

Waste PVC upcycling enables oxidant-free C-H and C-C bond editing

Ning Jiao

jiaoning@bjmu.edu.cn

Peking University <https://orcid.org/0000-0003-0290-9034>

Yichen Sun

Peking University <https://orcid.org/0009-0008-8278-2881>

Hongwei Shi

Peking University

Yichi Chen

Peking University

Zengrui Cheng

Peking University

Xi Wang

Peking University

Junhong Meng

Peking University

Yilei Huang

Peking University

Huizhen Liu

Institute of Chemistry, Chinese Academy of Sciences <https://orcid.org/0000-0002-6801-7816>

Buxing Han

Institute of Chemistry, Chinese Academy of Sciences <https://orcid.org/0000-0003-0440-809X>

Physical Sciences - Article

Keywords:

Posted Date: September 10th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10740945/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: There is **NO** Competing Interest.

Abstract

Carbocations are central intermediates in chemical synthesis^{1,2}, yet their direct generation from inert C-H bonds remains largely reliant on strong oxidants^{3,4}. Hydride abstraction represents a fundamentally different approach, but its synthetic use for C-H activation remains underdeveloped^{5,6}. At the same time, valorizing waste plastics as chemical feedstocks is of growing interest⁷, motivating us to explore whether an otherwise persistent polymer could be harnessed to generate and transform carbocations in organic synthesis. Here we show that waste poly(vinyl chloride) (PVC) enables direct carbocation generation from C-H bonds through biomimetic hydride abstraction. Activation of PVC with a recyclable AlCl₃-based ionic liquid (IL) generates transient carbocationic sites along the polymer backbone, enabling hydride abstraction from C-H bonds while simultaneously inducing PVC chain scission. This coupled process enables direct C-H functionalization and C-C bond activation under mild, oxidant-free conditions. Our strategy establishes hydride abstraction as an alternative to oxidative carbocation generation and transforms waste PVC into a reactive feedstock for molecular editing and late-stage functionalization.

Full Text

Carbocations are among the most fundamental reactive intermediates in chemistry. Since their conceptual emergence in physical organic chemistry, they have provided a unifying framework for understanding electrophilic substitution, rearrangements, solvolysis, and a wide range of bond-forming and bond-cleavage processes^{1,2}. Their exceptional reactivity enables rapid skeletal diversification and functional-group installation, making them indispensable in both small-molecule synthesis and the construction of complex molecular architectures. However, the direct generation of carbocations from inert hydrocarbon C-H bonds remains challenging because of the high energetic barrier. To date, most established methods rely on strong oxidants that operate through traditional electron transfer pathways to access carbocation intermediates (Fig. 1a)^{3,4,8-13}. Although this strategy has undergone substantial development over the past decades, the discovery of fundamentally new non-oxidative approaches for direct carbocation formation from C-H bonds remains an important challenge⁶.

A particularly attractive yet underdeveloped alternative is the hydride transfer strategy, which involves the heterolytic cleavage of C-H bonds through formal abstraction of a hydride ion (H⁻) to generate a carbocation intermediate directly from a hydrocarbon substrate (Fig. 1a)^{5,14}. Although hydride abstraction is highly endergonic^{15,16}, requiring more than 100 kcal·mol⁻¹ in the gas phase¹⁷, this approach can nevertheless offer significant advantages in chemical synthesis. By bypassing conventional multistep sequences and avoiding the intervention of other strong oxidants, hydride transfer can provide a more streamlined and energetically efficient route to rapidly increase molecular complexity and functional-group density. Significantly, biological systems have evolved highly efficient hydride transfer pathways to accomplish hydride abstraction under remarkably mild conditions¹⁸⁻²⁰. For example, berberine bridge enzyme (BBE) employs a flavin-derived cofactor to accept a hydride from

benzylic substrates, generating transient carbocation intermediates that drive oxidative cyclization in alkaloid biosynthesis (Fig. 1b)¹⁹. The enzymatic processes highlight the feasibility of non-radical, hydride-transfer based C–H oxidation and provide a compelling concept for developing biomimetic strategies in synthetic chemistry. In contrast to enzymatic systems, hydride abstraction mediated by small-molecule reagents generally requires highly electrophilic acceptors. A pioneering example was demonstrated by Olah and co-workers, that protons can serve as hydride acceptors in strongly superacidic media such as FSO₃H-SbF₅ (“magic acid”), enabling the direct generation and observation of carbocations (Fig. 1c)^{21–23}. In addition, Maulide and coworkers recently developed an elegant C-H activation enabled by distal acidification via a 1,6- μ -bridged cation species²⁴. Lercher and coworkers achieved the hydrogen abstraction and carbocation generation on the polyolefin chains for its further cracking and degradation²⁵. Although conceptually powerful, translating this strategy into oxidant-free carbocation generation and subsequent functional-group transformations in organic synthesis remains largely unexplored.

Inspired by proton-mediated hydride transfer, we envisioned that preformed carbocations could serve as tunable hydride acceptors to trigger direct new carbocation formation from otherwise inert C–H bonds (Fig. 1d, left). Such a strategy would offer a fundamentally distinct approach to carbocation chemistry. However, its realization is exceptionally challenging because the carbocation hydride acceptor is itself highly reactive and can readily undergo rearrangement, nucleophilic trapping, Friedel-Crafts alkylation, or other unproductive pathways before productive hydride abstraction occurs². Overcoming these competing processes requires precise control over both carbocation stability and chemoselectivity, representing a longstanding challenge in synthetic methodology development.

