Electronic supporting information for:

Synthetic approach to iodosulfuron-methyl and metsulfuron-methyl metabolites and their application for water analysis

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Scheme S1. Plausible MS/MS fragmentations of **3**/**4** and **6**/**7**

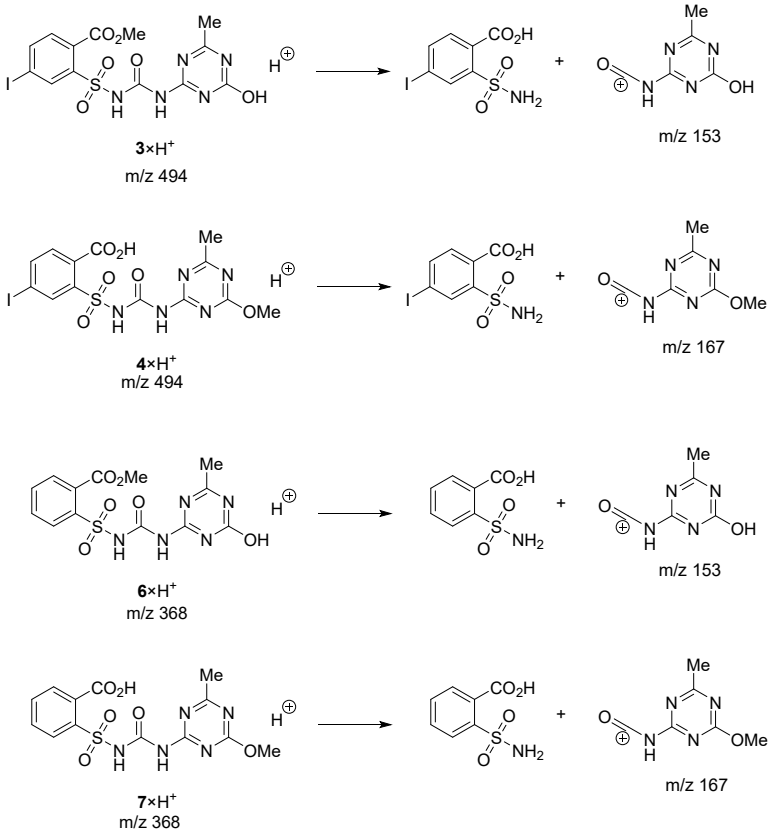


Figure S1. ESI MS/MS chromatograms of compounds **1**-**13**

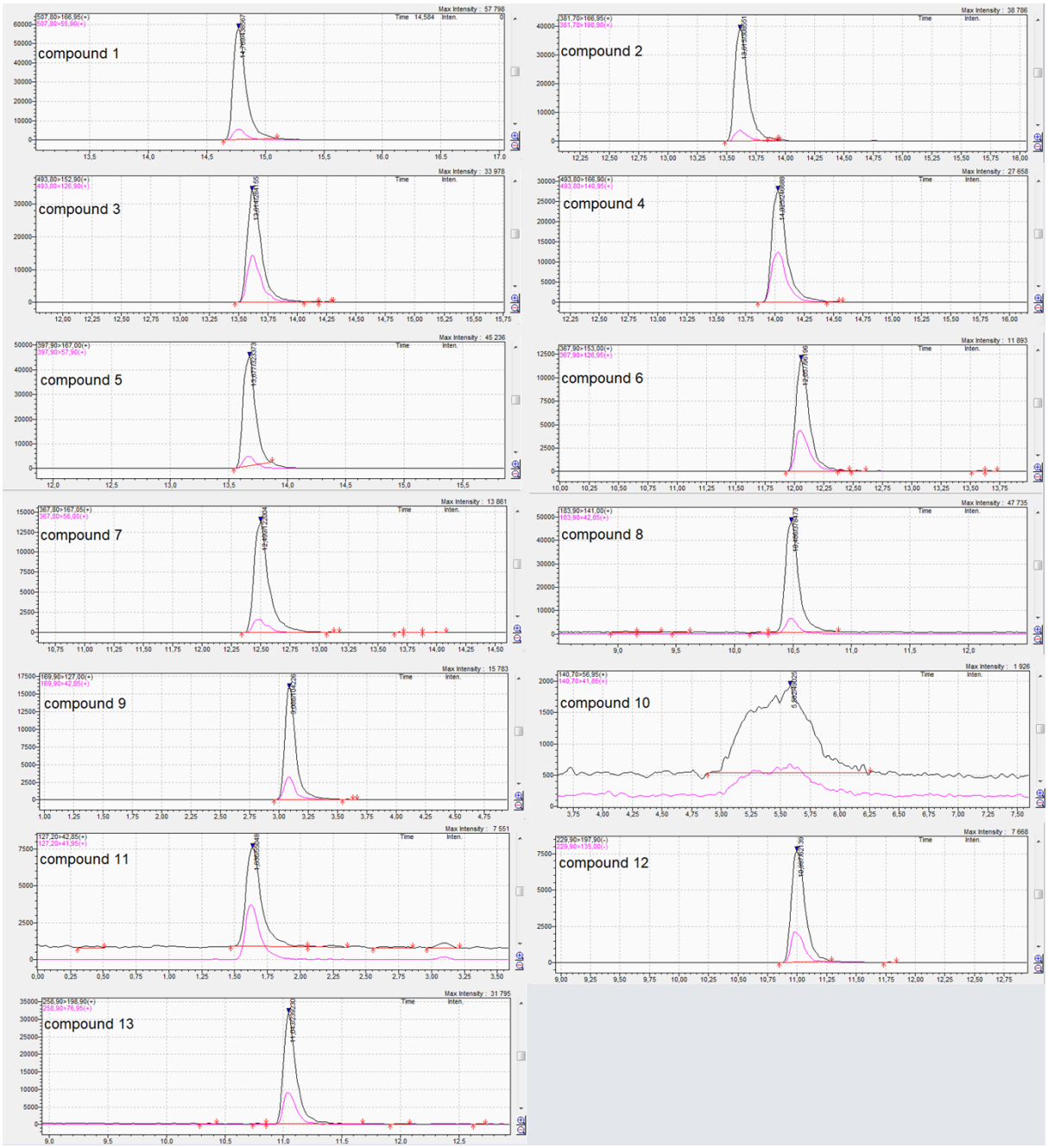


Table S1. Retention times and MRM conditions for compounds **1**-**13**.

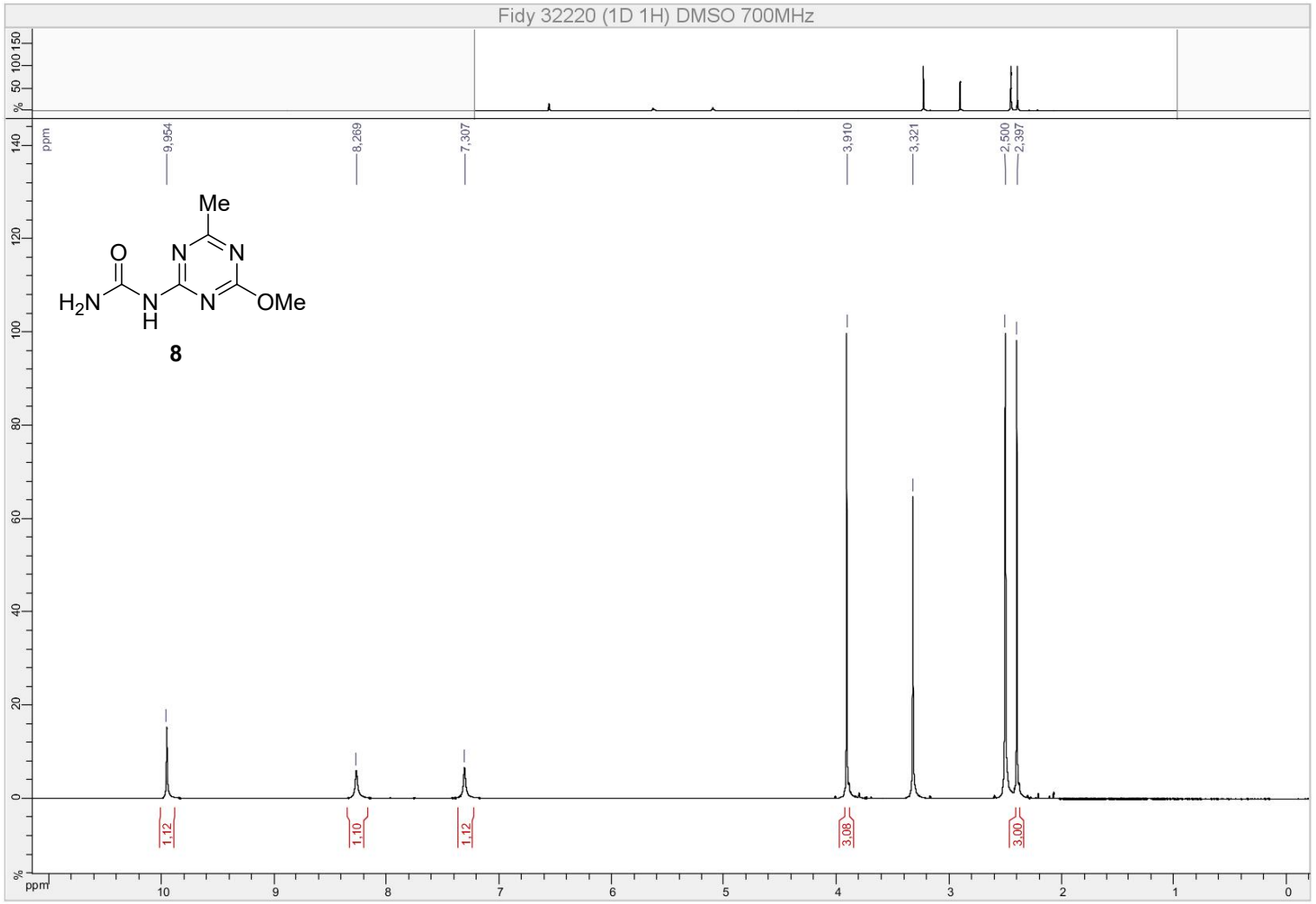
Compound	Retention time [min]	Precursor ion	Product ions	Dwell time [ms]	Q1 [V]	CE	Q3 [V]
1	14.90	507.80	166.95	56.0	-26.0	-25.0	-28.0
			55.90	56.0	-26.0	-55.0	-20.0
2	13.69	381.70	166.95	37.0	-19.0	-19.0	-30.0
			198.90	37.0	-19.0	-22.0	-17.0
3	13.67	493.80	152.90	37.0	-24.0	-21.0	-25.0
			126.90	37.0	-24.0	-24.0	-20.0
4	14.10	493.80	166.90	37.0	-24.0	-22.0	-29.0
			140.95	37.0	-24.0	-28.0	-22.0
5	13.73	397.90	167.00	37.0	-30.0	-18.0	-29.0
			57.90	37.0	-30.0	-54.0	-21.0
6	12.06	367.90	153.00	37.0	-29.0	-14.0	-26.0
			126.95	37.0	-29.0	-17.0	-21.0
7	12.51	367.80	167.05	37.0	-26.0	-18.0	-30.0
			58.00	37.0	-26.0	-41.0	-20.0
8	10.54	183.90	141.00	37.0	-21.0	-13.0	-24.0
			42.85	37.0	-21.0	-31.0	-16.0
9	3.96	169.90	127.00	264.0	-18.0	-12.0	-20.0
			42.85	264.0	-18.0	-34.0	-13.0
10	6.78	140.70	56.95	264.0	-30.0	-19.0	-20.0
			41.85	264.0	-30.0	-25.0	-13.0
11	1.74	127.20	42.85	264.0	-13.0	-16.0	-15.0
			41.95	264.0	-13.0	-25.0	-14.0
12[a)]	11.02	229.90	197.90	37.0	+17.0	+14.0	+19.0
			135.00	37.0	+17.0	+22.0	+23.0
13	11.06	258.90	198.90	37.0	-28.0	-9.0	-19.0
			76.95	37.0	-28.0	-38.0	-29.0

