Quick identification of native or technical lignin side-chain chemical shifts using annotated NMR HSQC plots and Database model data.

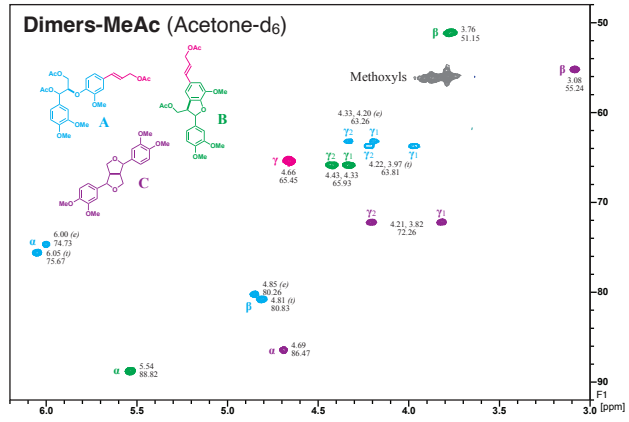
Many of the compounds in the database reflect the three most important dimers, characterized by their unique inter-unit linkages, derived from the free-radical coupling of coniferyl alcohol during lignin biosynthesis. These are the β-aryl ether (or simply β-ether, β-O-4), phenylcoumaran (β-5), and resinol (β-β) units. $^{1}H–^{13}C$ correlative NMR (HSQC, heteronuclear single-quantum coherence) spectra provides an excellent way to profile these units/linkages in the lignin polymer and also provides a tool for quantitation.

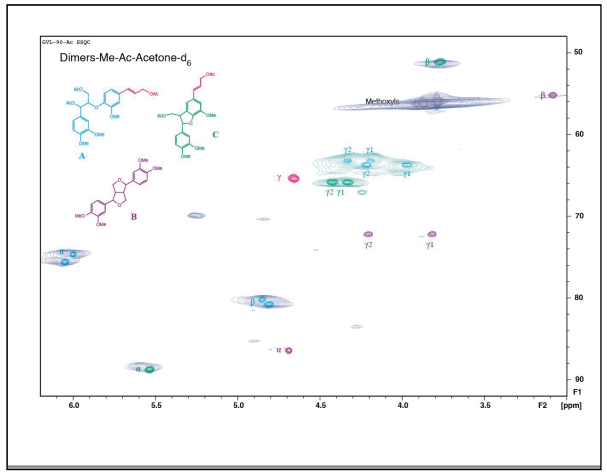
To aid the qualitative identification of the components, a mixture of the guaiacyl (4-hydroxy-3-methoxy monolignol) dimers was prepared* from coniferyl alcohol, cupric chloride, and oxygen in acetonitrile. The reaction mixture provided the three dehydrodiconiferyl alcohol dimers, β-β, β-5 and the β-O-4 as well as a small amount of vanillin, presumably via the oxidized monomer, coniferaldehyde.

The HSQC spectrum for the mixture was obtained in three common NMR solvents, perdeuterated chloroform ($CDCl_3$ ref. 7.24 and 77.0 ppm), acetone (acetone-d_6 ref. 2.04 and 29.83 ppm, and DMSO (dmso-d_6 ref. 2.49 and 39.5 ppm). Model compound chemical shifts were used to assign and annotate the spectra. The same mixture was derivatized to model the dimers as phenolic methyl ethers, as the fully acetylated compounds, and finally as the acetates of the phenolic methyl ethers.

Twelve HSQC plots illustrating the side-chain unit contours with their characteristic linkages in the three solvents were prepared. These plots provide a quick visual affirmation and chemical shift data for identification of these linkages in both native and technical lignins. The HSQC plots all cover the proton F2 region from 6.2 – 3.0 ppm and the carbon F1 region 92 – 48 ppm. This makes it easy to see the changes in chemical shift due to derivatization.

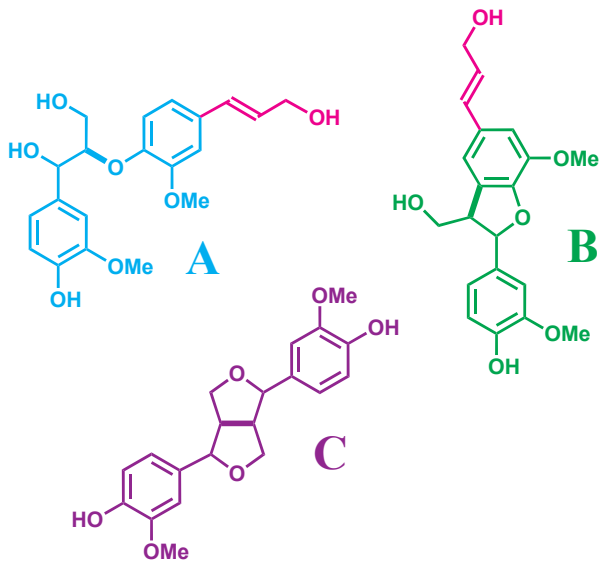
*The synthesis and derivitization details will be forthcoming in a future publication.





GVL delignified softwood lignin

Dimers (Acetone-d_6)



