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The Suzuki−Miyaura Reaction under Mechanochemical Conditions[§]

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Abstract:

As a model for a C−C-coupling procedure a Suzuki−Miyaura reaction has been studied under mechanochemical conditions. Important parameters influencing the yield of the reaction are the revolutions per minute, the milling time, and the material of the milling balls and beakers, as well as the size and number of milling balls.

Introduction

Whether in natural product synthesis, pharmaceutical chemistry, or the fine chemical industry C−C-coupling reactions are versatile and often used methods.[1−3] Recently, metal-catalyzed cross-coupling reactions have become of growing interest because of their advantages compared to those of conventional synthetic methods.[1,4−8] Using noble metal catalysts (e.g., Pd, Ru, Rh) very often allows simplification of the classical reaction procedures simultaneously leading to increased yield and higher selectivity. Especially palladium-catalyzed C−C-coupling reactions are widely applied in chemical synthesis (hydrogenation, dehydrogenation, oxidation, C−C- and C−N-bond formation). Cross-coupling reactions catalyzed by Pd, for instance the Suzuki−Miyaura and the Mizoroki−Heck reaction, are of special interest for the selective formation of carbon−carbon bonds.[9]

The common Suzuki−Miyaura reaction involves the reaction of an organic halide with a boronic acid at elevated temperatures in the presence of a $Pd(PPh_3)_4$ catalyst, an inorganic base (e.g., NaOH, Na_2CO_3) and a variety of solvents (e.g., benzene, toluene).[5,6] Various possibilities for an easier performance of the common Suzuki−Miyaura reaction have been reported in the literature. Carrying out the reaction in water allows for substitution of toxic solvents and for abdication of complex ligands.[10−14] Additionally, solvent-free procedures in the presence of Pd-salts as well as the possibility to perform the reaction with heterogeneous catalysts have been reported.[10,11,15−17] Either the catalyst can be immobilized on a solid support, or the catalytically active metal complexes can be anchored on the surface of a support material.[17] In some cases, the solid support material can serve as a base generated in situ.[10−14] The use of an alternative energy source, for instance microwave irradiation, can be an important advantage for a successful Suzuki reaction.[14,16−19] However, it is generally also possible to carry out reactions by simple mixing of the reactants using mortar and pestle, allowing chemical reactions to be performed under solvent-free conditions. For efficient and automated mixing more sophisticated instrumentation has been developed. Within this context, ball mills appear to be interesting. Different kinds of grinding materials (e.g., agate, stainless steel, tempered steel, zirconium oxide, tungsten carbide, ...) can be applied for the mechanochemical treatment. In inorganic chemistry and material sciences, ball milling is a well-established technique for the grinding of minerals and the preparation and modification of inorganic solids on both laboratory and industrial scale, allowing the preparation of nanostructured alloys and the synthesis of new materials.[20]

In synthetic organic chemistry the mechanochemical technique is not very common so far, and only a few studies (e.g. the functionalization of fullerenes and Knoevenagel and aldol condensations) have been reported.[21−25] For the first time the Suzuki reaction was carried out under mechanochemical and solvent-free conditions by Axelsson and co-workers in a

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[§] This paper is dedicated to Dr. Jan-Peter Lay.

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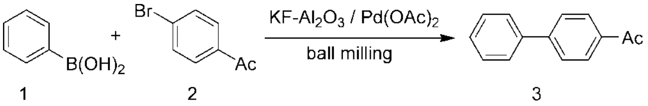
Scheme 1. **Model Suzuki−Miyaura reaction of phenylboronic acid (1) and 4-bromoacetophenone (2)**



planetary ball mill.[26] These authors reported the coupling of phenylboronic acid with a series of aryl bromides, using 2 equiv of the boronic acid, 5 mol % of $Pd(PPh_3)_4$ as the catalyst, and 3 equiv of K_2CO_3 as the base with a milling time of 30−60 min and obtained excellent yields.

The advantages of the mechanochemical treatment are among other things often decreased reaction times, simplified work-up procedures, the omission of solvents during the reaction course, and the better energy balance in comparison with those of microwave-assisted reactions or classical performance.[27]

The work of Nüchter et. al.[28] inspired us for our investigations regarding the influence of technical variables in a planetary ball mill performing the Suzuki−Miyaura model reaction. Nüchter and his co-workers discussed the various parameters by performing microwave-assisted synthesis, e.g. the aspects of the irradiation method or the aspects of the temperature measurement in the microwave field. In the application field of mechanochemical treatment such investigations are missing.