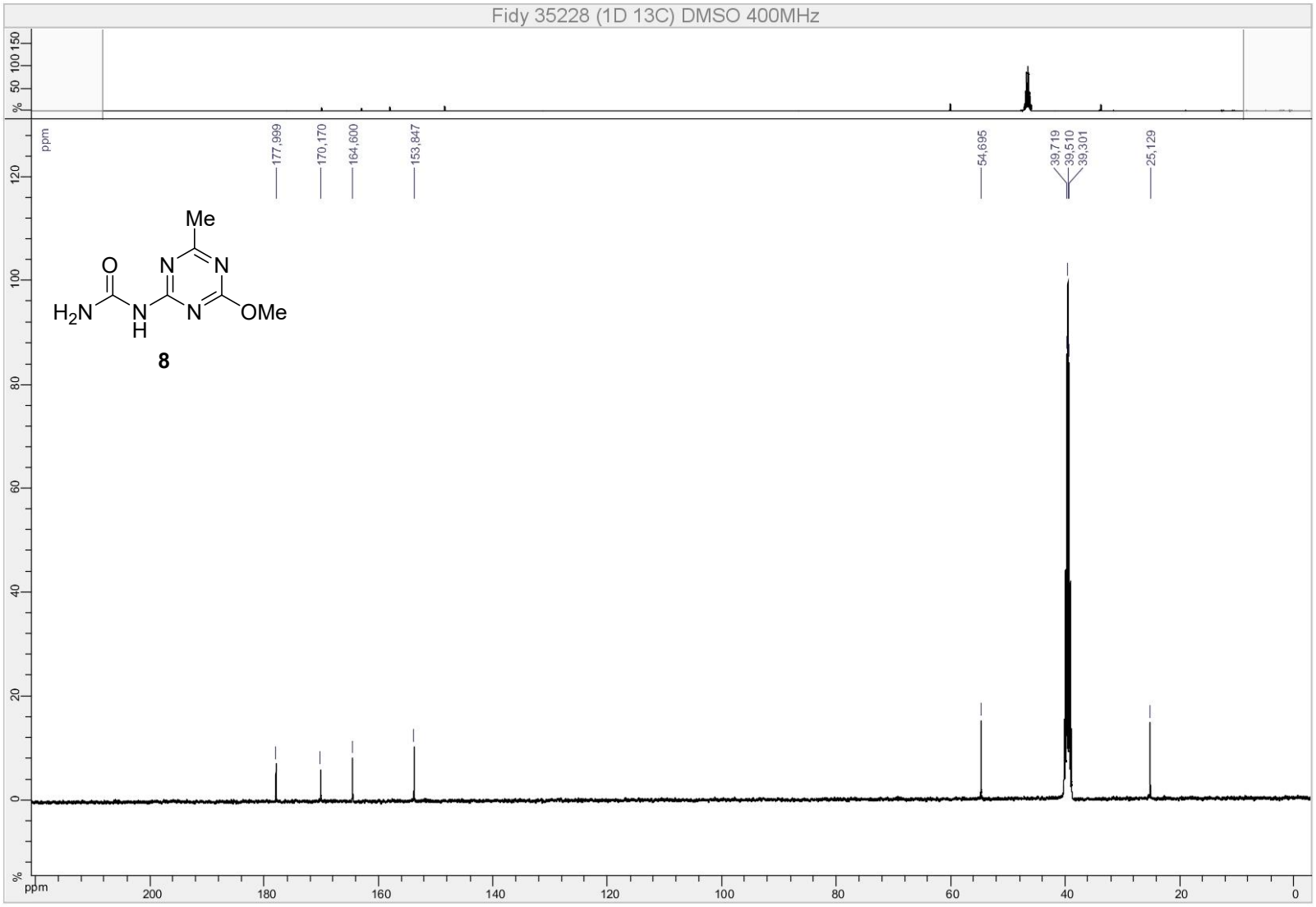
a) The MRM performed in negative mode.

Table S2. Analytical parameters for determination of compounds **1**-**13**.

Compound	Regression equation	R^2	LOD [ng/mL]	LOQ [ng/mL]	RSD (%) Intra-day precision 25 [ng/mL]	RSD (%) Intra-day precision 200 [ng/mL]	RSD (%) Intra-day precision 500 [ng/mL]	RSD (%) Inter-day precision 25 [ng/mL]	RSD (%) Inter-day precision 200 [ng/mL]	RSD (%) Inter-day precision 500 [ng/mL]	Recovery [%] 50 [ng/mL]	Recovery [%] 300 [ng/mL]
1	y = 994913x + 5304.8	0.9991	1.5	5.0	3.7	2.8	3.4	2.2	3.0	2.6	99 ± 5	101 ± 3
2	y = 501575x + 4875.9	0.9997	3.0	10.0	4.2	5.2	4.1	2.1	4.4	3.2	105 ± 1	103 ± 1
3	y = 575947x + 1201.2	0.9997	3.0	10.0	4.0	3.3	3.2	4.2	2.0	3.1	94 ± 4	105 ± 3
4	y = 502142x + 1677.8	0.9992	1.5	5.0	4.1	2.5	4.4	5.2	4.1	4.6	83 ± 5	91 ± 2
5	y = 549107x + 3335.7	0.9993	1.5	5.0	2.5	1.2	3.6	2.8	2.9	2.9	93 ± 4	101 ± 5
6	y = 292160x + 1085.7	0.9989	3.0	10.0	5.5	1.6	2.1	4.0	4.0	3.0	99 ± 2	102 ± 5
7	y = 343333x + 1311	0.9993	1.5	5.0	4.2	2.4	2.6	4.5	1.8	4.1	92 ± 3	79 ± 5
8	y = 845574x + 4800.4	0.9990	3.0	10.0	3.9	1.1	2.5	4.1	1.9	3.0	102 ± 4	103 ± 4
9	y = 269056x - 406.02	0.9999	3.0	10.0	4.1	3.9	3.9	3.2	3.4	4.8	101 ± 3	105 ± 1
10	y = 160621x + 843.99	0.9997	7.5	25.0	2.2	2.9	2.6	4.9	3.9	2.8	104 ± 3	105± 2
11	y = 94693x + 76.7	0.9996	60.0	200.0	nd.	4.0	4.9	nd.	4.8	5.0	102 ± 5	104 ± 4
12	y = 256865x + 5107.5	0.9989	3.0	10.0	1.2	4.8	2.6	4.5	4.5	4.5	105 ± 4	102 ± 4
13	y = 637448x + 2656.2	0.9990	1.5	5.0	4.6	2.2	2.2	4.1	3.3	3.7	98 ± 4	80 ± 5