To identify a suitable carbocation-based hydride acceptor, we turned our attention to polymers. We hypothesized that the intrinsically low solubility and restricted chain mobility of polymeric systems could suppress competing unproductive pathways such as rearrangement, nucleophilic trapping, and Friedel-Crafts alkylation. At the same time, the use of waste polymers as reactive chemical feedstocks would provide an opportunity to couple fundamental advances in carbocation chemistry with upcycling of sustainable molecular transformation^{26–34}. Among them, poly vinyl chloride (PVC), as one of the least recycled plastics with the recycling rates of <1%, its end-of-life management poses a significant challenge for humanity⁷. We envisioned that, if PVC could be harnessed as a programmable hydride acceptor, it would not only establish a fundamentally new mode of carbocation generation for organic synthesis, but also create a conceptually distinct strategy for plastic upcycling and carbon circularity^{35–40}. Previous studies have shown that alkyl halides can be activated by strong Lewis acids to generate carbocationic species⁴¹, suggesting a possible entry point for realizing polymer-enabled hydride abstraction (Fig. 1d, right). Here, we report a direct oxidant-free C-H and C-C bond transformation through hydride abstraction mediated by PVC. In this system, an AlCl₃-based ionic liquid (IL) activates the PVC backbone to generate transient carbocationic sites that function as hydride abstractors. This process triggers two coupled reaction pathways including hydride transfer and concomitant PVC chain

scission, thereby enabling direct C-H and C-C bond functionalization under non-oxidative conditions (Fig. 1e). This work establishes an oxidant-free strategy for carbocation chemistry, in which waste polymers serve not merely as passive substrates, but as reactive hydride-accepting platforms for molecular editing in the absence of conventional oxidants.

At the outset, we chose isopropylbiphenyl (**1a**), as model substrates to prove the concept, and use TMSN_3 to probe the generation of the benzyl carbocation with the formation of aniline product⁴². Mechanistically, efficient PVC activation requires both strong Lewis acidity for C-Cl bond polarization and an ionic medium capable of stabilizing charged intermediates. Because ILs facilitate carbocation stabilization, charge separation, and the dispersion of strong Lewis acidic species within the solution system⁴³⁻⁴⁷, we therefore evaluated a series of AlCl_3 -based ILs as synergistic activation platforms. A series of AlCl_3 -based ILs with different compositions and acidities was synthesized and evaluated. Compared with **IL-1**, solid AlCl_3 was ineffective due to its low solubility and poor dispersibility in the solvent (Fig. 2a, entry 2). Other ILs with high Lewis acidic Al_2Cl_7^- promoted PVC activation and hydride transfer but afforded lower yields (Fig. 2a, entries 3 and 4), while **IL-4** with AlCl_4^- cannot give the desired product due to its weaker Lewis acidity (Fig. 2a, entry 5)⁴⁷⁻⁴⁹. Notably, PVC proved to be the key hydride abstractor in our system (Fig. 2a, entry 6). In contrast, other chlorinated alkane gave lower yields and poorer recovery of the starting material (Fig. 2a, entry 7 and 8), likely owing to competing side reactions, including Friedel-Crafts alkylation, which appears to be suppressed by the polymeric nature of PVC. Solvent screening identified 1,2-Dichloroethane (DCE) as optimal, providing the highest product yield and substrate recovery (Fig. 2a, entry 9, Supplementary Table S1). After a systematic optimization, C-C bond amination of **1a** proceeded smoothly in the presence of 3 equivalents of PVC in **IL-1**, affording **2a** in 59% isolated yield (91% base on recovering starting material).

Fig. 2b illustrates the time course of aniline formation and the evolution of the number-average molecular weight (M_n) of the PVC reactant during the process. As the reaction proceeded, the M_n value of PVC gradually decreased, indicating continuous polymer degradation during the first 9 h. Over this period, the molecular weight dropped from 105 kDa to below 1 kDa. Notably, product formation closely paralleled polymer degradation, with generation of the target product beginning after approximately 2 h. Recycling experiments further showed that the IL is partially recyclable, retaining appreciable catalytic activity over five reaction cycles (Supplementary Table S6).

The post-reaction mixture, comprising the IL and deconstructed oligomers, was characterized by gel permeation chromatography (GPC) and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy. GPC analysis showed that PVC was almost completely degraded after the reaction (Fig. 2c). In the ^{27}Al NMR spectrum, pure **IL-4** showed a single resonance at 104 ppm corresponding to AlCl_4^- , whereas **IL-1** exhibited a dominant signal at 98 ppm assigned to Al_2Cl_7^- together with a shoulder at 104 ppm. This shoulder is attributed to chloride-bridged species involving reactive chloroaluminate intermediates and chloride atoms on PVC (Fig. 2d). During the reaction, the dimeric Al_2Cl_7^- can reversibly dissociate into

coordinatively saturated AlCl_4^- and highly Lewis acidic AlCl_3 , the latter of which can interact with PVC to form an activated AlCl_3 -PVC adduct capable of efficient hydride abstraction. After 12 h, the shoulder at 104 ppm evolved into a sharp resonance, while the signal at 98 ppm decreased substantially, indicating consumption of Al_2Cl_7^- and $\text{Al}^{\delta+}$ -PVC intermediates. Upon addition of AlCl_3 during the recycling experiments, the 98 ppm signal increased again, proving the regeneration of Al_2Cl_7^- species.

In addition, Fourier-transform infrared (FT-IR) analysis revealed distinct absorptions at 1700 cm^{-1} , indicating the presence of C=C double bonds (Fig. 2e). These species are likely formed through dechlorination of PVC. ^1H NMR also supported the proposed process of dichlorination, elimination and hydride transfer (Supplementary Figs. S3 and S4). Together, these results provide additional evidence for the formation of $\text{Al}^{\delta+}$ -PVC intermediates and carbocations along the PVC chains, while highlighting the important role of β -elimination in PVC decomposition.

