Supporting Information

N-Trifluoromethylation of Nitrosoarenes with Sodium Triflinate

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1. General Information

All reactions were carried out under air unless otherwise stated. Nitrosoarenes **1c**-**1n** were prepared according to literature procedures using commercial reagents (Section 2.1). All other starting materials and solvents were purchased from commercial suppliers and were used as received.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker 400 or 500 MHz spectrometer unless otherwise stated. Chemical shifts (δ) are reported in ppm with the following abbreviations used for the observed multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet for unresolved lines). ^{1}H NMR chemical shifts were referenced to the residual solvent signal for $CHCl_3$ (7.26 ppm) or DMSO (2.50 ppm), ^{13}C NMR chemical shifts were referenced to the solvent signal of $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) and ^{19}F NMR chemical shifts were referenced to the external standard α,α,α-trifluorotoluene (-63.72 ppm). Analytical TLC was performed on pre-coated silica plates. After elution, the plates were visualized by UV illumination at 254−360 nm, and by staining with ethanolic phosphomolybdic acid. Column chromatography was performed using Davisil 60Å silica (35-70 μm). LRMS data were recorded using EI technique. HRMS data were recorded on a micrOTOF instrument using ESI technique.

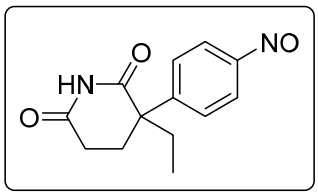
The regiochemistry of the products was established by analysis of the fragmentation pattern obtained from MS (EI) data and by NMR and HRMS analysis of the products obtained after reduction and acylation (sections 2.5 and 2.6).

2. Experimental Procedures and Spectral Data

2.1. Preparation of starting materials

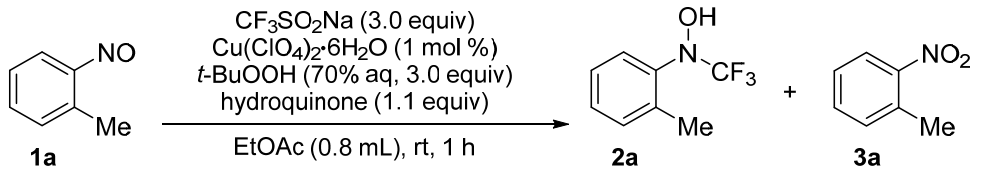
Nitrosoarenes **1c-1n** were synthesized according to adapted versions of the following literature procedures: oxidation of the corresponding anilines[1] (**1c-1e**, **1g-1i**, **1l** and **1n**), direct chlorination of the corresponding nitrosoarene[2] (**1f**), direct nitrosation[3] (**1j**) and nitrosation of the corresponding arylboronic acid (**1k**) or potassium aryltrifluoroborate[4] (**1m**). Spectral data for the compounds above can be found in the following references: **1c**,[5] **1d**,[6] **1e**,[7] **1f**,[2] **1g**,[8] **1h**,[1] **1i**,[9] **1j**,[4] **1k**,[4] **1l**,[4] and **1m**.[4]

3-Ethyl-3-(4-nitrosophenyl)piperidine-2,6-dione (1n)



1n: (0.5 mmol scale, 56% yield, 69.0 mg, green solid); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 8.32 (bs, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 2.73-2.62 (m, 1H), 2.51-2.25 (m, 3H), 2.11 (dq, J = 14.4, 7.4 Hz, 1H), 1.98 (dq, J = 14.4, 7.4 Hz, 1H), 0.90 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 174.26, 171.82, 164.44, 146.94, 127.48, 121.42, 51.76, 32.81, 29.29, 27.18, 9.14; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{14}N_2NaO_3$ $[M+Na]^+$ 269.0902, found 269.0899.

2.2. Screening of reaction conditions for the N-trifluoromethylation of 1a



Scheme S-1: Reaction conditions after screening.

To a screw-cap vial equipped with a magnetic stirring bar were added **1a** (12.1 mg, 0.10 mmol, 1.0 equiv), sodium triflinate (46.8 mg, 0.30 mmol, 3.0 equiv), hydroquinone (12.1 mg, 0.11 mmol, 1.1 equiv), ethyl acetate (0.62 mL), a solution of copper(II) perchlorate hexahydrate in ethyl acetate (0.18 mL, 0.054 M, 1 mol %) and *tert*-butyl hydroperoxide (42 µL, 70% solution in water, 0.30 mmol, 3.0 equiv) unless otherwise stated. The reaction mixture was subsequently stirred at room temperature for 1 hour, then 1,1,2,2-tetrachloroethane was added as an internal standard and a crude sample was taken. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture in $CDCl_3$. The yield of **S3** was determined by ^{19}F NMR (δ ppm -55.95) by comparison with product **2a** (Table S-2, entry 6).

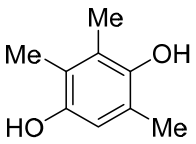
Table S-1: Relevant findings in the screening of Cu(II) sources.

Entry	Cu(II) source	Yield **2a** (%)	Yield **3a** (%)	Yield **1a** (%)
1	$Cu(ClO_4)_2{\cdot}6H_2O$ (5 mol %)	87	9	-
2	$CuCl_2$ (5 mol %)	84	13	-
3	$CuBr_2$ (5 mol %)	85	10	-
4	$Cu(OTf)_2$ (5 mol %)	82	11	-
5	$Cu(OAc)_2$ (5 mol %)	80	12	-
6	$Cu(ClO_4)_2{\cdot}6H_2O$ (1 mol %)	84	15	-
7	$Cu(ClO_4)_2{\cdot}6H_2O$ (0.1 mol %)	44	12	27

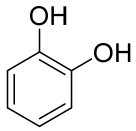
Table S-2: Relevant findings in the screening of reaction conditions.

Entry	Change		Yield **2a** (%)	Yield **3a** (%)	Yield **1a** (%)
1	-		84	15	-
2	No copper(II) source		-	-	>95
3	No hydroquinone		42	27	-
4	No oxidant		-	-	>95
5	No sodium triflinate		-	13	87
6	1 equiv of TEMPO added		27[a]	12	55
7	1 equiv of BHT added		83	19	-
8	Argon atmosphere		82	6	-
9	dried EtOAc $CuCl_2$ (5 mol %) *t*-BuOOH in decane (5.5 M)	Instead of: EtOAc $Cu(ClO_4)_2{\cdot}6H_2O$ *t*-BuOOH in H_2O	61	16	-
10	CuCl (1 mol %)	Instead of $Cu(ClO_4)_2{\cdot}6H_2O$	77	12	-
11	CuI (1 mol %)		76	11	-
12	$ZrCl_4$ (1 mol %)		-	-	89
13	$ZnCl_2$ (1 mol %)		-	-	93
14	$FeCl_2{\cdot}4H_2O$ (1 mol %)		-	-	73
15	$FeCl_3{\cdot}6H_2O$ (1 mol %)		-	-	54
16	**S1**	Instead of hydroquinone	71	11	-
17	**S2**		50	16	9
18	CH_3CN	Instead of EtOAc	-	-	89
19	DMSO		78	8	-
20	DCM		10	14	33
21	*i*-PrOH		56	18	28
22	$Zn(SO_2CF_3)_2$ (1.5 equiv)	Instead of $NaSO_2CF_3$	48	35	17
23	3 equiv of $Cu(ClO_4)_2{\cdot}6H_2O$	Instead of *t*-BuOOH	21	-	70
24	Stirring the reaction mixture for 1 h without $Cu(ClO_4)_2{\cdot}6H_2O$ (no reaction), then stirring for an additional hour after adding the Cu-species.		76	12	-

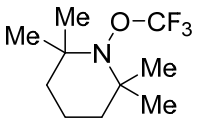
[a] In addition to product **2a**, 46% of TEMPO-CF_3 (**S3**) was observed.



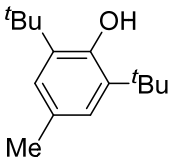
S1



S2



S3

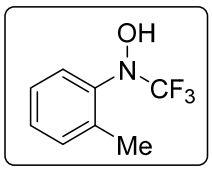


BHT

2.3. General procedure for the N-trifluoromethylation of nitrosoarenes 1a-1n

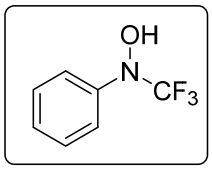
To a screw-cap vial equipped with a magnetic stirring bar were added **1** (0.30 mmol, 1.0 equiv), sodium triflinate (0.90 mmol, 3.0 equiv), hydroquinone (0.33 mmol, 1.1 equiv), ethyl acetate (1.85 mL), a solution of copper(II) perchlorate hexahydrate in ethyl acetate (0.55 mL, 0.054 M, 1 mol %) and *tert*-butyl hydroperoxide (70% solution in water, 125 µL, 0.90 mmol, 3.0 equiv, added last). The reaction mixture was stirred for 1 h at room temperature during which the color changed from blue or green to brown. The crude product was purified by adsorption on silica followed by column chromatography (pentane:ethyl acetate and/or pentane:DCM) to obtain hydroxylamine derivatives **2a**-**2n**.

***N*-(*o*-Tolyl)-*N*-(trifluoromethyl)hydroxylamine (2a)**



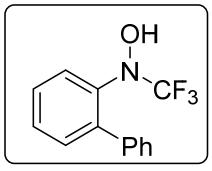
2a: (82% yield, 47.0 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.62-7.60 (m, 1H), 7.29-7.21 (m, 3H), 5.97 (bs, 1H), 2.36 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 140.37, 136.36, 130.80, 128.90, 126.77, 125.37, 123.67 (q, J = 262.4 Hz), 17.80; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.34 (s); **MS** (EI): *m/z* 191 (95%, $[M]^+$), 174 (15%, $[M\text{-}OH]^+$), 154 (100%), 127 (95%), 77 (60%); **HRMS** (ESI): *m/z* calcd for $C_8H_7F_3NO$ $[M\text{-}H]^-$ 190.0485, found 190.0487.

***N*-Phenyl-*N*-(trifluoromethyl)hydroxylamine (2b)**



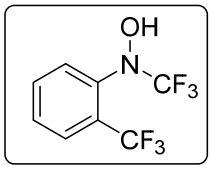
2b: (83% yield, 44.9 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.45 (d, J = 8.1 Hz, 2H), 7.41-7.38 (m, 2H), 7.34-7.30 (m, 1H), 5.93 (bs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 142.16, 128.93, 128.10, 124.03, 123.16 (q, J = 262.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.25 (s); **MS** (EI): *m/z* 177 (100%, $[M]^+$), 160 (50%, $[M\text{-}OH]^+$), 141 (90%, $[M\text{-}FOH]^+$), 95 (65%), 78 (90%); **HRMS** (ESI): *m/z* calcd for $C_7H_5F_3NO$ $[M\text{-}H]^-$ 176.0329, found 176.0334.

***N*-([1,1'-Biphenyl]-2-yl)-*N*-(trifluoromethyl)hydroxylamine (2c)**



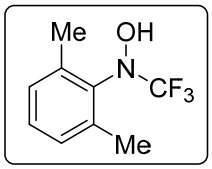
2c: (82% yield, 62.3 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.75-7.73 (m, 1H), 7.48-7.35 (m, 8H), 5.97 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 141.18, 139.24, 138.97, 131.07, 129.51, 129.34, 128.53, 128.17, 127.43, 125.67, 123.57 (q, J = 262.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -69.50; **HRMS** (ESI): *m/z* calcd for $C_{13}H_9F_3NO$ $[M\text{-}H]^-$ 252.0642, found 252.0640.

_N_-(Trifluoromethyl)-_N_-(2-(trifluoromethyl)phenyl)hydroxylamine (2d)



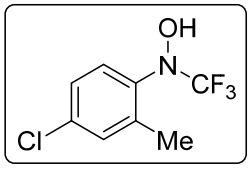
2d: (81% yield, 59.6 mg, colorless oil); **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.84 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.67 (dd, J = 7.8, 7.8 Hz, 1H), 7.54 (dd, J = 7.7, 7.7 Hz, 1H), 6.28 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 139.78, 133.24, 130.00, 129.55 (q, J = 30.5 Hz), 128.05, 126.74 (q, J = 5.2 Hz), 123.16 (q, J = 273.1 Hz), 123.14 (q, J = 262.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -59.66 (q, J = 3.0 Hz), -70.04 (q, J = 3.0 Hz); **HRMS** (ESI): *m/z* calcd for $C_8H_4F_6NO$ $[M-H]^-$ 244.0203, found 244.0197.

_N_-(2,6-Dimethylphenyl)-_N_-(trifluoromethyl)hydroxylamine (2e)



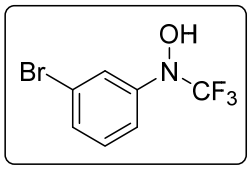
2e: (70% yield, 43.1 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.15 (dd, J = 8.3, 6.7 Hz, 1H), 7.07 (d, J = 7.7 Hz, 2H), 5.97 (bs, 1H), 2.43 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 137.98, 137.26, 129.36, 128.98, 123.80 (q, J = 259.8 Hz), 19.21; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -66.53; **HRMS** (ESI): *m/z* calcd for $C_9H_9F_3NO$ $[M-H]^-$ 204.0639, found 204.0642.

_N_-(4-Chloro-2-methylphenyl)-_N_-(trifluoromethyl)hydroxylamine (2f)



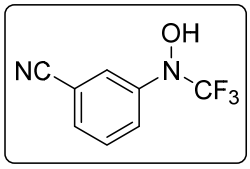
2f: (77% yield, 51.9 mg, colorless oil); **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.54 (d, J = 8.3 Hz, 1H), 7.24-7.22 (m, 2H), 6.13 (bs, 1H), 2.33 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 138.70, 137.92, 134.23, 130.34, 126.75, 126.30, 123.17 (q, J = 262.2 Hz), 17.49; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.53 (s); **HRMS** (ESI): *m/z* calcd for $C_9H_8ClF_3NO_3$ $[M+HCOO]^-$ 270.0150, found 270.0163. HCOONa was used as a calibrant.

_N_-(3-Bromophenyl)-_N_-(trifluoromethyl)hydroxylamine (2g)



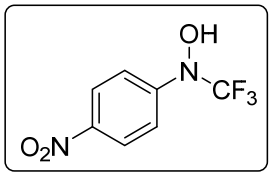
2g: (69% yield, 52.5 mg, colorless oil); **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.63 (bs, 1H), 7.45 (ddd, J = 8.0, 1.9, 1.0 Hz, 1H), 7.37-7.35 (m, 1H), 7.26 (dd, J = 8.0, 8.0 Hz, 1H), 6.14 (bs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 143.44, 131.04, 130.19, 126.79, 122.85 (q, J = 263.1 Hz), 122.45, 122.37; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.02 (s); **HRMS** (ESI): *m/z* calcd for $C_7H_4BrF_3NO$ $[M-H]^-$ 253.9434, found 253.9426.

3-(Hydroxy(trifluoromethyl)amino)benzonitrile (2h)



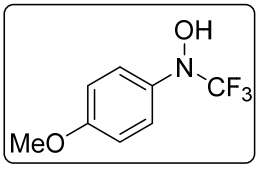
2h: (73% yield, 44.3 mg, white solid); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.75 (bs, 1H), 7.69-7.66 (m, 1H), 7.60 (ddd, J = 7.7, 1.3, 1.3 Hz, 1H), 7.52 (dd, J = 7.9, 7.9 Hz, 1H), 6.32 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 143.19, 131.27, 129.97, 127.82, 126.87, 122.64 (q, J = 263.5 Hz), 118.07, 113.18; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.13 (s); **HRMS** (ESI): *m/z* calcd for $C_8H_4F_3N_2O$ $[M-H]^-$ 201.0281, found 201.0277.

_N_-(4-Nitrophenyl)-_N_-(trifluoromethyl)hydroxylamine (2i)



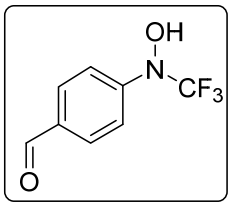
2i: (54% yield, 36.2 mg, yellow solid); **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 8.29-8.26 (m, 2H), 7.60-7.57 (m, 2H), 6.17 (q, J = 0.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 147.57, 146.46, 124.57, 122.76, 122.44 (q, J = 264.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -70.02; **HRMS** (ESI): *m/z* calcd for $C_7H_4F_3N_2O_3$ $[M\text{-}H]^-$ 221.0180, found 221.0188.

_N_-(4-Methoxyphenyl)-_N_-(trifluoromethyl)hydroxylamine (2j)



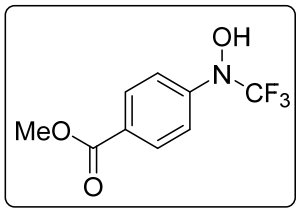
2j: (74% yield, 46.0 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.38 (d, J = 8.6 Hz, 2H), 6.92-6.88 (m, 2H), 6.16 (bs, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 159.53, 134.92, 126.33, 123.33 (q, J = 261.6 Hz), 114.14, 55.64; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.56 (s); **HRMS** (ESI): *m/z* calcd for $C_8H_7F_3NO_2$ $[M\text{-}H]^-$ 206.0434, found 206.0444.

4-(Hydroxy(trifluoromethyl)amino)benzaldehyde (2k)



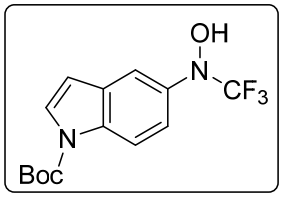
2k: (0.25 mmol scale, 61% yield, 31.3 mg, colorless oil); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 9.99 (s, 1H), 7.92-7.89 (m, 2H), 7.58 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 191.76, 147.65, 134.84, 130.62, 122.73 (q, J = 1.5 Hz), 122.67 (q, J = 263.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -70.11 (s); **HRMS** (ESI): *m/z* calcd for $C_8H_5F_3NO_2$ $[M\text{-}H]^-$ 204.0278, found 204.0282.

Methyl 4-(hydroxy(trifluoromethyl)amino)benzoate (2l)



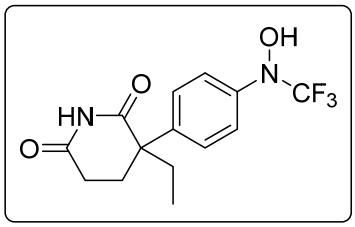
2l: (71% yield, 50.0 mg, white solid); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 8.06-8.02 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 6.48 (bs, 1H), 3.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 166.76, 146.29 (q, J = 1.4 Hz), 130.43, 128.96, 122.77 (q, J = 263.2 Hz), 122.56 (q, J = 1.5 Hz), 52.48; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -70.55 (s); **HRMS** (ESI): *m/z* calcd for $C_9H_7F_3NO_3$ $[M\text{-}H]^-$ 234.0384, found 234.0385.

***tert*-Butyl 5-(hydroxy(trifluoromethyl)amino)-1*H*-indole-1-carboxylate (2m)**



2m: (51% yield, 48.4 mg, white solid); **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 8.14 (d, J = 8.9 Hz, 1H), 7.66-7.63 (m, 2H), 7.40 (d, J = 9.0 Hz, 1H), 6.58 (d, J = 3.7 Hz, 1H), 6.06 (bs, 1H), 1.67 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 149.68, 137.09, 134.79, 130.77, 127.28, 123.42 (q, J = 261.5 Hz), 121.11, 117.38, 115.40, 107.46, 84.29, 28.32; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -71.38; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{14}F_3N_2O_3$ $[M\text{-}H]^-$ 315.0962, found 315.0964.

4-Ethyl-4-(4-(hydroxy(trifluoromethyl)amino)phenyl)piperidine-2,6-dione (2n)

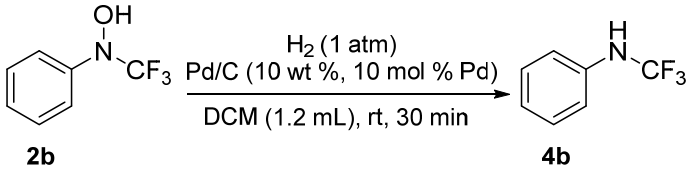


2n: (0.1 mmol scale, 66% yield, 20.8 mg, white solid); **^{1}H NMR** (400 MHz, DMSO-d_6): δ ppm 10.90 (bs, 1H), 10.45 (bs, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.37-7.34 (m, 2H), 2.51-2.45 (m, 1H), 2.38-2.33 (m, 1H), 2.22-2.07 (m, 2H), 1.94-1.77 (m, 2H), 0.76 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6): δ ppm 175.53, 172.67, 141.46, 138.87, 126.95, 123.17, 123.11 (q, J = 260.1 Hz), 49.96, 31.97, 29.06, 26.04, 8.91; **^{19}F NMR** (376 MHz, DMSO-d_6): δ ppm -69.03; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{15}F_3N_2NaO_3$ $[M+Na]^+$ 339.0932, found 339.0920.

2.4. N-Trifluoromethylation of nitrosobenzene on a 10.0 mmol scale

To a round-bottom flask equipped with a magnetic stirring bar were added copper(II) perchlorate hexahydrate (37.1 mg, 0.10 mmol, 1 mol %), nitrosobenzene (**1b**, 1.07 g, 10.0 mmol, 1.0 equiv), sodium triflinate (4.68 g, 30.0 mmol, 3.0 equiv), hydroquinone (1.21 g, 11.0 mmol, 1.1 equiv), ethyl acetate (80 mL) and *tert*-butyl hydroperoxide (70% solution in water, 4.15 mL, 30.0 mmol, 3.0 equiv). The reaction mixture was stirred for 1 h at room temperature during which the color changed from blue to brown. The crude product was purified by adsorption on silica followed by column chromatography (pentane:ethyl acetate, 25:1) to obtain *N*-phenyl-*N*-(trifluoromethyl)hydroxylamine (**2b**) in 74% yield (1.31 g). For spectral data of **2b**, see page S-5.

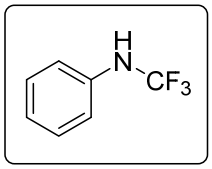
2.5. Reduction of 2b



Scheme S-2: Reduction of **2b**

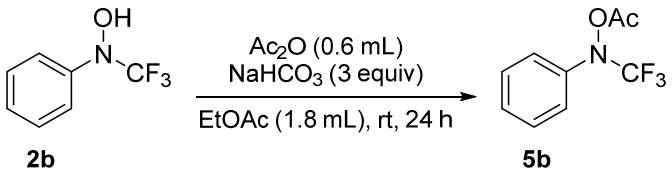
The reaction was performed according to an adapted version of a literature procedure.[10] To a round-bottom flask equipped with a magnetic stirring bar were added **2b** (53.1 mg, 0.30 mmol, 1.0 equiv), DCM (1.2 mL) and Pd/C (10 wt %, 16.0 mg, 10 mol % Pd). The flask was put under a hydrogen atmosphere with a balloon and the reaction mixture was stirred for 30 min at room temperature. The crude product was purified by filtration over Celite (DCM) to obtain **4b** in 83% yield (40.3 mg).

***N*-(Trifluoromethyl)aniline (4b)**



4b: (83% yield, 40.3 mg, colorless oil); ^{19}F NMR data are in accordance with literature[10] values: **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.31 (dd, J = 8.5, 7.5 Hz, 2H), 7.08 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 5.09 (bs, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ ppm 137.61, 129.57, 122.72, 121.70 (q, J = 255.7 Hz), 118.07; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -55.78 (s); **HRMS** (ESI): *m/z* calcd for $C_7H_5F_3N$ $[M-H]^-$, 160.0380 found 160.0383.