^{1}H NMR and ^{13}C NMR spectra

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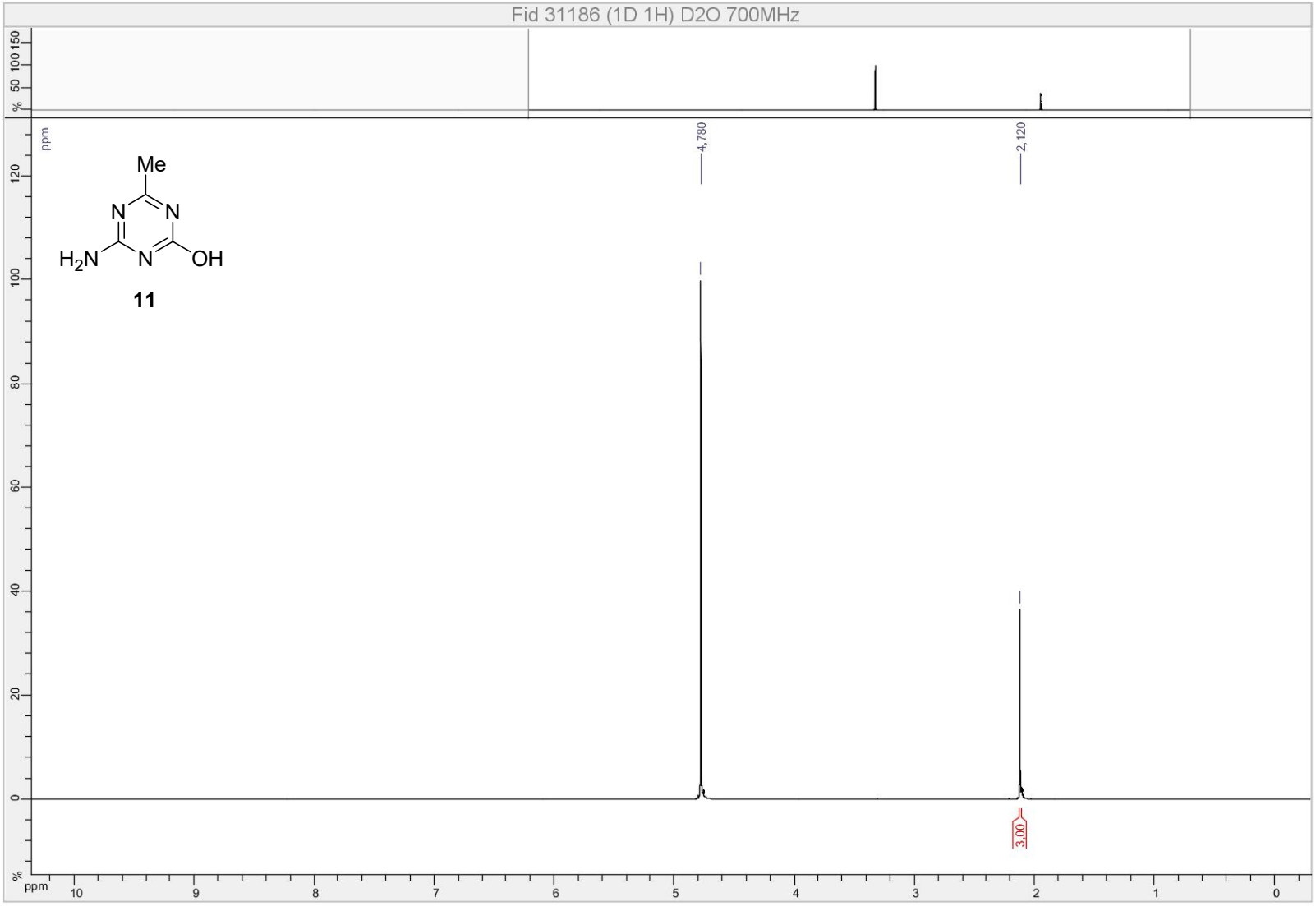
H2N
N
H
N
OMe
8
ppm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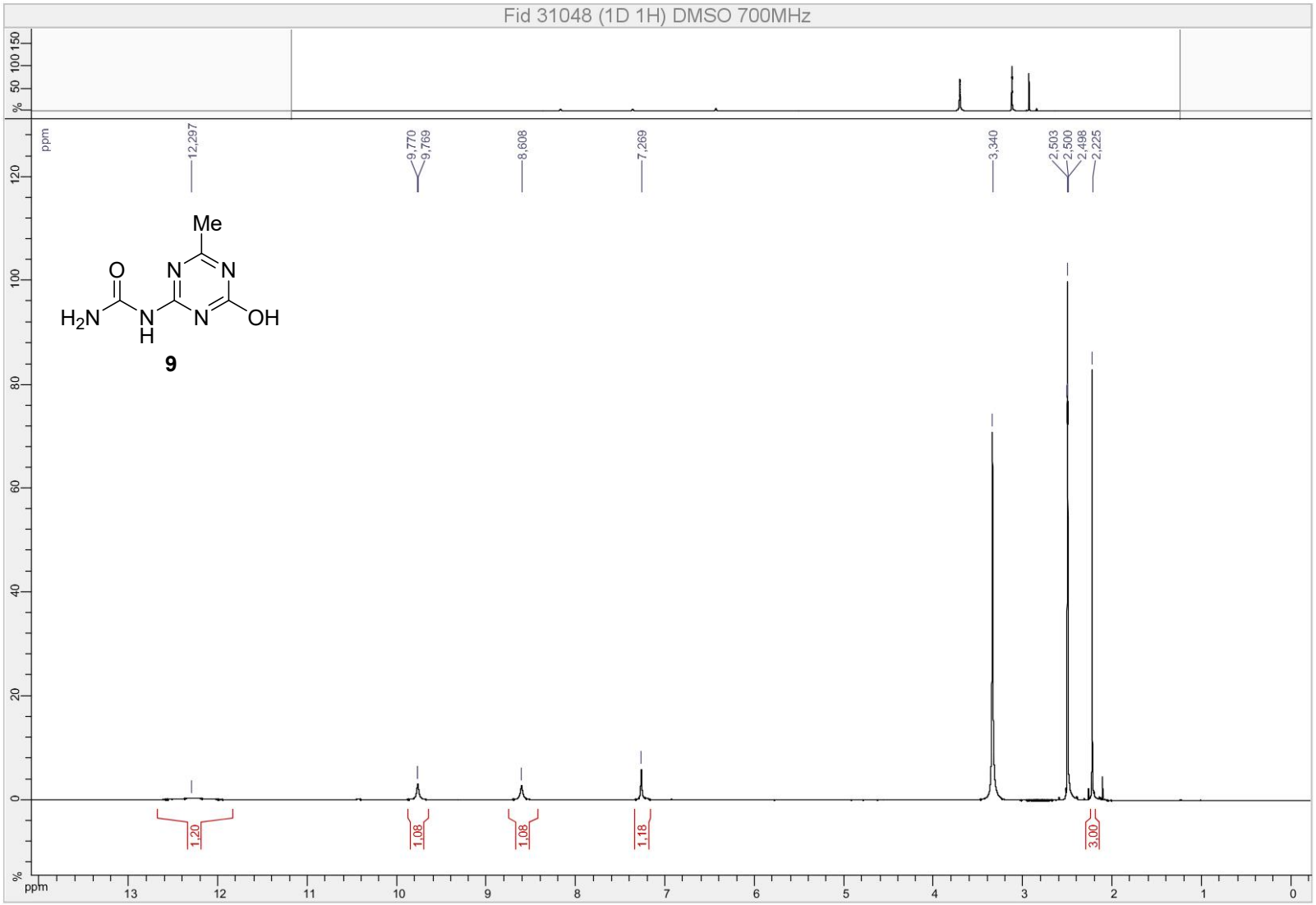
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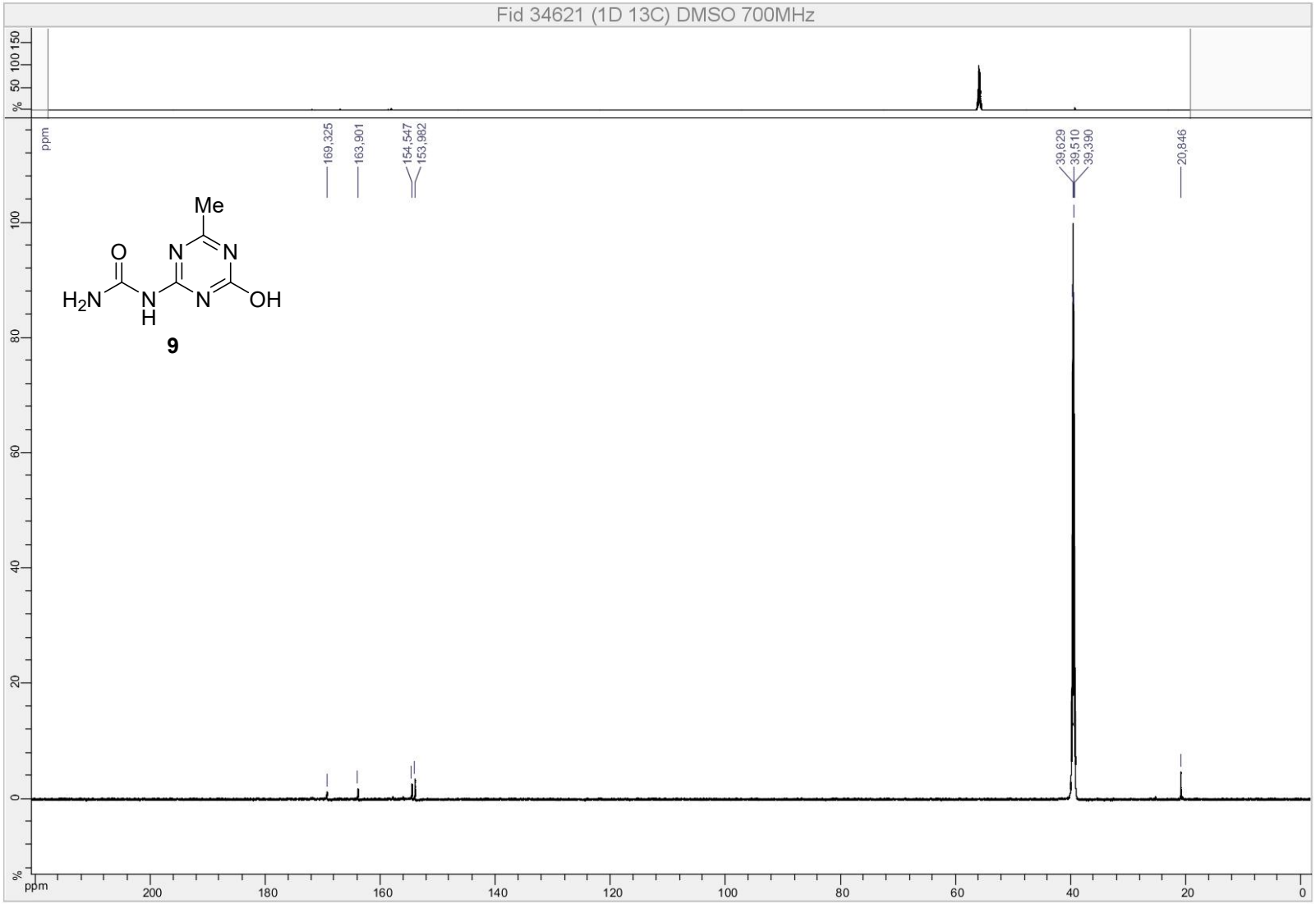
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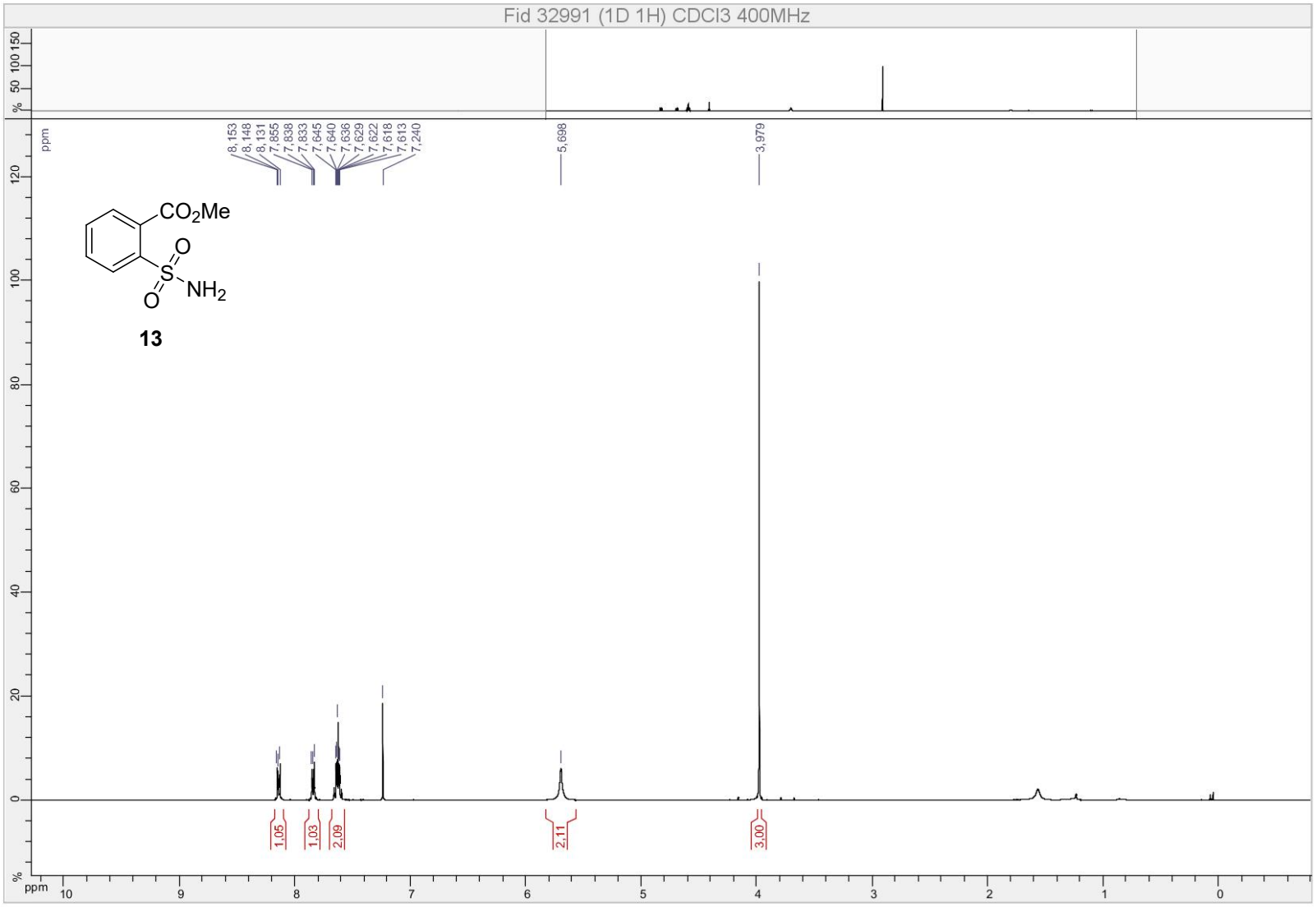
H2N
N
H
N
OH
9
ppm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7,240
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O
NH2
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2,09
2,11
