Supplementary Information (SI) for Dalton Transactions.

Supplementary Information

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

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S1. General information

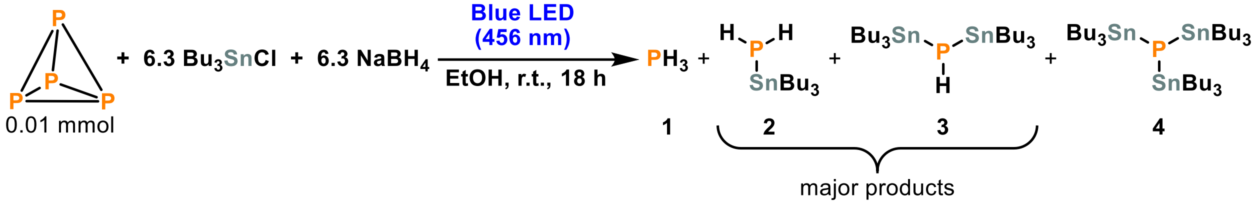
All reactions and manipulations were performed under an N_2 atmosphere (< 0.1 ppm O_2, H_2O) through the use of MBraun Unilab and GS MEGA Line gloveboxes, and standard Schlenk line techniques. All glassware was oven-dried (160 °C) overnight prior to use. Benzene was distilled from Na/benzophenone and stored over molecular sieves (3 Å). *n*-Hexane, toluene, Et_2O and THF were purified using an MBraun SPS-800 system and stored over molecular sieves (3 Å). EtOH was degassed and dried by standing over at least three sequential batches of molecular sieves (3 Å). C_6D_6 and D_2O were used without purification. All reagents and starting materials were purchased from major suppliers. Liquids were degassed (if not supplied under an inert atmosphere) but were otherwise used as supplied, unless stated otherwise. BnBr was distilled, degassed and stored over molecular sieves (3 Å). Solids were dried under vacuum (with the exception of paraformaldehyde) but otherwise used as supplied, unless stated otherwise. P_4 was sublimed prior to use.

Qualitative NMR spectra were recorded at room temperature on Bruker Avance III HD 400 (400 MHz) or Bruker Avance *Neo* 500 (500 MHz) spectrometers and were processed using MestReNova 14.0. Chemical shifts, δ, are reported in parts per million (ppm); ^1H and ^{13}C shifts are reported relative to $SiMe_4$ and were calibrated internally to residual solvent peaks, while ^{31}P shifts and ^{119}Sn shifts were referenced externally to 85% H_3PO_4 (aq.) and Me_4Sn, respectively. NMR samples were prepared in the glovebox using NMR tubes fitted with screw caps. Optimization reactions for the hydrostannylation of P_4 to $Bu_3Sn_{3-x}PH_x$ and subsequent functionalization to P_1 products were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy using triphenylphosphine oxide, Ph_3PO, as a subsequently added internal standard. Except where stated otherwise, integrals for $^{31}P\{^1H\}$ and ^{31}P spectra are provided for the purpose of qualitative comparison only and should not be considered quantitatively accurate. The abbreviations s, d, t, q, m are used to indicate singlet, doublets, triplets, quartets and multiplets, respectively.

Reactions driven by light were performed using an apparatus that has been described in a previous publication.[1]

S2. Hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$

S2.1 General procedure and optimization for the hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$ and LED irradiation



To a 10 mL, flat-bottomed, stoppered tube were added P_4 (0.01 mmol, stock solution in 65.9 µL benzene, 1 equiv.), EtOH (500 µL), Bu_3SnCl (17.1 µL, 0.063 mmol, 6.3 equiv.) and $NaBH_4$ (2.4 mg, 0.063 mmol, 6.3 equiv.). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 3.2 V, 700 mA, Osram OSLON SSL 80) for 18 h (unless stated otherwise). Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added as an internal standard. The resulting mixture was analyzed by ^{1}H, $^{31}P\{^{1}H\}$, ^{31}P and $^{119}Sn\{^{1}H\}$ NMR spectroscopy.

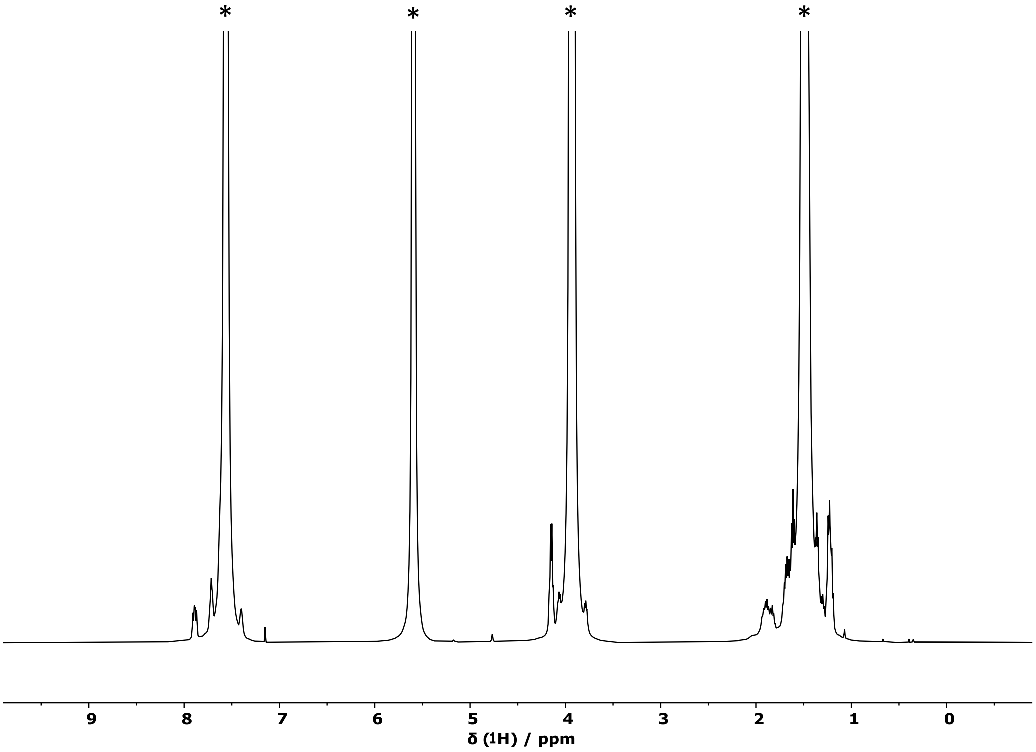


Figure S1. ^{1}H NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.) in EtOH under blue light irradiation (456 nm) for 18 h. Solvent resonances are marked with an asterisk and are truncated for clarity.

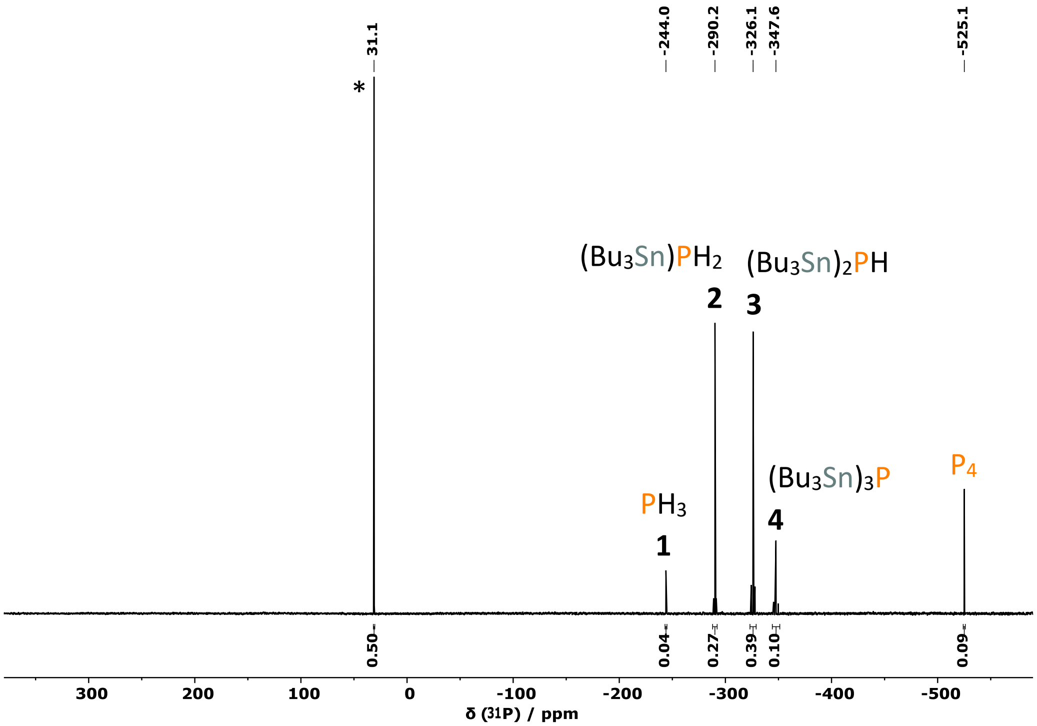


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.) in EtOH under blue light irradiation (456 nm) for 18 h. * marks the internal standard Ph_3PO (0.02 mmol).

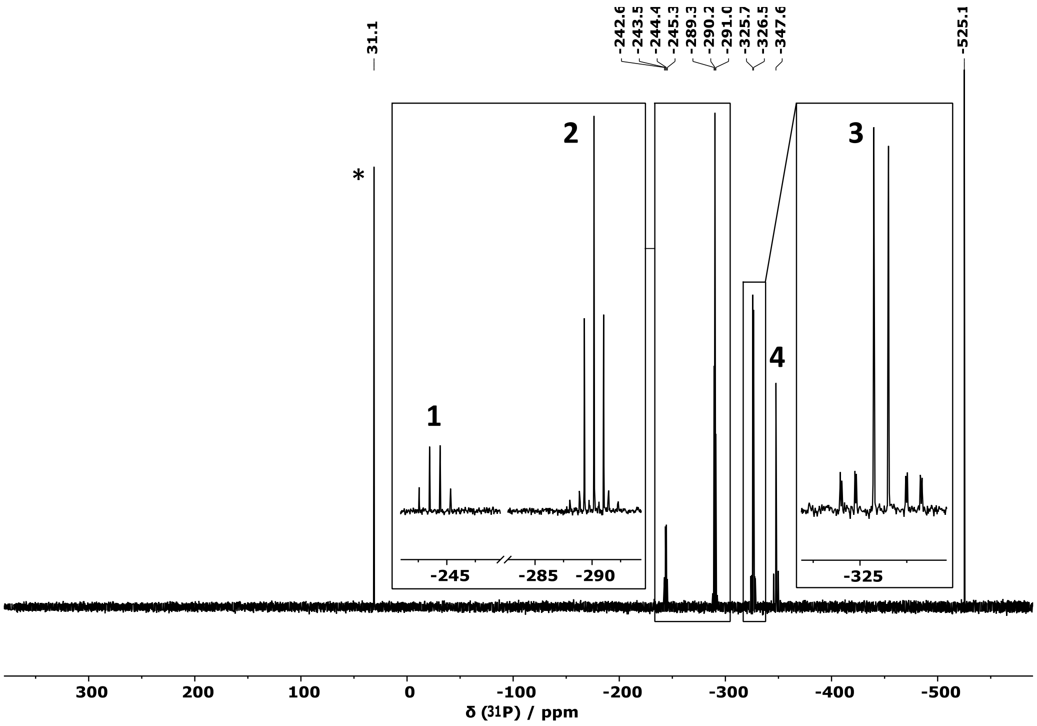


Figure S3. ^{31}P NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.) in EtOH under blue light irradiation (456 nm) for 18 h. * marks the internal standard Ph_3PO (0.02 mmol).

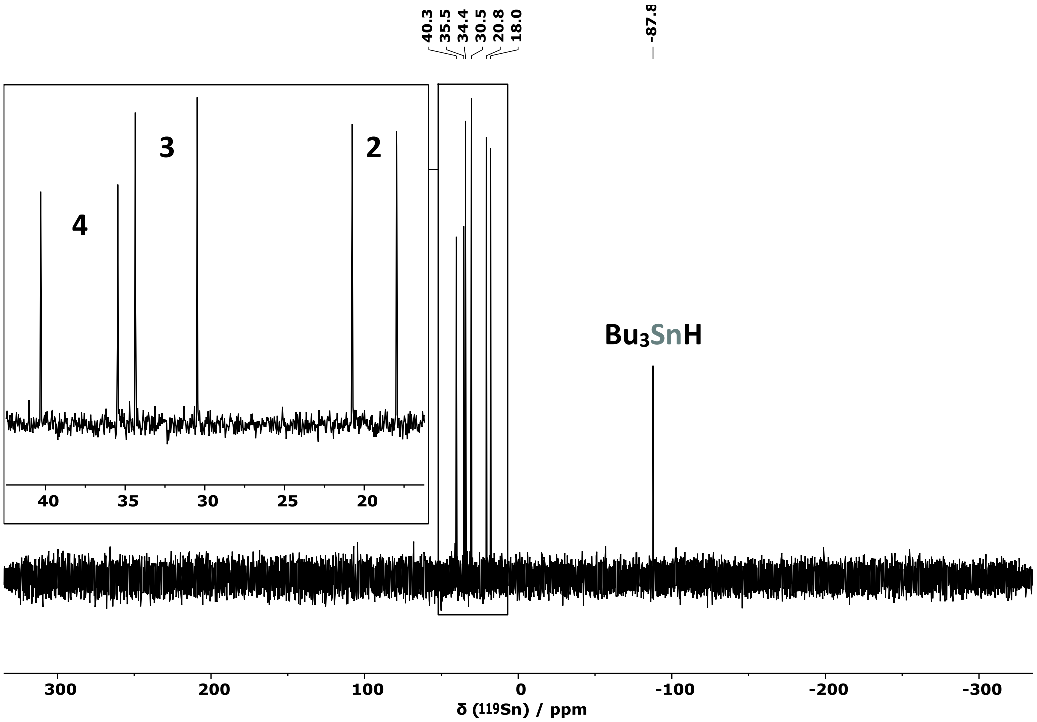
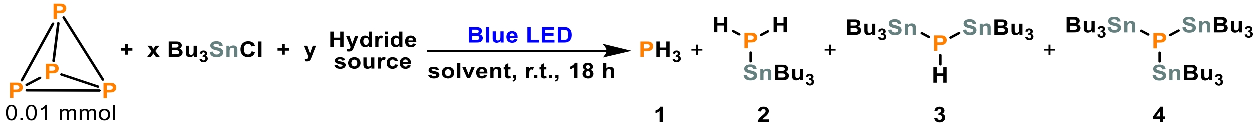


Figure S4. $^{119}Sn\{^{1}H\}$ NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.) in EtOH under blue light irradiation (456 nm) for 18 h.

For reasons of experimental expediency, during the optimization of hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$, standard, non-quantitative $^{31}P\{^{1}H\}$ NMR spectra were used to analyze each experiment and to estimate the relative conversions to **1-4**. Although this did not provide quantitative conversions, it did allow for meaningful, qualitative comparisons between experiments.

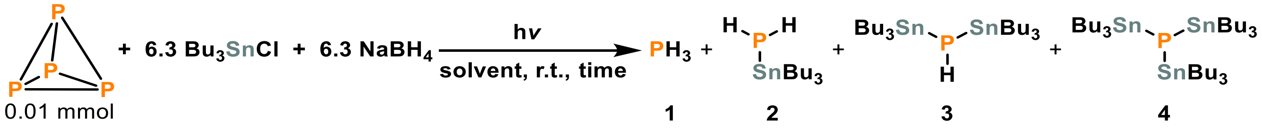
Table S1. Optimization of the hydrostannylation of P_4 (0.01 mmol) with Bu_3SnCl and a hydride source under blue LED irradiation (456 nm).[a]



Entry	Solvent	Hydride source	Equivalents[b]		Relative conv. to 1-4 (%)[c]
			Bu_3SnCl [x]	Hydride Source [y]	
1	**EtOH**	**$NaBH_4$**	**6.3**	**6.3**	**81%**
2	EtOH	$NaBH_4$	12	12	49%
3	THF	$NaBH_4$	6.3	6.3	n.d.
4	DMSO	$NaBH_4$	6.3	6.3	14%
5	MeOH	$NaBH_4$	6.3	6.3	22%
6	Et_2O	$NaBH_4$	6.3	6.3	n.d.
7	Toluene	$NaBH_4$	6.3	6.3	n.d.
8	EtOH	$NaBH_3CN$	6.3	6.3	n.d.
9	EtOH	$NaBH_3CN$	12	12	n.d.
10	EtOH	$NaBH_3CN$	12	20	n.d.
11	THF	$NaBH_3CN$	6.3	6.3	n.d.
12	MeOH	$NaBH_3CN$	6.3	6.3	n.d.
13	Et_2O	$LiAlH_4$	6.3	6.3	n.d.
14	Et_2O	$LiAlH_4$	12	12	n.d.
15	THF	$LiAlH_4$	6.3	6.3	n.d.

[a] The procedure was modified to use the indicated solvent, hydride source and equivalents. [b] The equivalents of Bu_3SnCl and the hydride source are given per P_4 (0.01 mmol). [c] The combined yield of the hydrostannylation products $(Bu_3Sn)_xPH_{3-x}$ (**1-4**) was assessed by qualitative $^{31}P\{^1H\}$ NMR spectroscopy with respect to Ph_3PO used as an internal standard.