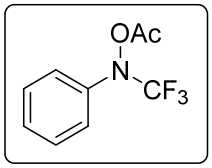
2.6. Acylation of 2b



Scheme S-3: Acylation of **2b**

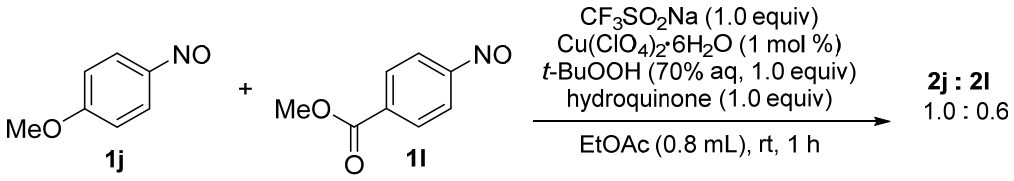
The acylation of **2b** was performed according to an adapted version of a literature procedure.[11] To a round-bottom flask equipped with a magnetic stirring bar were added **2b** (53.1 mg, 0.30 mmol, 1.0 equiv), ethyl acetate (1.8 mL), acetic anhydride (0.60 mL, 6.4 mmol, 21 equiv) and sodium bicarbonate (75.6 mg, 0.90 mmol, 3.0 equiv). The reaction mixture was stirred for 24 hours at room temperature. Water and ethyl acetate were added and the layers were separated. The organic layer was washed with a saturated solution of sodium bicarbonate in water (3x) followed by water (5x) and brine (3x) and was subsequently dried over $MgSO_4$. Evaporation of the solvent gave **5b** in 97% yield (63.7 mg).

***O*-Acetyl-*N*-phenyl-*N*-(trifluoromethyl)hydroxylamine (5b)**

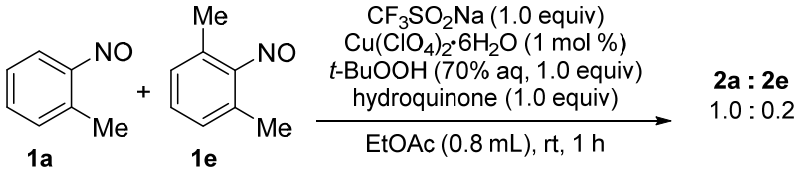


5b: (97% yield, 63.7 mg, colorless oil); NMR data are in accordance with literature[10] values: **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.50 (d, J = 7.7 Hz, 2H), 7.45-7.39 (m, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 167.23, 140.18, 129.48, 129.32, 125.66, 122.30 (q, J = 264.3 Hz), 18.85; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm -69.65 (s).

2.7. Competition experiments



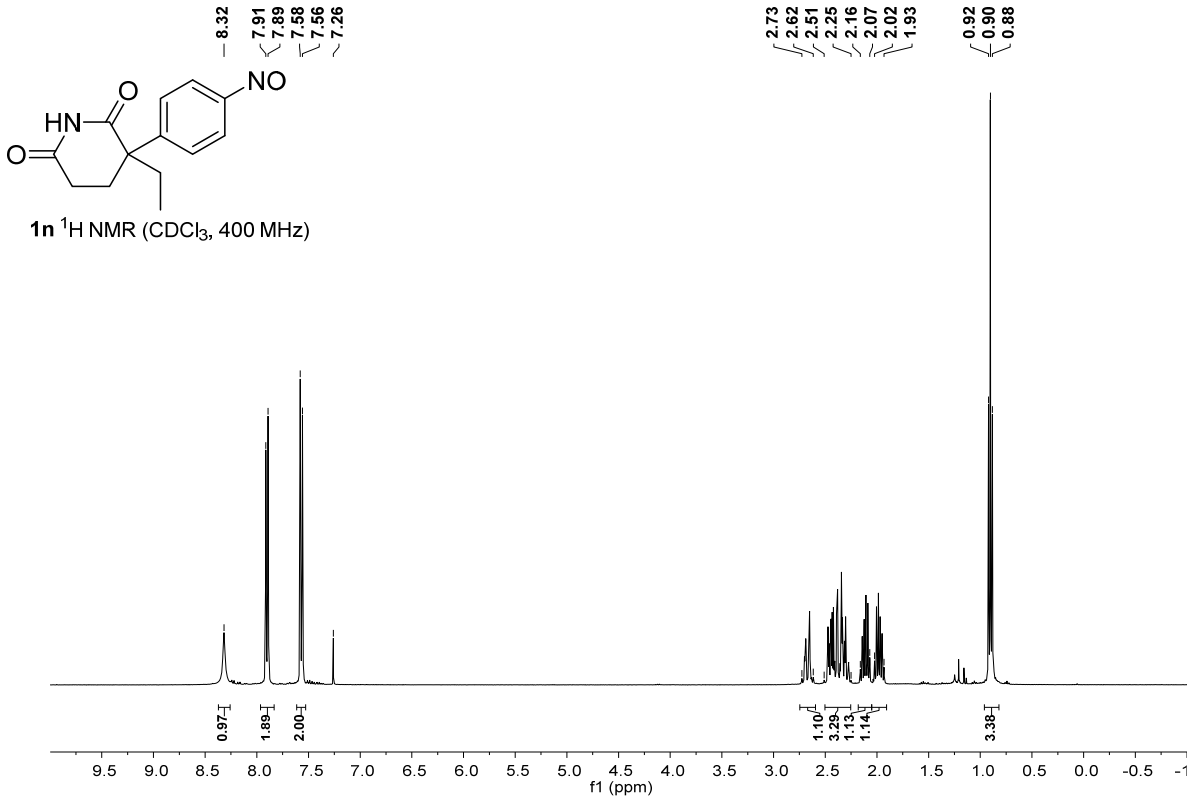
Scheme S-4: Competition experiment between **1j** and **1l**.



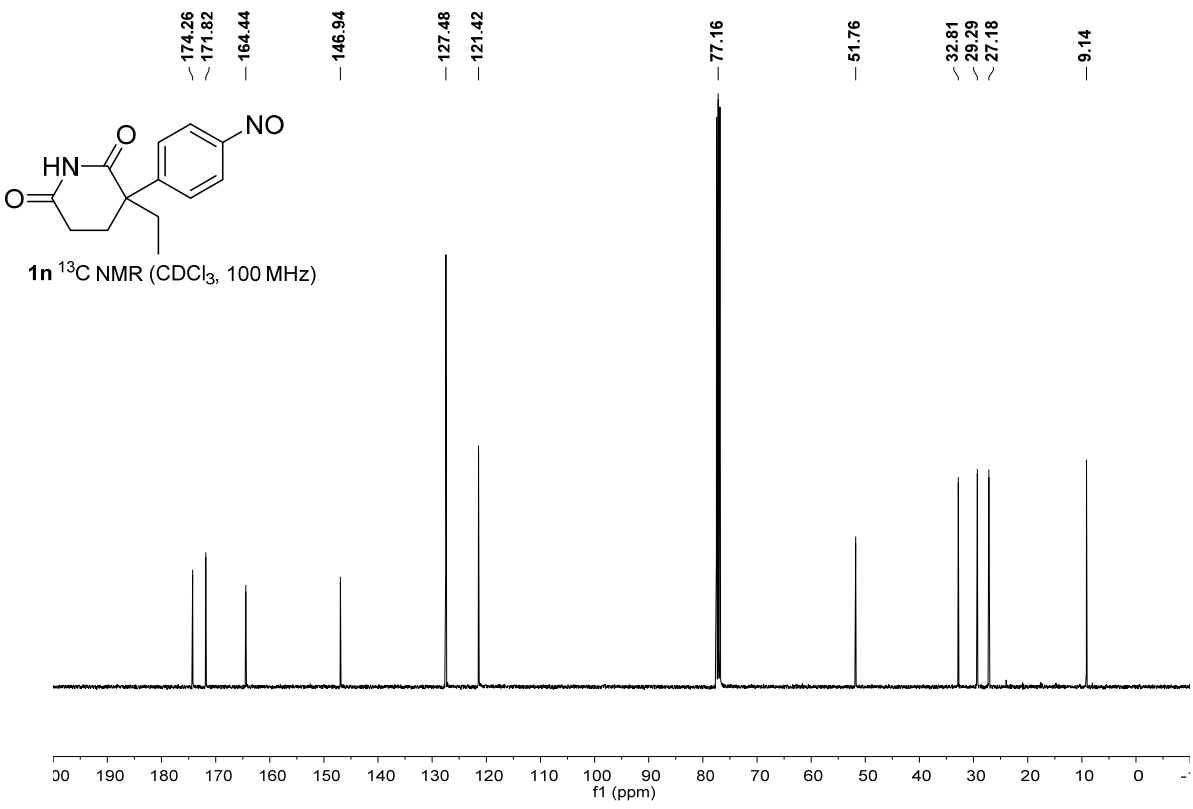
Scheme S-5: Competition experiment between **1a** and **1e**.

To a screw-cap vial equipped with a magnetic stirring bar were added **1j** or **1a** (0.10 mmol, 1.0 equiv), **1l** or **1e** (0.10 mmol, 1.0 equiv), sodium triflinate (15.6 mg, 0.10 mmol, 1.0 equiv), hydroquinone (11.0 mg, 0.10 mmol, 1.0 equiv), ethyl acetate (0.62 mL), a solution of copper(II) perchlorate hexahydrate in ethyl acetate (0.18 mL, 0.054 M, 1 mol %) and *tert*-butyl hydroperoxide (14 µL, 70% solution in water, 0.10 mmol, 1.0 equiv). The reaction mixture was subsequently stirred at room temperature for 1 hour, then 1,1,2,2-tetrachloroethane was added as an internal standard and a crude sample was taken. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture in $CDCl_3$. Ratios were determined by ^{19}F NMR analysis of the crude reaction mixture in $CDCl_3$. ^{1}H NMR yields were found to be lower than 10%.

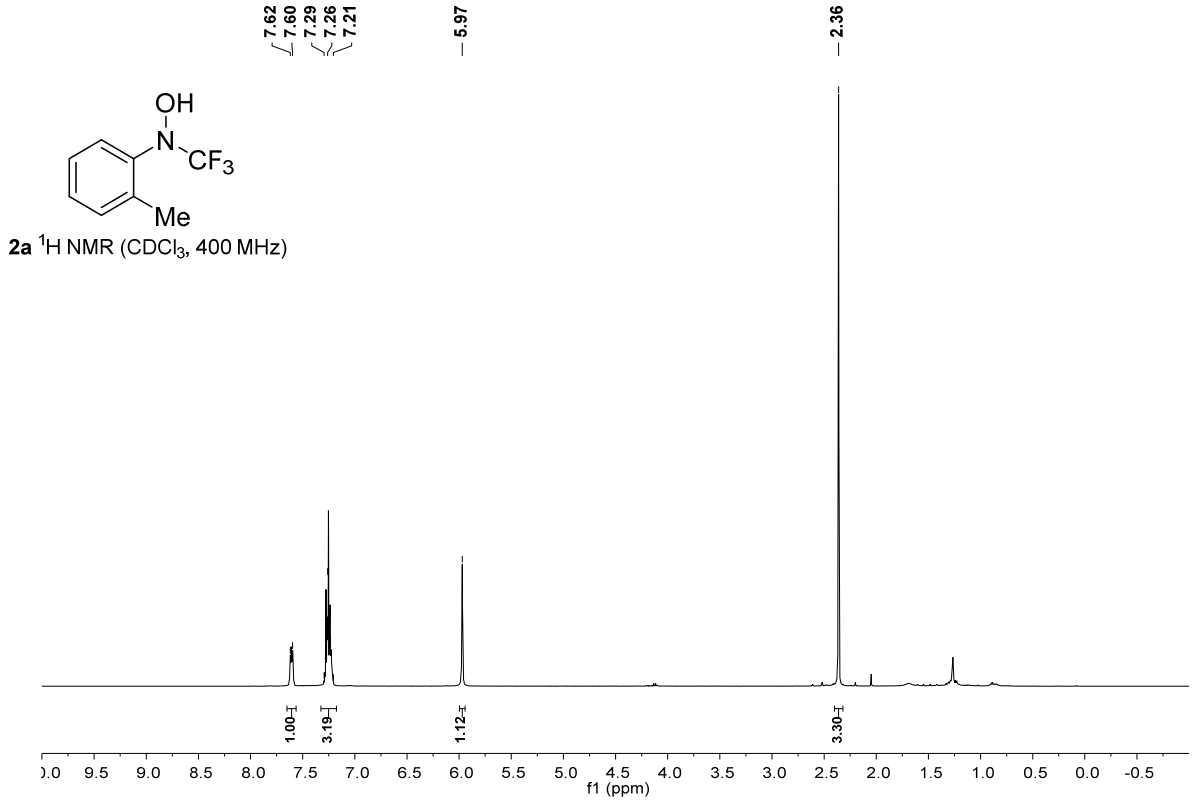
3. ^{1}H, ^{13}C and ^{19}F NMR Spectra



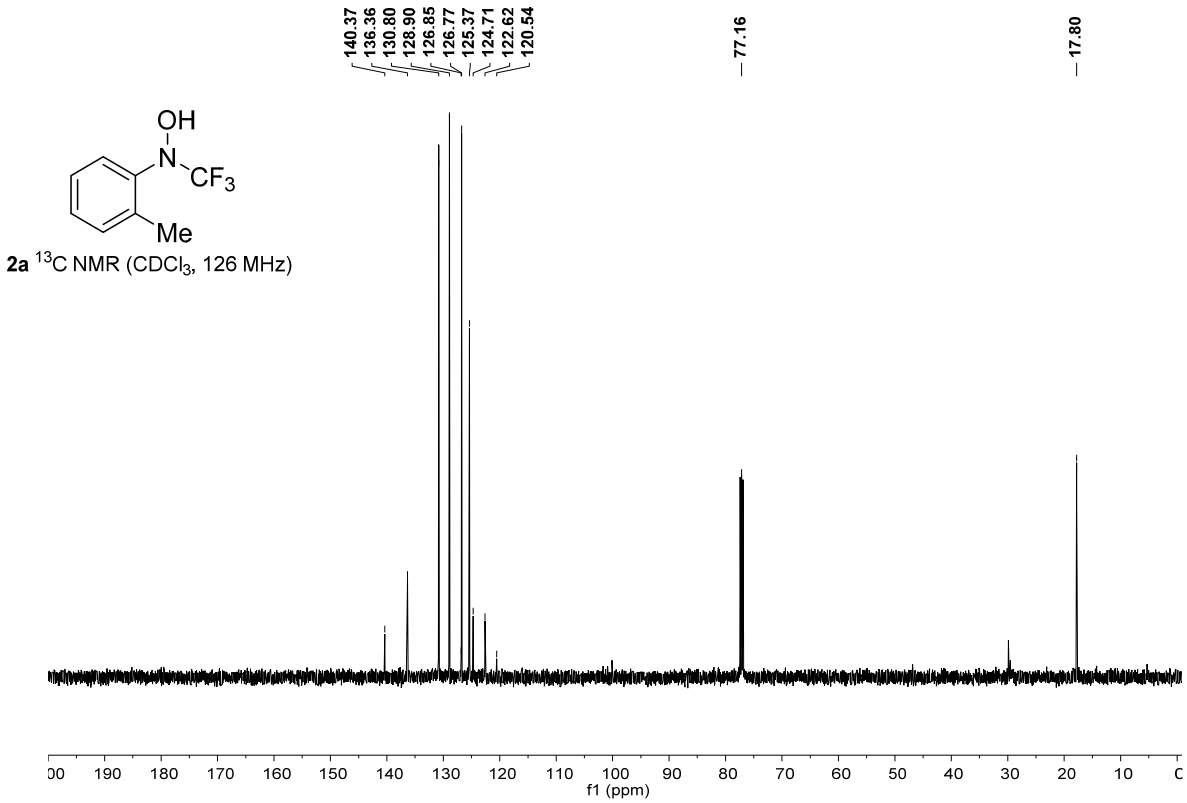
1n ^{1}H NMR ($CDCl_3$, 400 MHz)



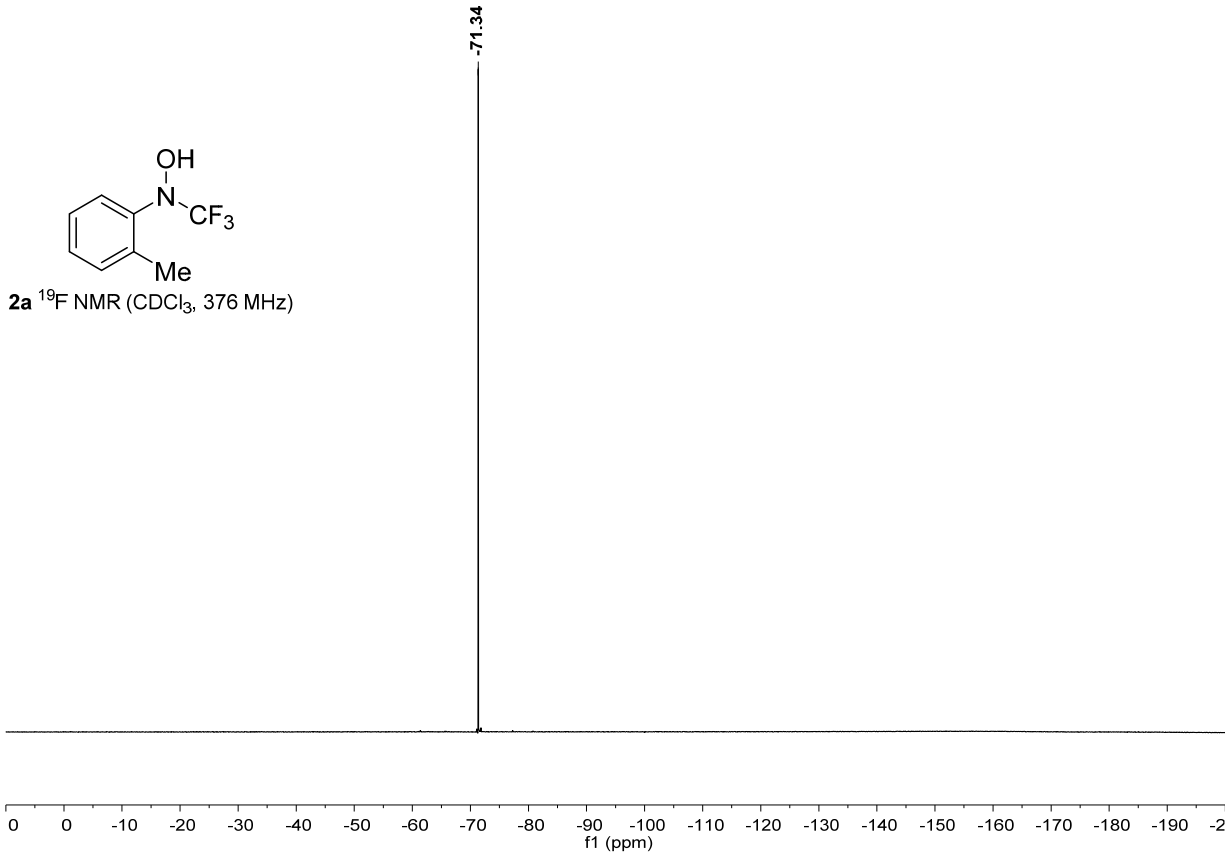
1n ^{13}C NMR ($CDCl_3$, 100 MHz)



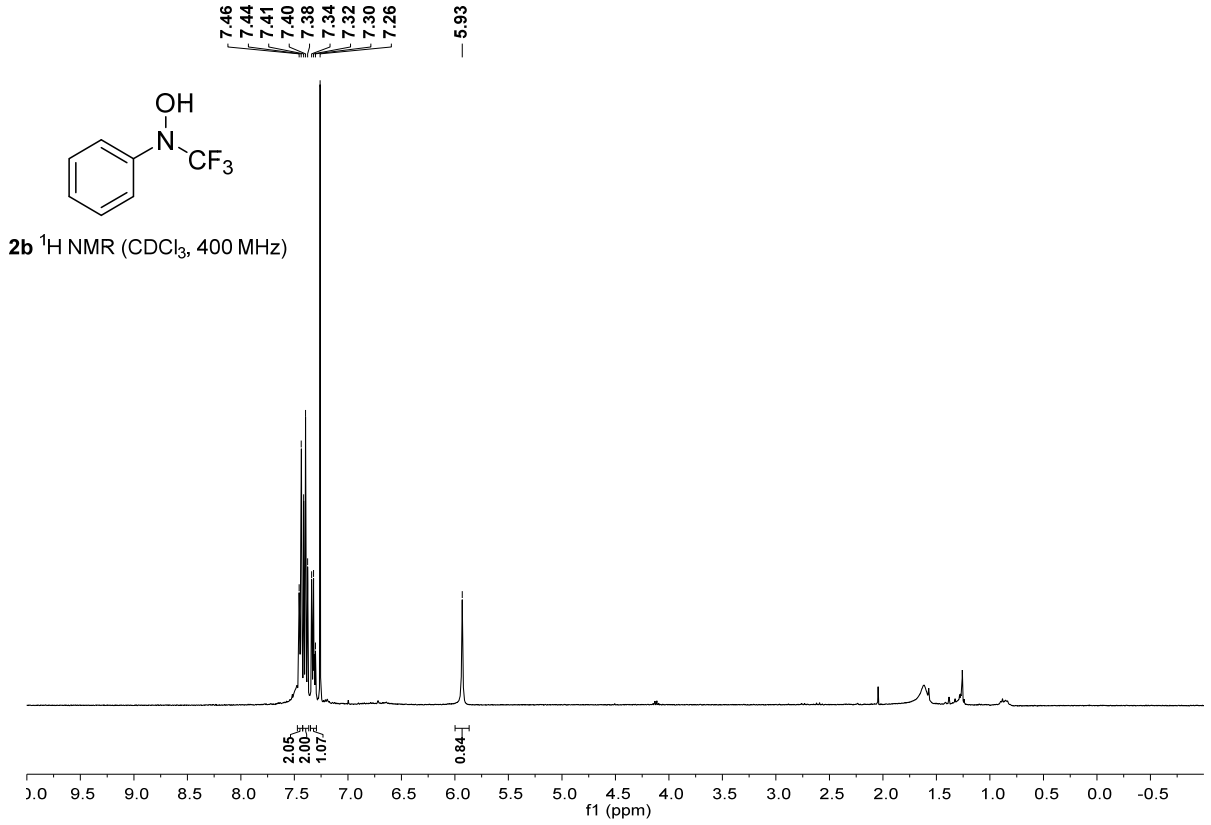
2a ^{1}H NMR ($CDCl_3$, 400 MHz)



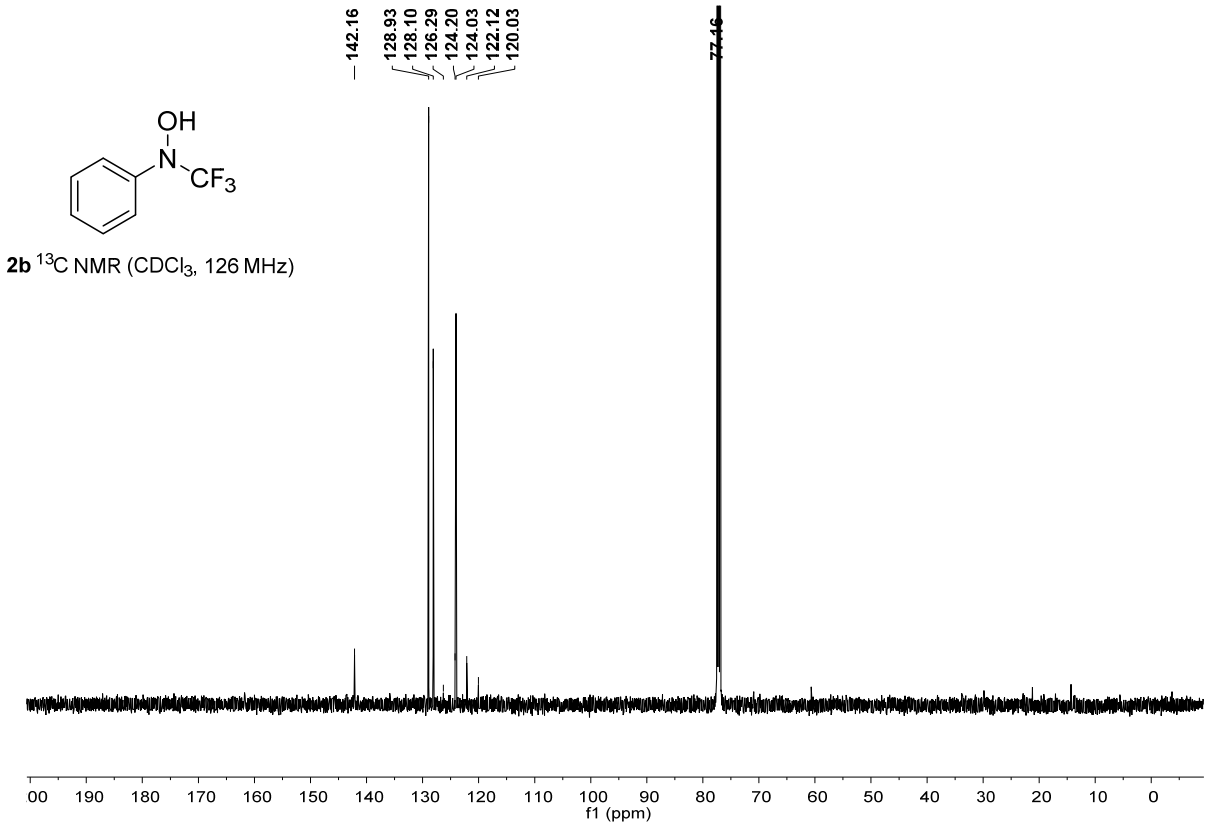
2a ^{13}C NMR ($CDCl_3$, 126 MHz)



