Electronic Supplementary Material (ESI) for RSC Advances.

Insights into the Morita-Baylis-Hillman reaction of Isomeric Dibenzofuran Carbaldehydes: A Theoretical and Mass spectral Study

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[b]*National Centre for Mass Spectrometry, CSIR-Indian Institute of Chemical Technology, Hyderabad-500 007, Telangana, INDIA.*

[c]*Centre for Molecular Modelling, CSIR-Indian Institute of Chemical Technology, Hyderabad-500 007, Telangana, INDIA.*

Supporting Information

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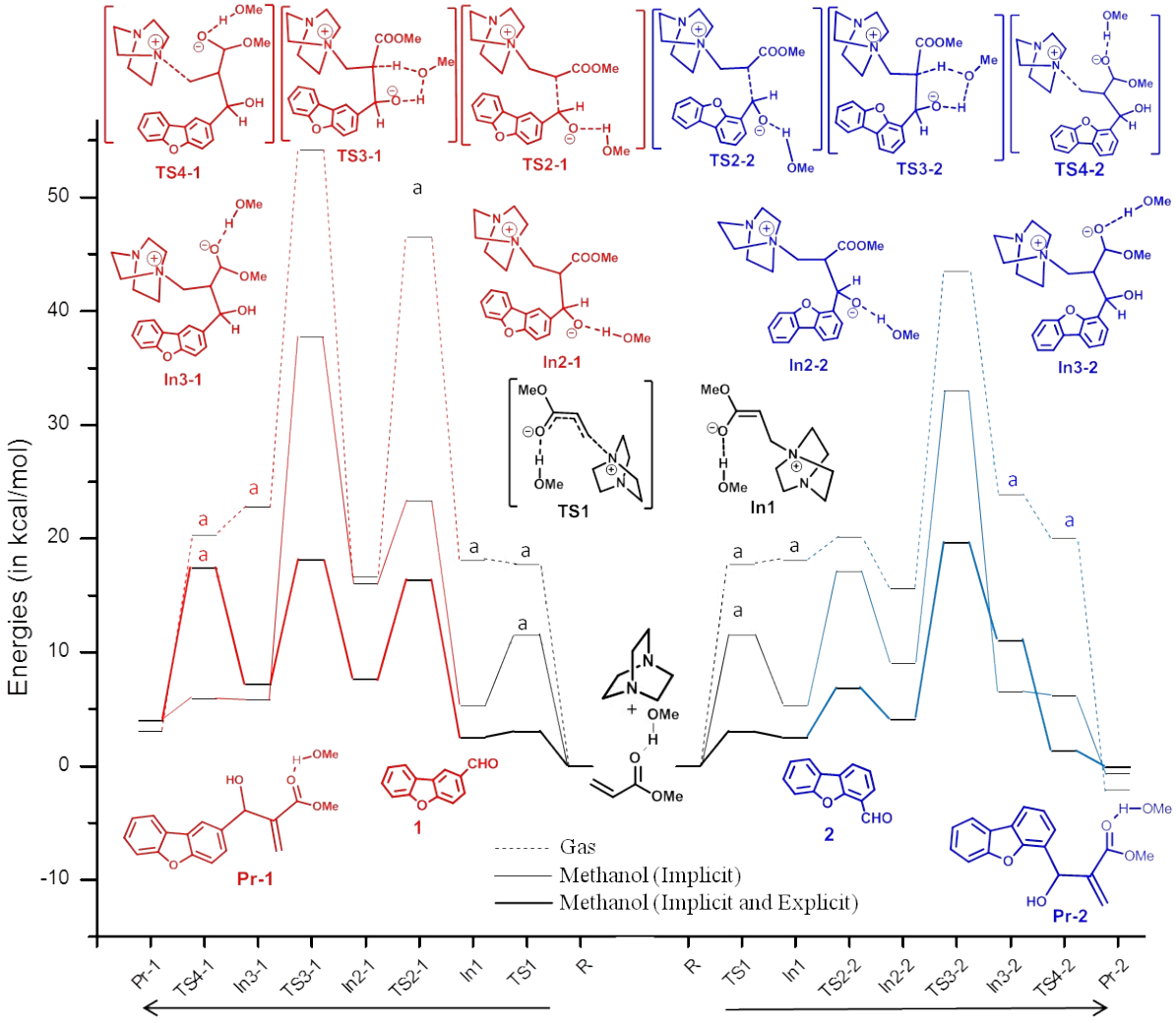


Figure S1. Gas phase as well as solvent (implicit and explicit methanol) phase reaction energy profiles for the considered reaction obtained using the aldehydes **1** (red) and **2** (blue) at mPW1K/6-31+G(d) level of theory. a: represents the structures obtained at mPW1K/6-31+g(d)//HF/3-21G level of theory.

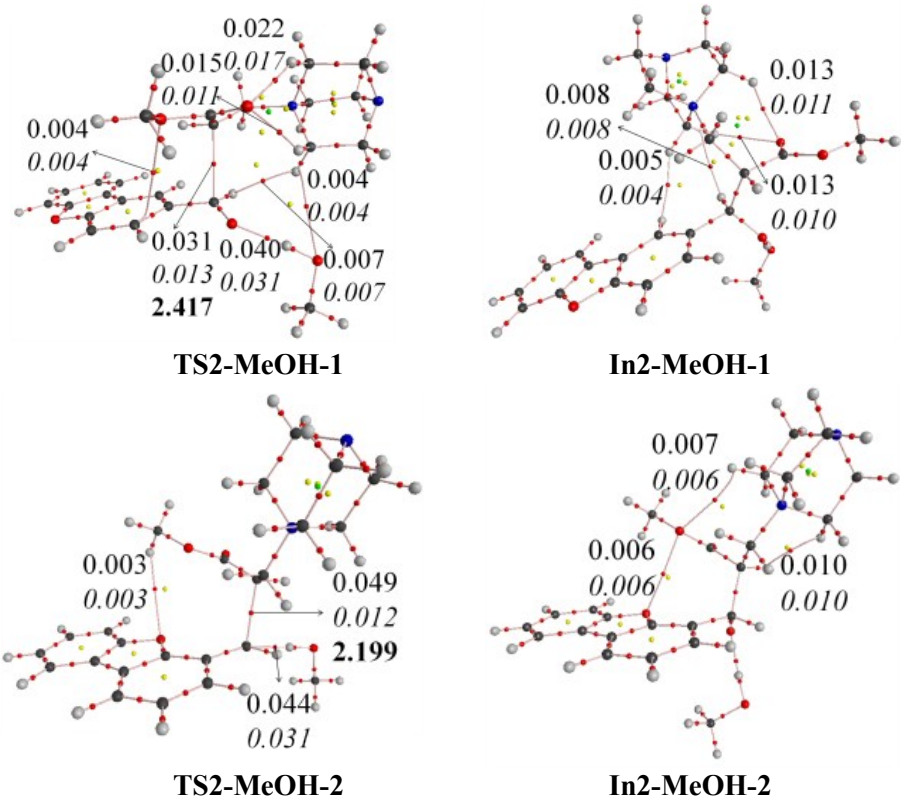
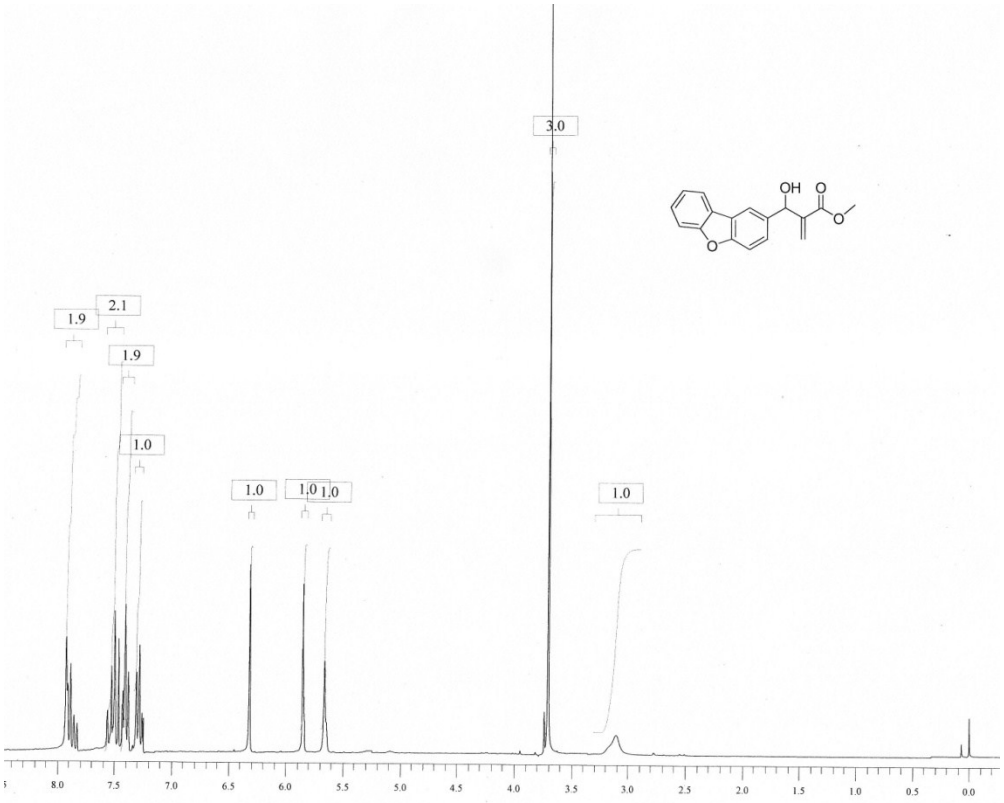


Figure S2. Bond critical points for **TS2-MeOH-1**, **TS2-MeOH-2**, **In2-MeOH-1** and **In2-MeOH-2**. Electron density values: normal, Laplacian of electron density: italics, Bond lengths: bold.