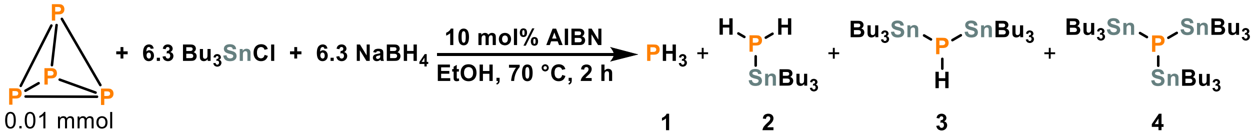
Table S2. Hydrostannylation of P_4 (0.01 mmol) using Bu_3SnCl (6.3 equiv.) and $NaBH_4$ (6.3 equiv.): Screening of conditions.[a]



Entry	Solvent	Time	Light source	Relative conv. to 1-4 (%)[b]
1	EtOH	18 h	**Blue (456 nm)**	**81%**
2			Green (520 nm)	16%
3			White	43%
4			Near UV (356 nm, 3 W)	55%
5			Near UV (356 nm, 10 W)	31%
6			No light, r.t.[c]	n.d.
7			No light, 70 °C[c]	<5%
8	EtOH	**15 min**	Near UV (356 nm, 3 W)	**63%**
9		30 min		66%
10		1 h		65%
11		3 h		50%
12		6 h		49%

[a] The procedure was modified to use the indicated reaction time and light source. [b] The combined yield of the hydrostannylation products $(Bu_3Sn)_xPH_{3-x}$ (**1**-**4**) was assessed by qualitative $^{31}P\{^1H\}$ NMR spectroscopy with respect to Ph_3PO used as an internal standard. [c] Reaction was wrapped in aluminium foil to exclude light.

S2.2 General procedure and optimization for the hydrostannylation of P_4 using Bu_3SnCl and $NaBH_4$ and AIBN



To a 10 mL, flat-bottomed, stoppered tube were added P_4 (0.01 mmol, stock solution in 65.9 µL benzene, 1 equiv.), EtOH (500 µL), AIBN (0.001 mmol, as a stock solution in benzene), Bu_3SnCl (17.1 µL, 0.063 mmol, 6.3 equiv.) and $NaBH_4$ (2.4 mg, 0.063 mmol, 6.3 equiv.). The tube was sealed, wrapped in aluminium foil to exclude light, and heated to 70 °C for 2 h. Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added as an internal standard. The resulting mixture was analyzed by $^{31}P\{^1H\}$ and ^{31}P NMR spectroscopy.

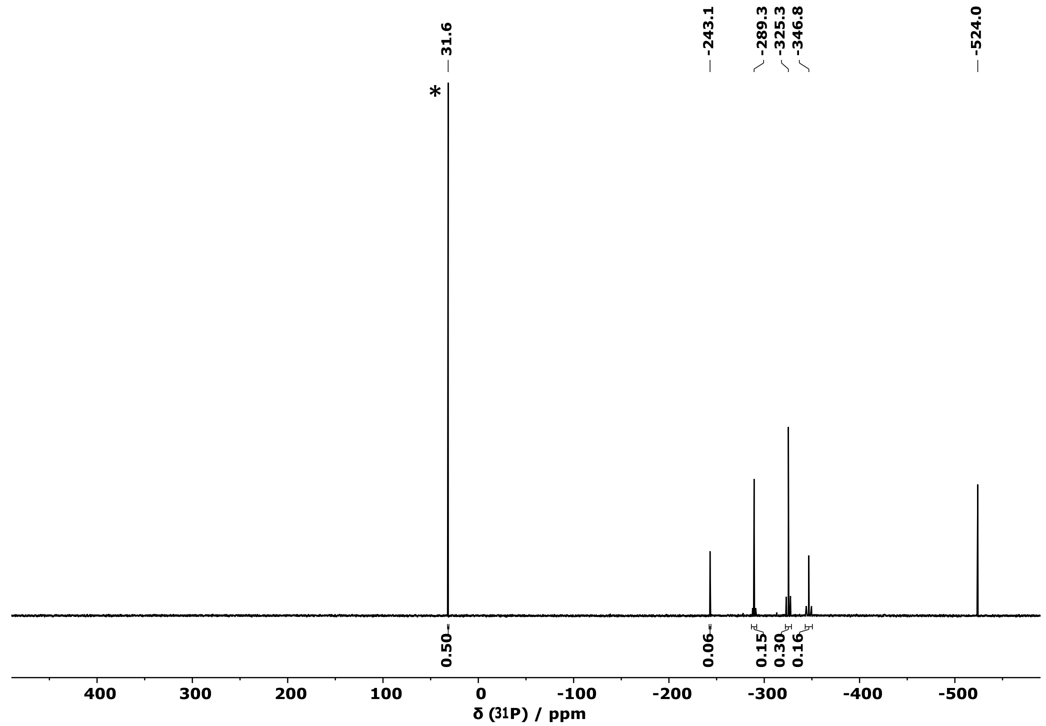


Figure S5. $^{31}P\{^1H\}$ NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.), $NaBH_4$ (6.3 equiv.) and AIBN (10 mol%) in EtOH at 70 °C for 2 h. * marks the internal standard Ph_3PO (0.02 mmol).

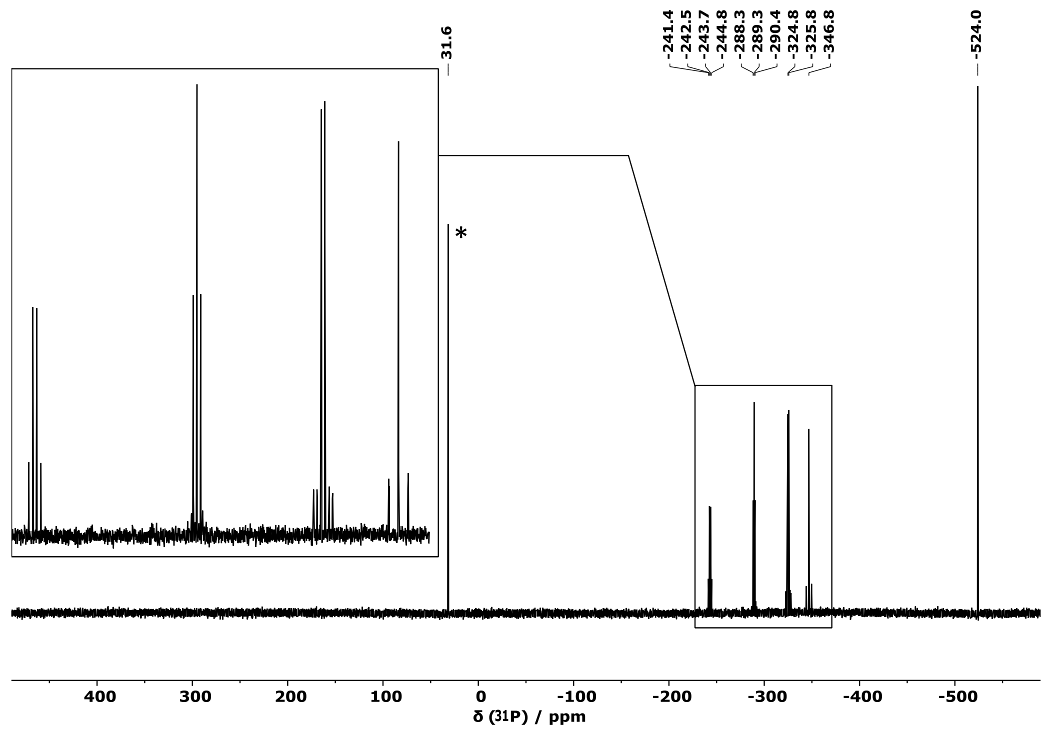
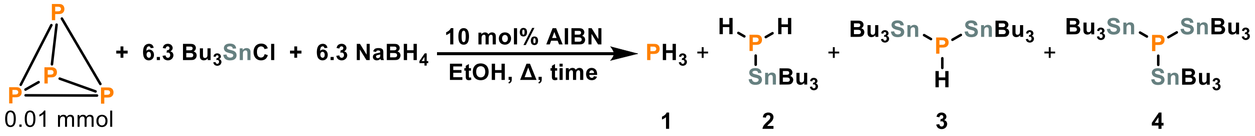


Figure S6. ^{31}P NMR spectrum for the reaction of P_4 (0.01 mmol) with Bu_3SnCl (6.3 equiv.), $NaBH_4$ (6.3 equiv.) and AIBN (10 mol%) in EtOH at 70 °C for 2 h. * marks the internal standard Ph_3PO (0.02 mmol).

Table S3. Optimization of the hydrostannylation of P_4 (0.01 mmol) using Bu_3SnCl (6.3 equiv.), $NaBH_4$ (6.3 equiv.) and AIBN (10 mol%).[a]



Entry	Temperature [°C]	Time [h]	Relative conv. to 1-4 (%)[b]
1	30	18	13
2	60	1	25
3	**70**	**2**	**67**
4	70	4	33
5	70	6	20
6	70	18	41

[a] The general procedure was modified to use the indicated temperature and reaction time. [b] The combined yield of the hydrostannylation products $(Bu_3Sn)_xPH_{3-x}$ (**1**-**4**) was assessed by qualitative $^{31}P\{^1H\}$ NMR spectroscopy with respect to Ph_3PO used as an internal standard.

S3. Synthesis and isolation of P_1 products

S3.1 Synthesis and isolation of $P(C(O)^tBu)_3$ (5)

5

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.) and $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting suspension was filtered, volatiles removed and toluene added (25 mL). $^tBuC(O)Cl$ (979 µL, 8.0 mmol, 16 equiv.) and KHMDS (599 mg, 3.0 mmol, 6 equiv.) were added, the tube was thoroughly wrapped in aluminium foil to exclude ambient light, and the mixture was stirred at room temperature for 16 h. The resulting light-yellow suspension was filtered, volatiles were removed under reduced pressure, and the remaining light-yellow oily residue was recrystallized from *n*-hexane at −35 °C, affording the desired product **5** as colorless needles (146.3 mg, 26%).

^{1}H NMR (500 MHz, 300 K, C_6D_6) δ [ppm] = 1.07 (s).

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6) δ [ppm] = 50.8 (s).

^{31}P NMR (202 MHz, 300 K, C_6D_6) δ [ppm] = 50.8 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, C_6D_6) δ [ppm] = 221.3 (d, $^1J(^{31}P\text{-}^1H) = 47.8$ Hz), 49.8 (d, $^2J(^{31}P\text{-}^1H) = 30.4$ Hz), 25.4 (d, $^3J(^{31}P\text{-}^1H) = 3.6$ Hz).

NMR data are consistent with our previous report.[2]

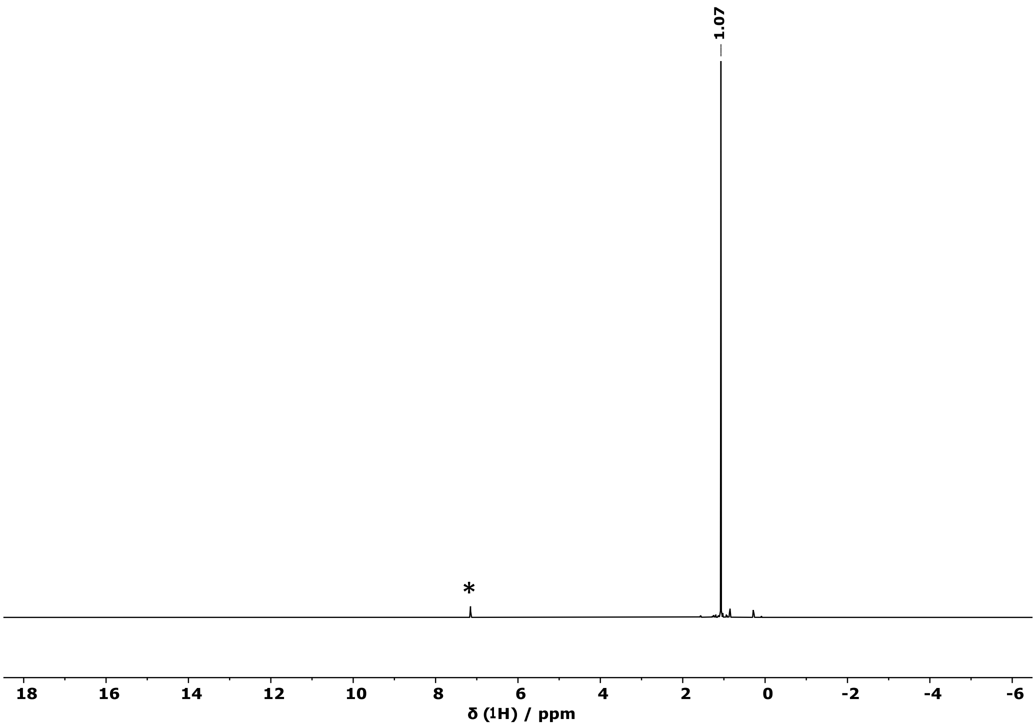


Figure S7. ^{1}H NMR spectrum of P(C(O)^{t}Bu)$_3$ (**5**) in C_6D_6 (*).

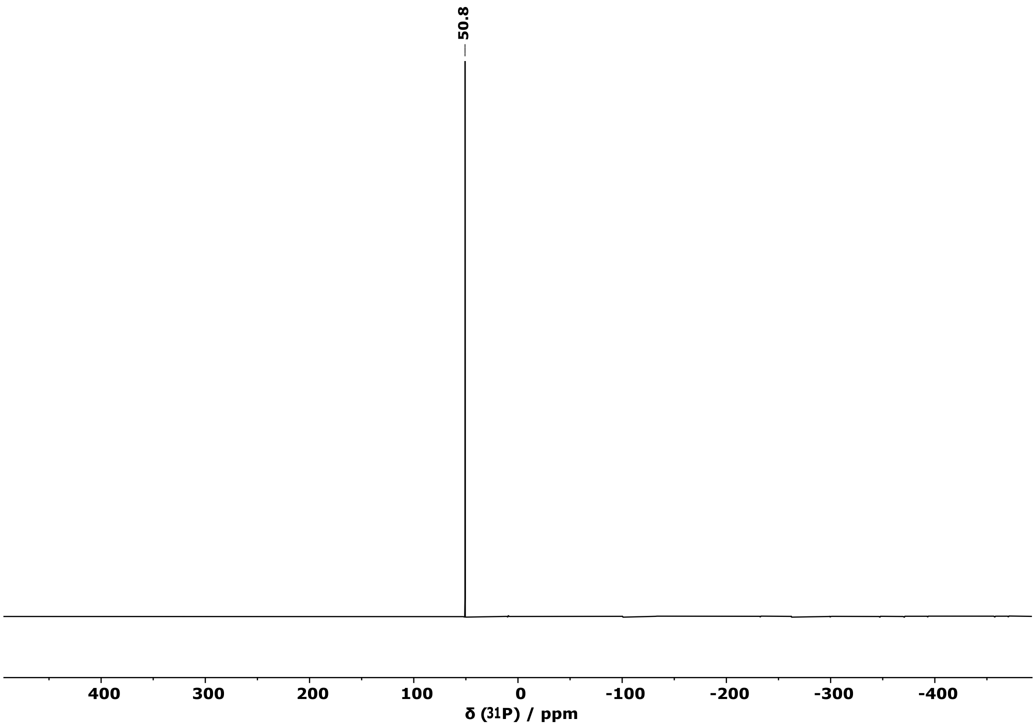


Figure S8. ^{31}P{^{1}H} NMR spectrum of P(C(O)^{t}Bu)$_3$ (**5**) in C_6D_6.

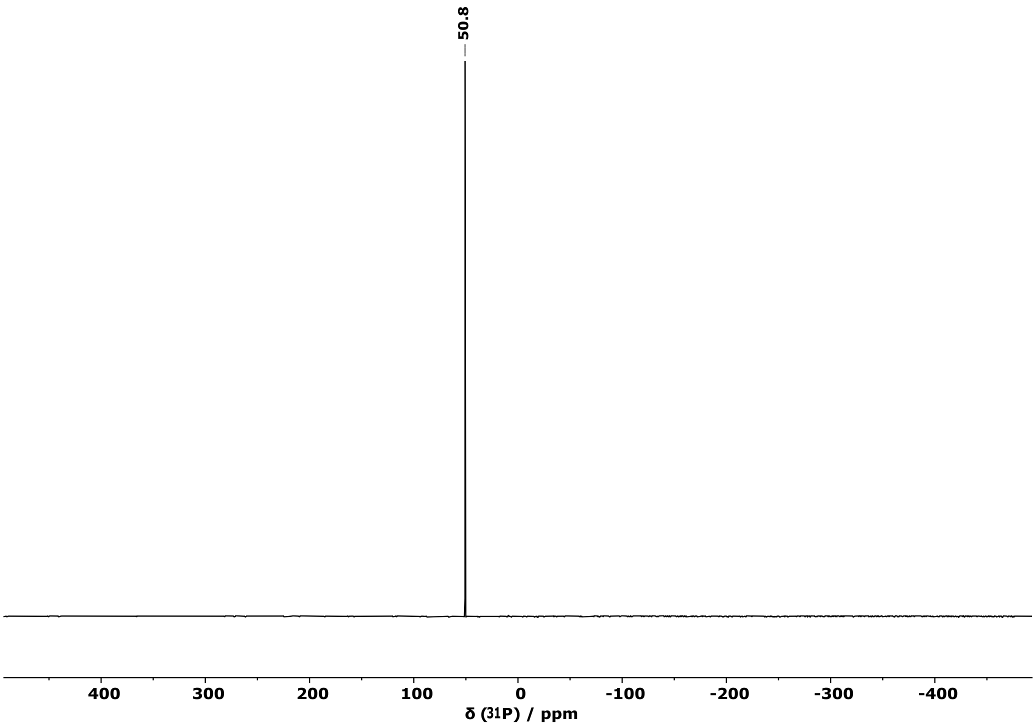


Figure S9. ^{31}P NMR spectrum of $P(C(O)^tBu)_3$ (**5**) in C_6D_6.

