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Supplementary Information

Photochemical transformation of chlorobenzenes and white phosphorus into arylphosphines and phosphonium salts

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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 use of a GS Glovebox (GS117717). All glassware was oven-dried (160 °C) overnight prior to use. Benzene was dried over Na and stored over molecular sieves (3 Å). Acetonitrile, dimethyl sulfoxide and dimethylformamide were distilled from CaH_2 and stored over molecular sieves (3 Å). Benzene was distilled from Na/benzophenone and stored over molecular sieves (3 Å). Acetone was stirred over $CaSO_4$ (3 h) and distilled after dynamically drying over molecular sieves (3 Å). THF and toluene were purified using an MBraun SPS-800 system and stored over molecular sieves (3 Å). C_6D_6 was distilled from K and stored over molecular sieves (3 Å). All other chemicals were purchased from major suppliers (Aldrich, ABCR); liquids were purified by Kugelrohr distillation and freeze-pump-thaw degassed three times prior to use; P_4, Ph_3P and Ph_3PO were purified by sublimation; all others were used as received.

With the exception of *in situ* experiments (for details of which, see section S6), 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 δ, are reported in parts per million (ppm); ^{1}H and ^{13}C shifts are reported relative to $SiMe_4$ and were calibrated internally to residual solvent peaks, while ^{31}P shifts were referenced externally to 85 % H_3PO_4 (aq.).

NMR samples were prepared in the glovebox using NMR tubes fitted with screw caps. Optimization reactions (see S3) and photochemical phenylation reactions of $PhPH_2$, Ph_2PH, Ph_4P_2 and Ph_3P (see S7) were analyzed by $^{31}P\{^{1}H\}$ spectra using only a single scan (DS = 0, D1 = 2 s). The accuracy of this method was confirmed by preparing solutions of (*o*-tol)$_3$P or [Ph_4P]Cl and 0.05 mmol Ph_3PO in MeCN/PhH (1.5 mL, 0.5 mL, respectively), and comparing the measured and expected relative integrations (Figure S1).

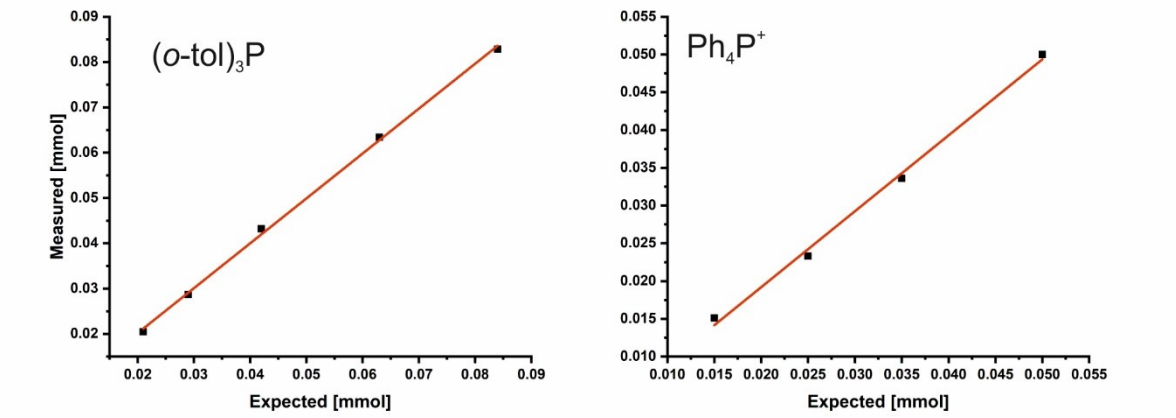


Figure S1. Plots showing the consistency between measured (by integration against 0.05 mmol Ph_3PO using a $^{31}P\{^{1}H\}$ experiment (zgig) with a single scan) and expected (based on mass added) molar quantities of (*o*-tol)$_3$P (left) or [Ph_4P]Cl (right) in MeCN/PhH (3:1) solutions.

Quantitative measurements for the substrate screening were conducted on Bruker Avance HD III 400 (400 MHz) spectrometers. Yields were determined by 1D $^{31}P\{^{1}H\}$ NMR spectroscopy. In order to meet quantitative conditions special attention was payed to the following aspects:

- Pulse lengths were calibrated. The O1P of the spectrum was set close to the frequencies of interest to enable maximum excitation. In cases where the distance between signals of interest was greater than 21000 Hz, one spectrum was recorded for each signal of interest, having its O1P close to the respective frequency.
- T_1 relaxation times were determined for all peaks of interest and a D1 of ≥ 5 × T_1 was used to ensure full relaxation between scans.
- The NS was adjusted so that the S/N-ratio (signal to noise ratio) was higher than 100/1. In order to reduce measurement time and to increase the S/N-ratio compared to a standard 1D experiment using only a 90° pulse (zg experiment), the zgig pulse program (inverse gated decoupled) was used, applying proton decoupling during the acquisition time. Since the zgig pulse program uses decoupling, it had to be ensured that any signal enhancement due to NOE (nuclear Overhauser effect) is negligible. Therefore, zg and zgig experiments were conducted and the integrals of the signals of interest were compared. For all reaction mixtures investigated, the integrals corresponding to both the internal standard (Ph_3PO) and the product stayed constant.
- After acquisition, the spectra were processed and integrated, and the yields were determined by referencing the integral of the product to that of the standard Ph_3PO.
- The quantitative spectra of the substrate screening are shown in S4.

S2. General procedure for photochemical functionalization of P_4 (0.04 mmol scale)

To a 10 mL stoppered tube equipped with a stirring bar were added the appropriate chlorobenzene derivative (0.4 mmol, 10 equiv. based on the phosphorus atom), organic photoreductant TDAE[1] (0.2 mmol, 5 equiv. based on the phosphorus atom), and P_4 (0.01 mmol, 1 equiv., as a stock solution in 71.3 µL benzene). The mixture was dissolved in acetone (0.5 mL). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S2), and irradiated with UV light (365 nm, 4.3 V, 700 mA, Osram OSLON SSL 80) for 20 h (unless stated otherwise). Ph_3PO (0.02 mmol, stock solution in benzene) was subsequently added to act as an internal standard. The resulting mixture was subjected to NMR analysis.

