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Repurposing of halogenated organic pollutants via alkyl bromide-catalysed transfer chlorination

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Halogenated organic pollutants (HOPs) are causing a significant environmental and human health crisis due to their high levels of toxicity, persistence and bioaccumulation. Urgent action is required to develop effective approaches for the reduction and reuse of HOPs. Whereas current strategies focus primarily on the degradation of HOPs, repurposing them is an alternative approach, albeit a challenging task. Here we discover that alkyl bromide can act as a catalyst for the transfer of chlorine using alkyl chloride as the chlorine source. We demonstrate that this approach has a wide substrate scope, and we successfully apply it to reuse HOPs that include dichlorodiphenyltrichloroethane, hexabromocyclododecane, chlorinated paraffins, chloromethyl polystyrene and poly(vinyl chloride) (PVC). Moreover, we show that the synthesis of essential non-steroidal anti-inflammatory drugs can be achieved using PVC and hexabromocyclododecane, and we demonstrate that PVC waste can be used directly as a chlorinating agent. Overall, this methodology offers a promising strategy for repurposing HOPs.

Besides being used as basic building blocks in synthesis, organic halides are widely used as pharmaceuticals, agrochemicals and materials[1]. However, extensive use of these compounds has led to the release of large quantities of halogenated organic pollutants (HOPs) into the environment, resulting in progressively severe environmental damage. Compounds of major concern comprise organochlorine insecticides, flame retardants, plasticizers and polymers[2] (Fig. 1a). Notable examples of these HOPs include dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), hexabromocyclododecane (HBCD), chlorinated paraffins (CPs), chloromethyl polystyrene (CMPS) and poly(vinyl chloride) (PVC). Although DDT (global consumption, 400,000 tons annually from 1945 to 1972)[3], HCH (4–7 million tons present in the environment)[4,5] and HBCD (global market demand, 31,000 tons annually in 2011)[6] are included as persistent organic pollutants (or POPs) in the Stockholm Convention and their use has been limited because of their toxic, persistent and bioaccumulative properties, large amounts of them have already accumulated in the environment. In addition, CPs (global production, 2 million tons annually)[7], PVC (global consumption, >50 million tons annually)[8] and CMPS are still being used on a large scale and with a low recycling rate, which has the potential to cause significant damage to both the environment and human health. In response to this impending environmental crisis, extensive efforts have been devoted to eliminating stockpiles of HOPs from the environment, involving various strategies such as biological or microbial[9], chemical[10,11], photochemical[12,13], electrochemical[14], thermal[15] and mechanochemical[16] means. However, most of the research on HOP remediation has focused on either the direct or mediated degradation of these pollutants. The repurposing (reusing) of HOPs is undoubtedly a more desirable approach, as it not only offers a means of pollution abatement but also has the potential to reduce greenhouse gas emissions associated with the production of virgin materials[17,18].

Despite the abundance of halogens in HOPs, their utility in the synthesis of other halides remains limited. Traditional methods for

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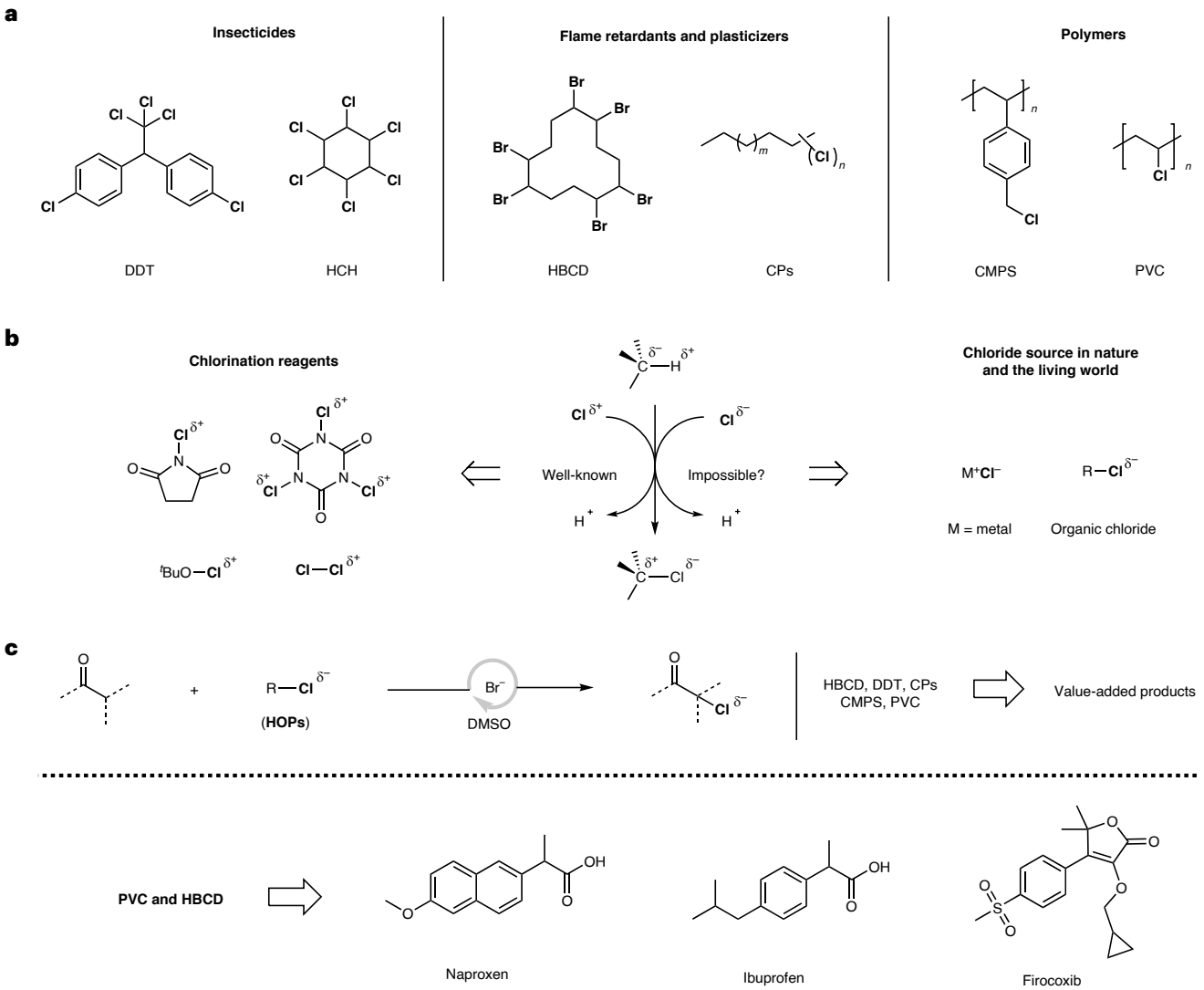