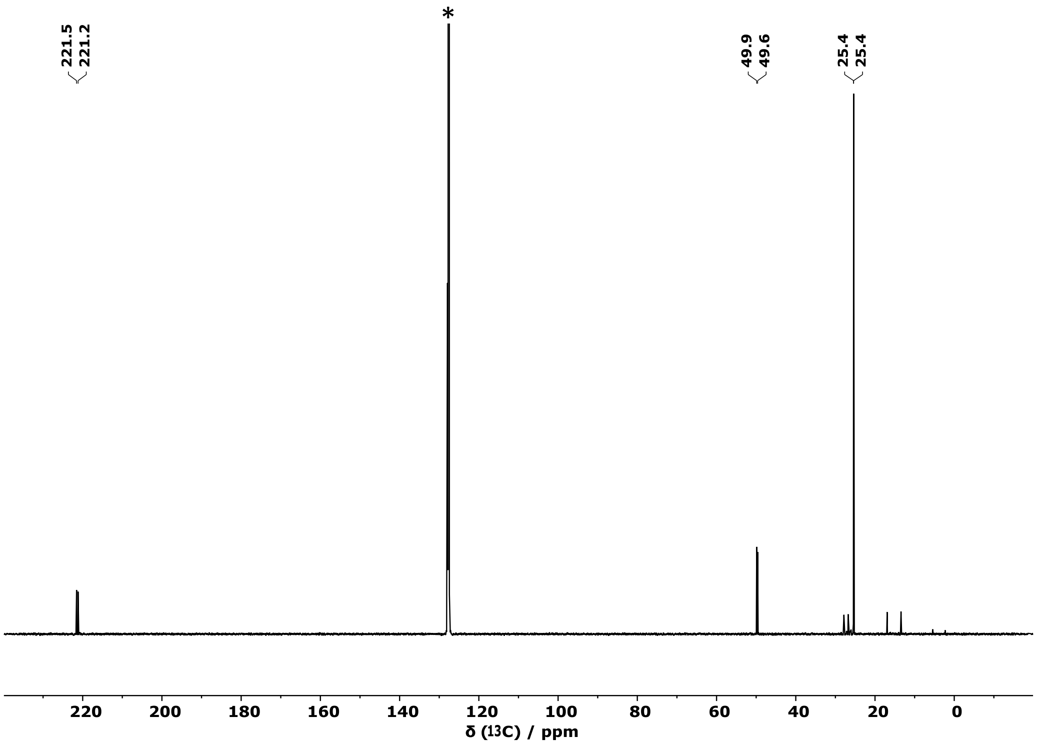
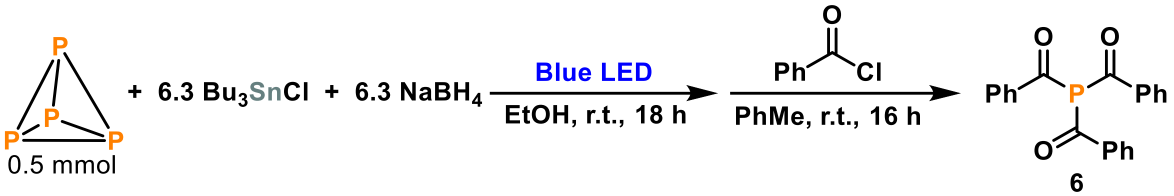


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of $P(C(O)^tBu)_3$ (**5**) in C_6D_6. Solvent resonances (*) truncated for clarity.

S3.2 Synthesis and isolation of P(C(O)Ph)$_3$ (6)



6

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.) and $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting suspension was filtered, volatiles removed and toluene added (25 mL). PhC(O)Cl (928 µL, 8.0 mmol, 16 equiv.) and KHMDS (599 mg, 3.0 mmol, 6 equiv.) were added, and the mixture was stirred at room temperature for 16 h. The resulting yellow suspension was filtered, volatiles were removed under reduced pressure, and the remaining yellow solid was washed with *n*-hexane (4 x 10 mL), affording the desired product **6** as fine yellow needles (164.6 mg, 24%).

^{1}H NMR (500 MHz, 300 K, C_6D_6) δ [ppm] = 7.97 (2H, m), 7.02 (1H, tt, $^3J(^1H-^1H)$ = 7.3 Hz, $^5J(^1H-^1H)$ = 1.3 Hz), 6.95 (2H, m).

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6) δ [ppm] = 53.7 (s).

^{31}P NMR (202 MHz, 300 K, C_6D_6) δ [ppm] = 53.7 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, C_6D_6) δ [ppm] = 205.4 (d, $J(^{31}P-^1H)$ = 32.7 Hz), 140.4 (d, $J(^{31}P-^1H)$ = 35.2 Hz), 133.5 (d, $J(^{31}P-^1H)$ = 1.0 Hz), 128.7 (d, $J(^{31}P-^1H)$ = 8.0 Hz), 128.6 (d, $J(^{31}P-^1H)$ = 0.8 Hz.

NMR data are consistent with our previous report.[2]

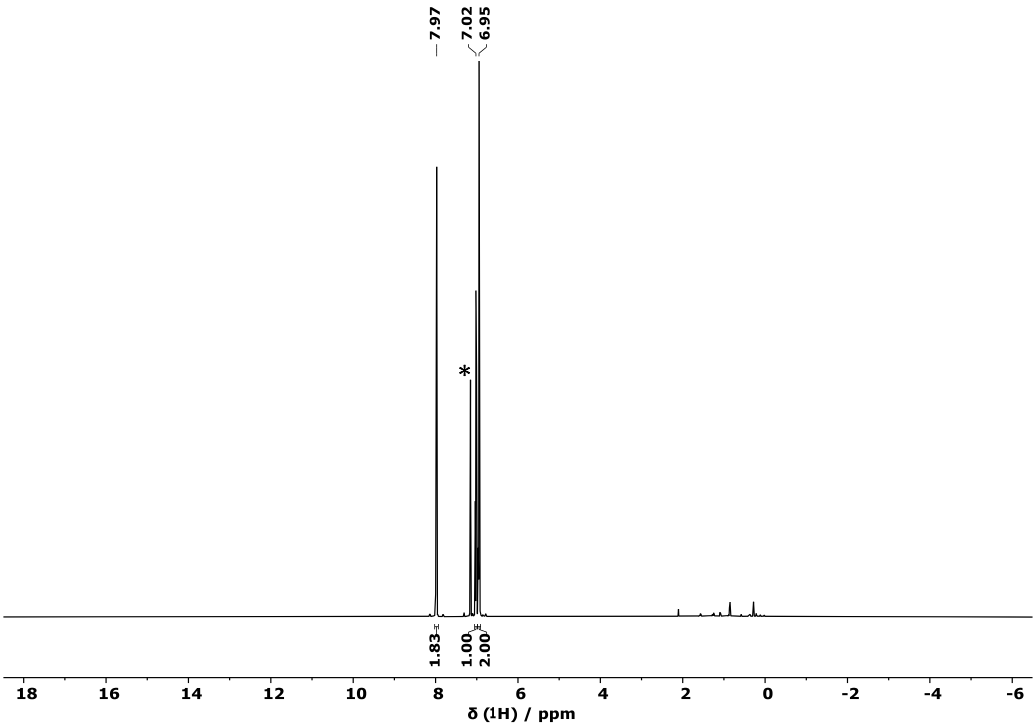


Figure S11. ^{1}H NMR spectrum of $P(C(O)Ph)_3$ (**6**) in C_6D_6 (*).

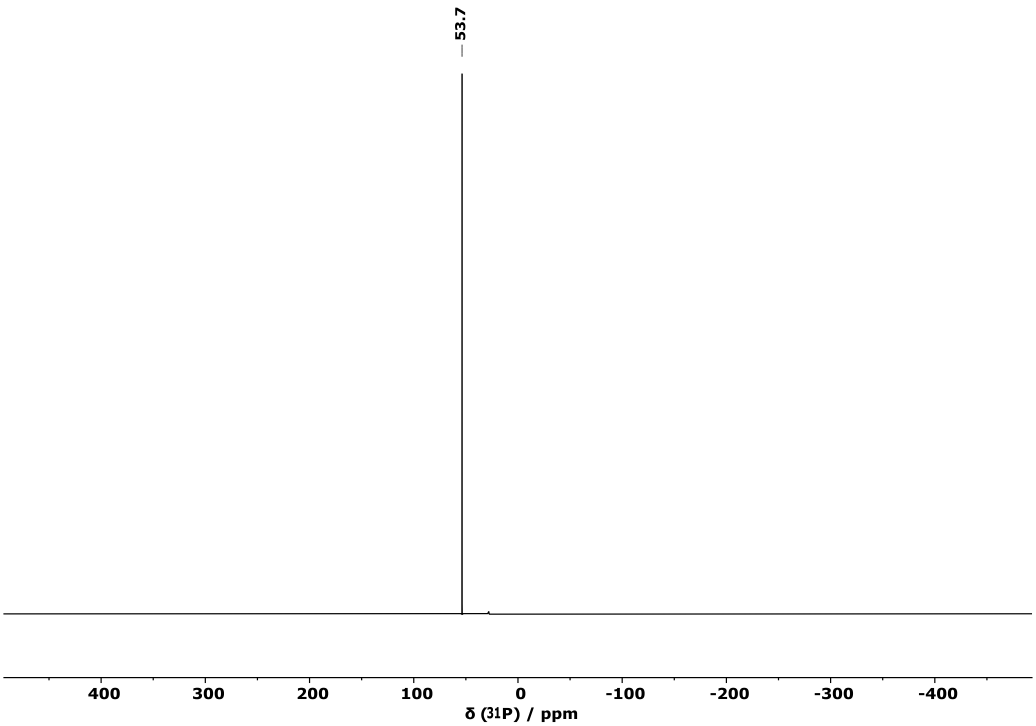


Figure S12. $^{31}P\{^1H\}$ NMR spectrum of $P(C(O)Ph)_3$ (**6**) in C_6D_6.

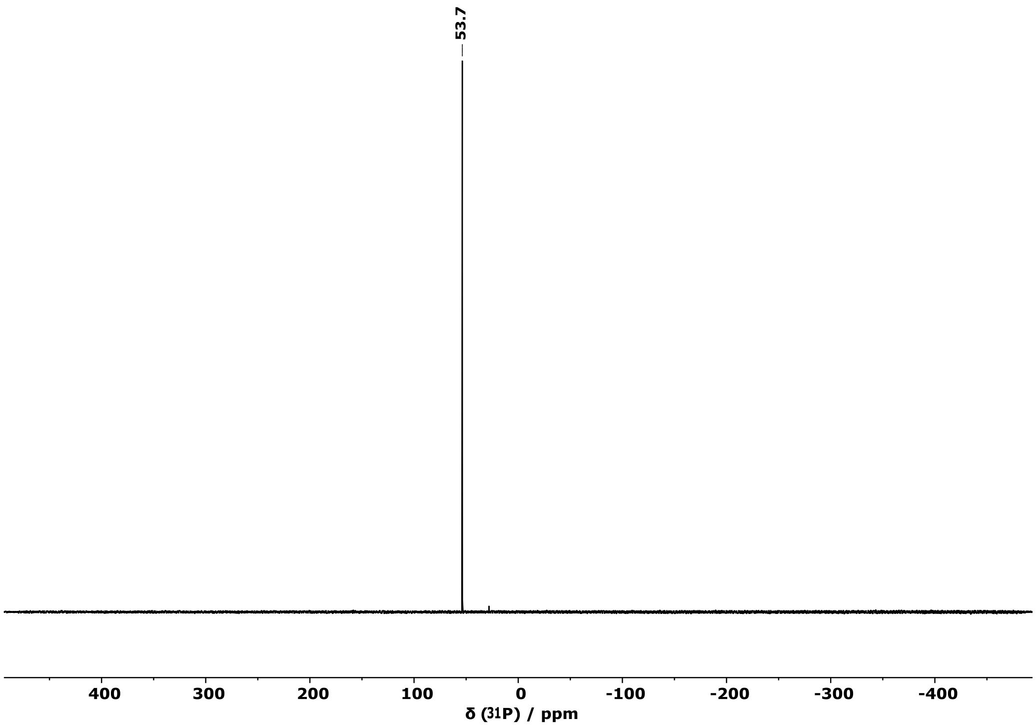


Figure S13. ^{31}P NMR spectrum of P(C(O)Ph)$_3$ (**6**) in C_6D_6.

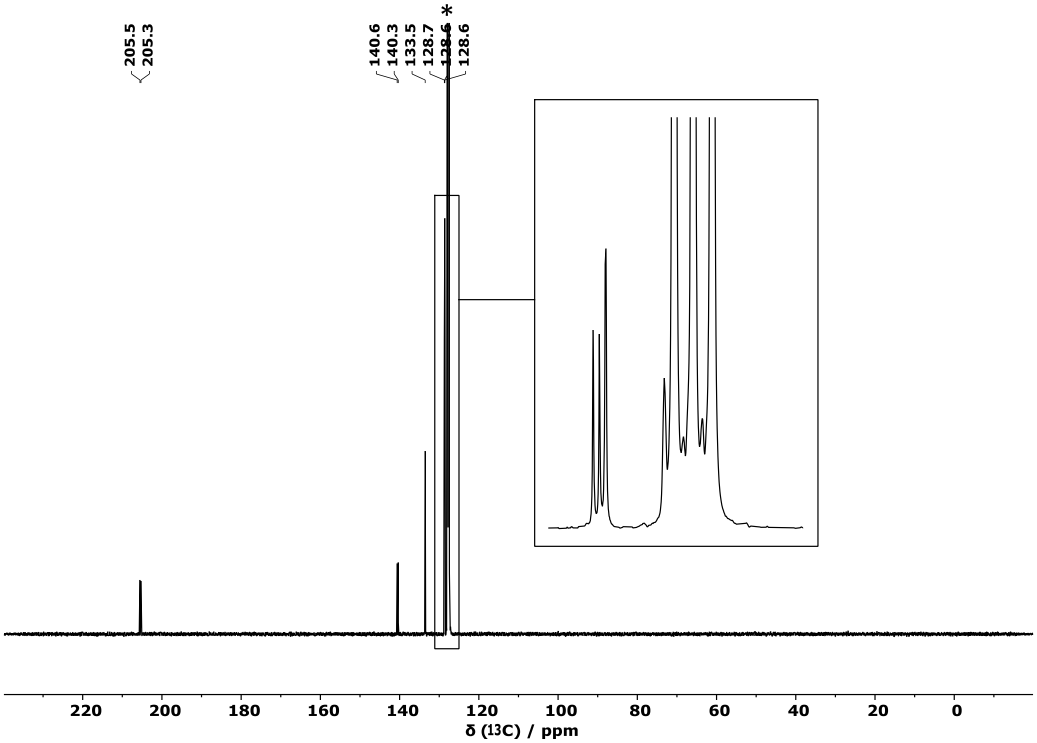


Figure S14. ^{13}C{^{1}H} NMR spectrum of P(C(O)Ph)$_3$ (**6**) in C_6D_6. Solvent resonances (*) truncated for clarity.

S3.3 Synthesis and isolation of [Bn_4P]Br (7)

7

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.) and $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. Volatiles were removed, toluene was added (15 mL) and the resulting suspension was filtered. Benzyl bromide (2.4 mL, 20 mmol, 40 equiv.) and KHMDS (399 mg, 2.0 mmol, 4 equiv.) were added. Subsequently, the reaction was heated to 80 °C with stirring for 3 d. The colorless suspension was filtered. The residue from the filtration was washed with toluene (3 x 20 mL). Subsequent extraction of the remaining solid into acetonitrile (3 x 20 mL) gave a colorless solution. Removal of volatiles under reduced pressure yielded **7** as a colorless solid (371.6 mg, 39%).

^{1}H NMR (500 MHz, 300 K, CD_3CN) δ [ppm] = 7.38 (3H, m), 7.23 (2H, m), 3.85 (d, $^2J(^{31}P\text{-}^1H) = 14.5$ Hz).

^{31}P{^{1}H} NMR (202 MHz, 300 K, CD_3CN) δ [ppm] = 24.3 (s).

^{31}P NMR (202 MHz, 300 K, CD_3CN) δ [ppm] = 24.3 (nonet, $^2J(^{31}P\text{-}^1H) = 14.1$ Hz).

^{13}C{^{1}H} NMR (126 MHz, 300 K, CD_3CN) δ [ppm] = 130.7 (d, $J(^{31}P\text{-}^1H) = 5.2$ Hz), 129.3 (d, $J(^{31}P\text{-}^1H) = 3.0$ Hz), 128.4 (d, $J(^{31}P\text{-}^1H) = 3.3$ Hz), 127.7 (d, $J(^{31}P\text{-}^1H) = 8.1$ Hz), 26.4 (d, $J(^{31}P\text{-}^1H) = 43.5$ Hz).