3,00
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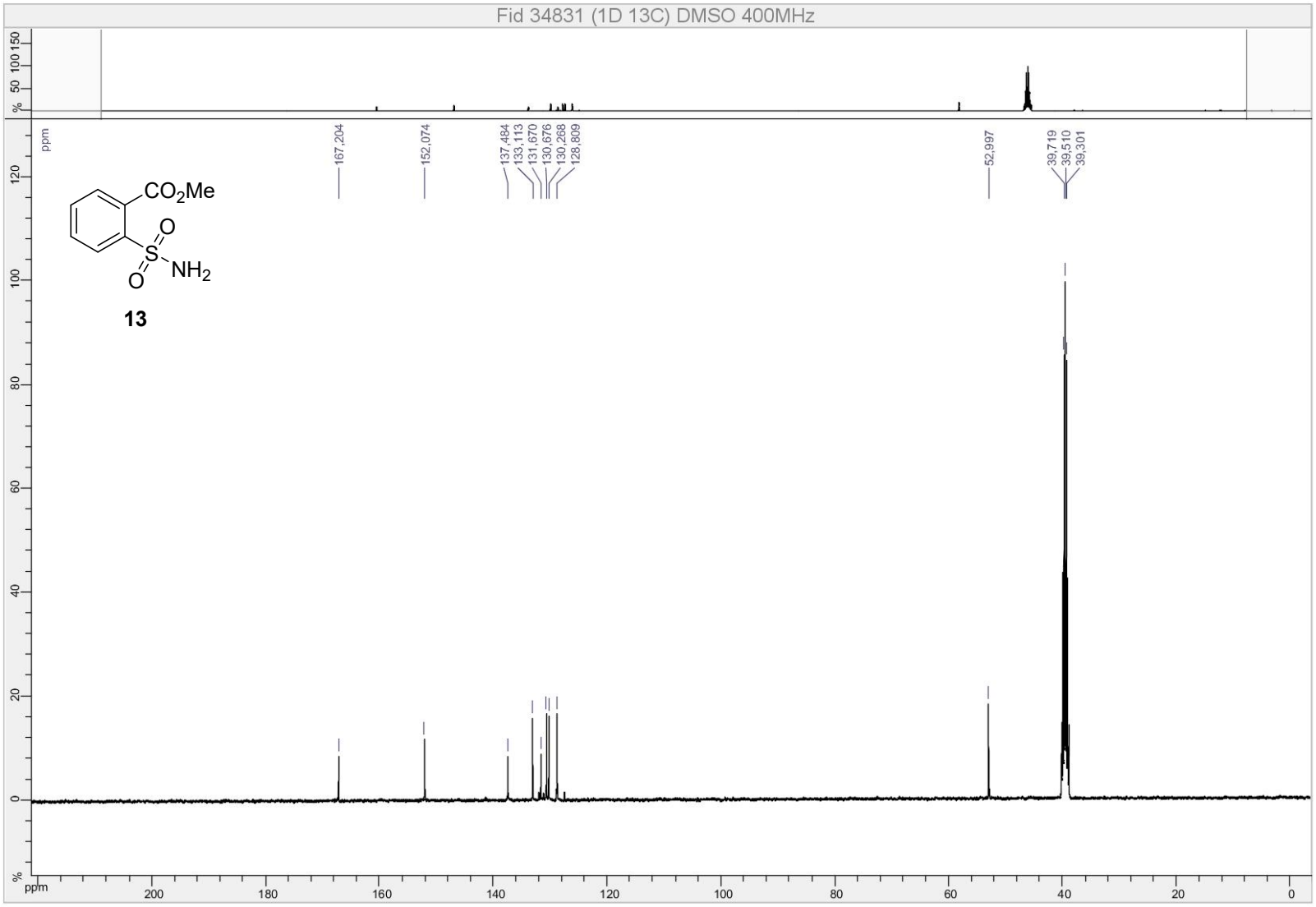
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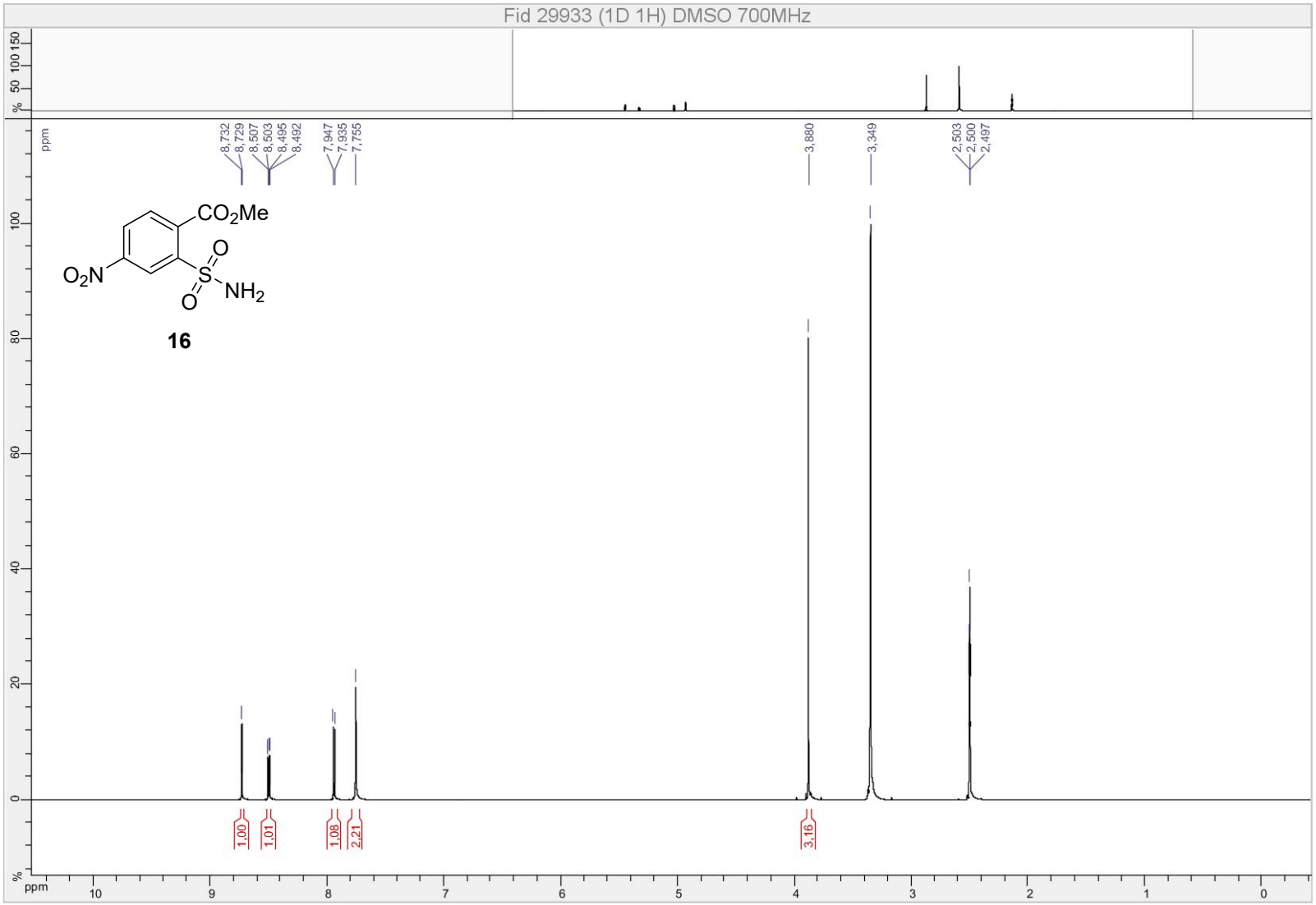
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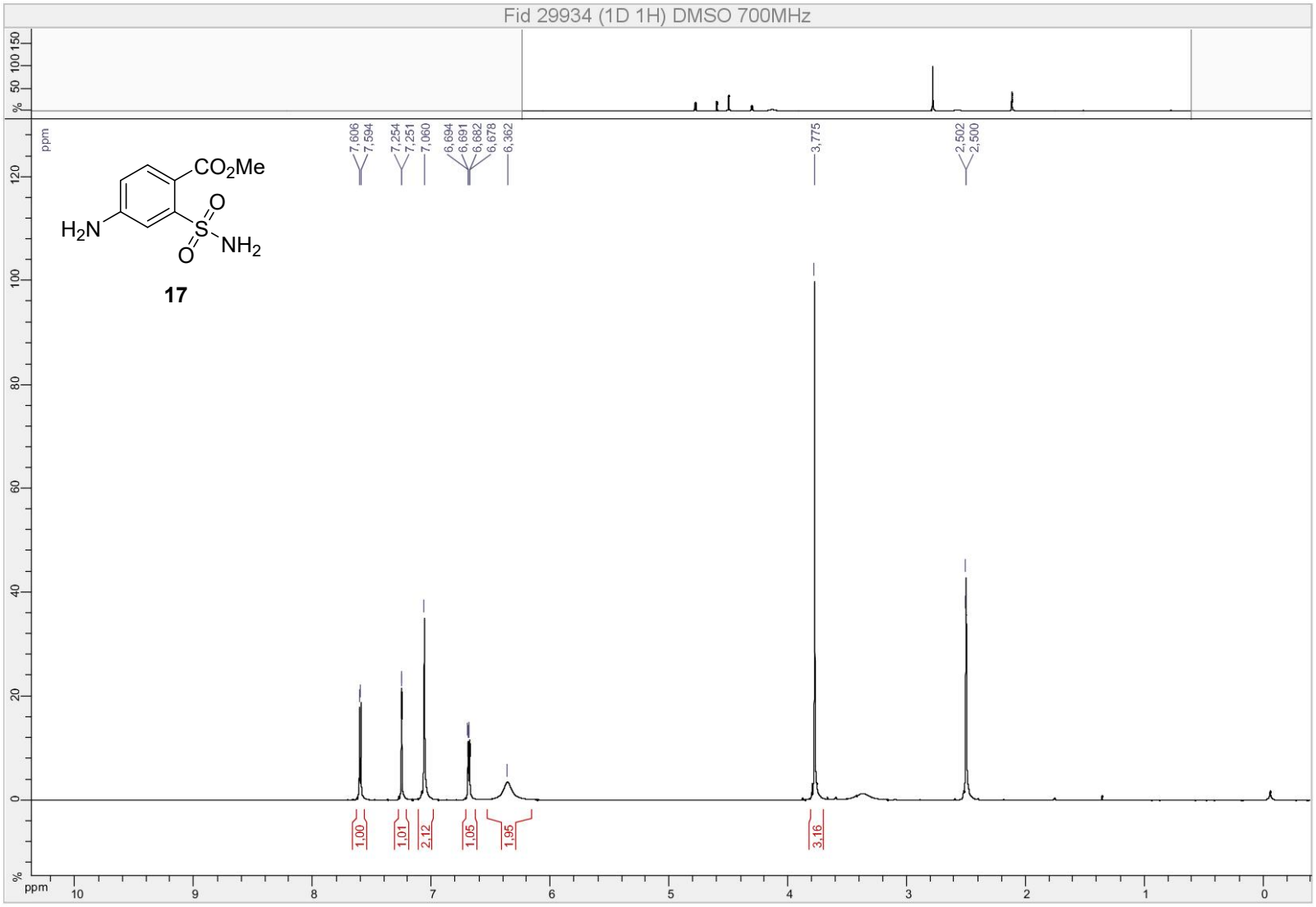
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2,502
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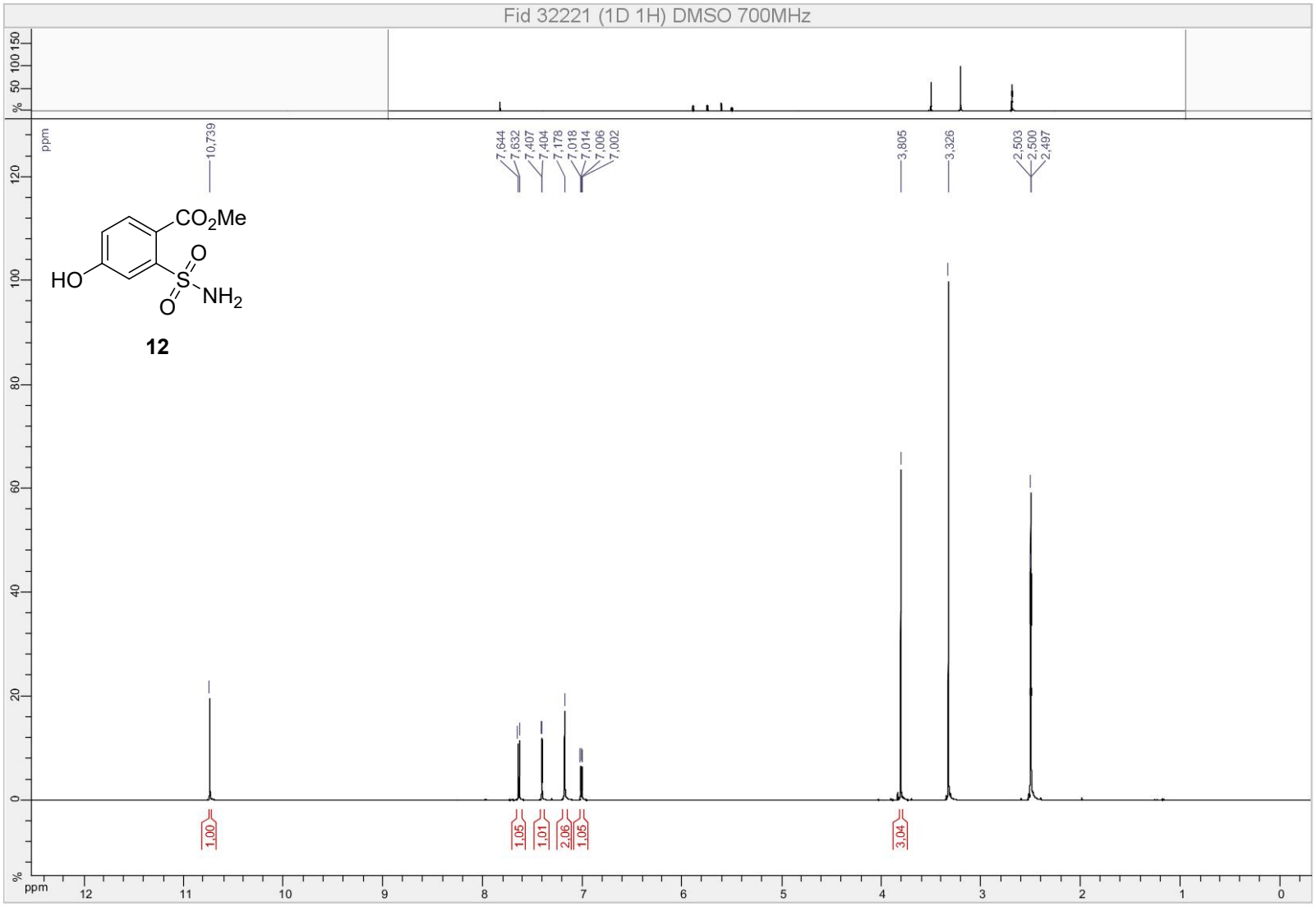
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7,002
3,805
3,326
2,503
2,500
2,497
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O
S
O
NH2
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1.01
