Supporting Information for

The formation of *p*-toluic acid from coumalic acid: A reaction network analysis

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Synthesis of reference materials for intermediates

The intermediate 4-methylcyclohexa-1,5-diene carboxylic acid **3a** was synthesized via non-catalytic reaction of CMA and propylene in toluene at 160 °C, 4 hrs and elevated pressure (~1200 psig). The purified product was isolated with the following procedure. First, the solvent was evaporated using a Rotavapor R205 (Büchi) equipped with a vacuum controller V-800 (Büchi), vacuum pump V-700 (Büchi), and a heating bath B-490 (Büchi) at 65 rpm, 100 mbar (absolute) and a temperature that was stepwise increased from 40 to 70 °C until an oily red-orange crude material was left behind. Second, the remaining material was recrystallized by adding 15 mL DI water which was heated in a water bath to 90 °C to fully dissolve all solid materials. Once the solid material was fully dissolved, the solution was slowly cooled to room temperature. Lastly, the liquid was placed in an ice bath and the solid fraction was separated via vacuum filtration through a cellulose filter and washed with cold water. The solid was analyzed using ^{1}H-NMR and confirmed the expected 4-methylcyclohexa-1,5-diene carboxylic acid **3a** with ~85 % purity and CMA remaining as the major byproduct.

4-methylcyclohexa-1,5-diene carboxylic acid - ^{1}H-NMR (600 MHz, benzene-d6): δ 6.93 (t, 1H), 6.56 (d, 1H), 5.51 (dd, 1H), 2.06-1.96 (m, 1H) 1.96-1.88 (m, 1H), 1.67-1.58 (m, 1H), 0.71 (d, 3H); GC-MS m/z: 138.1

NMR structural identification of intermediates, products and by-products

Verification assignments of bicyclic lactone intermediates (**2a** (endo/exo)**, 2b** (endo/exo)), methyl cyclohexa-1,5-dienecarboxylic acids (**3a, 3b**), toluic acid (**7a**, **7b**), and bicyclic by-products (**4a, 4b, 5a, 5b**) were carried out via NMR, UPLC-PDA/QDa and GC-FID/MS analysis of reaction products of CMA and propylene in the absence of Pd/C catalyst in 1,4-dioxane. Given that the CMA conversion in 1,4-dioxane showed identical performance as compared to reactions performed in GVL (**Table S1**), it was safe to assume that the reaction in 1,4-dioxane followed the same Diels-Alder/decarboxylation/ dehydrogenation sequence. Thus, the synthesis of intermediates and by-products was performed in 1,4-dioxane to separate the solvent from the temperature sensitive intermediates and to analyzed the products via NMR (**Table S2**).

Table S1. Comparison of CMA conversion to TA in different aprotic polar solvents

Entry	Solvent	Temp	Time	CMA Conversion [mol-%]	*p*-TA Yield [mol-%]	*m*-TA Yield [mol-%]
1	1,4-dioxane	180	8	99.5 ± 0.6	70.8 ± 3.4	15.8 ± 0.3
2	GVL	180	8	99.5 ± 5.4	71.9 ± 1.1	16.3 ± 0.8

Conditions: Solvent: 30 ml; CMA (600 mg); Stirring rate: (400 rpm); Propylene pressure at room temperature: (130 psig); Catalyst: 100 mg 10 wt.-% Pd/C

Table S2. Structural NMR experiments to identify intermediates and side-products

Entry	Solvent	Catalyst	T [°C]	t [hrs]	Analysis
1	1,4-dioxane	none	140	2	^{1}H-NMR, HSQC, COSY
2	1,4-dioxane	none	180	8	^{1}H-NMR, HSQC, COSY

Conditions: CMA concentration in 1,4-dioxane: 20 mg/ml; catalyst: none; Stirring rate: 400 rpm; Pressure at room temperature: 130 psig propylene; Reaction time: 8 hrs; Temperature: 180 °C

Bicyclic lactone intermediates **2a** (endo/exo) and **2b** (endo/exo) were synthesized at 140 °C for 2 hrs reaction time. A reaction preformed at 180 °C and 8 hrs reaction time on the other hand gave access to cyclohexa-1,5-diene intermediates **3a** and **3b** and Diels-Alder by-products (**4a, 4b, 5a, 5b**) from the cycloaddition of **3a** and **3b** with propylene. NMR analysis of the reaction products, obtained from a 140 °C and 2 hrs reaction, confirmed that a significant amount of the starting material CMA was converted to the bicyclic lactone intermediates **2a** (endo/exo) and **2b** (endo/exo), diene intermediates **3a** and **3b** and toluic acid **7a** and **7b** (**Table 2**). The reaction products obtained after an 8 hr reaction at 180 °C revealed the formation of cyclohexadiene intermediates (**3a, 3b**), and Diels-Alder by-products (**4a, 4b, 5a, 5b**) as the major compounds with small amounts of toluic acid (**7a**, **7b**) (**Table 2**). The assignment of the by-products **4a, 4b, 5a,** and **5b** was further supported by UPLC-QDa and GC-MS analysis (**Table S3 and S4**). These by-products were shown to be stable under reaction conditions in the absence of propylene. After an 8 hr reaction at 180 °C, the peak area of the by-products **4a, 4b, 5a,** and **5b** was not significantly changed (**Table S5**), indicating that no retro Diels-Alder reaction was operative.

The structural assignment of **4a**, **4b**, **5a**, **5b** of the complex NMR spectra shown in **Figure S16** was not trivial as a result of overlapping peaks. Through UPLC-QDa, GC-MS analysis we identified four compounds with similar mass (m/z: 180.1). Additional NMR analysis revealed the formation of four isomers from Diels-Alder reaction of **3a** and **3b** with propylene (**Scheme S1**). Very indicative of the assignment of **4a**, **4b**, **5a**, **5b** were the four doublets of the allylic protons between 7.0 and 7.25 ppm without any correlation to other allylic protons in that region (**Figure S17**). Unlike the bicyclic lactone

intermediates **2a**/**2b** (**Figure S3**) that have allylic C-H protons that correlate to de-shielded C-H protons (5.5 ppm) as a result of neighboring oxygen atoms, the allylic C-H protons in **Figure S18**, correlate to more shielded C-H protons in the region of 2.2 to 3 suggesting the formation of **4a**, **4b**, **5a**, and **5b** shown in **Scheme S1**. Moreover, the integration of all protons (**a**) or (**b**) in **Scheme S1** are equal to one for each isomer in **Figure S16**. **Figure S16** further shows that a total of four protons of (**a**) and four protons of (**b**) matched with a total of 24 CH_3 protons, further supporting the assignment of these by-products.

Scheme S1. By-products from cycloaddition of cyclohexa-1,5-diene intermediates and propylene

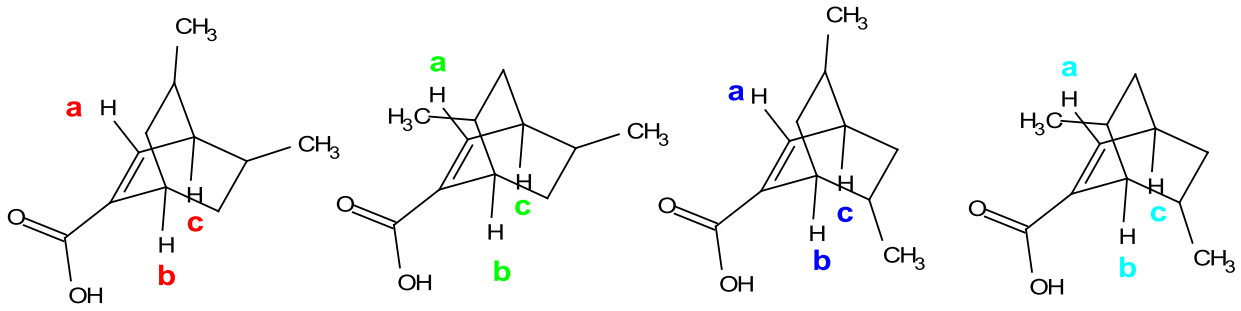

Table S3. GC-MS major ion fragments of the Diels-Alder reaction by-products of **3a**/**3b** with propylene

By-product peak	Retention time [min]	Major ion fragments [m/z]
1	35.22	180.1, 138.1, 123.1, 105.1, 93.1, 91.1, 79.1, 77.1
2	35.32	
3	35.80	
4	35.88	

Conditions: CMA concentration in 1,4-dioxane: 20 mg/ml; catalyst: none; Stirring rate: 400 rpm; Pressure at room temperature: 130 psig propylene; Reaction time: 8 hrs; Temperature: 180 °C.

Table S4. Major ion fragments of the Diels-Alder by-products of **3a**/**3b** with propylene from UPLC-QDa analysis

Peak	Retention time [min]	Peak area [µV*sec]	Major ion fragment [m/z]
1	13.96	15999626	180.1
2	14.27		

Conditions: CMA concentration in 1,4-dioxane: 20 mg/ml; catalyst: none; Stirring rate: 400 rpm; Pressure at room temperature: 130 psig propylene; Reaction time: 8 hrs; Temperature: 180 °C

Table S5. Major ion fragments of the Diels-Alder by-products **4a**, **4b, 5a,** and **5b** from UPLC-QDa analysis after retro Diels-Alder reaction in the absence of propylene

Peak	Retention time [min]	Peak area [µV*sec]	Major ion fragment [m/z]
1	13.96	15394927	180.1
2	14.27		

Conditions: CMA concentration in 1,4-dioxane: 20 mg/ml; catalyst: none; Stirring rate: 400 rpm; Pressure at room temperature: 130 psig N_2; Reaction time: 8 hrs; Temperature: 180 °C

Figure S1. ^{1}H-NMR structural assignment of the bicyclic intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