NMR data are consistent with our previous report.[2]

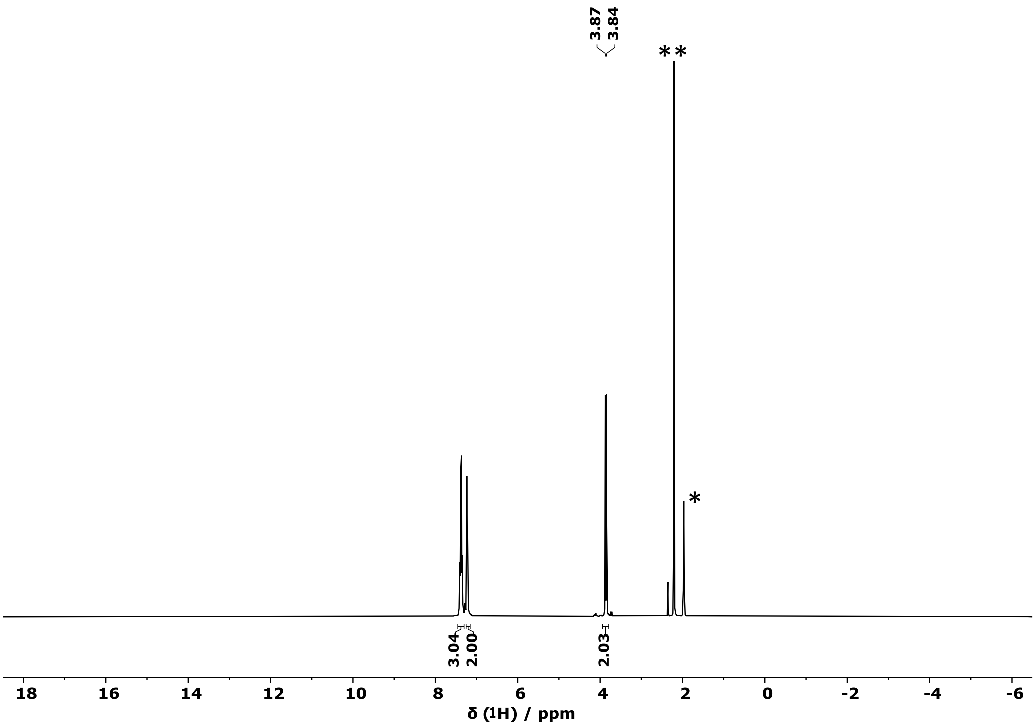


Figure S15. ^{1}H NMR spectrum of $[Bn_4P]Br$ (**7**) in CD_3CN (* solvent, ** H_2O).

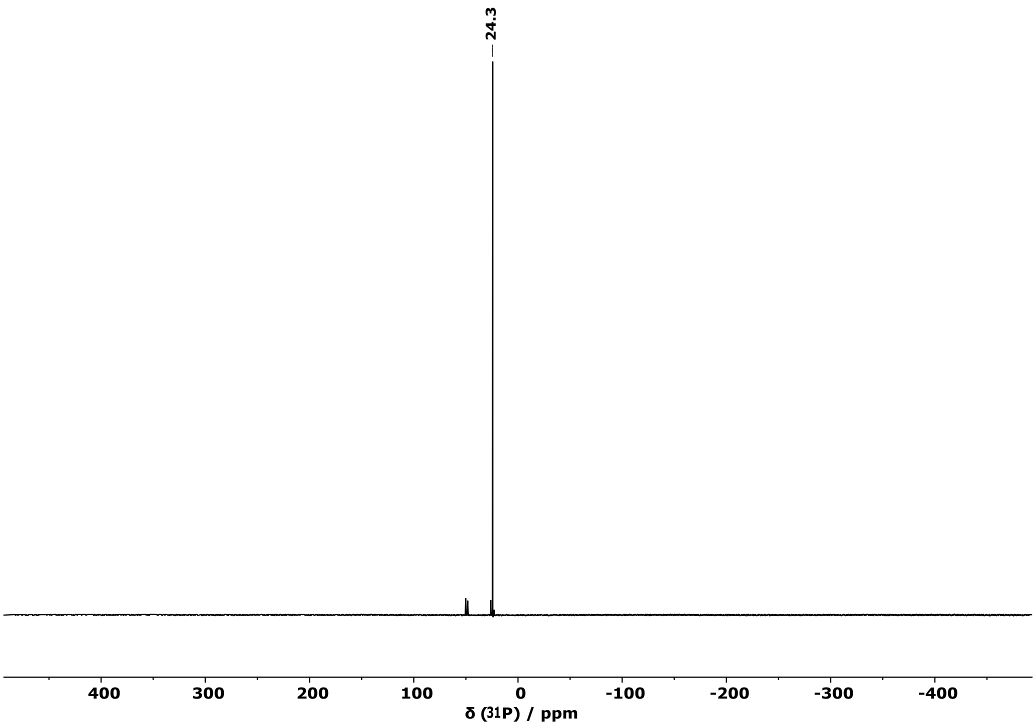


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of $[Bn_4P]Br$ (**7**) in CD_3CN.

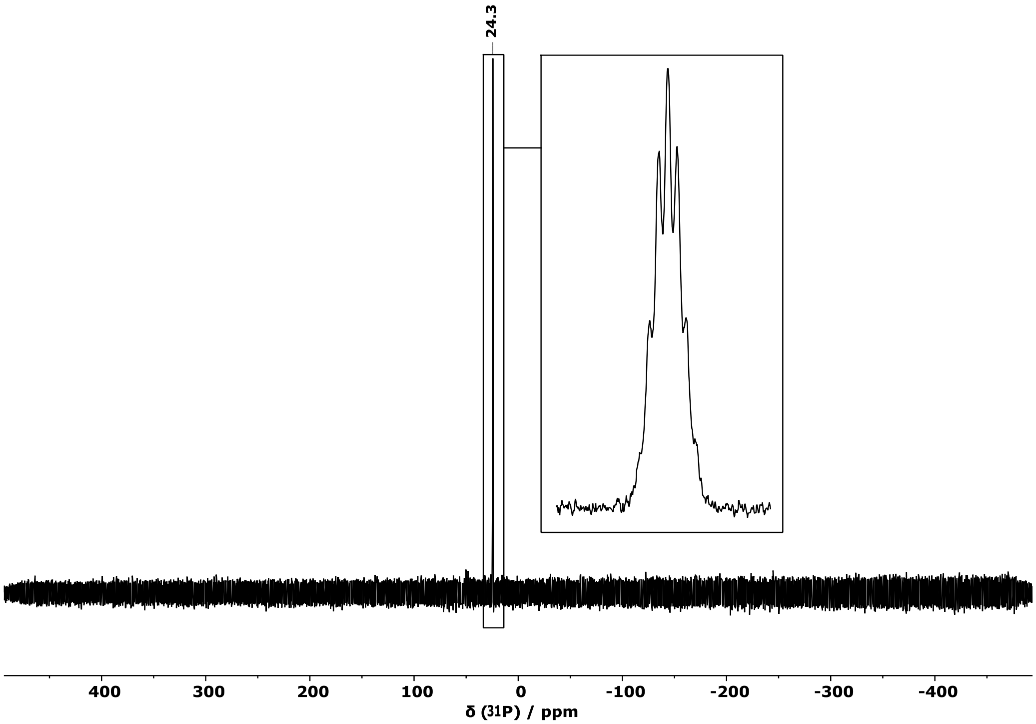


Figure S17. ^{31}P NMR spectrum of [Bn$_4$P]Br (**7**) in CD$_3$CN.

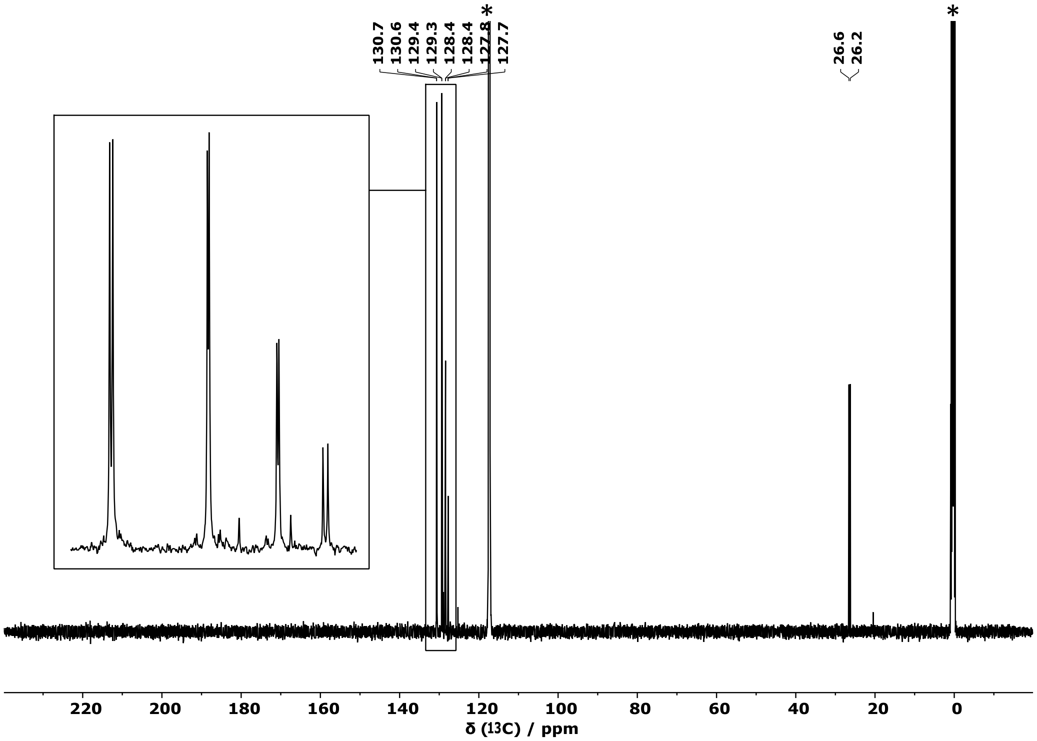


Figure S18. ^{13}C{^{1}H} NMR spectrum of [Bn$_4$P]Br (**7**) in CD$_3$CN. Solvent resonances (*) are truncated for clarity.

S3.4 Synthesis and isolation of [Et_4P]Br (8)

8

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.) and $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. Volatiles were removed, toluene was added (15 mL) and the resulting suspension was filtered. Ethyl bromide (741 µL, 10 mmol, 20 equiv.) and KHMDS (798 mg, 4.0 mmol, 8 equiv.) were added. Subsequently, the reaction was heated to 80 °C with stirring for 3 d. The colorless suspension was filtered. The residue from the filtration was washed with toluene (3 x 20 mL). Subsequent extraction into acetonitrile (3 x 20 mL) gave a colorless solution. Removal of volatiles under reduced pressure yielded **8** as a colorless solid (161.4 mg, 36%).

^{1}H NMR (500 MHz, 300 K, CD_3CN) δ [ppm] = 2.23 (2H, dq, $^1J(^{31}P\text{-}^1H) = 13.0$ Hz, $^3J(^1H\text{-}^1H) = 7.7$ Hz), 1.21 (3H, dt, $^2J(^{31}P\text{-}^1H) = 18.1$ Hz, $^3J(^1H\text{-}^1H) = 7.7$ Hz).

$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, CD_3CN) δ [ppm] = 40.7 (s).

^{31}P NMR (202 MHz, 300 K, CD_3CN) δ [ppm] = 40.7 (m).

$^{13}C\{^1H\}$ NMR (126 MHz, 300 K, CD_3CN) δ [ppm] = 10.8 (d, $^1J(^{31}P\text{-}^1H) = 49.6$ Hz), 4.8 (d, $^2J(^{31}P\text{-}^1H) = 5.4$ Hz).

NMR data are consistent with our previous report.[2]

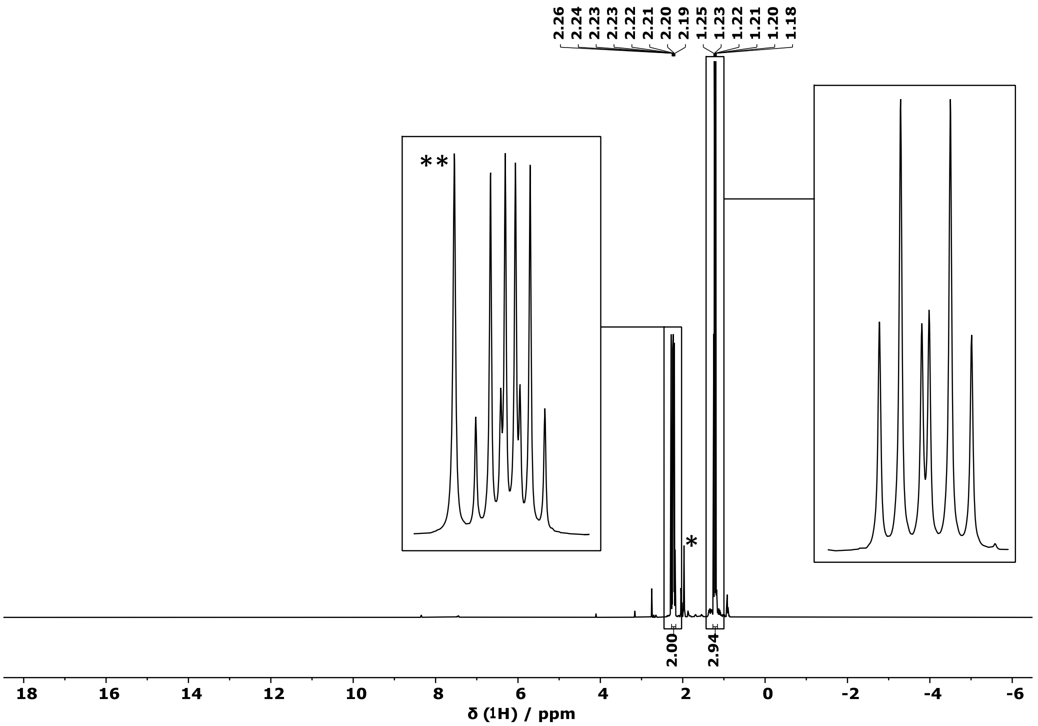


Figure S19. ^{1}H NMR spectrum of [Et_4P]Br (**8**) in CD_3CN (* solvent, ** H_2O).

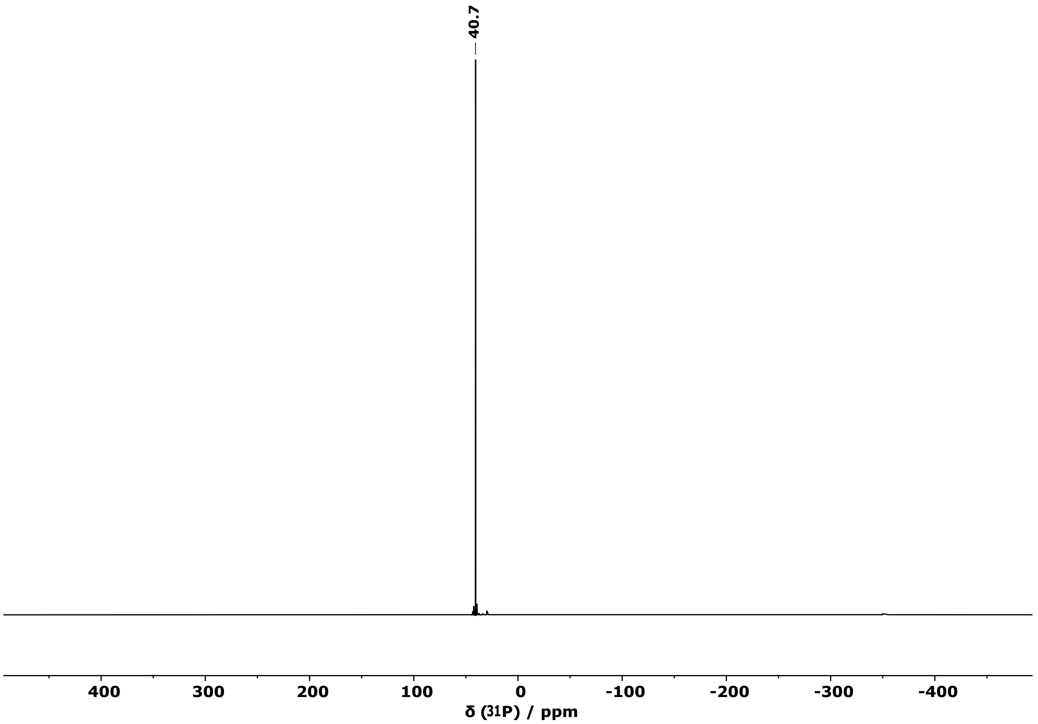


Figure S20. $^{31}P\{^1H\}$ NMR spectrum of [Et_4P]Br (**8**) in CD_3CN.

