Supporting Information

Deoxygenative Functionalization of Trifluoromethyl Ketones

Shuhei Shimoyama,[a] Miki B. Kurosawa,[a] and Junichiro Yamaguchi*[a]

[a] *Department of Applied Chemistry, Waseda University, 513 Wasedatsurumakicho, Shinjuku, Tokyo 162-0041 Japan.*

E-mail: junyamaguchi@waseda.jp (JY)

Table of Contents

1. General

Unless otherwise noted, all reactants or reagents including drying solvents were obtained from commercial suppliers and used as received. Diphenylphosphine oxide was purchased from BLD pharm. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU), magnesium turnings, mesitylene, tetrakis(triphenylphosphine)palladium(0), and thiophenol were purchased from KANTO Chemical. Lithium bis(trimethylsilyl)amide(1 M in toluene solution) and trimethylsilyl trifluoromethanesulfonate (TMSOTf), were purchased from Sigma-Aldrich (Note: TMSOTf was found to lose activity upon prolonged storage; therefore, freshly opened reagent was used in all experiments.). Allyltrimethylsilane, benzoic acid, diethyl phosphite, 4,4′-di-tert-butyl-2,2′-bipyridyl, methallyltrimethylsilane, *N*-methyl-*p*-toluenesulfonamide, nickel(II) bromide ethylene glycol dimethyl ether complex, phenyl triflimide, sodium formate, *p*-toluenethiol, thiobenzoic acid, thiophene, trifluoromethanesulfonic acid, 1-(trimethylsilyloxy)cyclohexene, 2,2,2-trifluoro-1-(4-methoxyphenyl)ethan-1-one (**1A**), 2,2,2-trifluoro-1-phenylethan-1-one (**1B**), 2,2,2-trifluoro-1-(*p*-tolyl)ethan-1-one (**1C**), 1-(4-chlorophenyl)-2,2,2-trifluoroethan-1-one (**1G**) were purchased from Tokyo Chemical Industry (TCI). Zinc cyanide was purchased from FUJIFILM Wako Pure Chemical Corporation. 1-(4-(*tert*-butyl)phenyl)-2,2,2-trifluoroethan-1-one (**1D**),[1] 1-(3,5-dimethylphenyl)-2,2,2-trifluoroethan-1-one (**1E**),[2] 1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one (**1F**),[3] 2,2,2-trifluoro-1-(4-morpholinophenyl)ethan-1-one (**1H**),[1] 1-(benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethan-1-one (**1I**),[1] 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one (**1J**),[1] 2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one (**1K**),[1] 1-(benzo[*b*]thiophen-2-yl)-2,2,2-trifluoroethan-1-one (**1L**),[1] 2,2,3,3,3-pentafluoro-1-phenylpropan-1-one (**1U**),[4] 2,2-difluoro-1-phenylethan-1-one (**1V**),[1] 2,2,2-trichloro-1-phenylethan-1-one (**1W**),[5] and 2,2,2-tribromo-1-phenylethan-1-one (**1X**)[6] were synthesized according to procedures and the spectra matched with those of compounds reported in the literature. Unless otherwise noted, all reactions were performed with drying solvents under an atmosphere of N_2 in dried glassware using standard vacuum-line techniques. All reactions were performed in 8-mL glass vessel tubes equipped with a screw cap and heated (IKA Plate RCT digital) in a 16-well aluminum reaction block (IKA DB4.3 Block) unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents under air unless otherwise noted.

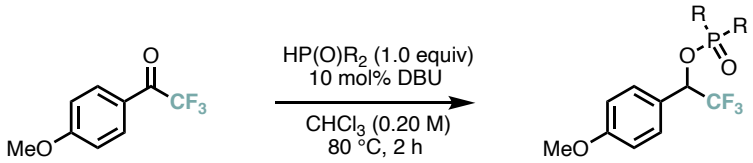
Analytical thin-layer chromatography (TLC) was performed using Silica-gel 70 TLC Plate-Wako (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with Biotage Isolera® equipped with Biotage Sfär Cartridge Silica D columns. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. High-resolution mass spectra (HRMS) were conducted on Thermo Fisher Scientific ExactivePlus Orbitrap (ESI) and Bruker Compact QTOF (APCI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS-400 (^{1}H 400 MHz, ^{13}C 101 MHz, ^{31}P 162 MHz, ^{19}F 376 MHz) and JEOL JNM-ECZ-400 (^{1}H 400 MHz, ^{13}C 101 MHz, ^{31}P 162 MHz, ^{19}F 376 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative

to tetramethylsilane (δ 0.00 ppm). Chemical shifts for $^{13}C\{^{1}H\}$ NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Chemical shifts for ^{31}P NMR are expressed in ppm relative to H_3PO_4 (δ 0.00 ppm) as an external standard. Chemical shifts for ^{19}F NMR are expressed in ppm relative to fluorobenzene (δ –113.15 ppm) as an internal standard. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LaboACE LC-5060 instrument equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent.

Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, tq = triplet of quartets, qd = quartet of doublets, qt = quartet of triplets, ddd = doublet of doublets of doublets, ddt = doublet of doublets of triplets, ddq = doublet of doublets of quartets, dtd = doublet of triplets of doublets, dqd = doublet of quartets of doublets, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration.

2. Optimization of Reaction Conditions

2.1. Pudovik Addition/Phospha-Brook Rearrangement of 1A

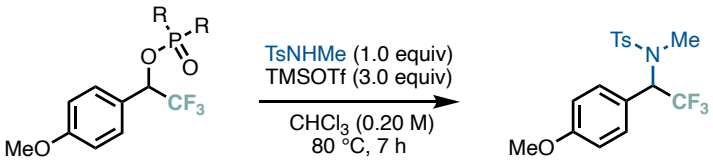


1A (0.20 mmol) **2**

entry	products	R	yield of **2** /%	recovery of **1** /%
1	**2A**	Ph	59	30
2	**2A'**	OEt	quant.	0

Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard.

2.2. Benzylic Substitution of 2

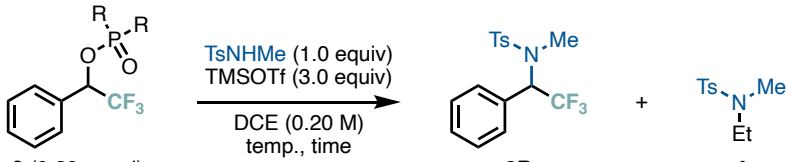


2 **3A**

entry	substrate	R	yield of **3A** /%	recovery of **2** /%
1	**2A**	Ph	77	0
2	**2A'**	OEt	82	0

Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard.

2.3. Re-examination with 3B

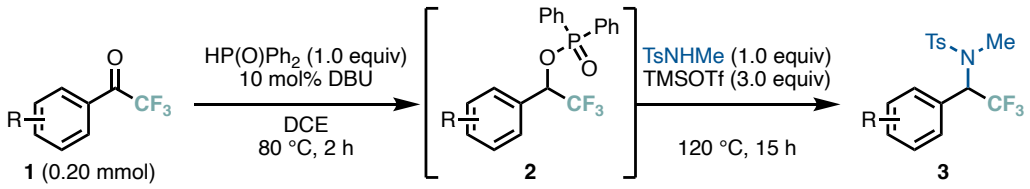


2 (0.20 mmol) **3B** **4**

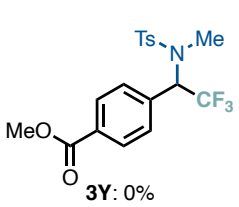
entry	substrate	R	temp. / °C	time / h	yield of **3B** /%	yield of **4** /%	recovery of **2** /%
1	**2B'**	OEt	80	7	0	87	0
2	**2B**	Ph	80	7	0	-	93
3	**2B**	Ph	120	7	50	-	32
4	**2B**	Ph	120	15	66	-	26

Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard.

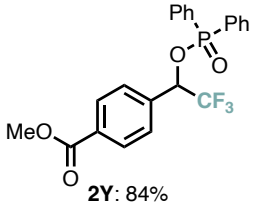
2.4. Electron-deficient Trifluoromethyl Ketones



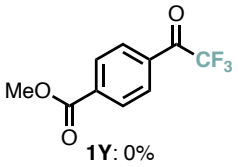
1 (0.20 mmol) **2** **3**



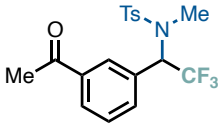
3Y: 0%



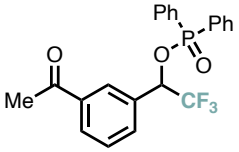
2Y: 84%



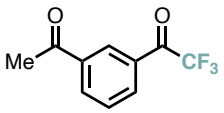
1Y: 0%



3Z: 0%

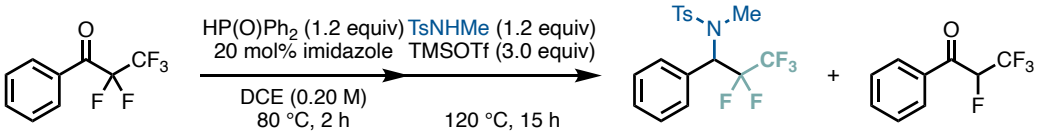


2Z: 53%



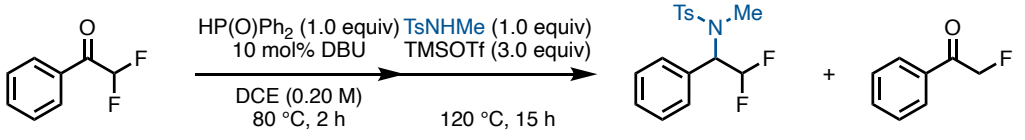
1Z: 0%

2.5. Other Fluorinated or Halogenated Ketones



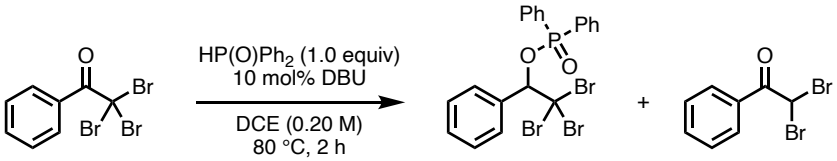
1U (0.20 mmol)
recovery 14%

3U: 41%(38%) 23%



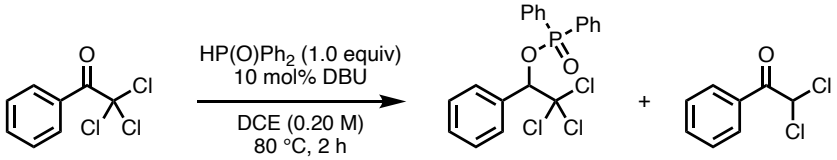
1V (0.20 mmol)
recovery 0%

3V: 0% 57%



1W (0.20 mmol)
recovery 0%

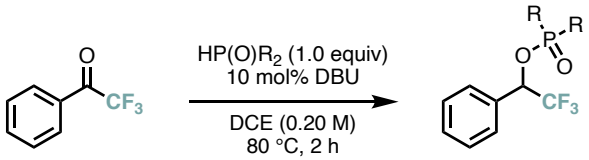
2W: 0% 66%



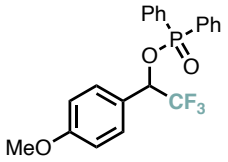
1X (0.20 mmol)
recovery 41%

2X: 0% 47%

3. Synthesis of Trifluoromethyl Phosphinate 2

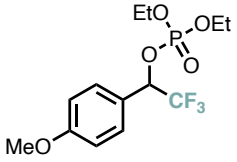


An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube was added phosphine oxide (1.0 equiv). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added trifluoromethylketone **1** (1.0 equiv), DBU (10 mol%), and 1,2-dichloroethane (0.20 M). The vessel was sealed with a screw cap and then heated at 80 °C for 2 h while its contents were being stirred. After the reaction mixture had been cooled to room temperature, the reaction mixture was concentrated *in vacuo*. The residue was purified by Isolera® to afford the corresponding product **2**.



2,2,2-Trifluoro-1-(4-methoxyphenyl)ethyl Diphenylphosphinate (2A)

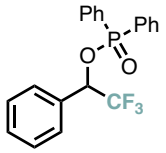
Reaction was conducted in 4 h. Purification by Isolera® (9:1 to 3:2 hexane/EtOAc) afforded **2A** as a colorless oil (0.50 mmol scale: 189.5 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 2H), 7.63–7.55 (m, 3H), 7.52–7.41 (m, 3H), 7.34–7.28 (m, 4H), 6.81 (d, J = 8.8 Hz, 2H), 5.65 (dq, $J_{H–P}$ = 10.8 Hz, $J_{H–F}$ = 6.4 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.6, 132.5 (d, $J_{C–P}$ = 2.9 Hz), 132.3 (d, $J_{C–P}$ = 2.9 Hz), 131.5 (d, $J_{C–P}$ = 10.7 Hz), 130.5 (d, $J_{C–P}$ = 136.2 Hz), 130.4 (d, $J_{C–P}$ = 138.1 Hz), 129.5, 128.5 (d, $J_{C–P}$ = 13.6 Hz), 128.2 (d, $J_{C–P}$ = 13.5 Hz), 123.5, 123.2 (qd, $J_{C–F}$ = 281.2 Hz, $J_{C–P}$ = 8.3 Hz), 113.8, 73.3 (qd, $J_{C–F}$ = 33.8 Hz, $J_{C–P}$ = 5.0 Hz), 55.1 (one peak is missing due to overlapping); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.7 (d, $J_{F–H}$ = 6.4 Hz); HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{21}H_{19}F_3O_3P$ 407.1018; Found 407.1008.



Diethyl (2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl) Phosphate (2A′)

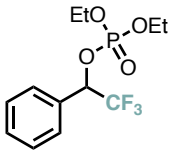
Purification by Isolera® (9:1 to 3:2 hexane/EtOAc) afforded **2A′** as a colorless oil (0.50 mmol scale: 168.9 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.54 (dq, $J_{H–P}$ = 10.0 Hz, $J_{H–F}$ = 6.4 Hz, 1H), 4.22–4.04 (m, 2H), 3.98–3.84 (m, 2H), 3.83 (s, 3H), 1.31

(td, J = 7.2 Hz, $J_{H–P}$ = 1.2 Hz, 3H), 1.15 (td, J = 7.2 Hz, $J_{H–P}$ = 1.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.8, 129.4, 123.3, 123.0 (qd, $J_{C–F}$ = 280.8 Hz, $J_{C–P}$ = 10.8 Hz), 113.9, 75.8 (qd, $J_{C–F}$ = 34.1 Hz, $J_{C–P}$ = 4.5 Hz), 64.3 (d, $J_{C–P}$ = 6.0 Hz), 64.1 (d, $J_{C–P}$ = 5.7 Hz), 55.1, 15.7 (d, $J_{C–P}$ = 7.5 Hz), 15.6 (d, $J_{C–P}$ = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ –2.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –77.4 (d, $J_{F–H}$ = 6.4 Hz); HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{13}H_{19}F_3O_5P$ 343.0917; Found 343.0919.



2,2,2-Trifluoro-1-phenylethyl Diphenylphosphinate (2B)[7]

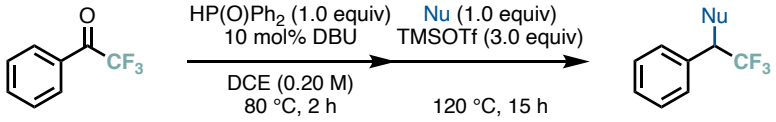
Purification by Isolera® (9:1 to 3:2 hexane/EtOAc) afforded **2B** as a colorless oil (1.0 mmol scale: 350.4 mg, 93% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 2H), 7.63–7.58 (m, 3H), 7.53–7.48 (m, 2H), 7.44–7.38 (m, 3H), 7.35–7.27 (m, 5H), 5.71 (dq, $J_{H–P}$ = 10.8 Hz, $J_{H–F}$ = 6.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 132.7 (d, $J_{C–P}$ = 2.9 Hz), 132.4 (d, $J_{C–P}$ = 2.9 Hz), 131.6 (d, $J_{C–P}$ = 10.6 Hz), 131.5 (d, $J_{C–P}$ = 10.6 Hz), 130.4 (d, $J_{C–P}$ = 136.6 Hz), 130.3 (d, $J_{C–P}$ = 138.2 Hz), 129.8, 128.6 (d, $J_{C–P}$ = 13.6 Hz), 128.4, 128.3 (d, $J_{C–P}$ = 13.6 Hz), 128.1, 123.1 (qd, $J_{C–F}$ = 281.5 Hz, $J_{C–P}$ = 8.0 Hz), 73.5 (qd, $J_{C–F}$ = 33.7 Hz, $J_{C–P}$ = 4.8 Hz) (one peak is missing due to overlapping); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.6 (d, $J_{F–H}$ = 6.4 Hz); HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{20}H_{17}F_3O_2P$ 377.0913; Found 377.0917. The spectra matched with those of this compound reported in the literature.[7]



Diethyl (2,2,2-trifluoro-1-phenylethyl) Phosphate (2B′)[8]

Purification by Isolera® (9:1 to 3:2 hexane/EtOAc) afforded **2B′** as a colorless oil (0.50 mmol scale: 120.3 mg, 77% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.45–7.39 (m, 3H), 5.59 (dq, $J_{H–P}$ = 10.4 Hz, $J_{H–F}$ = 6.4 Hz, 1H), 4.22–4.04 (m, 2H), 3.99–3.82 (m, 2H), 1.31 (td, J = 7.2 Hz, $J_{H–P}$ = 1.2 Hz, 3H), 1.15 (td, J = 7.2 Hz, $J_{H–P}$ = 1.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 131.4, 130.1, 128.6, 127.9, 122.9 (qd, $J_{C–F}$ = 280.9 Hz, $J_{C–P}$ = 9.8 Hz), 76.1 (qd, $J_{C–F}$ = 34.0 Hz, $J_{C–P}$ = 4.4 Hz), 64.4 (d, $J_{H–P}$ = 5.9 Hz), 64.2 (d, $J_{H–P}$ = 5.8 Hz), 15.8 (d, $J_{H–P}$ = 7.4 Hz), 15.7 (d, $J_{H–P}$ = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ –2.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –77.3 (d, $J_{F–H}$ = 6.4 Hz); HRMS (ESI) m/z $[M+H]^+$ Calcd for $C_{12}H_{17}F_3O_4P$ 313.0811; Found 313.0804. The spectra matched with those of this compound reported in the literature.[8]

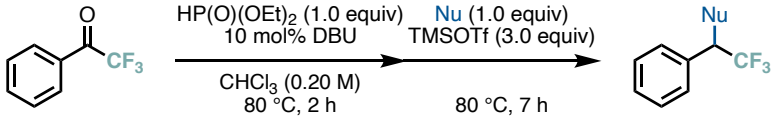
4. Deoxygenative Functionalization of Trifluoromethylketones



1 (0.20 mmol) **3**

General Procedure A

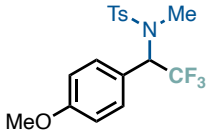
An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube was added diphenylphosphine oxide (40.4 mg, 0.20 mmol, 1.0 equiv). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added trifluoromethylketone **1** (0.20 mmol, 1.0 equiv), DBU (3 µL, 20 µmol, 10 mol%), and 1,2-dichloroethane (DCE: 1.0 mL). The vessel was sealed with a screw cap and then heated at 80 °C for 2 h while its contents were being stirred. After cooling to room temperature, to this tube was added nucleophile (0.20 mmol, 1.0 equiv). The mixture was stirred at 0 °C, and to this tube was added TMSOTf (108 µL, 0.60 mmol, 3.0 equiv) slowly. The vessel was sealed with a screw cap and then heated at 120 °C for 15 h while its contents were being stirred. After the reaction mixture had been cooled to room temperature, the reaction was quenched by saturated $NaHCO_3$ aq. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC to afford the corresponding product **3**.



1 (0.20 mmol) **3**

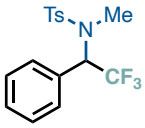
General Procedure B

An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added trifluoromethylketone **1** (0.20 mmol, 1.0 equiv), diethyl phosphite (26 µL, 0.20 mmol, 1.0 equiv), DBU (3 µL, 20 µmol, 10 mol%), and chloroform (1.0 mL). The vessel was sealed with a screw cap and then heated at 80 °C for 2 h while its contents were being stirred. After cooling to room temperature, to this tube was added nucleophile (0.20 mmol, 1.0 equiv). The mixture was stirred at 0 °C, and to this tube was added TMSOTf (108 µL, 0.60 mmol, 3.0 equiv) slowly. The vessel was sealed with a screw cap and then heated at 80 °C for 7 h while its contents were being stirred. After the reaction mixture had been cooled to room temperature, the reaction was quenched by saturated $NaHCO_3$ aq. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC to afford the corresponding product **3**.



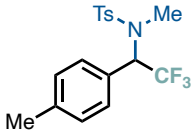
***N*,4-Dimethyl-*N*-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)benzenesulfonamide (3A)**

The reaction was conducted according to **General Procedure B**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3A** as a colorless oil (58.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.34–7.29 (m, 4H), 6.89 (d, J = 8.4 Hz, 2H), 5.81 (q, $J_{H–F}$ = 8.4 Hz, 1H), 3.81 (s, 3H), 2.66 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0, 143.8, 136.1, 130.1, 129.6, 127.5, 125.0 (q, $J_{C–F}$ = 284.3 Hz), 122.3, 114.2, 59.9 (q, $J_{C–F}$ = 31.2 Hz), 55.3, 30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.4 (d, $J_{F–H}$ = 8.4 Hz); HRMS (ESI) *m*/*z* [M+Na]$^{+}$ Calcd for $C_{17}H_{18}F_3NNaO_2S$ 396.0852; Found 396.0850.



***N*,4-Dimethyl-*N*-(2,2,2-trifluoro-1-phenylethyl)benzenesulfonamide (3B)**

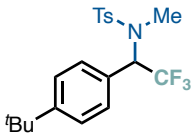
The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3B** as a colorless oil (41.0 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 2H), 7.43–7.36 (m, 5H), 7.31 (d, J = 7.6 Hz, 2H), 5.87 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.66 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 136.0, 130.5, 129.6, 129.1, 128.9, 128.6, 127.6, 124.9 (q, $J_{C–F}$ = 284.3 Hz), 60.4 (q, $J_{C–F}$ = 31.1 Hz), 30.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0 (d, $J_{F–H}$ = 8.4 Hz); HRMS (ESI) *m*/*z* [M+Na]$^{+}$ Calcd for $C_{16}H_{16}F_3NNaO_2S$ 366.0746; Found 366.0745.



***N*,4-Dimethyl-*N*-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)benzenesulfonamide (3C)**

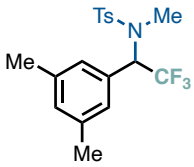
The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3C** as a colorless oil (38.3 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.32–7.26 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 5.82 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.65 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.8, 139.1, 136.1, 129.61, 129.55, 128.6, 127.5, 127.4, 125.0 (q, $J_{C–F}$ = 284.5 Hz), 60.2 (q, $J_{C–F}$ = 30.8 Hz), 30.5, 21.5, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$)

δ –68.2 (d, $J_{F–H}$ = 8.4 Hz); HRMS (ESI) *m/z* $[M+Na]^+$ Calcd for $C_{17}H_{18}F_3NNaO_2S$ 380.0903; Found 380.0906.



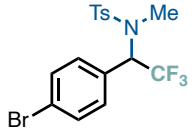
***N*-(1-(4-(*tert*-Butyl)phenyl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3D)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3D** as a white solid (71.1 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34–7.29 (m, 4H), 5.84 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.67 (s, 3H), 2.44 (s, 3H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.1, 143.8, 136.1, 129.6, 128.4, 127.6, 127.4, 125.8, 125.0 (q, $J_{C–F}$ = 284.4 Hz), 60.2 (q, $J_{C–F}$ = 31.1 Hz), 34.6, 31.1, 30.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0 (d, $J_{F–H}$ = 8.4 Hz); HRMS (ESI) *m/z* $[M+Na]^+$ Calcd for $C_{20}H_{24}F_3NNaO_2S$ 422.1372; Found 422.1372.



***N*-(1-(3,5-Dimethylphenyl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3E)**

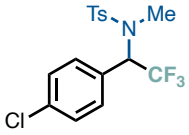
The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3E** as a colorless oil (32.7 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 1H), 6.91 (s, 2H), 5.73 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H), 2.28 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.8, 138.4, 136.2, 130.7, 130.1, 129.6, 127.6, 126.4, 125.0 (q, $J_{C–F}$ = 284.5 Hz), 60.5 (q, $J_{C–F}$ = 31.0 Hz), 30.8, 21.5, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0 (d, $J_{F–H}$ = 8.4 Hz); HRMS (ESI) *m/z* $[M+Na]^+$ Calcd for $C_{18}H_{20}F_3NNaO_2S$ 394.1059; Found 394.1048.



***N*-(1-(4-Bromophenyl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3F)**

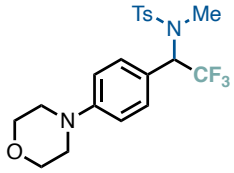
The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3E** as a white solid (62.3 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz,

2H), 7.52 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.83 (q, J_{H-F} = 8.4 Hz, 1H), 2.66 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.1, 135.8, 132.2, 130.2, 129.7, 129.6, 127.5, 124.6 (q, J_{C-F} = 284.5 Hz), 123.5, 59.9 (q, J_{C-F} = 31.2 Hz), 30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0 (d, J_{F-H} = 8.4 Hz); HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{16}H_{15}BrF_3NNaO_2S$ 443.9851; Found 443.9847.



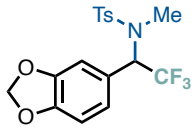
***N*-(1-(4-Chlorophenyl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3G)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3G** as a colorless oil (46.3 mg, 61% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.38–7.35 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 5.84 (q, J_{H-F} = 8.4 Hz, 1H), 2.66 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.0, 135.8, 135.3, 130.0, 129.7, 129.2, 129.1, 127.5, 124.7 (q, J_{C-F} = 284.4 Hz), 59.8 (q, J_{C-F} = 31.4 Hz), 30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{16}H_{15}ClF_3NNaO_2S$ 400.0356; Found 400.0354.



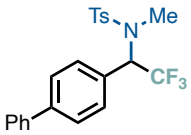
***N*,4-Dimethyl-*N*-(2,2,2-trifluoro-1-(4-morpholinophenyl)ethyl)benzenesulfonamide (3H)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) and GPC afforded **3H** as a white solid (41.4 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.79 (q, J_{H-F} = 8.4 Hz, 1H), 3.88–3.83 (m, 4H), 3.20–3.16 (m, 4H), 2.65 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.3, 143.7, 136.1, 129.8, 129.6, 127.5, 125.0 (q, J_{C-F} = 284.3 Hz), 120.8, 115.1, 66.7, 59.9 (q, J_{C-F} = 31.1 Hz), 48.4, 30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.4 (d, J_{F-H} = 8.4 Hz); HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{20}H_{23}F_3N_2NaO_3S$ 451.1274; Found 451.1270.



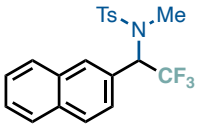
***N*-(1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3I)**

The reaction was conducted according to **General Procedure B**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3I** as a white solid (77.4 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.8 Hz, 1H), 6.87 (s, 1H), 6.79 (d, J = 8.8 Hz, 1H), 5.99 (s, 2H), 5.77 (q, J_{H-F} = 8.4 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.2, 148.1, 143.9, 136.0, 129.6, 127.5, 124.8 (q, J_{C-F} = 284.7 Hz), 123.9, 122.8, 109.0, 108.5, 101.5, 60.1 (q, J_{C-F} = 31.1 Hz), 30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.3 (d, J_{F-H} = 8.4 Hz); HRMS (ESI) *m*/*z* [M+Na]$^{+}$ Calcd for $C_{17}H_{16}F_3NNaO_4S$ 410.644; Found 410.0650.



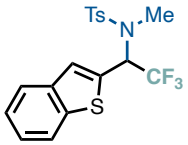
***N*-(1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3J)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3J** as a white solid (41.0 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.49–7.43 (m, 4H), 7.38 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 5.91 (q, J_{H-F} = 8.4 Hz, 1H), 2.71 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 141.9, 139.9, 136.0, 129.7, 129.4, 129.1, 128.9, 127.8, 127.6, 127.5, 127.1, 124.9 (q, J_{C-F} = 284.5 Hz), 60.2 (q, J_{C-F} = 31.2 Hz), 30.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.0 (d, J_{F-H} = 8.4 Hz); HRMS (ESI) *m*/*z* [M+Na]$^{+}$ Calcd for $C_{22}H_{20}F_3NNaO_2S$ 442.1059; Found 442.1055.



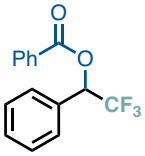
***N*,4-Dimethyl-*N*-(2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl)benzenesulfonamide (3K)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3K** as a white solid (31.4 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.80 (m, 4H), 7.77 (d, J = 8.4 Hz, 2H), 7.55–7.51 (m, 2H), 7.50–7.46 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.02 (q, J_{H-F} = 8.4 Hz, 1H), 2.69 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 136.1, 133.1, 132.9, 129.7, 128.9, 128.3, 128.2, 127.7, 127.6, 127.1, 126.7, 125.7, 125.0 (q, J_{C-F} = 284.7 Hz), 60.6 (q, J_{C-F} = 31.2 Hz), 30.7, 21.5 (one peak is missing due to overlapping); ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.8 (d, J_{F-H} = 8.4 Hz).; HRMS (ESI) *m*/*z* [M+Na]$^{+}$ Calcd for $C_{20}H_{18}F_3NNaO_2S$ 416.0903; Found 416.0910.



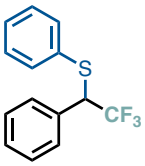
***N*-(1-(Benzo[*b*]thiophen-2-yl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (3L)**

The reaction was conducted according to **General Procedure A**, *N*-methyl-*p*-toluenesulfonamide (37.1 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (17:3 hexane/EtOAc) afforded **3L** as a yellow oil (37.1 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.74 (m, 4H), 7.39–7.35 (m, 3H), 7.33 (d, J = 8.8 Hz, 2H), 6.10 (q, $J_{H–F}$ = 7.6 Hz, 1H), 2.80 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 139.7, 138.9, 135.6, 133.1, 129.7, 127.7, 125.6, 125.4, 124.8, 124.1, 122.1, 57.7 (q, $J_{C–F}$ = 32.6 Hz), 30.6, 21.6 (one peak is missing due to overlapping); ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.3 (d, $J_{F–H}$ = 7.6 Hz); HRMS (ESI) *m/z* [M+Na]$^{+}$ Calcd for $C_{18}H_{16}F_3NNaO_2S_2$ 422.0467; Found 422.0467.



2,2,2-Trifluoro-1-phenylethyl Benzoate (3M)[9]

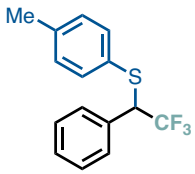
The reaction was conducted according to **General Procedure A**, benzoic acid (24.4 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (4:1 hexane/EtOAc) afforded **3M** as a colorless oil (28.6 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.12 (m, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.58–7.54 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.44–7.41 (m, 3H), 6.37 (q, $J_{H–F}$ = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 133.9, 131.3, 130.0, 129.9, 128.73, 128.69, 128.62, 128.0, 123.3 (q, $J_{C–F}$ = 280.7 Hz), 72.4 (q, $J_{C–F}$ = 33.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –75.9; HRMS (ESI) *m/z* [M+Na]$^{+}$ Calcd for $C_{15}H_{11}F_3NaO_2$ 303.0603; Found 303.0609. The spectra matched with those of this compound reported in the literature.[9]



Phenyl(2,2,2-trifluoro-1-phenylethyl)sulfane (3N)[10]

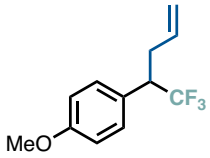
The reaction was conducted according to **General Procedure A**, thiophenol (21 μL, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (19:1 hexane/Chloroform) afforded **3N** as a colorless oil (15.2 mg, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.37–7.33 (m, 5H), 7.31–7.27 (m, 3H), 4.52 (q, $J_{H–F}$ = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.8, 133.6, 132.7, 129.1, 128.9, 128.8, 128.72, 128.67, 125.5 (q, $J_{C–F}$ = 279.9 Hz), 56.8 (q, $J_{C–F}$ = 29.5 Hz); ^{19}F

NMR (376 MHz, $CDCl_3$) δ –67.8 (d, $J_{F–H}$ = 8.4 Hz); HRMS (APCI) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{12}F_3S$ 269.0606; Found 269.0600. The spectra matched with those of this compound reported in the literature.[10]



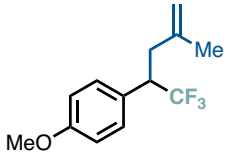
***p*-Tolyl(2,2,2-trifluoro-1-phenylethyl)sulfane (3O)**[11]

The reaction was conducted according to **General Procedure A**, *p*-toluenethiol (24.8 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile. Purification by PTLC (9:1 hexane/EtOAc) afforded **3O** as a colorless oil (29.7 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 5H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.45 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.1, 134.2, 133.8, 129.9, 129.1, 128.9, 128.73, 128.67, 125.6 (q, $J_{C–F}$ = 279.6 Hz), 57.2 (q, $J_{C–F}$ = 29.3 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.8 (d, $J_{F–H}$ = 8.4 Hz); HRMS (APCI) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{14}F_3S$ 283.0763; Found 283.0755. The spectra matched with those of this compound reported in the literature.[11]



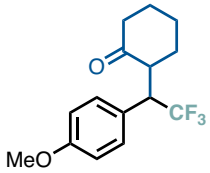
1-Methoxy-4-(1,1,1-trifluoropent-4-en-2-yl)benzene (3P)[12]

The reaction was conducted according to **General Procedure B**. Allyltrimethylsilane (95 µL, 0.60 mmol, 3.0 equiv) was used as a nucleophile, and TMSOTf (1.0 equiv; reduced from 3.0 equiv in the standard conditions) was employed. Purification by Isolera® (99:1 to 9:1 hexane/EtOAc) afforded **3P** as a colorless oil (34.2 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.57 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.06–5.00 (m, 1H), 4.97 (dd, *J* = 10.0, 0.8 Hz, 1H), 3.80 (s, 3H), 3.27 (dtd, *J* = 19.6, 9.2, 4.4 Hz, 1H), 2.79–2.71 (m, 1H), 2.65–2.56 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 134.0, 130.1, 126.8 (q, $J_{C–F}$ = 280.0 Hz), 126.2, 117.6, 114.0, 55.2, 49.2 (q, $J_{C–F}$ = 26.4 Hz), 33.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.2 (d, $J_{F–H}$ = 8.8 Hz); HRMS (APCI) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{14}F_3O$ 231.0991; Found 231.1000. The spectra matched with those of this compound reported in the literature.[12]



1-Methoxy-4-(1,1,1-trifluoro-4-methylpent-4-en-2-yl)benzene (3Q)

The reaction was conducted according to **General Procedure B**. Methallyltrimethylsilane (104 µL, 0.60 mmol, 3.0 equiv) was used as a nucleophile, and TMSOTf (1.0 equiv; reduced from 3.0 equiv in the standard conditions) was employed. Purification by Isolera® (99:1 to 9:1 hexane/EtOAc) afforded **3Q** as a colorless oil (43.5 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.71–4.68 (m, 1H), 4.61–4.59 (m, 1H), 3.80 (s, 3H), 3.42 (dqd, J = 11.2, 9.2, 4.0 Hz, 1H), 2.70 (dd, J = 14.4, 4.4 Hz, 1H), 2.58 (ddd, J = 14.4, 11.2, 0.8 Hz, 1H), 1.63–1.62 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.3, 140.8, 130.1, 126.9 (q, $J_{C–F}$ = 280.0 Hz), 126.3, 113.9, 55.1, 47.6 (q, $J_{C–F}$ = 26.4 Hz), 36.7, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –70.3 (d, $J_{F–H}$ = 8.8 Hz); HRMS (APCI) m/z [M+H]$^+$ Calcd for $C_{13}H_{16}F_3O$ 245.1148; Found 245.1145.

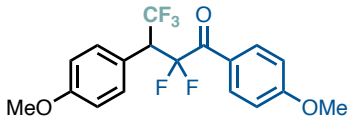


2-(2,2,2-Trifluoro-1-(4-methoxyphenyl)ethyl)cyclohexan-1-one (3R)

The reaction was conducted according to **General Procedure B**. (Cyclohex-1-en-1-yloxy)trimethylsilane (115 µL, 0.60 mmol, 3.0 equiv) was used as a nucleophile, and TMSOTf (1.0 equiv; reduced from 3.0 equiv in the standard conditions) was employed. Crude ^{1}H NMR showed ***major*-3R**:***minor*-3R** = 63:37; ^{1}H NMR peaks at 4.31 (qd, $J_{H–F}$ = 10.8 Hz, J = 5.6 Hz, 1H) and 3.96–3.84 (m, 0.59H) were used. Purification by PTLC (9:1 hexane/EtOAc) afforded ***major*-3R** as a colorless oil (20.3 mg, 35% yield) and ***minor*-3R** as a white solid (9.7 mg, 17% yield)

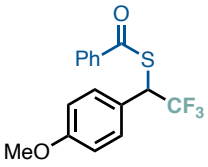
For ***major*-3R**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.31 (qd, $J_{H–F}$ = 10.8 Hz, J = 5.6 Hz, 1H), 3.80 (s, 3H), 2.97 (dt, J = 11.2, 5.6 Hz, 1H), 2.51 (dt, J = 14.8, 4.4 Hz, 1H), 2.43–2.34 (m, 1H), 2.04–1.96 (m, 2H), 1.84–1.78 (m, 1H), 1.72–1.60 (m, 2H), 1.18–1.08 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 323 K) δ 208.9, 159.4, 131.2, 127.4 (q, $J_{C–F}$ = 280.2 Hz), 124.8, 113.9, 55.2, 50.1, 46.2 (q, $J_{C–F}$ = 26.5 Hz), 41.7, 31.2, 27.6, 24.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.1 (d, $J_{F–H}$ = 8.8 Hz); HRMS (ESI) m/z [M+Na]$^+$ Calcd for $C_{15}H_{17}F_3NaO_2$ 309.1073; Found 309.1074.

For ***minor*-3R**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.96–3.84 (m, 1H), 3.78 (s, 3H), 3.11–3.03 (m, 1H), 2.54–2.44 (m, 1H), 2.36–2.30 (m, 1H), 2.28–2.23 (m, 1H), 2.12–2.05 (m, 1H), 2.01–1.95 (m, 1H), 1.80–1.68 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.2, 159.1, 130.2, 127.9, 126.9 (q, $J_{C–F}$ = 280.5 Hz), 113.9, 55.2, 53.7, 47.1 (q, $J_{C–F}$ = 26.5 Hz), 42.6, 32.3, 28.6, 25.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.4 (d, $J_{F–H}$ = 11.6 Hz); HRMS (ESI) m/z [M+Na]$^+$ Calcd for $C_{15}H_{17}F_3NaO_2$ 309.1073; Found 309.1084.



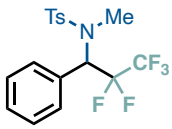
2,2,4,4,4-Pentafluoro-1,3-bis(4-methoxyphenyl)butan-1-one (3S)

The reaction was conducted according to **General Procedure B**. 2,2-Difluoro-1-(4-methoxyphenyl)vinyl diethyl phosphate (64.4 mg, 0.20 mmol, 1.0 equiv) was used as a nucleophile, and TMSOTf (1.0 equiv; reduced from 3.0 equiv in the standard conditions) was employed. Purification by PTLC (4:1 hexane/EtOAc) and GPC afforded **3S** as a colorless oil (32.4 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.57 (ddq, $J_{H–F}$ = 17.6, 13.2, 8.8 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 186.1 (t, $J_{C–F}$ = 29.1 Hz), 164.6, 160.2, 132.6 (t, $J_{C–F}$ = 3.8 Hz), 131.9, 124.5, 124.3 (qd, $J_{C–F}$ = 281.2, 3.6 Hz), 119.4, 116.8 (t, $J_{C–F}$ = 254.3 Hz), 114.1, 114.0, 55.6, 55.2, 51.7 (qdd, $J_{C–F}$ = 27.8, 23.2, 20.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.5 (dt, $J_{F–F}$ = 14.6 Hz, $J_{F–H}$ = 8.8 Hz), –101.0 (dqd, $J_{F–F}$ = 289.5, 13.2 Hz, $J_{F–H}$ = 13.2 Hz), –103.4 (dq, $J_{F–F}$ = 289.5, 8.6 Hz); HRMS (ESI) m/z [M+Na]$^{+}$ Calcd for $C_{18}H_{15}F_5NaO_3$ 397.0834; Found 397.0827.



***S*-(2,2,2-Trifluoro-1-(4-methoxyphenyl)ethyl) benzothioate (3T)**

The reaction was conducted according to **General Procedure B**, thiobenzoic acid (82.9 mg, 0.60 mmol, 3.0 equiv) was used as a nucleophile, and TMSOTf (1.0 equiv; reduced from 3.0 equiv in the standard conditions) was employed. Purification by PTLC (4:1 hexane/EtOAc) afforded **3T** as a pink oil (22.0 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.4, 1.2 Hz, 2H), 7.61 (tt, J = 7.2, 1.2 Hz, 1H), 7.50–7.44 (m, 2H), 7.39 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.44 (q, $J_{H–F}$ = 9.2 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 187.7, 160.0, 135.7, 134.2, 130.5, 128.8, 127.6, 125.3 (q, $J_{C–F}$ = 278.6 Hz), 125.1, 114.2, 55.3, 48.7 (q, $J_{C–F}$ =31.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.4 (d, $J_{F–H}$ = 9.2 Hz); HRMS (ESI) m/z [M+Na]$^{+}$ Calcd for $C_{16}H_{13}F_3NaO_2S$ 349.0481; Found 349.0486.

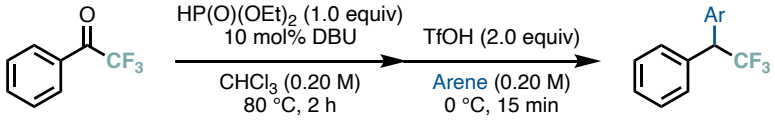


***N*,4-Dimethyl-*N*-(2,2,3,3,3-pentafluoro-1-phenylpropyl)benzenesulfonamide (3U)**

The reaction was conducted according to **General Procedure A**, imidazole (20 mol%) was used instead of DBU. Purification by PTLC (9:1 hexane/EtOAc) afforded **3U** as a colorless oil (29.8 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.45–7.42 (m, 2H), 7.39–7.35 (m,

3H), 7.24 (d, J = 8.4 Hz, 2H), 5.89 (t, $J_{H–F}$ = 16.0 Hz, 1H), 2.79 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.9, 135.5, 129.9, 129.5, 128.8, 127.7, 118.6 (qt, $J_{C–F}$ = 287.1, 35.3 Hz), 115.0 (tq, $J_{C–F}$ = 260.9, 36.0 Hz), 58.7 (t, $J_{C–F}$ = 22.6 Hz), 31.0, 21.5 (two peaks are missing due to overlapping); ^{19}F NMR (376 MHz, $CDCl_3$) δ –81.7, –116.5 (t, $J_{F–H}$ = 16.0 Hz); HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{17}H_{16}F_5NNaO_2S$ 416.0714; Found 416.0710.

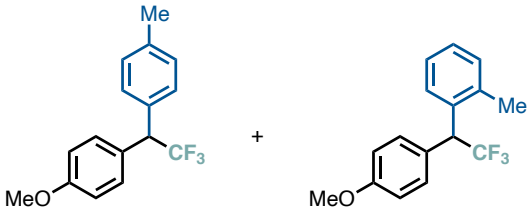
5. Deoxygenative Arylation of Trifluoromethylketones



1 (0.20 mmol) **5**

General Procedure

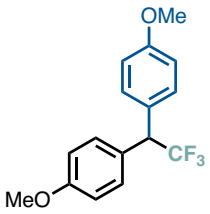
An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added trifluoromethylketone **1** (0.20 mmol, 1.0 equiv), diethyl phosphite (26 µL, 0.20 mmol, 1.0 equiv), DBU (3 µL, 20 µmol, 10 mol%), and chloroform (1.0 mL). The vessel was sealed with a screw cap and then heated at 80 °C for 2 h while its contents were being stirred. After cooling to room temperature, the mixture was concentrated *in vacuo*. To the residue were added arene (1.0 mL, 0.20 M) and TfOH (35 µL, 0.40 mmol, 2.0 equiv) at 0 °C. After being stirred the mixture for 15 minutes while the reaction progress was being monitored by TLC, the reaction was quenched by saturated $NaHCO_3$ aq. The mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC to afford the corresponding product **5**.



1-Methoxy-4-(2,2,2-trifluoro-1-(p-tolyl)ethyl)benzene (5A)[13]

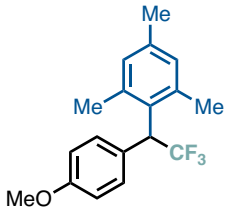
The reaction was conducted with toluene as solvent. Crude ^{1}H NMR showed ***p*-5A**:***o*-5A** = 95:5; ^{1}H NMR peaks at 4.59 (q, J_{H-F} = 10.0 Hz, 1H) and 4.83 (q, J_{H-F} = 10.0 Hz, 0.05H) were used. Purification by PTLC (9:1 hexane/EtOAc) afforded **5A** as a colorless oil (52.6 mg, 93% yield, as a mixture of structural isomer; ***p*-5A**:***o*-5A** = 95:5).

For ***p*-5A**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.8 Hz, 2H), 7.25–7.22 (m, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.59 (q, J_{H-F} = 10.0 Hz, 1H), 3.78 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 137.5, 132.7, 130.1, 129.4, 128.8, 127.7, 126.3 (q, J_{C-F} = 280.3 Hz), 114.0, 55.2, 54.4 (q, J_{C-F} = 27.6 Hz), 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.3 (d, J_{F-H} = 10.0 Hz). HRMS (APCI) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{16}F_3O$ 281.1148; Found 281.1138. The spectra matched with those of this compound reported in the literature.[13]



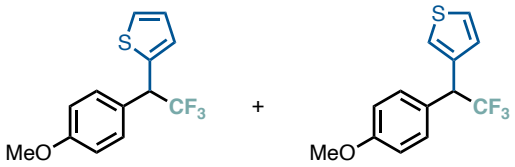
4,4'-(2,2,2-Trifluoroethane-1,1-diyl)bis(methoxybenzene) (5B)[14]

The reaction was conducted with anisole as solvent. Purification by PTLC (9:1 hexane/EtOAc) afforded **5B** as a colorless oil (60.0 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 4H), 6.87 (d, J = 8.4 Hz, 4H), 4.58 (q, $J_{H–F}$ = 10.0 Hz, 1H), 3.79 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 130.1, 127.8, 126.4 (q, $J_{C–F}$ = 280.8 Hz), 114.0, 55.2, 53.9 (q, $J_{C–F}$ = 27.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.5 (d, $J_{F–H}$ = 10.0 Hz); HRMS (APCI) *m/z* $[M]^+$ Calcd for $C_{16}H_{15}F_3O_2$ 296.1019; Found 296.1011. The spectra matched with those of this compound reported in the literature.[14]



1,3,5-Trimethyl-2-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)benzene (5C)[14]

The reaction was conducted with mesitylene as solvent. Purification by PTLC (9:1 hexane/EtOAc) afforded **5C** as a colorless oil (59.9 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.8 Hz, 2H), 6.94 (s, 1H), 6.83 (d, J = 8.8 Hz, 2H), 6.80 (s, 1H), 5.30 (q, $J_{H–F}$ = 10.4 Hz, 1H), 3.79 (s, 3H), 2.46 (s, 3H), 2.27 (s, 3H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 138.5, 137.6, 131.6, 130.0, 129.3, 128.6, 127.9, 126.9 (q, $J_{C–F}$ = 281.3 Hz), 113.8, 55.2, 48.4 (q, $J_{C–F}$ = 27.5 Hz), 21.6, 21.0, 20.7 (one peak is missing due to overlapping); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (d, $J_{F–H}$ = 10.4 Hz); HRMS (APCI) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{20}F_3O$ 309.1461; Found 309.1458. The spectra matched with those of this compound reported in the literature.[14]



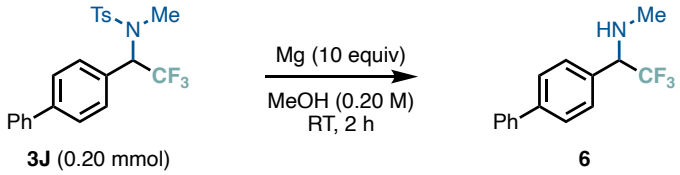
2-(2,2,2-Trifluoro-1-(4-methoxyphenyl)ethyl)thiophene (5D)[13.15]

The reaction was conducted with thiophene as solvent. Crude ^{1}H NMR showed **C_2-5D**:**C_3-5D** = 88:12; ^{1}H NMR peaks at 4.84 (q, $J_{H–F}$ = 9.6 Hz, 1H) and 4.70 (q, $J_{H–F}$ = 9.6 Hz, 0.14H) were used. Purification by PTLC (9:1 hexane/EtOAc) afforded **5D** as a colorless oil (24.6 mg, 45% yield, as a mixture of structural isomer; **C_2-5D**:**C_3-5D** = 88:12).

For **C_2-5D**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.8 Hz, 2H), 7.27 (dd, J = 5.2, 1.2 Hz 1H), 7.09–7.07 (m, 1H), 6.99 (dd, J = 5.2, 3.6 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 4.84 (q, $J_{H–F}$ = 9.6 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.6, 137.6, 130.2, 127.2, 126.9, 125.7, 125.6 (q, $J_{C–F}$ = 280.5 Hz), 114.1, 55.2, 50.4 (q, $J_{C–F}$ = 29.2 Hz) (one peak is missing due to overlapping); ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.1 (d, $J_{F–H}$ = 8.8 Hz); HRMS (APCI) *m*/*z* $[M+H]^+$ Calcd for $C_{13}H_{12}F_3OS$ 273.0555; Found 273.0551. The spectra matched with those of this compound reported in the literature.[13.15]

6. Application

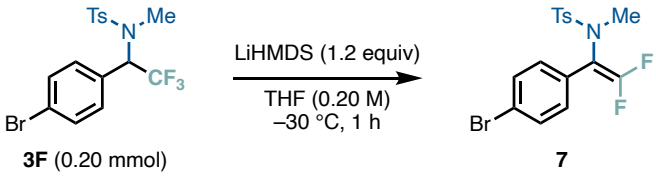
6.1. Detosylation of 3J



3J (0.20 mmol) **6**

An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar and magnesium turnings (48.6 mg, 2.0 mmol, 10 equiv) was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube was added **3J** (83.9 mg, 0.20 mmol, 1.0 equiv). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube was added methanol (1.0 mL). The vessel was sealed with a screw cap, and the mixture was stirred at room temperature for 2 h while the reaction progress was being monitored by TLC. The reaction was quenched with NH_4Cl aq. The mixture was extracted three times with Et_2O. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (4:1 hexane/EtOAc) to afford 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoro-*N*-methylethan-1-amine (**6**) as white solid (45.1 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 4H), 7.49–7.43 (m, 4H), 7.36 (t, J = 7.2 Hz, 1H), 4.07 (q, $J_{H–F}$ = 7.6 Hz, 1H), 2.45 (s, 3H), 1.70 (brs, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.9, 140.4, 133.0, 128.9, 128.8, 127.6, 127.4, 127.1, 125.4 (q, $J_{C–F}$ = 281.6 Hz), 66.2 (q, $J_{C–F}$ = 28.5 Hz), 34.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –74.1 (d, $J_{F–H}$ = 7.6 Hz). HRMS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{15}F_3N$ 266.1151; Found 266.1158.

6.2. Defluorination of 3F

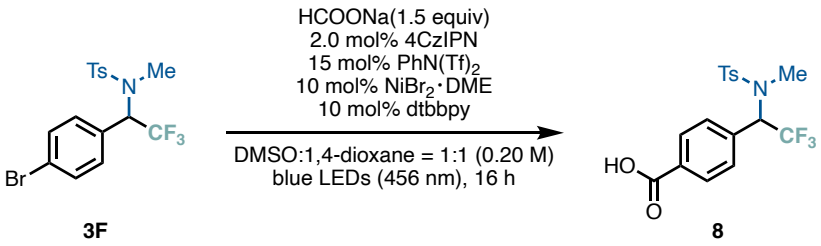


3F (0.20 mmol) **7**

An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube was added **3F** (84.5 mg, 0.20 mmol, 1.0 equiv). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube was added THF (1.0 mL). To this tube was added lithium bis(trimethylsilyl)amide (LiHMDS: 0.24 mL, 1.0 M in toluene 0.24 mmol, 1.2 equiv) at –30 °C. The mixture was stirred for 1 h while the reaction progress was being monitored by TLC. The reaction was quenched with water. The mixture was extracted three times with Et_2O. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (9:1 hexane/EtOAc) to afford *N*-(1-(4-bromophenyl)-2,2-difluorovinyl)-*N*,4-dimethylbenzenesulfonamide (**7**) as colorless oil (49.1 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.35–7.30 (m, 4H), 3.06 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ

156.9 (dd, $J_{C–F}$ = 303.3, 298.8 Hz), 144.0, 135.4, 131.8, 129.9 (dd, $J_{C–F}$ = 6.9, 1.8 Hz), 129.6, 128.7 (dd, $J_{C–F}$ = 6.3, 3.4 Hz), 127.5, 122.3, 100.6 (dd, $J_{C–F}$ = 30.7, 17.7 Hz), 36.8, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –82.4 (d, $J_{F–F}$ = 20.1 Hz), –88.2 (dd, $J_{F–F}$ = 20.1, 6.5 Hz). HRMS (ESI) *m/z* $[M+Na]^+$ Calcd for $C_{16}H_{14}BrF_2NNaO_2S$ 423.9789; Found 423.9789.

6.3. Carboxylation of 3F



3F **8**

An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube were added **3F** (84.5 mg, 0.20 mmol, 1.0 equiv), sodium formate (20.4 mg, 0.30 mmol, 1.5 equiv), 4CzIPN (3.2 mg, 4.0 μmol, 2.0 mol%), *N*-phenylbis(trifluoromethanesulfonimide) (10.7 mg, 30 μmol, 15 mol%), $NiBr_2$·DME (6.2 mg, 20 μmol, 10 mol%), and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (dtbbpy: 5.4 mg, 20 μmol, 10 mol%). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added DMSO (0.50 mL) and 1,4-dioxane (0.50 mL). The reaction mixture was purged with N_2 gas for 5 min. The vessel was sealed with a screw cap, and the mixture was irradiated with blue LEDs (Kessil®, 456 nm) for 16 h. The reaction was quenched with HCl aq. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (9:1 chloroform/methanol) to afford 4-(1-((*N*,4-dimethylphenyl)sulfonamido)-2,2,2-trifluoroethyl)benzoic acid (**8**) as colorless oil (62.4 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.95 (q, $J_{H–F}$ = 8.4 Hz, 1H), 2.68 (s, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.2, 144.2, 136.4, 135.7, 130.7, 129.8, 128.7, 127.6, 124.6 (q, $J_{C–F}$ = 284.4 Hz), 123.4, 60.2 (q, $J_{C–F}$ = 31.5 Hz), 30.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.7 (d, $J_{F–H}$ = 8.4 Hz). HRMS (ESI) *m/z* $[M+Na]^+$ Calcd for $C_{17}H_{16}F_3NNaO_4S$ 410.0644; Found 410.0648.

Photochemical Reaction Setup

The blue LED lamps (PR160L-456 nm Kessil® LED lamp, λ_{max} = 456 nm) were used with the intensity dial set to 100. The reaction tubes were placed 4.0 cm away from the LED lamps (**Figure S1**). During the photochemical reaction, fan cooling was used to maintain the temperature at approximately 35 °C. All reactions were performed with 1 or 2 tubes per 1 Kessil LED lamp.

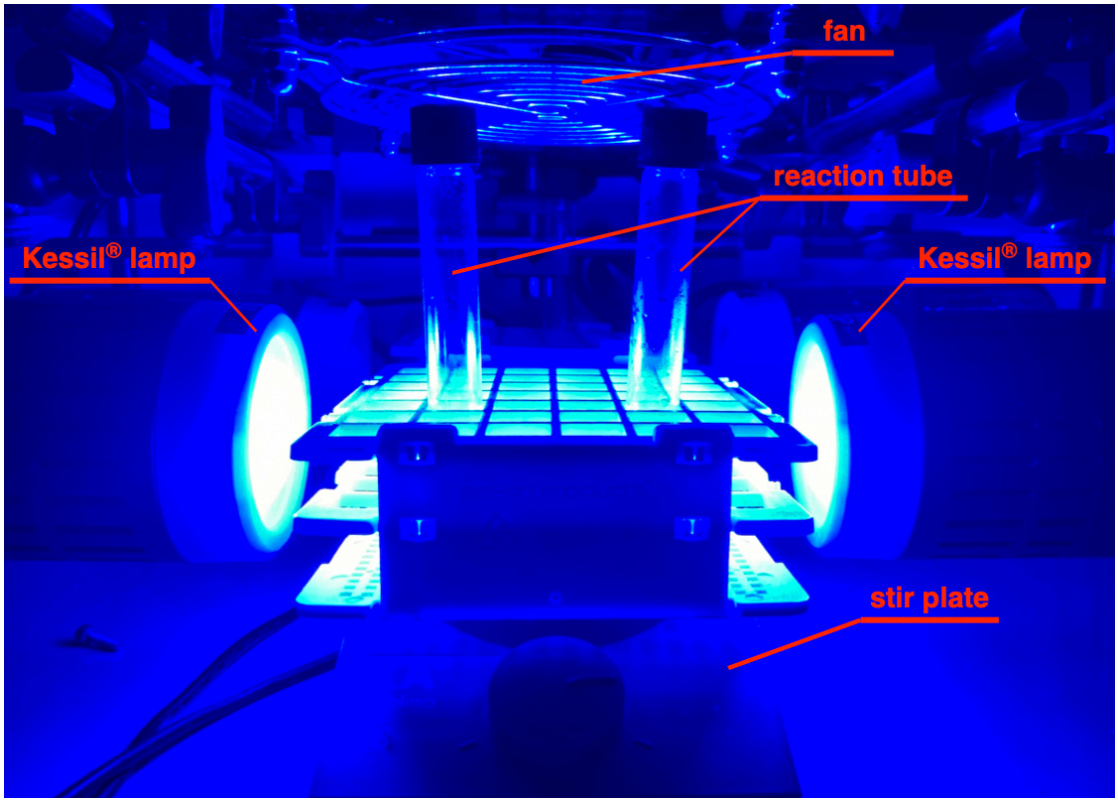
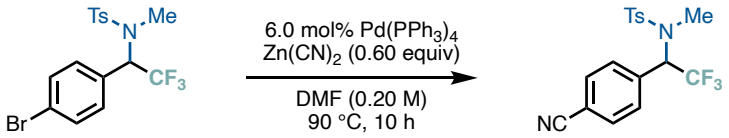


Figure S1. Photochemical reaction setup

6.4. Cyanation of 3F



3F **9**

An 8-mL glass tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat gun *in vacuo*. The tube was filled with N_2 gas after cooling to room temperature. To this tube were added **3F** (84.5 mg, 0.20 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (13.9 mg, 12 µmol, 6.0 mol%), zinc cyanide (14.1 mg, 0.12 mmol, 0.60 equiv). The tube was placed under vacuum and refilled three times with N_2 gas, and to this tube were added DMF (1.0 mL). The vessel was sealed with a screw cap and then heated at 90 °C for 10 h while its contents were being stirred. After the reaction mixture had been cooled to room temperature, the reaction was quenched by water. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (3:2 hexane/EtOAc) to afford *N*-(1-(4-cyanophenyl)-2,2,2-trifluoroethyl)-*N*,4-dimethylbenzenesulfonamide (**9**) as yellow solid (63.1 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.93 (q, J_{H-F} = 8.0 Hz, 1H), 2.66 (s, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 135.8, 135.4, 132.6, 129.7, 129.2, 127.5, 124.3 (q, J_{C-F} = 284.8 Hz), 117.8, 113.2, 60.0 (q, J_{C-F} = 31.7 Hz),

30.5, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.5 (t, $J_{F–H}$ = 8.0 Hz). HRMS (ESI) *m*/*z* $[M+Na]^+$ Calcd for $C_{17}H_{15}F_3N_2NaO_2S$ 391.0699; Found 391.0690.

