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## RESEARCH ARTICLE

## Using Near-Infrared Irradiation for Heating Mechanochemical Reactions in Organic-Dye-Doped Epoxy Milling Jars

Joao Tanepau,<sup>[a],[b]</sup> Hafsa Bonnaanaa<sup>[a],[b]</sup>, Angele Macé,<sup>[a]</sup> Arthur Guérin,<sup>[b]</sup> Philibert Lenormand,<sup>[b]</sup> Frédéric Lamaty,<sup>[a]</sup> Julien Pinaud<sup>\*[b]</sup> and Xavier Bantreil<sup>\*[a],[c]</sup>

Dedication ((optional))

[a] J. Tanepau, H. Bonnaanaa, A. Macé, Dr F. Lamaty, Prof. Dr X. Bantreil  
IBMM, Univ Montpellier, CNRS, ENSCM, Montpellier, France  
E-mail: [xavier.bantreil@umontpellier.fr](mailto:xavier.bantreil@umontpellier.fr)

[b] J. Tanepau, H. Bonnaanaa, A. Guérin, P. Lenormand, Dr. J. Pinaud  
ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France  
E-mail: [julien.pinaud@umontpellier.fr](mailto:julien.pinaud@umontpellier.fr)

[c] Prof. Dr X. Bantreil  
Institut Universitaire de France (IUF)

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**Abstract:** Albeit mechanochemistry is a novel promising technology that gives access to reactivity under solvent-free conditions, heating such reactions is sometimes compulsory to obtain satisfactory results in terms of conversion, selectivity and/or yield. In this work, we developed a novel approach using a dye that absorbs NIR photons and release the energy as heat. Hence, de novo milling jars in epoxy resin doped with the dye were thus produced to obtain reactors that would produce heat upon irradiation at 850 nm. Temperature profiles were recorded, depending on the irradiance, dye charge in the resin, and milling frequency, showing an excellent control of the temperature. The usefulness of the heating jar was then demonstrated in mechanochemical reactions that are known to require heat to yield the desired product, namely Diels-Alder reactions with high activation energies and the newly developed rearrangement of a sydnone into corresponding 1,3,4-oxadiazolin-2-one.

## Introduction

Mechanochemistry, and more specifically ball-milling, has regained a lot of attention in the last years as this technology makes it possible to work with solid reagents in the absence of solvent.<sup>[1]</sup> As well as avoiding the use of often toxic and polluting solvents, the advantages of this approach range from improving reaction times, efficiency and yields, obtaining a different selectivity from solution chemistry,<sup>[2]</sup> and facilitating purification and isolation of products. Since the first reported mechanochemical reaction, the reduction of cinnabar into mercury in a copper mortar and pestle with vinegar, described by Theophrastus of Eresus in 310 B.C.,<sup>[3]</sup> this solid-state approach has evolved along with the equipment. Vibratory and planetary ball-mills (vbm and pbm, respectively) are nowadays used to obtain reproducible results in various domains of chemistry such as material science,<sup>[4]</sup> including MOFs (Metal Organic Framework),<sup>[5]</sup> main group chemistry,<sup>[6]</sup> coordination chemistry,<sup>[7]</sup> organic synthesis,<sup>[8]</sup> among others. While the benefits of the technology are no longer in doubt, there are still limitations to

## Previous work

- Contact heating
    - Heating bands, pads, tape...
    - Jacketed reactors with heat-carrying liquid
  - Contactless heating
    - Heat gun with preset temperature
    - Induction heating
    - Custom-made oven
- ✓ Limited to good temp. control  
 ✗ Mainly limited to jars and/or beads in conductive materials  
 ✗ High loss of energy and safety issues (heat gun)  
 ✗ Possible metal contamination

## This work - NIR irradiation with dye-doped milling jars



- ✓ Novel material for milling jars (Epoxy resin)
- ✓ Safe and low energy NIR irradiation
- ✓ Good temp. control (localized and controlled irradiation)
- ✓ No dye leaching
- ✓ Easily adaptable to other shapes of milling jars

