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ARTICLE

Closed-loop hydrostannylation of white phosphorus using Bu_3SnCl and $NaBH_4$: one-pot access to organophosphorus compounds†

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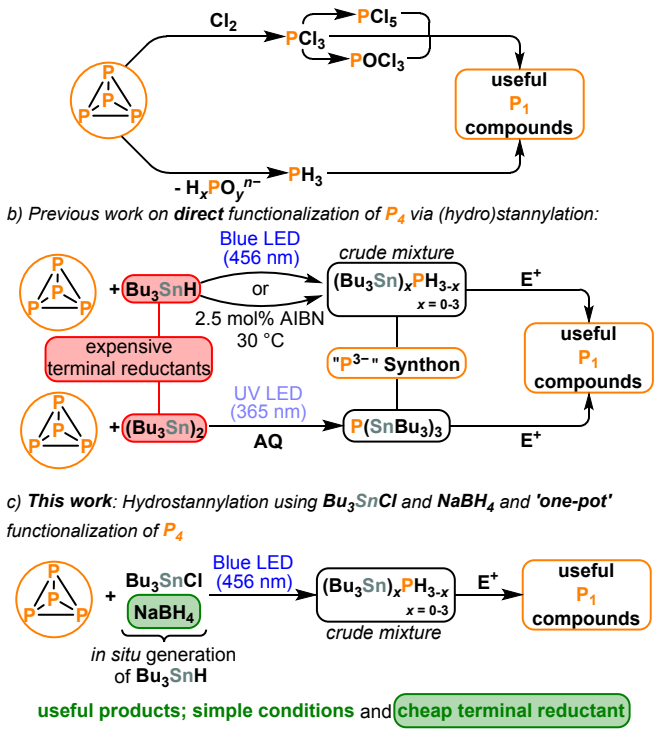
The direct functionalization of white phosphorus (P_4) is gaining attention as an alternative to state-of-the-art multi-step processes. The hydrostannylation of P_4 affords valuable monophosphorus compounds directly *via* a hydrostannylphosphine mixture $(Bu_3Sn)_xPH_{3-x}$ (where x = 0-3) that reacts with suitable electrophiles. However, previous reports required terminal reductants which are infeasible for industrial-scale applications. Here, we report an improvement in this chemistry using $NaBH_4$ as the terminal reducing agent, generating the key hydrostannylation agent Bu_3SnH *in situ* from Bu_3SnCl. The resulting $(Bu_3Sn)_xPH_{3-x}$ mixtures were successfully functionalized towards useful P_1 compounds. Furthermore, we present the 'one-pot' preparation of tetrakis(hydroxymethyl)phosphonium chloride (THPC), the subsequent direct recycling of Bu_3SnCl, and preliminary attempts towards the catalytic synthesis of THPC.

Introduction

White phosphorus (P_4) represents a key industrial starting material for the synthesis of all commercially significant organophosphorus compounds (OPCs). Nevertheless, the current industrial production of these P_1 species relies on complex multistep procedures in which P_4 is commonly oxidized with hazardous Cl_2 gas to form PCl_3, or disproportionated under acidic or basic conditions to form PH_3. These intermediates subsequently require further functionalization in separate steps to yield the targeted P_1 products (Scheme 1a).[1,2] Consequently, the development of more efficient strategies for the *direct* functionalization of P_4 into valuable P_1 compounds while avoiding hazardous intermediates and minimizing waste remains a central objective in both industrial and academic research.[3]

In recent years, this area of chemistry has witnessed several significant advances. These include photocatalytic reactions,[4] controlled degradation of P_4 using silicon species,[5] 'semi-catalytic' use of pentaphosphaferrocene,[6] and oxidation *via* 'onionation' of P_4[7] or by the use of aryl disulfides,[8] among others.[9] Additionally, there is a significant interest in bypassing the use of P_4 to generate P_1 compounds from P(V) precursors.[10]

