Supplementary Information

Photocatalytic Stannylation of White Phosphorus

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S1. General information

All reactions and manipulations were performed under an \( \text{N}_2 \) atmosphere (< 0.1 ppm \( \text{O}_2, \text{H}_2\text{O} \)) through use of a GS Glovebox (GS117717). All glassware was oven-dried (160 °C) overnight prior to use. Benzene was distilled from Na/benzophenone and stored over molecular sieves (3 Å). Acetonitrile was distilled from CaH\(_2\) and stored over molecular sieves (3 Å). Acetone was stirred over CaSO\(_4\) (30 min) and dynamically dried by passing over molecular sieves (3 Å). THF was purified using an MBraun SPS-800 system and stored over molecular sieves (3 Å). \( \text{C}_6\text{D}_6\) was distilled from K and stored over molecular sieves (3 Å). Hexabutyldistannane (Bu\(_3\)Sn)\(_2\) was purchased from ABCR or Thermo Scientific (97% purity). The photocatalysts benzophenone, 4-benzoylpyridine, xanthone, thioxanthone, anthraquinone and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) were ordered from major chemical suppliers (Sigma, ABCR) and used as received. All other chemicals were also purchased from major suppliers (Aldrich, ABCR); liquids were purified by Kugelrohr distillation and freeze-pump-thaw degassed three times prior to use; \( \text{P}_4\) and \( \text{Ph}_3\text{PO} \) were purified by sublimation; all others were used as received.

Qualitative NMR spectra were recorded at room temperature on Bruker Avance III HD 400 (400 MHz) spectrometers and were processed using Topspin 3.2. Chemical shifts \( \delta \) are reported in parts per million (ppm); \(^1\text{H}\) and \(^{13}\text{C}\) shifts are reported relative to SiMe\(_4\) and were calibrated internally to residual solvent peaks, while \(^{31}\text{P}\) shifts and \(^{119}\text{Sn}\) shifts were referenced externally to 85% H\(_3\text{PO}_4\) (aq.) and Me\(_4\text{Sn}\), respectively. NMR samples were prepared in the glovebox using NMR tubes fitted with screw caps. Optimization reactions (see sections S5, S6 and S7) and photocatalytic stannylation of \( \text{P}_4\) to \((\text{Bu}_3\text{Sn})_3\text{P}\) and subsequent functionalization to \( \text{P}_1\) products were analyzed by \(^{31}\text{P}{\{^1\text{H}\}}\) spectra using triphenylphosphine, \( \text{Ph}_3\text{PO} \), as a standard.

For determining the conversion of the \( \text{P}_1\) products, the following quantitative \(^{31}\text{P}{\{^1\text{H}\}}\) NMR pulse programs were used:

- Triacylphosphines\(^{[1]}\)  
  \( \text{LB} = 10 \)  
  \( \text{T}_{1\text{ss}} < \text{T}_{1\text{prod}} = 10\text{s}, \text{D}_1 = 40\text{s}, \text{zgig30}, \text{inverse gated decoupled}, \)

- Phosphonium salts\(^{[2]}\)  
  \( \text{LB} = 1. \)  
  \( \text{DS} = 0, \text{D}_1 = 2\text{s}, \text{D}_1 \geq 5 \times \text{T}_1, \text{zgig90}, \text{inverse gated decoupled}, \)
LEDs used for the optimization reactions of the photocatalytic stannylation of $P_4$ to $(\text{Bu}_3\text{Sn})_3P$ were:

- Green LED: 528 nm, 3.5 V, 700 mA, Osram OSLON SSL 80
- Blue LED: 455 nm (±15 nm), 3.2 V, 700 mA, Osram OSLON SSL 80
- Violet/Blue LED: 415 nm (±5 nm), 3.5 V, 700 mA, Intelligent LED Solutions ILH-XC01-5410-SC211-WIR200
- Violet LED: 405 nm (±10 nm), 4.0 V, 700 mA, Edixeon EDEV-SLC1-03
- UV LED: 385 nm (±15 nm), 3.4 V, 350 mA LST1-01G01-UV02-00
- UV LED: 365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80
- UV LED: 365 nm, 14 V, 700 mA, Osram OSLON SSL 80 (scale-up reactions)
S2. Supplementary mechanistic discussion

The proposed mechanism for the photocatalytic stannylation of $P_4$ by $(Bu_3Sn)_2$ catalyzed by simple ketones is outlined in Scheme 2 of the primary manuscript. However, it should be noted that in the absence of more comprehensive mechanistic studies it is currently not possible to exclude the involvement of several alternative elementary reaction steps. For example, while the formation of an intermediate stannylated ketyl radical $[R_2COSnBu_3]^-\text{•}$ is supported by the prior literature, an alternative energy transfer from $[R_2CO]^*$ to $(Bu_3Sn)_2$ resulting in cleavage to $Bu_3Sn^*$ by a purely outer sphere mechanism has not yet been definitively excluded.

One key question left unanswered at present relates to the precise mechanism by which radical breakdown of the $P_4$ tetrahedron is achieved. Based on our previous studies it can be confidently proposed that each $P$–$P$ bond cleavage step is likely to begin with attack of a photocatalytically-generated $Bu_3Sn^*$ radical (Scheme S1).[1] The simplest subsequent step would be recombination of the resulting $P$-centered radical with a second $Bu_3Sn^*$ radical, thus completing the stannylation of the original $P$–$P$ moiety (Scheme S1a). Note, however, that this requires bimolecular recombination of two transient radicals whose concentrations are expected to be low.

Alternatively, stannylation of this $P$-centered radical could be achieved through $S_n2$-type attack on the proposed intermediate $[R_2COSnBu_3]^*$ and/or its pinacol-type dimer, examples of which are known from the literature to exist in equilibrium (Scheme S1b).[3] In this scenario, this equilibrium would act as a stabilized and hence more persistent reservoir of chemically-accessible “$Bu_3Sn^*$”.

A third scenario is that $S_n2$-type attack could occur directly on the $(Bu_3Sn)_2$ substrate, which should be present in high concentrations throughout the reaction. This scenario would result in a radical chain mechanism analogous to that proposed previously for $P_4$ hydrostannylation (Scheme S1c).[1] In this case the $R_2CO$ photocatalyst would formally act as a photosensitizing initiator for the chain reaction, rather than as a strict catalyst per se. However, we currently consider this to be a less likely option, due to several qualitative experimental observations. Firstly, attempts to achieve an analogous chain reaction mechanism using “standard” chemical initiators such as AIBN under thermal conditions (instead of $R_2CO$ under photochemical conditions) have thus far been unsuccessful, not leading to any identifiable change by $^{31}P\{^1H\}$ NMR spectroscopy (for example, see Figure S1).

