

## Supporting Information

# **Rh-Catalyzed Deformylative Coupling of Salicylaldehydes with Acrylates and Acrylamides**

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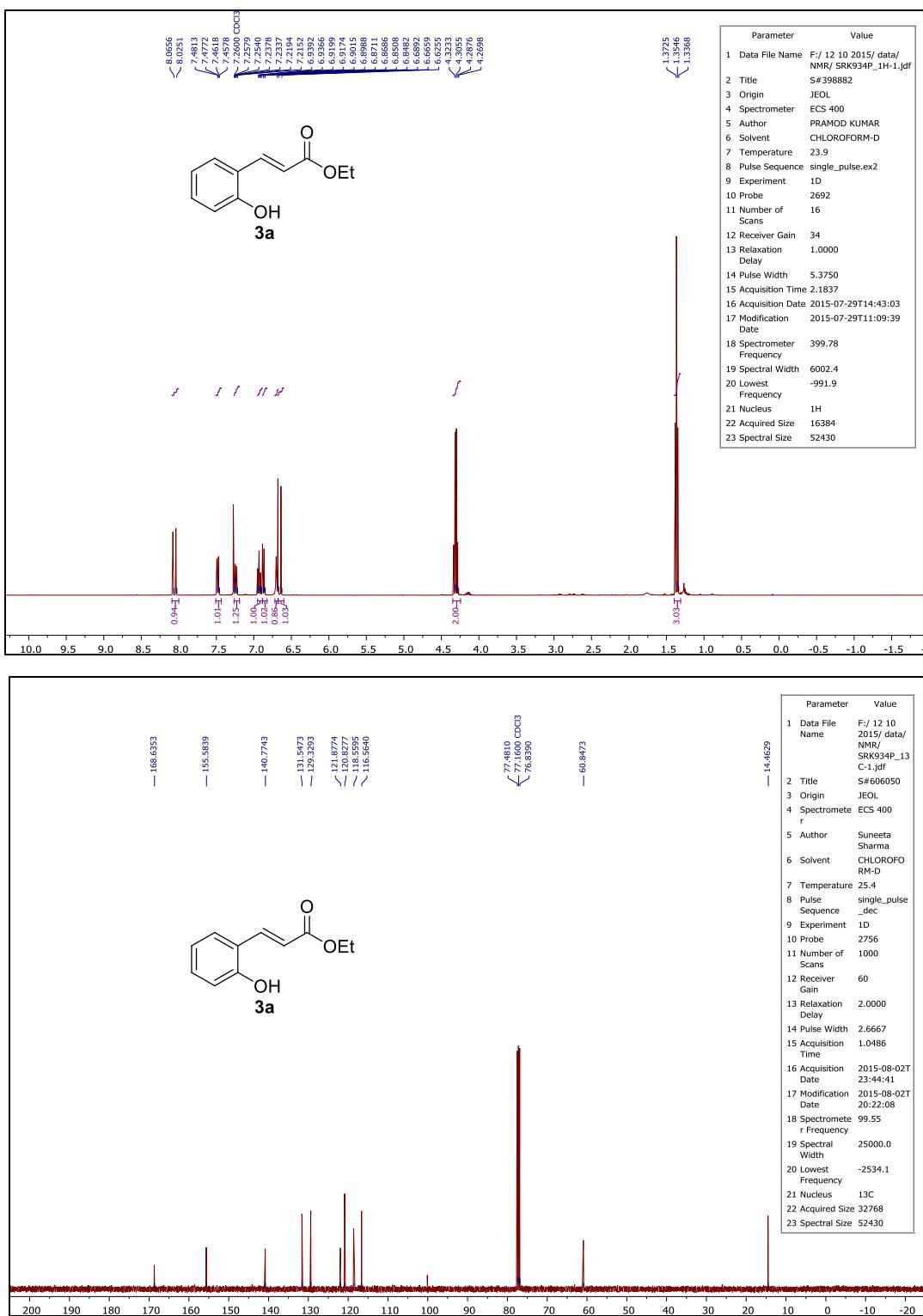
*Email:* maddali@iitk.ac.in

*Fax:* +91 512 259 7532

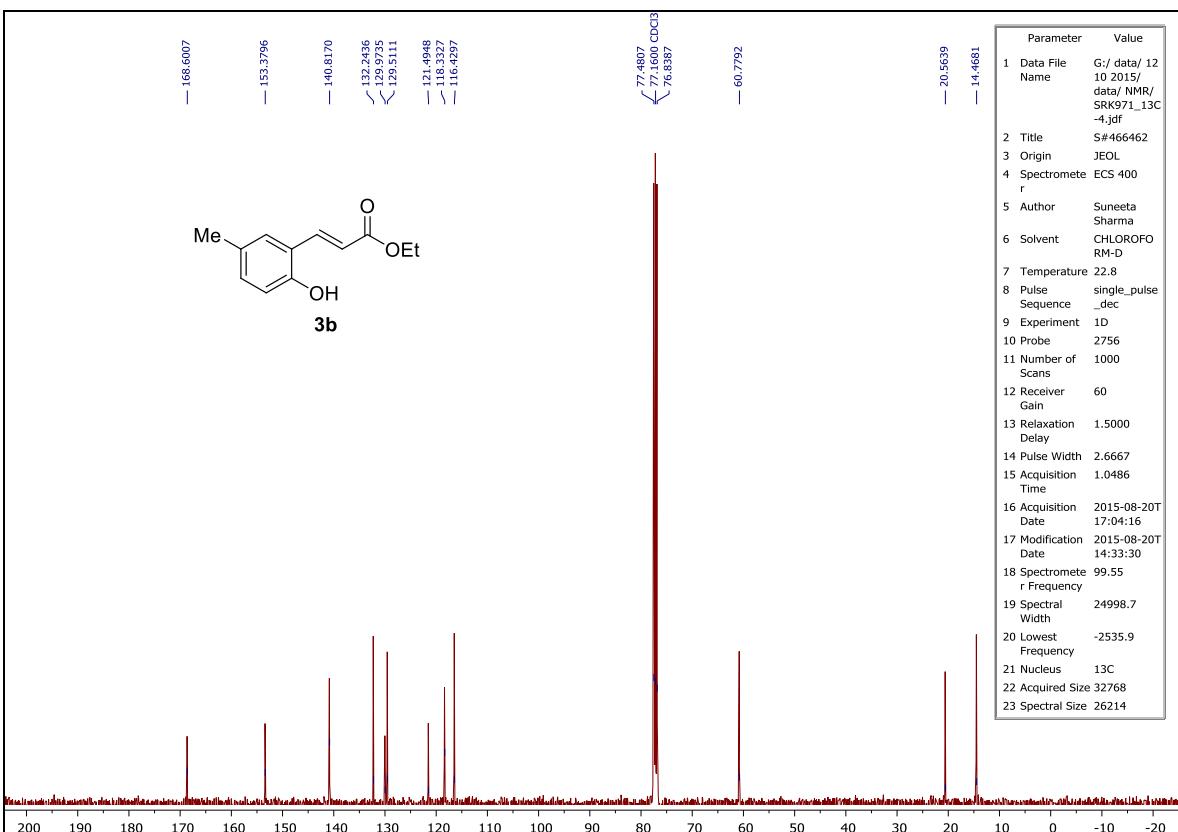
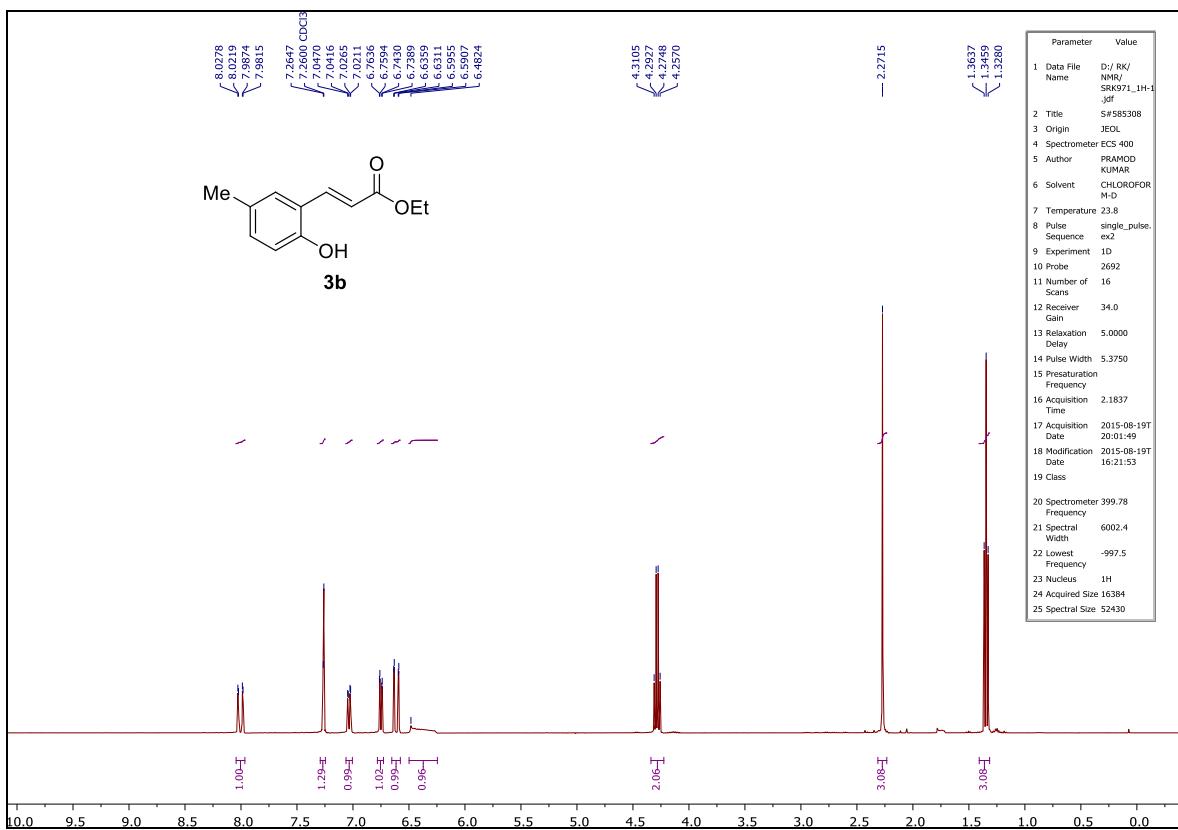
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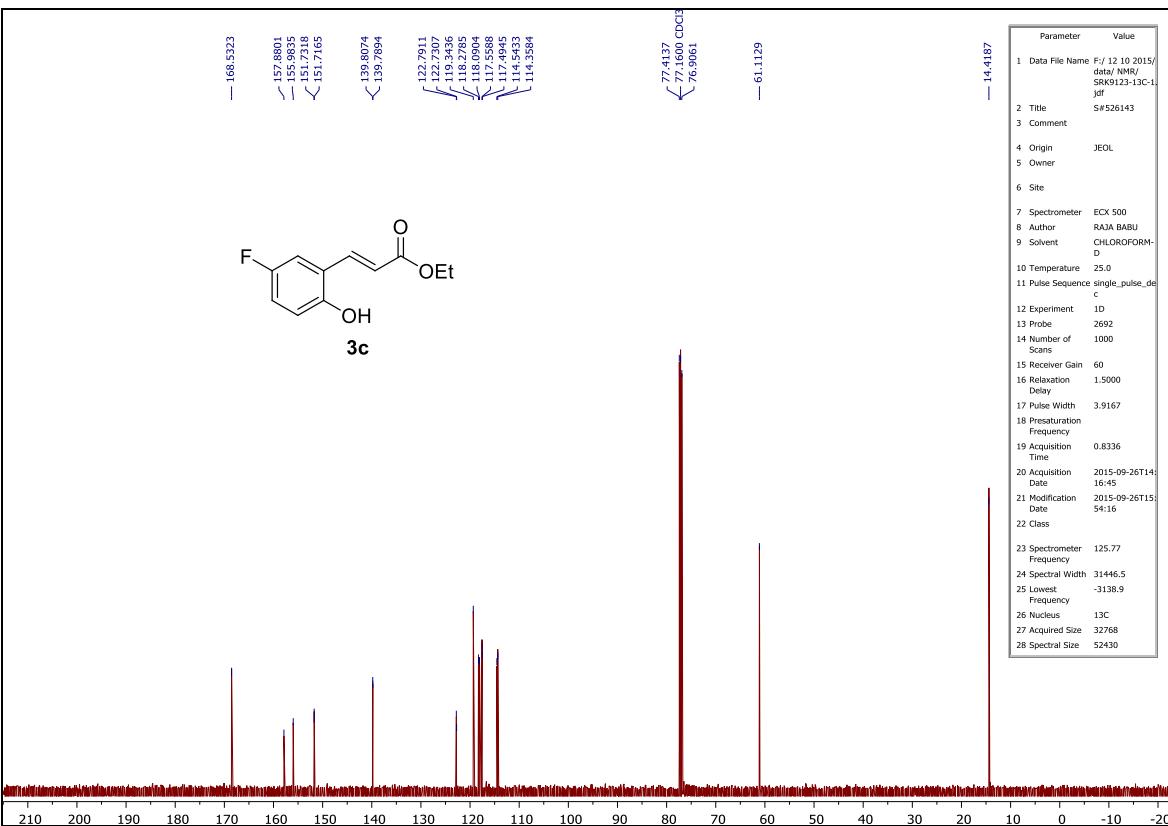
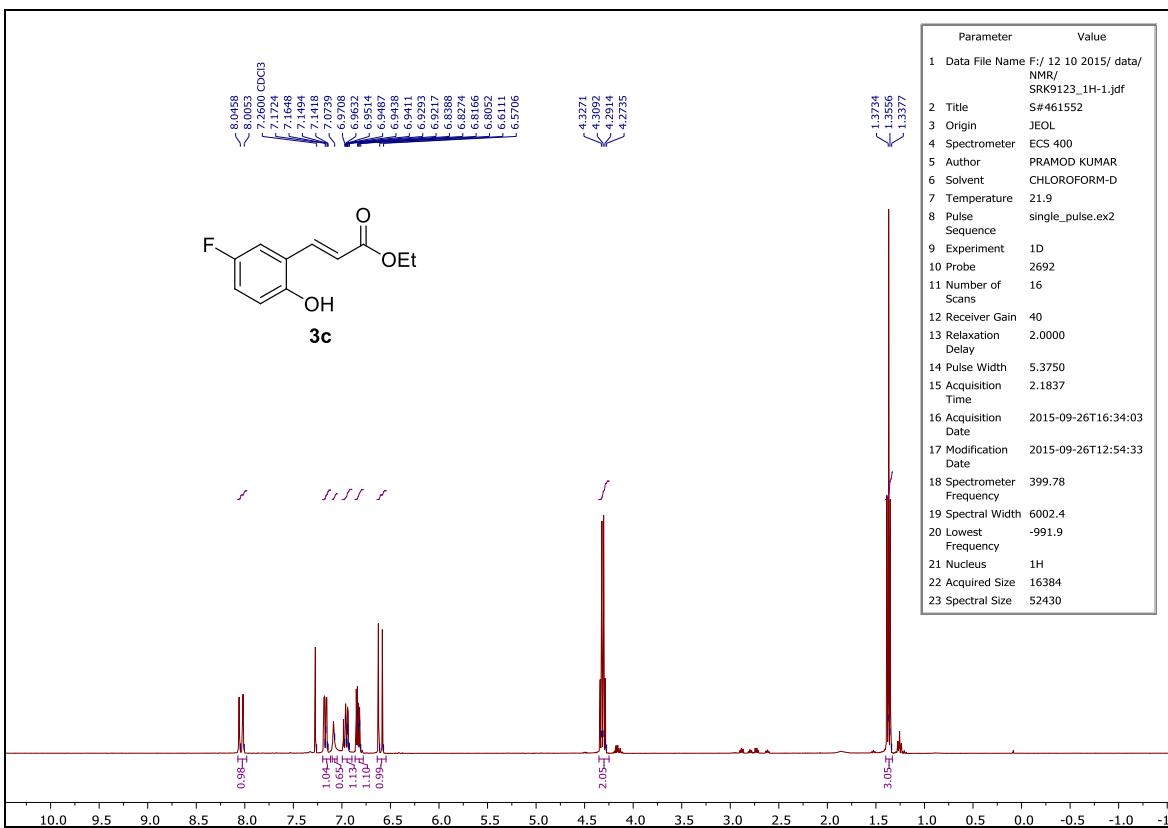
# 1. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products (3a-3n, 1A and 1B)



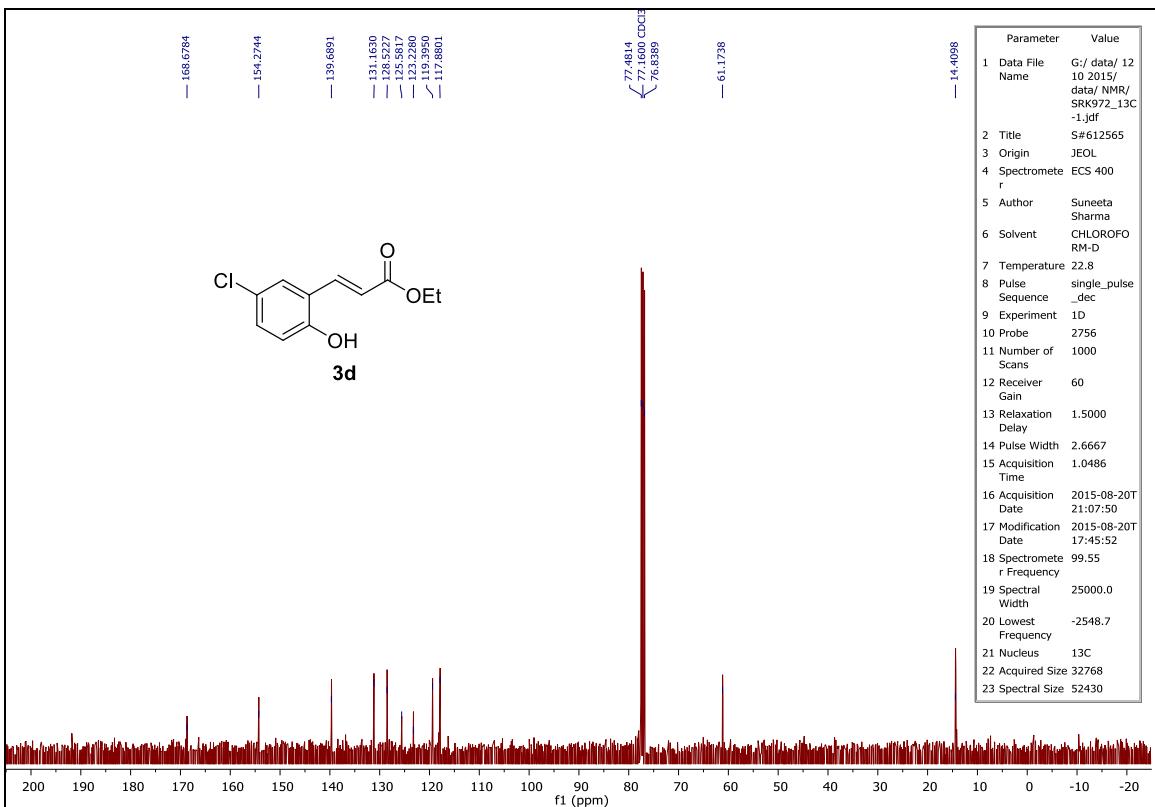
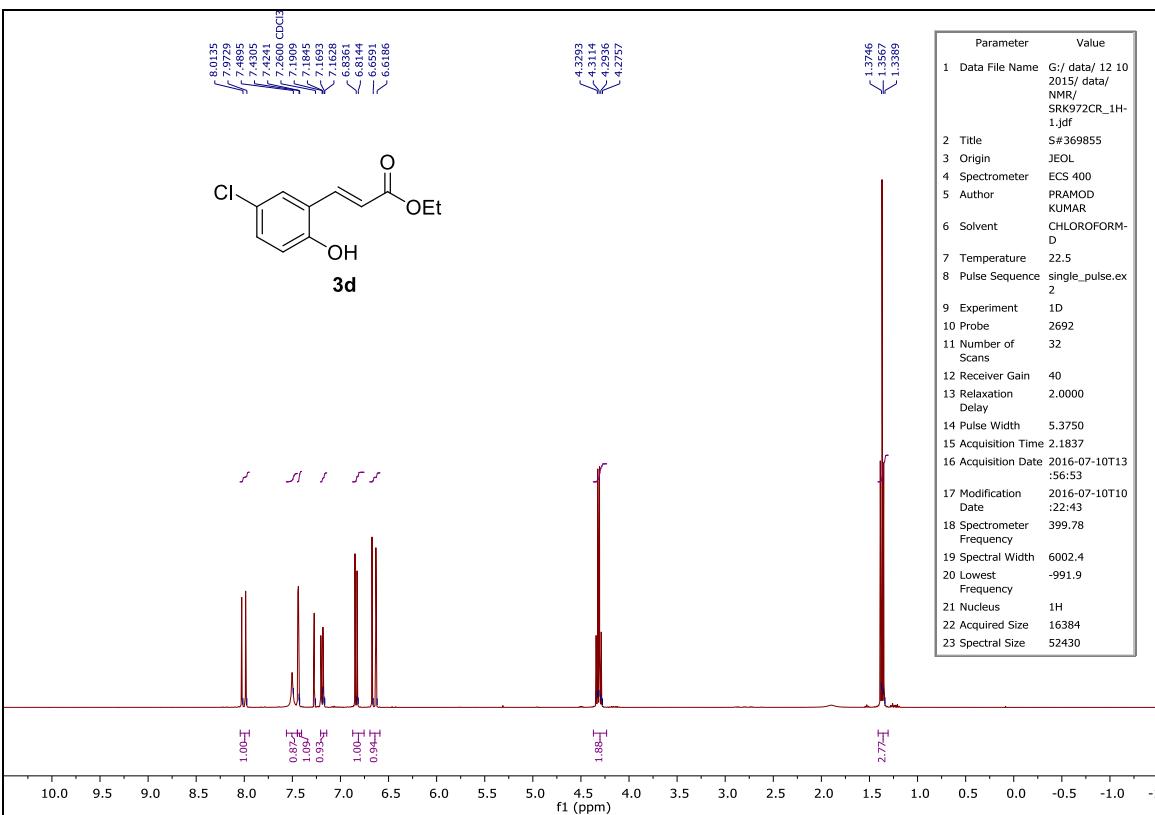
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (3a)