On the basis of these results and previous reports^{44,50}, we propose the plausible reaction mechanism shown in **Fig. 2**. The reaction is initiated by chloride abstraction from PVC by **IL-1**, generating a carbenium ion on the polymer backbone (**Int-1**). Subsequent deprotonation forms an alkene unit (**Int-2**). In the absence of an external hydride donor, this process would lead to progressive dechlorination of PVC with the formation of **Int-3**. However, in the presence of alkane substrates, hydride transfer to the PVC-derived carbenium ion occurs, converting **Int-3** into the saturated intermediate **Int-4**. Further chloride abstraction at an adjacent C-Cl bond generates a β -carbenium ion (**Int-5**), which undergoes β -scission to produce shorter dechlorinated PVC fragments. These fragments can subsequently enter additional cycles of dechlorination and hydride transfer. Throughout the degradation process, PVC-derived carbocations serve as hydride acceptors, generating substrate-derived carbocations (**Int-6**), which are trapped by nucleophiles to afford the corresponding C-H functionalization products. Through successive dechlorination, deprotonation, hydride transfer, and β -scission events, carbocationic reactivity is continuously initiated, propagated, and terminated between PVC and the alkane substrates. This process ultimately results in complete dechlorination and depolymerization of PVC while enabling concurrent C-H and C-C bond functionalization of the substrates (Fig. 2f).

We then examined the scope of this oxidant-free carbocation-generation strategy. A wide range of alkyl benzenes underwent efficient site-specific C-C bond amination, regardless of the electronic nature of the aromatic ring (Fig. 3). Alkyl-, aryl-, and ortho-substituted substrates were all well tolerated (**2a-2e**), as were electron-rich arenes (**2f-2j**). Halides and pinacolboronates remained intact under the reaction conditions, providing products amenable to further synthetic manipulation (**2k-2p**). Heteroaromatic functionalized benzylic substrates were also compatible (**2q-2s**). When multiple benzylic sites were present, amination occurred selectively at the position expected to generate the more stable carbocation intermediate (**2t-2u**). Electron-deficient aniline derivatives, which are difficult to access through conventional C-H amination, were readily prepared (**2w-2z**). The applicability of the method was further demonstrated by the late-stage functionalization of a lithocholic acid derivative (**2aa**).

The alkyl scope of the C(Ar)-C(alkyl) bond amination process was also investigated. A variety of alkylarenes bearing structurally diverse alkyl substituents underwent selective C-C bond cleavage to afford the corresponding anilines (**3a-3f**). The reaction also tolerated a range of functional groups, including carbonyls, halides, and carboxylic acids, providing the desired products with high chemoselectivity (**3g-3l**). Notably, cyclic hydrocarbon substrates were competent reaction partners, undergoing intramolecular C-N bond formation to furnish valuable *N*-insertion products (**4m, 4n**). These results highlight the potential of the method for the synthesis of structurally diverse *N*-heterocyclic value-added compounds.

In addition, we explored the scope of the nucleophilic partner of this oxidant-free carbocation-generation protocol (Fig. 4). The reaction tolerated alkyl azides in ring size and alkyl-chain length (**5a-5e**), as well as alkenyl and ethylene glycol substituents (**5f** and **5g**). A broad range of additional functional groups was also compatible with the reaction conditions, demonstrating the versatility of the aminating reagent (**5h-5l**). The synthetic practicality of the method is further enhanced by the ready availability of alkyl azides, which can be prepared directly from the corresponding alkyl halides by substitution with sodium azide, typically without chromatographic purification.

Notably, the broad compatibility of both nucleophilic coupling partners and hydrocarbon substrates demonstrates the generality of this oxidant-free carbocation-generation strategy, establishing a versatile platform for the functionalization of otherwise inert C-H bonds. Sulfur- and aryl-containing nucleophiles were compatible with the reaction conditions, affording the corresponding products in moderate yields (**6a-6d**). Intramolecular nucleophilic trapping was also feasible. Under the standard conditions, 1-(4-azidobutyl)-4-methoxybenzene underwent efficient C-H amination to furnish the corresponding cyclized imine product (**6e**). Significantly, substrates lacking benzylic C-H bonds also participated in the reaction. Unactivated hydrocarbons such as cyclopentane, cyclohexane, and 2-(tert-butyl)-1,1'-biphenyl underwent hydride transfer and subsequent functionalization, providing the desired products in useful yields (**6f-6h**).

In summary, this work introduces a fundamentally distinct oxidant-free C-H and C-C bond functionalization by mimicking biological hydride-transfer processes with waste PVC. By converting a ubiquitous waste plastic into a chemically productive reaction partner, this approach unifies carbocation chemistry, molecular editing, and polymer upcycling within a single framework. We anticipate that this concept will stimulate the development of new oxidant-free transformations based on hydride abstraction, broaden the synthetic utility of carbocation intermediates, and inspire future strategies that repurpose waste polymers as functional reagents for chemical synthesis.

Declarations

Acknowledgments: We acknowledge the NSFC (Nos. 22293014, 22131002, T2450076, 22293012, 22293015), the National Key R&D Program of China (No. 2021YFA1501700), Fundamental and Interdisciplinary Disciplines Breakthrough Plan of the Ministry of Education of China (JYB2025XDXM603), the New Corner-stone Science Foundation, Peking University Medicine plus X Pilot Program-Key

Technologies R&D Project (2024YXXLHGG001), and the support from "Laboratory for Synthetic Chemistry and Chemical Biology" under the Health@InnoHK Program for financial support. We thank Mr. Jincheng Weng and Mr. Yihan Wang in this group for reproducing the results of **2m**, **3k**, **6a** and **6g**.

Author Contributions

B.H. and N.J., directed the research. Y.S., and N.J. conceived and designed the experiments. Y.S. carried out most of experiments; Y.S., H.S., Y.C., Z.C., X.W., J.M., Y.H., H.L., B.H., and N.J. analyzed and discussed data. Y.S. and N.J. wrote the manuscript draft, which was revised by Y.S., H.S., Y.C., Z.C., X.W., J.M., Y.H., H.L., B.H., and N.J.

