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Rapid and facile solvent-free mechanosynthesis in a cell lysis mill: preparation and mechanochemical complexation of aminobenzoquinones†

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A cell lysis mill, typically used for the breakdown of biological structures in microbiological and biochemical studies, was used as a tool for rapid, solvent-free and general synthesis of short- and long-chain substituted zwitterionic *meta*- and *para*-aminobenzoquinones, never previously prepared under solvent-free conditions. Rapid agitation and self-heating in the lysis mill enabled thermally-demanding reactions without external solvent, providing yields comparable to those obtained by conventional solution chemistry, ball milling and melt chemistry. The lysis mill is also suitable for coordination-based reactions, demonstrated by the mechanosynthesis of a mononuclear Ni(II) *meta*-benzoquinonemonoimine complex.

Quinonoid compounds are ubiquitous in many areas of chemistry and biochemistry, and stable quinonoids are normally derived from *ortho*- and *para*-benzoquinones (Fig. 1a, I and II, respectively).[1,2] Aminobenzoquinones have been widely explored for biological applications, especially in medicinal chemistry due to anticancer and antimalarial properties.[3–5] The first synthesis of a novel stable *meta*-benzoquinone zwitterion (Fig. 1a, III), was reported in 2002 by the Braunstein group.[6] The unique structural and physical properties of this benzoquinonemonoimine have attracted much attention, with X-ray structural analysis revealing a formal zwitterion composed of two separate charged subunits.[7,8] In 2005, a simple one-pot route to III was developed *via* a transamination reaction, which enabled the introduction of diverse functionalities onto the quinonoid core.[9] The resulting quinonoids show rich organic,[7] supramolecular[10] and coordination chemistry,[8,9,11] and readily form extended networks on surfaces, where their large intrinsic dipoles allow the alteration of static dipoles on surfaces and the creation of conductive molecular films.[10,12,13] We have recently reported the charge-assisted hydrogen bond-directed self-assembly of an amphiphilic zwitterionic quinonemonoimine (**C18*m***, Scheme 1) at the liquid–solid interface investigated using scanning tunnelling microscopy.[14] Whereas the synthesis of *para*- and *meta*-aminobenzoquinones

Fig. 1 (a) Schematic representations of *ortho*-benzoquinone (I), *para*-benzoquinone (II), and diamino-*meta*-benzoquinone (III) and (b) a laboratory cell lysis mill (FastPrep®-24 from MP-Biomedicals) in operation.

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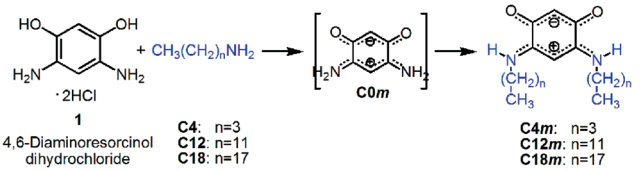


Scheme 1 General reaction for the synthesis of 4,6-di(alkylamino)-*m*-quinones.

in solution is well established, such processes require polar solvents and extended reaction times.[3,4,9,15] Presumably, a facile and rapid synthesis would make such compounds more readily accessible for potential applications in materials science and synthetic chemistry. We now demonstrate how a cell lysis mill (Fig. 1b),[16–18] a tool designed for the breakdown of bacterial cell walls in biochemical and microbiological research, can be adapted for rapid and solvent-free synthesis of *meta*- and *para*-aminobenzoquinones. To the best of our knowledge, this is the first demonstration of solvent-free synthesis[19–24] of aminobenzoquinones.

In order to evaluate the efficiency of lysis mill methodology with respect to conventional solution synthesis of 4,6-di(alkylamino)-*m*-quinones, we first conducted the synthesis of **C4*m***, **C12*m*** and **C18*m*** in solution. We followed a previously reported procedure[8,9] involving the reaction of 4,6-diaminoresorcinol dihydrochloride (**1**, Scheme 1) with excess alkylamine using methanol as a solvent most compatible with long-, as well as short-chain alkylamines. The reactions were conducted using either a 1 : 4 or a 1 : 7 ratio of **1** to the alkylamine. After two hours stirring at room temperature the products were isolated in typical yields >70%, following rotary evaporation and centrifugal chromatography (Table 1, entries 1, 2, 8, 9, 15, and 16).[9]‡ In this procedure, two equivalents of the alkylamine are required to neutralise the HCl salt and the remaining alkylamine drives the reversible reaction towards the desired product. Whereas this reaction is reminiscent of Schiff base condensations of aldehydes and amines, known to be accessible by solvent-free chemistry and mechanochemistry, we note that it involves three steps: deprotonation of **1**, aerobic oxidation to form **C0*m***, and the exchange of amine ligands.[25–28]