Alongside these approaches, our group has reported a simple method to directly functionalize P_4 using Bu_3SnH as a radical agent, initiated either by irradiation or by using chemical radical initiators, forming the hydrostannylphosphine mixture $(Bu_3Sn)_xPH_{3-x}$ (x = 0–3). This mixture then acts as a "P^{3-}" synthon, generating useful P_1 compounds upon treatment with suitable electrophiles (Scheme 1b).[11] Additionally, further developments of this method have been reported by our group, expanding the usability. These include the hydrostannylation of red phosphorus,[12] the full stannylation of P_4 towards $(Bu_3Sn)_3P$ using $(Bu_3Sn)_2$ and anthraquinone (AQ, Scheme 1b),[13] the use of



Scheme 1 a) Current industrial routes towards P_1 compounds starting from P_4. b) Previously reported direct transformation of P_4 towards P_1 compounds *via* hydrostannylation using Bu_3SnH under irradiation or initiated by chemical radical starters (top route)[11] or photocatalytic stannylation using anthraquinone (AQ) and $(Bu_3Sn)_2$ (bottom route).[13] c) Hydrostannylation of P_4 using cheap Bu_3SnCl and $NaBH_4$ and 'one-pot' functionalization using generic electrophiles (E^+).

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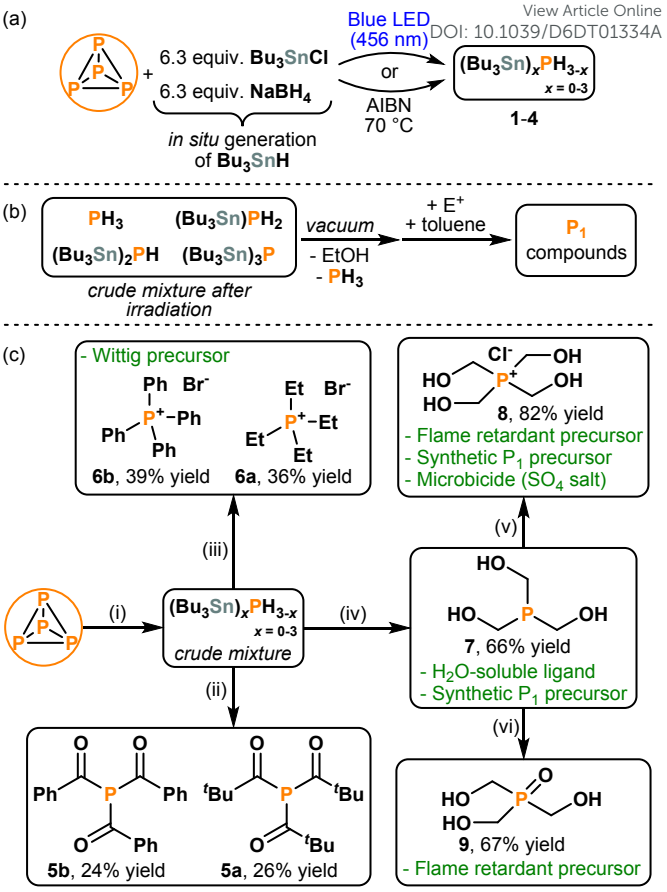
the lighter tetrels germanium and silicon for the hydroelementation[14] and experimental and computational investigation to better understand the break-down of P_4 during hydrostannylation.[15]

However, one downside of this hydrostannylation or -elementation is the use of terminal reductants that are unattractive on an industrial scale. Using Bu_3SnH or the related germanium or silicon hydrides is economically unsustainable. Furthermore, organotin hydrides display serious toxicity problems and thus must be handled with appropriate care. Targeting the second limitation, our group previously sought to demonstrate how to mitigate this by developing a procedure to recycle the crude tin-containing by-product, Bu_3SnCl, during the synthesis of tetrakis(hydroxymethyl)phosphonium chloride (THPC), by first hydrolyzing it to $(Bu_3Sn)_2O$ using aqueous Na_2CO_3, followed by reduction using polymethylhydrosiloxane (PMHS) to generate Bu_3SnH *in situ*.[11] However, while they are usually considered to be cheap reductants for laboratory use, even hydrosilanes such as PMHS are unattractive as terminal reducing agents at industrial scale.