7. References

[1] Kurosawa, M. B.; Shimoyama, S.; Tanaka, H.; Yamaguchi, J. Difluoroenol Phosphinates as Difluoroenolate Surrogates: Synthesis and Applications in Defluorination and Deoxygenative Coupling. *Chem*. *Sci*. **2025**, *16*, 13390–13400.

[2] Halbfinger, E.; Gorochesky, K.; Lévesque, S. A.; Beaudoin, A. R.; Sheihet, L.; Margel, S.; Fischer, B. Photoaffinity Labeling on Magnetic Microspheres (PALMm) Methodology for Topographic Mapping: Preparation of PALMm Reagents and Demonstration of Biochemical Relevance. *Org*. *Biomol*. *Chem*. **2003**, *1*, 2821–2832.

[3] Scheidt, F.; Neufeld, J.; Schäfer, M.; Thiehoff, C.; Gilmour, R. Catalytic Geminal Difluorination of Styrenes for the Construction of Fluorine-Rich Bioisosteres. *Org*. *Lett*. **2018**, *20*, 8073–8076.

[4] Yamazaki, T.; Terajima, T.; Kawasaki-Taskasuka, T. Unusual Reactions of Grignard Reagents toward Fluoroalkylated Esters. *Tetrahedron* **2008**, *64*, 2419–2424.

[5] Eschmann, C.; Song, L.; Schreiner, P. R. London Dispersion Interactions Rather than Steric Hindrance Determine the Enantioselectivity of the Corey–Bakshi–Shibata Reduction. *Angew*. *Chem*., *Int*. *Ed*. **2021**, *60*, 4823–4832.

[6] Sriramoju, V.; Jillella, R.; Kurva, S.; Madabhushi, S. A Study on Reactions of an Alkynylsilane with Oxone-KX (X = Cl, Br, I) and Its One-Pot Transformation into an Amide/Ester. *Chem*. *Lett*. **2017**, *46*, 560–562.

[7] Zhang, Y.; Zhang, X.; Zhao, J.; Jiang, J. $B(C_6F_5)_3$ -Catalyzed O–H Insertion Reactions of Diazoalkanes with Phosphinic Acids. *Org. Biomol. Chem.* **2021**, *19*, 5772–5776.

[8] Cherkupally, P.; Beier, P. Alkoxide-Induced Nucleophilic Trifluoromethylation Using Diethyl Trifluoromethylphosphonate. *Tetrahedron Lett.* **2010**, *51*, 252–255.

[9] Cronin, L.; Manoni, F.; O' Connor, C. J.; Connon, S. J. Tunable Bromomagnesium Thiolate Tishchenko Reaction Catalysts: Intermolecular Aldehyde–Trifluoromethylketone Coupling. *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 3045–3048.

[10] Hyde, S.; Veliks, J.; Liégault, B.; Grassi, D.; Taillefer, M.; Gouverneur, V. Copper-Catalyzed Insertion into Heteroatom–Hydrogen Bonds with Trifluorodiazoalkanes. *Angew*. *Chem*., *Int*. *Ed*. **2016**, *55*, 3785–3789.

[11] Kato, M.; Maeda, K.; Sato, K.; Omote, M.; Ando, A.; Kumadaki, I. Synthesis of New Synthons for Organofluorine Compounds from Halothane Containing Sulfur Functional Groups. *Chem*. *Pharm*. *Bull*. **2000**, *48*, 683–686.

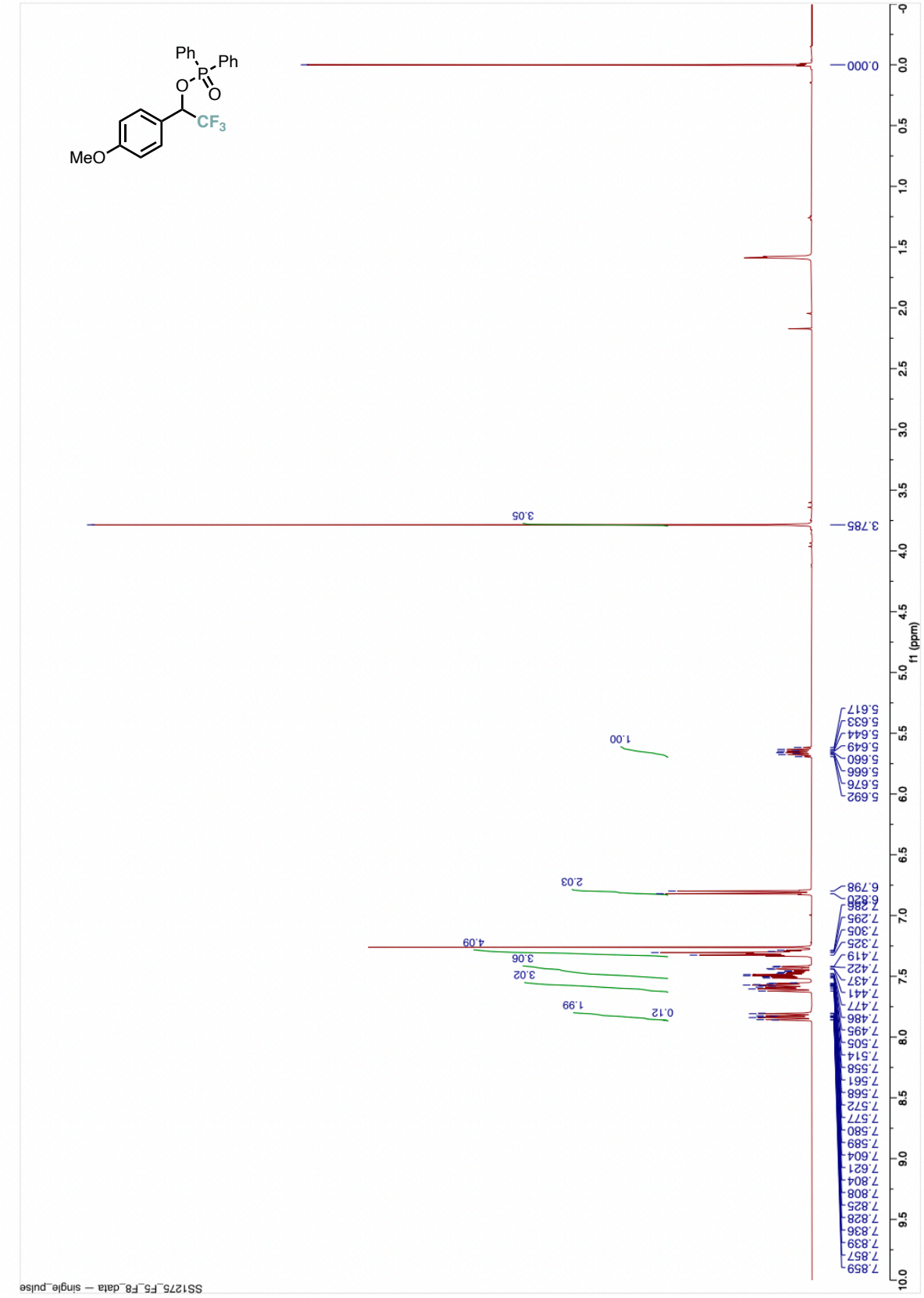
[12] Punna, N.; Harada, K.; Shibata, N. Stille Cross-Coupling of Secondary and Tertiary α-(Trifluoromethyl)-Benzyl Chlorides with Allylstannanes. *Chem*. *Commun*. **2018**, *54*, 7171–7174.

[13] Varenikov, A.; Shapiro, E.; Gandelman, M. Synthesis of Chiral α-CF_3-Substituted Benzhydryls via Cross-Coupling Reaction of Aryltitanates. *Org*. *Lett*. **2020**, *22*, 9386–9391.

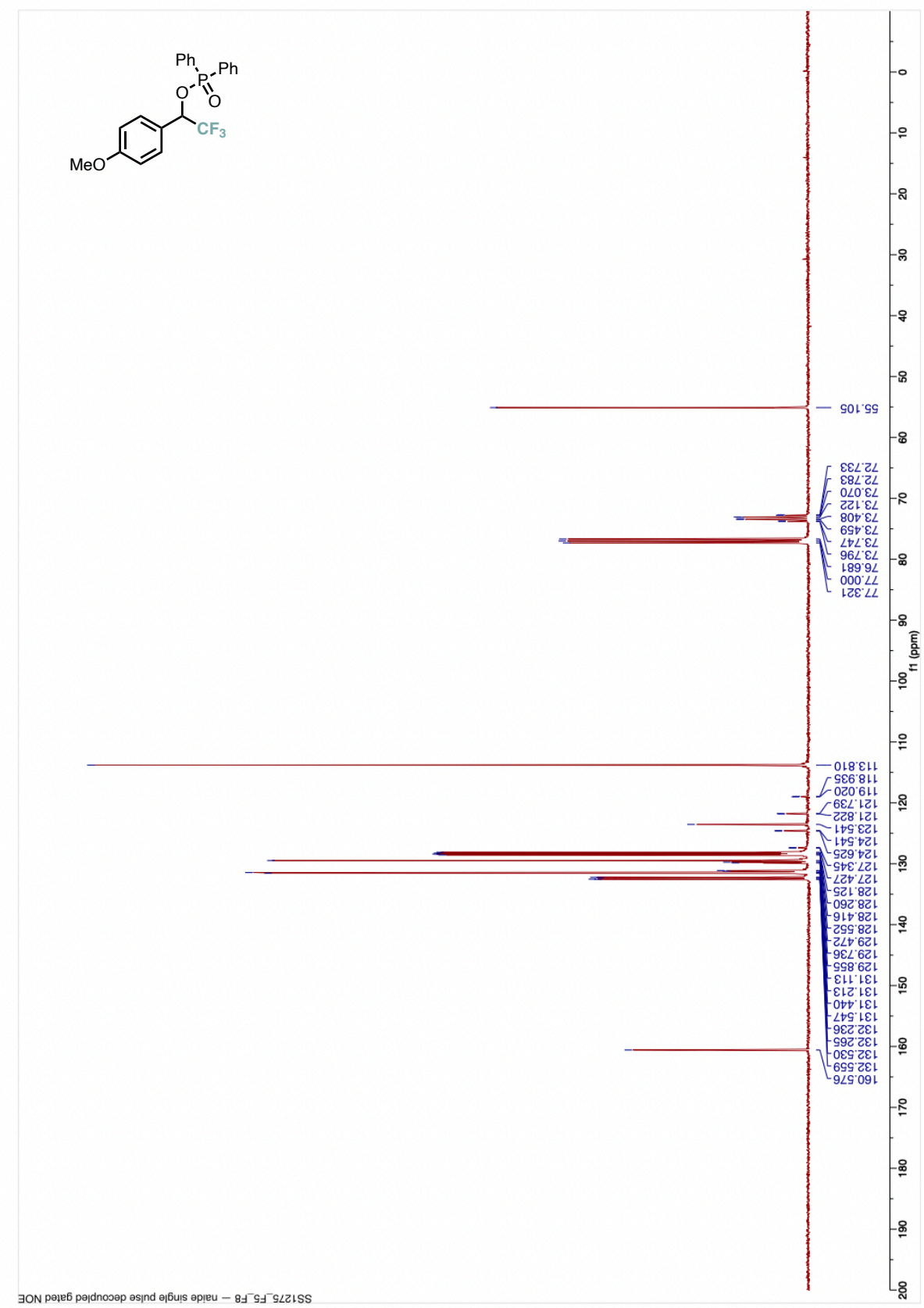
[14] Kuang, C.; Zhou, X.; Xie, Q.; Ni, C.; Gu, Y.; Hu, J. Generation of Carbocations under Photoredox Catalysis: Electrophilic Aromatic Substitution with 1-Fluoroalkylbenzyl Bromides. *Org*. *Lett*. **2020**, *22*, 8670–8675.
[15] Khoroshilova, O. V.; Vasilyev, A. V. Generation and NMR Study of Short-Lived and Reactive Trifluoroalkyl Carbocations of the α-Halogenothiophene Series in Brønsted Superacids: Reactions of the Cations with Arenes. *J. Org*. *Chem*. **2020**, *85*, 5872–5883.

8. ^{1}H , ^{13}C, ^{19}F, and ^{31}P NMR Spectra

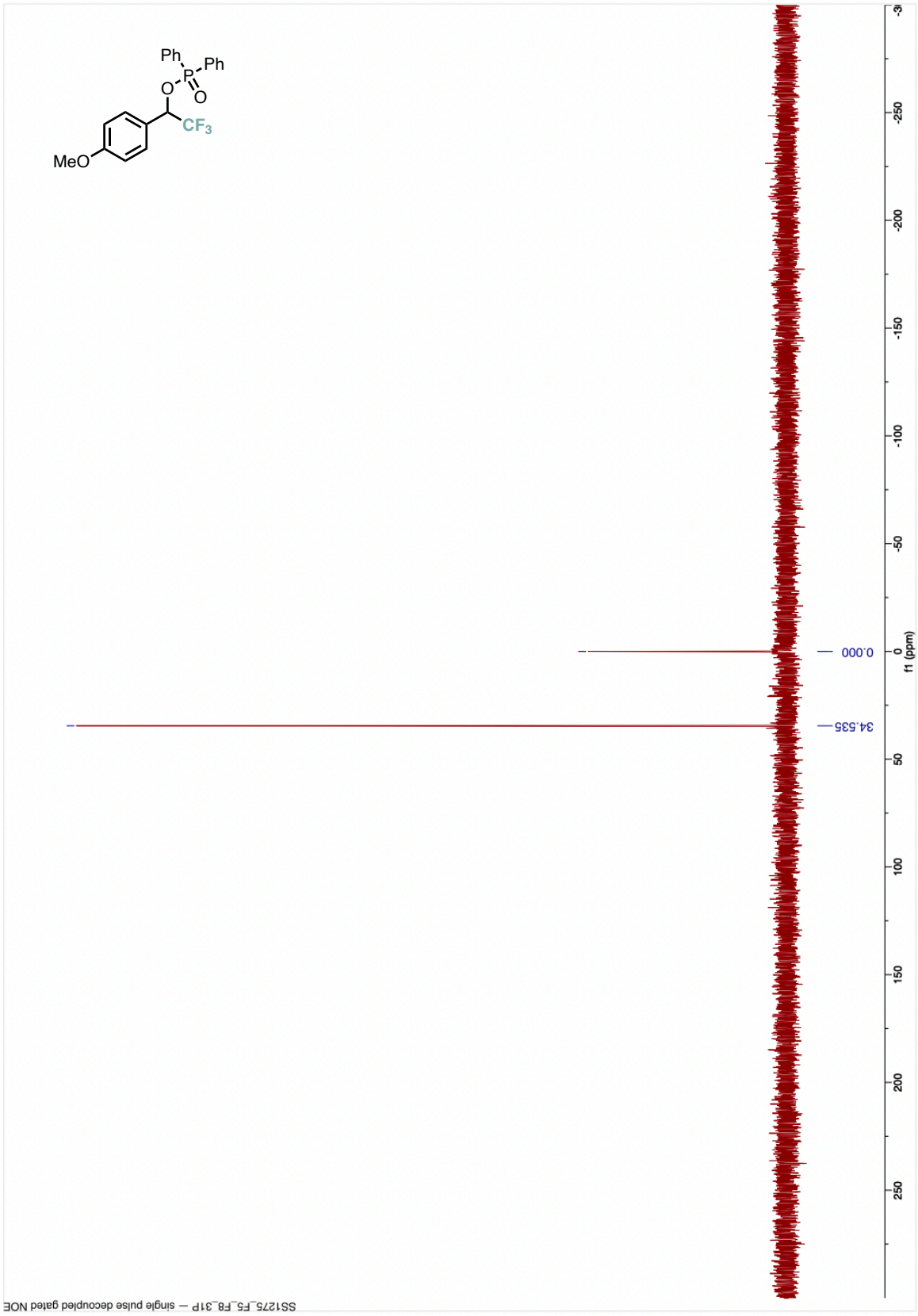
^{1}H NMR of **2A** (400 MHz, $CDCl_3$)



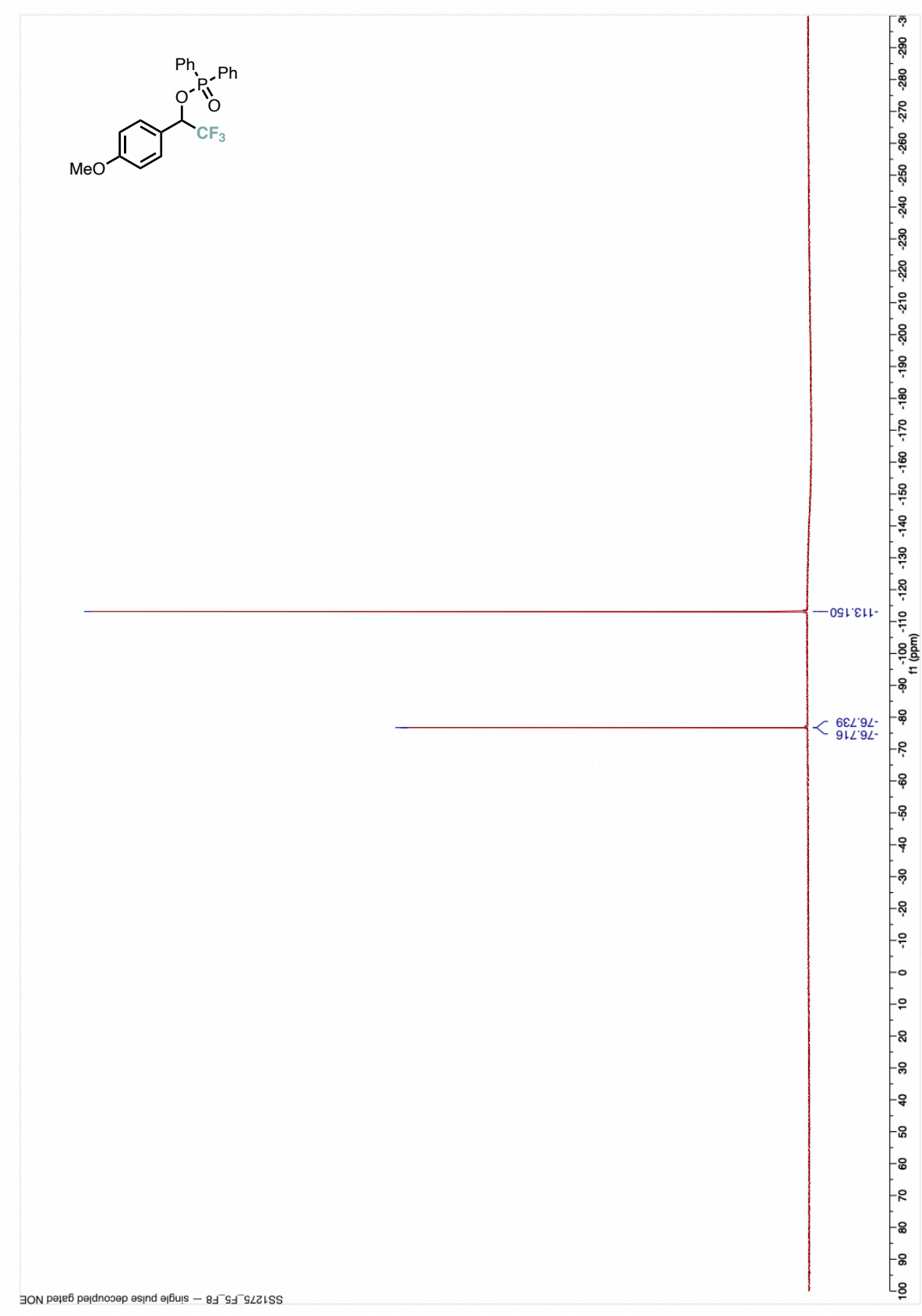
$^{13}C\{^{1}H\}$ NMR of **2A** (101 MHz, $CDCl_3$)



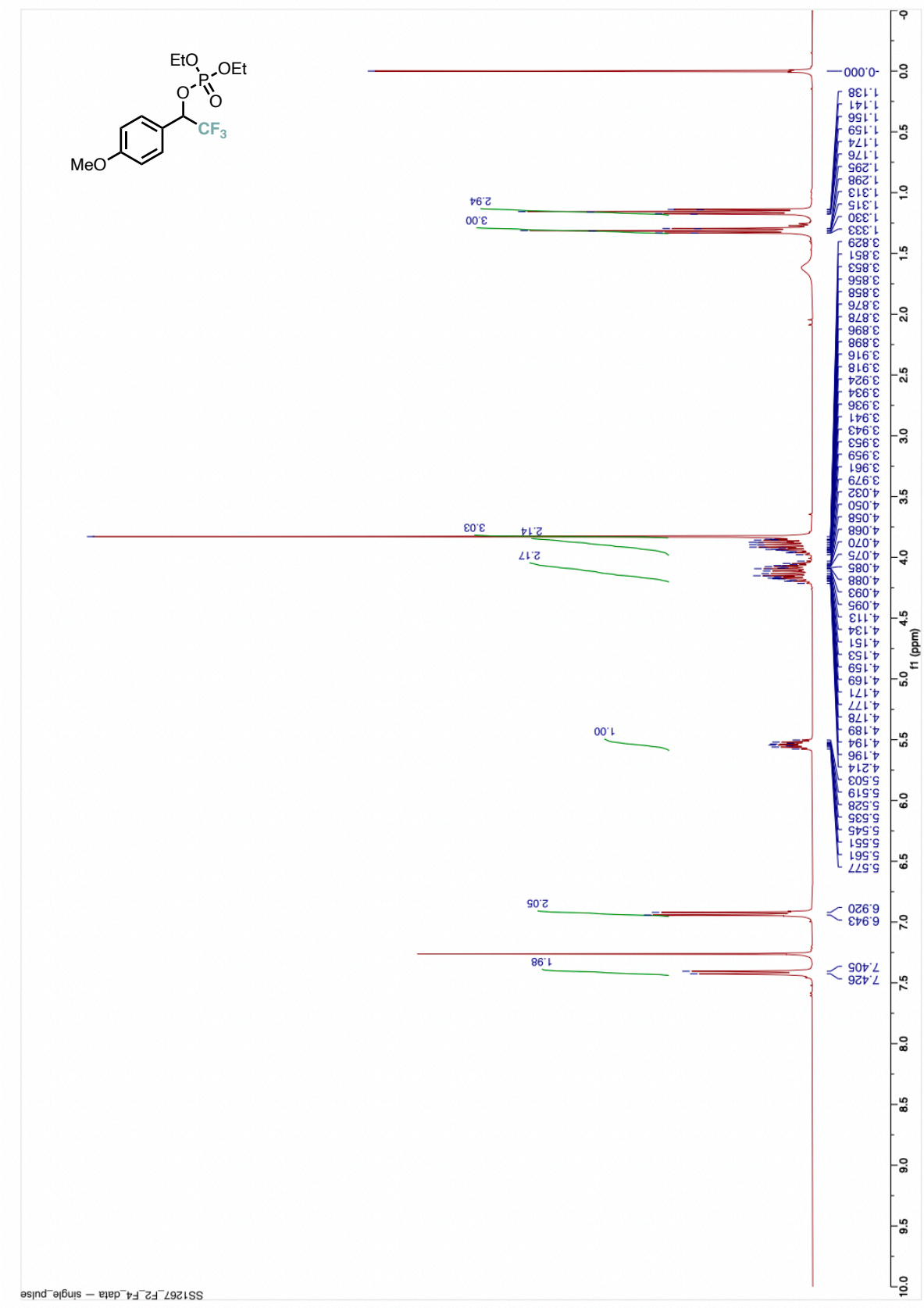
^{31}P NMR of **2A** (162 MHz, $CDCl_3$)



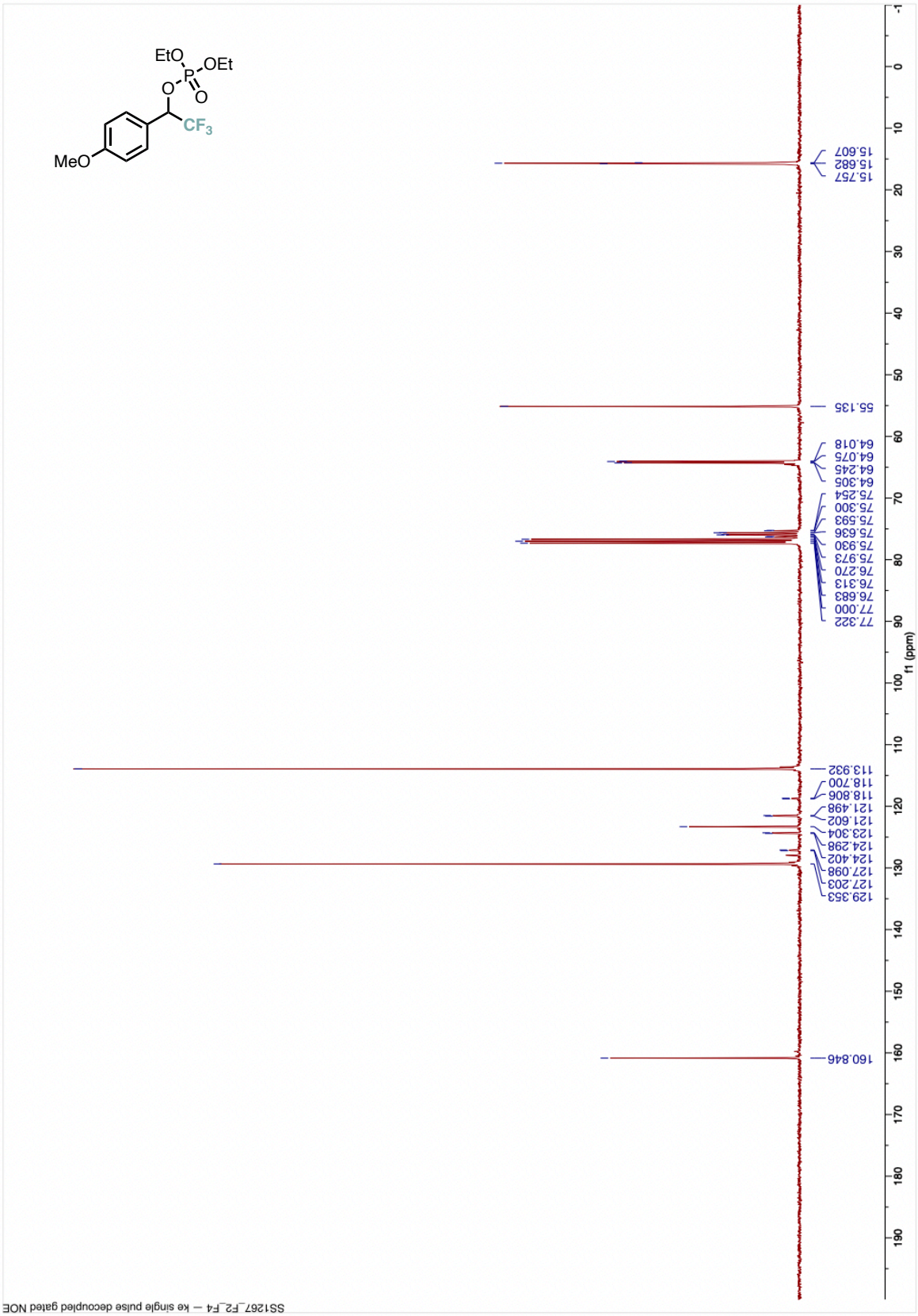
^{19}F NMR of **2A** (376 MHz, $CDCl_3$)



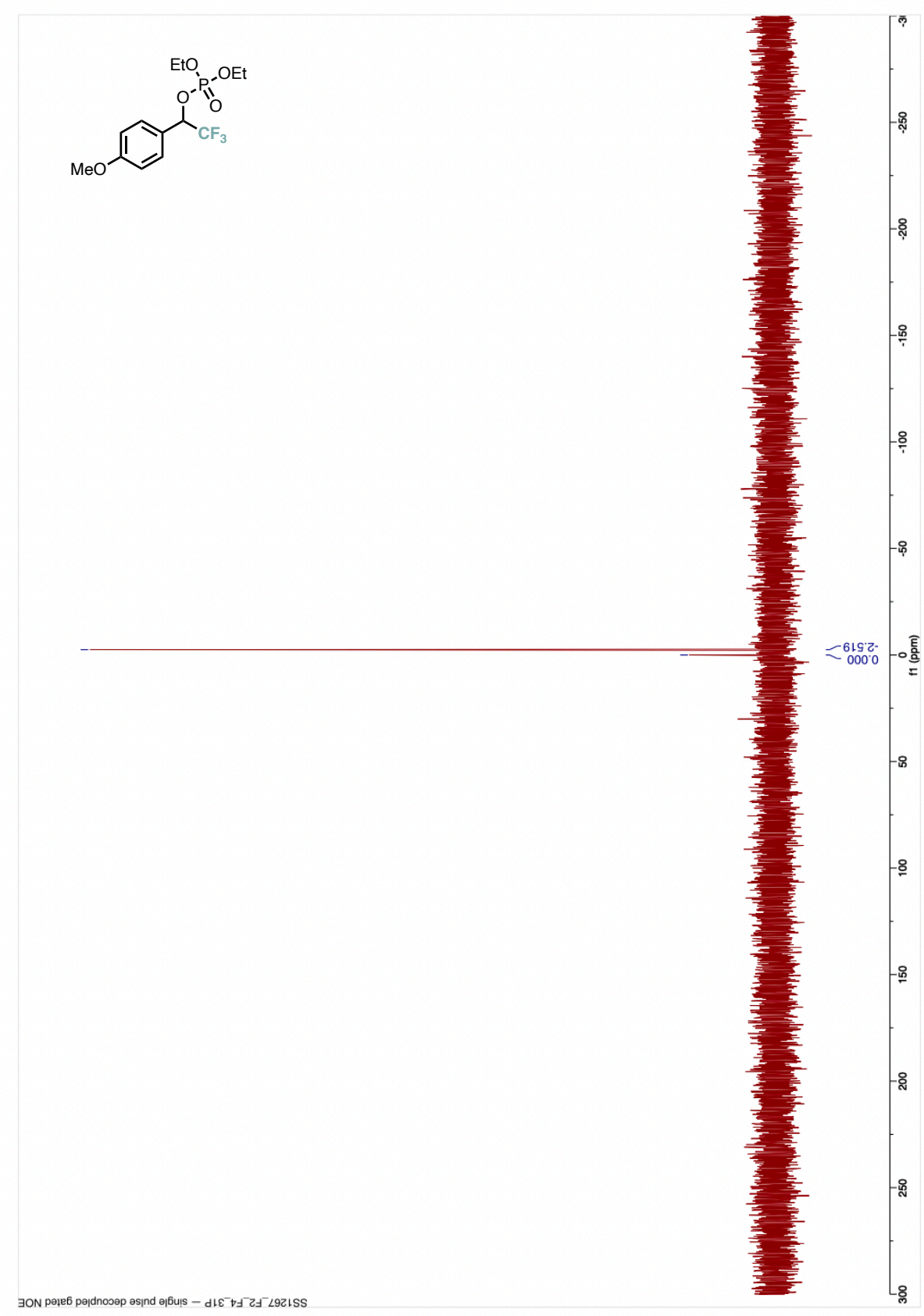
^{1}H NMR of **2A′** (400 MHz, $CDCl_3$)



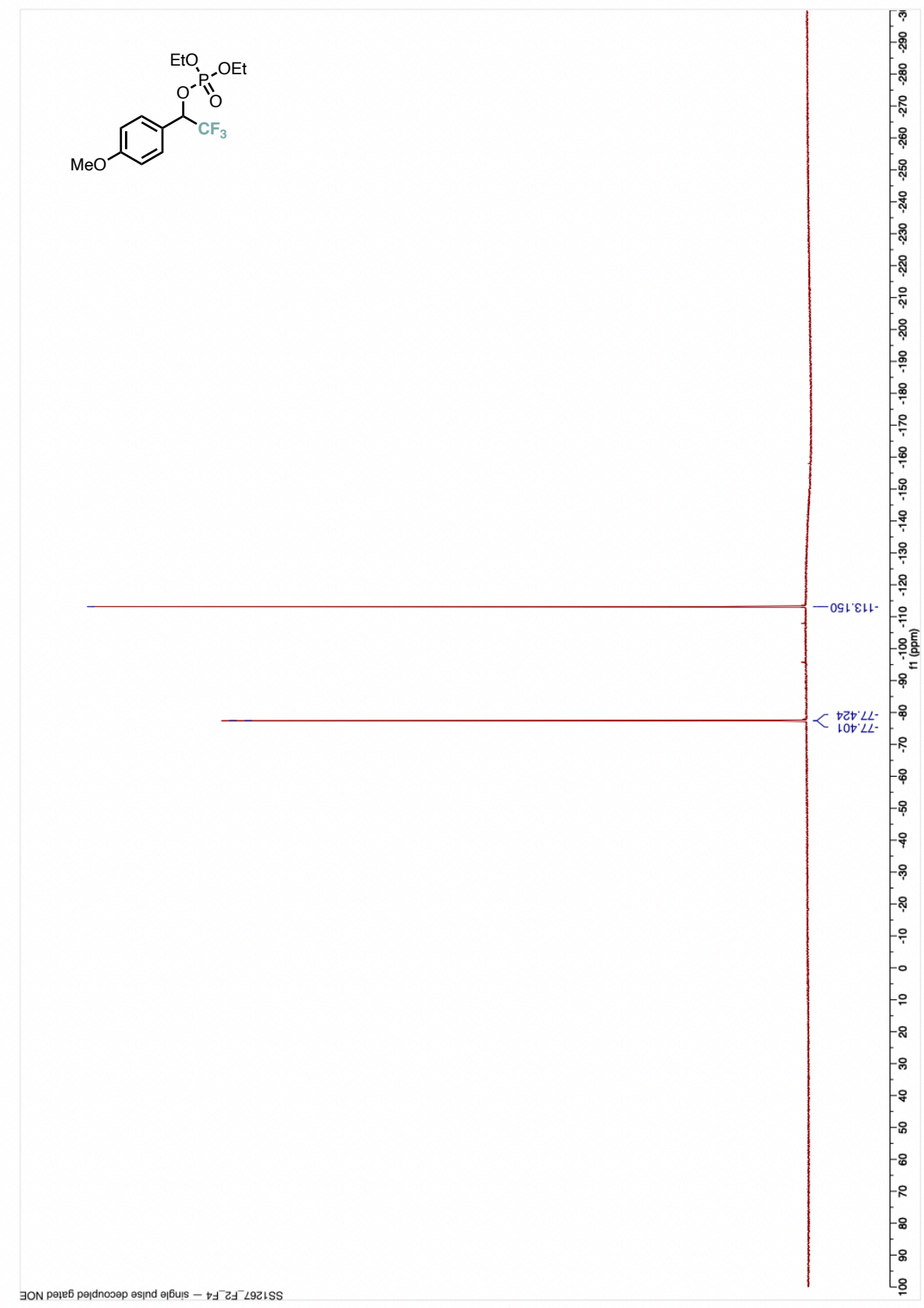
$^{13}C\{^{1}H\}$ NMR of **2A′** (101 MHz, $CDCl_3$)



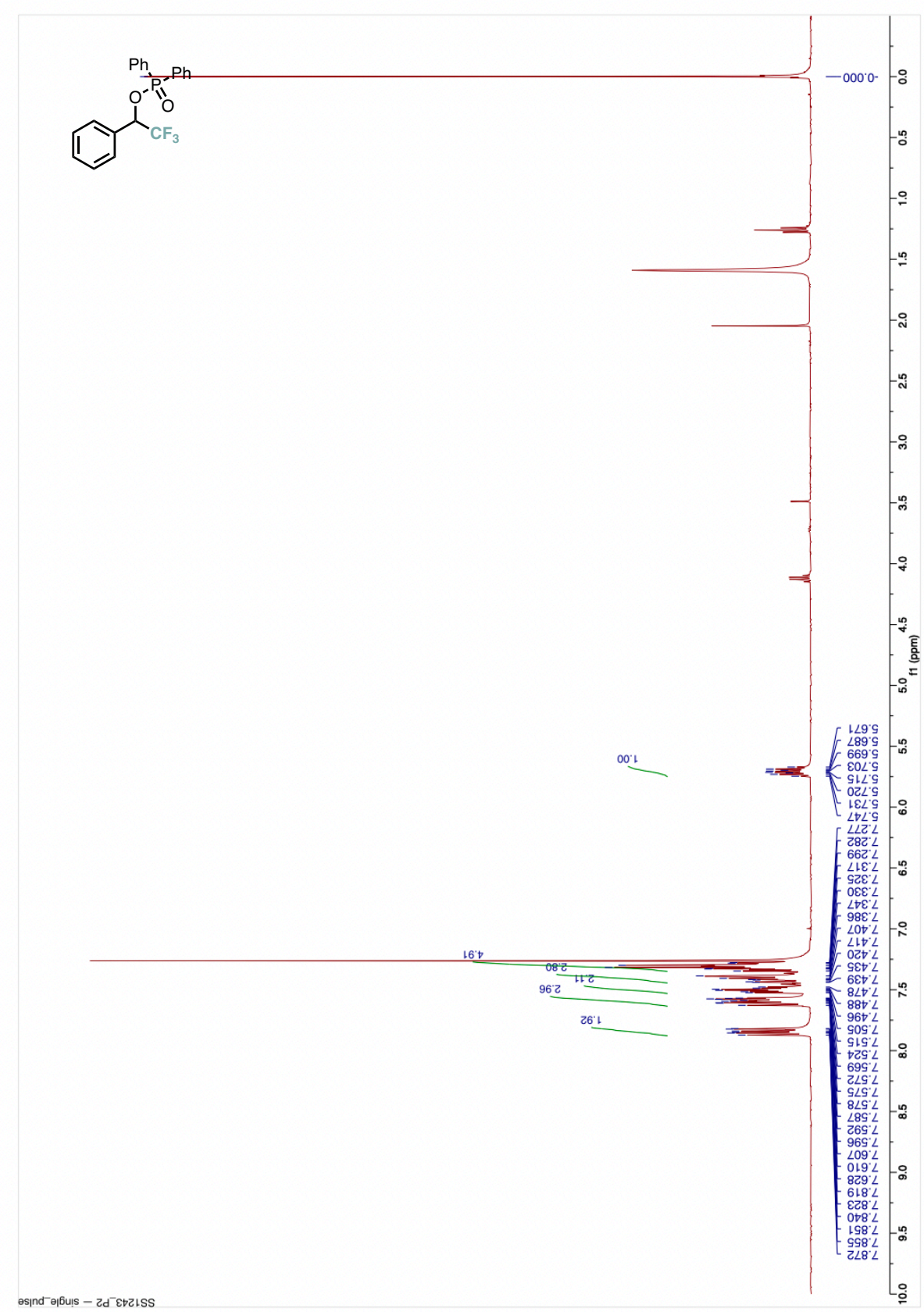
^{31}P NMR of **2A′** (162 MHz, $CDCl_3$)



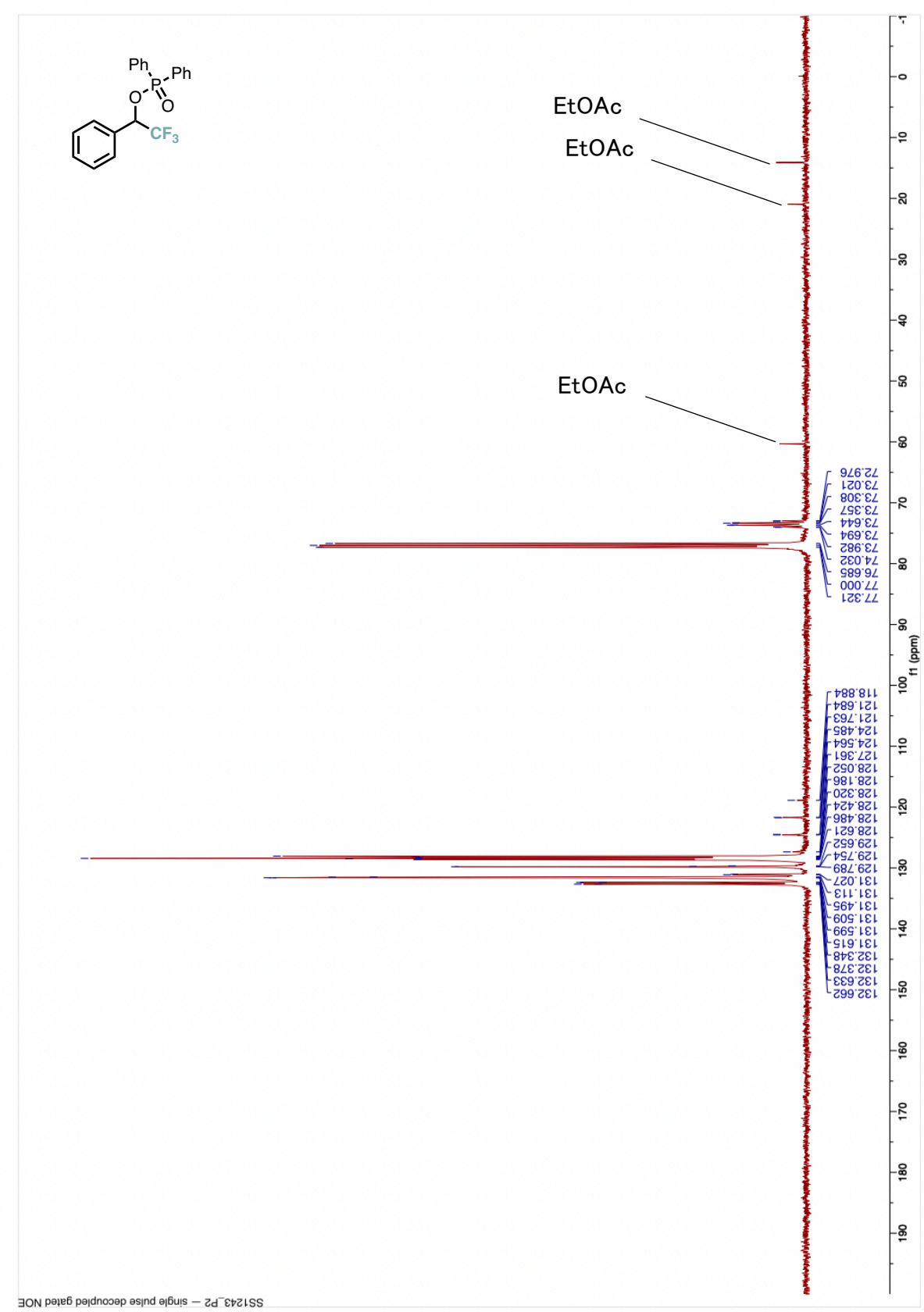
^{19}F NMR of **2A′** (376 MHz, $CDCl_3$)



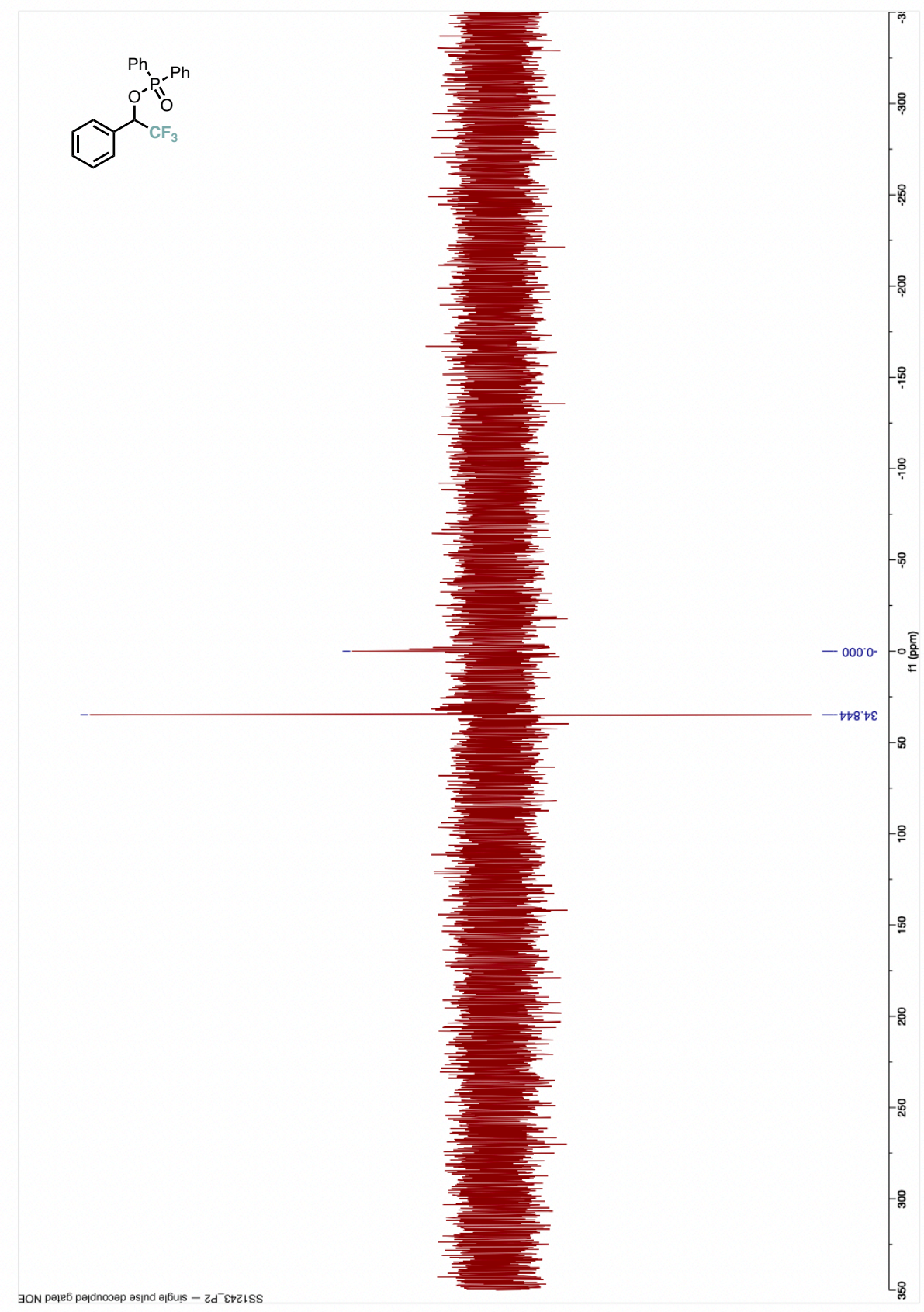
^{1}H NMR of **2B** (400 MHz, $CDCl_3$)



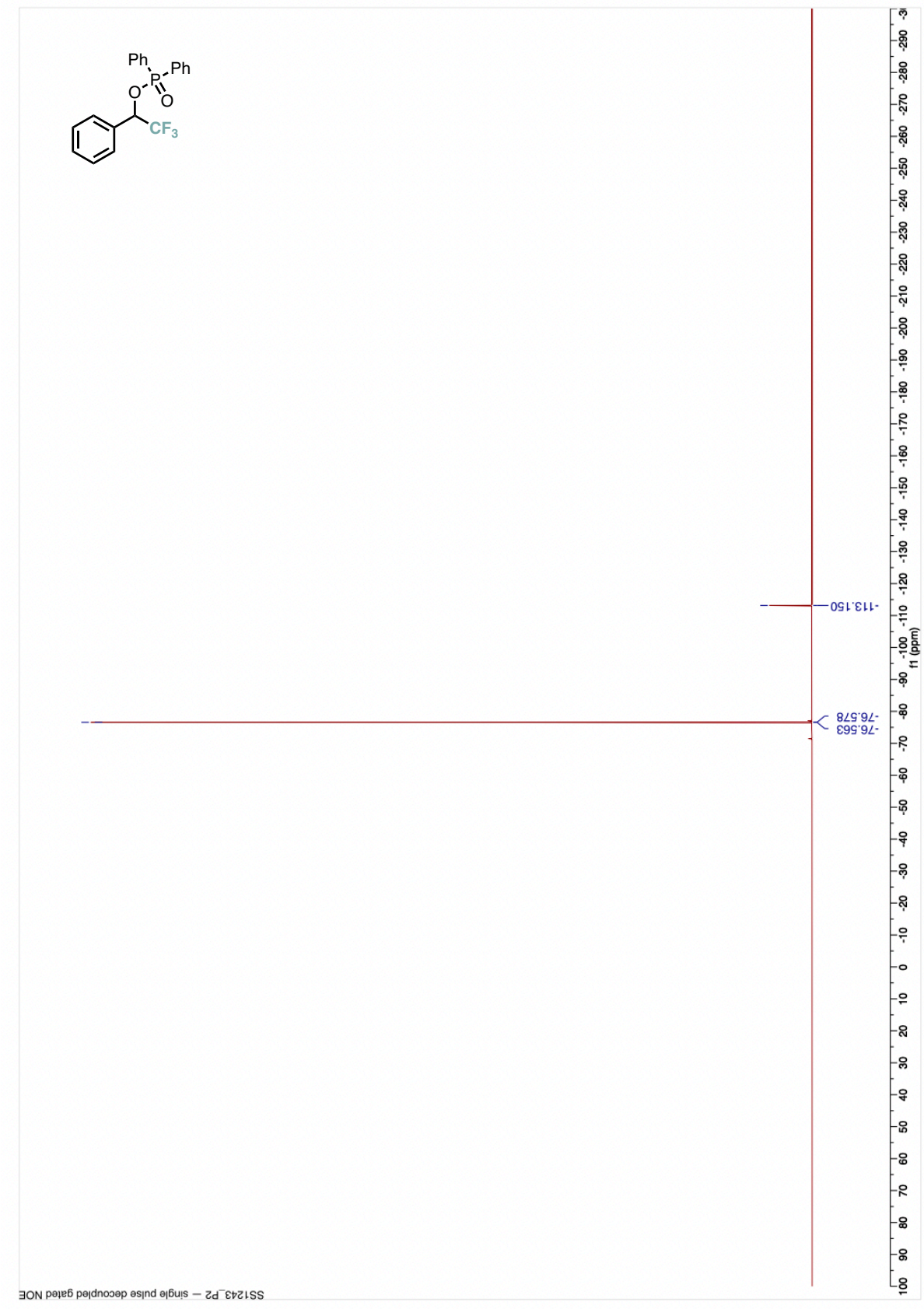
$^{13}C\{^{1}H\}$ NMR of **2B** (101 MHz, $CDCl_3$)



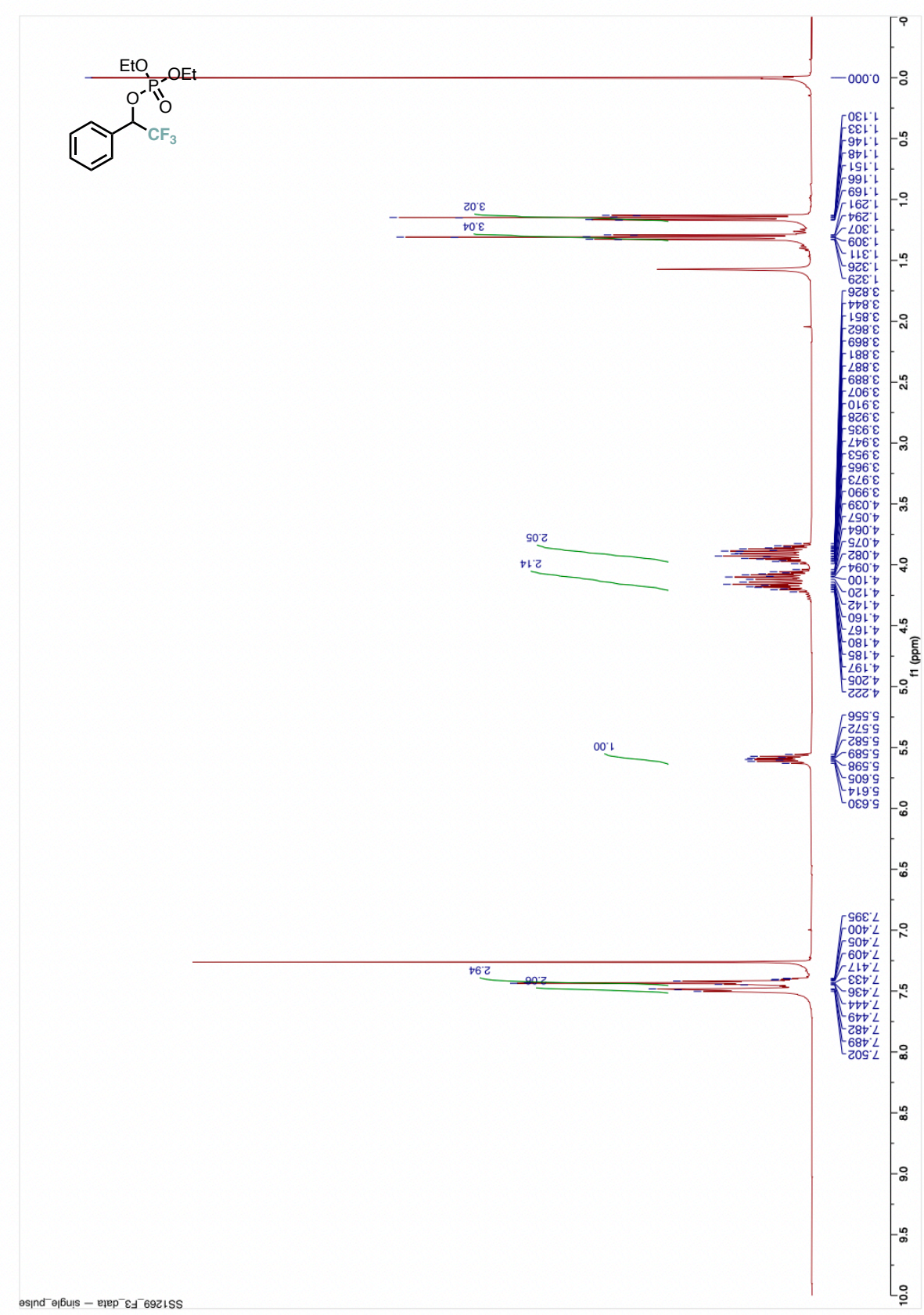
^{31}P NMR of **2B** (162 MHz, $CDCl_3$)



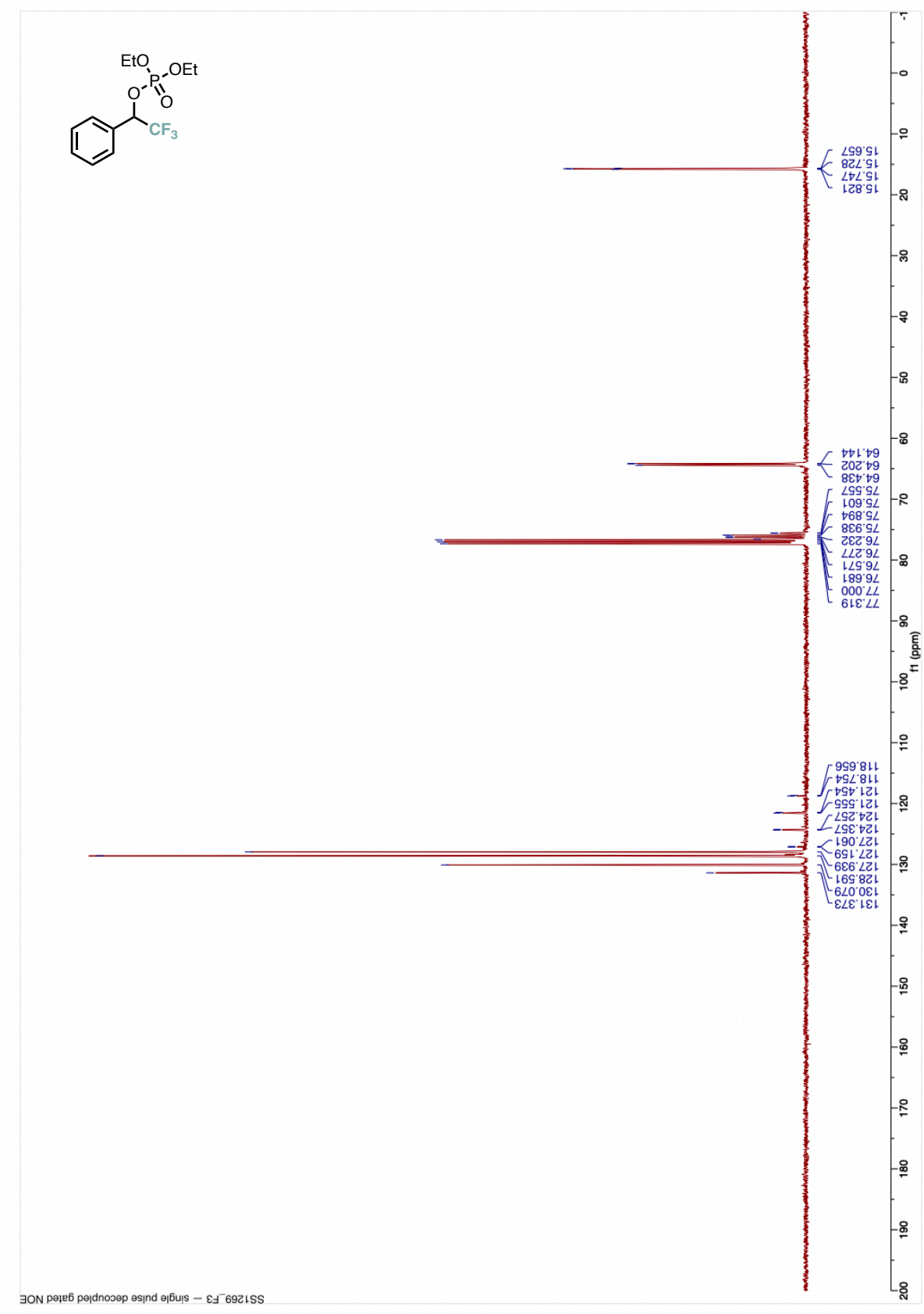
^{19}F NMR of **2B** (376 MHz, $CDCl_3$)



