

Electronic Supplementary Information

Incorporation of catechyl monomers into lignins: Lignification from the non-phenolic end via Diels-Alder cycloaddition?

Daisuke Ando,^{a†} Fachuang Lu,^{a,b} Hoon Kim,^a Alexis Eugene,^a Yuki Tobimatsu,^c Ruben Vanholme,^{d,e}
Thomas J. Elder,^f Wout Boerjan,^{d,e} John Ralph^{*a,g,h}

^a Department of Energy, Great Lakes Bioenergy Research Center, Wisconsin Energy Institute, Madison, Wisconsin 53726, USA.

^b State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 381 Wushan Rd, Tianhe District, Guangzhou, 510640, P.R. China.

^c Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, 611-0011, Japan.

^d Department of Plant Biotechnology and Bioinformatics, Ghent University, B-9052 Gent, Belgium.

^e Center for Plant Systems Biology, VIB, B-9052 Gent, Belgium.

^f USDA-Forest Service, Southern Research Station, 521 Devall Drive, Auburn, AL 36849, USA.

^g Department of Biochemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA.

^h Department of Biological System Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53726, USA.

[†] Current address: Institute of Wood Technology, Akita Prefectural University, 11-1 Aza Kaiezaka, Noshiro, Akita, Japan, 016-0876.

^{*} Corresponding author: John Ralph, Department of Biochemistry, Wisconsin Energy Institute, Room 2129 and the D.O.E. Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, 1552 University Avenue, Madison, Wisconsin 53706, United States, Phone: 608-890-2429, E-mail: jralph@wisc.edu

Figure S1. Diels-Alder reactions and products from 4-*O*-methyl coniferyl alcohol **6** and the benzoquinone **9** from methyl 5-hydroxyvanillate **11**.

Figure S2. Proton NMR spectrum of Diels-Alder product **13**.

Figure S3. Proton NMR spectrum of Diels-Alder product **15**.

Figure S4. Carbon NMR spectra of Diels-Alder products **13** and **15**.

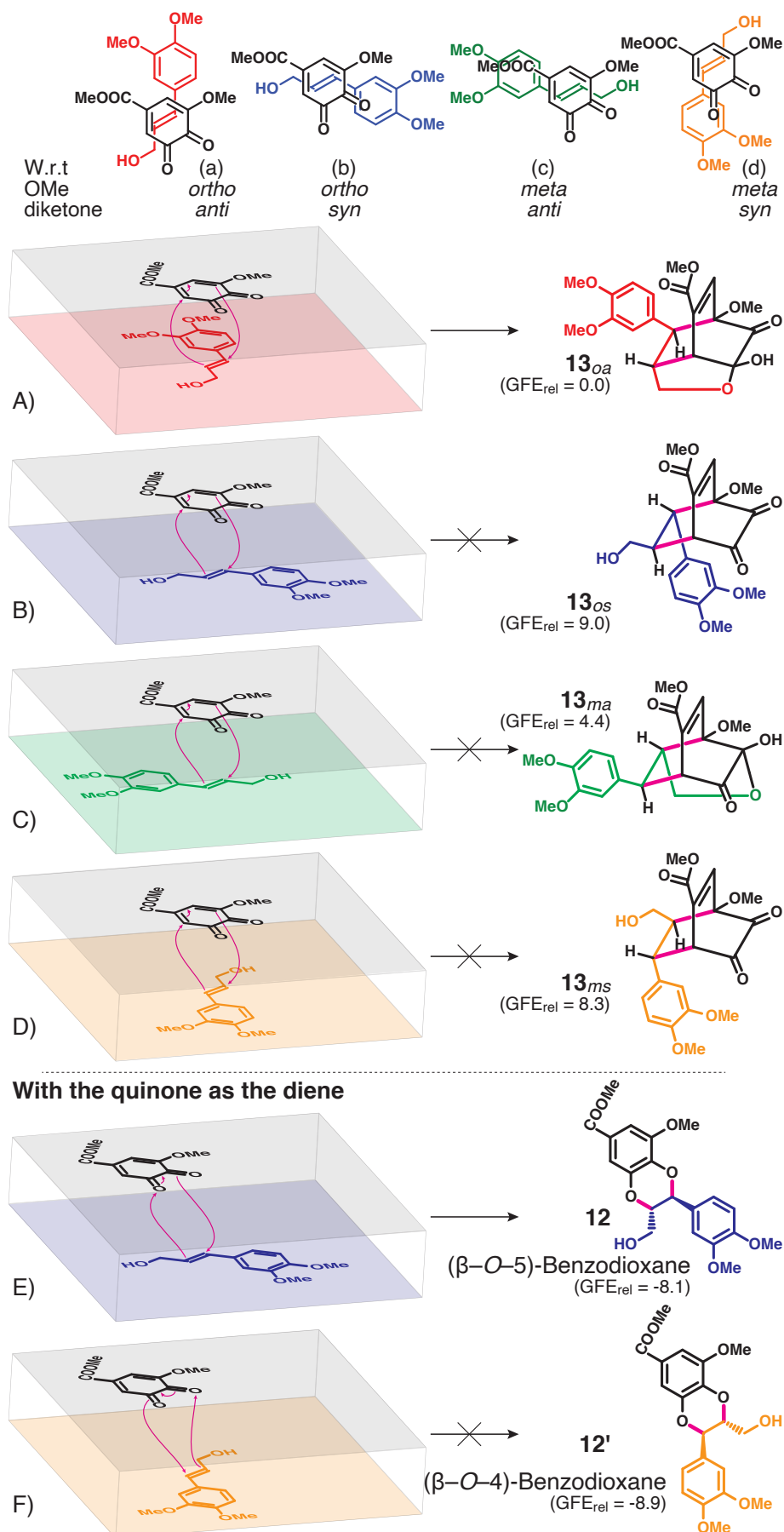
Figure S5. Proton NMR spectra of benzodioxane products **12** and **12'**.

