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# *Supplementary Information*

# Synthetic studies en route to the first total synthesis of a naturally occurring quinone from *Acorus gramineus*, *iso*-merrilliaquinone, *iso*-magnoshinin and 2-*epi*-3, 4-dihydro magnoshinin

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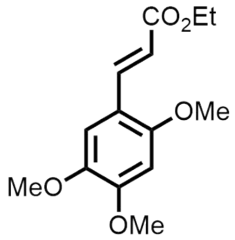
## General Information

**General:** All the reagents were purchased from Sigma-Aldrich and other commercial suppliers and used without further purification. While most of the desired solvents supplied by commercial suppliers were dried using the standard drying procedures.[1] All nonaqueous reactions were executed under nitrogen atmosphere. The $^{1}H$ and $^{13}C$ NMR spectra were recorded on 400 and 100 MHz Bruker spectrometer respectively using TMS signal as an internal standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet/pentet, td = triplet of doublet, and m = multiplet. The chemical shifts are reported as δ values (ppm) and the coupling constants (*J*) values are reported in Hz. Reactions monitoring were done using precoated $SiO_2$-gel GF254 glass TLC plates while spot visualizations were done under UV light and spot developing stains like *p*-anisaldehyde or $KMnO_4$. Purifications were done using column chromatography with 100-200 mesh size $SiO_2$-gel as the stationary phase.



**(*E*)-Ethyl 3-(2, 4, 5-trimethoxyphenyl) acrylate (16):** To a stirred solution of 2, 4, 5-trimethoxybenzaldehyde **15** (5.6 g, 28.57 mmol) in benzene (8 mL) was added carboxymethylene triphenylphosphorane (14.93 g, 42.86 mmol) and the reaction was then refluxed for 2 h. On complete consumption of starting material and on indication of formation of a new spot by the TLC analysis, the reaction was worked up by removing the solvent under reduced pressure and then subjecting the resultant residue to $SiO_2$ gel column chromatographic purification using hexane/ethyl acetate (4:1) as the eluent to arrive at **16** (*E*-isomer) (6.58 g, 24.709 mmol, 86% yield) in the form of a white solid. IR (neat): $\nu_{max}$ 2838, 1702, 1608, 1515, 1467, 1297, 1256, 1213, 1168, 1032 cm$^{-1}$; $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.1 Hz, 1H), 7.01 (s, 1H), 6.50 (s, 1H), 6.37 (d, *J* =16.1 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.76 , 153.81 , 151.99 , 143.15 , 139.45 , 115.76 , 114.87, 110.73, 96.77, 60.21 , 56.35, 56.30, 56.02, 14.39.

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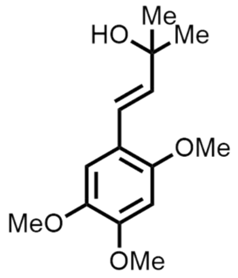
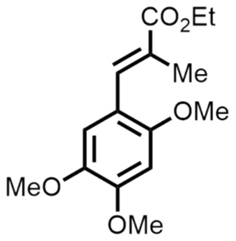
**Ref:**

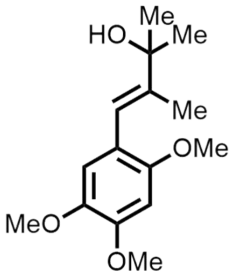
1. Armarego, D. L. F.; Perrin, D. D. *Purification of laboratory Chemicals* IV Edition



**(*E*)-2-methyl-4-(2, 4, 5-trimethoxyphenyl)but-3-en-2-ol (17):** To a solution of **16** (6.58 g, 24.74 mmol) in dry THF (4 mL) at -78 ˚C was added 3.0 M solution of methyl lithium in diethoxy methane (82.4 mL, 247.36 mmol). The reaction mixture was allowed to warm to rt and continued stirring at same temperature for 4.5 h until complete consumption of starting material and formation of a new spot was indicated by the TLC analysis. The reaction was quenched with saturated aq. NH$_4$Cl solution followed by extraction with ethyl acetate (4 × 40 mL). Drying of the organic phase over Na$_2$SO$_4$ and then removal of solvent under reduced pressure gave an oily residue which was subjected to column chromatography to access pure **17** (4.36 g, 17.280 mmol, 70% yield) as a colorless oil. IR (neat): $\nu_{max}$ 2963, 2935, 2834, 1608, 1509, 1465, 1260, 1206, 1039, 804 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ ) δ 6.98 (s, 1H), 6.86 (d, $J$ = 16.4 Hz, 1H), 6.50 (s, 1H), 6.24 (d, $J$ = 16.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 1.44 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.37, 149.38, 143.37, 135.82, 120.58, 117.58, 109.72, 97.75, 71.31, 56.63, 56.53, 56.10, 29.70 (2C).

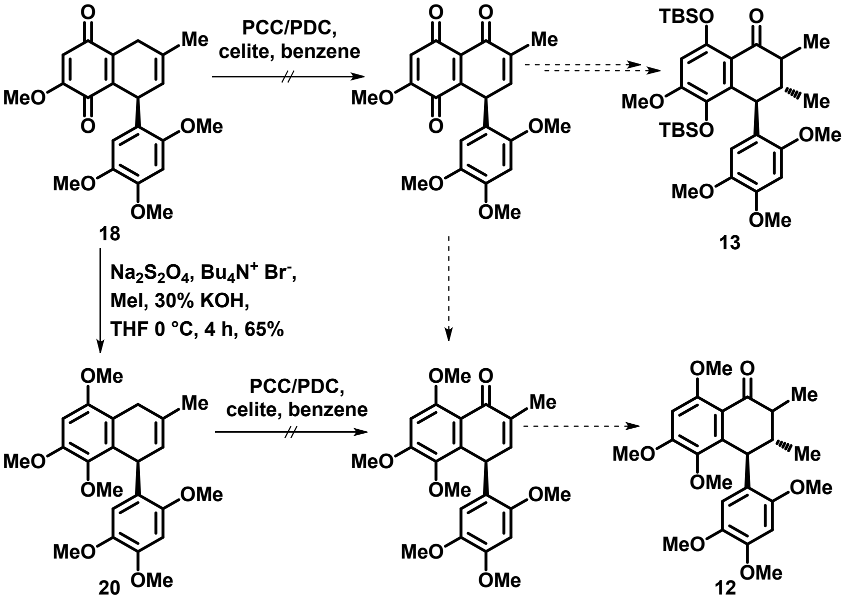


**(*E*)-Ethyl 3-(2, 4, 5-trimethoxyphenyl) acrylate (25)**: To a stirred solution of 2, 4, 5-trimethoxy-benzaldehyde **15** (600 mg, 3.06 mmol) in benzene (8 mL) was added carboxymethylene triphenylphosphorane (1.66 g, 4.591 mmol) and the reaction was then refluxed for 3 h. On complete consumption of starting material and on indication of formation of a new spot by the TLC analysis, the reaction was worked up by removing the solvent under reduced pressure and then subjecting the resultant residue to SiO$_2$ gel column chromatographic purification using hexane/ethyl acetate (4:1) as the eluent to arrive at **25** (*E*-isomer) (760 mg, 2.711 mmol, 89% yield) in the form of a yellow solid. [TLC profile: $R_f$ = 1.36 (petroleum ether/ethyl acetate 7:3, UV detection)]. IR (neat): $\nu_{max}$2937, 2835, 1700, 1608, 1514, 1465, 1250, 1214, 1032 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 1.2 Hz, 1H), 6.89 (s, 1H), 6.53 (s, 1H), 4.26 (q, $J$ = 7.2 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 6H), 2.08 (d, $J$ = 1.2 Hz, 3H), 1.34 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.82, 152.78, 150.33, 142.48, 134.13, 126.94, 116.38, 113.91, 96.97, 60.67, 56.68, 56.38, 56.05, 14.37, 14.35.



**(*E*)-2-methyl-4-(2, 4, 5-trimethoxyphenyl)but-3-en-2-ol (26)**: To a solution of **25** (3.49 g, 12.46 mmol) in dry THF (7 mL) at -78 °C was added 3.1 M solution of methyllithium in diethoxymethane (40.3 mL, 124.89 mmol). The reaction mixture was allowed to warm to rt and continued stirring at same temperature for 4 h until complete consumption of starting material and formation of a new spot was indicated by the TLC analysis. The reaction was quenched with saturated aq. $NH_4Cl$ solution followed by extraction with ethyl acetate (4 × 40 mL). Drying of the organic phase over $Na_2SO_4$ and then removal of solvent under reduced pressure gave an oily residue which was subjected to column chromatography to access pure **26** (2.98 g, 11.189 mmol, 89% yield) as a colorless oil. [TLC profile: $R_f = 1.5$ (petroleum ether/ethyl acetate 7:3, UV detection)]. IR (neat): $\nu_{max}$2972, 1608, 1512, 1465, 1397, 1317, 1207, 1124, 1035, 880 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 6.60 (s, 1H), 6.51 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H),1.84 (d, $J = 0.8$ Hz, 3H), 1.44 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 151.70, 148.39, 143.75, 142.51, 118.95, 117.81, 114.50, 97.82, 73.94, 56.68, 56.54, 56.12, 29.04 (2C), 14.58.

**Attempted synthesis of 12/13 from 18:**



## $^{1}$H NMR comparison of natural with that of synthetic and the desmethyl derivative

| Position | Natural gramineusquinone B (3) | Synthetic gramineusquinone B (3) | Desmethyl gramineusquinone B (19) |
|---|---|---|---|
| 1 | | | |
| 2 | | | |
| 3 | 6.08 (s) | 6.06 (s) | 6.10 (s) |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | 7.98 (s) | 7.96 (s) | 7.94 (s) |
| 8 | | | |
| 9 | 2.47 (s) | 2.45 (s) | 2.48 (s) |
| 4-OMe | 3.82 (s) | 3.80 (s) | 3.84 (s) |
| 1' | | | |
| 2' | | | |
| 3' | 6.65 (s) | 6.63 (s) | 6.67 (s) |
| 4' | | | |
| 5' | | | |
| 6' | 6.43 (s) | 6.40 (s) | 6.56 (s) |
| 7' | | | |
| 8' | | | 7.31 (s) |
| 9' | 2.03 (s) | 2.01 (s) | |
| 2'-OMe | 3.67 (s) | 3.65 (s) | 3.65 (s) |
| 4'-OMe | 3.97 (s) | 3.95 (s) | 3.93 (s) |
| 5'-OMe | 3.73 (s) | 3.76 (s) | 3.83 (s) |

## $^{13}$C NMR comparison of natural with that of synthetic and the desmethyl derivative

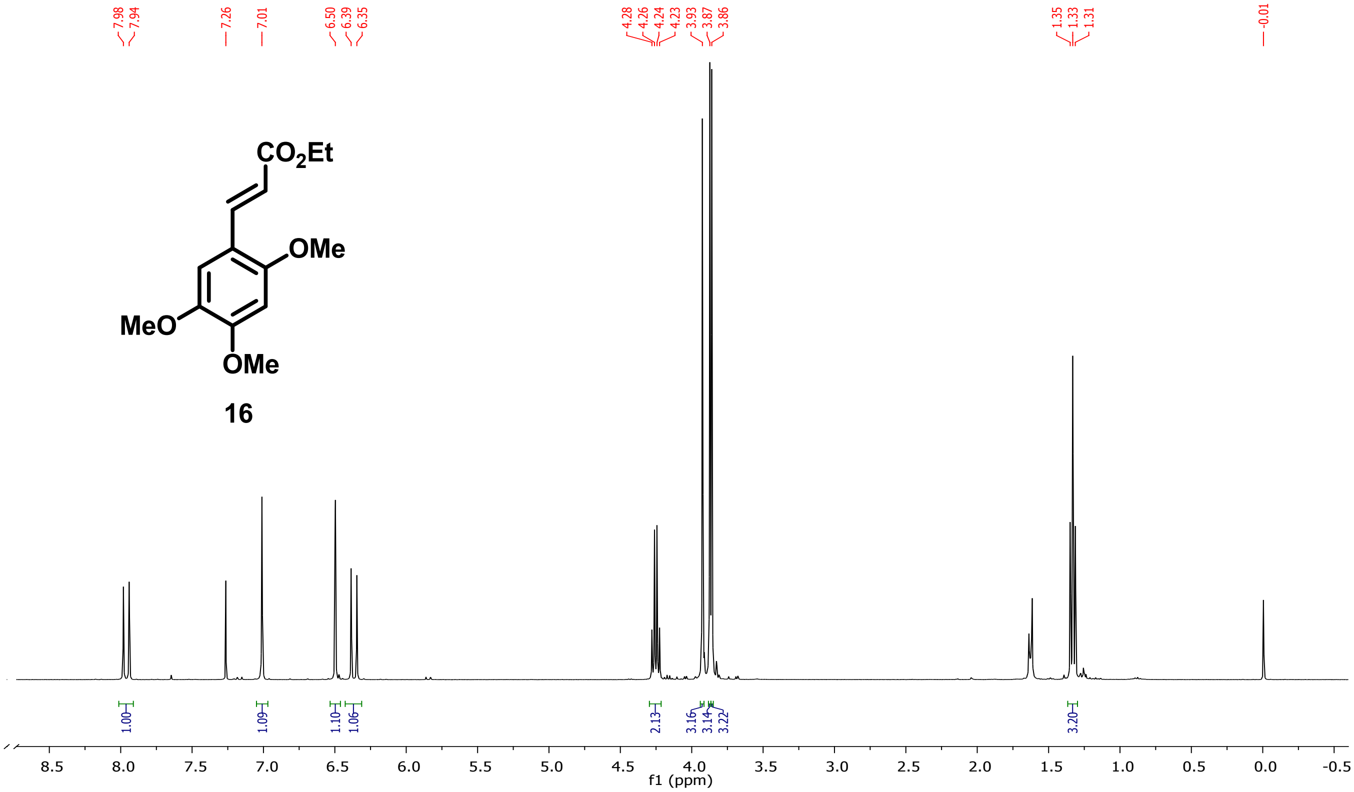
| Position | Natural gramineusquinone B (3) | Synthetic gramineusquinone B (3) | Desmethyl gramineusquinone B (19) |
|---|---|---|---|
| 1 | 130.8 | 130.7 | 133.0 |
| 2 | 185.5 | 185.5 | 185.4 |
| 3 | 108.0 | 108.0 | 108.3 |
| 4 | 160.8 | 160.8 | 161.1 |
| 5 | 179.8 | 179.8 | 179.6 |
| 6 | 127.0 | 127.0 | 127.0 |
| 7 | 127.2 | 127.2 | 126.5 |
| 8 | 143.7 | 143.7 | 144.4 |
| 9 | 21.5 | 21.5 | 21.8 |
| 4-OMe | 56.6 | 56.6 | 56.6 |
| 1' | 120.3 | 120.4 | 121.4 |
| 2' | 150.4 | 150.4 | 150.6 |
| 3' | 97.8 | 97.9 | 97.4 |
| 4' | 148.9 | 148.9 | 149.2 |
| 5' | 143.6 | 143.6 | 143.0 |
| 6' | 112.6 | 112.7 | 113.0 |
| 7' | 139.4 | 139.4 | 139.7 |
| 8' | 143.8 | 143.8 | 137.9 |
| 9' | 16.9 | 16.9 | |
| 2'-OMe | 56.1 | 56.1 | 56.2 |
| 4'-OMe | 56.4 | 56.4 | 56.4 |
| 5'-OMe | 56.2 | 56.2 | 56.30 |

## CRYSTAL INFORMATION FOR COMPOUND 14

| | |
|---|---|
| Formula | $C_{22} H_{24} O_6$ |
| Fw | 384.41 |
| radiation | $MoK_\alpha$ |
| wavelength (Å) | 0.71073 |
| temp./ K | 273(2) |
| cryst system | triclinic |
| space group | P -1 |
| $a$/Å | 7.5036(12) |
| $b$/Å | 11.2036(17) |
| $c$/Å | 12.4155(19) |
| $\alpha$(deg) | 80.842(4) |
| $\beta$(deg) | 73.658(4) |
| $\gamma$(deg) | 86.435(4) |
| $V$/ Å$^3$ | 988.6(3) |
| Crystal size (mm) | 0.7 x 0.03 x 0.02 |
| Z | 2 |
| $\mu$ / mm$^{-1}$ | 0.094 |
| $D_{calcd}$ / g cm$^{-3}$ | 1.291 |
| F(000) | 408 |
| $\theta$ range | 2.332 – 27.633 |
| Data/restraints/parameters | 3751/0/259 |
| R1,wR2 [I>2σ(I)] | 0.0606 |
| R1,wR2 (all data) | 0.1941 |
| Largest diff. peak hole (eÅ$^{-3}$) | 0.17, -0.24 |

| Bond Lengths | | | |
|---|---|---|---|
| O6 C17 | 1.369(3) | C14 C15 | 1.391(4) |
| O6 C21 | 1.418(3) | C14 C8 | 1.527(4) |
| O5 C19 | 1.378(3) | O3 C4 | 1.228(3) |
| O5 C20 | 1.388(4) | C6 C5 | 1.332(4) |
| O2 C7 | 1.209(3) | C6 C7 | 1.476(4) |
| O4 C22 | 1.365(4) | C6 C8 | 1.500(4) |
| O4 C16 | 1.368(3) | C17 C18 | 1.375(4) |
| O1 C2 | 1.347(4) | C17 C16 | 1.393(4) |
| O1 C1 | 1.453(4) | C8 C9 | 1.518(4) |
| C14 C19 | 1.387(4) | C16 C15 | 1.373(4) |
| C19 C18 | 1.387(4) | C7 C2 | 1.504(4) |
| C5 C4 | 1.487(4) | C5 C11 | 1.490(4) |
| C9 C10 | 1.325(4) | C9 C13 | 1.513(4) |
| C2 C3 | 1.318(4) | C4 C3 | 1.445(4) |
| C10 C11 | 1.497(4) | C10 C12 | 1.506(4) |
| **Bond Angles** | | | |
| C17 O6 C21 | 118.0(2) | C15 C14 C8 | 120.4(2) |
| C19 O5 C20 | 117.1(3) | C5 C6 C7 | 119.9(3) |
| C22 O4 C16 | 119.8(2) | C5 C6 C8 | 123.1(3) |
| C2 O1 C1 | 116.0(3) | C7 C6 C8 | 117.0(2) |
| C19 C14 C15 | 117.1(3) | O6 C17 C18 | 124.6(3) |
| C19 C14 C8 | 122.5(2) | O6 C17 C16 | 115.7(2) |
| C18 C17 C16 | 119.7(3) | C6 C8 C9 | 113.1(2) |
| C6 C8 C14 | 110.5(2) | C9 C8 C14 | 109.8(2) |
| O4 C16 C15 | 124.9(3) | O4 C16 C17 | 116.3(3) |

