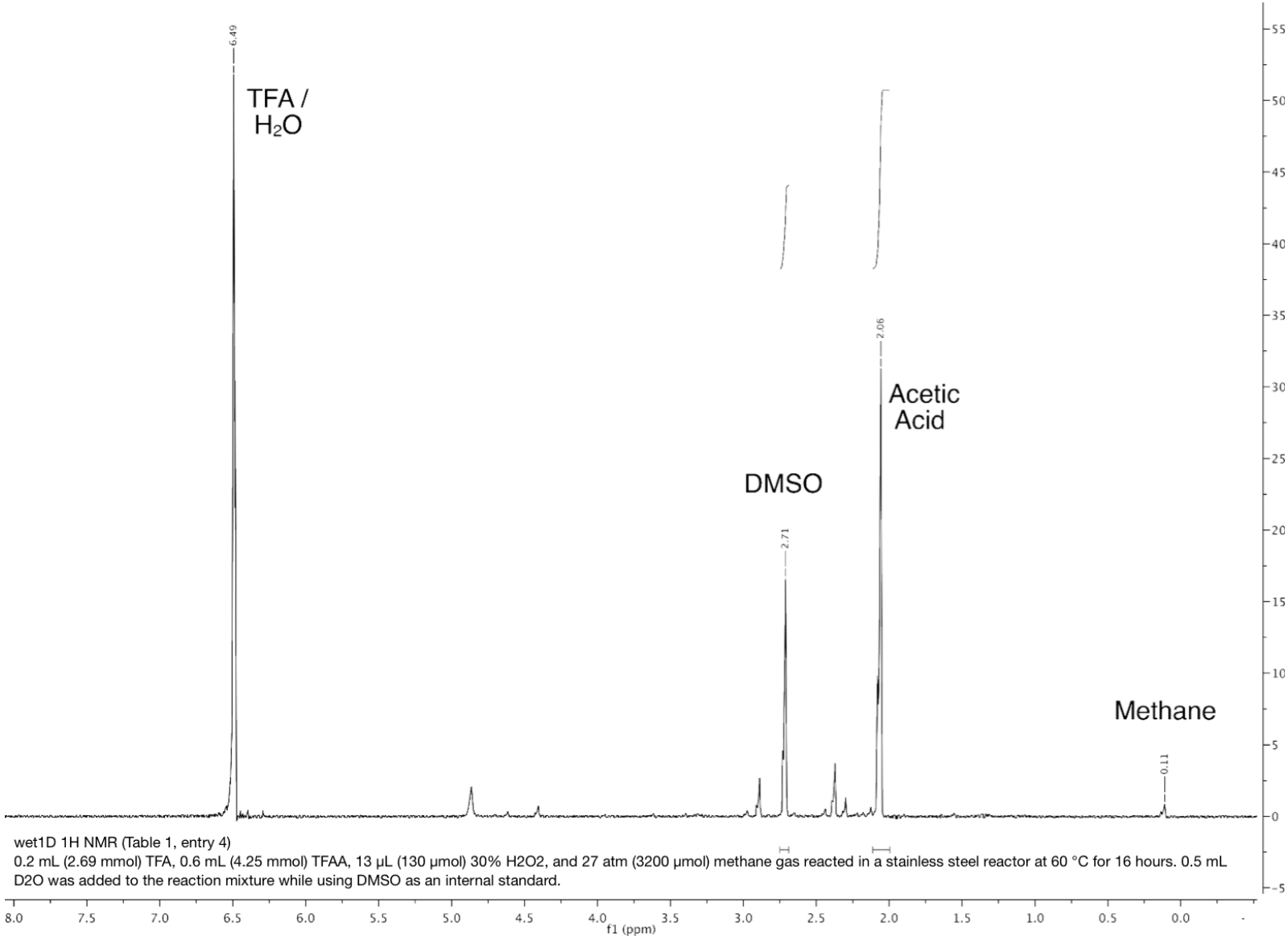
An Unexpected, Latent Radical Reaction of Methane Propagated by Trifluoromethyl Radicals

Supporting Information

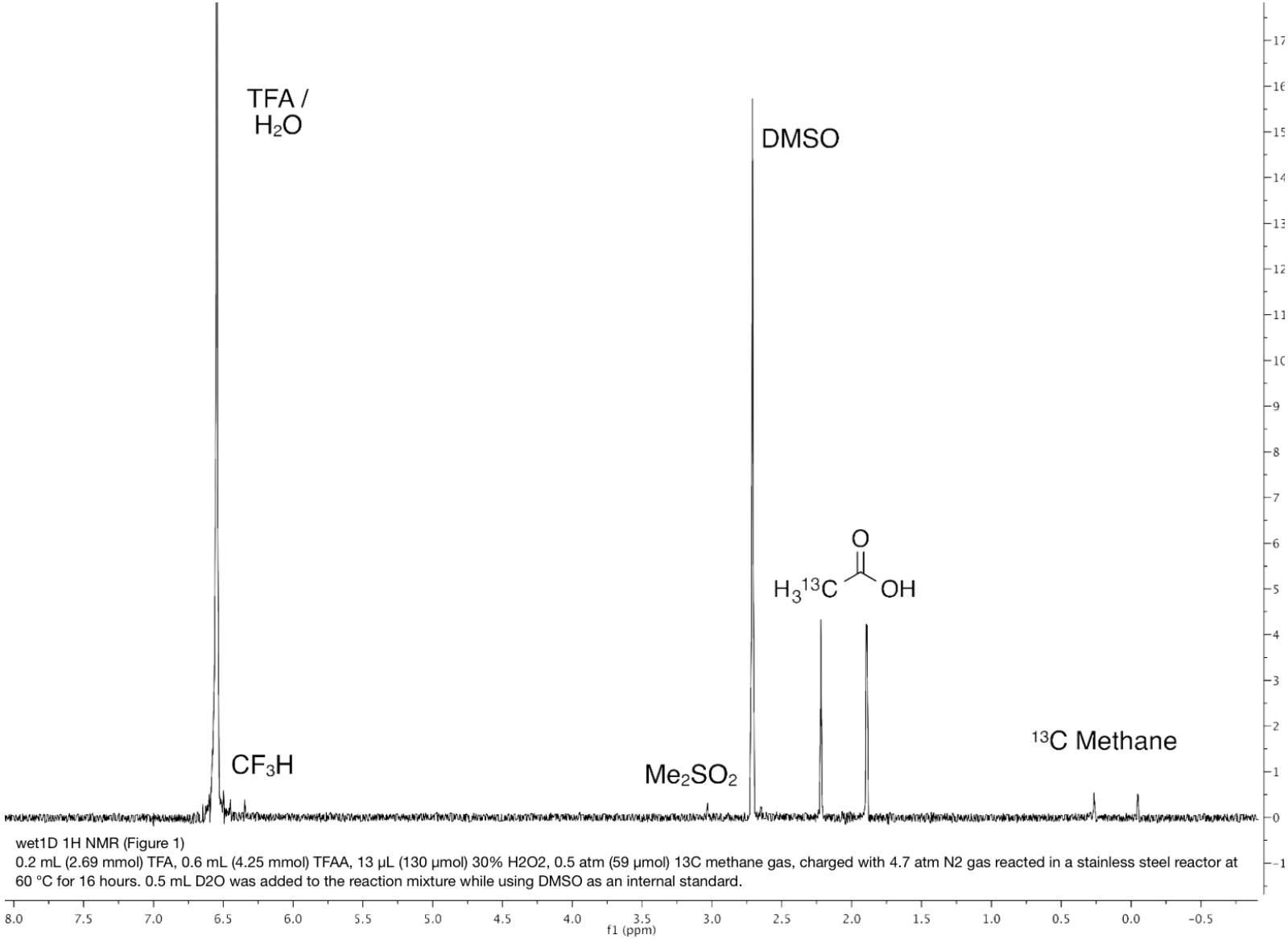
Nima Zargari, Pierre Winter, Yong Liang, Joo Ho Lee, Andrew Cooksy,* K. N. Houk,* and Kyung Woon Jung*