In an attempt to use the lysis mill (Scheme 1) as a means to eliminate the use of solvents and reduce reaction times, a stoichiometric amount (4 eq.) or an excess (7 eq.) of an alkylamine and **1** were added to a 2 mL screw cap Eppendorf tube (lysis tube). The tube was loaded with ceramic grinding media to a specific height (*vide infra*) and shaken in a cell lysis mill for 10 minutes, after which the reaction mixture became dark green (for **C18*m***) or dark red/purple (for **C12*m*** and **C4*m***) indicating that the reaction had taken place. Crude reaction mixtures were purified by centrifugal chromatography to provide products in high yields (>80%, Table 1, entries 3, 4, 10, 11, 17, and 18).‡ The products were characterised by ^{1}H and ^{13}C NMR, as well as powder X-ray diffraction (see ESI†). Preliminary attempts to structurally characterise the synthesised compounds gave crystals of **C12*m*** of sufficient quality for a single crystal X-ray diffraction experiment.§ Structure determination revealed the crystals, grown from methanol, are a methanol solvate of **C12*m*** (Fig. 2a). The crystals are built up of hydrogen-bonded chains containing two types of supramolecular synthons: the $R_4^4(14)$ motifs involving two molecules of **C12*m*** and two molecules of methanol, as well as homodimeric $R_2^2(10)$ motifs formed between neighboring **C12*m*** molecules (Fig. 2b). Each $R_4^4(14)$ ring synthon consists of two N–H···O hydrogen bonds (N···O distance: 2.82 Å), involving **C12*m*** as the hydrogen bond donor and the methanol molecule as the acceptor, and two O–H···O hydrogen bonds involving the methanol hydroxyl moiety as the donor and a **C12*m*** oxygen atom as the acceptor (O···O distance 2.72 Å). The $R_2^2(10)$ ring synthons consist of two N–H···O hydrogen bonds (N···O distance: 2.92 Å). The resulting hydrogen-bonded chains propagate along the crystallographic *b*-direction and are juxtaposed to form layers in the crystallographic (103) plane (Fig. 2c). Formation of a layered structure is consistent with the expected tendency of alkyl-substituted aminobenzoquinones to form self-assembled layers on surfaces.[14]

Each of the two alkyl chains on a **C12*m*** molecule adopts a different geometry due to a difference in the conformations of methylene groups attached closest to the aminobenzoquinone core. While one of the alkyl chains (C7–C18) is linear, with all methylene groups adopting a staggered conformation, the other one (C19–C30) adopts a kinked structure due to the partially eclipsed conformations of the first three methylene groups in the chain (Fig. 2a).

Table 1 Synthesis of 4,6-di(alkylamino)-*m*-quinones[a,b,c]

Entry	Product	Reaction type	Time (min)	Alkylamine (equiv.)	Yield (%)
1	**C4*m***	A	120	4	79
2		A	120	7	88
3		B	10	4	83
4		B	10	7	86
5		C	60	4	80
6		C	60	7	89
7		D	10	10	92
8	**C12*m***	A	120	4	70
9		A	120	7	74
10		B	10	4	79
11		B	10	7	85
12		C	60	4	81
13		C	60	7	86
14		D	10	8	84
15	**C18*m***	A	120	4	75
16		A	120	7	80
17		B	10	4	70
18		B	10	7	90
19		C	60	4	83
20		C	60	7	87
21		D	10	7	69

[a] Reaction conditions: A: conventional solution synthesis in methanol (**C4*m***) and ethanol (**C12*m*** and **C18*m***); B: lysis mill; C: ball mill; D: melt. [b] Pre-heated in oven at 45 °C for 20 min. [c] Monitoring the solution reactions by TLC indicates that the maximum conversion in solution is achieved after *ca.* 12 hours. Detailed procedures provided in the ESI.