Our aim is to close this gap, and herein we report our results on performing the Suzuki−Miyaura reaction under solvent-free conditions in a planetary ball mill. The influences of parameters such as revolutions per minute (rpm), milling time (*t*), size and number of milling balls, or the material of milling balls and beakers on the yield of the coupling products has been investigated. The coupling of phenylboronic acid (**1**) as the boron component and 4-bromoacetophenone (**2**) as the aryl halide partner under the influence of KF-Al_2O_3 as the base compound, catalyzed by $Pd(OAc)_2$ was employed as the model reaction.[29]

Results and Discussion

In order to investigate the effects of various parameters of the Planetary Micro Mill model "Pulverisette 7" (Fritsch GmbH) on the solvent-free Suzuki−Miyaura reaction, a model system has to be selected. As shown in Scheme 1 the Suzuki coupling of phenylboronic acid (**1**) and 4-bromoacetophenone (**2**) was used as the reaction catalyzed by $Pd(OAc)_2$ and carried out mechanochemically. KF-Al_2O_3 with a KF concentration of 32 wt % as inorganic support system allows for in situ generation of the base necessary for this type of reaction.[29]

Various types of ball mills have been described including (drum) ball mills, jet-mills, bead-mills, vibration ball mills, planetary ball mills, and horizontal rotary ball mills. All of these devices are based on the principle that a starting material is placed between two surfaces and crushed due to the impact or frictional forces that are caused by collisions between these surfaces. The various mills differ in the method by which these collision are caused. Besides the intensive grinding effect, the collisions lead to an energy transfer, which results in an increase of internal temperature and pressure. In general, ball mills are able to produce materials with a particle size of ≤100 nm.[22]

For our investigations we used the Planetary Micro Mill "Pulverisette 7" (classic line) by Fritsch. This apparatus can be applied for finest comminutions of hard and soft grinding materials (dry or in suspension) down to colloidal fineness, for mixing and perfect homogenization of emulsions and pastes. The grinding sample is comminuted by high-energy impacts from grinding balls and friction between balls and the grinding bowl wall. The areas of application of the "Pulverisette 7" (classic line) are in chemistry, biology, pharmacology, medicine, nuclear research, and engineering.[30] Different kinds of grinding materials (e.g. agate, stainless steel, tempered steel, zirconium oxide, hard metal tungsten carbide) can be chosen for the mechanochemical treatment. In the present study syntheses were carried out using the three different grinding materials (beaker and balls) listed in Table 1.

Within the limitations of these three combinations we covered the complete field of density and mass of the possible grinding materials. The mill charge has to have a lower hardness than the grinding material to hold abrasion on a low level. One can also combine various grinding materials, whereby the milling balls have to have a lower density than the grinding beaker. Thus, the possible combination of (tempered) steel beaker and agate milling balls was also used.[30] The grinding material combinations play an important role and influence the results of the other parameters investigated. Four different material combinations were used for the experiments herein: **SS**, **AA**, **ZZ**, and **SA**. The first letter of the abbreviation denotes the beaker material, whereas the second letter assigns the grinding ball material (Table 1).

Influence of Revolutions per Minute (rpm) and Grinding Material. Using different parameter settings in preliminary test reactions according to Scheme 1 and carried out in the Planetary Micro Mill, irregularities regarding the yield of 4-acetylbiphenyl (**3**) were observed. Inspired by these results investigations were conducted to determine possible parameters influencing the reaction in order to establish the optimum for the Suzuki model reaction.

First attention was focused on the revolutions per minute (rpm) parameter. In order to study the influence of rpm on the coupling of **1** and **2**, experiments with various grinding material combinations (cf. Table 1) at various rpm were performed. This allows for the investigation of two parameters (rpm and grinding material) simultaneously. Results are presented in Table 2.

As illustrated in Table 2 the experiments reveal that both rpm and grinding material have an influence on the yield of coupling product **3**. The best yield of **3** is obtained with the maximum rotation speed of 800 rpm (Table 2, entry 1) of the planetary ball mill used with the grinding material combination **SA**. Along with decreasing rpm the yields of **3** remain constant until 300 rpm, at which point a dramatic decrease in yield of **3** is observed, Table 2, entries 5−11. The influence of the various grinding material combinations plays an important role at lower

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Table 1. **Features of the three different grinding materials**

abbreviation	grinding material	main component	density (g/cm^3)	hardness (Mohs)	mass (g) of 1 MB[a]
S	steel (tempered)	Fe 87%, Cr 13%	7.9	∼8.0	13.96
A	agate	SiO$_2$	6.5	6.5−7	4.68
Z	zirconium oxide	ZrO$_2$	5.9	8.5	10.43

[a] MB = milling ball with a diameter of 15 mm.