TABLE OF CONTENTS

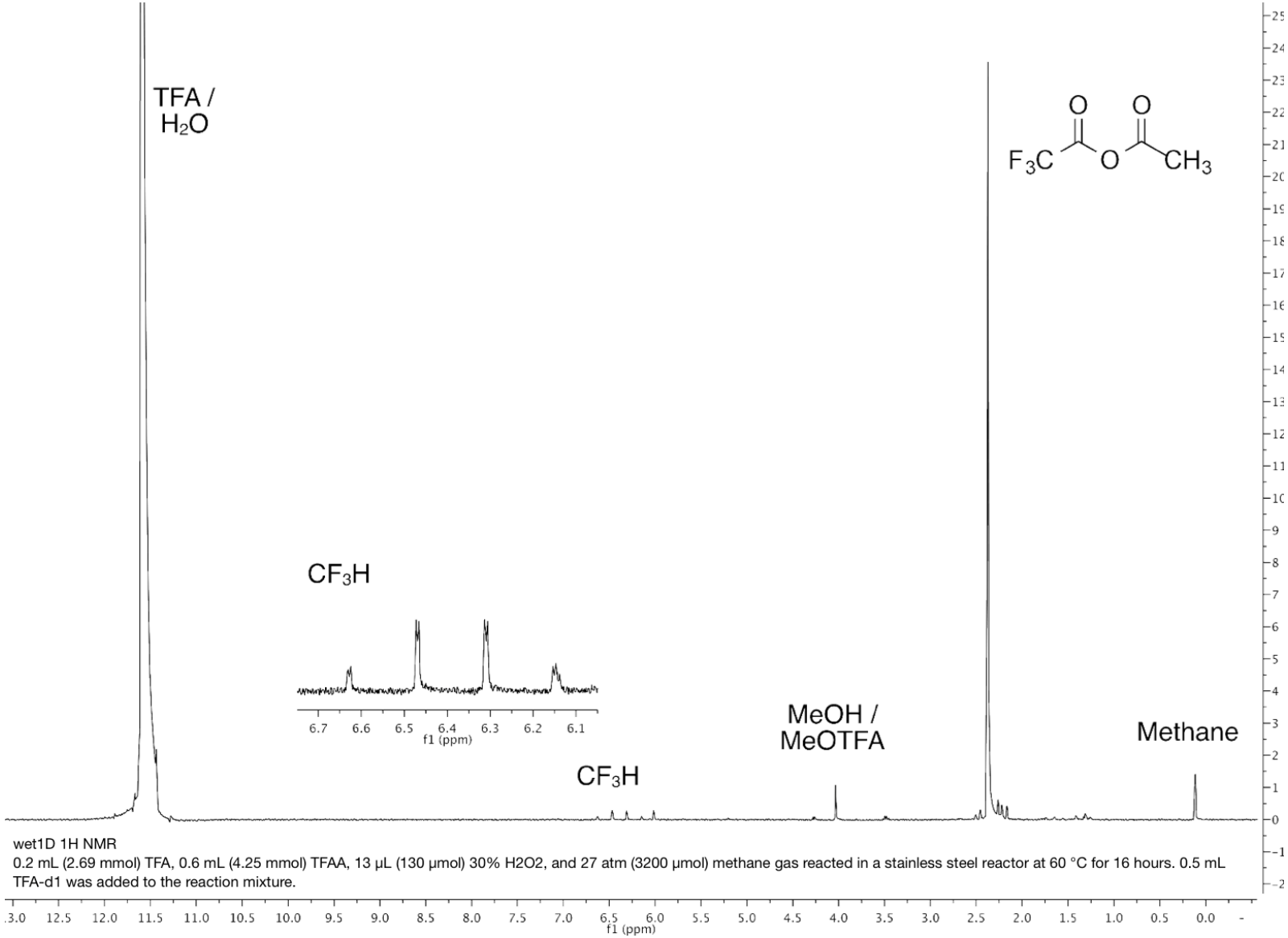
wet1D ^{1}H NMR Spectra, ^{12}C CH_4, D_2O workup (Table 1, entry 4)……..…….. 1
wet1D ^{1}H NMR Spectra, ^{13}C CH_4, D_2O workup (Figure 1)……..……..…….. 2
wet1D ^{1}H NMR Spectra, ^{12}C CH_4, TFA-d_1 workup……....…….. 3
^{13}C NMR Spectra, ^{13}C CH_4, D_2O workup (Figure 2)…….……..... 4
^{13}C NMR Spectra, ^{12}C CH_4, TFA-d_1 workup……..……..…...…….. 5
^{19}F NMR Spectra, TFA-d_1 workup……...……...…….….. 6
wet1D ^{1}H NMR Spectra (Table 2, entry 2)……..……..…….……... 7
wet1D ^{1}H NMR Spectra (Table 2, entry 3)……..……..……..…….…….. 8
wet1D ^{1}H NMR Spectra (Table 2, entry 4)……...……..…….....……... 9
wet1D ^{1}H NMR Spectra (Table 2, entry 5)…….……..…….....…….. 10
wet1D ^{1}H NMR Spectra (Table 3, entry 1)…….……..……..…….. 11
wet1D ^{1}H NMR Spectra (Table 3, entry 3)…….…….. 12
wet1D ^{1}H NMR Spectra (Table 4, entry 1)……...……..…….. 13
wet1D ^{1}H NMR Spectra (Table 4, entry 2)…….……...…….. 14
wet1D ^{1}H NMR Spectra (Table 4, entry 3)…….……..……..…….. 15
wet1D ^{1}H NMR Spectra (Table 4, entry 4)…….……..……..….. 16
Gas Chromotography……..……..……... 17
CO_2/ CO Incorporation Data …….……..……... 18
Density Functional Theory Calculations Supplemental Information……... 19



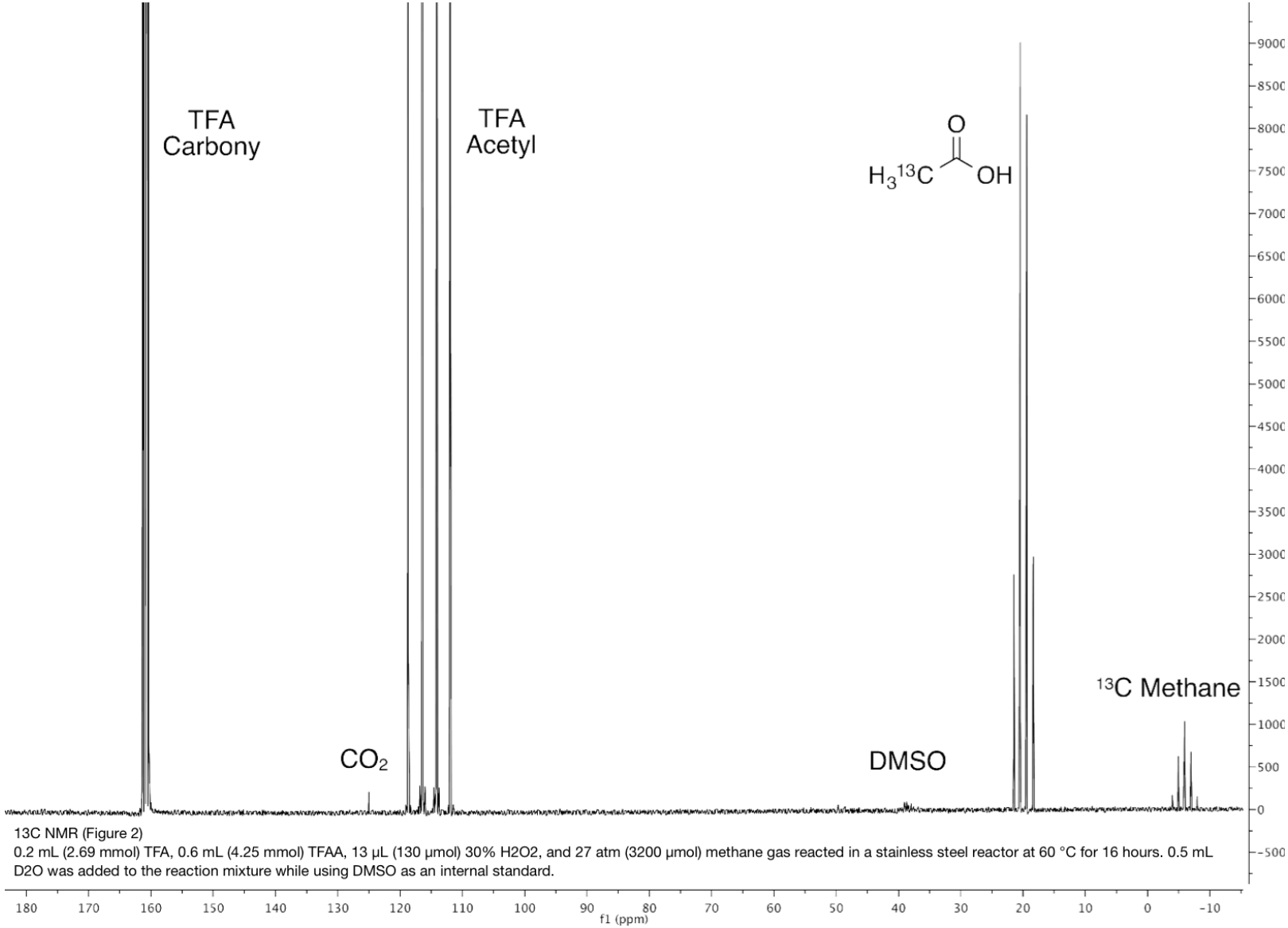
wet1D 1H NMR (Table 1, entry 4)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