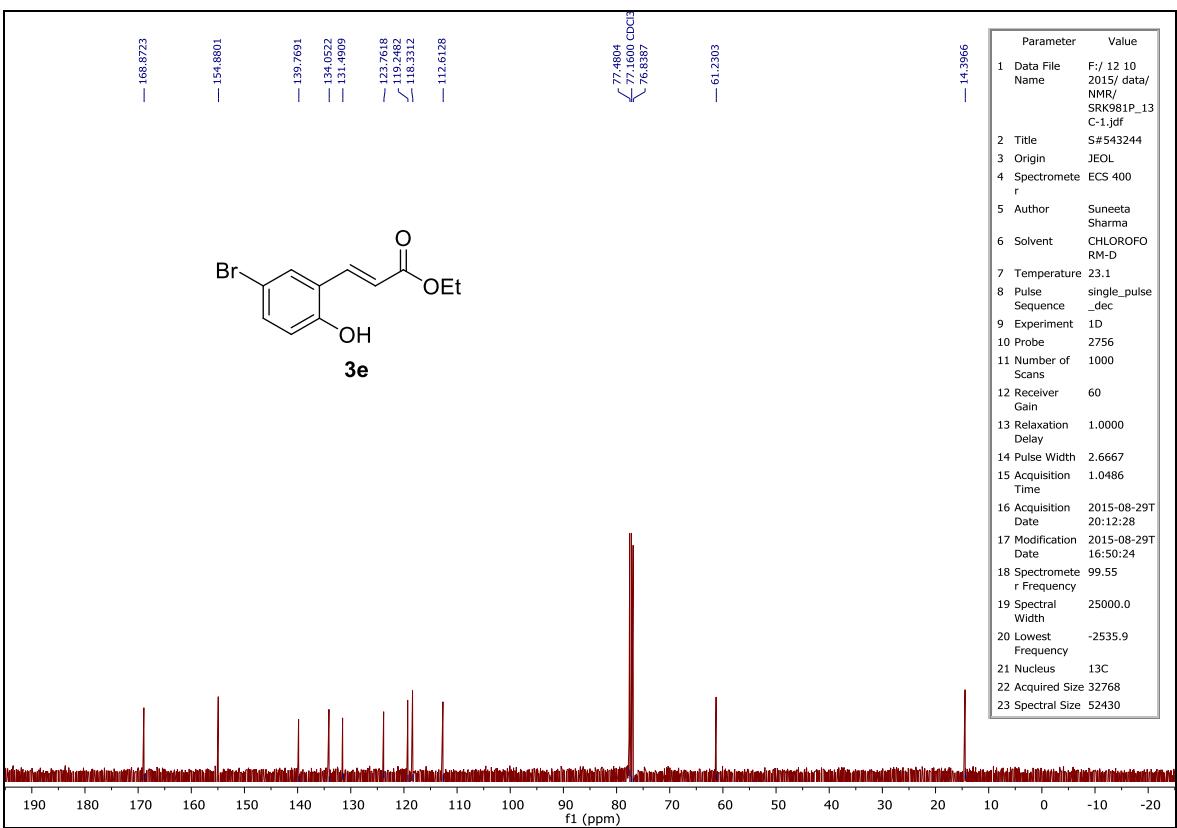
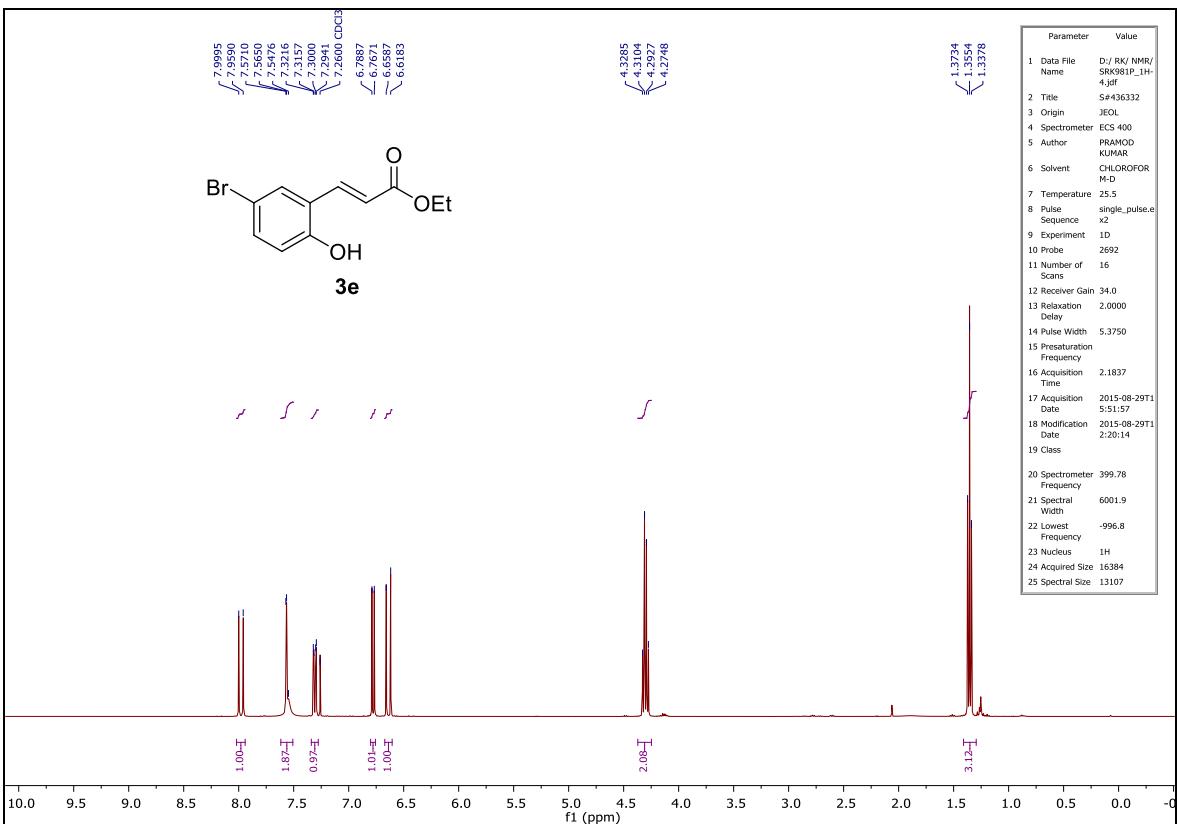
<sup>1</sup>H and <sup>13</sup>C NMR spectra of (E)-ethyl 3-(2-hydroxy-5-methylphenyl)acrylate (**3b**)



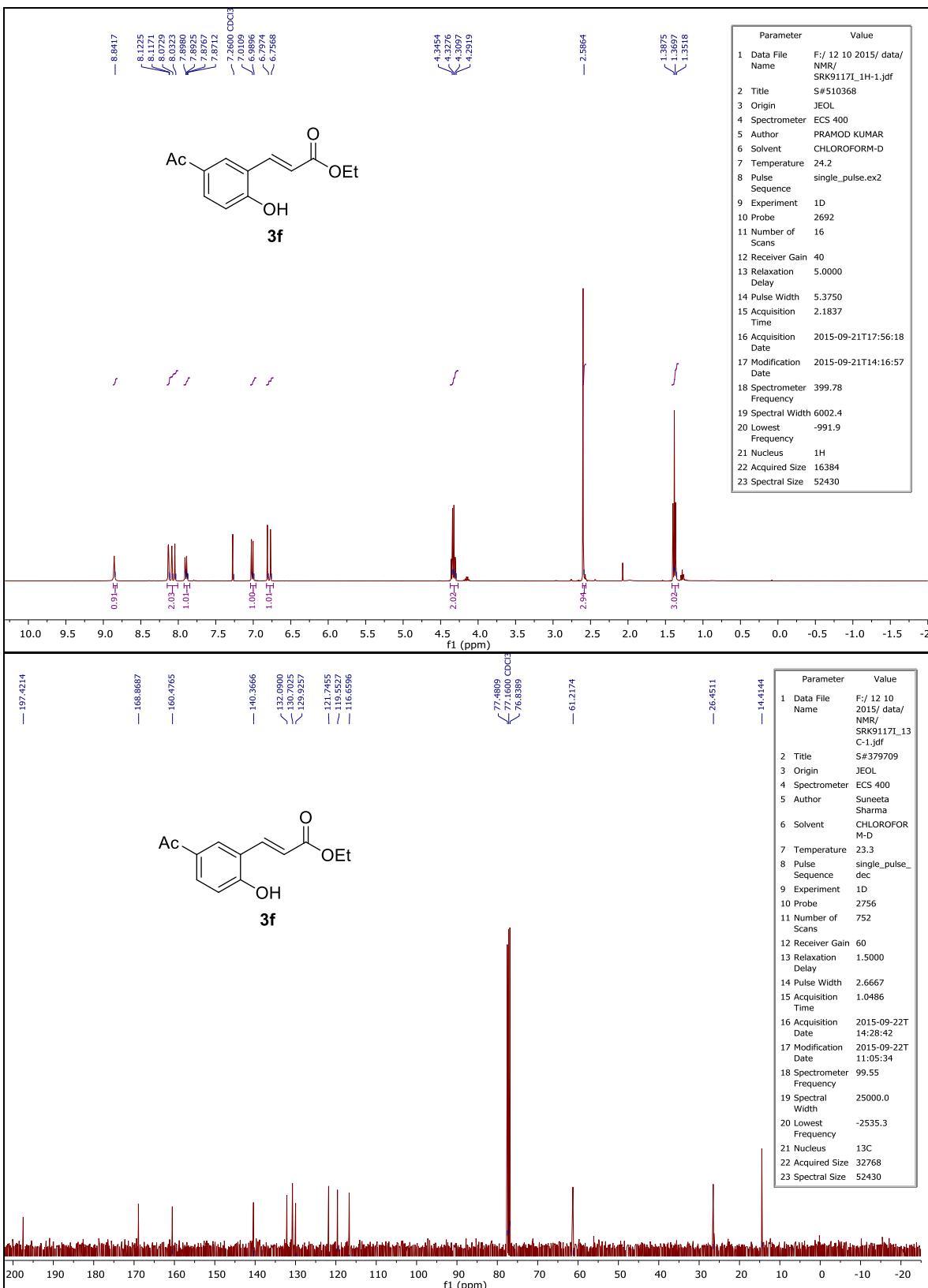
<sup>1</sup>H and <sup>13</sup>C NMR spectra of (E)-ethyl 3-(5-fluoro-2-hydroxyphenyl)acrylate (**3c**)



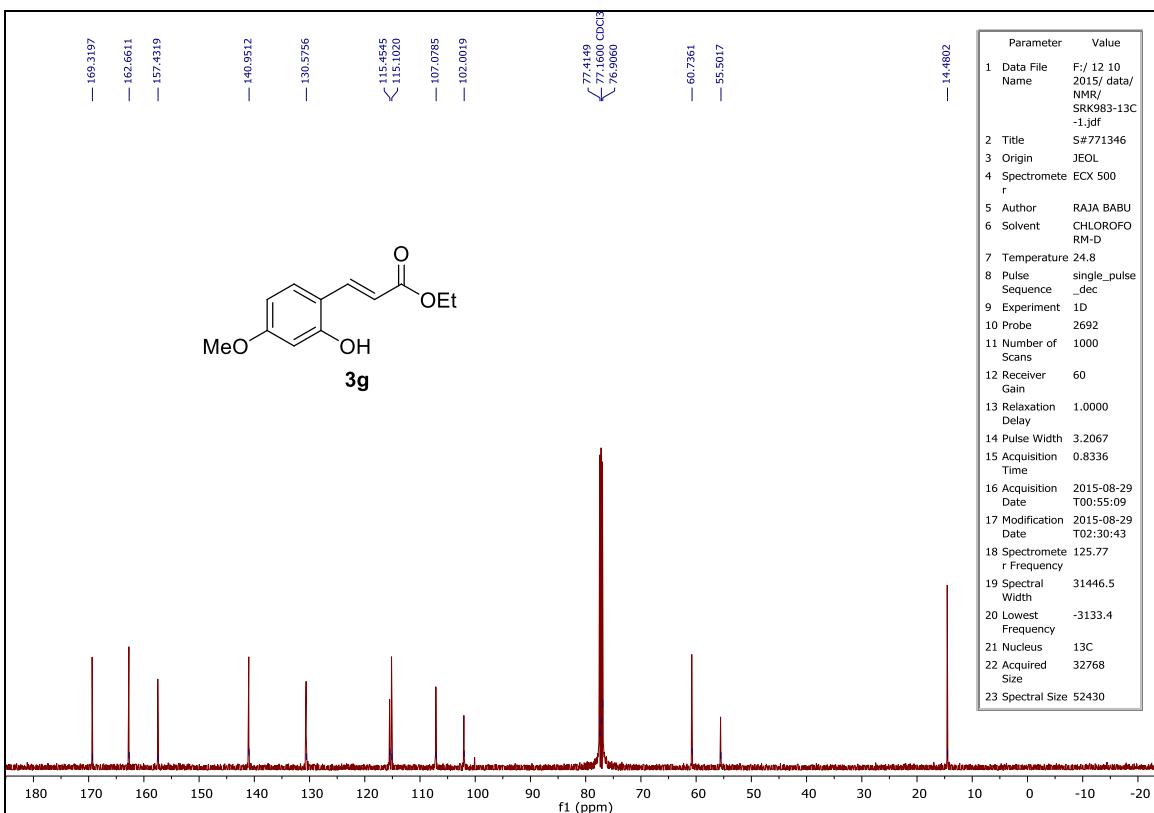
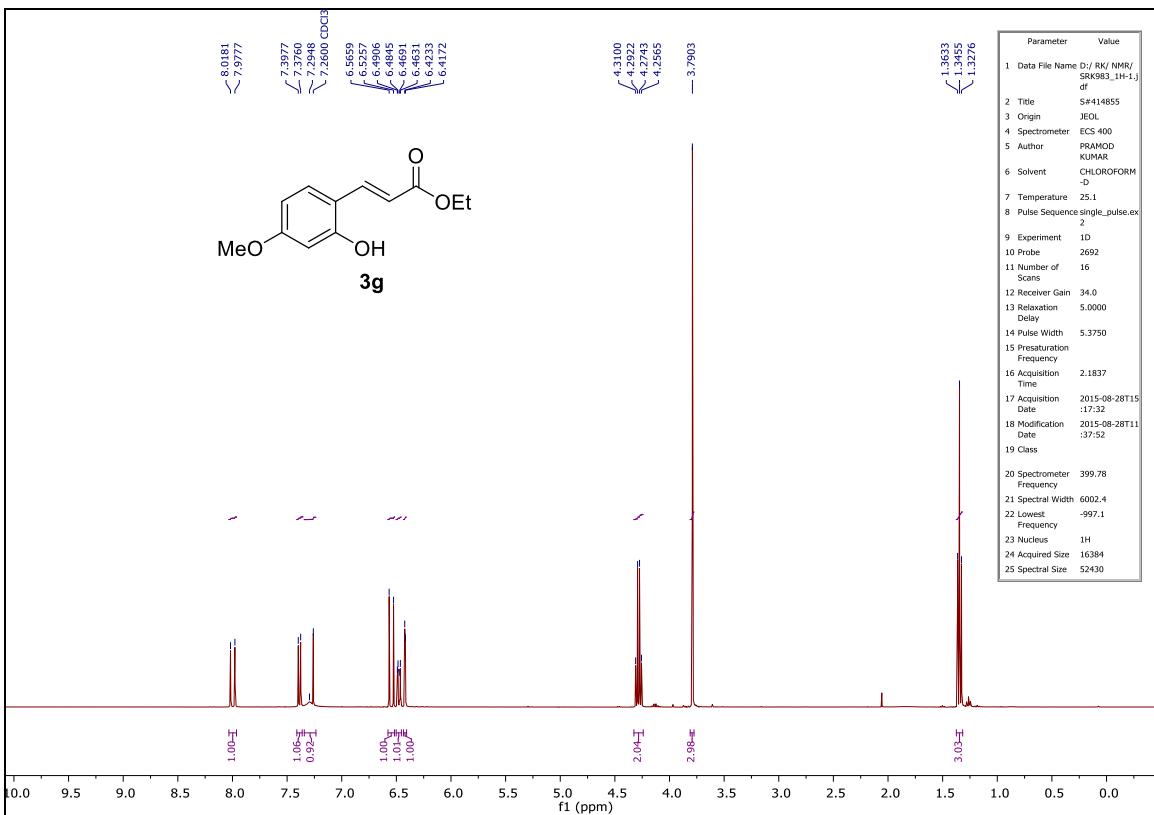
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(5-chloro-2-hydroxyphenyl)acrylate (**3d**)



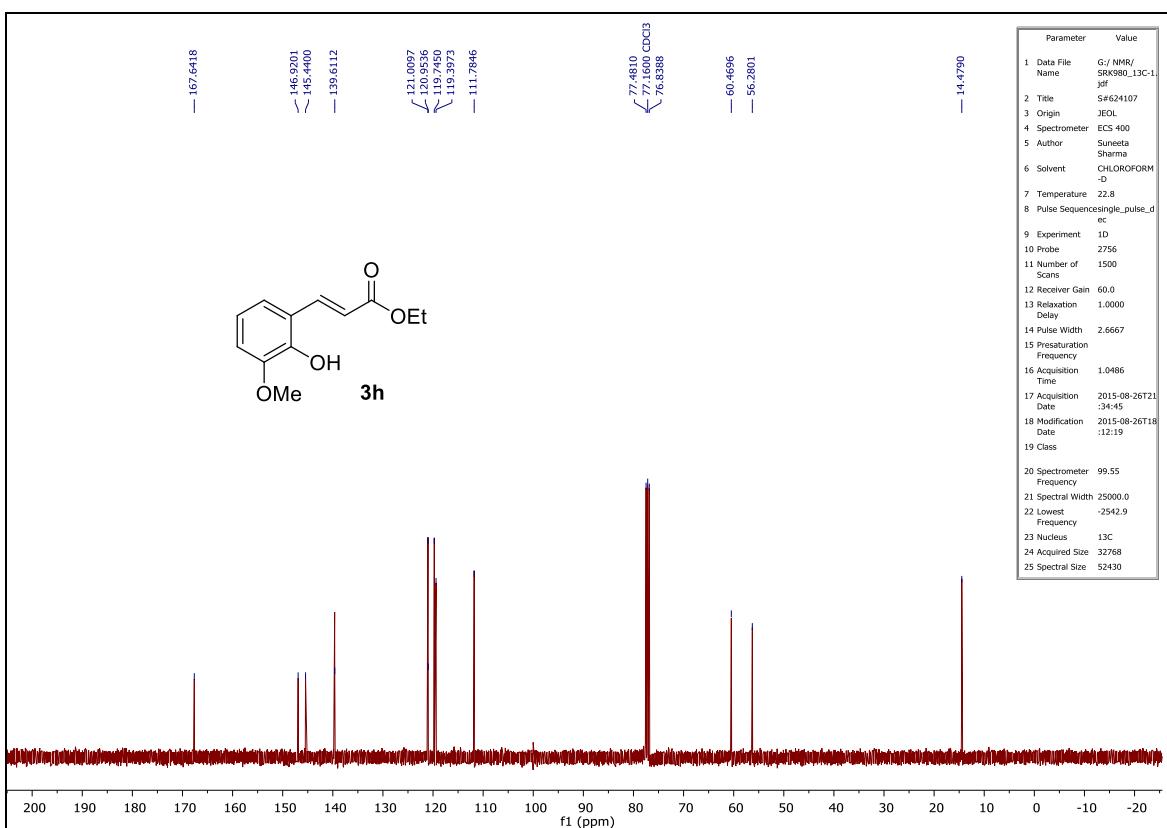
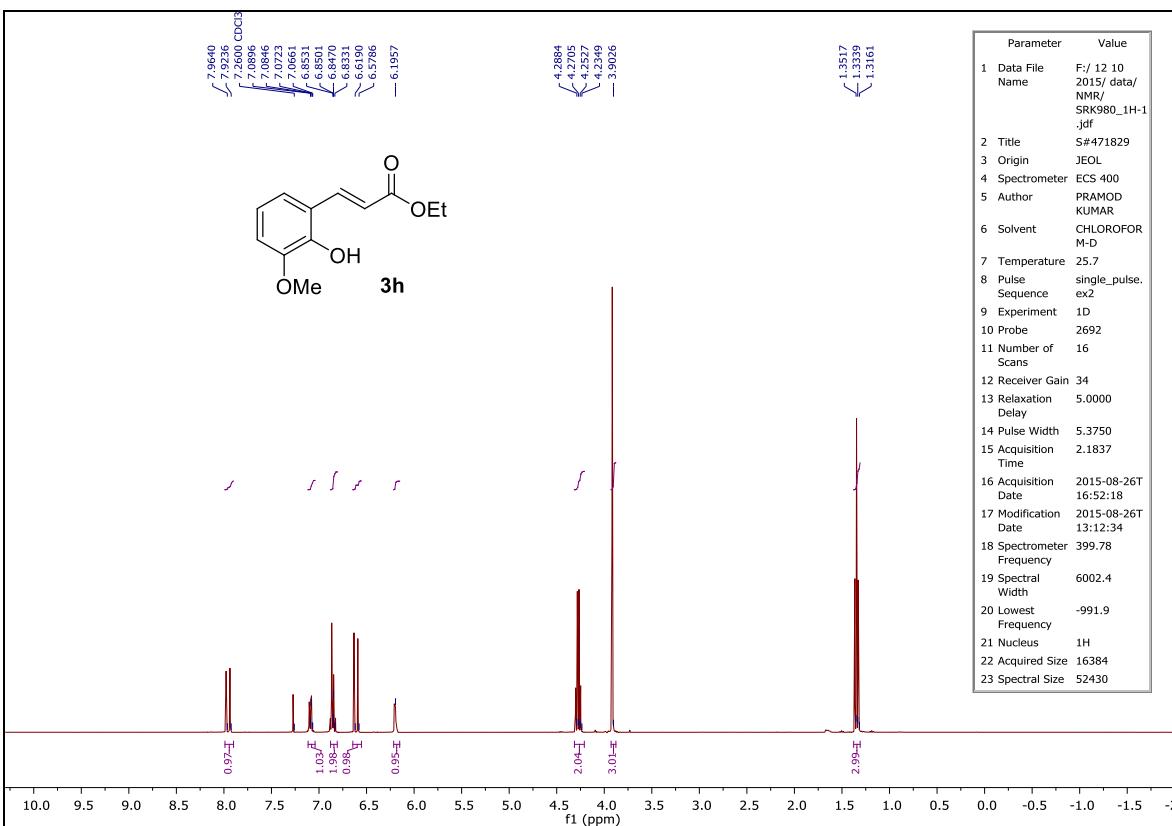
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(5-bromo-2-hydroxyphenyl)acrylate (**3e**)



