Enantioselective synthesis of the strigolactone mimic (+)-GR24.

Liam J. Bromhead, Johan Visser and Christopher S. P. McErlean*

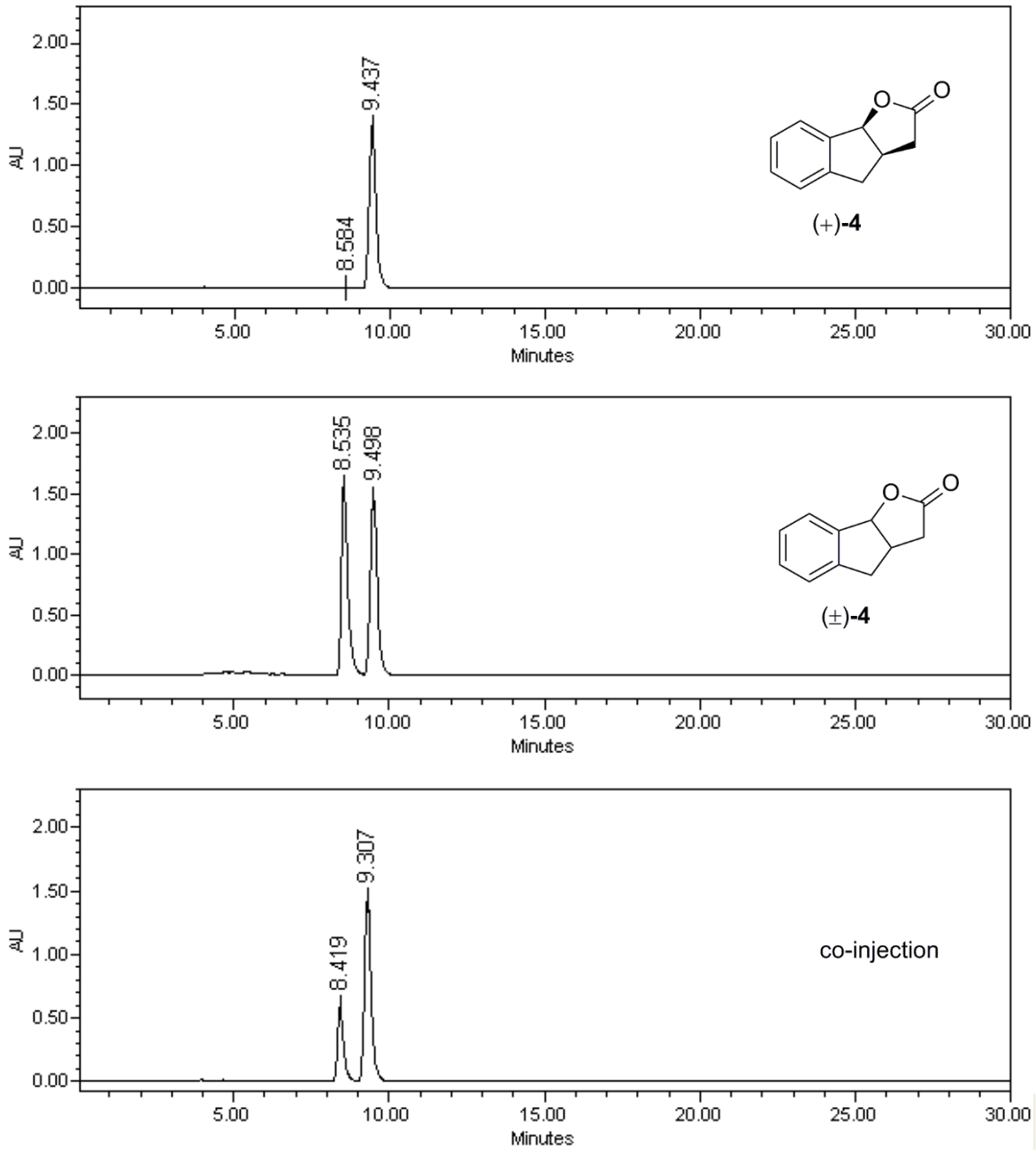
School of Chemistry, the University of Sydney, NSW, 2006, Australia.

Supporting Information

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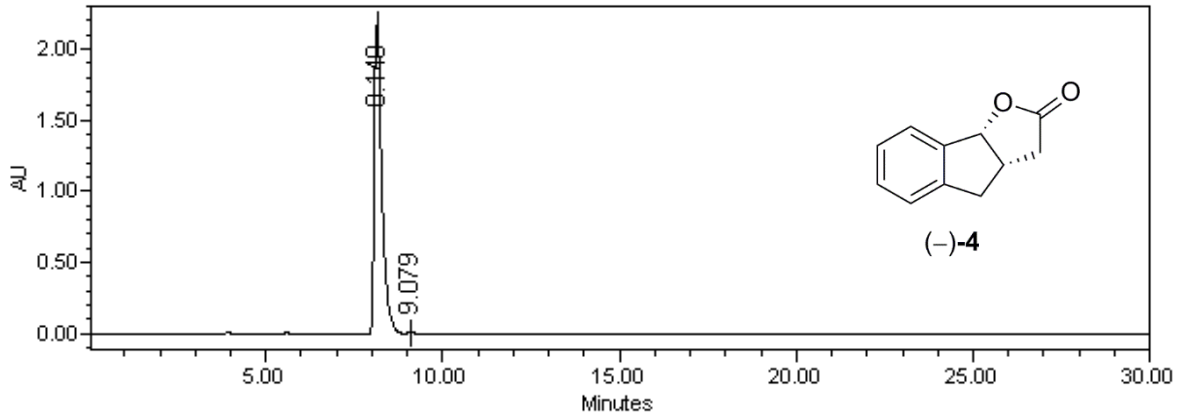
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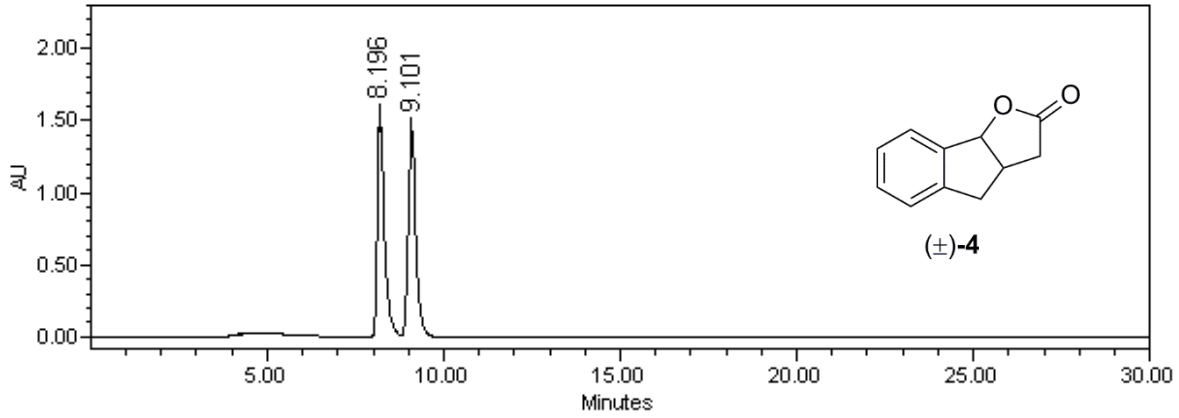
Enantioselective HPLC traces for compound 4

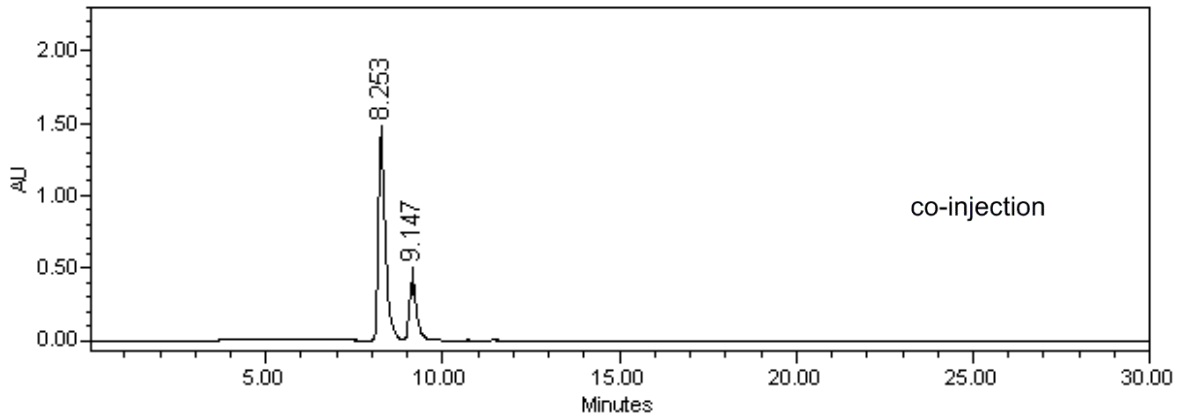


Compound	Retention Time (min)	Area (%)	*ee* (%)
(±)-4	8.535	50.29	–
	9.498	49.71	
(+)-4	8.584	0.19	>99
	9.437	99.81	
Co-injection	8.419	26.12	–
	9.307	73.88	

Conditions: AD-H column; 40% *i*-PrOH in hexanes; flow rate 0.8 mL/min.