Table S1: Activation (for transition states) and reaction energies (for intermediates) obtained at mPW1K/6-31+G(d,p) and B97-D/6-31+G(d,p) levels on HF/6-31+G(d,p) optimized geometries, and HF/6-31+G(d,p) level. ΔE_1 is for aldehyde **1** and ΔE_2 is for aldehyde **2**.

		mPW1K	HF	B97-D
TS1-G	ΔE	17.4	23.7	12.8
In1-G	ΔE	19.7	22.2	13.0
In3-G	ΔE_1	20.5	14.1	12.6
	ΔE_2	16.7	9.9	7.9
TS4-G	ΔE_1	19.6	15.4	10.7
	ΔE_2	15.0	10.2	6.2
In4-G-A	ΔE_1	21.4	11.9	11.2
	ΔE_2	17.9	8.1	7.2
TS5-G-A	ΔE_1	18.2	12.0	8.0
	ΔE_2	15.7	9.0	5.1

These results suggest the compatibility in trends while comparing the energetic of mPW1K/6-31+G(d,p)//HF/6-31+(d,p) level with those of HF/6-31+G(d,p) and B97-D/6-31+G(d,p)//HF/6-31+(d,p) levels.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O
O
1.9
2.1
1.9
1.0
1.0
1.0
1.0
1.0
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


166.759
156.514
142.162
140.933
135.850
127.214
126.019
125.889
122.703
121.299
120.717
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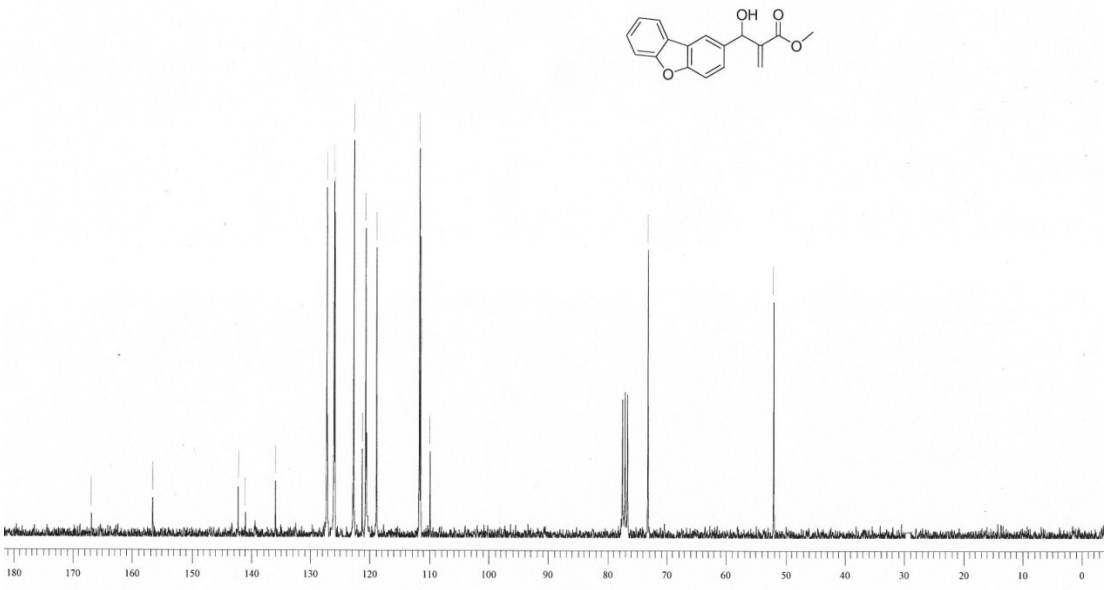
111.455
109.839
73.156
51.972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O
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60
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40
30
20
10
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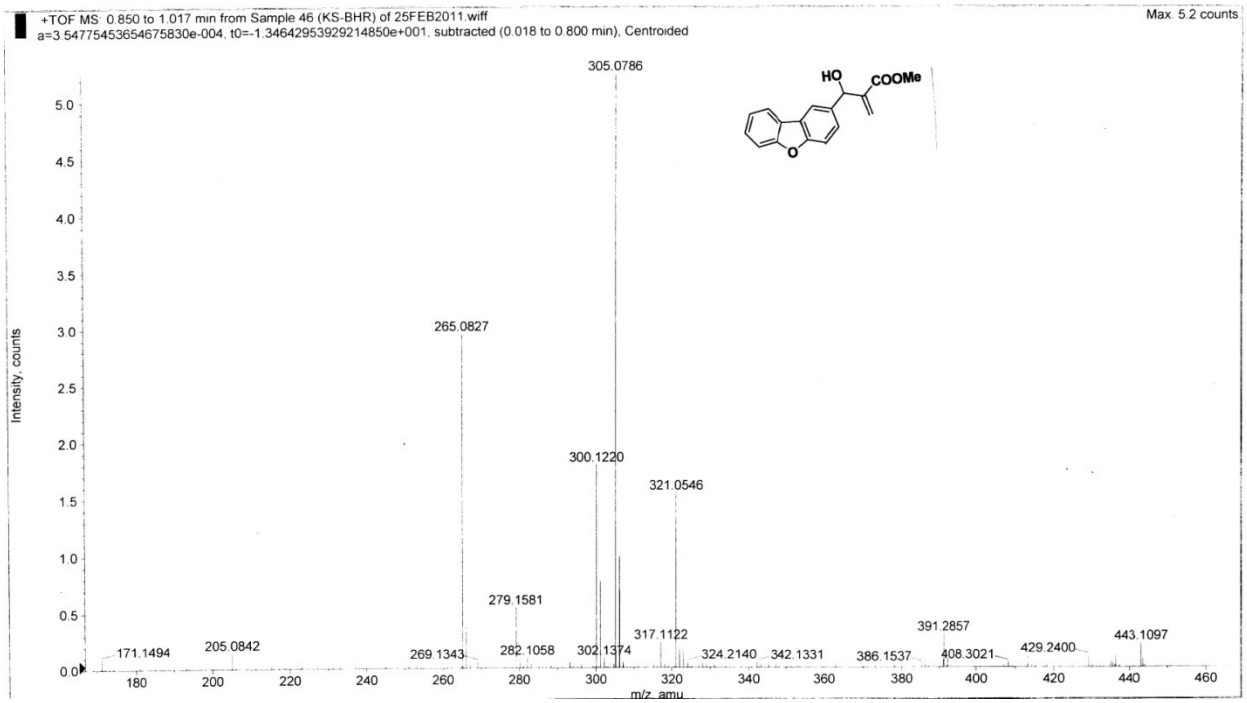

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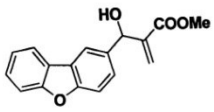
Sample Comment: n/a Acq. Time: n/a

Elemental composition calculator



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Min DBE: -0.5000 Max DBE: +50.0000
Electron state: OddAndEven
Num of charges: 0
Add water: N/A
Add proton: N/A
File Name: 25FEB2011.wiff

