Supplementary Information

Facile synthesis of 4,5,6a,7 tetrahydrodibenzo[de,g]chromene heterocycles and their transformation to phenanthrene alkaloids

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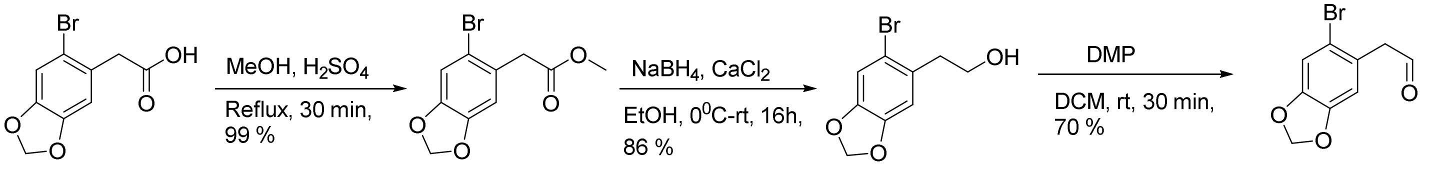
Experimental Procedures:



S1 **S2** **S3** **20**

*methyl 2-(6-*bromobenzo*[d][1,3]dioxol-5-yl)acetate **(S2)***

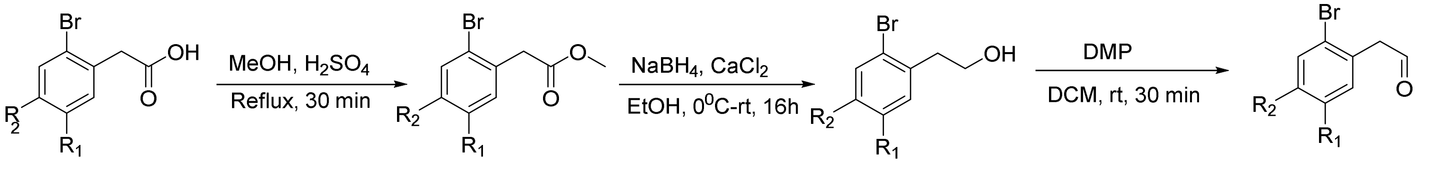
A solution of compound **S1** (5.00 g, 19.3 mmol) and conc. H_2SO_4 (catalytic) in methanol (50 mL) was refluxed for 30 min. After 30 min, the reaction mixture was cooled to rt and was evaporated under reduced pressure. To the resulting crude product water (30 mL) was added, followed by extraction with three portions of dichloromethane (30 mL each). The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure to afford **S2** as a white solid. (5.21 g, 99 %); Mp: 66 – 69 ^oC.

*2-(6-bromobenzo[d][1,3]dioxol-5-yl)ethanol **(S3)***

In a three neck round bottom flask, $CaCl_2$ (6.29 g, 57.25 mmol) was dissolved in ethanol (50 mL) under argon atmosphere. The resulting solution was cooled to 0 ^oC, followed by the addition of $NaBH_4$ (1.08 g, 28.62 mmol) at the same temperature. The suspension was allowed to stir at 0 ^oC for 30 min, after which a solution of **S2** (5.21 g, 19.08 mmol) in ethanol (50 mL) was added at the same temperature. The resulting reaction mixture was allowed to stir at 0 ^oC for another 30 min, and then at rt for 15 h. After 15 h, 50 mL of a mixture of water and dichloromethane (1:1) was added to the reaction mixture which was then sonicated for 1 h. The resulting mixture was then subjected to vacuum filtration over celite. The filtrate was collected and evaporated under reduced pressure. Water was added to the resulting crude product, which was then extracted with three portions of dichloromethane (30 mL each). The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure, to get a crude mixture which was purified using silica gel column chromatography eluting in 30 % ethyl acetate – petroleum ether, to afford **S3** as a white solid. (4.02 g, 86 %); 63 – 67 ^oC.

*2-(6-bromobenzo[d][1,3]dioxol-5-yl)acetaldehyde **(20)***

Dess-Martin Periodinane (3.80 g, 8.97 mmol) was added to a three neck round bottom flask containing dichloromethane (40 mL) under argon atmosphere. The resulting solution was stirred for 15 min, followed by the addition of compound **S3** (2.0 g, 8.16 mmol). The resulting suspension was stirred for 1 h, after which the reaction mixture was subjected to vacuum filtration over a silica gel bed. The filtrate was collected and evaporated under reduced pressure. The resulting crude **20** obtained as brown oil was used without further purification. (1.38 g,70 %).



S4a: R_1 = OMe R_2 = OMe
S4b: R_1 = OMe, R_2 = H
S4c: R_1 = H, R_2 = OMe
S4d: R_1 = H R_2= H

S5a: R_1 = OMe R_2 = OMe; 99 %
S5b: R_1 = OMe, R_2 = H; 99 %
S5c: R_1 = H, R_2 = OMe; 99 %
S5d: R_1 = H R_2= H; 99 %

S6a: R_1 = OMe R_2 = OMe; 60 %
S6b: R_1 = OMe, R_2 = H; 42 %
S6c: R_1 = H, R_2 = OMe; 55 %
S6d: R_1 = H R_2= H; 55 %

28a: R_1 = OMe R_2 = OMe; 77 %
28b: R_1 = OMe, R_2 = H; 44 %
28c: R_1 = H, R_2 = OMe; 74 %
28d: R_1 = H R_2= H ; 60 %

*General procedure for the synthesis of compounds **S5a-S5d** (Using **S5a** as a representative)*

A solution of **S4a** (5.0 g, 18.18 mmol) and conc. H_2SO_4 (catalytic) in methanol (50 mL) was refluxed for 30 min. After 30 min, the reaction mixture was cooled to rt and was evaporated under reduced pressure. To the resulting crude water (30 mL) was added, followed by extraction with three portions of 20 mL of dichloromethane. The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure to afford **S5a.**

methyl 2-(2-bromo-4,5-dimethoxyphenyl)acetate ***(S5a):*** Brown Oil; (5.19 g, 99 %).

methyl 2-(2-bromo-5-methoxyphenyl)acetate ***(S5b):*** Brown Oil; (2.09 g, 99 %).

methyl 2-(2-bromo-4-methoxyphenyl)acetate ***(S5c):*** Brown Oil; (2.09 g, 99 %).

methyl 2-(2-bromophenyl)acetate ***(S5d):*** Clear Oil; (5.27 g, 99 %).

General procedure for the synthesis of compounds ***S6a-S6d*** *(Using* ***S6a*** *as a representative)*

In a three neck round bottom flask, $CaCl_2$ (1.12 g, 10.2 mmol) was dissolved in ethanol (50 mL) under argon atmosphere. The resulting solution was cooled to 0 ºC, followed by the addition of $NaBH_4$ (0.19 g, 5.1 mmol) at the same temperature. The resulting suspension was allowed to stir at 0 ºC for 30 min, after which a solution of **S5a** (1.0 g, 3.4 mmol) in 60 mL of Ethanol was added at the same temperature. The resulting reaction mixture was allowed to stir at 0 ºC for another 30 min, and then at rt for 15 h. After 15 h, 50 mL of a mixture of water and dichloromethane (1:1) was added to the reaction mixture which was then sonicated for 1 h. The resulting mixture was then subjected to vacuum filtration over celite. The filtrate was collected and evaporated under reduced pressure. 50 mL of water was added to the resulting crude, which was then extracted with three portions of dichloromethane (30 mL each). The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure to afford **S6**

2-(2-bromo-4,5-dimethoxyphenyl)ethanol ***(S6a):*** Brown Oil; (2.56 g, 60 %).

2-(2-bromo-5-methoxyphenyl)ethanol ***(S6b):*** Clear Oil; (1.29 g, 42 %).

2-(2-bromo-4-methoxyphenyl)ethanol ***(S6c):*** Clear Oil; (1.03 g, 55 %).

2-(2-bromophenyl)ethanol ***(S6d):*** Clear Oil; (2.41 g, 55 %).

General procedure for the synthesis of compounds ***28a-28d****: (Using* ***28a*** *as a representative)*

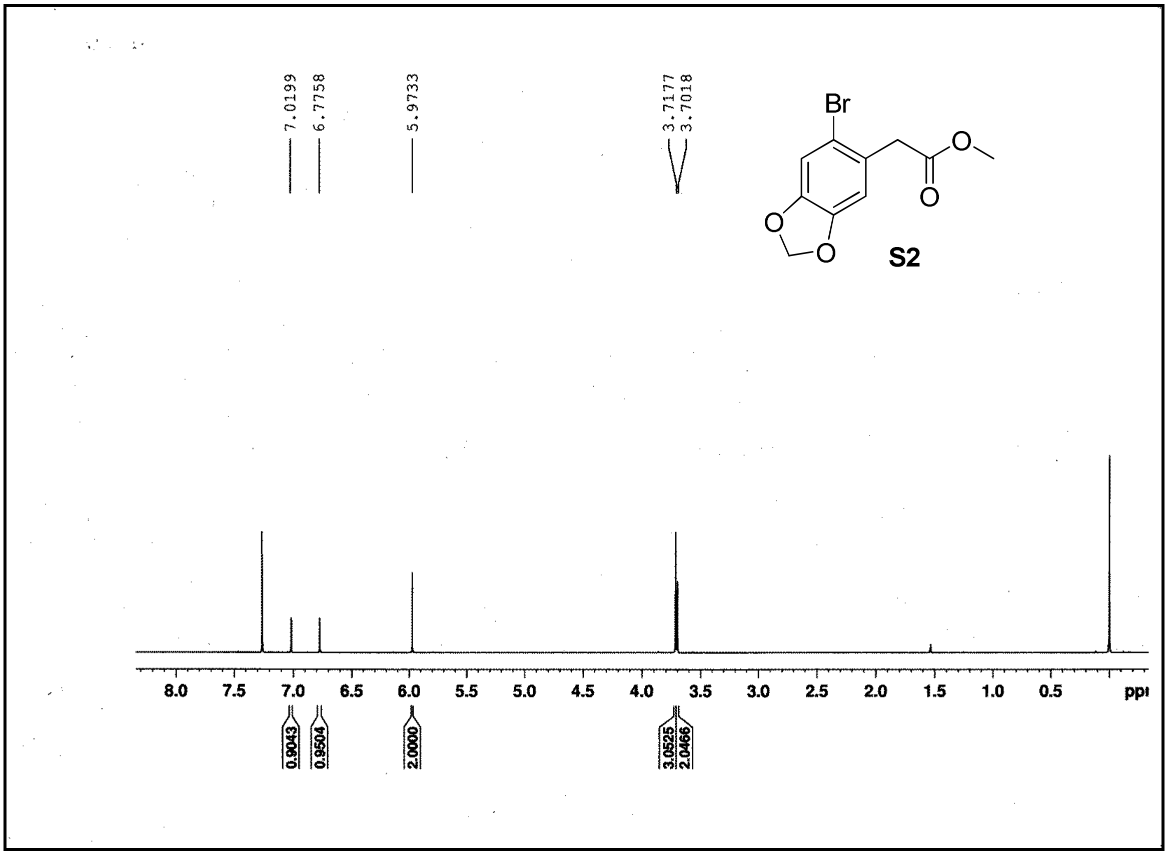
Dess-Martin Periodinane (1.78 g, 3.83 mmol) was added to a three neck round bottom flask containing 40 mL dichloromethane under argon atmosphere. The resulting solution was stirred for 15 min, followed by the addition of compound **S6** (1.0 g, 3.83 mmol). The resulting suspension was stirred for 1 h, after which the reaction mixture was subjected to vacuum filtration over silica gel. The filtrate was collected and evaporated under reduced pressure. The resulting crude aldehyde **28a** was used without further purification.

2-(2-bromo-4,5-dimethoxyphenyl)acetaldehyde ***(28a):*** Pale Yellow Solid; (0.76 g, 77 %).

2-(2-bromo-5-methoxyphenyl)acetaldehyde ***(28b):*** Clear Oil; (0.30 g, 44 %).

2-(2-bromo-4-methoxyphenyl)acetaldehyde ***(28c)***: Clear Oil; (0.33 g, 74 %).

2-(2-bromophenyl)acetaldehyde ***(28d):*** Clear Oil; (1.05 g, 60 %).



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O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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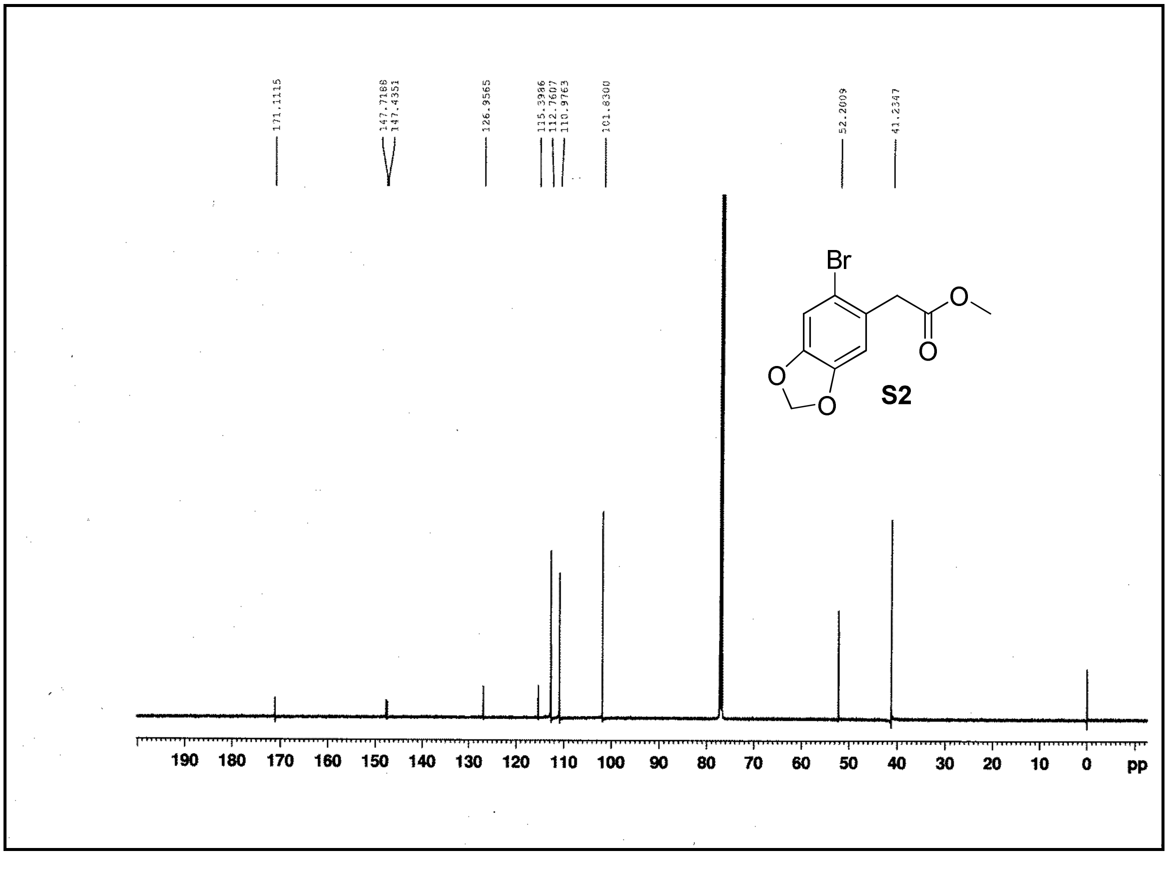