Figure 1. Listing of different heating systems for ball-mills

achieving by mechanochemistry many reactions reported in solution. One of these limitations is the need to heat the reaction medium in order to carry out reactions with a high activation energy. Despite the fact that collisions of the beads inside the milling jar provide a slight elevation of temperature,<sup>[9]</sup> the positive effect of heating was demonstrated over the years,<sup>[10]</sup> with the seminal work from G. Kaupp.<sup>[11]</sup> Depending on the ball-mill used, different heating systems have been developed,<sup>[12]</sup> including belt heaters,<sup>[13]</sup> heating tape,<sup>[14]</sup> or jacket,<sup>[9c]</sup> jacketed reactors with heat-carrying liquid,<sup>[11, 15]</sup> the use of a heat gun with a preset temperature,<sup>[16]</sup> custom-made ovens for home-made milling jars,<sup>[17]</sup> induction-assisted heating,<sup>[18]</sup> and some commercially available devices.<sup>[19]</sup> Some of these studies clearly demonstrate the potential of heated ball-milling to easily anticipate reaction

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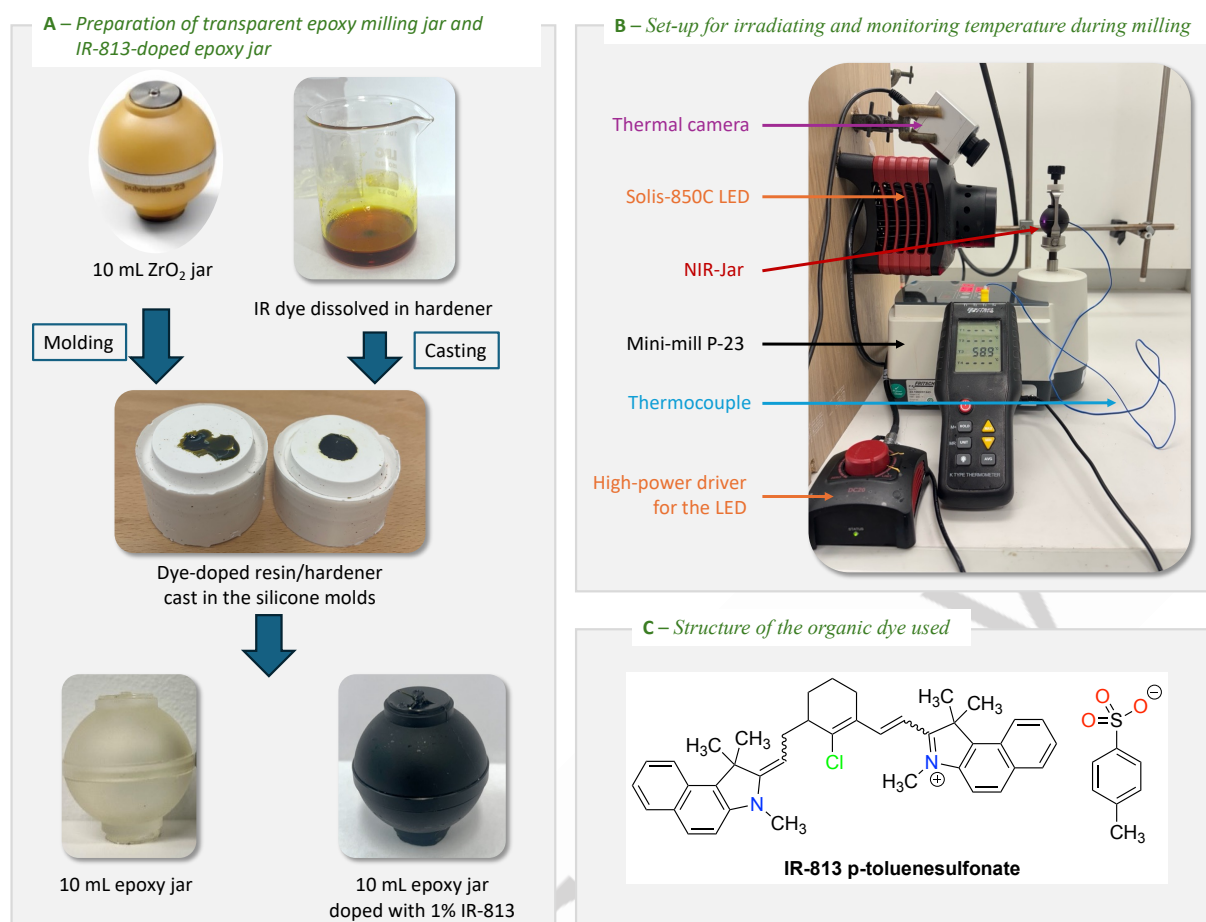