Table 2. **Influence of revolutions per minutes (rpm) and grinding material on the yield of 4-acetylbiphenyl (3) from cross-coupling of phenylboronic acid (1) and 4-bromoacetophenone (2)[a]**

		yield [%][b] for different grinding materials			
entry	rpm	**SA**[c]	**SS**[c]	**AA**[c]	**ZZ**[c]
1	800	94	96	92	94
2	700	92	–	–	–
3	600	91	–	–	–
4	500	90	–	–	–
5	400	92	85	90	93
6	300	89	90	81	74
7	270	44	–	–	–
8	250	41	–	–	–
9	200	34	67	58	43
10	170	13	–	–	–
11	100	6	–	–	–

[a] Reaction conditions: **1** (6.19 mmol, 0.755 g), **2** (5 mmol, 1.016 g), Pd(OAc)$_2$ (0.18 mmol, 3.56 mol %) and KF-Al$_2$O$_3$ (5 g, 32 wt % of KF) were mixed in a grinding beaker with six milling balls (d = 15 mm) and milled for 10 min at the respective rpm. [b] Determined by GC analysis. [c] Material combination: **SA** = steel beaker/agate balls; **SS** = steel beaker/steel balls; **AA** = agate beaker/agate balls; **ZZ** = zirconium oxide beaker/zirconium oxide balls.

rpm. At 400 and 300 rpm (Table 2, entries 5, 6) a significant influence of the diverse grinding material combinations on the yield of **3** is not observed. For rpm's 170 and 100 rpm, which are below 200, only **SA** is tested (Table 2, entries 9−11), and a noticeable difference between the grinding material combinations is observed. The yields of **3** for experiments carried out at 200 rpm increase from 34 to 67% for the use of material combinations **SA** and **SS**, respectively, revealing a significant difference between **SA** and the other materials used caused by their different physical properties (density and mass).

Influence of milling time (t) and grinding material. Furthermore we studied the influence of milling time (t) on the yield of **3**. The favoured model reaction (Scheme 1) was carried out under variation of reaction time (t = 5, 10, 15 min) and rpm (200, 400, 800). Experiments were conducted investigating the influence of grinding material in combination with t at 400 rpm. In Table 3 the yield of **3** at three different t's and rpm's using **SA** as the grinding material are presented.

Table 3. **Influence of the milling time (*t*) on the yield of 4-acetylbiphenyl (3) in the solvent-free Suzuki−Miyaura reaction between phenylboronic acid (1) and 4-bromoacetophenone (2) in the presence of KF-Al$_2$O$_3$ catalyzed by Pd(OAc)$_2$ performed in a planetary ball mill with SA as the grinding material.[a,b]**

entry	rpm	t [min]	yield [%][b,c]
1	200	5	6
2	200	10	34
3	200	15	14
4	400	5	64
5	400	10	92
6	400	15	53
7	800	5	94
8	800	10	94
9	800	15	95

[a] Reaction conditions: **1** (6.19 mmol, 0.755 g), **2** (5 mmol, 1.016 g), Pd(OAc)$_2$ (0.18 mmol, 3.56 mol %) and KF-Al$_2$O$_3$ (5 g, 32 wt % of KF) were added in the grinding beaker with six milling balls (d = 15 mm) and milled for the respective time. [b] Determined by GC analysis. [c] Material combination: **SA** = steel beaker/agate balls.

Table 4. **Influence of the milling time and the grinding material on the yield of 4-acetylbiphenyl (3) in the solvent-free Suzuki reaction between phenylboronic acid (1) and 4-bromoacetophenone (2) with KF-Al$_2$O$_3$ catalyzed by Pd(OAc)$_2$ performed in a planetary ball mill[a]**

			yield [%][c] for different grinding materials		
entry	rpm	t [min]	**SS**[c]	**AA**[c]	**ZZ**[c]
1	400	5	91	78	95
2	400	10	85	90	93
3	400	15	79	76	95

[a] Reaction conditions: **1** (6.19 mmol, 0.755 g), **2** (5 mmol, 1.016 g), Pd(OAc)$_2$ (0.18 mmol, 3,56 mol %) and KF-Al$_2$O$_3$ (5 g, 32 wt % of KF) were added in the grinding beaker with six milling balls (d = 15 mm) and milled for the respective time. [b] Determined by GC analysis. [c] Material combination: **SS** = steel beaker/steel balls; **AA** = agate beaker/agate balls; **ZZ** = zirconium oxide beaker/zirconium oxide balls.

