Sustainability and efficiency assessment of vanillin allylation: in solution versus ball-milling

Damien Breilly,[a] Sami Fadlallah,[a] Vincent Froidevaux,[b] Frédéric Lamaty,[c] Florent Allais*,[a] Thomas-Xavier Métro*[d]

[a] URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 51110 Pomacle
[b] CHRYSO Saint-Gobain, 45300 Sermaises
[c] IBMM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[d] ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Correspondence should be sent to: florent.allais@agroparistech.fr & thomas-xavier.metro@umontpellier.fr

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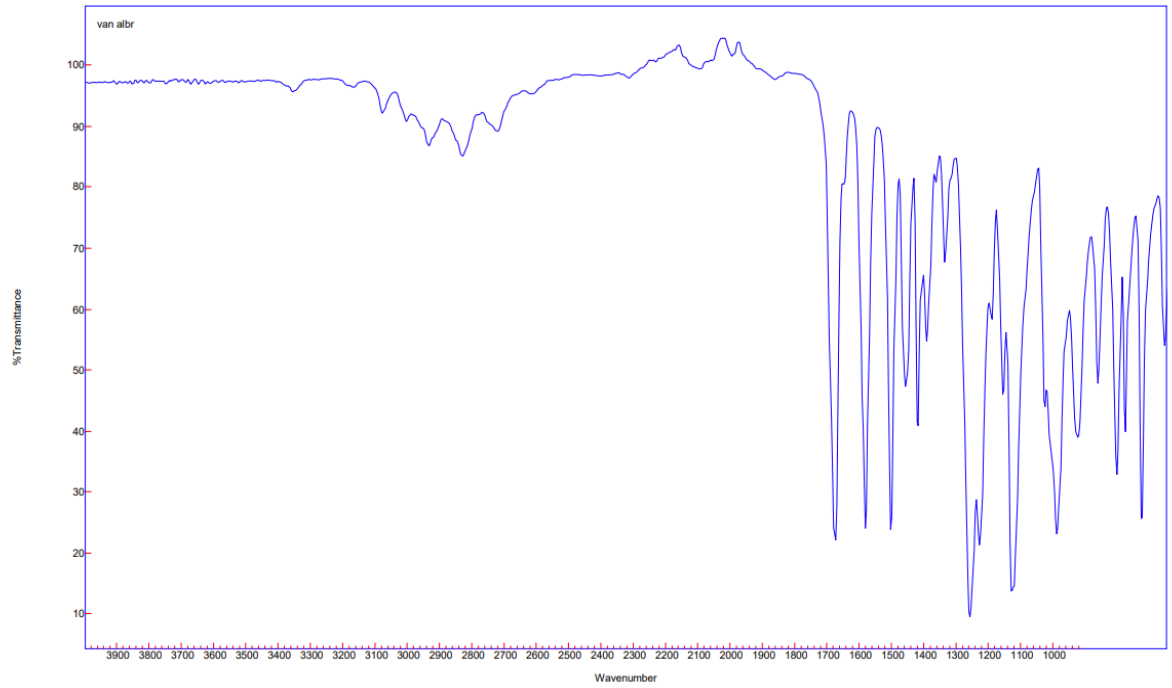

Figure S1: FTIR spectra of 3-methoxy-4-(2-propen-1-yloxy)benzaldehyde (allylated vanillin)