Competing interests

All authors declare no other competing financial interests.

Data availability

All data are available in the main text or the supplementary information.

Author Information:

¹State Key Laboratory of Natural and Biomimetic Drugs, Beijing Key Laboratory of AI-Driven Drug Discovery and Development, New Cornerstone Science Laboratory, Chemical Biology Center, School of Pharmaceutical Sciences, Peking University, Beijing 100191, China. ²Beijing National Laboratory for Molecular Sciences, CAS Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Centre for Excellence in Molecular Sciences, Centre for Carbon Neutral Chemistry, Institute of Chemistry; Chinese Academy of Sciences, Beijing, 100190, China. ³State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China. ⁴Laboratory for Synthetic Chemistry and Chemical Biology Limited, Health@InnoHK, Innovation and Technology Commission, Units 1503-1511, 15/F., Building 17W, Hong Kong SAR, China.

Supplementary Information The online version contains supplementary material available at <https://doi.org/>

Correspondence and requests for materials should be addressed to e to N.J. (jiaoning@pku.edu.cn); B.H. (hanbx@iccas.ac.cn)

Reprints and permissions information is available at <http://www.nature.com/reprints>.

References

1. D. J. Tantillo, The carbocation continuum in terpene biosynthesis—where are the secondary cations? *Chem. Soc. Rev.* 39, 2847–2854 (2010).

2. R. R. Naredla, D. A. Klumpp, Contemporary carbocation chemistry: applications in organic synthesis. *Chem. Rev.* 113, 6905–6948 (2013).
3. J. Xiang *et al.*, Hindered dialkyl ether synthesis with electrogenerated carbocations. *Nature* 573, 398–402 (2019).
4. T. Shen, Y.-L. Li, K.-Y. Ye, T. H. Lambert, Electrophotocatalytic oxygenation of multiple adjacent C–H bonds. *Nature* 614, 275–280 (2022).
5. H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, D. L. Pearson, Synthesis of tropenium (cycloheptatrienylium) salts by hydride exchange. *J. Am. Chem. Soc.* 79, 4557–4558 (1957).
6. G. A. Olah, My search for carbocations and their role in chemistry (Nobel Lecture). *Angew. Chem. Int. Ed.* 34, 1393–1405 (1995).
7. K. Lee, Y. Jing, Y. Wang, N. Yan, A unified view on catalytic conversion of biomass and waste plastics. *Nat. Rev. Chem.* 6, 635–652 (2022).
8. W. Liu *et al.*, Oxidative Aliphatic C–H fluorination with fluoride ion catalyzed by a manganese porphyrin. *Science* 337, 1322–1325 (2012).
9. T. von Münchow, S. Dana, Y. Xu, B. Yuan, L. Ackermann, Enantioselective electrochemical cobalt-catalyzed aryl C–H activation reactions. *Science* 379, 1036–1042 (2023).
10. S. Zhou, Z. J. Zhang, J. Q. Yu, Copper-catalysed dehydrogenation or lactonization of C(sp³)–H bonds. *Nature* 629, 363–369 (2024).
11. L. Zeng *et al.*, Programmed alternating current optimization of Cu-catalyzed C–H bond transformations. *Science* 385, 216–223 (2024).
12. C. Ahn, A. Gomez, M. A. Hartmann, M. C. White, Selective methylene oxidation in α,β -unsaturated carbonyl natural products. *Nature* 648, 607–615 (2025).
13. Q. Guo *et al.*, Asymmetric Hofmann–Löffler–Freitag-type reaction via a transient carbenium ion complex merging organocatalysis and photocatalysis. *Nat. Catal.* 8, 448–456 (2025).
14. K. A. Gardner, J. M. Mayer, Understanding C–H Bond oxidations: H $\cdot$ and H $^-$ transfer in the oxidation of toluene by permanganate. *Science* 269, 1849–1851 (1995).
15. H. Hotop, W. C. Lineberger, Binding energies in atomic negative ions: II. *J. Phys. Chem. Ref. Data* 14, 731–750 (1985).
16. X. S. Xue, P. Ji, B. Zhou, J. P. Cheng, The essential role of bond energetics in C–H activation/Functionalization. *Chem. Rev.* 117, 8622–8648 (2017).
17. S. Ilic, A. Alherz, C. B. Musgrave, K. D. Glusac, Thermodynamic and kinetic hydricities of metal-free hydrides. *Chem. Soc. Rev.* 47, 2809–2836 (2018).
18. S. Gergel *et al.*, Engineered cytochrome P450 for direct arylalkene-to-ketone oxidation via highly reactive carbocation intermediates. *Nat. Catal.* 6, 606–617 (2023).
19. N. Guo *et al.*, Aspartic acid residues in BBE-like enzymes from *Morus alba* promote a function shift from oxidative cyclization to dehydrogenation. *Proc. Natl. Acad. Sci.* 122, e2504346122 (2025).