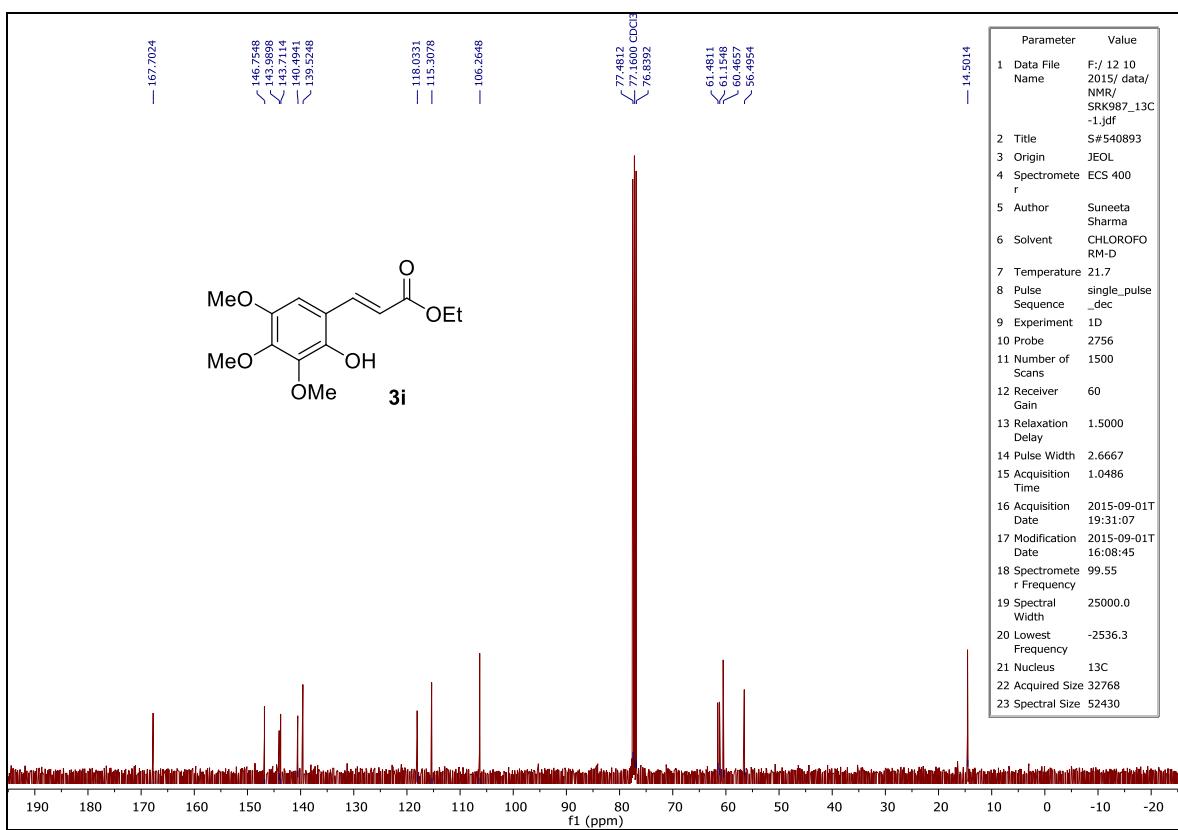
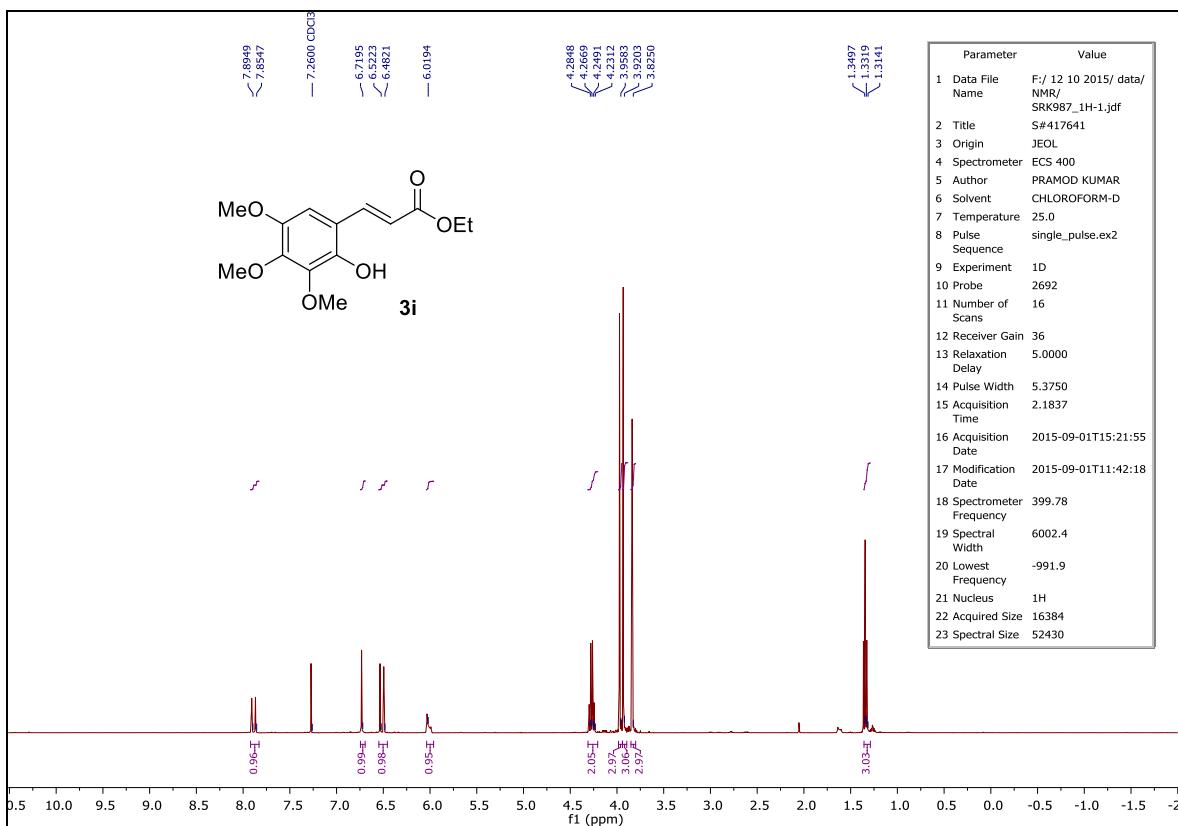
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(5-acetyl-2-hydroxyphenyl)acrylate (**3f**)



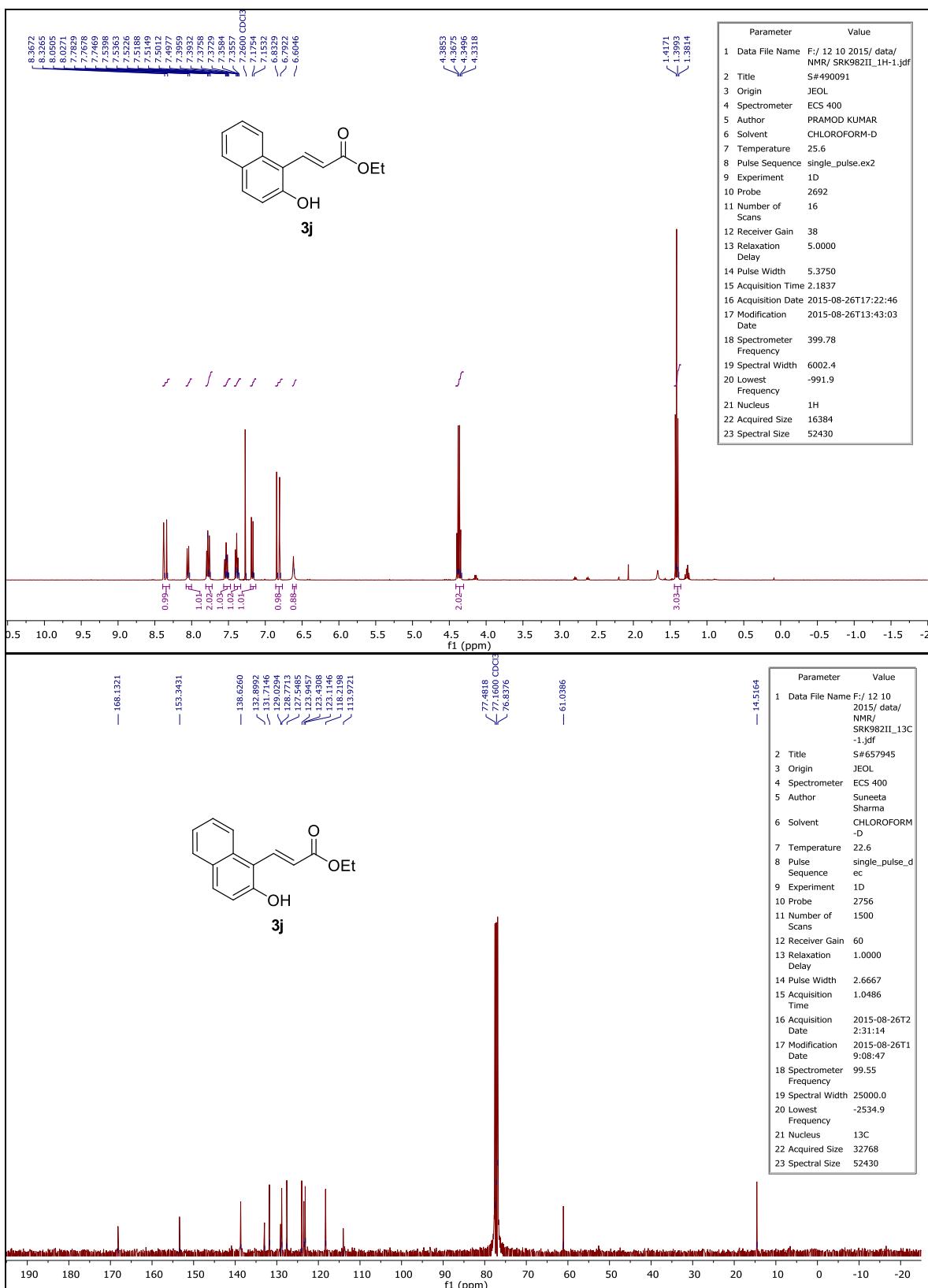
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(2-hydroxy-4-methoxyphenyl)acrylate (**3g**)



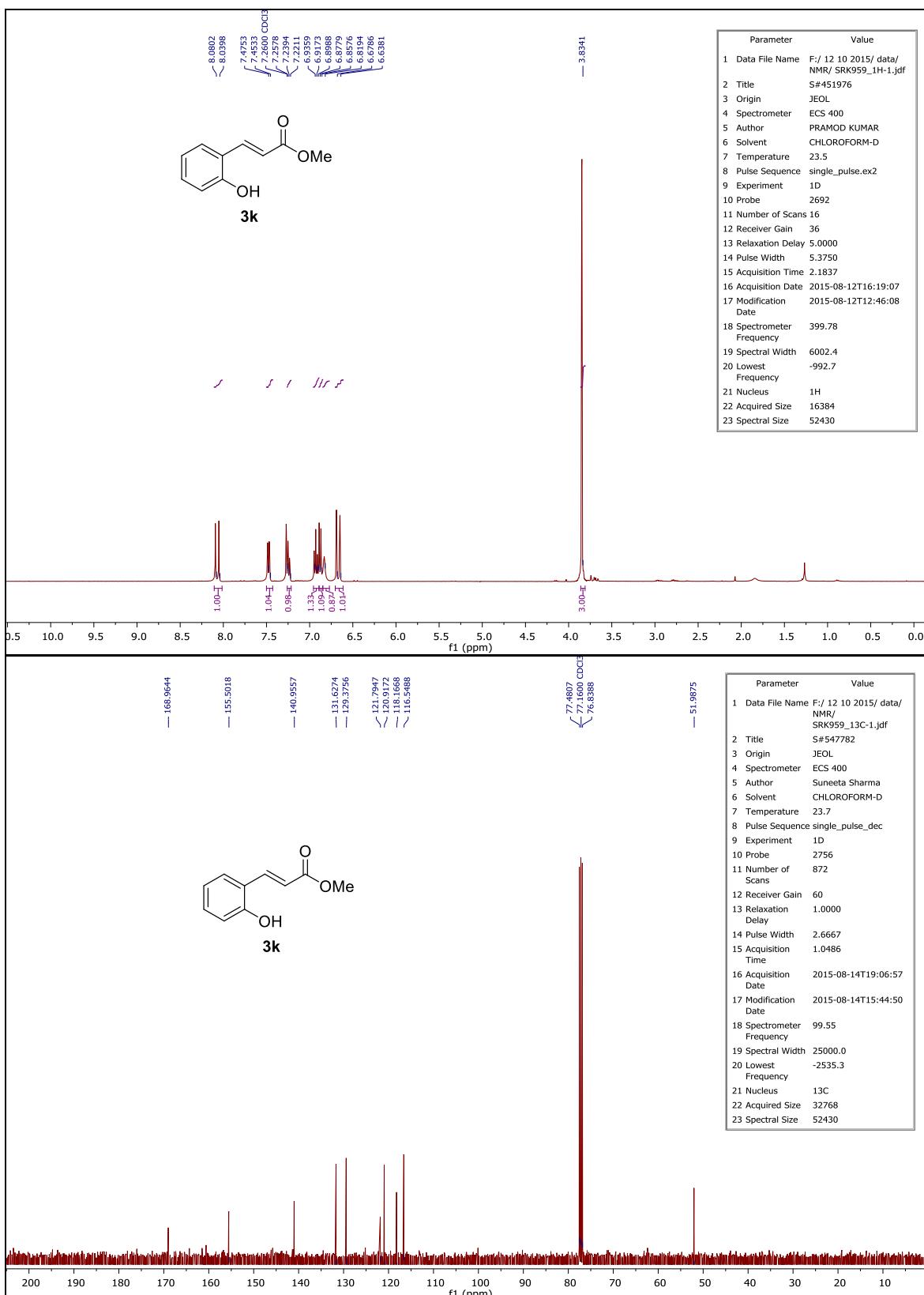
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(2-hydroxy-3-methoxyphenyl)acrylate (**3h**)



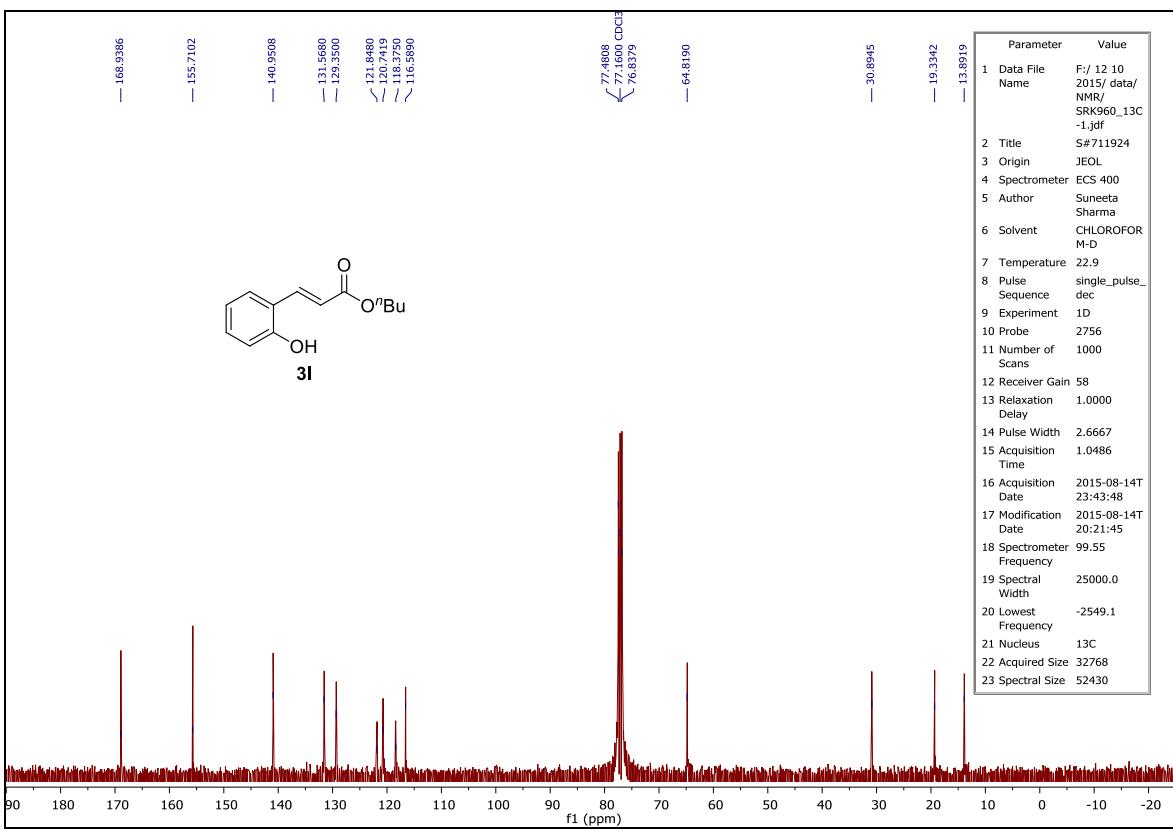
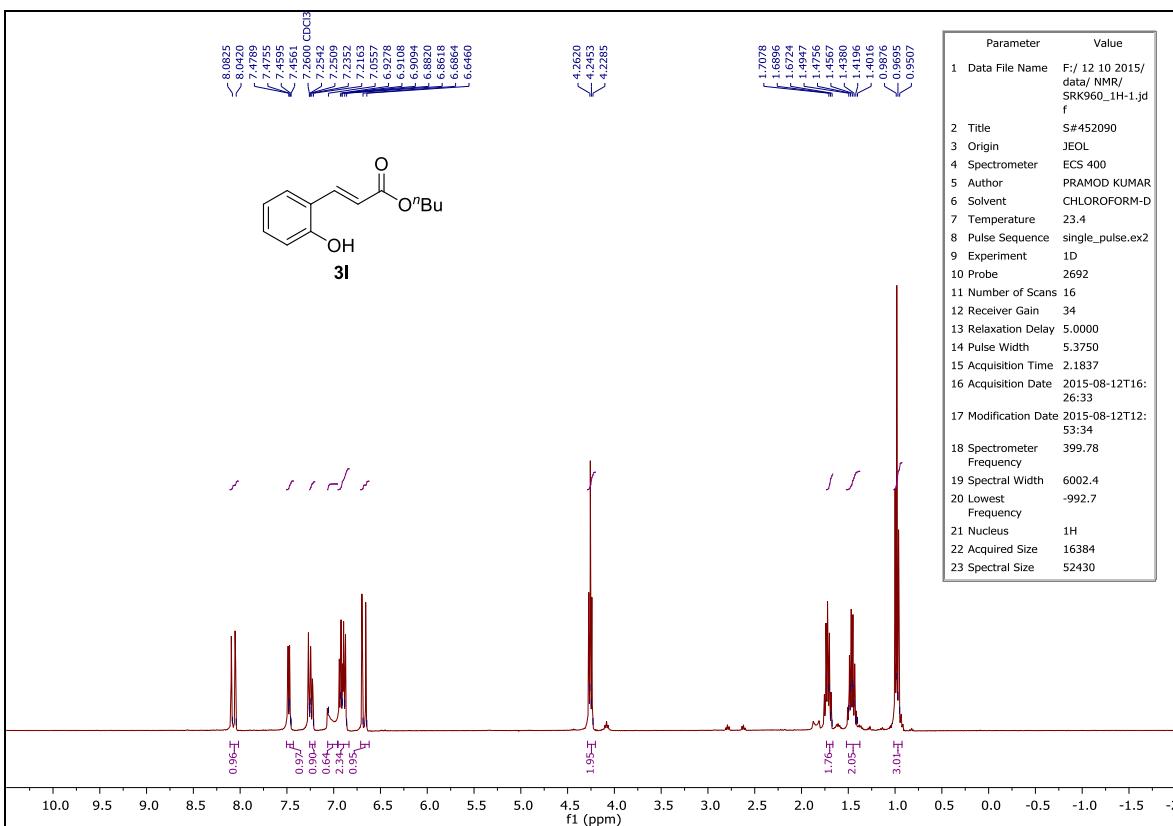
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(2-hydroxy-3,4,5-trimethoxyphenyl)acrylate (**3i**)