For all three milling times (5, 10, 15 min) the coupling reaction of **2** and **1** at 200 rpm yields **3** in poor amounts (Table 3, entries 1−3), whereas at 800 rpm the milling time seems to have no significant influence on the reaction at all, in case of material combination **SA**. After 5 min already nearly quantitative conversion was obtained (Table 3, entries 7−9). Experiments have shown that while increasing t the corresponding yield of **3** passes through maxima for 200 and 400 rpm, allowing the conclusion that there is a significant influence of t. Obviously, longer reaction times support the decomposition of the coupling product **3**. When the reaction was performed at 800 rpm, no clear difference in yield was observed while changing t. Reaction was nearly quantitative after a reaction time of 5 min. Due to the high rotation of the milling balls, sintering processes were observed, leading to a compact layer of the reaction mixture on the beaker walls, preventing further mixing of the reactants. Therefore, longer treatment in case of 800 rpm has no negative effect on the yield of **3**. When the Suzuki−Miyaura reaction is carried out with the combination **SA** good to excellent yields of **3** were obtained within 10 min (Table 3, entries 2, 5, 8), whereas reactions for 15 min led to decreased yields (Table 3, entries 3, 6).

In order to study the combined influence of grinding material and milling time (t) on the yield of **3** experiments at 400 rpm were carried out for various material combinations. Results are summarized in Table 4.

Revealing are the grinding material combinations **SS** and **ZZ** with which the reaction forms **3** in nearly quantitative amounts for t = 5 min. This is due to the high densities of the materials used which cause a better energy transfer to the milling

Table 5. **Influence of the number and size of milling balls with SA as grinding material on the yield of 3 in the solvent-free Suzuki reaction between phenylboronic acid (1) and 4-bromoacetophenone (2) in the presence of KF-Al_2O_3 catalyzed by $Pd(OAc)_2$ performed in a planetary ball mill**[a]

entry	number of milling balls	yield [%][b,c]	active surface area[d] [mm^2]	m[e] [g]
1	3	6	9134	14.04
2	4	14	9841	18.72
3	5	43	10548	23.4
4	6	92	11254	28.08
5	6[f]	6	8898	8.34

[a] Reaction conditions: **1** (6.19 mmol, 0.755 g), **2** (5 mmol, 1.016 g), $Pd(OAc)_2$ (0.18 mmol, 3,56 mol %) and KF-Al_2O_3 (5 g, 32 wt % of KF) were added in the grinding beaker with *n* milling balls ($d = 15$ mm) and milled at 400 rpm for 10 min. [b] Determined by GC analysis. [c] Material combination: **SA** = steel beaker/agate balls. [d] Active surface area = $\text{surface}_{\text{balls}} + \text{surface}_{\text{beaker}}$. [e] Mass of one agate ball (15 mm) = 4.68 g/mass of one agate ball (10 mm) = 1.39 g. [f] Milling balls with a diameter of 10 mm.

charge. At a milling time of 10 min (Table 4, entry 2) good to excellent yields were obtained in all cases. Further increase of the milling time up to 15 min (Table 4, entry 3) does not lead to an increase of the yield of 4-acetylbiphenyl. Hence the yields of **3** decrease with further milling time, especially at 15 min, the time of the mechanochemical treatment seems too long since decomposition of the products were observed (SS and AA as grinding materials). Independent from reaction time experiments with both beakers and balls prepared from zirconium oxide (**ZZ**) showed the best results. Generally, it seems that combination of balls and beakers from the same material is advantageous with respect to the formed coupling product **3**. Nevertheless, the reaction time influences the amount of **3** formed significantly for all material combinations. While the amount of coupling product seems to be independent from time at a high level for **SS** a maximum in yield at 5 min was observed. In case of both beakers and balls being agate **AA** the best results were obtained within 10 min. With the grinding material **ZZ** it seems that the milling time has no pronounced influence on the desired product **3**. Already a milling time of 5 min provides nearly quantitative yields.