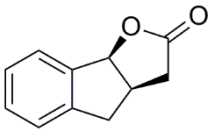
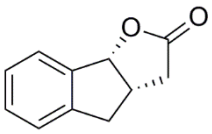
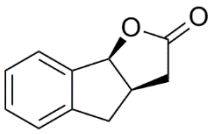
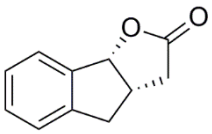




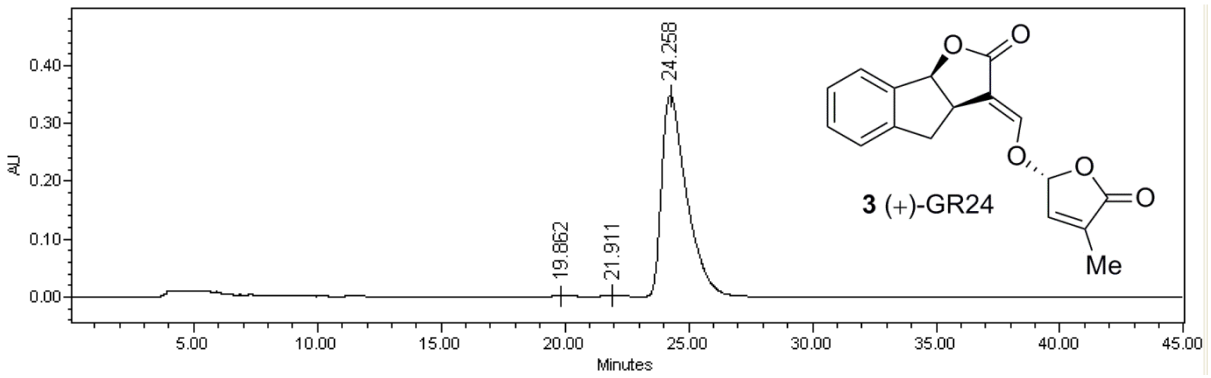
Compound	Retention Time (min)	Area (%)	*ee* (%)
(±)-4	8.196	49.97	–
	9.101	50.03	
(−)-4	8.140	99.87	>99
	9.079	0.13	
Co-injection	8.253	77.25	–
	9.147	22.75	

Conditions: AD-H column; 40% *i*-PrOH in hexanes; flow rate 0.8 mL/min.

Comparison of optical rotation for compound 4

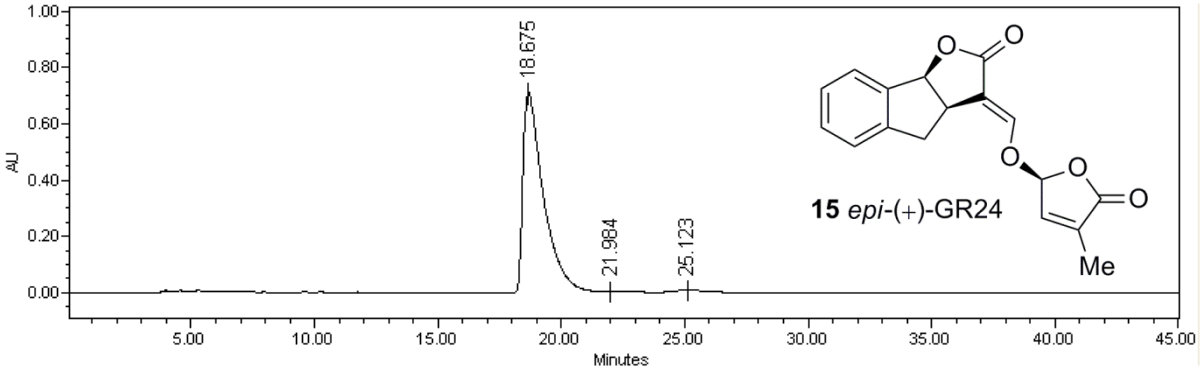
Compound	Stereochem.	$[\alpha]_D^{20}$	*ee* (%)	Method	Reference
 (+)-**4**	3a*R*,8b*S*	− 107.0 (*c* 0.4, $CHCl_3$)	>98%	Resolved	**1**
 (–)-**4**	3a*S*,8b*R*	+ 102.5 (*c* 0.4, $CHCl_3$)	>98%	Resolved	**1**
 (+)-**4**	3a*R*,8b*S*	+ 97.0 (*c* 1.01, $CHCl_3$)	96%	DKR (*S*,*S*) Catalyst	**2**
 (–)-**4**	3a*S*,8b*R*	− 93.0 (*c* 1.02, $CHCl_3$)	96%	DKR (*R*,*R*) Catalyst	**2**

HPLC traces for GR24 diastereomers



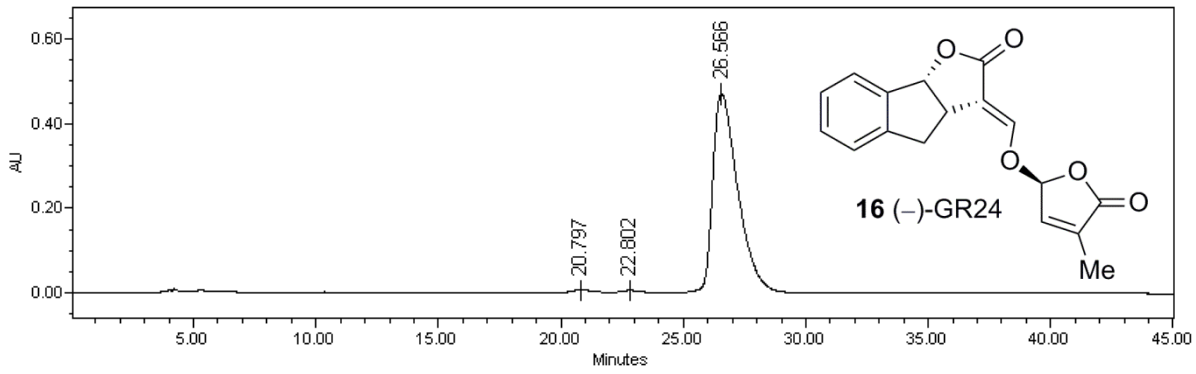
Compound	Retention Time (min)	Area (%)	*de* (%)
3 (+)-GR24	19.862	0.45	>98
	21.911	0.46	
	24.258	99.09	

Conditions: AD-H column; 30% *i*-PrOH in hexanes; flow rate 0.8 mL/min.



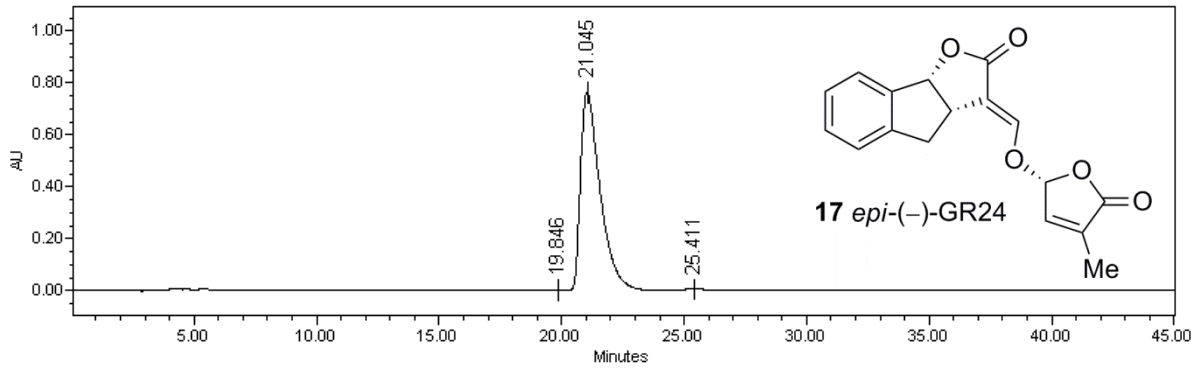
Compound	Retention Time (min)	Area (%)	*de* (%)
15 *epi*-(+)-GR24	18.675	99.36	>98
	21.984	0.16	
	25.123	0.48	

Conditions: AD-H column; 30% *i*-PrOH in hexanes; flow rate 0.8 mL/min.



Compound	Retention Time (min)	Area (%)	*de* (%)
16 (−)-GR24	20.797	0.48	>98
	22.802	0.45	
	26.566	99.07	

Conditions: AD-H column; 30% *i*-PrOH in hexanes; flow rate 0.8 mL/min.