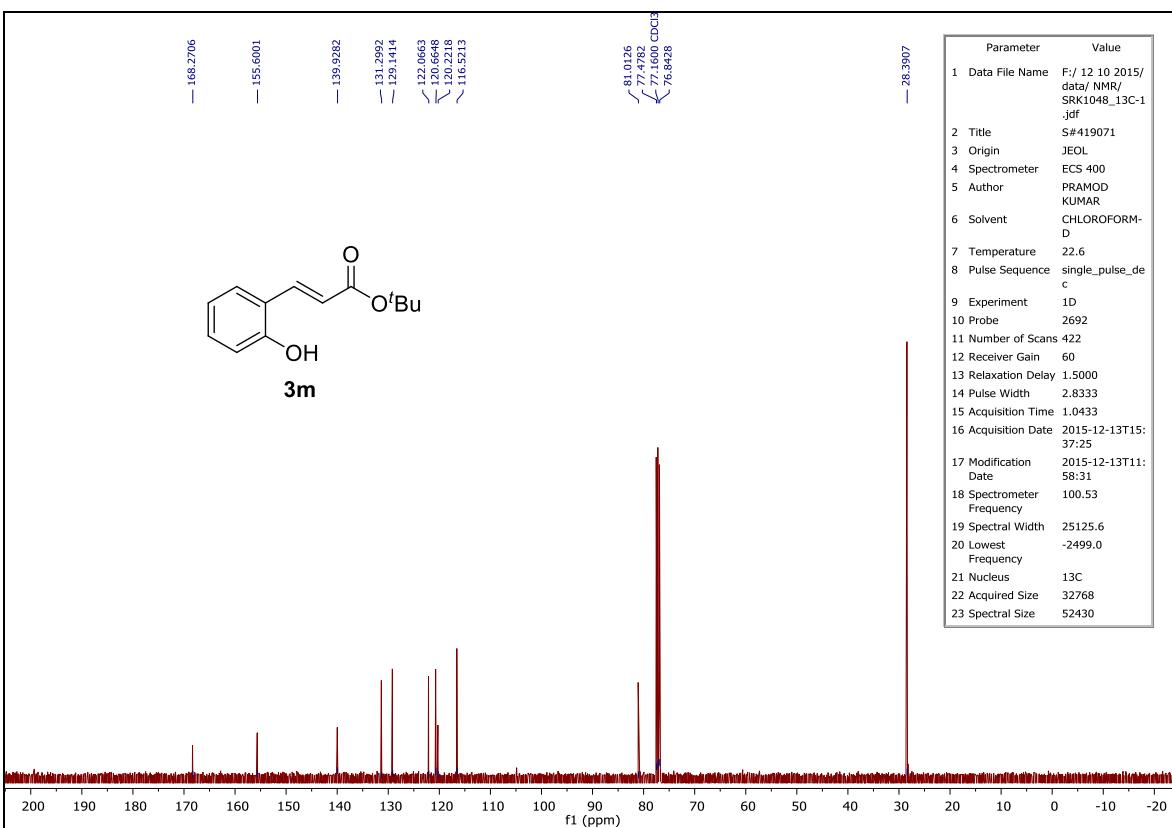
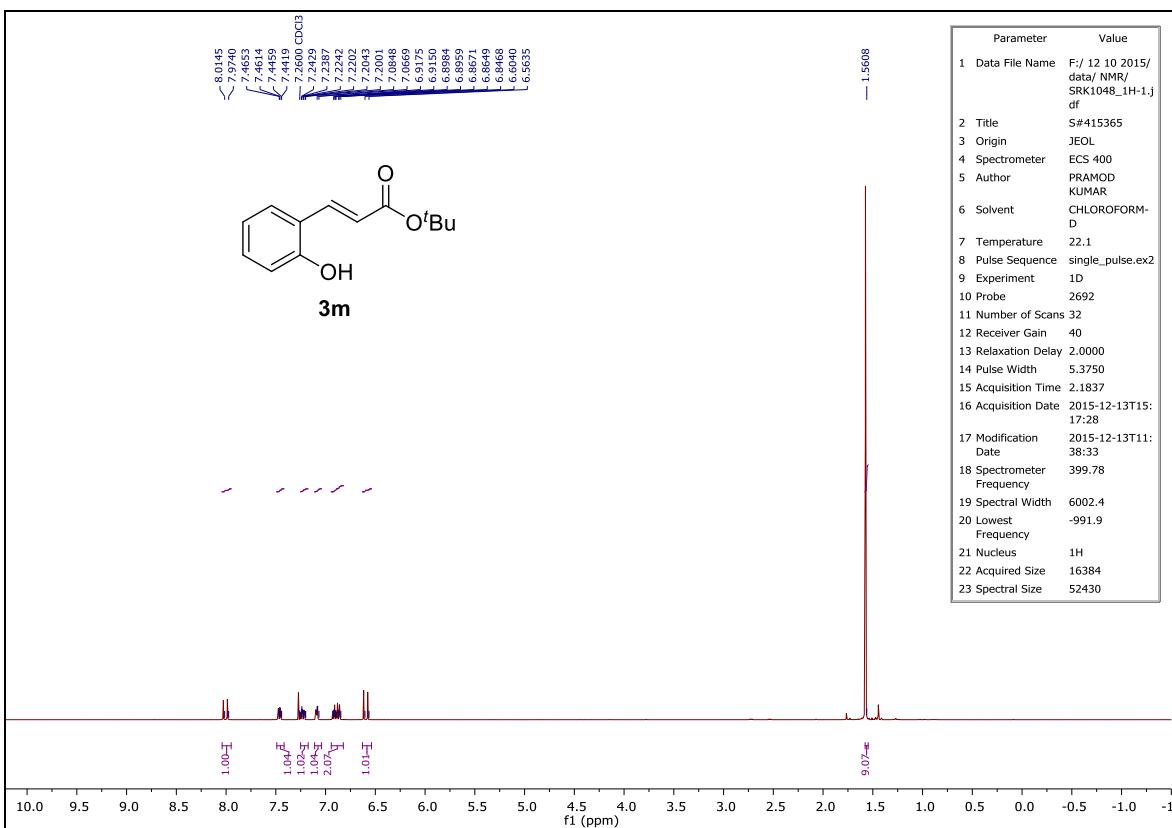
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(2-hydroxynaphthalen-1-yl)acrylate (3j)



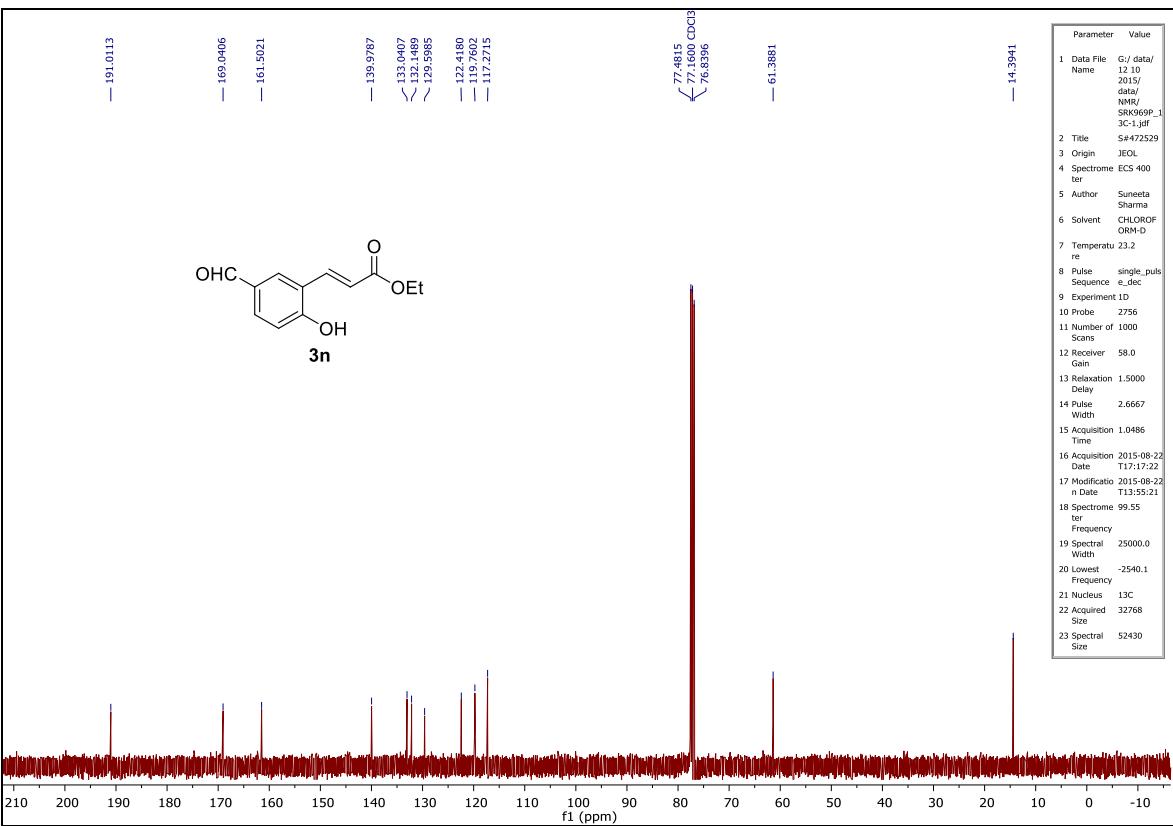
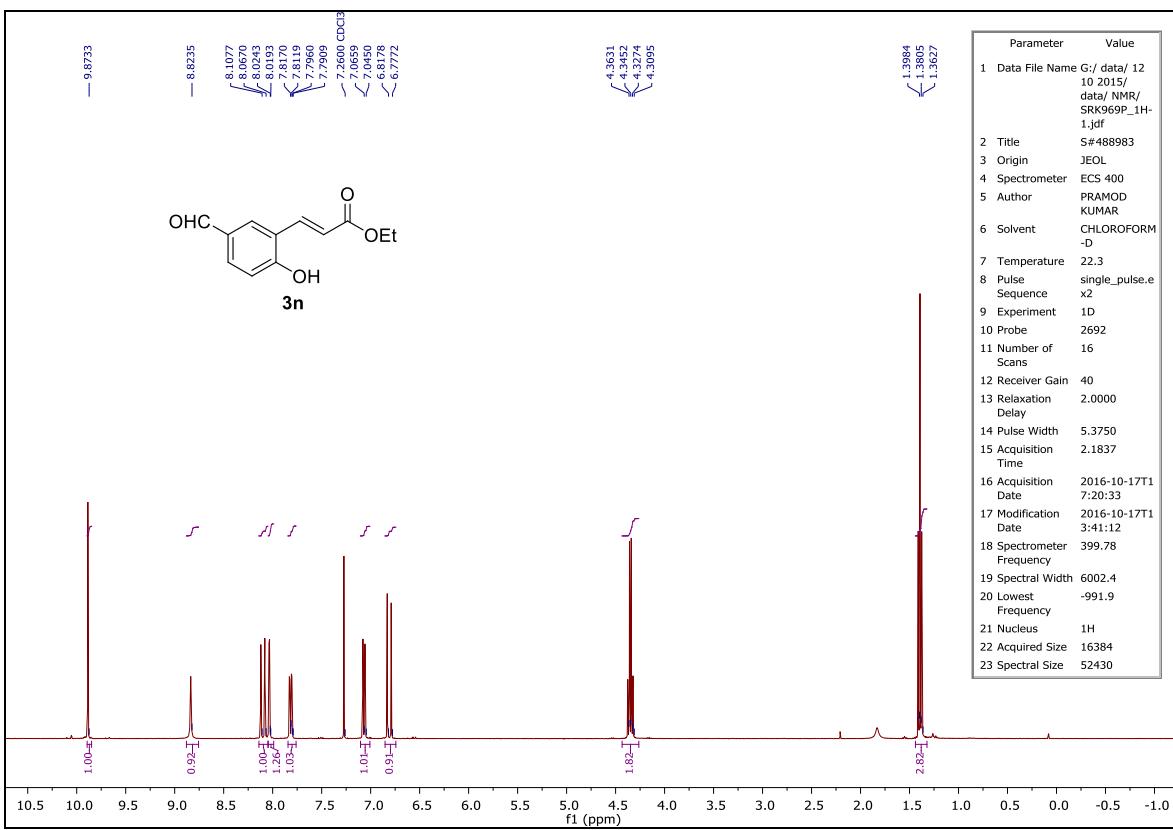
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-methyl 3-(2-hydroxyphenyl)acrylate (**3k**)



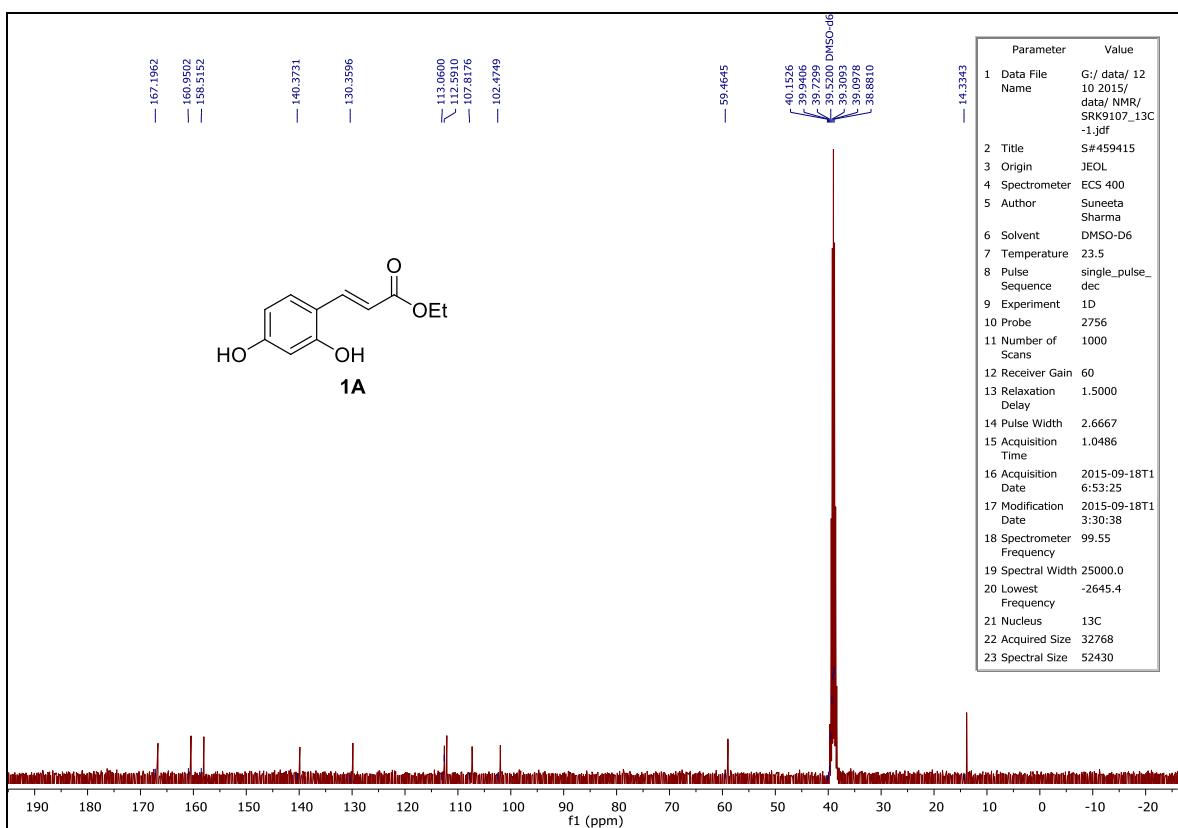
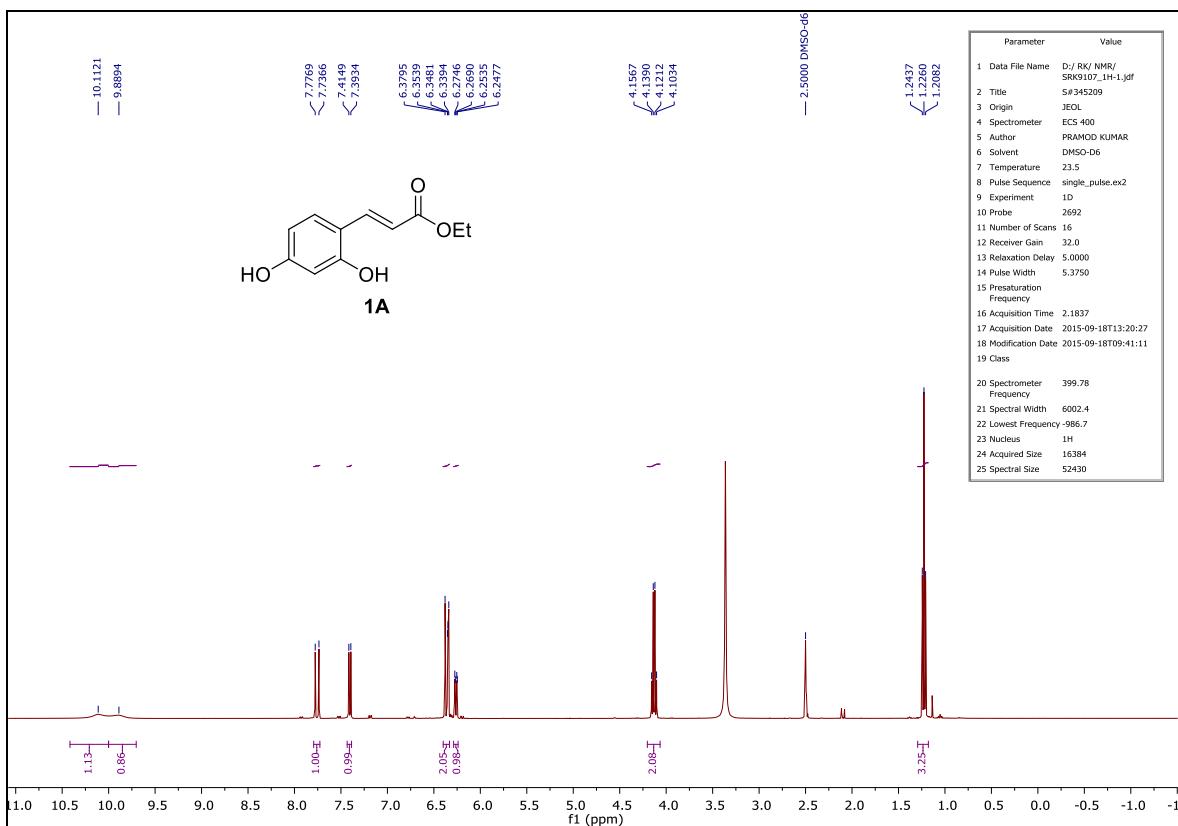
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-*n*-butyl 3-(2-hydroxyphenyl)acrylate (**3l**)



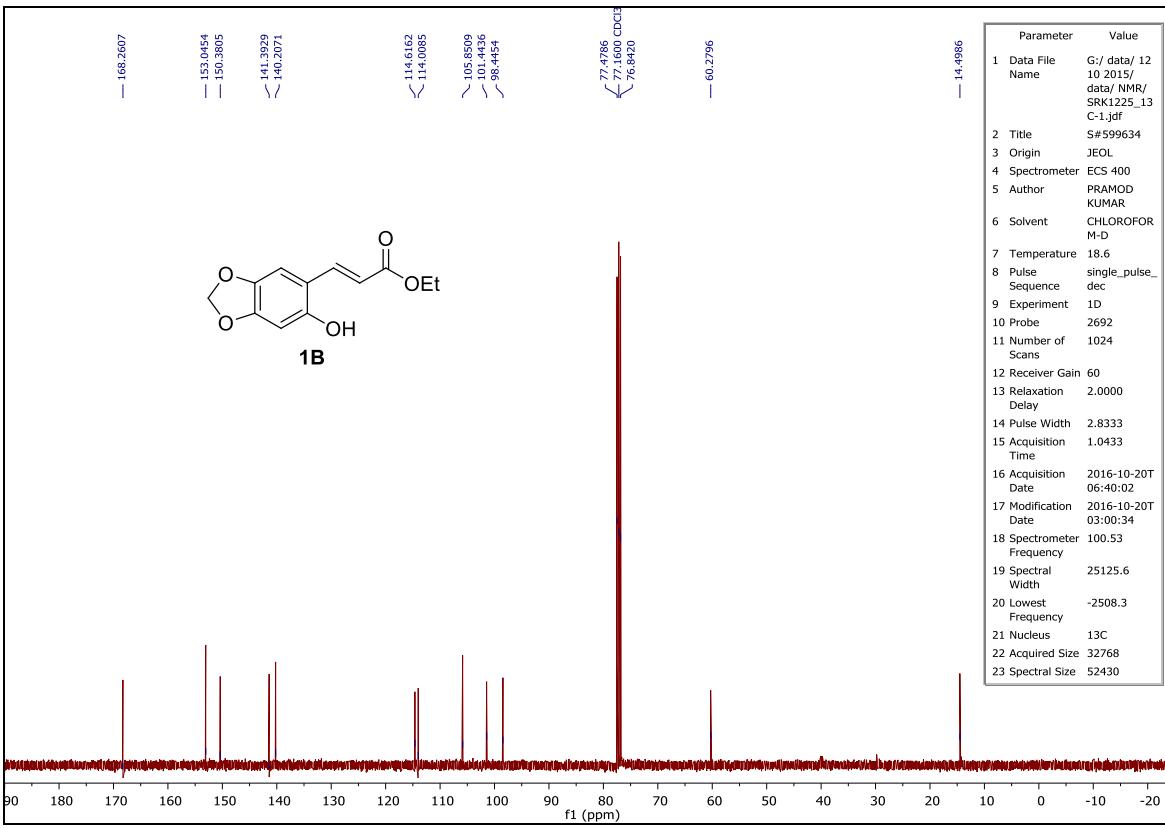
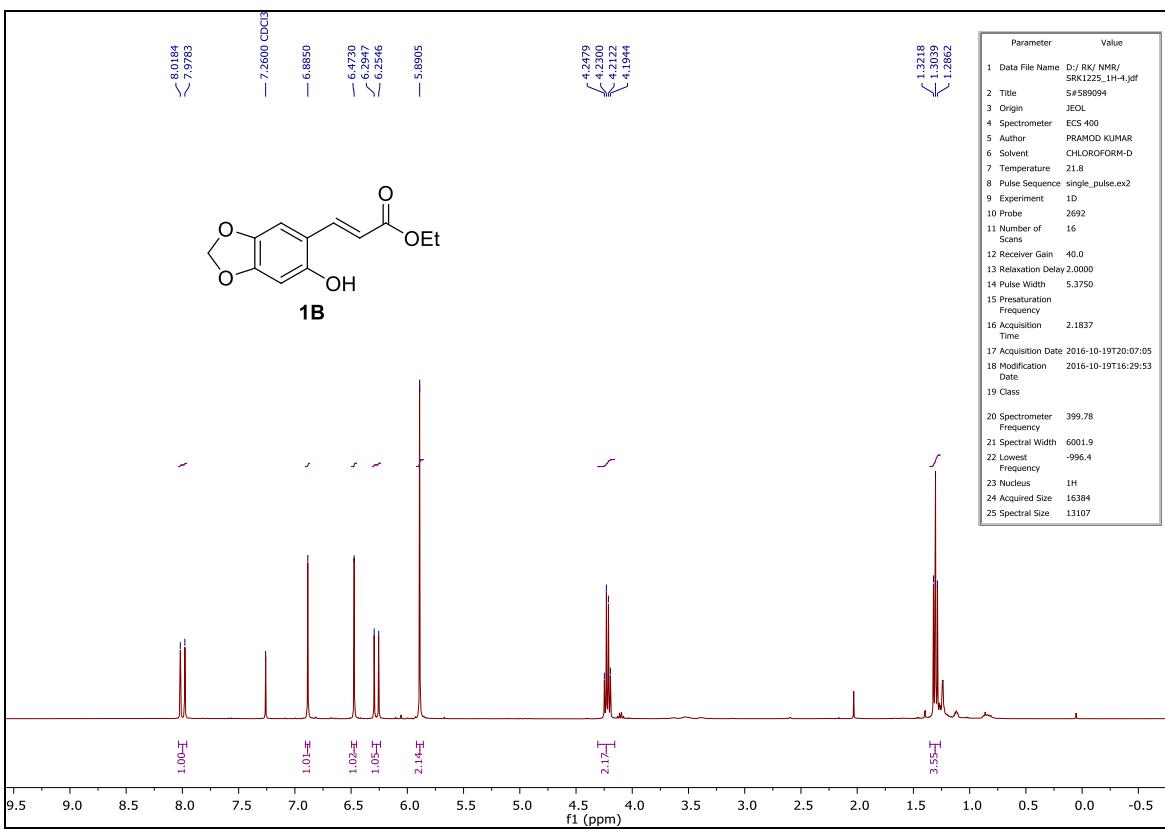
<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-*tert*-butyl 3-(2-hydroxyphenyl)acrylate (**3m**)