Figure S6. Carbon NMR spectra of benzodioxane products **12** and **12'**.

Figure S7. ¹H–¹³C correlation spectra of the benzodioxane **12**.

Figure S8. ¹H–¹³C correlation spectra of the benzodioxane **12'**.

Figure S1. Diels-Alder reactions and products from 4-*O*-methylconiferyl alcohol **6** and the benzoquinone **9** from methyl 5-hydroxyvanillate **11**. Two Diels-Alder reactions are possible; all possible orientations/regiochemistries are shown, with the usual *ortho*- and *anti*-designations (with respect to the OMe on **6** and the diketone on **9**). **A-D**) The conventional Diels-Alder reaction in which the diene itself acts as the diene component. Because of the electronic requirements (see Figure 6 and its caption in the main text), there is really only one regiochemical possibility, producing **13_{oa}** (designated as simply **13** in the main text) and its optical isomer – see text. **E-F**) The ‘hetero-Diels-Alder’ reaction in which the *o*-benzoquinone acts as the diene. Two orientations can be envisioned but only one satisfies the electronic requirements (see Figure 6 and its caption in the main text), both producing strictly *trans*-benzodioxanes (because of the concerted nature of the reaction), but in which the regiochemistry, if it were described as resulting from radical coupling, appears as either a β -*O*-5 product **12** or a β -*O*-4 product **12'**. In fact only the β -*O*-5 product **12** was observed (see Figure 6 and its caption in the main text).