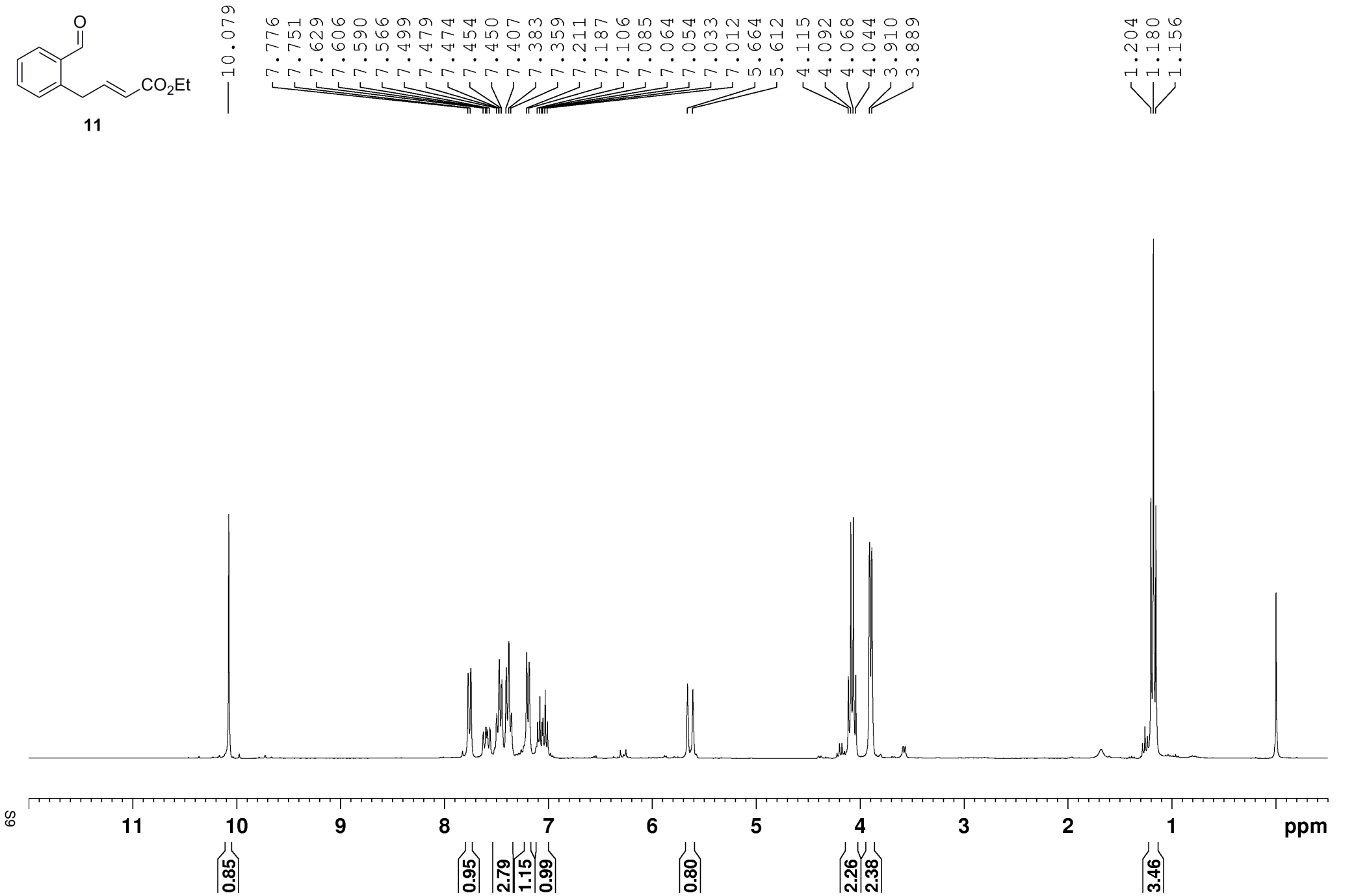
Compound	Retention Time (min)	Area (%)	*de* (%)
17 *epi*-(−)-GR24	19.846	0.16	>98
	21.045	99.45	
	25.411	0.39	

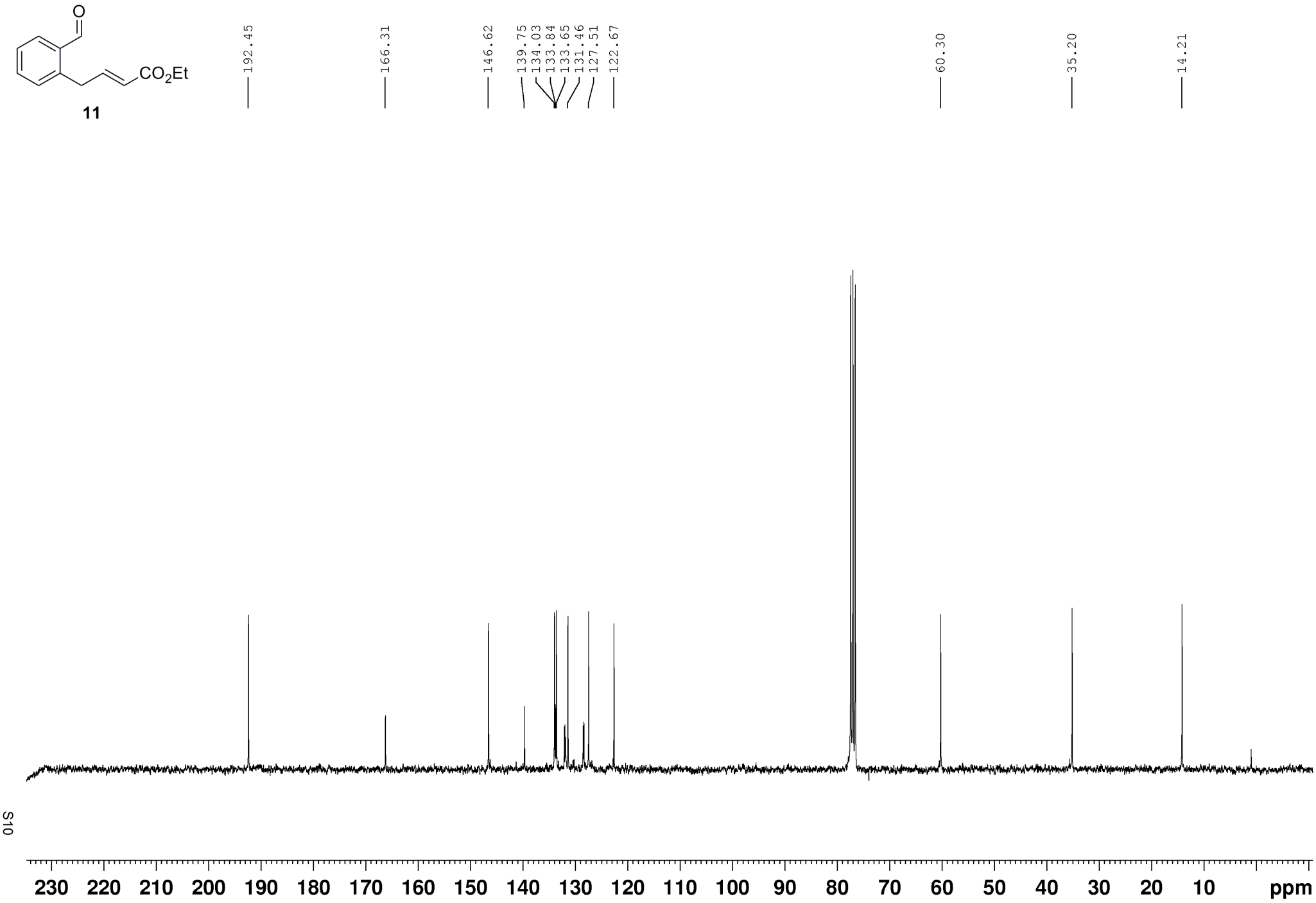
Conditions: AD-H column; 30% *i*-PrOH in hexanes; flow rate 0.8 mL/min.

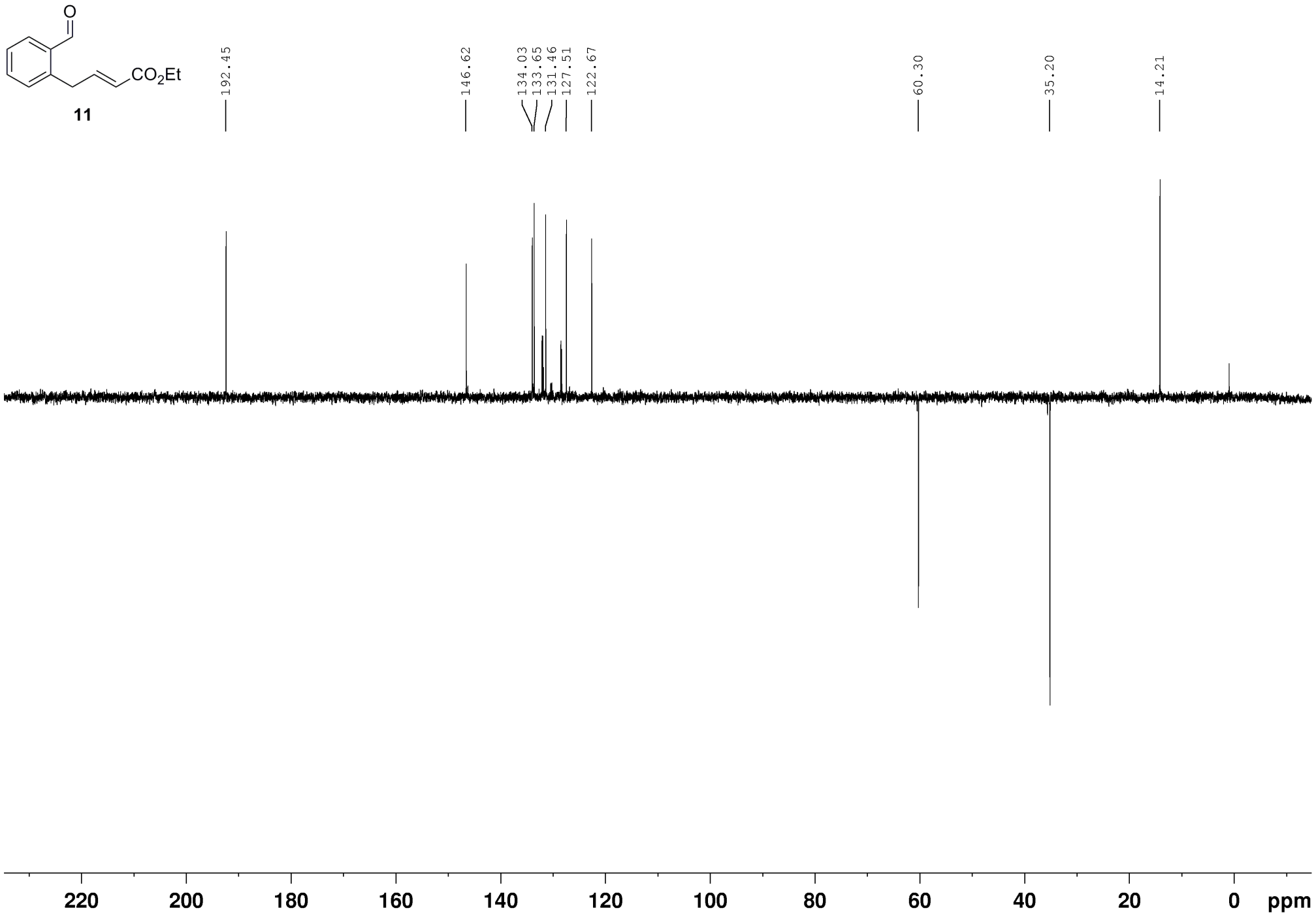
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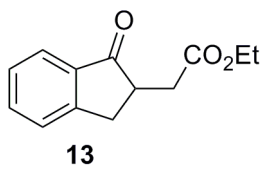
(1) Thuring, J. W. J. F.; Nefkens, G. H. L.; Zwanenburg, B. *J. Agric. Food Chem.* **1997**, *45*, 2278.