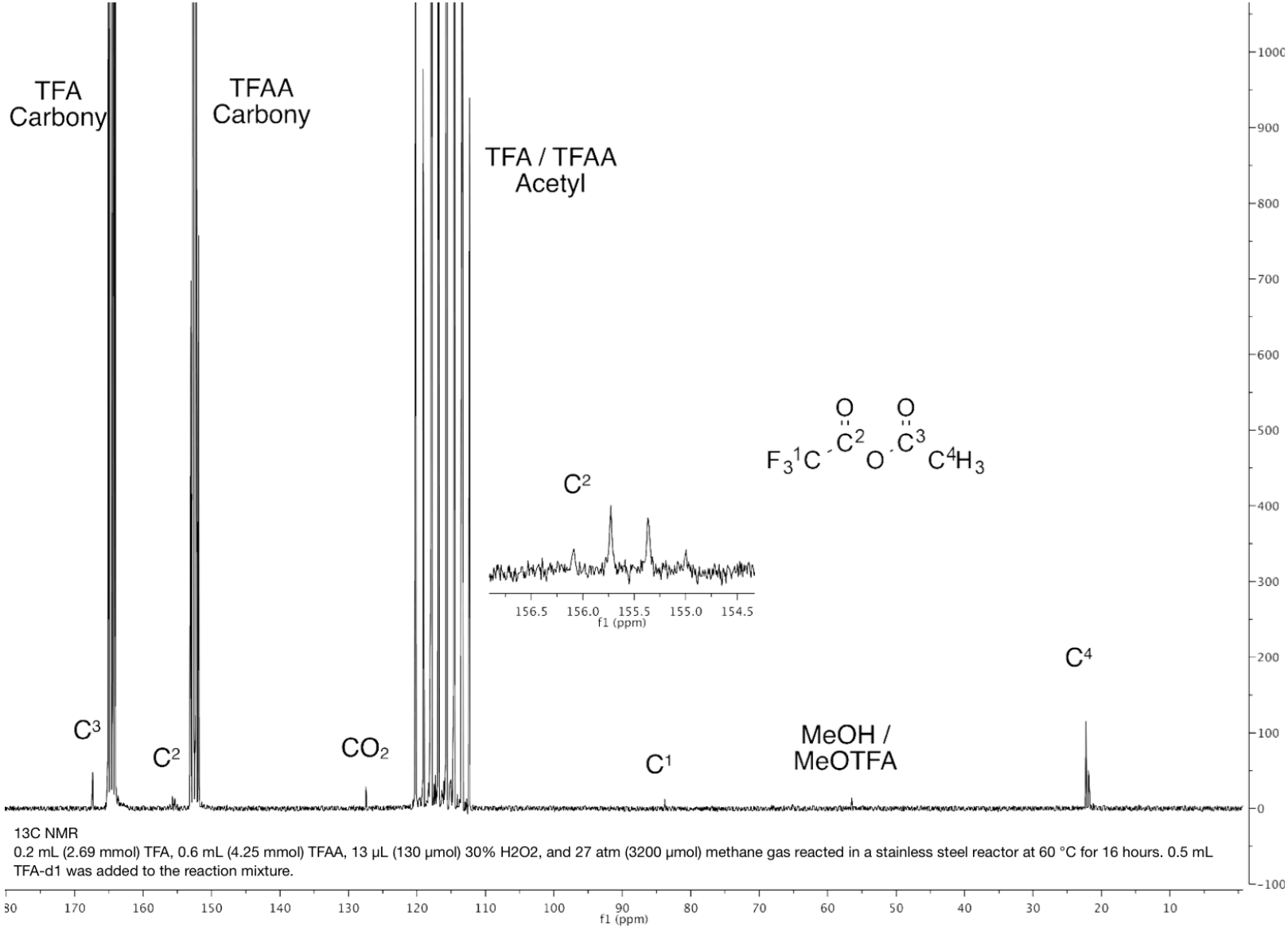
wet1D 1H NMR (Figure 1)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, 0.5 atm (59 µmol) 13C methane gas, charged with 4.7 atm N2 gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



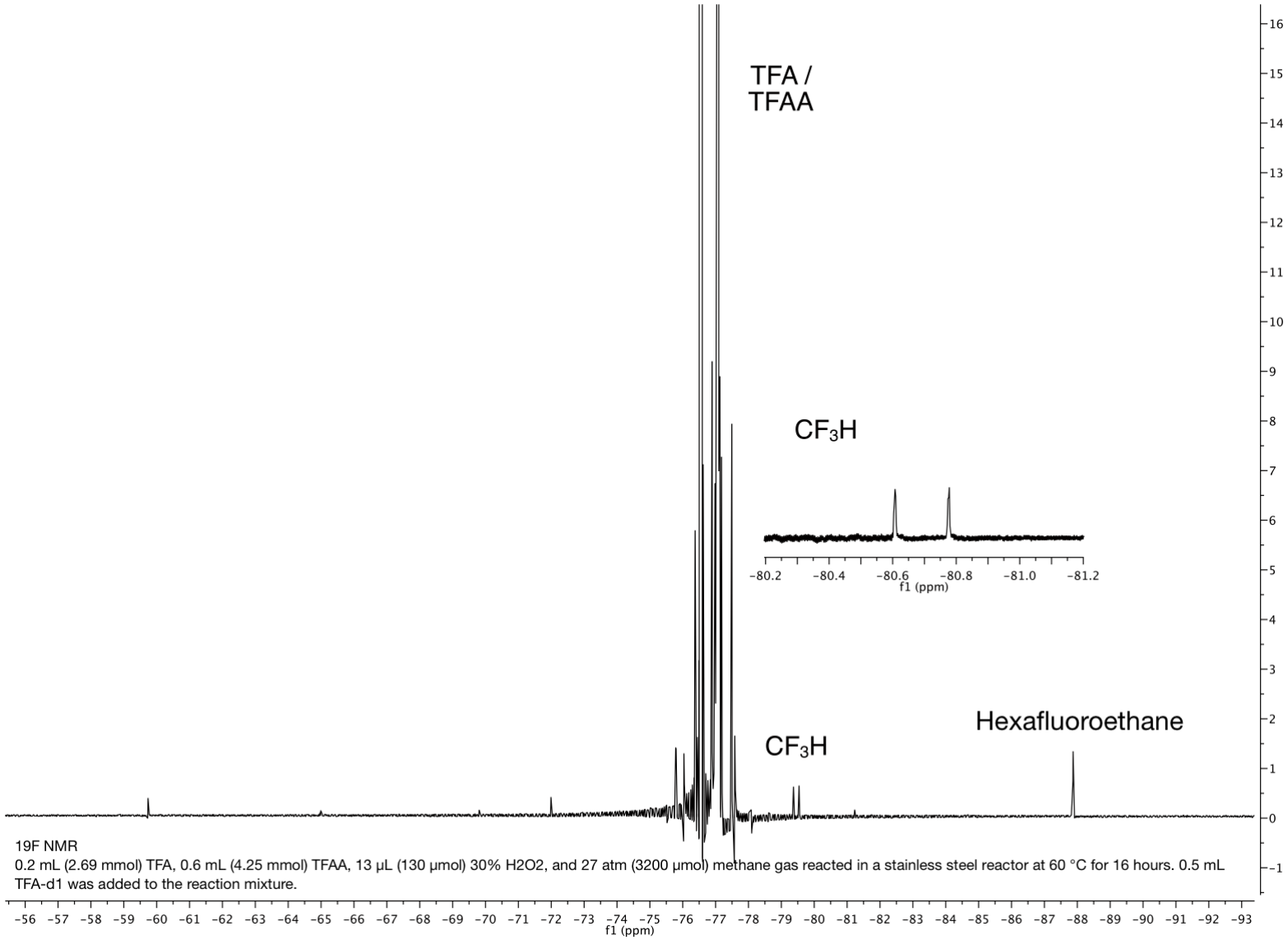
wet1D 1H NMR
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL TFA-d1 was added to the reaction mixture.



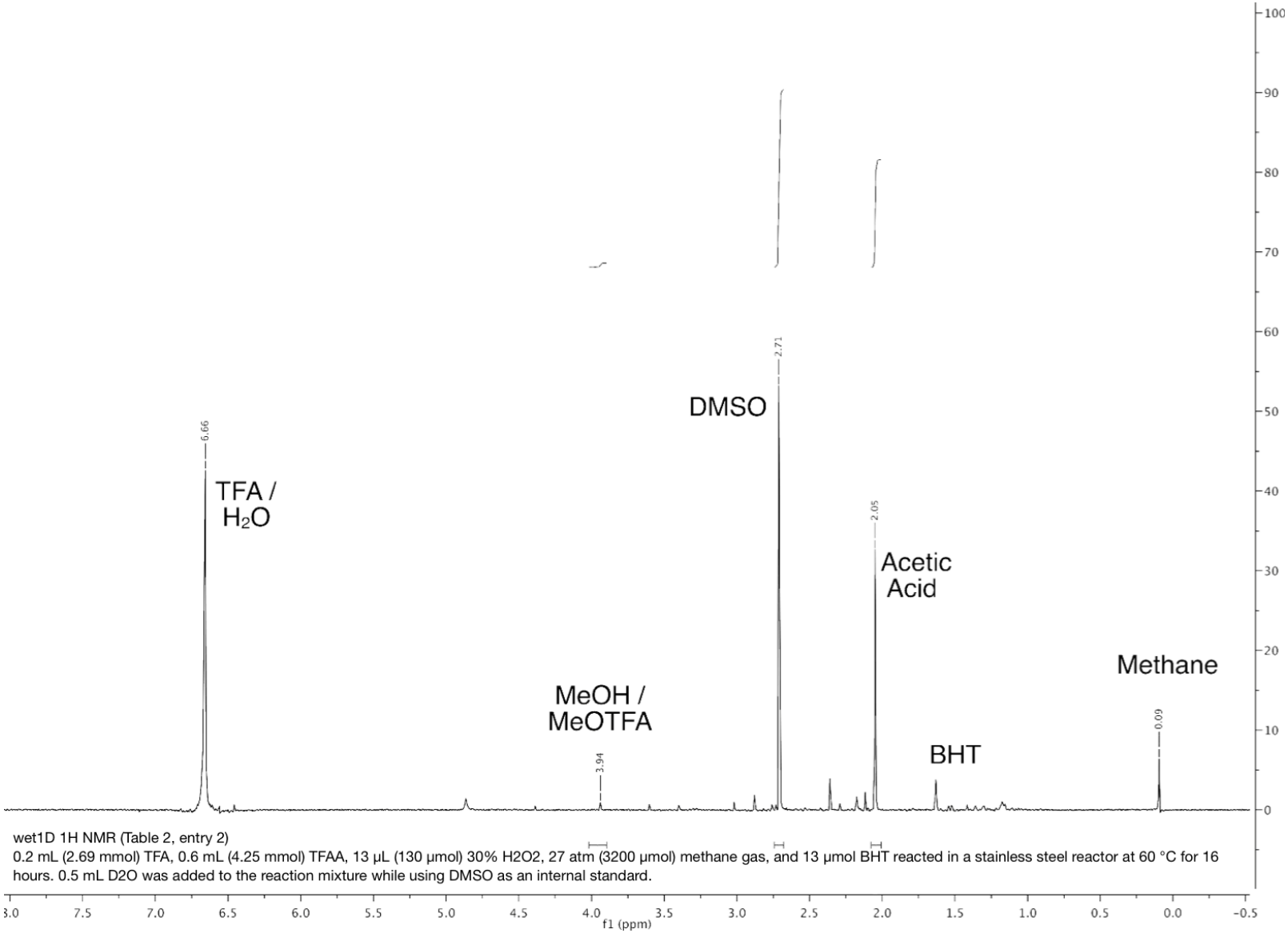
13C NMR (Figure 2)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



