



Cite this: *Green Chem.*, 2024, **26**, 11518

Received 30th September 2024,

Accepted 29th October 2024

DOI: 10.1039/d4gc04903a

rsc.li/greenchem

Hypervalent iodine chemistry with a mechanochemical twist†

Sayad Doobary,^a Miguel M. de Vries Ibáñez^a and Berit Olofsson^{a,b}

The combination of mechanochemistry and hypervalent iodine chemistry has rarely been reported, despite the numerous advantages offered by this enabling technology. With this in mind, this study addresses the key issue of transforming hypervalent iodine-mediated, solution-based reactions into the mechanochemical realm, accompanied by benchmarking and sustainability studies of the different types of reactions. Interestingly, several reagents displayed quite different reactivity and regioselectivity under mechanochemical conditions.

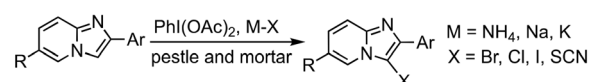
Mechanochemistry provides a unique avenue to explore organic reactivity due to its inherent solvent-free nature. The mechanical impacts created by ball-milling, pestle and mortar or extruders impart mechanical energy to activate a reaction in a similar way to thermal or irradiation activation.¹ Thus, mechanochemistry has emerged as a useful enabling technology in organic chemistry.² Whilst the solvent-free nature can lead to chemical advantages such as increased selectivity, faster reaction times and novel reactivity,³ there can also be potential sustainability benefits like less waste produced and decreased use of energy.⁴

Hypervalent iodine reagents have in recent years been demonstrated as powerful electrophilic reagents that can be utilized to give chemo- and stereoselective reactions under transition metal-free conditions.⁵ The vast majority of iodine(III) reactions are reported in solution, but there are some examples of solvent-free reactions, such as the microwave-assisted acetoxylation of oxo-benzoxazines⁶ or transamidation reactions.⁷ While mechanochemical activation has been employed in iodine(III)-mediated oxidations⁸ and in halogenation of imidazo[1,2- α]pyridines (Scheme 1A),⁹ very few reports concentrate on their use as group transfer reagents. Prominent

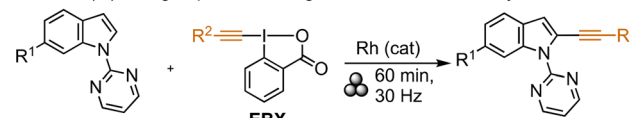
examples include a metal-catalysed indole alkynylation with ethynylbenziodoxolone (EBX, Scheme 1B),¹⁰ a fluorocyclisation to form fluorinated heterocycles,¹¹ and a copper-catalysed *N*-arylation of diaryliodonium salts.¹²

Further investigations are needed to properly assess the power of combining mechanochemistry with hypervalent iodine chemistry, and discover novel applications of this emerging technology. Hence, we have conducted a study on a multitude of hypervalent iodine-mediated transformations, which are reported in solution, to understand how to convert solution-phase to solid-phase, compare yields, and evaluate the sustainability of mechanochemical *vs.* solution reactions. Herein, we report the optimisation and scope of mechanochemical *S*-, *O*- and *C*-arylations,¹³ *S*- and *C*-vinylations, as well as a catalytic *C*-tosyloxylation (Scheme 1C). The important

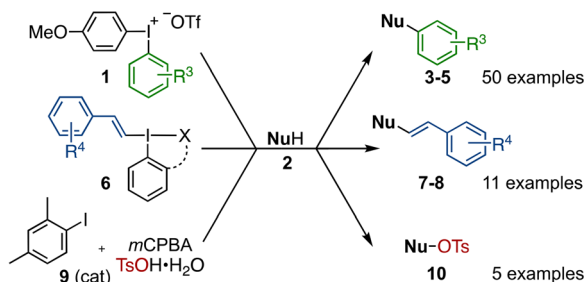
A Iodine(III) as an oxidant in mechanochemistry



B Iodine(III) as a group transfer reagent in mechanochemistry



C This work:



Scheme 1 The use of hypervalent iodine reagents in mechanochemistry as (A) an oxidant; (B) as a group transfer agent. (C) This work.

