Supporting information

Degradation Mechanism of Lignin Model Compound during Alkaline Aerobic Oxidation: Formation of Vanillin Precursor from β-O-4 Middle Unit of Softwood Lignin.

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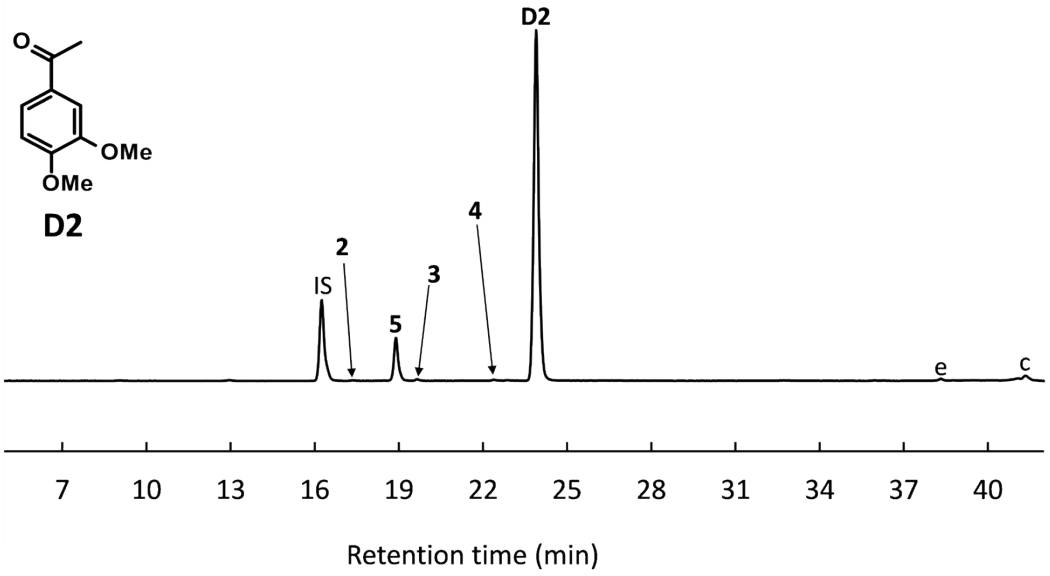


Figure S1. HPLC chromatogram of the reaction mixture obtained after alkaline oxidation of **D2** at 120 ºC for 24 h under air. The data in entry 6 in Table 1were obtained on the basis of this HPLC chromatogram.

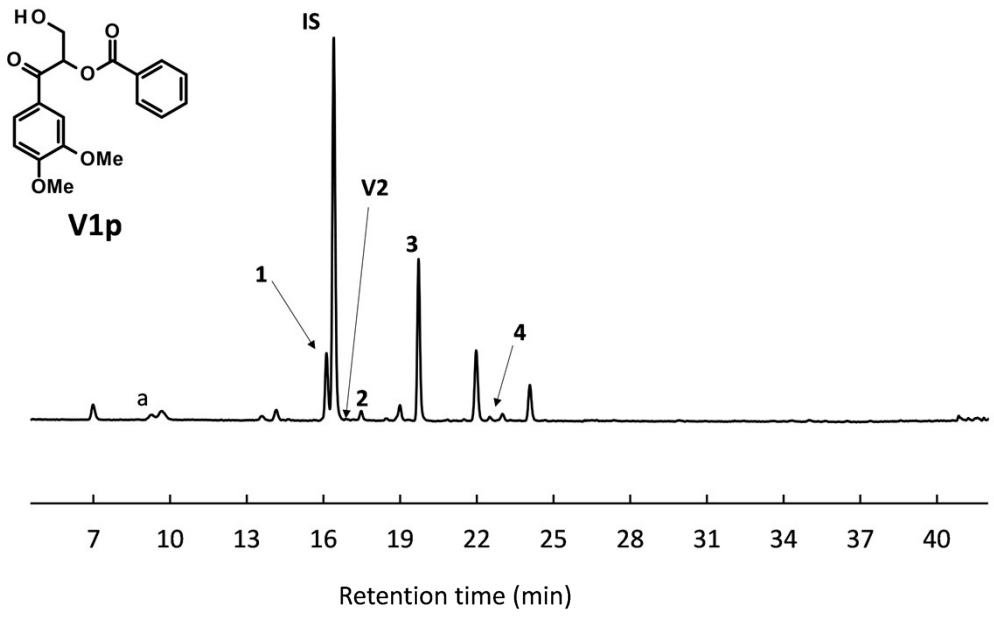


Figure S2. HPLC chromatogram of the reaction mixture obtained after the alkaline aerobic oxidation of **V1p** at 120 ºC for 24 h under air. The data in entry 2 in Table 1 were obtained on the basis of this HPLC chromatogram.

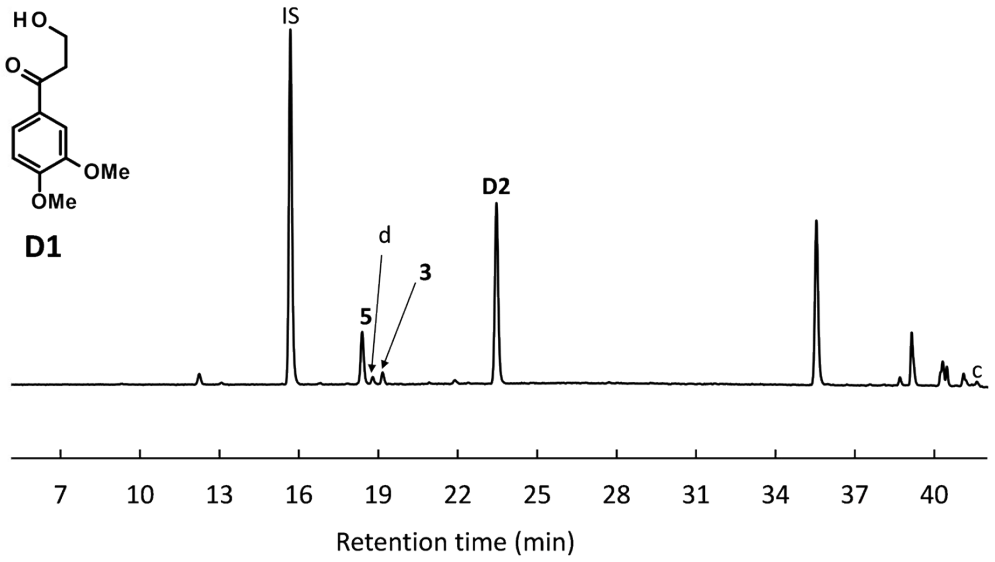


Figure S3. HPLC chromatograms of the reaction mixture obtained after alkaline aerobic oxidation of **D1** at 120 ºC for 24 h under air. The data in entry 5 in Table 1 were obtained on the basis of this HPLC chromatogram.

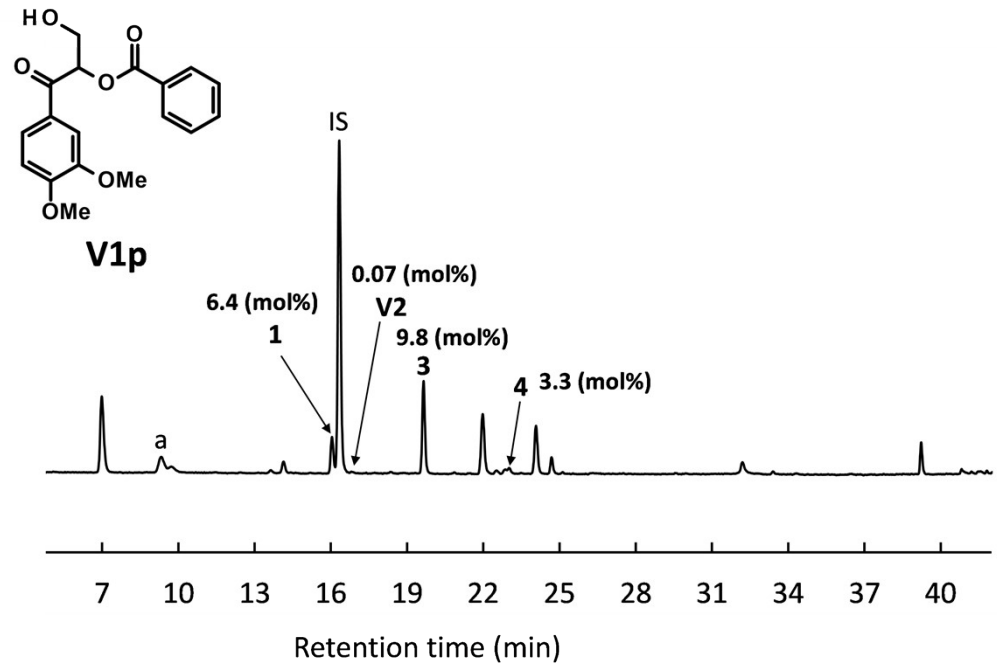


Figure S4. HPLC chromatogram of a solution obtained after dissolving **V1p** in 4.0 mol/L NaOH aq. (2.0 mL) at room temperature. We observed the formation of compounds **1** and **3** when veratraldehyde (**4**) was dissolved in 4.0 mol/L NaOH aq. at room temperature, which strongly suggests that the Cannizzaro reaction of **4** does occur even under such low-temperature conditions.

Table S1. Yields (mol %) of products with C_1 and C_2 side-chains after the degradation of **V1p** and **D1** (3.0 mg) in 4.0 mol/L NaOH aq. (2.0 mL) at 120 °C for 24h under N_2.

Starting material	Product yield (mol %)									Conversion (%)
	C_1 side-chain				C_2 side-chain				Total	
	1	**2**	**3**	**4**	**5**	**6**	**V2**	**D2**		
V1p	8.8	0.4	15.8	3.4	-	ND[a]	0.02	-	28.4	-[b]
D1	ND	ND	1.0 (1.0)[c]	ND	2.8 (2.8)	-	-	9.7 (9.7)	13.5 (13.5)	99.99

[a] ND：Not detected. [b] The recovery of **V1p** was not investigated. [c] Number in the parenthesis shows the yield (mol%) on the basis of degraded starting material.

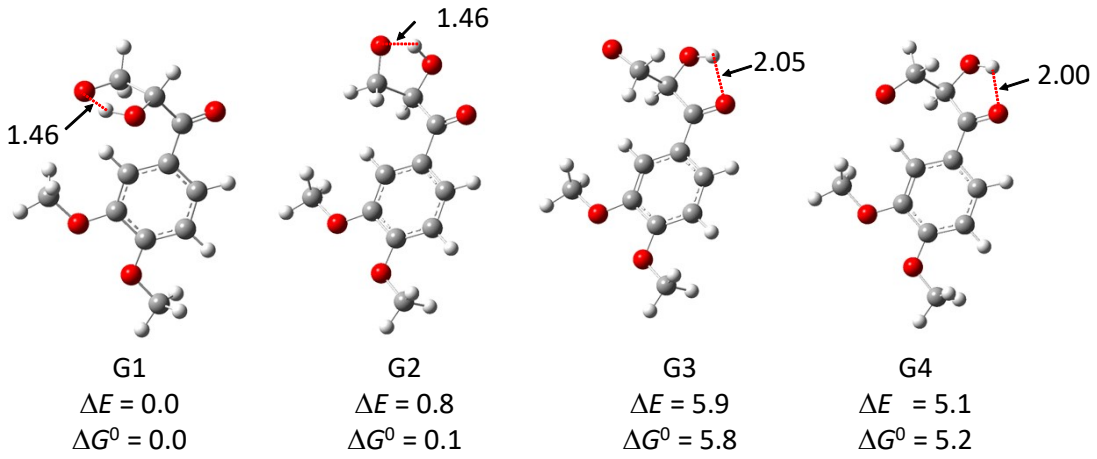


Figure S5. Geometries (G1~G4) of several rotamers of deprotonated **V1** and their energies (kcal/mol) relative to the most stable G1, where atomic distances are shown in Å. The energies of the chemical species in Figure 3 were calculated relative to the most stable geometry of G1.

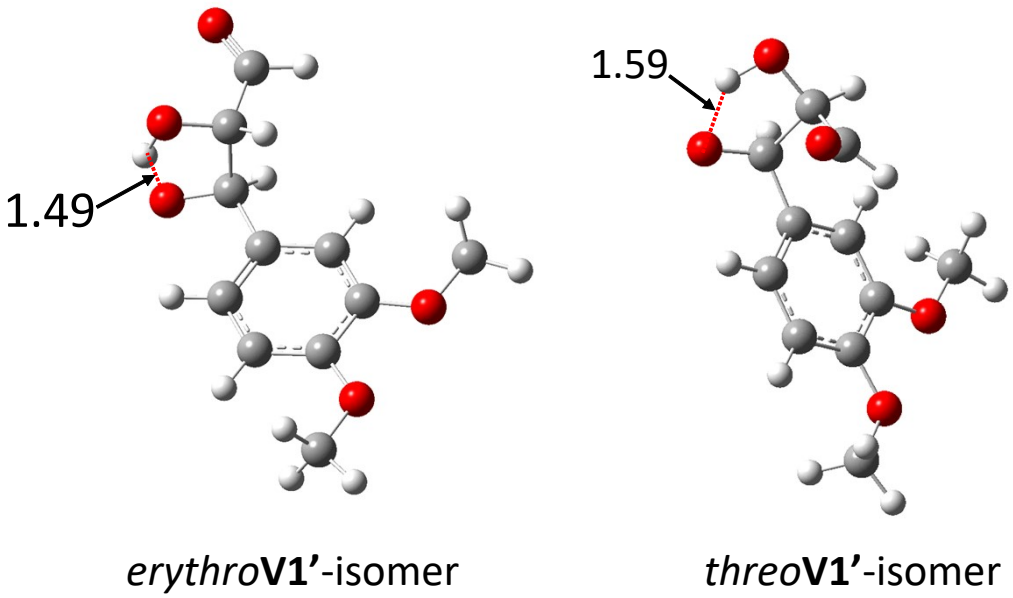


Figure S6. Geometries of *erythro*- and *threo*- **V1'**. Atomic distances are shown in Å.

