

Supplementary Information

A new selective route towards benzoic acid and derivatives from biomass-derived coumalic acid

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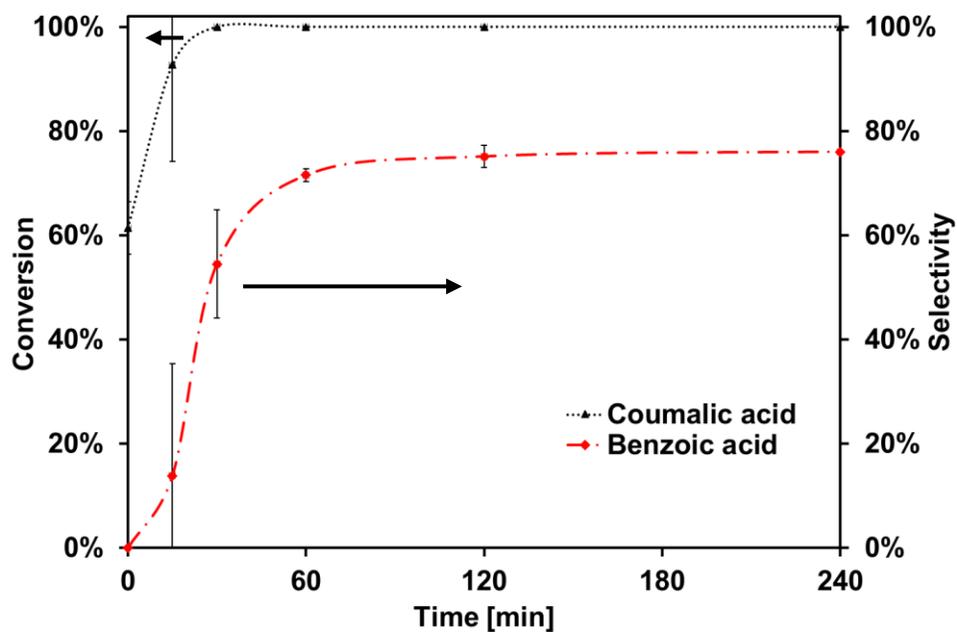


Figure S1. The conversion of coumalic acid to benzoic acid at 180 °C using 10 wt.-% Pd/C and the solvent GVL.

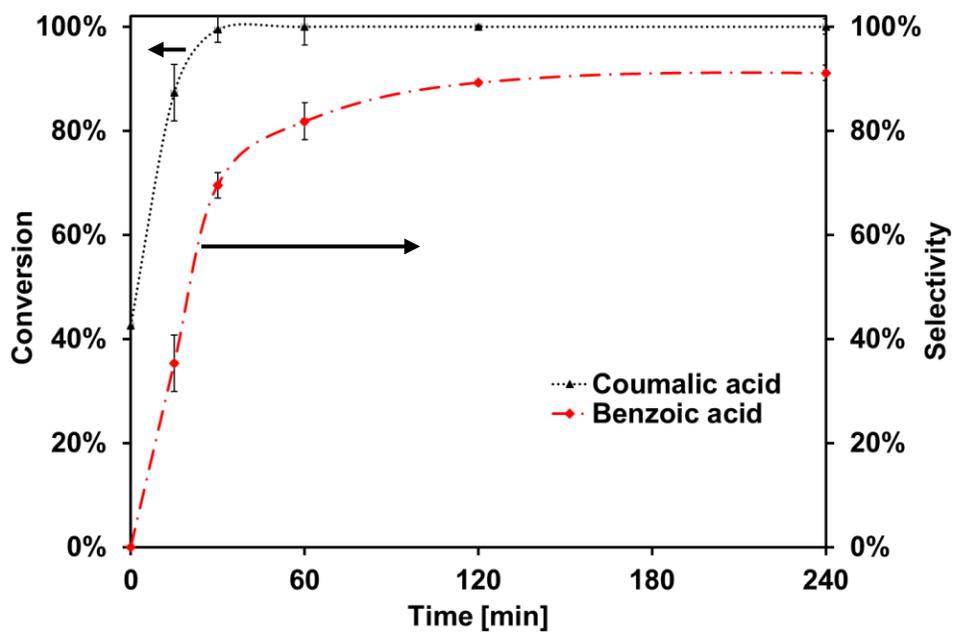


Figure S2. The conversion of coumalic acid to benzoic acid at 180 °C using 10 wt.-% Pd/C and the solvent 1,4-dioxane.

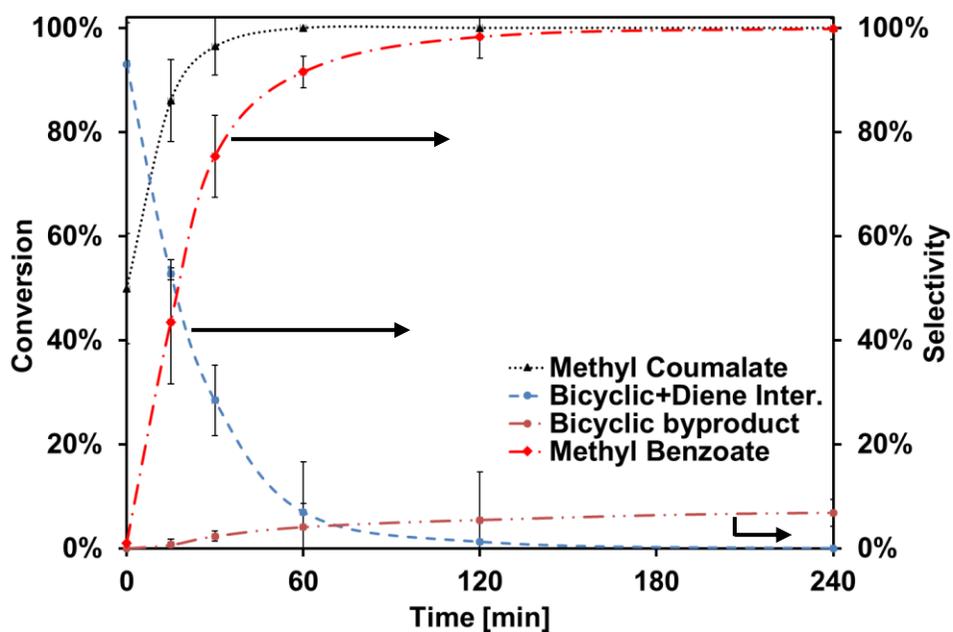


Figure S3. The conversion of methyl coumalate to methyl benzoate at 180 °C using 10 wt.-% Pd/C and the solvent toluene.

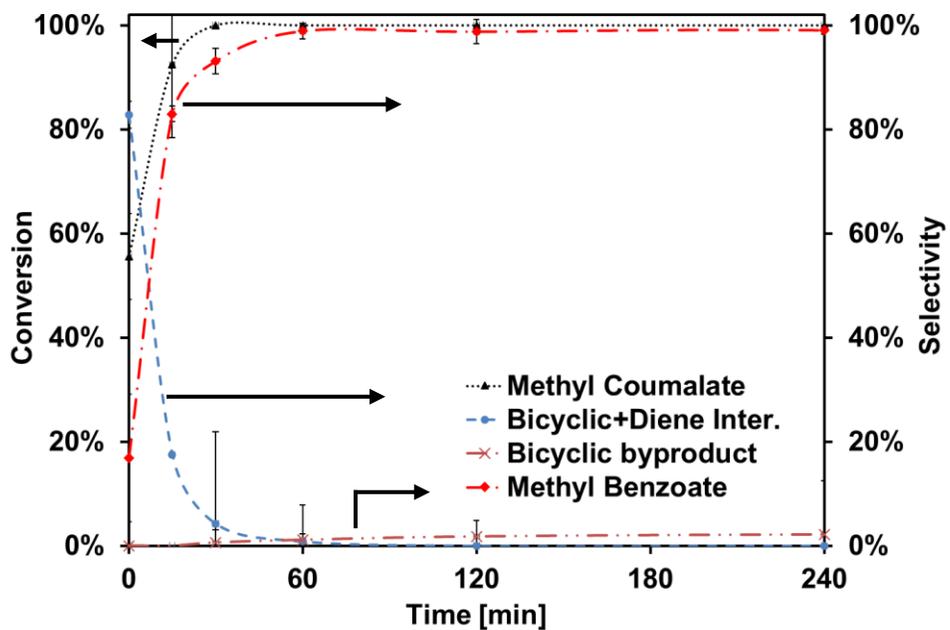


Figure S4. The conversion of methyl coumalate to methyl benzoate at 180 °C using 10 wt.-% Pd/C and the solvent GVL.