Figure 2. Preparation of epoxy milling jars (A), set-up for irradiating and monitoring mechanochemical reactions (B) and structure of IR-813 p-toluenesulfonate (C)

conditions in reactive extrusion for a solvent-less scale-up approach.<sup>[13d, 13f]</sup> Albeit efficient, most of the systems listed above require the use of a jar or beads made of conductive material, most frequently stainless steel. In this context, we wanted to propose an alternative to mechanochemical reaction heating techniques that would be inexpensive, practical, non-hazardous for the user, did not require the use of conductive materials such as stainless steel, and was adaptable to different types of vibratory ball-mills. Herein, we thus propose a new approach involving the manufacture of epoxy resin milling jars, doped with IR-813 *p*-toluenesulfonate dye (2-Chloro-3-[2-(1,1,3-trimethylbenz[e]indolin-2-ylidene)ethylidene]-1-[2-(1,1,3-trimethylbenz[e]indolium-2-yl)vinyl]cyclohexene *p*-toluenesulfonate, Figure 2C). Upon innocuous and low energy NIR (near infra-red) irradiation, the organic dye will absorb energy and release it in the form of heat. Such property was demonstrated with applications in photothermal therapy,<sup>[20]</sup> and was cleverly used for light-induced polymerization or polymer remodeling/recycling.<sup>[21]</sup> Compared to graphene oxide or nanoparticles that could have similar properties,<sup>[22]</sup> the organic dye has a higher solubility and stability in polymers and monomers, and allowed to obtain more controllable temperatures for the reshaping of polymers while working at low concentrations.<sup>[21c]</sup> It should be noted that different commercially available materials (Teflon, agate, stainless steel, zirconium oxide,

tungsten carbide) are classically used in milling reactions, and that polymeric ones, with jars made by machining,<sup>[23]</sup> or 3D-printed,<sup>[24]</sup> have been recently evaluated for milling applications, but epoxy resin was never tested to date. We thought that with dye-doped epoxy milling jars in hand, we could provide a convenient alternative to existing heating systems and investigate reactions in the ball-mill that require additional energy input. Here, we report on the manufacture of novel dye-doped milling jars and demonstrate that NIR irradiation can promote mechanochemical reactions by heat transfer.

## Results and Discussion

### Manufacture and evaluation of dye-doped milling jars

To prove the possibility to use an organic NIR dye to provide sufficient heating in milling reactions, we decided to focus on the use of the vertical mini-mill P-23 from Fritsch®. First, a silicone mold of the two parts of a 10 mL ZrO<sub>2</sub> milling jar was made. After analyzing different chemical resistance charts of polymers that could be used, epoxy resins seemed to offer promising properties in terms of mechanical and chemical resistance over other materials. In addition, the transparency of epoxy resins allowed

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us to perform photoredox mechanochemical reactions.<sup>[25]</sup> A screening of different commercially available epoxy resins was then performed,<sup>[26]</sup> to secure the finding of a composition that would fit the requirements of mechanochemical stress, as well as high chemical resistance. Resin plates were prepared and immersed in various solutions (organic solvent, aqueous acidic and basic solutions) for up to 2 h to assess their chemical resistance. Gratifyingly, most of them showed excellent chemical resistance, even under highly acidic conditions (Table 1).<sup>[26]</sup> In addition, only few drops of solvent are generally used in the ball-mill.<sup>[27]</sup> Thus, even solvents that are not completely compatible with the epoxy resin such as 2-MeTHF could be used as liquid additive in standard milling reactions. To evaluate the mechanical resistance, milling jars in epoxy resin were cast, filled with 300 mg of NaCl and one 10 mm diameter stainless steel ball. The mixture was then agitated at 25 or 30 Hz for 30 min. If most of the milling jars showed a good mechanical resistance at 25 Hz, milling at 30 Hz revealed their limitations with clear visual abrasion at the bottom of the jar. However, epoxy resins with high energy absorption (51-53 kJ.m<sup>-2</sup>, measured by Charpy Impact test) and relatively high T<sub>g</sub> (80-83 °C) gave excellent results in terms of mechanical resistance, even when working at higher frequency (50 Hz).<sup>[26]</sup> Hence, among the formulations tested, the most suitable was found to be a mixture SR8500/SD7160 from Sicomin®. To obtain milling jars with heating properties, different proportions (0.5, 1, 2 and 10% in weight) of IR-813 *p*-toluene sulfonate were dissolved in the amine-containing hardener (SD7160). The epoxy partner (SR8500) was then added and the