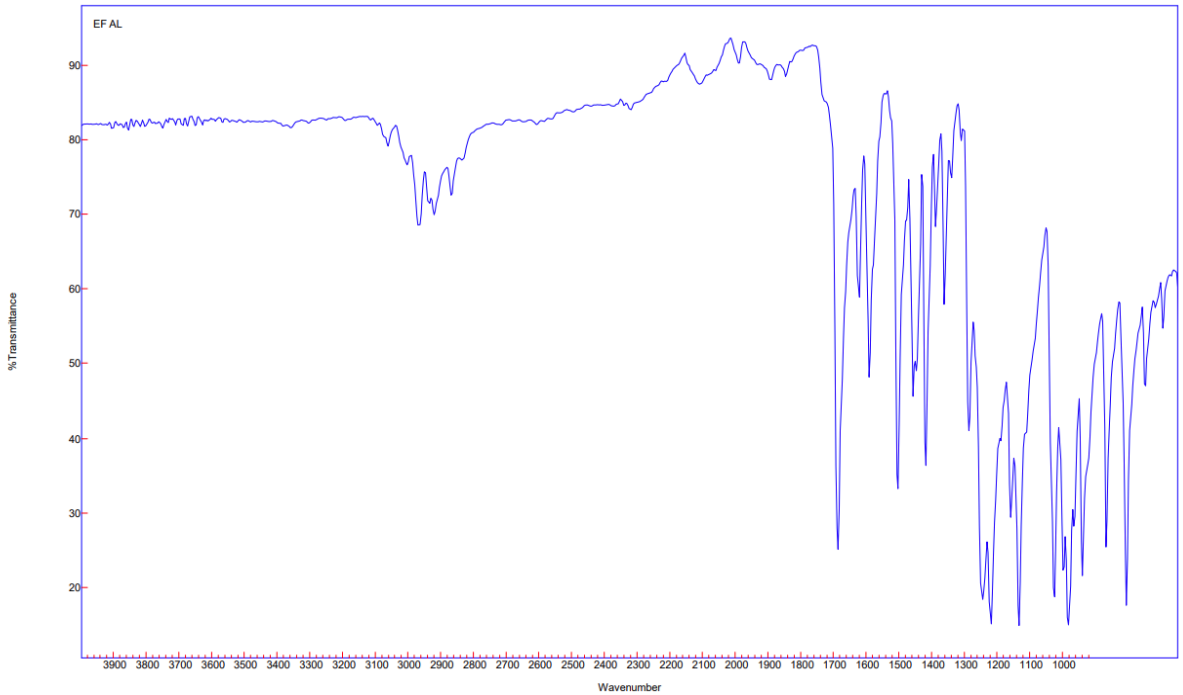

Figure S2: FTIR spectra of 3-[3-methoxy-4-(2-propen-1-yloxy)phenyl]-2-propenoic acid ethyl ester (allylated ethyl ferulate)