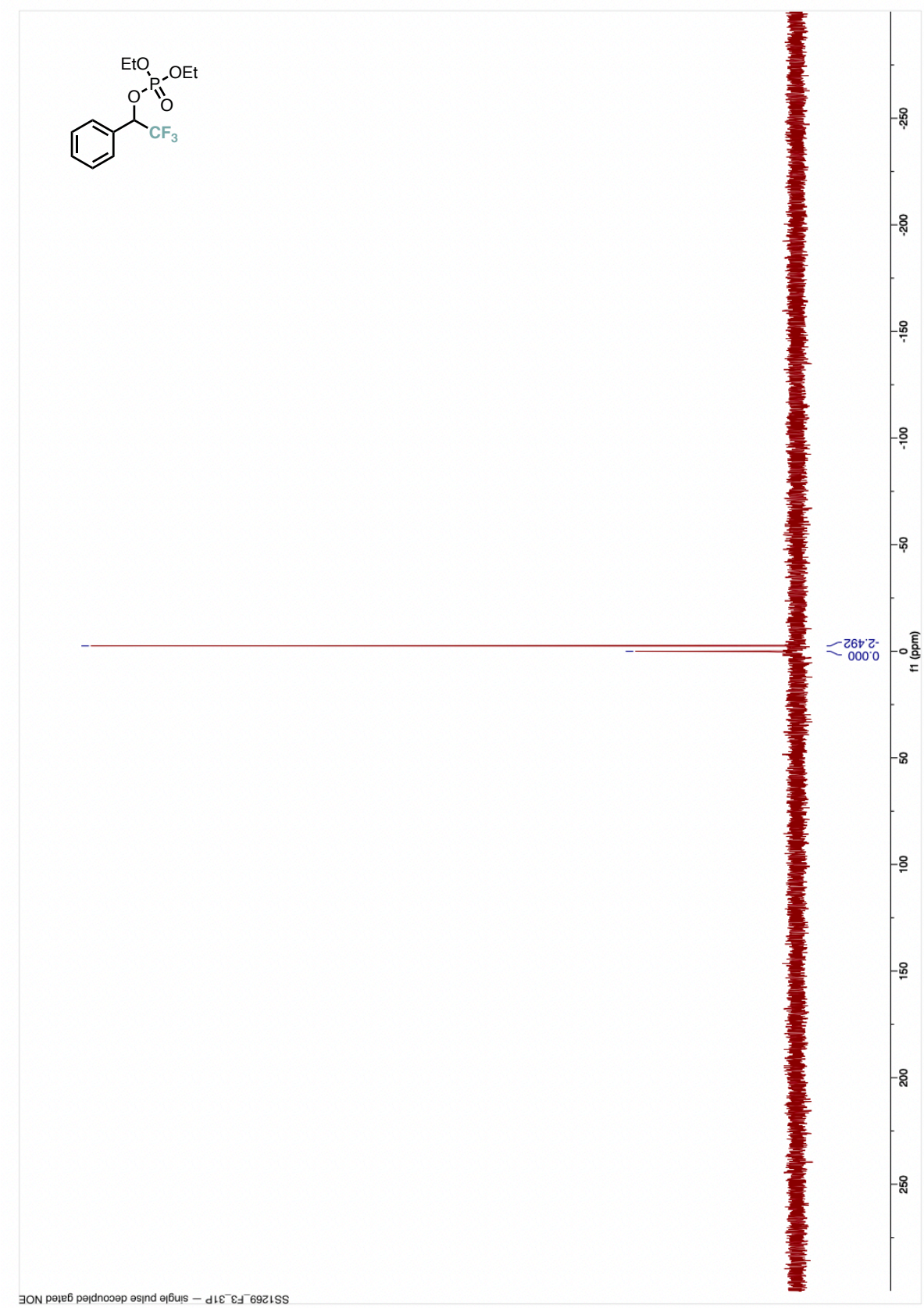
^{1}H NMR of **2B′** (400 MHz, $CDCl_3$)



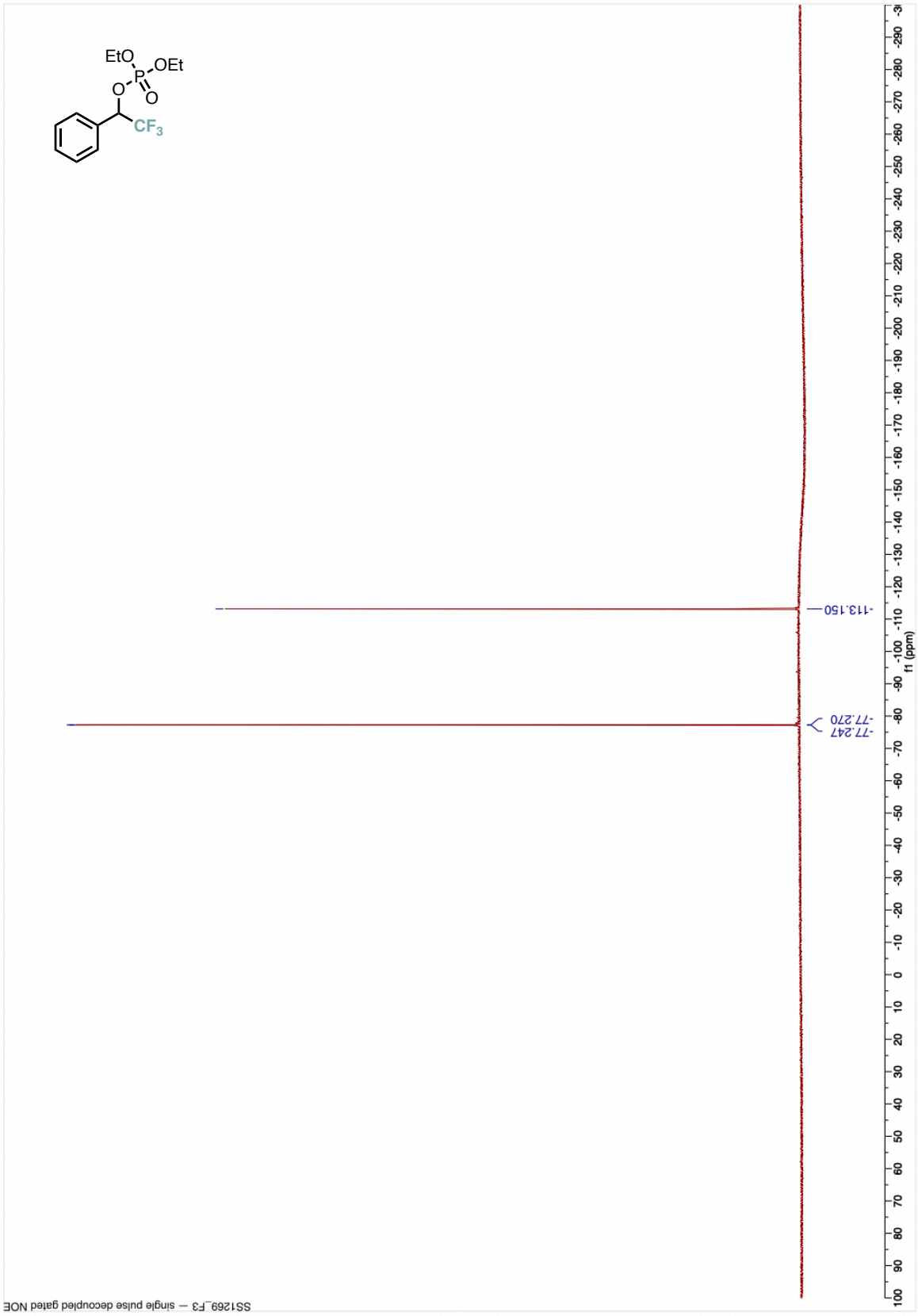
$^{13}C\{^{1}H\}$ NMR of **2B′** (101 MHz, $CDCl_3$)



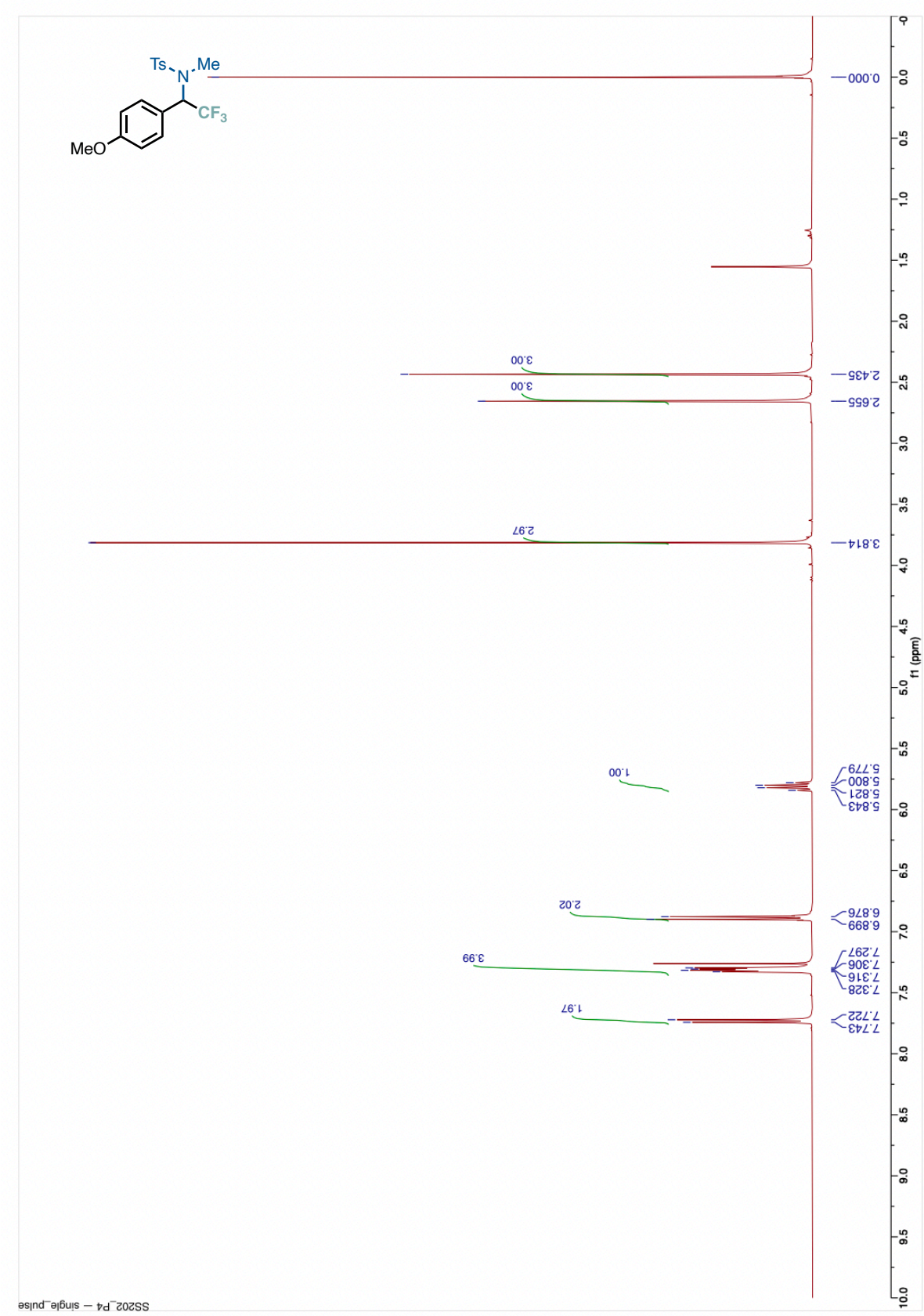
^{31}P NMR of **2B′** (162 MHz, $CDCl_3$)



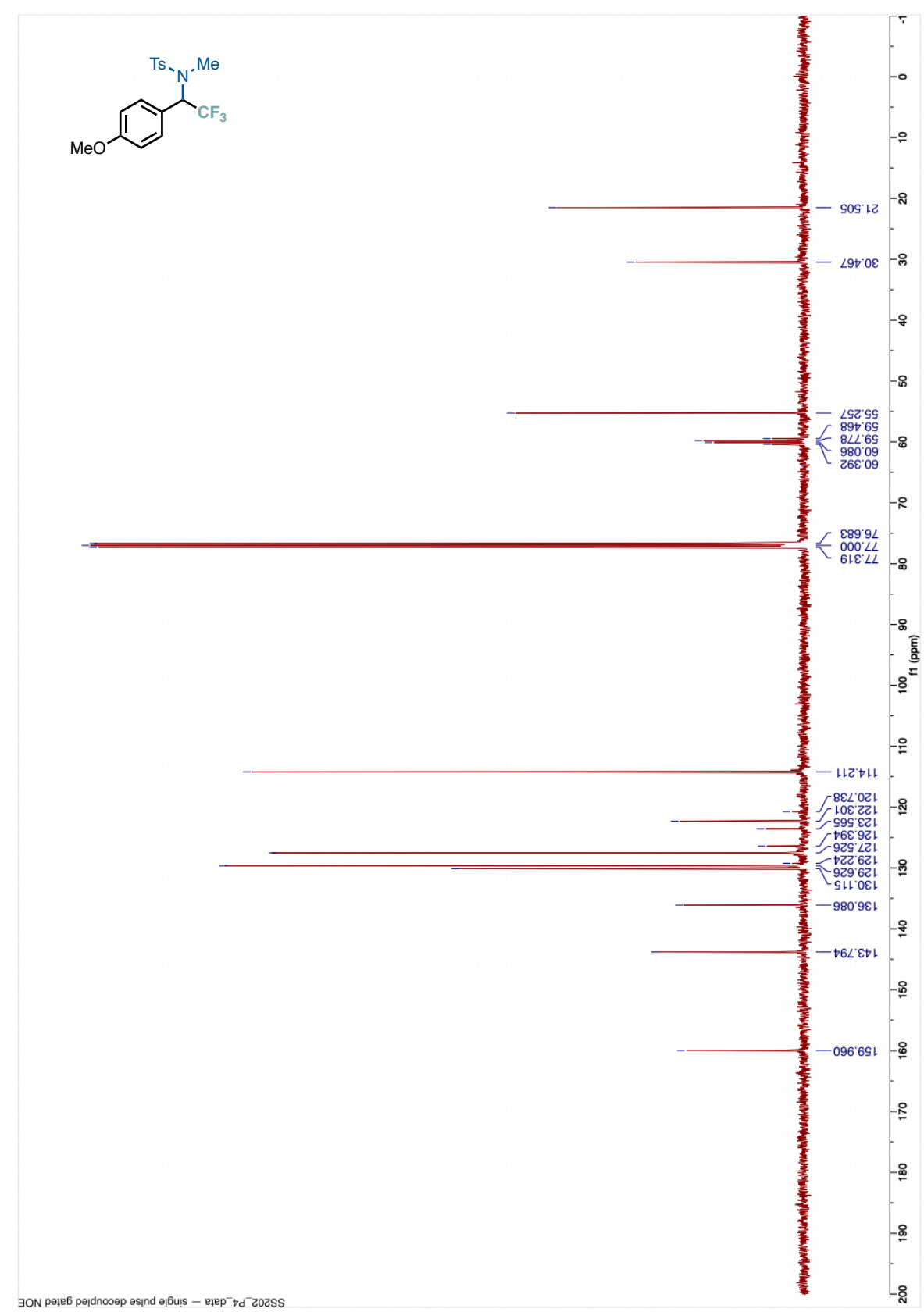
^{19}F NMR of **2B′** (376 MHz, $CDCl_3$)



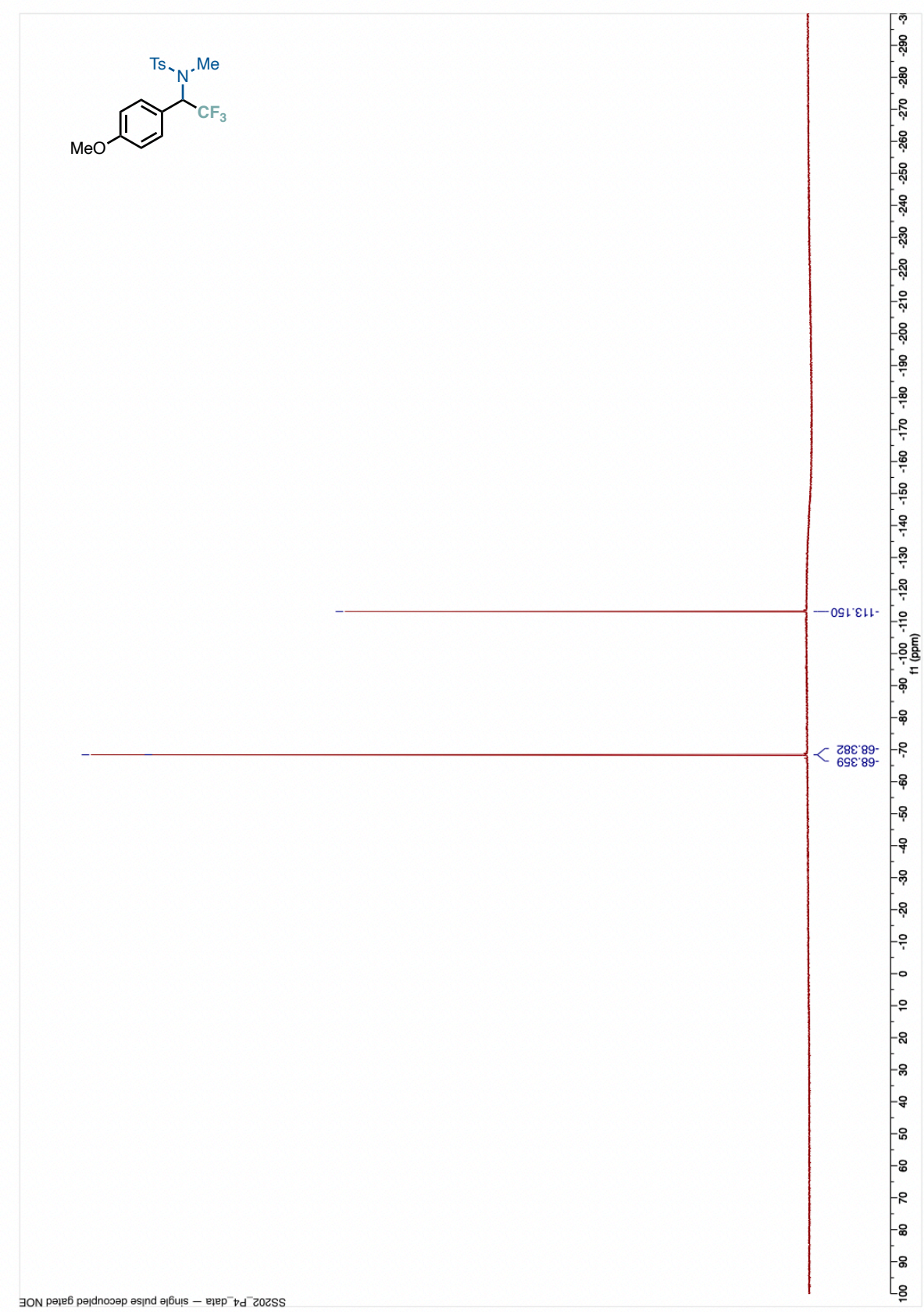
^{1}H NMR of **3A** (400 MHz, $CDCl_3$)



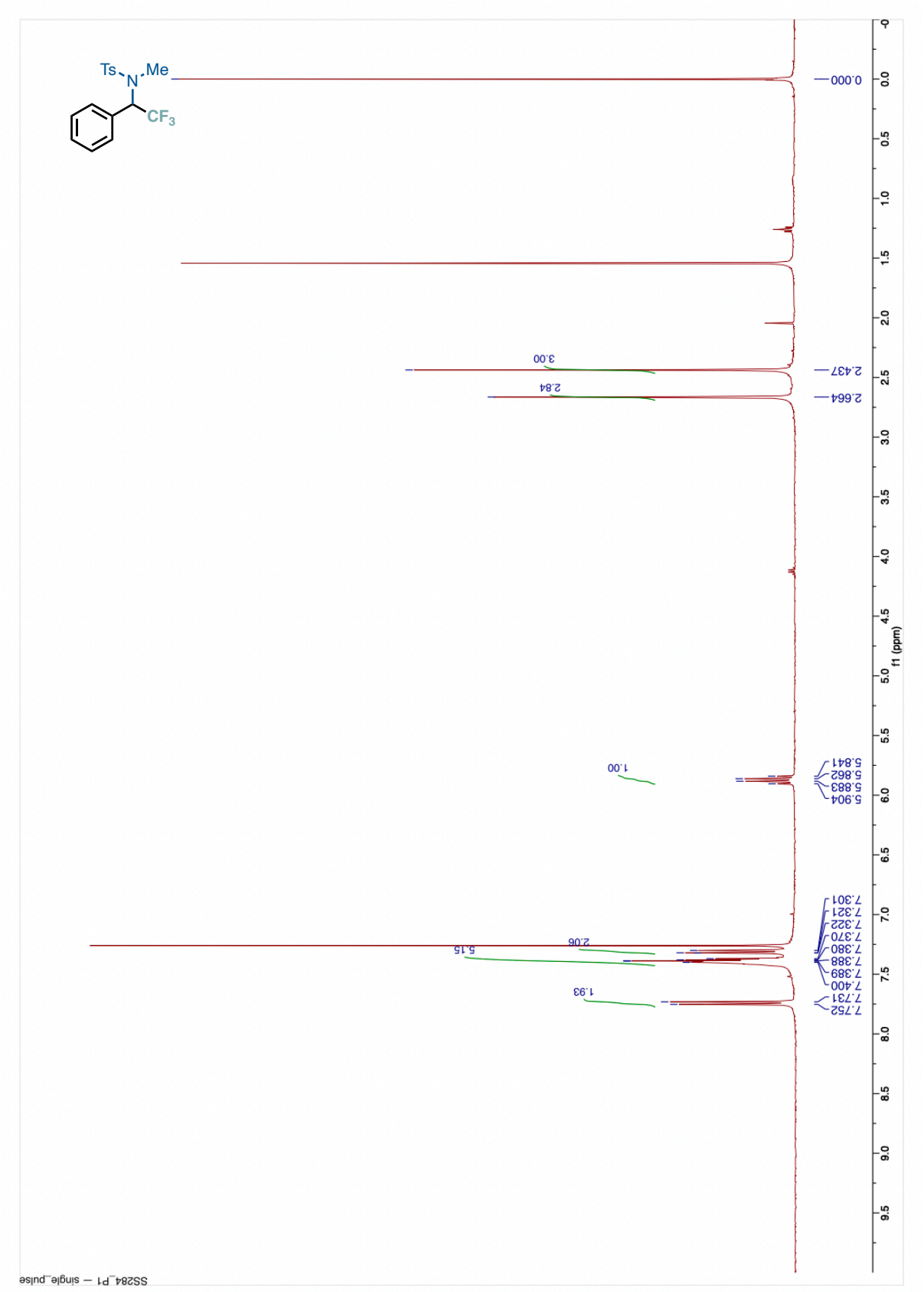
$^{13}C\{^{1}H\}$ NMR of **3A** (101 MHz, $CDCl_3$)



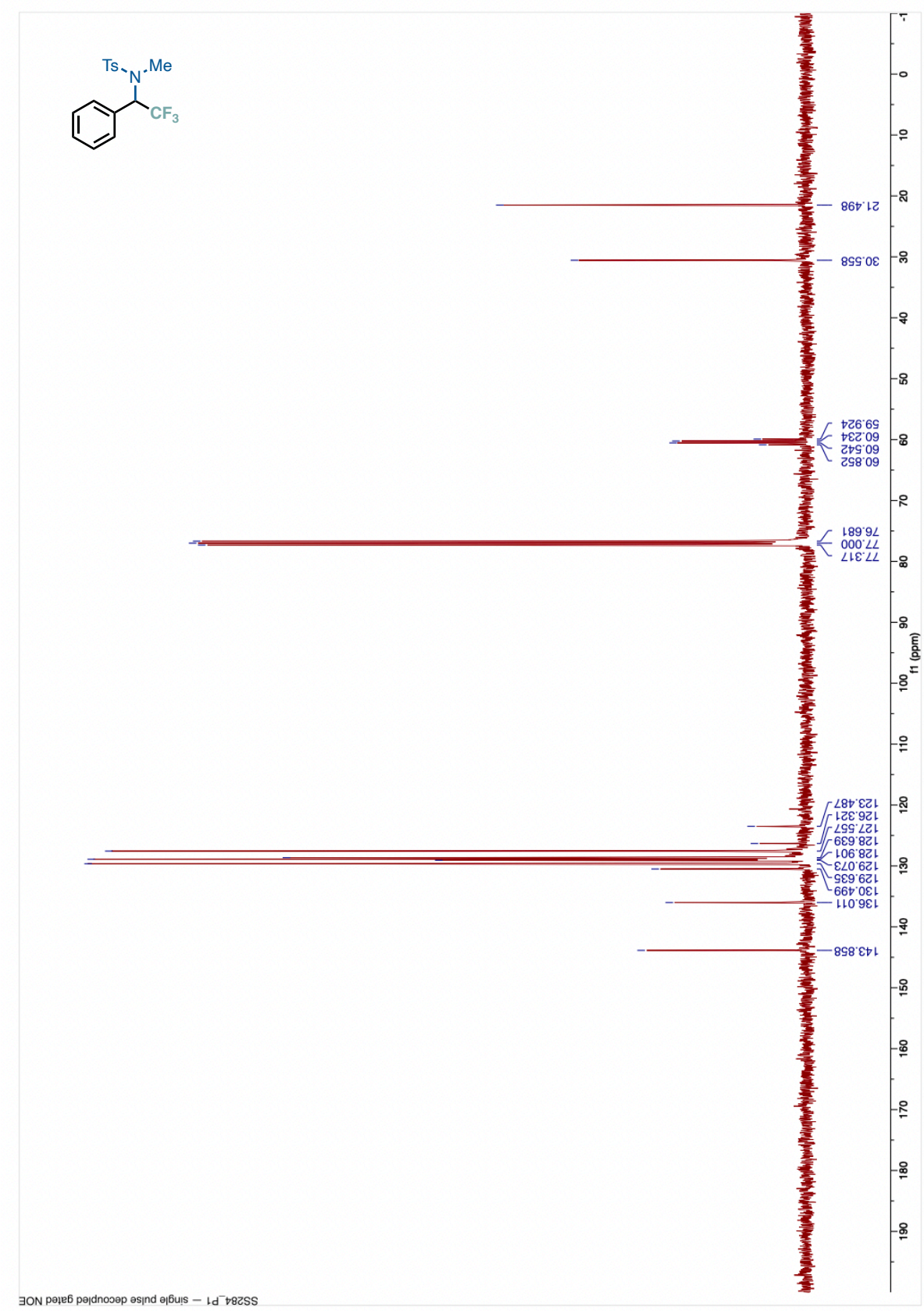
^{19}F NMR of **3A** (376 MHz, $CDCl_3$)



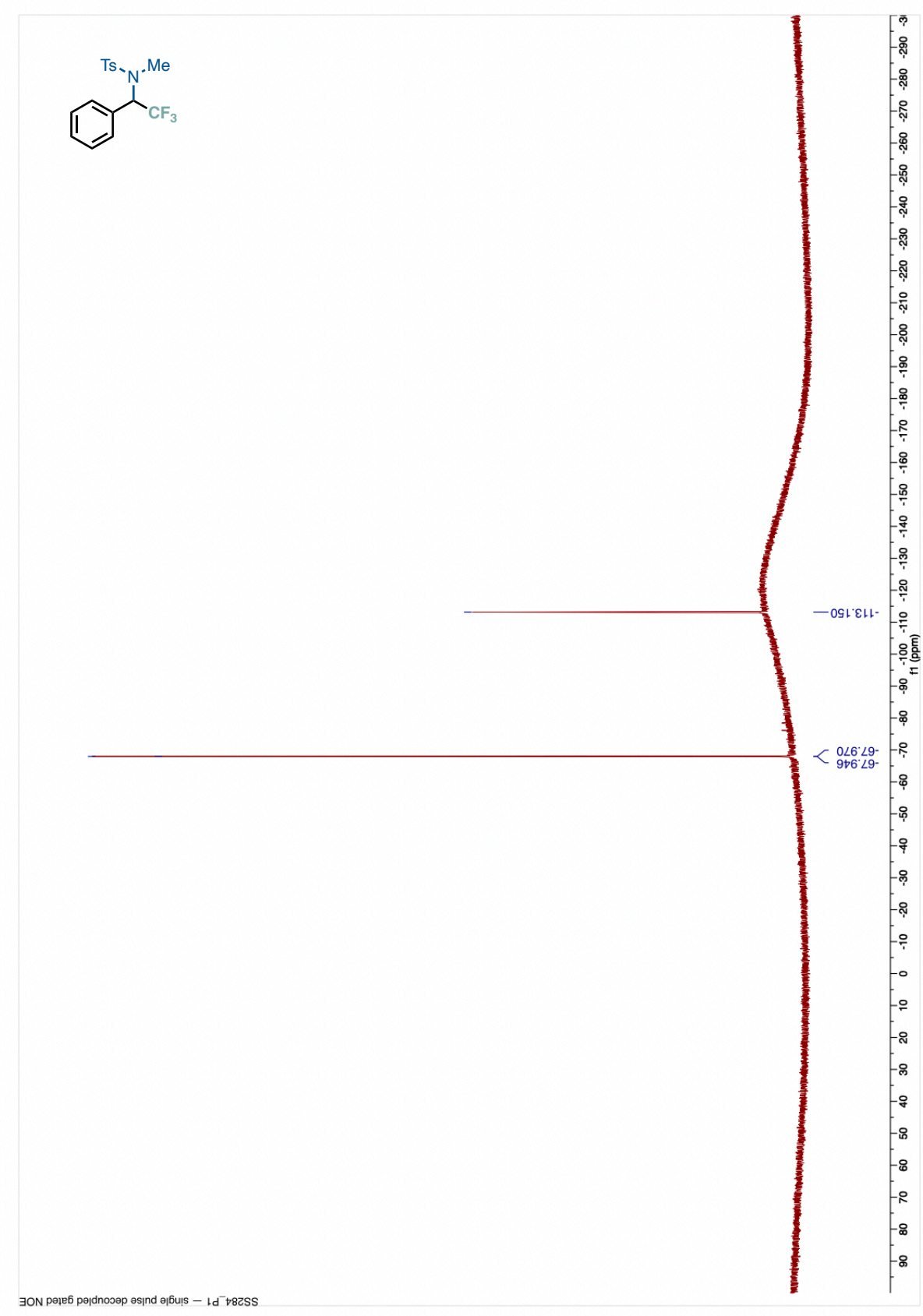
^{1}H NMR of **3B** (400 MHz, $CDCl_3$)



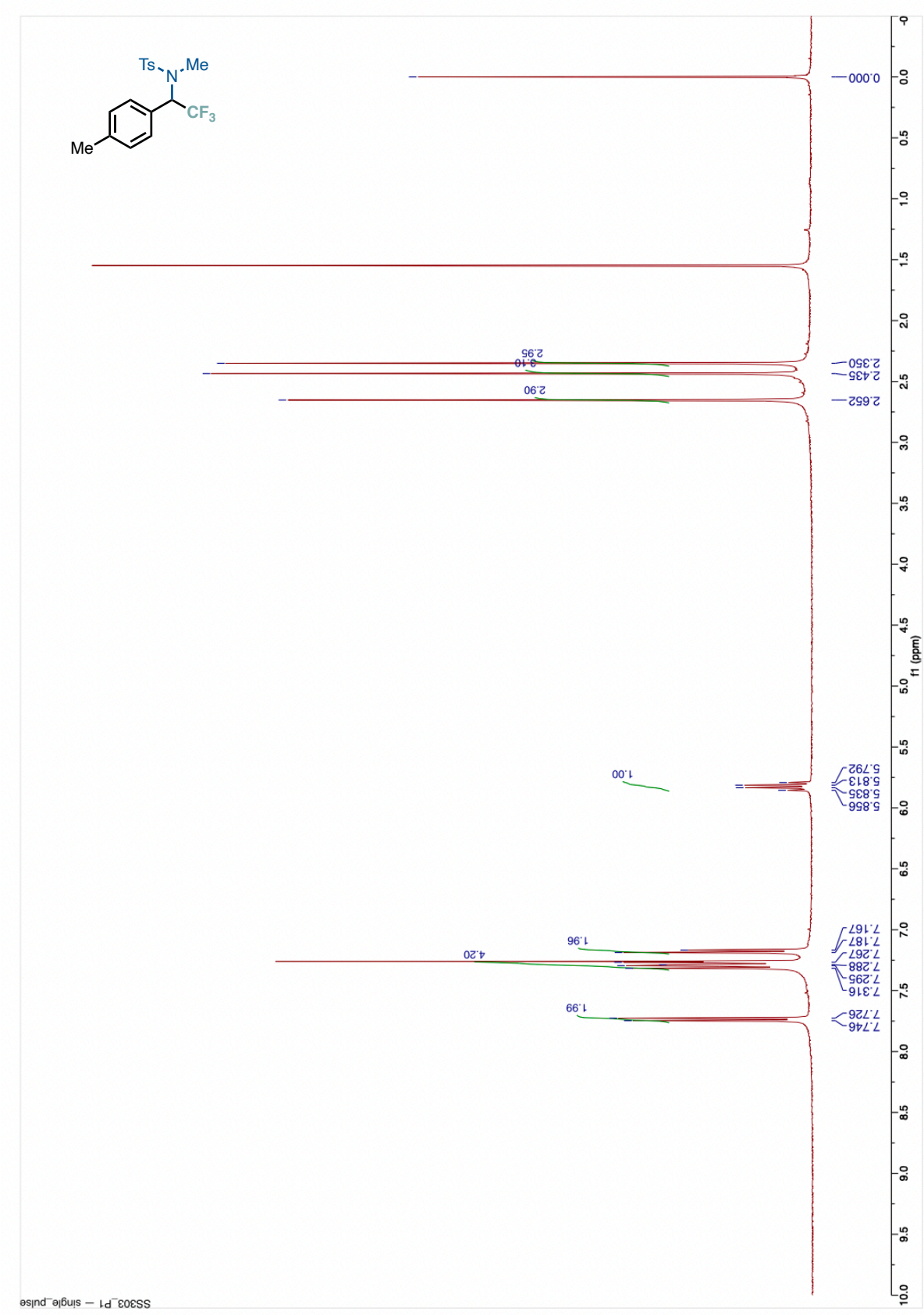
$^{13}C\{^{1}H\}$ NMR of **3B** (101 MHz, $CDCl_3$)



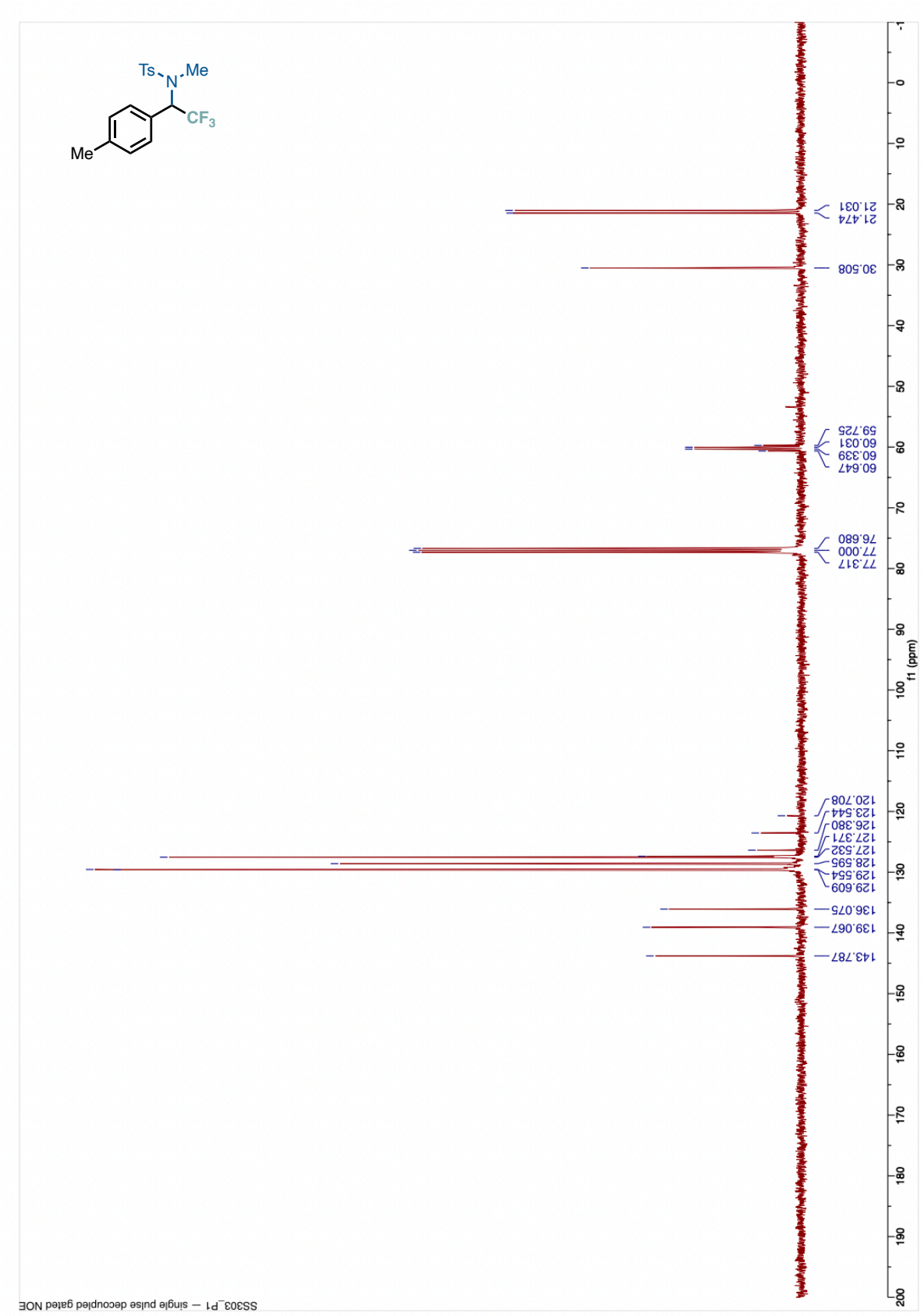
^{19}F NMR of **3B** (376 MHz, $CDCl_3$)



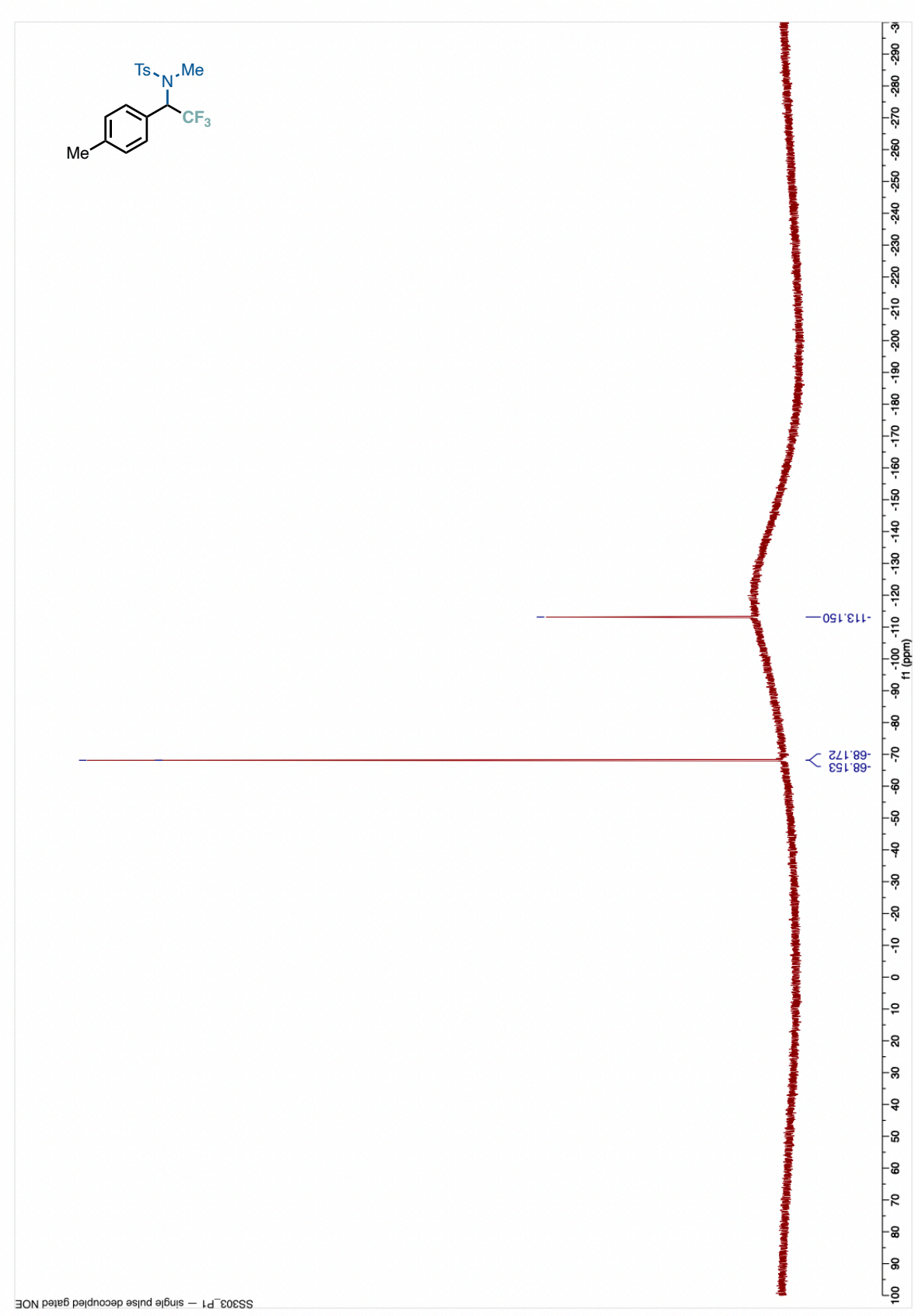
^{1}H NMR of **3C** (400 MHz, $CDCl_3$)



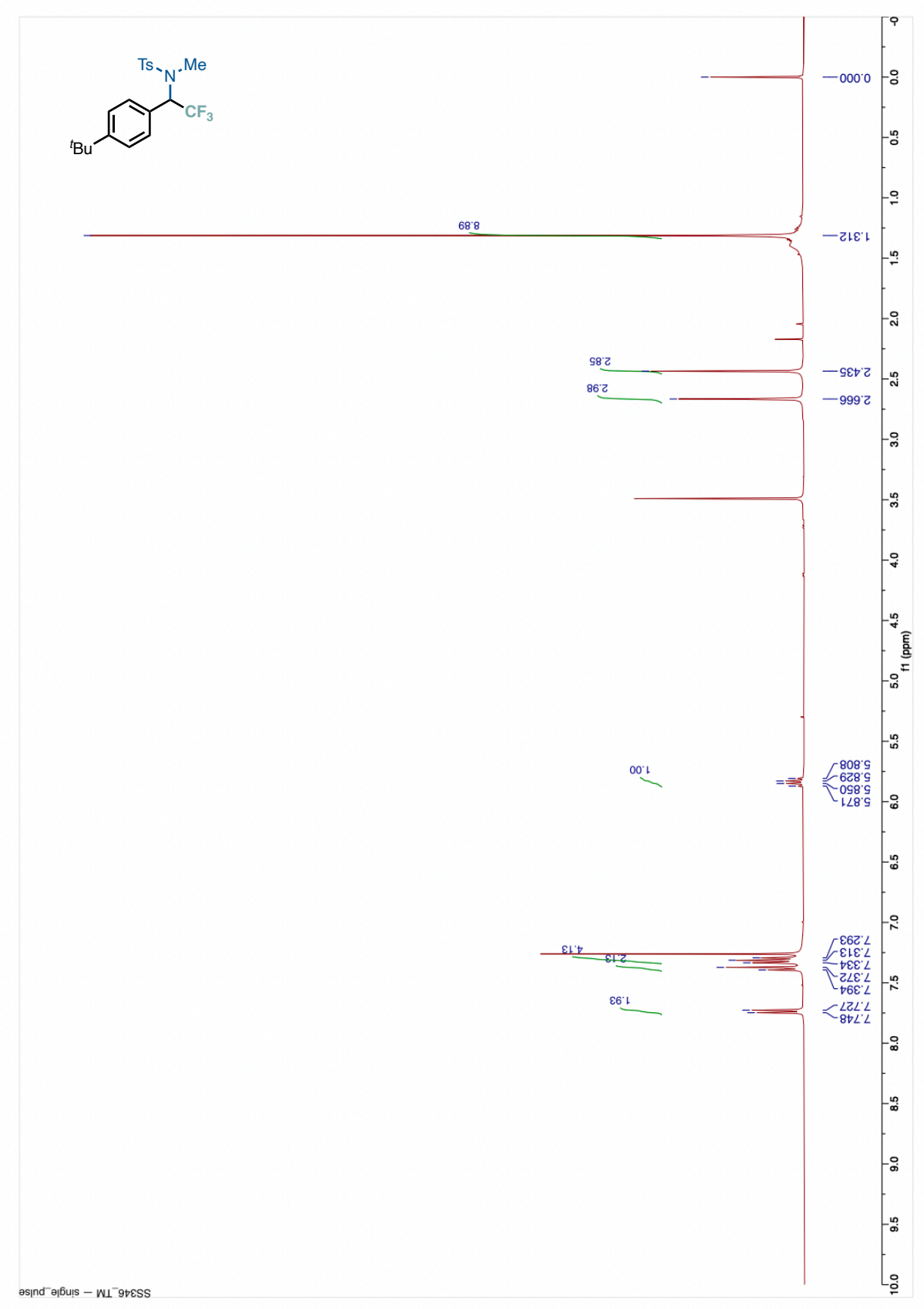
$^{13}C\{^{1}H\}$ NMR of **3C** (101 MHz, $CDCl_3$)



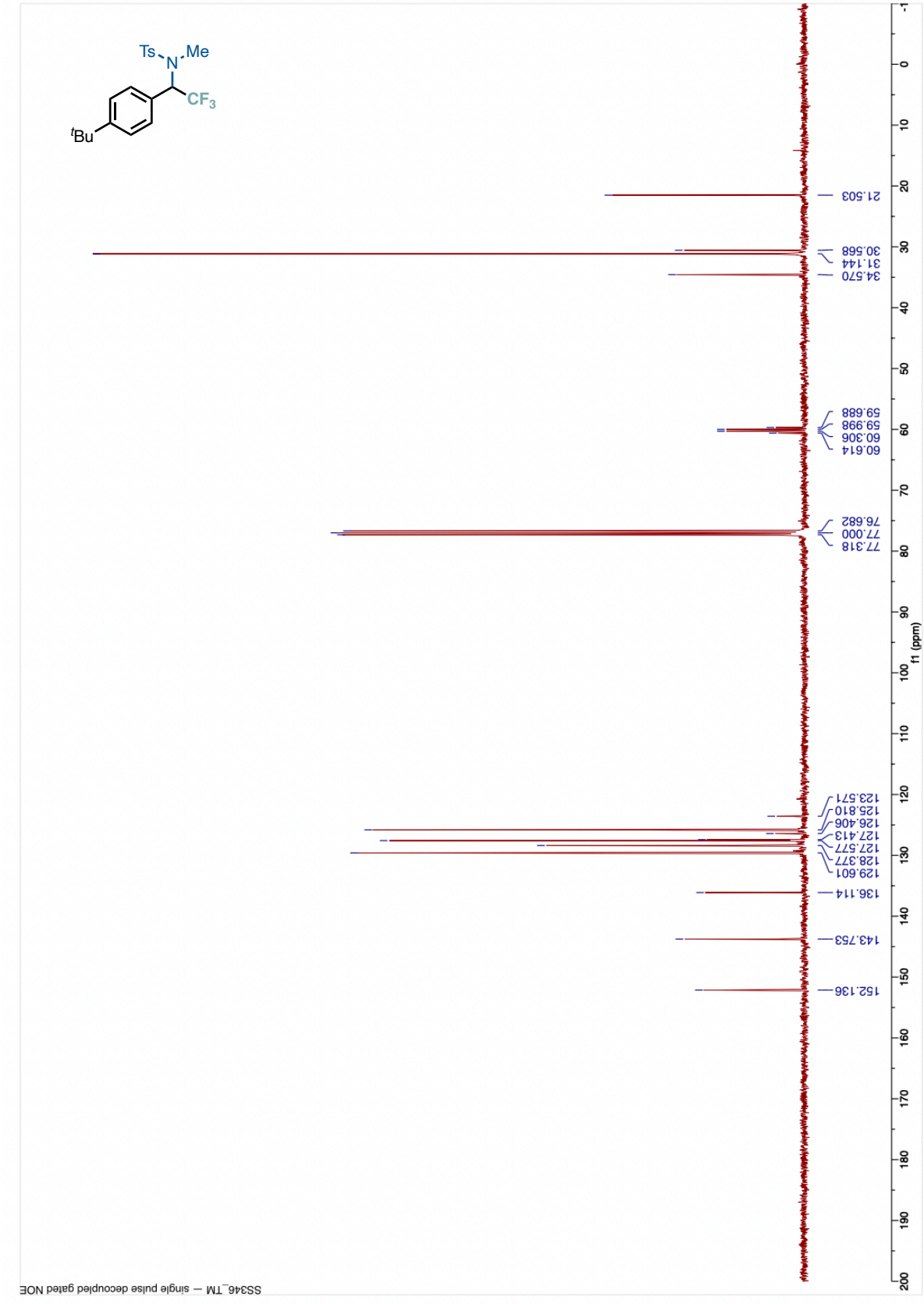
^{19}F NMR of **3C** (376 MHz, $CDCl_3$)



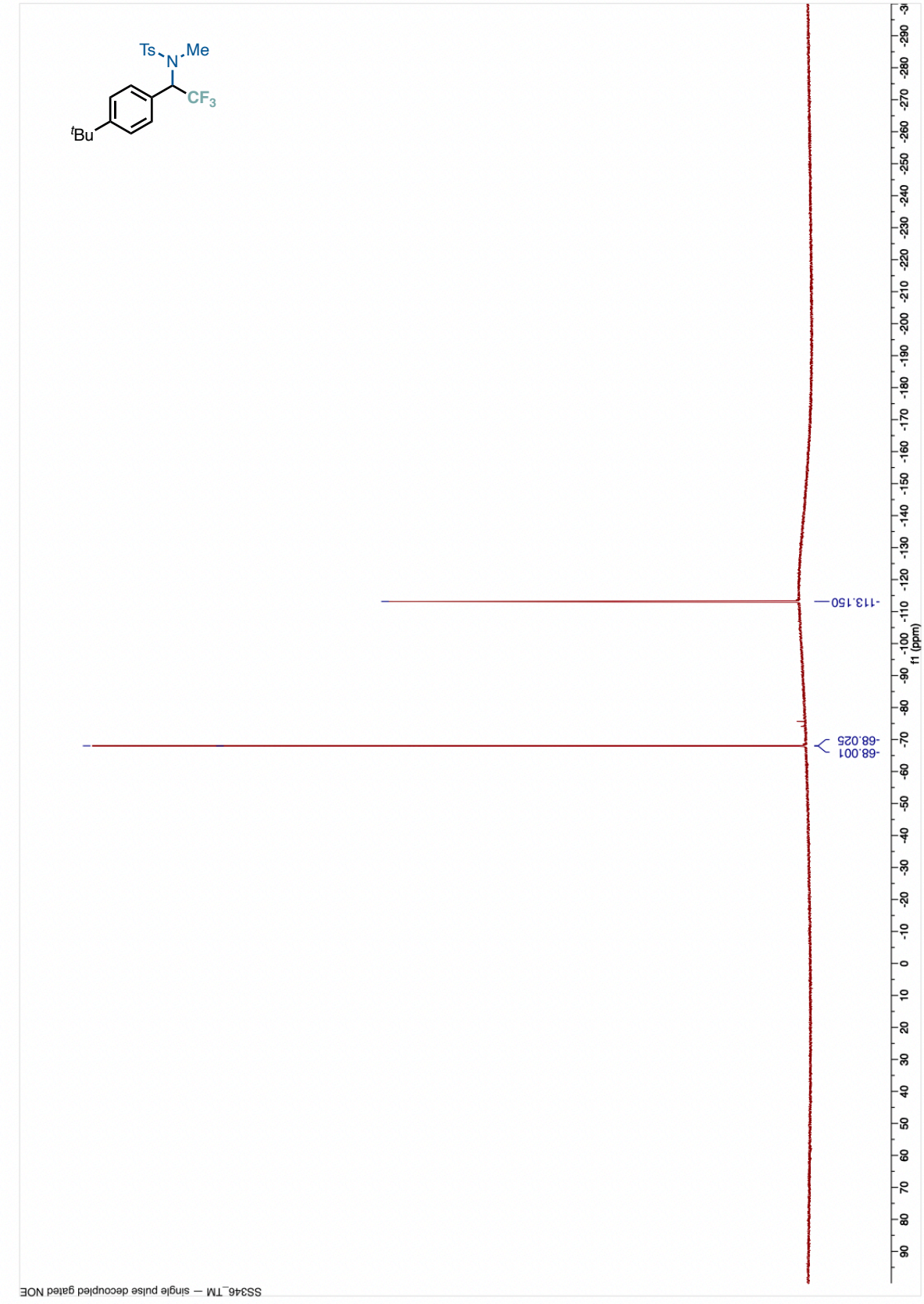
^{1}H NMR of **3D** (400 MHz, $CDCl_3$)



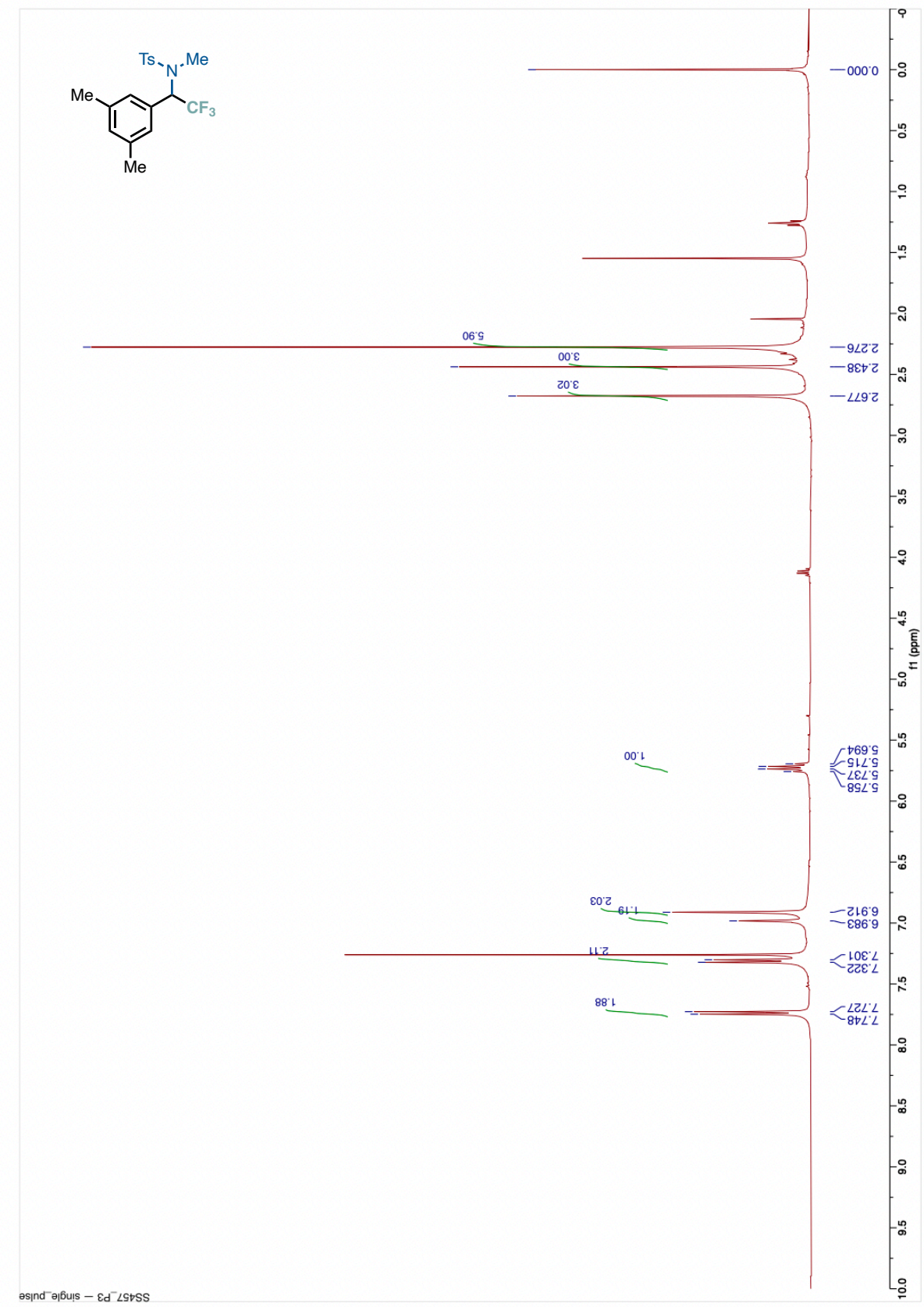
$^{13}C\{^{1}H\}$ NMR of **3D** (101 MHz, $CDCl_3$)



