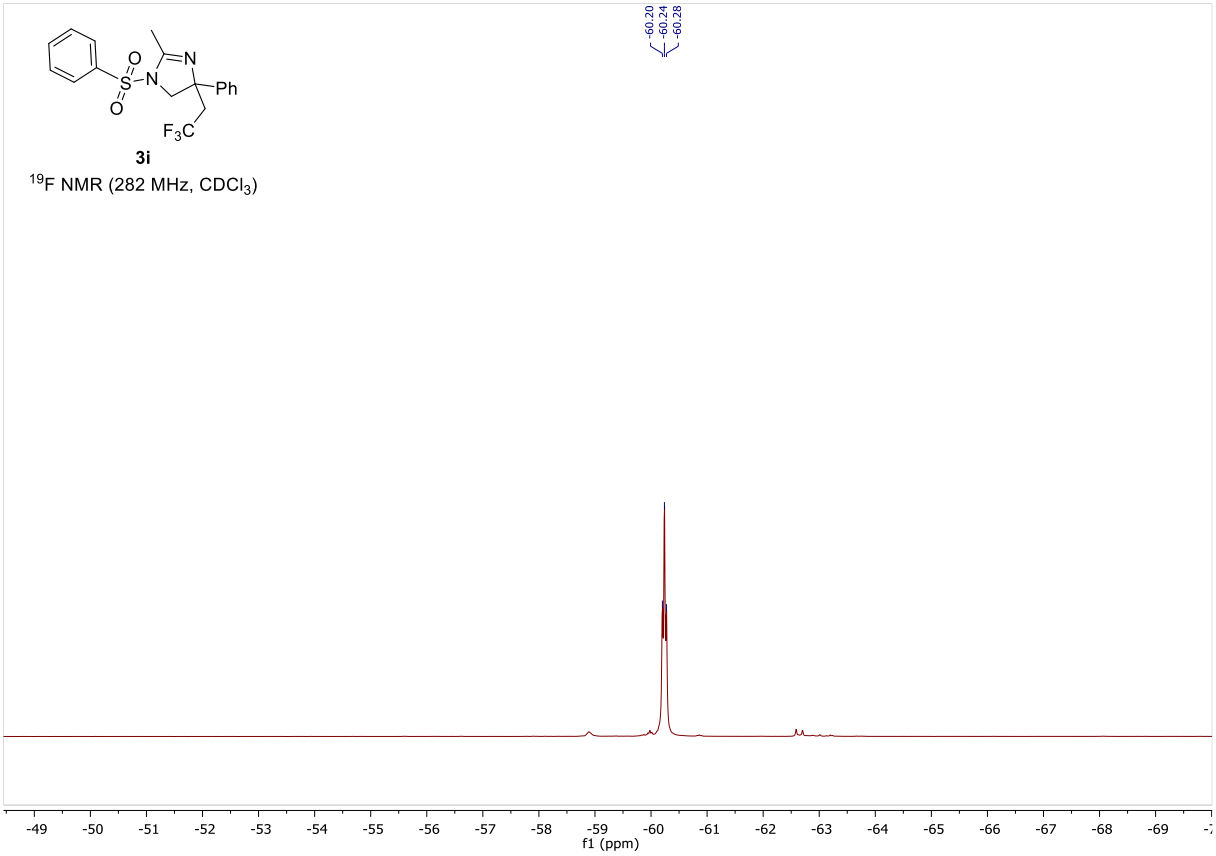


3h

^{19}F NMR (282 MHz, $CDCl_3$)

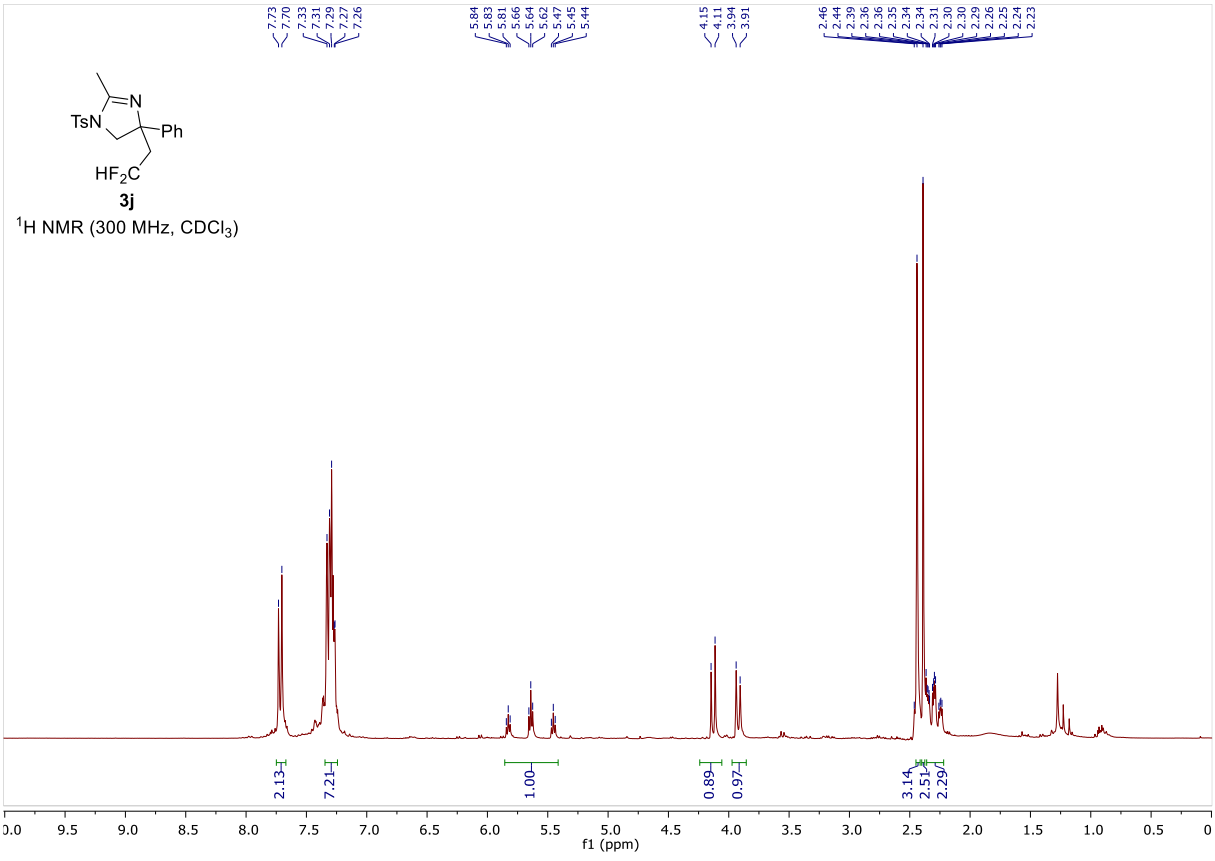

7.87 7.87 7.86 7.85 7.85 7.84 7.67 7.65 7.64 7.63 7.62 7.62 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.52 7.52 7.34 7.33 7.33 7.32 7.31 7.31 7.30
4.26 4.23 4.06 4.02
2.68 2.67 2.65 2.65 2.63 2.62 2.61 2.60 2.58 2.57 2.56 2.55 2.53 2.39
O
N
S
O
N
Ph
F3C
3i
1H NMR (300 MHz, CDCl3)
2.06 3.48 5.27 0.93 1.00 1.96 3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.67 143.82 138.24 133.79 129.49 128.71 127.72 127.10 126.91 125.28 123.22
69.40 58.01 45.50 45.15 44.81 44.46 16.63
O
N
S
O
N
Ph
F3C
3i
13C NMR (75 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



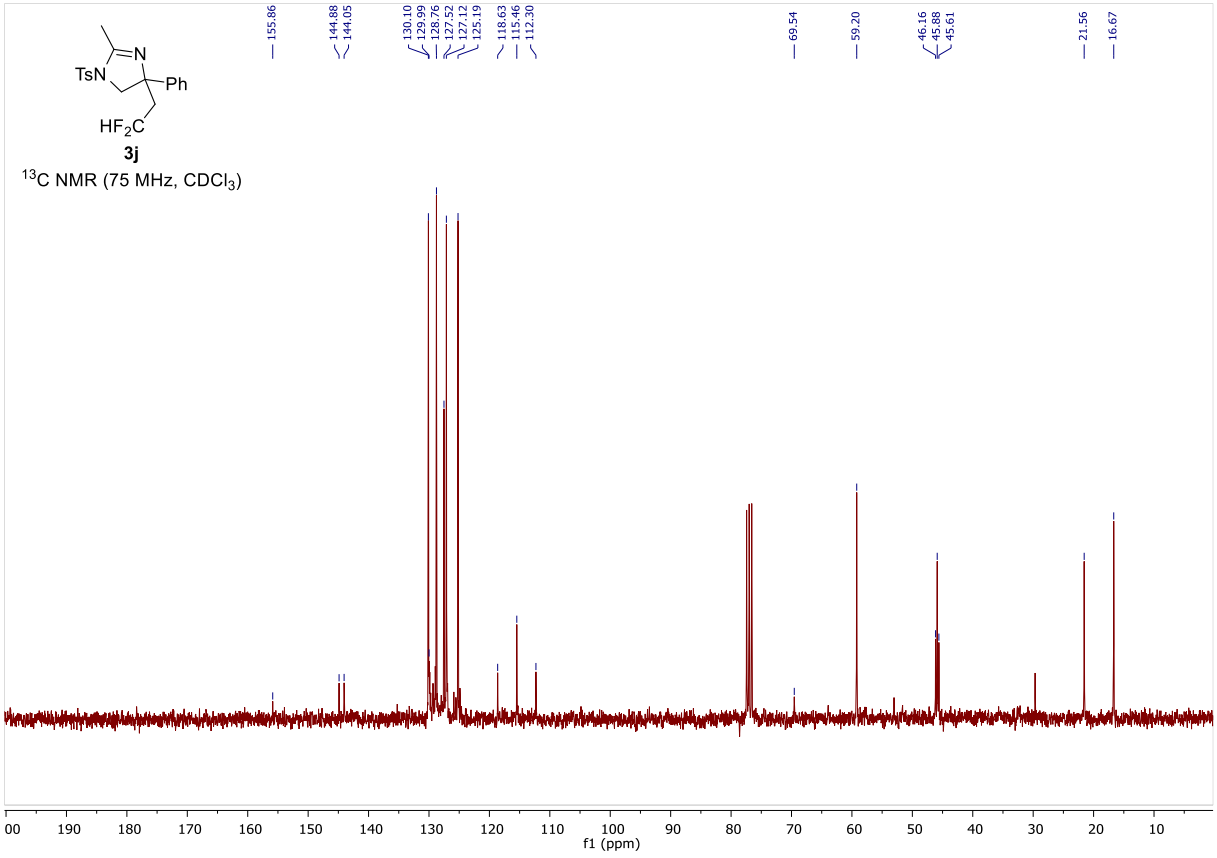
3i

^{19}F NMR (282 MHz, $CDCl_3$)



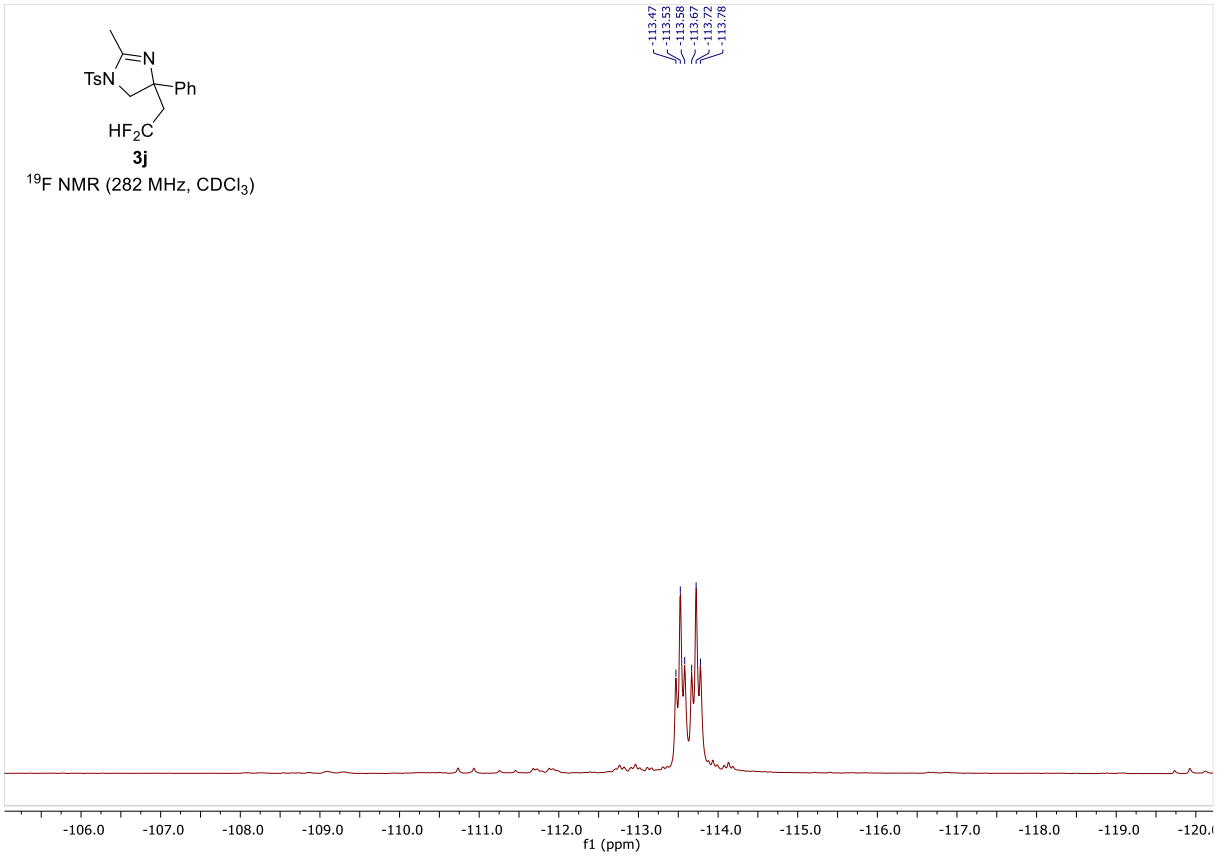
3j

^{1}H NMR (300 MHz, $CDCl_3$)



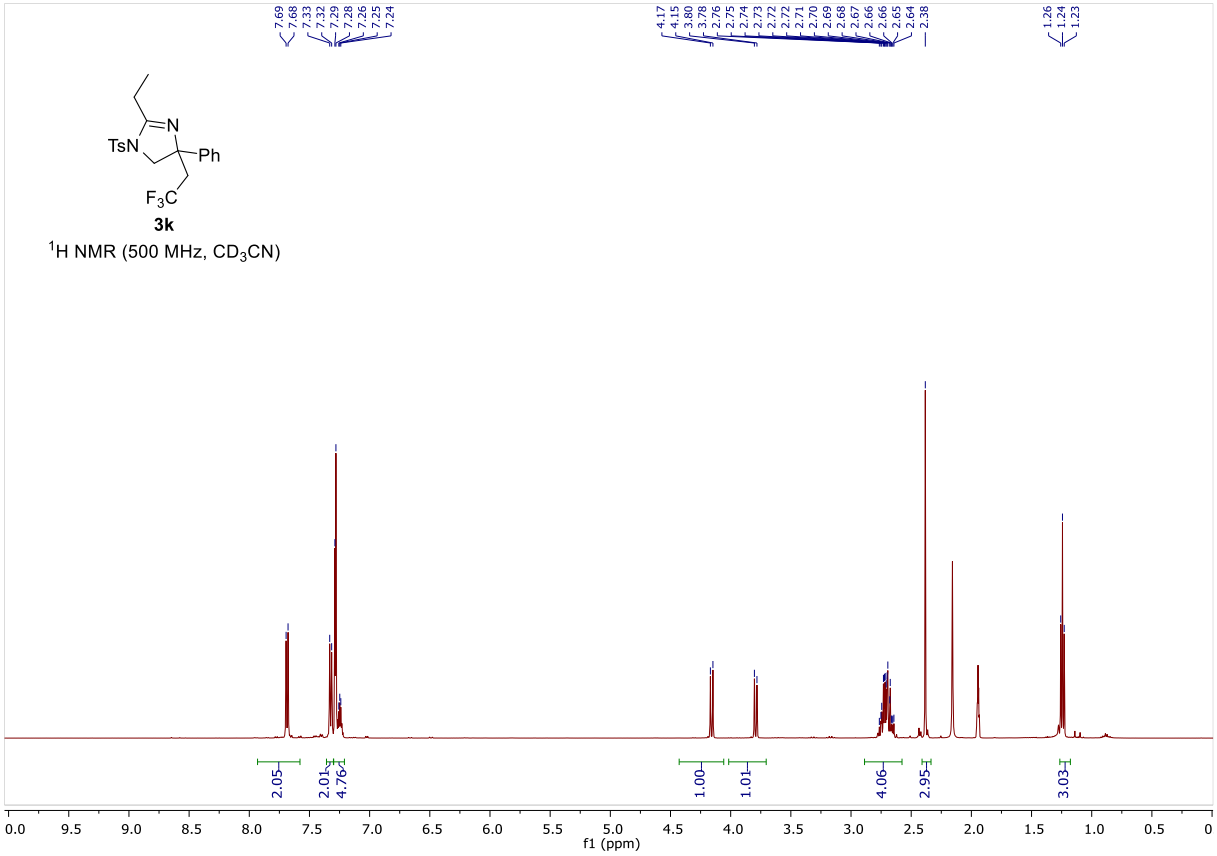
3j

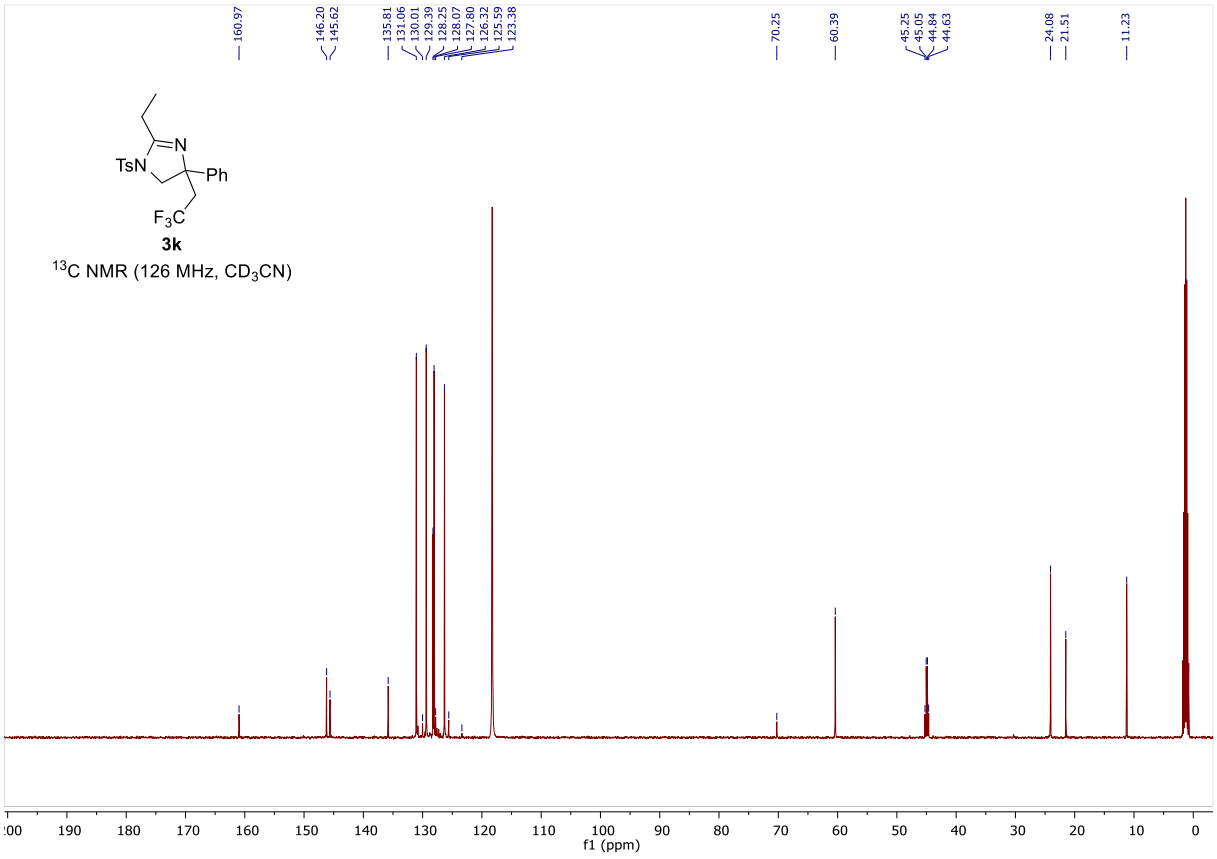
^{13}C NMR (75 MHz, $CDCl_3$)