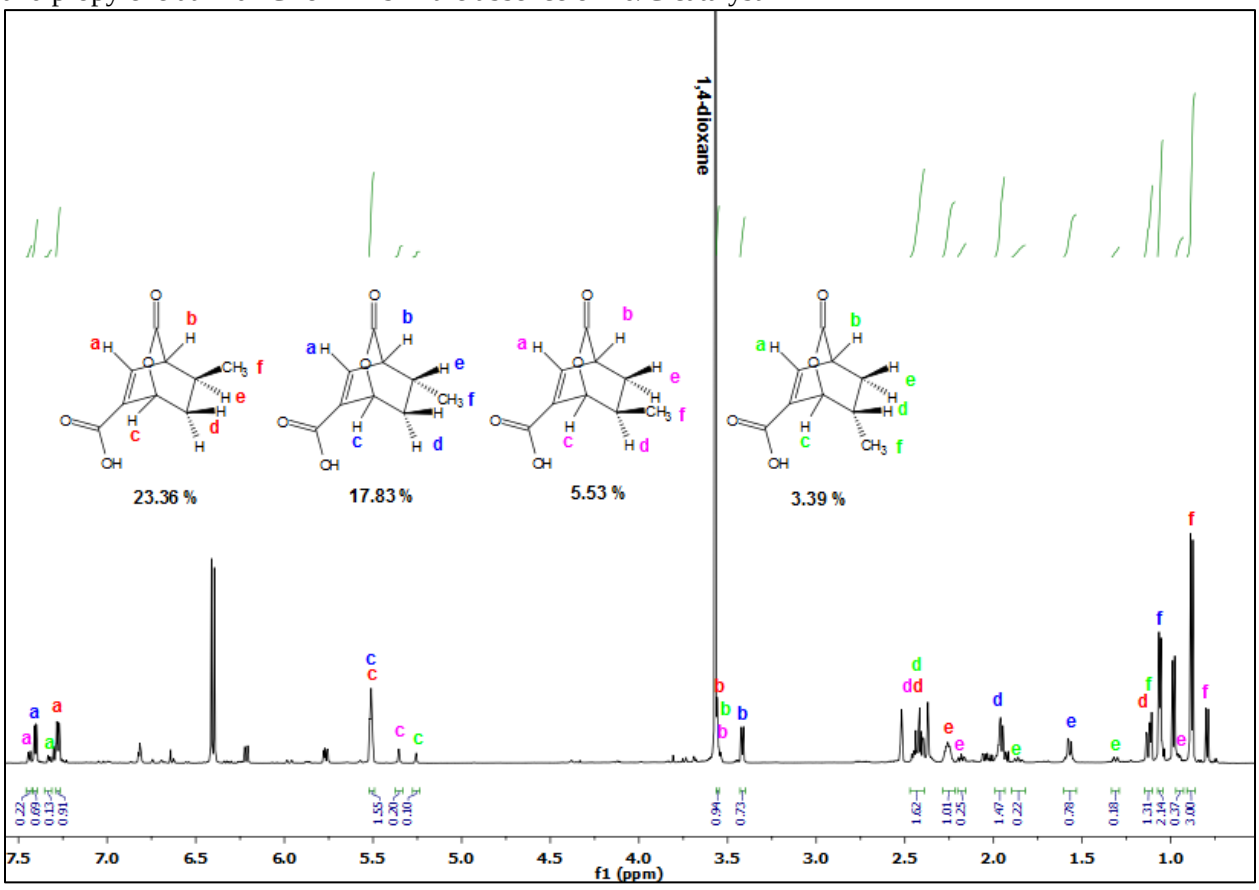

Figure S2. ^{1}H-^{1}H COSY structural assignment of the bicyclic intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

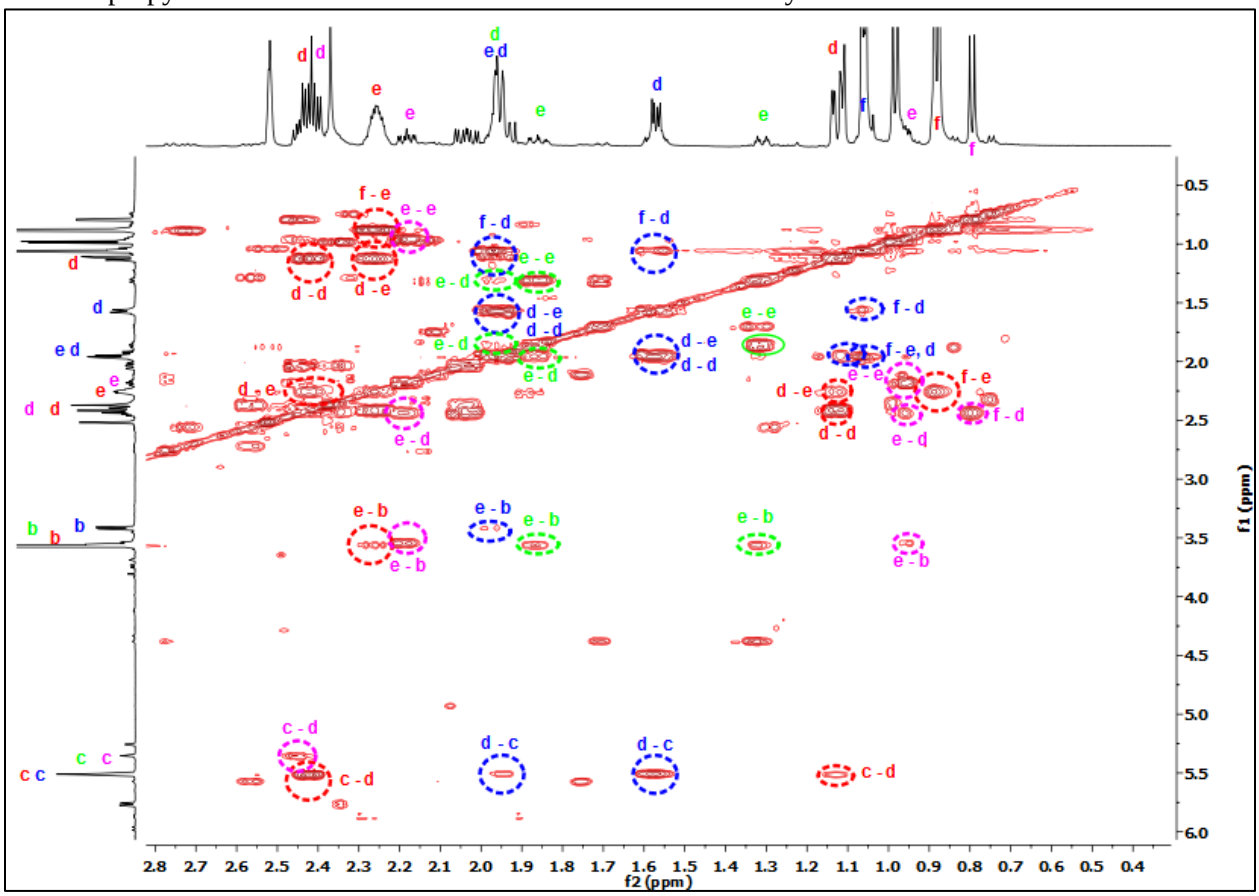

Figure S3. ^{1}H-^{1}H COSY structural assignment of the bicyclic intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

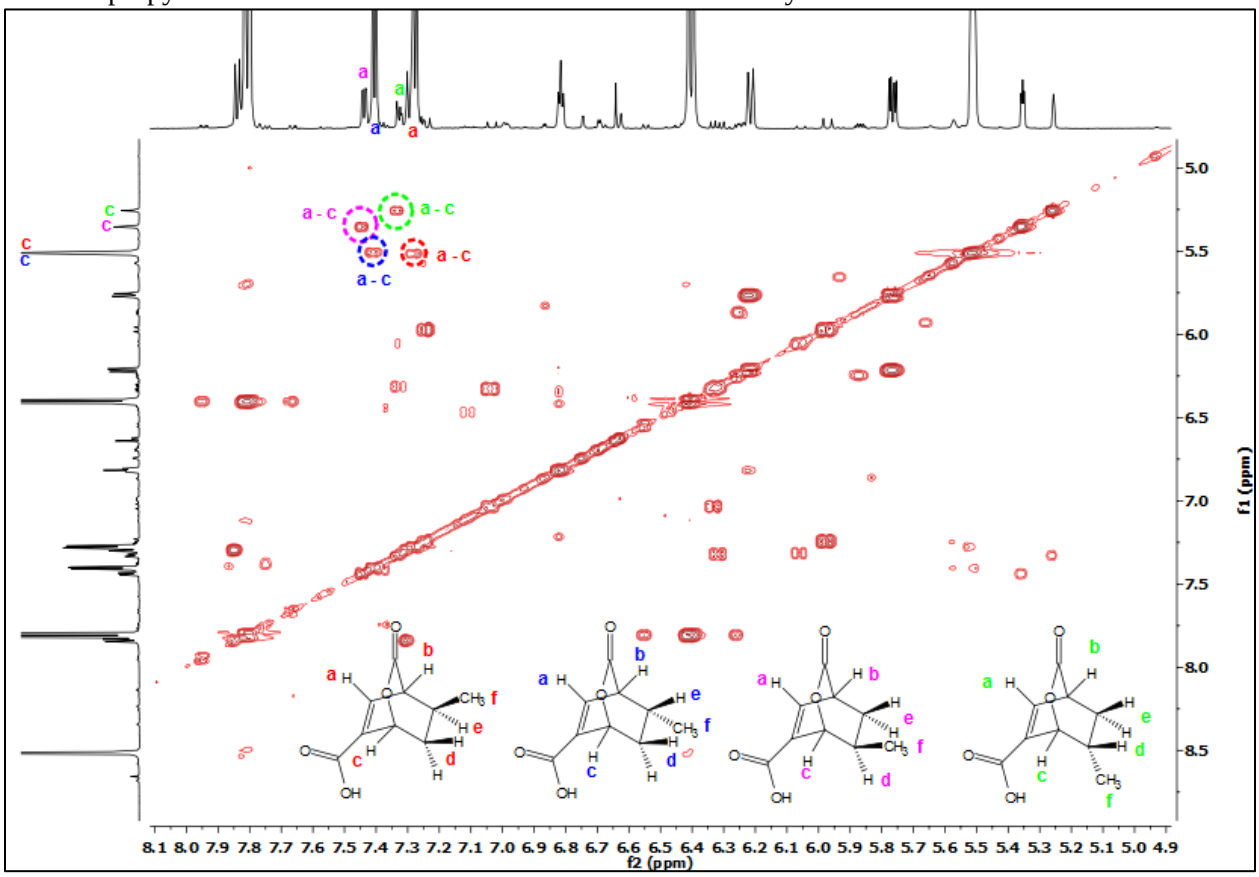

Figure S4. ^{1}H-^{1}H COSY structural assignment of the bicyclic intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

