Supporting Information

Hydro/Deutero Deamination of Arylazo Sulfones under Metal- and (Photo)Catalyst-Free Conditions

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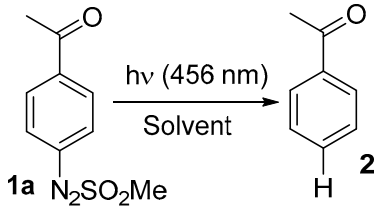
1 Optimization of the procedure for the reductive dediazoniation of arylazo sulfones.

Table S1. Irradiation of arylazosulfone **1a** in different solvents.[a]



Entry	Conditions	2 (% yield)
1	**1a** (0.025 M), MeOH	48
2	**1a** (0.025 M), MeOH-H_2O 9:1	50
3	**1a** (0.025 M), MeOH-H_2O 4:1	51
4	**1a** (0.025 M), MeCN	30
5	**1a** (0.025 M), MeCN-H_2O 9:1	38
6	**1a** (0.025 M), MeCN-H_2O 4:1	43
7	**1a** (0.025 M), Acetone	54[b]
8	**1a** (0.05 M), Acetone	49[b]
9	**1a** (0.1 M), Acetone	34[b]
10	**1a** (0.025 M), THF	59
11	**1a** (0.025 M), THF-H_2O 9:1	56
12	**1a** (0.025 M), THF-H_2O 4:1	61
13	**1a (0.025 M), *i*PrOH-H_2O 9:1**	**76**
14	**1a** (0.025 M), *i*PrOH-H_2O 4:1	71
15[c]	**1a** (0.025 M), *i*PrOH-H_2O 9:1	[c]

[a] A solution of **1a** in the chosen medium (1 mL) was nitrogen purged for 5 min, then irradiated by means of a 34 W Kessil Lamp (λ_{em} = 456 nm). The reaction course was monitored by GC analyses and the amount of **2** quantified by a calibration curve. [b] 4-Acetylphenyl methylsulfone (<10%) detected by GC-MS [c] Blank experiment, no consumption of **1a** observed.

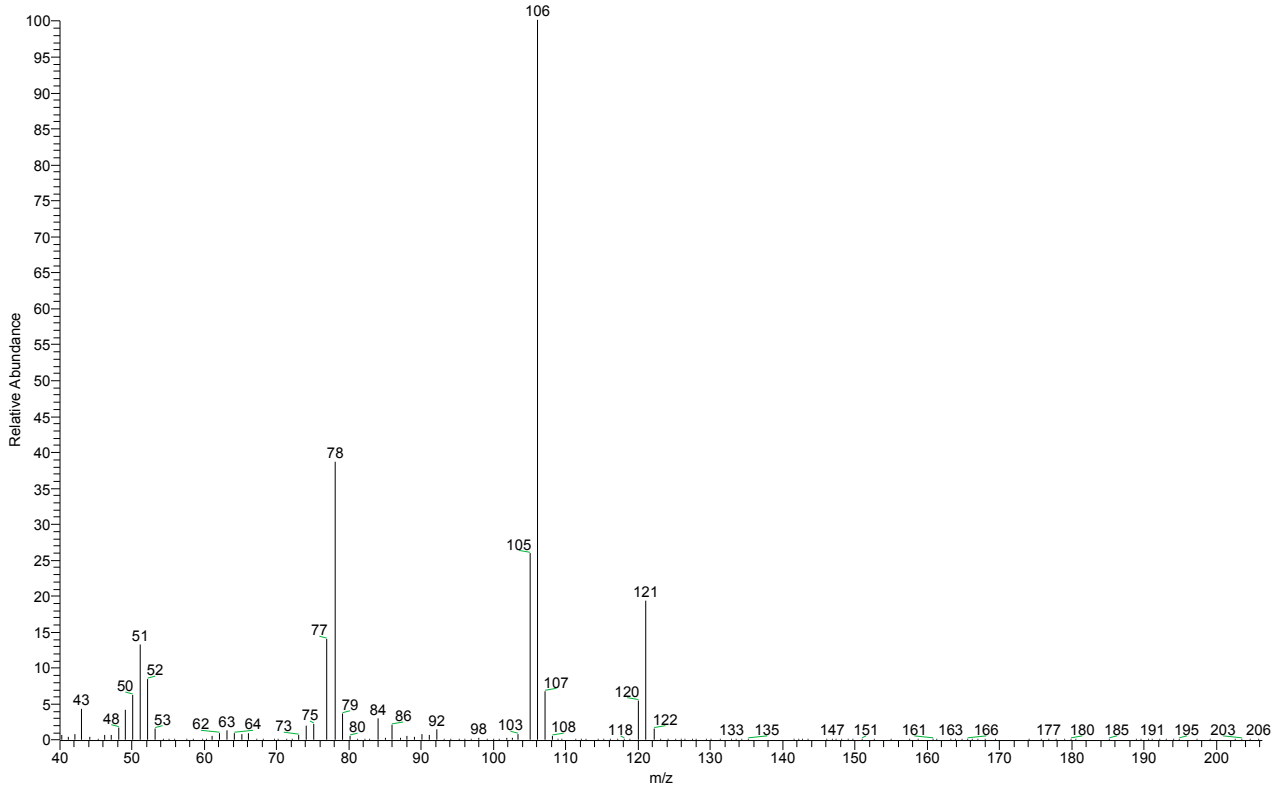
As depicted in Table S1, irradiation of a 0.025 M solution of **1a** in methanol as well as in different methanol-water mixtures (entries 1-3) afforded a moderate yield of acetophenone **2**. A similar behavior was observed in acetonitrile containing mixtures (entries 4-6), while when moving to acetone, a noxious effect on the yield of **2** was observed when increasing the concentration of **1a** (entries 7-9). Furthermore, small amounts (<10% yield) of the by-product 4-acetylphenyl methyl sulfone (GC-MS: 198 (6), 183 (100), 121 (54))[S1] were detected. Better yields were obtained by choosing THF as the (co)solvent (up to 61% yield, entries 10-12). However, when shifting to aqueous isopropanol (entries 13,14), conversion of **1a** to **2** was found to occur in a satisfactory yield (76% in

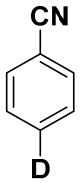
*i*PrOH-H_2O 9:1 mixture). Finally, no consumption of **1a** took place in the absence of irradiation (entry 15). The protocol described in entry 13 was thus adopted to investigate the versatility of the reaction.

2. MS spectra of compounds 2-d^1-14-d^1 and ^{1}H and ^{13}C NMR of 13-d^1

2-d^1

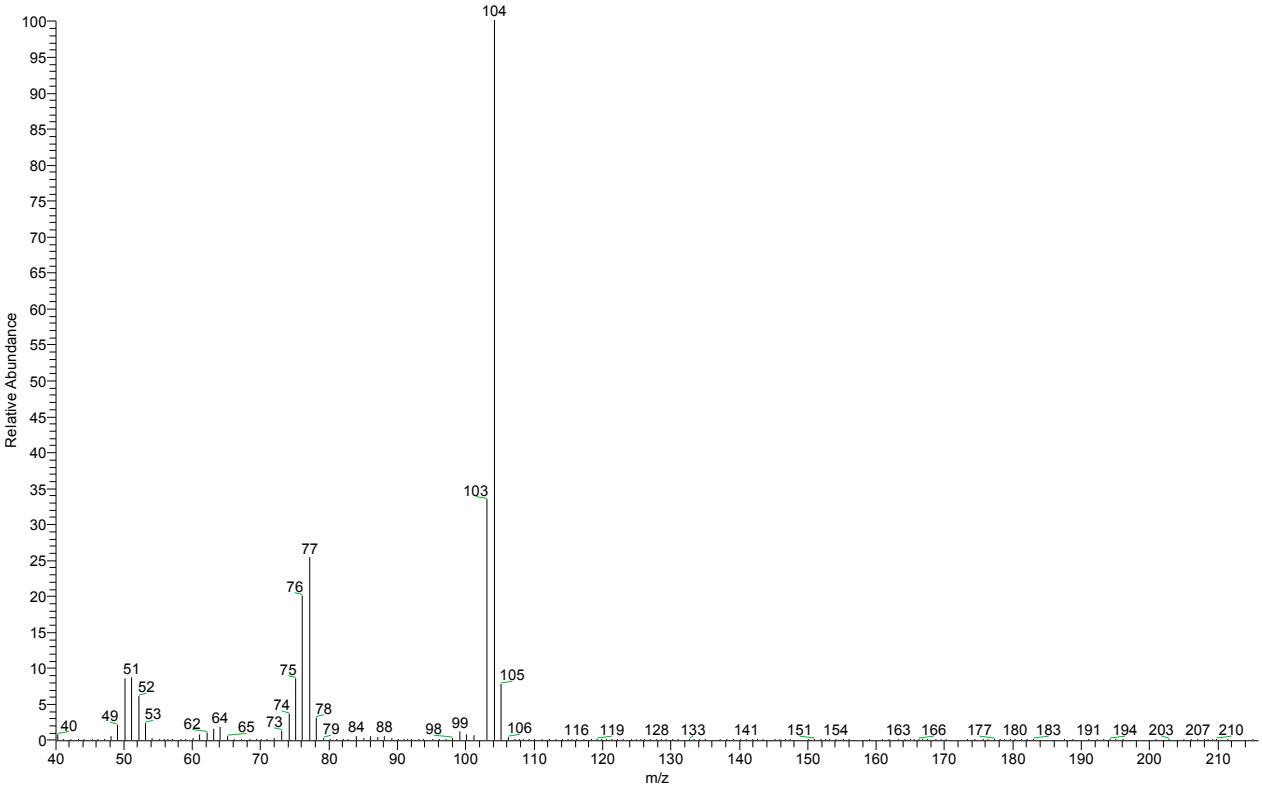
Reference: S2

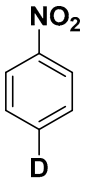




3-*d*^{1}

Reference: S3





4-*d*[1]

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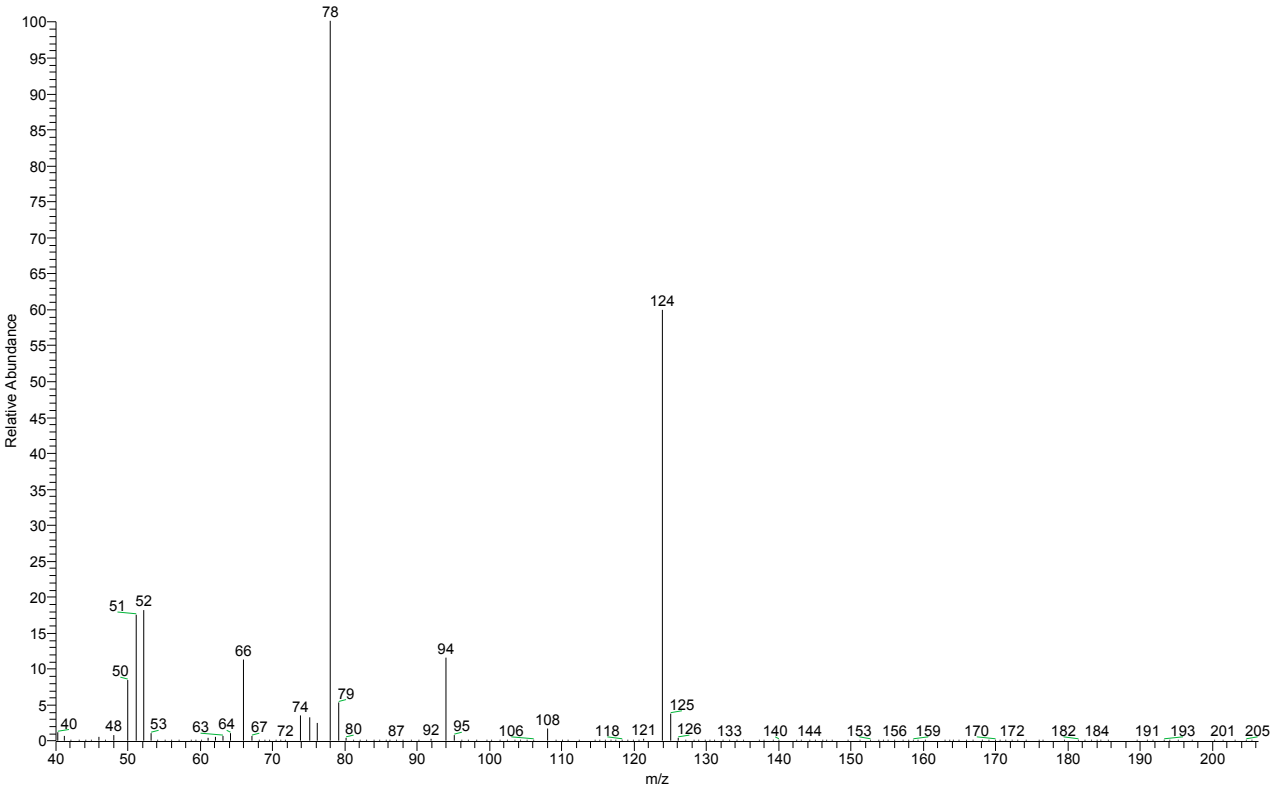

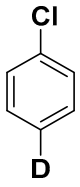

5-*d*[1]