20. A. V. Modappilappally, N. P. Mankad, A synthetic molybdenum hydroxylase compound that cleaves C–H bonds by hydride abstraction. *J. Am. Chem. Soc.* 148, 22008–22015 (2026).
21. R. V. Oppenauer, Eine methode der dehydrierung von sekundären alkoholen zu ketonen. I. Zur herstellung von sterinketonen und sexualhormonen. *Recl. Trav. Chim. Pays-Bas* 56, 137–144 (1937).
22. G. A. Olah, G. Klopman, R. H. Schlosberg, Super acids. III. Protonation of alkanes and intermediacy of alkanonium ions, pentacoordinated carbon cations of CH_5^+ type. Hydrogen exchange, protolytic cleavage, hydrogen abstraction; polycondensation of methane, ethane, 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane in $\text{FSO}_3\text{H-SbF}_5$. *J. Am. Chem. Soc.* 91, 3261–3268 (1969).
23. G. A. Olah, 100 years of carbocations and their significance in chemistry. *J. Org. Chem.* 66, 5943–5957 (2001).
24. P. S. Grant, M. Vavřík, V. Porte, R. Meyrelles, N. Maulide, Remote proton elimination: C–H activation enabled by distal acidification. *Science* 384, 815–820 (2024).
25. W. Zhang *et al.*, Integrated low-temperature PVC and polyolefin upgrading. *Science* 390, 88–94 (2025).
26. F. Zhang *et al.*, Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* 370, 437–441 (2020).
27. K. P. Sullivan *et al.*, Mixed plastics waste valorization through tandem chemical oxidation and biological funneling. *Science* 378, 207–211 (2022).
28. R. J. Conk *et al.*, Catalytic deconstruction of waste polyethylene with ethylene to form propylene. *Science* 377, 1561–1566 (2022).
29. H. Li *et al.*, Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. *Science* 381, 660–666 (2023).
30. Z. Ait-Touchente, M. Khellaf, G. Raffin, N. Lebaz, A. Elaissari, Recent advances in polyvinyl chloride (PVC) recycling. *Polym. Adv. Technol.* 35, e6228 (2023).
31. Z. Xu *et al.*, Chemical upcycling of polyethylene, polypropylene, and mixtures to high-value surfactants. *Science* 381, 666–671 (2023).
32. Z. Cen *et al.*, Upcycling of polyethylene to gasoline through a self-supplied hydrogen strategy in a layered self-pillared zeolite. *Nat. Chem.* 16, 871–880 (2024).
33. S. E. Towell, M. Ratushnyy, L. S. Cooke, G. M. Lewis, A. V. Zhukhovitskiy, Deconstruction of rubber via C–H amination and aza-Cope rearrangement. *Nature* 640, 384–389 (2025).
34. M.-Q. Zhang *et al.*, In-line NMR guided orthogonal transformation of real-life plastics. *Nature* 643, 395–403 (2025).
35. R. Gao *et al.*, Catalyst-free, microdroplet-mediated waste plastic conversion to diacids. *Nature* 655, 917–924 (2026).
36. D. E. Fagnani, D. Kim, S. I. Camarero, J. F. Alfaro, A. J. McNeil, Using waste poly(vinyl chloride) to synthesize chloroarenes by plasticizer-mediated electro(de)chlorination. *Nat. Chem.* 15, 222–229 (2023).

37. H. Liu *et al.*, Repurposing of halogenated organic pollutants via alkyl bromide-catalysed transfer chlorination. *Nat. Chem.* 16, 1505–1514 (2024).
38. M. Liu, X. Wu, P. J. Dyson, Tandem catalysis enables chlorine-containing waste as chlorination reagents. *Nat. Chem.* 16, 700–708 (2024).
39. H. Jiang, E. A. Medina, E. E. Stache, Upcycling Poly(vinyl chloride) and Polystyrene Plastics Using Photothermal Conversion. *J. Am. Chem. Soc.* 147, 2822–2828 (2025).
40. K. Kubota *et al.*, Using mechanochemistry to activate poly(vinyl chloride) as a mechanotunable brønsted-acid-releasing reagent for organic synthesis. *J. Am. Chem. Soc.* 148, 1953–1962 (2026).
41. C. Friedel, J. M. Crafts, A new general synthetical method of producing hydrocarbons. *J. Chem. Soc.* 32, 725–791 (1877).
42. J. Liu *et al.*, From alkylarenes to anilines via site-directed carbon–carbon amination. *Nat. Chem.* 11, 71–77 (2018).
43. S. Bigot, G. Louarn, N. Kébir, F. Burel, Click grafting of seaweed polysaccharides onto PVC surfaces using an ionic liquid as solvent and catalyst. *Carbohydr. Polym.* 98, 1644–1649 (2013).
44. W. Zhang *et al.*, Low-temperature upcycling of polyolefins into liquid alkanes via tandem cracking-alkylation. *Science* 379, 807–811 (2023).
45. R. Cao *et al.*, Co-upcycling of polyvinyl chloride and polyesters. *Nat. Sustain.* 6, 1685–1692 (2023).
46. F. Wu *et al.*, Upcycling poly(succinates) with amines to *N*-substituted succinimides over succinimide anion-based ionic liquids. *Nat. Commun.* 15, 712 (2024).
47. L. Qiu *et al.*, Polyethylene upcycling to liquid alkanes in molten salts under neat and external hydrogen source-free conditions. *J. Am. Chem. Soc.* 147, 16207–16216 (2025).
48. C. J. Adams, M. J. Earle, K. R. Seddon, Catalytic cracking reactions of polyethylene to light alkanes in ionic liquids. *Green Chem.* 2, 21–24 (2000).
49. W. Zhang *et al.*, Chloride and hydride transfer as keys to catalytic upcycling of polyethylene into liquid alkanes. *Angew. Chem. Int. Ed.* 63, e202319580 (2024).
50. J. Wu *et al.*, Kinetic study of polyvinyl chloride pyrolysis with characterization of dehydrochlorinated PVC. *ACS Sustainable Chem. Eng.* 12, 7402–7413 (2024).