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O
O
O
S2
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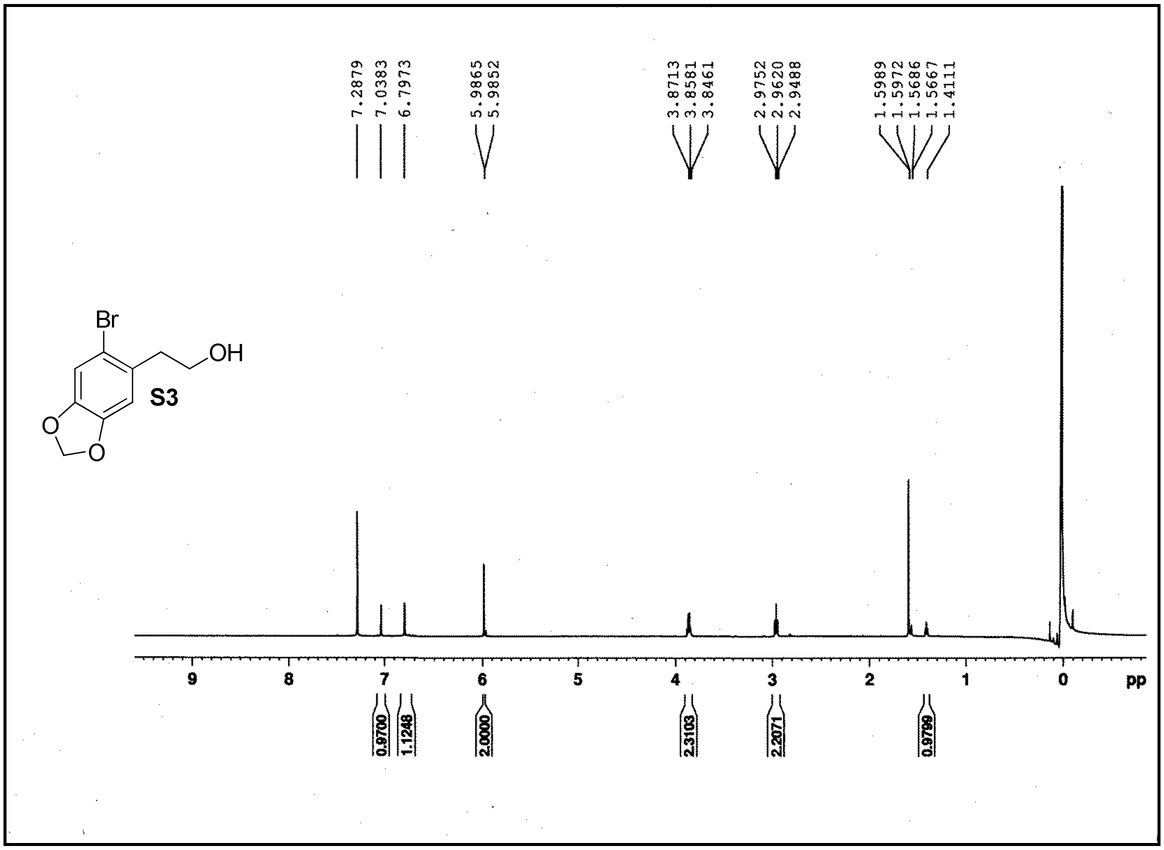
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1.5972
1.5686
1.5667
1.4111
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OH
O
O
S3
9
8
7
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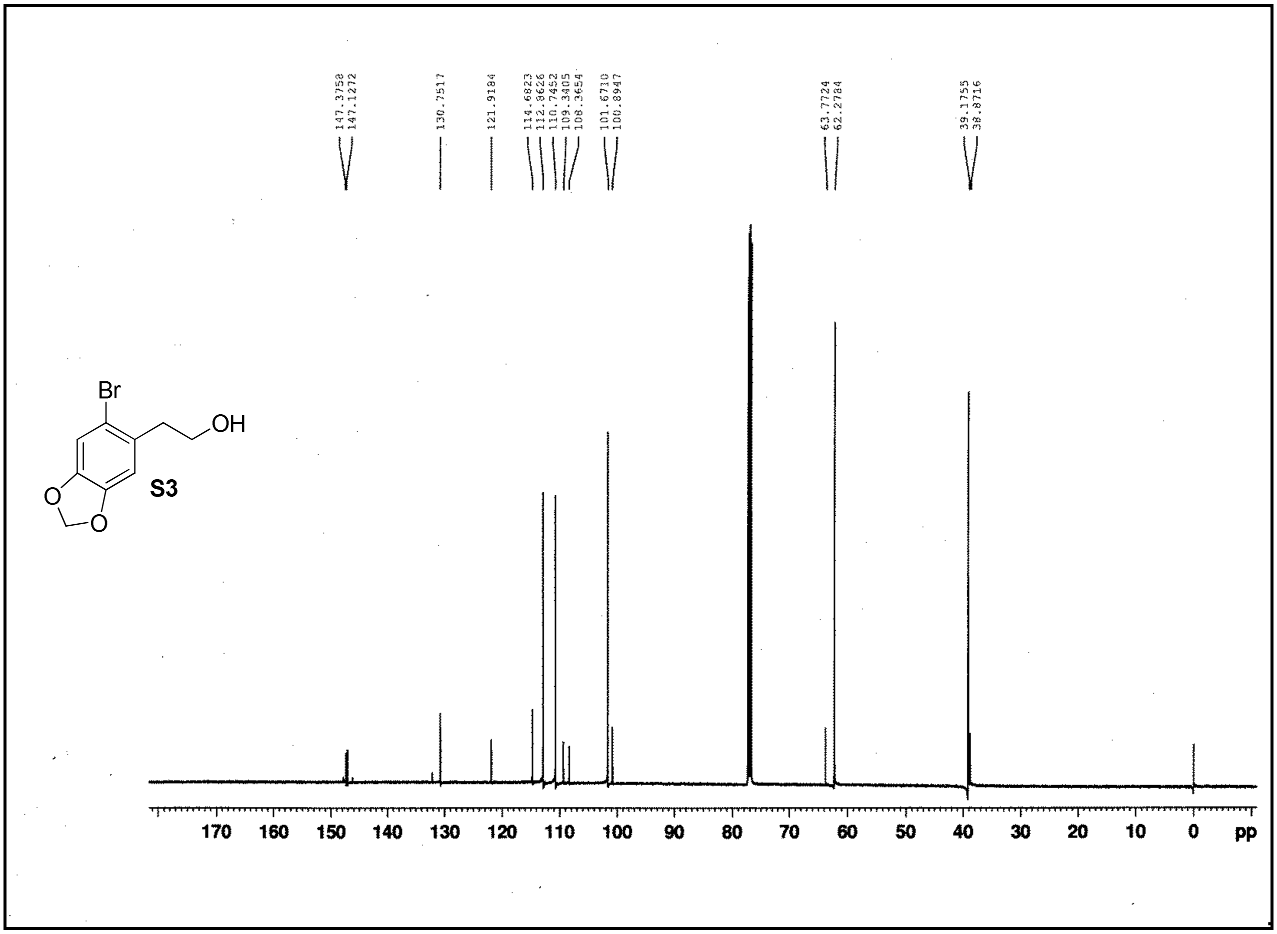
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63.7724
62.2784
39.1755
38.8716
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OH
O
O
S3
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120
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20
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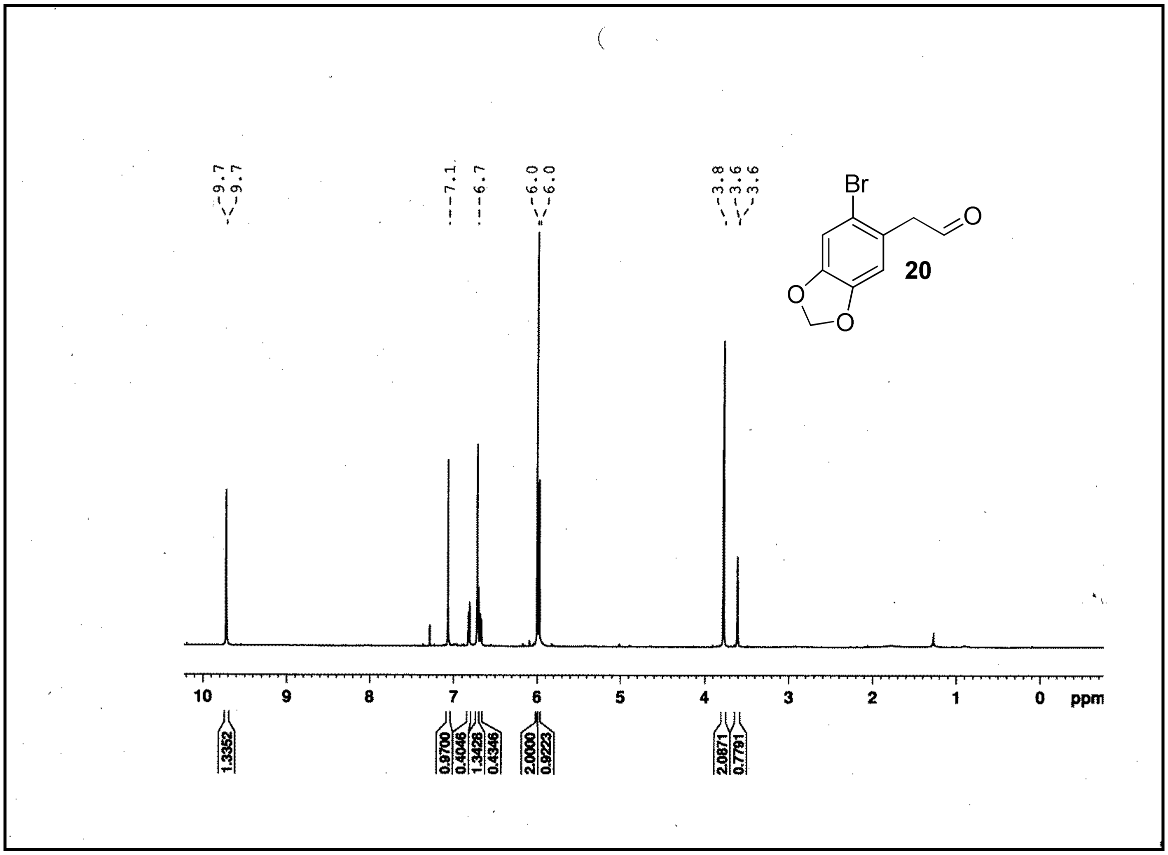
pp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9
8
7
6
5
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3
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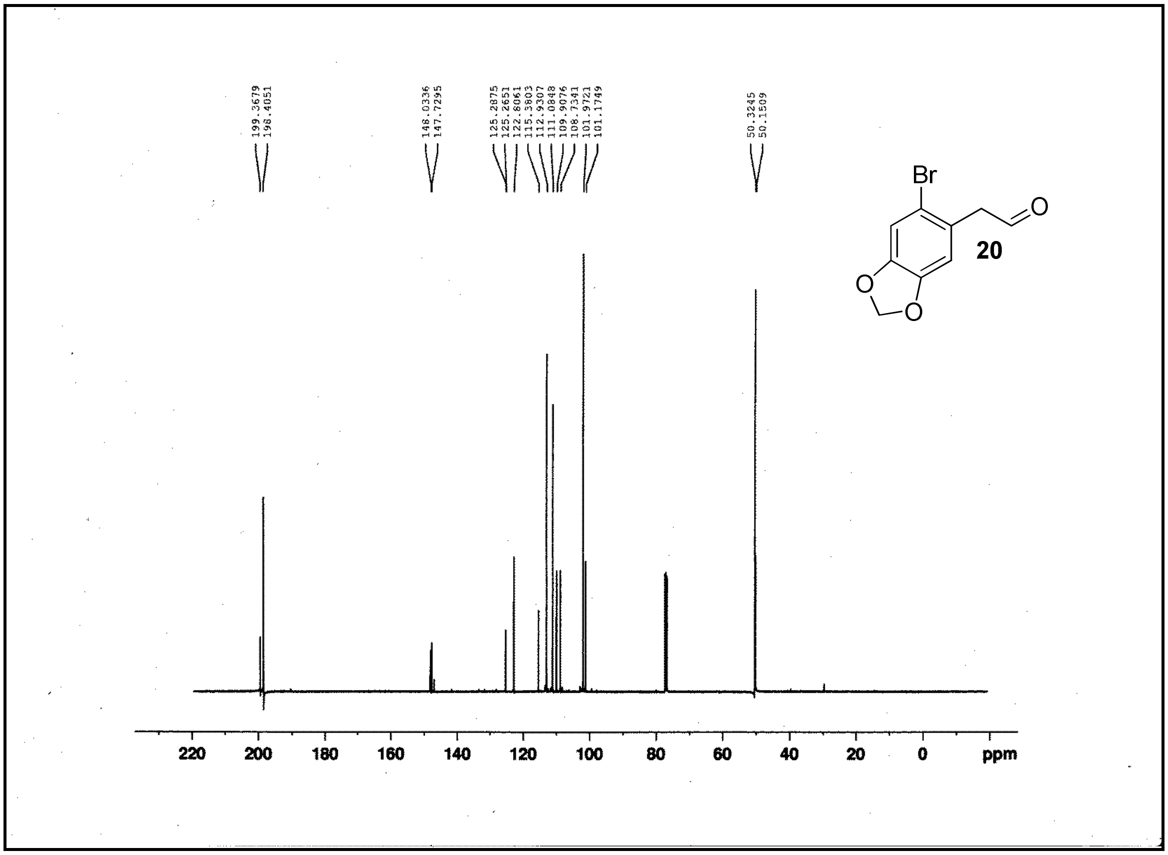
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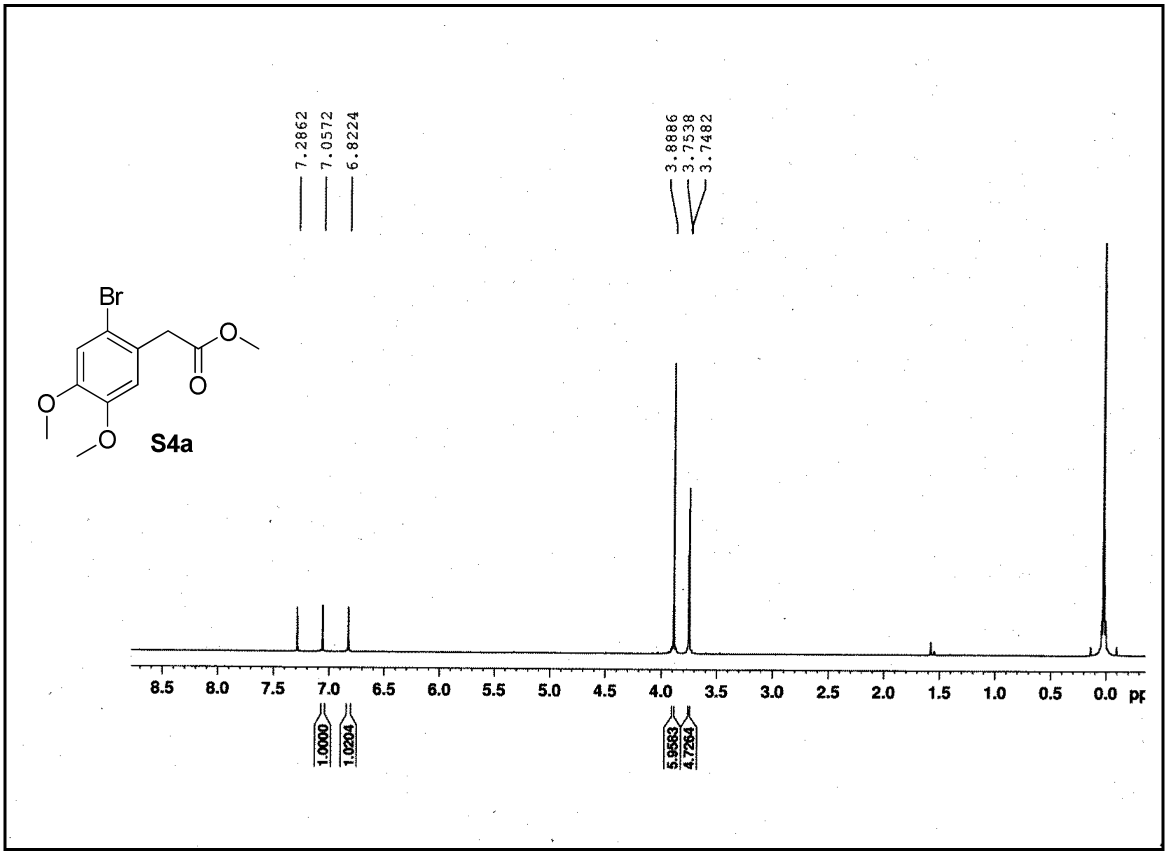
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7.0
6.5
6.0
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4.5
4.0
3.5
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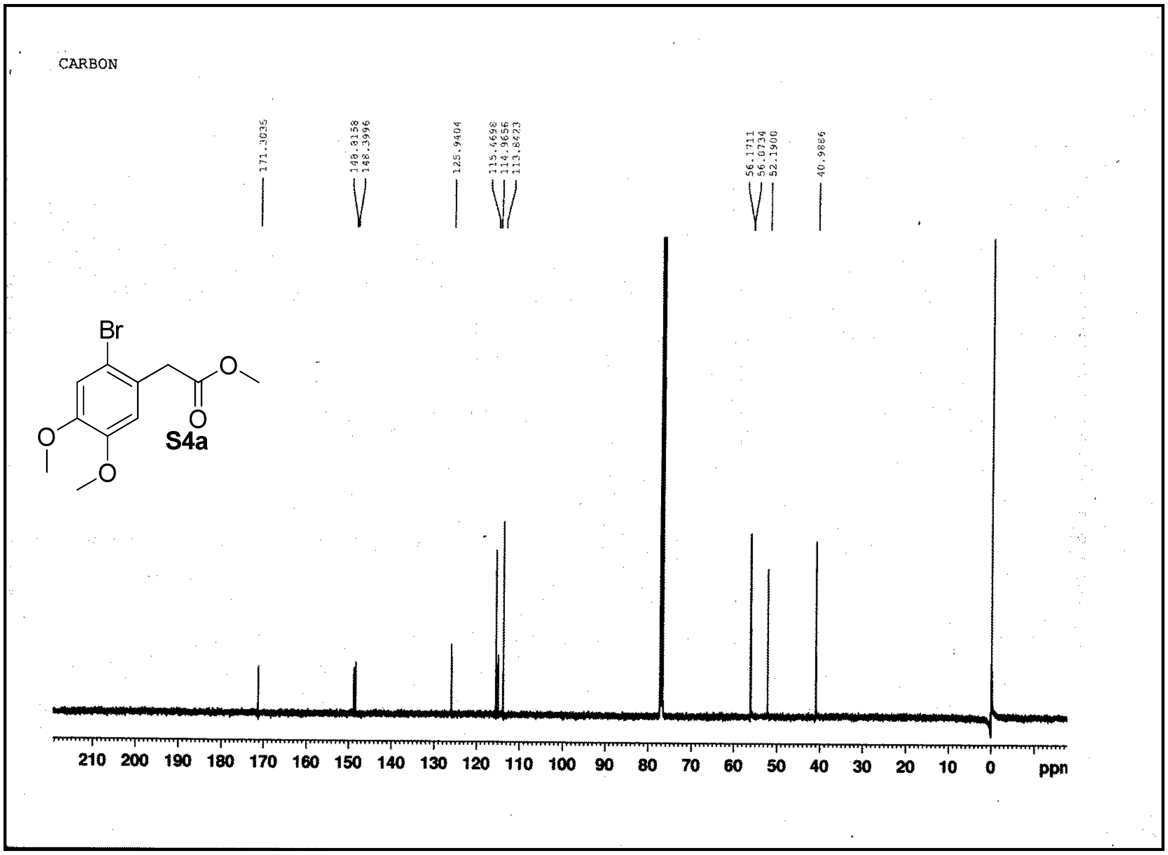
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O
S4a
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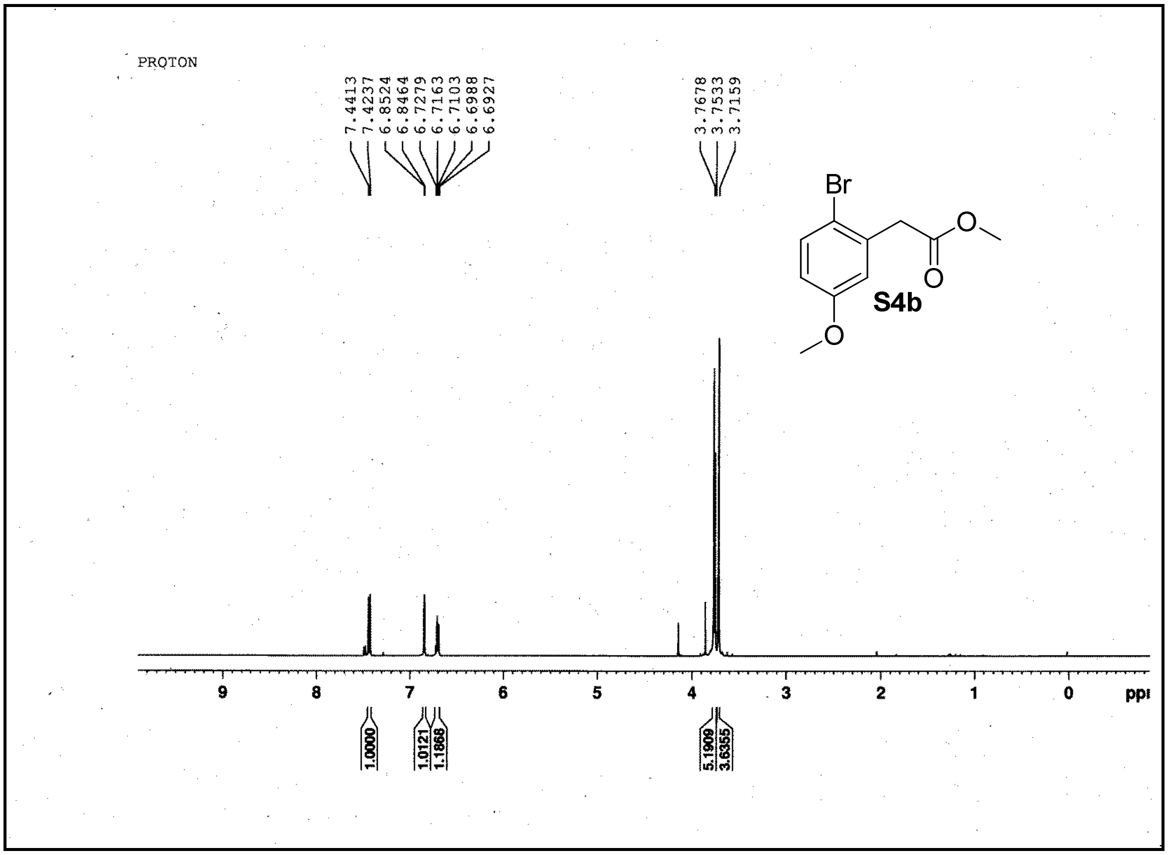
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3.7533
3.7159
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S4b
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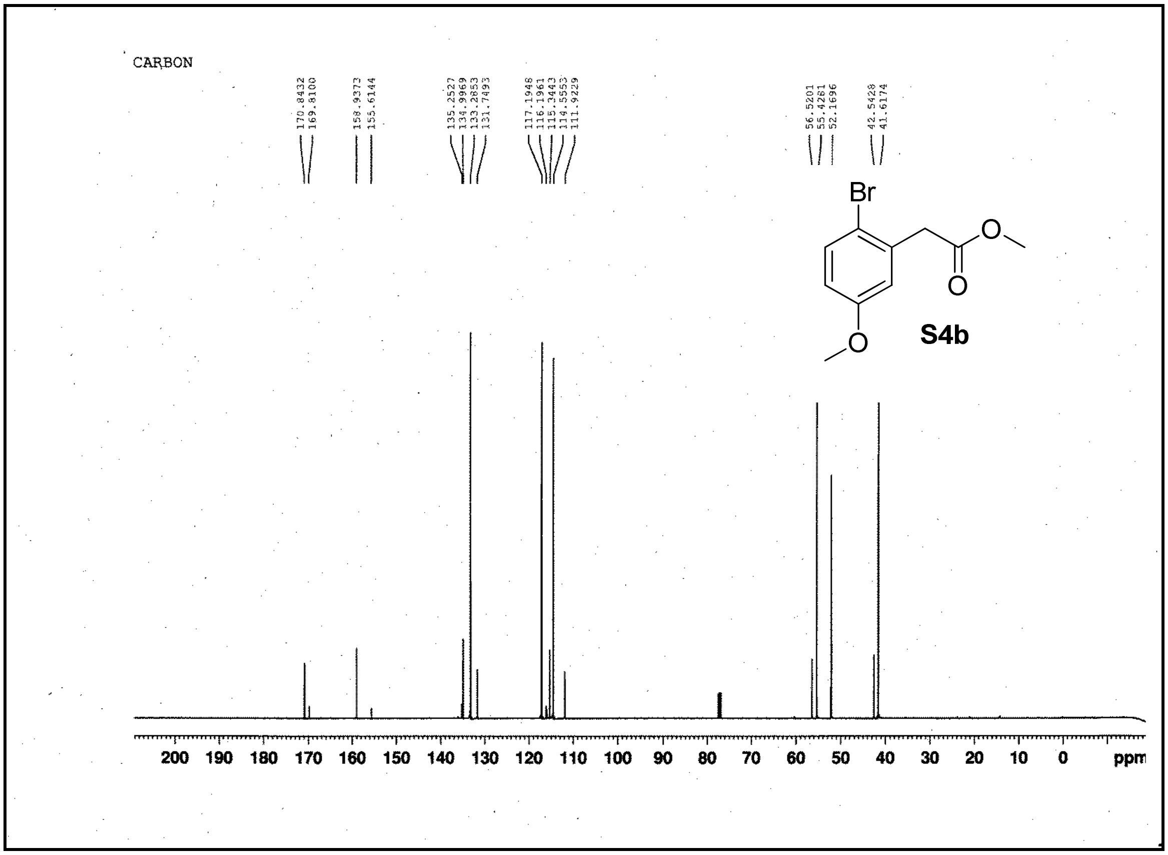
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O
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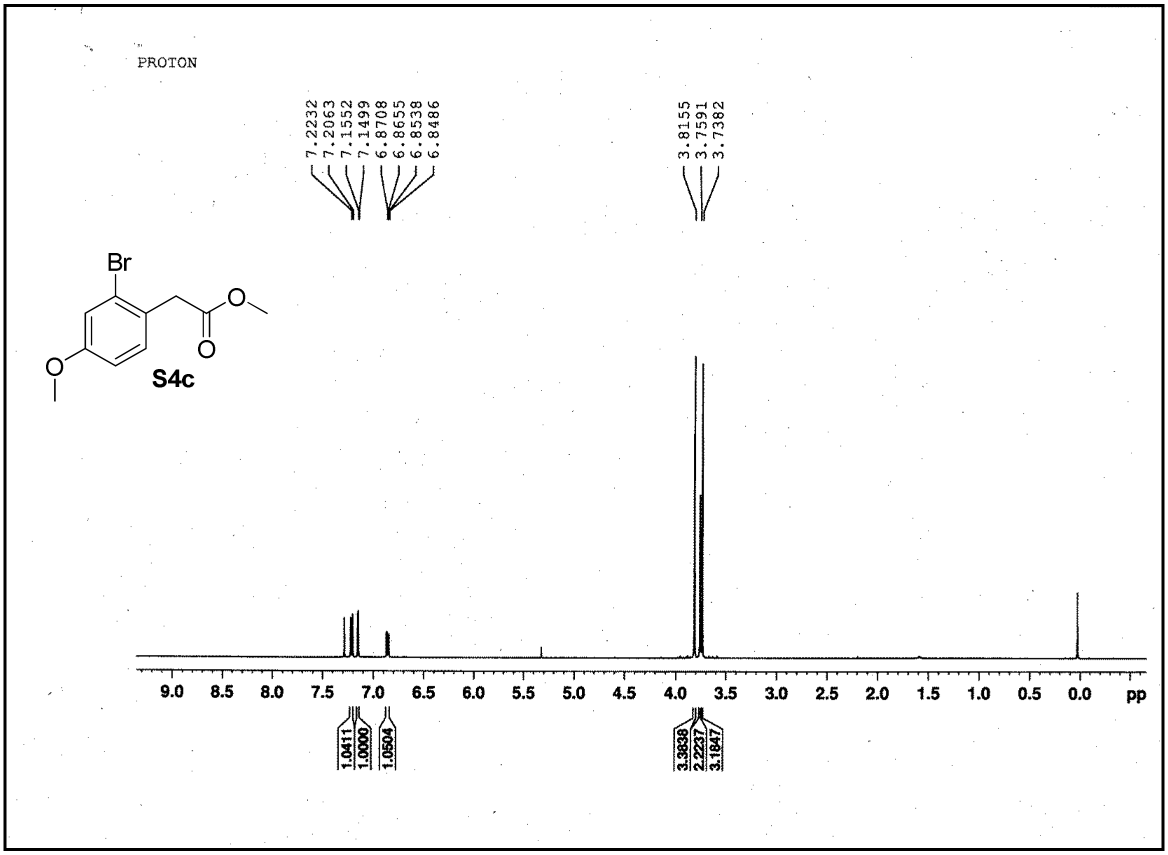
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O
O
S4c
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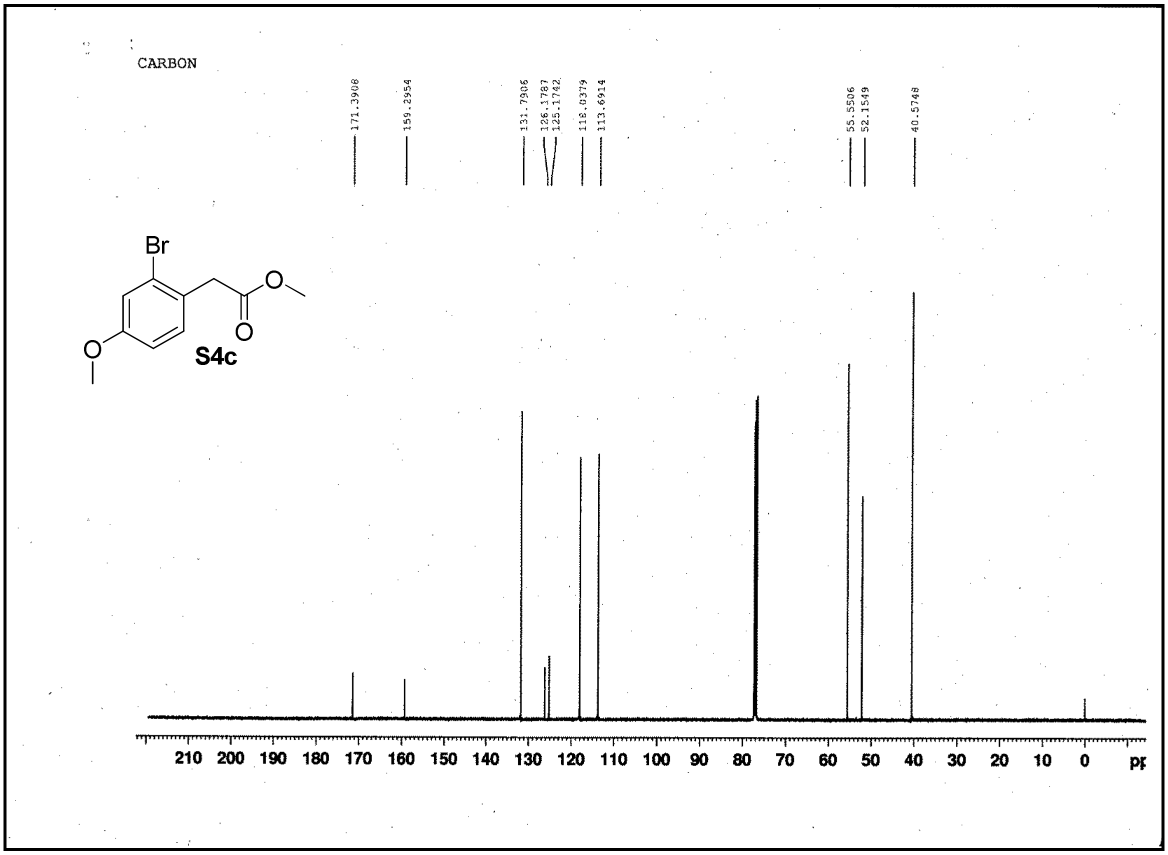
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O
S4c
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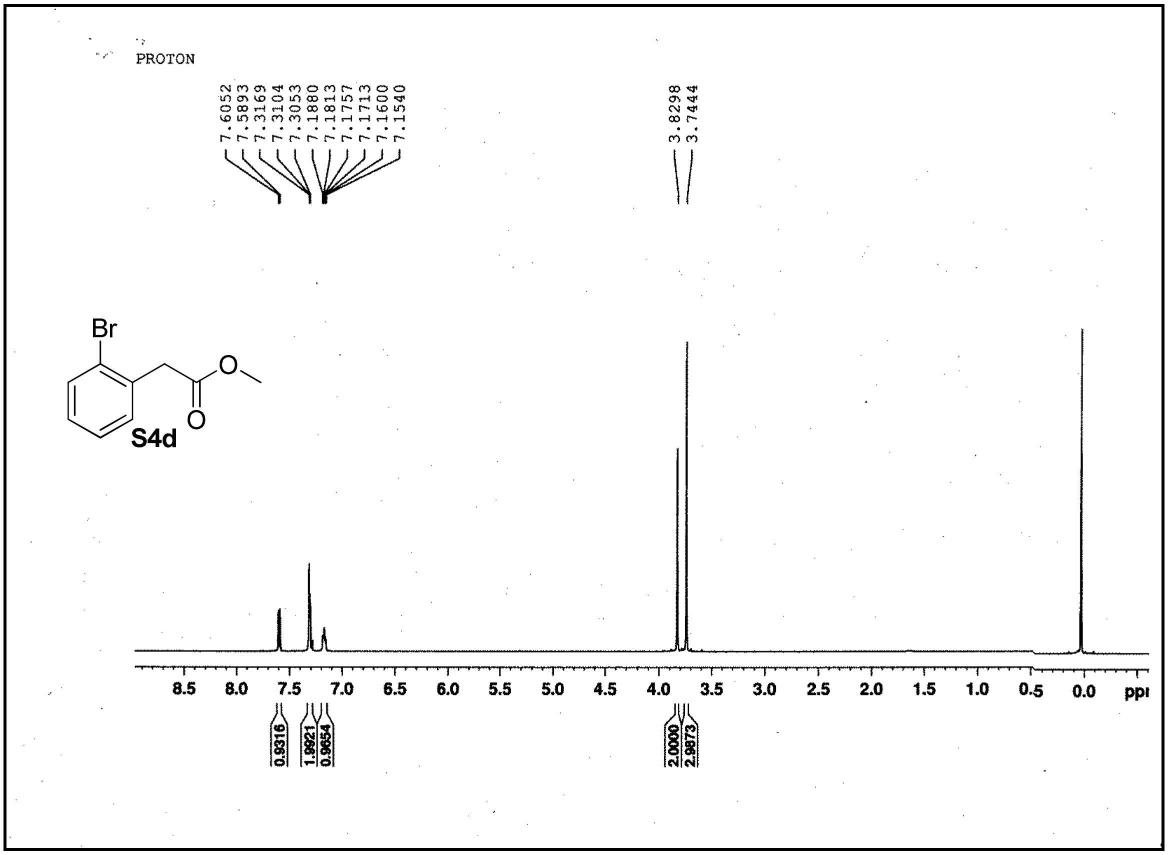
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3.7444
Br
O
O
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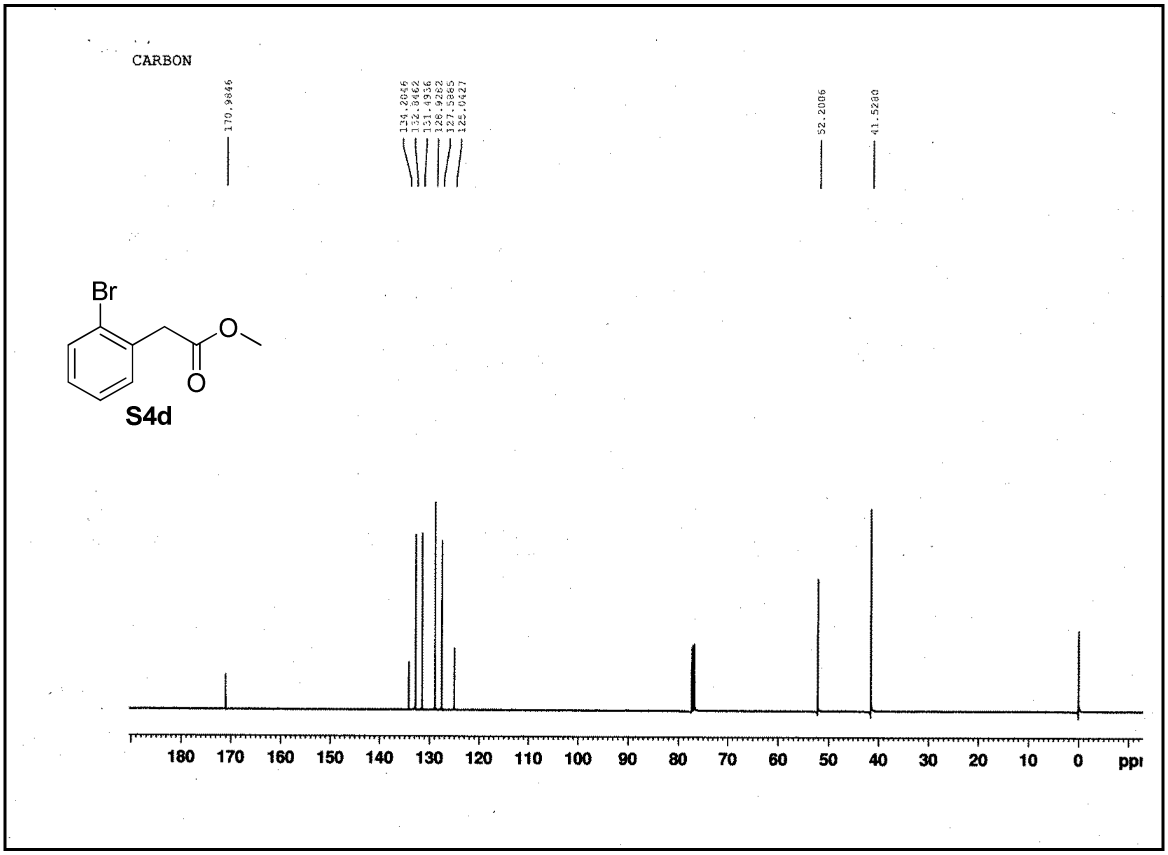
S4d

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O
O
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110
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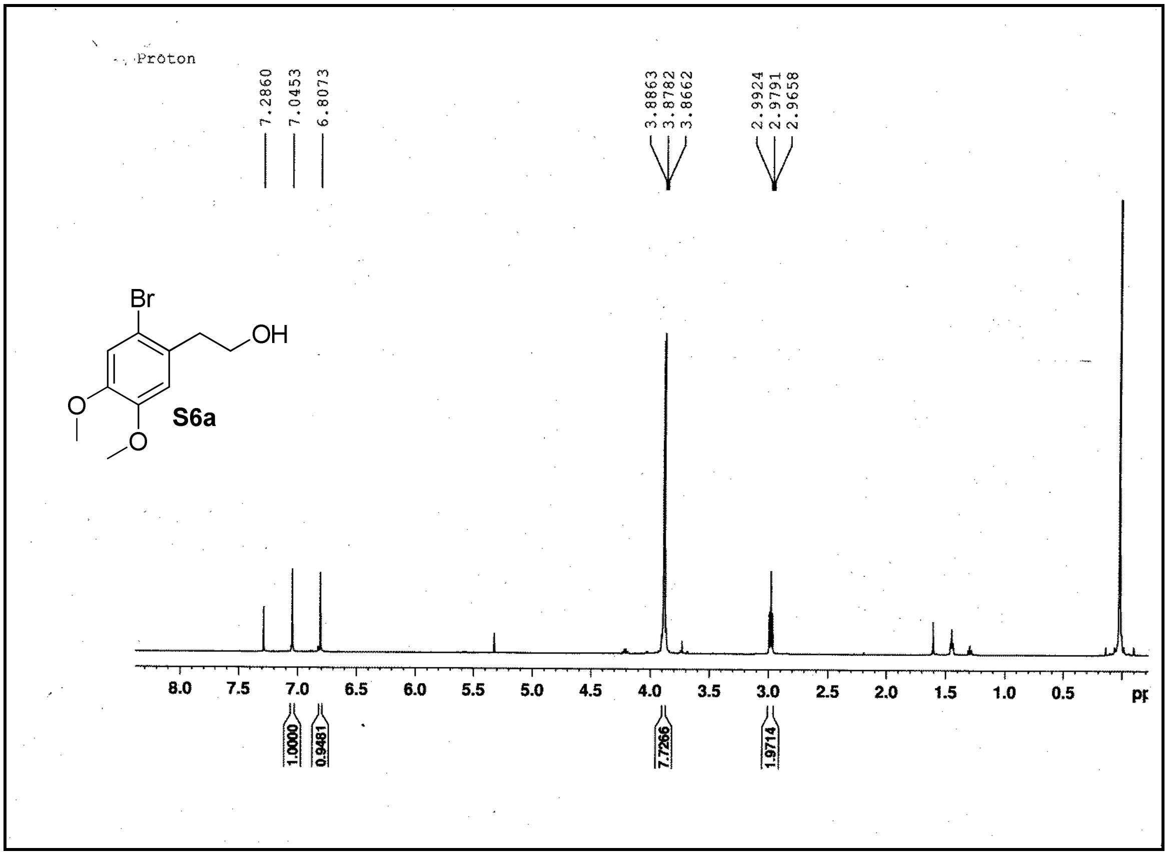
50
40
30
20
10
0
ppı