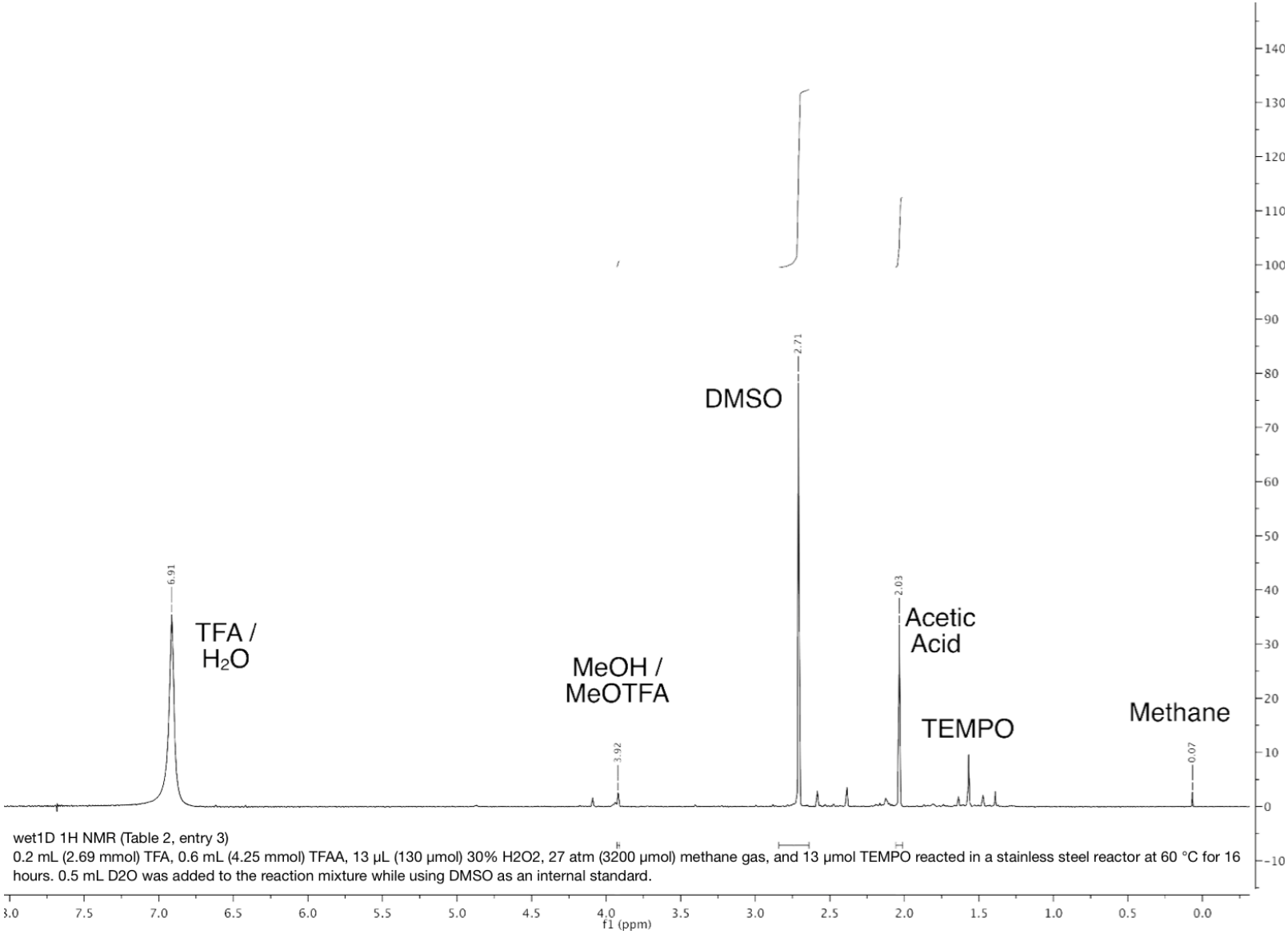
13C NMR
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL TFA-d1 was added to the reaction mixture.



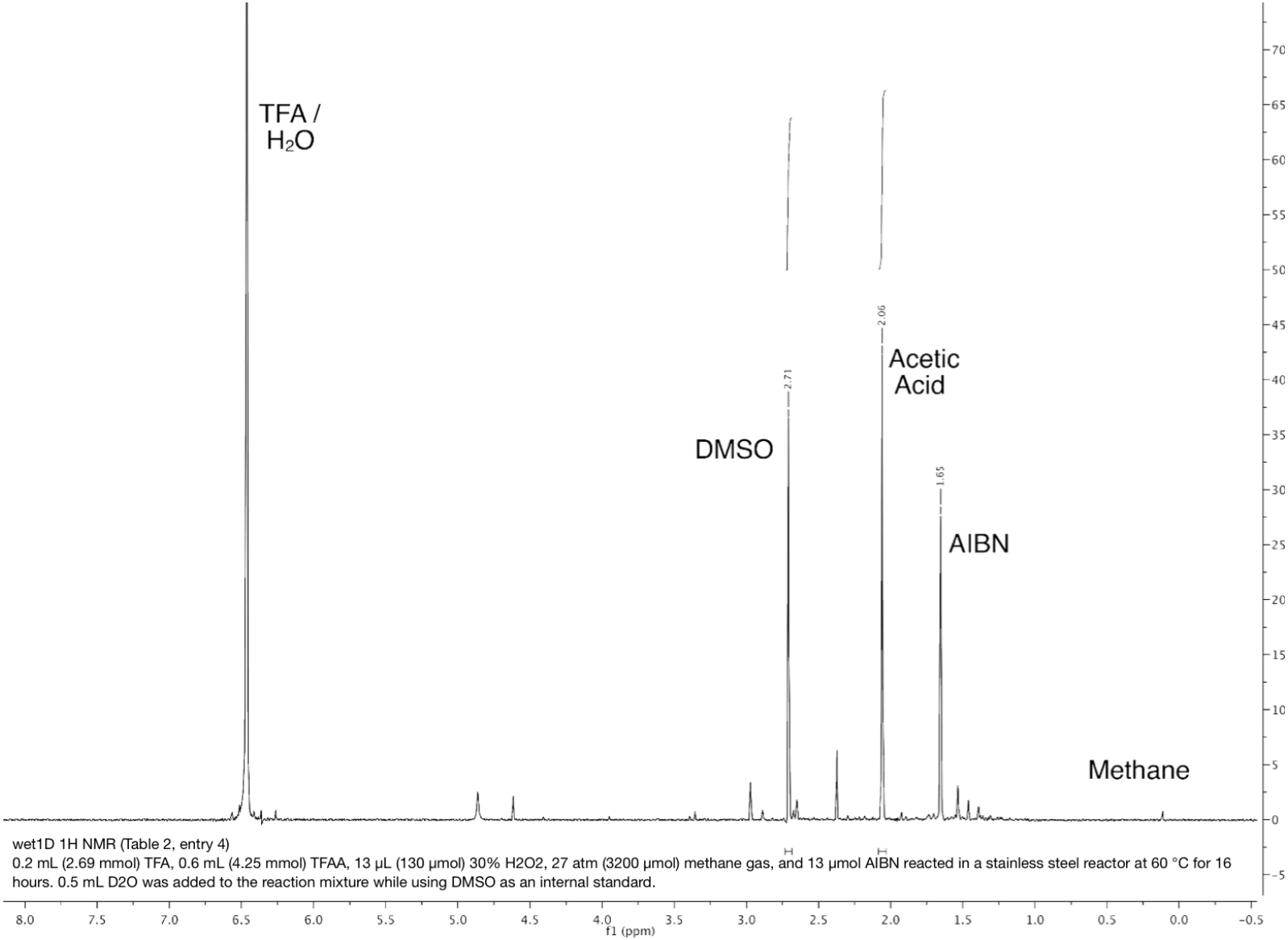
19F NMR
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL TFA-d1 was added to the reaction mixture.