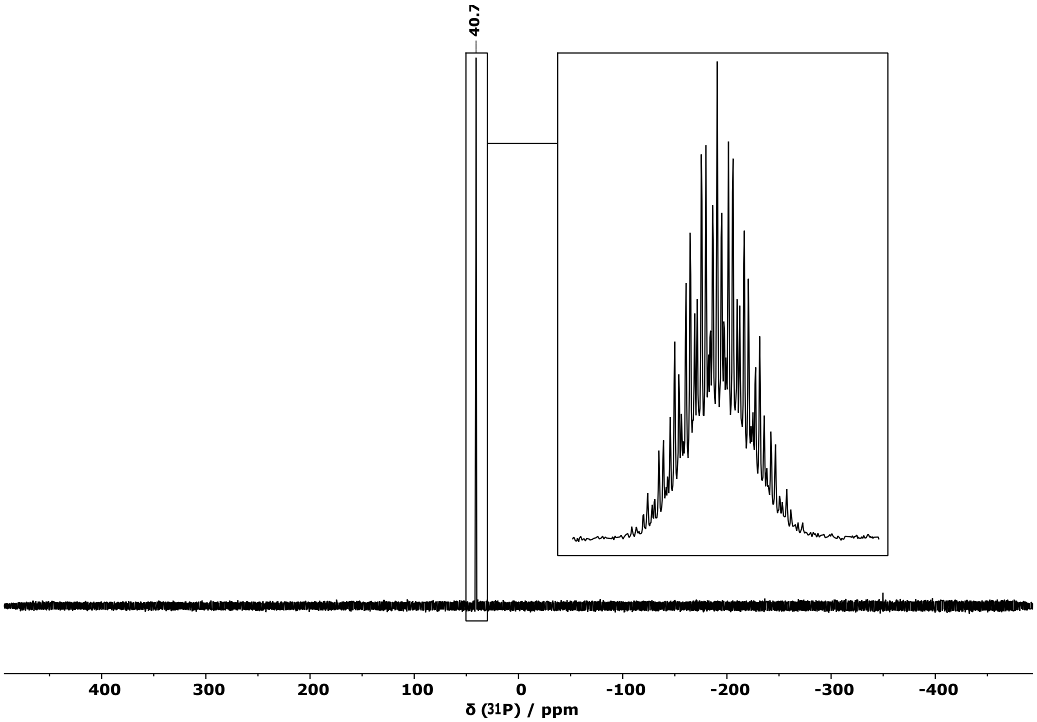


Figure S21. ^{31}P NMR spectrum of [Et$_4$P]Br (**8**) in CD$_3$CN.

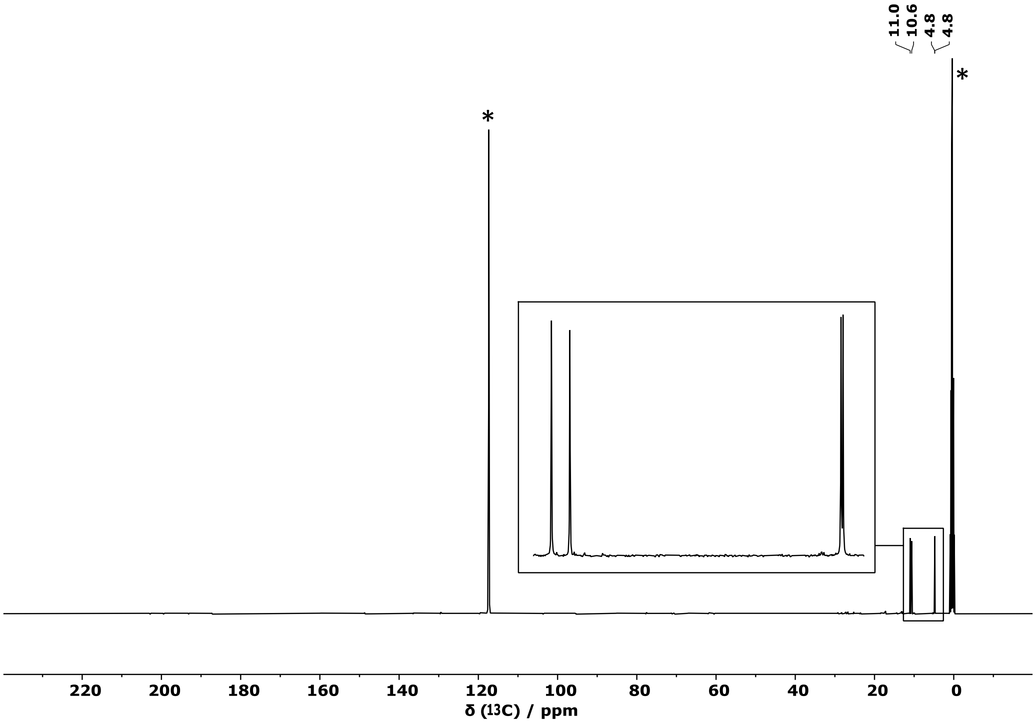
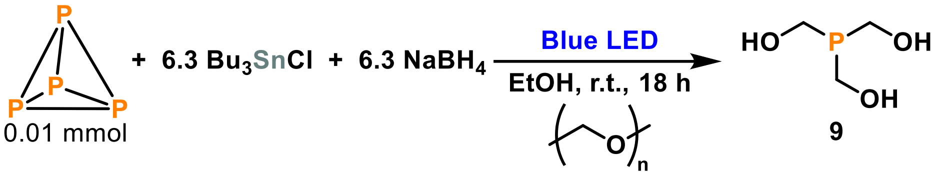


Figure S22. ^{13}C{^{1}H} NMR spectrum of [Et$_4$P]Br (**8**) in CD$_3$CN (*).

S3.5 Synthesis and isolation of THP (9)



To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.), $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) and paraformaldehyde (180 mg, 6.0 mmol, 12 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting suspension was filtered, and volatiles were removed under reduced pressure. The remaining oily residue was dissolved in toluene (10 mL) and degassed water (10 mL) and thoroughly stirred for 1 h. Subsequently, the organic phase was removed, and the aqueous phase was washed with further toluene (2 x 10 mL). After removal of volatiles from the aqueous phase, the desired product **9** was obtained as a colorless oil (163.2 mg, 66%).

^{1}H NMR (500 MHz, 300 K, D_2O) δ [ppm] = 4.01 (d, $^{2}J(^{31}P\text{-}^{1}H)$ = 5.3 Hz).

^{31}P{^{1}H} NMR (202 MHz, 300 K, D_2O) δ [ppm] = −24.5 (s).

^{31}P NMR (202 MHz, 300 K, D_2O) δ [ppm] = −24.5 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, D_2O) δ [ppm] = 56.3 (d, $^{1}J(^{31}P\text{-}^{1}H)$ = 8.4 Hz).

NMR data are consistent with our previous report.[2]

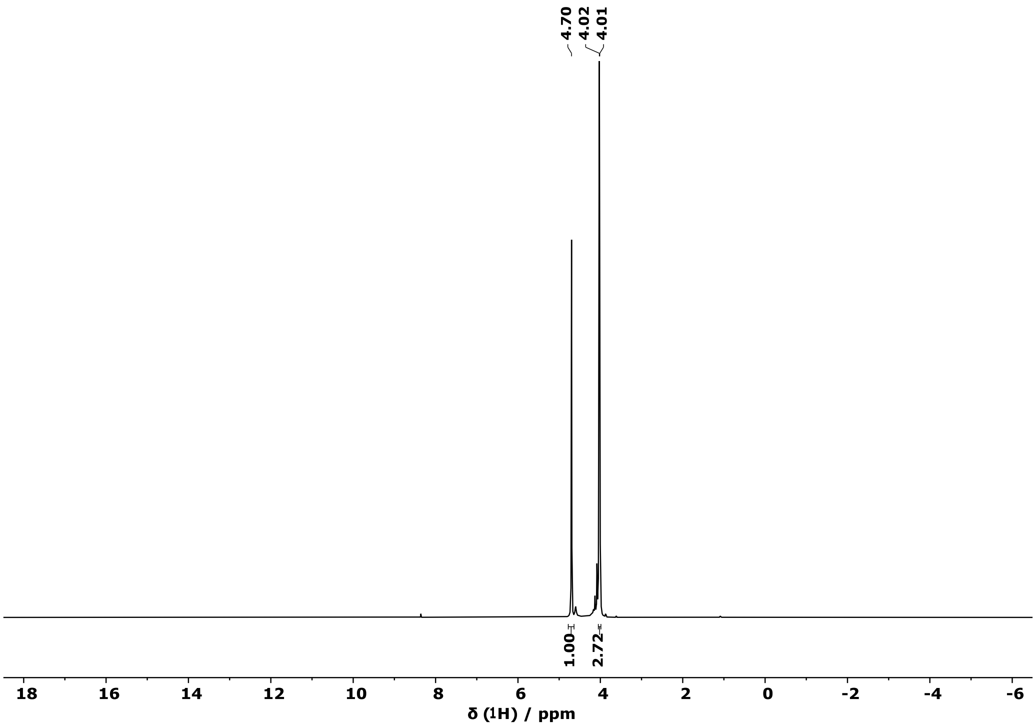


Figure S23. ^{1}H NMR spectrum of THP (**9**) in D_2O.

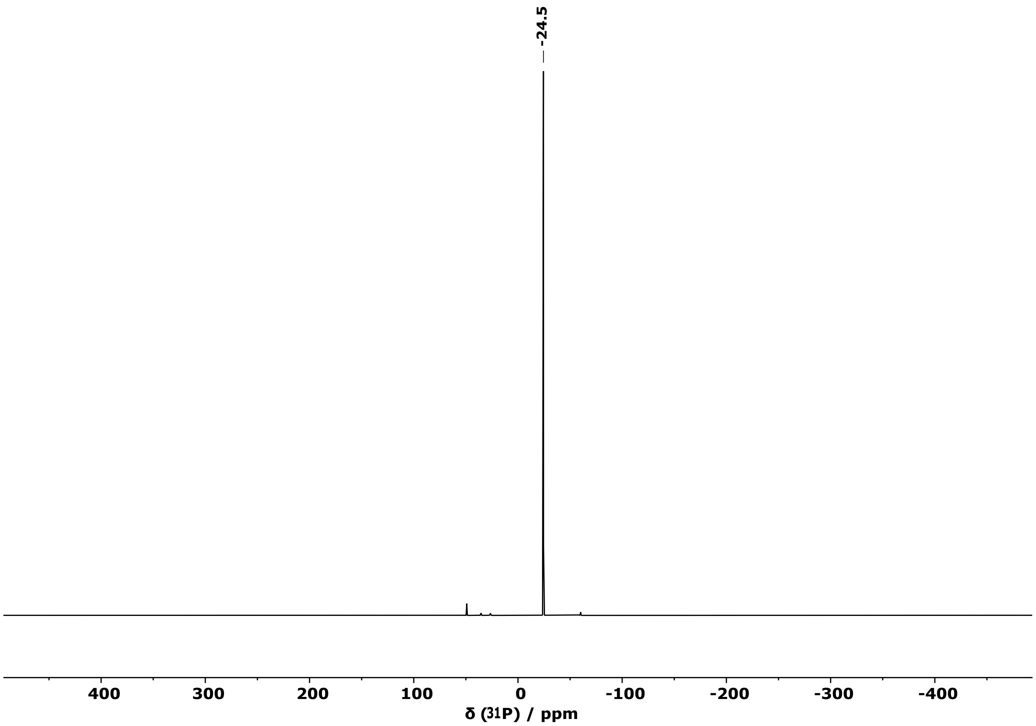


Figure S24. $^{31}P\{^1H\}$ NMR spectrum of THP (**9**) in D_2O.

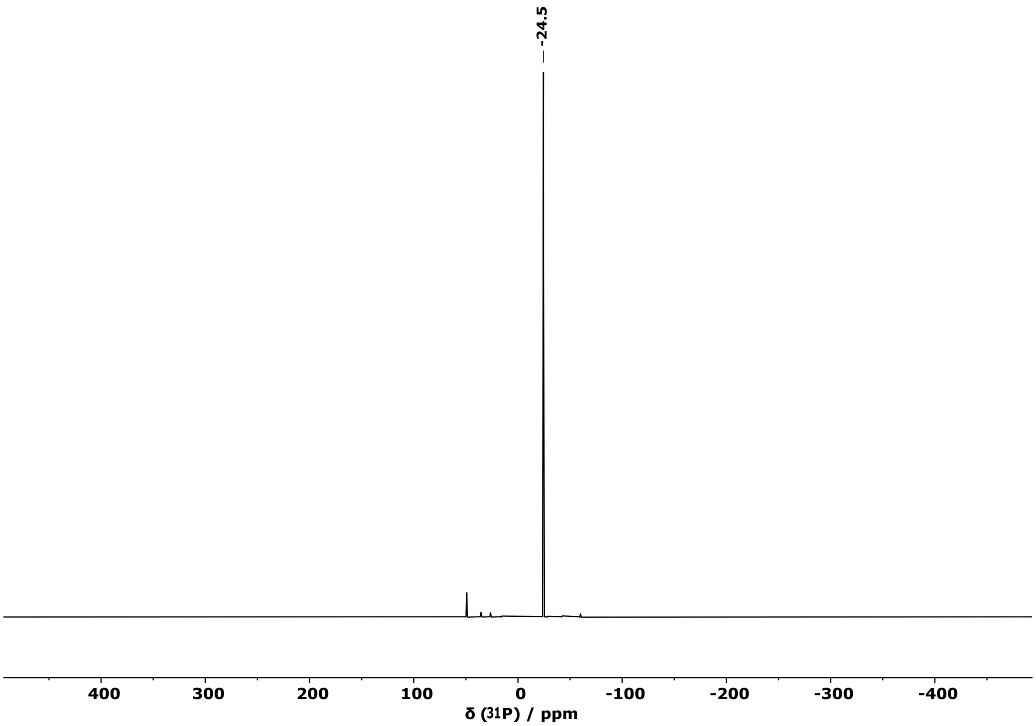


Figure S25. ^{31}P NMR spectrum of THP (**9**) in D_2O.

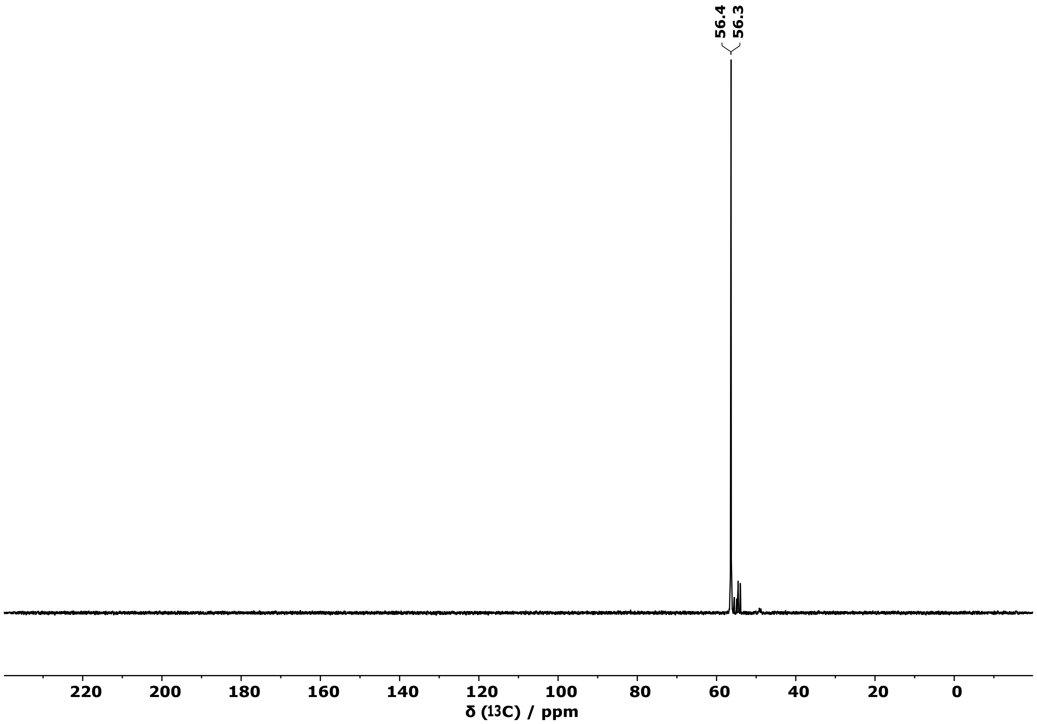
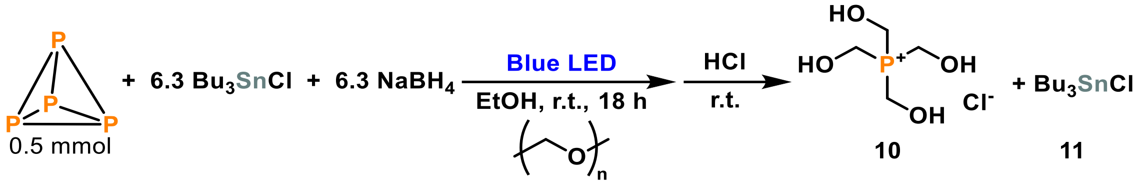


Figure S26. ^{13}C{^{1}H} NMR spectrum of THP (**9**) in D_2O.

S3.6 Synthesis and isolation of THPC (10) with recovery of Bu_3SnCl (11)



To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.), $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) and paraformaldehyde (750 mg, 25.0 mmol, 50 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting mixture was frozen in liquid nitrogen and HCl (4.0 M in 1,4-dioxane, 5 mL, 20 mmol, 40 equiv.) was added. After thawing, the mixture was stirred at room temperature for 2 h. The resulting suspension was filtered. Removal of volatiles yielded an oily residue. Triturating the semi-solid residue with Et_2O (20 mL) overnight gave a white solid. The solid was isolated by filtration, washed with Et_2O (2 x 10 mL) and dried under reduced pressure to afford **10** (312.2 mg, 82%) as a white powder.