S6a

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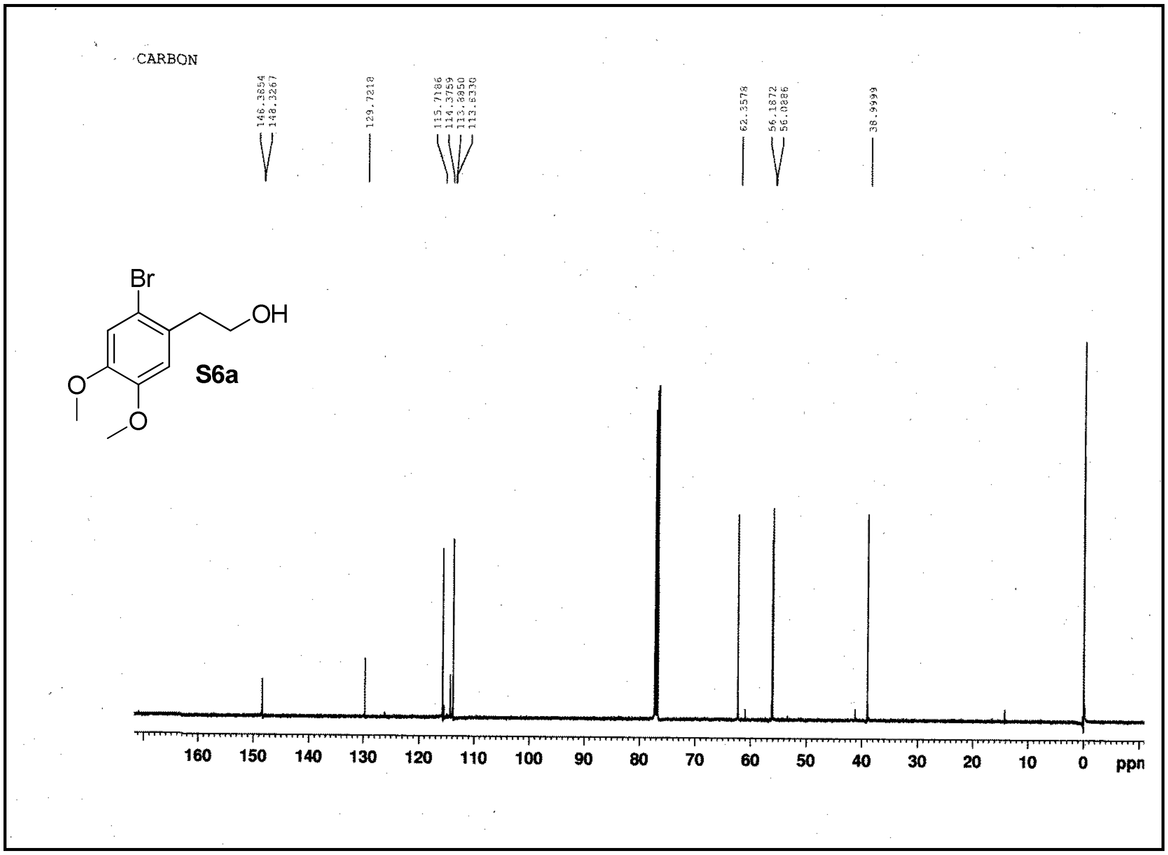
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30
20
10
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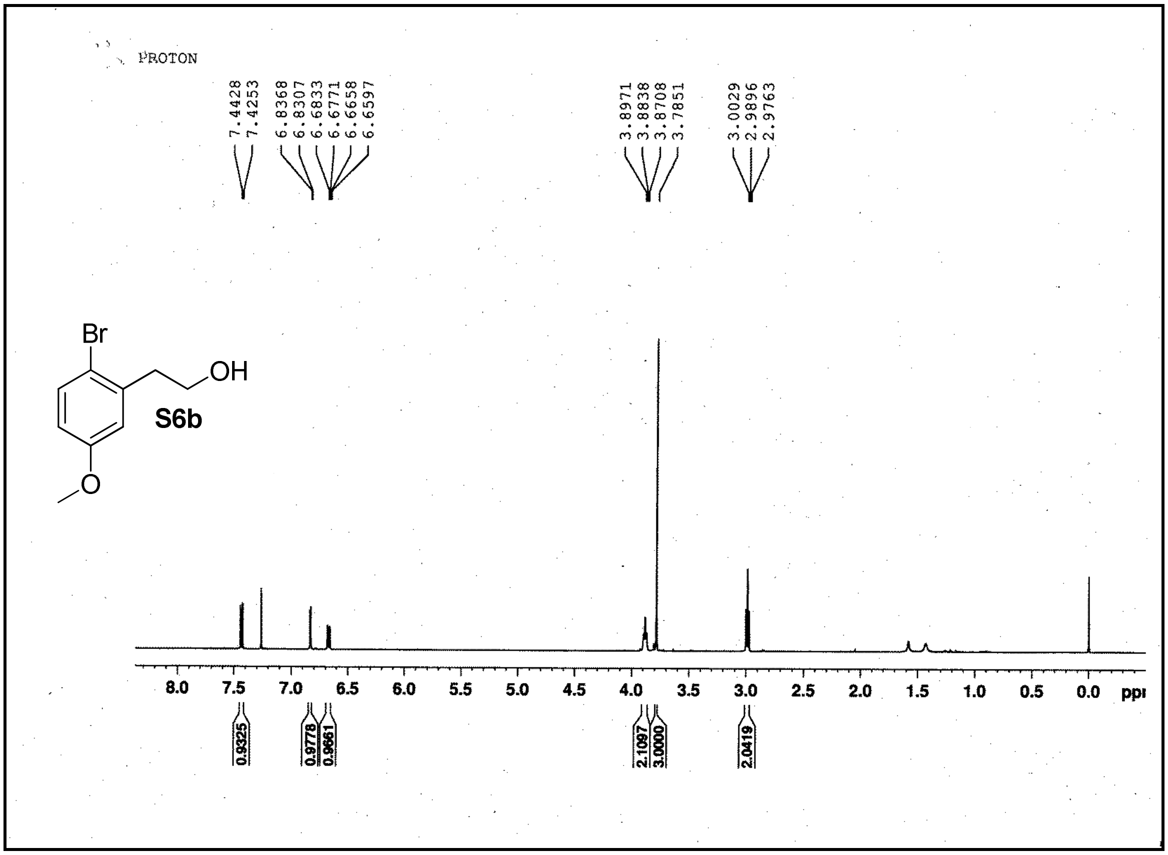
ppm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O
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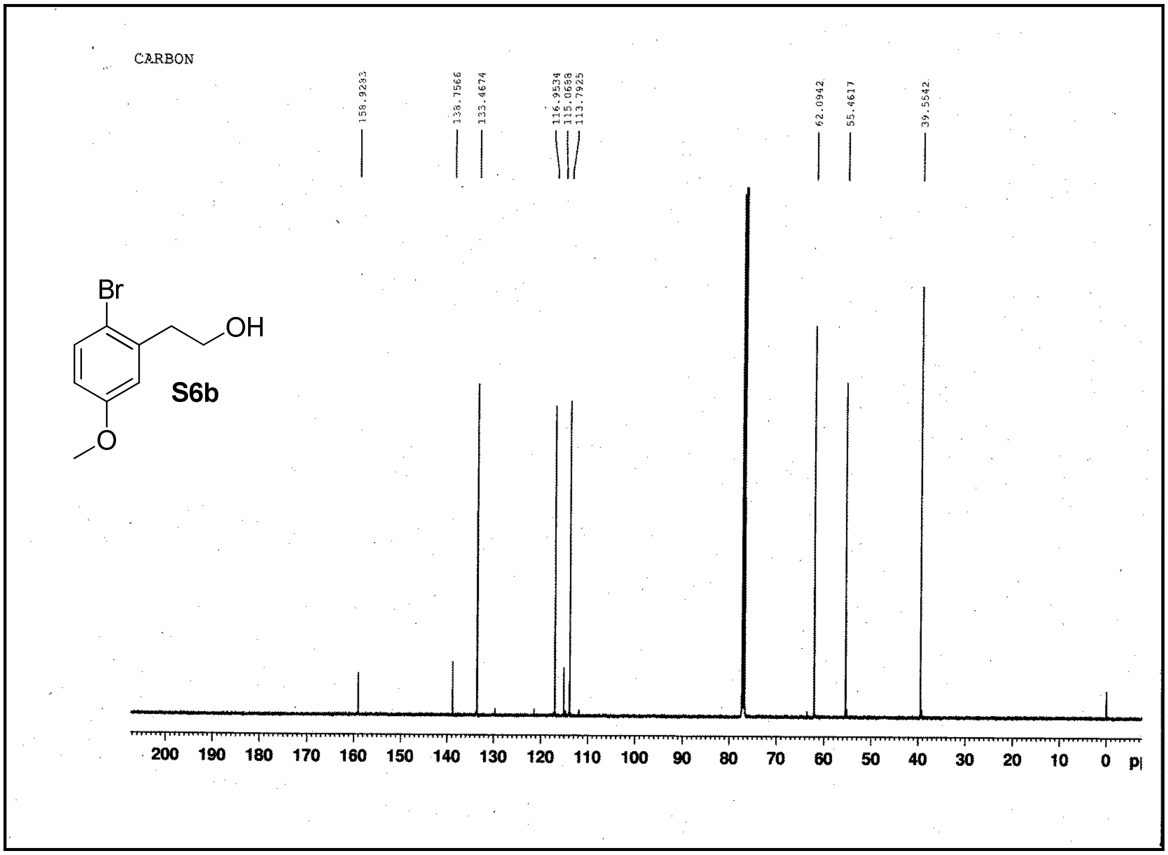

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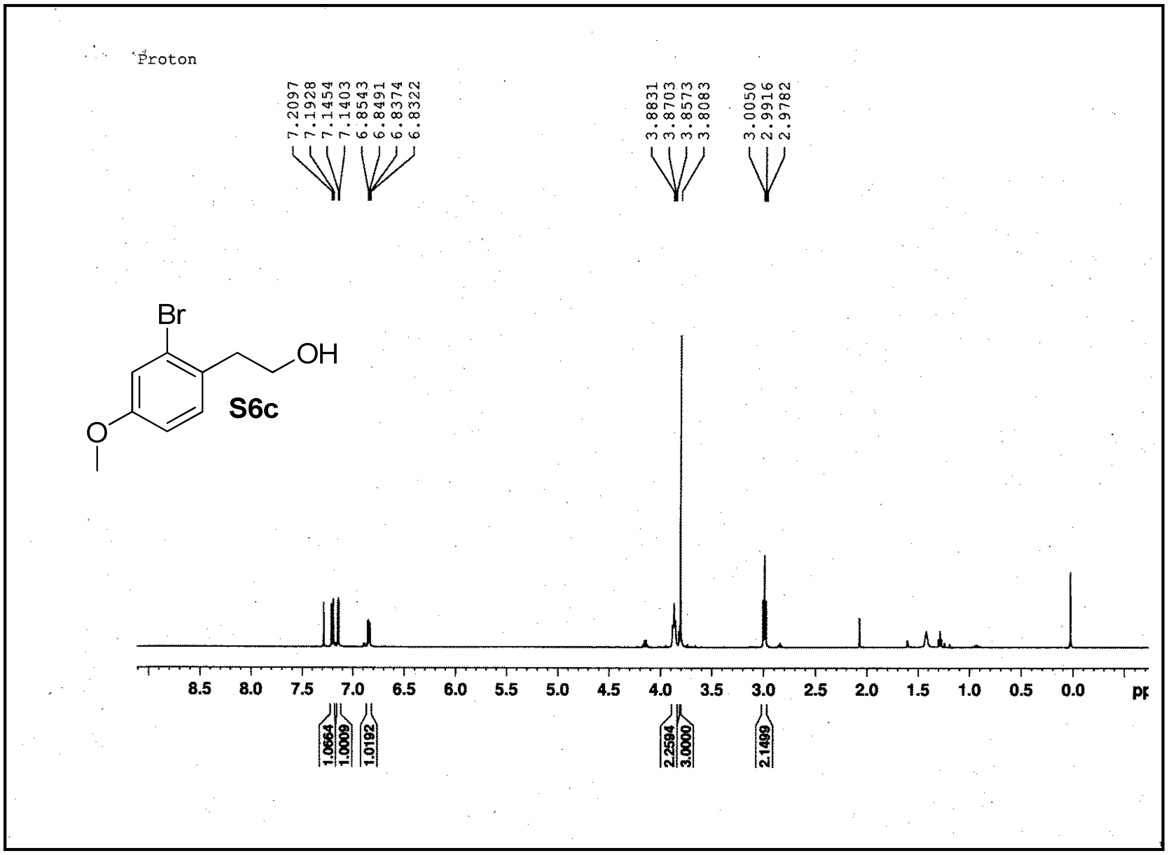
S6b