Secondly, attempts to initiate the same radical chain under thermal conditions by using catalytic quantities of both AIBN and $Bu_3SnH$, which should definitely result in formation of $Bu_3Sn^*$, have also been unsuccessful. These led only to trace hydrostannylation, consistent with the amount of $Bu_3SnH$
present and similar to the outcome when no distannane is present, which argues against any efficient radical interception by \((\text{Bu}_3\text{Sn})_2\) (for example, see Figure S2).

Scheme S1. Illustration of the equipment setup used for photocatalytic reactions at 0.04 mmol scale.

Figure S1. Representative $^31\text{P}({}^1\text{H})$ NMR spectrum for the attempted stannylation of $\text{P}_4$ using $(\text{Bu}_3\text{Sn})_2$ and 12.5 mol% AIBN in toluene, after heating to 80 °C for 16 h.
Figure S2. Representative $^{31}\text{P}$$^{1}\text{H}$ NMR spectrum for the attempted stannylation of $P_4$ using $(\text{Bu}_3\text{Sn})_2$ and 12.5 mol% of both AIBN and Bu$_3$SnH in toluene, after heating to 80 °C for 18 h. The relatively high proportion of $(\text{Bu}_3\text{Sn})_2\text{PH}$ and $(\text{Bu}_3\text{Sn})_3\text{P}$ relative to Bu$_3$SnPH$_2$ (c.f. ref. [1]) can likely be attributed to Bu$_3$Sn/H ligand scrambling at the elevated reaction temperature and/or the high loading of AIBN relative to Bu$_3$SnH which reduces the number of available H atoms. This is supported by the observation that when the reaction is repeated in the absence of $(\text{Bu}_3\text{Sn})_2$ the resulting $(\text{Bu}_3\text{Sn})_n\text{PH}_{4-n}$ mixture is also heavily weighted towards $(\text{Bu}_3\text{Sn})_2\text{PH}$ and $(\text{Bu}_3\text{Sn})_3\text{P}$.
S3. General procedure for photocatalytic functionalization of P₄ (0.04 mmol scale) into stannylated phosphine (Bu₃Sn)₃P using benzophenone

At the start of this project, benzophenone (BP) was chosen as a photocatalyst for the initial reaction optimization due to both its simplicity and the fact that its (photo)reactivity towards hexaalkyldistannanes has been studied previously.[3]

To a 10 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (101.1 μL, 5 equiv. based on phosphorus atoms, 20 equiv. based on P₄), BP (0.01 mmol, as a stock solution in 149.2 μL benzene, 1 equiv. based on P₄) and P₄ (0.01 mmol, as a stock solution in 71.3 μL benzene) in benzene as solvent (in total 0.5 mL). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S3),[2] and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h (unless stated otherwise). Ph₃PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to ³¹P{¹H} NMR analysis (Figure S4). Formation of (Bu₃Sn)₃P was indicated by the characteristic ¹¹⁷/¹¹⁹Sn-satellited resonance at -346.5 ppm.[1]
Figure S4. Representative $^{31}$P{$^1$H} NMR spectrum for the photocatalytic functionalization of P4 using benzophenone (BP) as a photocatalyst (Table 1, Entry 1). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
S4. Optimization of photocatalytic reaction conditions using benzophenone

**Table S1.** Photocatalytic functionalization of $P_4$ to $(Bu_3Sn)_3P$: screening of control experiments.\[^a\]

| Entry | Conditions | Full conv. of $P_4$? | Conv. to $(Bu_3Sn)_3P$ / % |
|-------|------------|-----------------------|-----------------------------|
| 1     | Standard\[^a\] | ✓                     | 50                          |
| 2     | No light   | X                     | 0                           |
| 3     | No benzophenone | ✓                     | 0                           |
| 4     | No $(Bu_3Sn)_2$ | X                     | 0                           |
| 5     | Blue LEDs (455 nm) | X                     | 0                           |
| 6     | Violet LEDs (405 nm) | ✓                     | 26                          |
| 7     | $P_{red}$ instead of $P_4$ | —                     | 1                           |

\[^a\] For the general procedure, see section S3.

**Table S2.** Photocatalytic functionalization of $P_4$ to $(Bu_3Sn)_3P$: screening of different radiation sources (LEDs).\[^a\]

| Entry | LEDs                  | Full conv. of $P_4$? | Conv. to $(Bu_3Sn)_3P$ / % |
|-------|-----------------------|-----------------------|-----------------------------|
| 1     | 365 nm\[^a\] (UV LED) | ✓                     | 50                          |
| 2     | 385 nm (UV LED)       | ✓                     | 40                          |
| 3     | 405 nm (violet LED)   | ✓                     | 26                          |
| 4     | 420 nm (violet blue LED) | ✓                     | 21                          |
| 5     | 455 nm (blue LED)     | X                     | 0                           |
| 6     | 528 nm (green LED)    | X                     | 0                           |

\[^a\] The general procedure (see section S3) was modified to use the LEDs indicated.
Table S3. Photocatalytic functionalization of $P_4$ to $(\text{Bu}_3\text{Sn})_3P$: screening of irradiation period.[a]

![Diagram](image-url)

| Entry | Irradiation period | Full conv. of $P_4$? | Conv. to $(\text{Bu}_3\text{Sn})_3P$ / % |
|-------|-------------------|-------------------|-----------------------------|
| 1     | 16 h              | ✓                 | 41                          |
| 2     | 18 h              | ✓                 | 43                          |
| 3     | 20 h              | ✓                 | 45                          |
| 4     | 22 h              | ✓                 | 50                          |

[a] The general procedure (see section S3) was modified in the period of irradiation with UV light (365 nm).

Table S4. Photocatalytic functionalization of $P_4$ to $(\text{Bu}_3\text{Sn})_3P$: screening of solvents.[a]

![Diagram](image-url)

| Entry | Solvent | Full conv. of $P_4$? | Conv. to $(\text{Bu}_3\text{Sn})_3P$ / % |
|-------|---------|-------------------|-----------------------------|
| 1     | Benzene[a] | ✓                 | 50                          |
| 2     | Benzene[b] | ✓                 | 47                          |
| 3     | Acetone  | ✓                 | 50                          |
| 4     | Acetonitrile | ✓             | 35                          |
| 5     | THF      | ✓                 | 11                          |
| 6     | Toluene  | ✓                 | 48                          |

[a] The general procedure (see section S3) was modified to use a solvent mixture ($P_4$ and BP stock solutions still in benzene, total solvent volume of 0.5 mL). [b] 0.22 mL solvent volume.