The Et_2O extracts were combined, the solvent was removed and the oily residue was dried under vacuum to afford Bu_3SnCl (**11**) as a pale-yellow oil (963.3 mg, 94%).

Spectroscopic data of THPC:

^{1}H NMR (500 MHz, 300 K, D_2O) δ [ppm] = 4.60 (d, $^2J(^{31}P\text{-}^1H) = 1.8$ Hz).

^{31}P{^{1}H} NMR (202 MHz, 300 K, D_2O) δ [ppm] = 26.3 (s).

^{31}P NMR (202 MHz, 300 K, D_2O) δ [ppm] = 26.3 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, D_2O) δ [ppm] = 48.9 (d, $^1J(^{31}P\text{-}^{13}C) = 51.4$ Hz).

NMR data are consistent with our previous report.[2]

Spectroscopic data of recovered Bu_3SnCl:

^{1}H NMR (500 MHz, 300 K, $CDCl_3$) δ [ppm] = 1.76-1.56 (2H, m), 1.41-1.29 (4H, m), 0.94 (3H, t, $^3J(^1H\text{-}^1H) = 7.4$ Hz).

^{119}Sn{^{1}H} NMR (186 MHz, 300 K, $CDCl_3$) δ [ppm] = 158.4 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, $CDCl_3$) δ [ppm] = 27.9 (s), 26.9 (s), 17.5 (s), 13.6 (s).

NMR data are consistent with previous reports.[3]

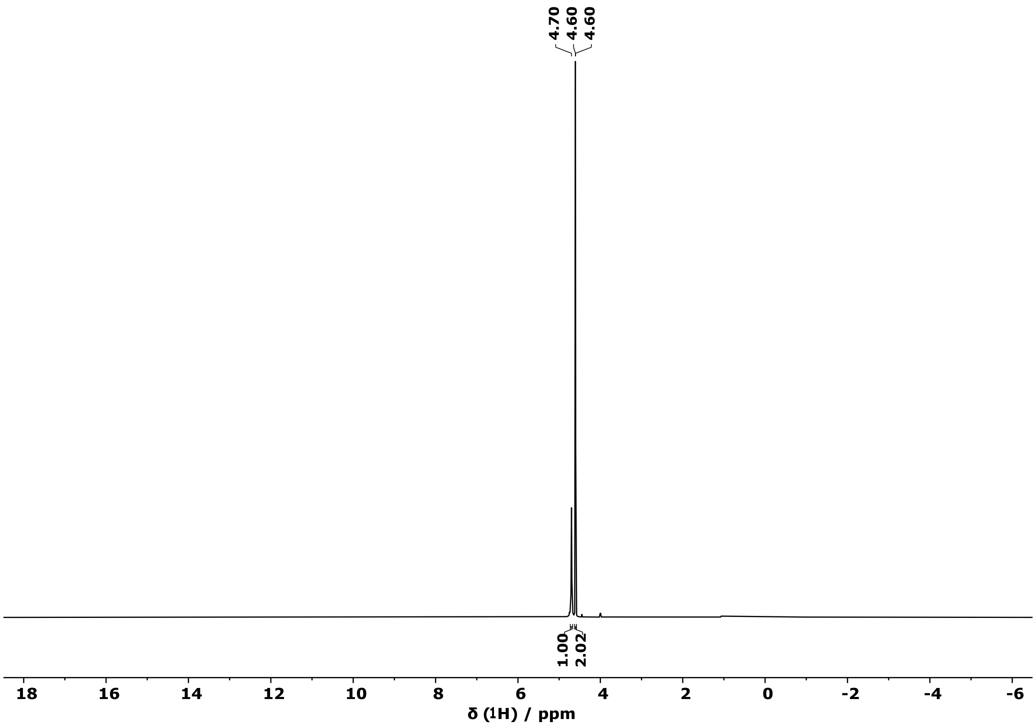


Figure S27. ^{1}H NMR spectrum of THPC (**10**) in D_2O.

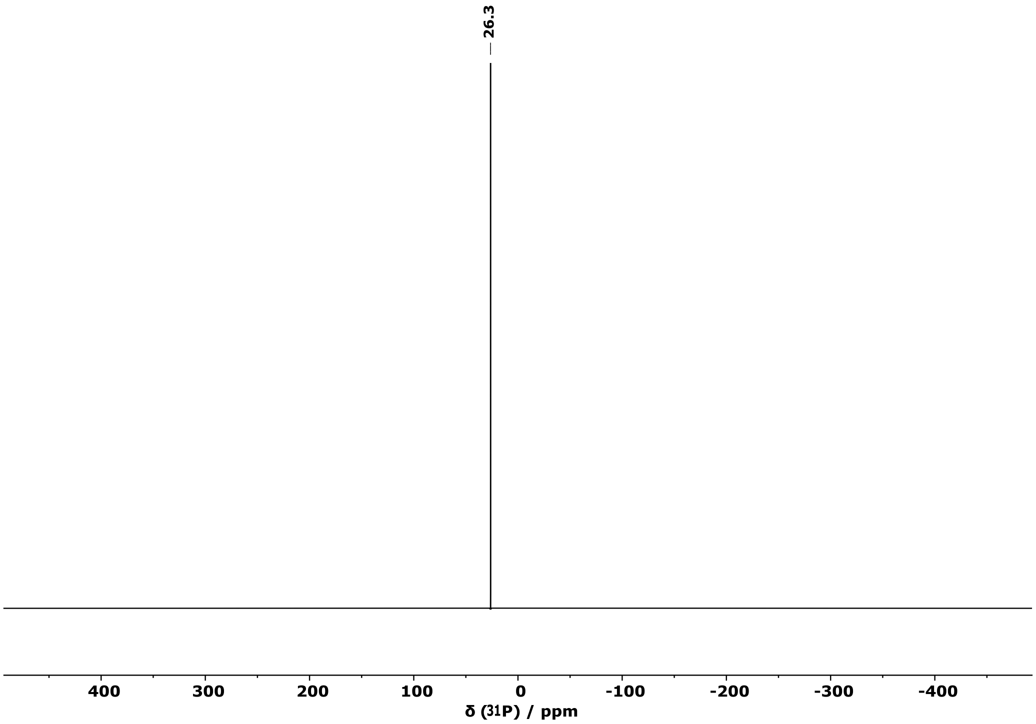


Figure S28. ^{31}P{^{1}H } NMR spectrum of THPC (**10**) in D_2O.

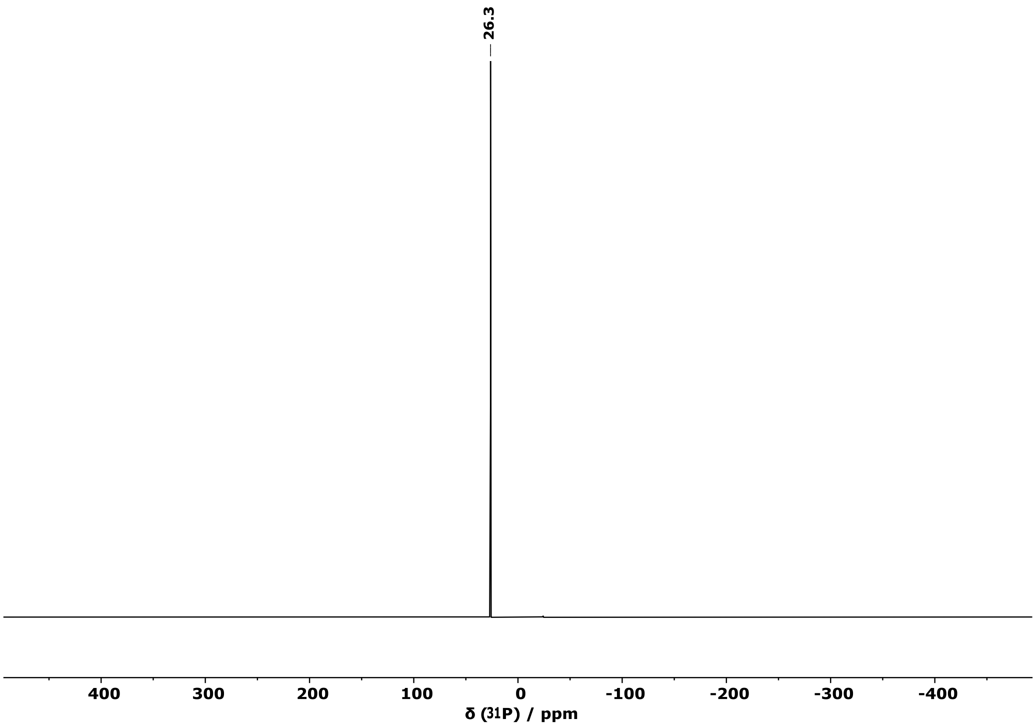


Figure S29. ^{31}P NMR spectrum of THPC (**10**) in D_2O.

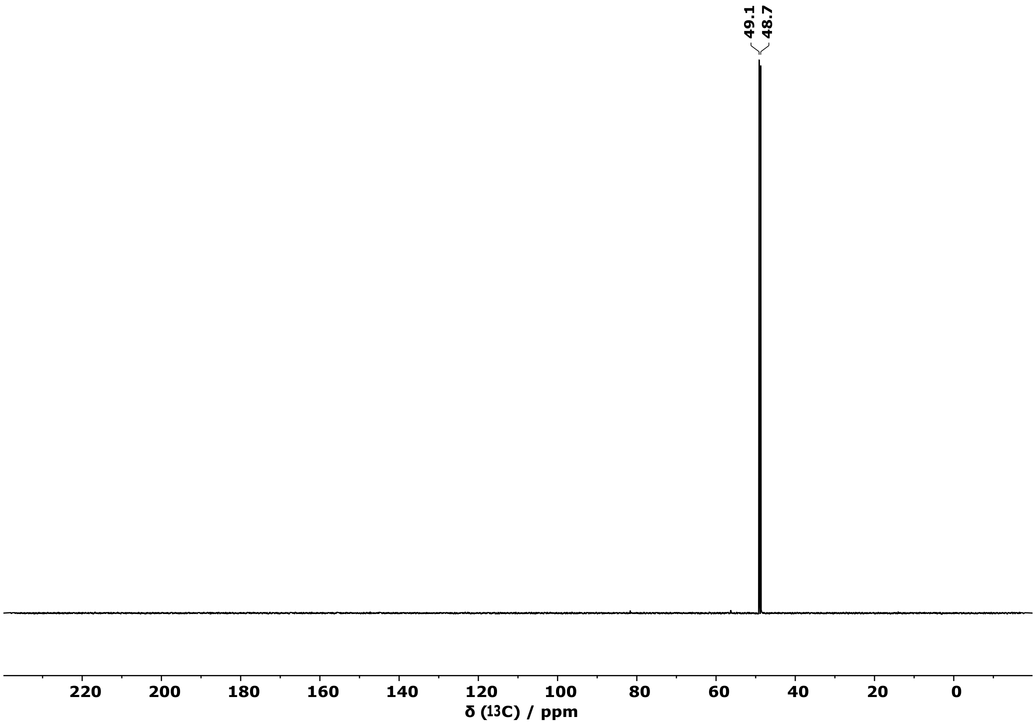


Figure S30. ^{31}C{^{1}H } NMR spectrum of THPC (**10**) in D_2O.

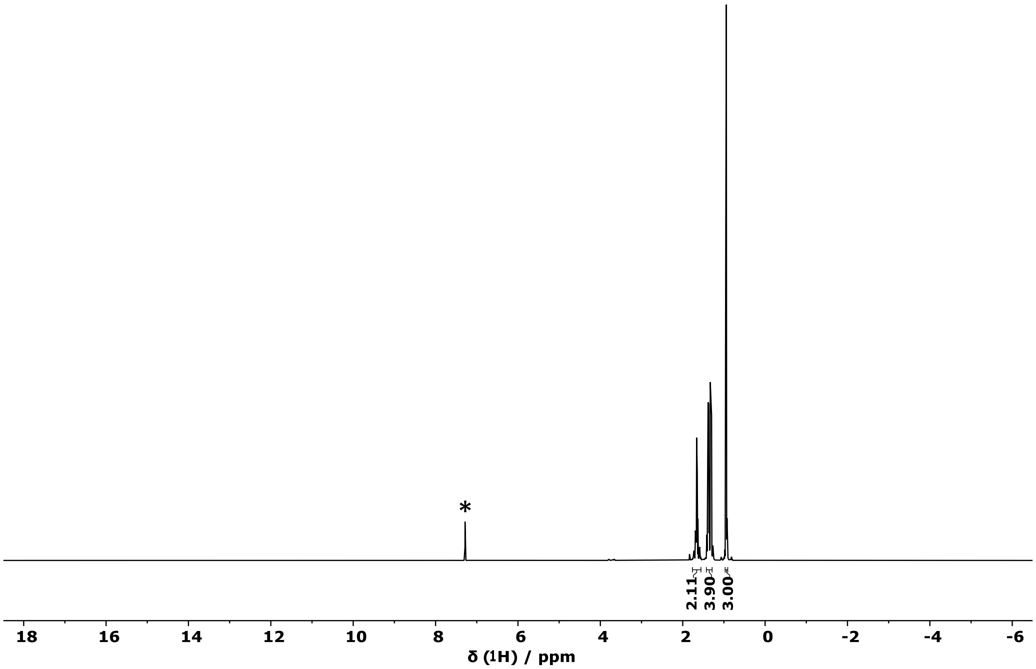


Figure S31. ^{1}H NMR spectrum of Bu_3SnCl (**11**) in CD_3Cl (*).

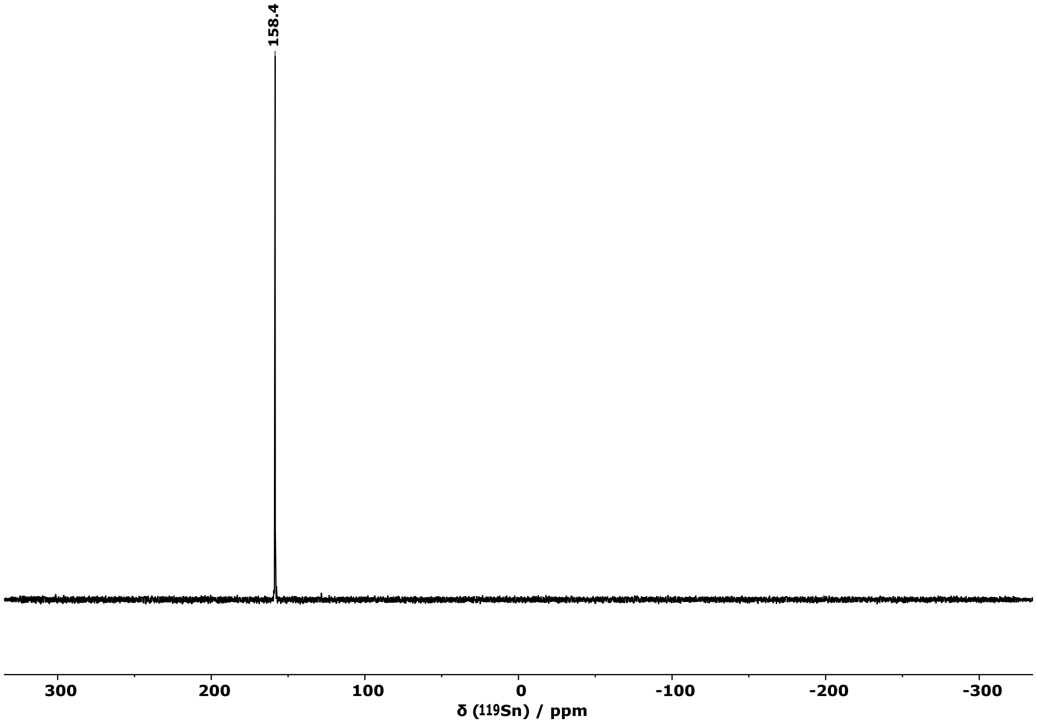


Figure S32. $^{119}Sn\{^{1}H\}$ NMR spectrum of Bu_3SnCl (**11**) in CD_3Cl.