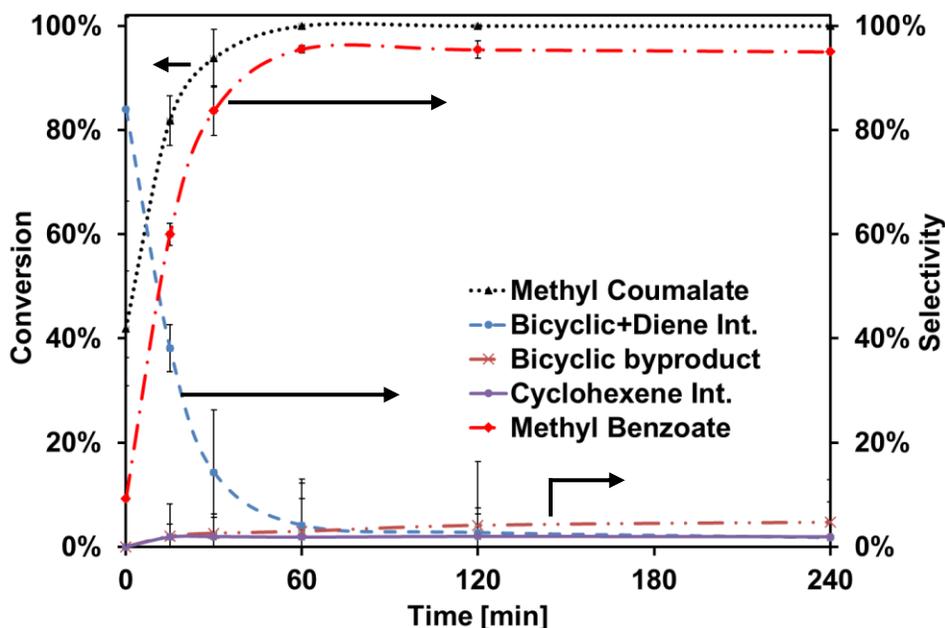


Figure S5. The conversion of methyl coumalate to methyl benzoate at 180 °C using 10 wt.-% Pd/C and the solvent 1,4-dioxane.

Structural assignment of intermediates and by-products

The structural assignment of intermediates, products and by-products were identified via 2D-NMR experiments of the reaction products obtained from a 48 h reaction of MeCMA and ethylene in benzene-d₆ (Figure S1). Fully deuterated benzene-d₆ was used due to its cheapness (compared to dioxane-d₈) and as a result of identical findings when compared to dioxane-d₈. We identified the bicyclic lactone intermediate and cyclohexa-1,5-diene intermediate as well as the double Diels-Alder by-product from cycloaddition of the diene intermediate and ethylene (Figure S1-11). Additionally, GC-MS and UPLC-QDa analysis provided the mass of the identified compounds. The toluene peak in Figure S1-S11 was the result of residual toluene (solvent used to mediate reactions) in the reactor head space and can thus, be neglected.

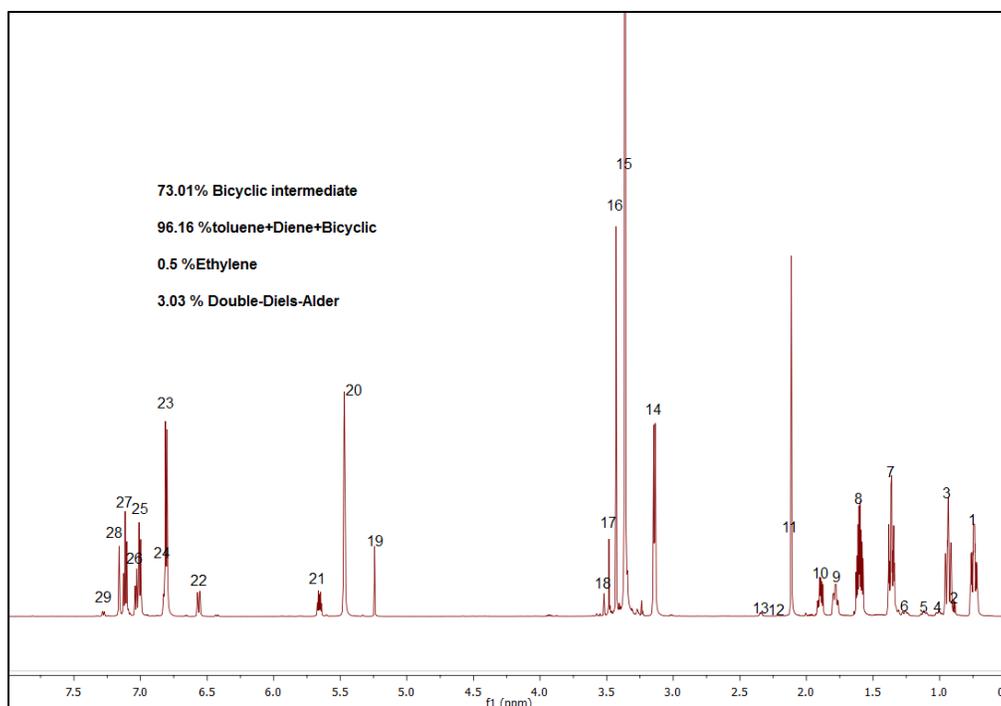


Figure S6. $^1\text{H-NMR}$ of the reaction of MeCMA and ethylene at 90 °C for 48 hrs (600 MHz, benzene- d_6).

Methyl -3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate intermediate (DAP): $^1\text{H NMR}$ (600 MHz, Benzene- d_6) δ 6.81 (dd, $J = 6.5, 2.3$ Hz, 1H), 5.47 (dt, $J = 4.0, 1.9$ Hz, 1H), 3.36 (s, 3H), 1.66 – 1.55 (m, 1H), 1.40 – 1.31 (m, 1H), 0.98 – 0.87 (m, 1H), 0.80 – 0.69 (m, 1H), m/z : 180.1.

Table S1. Tabulated NMR assignment of methyl -3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate intermediate (DAP).