	Elements	Min Number	Max Number
1	C	0	25
2	H	0	22
3	Na	0	1
4	O	0	5

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
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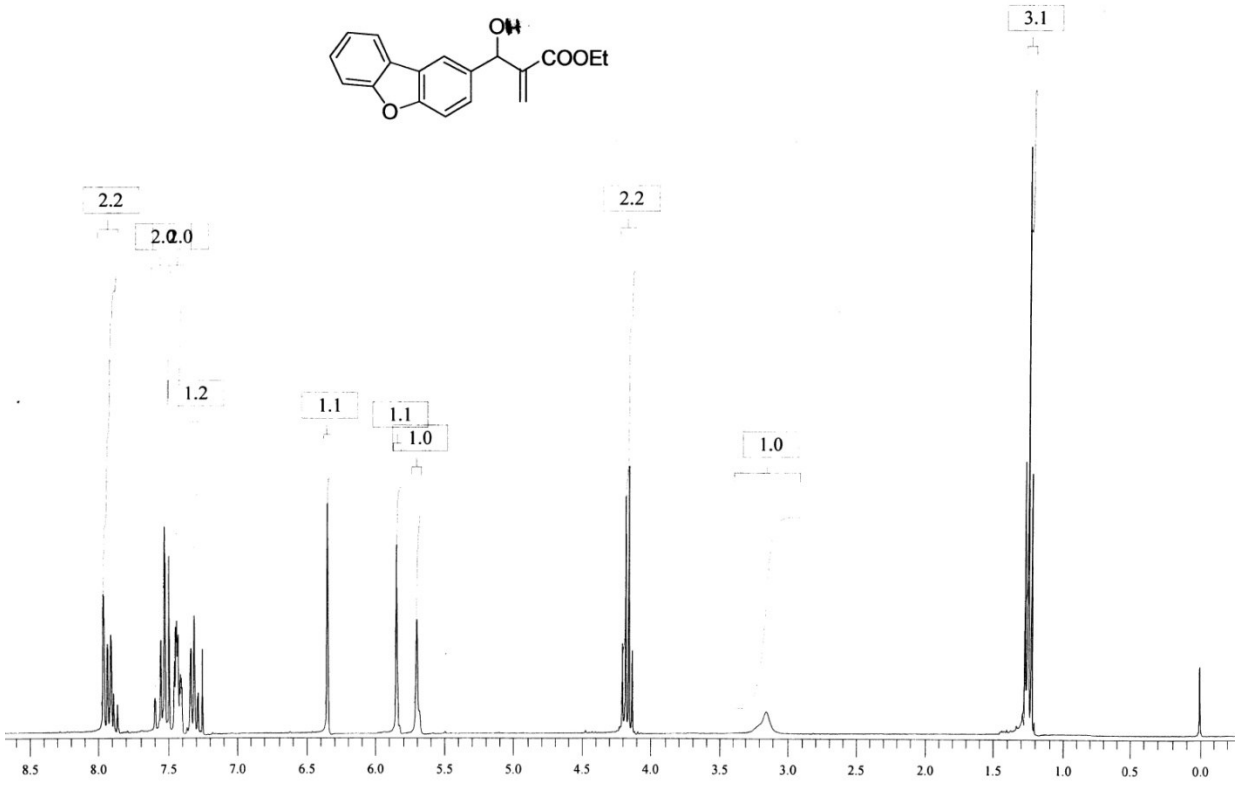
OH
COOEt
O
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2.2
2.0
2.2
1.2
1.1
1.1
1.0
1.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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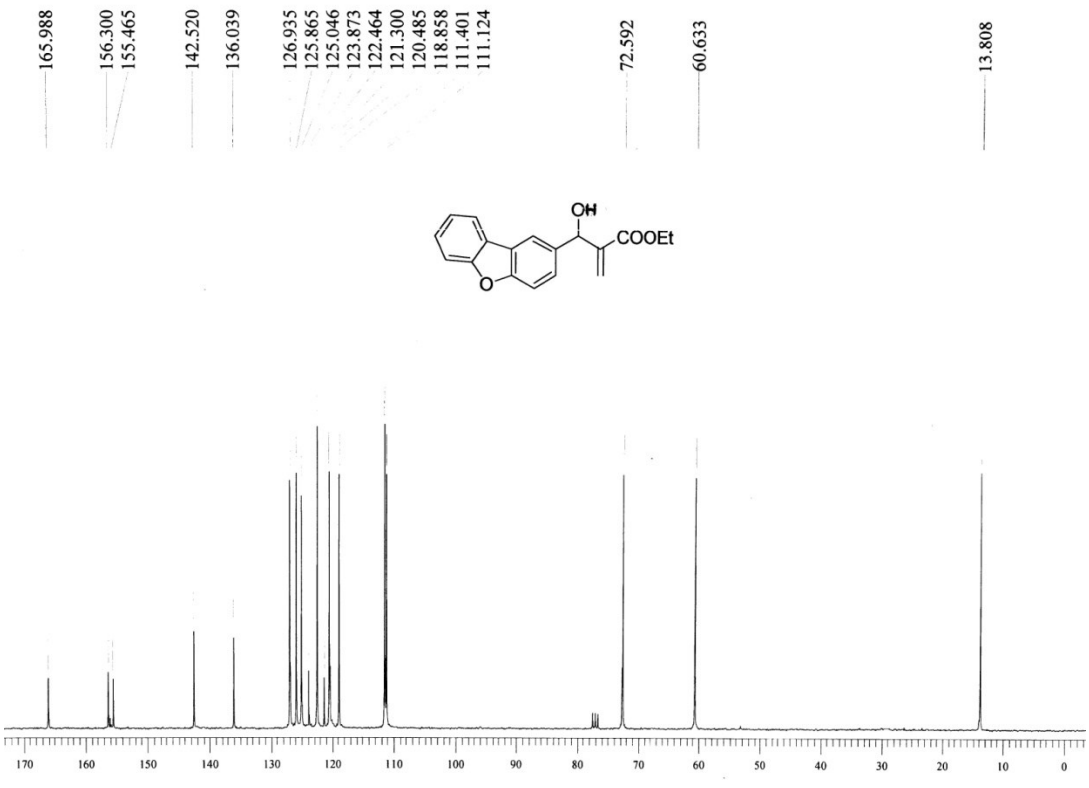
2.5
2.0
1.5
1.0
0.5
0.0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142.520
136.039
126.935
125.865
125.046
123.873
122.464
121.300
120.485
118.858
111.401
111.124
72.592
60.633
13.808
OH
COOEt
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

CSIR-INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
NATIONAL CENTRE FOR MASS SPECTROMETRY

Data:KS-BHEARNI-20-1-15
Sample Name:KS-BHEARNI-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.52..0.64)

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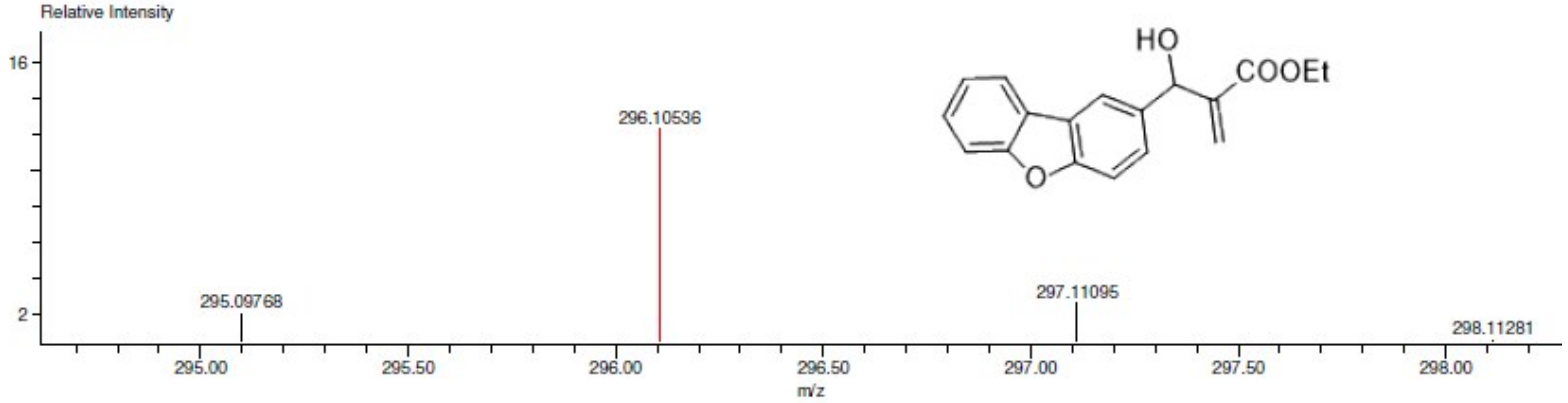
Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 16:30:50
Created by:JEOL

Charge number:1 Tolerance:1000.00(ppm)
Element:^{12}C:0 .. 18, ^{1}H:0 .. 17, ^{79}Br:0 .. 0, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{127}I:0 .. 0, ^{14}N:0 .. 0, ^{16}O:0 .. 4, ^{32}S:0 .. 0

Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
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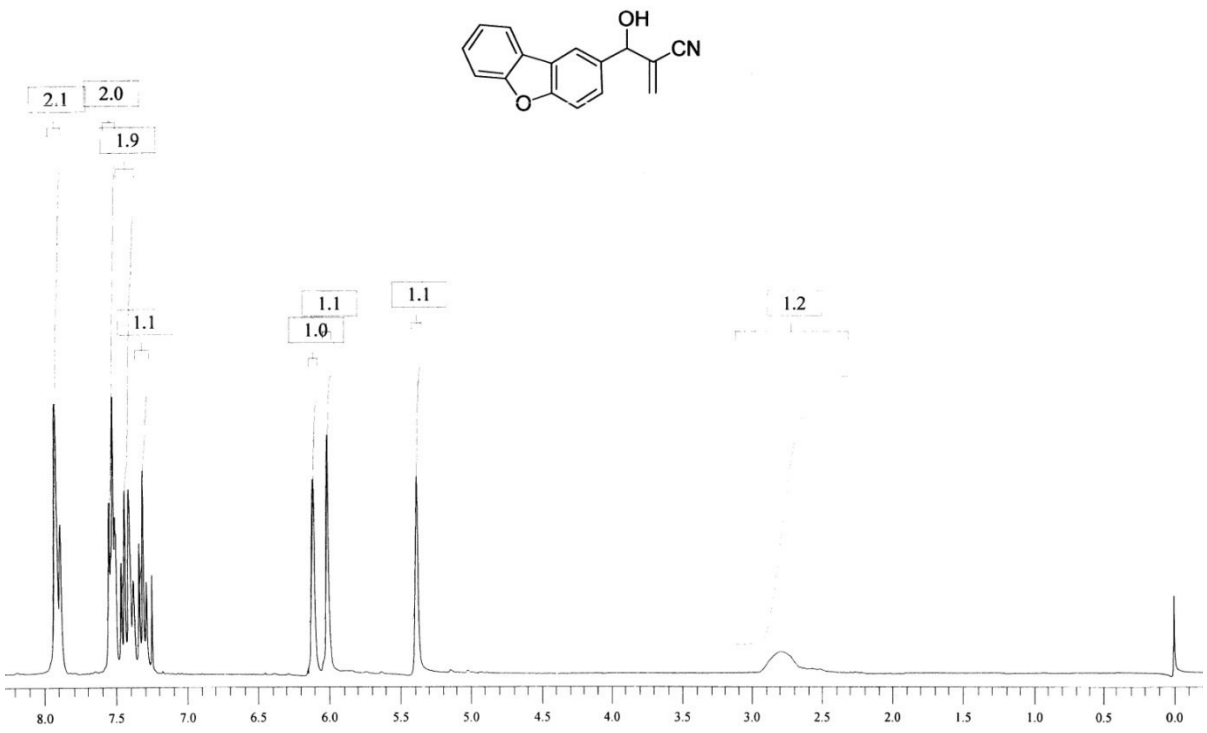
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1.0
1.1
1.2
8.0
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6.5
6.0
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4.0
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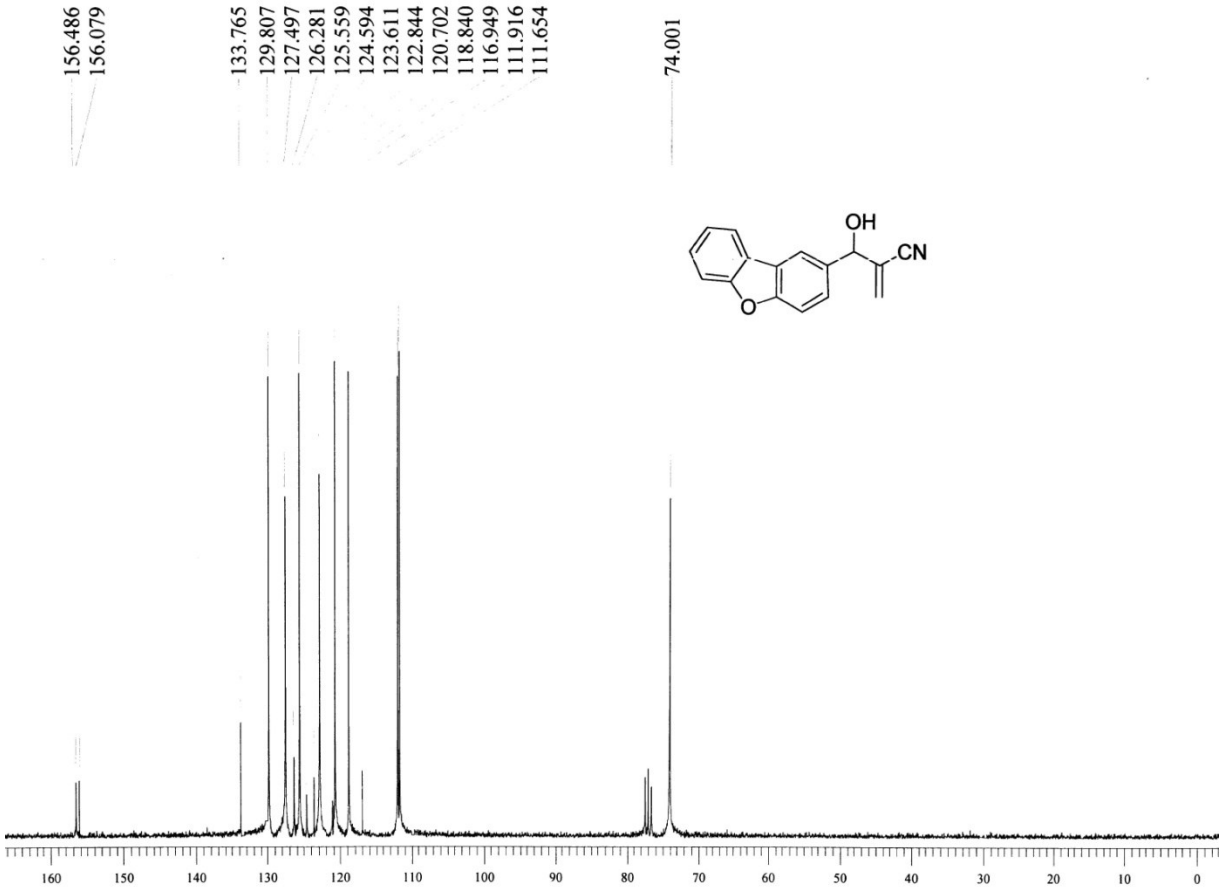
2.0
1.5
1.0
0.5
0.0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116.949
111.916
111.654
74.001
OH
CN
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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Data:KS-BHACRNI-20-1-15
Sample Name:KS-BHACRNI-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.87..0.91)

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Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 14:07:03
Created by:JEOL

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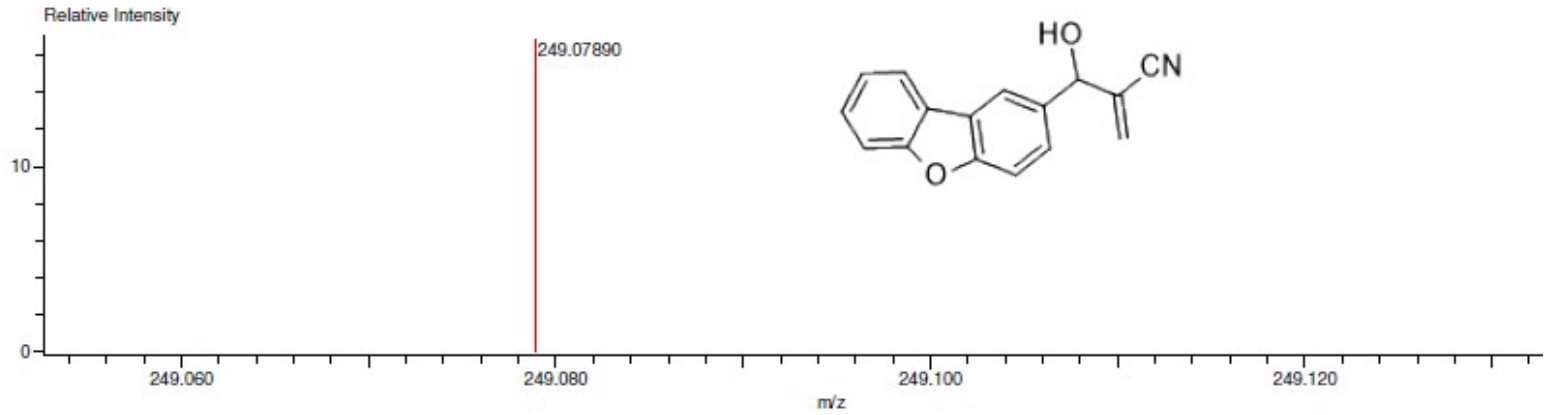
Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
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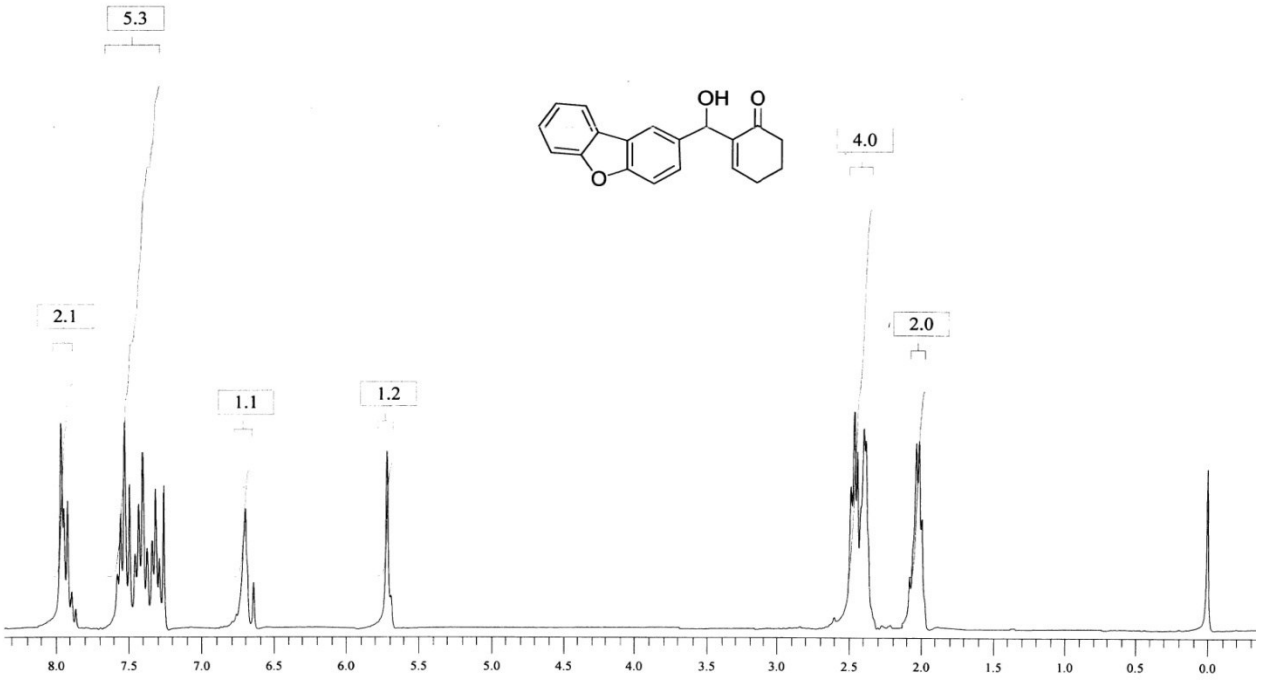
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O
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2.0
1.1
1.2
8.0
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7.0
6.5
6.0
5.5
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4.5
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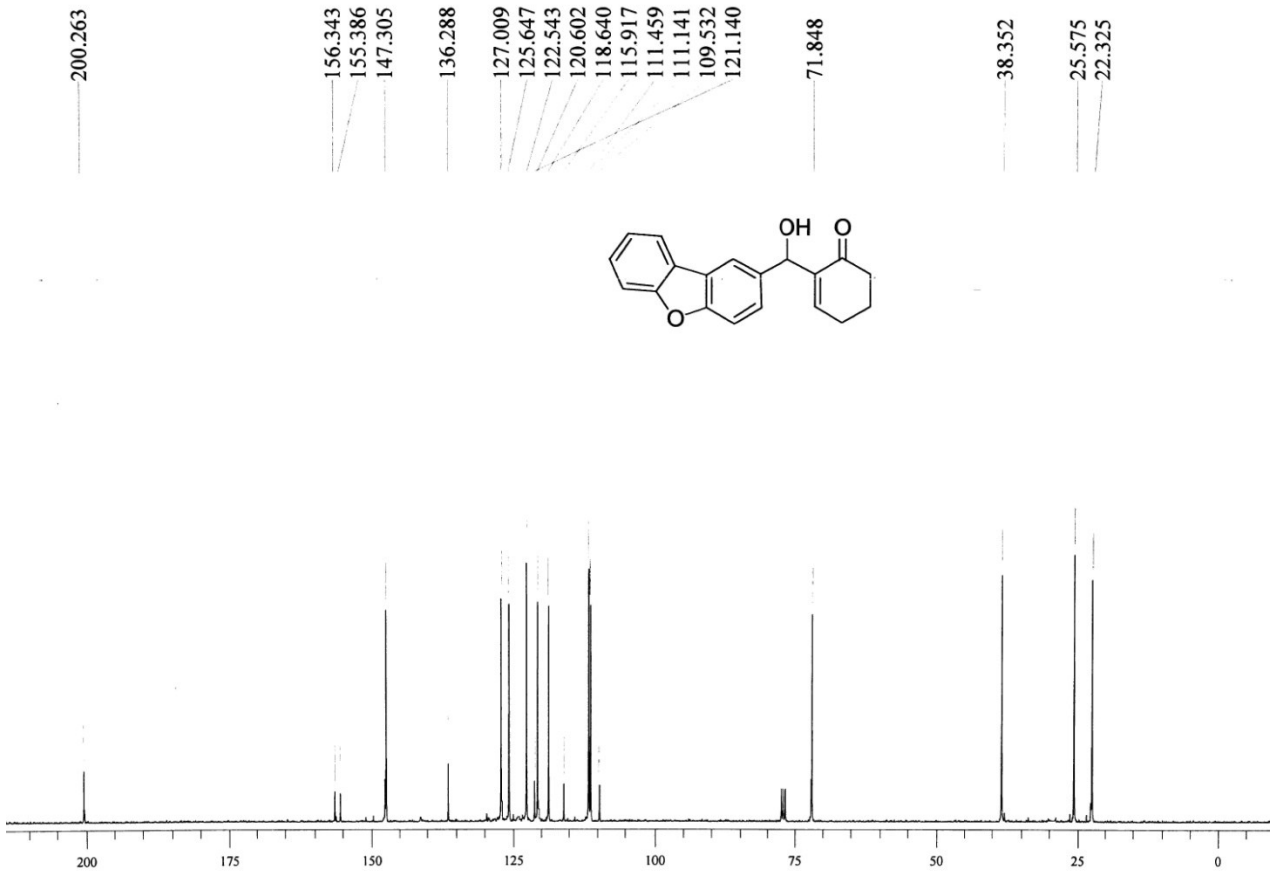
2.5
2.0
1.5
1.0
0.5
0.0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109.532
121.140
71.848
38.352
25.575
22.325
OH
O
200
175
150
125
100
75
50
25
0