2.06
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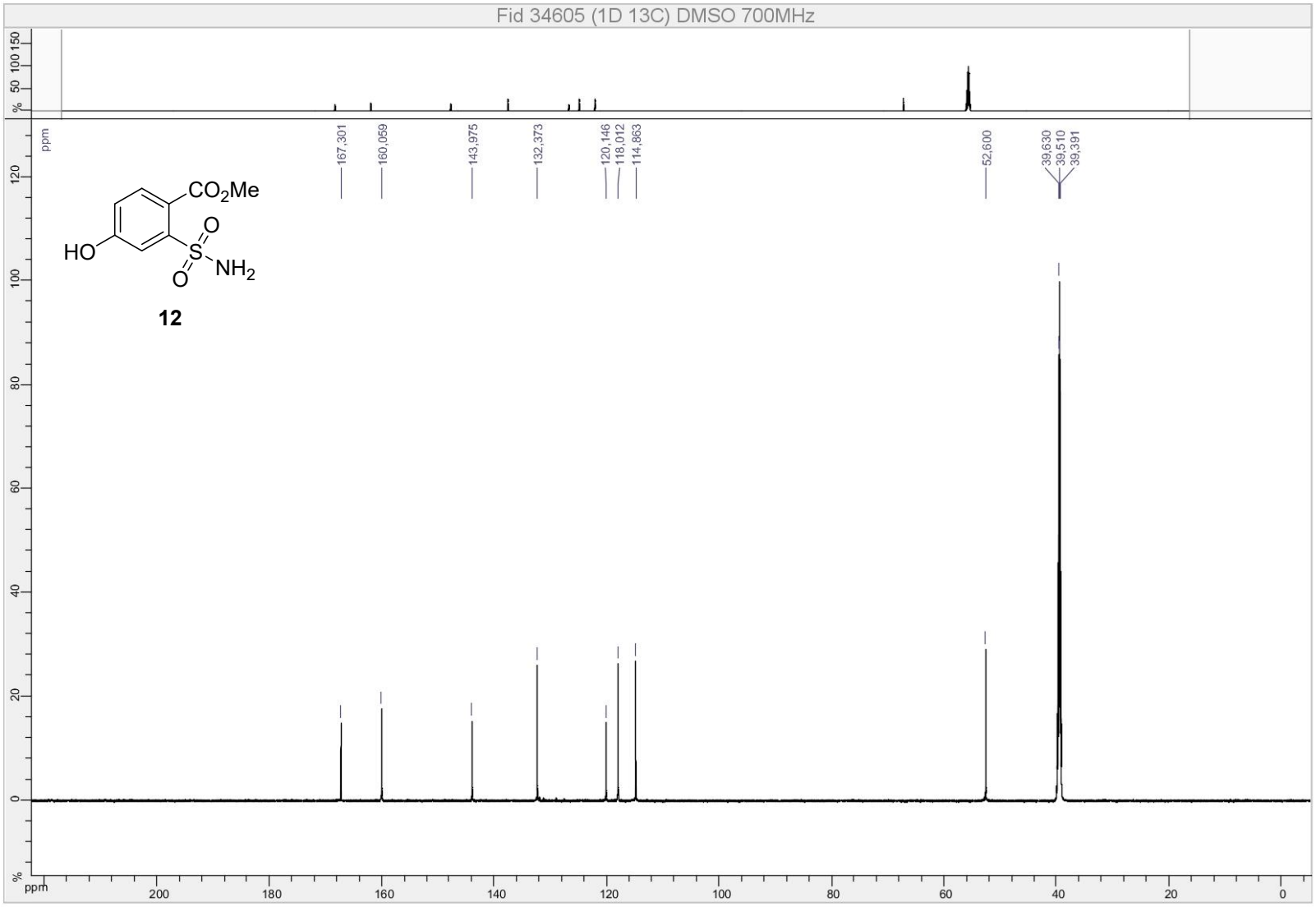
ppm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S
O
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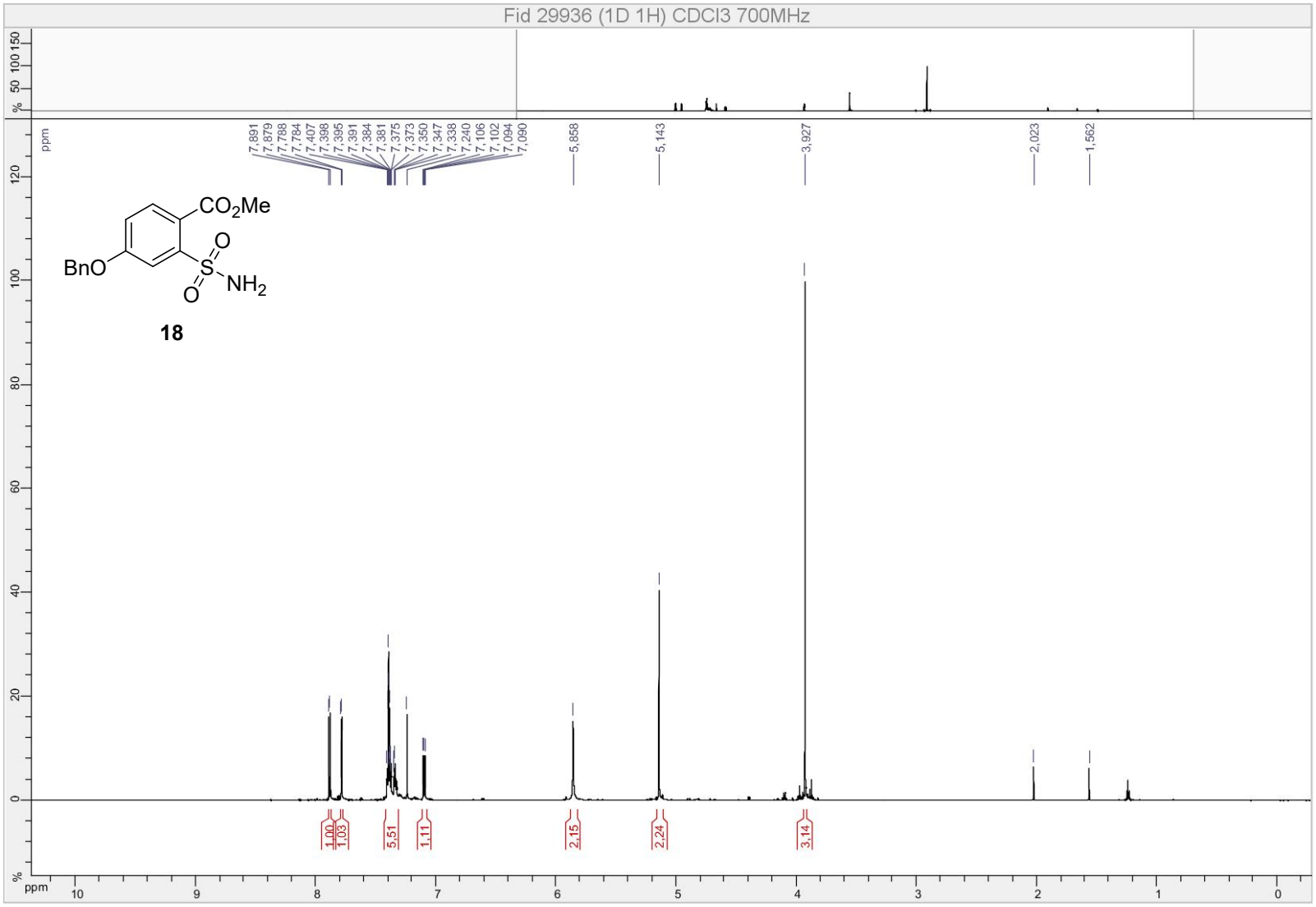
NH2
12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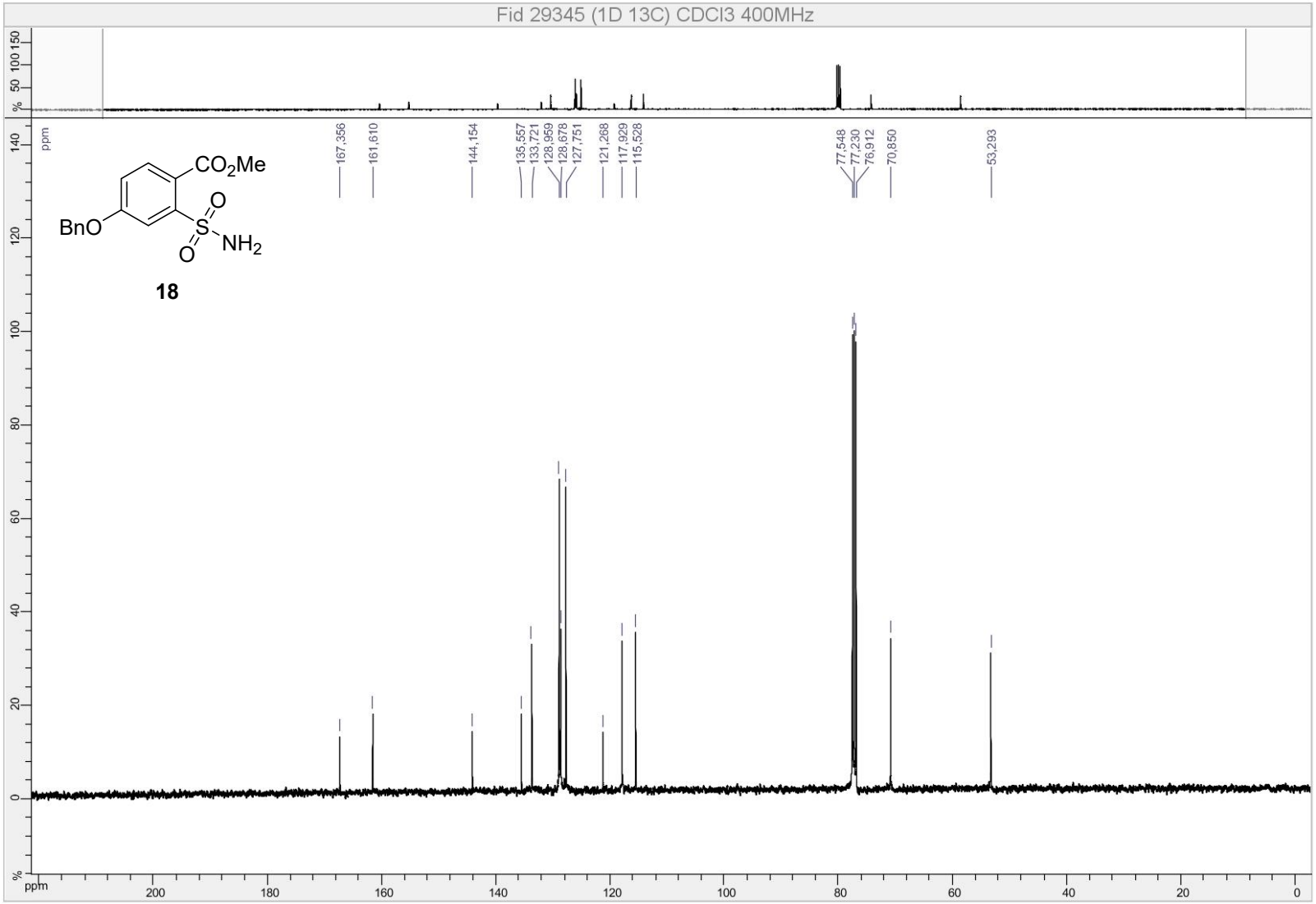
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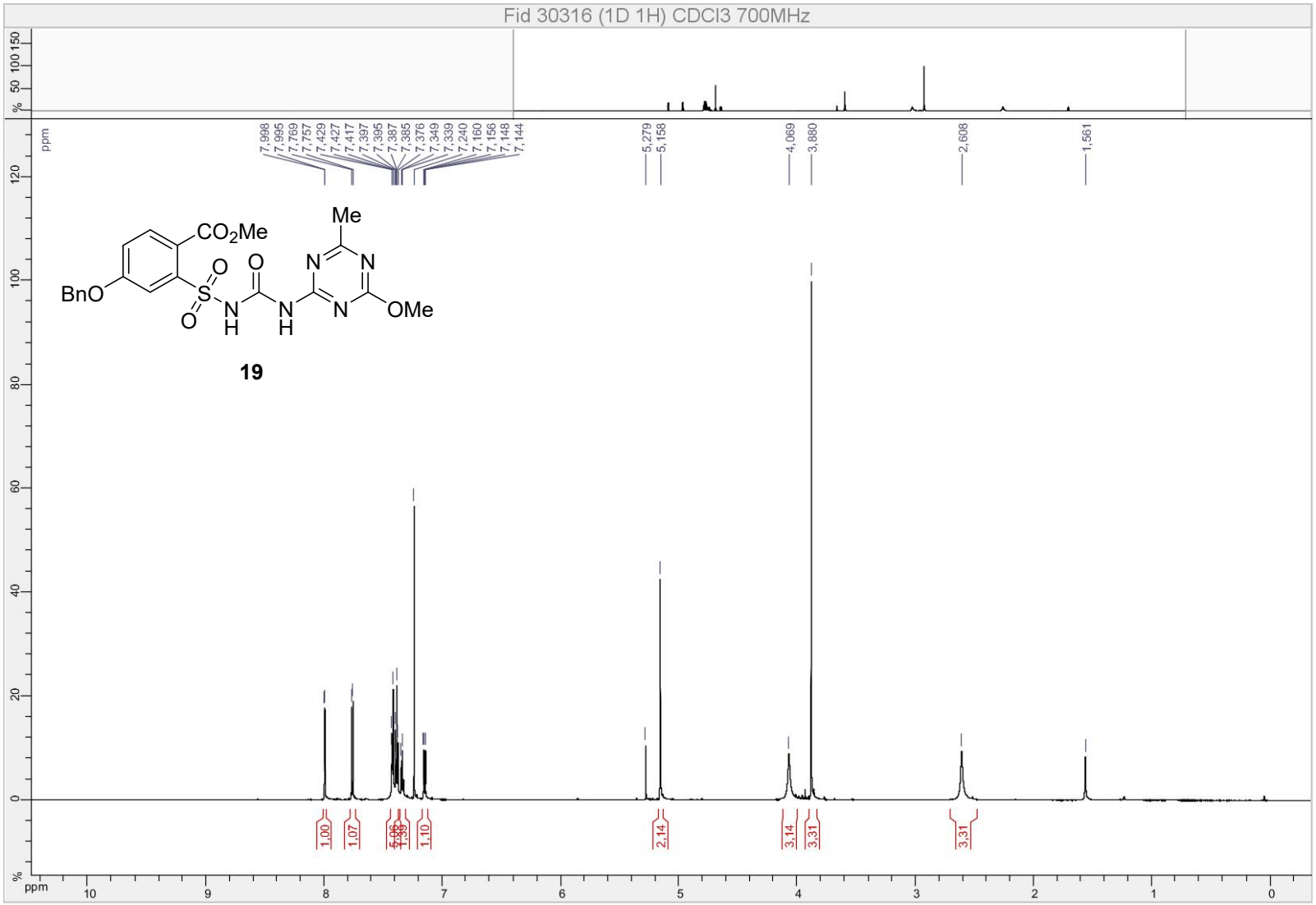
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7,387
7,385
7,376
7,349
7,339
7,240
7,160
7,156
7,148
7,144
5,279
5,158
4,069
3,880
2,608
1,561
CO2Me
Me
BnO