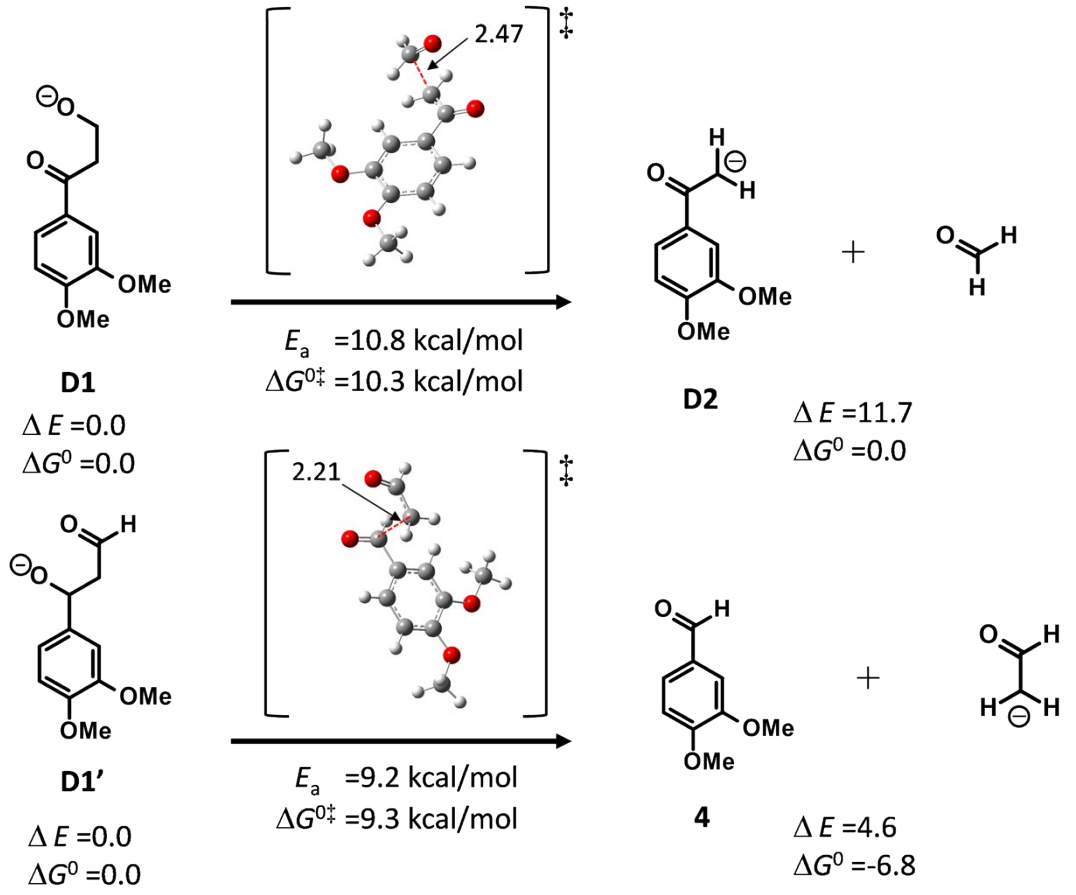
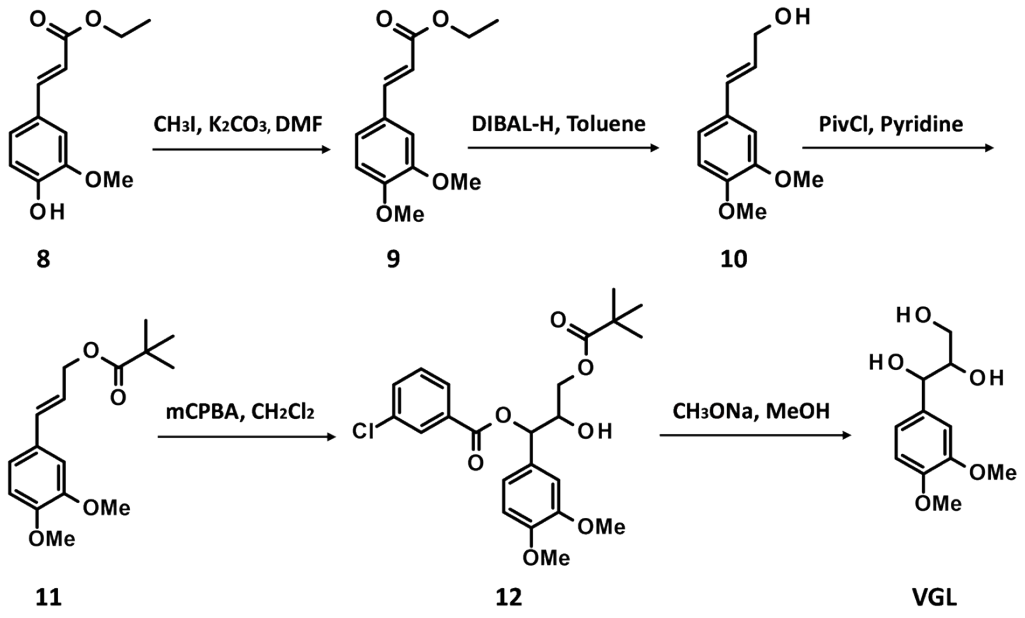


Figure S7. Retro-aldol reactions staring from **D1** and **D1'** calculated at the SCS-MP2//DFT(M06-2X) level of theory. Energies and atomic distances are shown in kcal/mol and Å, respectively. The barriers of the two reactions were calculated on the different basis (the energy of **D1** for the above reaction and that of **D1'** for the below one), as there is no equilibrium between **D1** and **D1'** in these β-deoxy compounds.

Synthetic routes for the model compounds

General Information. All synthetic reactions were monitored by TLC on silica gel with co-solvents of *n*-hexane and EtOAc being used as the eluent and a 10 wt% phosphomolybdic acid/ethanol solution and UV_{254nm} being employed to quench the spots. CHROMATOREX PSQ100B silica gel (Fuji silica chemical, Ltd) was used for column chromatography with the amount of the silica gel being set to be approximately 50 g per 1 g of the crude mixture. NMR spectra were recorded on a JNM-ECZ 400 S (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer at room temperature in $CDCl_3$, CD_3OD, or Acetone-d6; chemical shifts (δ ppm) were taken relative to that of chloroform (δ_H = 7.26 ppm, δ_C = 77.0 ppm), methanol (δ_H = 3.31 ppm, δ_C = 49.0 ppm), or acetone (δ_H = 2.02 ppm, δ_C = 205.34 ppm). For the ^{1}H NMR spectra presented below, the following abbreviations are employed: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. dd = double of doublet, dt = double of triplet.

Synthesis of VGL



Scheme S1. Synthetic route for **VGL**.

(*E*)-ethyl-3-(3,4-dimethoxyphenyl) prop-2-enoate (9). K_2CO_3 (1.50 g, 10.9 mmol) and CH_3I (0.67 mL, 10.7 mmol) were added in this order to a solution of commercial ferulic acid ethyl ester **8** (2.05 g, 9.2 mmol) in DMF (7.0 mL) with stirring. The reaction solution was stirred over night at room temperature and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq. twice and washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The product mixture was dissolved in EtOH, and recrystallized to give a white crystal of (*E*)-ethyl-3-(3,4-dimethoxyphenyl)prop-2-enoate (**9**) (1.30 g, 5.16 mmol).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 15.9 Hz, 1H), 7.05 (dd, *J* = 2.0 and 8.3 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.27(d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.86(s, 6H), 1.29(t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 150.8, 149.0, 144.3, 127.2, 122.4, 115.7, 110.8, 109.3, 60.2, 55.8, 55.7, 14.2 ppm.

[(*E*)-3-(3,4-dimethoxyphenyl) allyl] pivalate (11). (*E*)-ethyl-3-(3,4-dimethoxyphenyl) prop-2-enoate (**9**) (1.30 g, 5.16 mmol) was dissolved in anhydrous toluene (5.0 mL). The solution was dropped into a 1.5 mol/L diisobutylaluminium hydride (DIBAL-H) toluene solution (15.5 mL, equivalent to 15.45 mmol of DIBAL-H) for 2 h with stirring at room temperature. EtOH and H_2O were added to the reaction solution in this order to quench the remaining DIBAL-H.

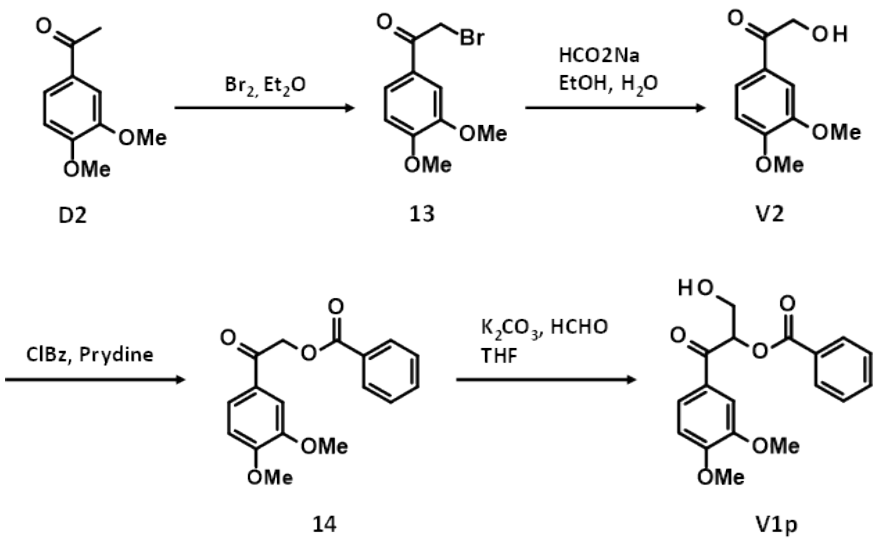
After adjusting the pH of the solution to around 3 by adding an aqueous solution of citric acid, saturated Na_2SO_4 aq. was added and stirred at room temperature for 1 h. The resulting two-phase-separated reaction mixture was extracted with EtOAc and the organic layer was washed with brine twice, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Light yellow oil (0.90 g) containing (*E*)-3-(3,4-dimethoxyphenyl) prop-2-en-1-ol (**10**) was used for the next step without further purification.

The crude mixture containing **10** (0.90 g) was dissolved in pyridine (4.0 mL) and pivaloyl chloride (0.86 mL, 6.97 mmol) was added to the solution at room temperature. In 48 h the reaction mixture was extracted with EtOAc and the organic layer was washed with 10 wt % HCl aq., saturated $NaHCO_3$ aq. and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography using EtOAc/Hexane = 1/2 to give **11** as colorless oil (0.80 g, 2.89 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.96 ~ 6.91 (m, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 6.20 ~ 6.11 (m, 1H), 4.70 (dd, *J* = 1.3 and 6.5 Hz, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 1.23 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.5, 149.2, 149.1, 133.8, 129.4, 121.6, 120.0, 111.1, 108.9, 65.2, 56.0, 55.9, 38.9, 27.3, 27.1, 19.57 ppm.

***threo*-[1-(3,4-dimethoxyphenyl)-3-(2,2-dimethoxylpropanoyloxy)-2-hydyoxy-propyl]3-chlorobenzoate (12)**. **11** (0.80 g, 2.89 mmol) was dissolved in CH_2Cl_2 (10 mL), and 72 % *m*-chloroperoxybenzoicacid (0.78 g, 4.51 mmol) was added with stirring at room temperature. In 2 h saturated $Na_2S_2O_3$ aq. was added to the solution to quench the remaining reagent. The reaction mixture was extracted with EtOAc and the organic layer was washed with saturated $NaHCO_3$ aq. and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography with EtOAc/Hexane = 1/2 to give **12** as colorless oil (1.02 g, 2.26 mmol). The product also contained 8.0 % of the *erythro*-isomer as the minor diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (t, *J* = 1.7 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.55 (dt, *J* = 0.9, 1.3, and 8.1 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.00 (dd, *J* = 2.1 and 8.2 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.99 (d, *J* = 7.1 Hz, 1H), 4.30~4.24 (m, 1H), 4.20 (dd, *J* = 3.5 and 11.7 Hz,1H), 3.96 (dd, *J* = 5.6 and 11.5 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 1.24 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.7, 164.8, 149.5, 149.2, 139.4, 134.7, 133.4, 131.7, 129.9, 129.8, 127.9, 119.7, 111.3, 110.2, 77.3, 72.8, 64.9, 56.1, 56.0, 39.0, 27.3, 27.2, 18.0 ppm.

***threo*-1-(3,4-dimethoxyphenyl)propane-1,2,3-triol (VGL)**. **12** (1.02 g, 2.26 mmol) was dissolved in MeOH (10 mL), and 28 % CH_3ONa/MeOH solution (25 mL) was then added to the solution with stirring at room temperature. In 1h, the reaction mixture was neutralized with strong acid ion-exchange resin (DOWX^{TM}HCR Na activated with HCl aq.). The resulting solution was concentrated *in vacuo* and the remaining oil was crystallized in EtOH to give **VGL** as white crystal (0.235 g, 1.03 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94 ~ 6.83 (m, 3H), 4.68 (d, *J* = 6.7 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.80 ~ 3.75 (m, 1H), 3.64 (dd, *J* = 3.5 and 11.8 Hz, 1H), 3.52 (dd, *J* = 5.2 and 11.7 Hz, 1H) ppm. ^{1}H NMR (400 MHz, CD_3OD) δ = 7.02 (s, 1H), 6.91 (d, *J* = 1.4 Hz, 2H), 4.55 (d, *J* = 6.3 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.69 ~ 3.64 (m, 1H), 3.48 (dd, *J* = 4.1 and 11.5 Hz, 1H), 3.35 (dd, *J* = 6.4 and 11.2 Hz, 1H) ppm.^{13}C NMR (100 MHz, CD_3OD) δ = 148.9, 148.5, 134.9, 119.1, 111.2, 110.3, 76.1, 73.8, 62.8, 55.1, 54.9 ppm.

Synthesis of V2 and V1p starting from D2



Scheme S2. Synthetic route for **V2** and **V1p**.