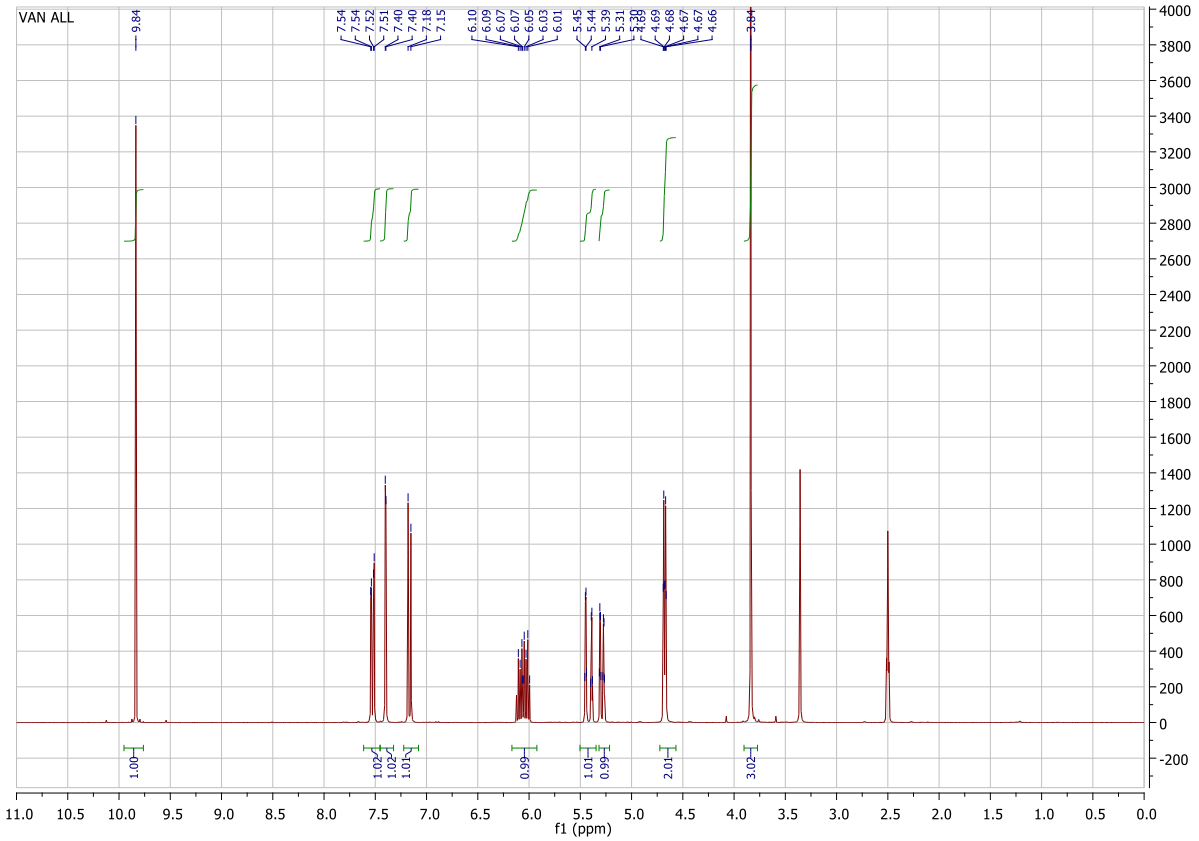

Figure S3: ^{1}H NMR spectra of 3-methoxy-4-(2-propen-1-yloxy)benzaldehyde (allylated vanillin)

