

Supplementary Information

for

Energetic Assessment of the Suzuki-Miyaura Reaktion: A Curtate Life Cycle Assessment as an easily Understandable and Applicable Tool for Reaction Optimization

F. Schneider,^a T. Szuppa,^a A. Stolle,^a B. Ondruschka,^{*a} H. Hopf^b

^a Institute for Technical Chemistry and Environmental Chemistry,
Friedrich-Schiller University Jena

^b Institute of Organic Chemistry, Technical University Braunschweig

* Fax: (+49)-3641-948-402; E-mail: bernd.ondruschka@uni-jena.de

Table of Content

Experimental Procedures – Ball Milling	2
Experimental Procedures – Microwave Irradiation	3
Experimental Procedures – Combination	4
Experimental Procedure – Mortar and Pestle	5
Correlation of Energy Demand, Yield, and Rotation Frequency (Pulverisette 7)	6
Temperature Effect for MW1	7

Experimental Procedures – Ball Milling:

BM1 (“Pulverisette 7”, Fritsch GmbH, Idar-Oberstein Germany): For more details *cf.* Table 1 and the Experimental Section of the manuscript.

BM2 (“Pulverisette 5”, Fritsch GmbH, Idar-Oberstein Germany): Inorganic support material (50 g), *p*-bromoacetophenone (**1d**; 50 mmol, 10.16 g), phenylboronic acid (62 mmol, 7.55 g), Pd(OAc)₂ (1.8 mmol, 0.4 g, 3.6 mol%) were added in the milling beaker (volume: 250 mL; material: stainless steel; six 30 mm agate milling balls per beaker) of the planetary ball mill “Pulverisette 5”. The mixtures were subsequently milled with the chosen reaction parameters for rpm and milling time (*cf.* Table 1). Samples were extracted with 2 ml of deionized water and 3 ml of ethyl acetate and were analyzed by gas chromatography.

BM3 (“MM 301”, Retsch GmbH, Haan Germany): Inorganic support material (5 g), aryl halides (5 mmol), phenylboronic acid (6.2 mmol, 0.755 g), Pd(OAc)₂ (0.18 mmol, 0.04 g, 3.6 mol%) were added in the milling beaker (volume: 50 mL; material: stainless steel; six 12 mm stainless steel milling balls per beaker) of the mixer mill “MM 301” Retsch GmbH. The mixtures were subsequently milled with the chosen reaction parameters for rpm and milling time (*cf.* Table 1). Samples were extracted with 2 ml of deionized water and 3 ml of the corresponding solvent (**1a-c**: *tert*-butylmethylether; **1d**, **1e**: ethyl acetate) and were analyzed by gas chromatography.

Experimental Procedures – Microwave Irradiation:

MW1 (“Praktika”, MLS GmbH, Leutkirch Germany): Inorganic support material (5 g), aryl halides (5 mmol), phenylboronic acid (6.2 mmol, 0.755 g), Pd(OAc)₂ (0.18 mmol, 0.04 g, 3.6 mol%) were added into a ground-joint test tube (50 mL), equipped with a fiber-optic sensor, and installed into a mounting inside the microwave device “Praktika”. The sample was irradiated for 15 min at 150 °C (300 W). After cooling to room temperature, samples were extracted with 2 ml of deionized water and 3 ml of the corresponding solvent (**1a-c**: *tert*-butylmethylether; **1d**, **1e**: ethyl acetate) and were analyzed by gas chromatography.

MW2 (“Discover”, CEM GmbH, Kamp-Lintfort Germany): Inorganic support material (5 g), aryl halides (5 mmol), phenylboronic acid (6.2 mmol, 0.755 g), Pd(OAc)₂ (0.18 mmol, 0.04 g, 3.6 mol%) were added into a 50mL-flask, equipped with a fiber-optic sensor, and installed into a mounting inside the microwave device. The sample was irradiated for 15 min at 150 °C (150 W). After cooling to room temperature, samples were extracted with 2 ml of deionized water and 3 ml of the corresponding solvent (**1a-c**: *tert*-butylmethylether; **1d**, **1e**: ethyl acetate) and were analyzed by gas chromatography.