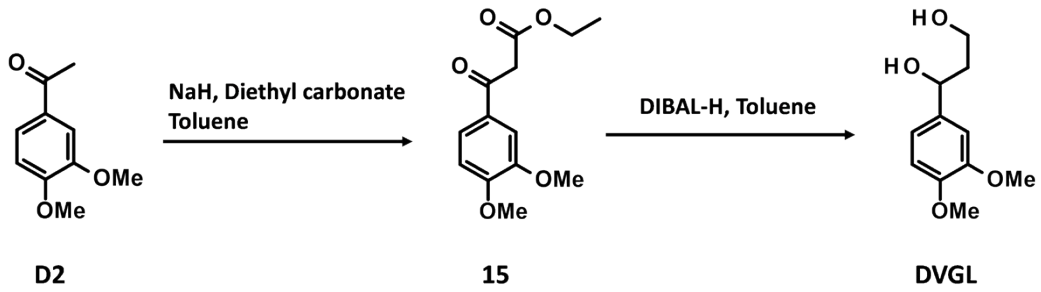
1-(3,4-dimethoxyphenyl)-2-hydroxy-ethanone (V2). 1-(3,4-dimethoxyphenyl) ethenone (**D2**) (2.0 g, 11.10 mmol) was dissolved in Et_2O (10.0 mL) and CH_2Cl_2 (5.0 mL), and Br_2 (0.37 mL, 14.36 mmol) was added with stirring at 0 ºC. After stirring at 0 ºC for 15 minutes, the temperature was allowed to be increased to room temperature and stirred for 20 h. After the addition of water to the solution, the pH of the solution was adjusted to ~8 with saturated $NaHCO_3$ aq. The resulting reaction mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The product mixture containing 2-bromo-1-(3,4-dimethoxyphenyl) ethenone (**13**) (2.50 g) was used for the next step without further purification.

The crude mixture containing **13** (1.25 g) was dissolved in EtOH (12.32 mL) and H_2O (2.17 mL) and HCO_2Na (1.97 g, 28.97 mmol) was added to the solution and refluxed with stirring for 3 h. The reaction mixture was then concentrated *in vacuo*, diluted with H_2O, extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The product mixture was purified by column chromatography using EtOAc/Hexane = 1/1 to give crystal of 1-(3,4-dimethoxyphenyl)-2-hydroxy-ethanone (**V2**) (0.24g, 1.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 ~ 7.48 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 4.84 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ = 196.9, 154.2, 149.4, 126.5, 122.3, 110.3, 109.8, 65.0, 56.2, 56.1 ppm.

[2-(3,4-dimethoxyphenyl)-2-oxo-ethyl] benzoate (14). V2 (0.24 g, 1.14 mmol) was dissolved in pyridine (3.0 mL) and benzoyl chloride (0.16 mL, 1.28 mmol) was added to the solution with stirring at room temperature. In 20 h, the reaction mixture was washed with 10 wt% HCl aq. and extracted with EtOAc. The organic layer was washed with saturated $NaHCO_3$ aq. and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The product mixture was recrystallized in EtOH to give white crystal of **14** (0.1 g, 0.33 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 ~ 8.13 (m, 2H), 7.63 ~ 7.45 (m, 5H), 6.92 (d, *J* = 8.18 Hz, 1H), 5.55 (s, 2H), 3.97 (s, 3H), 3.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ = 190.7, 166.1, 153.9, 149.3, 133.3, 130.0, 129.5, 128.4, 127.4, 122.3, 110.1, 110.0, 66.2, 56.1, 56.0 ppm.

[2-(3,4-dimethoxyphenyl)-1-(hydroxymethyl)-2-oxo-ethyl] benzoate (V1p). 14 (0.10 g, 0.33 mmol) was dissolved in THF (1.1 mL) and K_2CO_3 (0.02 g, 0.14 mmol) and 38 % HCHO (0.03 mL, 0.81 mmol) were then added to the solution with stirring at 55 ºC. In 20 h, the reaction mixture was neutralized with AcOH, extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by thin layer chromatography with EtOAc/Hexane = 1/1 to give **V1p** as crystal (0.02 g, 0.06 mmol). **V1p** was analyzed by NMR as an acetylated **V1p**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 6.9 Hz, 2H), 7.44 (t, *J* = 7.69 Hz, 2H), 6.94 (d, *J* = 8.45 Hz, 1H), 6.31 (dd, *J* = 3.32 and 7.84 Hz, 1H), 4.89 (dd, *J* = 3.32 and 12.07 Hz, 1H), 4.53 (m, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 2.19(s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ = 170.2, 166.2, 154.0, 149.2, 133.3, 129.7, 129.2, 128.4, 127.4, 123.3, 110.5, 110.2, 99.8, 72.9, 63.6, 56.1, 55.9, 20.6 ppm.

Synthesis of DVGL starting from D2

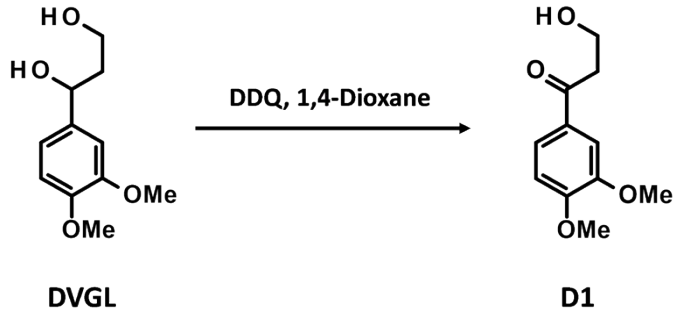


Scheme S3. Synthetic route for **DVGL**.

1-(3,4-dimethoxyphenyl) propane-1,3-diol, DVGL. 3.4-dimethoxyacetophenone (**D2**) (2.02 g, 11.21 mmol) was dissolved in anhydrous toluene (20.0 mL). The solution was dropped into toluene solution (12 mL) of diethyl carbonate (2.68 mL, 22.12 mmol) and NaH (1.51 g, 62.94 mmol) and the resulting solution was refluxed for 3 h. Aqueous solution of citric acid was then added to degrade the remaining NaH. The organic layer was extracted by EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Red oil (3.52 g) containing ethyl 3-(3,4-dimethoxyphenyl)-3-oxo-propanoate (**15**) was used for the next step without further purification.

The crude mixture containing **15** (3.52 g) was dissolved in anhydrous toluene (10.0 mL). The solution was dropped into a 1.5 mol/L DIBAL-H toluene solution (22.0 mL, equivalent to 33.3 mmol of DIBAL-H) for 2h with stirring at room temperature. EtOH and H_2O were added to the reaction solution in this order to quench the remaining DIBAL-H. After adjusting the pH of the solution to ~3 by adding an aqueous solution of citric acid, saturated Na_2SO_4 aq. was added and stirred at room temperature for 1 h. The resulting two-phase-separated reaction mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography with EtOAc to give **DVGL** as light green oil (0.91 g, 4.29 mmol). **DVGL** was analyzed with NMR after its acetylation in Ac_2O/pyridine. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92 ~ 6.80 (m, 3H), 5.79 (dd, *J* = 5.92 and 8.41, 1H), 4.17 ~ 4.09 (m, 1H), 4.04 ~ 3.97 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.30 ~ 2.19 (m, 1H), 2.12 ~ 2.07 (m, 1H), 2.06 (m, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ = 171.0, 170.2, 151.9, 148.8, 132.2, 119.0, 110.9, 109.5, 72.6, 60.7, 55.8, 35.0, 21.2, 20.8, 20.7 ppm.

Synthesis of D1 starting from DVGL



DVGL D1

Scheme S4. Synthetic route for **D1**.

1-(3,4-dimethoxyphenyl)-3-hydroxy-propan-1-one (D1). DVGL (0.11 g, 0.52 mmol) was dissolved in 1,4-dioxane (5.0 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.13 g, 0.57 mmol) was added to the solution at room temperature. In 1.5 h, an aqueous solution of sodium thiosulfate was added to quench remaining DDQ. The resulting reaction mixture was extracted with EtOAc and the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography with EtOAc to give **D1** as white crystal (0.11 g, 0.52 mmol). ^{1}H NMR (400 MHz, acetone-d_6) δ = 7.63 (dd, J = 2.3 and 8.5 Hz, 1H), 7.50 (d, J = 1.9 Hz, 1H), 7.02 (d, J = 8.63 Hz, 1H), 3.92 ~ 3.87 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.13 (t, J = 6.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, acetone-d_6) δ = 198.2, 154.5, 150.1, 131.3, 123.5, 111.4, 111.2, 58.6, 56.1, 56.0, 41.6 ppm.

NMR spectra of the compounds synthesized in this study

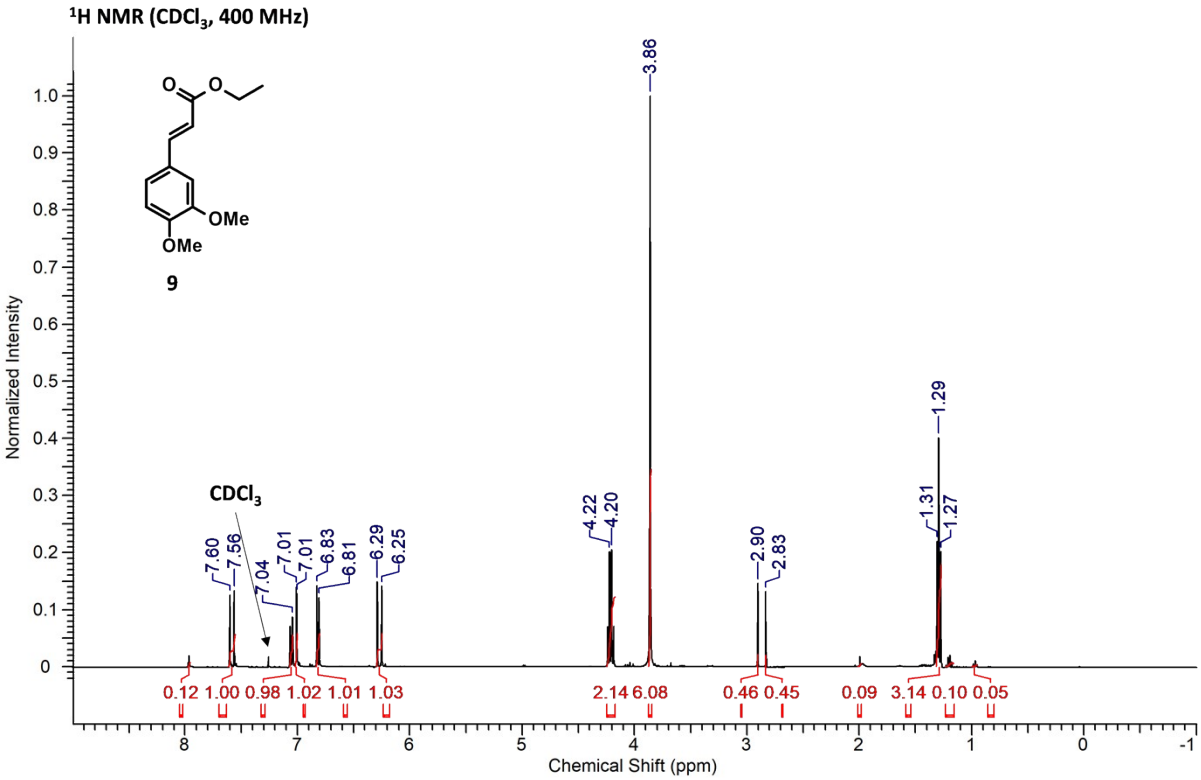


Figure S8. [1]H NMR spectrum of **9**

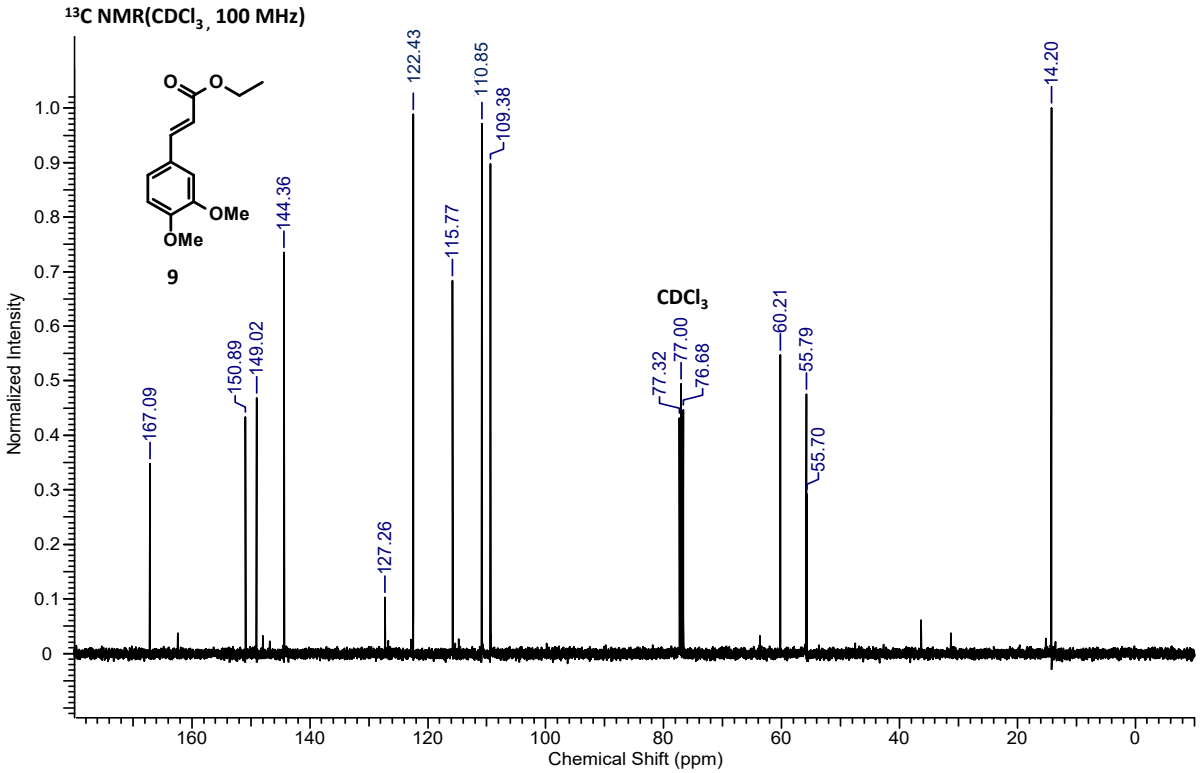


Figure S9. [13]C NMR spectrum of **9**.