We therefore sought to develop an alternative method for *in situ* reduction of the Bu_3Sn moiety, using $NaBH_4$ as the terminal reducing agent. $NaBH_4$ is one of the cheapest reductants available for industry (besides H_2) and is already employed at tonne-to-kilotonne scale for applications including paper/pulp production, electroless metal deposition, and fine chemical synthesis.[16] $NaBH_4$ is also capable of directly reducing Bu_3SnCl to Bu_3SnH,[17] obviating the need for the extra hydrolysis step required previously (*cf.* PMHS, which can reduce $(Bu_3Sn)_2O$ but not Bu_3SnCl). Herein, we describe the hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$ and preparation of relevant P_1 compounds in a 'one-pot' procedure (Scheme 1c). This procedure allows for the *direct* recycling of the Bu_3Sn moiety, as Bu_3SnCl (or other tributyltin halides) is the common byproduct in most cases. This allows for a simplified, much more economically viable synthetic cycle that uses cheap, scalable $NaBH_4$ as the terminal reductant.



Scheme 2 (a) Hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$ *via in situ* generation of Bu_3SnH, promoted by blue light irradiation; (b) General functionalization procedure for the synthesis of triacylphosphines or tetraalkylphosphonium salts (E^+ = RC(O)Cl or RBr, respectively) starting from the crude mixture of **1**-**4**; (c) Synthesis of important P_1 compounds in 'one-pot' procedures starting from P_4. (i) Hydrostannylation of P_4 (0.5 mmol, 1 equiv.) with Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.), PhH (5 mL), EtOH (15 mL), 456 nm, r.t., 18 h; (ii) preparation of triacylphosphines from crude $(Bu_3Sn)_xPH_{3-x}$: −EtOH, PhMe, 16 equiv. RC(O)Cl (R = ^{t}Bu, Ph), 6 equiv. KHMDS, r.t., 16 h; (iii) preparation of phosphonium salts $[R_4P]Br$ from crude $(Bu_3Sn)_xPH_{3-x}$: −EtOH, PhMe (25 mL), 40 equiv. BnBr or 20 equiv. EtBr, 8 equiv. KHMDS, 80 °C, 72 h; (iv) preparation of THP: P_4 (0.5 mmol, 1 equiv.) with Bu_3SnCl (6.3 equiv.), $NaBH_4$ (6.3 equiv.) and paraformaldehyde (50 equiv.), EtOH (25 mL), 456 nm, r.t., 17 h; (v) preparation of THPC from crude THP: 40 equiv. HCl (4.0 M in 1,4-dioxane), r.t., 2 h; (vi) preparation of THPO from crude THP: PhMe/H_2O, air, 90 °C, 16 h.

Results and Discussion

Hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$

To begin with, the simple addition of $NaBH_4$ and Bu_3SnCl to a slightly limiting amount of P_4 in EtOH was tested (6.3:6.3:1 molar ratio), followed by irradiation using blue LED light (456 nm) for 18 h. As the reduction of Bu_3SnCl with $NaBH_4$ is a very fast process with quantitative yields after a few minutes, we anticipated seeing comparable results to our original work using pre-prepared Bu_3SnH.[17] Gratifyingly, the formation of the desired phosphine mixture of PH_3 (**1**), Bu_3SnPH_2 (**2**), $(Bu_3Sn)_2PH$ (**3**) and $(Bu_3Sn)_3P$ (**4**) could be observed in very good spectroscopic yield of more than 80% (Scheme 2a; for more information see section S2.1, ESI). Using other solvents than EtOH or different stoichiometries led to worse outcomes, as did using hydride sources such as $NaBH_3CN$ or $LiAlH_4$ (see Table S1, ESI). Furthermore, using different wavelength lights showed no improvement in the reaction outcome. Notably, using near-UV light (365 nm), the reaction time could be drastically shortened to 15 min, at the cost of a somewhat lower yield of 63% (see Table S2, ESI).

Additionally, the hydrostannylation using chemical radical initiators like azobis(isobutyronitrile) (AIBN) was also found to yield the expected mixture of **1**-**4** in a good yield of 67% (Scheme 2a; see section S2.2, ESI). In contrast to our original publication using Bu_3SnH, however, elevated temperatures were necessary to provide this in good yield. Furthermore, it is noteworthy that longer reaction times impaired product formation (see Table S3, ESI).

