

Harnessing triaryloxonium ions for aryne generation

Received: 27 March 2023

Accepted: 31 August 2023

Published online: 2 October 2023

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Arynes are highly reactive and versatile intermediates for the functionalization of aromatic rings that are often generated using strong bases or fluoride sources, which, in some cases, can limit functional group tolerance. Here we demonstrate that triaryloxonium ions can be transformed into arynes through treatment with solid potassium phosphate at room temperature. A substantial range of functional group-bearing arynes, including 4,5-pyrimidynes, may be generated and trapped using cycloaddition reactions with high yields. Other arynophiles including nitrones, alkenes and azides are compatible with these conditions. Quantum computation in conjunction with an intramolecular kinetic isotope study is consistent with an elimination, unimolecular, conjugate base-like mechanism of elimination to form the aryne. These investigations demonstrate that the oxonium ion is a powerful electron-withdrawing group and a particularly effective leaving group. We anticipate that this study will stimulate further investigations into the synthetic utility of aryl oxonium ions.

Arynes¹ possess particularly rich history and varied chemistry, which has led to their broad application as reactive intermediates in synthesis². The emerging field of arynes was initially dominated by a focus on structure and mechanism, leading to the original formulation of benzyne as a diradical intermediate³. Later, a dipolar form for benzyne was proposed⁴ and finally, by virtue of a classical ¹⁴C-labelling experiment, the bent acetylene-type structure, now regarded as correct, was proposed⁵. The practical use of arynes in synthesis had to await the arrival of accessible and stable precursors (Fig. 1a)⁶. These include haloarenes that generate benzyne upon treatment with organometallic bases⁷ and aryl *ortho*-diazonium carboxylates that offer reliable access to arynes despite their shock sensitivity⁸. Other eliminative approaches include transition metal-mediated functionalizations that can be employed in mild and chemoselective approaches to metal-bound arynes^{9,10}. An alternative method for benzyne generation exploits the hexadehydro Diels–Alder reaction of tethered triynes^{11–13}, which provides reagent-free (thermal) access to polycyclic arynes. However, among contemporary precursors, Kobayashi's *ortho*-silyl triflate^{14,15} is largely responsible for the rehabilitation of arynes as viable intermediates in synthetic

chemistry as a consequence of its ability to generate a low steady-state concentration of aryne upon treatment with a sparingly soluble fluoride source¹⁶. This has also led to a resurgence in fluoride-free¹⁷ methods for aryne generation, often from monosubstituted precursors^{18–20}. Many of these methods use activated leaving groups such as λ^3 -iodanes to enable milder conditions for aryne generation^{21–23}, but these often necessitate the use of strong bases such as lithium bis(triethylsilyl) amide or potassium *tert*-butoxide. There are relatively few reports of benzyne formation with weaker bases^{23,24} although notable progress has been made in the elimination of tricyclic λ^3 -chloranes and bromanes^{25–27}.

We reasoned that a monosubstituted arene bearing a particularly good leaving group (that could also function as a powerful electron-withdrawing group) could enable the formation of arynes using mild and functional group-compatible conditions. The leaving group ability of onium salts from nitrogen, oxygen, phosphorus and sulfur has been calculated to be the greatest for oxygen²⁸. Hence, we decided to examine whether oxonium salts could function as aryne precursors. Alkylloxonium salts are exemplified by Meerwein's salt, which although kinetically stable, is a powerful alkylating agent that reacts with many

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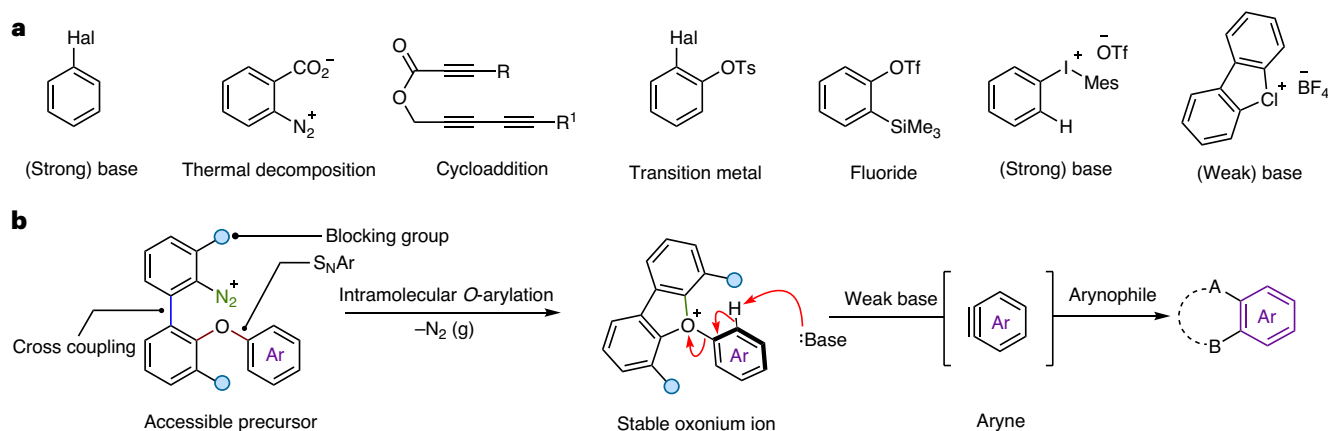


Fig. 1 | Exemplar methods for the synthesis of arynes, and a strategy for benzyne generation via the elimination of triaryloxonium salts. **a**, Previous strategies and methods for the synthesis of benzynes include the organometallic elimination of haloarenes, decomposition of diazo-anthranilic acid derivatives, the hexadehydro Diels–Alder reaction of tethered trienes, the oxidative insertion-mediated elimination of *ortho*-substituted leaving groups, the fluoride-mediated elimination of *ortho*-silyl triflates, the base-mediated elimination

of λ^3 -iodanes and the base-mediated elimination of tricyclic λ^3 -chloranes and bromanes. **b**, In this work, a diverse range of triaryloxonium ions can be synthesized through an intramolecular *O*-arylation process. These oxonium ions can be used in mild and functional group-tolerant synthesis of arynes through a base-mediated elimination reaction. A range of arynophiles are effective trapping agents in this process. Hal, halogen; Ts, tosylate; Tf, triflate; Mes, mesityl; R, R¹ = alkyl and/or aryl group.