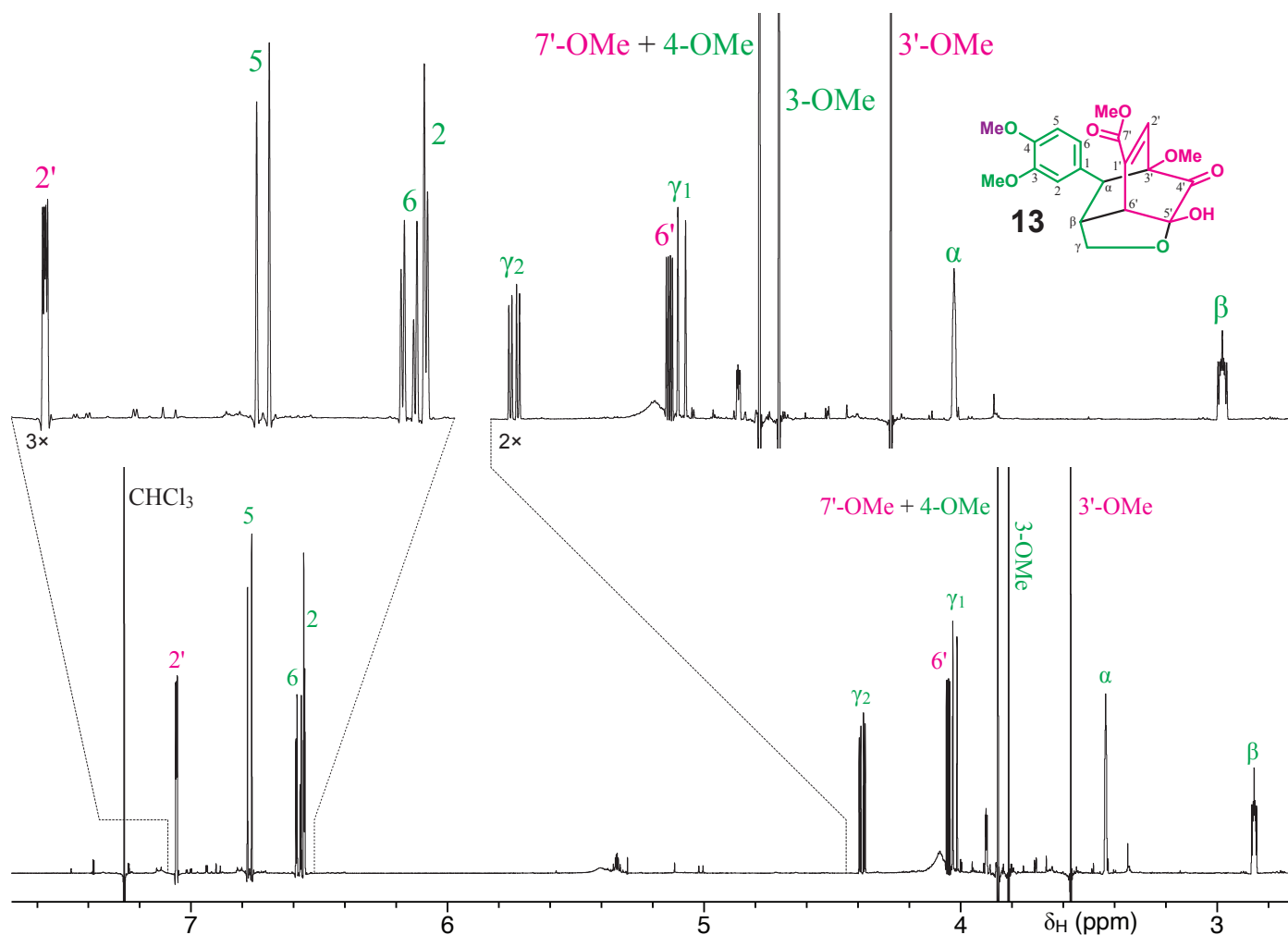


Figure S2. Proton NMR spectrum of Diels-Alder product **13** (in CDCl₃) showing horizontal expansions and assignments. Color coding uses that established in Figure 3 and used throughout to designate moieties derived from the 4-*O*-methylconiferyl alcohol **6** and from benzoquinone **9**.