(2) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521.


O
CO2Et
11
10.079
7.776
7.751
7.629
7.606
7.590
7.566
7.499
7.479
7.474
7.454
7.450
7.407
7.383
7.359
7.211
7.187
7.106
7.085
7.064
7.054
7.033
7.012
5.664
5.612
4.115
4.092
4.068
4.044
3.910
3.889
1.204
1.180
1.156
6S
11
10
9
8
7
6
5
4
3
2
1
ppm
0.85
0.95
2.79
1.15
0.99
0.80
2.26
2.38
3.46


O
CO2Et
11
192.45
166.31
146.62
139.75
134.03
133.84
133.65
131.46
127.51
122.67
60.30
35.20
14.21
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
CO2Et
11
192.45
146.62
134.03
133.65
131.46
127.51
122.67
60.30
35.20
14.21
220
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180
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140
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60
40
20
0
ppm

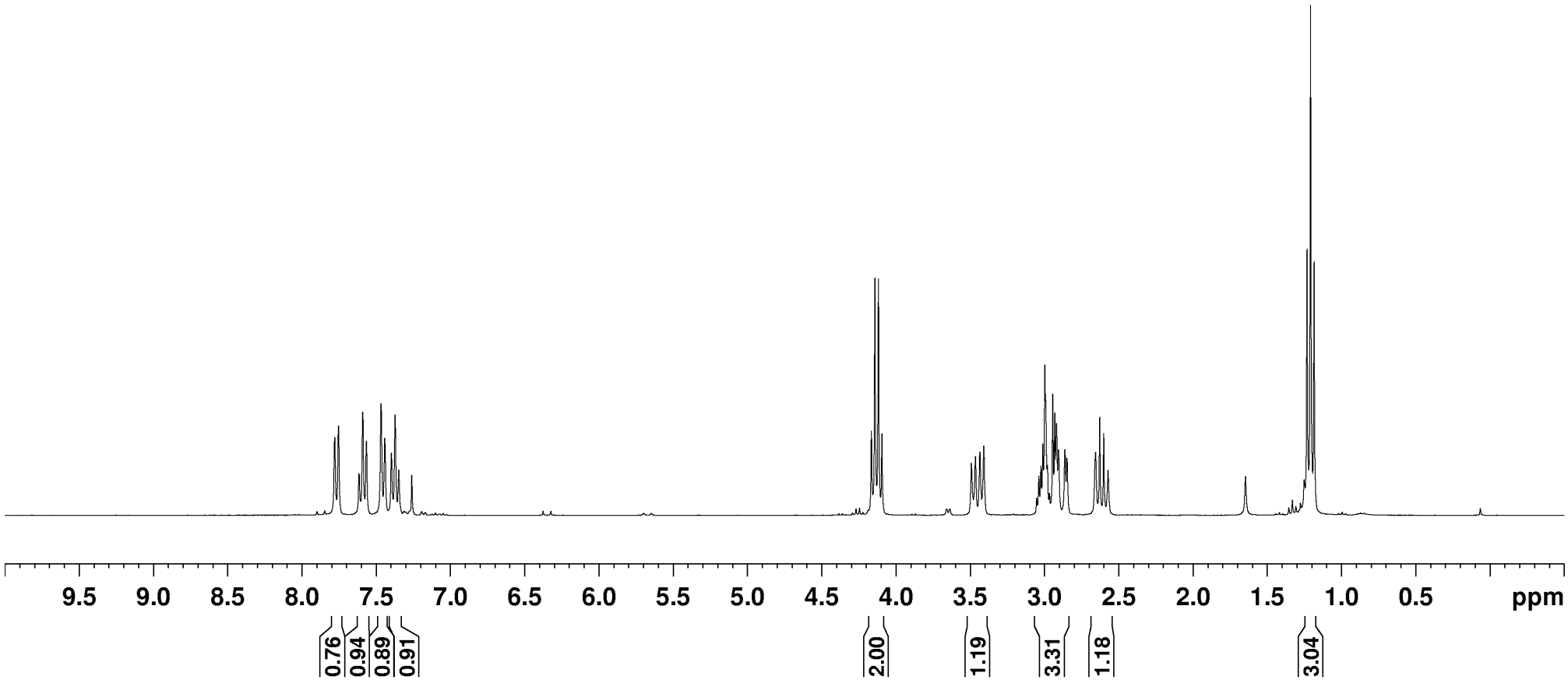


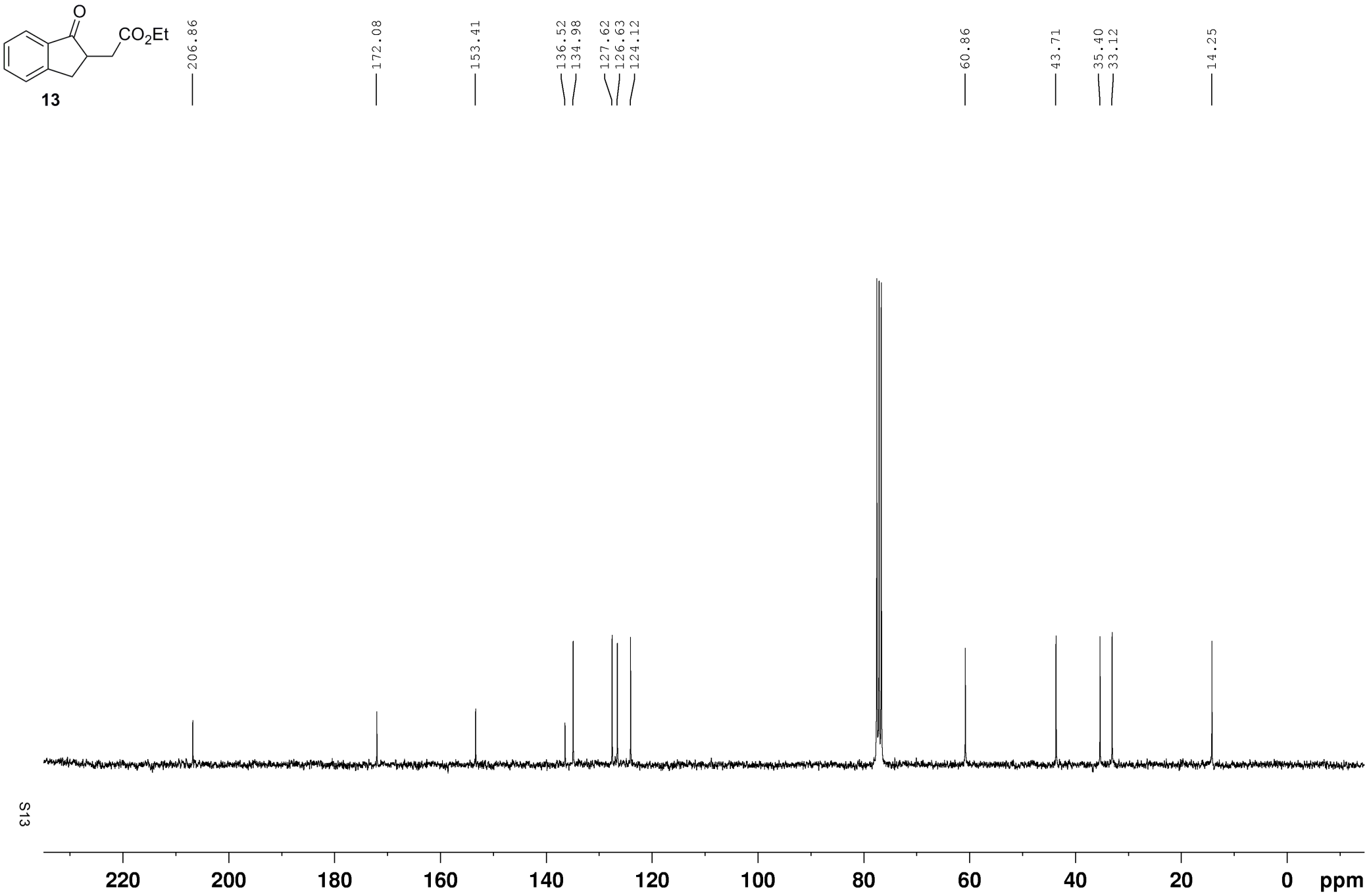
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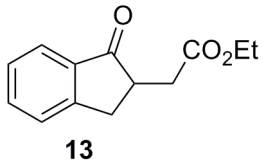
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4.120
4.097
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3.468
3.437
3.411
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3.000
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1.187