^aDepartment of Organic Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden. E-mail: Berit.Olofsson@su.se

^bStockholm University Center for Circular and Sustainable Systems (SUCCeSS), Stockholm University, 106 91 Stockholm, Sweden

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4gc04903a>



parameters and variables are highlighted during the work and comparisons to solution-based methods elucidate the superiority of mechanochemistry in many transformations.

In order to assess the key parameters governing the transformation of a solution-phase reaction to mechanochemical conditions, we first evaluated the *O*-arylation of phenols to give diaryl ethers, a transformation that proceeds well under solution-phase conditions.¹⁴ The optimisation was performed with unsymmetric diaryliodonium salt **1a** to chemoselectively give diaryl ether **3a** (Table 1).¹⁵ Initial ball milling reactions were performed at 25 Hz for 30 min, using a 1.5 mL stainless steel vessel with a 5 mm stainless steel ball. Very low yields were observed using sodium *t*-butoxide, sodium hydroxide or sodium carbonate as base (entries 1–3). A screen of frequencies showed that 35 Hz gave higher yield, which is in line with previous reports (entries 3–5).¹⁶ The effect of liquid-assisted grinding (LAG) was evaluated next,^{1c,17} and the presence of a small amount of LAG (20 μ L = 0.33 μ L mg^{−1}) increased the yield markedly (entries 6–9). The green solvent EtOAc¹⁸ was selected as LAG for further studies, and the optimum amount of LAG proved to be 20 μ L since a smaller amount resulted in a lower yield (entries 9–11). Potassium bases often work well with iodine(III) reagents,^{14e,19} and the combination of increased reaction time (3 h) and the use of potassium carbonate indeed improved the yield substantially (entries 12–14). Whilst the use of two stainless steel balls was detrimental

(entry 15), a larger ball-milling vessel (5 mL) produced similar results (entry 16). Finally, it was found that pre-milling phenol **2a** with base for 15 min, followed by 30 min of milling with diaryliodonium salt **1a** delivered diaryl ether **3a** in 91% isolated yield (entry 17). Interestingly, when the reaction was carried out in a microwave vial with a stirring bar under the same conditions, only 28% yield was garnered, indicating the importance of milling for the reaction to occur (entry 18). This optimisation serves as an example of the process of switching from solution- to solid-phase, and accounts for the most important factors, such as choice of base and LAG, amount of LAG, frequency and reaction setup.

The scope of the diaryl ether synthesis is depicted in Scheme 2A. A range of phenols with varying electronic properties were well tolerated, including halogen, nitro, *t*-butyl and methoxy substituents (**3a–3h**). Steric hindrance was well accepted, as demonstrated by *ortho*-substituted products **3f–3h**. Finally, the functional group tolerance was briefly evaluated with allyl and pyridyl groups (**3h**, **3i**). The diaryliodonium structure was varied next, keeping the anisyl group as “dummy” ligand to ensure chemoselective transfer of the green aryl group.²⁰ Reactions of phenol **2a** with varied diaryliodonium salts **1** produced **3j–3m** in good to excellent yields. Next, 2-methoxyphenol was used as nucleophile to evaluate a sterically demanding environment. Arylation with a variety of electron-deficient aryl groups, including halides, cyano and ester substituents (**3n–3q**) was achieved upon extending the reaction time to 2 h to ensure complete conversion with less reactive salts **1**. To the contrary, transfer of electron rich aryl groups was limited to a tolyl group (**3r**, **3s**), whereas a heteroaryl group was successfully transferred (**3t**). The method was subsequently evaluated for arylation of a variety of other nucleophiles, which are reported in solution. Indeed, aliphatic alcohols²¹ could be arylated in good yields (**3u–3y**) using acetonitrile as LAG.