Methoxyls

β 3.53 54.75

β 3.08 55.20

3.81, 3.69 *(e)* 61.82

γ2 γ1

γ2 γ1

γ 4.19 63.33

γ2 γ1 3.87, 3.83 64.59

γ2 γ1 3.69, 3.49 *(t)* 61.90

γ2 γ1 4.19, 3.79 72.18

α 4.88 73.83

α 4.66 86.62

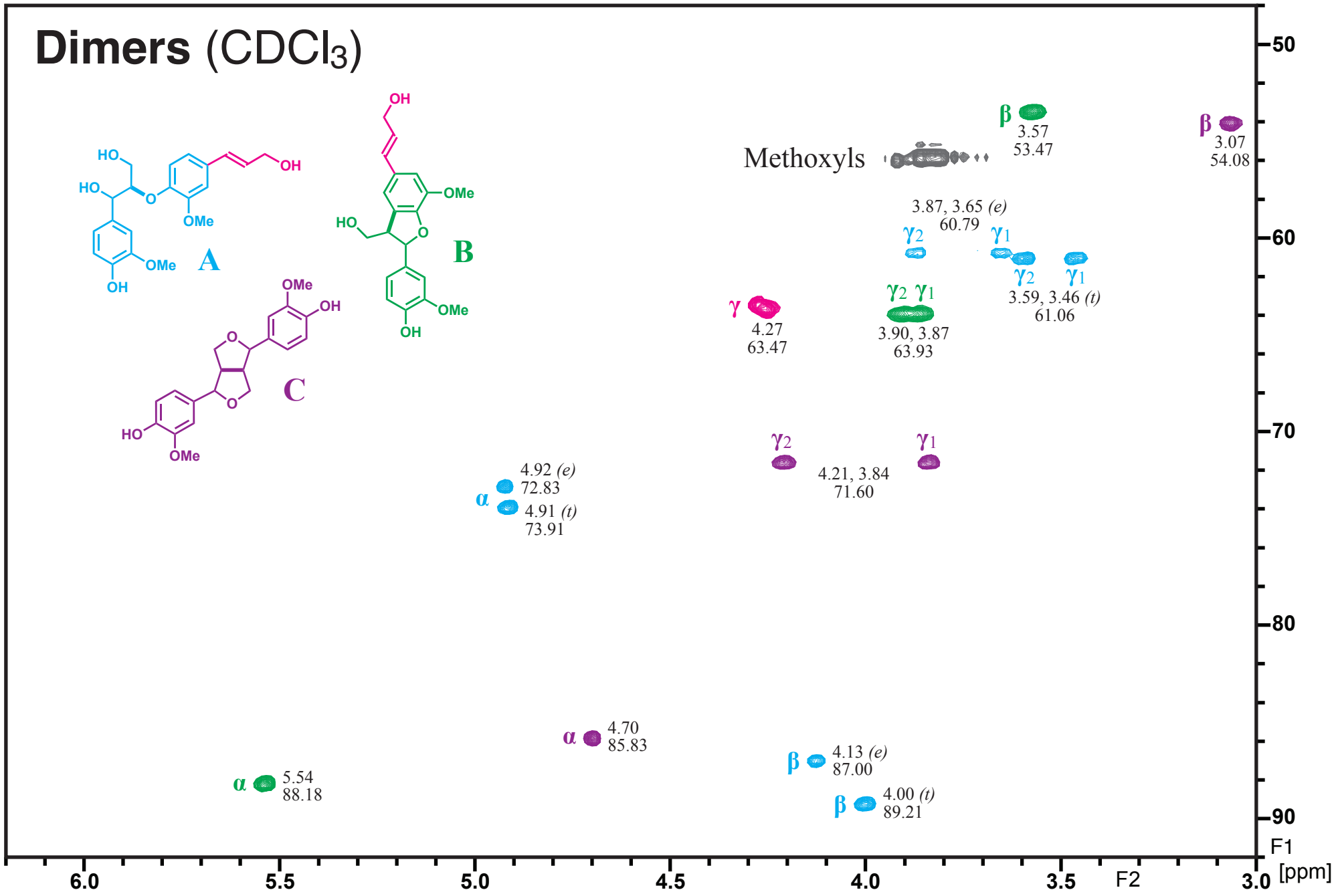
β 4.29 *(e)* 86.65

β 4.20 *(t)* 88.43

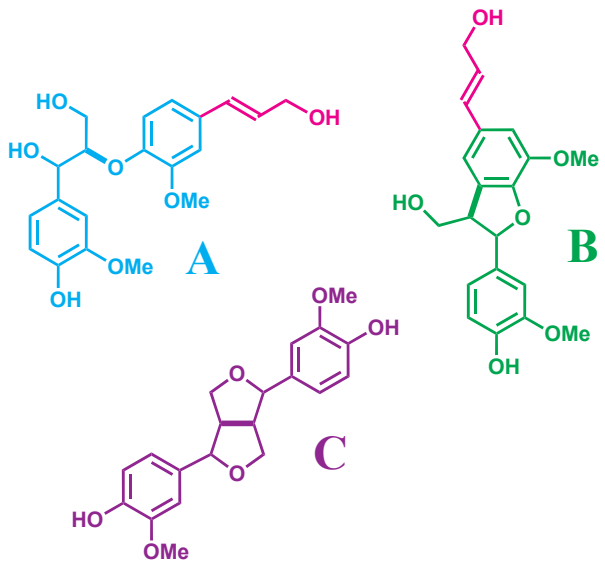
α 5.55 88.52

50 60 70 80 90 F1

6.0 5.5 5.0 4.5 4.0 3.5 F2 3.0 [ppm]


Dimers (CDCl3)
A
B
C
Methoxyls
β
3.57
53.47
β
3.07
54.08
3.87, 3.65 (e)
60.79
γ2
γ1
γ2
γ1
3.59, 3.46 (t)
61.06
γ
4.27
63.47
γ2 γ1
3.90, 3.87
63.93
γ2
γ1
4.21, 3.84
71.60
α
4.92 (e)
72.83
4.91 (t)
73.91
α
4.70
85.83
α
5.54
88.18
β
4.13 (e)
87.00
β
4.00 (t)
89.21
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
F2
3.0
[ppm]

Dimers (DMSO-d_6)