Fig. 1 | HOPs and their repurposing. a, Representative HOPs include insecticides, flame retardants, plasticizers and polymers. These contaminants pose a threat to the environment due to their bioaccumulation, toxicity and persistence, as well as their high production and low recovery rate. **b**, Traditional methods for the chlorination of C–H bonds using $Cl^{\delta+}$-containing reagents. Using $Cl^{\delta-}$-containing compounds (the major forms of chloride in nature and the living world) as chlorinating agents is a better choice because they are cheap, readily available and more stable. **c**, A strategy for repurposing HOPs using alkyl bromide-catalysed transfer chlorination enables the production of versatile α-chloroketones. Using this approach, various non-steroidal anti-inflammatory drugs, including naproxen, ibuprofen and firocoxib, were successfully synthesized utilizing PVC and HBCD.

the chlorination of C–H bonds often utilize reagents that can provide Cl^+ species either directly or in situ[19–26], such as *N*-chlorosuccinimide, trichloroisocyanuric acid, *tert*-butyl hypochlorite and chlorine (Fig. 1b). Nevertheless, these chlorinating agents are relatively expensive, toxic, hazardous and difficult to store compared with $Cl^{\delta-}$-containing reagents. Furthermore, owing to the strong oxidizing properties of Cl^+, many unwanted side reactions frequently occur during chlorination reactions[27–29]. In nature and the living world, the major forms of chloride are $Cl^{\delta-}$-containing species, particularly HOPs. However, there have been few reports on the use of alkyl chlorides as chlorinating agents[30–33], and the direct chlorination of C–H bonds using HOPs presents greater difficulties: (1) the C–Cl bonds of HOPs need to be broken first; (2) it is problematic to use the free chloride anion and C–H bonds to form new C–Cl bonds without strong oxidants; and (3) the rupture of newly formed C–Cl bonds needs to be avoided. This transfer chlorination process poses a formidable challenge but is crucial for the repurposing of HOPs.

Here we have developed a strategy for the repurposing of HOPs via alkyl bromide-catalysed transfer chlorination (Fig. 1c). Our strategy exhibits versatility with respect to substrate scope, and both the chlorine-transfer reagents and catalysts can be HOPs. This method not only enables the chlorination of ketones but also facilitates the chlorohydroxylation of olefins via the chlorine-transfer reaction. The resulting α-chloroketones serve as important intermediates for the synthesis of various medicines, including naproxen, ibuprofen and firocoxib. Moreover, PVC waste can be reused through transfer chlorination. Thus, this approach offers the potential for transforming HOPs into high-value products and holds considerable promise for practical applications.

Results and discussion

Scope of organic halides

After the evaluation of various reaction parameters, we established that alkyl bromide can act as a catalyst in the transfer of chlorine from an alkyl chloride to the α-position of the carbonyl moiety when in dimethyl sulfoxide (DMSO) (Supplementary Fig. 1). Considering the diversity of HOP structures, a library of these halogenated compounds was established. It shows that several variations of alkyl bromide can

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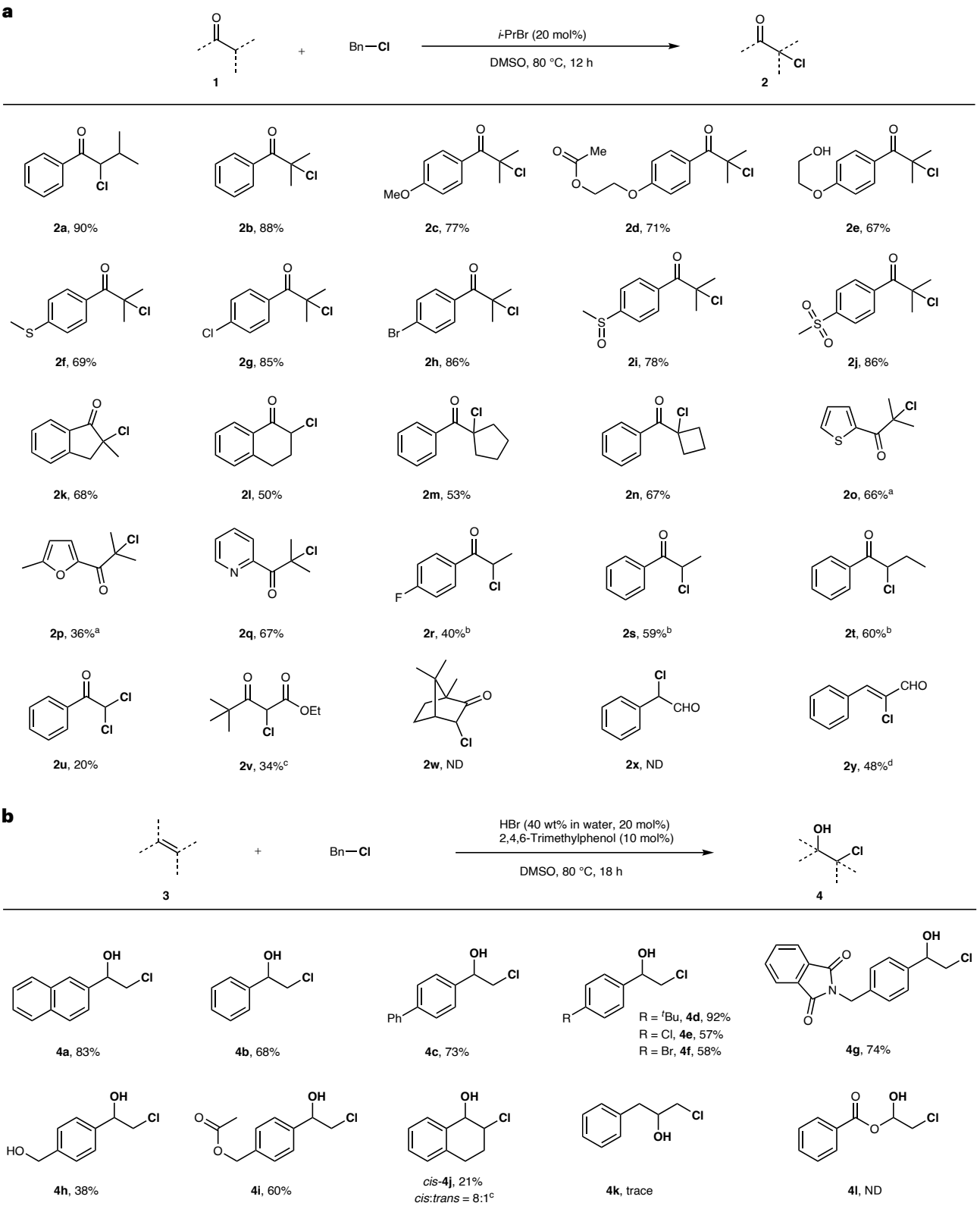