Next, the *S*-arylation of thiols²² to yield diaryl sulfides **4** was investigated (Scheme 2B). An optimisation¹⁵ showed that cyclopentanone, which is a more sustainable LAG than EtOAc,¹⁸ was equally efficient (see Table S5†). Similar to the *O*-arylation, varied nucleophiles could be used (**4a–4e**). While the reaction was limited to incorporation of electron deficient aryl rings (**4f–4k**) and a pyridyl group (**4j**), the arylation of mercaptobenzoxazole and aliphatic thiols was feasible (**4k–4m**). The chemoselectivity of the reaction is demonstrated by the selective *S*-arylation to product **4l**, which has a free amino group.

Finally, the *C*-arylation of nitroalkanes²³ to give products **5** was investigated under mechanochemical conditions (Scheme 2C).¹⁵ The reaction was found to proceed well in the absence of a LAG, and was high-yielding for both cyclic and acyclic nitroalkanes (**5a–5h**), including transfer of the electron-rich anisyl group (**5d**) and a pyridyl group (**5f**). While a nitro-ester reacted sluggishly (**5i**), the *C*-arylation to β -keto ester **5j** proceeded smoothly.

We have recently reported metal-free, regio- and stereo-selective vinylations using vinylbenziodoxolones (VBX).²⁴ Due to the increased stability of the benziodoxolone core, reactions

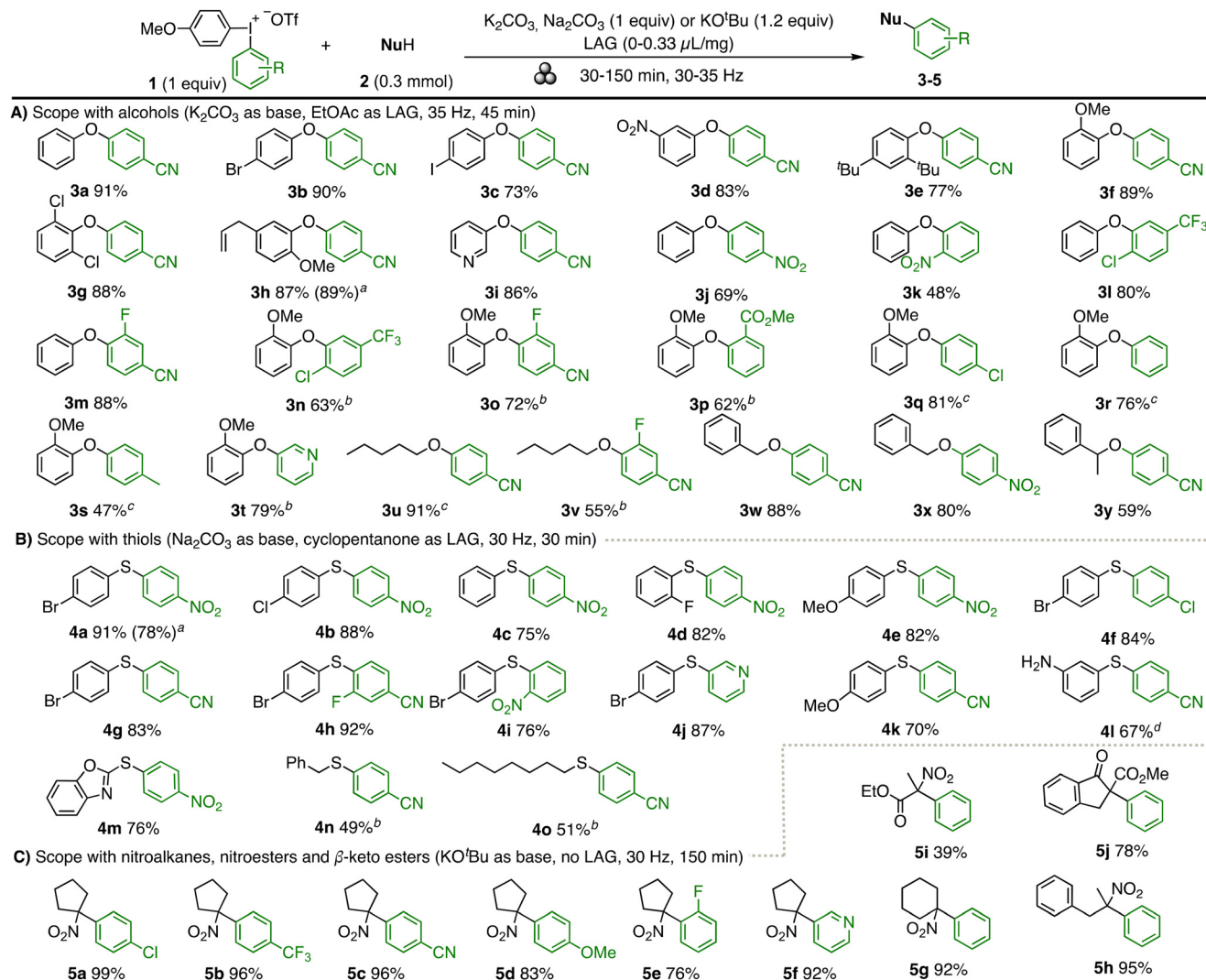
Table 1 Optimization of mechanochemical *O*-arylation^a