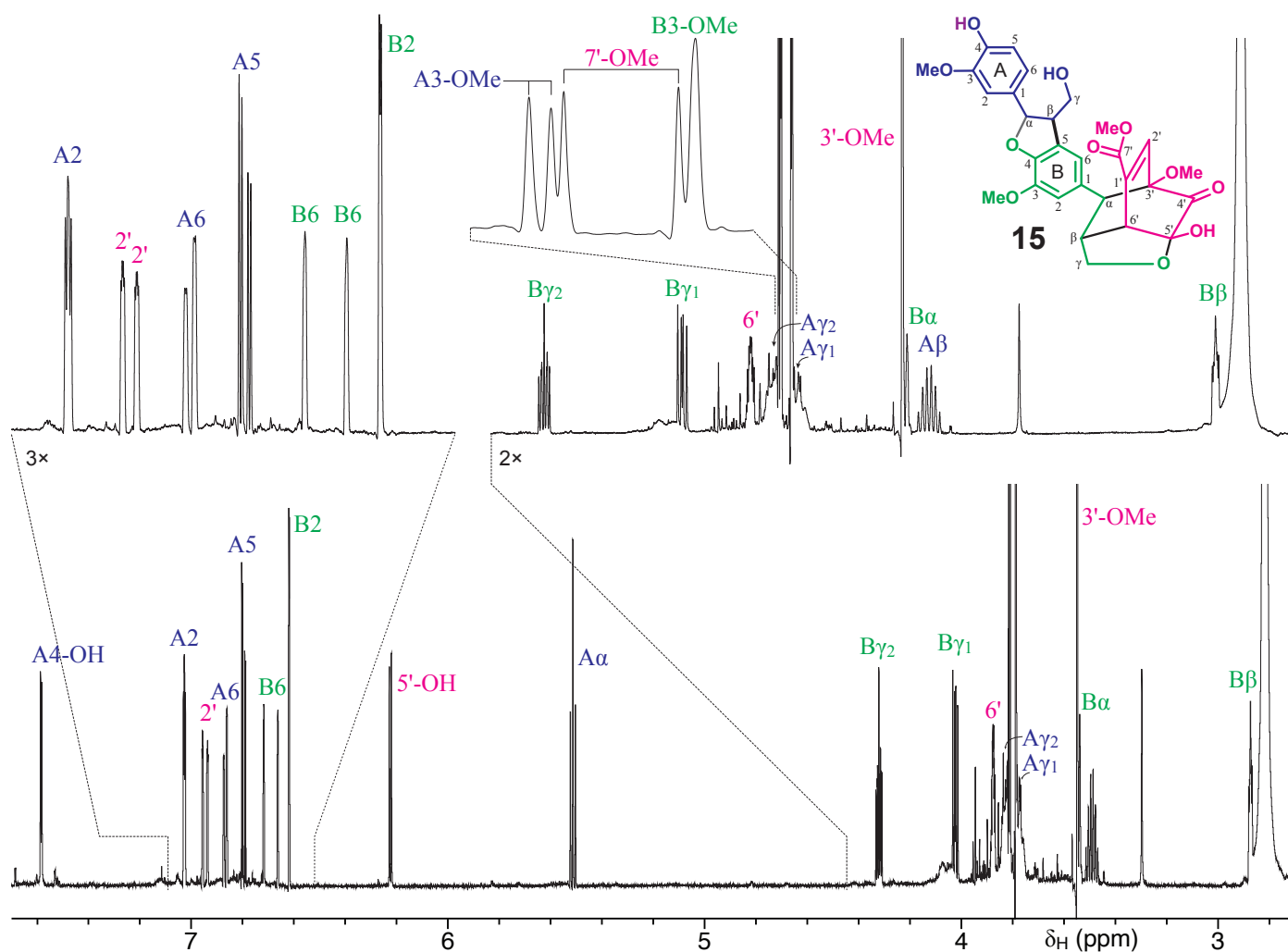


Figure S3. Proton NMR spectrum of Diels-Alder product **15** (in acetone- d_6) showing horizontal expansions and assignments; uses the same plot-regions as Figure S2, including expansions, plus an expansion of the methoxyl region to show how methoxyls can be assigned. Note that this product is a mixture of two closely related isomers (see text); many of the resonances can be resolved into the two isomers but no attempt is made to individually assign them. Color coding uses that established in Figure 3 and used throughout to designate moieties derived from the coniferyl alcohol **1** and from benzoquinone **9**, and distinguishing between the A-ring and the B-ring

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Figure S4. Carbon NMR spectra of: **A)** Diels-Alder product **13** (in $CDCl_3$), and **B)** Diels-Alder product **15** (in acetone- d_6) showing horizontal expansions and assignments; each uses the same plot-regions, with the more complex mixture of the two isomers of **15** having additional expansions to show the split nature of peaks not included in the expansions above. Color coding uses that established in Figure 3 and used throughout to designate moieties derived from the cinnamyl alcohol (**1**, **6**, or a preformed dimer **14**, Figure 3) and from benzoquinone **9**.

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Figure S5. Proton NMR spectra (in $CDCl_3$) of benzodioxane products, **A)** compound **12** from a Diels-Alder reaction, and **B)** compound **12'** from a radical coupling reaction followed by simple phenol-methylation, showing the same horizontal expansions and assignments. Color coding uses that established in Figure 3 and used throughout to designate, in green, moieties derived from the 4-*O*-methylconiferyl alcohol **6** and, in magenta, from catechol **11** or its derived benzoquinone **9**.