Figures

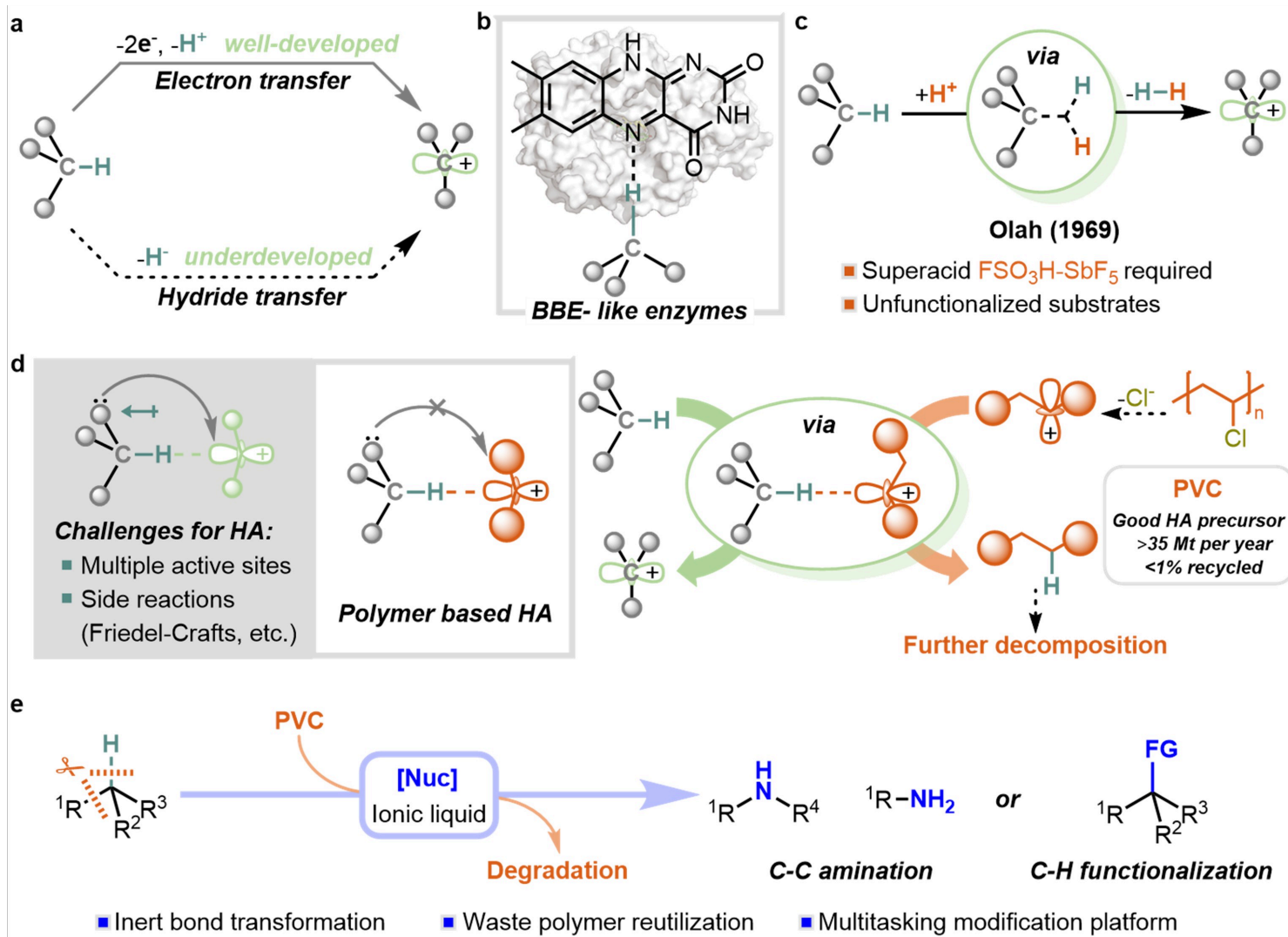


Figure 1

Background and concept. **a**, Strategies of inert C–H functionalization mediated by carbocations: electron transfer process and hydride transfer process. **b**, Hydride abstraction in metabolite synthesis. **c**, Hydride transfer by Olah with superacid as activator. **d**, The challenges in hydride abstraction using a carbocations as hydride acceptor and our hypothesis of PVC mediated C–H activation. **e**, This work: direct carbocation-generation strategy with PVC and the resulted C–C amination and C–H functionalization.