^1H -label	δ ^1H , ppm, (mult)	δ ^{13}C	^1H Int.	^1H - ^1H -COSY	rel. mol-%
1	0.74 (m)	19.24	1.00	1-3, 1-7, 1-8, 1-14	73.01
3	0.94 (m)	24.82	1.04	3-1, 3-7, 3-8, 3-20	
7	1.36 (m)	19.08	1.06	7-1, 7-3, 7-8, 7-14	
8	1.60 (m)	24.33	1.03	8-1, 8-3, 8-7, 8-20	
15	3.36 (m)	51.49	2.99	-	
20	5.47 (s)	73.08	0.94	20-2, 20-8, 20-2	
23	6.81 (dd)	140.86	1.08	23-14, 23-20	

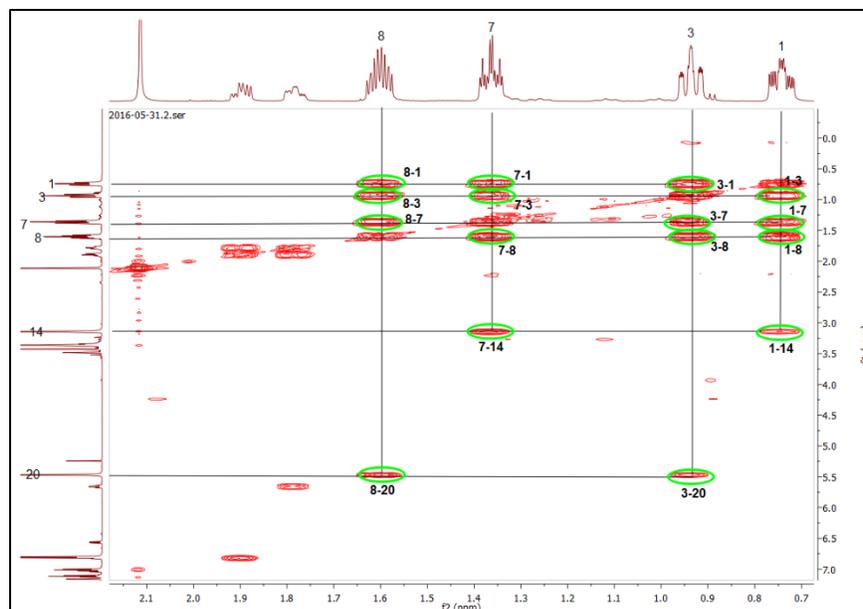


Figure S7. ^1H - ^1H - COSY of the methyl -3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

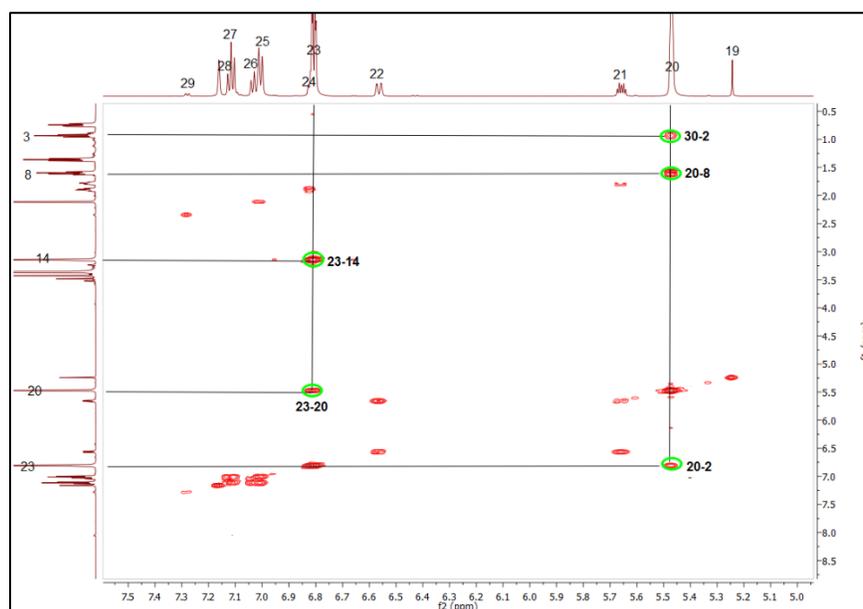


Figure S8. ^1H - ^1H - COSY of the methyl -3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

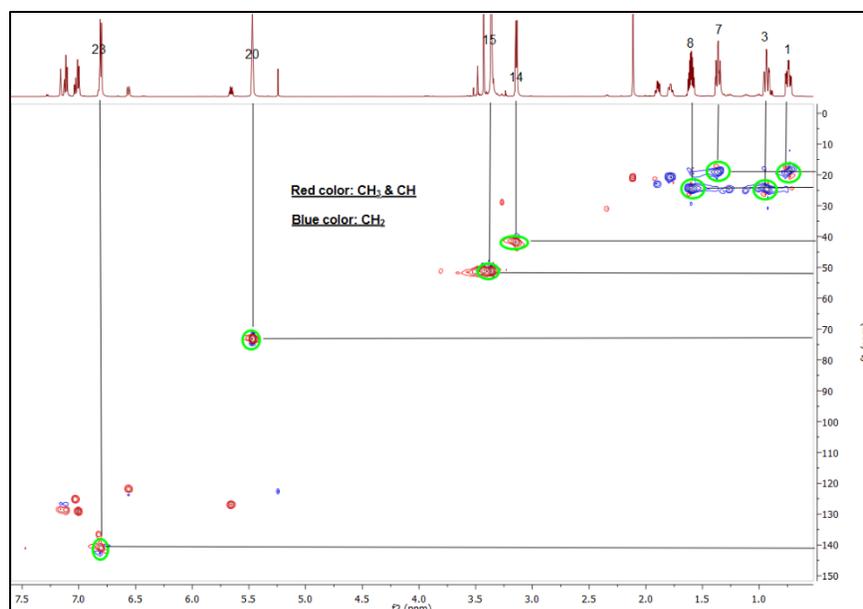


Figure S9. ^{13}C - ^1H - HSQC of the methyl -3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

Methyl cyclohexa-1,5-diene carboxylate (Diene): ^1H NMR (600 MHz, Benzene- d_6) δ 6.56 (dq, $J = 9.9, 1.9$ Hz, 1H), 5.68 – 5.64 (m, 1H), 8.45 – 0.52 (m, 102H), 3.43 (s, 3H), 1.93 – 1.86 (m, 2H), 1.81 – 1.75 (m, 2H), m/z : 138.1.

Table S2. Tabulated NMR assignment of the methyl cyclohexa-1,5-diene carboxylate intermediate.

^1H -label	δ ^1H , ppm, (mult)	δ ^{13}C	^1H Int.	^1H - ^1H -COSY	rel. mol-%
9	1.79	20.60	2.40	9-10, 9-21, 9-24	11.10
10	1.90	22.71	2.40	10-9, 10-24	
16	3.43	50.64	3.16	-	
21	5.66	126.98	1.13	21-9, 21-22	
22	6.56	121.66	1.04	22-10, 22-21	
24	6.82*	136.45	1.04	24-10	

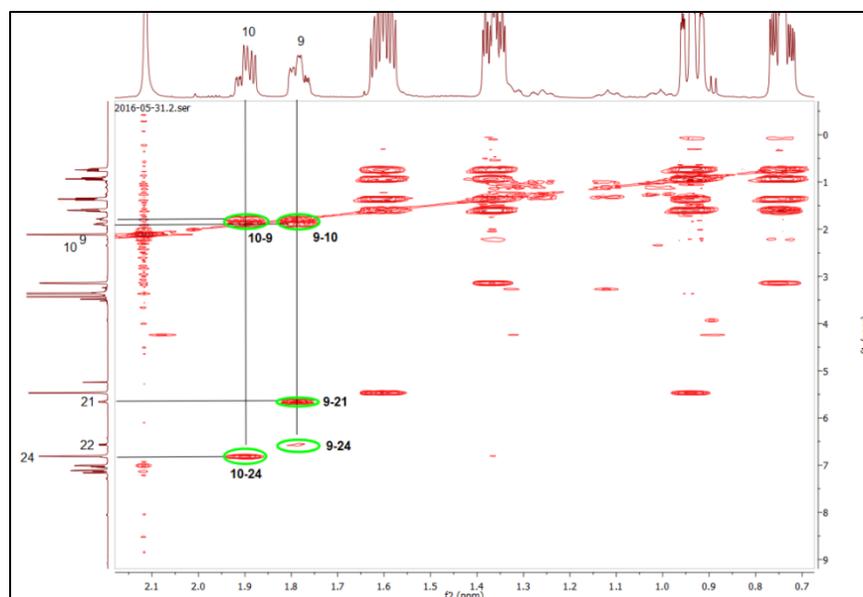


Figure S10. ^1H - ^1H - COSY of the methyl cyclohexa-1,5-diene carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