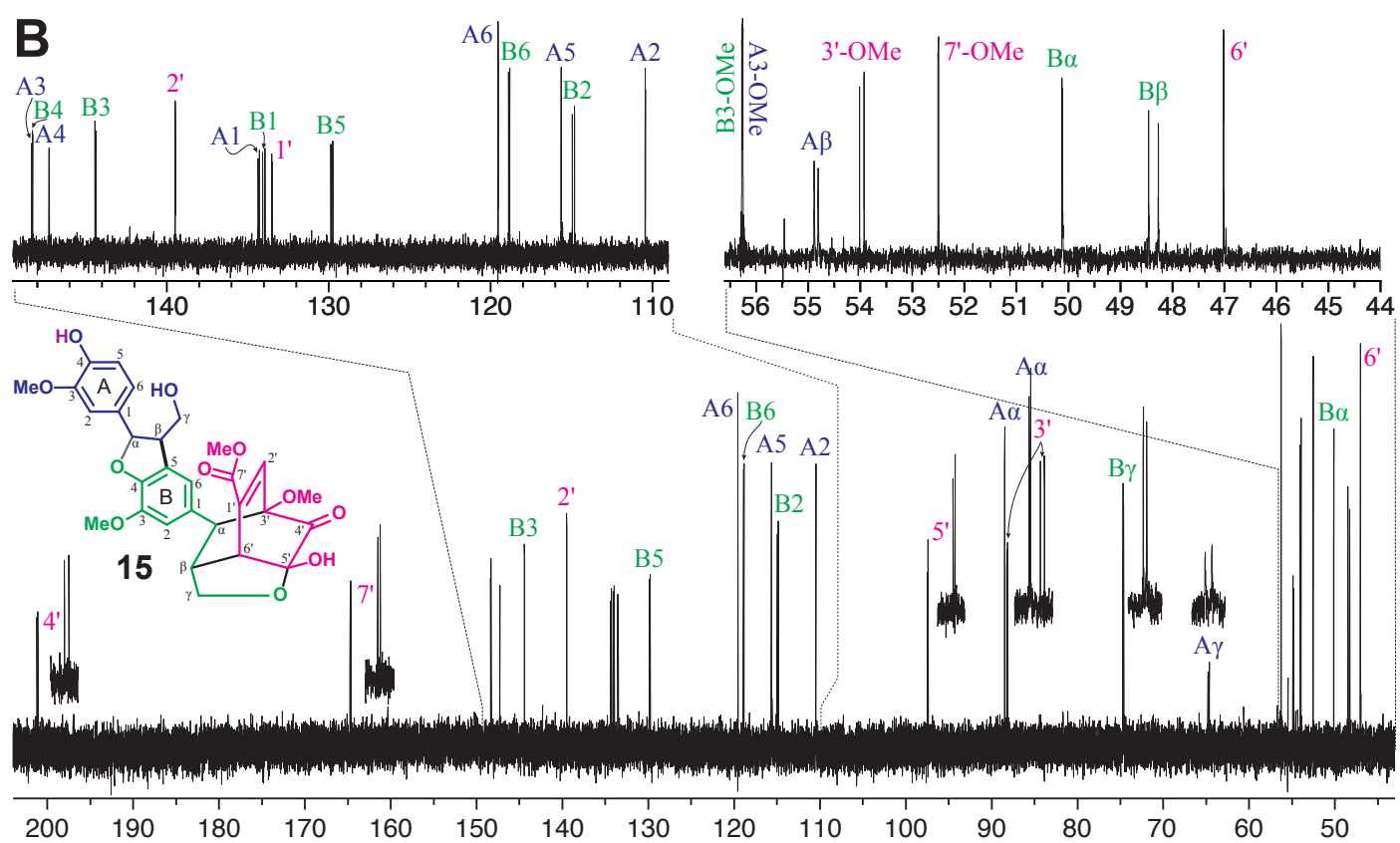
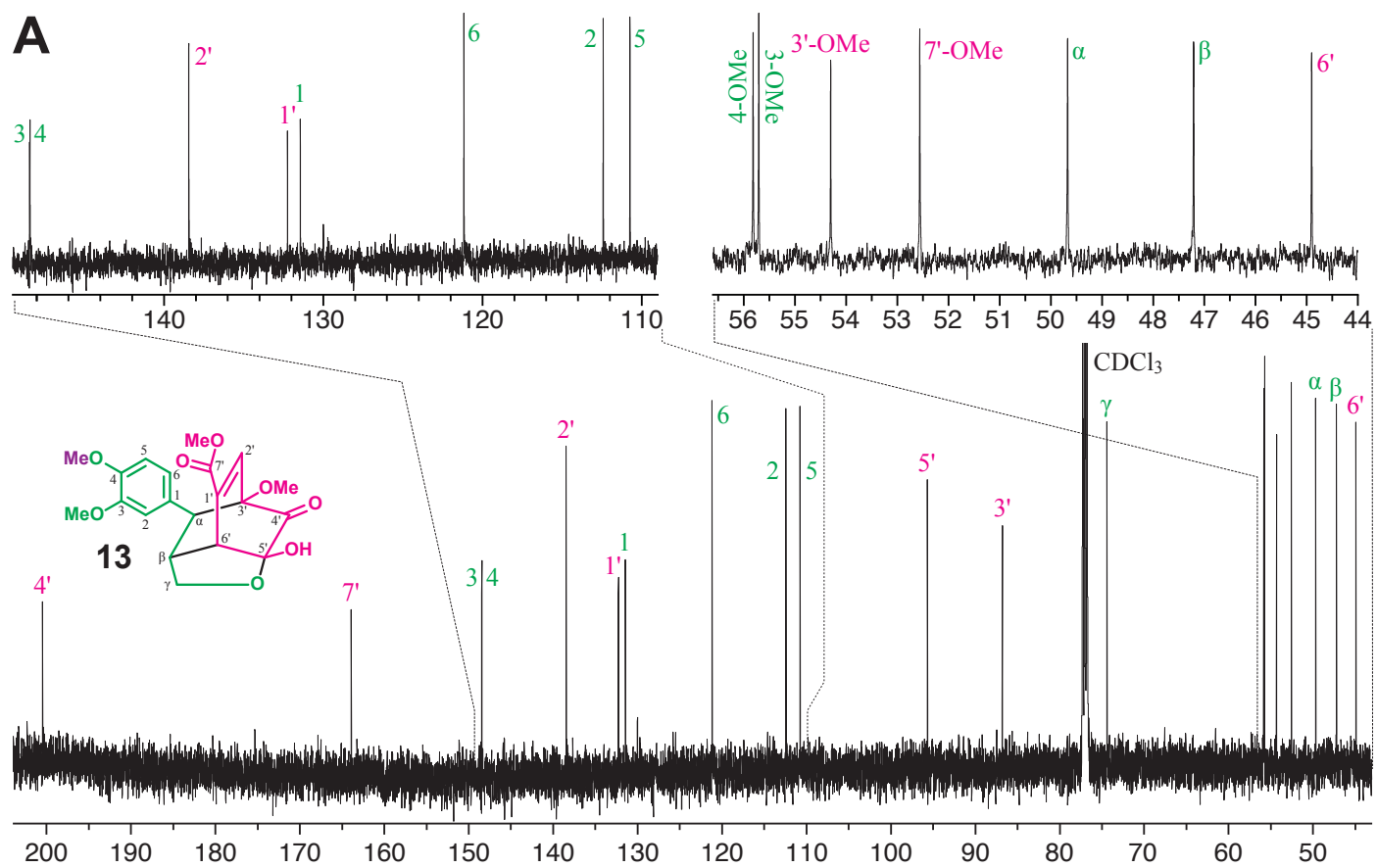


Figure S4. Carbon NMR spectra of **13** and **15**. See full caption on previous page, page 4.