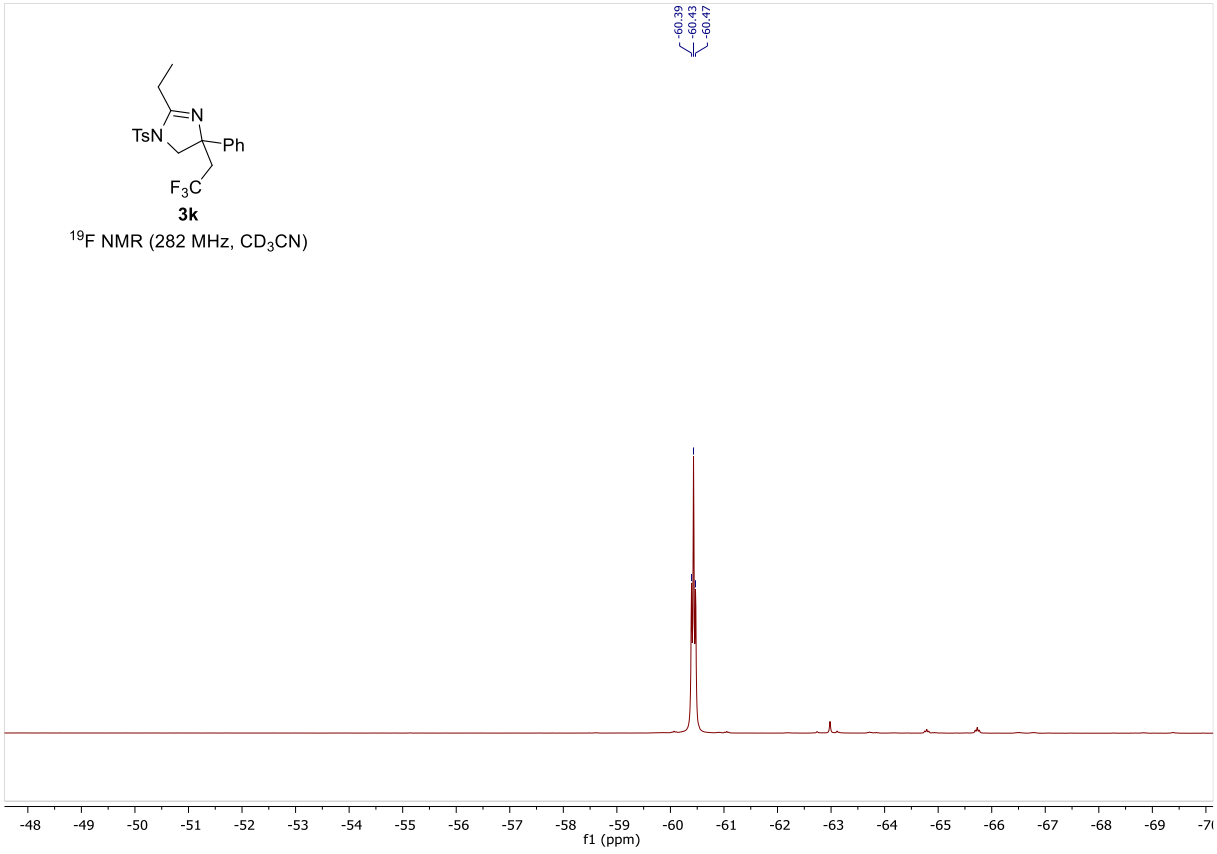


3j

^{19}F NMR (282 MHz, $CDCl_3$)

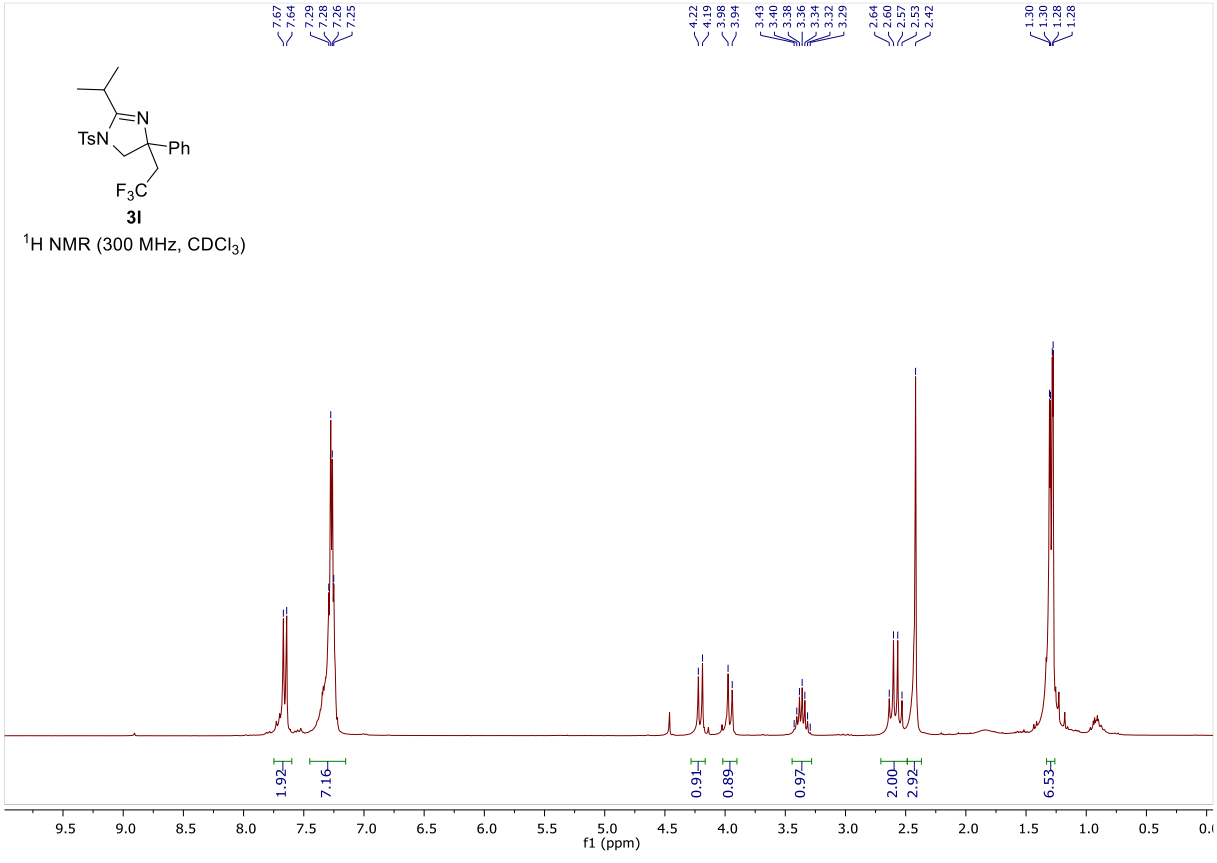

7.69
7.68
7.33
7.32
7.29
7.28
7.26
7.25
7.24
4.17
4.15
3.80
3.78
2.76
2.75
2.74
2.73
2.72
2.72
2.71
2.70
2.69
2.68
2.67
2.66
2.66
2.65
2.64
2.38
1.26
1.24
1.23
TsN
N
Ph
F3C
3k
1H NMR (500 MHz, CD3CN)
2.05
2.01
4.76
1.00
1.01
4.06
2.95
3.03
f1 (ppm)


160.97
146.20
145.62
135.81
131.06
130.01
129.39
128.25
128.07
127.80
126.32
125.59
123.38
70.25
60.39
45.25
45.05
44.84
44.63
24.08
21.51
11.23
TsN
N
Ph
F3C
3k
13C NMR (126 MHz, CD3CN)
f1 (ppm)



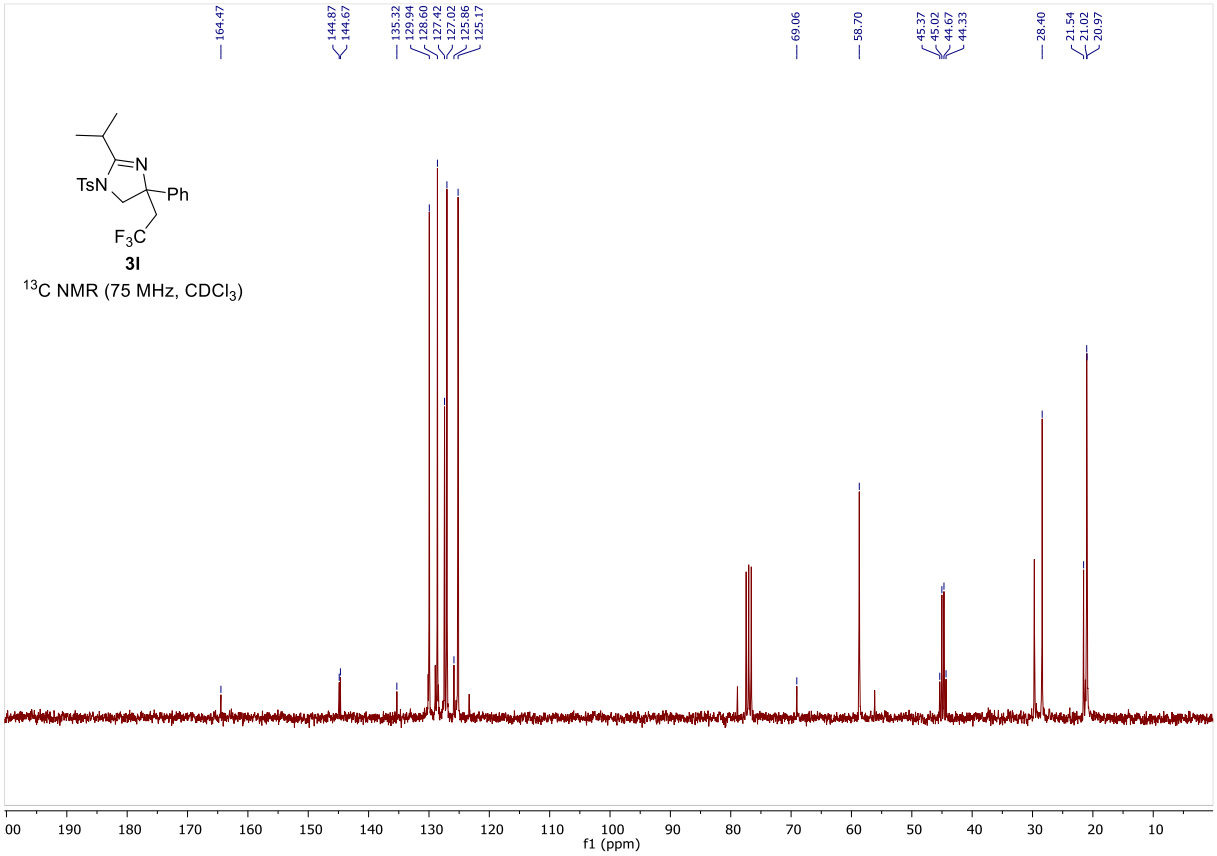
3k

^{19}F NMR (282 MHz, CD_3CN)



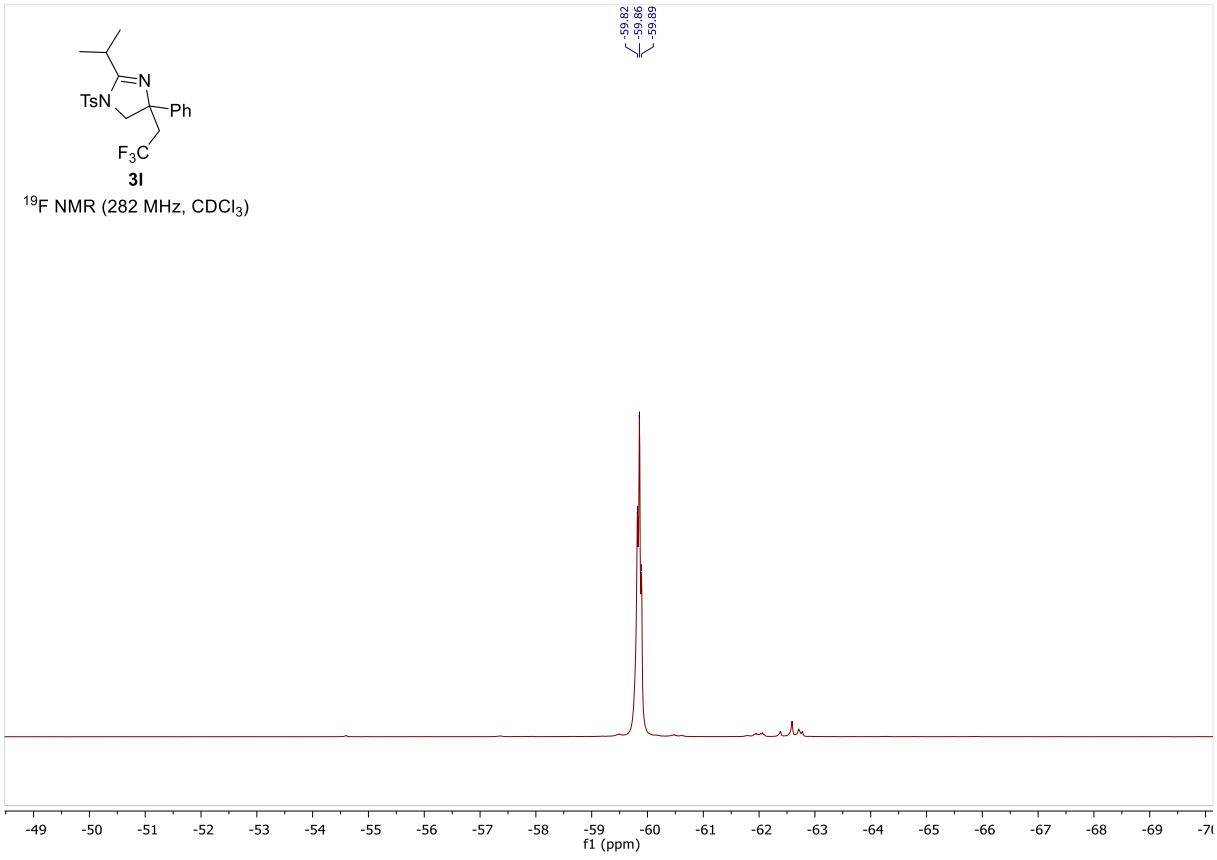
3l

^{1}H NMR (300 MHz, $CDCl_3$)



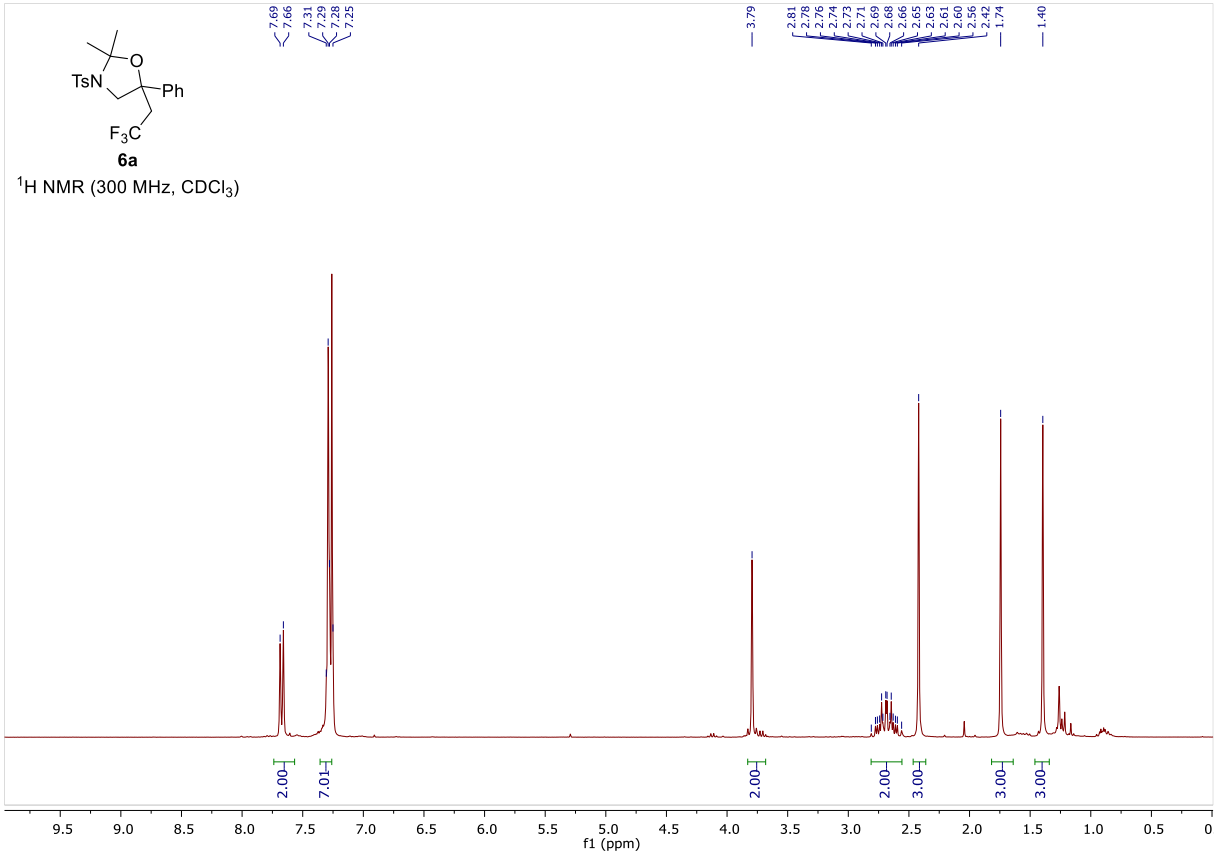
3l

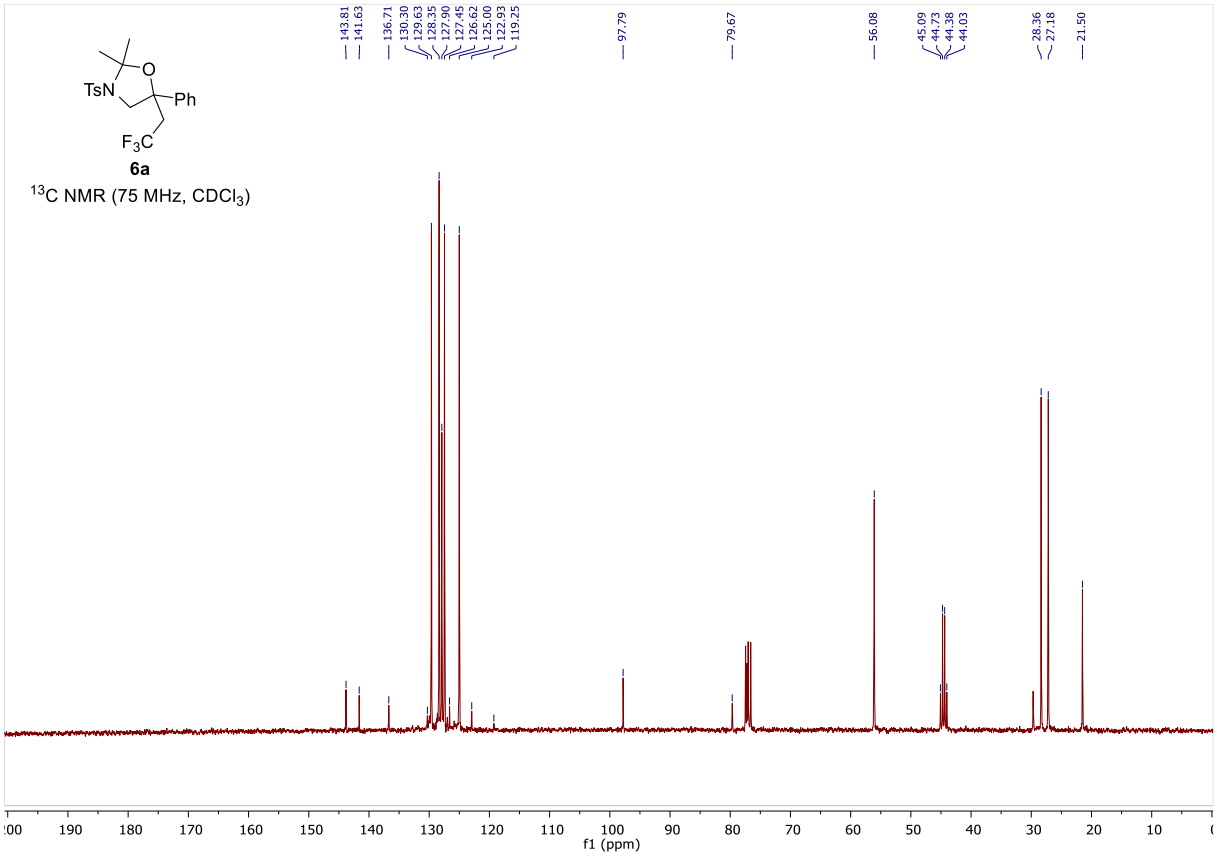
^{13}C NMR (75 MHz, $CDCl_3$)