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Br
OH
O
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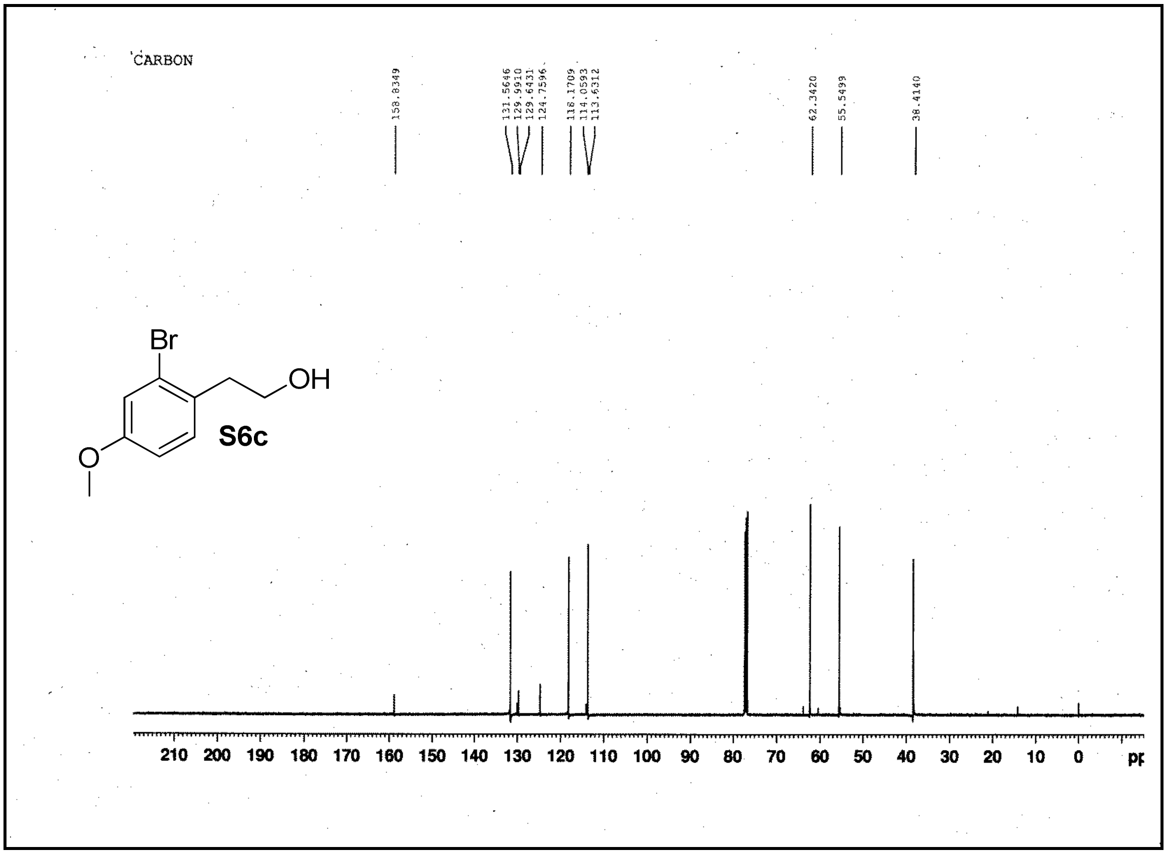
S6c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O
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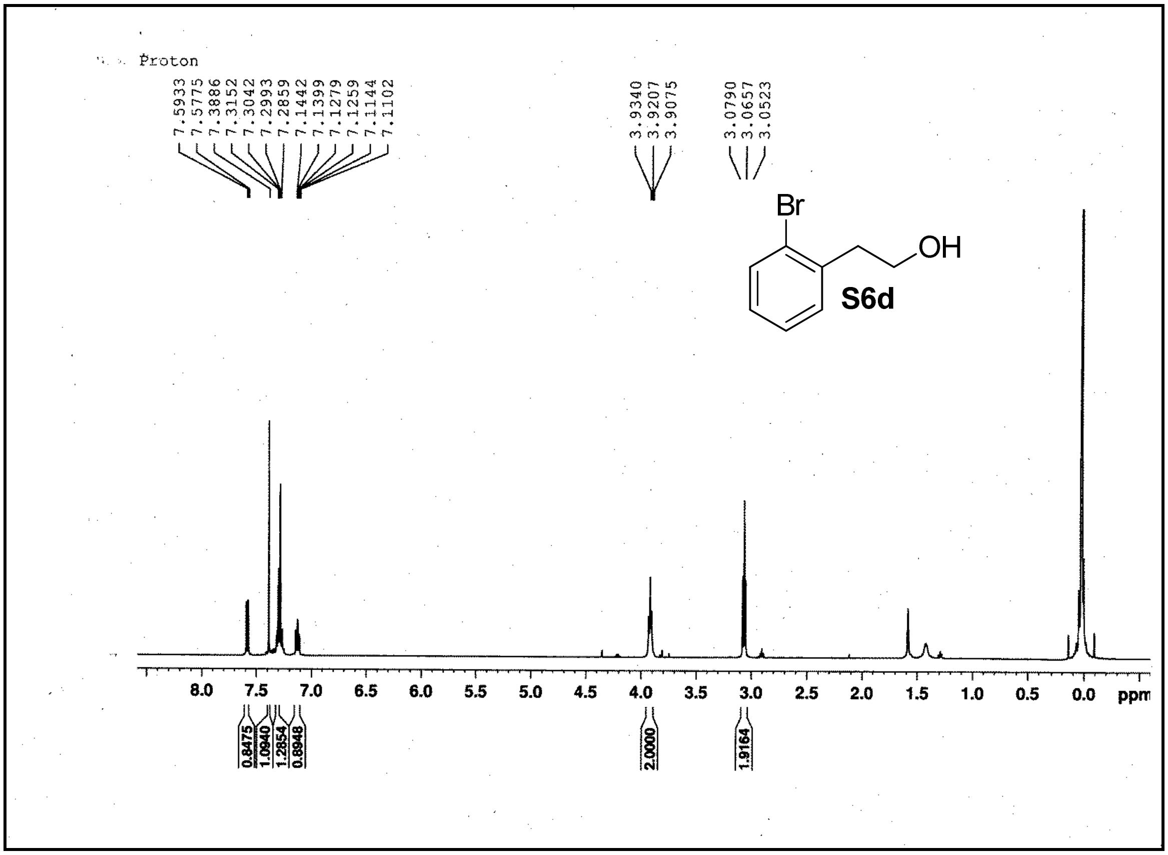
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OH
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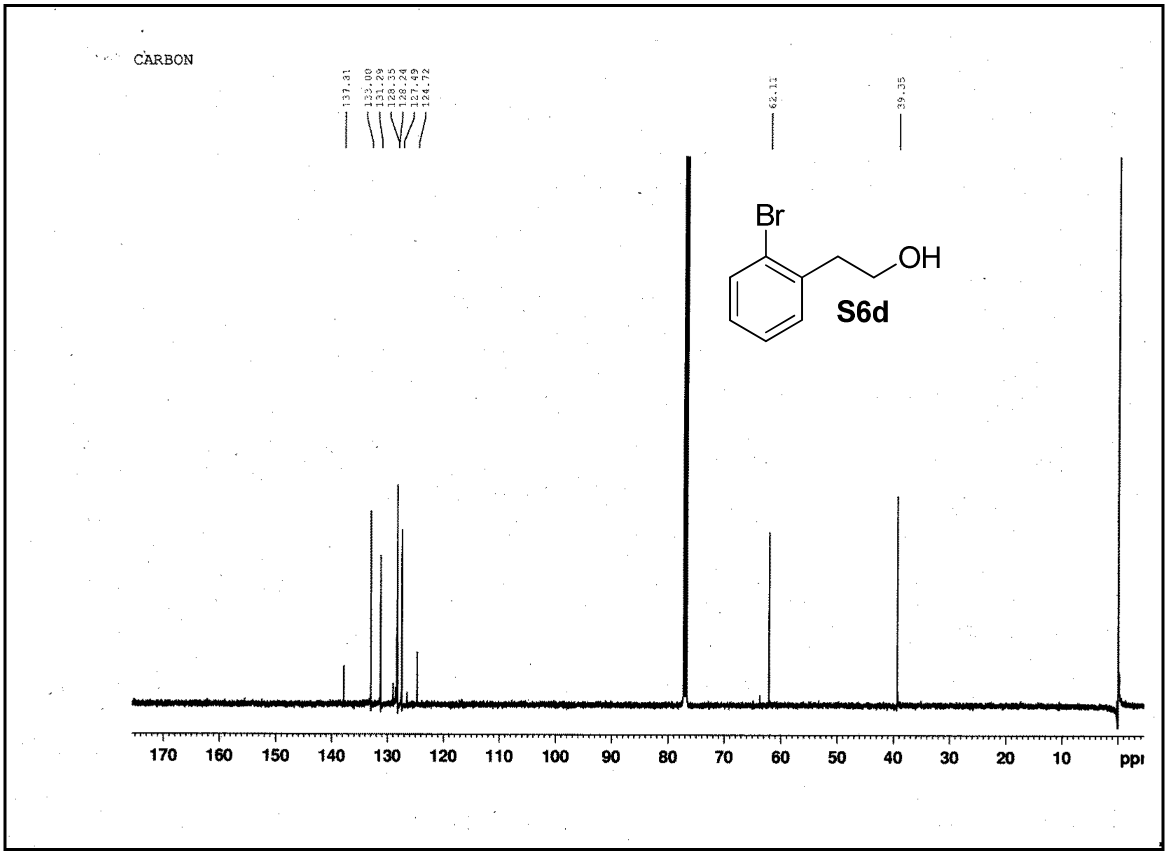
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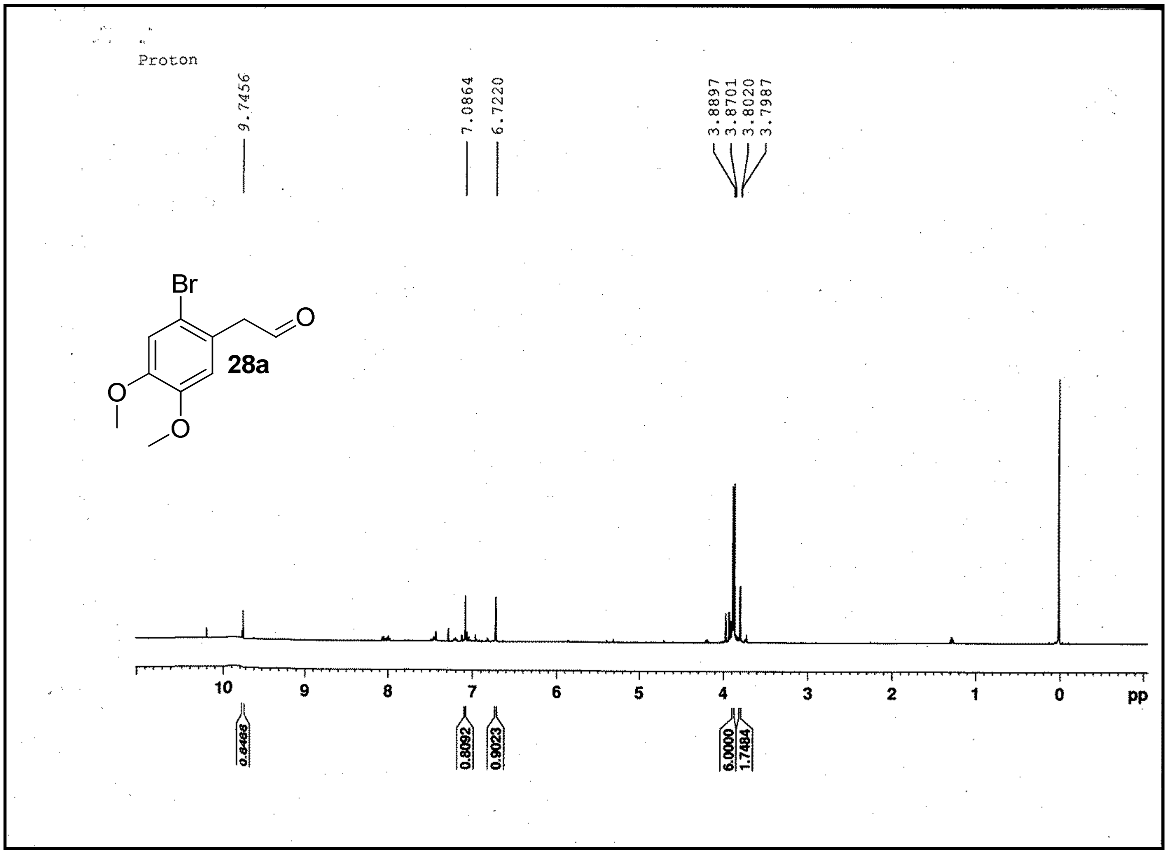
62.11
39.35
Br
OH
S6d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppı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Br
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28a
O
O
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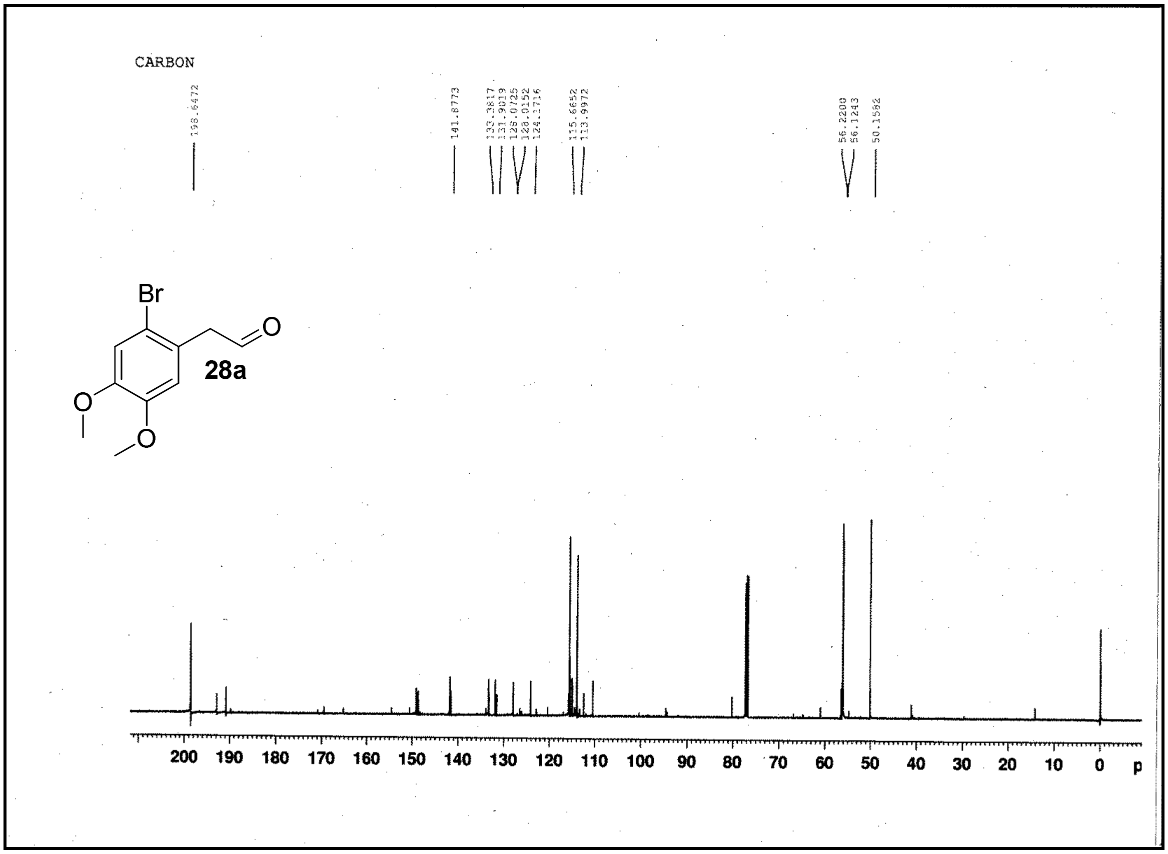
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115.6652
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56.1243
50.1582
Br
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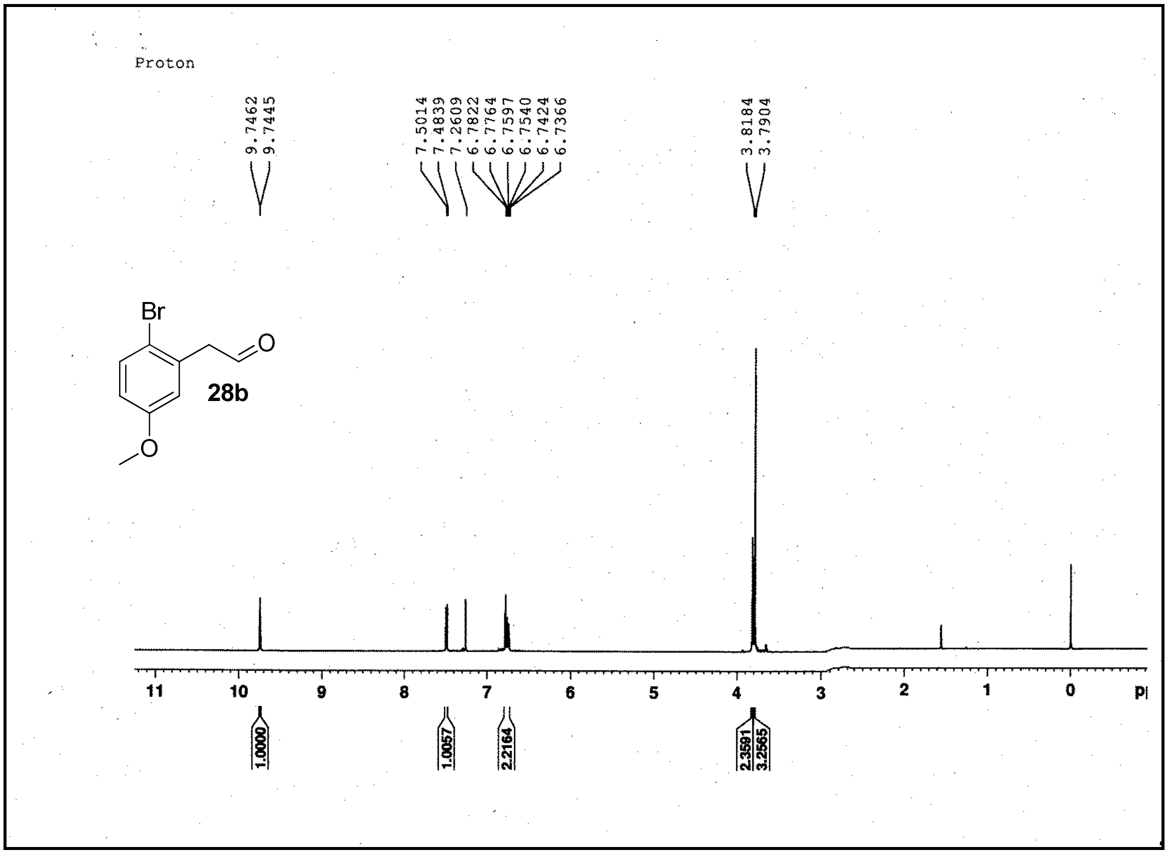
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 p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6.7424
6.7366
3.8184
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O
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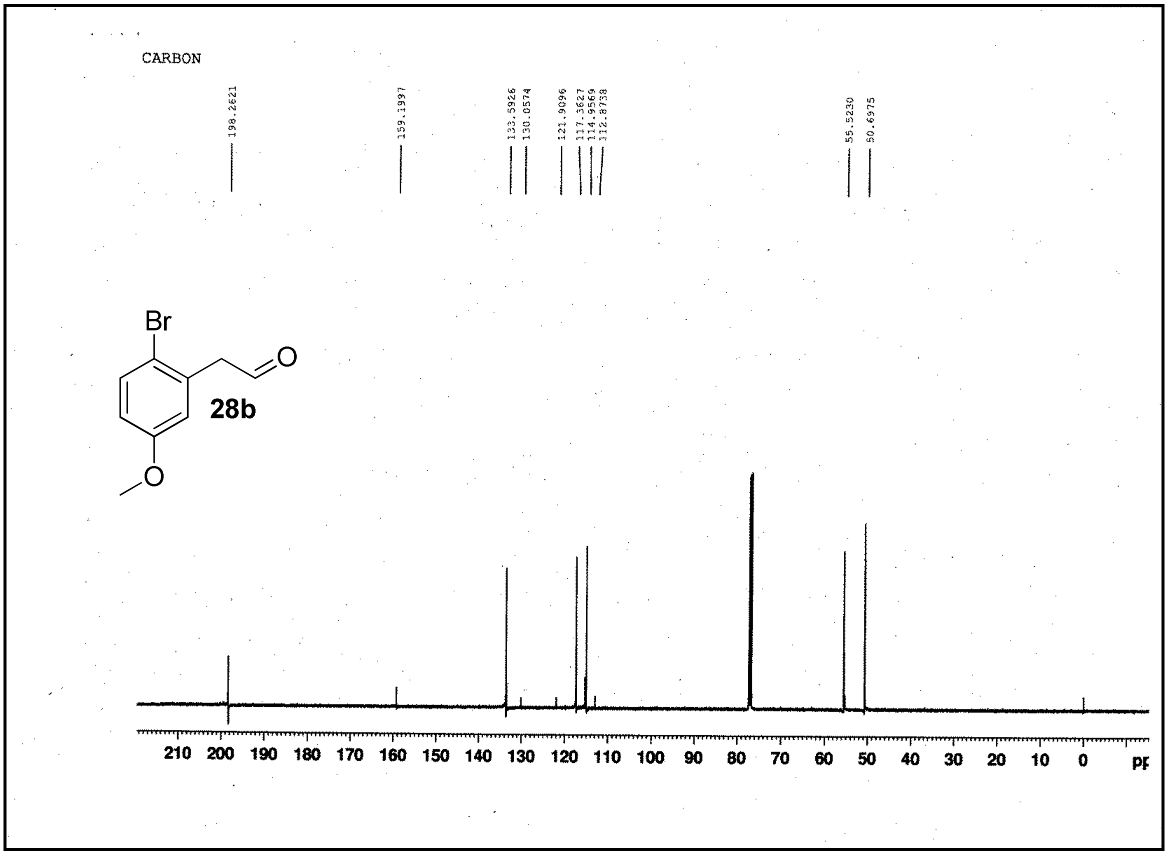
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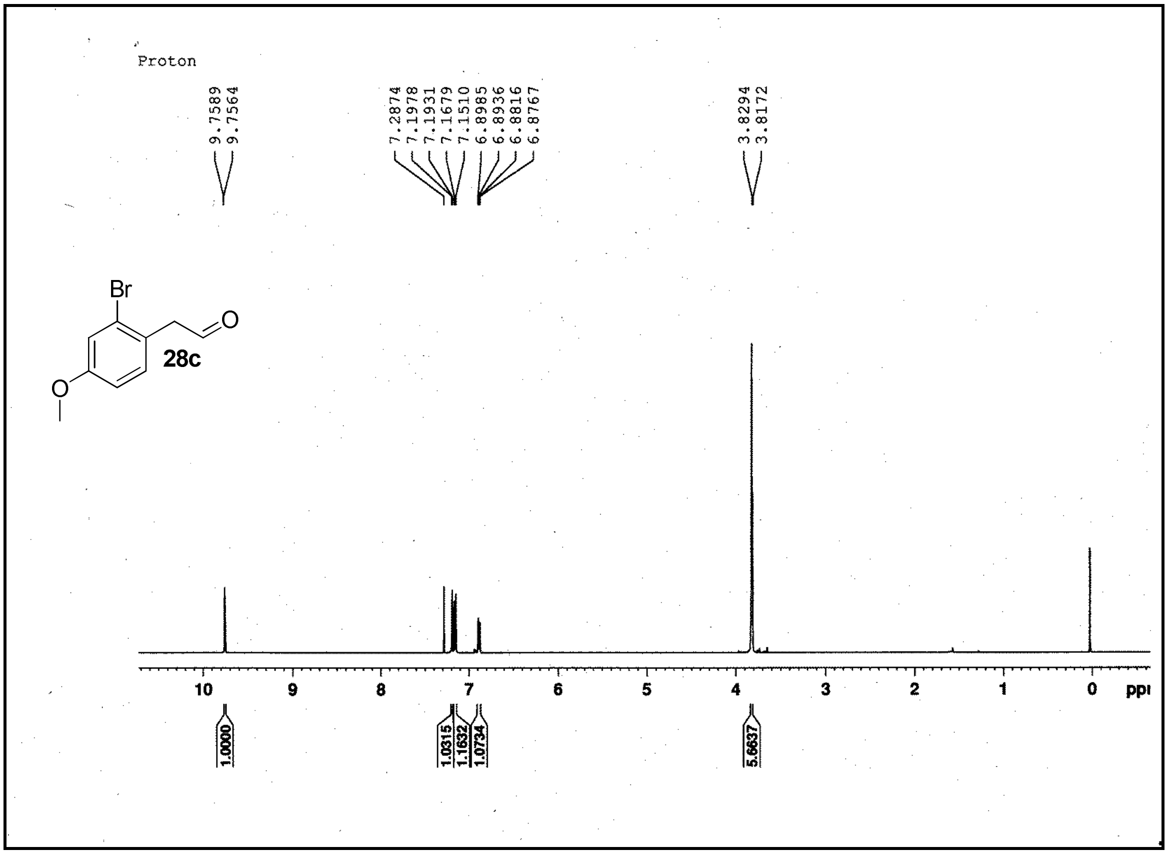
28b
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 pp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O
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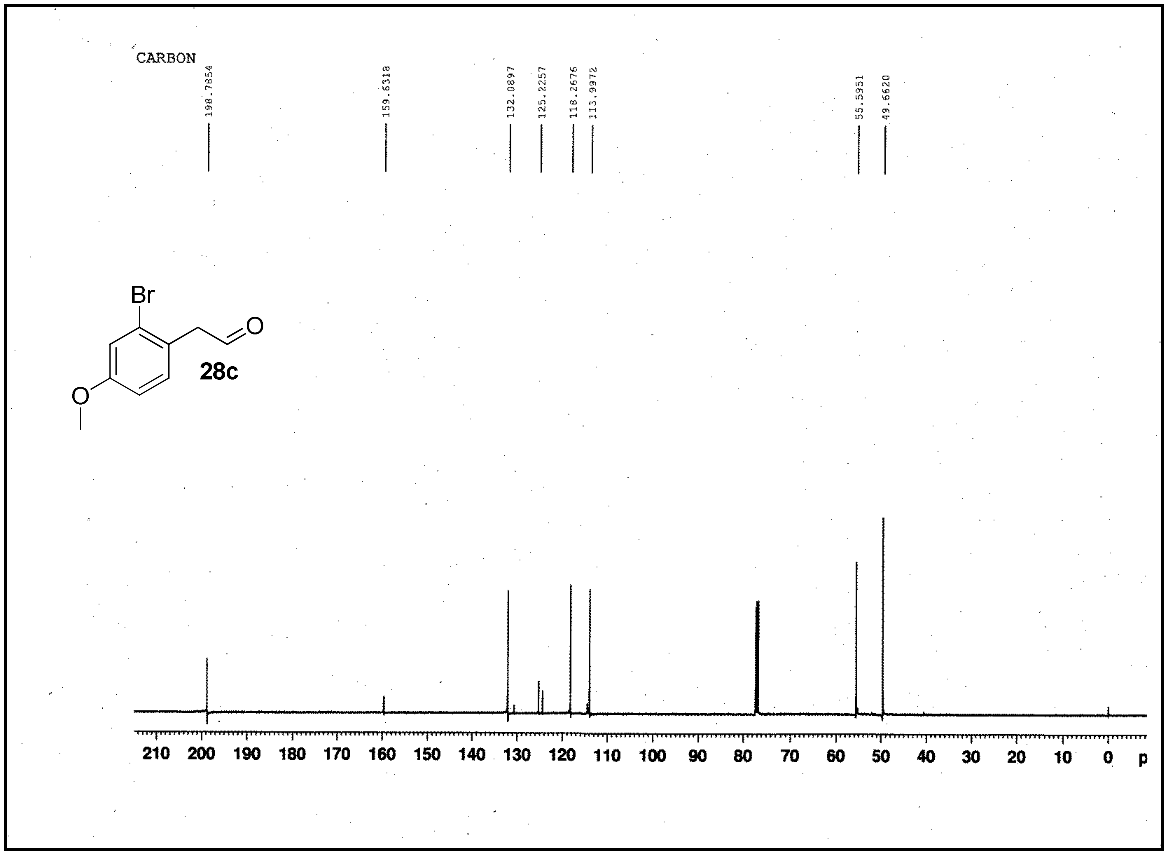
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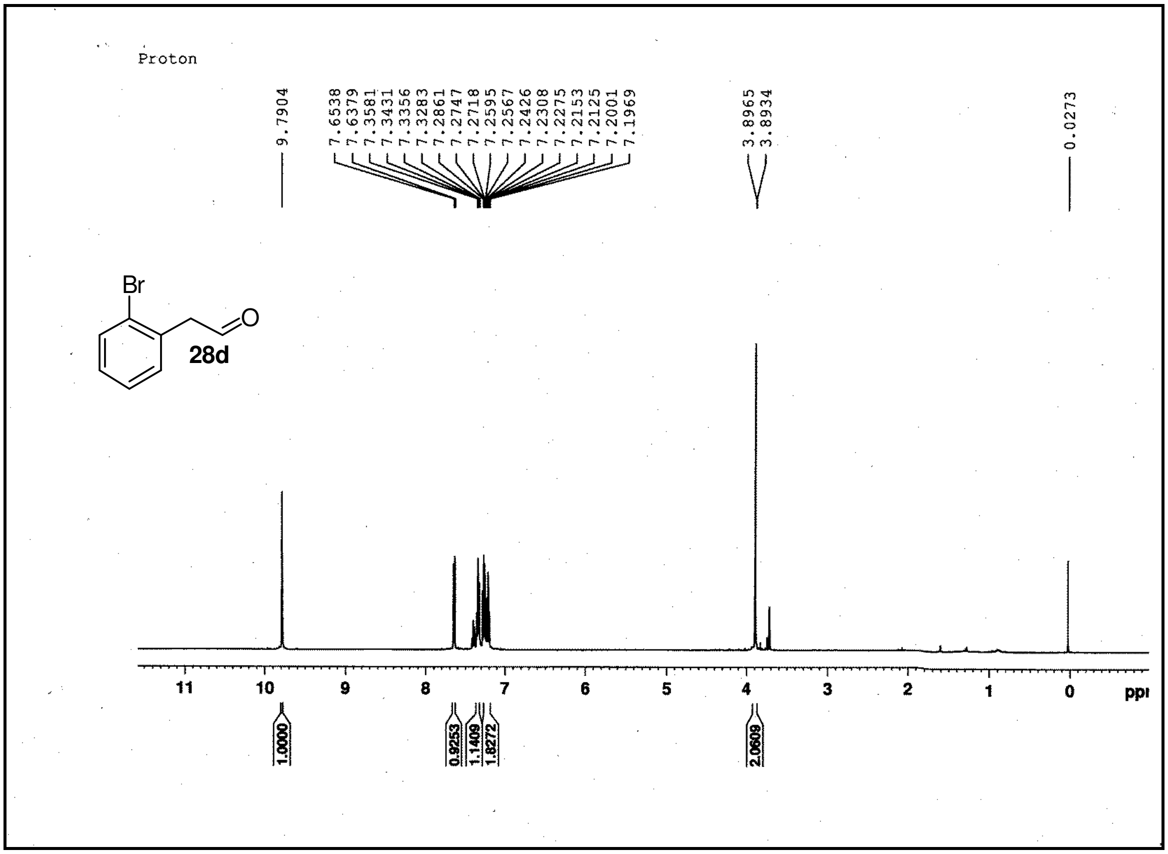
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7.3356
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7.2861
7.2747
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7.2595
7.2567
7.2426
7.2308
7.2275
7.2153
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7.2001
7.1969
3.8965
3.8934
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11 10 9 8 7 6 5 4 3 2 1 0 ppı
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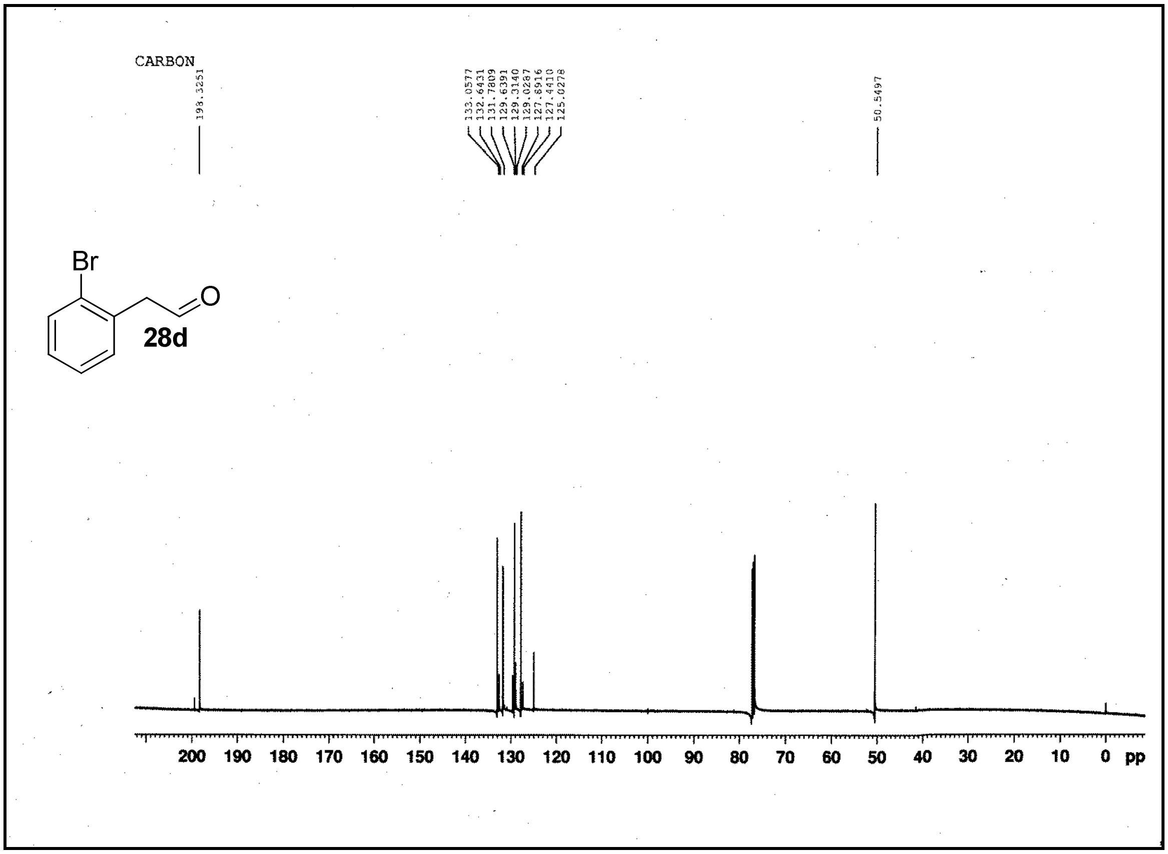
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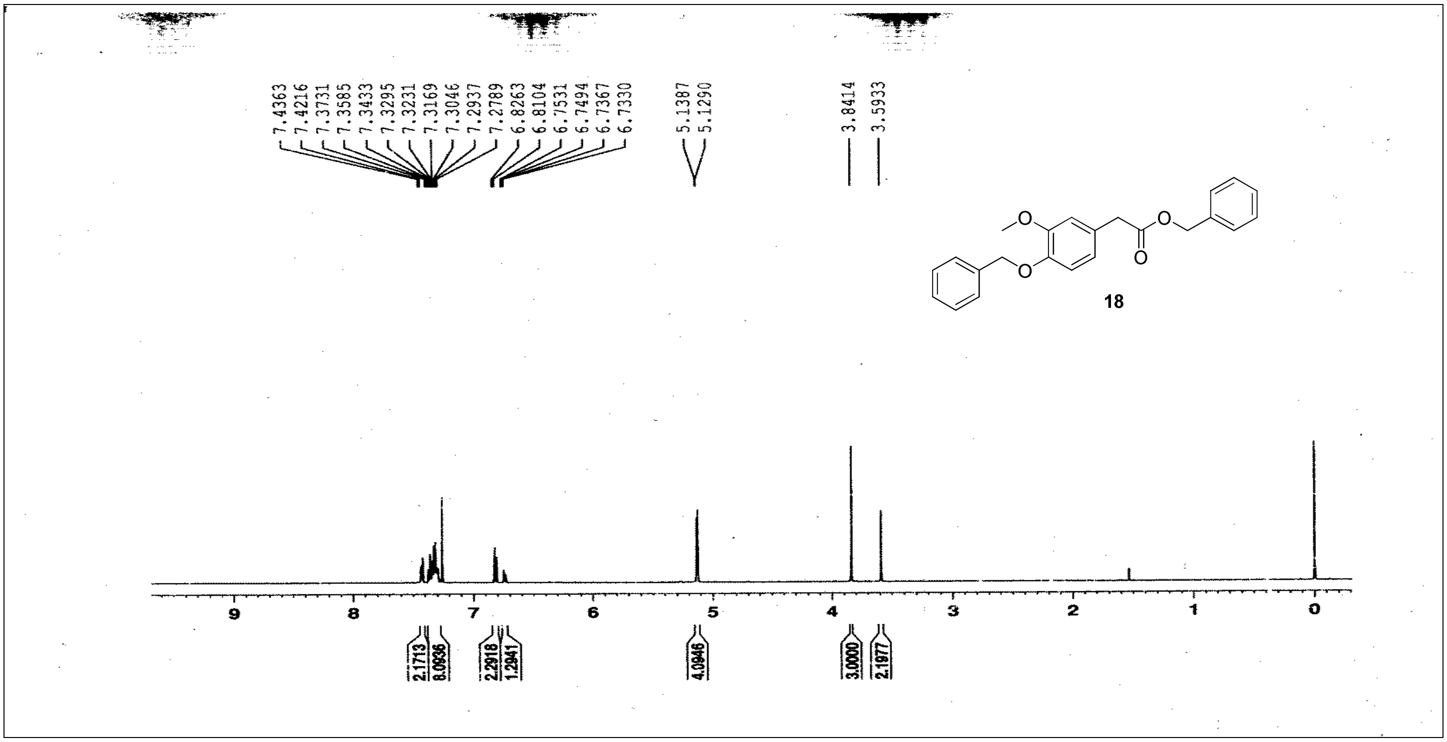
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6.8263
6.8104
6.7531
6.7494
6.7367
6.7330
5.1387
5.1290
3.8414
3.5933
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9
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7
6