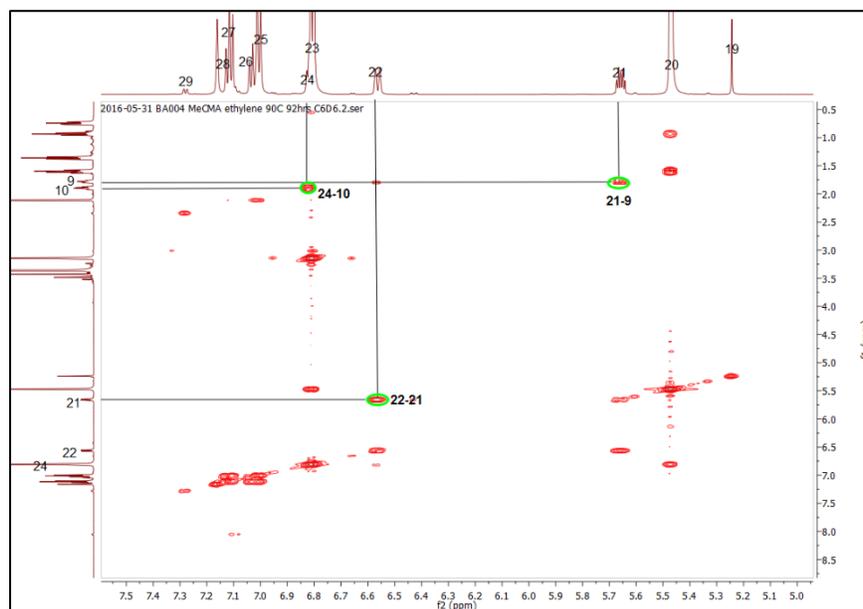


Figure S11. ^1H - ^1H - COSY of the methyl cyclohexa-1,5-diene carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

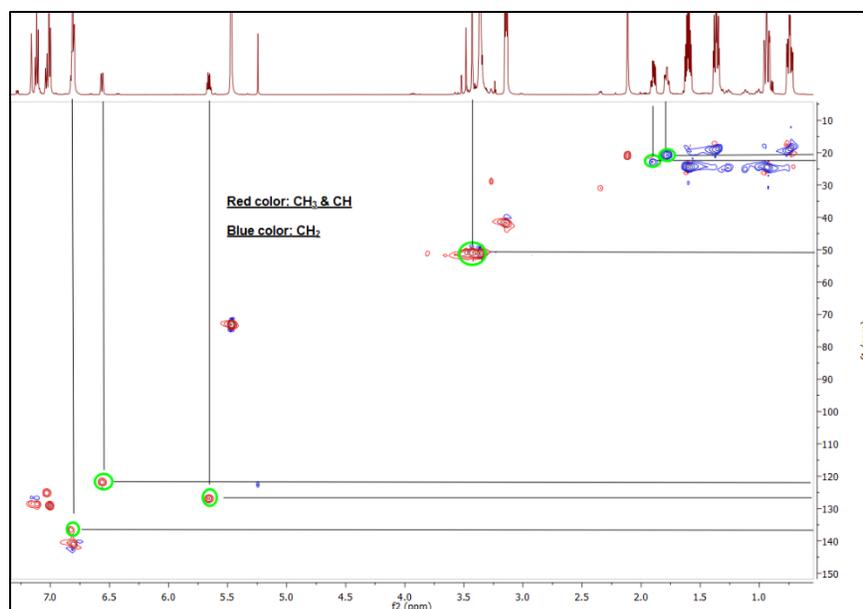


Figure S12. ^{13}C - ^1H -HSQC of the methyl cyclohexa-1,5-diene carboxylate intermediate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

Methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate: ^1H NMR (600 MHz, Benzene- d_6) δ 7.28 (dd, J = 6.9, 1.7 Hz, 1H), 3.48 (s, 3H), 3.28 – 3.25 (m, 1H), 2.36 – 2.32 (m, 1H), 1.33 – 1.29 (m, 2H), 1.29 – 1.23 (m, 2H), 1.16 – 1.08 (m, 2H), 1.05 – 0.97 (m, 2H), m/z : 166.1.

Table S3. Tabulated NMR assignment of methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate.

^1H -label	δ ^1H , ppm, (mult)	δ ^{13}C	^1H Int.	^1H - ^1H -COSY	rel. mol-%
4	1.01 (m)	24.36	1.62	4-5, 4-6, 4-6a, 4-13	3.03
5	1.12 (m)	24.88	1.92	5-4, 5-6, 5-6a, 5-14a	
6	1.26 (m)	24.57	2.11	6-4,6-5, 6-6a, 6-13	
6a	1.31 (m)	25.08	1.78	6a-4, 6a-5, 6a-6, 6a-14a	
13	2.34 (m)	31.01	0.84	13-4, 13-6, 13-29	
14a	3.27 (m)	28.74	1.21	14a-5, 14a-6a, 14a-29	
17	3.48 (s)	51.63	2.92	-	
29	7.28 (dd)	144.33	0.88	29-13, 29-14a	

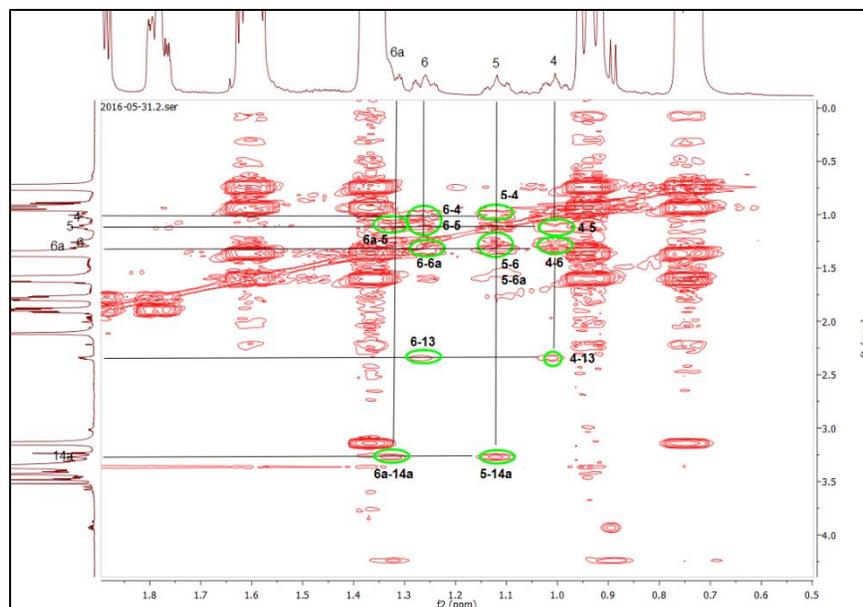


Figure S13. ^1H - ^1H - COSY of the methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