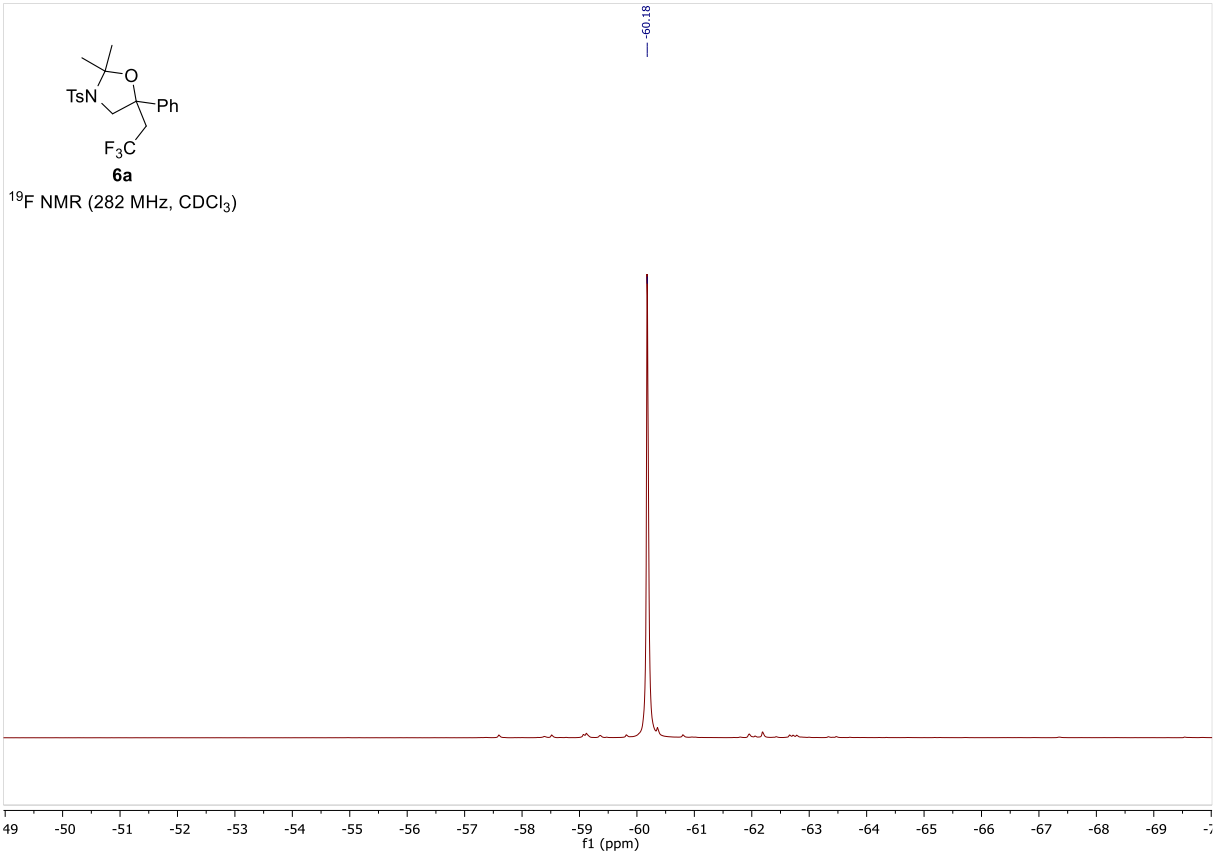


3l

^{19}F NMR (282 MHz, $CDCl_3$)

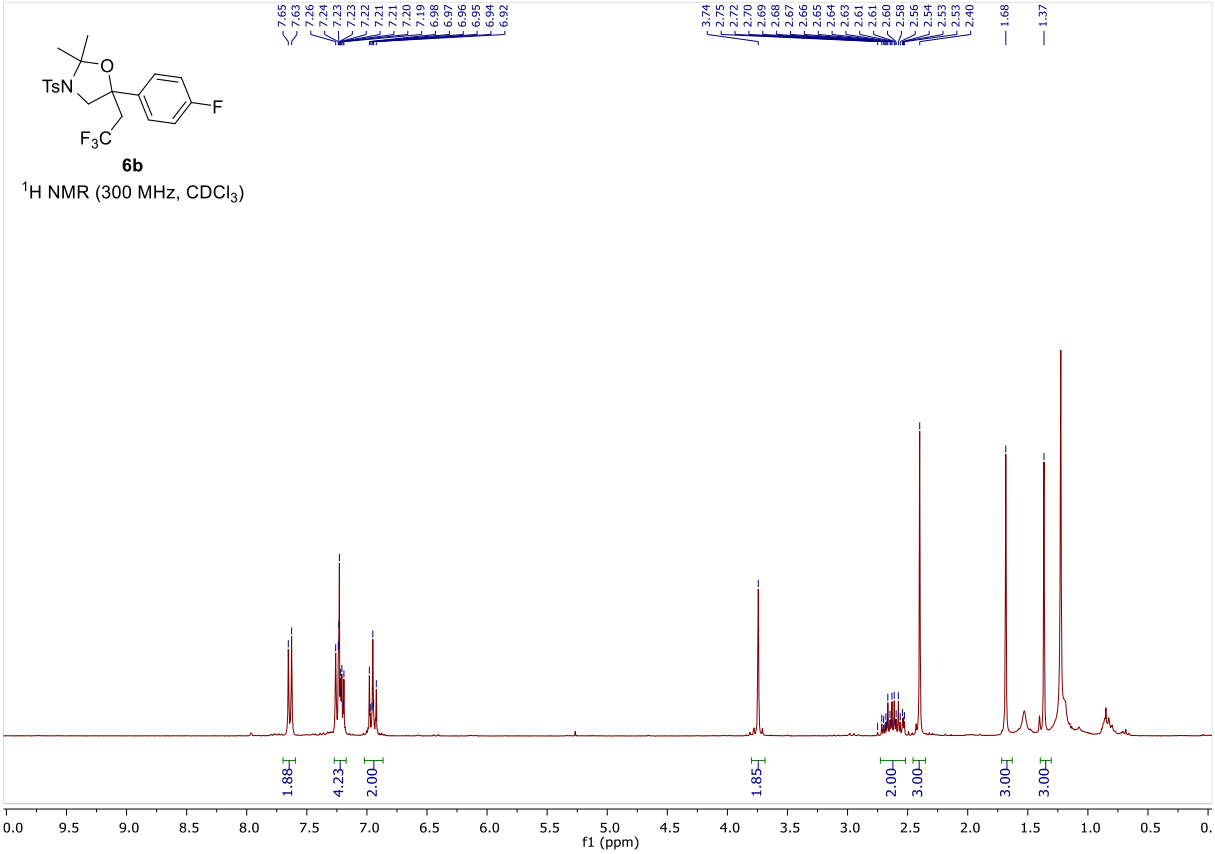

TsN
O
Ph
F3C
6a
1H NMR (300 MHz, CDCl3)
7.69
7.66
7.31
7.29
7.28
7.25
3.79
2.81
2.78
2.76
2.74
2.73
2.71
2.69
2.68
2.66
2.65
2.63
2.61
2.60
2.56
2.42
1.74
1.40
2.00
7.01
2.00
2.00
3.00
3.00
3.00
f1 (ppm)


TsN
O
Ph
F3C
6a
13C NMR (75 MHz, CDCl3)
143.81
141.63
136.71
130.30
129.63
128.35
127.90
127.45
126.62
125.00
122.93
119.25
97.79
79.67
56.08
45.09
44.73
44.38
44.03
28.36
27.18
21.50
f1 (ppm)



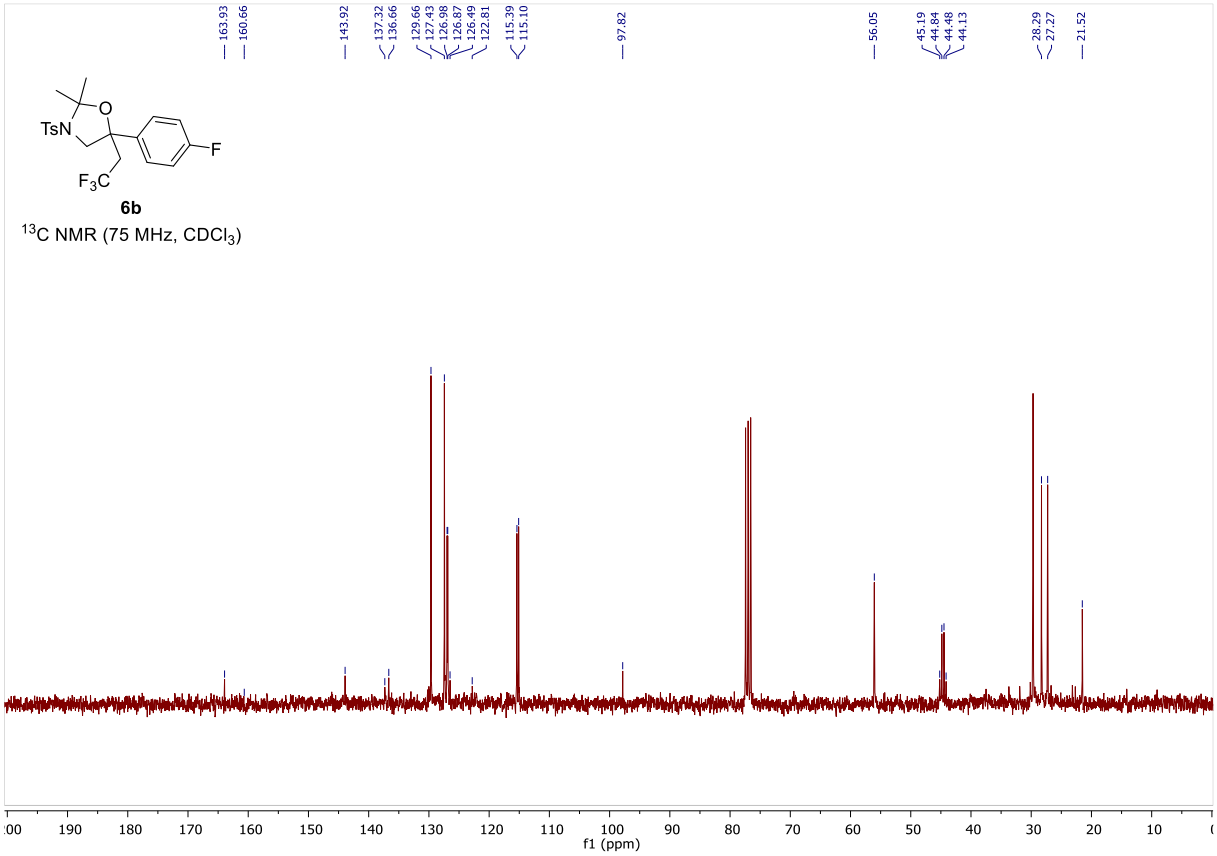
6a

^{19}F NMR (282 MHz, $CDCl_3$)



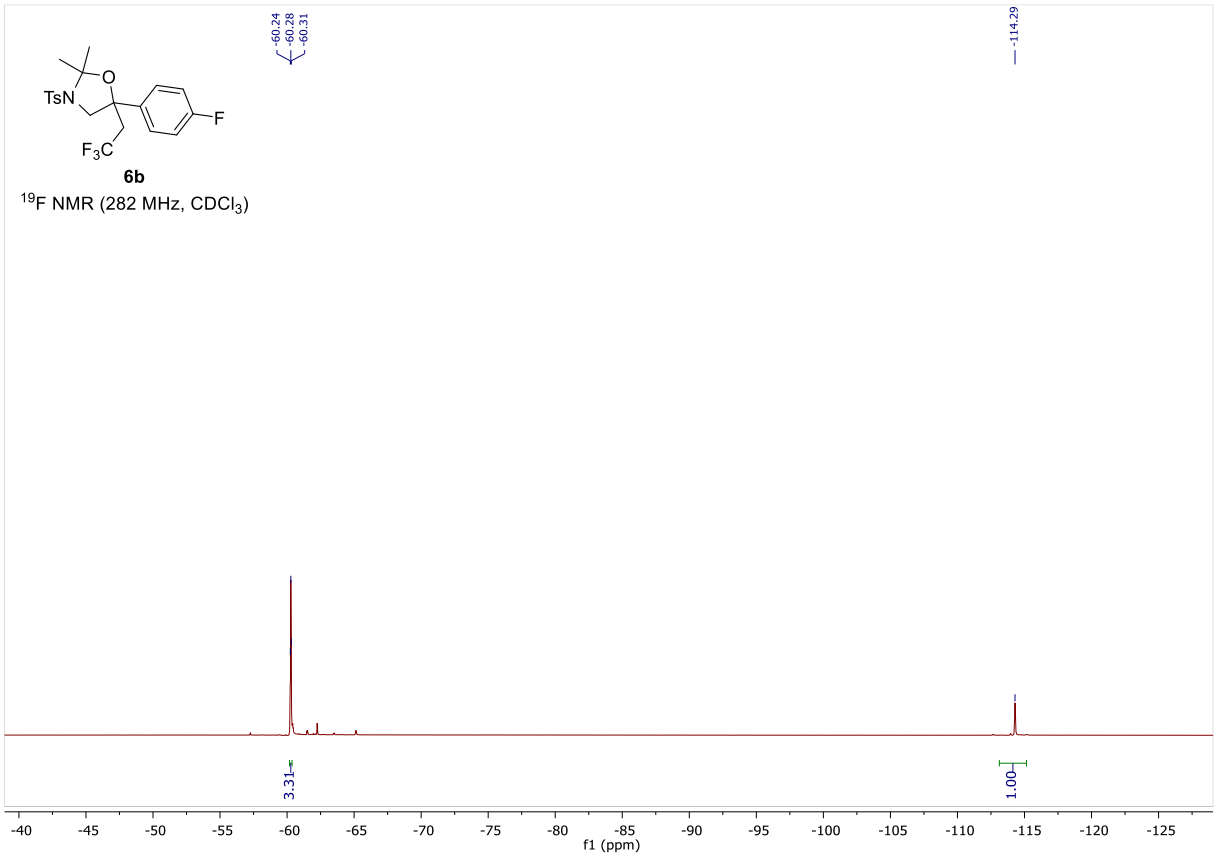
6b

^{1}H NMR (300 MHz, $CDCl_3$)



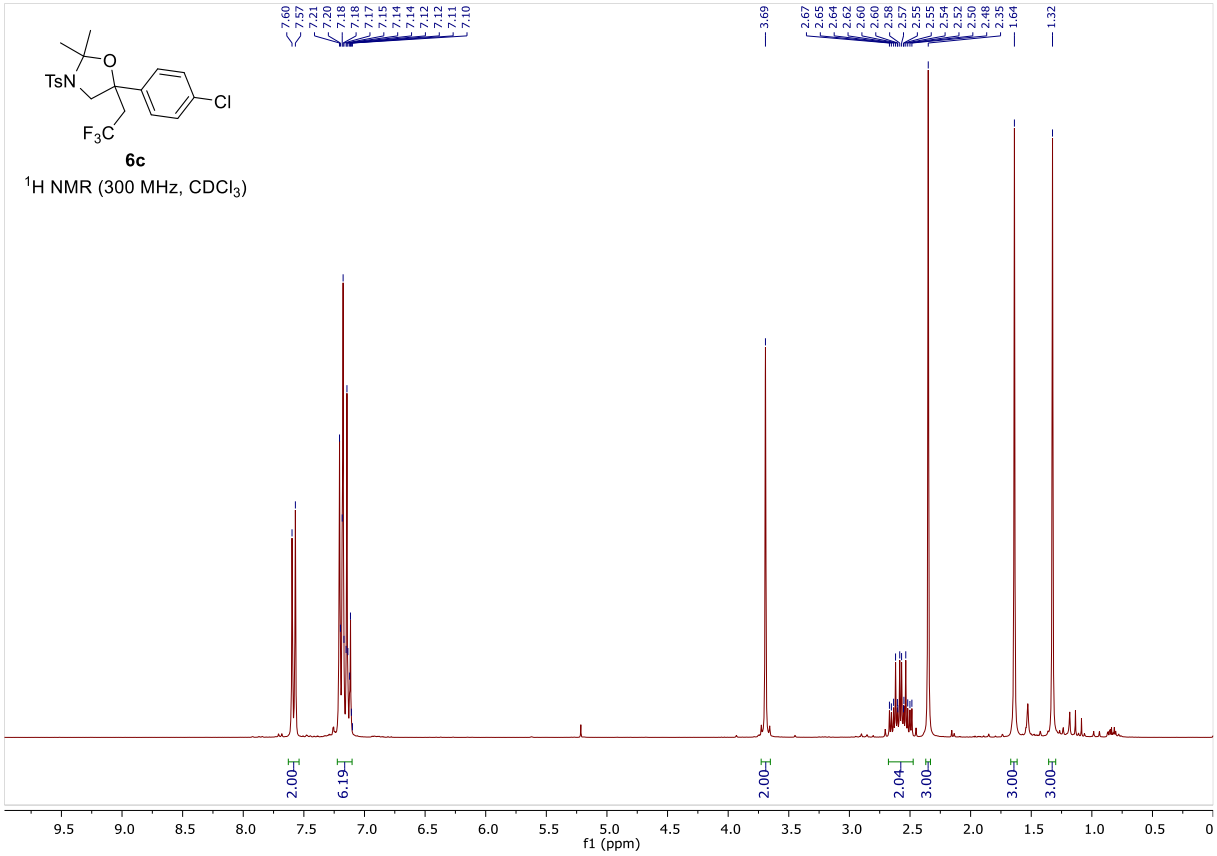
6b

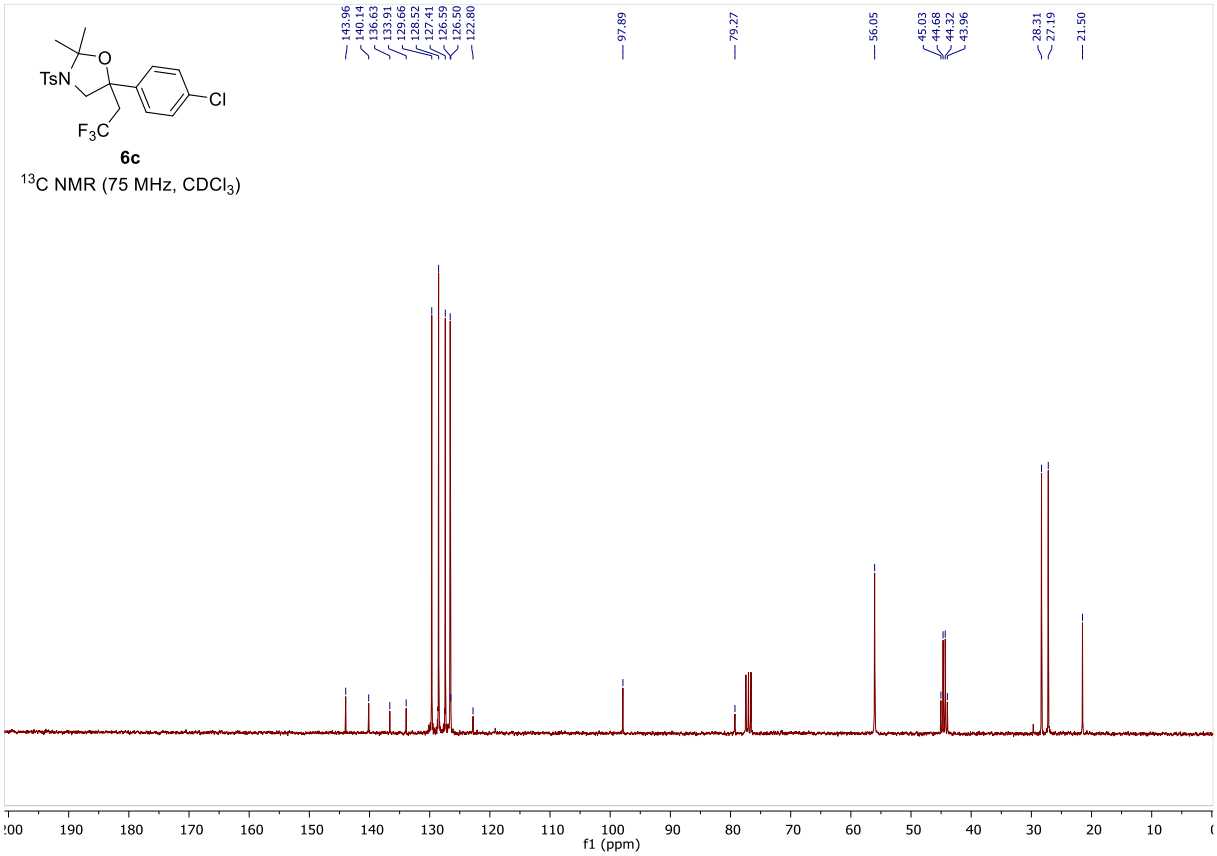
^{13}C NMR (75 MHz, $CDCl_3$)