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Data:KS-BH2CYH-20-1-15
Sample Name:KS-BH2CYH-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.70..1.03)

Acquired:20-01-2015 15:01:00
Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 15:04:22
Created by:JEOL

Charge number:1 Tolerance:1000.00(ppm)
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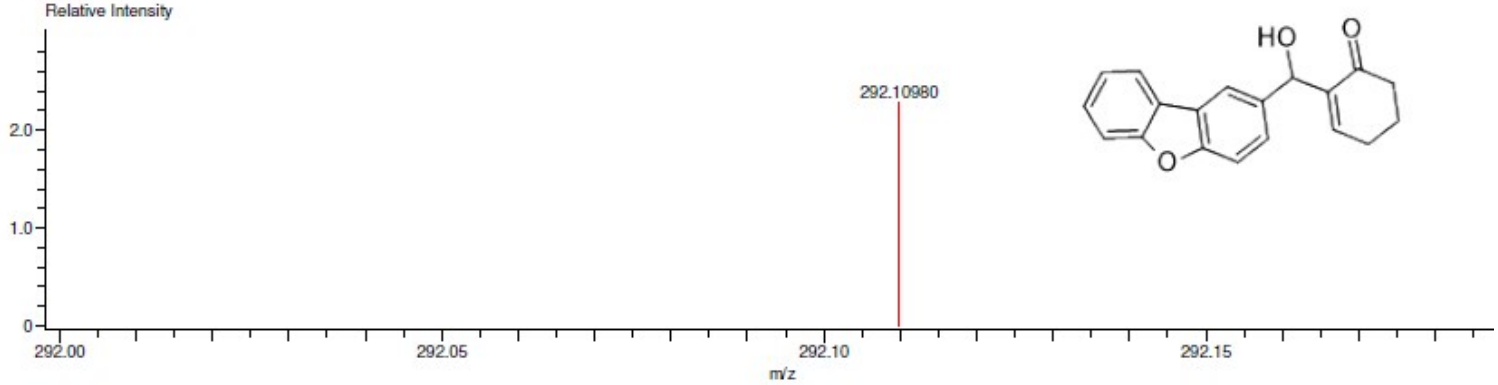
Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
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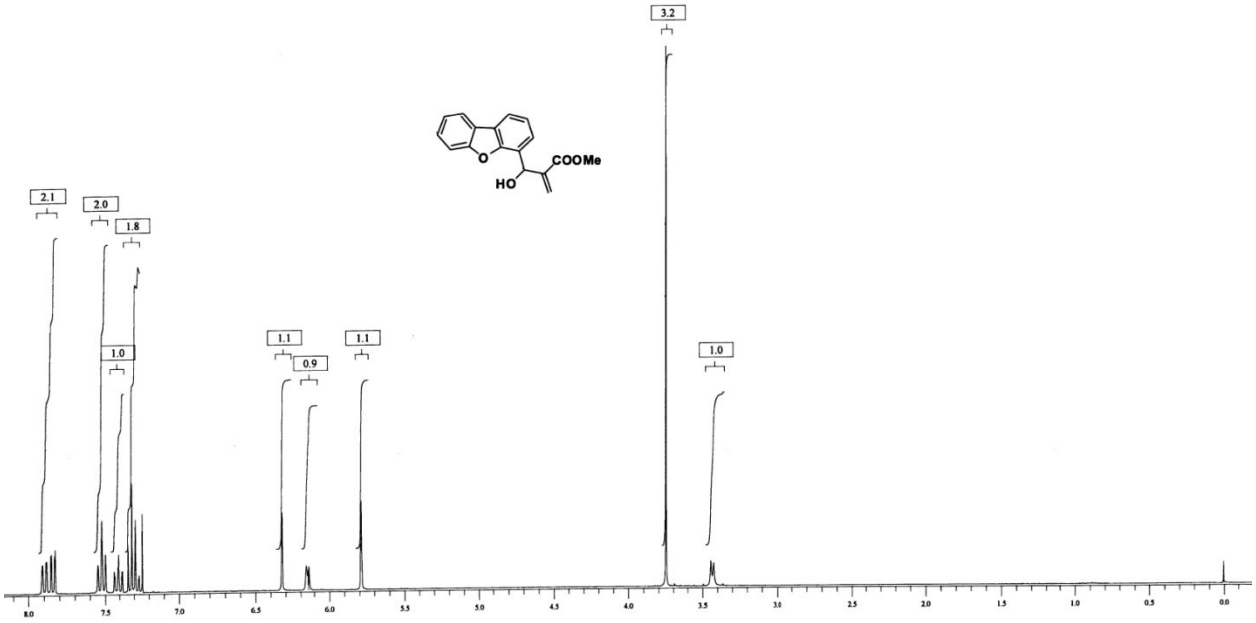
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1.0
1.1
0.9
1.1
1.0


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140.766
126.882
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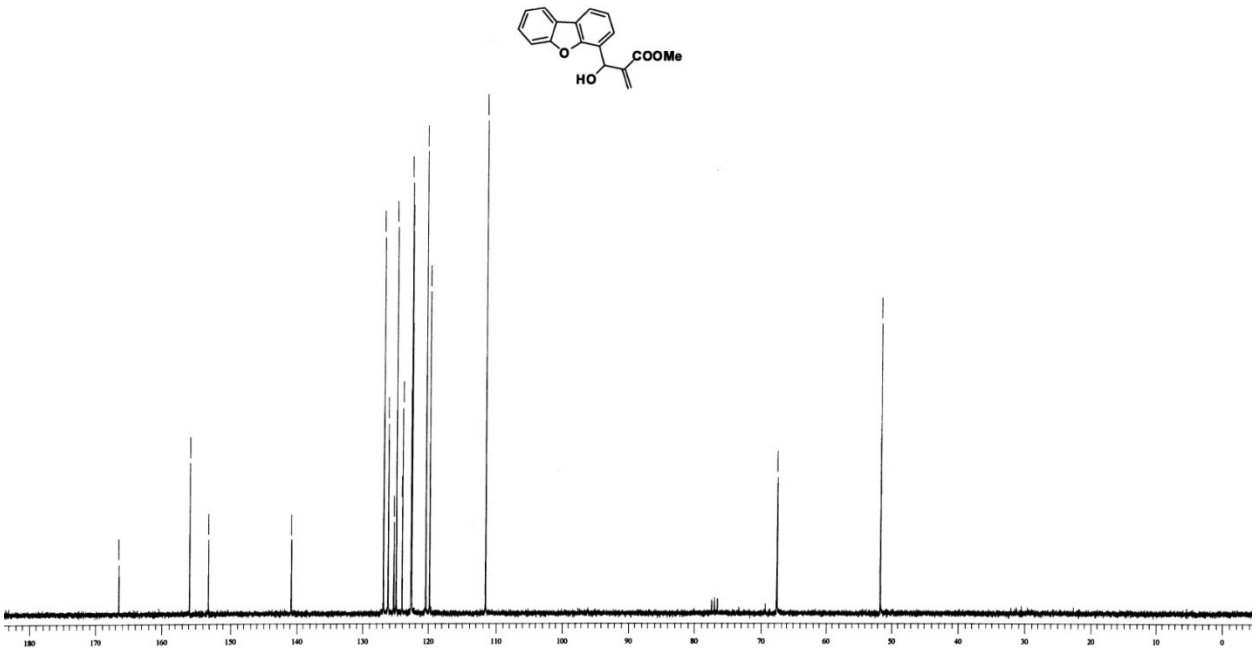
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HO