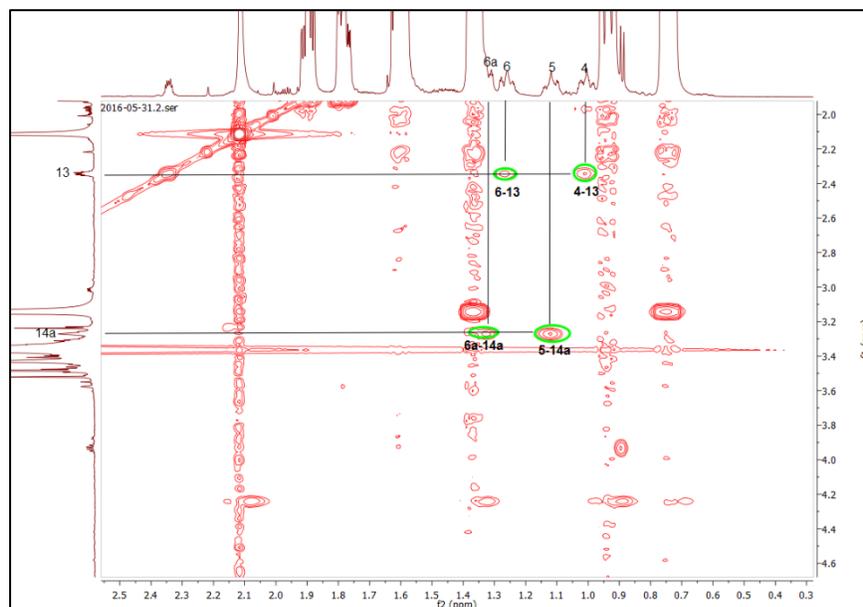


Figure S14. ^1H - ^1H - COSY of the methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

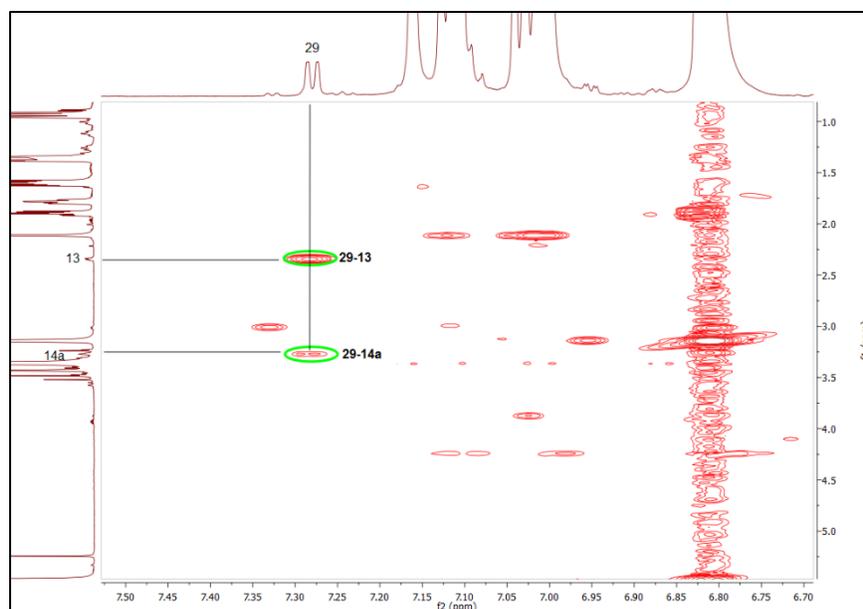


Figure S15. ^1H - ^1H - COSY of the methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

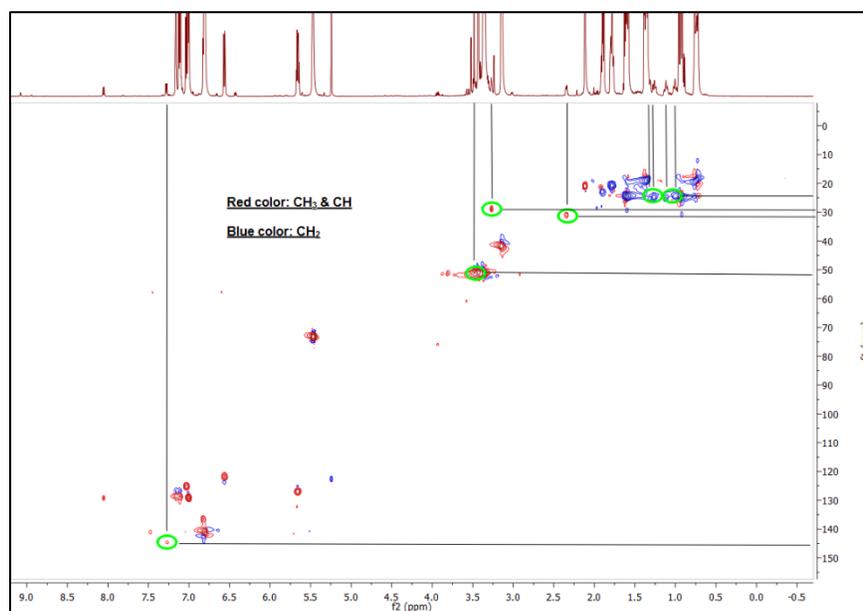


Figure S16. ^{13}C - ^1H - HSQC of the methyl bicyclo[2.2.2]oct-2-ene-2-carboxylate from the reaction of MeCMA with ethylene (600 MHz, benzene- d_6).

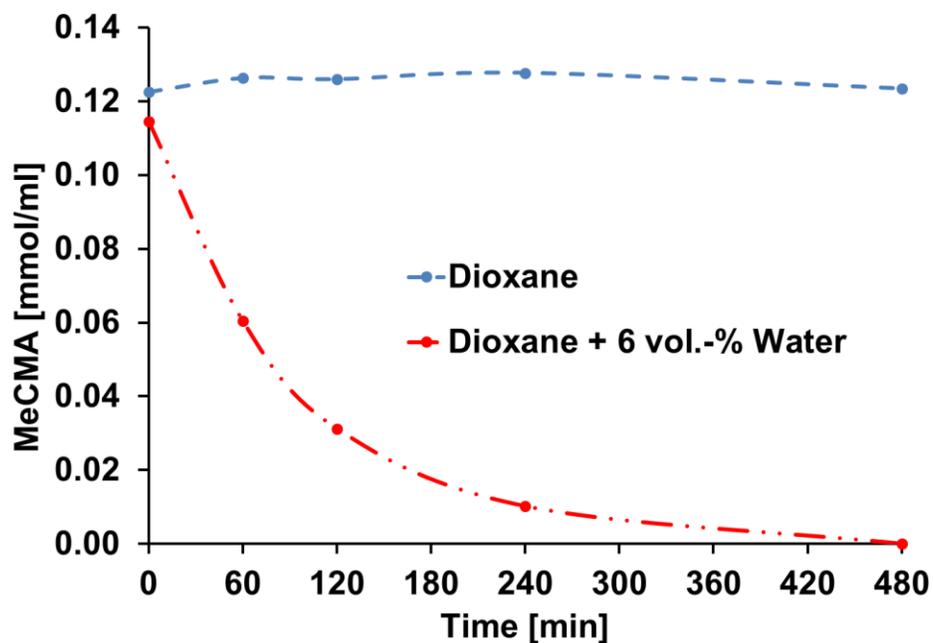


Figure S17. Stability test of coumalic acid in 1,4-dioxane in the presence and absence of water at 180 °C.