Methoxyls

β 3.43 52.99

β 3.02 53.57

γ 3.58 *(e)* 60.08

γ2 3.57, 3.23 *(t)* 60.08 γ1

γ 4.07 61.63

γ2 γ1 3.69, 3.62 62.92

α 4.70 *(t)* 70.93
4.69 *(e)* 71.59

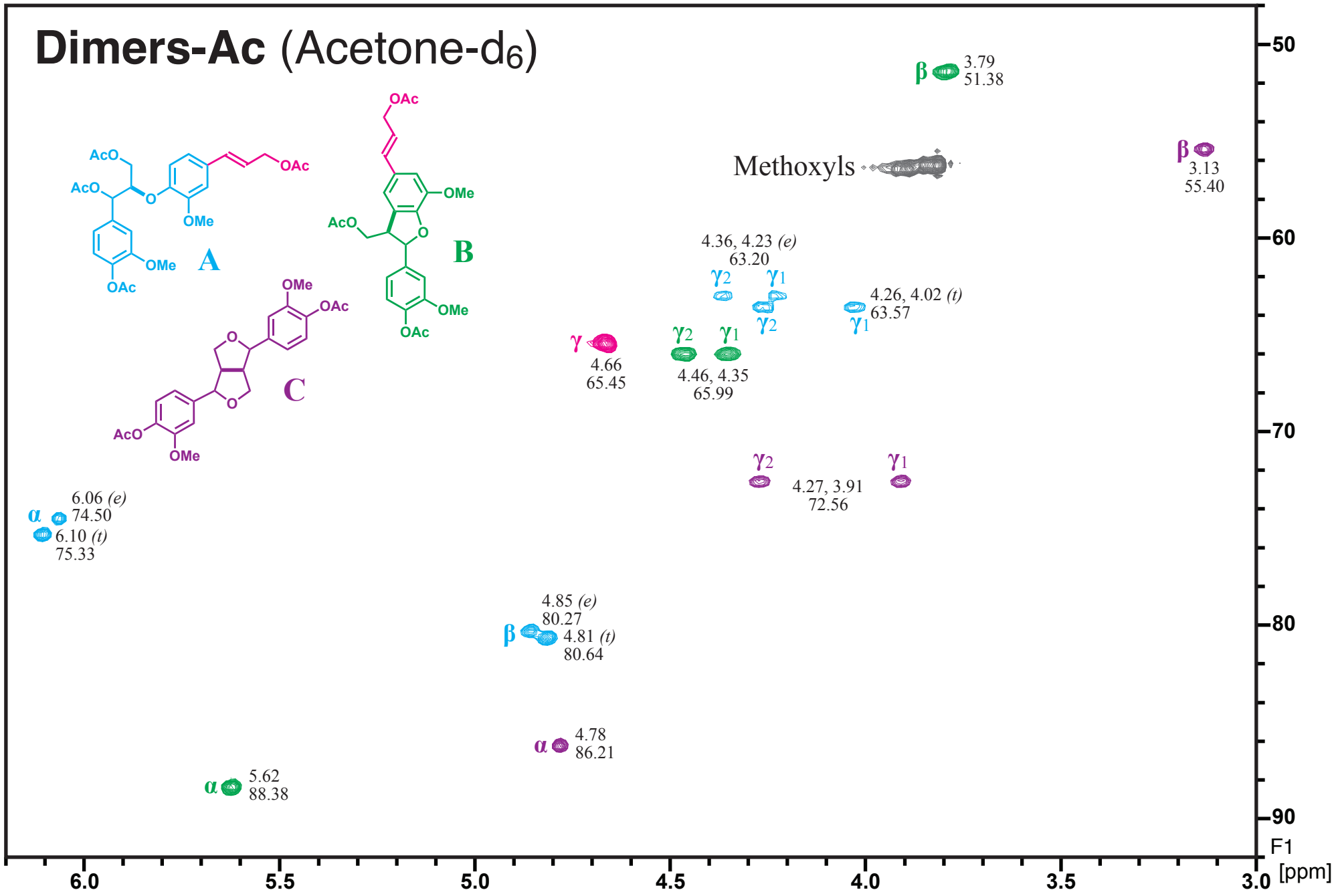
γ2 4.11, 3.71 70.87 γ1

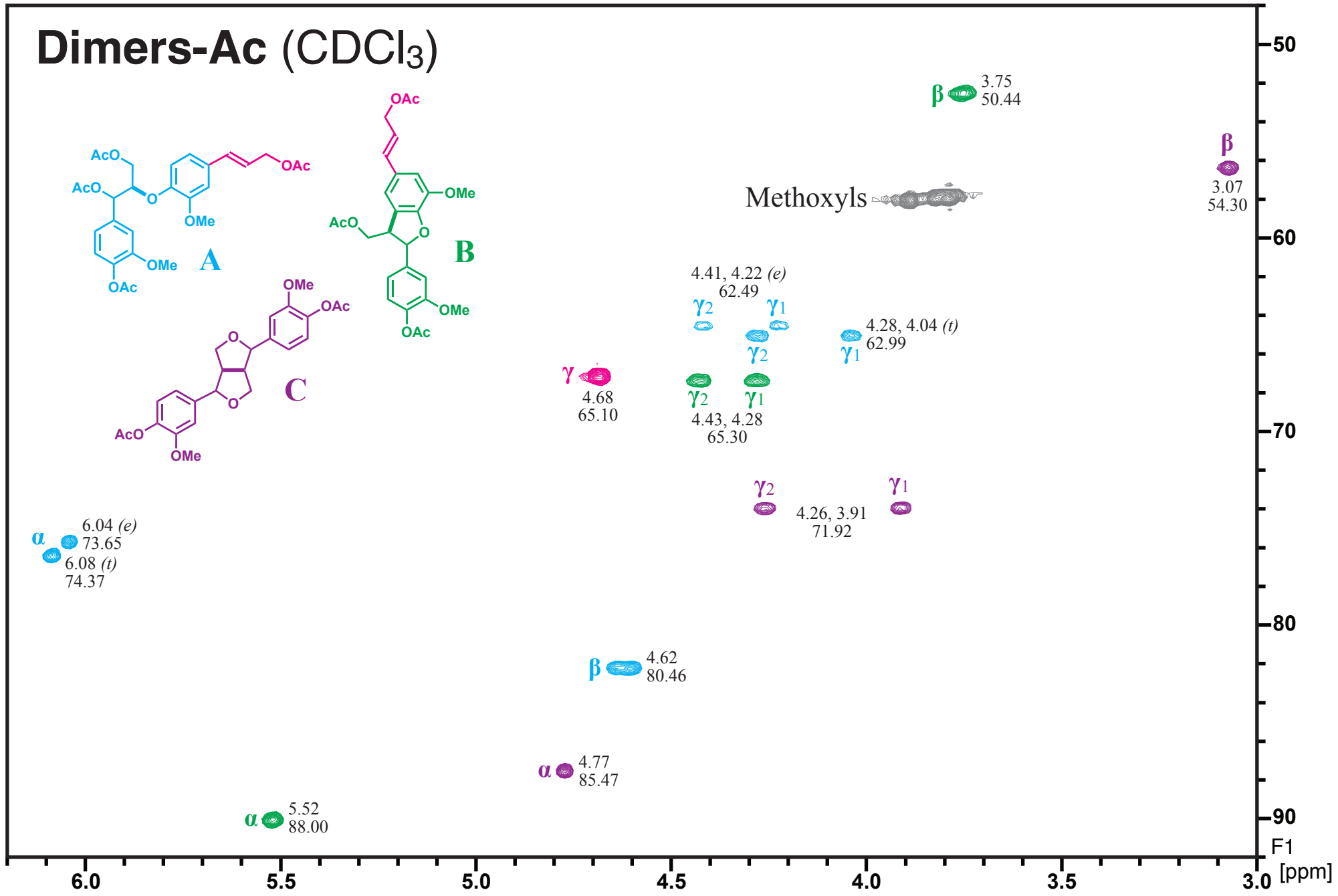
β 4.28 *(e)* 83.70
4.24 *(t)* 84.33

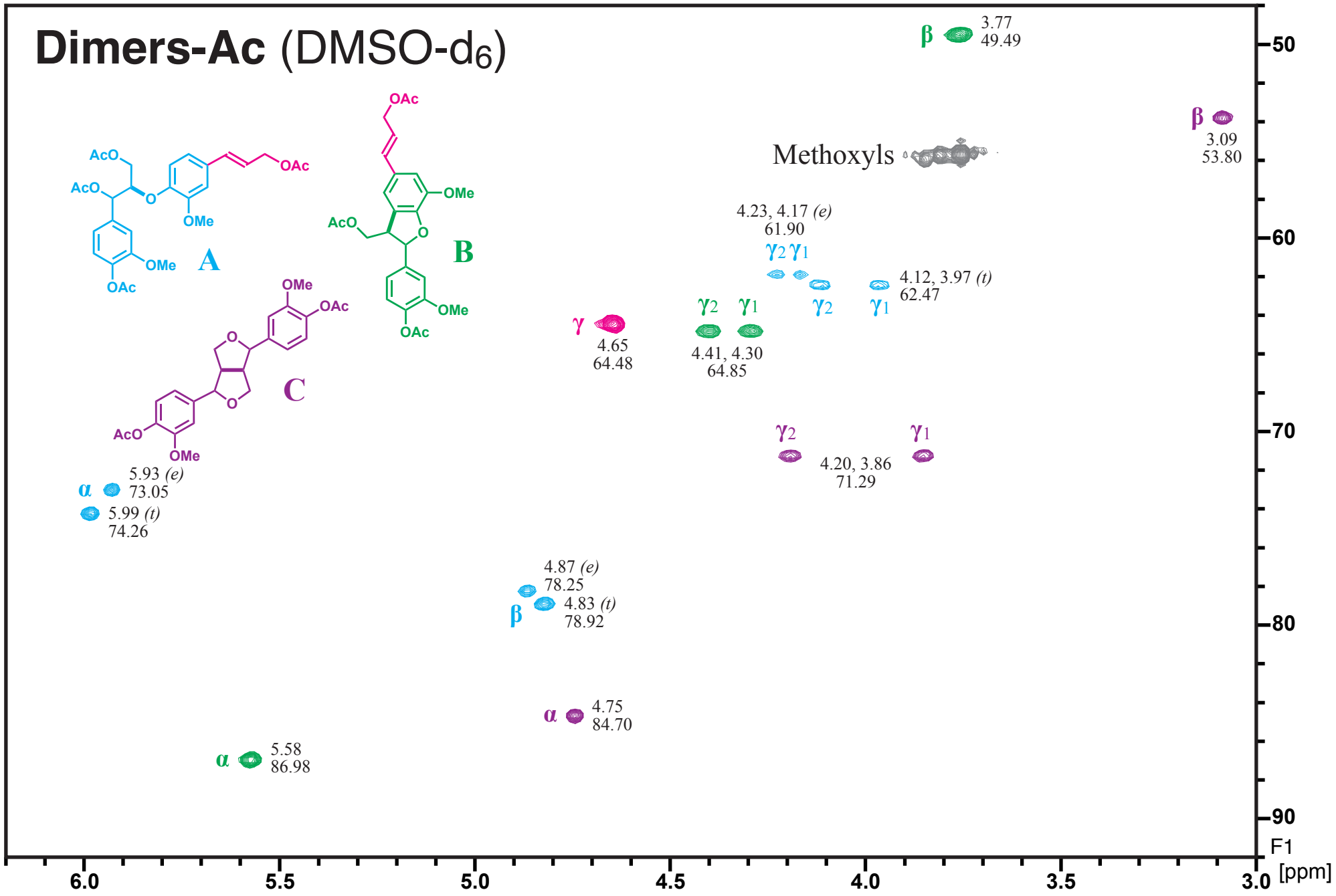
