Supplementary Material

Total synthesis of amorfrutin B via a Pd-catalyzed regioselective geranyl migration-decarboxylation-cycloaromatization cascade

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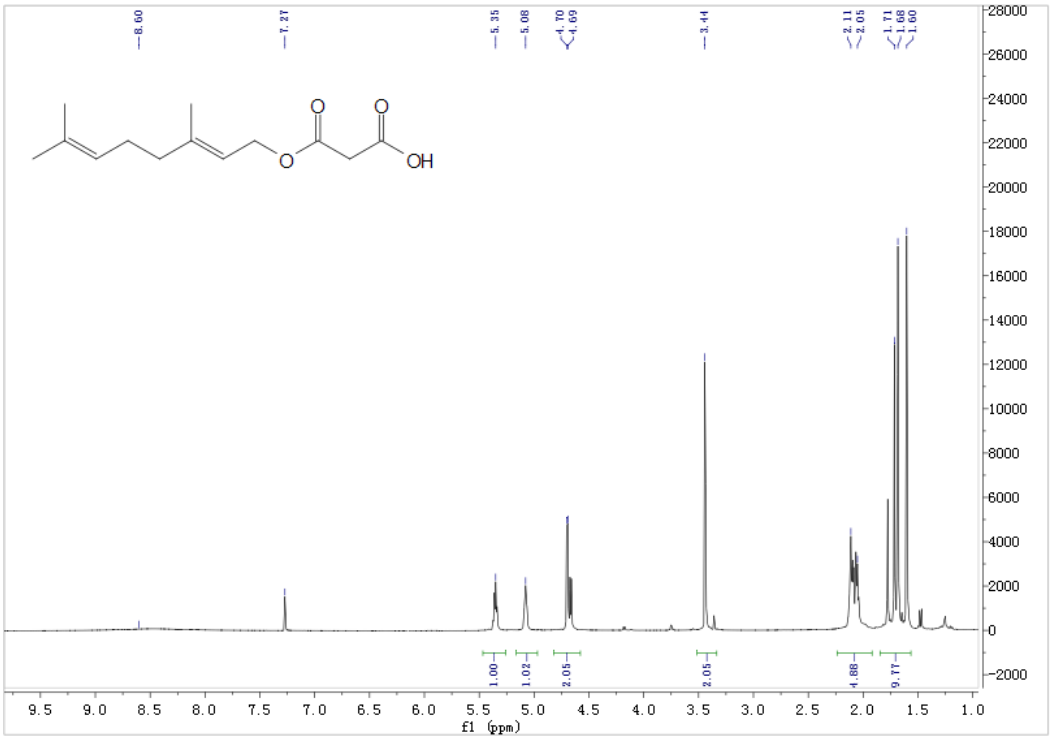
Compound **3**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4.69
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2.11
2.05
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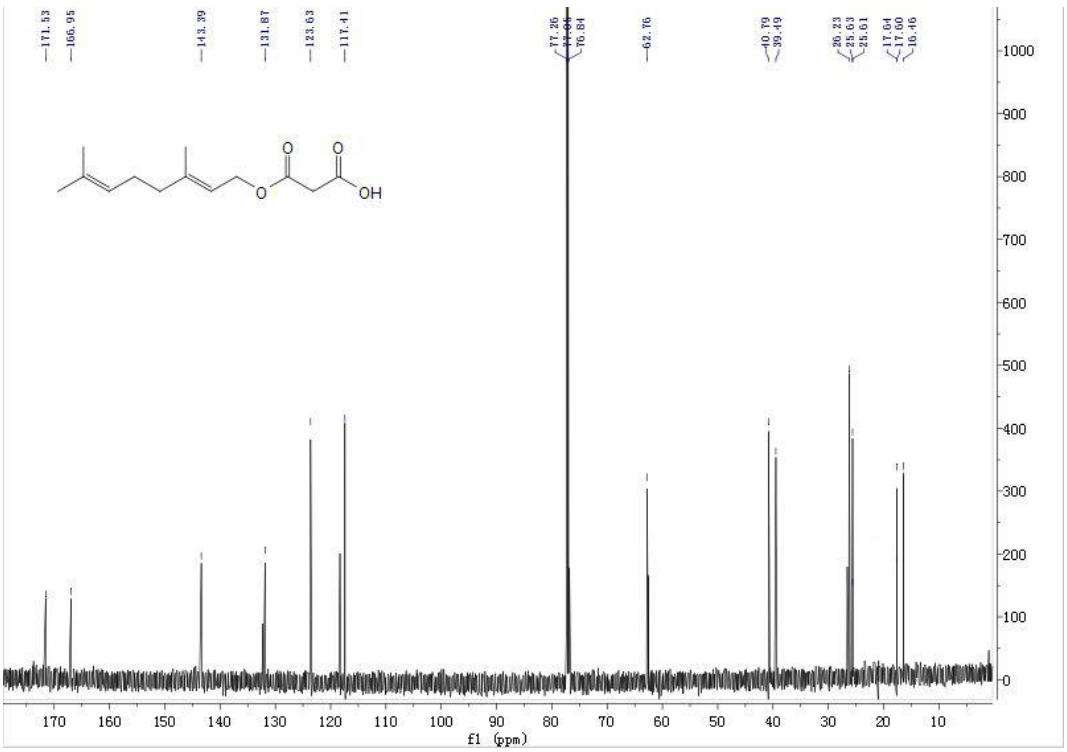
1.68
1.60
1.00
1.02
2.05
2.05
4.88
9.17
f1 (ppm)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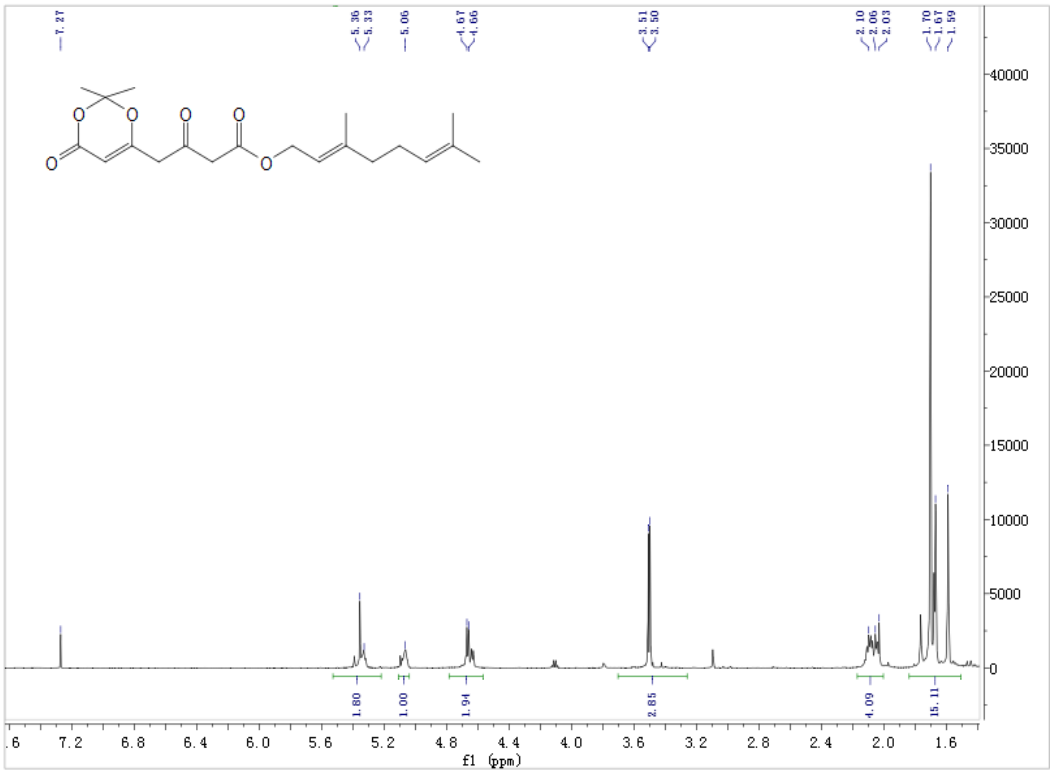
143.39
131.87
123.63
117.41
77.26
76.84
62.76
40.79
39.49
26.23
25.63
25.61
17.64
17.60
16.46
f1 (ppm)