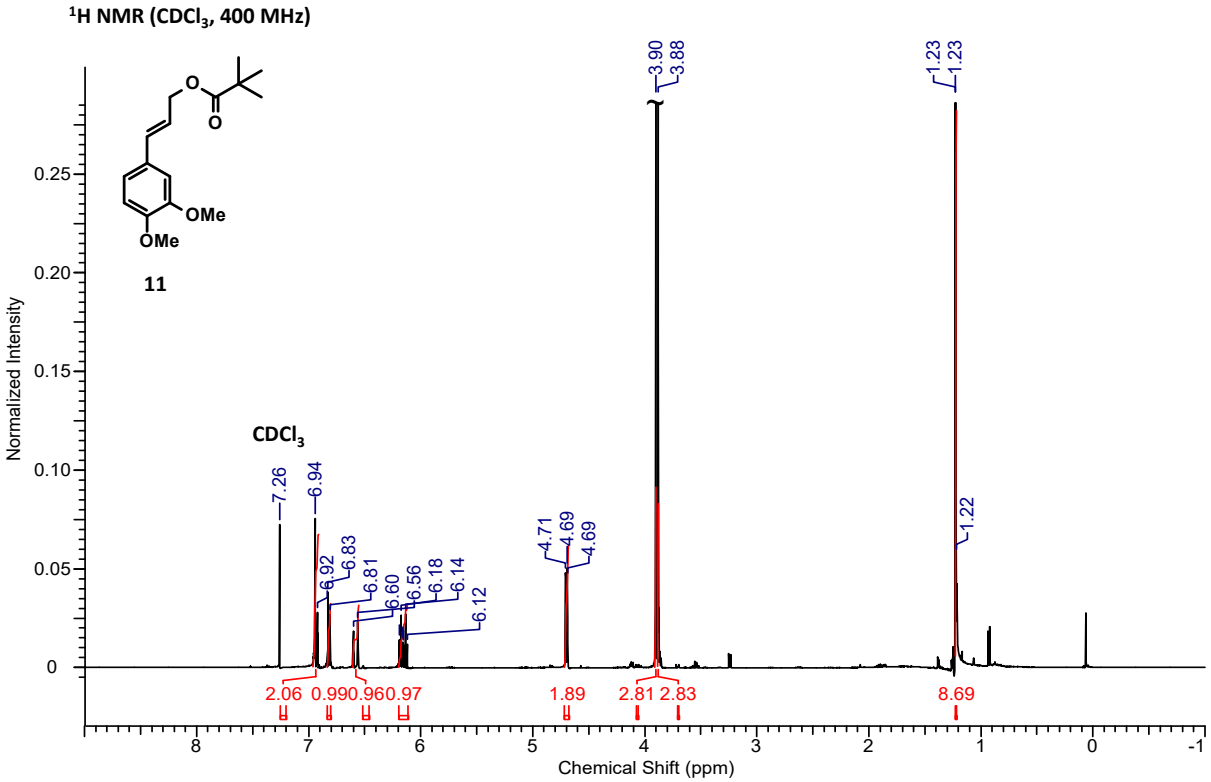


Figure S10. [1]H NMR spectrum of **11**.

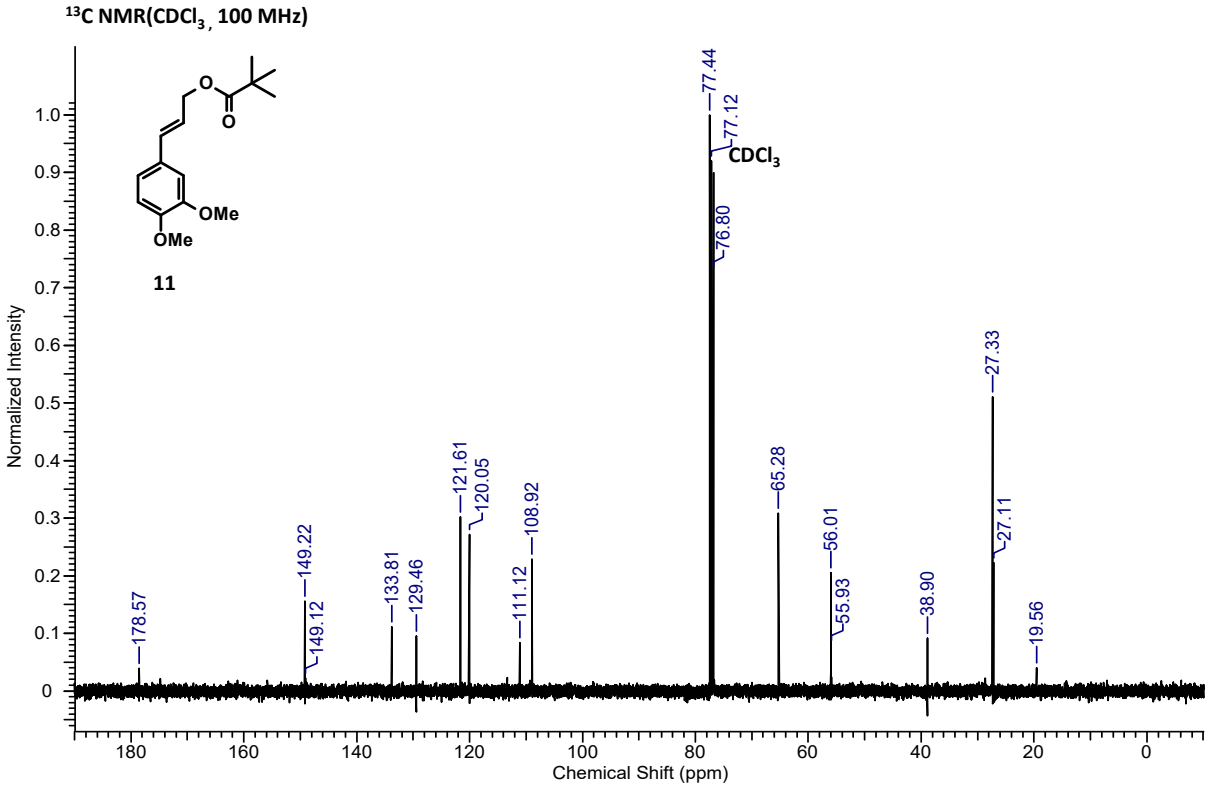


Figure S11. [13]C NMR spectrum of **11**.

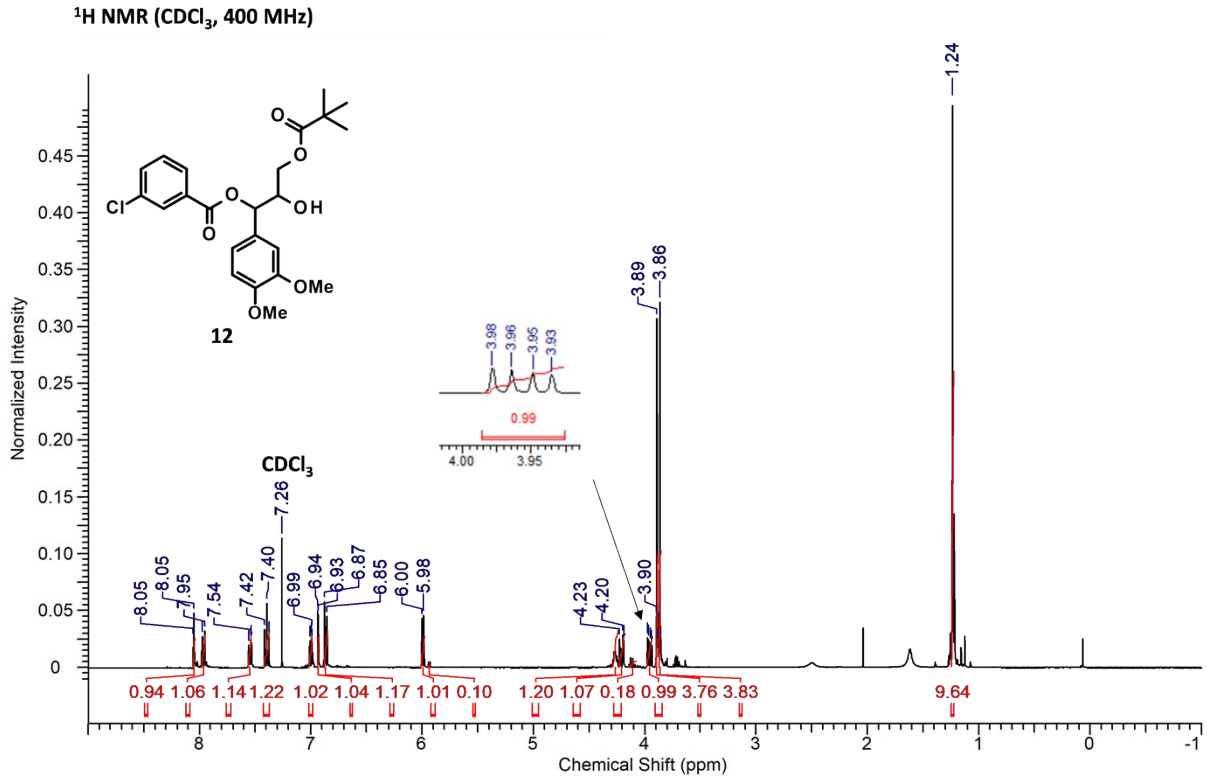


Figure S12. ^{1}H NMR spectrum of **12**.

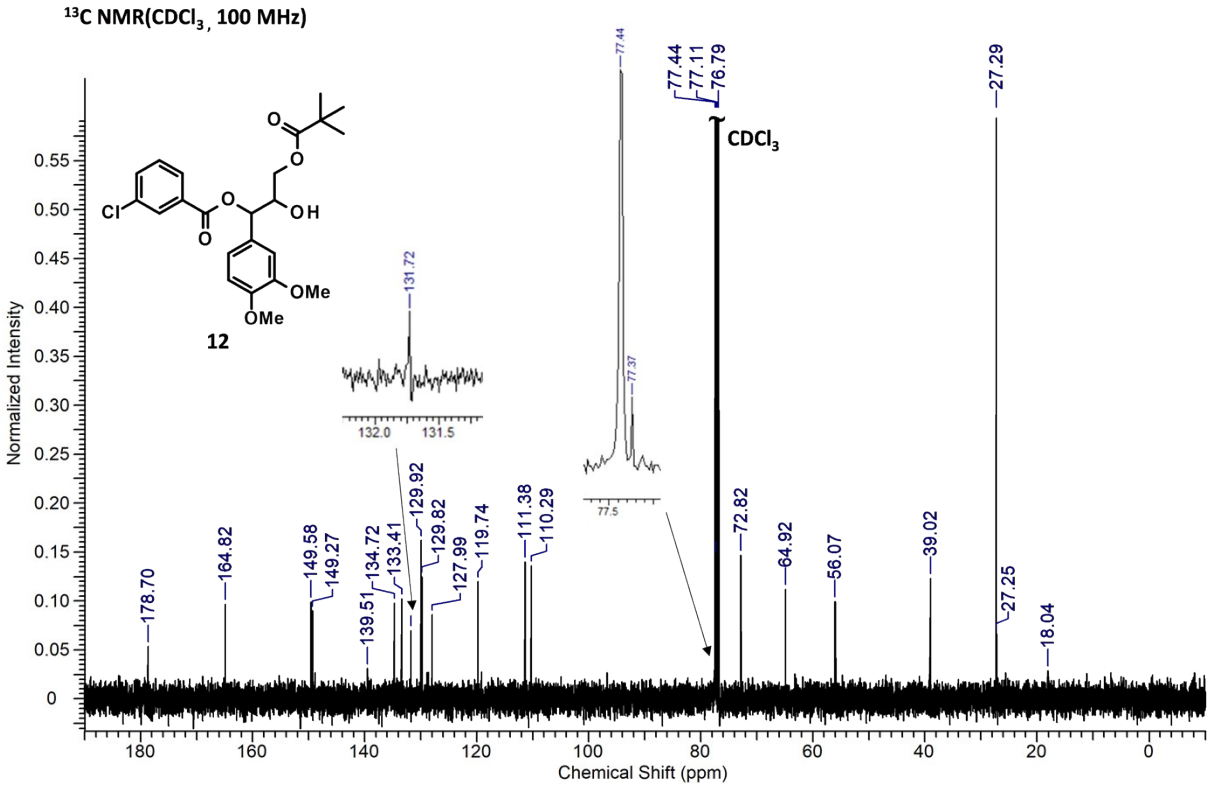


Figure S13. ^{13}C NMR spectrum of **12**.

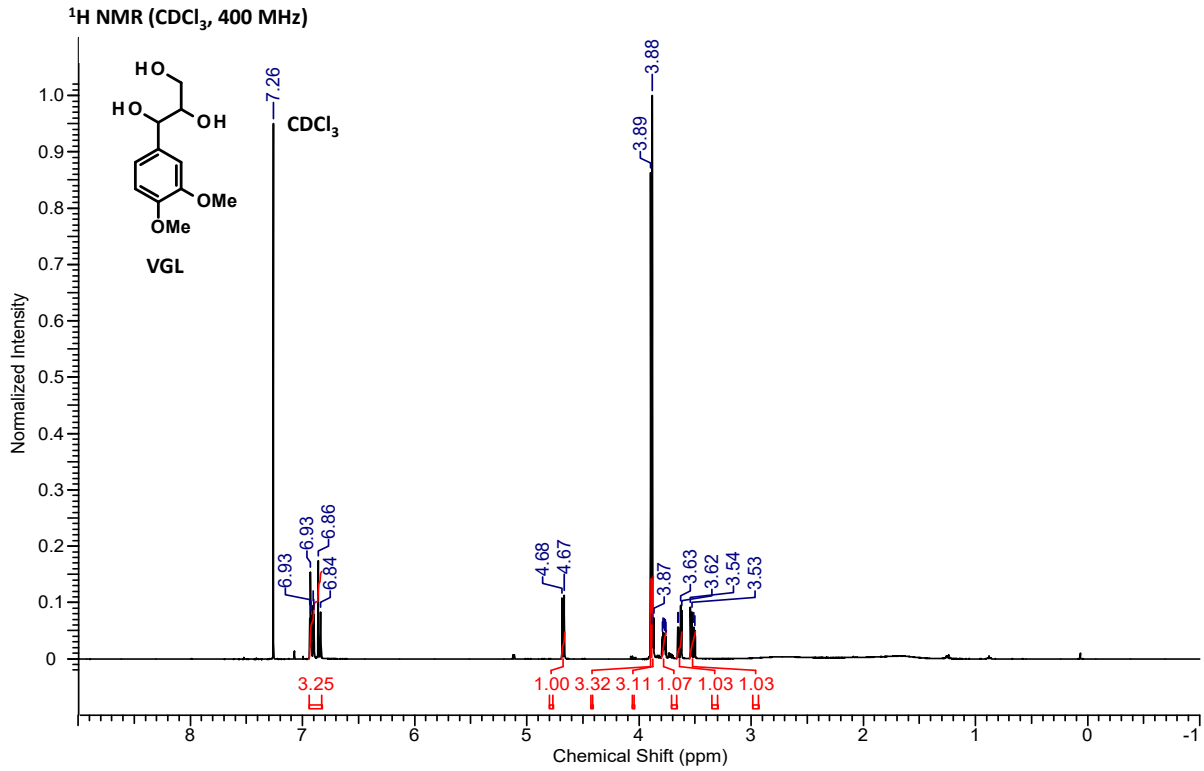


Figure S14. [1]H NMR spectrum of **VGL**.