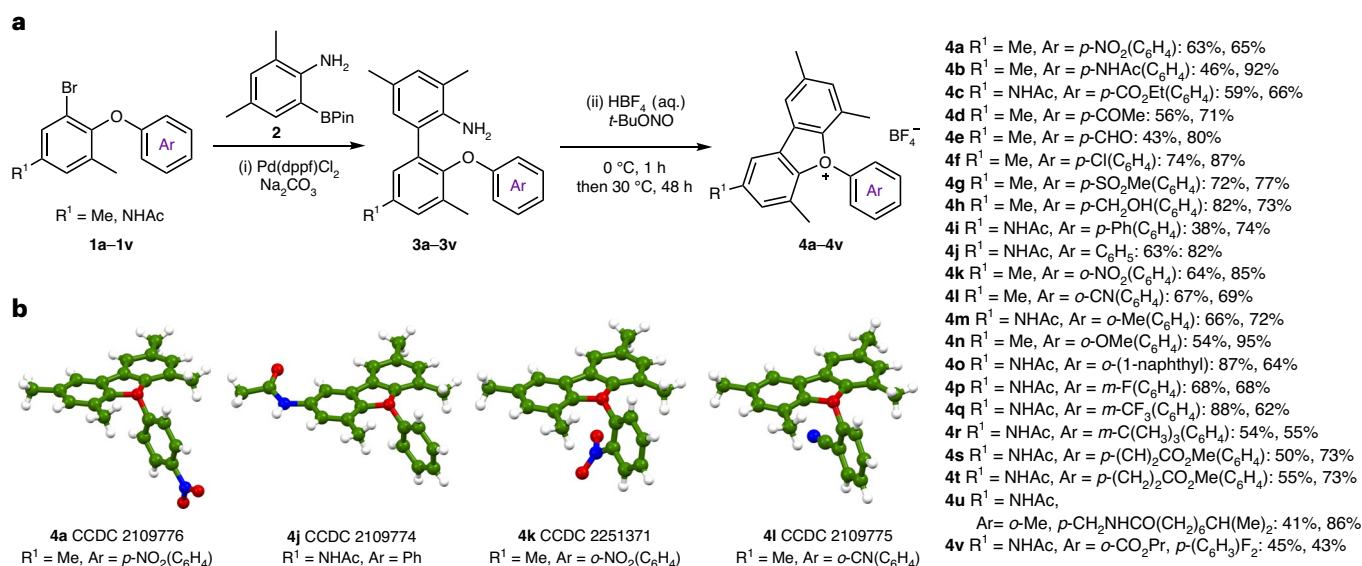
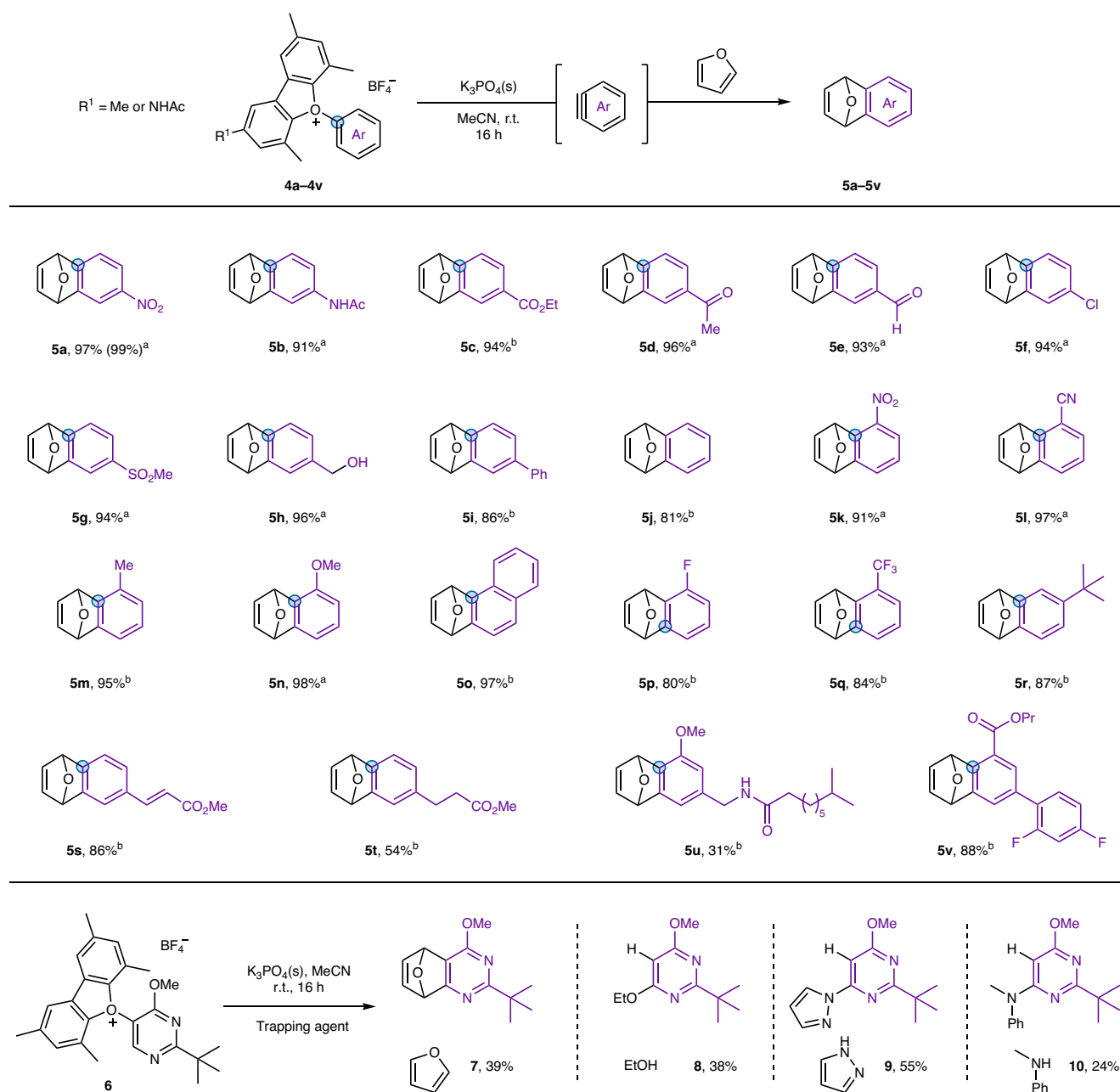