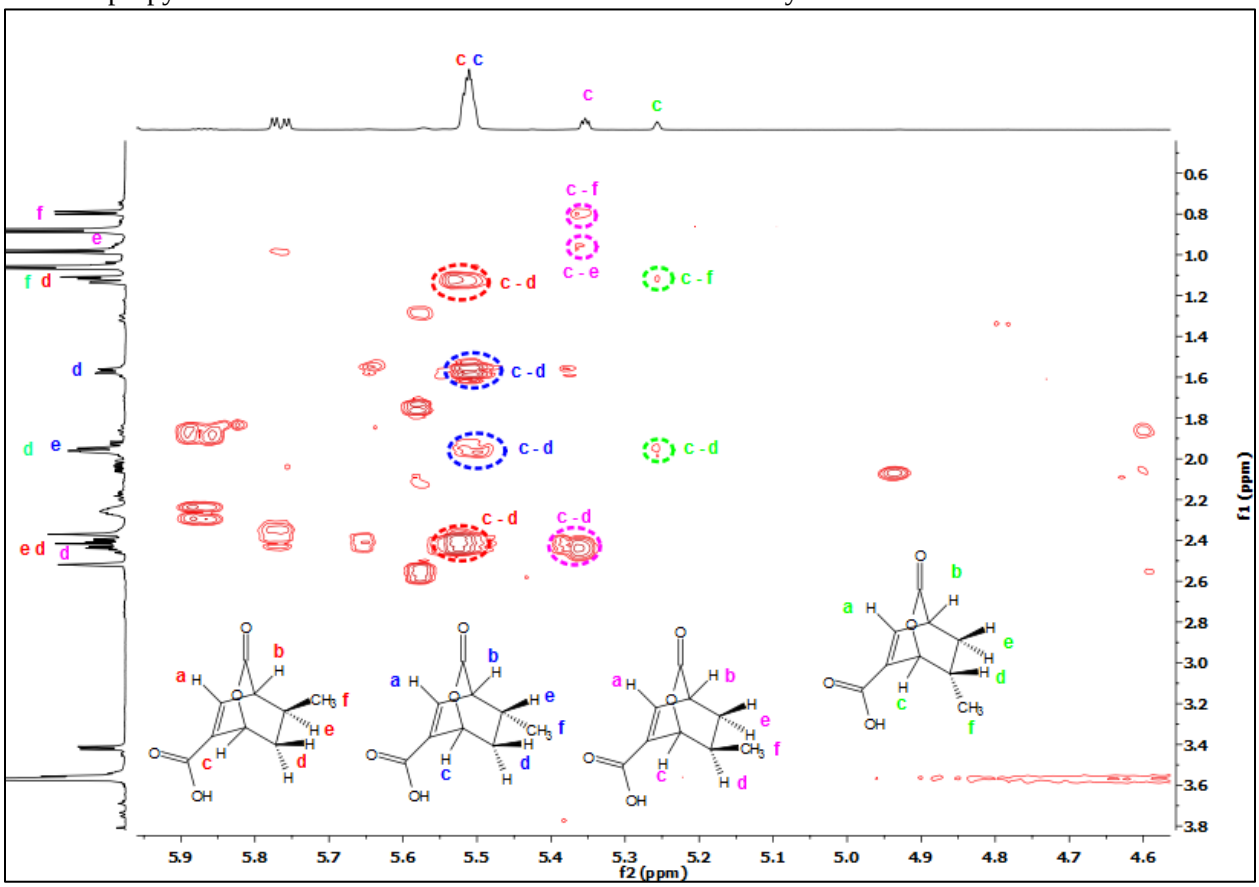

Figure S5. ^{1}H-^{1}H COSY structural assignment of the bicyclic intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

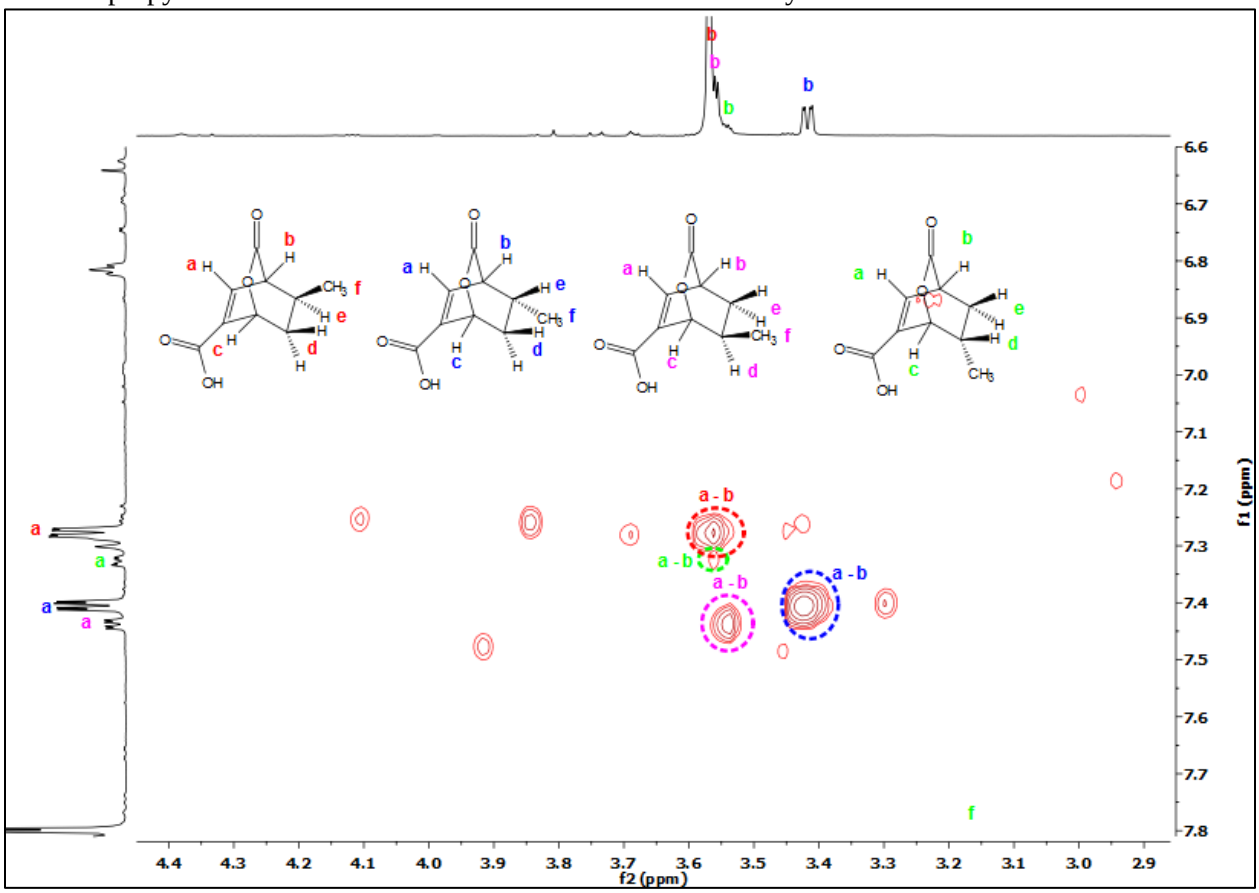

Figure S6. ^{13}C-^{1}H-HSQC structural assignment of coumalic acid, bicyclic lactone intermediates after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

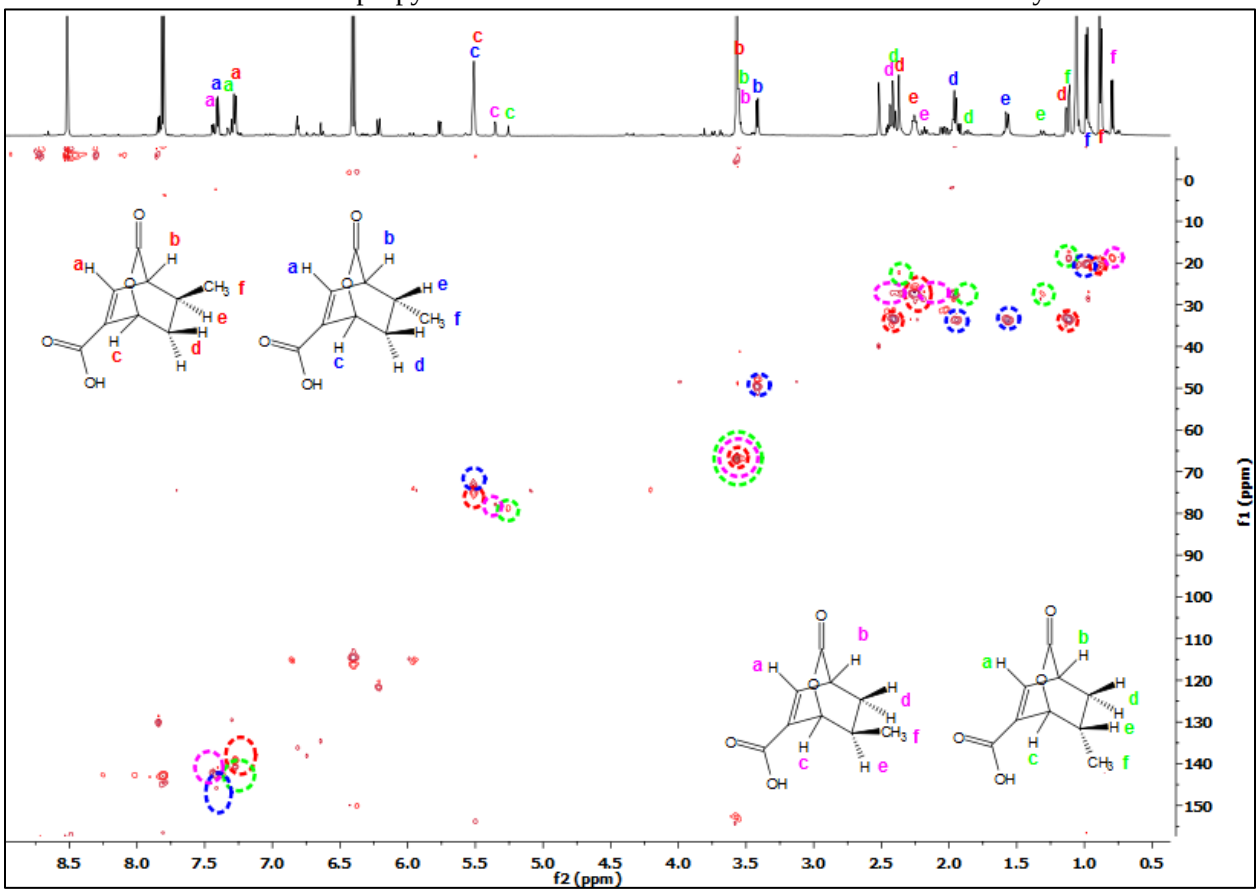

Figure S7. [1]H-NMR structural assignment of coumalic acid, m-/p-diene intermediates and p-toluic acid after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