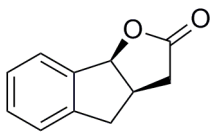



O
CO2Et
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172.08
153.41
136.52
134.98
127.62
126.63
124.12
60.86
43.71
35.40
33.12
14.25
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
CO2Et

13

134.98
127.62
126.63
124.12
60.86
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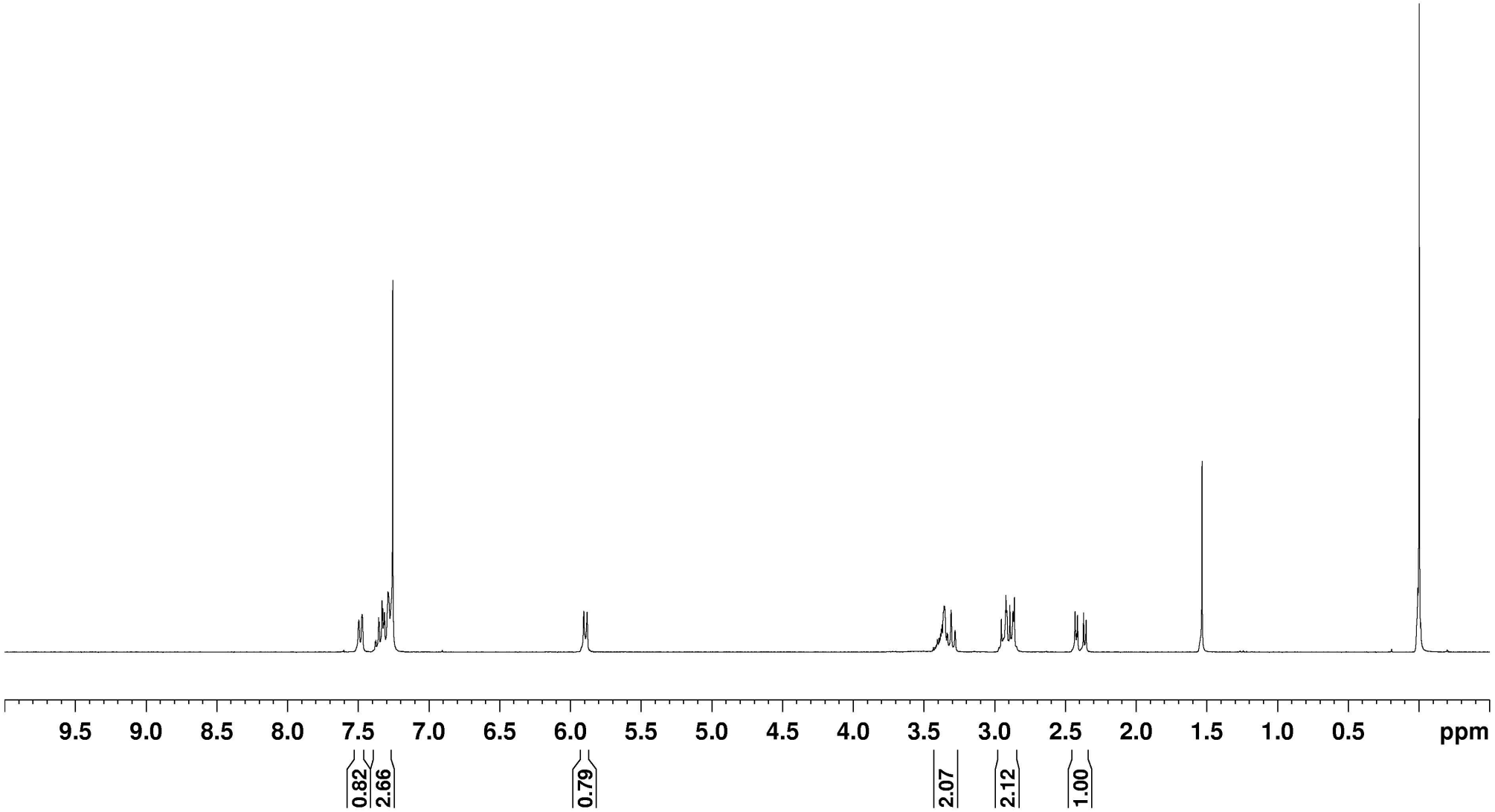


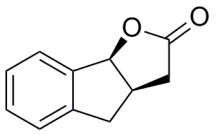
(+)-**4**

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7.477
7.383
7.359
7.354
7.335
7.330
7.317
7.293
7.259

5.908
5.885

3.408
3.360
3.357
3.311
3.283
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2.923
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2.895
2.873
2.863
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2.355

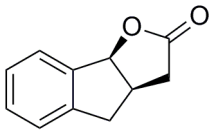




(+)-**4**

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37.92
37.34
35.66

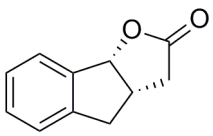
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(+)-**4**

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127.57
126.36
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87.65
37.92
37.34
35.66

220 200 180 160 140 120 100 80 60 40 20 0 ppm

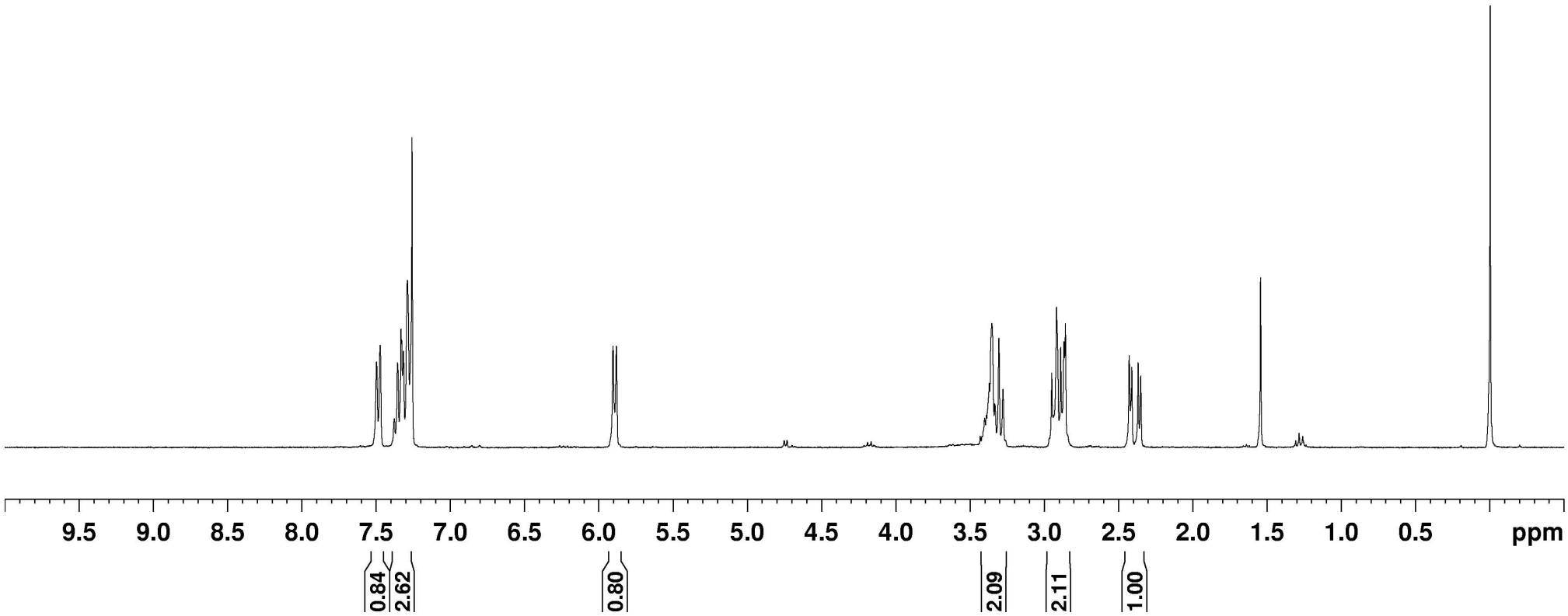


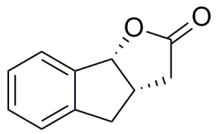
(–)-**4**

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7.473
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7.356
7.333
7.328
7.315
7.289

5.905
5.882

3.434
3.405
3.355
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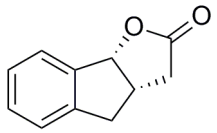