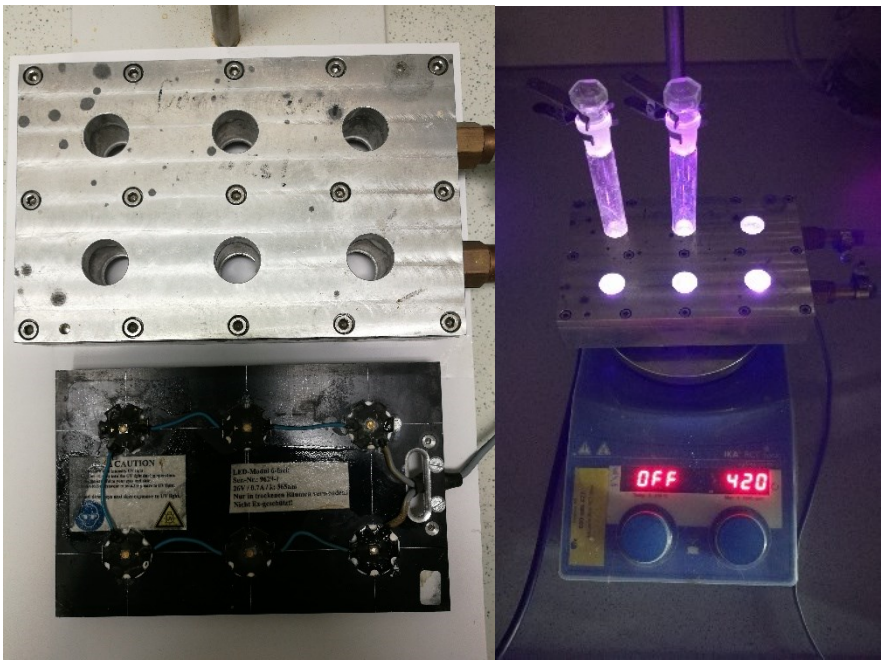
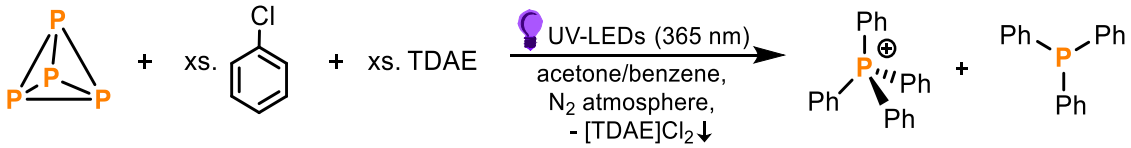


Figure S2. Illustration of the equipment setup used for photochemical reactions at 0.04 mmol scale.

S3. Optimization of reaction conditions

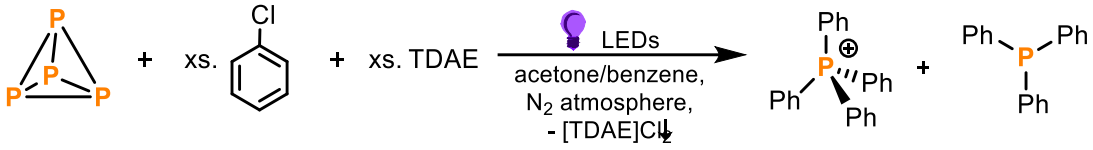
Table S1. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: screening of **control experiments**.[a]



Entry	Conditions	Full conv. of P_4?	Conv. to **$[Ph_4P]Cl$ / %**	Conv. to **Ph_3P / %**
1	Standard[a]	✓	53	9
2	No light	X	0	0
3	No TDAE	X	0	0
4	No PhCl	X	0	0
5	PhF instead of PhCl	X	0	0
6	PhBr instead of PhCl	✓	43	10
7	PhI instead of PhCl	✓	14	10
8	P_{red} instead of P_4	–	0	0

[a] For the general procedure, see section S2.

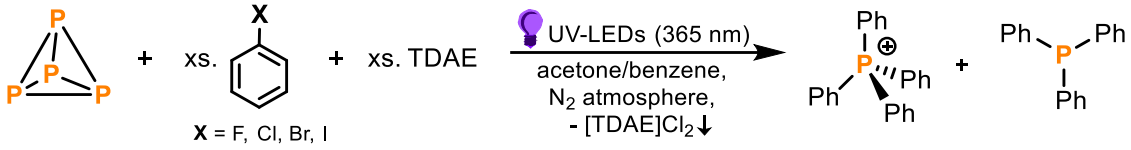
Table S2. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: screening of **LEDs** at different **temperatures**.[a]



Entry	LEDs	Full conv. of P_4?	Conv. to **$[Ph_4P]Cl$ / %**	Conv. to **Ph_3P / %**	Conv. to **Ph_4P_2 / %**	Conv. to **Int1 / %**
1	455 nm	✓	21	8	3	3
2	455 nm[b]	✓	17	11	3	0[~]
3	420 nm	✓	52	15	0[~]	0[~]
4	420 nm[c]	✓	37	12	0[~]	4
5	400 nm	✓	43	15	0[~]	4
6	385 nm	✓	38	9	0[~]	0[~]
7	365 nm[a]	✓	53	9	1	
8	365 nm[d]	✓	43	11	2	0[~]
9	365 nm[c]	✓	39	10	0[~]	2

[a] The general procedure (section S2) was modified to use the LEDs indicated. For the general procedure, see section S2. [b] Photoreactor 7W, 36 °C. [c] Cooling with cryostat to −5 °C. [d] Cooling with cryostat to 0 °C. [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

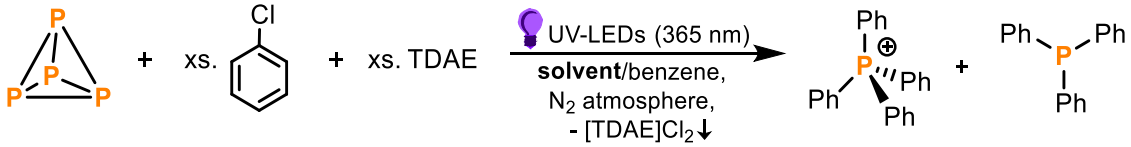
Table S3. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: screening of **aryl halides**.[a]



Entry	Aryl halide	Full conv. of P_4?	Conv. to $[Ph_4P]X$ / %	Conv. to Ph_3P / %	Conv. to Ph_4P_2 / %	Conv. to Int1 / %
1	Fluorobenzene	X	0	0	0	0
2	Chlorobenzene[a]	✓	53	9	1	0
3	Bromobenzene	✓	43	10	0[~]	4
4	Iodobenzene	✓	14	10	0[~]	4

[a] For the general procedure, see section S2. [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