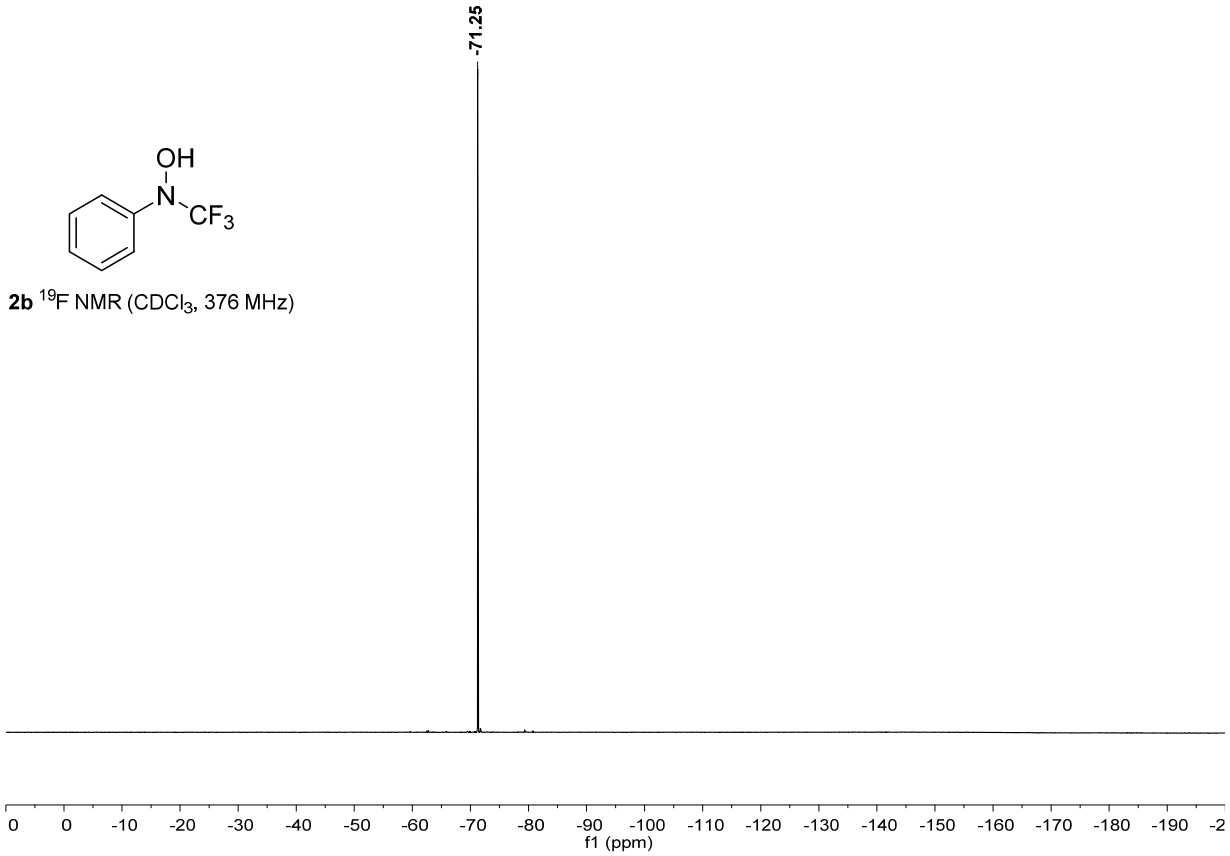
2a ^{19}F NMR ($CDCl_3$, 376 MHz)



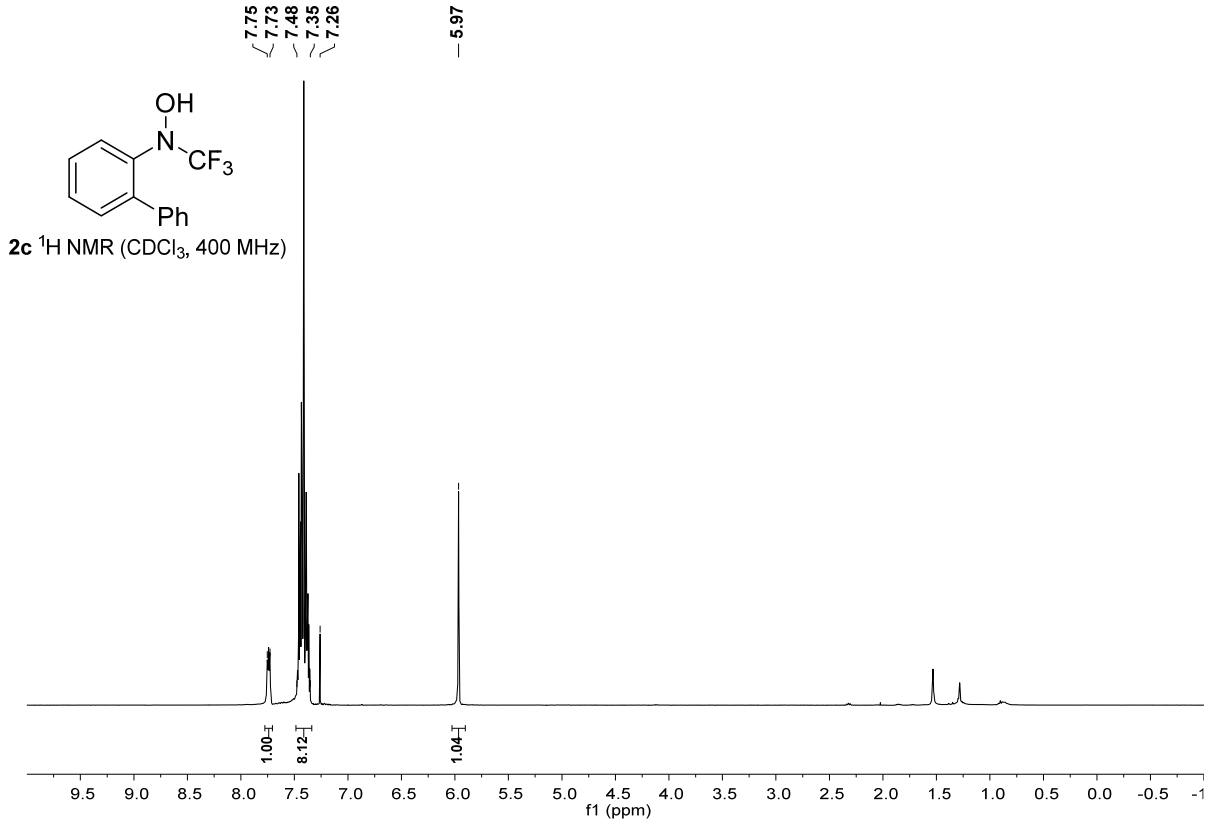
2b ^{1}H NMR ($CDCl_3$, 400 MHz)



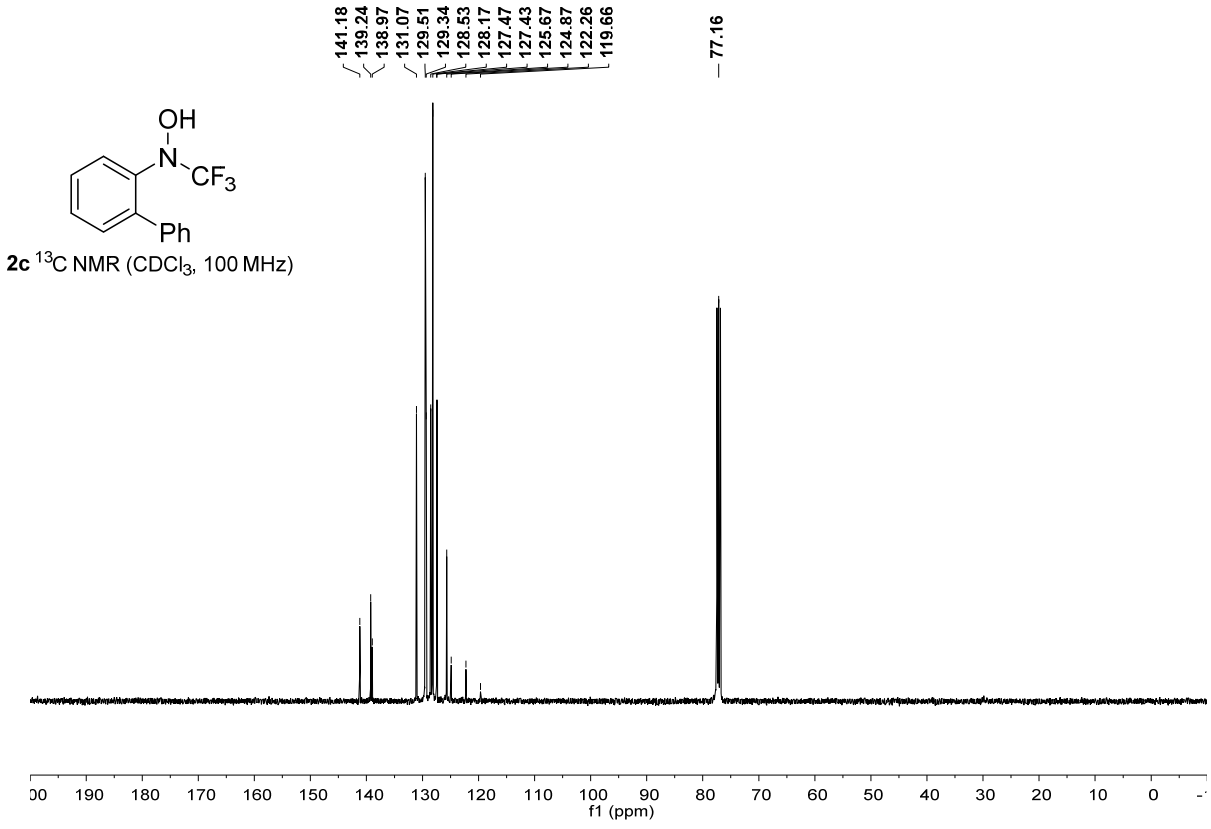
2b ^{13}C NMR ($CDCl_3$, 126 MHz)



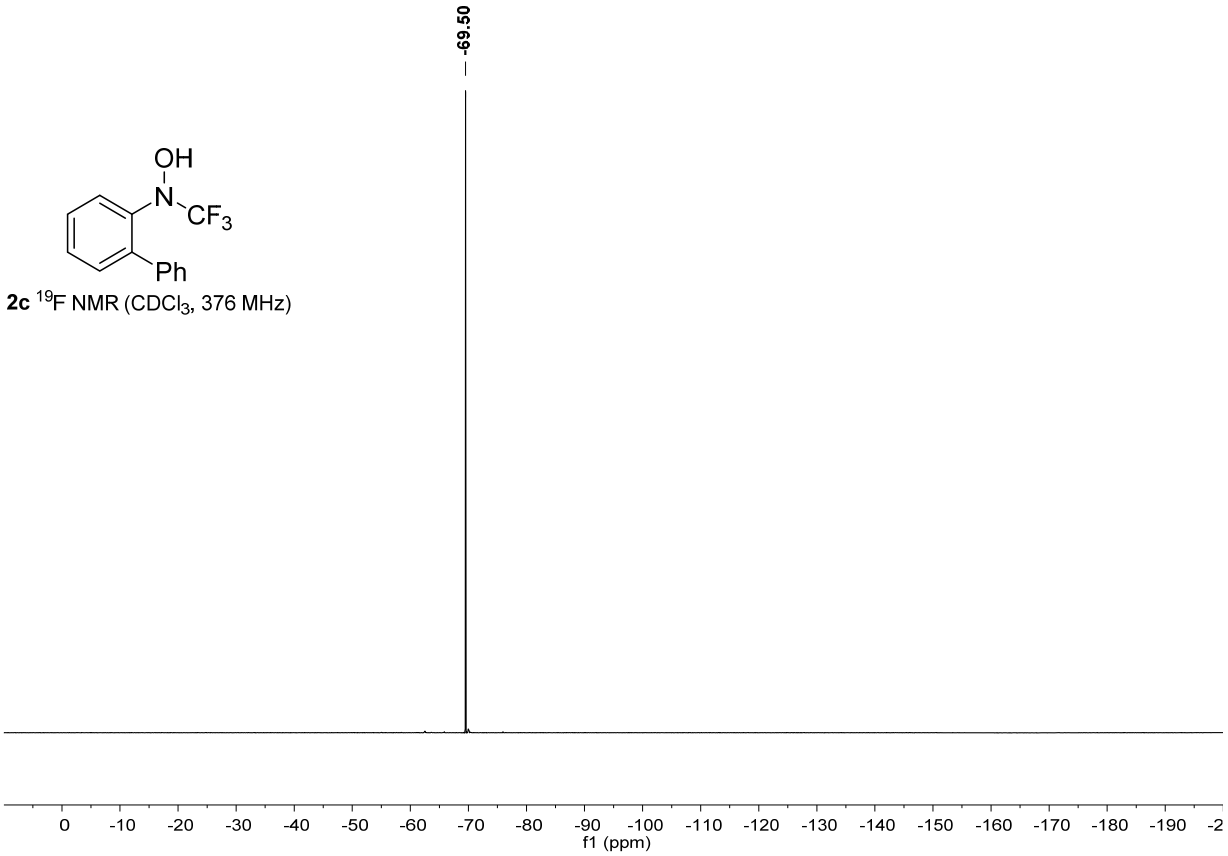
2b ^{19}F NMR ($CDCl_3$, 376 MHz)



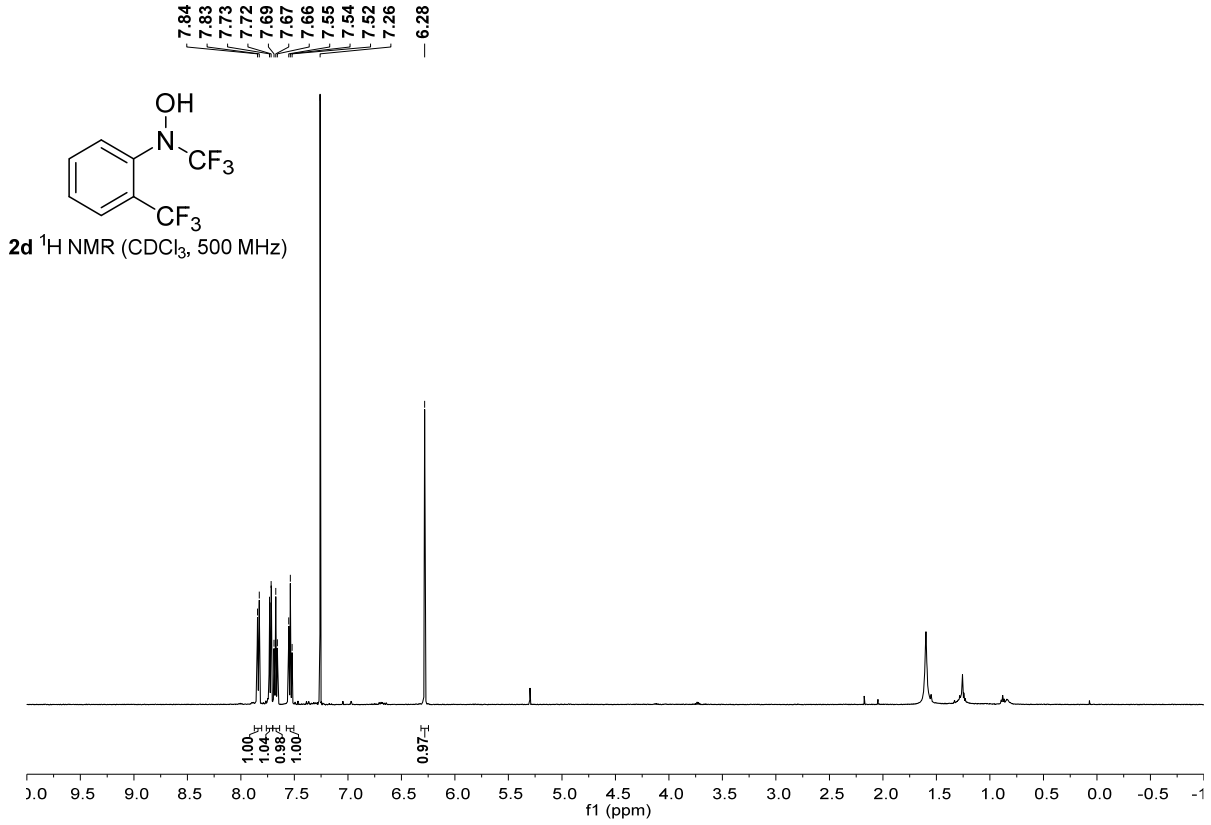
2c ^{1}H NMR ($CDCl_3$, 400 MHz)



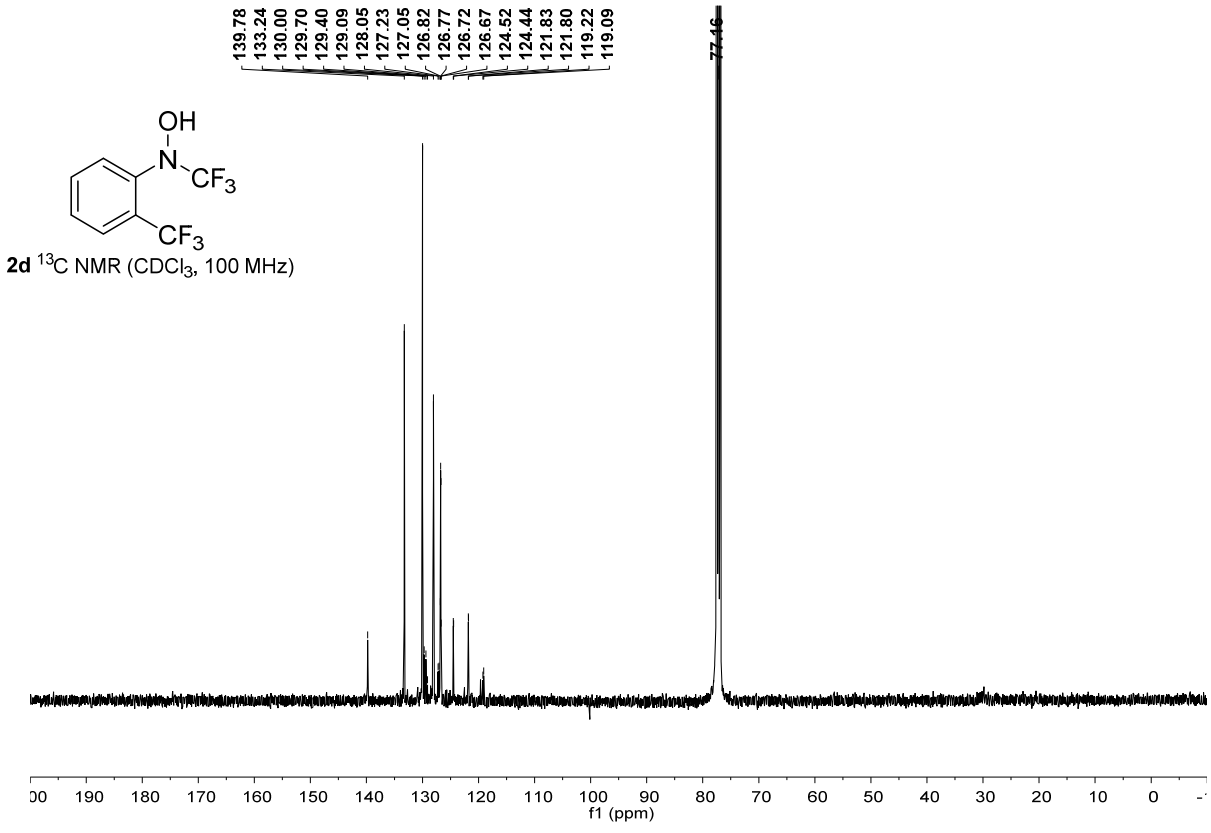
2c ^{13}C NMR ($CDCl_3$, 100 MHz)



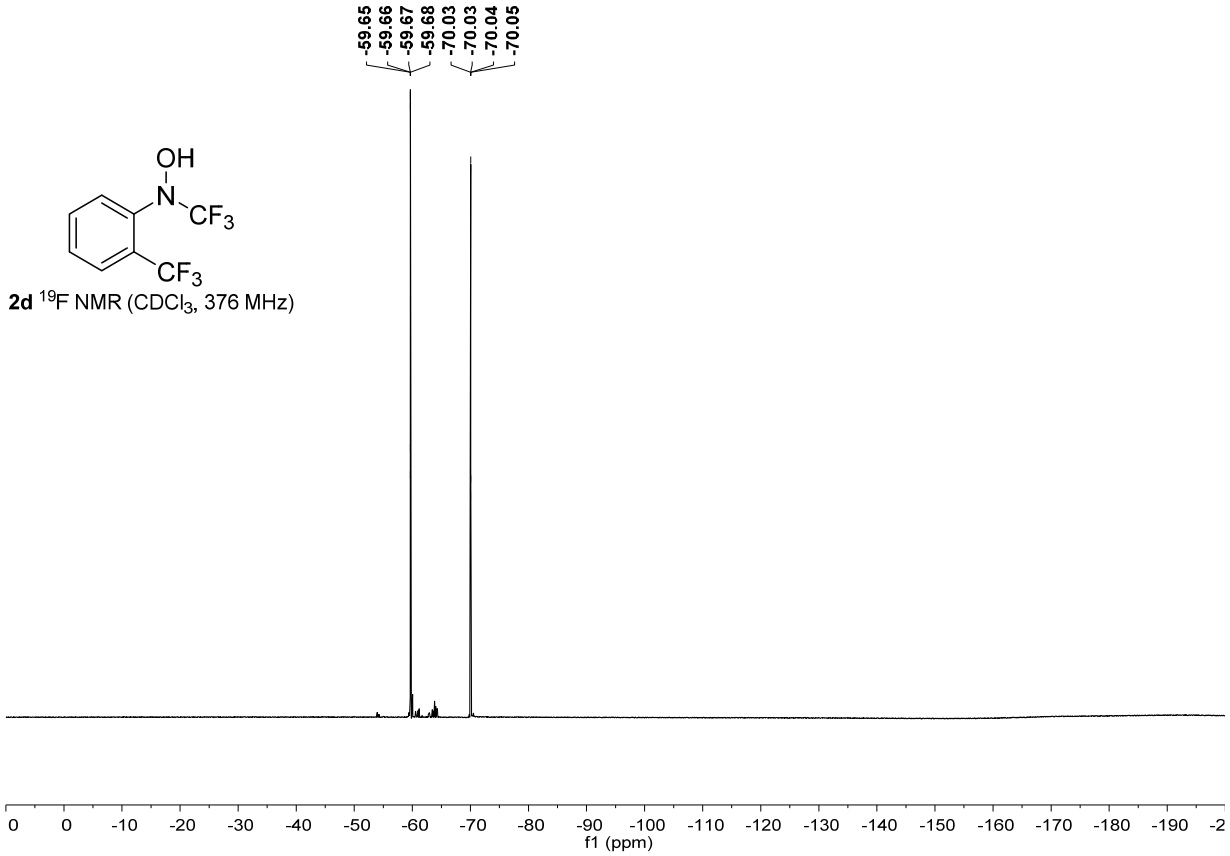
2c ^{19}F NMR ($CDCl_3$, 376 MHz)