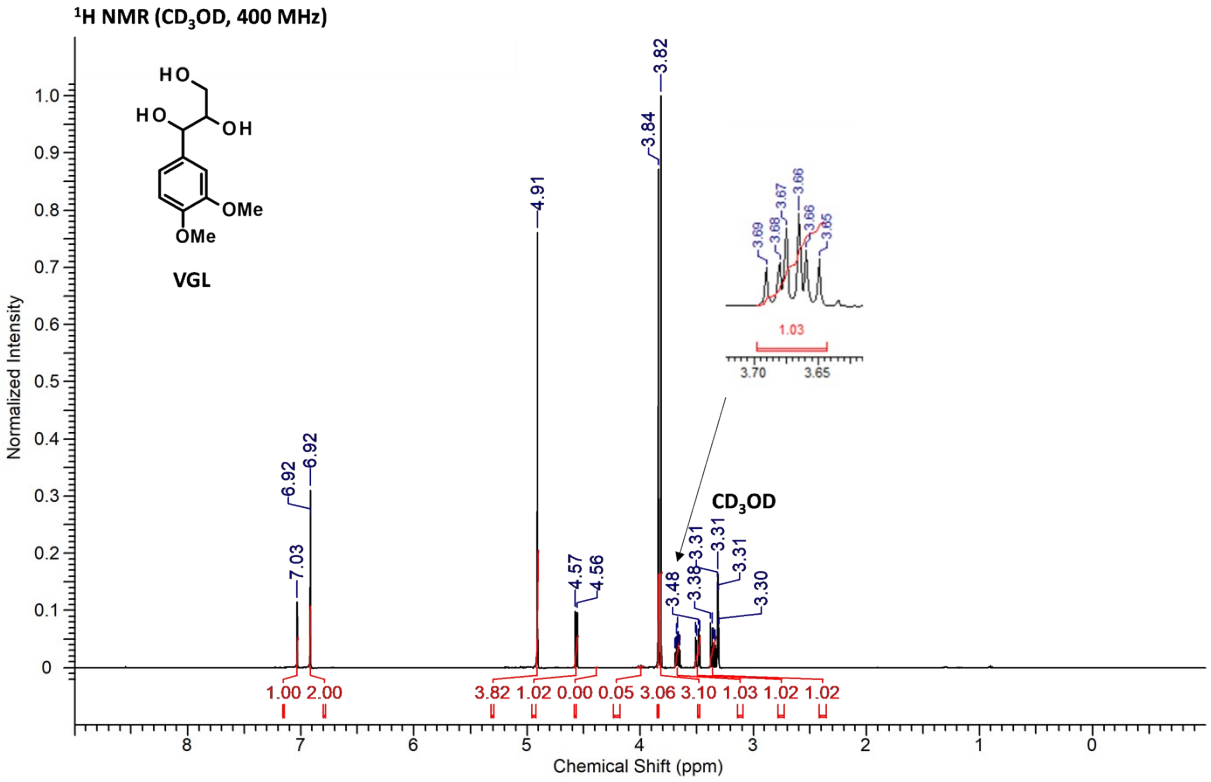


Figure S15. [1]H NMR spectrum of **VGL**.

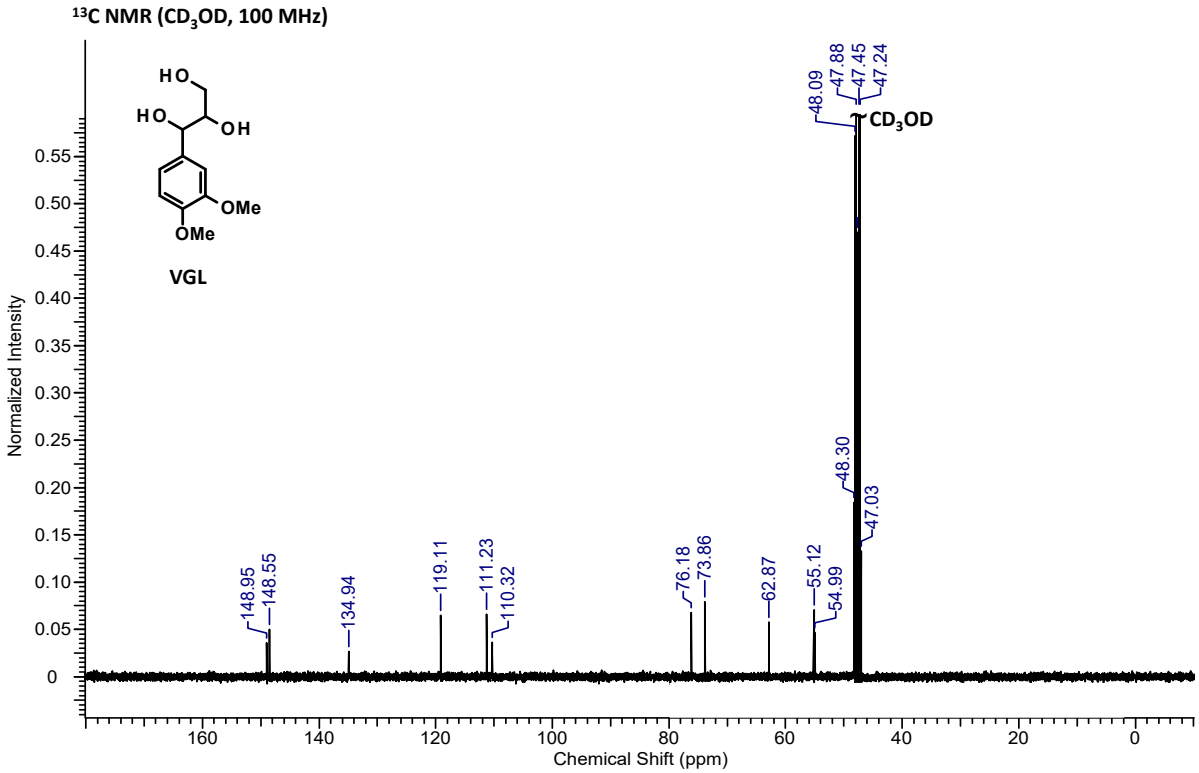


Figure S16. ^{13}C NMR spectrum of **VGL**.

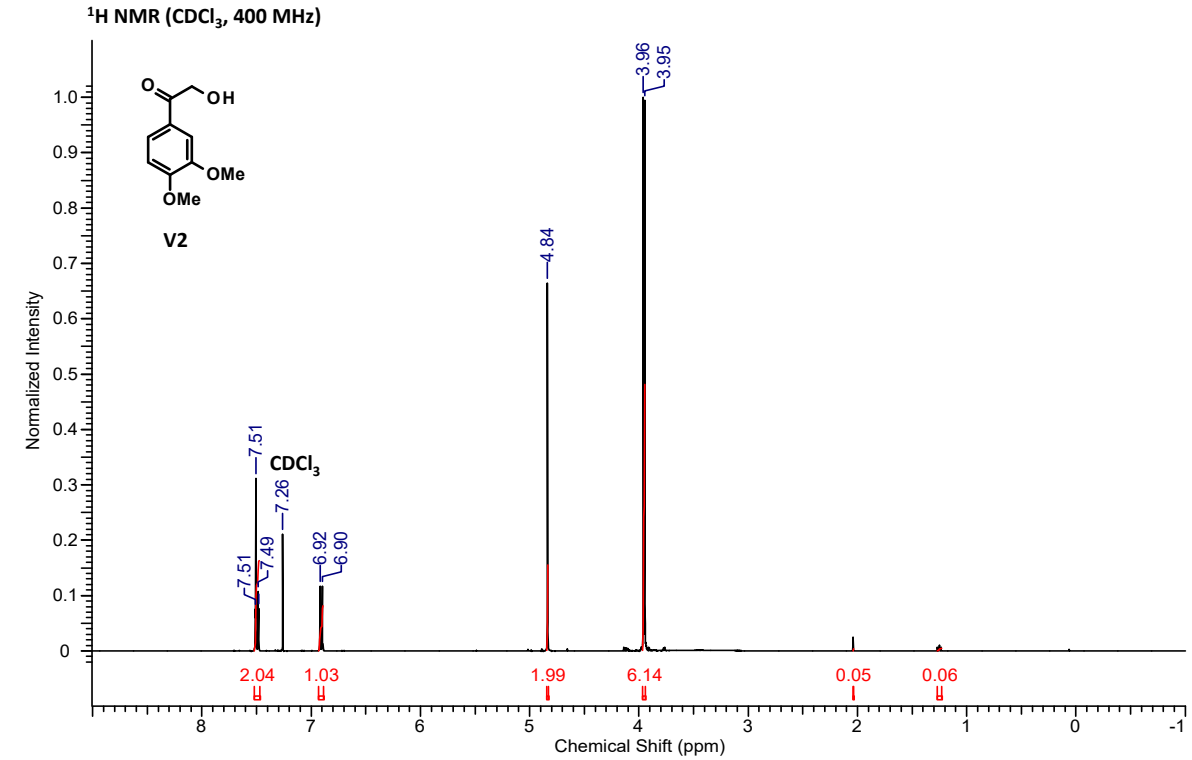


Figure S17. [1]H NMR spectrum of **V2**

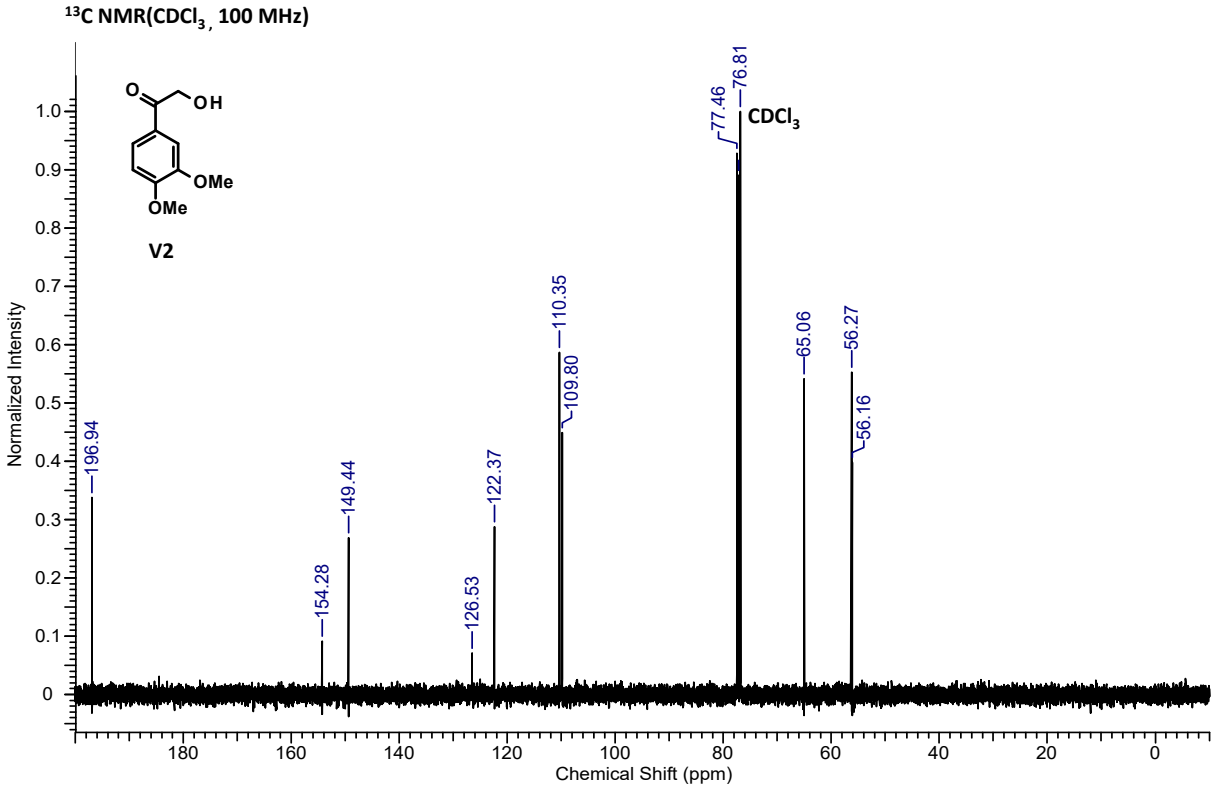


Figure S18. [13]C NMR spectrum of **V2**.