(–)-**4**

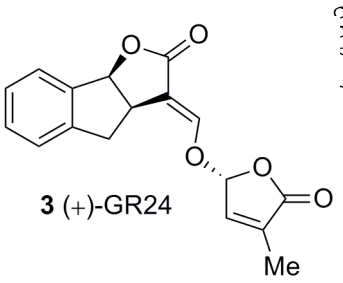
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129.98
127.57
126.37
125.33
87.65
37.92
37.34
35.67

220 200 180 160 140 120 100 80 60 40 20 0 ppm



(–)-**4**

129.98
127.57
126.37
125.33
87.65
37.92
37.34
35.66
220
200
180
160
140
120
100
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40
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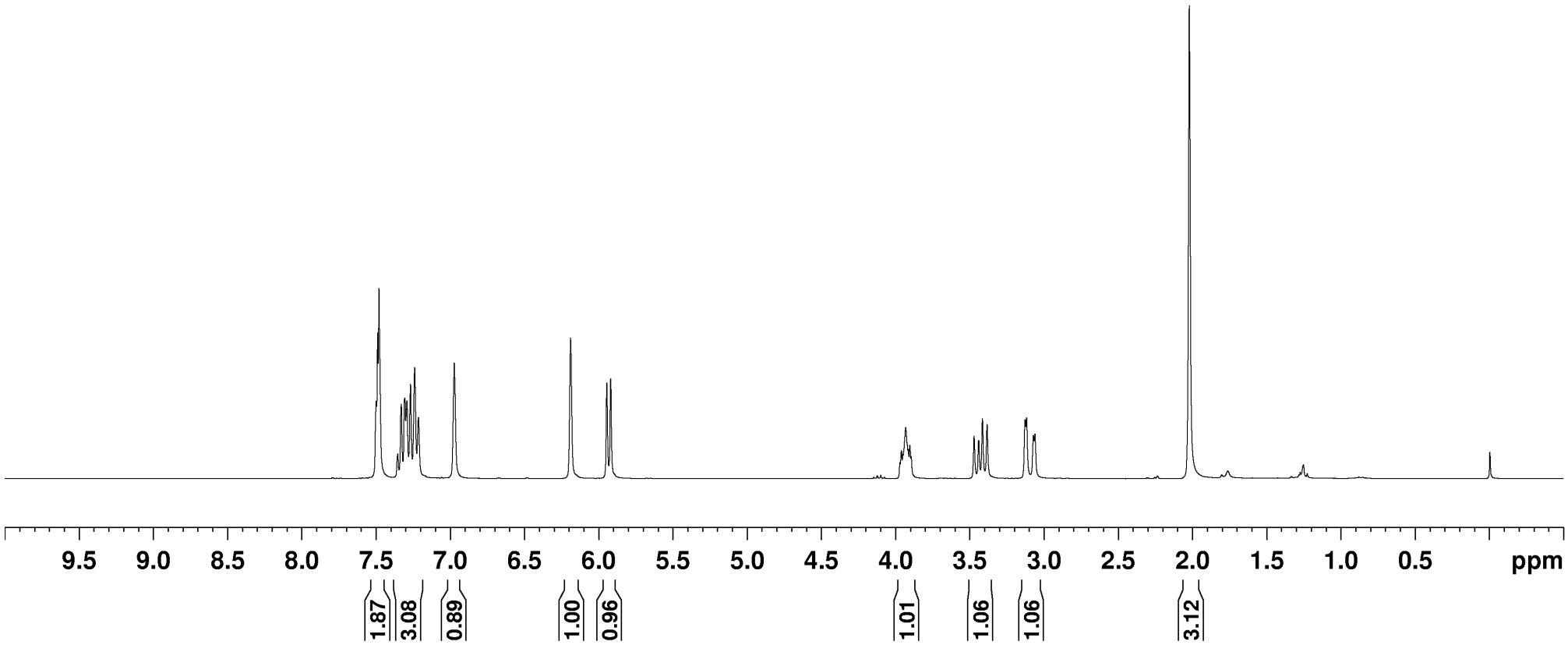


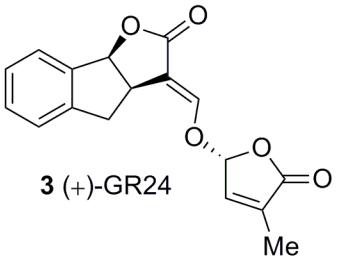
3 (+)-GR24

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7.489
7.480
7.354
7.330
7.308
7.306
7.292
7.268
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7.215
6.973
6.189
5.946
5.919

3.971
3.961
3.952
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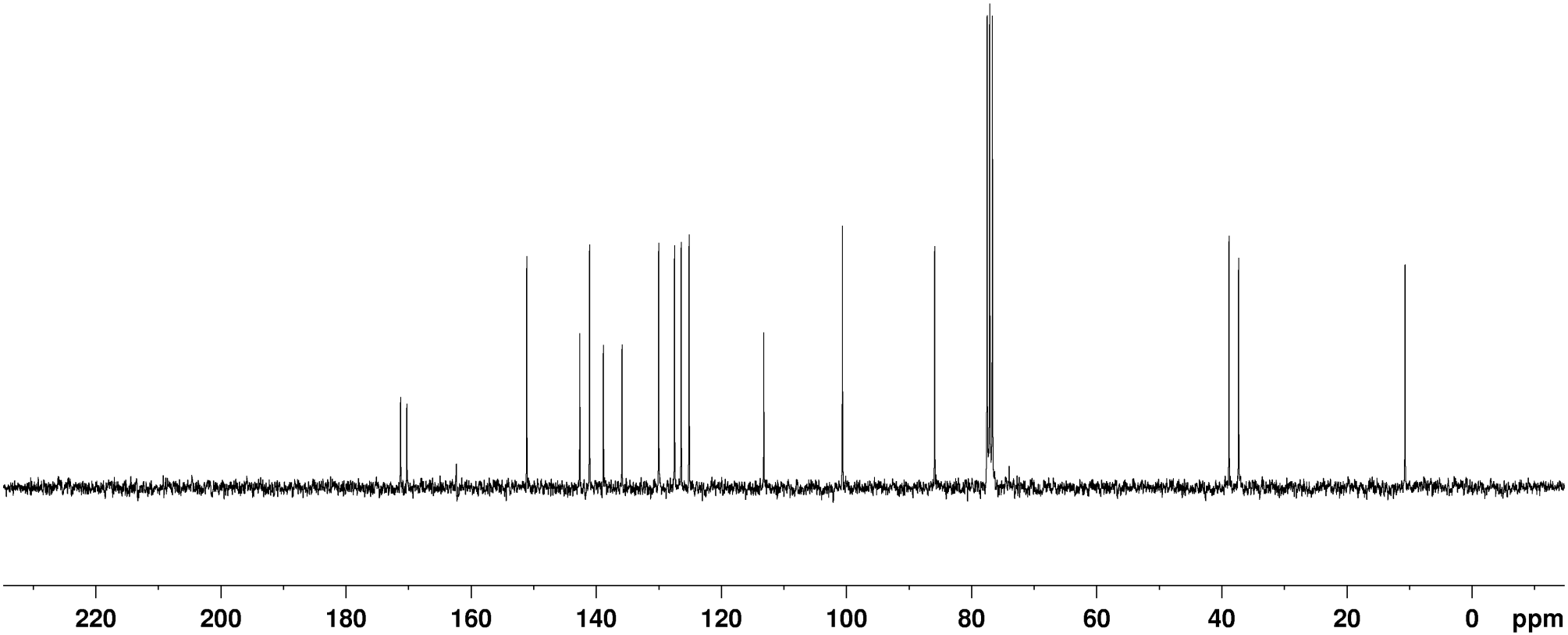
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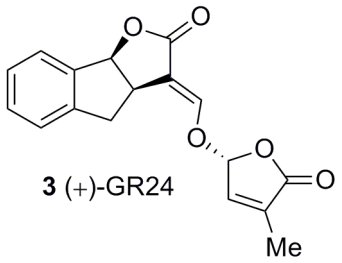




3 (+)-GR24

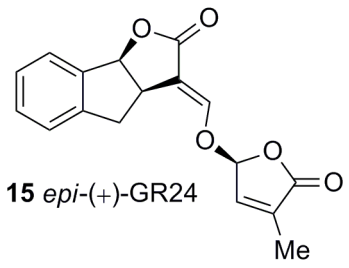
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141.07
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126.42
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100.65
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38.85
37.31
10.72