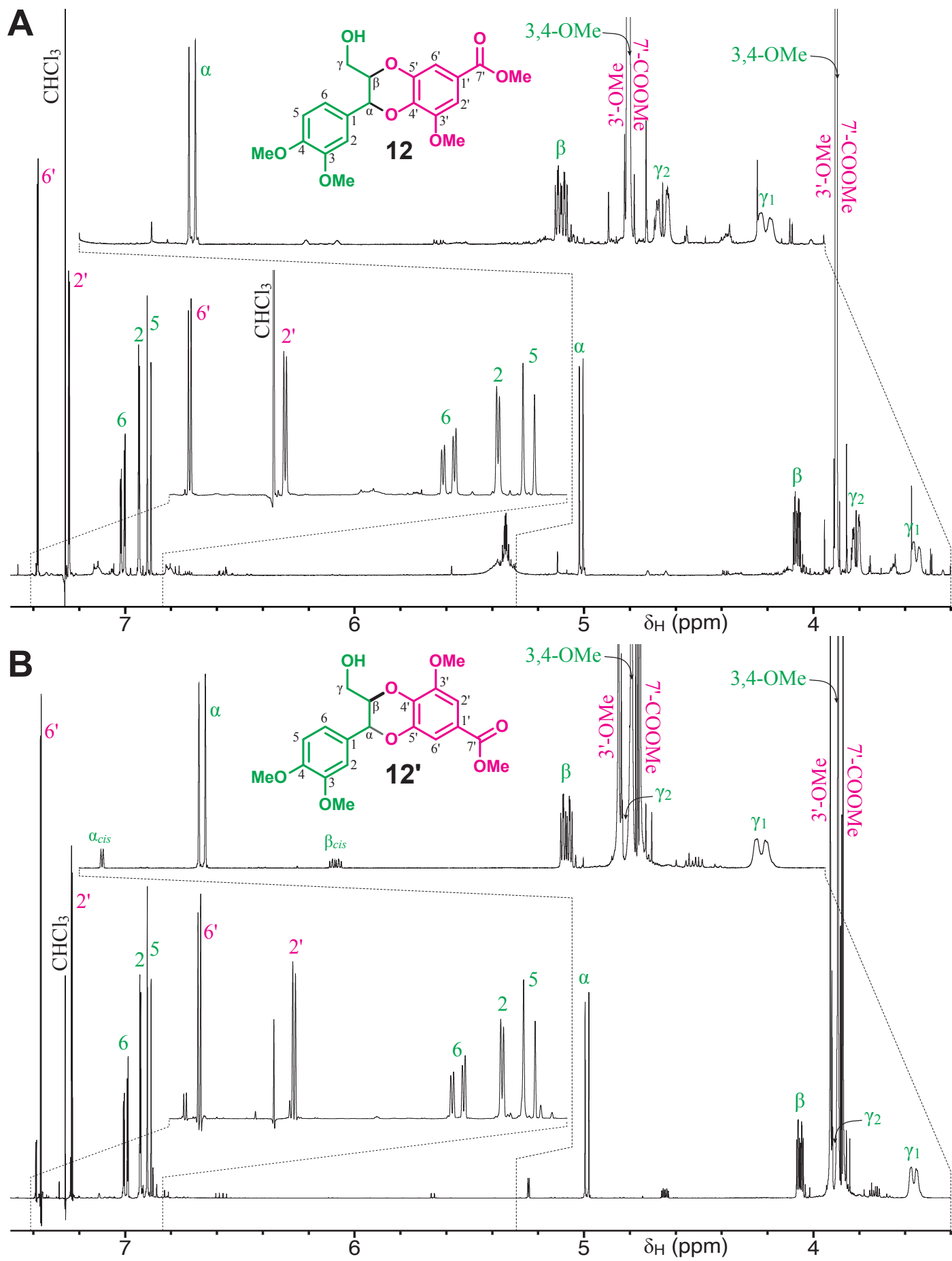


Figure S5. Proton NMR spectra of **12** and **12'**. See full caption on page 4.