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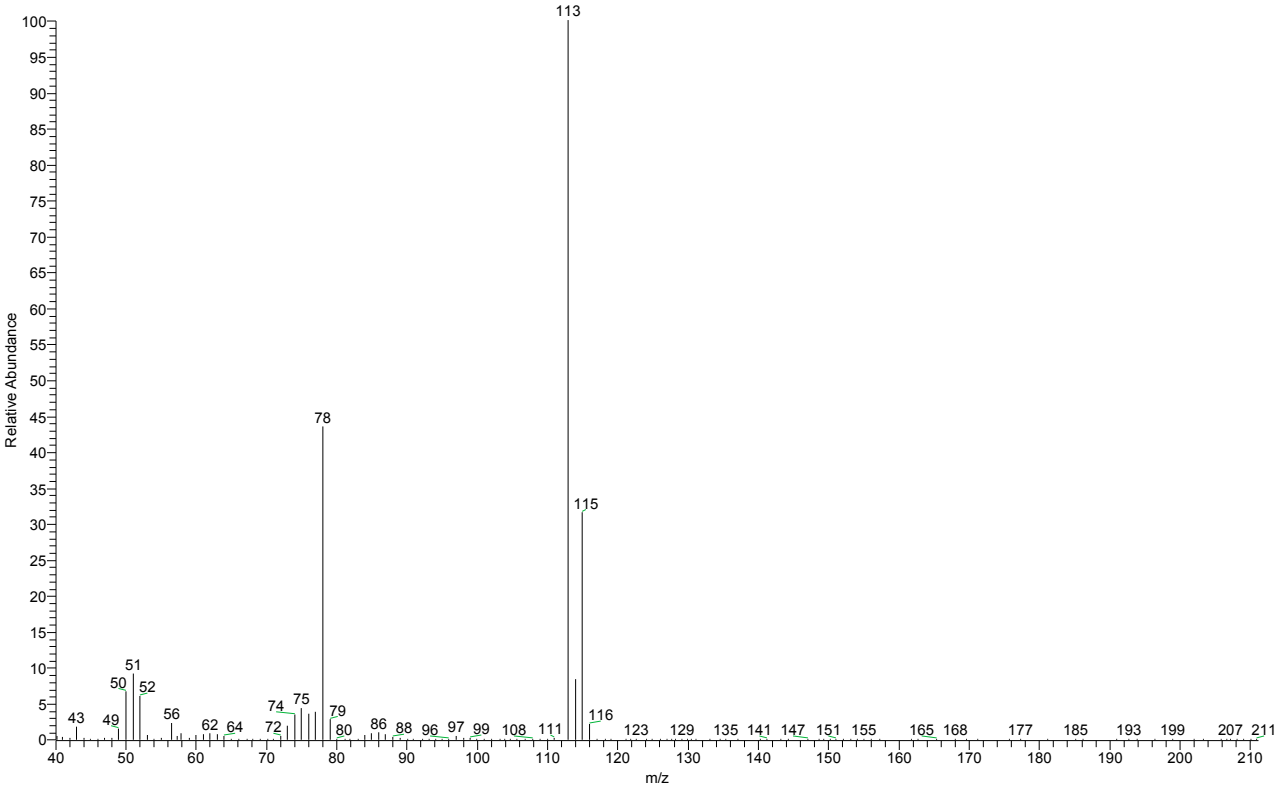

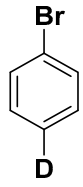

6-*d*^{1}

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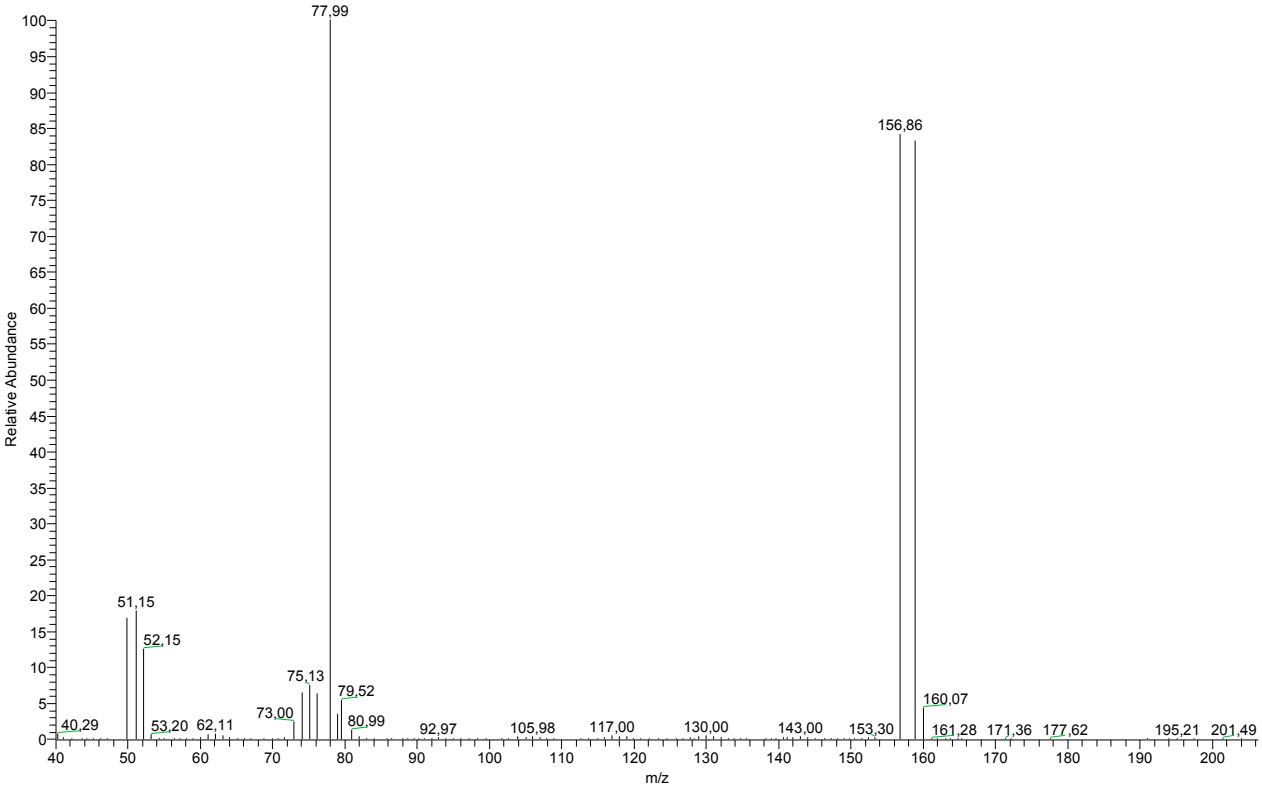

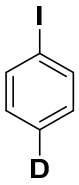

7-*d*^{1}

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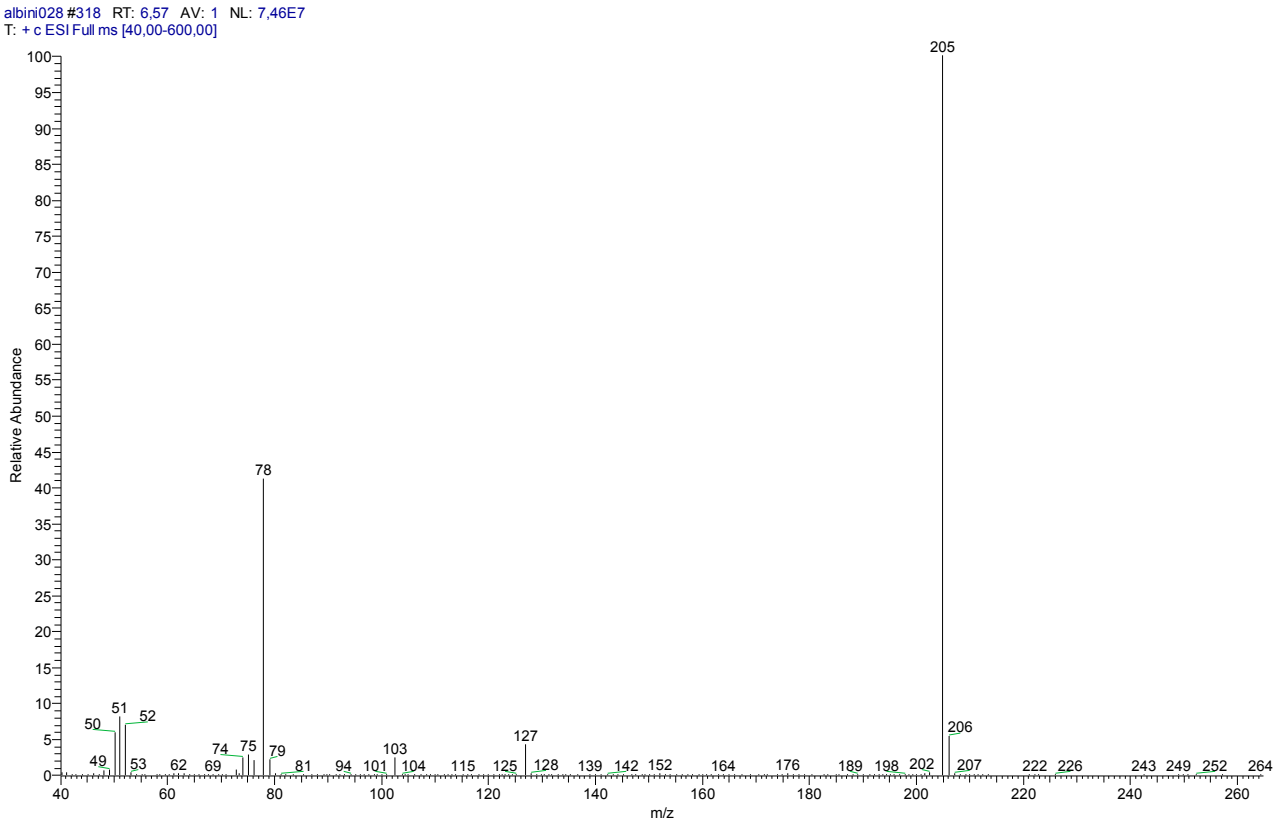

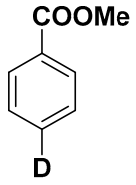

8-*d*^{1}

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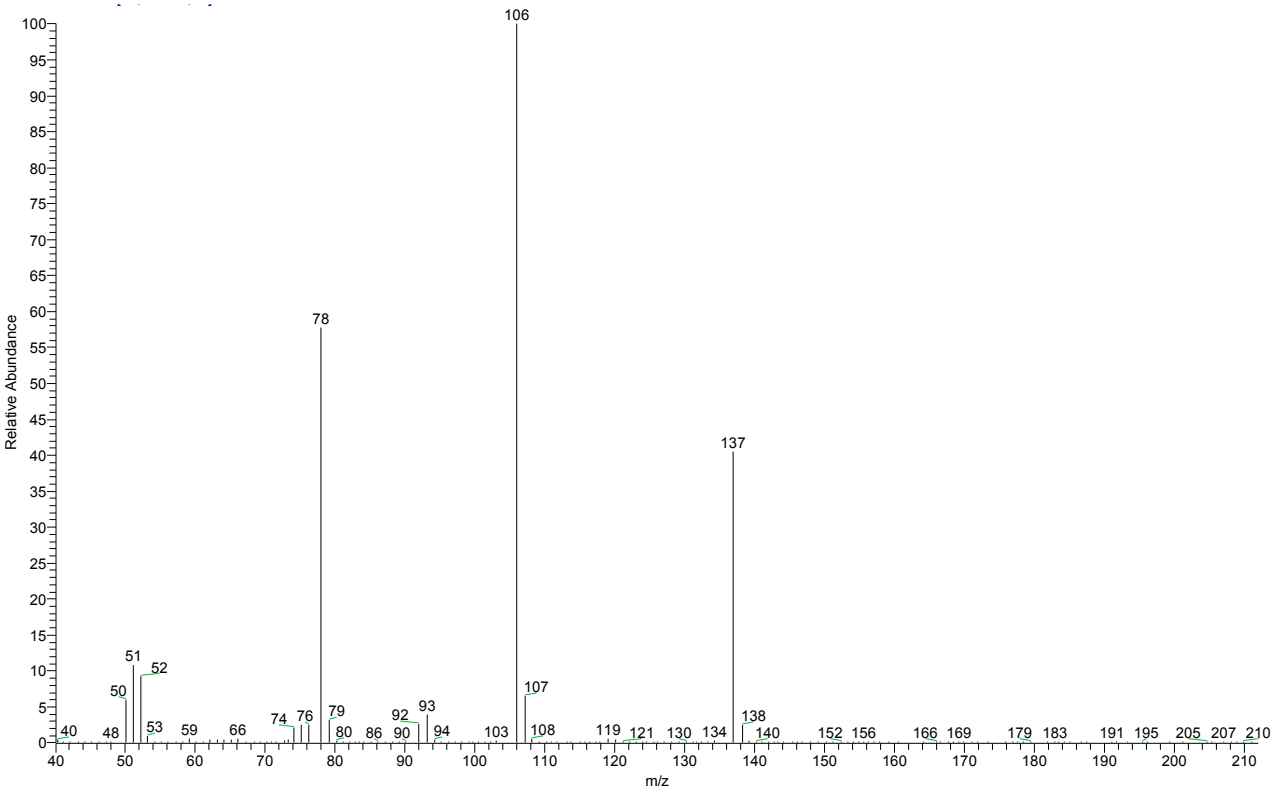