Functionalization of the resulting hydrostannylphosphine mixture $(Bu_3Sn)_xPH_{3-x}$

In our previous publications, we showed that the P–Sn and P–H bonds in $(Bu_3Sn)_xPH_{3-x}$ (**1**-**4**) can both react with suitable

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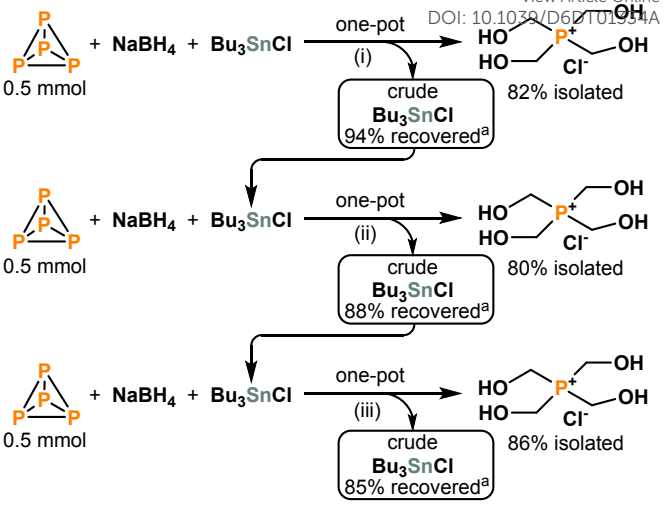
electrophiles, serving as a mixture of "P^{3-}" synthons. Using this property, OPCs could be synthesized directly in a 'one-pot' fashion.[11-14] Therefore, we investigated the functionalization of the phosphine mixture **1**-**4** obtained from Bu_3SnCl and $NaBH_4$ to demonstrate its comparability with the original method using Bu_3SnH.

Thus, the acylation of the phosphine mixture **1**-**4** was investigated first. To begin with, the reaction protocol from our original publication was repeated to synthesize acyl phosphines. This was done by simple addition of potassium bis(trimethylsilyl)amide (KHMDS), acting as a base, and acyl chlorides to the phosphine mixture **1**-**4** in EtOH after irradiation. However, when performing this reaction, no product formation of the desired acyl phosphines could be observed in the $^{31}P\{^1H\}$ NMR spectra. This is likely due to the EtOH reacting with the base first, forming the corresponding ethoxide, which then reacts with the acyl chlorides to form esters. Fortunately, this limitation can be addressed by removing the EtOH under reduced pressure and replacing it with toluene before adding further reactants to the mixture. However, during this process, PH_3 – formed through continuous scrambling of the phosphine mixture – is likewise removed, resulting in a loss of phosphorus equivalents during the functionalization (Scheme 2b). Consequently, the yield of the triacylphosphines $P(C(O)^tBu)_3$ (**5a**) and $P(C(O)Ph)_3$ (**5b**) is considerably lower than in the original publication using authentic Bu_3SnH for the hydrostannylation (Isolated yield for **5a**: 26% *vs.* 57%; for **5b**: 24% *vs.* 51%; Scheme 2c; see section S3.1 & S 3.2, ESI). Nevertheless, the 'one pot' generation of the target products was successful, providing encouraging proof of principle.

Similar behavior was observed in the alkylation of the phosphine mixture **1**-**4** using bromoethane (EtBr) or benzyl bromide (BnBr). When adding the alkyl halides and KHMDS to the mixture in EtOH after irradiation, no product formation could be observed in the $^{31}P\{^1H\}$ NMR spectra. Again, this is likely due to ethoxide reacting with alkyl halides to form ethers. However, when the solvent was replaced with toluene after the irradiation, this reaction too became feasible, forming the corresponding phosphonium salts $[Et_4P]Br$ (**6a**) or $[Bn_4P]Br$ (**6b**), with the latter being a precursor for useful Wittig chemistry,[18] albeit again in lower yield compared to the hydrostannylation of P_4 using Bu_3SnH directly (for **6a**: 36% *vs.* 65%; for **6b**: 39% *vs.* 82%; Scheme 2c, see section S3.3 & S3.4, ESI).