Influence of Number and Size of the Milling Balls and Grinding Material. Studies were finally focused on the influence of the number and size of the milling balls in the beakers on the yield of **3**. Results for variation of the number of milling balls are listed in Table 5 with **SA** as the material. While parameters like *rpm*, *t*, and material combination were kept constant and the number of milling balls was changed, an increase in the yield of **3** was observed, corresponding to the number of balls used (Table 5, entries 1−4). This parameter directly influences the active surface area and the total mass of the milling balls, which are responsible for energy transfer. As a consequence more energy can be transferred to the mill charge, and higher yields of **3** are obtained when experiments were carried out with a higher number of spheres. According to the manufacturer the number of used milling balls for each grinding beaker should depend on the volume of the beaker, though the number is limited by the filling degree. A maximal volume of 2/3 for milling balls and mill charge are recommended. The remaining third of the beaker's volume is required for the trajectories of the milling balls; without a chance that these can move in the beaker, the energy transfer from the grinding material to the mill charge is poor.[31]

Besides the number of milling balls, the size of them influences the active surface area of the grinding material also. One obtains different results when using six milling balls with a diameter of 15 mm or six spheres with a diameter of 10 mm. A constant number of milling balls is given, but the smaller milling balls result in a reduced surface area of the grinding material. This causes less effective energy transfer to the mill charge and leads to inferior yields of **3**. Table 5, entries 4 + 5 summarize the results with different sizes of milling balls (10 or 15 mm). As a matter of fact high rpm leads to an increase in the amount of the desired **3**. But the decisive factor is the dimension of the active surface area (15 mm/6 balls = 11254 mm^2 vs 10 mm/6 balls = 8898 mm^2) of the grinding material as mentioned above. With 400 and 800 rpm and 6 milling balls with a diameter of 15 mm nearly quantitative yields were obtained.

The relationship between the energy (E_{kin}), the mass *m*, and the velocity ν of a milling ball is given approximately by the classical equation:

$$E_{kin} = \frac{m}{2}\nu^2$$

In other words the maximum relative velocity of the grinding material (balls) is the most determining factor contributing to the kinetic energy. In the case of the model "Pulverisette 7" used here, the parameter *rpm* plays the most important role. The mass *m* of the grinding material depends on the *size* and the *number* of the used milling balls. These parameters influence also the active surface area, which is important for the energy transfer during collision of the milling balls with the beaker walls and the mill charge.

With respect to the data listed in Table 1, it is obvious that steel balls as grinding material are more heavy-weight than zirconium dioxide or agate balls. In summary the following order of the investigated parameters regarding their positive influence of the desired product **3** is: rpm > milling time (*t*) > size of milling balls > number of milling balls > grinding material (**SS** ≈ **ZZ** > **AA** ≫ **SA**).

Conclusion

For all reactions carried out by mechanochemical treatment, it is important, that the reaction has to proceed in general. The handling of a high-energy ball mill to perform the mechanochemical treatment of chemical reactions is from the technical point of view very easy. It is also possible to carry out chemical reactions without the need of solvents. So one can avoid additional substrates for the performance of the Suzuki−Miyaura reaction to obtain high yields with a low energy consumption. *In toto* the process is sustainable. In addition to the common reaction conditions (e.g. the amount of substrate and catalyst) chemical reactions are in general influenced by technical variables of the used apparatus, for example performing microwave-assisted reactions, irradiation power of the microwave device being an important parameter. Within the scope

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(31) Retsch: Solutions in Milling and Sieving: http://www.retsch.de/en.

of the application of the Planetary Micro Mill “Pulverisette 7” (classic line) the following parameters were investigated: revolutions per minute (rpm), milling time (*t*), number and size of milling balls, and the grinding material. All investigated parameters showed to have an influence on the expected yield of **3**. When carrying out the Suzuki−Miyaura reaction with high rpm at adequate reaction times and grinding material one can obtain quantitative yields. The following order of the investigated parameters regarding their positive influence on the formation of **3** can be derived : rpm > milling time > size of milling balls > number of milling balls > grinding material.

Experimental Section

General remarks. All reagents were purchased from commercial suppliers and used without further purification. Reactions in a ball mill were conducted using a Fritsch Planetary Micro Mill model “Pulverisette 7” (classic line). The milling device consists of a main disk which can rotate at a speed of 100−800 rpm. For reason of balancing, two grinding beakers ($V = 45$ mL) with nearly identical weight have to be placed inside the ball mill. The grinding material was changed between experiments. Possible grinding material combinations were: **SA** = steel beaker/agate balls; **SS** = steel beaker/steel balls; **AA** = agate beaker/agate balls and **ZZ** = zirconium oxide beaker/zirconium oxide balls.