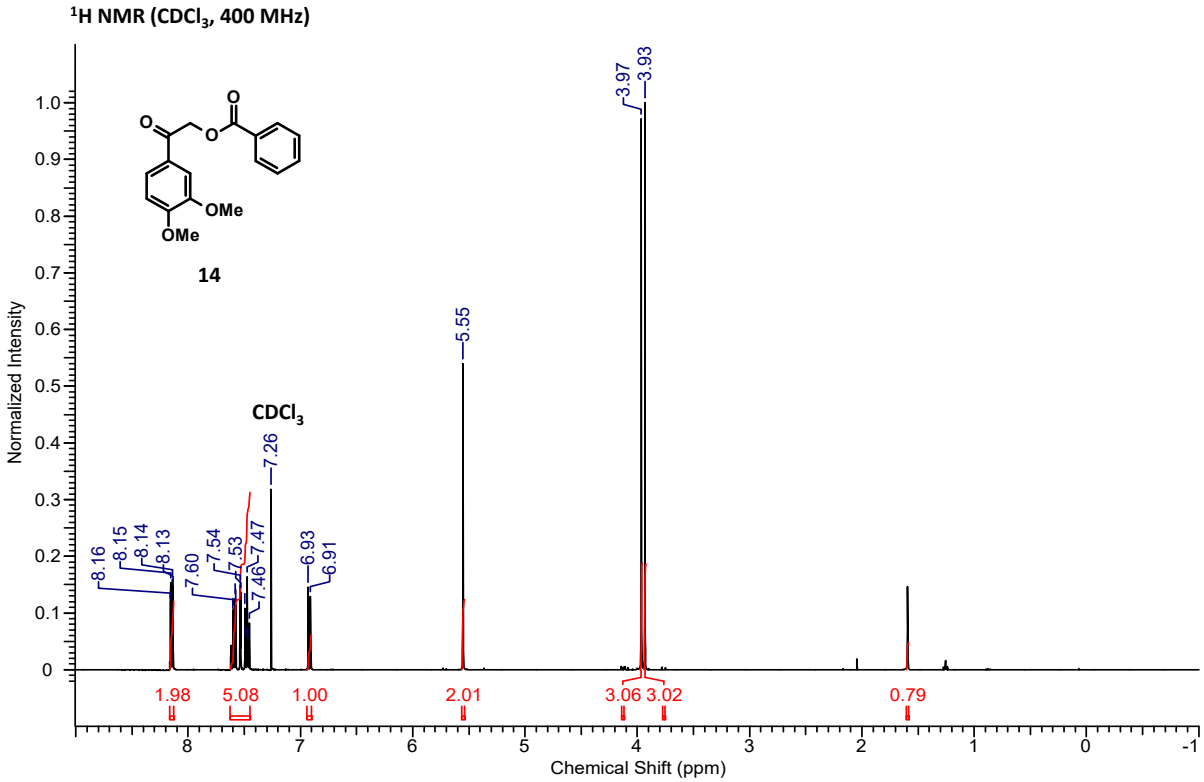


Figure S19. ^{1}H NMR spectrum of **14**.

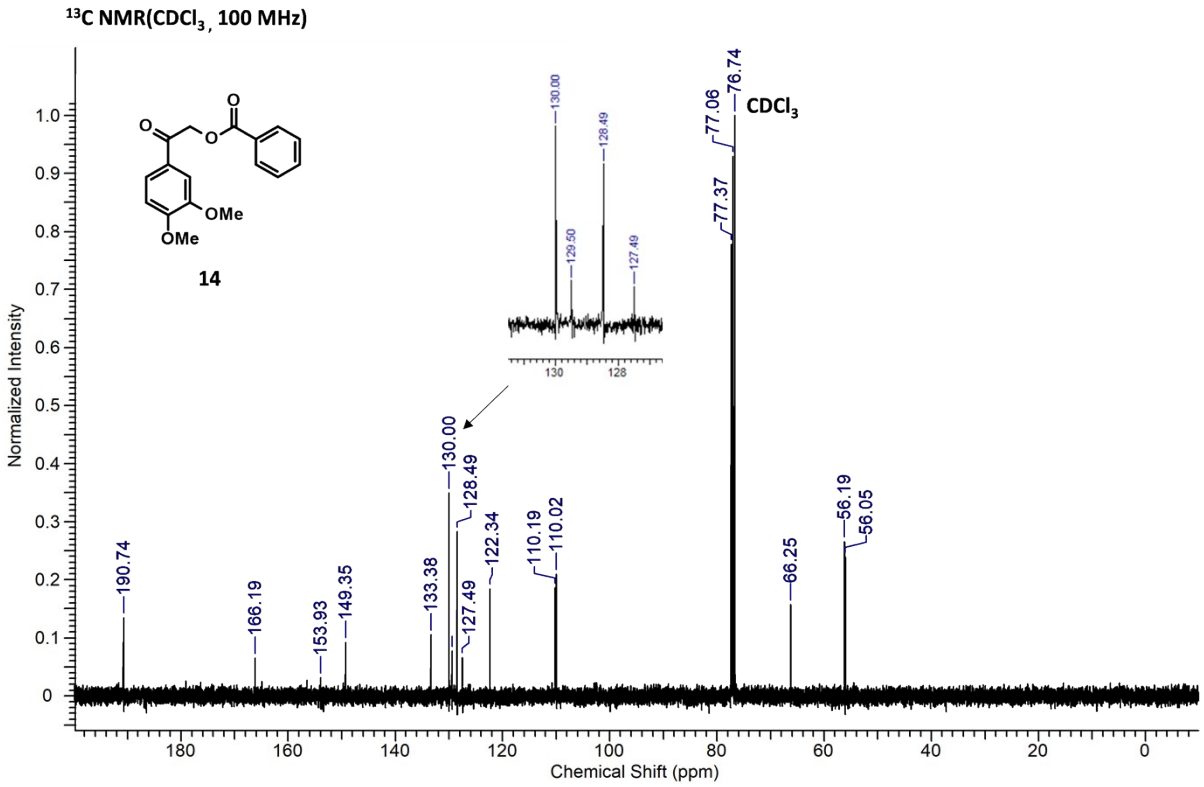


Figure S20. ^{13}C NMR spectrum of **14**.

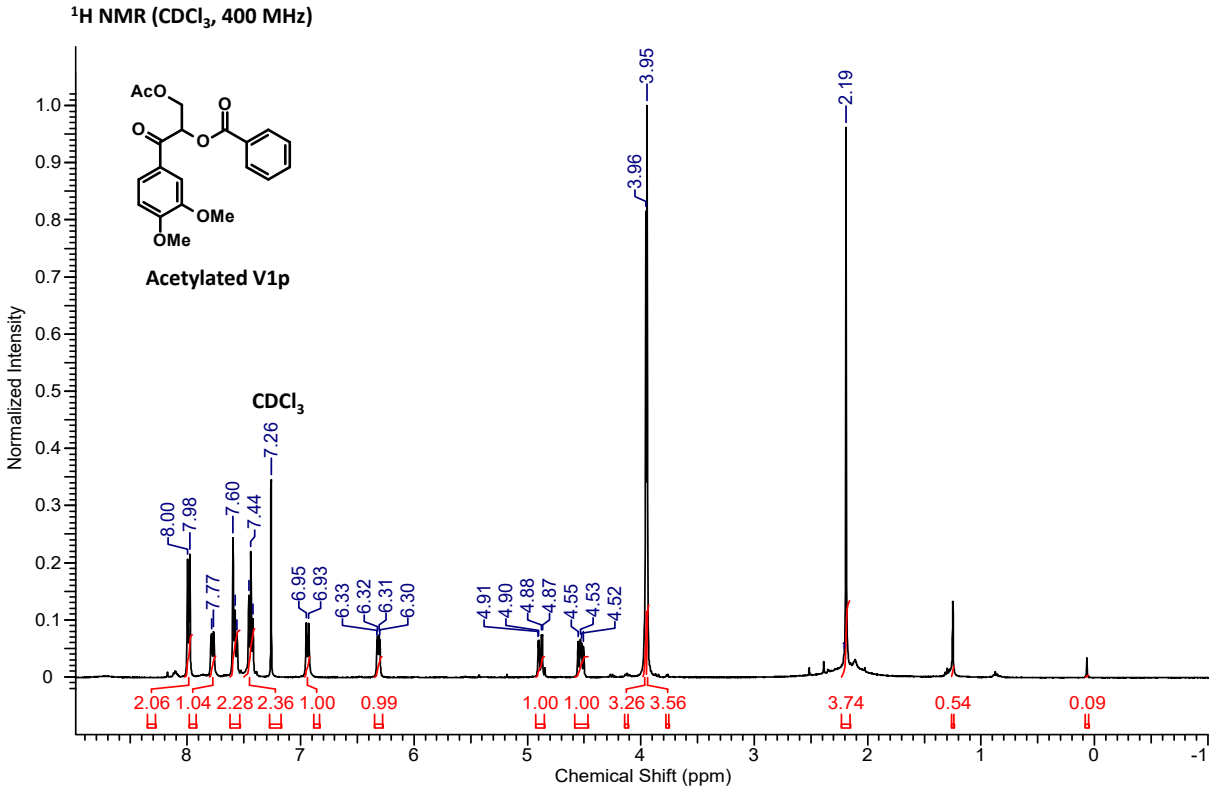


Figure S21. [1]H NMR spectrum of acetylated **V1p**.

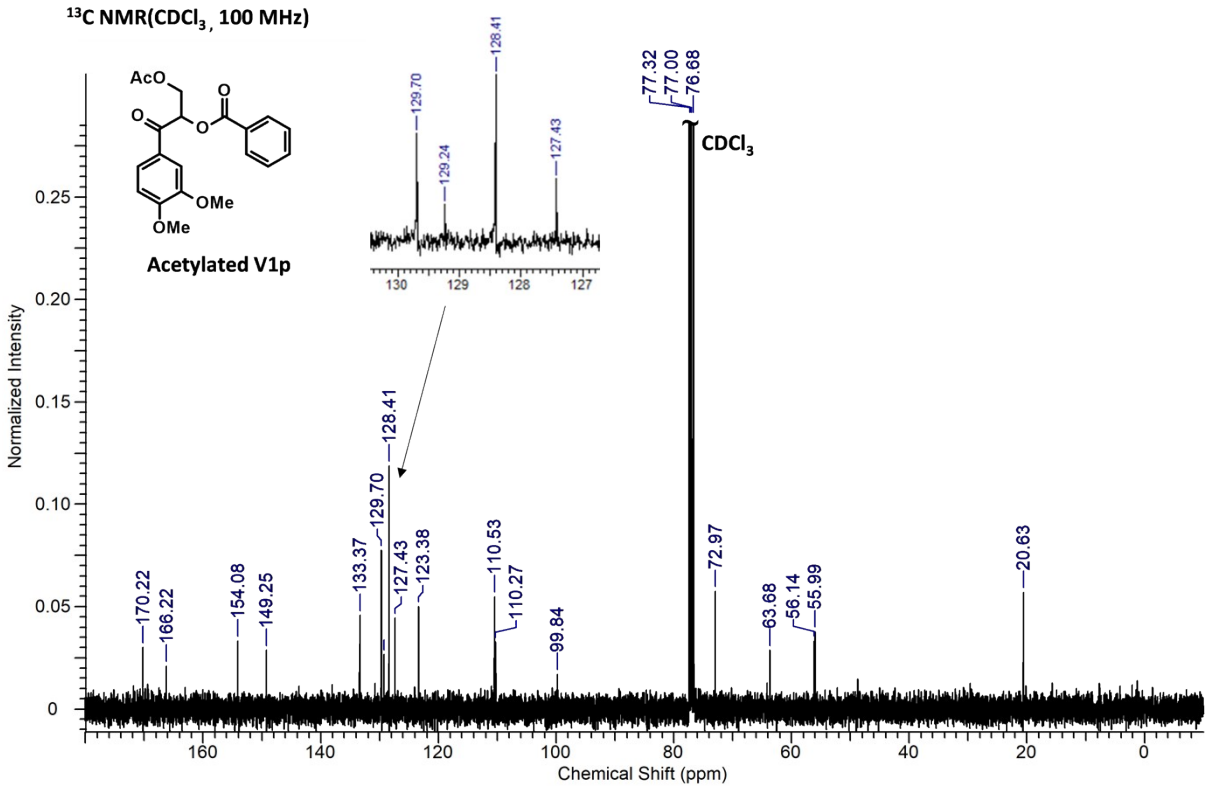


Figure S22. [13]C NMR spectrum of acetylated **V1p**.

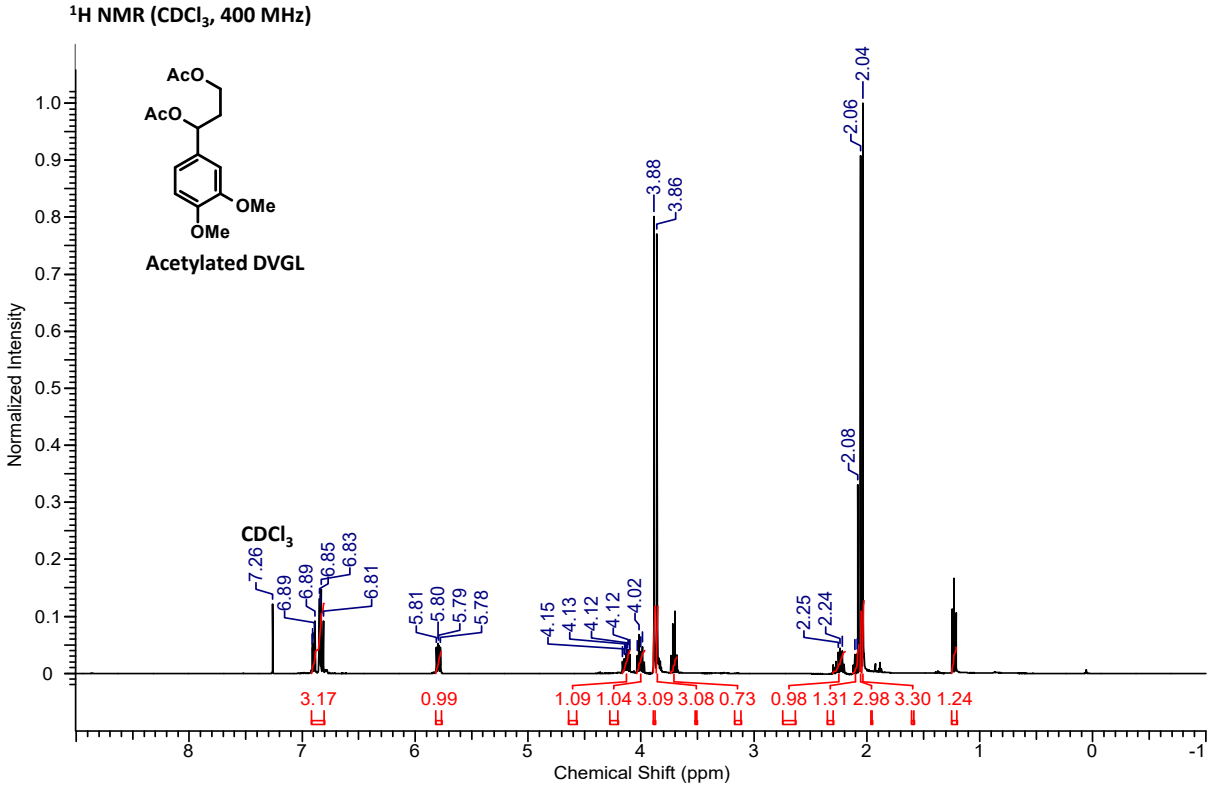


Figure S23. [1]H NMR spectrum of acetylated **DVGL**.