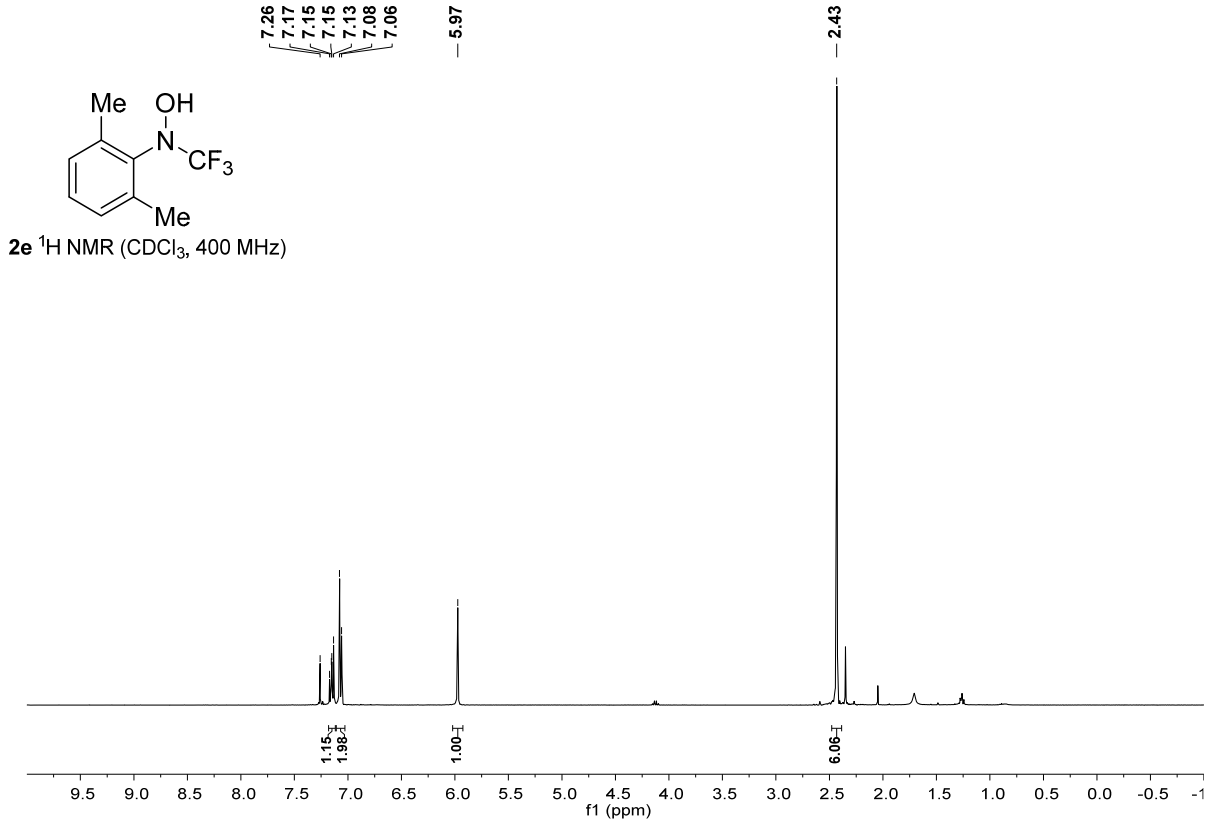
2d ^{1}H NMR ($CDCl_3$, 500 MHz)



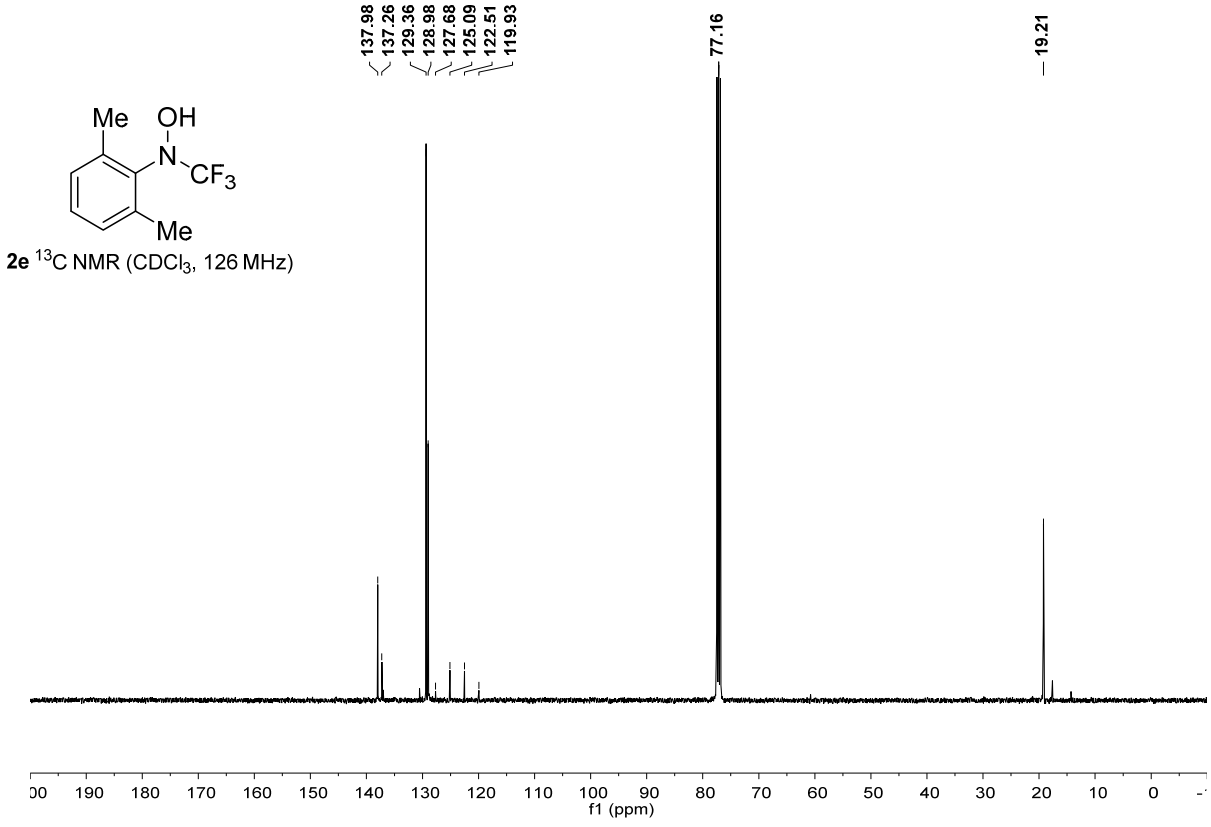
2d ^{13}C NMR ($CDCl_3$, 100 MHz)



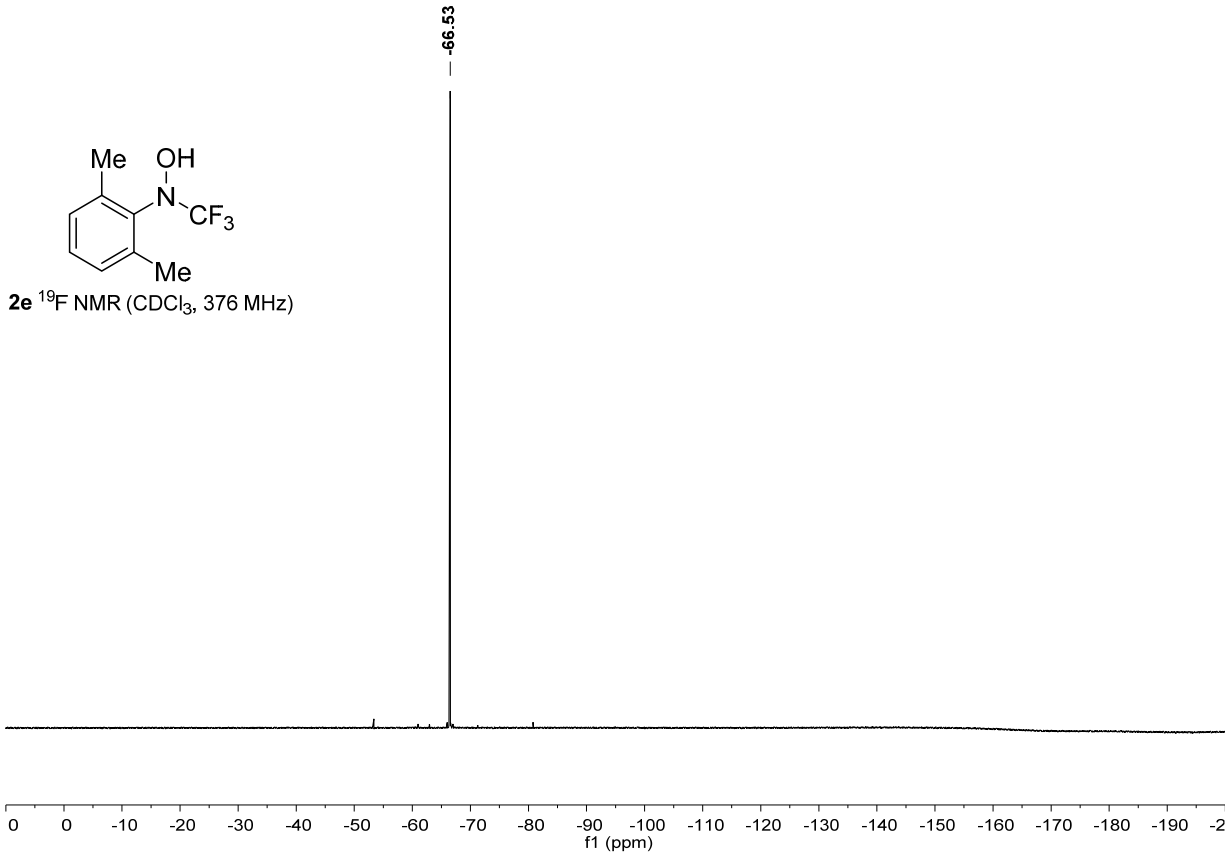
2d ^{19}F NMR ($CDCl_3$, 376 MHz)



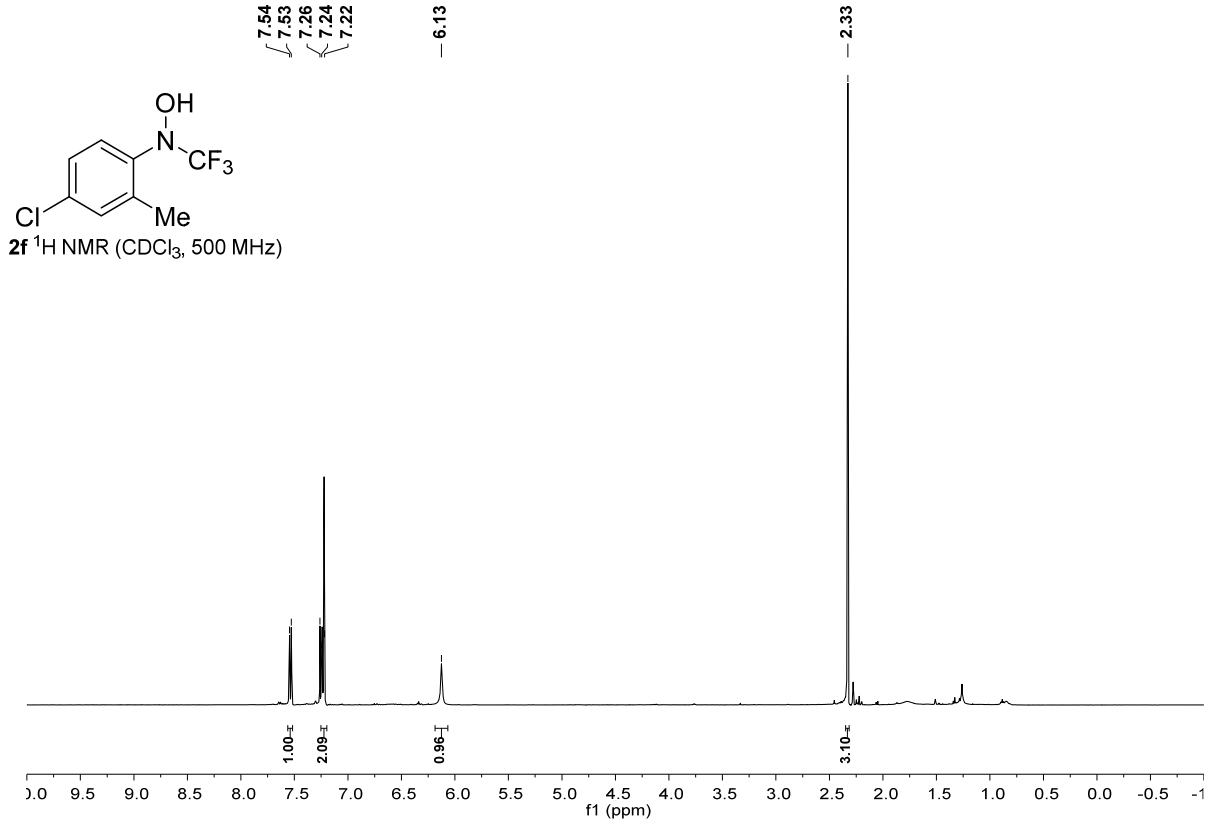
2e ^{1}H NMR ($CDCl_3$, 400 MHz)



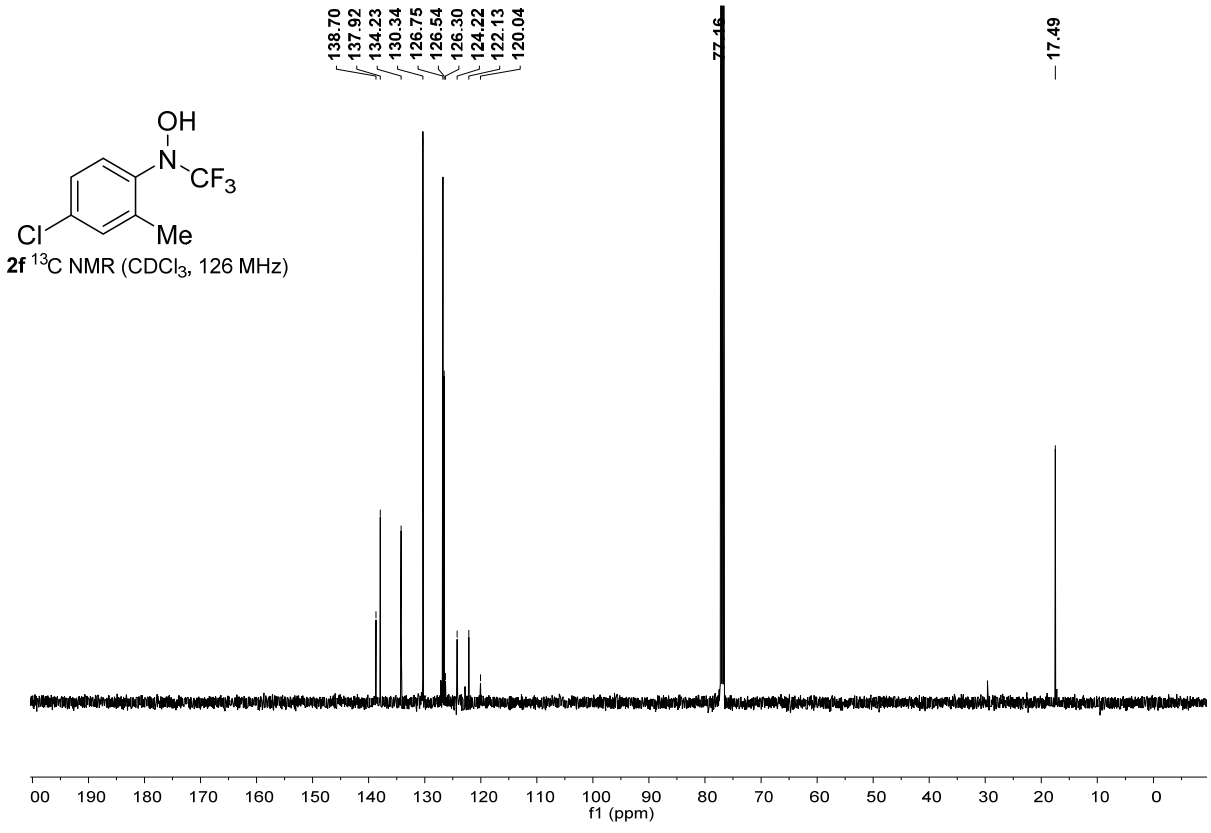
2e ^{13}C NMR ($CDCl_3$, 126 MHz)



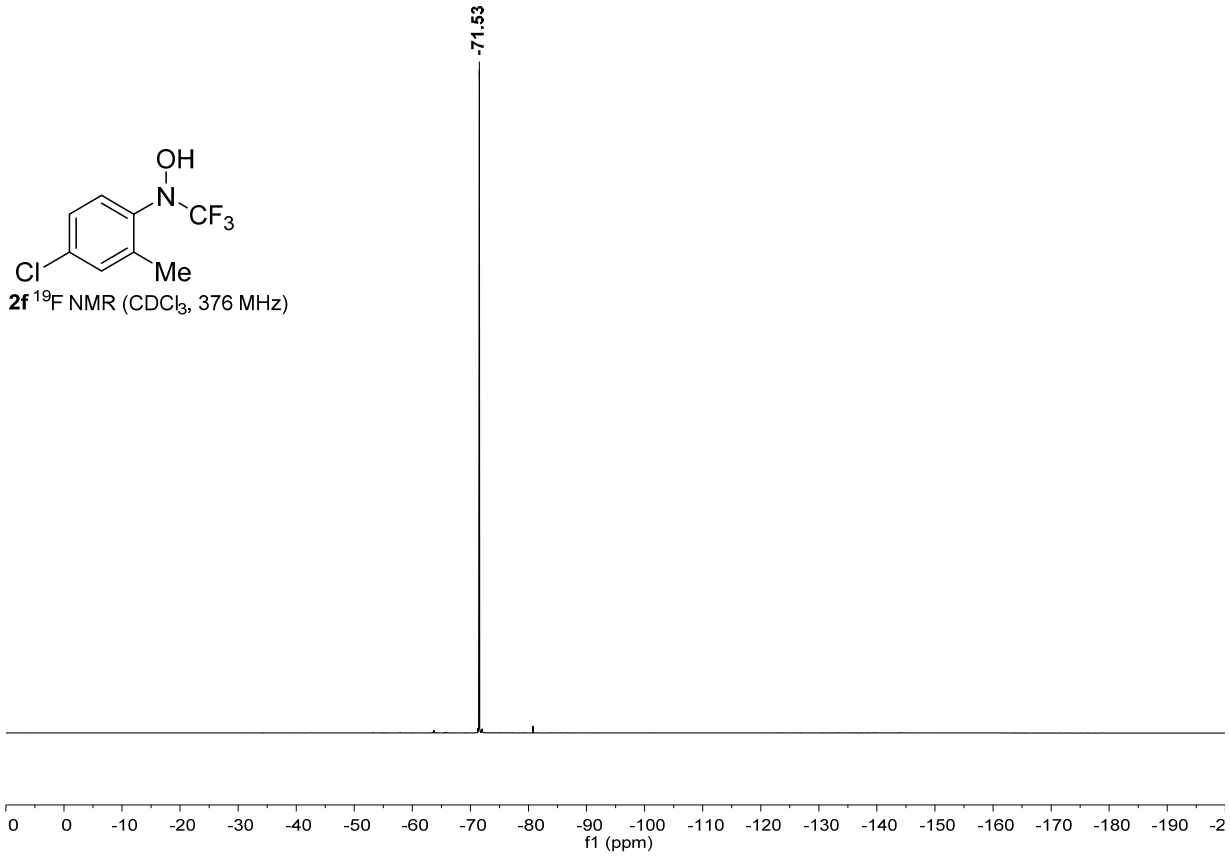
2e ^{19}F NMR ($CDCl_3$, 376 MHz)



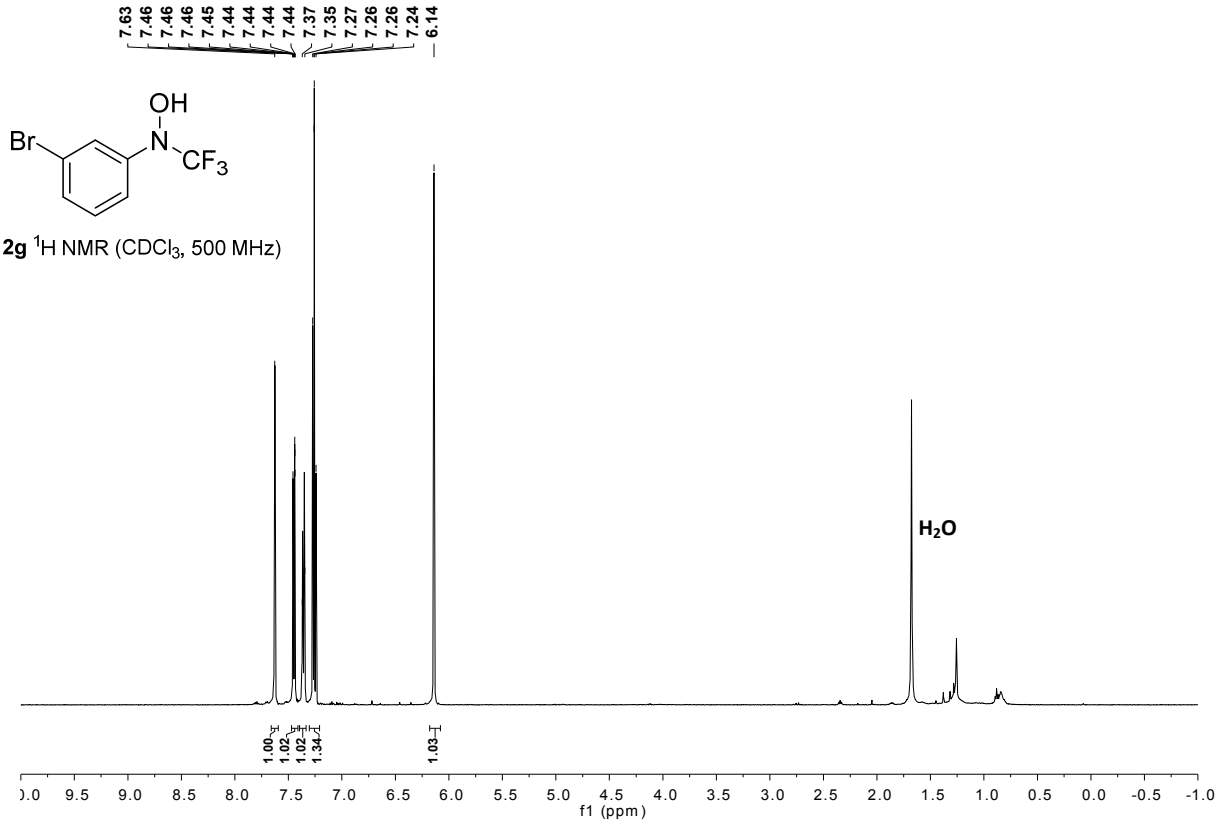
2f ^{1}H NMR ($CDCl_3$, 500 MHz)