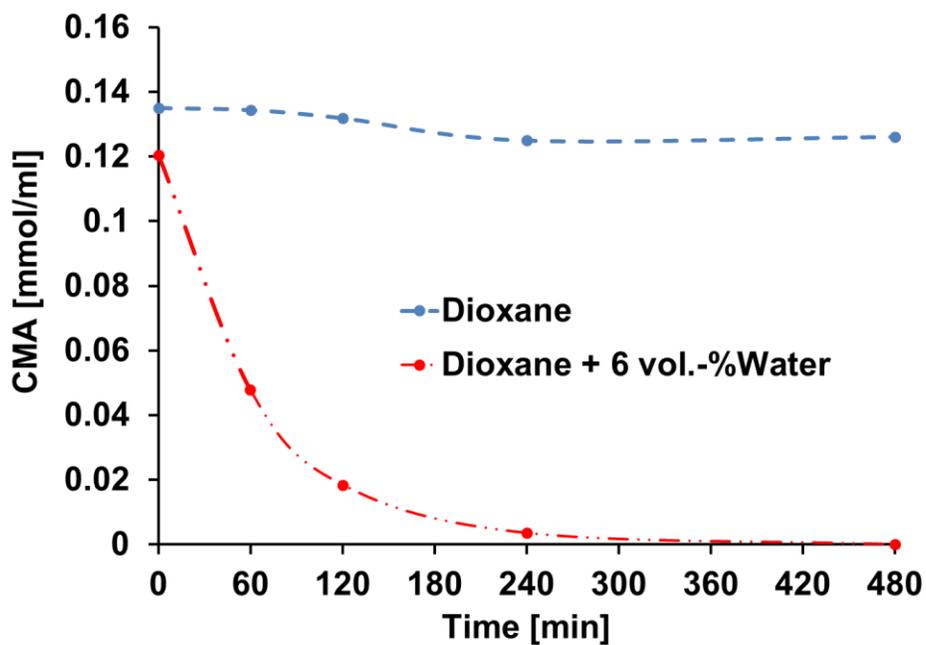


Figure S18. Stability test of methyl coumalate in 1,4-dioxane in the presence and absence of water at 180 °C.

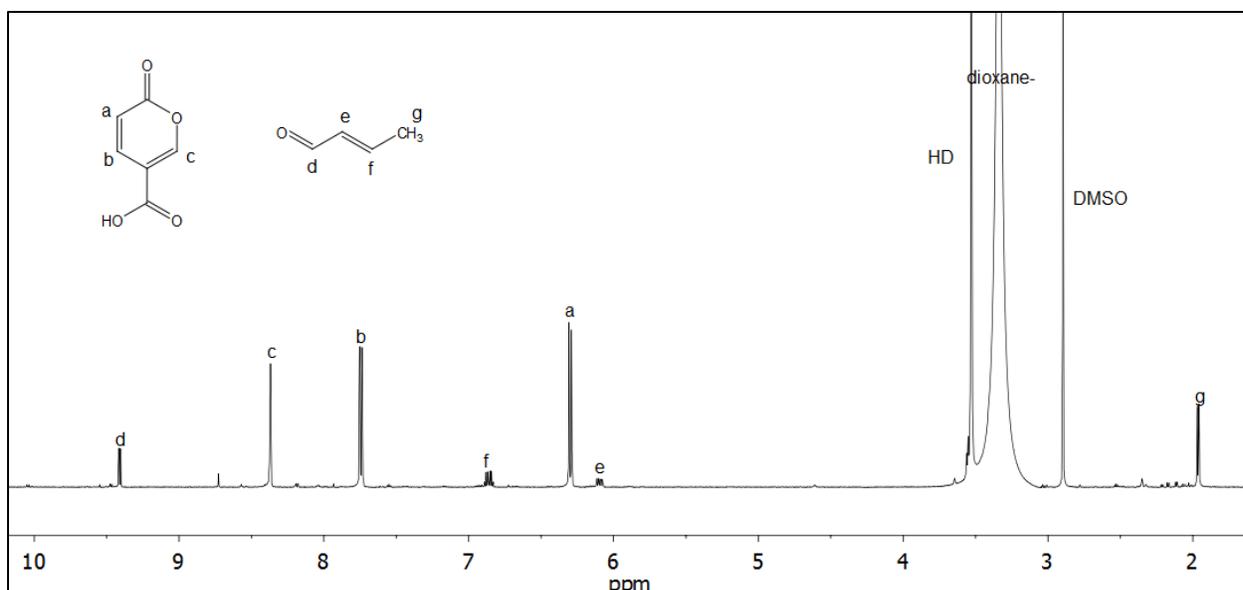


Figure S19. ¹H NMR (600 MHz, dioxane-d₈) of 0.15M coumalic acid and 3 vol.-% H₂O after 386 min at 171 °C.

Table S4. Rate constants and activation energy of the Diels-Alder reaction of coumalates with ethylene.

Entry	Substrate	Temp. [°C]	10 ³ 1/T [K ⁻¹]	10 ⁻³ k _{obs} [min ⁻¹]	lnk	E _A [kJ/mol]
1	MeCMA	90	2.75	0.99	-6.92	76.74
2	MeCMA	100	2.68	2.03	-6.20	
3	MeCMA	110	2.61	4.15	-5.49	
4	MeCMA	120	2.54	6.72	-5.00	
5	CMA	90	2.75	0.82	-7.11	77.06
6	CMA	100	2.68	1.61	-6.43	
7	CMA	110	2.61	3.10	-5.77	
8	CMA	120	2.54	6.07	-5.10	

Table S5. Rate constants and activation energy of the decarboxylation reaction of the bicyclic intermediate DAP from coumalate reaction with ethylene.

Entry	Substrate	Temp. [°C]	10 ³ 1/T [K ⁻¹]	10 ⁻³ k _{obs} [min ⁻¹]	lnk	E _A [kJ/mol]
1	MeCMA-DAP	140	2.42	2.56	-5.97	132.79
2	MeCMA-DAP	149	2.36	5.65	-5.18	
3	MeCMA-DAP	160	2.31	15.24	-4.18	
4	CMA-DAP	139	2.42	2.81	-5.88	141.56
5	CMA-DAP	149	2.36	7.56	-4.88	
6	CMA-DAP	158	2.32	17.31	-4.06	