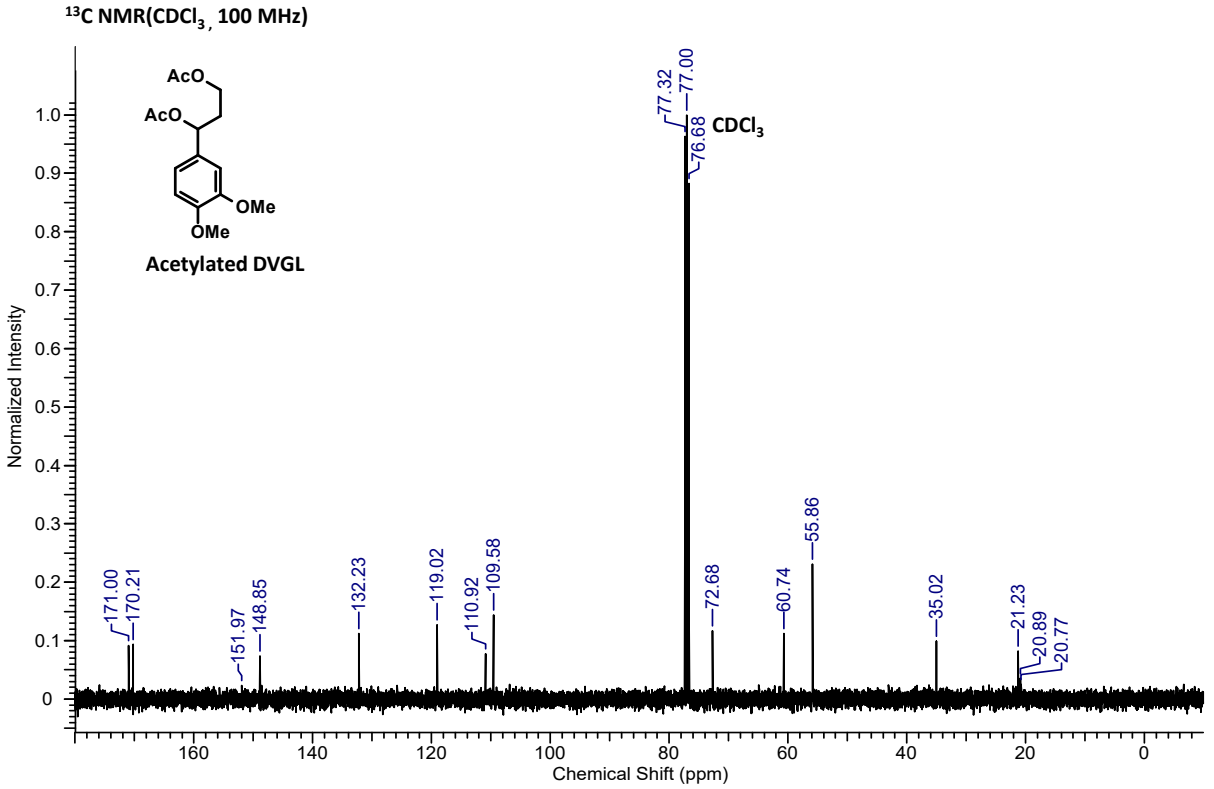


Figure S24. [13]C NMR spectrum of acetylated **DVGL**.

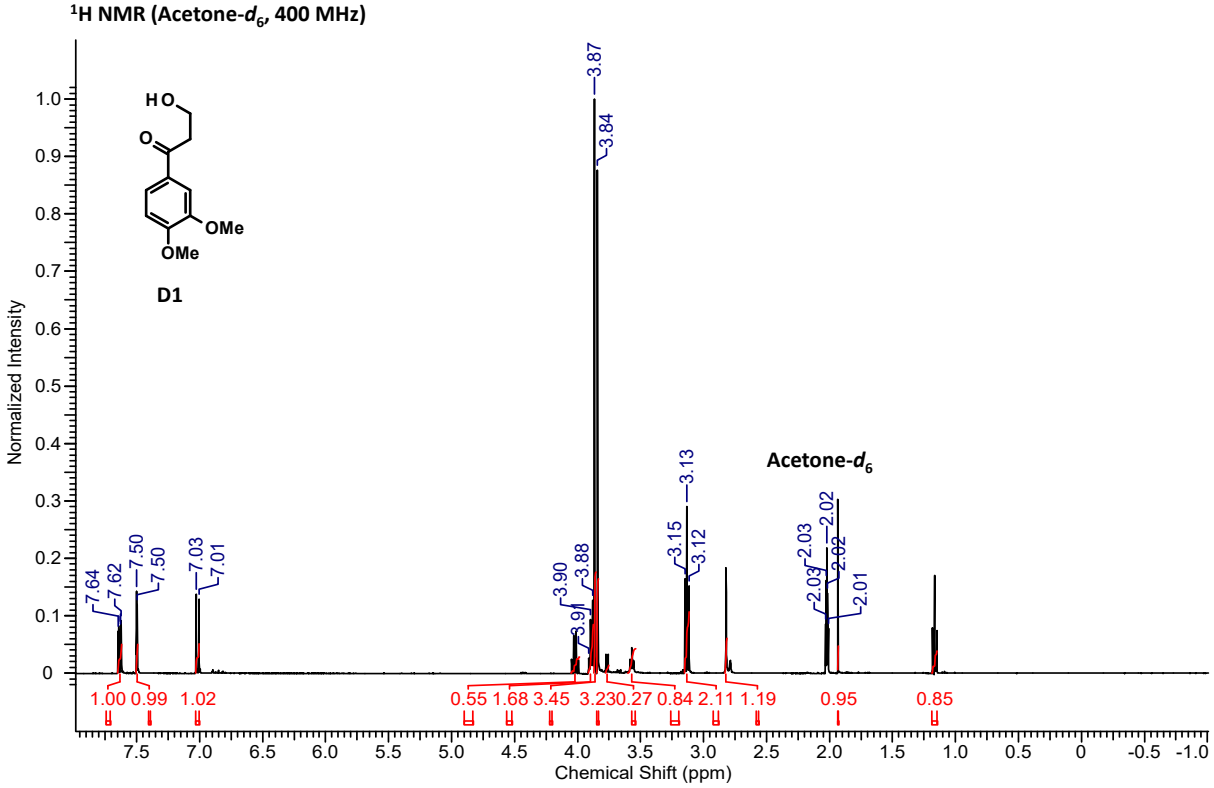


Figure S25. [1]H NMR spectrum of **D1**.

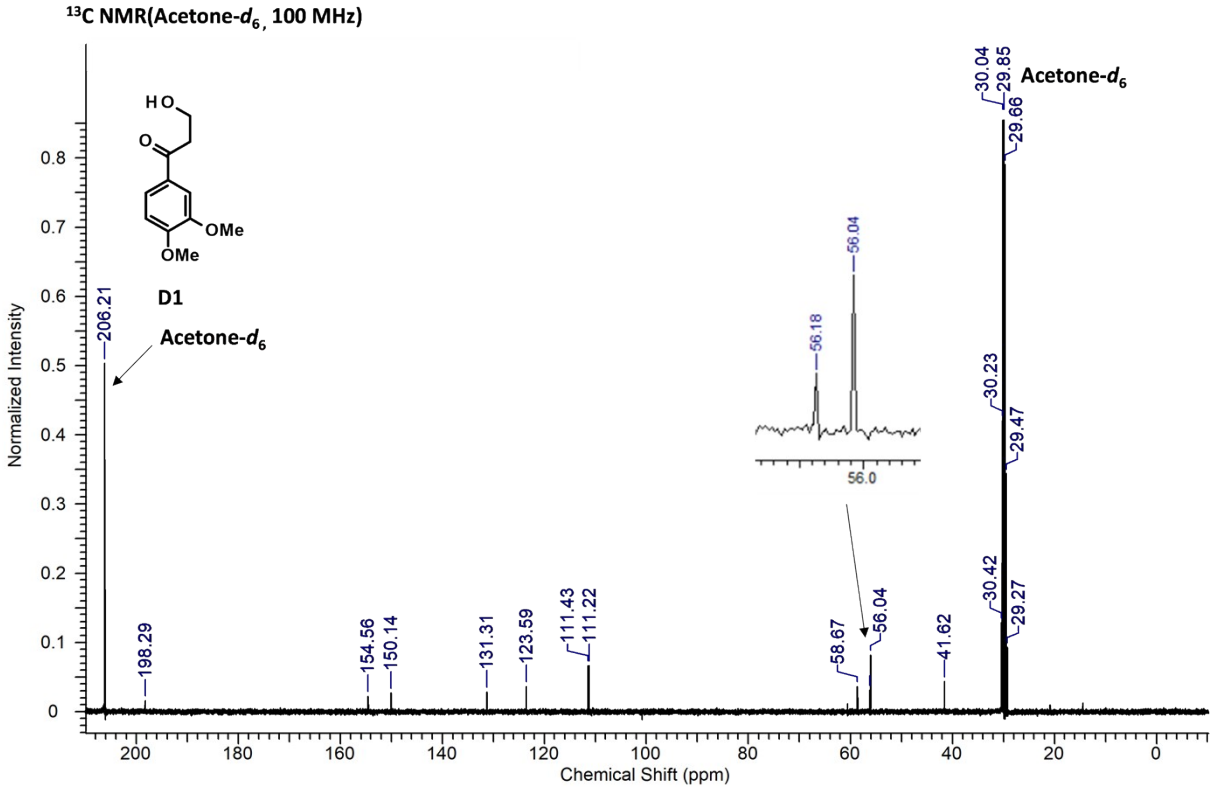


Figure S26. [13]C NMR spectrum of **D1**.

Cartesian coordinates and total energies of optimized geometries.

Cartesian coordinate of V1

C	2.26438600	-0.23474800	0.00061300
C	1.23646400	0.74000600	0.02467700
C	-0.09312800	0.34722500	0.01900200
C	-0.42472800	-1.02154200	0.01000800
C	0.58833800	-1.97453000	0.00237700
C	1.92998800	-1.58684500	-0.01143600
H	-0.88633600	1.09031000	0.03583300
H	0.32956600	-3.02862100	0.00102600
H	2.70506300	-2.34421100	-0.03191900
O	3.52860300	0.24744600	-0.00919500
O	1.65621200	2.03264700	0.04640100
C	0.65221300	3.03473100	0.05580400
H	0.02023600	2.94938500	0.94672400
H	1.18058500	3.98750300	0.06762000
H	0.02469000	2.96990400	-0.84033300
C	4.59112600	-0.69418300	-0.02857000
H	4.54778500	-1.31427800	-0.93029000
H	5.50859200	-0.10737100	-0.03107000
H	4.56392700	-1.33231400	0.86106100
C	-1.84524400	-1.48243200	0.04515100
O	-2.11336500	-2.62637300	0.40148900
C	-2.96405600	-0.52718500	-0.31043900
H	-3.86291300	-1.14713100	-0.42762300
C	-3.18613800	0.55633200	0.86673800
H	-4.20108900	0.39659400	1.27329100
H	-2.47741600	0.33814100	1.69159400
O	-2.71185300	0.23020500	-1.45682900
H	-2.78151000	1.17422200	-0.99468000
O	-3.00541100	1.79443800	0.31003600

Total Energy: -802.897678743 a.u.

Cartesian coordinate of G2

C	-2.42699200	-0.31357700	0.04390400
C	-1.51757300	0.76246900	-0.10951500
C	-0.15844800	0.50511600	-0.20401000
C	0.32821300	-0.81446800	-0.13264100
C	-0.57104900	-1.86243000	0.02845100
C	-1.94364300	-1.61763600	0.10933400
H	0.53054400	1.33287500	-0.32183100
H	-0.19632000	-2.87925700	0.08615800
H	-2.62885600	-2.44915200	0.22514300
O	-3.73191200	0.03118100	0.11596500
O	-2.07648800	1.99848200	-0.15278100
C	-1.20004700	3.10522800	-0.29494600
H	-0.64400200	3.04675500	-1.23733200
H	-1.83424200	3.99059500	-0.29853200
H	-0.49751600	3.15862600	0.54458200
C	-4.68170200	-1.01508300	0.26314700
H	-4.50827200	-1.57113600	1.19049700
H	-5.65547800	-0.52901700	0.30367600
H	-4.64509000	-1.69825400	-0.59194800
C	1.79323100	-1.11611100	-0.21503700
O	2.20576900	-2.24051500	0.03483200
C	2.72585800	0.02264600	-0.56817800
H	2.28654500	0.59011800	-1.40060500
C	2.90292800	0.98064400	0.73265700
H	2.56027800	1.99508200	0.44429500
H	2.21485800	0.63211300	1.52861500
O	4.01118000	-0.40167200	-0.87568800
H	4.49008100	0.06583600	-0.06445000
O	4.21930100	0.92427800	1.08676400

Total Energy: -802.895792637 a.u.