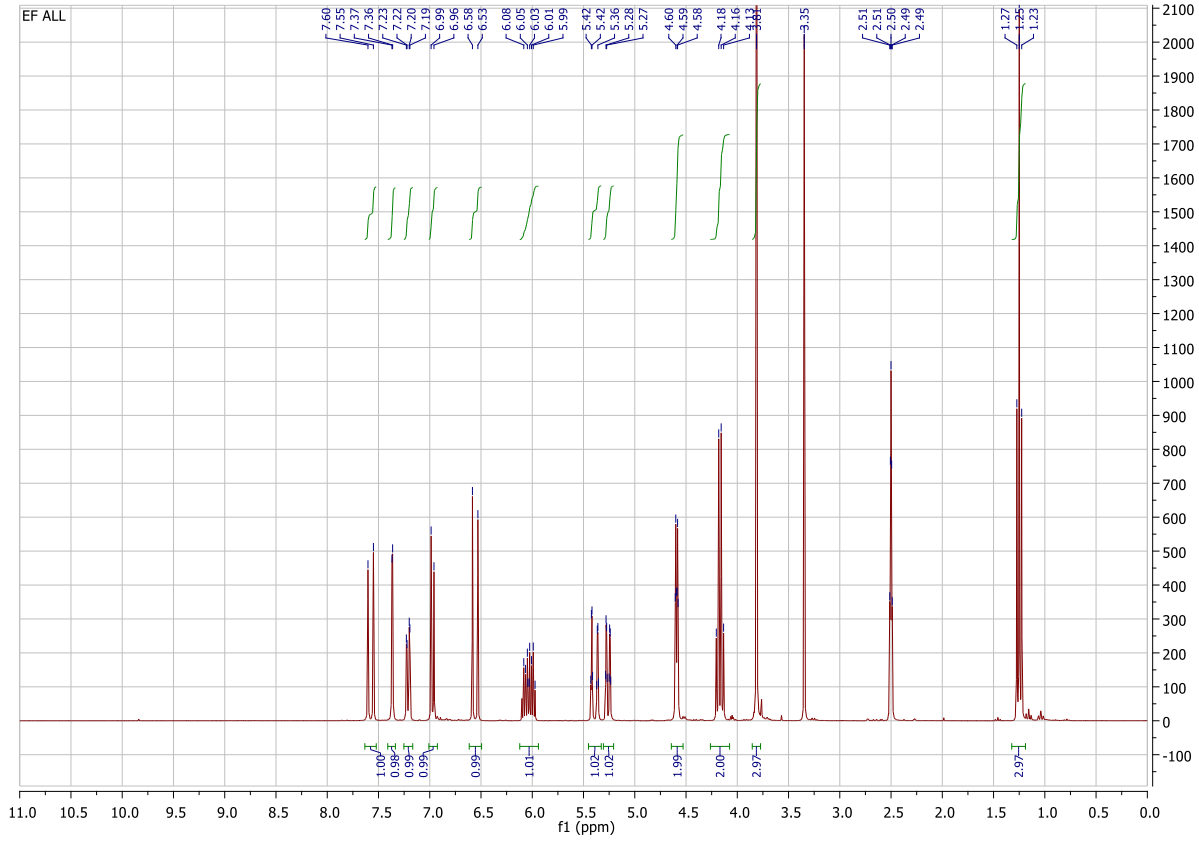

Figure S4: ^{1}H NMR spectra of 3-[3-methoxy-4-(2-propen-1-yloxy)phenyl]-2-propenoic acid ethyl ester (allylated ethyl ferulate)