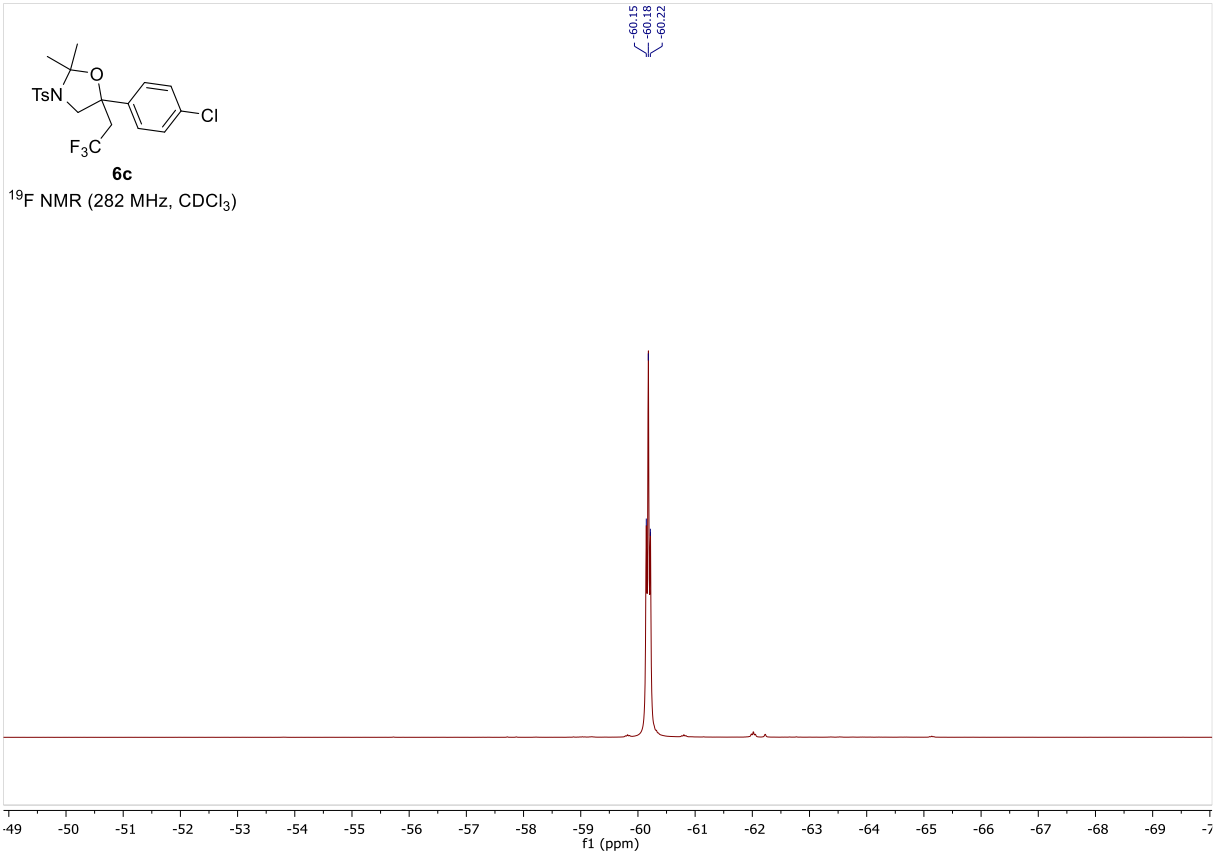


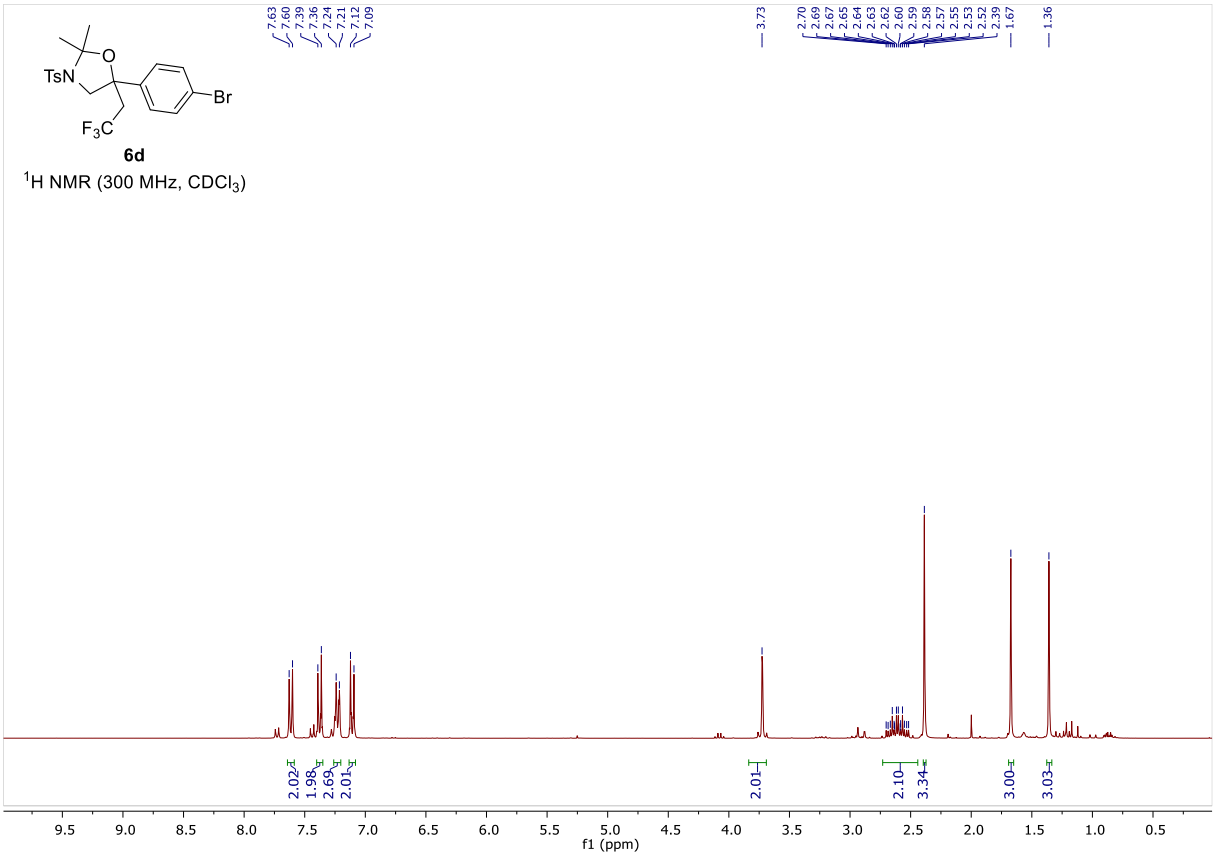
6b

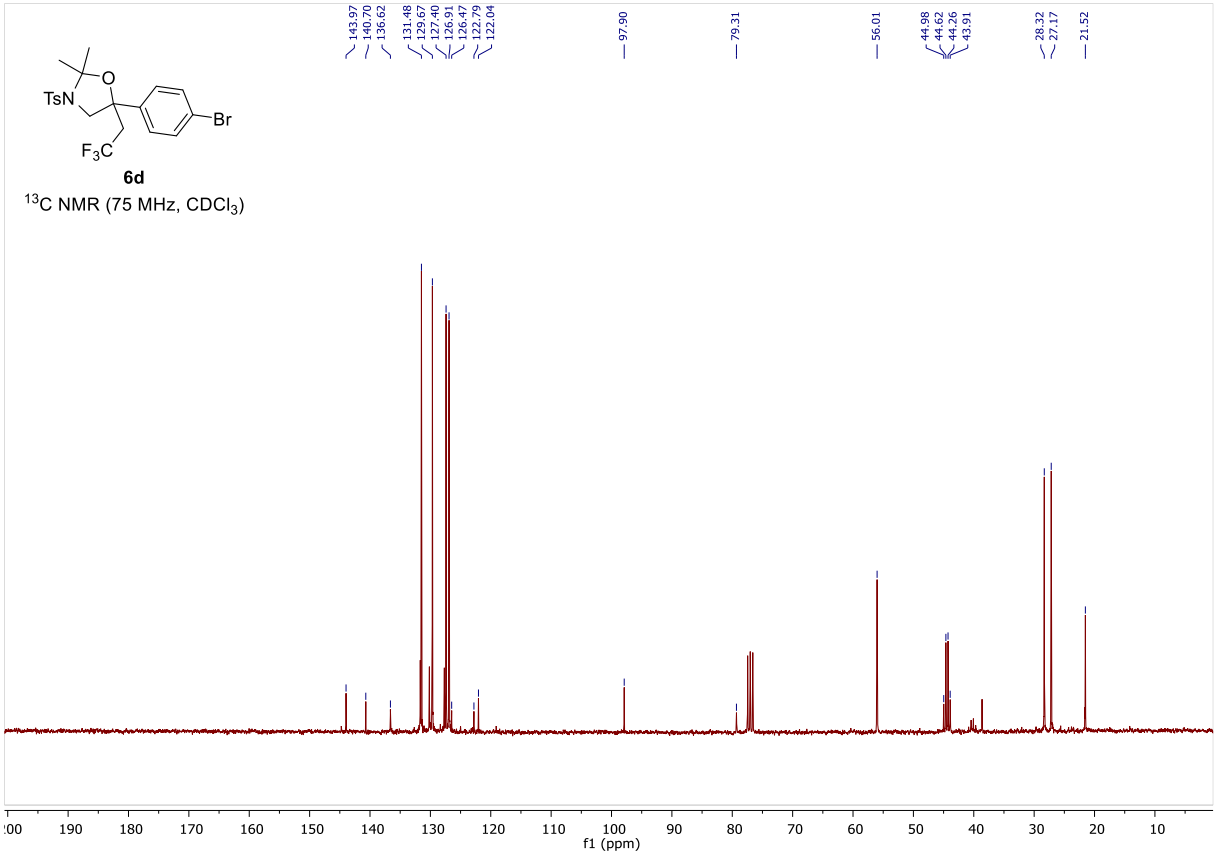
^{19}F NMR (282 MHz, $CDCl_3$)


TsN
O
Cl
F3C
6c
1H NMR (300 MHz, CDCl3)
7.60
7.57
7.21
7.20
7.18
7.18
7.17
7.15
7.14
7.14
7.12
7.12
7.11
7.10
3.69
2.67
2.65
2.64
2.62
2.60
2.60
2.58
2.57
2.55
2.55
2.54
2.52
2.50
2.48
2.35
1.64
1.32
2.00
6.19
2.00
2.04
3.00
3.00
3.00
f1 (ppm)


TsN
O
Cl
F3C
6c
13C NMR (75 MHz, CDCl3)
143.96
140.14
136.63
133.91
129.66
128.52
127.41
126.59
126.50
122.80
97.89
79.27
56.05
45.03
44.68
44.32
43.96
28.31
27.19
21.50
f1 (ppm)

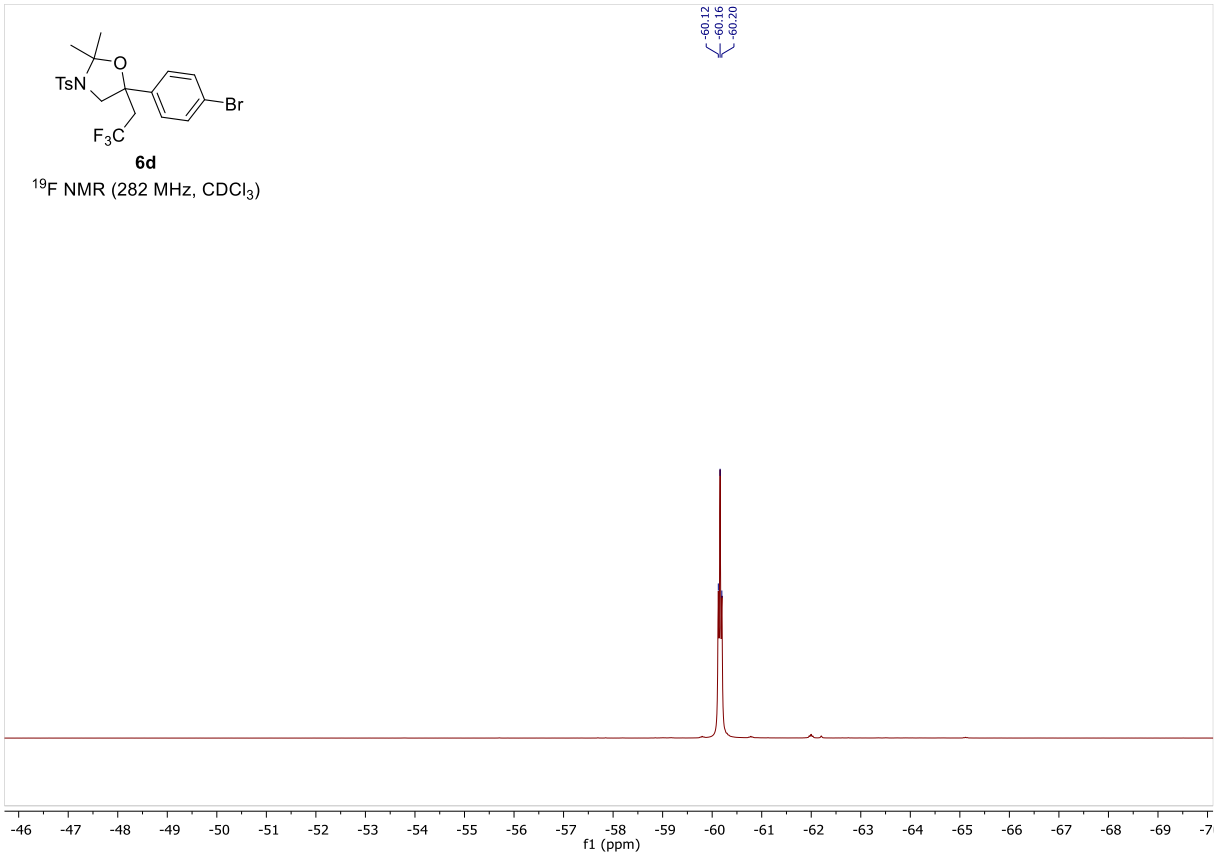

-60.15
-60.18
-60.22
TsN
O
Cl
F3C
6c
19F NMR (282 MHz, CDCl3)
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -7
f1 (ppm)


7.63
7.60
7.39
7.36
7.24
7.21
7.12
7.09
3.73
2.70
2.69
2.67
2.65
2.64
2.63
2.62
2.60
2.59
2.58
2.57
2.55
2.53
2.52
2.39
1.67
1.36
TsN
O
Br
F3C
6d
1H NMR (300 MHz, CDCl3)
2.02
1.98
2.69
2.01
2.01
2.10
3.34
3.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



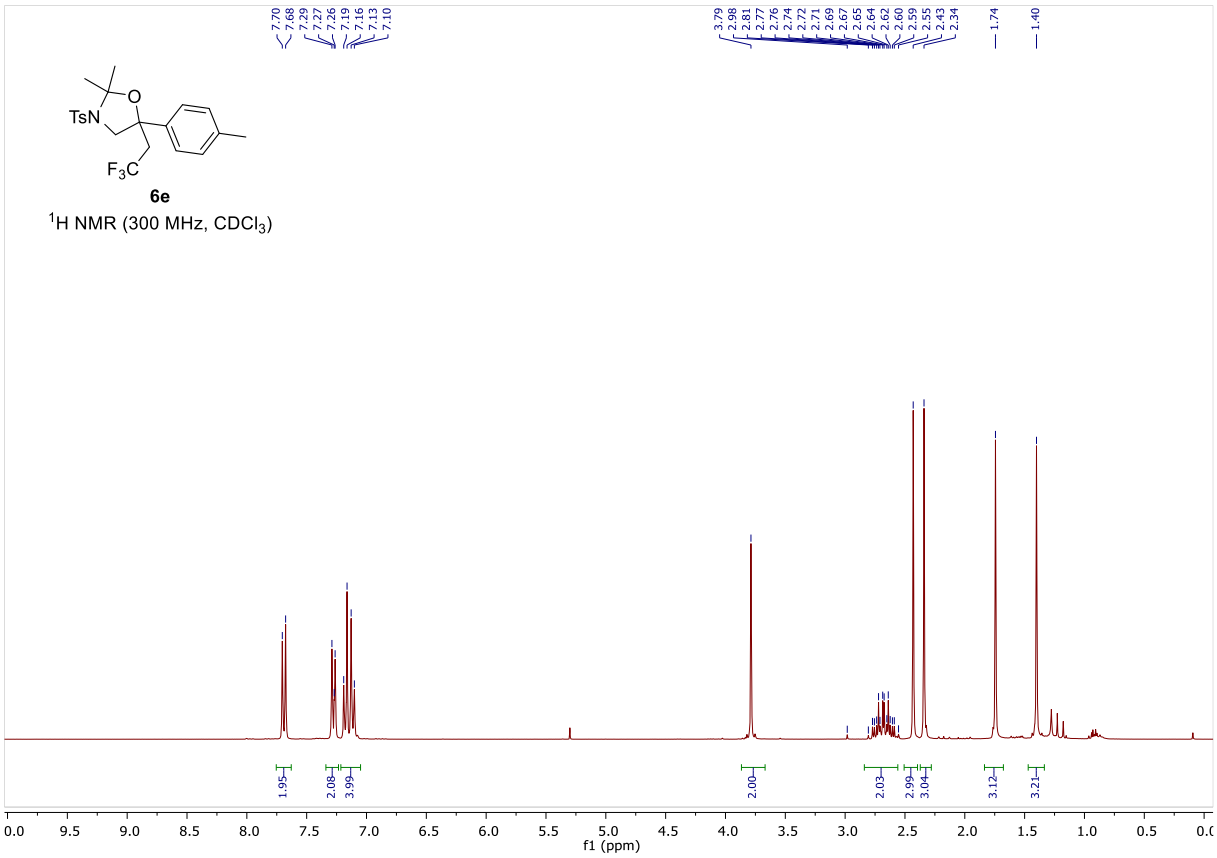
6d

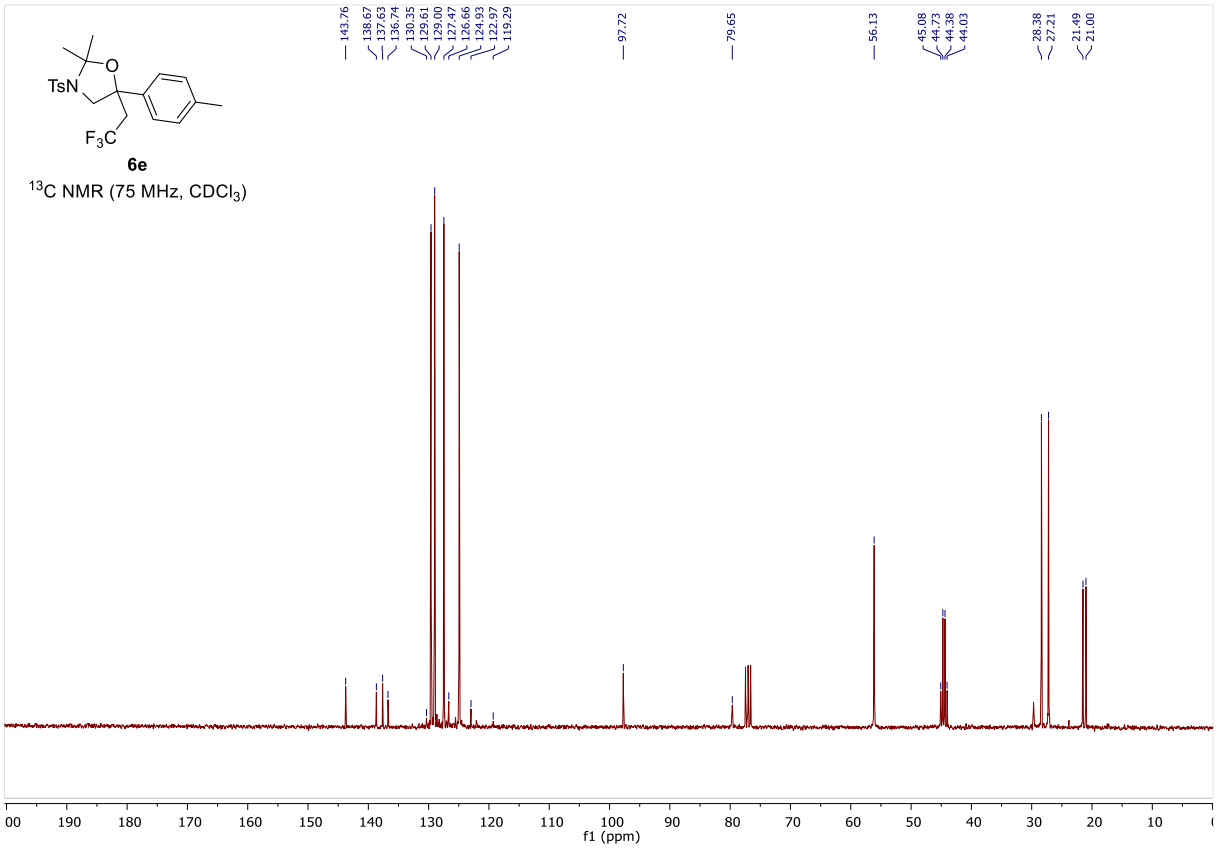
^{13}C NMR (75 MHz, $CDCl_3$)