δ /ppm	^{1}H Assignment
8.60 (brs, 1H)	COO**H**
5.35 (t, *J* = 7.3 Hz, 1H)	$CH_2CH_3C=C$**H**
5.08 (t, *J* = 6.1 Hz, 1H)	$(CH_3)_2C=C$**H**
4.70 (d, *J* = 7.2 Hz, 2H)	OC**H**$_2$
3.44 (s, 2H)	COC**H**$_2$CO
2.13 - 2.05 (m, 4H)	C=CHC**H**$_2C$**H**$_2$CH=CH
1.71 (s, 3H)	CH=CC**H**$_3$
1.68 (s, 3H), 1.60 (s, 3H)	C=CC**H**$_3C$**H**$_3$

δ /ppm	^{13}C Assignment
171.5	**C**OOH
166.9	**C**OOR
143.4, 131.8, 122.2, 117.4	$(CH_3)_2$**C**=**C**H, (CH_3)R**C**=**C**H
62.8	O**C**H$_2$
40.8	CO-**C**H$_2$-CO
39.5, 26.2	C=C**C**H$_2$**C**H$_2$C=C
25.6, 17.6, 16.5	C=CC(**C**H$_3$)$_2$,C=C**C**H$_3$R

Compound **6**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3.50
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2.06
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1.67
1.59
1.80
1.00
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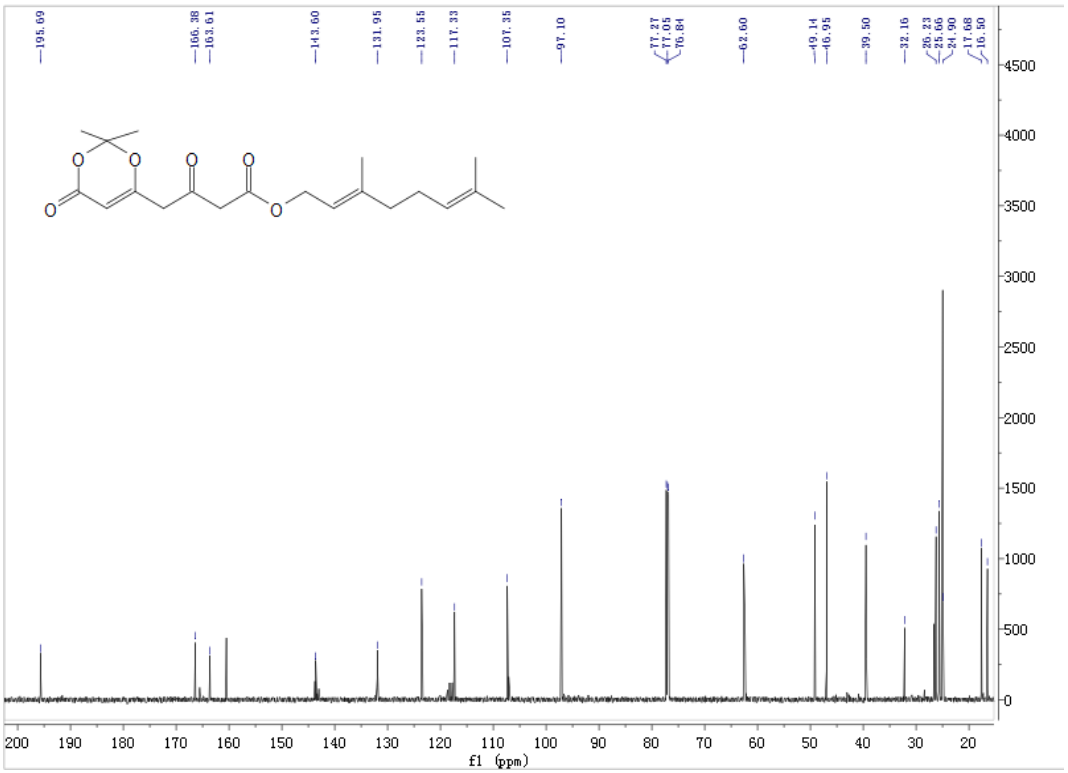
2.85
4.09
15.11
f1 (ppm)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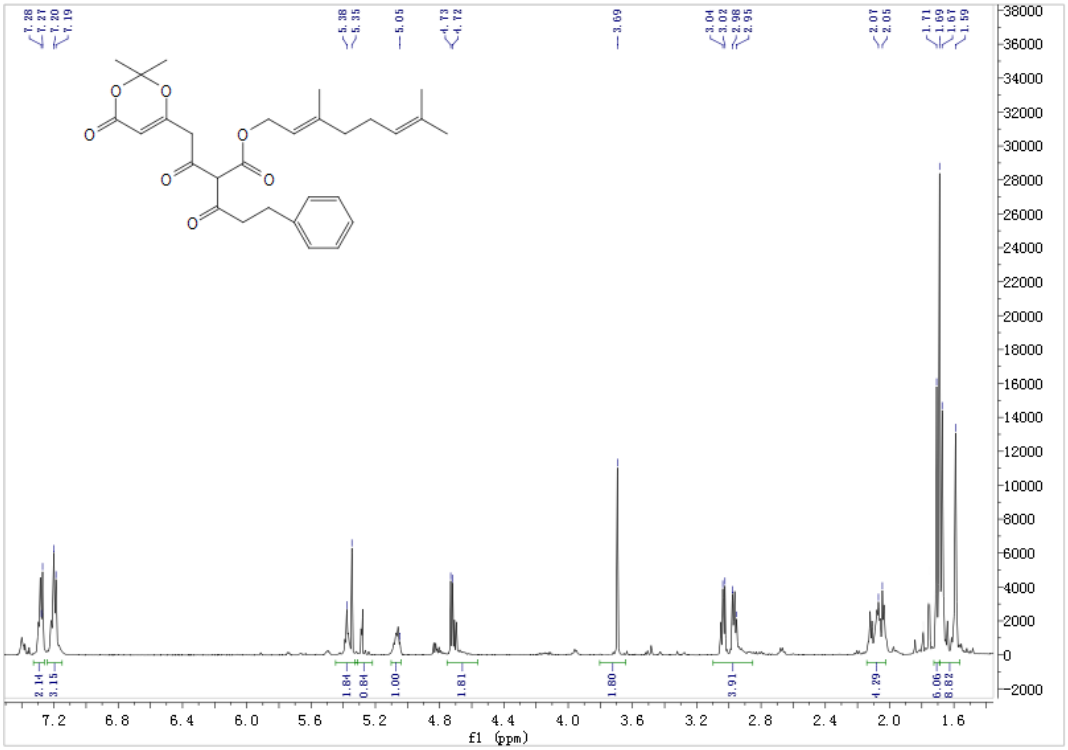
