Investigating the Existence of Nonthermal/Specific Microwave Effects Using Silicon Carbide Heating Elements as Power Modulators

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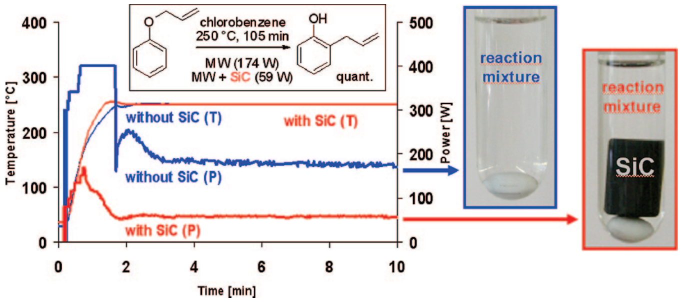

The use of passive heating elements made out of chemically inert sintered silicon carbide (SiC) allows microwave transparent or poorly absorbing reaction mixtures to be heated under microwave conditions. The cylindrical heating inserts efficiently absorb microwave energy and subsequently transfer the generated thermal energy via conduction phenomena to the reaction mixture. In the case of low to medium microwave absorbing reaction mixtures, the addition of SiC heating elements results in significant reductions (30−70%) in the required microwave power as compared to experiments performed without heating element at the same temperature. The method has been used to probe the influence of microwave power (electromagnetic field strength) on chemical reactions. Six diverse types of chemical transformations were performed in the presence or absence of a SiC heating element at the same reaction temperature but at different microwave power levels. In all six cases, the measured conversions/yields were similar regardless of whether a heating element was used or not. The applied microwave power had no influence on the reaction rate, and only the attained temperature governed the outcome of a specific chemical process under microwave conditions.

Introduction

The use of microwave energy to heat chemical reactions on a laboratory scale is growing at a rapid rate. In many instances, controlled microwave heating under sealed vessel conditions has been shown to dramatically reduce reaction times, increase product yields, and enhance product purities by reducing unwanted side reactions compared to conventional synthetic methods.[1,2] Regardless of the relatively large body of published work in this area, there is still considerable debate on the exact reasons why microwave irradiation is able to enhance chemical processes.[3] Today it is generally agreed upon that in many cases the observed enhancements in microwave-heated reactions are the result of purely thermal/kinetic effects, in other words, a consequence of the high reaction temperatures that can rapidly be attained when irradiating polar materials/reaction mixtures under sealed vessel conditions in a dedicated microwave

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reactor.[2] However, there is experimental evidence that certain chemical transformations when carried out at the same measured reaction temperature using either microwave or conventional heating lead to different results in terms of product distribution (selectivity) and yield.[3,4] These difficult to rationalize effects have been referred to as "specific" or "non-thermal" microwave effects.[3,5] Specific microwave effects, although still the result of a thermal phenomenon, cannot be duplicated by conventional heating and result from the uniqueness of the microwave dielectric heating phenomenon. In this category fall, for example, (i) the superheating effect of solvents at atmospheric pressure, (ii) the selective heating of, e.g., strongly microwave absorbing heterogeneous catalysts or reagents in a less polar reaction medium, and (iii) the elimination of wall effects caused by inverted temperature gradients.[5] In contrast, nonthermal microwave effects have been proposed to be the consequence of a direct interaction of the electric field with specific molecules in the reaction medium that is not related to a macroscopic temperature effect.[3,5] This interaction may lead to a decrease in activation energy or an increase in the pre-exponential factor in the Arrhenius law due to orientation effects of polar species in the electromagnetic field.[3] A similar effect may be observed for polar reaction mechanisms, where the polarity is increased going from the ground-state to the transition state, resulting in an enhancement of reactivity by lowering of the activation energy.[3]

Both specific and nonthermal microwave effects will be directly influenced by the electromagnetic (microwave) field strength. The stronger the microwave field, the more pronounced the observed microwave effect. These considerations have led to the notion that simultaneous external cooling of the reaction mixture (or maintaining subambient reaction temperatures) while heating by microwave irradiation can lead, in some cases, to an enhancement of the overall process.[6] Under the "heating-while-cooling" conditions, the reaction vessel is cooled from the outside by compressed air or with the aid of a cooling fluid while being irradiated by microwaves. This allows a higher level of microwave power to be directly administered to the reaction mixture, thereby potentially enhancing any specific or nonthermal microwave effects that are dependent on the electric field strength.[6] By monitoring internal reaction temperatures using fiber-optic probes and carefully adjusting the temperature and/or flow of the external cooling gas or liquid, experiments can be performed where at constant bulk reaction temperature distinctly different microwave power levels can be applied.[7–11] In some cases, significant improvements from applying an increased microwave power level have been reported using this technology,[7,8] while for other chemistry examples there was essentially no effect compared to conventional microwave processing or even thermal heating at the same temperature.[9–11]

As an alternative to the simultaneous cooling approach where higher power levels can be applied, any method that would allow a lower level of microwave power to be administered to the reaction mixture under otherwise identical conditions (temperature) would appear to be an additional useful probe for the investigation of specific and nonthermal microwave effects. In 2006, we introduced silicon carbide (SiC) cylinders as passive heating elements (PHEs) for microwave chemistry.[12] These chemically inert heating inserts efficiently absorb microwave energy and subsequently transfer the generated thermal energy via conduction phenomena to the reaction mixture.[12] The use of these passive heating elements allows otherwise microwave transparent or poorly absorbing reaction mixtures to be effectively heated under microwave conditions. Apart from this useful practical feature, we have realized at the time that chemical transformations using SiC cylinders often required only a fraction of the microwave magnetron output power as compared to experiments attempted without these passive heating elements.[12–15] While our previous investigations in this area were mainly concerned with the practical benefits[12,14] of using such heating aids in microwave synthesis, we are now focusing on the more fundamental role of applying these devices in microwave chemistry. It has occurred to us that the use of these strongly microwave absorbing additives represents an experimentally very easy way to modulate the electric field strength in a microwave-heated experiment performed at constant temperature. Therefore, comparison studies of microwave-heated reactions performed in the presence or absence of a SiC heating element seem to be an ideal tool to probe the existence of specific and nonthermal microwave effects. The results of our investigations involving a representative selection of six synthetic organic transformations are presented herein.