OMe
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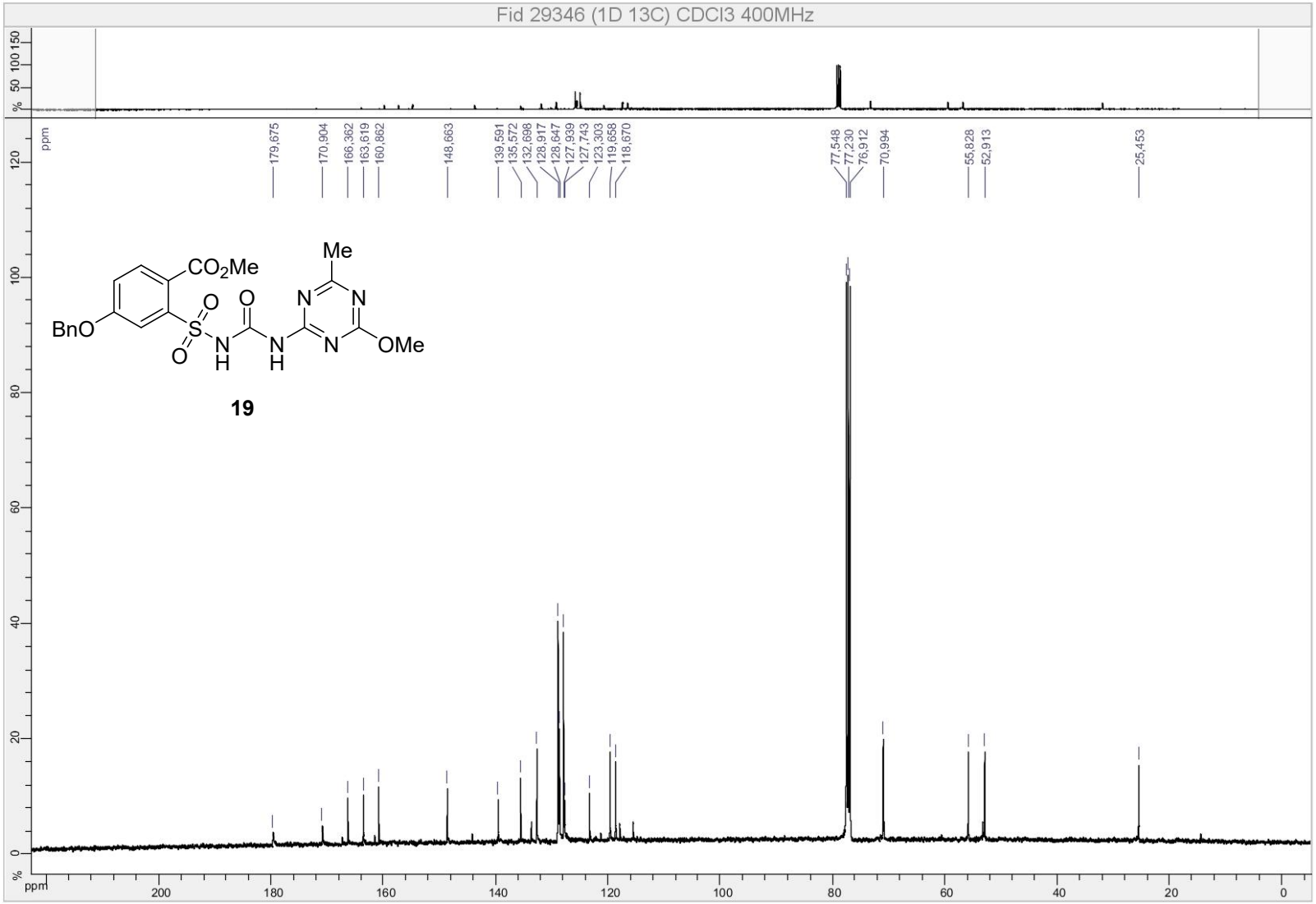
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128,647
127,939
127,743
123,303
119,658
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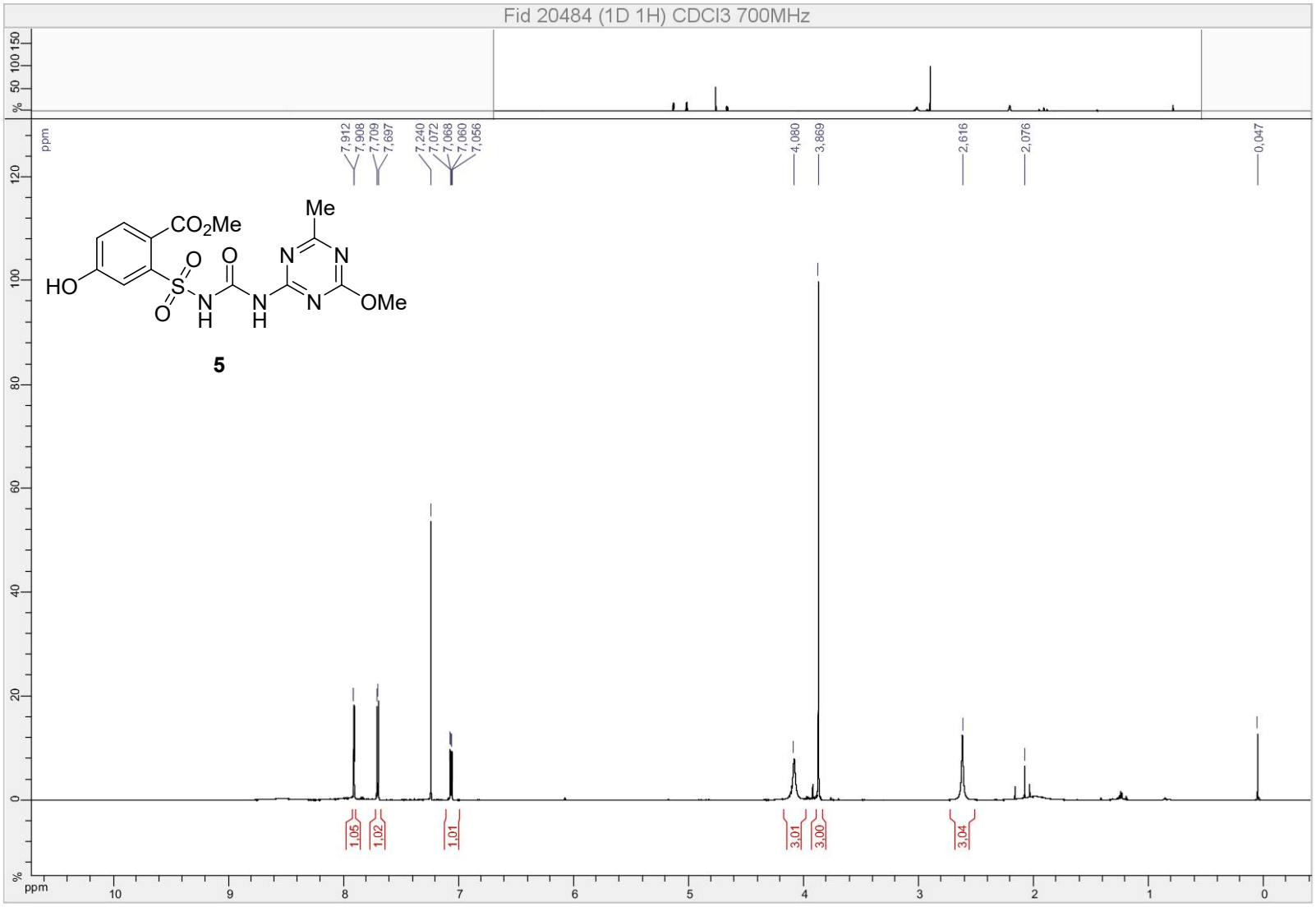
BnO
OMe
19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S
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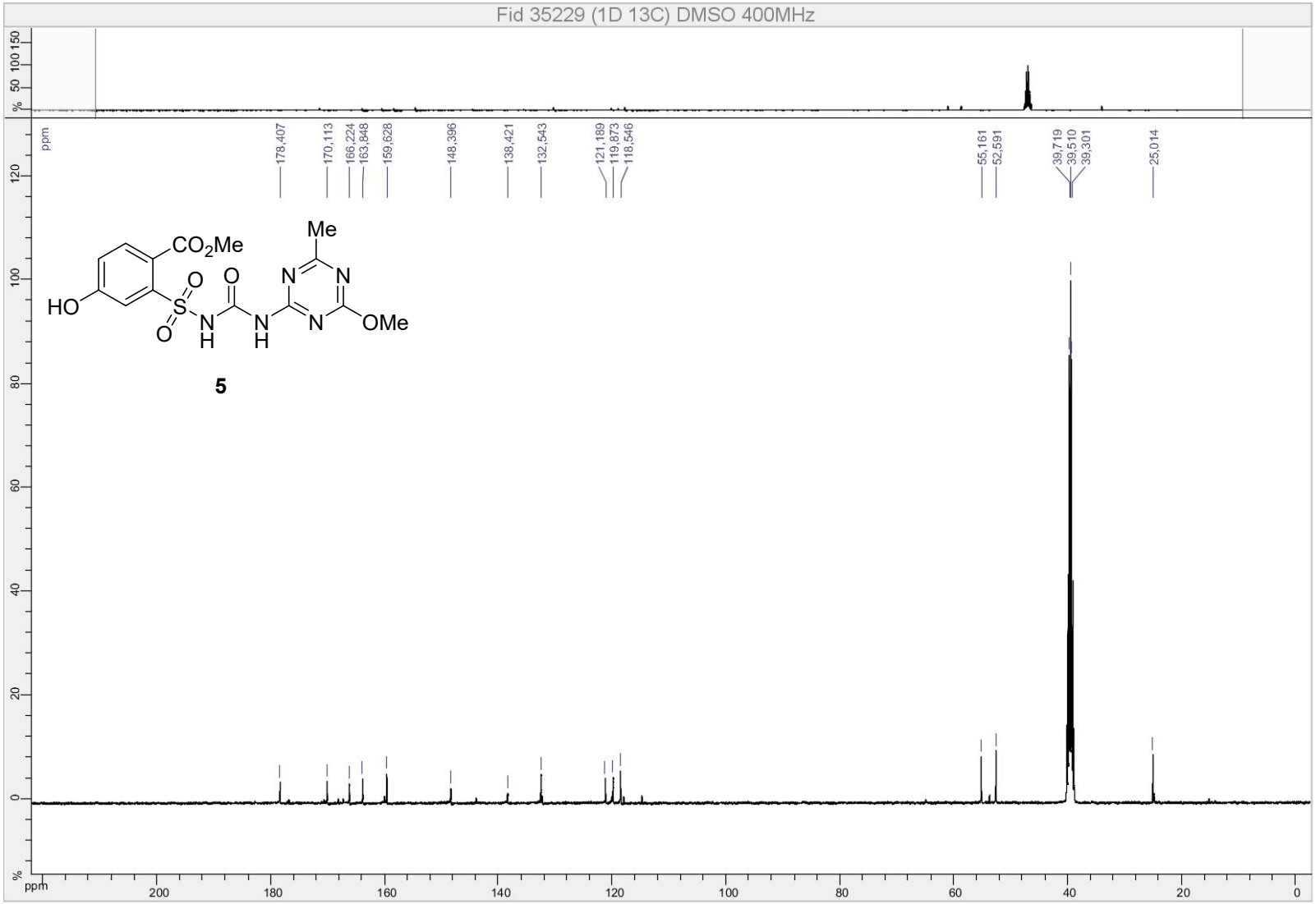
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HO
OMe
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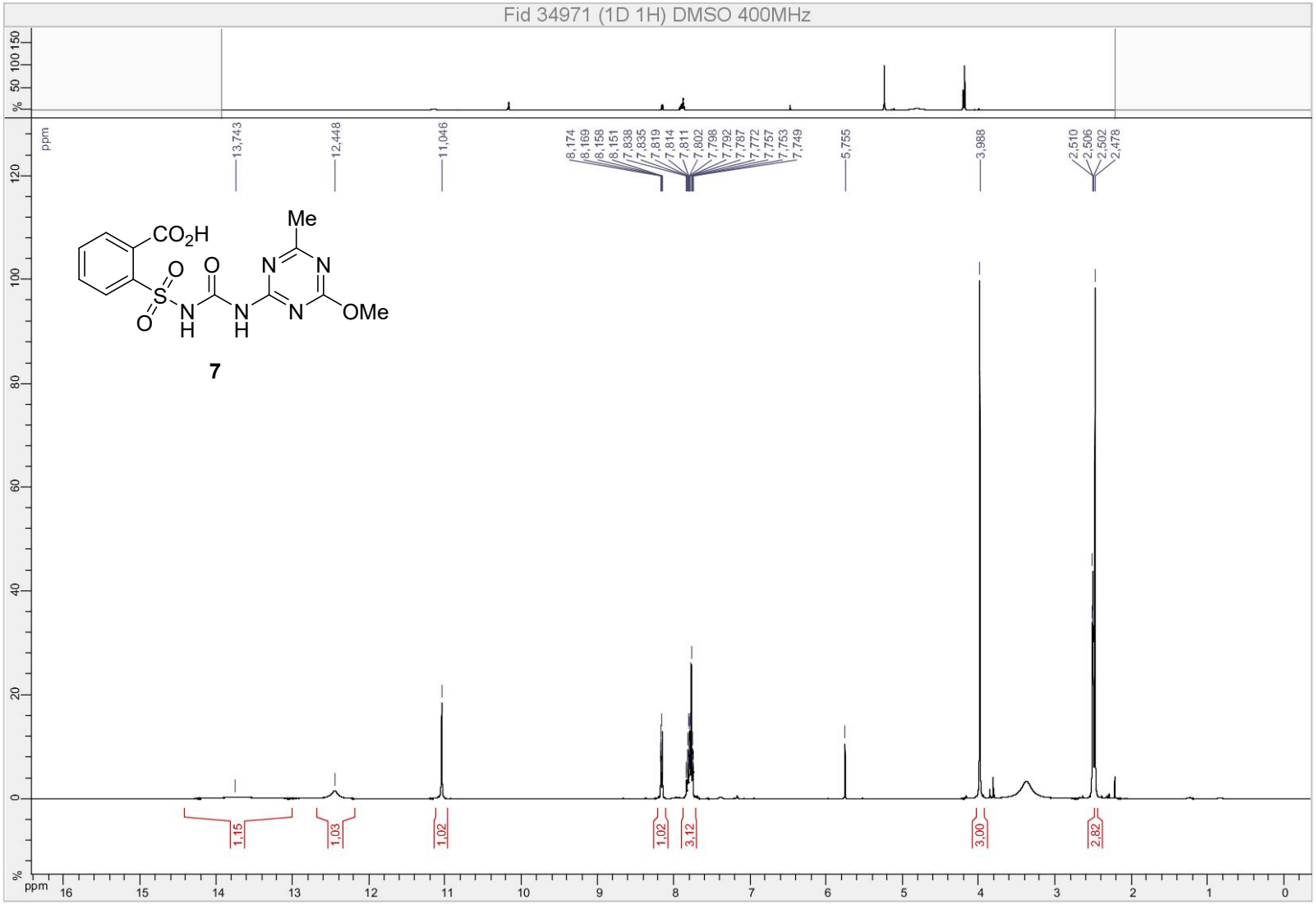