Cartesian coordinate of G3

C	2.40372100	-0.30732600	-0.04435400
C	1.49035000	0.75767300	0.16410700
C	0.13323800	0.49175800	0.24678300
C	-0.34625200	-0.82657700	0.11526700
C	0.55693400	-1.86462600	-0.09240700
C	1.92662800	-1.60987900	-0.17064800
H	-0.55968400	1.30879200	0.40641500
H	0.18590500	-2.87927900	-0.19191500
H	2.61491900	-2.43110900	-0.33150100
O	3.70459200	0.04562300	-0.10471500
O	2.04630100	1.99038000	0.26588700
C	1.16707600	3.09027800	0.44301600
H	0.61215900	3.00080400	1.38344500
H	1.79953000	3.97634500	0.47401200
H	0.46444300	3.16802100	-0.39441100
C	4.65936400	-0.98426800	-0.32469900
H	4.48053000	-1.48200000	-1.28342700
H	5.62965100	-0.49010400	-0.34245200
H	4.63367400	-1.71885200	0.48687100
C	-1.79495600	-1.14359600	0.20993700
O	-2.19908700	-2.29979400	0.10866100
C	-2.81449300	-0.03499600	0.36442300
H	-2.47917800	0.70648600	1.09851200
C	-3.02744400	0.70564200	-1.00310600
H	-2.01043700	0.87662800	-1.43020400
H	-3.48519200	-0.08589900	-1.65103600
O	-4.03043100	-0.57812900	0.84137500
H	-4.03412700	-1.50865900	0.56699600
O	-3.76852400	1.83121200	-0.89136000

Total Energy: -802.887060430 a.u.

Cartesian coordinate of G4

C	-2.32112900	-0.37985000	0.00033200
C	-1.42904900	0.71423000	-0.11382700
C	-0.06071400	0.49524900	-0.11926700
C	0.44169700	-0.81111100	0.01849200
C	-0.43602400	-1.88510400	0.14966300
C	-1.81461600	-1.67258900	0.13414300
H	0.65021600	1.32059200	-0.13018500
H	-0.04200900	-2.89107400	0.25179000
H	-2.48723500	-2.51745400	0.22366500
O	-3.63626000	-0.06822800	-0.02682400
O	-2.00903700	1.93999300	-0.20840500
C	-1.13259700	3.05164100	-0.31916400
H	-0.53767100	2.98897700	-1.23754600
H	-1.77052500	3.93409500	-0.35240600
H	-0.45951600	3.10716800	0.54326300
C	-4.57005000	-1.13327300	0.07956100
H	-4.46046500	-1.65343400	1.03700700
H	-5.55499900	-0.67182800	0.02310100
H	-4.44844200	-1.84403500	-0.74468400
C	1.89982200	-1.07610800	-0.01474100
O	2.35282700	-2.16722400	0.33036700
C	2.88018000	-0.02324700	-0.49936100
H	2.45900100	0.52628800	-1.34963100
C	3.25129300	1.01870400	0.62840200
H	3.59236600	0.38127600	1.48426500
H	4.18700600	1.46134000	0.21216100
O	4.06107900	-0.67791900	-0.92952600
H	4.05995500	-1.54843000	-0.50029800
O	2.30132100	1.92528800	0.94365000

Total Energy: -802.888315361 a.u.

Cartesian coordinate of erythro-V1'

C	-0.33546000	0.81465600	0.38062600
C	0.38759000	-0.38468200	0.50128000
C	-0.28339500	-1.58792500	0.36094000
C	-1.66063200	-1.61364300	0.08772900
C	-2.37362600	-0.42921200	-0.04078500
C	-1.69853000	0.80569800	0.11558100
H	0.18983200	1.75914400	0.49917600
H	0.27102300	-2.51466400	0.47023500
H	-2.16367300	-2.56813400	-0.02196300
O	-2.47339900	1.91835200	-0.00914000
O	-3.70755100	-0.34289900	-0.30679300
C	-4.40957100	-1.55927100	-0.49233700
H	-5.44019600	-1.28212000	-0.71214300
H	-3.99486000	-2.12790700	-1.33270900
H	-4.38065000	-2.17397100	0.41452500
C	-1.83160400	3.17416000	0.12879500
H	-1.05679400	3.30580900	-0.63484300
H	-2.60884700	3.92562900	-0.00597000
H	-1.38609700	3.28140600	1.12425400
C	1.89243000	-0.34130500	0.74925100
H	2.07909900	0.50234000	1.44573800
C	2.63507500	0.00795100	-0.66009800
H	1.91450900	0.44201900	-1.36742200
O	2.43983000	-1.51414100	1.16123000
O	3.14999000	-1.20243000	-1.09635400
H	3.02353300	-1.71502200	-0.19342700
C	3.68018200	1.04145800	-0.36147200
O	4.87359200	0.83359900	-0.26603300
H	3.27867900	2.05831400	-0.16578200

Total Energy: -802.889663955 a.u.

Cartesian coordinate of threo-V1'

C	0.32473400	1.06206700	-0.39509500
C	-0.57816200	0.03655300	-0.72437700
C	-0.12489800	-1.27286300	-0.74995700
C	1.20835700	-1.57629000	-0.43415800
C	2.09745200	-0.56491800	-0.09344900
C	1.64738800	0.77733400	-0.07972700
H	-0.02851300	2.08976600	-0.38893700
H	-0.81880700	-2.06472700	-1.01512200
H	1.54038800	-2.60840900	-0.45984000
O	2.58584300	1.70757400	0.24652800
O	3.40818900	-0.75121400	0.22778600
C	3.89036800	-2.08349400	0.22976300
H	4.94026900	-2.02357000	0.51504300
H	3.34619000	-2.69715400	0.95695600
H	3.80543300	-2.53479900	-0.76532400
C	2.17221200	3.06262200	0.28244600
H	1.38430100	3.21338800	1.02903000
H	3.05421400	3.63849800	0.56070000
H	1.81402200	3.39138500	-0.69958400
C	-2.04098900	0.36973200	-0.98562700
H	-2.06098800	1.35994600	-1.49396500
C	-2.81721500	0.63453600	0.40626600
H	-2.64832200	1.67007300	0.73453200
O	-2.75833600	-0.57499800	-1.64279300
O	-4.15712200	0.39489000	0.10398200
H	-4.00257700	-0.17085100	-0.73173400
C	-2.28817200	-0.28085200	1.47861500
O	-2.82214900	-1.31079500	1.84208500
H	-1.32346800	0.02623500	1.92934500

Total Energy: -802.888884270 a.u.

Cartesian coordinate of TS1

C	-2.36071000	-0.41349000	0.03279500
C	-1.56978800	0.74846500	-0.13975200
C	-0.19779900	0.63275500	-0.30750900
C	0.42860200	-0.63066700	-0.32809700
C	-0.35859900	-1.76205400	-0.15121900
C	-1.74503400	-1.65819900	0.02591700
H	0.40312500	1.52996000	-0.40642900
H	0.11699700	-2.73734800	-0.15191500
H	-2.33123700	-2.56065800	0.15958800
O	-3.69332400	-0.20020400	0.20495200
O	-2.24882500	1.92750300	-0.10869400
C	-1.49976300	3.11636000	-0.29306600
H	-0.99884400	3.11803500	-1.26795600
H	-2.21952700	3.93329600	-0.25041000
H	-0.75547200	3.24150300	0.50146700
C	-4.51129100	-1.34100500	0.39984700
H	-4.21174200	-1.89062000	1.29935800
H	-5.52626700	-0.96459600	0.52298300
H	-4.46960100	-2.00819200	-0.46847200
C	1.90522600	-0.78843600	-0.50440700
O	2.46984100	-1.90424800	-0.19494500
C	2.67047700	0.27396100	-0.94592100
H	2.30819800	1.19669900	-1.37821700
C	2.85108100	0.88277400	1.38213100
H	2.95458200	1.89373000	0.95395500
H	1.82778100	0.58122600	1.65635000
O	4.02001400	0.05579600	-1.12748800
H	4.17742400	-0.78819700	-0.66569300
O	3.83356400	0.25770100	1.78506000

Total Energy: -802.867194778 a.u.

Cartesian coordinate of TS2e

C	-0.34025000	0.83627800	0.53972700
C	0.38534300	-0.35392000	0.72120000
C	-0.23733800	-1.57981700	0.52540900
C	-1.57891400	-1.63219400	0.13417500
C	-2.30138400	-0.45713100	-0.05467100
C	-1.67137400	0.79621500	0.15602500
H	0.16199800	1.78662200	0.69455200
H	0.32412200	-2.49683900	0.67661600
H	-2.05294500	-2.59499300	-0.01813000
O	-2.45623100	1.88669500	-0.04105900
O	-3.60205900	-0.39940200	-0.42954100
C	-4.27530100	-1.62840600	-0.65551500
H	-5.29147300	-1.36329700	-0.94439100
H	-3.79724000	-2.19249800	-1.46354600
H	-4.29844000	-2.23549000	0.25583800
C	-1.86071000	3.15844000	0.15937900
H	-1.02721100	3.31396900	-0.53472600
H	-2.64286800	3.89040500	-0.03790800
H	-1.50668200	3.26733800	1.19052700
C	1.80209400	-0.27372800	1.14486100
H	2.17340700	0.73598400	1.37979700
C	2.74320600	-0.17494700	-1.18512300
H	1.80602800	-0.15406400	-1.73635700
O	2.46706300	-1.27017900	1.47007700
O	3.34085700	-1.41407400	-1.04543300
H	3.24268600	-1.68105300	-0.10490300
C	3.37334200	1.00184600	-0.82825200
O	4.48893300	1.15498300	-0.23410300
H	2.76783100	1.90391500	-1.06018100

Total Energy: -802.872472615 a.u.

Cartesian coordinate of TS2t

C	0.26502900	0.99244400	-0.62796900
C	-0.59885900	-0.08317200	-0.90039000
C	-0.13946700	-1.38596200	-0.76690300
C	1.17718200	-1.63069900	-0.36002000
C	2.03278100	-0.57075600	-0.07991400
C	1.56562000	0.76308800	-0.21189000
H	-0.11186200	2.00580800	-0.73172400
H	-0.80778700	-2.21351000	-0.98349800
H	1.52418100	-2.65291400	-0.26369100
O	2.47105600	1.73228700	0.08482600
O	3.32200700	-0.70026400	0.32052100
C	3.83047700	-2.01627900	0.47146800
H	4.86429700	-1.90154600	0.79512200
H	3.26619000	-2.56928500	1.23036800
H	3.80001200	-2.55912100	-0.47961500
C	2.03454100	3.07780500	-0.01471700
H	1.19800100	3.26958400	0.66698800
H	2.88792300	3.69187700	0.27028000
H	1.73484200	3.31806500	-1.04096200
C	-1.97688400	0.19831100	-1.35597600
H	-2.18918600	1.25491600	-1.58131500
C	-3.25799500	0.61012700	0.72626100
H	-3.54336400	1.62989400	0.47123700
O	-2.74951000	-0.69422000	-1.75784800
O	-4.17310100	-0.38076600	0.42537300
H	-3.91278300	-0.75420400	-0.44826500
C	-2.19778700	0.39251400	1.59359200
O	-1.80867400	-0.69681400	2.10899000
H	-1.61251600	1.31412600	1.79893300

Total Energy: -802.871283308 a.u.

Cartesian coordinate of V2

C	1.84105700	-0.45696100	-0.02761300
C	1.12998000	0.76571500	0.03992500
C	-0.25616300	0.76051900	0.08998000
C	-0.98463200	-0.44760700	0.05494100
C	-0.27146200	-1.64086800	0.00411200
C	1.13034600	-1.64926900	-0.03967400
H	-0.79115100	1.69974800	0.17438400
H	-0.82033200	-2.57657500	-0.00658600
H	1.65472000	-2.59759200	-0.08525100
O	3.20017800	-0.35252600	-0.06478700
O	1.90131900	1.88869200	0.06910200
C	1.23377500	3.13686500	0.12482500
H	0.64069700	3.22647700	1.04207400
H	2.01570900	3.89598700	0.12085800
H	0.58294900	3.27471700	-0.74626100
C	3.93594300	-1.56029500	-0.14203500
H	3.68478900	-2.11680800	-1.05233400
H	4.98658800	-1.27261400	-0.16767700
H	3.74972400	-2.19151700	0.73453500
C	-2.47783200	-0.48580800	0.07894300
O	-3.08539100	-1.60188600	0.40974500
C	-3.20550400	0.60667900	-0.28505400
H	-2.84545600	1.56709000	-0.62772000
O	-4.59107100	0.48549200	-0.26366300
H	-4.71157400	-0.44091800	0.02069400

Total Energy: -688.399983942 a.u.

Cartesian coordinate of formaldehyde

C	0.53259600	0.00000000	-0.00006700
H	1.10833900	-0.93993200	0.00013600
H	1.10834000	0.93993200	0.00013600
O	-0.67653200	0.00000000	0.00001600

Total Energy: -114.457491489 a.u.

Cartesian coordinate of 4

C	-0.79132900	0.98231200	-0.00003000
C	-1.68508700	-0.10362700	-0.00010600
C	-1.20248500	-1.40887400	-0.00013100
C	0.17159300	-1.64331700	-0.00006400
C	1.06555200	-0.57174100	0.00003500
C	0.57663600	0.76046800	0.00003200
H	-1.18714100	1.99317800	-0.00000400
H	-1.90044600	-2.24023000	-0.00022100
H	0.54157700	-2.66166400	-0.00012400
O	1.52364300	1.72985100	0.00012000
O	2.40767000	-0.69386300	0.00008300
C	2.95756800	-2.00510300	0.00055700
H	4.03824300	-1.87226300	0.00092500
H	2.65259100	-2.55474300	0.89692000
H	2.65323200	-2.55511200	-0.89580000
C	1.07515700	3.07650900	-0.00019900
H	0.48244300	3.29134900	0.89572100
H	1.97435500	3.69077900	-0.00030500
H	0.48250400	3.29093200	-0.89626100
C	-3.13114900	0.17172100	-0.00017300
H	-3.40974600	1.24262500	-0.00020000
O	-3.99960500	-0.68285500	-0.00022600

Total Energy: -574.398357995 a.u.

Cartesian coordinate of 7

C	0.61591000	0.65506700	-0.00003200
H	1.19426600	1.56966400	-0.00009700
O	1.37707400	-0.51889500	-0.00000500
H	0.69708000	-1.21510600	-0.00000400
C	-0.73542400	0.54362300	-0.00000700
O	-1.35858300	-0.60906400	0.00004900
H	-1.32218700	1.47697300	-0.00001600

Total Energy: -228.467174008 a.u.