| | | | |
|---|---|---|---|
| C15 C16 C17 | 118.8(3) | O5 C19 C14 | 117.2(2) |
| O5 C19 C18 | 121.7(2) | C14 C19 C18 | 121.0(3) |
| C17 C18 C19 | 120.4(3) | C16 C15 C14 | 122.8(3) |
| O2 C7 C6 | 121.6(3) | O2 C7 C2 | 120.8(3) |
| C6 C7 C2 | 117.5(3) | C6 C5 C4 | 121.0(3) |
| C6 C5 C11 | 122.8(3) | C4 C5 C11 | 116.3(3) |
| C10 C9 C13 | 123.3(3) | C10 C9 C8 | 123.0(3) |
| C13 C9 C8 | 113.6(3) | C3 C2 O1 | 127.4(3) |
| C3 C2 C7 | 121.3(3) | O1 C2 C7 | 111.3(3) |
| O3 C4 C3 | 121.6(3) | O3 C4 C5 | 119.3(3) |
| C3 C4 C5 | 119.1(3) | C9 C10 C11 | 122.6(3) |
| C9 C10 C12 | 124.7(3) | C11 C10 C12 | 112.8(3) |
| C5 C11 C10 | 114.7(2) | C2 C3 C4 | 120.5(3) |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3.86
1.35
1.33
1.31
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CO$_2$Et
OMe
MeO
OMe
16
1.00
1.09
1.10
1.06
2.13
3.16
3.14
3.22
3.20
8.5
8.0
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6.0
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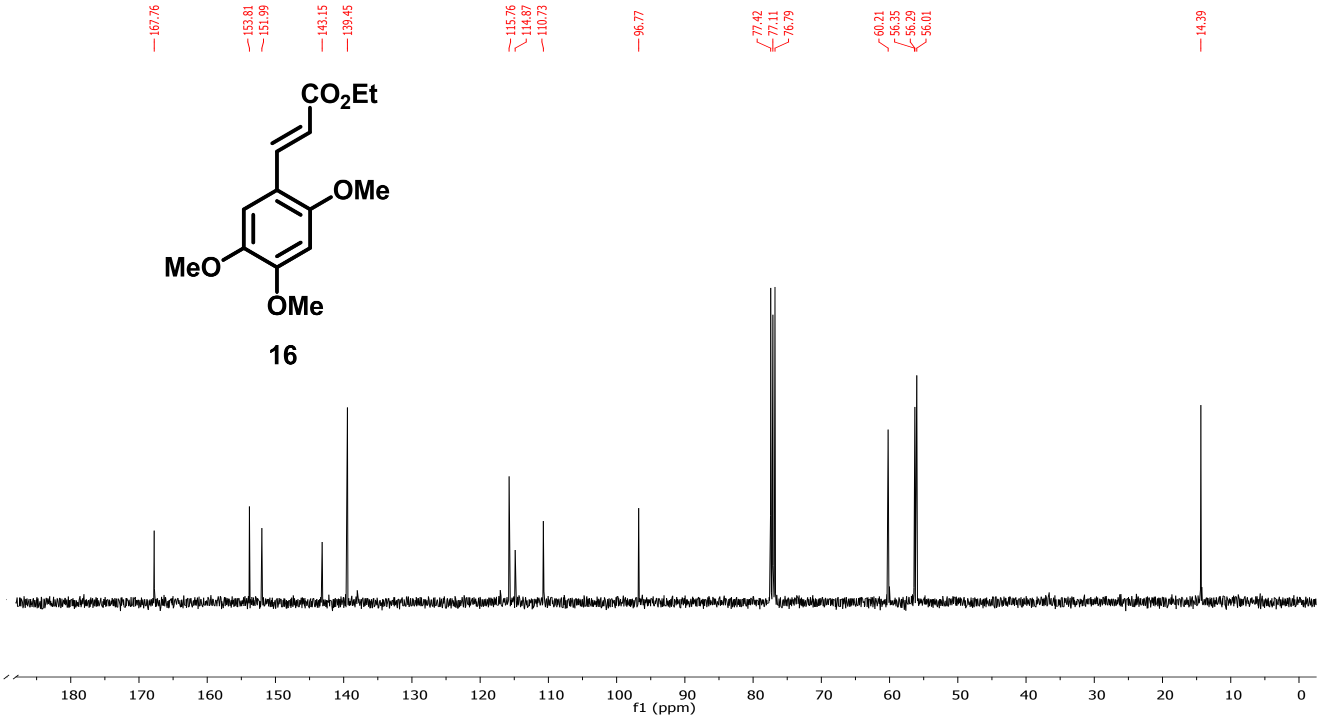
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56.35
56.29
56.01
14.39
CO$_2$Et
OMe
MeO
OMe
16
180
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130
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70
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50
40
30
20
10
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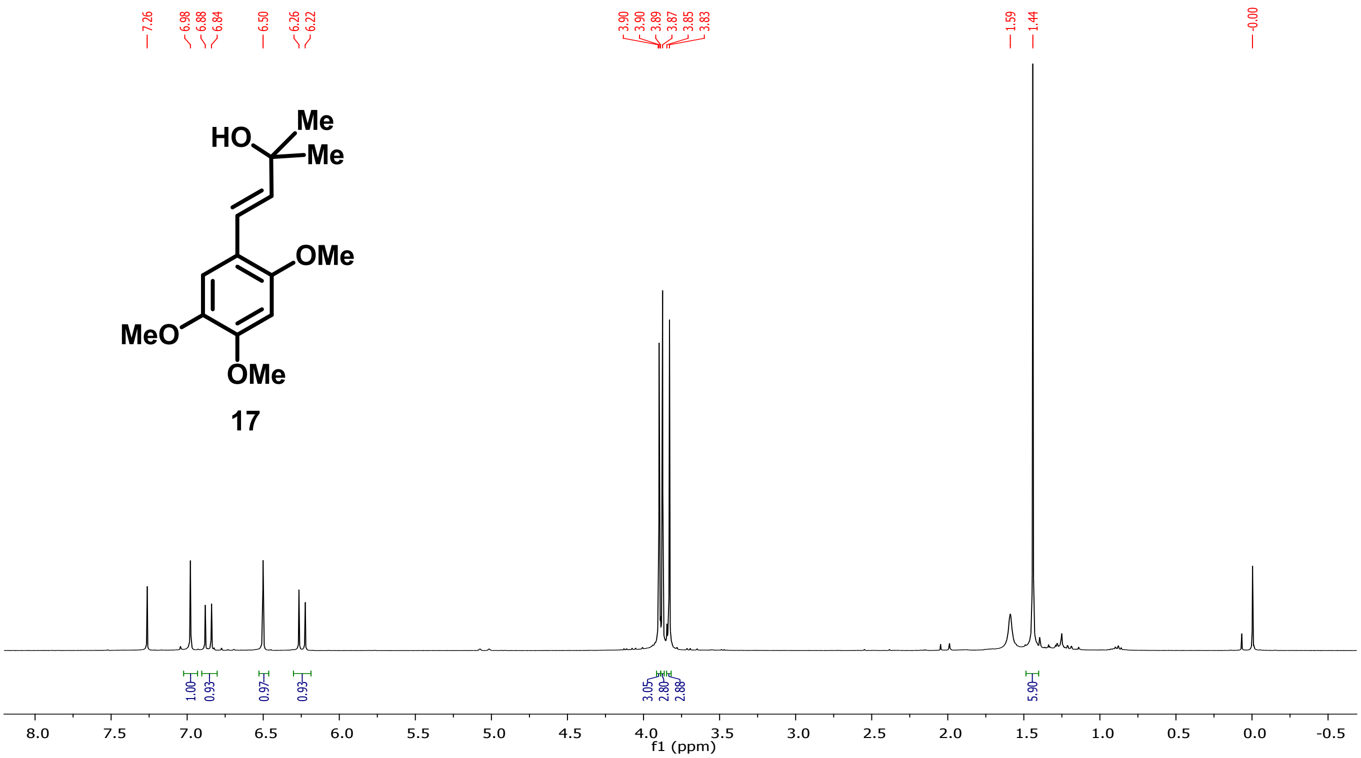
f1 (ppm)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1.44
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Me
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OMe
MeO
OMe
1.00
0.93
0.97
0.93
3.05
2.80
2.88
5.90
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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0.0
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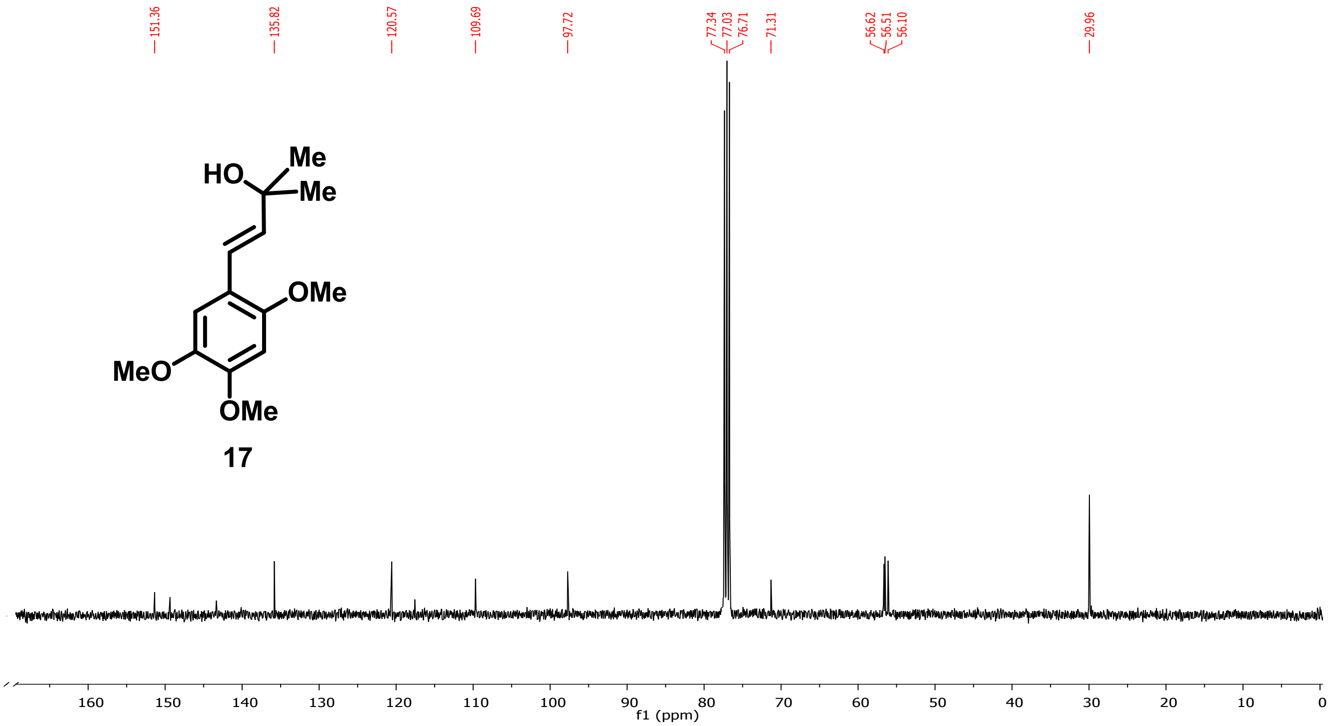
f1 (ppm)