Fig. 2 | Substrate scope. a, Substrate scope of transfer chlorination. Conditions: **1** (0.40 mmol), BnCl (0.80 mmol), *i*-PrBr (20 mol%), DMSO (0.5 ml), 80 °C, under air. Bn, benzyl; ND, not detected. **b**, Substrate scope of chlorohydroxylation. Conditions: **3** (0.40 mmol), BnCl (0.80 mmol), HBr (40 wt% in water, 20 mol%), 2,4,6-trimethylphenol (10 mol%), DMSO (1.0 ml), 80 °C, under air. [a]100 °C. [b]Solvent is DMSO/CH_3CN (v/v, 1:1). [c]Determined using ^1H NMR. [d]From hydrocinnamaldehyde.

serve as a catalyst for this reaction, resulting in satisfactory yields of the corresponding products (45–87%). However, the catalytic efficiency of alkyl bromide was found to be influenced by its structure, with primary, secondary and benzylic alkyl bromide performing better (80, 85 and 87%, respectively) than tertiary (58%) and cyclic alkyl bromide (45%). Regrettably, aryl bromide was found to be ineffective

for catalysing this reaction. Subsequently, the scope of this transfer chlorination was explored using 2-bromopropane as the catalyst. It was found that primary, secondary and tertiary alkyl chloride functioned well as chlorine-transfer reagents (54, 50 and 54% yield, respectively), with benzyl chloride producing the best result (85%). Furthermore, dichloride and trichloride compounds were also found to be effective for transfer chlorination (41 and 56% yield, respectively). These results demonstrate that alkyl bromide-catalysed transfer chlorination has a broad substrate scope and possesses immense potential for the repurposing of HOPs.

Chlorination of ketones

Encouraged by the above results, we investigated the scope of ketones using 2-bromopropane as a catalyst and benzyl chloride as the chlorine-transfer reagent (Fig. 2a). In general, steric hindrance has a detrimental effect on the transfer reaction. However, it is interesting to note that a ketone with a bulky group afforded the product in high yield (**2b**, 88%). Both electron-donating and electron-withdrawing ketones afforded the target products in good yields (**2c**–**2j**, 67–86%), indicating that the electronic variations did not influence the reactions obviously. In addition, the reactions were compatible with various polar functional groups, such as ester (**2d**), alcohol (**2e**), sulfoxide (**2i**) and sulfone (**2j**). Furthermore, these conversions were applicable to cyclic ketones, such as 2-methyl-1-indanone (**2k**) and 1-tetralone (**2l**). Notably, substrates bearing four- or five-membered rings were chlorinated in good yields (**2m** and **2n**, 53% and 67%). It should be noted that **2n** was accompanied by inseparable brominated products, but in other reactions, brominated products were not obtained after the reaction, which may be due to the oxidation of brominated by-products by DMSO. Interestingly, ketones that contain heterocycles such as thiophene, furan and pyridine were also able to undergo the desired transformation to α-chloroketones (**2o**–**2q**, 36–67%). Ketones containing groups with lower steric hindrance exhibited good tolerance and yielded the corresponding products (**2r**–**2t**, 40–60%). The reaction of acetophenone produced the dichloride product **2u** in 20% yield. In addition, a ketone without an aryl group can still undergo transfer (**2v**, 34%), but D(+)-camphor did not generate the target product (**2w**). It was observed that using phenylacetaldehyde did not give the desired target product **2x**. Intriguingly, the synthesis of the chlorinated olefin **2y** (48%) can be achieved through using hydrocinnamaldehyde.

Chlorohydroxylation of olefins

It was proposed that the ketones will undergo isomerization to enols before chlorination. We wondered whether olefins could also undergo chlorination (Fig. 2b). To our delight, after careful evaluation of the reaction parameters, it was found that the chlorohydroxylation of olefins can be achieved using HBr (40 wt% in water) as the catalyst and benzyl chloride as the chlorine-transfer reagent. Control experiments (Supplementary Table 5) demonstrated that water plays a crucial role in the reaction. To avoid polymerization of the olefins, a radical inhibitor (2,4,6-trimethylphenol) was added. Having established the optimized conditions, the scope of HBr-catalysed chlorohydroxylation was explored (Fig. 2b). The compound 2-vinylnaphthalene delivered the target product **4a** well, in 83% yield. The chlorohydroxylation of styrene and phenyl-substituted styrene proceeded smoothly, yielding **4b** and **4c** in 68% and 73% yield, respectively. However, the yields of products with electron-withdrawing groups (**4e** and **4f**, 57% and 58%, respectively) were slightly lower than that of the product with an electron-donating group (**4d**, 92%). In addition, amides (**4g**), alcohols (**4h**) and esters (**4i**) were well tolerated in this transformation. Moreover, the target product (**4j**) was also obtained via this reaction when starting with 1,2-dihydronaphthalene. However, olefins that are not conjugated with aryl groups did not work (**4k** and **4l**).

Mechanistic investigations

To explain the mechanistic details of the process, several control experiments were conducted. The bromination of **1a** was achieved in 69% yield (Fig. 3a, reaction (1)) in the presence of 2-bromopropane and DMSO at 100 °C (72% yield was achieved using HBr; Supplementary Table 6). This indicates that the brominated ketone **5a** may serve as a crucial intermediate for the transfer chlorination reaction. The reaction of **5a** and benzyl chloride yielded **2a** in 49% yield (reaction (2)), further substantiating the role of **5a** as an intermediate in the reaction. In DMSO, **5a** is capable of undergoing halogen-exchange reactions with LiCl, NaCl or KCl to yield product **2a** (Supplementary Table 8). Moreover, it was observed that **5a** exhibited catalytic activity for transfer chlorination (reaction (3)), whereas the reaction did not proceed in the absence of bromide (reaction (4)). These findings demonstrate that bromide plays a catalytic role in the reaction. The transfer chlorination reaction did not occur without DMSO (reaction (3)) or in CH_3CN (Supplementary Table 9), which suggests that DMSO is also involved in the reaction. Furthermore, under acidic conditions, chloride products can also be obtained when inorganic bromides and chlorides are used (Supplementary Table 11).

To determine the generation pathway of transfer bromination for various alkyl bromides, related experiments were conducted. As the reaction proceeded, formation of the brominated product **5a** was observed, accompanied by the consumption of primary alkyl bromide **6a** (Extended Data Fig. 1a, I). Furthermore, a comparable amount of primary alcohol **7a** was generated alongside the brominated product, while the olefin **8a** generated by the elimination reaction was not detected. These findings suggest that primary alkyl bromide **6a** undergoes transformation to the corresponding alcohol. In the case of secondary alkyl bromide **6b** (Extended Data Fig. 1a, II), the reaction mechanism was similar to that of the primary alkyl bromide. The secondary alkyl bromide **6b** was converted to the corresponding alcohol **7b** rather than olefin **8b**. When the transfer bromination was carried out with tertiary alkyl bromine **6c**, the kinetic curve showed a distinct reaction pathway. Specifically, alkyl bromide **6c** was rapidly consumed to generate the corresponding olefins **8c** and **8c′**, with the corresponding tertiary alcohol being almost undetectable (Extended Data Fig. 1a, III). These results indicate that debromination of the tertiary alkyl bromide is an elimination reaction. With respect to chlorine-transfer reactions (Extended Data Fig. 1b), the trend of feedstock consumption and product formation is similar to that of the bromination reactions (Extended Data Fig. 1a), albeit with a lower reaction rate. In addition, the formation of brominated products was observed first, providing further confirmation that brominated products serve as intermediates in transfer chlorination reactions.