mixture was cast in the silicone mold. After curing, NIR dye-doped epoxy milling jars suitable for testing with the Pulverisette-23 were obtained (Figure 2A). For the reader's convenience, the jars will be named **NIR-Jar-X** in the rest of the manuscript, X being the percentage of dye used.

To evaluate the thermal properties of the **NIR-Jars**, a set-up involving an NIR LED irradiating at 850 nm, a thermal camera, and a thermocouple was used (Figure 2B). The thermal camera allowed to monitor the temperature on the external surface of the milling jar, while the thermocouple was used to monitor the temperature on the inner wall of the jar. At first, the heating capacity of the milling jars doped with 0.5 - 10% of dye was evaluated upon irradiation at 0.5 W.cm<sup>-2</sup>, without and with agitation at 30 Hz, in the absence of milling balls (Figure 3a and b, respectively). Interestingly, all the **NIR-Jars** allowed to reach temperatures of 140 - 150 °C when the jar was not moving, after only 10 min of irradiation. The external temperature was found to be slightly lower, 125 - 140 °C, when agitation to 30 Hz was on. Decrease of temperature was also monitored and going back to room temperature required less than 10 minutes. The dye content had little impact on the heating rate and maximal temperature obtained, showing that as low as 0.5% in weight was sufficient for good results. However, the need for the dye addition was demonstrated by monitoring the external temperature of a milling jar made of pure epoxy resin (no dye added) irradiated at 850 nm. As expected, no elevation of temperature was detected with or without agitation.

As the **NIR-Jar-0.5** reached a slightly lower temperature than the other **NIR-Jars**, we decided to continue the rest of the studies with **NIR-Jar-1**, that required the lower doping with IR-813 *p*-toluenesulfonate while having excellent thermal properties. The temperature could be tuned by changing the irradiance of the NIR LED (Figure 3c and d). Hence, irradiances of 0.15, 0.25, 0.38, 0.5 and 0.6 W.cm<sup>-2</sup> allowed to reach a range of external temperatures of 71 to 158 °C. Corresponding internal temperatures, measured simultaneously, were slightly lower (49 to 112 °C). Hence, **NIR-Jar-1** allowed to reach relatively high and controlled temperature inside the milling jar, as the maximum T<sub>int</sub> and T<sub>ext</sub> were found to be linearly correlated to the irradiance (Figure 3f). Finally, the impact of the frequency of agitation on the internal and external temperature was evaluated at an irradiance of 0.5 W.cm<sup>-2</sup> (Figure 3e). Using a higher frequency (50 Hz) resulted in lower T<sub>int</sub> and T<sub>ext</sub> of 86 and 120 °C, respectively, than with an agitation at 30 Hz. It should be noted that these measurements were performed without adding beads inside the milling jar, and that shocks during the milling might provide a slight increase in temperature. In addition, no deactivation of the dye was observed, as the temperature reached remained the same after prolonged irradiation of the **NIR-Jar-1** (4 consecutive periods of 8 h), or during irradiation of an **NIR-Jar-1** left aside for around 6 months before carrying out the experiment.<sup>[26]</sup>

Table 1. Evaluation of the chemical resistance of epoxy resin

Solvent	Resistance after immersion for	
	1 h	2 h
Acetone	E	E
Acetonitrile	E	E
Acetic acid	E	E
Benzaldehyde	E	E
Dichloromethane	F	N
Dimethylcarbonate	E	E
DMF	E	E
DMSO	F <sup>[a]</sup>	F <sup>[a]</sup>
1,3-Dioxolane	E	E
Ethanol	E	E
Hexane	E	E
Isopropanol	E	E
2-MeTHF	E	G
Pyridine	G	N <sup>[b]</sup>
Toluene	E	E
<b>Aqueous solutions</b>		
HCl 37%	E	E
H <sub>2</sub> SO <sub>4</sub> cc.	N <sup>[b]</sup>	N <sup>[b]</sup>
H <sub>2</sub> SO <sub>4</sub> 30%	E	E
Na <sub>2</sub> CO <sub>3</sub> 20%	E	E
NaOH 60%	E	E

A parallelepiped resin sample (SR8500/SD7160) of dimensions 25 x 25 x 3.5 mm was immersed in the solution. The chemical resistance was evaluated based on visual appearance at room temperature. If necessary (visual analysis inconclusive), a microscope was used. Green (E) indicates excellent resistance, Orange (G) good resistance, Yellow (F) fair resistance and Red (N) no chemical resistance. [a] Loss of transparency. [b] Becomes dark orange.