Table S5. Photocatalytic functionalization of $P_4$ to $(\text{Bu}_3\text{Sn})_3P$: screening of amounts of benzophenone.[a][b]

![Diagram](image-url)

| Entry | BP / equiv.[b] | Full conv. of $P_4$? | Conv. to $(\text{Bu}_3\text{Sn})_3P$ / % |
|-------|----------------|-------------------|-----------------------------|
| 1     | 0.5            | ✓                 | 45                          |
| 2     | 1              | ✓                 | 50                          |
| 3     | 4              | ✓                 | 60                          |
| 4     | 10             | ✓                 | 59                          |

[a] For the general procedure, see section S3. [b] Listed equivalents are defined per $P_4$ molecule.
Table S6. Photocatalytic functionalization of $P_4$ to (Bu$_3$Sn)$_3$P: screening of amounts of (Bu$_3$Sn)$_2$.\[a][b]

![Diagram of photocatalytic functionalization]

| Entry | (Bu$_3$Sn)$_2$ / equiv.$^\text{[a]}$ | Full conv. of $P_4$? | Conv. to (Bu$_3$Sn)$_3$P / % |
|-------|---------------------------------|---------------------|---------------------------|
| 1     | 30                              | ✓                   | 58                        |
| 2     | 20                              | ✓                   | 51                        |
| 3     | 15                              | ✓                   | 49                        |
| 4     | 12                              | ✓                   | 45                        |
| 5     | 6                               | ✓                   | 35                        |

$^\text{[a]}$ For the general procedure, see section S3. $^\text{[b]}$ Listed equivalents are defined per $P_4$ molecule.
S5. Benzophenone derivatives used as photocatalysts for the photocatalytic functionalization of \( P_4 \) to \( (\text{Bu}_3\text{Sn})_3\text{P} \)

Table S7. Photocatalytic functionalization of \( P_4 \) to \( (\text{Bu}_3\text{Sn})_3\text{P} \): screening of benzophenone derivatives.\(^4\)[a]

![Scheme](image)

| Entry | Photoinitiator (PI) | Full conv. of \( P_4 \)? | Conv. to \( (\text{Bu}_3\text{Sn})_3\text{P} \) / % |
|-------|---------------------|--------------------------|-----------------------------------------------|
| 1     | Benzophenone\(^{[a]}\) (BP) | ✓                        | 50                                           |
| 2     | Benzophenone\(^{[b]}\) (BP) | ✓                        | 50                                           |
| 3     | 4-Benzoylpyridine (4-BP) | ✓                        | 73                                           |
| 4     | Xanthone (XT)         | ✓                        | 39                                           |
| 5     | Thioxanthone (TXT)    | ✓                        | 70                                           |
| 6     | Thioxanthone\(^{[b]}\) (TXT) | ✓                        | 66                                           |
| 7     | Anthraquinone (AQ)    | ✓                        | 62                                           |
| 8     | Anthraquinone\(^{[b]}\) (AQ) | ✓                        | 75                                           |
| 9     | Anthraquinone\(^{[b][c]}\) (AQ) | ✓                        | 83                                           |
| 10    | Acetone               | ✓                        | 2                                            |
| 11    | DDQ                  | ✓                        | 8                                            |

[a] For the general procedure, see section S3. [b] A solvent mixture of benzene (71.3 μL of the \( P_4 \) stock solution) and acetone (429 μL) was used. [c] Instead of the usual 1 equiv. of the photocatalyst only 0.5 equiv. of the anthraquinone (AQ) was used.
Figure S5. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using benzophenone (BP) as a photocatalyst (Table 7, Entry 1). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

Figure S6. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using benzophenone (BP) as a photocatalyst (Table 7, Entry 2, PhH/acetone). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
Figure S7. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P₄ using 4-benzoylpyridine (4-BP) as a photocatalyst (Table S7, Entry 3). * marks the internal standard Ph₃PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

Figure S8. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P₄ using xanthone (XT) as a photocatalyst (Table S7, Entry 4). * marks the internal standard Ph₃PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
Figure S9. $^{31}\text{P}^1\text{H}$ NMR spectrum for the photocatalytic functionalization of $\text{P}_4$ using thioxanthone (TXT) as a photocatalyst (Table S7, Entry 5). * marks the internal standard $\text{Ph}_3\text{PO}$ (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

Figure S10. $^{31}\text{P}^1\text{H}$ NMR spectrum for the photocatalytic functionalization of $\text{P}_4$ using thioxanthone (TXT) as a photocatalyst (Table S7, Entry 6, PhH/acetone). * marks the internal standard $\text{Ph}_3\text{PO}$ (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
**Figure S11.** $^{31}$P($^{1}$H) NMR spectrum for the photocatalytic functionalization of $P_4$ using anthraquinone (AQ) as a photocatalyst (Table S7, Entry 7). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

**Figure S12.** $^{31}$P($^{1}$H) NMR spectrum for the photocatalytic functionalization of $P_4$ using anthraquinone (AQ) as a photocatalyst (Table S7, Entry 8, PhH/acetone). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
Figure S13. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using anthraquinone (AQ) as a photocatalyst (Table S7, Entry 9, 0.5 equiv. anthraquinone in PhH/acetone). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

Figure S14. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using acetone as a photocatalyst (Table S7, Entry 10). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.
Figure S15. $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P₄ using DDQ as a photocatalyst (Table S7, Entry 11). * marks the internal standard Ph₃PO (0.02 mmol). # marks unknown side products.
S6. General procedure for photocatalytic functionalization of P₄ (0.04 mmol scale) into stannylated phosphine (Bu₃Sn)₃P using anthraquinone

To a 10 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (101.1 µL, 5 equiv. based on phosphorus atoms, 20 equiv. based on P₄), anthraquinone (AQ) (1.0 mg, 0.5 equiv. based on P₄) and P₄ (0.01 mmol, as a stock solution in 71.3 µL benzene) in acetone as solvent (429 µL, in total 0.5 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S16), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h (unless stated otherwise). Ph₃PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to ³¹P{¹H} NMR analysis and showed 83% conversion to the product (Bu₃Sn)₃P[1] (Figure S17).

Figure S16. Illustration of the equipment setup used for photocatalytic reactions at 0.04 mmol scale.

Spectroscopic data of (Bu₃Sn)₃P:

³¹P{¹H} and ¹¹⁹Sn{¹H} NMR data of the photocatalytically generated (Bu₃Sn)₃P were extracted from spectra of the crude reaction mixture (see Figure S17 and S18), and are consistent with previous reports.[6] Note that isolation of (Bu₃Sn)₃P was not pursued due to separation from unreacted (Bu₃Sn)₂ being complicated by very similar solubilities as well as the high boiling point of both compounds.

³¹P{¹H} NMR (161.98 MHz, 300 K, C₆D₆): δ = −346.8 ppm (s).

¹¹⁹Sn{¹H} NMR (149.21 MHz, 300 K, C₆D₆): δ = 38.0 ppm (d, J(³¹P-¹¹⁹Sn) = 912.5 Hz, J(¹¹⁹Sn-¹¹⁷Sn) = 278.2 Hz).
Figure S17. Representative $^{31}$P($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using anthraquinone (AQ) as a photoinitiator (section S5, Table S8, Entry 1). * marks the internal standard Ph$_3$PO (0.02 mmol). ~ marks an unknown Sn-containing side product. # marks unknown side products.