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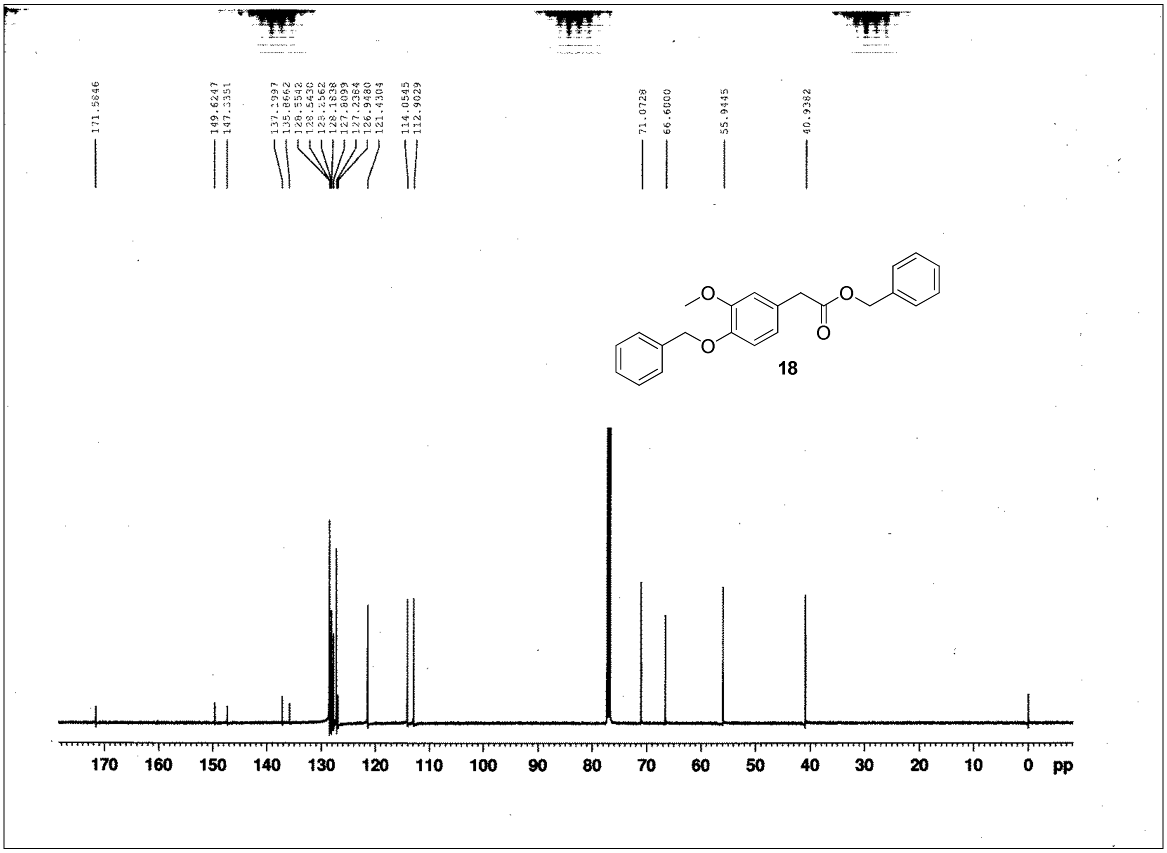
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114.0545
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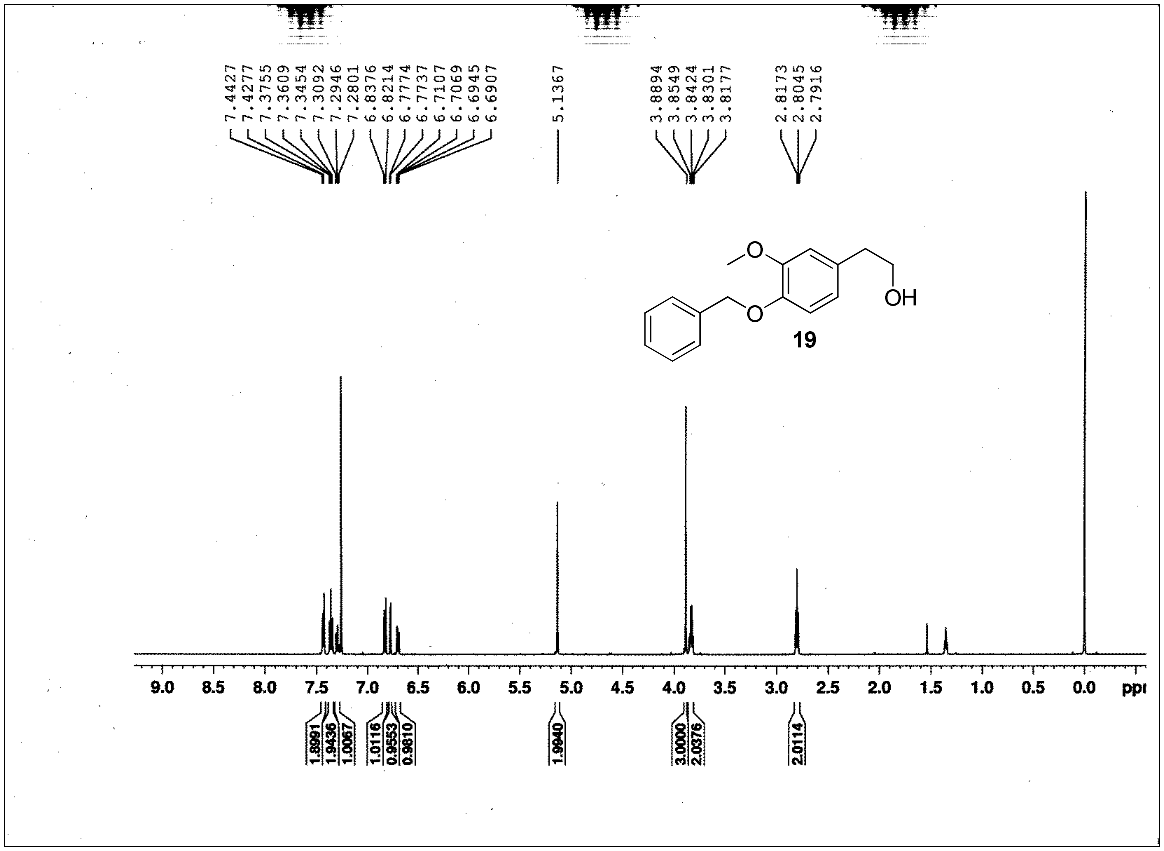
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6.7737
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5.1367
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3.8301
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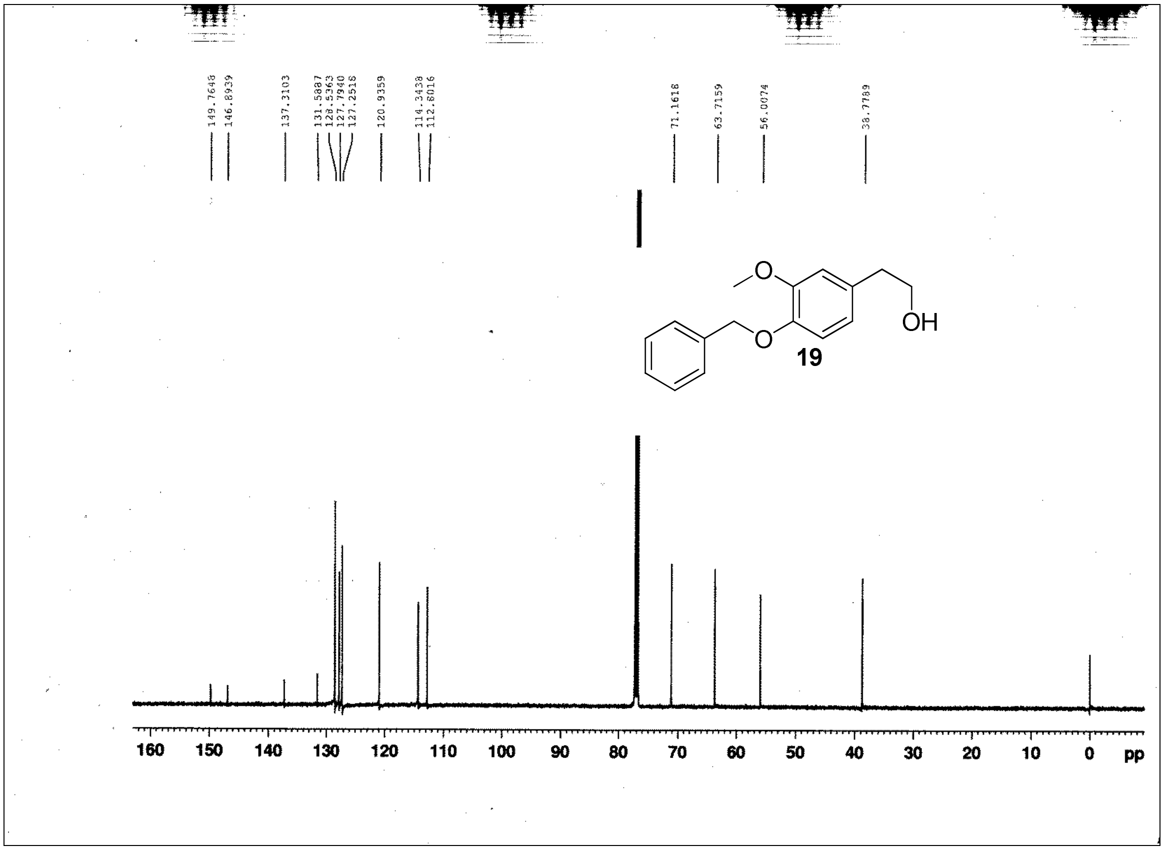
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56.0074
38.7789
O
OH
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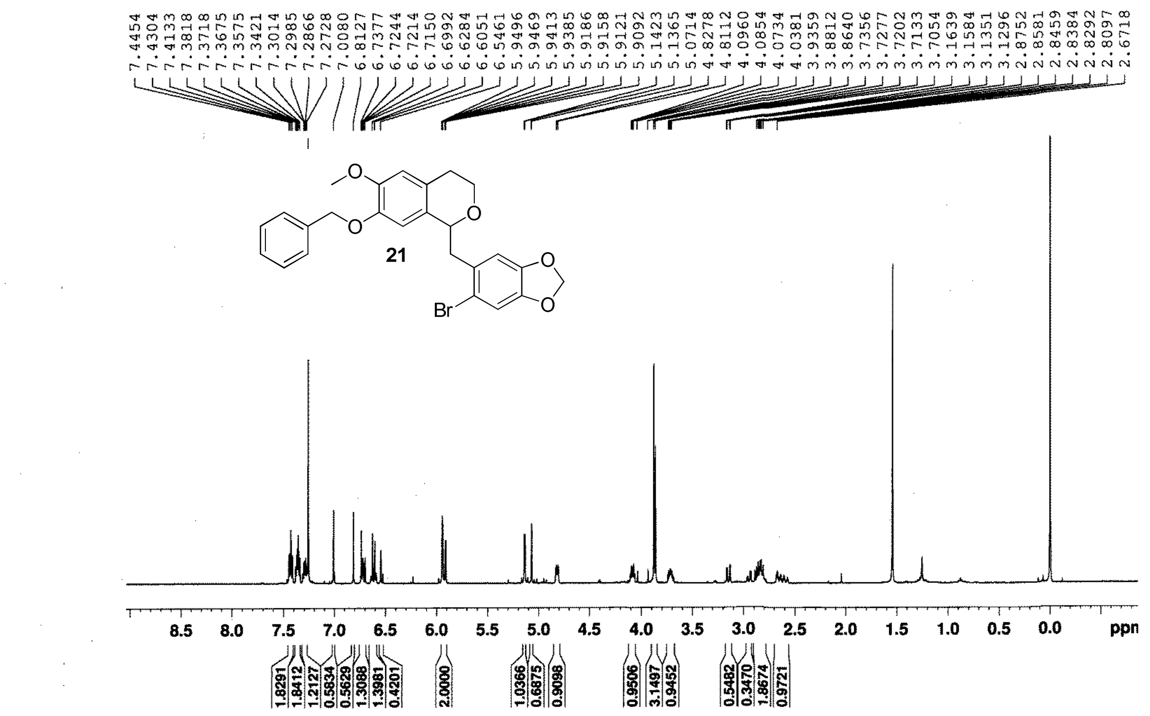
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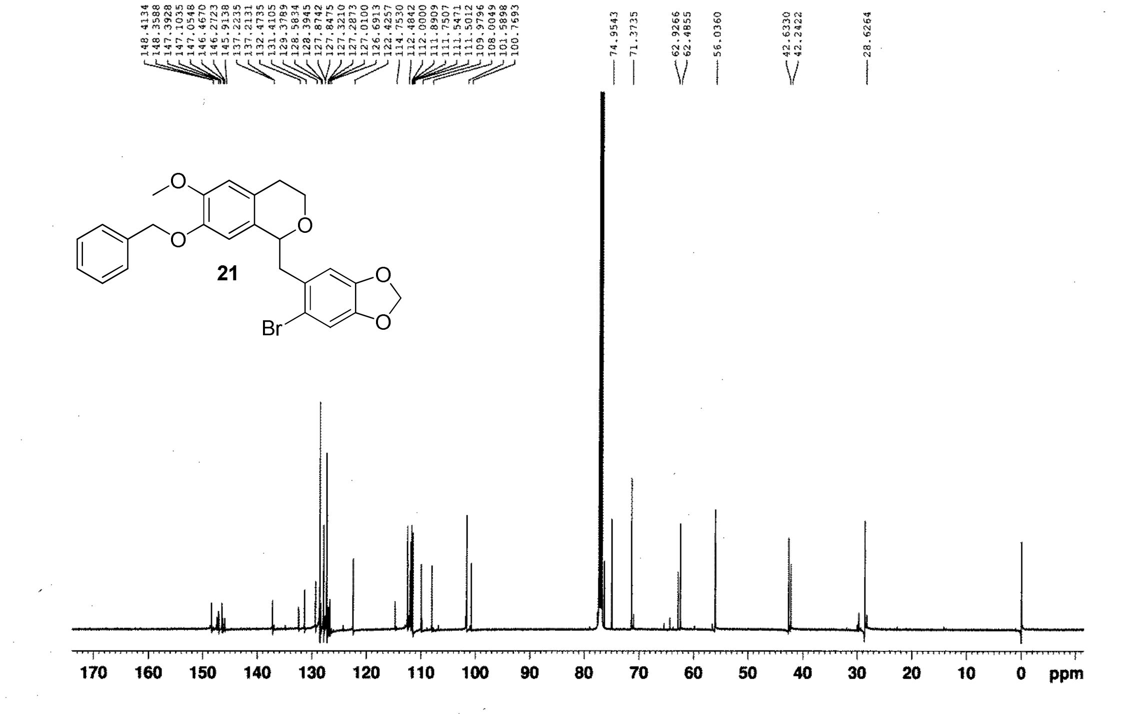
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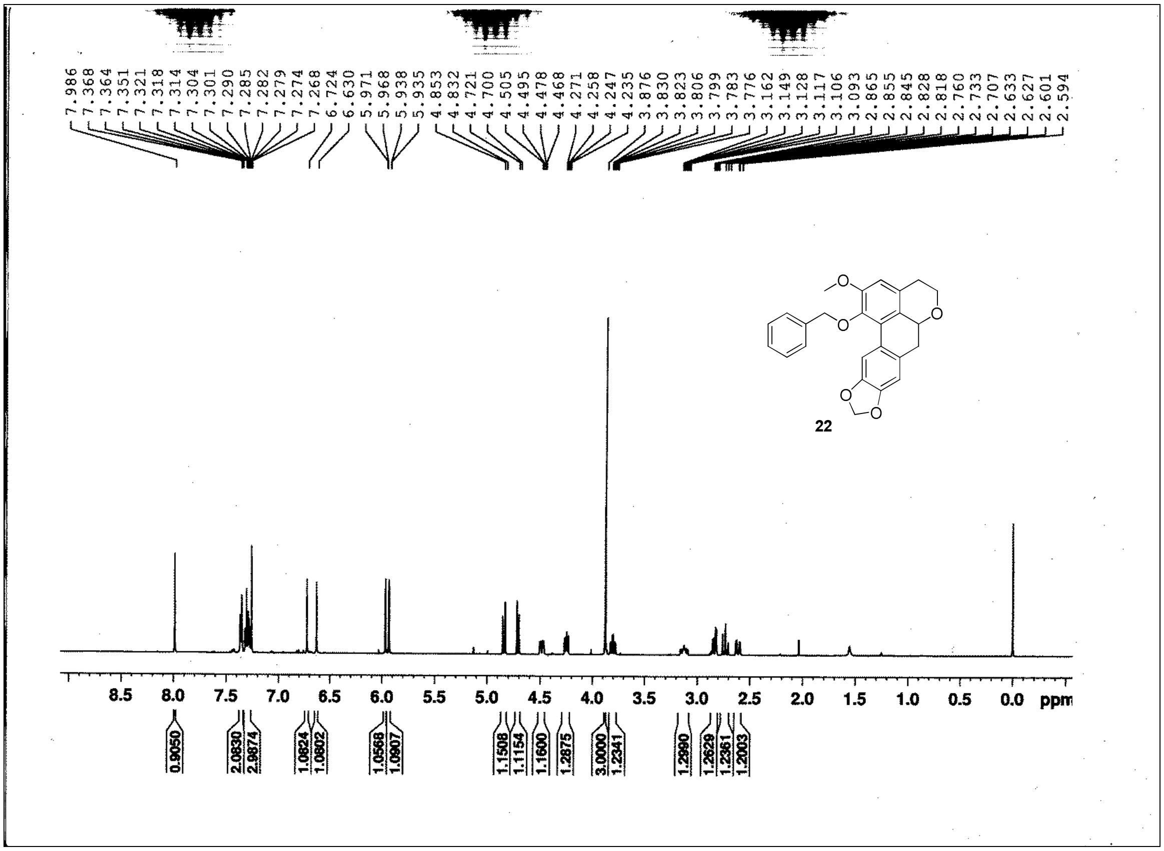
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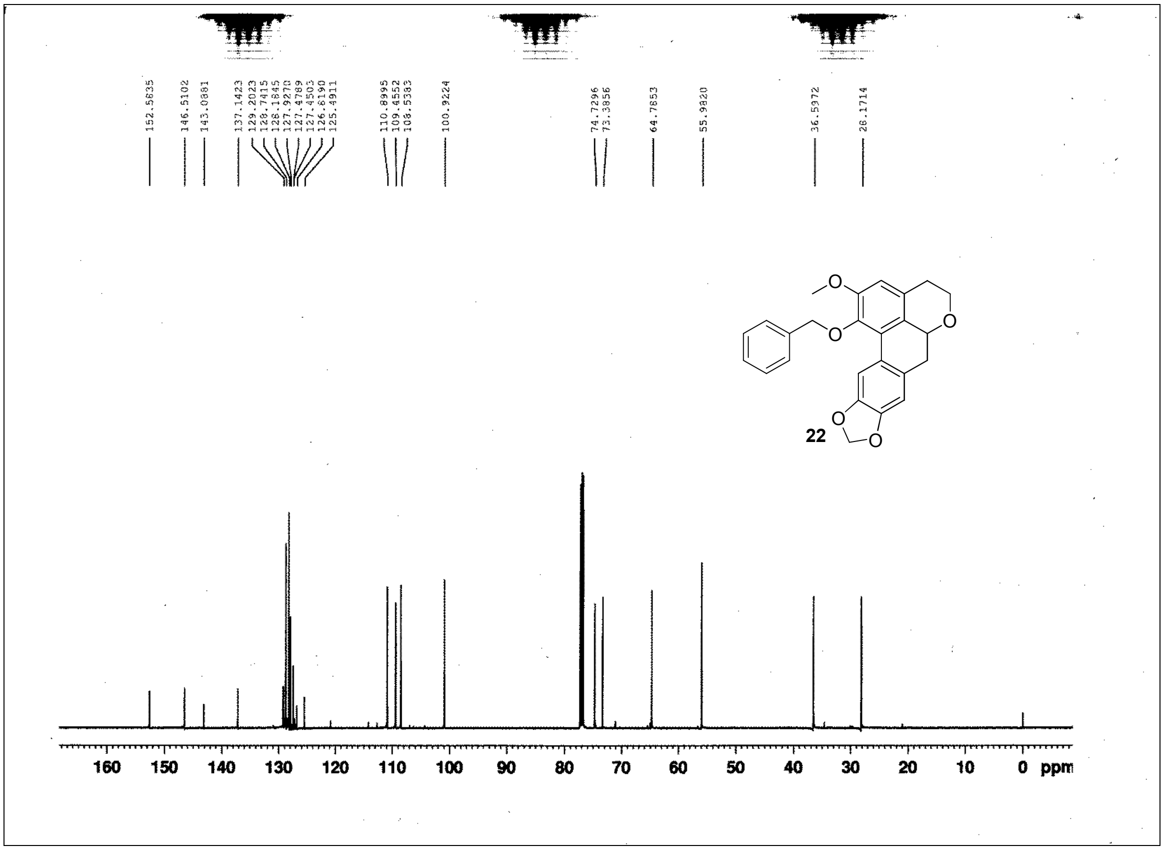
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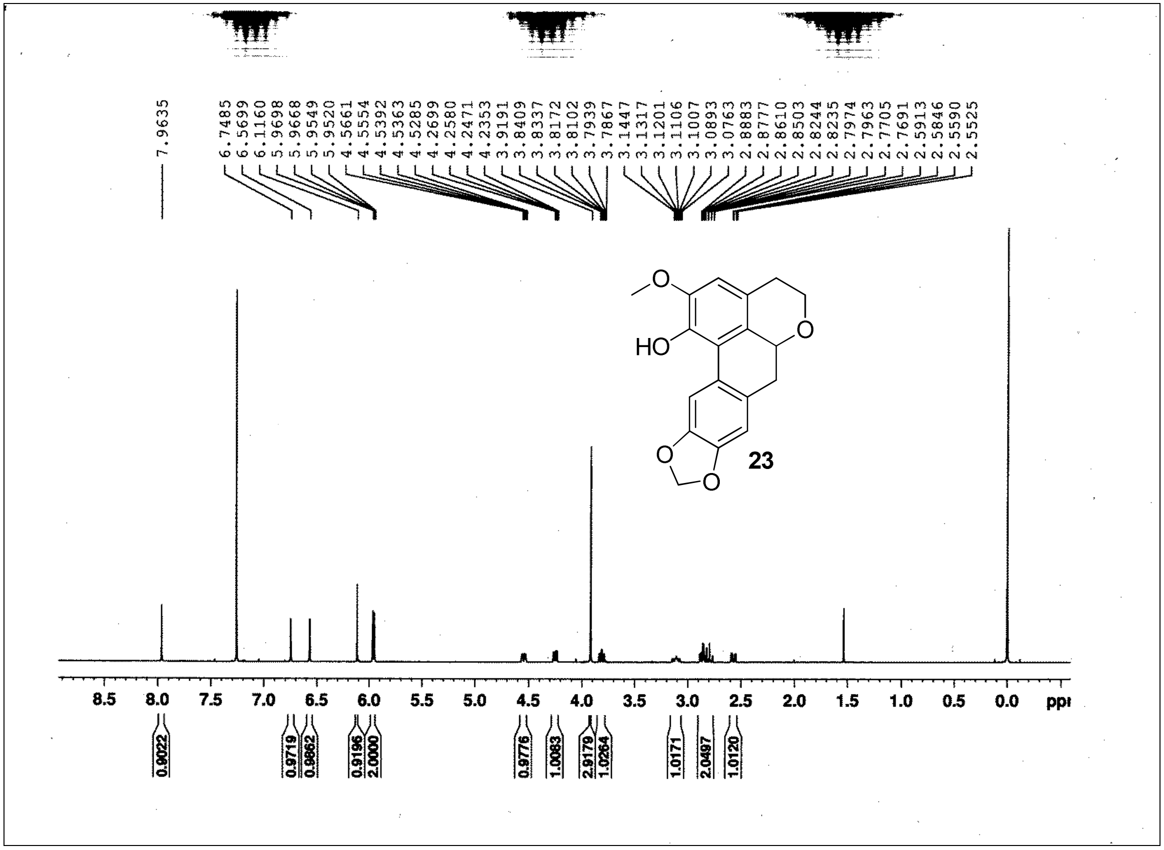
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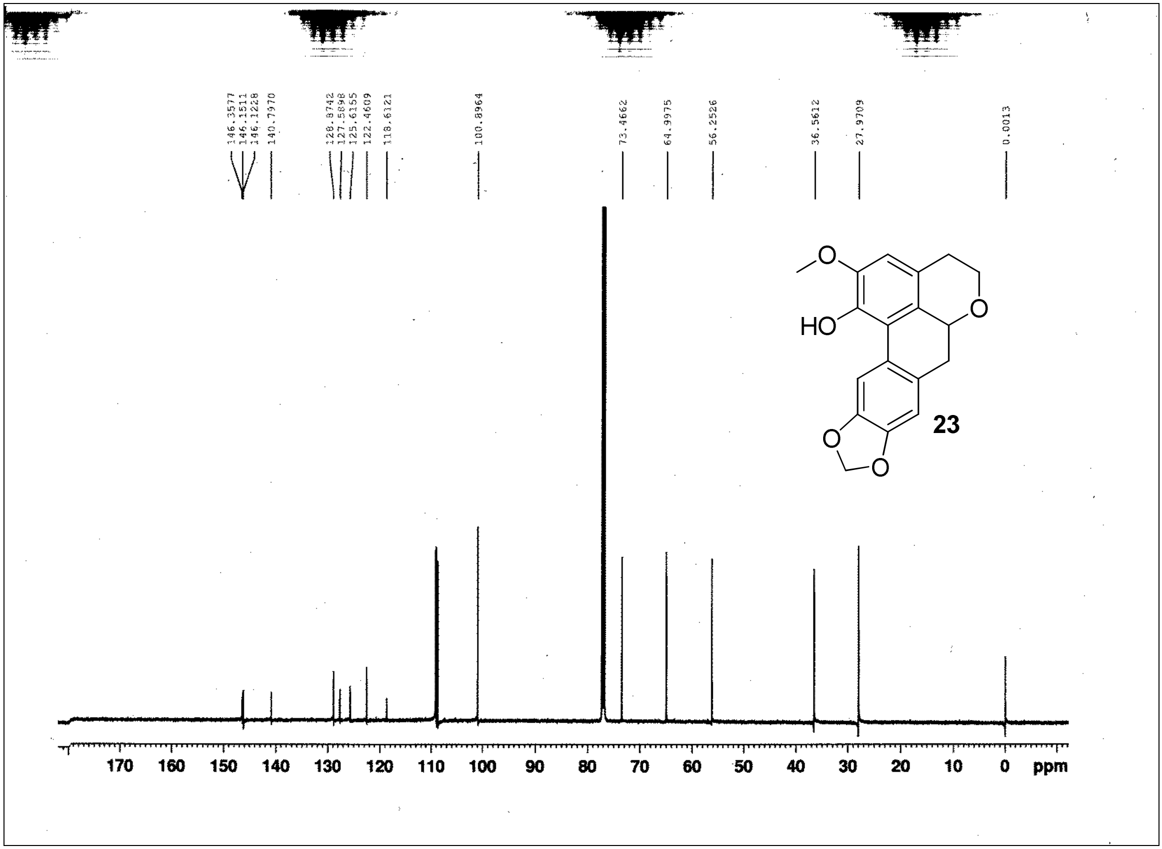
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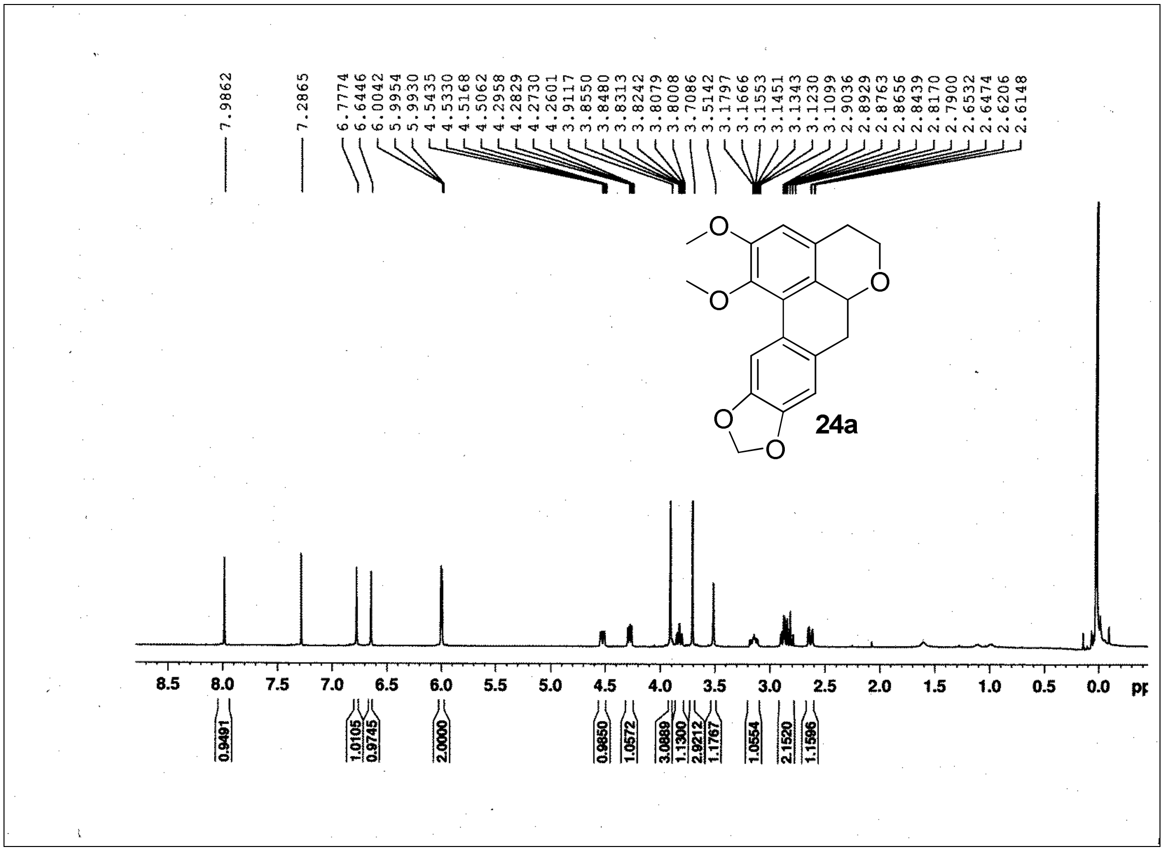
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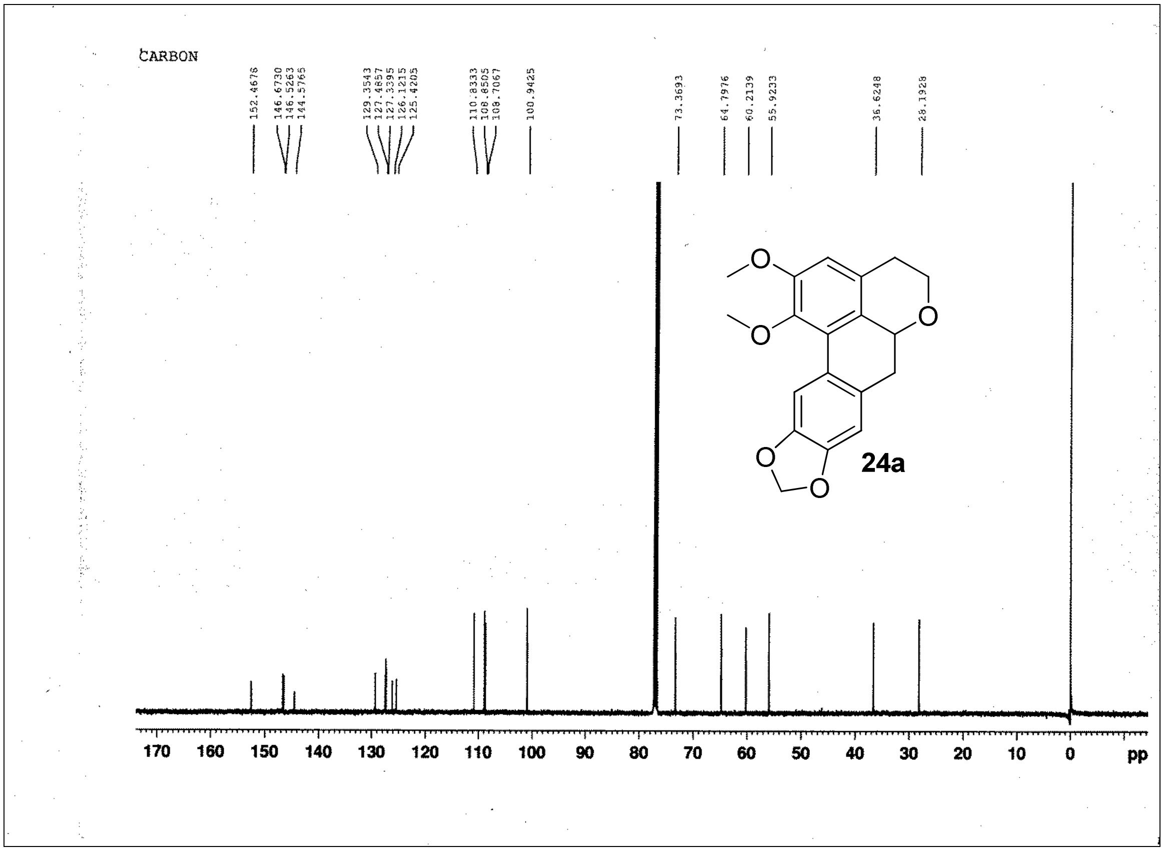
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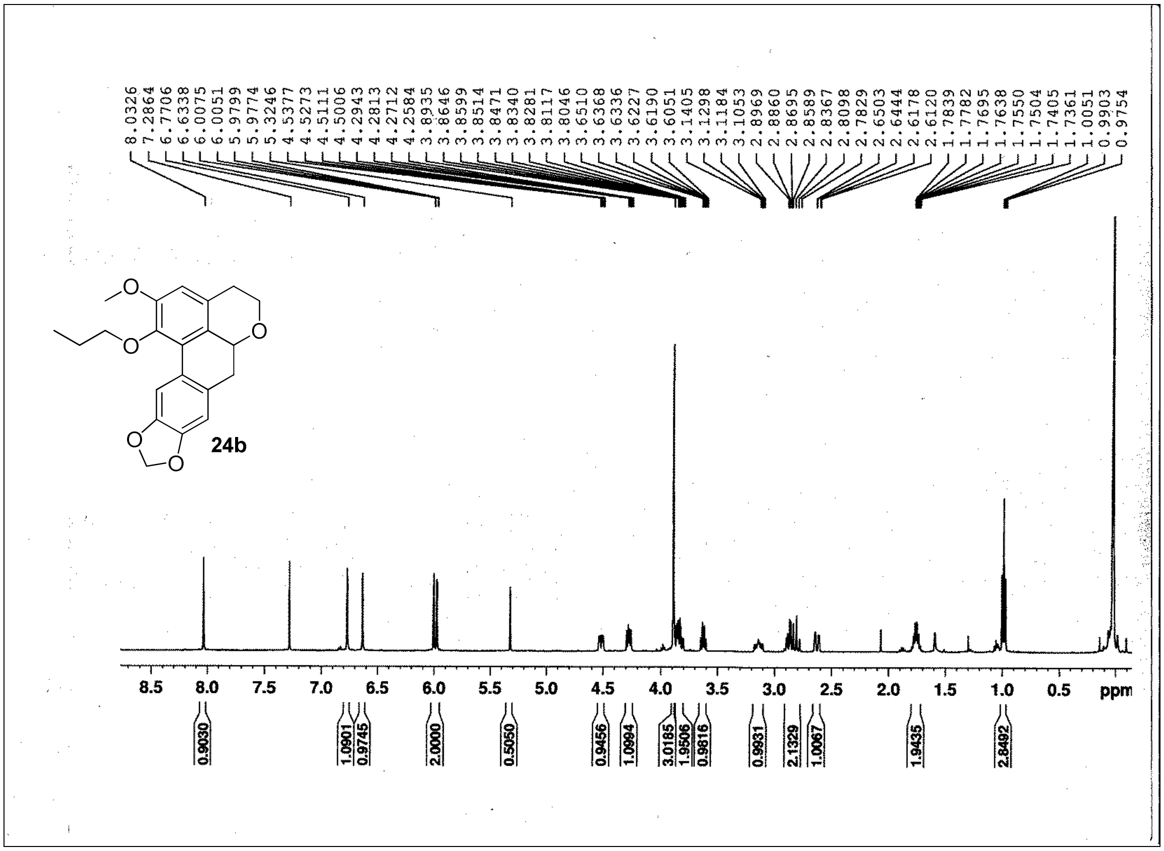
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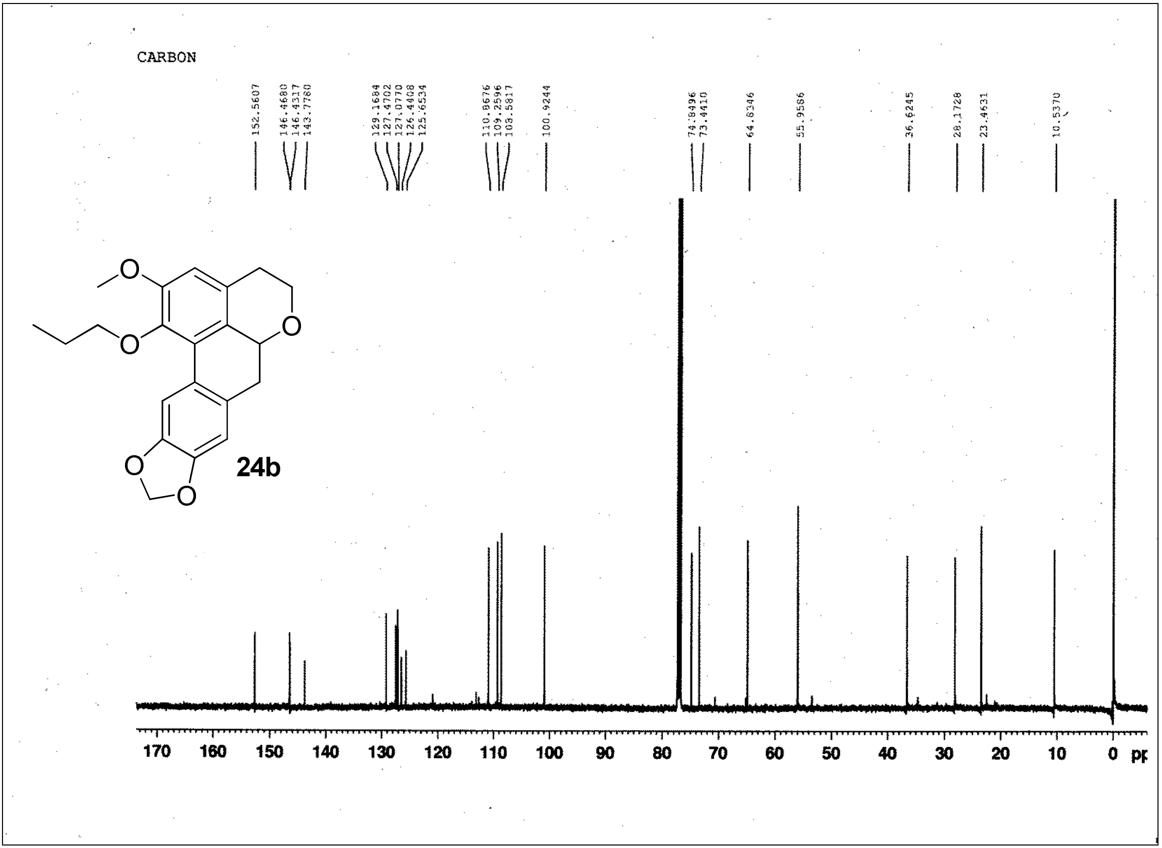
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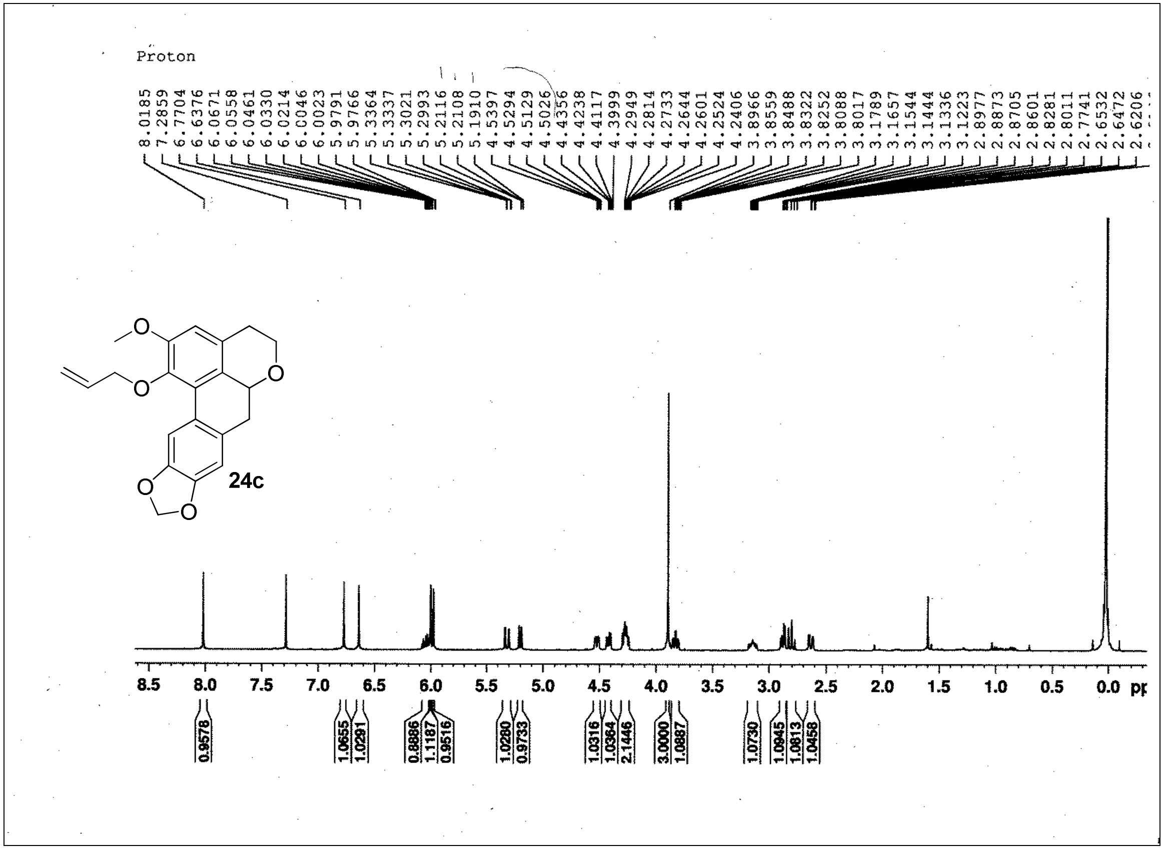
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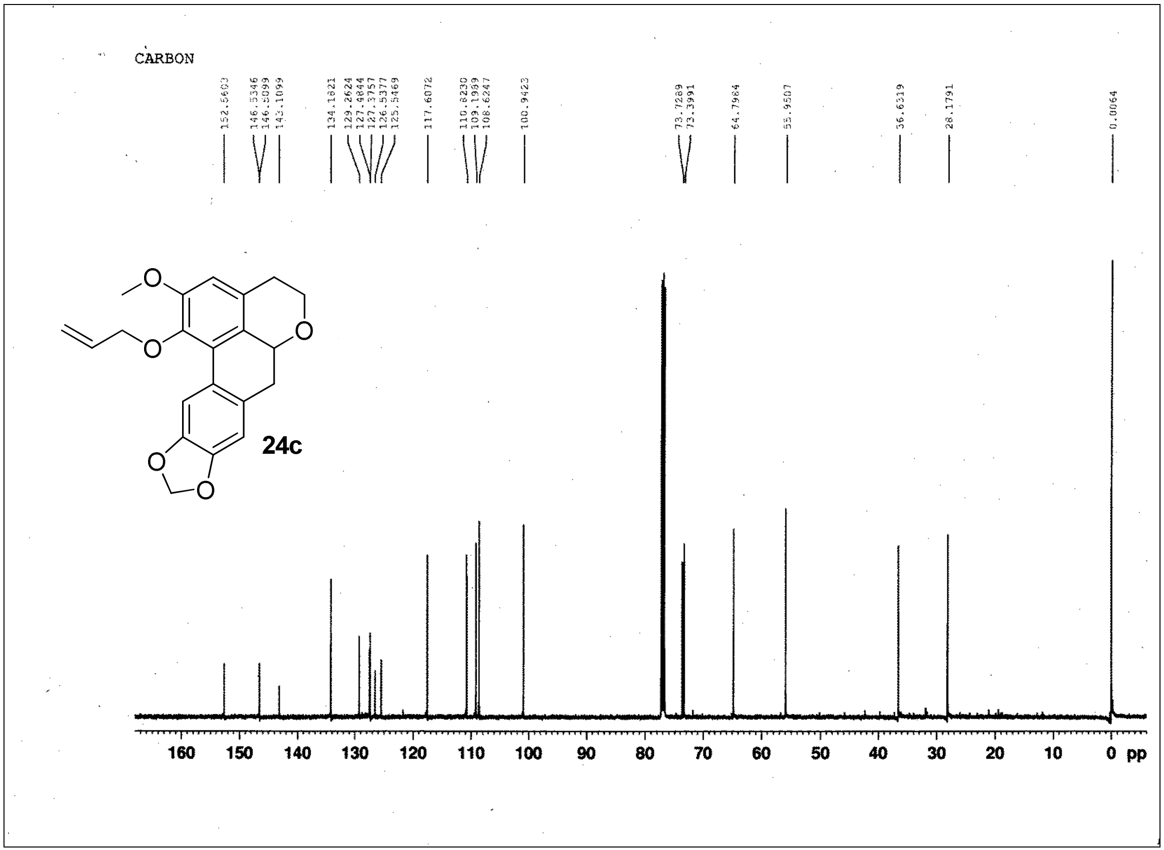
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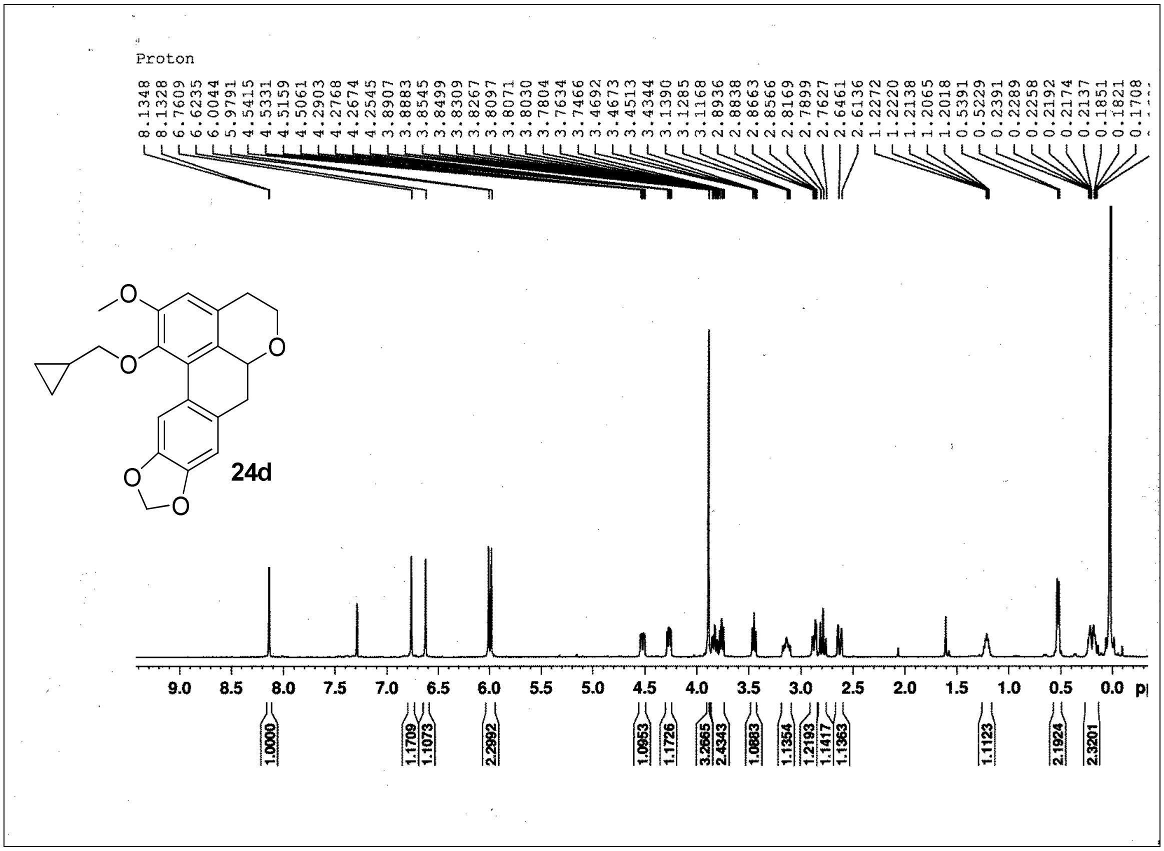
0 pp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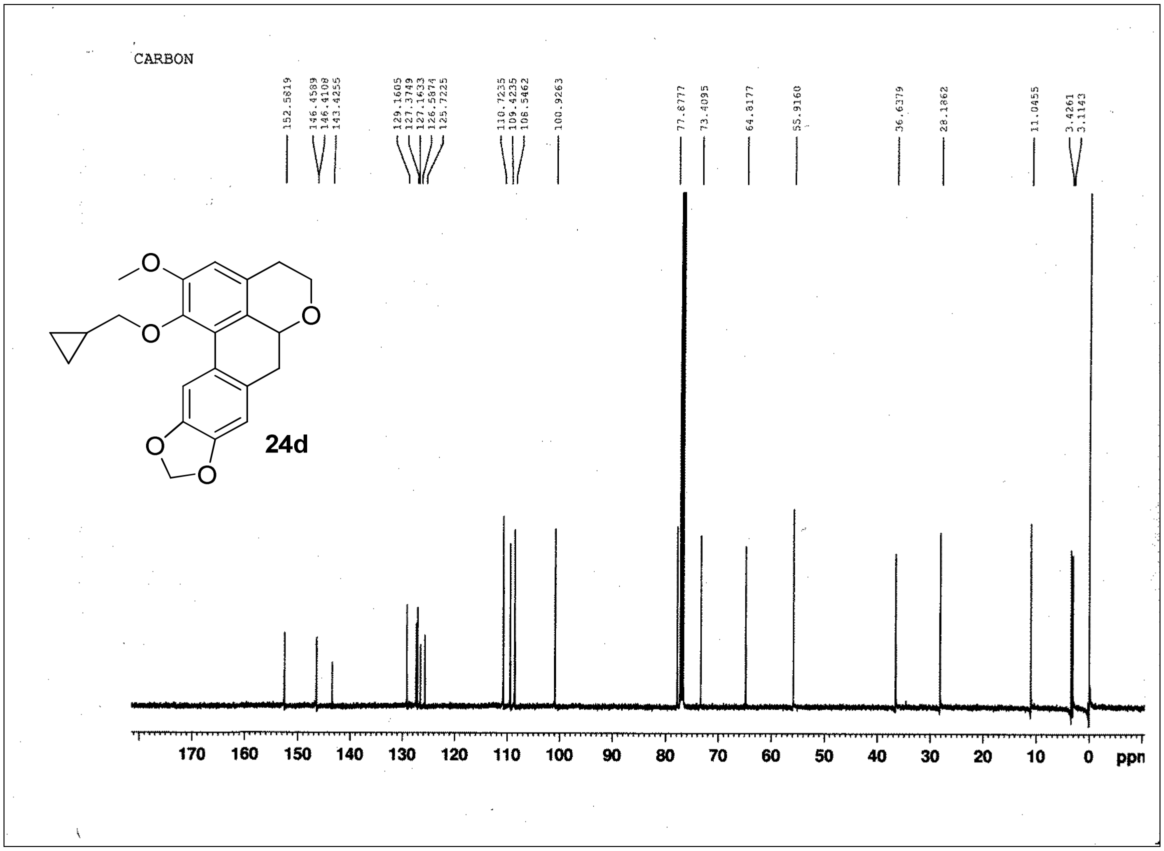
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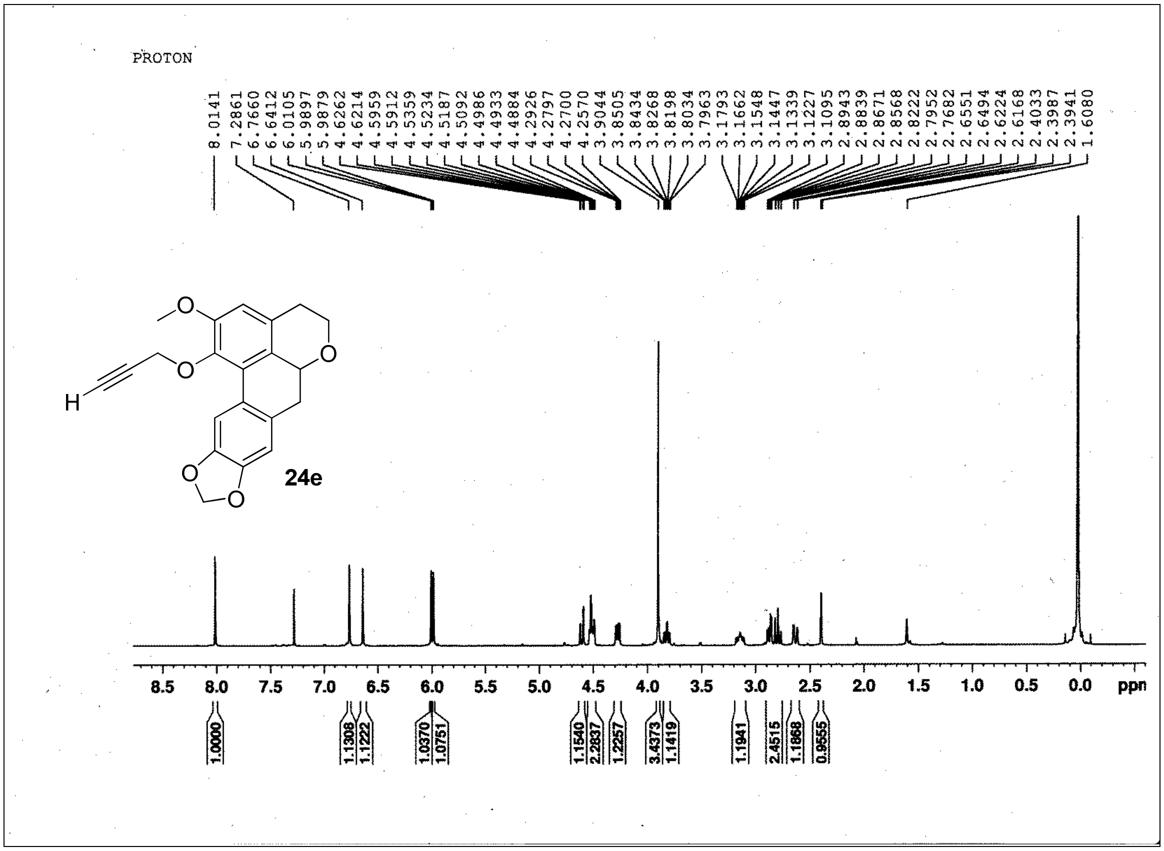
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O
O
O
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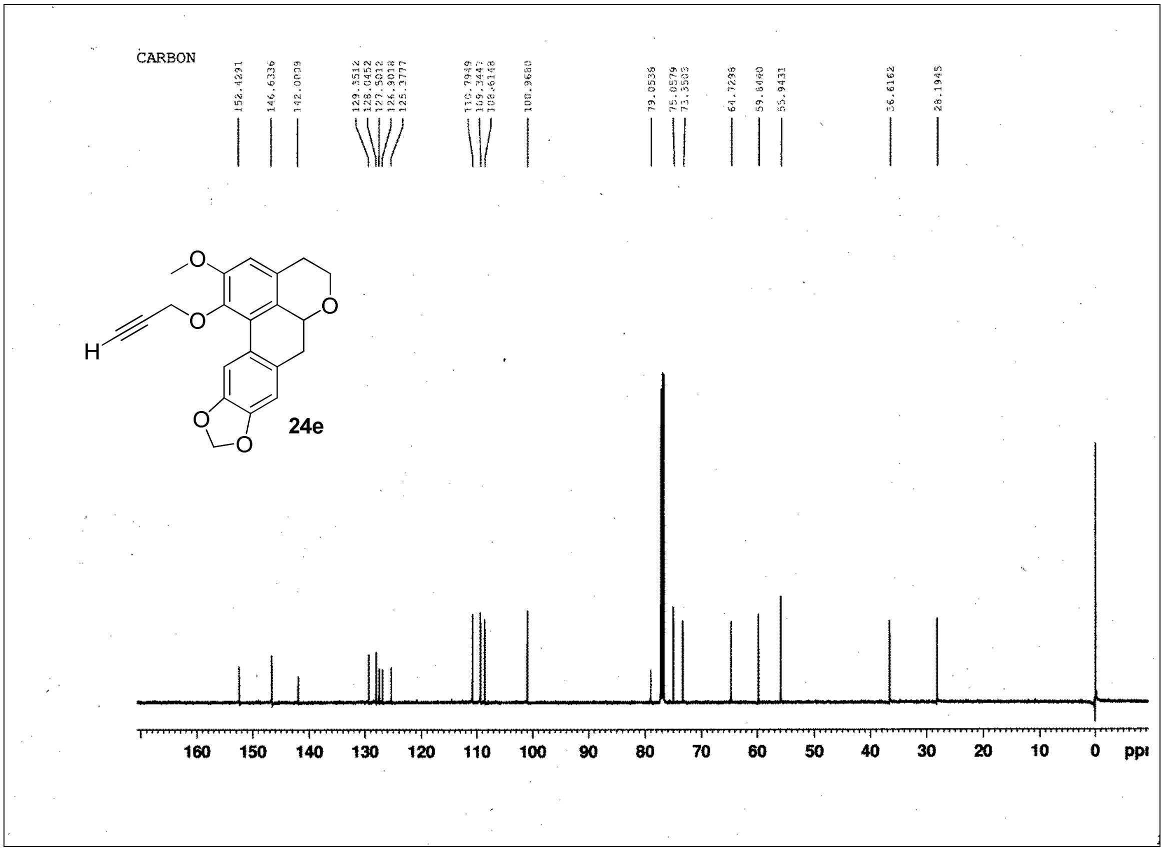
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O
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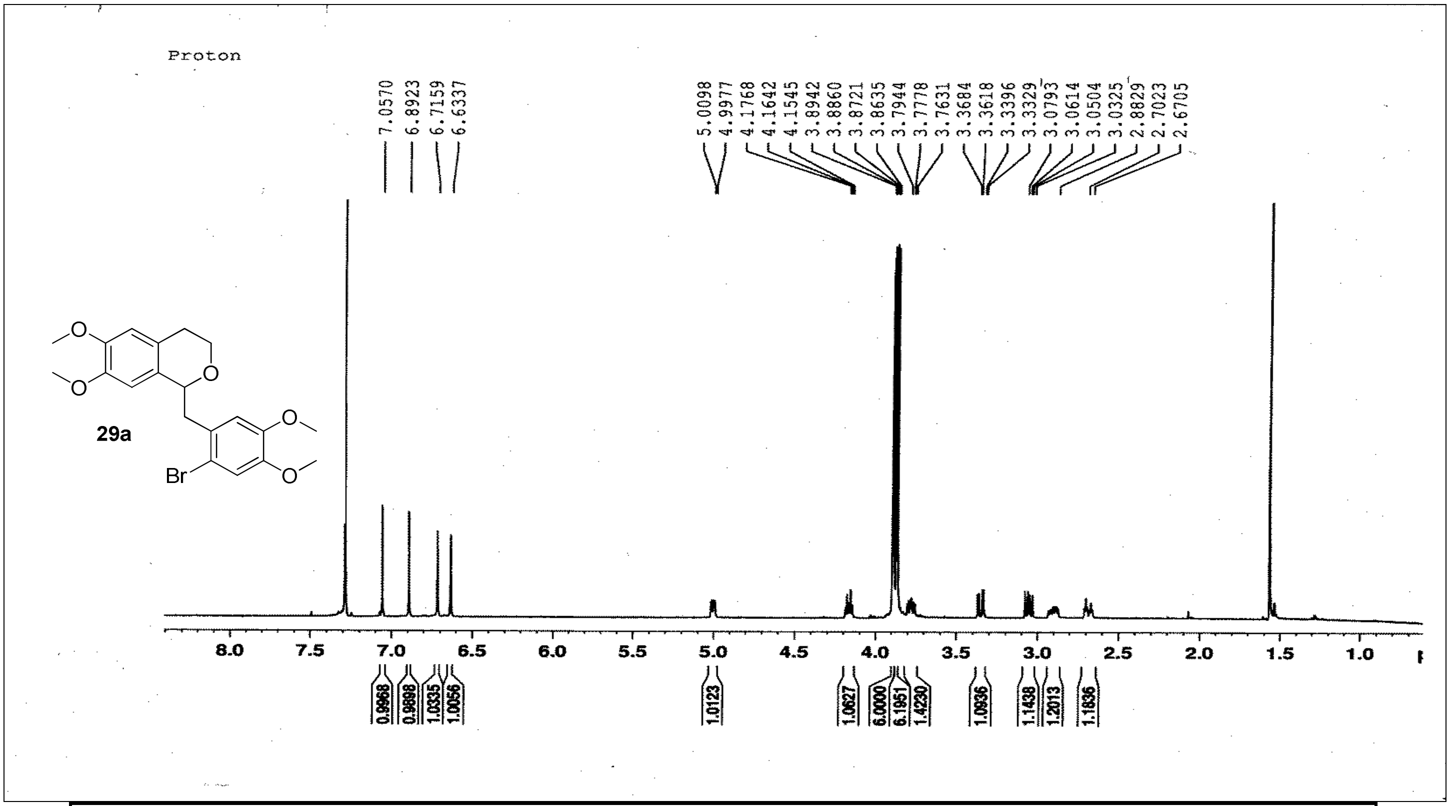
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3.7944
3.7778
3.7631
3.3684
3.3618
3.3396
3.3329
3.0793
3.0614
3.0504
3.0325
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Br
O
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6.5
6.0
5.5
5.0
4.5
4.0