Entry	Frequency (Hz)	Base	LAG	Time (min)	Yield ^b (%)
1	25	NaO ^t Bu	—	60	5
2	25	NaOH	—	60	5
3	25	Na ₂ CO ₃	—	60	8
4	30	Na ₂ CO ₃	—	60	10
5	35	Na ₂ CO ₃	—	60	15
6	35	Na ₂ CO ₃	THF	60	23
7	35	Na ₂ CO ₃	MeOH	60	39
8	35	Na ₂ CO ₃	Toluene	60	40
9	35	Na ₂ CO ₃	EtOAc	60	40
10	35	Na ₂ CO ₃	EtOAc (10 μ L)	60	33
11	35	Na ₂ CO ₃	EtOAc (30 μ L)	60	41
12	35	Na ₂ CO ₃	EtOAc	180	60
13	35	KO ^t Bu	EtOAc	180	69
14	35	K ₂ CO ₃	EtOAc	180	88
15 ^c	35	K ₂ CO ₃	EtOAc	180	63
16 ^d	35	K ₂ CO ₃	EtOAc	180	90
17 ^e	35	K ₂ CO ₃	EtOAc	15 + 30	(91)
18 ^f	—	K ₂ CO ₃	EtOAc	15 + 30	28

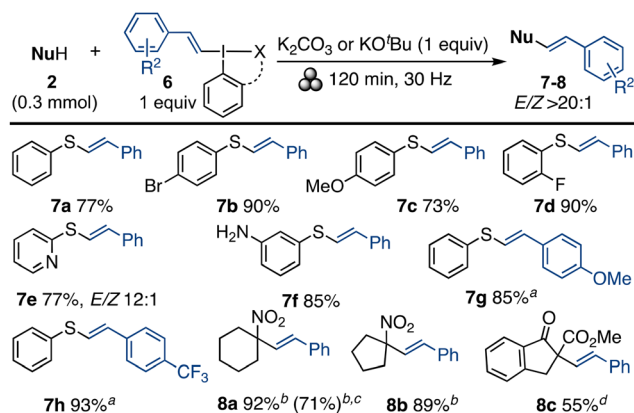
^a Standard setup: 1.5 mL stainless steel vessel with a 5 mm stainless steel ball. ^b NMR yield using 1,3,5-trimethoxybenzene (TMB) as internal standard. ^c With 2 balls. ^d With a 5 mL vessel and a 10 mm ball. ^e Pre-milling of **2a** with base for 15 min before addition of **1a**, isolated yield. ^f Reaction carried out in a microwave vial.





Scheme 2 Mechanochemical arylation scope. ^a 3.0 mmol scale; ^b 15 min pre-mill with base, then 2 h milling time with 1, ^c 2 h reaction time, MeCN as LAG, ^d EtOAc as LAG.