Figure S18. $^{119}$Sn($^1$H) NMR spectrum for the photocatalytic functionalization of P$_4$ using anthraquinone (AQ) as a photoinitiator (0.5 equiv. anthraquinone and 12 equiv. (Bu$_3$Sn)$_2$ in PhH/acetone). ~ marks an unknown side product (see Figure S15, $^{31}$P($^1$H) NMR $\delta = -198.6$ ppm).
S7. Optimization of photocatalytic reaction conditions using anthraquinone

**Table S8.** Photocatalytic functionalization of \( P_4 \) to \((\text{Bu}_3\text{Sn})_3\text{P} \): screening of control experiments.\(^{[a]}\)

| Entry | Conditions | Full conv. of \( P_4 \)? | Conv. to \((\text{Bu}_3\text{Sn})_3\text{P} \) / % |
|-------|------------|---------------------------|-----------------------------------------------|
| 1     | Standard\(^{[a]}\) | ✓                         | 83                                            |
| 2     | No light   | X                         | 0                                             |
| 3     | No AQ\(^{[b]}\) | ✓                         | 2                                             |
| 4     | No \((\text{Bu}_3\text{Sn})_2\) | X                       | 0                                             |
| 5     | Blue LEDs (455 nm) | X                       | 15                                            |
| 6     | Violet/Blue LEDs (420 nm) | ✓                       | 76                                            |
| 7     | \( P_{\text{red}} \) instead of \( P_4 \) | -                         | 0                                             |

\(^{[a]}\) For the general procedure, see section S6. \(^{[b]}\) The reaction without anthraquinone (AQ) as a photoinitiator shows small conversion to \((\text{Bu}_3\text{Sn})_3\text{P} \) presumably because acetone used as a solvent can act as an alternative but less efficient photocatalyst (see section S5, Table S7, Entry 10).

**Table S9.** Photocatalytic functionalization of \( P_4 \) to \((\text{Bu}_3\text{Sn})_3\text{P} \): screening of different radiation sources (LEDs).\(^{[a]}\)

| Entry | LEDs                | Full conv. of \( P_4 \)? | Conv. to \((\text{Bu}_3\text{Sn})_3\text{P} \) / % |
|-------|---------------------|---------------------------|-----------------------------------------------|
| 1     | 365 nm\(^{[a]}\) (UV LED) | ✓                         | 83                                            |
| 2     | 385 nm (UV LED)     | ✓                         | 66                                            |
| 3     | 405 nm (violet LED) | ✓                         | 21                                            |
| 4     | 420 nm (violet blue LED) | ✓                       | 76                                            |
| 5     | 455 nm (blue LED)   | ✓                         | 15                                            |
| 6     | 528 nm (green LED)  | X                         | 0                                             |

\(^{[a]}\) The general procedure (section S6) was modified to use the LEDs indicated.
Table S10. Photocatalytic functionalization of P₄ to (Bu₃Sn)₃P: screening of solvents.^[a]

| Entry | Solvent     | Full conv. of P₄? | Conv. to (Bu₃Sn)₃P / % |
|-------|-------------|-------------------|------------------------|
| 1     | Benzene^[a] | ✓                 | 58                     |
| 2     | Acetone     | ✓                 | 83                     |
| 3     | Acetone^[b] | ✓                 | 79                     |
| 4     | Acetonitrile| ✓                 | 5                      |
| 5     | THF         | ✓                 | 35                     |
| 6     | Toluene     | ✓                 | 60                     |
| 7     | Ethanol     | ✓                 | 3                      |

^[a] The general procedure (section S6) was modified to use a solvent mixture (P₄ stock solutions in benzene).^[b] 0.22 mL solvent volume.

Table S11. Photocatalytic functionalization of P₄ to (Bu₃Sn)₃P: screening of amounts of anthraquinone.^[a][b]

| Entry | AQ / equiv.^[b] | Full conv. of P₄? | Conv. to (Bu₃Sn)₃P / % |
|-------|-----------------|-------------------|------------------------|
| 1     | 0.01^[c]        | ✓                 | 4                      |
| 2     | 0.1^[c]         | ✓                 | 47^[d]                 |
| 3     | 0.25            | ✓                 | 70^[e]                 |
| 4     | 0.5             | ✓                 | 83                     |
| 5     | 1               | ✓                 | 73                     |
| 6     | 4               | ✓                 | 45                     |

^[a] For the general procedure, see section S6.^[b] Listed equivalents are defined per P₄ molecule.^[c] For catalytic use of photoinitiator anthraquinone (AQ) a stock solution (1 mg AQ in 1 mL benzene) was prepared for screening 0.01 equiv. AQ (20.8 µL, Entry 1) and 0.1 mmol AQ (208 µL, Entry 2).^[d] This catalyst loading corresponds to a TON of 28.2.^[e] This catalyst loading corresponds to a TON of 16.8.
Table S12. Photocatalytic functionalization of P₄ to (Bu₃Sn)₃P: screening of amounts of (Bu₃Sn)₂[^a][^b]

![Diagram](image)

| Entry | AQ / equiv. | (Bu₃Sn)₂ / equiv[^a] | Full conv. of P₄? | Conv. to (Bu₃Sn)₃P / % |
|-------|-------------|----------------------|-------------------|------------------------|
| 1     | 1           | 30                   | ✓                 | 82                     |
| 2     | 1           | 20                   | ✓                 | 75                     |
| 3     | 1           | 12                   | ✓                 | 82                     |
| 4     | 1           | 6                    | ✓                 | 61                     |
| 5     | 0.5         | 30                   | ✓                 | 84                     |
| 6     | 0.5         | 20                   | ✓                 | 83                     |
| 7     | 0.5         | 12                   | ✓                 | 79                     |
| 8     | 0.5         | 6                    | ✓                 | 64                     |

[^a]: For the general procedure, see section S6. [^b]: Listed equivalents are defined per P₄ molecule (0.01 mmol).

**Note:**

In the final stage of optimization, it was found that reducing the (Bu₃Sn)₂ loading from 20 equiv. to 12 equiv. had only a very minor impact on conversion to (Bu₃Sn)₃P (from 83% to 79%). Thus, while the reaction with 20 equiv. formally gave the best conversion, the reaction with 12 equiv. was chosen as being optimal for further elaboration into ‘one pot’ reactions, as it should reduce the formation of stoichiometric, Sn-containing waste.
S8. Characterization of optimized 0.04 mmol scale reactions using anthraquinone

S8.1 Synthesis of triacylphosphines (R(O)C)₃P (R = Ph, Ad, Cy, tBu, iPr, nBu, Me)⁴¹

To a 10 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (60.6 μL, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄), anthraquinone (AQ) (1.0 mg, 0.5 equiv. based on P₄) and P₄ (0.01 mmol, as a stock solution in 71.3 μL benzene) in acetone as solvent (429 μL, in total 0.5 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S14), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h. To further functionalize the P₁ intermediate (Bu₃Sn)₃P into triacyl phosphines (R(O)C)₃P in an ‘one-pot’ manner, different acyl chlorides RC(O)Cl (0.16 mmol, 16 equiv. based on P₄, 4 equiv. based on phosphorus atoms, with R = Ph, Ad, Cy, tBu, iPr, nBu and Me, see Table S13) were added to the photocatalytic reaction mixture, which each showed a color change from an orange to a yellow solution while stirring overnight.