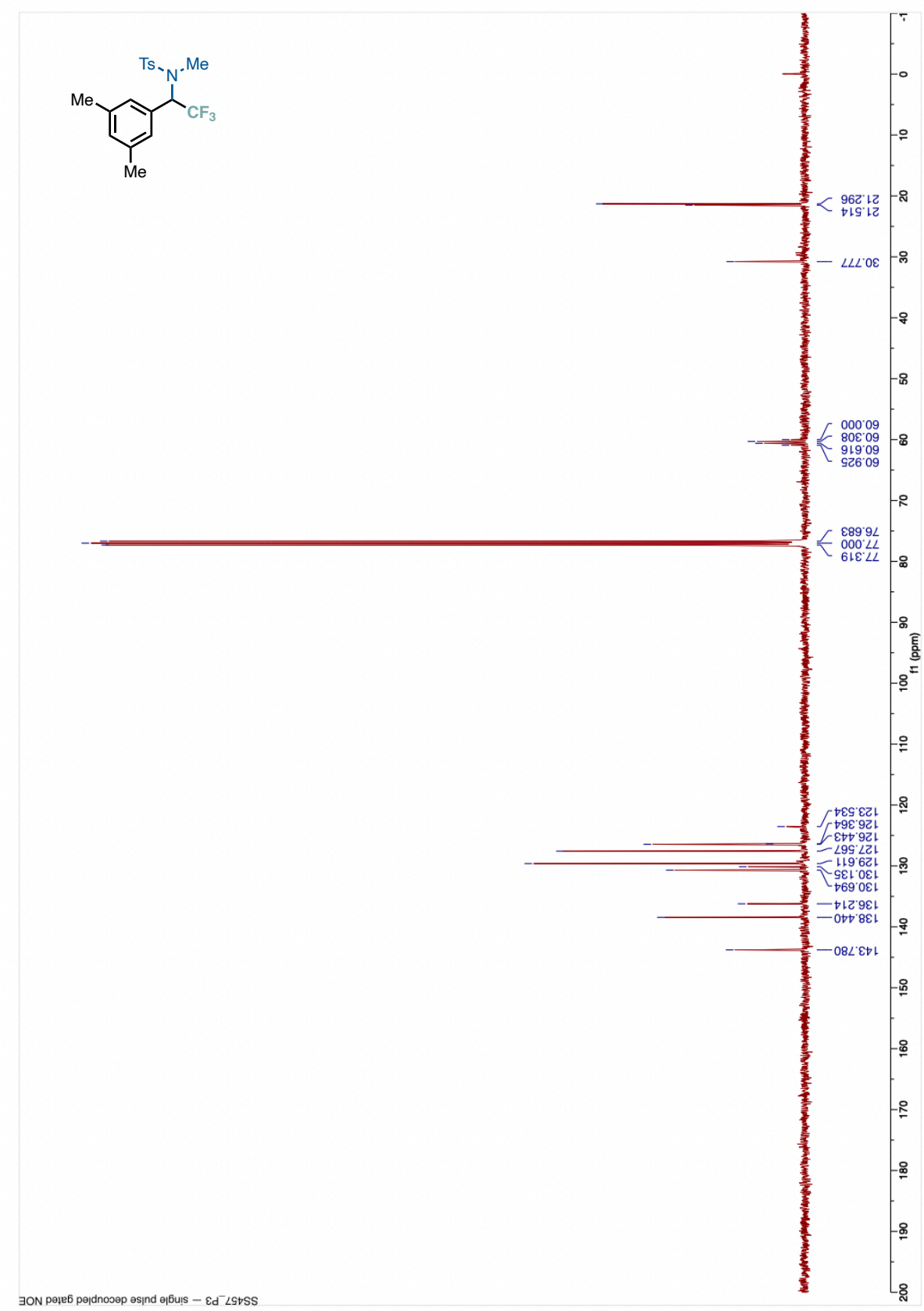
^{19}F NMR of **3D** (376 MHz, $CDCl_3$)



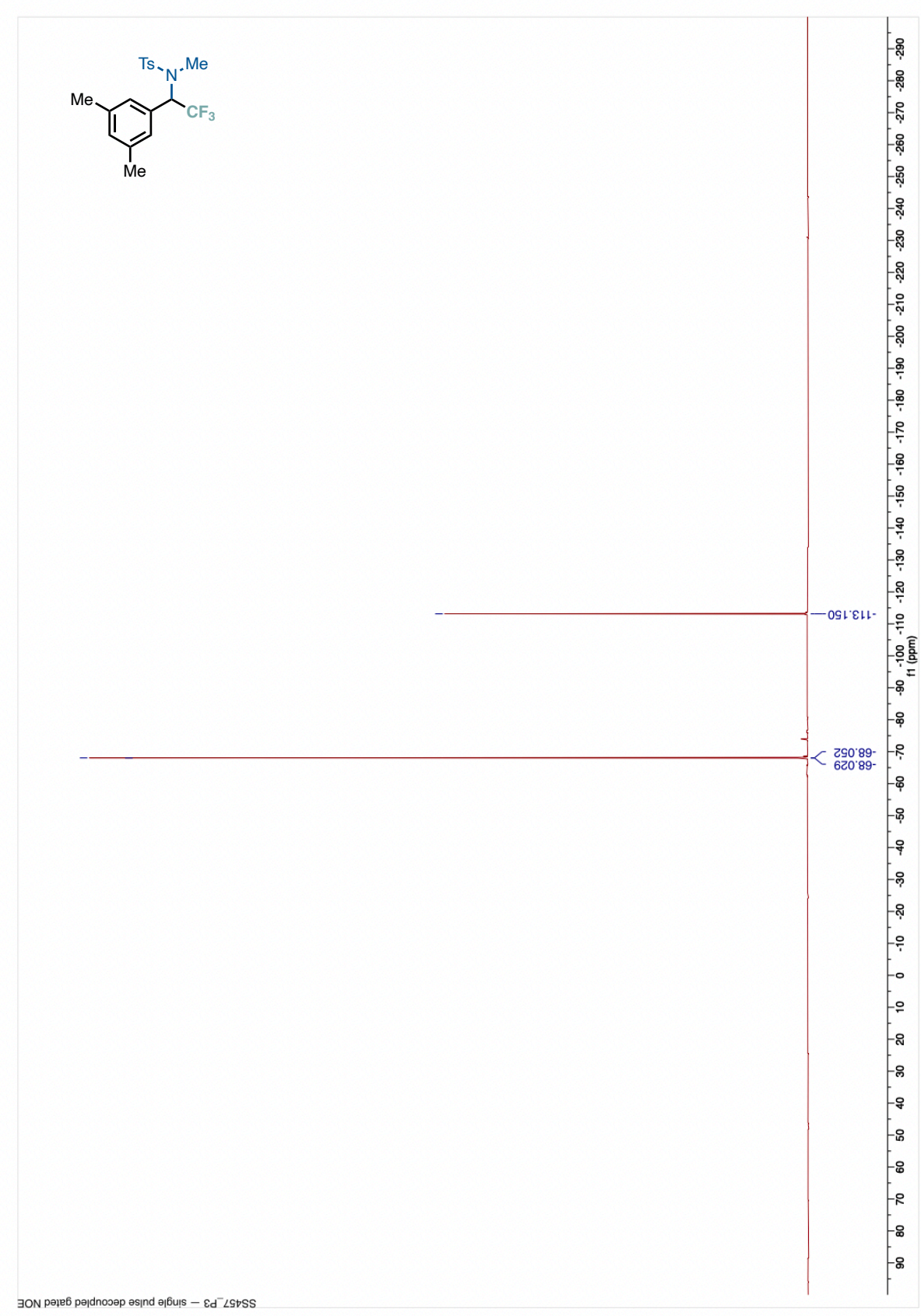
^{1}H NMR of **3E** (400 MHz, $CDCl_3$)



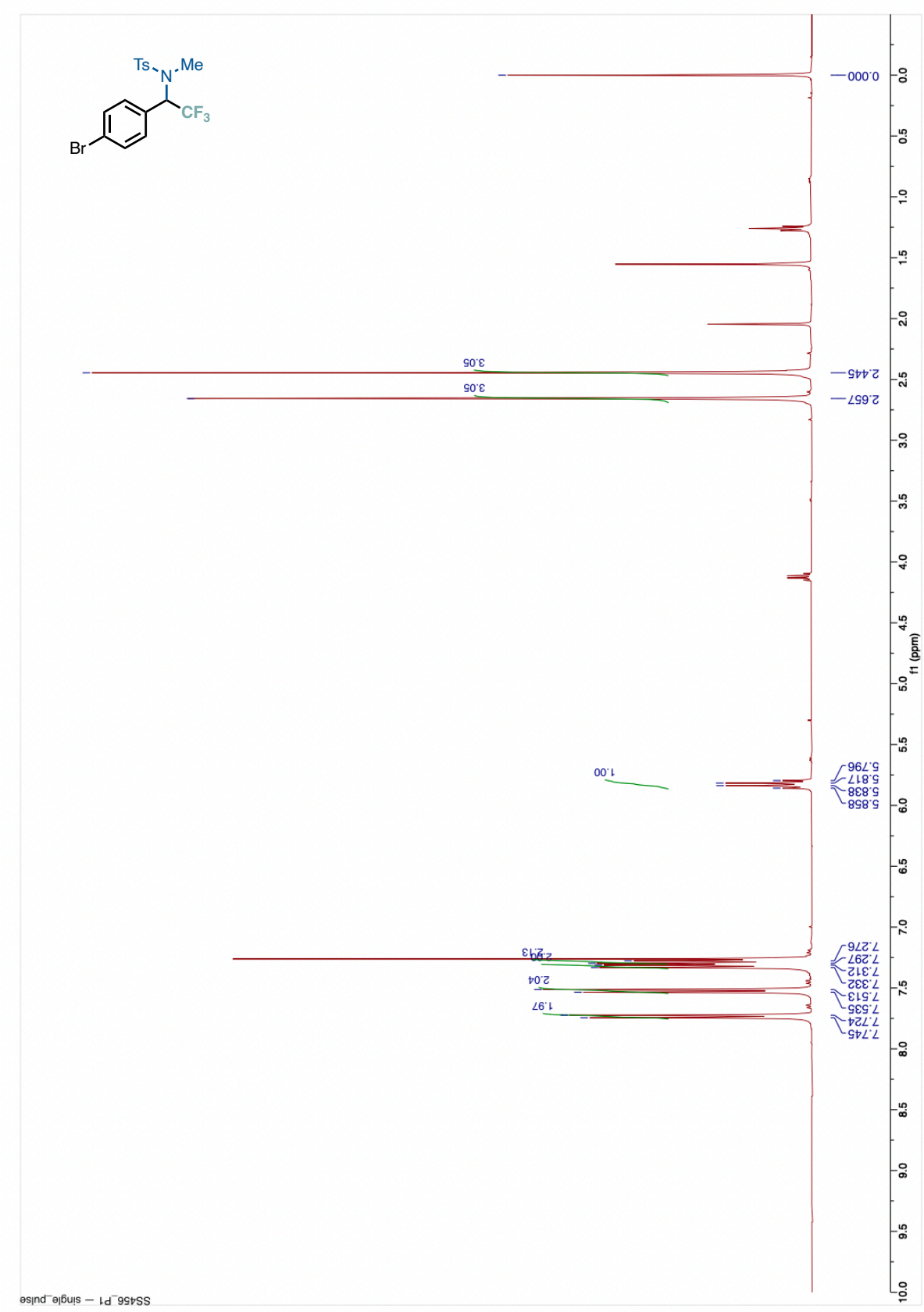
$^{13}C\{^{1}H\}$ NMR of **3E** (101 MHz, $CDCl_3$)



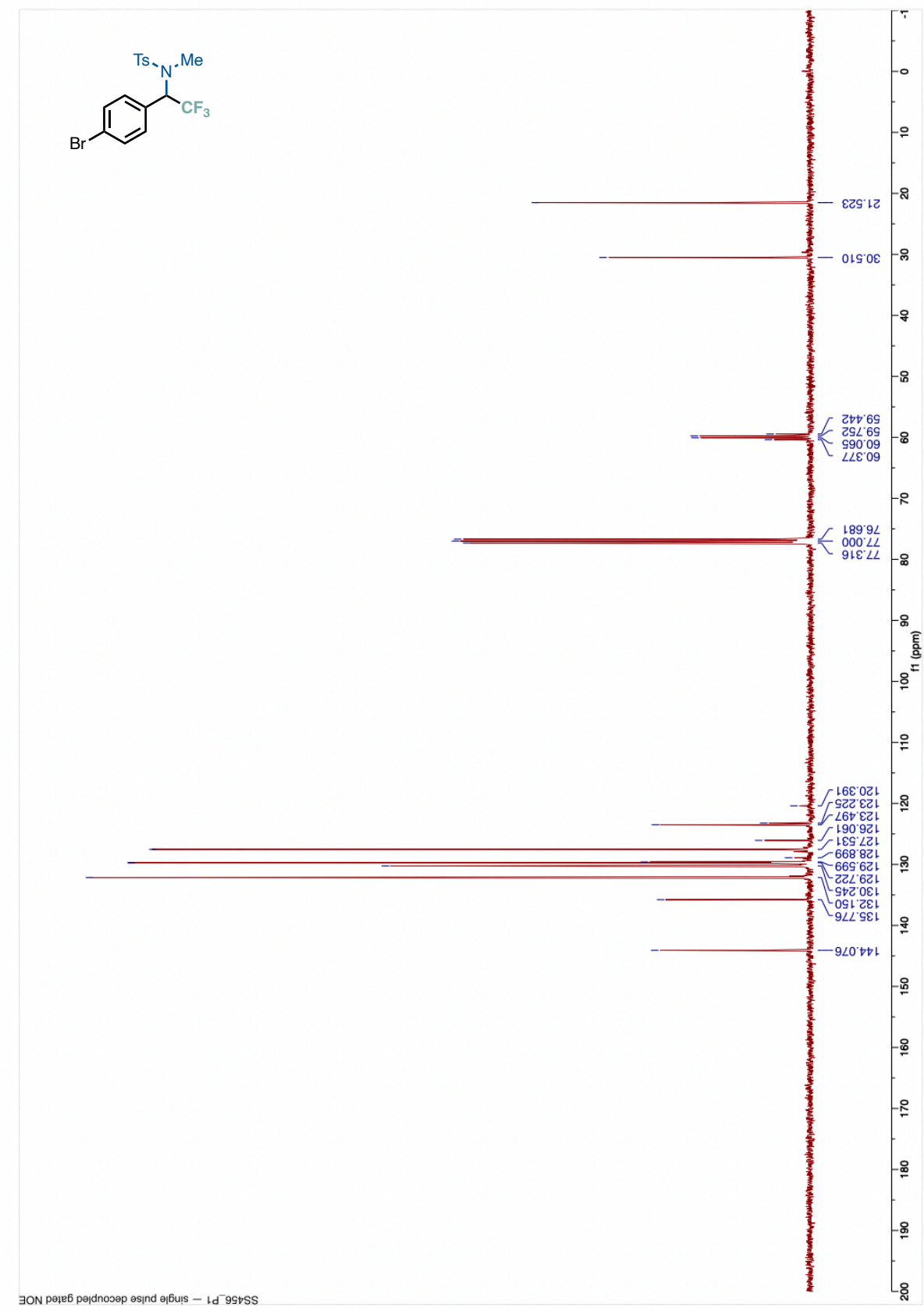
^{19}F NMR of **3E** (376 MHz, $CDCl_3$)



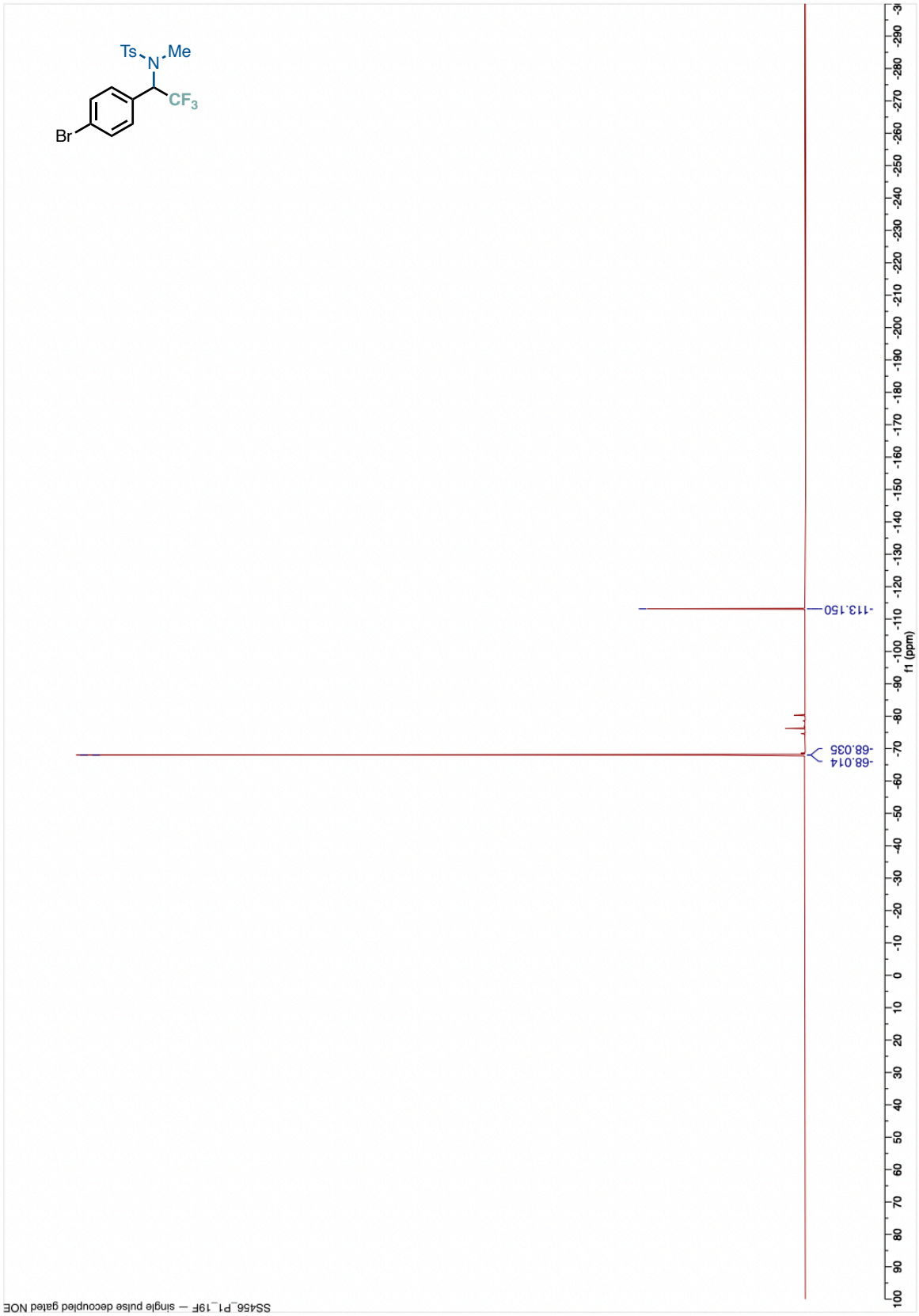
^{1}H NMR of **3F** (400 MHz, $CDCl_3$)



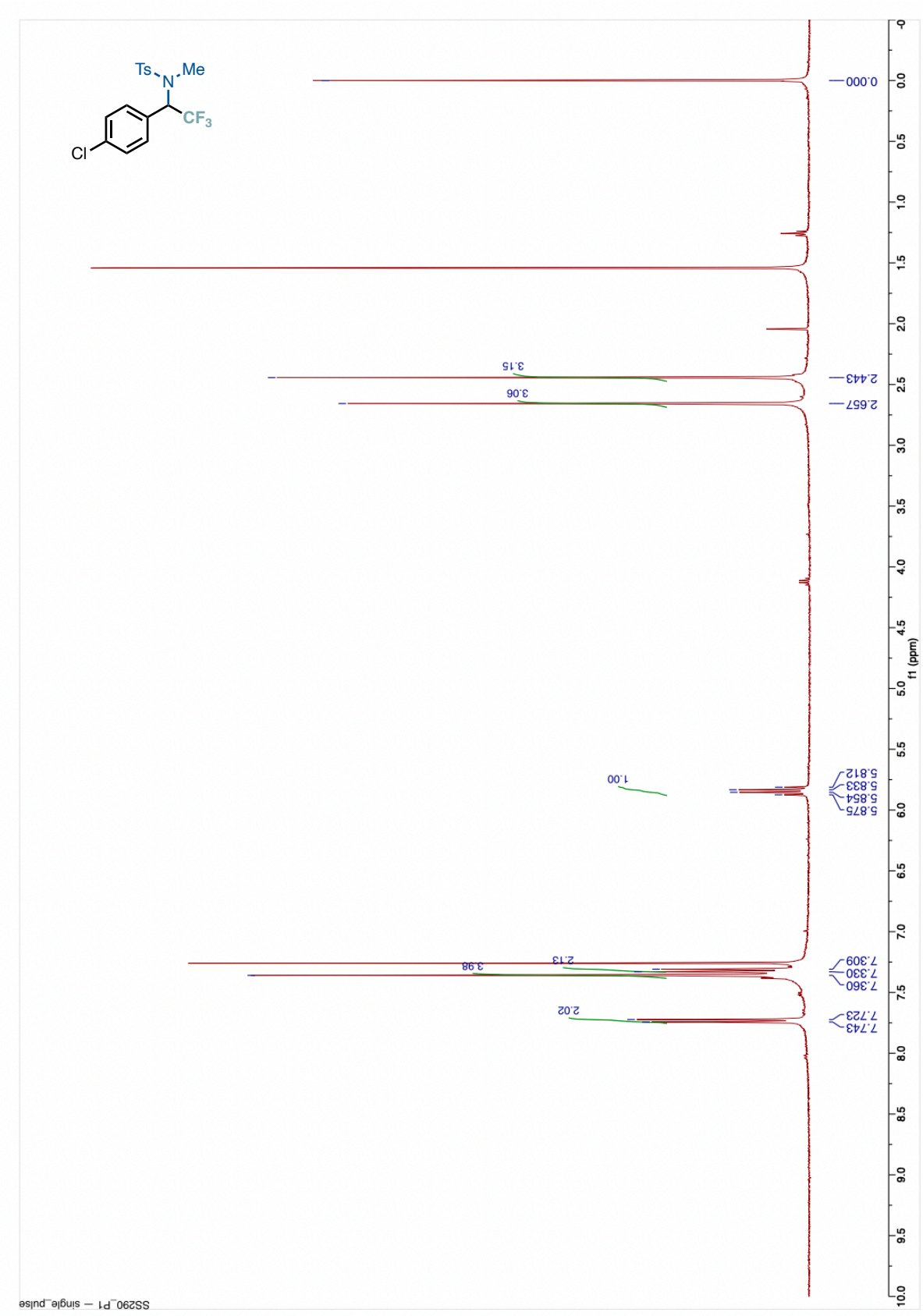
$^{13}C\{^{1}H\}$ NMR of **3F** (101 MHz, $CDCl_3$)



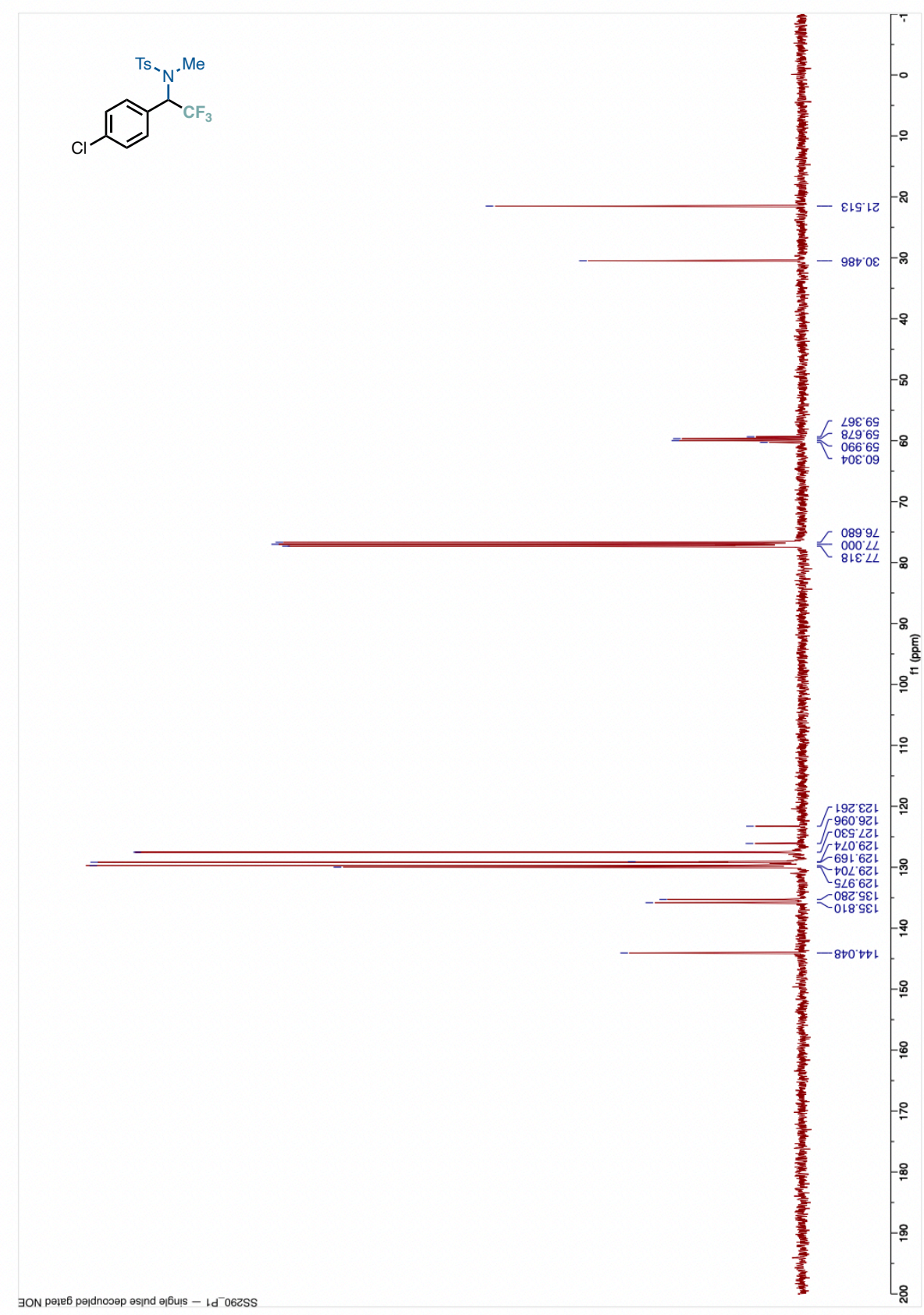
^{19}F NMR of **3F** (376 MHz, $CDCl_3$)



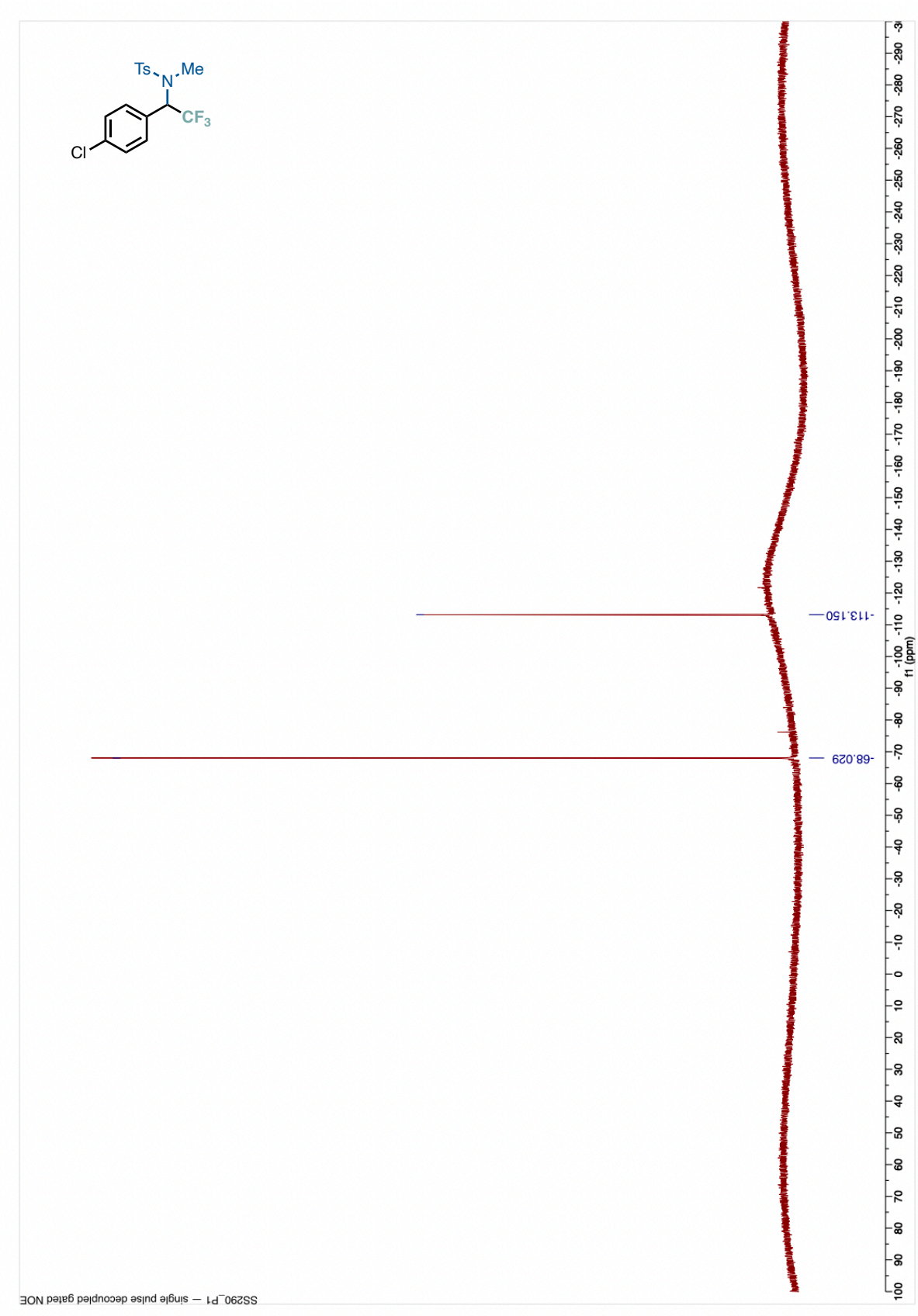
^{1}H NMR of **3G** (400 MHz, $CDCl_3$)



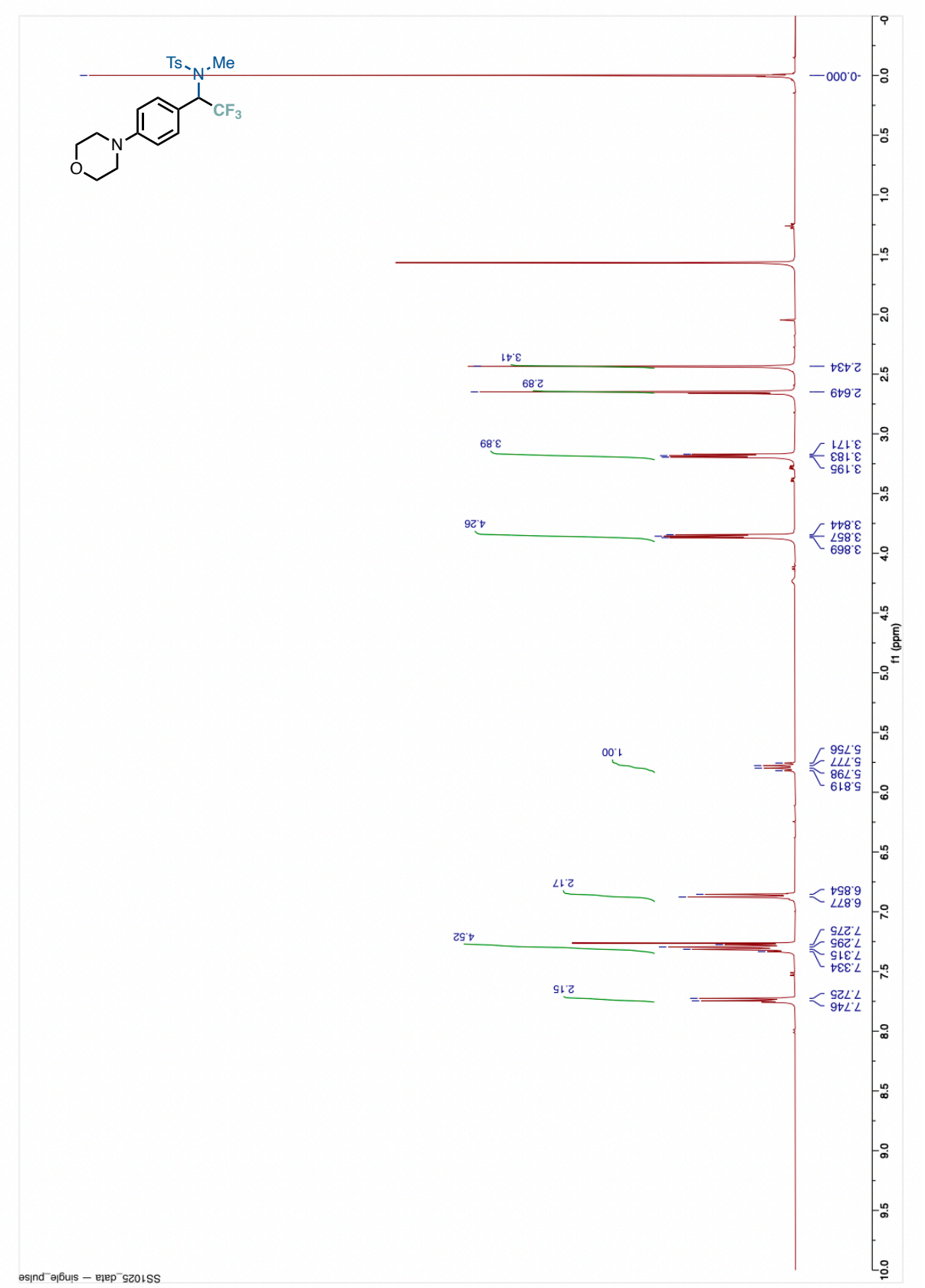
$^{13}C\{^{1}H\}$ NMR of **3G** (101 MHz, $CDCl_3$)



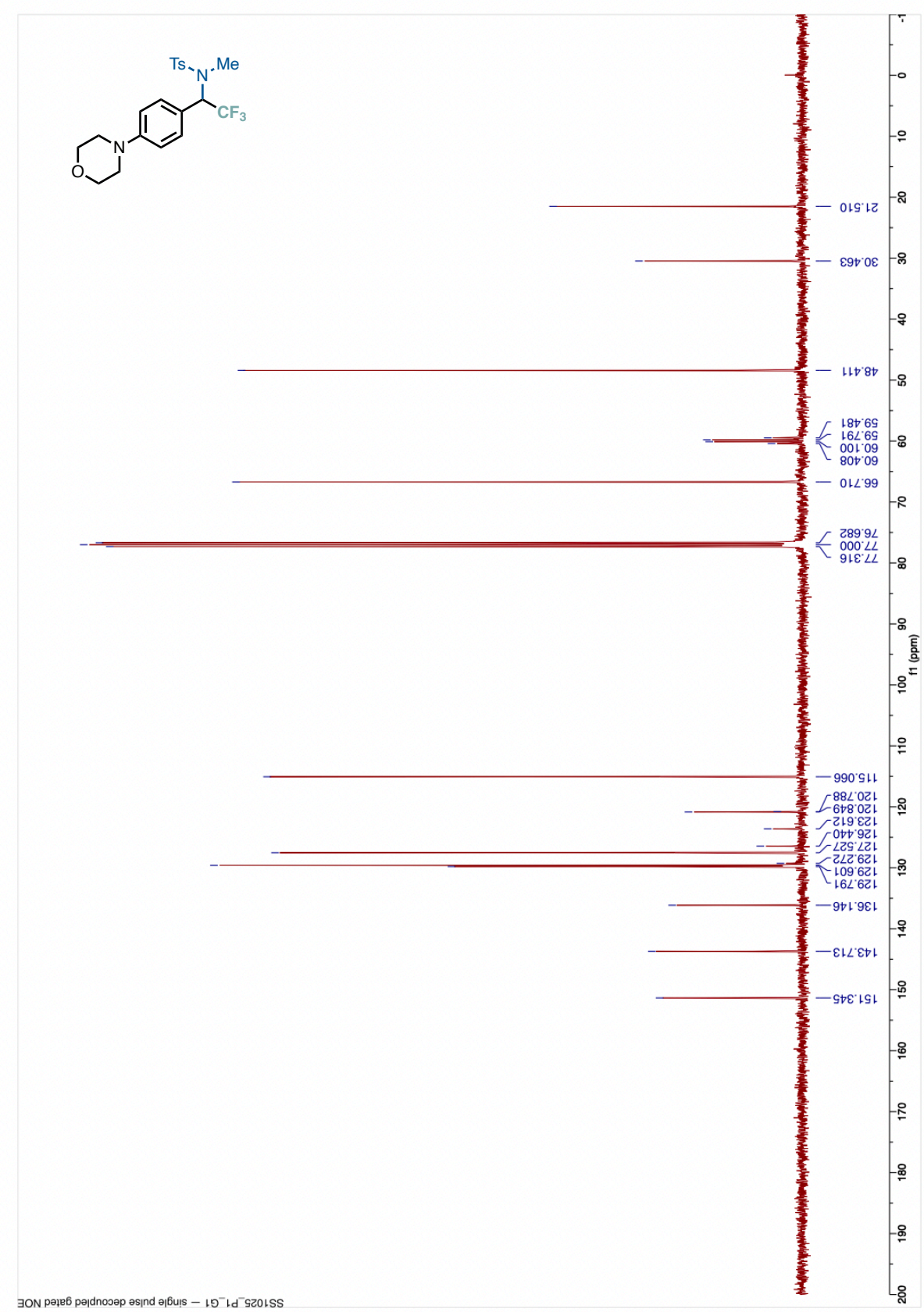
^{19}F NMR of **3G** (376 MHz, $CDCl_3$)



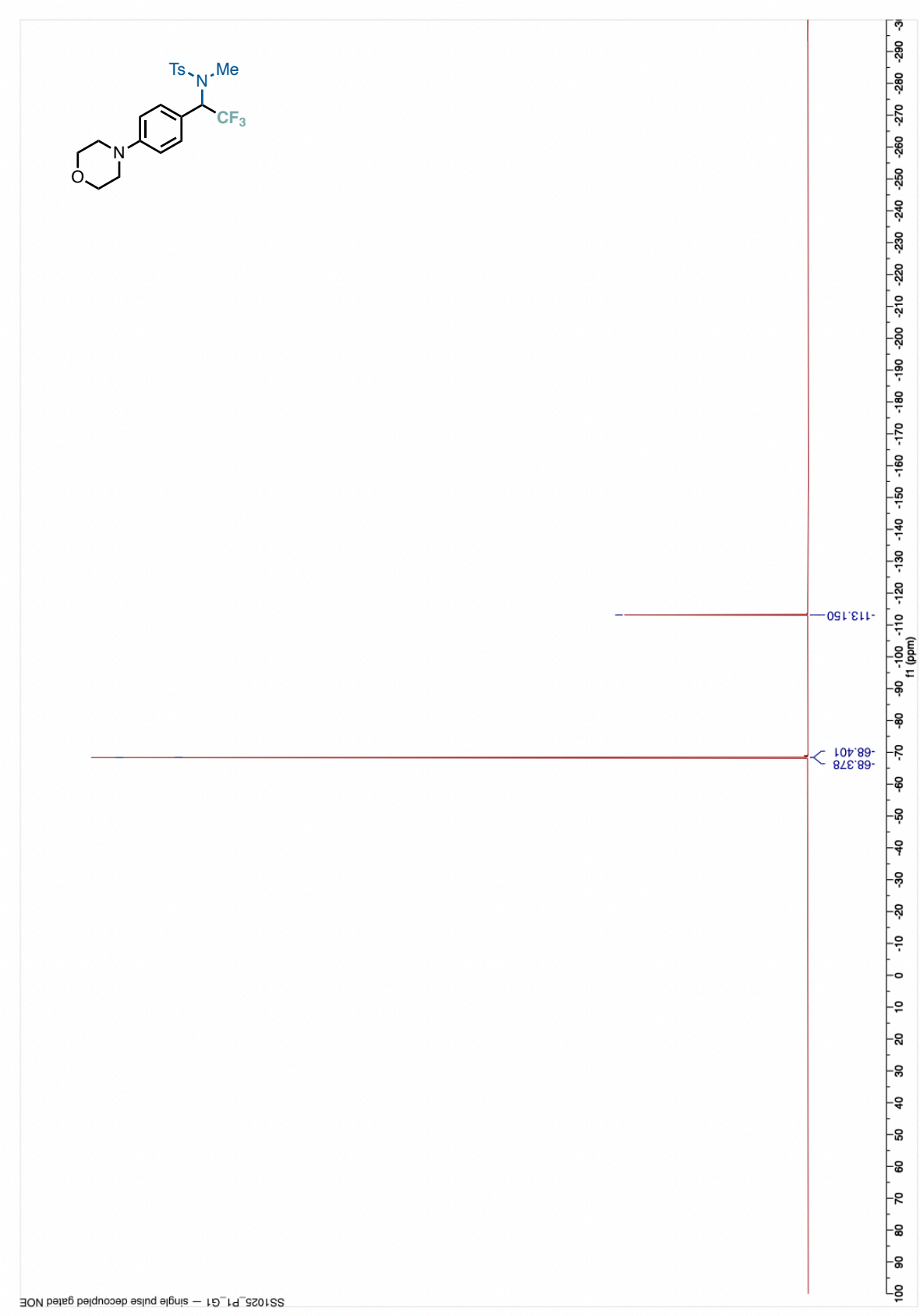
^{1}H NMR of **3H** (400 MHz, $CDCl_3$)



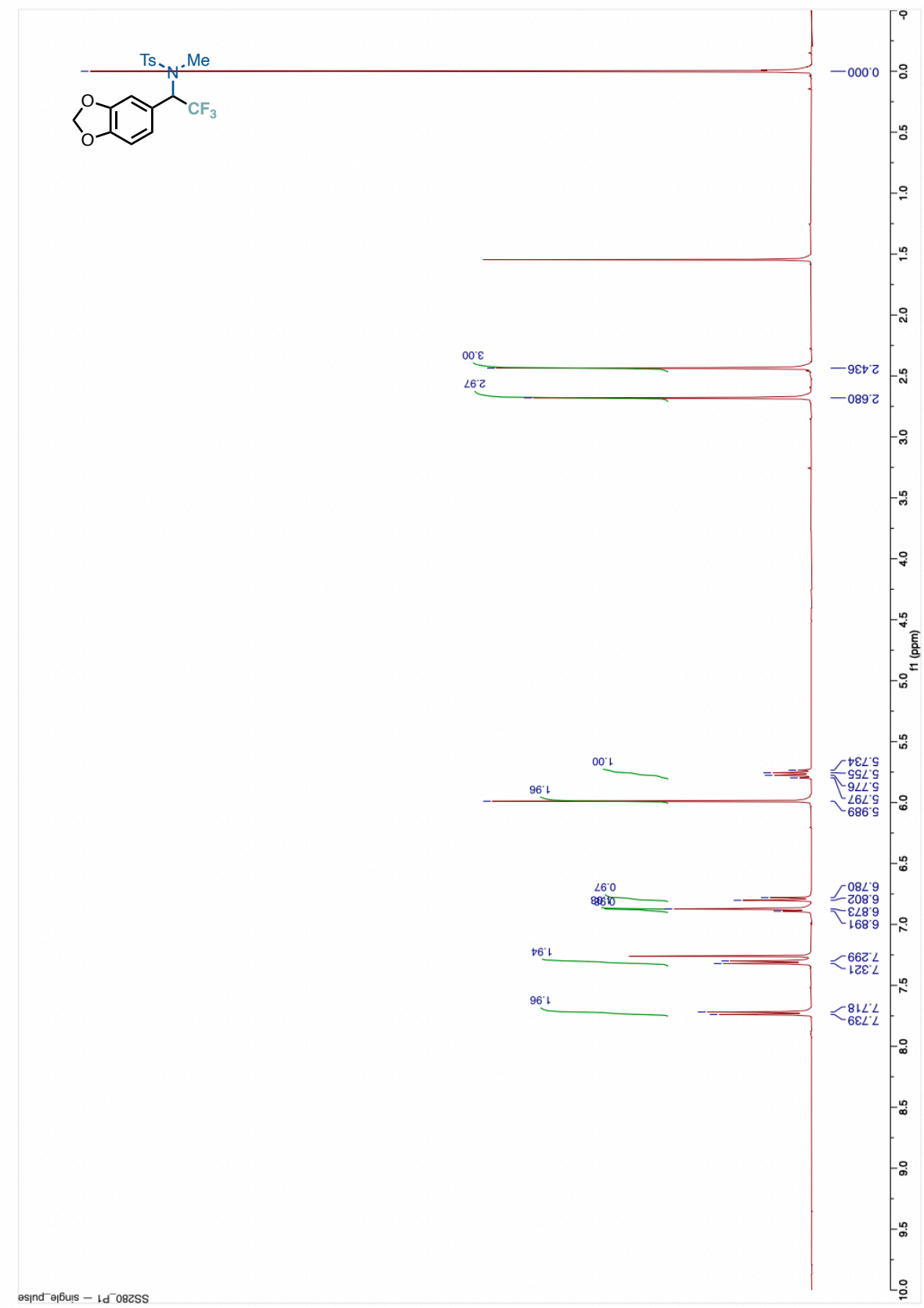
$^{13}C\{^{1}H\}$ NMR of **3H** (101 MHz, $CDCl_3$)



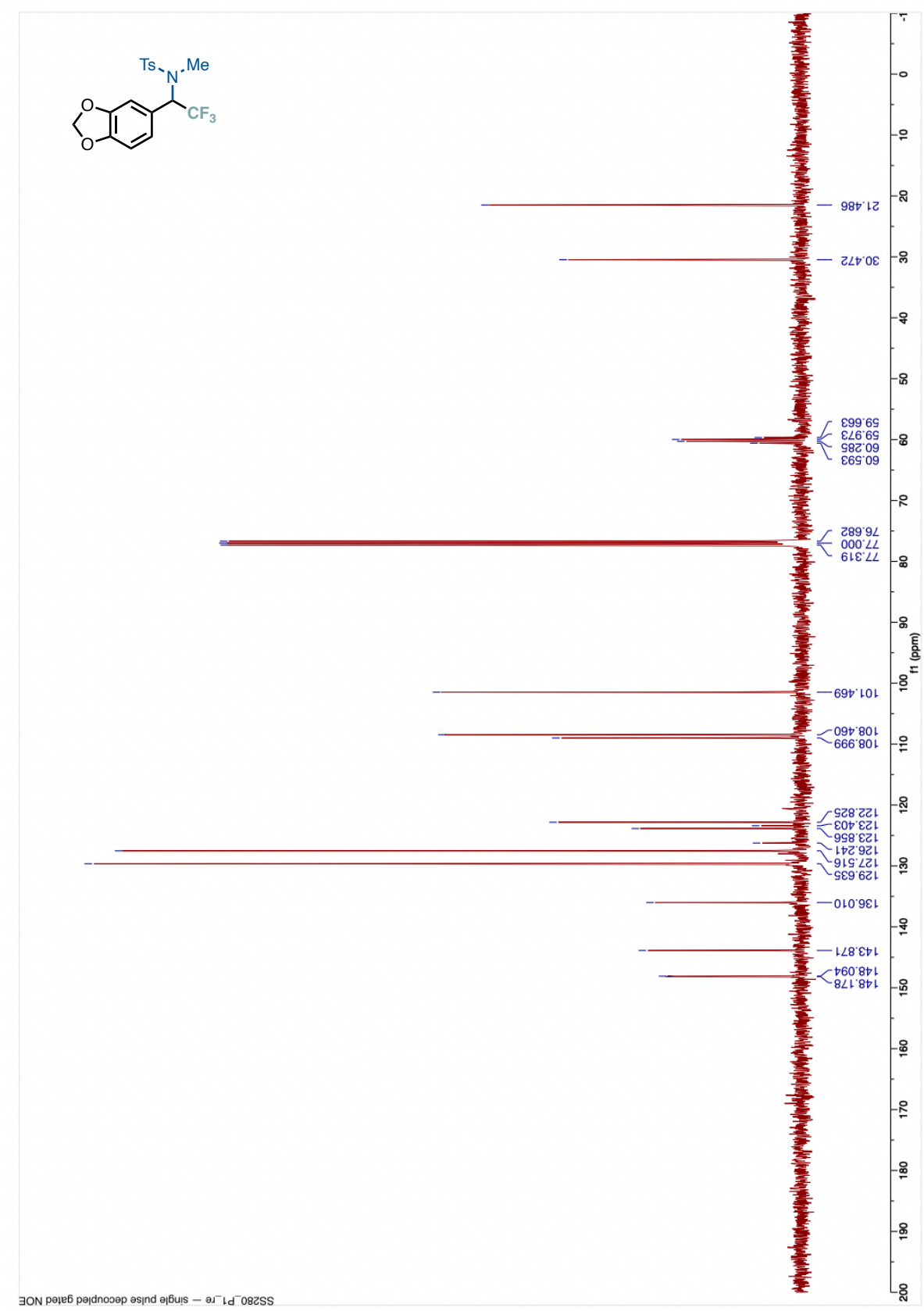
^{19}F NMR of **3H** (376 MHz, $CDCl_3$)



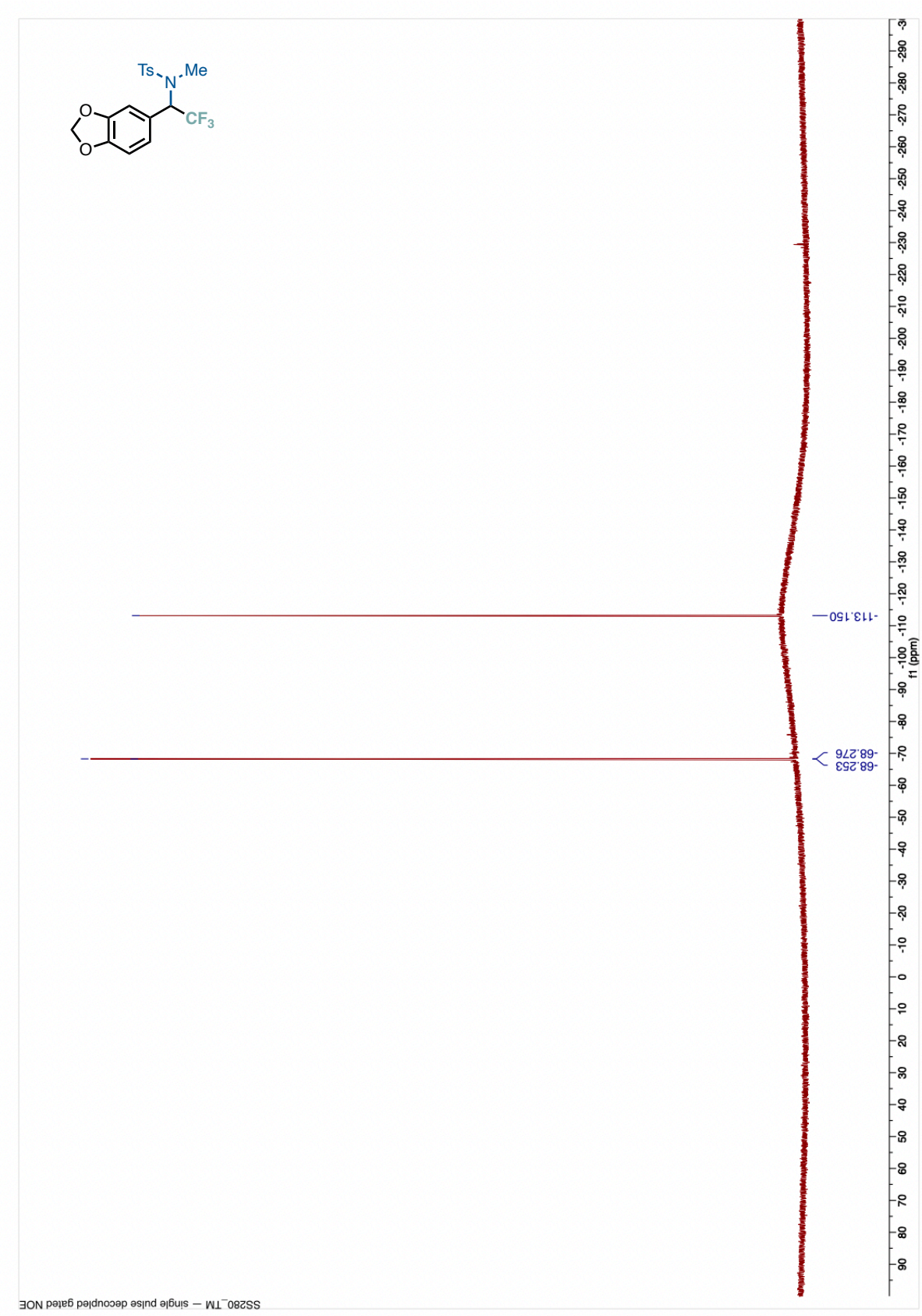
^{1}H NMR of **3I** (400 MHz, $CDCl_3$)



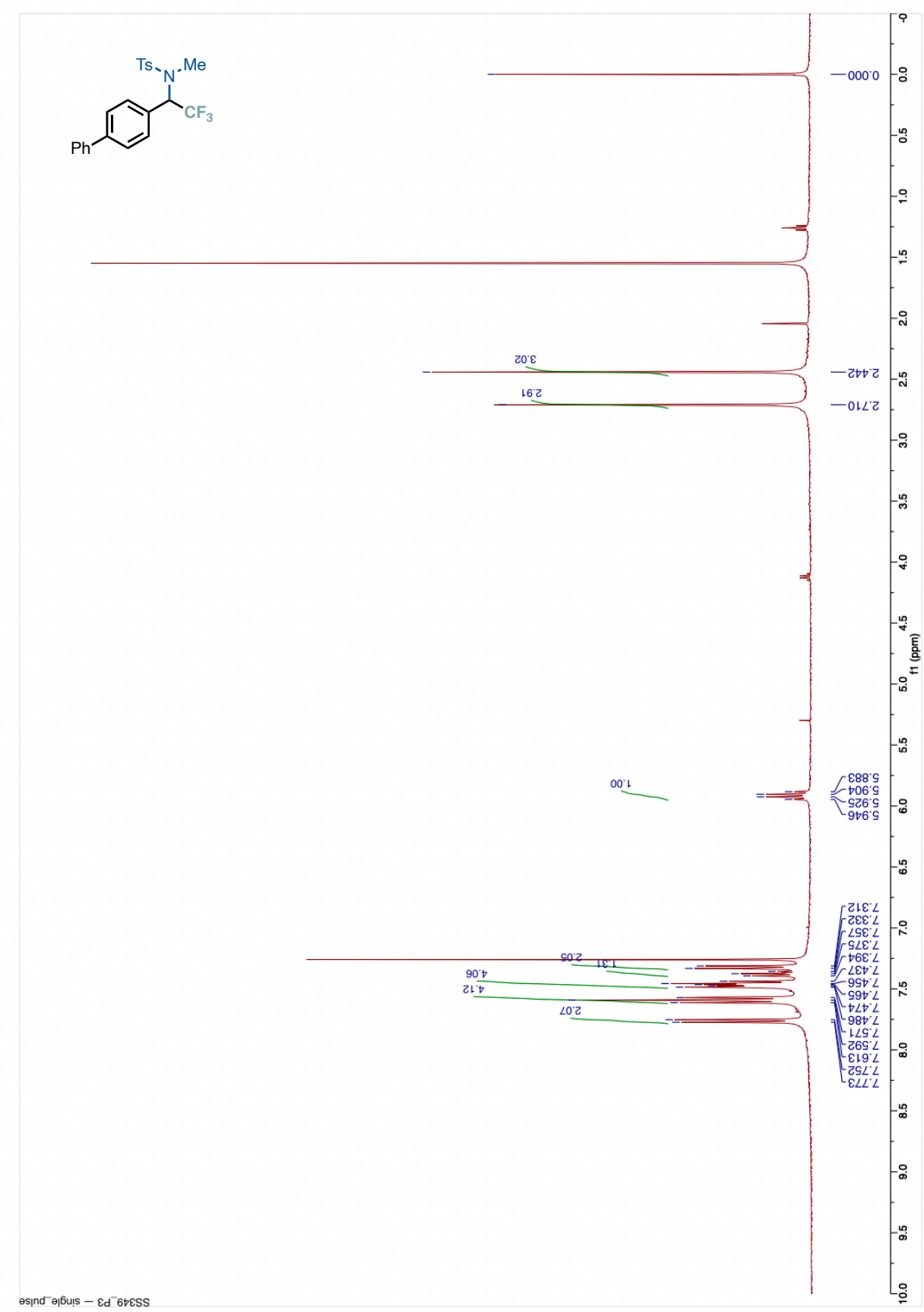
$^{13}C\{^{1}H\}$ NMR of **3l** (101 MHz, $CDCl_3$)