Fig. 2 | Synthesis and structure of triaryloxonium ions. **a**, Triaryloxonium ions can be generated from bromobiphenyl ethers via cross-coupling, diazotization and *O*-arylation procedures. Reagents and conditions: (i) Pd(dppf)Cl₂, CH₂Cl₂ (5 mol%), Na₂CO₃ (4 eq.), PhMe/H₂O (1:1, vol/vol), 95 °C, 24 h and (ii) HBF₄ (48% aq., 5 eq.), *t*-BuONO (5 eq.), CH₂Cl₂/IPA (1:1), 0 °C, 1 h then 30 °C, 48 h. Yields are reported for isolated and purified materials for each of the two steps pictured. For oxonium ions in which R¹ = NHAc, yields are reported from a precursor

R¹ = NO₂ and include a reduction and *N*-acylation step (not pictured; for full details, see Supplementary Information). **b**, Crystal and molecular structure of dibenzofuran-derived oxonium salts from single crystal X-ray diffraction studies. Tetrafluoroborate counterion is omitted for clarity. Yields for salts **4d** and **4e** reflect a different synthetic method; for details, see Supplementary Information. Pin, pinacol; dppf, 1,1'-ferrocenediyl-bis(diphenylphosphine).

nucleophiles, including water^{29,30}. More complex oxonium ions have been proposed as intermediates in natural product biosynthesis³¹, and aside from Mascall's oxatriquinane oxonium ions³², are considered to be highly reactive. In contrast, triaryloxonium ions are resistant to the action of many nucleophiles and are kinetically stable isolable solids. An early report from Hellwinkel³³ showed that the addition of phenyllithium to phenyl dibenzofuranium ion led to products consistent with the generation of an aryne. Tolstaya later showed that treatment of a symmetrical triaryloxonium ion with potassium acetate in refluxing benzene led to an aryne that could be trapped *in situ* with tetraphenylcyclopentadienone³⁴.

In this article, we describe a mild and functional group-tolerant method for the generation and trapping of functionalized arynes. We reasoned that, with an appropriately designed oxonium precursor, we could generate arynes using weak inorganic bases without any special precautions to exclude moisture or oxygen. While this approach would demonstrate only modest atom economy in common with other eliminative aryne generation methods, this could be compensated by the mildness of the reaction conditions for onward reaction and trapping. An appropriate oxonium precursor should possess *ortho*-blocking groups to prevent uncontrolled elimination (Fig. 1b). This structure could be assembled via cross-coupling between two suitably activated

Table 1 | Mild and functional group-tolerant generation and trapping of arynes

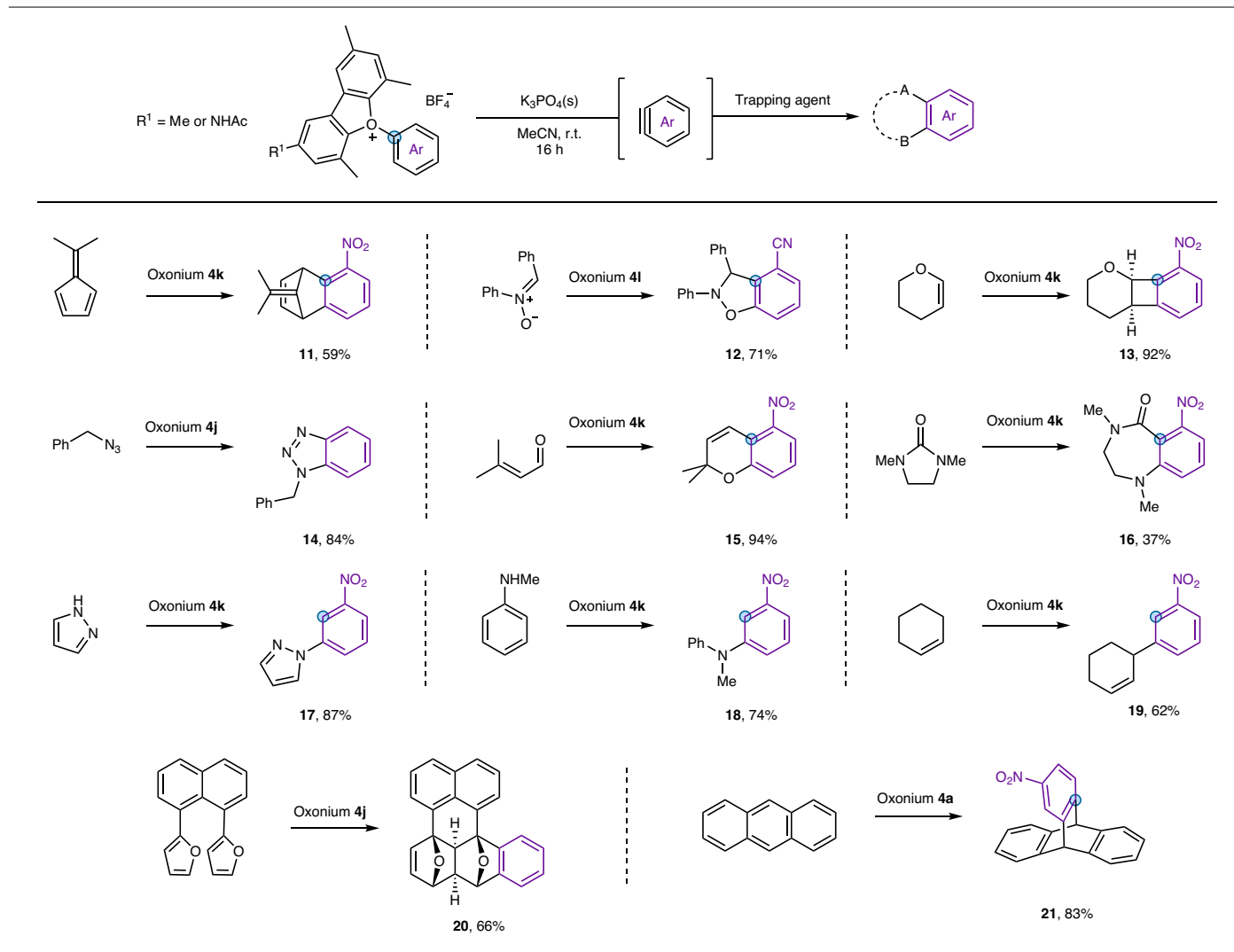
Benzynes and 2,3-pyrimidynes can be generated from triaryloxonium ions by stirring with a weak solid base at r.t. without any special precautions. In situ trapping with furan as an exemplar arynophile yields bicyclic products. The blue dot indicates the original position of the oxonium ion relative to substituent. Yields refer to isolated and purified material; yield in parentheses refers to a 1 mmol scale reaction. ^aGenerated from oxonium ion with $R^1 = \text{Me}$. ^bGenerated from oxonium ion with $R^1 = \text{NHAc}$. Reagents and conditions: oxonium ion (0.3 mmol), K_3PO_4 (s, 1.5 mmol), MeCN [oxonium = 0.05 M], furan (1.5 mmol), 16 h, r.t., stirring rate >600 rpm.