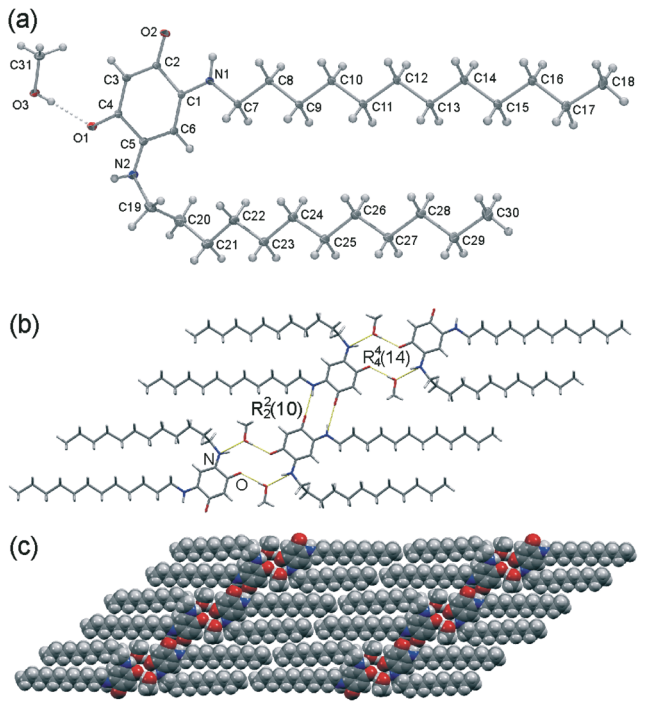


Fig. 2 (a) ORTEP representation of the asymmetric unit in the solvate **C12*m***·methanol; (b) the assembly of **C12*m*** and methanol molecules into hydrogen-bonded chains, with designated hydrogen-bonded synthons and (c) the assembly of hydrogen-bonded chains in the structure of methanol solvate of **C12*m*** into layers parallel to the (103) crystallographic planes.

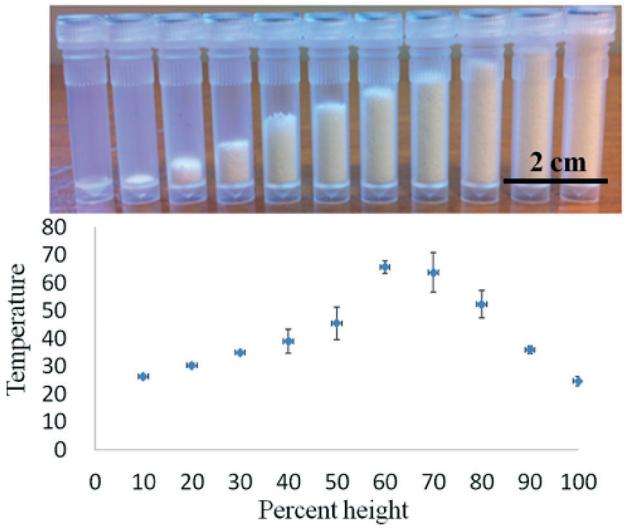


Fig. 3 Lysis tube temperature after 1 minute of agitation in the lysis mill operating at 6.0 m s^{-1} as a function of bead height.