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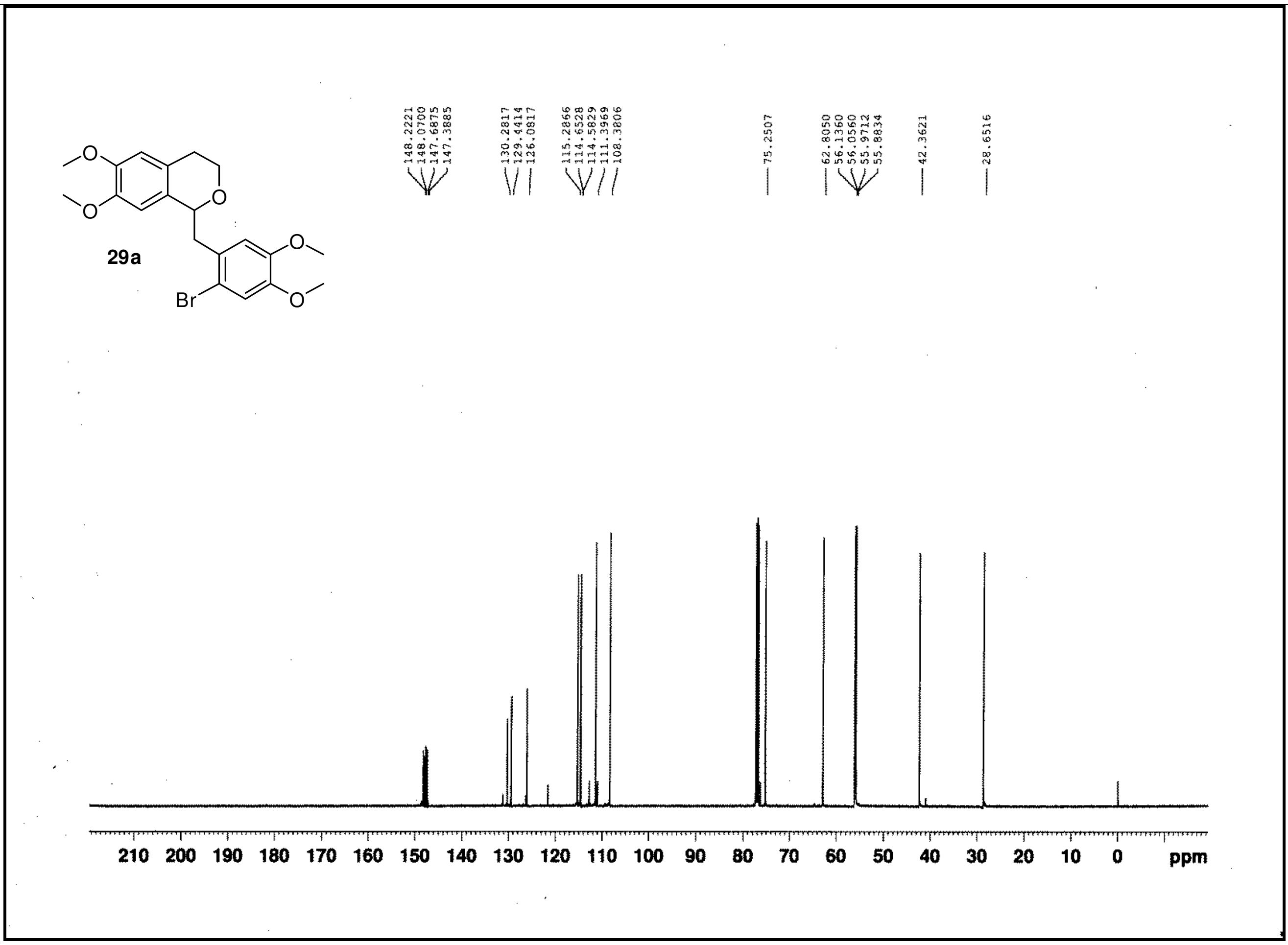
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29a
Br
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200
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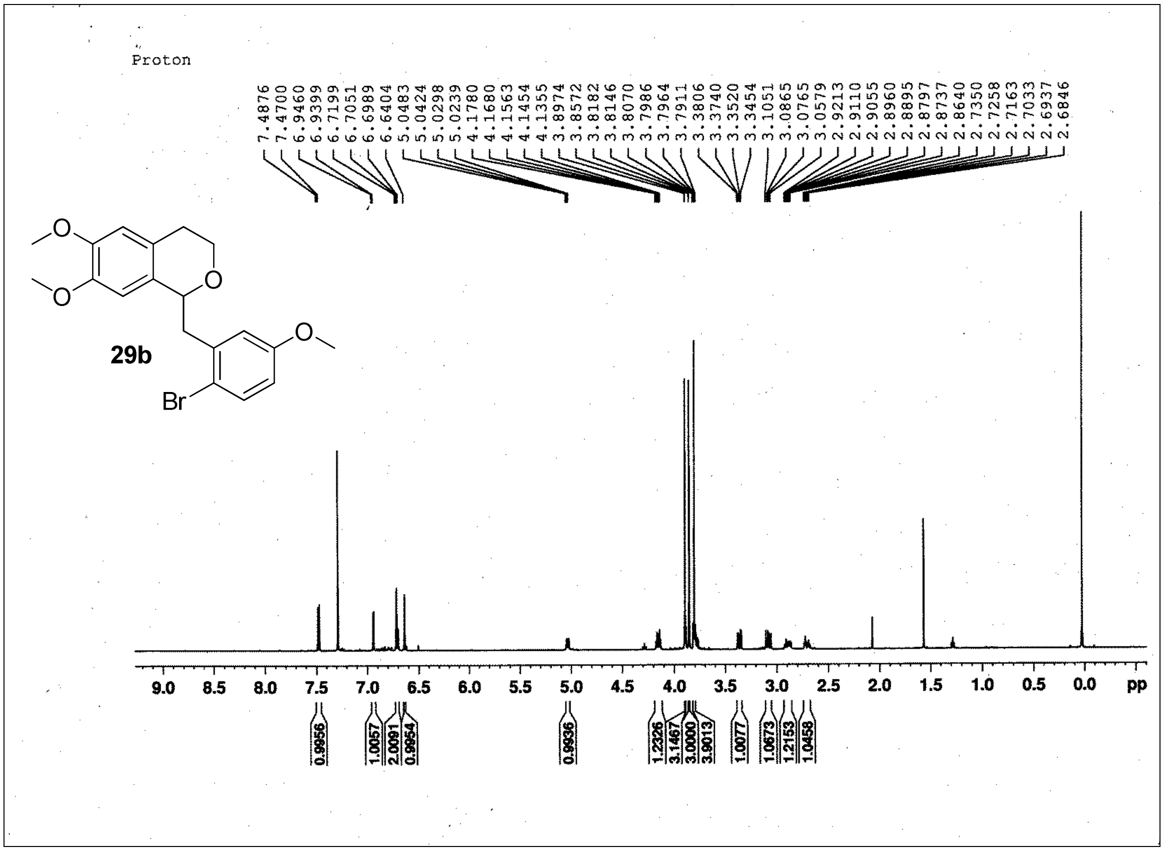
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5.0298
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3.7986
3.7964
3.7911
3.3806
3.3740
3.3520
3.3454
3.1051
3.0865
3.0765
3.0579
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4.0
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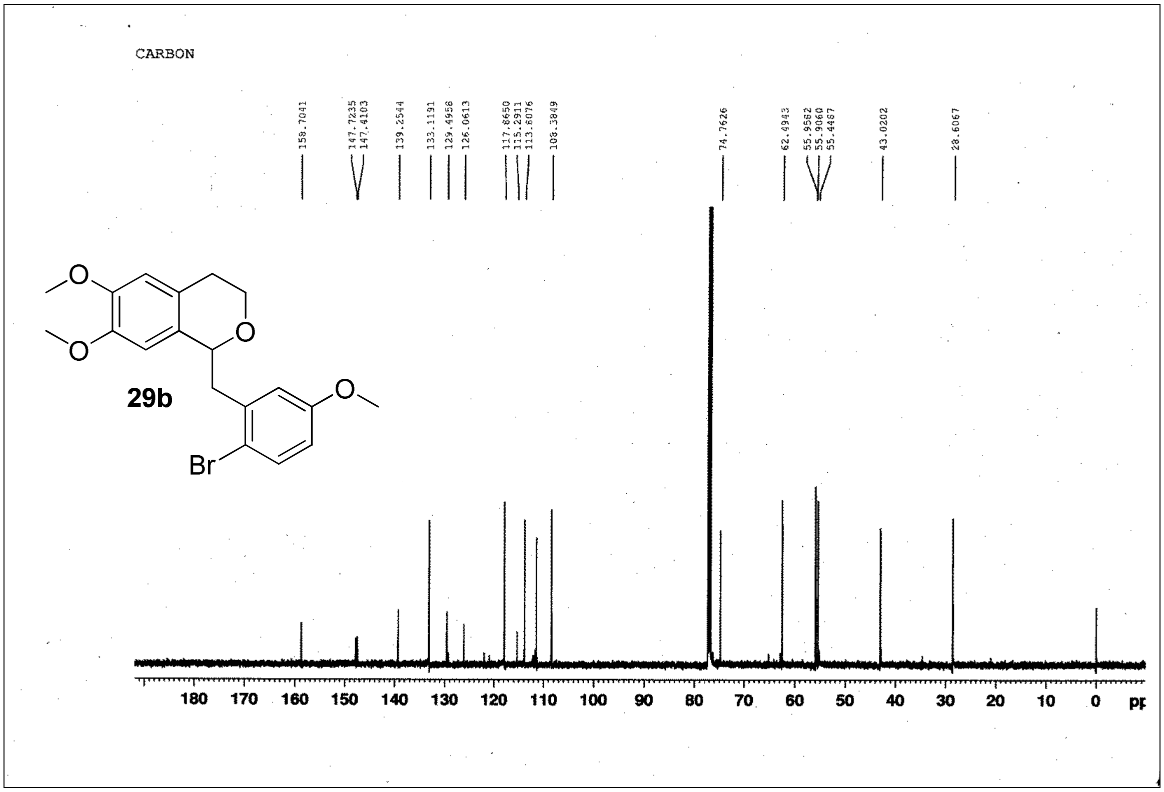
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55.9060
55.4487
43.0202
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O
O
O
O
Br
29b
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120
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20
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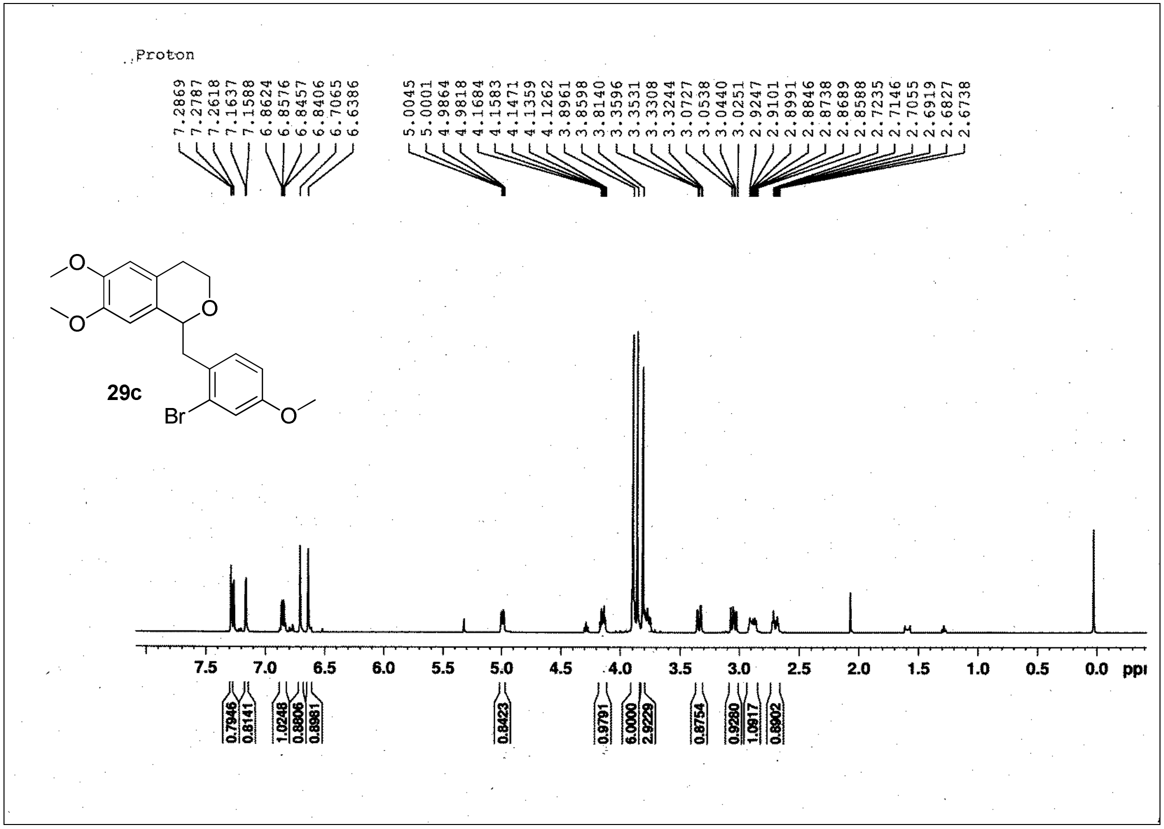
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Br
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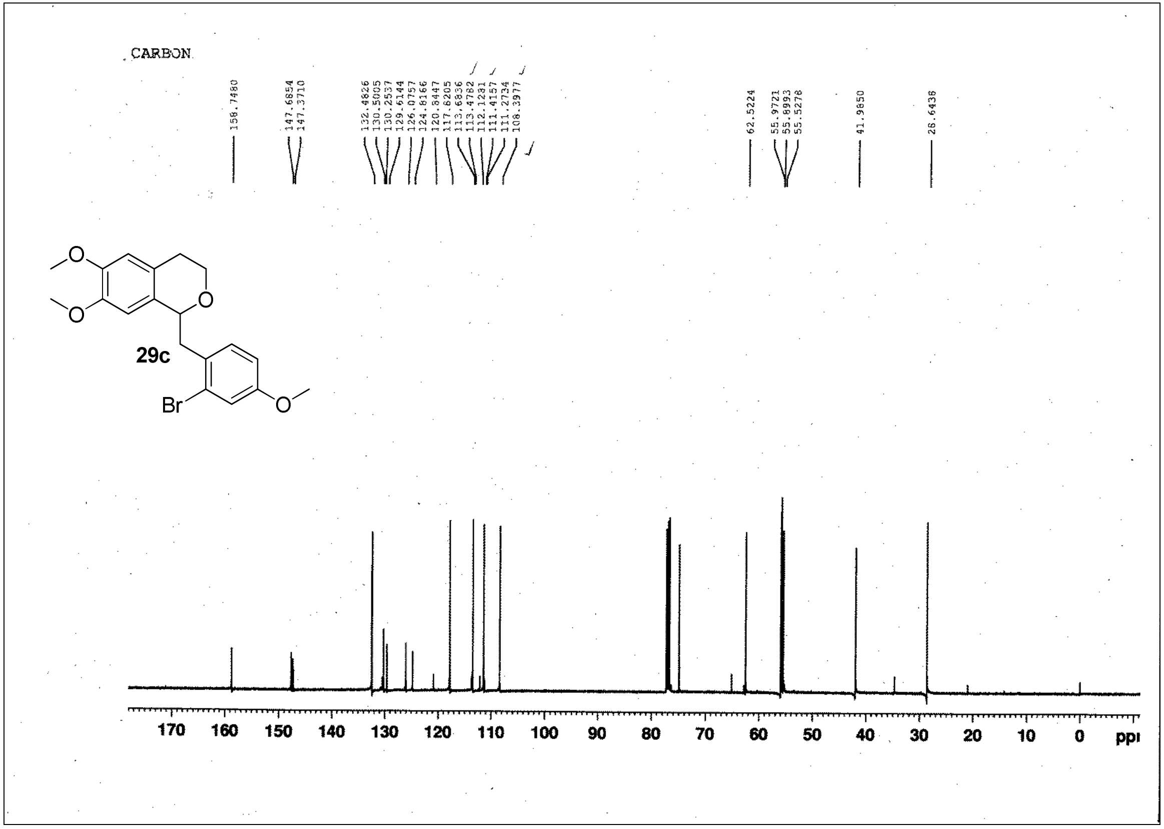
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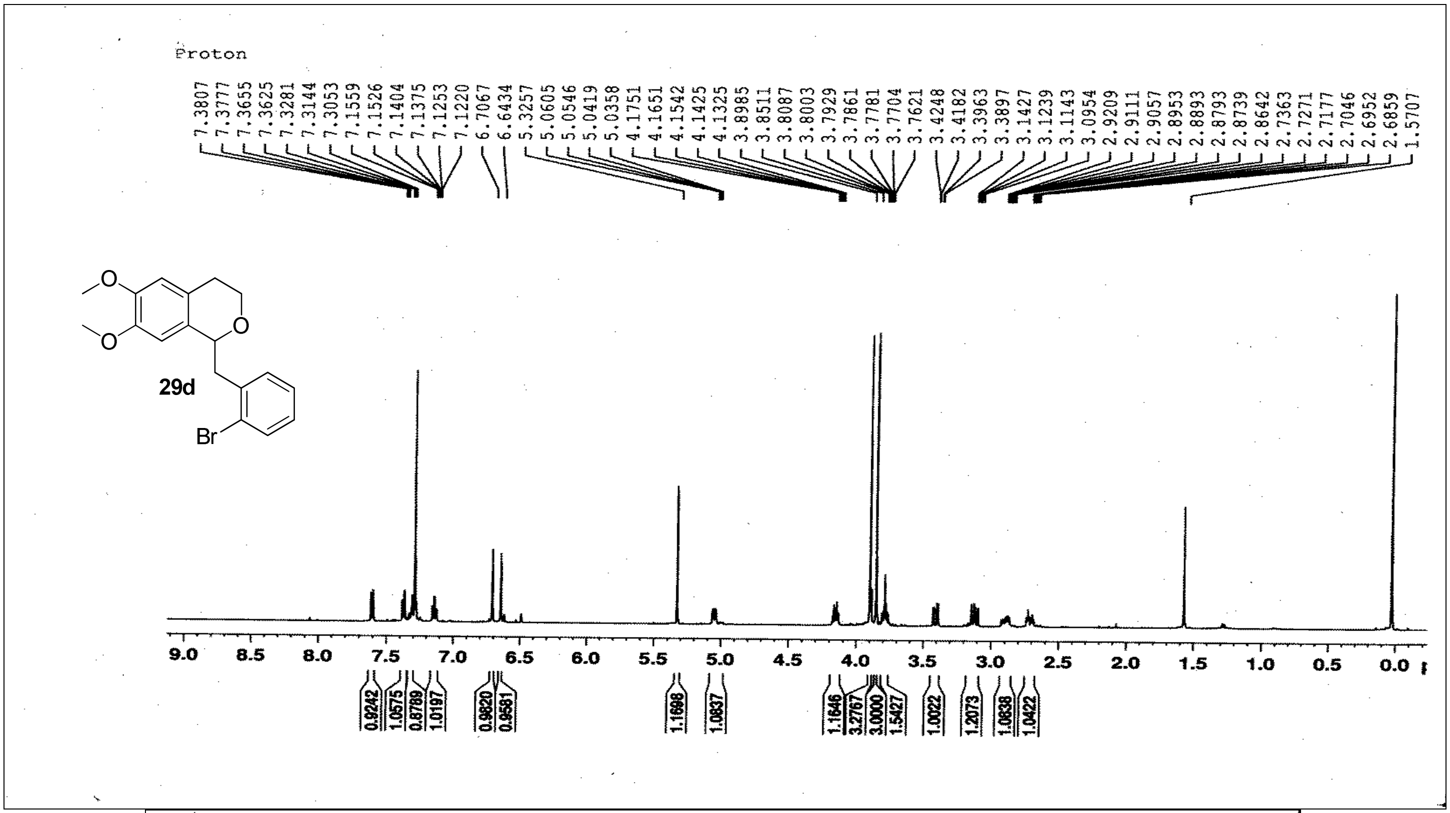
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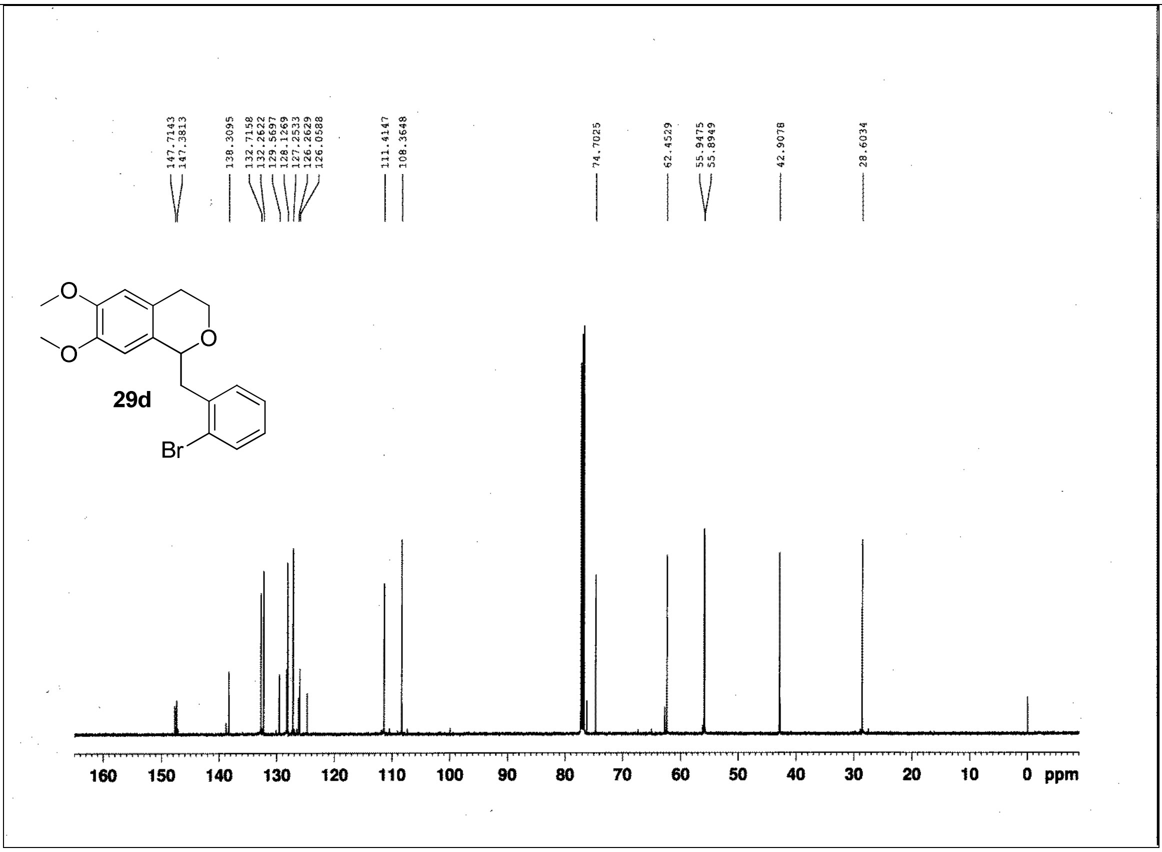
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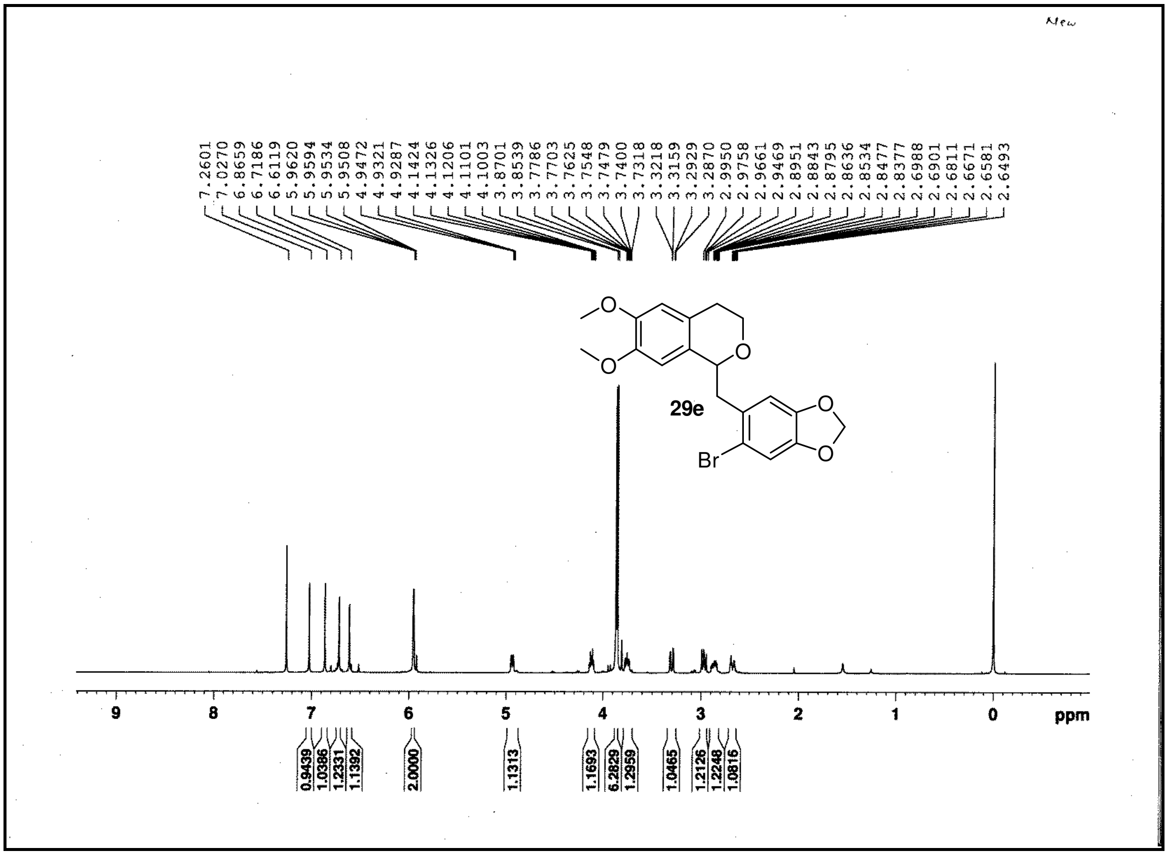
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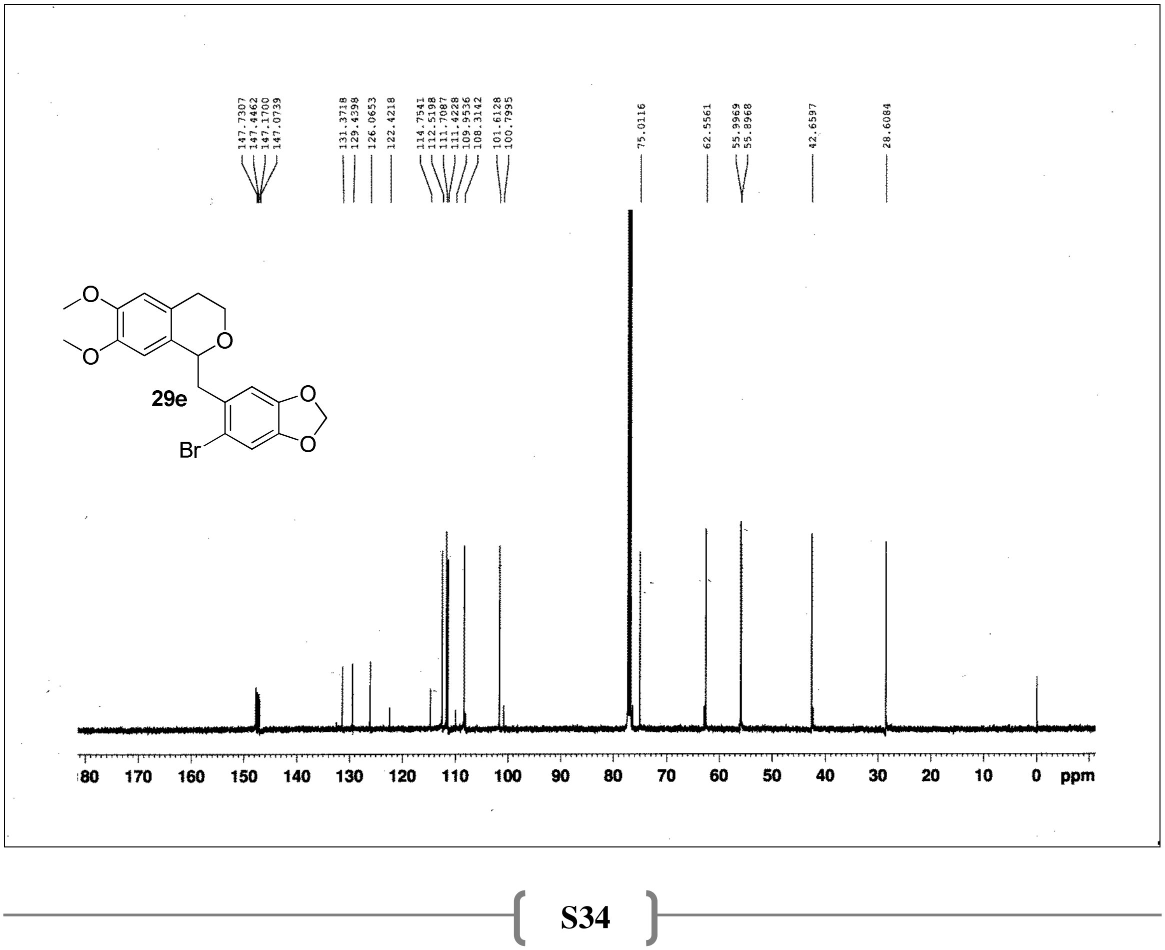
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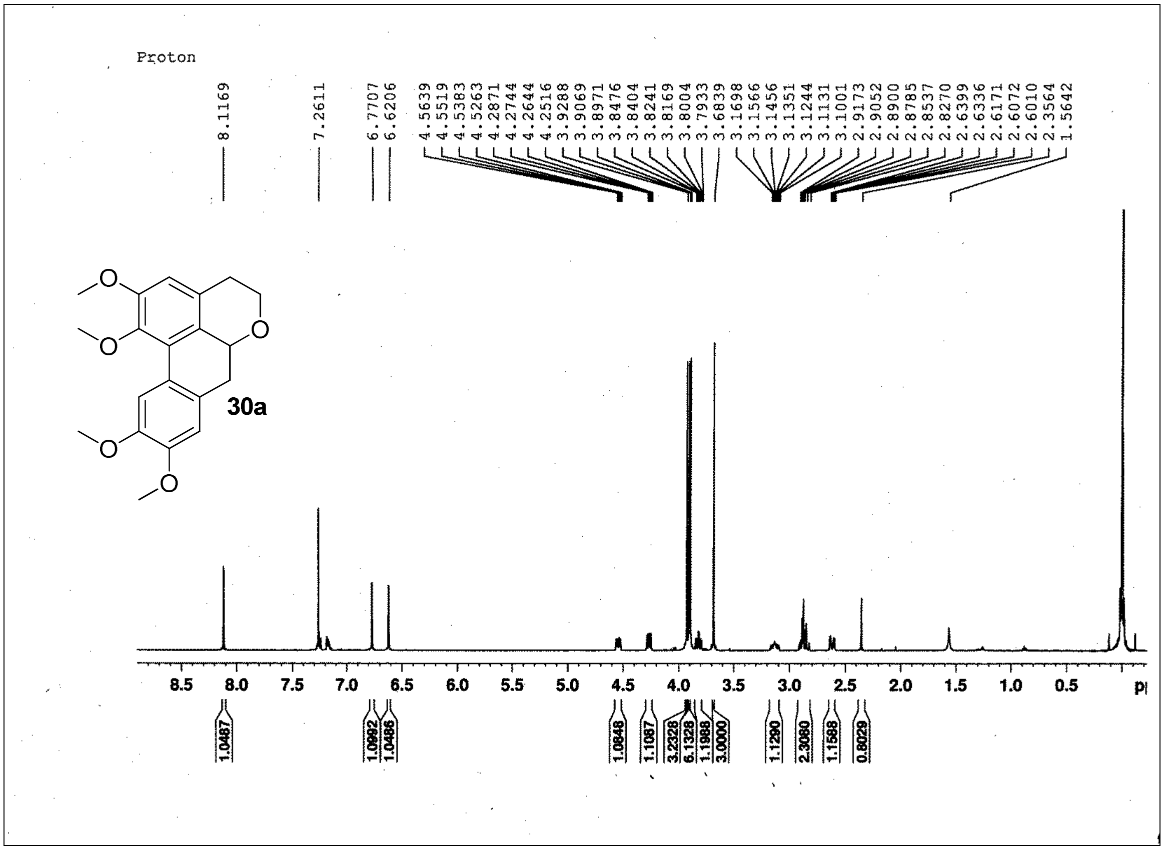
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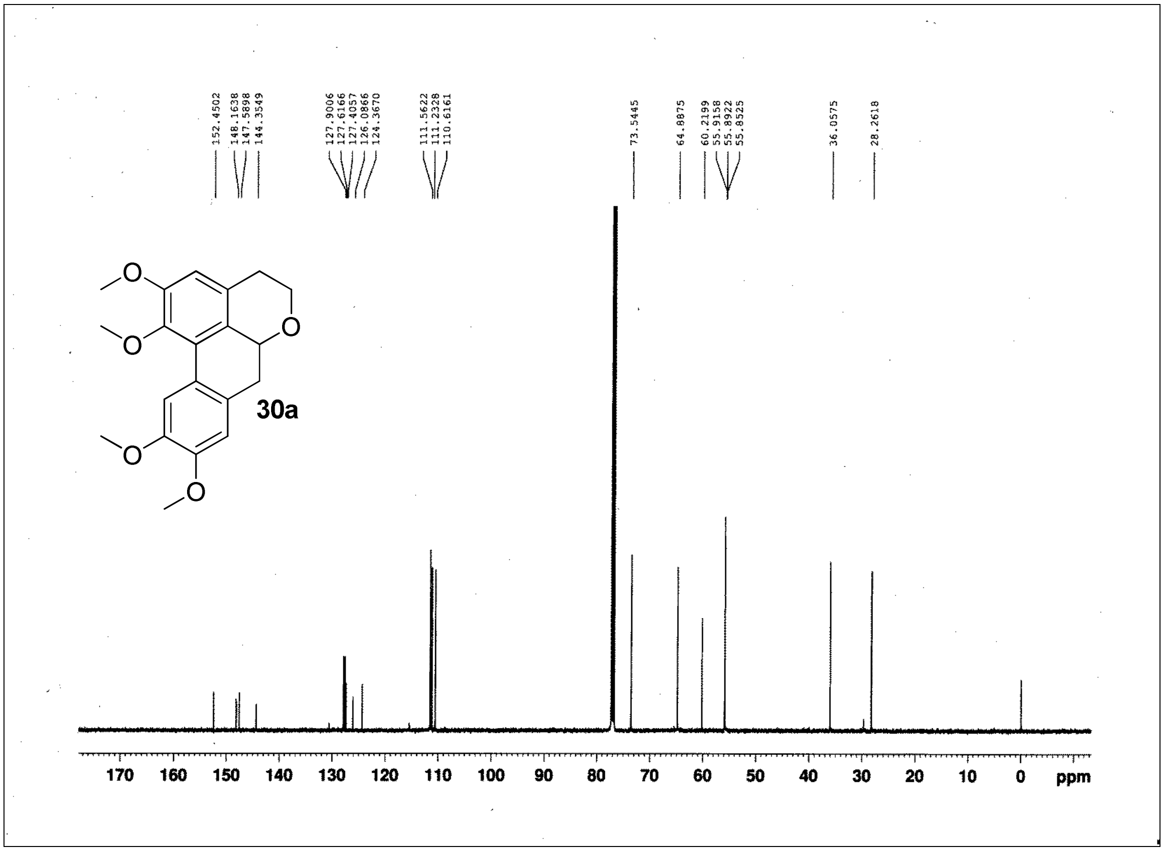
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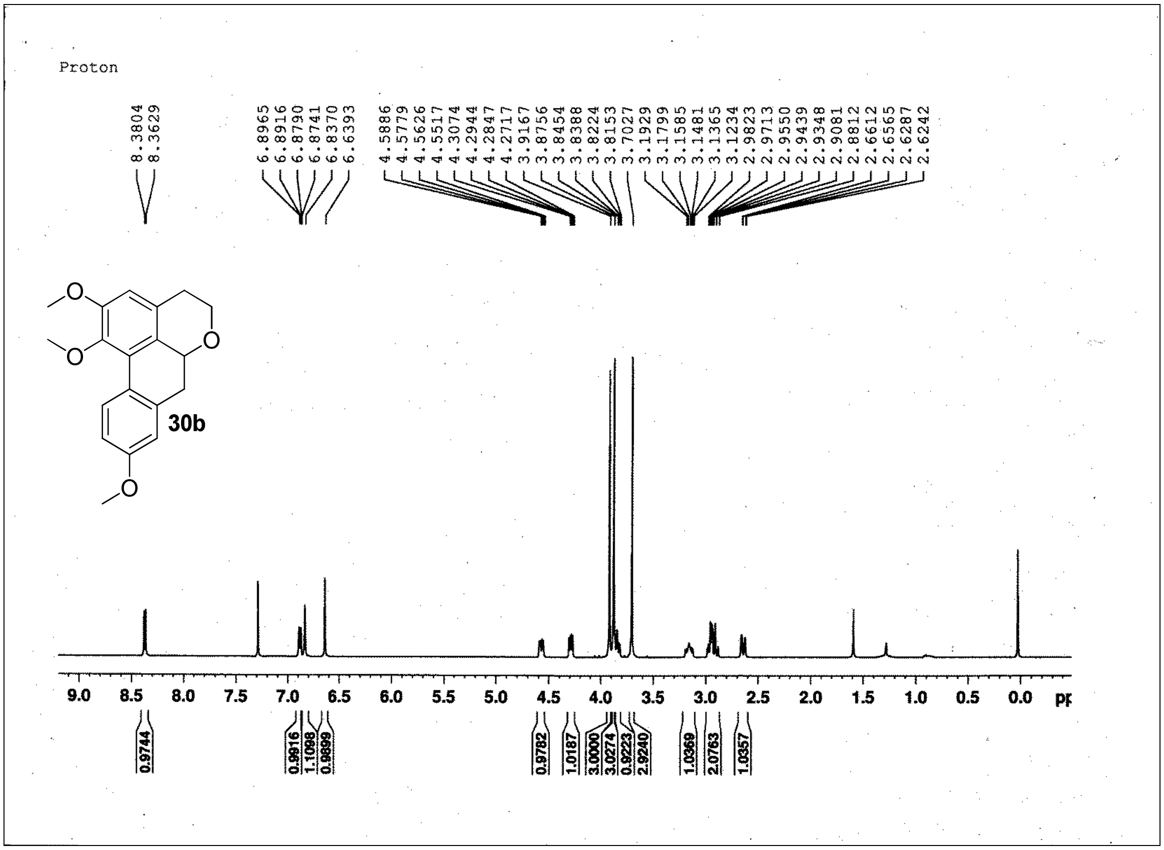
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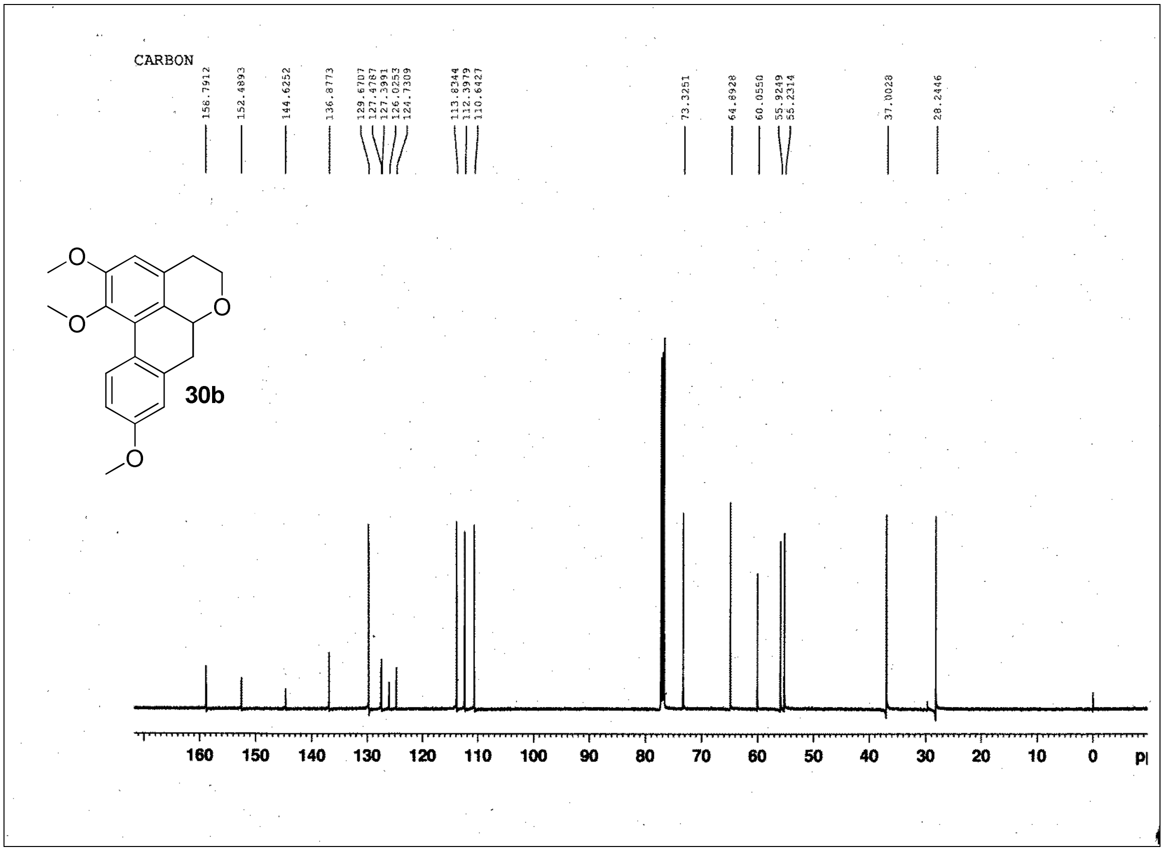
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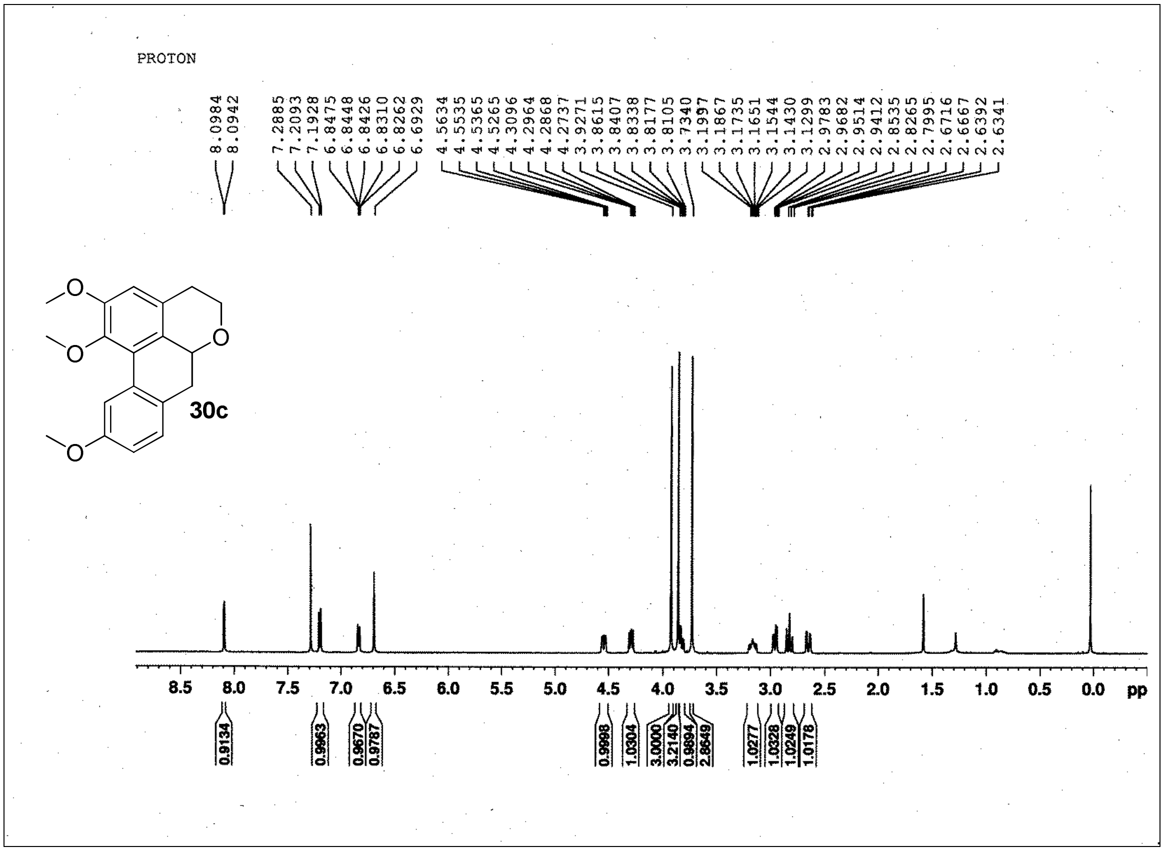
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2.7995
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2.6667
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2.6341
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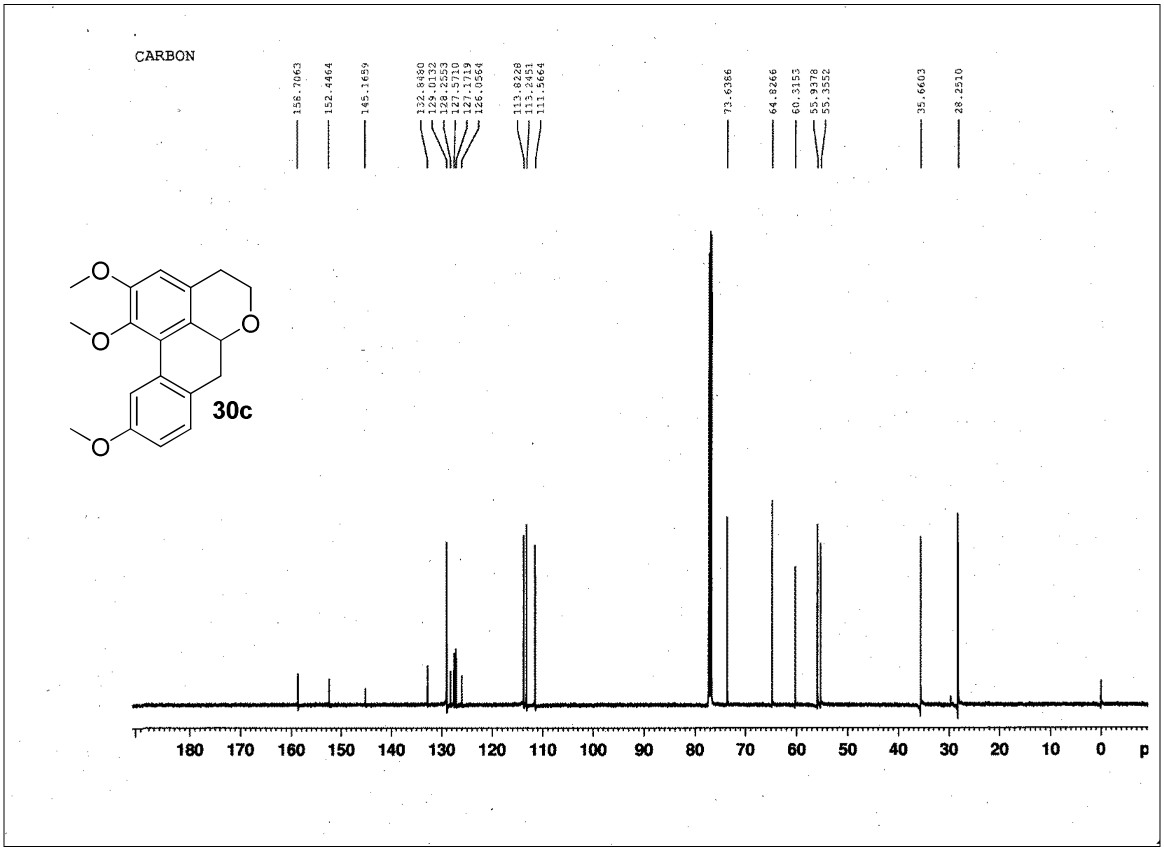
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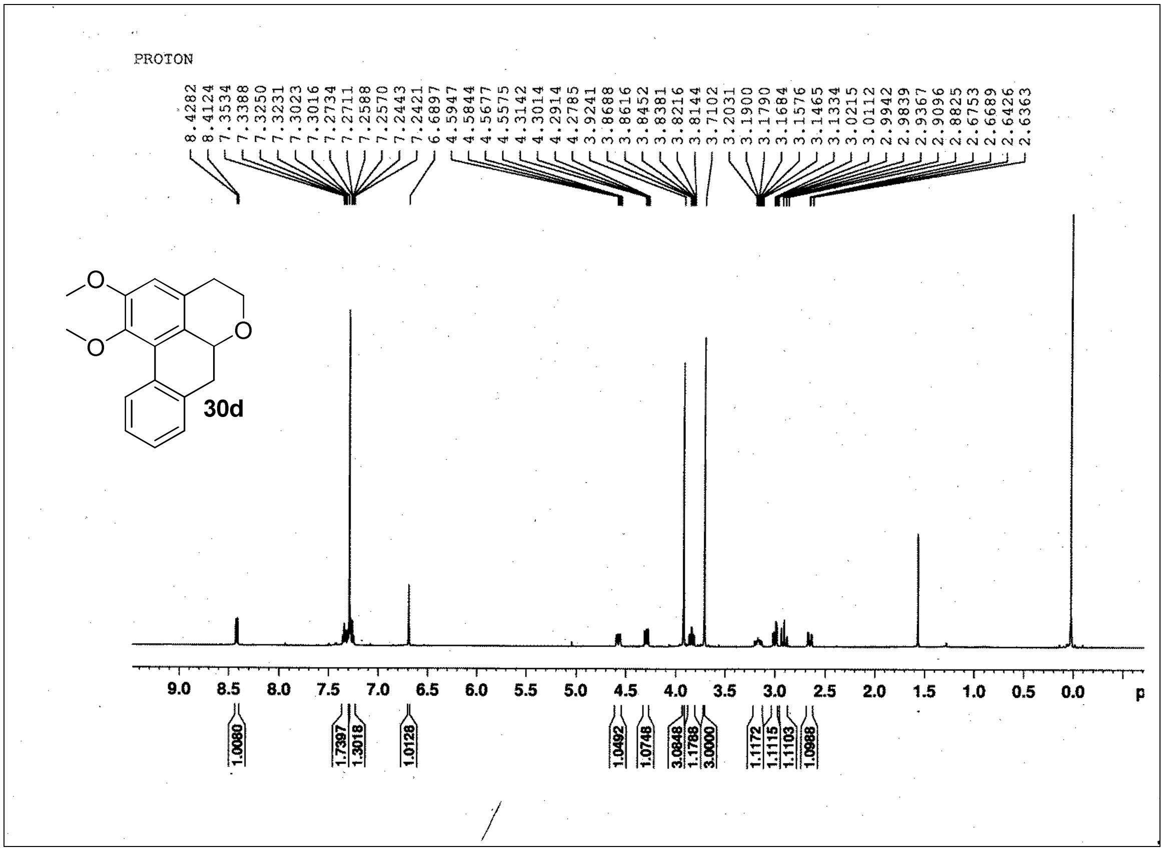
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6.0
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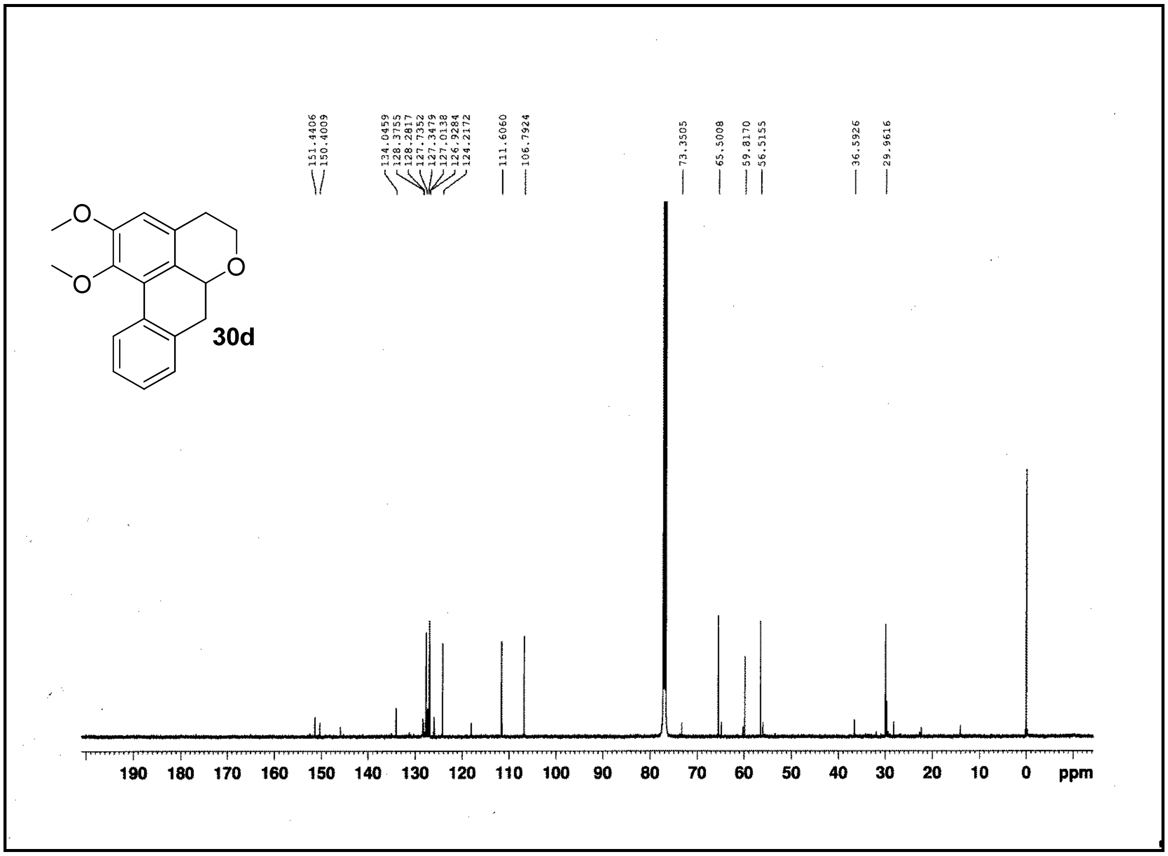
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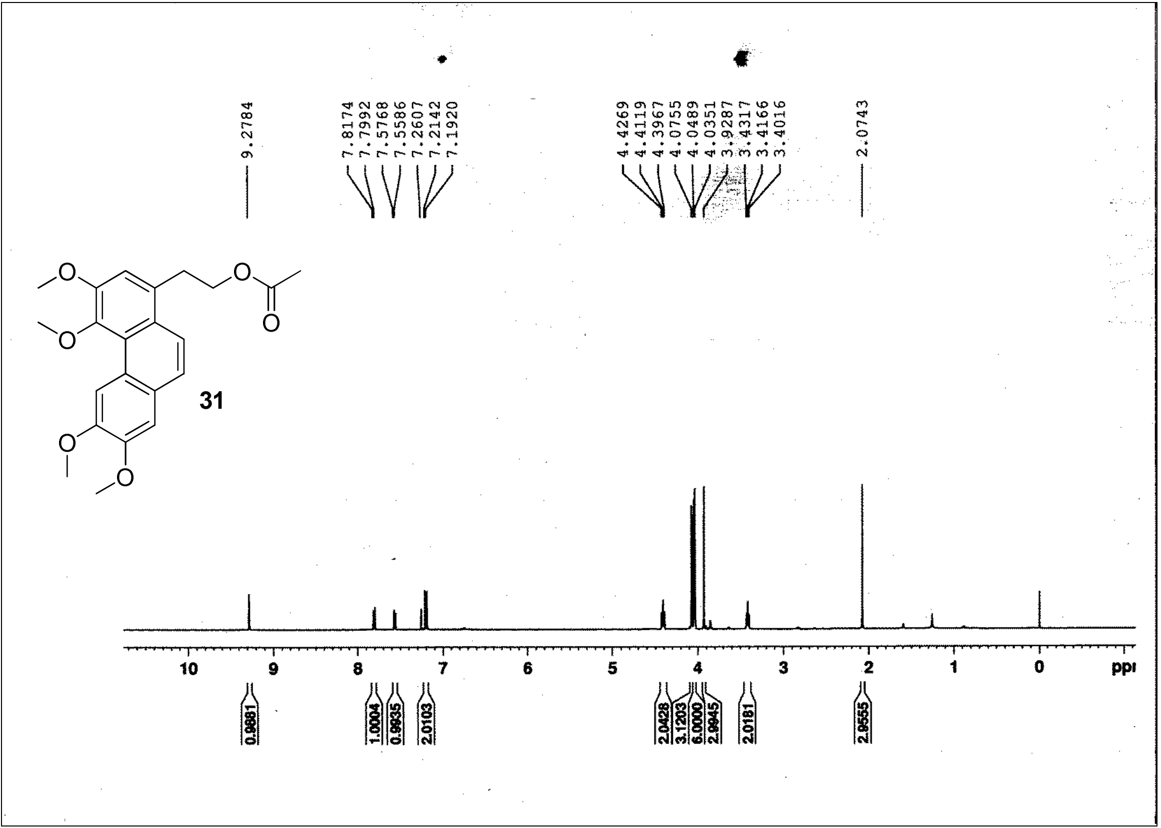