<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-ethyl 3-(5-formyl-2-hydroxyphenyl)acrylate (**3n**)

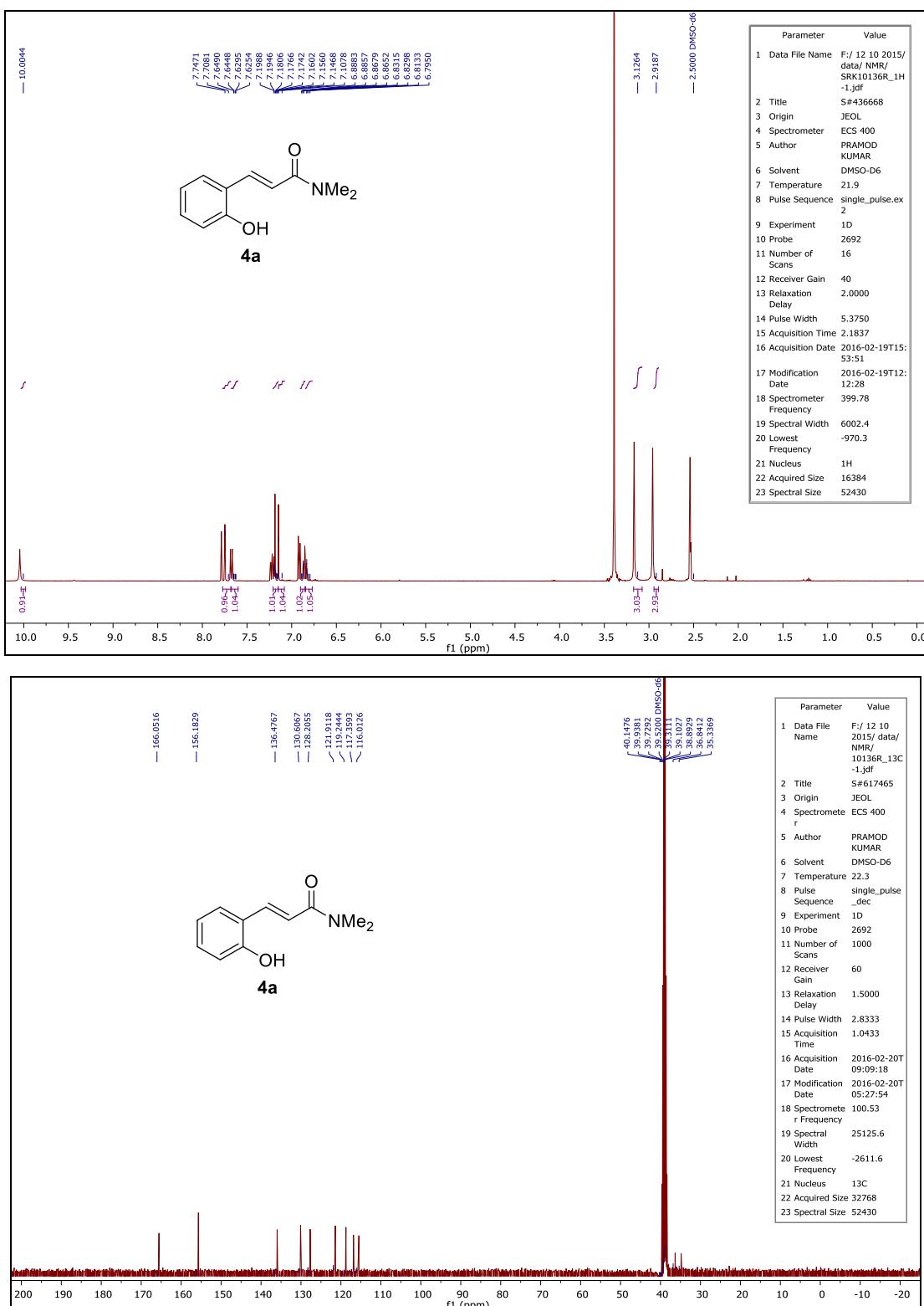


<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-ethyl 3-(2,4-dihydroxyphenyl)acrylate (**1A**)

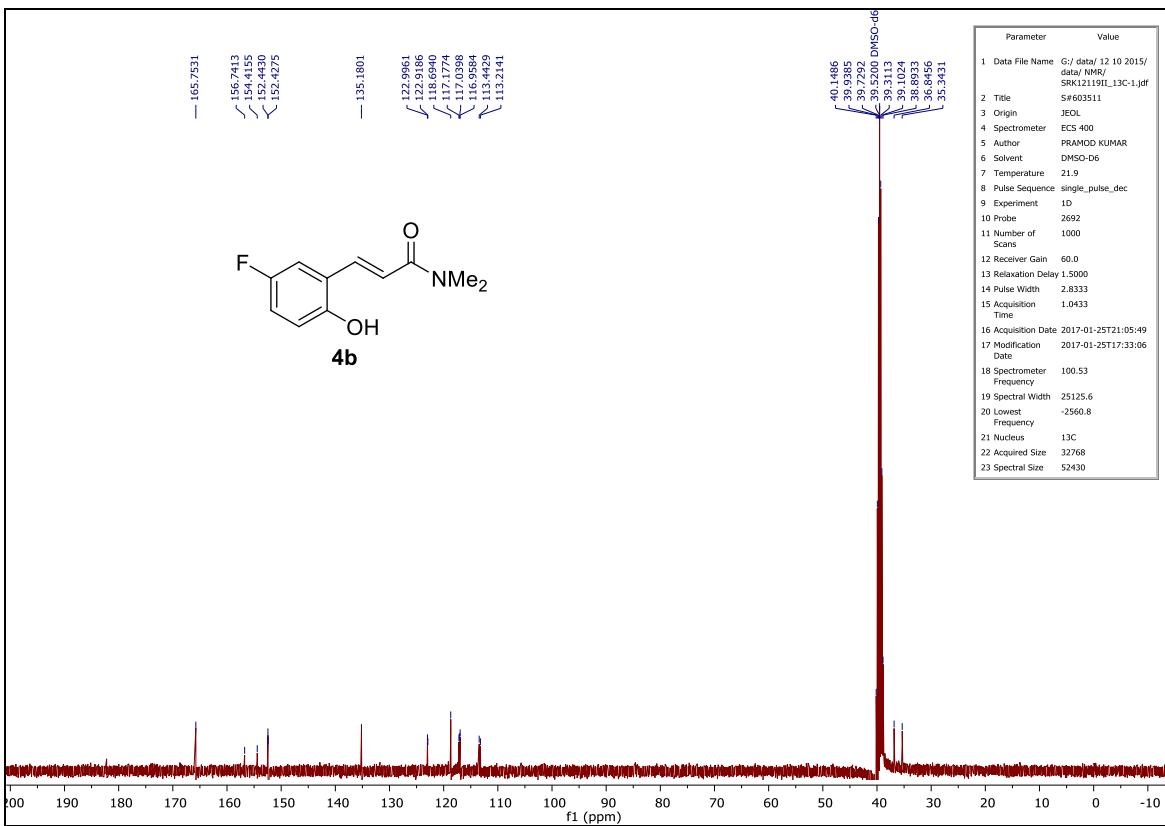
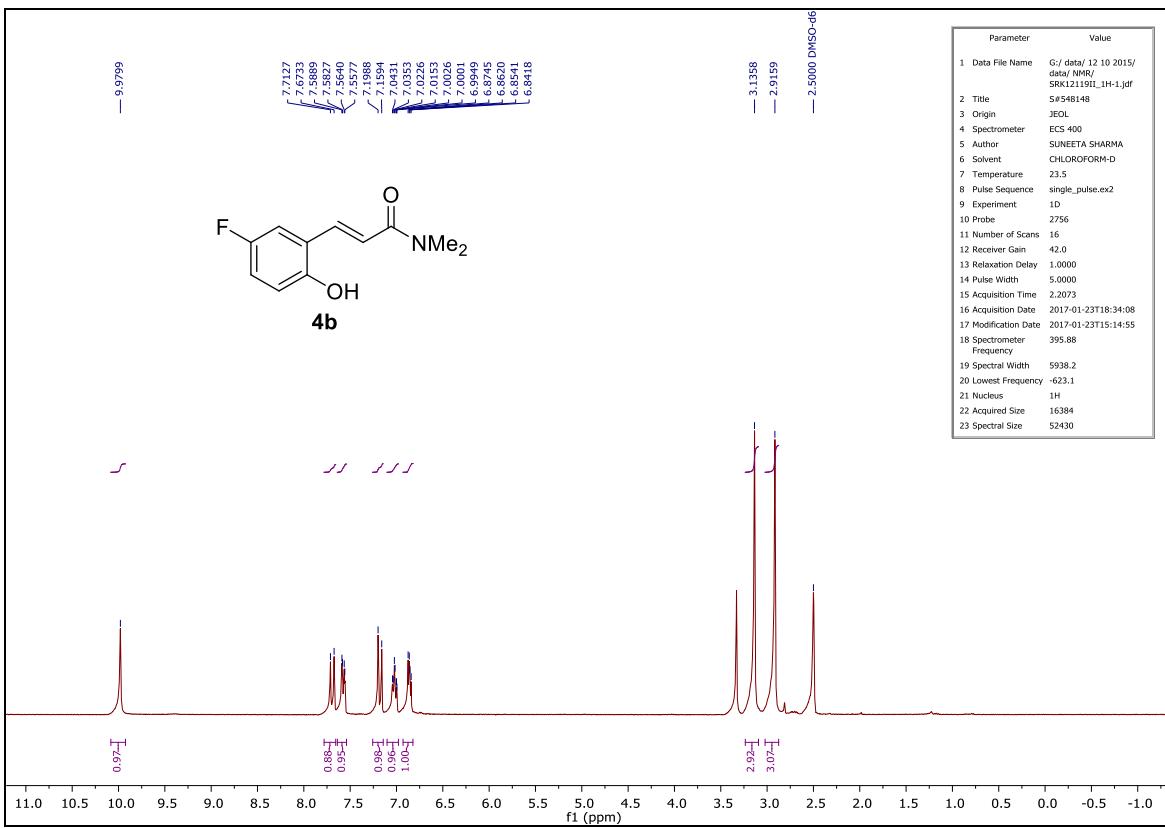


<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-ethyl 3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)acrylate (**1B**)

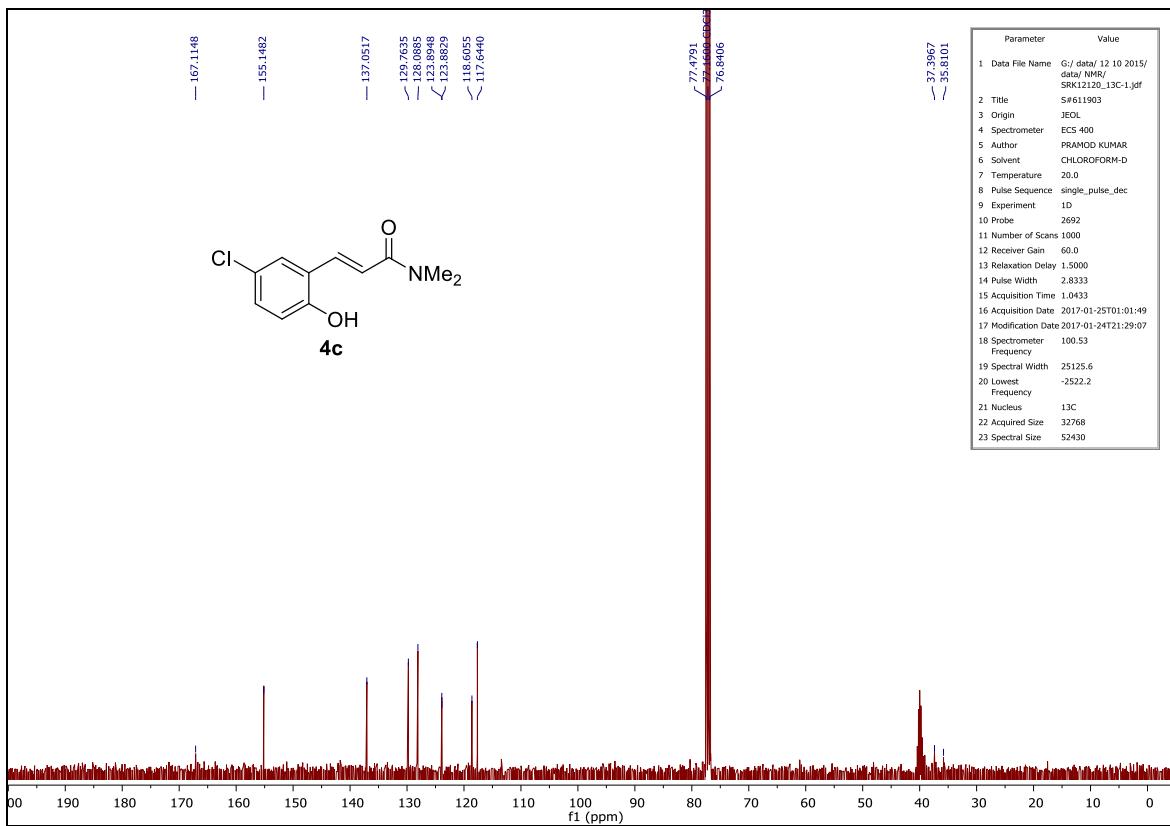
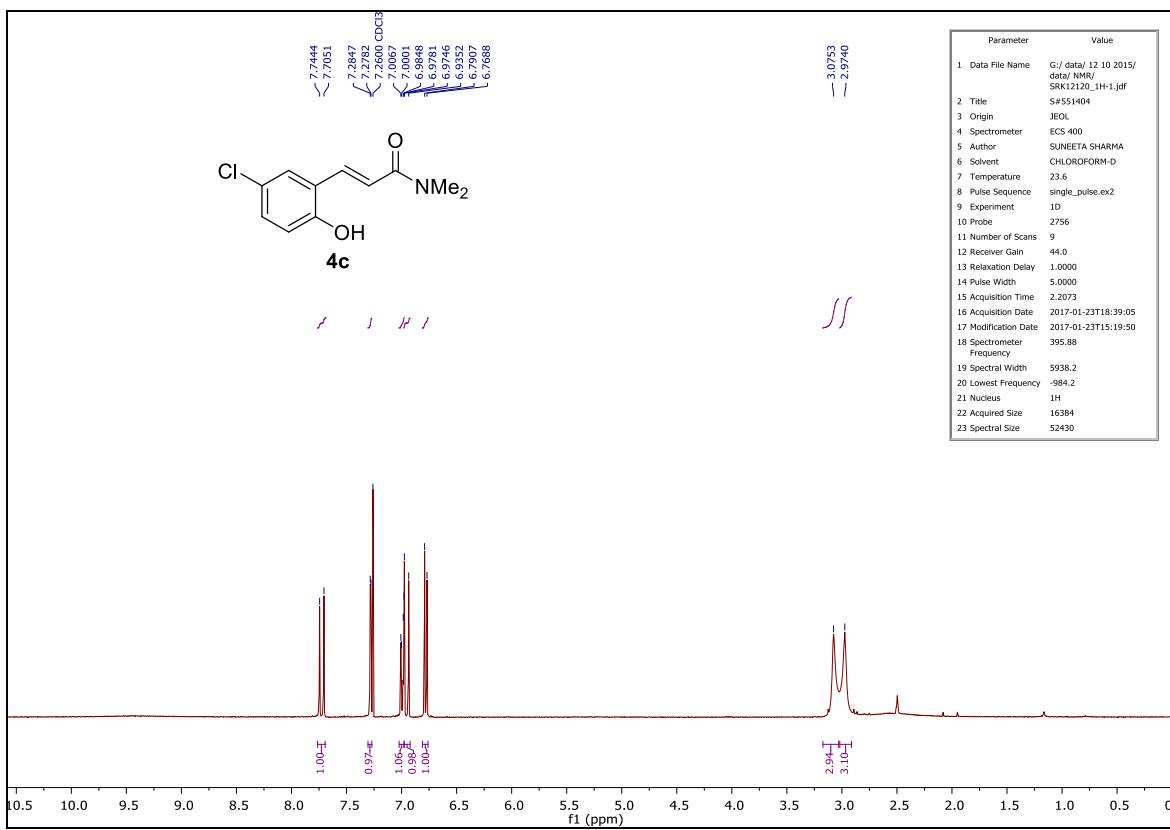
## 2. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products (4a-4d)



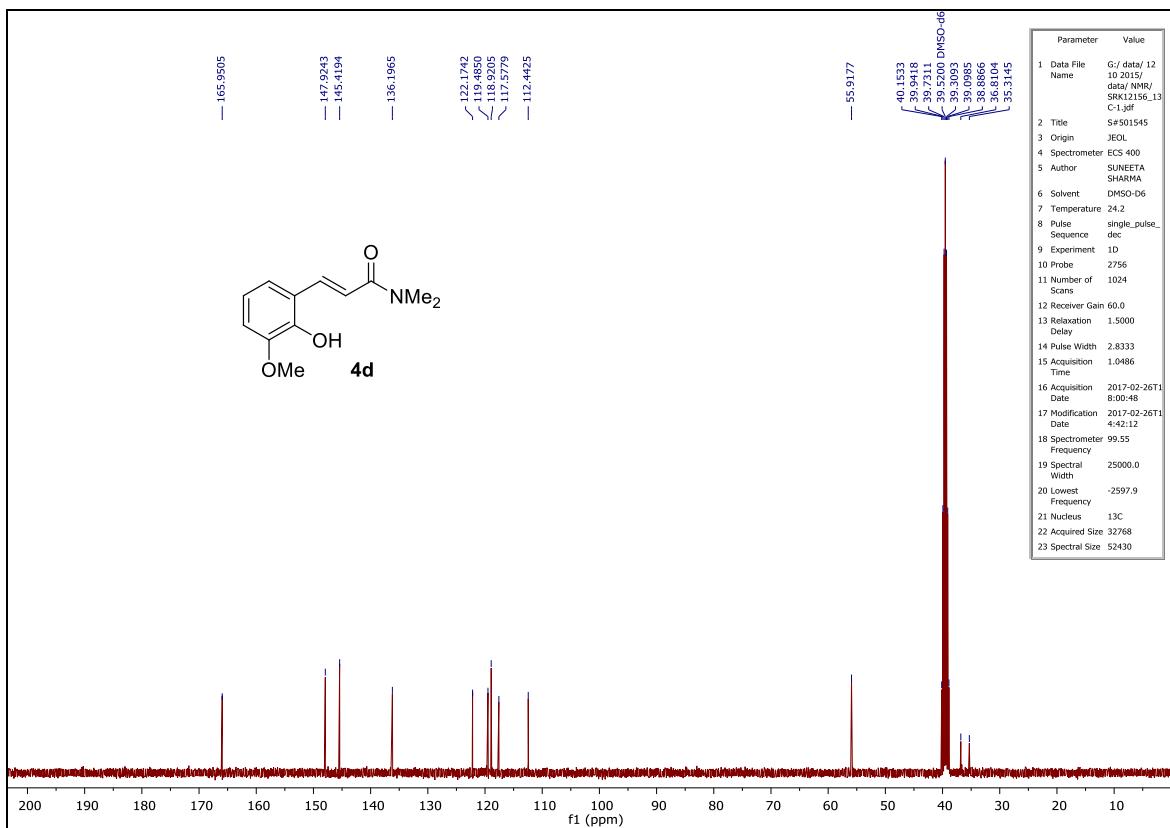
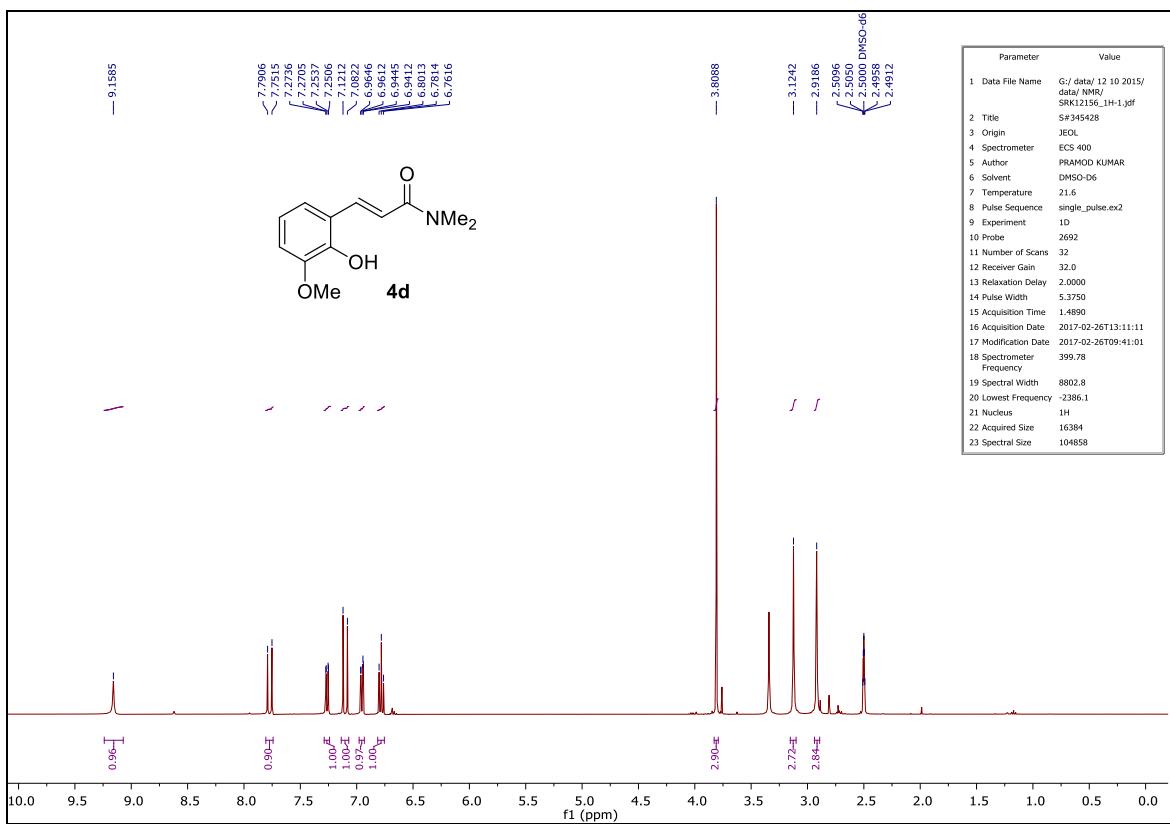
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of (*E*)-3-(2-hydroxyphenyl)-*N,N*-dimethylacrylamide (**4a**)