α 4.59 85.16

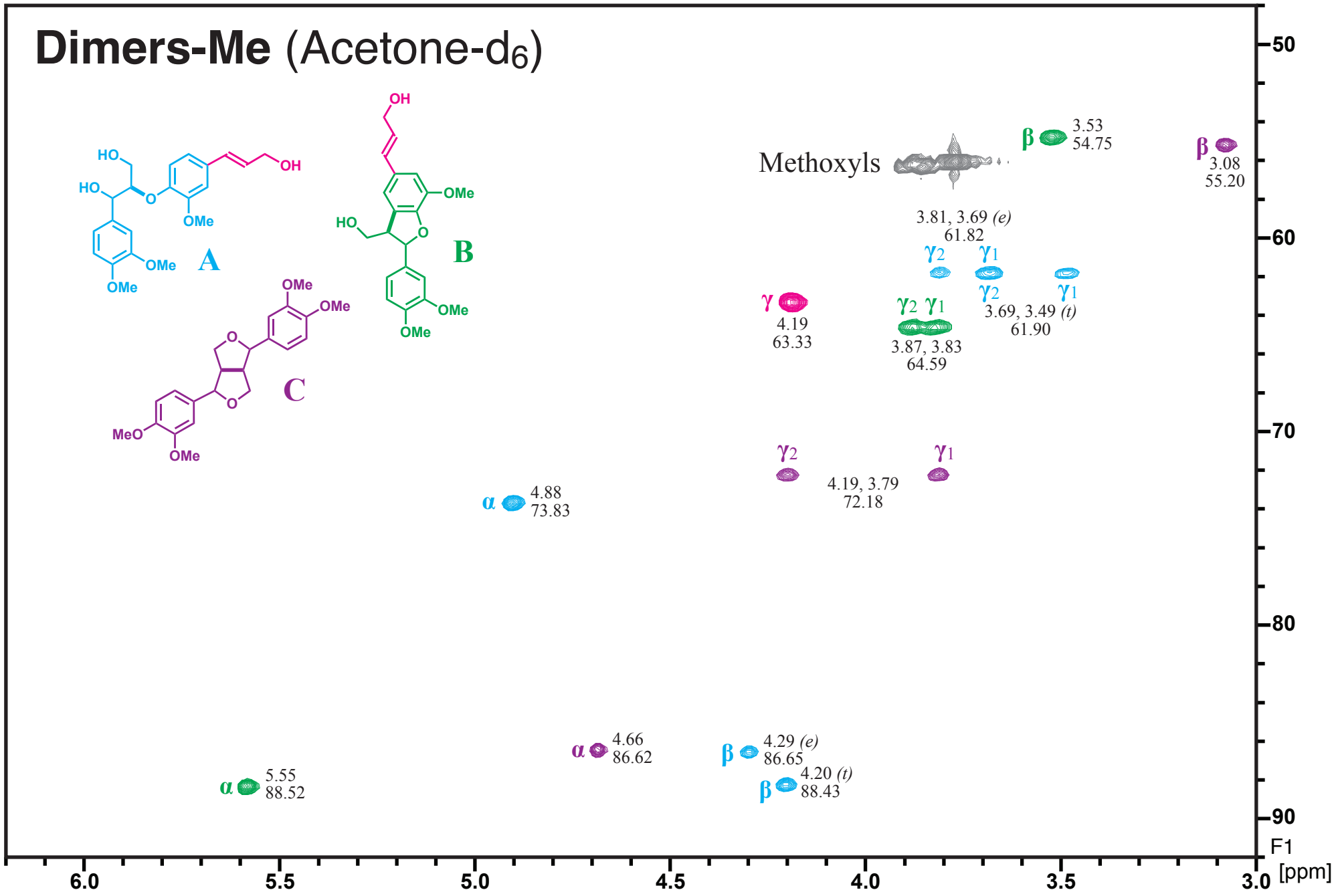
α 5.44 87.21

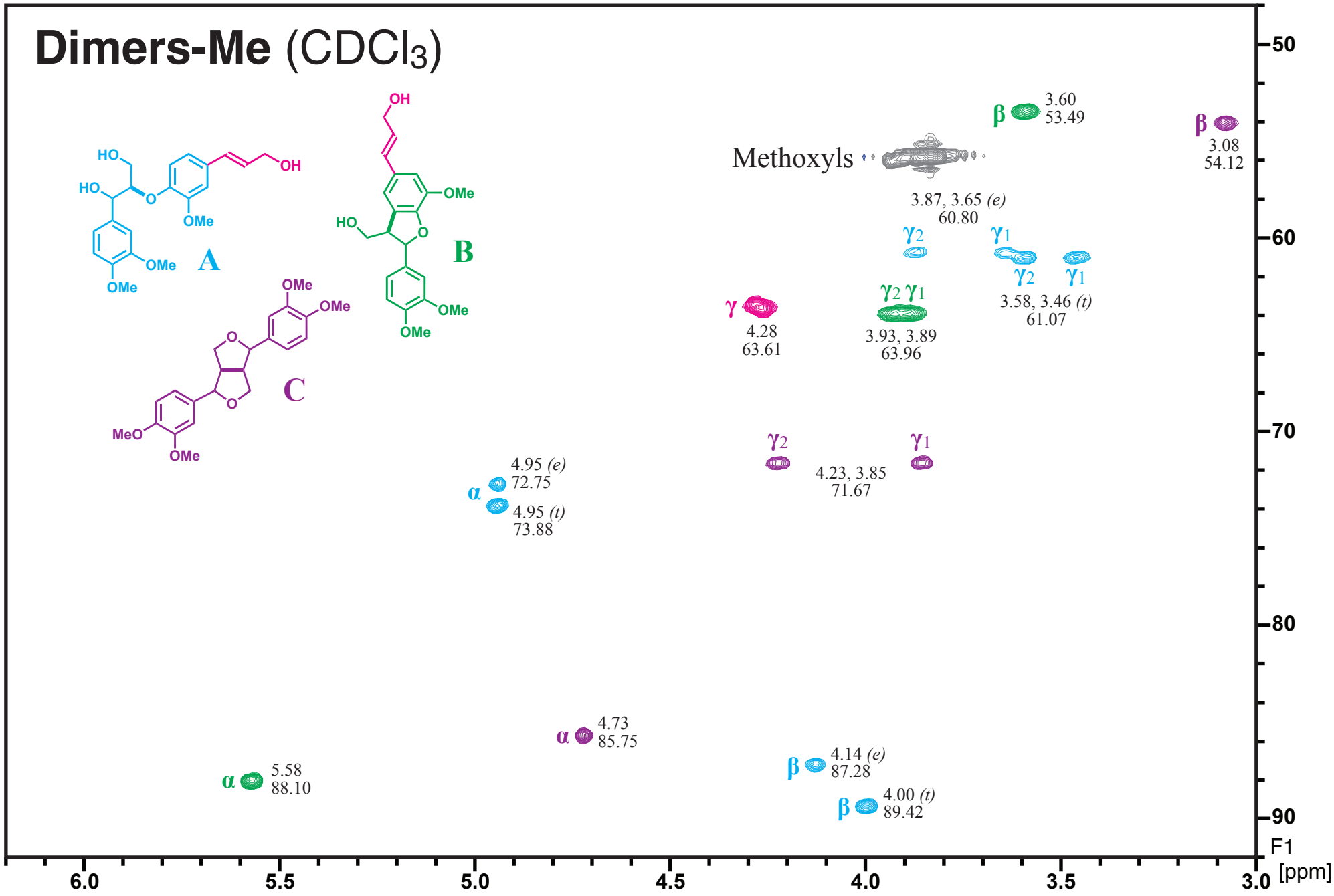
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