To overcome this limitation in the synthesis of acyl phosphines and phosphonium salts, hydroxymethyl-substituted phosphine derivatives were targeted. These are used as P_1 precursors and for preparing flame-retardant materials,[19,20] and their synthesis can be performed directly in EtOH, eliminating the need for a solvent switch (and concomitant loss in yield).[11] Notably, the synthesis of the parent phosphine $(HOCH_2)_3P$ (THP, **7**) was achieved in good isolated yield by simple addition of paraformaldehyde to the initial hydrostannylation mixture in EtOH before irradiation (66%; Scheme 2c, see S3.5, ESI). Alternatively, subsequent quenching of the thus obtained solution with HCl furnished $[(HOCH_2)_4P]Cl$ (THPC, **8**) in one-pot in excellent yield (82%; see S3.6, ESI). Additionally, Bu_3SnCl was recovered from that reaction in similarly excellent yield (94%).



Scheme 3 One-pot synthesis of THPC directly from P_4 with direct recycling of Bu_3SnCl. Conditions (equiv. are given per P_4 molecule): (i) from P_4: 6.3 equiv. Bu_3SnCl, 6.3 equiv. $NaBH_4$, 50 equiv. paraformaldehyde, EtOH, 456 nm LEDs, r.t., 17 h, then 40 equiv. HCl (4.0 M in 1,4-dioxane), r.t., 2 h; (ii) from P_4: crude recovered Bu_3SnCl, 6.3 equiv. $NaBH_4$, 50 equiv. paraformaldehyde, EtOH, 456 nm LEDs, r.t., 17 h, then 40 equiv. HCl (4.0 M in 1,4-dioxane), r.t., 2 h; (iii) from P_4: crude recovered Bu_3SnCl, 6.3 equiv. $NaBH_4$, 50 equiv. paraformaldehyde, EtOH, 456 nm LEDs, r.t., 17 h, then 40 equiv. HCl (4.0 M in 1,4-dioxane), r.t., 2 h. [a] Recovered yield is given relative to starting amount Bu_3SnCl in first cycle.

As a third option, the THP solution could be quenched by exposure to air, furnishing the corresponding phosphine oxide $(HOCH_2)_3PO$ (THPO, **9**) also in good yield (67%; Scheme 2c, see S3.7, ESI).

'One-pot' synthesis of THPC with direct recycling of Bu_3SnCl and attempted catalytic use

As mentioned in the introduction, one major downside of any *stoichiometric* procedure for forming useful OPCs *via* hydrostannylation is the generation of stoichiometric organotin waste, which poses serious drawbacks in terms of both cost and toxicity. Our group has previously attempted to circumvent this during the synthesis of THPC by recycling the organotin by-products or even using them in a catalytic fashion.[11] However, in those procedures, the Bu_3SnCl formed had to be hydrolyzed to $(Bu_3Sn)_2O$ using aqueous $NaCO_3$ before it could be reduced again using PMHS (which is unreactive towards Bu_3SnCl, whereas reactivity towards $(Bu_3Sn)_2O$ is driven by formation of a strong Si–O bond). However, having now shown that Bu_3SnCl can be used *directly* as the Bu_3Sn moiety to perform the hydrostannylation of P_4, we anticipated that this recycling could now be streamlined using $NaBH_4$ as the terminal reductant. Accordingly, we investigated the *direct* recycling of Bu_3SnCl in the synthesis of THPC, increasing the step and atom economy of the recycling process.

Thus, the synthesis of THPC (**8**) was repeated as previously described, giving an excellent yield (82%) and excellent recovery of Bu_3SnCl (94%; Scheme 3, i). This recovered Bu_3SnCl was then used directly as a crude starting material for a second cycle to synthesize THPC (**8**) again in excellent yield (80%) and again with very good recovery of Bu_3SnCl (88%, Scheme 3, ii). This could be repeated in a third cycle, with the crude 're-recovered' Bu_3SnCl

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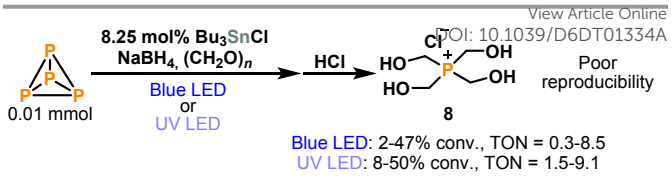
used to synthesize a third batch of THPC (**8**) in again excellent yield (86%), with Bu_3SnCl ultimately being recovered in a very good yield of 85% with respect to the initially used amount (Scheme 3, iii; see S4, ESI), clearly showing the viability of efficient, direct recycling of Bu_3SnCl to form hydroxymethyl substituted phosphines.