Proposed mechanism

In light of the above results, a proposed mechanism is described in detail in Fig. 3b. Initially, the primary or secondary halogenated compound **6**/**9** undergoes a nucleophilic substitution reaction with DMSO to afford alkoxysulfonium salt **A**, which produces the corresponding alcohol **7** and the hydrogen halide through hydrolysis[34,35]. Conversely, the tertiary halide **6**/**9** yields hydrogen halide and an olefin through an elimination reaction under heating. Subsequently, under acidic conditions, the bromide anion is oxidized to Br^+ by DMSO[36,37]. Following this, ketone **1** undergoes enol isomerization and reacts with Br^+ to form the brominated product **5**. Finally, the free chloride ion and brominated product **5** undergo a halogen-exchange reaction to form the chlorinated product **2**, and the bromide ion is regenerated.

Repurposing of HOPs

Next, we extended the protocol to encompass the repurposing of various HOPs (Fig. 4). HBCD is persistent, bioaccumulative and globally distributed, and as such, many countries have begun to limit its production and use due to the potential threat it poses to the environment

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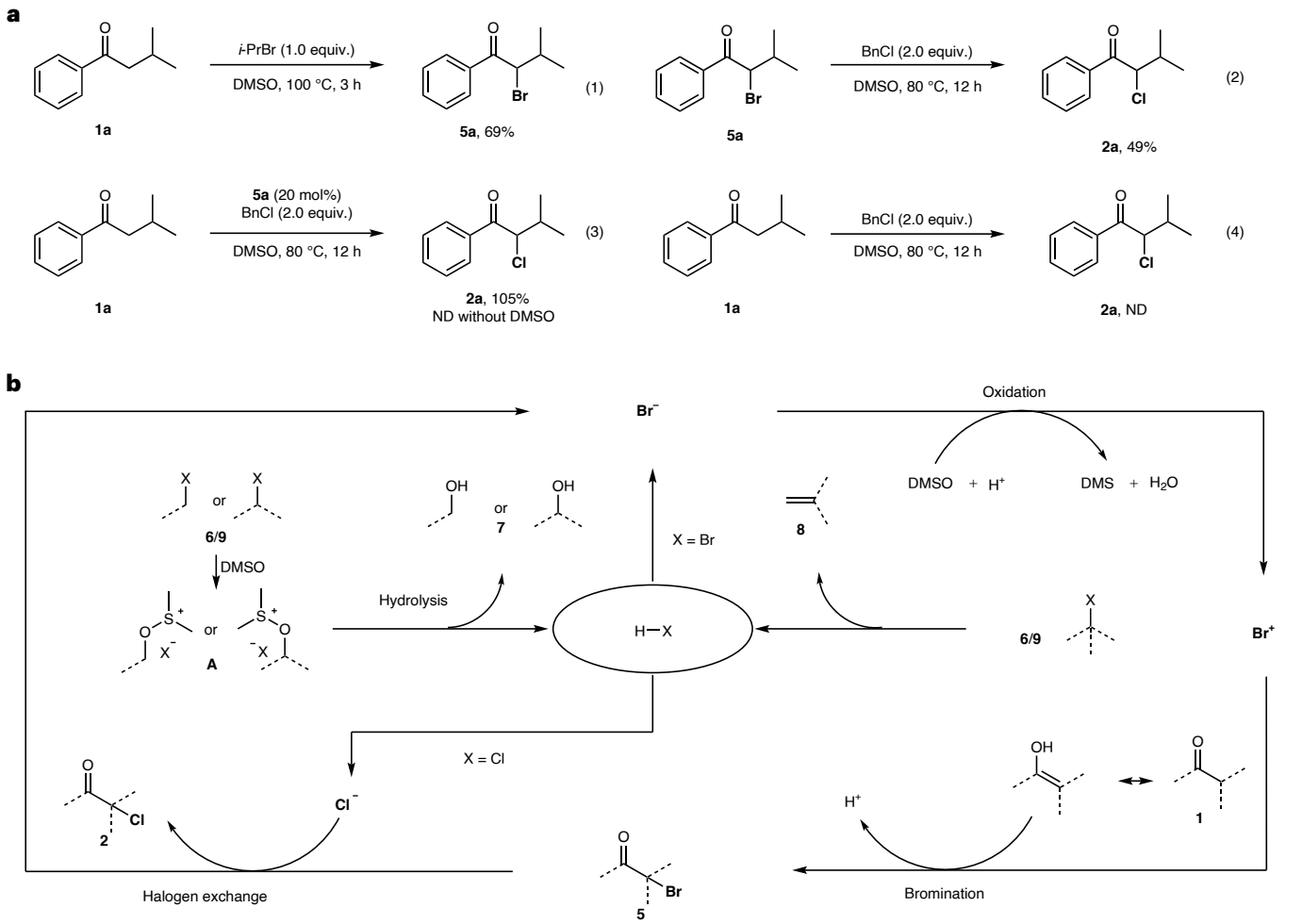

Fig. 3 | Mechanistic studies and proposed mechanism. a, Control experiments show that the brominated ketone serves as a crucial intermediate, and that DMSO is necessary. **b**, According to control experiments and kinetic studies, a proposed mechanism involving halogen-exchange reactions has been suggested.

and human health[38]. Therefore, there is an urgent need to mitigate HBCD risks. Mechanistic studies showed that alkyl bromides can be used as transfer bromination reagents, enabling the repurposing of this pollutant through reaction with ketones in mixed solvents of DMSO and 1,4-dioxane (Fig. 4a). The resulting brominated products (**5a**–**5c**) were obtained in good yields (71–90%) with 1.0 equivalent of HBCD. Even at a stoichiometric ratio of 0.2 equiv. HBCD, compound **5a** can still be synthesized in 59% yield. Structural analysis of the reacted HBCD (Supplementary Fig. 8) showed that bromine transfer during the reaction is primarily accomplished through the elimination of hydrogen bromide. In addition, HBCD can serve as a catalyst for transfer chlorination reactions. As shown in Fig. 4a, using 10 mol% of HBCD as the catalyst, ketones **1** were transformed to **2** (**2a**, **2b** and **2s**) in good yields (69–91%). Using 2 mol% of HBCD also exhibited a decent catalytic efficiency (**2a**, 56%). The mechanism shows that alkyl bromide is oxidized to Br^+, which can be utilized for the bromination of aromatic hydrocarbons (**10**). By simply switching the dosage of HBCD, monobromo (**11a**) and dibromo (**11a′**) products can be selectively generated in moderate yields (51 and 57%, respectively). Aniline (**11b**), which is easily brominated, requires a relatively small amount of brominating agent (0.3 equiv. HBCD). Furthermore, the indole (**11c**) substrate is suitable for this reaction.