Results and Discussion

Experimental/Technical Considerations. In our previous work, we have employed sintered SiC cylinders as passive heating elements for microwave-assisted reactions involving low-absorbing solvents.[12] The cylindrical shape allows the use of these inserts in both single-mode and multimode microwave reactors utilizing the appropriate dedicated microwave vials.[12–15] For the present study, we have reevaluated the heating efficiency of various SiC materials using not only cylinders of two different sizes (10 × 18 mm, 4.35 g; 10 × 8 mm, 1.94 g) but also SiC powder and granules. Our comparison studies involved heating low microwave-absorbing toluene (tan δ 0.040)[16] together with varying amounts of SiC material in a standard 10 mL sealed Pyrex microwave vial at constant microwave magnetron output power using a single-mode microwave reactor. Based on

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(11) Herrero, M. A.; Kremsner, J. M.; Kappe, C. O. *J. Org. Chem.* **2008**, *73*, 36.

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comparative heating experiments involving the exact same amount (weight) of the three materials under otherwise identical conditions it became clear that the cylindrical form provided the highest heating efficiency (Figures S1−S3, Supporting Information). In particular, the larger 10 × 18 mm cylinder exhibited excellent heating characteristics and allowed a substantial reduction of the required microwave magnetron power (75%) compared to a run without SiC in a temperature controlled experiment (Figure S4, Supporting Information). In order to perform both sets of experiments (with and without PHE) at the same overall filling volume of the microwave vial (ca. 4 mL), the amount of reagent mixture was adjusted appropriately for runs utilizing the 10 × 18 mm SiC cylinder (volume reduced by 1.4 mL). Control experiments have shown that this reduction in reagent mixture had no effect on the required microwave power (Figure S20, Supporting Information).

An additional argument in favor of SiC cylinders is related to the stirring efficiency. A careful analysis of stirring efficiencies for all three forms of SiC suspended in organic solvents has demonstrated that it is rather difficult to stir larger amounts (>1 g) of both SiC powder and granules using the magnetic stirring system of the microwave instrument. In particular, the quite heavy granules can not be distributed in a homogeneous fashion across the whole volume of the reaction vessel. Indeed, if the amount of SiC material is too high the mobility of the stir bar is severely restricted and ultimately no magnetic stirring inside the microwave cavity occurs. The SiC cylinders are designed in such a way that stirring using a conventional magnetic stir bar placed below the cylinder is still possible, despite the considerable weight of the cylinder itself.[12] The stirring efficiency can be further improved by switching from conventional rod-shaped stir bars typically provided together with the microwave vials to an egg-shaped (oval) stirrer where the physical contact area with the SiC cylinder above is minimized. Using this type of stirrer even heterogeneous mixtures can be stirred in the presence of the SiC cylinder as demonstrated for systems containing both SiC powder and a 10 × 18 mm SiC cylinder. Due to the fact that efficient stirring in microwave-assisted transformations is essential,[11,17] we have also experimented with a two stirrer system where an additional stir bar is placed on top of the SiC cylinder (Figure S5, Supporting Information), although the stirring efficiency here will strongly depend on the effectiveness of the magnetic stirring system of the microwave reactor.

In order to get accurate and reliable temperature measurements during a microwave-heated experiment it is generally advised to use internal temperature probes.[10–12] In the presence of a SiC cylinder placed inside the 10 mL standard microwave vial this is generally not possible as there is not enough space to properly insert the probe into the center of the vessel. In a recent study, we have demonstrated, however, that external IR temperature sensors can be used as long as the sensor is correctly calibrated and the reaction mixture (homogeneous or heterogeneous) can be efficiently stirred.[11] A major concern connected to the use of external IR temperature monitoring was the possibility that the comparatively slow transfer of heat from the SiC to the surrounding solvent by conduction phenomena would lead to significant overheating of the strongly microwave absorbing SiC cylinder to temperatures above the temperature recorded by the external IR sensor. Indeed, employing a fiber-optic sensor in combination with a custom-made SiC cylinder containing an appropriate cavity for the internal probe, it was discovered that in the initial phase of microwave irradiation strong superheating at the surface of the SiC material occurred (Figure S6, Supporting Information). This effect was particularly pronounced when a high level of initial microwave power was used. Therefore, for all the chemistry examples involving SiC passive heating elements described in this manuscript, comparatively low levels of initial microwave power were applied (see below). This adjustment generally provided closely matching heating profiles for experiments performed with and without SiC PHEs.

Selection of Chemistry Examples. In our previous work, we have mainly focused on examples where heating to the desired target temperatures without SiC PHEs was not possible, and therefore, the use of a heating aid was mandatory.[12] This was mainly a consequence of the low overall microwave absorbance[16] of the reaction mixtures and of the high temperatures required (200−300 °C).[12,14] Clearly, under these conditions control experiments in the absence of SiC PHEs at the same reaction temperature cannot be performed. On the other hand, previous studies have shown that for microwave-assisted transformations performed in medium to high absorbing solvents such as, for example, dimethylformamide or methanol ($\tan \delta > 0.1$),[16] the effect of SiC PHEs on influencing heating rates and on the average power consumption is rather small.[12,13]

We have therefore considered chemical transformations as model systems where the overall loss tangent of the reaction medium is comparatively small, but the reaction can still be carried out under conventional microwave conditions using a high field-density 400 W single-mode microwave reactor. In this situation, the introduction of strongly microwave absorbing SiC material can be expected to lead to a significant reduction in microwave power and would therefore allow us to probe the existence of specific and nonthermal microwave effects. It should be emphasized that microwave effects have generally been proposed for nonpolar, low microwave-absorbing media (or solvent-free conditions).[3–5] In case of a high absorbing solvent, most of the microwave energy will in fact be absorbed by the solvent and converted into heat, thereby masking any potential nonthermal or specific microwave effect.[3,5]

The selected known chemistry examples span a range of different types of transformations. We were particularly interested to investigate the influence of microwave power on transition-metal-catalyzed cross-couplings and reactions that involve strongly microwave absorbing heterogeneous metal catalysts or reagents in order to probe effects resulting from the selective heating of those materials. Using conventional (reflux) conditions, all transformations are known to require many hours of heating in an oil bath. When sealed vessel microwave heating is applied at higher temperatures, these reactions are typically completed within a few minutes. In order to get reliable and meaningful data on conversions/yields for transformations performed with and without the SiC power modulators, we attempted to compare HPLC data sets for ca. 50%, 75%, and 100% conversion over a time period of 3−105

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[16] The ability of a specific solvent to convert microwave energy into heat at a given frequency and temperature is determined by the so-called loss tangent ($\tan \delta$), expressed as the quotient, $\tan \delta = \epsilon''/\epsilon'$. A reaction medium with a high $\tan \delta$ at the standard operating frequency of a microwave synthesis reactor (2.45 GHz) is required for good absorption and, consequently, for efficient heating. Solvents used for microwave synthesis can be classified as high ($\tan \delta > 0.5$), medium ($\tan \delta$ 0.1−0.5), and low microwave absorbing ($\tan \delta < 0.1$). See refs 1 and 2 for more details.