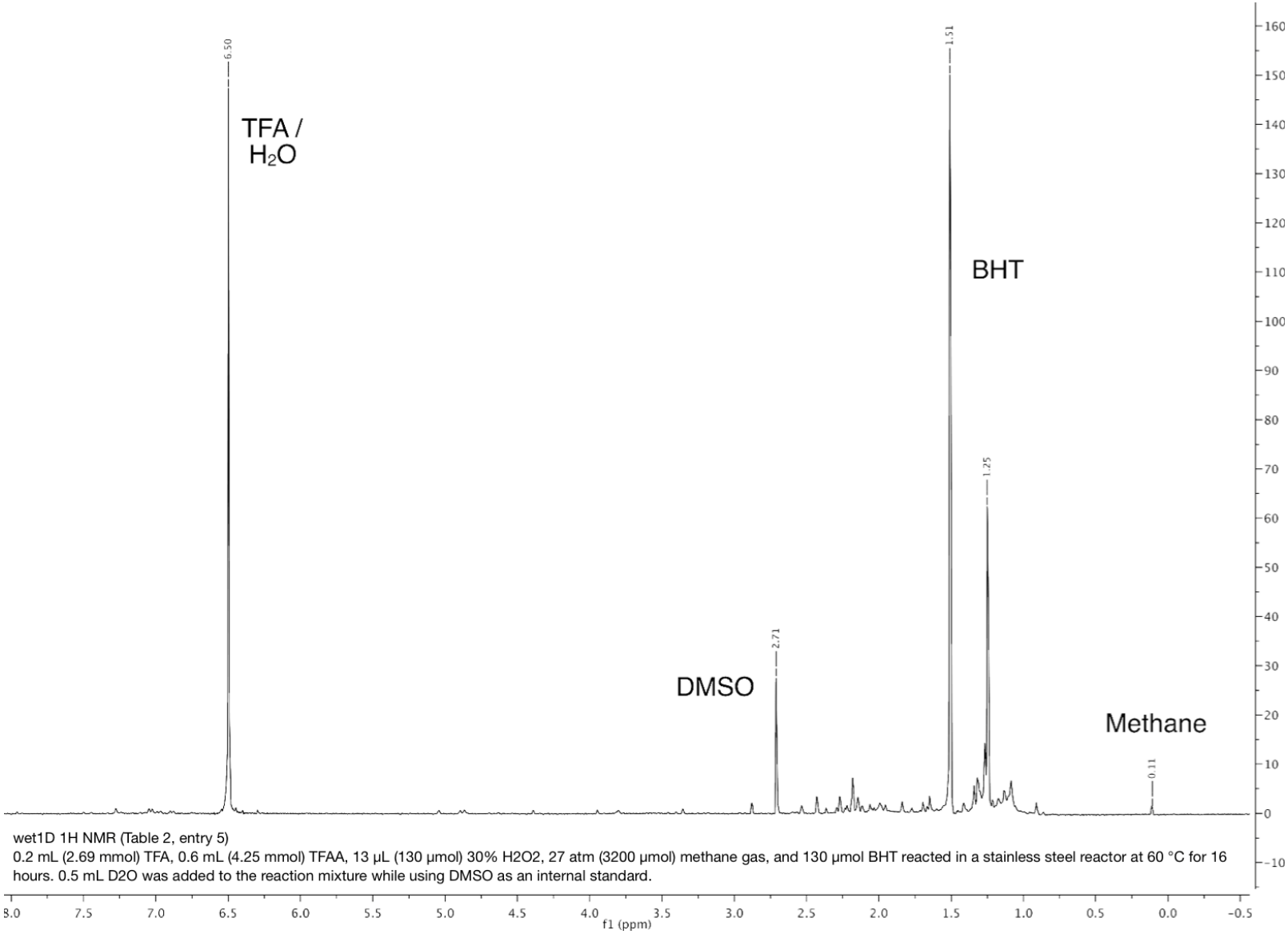
wet1D 1H NMR (Table 2, entry 2)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, 27 atm (3200 µmol) methane gas, and 13 µmol BHT reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



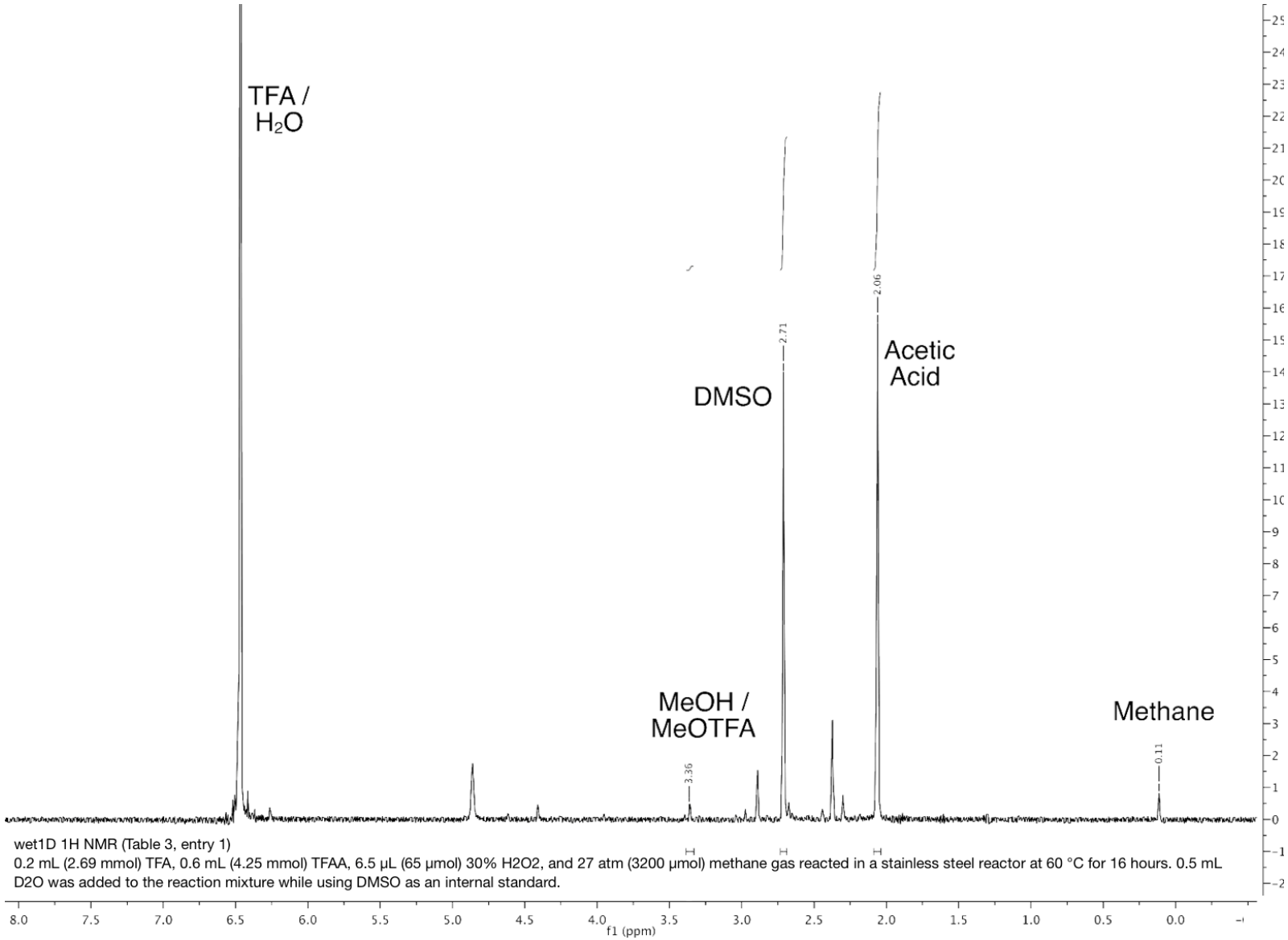
wet1D 1H NMR (Table 2, entry 3)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, 27 atm (3200 µmol) methane gas, and 13 µmol TEMPO reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



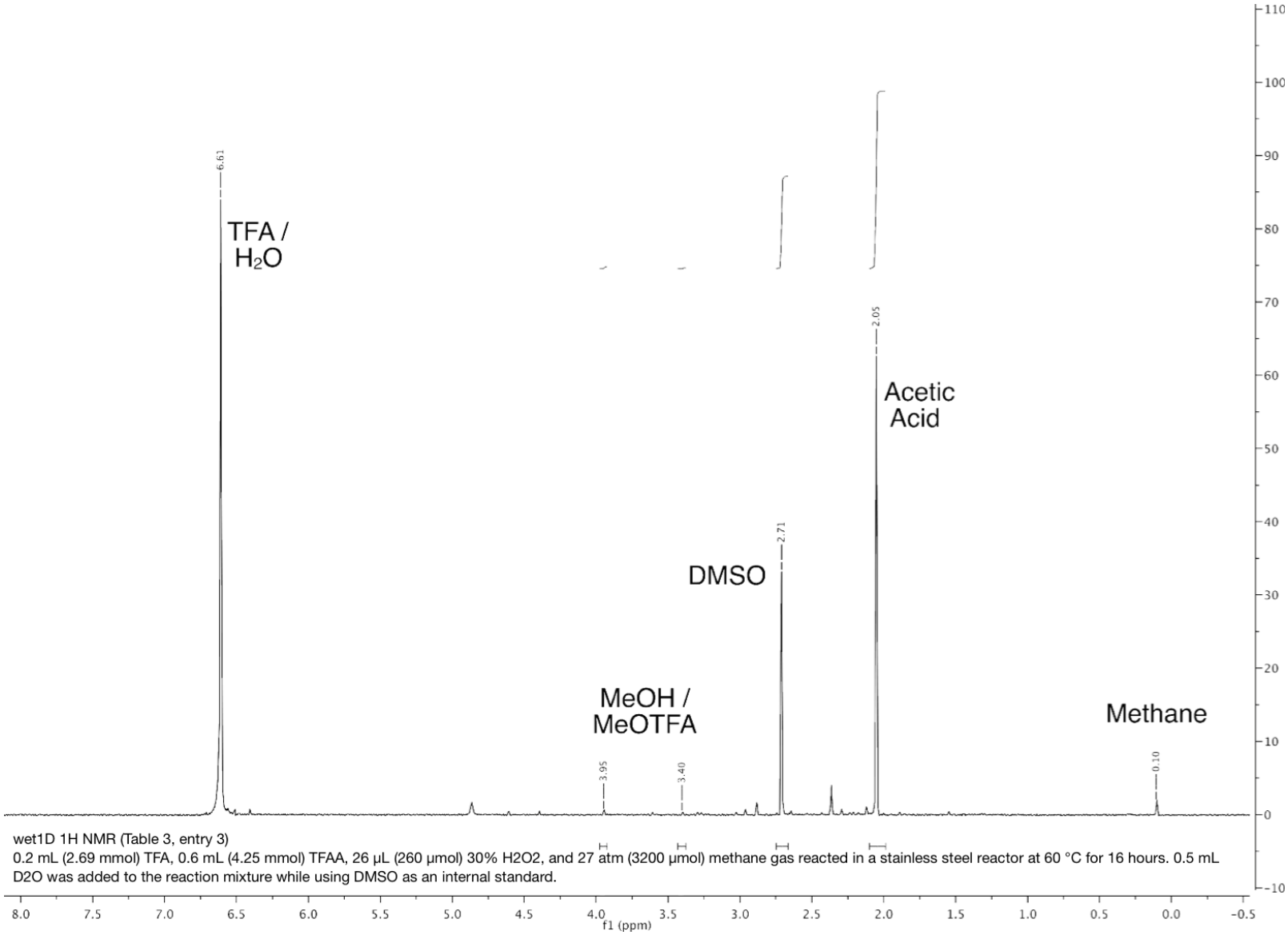
wet1D 1H NMR (Table 2, entry 4)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, 27 atm (3200 µmol) methane gas, and 13 µmol AIBN reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