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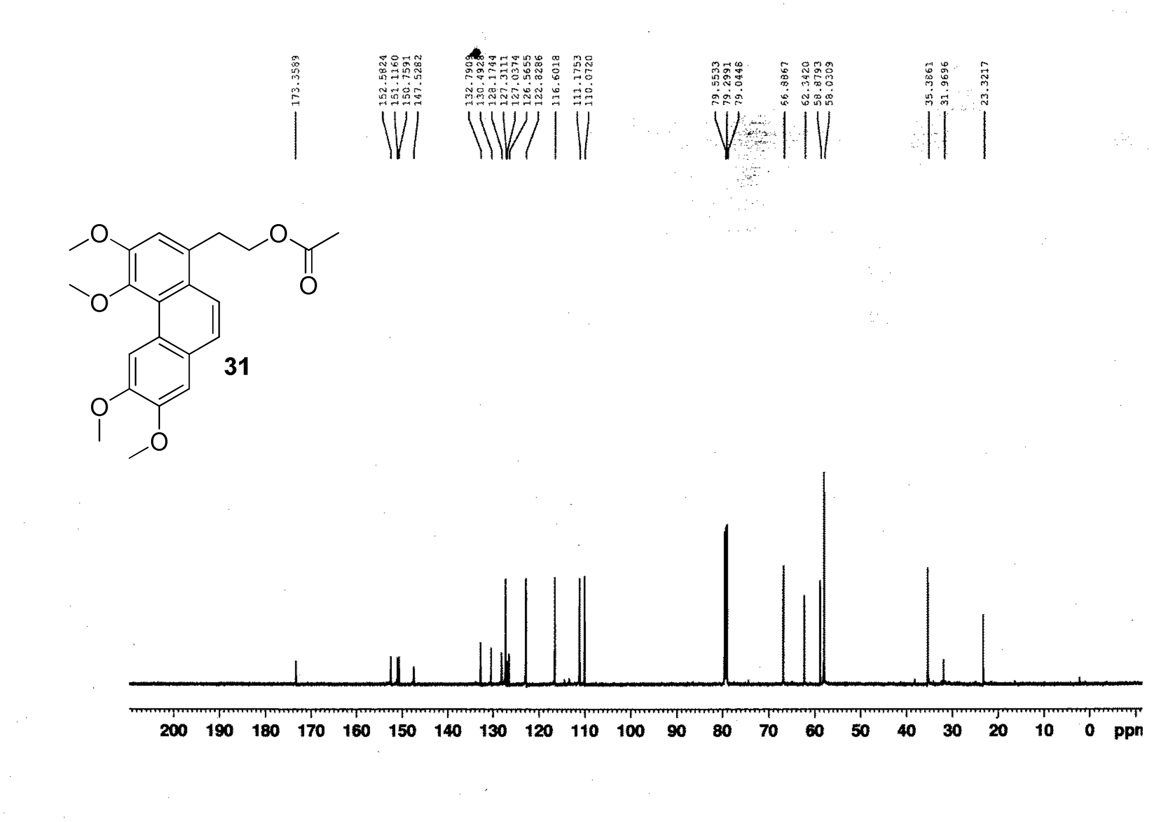