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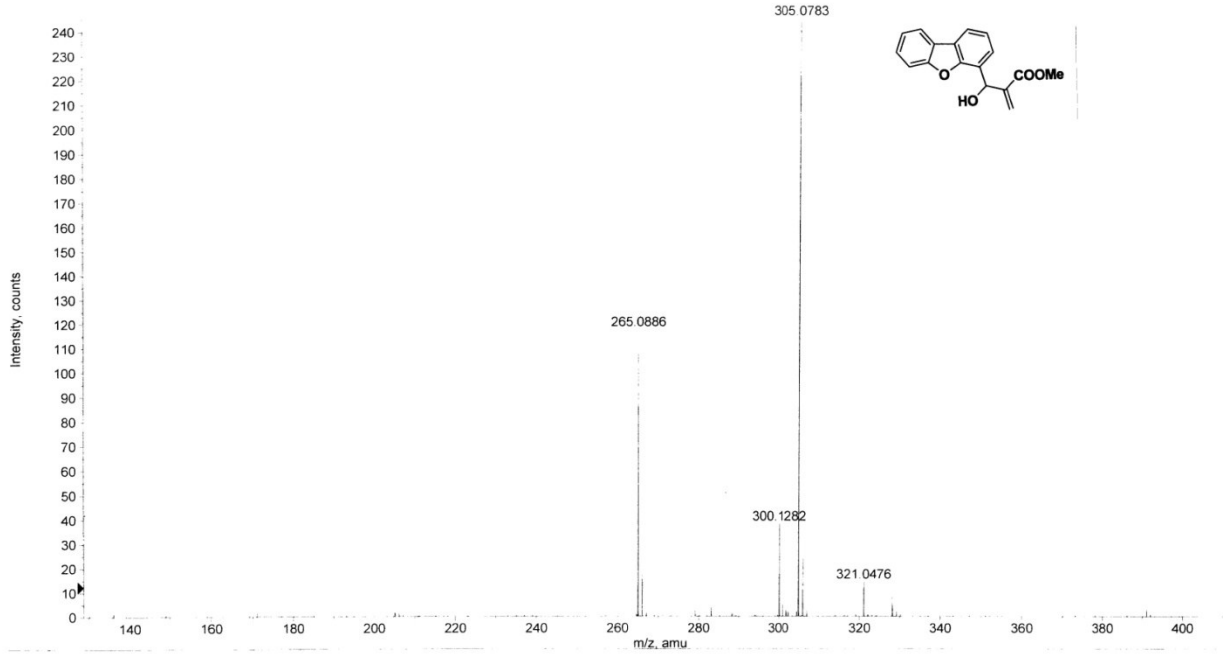
Max. 245.2 counts

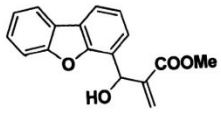


Sample ID: n/a

Acq. Date: n/a

Acq. Time: n/a

Elemental composition calculator



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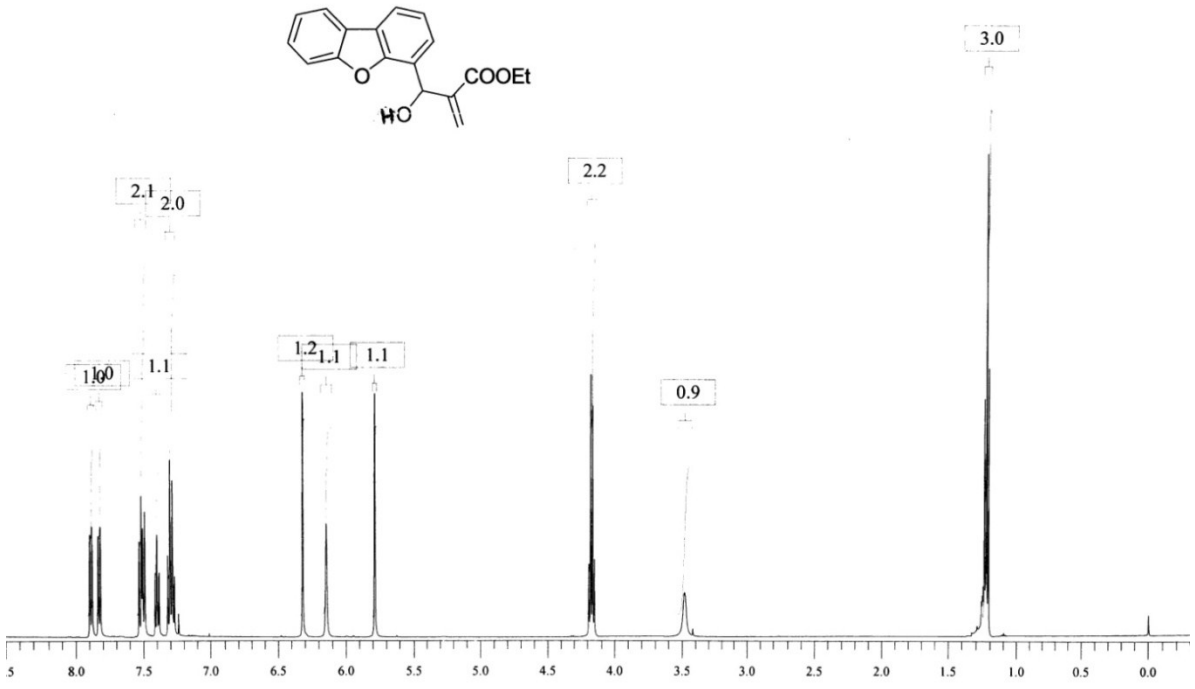
Tolerance: +5.0000 ppm
Result type: Elemental
Max num of results: 100
Min DBE: -0.5000 Max DBE: +50.0000
Electron state: OddAndEven
Num of charges: 0
Add water: N/A
Add proton: N/A
File Name: 28FEB2011.wiff

	Elements	Min Number	Max Number
1	C	0	31
2	H	0	28
3	N	0	1
4	Na	0	1
5	O	0	5

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C17 H14 O4 Na	305.0789	-0.6788	-2.2250	10.


COOEt
HO
3.0
2.2
2.1
2.0
1.2
1.1
1.1
1.0
1.0
1.1
0.9


166.192
155.852
153.132
140.905
126.949
126.012
125.263
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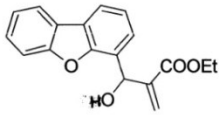
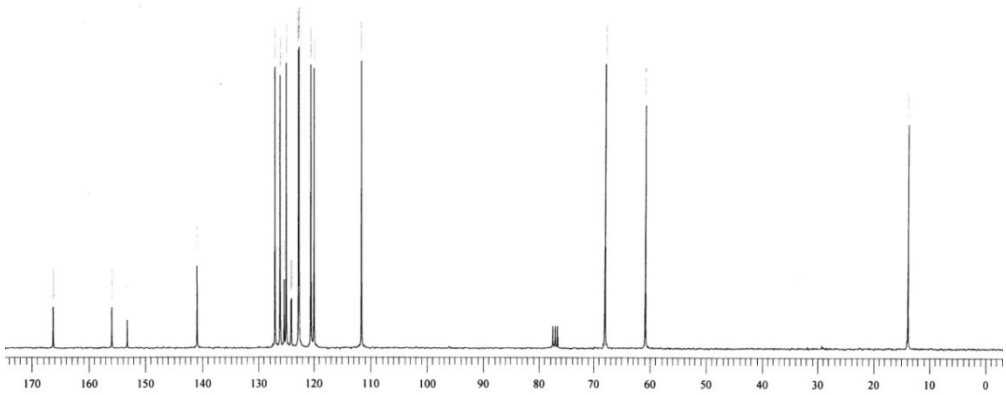
60.760
13.787


COOEt
HO



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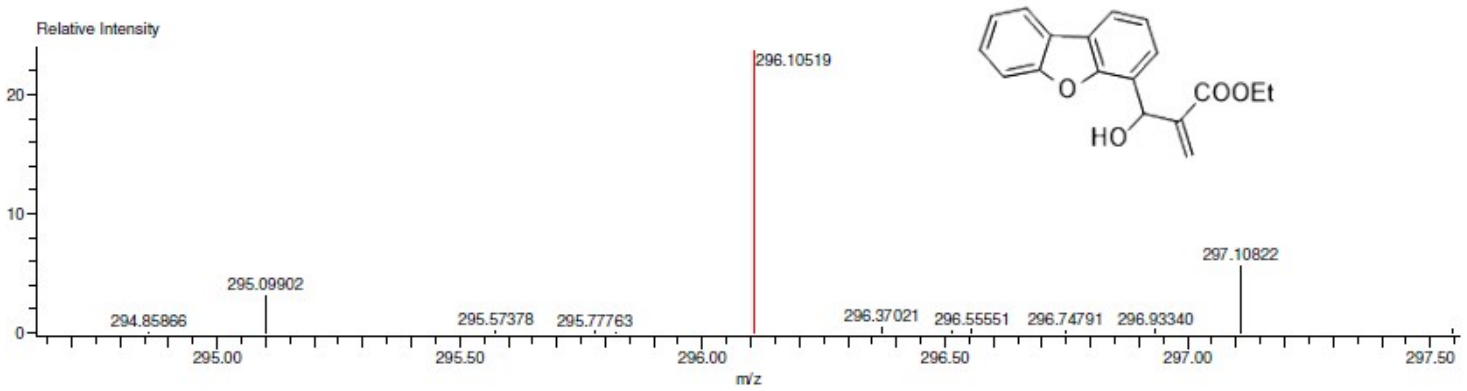
Data:KS-BH1EARNI-20-1-15
Sample Name:KS-BH1EARNI-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.47..0.67)