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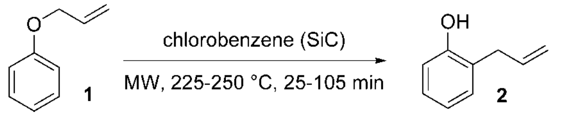
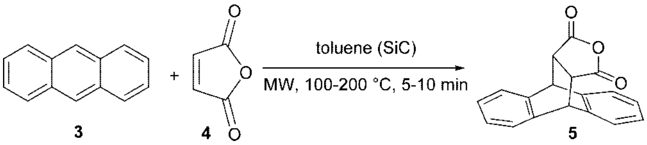
TABLE 1. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Claisen Rearrangement of Allyl Phenyl Ether (1)[a]



entry	SiC[b]	T[c](°C)	time[d] (min)	conv[e](%)	power[f](W)
1		250	25	54	190
2		250	50	75	171
3		250	105	96	174
4	Cyl	250	25	67	62
5	Cyl	250	50	90	60
6	Cyl	250	105	100	59
7		225	100	48	141
8	Cyl	225	100	57	53
9	Cyl(s)	250	25	62	124

[a] A solution of allyl phenyl ether (0.182 M) was heated in chlorobenzene under sealed vessel single-mode microwave irradiation (10 mL Pyrex reaction vessel, 4.0 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl: large 10 × 18 mm SiC cylinder (4.35 g), Cyl(s): small 10 × 8 mm SiC cylinder (1.95 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S7, Supporting Information). [e] Conversion based on HPLC monitoring at 215 nm. [f] Average magnetron microwave power output.

TABLE 2. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Diels−Alder Cycloaddition of Anthracene (3) with Maleic Anhydride (4)[a]



entry	SiC[b]	T[c](°C)	time[d] (min)	conv[e](%)	power[f](W)
1		200	5	(94)[g]	113
2	Cyl	200	5	(90)[g]	60
3		100	10	63	42
4	Cyl	100	10	67	17
5		100	5	58	41
6	Cyl	100	5	57	21

[a] A solution of anthracene and maleic anhydride (both 1.23 M) was heated in toluene under sealed vessel single-mode microwave irradiation (10 mL Pyrex reaction vessel, 4.4 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl: large 10 × 18 mm SiC cylinder (4.35 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S8, Supporting Information). [e] Conversion based on HPLC monitoring at 254 nm. [f] Average magnetron microwave power output. [g] Isolated yield.

min. On the basis of all these criteria, six representative examples for investigating the influence of microwave power on chemical transformations were chosen. These are discussed in detail in the following sections.

Claisen Rearrangement. In our 2006 publication, we investigated the Claisen rearrangement of allyl phenyl ether under microwave irradiation using toluene as a solvent.[12] While in the absence of a SiC heating element the required reaction temperature of 250 °C could not be reached and therefore no significant conversion to product was achieved, the rearrangement proceeded smoothly at 250 °C applying a 10 × 18 mm SiC PHE within less than 2 h.[12] In order to be able compare the outcome of this transformation with an experiment in the absence of a heating aid, the rearrangement has now been repeated using chlorobenzene as a solvent. Chlorobenzene is a significantly better microwave absorbing solvent than toluene (tan δ 0.101 versus 0.040),[16] and therefore, the reaction temperature of 250 °C can be attained also without a heating aid using a 400 W single-mode microwave reactor. Using the maximum available magnetron power of the instrument (400 W), the reaction mixture was heated to 250 °C within 110 s (8−9 bar). The conversion to product was determined by HPLC analysis after 25, 50, and 105 min in three separate irradiation experiments and produced values comparable to our previously published data using toluene as solvent (Table 1).[12] Repeating the experiment in the presence of a 10 × 18 mm SiC cylinder, we noticed that due to intense superheating of the surface of the SiC material (cf. Figure S6, Supporting Information) it was necessary to limit the initial magnetron output power to below 80 W.[18] Under these conditions the heating profile of the bulk reaction mixture as monitored by the external IR sensor was similar to the experiment performed without the SiC PHE using the full 400 W microwave power of the instrument (Figure S7, Supporting Information). Importantly, the overall microwave power used in the two experiments was strikingly different: while in rearrangements at 250 °C without SiC ca. 170−190 W magnetron output power had to be employed, the identical experiments with SiC consumed only ca. 60 W (Table 1, compare entries 1−3 with 4−6). This represents a reduction in the applied microwave power by ca. 70%.

Looking at the conversions in the Claisen rearrangement, we noticed a significant difference in the measured values at 25, 50, and 105 min. Interestingly, the conversions achieved with less microwave power (with SiC PHE) were somewhat higher than the measured conversions using higher microwave power levels (without SiC). We ascribe these differences to the very efficient heating of the large SiC cylinder (Figure S3, Supporting Information), leading essentially to a higher temperature on the surface of the SiC than recorded by the external IR temperature sensor (cf. Figure S6, Supporting Information). The differences in the observed conversions between experiments with and without SiC cylinders were less pronounced (<10%) when the reaction was performed either at a lower temperature (Table 1, entries 7 and 8) or when using the smaller 10 × 8 mm SiC cylinder (compare entries 1 and 9). We therefore believe that in this particular case the differences observed between experiments carried out in the presence/absence of the SiC cylinders are due to the strong superheating of SiC at the relatively high temperature of 250 °C (see below).[11]

Diels−Alder Reaction of Anthracene with Maleic Anhydride. The second model reaction performed for the purpose of studying the effect of different levels of microwave power involved the Diels−Alder cycloaddition of anthracene with maleic anhydride in toluene (Table 2). On the basis of our previous experience with this transformation under both microwave and oil bath conditions, it was apparent that complete conversion for this cycloaddition can be obtained within 2−5 min at temperatures around 200 °C using equimolar amounts of diene and dienophile.[15] Although, as already stated above,