Experimental Procedures – Combination:

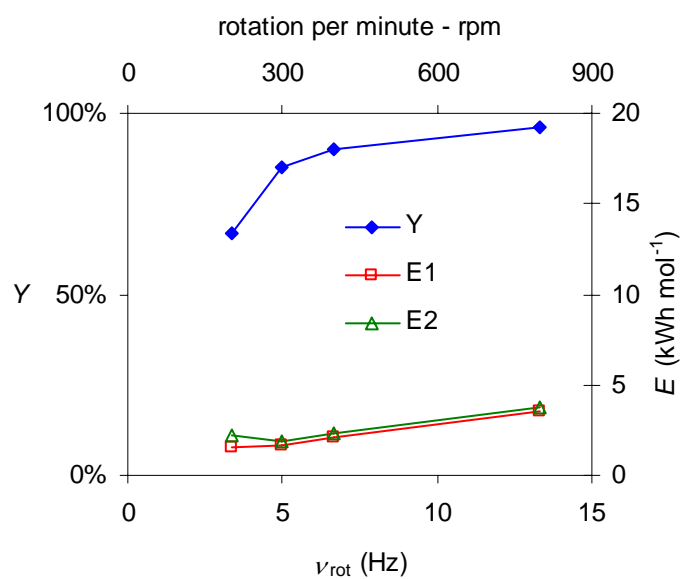
COMB: Inorganic support material (5 g), aryl halides (5 mmol), phenylboronic acid (6.2 mmol, 0.755 g), Pd(OAc)₂ (0.18 mmol, 0.04 g, 3.6 mol%) were added in the milling beaker (volume: 45 mL; material: agate; six 15 mm agate milling balls per beaker) of the planetary ball mill “Pulverisette 7” (Fritsch GmbH). The mixtures were subsequently milled with 800 rpm for 10 min. The ground samples were transferred into a ground-joint test tube, equipped with a fiber-optic sensor, and installed into a mounting inside the microwave device “Praktika” (MLS GmbH). The sample was irradiated for 15 min at 150 °C (300 W). After cooling to room temperature, samples were extracted with 2 ml of deionized water and 3 ml of the corresponding solvent (**1a-c**: *tert*-butylmethylether; **1d**, **1e**: ethyl acetate) and were analyzed by gas chromatography.

Experimental Procedures – Mortar and Pestle:

Inorganic support material (5 g), *p*-bromoacetophenone (**1d**; 5 mmol, 1.016 g), phenylboronic acid (6.2 mmol, 0.755 g), Pd(OAc)₂ (0.18 mmol, 0.04 g, 3.6 mol%) were added in the porcelain mortar. The mixtures were subsequently milled with a porcelain pestle for 5 min. Samples were extracted with 2 ml of deionized water and 3 ml of ethyl acetate and were analyzed by gas chromatography.

Correlation of Energy Demand, Yield, and Rotation Frequency (Pulverisette 7):

Figure S1 (stainless steel milling balls). Yield of coupling products **3d** from Suzuki-Miyaura reaction of **1d** (5 mmol) with **2** (124 mol%) induced by ball milling (“Pulverisette 7”) and demand of electrical energy used for reaction (E_1 and E_2 calculated according to Eq. 1 and 2; base: KF-Al₂O₃; catalyst: 3.6 mol% Pd(OAc)₂; milling time: 10 min; steel beakers; $V_{\text{beaker}} = 45$ mL; six **stainless steel** milling balls; $d_{\text{balls}} = 15$ mm).



Temperature Effect for MW1

Table S1. Influence of reaction temperature on the outcome of the Suzuki-Miyaura reaction of **1** with **2d** (cf. Scheme 1 in manuscript).

Treatment ^a	<i>t</i> [min]	<i>T</i> [°C]	Yield 3d [%]
BM1	10	70 ^b	89
BM2	10	70 ^b	45
MW1	10	50	14
		75	16
		100	51
		150	62
		15	150
MW2	15	150	45

^a For reaction conditions please refer to Table 1 of the manuscript. ^b Surface temperatures measured after grinding at 800 rpm.

As presented in Table S1 the measured surface temperatures in case of ball milling are about 70 °C. Performing the similar reaction under microwave irradiation assuming that surface temperatures from ball milling experiments are equal to the bulk temperature in case of microwave irradiation (measured with fibre optics) reveals decreased yields. However increase of reaction temperature for **MW1** to 150 °C allows to increase the yield of coupling product **3d** reaching the same level as for **BM1**. Experiments point out that it is not possible to compare the temperatures from ball milling experiments with those reaction bulk reaction temperatures measured in microwave experiments.