**17**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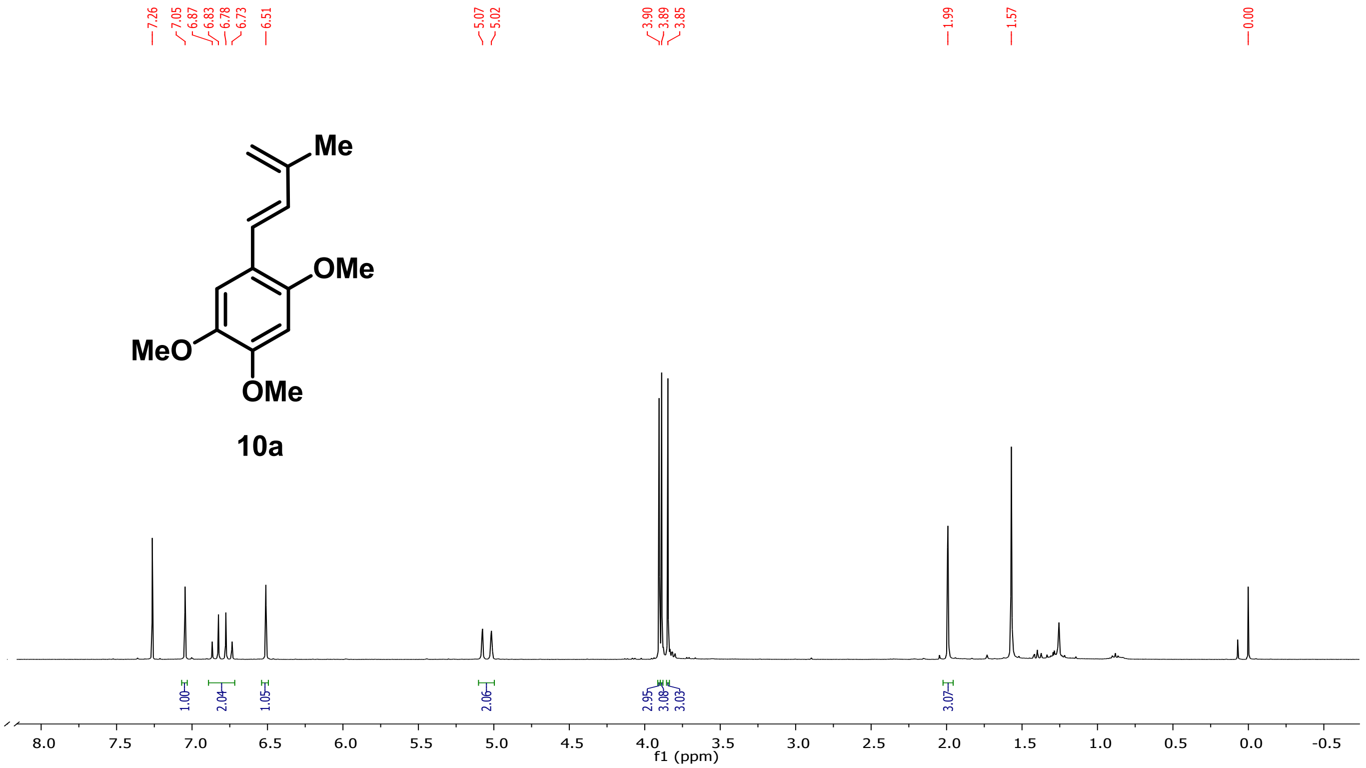
f1 (ppm)

**17**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1.05
2.06
2.95
3.08
3.03
3.07
8.0
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7.0
6.5
6.0
5.5
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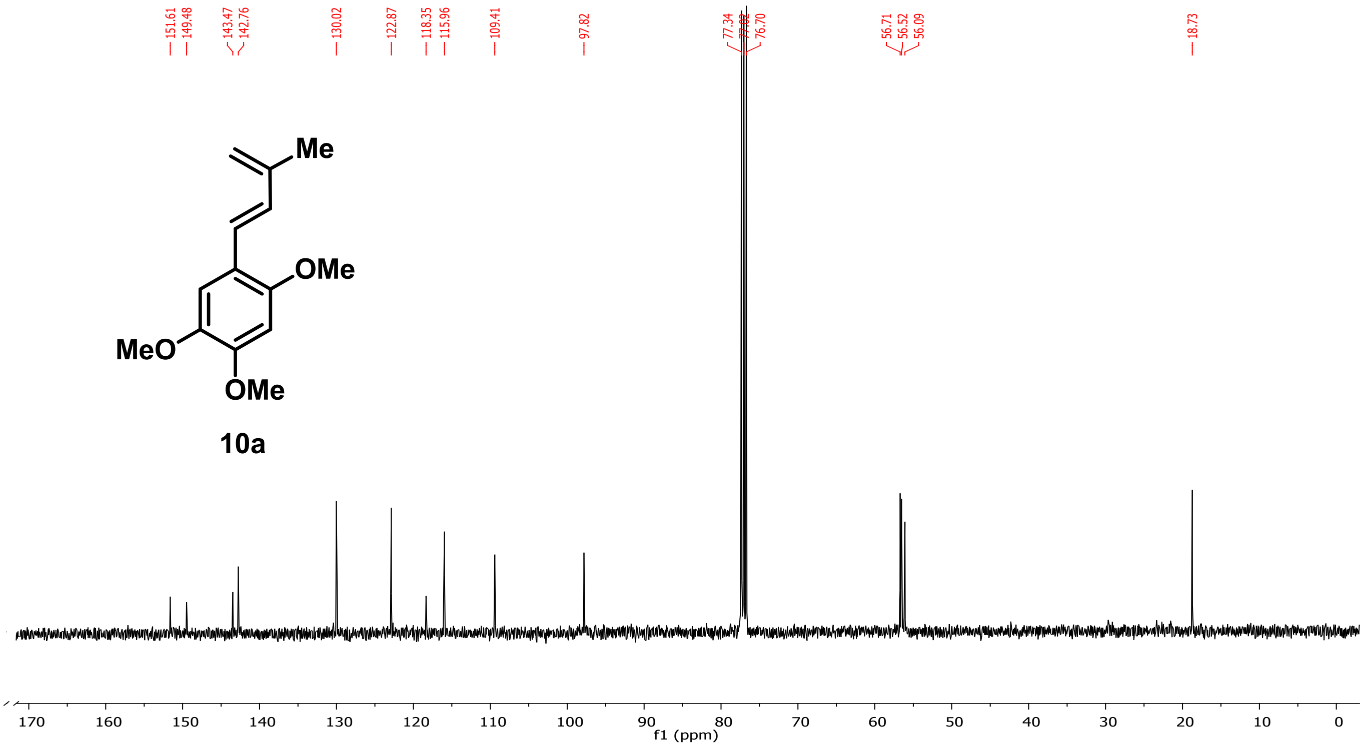
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77.02
76.70
56.71
56.52
56.09
18.73
Me
OMe
MeO
OMe
10a
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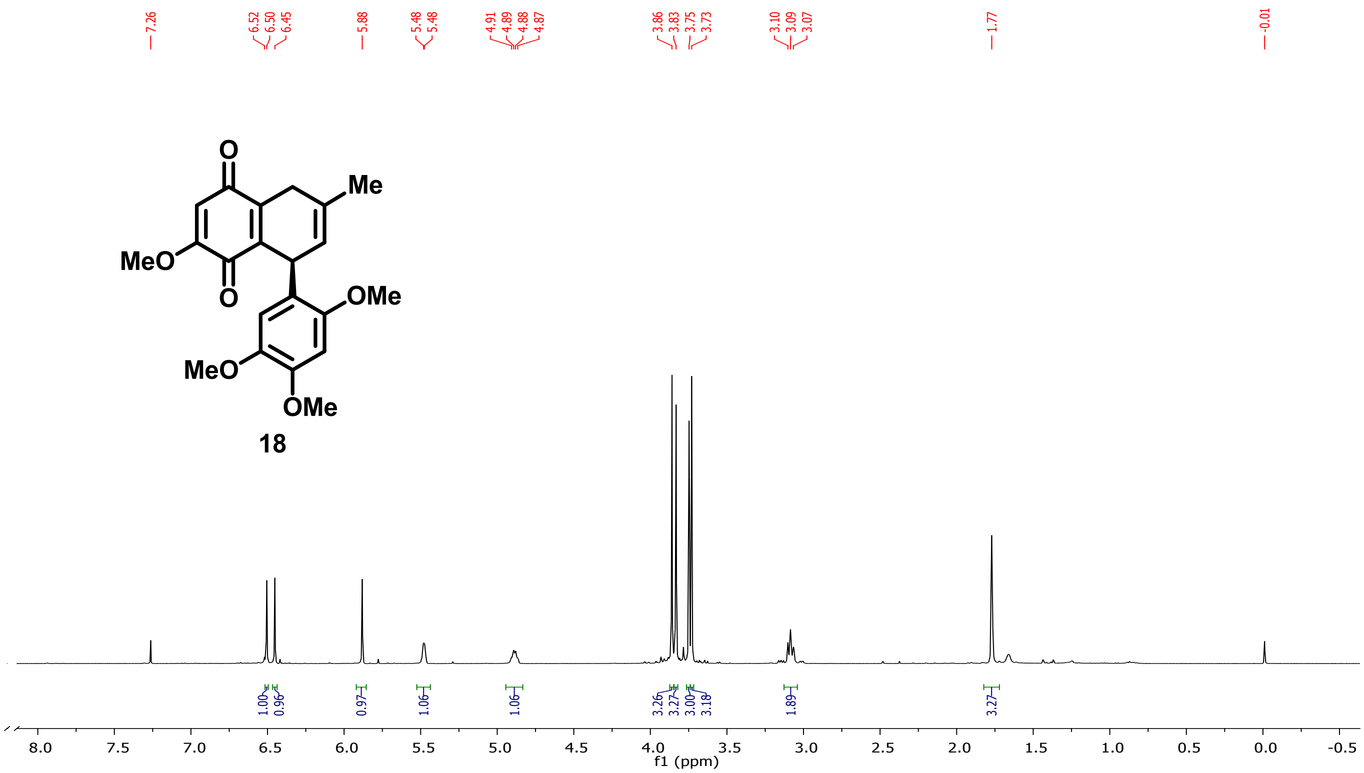
f1 (ppm)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3.73
3.10
3.09
3.07
1.77
-0.01
O
Me
MeO
O
OMe
MeO
OMe
18
1.00
0.96
0.97
1.06
1.06
3.26
3.27
3.00
3.18
1.89
3.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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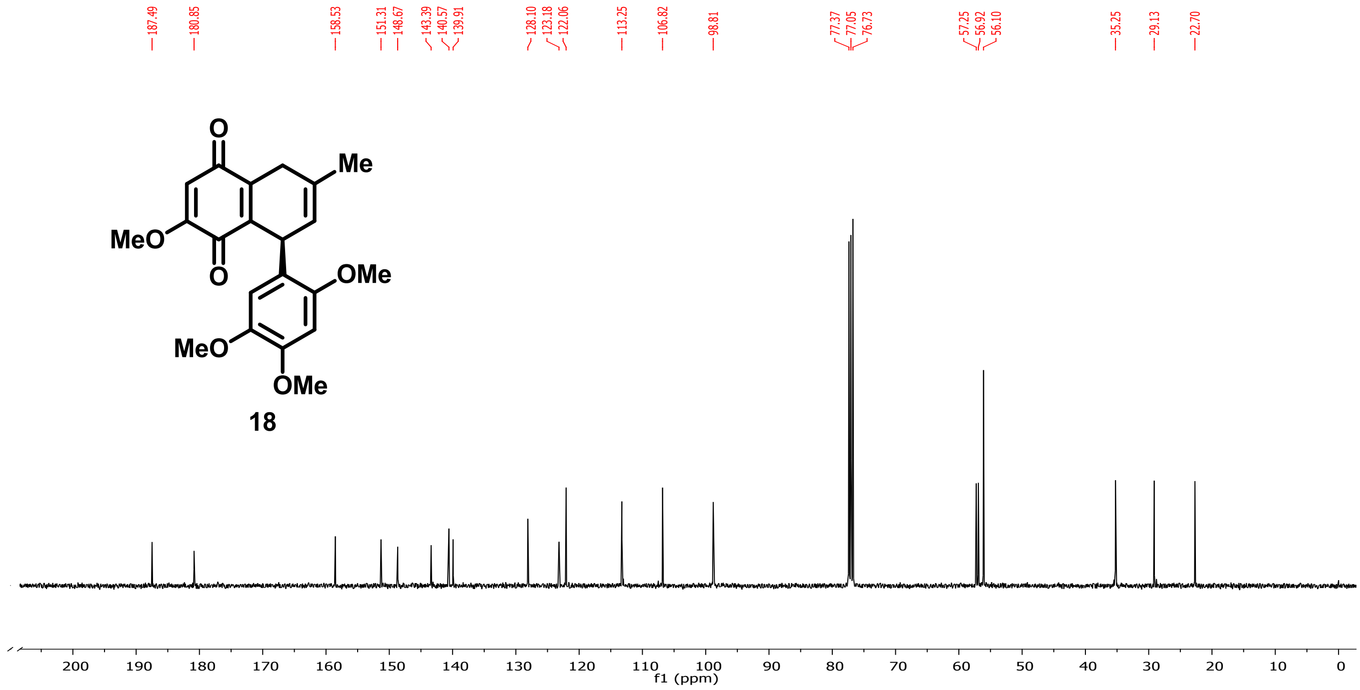
f1 (ppm)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98.81
77.37
77.05
76.73
57.25
56.92
56.10
35.25
29.13
22.70
O
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MeO
O
OMe
MeO
OMe
18
200
190
180
170
160
150
140
130
120
110
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90
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70
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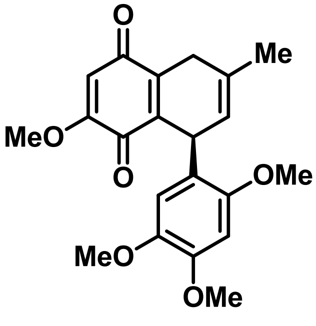
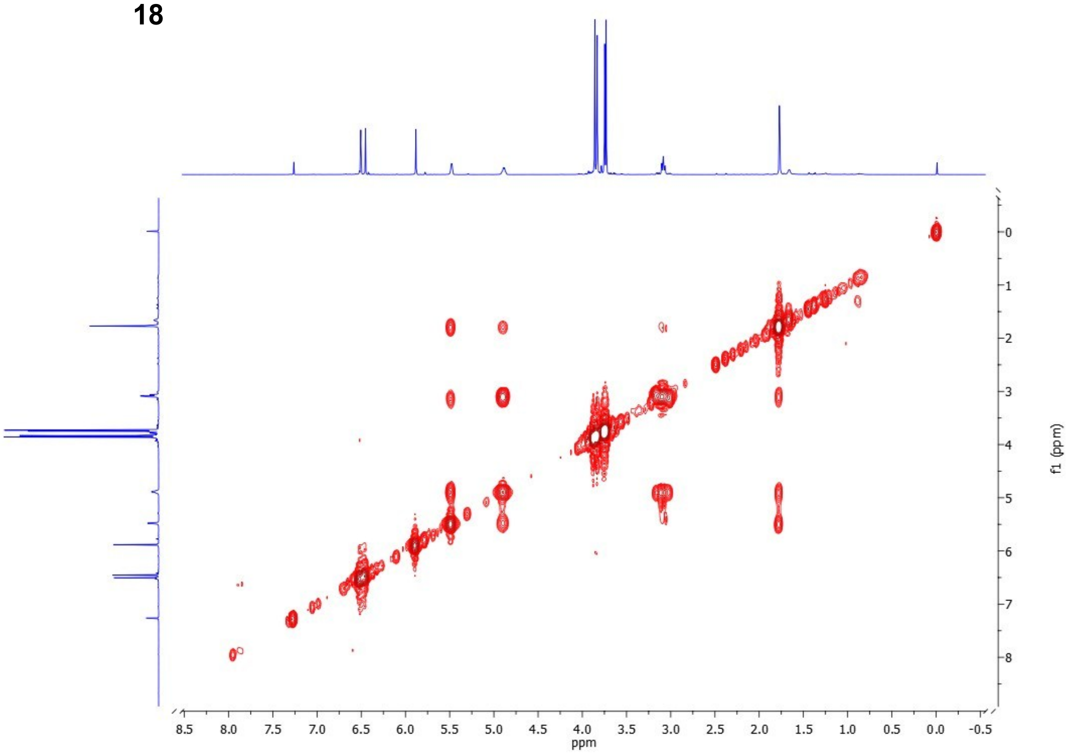
30
20
10
0
f1 (ppm)

## 2D NMR spectra for 18

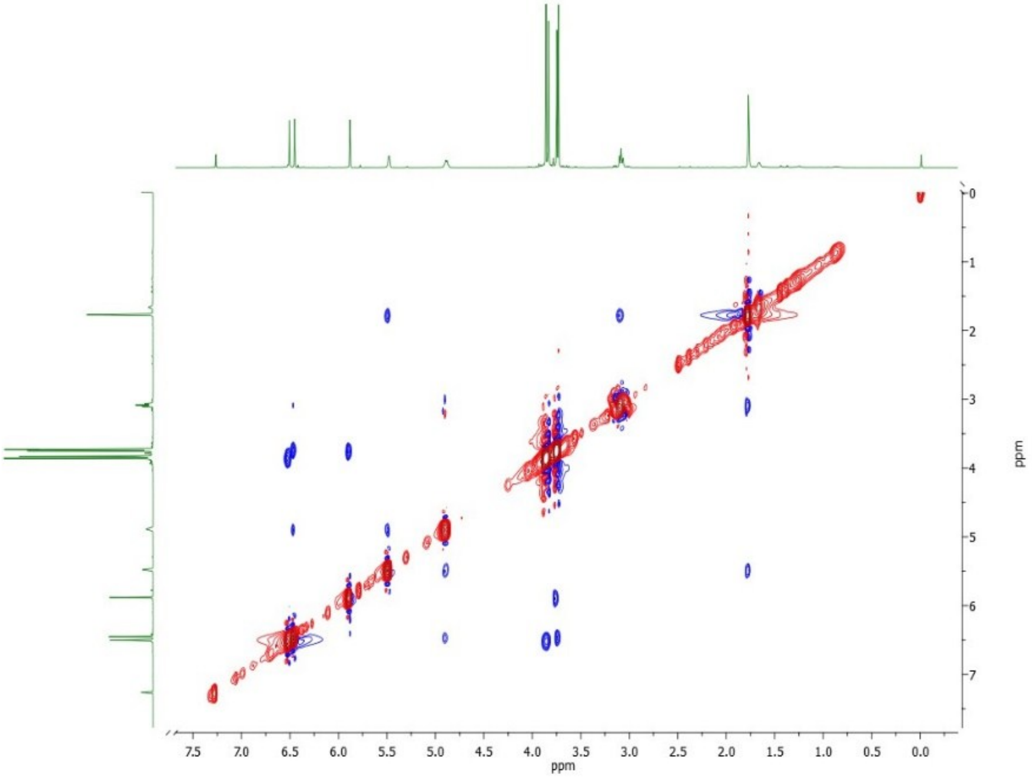
*i) COSY spectrum*



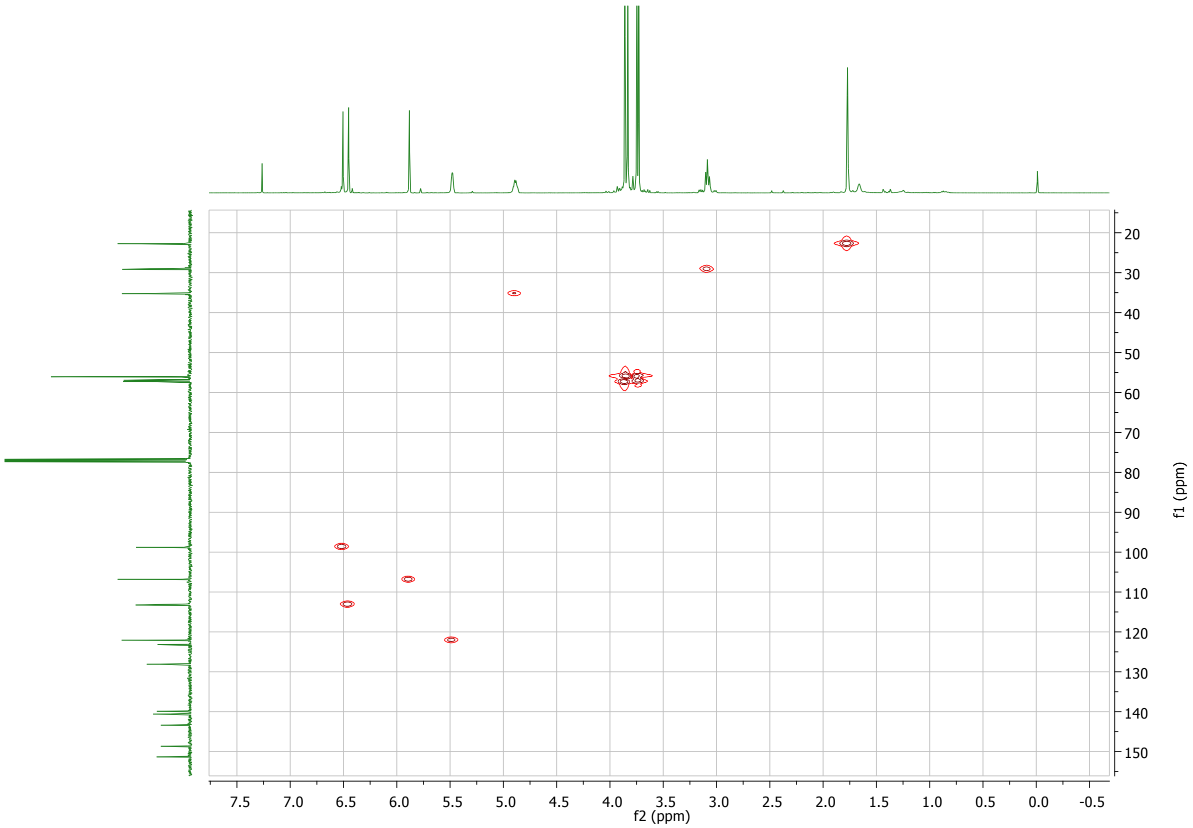
**18**

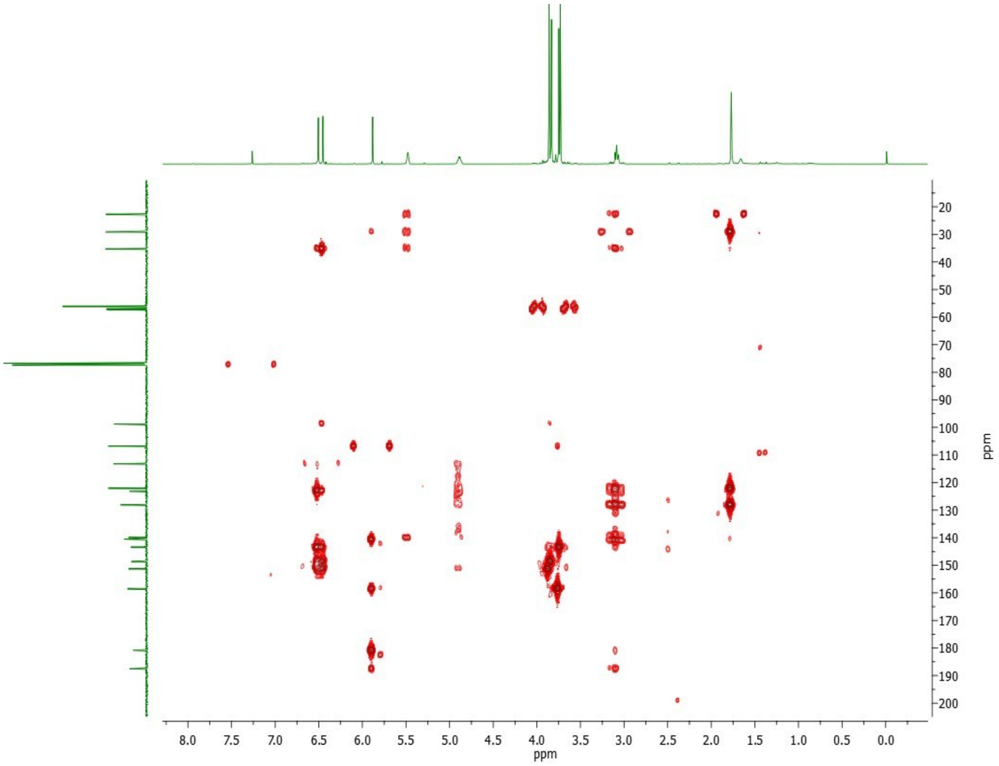


ii) *NOESY spectrum*:

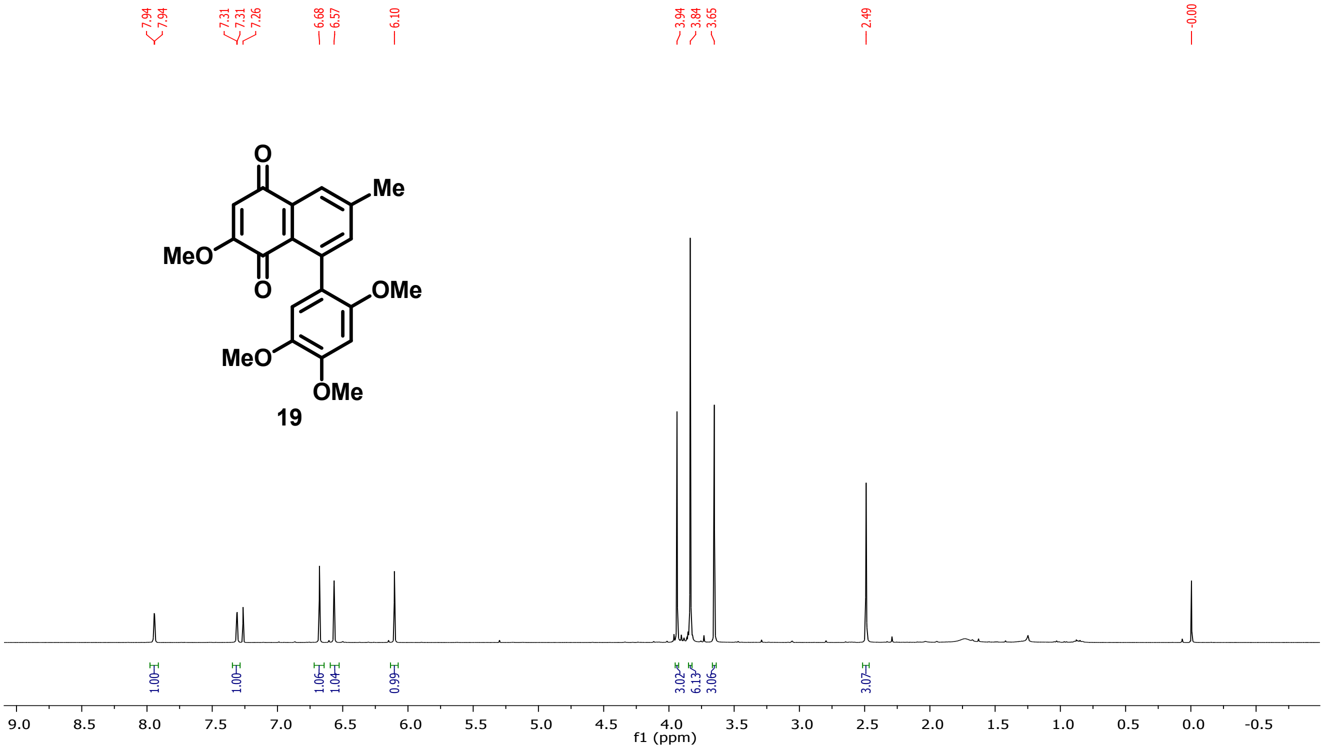


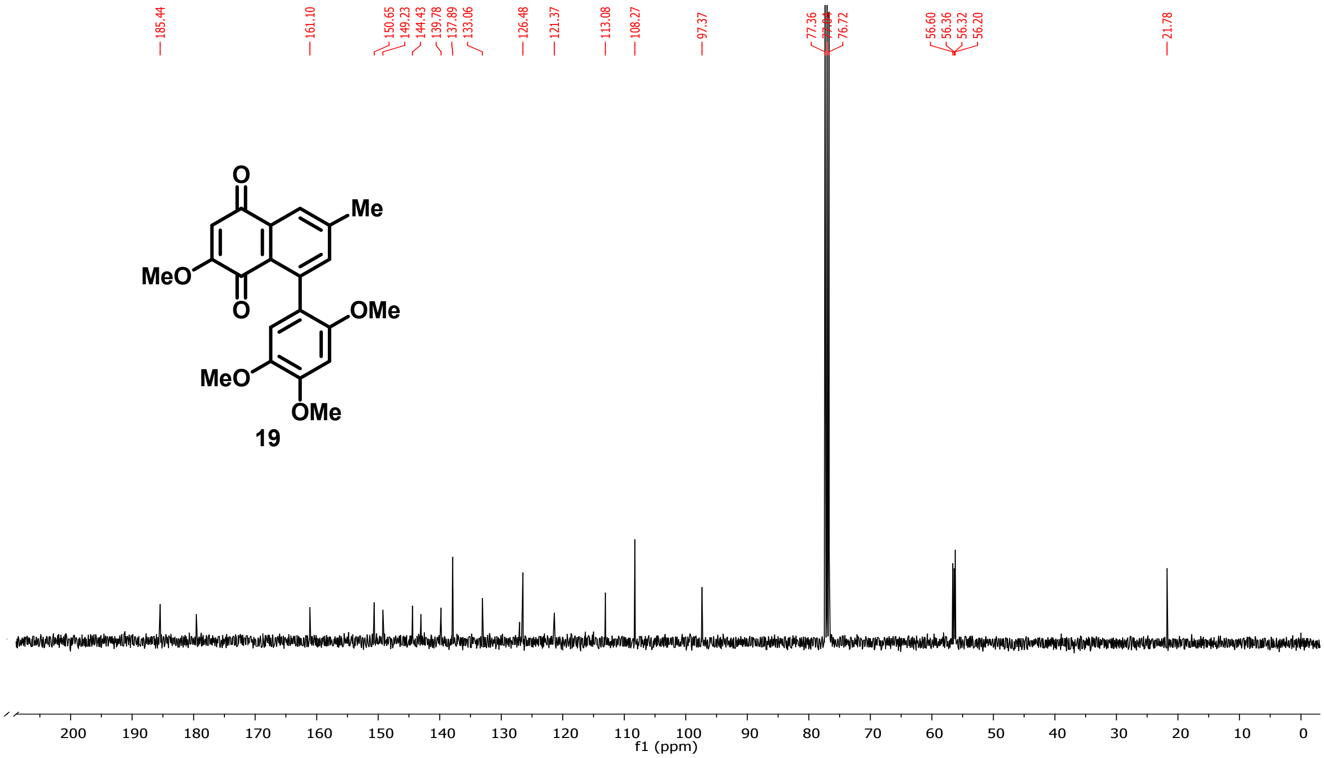
iii) *HMQC spectrum*:

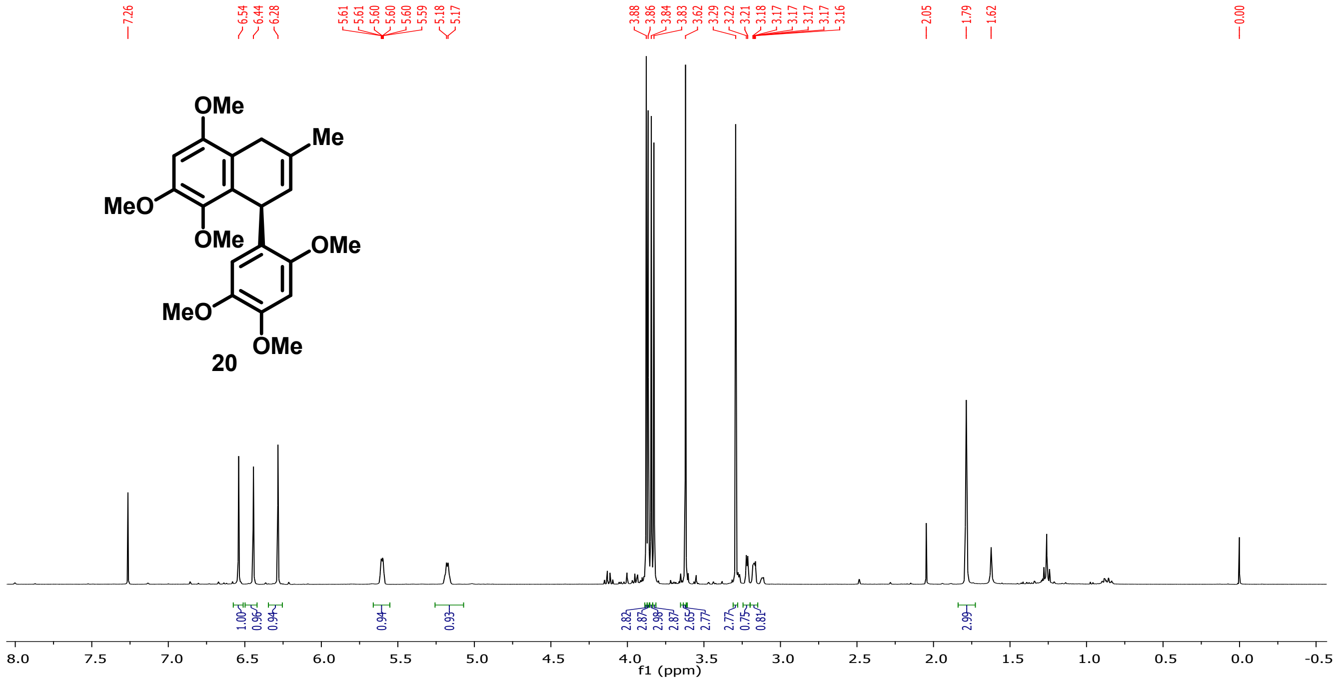




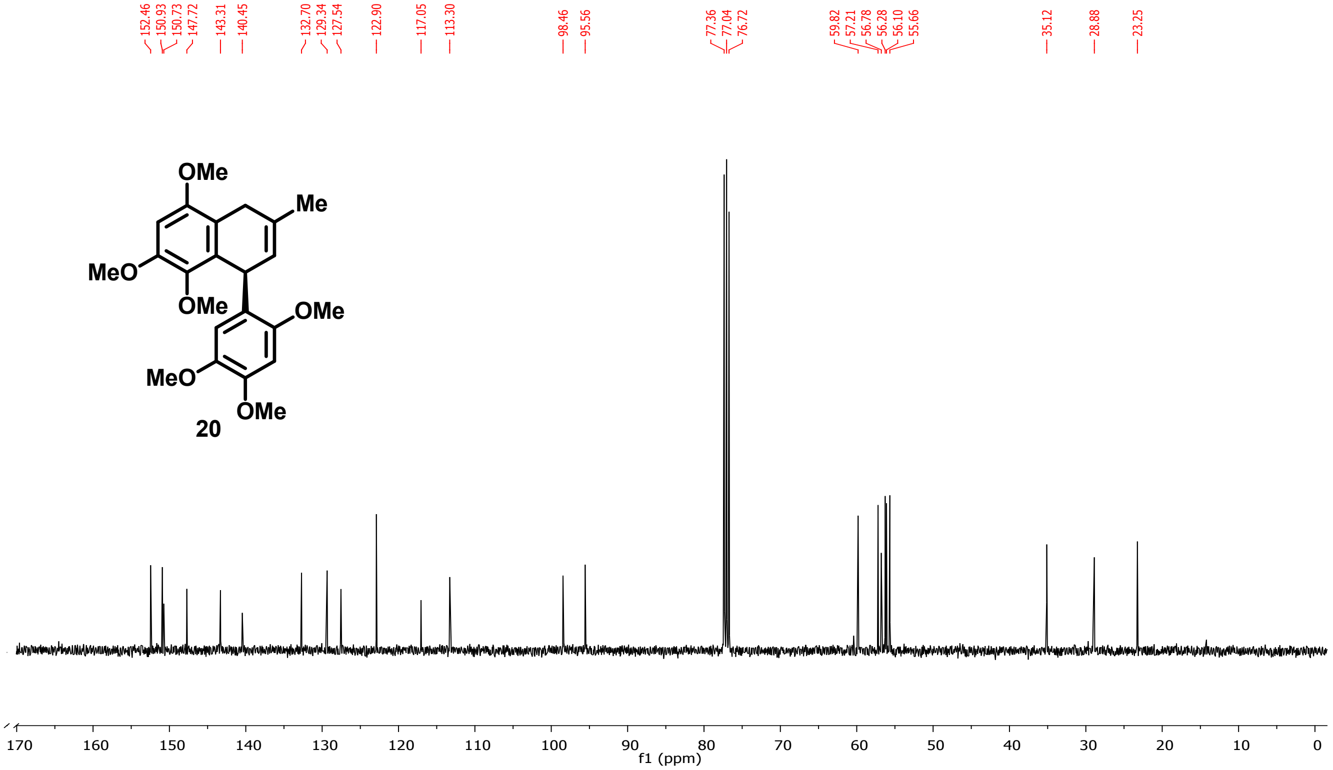
iv) *HMBC spectrum:*


7.94
7.94
7.31
7.31
7.26
6.68
6.57
6.10
3.94
3.84
3.65
2.49
-0.00
O
Me
MeO
O
OMe
MeO
OMe
19
1.00
1.00
1.06
1.04
0.99
3.02
6.13
3.06
3.07
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
0.0
-0.5
f1 (ppm)

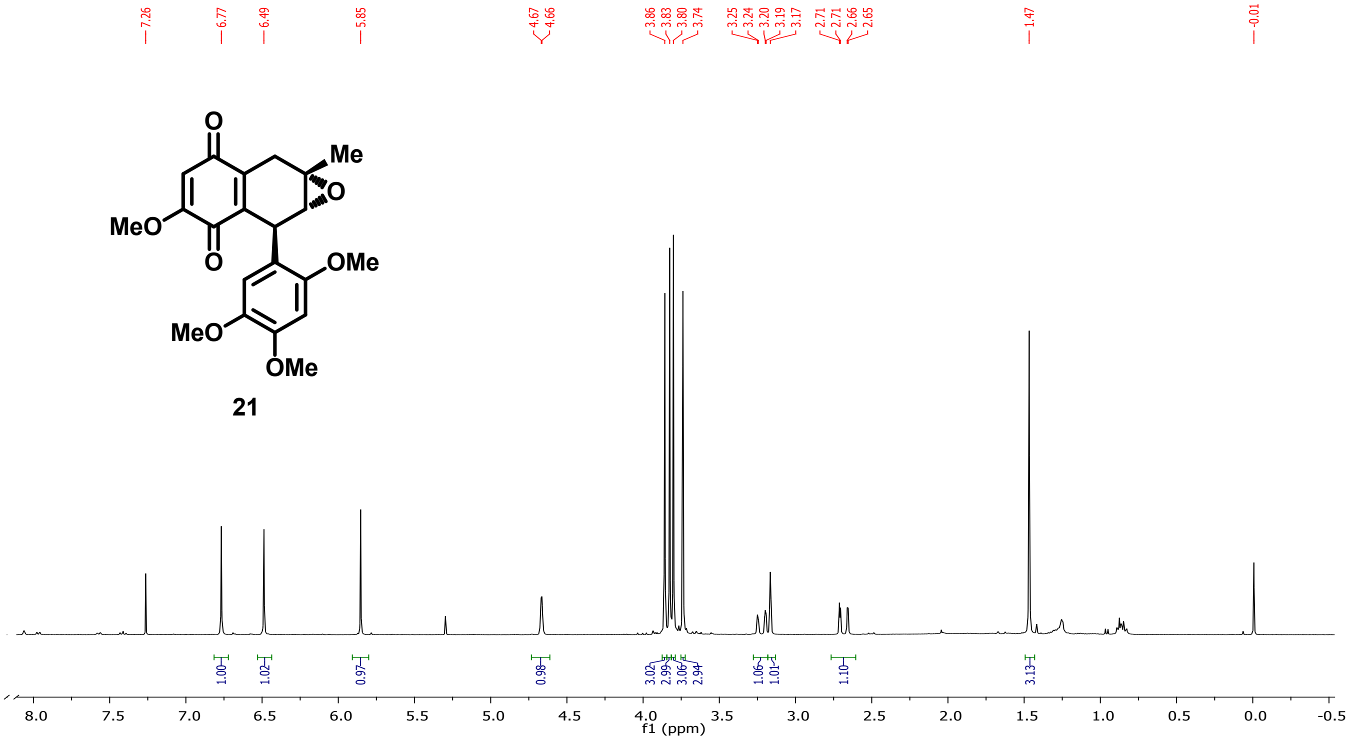

185.44
161.10
150.65
149.23
144.43
139.78
137.89
133.06
126.48
121.37
113.08
108.27
97.37
77.36
77.04
76.72
56.60
56.36
56.32
56.20
21.78
O
Me
MeO
O
OMe
MeO
OMe
19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