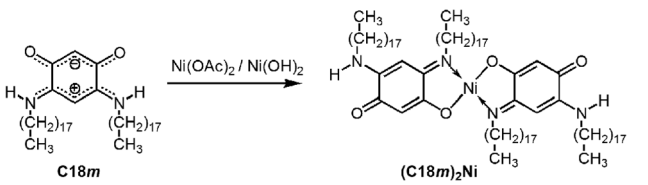
Next, we investigated the synthesis in a laboratory ball mill, using the synthesis of **C18*m*** as the first model reaction. After 60 minutes milling the reaction mixture became brownish red, *i.e.* different than in the lysis mill. The colour was found to be due to **C0*m*** (Scheme 1), an intermediate on the route to the target zwitterionic *meta*-aminoquinone, formed by deprotonation of **1**. The formation of **C0*m*** indicates that the reaction in the ball mill is not limited by deprotonation or aerobic oxidation steps, but by the amine exchange reaction. While searching for an explanation for the difference in reactivity between the lysis mill and the ball mill, we noted that the temperature of the lysis tube after 1 min agitation varied significantly between different experiments. Moreover, higher yields were obtained in hotter tubes, while cooler tubes resulted in notable quantities of **C0*m***. Presumably, the principal factor behind such temperature variations was the number of beads in the tube, *i.e.* the "bead height". This was subsequently verified by measuring the temperature of the tube contents as a function of bead height after 1 min agitation (at 6.0 m s^{-1}), by inserting a thermocouple into the ceramic beads. The results, shown in Fig. 3, confirm that the bead height has a considerable effect on the temperature of the vial contents, with a maximum measured temperature of *ca.* 70 °C after 1 min for a bead height of 70% of the tube height. Too many or not enough ceramic beads reduced the temperature increase, presumably due to a lower overall number of collisions between the beads or less efficient conversion of kinetic energy into heat. In the ball milling experiments, the temperature of the steel jars did not increase significantly after 1 h milling. Therefore, we considered that, in spite of the mechanical input, the lower temperature was insufficient to overcome the activation barrier to convert the **C0*m*** intermediate to the final product. We then attempted the ball milling synthesis of **C18*m*** in a steel jar pre-heated to 45 °C for 20 min prior to milling. After 1 h milling the crude product was dark green and the formation of **C18*m*** was confirmed by thin layer chromatography (TLC) and solution ^{1}H NMR analysis (Table 1, entries 19 and 20, see ESI† for details of characterisation). Ball milling synthesis of **C12*m*** and **C4*m*** did not require heat (Table 1, entries 5, 6, 12, and 13), probably due to the lower melting points of *n*-dodecylamine and *n*-butylamine (28 °C and −49 °C, respectively), compared to *n*-octadecylamine (52 °C).[29]

At this point, we speculated if the herein investigated mechanochemical reactions are mediated by a liquid phase, as demonstrated for a number of organic and supramolecular mechanochemical processes.[20,27,30–35] We attempted a simple melt reaction for the synthesis of **C18*m*** by mixing the reactant **1** with excess octadecylamine. The two powders were ground together using a mortar and pestle for 2 min, with no significant color change. The mixture was then heated at 70 °C for 10 min. As soon as the octadecylamine melted, a color change from white to dark green was observed and product formation was confirmed by TLC and ^{1}H NMR (Table 1, entry 21). Thus, the transamination reaction to prepare zwitterionic *meta*-benzoquinones can proceed in the melt. In the case of **C18*m***, only the melting of the octadecylamine was necessary. This was further confirmed with the synthesis of **C4*m*** and **C12*m*** (Table 1, entries 7 and 14). When the reaction was attempted using 4,6-diaminoresorcinol dihydrochloride and *n*-butylamine, a liquid at room temperature, no heat was required for the reaction to proceed. As soon as both starting materials were combined, the transparent reaction mixture became red indicating the formation of product (Table 1,

entry 7). The melt reactions, however, required the use of excess liquid amine in order to facilitate stirring. In the end, we conclude that the combination of vigorous agitation and frictional heating in the lysis mill enables the simple and rapid synthesis of *m*-aminobenzoquinones without external solvents or excess reagents.

Mechanosynthesis by manual grinding or ball milling has become particularly popular for making metal–organic materials, held together by coordination bonds.[36–38] In order to verify the applicability of the lysis mill for such reactions, we explored the synthesis of a mononuclear complex of nickel with one of the prepared aminoquinones, (**C18*m***)$_2$Ni (Scheme 2).

The conventional solution-based reaction was carried out overnight in refluxing toluene using a 1 : 1 ratio of **C18*m*** and nickel(II) acetate tetrahydrate, Ni(OAc)$_2$·4H$_2$O (Table 2, entry 1).[39] These conditions were based on those reported for the synthesis of a related compound, (**C4*m***)$_2$Ni, with shorter alkyl chains, using nickel(II) acetylacetonate, Ni(**acac**)$_2$ (using a **C4*m*** : Ni(**acac**)$_2$ ratio of 2 : 1). However, we successfully substituted the more expensive Ni(**acac**)$_2$ reagent used in the solution synthesis with Ni(OAc)$_2$·4H$_2$O. In particular, the cost of Ni(**acac**)$_2$ (CAD$ 1297 mol^{-1}) greatly exceeds the cost of Ni(OAc)$_2$·4H$_2$O of comparable purity (CAD$ 45 mol^{-1}).¶ We also considered using the even less expensive nickel(II) hydroxide, Ni(OH)$_2$ (CAD$ 21 mol^{-1}), which also offered a further advantage of producing water as the only by-product.‖ However, due to its low solubility, Ni(OH)$_2$ is not a reagent of choice in solution reactions (Table 2, entry 2). For mechanochemical syntheses carried out with the lysis mill, reagent solubility is no longer expected to be a relevant factor.[40] Indeed, Ni(OAc)$_2$·4H$_2$O or Ni(OH)$_2$ react with **C18*m*** in the lysis mill to give 85% and 80% yield of the (**C18*m***)$_2$Ni complex, respectively, after 20 shaking cycles (Table 2, entries 3, 4).