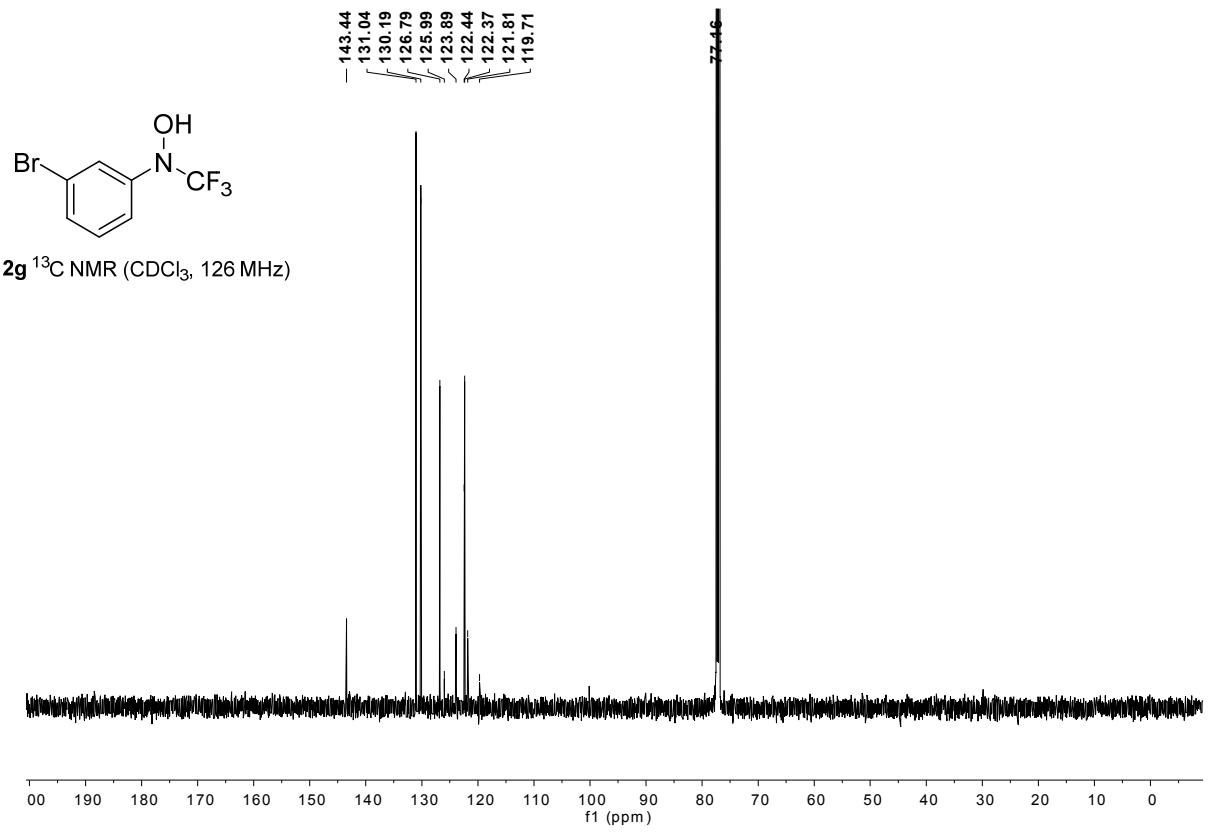
2f ^{13}C NMR ($CDCl_3$, 126 MHz)



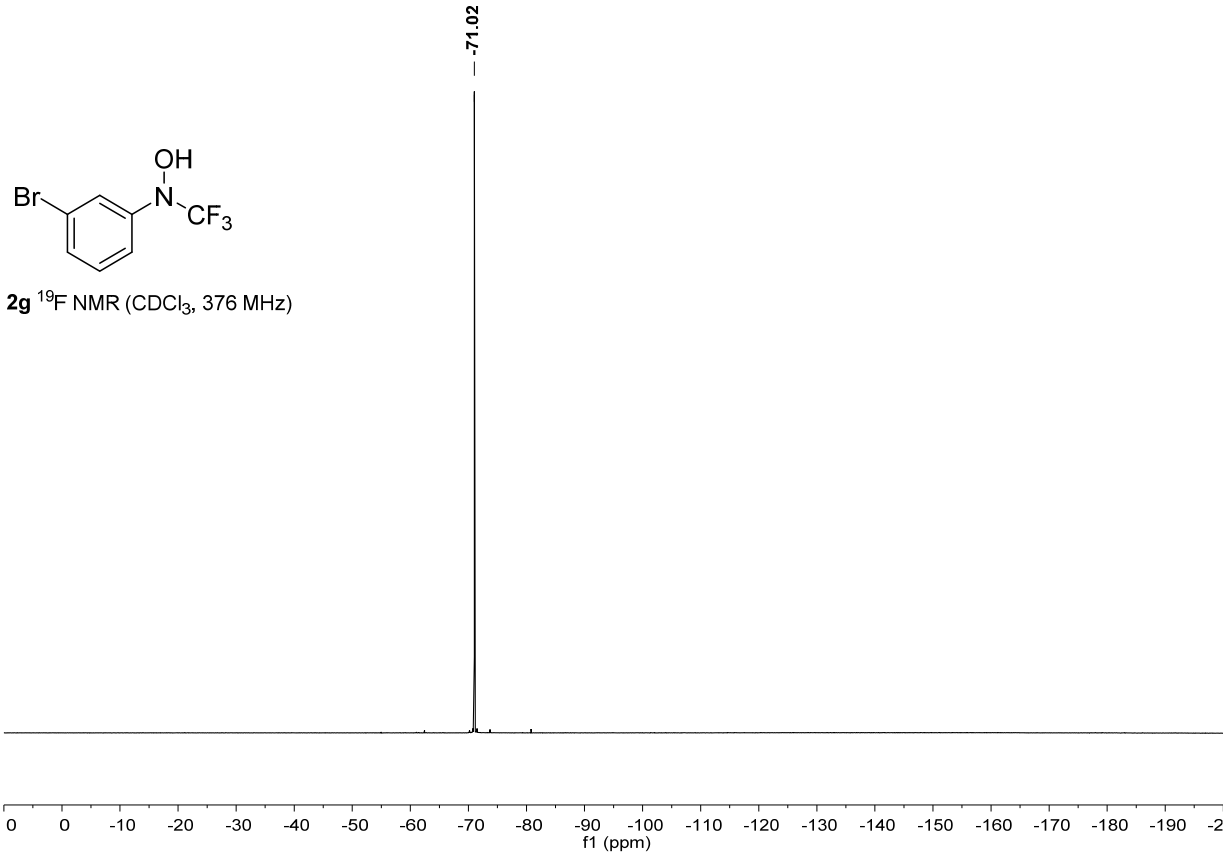
2f ^{19}F NMR ($CDCl_3$, 376 MHz)



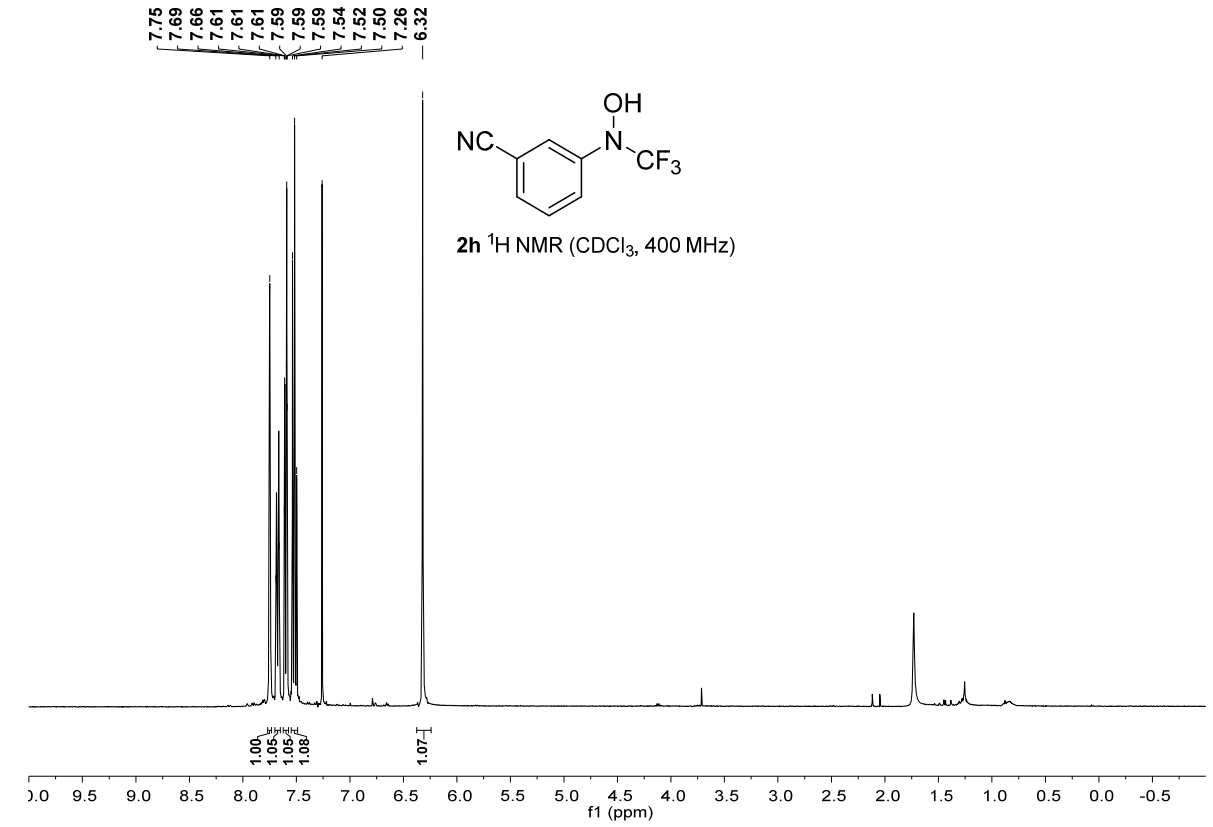
2g ^{1}H NMR ($CDCl_3$, 500 MHz)



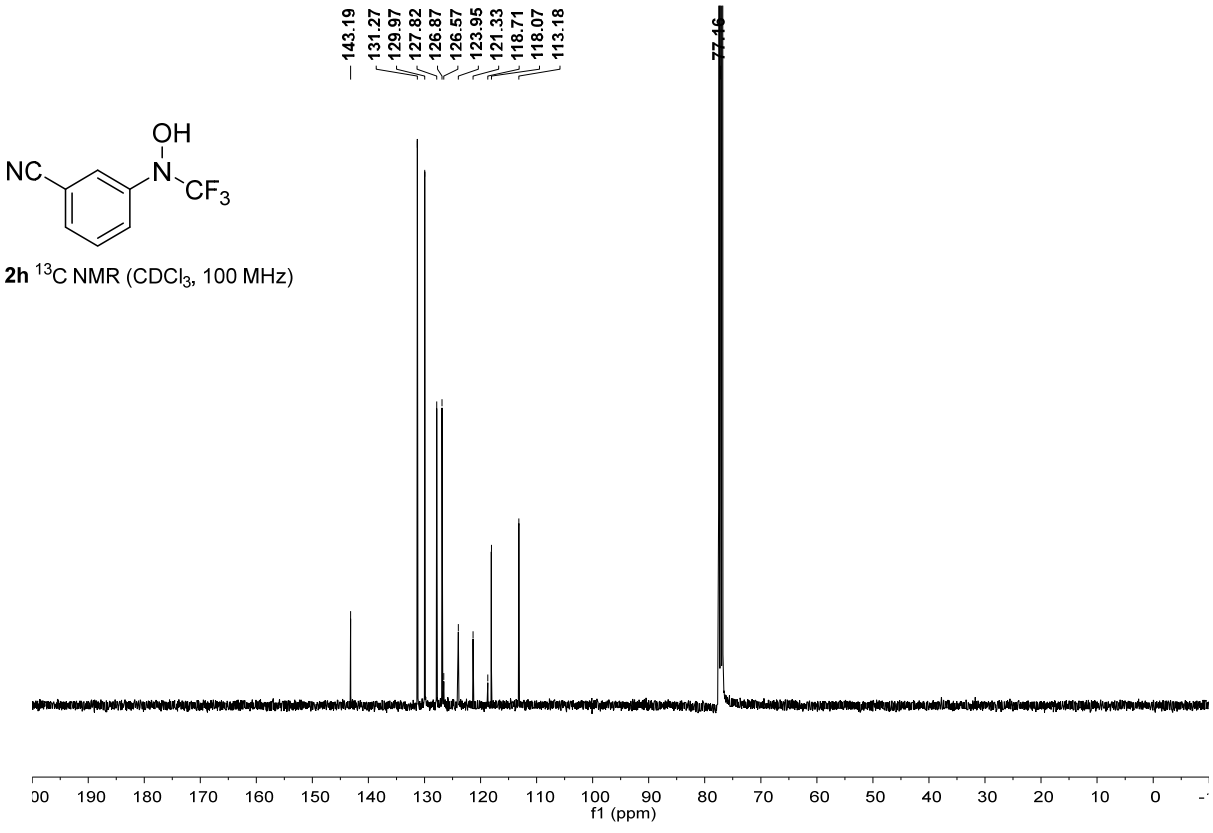
2g ^{13}C NMR ($CDCl_3$, 126 MHz)



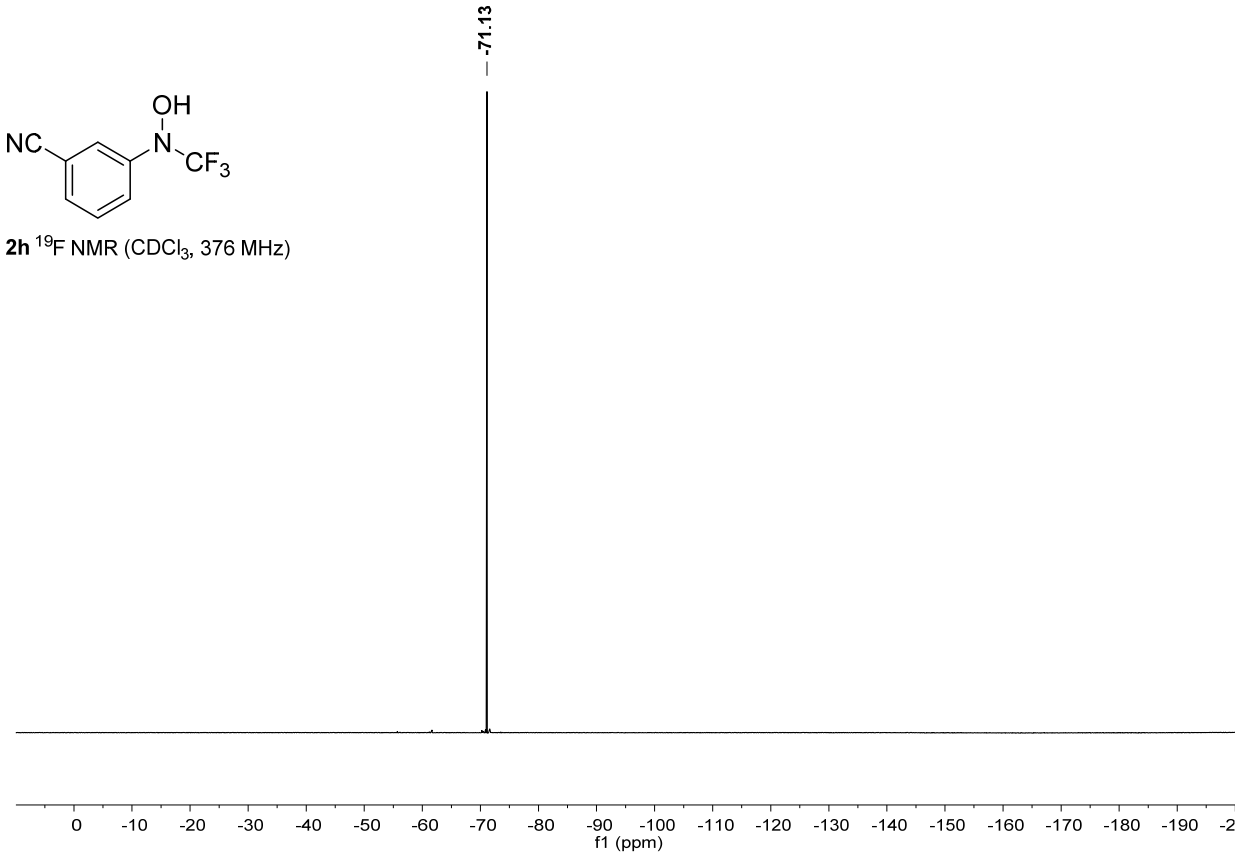
2g ^{19}F NMR ($CDCl_3$, 376 MHz)



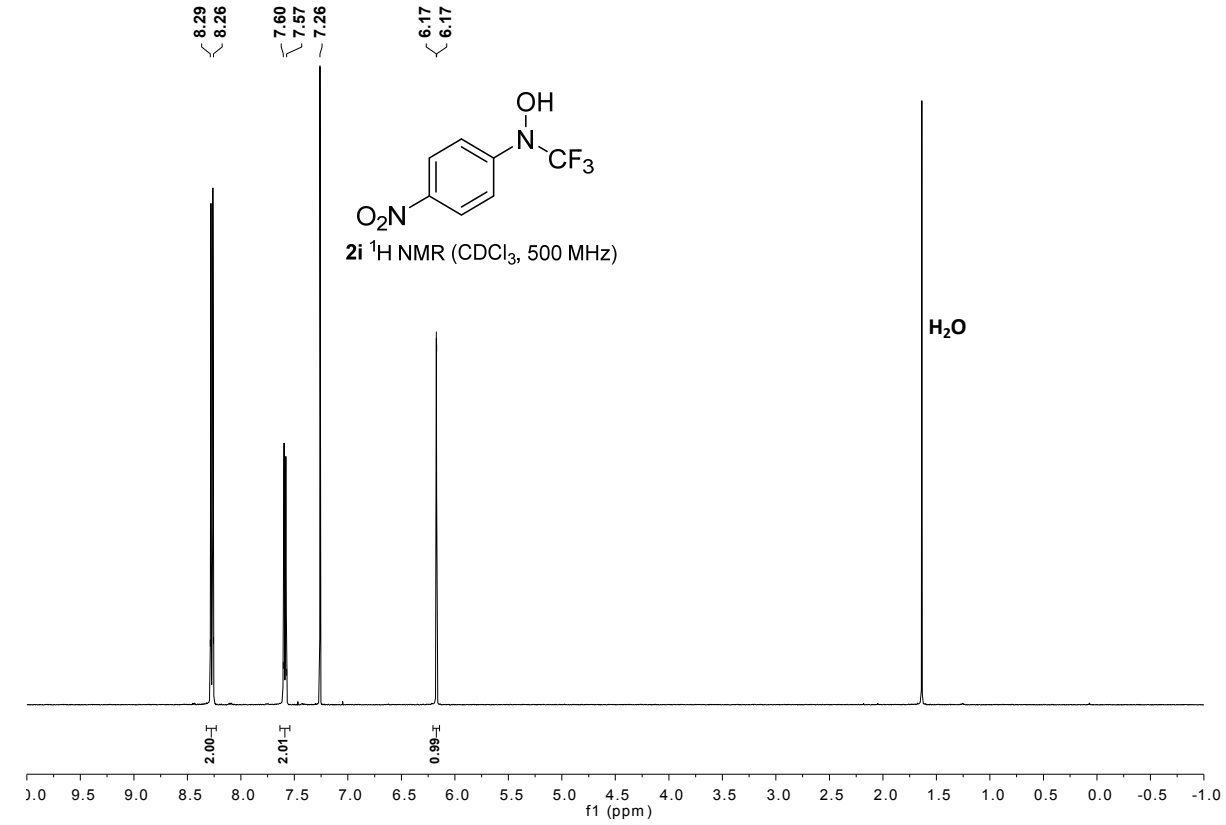
2h ^{1}H NMR ($CDCl_3$, 400 MHz)



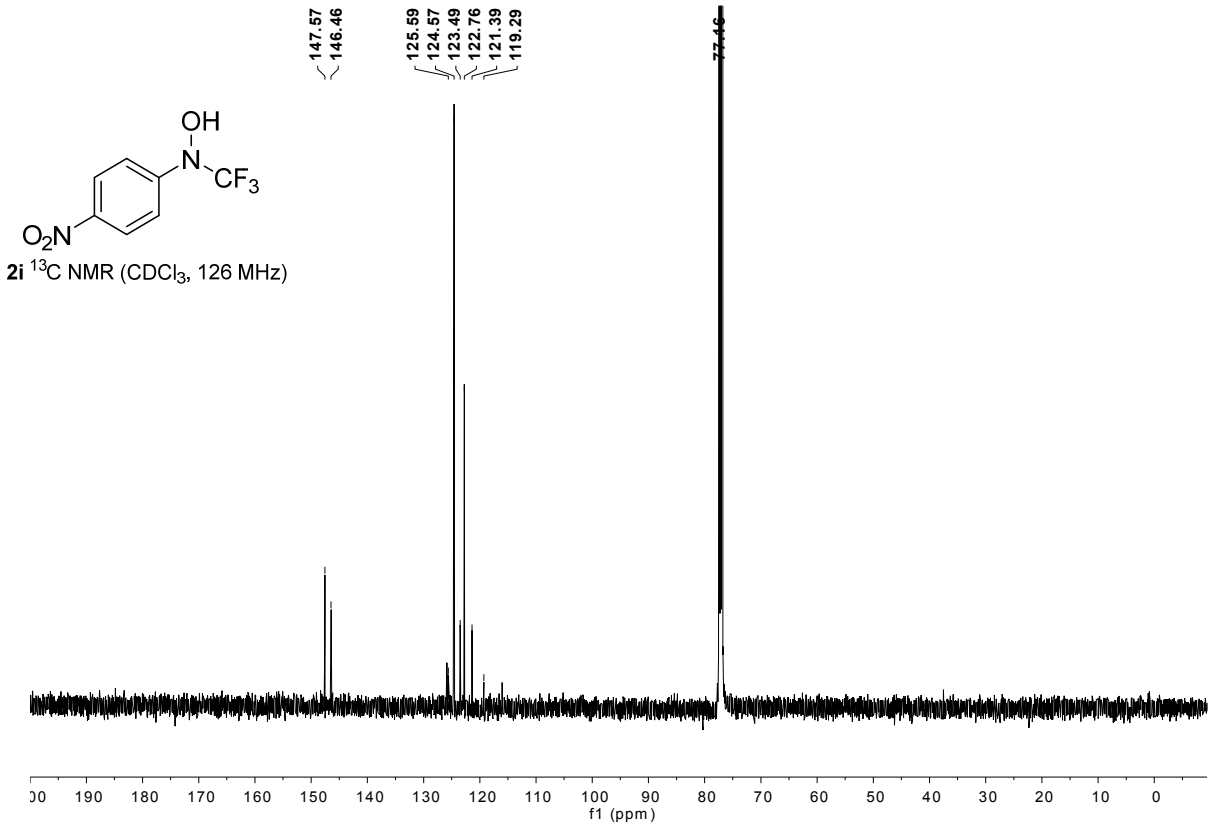
2h ^{13}C NMR ($CDCl_3$, 100 MHz)