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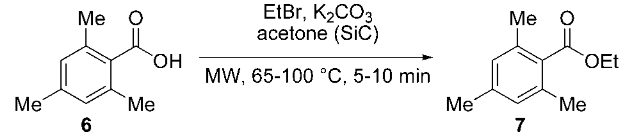
(18) This is achieved by using the instrument setting "very high absorbing" or "high absorbing" on the Biotage Initiator 2.0 model. For other instruments, the microwave output power can be manually adjusted to the desired level. Using higher power settings in some cases led to temperature overshoots and to a deformation of the Teflon-coated stir bars at the SiC cylinder contact surface indicating temperatures >270 °C at the SiC surface. SiC is known to be a very strong microwave absorbing material:(a) Meredith, R. *Engineers' Handbook of Industrial Microwave Heating*; The Institution of Electrical Engineers: Stevenege, U.K., 1998. (b) Baeraky, T. A. *Egypt. J. Sol.* **2002**, *25*, 263.

toluene itself is a weakly microwave absorbing solvent (tan δ 0.040),[16] the fact that the cycloaddition is executed under fairly concentrated conditions (1.23 M for both the diene and the dienophile) allows the overall reaction mixture to be heated to 200 °C by single-mode microwave irradiation within 1 min (Figure S8, Supporting Information). This is in stark contrast to the Claisen rearrangement example discussed above where the more dilute solution of allyl phenyl ether in toluene (0.182 M) proved very difficult to heat under microwave conditions,[12] or to the attempt to heat pure toluene using the same instrument (Figure S4, Supporting Information). Apparently, in the case of the Diels−Alder reaction the dissolved starting materials, in particular the polar maleic anhydride, contribute significantly to the overall microwave absorbance characteristics of the reaction mixture.

As shown in Table 2, full conversion with ca. 90% isolated product yield was obtained after 5 min at 200 °C (8−9 bar), regardless of whether the reaction was carried out in the presence or absence of the heating element. The required magnetron output power was reduced in half from 113 to 60 W using the SiC PHE. In order to obtain more reliable intermediate data points, the reaction temperature was reduced to 100 °C and the conversion measured by HPLC analysis. A comparison of the 5 and 10 min data points at 100 °C (Table 2, entries 3−6) demonstrates that, while significantly different levels of microwave power are used in the two types of experiments, the conversion is not influenced by the amount of the applied microwave power. It is only the reaction temperature that governs the progress of this transformation. Similarly, it appears to be irrelevant if the temperature of the reaction mixture is raised by direct coupling of microwave energy with one of the polar substrates (here maleic anhydride) or with the solvent and/or passive heating element. At the lower temperatures and microwave powers used for this transformation in comparison to the Claisen rearrangement described above, the potential overheating of the SiC cylinder itself is apparently not a significant factor.

Esterification of 2,4,6-Trimethylbenzoic Acid. In order to investigate the behavior of reaction mixtures that are not completely homogeneous using the SiC PHE technology, our next example involved the esterification of 2,4,6-trimethylbenzoic acid with ethyl bromide and potassium carbonate base in acetone. At the reflux temperature of the solvent (56 °C), the esterification of this sterically demanding acid typically requires many hours for completion[19] but can be performed within a few minutes under microwave conditions.[20] Best results in this esterification under microwave conditions were achieved using dry acetone as solvent and finely ground anhydrous potassium carbonate as base (1.80 equiv). At 100 °C under sealed vessel microwave conditions (ca. 3.5 bar), full conversion and quantitative isolated yields of the corresponding ethyl ester were obtained after 10 min (Table 3). Again, in order to get more reliable intermediate data points, the reaction temperature and time was reduced. The comparison of HPLC conversions obtained in the two types of experiments demonstrated again that there is no influence of the microwave power on the conversion in this process (Table 3, entries 3−8). Using the egg-shaped stirrer (Figure S5a, Supporting Information), agitation of the heterogeneous mixture containing 250 mg of potassium carbonate in combination with the SiC cylinder was unproblematic. It should be noted that solid anhydrous potassium carbonate, while being a heterogeneous component in this transformation, does not absorb microwave irradiation (cf Figure S17, Supporting Information).

TABLE 3. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Esterification of 2,4,6-Trimethylbenzoic Acid (6) with Bromoethane[a]



entry	SiC[b]	T[c] (°C)	time[d] (min)	conv[e] (%)	power[f] (W)
1		100	10	100 (92)[g]	61
2	Cyl	100	10	100 (94)[g]	44
3		90	5	93	62
4	Cyl	90	5	93	37
5		80	5	56	60
6	Cyl	80	5	53	39
7		65	5	17	48
8	Cyl	65	5	17	29

[a] A mixture of 2,4,6-trimethylbenzoic acid (0.256 M), ethyl bromide (2.0 equiv), and anhydrous potassium carbonate (1.81 equiv) was heated in dry acetone under sealed vessel single-mode microwave irradiation (10 mL Pyrex reaction vessel, 4.0 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl(l): large 10 × 18 mm SiC cylinder (4.35 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S9, Supporting Information). [e] Conversion based on HPLC monitoring at 215 nm. [f] Average magnetron power output. [g] Isolated yield.

Aromatization of Dihydropyridine 8 with Manganese Dioxide. The microwave-assisted oxidation/aromatization of Hantzsch-type dihydropyridines to the corresponding pyridines with manganese dioxide has recently been reported.[21] Virtually quantitative yields can be obtained in 1 min by sealed vessel microwave irradiation of dihydropyridine **8** in methylene chloride in the presence of manganese dioxide (10 equiv) at 100 °C.[21] We were particularly interested in this process since manganese dioxide is a strongly microwave-absorbing material[22] which can be expected to be selectively heated to very high temperatures in nonpolar, low microwave-absorbing solvents such as methylene chloride (tan δ 0.042).[16] In fact, there is clear evidence for a related oxidation process involving chromium dioxide in toluene in which selective heating of the metal oxide to temperatures higher than the bulk temperature of the solvent will occur by microwave irradiation.[23] The realization of this “specific microwave effect” may lead to faster overall reactions under microwave conditions compared to a conventionally heated process at the same measured bulk temperature.[5] The presence of the strongly microwave absorbing SiC should have a distinct influence on these transformations since selective heating of the manganese dioxide reagent under these conditions will be minimized.