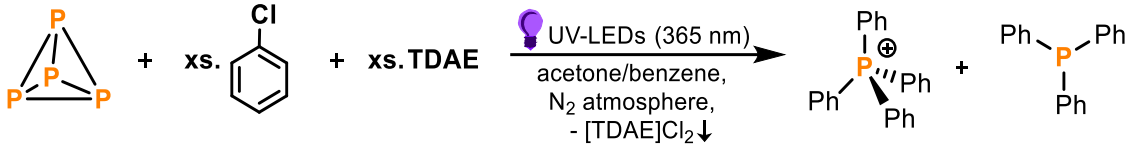
Table S4. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: screening of **solvents**.[a]



Entry	Solvent	Full conv. of P_4?	Conv. to $[Ph_4P]Cl$ / %	Conv. to Ph_3P / %	Conv. to Ph_4P_2 / %	Conv. to Int1 / %
1	Acetone[a]	✓	53	9	1	0
2	Acetone[b]	✓	47	4	0[~]	0
3	Acetone[c]	✓	41	10	0[~]	0[~]
4	Acetone[d]	✓	31	13	0[~]	0[~]
5	Benzene	✓	27	11	0[~]	5
6	Acetonitrile	✓	31	11	2	0
7	THF	✓	0[~]	2	11	0
8	Toluene	✓	19	7	0[~]	2
9	DMSO	✓	6	0	0	0
10	DMF	✓	11	11	0[~]	0
11	Chlorobenzene	✓	23	12	0[~]	7

[a] The general procedure (section S2) was modified to use the solvent system indicated (identical solvent volume). [b] 0.25 mL solvent volume. [c] 1.0 mL solvent volume. [d] 2.0 mL solvent volume. [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

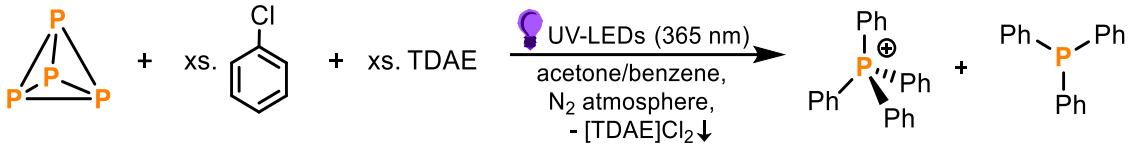
Table S5. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: screening of **stoichiometry**.[a][b]



Entry	Stoichiometry[b] TDAE:PhCl	Full conv. of P_4?	Conv. to $[Ph_4P]Cl$ / %	Conv. to Ph_3P / %	Conv. to Ph_4P_2 / %	Conv. to Int1 / %
1	8:16	✓	8	17	0	8
2	12:24	✓	23	16	0[~]	6
3	16:16	✓	40	12	3	0[~]
4	16:16[c]	✓	12	14	1	10
5	16:16[d]	✓	19	16	0[~]	11
6	16:16[e]	✓	11	14	0	9
7	16:16[f]	✓	11	12	0	13
8	16:16[g]	✓	8	10	0[~]	12
9	32:16	✓	3	9	0	7
10	20:20	✓	12	14	0[~]	11
11	20:40[a]	✓	53	9	1	0
12	20:40[c]	✓	48	10	0[~]	0
13	(2 · 20):40[h]	✓	50	8	0[~]	0
14	20:40[i]	✓	42	11	0	0[~]
15	20:40[j]	✓	43	9	0[~]	0[~]
16	40:20	✓	5	10	0[~]	9
17	40:20[c]	✓	4	9	0[~]	8
18	40:40	✓	26	12	5	0[~]
19	40:40[d]	✓	30	15	0[~]	1

[a] For the general procedure, see section S2. [b] Listed equivalents are defined per P_4 molecule. [c] 0.25 mL solvent volume. [d] Cooling with cryostat to 0 °C. [e] Cooling with cryostat to −5 °C. [f] 400 nm LED. [g] 420 nm LED. [h] To a reaction with standard conditions (Entry 10, 20:40, UV, 20h) another 20 equiv. TDAE were added and irradiated for additional 20h. [i] modified P_4 concentration (0.005 mmol). [j] modified P_4 concentration (0.02 mmol). [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

Table S6. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: **kinetic investigations**.[a]



Entry	**Time**	Full conv. of **P_4**?	Conv. to **$[Ph_4P]Cl$** / %	Conv. to **Ph_3P** / %	Conv. to **Ph_2PH** / %	Conv. to **Ph_4P_2** / %	Conv. to **Int1** / %
1	5 min	X	0[~]	0[~]	0[~]	0[~]	0[~]
2	10 min	✓	0[~]	0[~]	0[~]	0[~]	0[~]
3	30 min	✓	0[~]	2	2	2	2
4	1 h	✓	17	19	0	0[~]	11
5	3 h	✓	30	11	0	0	8
6	5 h	✓	35	11	0	0	6
7	7 h	✓	34	10	0	0	8
8	20 h[a]	✓	53	9	0	1	0
9	40 h	✓	48	8	0	1	0

[a] For the general procedure, see section S2. [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