Table S13. Substrate scope for functionalization of (Bu₃Sn)₃P generated photocatalytically using anthraquinone into triacyl phosphines.

| Substrate | R       | Full conv. of (Bu₃Sn)₃P? | Conv.[a] to (R(O)C)₃P / % |
|-----------|---------|--------------------------|--------------------------|
| 1         | R = Phenyl (Ph) | ✓                        | 75                       |
| 2         | R = Adamantyl (Ad) | ✓                        | 40                       |
| 3         | R = Cyclohexyl (Cy) | ✓                        | 66                       |
| 4         | R = tert-Butyl (tBu) | ✓                        | 64                       |
| 5         | R = iso-Propyl (iPr) | ✓                        | 67                       |
| 6         | R = n-Butyl (nBu) | ✓                        | 54                       |
| 7         | R = Methyl (Me) | ✓                        | 60                       |

‘One-pot’ synthesis of triacyl phosphines: (i) For the general procedure of the photocatalytic stannylation of P₄ into (Bu₃Sn)₃P (0.04 mmol scale) see section S6. (ii) Subsequent functionalization of (Bu₃Sn)₃P using acyl chlorides to generate triacyl phosphines (R(O)C)₃P. The conversions were determined by ³¹P{¹H} NMR experiments (161.98 MHz, 300 K, C₆D₆) (0.02 mmol Ph₃PO as internal standard). [a] The conversions were determined by quantitative ³¹P{¹H} NMR (T₁S < T₁Prod = 10s, D₁ = 40 s, zgig30, inverse gated decoupled).
S8.1.2 Synthesis and quantification of (Ph(O)C)₃P

Figure S19. Quantitative $^{31}$P($^1$H) NMR spectrum of (Ph(O)C)₃P generated via photocatalytic stannylation of $P_4$ in benzene/acetone followed by acylation with benzoyl chloride PhC(O)Cl (1) (Table S13, 12 equiv. (Bu₃Sn)$_2$, $T_1$< $T_{1\text{prod}}$ = 10s, $D_1$ = 40 s, zgig30, inverse gated decoupled, LB = 10). * marks the internal standard Ph$_3$PO (0.02 mmol).

S8.1.3. Synthesis and quantification of (Ad(O)C)₃P

Figure S20. Quantitative $^{31}$P($^1$H) NMR spectrum of (Ad(O)C)₃P generated via photocatalytic stannylation of $P_4$ in benzene/acetone followed by acylation with 1-adamantanecarbonyl chloride AdC(O)Cl (2) (Table S13, 12 equiv. (Bu₃Sn)$_2$, $T_1$< $T_{1\text{prod}}$ = 10s, $D_1$ = 40 s, zgig30, inverse gated decoupled, LB = 10) * marks the internal standard Ph$_3$PO (0.02 mmol).
S8.1.4. Synthesis and quantification of $$(	ext{Cy}(	ext{O})	ext{C})_3	ext{P}$$

![NMR spectrum of $$(	ext{Cy}(	ext{O})	ext{C})_3	ext{P}$$](image)

Figure S21. Quantitative $^{31}	ext{P}$(1H) NMR spectrum of $$(	ext{Cy}(	ext{O})	ext{C})_3	ext{P}$$ generated via photocatalytic stannylation of $\text{P}_4$ in benzene/acetone followed by acylation with cyclohexanecarbonyl chloride $\text{CyC(O)Cl}$ (3) (Table S13, 12 equiv. (Bu$_3$Sn)$_2$, $T_{1s} < T_{1\text{prod}} = 10\text{s}$, $D_1 = 40\text{s}$, zgig30, inverse gated decoupled, LB = 10). * marks the internal standard Ph$_3$PO (0.02 mmol).

S8.1.5. Synthesis and quantification of $$(\text{tBu}(	ext{O})	ext{C})_3	ext{P}$$

![NMR spectrum of $$(\text{tBu}(	ext{O})	ext{C})_3	ext{P}$$](image)

Figure S22. Quantitative $^{31}	ext{P}$(1H) NMR spectrum of $$(\text{tBu}(	ext{O})	ext{C})_3	ext{P}$$ generated via photocatalytic stannylation of $\text{P}_4$ in benzene/acetone followed by acylation with pivaloyl chloride $\text{tBuC(O)Cl}$ (4). (Table S13, 12 equiv. (Bu$_3$Sn)$_2$, $T_{1s} < T_{1\text{prod}} = 10\text{s}$, $D_1 = 40\text{s}$, zgig30, inverse gated decoupled, LB = 10) * marks the internal standard Ph$_3$PO (0.02 mmol).
S8.1.6. Synthesis and quantification of (iPr(OC))₃P

Figure S23. Quantitative $^{31}$P{¹H} NMR spectrum of (iPr(OC))₃P generated via photocatalytic stannylation of P₄ in benzene/acetone followed by acylation with isobutyryl chloride iPrC(O)Cl (5). (Table S13, 12 equiv. (Bu₃Sn)₂, T1s < T1prod = 10s, D1 = 40 s, zgig30, inverse gated decoupled, LB = 10) * marks the internal standard Ph₃PO (0.02 mmol).

S8.1.7. Synthesis and quantification of (nBu(OC))₃P

Figure S24. Quantitative $^{31}$P{¹H} NMR spectrum of (nBu(OC))₃P generated via photocatalytic stannylation of P₄ in benzene/acetone followed by acylation with valeroyl chloride nBuC(O)Cl (6). (Table S13, 12 equiv. (Bu₃Sn)₂, T1s < T1prod = 10s, D1 = 40 s, zgig30, inverse gated decoupled, LB = 10). * marks the internal standard Ph₃PO (0.02 mmol).
S8.1.8. Synthesis and quantification of (Me(O)C)$_3$P

Figure S25. Quantitative $^{31}$P{$_1^1$H} NMR spectrum of (Me(O)C)$_3$P generated via photocatalytic stannylation of P$_4$ in benzene/acetone followed by acylation with acetyl chloride MeC(O)Cl (7). (Table S13, 12 equiv. (Bu$_3$Sn)$_2$, $T_{1\theta} <$ $T_{1\prod}$ = 10s, $D_1$ = 40 s, zgi30, inverse gated decoupled, $L_8$ = 10). * marks the internal standard Ph$_3$PO (0.02 mmol).
**S8.2 Synthesis of the phosphonium salts [R₄P]Br \[^{[0]}\]**