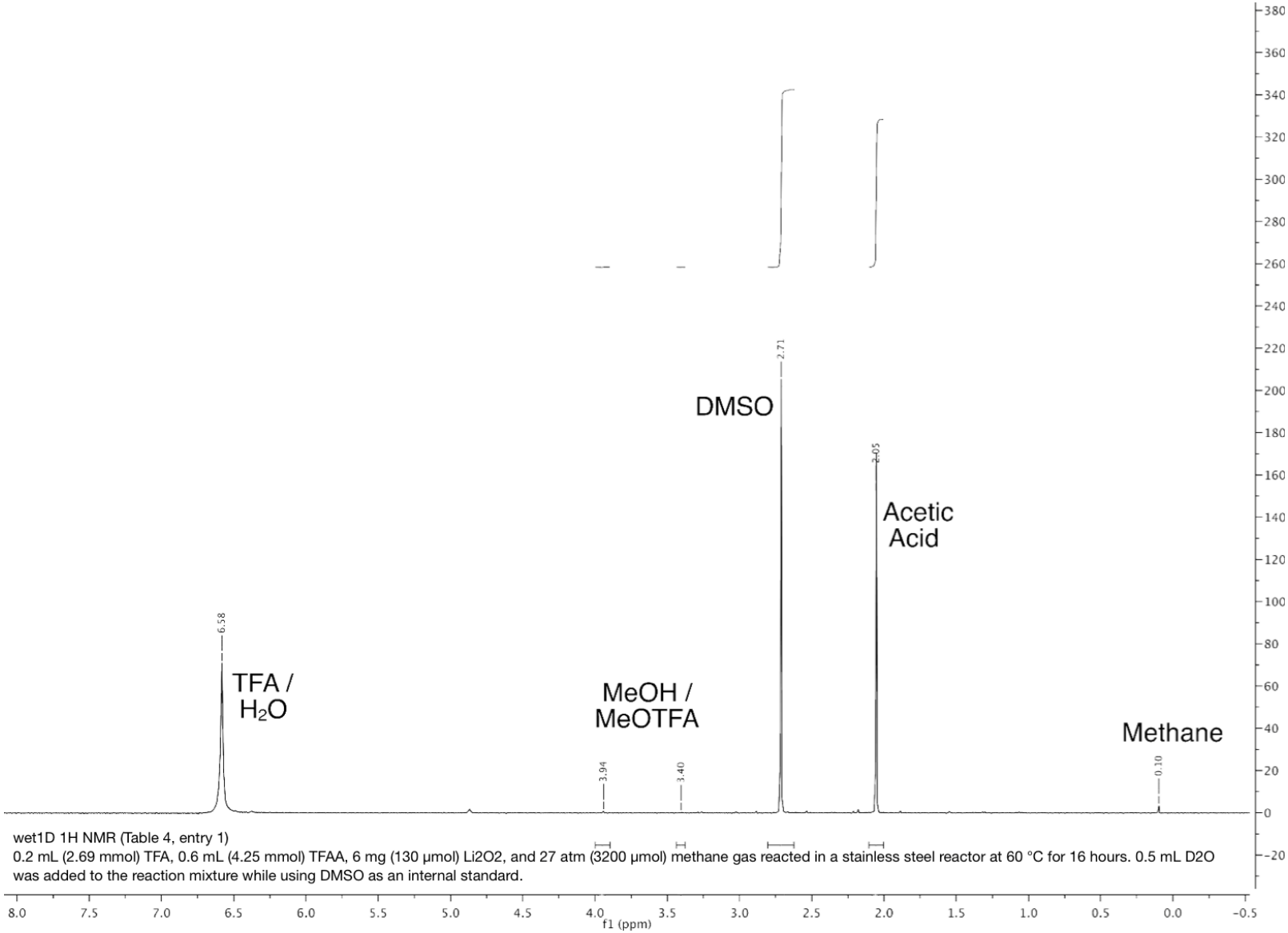
wet1D 1H NMR (Table 2, entry 5)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 13 µL (130 µmol) 30% H2O2, 27 atm (3200 µmol) methane gas, and 130 µmol BHT reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



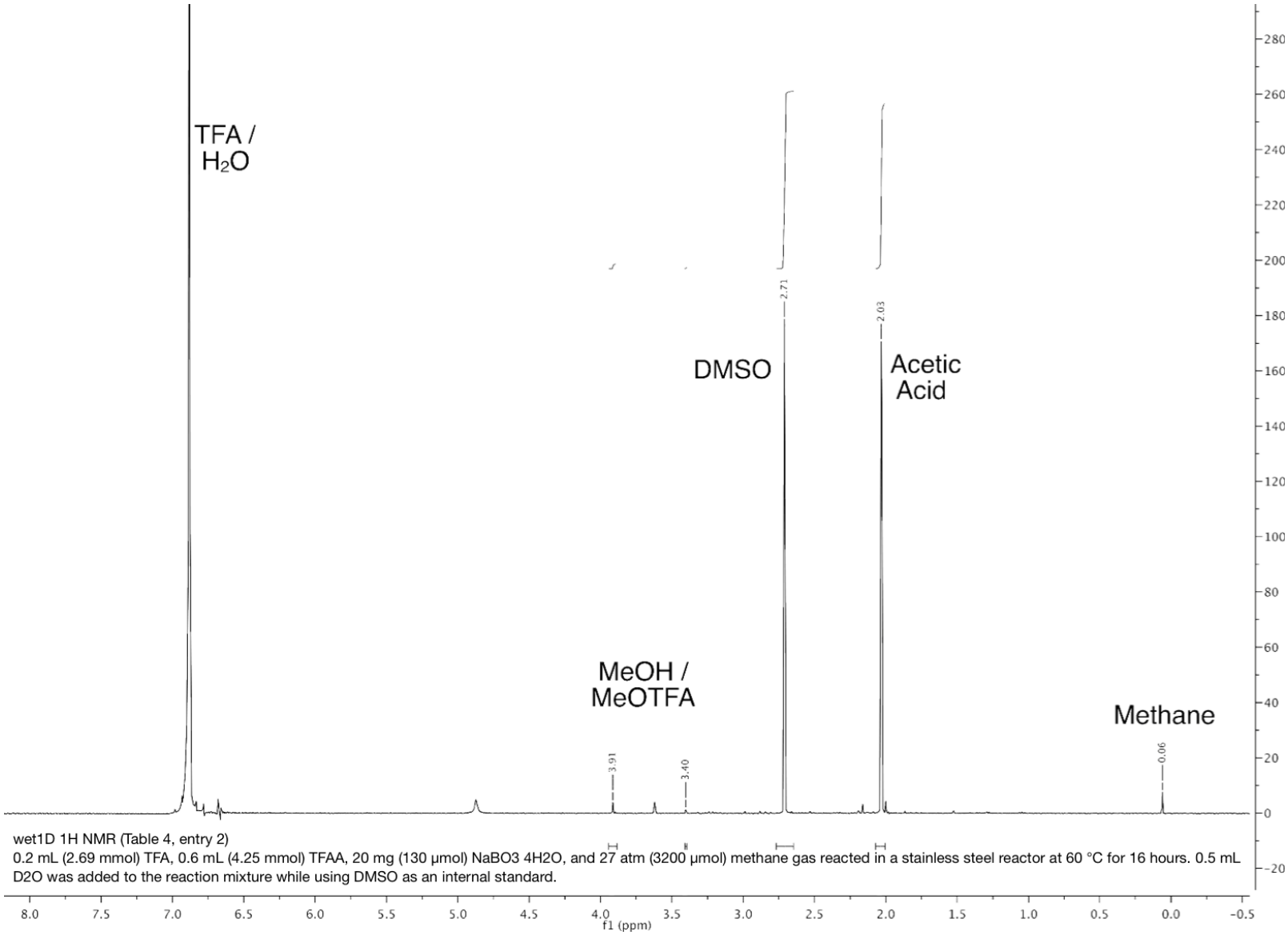
wet1D 1H NMR (Table 3, entry 1)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 6.5 µL (65 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