<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-3-(5-fluoro-2-hydroxyphenyl)-*N,N*-dimethylacrylamide (**4b**)

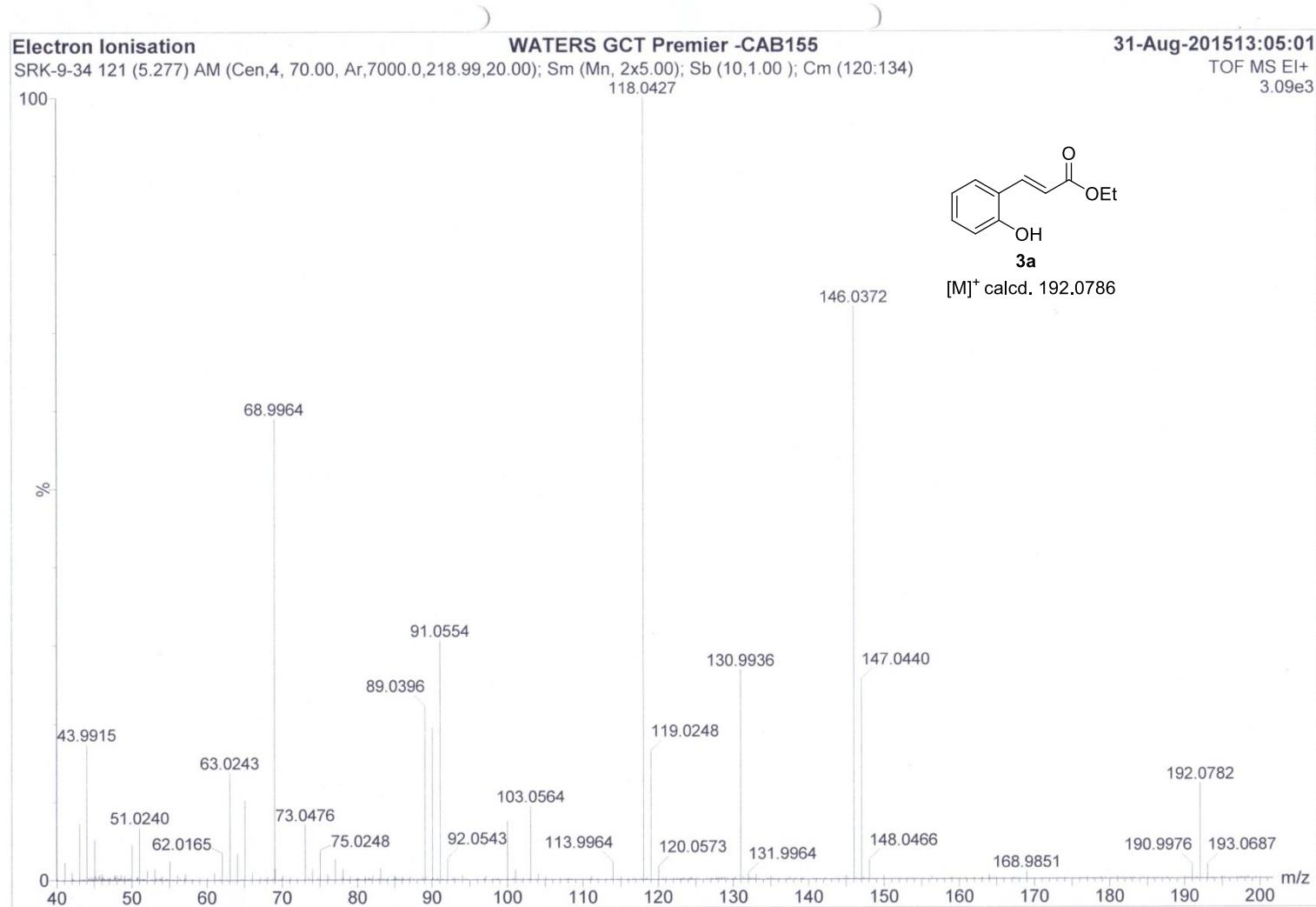


<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (*E*)-3-(5-chloro-2-hydroxyphenyl)-*N,N*-dimethylacrylamide (**4c**)



<sup>1</sup>H and <sup>13</sup>C NMR spectrum of (E)-3-(2-hydroxy-3-methoxyphenyl)-N,N-dimethylacrylamide (**4d**)

### 3. Copies of HRMS spectra of products (3a-3n, 1A, 1B and 4a-4d)



EI(HRMS) spectrum of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (**3a**)

Electron Ionisation

WATERS GCT Premier -CAB155

14-Oct-2015 15:08:33

SRK\_9-71+ 435 (11.035) AM (Cen,4, 50.00, Ar,7000.0,218.99,20.00); Sm (Mn, 2x5.00); Sb (10,1.00 ); Cm (434:468)

68.9947

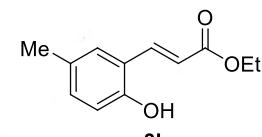
TOF MS El+  
1.36e4

100

8%

0

40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 m/z



$[M]^+$  calcd. 206.0943

131.0040

132.0563

160.0524

161.0584

$[M]^+$

206.0941

207.0388

208.0383

43.9896

51.0227

63.0221

77.0388

78.0455

79.0528

91.0537

99.9930

105.0694

110.0542

115.0542

118.9904

121.0623

131.0040

132.0563

133.0604

134.0679

149.9869

160.0524

161.0584

162.0606

175.9979

190.9967

EI(HRMS) spectrum of (*E*)-ethyl 3-(2-hydroxy-5-methylphenyl)acrylate (**3b**)

Electrospray ionisation -MS

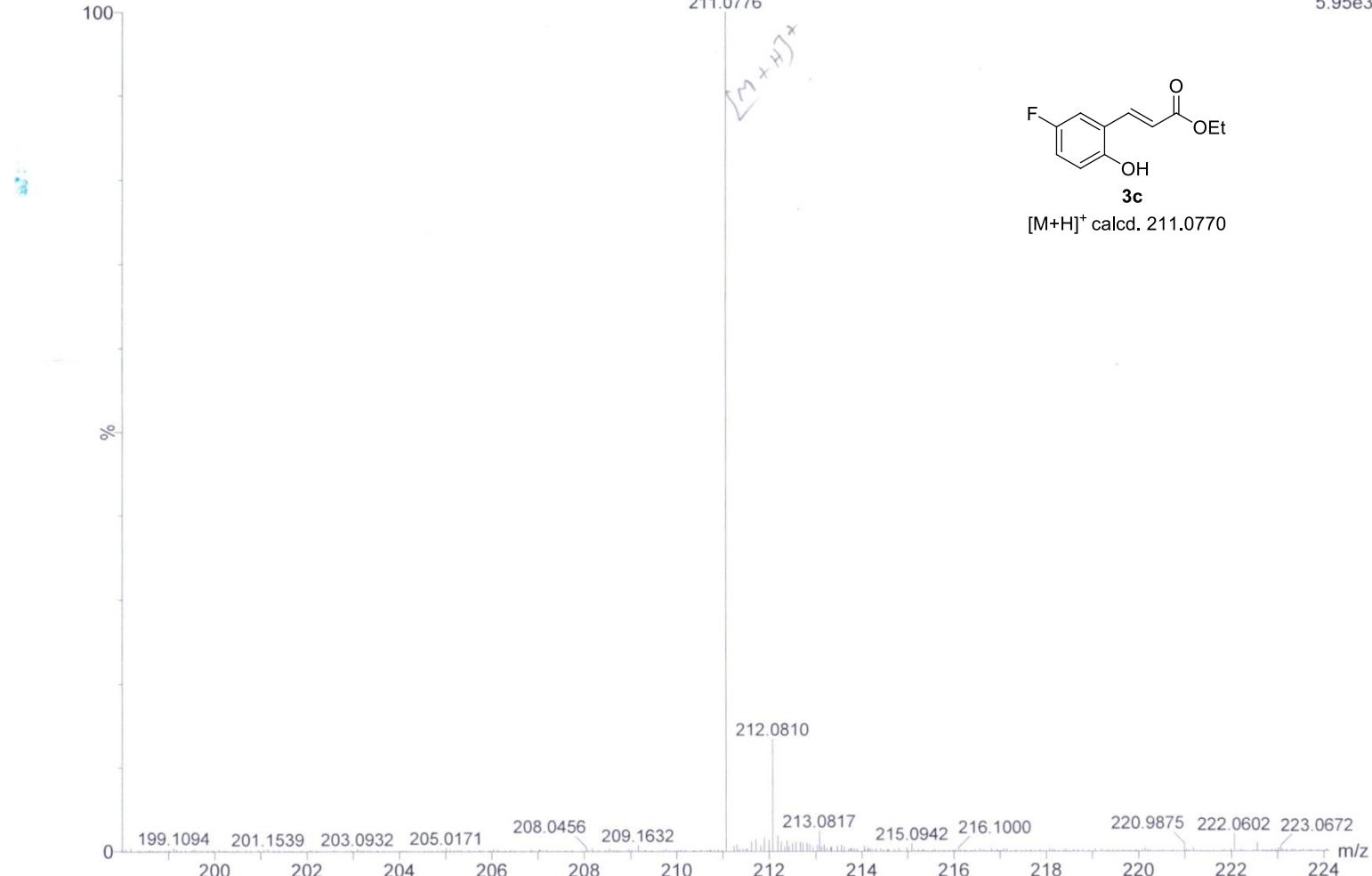
WATERS Q-TOF Premier-HAB213

03-Oct-2016  
10:49:59

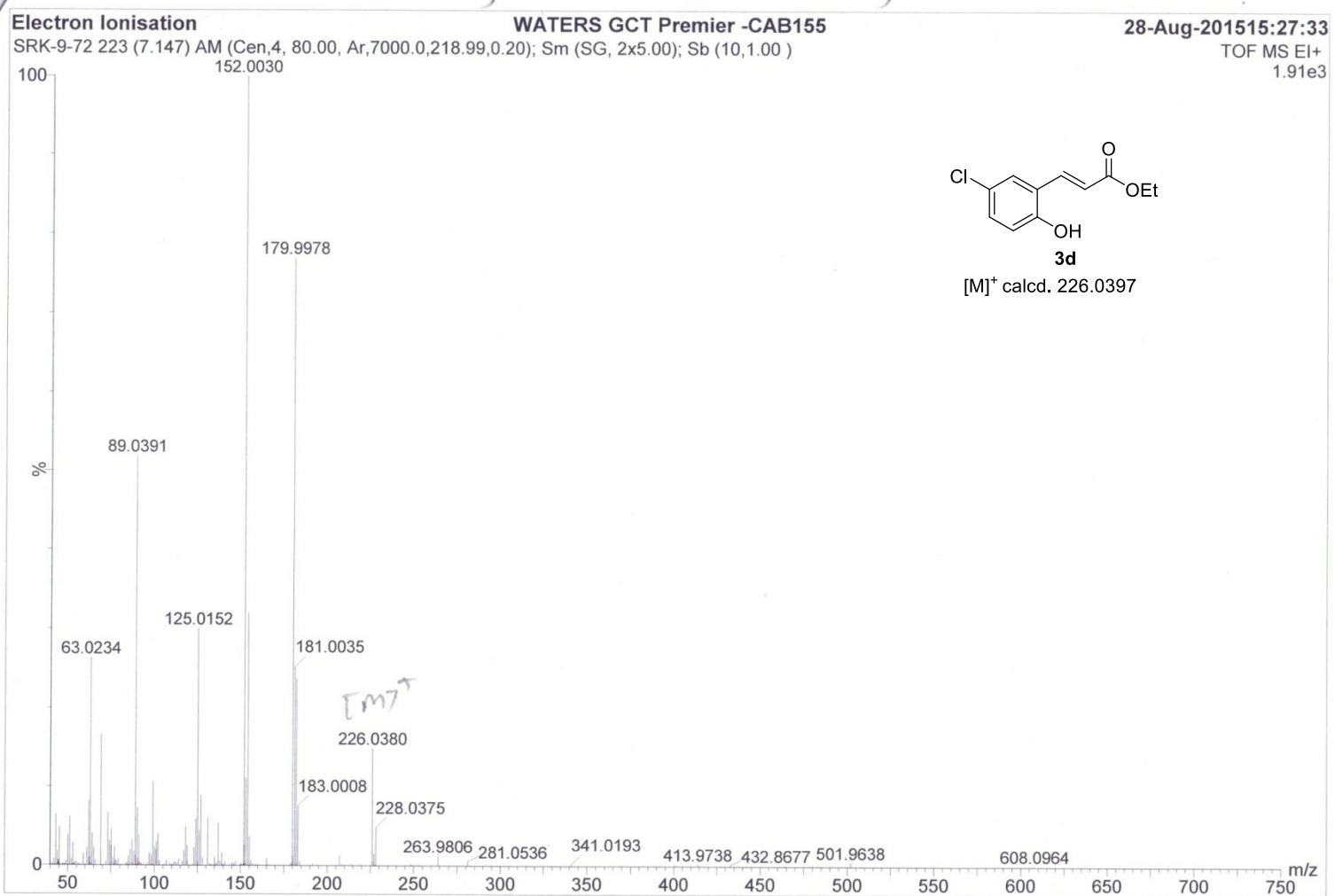
1: TOF MS ES+  
5.95e3

SRK9-123 15 (0.313) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.60,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (15:18-1:3)

211.0776



ESI(HRMS) spectrum of (E)-ethyl 3-(5-fluoro-2-hydroxyphenyl)acrylate (**3c**)



EI(HRMS) spectrum of (*E*)-ethyl 3-(5-chloro-2-hydroxyphenyl)acrylate (**3d**)

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

19-Oct-2016

16:09:21

1: TOF MS ES+  
2.48e3

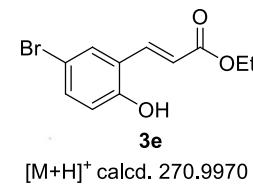
SRK9-81 10 (0.221) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.70,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (9:10-72:81)

270.9977 272.9951

100

%

$[M+H]^+$



ESI(HRMS) spectrum of (*E*)-ethyl 3-(5-bromo-2-hydroxyphenyl)acrylate (**3e**)

Electrospray ionisation -MS

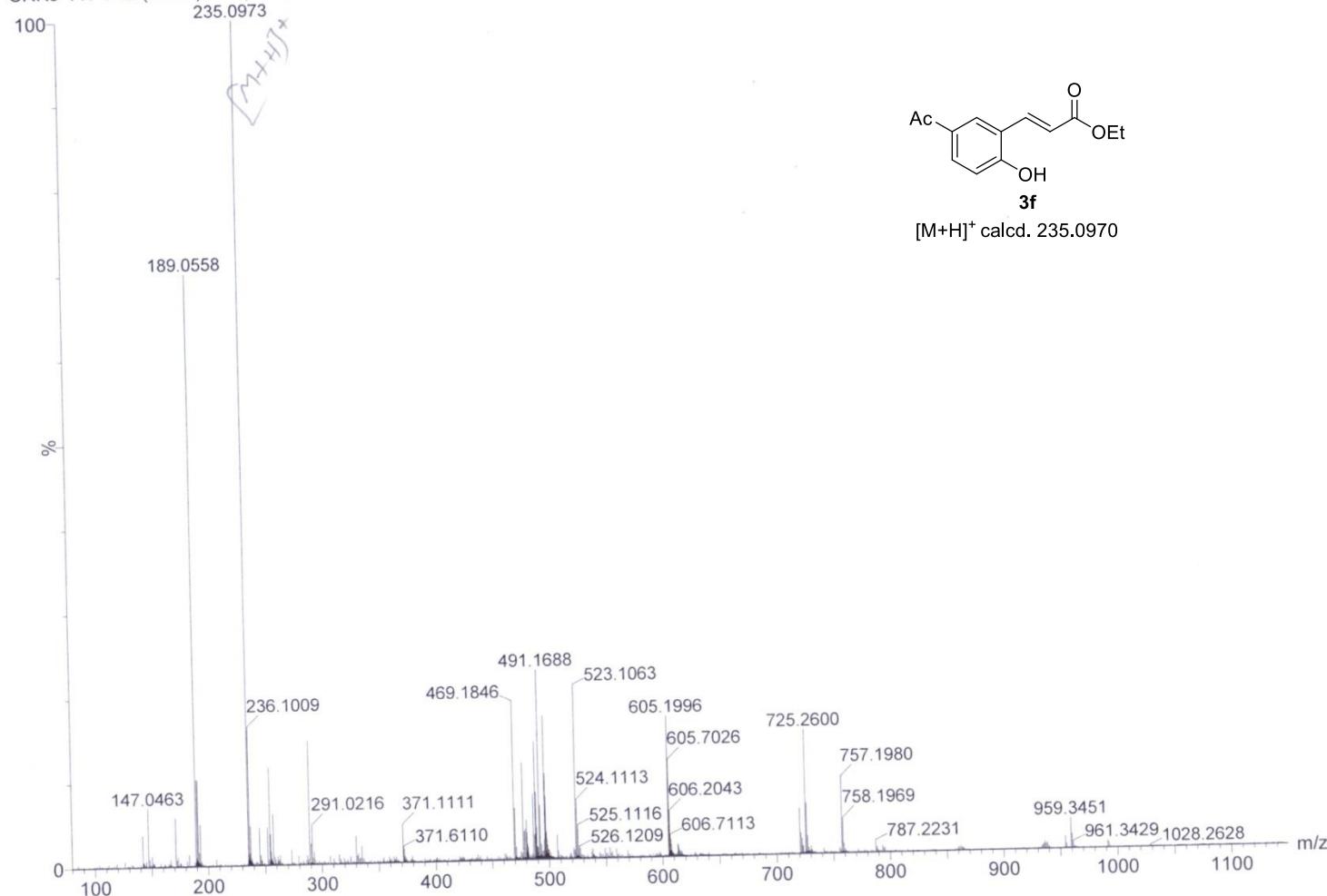
WATERS Q-TOF Premier-HAB213

03-Oct-2016

10:55:31

1: TOF MS ES+  
7.96e3

SRK9-117-I 12 (0.258) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.70,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (11:13-1:3)



ESI(HRMS) spectrum of (*E*)-ethyl 3-(5-acetyl-2-hydroxyphenyl)acrylate (**3f**)

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

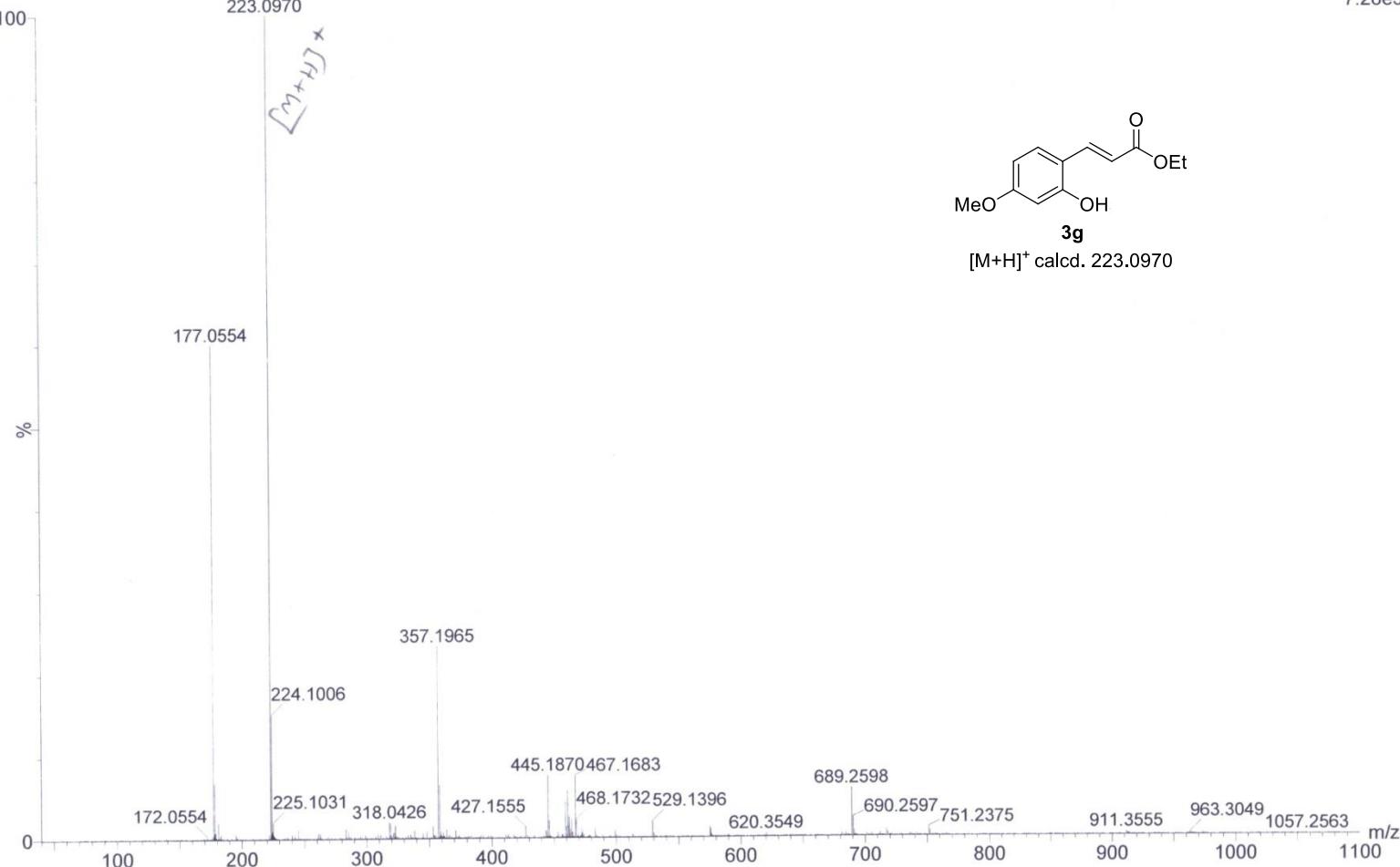
18-Nov-2015

10:00:07

1: TOF MS ES+  
7.28e3

SRK9-83 16 (0.332) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.70,LS 10); Sm (SG, 1x5.00); Sb (10,10.00 ); Cm (16:18-98:104)