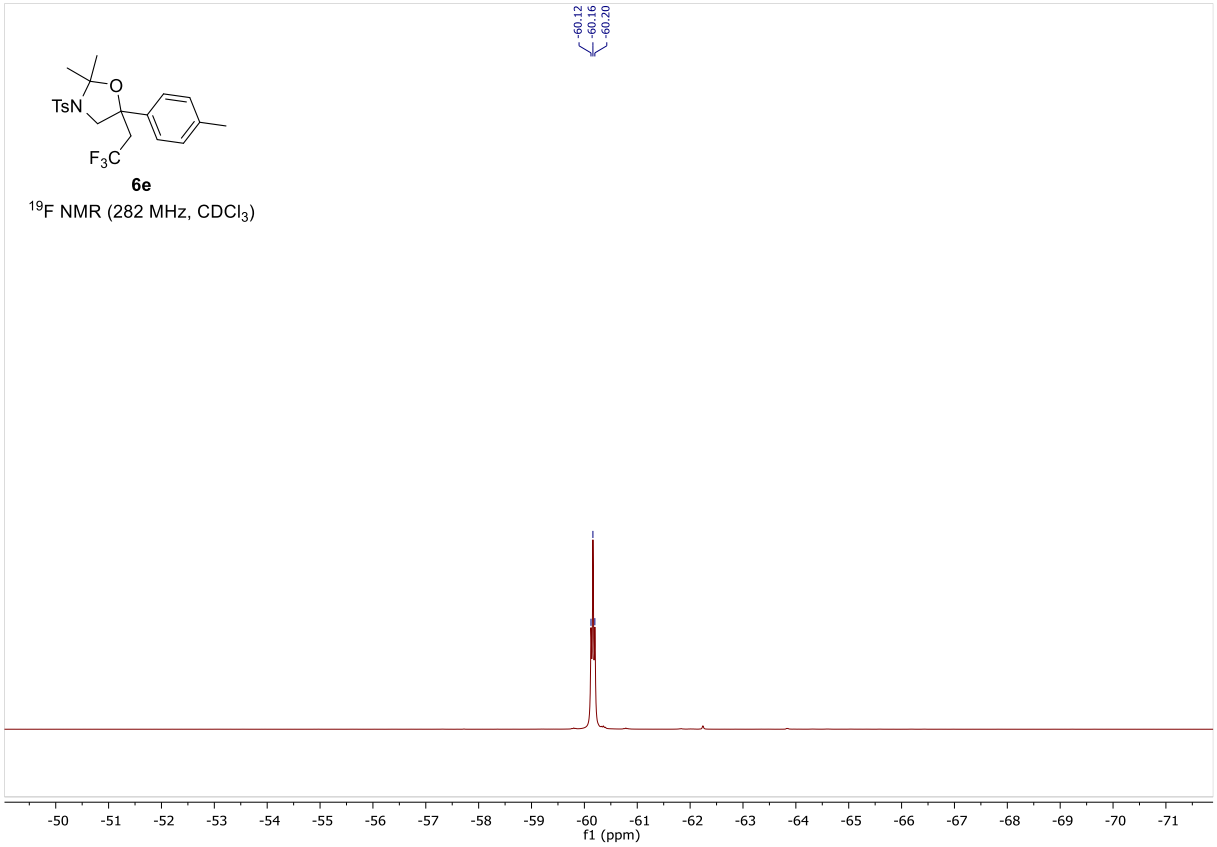


6d

^{19}F NMR (282 MHz, $CDCl_3$)

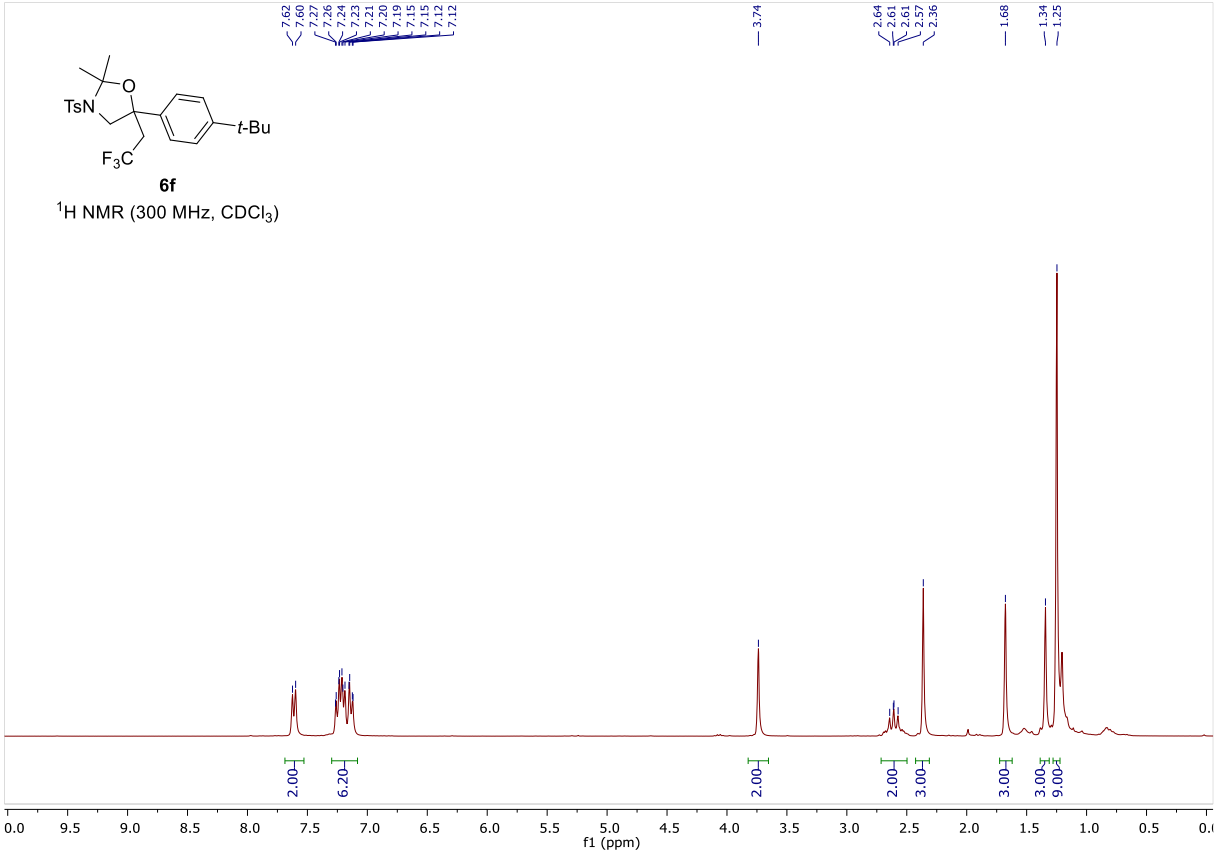

7.70
7.68
7.29
7.27
7.26
7.19
7.16
7.13
7.10
3.79
2.98
2.81
2.77
2.76
2.74
2.72
2.71
2.69
2.67
2.65
2.64
2.62
2.60
2.59
2.55
2.43
2.34
1.74
1.40
TsN
O
F3C
6e
1H NMR (300 MHz, CDCl3)
1.95
2.08
3.99
2.00
2.03
2.99
3.04
3.12
3.21
f1 (ppm)


143.76
138.67
137.63
136.74
130.35
129.61
129.00
127.47
126.66
124.93
122.97
119.29
97.72
79.65
56.13
45.08
44.73
44.38
44.03
28.38
27.21
21.49
21.00
TsN
O
F3C
6e
13C NMR (75 MHz, CDCl3)
f1 (ppm)



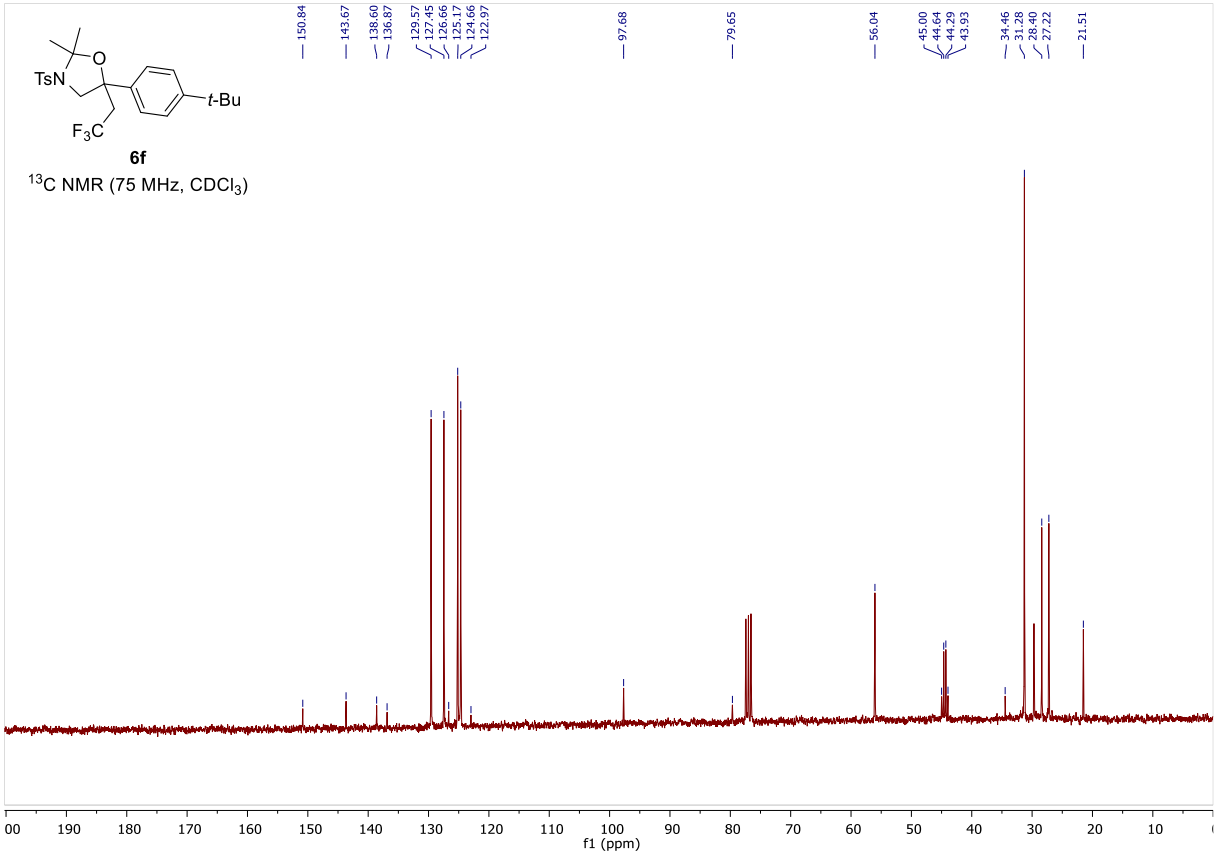
6e

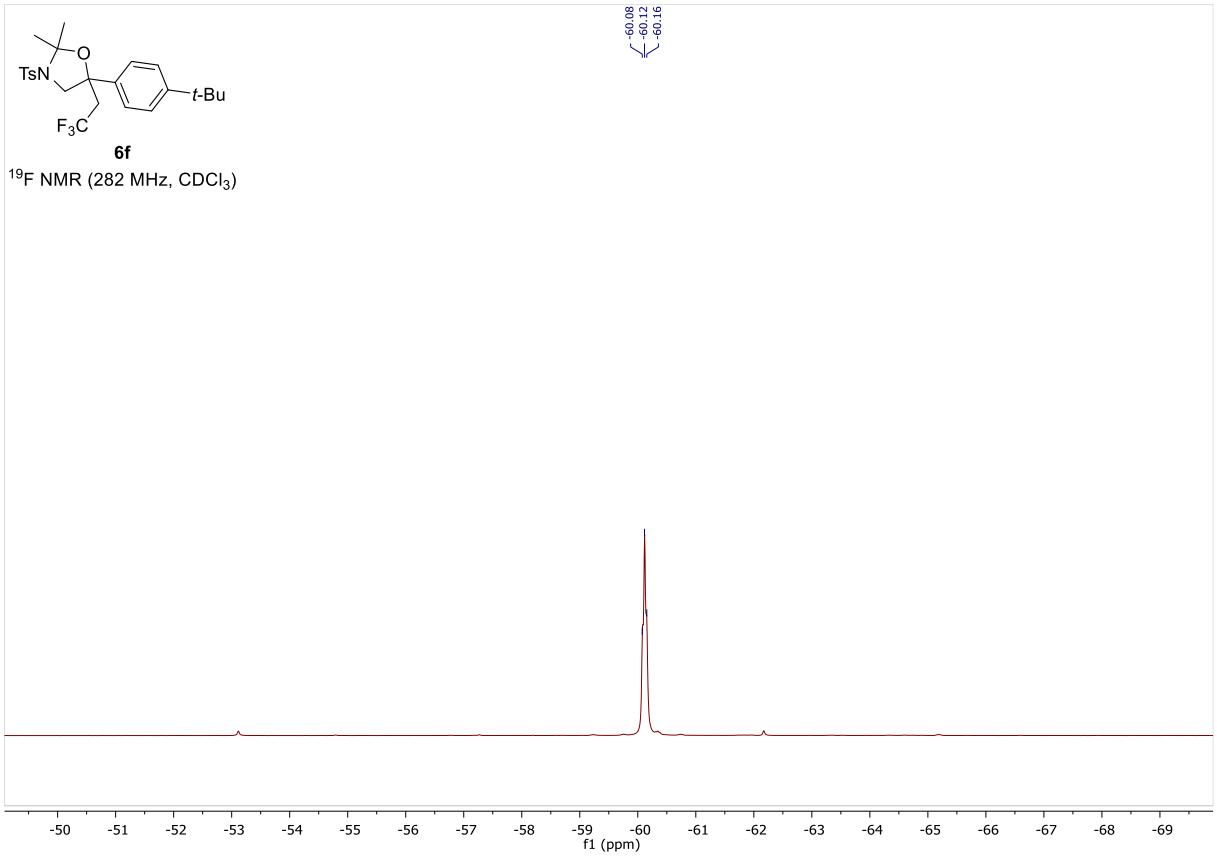
^{19}F NMR (282 MHz, $CDCl_3$)

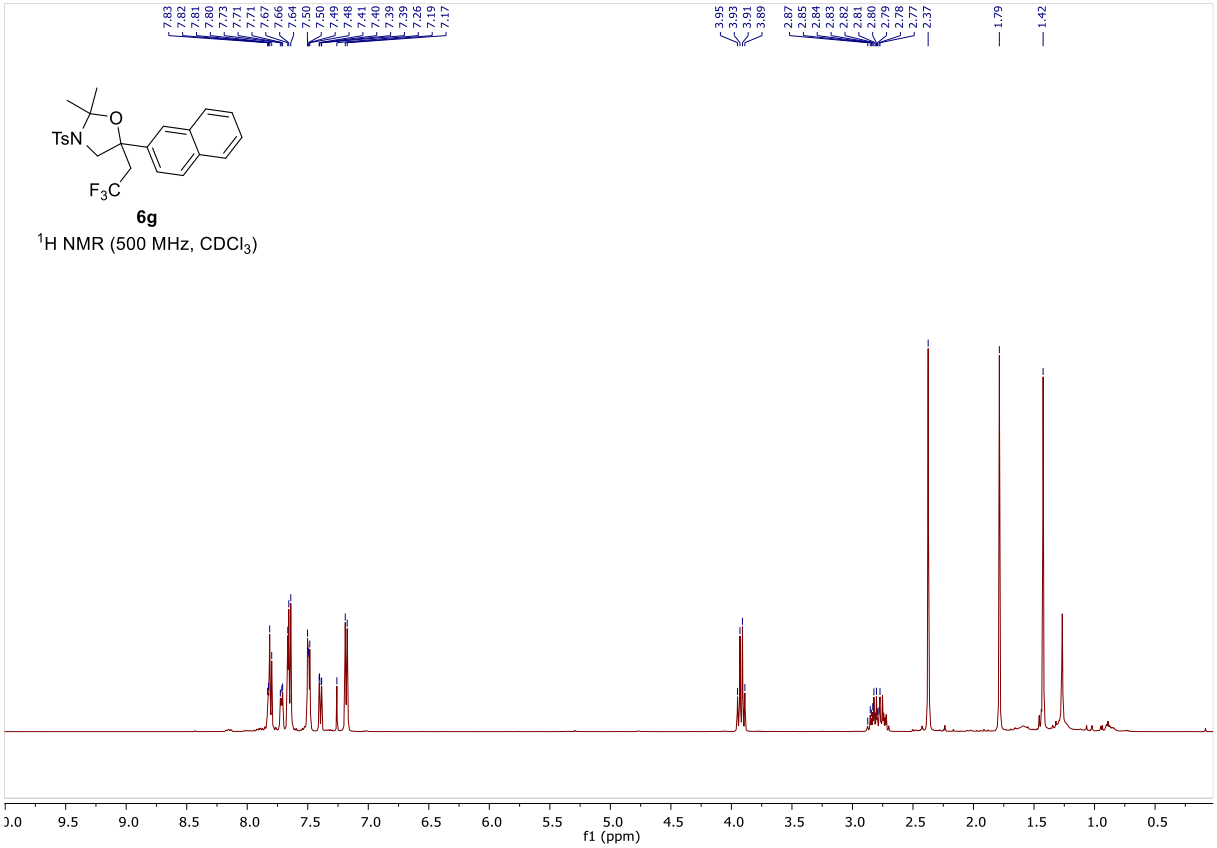


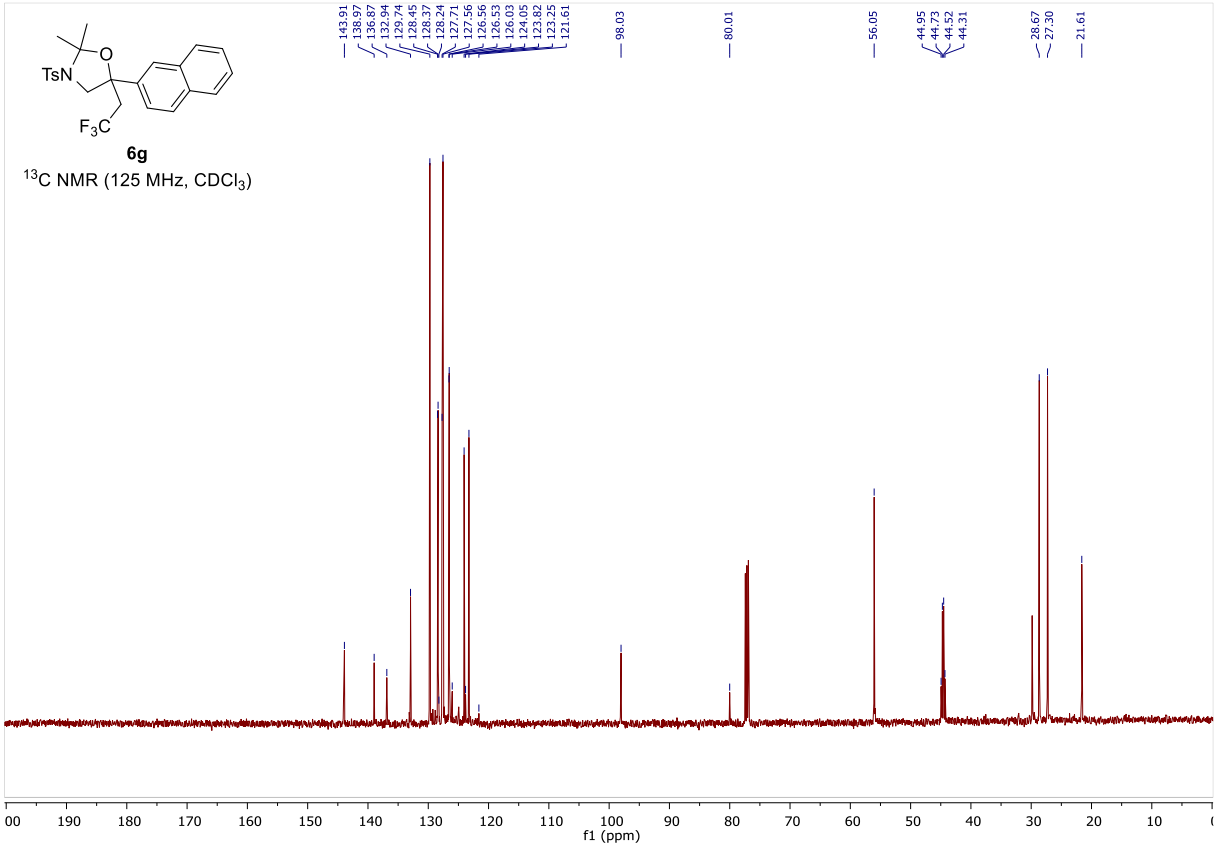
6f

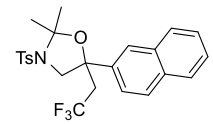
^{1}H NMR (300 MHz, $CDCl_3$)