with VBX often give enhanced selectivity compared to vinyl (aryl)iodonium salts.^{24b,d,25} The mechanochemical vinylation efficiency of VBX and vinylidonium salts was interesting to study, and the solution-phase *S*-vinylation of thiols with VBX and $KOtBu$ was examined first.^{24a} We were pleased to discover that the reaction proceeded well with VBX 6a and the milder base K_2CO_3 in the ball mill at 30 Hz (Scheme 3). Similar to the original report, the mechanochemical yields of vinyl aryl sulfides 7 were quite high, and the products were formed with complete regioselectivity and generally with *E/Z* > 20 : 1.²⁶ The thiol scope was wide, and tolerant of free amino groups and heteroaromatics (7a–7f). Additionally, reactions with VBX reagents 6b, 6c provided 7g, 7h in good yields. Importantly, since the synthesis of 7g and 7h was higher-yielding using the mechanochemical methodology than in solution, isolation could be completed using a chromatography-free protocol,



Scheme 3 Mechanochemical vinylation scope. Products 7 formed with VBX 6a–6c and K_2CO_3 , products 8 formed with salt 6d and $KOtBu$. ^a THF as LAG, 135 min; ^b 10 min; ^c 3.0 mmol scale; ^d 30 min.



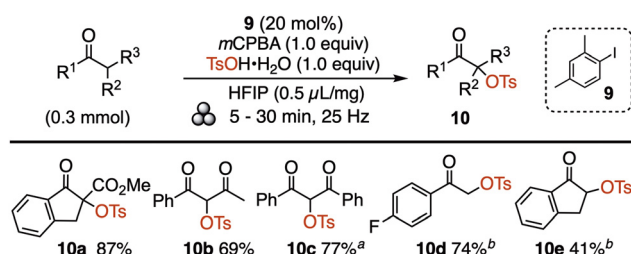
which considerably improves the sustainability of the transformation.

Finally, the *C*-vinylation of nitroalkanes^{24b} was investigated under mechanochemical conditions. The optimisation uncovered that the acyclic styryl(phenyl)iodonium tetrafluoroborate²⁷ (**6d**) produced higher yields than VBX, delivering *C*-vinylated products **8a**, **8b**. Remarkably, this mechanochemical protocol can be finished in as little as 10 min and the products were formed with excellent regioselectivity (ratio of internal/terminal alkene >20:1). In solution, the same reaction required 18 h reaction time with **6d**, and produced a measly internal/terminal ratio of 4:1, whereas solution reactions with VBX gave the terminal product in 14:1 ratio.^{24b} *C*-vinylation to give β -keto ester **8c** was also feasible.

To evaluate the scalability of the developed mechanochemical protocols, the scale was increased from 0.3 mmol to 3 mmol for products **3h**, **4a**, and **8a**. A 5 mL vessel and a 10 mm stainless steel ball were utilised to ensure sufficient space for milling to occur. Good yields were still obtained in these reactions, illustrating that upscaling is indeed possible.

Organic oxidative transformations utilising catalytic iodine(III) reagents are ubiquitous in the literature owing to the readily accessible redox couple iodine(I)/(III).^{5a,28} However, a literature search showed a complete lack of mechanochemical reactions utilizing catalytic iodine(III) reagents.²⁹ The tosyloxylation of *C*-nucleophiles has been profusely studied in solution,³⁰ and served as a good model reaction to evaluate mechanochemically. The optimisation showed that it was indeed possible to form the iodine(III) oxidant *in situ*, using a catalytic amount of 2,4-dimethylphenyl iodide (**9**) together with stoichiometric *m*CPBA and tosic acid (Scheme 4). In this fashion, several classes of substrates were tosyloxyated to give products **10** in high yields.

To evaluate the reasons for the observed reaction efficiency, we carried out the respective solution reactions in concentrations similar to that of a LAG, which usually resulted in a stark drop in yield.¹⁵ The same was true when our standard mechanochemical reactions were carried out in microwave vials with stirring bars as opposed to ball milling conditions.¹⁵ Together these results show that the mechanochemical activation is indeed required for high yields.



Scheme 4 Catalytic tosyloxylation of *C*-nucleophiles. ^a No HFIP added; ^b 1.5 equiv. *m*CPBA and tosic acid, preheated vessel. *m*CPBA = *m*-chloroperbenzoic acid; TsOH = *p*-toluenesulfonic acid; HFIP = hexafluoroisopropanol.