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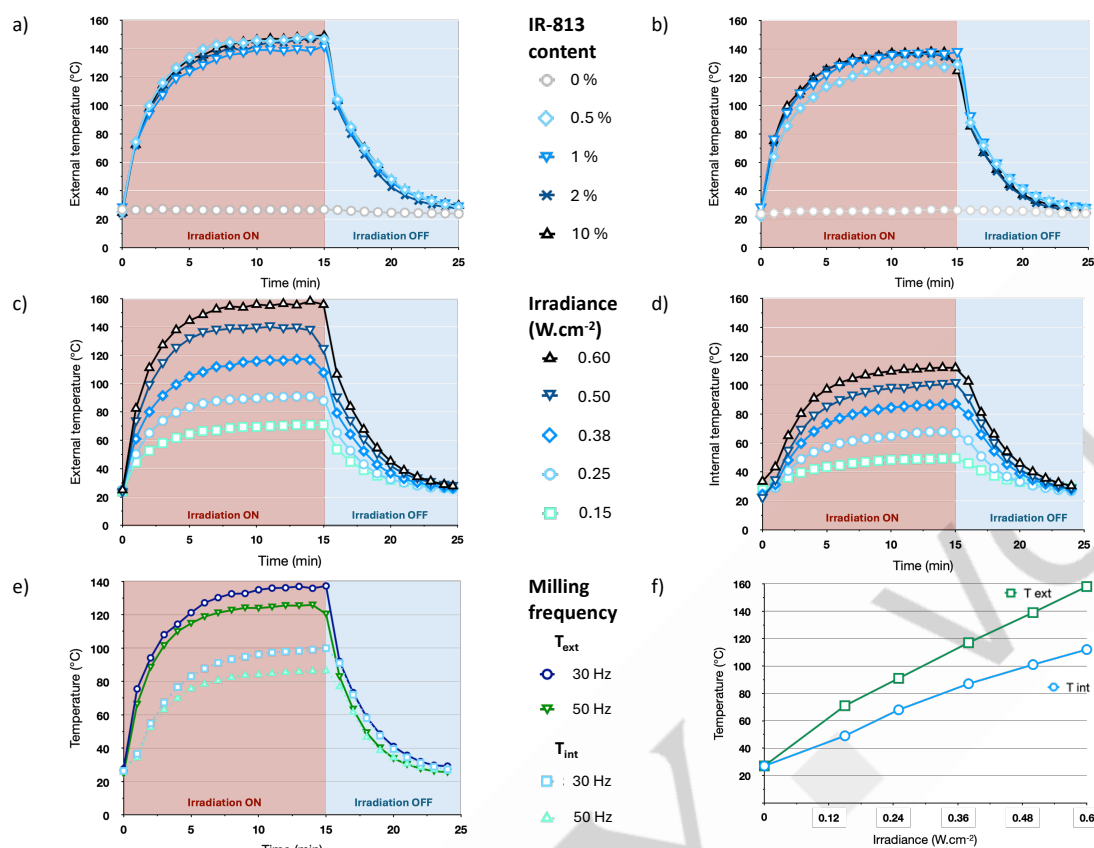


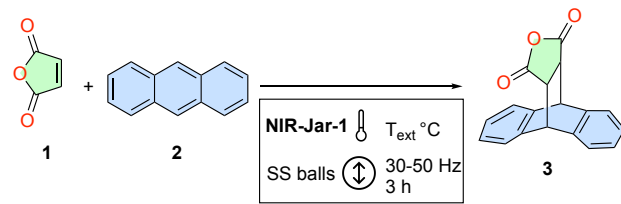
Figure 3. Evolution, in the absence of milling balls, of external temperature of milling jars doped with different IR-813 content and irradiated with a NIR LED emitting at 850 nm with an irradiance of 0.5 W.cm<sup>-2</sup> (a) without agitation and (b) with agitation at 30 Hz. Evolution of (c) external and (d) internal temperature of **NIR-Jar-1** upon NIR irradiation at various irradiances, without agitation. e) Effect of milling frequency on internal and external temperature of **NIR-Jar-1**, at an irradiance of 0.5 W.cm<sup>-2</sup>, in the absence of milling balls. f) Correlation between maximal external temperature and irradiance without agitation.