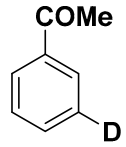

***2'-d*[1]**

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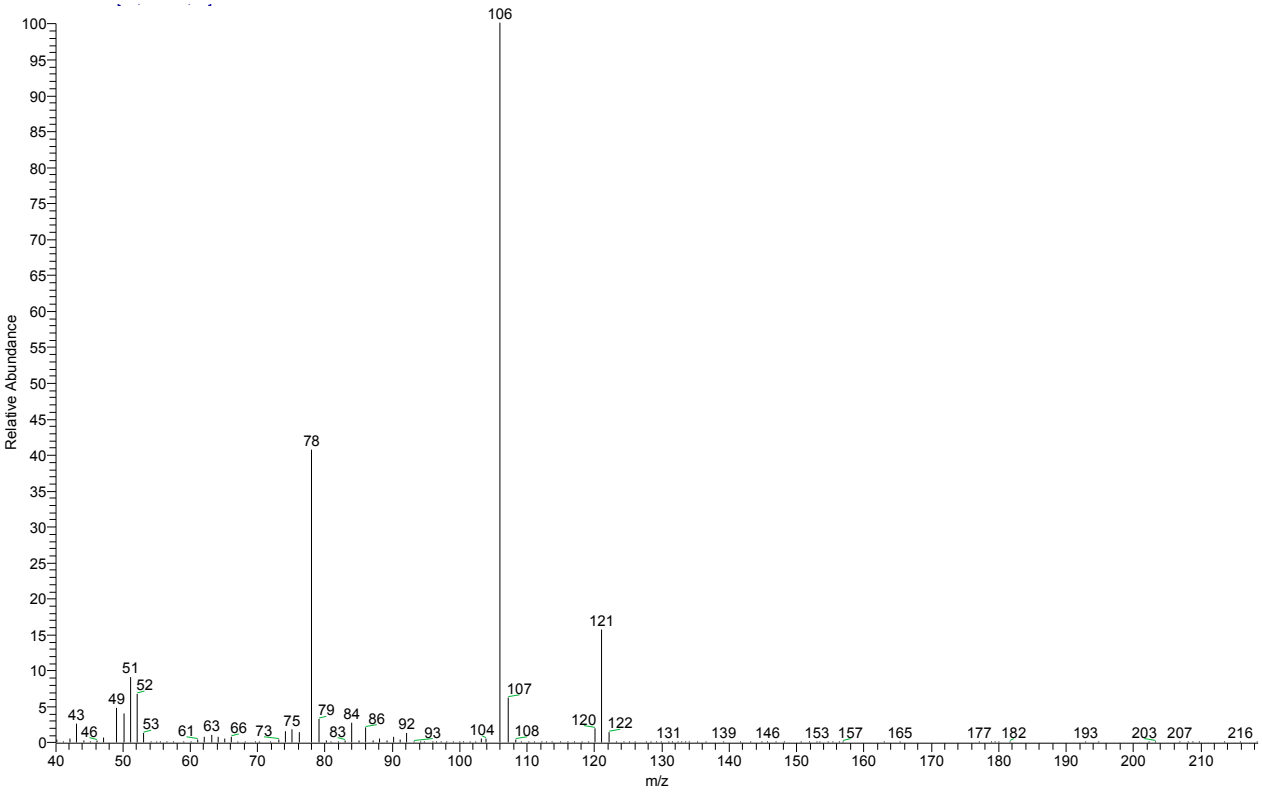

***3'-d*[1]**

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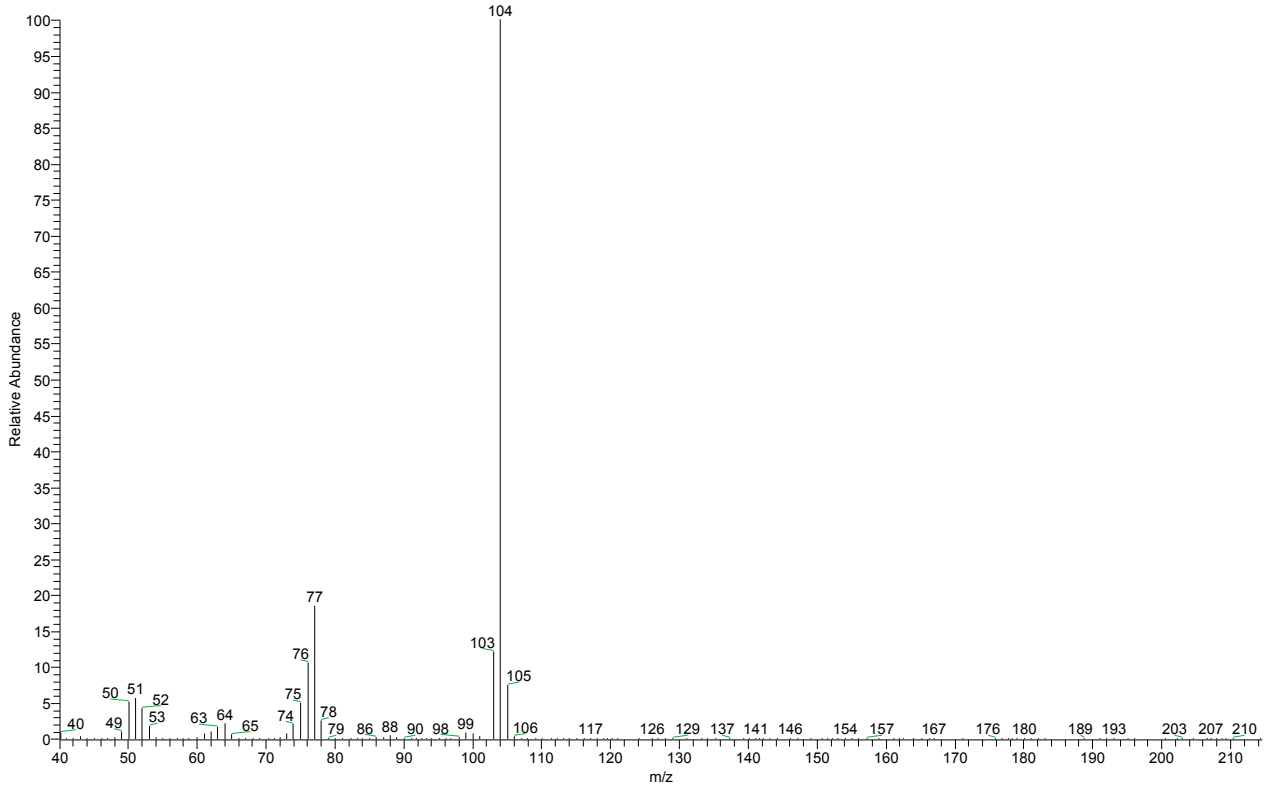

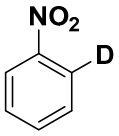

***4'-d*[1]**

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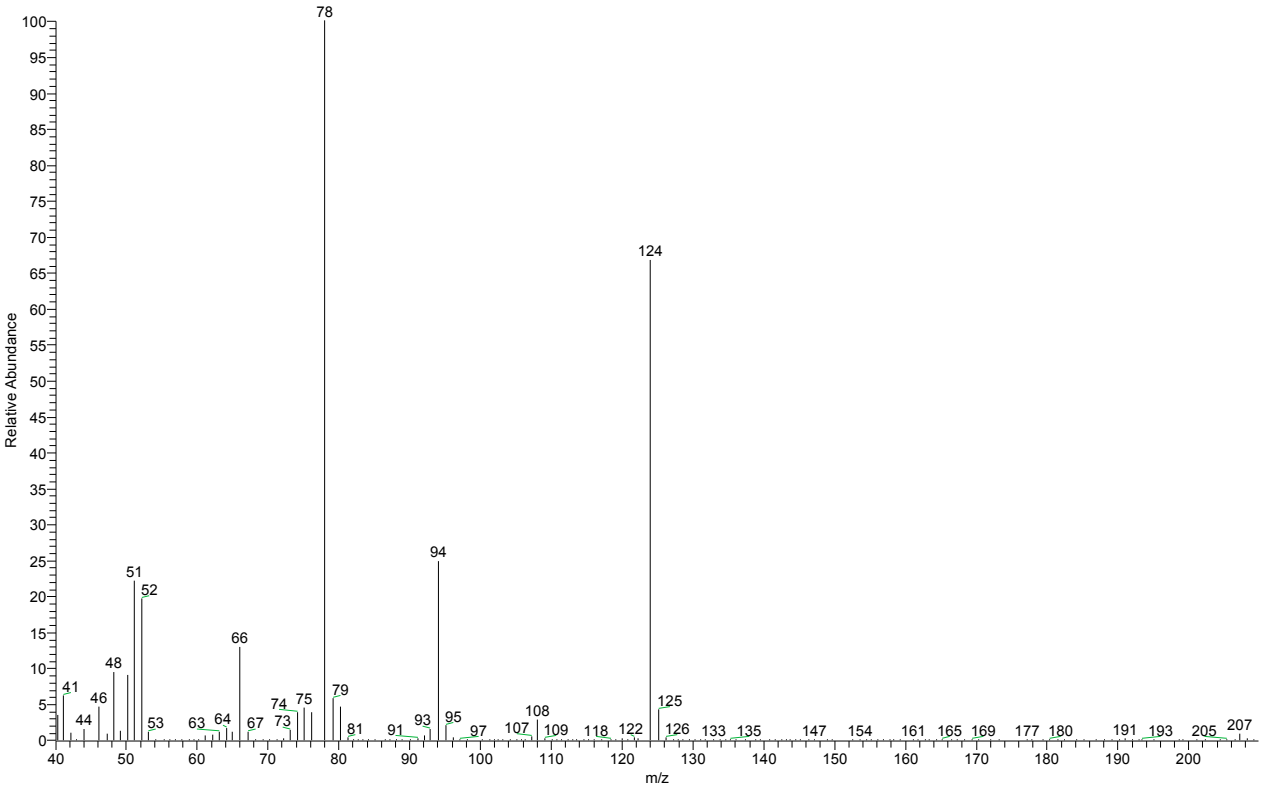

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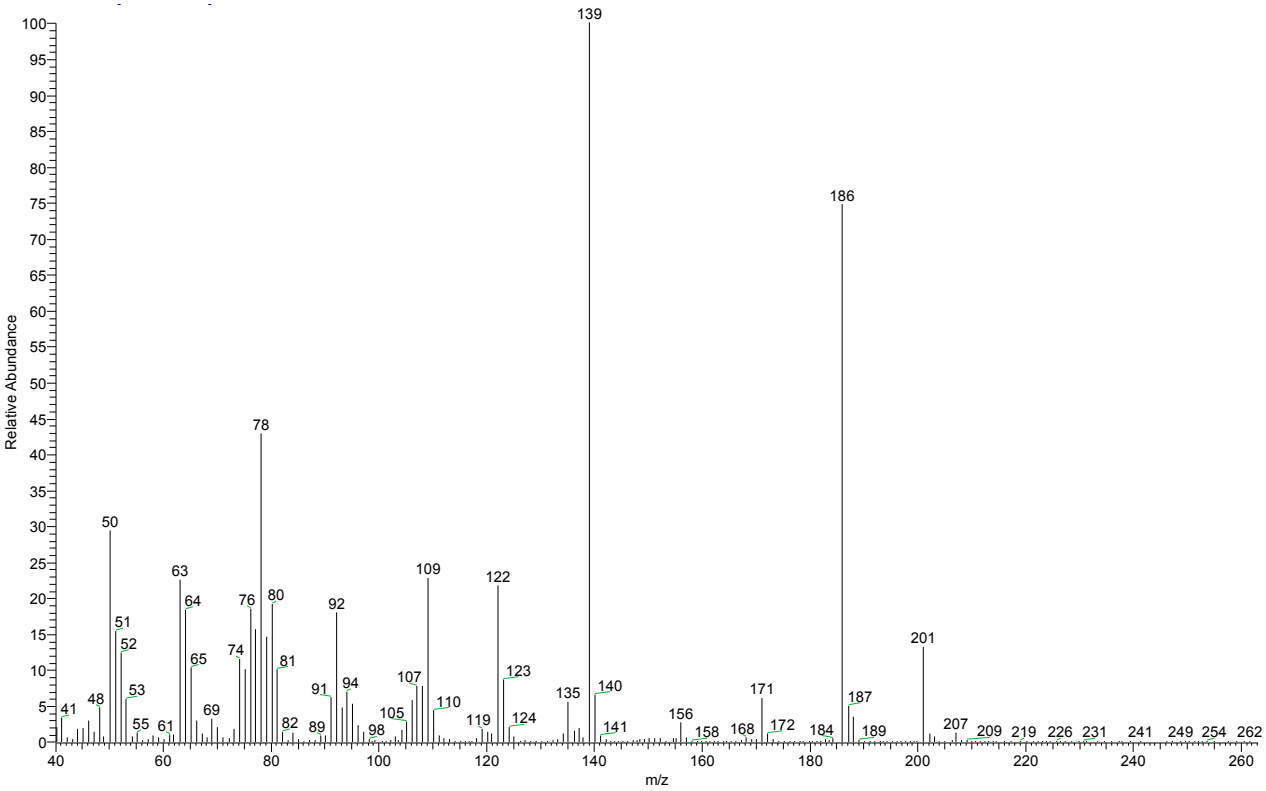