To a 10 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (60.6 μL, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄), anthraquinone (AQ) (1.0 mg, 0.5 equiv. based on P₄) and P₄ (0.01 mmol, as a stock solution in 71.3 μL benzene) in acetone as solvent (429 μL, in total 0.5 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S14), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h. After photocatalytic generation of the stannylated phosphine (Bu₃Sn)₃P directly from P₄ this P₁ intermediate was further converted into phosphonium salts in an ‘one-pot’ manner. Alkyl bromides such as benzyl bromide or ethyl bromide (0.2 mmol, 20 equiv. based on P₄, 5 equiv. based on phosphorus atoms) were added to the photocatalytic reaction mixture. While heating the reaction mixture (for [Bn₄P]Br: overnight at 60 °C, for [Et₄P]Br: 2d at 80 °C) a color change from an orange to a yellow solution was obtained. Ph₃PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to ³¹P{¹H} NMR analysis (Figure S26 and S27).

### Table S14. Substrates for functionalization of photocatalytic generated (Bu₃Sn)₃P into phosphonium salts.

| Entry | Substrate          | Full conv. of (Bu₃Sn)₃P? | Conv. to [R₄P]⁺ / % |
|-------|--------------------|--------------------------|---------------------|
| 1     | Benzyl bromide (BnBr) | ✓                        | 69%                 |
| 2     | Ethyl bromide (EtBr)   | ✓                        | 46%                 |

One-pot' synthesis of phosphonium salts: (i) For the general procedure of the photocatalytic stannylation of P₄ into (Bu₃Sn)₃P (0.04 mmol scale) see section S6. (ii) Subsequent functionalization of (Bu₃Sn)₃P using alkyl bromides (RBr) to generate phosphonium salts [R₄P]Br.
S8.2.1 Synthesis and quantification of [Bn₄P]Br

Figure S26. Quantitative ³¹P{¹H} NMR (zgig) spectrum of [Bn₄P]Br generated via photocatalytic stannylation of P₄ in benzene/acetone followed by alkylation with benzyl bromide (BnBr, Table S14). * marks the internal standard Ph₃PO (0.02 mmol).

S8.2.2 Synthesis and quantification of [Et₄P]Br

Figure S27. Quantitative ³¹P{¹H} NMR (zgig) spectrum of [Et₄P]Br generated via photocatalytic stannylation of P₄ in benzene/acetone followed by alkylation with benzyl bromide (EtBr, Table S14). * marks the internal standard Ph₃PO (0.02 mmol).
S8.3 Synthesis of THP, THPO and THPC

S8.3.1 Synthesis of THP and oxidation to THPO

To a 10 mL stoppered tube equipped with a stirring bar were added (Bu$_3$Sn)$_2$ (60.6 μL, 3 equiv. based on phosphorus atoms, 12 equiv. based on P$_4$), anthraquinone (AQ) (1.0 mg, 0.5 equiv. based on P$_4$) and P$_4$ (0.01 mmol, as a stock solution in 71.3 µL benzene) in acetone as solvent (429 µL, in total 0.5 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S16), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h. The photocatalytically generated P$_1$ intermediate (Bu$_3$Sn)$_3$P was further functionalized by removal of volatiles under vacuum and addition of EtOH (1 mL) and paraformaldehyde (3.6 mg, 0.12 mmol, 12 equiv. based on P$_4$, 3 equiv. based on phosphorus atoms). The resulting suspension was stirred at room temperature for 16 h. Ph$_3$PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to $^{31}$P{$^1$H} NMR analysis and showed 48% conversion of THP (Figure S28).

Afterwards the ‘one-pot’ reaction mixture was stirred at 80 °C under air for 16 h to convert the initially formed product THP into its oxidized form THPO ($^{31}$P{$^1$H} NMR analysis: 38% conversion to THPO, see Figure S29).
Figure S28. Quantitative $^{31}$P{$^1$H} NMR (zgig) spectrum of THP generated via photocatalytic stannylation of P₄ in benzene/acetone followed by addition of paraformaldehyde in EtOH. * marks the internal standard Ph₃PO (0.02 mmol).

Figure S29. Quantitative $^{31}$P{$^1$H} NMR spectrum of THPO generated via photocatalytic stannylation of P₄ in benzene/acetone followed by addition of paraformaldehyde in EtOH and subsequent oxidation in air. * marks the internal standard Ph₃PO (0.02 mmol).
S8.3.2 Synthesis of THPC

To a 10 mL stoppered tube equipped with a stirring bar were added \((\text{Bu}_3\text{Sn})_2\) (60.6 µL, 3 equiv. based on phosphorus atoms, 12 equiv. based on \(\text{P}_4\)), anthraquinone (AQ) (1.0 mg, 0.5 equiv. based on \(\text{P}_4\)) and \(\text{P}_4\) (0.01 mmol, as a stock solution in 71.3 µL benzene) in acetone as solvent (429 µL, in total 0.5 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S16), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 22 h. The photocatalytically generated \(\text{P}_1\) intermediate \((\text{Bu}_3\text{Sn})_3\text{P}\) was further functionalized by removal of volatiles under vacuum and addition of \(\text{EtOH}\) (1 mL) and paraformaldehyde (15 mg, 0.5 mmol, 20 equiv. based on \(\text{P}_4\), 5 equiv. based on phosphorus atoms). The resulting suspension was stirred at room temperature for 16 h. The mixture was frozen in a liquid-nitrogen bath, and \(\text{HCl}\) (0.4 M in 1,4-dioxane, 1 mL, 0.4 mmol, 40 equiv. based on \(\text{P}_4\), 10 equiv. based on phosphorus atoms) was added. After thawing, the yellowish reaction mixture was stirred at room temperature for 2 h. \(\text{Ph}_3\text{PO}\) (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to \(^{31}\text{P}\{^1\text{H}\}\) NMR analysis and showed 53% conversion of THPC (Figure S30).
Figure S30. Quantitative $^{31}$P($^1$H) NMR (zgig) spectrum of THPC generated via photocatalytic stannylation of $P_4$ in benzene/acetone followed by reaction with paraformaldehyde in EtOH and subsequent HCl work-up. * marks the internal standard Ph$_3$PO (0.02 mmol).
S9. Reactions at 0.8 mmol scale using anthraquinone as a photoinitiator

S9.1 Photocatalytic synthesis of stannylated phosphine (Bu₃Sn)₃P[^0]

To a 100 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (1.212 mL, 2.4 mmol, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄), anthraquinone (AQ) (20.8 mg, 0.1 mmol, 0.5 equiv. based on P₄) and P₄ (0.2 mmol, as a stock solution in 1.426 mL benzene) in acetone as solvent (2.574 mL, in total 4 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S31), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 48 h. ³¹P{¹H} NMR spectroscopy (Ph₃PO as internal standard) showed 64% conversion to the stannylated phosphine (Bu₃Sn)₃P (see Figure S32).