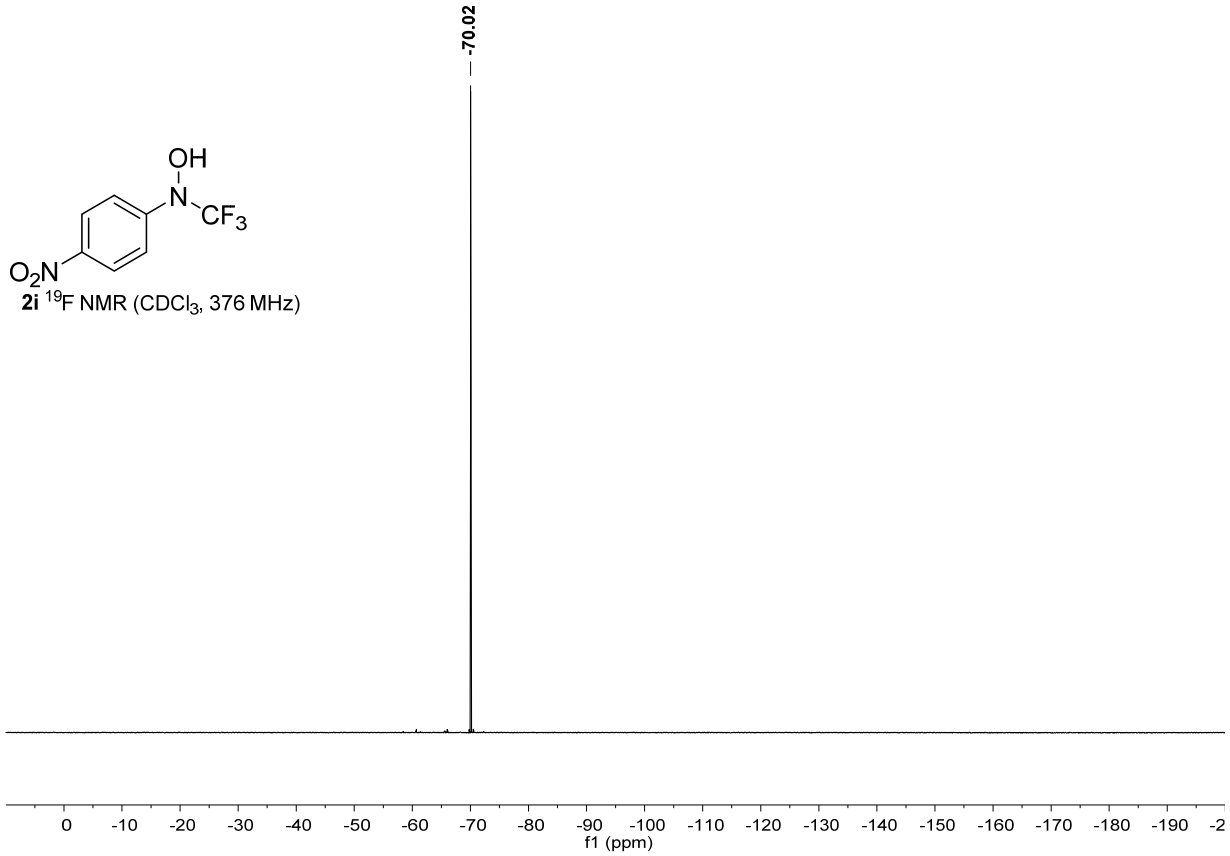
2h ^{19}F NMR ($CDCl_3$, 376 MHz)



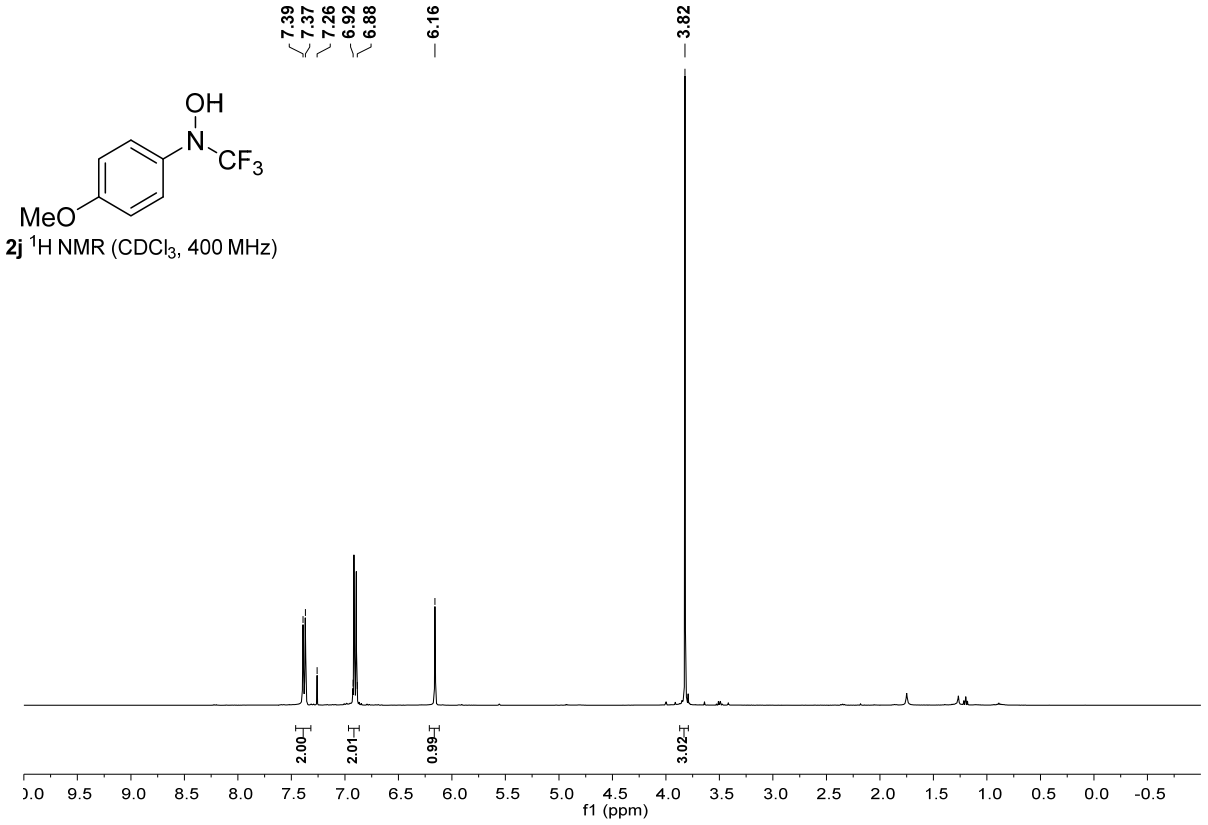
2i ^{1}H NMR ($CDCl_3$, 500 MHz)



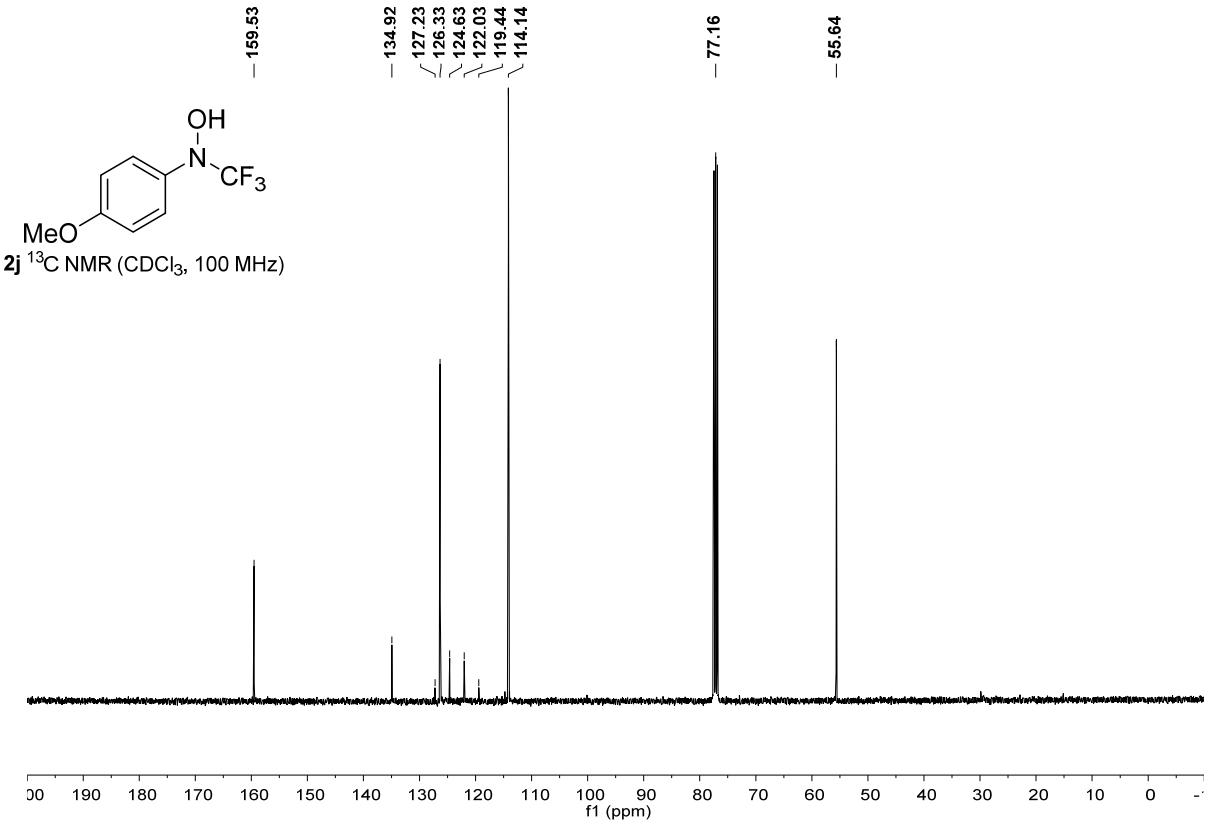
2i ^{13}C NMR ($CDCl_3$, 126 MHz)



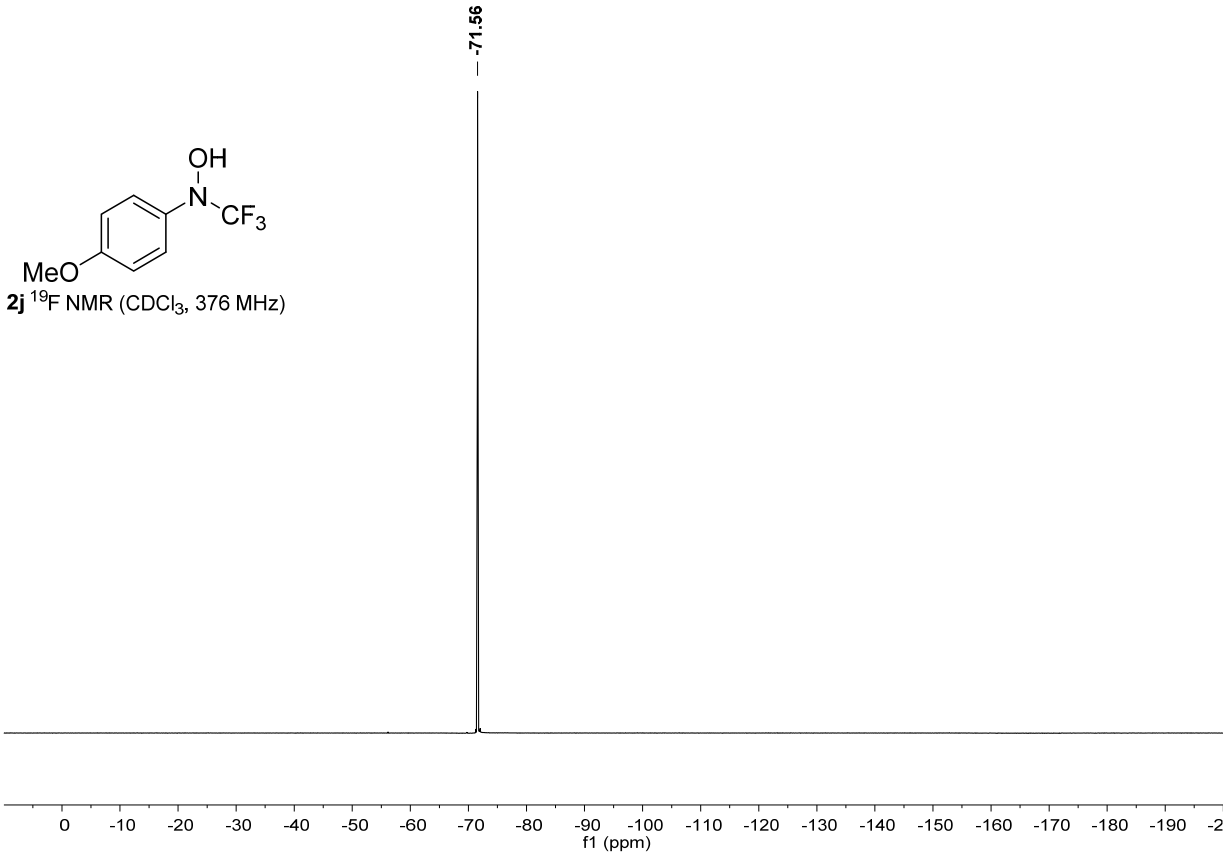
2i ^{19}F NMR ($CDCl_3$, 376 MHz)



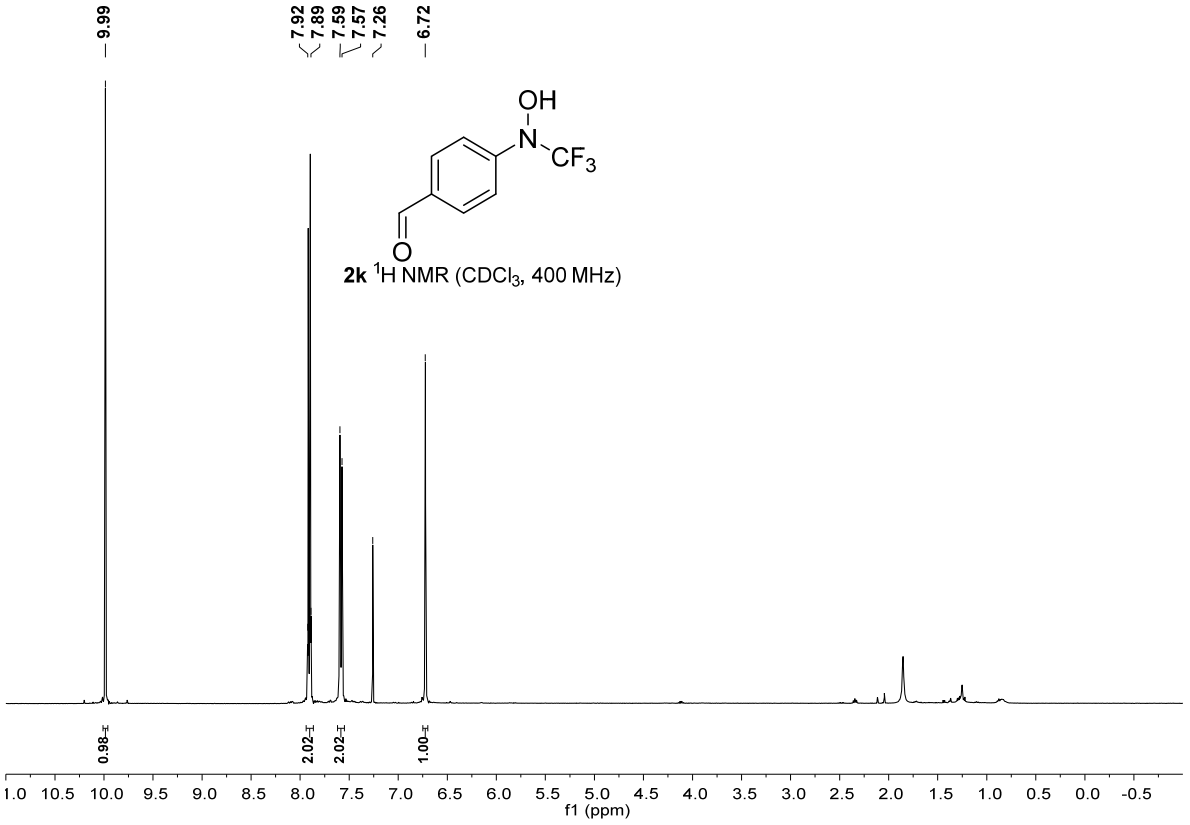
2j ^{1}H NMR ($CDCl_3$, 400 MHz)



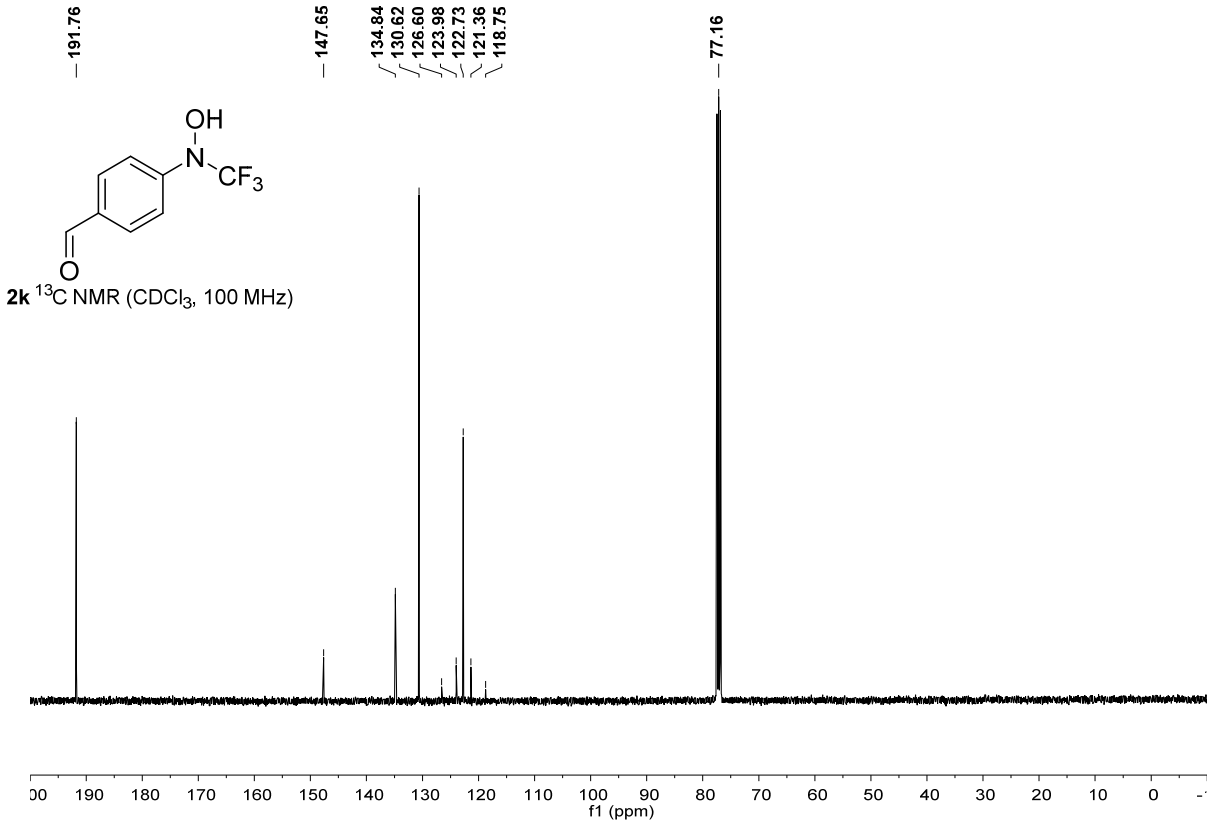
2j ^{13}C NMR ($CDCl_3$, 100 MHz)



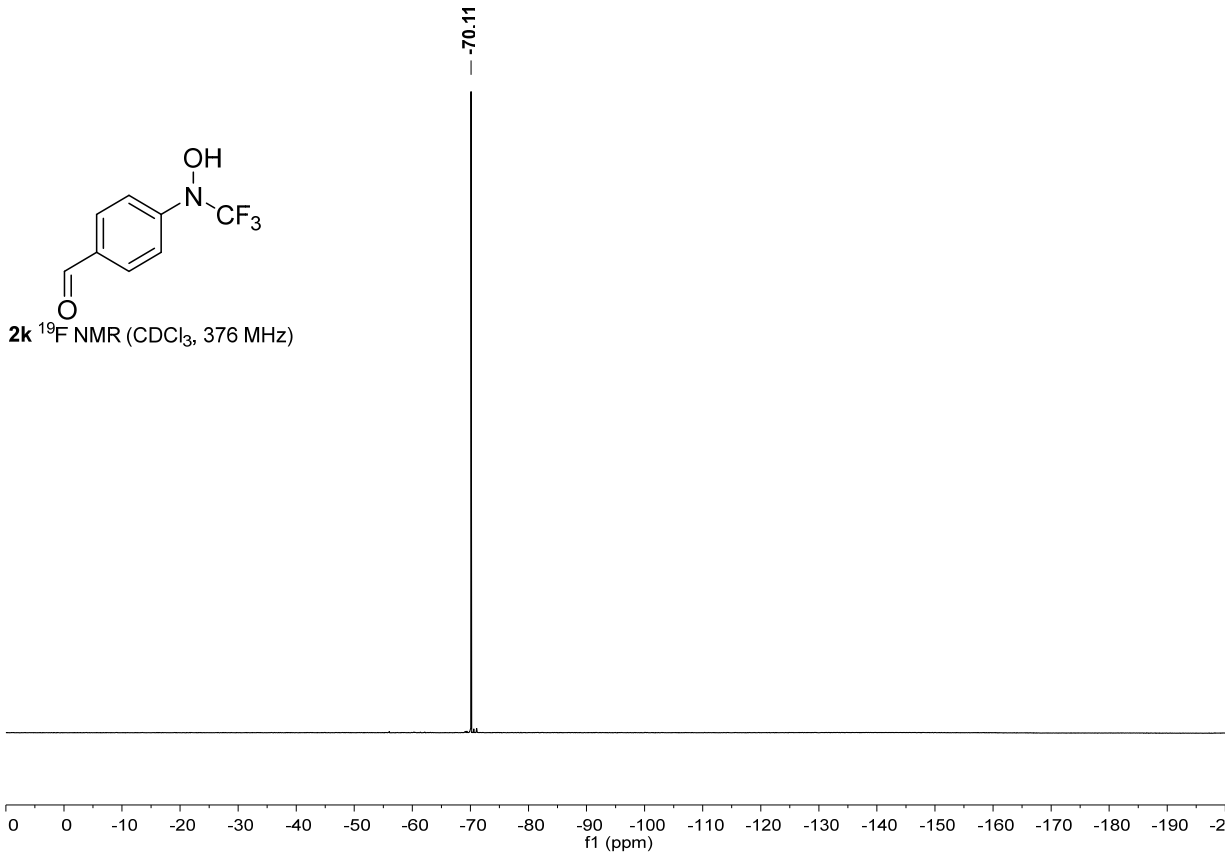
2j ^{19}F NMR ($CDCl_3$, 376 MHz)



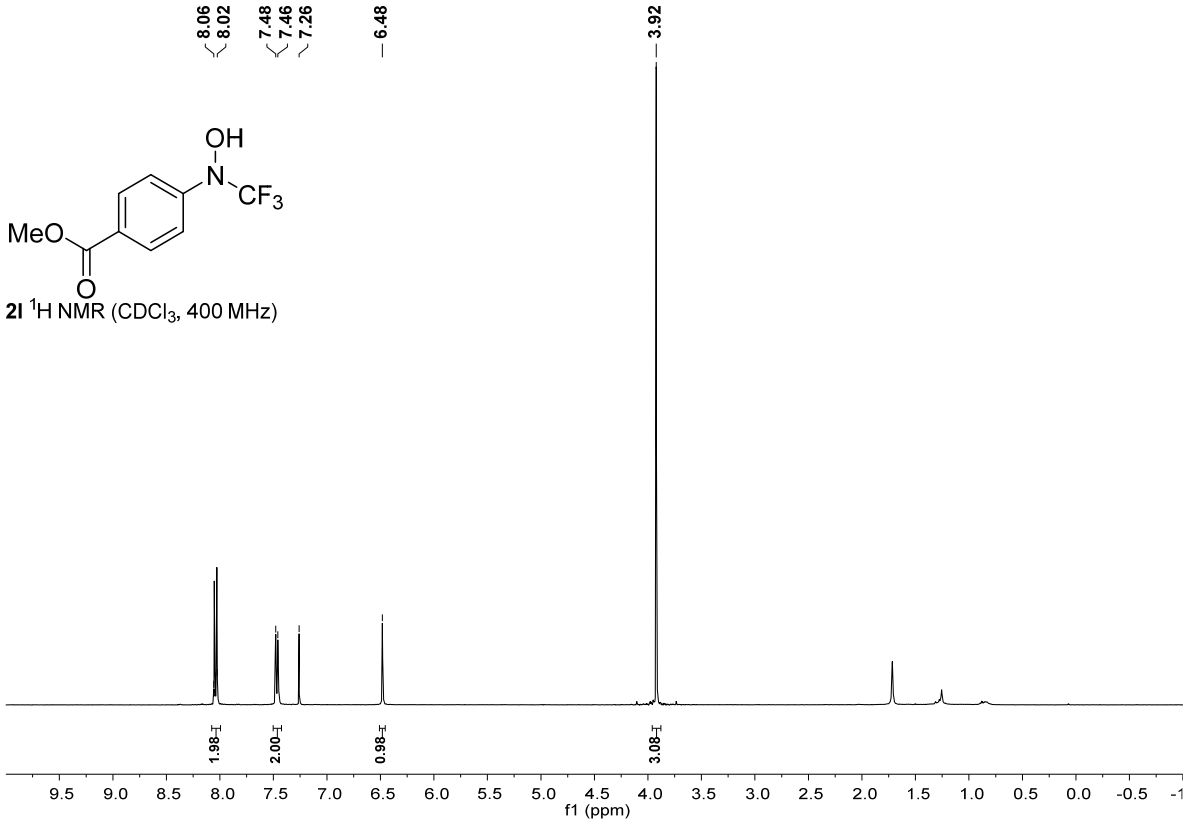
2k ^{1}H NMR ($CDCl_3$, 400 MHz)