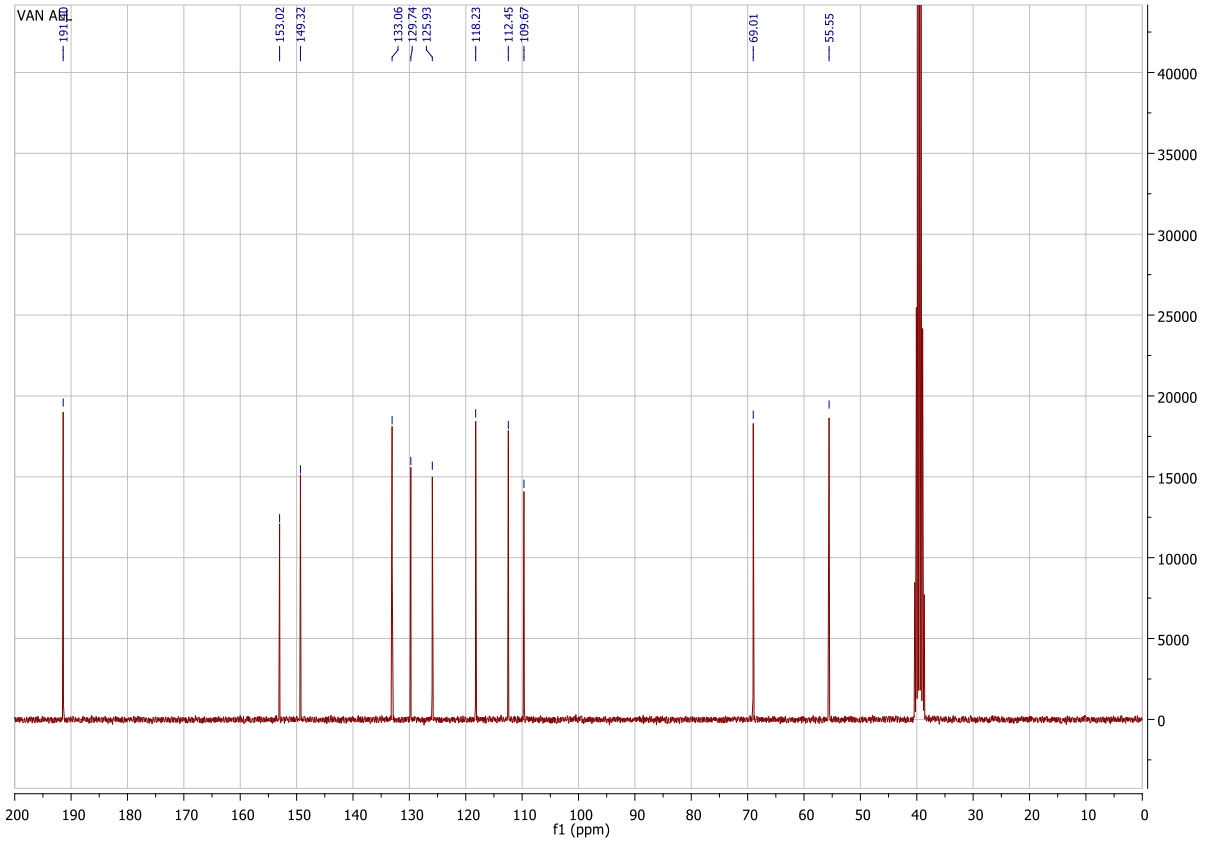

Figure S5: ^{13}C NMR spectra of 3-methoxy-4-(2-propen-1-yloxy)benzaldehyde (allylated vanillin)