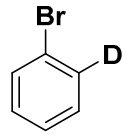

***6'-d*[1]**

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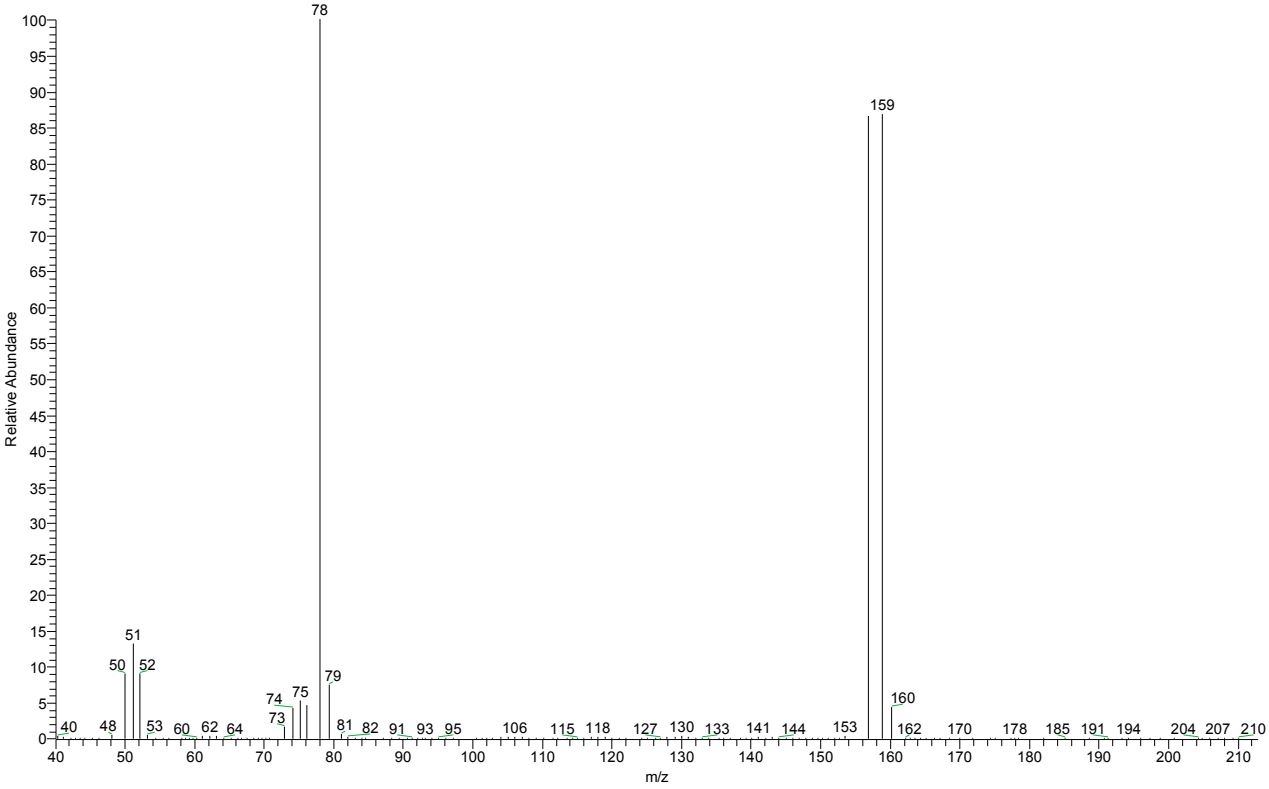
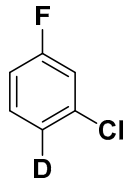
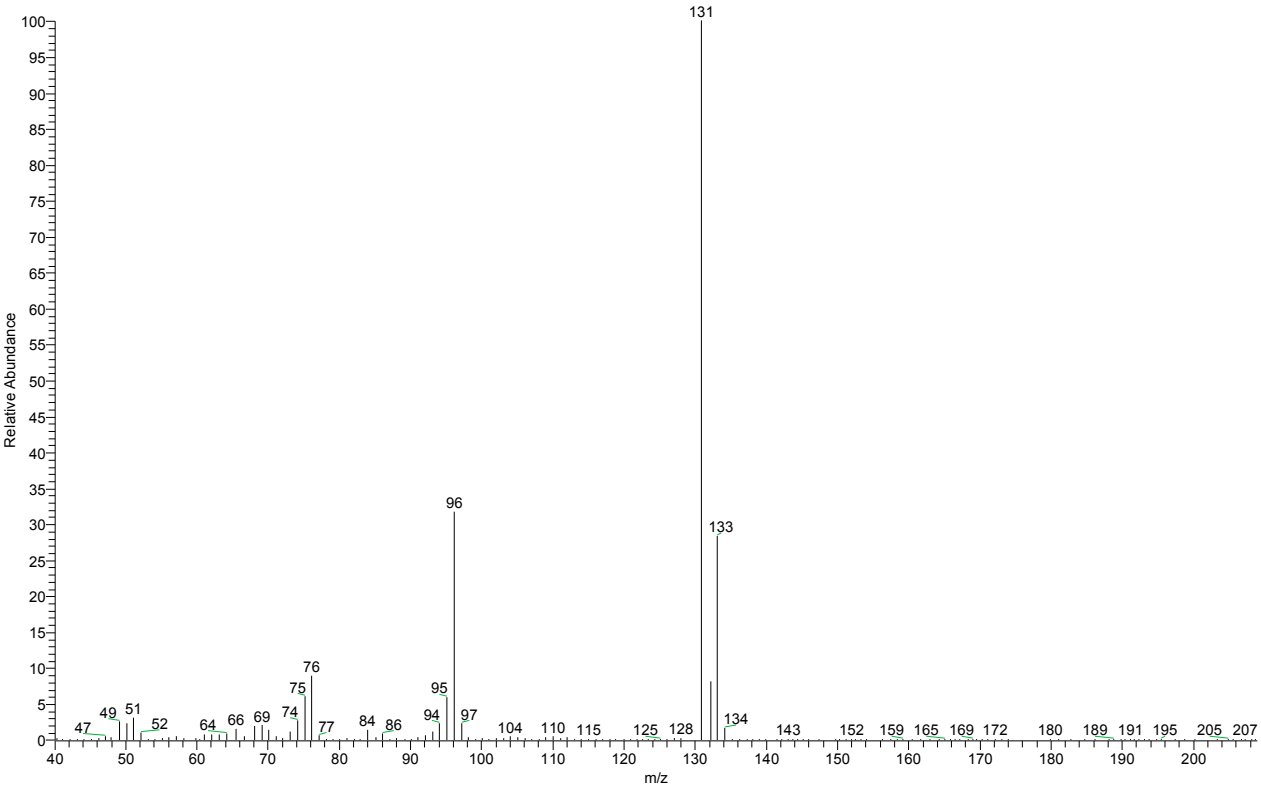



F
Cl
D

9-*d*^{1}


Relative Abundance
m/z
131
96
133
76
75
95
97
49
51
52
64
66
69
74
77
84
86
94
104
110
115
125
128
134
143
152
159
165
169
172
180
189
191
195
205
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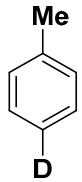
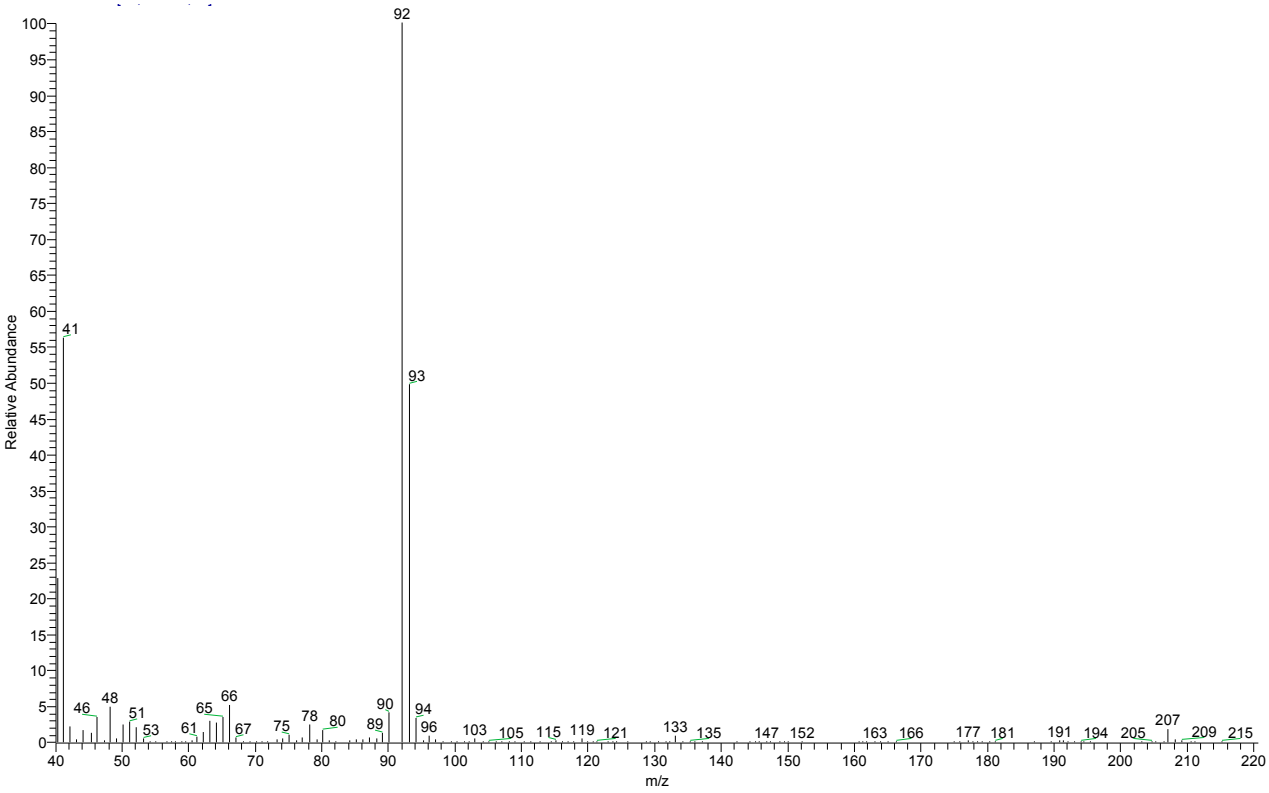
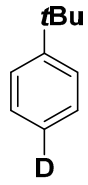


10-*d*^{1}

Reference: S13





11-*d*^{1}

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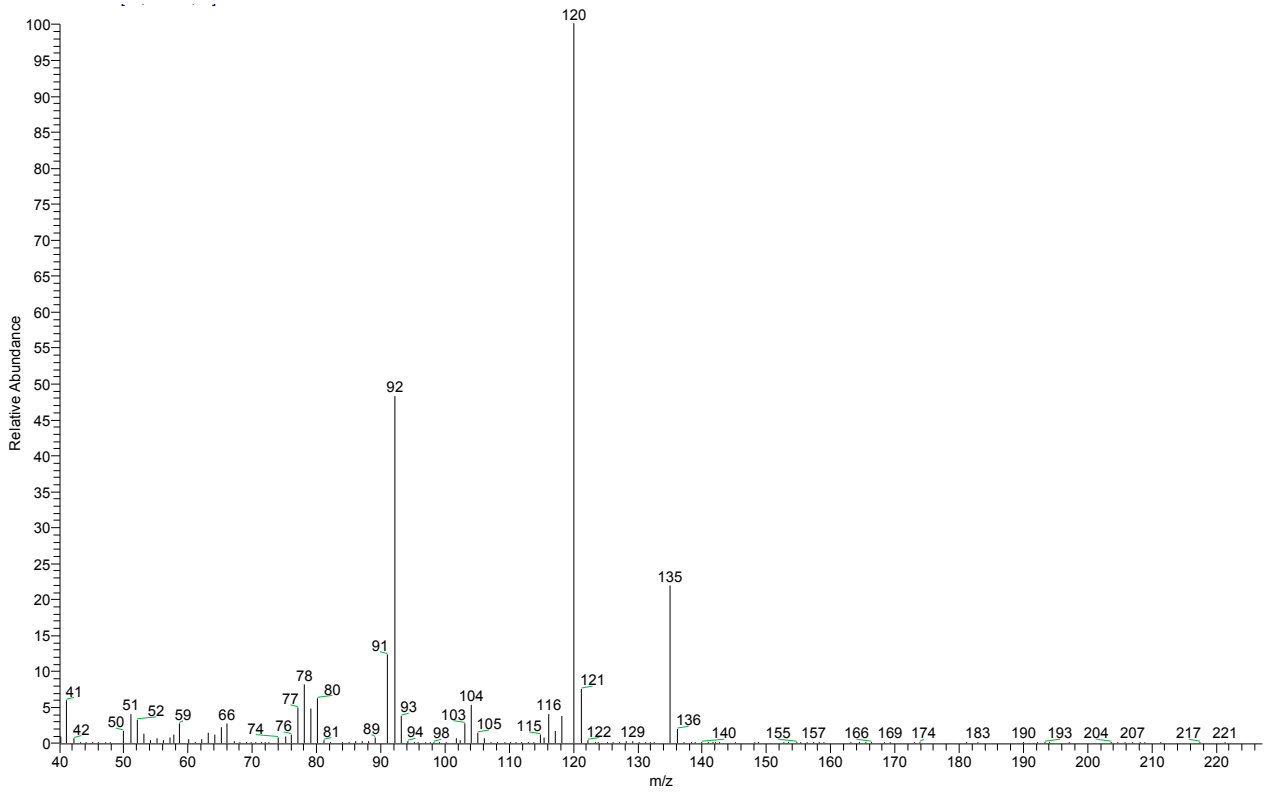