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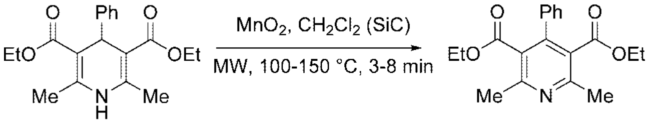
TABLE 4. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Oxidation of a Dihydropyridine 8 with Manganese Dioxide[a]



8 **9**

entry	SiC[b]	T[c] (°C)	time[d] (min)	conv[e] (%)	power[f] (W)
1		150	8	100 (99)[g]	118
2	Cyl	150	8	100 (99)[g]	52
3		120	3	86	97
4	Cyl	120	3	86	48
5		100	5	65	65
6	Cyl	100	5	64	39

[a] A mixture of dihydropyridine **8** (0.1 M) and manganese dioxide (2.5 equiv) was heated in methylene chloride under sealed vessel single-mode microwave irradiation (10 mL reaction vessel, 4.0 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl: large 10 × 18 mm SiC cylinder (4.35 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S10, Supporting Information). [e] Conversion based on HPLC monitoring at 215 nm. [f] Average magnetron microwave power output. [g] Isolated yield.

In order to obtain suitable settings for a kinetic investigation, the original conditions for the Hantzsch dihydropyridine oxidation[21] were modified by reducing the amount of manganese dioxide from 10 equiv to 2.5 equiv. Using a reduced amount of oxidation reagent, the aromatization of dihydropyridine **8** was completed after 8 min at 150 °C (17 bar) (Table 4). Performing the reaction at a lower temperature or for a shorter time period allowed us to obtain intermediate data points in the 60−80% conversion range. The HPLC conversions for experiments carried out with or without SiC were again virtually identical (Table 4, entries 3−6). This was somewhat surprising since due to the low tan δ value of methylene chloride, the addition of the strongly microwave-absorbing SiC heating aid resulted in a ca. 50% reduction in the required microwave power in all cases (Table 4). Apparently, the applied microwave power had no effect on the oxidation reaction, and it therefore appeared that selective heating (superheating) of the strongly microwave absorbing manganese dioxide by microwave irradiation did not occur.

In order to probe the microwave absorbance characteristics of manganese dioxide in more detail, we have performed some additional experiments. Applying a microwave transparent quartz reaction vessel[24] in combination with a fully microwave transparent solvent such as carbon tetrachloride,[16] it was demonstrated that manganese dioxide in fact is a strongly microwave-absorbing solid. Accurately monitoring the temperature with a fast-responding internal fiber-optic probe,[11] it was shown that a sample of pure carbon tetrachloride solvent cannot be heated under microwave irradiation conditions, even by applying 150 W of magnetron output power in a single-mode reactor.[12] However, in the presence of small amounts of manganese dioxide (1.5% w/w), the bulk temperature of the stirred mixture was raised significantly by ca. 30 °C after less than 4 min of irradiation (Figure S11, Supporting Information). These data confirm the strong microwave absorbing character of manganese dioxide and suggest that the temperature of the manganese dioxide particles under microwave irradiation conditions must be significantly higher than the measured bulk temperature of the mixture.

However, when switching from the somewhat artificially created microwave transparent environment to the actual reaction mixture (Pyrex vessel, methylene chloride solvent), the selective heating of the manganese dioxide was not noticeable any more and no difference in temperature rise between a heating experiment in the presence or absence of the metal oxide was seen (Figure S12, Supporting Information). It appears that the comparatively large quantity of solvent, even though it is comparatively low microwave absorbing (tan δ 0.042),[16] overrides the potential for selective heating of the manganese dioxide reagent. In addition, the use of a conventional Pyrex reaction vessel which absorbs part of the microwave irradiation probably has a significant effect as well.[12,24] Therefore, no "specific microwave effect" is seen here, and the addition of the strongly absorbing SiC has no effect on these transformations.

Heck Arylation of 4-Iodobenzonitrile with Acrylic Acid Catalyzed by Palladium-on-Charcoal. Microwave-assisted transformations employing immobilized, heterogeneous transition-metal catalysts are becoming increasingly important in organic synthesis.[8,25,26] As the metal catalysts and/or the supports used are typically very strongly microwave absorbing, the possibility for selective heating of the catalyst clearly exists.[26] In the context of transition-metal-catalyzed carbon−carbon bond-forming reactions and related coupling processes, palladium-on-charcoal (Pd/C) is one of the most often used heterogeneous catalysts, and numerous examples of successful microwave-assisted processes have been described in the literature.[1,2,25] Importantly, there are reports that suggest that the progress of chemical transformations involving Pd/C or related immobilized Pd species using microwave irradiation can be enhanced by simultaneous cooling of the reaction mixture compared to conventional microwave processing.[8] As outlined above, simultaneous cooling will allow more microwave energy to be delivered to the reaction mixture at the same bulk temperature. We were therefore interested to see how using SiC as power modulator would influence the outcome of Pd/C-catalyzed transformations under microwave conditions.

Based on our previous experience with microwave-assisted Heck arylations involving acrylic acid and Pd/C,[27] we have selected the arylation of 4-iodobenzonitrile with acrylic acid as a model reaction (Table 5). Using acetonitrile as solvent (tan δ 0.062)[16] and triethylamine as base, the Heck arylation could be successfully completed within 5 min at 155 °C using ca. 0.7 mol % of an optimized Pd/C catalyst.[28] By decreasing the reaction temperature to 140−150 °C, conversions in the 40−60% region were obtained suitable for our comparison studies. Again, the presence of the SiC heating element proved to have no effect on the achieved conversions (Table 5, entries 3−6), despite of the fact that in all experiments applying the

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[24] The commonly used borosilicate microwave reaction vials used in single-mode reactors do absorb a significant amount of microwave energy (borosilicate: tan δ 10×10^{-4}) as compared to quartz reaction vessels (quartz: tan δ 0.6×10^{-4}). (a) Bogdal, D.; Prociak, A. *Microwave-Enhanced Polymer Chemistry and Technology*; Blackwell Publishing: Oxford, UK, 2007.