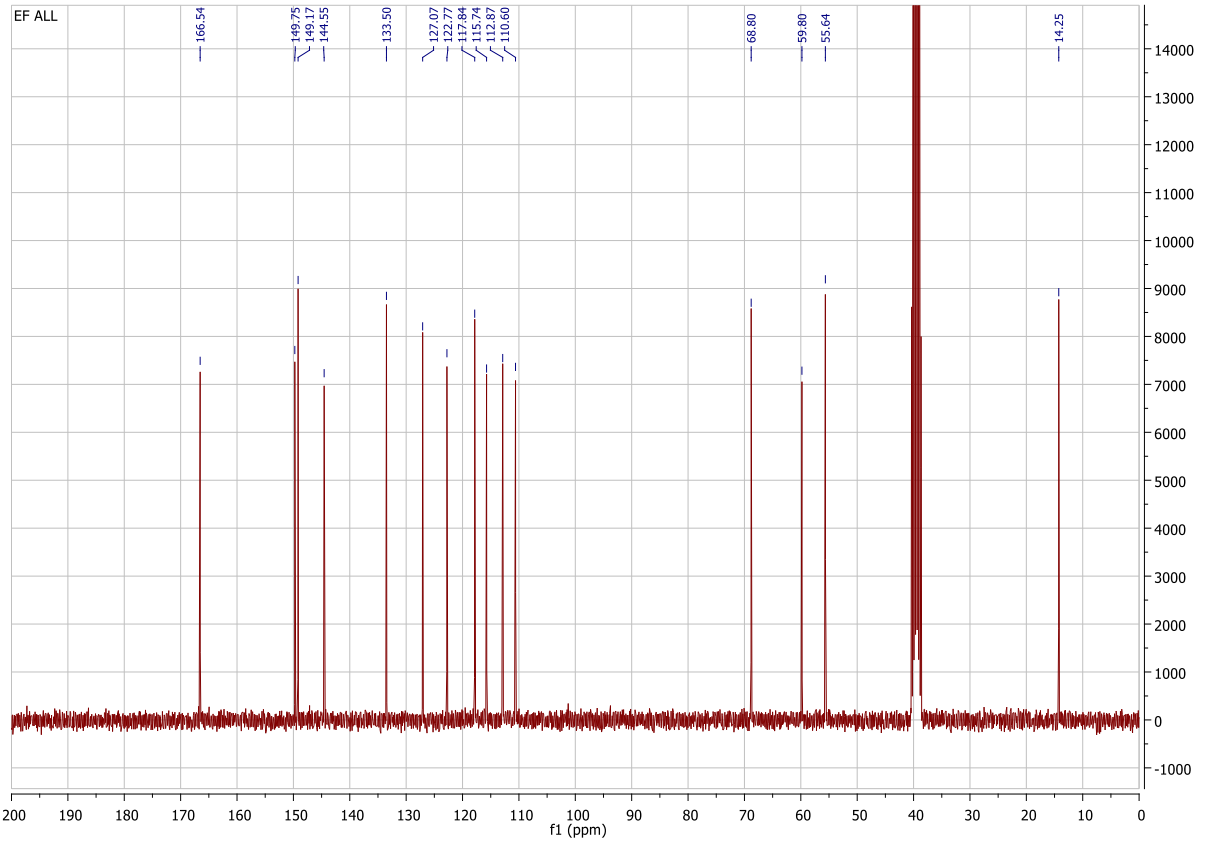

Figure S6: ^{13}C NMR spectra of 3-[3-methoxy-4-(2-propen-1-yloxy)phenyl]-2-propenoic acid ethyl ester (allylated ethyl ferulate)

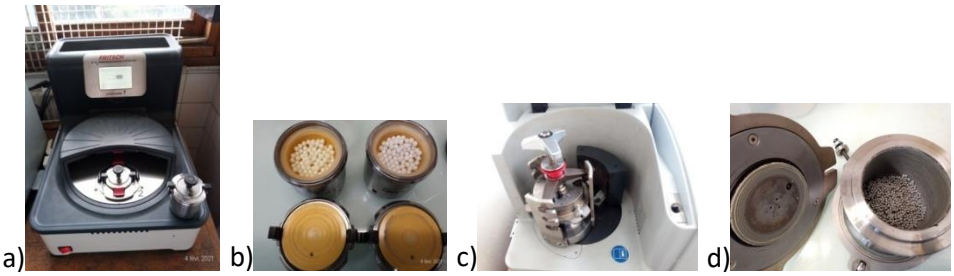

Figure S7: Photography of (a) a planetary ball mill P7 with (b) 20 mL reactors and (c) a planetary ball mill Retsch PM100 with (d) a 250 mL reactor

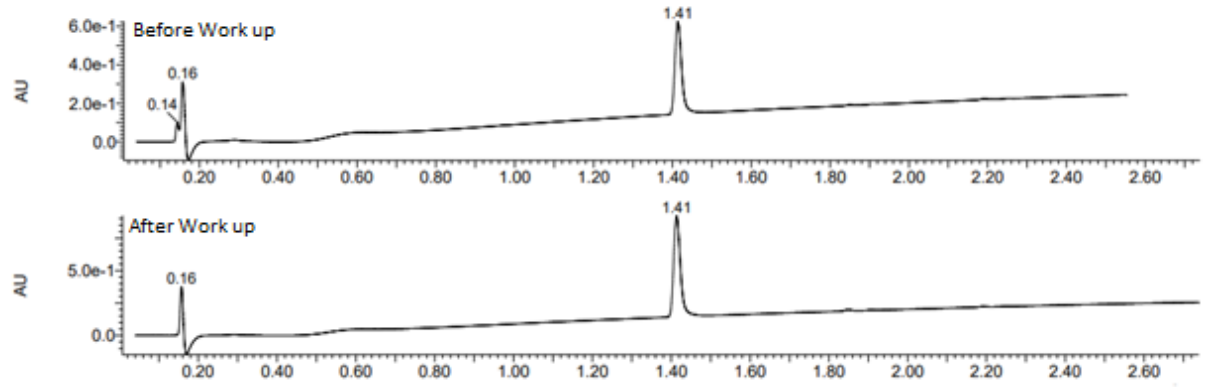

Figure S8: Chromatogram of 3-methoxy-4-(2-propen-1-yloxy)benzaldehyde (allylated vanillin) before (top) and after work up (bottom) (abscissa in AU and ordinate in minute)