Chart 1 Comparison of yields and *E*-factors for mechanical and solution conditions. ^a **1** (1 equiv.), KO^tBu (1.2 equiv.), THF (0.2 M), 40 °C, 1 h;^{14a} ^b **1** (1 equiv.), DBU (1.1 equiv.), MeCN (0.1 M), 80 °C for 1.5 h;^{22a} ^c Yields taken from the literature; **5f**,²³ **7g**,^{24a} **10c**,^{30a} ^d **6d** (1.1 equiv.), KO^tBu (1.1 equiv.), THF (0.024 M), rt, 18 h.^{24a}

Having demonstrated the facile conversion of known solution-phase transformations to mechanochemical conditions, we wanted to evaluate the efficiency and sustainability of the developed mechanochemical methods. The *E*-factor, which is defined as the mass ratio of waste to desired product, is a very useful sustainability benchmarking method.^{4,31} To highlight the differences between mechanochemical and solution-phase reactions, we decided to calculate the *E*-factors excluding the waste created *via* purification (which was expected to be rather similar for both methods). Chart 1 details the comparison of yields and *E*-factors for selected products¹⁵ using the arylation, vinylation and tosyloxylation methodologies. The mechanochemical arylations sometimes produced markedly higher yields (**3h**, **3q**, **4g**) than the reactions in solution.^{21,22e,23} A similar trend was seen for *S*-vinylation, where the high yields obtained mechanochemically enabled column-free purification and hence higher *E*/*Z* ratios (**7g**).^{24a} For the *C*-vinylation, the mechanochemical protocol provides higher yields and better regioselectivity (internal/terminal alkene) than in solution.

The comparison of *E*-factors highlights that the mechanochemical methods produce far less waste than the corresponding solution-phase reactions; particularly striking are the results for **7g** and **8c**, which are low-yielding in solution and have high *E*-factors. The difference is especially interesting for products with higher yields using solution-phase methodologies (**3q**, **10c**), as the solution-phase still has much higher *E*-factors.

Conclusions

In conclusion, we have successfully transferred known hypervalent iodine-mediated arylations, vinylation and tosyloxylation from solution- to solid-phase. Furthermore, the first catalytic hypervalent iodine protocol utilising mechanochemistry was developed. The scope studies revealed several examples where the mechanochemical methods were superior, and a



comparison of E-factors showed that the novel protocols are far more sustainable. The results establish the value of combining mechanochemistry with hypervalent iodine chemistry, and the discovered key parameters for methodology transfer from solution are likely also applicable when developing other mechanochemical hypervalent iodine reactions.

Author contributions

Sayad Doobary: conceptualization, investigation, methodology, supervision, writing – original draft, writing – review & editing; Miguel M. de Vries Ibáñez: investigation, methodology; Berit Olofsson: funding acquisition, validation, project administration, resources, supervision, writing – review & editing.

Data availability

The data supporting this article have been included as part of the ESI.† Raw data can be found online at: <https://doi.org/10.5281/zenodo.13991537>.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Carl Trygger Foundation (20:316) and Olle Engkvist Foundation (224-0058) are kindly acknowledged for financial support.