precursors. A methyl group is employed as the *ortho*-blocking group due to its small size and the availability of precursors. We have demonstrated that helically chiral triaryloxonium ions can be generated by intramolecular *O*-arylation of a diphenylether derivative³⁵ with a diazonium salt, and we rationalized that this strategy offered a viable route to suitable oxonium ions for aryne generation³⁶.

Results

The 2-bromobiaryl ethers (such as **1a–1v**) can be synthesized by a base-mediated $\text{S}_\text{N}\text{Ar}$ reaction between an electron-deficient fluoroarene and a phenol derivative; this reaction is relatively tolerant of different functional groups and can be performed where the bromine

atom is part of either the nucleophilic or electrophilic species. These compounds can also be manipulated to introduce other functional groups (for full details of oxonium ion synthesis, see Supplementary Section 2). Aniline-containing pinacol borane **2** can be efficiently cross-coupled with aryl bromides in the presence of a catalytic quantity of 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) to yield anilines **3a–3v**. Treatment with *tert*-butylnitrite in the presence of tetrafluoroboric acid led to an intermediate diazonium salt, which upon gentle warming, underwent intramolecular *O*-arylation to yield oxonium tetrafluoroborates **4a–4v** (Fig. 2). Aldehyde and ketone functional groups were incompatible with the cross-coupling strategy due to the presence of an aniline, and hence an alternative procedure

Table 2 | Generation and reaction of arynes with a variety of trapping agents

Arynes generated from triaryloxonium ions are compatible with a range of different trapping reagents. The blue dot indicates the original position of oxonium ion relative to substituent. Yields refer to isolated and purified material. Reagents and conditions: oxonium ion (0.3 mmol), K_3PO_4 (s, 1.5 mmol), MeCN [oxonium = 0.05 M], trapping agent (0.6–1.5 mmol), 16 h, r.t., stirring rate >600 rpm.

was utilized to generate oxonium ions **4d** and **4e** (route not shown; Supplementary Section 3.5). Using these methods, we were able to synthesize a wide range of triaryloxonium tetrafluoroborates. These are generally crystalline materials that can be stored indefinitely at ambient temperature without special precautions; there is little observable difference in reactivity or stability between oxonium ions with a *para*-acetamide or *para*-methyl group. The structure of compounds **4a**, **4j**, **4k** and **4l** was confirmed by single crystal X-ray diffraction, which in all cases shows that these compounds are pyramidal around the trivalent oxygen, with the exocyclic *O*-aryl substituent oriented almost perpendicular to the plane of the dibenzofuran ring system. These structural features are consistent with previous solid-state investigations of related materials³⁷.

With a range of oxonium salts in hand, we examined conditions for elimination of *para*-nitro oxonium **4a** in the presence of furan as an exemplar arynophile. Homogeneous bases such as 2,6-lutidine and diisopropylethylamine were mostly ineffective. However, solid inorganic bases such as potassium carbonate at room temperature (r.t.) led to the formation of bicyclic product **5a**, while treatment with sodium hydrogen carbonate led to recovery of oxonium ion. Potassium phosphate led to complete consumption of oxonium ion and a high yield of the furan trapping product **5a**, and hence we focused

on the use of this base to enable aryne generation (Supplementary Section 3.7). Our optimized conditions employ 5 equivalents of solid potassium phosphate in the presence of 5 equivalents of the trapping agent in acetonitrile. This process does not require any special precautions beyond rapid stirring, is not carried out under an inert atmosphere and does not require dry solvents or reagents (Table 1). Under our optimized conditions, *p*-nitro oxonium ion **4a** led to the formation of tricycle **5a** in 97% isolated yield. This increased to 99% when the reaction was carried out on a 1 mmol scale. This aryne generation and trapping process is tolerant of amides (to afford **5b** in 91% yield) and esters (yielding **5c** in 94% yield). Ketone- and aldehyde-containing oxonium salts can also be transformed into arynes and trapped with furan to yield **5d** (96% yield) and **5e** (93% yield), respectively. Oxonium ions bearing other electron-withdrawing groups such as *p*-chloro (affording **5f**, 94%) and *p*-methylsulfone **5g** (94%) are also effective in this transformation. Free alcohols do not have any deleterious effect on the aryne generation and trapping reaction. Oxonium **4h** affords *p*-hydroxymethyl tricycle **5h** in 96% yield. Oxonium **4i** bearing a *para*-aryl group is also successfully converted to **5i** (86% yield), and simple unsubstituted benzyne can also be generated from **4j**, yielding **5j** in 81% yield. *Ortho*-nitro^{23,38,39} oxonium ions smoothly generate the corresponding aryne, which upon trapping generates **5k** in 91% yield; this reactivity