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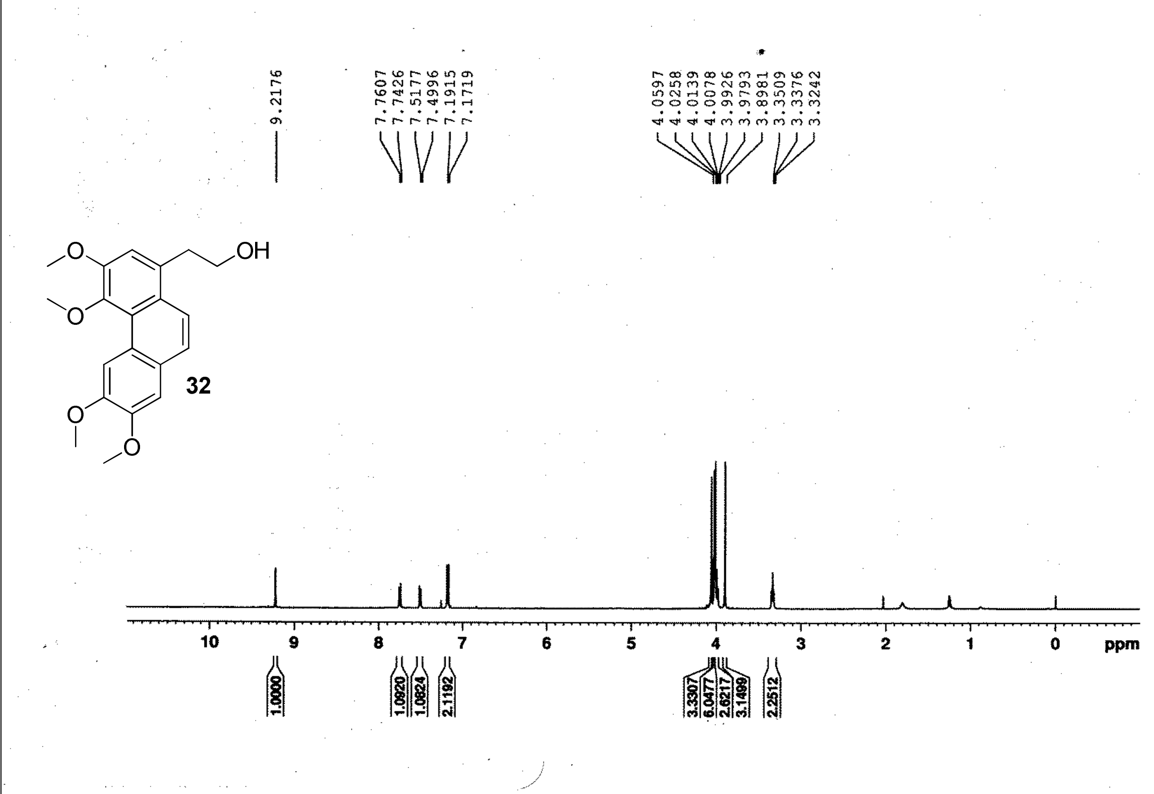
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5
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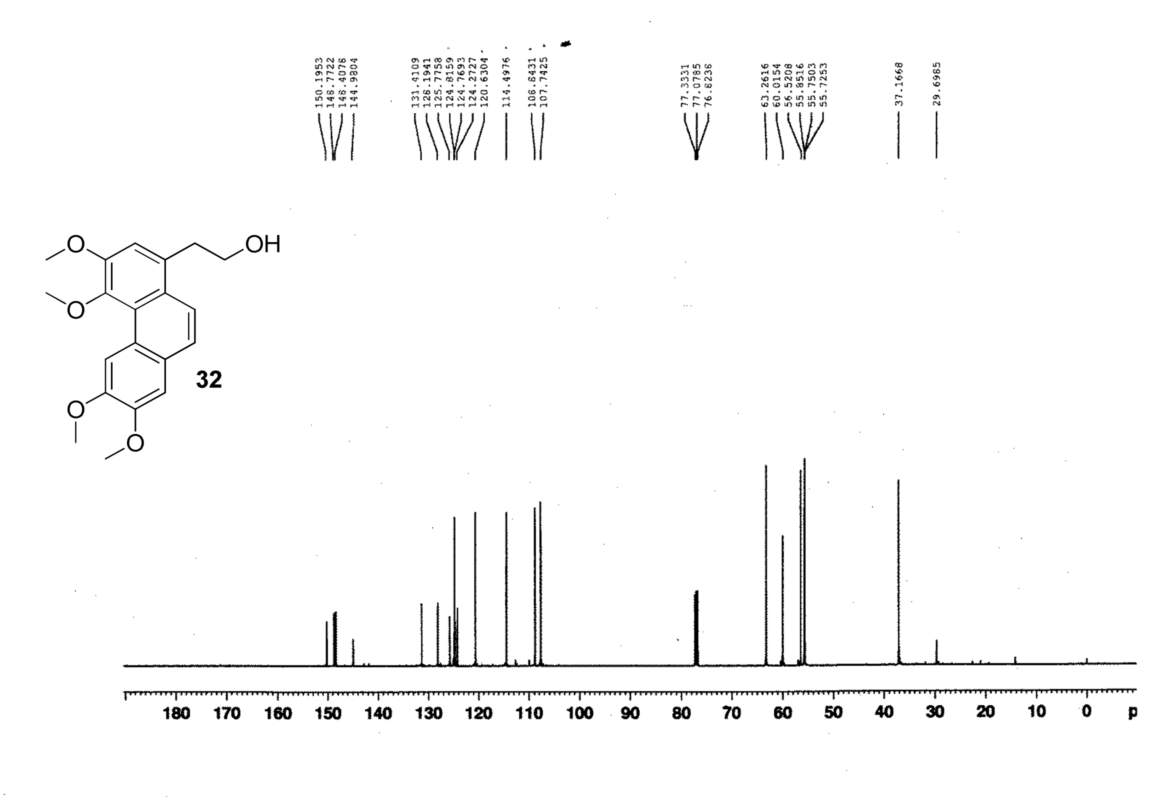
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O
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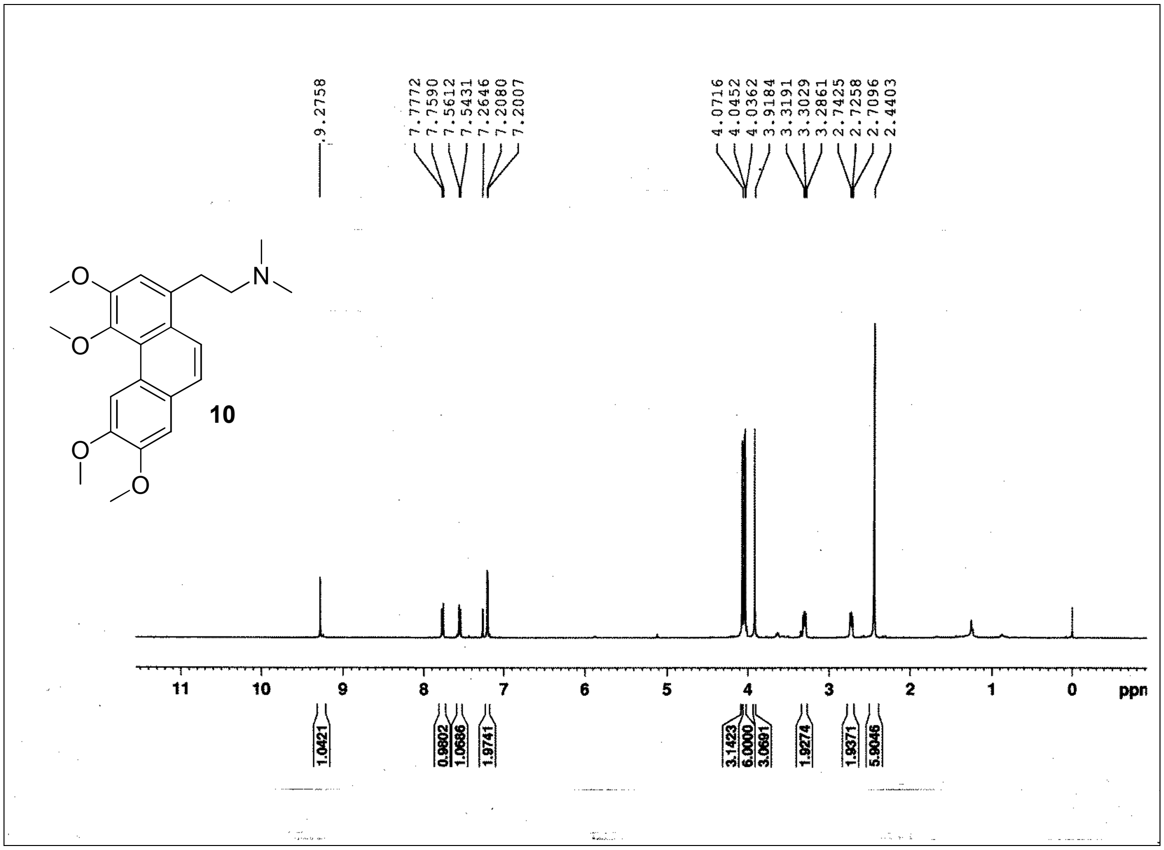
32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3.3191
3.3029
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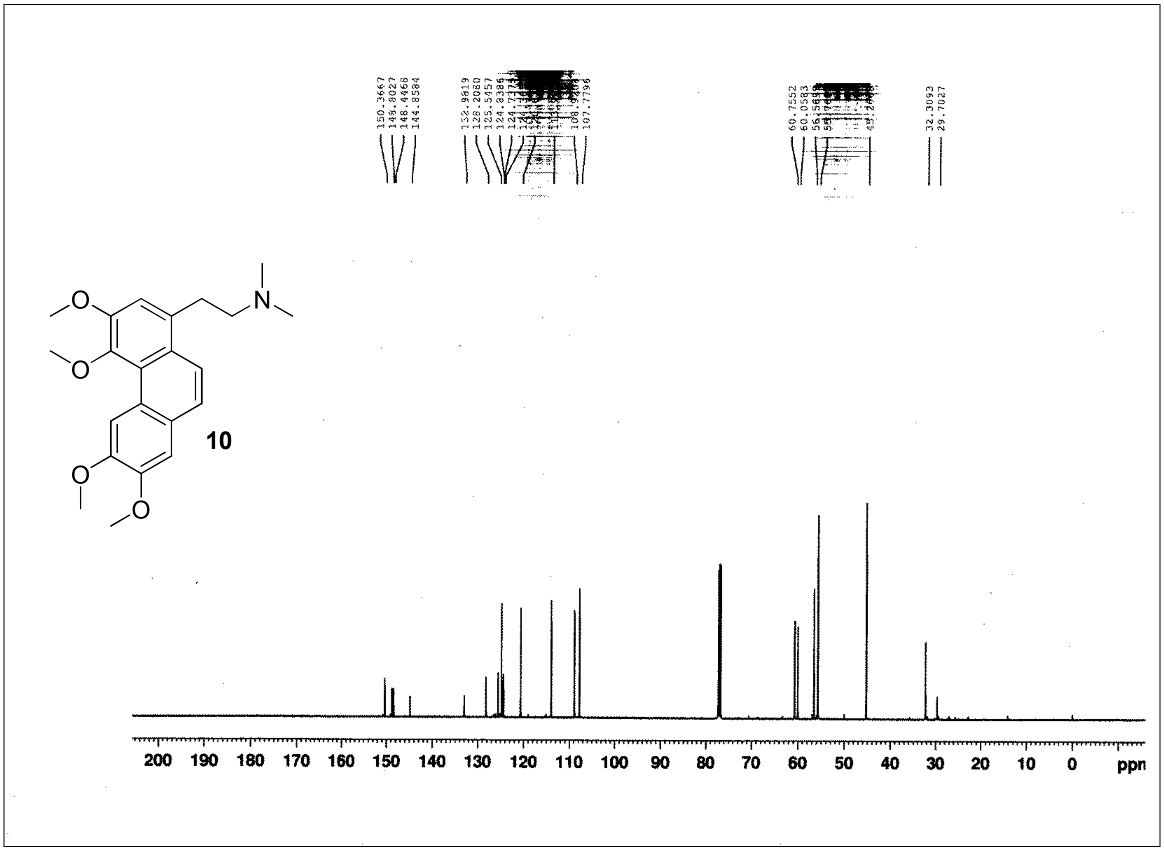
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ppm