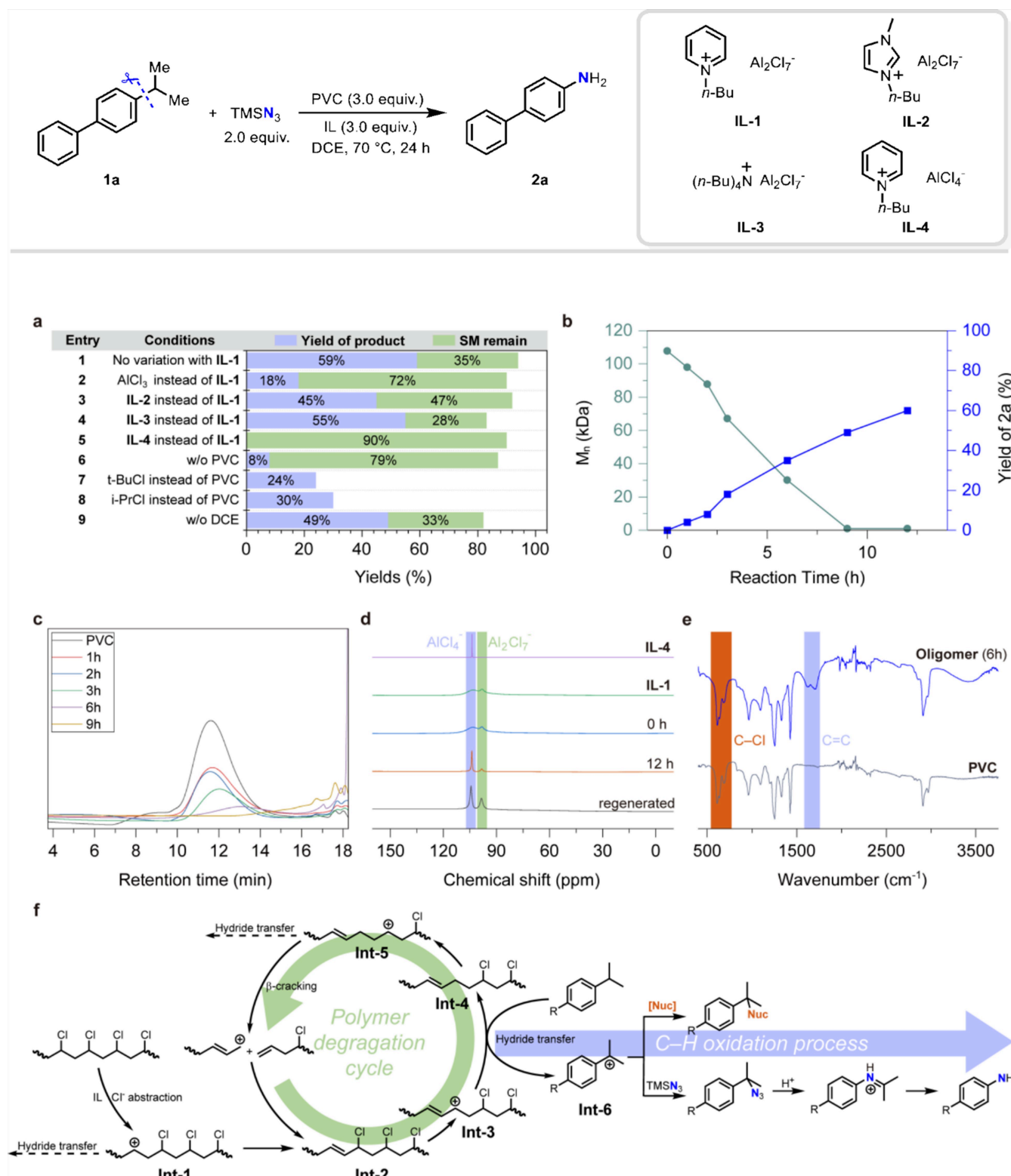


Figure 2

Conditions screening and characterizations of IL-PVC system. **a**, Reaction optimization. **b**, Time course of product and the number-average molecular weight (M_n) throughout the hydride abstraction process. **c**, Gel permeation chromatography (GPC) traces of PVC degradation. **d**, ^{27}Al nuclear magnetic resonance (NMR) spectra of representative ILs and the IL-PVC reaction system. **e**, FT-IR spectra of PVC and oligomers from PVC degradation. **f**, Proposed reaction mechanism.