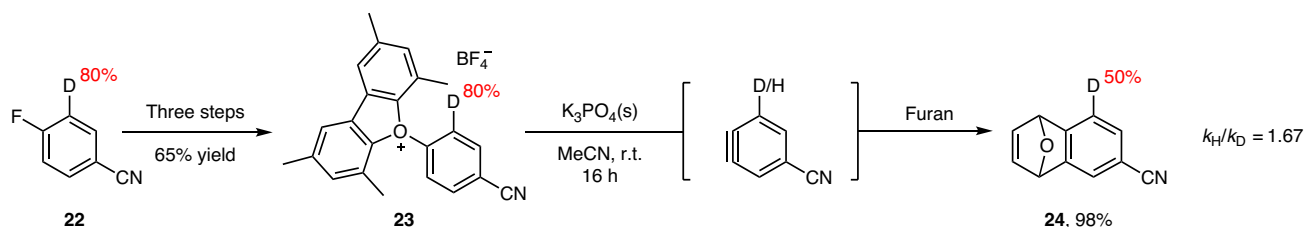


Fig. 3 | Intramolecular kinetic isotope determination. Generating an aryne from monodeuterated oxonium **23** allows determination of an intramolecular KIE. Yields refer to isolated and purified material. Reagents and conditions: oxonium ion (0.3 mmol), K_3PO_4 (s, 1.5 mmol), MeCN [oxonium = 0.05 M], furan (1.5 mmol), 16 h, r.t., stirring rate >600 rpm.

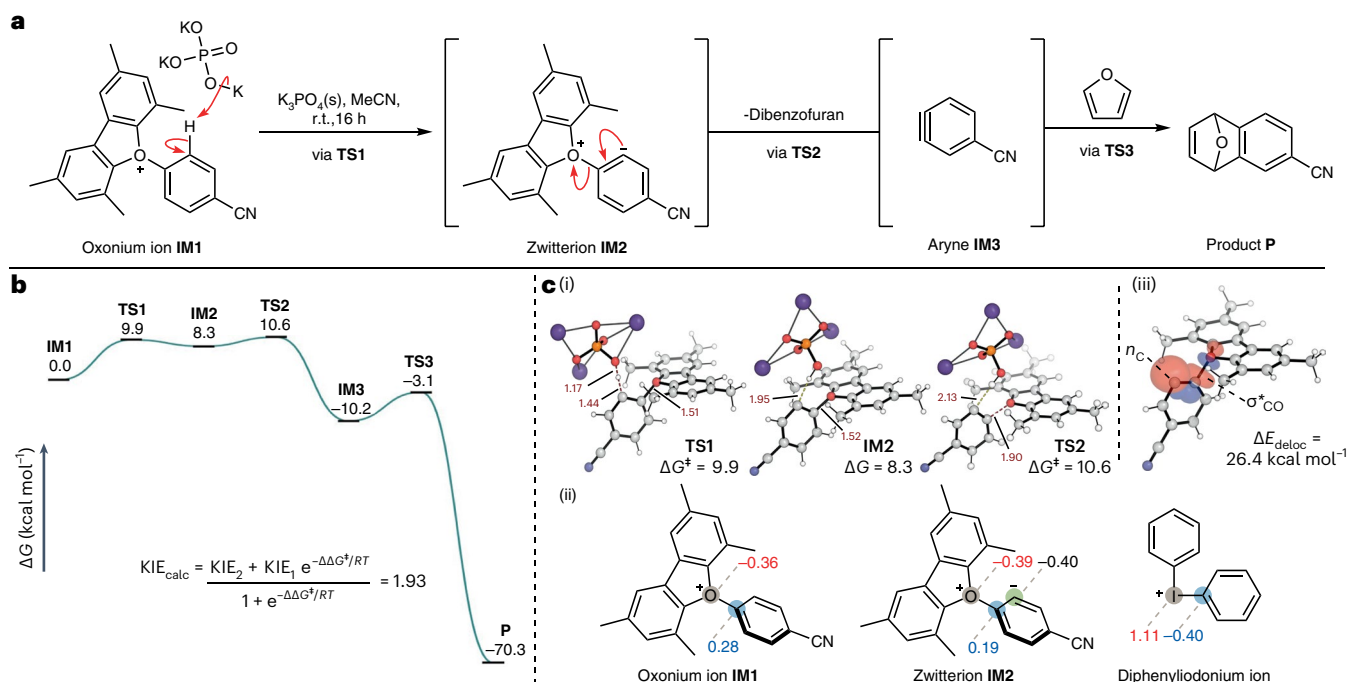


Fig. 4 | Computational studies. **a**, Mechanism of base-mediated aryne formation from oxonium ions via an E1cB elimination reaction and subsequent trapping with furan. **b**, ω B97X-D/6-31 + $G(d,p)$ calculated Gibbs free energy profile (kcal mol⁻¹). **c**, (i) Optimized geometries of key TSs and intermediates

(selected distances are indicated (Å), energies in kcal mol⁻¹); (ii) polarization (natural charges) in oxonium **IM1**, zwitterion **IM2** and an exemplar diphenyliodonium ion; and (iii) NBO plot showing $n-\sigma^*$ electron delocalization in **IM2**. R , universal gas constant; T , temperature; ΔE_{deloc} , change in delocalization energy.