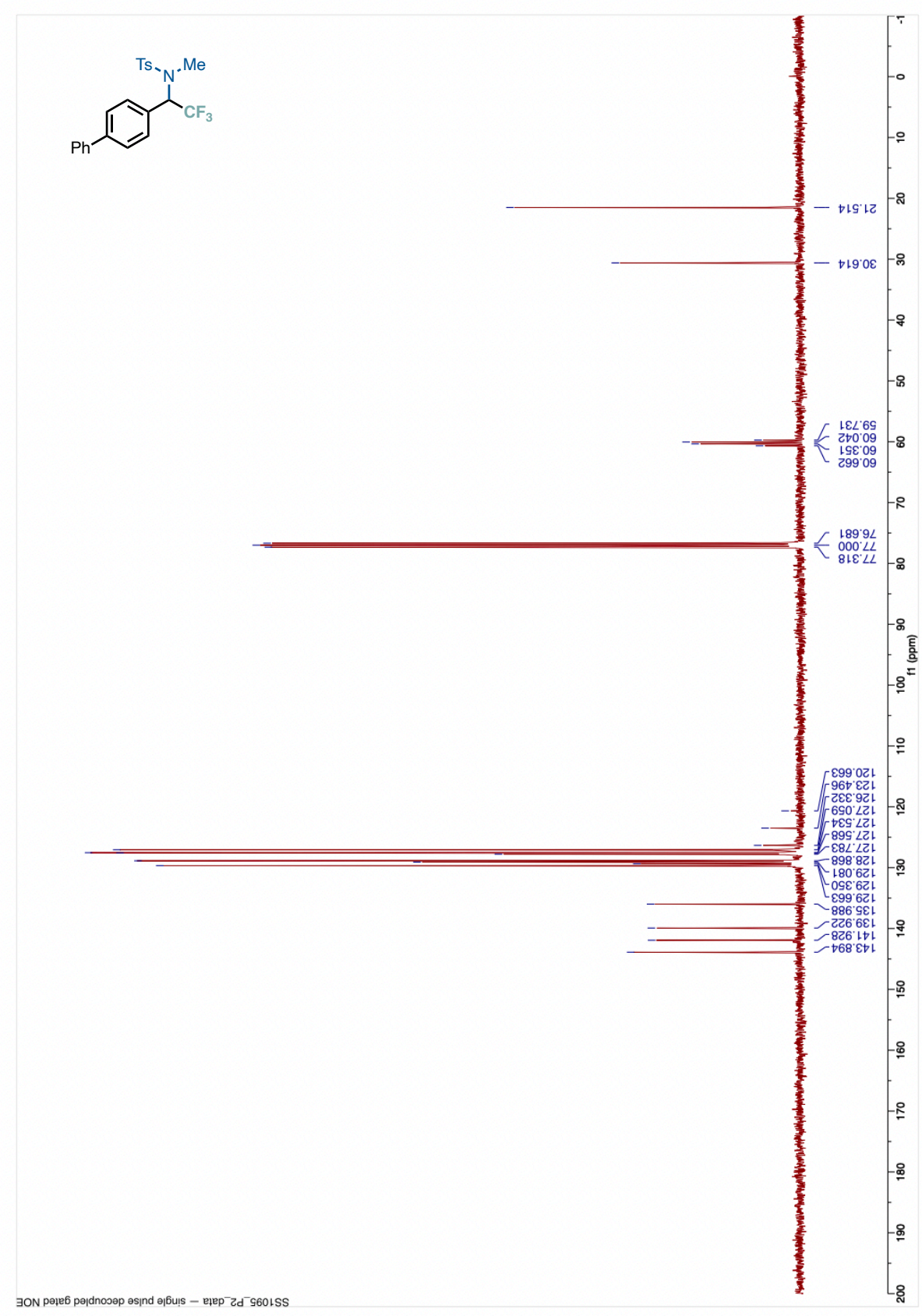
^{19}F NMR of **3l** (376 MHz, $CDCl_3$)



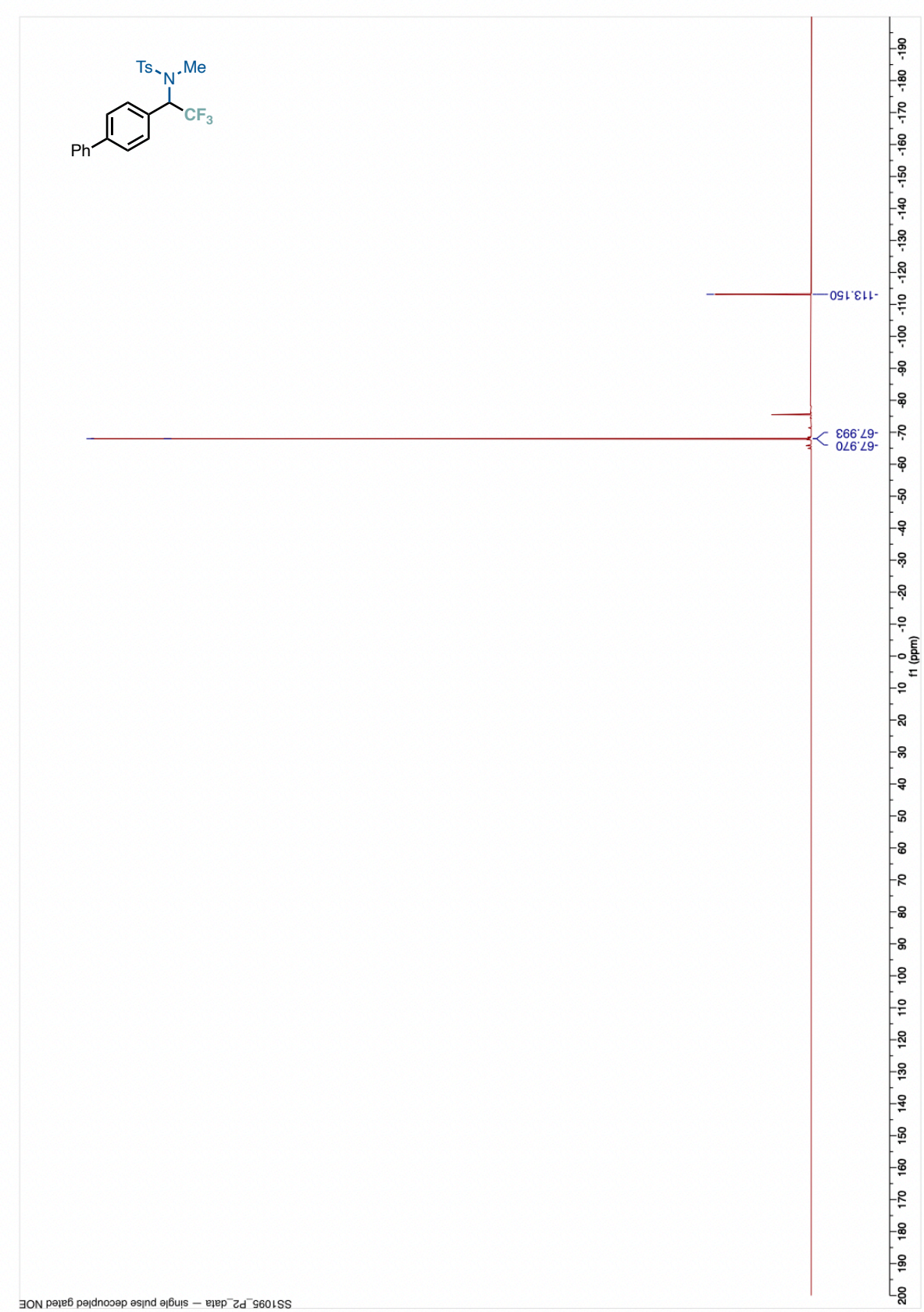
^{1}H NMR of **3J** (400 MHz, $CDCl_3$)



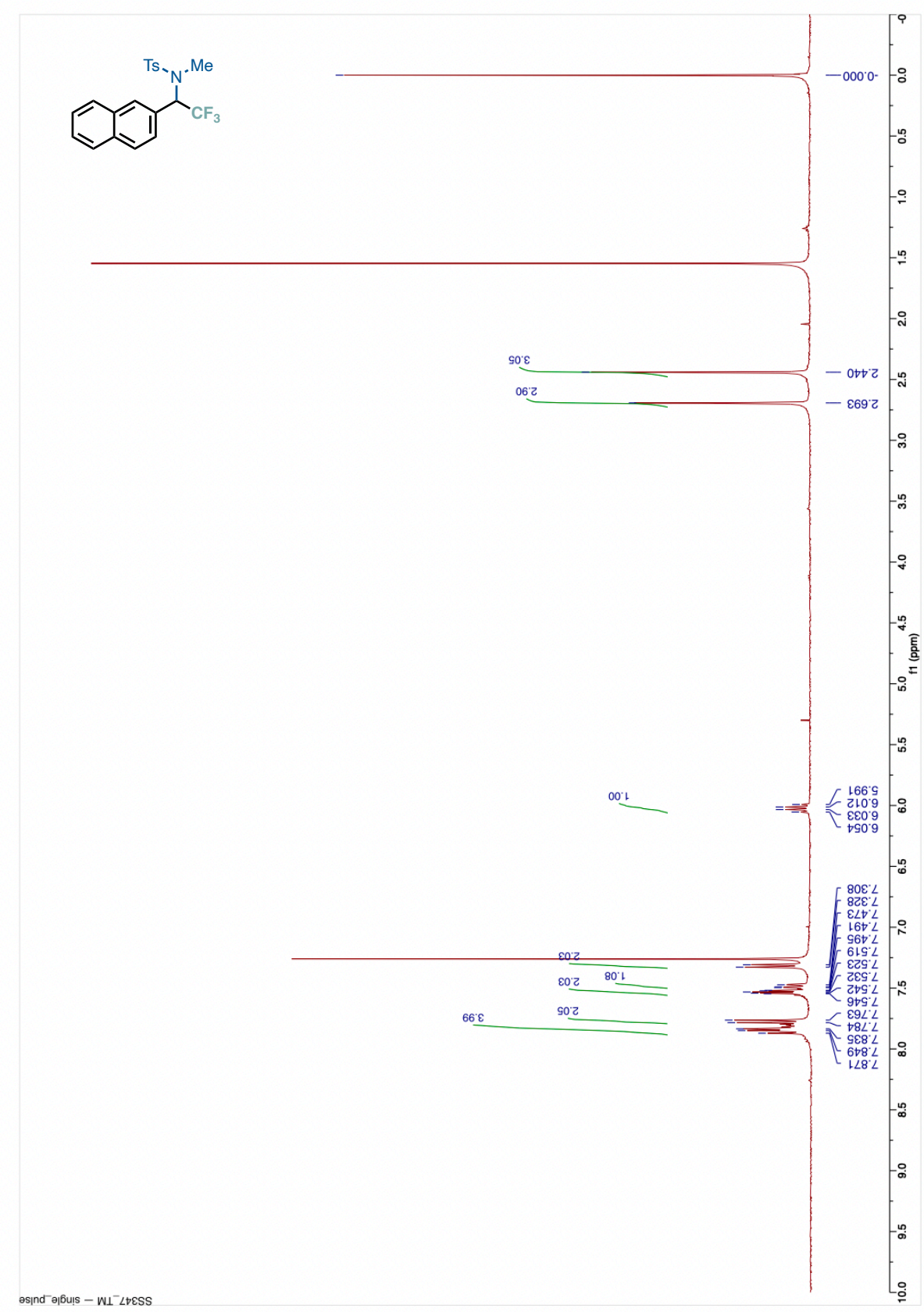
$^{13}C\{^{1}H\}$ NMR of **3J** (101 MHz, $CDCl_3$)



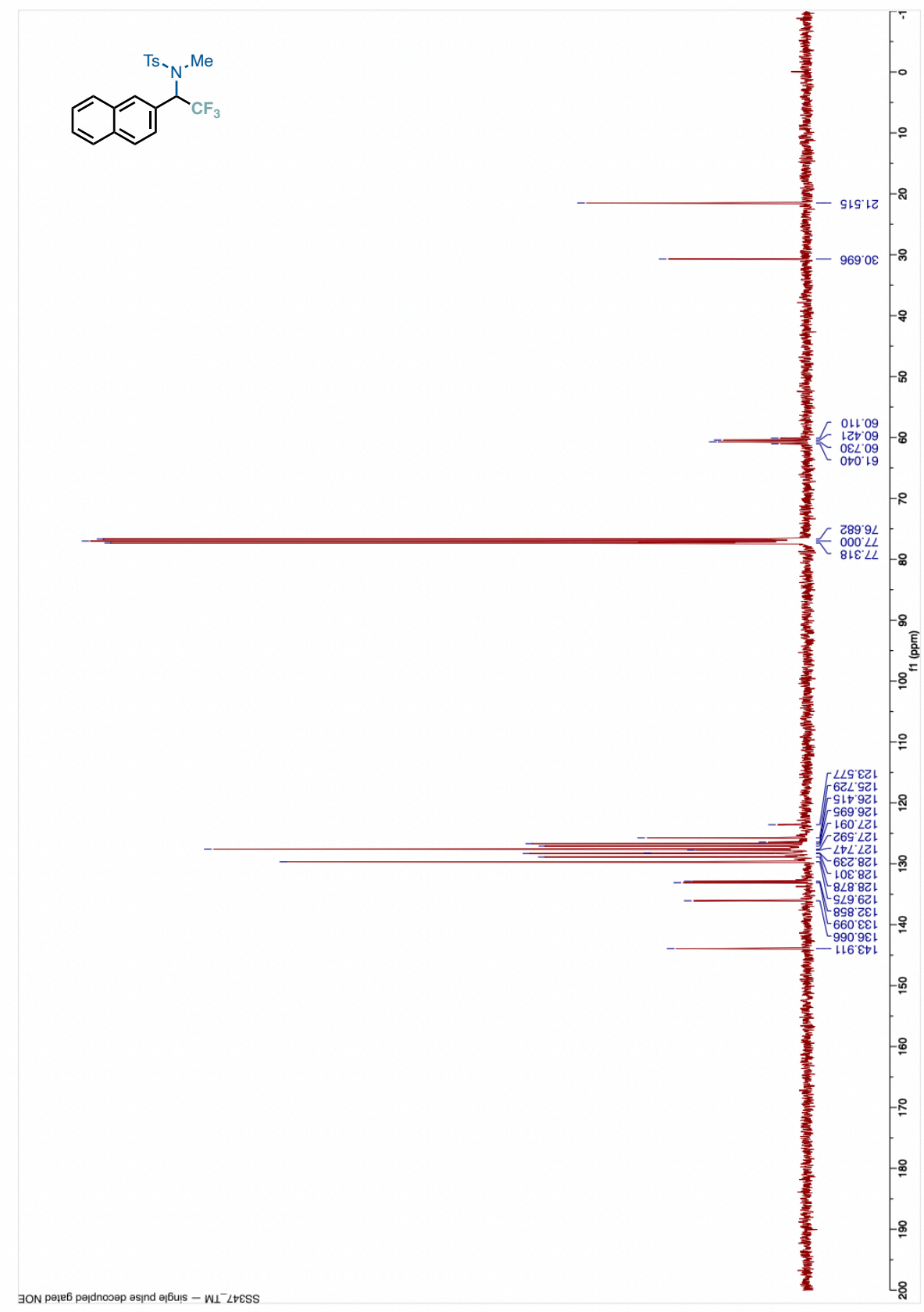
^{19}F NMR of **3J** (376 MHz, $CDCl_3$)



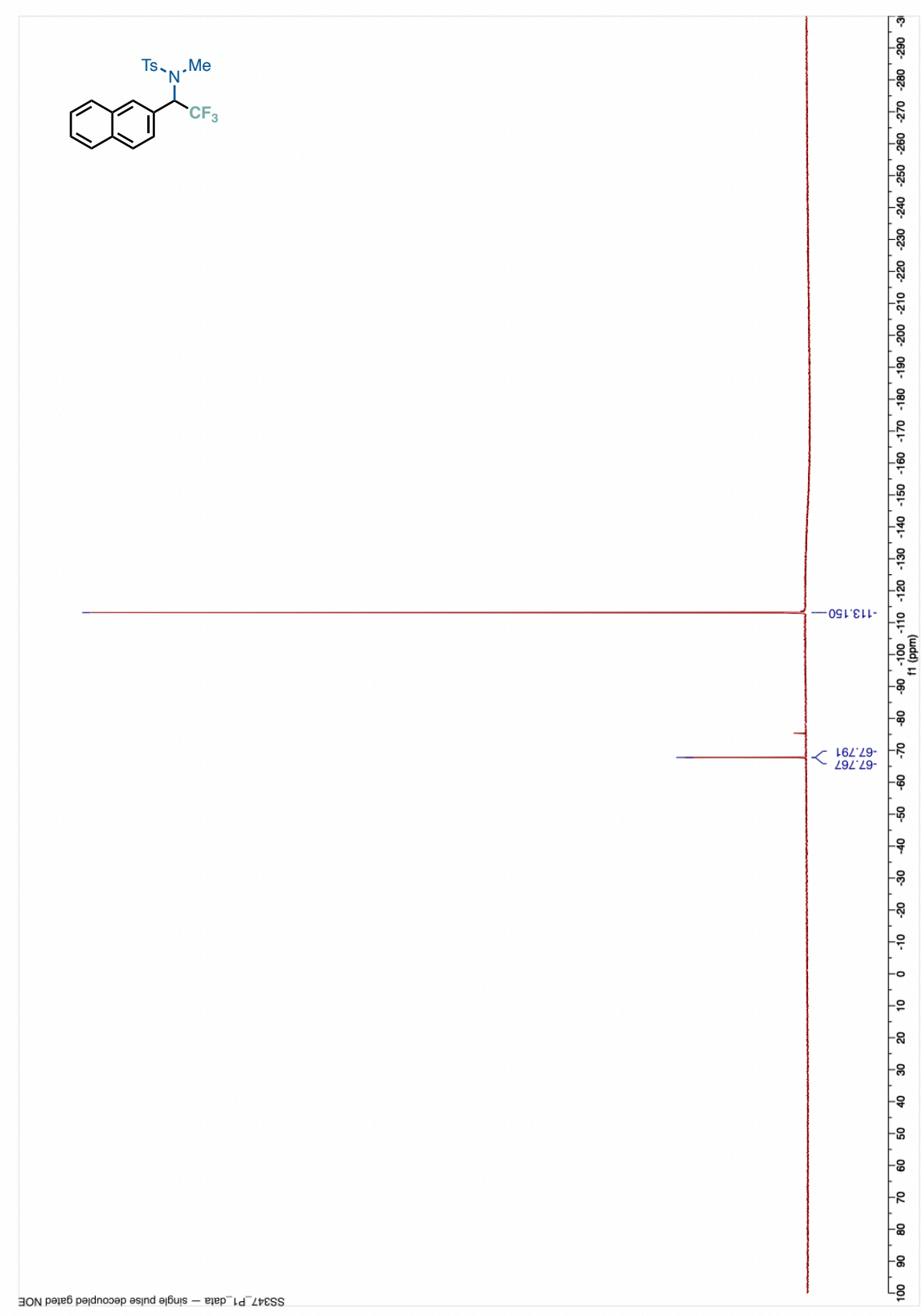
^{1}H NMR of **3K** (400 MHz, $CDCl_3$)



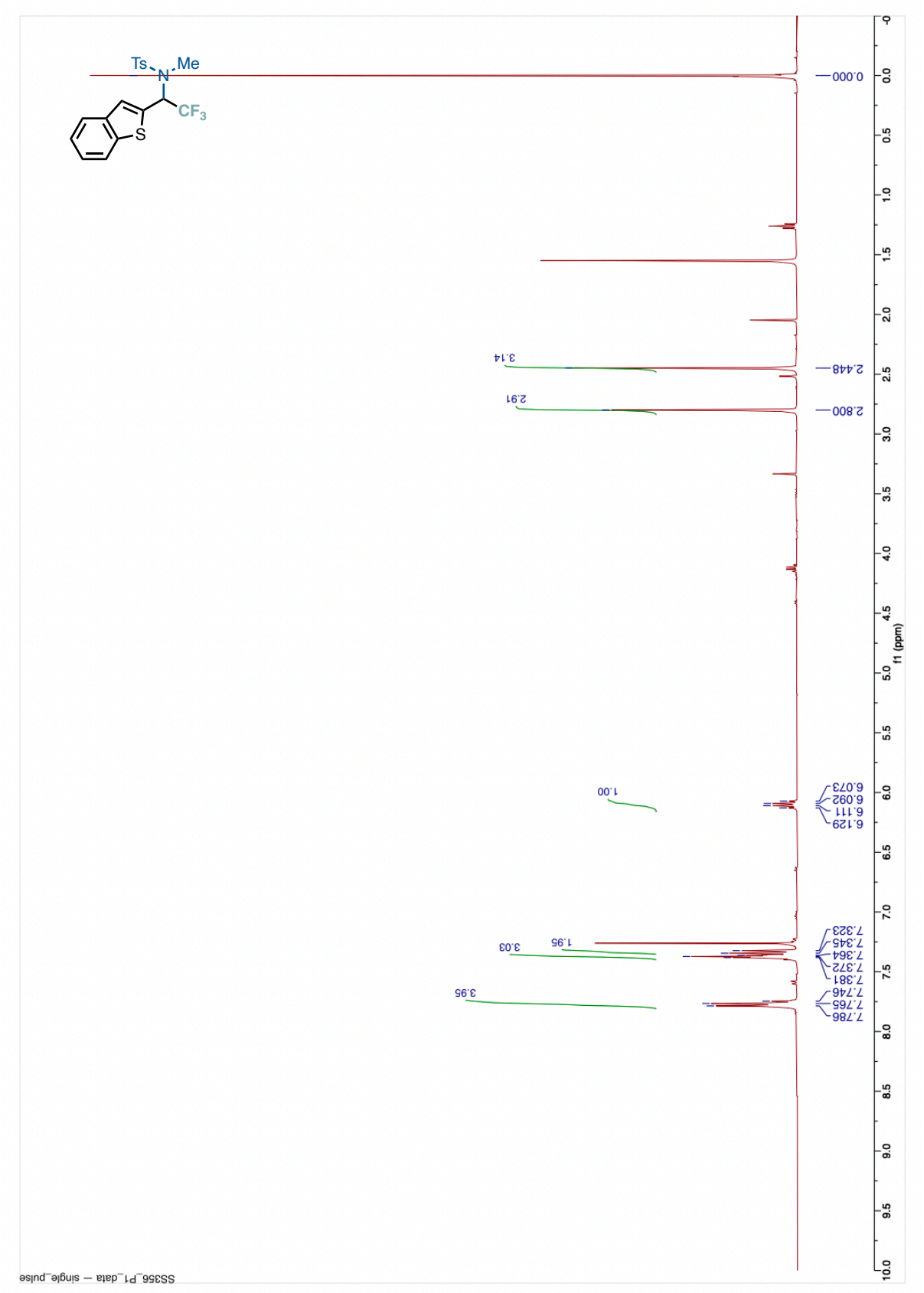
$^{13}C\{^{1}H\}$ NMR of **3K** (101 MHz, $CDCl_3$)



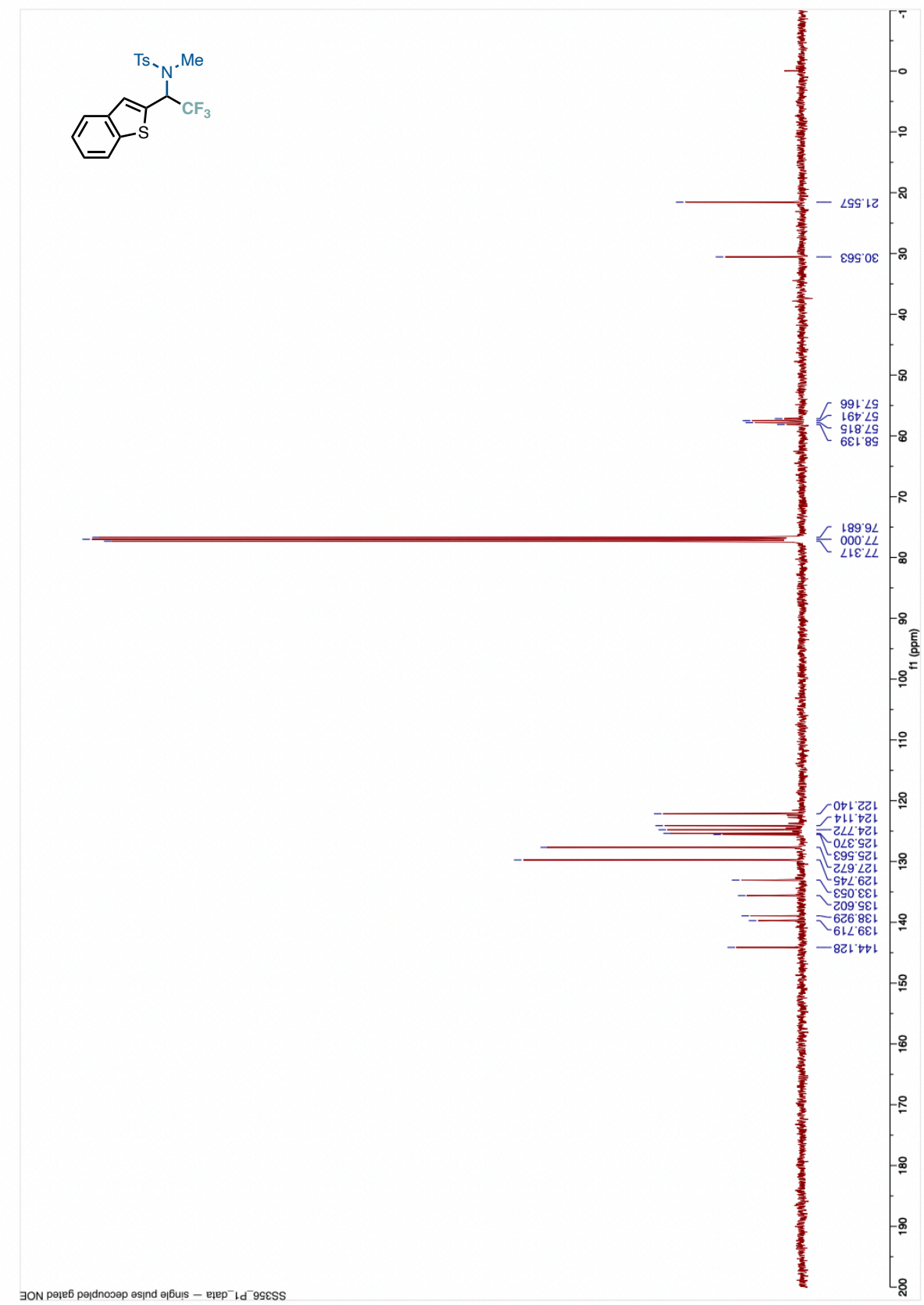
^{19}F NMR of **3K** (376 MHz, $CDCl_3$)



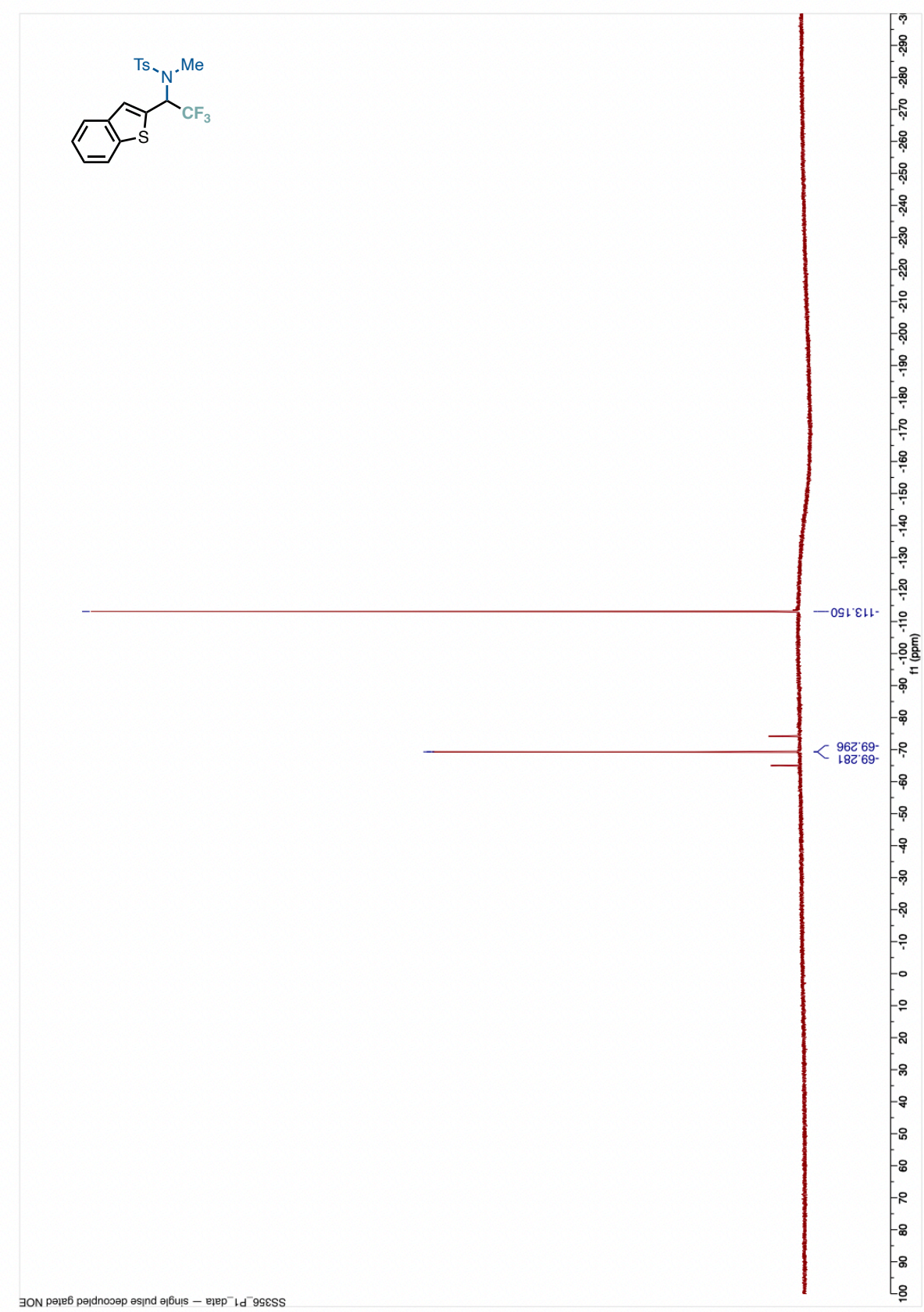
^{1}H NMR of **3L** (400 MHz, $CDCl_3$)



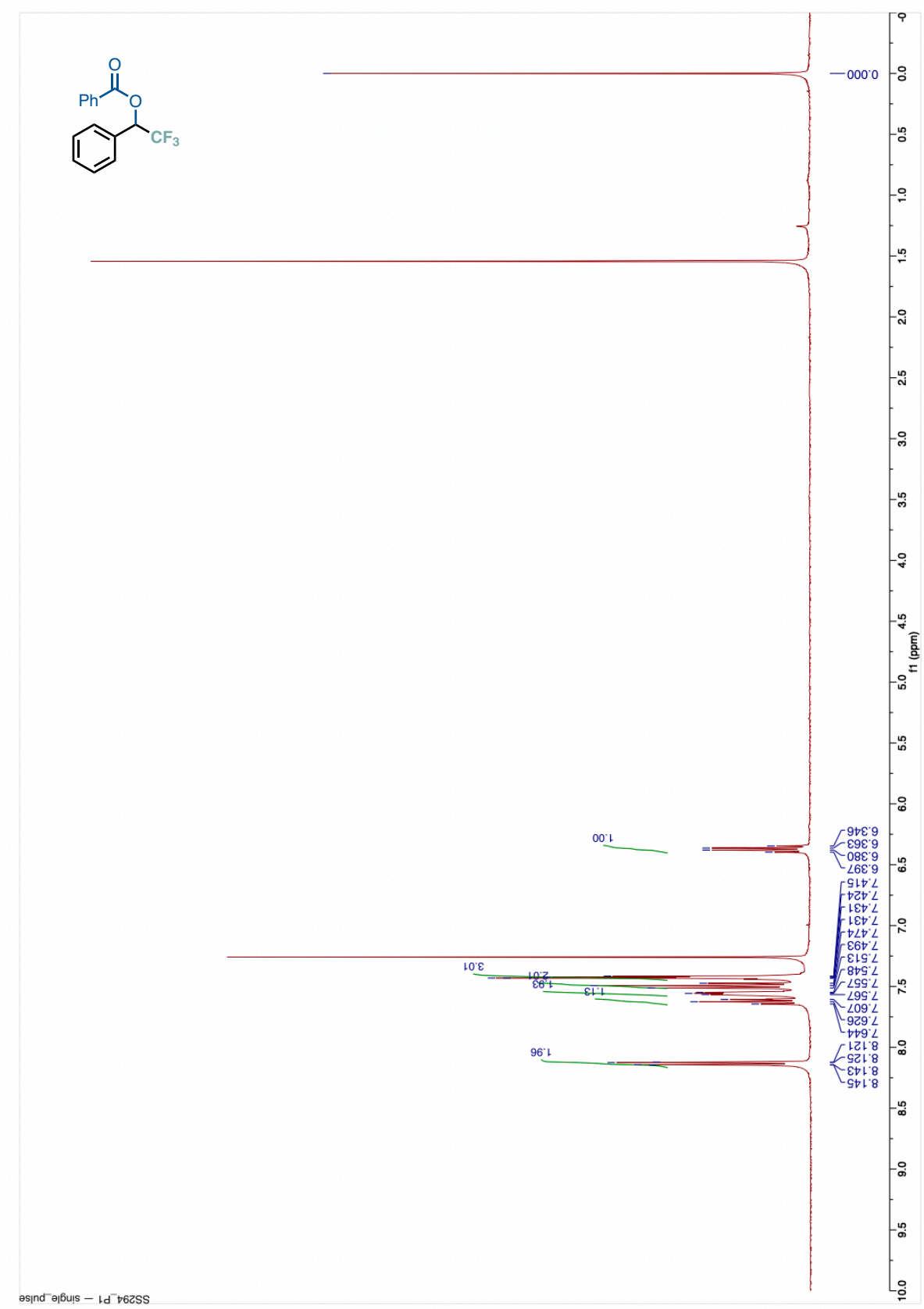
$^{13}C\{^{1}H\}$ NMR of **3L** (101 MHz, $CDCl_3$)



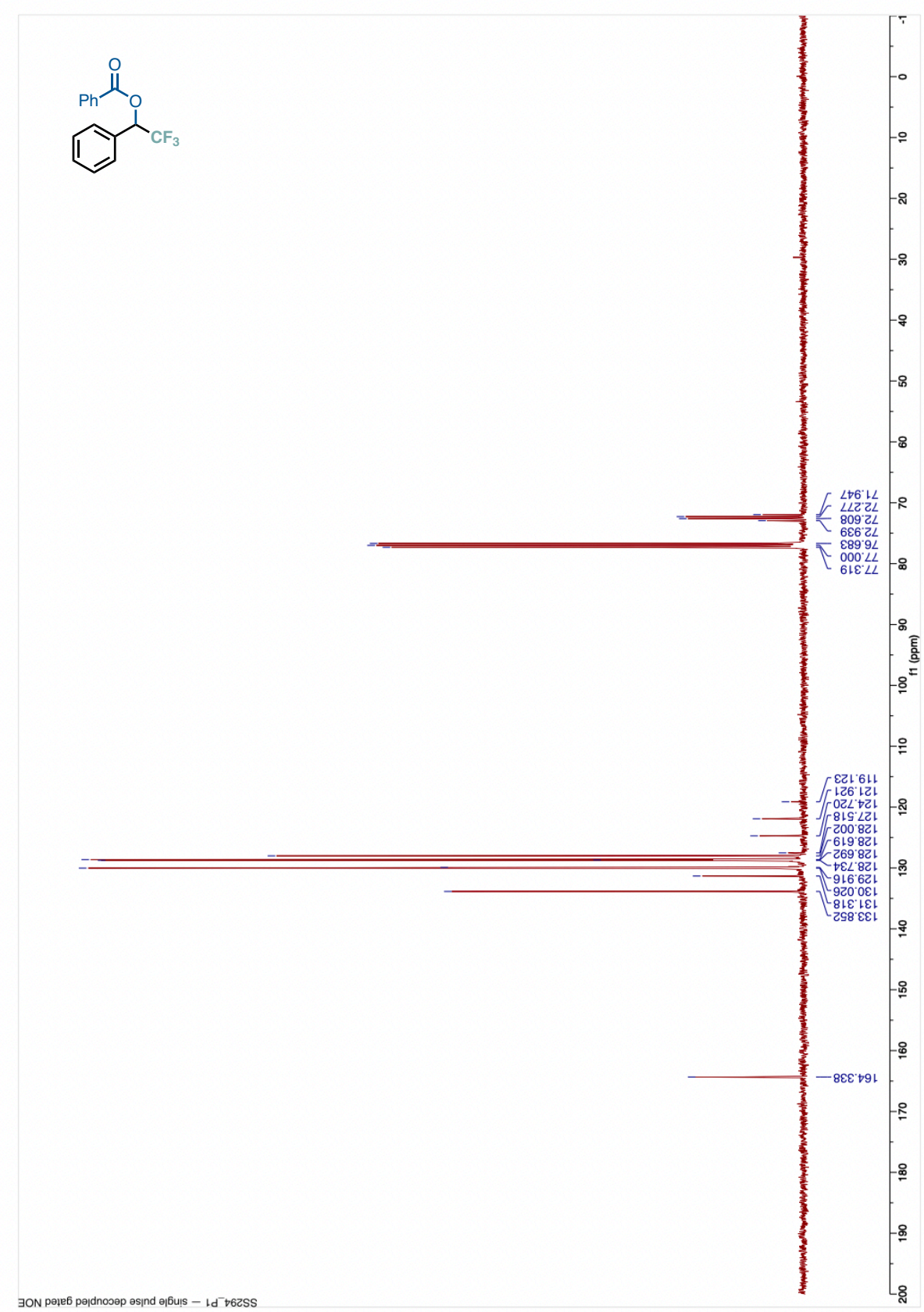
^{19}F NMR of **3L** (376 MHz, $CDCl_3$)



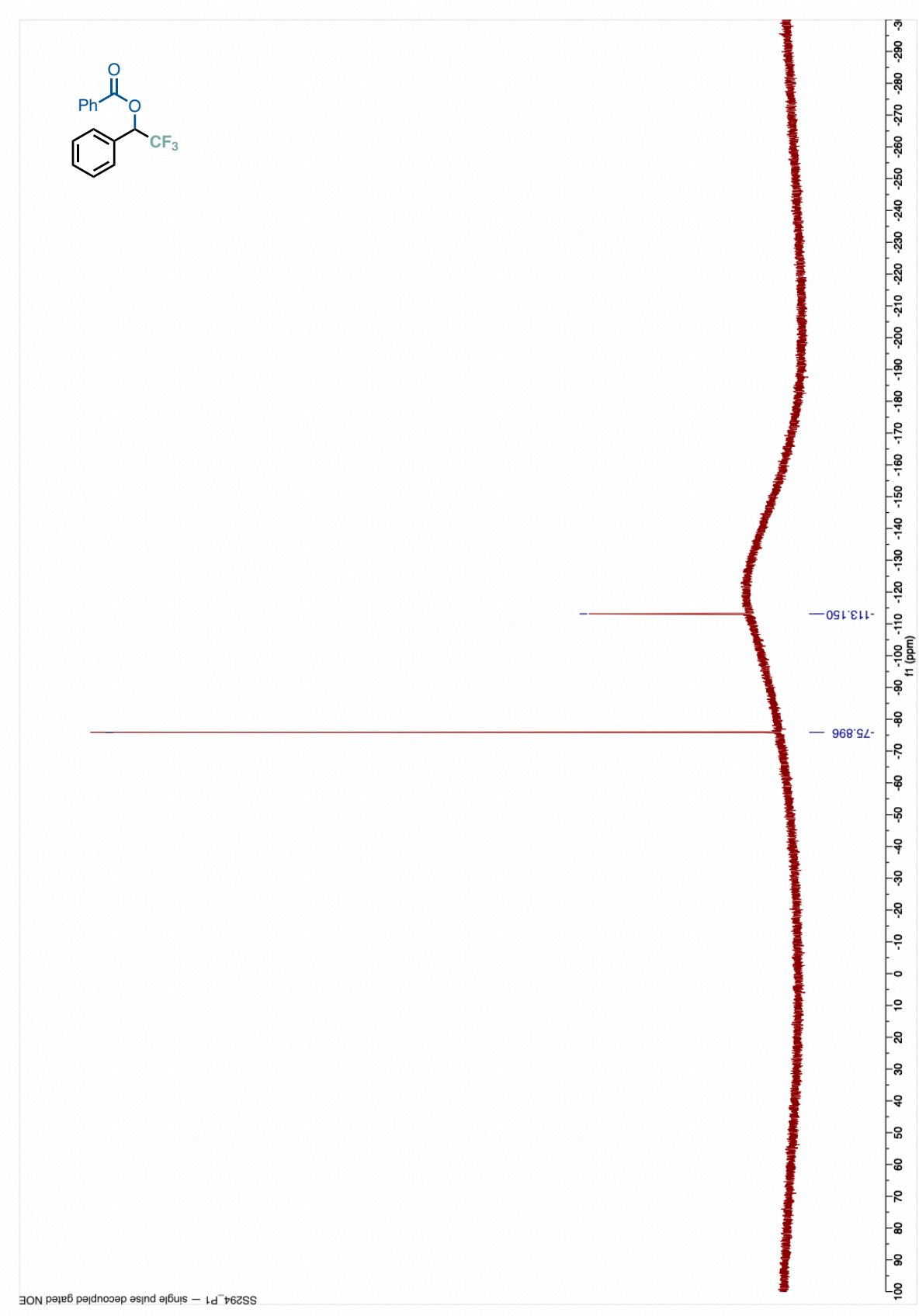
^{1}H NMR of **3M** (400 MHz, $CDCl_3$)



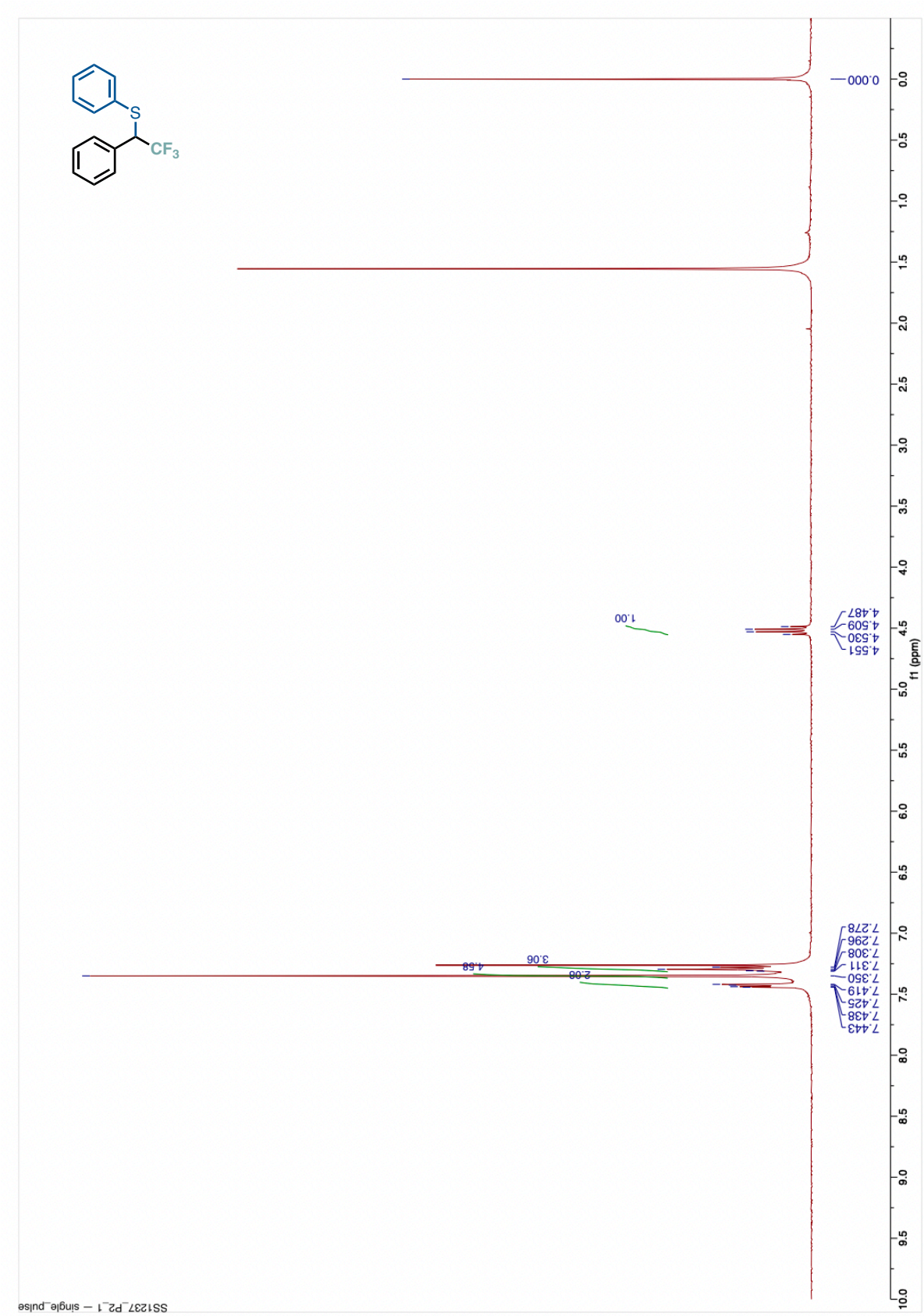
$^{13}C\{^{1}H\}$ NMR of **3M** (101 MHz, $CDCl_3$)



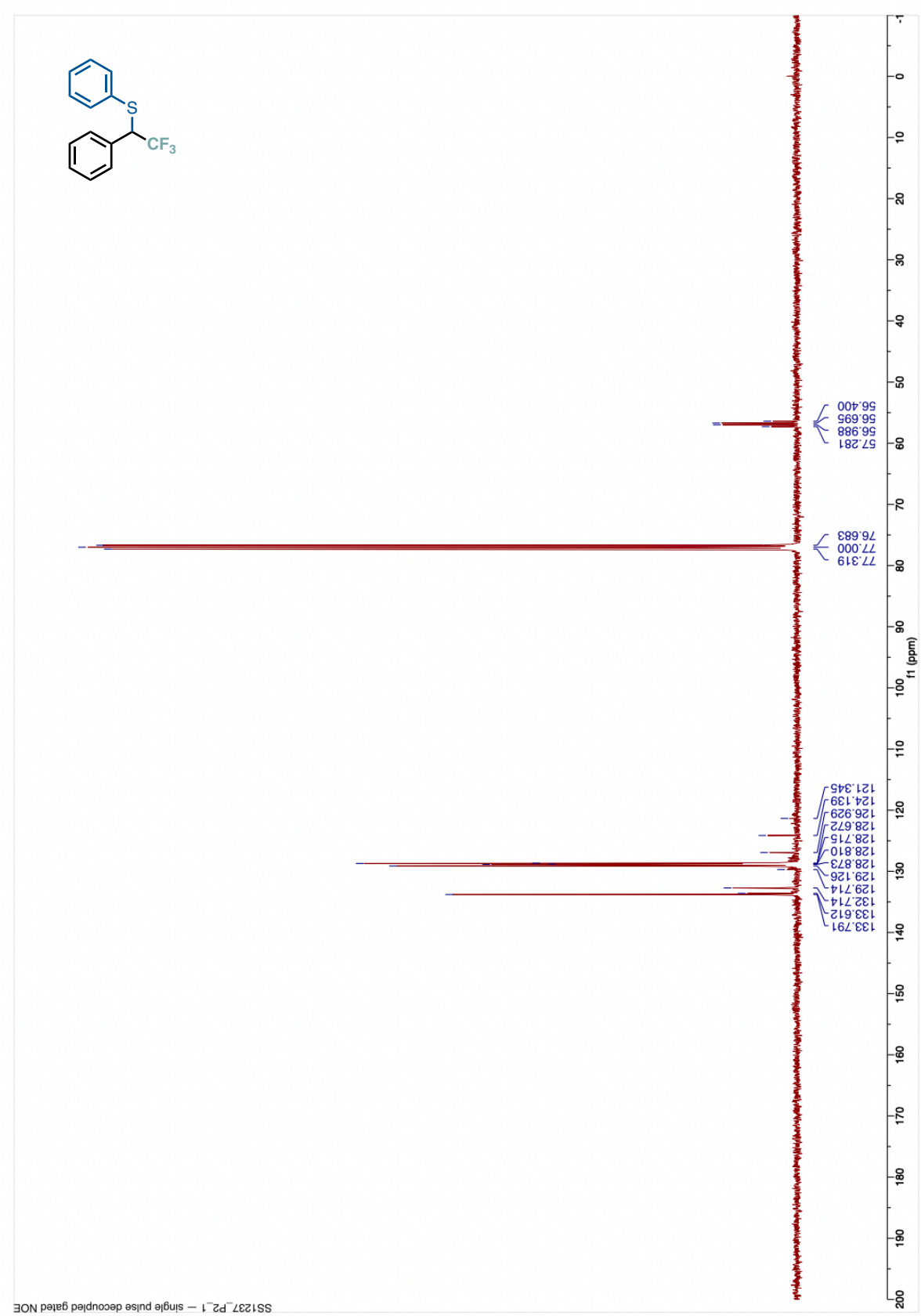
^{19}F NMR of **3M** (376 MHz, $CDCl_3$)



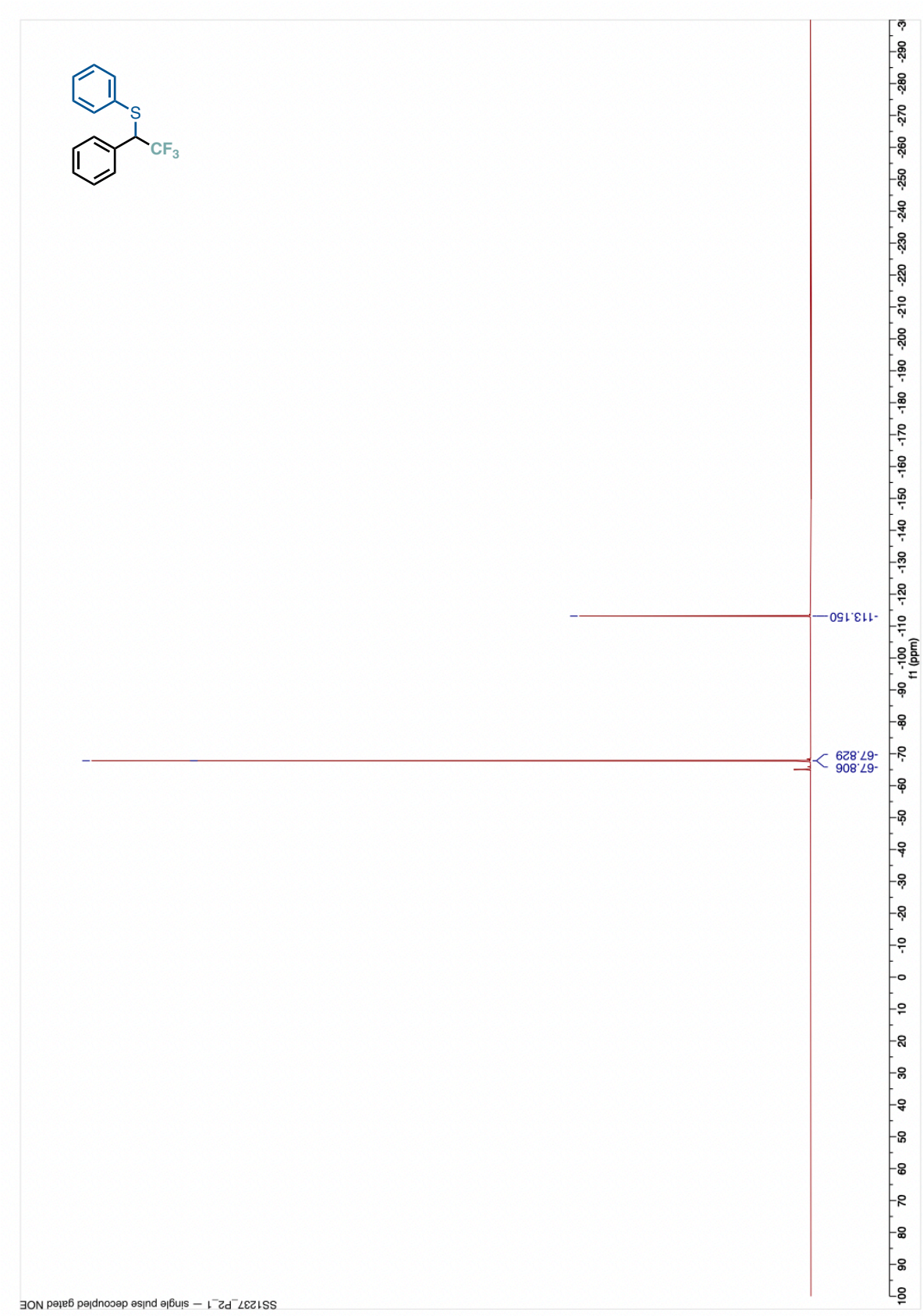
^{1}H NMR of **3N** (400 MHz, $CDCl_3$)



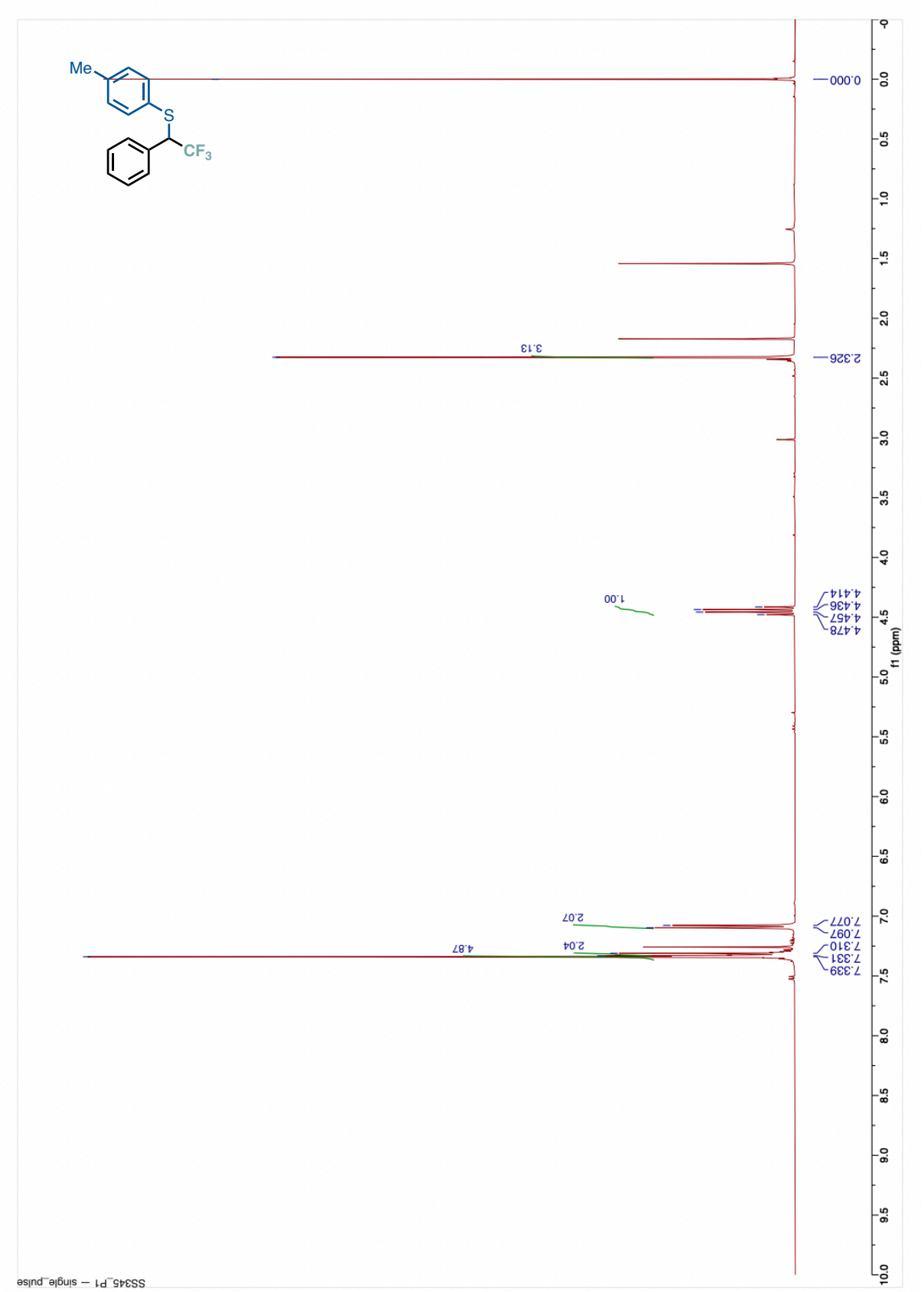
$^{13}C\{^{1}H\}$ NMR of **3N** (101 MHz, $CDCl_3$)