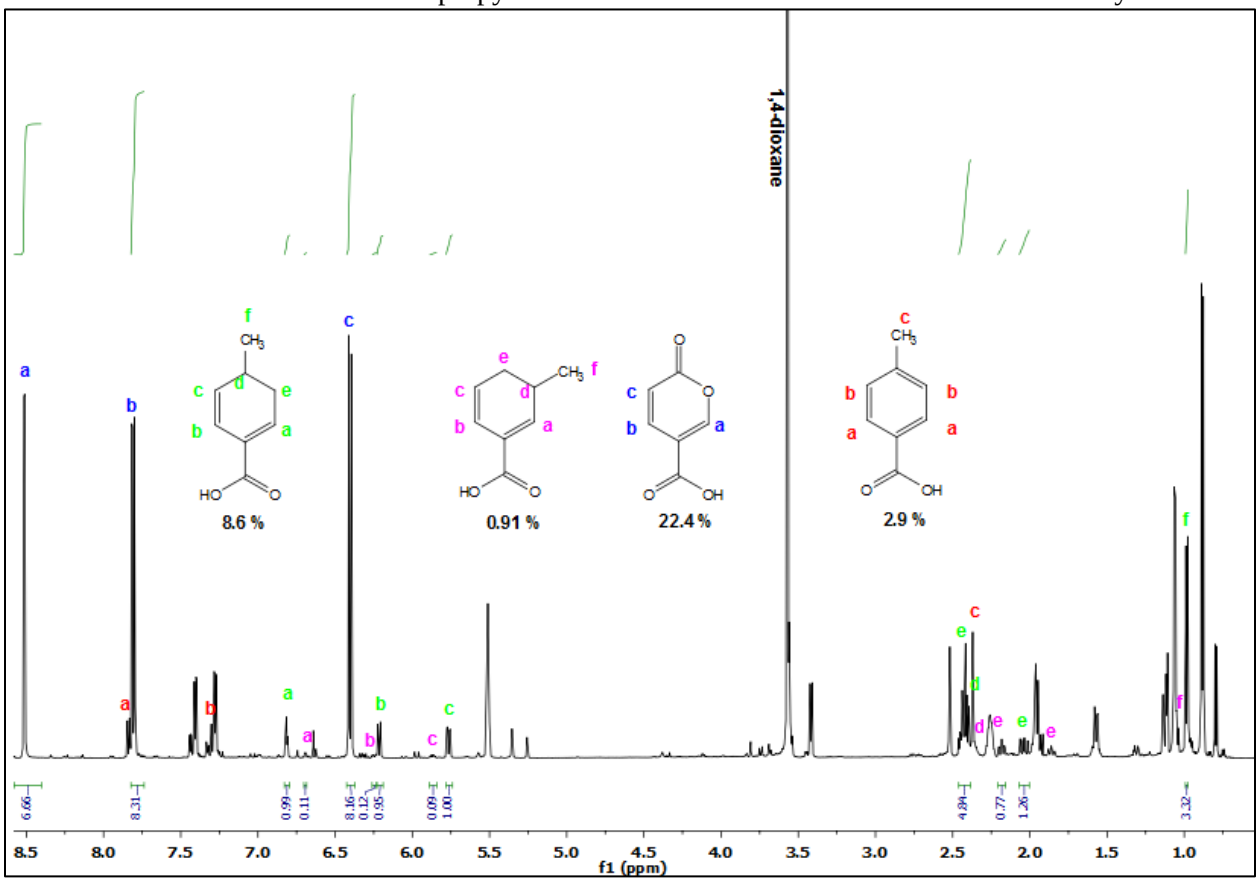

Figure S8. ^{1}H-^{1}H COSY structural assignment of coumalic acid, m-/p-diene intermediates and p-toluic acid after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

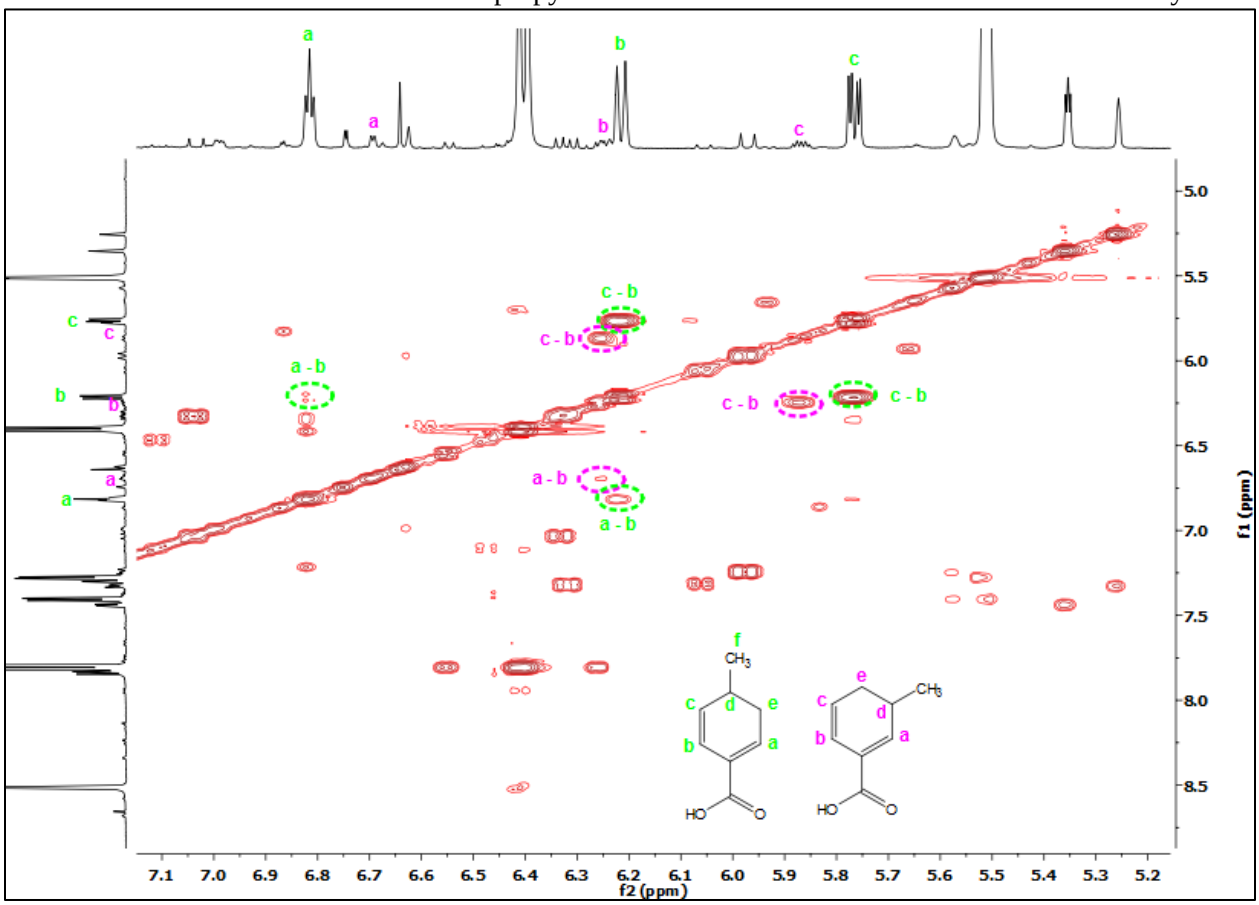

Figure S9. ^{1}H-^{1}H COSY structural assignment of coumalic acid, m-/p-diene intermediates and p-toluic acid after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

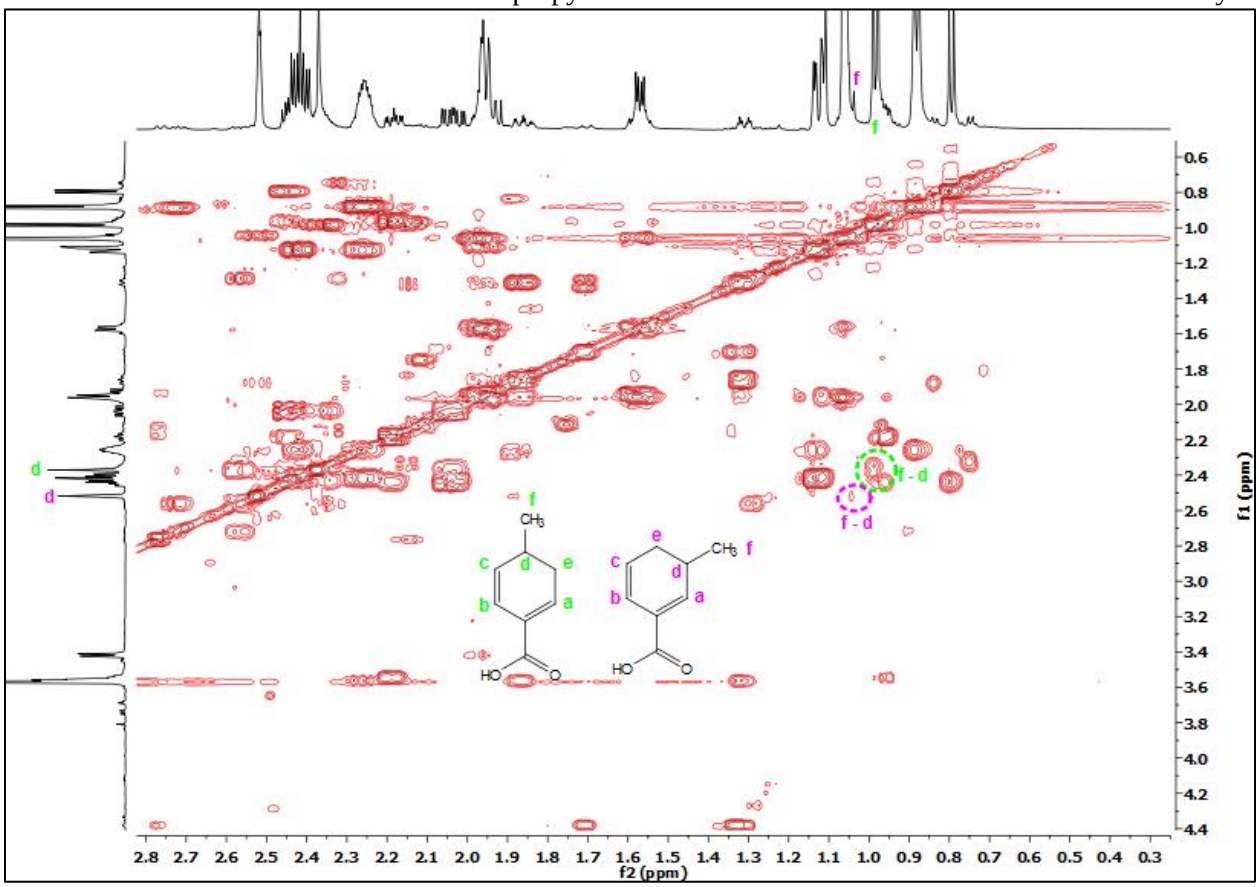

Figure S10. ^{1}H-^{1}H COSY structural assignment of coumalic acid, m-/p-diene intermediates and p-toluic acid after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