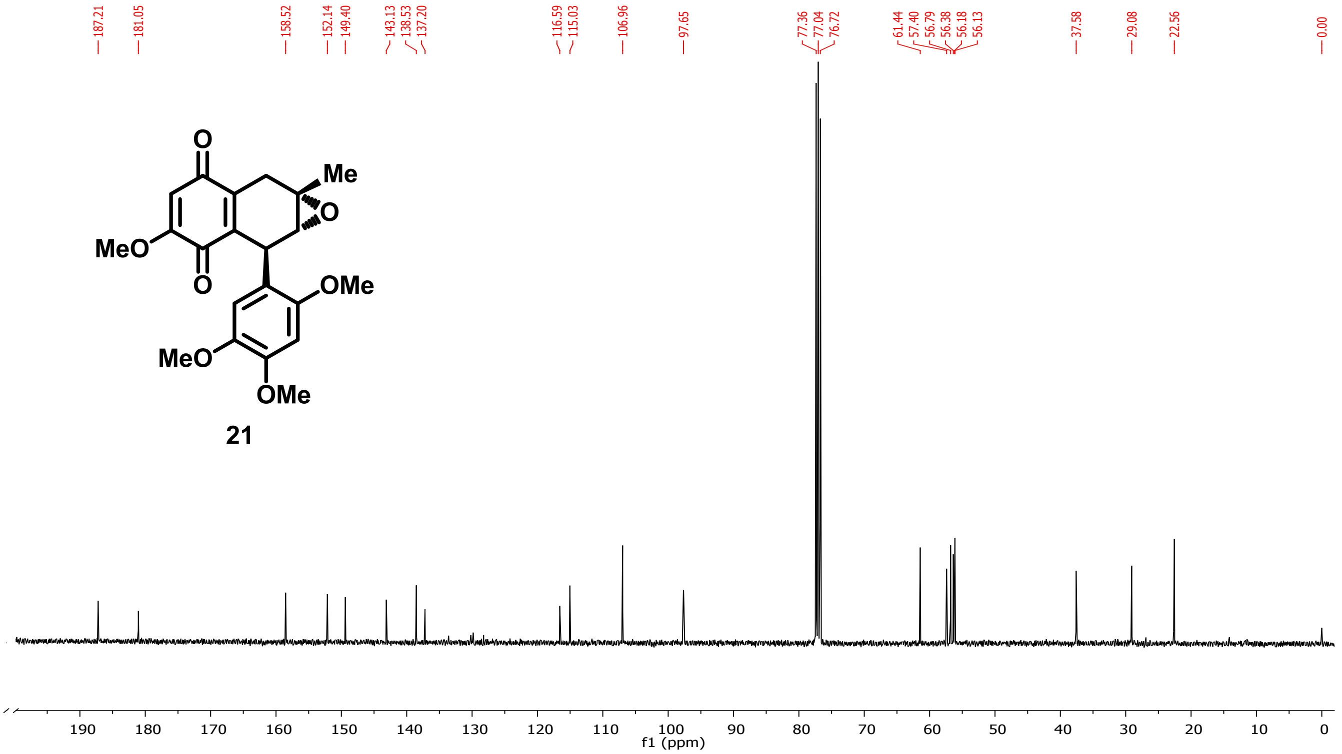

7.26
6.54
6.44
6.28
5.61
5.61
5.60
5.60
5.60
5.59
5.18
5.17
3.88
3.86
3.84
3.83
3.62
3.29
3.22
3.21
3.18
3.17
3.17
3.17
3.17
3.16
2.05
1.79
1.62
0.00
OMe
Me
MeO
OMe
OMe
MeO
OMe
1.00
0.96
0.94
0.94
0.93
2.82
2.87
2.98
2.87
2.65
2.77
2.77
0.75
0.81
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

20


152.46
150.93
150.73
147.72
143.31
140.45
132.70
129.34
127.54
122.90
117.05
113.30
98.46
95.56
77.36
77.04
76.72
59.82
57.21
56.78
56.28
56.10
55.66
35.12
28.88
23.25
OMe
Me
MeO
OMe
OMe
MeO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

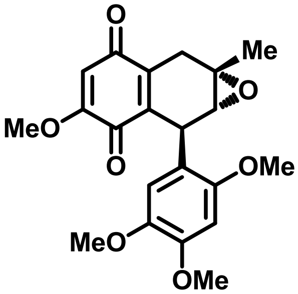
20


7.26
6.77
6.49
5.85
4.67
4.66
3.86
3.83
3.80
3.74
3.25
3.24
3.20
3.19
3.17
2.71
2.71
2.66
2.65
1.47
-0.01
O
Me
O
MeO
O
OMe
MeO
OMe
21
1.00
1.02
0.97
0.98
3.02
2.99
3.06
2.94
1.06
1.01
1.10
3.13
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
-0.5
f1 (ppm)

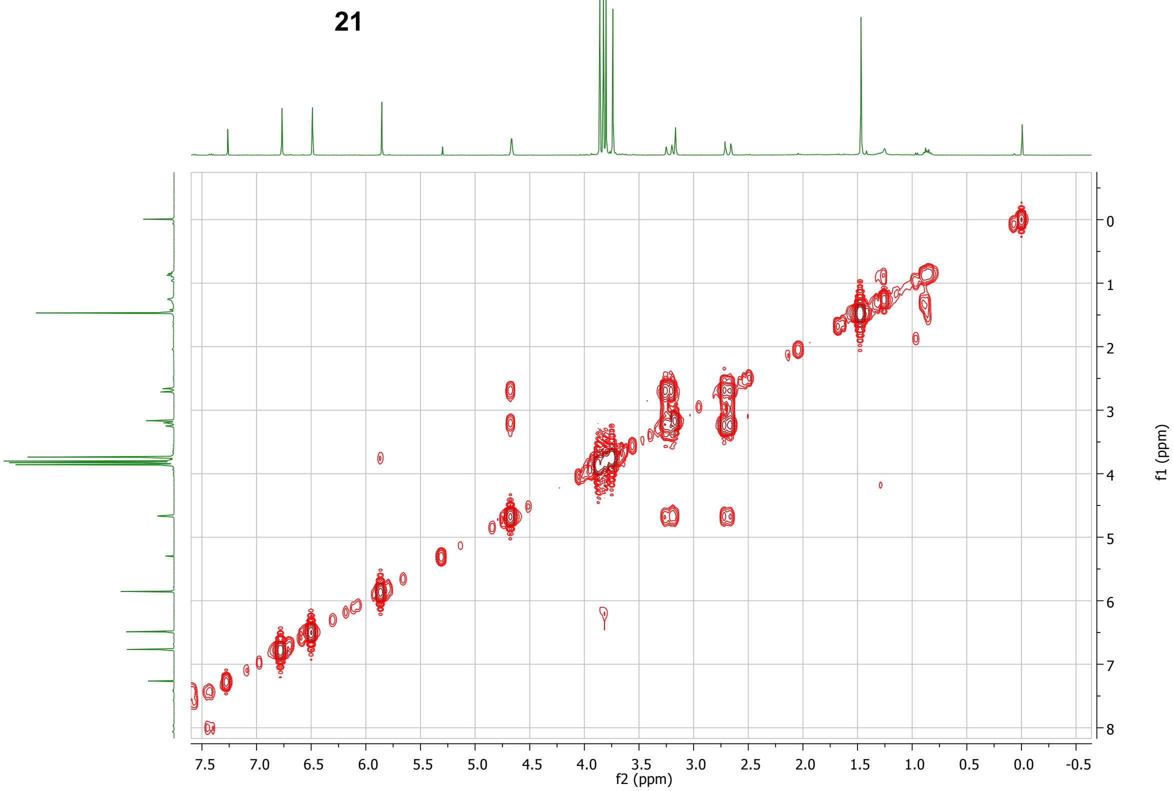

187.21
181.05
158.52
152.14
149.40
143.13
138.53
137.20
116.59
115.03
106.96
97.65
77.36
77.04
76.72
61.44
57.40
56.79
56.38
56.18
56.13
37.58
29.08
22.56
0.00
O
Me
O
MeO
O
OMe
MeO
OMe
21
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# 2D NMR spectra for 21

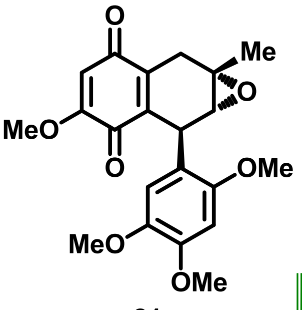
*i) COSY spectrum*



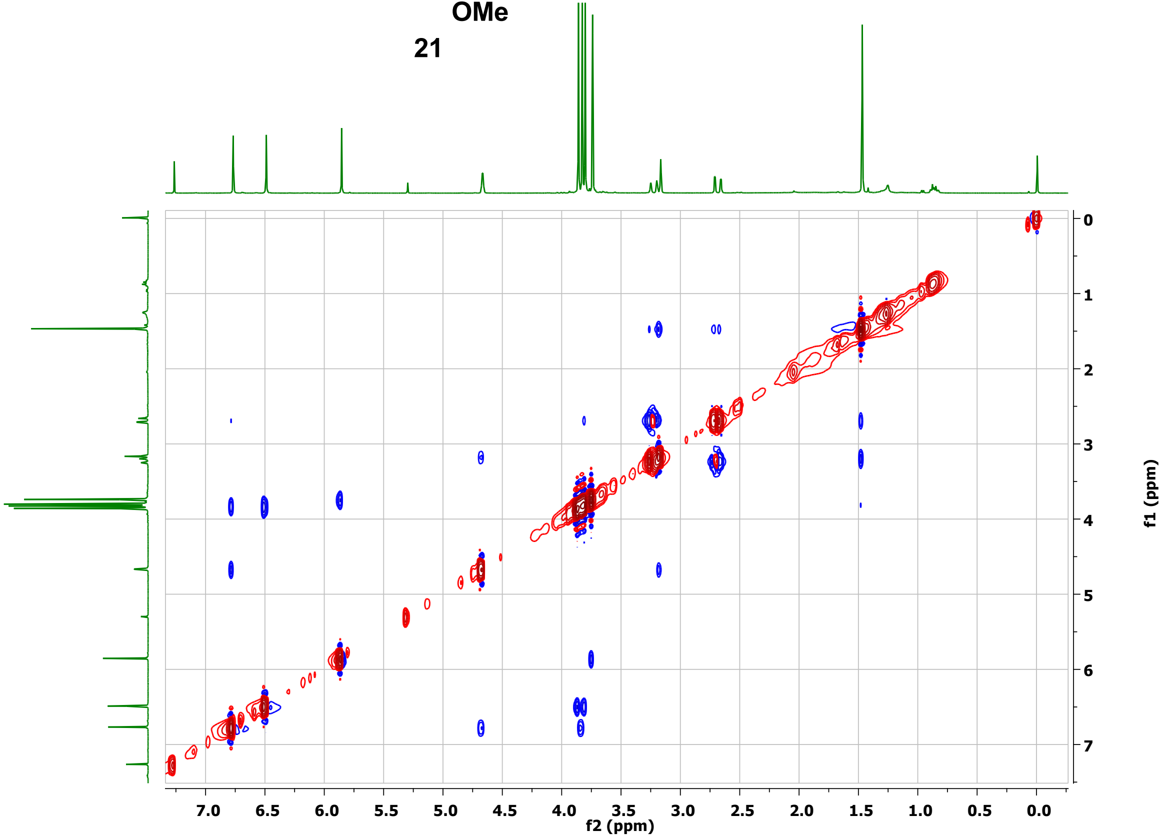
**21**

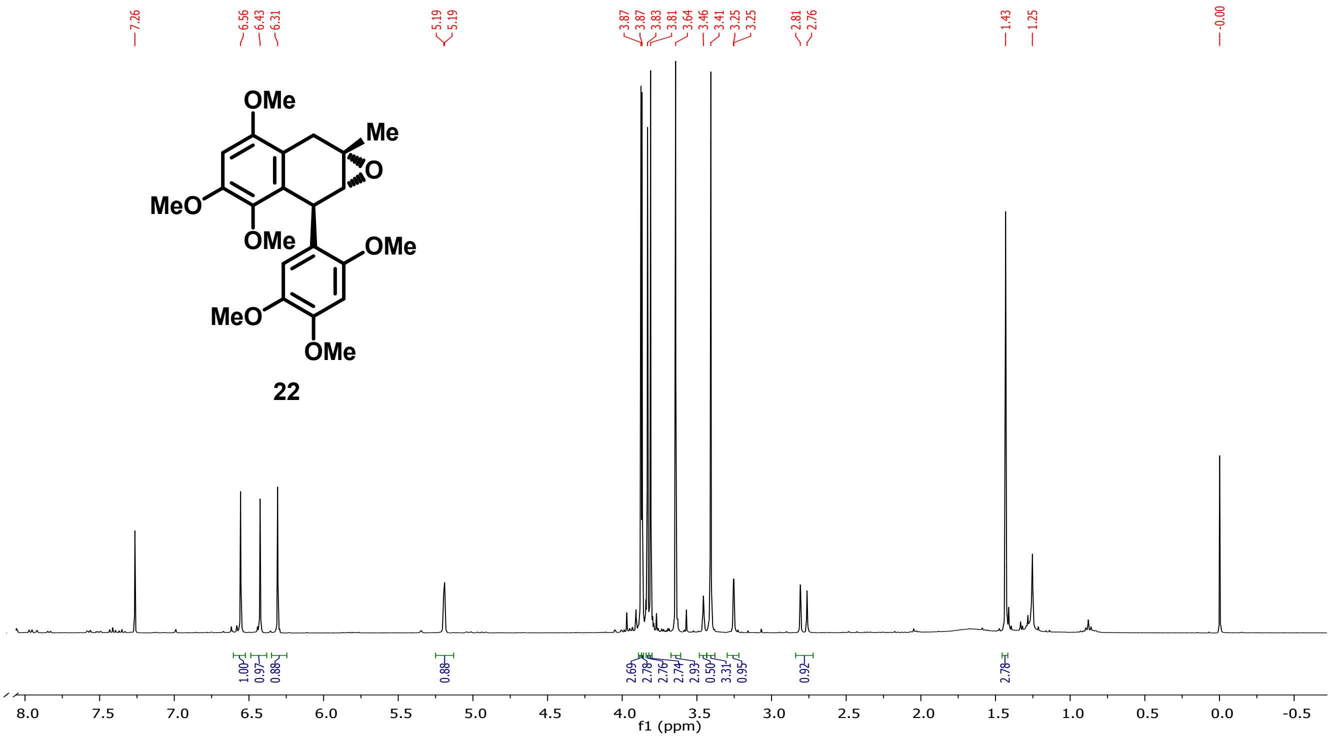


*(ii) NOESY spectrum*:

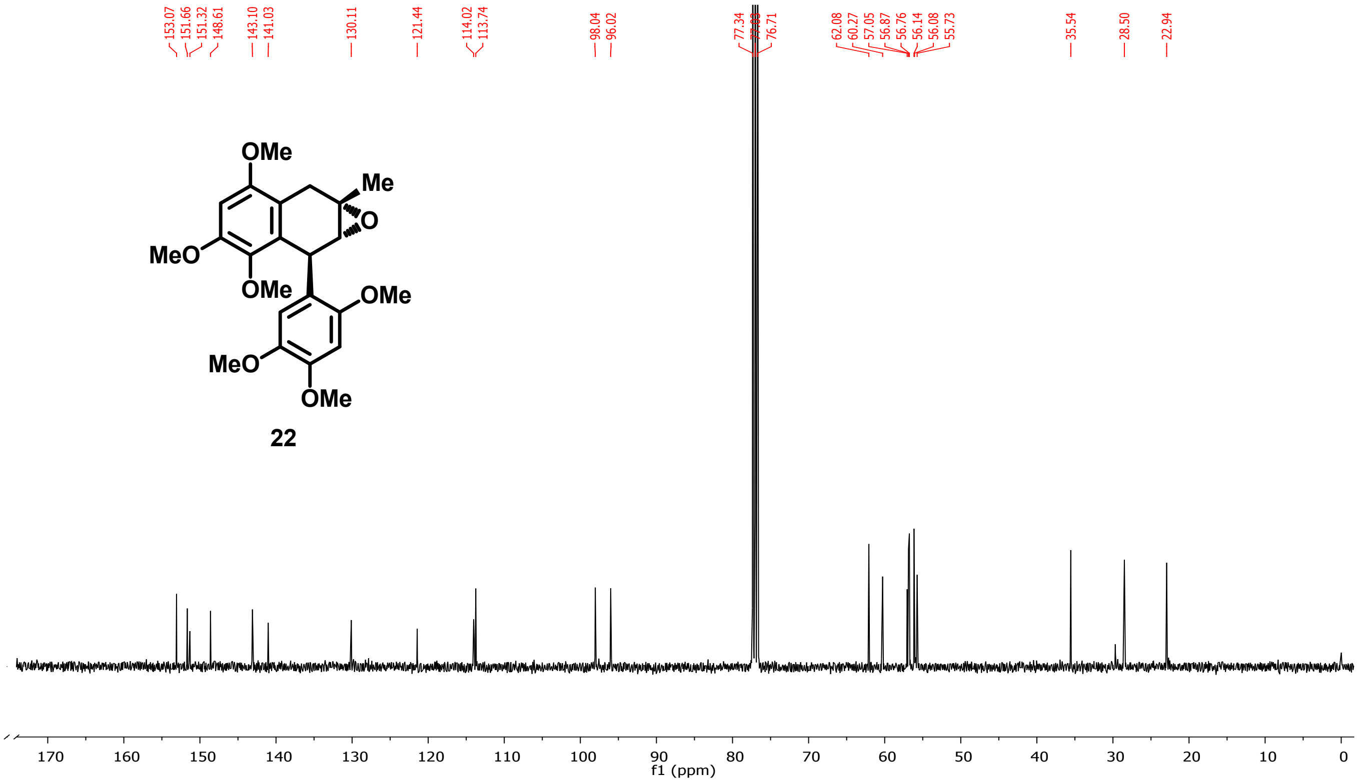


**21**

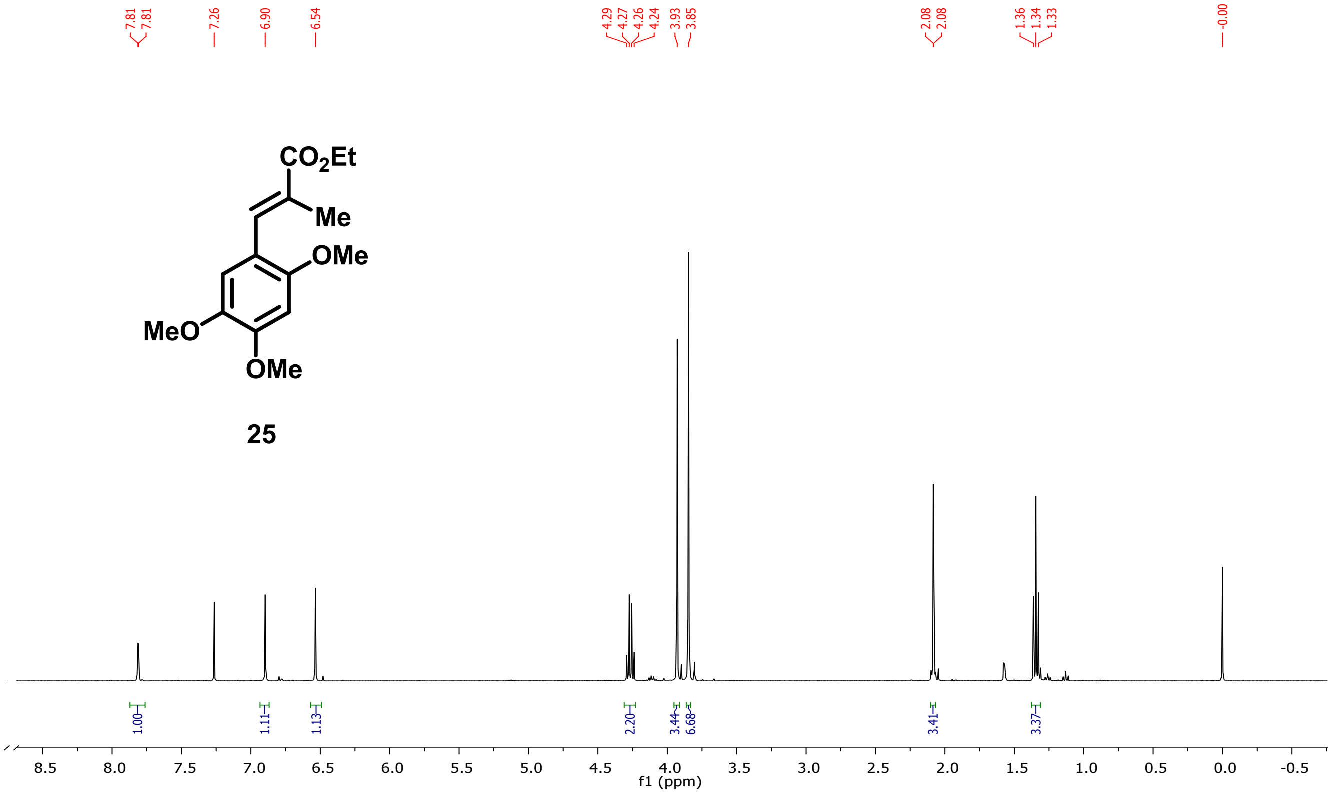




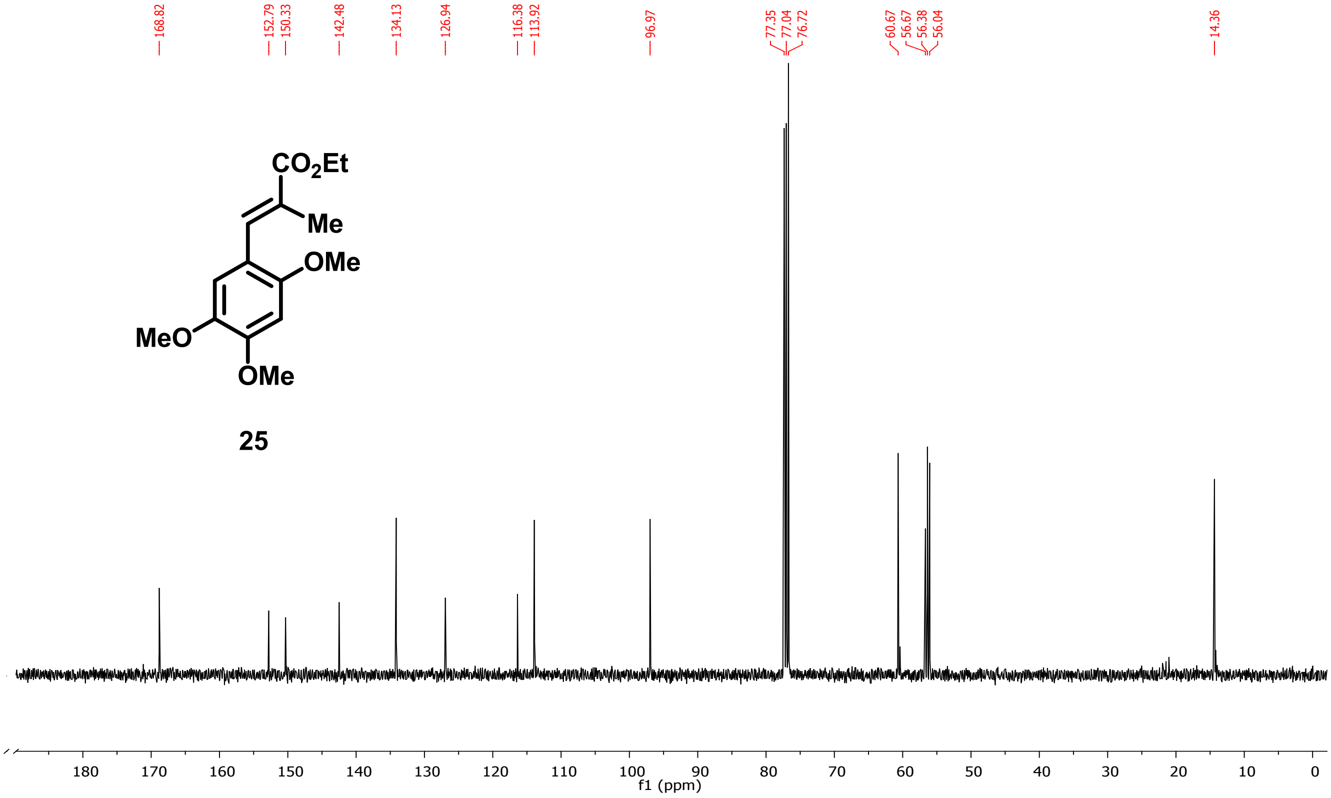
7.26
6.56
6.43
6.31
5.19
5.19
3.87
3.87
3.83
3.81
3.64
3.46
3.41
3.25
3.25
2.81
2.76
1.43
1.25
-0.00
OMe
Me
O
MeO
OMe
OMe
MeO
OMe
22
1.00
0.97
0.88
0.88
2.69
2.78
2.76
2.74
2.93
0.50
3.31
0.95
0.92
2.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



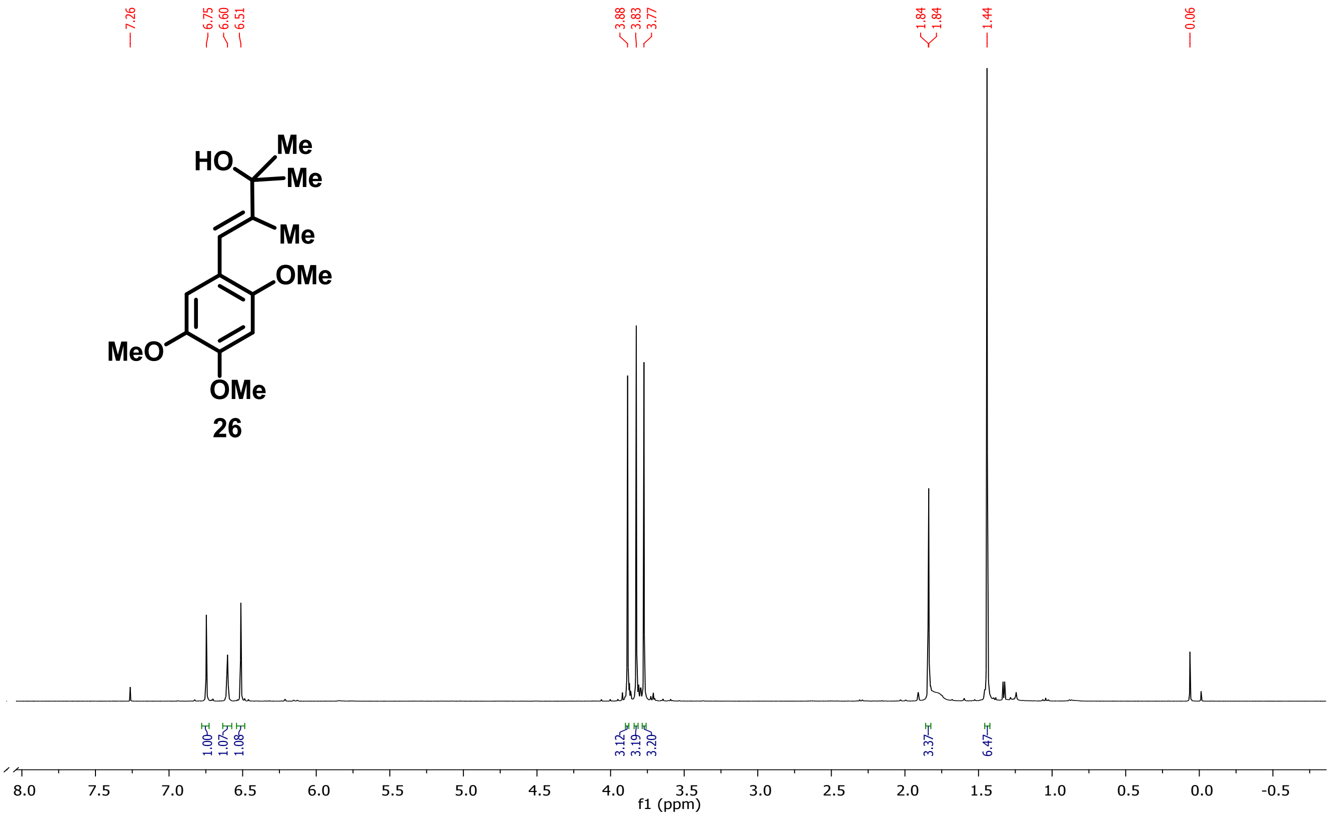
153.07
151.66
151.32
148.61
143.10
141.03
130.11
121.44
114.02
113.74
98.04
96.02
77.34
77.03
76.71
62.08
60.27
57.05
56.87
56.76
56.14
56.08
55.73
35.54
28.50
22.94
OMe
Me
O
MeO
OMe
OMe
MeO
OMe
22
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

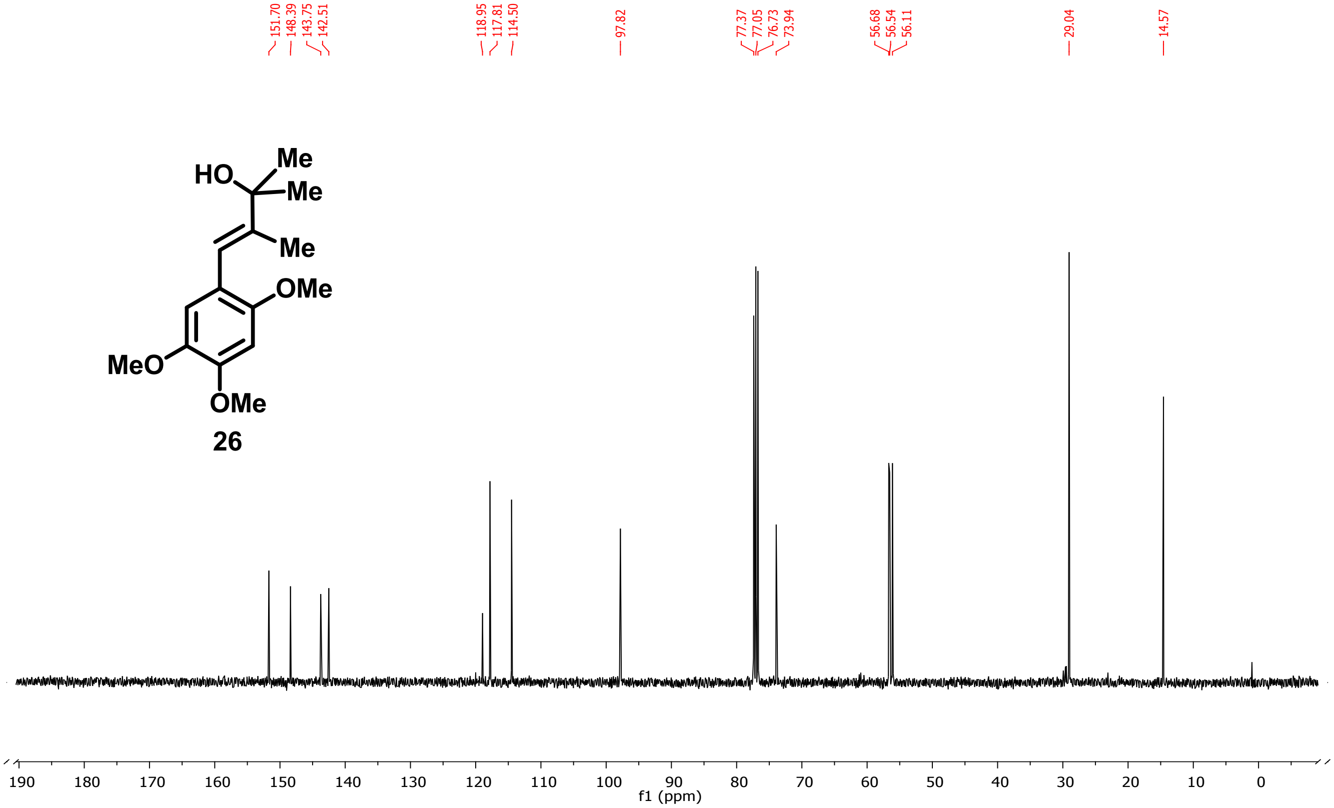

7.81
7.81
7.26
6.90
6.54
4.29
4.27
4.26
4.24
3.93
3.85
2.08
2.08
1.36
1.34
1.33
-0.00
$CO_2Et$
Me
OMe
MeO
OMe
1.00
1.11
1.13
2.20
3.44
6.68
3.41
3.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

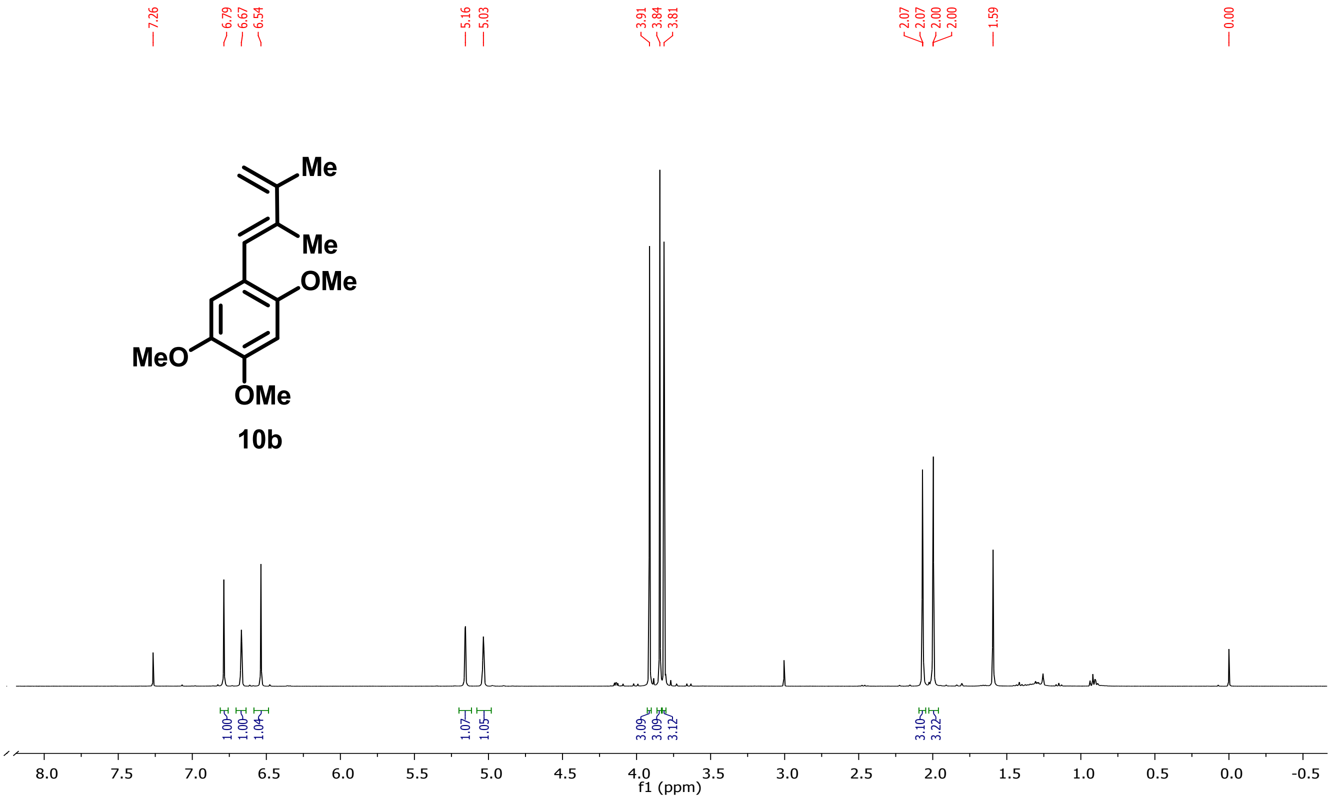
**25**

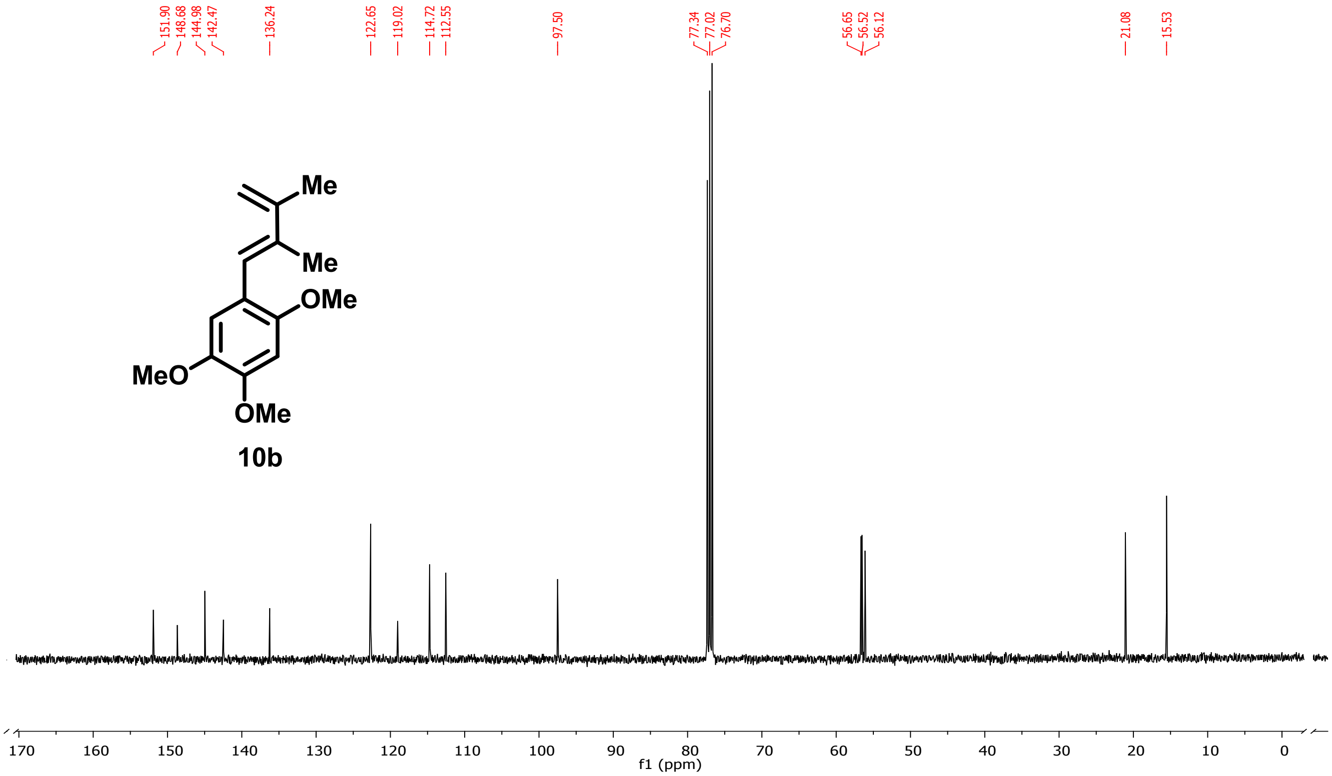

168.82
152.79
150.33
142.48
134.13
126.94
116.38
113.92
96.97
77.35
77.04
76.72
60.67
56.67
56.38
56.04
14.36
$CO_2Et$
Me
OMe
MeO
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**25**