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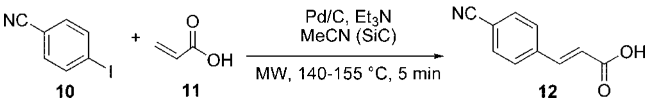
TABLE 5. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Heck Arylation of 4-Iodobenzonitrile (10) with Acrylic Acid (11)[a]



entry	SiC[b]	T[c] (°C)	time[d](min)	conv[e] (%)	power[f](W)
1		155	5	98 (80)[g]	109
2	Cyl	155	5	98 (80)[g]	54
3		150	5	64	113
4	Cyl	150	5	66	56
5		140	5	44	83
6	Cyl	140	5	41	50

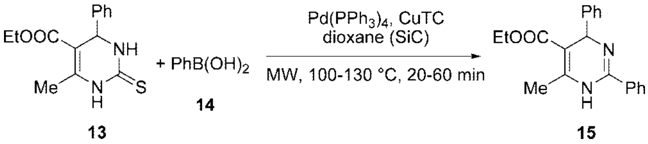
[a] A mixture of 4-iodobenzonitrile (**10**) (0.125 M), acrylic acid (**11**) (1.5 equiv), triethylamine (1.5 equiv), and 5% Pd/C (0.66 mol%) was heated in acetonitrile under sealed vessel single-mode microwave irradiation (10 mL reaction vessel, 4.0 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl: large 10 × 18 mm SiC cylinder (4.35 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S13, Supporting Information). [e] Conversion based on HPLC monitoring at 215 nm [f] Average magnetron microwave power output. [g] Isolated yield of cinnamic acid **12** after extractive workup.

PHE ca. 50% less microwave power was used to heat the reaction mixture to the same target temperature (Table 5).

Similar to the experiments for manganese dioxide described above, we were interested in evaluating if Pd/C indeed could be selectively heated by microwave irradiation. Figure S14 (Supporting Information) demonstrates that even small amounts of the strongly absorbing Pd/C can raise the bulk temperature of suspensions of the catalyst in carbon tetrachloride significantly (quartz vessel). The temperature of the Pd/C catalyst under these conditions must be significantly higher than the monitored bulk mixture temperature. Experiments using different power levels further demonstrated that the more microwave energy was applied, the faster the heating of the carbon tetrachloride occurred (Figure S15, Supporting Information). Again, for the actual reaction mixture in a Pyrex vessel containing several other microwave-absorbing components (acetonitrile, triethylamine, acrylic acid) an effect derived from selective heating of Pd/C is not observable (Figure S16, Supporting Information) and has apparently no influence on the reaction rate as the experiments with SiC PHEs indicate.

Cross-Coupling of Dihydropyrimidine-2-thione 13 with Phenylboronic Acid (14). The final example in this series is based on our recently reported Liebeskind−Srogl-type carbon−carbon cross-coupling of dihydropyrimidine-2-thione **13** with phenylboronic acid (**14**) (Table 6).[29] This transition-metal-catalyzed process is catalytic in Pd(0) and stoichiometric in Cu(I), requiring >1 equiv of Cu(I)−thiophene-2-carboxylate (CuTC) as a cofactor. This rather complex transformation was selected since it involves a homogeneous Pd catalyst, a heterogeneous cofactor (CuTC), and a microwave transparent solvent (dioxane).[16] Using the carbon tetrachloride/quartz vessel method, it was established that solid CuTC itself (like solid potassium carbonate, see above) does not absorb microwave energy (Figure S17, Supporting Information). On the other hand, solutions/suspensions of the $Pd(PPh_3)_4$ catalyst in carbon tetrachloride proved to be rather strongly microwave absorbing demonstrating that the homogeneous catalyst itself is able to convert microwave energy into heat (Figure S17, Supporting Information). Similar to the arguments made above for the heterogeneous catalyst Pd/C, it can be argued that for a homogeneous system containing a strongly microwave absorbing substance—here the $Pd(PPh_3)_4$ catalyst—selective heating of this material may occur. However, the existence of such “molecular radiators” is experimentally difficult to prove, and it would have to be assumed that the energy of these “hot” molecules would be instantaneously dissipated to the surrounding “cooler” solvent molecules.[30] In any event, it appears that under the reaction conditions using a Pyrex vessel, any selective heating of the Pd(0) catalyst is masked by the other absorbing components in the reaction mixture (Figure S18, Supporting Information).

TABLE 6. Comparison of Microwave Heating in the Presence and Absence of SiC Passive Heating Aids for the Cross-Coupling of Dihydropyrimidine-2-thione 13 with Phenylboronic Acid (14)[a]



entry	SiC[b]	T[c] (°C)	time[d] (min)	conv[e] (%)	power[f] (W)
1		130	60	96	102
2	Cyl	130	60	97	36
3		120	20	83	108
4	Cyl	120	20	86	33
5		100	20	52	98
6	Cyl	100	20	57	27

[a] A mixture of dihydropyrimidine-2-thione **13** (0.0625 M), phenylboronic acid (**14**) (1.5 equiv), Cu(I)-thiophene-2-carboxylate (3.0 equiv), and $Pd(Ph_3)_4$ (3.0 mol %) was heated in anhydrous dioxane under Ar under sealed vessel single-mode microwave irradiation (10 mL reaction vessel, 4.0 mL overall volume, magnetic stirring). For further details, see the Experimental Section. [b] Cyl: large 10 × 18 mm SiC cylinder (4.35 g). [c] External IR temperature monitoring. [d] Reaction times refer to hold times at the set reaction temperature, not to total irradiation times (Figure S19, Supporting Information). [e] Conversion based on HPLC monitoring at 215 nm. [f] Average magnetron microwave power output.

Optimization studies have shown that, similar to our original method using THF as solvent,[29] close to full conversion in this carbon−carbon coupling protocol can also be achieved at 130 °C within 60 min in dioxane using 3.0 mol % of $Pd(PPh_3)_4$, 3.0 equiv of CuTC cofactor, and 1.5 equiv of phenylboronic acid (**14**) (Table 6). Appropriate reductions of reaction time and temperature made data points in the 50−80% conversion range available. Applying the SiC passive heating elements led to a considerable reduction in the required magnetron microwave output power (ca. 70%) but otherwise provided rather similar conversion rates in comparison to experiments without SiC (Table 6, entries 3−6). This again demonstrates that only the bulk temperature of the reaction mixture determines the rate of this cross-coupling reaction. The applied microwave power has no influence. In this particular case, this was expected since a previously conducted control experiment using conventional heating in a sealed tube at the same internal reaction temperature has already demonstrated that in cross-couplings of this type no “special” or “nonthermal” microwave effect exists.[29] The rate enhancements seen on going from a reflux experiment in

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(29) Prokopcová, H.; Kappe, C. O. *J. Org. Chem.* **2007**, *72*, 4440.