Dimers-Ac (Acetone-d6)
A
B
C
Methoxyls
β 3.79 51.38
β 3.13 55.40
4.36, 4.23 (e) 63.20
γ2 γ1
γ2
4.26, 4.02 (t) 63.57
γ1
γ 4.66 65.45
γ2 γ1
4.46, 4.35 65.99
γ2 γ1
4.27, 3.91 72.56
α 6.06 (e) 74.50
6.10 (t) 75.33
4.85 (e) 80.27
β 4.81 (t) 80.64
α 4.78 86.21
α 5.62 88.38
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]

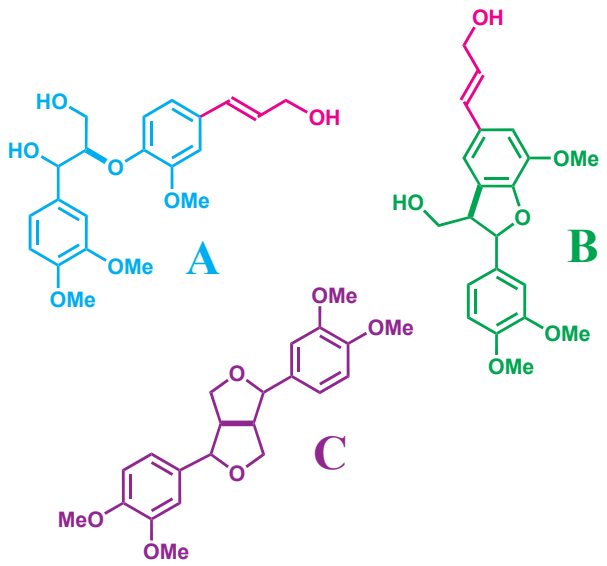

Dimers-Ac (CDCl3)
AcO
AcO
OAc
O
OMe
OMe
OAc
A
OAc
OMe
AcO
O
OMe
OAc
B
OMe
OAc
O
O
AcO
OMe
C
β 3.75 50.44
β 3.07 54.30
Methoxyls
4.41, 4.22 (e) 62.49
γ2 γ1
γ2
γ2 γ1
4.43, 4.28 65.30
γ 4.68 65.10
γ1 4.28, 4.04 (t) 62.99
γ2 γ1
4.26, 3.91 71.92
α 6.04 (e) 73.65
6.08 (t) 74.37
β 4.62 80.46
α 4.77 85.47
α 5.52 88.00
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


Dimers-Ac (DMSO-d6)
A
B
C
Methoxyls
β 3.77 49.49
β 3.09 53.80
4.23, 4.17 (e) 61.90
γ2 γ1
4.12, 3.97 (t) 62.47
γ2 γ1 γ2 γ1
γ 4.65 64.48
4.41, 4.30 64.85
γ2 γ1
4.20, 3.86 71.29
α 5.93 (e) 73.05
5.99 (t) 74.26
4.87 (e) 78.25
β 4.83 (t) 78.92
α 4.75 84.70
α 5.58 86.98
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


Dimers-Me (Acetone-d6)
HO
HO
OH
O
OMe
OMe
OMe
A
OH
HO
OMe
O
OMe
OMe
B
OMe
OMe
O
O
MeO
OMe
C
Methoxyls
β 3.53
54.75
β 3.08
55.20
3.81, 3.69 (e)
61.82
γ2
γ1
γ2
γ1
γ 4.19
63.33
γ2 γ1
3.87, 3.83
64.59
3.69, 3.49 (t)
61.90
γ2
γ1
4.19, 3.79
72.18
α 4.88
73.83
α 4.66
86.62
β 4.29 (e)
86.65
β 4.20 (t)
88.43
α 5.55
88.52
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


Dimers-Me (CDCl3)
HO
HO
OH
OMe
OMe
OMe
A
OH
HO
OMe
OMe
OMe
B
OMe
OMe
O
O
MeO
OMe
C
Methoxyls
β 3.60 53.49
β 3.08 54.12
3.87, 3.65 (e) 60.80
γ2
γ1
γ2 γ1
3.58, 3.46 (t) 61.07
γ 4.28 63.61
γ2 γ1 3.93, 3.89 63.96
γ2
γ1
4.23, 3.85 71.67
α 4.95 (e) 72.75
4.95 (t) 73.88
α 4.73 85.75
α 5.58 88.10
β 4.14 (e) 87.28
β 4.00 (t) 89.42
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]

Dimers-Me (DMSO-d_6)