Although there have been few studies on the toxicity of CPs, extant research posits that protracted exposure to this chemical may cause deleterious impacts on the human endocrine system[7,39]. In addition, CPs are known to be highly persistent and readily disseminated within the environment, with detectable levels even present in human blood[7]. Consequently, there has arisen a palpable and highly warranted concern regarding the potential for CPs to engender environmental pollution. However, transfer chlorination reactions offer a solution to this issue, as they enable the synthesis of value-added chlorinated products (**2a** and **2b**, 57 and 64% yields, respectively) that can mitigate CP emissions in the environment (Fig. 4b). In addition, a 33% yield of **2a** was achievable using 1 equiv. CPs.

The extensive utilization of DDT as an insecticide has resulted in severe environmental contamination. Despite this, in certain areas, it is still being manufactured for the purpose of malaria control[3]. The repurposing of DDT presents a promising solution for mitigating its adverse environmental impact. In addition, the catalytic reaction of alkyl bromide can facilitate an efficient transfer chlorination process leading to the production of the corresponding chlorinated products (Fig. 4c). In this reaction, DDT is converted to dichlorodiphenyldichloroethylene (Supplementary Section 7.3), which exhibits lower toxicity than DDT[40]. Given that DDT is frequently detected in soil as a contaminant, a DDT/soil mixture was used as a chlorinating reagent. Gratifyingly, the soil component did not exhibit any clear influence on the reaction.

The proliferation of waste plastics, particularly those that contain chlorine, has led to an alarming increase in environmental contamination. In response to this, we have identified the chlorine-containing polymer CMPS as a promising candidate for repurposing. Our investigations showed that CMPS is capable of effectively transferring

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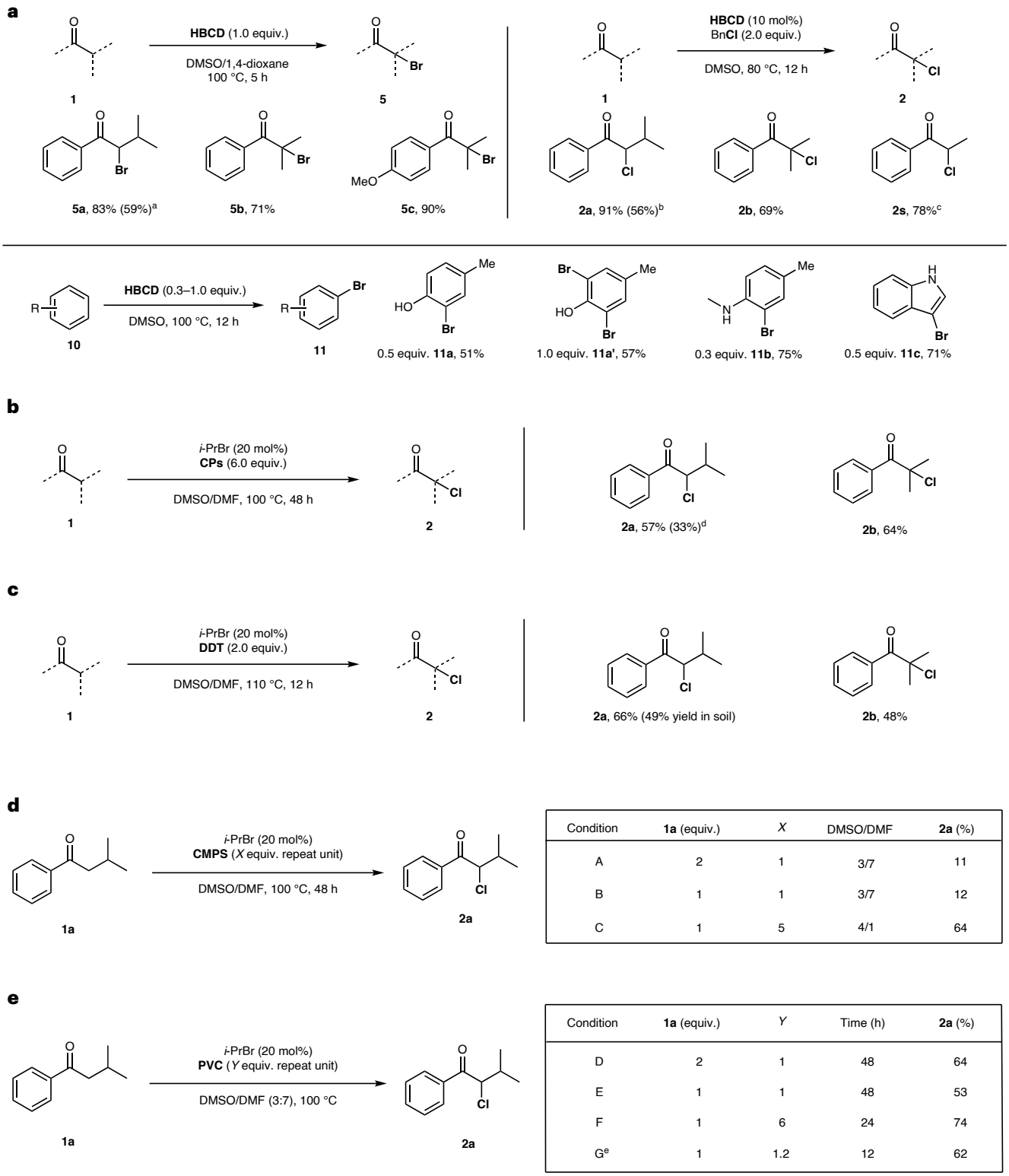

Condition	1a (equiv.)	X	DMSO/DMF	2a (%)
A	2	1	3/7	11
B	1	1	3/7	12
C	1	5	4/1	64

Condition	1a (equiv.)	Y	Time (h)	2a (%)
D	2	1	48	64
E	1	1	48	53
F	1	6	24	74
G[e]	1	1.2	12	62

Fig. 4 | HOP valorization. a, HBCD can serve not only as a catalyst for transfer chlorination reactions but also as a bromination reagent to achieve the bromination of ketones and arenes. **b**, CPs can be reconsidered as chlorinating reagents utilizing the chloride-transfer reaction. **c**, The catalytic reaction of alkyl bromide enables efficient chlorine transfer from DDT to ketones. In addition, soil has little impact on this reaction. **d**, Experiments show that CMPS effectively transfers chlorine to ketones in DMSO and DMF, but solubility issues result in low product yield. Adjusting solvent ratio and increasing the amount of CMPS enhance the product yield significantly. **e**, Using PVC as the chlorinating reagent, the chlorinated product was synthesized successfully. Increasing the PVC dosage and temperature can enhance the reaction efficiency. For detailed optimization, see Supplementary Tables 26–30. [a]HBCD (0.2 equiv.), H_2O (6.0 equiv.), DMSO (0.25 ml), 120 °C, then **1a** (1.0 equiv.), 80 °C. [b]HBCD (2 mol%), 48 h. [c]DMSO/CH_3CN (v/v, 1:1). [d]**1a** (2.0 equiv.), CPs (1.0 equiv.). [e]DMSO/DMF (v/v, 1:9), 120 °C.