### Thermally induced milling reactions

With the heating jars fully characterized, we tested the viability of the jars with reactions that require an external heating, even when performed in mechanochemistry. First, we focused on Diels-Alder reaction, for which the positive impact of mechanical energy was clearly demonstrated over chemistry in solution.<sup>[28]</sup> In particular, Mack and co-workers explored the energetics of a Spex 8000M ball-mill equipped with a heating band.<sup>[13a]</sup> They clearly showed that depending on the diene and dienophile used, the activation energy required to perform the Diels-Alder reaction could be tuned. In most cases, with low to medium activation energies, the milling was sufficient to promote the reaction. However, external heating was necessary to perform reactions with high activation energies (14.9 and 17.4 kcal.mol<sup>-1</sup>). Thus, similar Diels-Alder partners were used herein to study reactions having activation energies of 14.9 and 17.4 kcal.mol<sup>-1</sup>. It is important to note that Zholdassov *et al.* demonstrated that mechanical distortion of the reagents, that could likely happen under milling conditions, might reduce the activation energies required to perform the Diels-Alder reactions.<sup>[28b]</sup> There may therefore be a difference between the activation energies required in solution and in a ball-mill, but as the movement of the jar is quite different in the Spex 8000M and in the mini-mill P-23, this probably depends on the type of ball-

mill. Thus, direct comparison of results is rather complicated. We first investigated the reaction of maleic anhydride **1** and anthracene **2** ( $E_a = 14.9$  kcal.mol<sup>-1</sup>). Such reaction needed a temperature of about 82 °C to reach full conversion in the Spex 8000M.<sup>[13a]</sup> In the P-23, using an irradiance of 0.5 W.cm<sup>-2</sup> ( $T_{ext} = 117$  °C) at a frequency of 30 Hz resulted in only 20% conversion (Table 2, entry 1). Increasing the frequency to 50 Hz allowed to slightly increase the conversion (Entry 2). However, when opening the milling jar, it was visually evident that the milling balls were following a preferred path, and that the mixture was not homogeneous. Thus, a third ball of 10 mm diameter was added, which allowed to obtain a better homogenization and higher conversion (Entry 3). Nevertheless, the use of relatively heavy balls at high speed induced a break of the epoxy milling jar and leakage of a part of the reaction mixture. To avoid such safety issue, six 7 mm diameter milling balls were used instead, giving a slightly lower conversion, but no break of the milling jar (Entry 4). Interestingly, increasing the milling load while using an irradiance of 0.6 W.cm<sup>-2</sup> allowed to reach 85 % conversion (Entry 5), and full conversion when using an excess of maleic anhydride (Entry 6). Reducing the irradiance to 0.45 W.cm<sup>-2</sup>, and thus the temperature, also allowed to reach full conversion in 3 h, and compound **3** could be isolated in 80 % yield (entry 7). Under these conditions, no or lower NIR irradiation resulted in lower conversions (Entries 8-10). Then, the Diels-Alder reaction with the highest activation energy

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Table 2. Diels-Alder reaction of maleic anhydride and anthracene<sup>[a]</sup>


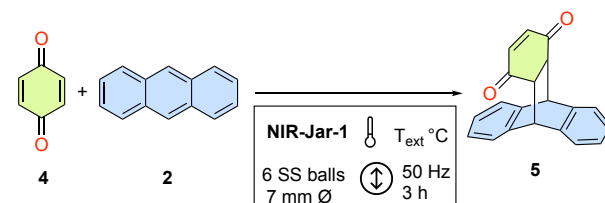
Entry	1 (mmol)	2 (mmol)	Frequency (Hz)	Balls (ø in mm)	Irradiance (W.cm <sup>-2</sup> )	T <sub>ext</sub> (°C)	Conv. (%) <sup>[b]</sup>
1	0.5	0.5	30	2 (10)	0.5	117	20
2	0.5	0.5	50	2 (10)	0.5	117	30
3	0.5	0.5	50	3 (10)	0.5	117	41
4	0.5	0.5	50	6 (7)	0.5	117	36
5	1	1	50	6 (7)	0.6	125	85
6	1.5	1	50	6 (7)	0.6	125	100
7	1.5	1	50	6 (7)	0.45	115	100 (80) <sup>[c]</sup>
8	1.5	1	50	6 (7)	0.25	97	50
9	1.5	1	50	6 (7)	0	50	43