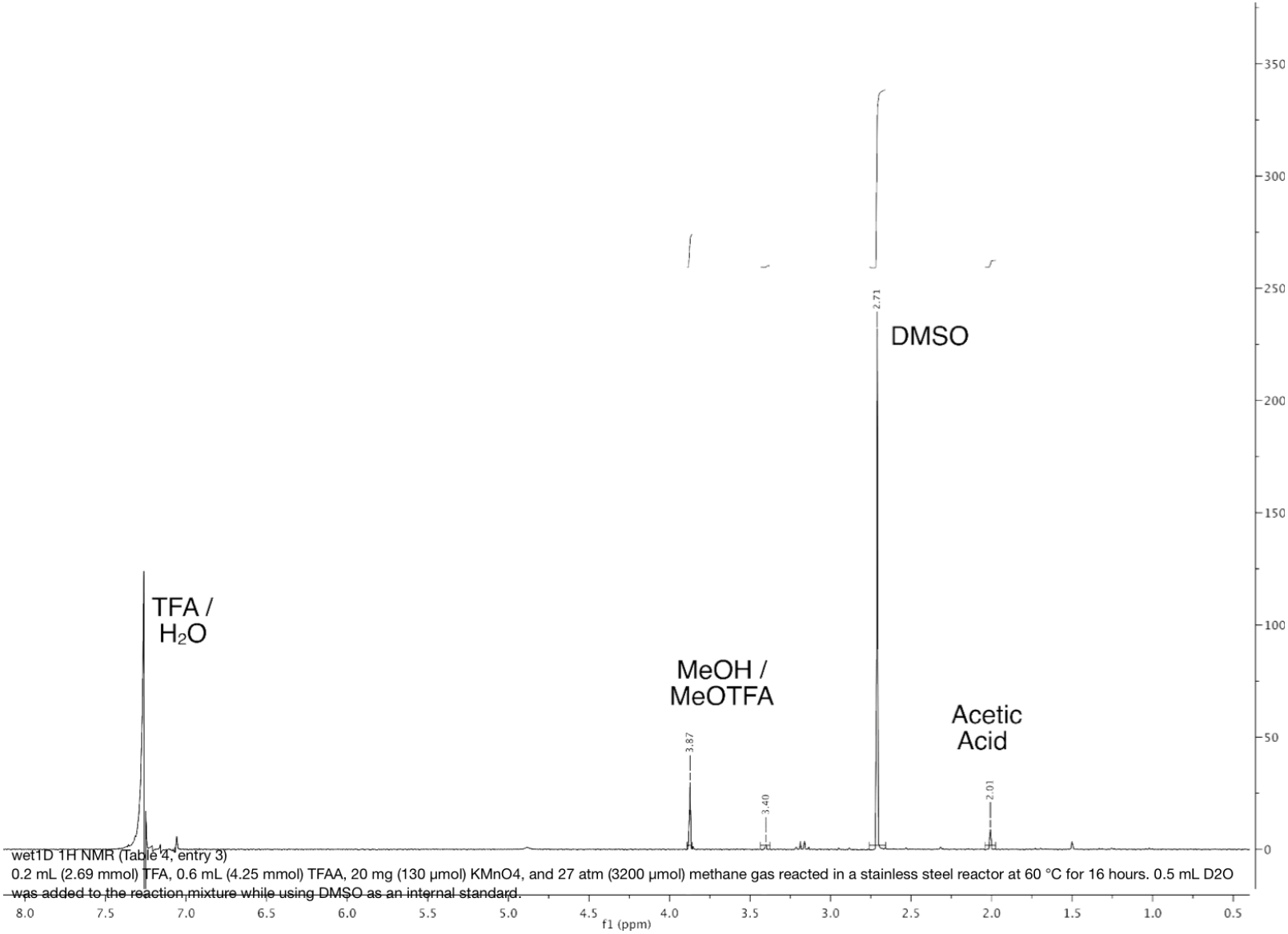
wet1D 1H NMR (Table 3, entry 3)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 26 µL (260 µmol) 30% H2O2, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



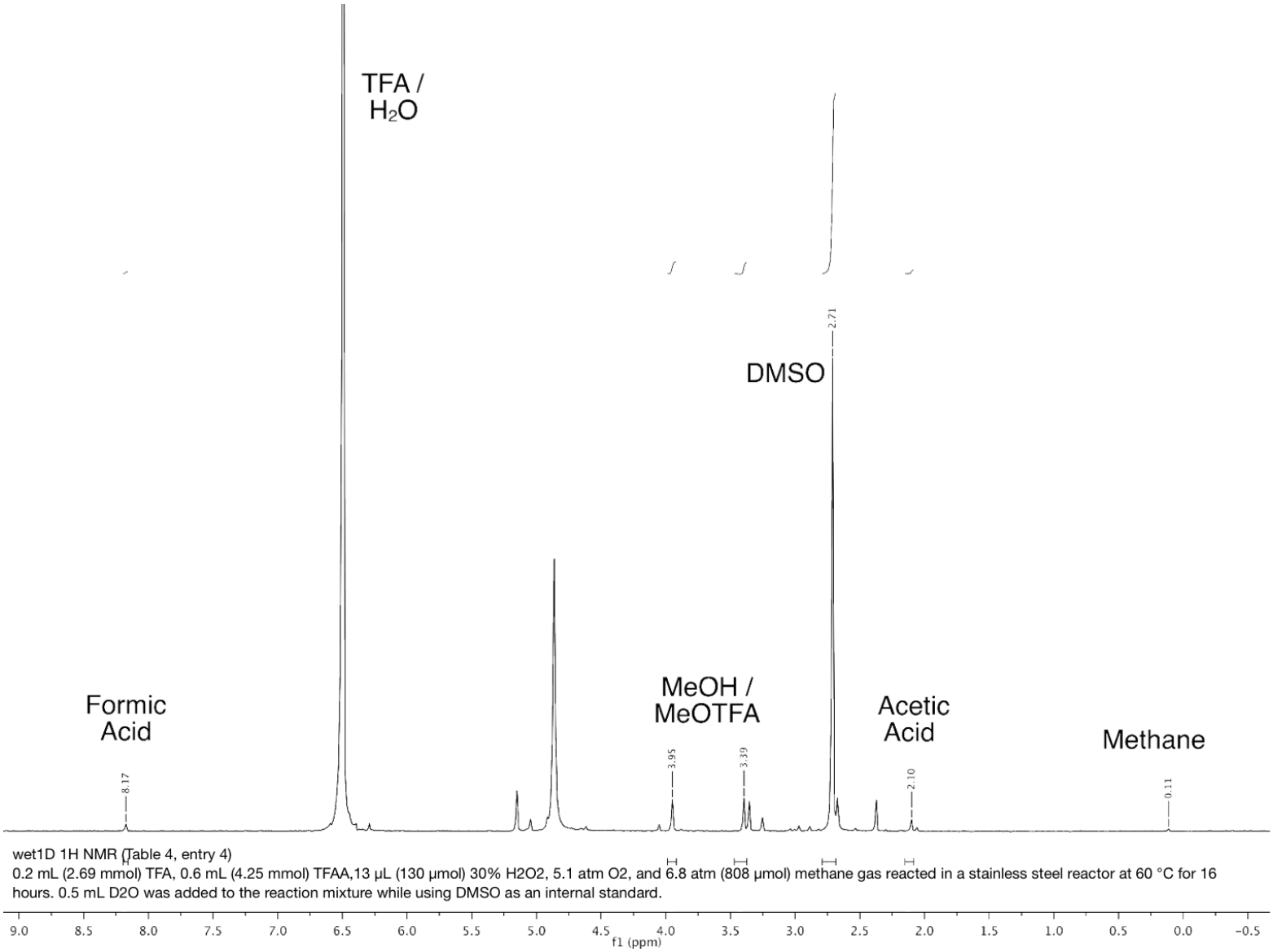
wet1D 1H NMR (Table 4, entry 1)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 6 mg (130 μmol) Li2O2, and 27 atm (3200 μmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



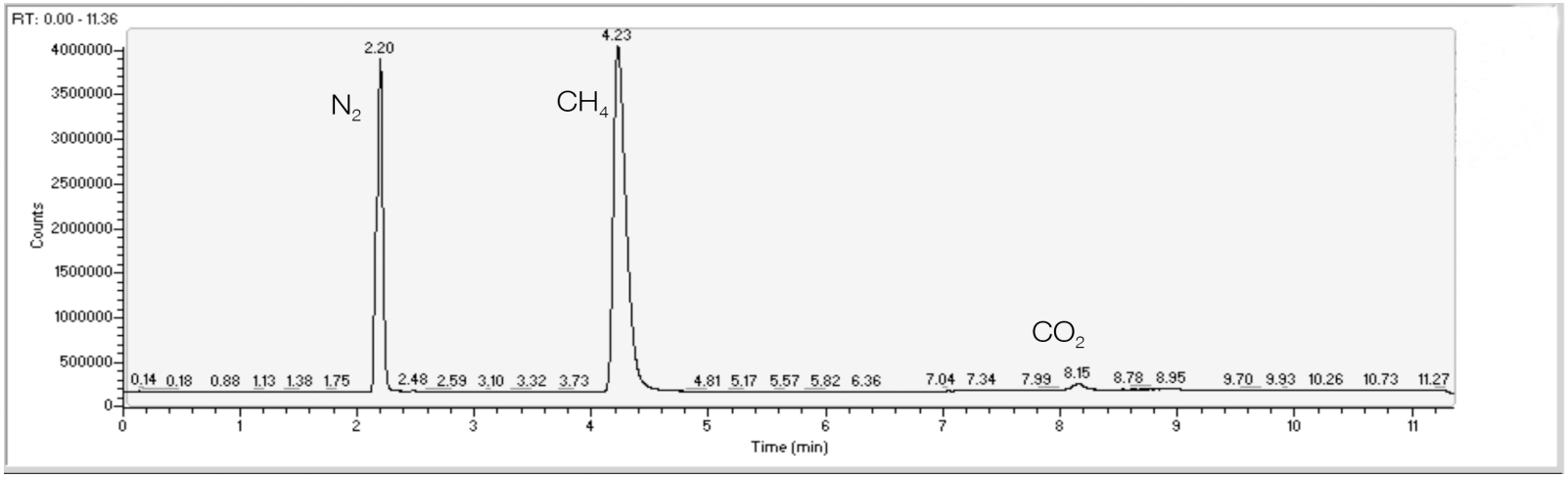
wet1D 1H NMR (Table 4, entry 2)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 20 mg (130 μmol) NaBO3 4H2O, and 27 atm (3200 μmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



wet1D 1H NMR (Table 4, entry 3)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA, 20 mg (130 µmol) KMnO4, and 27 atm (3200 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



wet1D 1H NMR (Table 4, entry 4)
0.2 mL (2.69 mmol) TFA, 0.6 mL (4.25 mmol) TFAA,13 µL (130 µmol) 30% H2O2, 5.1 atm O2, and 6.8 atm (808 µmol) methane gas reacted in a stainless steel reactor at 60 °C for 16 hours. 0.5 mL D2O was added to the reaction mixture while using DMSO as an internal standard.