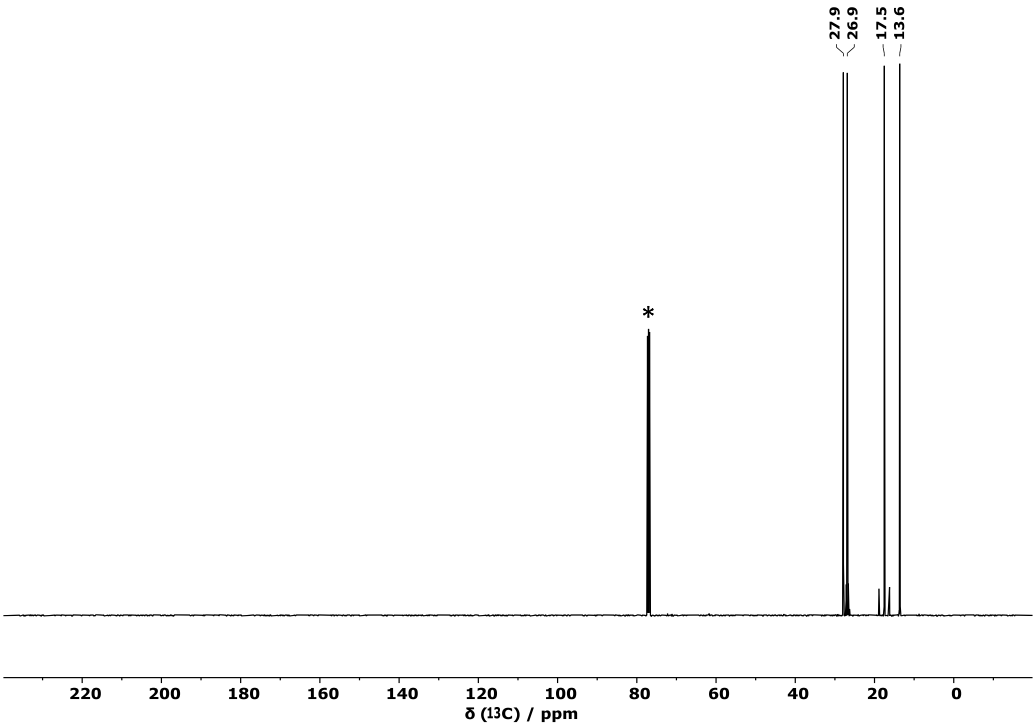
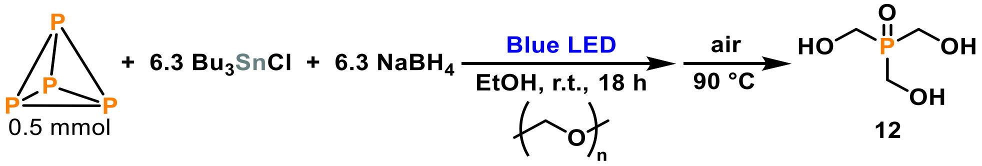


Figure S33. $^{13}C\{^1H\}$ NMR spectrum of Bu_3SnCl (**11**) in CD_3Cl (*).

S3.7 Synthesis and isolation of THPO (12)



12

To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.), $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) and paraformaldehyde (180 mg, 6.0 mmol, 12 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting suspension was filtered, and volatiles were removed under reduced pressure. The subsequent work-up was performed under air. Toluene (10 mL) and water (10 mL) were added to the colorless residue, and the mixture was vigorously stirred for 30 min. Subsequently, the organic phase was removed, and the aqueous phase was extracted with toluene (2 x 10 mL). The aqueous phase was heated to 90 °C overnight under air. Removal of all volatiles under vacuum afforded **12** as a colorless oil (187.2 mg, 67%).

^{1}H NMR (500 MHz, 300 K, D_2O) δ [ppm] = 4.04 (d, $^{2}J(^{31}P-^{1}H)$ = 3.1 Hz).

^{31}P{^{1}H} NMR (202 MHz, 300 K, D_2O) δ [ppm] = 49.0 (s).

^{31}P NMR (202 MHz, 300 K, D_2O) δ [ppm] = 49.0 (s).

^{13}C{^{1}H} NMR (126 MHz, 300 K, D_2O) δ [ppm] = 54.2 (d, $^{1}J(^{31}P-^{13}C)$ = 75.5 Hz).

NMR data are consistent with our previous report.[2]

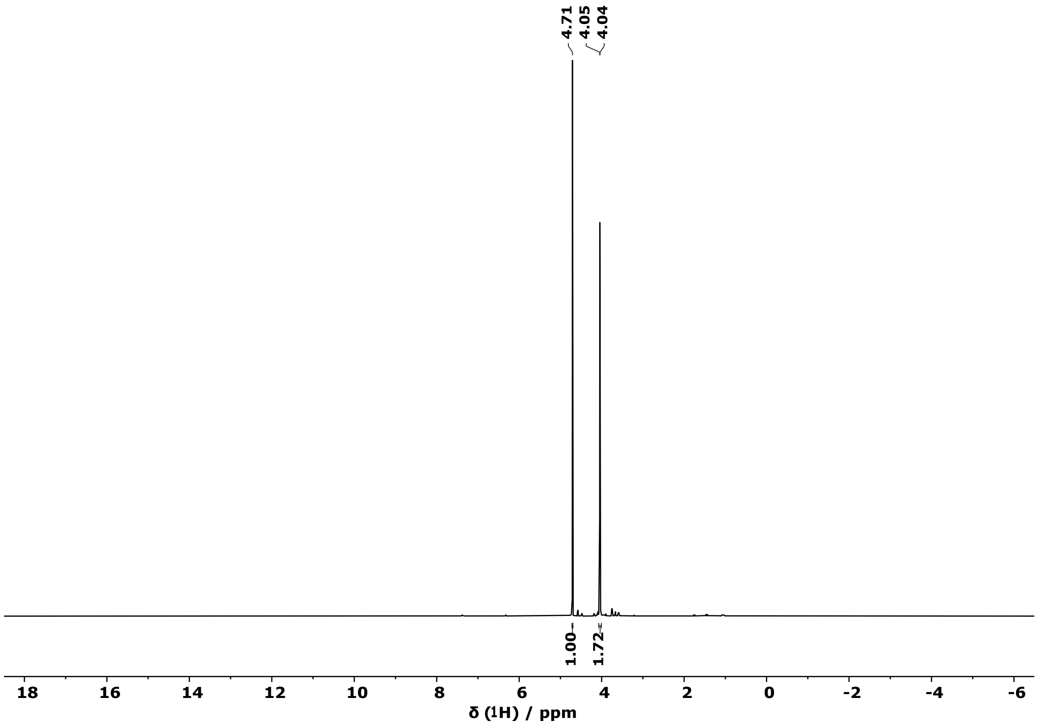


Figure S34. ^{1}H NMR spectrum of THPO (**12**) in D_2O.

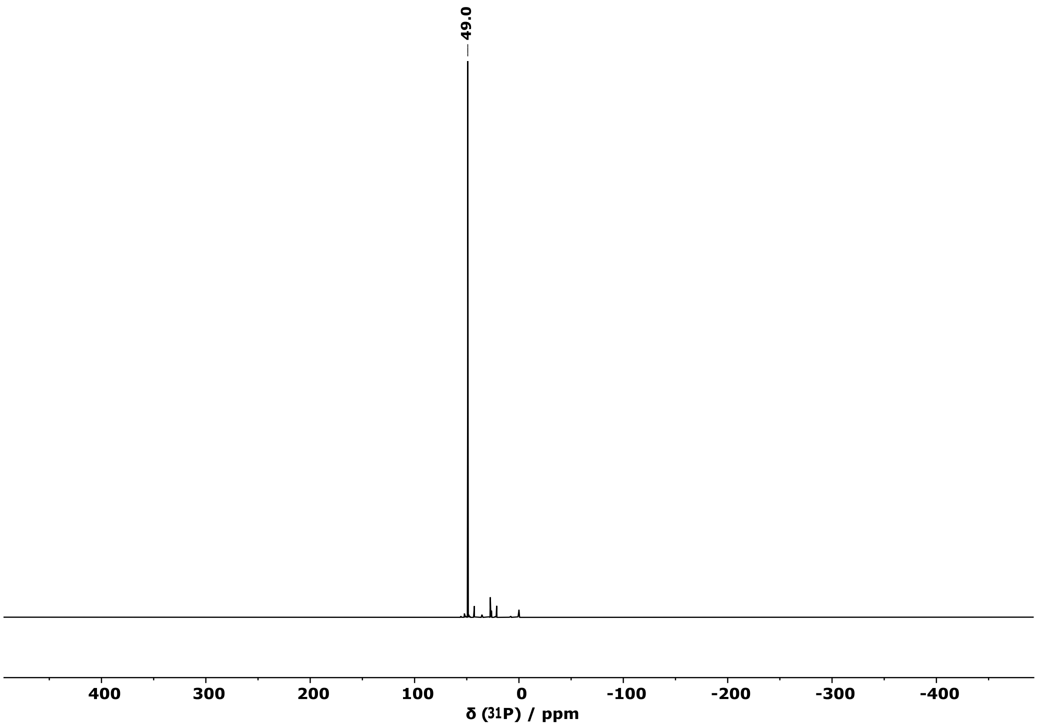


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of THPO (**12**) in D_2O.

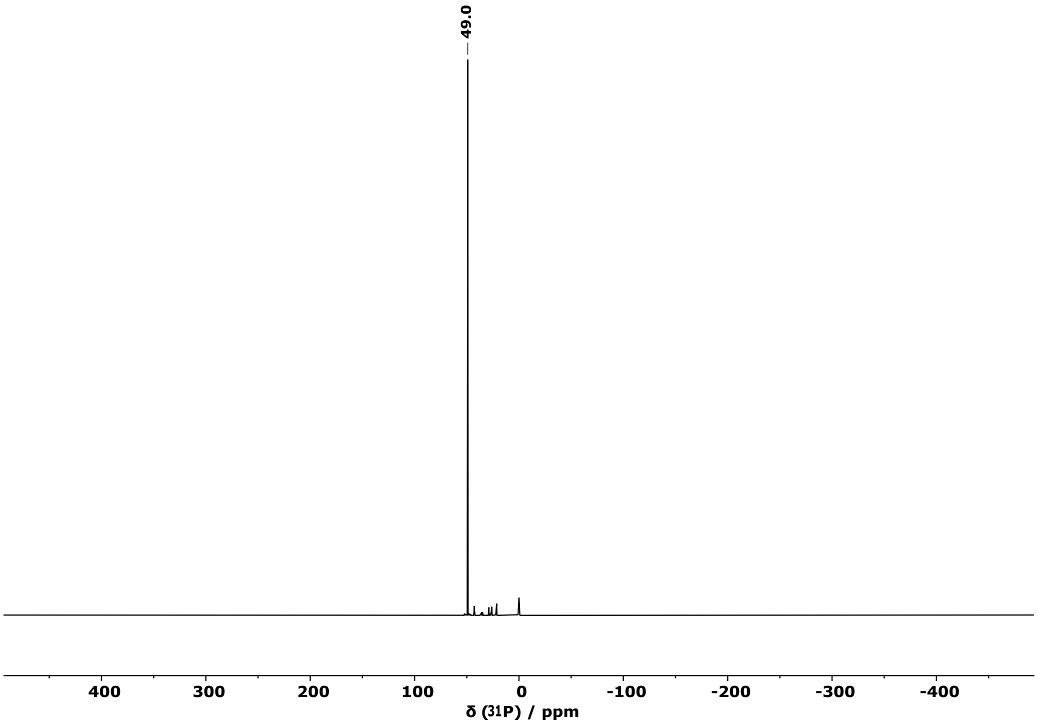


Figure S36. ^{31}P NMR spectrum of THPO (**12**) in D_2O.

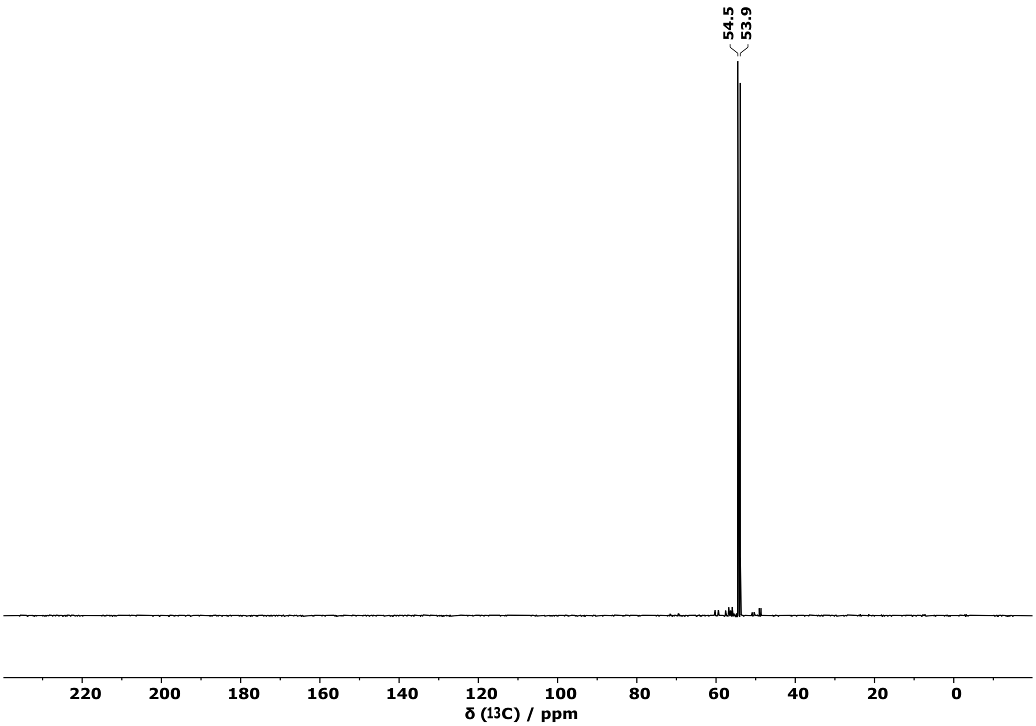
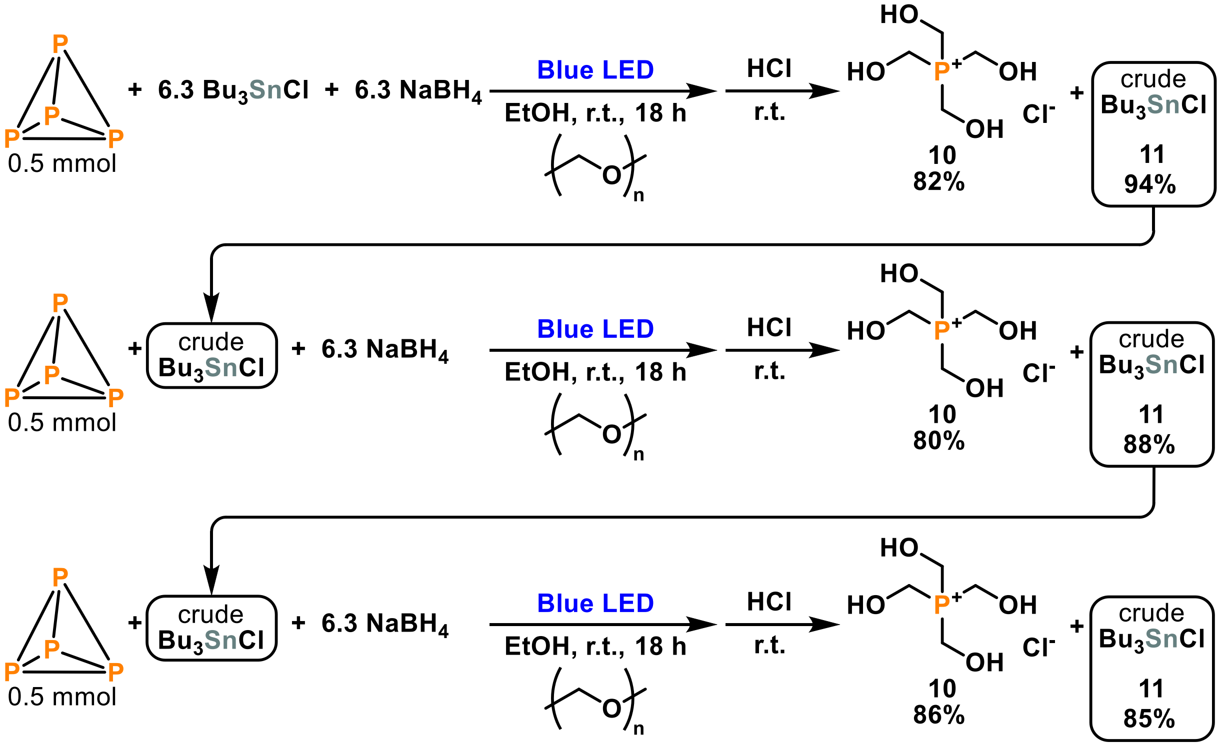


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of THPO (**12**) in D_2O.

S4. Synthesis and isolation of THPC with direct recycling of Bu_3SnCl (three cycles)



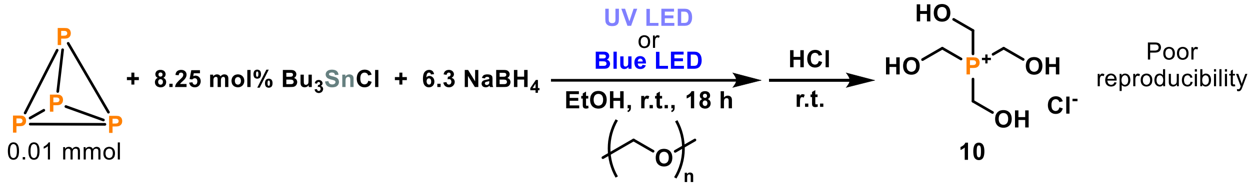
To a 50 mL flat-bottomed Schlenk tube were added P_4 (62.0 mg, 0.5 mmol) and benzene (5 mL). The mixture was stirred until P_4 had completely dissolved. Subsequently, EtOH (15 mL), Bu_3SnCl (854 µL, 3.15 mmol, 6.3 equiv.), $NaBH_4$ (119 mg, 3.15 mmol, 6.3 equiv.) and paraformaldehyde (750 mg, 25.0 mmol, 50 equiv.) were added. The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 20.3 V, 1000 mA, 7X Osram OSLON SSL 80) for 18 h. The resulting mixture was frozen in liquid nitrogen and HCl (4.0 M in 1,4-dioxane, 5 mL, 20 mmol, 40 equiv.) was added. After thawing, the mixture was stirred at room temperature for 2 h. The resulting suspension was filtered. Removal of volatiles yielded an oily residue. Triturating the semi-solid residue with Et_2O (20 mL) overnight gave a white solid. The solid was isolated by filtration, washed with Et_2O (2 x 10 mL) and dried under reduced pressure to afford **10** (312.2 mg, 82%) as a white powder.