[a] Reaction conditions: **1** and **2** were milled in a 10 mL **NIR-Jar-1** at 30-50 Hz for 3 h, upon irradiation at 850 nm. [b] Conversion of **2** into **3** was determined by HPLC. [c] Isolated yield is given in brackets.

( $E_a = 17.4 \text{ kcal}\cdot\text{mol}^{-1}$ ), involving benzoquinone **4** and anthracene **2**, was evaluated (Table 3). Such reaction required a temperature of approximately 105 °C to reach full conversion in a Spex 8000M.<sup>[13a]</sup> In our hands, without external heating, 16 % conversion were obtained in 3 h of milling at 50 Hz, with an excess of benzoquinone (Entry 1). Gratifyingly, with an irradiance of 0.6 W.cm<sup>-2</sup>, full conversion into the adduct **5** was obtained (Entry 2). On the other hand, working in stoichiometric conditions allowed to reach only 66% conversion (Entry 3). Finally, reducing the irradiance to 0.45 W.cm<sup>-2</sup> allowed to maintain full conversion, and compound **5** was isolated in 81 % yield, while irradiances of 0.35 and 0.25 W.cm<sup>-2</sup> gave conversions of 27 and 18 %, respectively (Entries 4-6).

To further demonstrate the applicability of **NIR-Jar-1** to promote mechanochemical reactions that require external heating, we next focused on the mechanochemical rearrangement of N-phenylsydnone **6** that we reported recently.<sup>[16e]</sup> In the presence of stoichiometric quantities of acetic anhydride (Ac<sub>2</sub>O) and N-bromosuccinimide (NBS), without external heating, milling of sydnone **6** led to its exclusive bromination into intermediate **7**. Upon gentle heating during the milling, full conversion into 3-phenyl-5-methyl-1,3,4-oxadiazolin-2-one **8** was obtained. Of note, this rearrangement was reported using a horizontal vibratory ball-mill with external heating provided by a heatgun with a set temperature at 100 °C, delivering an internal temperature of approx. 50 °C. In the vertical ball-mill, when sydnone **6** was milled at 30 Hz with Ac<sub>2</sub>O and NBS, using two stainless steel balls (1 cm diameter), and no irradiation, full conversion into brominated sydnone **7** was obtained after 30 min (Table 4, Entry 1). The same result was obtained with the irradiance set to 0.1 W.cm<sup>-2</sup> to obtain an external temperature of 50 °C (entry 2). Increasing the irradiance to reach temperatures of 80 and 100 °C allowed to

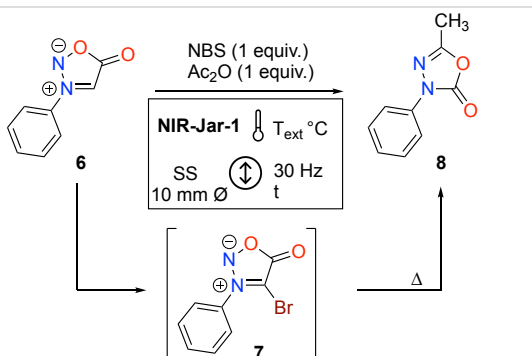
promote the rearrangement into **8** and gave conversions of 69 and 78 %, respectively (Entries 3 and 4). Reducing the reaction time to 15 min or increasing the temperature to 130 °C resulted in lower conversions of 73 and 72 %, respectively (Entries 5 and 6). Finally, using only one 1 cm diameter ball allowed to reach full conversion, yielding 95 % of oxadiazolinone **8** after extraction (Entry 7). To confirm that the heating was necessary under these conditions, the same reaction was performed without IR irradiation, and