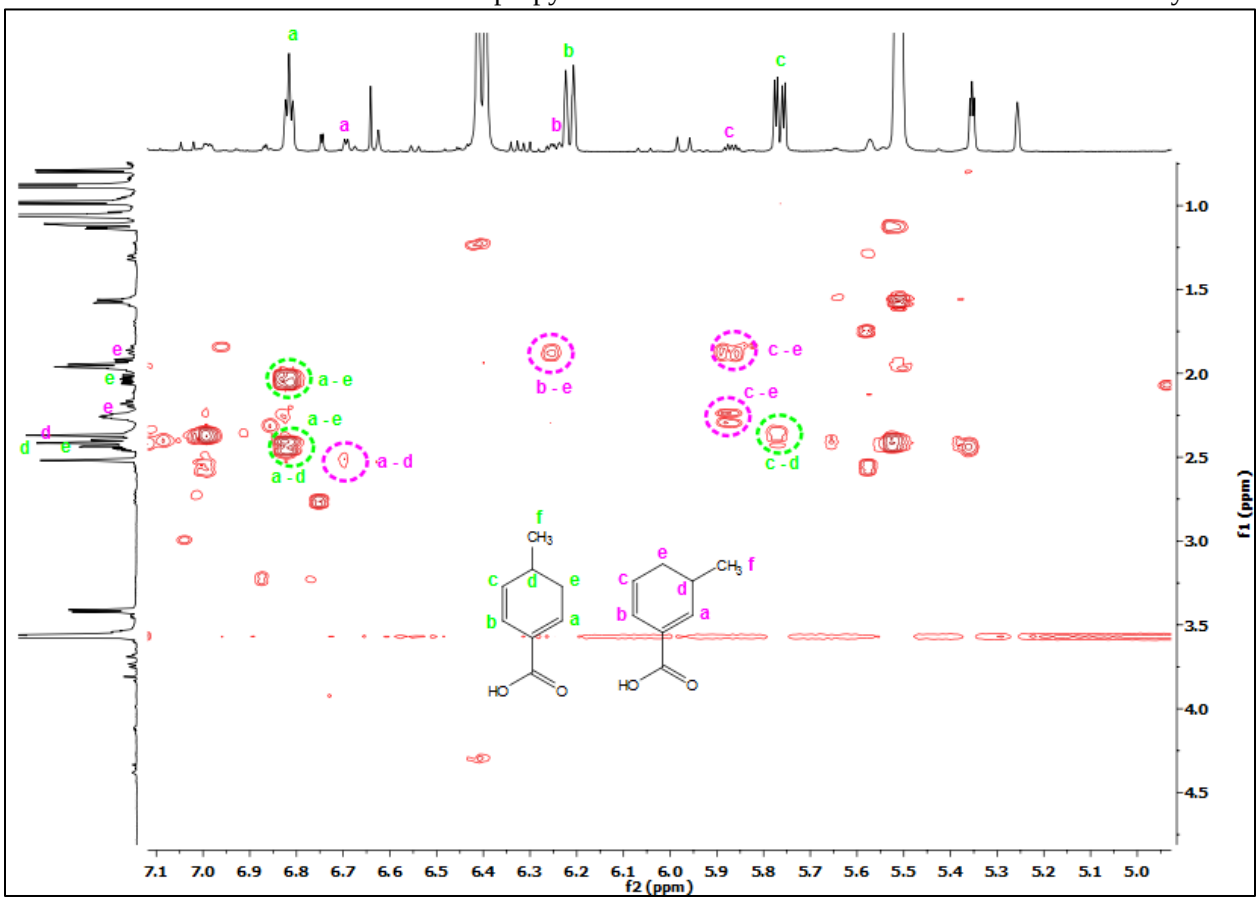

Figure S11. ^{1}H-NMR structural assignment of p/m--toluic acid after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

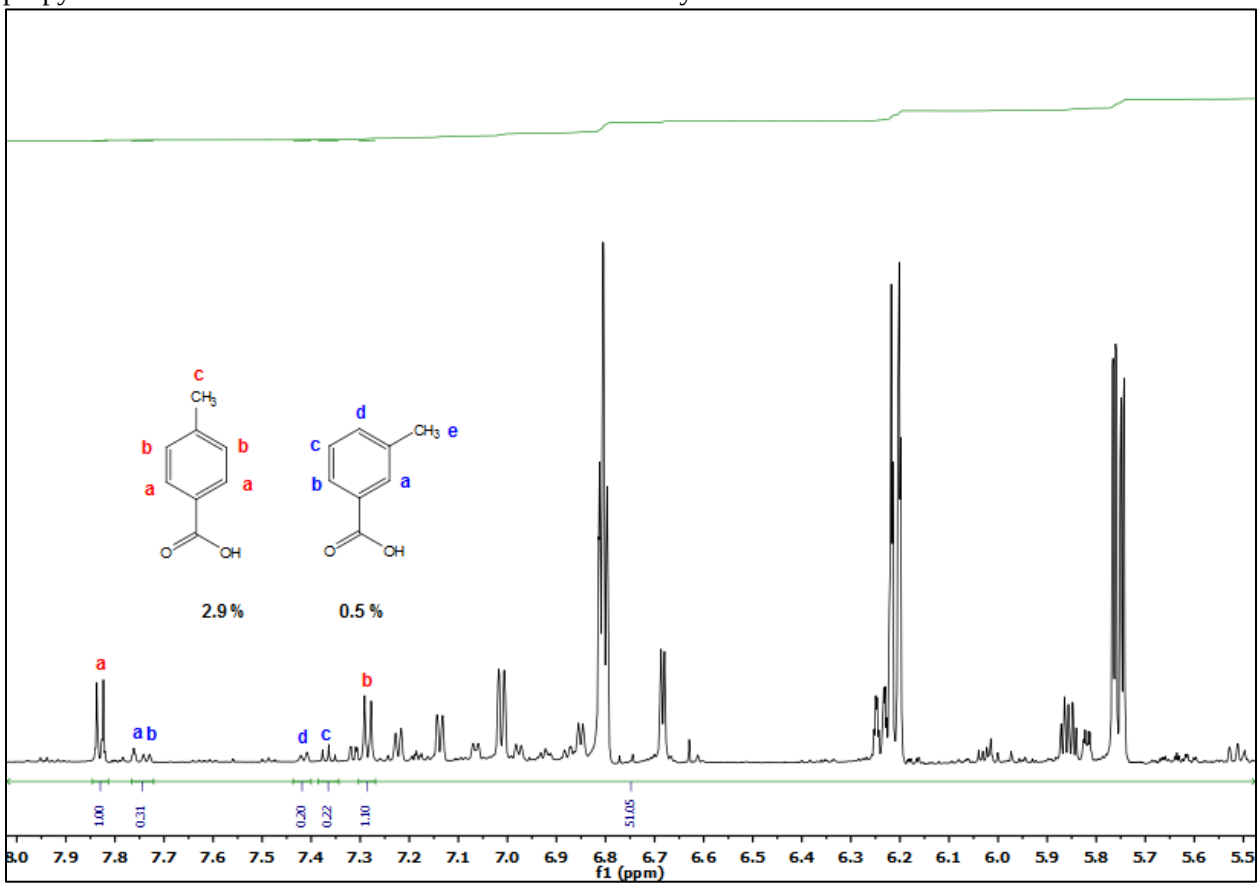

Figure S12. ^{13}C-^{1}H-HSQC structural assignment of coumalic acid, m-/p-diene intermediates and p-toluic acid after a reaction of coumalic acid and propylene at 140 °C for 2 hrs in the absence of Pd/C catalyst

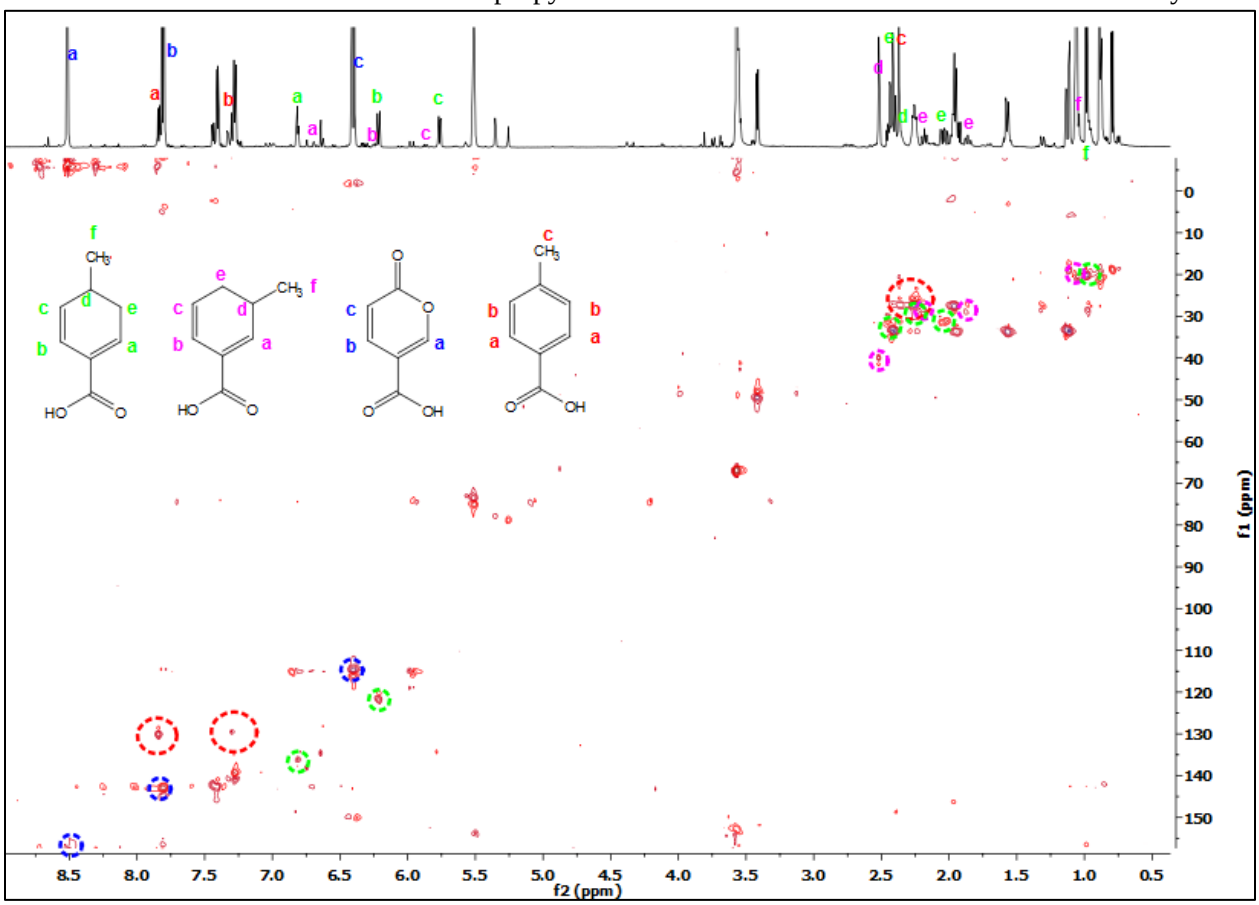

Figure S13. [1]H-NMR structural assignment of diene intermediates after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