62.60
49.14
46.95
39.50
32.16
26.23
25.66
24.90
17.68
16.50
f1 (ppm)

δ/ppm	^{1}H Assignment
5.36 (s, 1H)	$CH_3C=C\mathbf{H}$
5.35 (mc, 1H)	$(CH_3)_2C=C\mathbf{H}$
5.06 (mc, 1H)	$OC=C\mathbf{H}COO$
4.67, 4.66 (d, 2H, *J* = 7.2 Hz)	$OC\mathbf{H}_2$
3.51 (s, 2H)	$COC\mathbf{H}_2CO$
3.50 (s, 2H)	$COC\mathbf{H}_2C=CH$
2.10 - 2.05 (m, 4H)	$C=CHC\mathbf{H}_2C\mathbf{H}_2$
1.70 (s, 9H)	$O_2C(C\mathbf{H}_3)_2$, $C=CC\mathbf{H}_3$
1.67 (s, 3H), 1.59 (s, 3H)	$C=C(C\mathbf{H}_3)_2$

δ /ppm	^{13}C Assignment
195.7	$CH_2\mathbf{C}OCH_2$
166.4	$COCH_2\mathbf{C}OOR$
163.6	$CH\mathbf{C}OOC(CH_3)_2$
160.5	$\mathbf{C}OCH_2CO$
143.6, 123.5	$\mathbf{C}H=\mathbf{C}CH_3R$
131.9,117.3	$\mathbf{C}H=\mathbf{C}(CH_3)_2$
107.3	$O_2\mathbf{C}(CH_3)_2$
97.1	$OC=\mathbf{C}HCOO$
62.6	$O\mathbf{C}H_2$
49.1, 46.9	$CO\mathbf{C}H_2CO$, $C=C\mathbf{C}H_2CO$
39.5, 32.2	$C=C\mathbf{C}H_2\mathbf{C}H_2C=C$
26.2, 25.7, 24.9, 17.7, 16.5	$OC(\mathbf{C}H_3)_2$, $C=C(\mathbf{C}H_3)_2$, $C=C\mathbf{C}H_3R$