is complementary to that of the corresponding Kobayashi silyl triflate aryne precursor, which preferentially undergoes the thia-Fries rearrangement⁴⁰. Other *ortho*-substituents on the oxonium ion that successfully yield bicyclic products include *o*-cyano (**5l**, 97%), *o*-methyl (**5m**, 95% yield), *o*-methoxy (**5n**, 98%) and 1-naphthyl (**5o**, 97% yield). *Meta*-substituted oxonium ions also eliminate smoothly to generate arynes, and regioselectivity is dictated by the steric and/or electronic nature of the substituent group.⁴¹ *Meta*-fluoro oxonium **4p** generates **5p** upon treatment with base and reaction with furan (80% yield); other electron-withdrawing groups such as trifluoromethyl proceed with the same regioselectivity (to give **5q**, 84% yield). This regioselectivity is reversed with a relatively large group such as *tert*-butyl, yielding **5r** in 87% yield. *Para*-alkenes bearing electron-withdrawing groups are tolerated without incident (**5s**, 86% yield) as are more functionalized alkyl groups (to afford **5t**), albeit in reduced yield.

We can also apply these conditions to the synthesis of modified natural products and drugs. A capsaicin-derived oxonium ion was generated, which yielded tricycle **5u** in 31% yield upon trapping with furan. This approach was also successful in the generation of an aryne derived from a difusinal derivative, which yielded **5v** in 88% yield. There are relatively few substituents that are unsuccessful in this process.

These include oxonium ions bearing nucleophilic groups such as *p*-SMe, and groups such as *p*-CH₂CO₂Et that may be preferentially deprotonated in the benzylic rather than the *ortho*-position.

We also considered whether we could use this strategy to access hetarynes. 4,5-Pyrimidines are a class of aryne that are notably more challenging to generate than modified benzyne^{42,43} and there are few reports of their generation and reactivity^{44–47}. Pyrimidine oxonium **6** was assembled via a Suzuki coupling route similar to that employed for other oxonium ions (Supplementary Section 3.8) and its structure confirmed by single crystal X-ray diffraction. We reasoned that the electron-donating methoxy group adjacent to the oxonium oxygen could lead to enhanced trapping reactivity, as demonstrated in 2,3-pyridynes⁴⁸. Treatment of this oxonium ion with solid potassium phosphate at r.t. in the presence of furan as trapping agent led to tricyclic product **7** in 39% yield. Trapping with ethanol is also effective, leading to **8** in 38% yield. In both of these reactions, a high concentration of trapping agent led to substantially increased yields. Employing pyrazole as the trapping agent led to formal insertion of the aryne into the N–H bond, affording **9** as a single regioisomer in 55% yield. This regioselectivity is consistent with nucleophilic attack distal to the electron-withdrawing oxygen substituent⁴⁹. We observed similar reactivity in the

addition of *N*-methylaniline to give **10**, albeit in a moderate 24% yield. These results indicated that trapping reactions beyond cycloadditions with furan could be viable, and we explored the compatibility of a range of different trapping agents under our base-mediated conditions for aryne generation (Table 2).

The 1-nitrobenzynes, generated from oxonium ion **4k**, reacts with 6,6-dimethylfulvene to afford tricycle **11** in 59% yield, which is a precursor to the anti-fungal agent isopyrazam⁵⁰. Formal (3 + 2) cycloaddition is also an effective trapping manifold. Tricycle **12** is isolated in 71% yield through reaction with a diarylnitron. Dihydropyran reacts with in situ-generated 1-nitrobenzynes via a formal (2 + 2) cycloaddition to afford **13** in 92% yield. Benzyne itself, generated from oxonium **4j**, can trap benzyl azide to afford triazene **14** in 84% yield, and 3-methyl-2-butenal affords fused bicycle **15** (92% yield) via a cascade of rearrangements upon reaction with 1-nitrobenzynes (from **4k**). The reaction of **4k** with potassium phosphate base in the presence of 1,3-dimethyl-2-imidazolidinone affords benzodiazepine **16** in 37% yield. Nucleophiles such as pyrazole and *N*-methylaniline both yield regioselective addition products **17** (87% yield) and **18** (74% yield), respectively, in the presence of oxonium **4k**. This oxonium ion also engages in an ene reaction with cyclohexene in the presence of potassium phosphate to yield **19**. More complex structures are accessible: the reaction of in situ-generated benzyne with tethered bisbiaryl furan led to *exo,exo*-polycycle **20** in 47% yield⁵¹. Tryptycene **21** was formed in 83% yield from cycloaddition between anthracene and the aryne generated from precursor **4a**.

To probe the mechanism of the formation of arynes from oxonium ions, we synthesized *ortho*-deuterated fluoroarene **22** (80% deuterium), which was transformed into oxonium **23** in three steps without any loss of deuterium (Fig. 3). We reasoned that this monodeuterated intermediate could allow us to perform an intramolecular competition experiment by measuring the selectivity of proton versus deuterium removal⁵². Subjecting **23** to our standard aryne-generating conditions in the presence of furan as trapping agent afforded tricycle **24** in 98% isolated yield, in which 50% of the deuterium label was retained. This allows us to calculate the kinetic isotope effect (KIE) $k_H/k_D = 1.67$, where k_H is the rate constant of the reaction involving removal of hydrogen and k_D is the rate constant of the reaction involving removal of deuterium.

We used quantum chemical calculations to investigate the mechanism of benzyne formation from an oxonium ion with inorganic phosphate at the ω B97X-D/6-31 + G(d,p) level of theory with solvation model density solvation (CH₃CN) (refs. 53–56).