**26**
7.26
6.75
6.60
6.51
3.88
3.83
3.77
1.84
1.84
1.44
0.06
HO
Me
Me
Me
OMe
MeO
OMe
1.00
1.07
1.08
3.12
3.19
3.20
3.37
6.47
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
-0.5
f1 (ppm)


**26**
151.70
148.39
143.75
142.51
118.95
117.81
114.50
97.82
77.37
77.05
76.73
73.94
56.68
56.54
56.11
29.04
14.57
HO
Me
Me
Me
OMe
MeO
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
6.79
6.67
6.54
5.16
5.03
3.91
3.84
3.81
2.07
2.07
2.00
2.00
1.59
0.00
Me
Me
OMe
MeO
OMe
10b
1.00
1.00
1.04
1.07
1.05
3.09
3.09
3.12
3.10
3.22
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
-0.5
f1 (ppm)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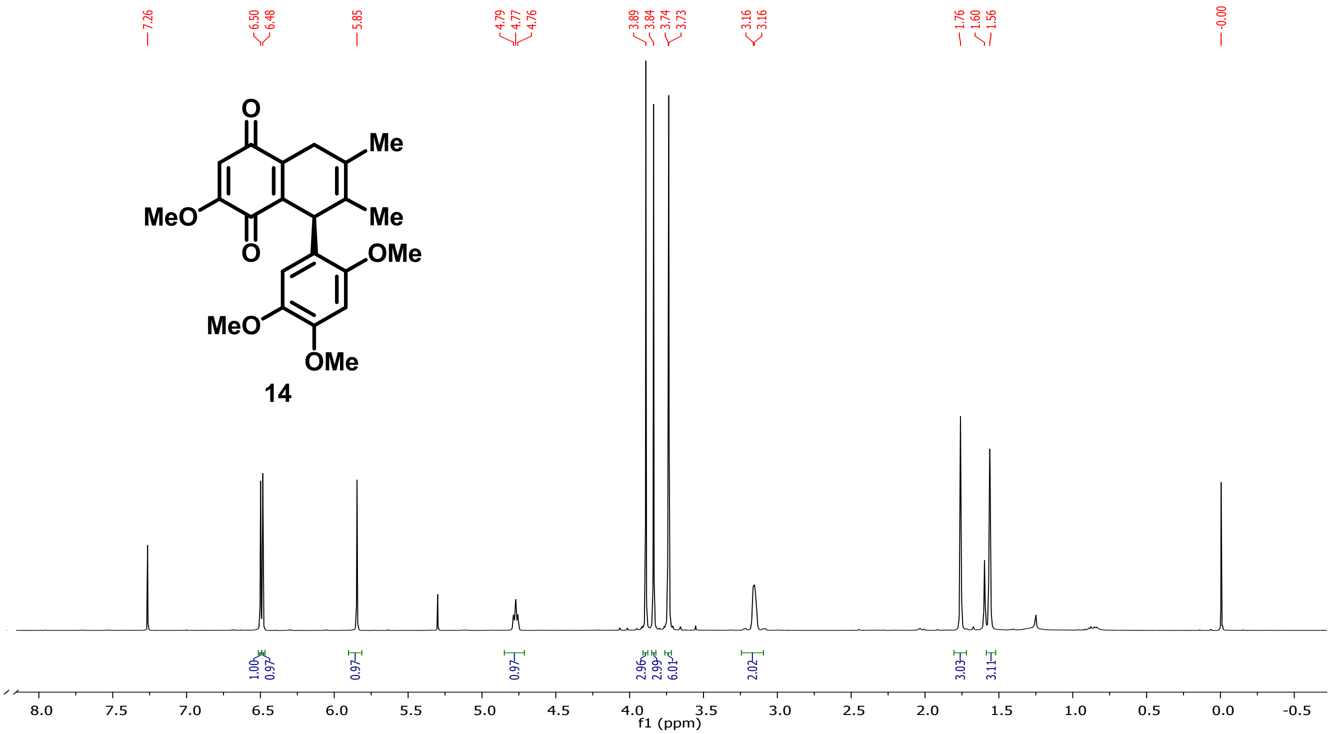
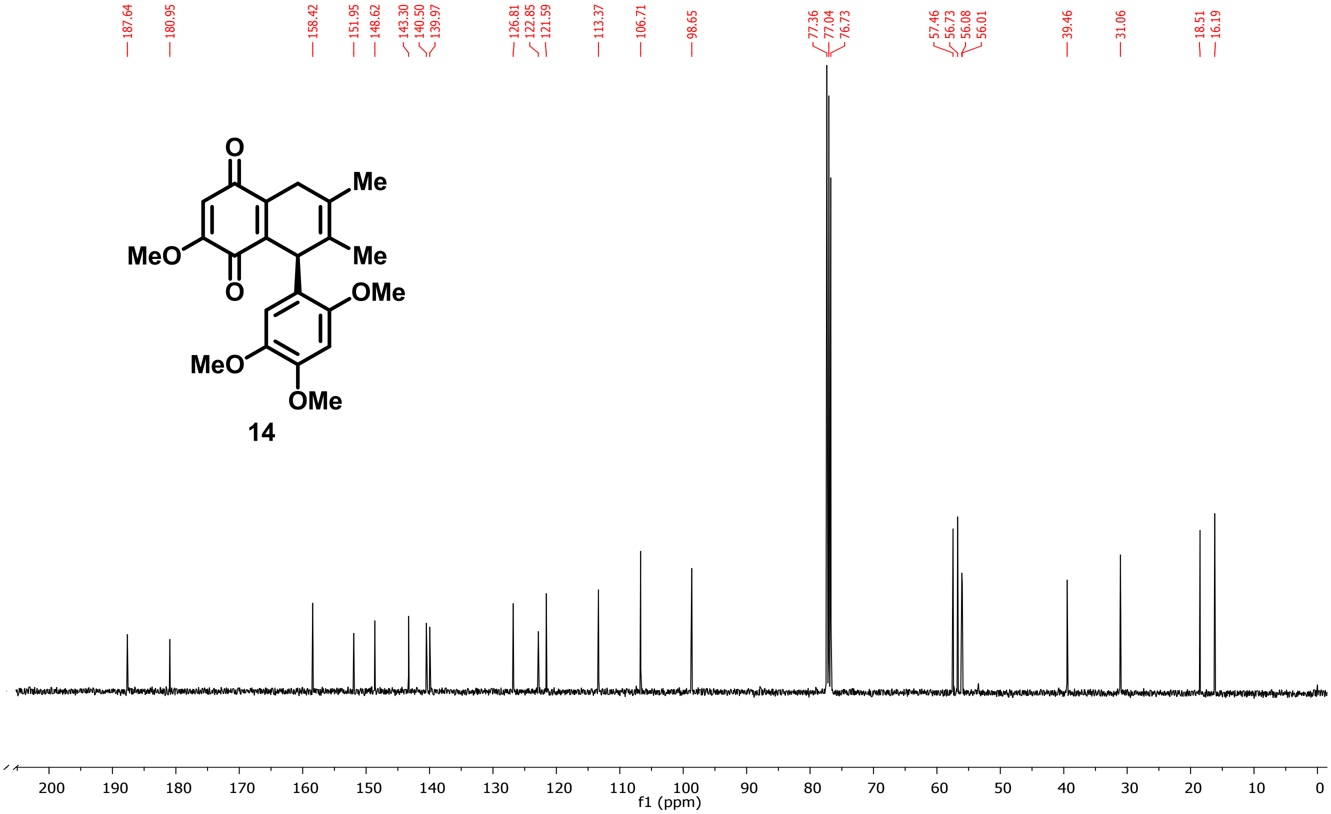
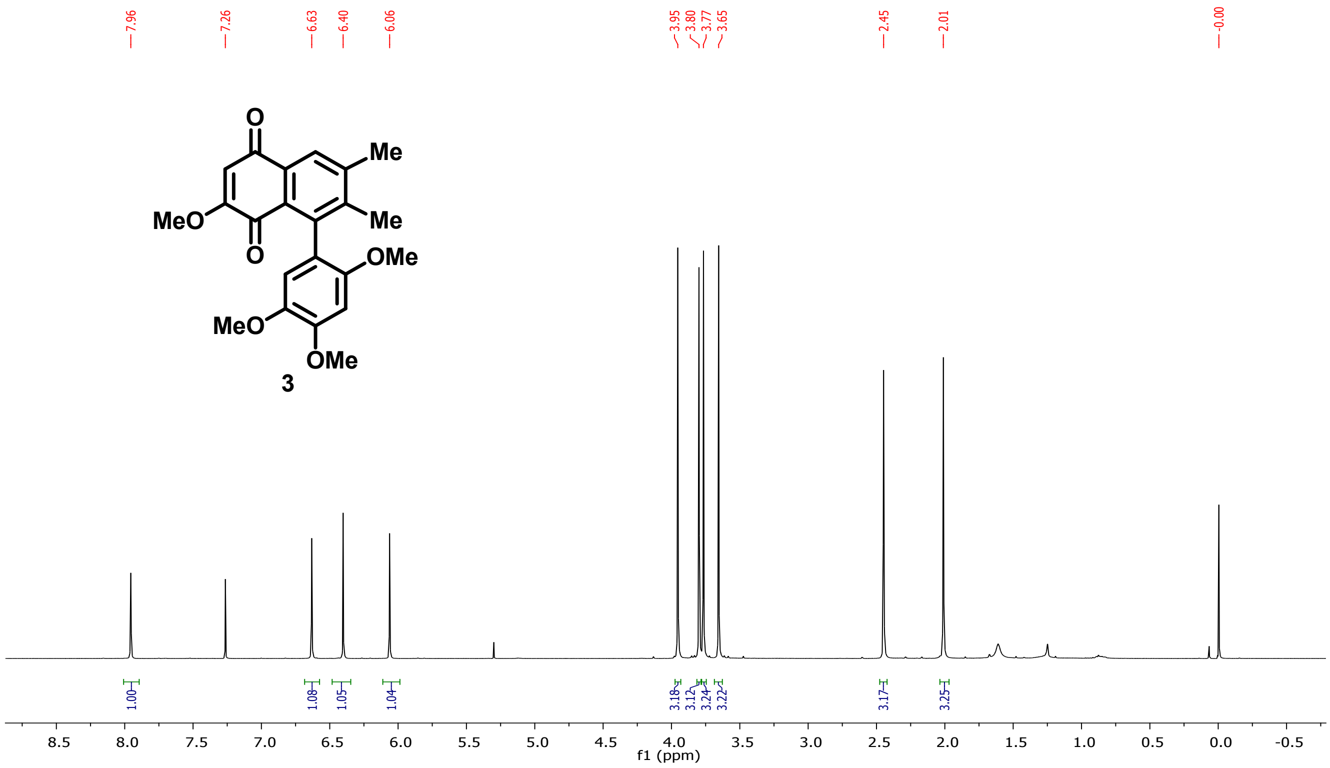
148.68
144.98
142.47
136.24
122.65
119.02
114.72
112.55
97.50
77.34
77.02
76.70
56.65
56.52
56.12
21.08
15.53
Me
Me
OMe
MeO
OMe
10b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
6.50
6.48
5.85
4.79
4.77
4.76
3.89
3.84
3.74
3.73
3.16
3.16
1.76
1.60
1.56
-0.00
MeO
O
O
Me
Me
OMe
MeO
OMe
14
1.00
0.97
0.97
0.97
2.96
2.99
6.01
2.02
3.03
3.11
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
-0.5
f1 (ppm)