Compound **9**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2.95
2.07
2.05
1.71
1.69
1.67
1.59
2.14
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4.29
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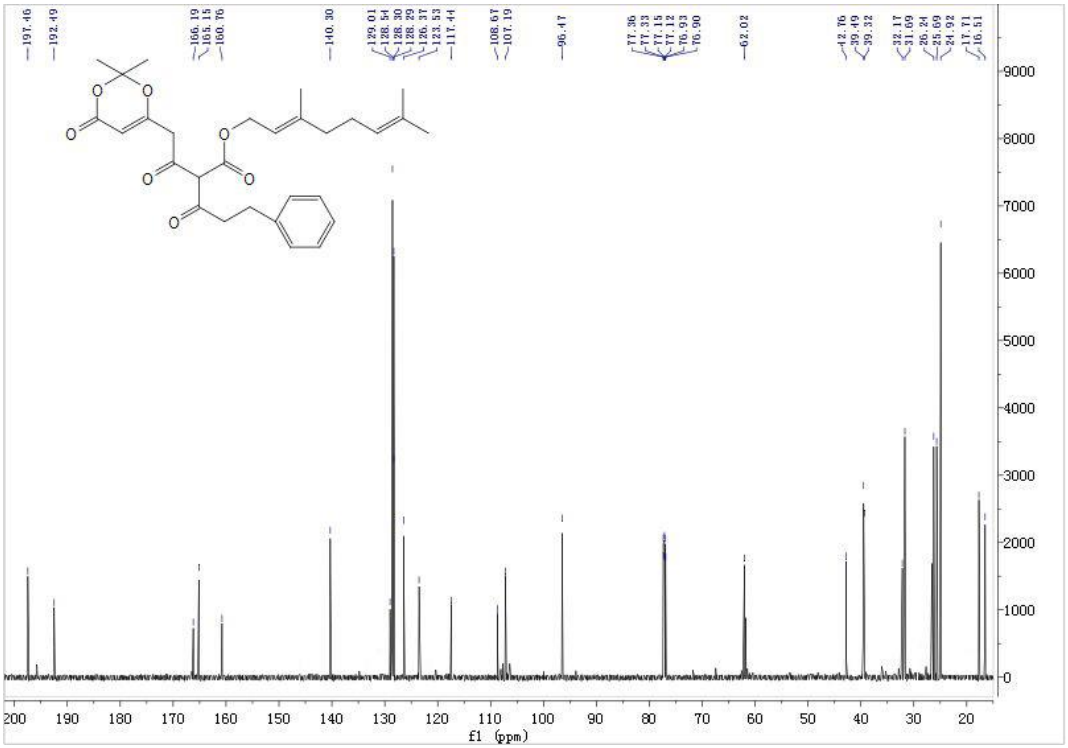
8.82
f1 (ppm)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108.67
107.19
96.47
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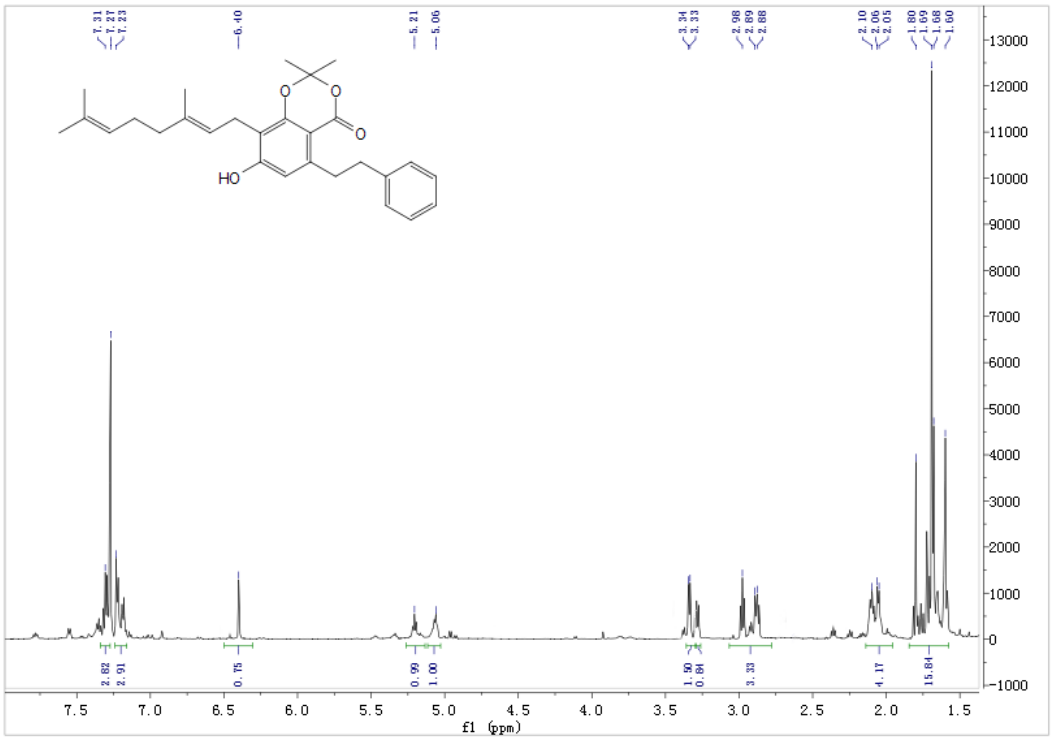
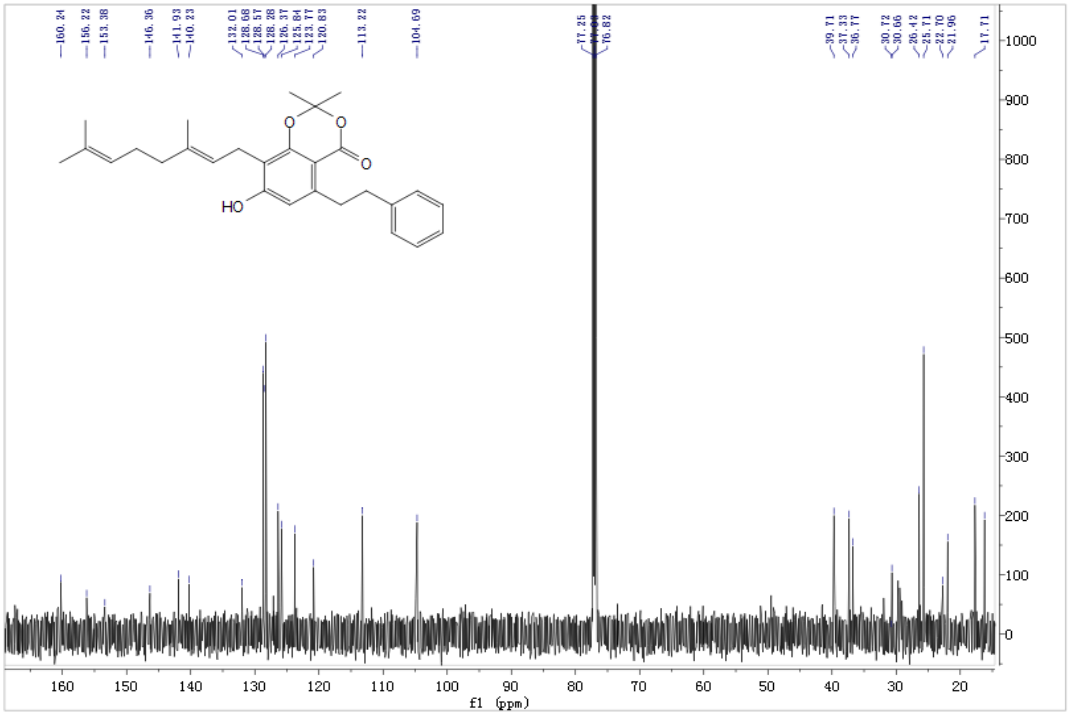
77.33
77.15
77.12
76.93
76.90
62.02
42.76
39.49
39.32
32.17
31.69
26.24
25.69
24.92
17.71
16.51
f1 (ppm)