The computed potential energy surface reveals a formally stepwise elimination, unimolecular, conjugate base (E1cB) elimination mechanism with respect to C–H abstraction and C–O bond cleavage steps (Fig. 4a). Deprotonation at the *ortho*-position by K₃PO₄ takes place via transition structure (TS) **TS1** ($\Delta G^\ddagger = 9.9$ kcal mol^{−1}) and leads to the formation of a stable but shallow intermediate on the potential energy surface, **IM2** (Fig. 4b). Relatively little lengthening of the exocyclic C–O bond is observed in this 1,3-zwitterionic intermediate compared with the parent oxonium ion (0.01 Å) (refs. 57,58). Subsequently, C–O bond cleavage proceeds via **TS2** with a low barrier ($\Delta G^\ddagger = 2.3$ kcal mol^{−1}) relative to intermediate **IM2**, resulting in the exergonic and irreversible formation of benzyne and dibenzofuran products **IM3**. We also computed the Diels–Alder cycloaddition of this benzyne intermediate with furan, which occurs via **TS3** ($\Delta G^\ddagger = 7.1$ kcal mol^{−1}) in a highly exergonic fashion. These data are consistent with the rapid and irreversible consumption of benzyne once formed. The stepwise formation of benzyne from an oxonium ion (Fig. 4c) stands in contrast to the mechanism of benzyne formation from a diaryliodonium ion. We computationally investigated base-mediated aryne generation from an exemplar diphenyliodonium ion at the same level of theory; this demonstrated that C–H abstraction and C–I cleavage occur in a concerted asynchronous single step without an intervening intermediate (for further details, see Supplementary Section S) ^{21,26,59}. This is partly due to the greater

strength of the (exocyclic) C–O bond in an oxonium ion versus the C–I bond in an iodonium ion; however, electronic effects are also apparent. While the formal positive charge in the Lewis structures of both -onium ions is placed at the heteroatom, polarization in the oxonium ion differs profoundly from the halonium ion. For example, computed natural charges illustrate that the oxygen atom retains substantial negative charge in oxonium ion **IM1** (−0.36, cf. −0.48 in neutral 2,4,6,8-tetramethyldibenzofuran), while the neighbouring carbon atom (C1) has a partial positive charge of 0.28. This dipole provides electrostatic stabilization to the adjacent developing negative charge during *ortho*-C–H abstraction, which reaches −0.40 in **IM2**. In contrast, for the iodonium ion, a large positive charge is coincident with the position of the formal charge at the iodine atom (1.11). Natural bond orbital (NBO) analysis shows that **IM2** is further stabilized through delocalization of the in-plane C6 sp² lone pair into the exocyclic C–O σ* orbital (by 26.4 kcal mol^{−1}). Finally, we compared the computationally predicted k_H/k_D isotope effect based on our Gibbs energy profile against the experiment. While the TS for C–O bond cleavage is formally rate limiting, it is only 0.7 kcal mol^{−1} higher in energy than the C–H abstraction TS, such that the KIE value is influenced by both **TS1** and **TS2**. Quantitatively, the computed value of 1.93 is in close agreement with the observed KIE of 1.67 (ref. 60).

Conclusion

Triaryloxonium ions are stable and accessible compounds that can be transformed into arynes via a practically simple and mild base-mediated elimination. The functional group tolerance of this process enables efficient trapping of a wide range of functionalized arynes, including those bearing alcohols, amides and *ortho*-electron-withdrawing groups. Extension to the synthesis and trapping of 2,3-pyrimidynes is also successful. We anticipate that triaryloxonium salts may find application in the generation and reactions of other functionalized arynes.

Methods

Typical procedures for the preparation and reactions of triaryloxonium tetrafluoroborate salts are (i) Suzuki cross-coupling, (ii) diazotization and intramolecular *O*-arylation and (iii) aryne formation and trapping with furan. These procedures are exemplified for the formation and elimination of *p*-nitro oxonium tetrafluoroborate **4a** and trapping to form **5a**. Selected nuclear magnetic resonance (NMR) data are provided.

Suzuki cross-coupling

The 1-bromo-3,5-dimethyl-2-(4-nitrophenoxy)benzene **1a**, (2.61 g, 8.00 mmol, 1 eq.) and a solution of 2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline **2**, (12.00 mmol, 1.5 eq.) in PhMe (48 ml) were sequentially added to a stirring solution of Pd(dppf) Cl₂·CH₂Cl₂ (327 mg, 0.4 mmol, 5 mol%) and Na₂CO₃ (3.39 g, 32.00 mmol, 4 eq.) in PhMe (20 ml) and water (80 ml), under N₂ at r.t. Argon was bubbled through the solution for 5 min, and the reaction mixture was heated to 95 °C. After 24 h, the reaction mixture was extracted (CH₂Cl₂, 3 × 80 ml), dried (MgSO₄), filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography (EtOAc:pentane, 7:93, R_f = 0.3). The crude product was suspended in 2-propanol (20 ml), and water (40 ml) was added. The solid precipitate was collected to give 3,3',5,5'-tetramethyl-2'-(4-nitrophenoxy)-[1,1'-biphenyl]-2-amine **3a** as a bright yellow solid (1.86 g, 64%).

¹H NMR (600 MHz, CDCl₃): δ_H = 8.04–7.96 (m, 2H, H₁₁), 7.14–7.10 (m, 1H, H₃), 7.05 (t, J = 1.5 Hz, 1H, H₃), 6.75–6.72 (m, 1H, H₁₆), 6.70 (m, 2H, H₁₀), 6.57 (d, J = 2.1 Hz, 1H, H₁₈), 2.37 (s, 3H, H₈), 2.17 (s, 3H, H₇), 2.11 (s, 3H, H₁₉), 2.07 (s, 3H, H₂₀). NH₂ not observed.

¹³C NMR (151 MHz, CDCl₃): δ_C = 163.1 (C₉), 147.6 (C₁), 141.9 (C₁₂), 138.7 (br, C₁₄), 136.2 (C_{Ar}), 132.7 (C₆), 131.8 (C₃), 131.4 (C₁₆), 130.7 (C_{Ar}), 130.5 (C₅), 128.7 (C₁₈), 127.3 (br, C_{Ar}), 125.5 (C₁₁), 123.2 (br, C₁₃), 122.8 (br, C_{Ar}), 115.3 (C₁₀), 20.9 (C₈), 20.2 (C₂₀), 17.8 (C₁₉), 16.4 (C₇).