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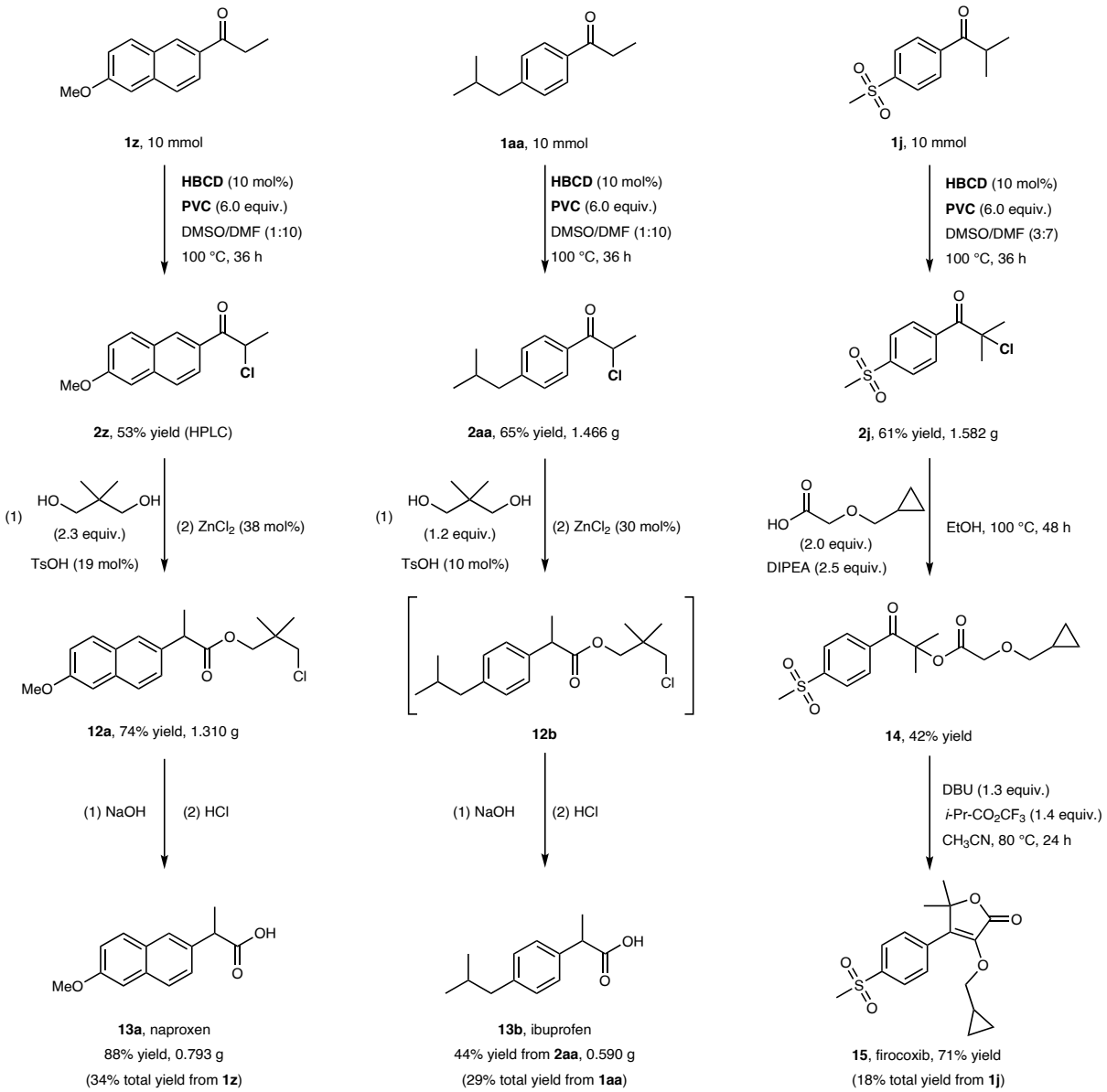

Fig. 5 | Using HOPs to synthesize non-steroidal anti-inflammatory drugs. The chlorine-transfer strategy using HBCD as a catalyst and PVC as a chlorinating reagent was used to synthesize anti-inflammatory drugs including naproxen, ibuprofen and firocoxib. TsOH, *p*-toluenesulfonic acid; DIPEA, *N*,*N*-diisopropylethylamine; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene.

chlorine to ketones in DMSO and *N*,*N*-dimethylformamide (DMF) mixtures (Fig. 4d). However, probably because of solubility problems, the yield of the product was low with 1 equiv. repeat unit of CMPS. By optimizing the DMSO-to-DMF ratio and increasing the amount of CMPS, the yield of the target product was improved greatly. According to estimates, the annual global consumption of PVC exceeds 50 million tons[8]. Owing to the low recycling rate, a significant amount of PVC is disposed of in the environment, leading to severe pollution[41,42]. Nonetheless, transfer chlorination reactions offer a viable solution for the repurposing of PVC (Fig. 4e). Such reactions can yield chlorinated products at a moderate level using only one repeat unit of PVC. By increasing the amount of PVC used, the reaction yield can be enhanced while shortening the reaction time. A significant improvement in the reaction efficiency can be achieved by increasing the temperature (condition G). These findings demonstrate that the alkyl bromide-catalysed transfer chlorination reaction can effectively facilitate the repurposing of HOPs. After the reaction, the resulting polymers (dCMPS and dPVC) were characterized using infrared spectroscopy (Supplementary Figs. 9 and 10), thermogravimetric analysis (TGA; Supplementary Figs. 11 and 12) and differential scanning calorimetry (DSC; Supplementary Figs. 13 and 14) to determine any new structural features. Briefly, the properties of the polymers have all changed, especially dPVC, which has properties that are completely distinct from PVC (a lower decomposition temperature, the generation of unsaturated bonds and so on).