References

- (a) B. R. Naidu, T. Sruthi, R. Mitty and K. Venkateswarlu, *Green Chem.*, 2023, **25**, 6120–6148; (b) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413–447; (c) J.-L. Do and T. Friščić, *ACS Cent. Sci.*, 2017, **3**, 13–19; (d) K. Kubota, Y. Pang, A. Miura and H. Ito, *Science*, 2019, **366**, 1500–1504.
- (a) J.-L. Do and T. Friščić, *Synlett*, 2017, 2066–2092; (b) D. Tan and T. Friščić, *Eur. J. Org. Chem.*, 2018, 18–33.
- J. L. Howard, Q. Cao and D. L. Browne, *Chem. Sci.*, 2018, **9**, 3080–3094.
- (a) N. Fantozzi, J.-N. Volle, A. Porcheddu, D. Virieux, F. García and E. Colacino, *Chem. Soc. Rev.*, 2023, **52**, 6680–6714; (b) K. J. Ardila-Fierro and J. G. Hernández, *ChemSusChem*, 2021, **14**, 2145–2162.
- (a) A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2024, **124**, 11108–11186; (b) A. Bauer and N. Maulide, *Chem. Sci.*, 2021, **12**, 853–864; (c) W. W. Chen, A. B. Cuenca and A. Shafir, *Angew. Chem., Int. Ed.*, 2020, **59**, 16294–16309; (d) P. Villo and B. Olofsson, in *Patai's Chemistry of Functional Groups: The Chemistry of Hypervalent Halogen Compounds*, ed. B. Olofsson, I. Marek and Z. Rappoport, 2019, pp. 461–522.
- R. Prajapati, A. K. Gola, A. Kumar, S. Jaiswal and N. Tadigoppula, *New J. Chem.*, 2022, **46**, 5719–5724.
- R. Vanjari, B. Kumar Allam and K. Nand Singh, *RSC Adv.*, 2013, **3**, 1691–1694.
- (a) M. S. Yusubov and T. Wirth, *Org. Lett.*, 2005, **7**, 519–521; (b) L. Gonnet, C. André-Barrès, B. Guidetti, A. Chamayou, C. Menendez, M. Baron, R. Calvet and M. Baltas, *ACS Sustainable Chem. Eng.*, 2020, **8**, 3114–3125; (c) S. M. Zeitler, P. Chakma and M. R. Golder, *Chem. Sci.*, 2022, **13**, 4131–4138; (d) L. Pan, L. Zheng, Y. Chen, Z. Ke and Y.-Y. Yeung, *Angew. Chem., Int. Ed.*, 2022, **61**, e202207926.
- D. R. Indukuri, G. R. Potuganti and M. Alla, *Synlett*, 2019, 1573–1579.
- G. N. Hermann, M. T. Unruh, S.-H. Jung, M. Krings and C. Bolm, *Angew. Chem., Int. Ed.*, 2018, **57**, 10723–10727.
- W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun.*, 2021, 57, 7406–7409.
- J. Jiang and J. Li, *ChemistrySelect*, 2020, **5**, 542–548.
- Mechanochemical N-arylations were not investigated as they are already reported, see ref. 12.
- (a) N. Jalalian, E. E. Ishikawa, L. F. Silva and B. Olofsson, *Org. Lett.*, 2011, **13**, 1552–1555; (b) E. Lindstedt, R. Ghosh and B. Olofsson, *Org. Lett.*, 2013, **15**, 6070–6073; (c) S. K. Sundalam and D. R. Stuart, *J. Org. Chem.*, 2015, **80**, 6456–6466; (d) T. Sasaki, K. Miyagi, K. Moriyama and H. Togo, *Org. Lett.*, 2016, **18**, 944–947; (e) R. T. Gallagher, S. Basu and D. R. Stuart, *Adv. Synth. Catal.*, 2020, **362**, 320–325.
- See the ESI† for details.
- S. Ni, M. Hribersek, S. K. Baddigam, F. J. L. Ingner, A. Orthaber, P. J. Gates and L. T. Pilarski, *Angew. Chem., Int. Ed.*, 2021, **60**, 6660–6666.
- (a) L. E. Wenger and T. P. Hanusa, *Chem. Commun.*, 2023, **59**, 14210–14222; (b) P. Ying, J. Yu and W. Su, *Adv. Synth. Catal.*, 2021, **363**, 1246–1271.
- C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.
- (a) F. Gang, Y. Che, Z. Du, H. Feng and Y. Fu, *Synlett*, 2017, 1624–1629; (b) K. Jiang, X. Li, L. Wang and J. Han, *Asian J. Org. Chem.*, 2024, **13**, e202400139; (c) Y. Kakinuma, K. Moriyama and H. Togo, *Synthesis*, 2013, 183–188; (d) C. Wu, C. Zhao, J. Zhou, H.-S. Hu, J. Li, P. Wu and C. Chen, *Commun. Chem.*, 2020, **3**, 92; (e) S. Yang, W. Hua, Y. Wu, T. Hu, F. Wang, X. Zhang and F. Zhang, *Chem. Commun.*, 2018, **54**, 3239–3242; (f) S. Yang, F. Wang, Y. Wu, W. Hua and F. Zhang, *Org. Lett.*, 2018, **20**, 1491–1495; (g) E. Linde, D. Bulfield, G. Kervefors, N. Purkait and B. Olofsson, *Chem*, 2022, **8**, 850–865.