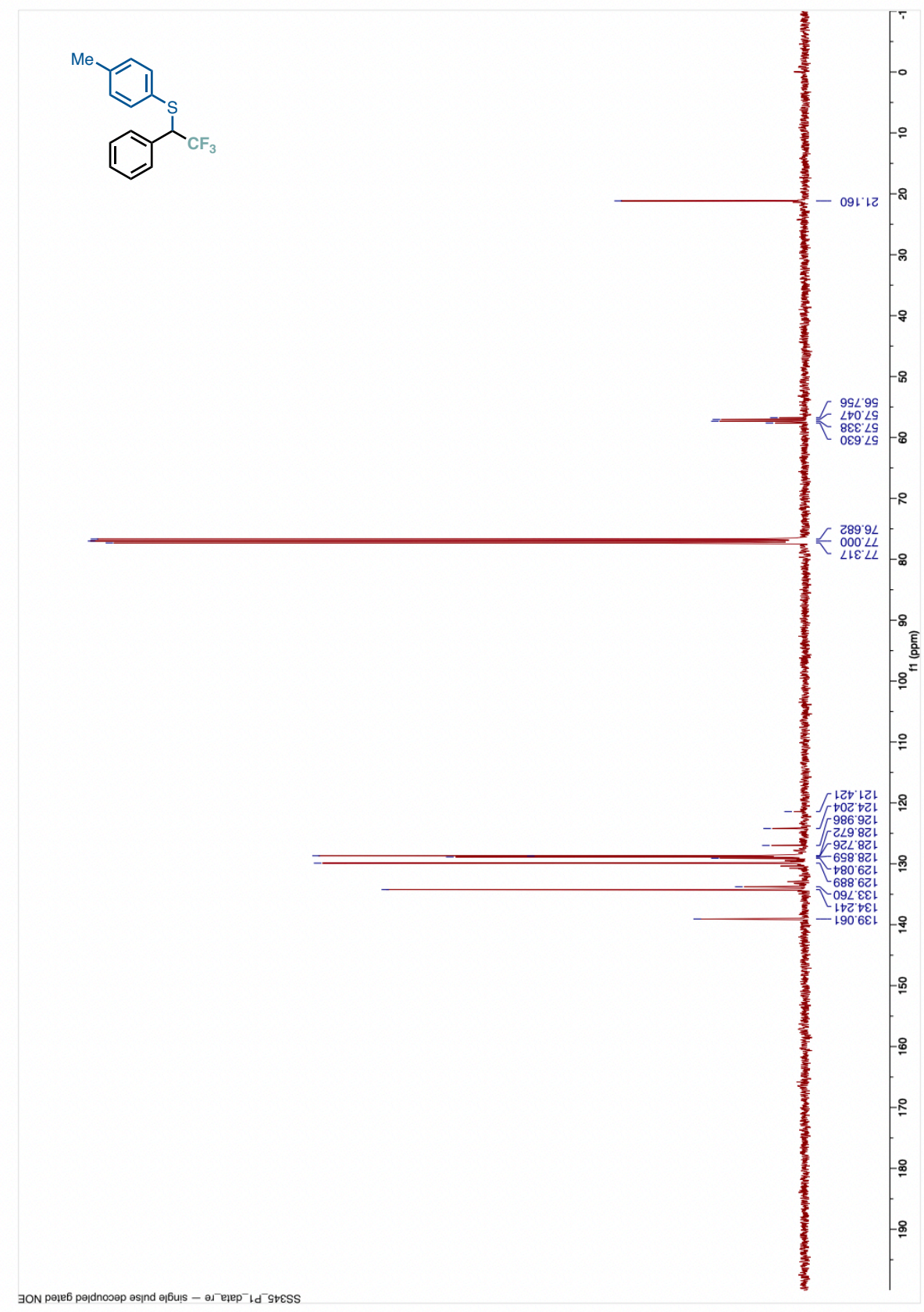
^{19}F NMR of **3N** (376 MHz, $CDCl_3$)



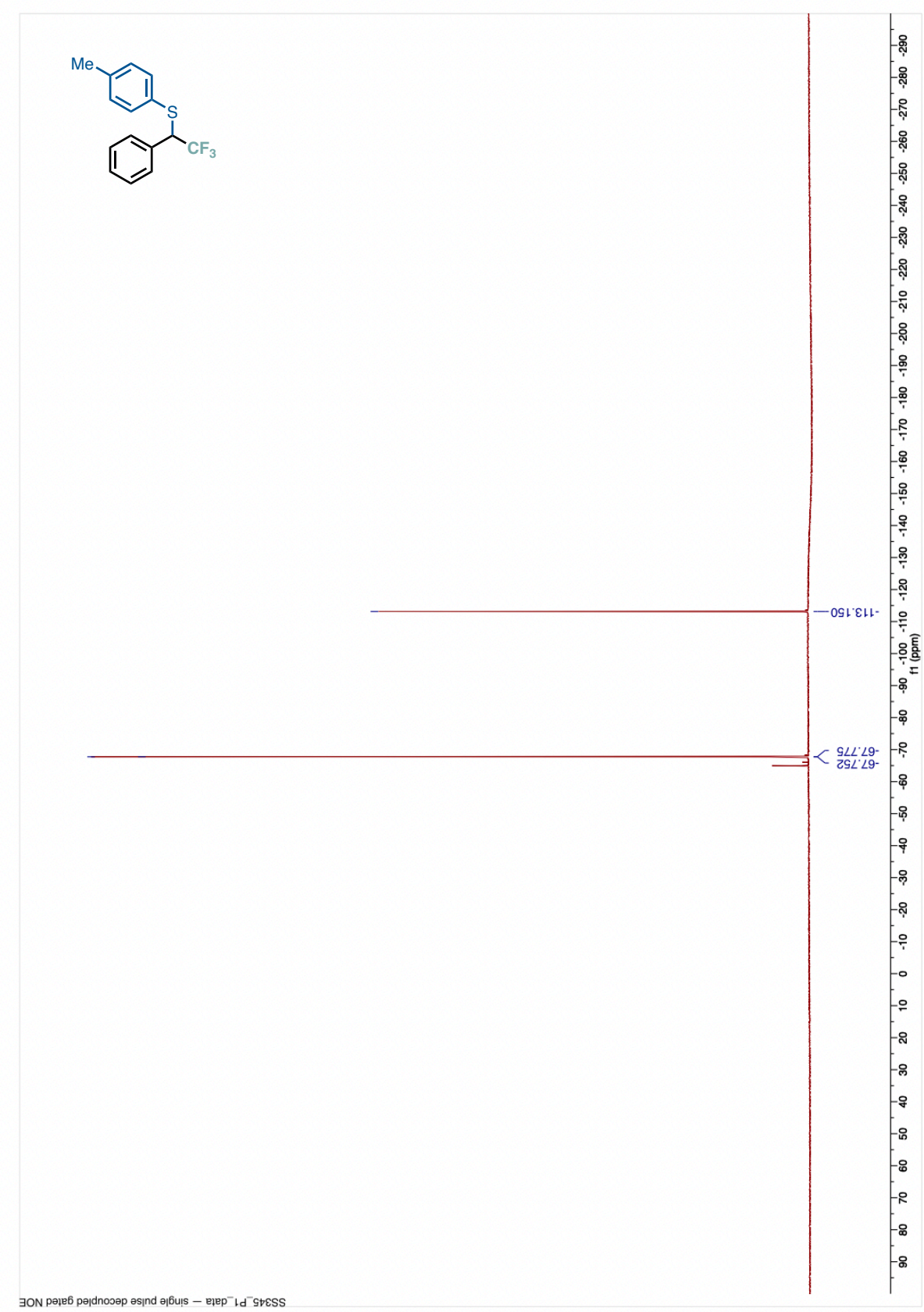
^{1}H NMR of **3O** (400 MHz, $CDCl_3$)



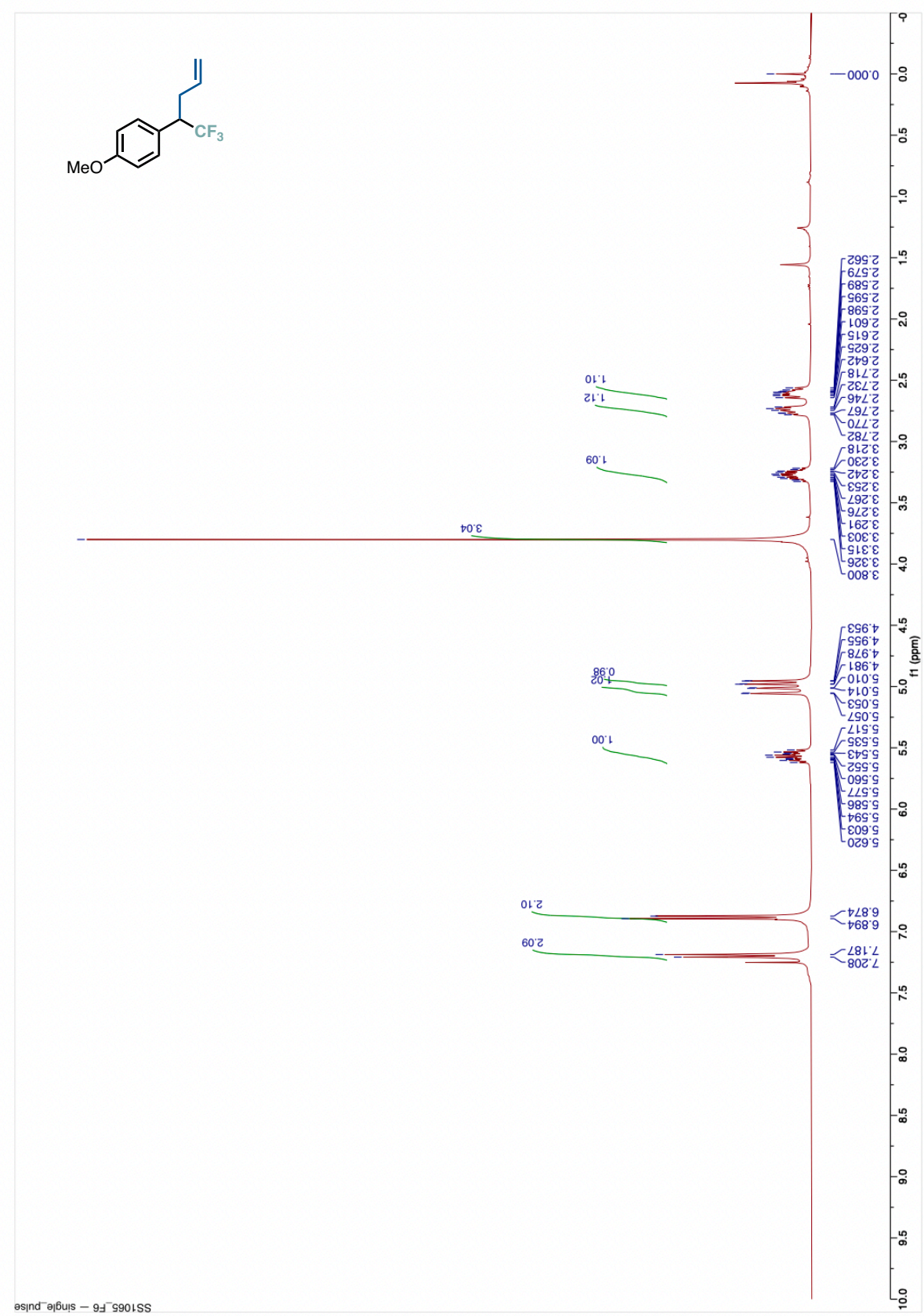
$^{13}C\{^{1}H\}$ NMR of **3O** (101 MHz, $CDCl_3$)



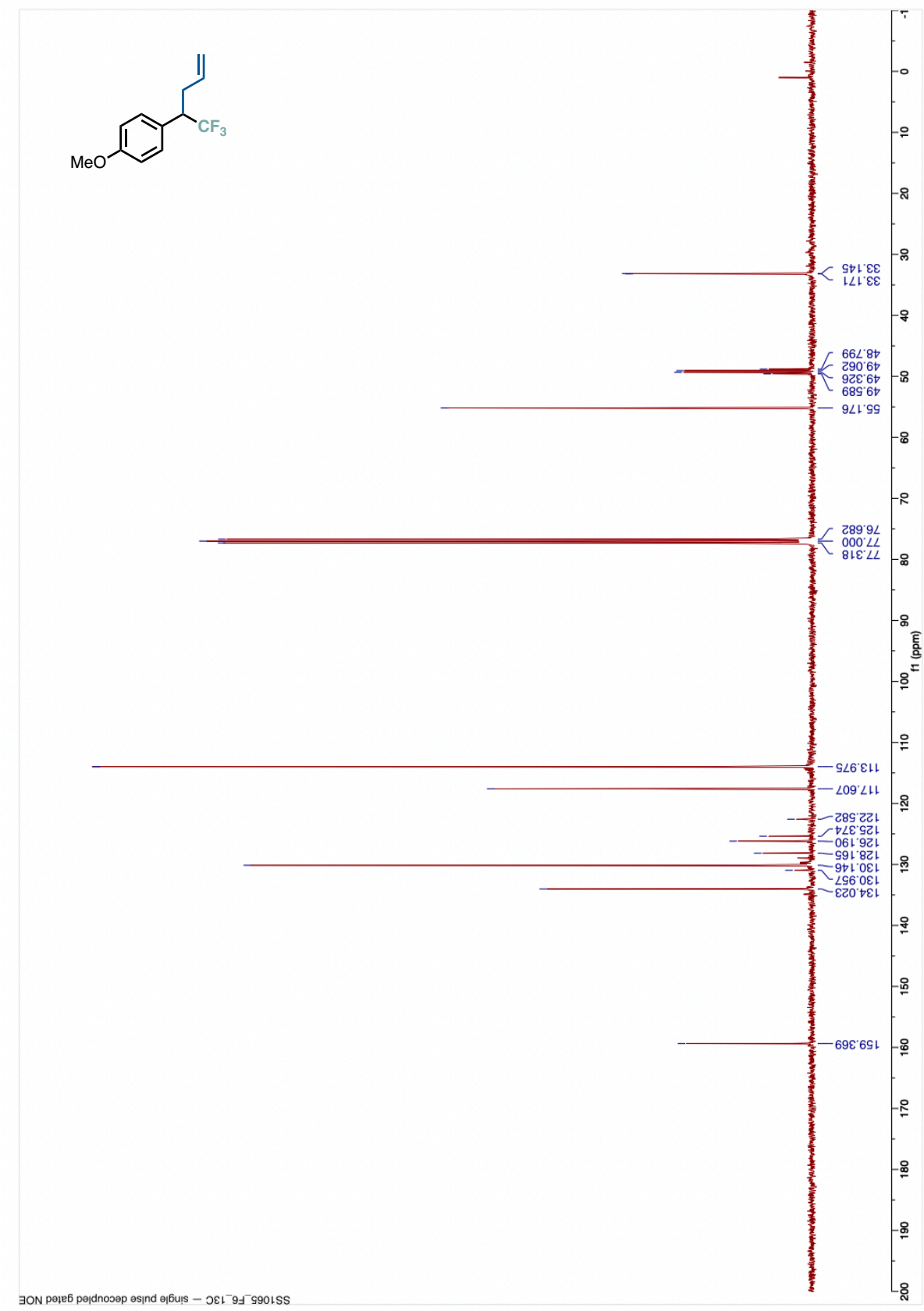
^{19}F NMR of **3O** (376 MHz, $CDCl_3$)



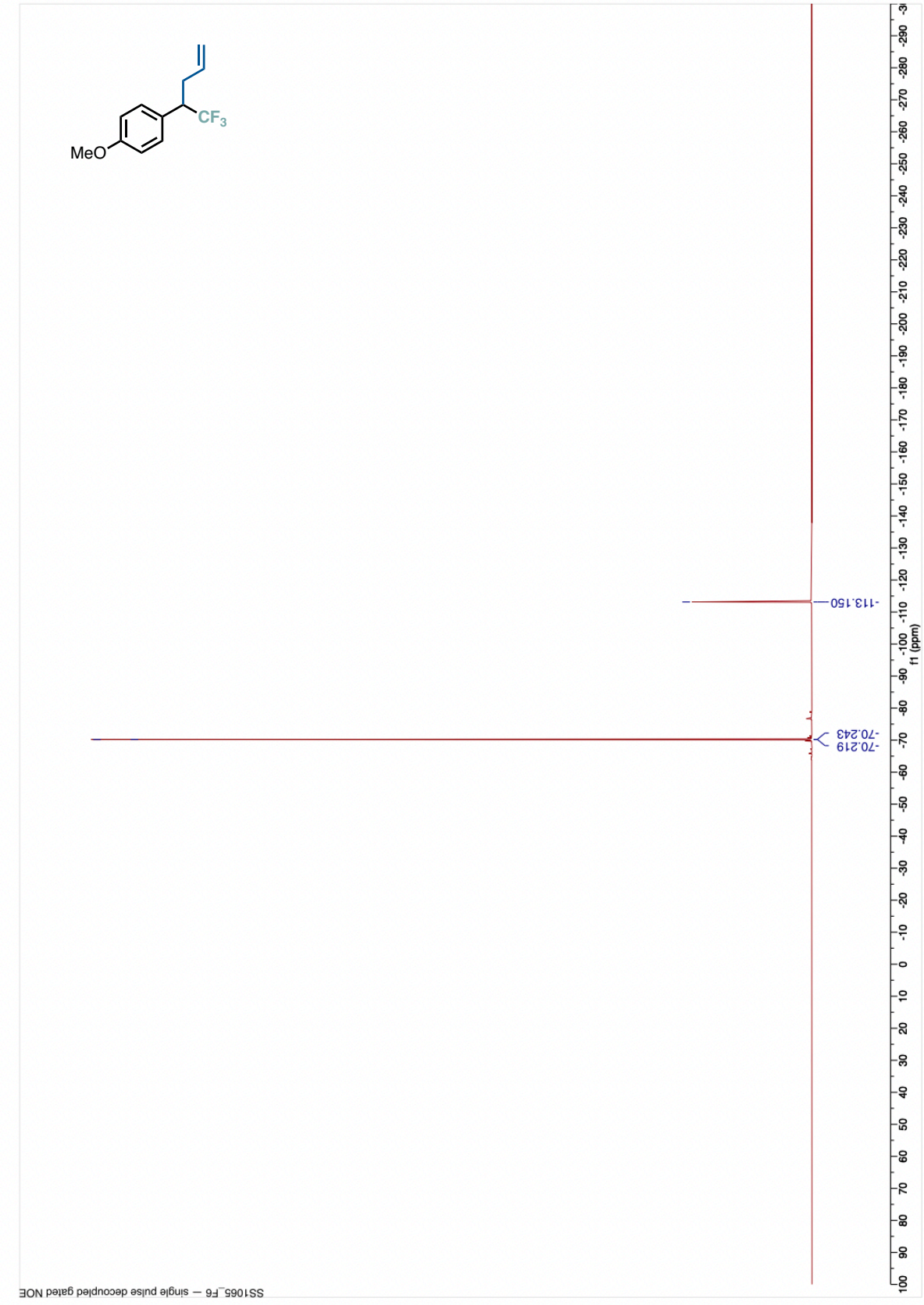
^{1}H NMR of **3P** (400 MHz, $CDCl_3$)



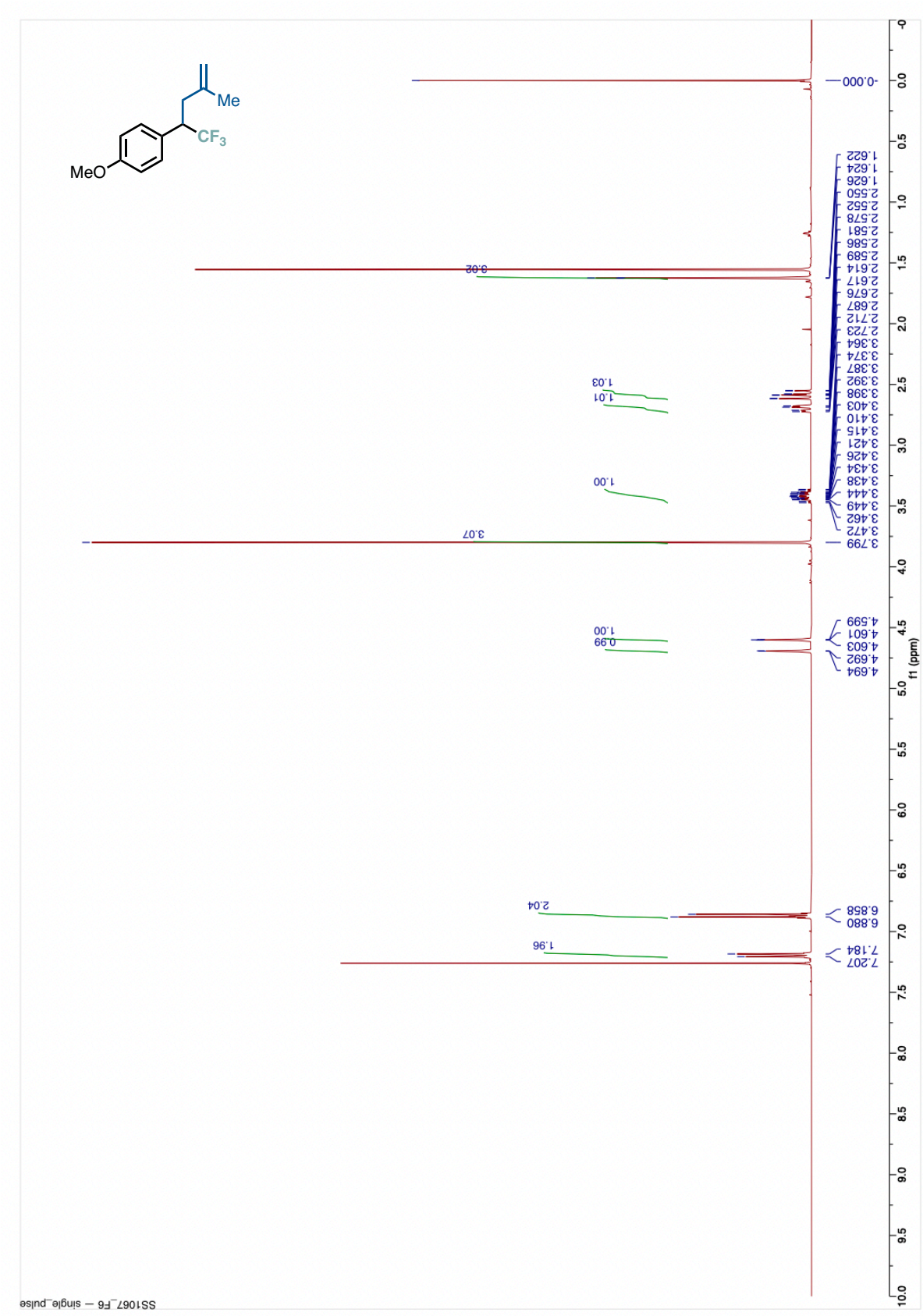
$^{13}C\{^{1}H\}$ NMR of **3P** (101 MHz, $CDCl_3$)



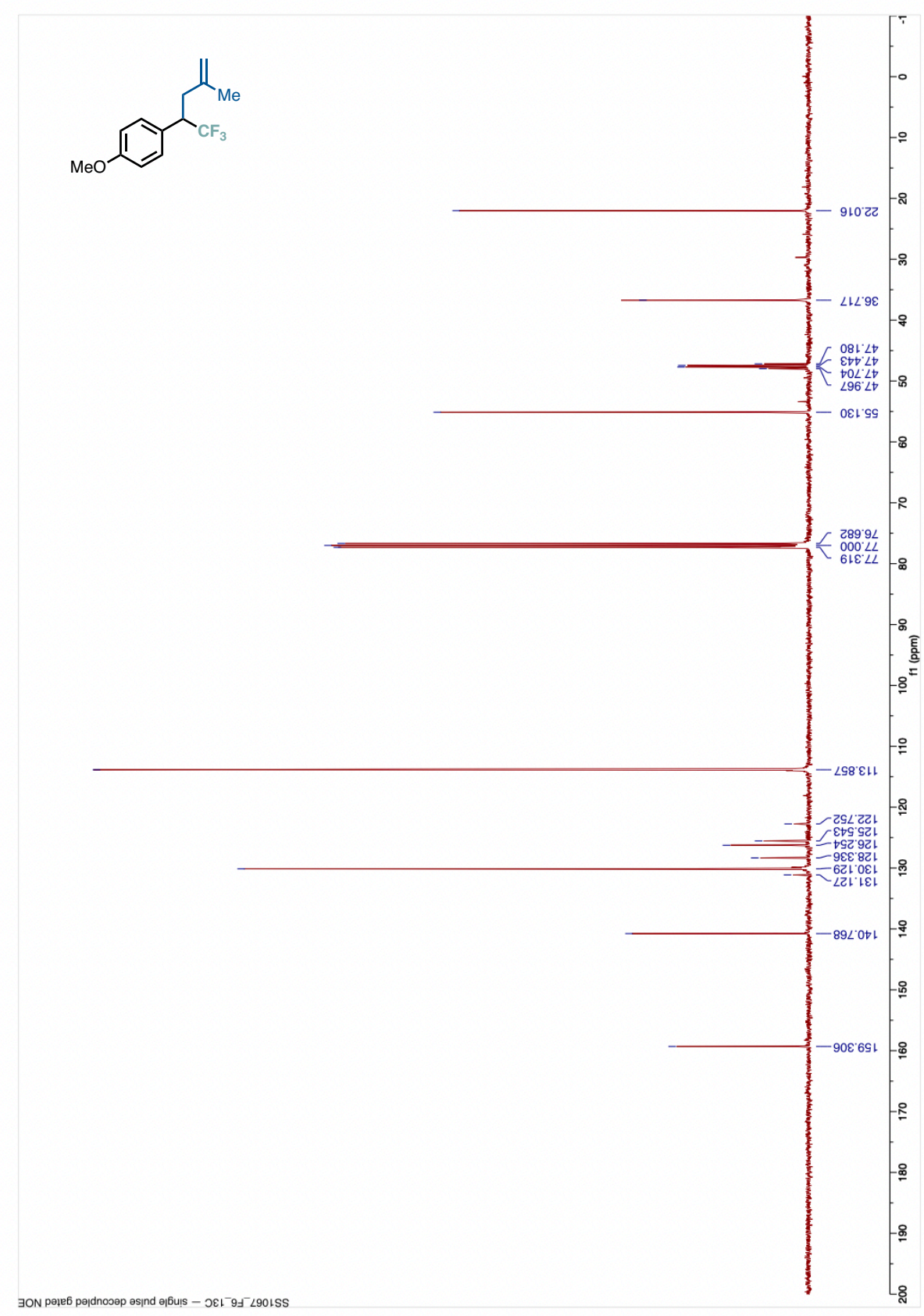
^{19}F NMR of **3P** (376 MHz, $CDCl_3$)



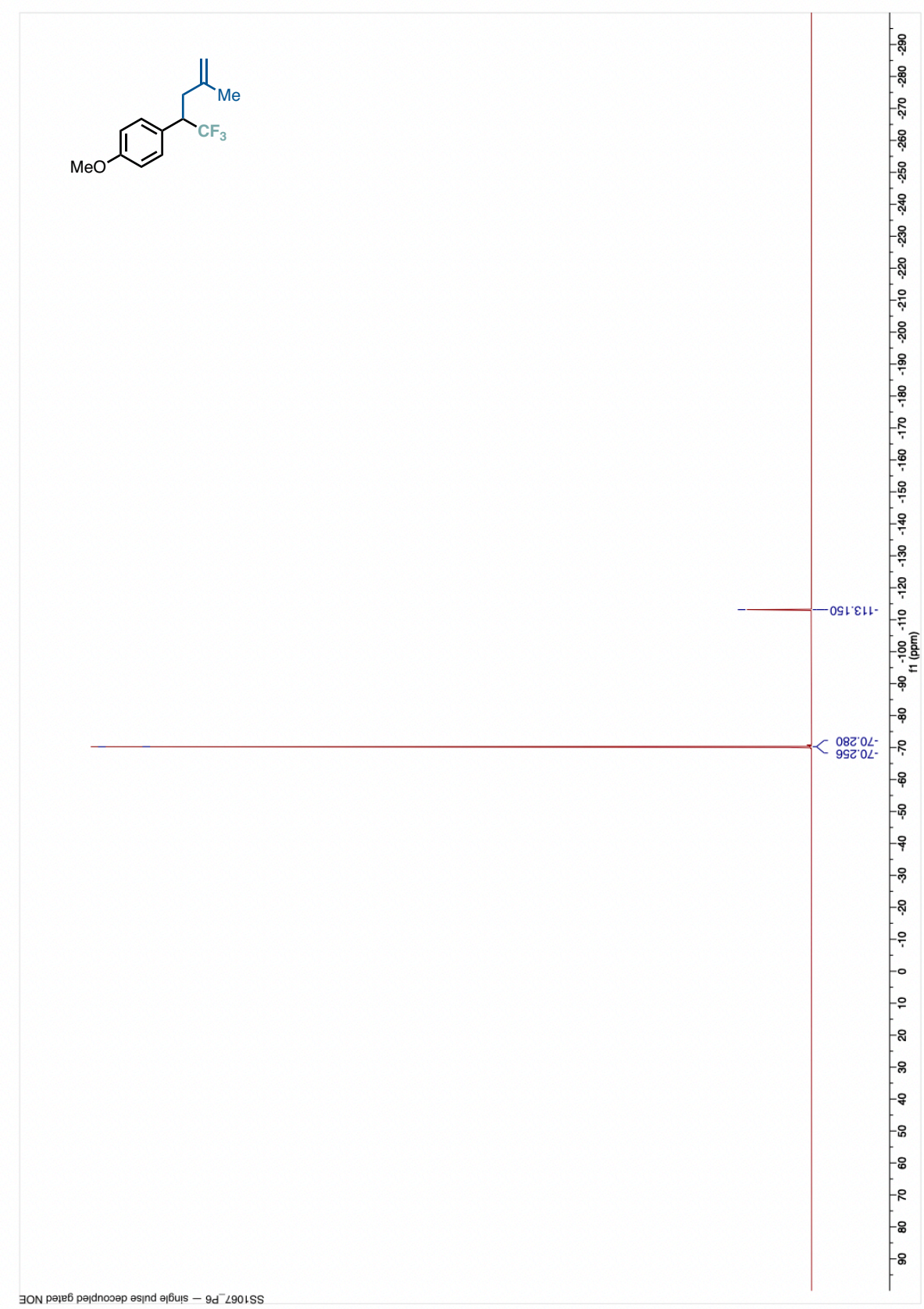
^{1}H NMR of **3Q** (400 MHz, $CDCl_3$)



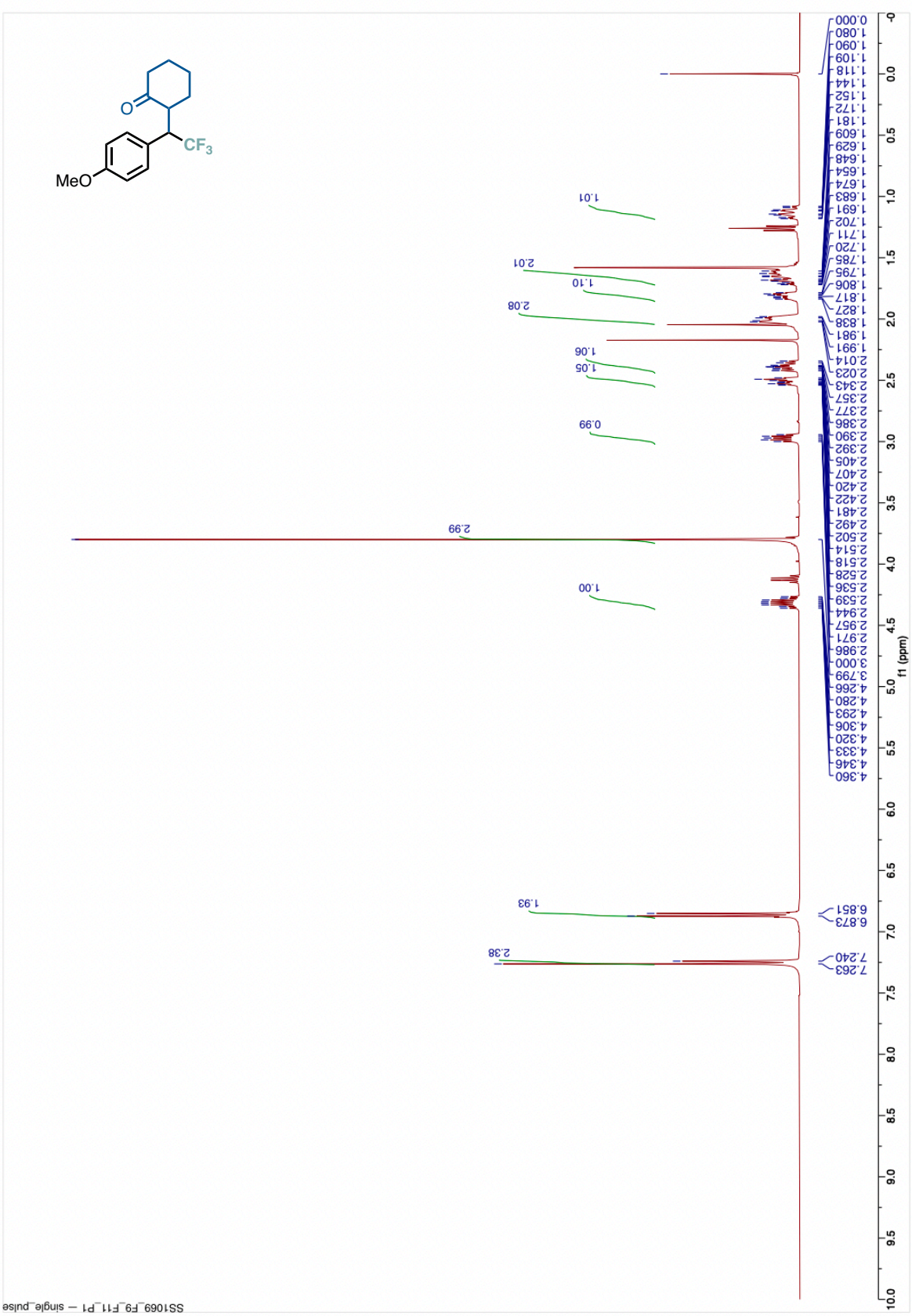
$^{13}C\{^{1}H\}$ NMR of **3Q** (101 MHz, $CDCl_3$)



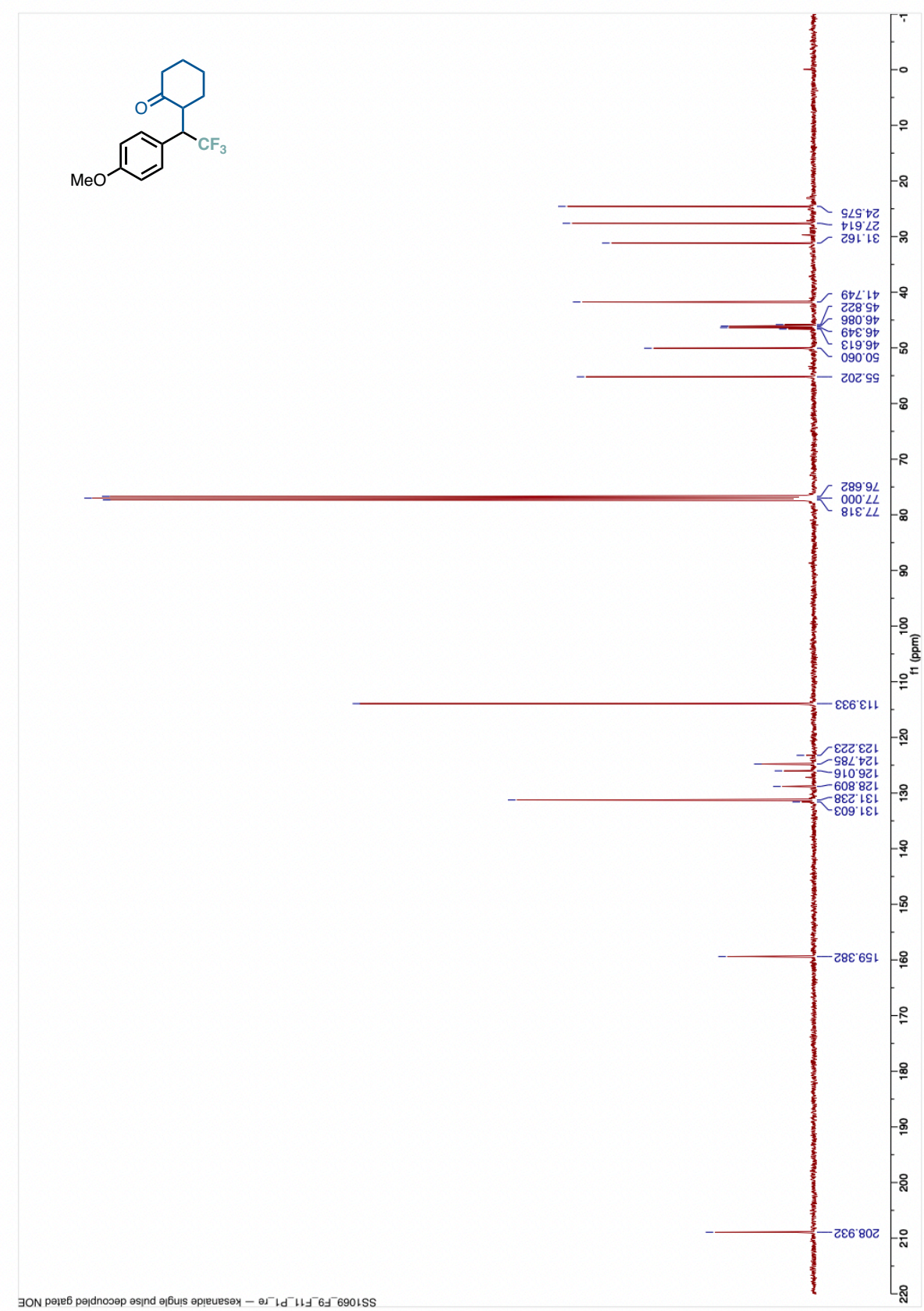
^{19}F NMR of **3Q** (376 MHz, $CDCl_3$)



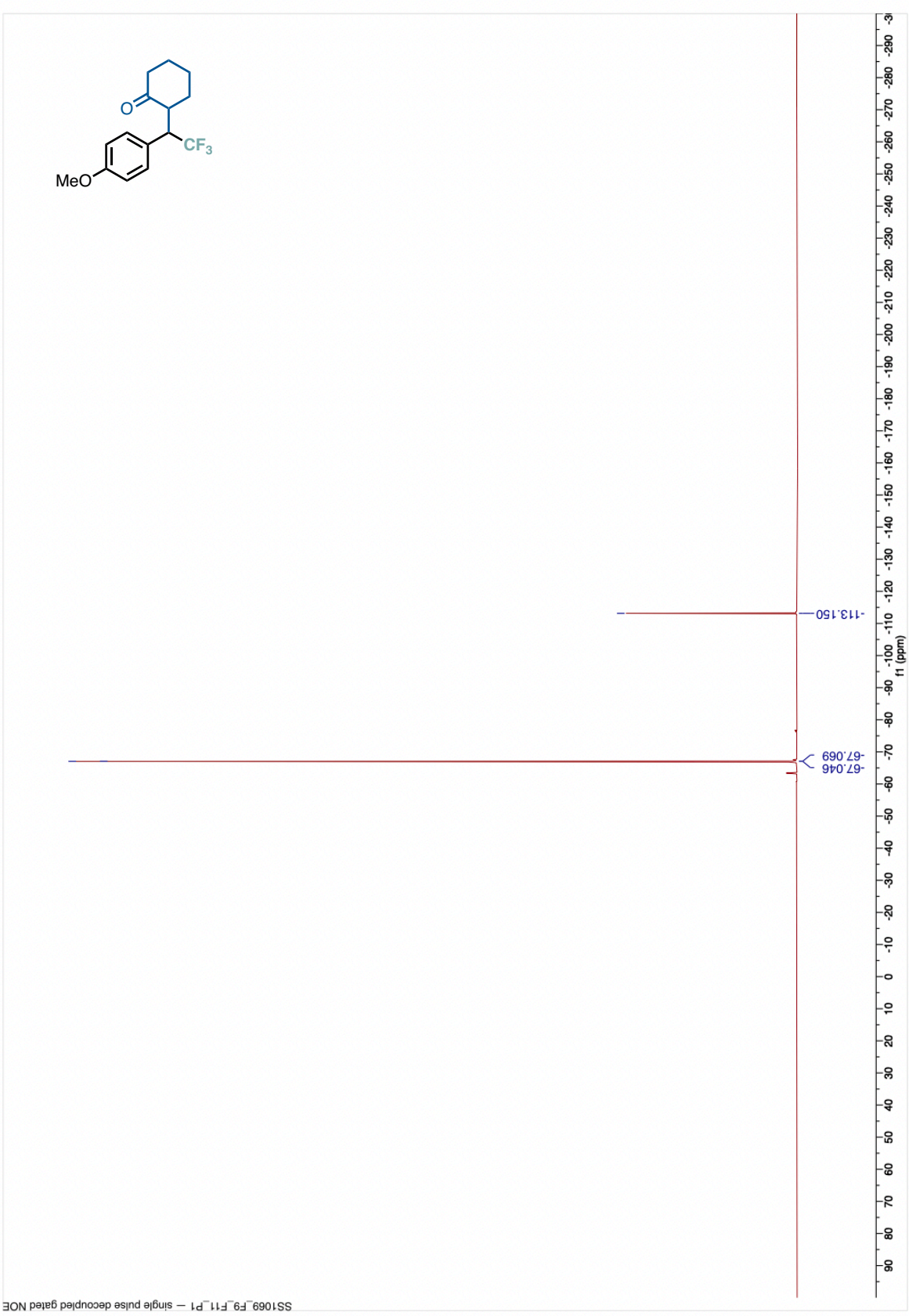
^{1}H NMR of ***major*-3R** (400 MHz, $CDCl_3$)



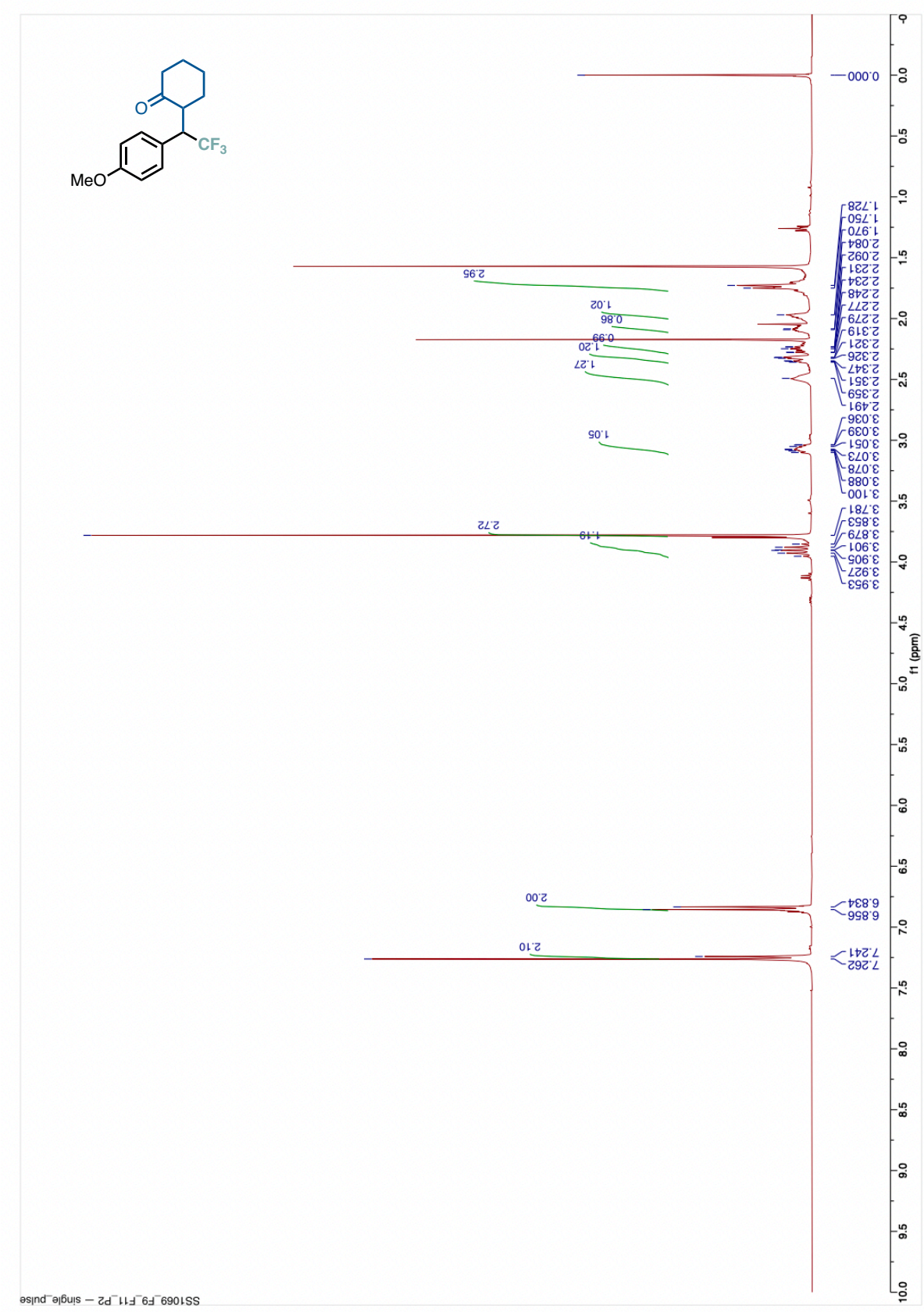
$^{13}C\{^{1}H\}$ NMR of ***major*-3R** (101 MHz, $CDCl_3$)



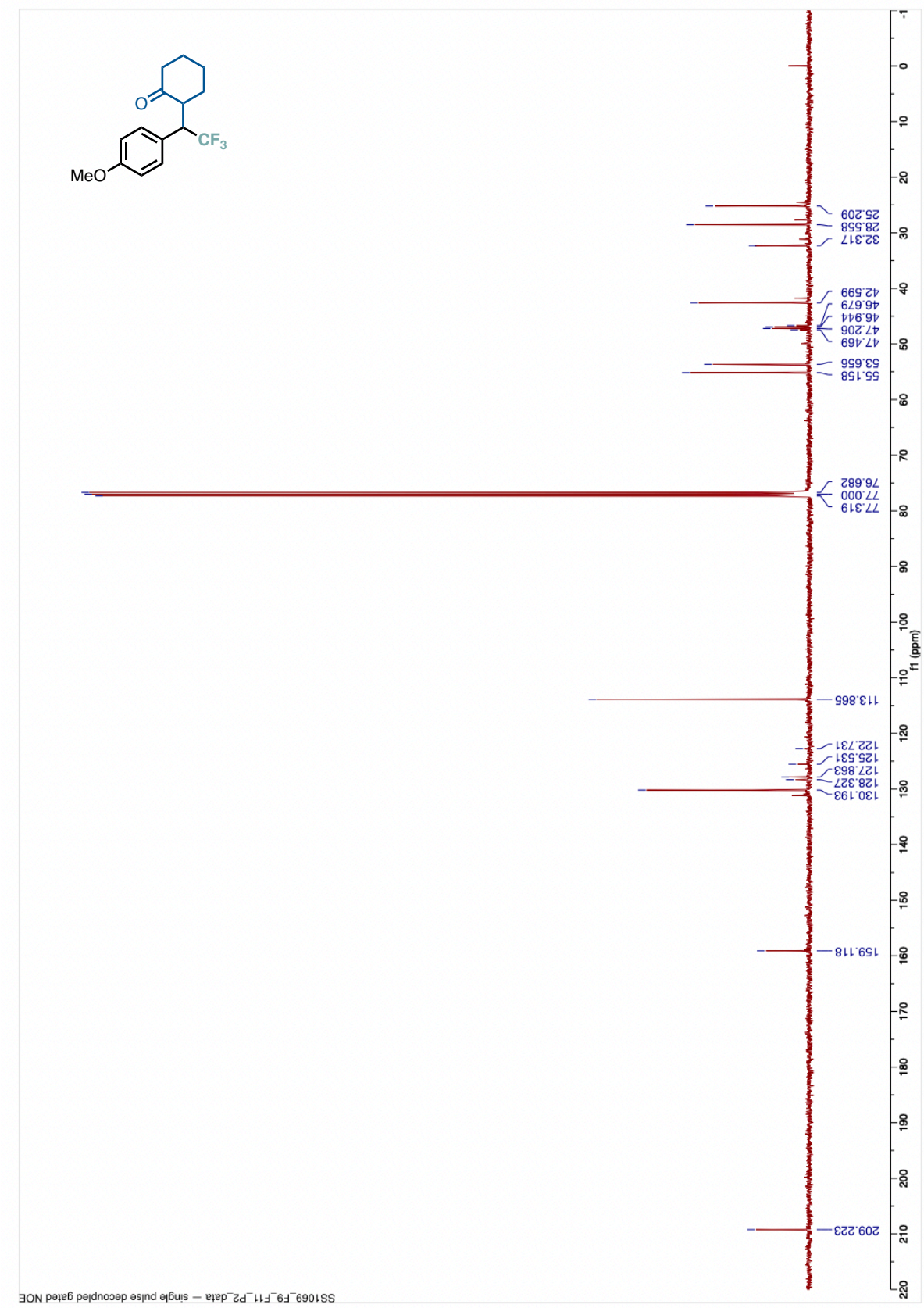
^{19}F NMR of ***major*-3R** (376 MHz, $CDCl_3$)



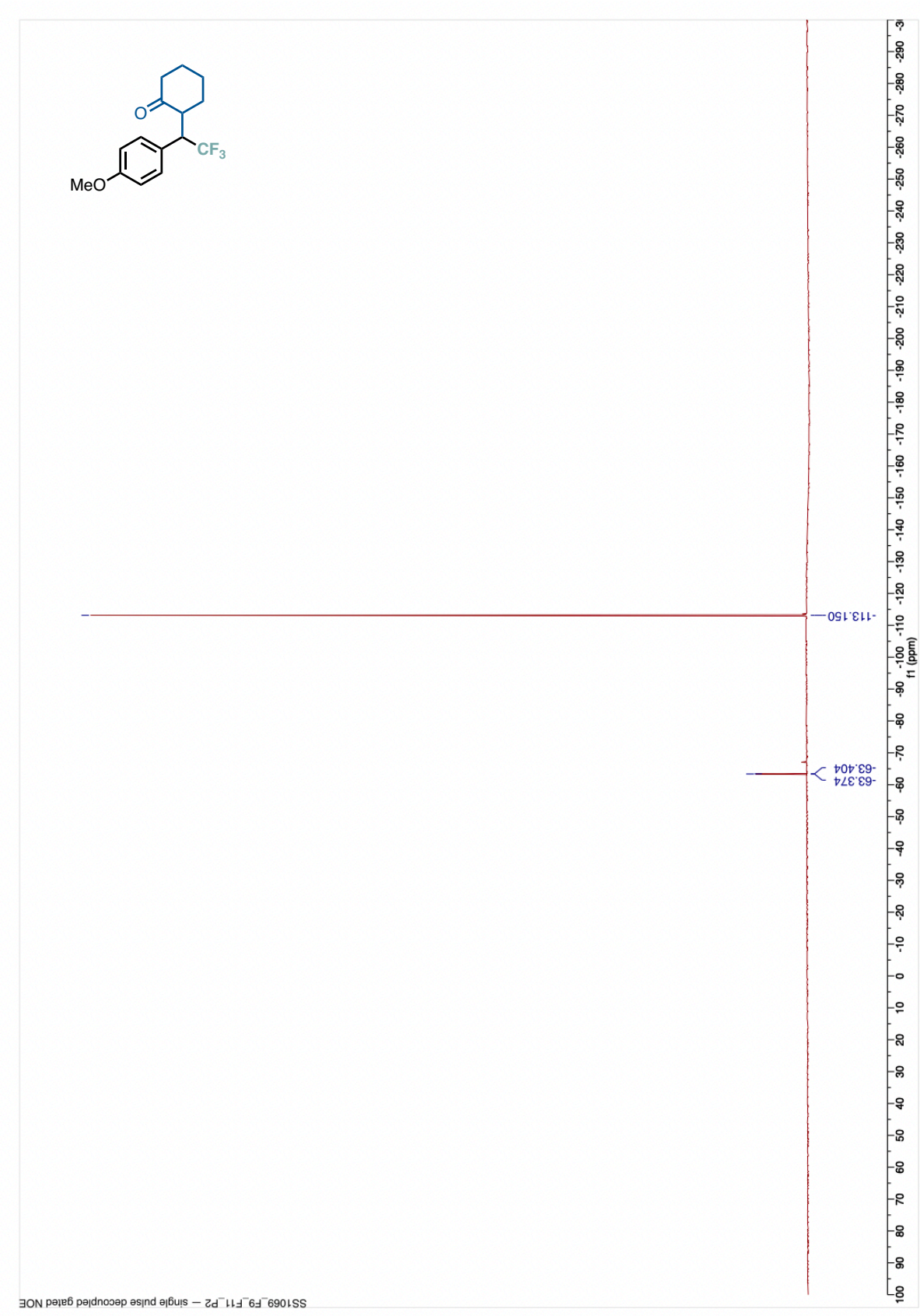
^{1}H NMR of ***minor*-3R** (400 MHz, $CDCl_3$)



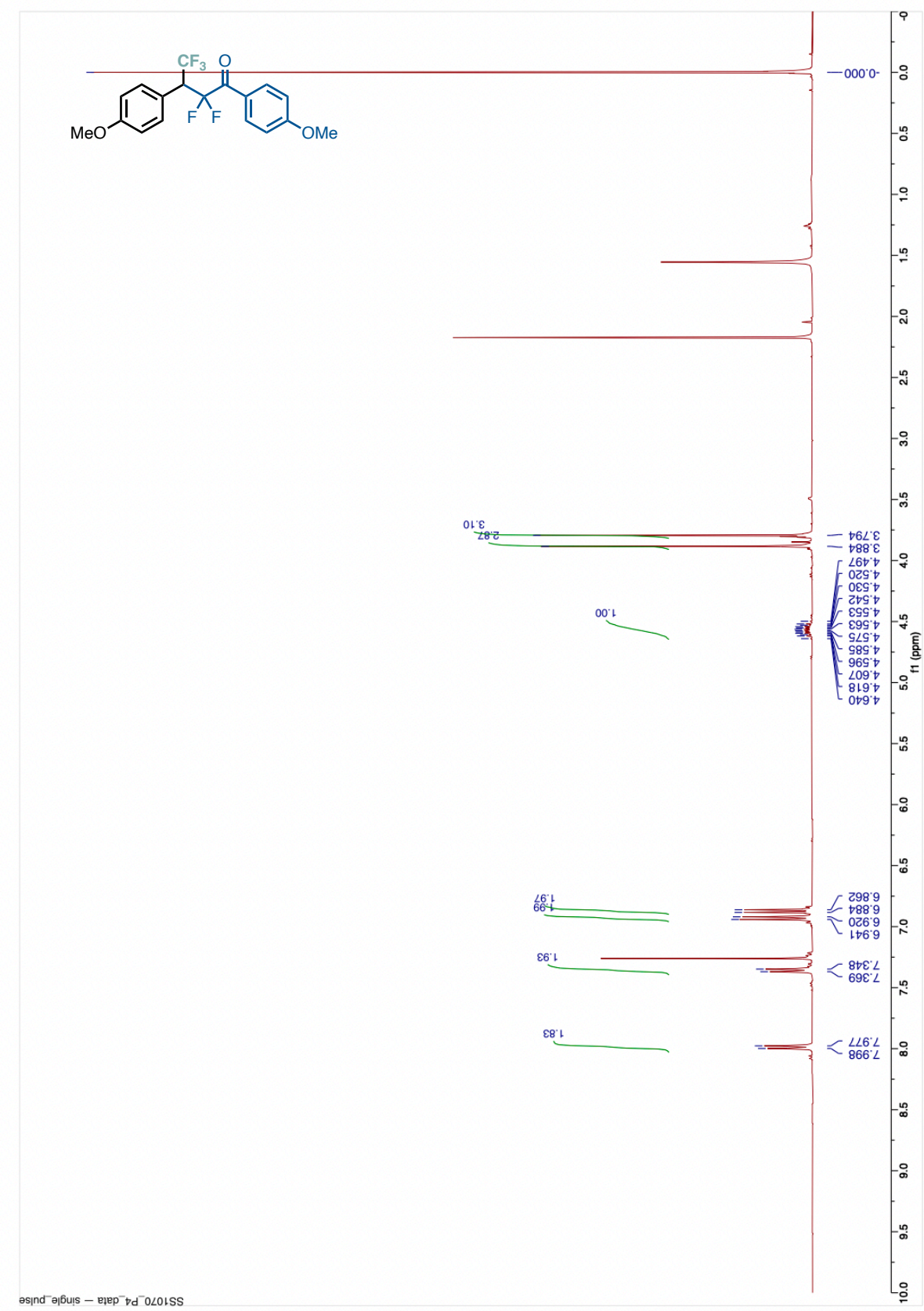
$^{13}C\{^{1}H\}$ NMR of ***minor*-3R** (101 MHz, $CDCl_3$)



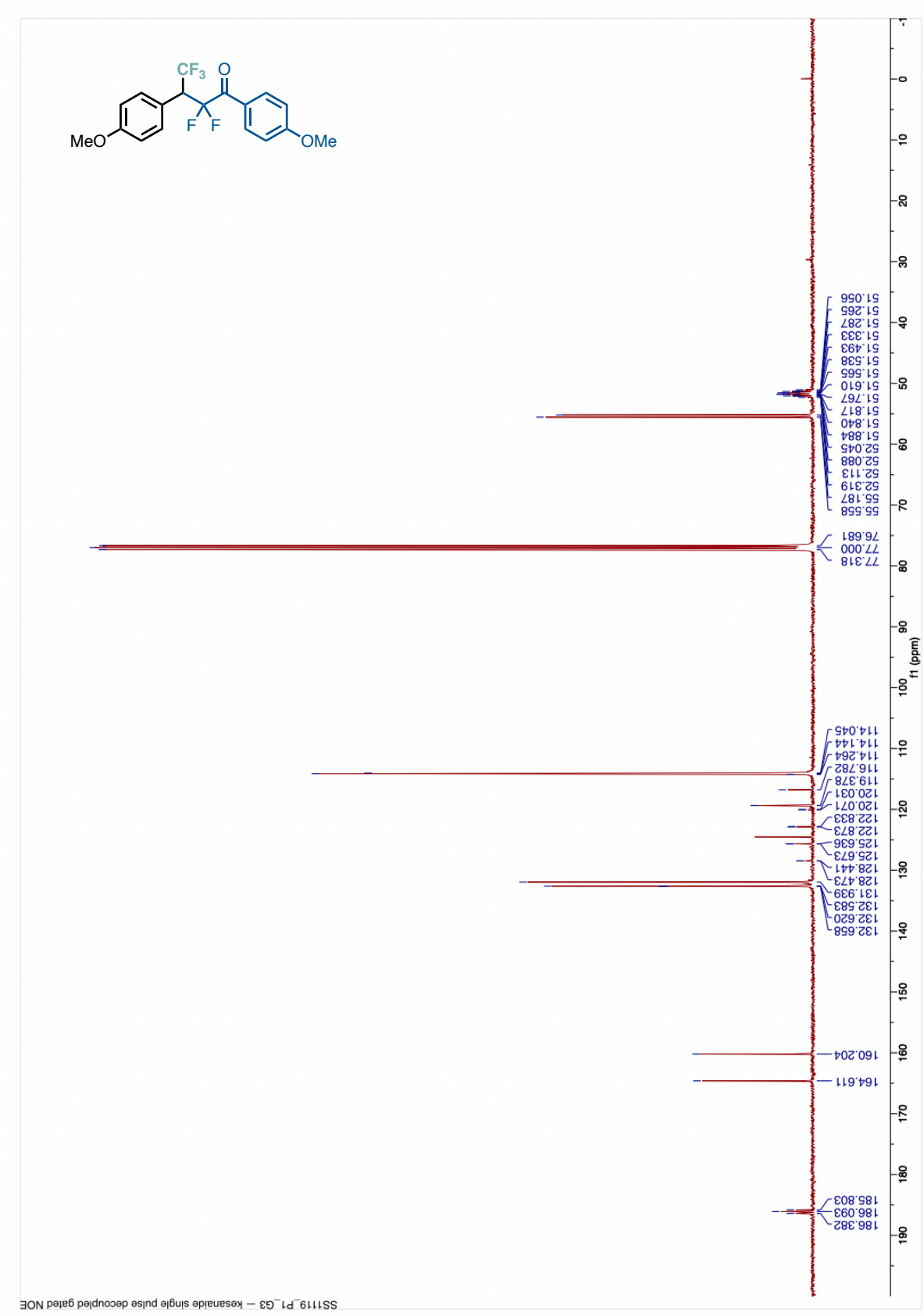
^{19}F NMR of ***minor*-3R** (376 MHz, $CDCl_3$)