***12-d*[1]**

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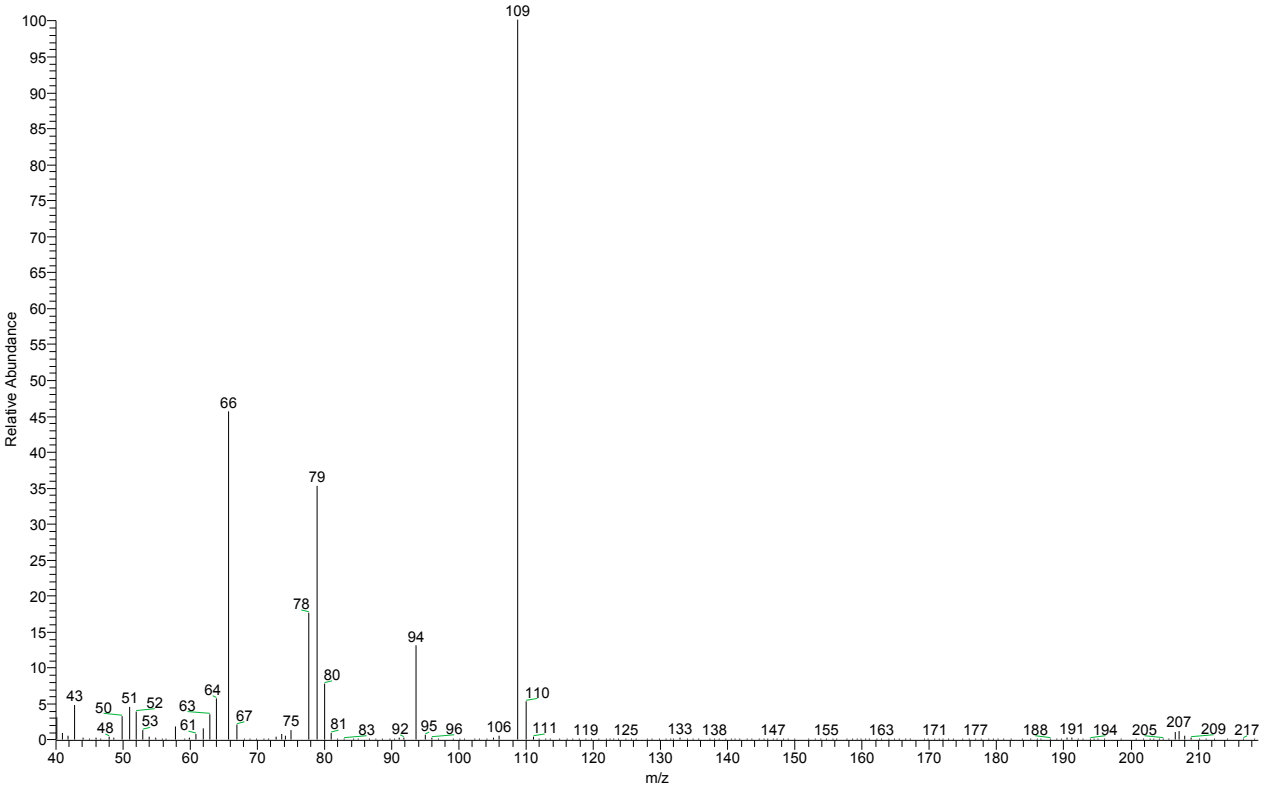
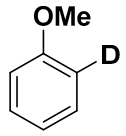
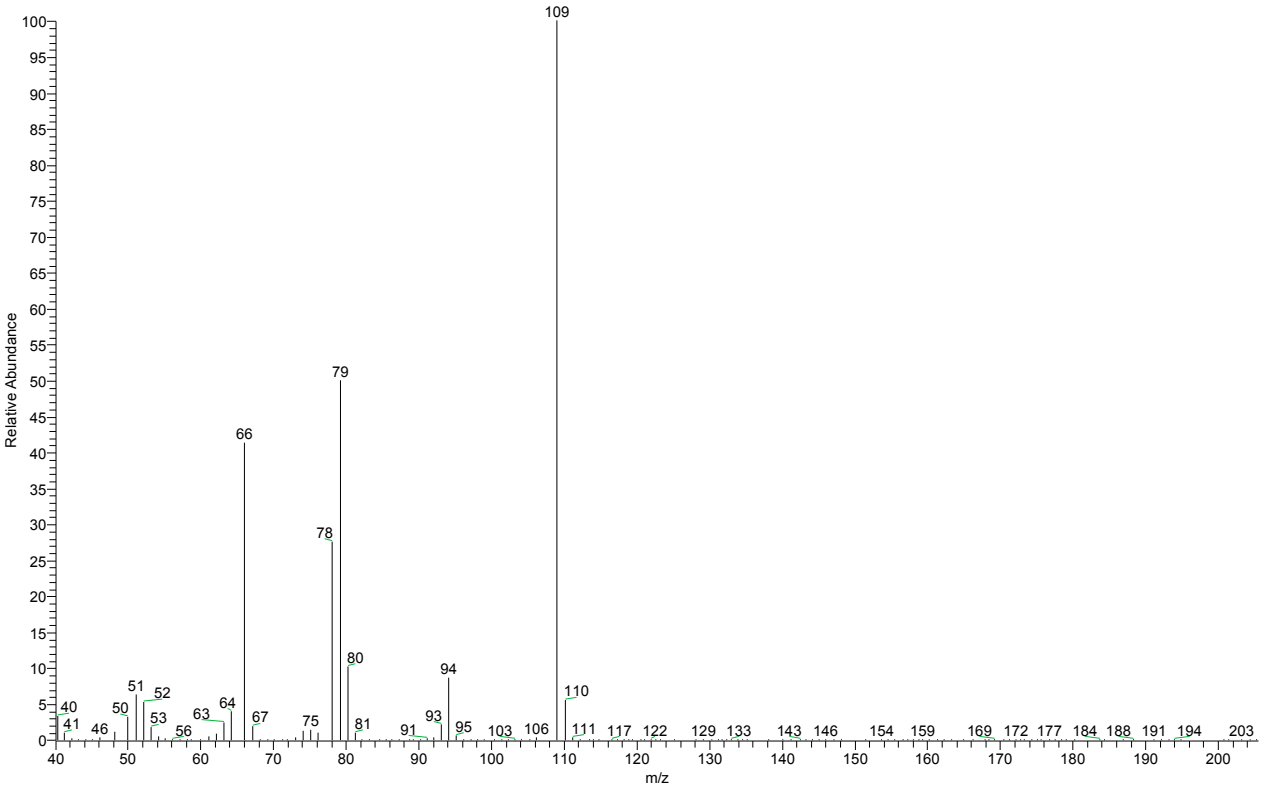
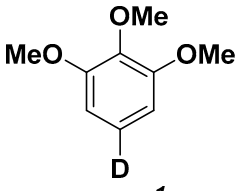