**Figure 31.** Illustration of the equipment setup used for photocatalytic reactions at 0.8 mmol scale.

**Figure S32.** ³¹P{¹H} NMR spectrum for the scale-up (0.8 mmol) photocatalytic stannylation of P₄ using (Bu₃Sn)₂ and photoinitiator anthraquinone (AQ). * marks the internal standard Ph₃PO. ~ marks an unknown Sn-containing side product. # marks unknown side products.
S9.2 ‘One-pot’ synthesis and purification of (Ph(O)C)₃P

To a 100 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (1.212 mL, 2.4 mmol, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄) anthraquinone (AQ) (20.8 mg, 0.1 mmol, 0.5 equiv. based on P₄) and P₄ (0.2 mmol, as a stock solution in 1.426 mL benzene) in acetone as solvent (2.574 mL, in total 4 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S31), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 48 h. Subsequent addition of benzoyl chloride PhC(O)Cl (371 μL, 3.2 mmol, 16 equiv. based on P₄, 4 equiv. based on phosphorus atom) and stirring overnight at room temperature resulted in a color change of the orange reaction mixture to a yellow solution (by internal standard addition to a separate reaction the ³¹P[¹H] NMR showed 62% conversion into (Ph(O)C)₃P, see Figure S33). The volatiles were removed under vacuum and the remaining yellow solid was washed with n-hexane (4 x 5 mL). The remaining yellow residue was recrystallized from THF/n-hexane at −35°C. Decanting of the mother liquor and washing with n-hexane (2 x 10 mL) afforded the desired product (Ph(O)C)₃P was as yellow powder (151.2 mg, 55%).

Figure S33. ³¹P[¹H] NMR spectrum of crude (Ph(O)C)₃P generated via photocatalytic stannylation of P₄ in benzene/acetone (scale-up (0.8 mmol)) followed by acylation with benzoyl chloride PhC(O)Cl (1). * marks the internal standard Ph₃PO (0.02 mmol).
Spectroscopic data of (Ph(O)C)$_3$P:

The NMR data are consistent with previous reports.$^{[6],[5]}$

$^1$H NMR (400.13 MHz, 300 K, C$_6$D$_6$): $\delta = 7.98$ ppm (2H, m), 7.02 ppm (1H, t, $^3J(^1H,^1H) = 7.3$ Hz), 6.95 ppm (2H, t, $^3J(^1H,^1H) = 7.5$ Hz).

$^{31}$P($^1$H) NMR (161.98 MHz, 300 K, C$_6$D$_6$): $\delta = 54.3$ ppm (s).

$^{13}$C($^1$H) NMR (100.61 MHz, 300 K, C$_6$D$_6$): $\delta = 205.3$ ppm (d, $J(^{31}P,^1H) = 35.4$ Hz), 140.5 ppm (d, $J(^{31}P,^1H) = 35.3$ Hz), 133.5 ppm (d, $J(^{31}P,^1H) = 1.2$ Hz), 128.6 ppm (d, $J(^{31}P,^1H) = 8.0$ Hz), 128.5 ppm (d, $J(^{31}P,^1H) = 0.8$ Hz).

Figure S34. $^1$H NMR (400.13 MHz, 300 K, C$_6$D$_6$) spectrum of (Ph(O)C)$_3$P. * marks C$_6$D$_6$. # marks minor THF.
Figure S35. $^{31}$P($^1$H) NMR (161.98 MHz, 300 K, C$_6$D$_6$) spectrum of (Ph(O)C)$_3$P. # marks minor unknown impurity.

Figure S36. $^{13}$C($^1$H) NMR (100.61 MHz, 300 K, C$_6$D$_6$) spectrum of (Ph(O)C)$_3$P. * marks C$_6$D$_6$. 

S9.3 ‘One-pot’ synthesis and purification of phosphonium salt [Bn₄P]Br

To a 100 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (1.212 mL, 2.4 mmol, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄) anthraquinone (20.8 mg, 0.1 mmol, 0.5 equiv. based on P₄) and P₄ (0.2 mmol, as a stock solution in 1.426 mL benzene) in acetone as solvent (2.574 mL, in total 4 mL PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S31), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 48 h. Subsequent addition of benzyl bromide (475 µL, 4 mmol, 20 equiv. based on P₄, 5 equiv. based on phosphorus atoms) and heating overnight at 60 °C resulted in a color change of the orange reaction mixture to a yellow solution (by internal standard addition to a separate reaction the ³¹P{¹H} NMR showed 67% conversion into [Bn₄P]Br, see Figure S37). The volatiles were removed under vacuum. n-Hexane was added to the remaining orange oil and the product was precipitated and washed with n-hexane (2 x 10 mL). Recrystallization twice from acetone/n-hexane afforded the desired product [Bn₄P]Br (212.2 mg, 56%) as an off-white powder.

Figure S37. Quantitative ³¹P{¹H} NMR (zgig) spectrum of crude [Bn₄P]Br generated via photocatalytic stannylation of P₄ in benzene/acetone followed by alkylation with benzyl bromide (BnBr). * marks the internal standard Ph₃PO (0.02 mmol).
Spectroscopic data of [Bn₄P]Br:
The NMR data are consistent with previous reports of both the chloride salt [Bn₄P]Cl[⁶] and [Bn₄P]Br.[¹]

**¹H NMR** (400.13 MHz, 300 K, CDCl₃): δ = 7.32 ppm (3H, m), 7.18 ppm (2H, m), 4.03 ppm (2H, d, J_{31P-¹H} = 14.3 Hz).

**³¹P{¹H} NMR** (161.98 MHz, 300 K, CDCl₃): δ = 24.7 ppm (s).

**³¹P NMR** (161.98 MHz, 300 K, CDCl₃): δ = 24.7 ppm (nonet, J_{31P-¹H} = 14.3 Hz).

**¹³C{¹H} NMR** (100.61 MHz, 300 K, CDCl₃): δ = 130.6 ppm (d, J_{31P-¹H} = 5.3 Hz), 129.6 ppm (d, J_{31P-¹H} = 2.9 Hz), 128.7 ppm (d, J_{31P-¹H} = 3.5 Hz), 127.5 ppm (d, J_{31P-¹H} = 8.1 Hz), 26.8 ppm (d, J_{31P-¹H} = 43.2 Hz).

*Figure S38.* ¹H NMR (400.13 MHz, 300 K, CDCl₃) spectrum of [Bn₄P]Br. * marks CDCl₃, ~ marks residual acetone. # marks water present in the CDCl₃ NMR solvent.
Figure S39. $^{31}$P($^1$H) NMR (161.98 MHz, 300 K, CDCl₃) spectrum of $[\text{Bn}_4\text{P}]\text{Br}$. # marks minor unknown impurity.