δ/ppm	^{1}H Assignment
7.28, 7.27, 7.20, 7.19 (m, 5H)	Ar-**H**
5.38 (m, 1H)	$CH_3C=C\mathbf{H}$
5.35 (s, 1H)	$(CH_3)_2C=C\mathbf{H}$
5.28 (s,1H)	CO**C**COO
5.05 (mc, 1H)	OC=C**H**COO
4.73 (d, 2H, *J* = 7.4 Hz)	O$\mathbf{CH_2}$CH=C
3.69 (s, 2H)	COC$\mathbf{H_2}$CO
3.04 - 2.95 (m, 4H)	COC$\mathbf{H_2}$C$\mathbf{H_2}$Ar
2.07 - 2.05 (m, 4H)	C=CHC$\mathbf{H_2}$C$\mathbf{H_2}$C=C
1.71 -1.59 (s, 15H)	$O_2C(C\mathbf{H_3})_2$, C=CC$\mathbf{H_3}$，C=C(C$\mathbf{H_3}$)$_2$

δ /ppm	^{13}C Assignment
197.5	$CH_2\mathbf{C}$=OCHCOCH$_2$CH$_2$Ar
192.5	ArCH$_2$CH$_2\mathbf{C}$=O
165.2	**C**OOCH$_2$=CRCH$_3$
165.1	CH**C**OOC(CH$_3$)$_2$
160.8	CH=**C**O
140.3	Ar(**C**)CH$_2$CH$_2$
129.0, 117.4	**C**H=**C**(CH$_3$)R
128.5, 128.3, 128.2	Ar(**C**)
123.5, 108.7	**C**H=**C**(CH$_3$)$_2$
107.2	O$_2\mathbf{C}$(CH$_3$)$_2$
96.5	OC=**C**HCOO
62.0	CO**C**H$_2$COO
61.8	O**C**H$_2$CH
42.7	C=C**C**H$_2$CO
39.5, 31.7	C=C**C**H$_2$**C**H$_2$C=C
39.3, 32.2	Ar**C**H$_2$**C**H$_2$
26.2, 25.7, 24.9, 17.7, 16.5	OC(**C**H$_3$)$_2$, C=C(**C**H$_3$)$_2$, C=C**C**H$_3$R