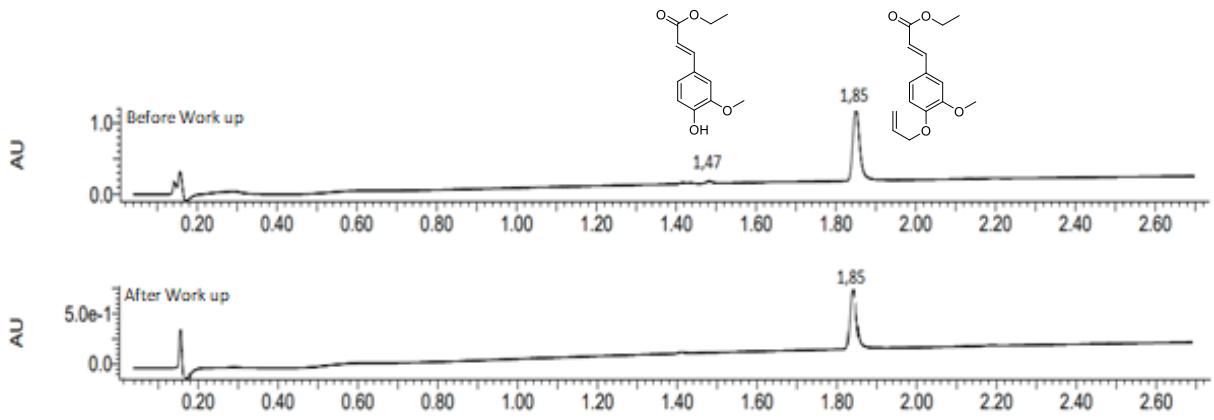

Figure S9: Chromatogram of 3-[3-methoxy-4-(2-propen-1-yloxy)phenyl]-2-propenoic acid ethyl ester (allylated ethyl ferulate) before (top) and after work up (bottom) (abscissa in AU and ordinate in minute)

$$\text{E Factor} = \frac{\sum m(solvent) + \sum m(water) + \sum m(reagent) + \sum m(raw\ material) - m(desired\ product)}{m(desired\ product)}$$