Figure S40. $^{31}$P NMR (161.98 MHz, 300 K, CDCl₃) spectrum of $[\text{Bn}_4\text{P}]\text{Br}$. 
Figure S41. $^{13}$C($^1$H) NMR (100.61 MHz, 300 K, CDCl$_3$) spectrum of [Bn$_4$P]Br. * marks C$_6$D$_6$. ~ marks residual acetone.
S9.4 ‘One-pot’ synthesis and purification of THPC and recycling of Bu₃SnCl and (Bu₃Sn)₂

To a 100 mL stoppered tube equipped with a stirring bar were added (Bu₃Sn)₂ (1.212 ml, 2.4 mmol, 3 equiv. based on phosphorus atoms, 12 equiv. based on P₄), anthraquinone (20.8 mg, 0.1 mmol, 0.5 equiv. based on P₄) and P₄ (0.2 mmol, as a stock solution in 1.426 ml benzene) in acetone as solvent (2.574 ml, in total 4 ml PhH/acetone mixture). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S31), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 48 h. Following removal of volatiles under vacuum, EtOH (5 ml) and paraformaldehyde (300 mg, 10 mmol, 50 equiv. based on P₄, 12.5 equiv. based on phosphorus atoms) were added, and the reacting suspension was stirred at room temperature for 16 h. The mixture was frozen in a liquid-nitrogen bath, and HCl (4.0 M in 1,4-dioxane, 2 ml, 8 mmol (based on P₄)) was added. After thawing, the yellowish reaction mixture was stirred at room temperature for 2 h and volatiles were removed under vacuum. The remaining orange oily solid residue was washed with Et₂O (3 x 10 ml) to extract the Sn-containing compounds, Bu₃SnCl and (Bu₃Sn)₂. The residue was recrystallized from EtOH/n-hexane (4 ml/4 ml) at −35°C. Decanting of the mother liquor afforded the desired product THPC as a pale yellow solid (50.3 mg, 33%) after drying under vacuum. The combined Et₂O washes from the above reaction were dried under vacuum to afford a mixture of Bu₃SnCl and (Bu₃Sn)₂ as a yellow oil (1.346 g). ¹H and ¹¹⁹Sn¹H) NMR indicate a ratio of 1 : 1.3 for the (Bu₃Sn)₂ / Bu₃SnCl mixture (Figure S45 and S46). Overall, 92% of the used (Bu₃Sn)₂ (2.4 mmol) could be recovered as a mixture (1.346 g) of Bu₃SnCl (567.7 mg, 1.74 mmol, 36%) and (Bu₃Sn)₂ (778.3 mg, 1.34 mmol, 56%).

**Spectroscopic data of THPC:**

The NMR data are consistent with previous reports.

¹H NMR (400.13 MHz, 300 K, D₂O): δ = 4.67 ppm (d, J(31P-¹H) = 1.8 Hz).

³¹P(¹H) NMR (161.98 MHz, 300 K, D₂O): δ = 27.1 ppm (s).

¹³C(¹H) NMR (100.61 MHz, 300 K, D₂O): δ = 49.1 ppm (d, J(³¹P-¹³C) = 51.3 Hz).

**Spectroscopic data of the recycled mixture of Bu₃SnCl and (Bu₃Sn)₂:**

The NMR data of Bu₃SnCl and (Bu₃Sn)₂ are consistent with previous reports. The ¹H NMR and ¹¹⁹Sn¹H) NMR showed a 1 to 1.3 ratio of (Bu₃Sn)₂ to Bu₃SnCl.

¹H NMR (400.13 MHz, 300 K, C₆D₆): δ = 1.70-1.62 (m, 2H, (Bu₃Sn)₂), 1.60-1.53 (m, 1.3H, Bu₃SnCl), 1.46-1.36 (m, 2.1H, (Bu₃Sn)₂), 1.30-1.21 (m, 1.5H, Bu₃SnCl), 1.16-1.12 (m, 2H, (Bu₃Sn)₂), 1.10-1.07 (m, 1.5H, Bu₃SnCl), 0.96 (t, 3H, (Bu₃Sn)₂), ³J(¹H-¹H) = 7.3 Hz), 0.85 (t, 2H, Bu₃SnCl, ³J(¹H-¹H) = 7.3 Hz).

¹¹⁹Sn¹H) NMR (149.21 MHz, 300 K, C₆D₆): δ = −83.2 ppm (s, 2Sn of (Bu₃Sn)₂, ¹J(¹¹⁹Sn-¹³C) = 240.7 Hz, ¹J(¹¹⁹Sn-¹¹⁹Sn) = 2556.3 Hz, 146.9 ppm (s, 1.3Sn of Bu₃SnCl).
$^{13}$C{$_1^1$H} NMR (100.61 MHz, 300 K, C$_6$D$_6$): $\delta = 30.8$ (s, (Bu$_3$Sn)$_2$), 27.8 (s, Bu$_3$SnCl), 27.6 (s, (Bu$_3$Sn)$_2$), 26.8 (s, Bu$_3$SnCl), 16.9 (s, Bu$_3$SnCl), 13.6 (s, (Bu$_3$Sn)$_2$), 13.4 (s, Bu$_3$SnCl), 10.1 (s, (Bu$_3$Sn)$_2$).

Figure S42. $^1$H NMR (400.13 MHz, 300 K, D$_2$O) spectrum of THPC. * marks D$_2$O.

Figure S43. $^{31}$P({$_1^1$H}) NMR (161.98 MHz, 300 K, D$_2$O) spectrum of THPC. # marks minor unknown impurities.
Figure S44. $^{13}$C($^1$H) NMR (100.61 MHz, 300 K, D$_2$O) spectrum of THPC.

Figure S45. $^1$H NMR (400.13 MHz, 300 K, C$_6$D$_6$) spectrum of recycled Bu$_3$SnCl and (Bu$_3$Sn)$_2$ mixture. * marks C$_6$D$_6$. # marks minor Et$_2$O. The blue box shows the integration of the CH$_3$ groups of (Bu$_3$Sn)$_2$ and Bu$_3$SnCl, which indicates a 1 to 1.3 ratio of the Sn-containing compounds.
**Figure S46.** $^{119}$Sn($^1$H) NMR (149.21 MHz, 300 K, C$_6$D$_6$) spectrum of recycled Bu$_3$SnCl and (Bu$_3$Sn)$_2$ mixture (ratio of 1.3 to 1).

**Figure S47.** $^{13}$C($^1$H) NMR (100.61 MHz, 300 K, C$_6$D$_6$) spectrum of recycled Bu$_3$SnCl and (Bu$_3$Sn)$_2$ mixture. * marks C$_6$D$_6$. 
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