Gas chromatograph of standard functionalization reaction.
Conditions: 0.2 mL TFA, 0.6 mL TFAA, 13 µL (130 µmol) 30% H_2O_2, and 27 atm methane gas stirred at 60 °C for 16 hours.

CO_2/ CO INCORPORATION DATA

$$\underset{(13.6\ \text{atm})}{CH_4} + \underset{(3.4\ \text{atm})}{CO_2} \xrightarrow[60\ °C,\ 16\ h]{TFAA,\ TFA,\ H_2O_2} \underset{(1.9\%)}{CH_3CO_2H}$$

$$\underset{(13.6\ \text{atm})}{CH_4} + \underset{(3.4\ \text{atm})}{N_2} \xrightarrow[60\ °C,\ 16\ h]{TFAA,\ TFA,\ H_2O_2} \underset{(2.6\%)}{CH_3CO_2H}$$

CH_4 (atm)	N_2 (atm)	CO_2 (atm)	CO (atm)	TFA / TFAA (mL)	H_2O_2 (μmol)	AcOH (μmol)
13.6	3.4	-	-	0.2 / 0.6	130	42.0
13.6	-	3.4	-	0.2 / 0.6	130	30.7
13.6	-	-	3.4	0.2 / 0.6	130	25.7

As a potential candidate of the extra carbon source, we considered the possibility of carbon dioxide participating in the reaction since small amounts of carbon dioxide were detected at the end of the reaction. To evaluate this possibility, we set up the reactions in the presence of CO_2 and inert N_2 to maintain the similar pressure. Carbon dioxide failed to facilitate the reaction, and yields of acetic acid under CO_2 conditions were slightly lower than pure methane conditions and the methane-nitrogen case. Similar results were observed in the presence of carbon monoxide.

COMPUTATIONAL CALCULATIONS USING GAUSSIAN 09

Electronic energies are shown for the solvated structures. CPCM model employed with Eps=8.55 and RSolv=13.7. Thermal free energy corrections were added to the solvated electronic energies.

Format:

- Compound Name
- Electronic Energy in Hartrees (B3LYP/aug-DZ)
- Sum of electronic and thermal Free Energies in Hartrees (B3LYP/aug-DZ at 333K and 27.0 atm)
- Cartesian coordinates for optimized geometry in Angstroms

Trifluoromethyl radical (CF_3•)

Electronic Energy= -337.6081691
Sum of electronic and thermal Free Energies= -337.6222695

C	0.000000	0.000000	0.330572
F	0.000000	1.267760	-0.073460
F	-1.097913	-0.633880	-0.073460
F	1.097913	-0.633880	-0.073460

Methane (CH_4)

Electronic Energy= -40.5207971
Sum of electronic and thermal Free Energies= -40.4929242

C	0.000000	0.000000	0.000000
H	0.633332	0.633332	0.633332
H	-0.633332	-0.633332	0.633332
H	-0.633332	0.633332	-0.633332
H	0.633332	-0.633332	-0.633332

Transition State 1

Electronic Energy= -378.11159
Sum of electronic and thermal Free Energies= -378.0915059

C	2.36837100	-0.00004000	0.00032200
H	2.63788600	-1.04070000	0.20126300
H	1.04149200	0.00008200	0.00043800
H	2.63833300	0.69426000	0.80098000
H	2.63795600	0.34613300	-1.00140500
C	-0.32888500	-0.00002000	0.00010700
F	-0.78472000	1.24406300	-0.23129600
F	-0.78450400	-0.82218600	-0.96191500
F	-0.78550800	-0.42181100	1.19278300

Trifluoromethane (CF_3H)

Electronic Energy= -338.28754
Sum of electronic and thermal Free Energies= -338.2879923

C	0.000028	-0.000031	0.351558
H	0.000100	-0.000037	1.445956
F	-0.365180	1.208499	-0.131728
F	-0.864126	-0.920448	-0.131705
F	1.229277	-0.288026	-0.131601

Methyl radical (CH_3•)

Electronic Energy= -39.8449057
Sum of electronic and thermal Free Energies= -39.8332299

C	0.000000	0.000000	0.000025
H	0.000000	1.088070	-0.000051
H	-0.942296	-0.544035	-0.000051
H	0.942296	-0.544035	-0.000051

Trifluoroacetic acid anhydride (TFAA) ($C_4O_3F_6$)

Electronic Energy= -977.2802269
Sum of electronic and thermal Free Energies= -977.2741009

C	-2.358102	-0.312189	0.050364
C	-1.185709	0.669531	-0.210246
O	-1.309356	1.794033	-0.570994
O	-0.000010	-0.011278	0.000148
C	1.185758	0.669550	0.210324
C	2.358082	-0.312217	-0.050401
F	2.312163	-0.763918	-1.319772
F	2.276599	-1.368494	0.782526
F	3.525026	0.304443	0.147036
F	-2.312319	-0.763879	1.319772
F	-2.276557	-1.368494	-0.782510
F	-3.525001	0.304490	-0.147188
O	1.309446	1.794072	0.570969

Transition State 2

Electronic Energy= -1017.119449
Sum of electronic and thermal Free Energies= -1017.081752

C	-2.485654	-0.337277	0.063947
C	-1.282842	0.624685	-0.133372
O	-1.397839	1.793127	-0.352252
O	-0.133262	-0.081227	0.026836
F	-2.430359	-0.919317	1.280711
F	-2.467785	-1.308054	-0.871669
F	-3.637011	0.333384	-0.035732
C	1.110766	0.430696	-0.444433
C	1.497879	1.967523	1.107010
H	2.528628	2.200016	0.847796
H	0.723454	2.652591	0.770116
H	1.315869	1.376373	2.003307
C	2.201086	-0.580103	0.014957
O	1.229983	1.094751	-1.447246
F	3.422813	-0.053497	-0.156004
F	2.106895	-1.687467	-0.750684
F	2.071400	-0.955642	1.301313

Species 5 ($C_5H_3O_3F_6$)

Electronic Energy= -1017.1454798
Sum of electronic and thermal Free Energies= -1017.102606

C	-2.466032	-0.340163	0.030451
C	-1.260838	0.634745	-0.073174
O	-1.387198	1.816654	-0.237887
O	-0.123243	-0.062943	0.061675
F	-2.462754	-0.966583	1.227772
F	-2.405194	-1.278031	-0.936653
F	-3.618001	0.327098	-0.094737
C	1.161410	0.634314	-0.109575
C	1.407332	1.659278	1.028161
H	2.450873	1.984188	0.996835
H	0.741407	2.512341	0.884302
H	1.190556	1.159362	1.979071
C	2.188846	-0.554389	-0.002463
O	1.294366	1.222061	-1.290167
F	3.441913	-0.081478	-0.118374
F	1.982629	-1.457020	-0.972806
F	2.079347	-1.173406	1.187068

Transition State 3

Electronic Energy= -1017.1283577
Sum of electronic and thermal Free Energies= -1017.089129

C	-2.467628	-0.407642	0.036828
C	-1.358129	0.670610	-0.091941
O	-1.589494	1.832918	-0.281975
O	-0.156624	0.094016	0.062542
F	-2.415042	-0.993075	1.254635
F	-2.310661	-1.367295	-0.897655
F	-3.677322	0.141514	-0.115460
C	1.021977	0.959706	-0.151489
C	1.383572	1.725667	1.102706
H	0.642176	2.531702	1.193738
H	1.336245	1.094649	1.995049
H	2.378128	2.166745	0.986275
C	2.322114	-0.645018	-0.011692
O	1.271853	1.307570	-1.295634
F	3.540676	-0.137612	-0.117073
F	2.050403	-1.471129	-1.000260
F	2.148184	-1.226744	1.169035

Species 6 ($C_4H_3O_3F_3$)

Electronic Energy= -679.5386106
Sum of electronic and thermal Free Energies= -679.504237

C	1.587269	-0.180317	0.057256
C	0.233097	0.502072	-0.273202
O	0.139738	1.621429	-0.675525
O	-0.769640	-0.397127	-0.075509
F	1.748678	-1.303564	-0.676153
F	1.631330	-0.521669	1.363520
F	2.605815	0.644964	-0.201961
C	-2.112409	0.040334	0.142109
C	-3.059735	-1.025411	-0.314475
H	-4.078546	-0.749145	-0.029474
H	-2.987537	-1.131262	-1.406051
H	-2.780699	-1.990054	0.128868
O	-2.359469	1.084800	0.659518