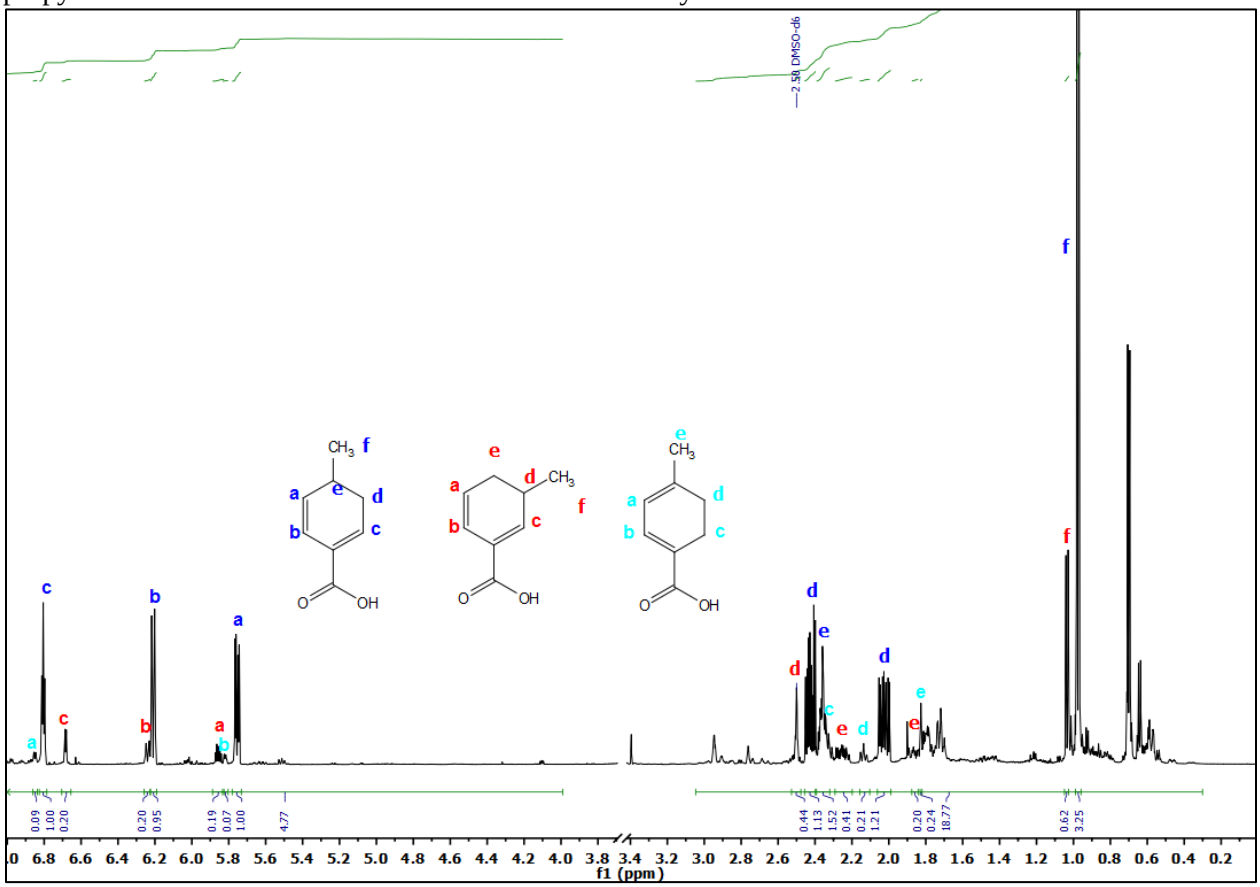

Figure S14. ^{1}H-^{1}H COSY structural assignment of diene intermediates after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

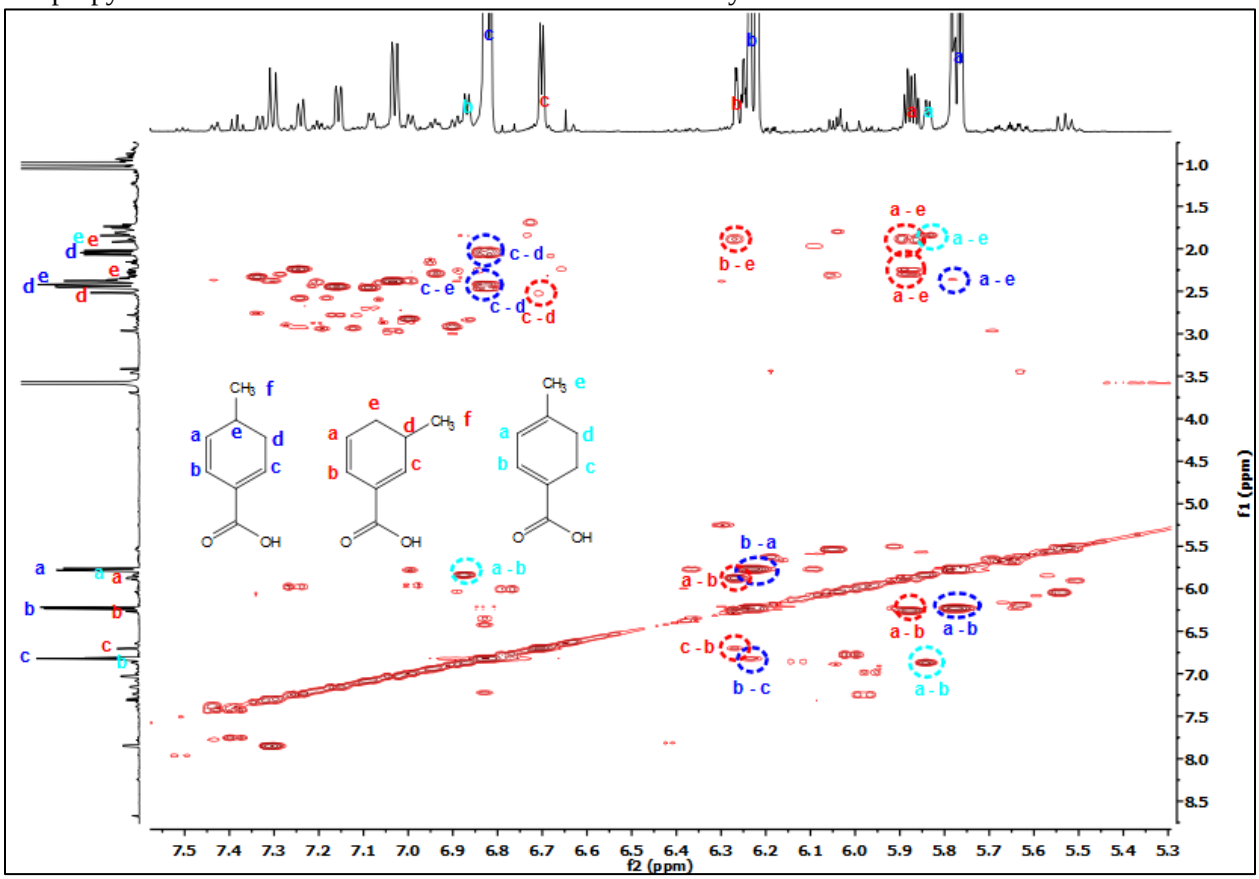

Figure S15. ^{1}H-^{1}H COSY structural assignment of diene intermediates after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