- 20 (a) J. Malmgren, S. Santoro, N. Jalalian, F. Himo and B. Olofsson, *Chem. – Eur. J.*, 2013, **19**, 10334–10342; (b) D. R. Stuart, *Chem. – Eur. J.*, 2017, **23**, 15852–15863.
- 21 R. Ghosh, E. Lindstedt, N. Jalalian and B. Olofsson, *ChemistryOpen*, 2014, **3**, 54–57.
- 22 (a) S. Sarkar, N. Wojciechowska, A. A. Rajkiewicz and M. Kalek, *Eur. J. Org. Chem.*, 2022, e202101408; (b) A. M. Wagner and M. S. Sanford, *J. Org. Chem.*, 2014, **79**, 2263–2267; (c) D. Wang, X. Yu, K. Zhao, L. Li and Y. Ding, *Tetrahedron Lett.*, 2014, **55**, 5739–5741; (d) B. Zhang, Y. Kang, L. Yang and X. Chen, *ChemistrySelect*, 2016, **1**, 1529–1532; (e) A. Krief, W. Dumont and M. Robert, *Synlett*, 2006, 484–486.
- 23 C. Dey, E. Lindstedt and B. Olofsson, *Org. Lett.*, 2015, **17**, 4554–4557.
- 24 (a) L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen and B. Olofsson, *Angew. Chem., Int. Ed.*, 2020, **59**, 15512–15516; (b) E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. – Eur. J.*, 2016, **22**, 16066–16070; (c) L. Castoldi, A. A. Rajkiewicz and B. Olofsson, *Chem. Commun.*, 2020, **56**, 14389–14392; (d) N. Declas, G. Pisella and J. Waser, *Helv. Chim. Acta*, 2020, **103**, e2000191; (e) E. M. Di Tommaso, P.-O. Norrby and B. Olofsson, *Angew. Chem., Int. Ed.*, 2022, **61**, e202206347.
- 25 A. Yoshimura, A. Saito and V. V. Zhdankin, *Adv. Synth. Catal.*, 2023, **365**, 2653–2675.
- 26 In solution, the *S*-vinylation provided product **7e** with an *E/Z* ratio of only 5 : 1 (see ref. 24a). The *E*-product is formed through a stereospecific ligand coupling mechanism (see ref. 24e), but some products are prone to isomerization during purification on silica.
- 27 M. Ochiai, T. Shu, T. Nagaoka and Y. Kitagawa, *J. Org. Chem.*, 1997, **62**, 2130–2138.
- 28 F. V. Singh, S. E. Shetgaonkar, M. Krishnan and T. Wirth, *Chem. Soc. Rev.*, 2022, **51**, 8102–8139.
- 29 Ref. 8d demonstrates *in situ*-formation of iodine(III) utilizing 50 mol% of ArI combined with 1.5 equiv. *m*CPBA under mechanochemical conditions. Since the product yield is 30%, the reaction is not catalytic.
- 30 (a) A. Tanaka and H. Togo, *Synlett*, 2009, 3360–3364; (b) Y. Yamamoto and H. Togo, *Synlett*, 2006, 798–800; (c) E. A. Merritt and B. Olofsson, *Synthesis*, 2011, 517–538; (d) R. D. Richardson, T. K. Page, S. Altermann, S. M. Paradine, A. N. French and T. Wirth, *Synlett*, 2007, 538–542; (e) H. Alharbi, M. Elsherbini, J. Qurban and T. Wirth, *Chem. – Eur. J.*, 2021, **27**, 4317–4321; (f) B. D. Rupanawar, K. D. Mane and G. Suryavanshi, *New J. Chem.*, 2022, **46**, 16832–16839.
- 31 R. A. Sheldon, *Green Chem.*, 2023, **25**, 1704–1728.