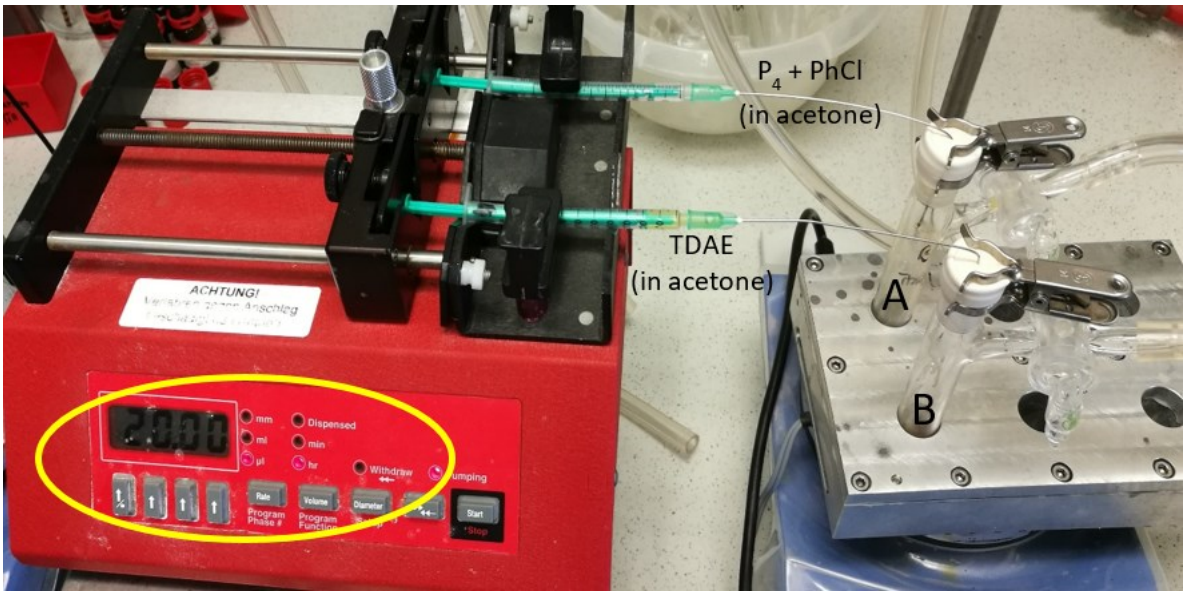
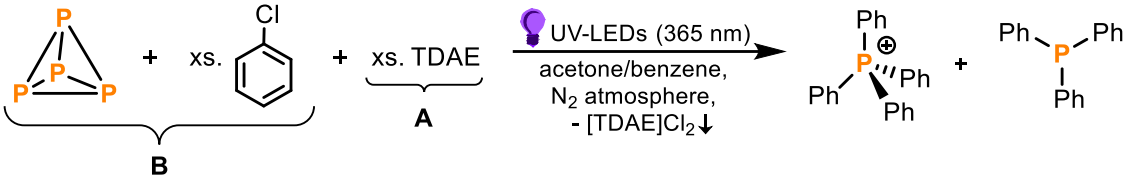


Figure S3. Illustration of the equipment setup used for slow addition via syringe pump for the photochemical reactions at 0.04 mmol scale. Standard reaction conditions: Chlorobenzene (0.4 mmol), TDAE (0.2 mmol) and P_4 (0.01 mmol) in acetone (0.5 mL). Reaction 1: slow addition of a P_4/PhCl mixture in acetone to TDAE/acetone solution (A). Reaction 2: slow addition of TDAE in acetone to a P_4/PhCl/acetone mixture (B). Syringe pump conditions: injected syringe volume 250 µL (syringe dead volume 100 µL), injection rate 20 µL/hour, injection period 12.5 hours, irradiation period 20h.

Table S7. Photochemical functionalization of P_4 to $[Ph_4P]Cl$ and Ph_3P: **slow addition** via syringe pump.[a]

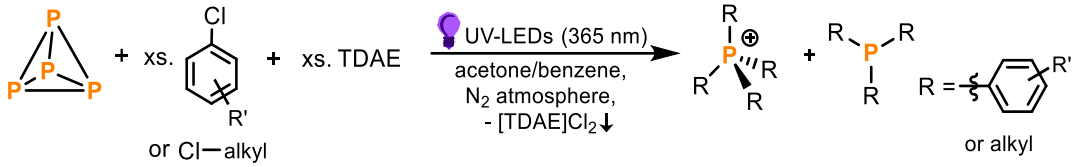


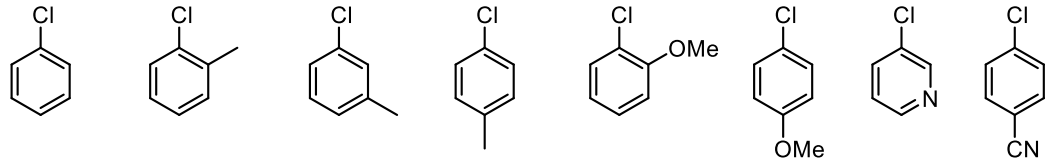
Entry	Schlenk	Slow addition	Full conv. of P_4?	Conv. to $[Ph_4P]Cl$ / %	Conv. to Ph_3P / %	Conv. to Ph_4P_2 / %	Conv. to Int1 / %
1	**A** (TDAE)	P_4/PhCl	X	11	6	0[~]	2
2	**B** (P_4 + PhCl)	TDAE	✓	37	0[~]	0[~]	0[~]

[a] For the general procedure, see section S2. [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

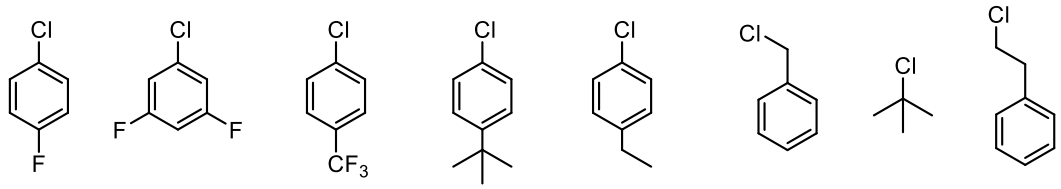
S4. Characterization of optimized 0.04 mmol scale reactions

Table S8. Substrate scope for photochemical P_4 functionalization.





1 **2** **3** **4** **5** **6** **7** **8**



9 **10** **11** **12** **13** **14** **15** **16**

Substrate[a]	R’	Conv. to **[R4P]Cl** / %	Conv. to **R3P** / %
1	R’ = H	53	9
2	R’ = 2-Me	0	10
3	R’ = 3-Me	39	16
4	R’ = 4-Me	35	10
5	R’ = 2-OMe	0	3
6	R’ = 4-OMe	20	6
7	3-PyrCl	27	7
8	R’ = 4-CN	0	7
9	R’ = 4-F	9	11
10	R’ = 3,5-F	0	8
11	R’ = 4-CF_3	0	9
12	R’ = 4-^{t}Bu	17	14
13	R’ = 4-Et	24	9
14	BnCl	0	27
15	^{t}BuCl	0	5
16	(2-chloroethyl) benzene	0	75

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing chlorobenzene (Entry 1) with chlorobenzene derivatives.

The conversions were determined by quantitative $^{31}P\{^1H\}$ (zgig) NMR experiments (161.98 MHz, 300 K, C_6D_6) as mentioned in the text (Ph_3PO (0.02 mmol) as internal standard, see S1 for further information).