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THF at 65 °C to a microwave experiment in a sealed tube at 130 °C (16 h vs 30 min) are only due to the increased reaction temperature and are therefore purely thermal.[29]

Conclusion

In this paper, we have evaluated the performance of SiC passive heating aids as power modulators for microwave-assisted chemical transformations. In cases where the reaction mixture is low to medium microwave absorbing, the addition of the strongly microwave absorbing SiC heating elements has led to significant reductions (30−70%) in the required microwave power in temperature-controlled experiments. Despite the lower levels of applied microwave power used at the same reaction temperature, no influence on the conversion for all six chemical transformations has been observed. This clearly demonstrates that for the studied examples it is only the reaction temperature that influences the rate of these reactions and that the level of applied microwave power is not a contributing factor. Importantly, our chosen transformations included cases where selective heating (superheating) of strongly microwave absorbing heterogeneous reagents (manganese dioxide) or catalysts (palladium-on-charcoal) could be expected, in addition to an example that involved a strongly microwave-absorbing homogeneous transition metal catalyst [$Pd(PPh_3)_4$] that could act as a "molecular radiator". Although the selective heating by microwave irradiation of these materials was experimentally confirmed using fully microwave transparent solvents and reaction vessels, in a real case chemical reaction scenario involving nontransparent solvents and other absorbing substances, the selective heating of these components was not observed.

In this context, the possibility of adding SiC heating aids represents an experimentally very simple way to modulate (reduce) the power in a microwave-heated reaction, and is therefore complementary to the concept of "heating-while cooling" where the applied microwave power can be increased by simultaneous cooling of the reaction vessel.[6] While the simultaneous cooling approach has to rely on the use of internal temperature probes[7−11] and is more suitable for low temperature studies (0−100 °C), the SiC method can be performed using standard external IR sensors in conventional single-mode microwave reactors and has proven useful to probe microwave chemistry, the influence of microwave power and the occurrence of microwave effects in the high-temperature region (100−250 °C).

It may be argued that the use of SiC heating aids to some extent mimics an oil bath experiment since a significant amount of microwave energy will be absorbed by the heating element immersed in the reaction vial and not by the reaction mixture itself. In particular for the large 10 × 18 mm SiC cylinder (4.33 g) used in combination with a standard 10 mL microwave vial (Figure S5, Supporting Information), most of the microwave energy will probably be absorbed by the SiC which will subsequently transfer the generated heat via conduction phenomena to the reaction mixture. This means that most of the "microwave heating" using this technology essentially occurs by conventional conduction and convection principles, similar to an oil bath experiment generating a hot surface and temperature gradients. While properly conducted comparison experiments between microwave and oil bath heating can be quite elaborate,[10,11] the use of SiC passive heating elements is experimentally comparatively simple and may provide a rapid indication if the observed effects are thermal in nature or do involve the microwave field.

Experimental Section

Microwave Irradiation Experiments. Heating curves of solvents were recorded using single-mode microwave reactors (Discover Labmate, CEM Corp. or Initiator Eight EXP 2.0, Biotage AB) using either custom-made high purity quartz or standard Pyrex vessels (capacity 10 mL) as appropriate.[12] The temperature profiles for solvents were generally monitored with a fiber-optic probe (Opsens) inserted into the reaction vessel protected by a sapphire or quartz immersion well.[10,11] Chemical transformations in the presence of SiC heating materials were performed in an Initiator Eight EXP instrument in the standard configuration (temperature control, external IR temperature sensor, fixed hold time, sealed 10 mL Pyrex vessels). For those experiments, the power level in the Biotage software was set to "very high" or "high", whereas a "normal" power setting was used for experiments without SiC. In order to perform both sets of experiments (with and without PHE) at the same overall filling volume of the microwave vial (ca. 4 mL), the amount of reagent mixture was adjusted appropriately for runs utilizing the 10 × 18 mm SiC cylinder (volume reduced by 1.4 mL). The average microwave magnetron power used by the system was calculated from the time, temperature, and power curves downloaded from the instrument using an appropriate algorithm.

Claisen Rearrangement of Allyl Phenyl Ether (1) (Table 1, Entry 6). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 0.065 mL (64 mg, 0.473 mmol) of allyl phenyl ether (**1**) and 2.6 mL of chlorobenzene. After the vessel was sealed, the sample was irradiated for 105 min at 250 °C applying the "very high" absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring the conversion by HPLC, an aliquot of the reaction mixture was removed and diluted with acetonitrile. This diluted solution was then subjected to HPLC to determine the conversion (see Table 1). For preparative isolation, evaporation of the solvent under reduced pressure resulted in 64 mg (quantitative, HPLC homogeneity at 215 nm: >95%) of 2-allylphenol (**2**) as a yellowish oil: ^1H NMR (360 MHz, $CDCl_3$) δ 3.43 (d, $J = 6.3$ Hz, 2 H), 4.95 (s, 1H), 5.16−5.21 (m, 2 H), 5.99−6.10 (m, 1 H), 6.82−6.93 (m, 2 H), 7.12−7.18 (m, 2H). The NMR data of this material were in accordance with our previously reported spectrum.[12]

Diels−Alder Cycloaddition of Anthracene (3) and Maleic Anhydride (4) (Table 2, Entry 2). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 660 mg (3.7 mmol) of anthracene (**3**), 365 mg (3.7 mmol, 3.7 mmol) of maleic anhydride (**4**), and 3 mL of toluene. After the vessel was sealed, the sample was irradiated for 5 min (fixed hold time) at 200 °C by applying the "high" absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring the conversion by HPLC the reaction mixture was diluted with acetone until it became totally homogeneous. This diluted solution was then subjected to HPLC analysis to determine the conversion (Table 2). For preparative isolation, the (undiluted) reaction mixture was allowed to stand in a refrigerator (4 °C) for 3−4 h to enable complete crystallization of the cycloaddition product (**5**). The precipitated product was filtered and washed with cold toluene, and subsequently dried overnight at 50 °C to provide 920 mg (90%) of pure cycloadduct **5** as colorless solid: mp 263−265 °C (lit.[31] mp 260.5−263.0 °C); ^1H NMR (360 MHz, DMSO) δ 3.65 (s, 2H), 4.87 (s, 2H), 7.16−7.48 (m, 8H). All spectral and physical properties were identical to those reported in the literature.[31]