Having established the direct recycling of Bu_3SnCl, we finally investigated whether it could also be employed as the starting Bu_3Sn moiety in a fully catalytic cycle towards THPC starting from P_4 and $NaBH_4$, analogous to the PMHS-based catalytic cycle we have reported previously[11] (for a proposed catalytic mechanism, see Figure S38, ESI). Therefore, our previously reported catalytic procedure towards THPC (**8**) was repeated using catalytic Bu_3SnCl (8.25 mol% per P atom) and stoichiometric $NaBH_4$ (instead of Bu_3SnOMe and PMHS, respectively; Scheme 4; see S5, ESI). Unfortunately, this approach showed poor reproducibility. While good turnover, comparable to our previous best results, was observed in some specific cases, other seemingly identical reactions showed no or very low catalytic activity, with minimal turnover numbers (TONs). In the best cases, using blue light (456 nm) and UV light (365 nm), THPC (**8**) was obtained in NMR yields of 47% and 50%, respectively, corresponding to TONs of 8.5 and 9.1, respectively (see S5, ESI for calculations). Given the noted reproducibility issues, there are clearly unidentified factors affecting catalytic turnover in these reactions. Nevertheless, these preliminary results suggest that, with further investigation, efficient, consistent catalysis should be achievable, and efforts towards this goal are ongoing.



Scheme 4 Catalytic transformation of P_4 into THPC (**8**): 8.25 mol% (per P atom) Bu_3SnCl, 6.3 eq. $NaBH_4$, 50 eq. paraformaldehyde, EtOH, 456 nm or 365 nm LEDs, r.t., 67 h.

Conclusions

We have described herein further developments in the hydrostannylation of P_4, showing how this can now be achieved much more cheaply using Bu_3SnCl as a source of Bu_3Sn moieties and $NaBH_4$ as a terminal reductant, marking a significant step towards larger-scale feasibility for this chemistry. We have shown that this method enables the preparation of useful P_1 products, albeit with reduced yields for some. However, other products, especially hydroxymethyl-substituted phosphine derivatives, suffer no drawbacks from this updated hydrostannylation method, achieving yields similar to our best previous results at a significantly reduced cost.[21] Furthermore, direct recycling of the Bu_3SnCl by-product in the synthesis of THPC (**8**) could be done consistently over three cycles, showing a major advantage of this method. Unfortunately, preliminary studies of the potential catalytic use of Bu_3SnCl to generate THPC (**8**) from P_4 suffered from reproducibility issues, but initial results suggest that, if these can be resolved, true catalysis should be achievable. As such, this work serves as an intriguing proof of principle. Further research into this particular reaction is on-going with the aim of further maximizing efficiency in organotin-catalyzed transformations of P_4.

Author contributions

MM: investigation – experimental study, writing – original draft. LH: experimental assistance – recycling of Bu_3SnCl, catalytic use of Bu_3SnCl. DJS: conceptualization, writing – review and editing. RW: conceptualization, supervision, funding acquisition, writing – review and editing.

Conflicts of interest

A patent covering all the results described herein has been filed (as of 13 February 2020) by the University of Regensburg (EP 20,157,197.3; inventors, DJS and RW). The authors declare no other competing interests.

Data availability

The data supporting this article have been included as part of the ESI.†

Acknowledgements

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21 As a rough illustration, publicly listed prices for the largest purchasable quantities on sigmaaldrich.com (accessed: 26.05.2026) are as follows : Bu_3SnH: 553 €/mol and PMHS: 45 €/mol *vs.* Bu_3SnCl: 108 €/mol and $NaBH_4$: 28 €/mol.

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Data Availability Statement

for the article

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