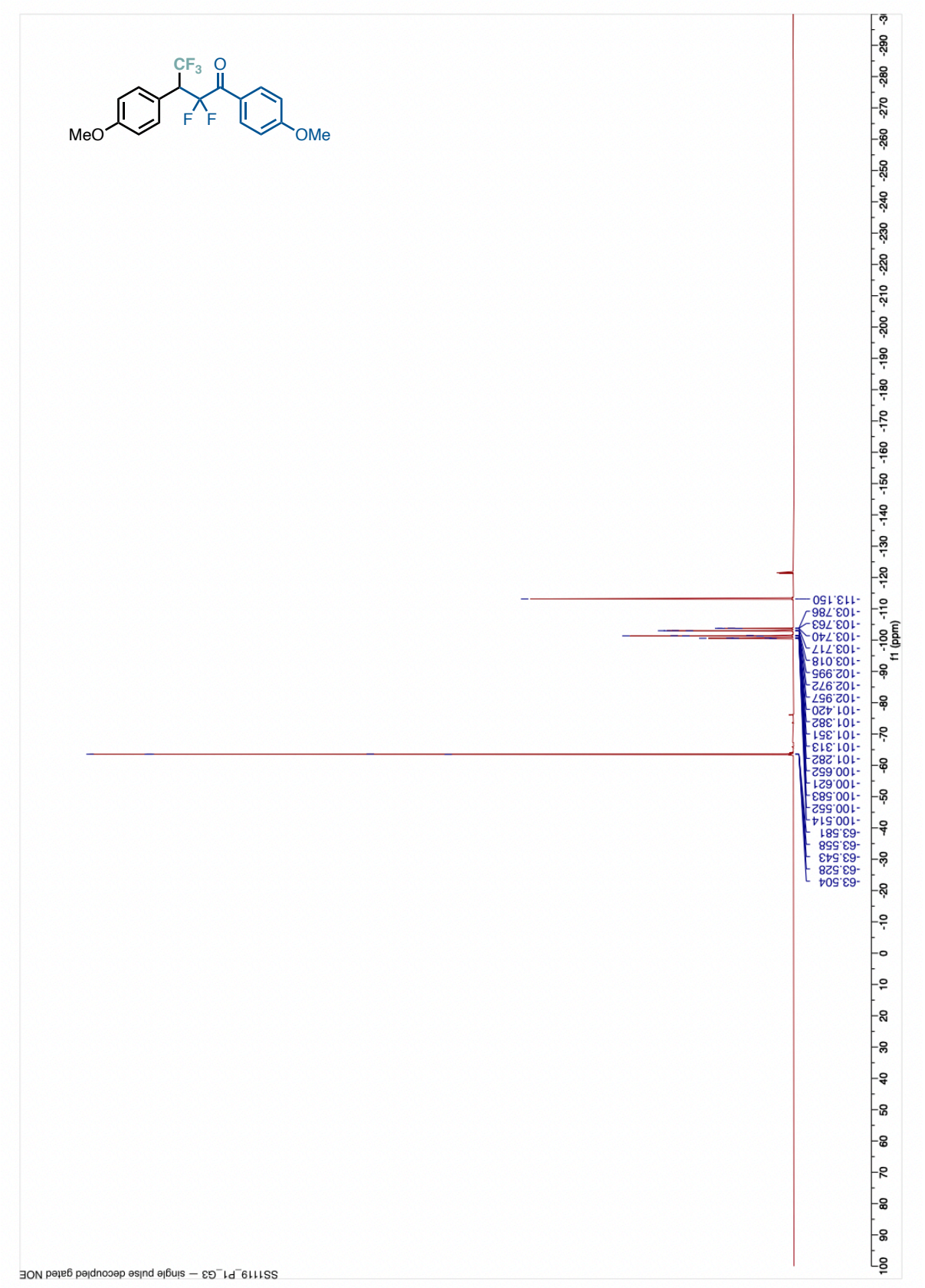
^{1}H NMR of **3S** (400 MHz, $CDCl_3$)



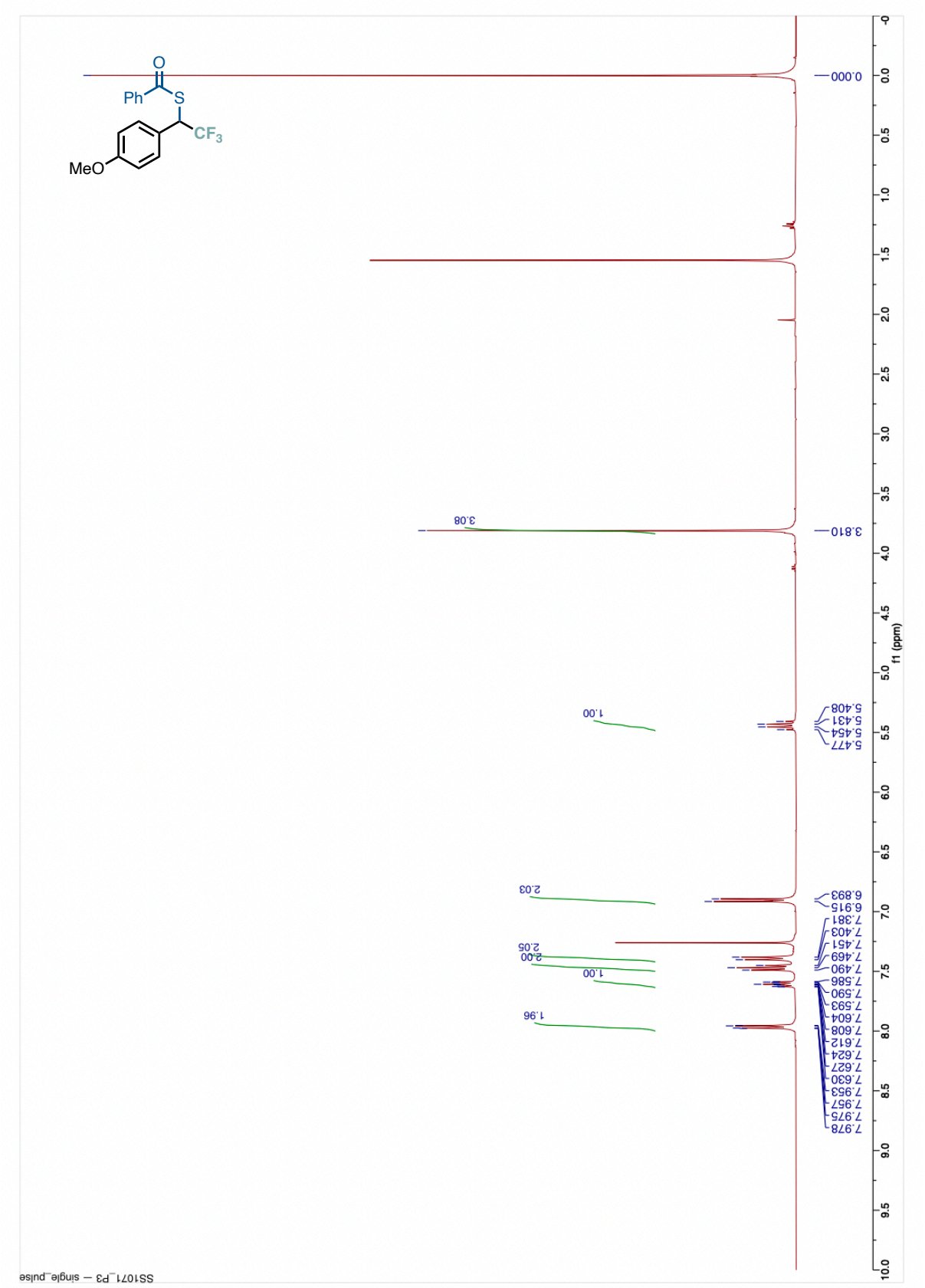
$^{13}C\{^{1}H\}$ NMR of **3V** (101 MHz, $CDCl_3$)



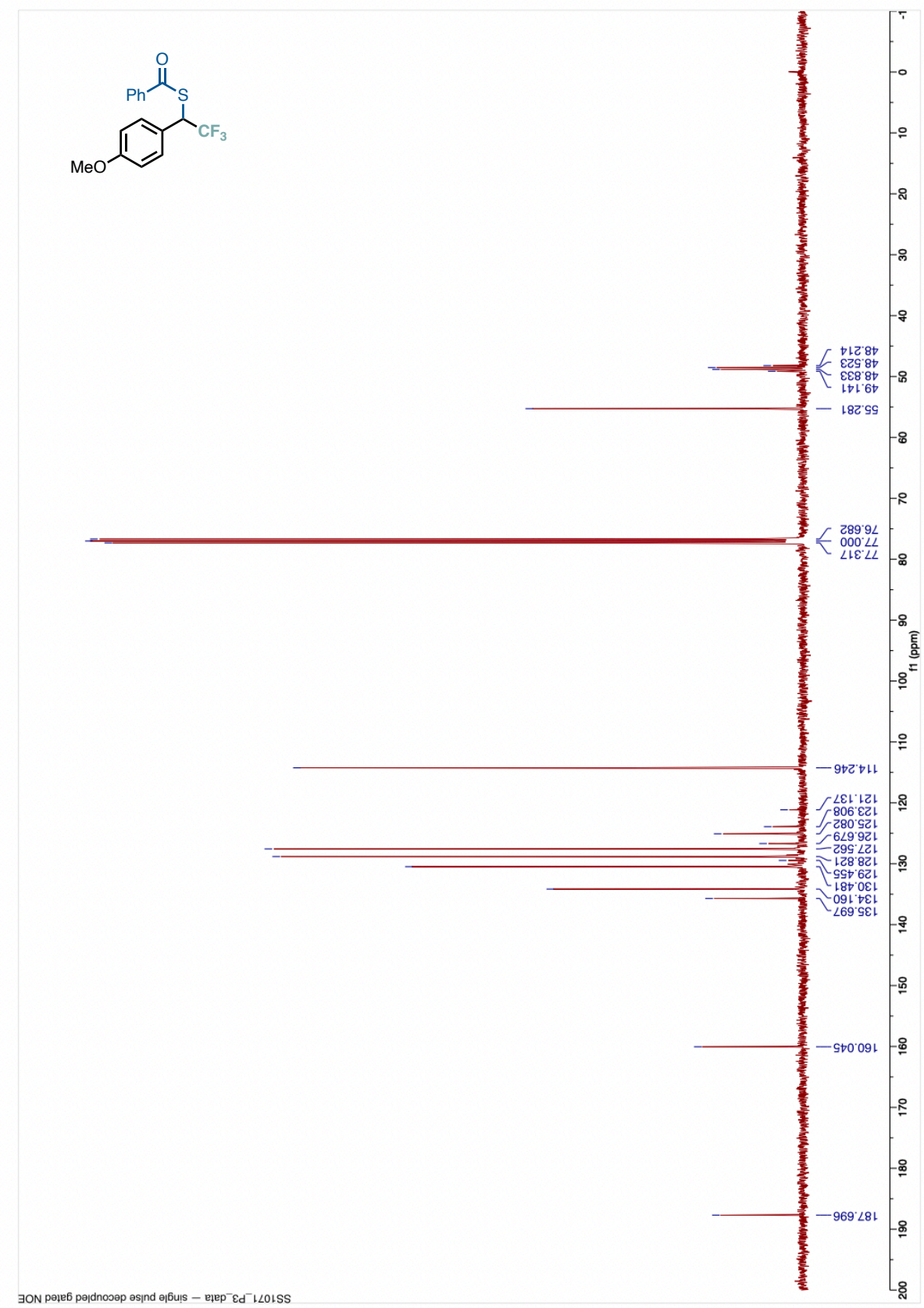
^{19}F NMR of **3S** (376 MHz, $CDCl_3$)



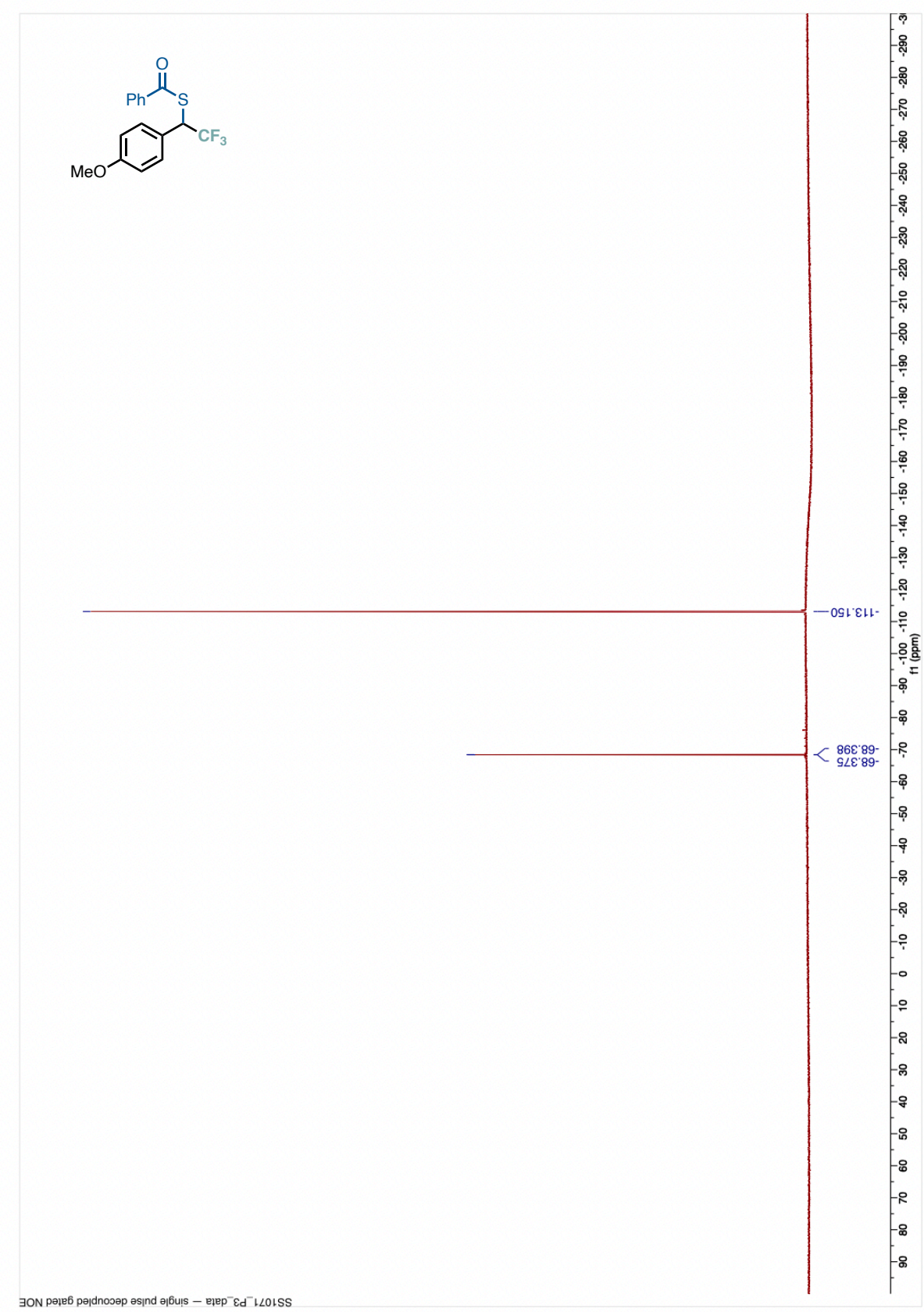
^{1}H NMR of **3T** (400 MHz, $CDCl_3$)



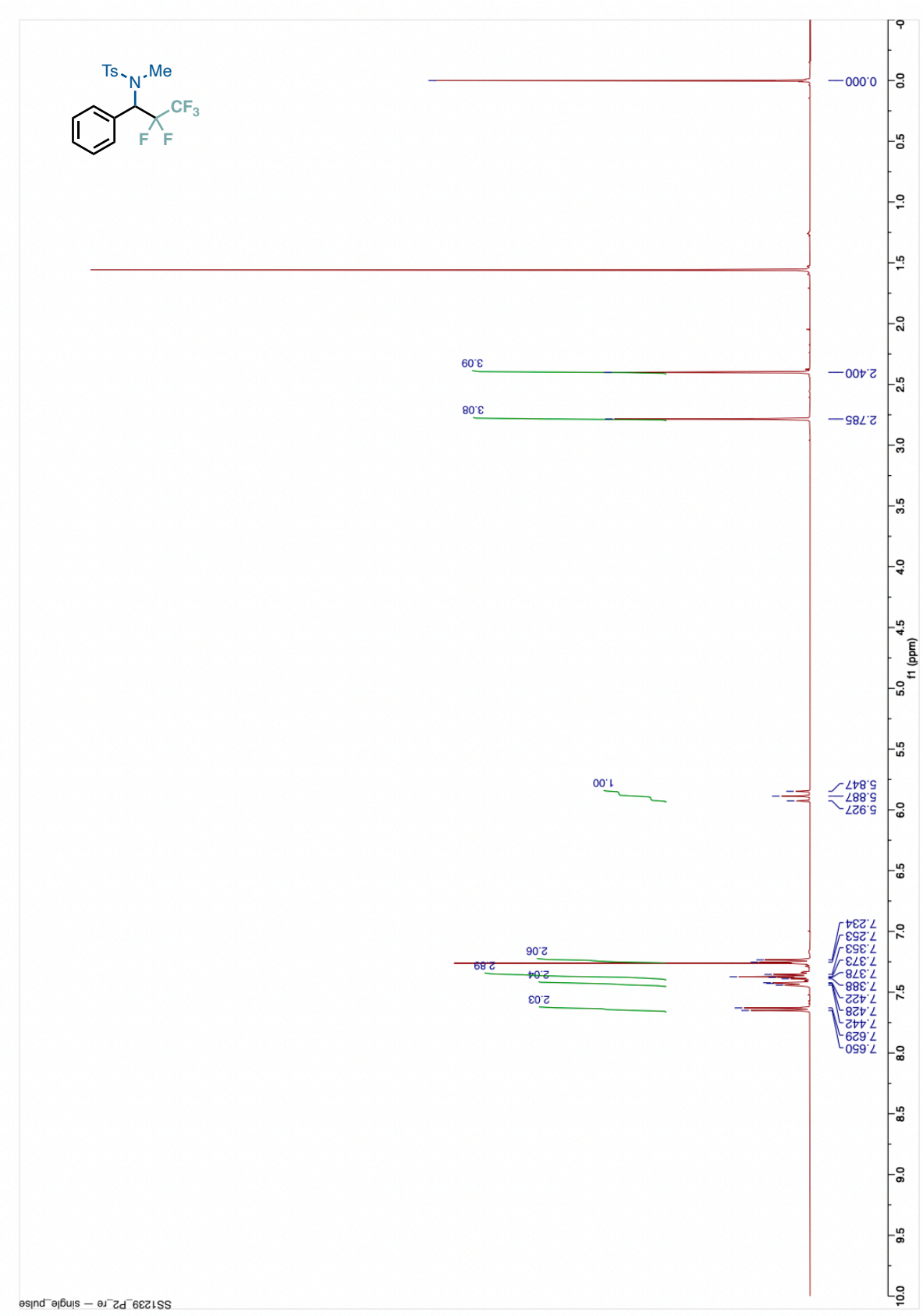
$^{13}C\{^{1}H\}$ NMR of **3T** (101 MHz, $CDCl_3$)



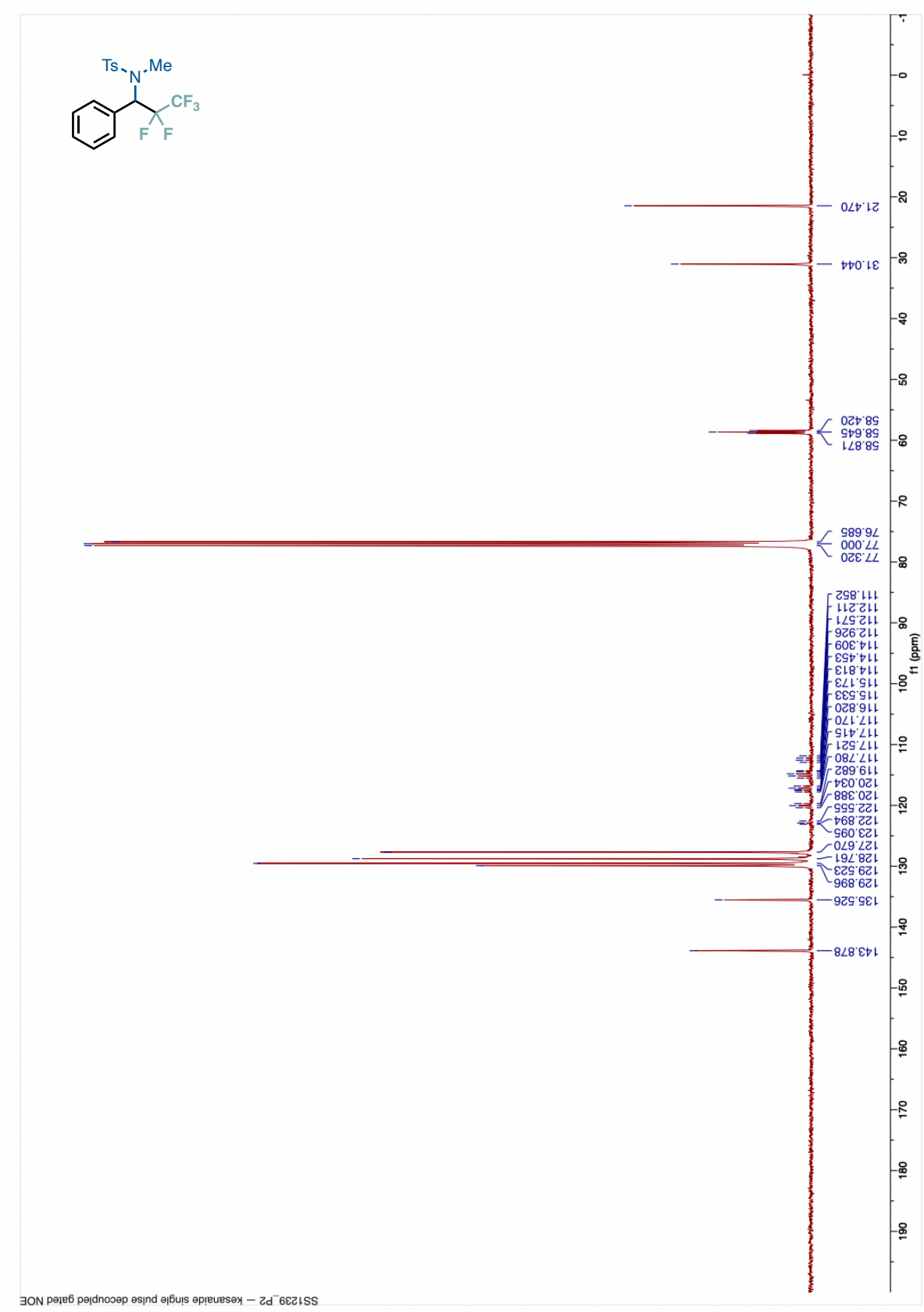
^{19}F NMR of **3T** (376 MHz, $CDCl_3$)



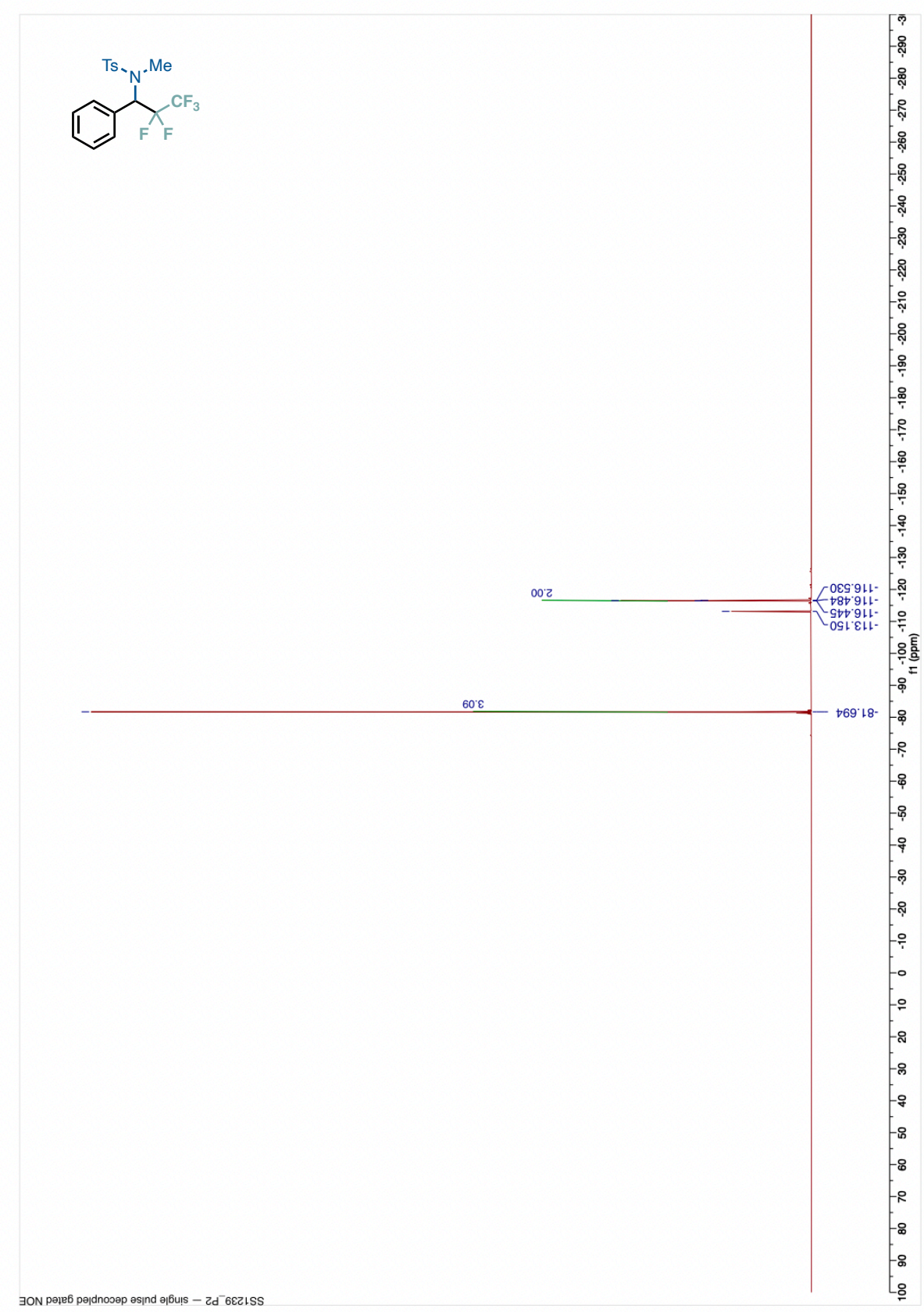
^{1}H NMR of **3U** (400 MHz, $CDCl_3$)



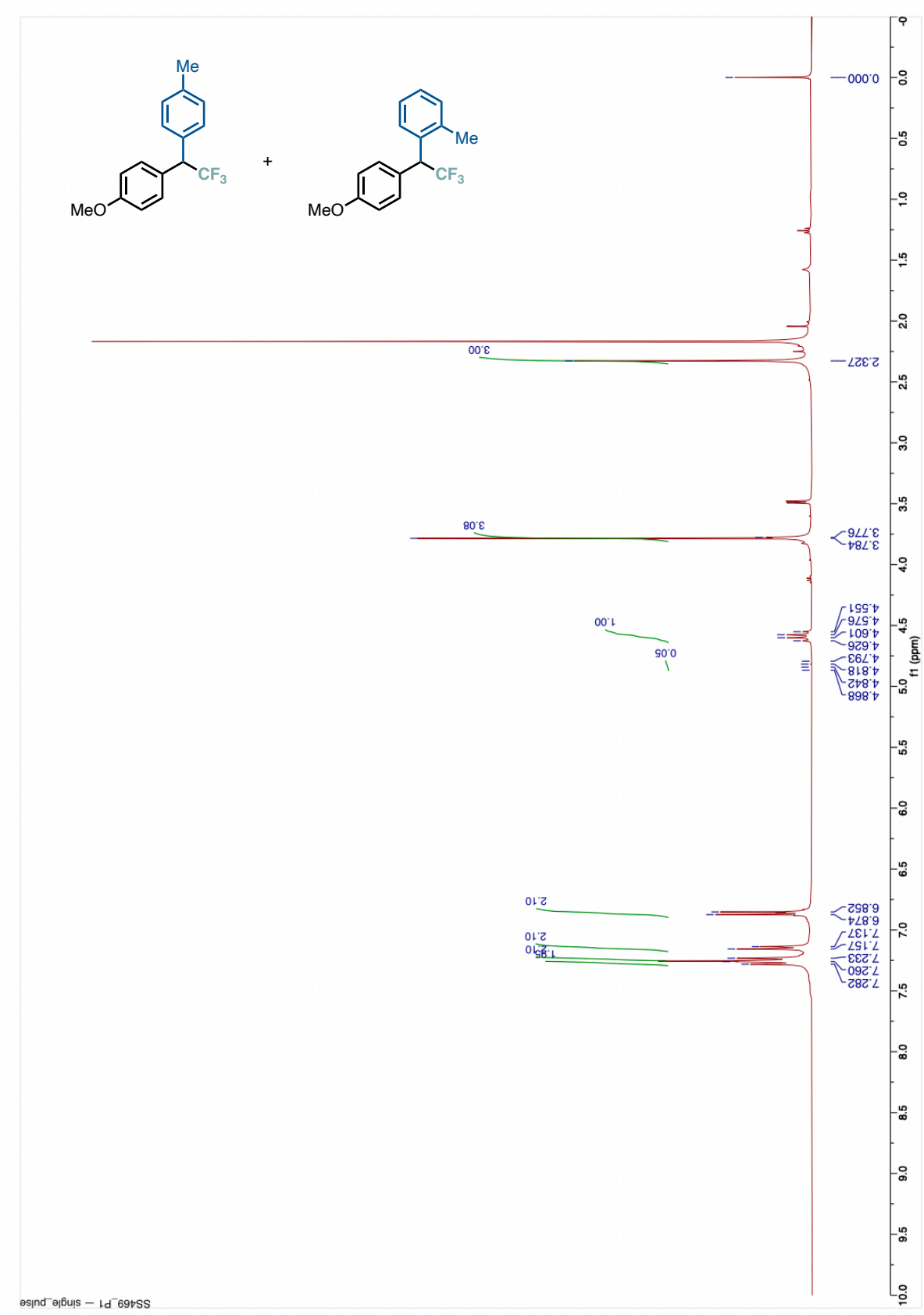
$^{13}C\{^{1}H\}$ NMR of **3U** (101 MHz, $CDCl_3$)



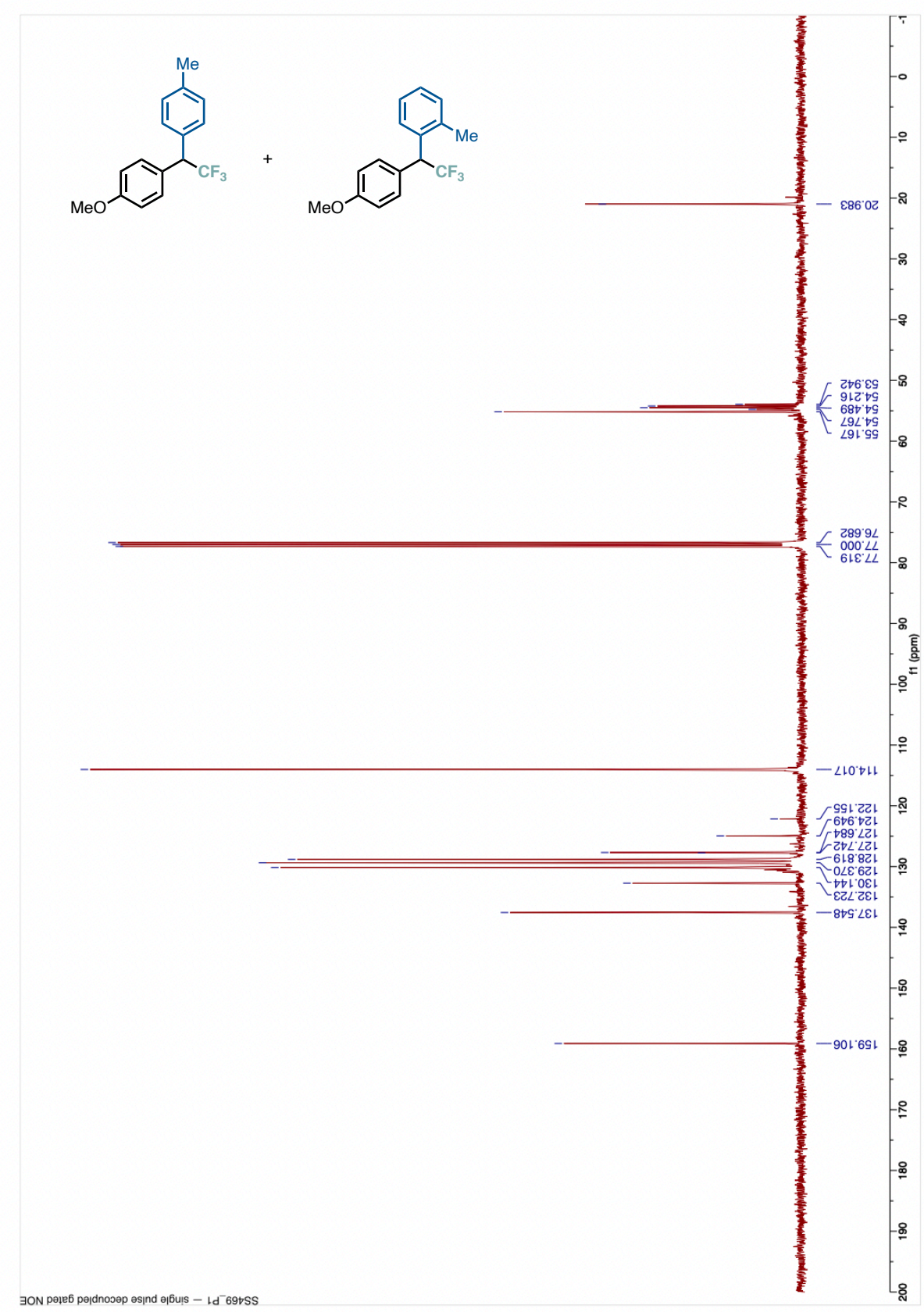
^{19}F NMR of **3U** (376 MHz, $CDCl_3$)



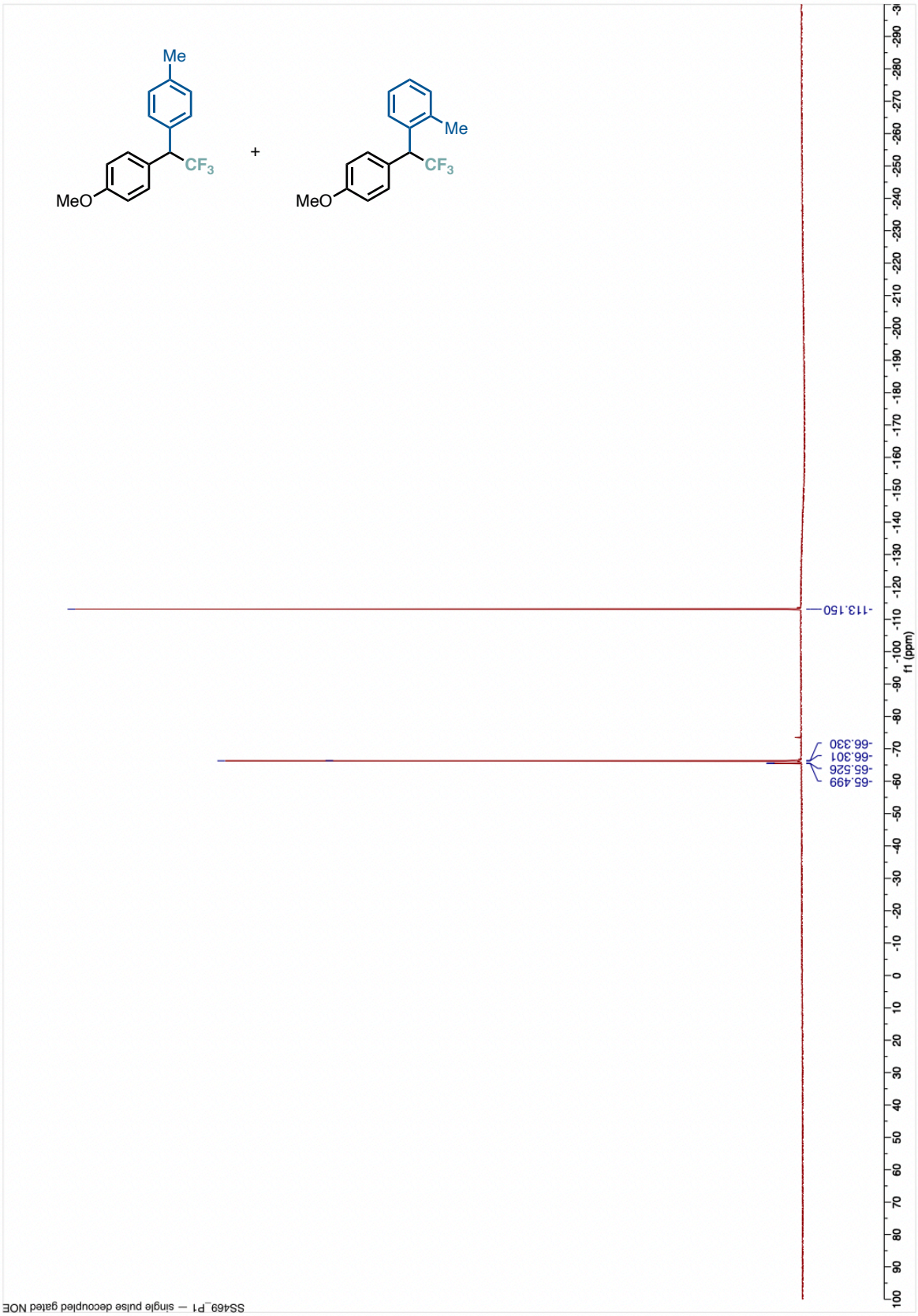
^{1}H NMR of **5A** (400 MHz, $CDCl_3$)



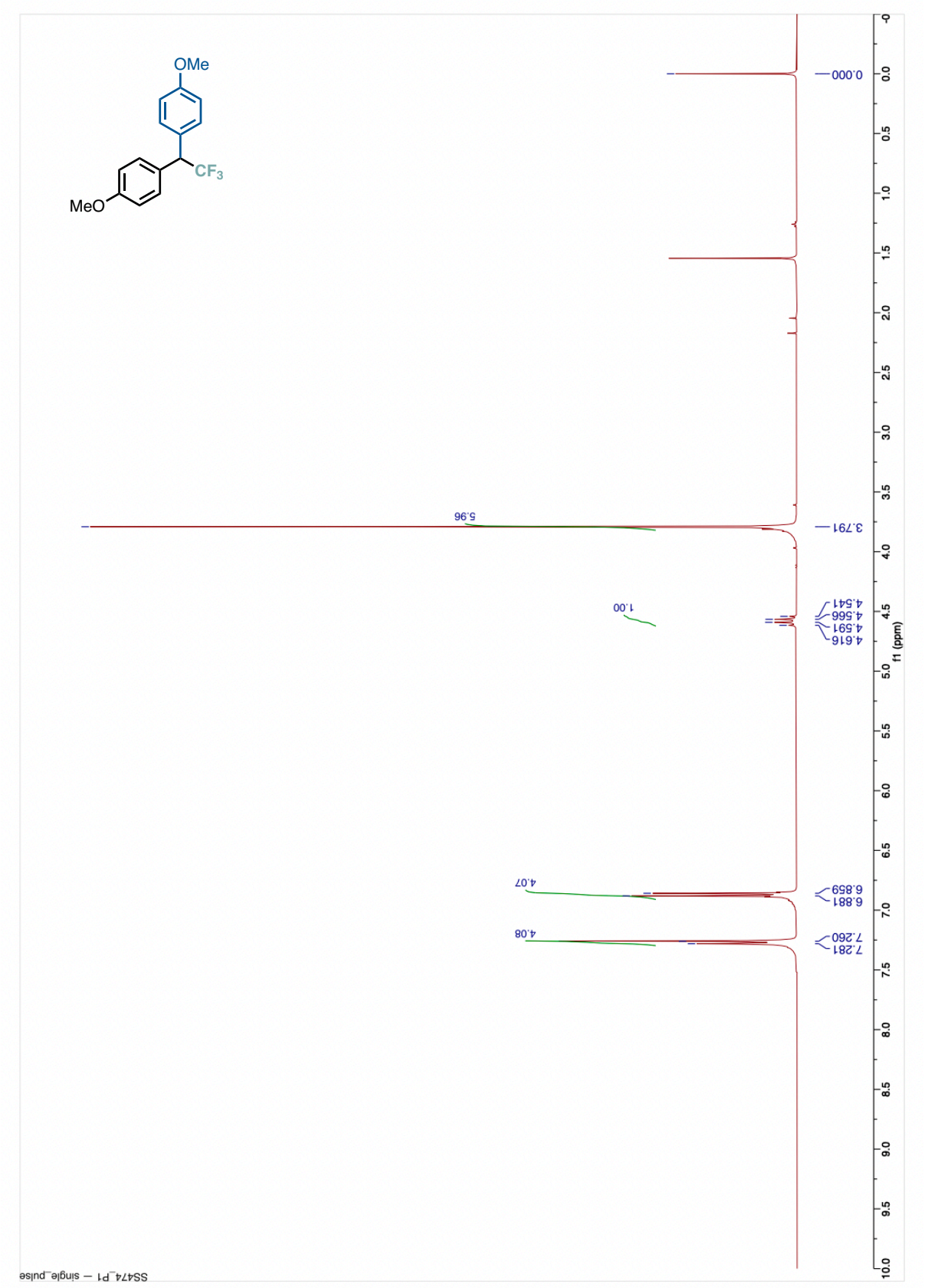
$^{13}C\{^{1}H\}$ NMR of **5A** (101 MHz, $CDCl_3$)



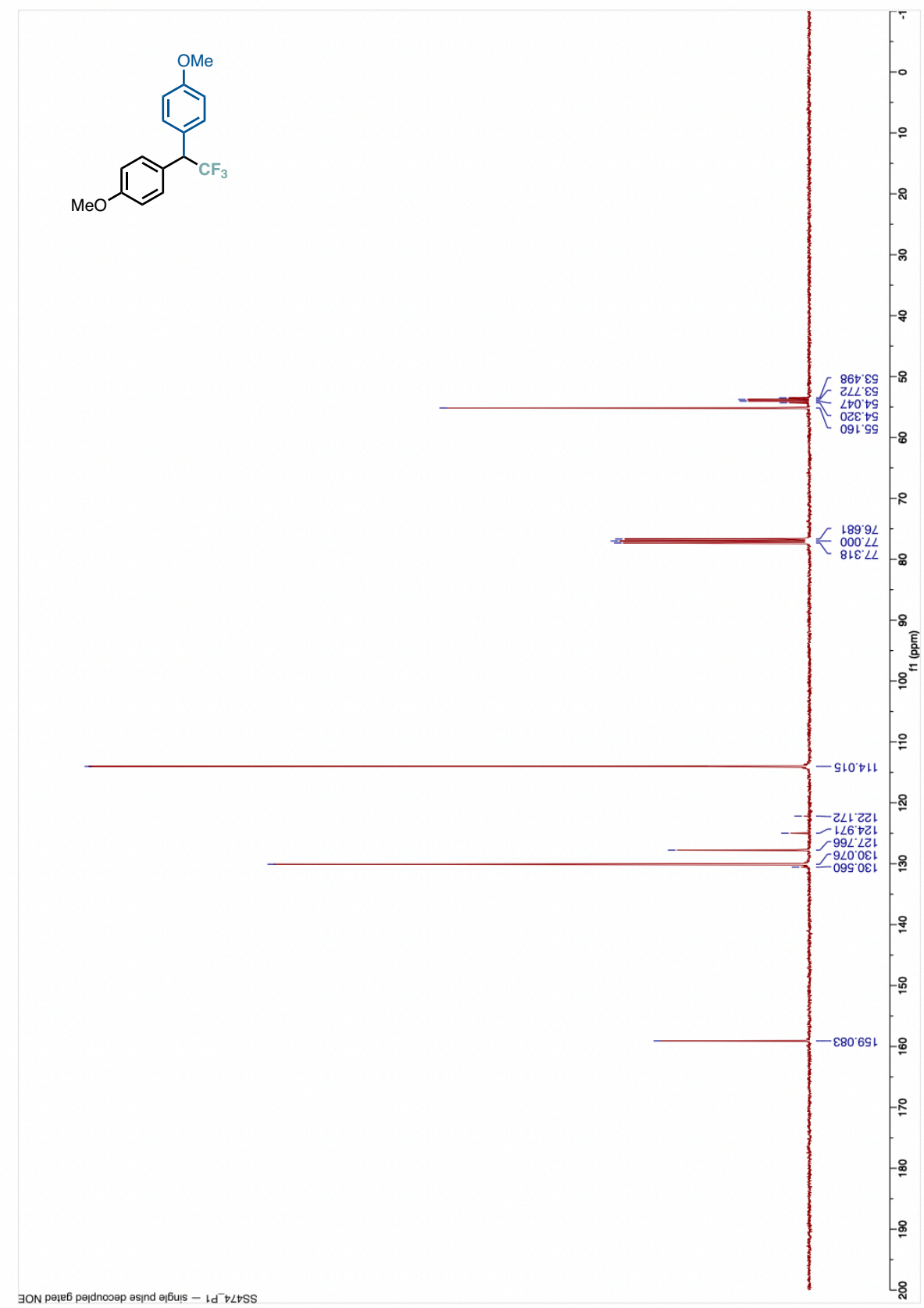
^{19}F NMR of **5A** (376 MHz, $CDCl_3$)



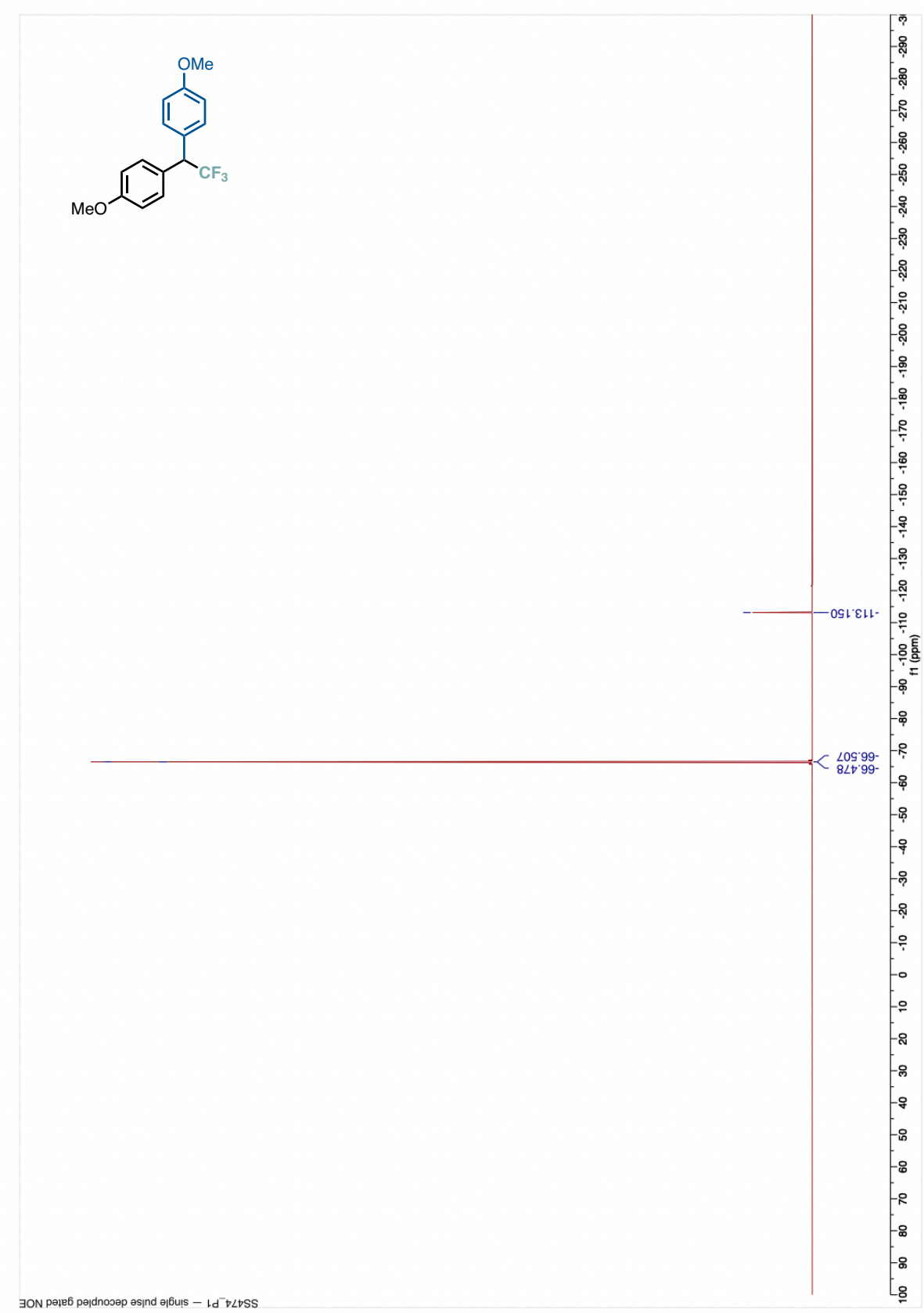
^{1}H NMR of **5B** (400 MHz, $CDCl_3$)



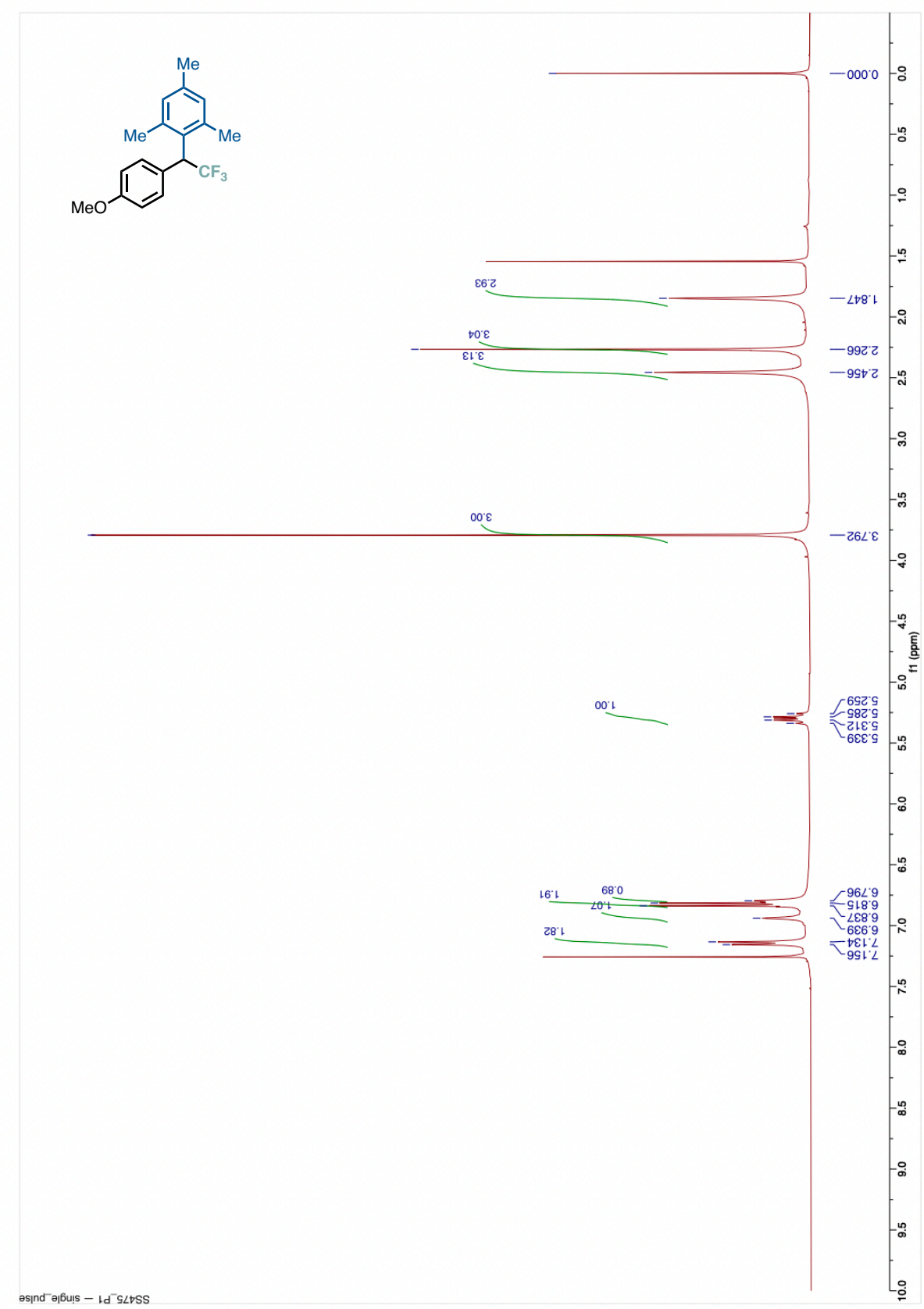
$^{13}C\{^{1}H\}$ NMR of **5B** (101 MHz, $CDCl_3$)



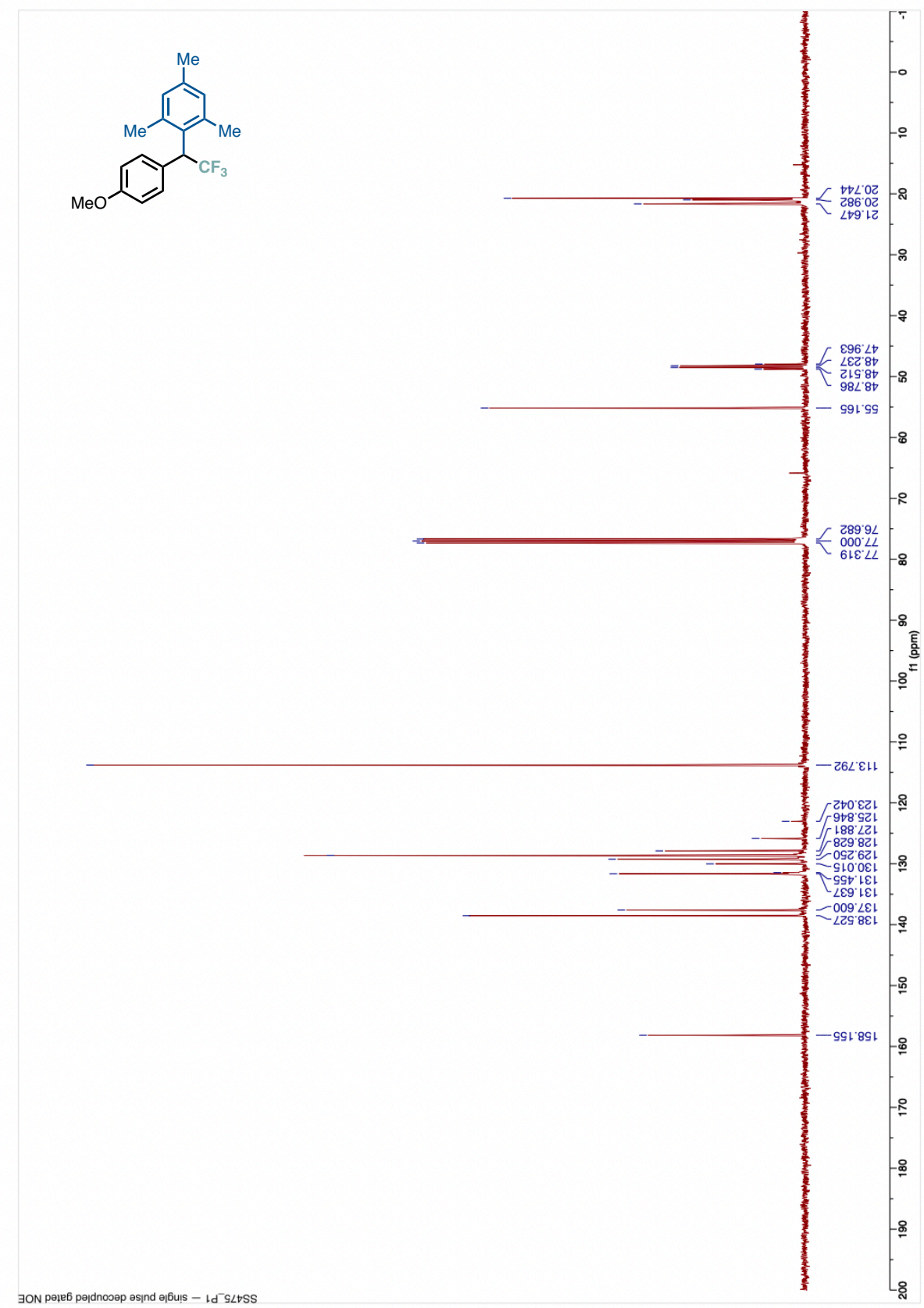
^{19}F NMR of **5B** (376 MHz, $CDCl_3$)