Application to the synthesis of anti-inflammatory drugs

To further demonstrate the value of this chlorine-transfer strategy, our focus was directed towards using HBCD as a catalyst and PVC as a chlorinating reagent for the synthesis of crucial drugs such as naproxen (**13a**), ibuprofen (**13b**) and firocoxib (**15**; Fig. 5). Naproxen and ibuprofen are widely used non-steroidal anti-inflammatory drugs that possess an aromatic propionic acid framework[43,44]. Owing to the prevalent use of non-steroidal anti-inflammatory drugs as antipyretic analgesics, they have emerged as popular drugs in the pharmaceutical market, particularly during the COVID-19 pandemic[45,46]. Consequently, research efforts

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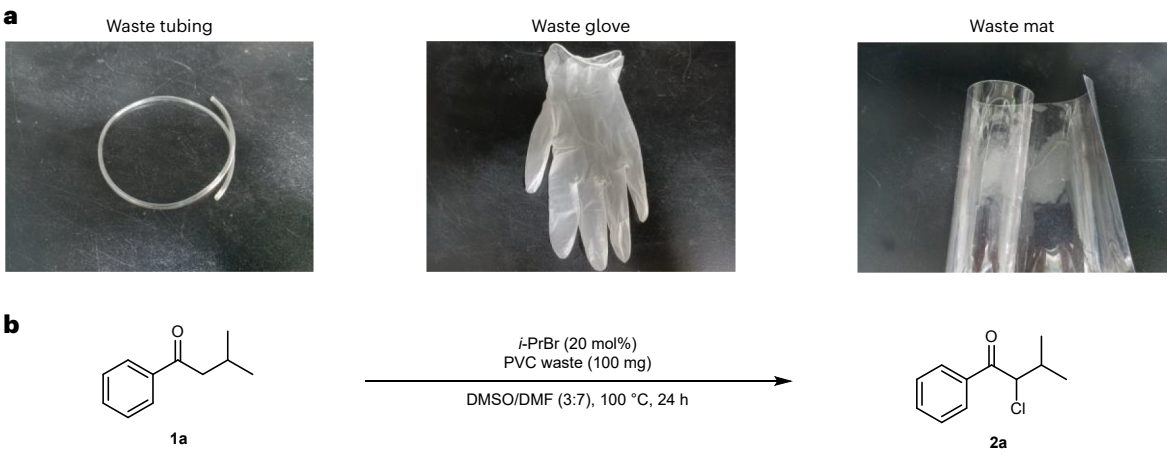

PVC waste	PVC content (wt%)	Plasticizer	Use of repeat unit (equiv.)	**2a** (%)
PVC_{tubing}	63	DEHP (35 wt%)	5.0	70
PVC_{glove}	57	DOTP (41 wt%)	4.6	69
PVC_{mat}	66	DPHP (34 wt%)	5.3	72

Fig. 6 | Repurposing of waste PVC through the transfer chlorination reaction. **a**, Discarded PVC-containing plastic waste items were used for the reaction directly by cutting them into pieces. **b**, Apart from PVC, the discarded PVC waste items also contain substantial amounts of plasticizers. The plasticizers, including DEHP, DOTP and DPHP, were found to have no significant impact on the transfer chlorination reactions. Using these materials with <6 equiv. chlorine can yield the chlorination products in good yields. Conditions: **1a** (0.20 mmol), *i*-PrBr (20 mol%), PVC waste (100 mg), DMSO (0.3 ml), DMF (0.7 ml), 100 °C, 24 h.

are still underway to devise novel methods for their synthesis[47]. The proposed methodology is demonstrated to be a successful approach for the synthesis of naproxen and ibuprofen.

Through a transfer chlorination reaction, ketone **1z** was readily transformed to **2z** in 53% yield in the presence of HBCD and PVC on a 10 mmol scale. As **2z** was accompanied by inseparable unreacted **1z**, the yield was determined via HPLC using naphthalene as the internal standard. The resulting mixture was subjected to reaction with neopentyl glycol to produce a ketal, which then underwent a rearrangement reaction catalysed by zinc chloride to provide **12a** in 74% yield[48]. Hydrolysis of **12a** under alkaline conditions and subsequent acidification yielded naproxen (**13a**) in 88% yield. Through transfer chlorination facilitated by the use of HBCD and PVC, ketone **1z** underwent a series of sequential transformations, ultimately yielding naproxen (**13a**) with a notable total yield of 34%. Using a similar reaction process, the gram-scale production of ibuprofen (**13b**) was achieved without the need to isolate intermediate **12b**. Notably, the yield of ibuprofen (**13b**) from ketone **1aa** was 29%.

Firocoxib, a commercial veterinary drug with proven anti-inflammatory activity[49], can be synthesized using α-chloroketone **2j** as an intermediate, which can be obtained in 61% yield on a 10 mmol scale using HBCD and PVC. Under alkaline conditions, **2j** underwent reaction with 2-(cyclopropylmethoxy)acetic acid to afford ester **14** in 42% yield, which was ultimately transformed to firocoxib (**15**) via a condensation reaction in 71% yield[50]. In other words, commencing with ketone **1j**, following a three-step reaction, firocoxib (**15**) was obtained in 18% yield. The above results show that transfer chlorination can facilitate the synthesis of drugs with substantial therapeutic value from HOPs.

Reuse of PVC waste

To investigate whether or not this approach could be directly applied for the repurposing of HOPs from waste sources, PVC-containing waste tubing, a waste glove and waste table mat were used as chlorinating agents (Fig. 6a). It was found that these materials, besides PVC (tubing, 63 wt%; glove, 57 wt%; mat, 66 wt%), also contained plasticizers. However, these plasticizers, including di(2-ethylhexyl) phthalate (DEHP), di(2-ethylhexyl) terephthalate (DOTP) and di(2-propylheptyl) phthalate (DPHP), have no significant effect on the transfer chlorination reaction. Using these waste plastics directly, with less than 6 equiv. chlorine, can yield chlorination products in good yields (69–72%) (Fig. 6b). These results suggest that the transfer chlorination reaction can be effectively applied in the repurposing of waste PVC plastics.

Conclusions

In summary, we developed an alkyl bromide-catalysed chlorine-transfer reaction for repurposing HOPs, using readily operable conditions and inexpensive reagents. In contrast to degradation, the repurposing of pollutants via chlorine-transfer reactions not only mitigates environmental pollution but also yields products of substantial economic worth. In addition, the chlorine-transfer reaction can achieve the chlorination of ketones and the chlorohydroxylation of olefins, both of which are compatible with a diverse array of functional groups. Mechanistic investigations have shown that the reaction proceeds through a halogen-exchange process, thereby facilitating the transfer of chlorine between distinct molecules. Guided by the mechanism, diversified use of the brominated pollutant HBCD has been realized. In addition, this strategy enables the repurposing of a variety of chlorinated organic pollutants, including CPs, DDT, CMPS and PVC. The practical value of this reaction is further shown by the successful synthesis of three pharmaceuticals and reusing PVC waste. This study presents a demonstration of transfer chlorination facilitated by alkyl bromide catalysis, which has broad applicability for the remediation of environmental pollutants, including brominated and chlorinated compounds. The findings of this study have implications for the development of pollutant-recycling methods aimed at mitigating environmental pollution.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41557-024-01551-8.