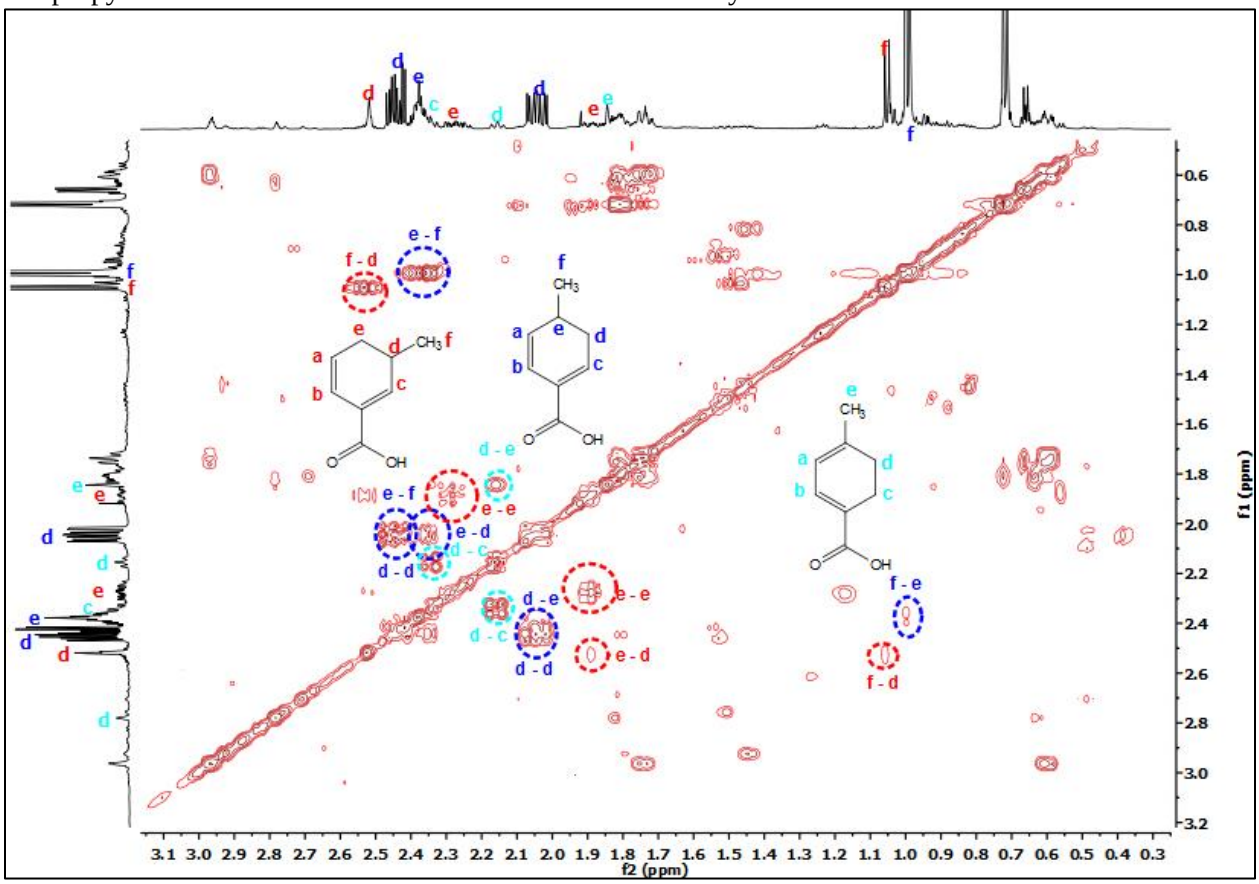

Figure S16. [1]H NMR structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

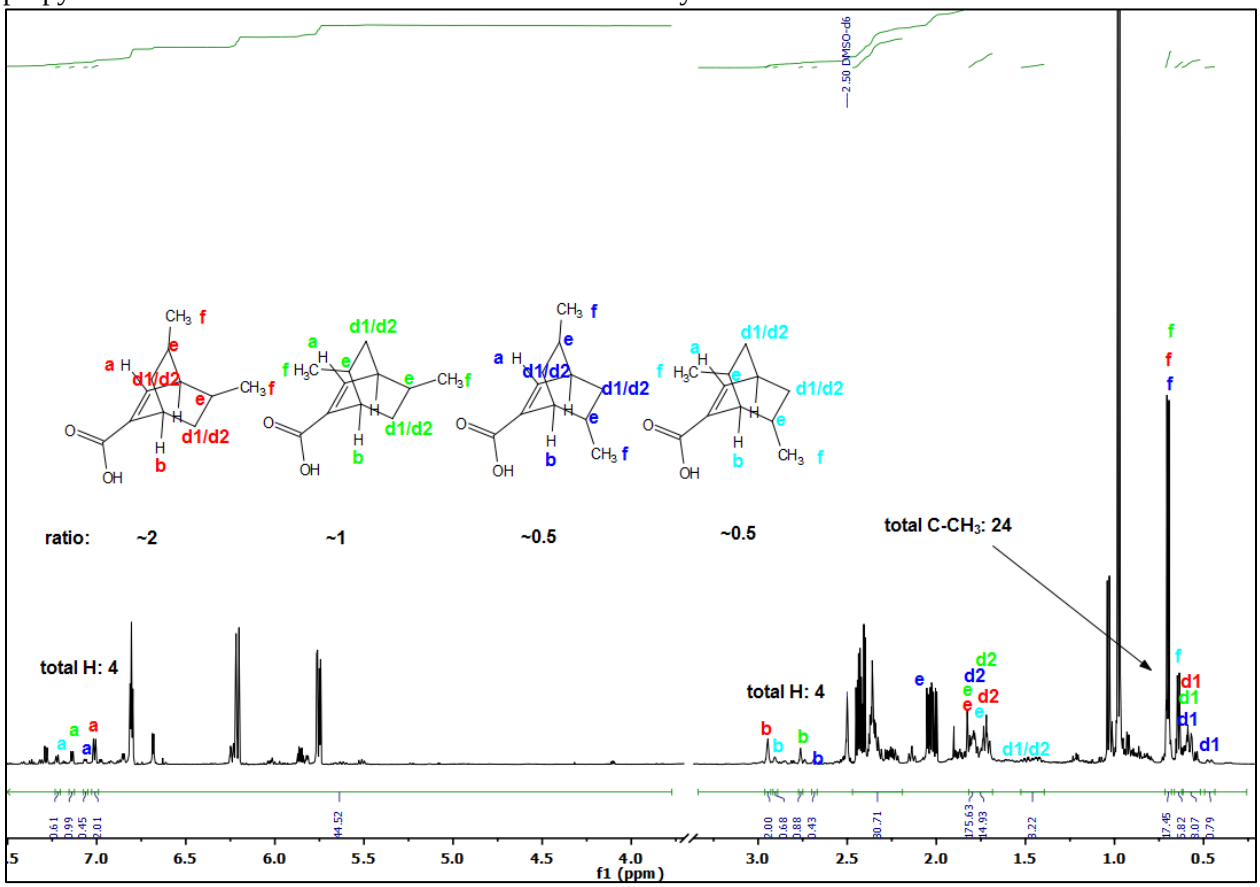

Figure S17. ^{1}H-^{1}H COSY structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

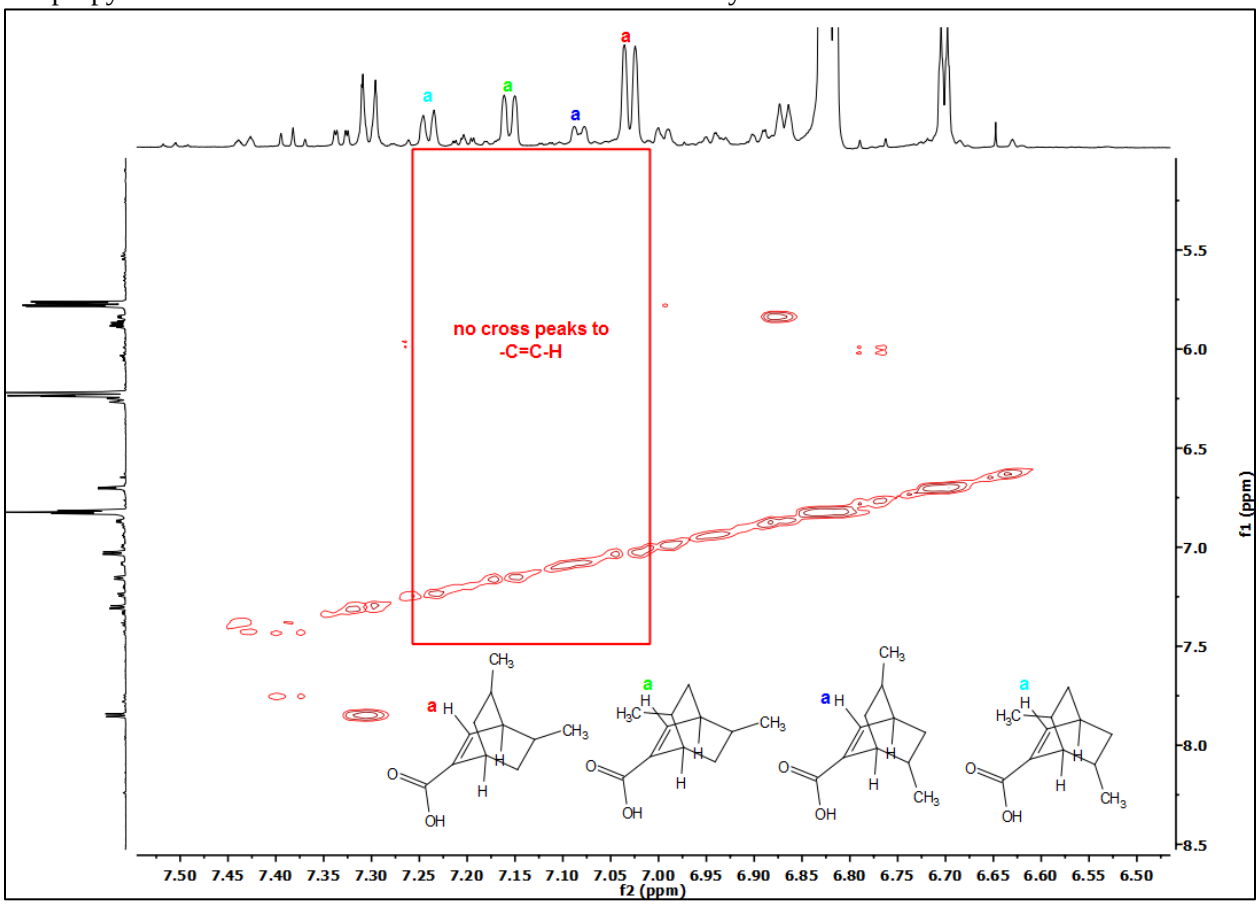

Figure S18. ^{1}H-^{1}H COSY structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

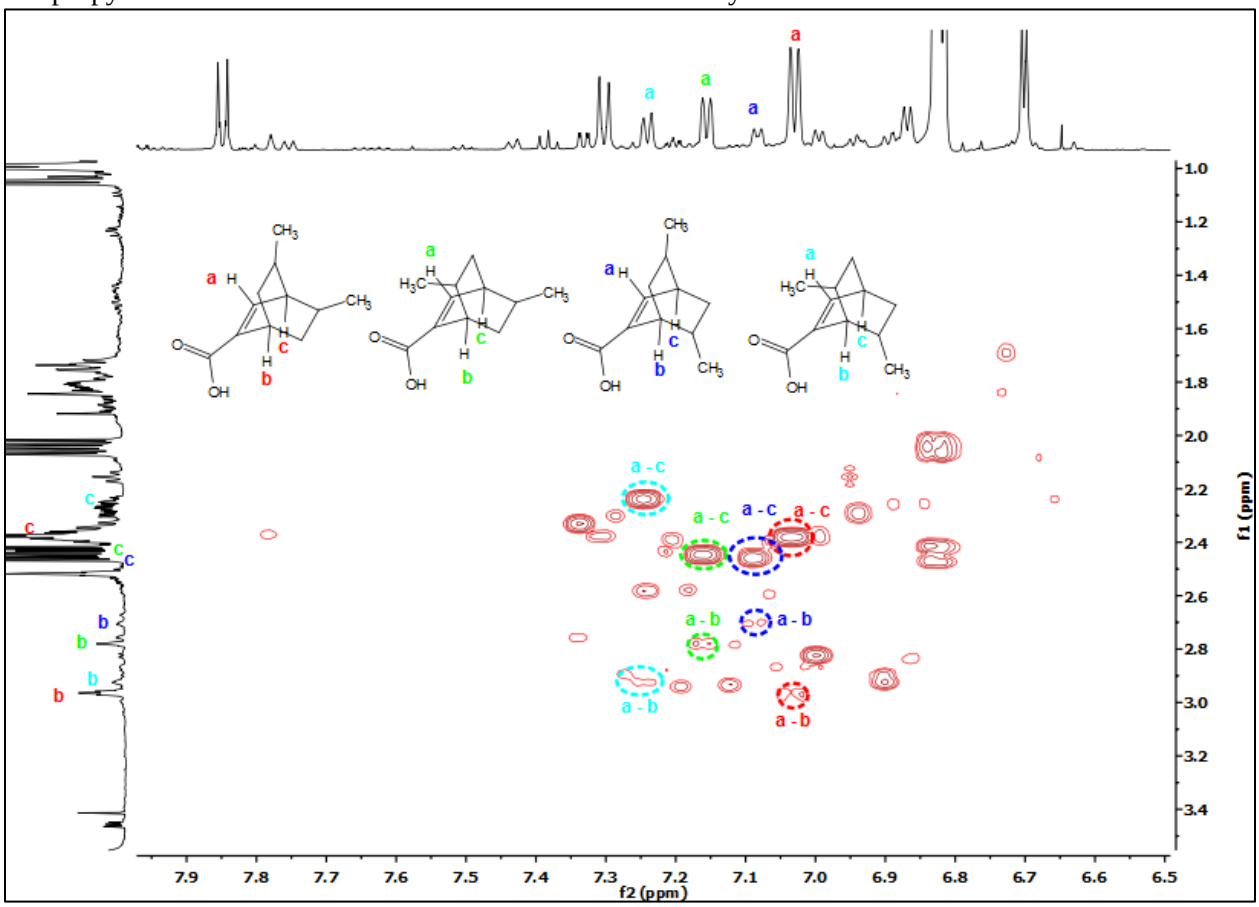

Figure S19. ^{1}H-^{1}H COSY structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