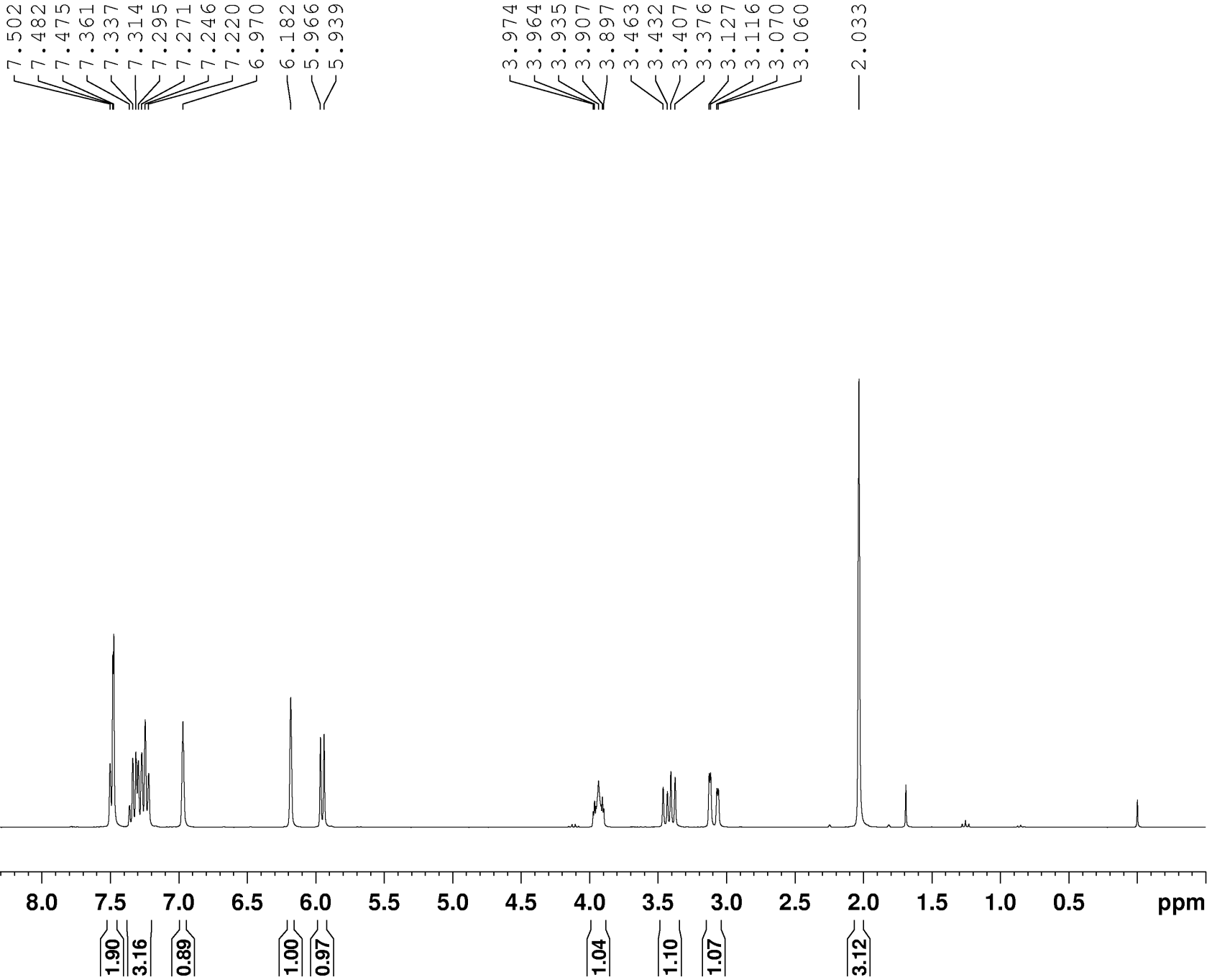

O
O
O
O
O
Me

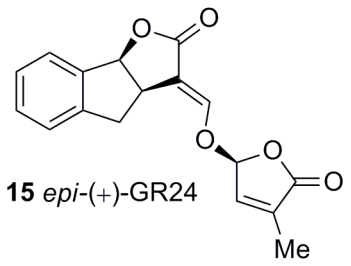
3 (+)-GR24

151.10
141.07
130.02
127.48
126.42
125.15
100.65
85.90
38.85
37.31
10.72
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
O
O
O
Me

15 *epi*-(+)-GR24

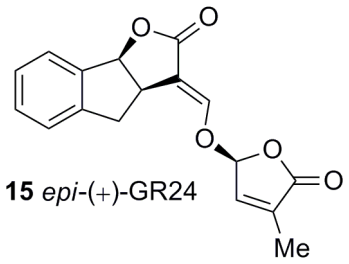

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5.939
3.974
3.964
3.935
3.907
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3.432
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3.376
3.127
3.116
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8.0
7.5
7.0
6.5
6.0
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5.0
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4.0
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3.0
2.5
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0.5
ppm
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0.89
1.00
0.97
1.04
1.10
1.07
3.12



15 *epi*-(+)-GR24

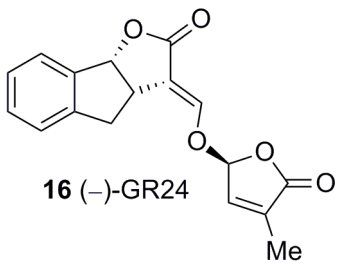
171.26
170.25
151.05
142.63
141.06
138.77
135.88
130.04
127.46
126.36
125.24
113.39
100.70
85.92
38.80
37.41
10.73

220 200 180 160 140 120 100 80 60 40 20 0 ppm


O
O
O
O
O
Me

15 *epi*-(+)-GR24

151.06
141.06
130.04
127.46
126.36
125.24
100.70
85.92
38.80
37.41
10.74
220
200
180
160
140
120
100
80
60
40
20
0
ppm

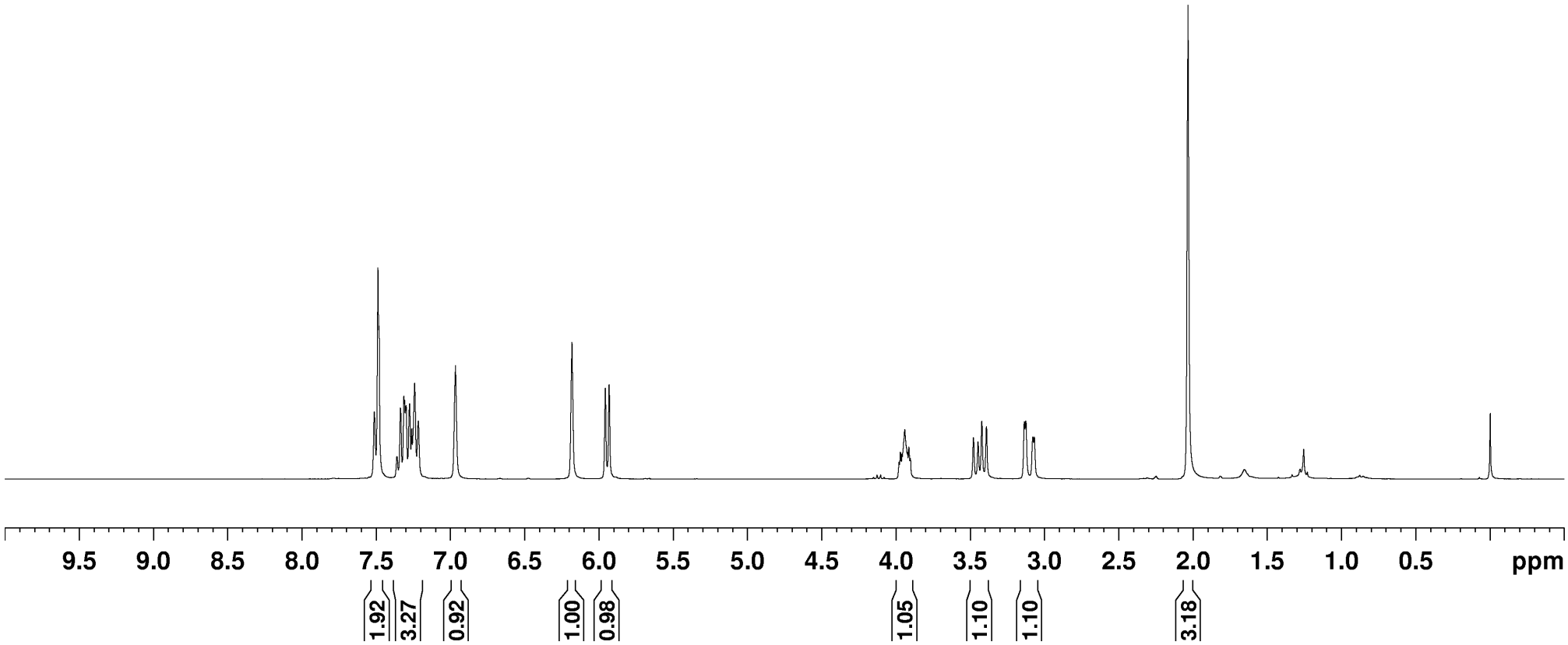


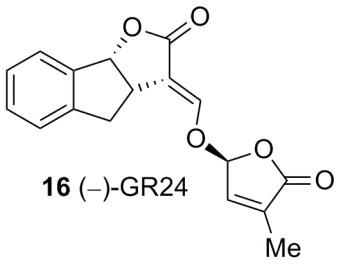
16 (–)-GR24

7.512
7.488
7.480
7.364
7.340
7.316
7.311
7.302
7.278
7.263
7.244
7.219
6.969
6.184
5.960
5.934

3.982
3.973
3.961
3.943
3.925
3.916
3.905
3.480
3.449
3.424
3.393
3.138
3.127
3.081
3.071