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Methods

General procedure for alkyl bromide-catalysed transfer chlorination

To a sealed tube were added **1** (0.40 mmol), BnCl (92.1 µl, 0.80 mmol, 2.0 equiv.), *i*-PrBr (7.6 µl, 0.08 mmol, 20 mol%) and DMSO (0.5 ml) at room temperature. The reaction tube was sealed with a Teflon screw cap. Then, the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (EA) (5 ml) and washed with water (5 ml), extracted with EA (3 × 5 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction mixture was purified via column chromatography on silica gel using EA and petroleum ether (PE) to afford the corresponding product **2**. The experimental procedure for the treatment of HOPs follows a similar approach as described above, with reaction condition adjustments based on the specific type of HOPs used. Detailed values are available within the article and Supplementary Information.

General procedure for the chlorohydroxylation of olefins

To a sealed tube were added HBr (11.4 µl, 0.08 mmol, 40 wt% in water, 20 mol%), **3** (0.40 mmol, 1.0 equiv.), BnCl (92.1 µl, 0.80 mmol, 2.0 equiv.), 2,4,6-trimethylphenol (5.4 mg, 0.04 mmol, 10 mol%) and DMSO (1.0 ml) at room temperature. The reaction tube was sealed with a Teflon screw cap. Then, the reaction mixture was stirred at 80 °C for 18 h. After cooling to room temperature, the reaction mixture was diluted with EA (5 ml) and washed with water (5 ml), extracted with EA (3 × 5 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction mixture was purified via column chromatography on silica gel using EA and PE to afford the corresponding product **4**.

General procedure for bromination

To a sealed tube were added **1** (0.20 mmol), HBCD (128.3 mg, 0.20 mmol, 1.0 equiv.), DMSO (0.25 ml) and 1,4-dioxane (0.25 ml) at room temperature. The reaction tube was sealed with a Teflon screw cap. Then, the reaction mixture was stirred at 100 °C for 5 h. After cooling to room temperature, the reaction mixture was diluted with EA (5 ml) and washed with water (5 ml), extracted with EA (3 × 5 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude reaction mixture was purified via column chromatography on silica gel using EA and PE to afford the corresponding product **5**. The experimental procedure for the bromination of arenes follows a similar approach as described above. The type and amount of the respective reagents were simply modified, and the reaction time was adjusted. Detailed values are available within the article and Supplementary Information.

All methods are included in the Supplementary Information.

Data availability

Relevant data are available within the Article and its Supplementary Information. Raw TGA and DSC data are available via Figshare at https://doi.org/10.6084/m9.figshare.25406248 (ref. 51). Source data are provided with this paper.

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Author contributions

Q.-A.C. conceived and supervised the project. Q.-A.C. and H.L. designed the experiments. H.L. performed the experiments and analysed the data. Y.-K.M., Y.L. and X.-Y.W. assisted with the materials synthesis. D.-W.J. and C.-H.L. reviewed and edited the paper. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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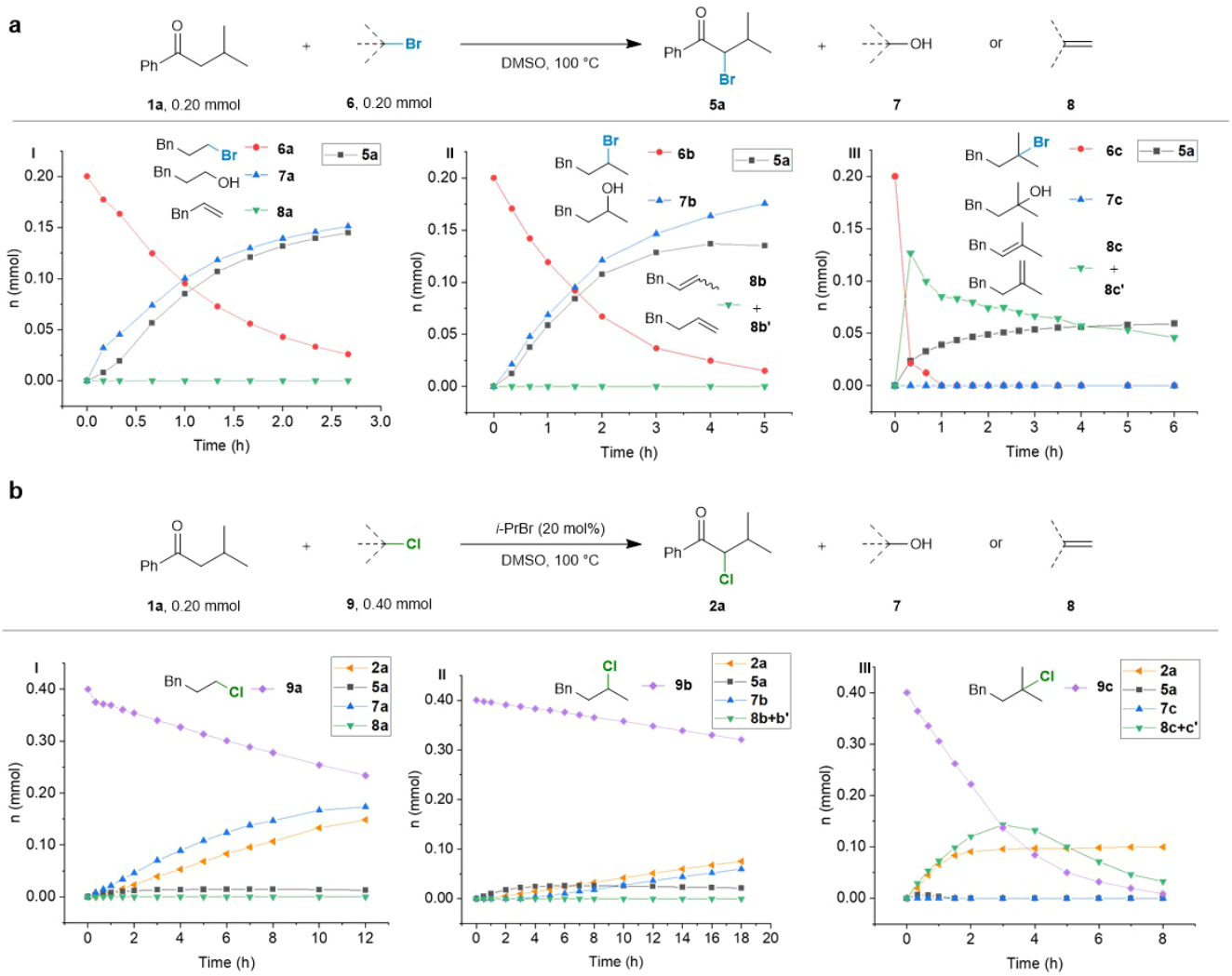

Extended Data Fig. 1 | Kinetic studies. (**a**) Kinetic studies of bromination reactions indicate that primary and secondary bromides undergo dehalogenation via substitution reactions, whereas tertiary bromides undergo dehalogenation through elimination reactions. (**b**) The trends of kinetic curves were similar to those of bromination reactions, indicating that primary and secondary chlorides undergo dehalogenation via substitution reactions, whereas tertiary chlorides undergo dehalogenation through elimination reactions.