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Esterification of 2,4,6-Trimethylbenzoic Acid (6) with Ethyl Bromide (Table 3, Entry 2). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 105 mg (0.64 mmol) of 2,4,6-trimethylbenzoic acid (**6**), 160 mg (1.16 mmol, 1.81 equiv) of finely ground anhydrous potassium carbonate, 95 μL (1.3 mmol, 2 equiv) of bromoethane, and 2.5 mL of acetone. After the vessel was sealed, the sample was irradiated for 10 min (fixed hold time) at 100 °C by applying the “high” absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring the conversion by HPLC the contents of the vial were diluted with 80 mL of acetone and subsequently acidified with 4 mL of 1 M HCl. The resulting clear solution was used directly for determining the conversion by HPLC (Table 3). Alternatively, for preparative isolation, the solvent was evacuated from the reaction mixture and the residue partitioned between water and methylene chloride. The organic phase was dried over sodium sulfate and evaporated to produce 107 mg (94%) of ester **7** as a clear oil. The purity of this product (^{1}H NMR and HPLC at 215 °C) was >99%: ^{1}H NMR (360 MHz, DMSO) δ 1.28 (t, J = 7.1 Hz, 3H), 2.20 (s, 6 H), 2.23 (s, 3 H), 4.27−4.33 (q, J = 7.1 Hz, 2 H), 6.88 (s, 2 H). All spectral and physical properties were identical to those reported in the literature.[32]

Oxidation of a Dihydropyridine (8) with Manganese Dioxide (Table 4, Entry 2). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 86 mg (0.26 mmol) of dihydropyridine **8**, 57 mg (0.65 mmol, 2.5 equiv) of fine MnO_2 powder, and 2.6 mL of methylene chloride. After the vessel was sealed, the sample was irradiated for 8 min (fixed hold time) at 150 °C by applying the “high” absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring the conversion an aliquot of the reaction mixture was removed and after filtration directly subjected to HPLC analysis (Table 4). For preparative isolation, the reaction mixture was filtered through Celite, washed with 5 mL of methylene chloride, and evaporated to produce 84 mg (99%) of aromatized product **9** as a colorless solid, mp 63−64 °C (lit.[21] mp 63−64 °C). The purity of this material (^{1}H NMR and HPLC) was >97%: ^{1}H NMR (360 MHz, DMSO) δ 0.83 (t, J = 7.1 Hz, 6H), 2.49 (s, 6 H), 3.97 (q, J = 7.1 Hz, 4 H), 7.14−7.17 (m, 2H), 7.42−7.44 (m, 3H). All spectral and physical properties were identical to those reported in the literature.[21]

Heck Arylation of 4-Iodobenzonitrile (10) with Acrylic Acid (11) (Table 5, Entry 2). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 4.6 mg (0.00216 mmol, 0.66 mol%) of Pd/C (Degussa type E105CA/W, 5% Pd, Aldrich 643181), 68 μL (0.48 mmol, 1.5 equiv) of triethylamine, and 2.6 mL of acetonitrile and stirred for 10 min. After the addition of 75 mg (0.325 mmol) of 4-iodobenzonitrile (**10**) and 34 μL (0.48 mmol, 1.5 equiv) of acrylic acid (**11**), the vessel was sealed and irradiated for 5 min (fixed hold time) at 155 °C by applying the “high” absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring the conversion by HPLC the contents of the vial were dissolved in 30 mL of acetone/water (5:1) and after filtration injected directly into the HPLC instrument. For preparative isolation, the crude reaction mixture was evacuated and the residue partitioned between water and ethyl acetate. The filtered organic layer was dried over sodium sulfate and concentrated to furnish 45 mg (80%) of cinnamic acid **12** as a colorless solid, mp 255−260 °C (lit.[33] mp 255−256 °C). The purity of the product (^{1}H NMR and HPLC at 215 °C) was >95%: ^{1}H NMR (360 MHz, DMSO) δ 6.70 (d, J = 16.1 Hz, 1H), 7.64 (d, J = 16.1 Hz, 1H), 7.86−7.91 (m, 4H), 12.64 (s, 1H). All spectral and physical properties were identical to those reported in the literature.[33]

Cross-Coupling of Dihydropyrimidine-2-thione 13 with Phenylboronic Acid (14) (Table 6, Entry 2). A 10 mL microwave vessel equipped with an egg-shaped Teflon-coated stir bar and a 10 × 18 mm SiC heating element cylinder was filled with 45 mg (0.163 mmol) of dihydropyrimidine-2-thione **13**, 30 mg (0.243 mmol, 1.5 equiv) of phenylboronic acid, 93 mg (3.0 equiv) of Cu(I)-thiophene-2-carboxylate (CuTC), 5.5 mg (0.00476 mmol, 3 mol%) of $Pd(PPh)_4$, and 2.6 mL of dioxane. After the mixture was flushed with argon, the vessel was sealed and irradiated for 60 min (fixed hold time) at 130 °C by applying the “high” absorption level. The reaction mixture was subsequently cooled to 50 °C by compressed air, the vessel was opened, and the SiC cylinder was removed. For monitoring conversion by HPLC an aliquot of the reaction mixture was taken out and diluted with acetonitrile. This diluted solution was then filtered and directly subjected to HPLC analysis (Table 6). For preparative isolation, the crude reaction mixture was transferred to a round-bottom flask and was adsorbed on silica gel. The solid residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate 3:1) to yield 42 mg (81%) of 2-phenyl-1,4-dihydropyridine **14** as a colorless solid: mp 124−125 °C (lit.[34] mp 125−126 °C); ^{1}H NMR (360 MHz, DMSO) δ 1.14 (t, J = 7.1 Hz, 3H), 1.23 (br s, 1H), 2.37 (s, 3H), 4.03 (q, J = 7.1 Hz, 2H), 5.85 (s, 1H), 7.18−7.29 (m, 5H), 7.42−7.50 (m, 3H), 7.83−7.86 (m, 2 H). The purity of this material (^{1}H NMR and HPLC at 215 °C) was >99%. All spectral and physical properties were identical to those reported in the literature.[29,34]

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Supporting Information Available: Description of general experimental procedures, images, and heating profiles for reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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