***12'-d*[1]**

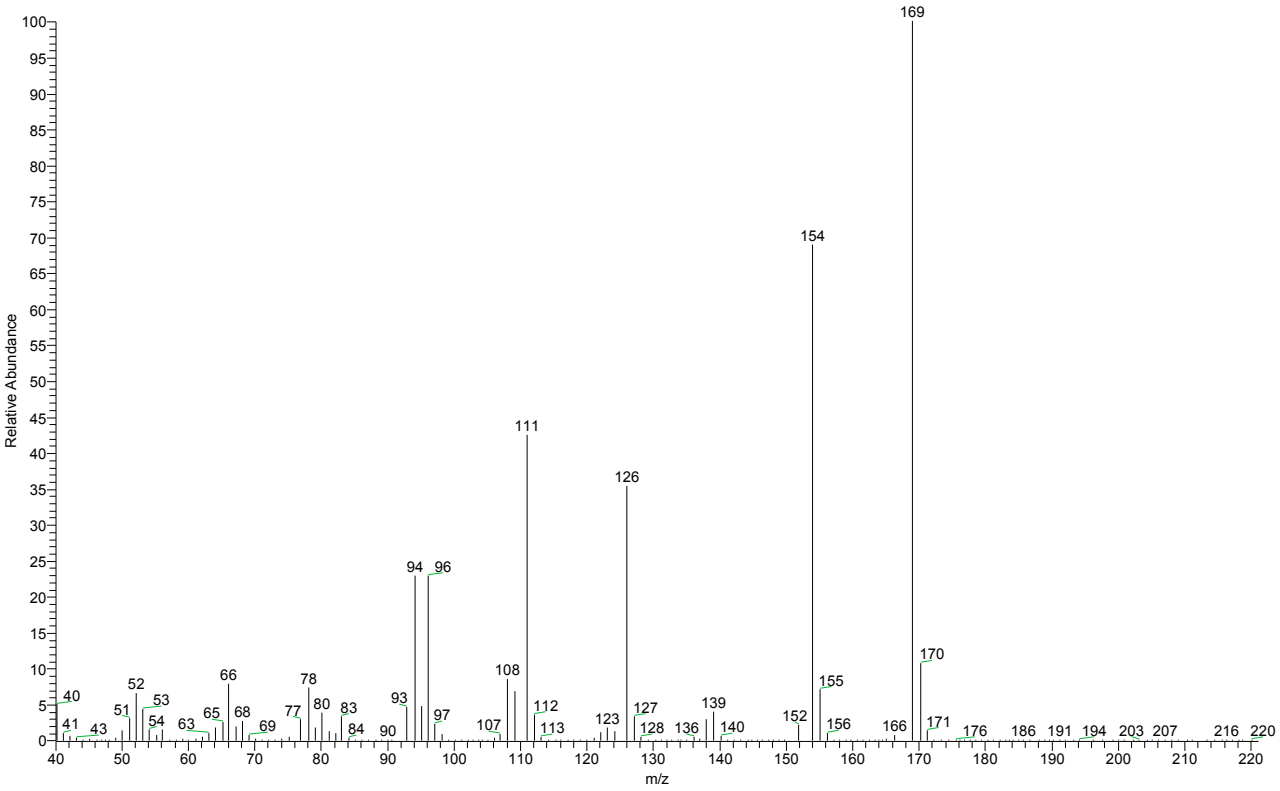
Reference: S14



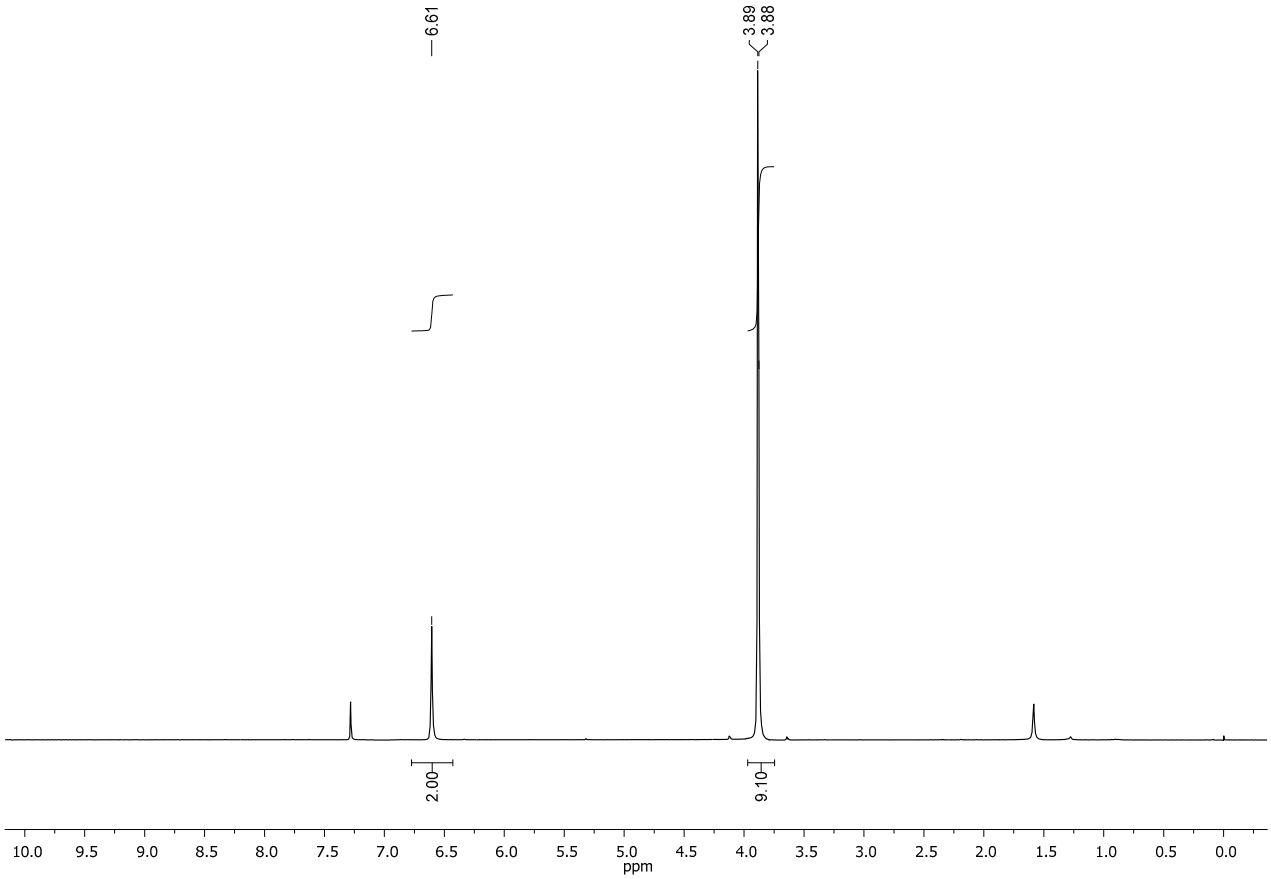


13-*d*^{1}

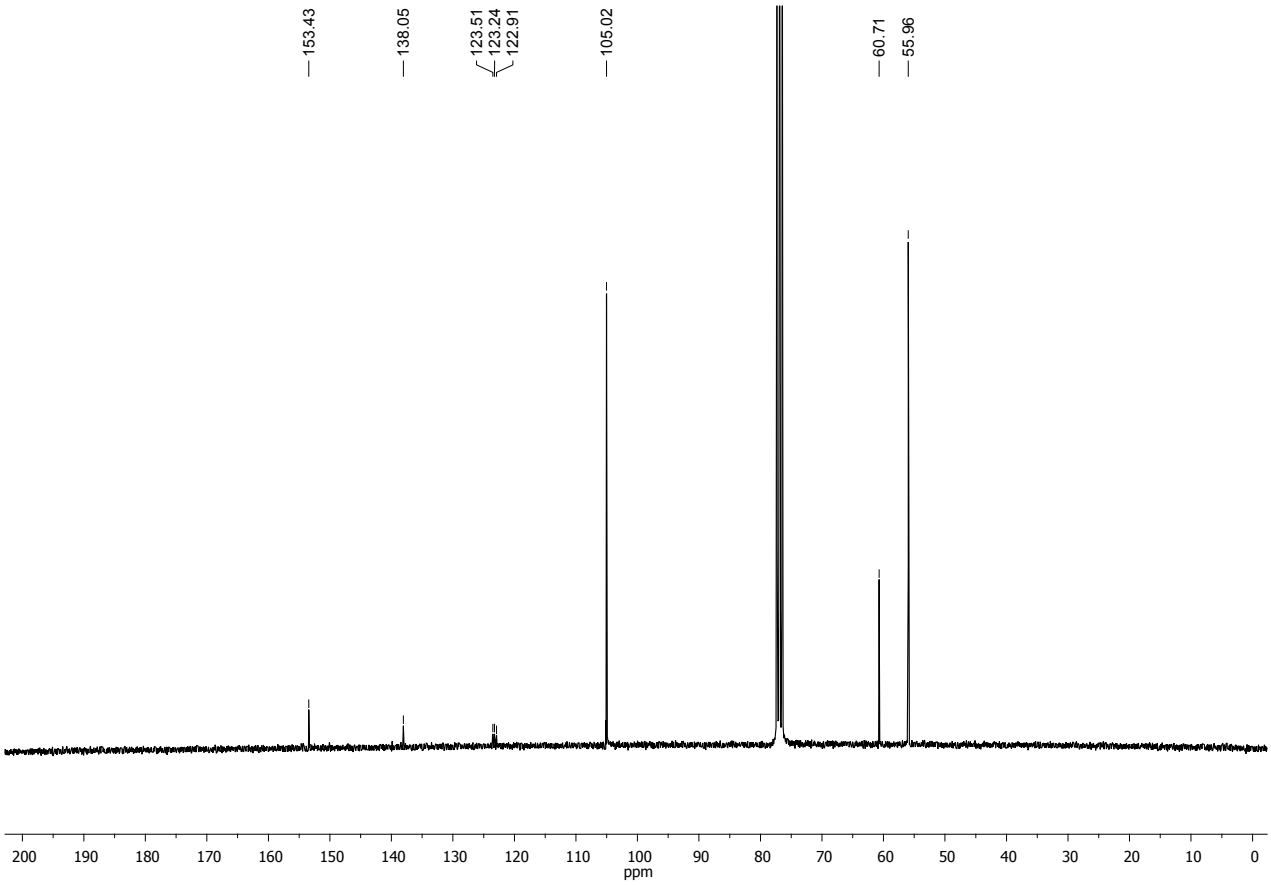
Reference: S9

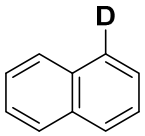


13-*d*^{1} (^{1}H NMR, 300 MHz)



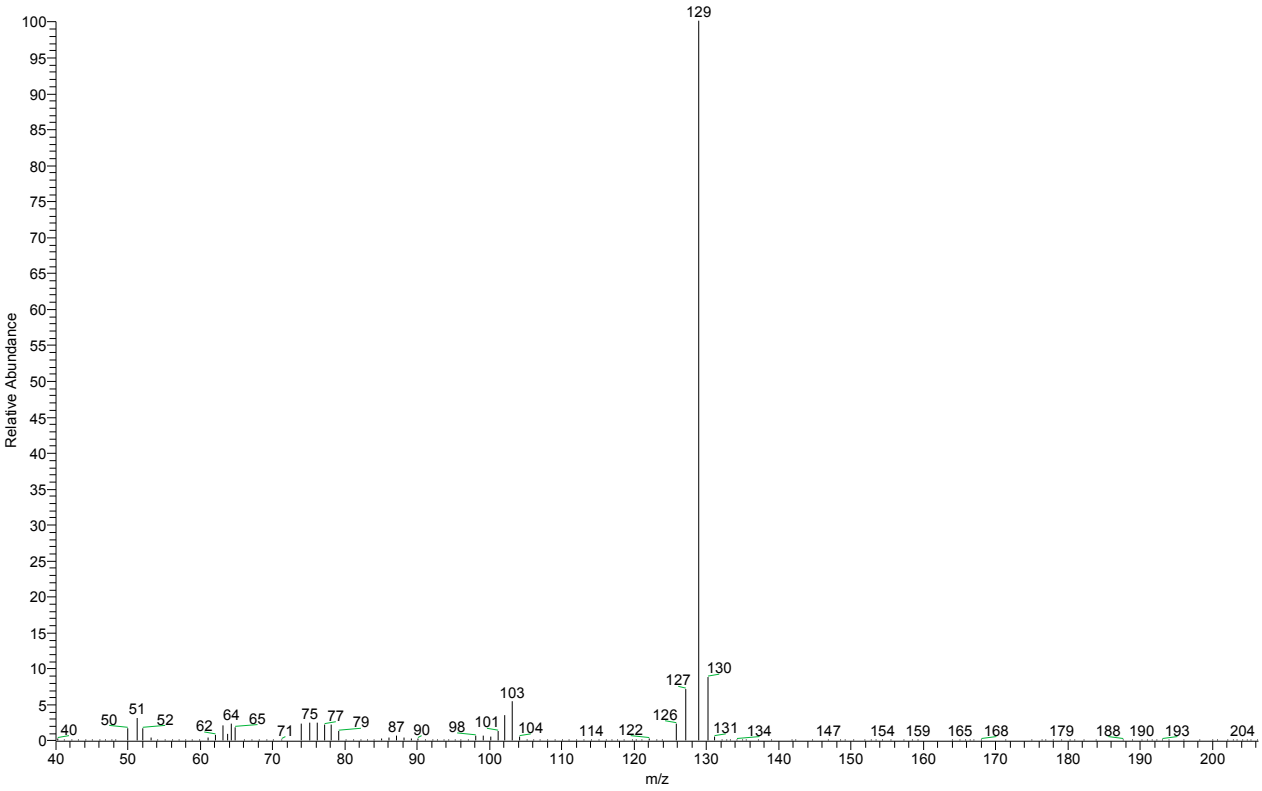
13-*d*^{1} (^{13}C NMR, 75 MHz)