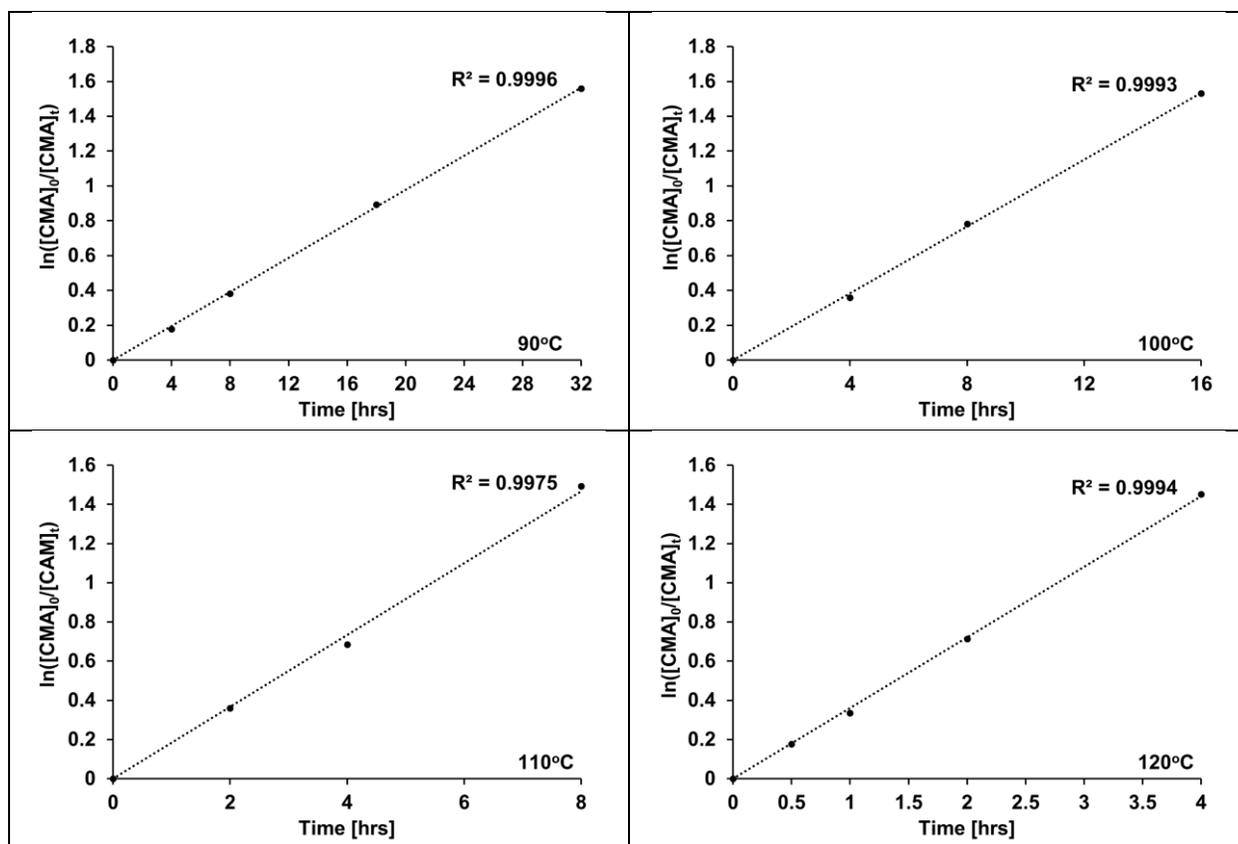


Figure S20. Diels-Alder reactions kinetics of coumalic acid and ethylene at different temperatures.

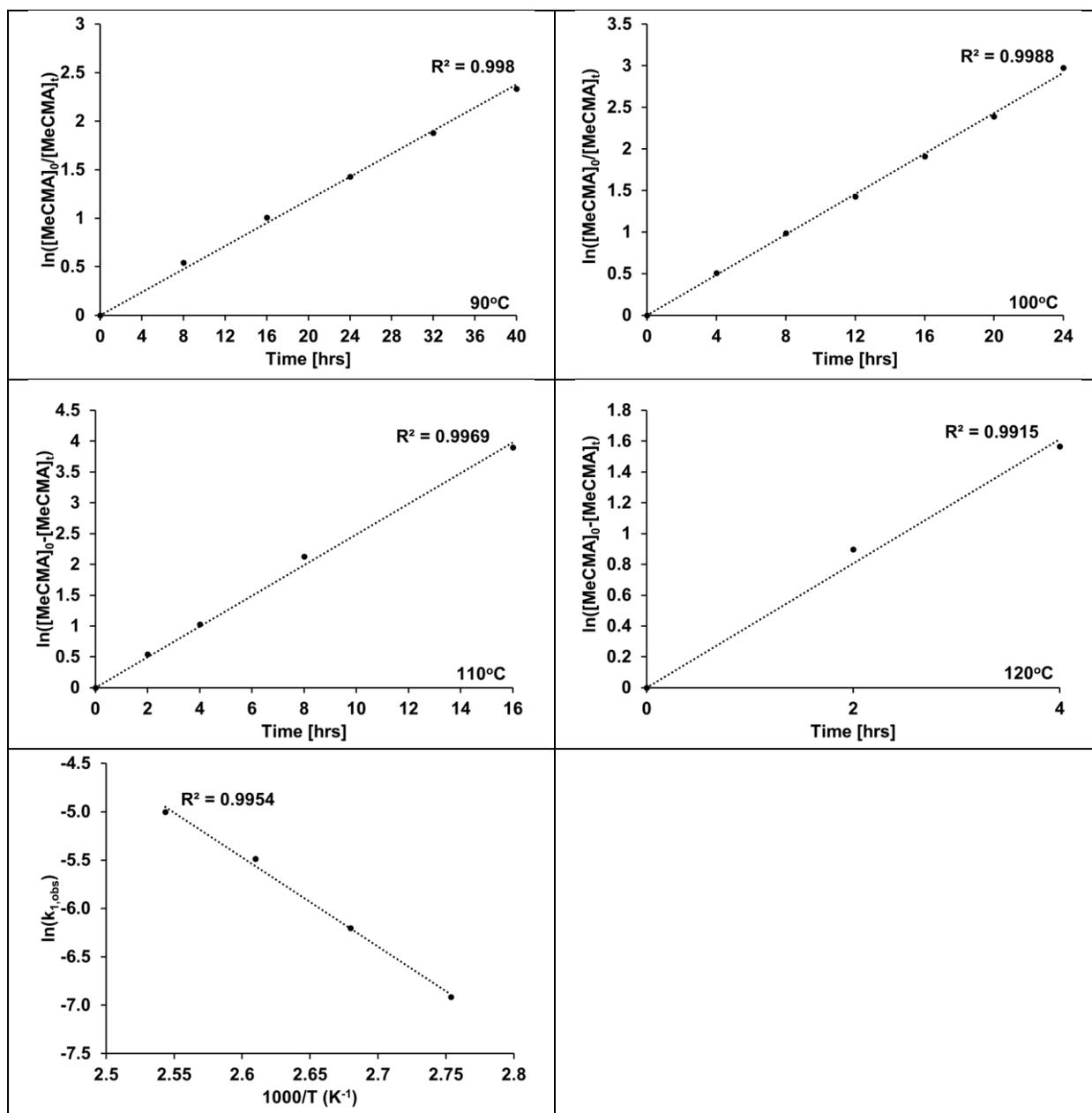


Figure S21. Diels-Alder reaction kinetics of methyl coumalate and ethylene at different temperatures.