Scheme 2 General reaction for the synthesis of 4,6-di(alkylamino)-*m*-aminoquinone monometallic complexes.

The formation of (**C18*m***)$_2$Ni was confirmed by mass spectrometry (see ESI†). For the reaction with nickel acetate, a distinct odor of acetic acid by-product was detected upon opening the reaction tube. The reaction was also successful with a standard ball mill apparatus. After grinding the reagents together for 2 h, comparable yields of the desired product were obtained (Table 2, entries 5 and 6).

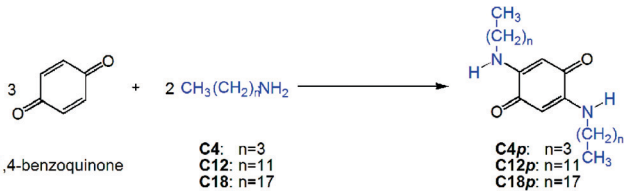
Mechanochemistry was also successful in the synthesis of the analogous *para*-compounds. Conventionally, 2,5-di(alkylamino)-1,4-benzoquinones are synthesized by mixing 1,4-benzoquinone and an alkylamine in a 3 : 2 ratio in solution and stirring at room temperature for several hours (Table 3, entries 1, 5, and 9).[4,5,15] The additional two equivalents of benzoquinone serve to oxidize reaction intermediates back to the quinone oxidation state (Scheme 3). In this reaction, a colour change was apparent as soon as the reagents came into contact, and was even observed when the reagents were simply kept in close proximity. To visualize this phenomenon, benzoquinone and octadecylamine were placed in separate vials within a sealed jar (see ESI† Fig. S1). Upon aging, the initially white octadecylamine turned from slightly brown-orange (after several hours) to light brown (after 1 day) and, finally to dark brown (after 1 week). Analysis of the dark brown powder using TLC revealed the formation of **C18*p***. It is likely that the high vapor pressure of benzoquinone facilitates the contact between the two reactants.

In that way the synthesis of *p*-aminoquinones is analogous to the solvent-free and mechanochemical syntheses of two- and three-component cocrystals of *p*-benzoquinone investigated by the groups of Kuroda and of Rastogi.[41–43] Next, we attempted to enhance the mixing of reagents by milling. The reagents were placed in a 2 mL lysis tube loaded with ceramic beads to 3/4 of the tube height. The tube was shaken at 6.0 m s^{-1} in the lysis mill for 5 shaking cycles (Table 3, entries 2, 6, 10). The colour of the reaction mixture changed to black in less than 1 minute. Comparable reaction yields were also obtained in a ball mill after 7 min milling (Table 3, entries 3, 7 and 11). As with the *meta*-compounds, the synthesis also proceeds in the melt, by heating the reaction mixture to 70 °C for 5 minutes (Table 3, entries 4, 8 and 12). The mixture turned black immediately upon melting of the alkylamine and, in the synthesis of **C4*p*** (Table 3, entry 4), white vapour was also observed upon the addition of liquid

Table 2 Synthesis of bis[4-(octadecylamino)-2-(octadecylimino)-5-oxo-1,4-cyclohexadienolato]nickel (**C18*m***)2Ni under different reaction conditions[a]

Entry	Reaction type[a]	Time (min)	Alkylamine (equiv.)	Yield (%)
1	A	720	**C18*m*** : nickel acetate, 1 : 1	69
2	A	720	**C18*m*** : nickel hydroxide, 1 : 1	10
3	B	20	**C18*m*** : nickel acetate, 1 : 1	85
4	B	20	**C18*m*** : nickel hydroxide, 1 : 1	80
5	C	120	**C18*m*** : nickel acetate, 1 : 1	71
6	C	120	**C18*m*** : nickel hydroxide, 1 : 1	70

[a] Reaction conditions: reaction type A, conventional solvent synthesis in refluxing toluene; type B, lysis mill; type C, ball mill. Detailed procedures provided in the ESI.