TsN
O
t-Bu
F3C
6f
13C NMR (75 MHz, CDCl3)
150.84
143.67
138.60
136.87
129.57
127.45
126.66
125.17
124.66
122.97
97.68
79.65
56.04
45.00
44.64
44.29
43.93
34.46
31.28
28.40
27.22
21.51
f1 (ppm)


TsN
O
t-Bu
F3C
6f
19F NMR (282 MHz, CDCl3)
-60.08
-60.12
-60.16
f1 (ppm)

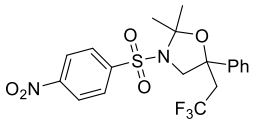

7.83
7.82
7.81
7.80
7.73
7.71
7.71
7.67
7.66
7.64
7.50
7.50
7.49
7.48
7.41
7.40
7.39
7.39
7.26
7.19
7.17
3.95
3.93
3.91
3.89
2.87
2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.78
2.77
2.37
1.79
1.42
TsN
O
F3C
6g
1H NMR (500 MHz, CDCl3)
f1 (ppm)


143.91
138.97
136.87
132.94
129.74
128.45
128.37
128.24
127.71
127.56
126.56
126.53
126.03
124.05
123.82
123.25
121.61
98.03
80.01
56.05
44.95
44.73
44.52
44.31
28.67
27.30
21.61
TsN
O
F3C
6g
13C NMR (125 MHz, CDCl3)
f1 (ppm)



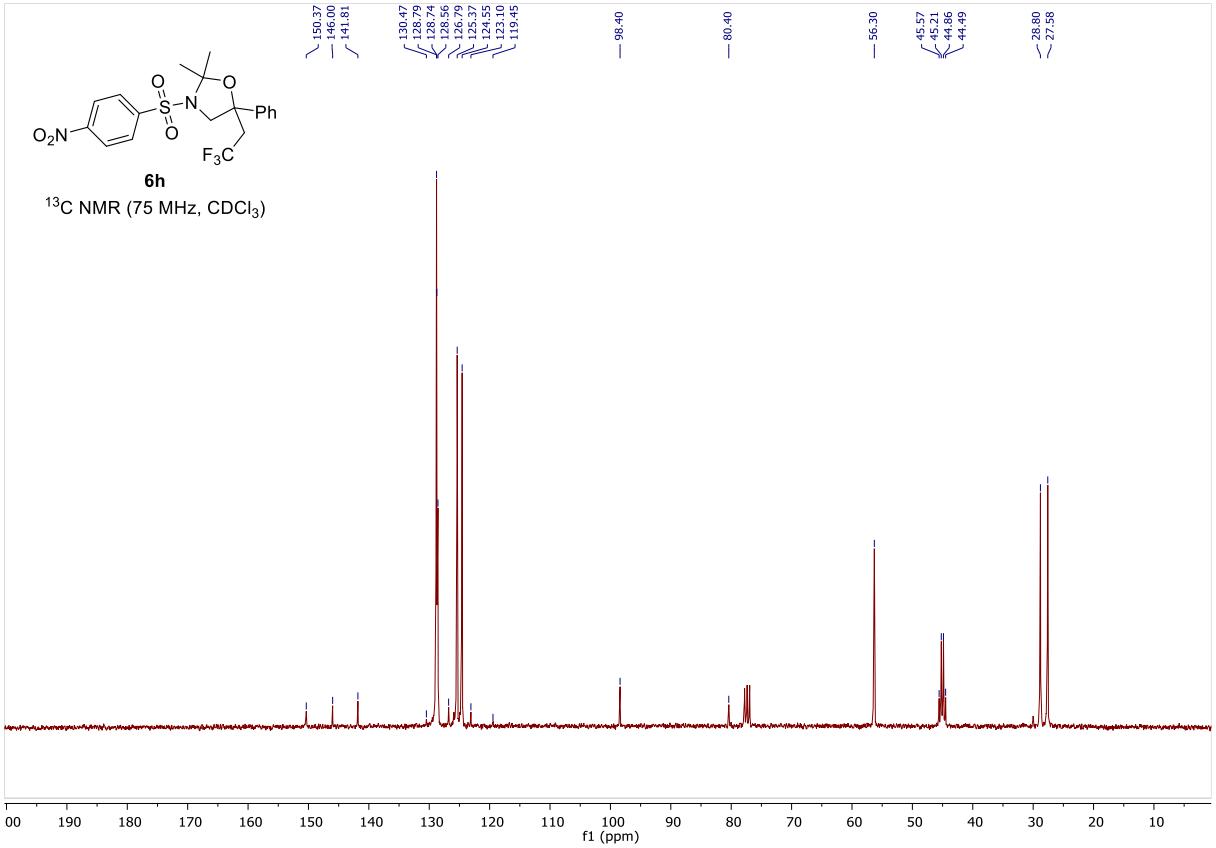
6g

^{19}F NMR (282 MHz, $CDCl_3$)



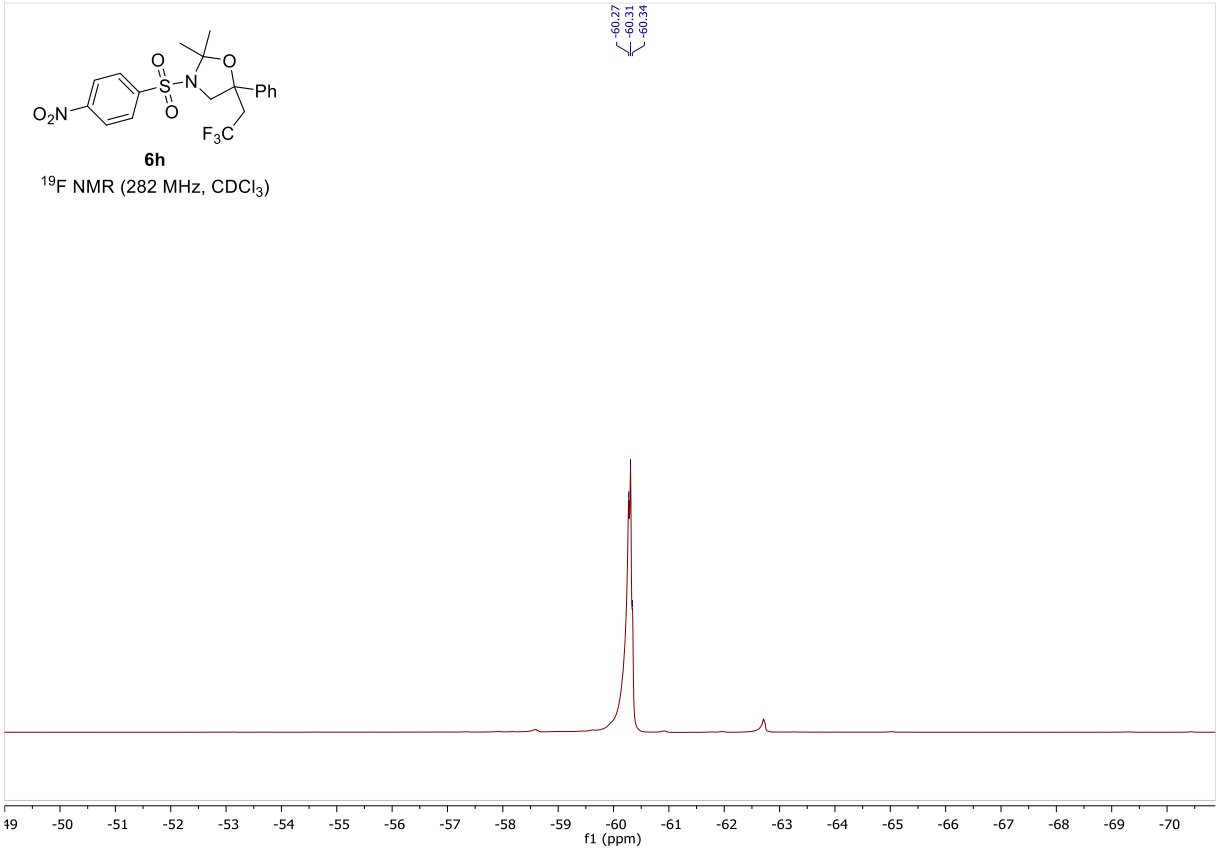
6h

^{1}H NMR (300 MHz, $CDCl_3$)



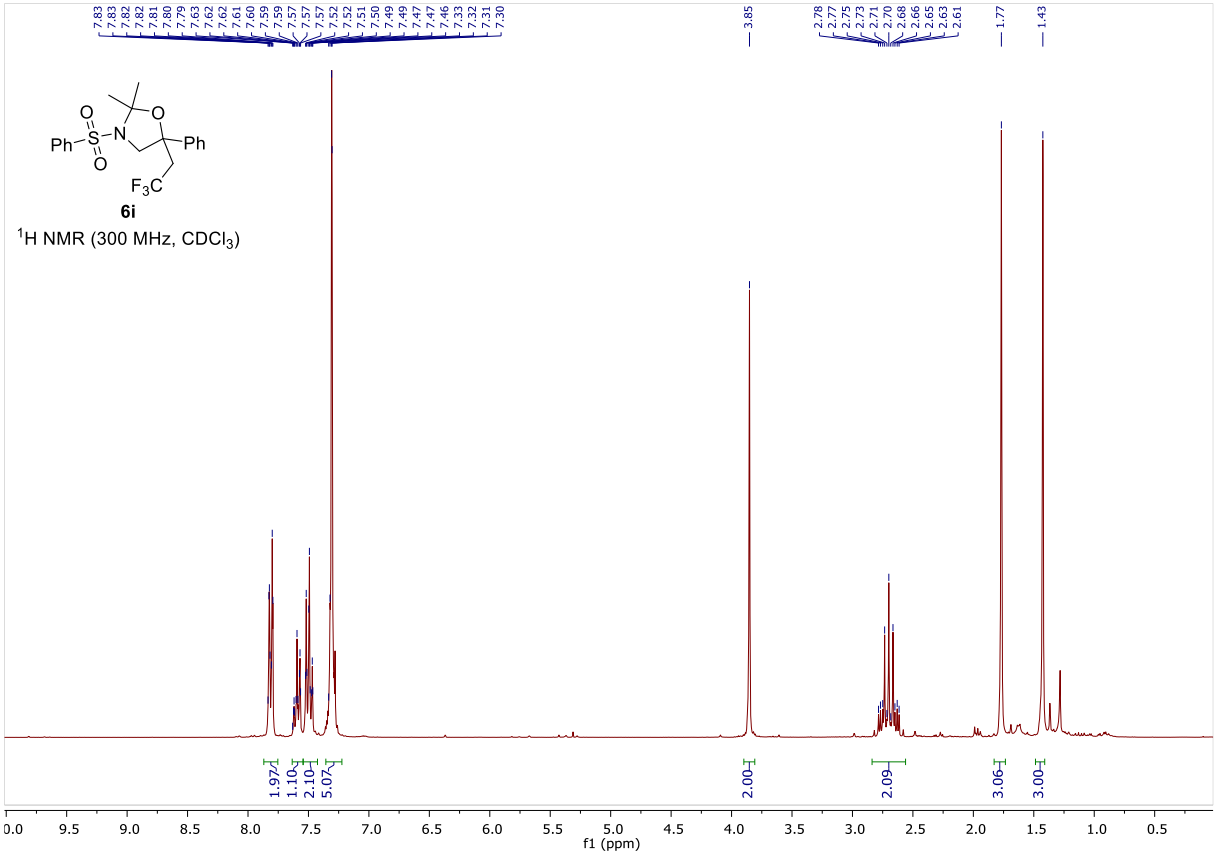
6h

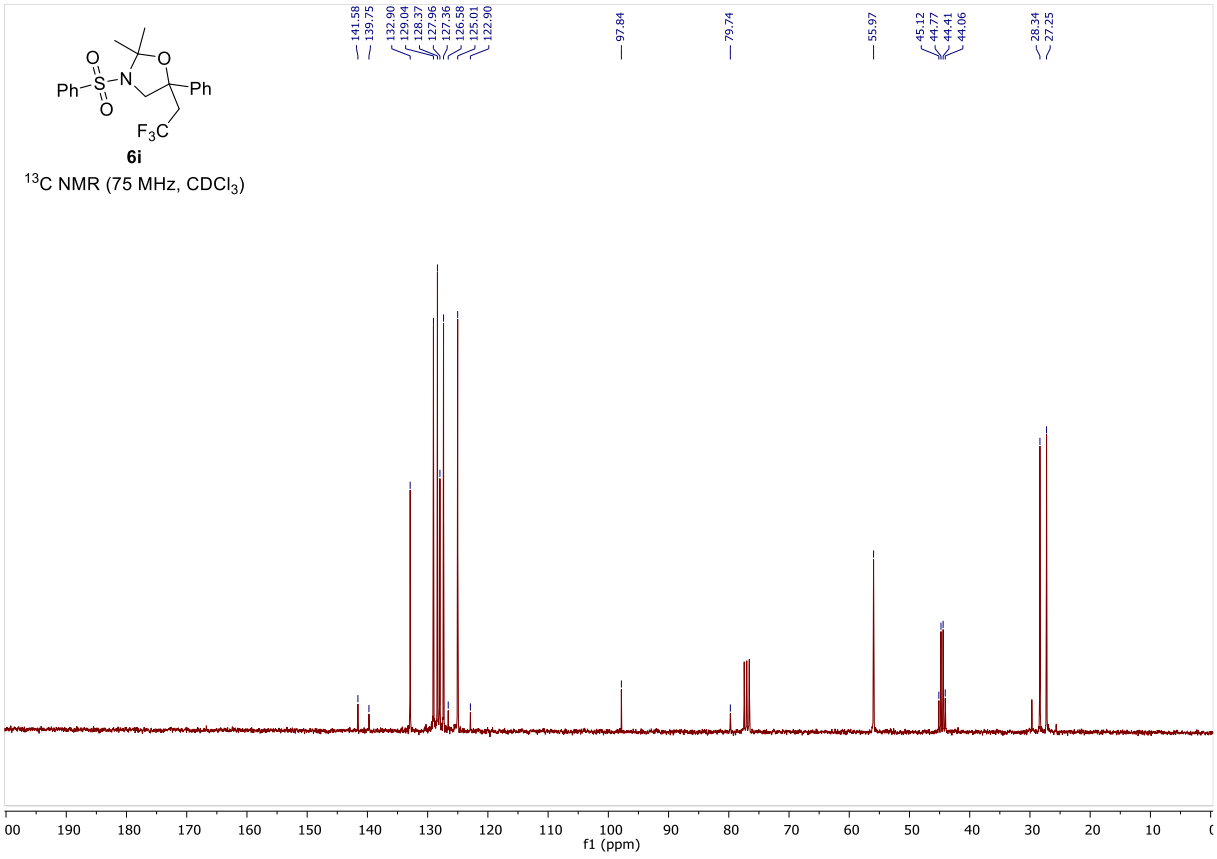
^{13}C NMR (75 MHz, $CDCl_3$)

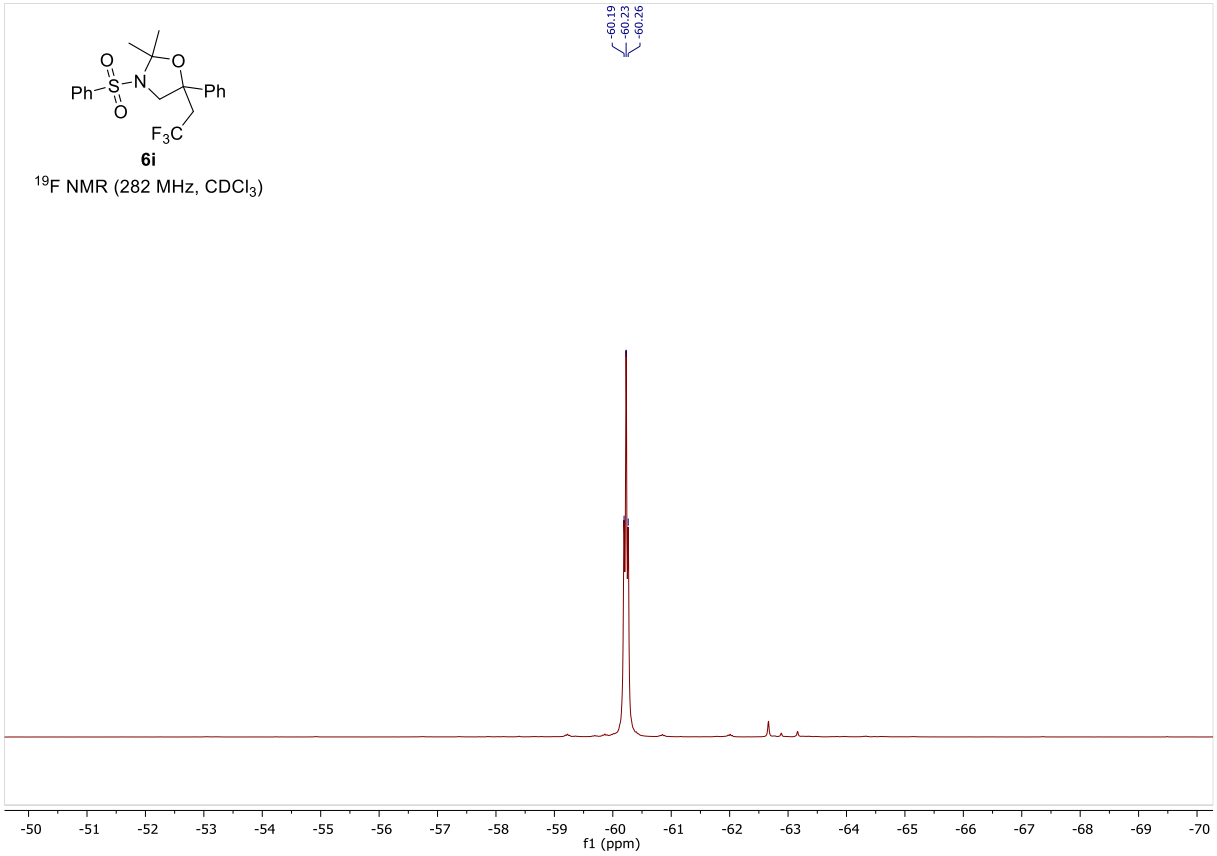


6h

^{19}F NMR (282 MHz, $CDCl_3$)