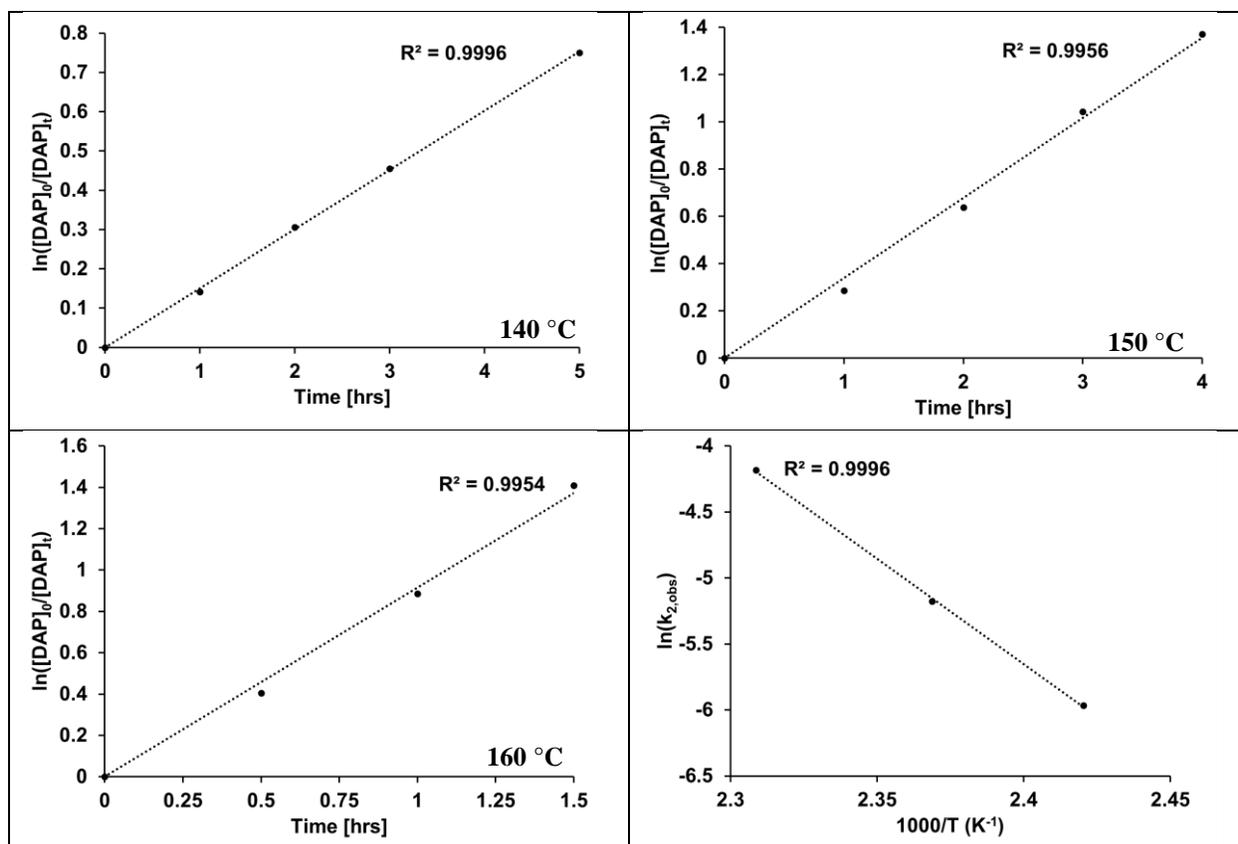


Figure S22. Decarboxylation reaction kinetics of the Diels-Alder product of methyl coumalate and ethylene at different temperatures and the corresponding Arrhenius plot.

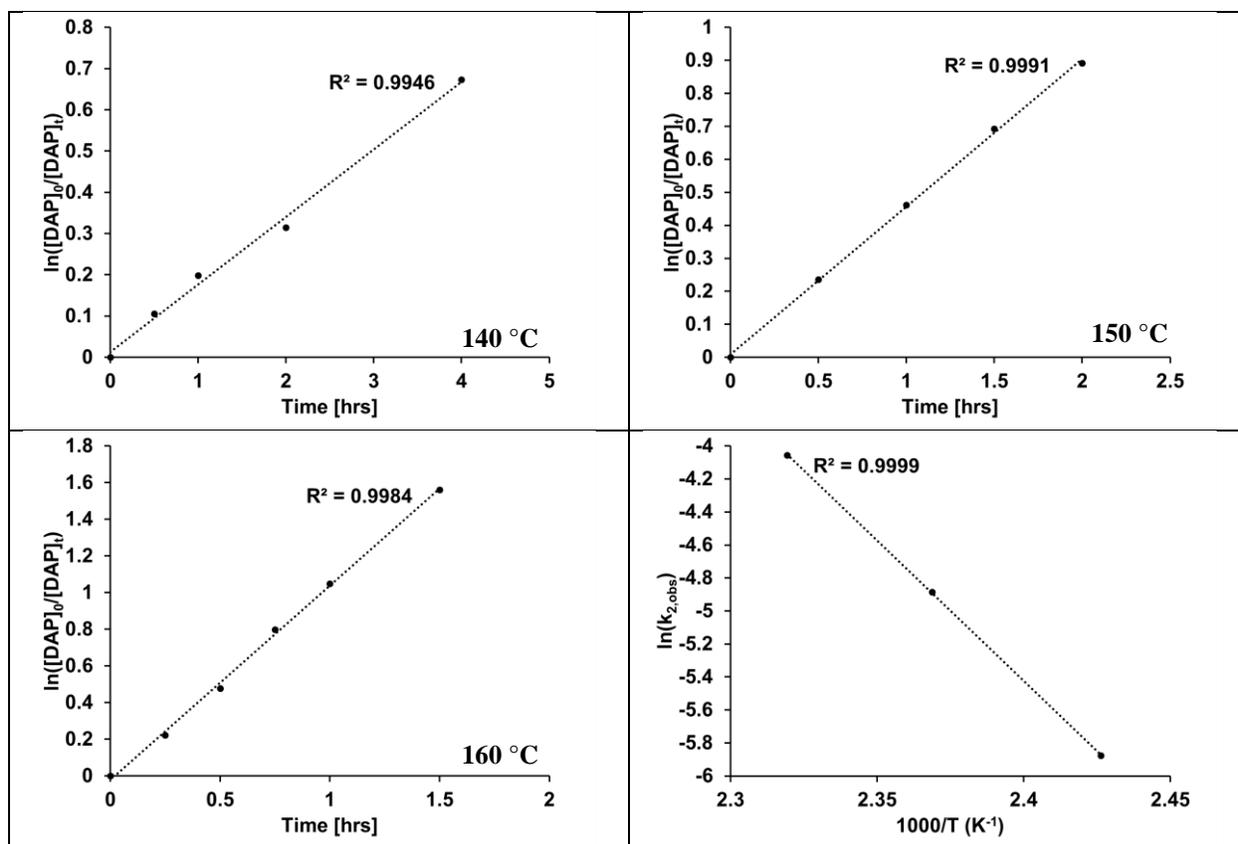


Figure S23. Decarboxylation reaction kinetics of the Diels-Alder product of coumalic acid and ethylene at different temperatures and the corresponding Arrhenius plot

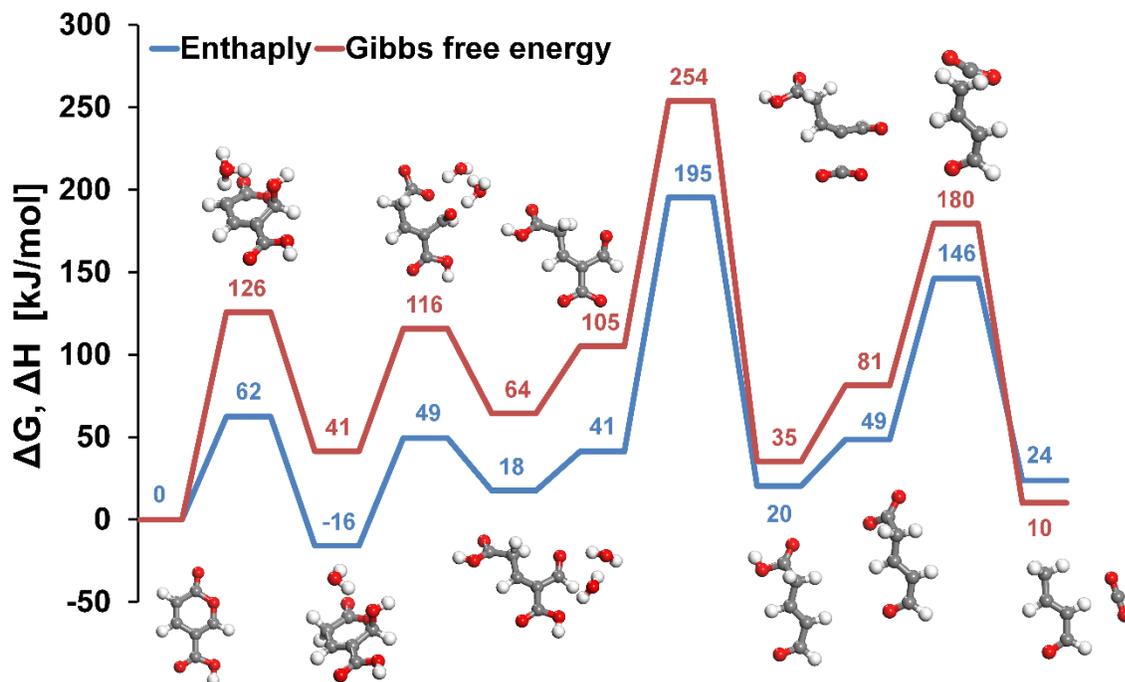


Figure S24. Reaction profile diagram of the coumalic acid breakdown in water