187.64
180.95
158.42
151.95
148.62
143.30
140.50
139.97
126.81
122.85
121.59
113.37
106.71
98.65
77.36
77.04
76.73
57.46
56.73
56.08
56.01
39.46
31.06
18.51
16.19
MeO
O
O
Me
Me
OMe
MeO
OMe
14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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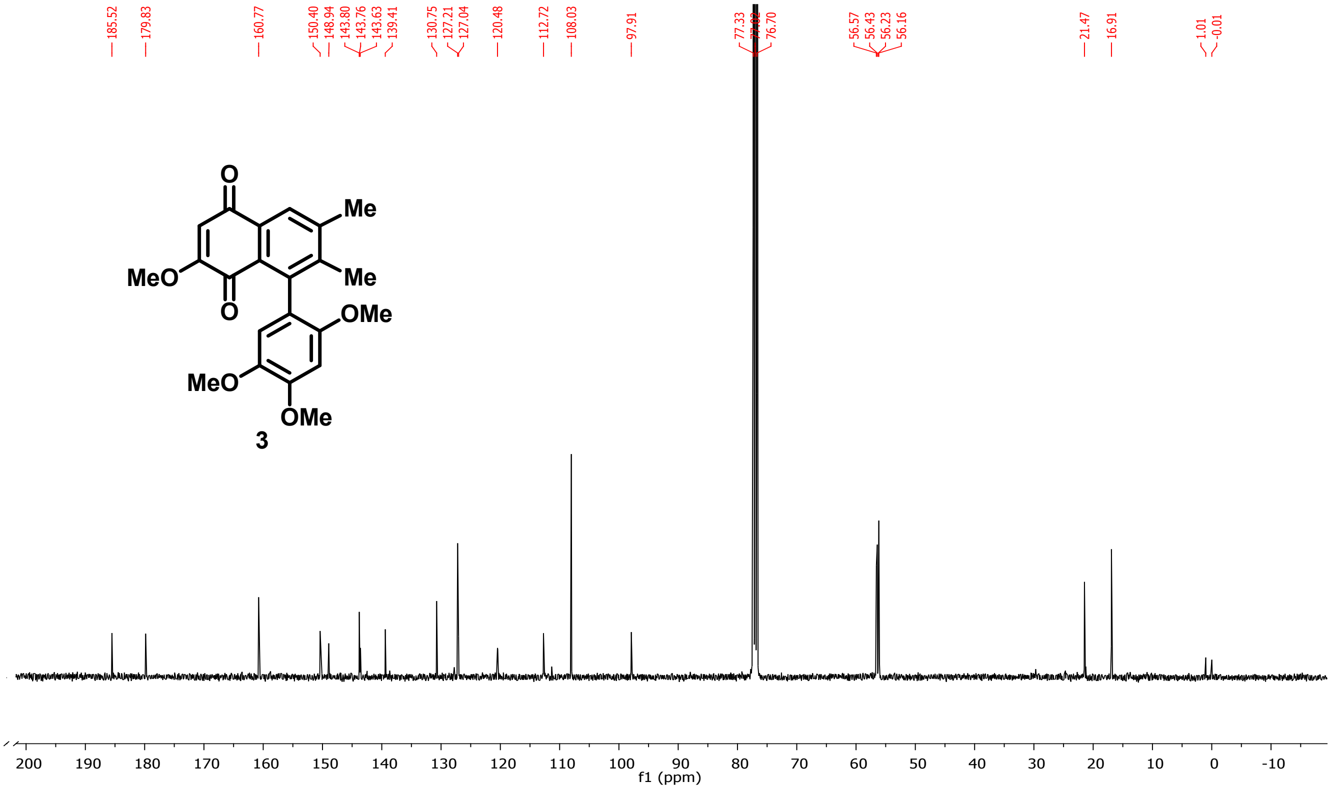
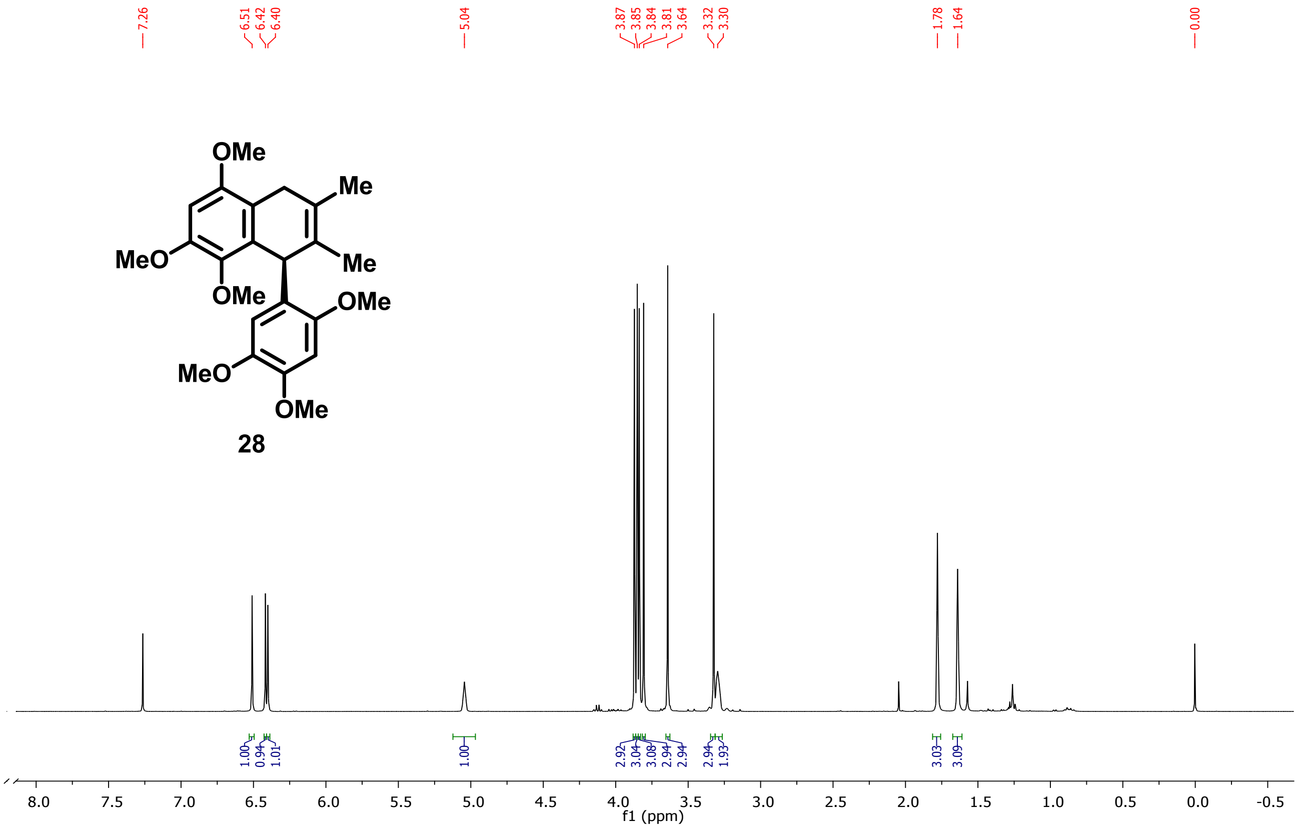
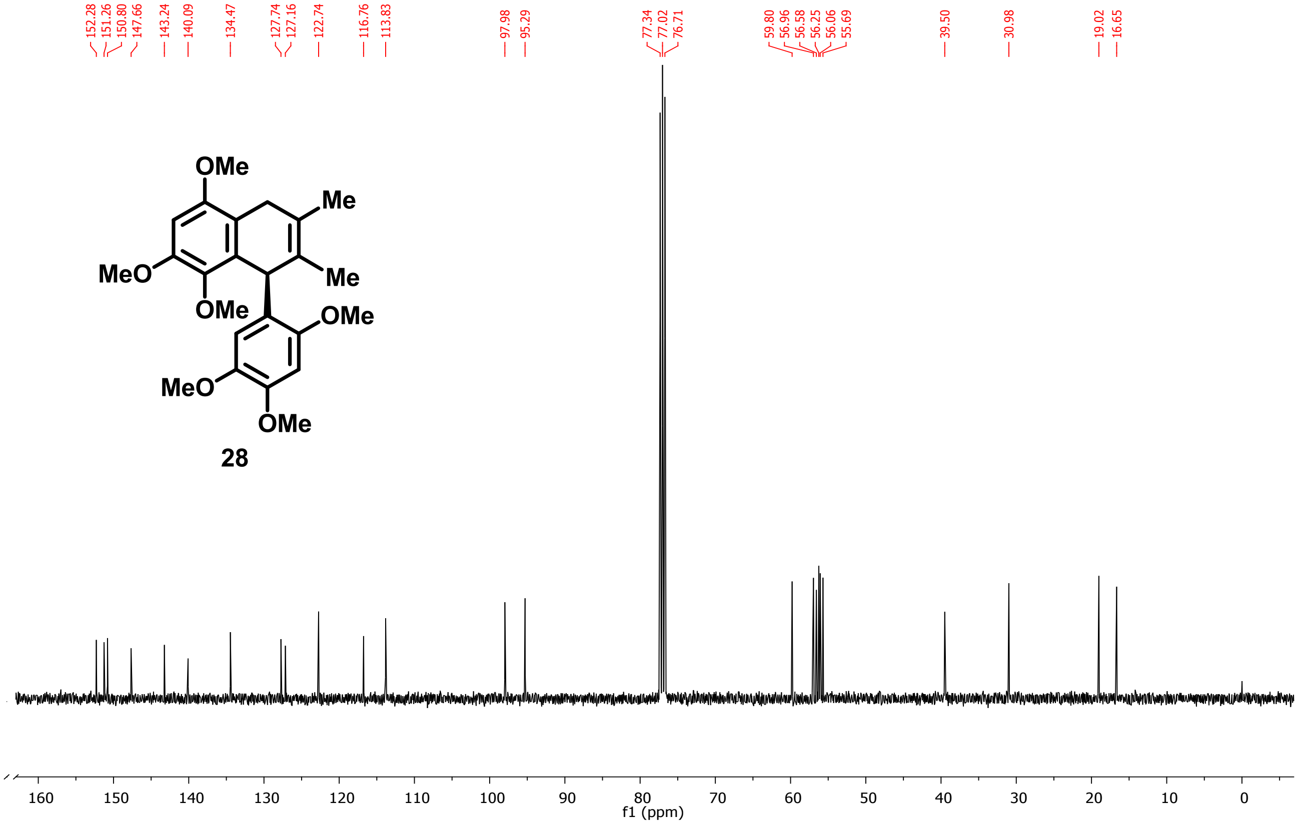
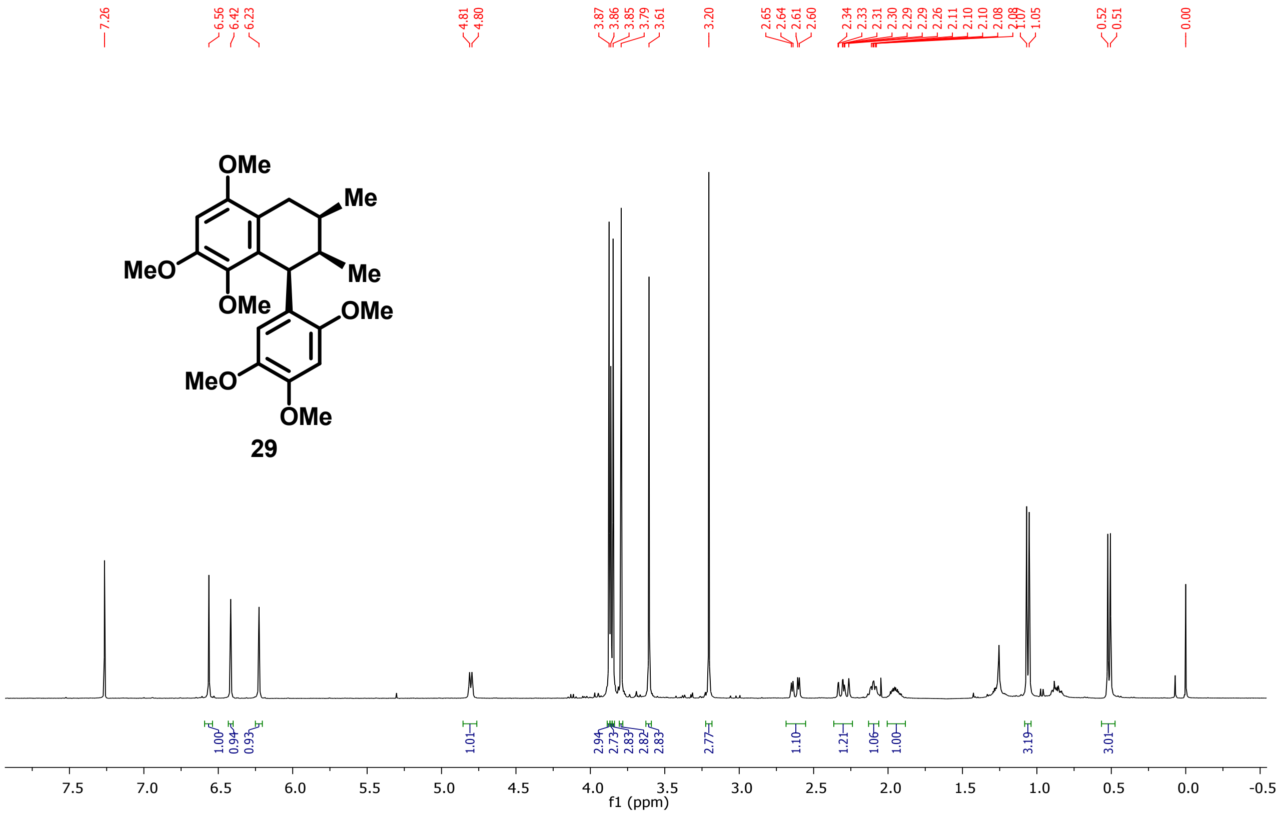
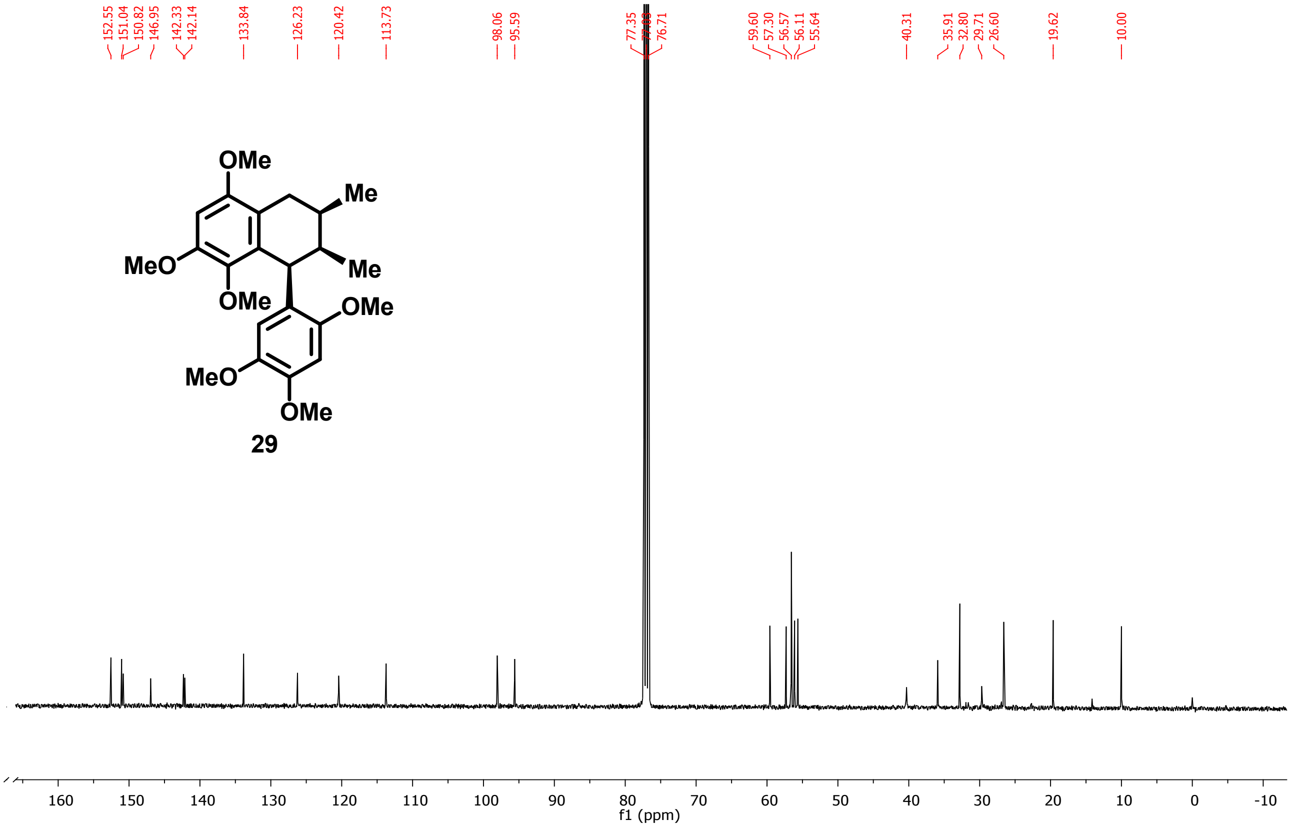
7.26
6.63
6.40
6.06
3.95
3.80
3.77
3.65
2.45
2.01
0.00
1.00
1.08
1.05
1.04
3.18
3.12
3.24
3.22
3.17
3.25
O
Me
MeO
Me
O
OMe
MeO
OMe
3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


185.52
179.83
160.77
150.40
148.94
143.80
143.76
143.63
139.41
130.75
127.21
127.04
120.48
112.72
108.03
97.91
77.33
77.02
76.70
56.57
56.43
56.23
56.16
21.47
16.91
1.01
-0.01
O
Me
MeO
Me
O
OMe
MeO
OMe
3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

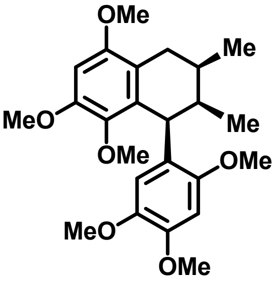

7.26
6.51
6.42
6.40
5.04
3.87
3.85
3.84
3.81
3.64
3.32
3.30
1.78
1.64
0.00
OMe
Me
MeO
Me
OMe
OMe
MeO
OMe
28
1.00
0.94
1.01
1.00
2.92
3.04
3.08
2.94
2.94
2.94
1.93
3.03
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


152.28
151.26
150.80
147.66
143.24
140.09
134.47
127.74
127.16
122.74
116.76
113.83
97.98
95.29
77.34
77.02
76.71
59.80
56.96
56.58
56.25
56.06
55.69
39.50
30.98
19.02
16.65
OMe
Me
MeO
Me
OMe
OMe
MeO
OMe
28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

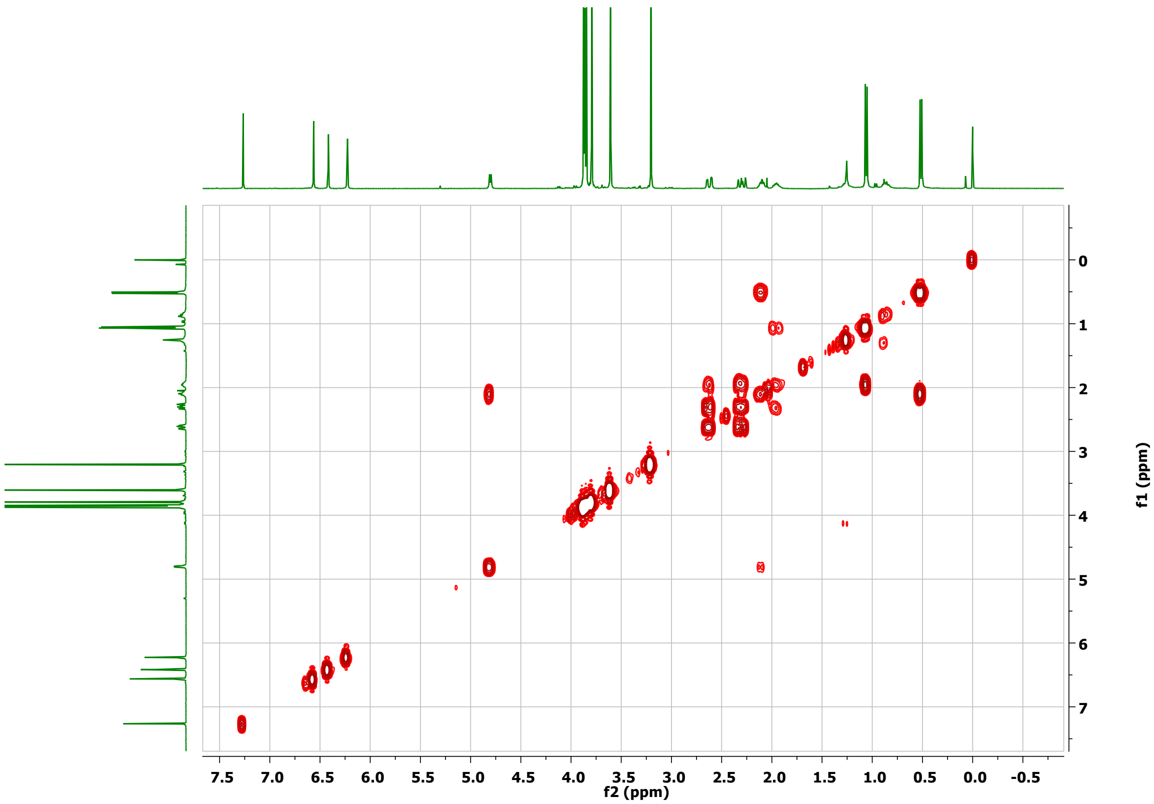

7.26
6.56
6.42
6.23
4.81
4.80
3.87
3.86
3.85
3.79
3.61
3.20
2.65
2.64
2.61
2.60
2.34
2.33
2.31
2.30
2.29
2.29
2.26
2.11
2.10
2.10
2.08
2.08
1.07
1.05
0.52
0.51
0.00
OMe
Me
Me
MeO
OMe
OMe
MeO
OMe
29
1.00
0.94
0.93
1.01
2.94
2.73
2.83
2.82
2.83
2.77
1.10
1.21
1.06
1.00
3.19
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


152.55
151.04
150.82
146.95
142.33
142.14
133.84
126.23
120.42
113.73
98.06
95.59
77.35
76.71
59.60
57.30
56.57
56.11
55.64
40.31
35.91
32.80
29.71
26.60
19.62
10.00
OMe
Me
Me
MeO
OMe
OMe
MeO
OMe
29
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

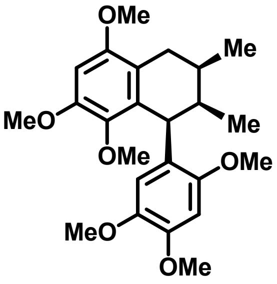
*COSY spectrum*



**29**



*NOESY spectrum*



**29**