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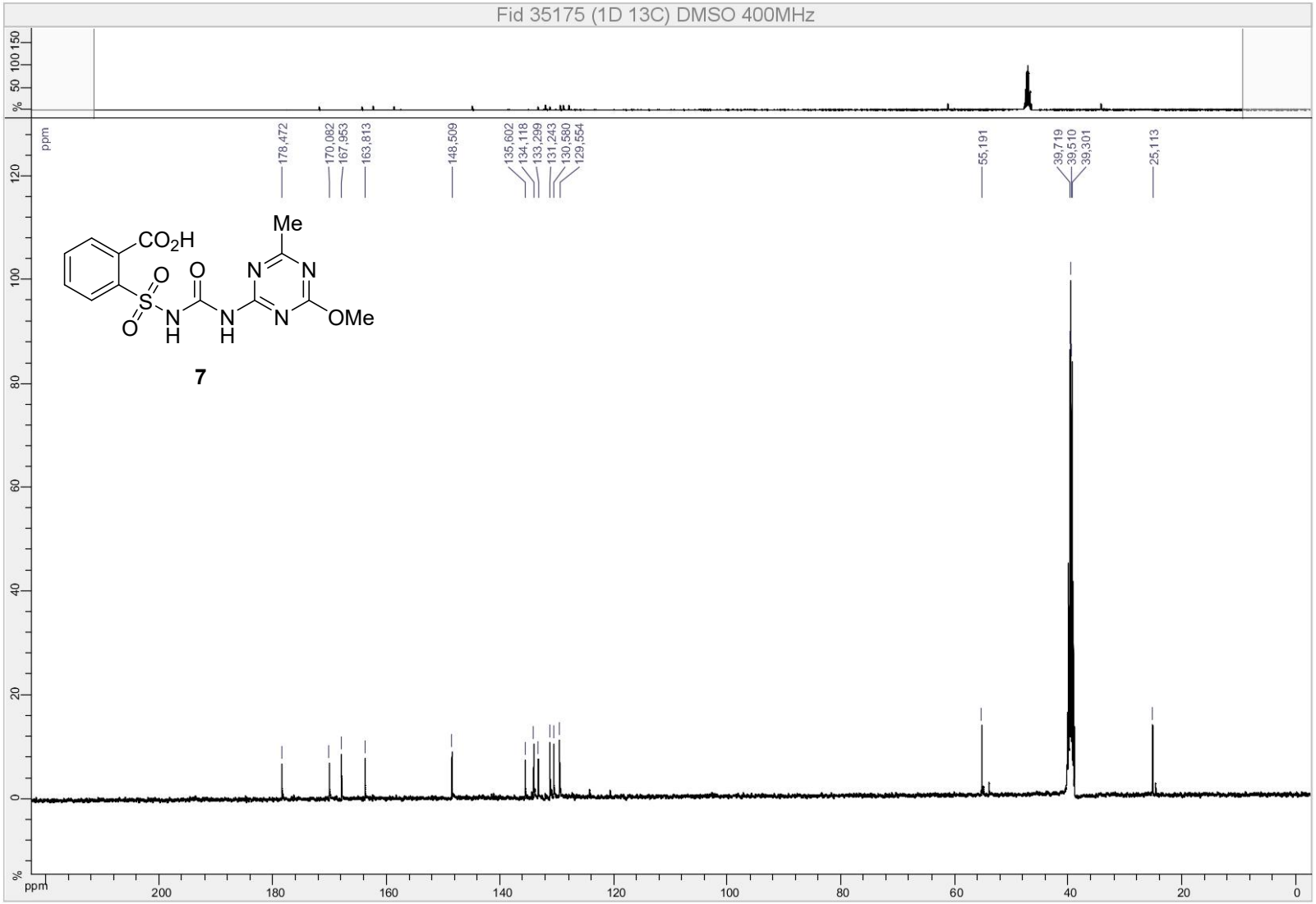
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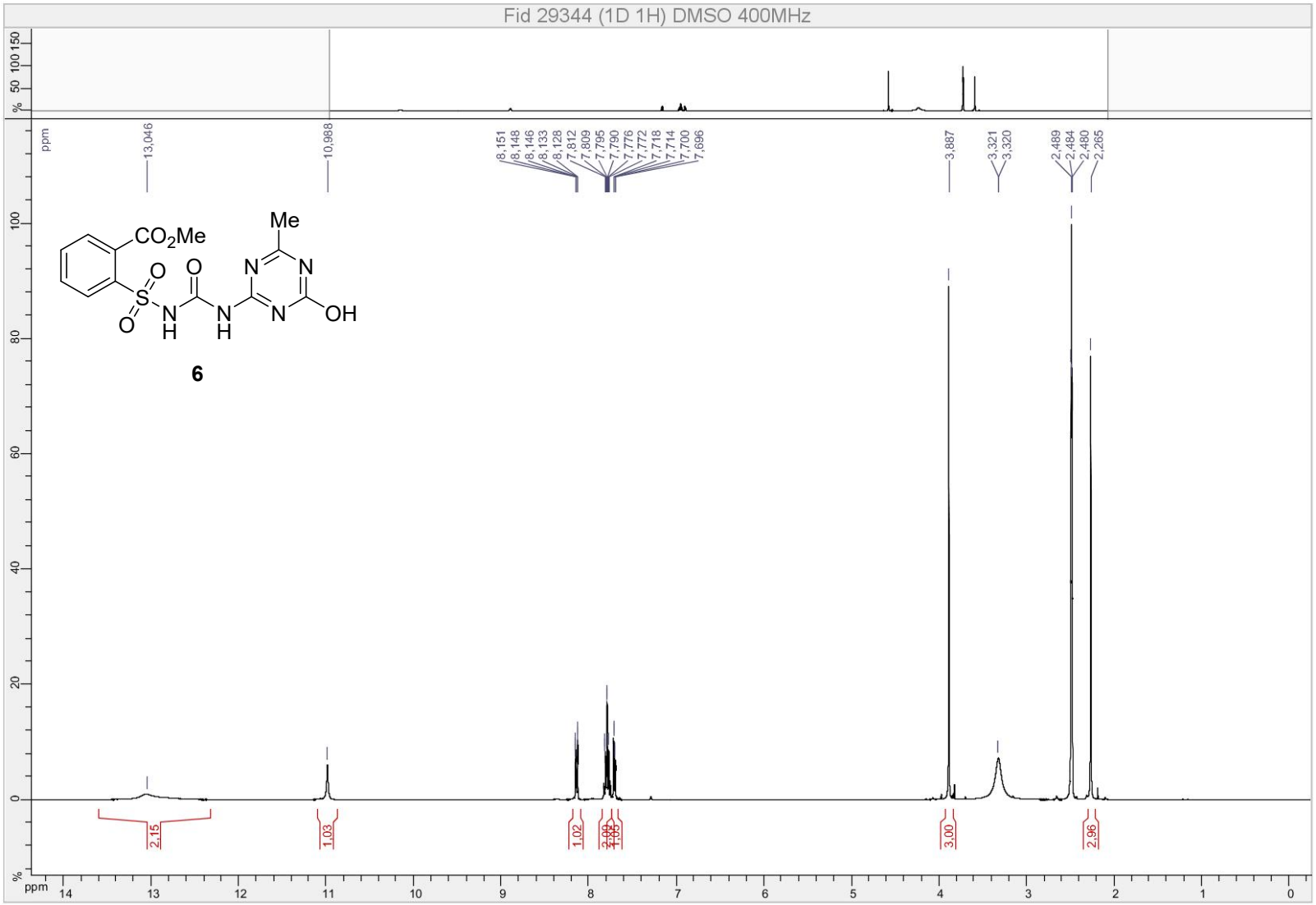
Me
OMe
7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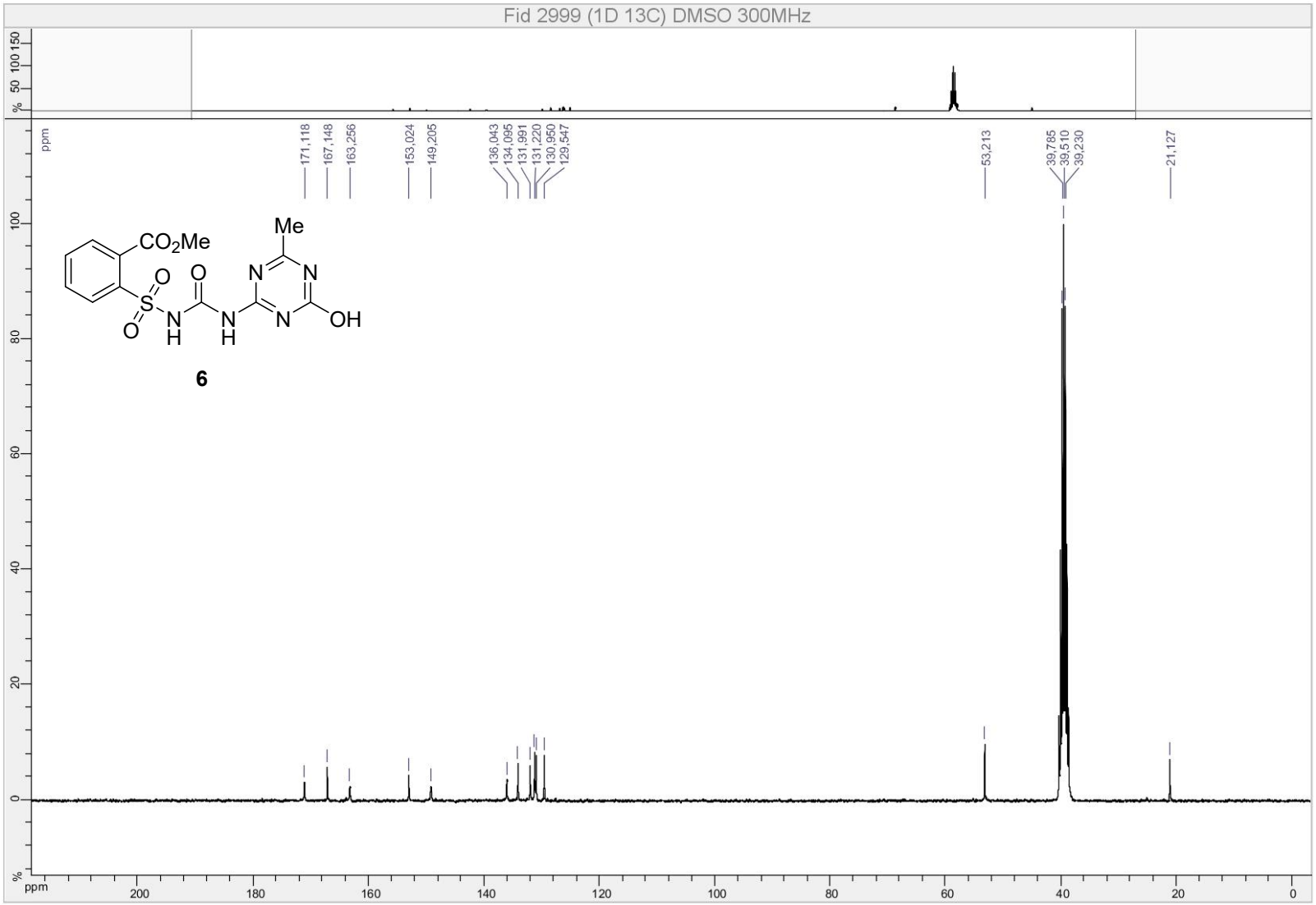
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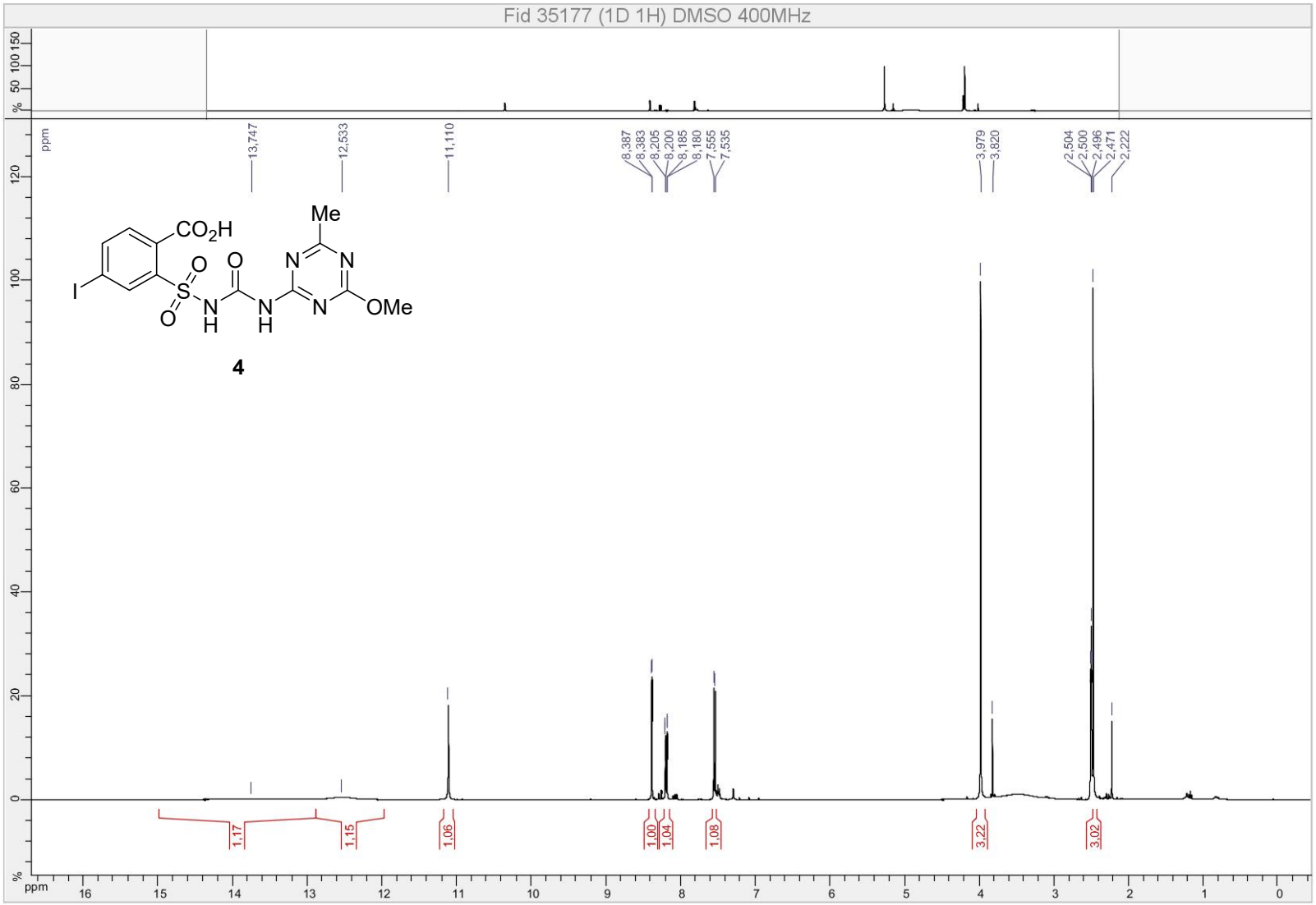
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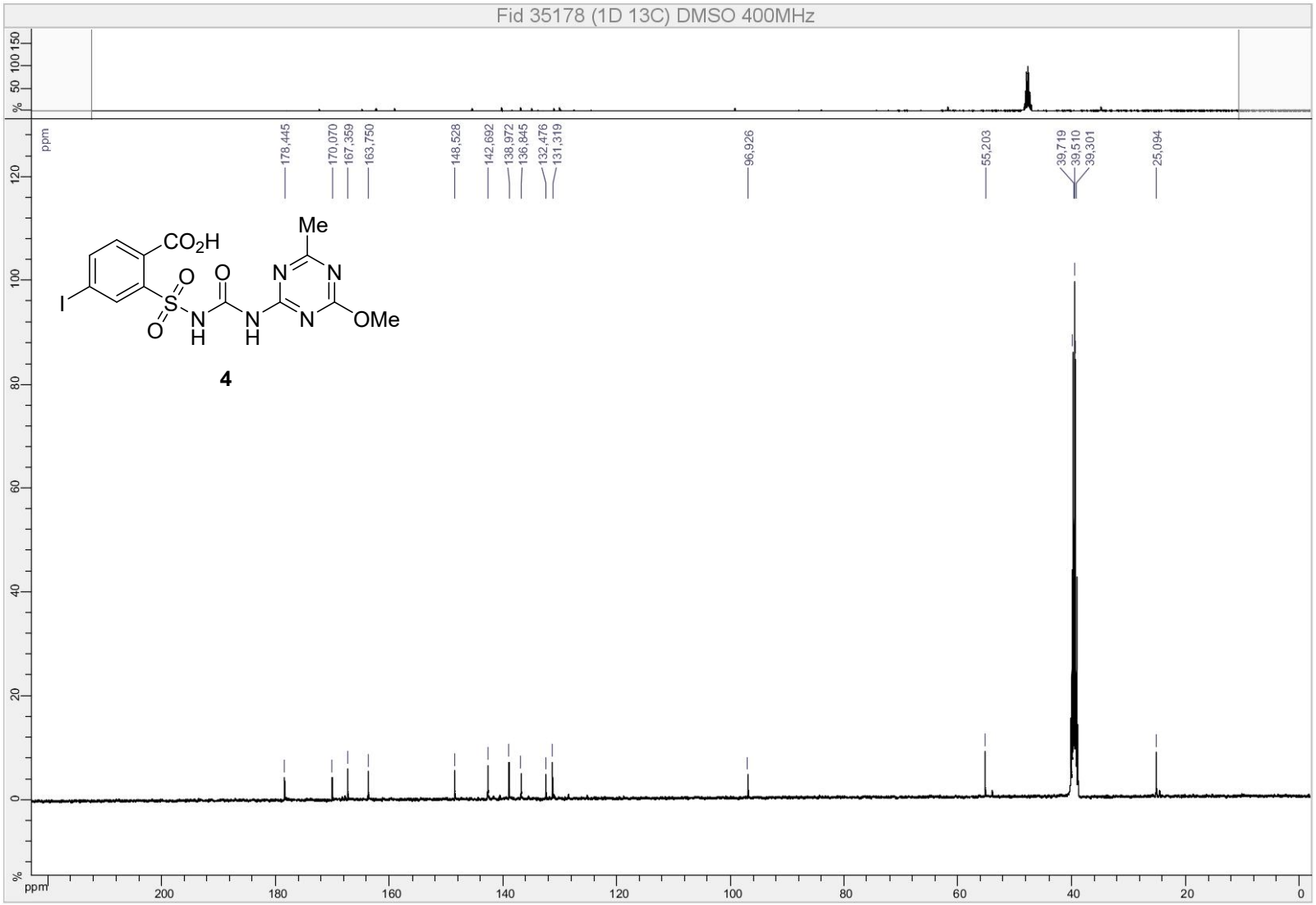
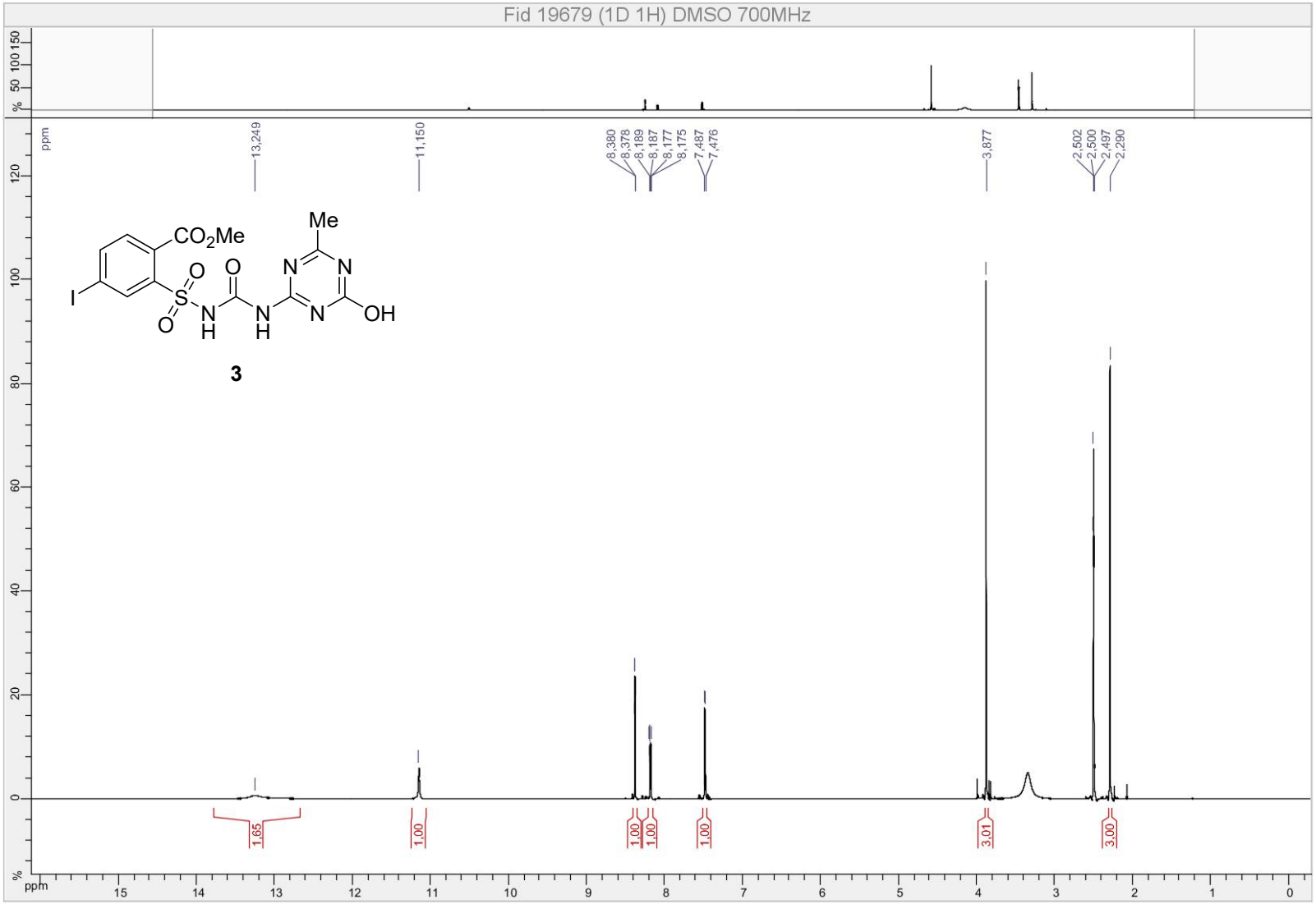
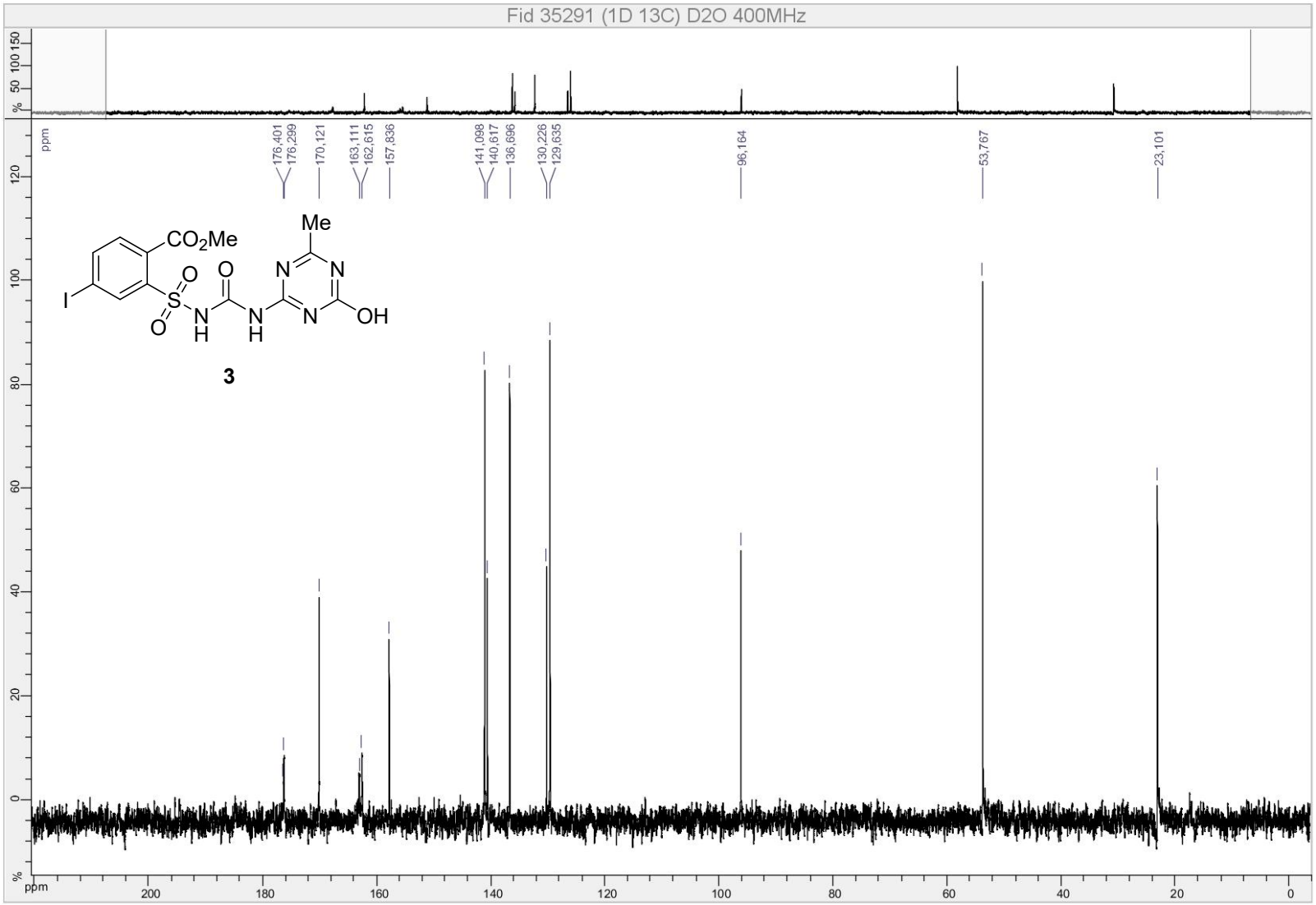
11,110
8,387
8,383
8,205
8,200
8,185
8,180
7,555
7,535
3,979
3,820
2,504
2,500
2,496
2,471
2,222
CO2H
I
S
O
N
H
O
N
H
N
N
N
Me
OMe
4
1,17
1,15
1,06
1,00
1,04
1,08
3,22
3,02
ppm


Fid 35178 (1D 13C) DMSO 400MHz
ppm
178,445
170,070
167,359
163,750
148,528
142,692
138,972
136,845
132,476
131,319
96,926
55,203
39,719
39,510
39,301
25,094
CO2H
Me
I
S
O
N
H
OMe
4


Fid 19679 (1D 1H) DMSO 700MHz
ppm
13,249
11,150
8,380
8,378
8,189
8,187
8,177
8,175
7,487
7,476
3,877
2,502
2,500
2,497
2,290
CO2Me
Me
I
O
O
S
O
N
H
O
N
H
N
N
N
OH
3
1,65
1,00
1,00
1,00
1,00
3,01
3,00


Fid 35291 (1D 13C) D2O 400MHz
ppm
176,401
176,299
170,121
163,111
162,615
157,836
141,098
140,617
136,696
130,226
129,635
96,164
53,767
23,101
CO2Me
Me
I
S
O
N
H
OH
3