The Et_2O extracts were combined, the solvent was removed, and the oily residue was dried under vacuum to afford Bu_3SnCl (**11**) as a pale-yellow oil (963.3 mg, 94%). The oil was transferred into a 50 mL flat-bottomed Schlenk tube. The reaction was repeated according to the above procedure to afford **10** as a white solid (303.2 mg, 80%).

Repeating the same procedure one more time afforded **10** as a white solid in a similar yield (328.1 mg, 86%). Bu_3SnCl (**11**) was recovered as a pale-yellow oil as described above(872.3 mg, 85% with respect to the starting amount).

NMR data of samples of **10** from the 1st, 2nd and 3rd cycle were identical to those reported in Supplementary Information section S3.6.

S5. Catalytic synthesis of THPC (10)



Blue LED: 2-47% conv., TON = 0.3-8.5
UV LED: 8-50% conv., TON = 1.5-9.1

To two 10 mL, flat-bottomed Schlenk tubes were added P_4 (0.01 mmol, stock solution in 65.9 µL benzene, 1 equiv.), EtOH (500 µL), Bu_3SnCl (0.89 µL, 0.0033 mmol, 8.25 mol% with respect to P), $NaBH_4$ (2.4 mg, 0.063 mmol, 6.3 equiv.) and paraformaldehyde (15 mg, 0.5 mmol, 50 equiv.). The tubes were sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (±15 nm), 3.2 V, 700 mA, Osram OSLON SSL 80) or UV light (356 nm) for 72 h. The resulting mixtures were frozen in a liquid nitrogen bath and HCl (4.0 M in 1,4-dioxane, 0.1 mL, 0.4 mmol, 40 equiv.) was added. After thawing, the reaction mixtures were stirred at room temperature for 2 h. Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added as an internal standard. The mixtures were analyzed by quantitative $^{31}P\{^1H\}$ NMR to determine the yield of THPC.

The turnover numbers (TONs) are calculated factoring the 1:6 stoichiometry of the reaction between P_4 and Bu_3SnH (*in situ* generated by Bu_3SnCl and $NaBH_4$). Therefore, the full consumption of P_4 corresponds to 6 turnovers of the catalyst. Equivalently, formation of 1 eq. THPC (from 0.25 eq. P_4) requires 1.5 turnovers. Thus, the TON is calculated as 1.5 times the molar ratio of THPC to the Bu_3SnCl catalyst.

The results showed that, in the best case, the main product was **10**, with 47% yield under blue-light irradiation (456 nm, TON = 8.5) and 50% under UV light irradiation (356 nm, TON = 9.1). Unfortunately, this attempt to reproduce the result yielded highly inconsistent results, with TONs < 1 observed in many cases. Efforts to improve reproducibility by varying parameters such as reaction time, light source, solvents, stoichiometries, and reducing agents have been unsuccessful to date.

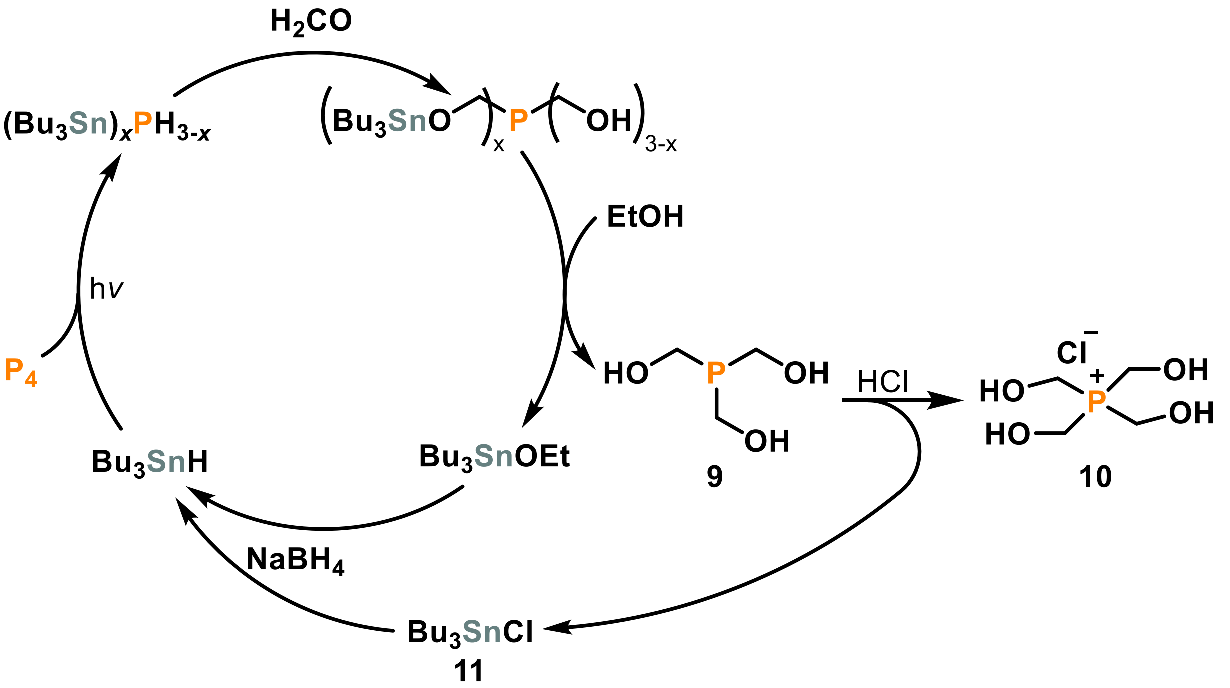


Figure S38. Proposed mechanism for the catalytic formation of THPC (**10**) from P_4 with recycling of Bu_3SnCl (**11**).

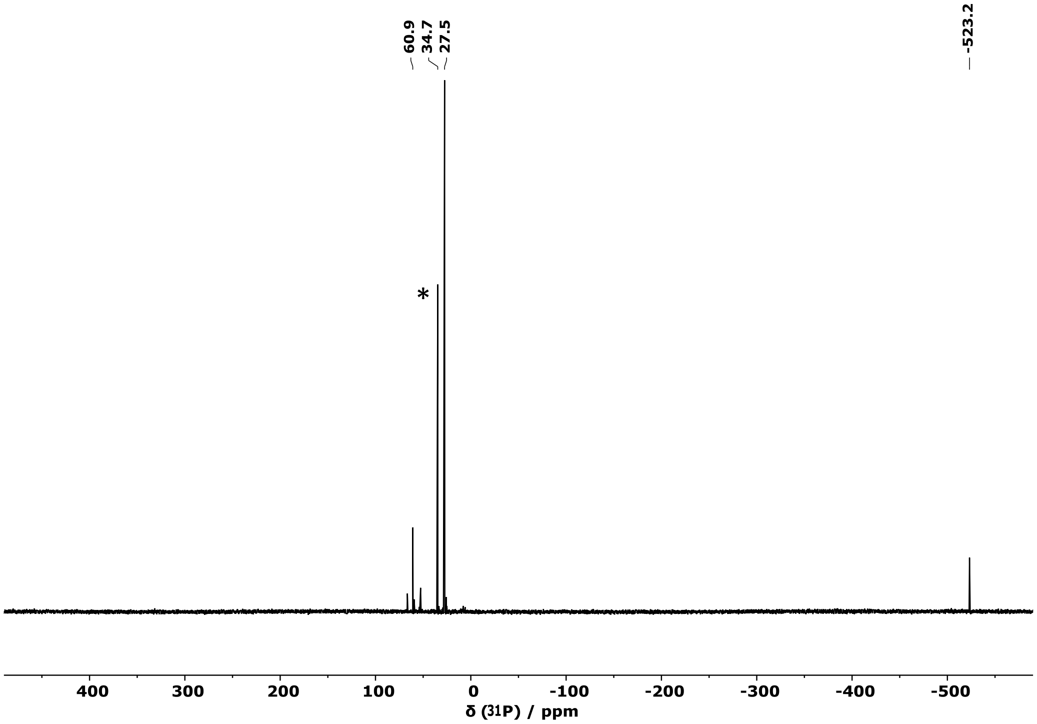


Figure S39. $^{31}P\{^1H\}$ NMR spectrum for the catalytic transformation of P_4 into THPC (**10**), driven by blue light irradiation (456 nm), with Ph_3PO as internal standard (*).

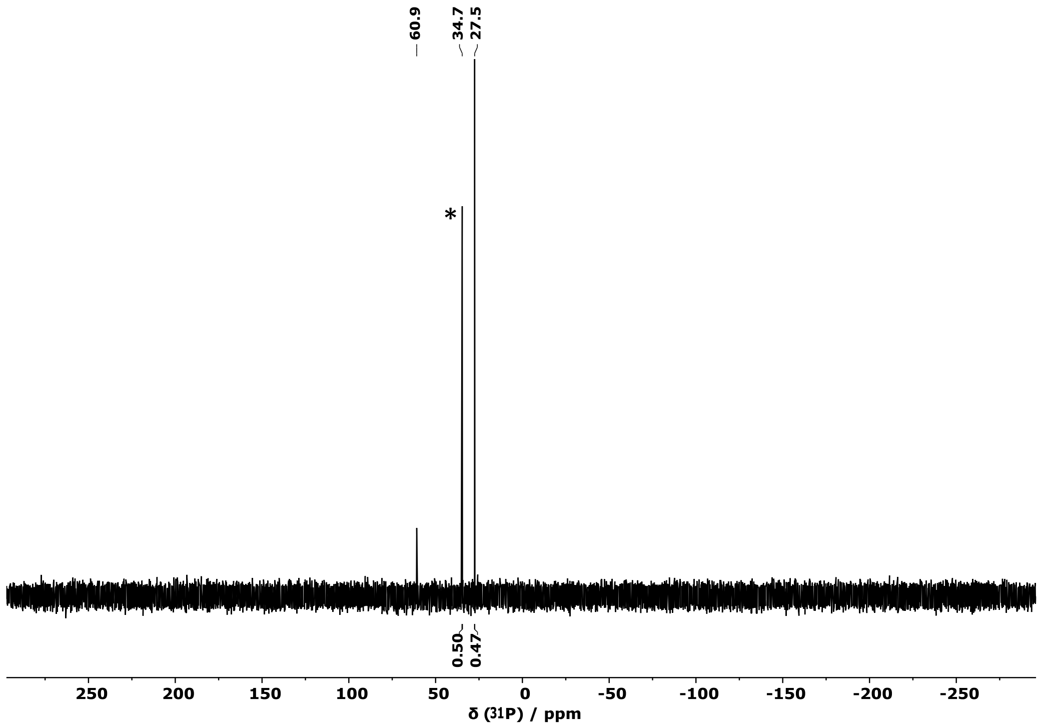


Figure S40. Quantitative single-scan, inverse gated $^{31}P\{^{1}H\}$ NMR spectrum for the catalytic transformation of P_4 into THPC (**10**), driven by blue light irradiation (456 nm), with Ph_3PO as internal standard (*).

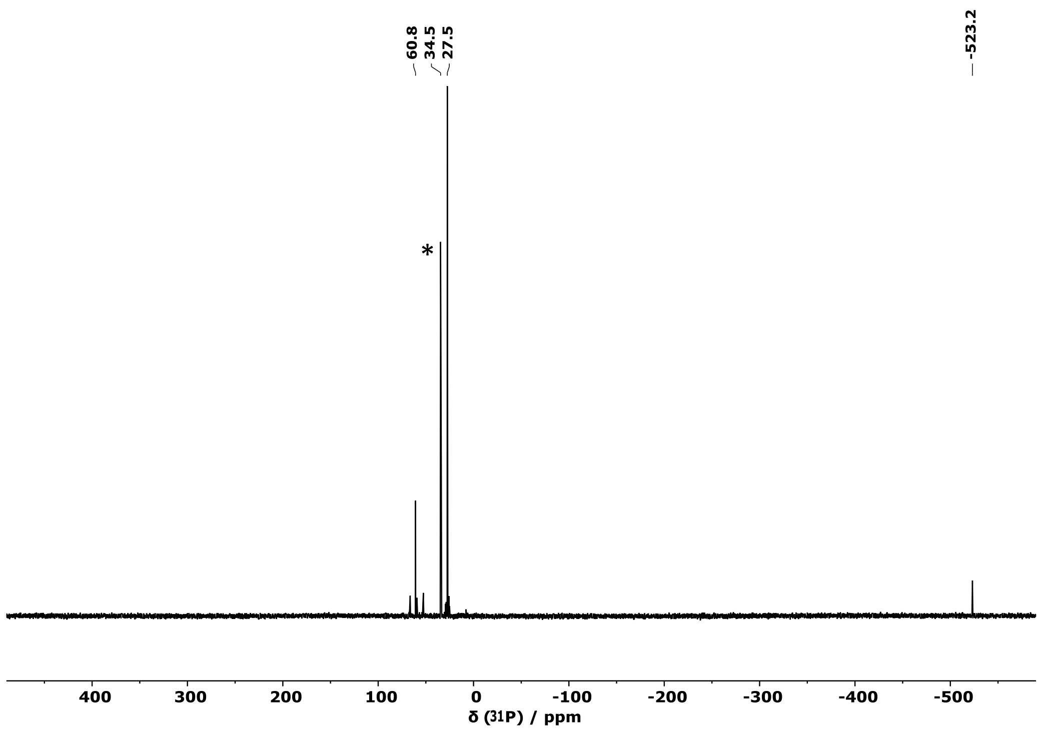


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum for the catalytic transformation of P_4 into THPC (**10**), driven by UV light irradiation (356 nm), with Ph_3PO as internal standard (*).

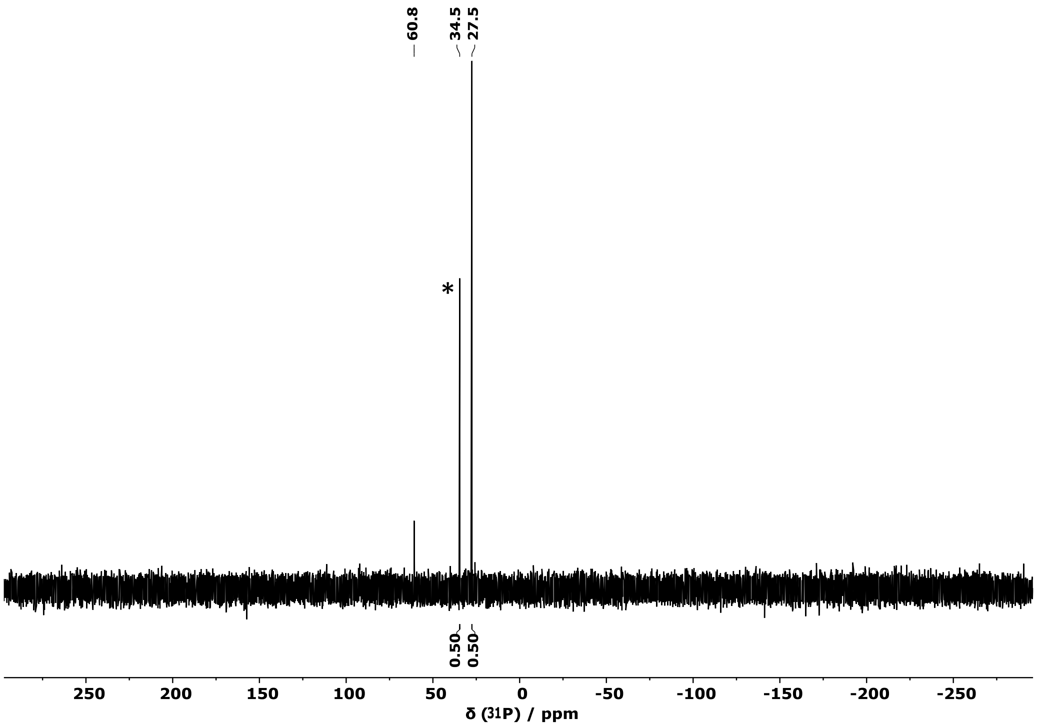


Figure S42. Quantitative single-scan, inverse gated $^{31}P\{^{1}H\}$ NMR spectrum for the catalytic transformation of P_4 into THPC (**10**), driven by UV light irradiation (356 nm), with Ph_3PO as internal standard (*).

S6. References

[1] U. Lennert, P. B. Arockiam, V. Streitferdt, D. J. Scott, C. Rödl, R. M. Gschwind, R. Wolf, *Nat. Catal.* **2019**, *2*, 1101-1106.

[2] D. J. Scott, J. Cammarata, M. Schimpf, R. Wolf, *Nat. Chem.* **2021**, *13*, 458-464.

[3] A. G. Davies, A. Sella, R. Sivasubramaniam, *J. Organomet. Chem.* **2006**, *691*, 3556-3561.