Compound **10**

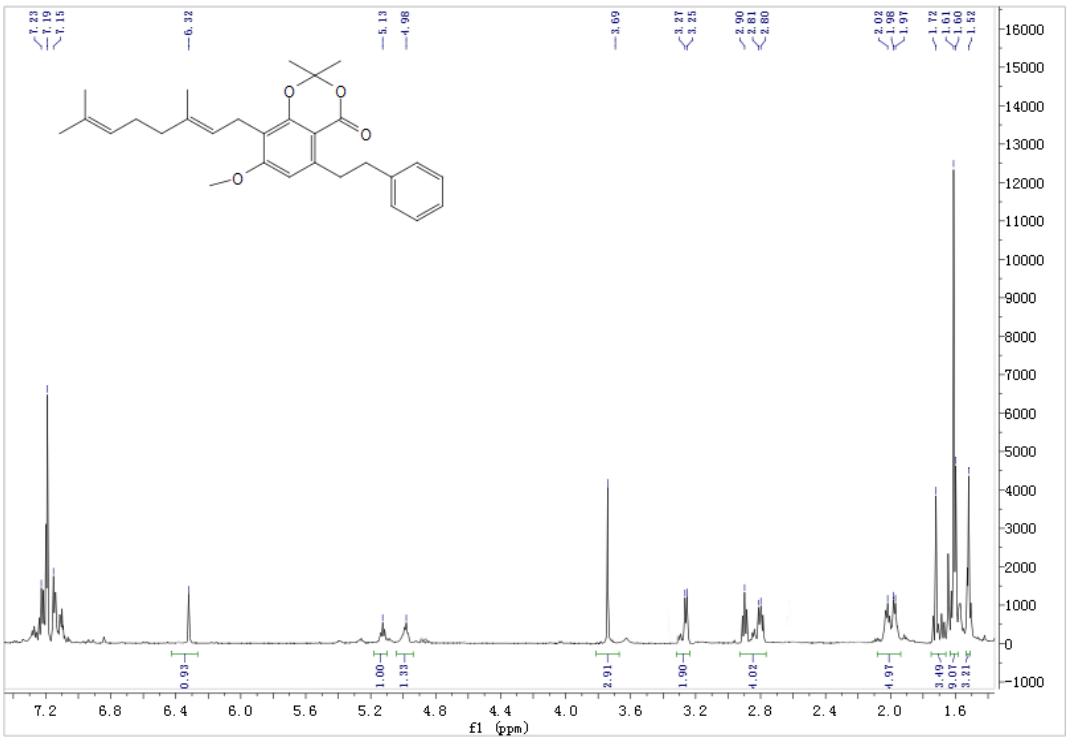




δ/ppm	^{1}H Assignment
7.31 - 7.23 (m, 5H)	Ar-**H**
6.40 (s, 1H)	Ar-**H**
5.21 (t, 1H, *J* = 7.2 Hz)	$RCH_3C=C\mathbf{H}$
5.06 (t, 1H, *J* = 7.2 Hz)	$(CH_3)_2C=C\mathbf{H}$
3.34, 3.33 (d, 2H, *J* = 7.3 Hz)	$ArC\mathbf{H}_2CH=C$
2.98 - 2.88 (m, 4H)	$ArC\mathbf{H}_2C\mathbf{H}_2Ar$
2.10 - 2.05 (m, 4H)	$C=CHC\mathbf{H}_2C\mathbf{H}_2C=C$
1.80, 1.69, 1.68, 1.60 (s, 15H)	$O_2C(C\mathbf{H}_3)_2$, $C=CC\mathbf{H}_3$, $C=C(C\mathbf{H}_3)_2$,

δ /ppm	^{13}C Assignment
160.2	Ar-**C**OOR
156.2	Ar(**C**)-OH
152.4	Ar(**C**)-$OC(CH_3)_2$
146.3, 125.8	**C**H=**C**(CH_3)R
141.9, 140.2	Ar(**C**)-CH_2CH_2-Ar(**C**)
132.1,126.4	**C**H=**C**$(CH_3)_2$
128.7, 128.6, 128.3	Ar
122.8	Ar(**C**)-$CH_2C=C$
120.8	Ar(**C**)-COOR
113.2	O**C**$(CH_3)_2$
104.7	Ar(**C**)
39.7, 30.7	$C=C\mathbf{C}H_2\mathbf{C}H_2C=C$
37.5, 36.7	$Ar\mathbf{C}H_2\mathbf{C}H_2Ar$
26.4, 17.7	$C=C(\mathbf{C}H_3)_2$
25.7	Ar-**C**H_2-C=C
22.7, 21.9, 16.2	$C(\mathbf{C}H_3)_2$, $C=CC\mathbf{H}_3R$