S4.1. Tetraphenylphosphonium chloride & Triphenylphosphine

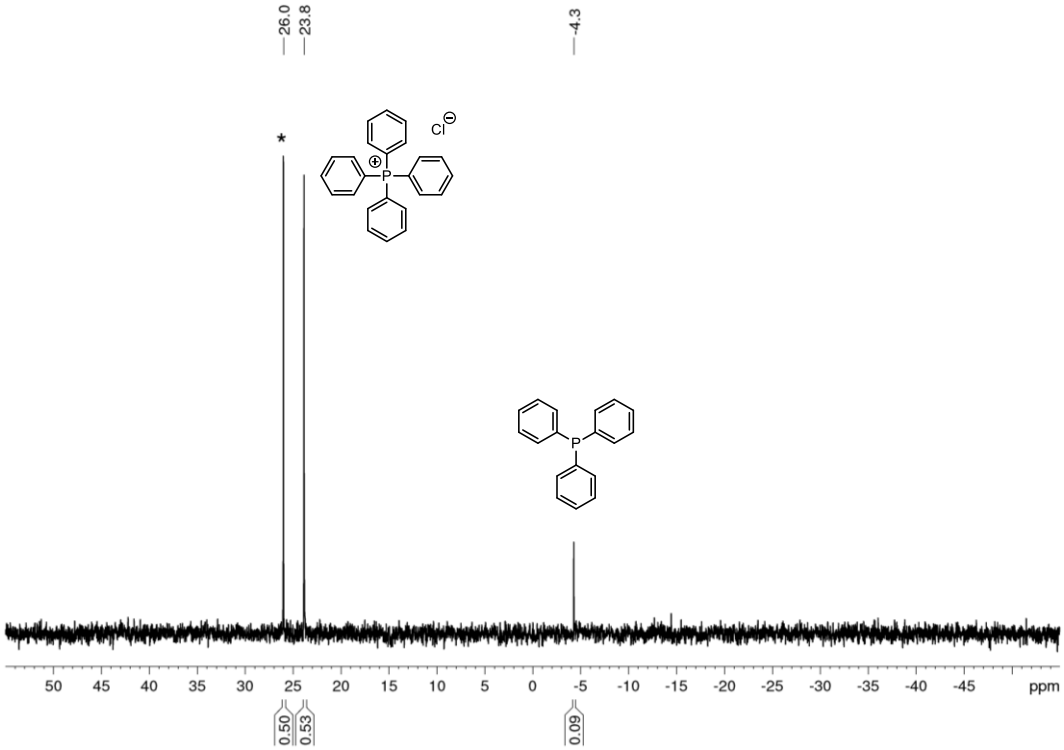


Figure S4. Quantitative single scan $^{31}P\{^1H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using chlorobenzene (Table S8, Entry 1). * marks the internal standard Ph_3PO (0.02 mmol).

S4.2. Tri(*o*-tolyl)phosphine

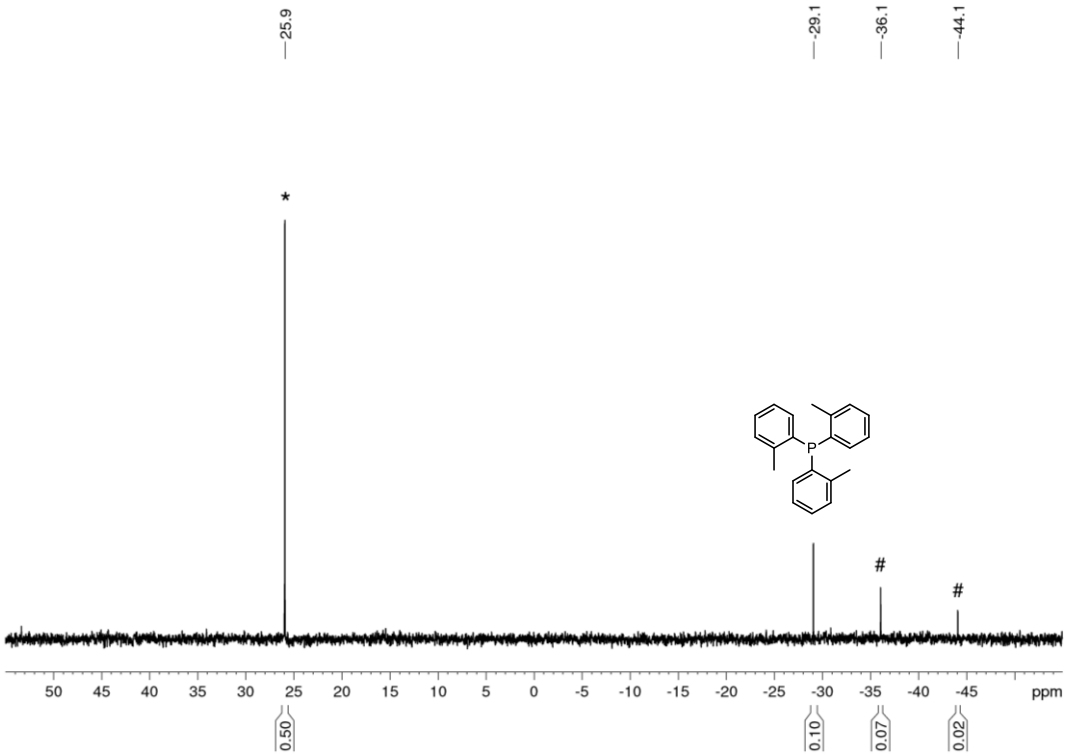


Figure S5. Quantitative single scan $^{31}P\{^1H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 2-chlorotoluene (Table S8, Entry 2). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signals of unknown by-products.