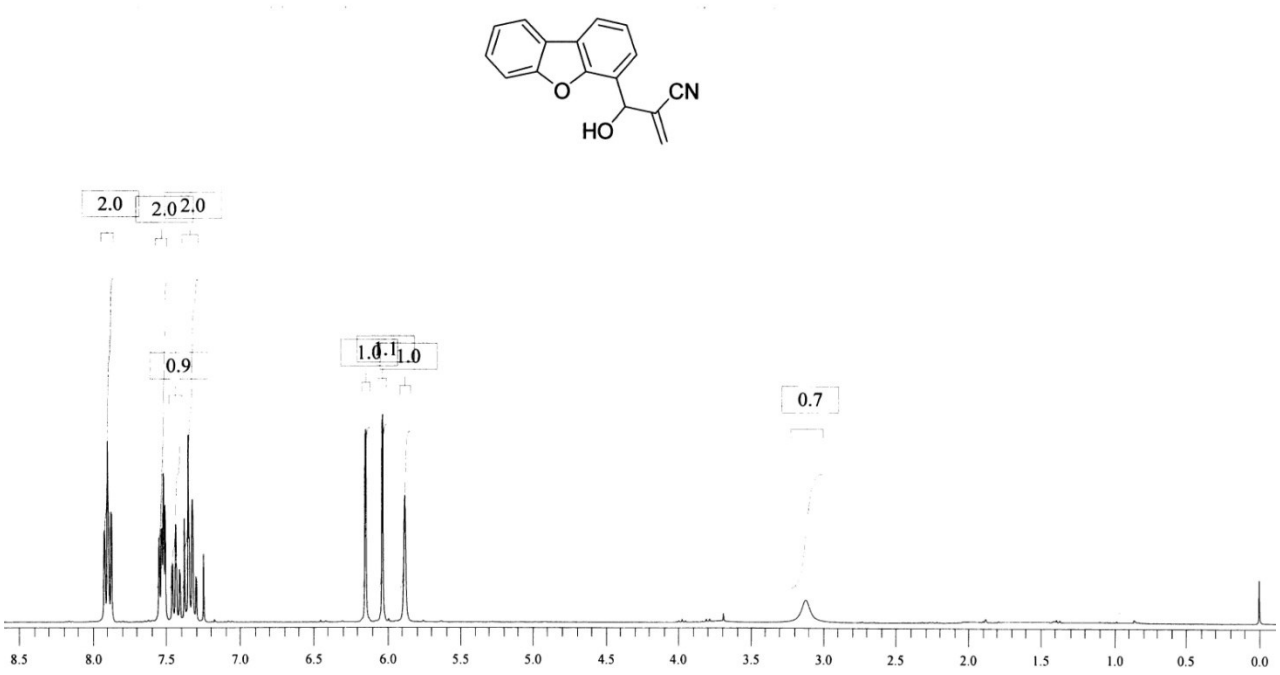
Acquired:20-01-2015 12:33:35
Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 16:28:12
Created by:JEOL

Charge number:1 Tolerance:1000.00(ppm)
Element:^{12}C:0 .. 18, ^{1}H:0 .. 17, ^{79}Br:0 .. 0, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{127}I:0 .. 0, ^{14}N:0 .. 0, ^{16}O:0 .. 4, ^{32}S:0 .. 0

Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
296.10519	176781.41	296.10486	0.33	1.12	$^{12}C_{18}{}^{1}H_{16}{}^{16}O_4$	11.0


CN
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2.0
2.0
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1.0
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0.7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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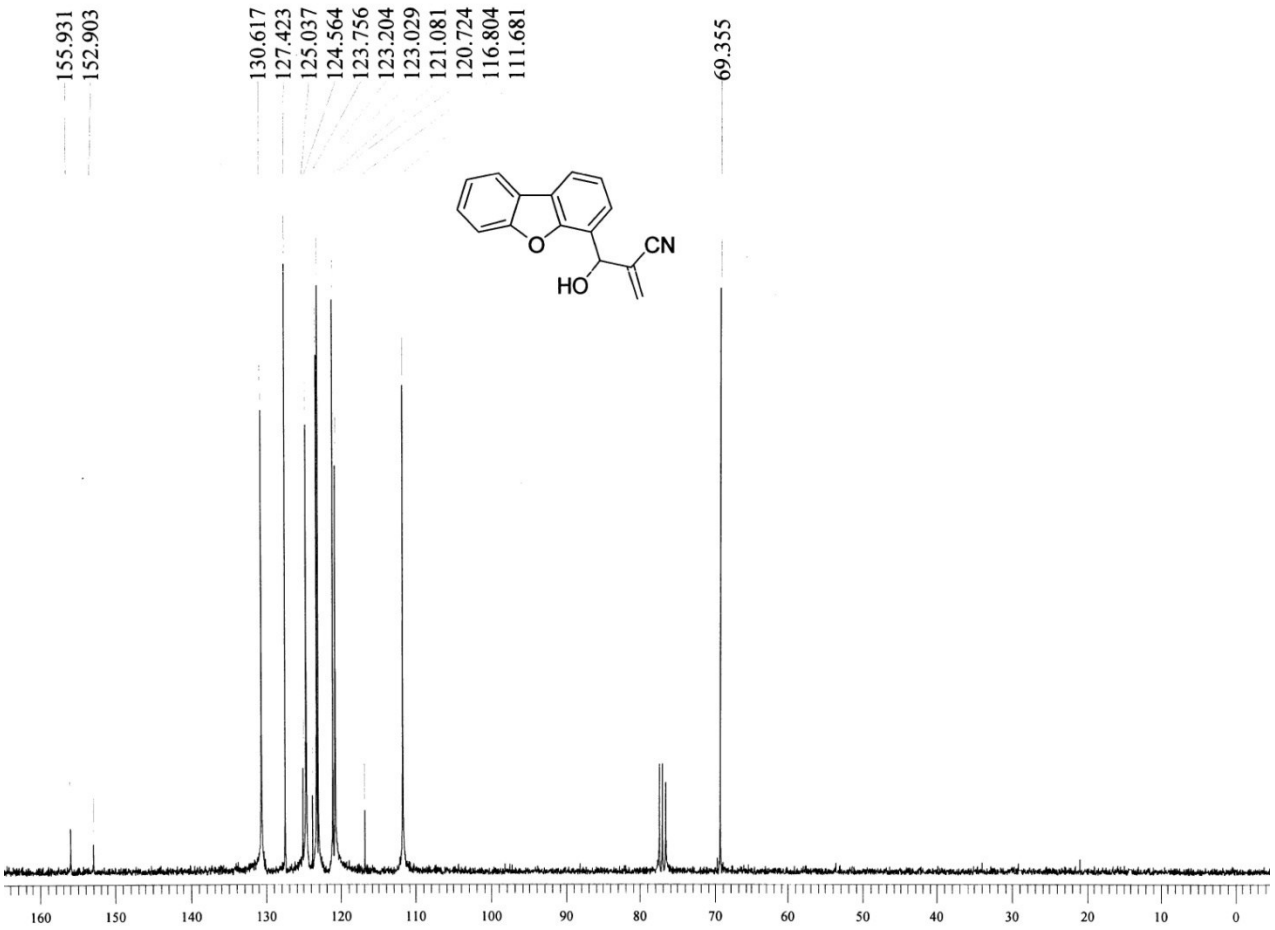
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69.355
CN
HO
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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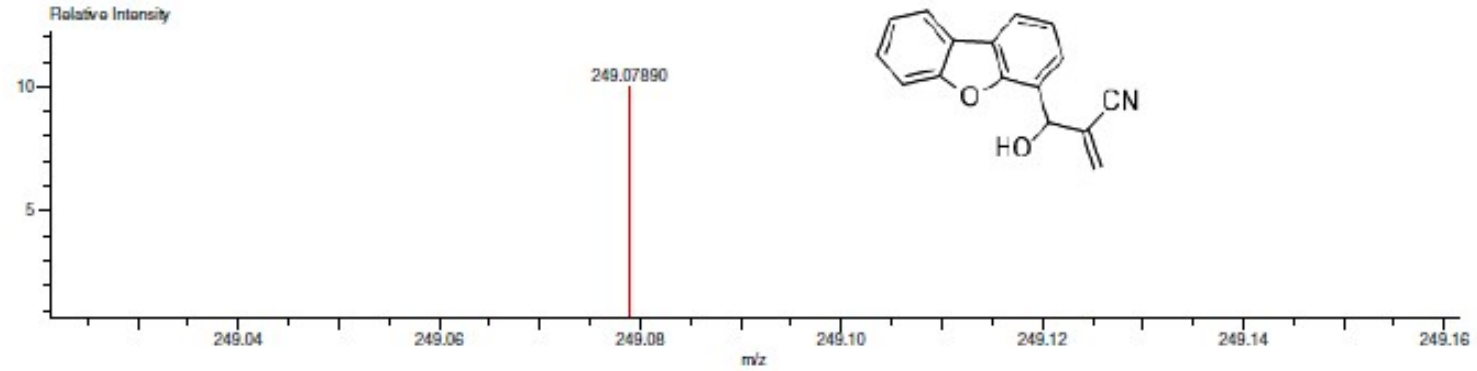
Data:KS-BH1ACRNI-20-1-15
Sample Name:KS-BH1ACRNI-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.48..0.57)