Methoxyls

β 3.44 53.13

β 3.04 53.65

γ 3.58 *(e)* 60.00

3.58, 3.22 *(t)* 60.02

γ2 γ1

γ 4.07 61.61

γ2 γ1 3.71, 3.63 62.90

4.75 *(t)* 70.73

α 4.74 *(e)* 71.48

γ2 γ1 4.13, 3.75 70.97

4.31 *(e)* 83.56

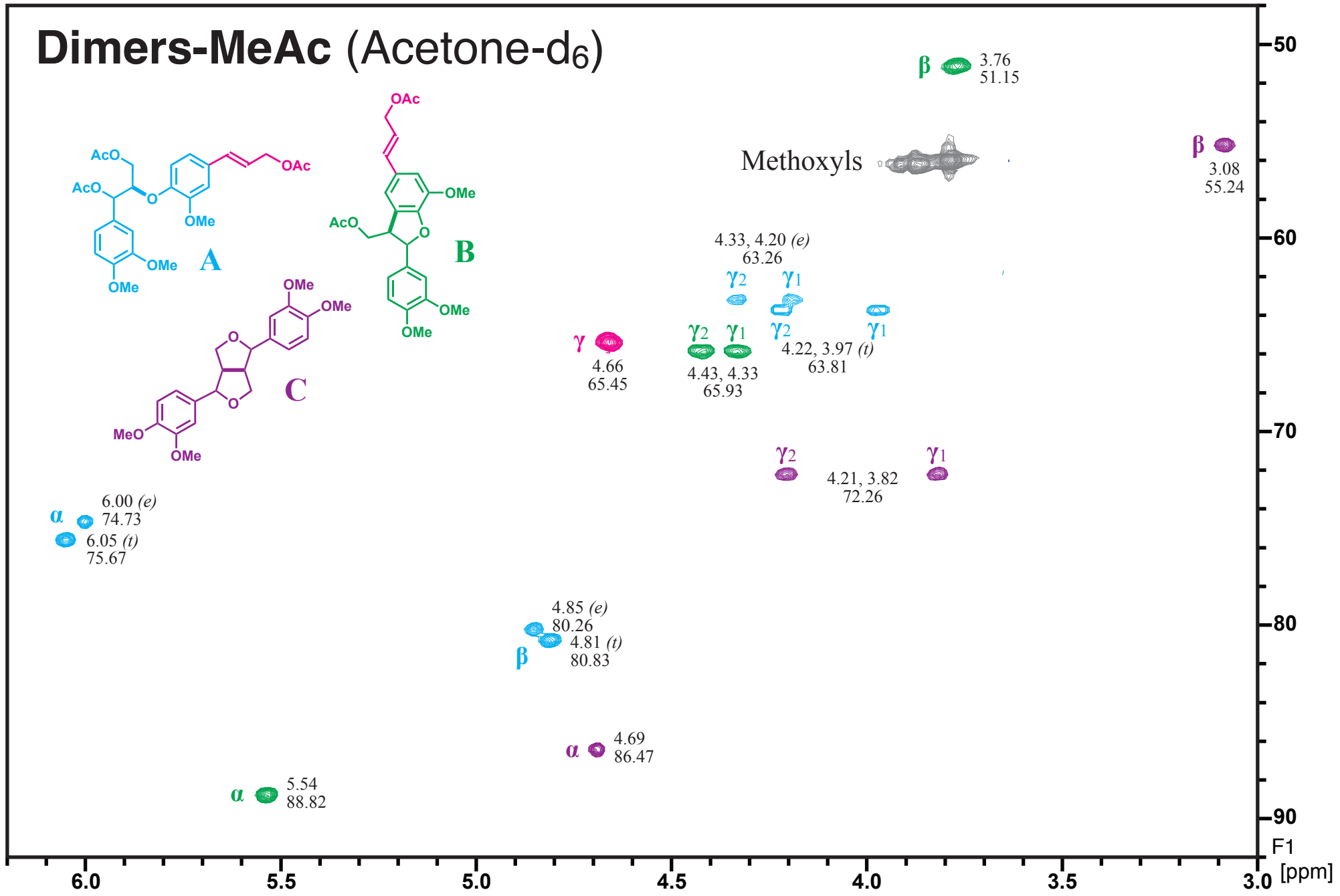
β 4.27 *(t)* 84.12

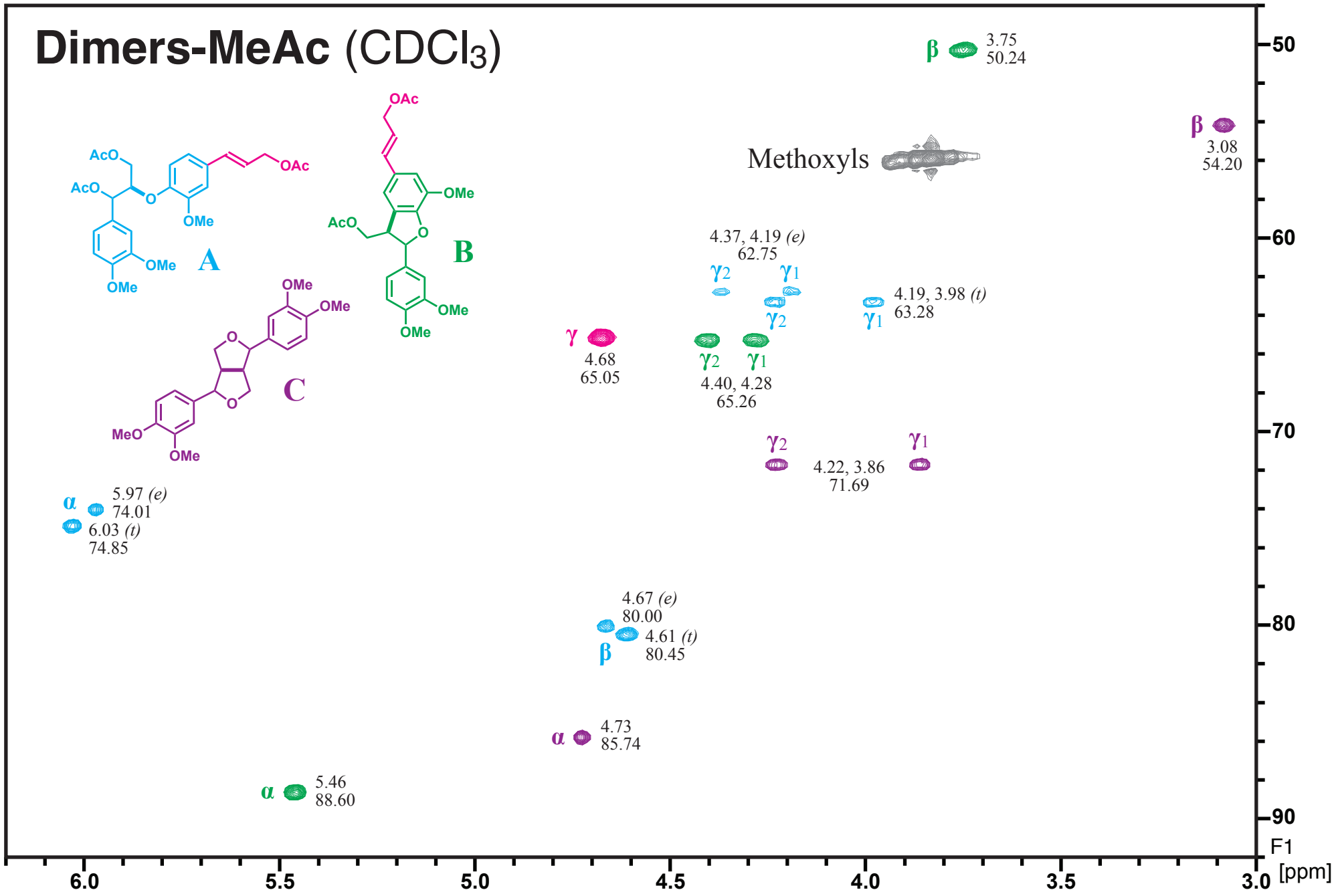
α 4.65 84.93

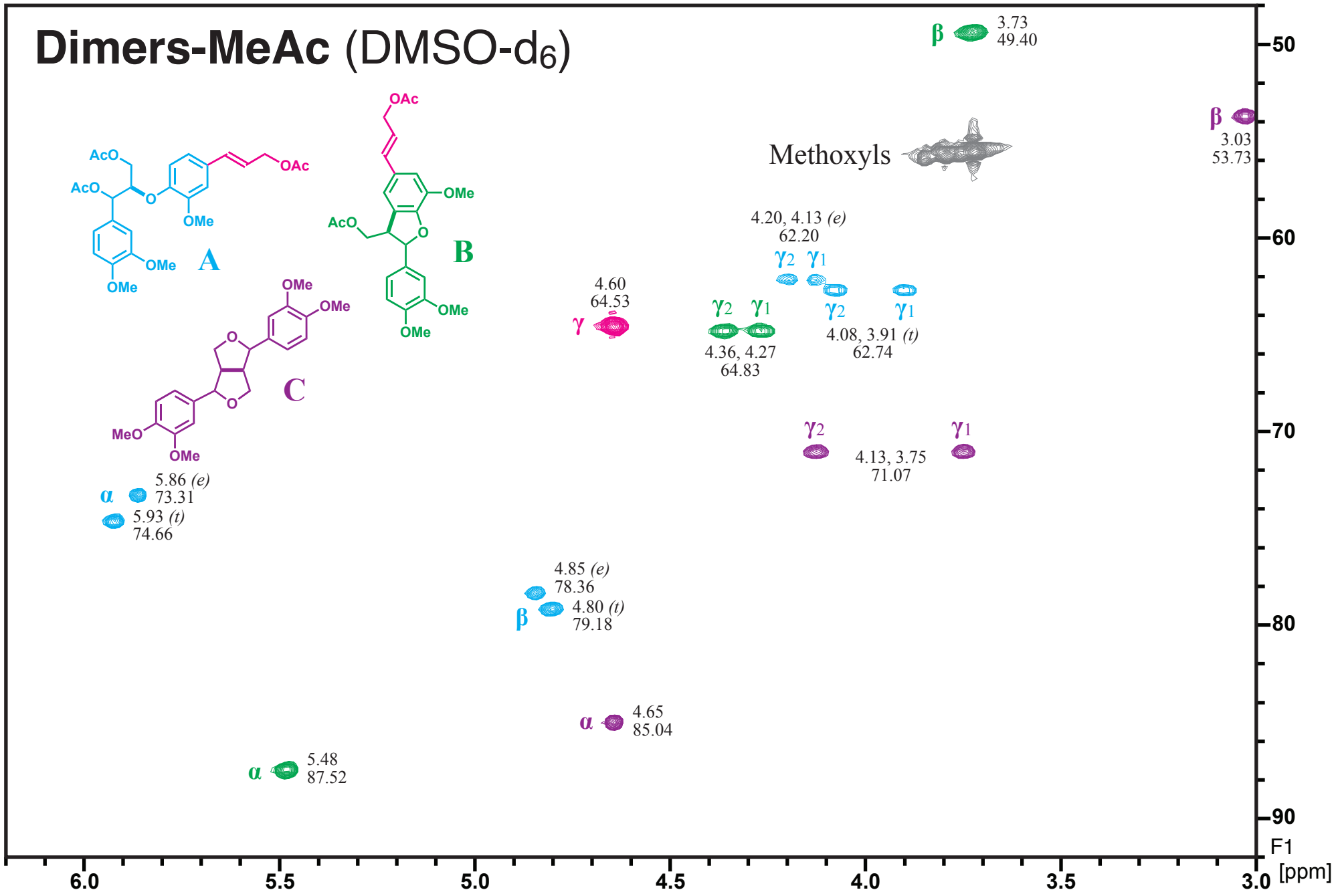
α 5.50 87.00

50 60 70 80 90 F1 [ppm]

6.0 5.5 5.0 4.5 4.0 3.5 3.0


Dimers-MeAc (Acetone-d6)
AcO
AcO
OAc
OMe
OMe
OMe
A
OAc
AcO
OMe
OMe
OMe
B
OMe
OMe
MeO
OMe
C
Methoxyls
β
3.76
51.15
β
3.08
55.24
4.33, 4.20 (e)
63.26
γ2
γ1
γ2
γ1
γ2
γ1
4.22, 3.97 (t)
63.81
γ
4.66
65.45
4.43, 4.33
65.93
γ2
γ1
4.21, 3.82
72.26
α
6.00 (e)
74.73
6.05 (t)
75.67
4.85 (e)
80.26
β
4.81 (t)
80.83