S4.3. Tetra(*m*-tolyl)phosphonium chloride & Tri(*m*-tolyl)phosphine

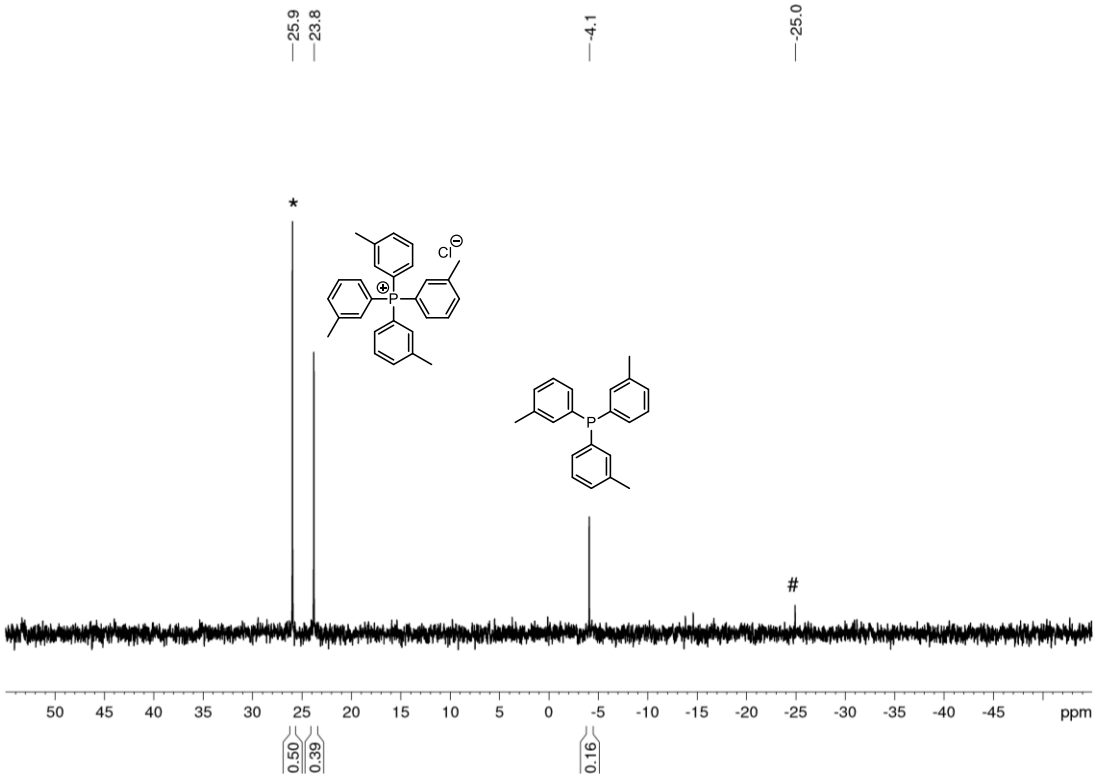


Figure S6. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 3-chlorotoluene(Table S8, Entry 3). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.4. Tetra(*p*-tolyl)phosphonium chloride & Tri(*p*-tolyl)phosphine

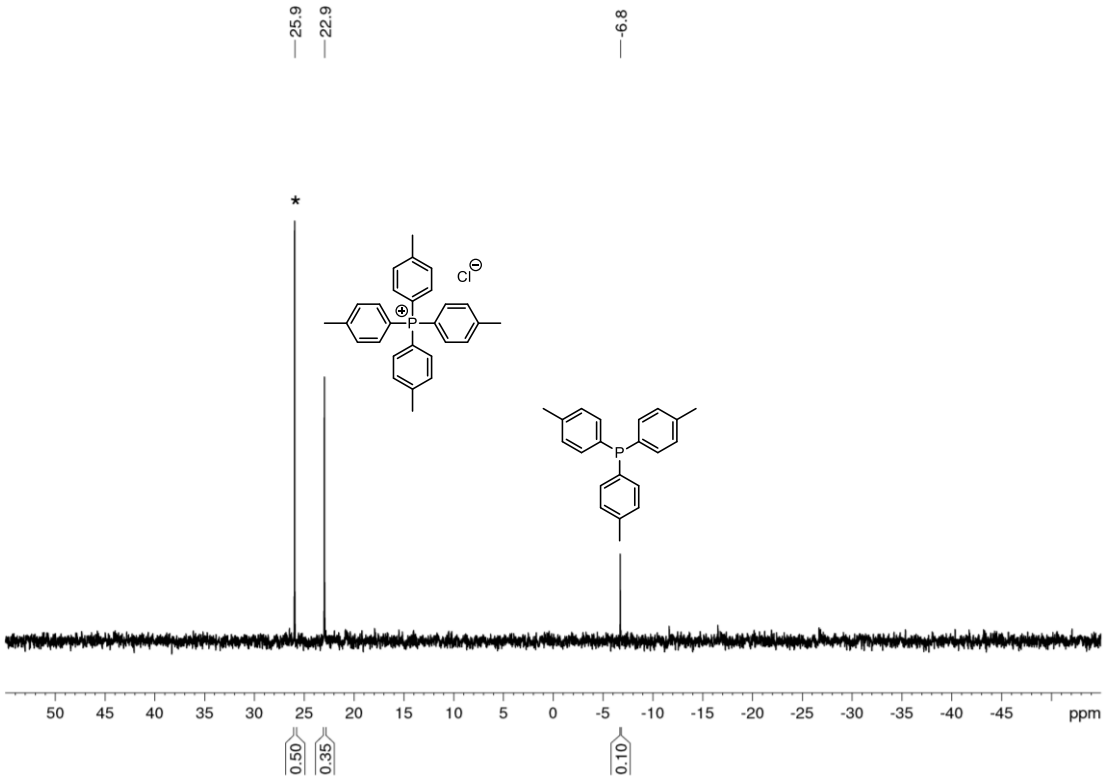


Figure S7. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 4-chlorotoluene (Table S8, Entry 4). * marks the internal standard Ph_3PO (0.02 mmol).