Compound **13**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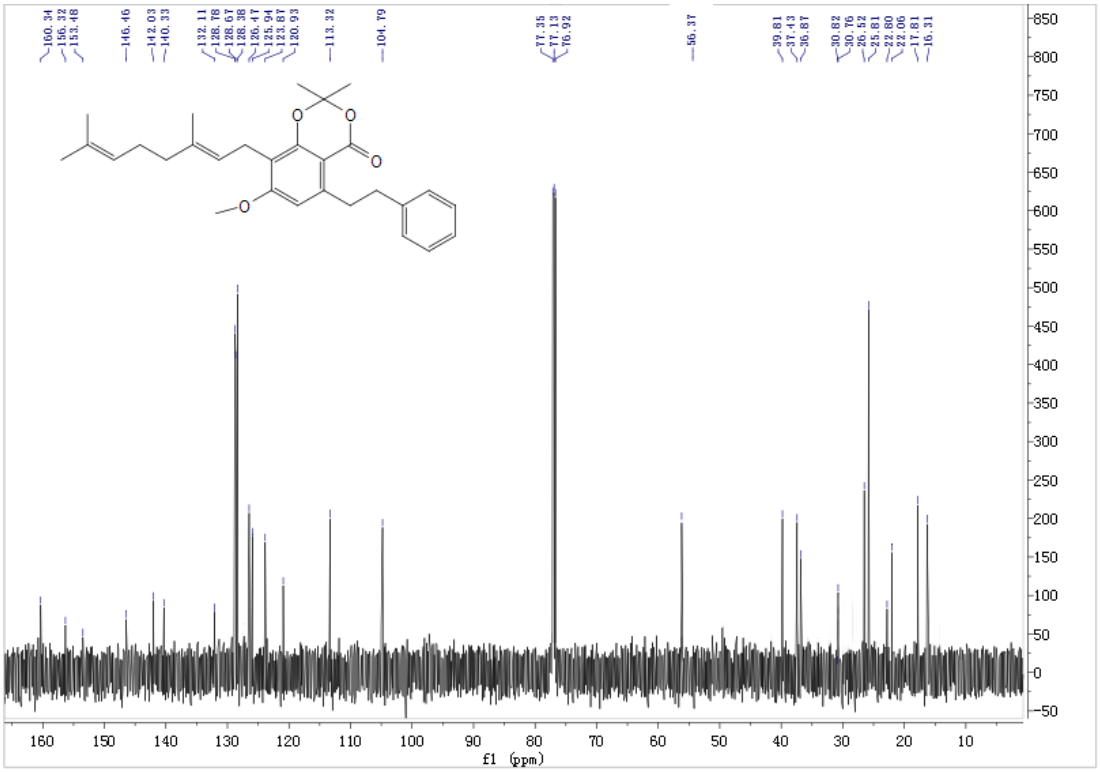
7.19
7.15
6.32
5.13
4.98
3.69
3.27
3.25
2.90
2.81
2.80
2.02
1.98
1.97
1.72
1.61
1.60
1.52
0.93
1.00
1.33
2.91
1.90
4.02
4.97
3.49
9.07
3.21
f1 (ppm)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140.33
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128.67
128.38
126.47
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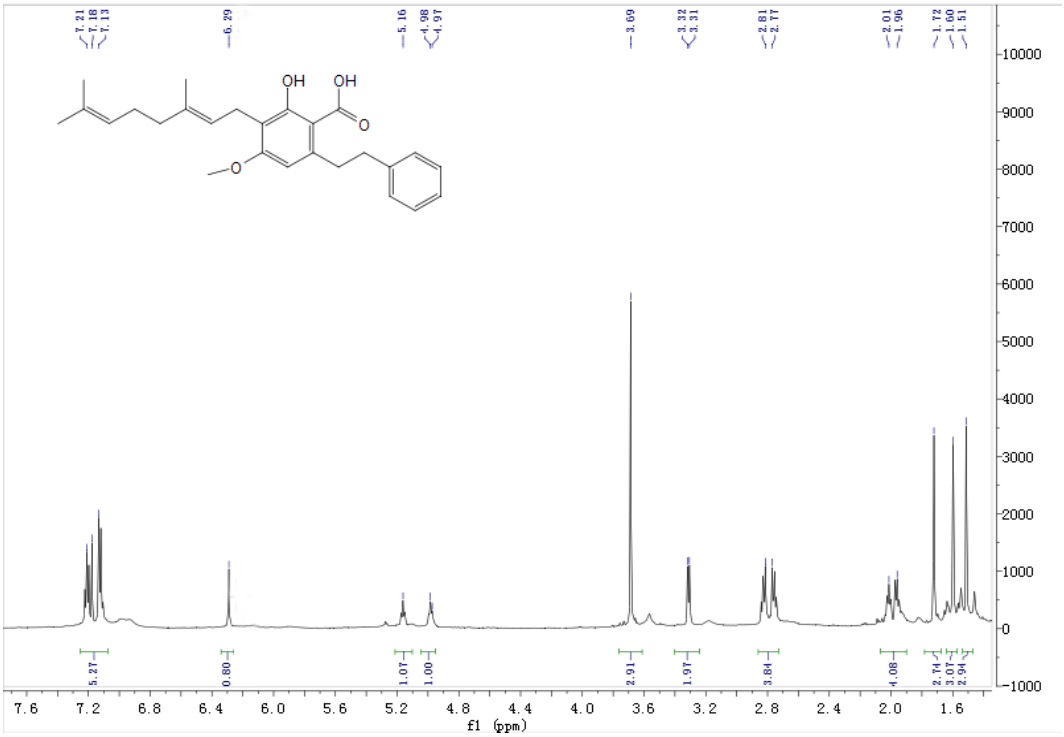
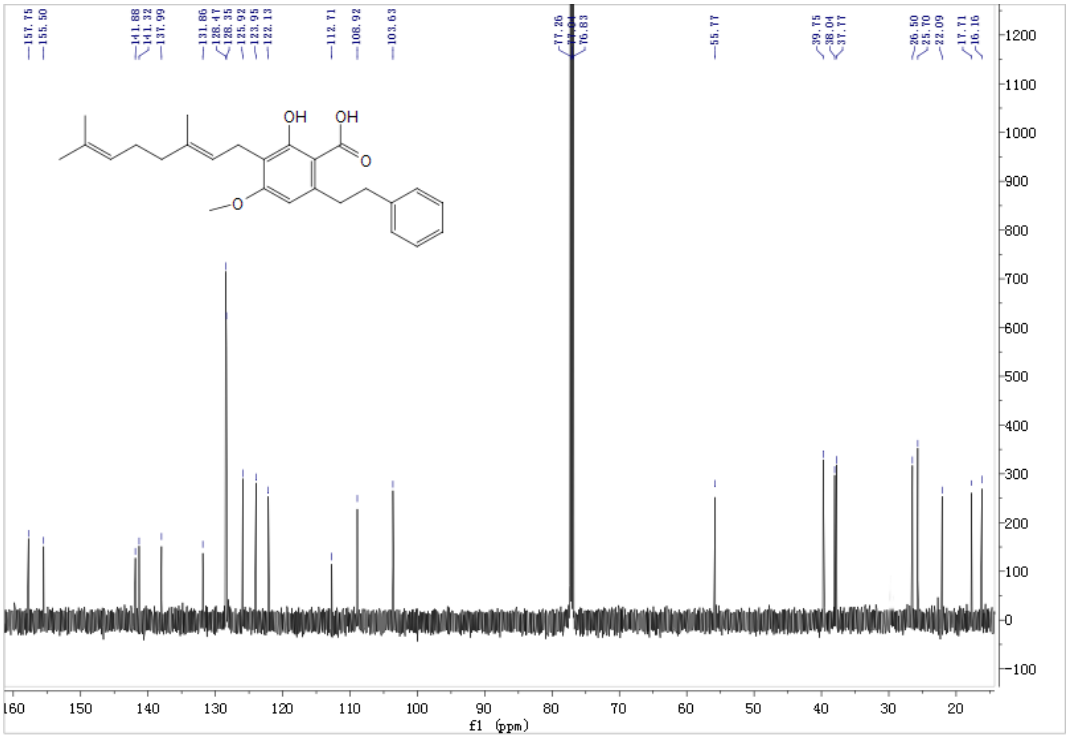
123.87
120.93
113.32
104.79
77.35
77.13
76.92
56.37
39.81
37.43
36.87
30.82
30.76
26.52
25.81
22.80
22.06
17.81
16.31
f1 (ppm)