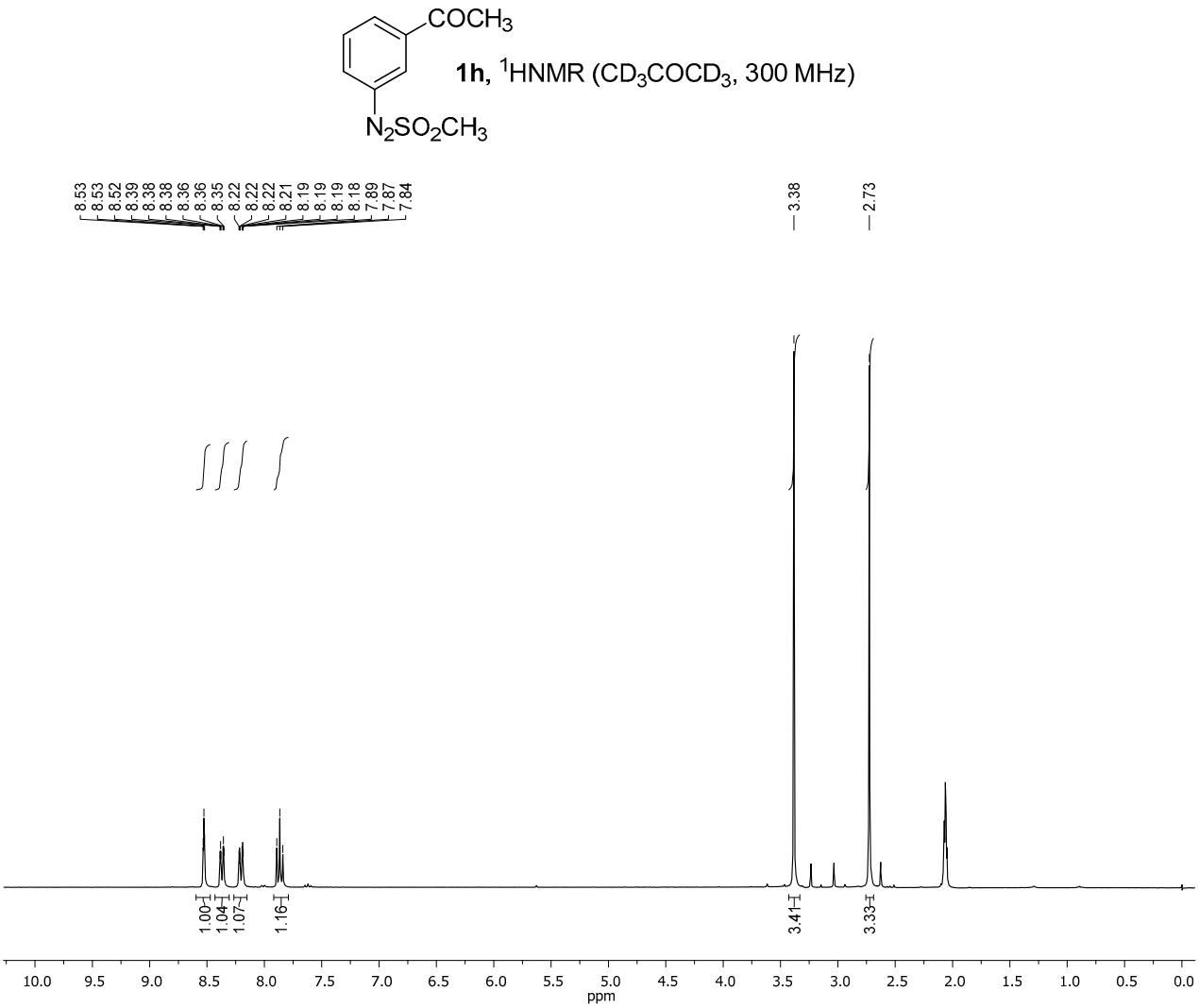


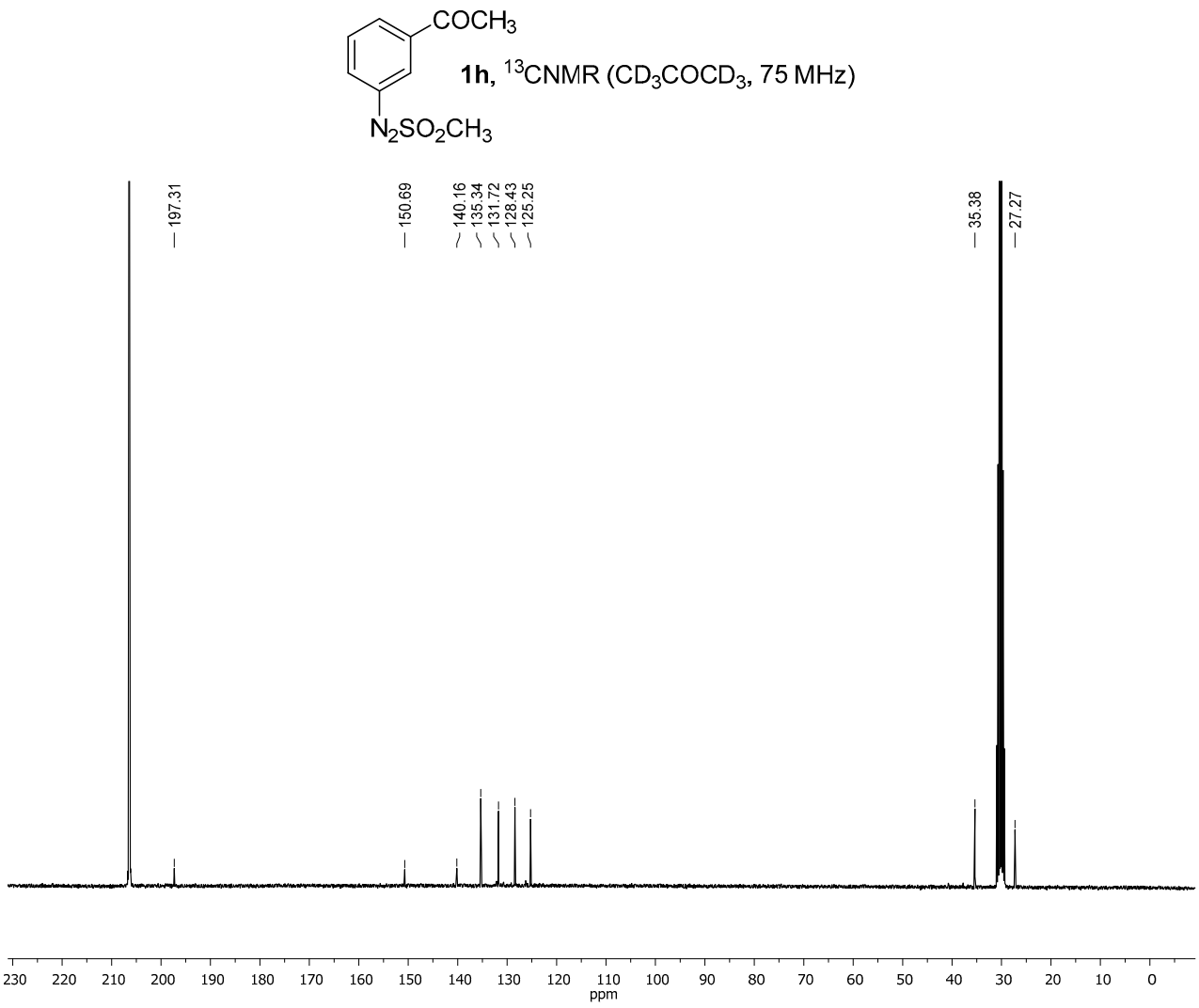
14-*d*^{1}

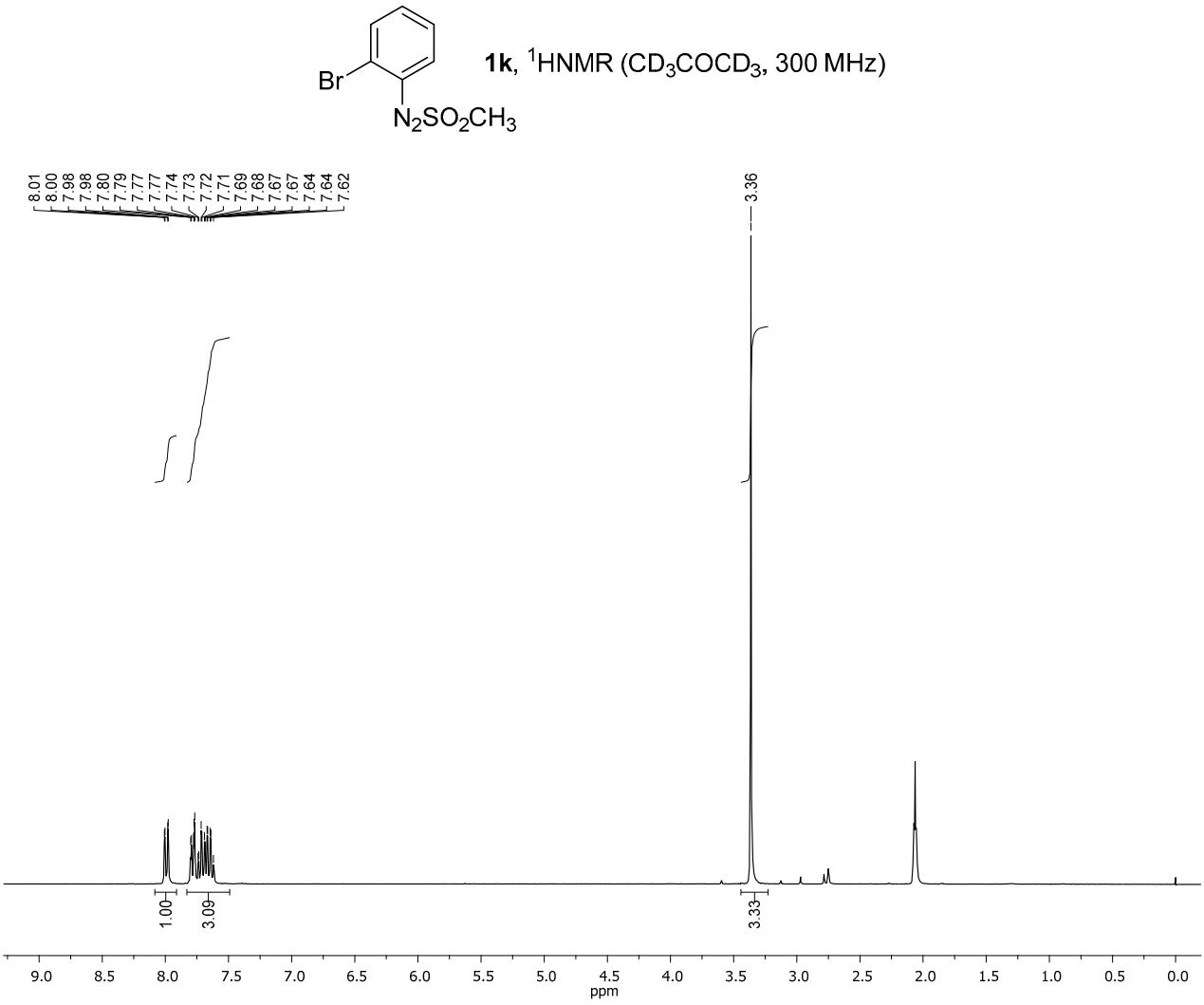
Reference: S9

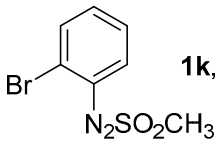


3 ^{1}H and ^{13}C NMR spectra of compounds 1h, 1i, 1k, 1l, 1q

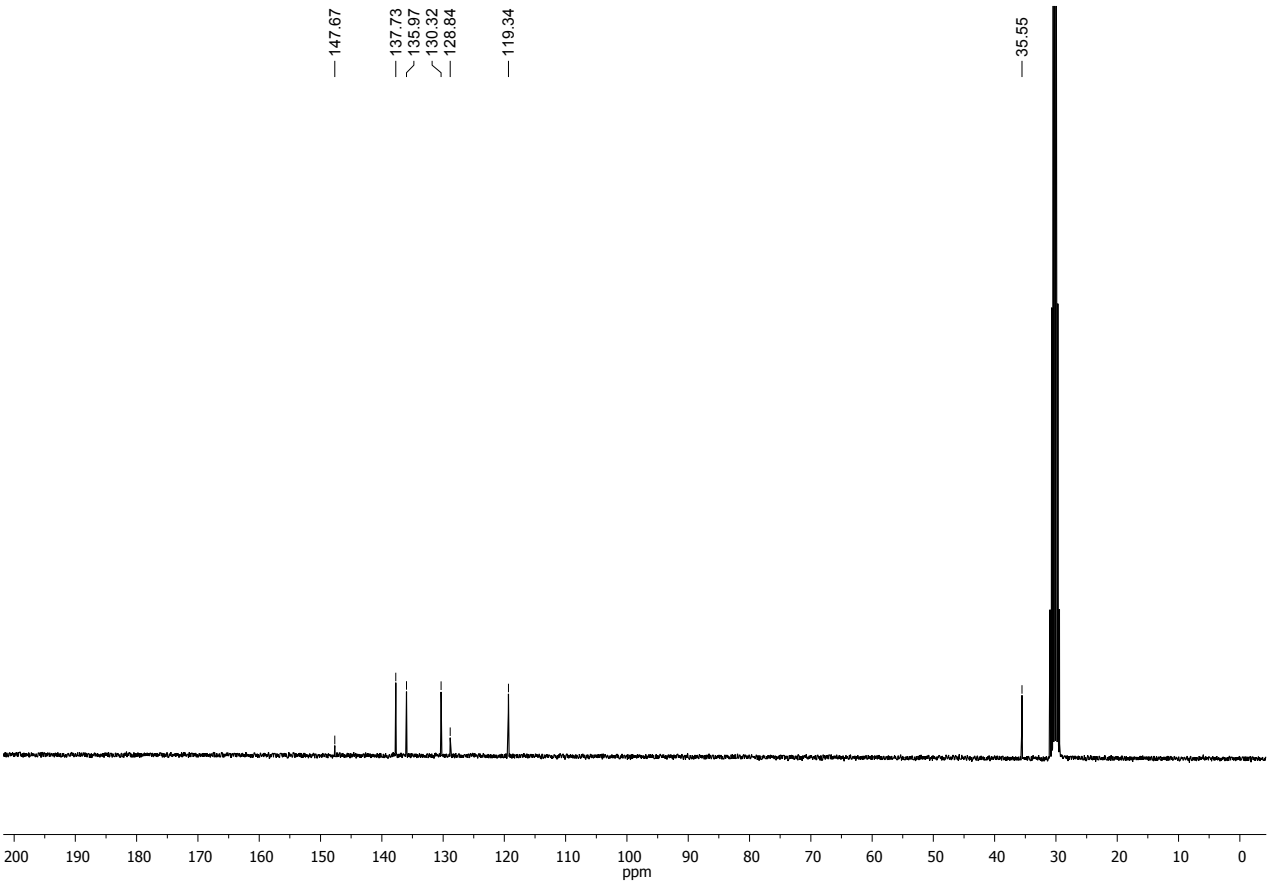


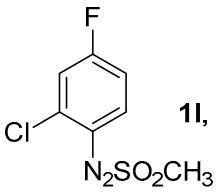

COCH3
N2SO2CH3
1h, 13CNMR (CD3COCD3, 75 MHz)
197.31
150.69
140.16
135.34
131.72
128.43
125.25
35.38
27.27
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


Br
N2SO2CH3
1k, 1HNMR (CD3COCD3, 300 MHz)
8.01
8.00
7.98
7.98
7.80
7.79
7.77
7.77
7.74
7.73
7.72
7.71
7.69
7.68
7.67
7.67
7.64
7.64
7.62
3.36
1.00
3.09
3.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