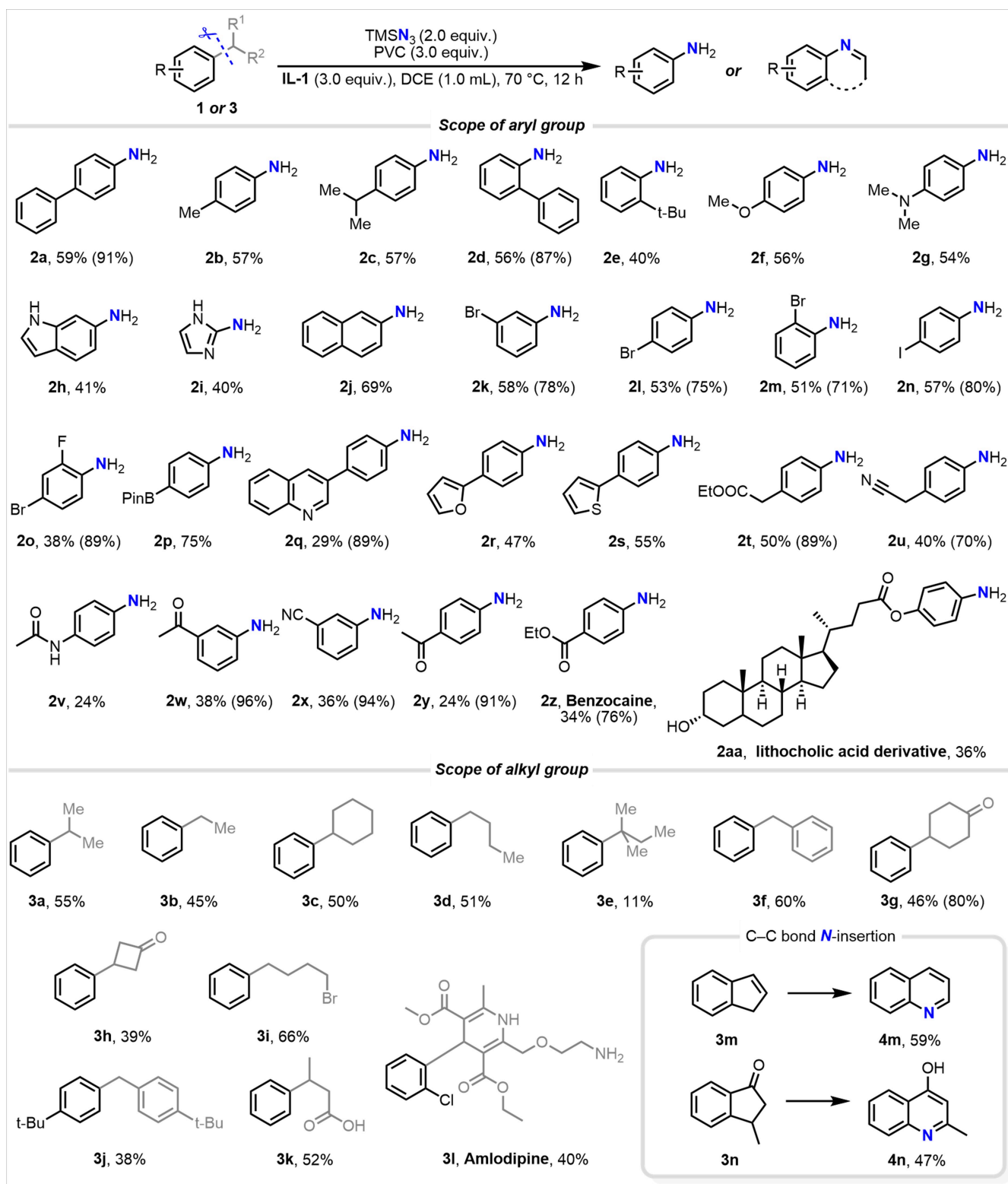


Figure 3

Substrate scope of substituted alkylbenzenes. Conditions: **1** or **3** (0.5 mmol, 1.0 equiv.), TMSN_3 (1.0 mmol, 2.0 equiv.), ionic liquid **IL-1** (1.5 mmol, 3.0 equiv., calculated by corresponding cation), PVC (1.5 mmol, 3.0 equiv., calculated by corresponding monomer), DCE (1.0 mL), 70 °C, under N_2 . Isolated yields are reported. Isolated yields base on recovering starting materials (b.r.s.m.) are reported in the parentheses.

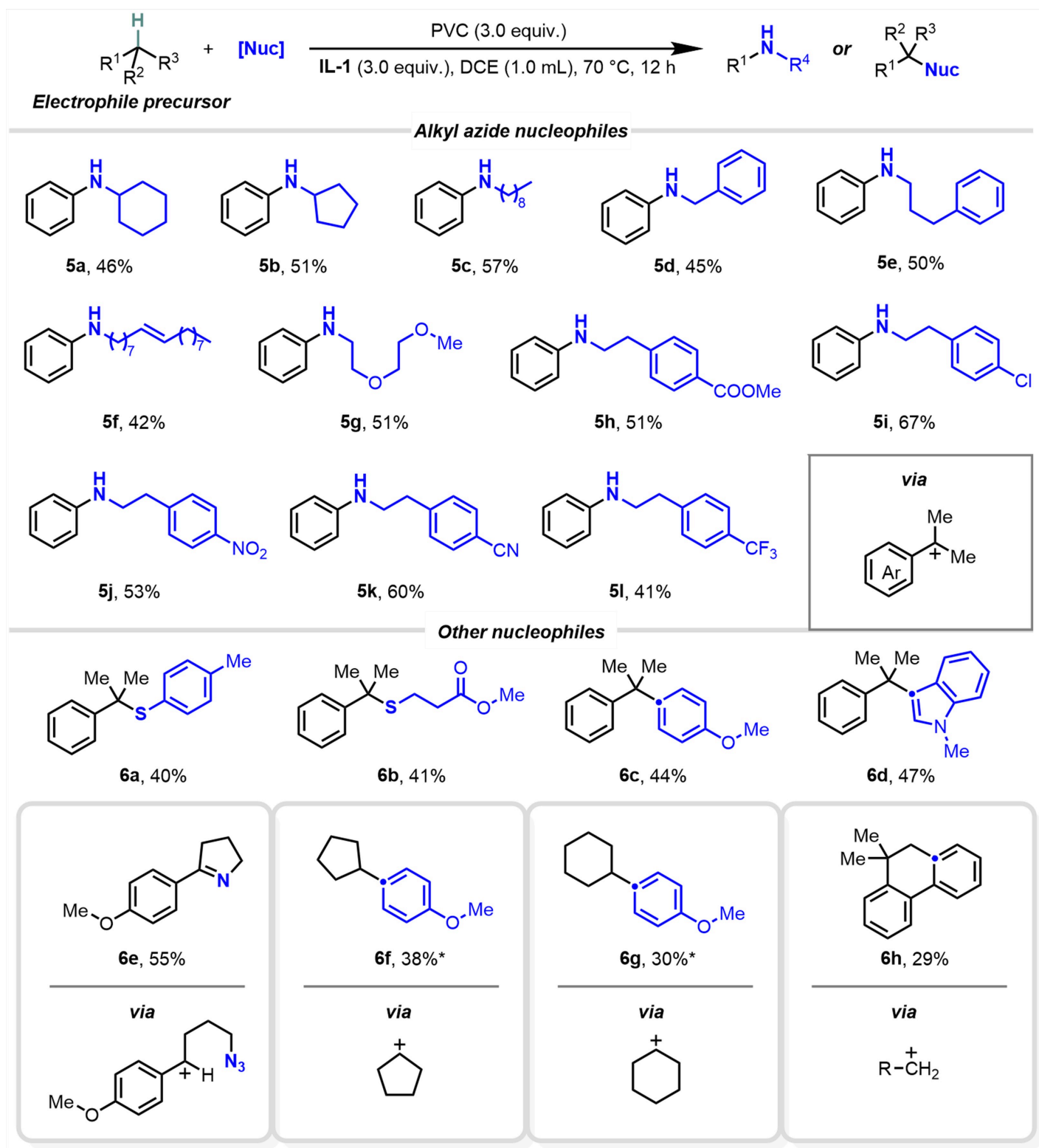


Figure 4

Substrate scope of alkane electrophile precursors and nucleophiles. Conditions: **Electrophile precursors** (0.5 mmol, 1.0 equiv.), **Nucleophiles** (1.0 mmol, 2.0 equiv.), ionic liquid **IL-1** (1.5 mmol, 3.0 equiv., calculated by corresponding cation), PVC (1.5 mmol, 3.0 equiv., calculated by corresponding monomer), DCE (1.0 ml), 70 °C, under N₂. Isolated yields are reported. *The reaction was carried out with

Nucleophiles (0.5 mmol, 1.0 equiv.) at room temperature, with electrophile precursors (0.5 mL) as both the reactant and the co-solvent instead of DCE.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SunSupplementaryInformation.pdf](#)