Scheme 3 General reaction for the synthesis of 2,5-di(alkylamino)-1,4-benzoquinones.

Table 3 Synthesis of 2,5-di(alkylamino)-1,4-quinones[a]

Entry	Product	Reaction type	Time (min)	Yield (%)
1	**C4*p***	A	300	32
2		B	5	27
3		C	7	25
4		D	5	20
5	**C12*p***	A	300	29
6		B	5	30
7		C	7	32
8		D	5	22
9	**C18*p***	A	300	22
10		B	5	28
11		C	7	27
12		D	5	21

[a] Reaction conditions: A: conventional solution synthesis in methanol (**C4*m***) and ethanol (**C12*m*** and **C18*m***); B: lysis mill; C: ball mill; D: melt. Detailed procedures provided in the ESI.

n-butylamine to benzoquinone, suggesting the reaction is sufficiently exothermic to vaporize *n*-butylamine. After work-up, it was determined that the yields were comparable to those of the solution-based and mechanochemical reactions.

In summary, two families of aminobenzoquinones were synthesized under several solvent-free reaction conditions. Compared to conventional solvent reactions, the reaction times are significantly reduced and, in a matter of minutes, yields comparable to what normally takes hours in solution can be obtained. Most importantly, the use of a lysis mill enabled a general synthetic procedure to be applied for making short-chain as well as long-chain *N*-substituted aminoquinones. Such a general synthetic procedure is not readily achievable in conventional solution media due to significant differences in solubility between short- and long-chain alkyl-substituted molecules. The reaction temperature attained during the shaking process was found to be an important parameter to consider when optimizing the mechanochemical reaction conditions. In this respect the lysis mill provides an attractive means to conduct solvent-free reactions that require simultaneous input of heat and mechanical agitation.** The mechanochemical reactivity in a lysis mill might resemble that recently reported for "vortex grinding"[38] but with the added benefits of control over speed, time and frictional heating. The lysis mill was found to be a convenient tool for performing the solvent-free syntheses of *m*- and *p*-aminoquinones on a small scale, and is also applicable for the solid-state assembly of corresponding coordination complexes, while offering increased flexibility in reactant choice.

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Notes and references

‡ As the separation procedures for the *m*- and *p*-aminoquinones depend strongly on the nature of the *N*-substituent[8,9] we opted for centrifugal chromatography as a universal method of purification applicable to products from solution, ball milling and lysis milling syntheses. Moreover, the herein reported compounds are prepared for studies in surface self-assembly, which requires samples of high purity,[44] necessitating chromatographic purification regardless of the preparation method.

§ Crystallographic and general data for **C12*m*** methanol solvate: $C_{31}H_{58}N_2O_3$, CCDC 1005686, triclinic, space group $P\bar{1}$, a = 6.6943(6) Å, b = 15.448(2) Å, c = 15.565(2) Å, α = 94.626(1)°, β = 98.453(1)°, γ = 101.528(1)°, V = 1549.9(3) Å^3, Z = 2, R_1 = 0.072, wR_2 = 0.198, (for 5370 out of 7125 independent reflections with $I \geq \sigma_I$).

¶ Prices based on the Sigma-Aldrich catalogue (online), 2014.

|| The benefits of using mineral-like precursors (oxides, hydroxides, carbonates) to metal–organic materials was previously discussed, see: (a) C. J. Adams, M. A. Kurawa, M. Lusi and A. G. Orpen, *CrystEngComm*, 2008, **10**, 1790–1795; (b) T. Friščić and L. Fábián, *CrystEngComm*, 2009, **11**, 743–745; (c) W. Yuan, J. O'Connor and S. L. James, *CrystEngComm*, 2010, **12**, 3515–3517.

** The work described herein used exclusively 2 mL Eppendorf tubes in a sample holder that can accommodate 24 samples. However, in principle, the reactions can be scaled up using 15 mL conical centrifuge tubes in a holder that can accommodate 12 samples.

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