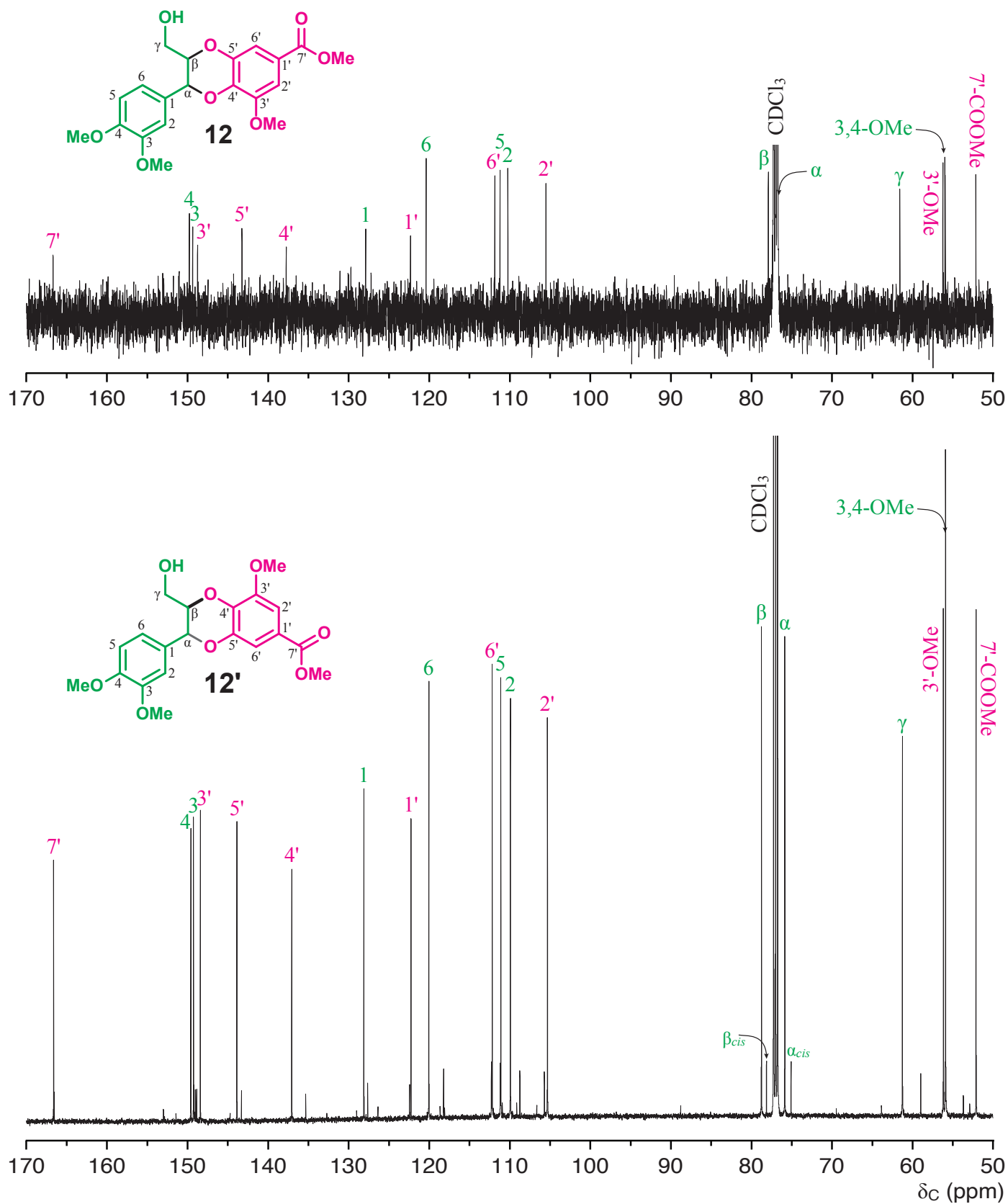


Figure S6. Carbon NMR spectra (in CDCl₃) of benzodioxanes from: **A)** Diels-Alder product **12**, and **B)** radical coupling products (followed by simple phenol-methylation) **12'**. Color coding uses that established in Figure 3 and used throughout to designate, in green, moieties derived from the 4-*O*-methylconiferyl alcohol **6** or coniferyl alcohol **1** and, in magenta, from catechol **11** or its derived benzoquinone **9**.

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Figure S7. ^1H - ^{13}C Correlation spectra (in CDCl_3) of the benzodioxane **12** from the Diels-Alder reaction between 4-*O*-methylconiferyl alcohol **6** and the benzoquinone **9** from methyl 5-hydroxyvanillate **11**. HSQC (red contours and assignments) is overlaid (from a separate spectrum/experiment). HMBC spectrum (black correlations) shows (with green highlighting) correlations of $\text{H}\beta$ to $\text{C}5'$ and $\text{H}\alpha$ to $\text{C}4'$ that define the regiochemistry. Some correlations required vertical expansion (by the factor indicated beside the box) to be seen. Other correlations aid in assignments. Of major significance is that this benzodioxane **12** is the product of apparent β - O -5-coupling, but the mechanism is in fact [4+2] cycloaddition (which therefore produces a different regioisomer). As shown by the green shading, the α -proton correlates with six carbons: γ , β , 2, 6, 1, and, importantly, $4'$ (in chemical shift order). Similarly, the β -proton correlates with three carbons: α , 1, and, importantly, $5'$. Contours colored light gray are from residual 1-bond correlations (split by the 1-bond ^1H - ^{13}C coupling constant) from some peaks due to deviation from the set average value (145 Hz) or are from minor impurities.