δ/ppm	^{1}H Assignment
7.23, 7.19, 7.15 (m, 5H)	Ar-**H**
6.32 (s,1H)	Ar-**H**
5.12 (t, 1H, *J* = 7.2 Hz)	RCH_3C=C**H**
4.98 (t, 1H, *J* = 7.2 Hz)	$(CH_3)_2C$=C**H**
3.78 (s, 3H)	COC**H**$_3$
3.27, 3.25 (d, 2H, *J* = 7.3 Hz)	ArC**H**$_2$CH=C
2.90 - 2.80 (m, 4H)	ArC**H**$_2$C**H**$_2$Ar
2.02 - 1.97 (m, 4H)	C=CHC**H**$_2$C**H**$_2$C=C
1.72, 1.60, 1.52 (s, 15H)	$O_2C(C$**H**$_3)_2$, C=CC**H**$_3$, C=C(C**H**$_3)_2$,

δ /ppm	^{13}C Assignment
160.3	Ar-**C**OOR
156.3	Ar(**C**)-OH
152.4	Ar(**C**)-OC$(CH_3)_2$
146.5,126.5	**C**H=**C**(CH_3)R
141.9, 140.3	Ar(**C**)-CH_2CH_2-Ar(**C**)
132.1,125.9	**C**H=**C**$(CH_3)_2$
128.8, 128.7, 128.4	Ar
122.9	Ar(**C**)-CH_2C=C
120.8	Ar(**C**)-COOR
113.3	O**C**$(CH_3)_2$
104.7	Ar(**C**)
56.4	O**C**H_3
39.8, 30.9	C=C**C**H_2**C**H_2C=C
37.4, 36.9	Ar**C**H_2**C**H_2Ar
26.5,17.8	C=C(**C**$H_3)_2$
25.7	Ar-**C**H_2-C=C
22.9, 22.1, 16.3	C(**C**$H_3)_2$, C=CC**H**$_3$R

Amorfrutin B





δ/ppm	^{1}H Assignment
7.21 - 7.13 (m, 5H)	Ar-**H**
6.29 (s, 1H)	O**H**
5.16 (t, 1H, *J* = 7.1 Hz)	RCH_3C=C**H**
4.98 (t, 1H, *J* = 7.1 Hz)	$(CH_3)_2$C=C**H**
3.69 (s, 3H)	OC**H**$_3$
3.32, 3.31 (d, 2H, *J* = 7.3 Hz)	ArC**H**$_2$CH=C
2.81- 2.77 (m, 4H)	ArC**H**$_2$C**H**$_2$Ar
2.01 - 1.96 (m, 4H)	C=CHC**H**$_2$C**H**$_2$C=C
1.72 (s, 3H), 1.60 (s, 3H), 1.51 (s, 3H)	C=CC**H**$_3$, C=CC**H**$_3$C**H**$_3$

δ /ppm	^{13}C Assignment
157.7	**C**OOH
155.5	Ar(**C**)-OCH_3
141.8	Ar(**C**)-OH
141.3	Ar(**C**)-CH_2CH_2
137.9	CH_2CH_2-Ar(**C**)
131.8, 123.9	**C**H=**C**(CH_3)R
128.5, 128.3	Ar
125.9, 122.1	**C**H=**C**$(CH_3)_2$
112.7	Ar(**C**)-CH_2C=C
108.9	Ar(**C**)-COOH
103.6	Ar(**C**)
55.7	O**C**H_3
39.7, 26.5	C=C**C**H_2**C**H_2C=C
38.0, 37.7	Ar**C**H_2**C**H_2Ar
25.7,17.7	C=C(**C**$H_3)_2$
22.1	Ar-**C**H_2-C=C
16.1	C=C**C**H_3R