Equation S1: Environmental factor equation

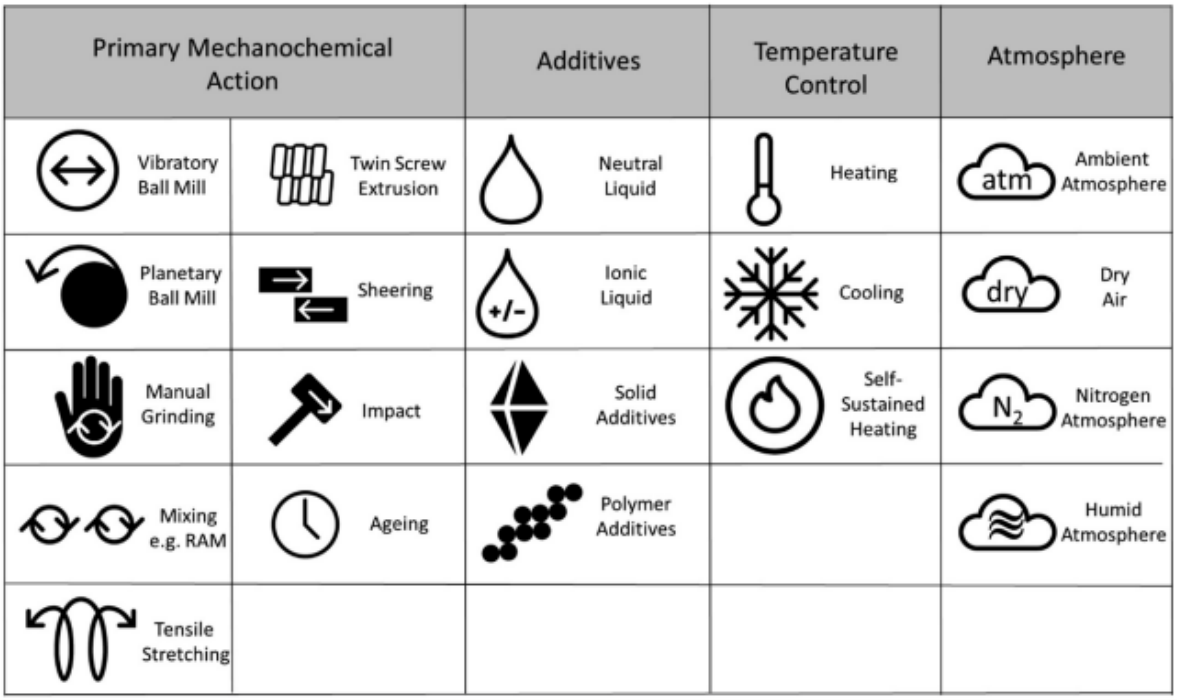

Figure S10: Symbols utilized for the representation of experimental mechanochemical conditions (according to Michalchuk *et al.*, *Front. Chem.* **2021**, *9*, 359)

Author, year	phenol	m(phenol) (g)	Eq K_2CO_3	m(K_2CO_3) (g)	Eq(AllylBr)	m(AllylBr) (g)	solvent	V(solvent) (mL)	m(solvent) (g)	Eq solvent	yield	m(product) (g)	Simple *E* Factor[a]	Work-up solvent 1 (g)	Work-up solvent 2 (g)	Work-up solvent 3 (g)	Complete *E* factor[b]
Srikrishna et al, 2007	vanillin	2.5	2.02	4.59	2.00	3.98	acetone	5	3.92	4.11	100%	3.25	**3.61**	/	/	/	**n.a.[c]**
Hoffmann et al, 2014	vanillin	15.2	1.00	13.8	1.10	13.3	ethanol	50	39.5	8.57	98%	18.84	**3.34**	/	/	/	**n.a.[c]**
Ayer et al, 1992	vanillin	12.2	0.99	11	1.05	10.21	DMF	20	18.88	3.22	98%	15.06	**2.47**	/	/	/	**n.a.[c]**
Chate et al, 2012	vanillin	1	1.09	0.99	1.00	0.798	DMF	5	4.72	9.83	92%	1.16	**5.46**	/	/	/	**n.a.[c]**
Kevwitch et al, 2012	vanillin	102	0.54	50.2	1.02	82.5	DMF	600	566.4	11.56	96%	123	**5.51**	300	265	480.8	**14**
This work in solution in DMF	vanillin	1	1	0.908	1.5	1.188	DMF	2.6	2.45	5.11	86%	1.09	**4.09**	54.12	20	20.8	**91**
This work, pbm mg-scale	vanillin	0.129	1	0.117	1.5	0.154	DMF η=0.2	0.08	0.076	1.22	87%	0.143	**2.33**	22.6	5	10.4	**268**
This work, pbm g-scale	vanillin	1.61	1	1.46	1.5	1.93	DMF η=0.2	1.00	0.94	1.22	95%	1.94	**2.06**	135.3	50	52	**124**
This work, pbm mg-scale	ethyl ferulate	0.164	1	0.102	1.5	0.13	DMF η=0.2	0.08	0.076	1.40	82%	0.16	**1.98**	22.6	5	10.4	**239**
This work, pbm g-scale	ethyl ferulate	2.05	1	1.28	1.5	1.68	DMF η=0.2	1.00	0.94	1.40	92%	2.24	**1.66**	135.3	50	52	**108**

[a] Work-up solvents were not taken into account in the calculation of the E factor. [b] Work-up solvents were taken into account in the calculation of the E factor. [c] n.a.: not applicable (information not available in the original publication, e.g. volume of solvent used for column chromatography purification).

Table S1: Details for the calculations of the *E* factors