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Figure S8. ^1H - ^{13}C Correlation spectra (in CDCl_3) of the benzodioxane **12'** from the radical coupling reaction between coniferyl alcohol **1** and methyl 5-hydroxyvanillate **11** followed by simple phenolic methylation to produce the compound analogous to **12** and allow the determination that these are isomers and are not the same products. HSQC (red contours and assignments) is overlaid (from a separate spectrum/experiment). HMBC spectrum (black correlations) shows (with green highlighting) correlations of $\text{H}\alpha$ to $\text{C}5'$ and $\text{H}\beta$ to $\text{C}4'$ that define the regiochemistry. Some correlations required vertical expansion (by the factor indicated beside the box) to be seen. Other correlations aid in assignments. Note also the beautiful correlations from the *cis*-benzodioxane (at ~5% of the *trans*); just $\text{H}\alpha$ and $\text{H}\beta$ correlations are colored dark blue to highlight them. Of major significance is that this radical coupling benzodioxane **12'** is the product of β - O -4-coupling, as is usual for coupling of a monolignol with a phenolic. As shown by the green shading, the α -proton correlates with six carbons: γ , β , 2, 6, 1, and, importantly, $5'$ (in chemical shift order). Similarly, the β -proton correlates with three carbons: α , 1, and, importantly, $4'$, establishing the β - O -4-coupling. Contours colored light gray are from residual 1-bond correlations (split by the 1-bond ^1H - ^{13}C coupling constant) from some peaks due to deviation from the set average value (145 Hz) or are from minor impurities.

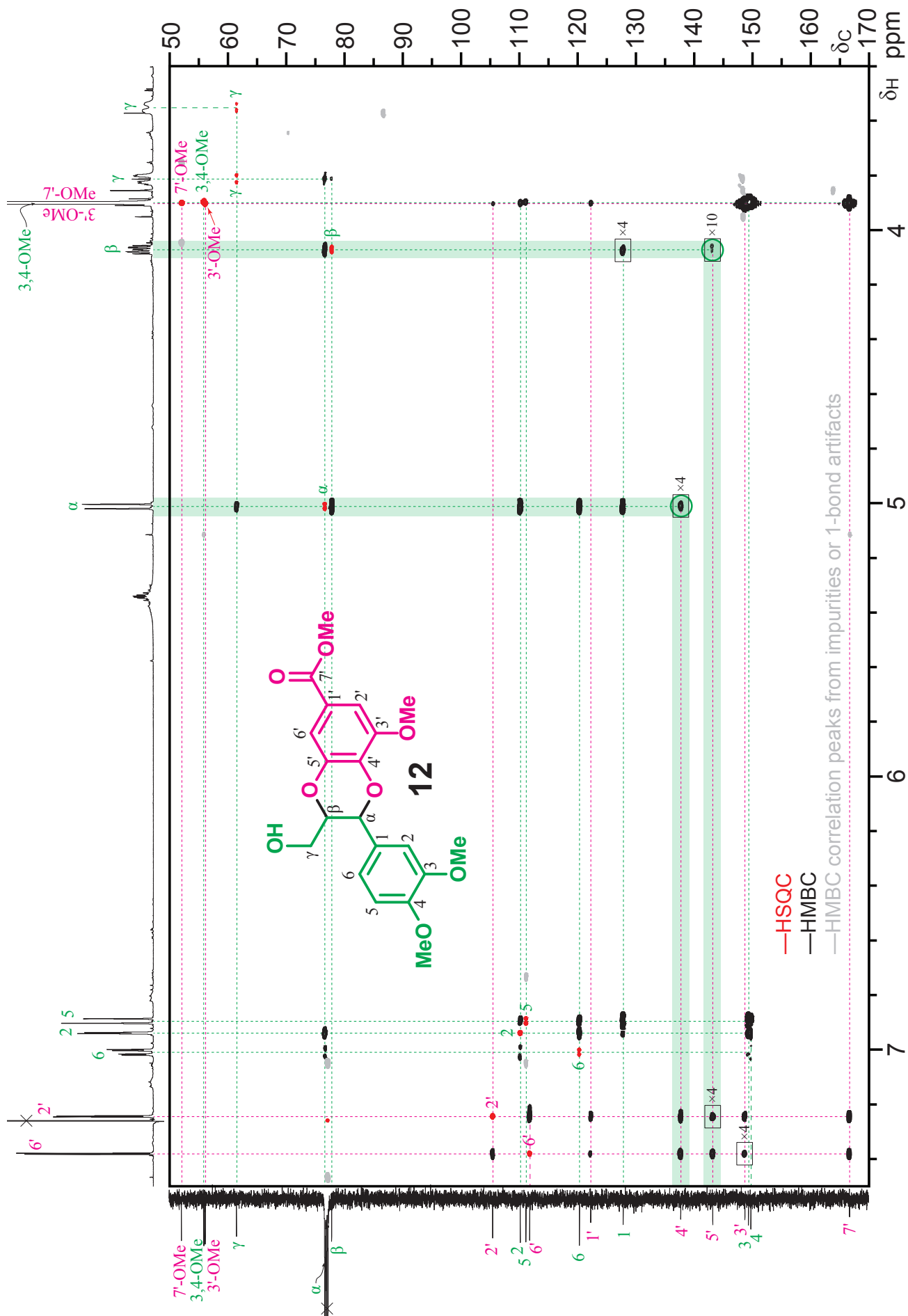


Figure S7. ^1H - ^{13}C correlation spectra of the benzodioxane **12**. See full caption on previous page, page 8.