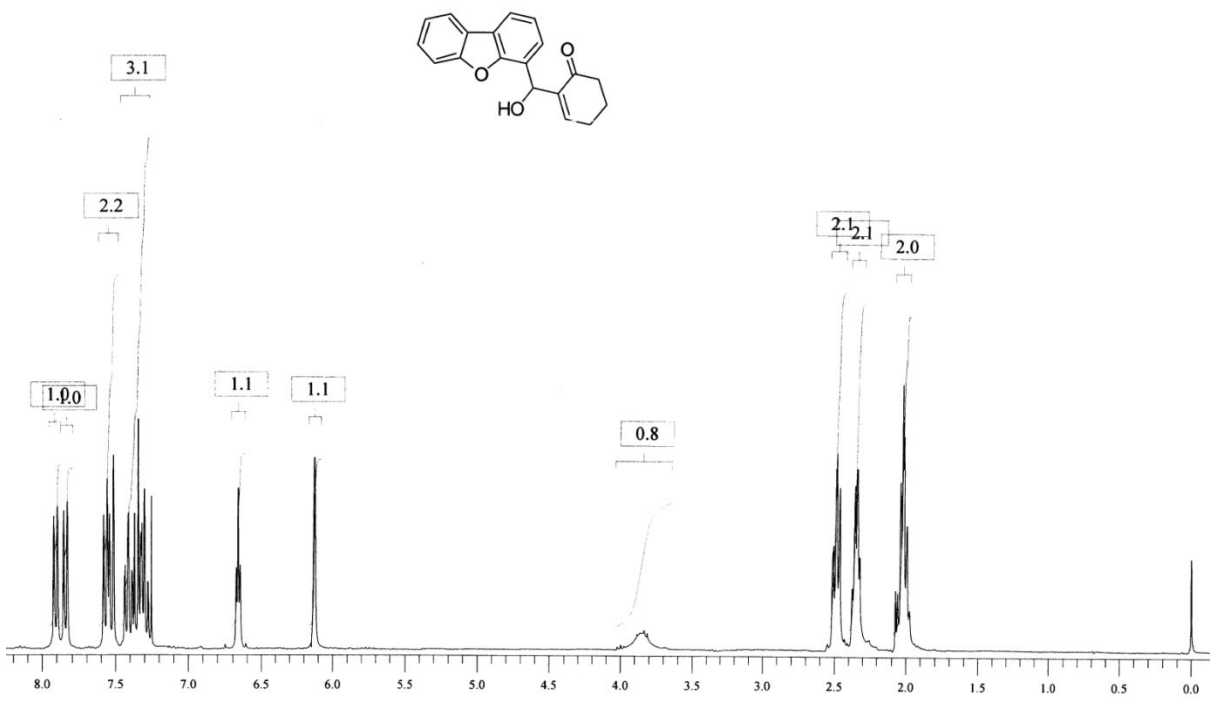
Acquired:20-01-2015 15:10:31
Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 15:14:05
Created by:JEOL

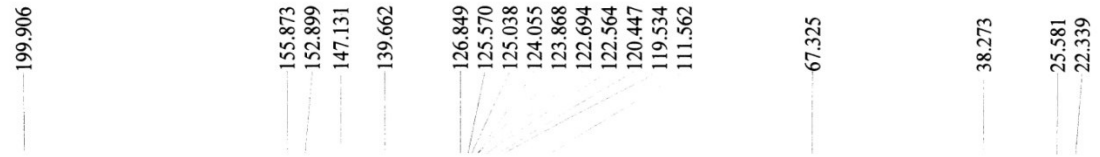
Charge number:1 Tolerance:1000.00(ppm)
Element:^{12}C:0 .. 16, ^{1}H:0 .. 11, ^{79}Br:0 .. 0, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{127}I:0 .. 0, ^{14}N:0 .. 1, ^{16}O:0 .. 2

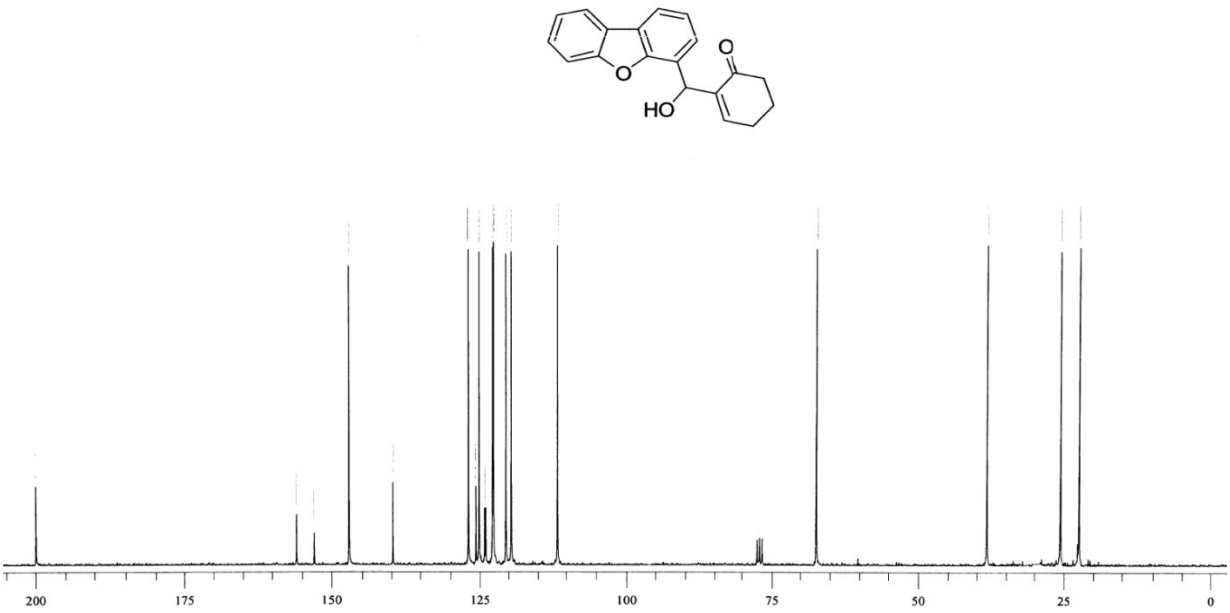
Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
249.07890	69786.92	249.07898	-0.08	-0.31	$^{12}C_{16}{}^{1}H_{11}{}^{14}N_{1}{}^{16}O_{2}$	12.0


O
HO
3.1
2.2
1.0
1.0
1.1
1.1
0.8
2.1
2.1
2.0
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


199.906
155.873
152.899
147.131
139.662
126.849
125.570
125.038
124.055
123.868
122.694
122.564
120.447
119.534
111.562
67.325
38.273
25.581
22.339


O
HO
200
175
150
125
100
75
50
25
0

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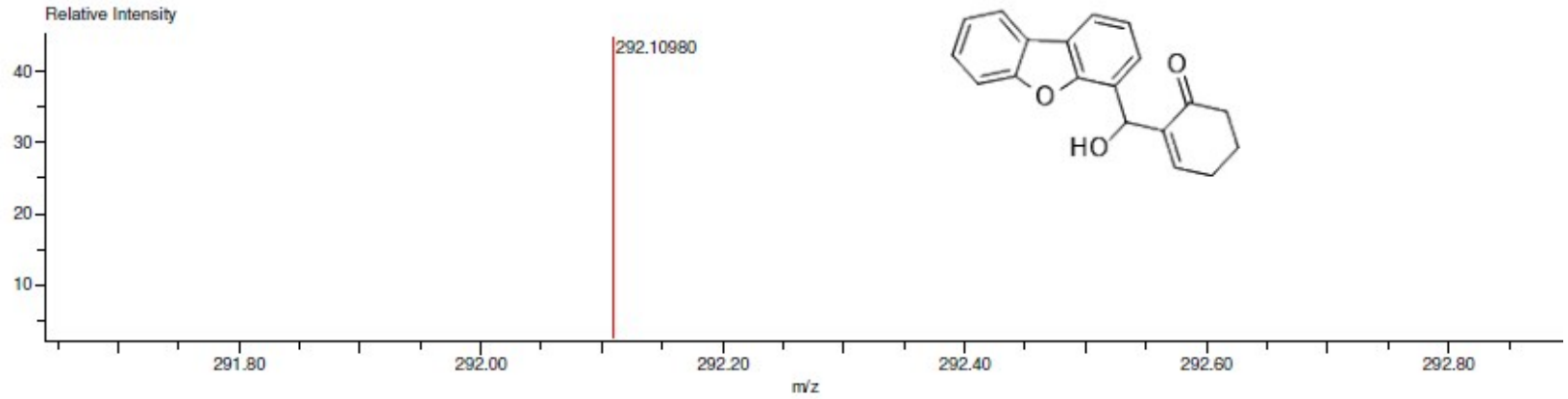
NATIONAL CENTRE FOR MASS SPECTROMETRY

Data:KS-BH12CYH-20-1-15
Sample Name:KS-BH12CYH-20-1-15, Dr K SRINIVAS, EI-HR-MS, DIP-250
Description:
Ionization Mode:EI+
History:Determine m/z[Peak Detect[Centroid,1,Area];Smooth[3]];Correct Base[];Smooth[3];Average(MS[1] 0.84..1.07)

Acquired:20-01-2015 14:12:39
Operator:JEOL
Mass Calibration data:EIPOS_17DECCAL
Created:20-01-2015 14:16:37
Created by:JEOL

Charge number:1 Tolerance:1000.00(ppm)
Element:^{12}C:0 .. 19, ^{1}H:0 .. 16, ^{79}Br:0 .. 0, ^{35}Cl:0 .. 0, ^{19}F:0 .. 0, ^{127}I:0 .. 0, ^{14}N:0 .. 0, ^{16}O:0 .. 3

Unsaturation Number:-1.5 .. 50.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
292.10980	245262.13	292.10994	-0.14	-0.49	$^{12}C_{19}{}^{1}H_{16}{}^{16}O_3$	12.0