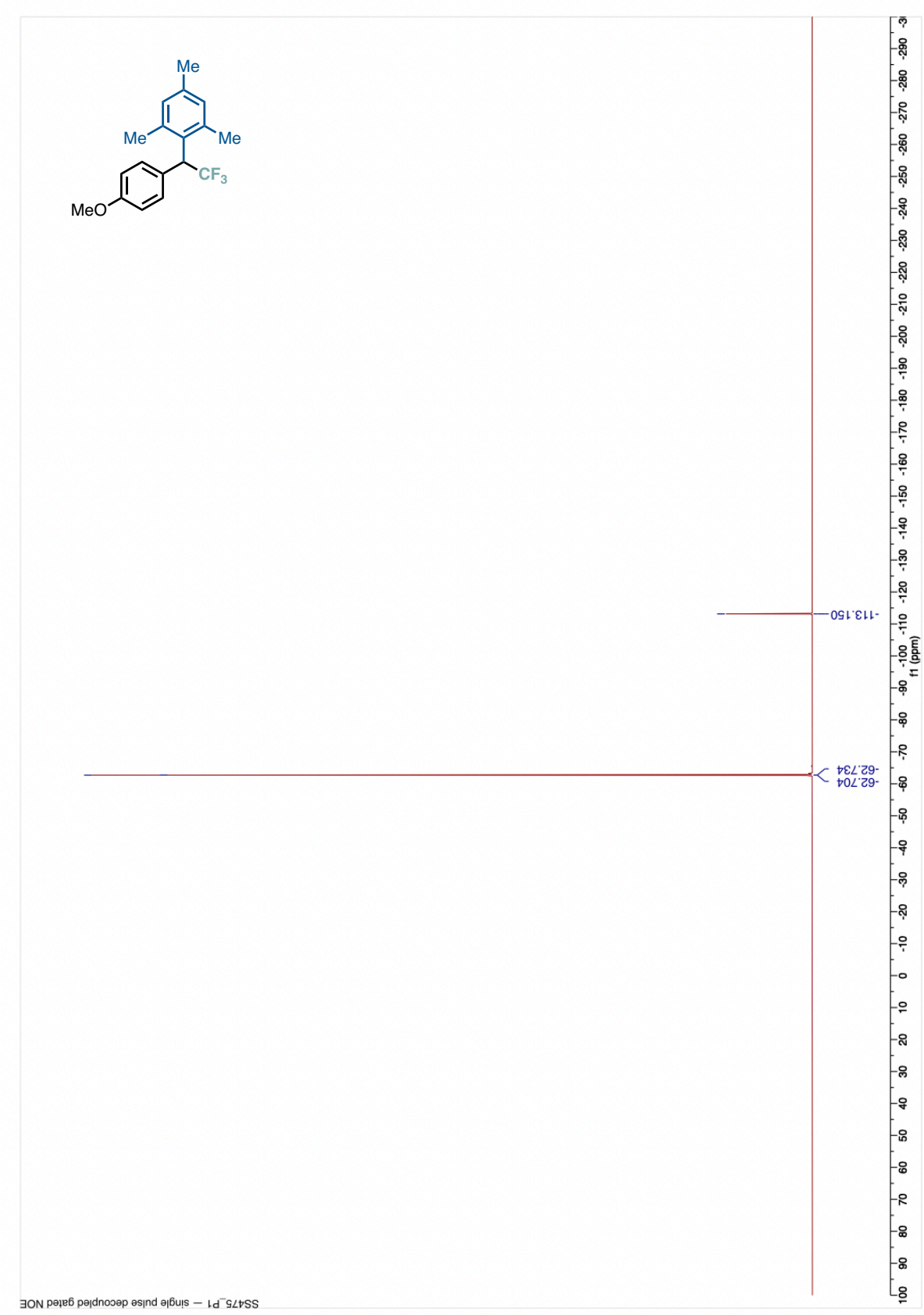
^{1}H NMR of **5C** (400 MHz, $CDCl_3$)



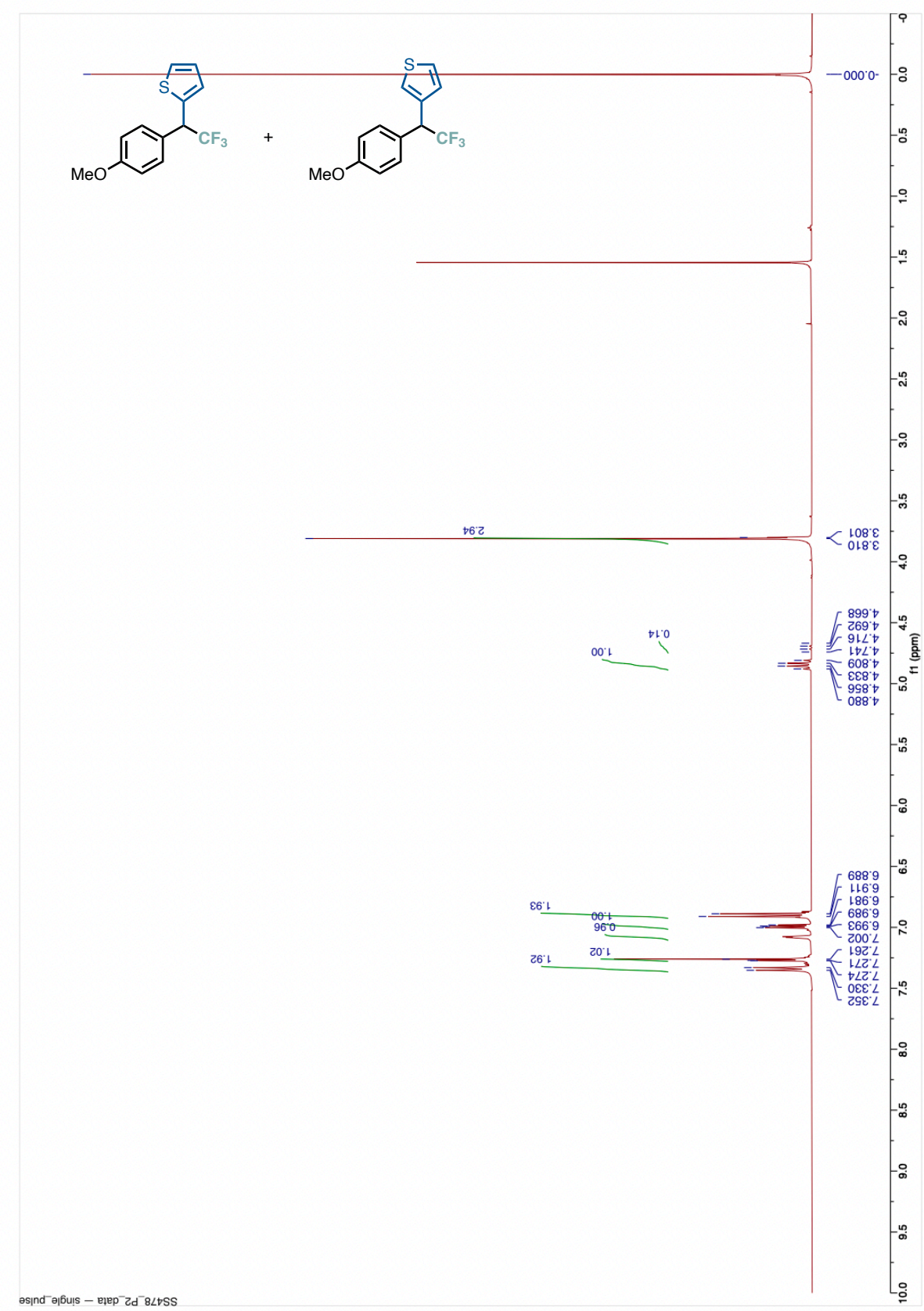
$^{13}C\{^{1}H\}$ NMR of **5C** (101 MHz, $CDCl_3$)



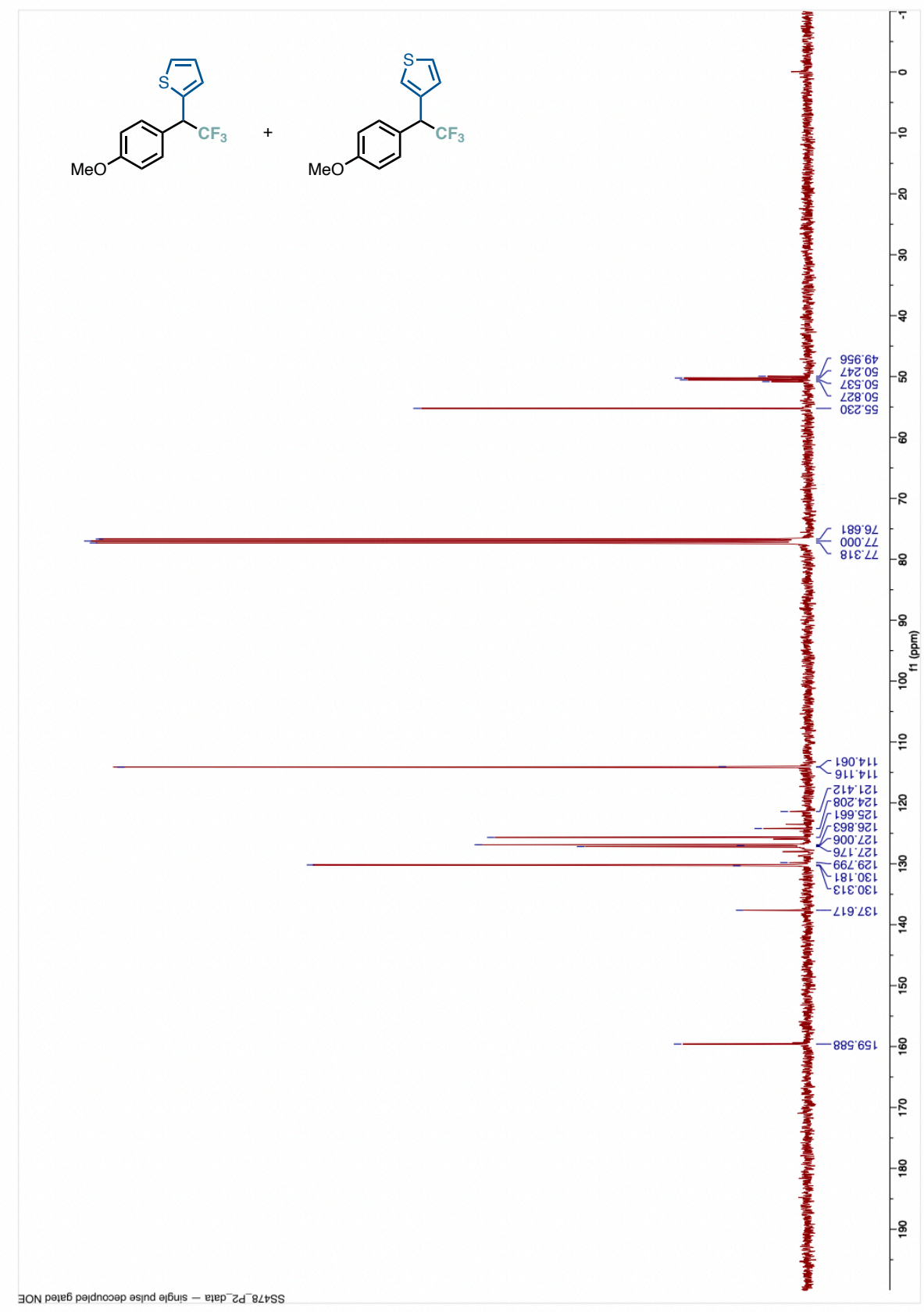
^{19}F NMR of **5C** (376 MHz, $CDCl_3$)



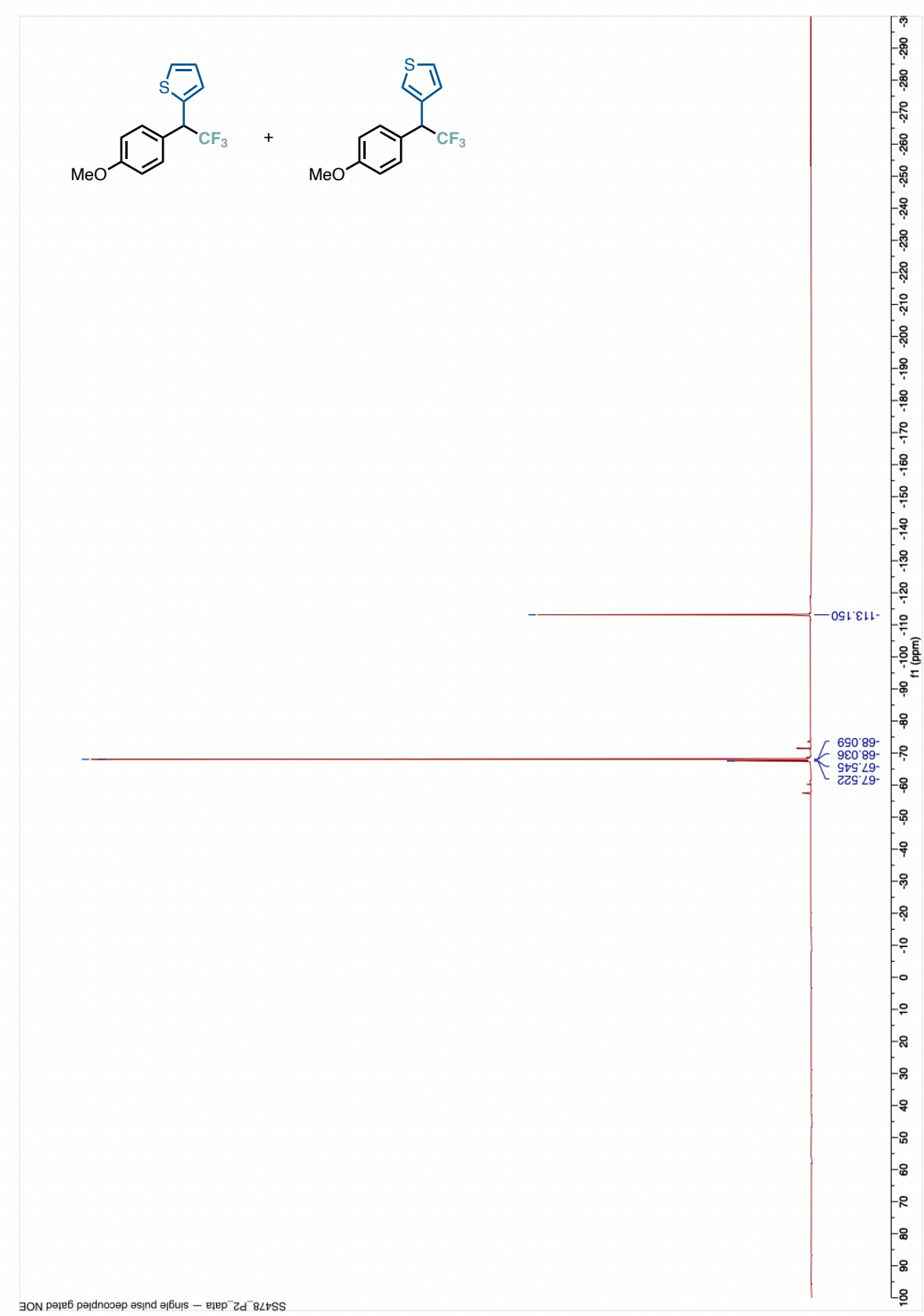
^{1}H NMR of **5D** (400 MHz, $CDCl_3$)



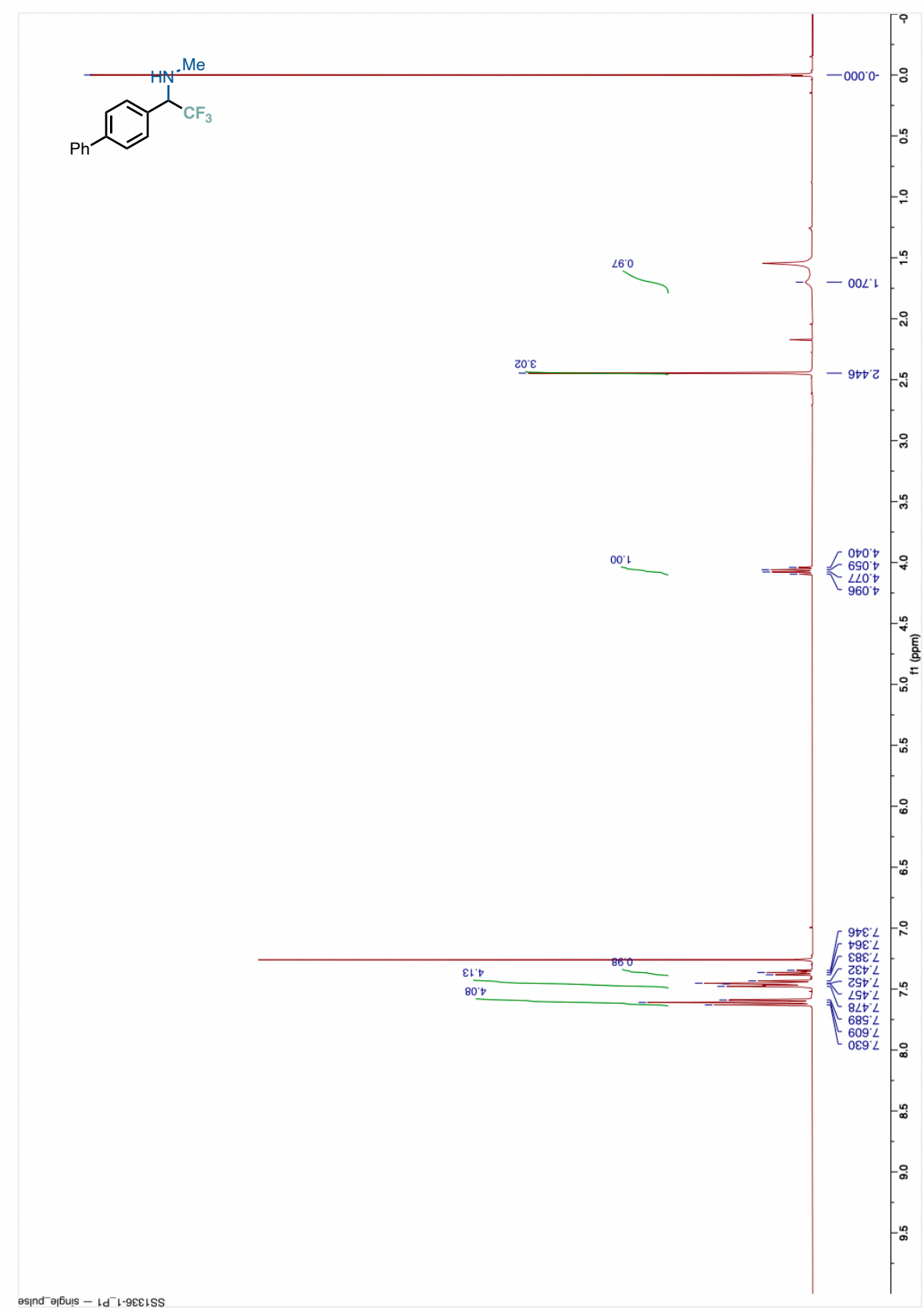
$^{13}C\{^{1}H\}$ NMR of **5D** (101 MHz, $CDCl_3$)



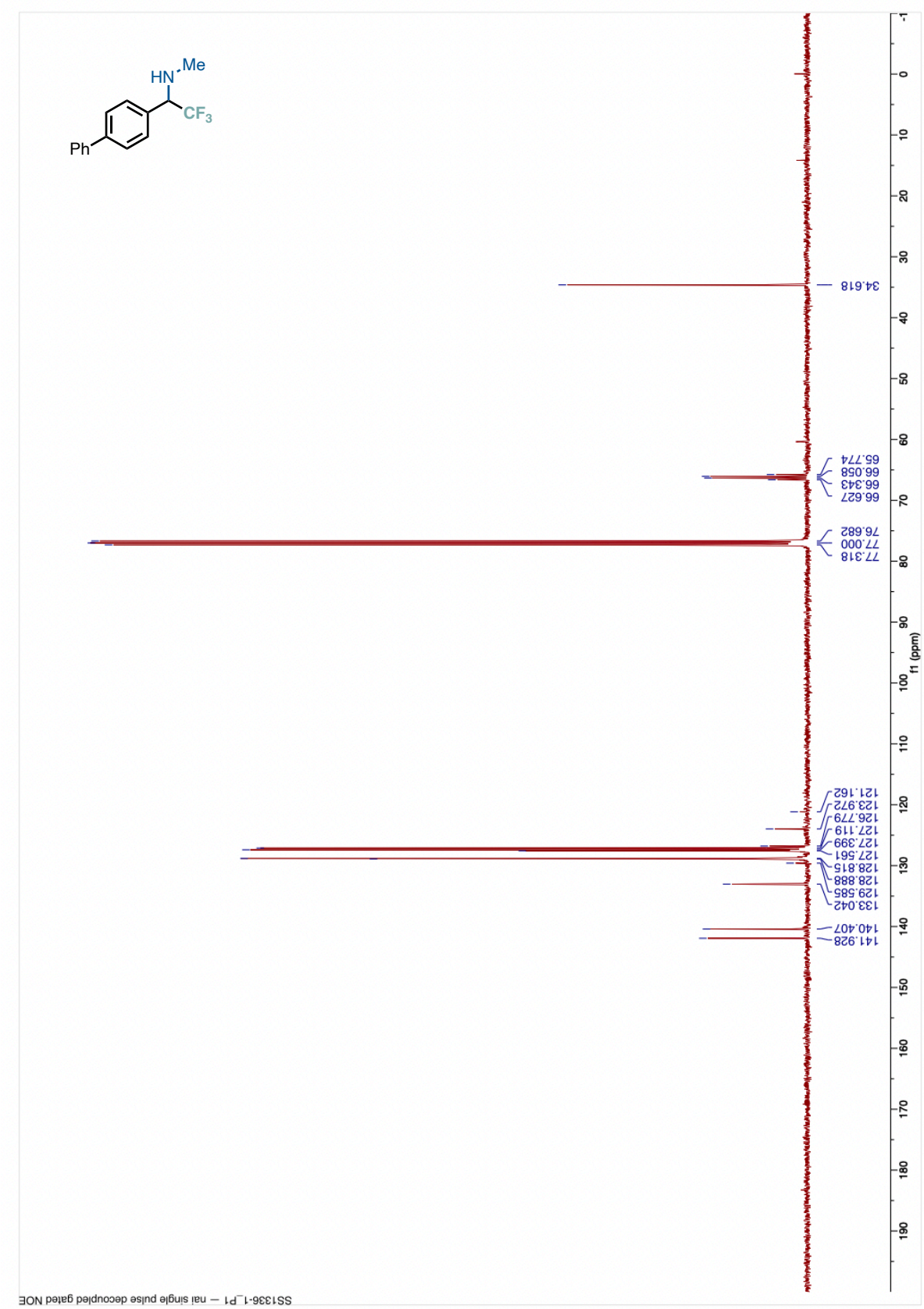
^{19}F NMR of **5D** (376 MHz, $CDCl_3$)



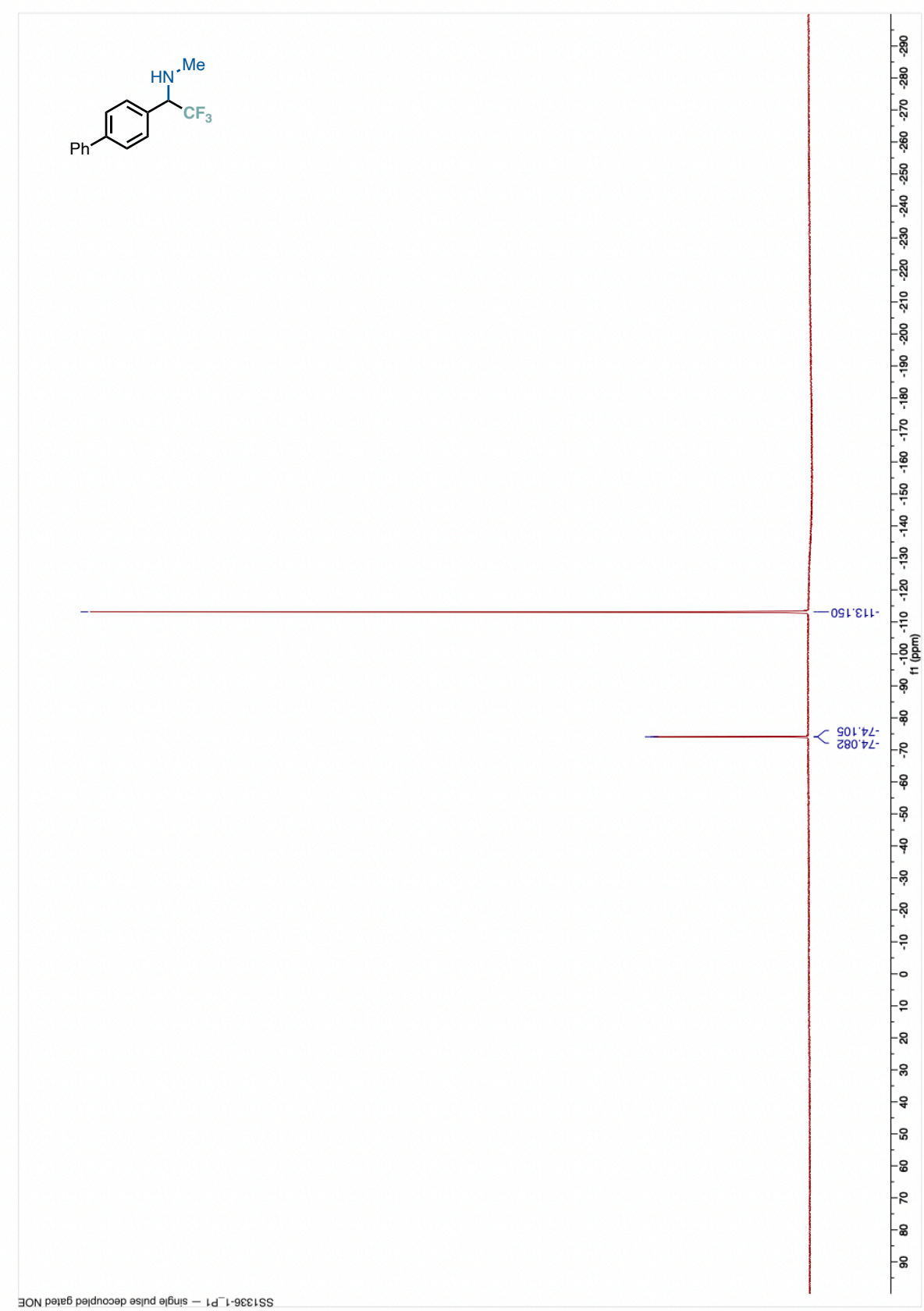
^{1}H NMR of **6** (400 MHz, $CDCl_3$)



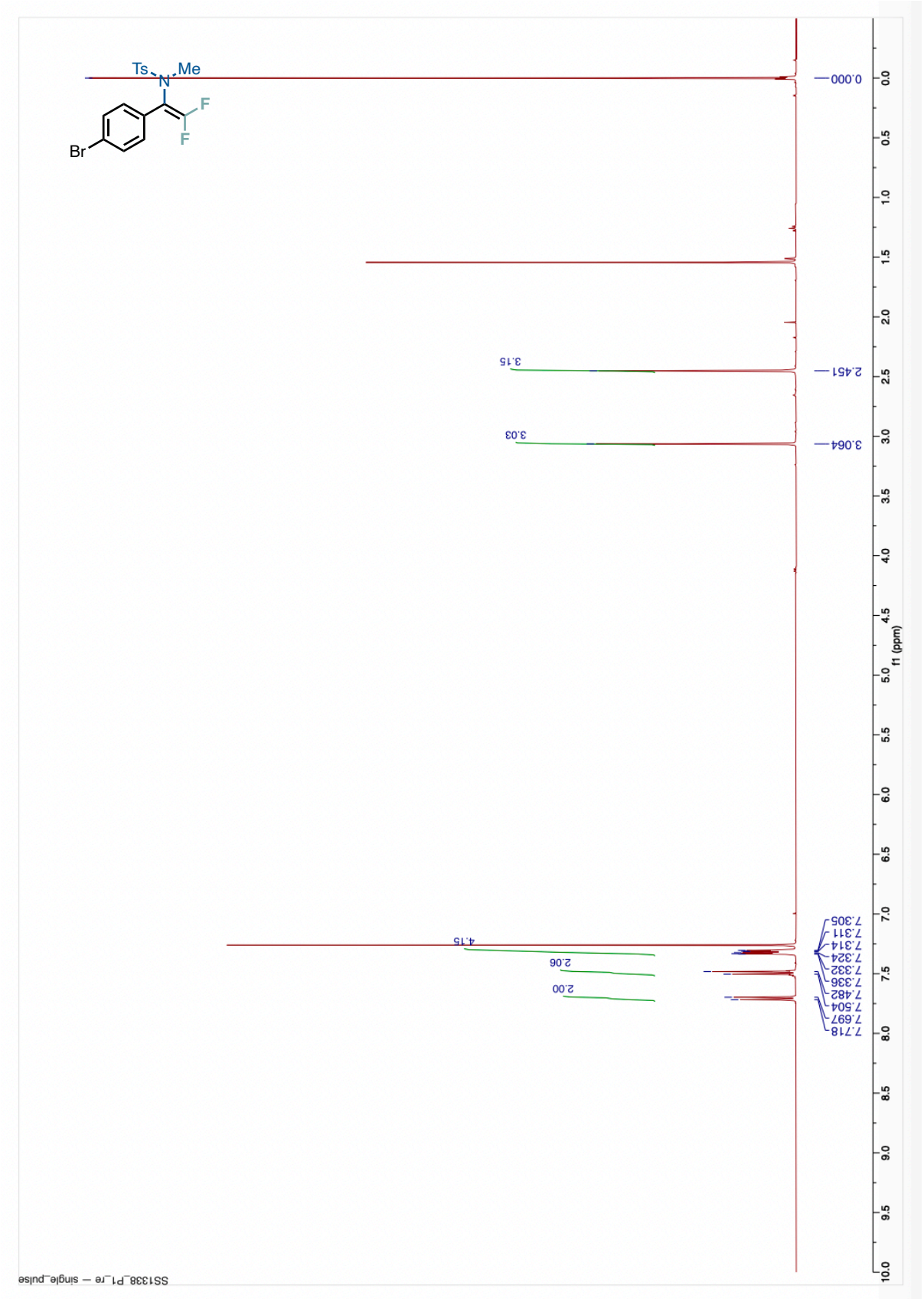
$^{13}C\{^{1}H\}$ NMR of **6** (101 MHz, $CDCl_3$)



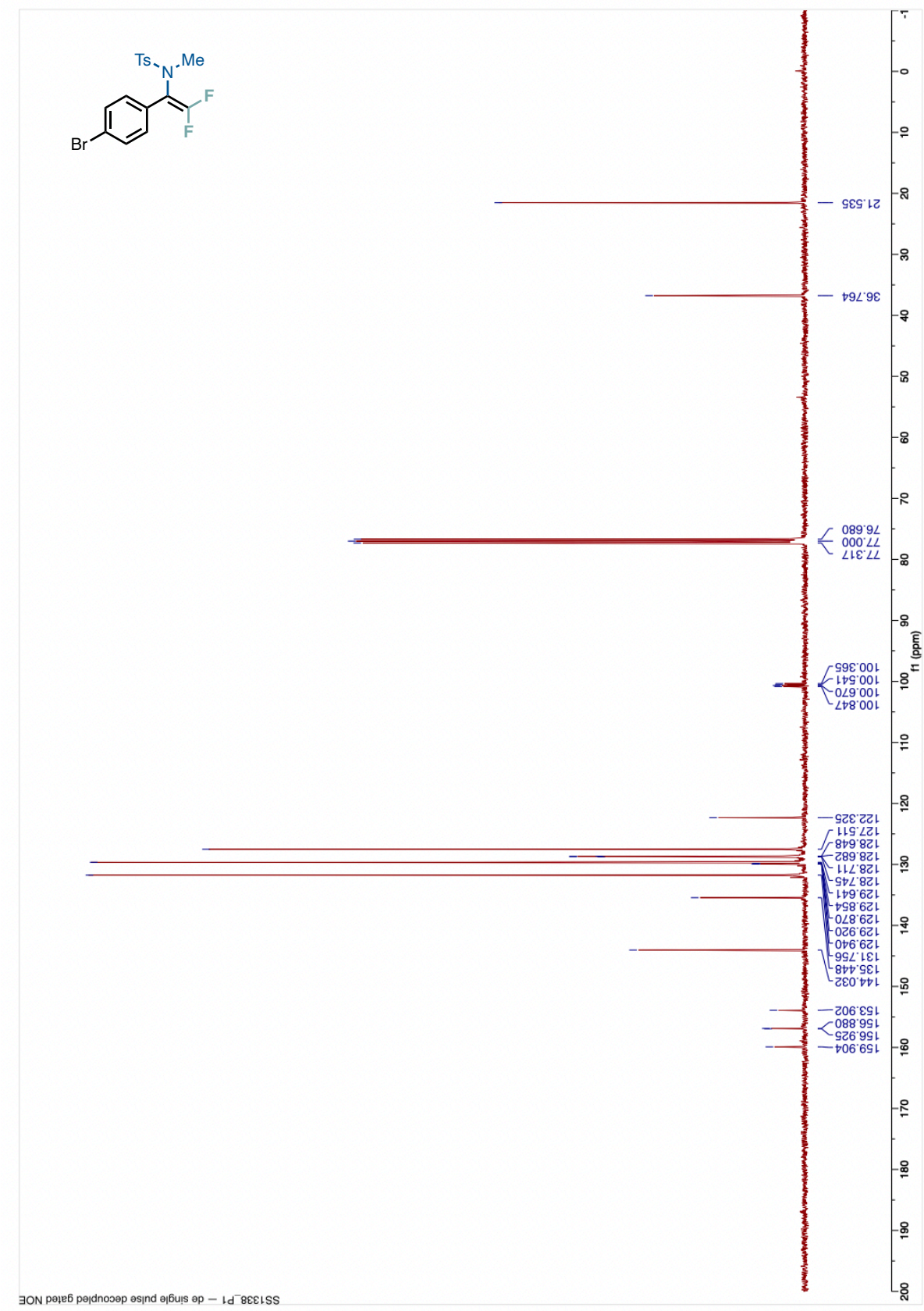
^{19}F NMR of **6** (376 MHz, $CDCl_3$)



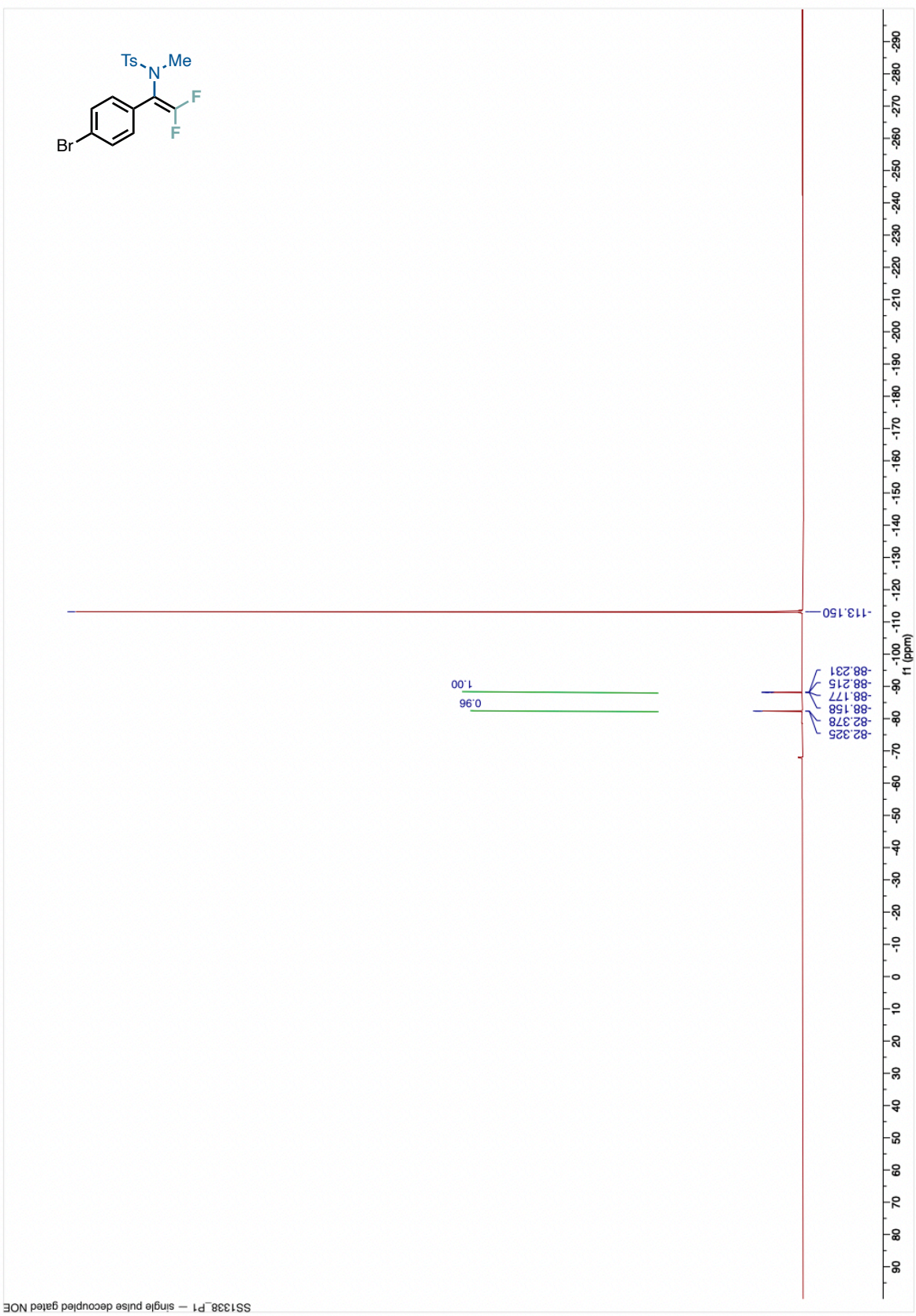
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



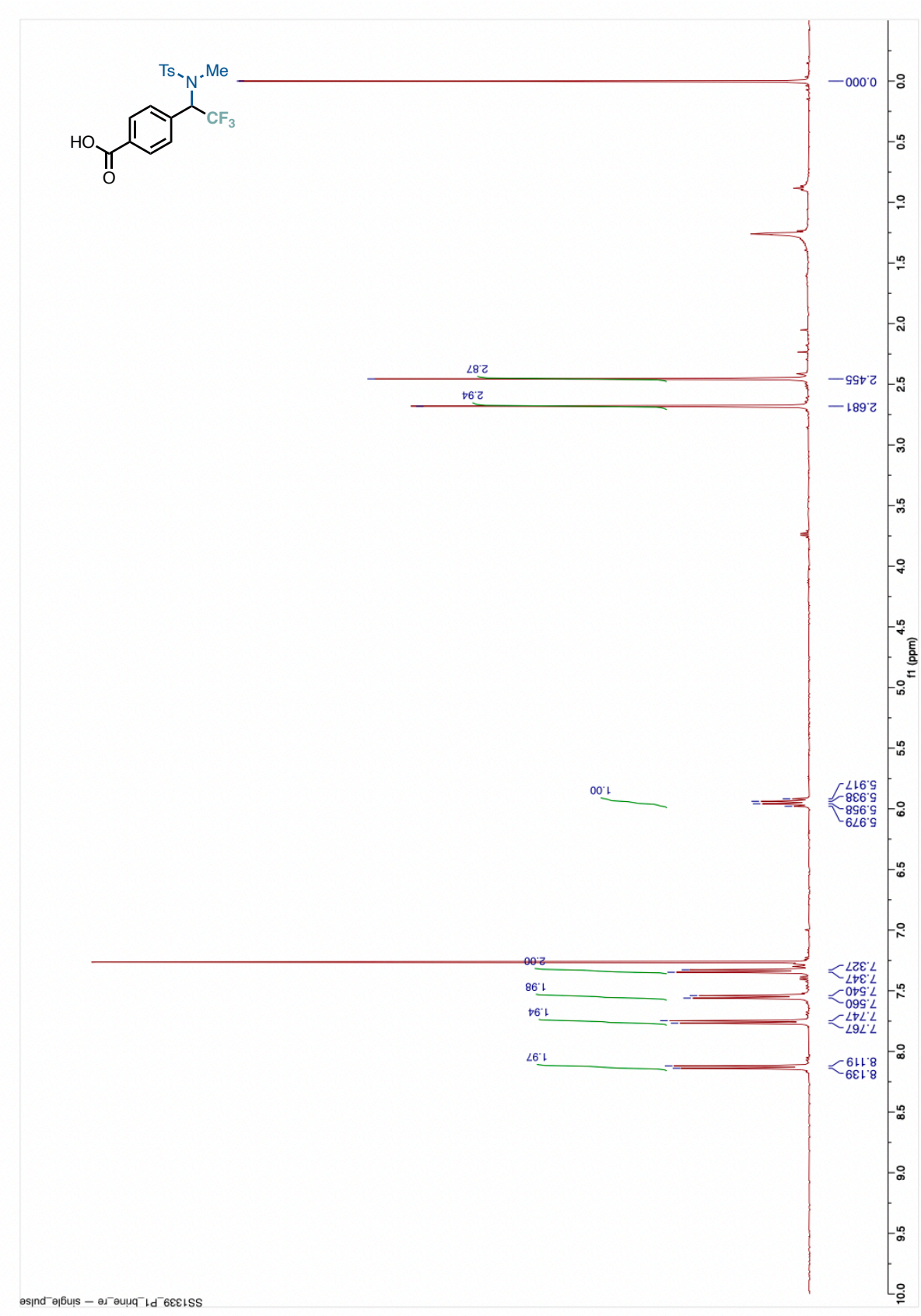
$^{13}C\{^{1}H\}$ NMR of **7** (101 MHz, $CDCl_3$)



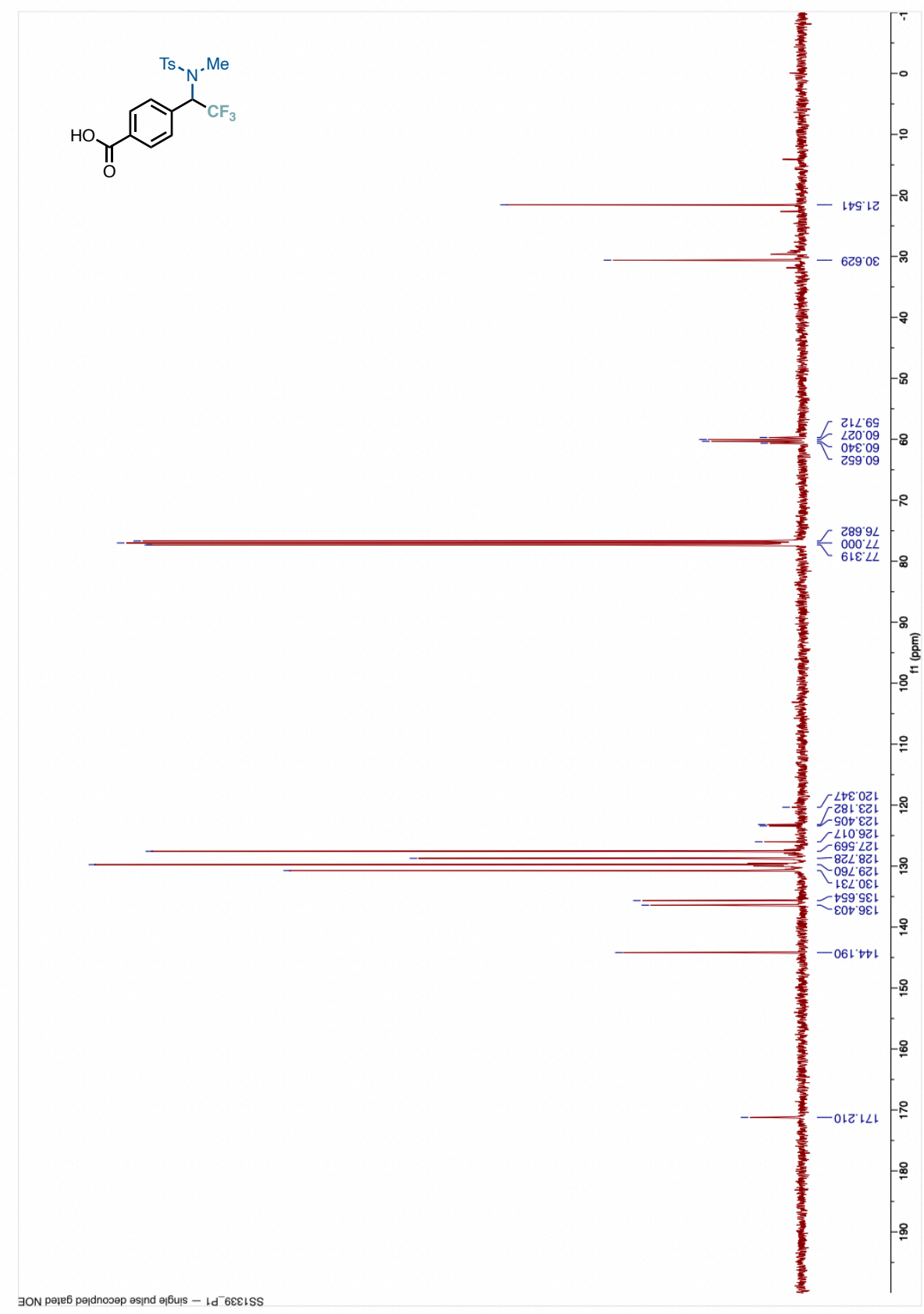
^{19}F NMR of **7** (376 MHz, $CDCl_3$)



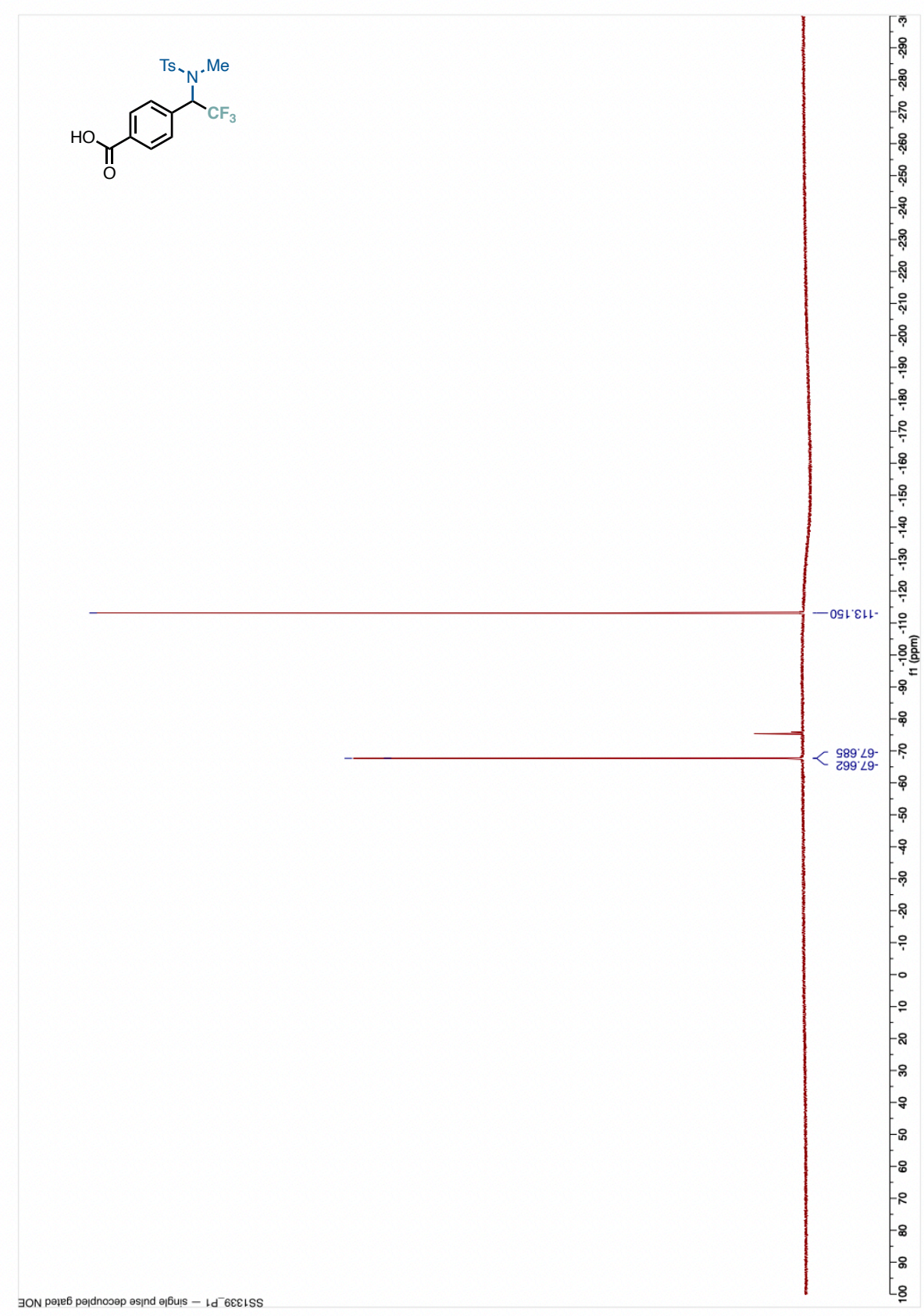
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



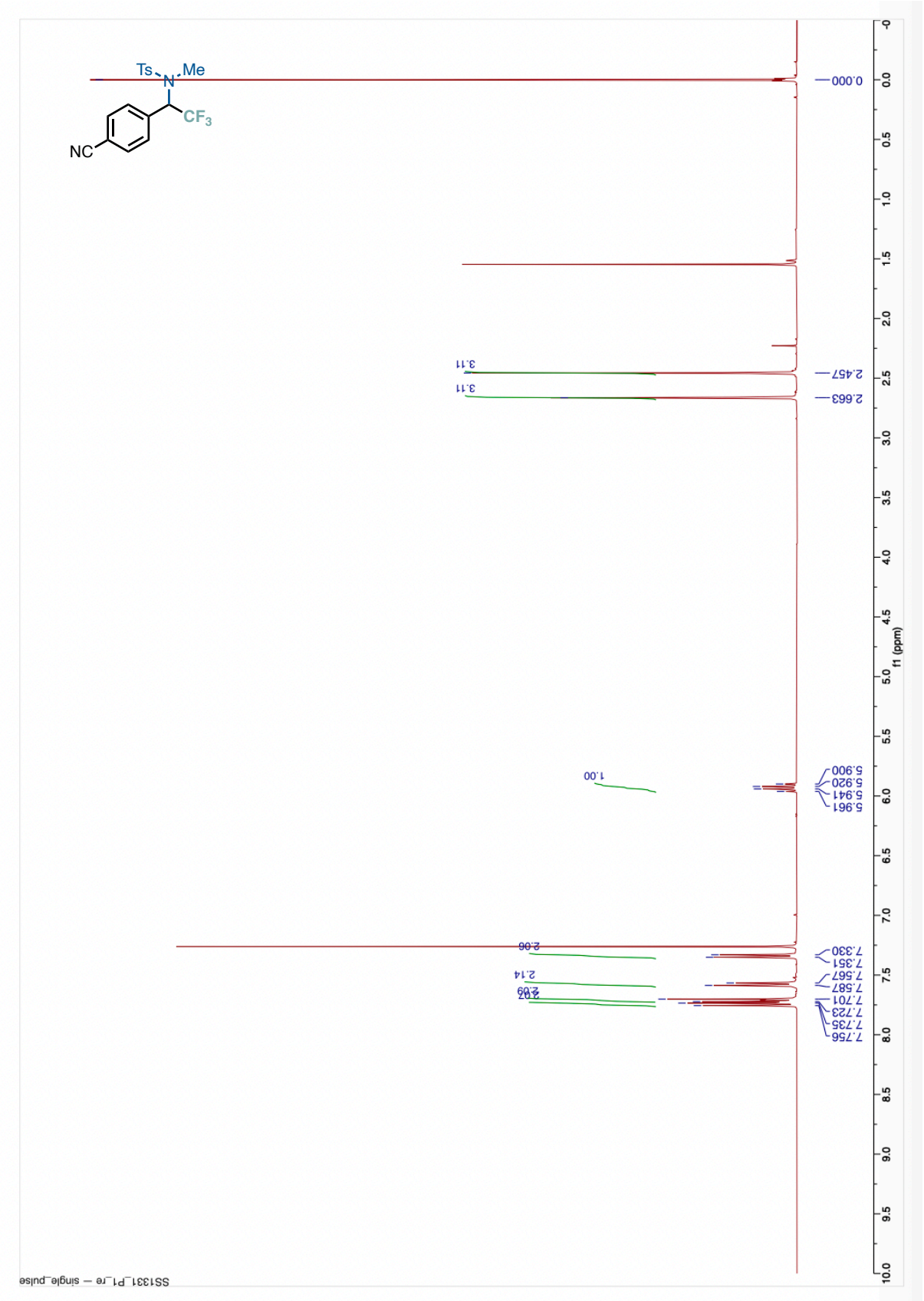
$^{13}C\{^{1}H\}$ NMR of **8** (101 MHz, $CDCl_3$)



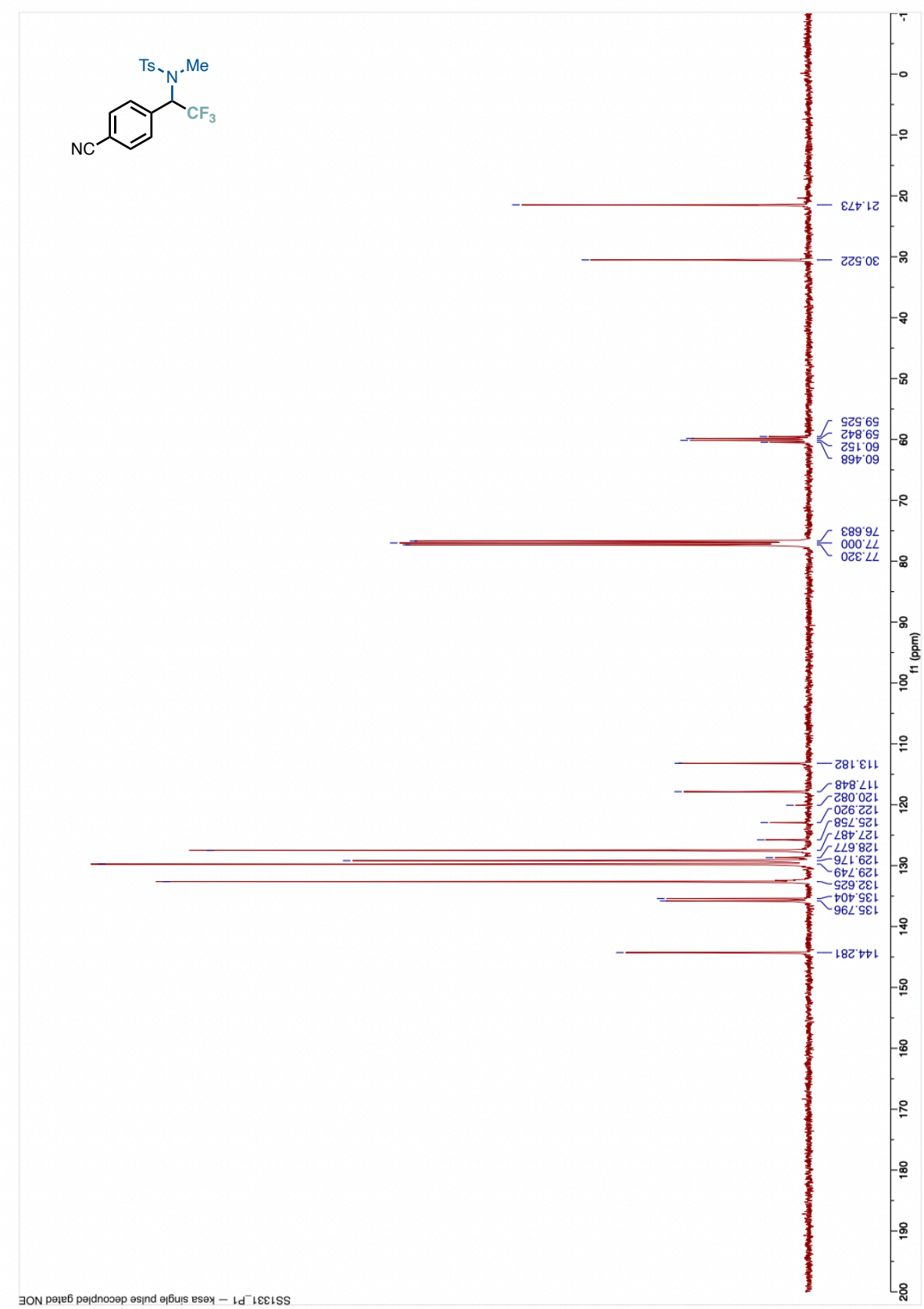
^{19}F NMR of **8** (376 MHz, $CDCl_3$)



^{1}H NMR of **9** (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR of **9** (101 MHz, $CDCl_3$)



^{19}F NMR of **9** (376 MHz, $CDCl_3$)