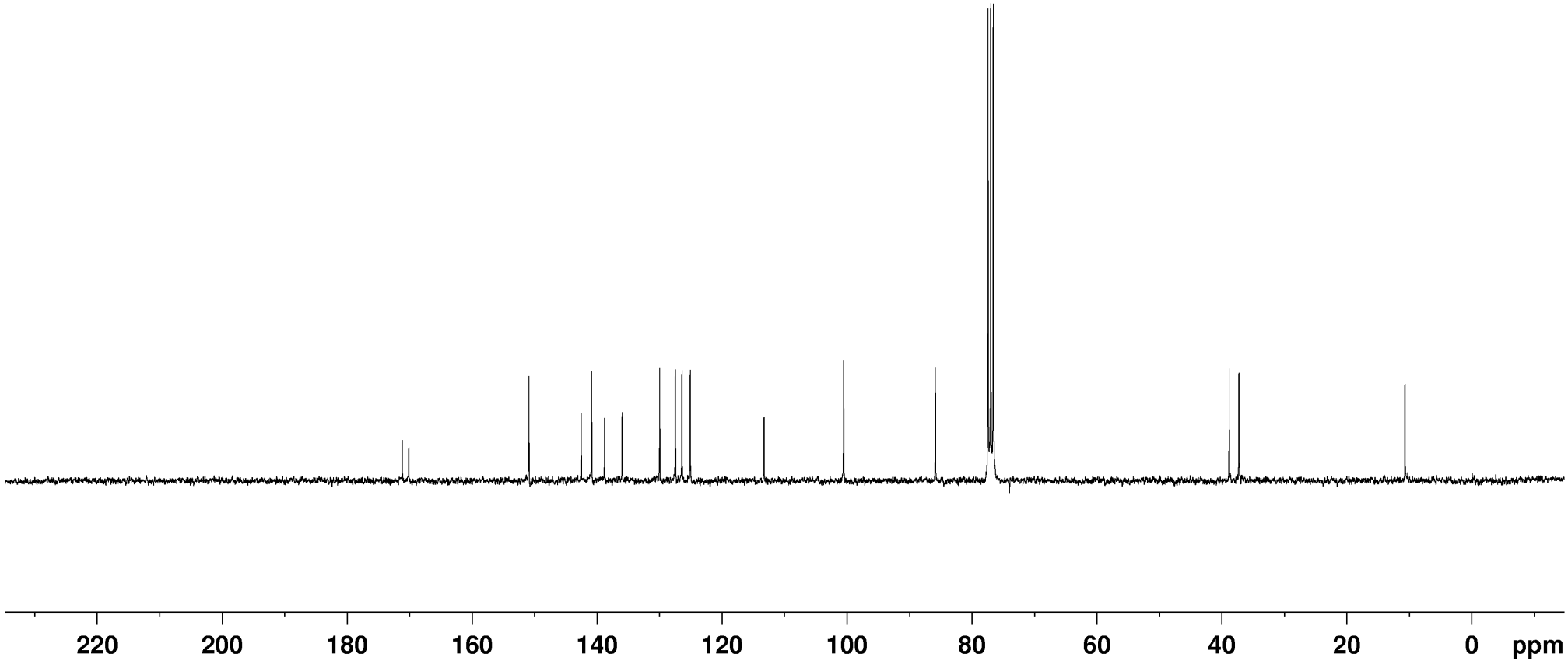
2.035

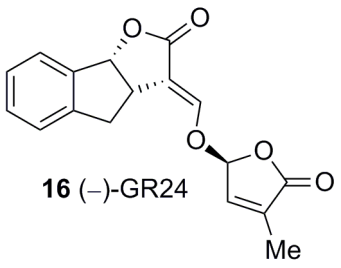




16 (–)-GR24

171.22
170.17
150.95
142.58
140.91
138.85
136.02
130.02
127.50
126.46
125.13
113.32
100.58
85.89
38.87
37.31
10.74

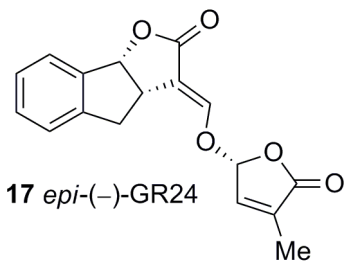




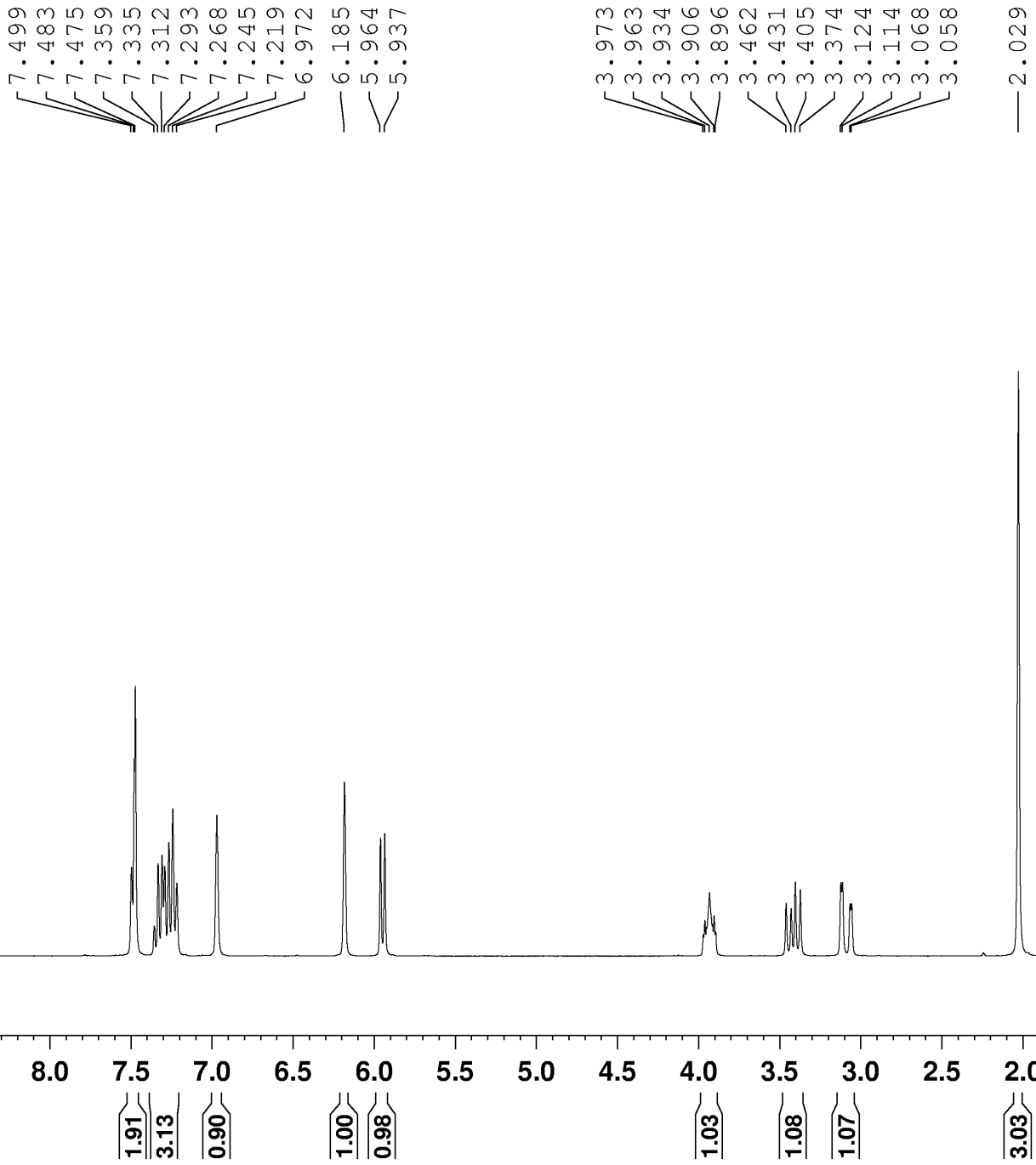
16 (–)-GR24

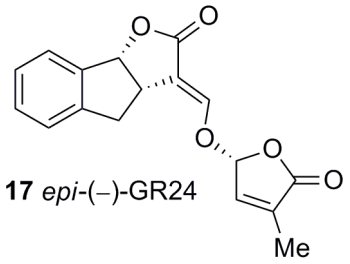
150.96
140.92
130.02
127.50
126.46
125.13
100.58
85.89
38.87
37.31
10.74

220 200 180 160 140 120 100 80 60 40 20 0 ppm


O
O
O
O
O
Me

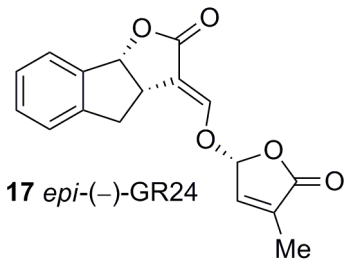
17 *epi*-(–)-GR24


7.499
7.483
7.475
7.359
7.335
7.312
7.293
7.268
7.245
7.219
6.972
6.185
5.964
5.937
3.973
3.963
3.934
3.906
3.896
3.462
3.431
3.405
3.374
3.124
3.114
3.068
3.058
2.029
S30
9.5
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
ppm
1.91
3.13
0.90
1.00
0.98
1.03
1.08
1.07
3.03


O
O
O
O
O
Me

17 *epi*-(–)-GR24

171.27
170.28
151.10
142.65
141.11
138.77
135.84
130.03
127.45
126.35
125.25
113.36
100.72
85.93
38.80
37.41
10.73
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
O
O
O
O
Me

17 *epi*-(–)-GR24

151.10
141.11
130.03
127.45
126.35
125.25
100.72
85.93
38.80
37.41
10.73
220
200
180
160
140
120
100
80
60
40
20
0
ppm