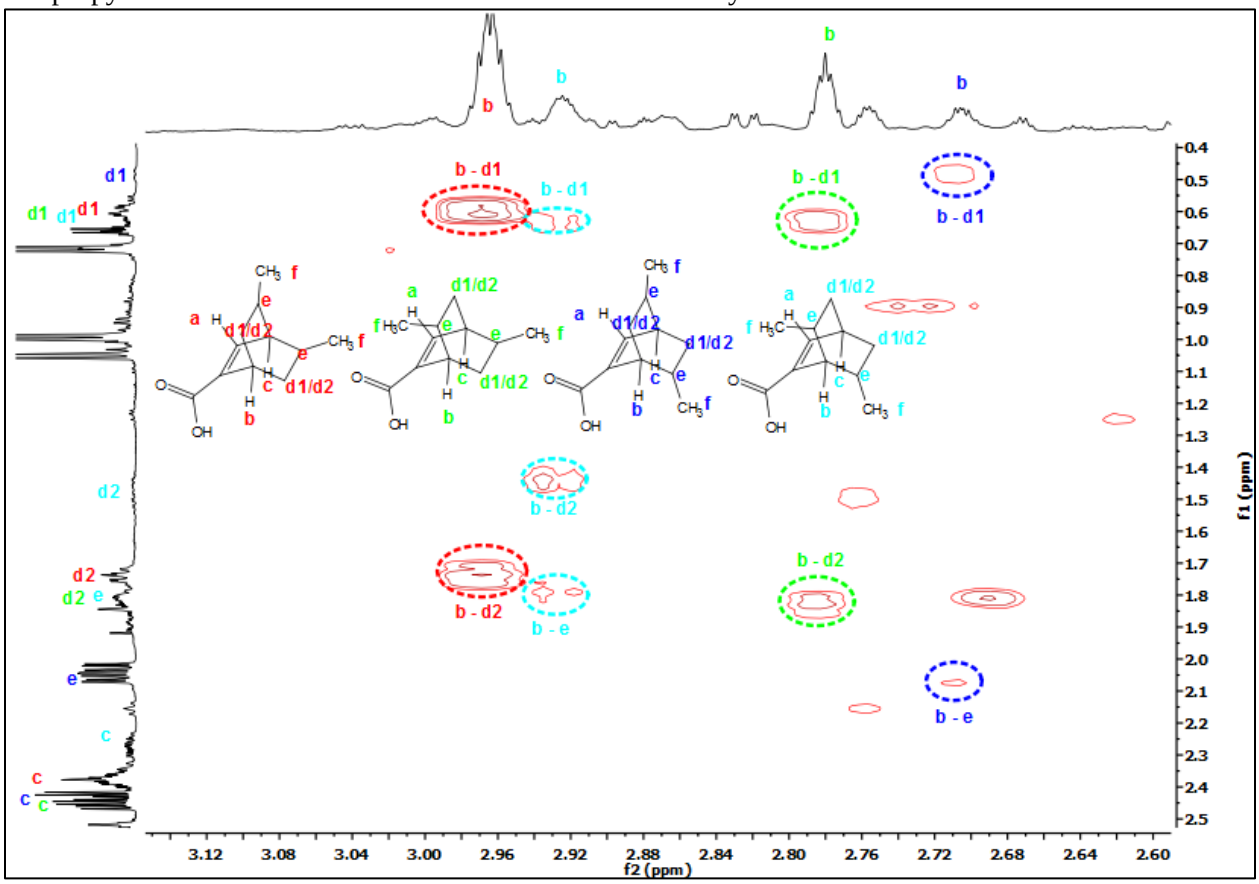

Figure S20. ^{1}H-^{1}H COSY structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

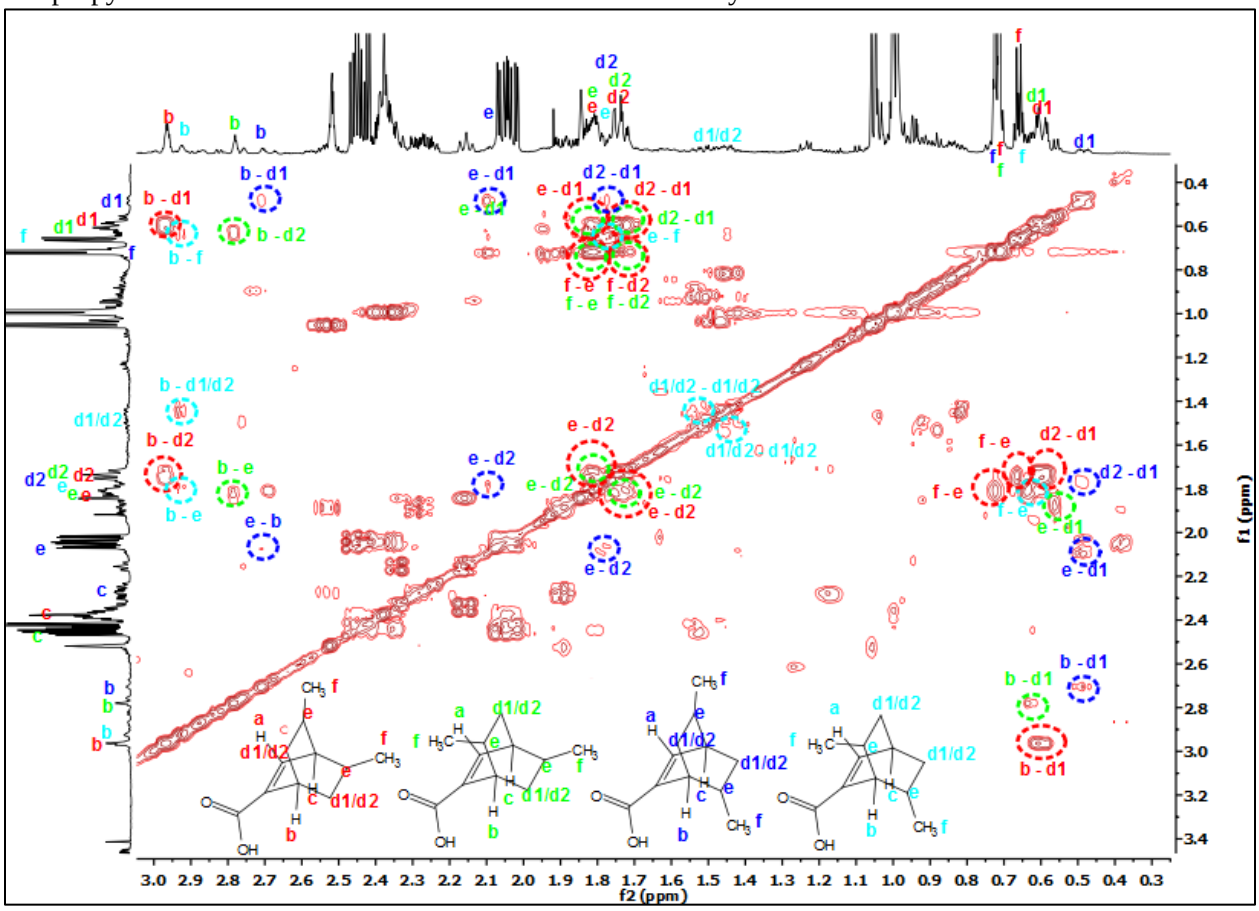

Figure S21. ^{13}C-^{1}H HSQC structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst

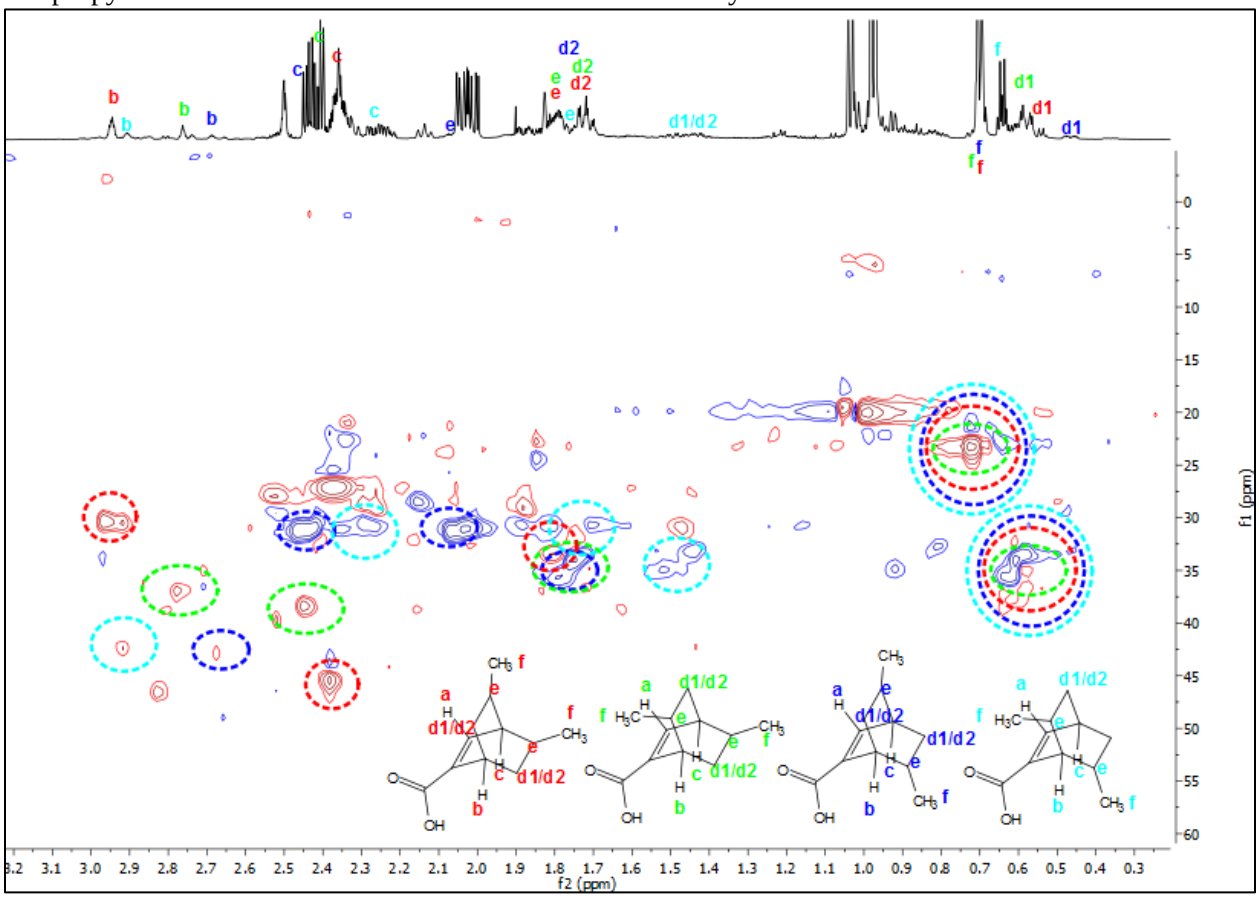

Figure S22. ^{13}C-^{1}H HSQC structural assignment of DDA by-products after a reaction of coumalic acid and propylene at 180 °C for 8 hrs in the absence of Pd/C catalyst