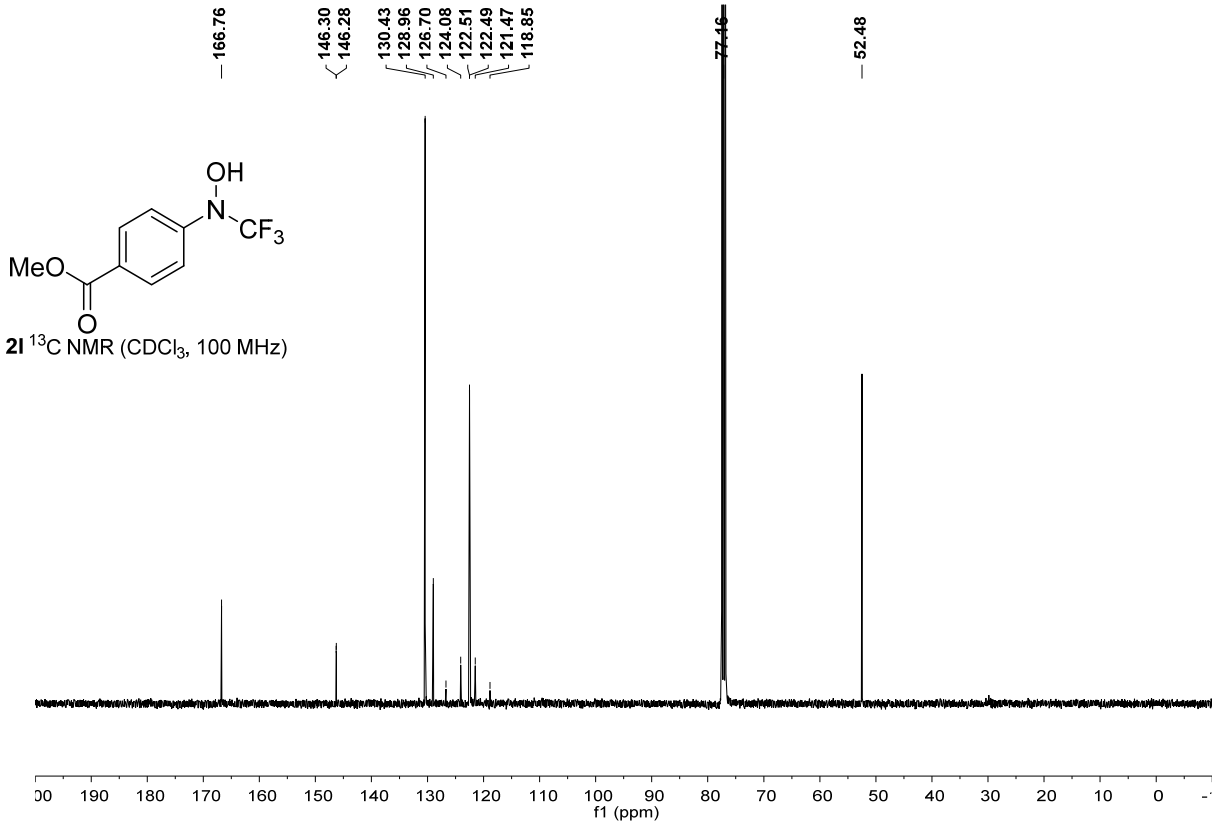
2k ^{13}C NMR ($CDCl_3$, 100 MHz)



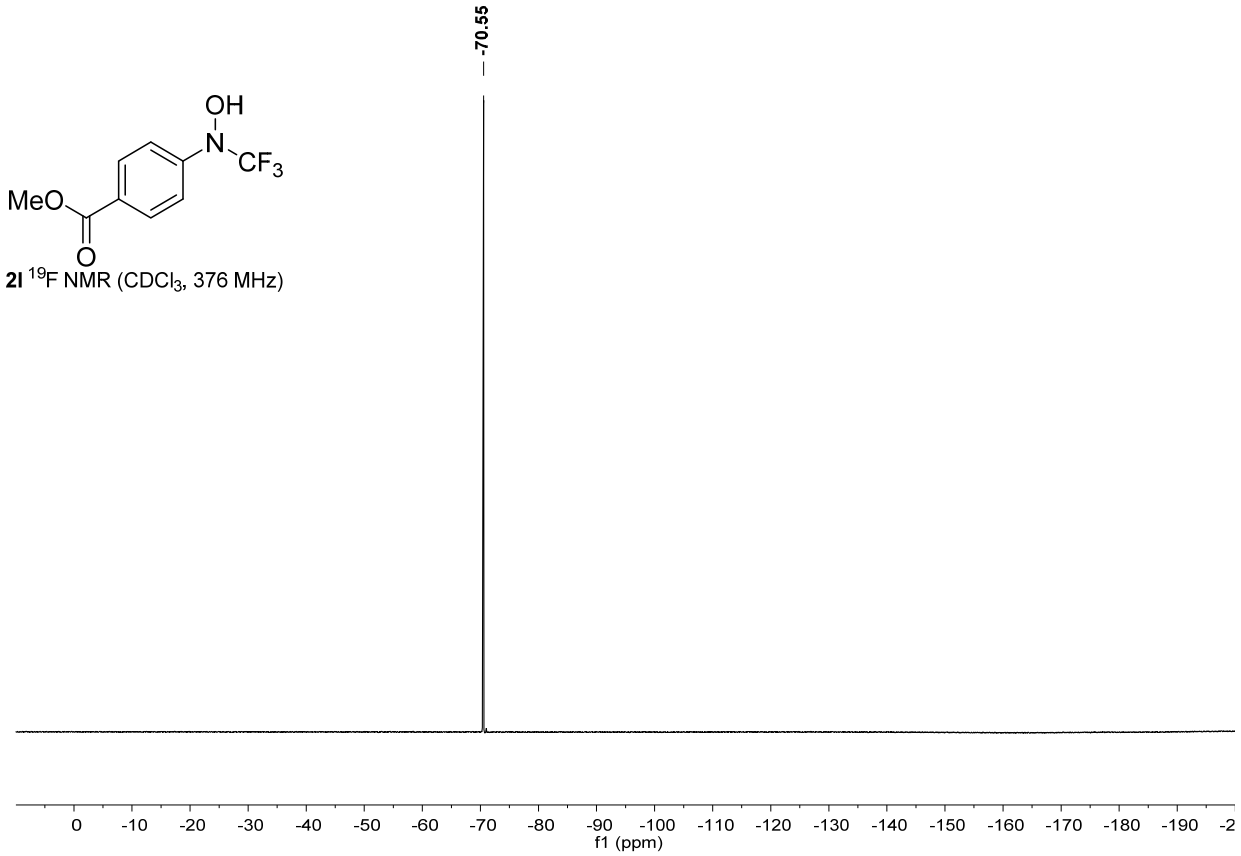
2k ^{19}F NMR ($CDCl_3$, 376 MHz)



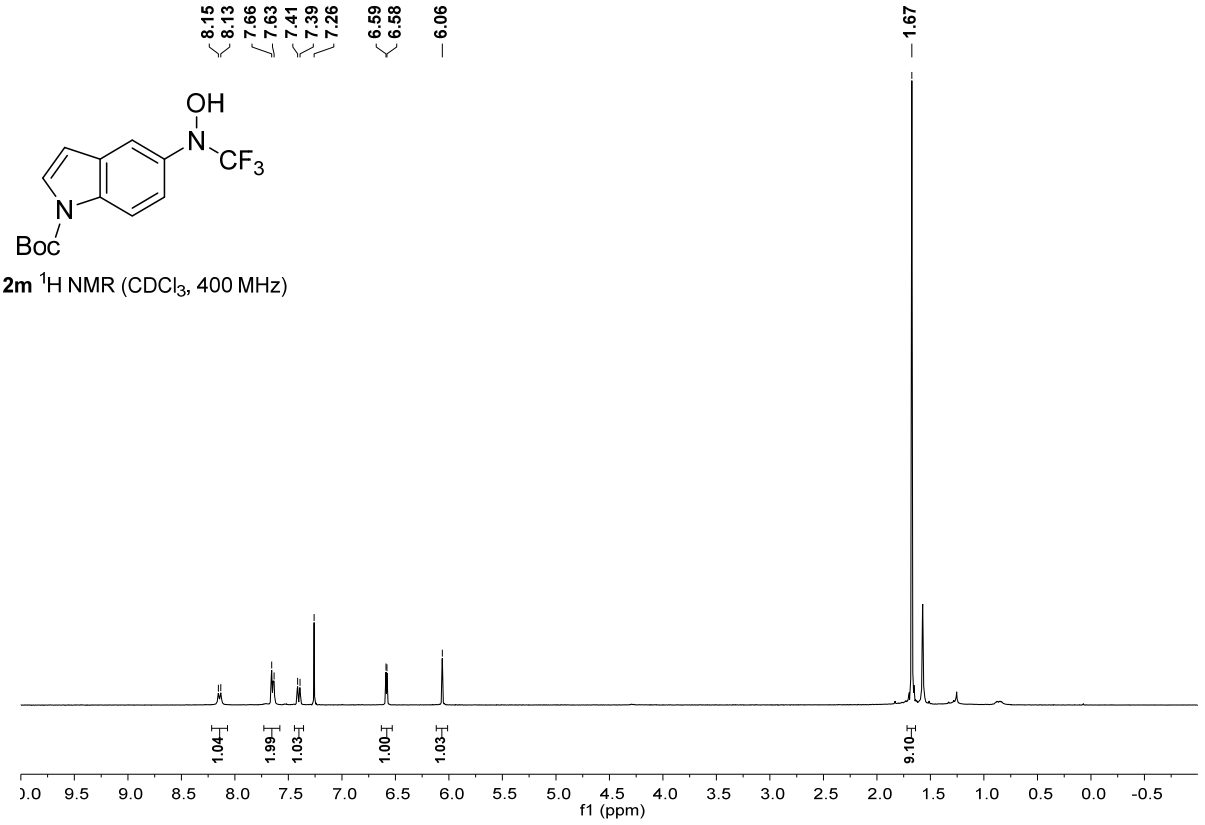
2l ^{1}H NMR ($CDCl_3$, 400 MHz)



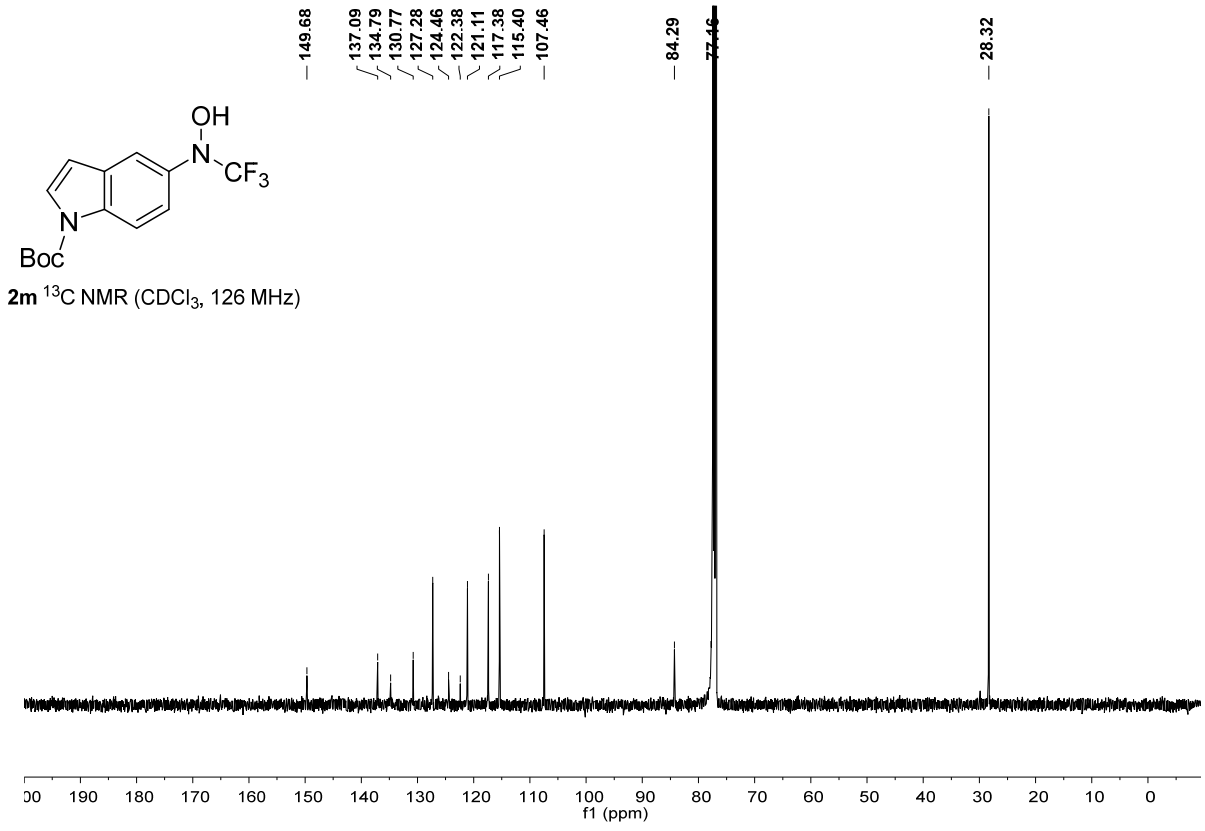
2l ^{13}C NMR ($CDCl_3$, 100 MHz)



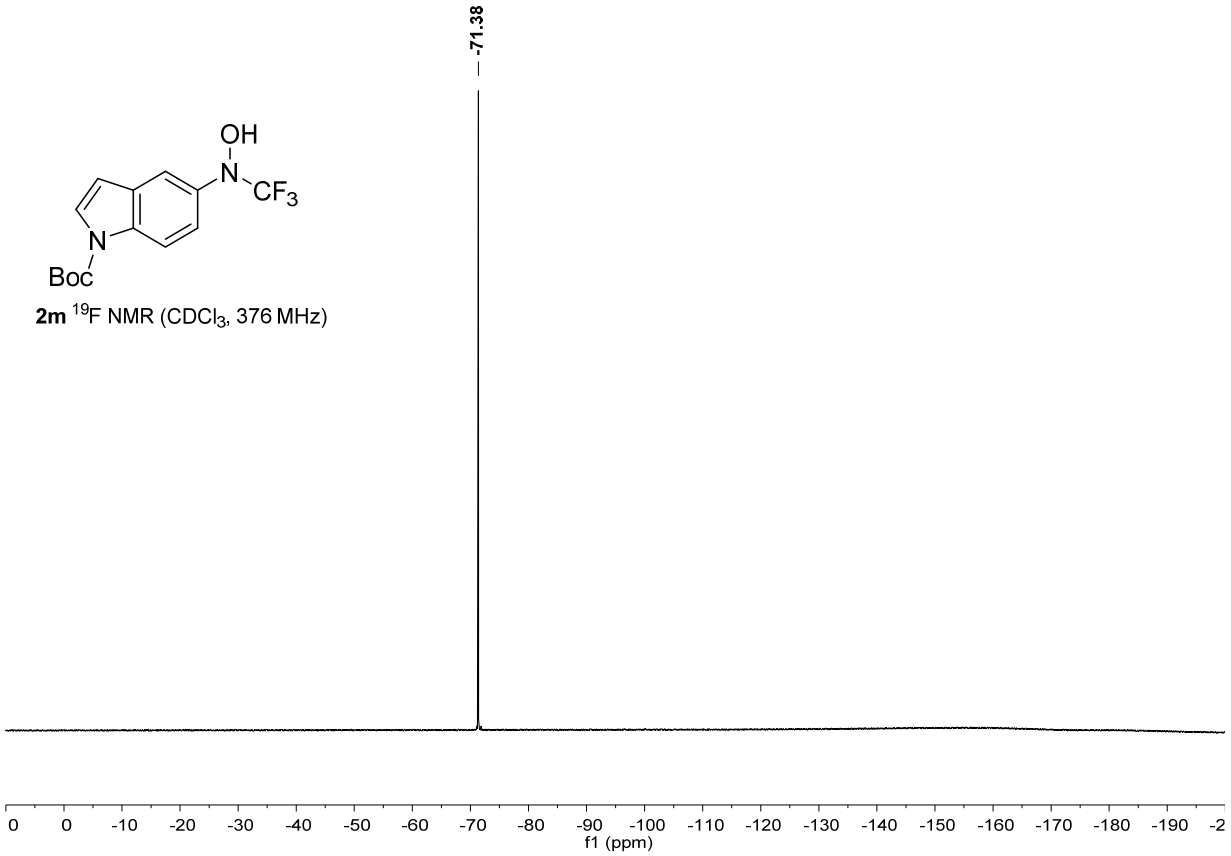
2l ^{19}F NMR ($CDCl_3$, 376 MHz)



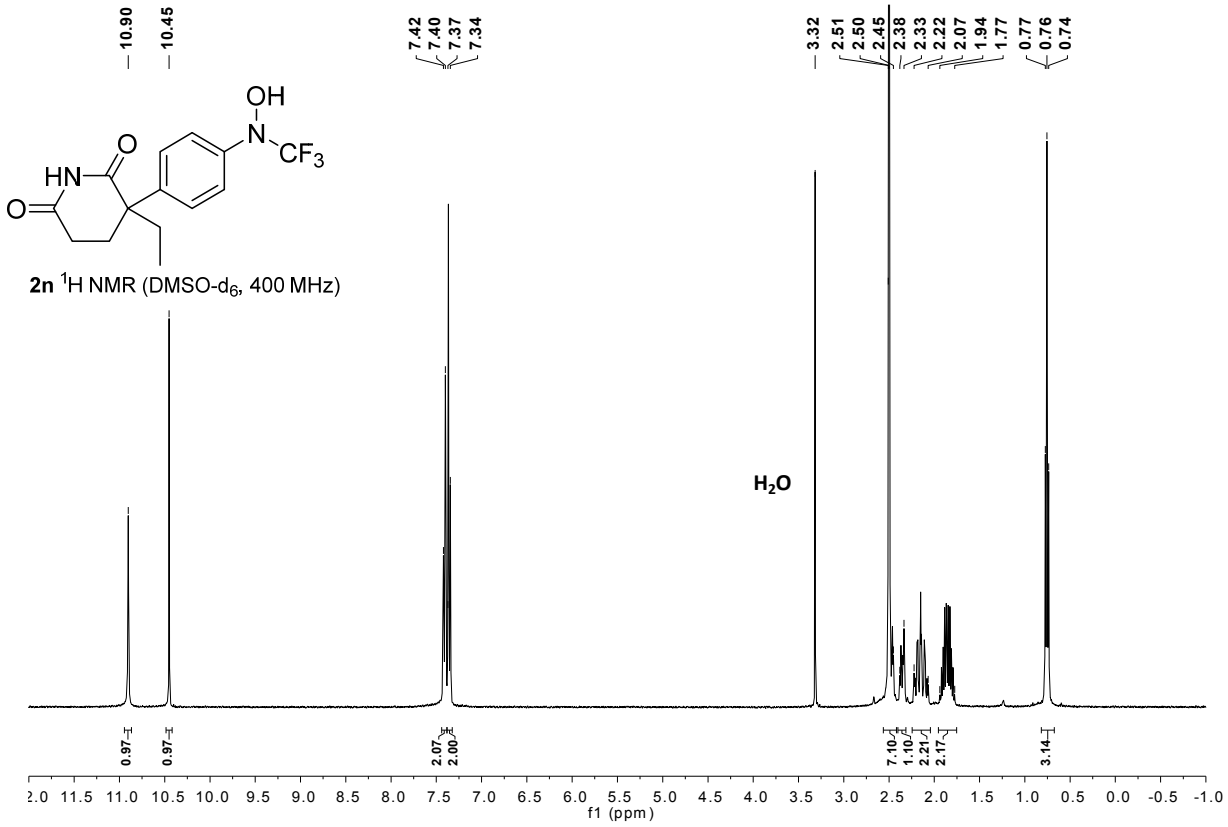
2m ^{1}H NMR ($CDCl_3$, 400 MHz)



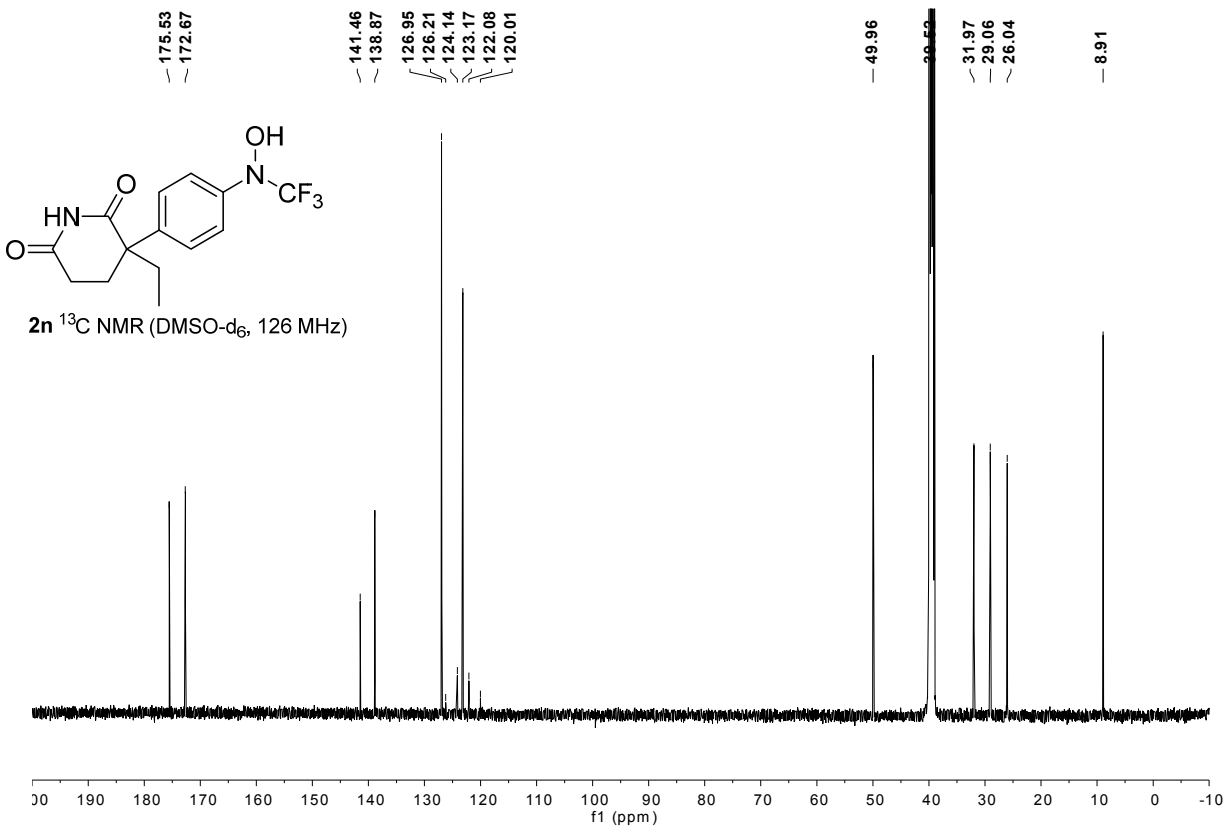
2m ^{13}C NMR ($CDCl_3$, 126 MHz)