223.0970



ESI(HRMS) spectrum of (*E*)-ethyl 3-(2-hydroxy-4-methoxyphenyl)acrylate (**3g**)

Electron Ionisation

WATERS GCT Premier -CAB155

31-Aug-2015 15:22:49

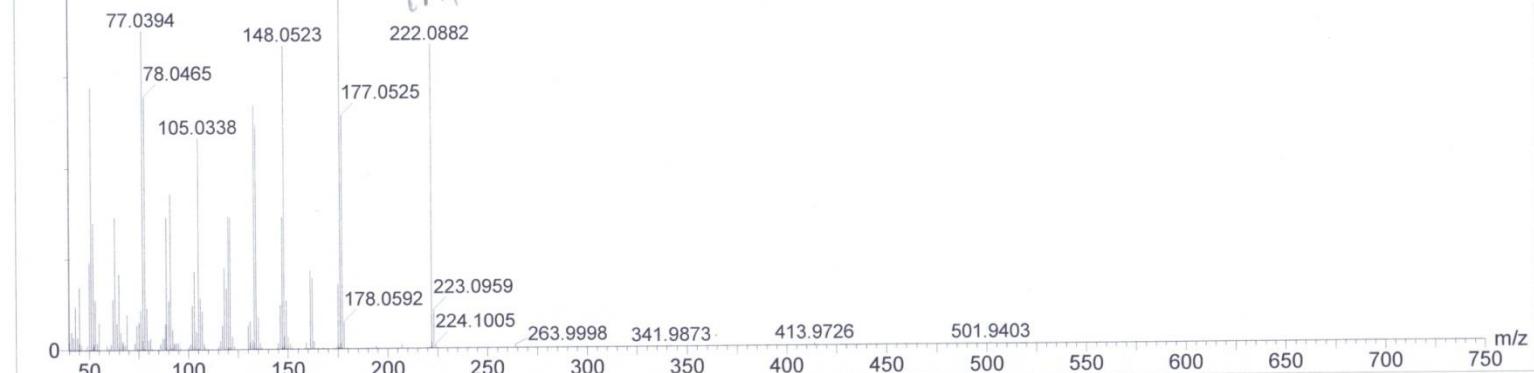
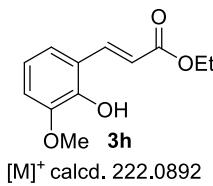
TOF MS EI+  
3.49e3

SRK-9-80 211 (6.927) AM (Cen,4, 10.00, Ar,7000.0,218.99,0.80); Sm (SG, 2x5.00); Sb (10,1.00 )

176.0434

100

%



EI(HRMS) spectrum of (*E*)-ethyl 3-(2-hydroxy-3-methoxyphenyl)acrylate (**3h**)

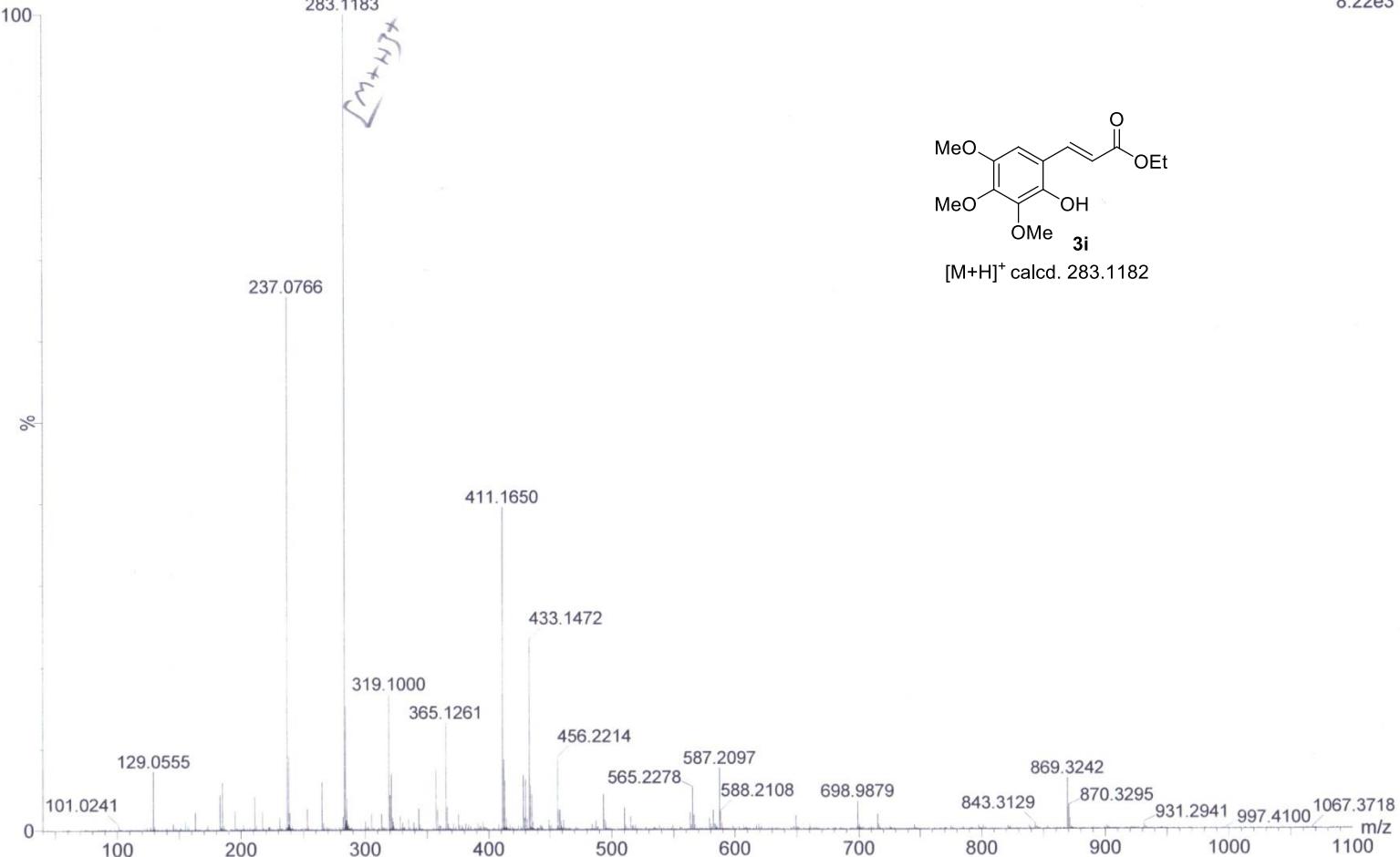
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

18-Nov-2015  
10:04:47

1: TOF MS ES+  
8.22e3

SRK9-87 15 (0.314) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.35,LS 10); Sm (SG, 1x5.00); Sb (10,10.00 ); Cm (15:19-67:72)  
283.1183



ESI(HRMS) spectrum of (E)-ethyl 3-(2-hydroxy-3,4,5-trimethoxyphenyl)acrylate (**3i**)

Electrospray ionisation -MS

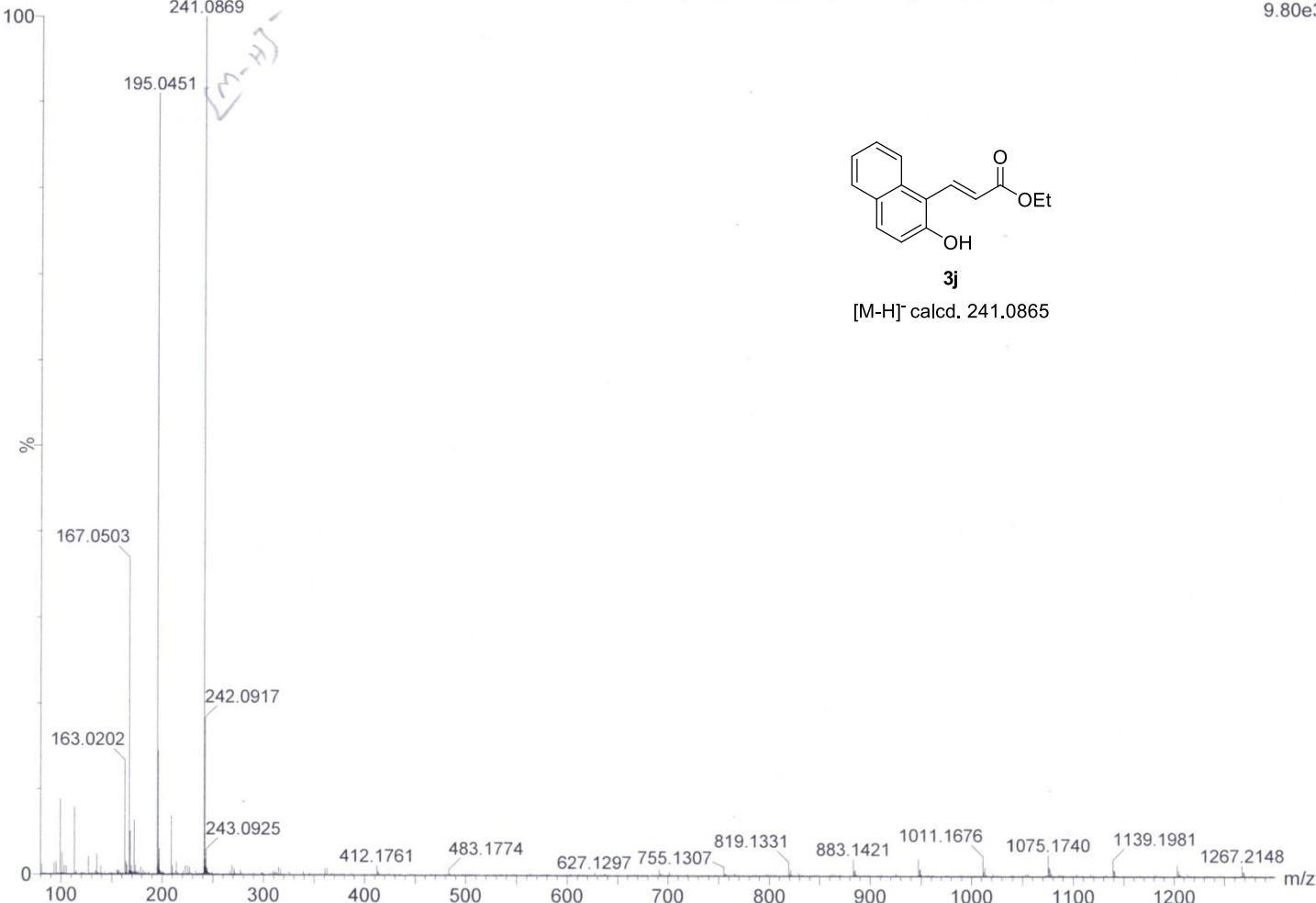
WATERS Q-TOF Premier-HAB213

03-Oct-2016

16:38:34

1: TOF MS ES-  
9.80e3

SRK9-82-II- 16 (0.332) AM (Cen,4, 100.00, Ar,8500.0,554.26,0.60,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (16:19-1:3)



ESI(HRMS) spectrum of (*E*)-ethyl 3-(2-hydroxynaphthalen-1-yl)acrylate (**3j**)

Electron Ionisation

WATERS GCT Premier -CAB155

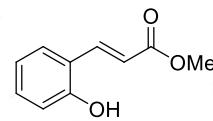
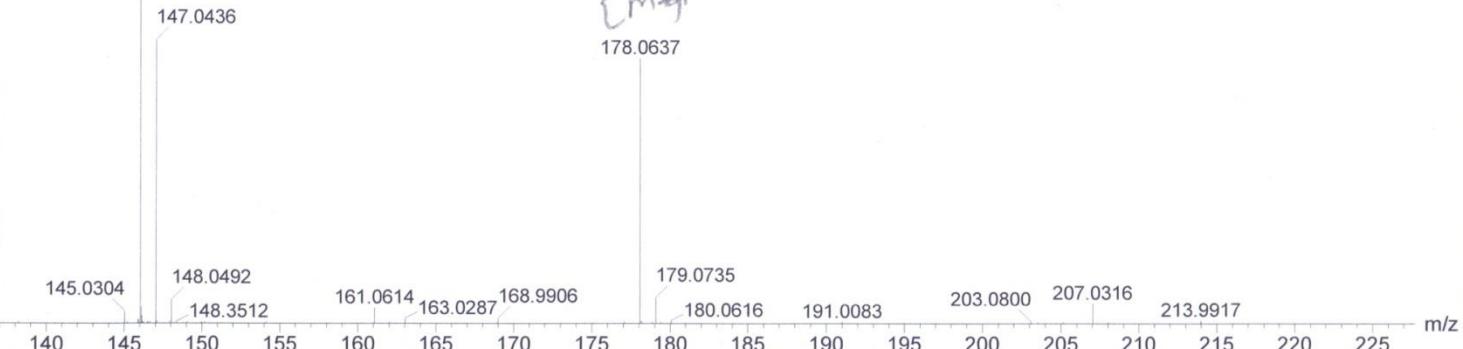
28-Aug-2015 12:59:44

SRK-9-59 85 (4.617) AM (Cen,4, 100.00, Ar,7000.0,218.99,1.00); Sm (SG, 2x5.00); Sb (10,1.00 )  
146.0364TOF MS EI+  
1.54e3

100

%

0

[M]<sup>+</sup> calcd. 178.0630EI(HRMS) spectrum of (*E*)-methyl 3-(2-hydroxyphenyl)acrylate (**3k**)

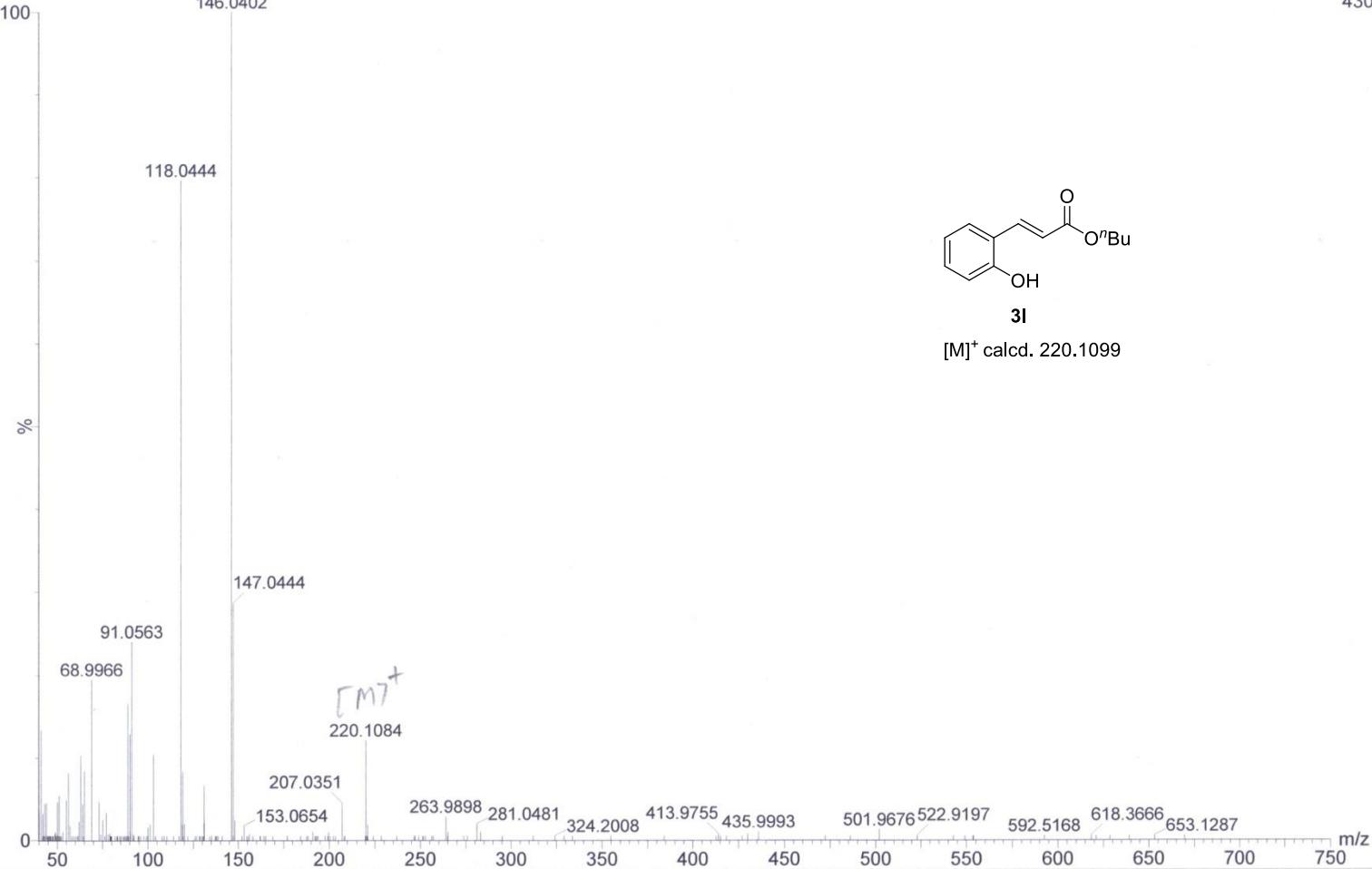
Electron Ionisation

SRK-9-60+ 227 (7.220) AM (Cen,4, 100.00, Ar,7000.0,218.99,1.00); Sm (SG, 2x5.00); Sb (10,1.00 )  
146.0402

WATERS GCT Premier -CAB155

31-Aug-2015 10:44:57

TOF MS EI+  
430



EI(HRMS) spectrum of (*E*)-*n*-butyl 3-(2-hydroxyphenyl)acrylate (**3l**)

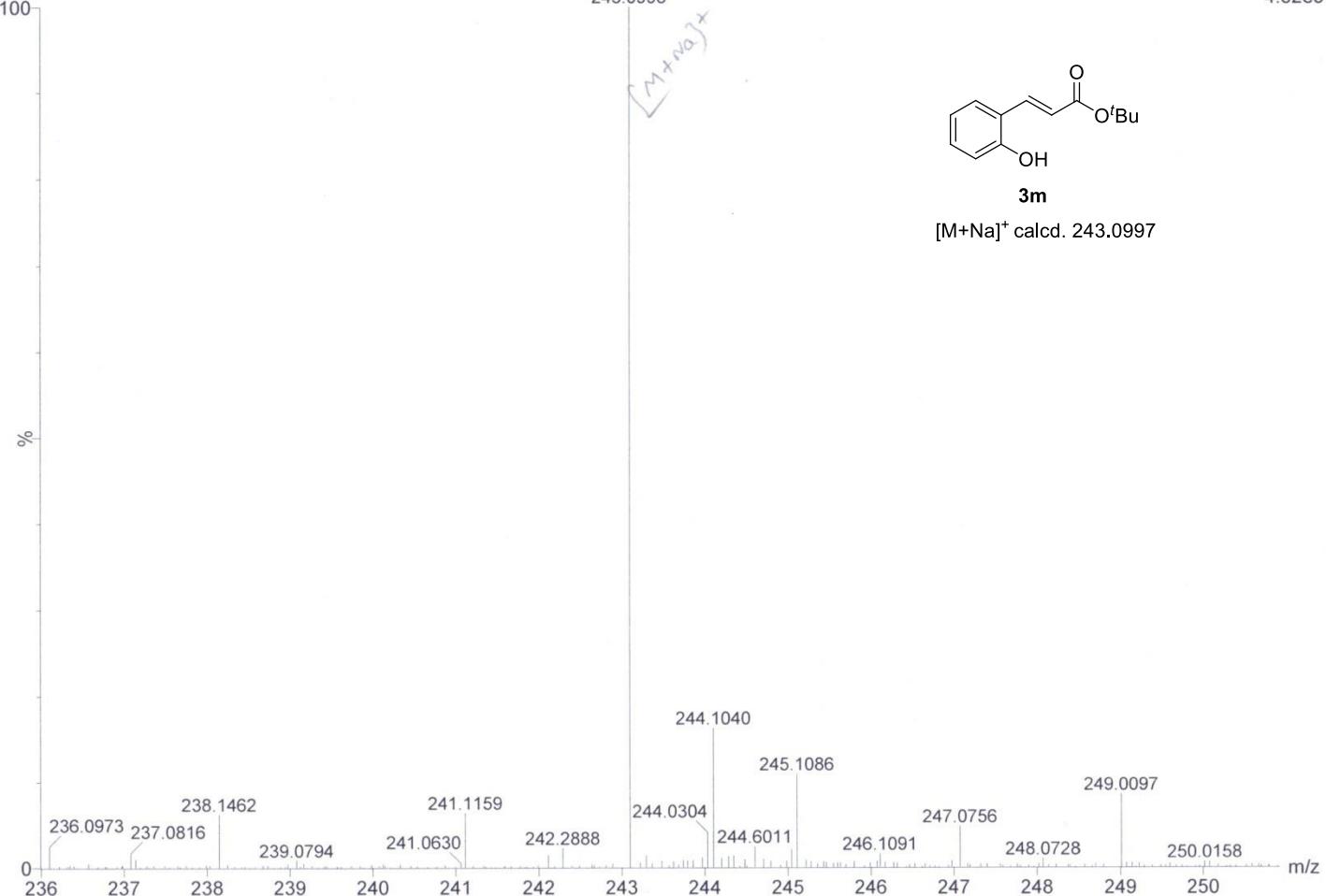
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