Diazotization and intramolecular *O*-arylation

t-BuONO (2.23 ml, 1.94 g, 19.35 mmol, 5 eq.) was added to a solution of 3,3',5,5'-tetramethyl-2'-(4-nitrophenoxy)-[1,1'-biphenyl]-2-amine **3a** (1.40 g, 3.87 mmol, 1 eq.) and HBF₄ (2.50 ml, 3.53 g, 19.35 mmol, 48% aq., 5 eq.) in CH₂Cl₂:IPA (1:1, 16 ml) at 0 °C. After 1 h, the reaction mixture was diluted (CH₂Cl₂, 20 ml), washed (H₂O, 8 ml) and warmed to 30 °C. After 36–48 h, the solvent was removed by a steady stream of N₂ and Et₂O (20 ml) was added, resulting in a solid precipitate. The Et₂O layer was passed through Celite® (4 ml). The solid precipitate was washed, and the solvent passed through Celite® (Et₂O, 4 × 4 ml). The solid was dissolved in MeCN (30 ml), passed through Celite® and eluted (MeCN, 4 × 20 ml). The solvent was removed in vacuo at r.t. to give oxonium ion **4a** as a tan solid (1.10 g, 65%).

¹H NMR (500 MHz, CD₃CN): δ_H = 8.49–8.42 (m, 2H, H₁₀), 8.04–7.98 (m, 2H, H₁₁), 7.93–7.89 (m, 2H, H₅), 7.34–7.30 (m, 2H, H₃), 2.51 (s, 6H, H₈), 2.13 (s, 6H, H₇).

¹³C NMR (126 MHz, CD₃CN): δ_C = 162.3 (C₉), 161.4 (C₁), 150.4 (C₁₂), 143.4 (C_{Ar}), 135.5 (C₃), 128.5 (C₁₀), 124.7 (C_{Ar}), 124.2 (C_{Ar}), 123.8 (C₁₁), 122.7 (C₅), 21.1 (C₈), 16.7 (C₇).

¹⁹F NMR (471 MHz, CD₃CN): δ_F = –151.8.

Aryne formation and trapping with furan

K₃PO₄ (1.06 g, 5.00 mmol, 5 eq.) was added to a stirring (>600 rpm) solution of 2,4,6,8-tetramethyl-5-(4-nitrophenyl)-5*H*-dibenzo[*b,d*]furan-5-ium tetrafluoroborate **4a** (433 mg, 1.00 mmol, 1 eq.) and furan (0.37 ml, 340 mg, 5.00 mmol, 5 eq.) in MeCN (6 ml). After 16 h, the reaction was filtered through Celite® (5 ml), eluted (CH₂Cl₂, 4 × 10 ml) and concentrated in vacuo. The crude residue was purified by flash column chromatography (Et₂O:pentane, 15:85, R_f = 0.3) to give 6-nitro-1,4-dihydro-1,4-epoxynaphthalene **5a** as a white solid (189 mg, 99%).

¹H NMR (400 MHz, CDCl₃): δ_H = 8.04 (d, *J* = 2.0 Hz, 1H, H₇), 7.98 (dd, *J* = 7.8, 2.0 Hz, 1H, H₉), 7.36 (d, *J* = 7.8 Hz, 1H, H₁₀), 7.10 (dd, *J* = 5.5, 1.9 Hz, 1H, H_{3/4}), 7.05 (dd, *J* = 5.5, 1.9 Hz, 1H, H_{3/4}), 5.83–5.78 (m, 2H, H₂, H₅).

¹³C NMR (126 MHz, CDCl₃): δ_C = 156.6 (C₁), 151.4 (C₆), 145.9 (C₈), 143.6 (C_{3/4}), 142.5 (C_{3/4}), 122.5 (C₉), 120.2 (C₁₀), 115.4 (C₇), 82.2 (C_{2/5}), 82.2 (C_{2/5}).

Data availability

All data (experimental procedures, characterization data and cartesian coordinates for all density functional theory calculations) supporting the findings of this study are available within the article and its supplementary information. Crystallographic data for compounds **4a**, **4j**, **4k**, **4l** and **6** have been deposited with the Cambridge Crystallographic Data Centre under deposition numbers [2109776](#), [2109774](#), [2251371](#), [2109775](#) and [2251372](#), respectively. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

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Acknowledgements

The Engineering and Physical Sciences Research Council has provided financial support for studentships: to O.S. via the Centre for Doctoral Training in Synthesis for Biology and Medicine (EP/L015838/1) and to M.H. via a doctoral training partnership studentship (EP/T517811/1; project 2446204). R.S.P. acknowledges support from the National Science Foundation (CHE-1955876) and computational resources from the Rocky Mountain Advanced Computer Consortium Summit supercomputer supported by the National Science Foundation (ACI-1532235 and ACI-1532236), the University of Colorado Boulder and Colorado State University, and the Extreme Science and Engineering Discovery Environment through allocation TG-CHE180056. A CC-BY licence is applied to the author accepted manuscript arising from this submission, in accordance with Engineering and Physical Sciences Research Council's open access conditions.

Author contributions

O.S., M.J.H., R.S.P., J.W.B. and M.D.S. conceived and designed the study. O.S., V.T. and M.J.H. performed the synthetic experiments and analysed data for all compounds. O.S. performed the X-ray crystallography. A.S. and R.S.P. performed the computational study. O.S., M.J.H., A.S., R.S.P., J.W.B. and M.D.S. co-wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s44160-023-00408-1>.

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Peer review information *Nature Synthesis* thanks Torben Rogge and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Primary Handling Editor: Peter Seavill, in collaboration with the *Nature Synthesis* team.

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