S4.5. Tris(2-methoxyphenyl)phosphine

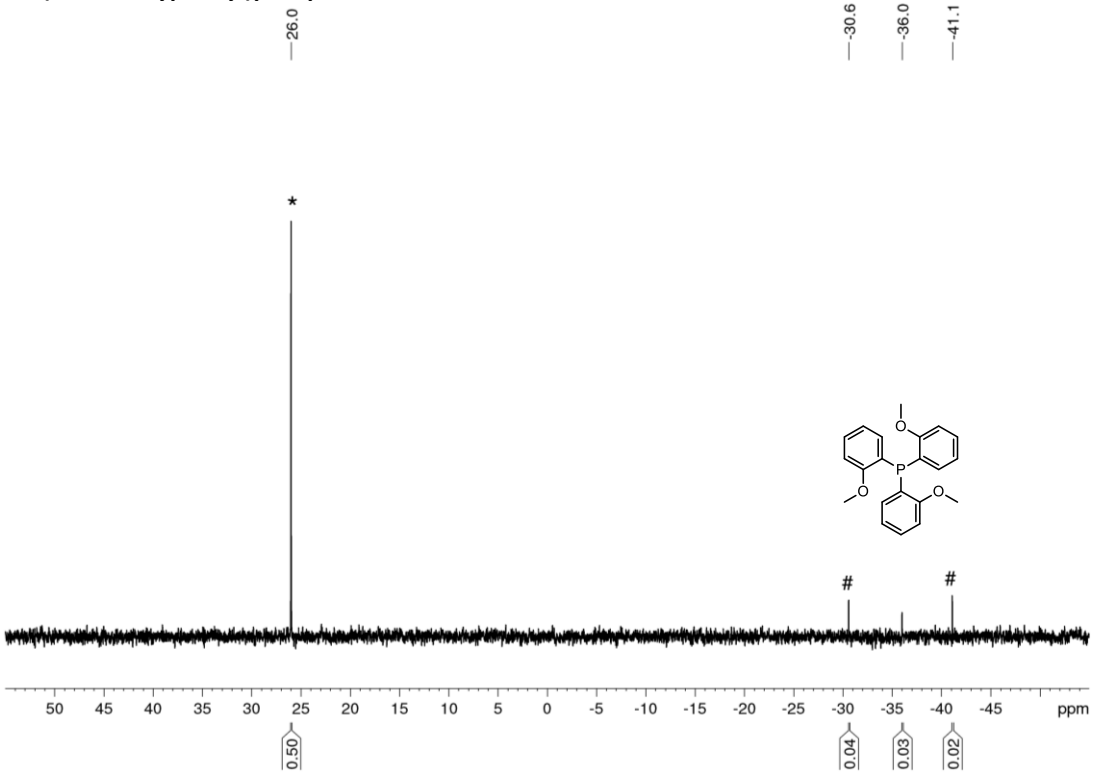


Figure S8. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 2-chloroanisole (Table S8, Entry 5). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signals of unknown by-products.

S4.6. Tetrakis(4-methoxyphenyl)phosphonium chloride & Tris(4-methoxyphenyl)phosphine

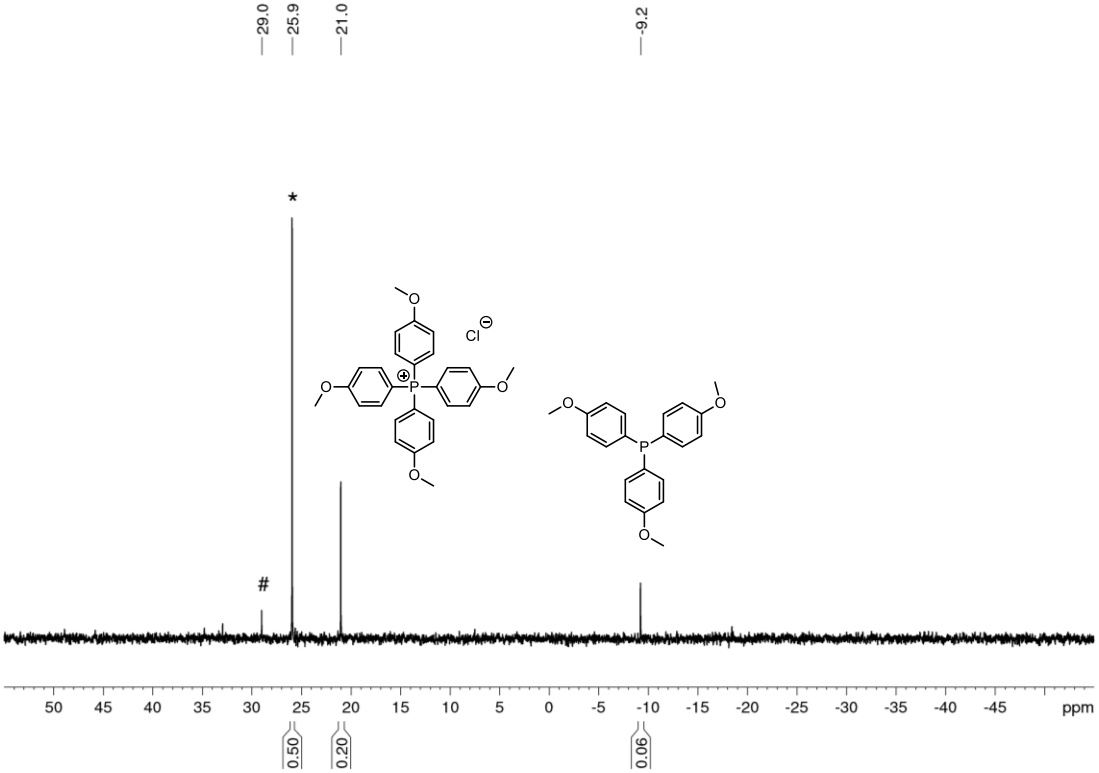


Figure S9. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 4-chloroanisole (Table S8, Entry 6). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.7. Tetrakis(pyridin-3-yl)phosphonium chloride & Tris(pyridine-3-yl)phosphine

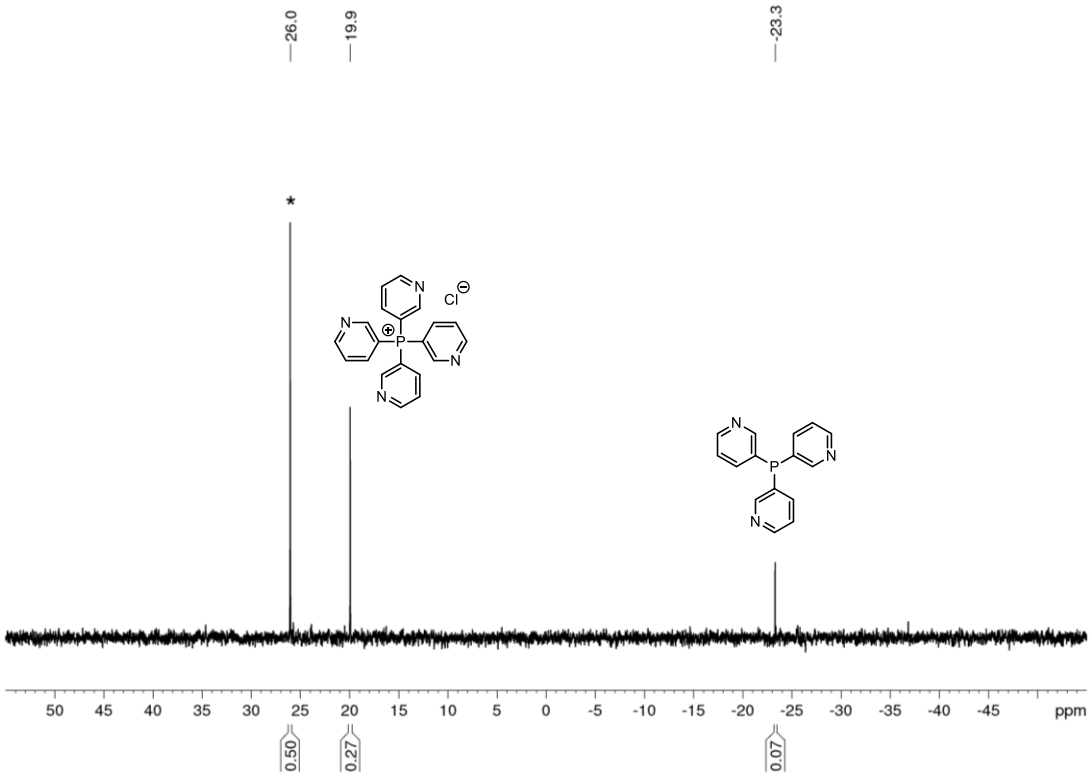


Figure S10. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 3-chloropyridine (Table S8, Entry 7). * marks the internal standard Ph_3PO (0.02 mmol).