03-Oct-2016  
11:24:36

1: TOF MS ES+  
4.82e3

SRK10-48 14 (0.296) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.70,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (12:16-1:3)  
243.0998



ESI(HRMS) spectrum of (E)-tert-butyl 3-(2-hydroxyphenyl)acrylate (**3m**)

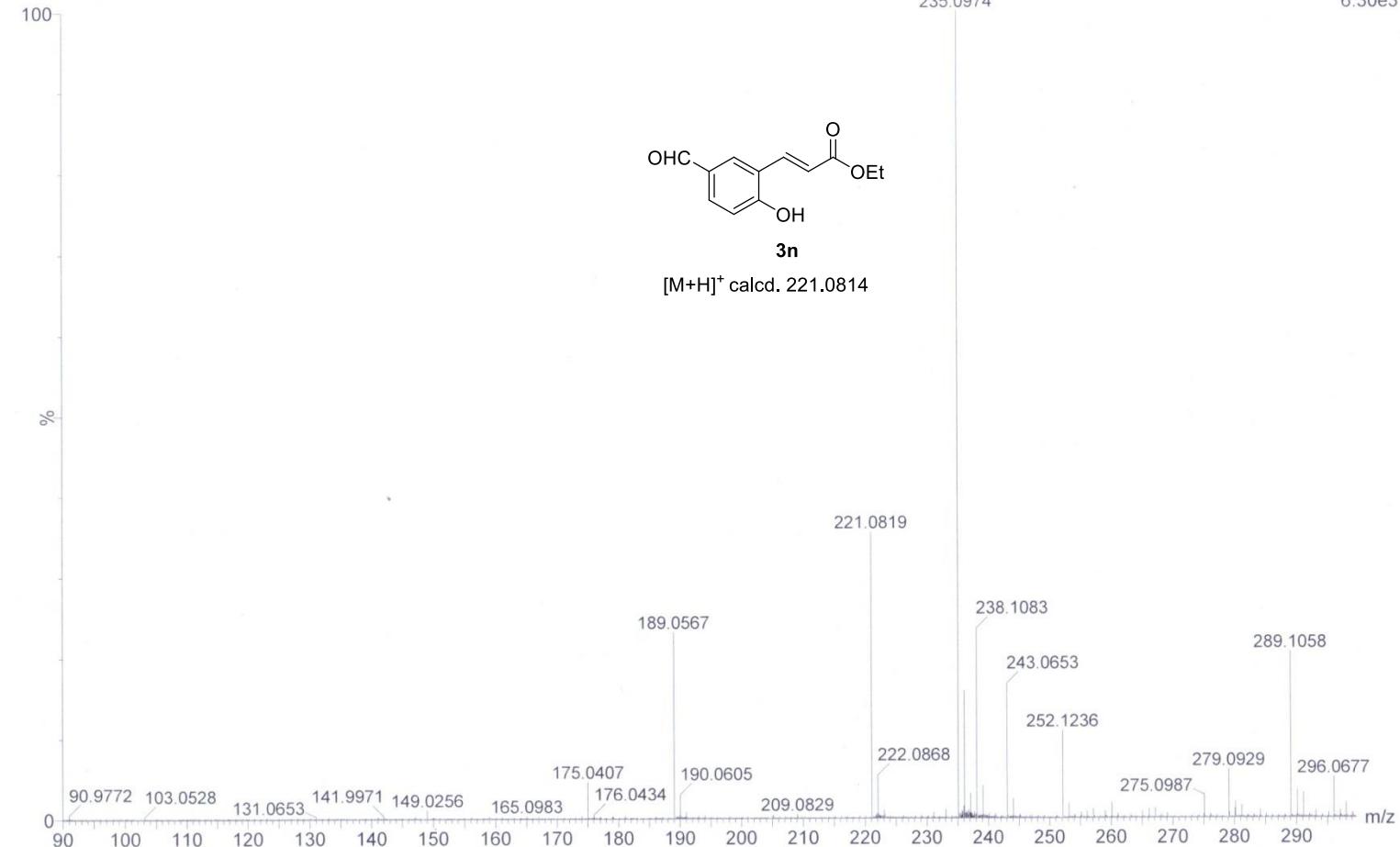
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

14-Aug-2017  
15:34:57

SRK9-69 12 (0.258) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.60,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (12:15-1:3)  
235.0974

1: TOF MS ES+  
6.30e3



ESI(HRMS) spectrum of (*E*)-ethyl 3-(5-formyl-2-hydroxyphenyl)acrylate (**3n**)

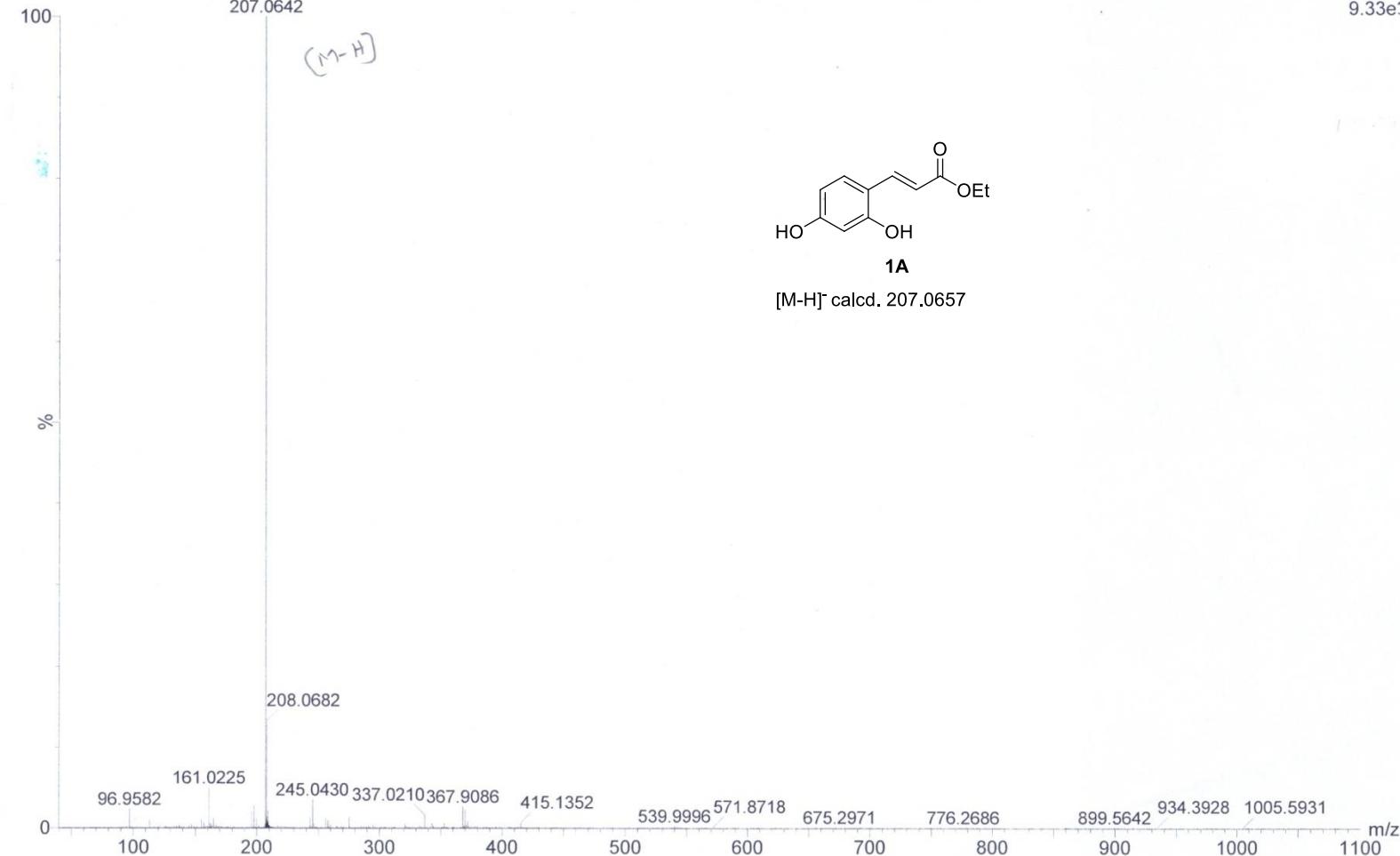
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

19-Oct-2015  
14:37:14

1: TOF MS, ES-  
9.33e3

SRK9-107- 17 (0.3e9) AM (Cen,4, 100.00, Ar,10000.0,554.26,0.70,LS 10); Sm (SG, 1x5.00); Sb (15,10.00 ); Cm (17:20-1:3)



ESI(HRMS) spectrum of (E)-ethyl 3-(2,4-dihydroxyphenyl)acrylate (**1A**)

Electrospray ionisation -MS

11-148

SRK9<sub>c</sub> 148 14 (0.295) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.75,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (14:15-1:3)

WATERS Q-TOF Premier-HAB213

237.0769

19-Oct-2016

16:14:09

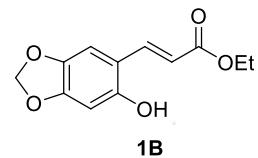
1: TOF MS ES+  
3.96e3

100

%

223.1171 224.1760 227.1557 229.1971 230.1682 233.0349 236.0691 238.0800  
239.0760 239.4638 243.0441 247.0640  
246.9716 248.0582 249.0591 251.7413 m/z

$[\text{M}+\text{H}]^+$



ESI(HRMS) spectrum of (*E*)-ethyl 3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)acrylate (**1B**)

Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

24-Feb-2016

15:05:48

1: TOF MS ES+  
5.51e3

SRK10-136 22 (0.461) AM (Cen,4, 100.00, Ar,8500.0,556.28,1.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (22:23-1:3)

192.1026

$[M + H]^+$

x

192.1026

$[M + H]^+$

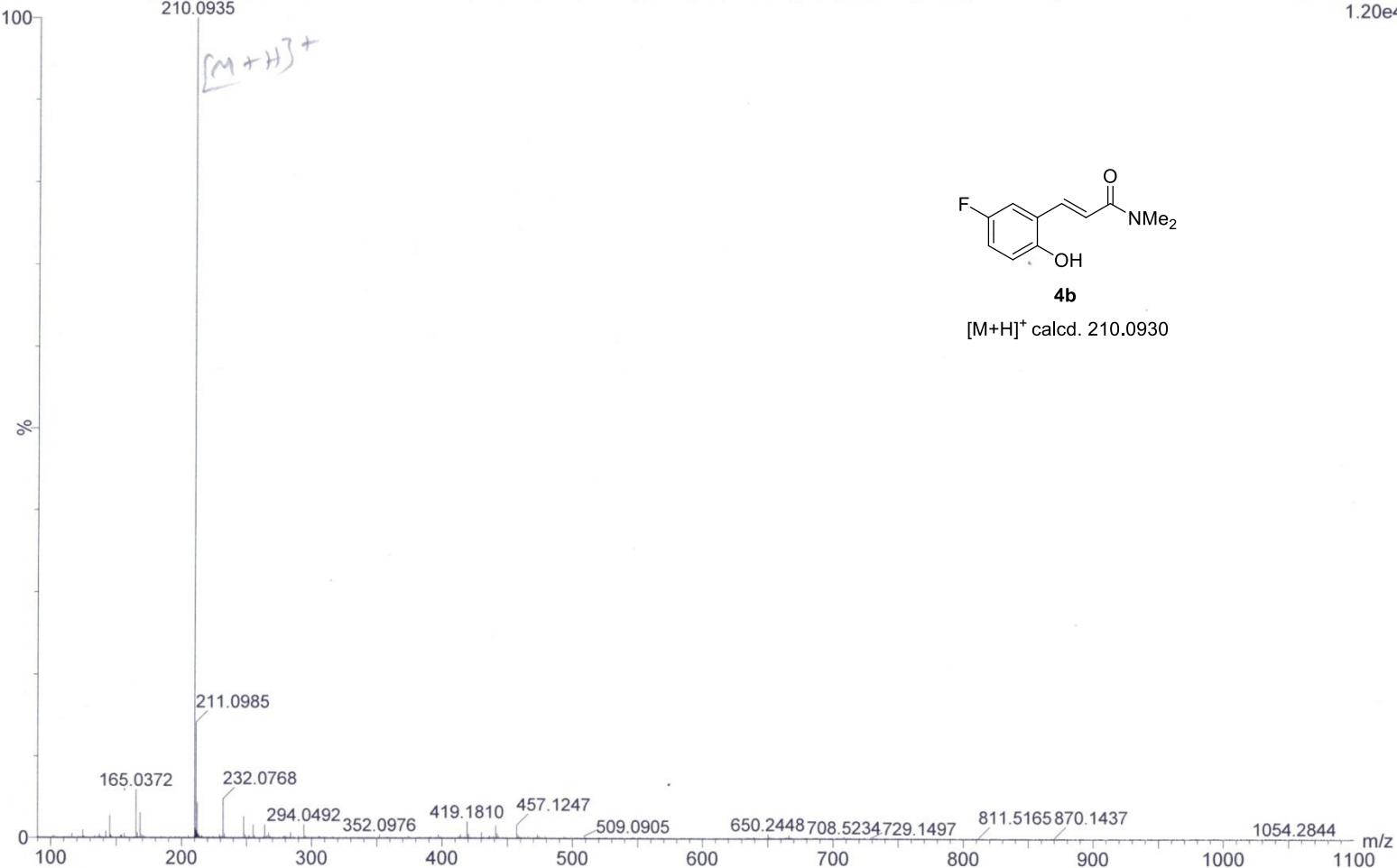
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

23-Mar-2017  
14:43:51

1: TOF MS ES+  
1.20e4

SRK12-119-II 19 (0.405) AM (Cen,4, 100.00, Ar,8500.0,556.28,1.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (19:20-1:3)



ESI(HRMS) spectrum of (*E*)-3-(5-fluoro-2-hydroxyphenyl)-*N,N*-dimethylacrylamide (**4b**)

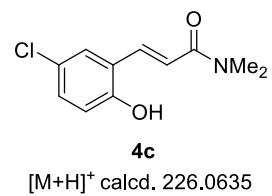
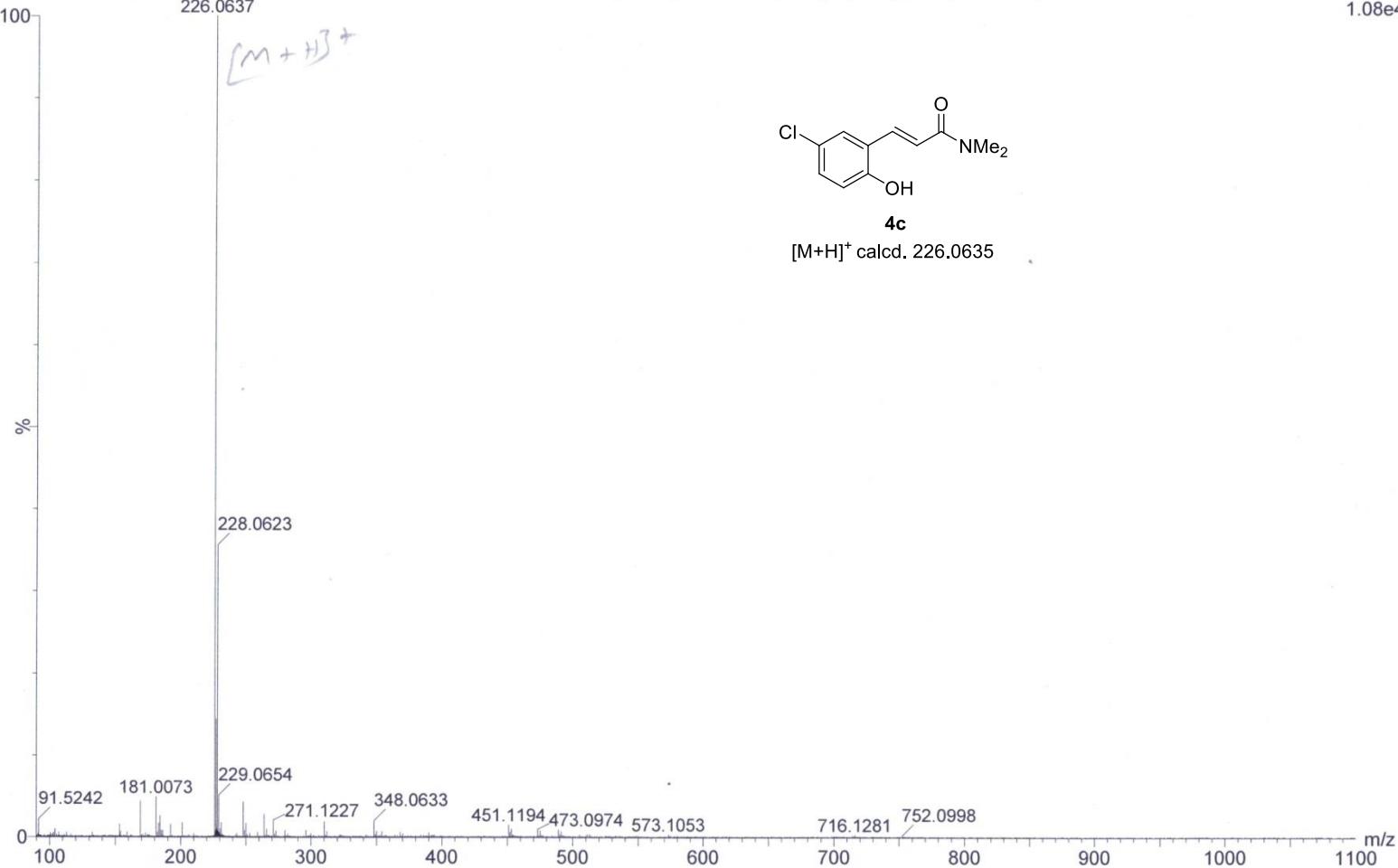
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

23-Mar-2017  
14:46:14

1: TOF MS ES+  
1.08e4

SRK12-120 19 (0.406) AM (Cen,4, 100.00, Ar,8500.0,556.28,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (19:21-1:3)



ESI(HRMS) spectrum of (*E*)-3-(5-chloro-2-hydroxyphenyl)-*N,N*-dimethylacrylamide (**4c**)

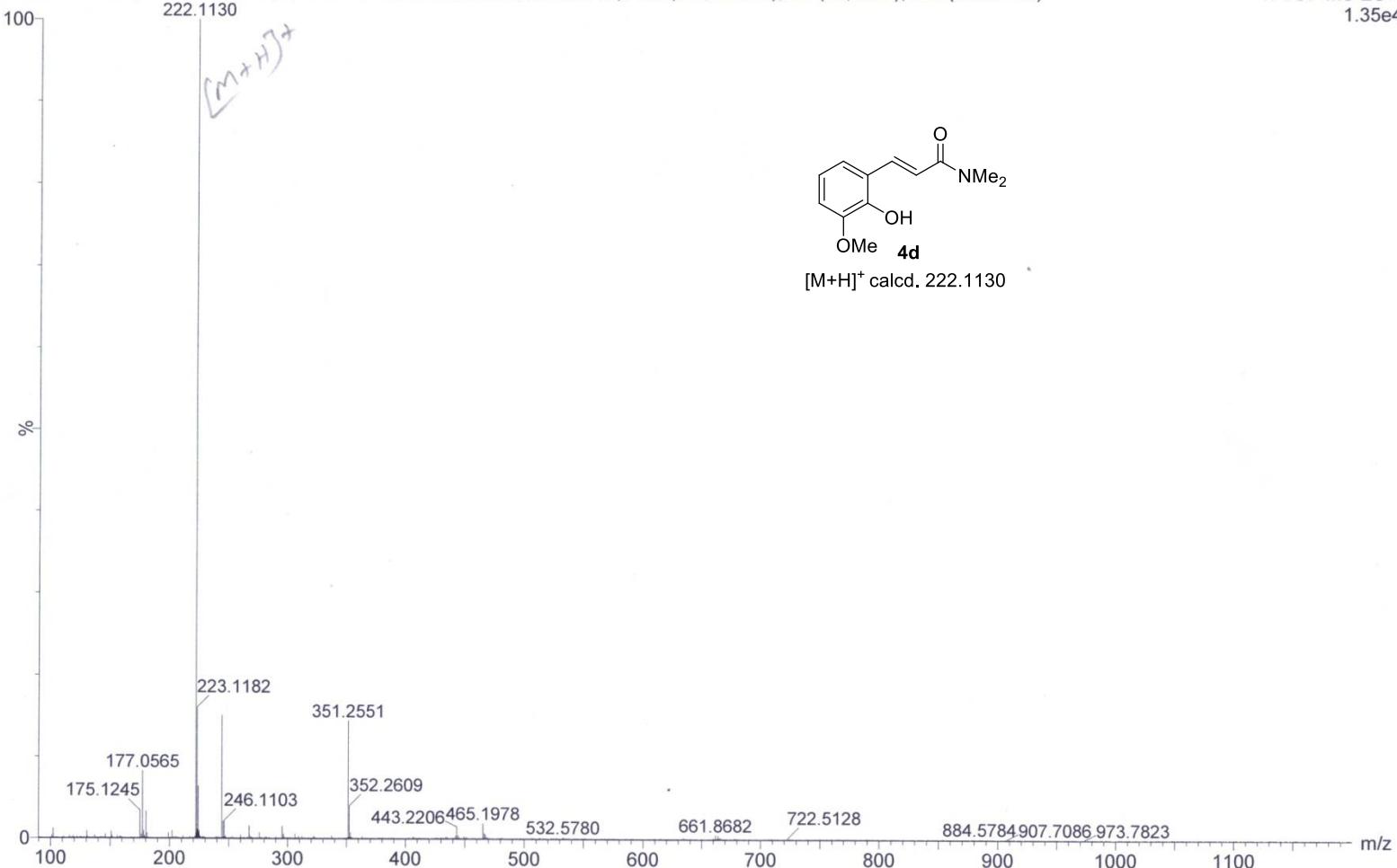
Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

05-Apr-2017  
12:56:31

1: TOF MS ES+  
1.35e4

SRK12-156 19 (0.405) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.75,LS 10); Sm (SG, 2x5.00); Sb (10,1.00 ); Cm (19:21-1:3)



ESI(HRMS) spectrum of (E)-3-(2-hydroxy-3-methoxyphenyl)-N,N-dimethylacrylamide (**4d**)