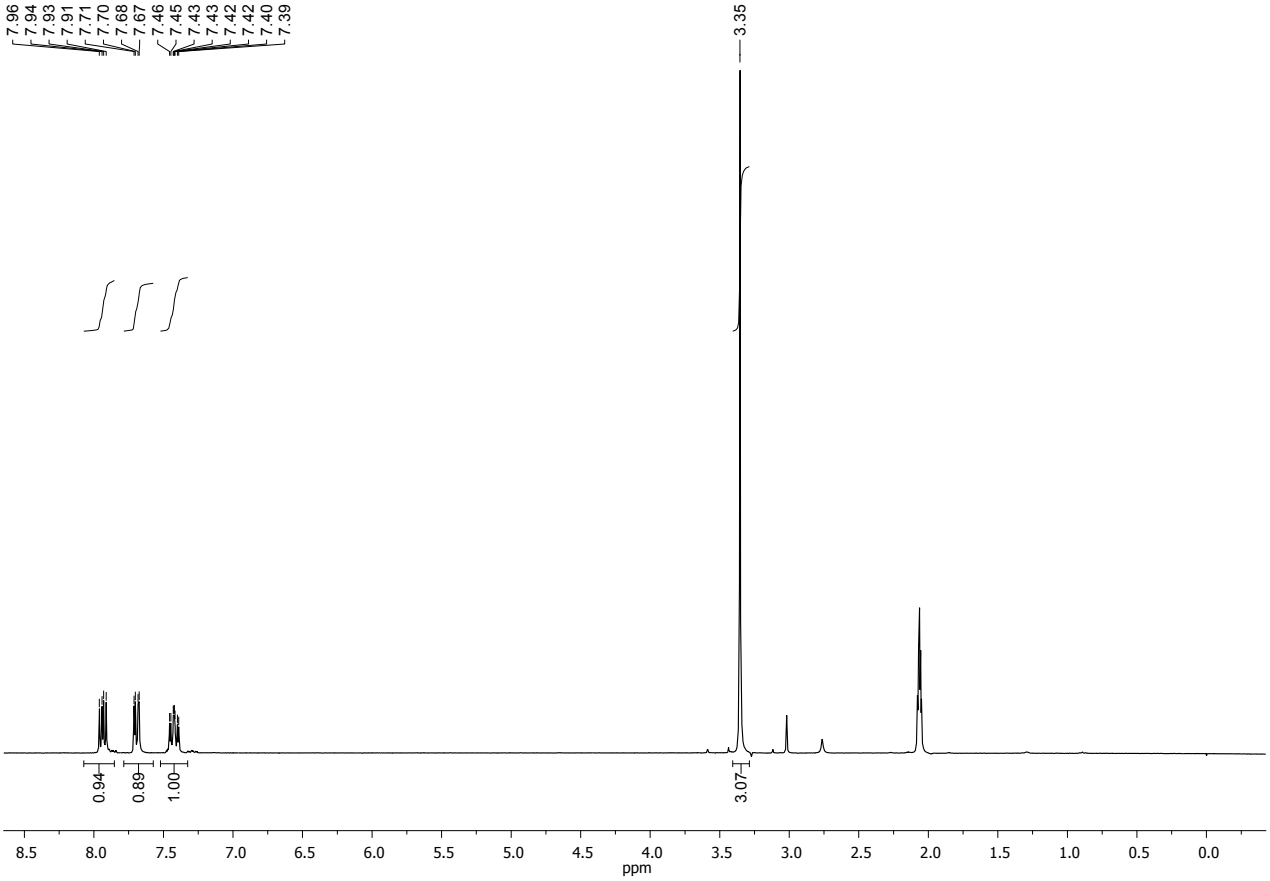


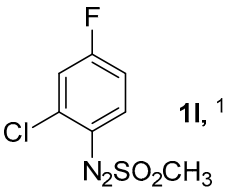
1k, ^{13}CNMR (CD_3COCD_3, 75 MHz)



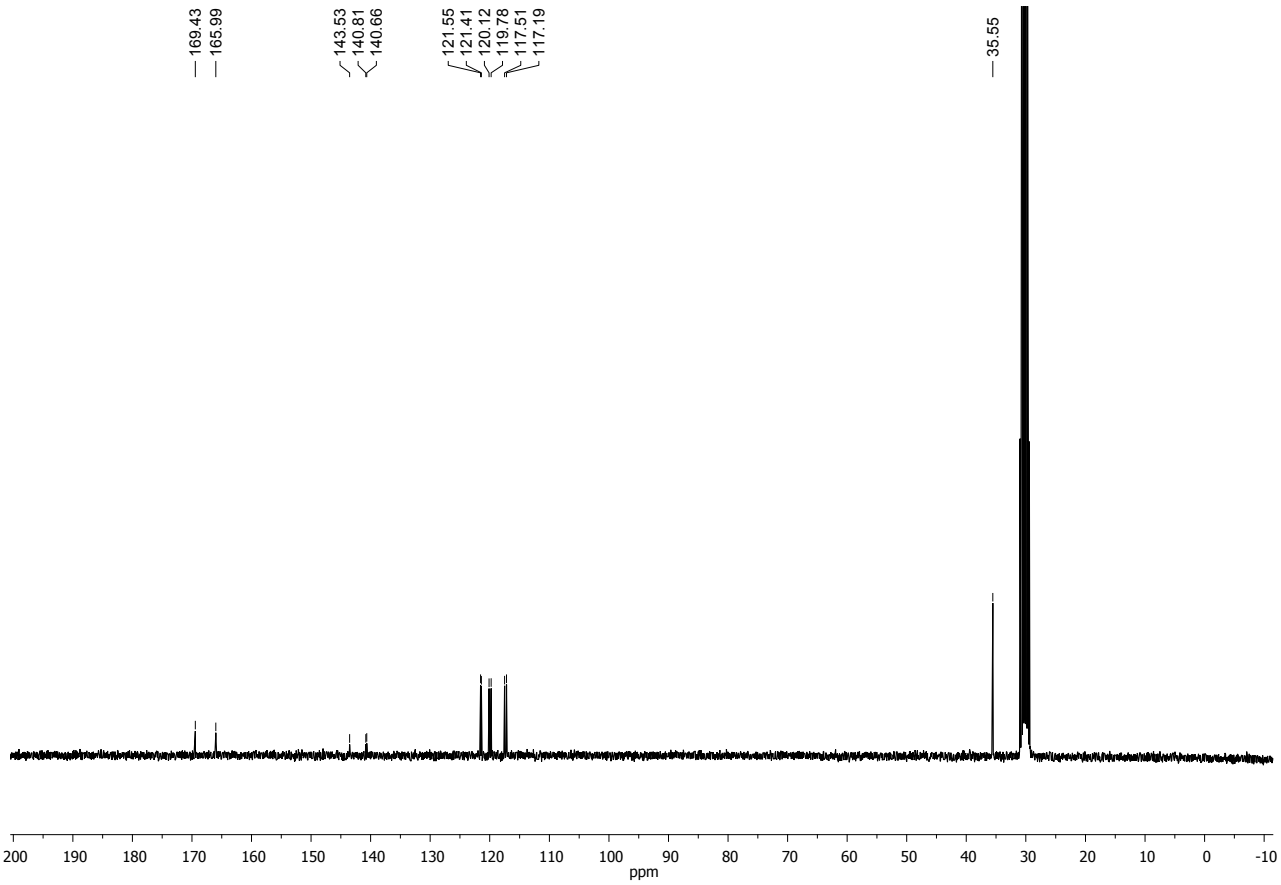


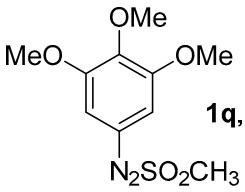
1l, ^{1}HNMR (CD_3COCD_3, 300 MHz)



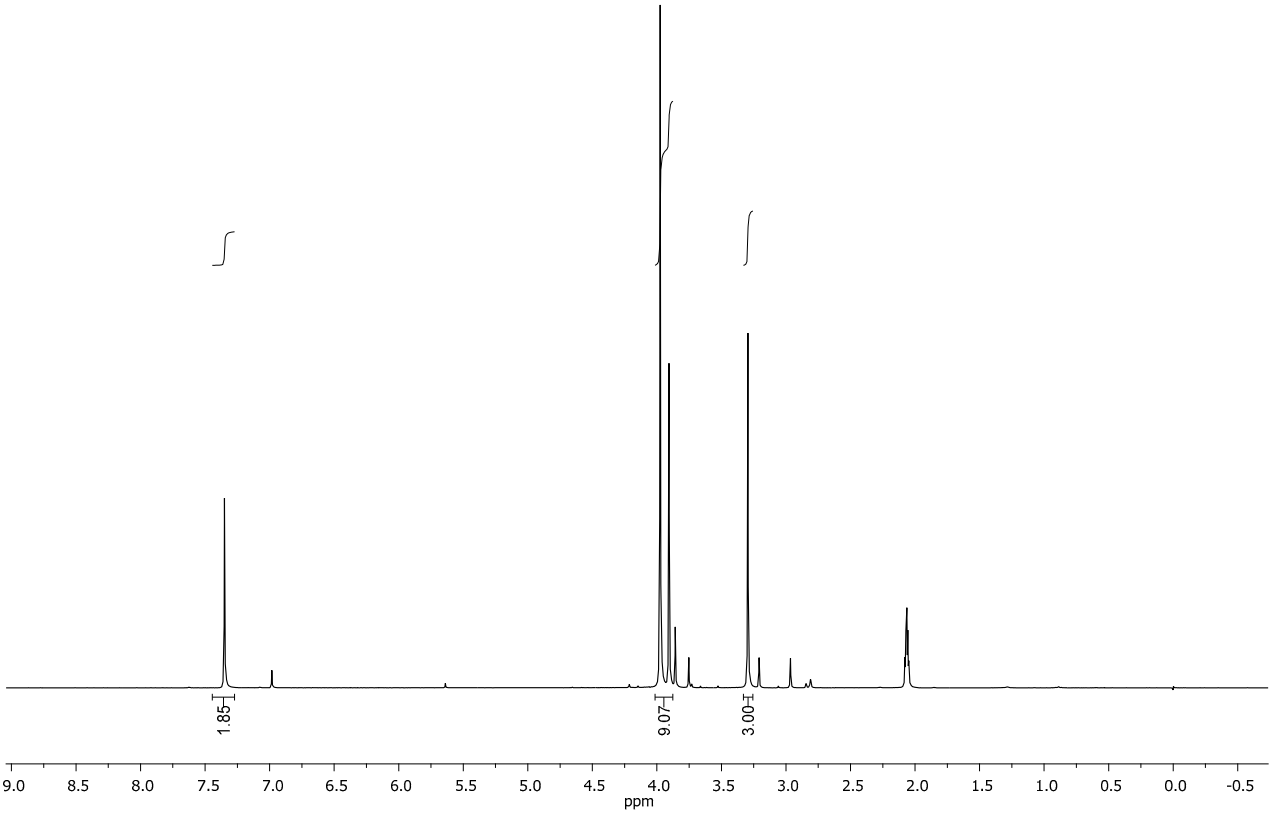


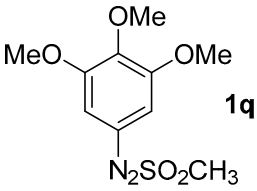
1l, ^{13}CNMR (CD_3COCD_3, 75 MHz)



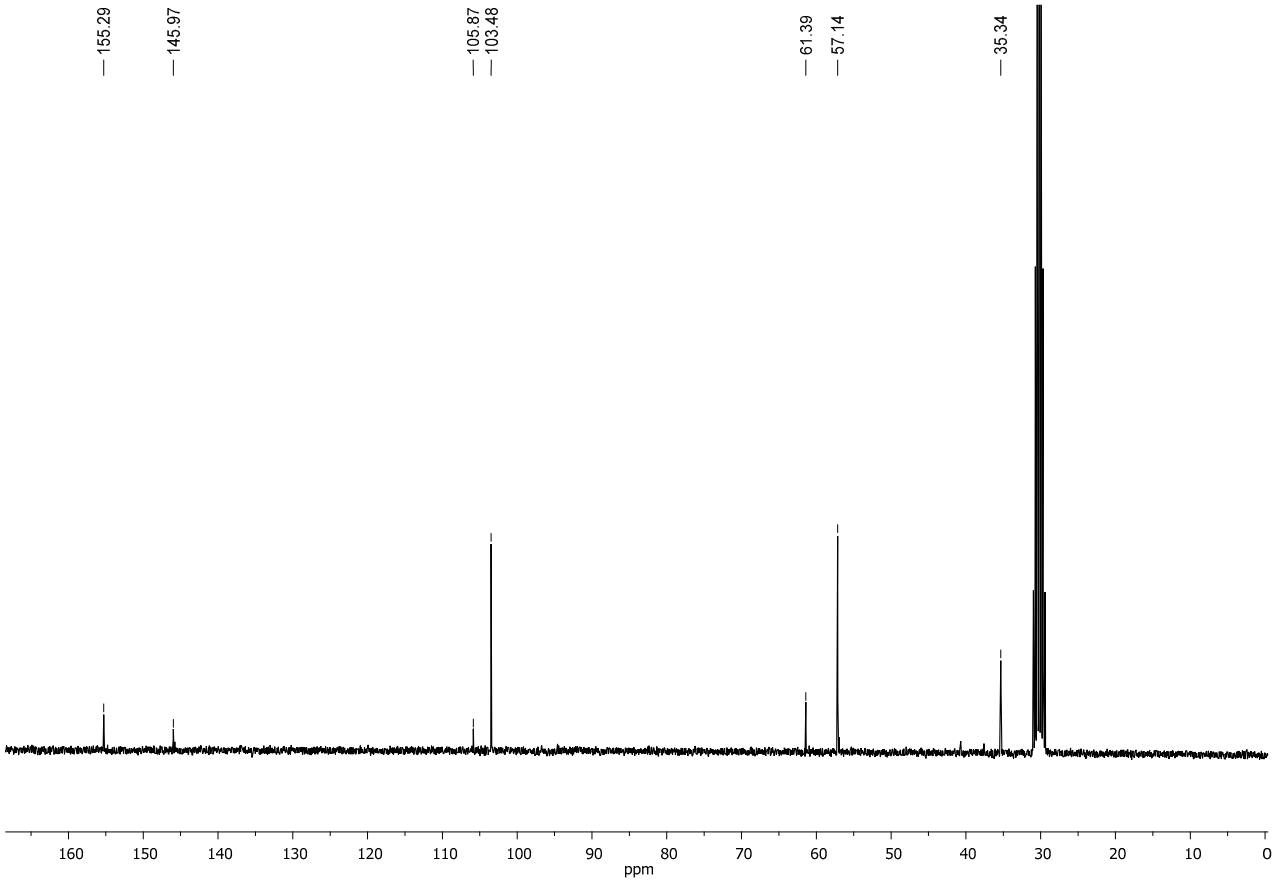


1q, ^{1}HNMR (CD_3COCD_3, 300 MHz)





1q, ^{13}CNMR (CD_3COCD_3, 75 MHz)



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