Table 3. Diels-Alder reaction of benzoquinone and anthracene<sup>[a]</sup>


Entry	4 (mmol)	2 (mmol)	Irradiance (W.cm <sup>-2</sup> )	T <sub>ext</sub> (°C)	Conv. (%) <sup>[b]</sup>
1	1.5	1	0	50	16
2	1.5	1	0.6	125	100
3	1	1	0.6	125	66
4	1.5	1	0.45	115	100 (81) <sup>[c]</sup>
5	1.5	1	0.35	105	27
6	1.5	1	0.25	95	18

[a] Reaction conditions: **4** and **2** were milled, using six 7 mm diameter stainless steel balls, in a 10 mL **NIR-Jar-1** at 50 Hz for 3 h, upon irradiation at 850 nm. [b] Conversion of **2** into **5** was determined by HPLC. [c] Isolated yield is given in brackets.

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Table 4. Mechanochemical rearrangement of sydnone **6**<sup>[a]</sup>


Entry	t (min)	Balls	Irradiance (W.cm <sup>-2</sup> )	T <sub>ext</sub> (°C)	Conv. into <b>8</b> <sup>[b]</sup> (%)
1	30	2	0	25	0 <sup>[c]</sup>
2	30	2	0.1	50	0 <sup>[c]</sup>
3	30	2	0.2	80	69
4	30	2	0.28	100	78
5	15	2	0.28	100	73
6	30	2	0.6	130	72
7	30	1	0.28	100	100 (95) <sup>[d]</sup>
8	30	1	0	25	0 <sup>[c],[e]</sup>

[a] Reaction conditions: **6** (0.45 mmol), NBS (0.45 mmol) and acetic anhydride (0.45 mmol) were milled in a 10 mL **NIR-Jar-1** at 30 Hz for 15–30 min, upon irradiation at 850 nm. [b] Conversion determined by HPLC. [c] Full conv. into brominated intermediate **7**. [d] Isolated yield is given in brackets. [e] Intermediate **7** was isolated in 98% yield.

resulted in full conversion into intermediate **7**, which could be isolated in 98 % yield (Entry 8). Under these conditions, no elevation of the external temperature was observed, contrary to Diels-Alder reactions for which a higher frequency and different amount and type of balls were used. Importantly, for the three reactions described above, <sup>1</sup>H NMR and LC-MS analysis of the crude mixture revealed no contamination of the desired product with the NIR organic dye, showing that there was no leaching of IR-813 incorporated in the epoxy resin despite the repeated shocks between the beads and the **NIR-Jar-1**. Moreover, **NIR-Jar-1** could be reused up to 5 times without noticing any wear of its internal wall.

## Conclusion

A new material, namely epoxy resin, and an original manufacturing approach by molding and casting were used to produce milling jars for a vertical ball-mill. Such material was found to be chemically resistant and robust enough for a use in ball-milling. Doping the resin with a NIR-absorbing dye allowed to produce milling jars that could provide consistent heating during milling. Upon irradiation at 850 nm, the novel NIR-Jars allowed to perform mechanochemical reactions that require heating to provide the desired product. The efficiency of the jars was thus

demonstrated in Diels-Alder reactions with high activation energies and in the rearrangement of sydnone into 1,3,4-oxadiazolin-2-one. This paves the way to the preparation of milling jars with different shapes, adapted to their use in various type of ball-mills, and with broad applications depending on their composition.

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**Keywords:** Mechanochemistry • Ball-milling • Diels-Alder reaction • Near-infrared irradiation • Photothermal effect

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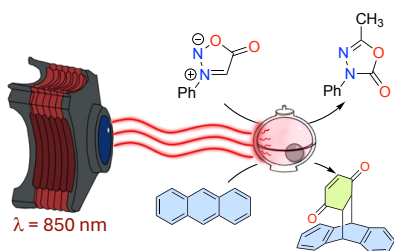


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## RESEARCH ARTICLE

## Entry for the Table of Contents



- Novel milling jars made of epoxy resin
- Safe NIR irradiation
- Efficient generation of heat

New milling jars, made of epoxy resin doped with an organic dye, were manufactured to perform heat-controlled organic transformations upon NIR irradiation. Reactions that require external heat even under solvent-free ball-milling conditions could then be performed efficiently.

Institute and/or researcher Twitter usernames: ((optional))

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