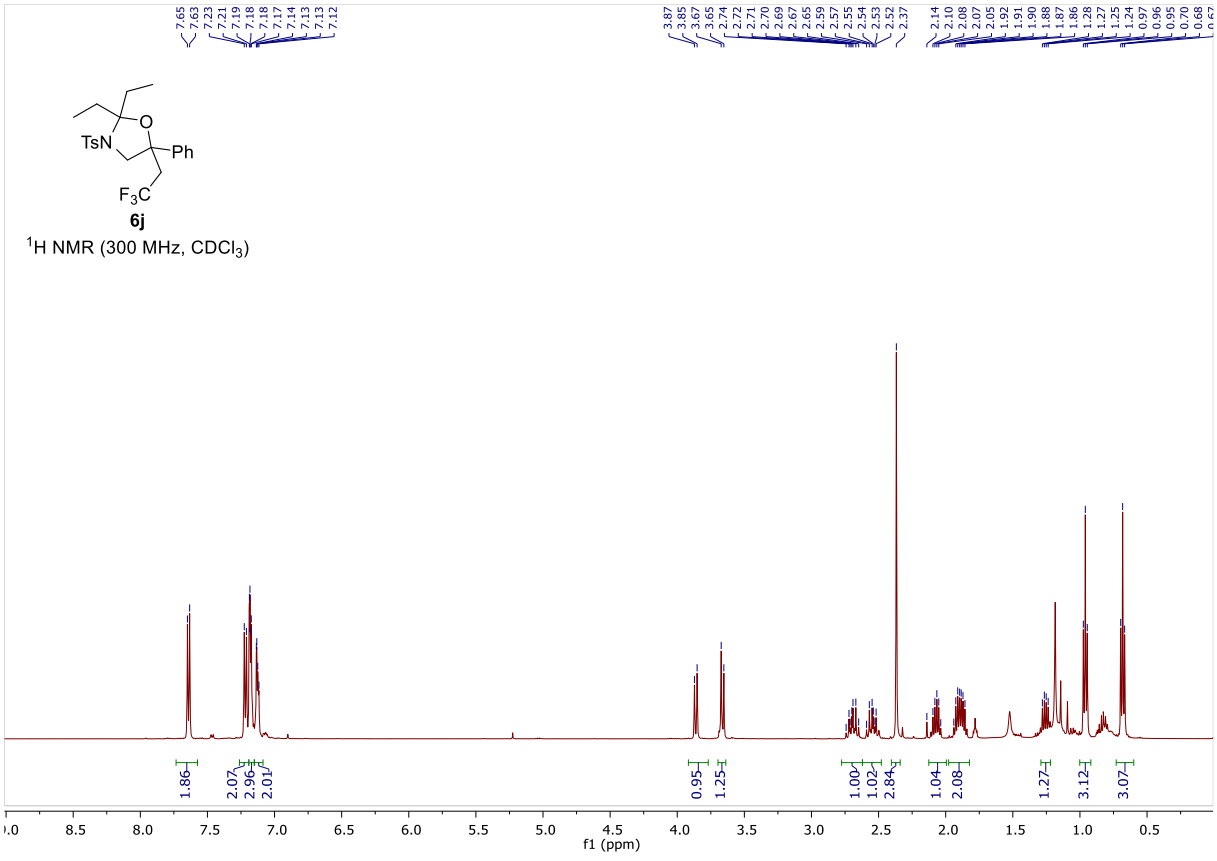

7.83 7.83 7.82 7.82 7.81 7.80 7.79 7.63 7.62 7.62 7.61 7.60 7.59 7.59 7.57 7.57 7.57 7.52 7.52 7.51 7.50 7.49 7.49 7.47 7.47 7.46 7.33 7.32 7.31 7.30
3.85
2.78 2.77 2.75 2.73 2.71 2.70 2.68 2.66 2.65 2.63 2.61
1.77
1.43
O
O
Ph
S
N
Ph
O
F3C
6i
1H NMR (300 MHz, CDCl3)
1.97
1.10
2.10
5.07
2.00
2.09
3.06
3.00
f1 (ppm)


141.58
139.75
132.90
129.04
128.37
127.96
127.36
126.58
125.01
122.90
97.84
79.74
55.97
45.12
44.77
44.41
44.06
28.34
27.25
O
O
Ph
S
N
Ph
O
F3C
6i
13C NMR (75 MHz, CDCl3)
f1 (ppm)



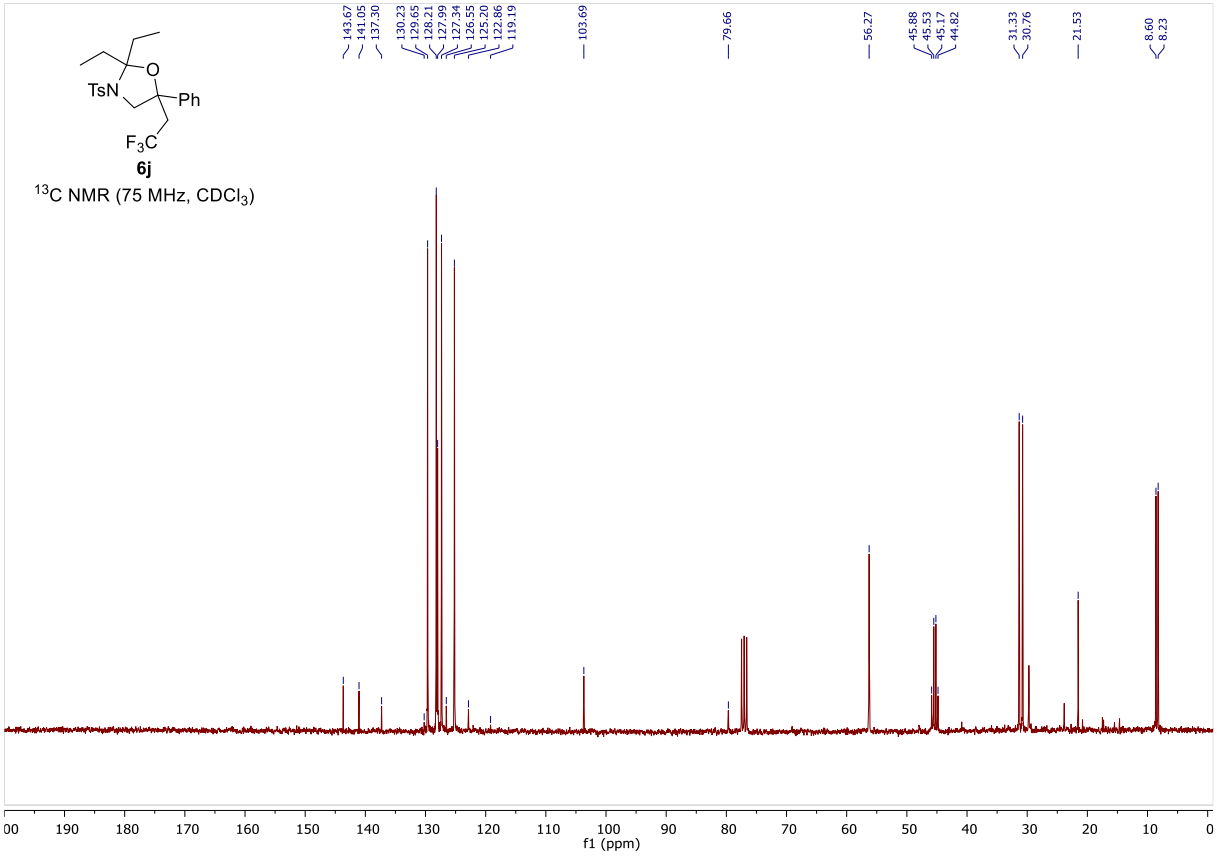
6i

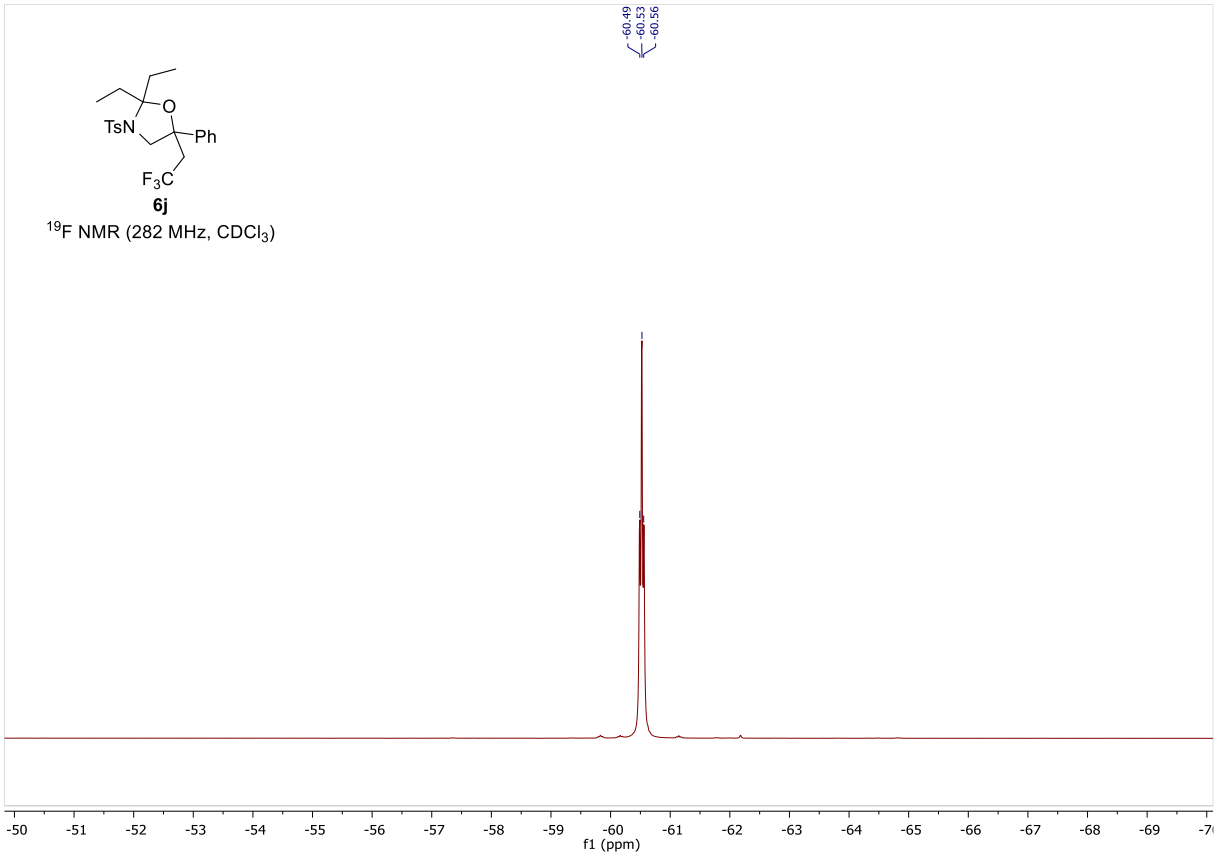
^{19}F NMR (282 MHz, $CDCl_3$)

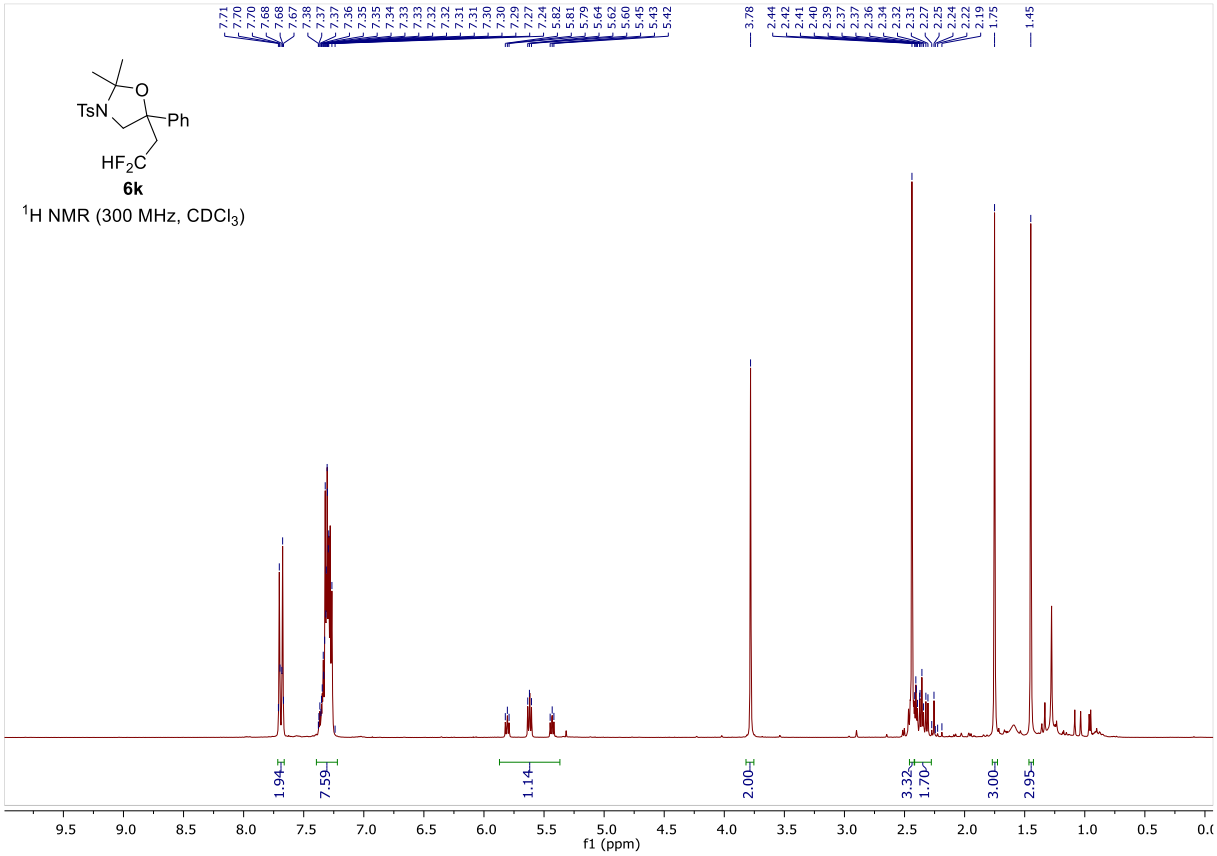


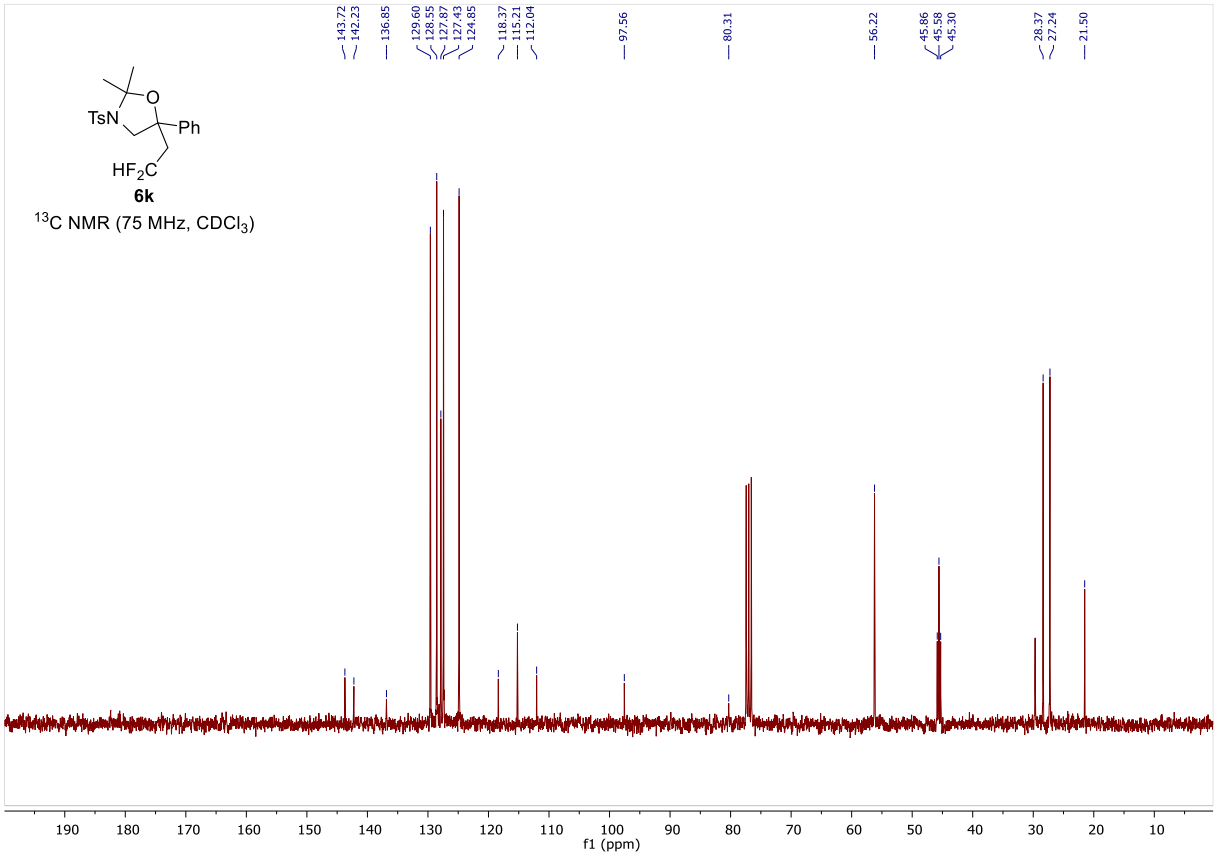
6j

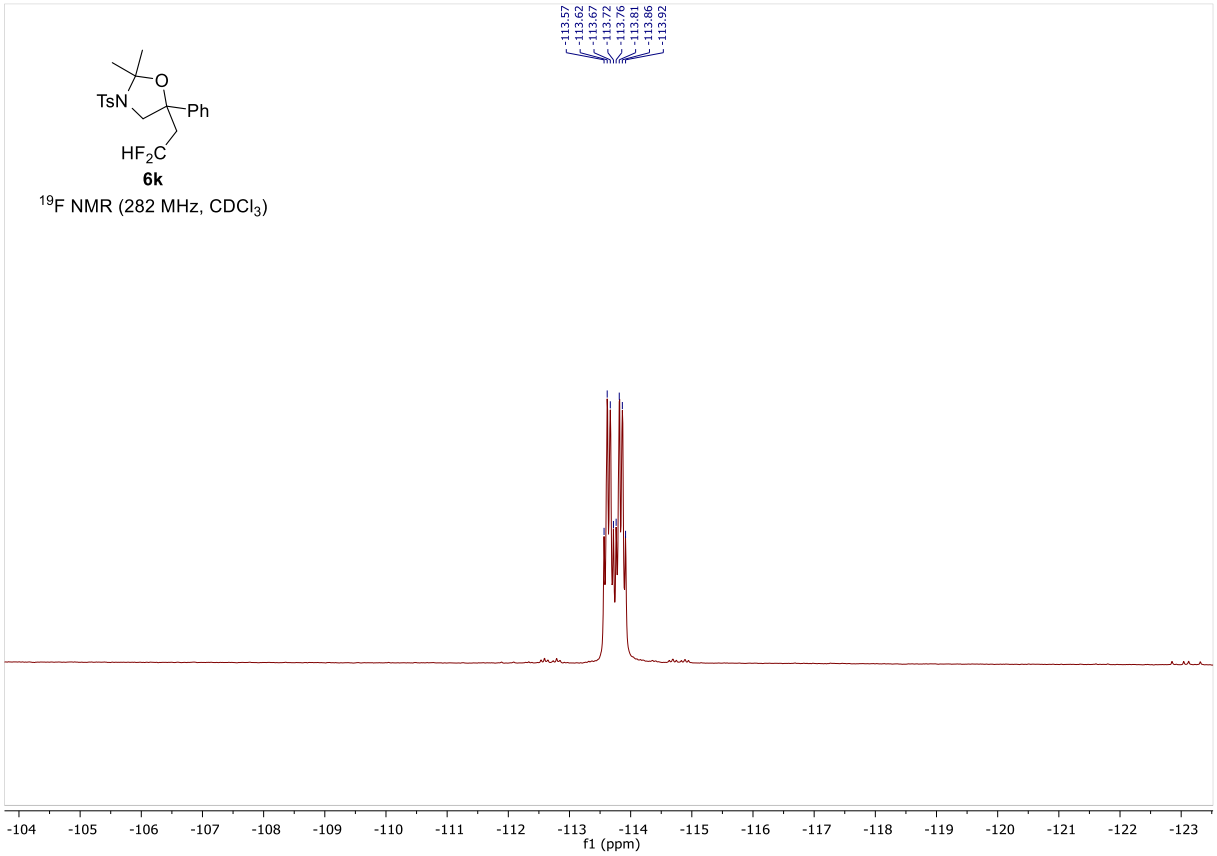
^{1}H NMR (300 MHz, $CDCl_3$)


143.67
141.05
137.30
130.23
129.65
128.21
127.99
127.34
126.55
125.20
122.86
119.19
103.69
79.66
56.27
45.88
45.53
45.17
44.82
31.33
30.76
21.53
8.60
8.23
TsN
O
Ph
F3C
6j
13C NMR (75 MHz, CDCl3)
f1 (ppm)


-60.49
-60.53
-60.56
TsN
O
Ph
F3C
6j
19F NMR (282 MHz, CDCl3)
f1 (ppm)