The purity of all compounds was checked by capillary gas chromatography. The analyses of the reaction mixtures were carried out by GC-FID (HP 5890 series II). GC-FID: HP 5, 30 m × 0,32 mm × 0,25 μm, H_2: 12 psi, program: 50 °C (hold for 3 min), 30 K min^{-1} up to 280 °C (hold for 5 min), injector temperature: 280 °C, detector temperature : 300 °C. GC-MSD: HP 5, 30 m × 0.32 mm × 0.25 μm, H_2: 12 psi, program: 50 °C (hold for 3 min), 30 K min^{-1} up to 280 °C (hold for 5 min), injector temperature: 280 °C, detector temperature : 300 °C. All product yields reported herein are GC determined yields and are comparable with the isolated ones. Nevertheless, the reported yields were corrected by means of different FID-sensitivity for substrate and product. The reported yields are mean values from at least two independent experimental runs.

NMR spectra were recorded with a Bruker Avance 200 MHz system in 5-mm tubes at room temperature. Measurements were carried out using $CDCl_3$ as solvent. IR spectra were measured with a Perkin-Elmer FT-IR spectrum 100 series device equipped with a universal ATR sampling accessory. Melting points were detected with a SMP10 from Stuart Scientific and are uncorrected.

Preparation of the KF-Al_2O_3 Support (32 wt % of KF). In a 250 mL Erlenmeyer flask, potassium fluoride (0.275 mol, 16 g) was dissolved in deionized water (25 mL) for the preparation of the support mixture. Subsequently, alumina (0.333 mol, 34 g) and further deionized water (25 mL) were added to the solution under slow stirring. Stirring was maintained for 1 h. The solvent was then evaporated in vacuo and the remaining residue stored in a desiccator over potassium hydroxide.

Typical Experimental Procedure. KF-Al_2O_3 (5 g, 32 wt % of KF), 4-bromoacetophenone (**2**, 5 mmol, 1.106 g), phenylboronic acid (**1**, 6.19 mmol, 0.755 g), $Pd(OAc)_2$ (0.18 mmol, 3.56 mol % 0.04 g) were added to the grinding beaker (volume: 45 mL) together with an adequate number of milling balls and placed inside the Planetary Micro Mill model “Pulverisette 7” (Fritsch GmbH). Another grinding beaker filled with a similar batch was mounted on the opposite position of the rotating disc. The mixtures were subsequently milled with the respective rpm and time. The crude product was immediately extracted with 2 mL of deionized water and 3 mL of ethyl acetate. A sample of the organic phase was analyzed using GC-FID.

Isolated yields: For various samples the crude product was washed from the grinding beaker with *tert*-butylmethylether (3 × 20 mL). The crude mixture was stirred into a round-bottom flask for 30 min and then filtered over a G3 frit. The residue was washed with *tert*-butylmethylether (3 × 20 mL). After removing the solvent the colorless crystalline product was analyzed by GC-FID, GC/MS, ^{1}H NMR and IR spectroscopy. The obtained GC yields are comparable with the isolated ones.

4-Acetylbiphenyl (3): isolated yield 97% based on 4-bromoacetophenone (800 rpm, 10 min, 6 milling balls with a diameter of 15 mm, **SA** as material combination); mp 116−117 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TSM): $\delta = 2.61$ (s, 3 H, CH_3), 7.43 (m, 3 H, CH), 7.63 (m, 4 H, CH), 8.00 (m, 2H, CH); IR (neat, ATR): $\tilde{\nu} = 3076$ (w, C−H), 3037 (w, C−H), 3002 (w, C−H), 2917 (w, C−H), 1675 (s, C=C), 1601 (m, C−C), 1451 (w, CH_3), 1424 (w, CH_3), 1403 (m, CH_3), 958 (m, =C−H), 833 (m, =C−H), 762 (s, =C−H), 688 cm^{-1} (m, =C−H); MS (70 eV): *m/z* (%): 197 (7) $[M + 1]^+$, 196 (49) $[M^+]$, 181 (100) $[M - CH_3]^+$, 152 (68) $[M - Ac]^+$, 76 (11) $[C_6H_4]^+$.

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