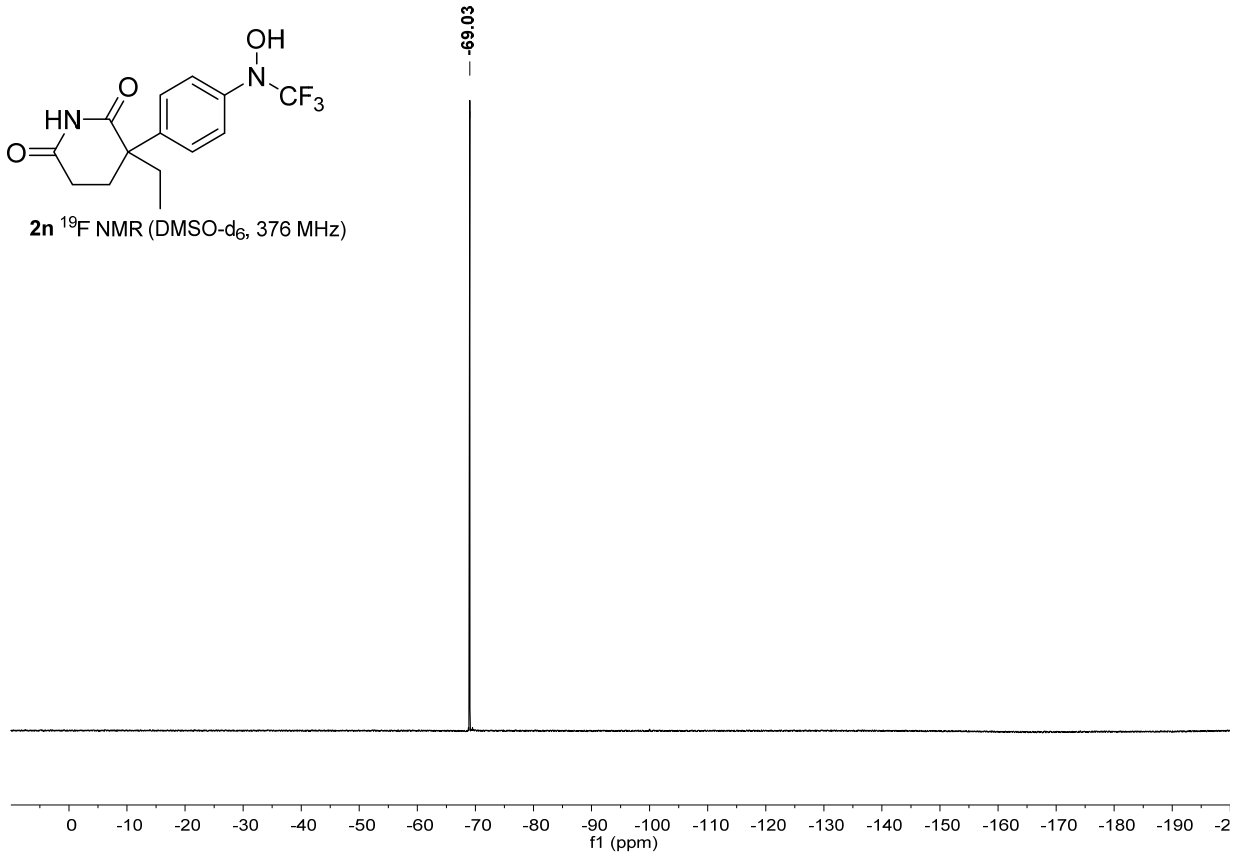
2m ^{19}F NMR ($CDCl_3$, 376 MHz)



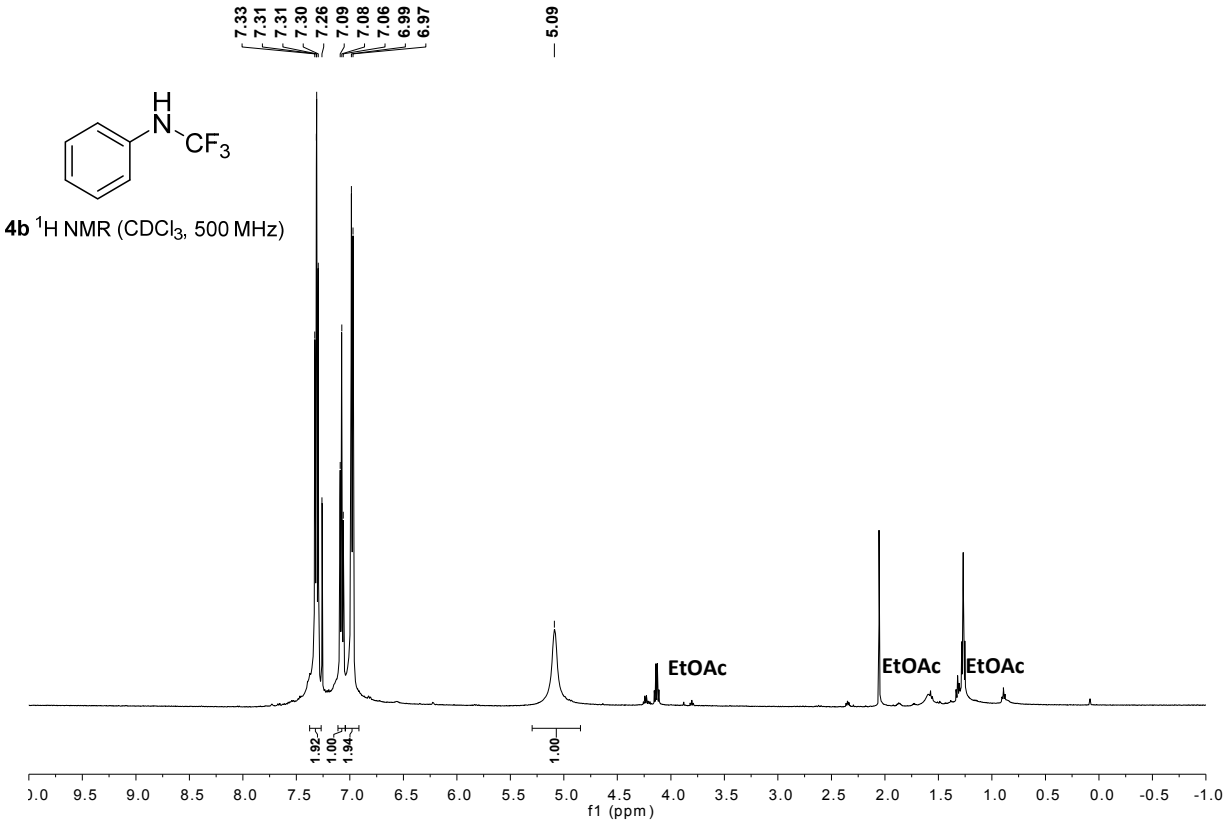
2n ^{1}H NMR (DMSO-d_6, 400 MHz)



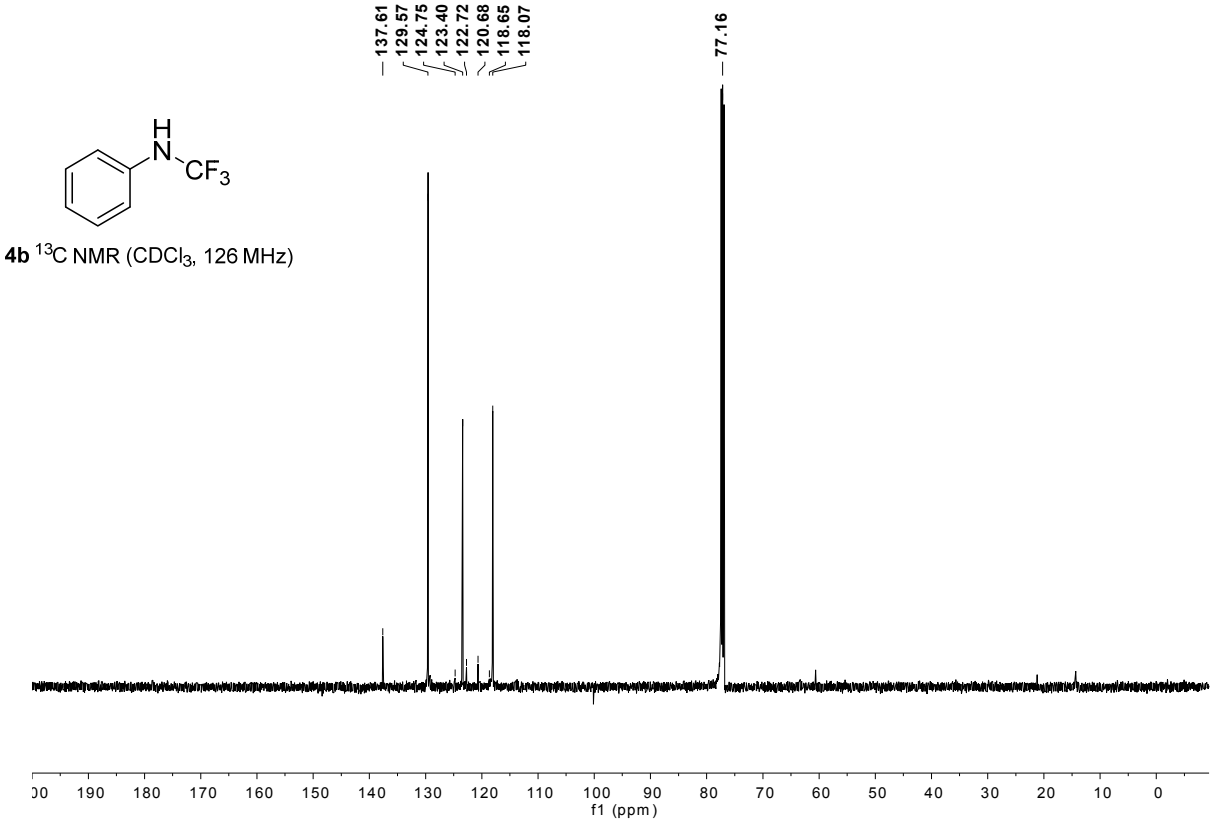
2n ^{13}C NMR (DMSO-d_6, 126 MHz)



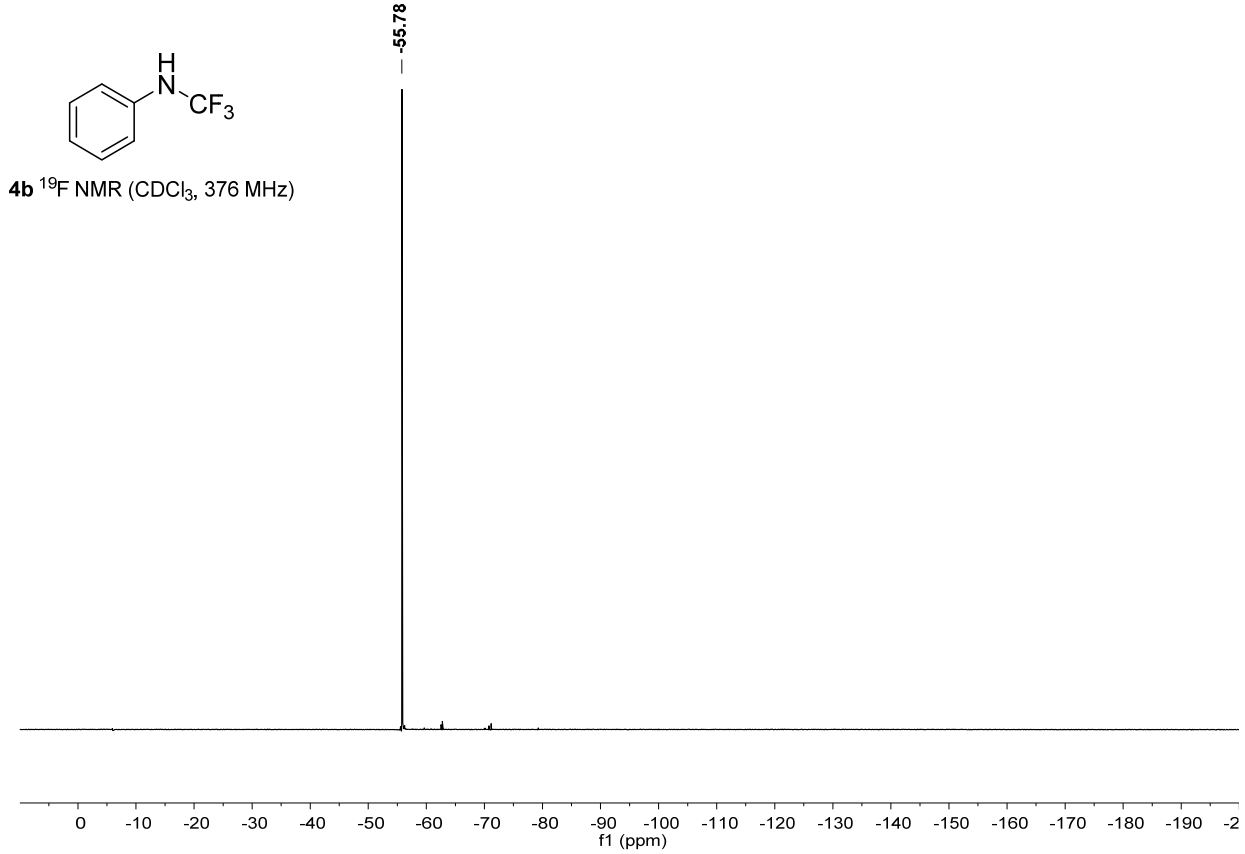
2n ^{19}F NMR (DMSO-d_6, 376 MHz)



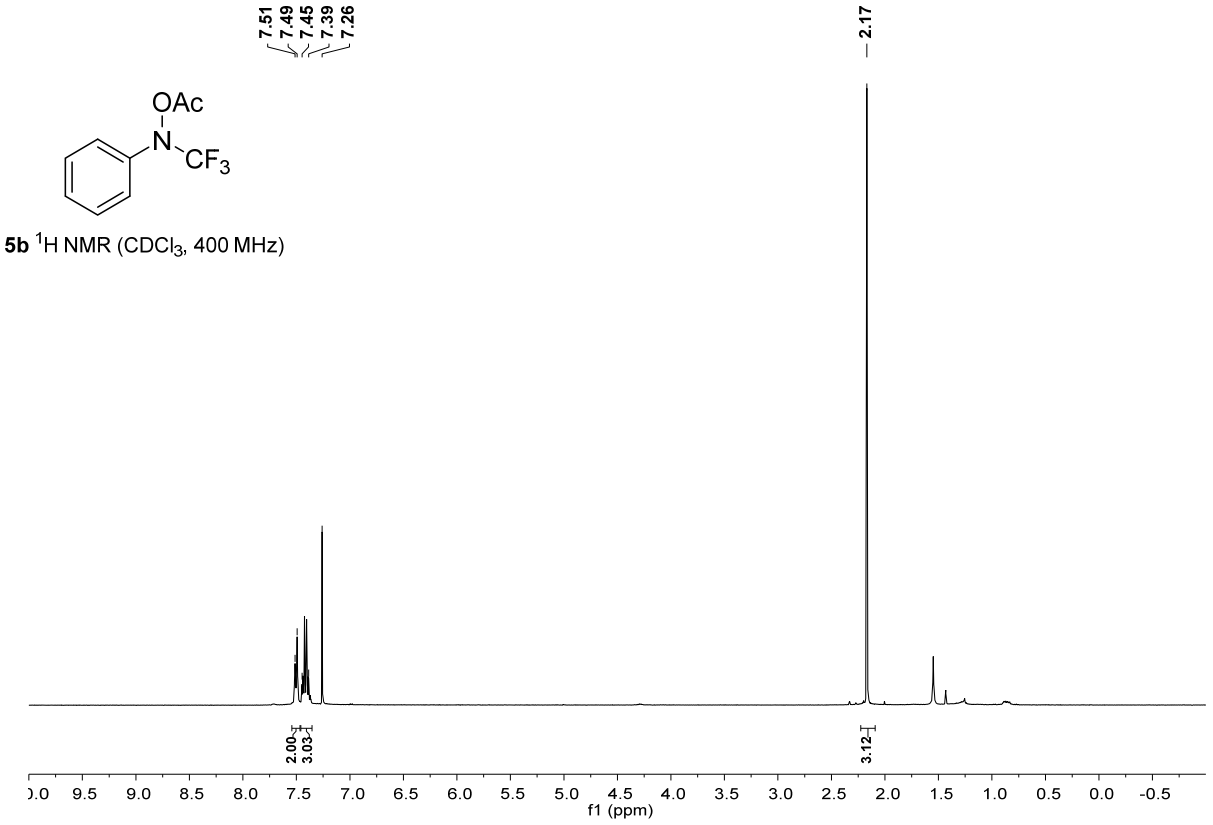
4b ^{1}H NMR ($CDCl_3$, 500 MHz)



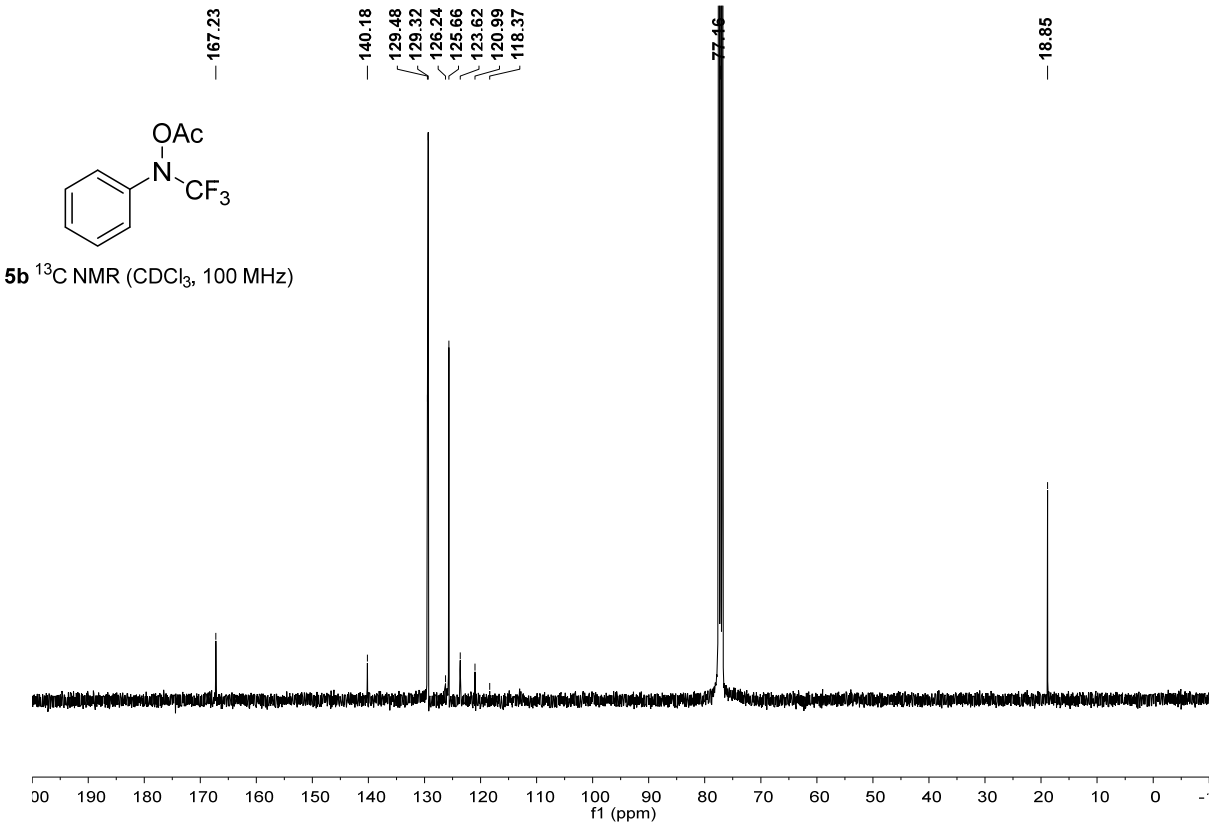
4b ^{13}C NMR ($CDCl_3$, 126 MHz)



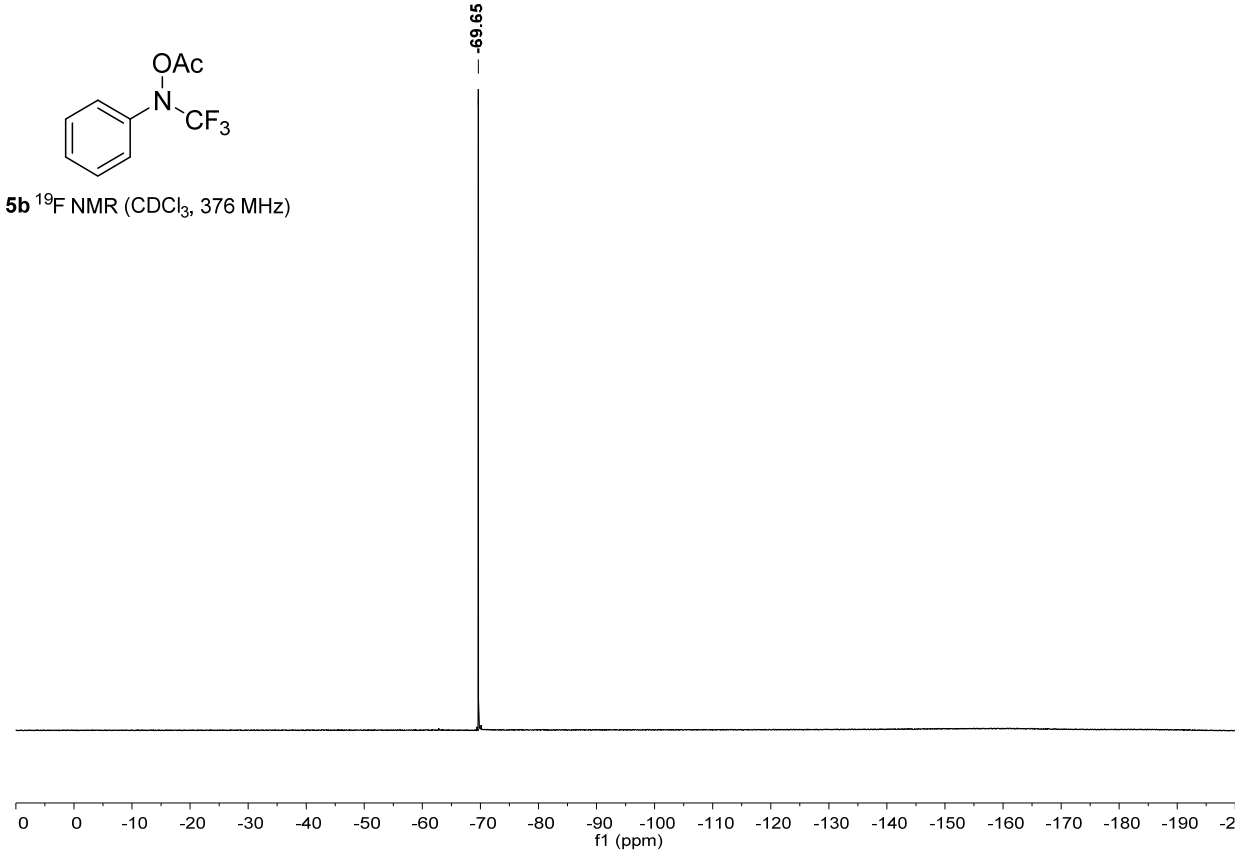
4b ^{19}F NMR ($CDCl_3$, 376 MHz)



5b ^{1}H NMR ($CDCl_3$, 400 MHz)



5b ^{13}C NMR ($CDCl_3$, 100 MHz)



5b ^{19}F NMR ($CDCl_3$, 376 MHz)

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