α
4.69
86.47
α
5.54
88.82
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


Dimers-MeAc (CDCl3)
A
B
C
Methoxyls
β 3.75 50.24
β 3.08 54.20
γ 4.68 65.05
4.37, 4.19 (e) 62.75
γ2 γ1 γ2
γ2 γ1 4.40, 4.28 65.26
4.19, 3.98 (t) 63.28
γ1
γ2 γ1 4.22, 3.86 71.69
α 5.97 (e) 74.01
6.03 (t) 74.85
4.67 (e) 80.00
β 4.61 (t) 80.45
α 4.73 85.74
α 5.46 88.60
50
60
70
80
90
F1 [ppm]
6.0
5.5
5.0
4.5
4.0
3.5
3.0


Dimers-MeAc (DMSO-d6)
A
B
C
Methoxyls
β 3.73 49.40
β 3.03 53.73
4.20, 4.13 (e) 62.20
γ2 γ1
γ2 γ1
γ2 γ1
4.08, 3.91 (t) 62.74
4.36, 4.27 64.83
4.60 64.53
γ
γ2
γ1
4.13, 3.75 71.07
α 5.86 (e) 73.31
5.93 (t) 74.66
4.85 (e) 78.36
β 4.80 (t) 79.18
α 4.65 85.04
α 5.48 87.52
50
60
70
80
90
F1
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]