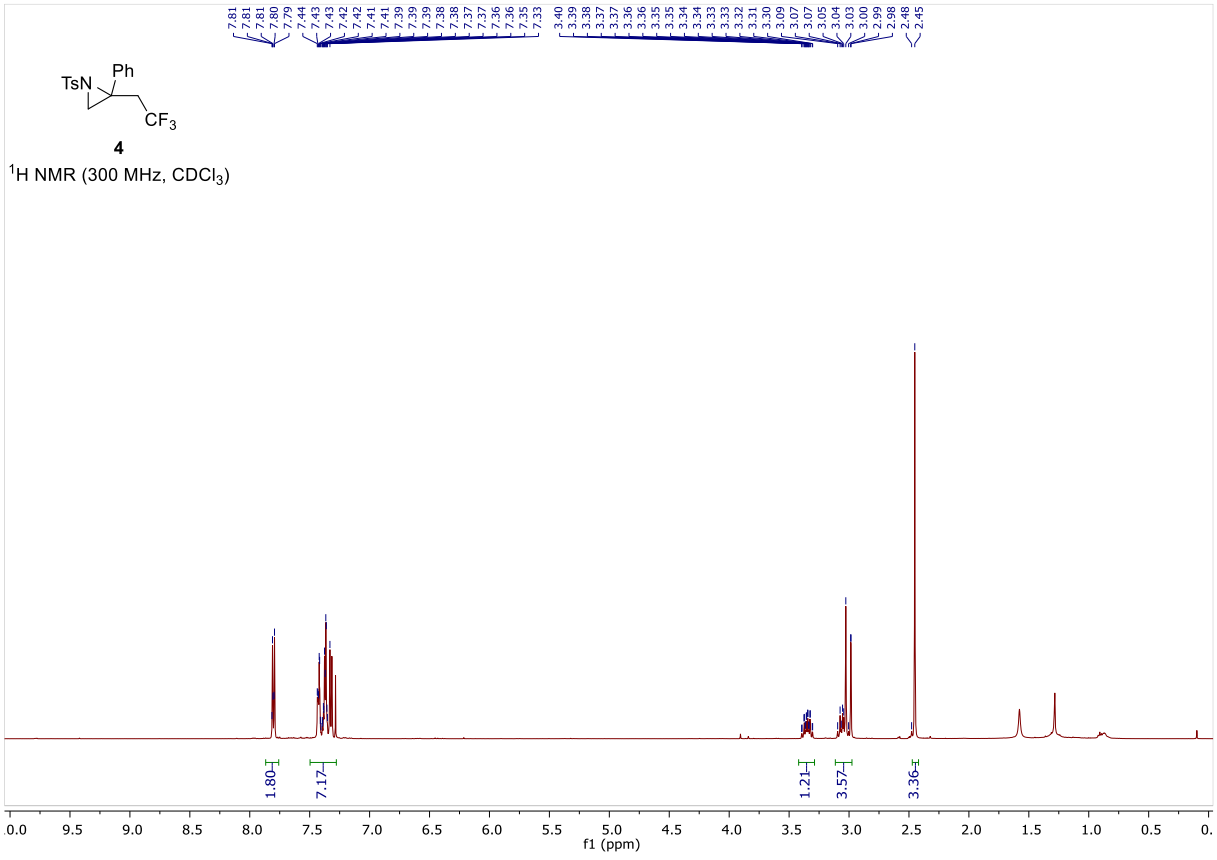

TsN
O
Ph
HF2C
6k
1H NMR (300 MHz, CDCl3)
f1 (ppm)


TsN
O
Ph
HF2C
6k
13C NMR (75 MHz, CDCl3)
f1 (ppm)



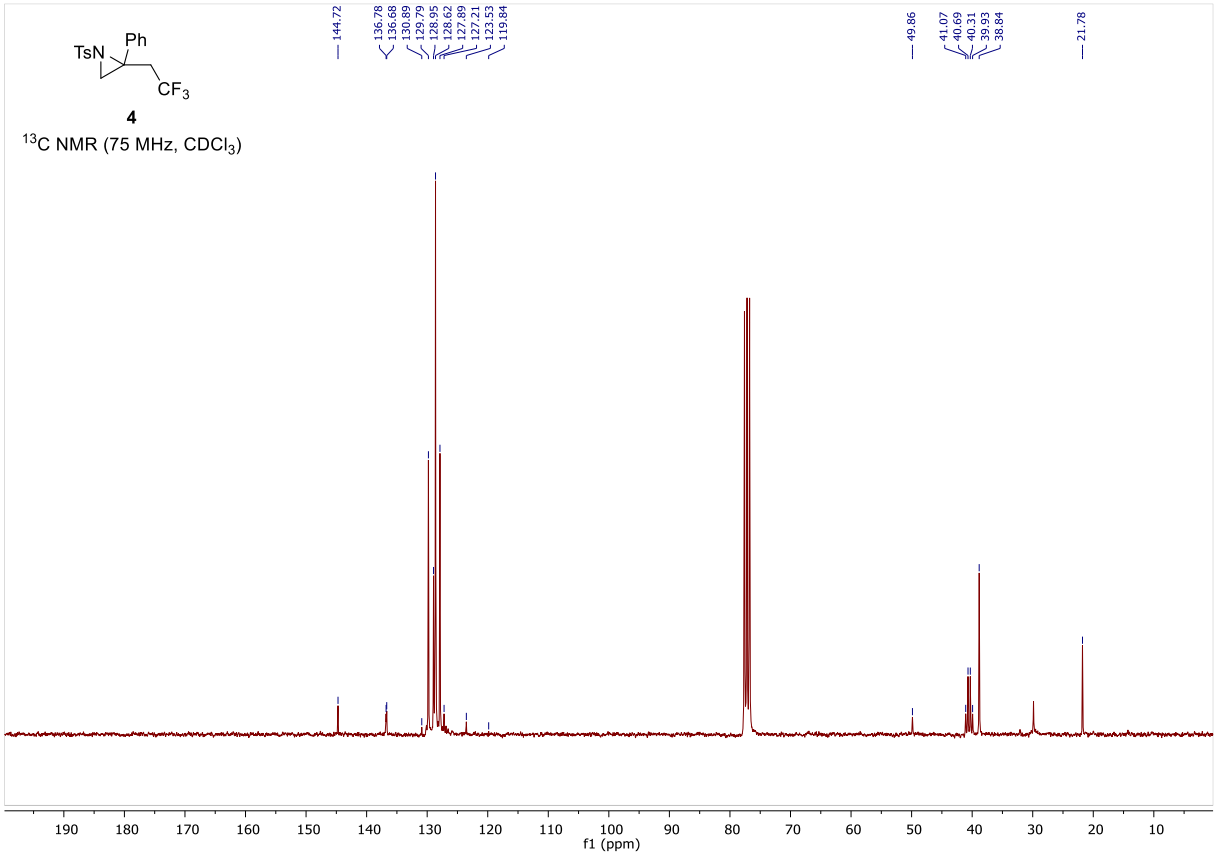
6k

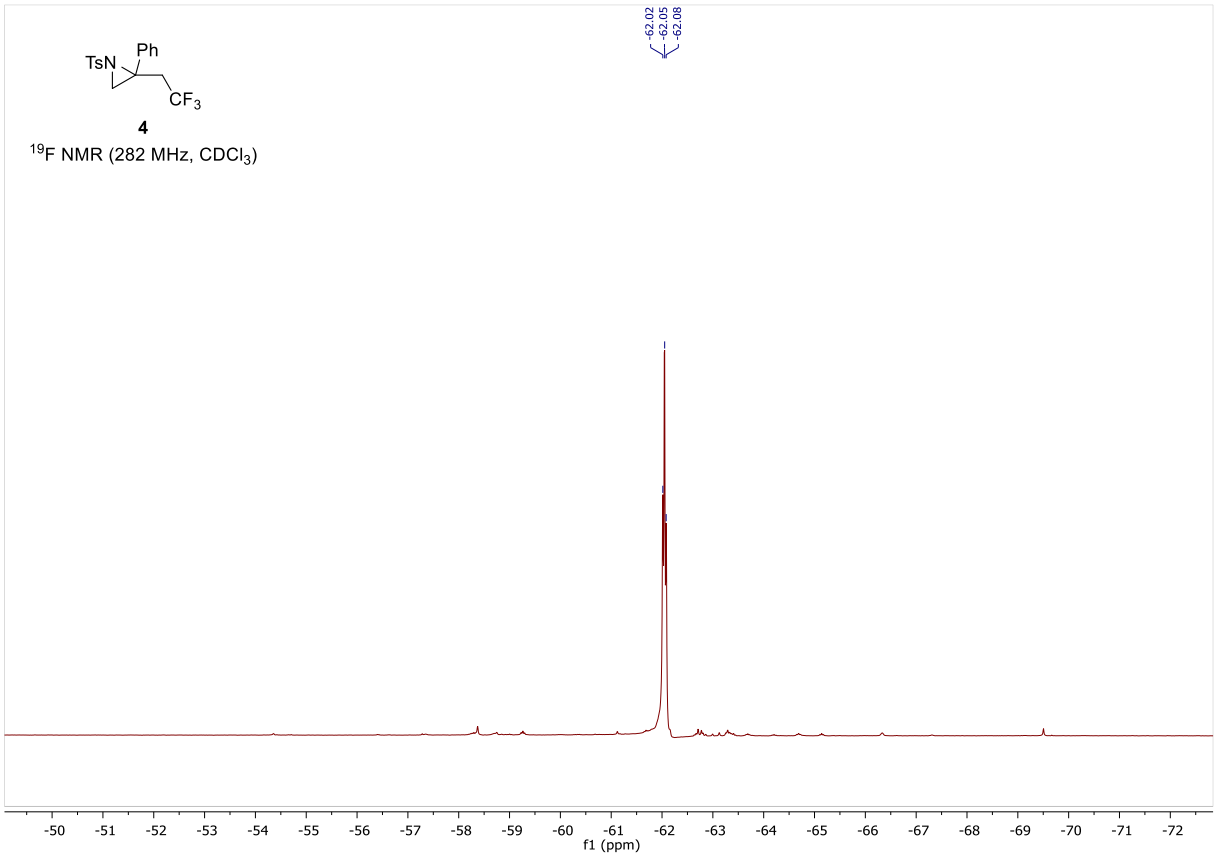
^{19}F NMR (282 MHz, $CDCl_3$)

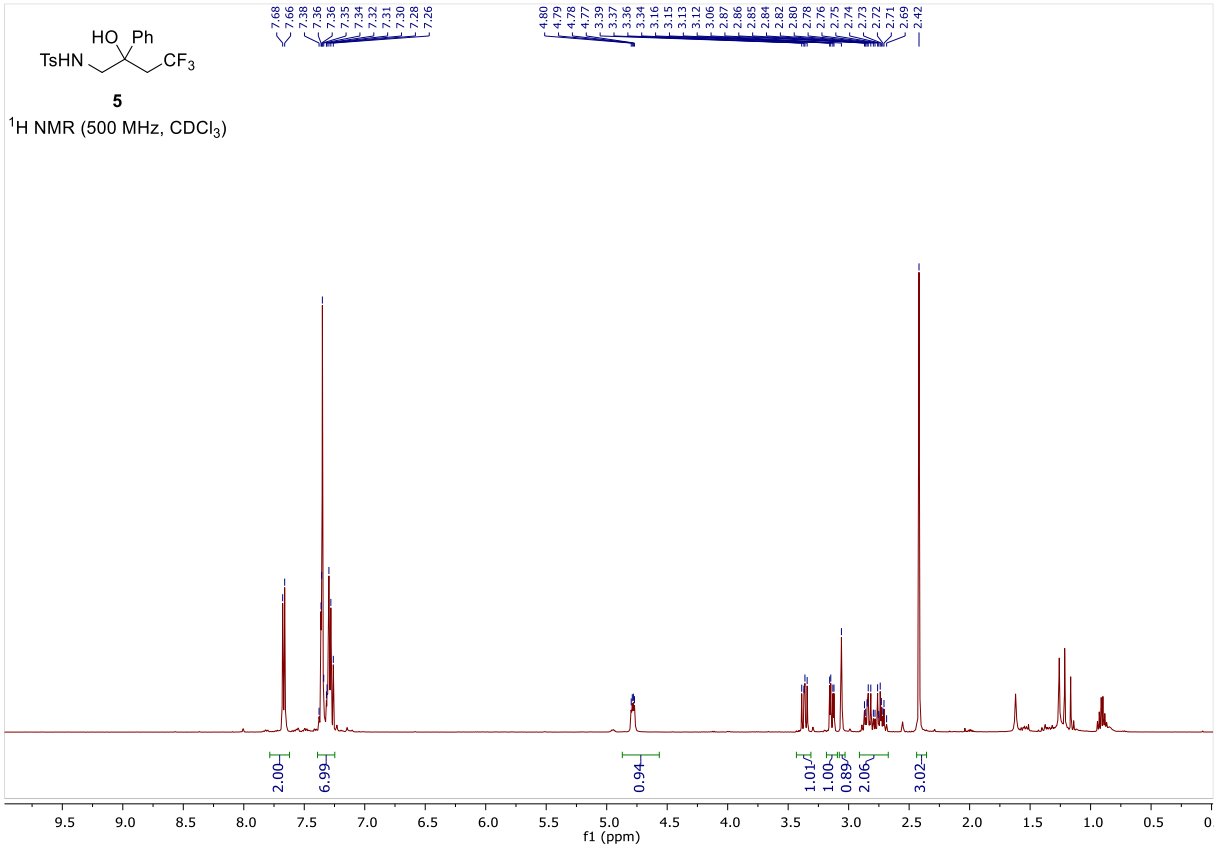


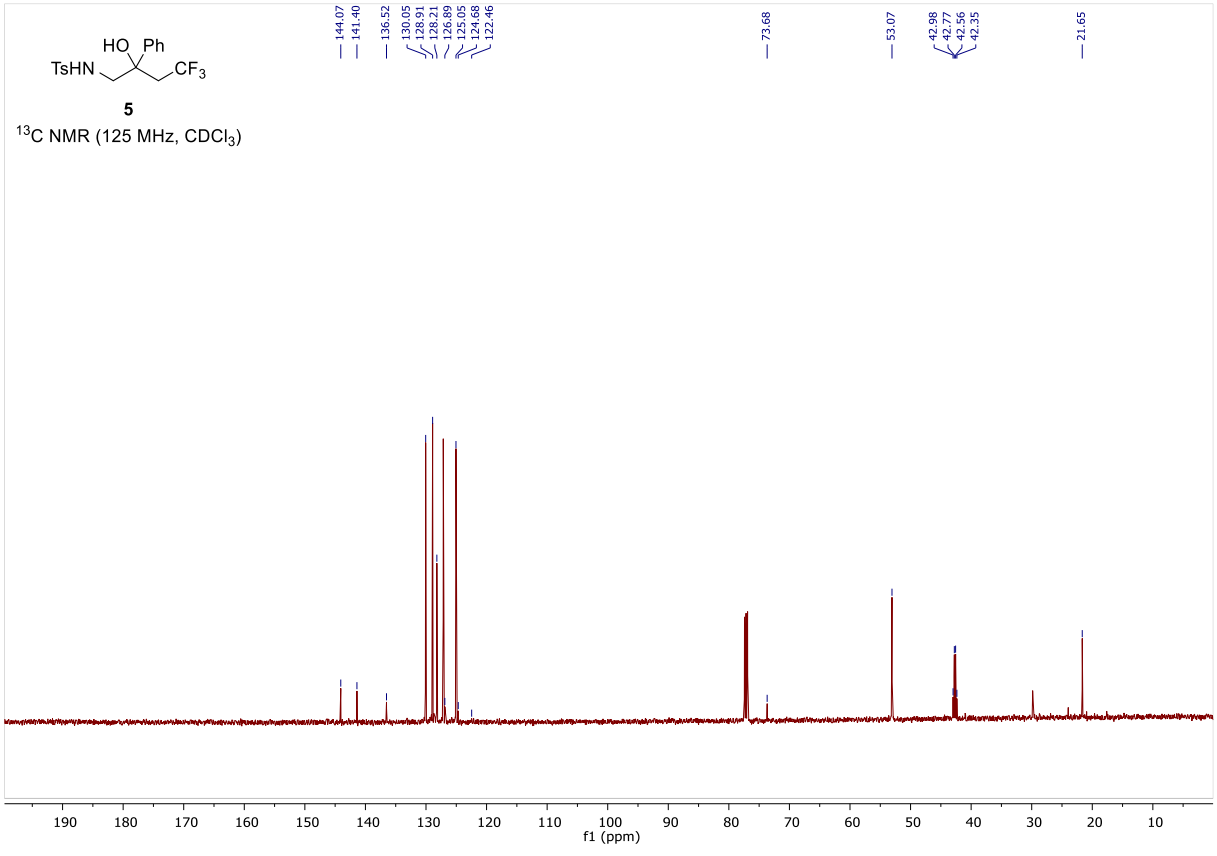
4

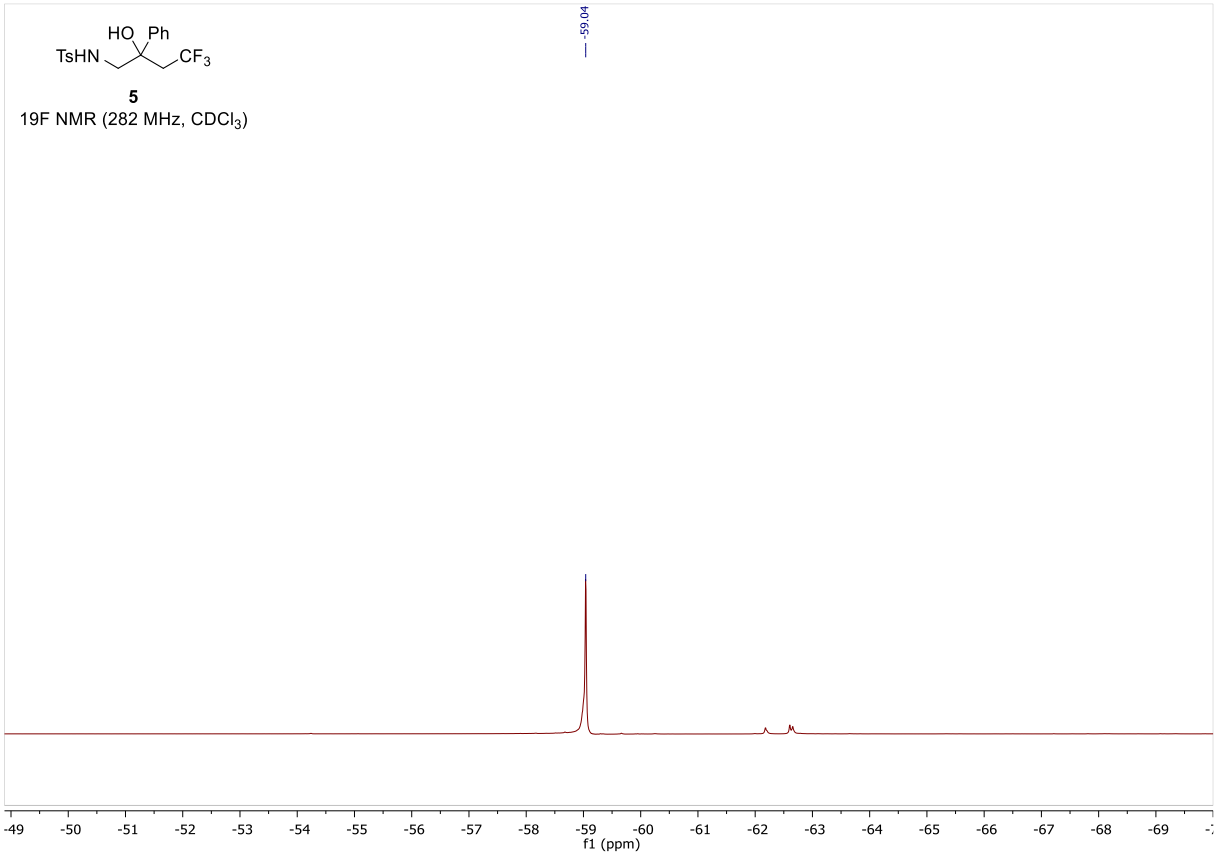
^{1}H NMR (300 MHz, $CDCl_3$)


TsN
Ph
CF3
4
13C NMR (75 MHz, CDCl3)
144.72
136.78
136.68
130.89
129.79
128.95
128.62
127.89
127.21
123.53
119.84
49.86
41.07
40.69
40.31
39.93
38.84
21.78
f1 (ppm)


TsN
Ph
CF3
4
19F NMR (282 MHz, CDCl3)
-62.02
-62.05
-62.08
f1 (ppm)


HO Ph
TsHN CF3
5
1H NMR (500 MHz, CDCl3)
7.68
7.66
7.38
7.36
7.36
7.35
7.34
7.32
7.31
7.30
7.28
7.26
4.80
4.79
4.78
4.77
4.39
3.37
3.36
3.34
3.16
3.15
3.13
3.12
3.06
2.87
2.86
2.85
2.84
2.82
2.80
2.78
2.76
2.75
2.74
2.73
2.72
2.71
2.69
2.42
2.00
6.99
0.94
1.01
1.00
0.89
2.06
3.02
f1 (ppm)


HO Ph
TsHN CF3
5
13C NMR (125 MHz, CDCl3)
144.07
141.40
136.52
130.05
128.91
128.21
126.89
125.05
124.68
122.46
73.68
53.07
42.98
42.77
42.56
42.35
21.65
f1 (ppm)



5

19F NMR (282 MHz, $CDCl_3$)