S4.8. Tris(4-benzonitrile)phosphine

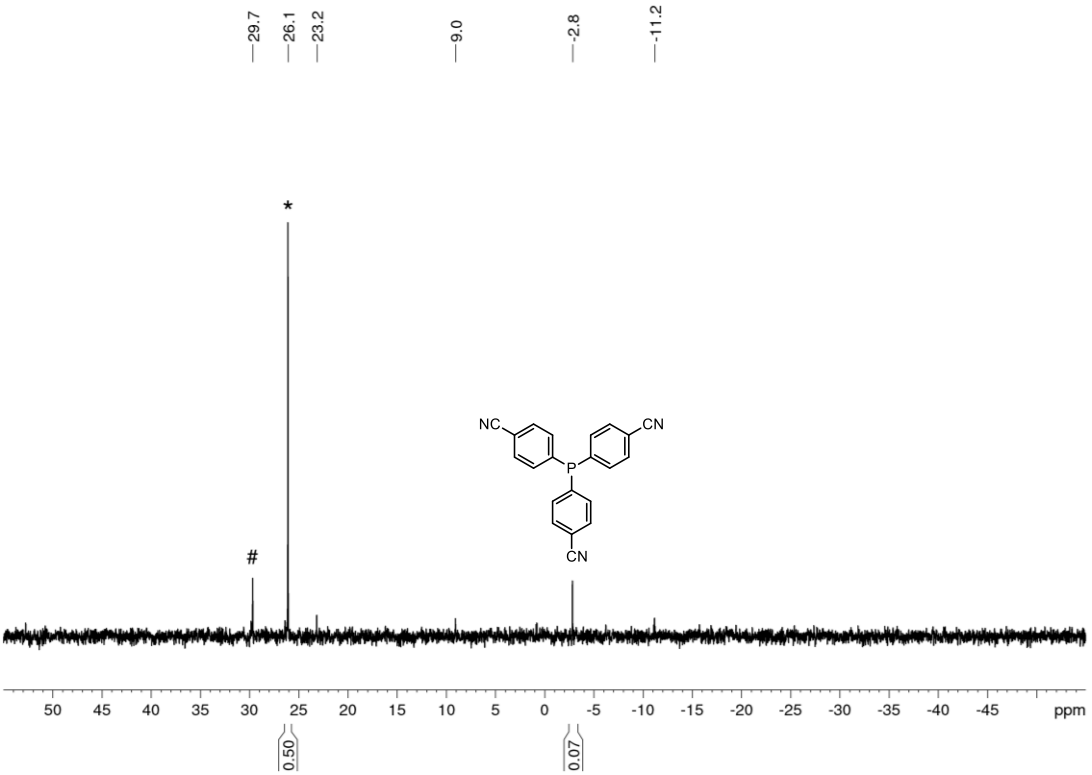


Figure S11. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 4-chlorobenzonitrile (Table S8, Entry 8). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.9. Tetrakis(4-fluorophenyl)phosphonium chloride & Tris(4-fluorophenyl)phosphine

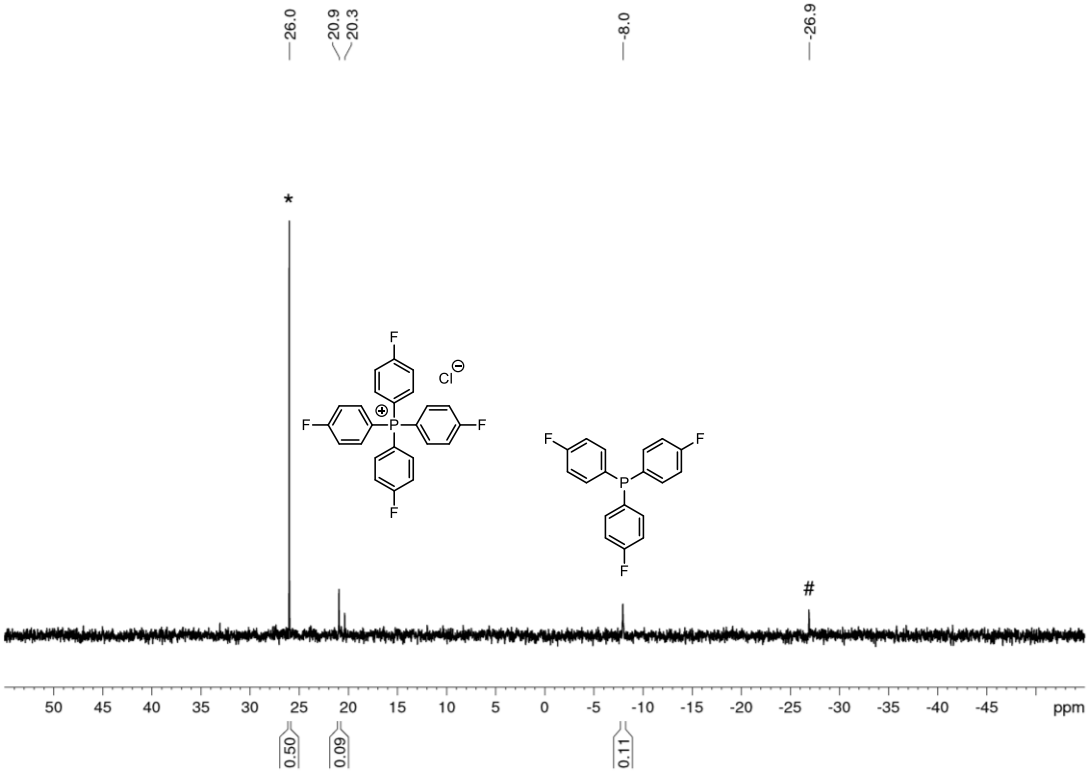


Figure S12. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-chloro-4-fluorobenzene (Table S8, Entry 9). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.10. Tris(3,5-difluorophenyl)phosphine

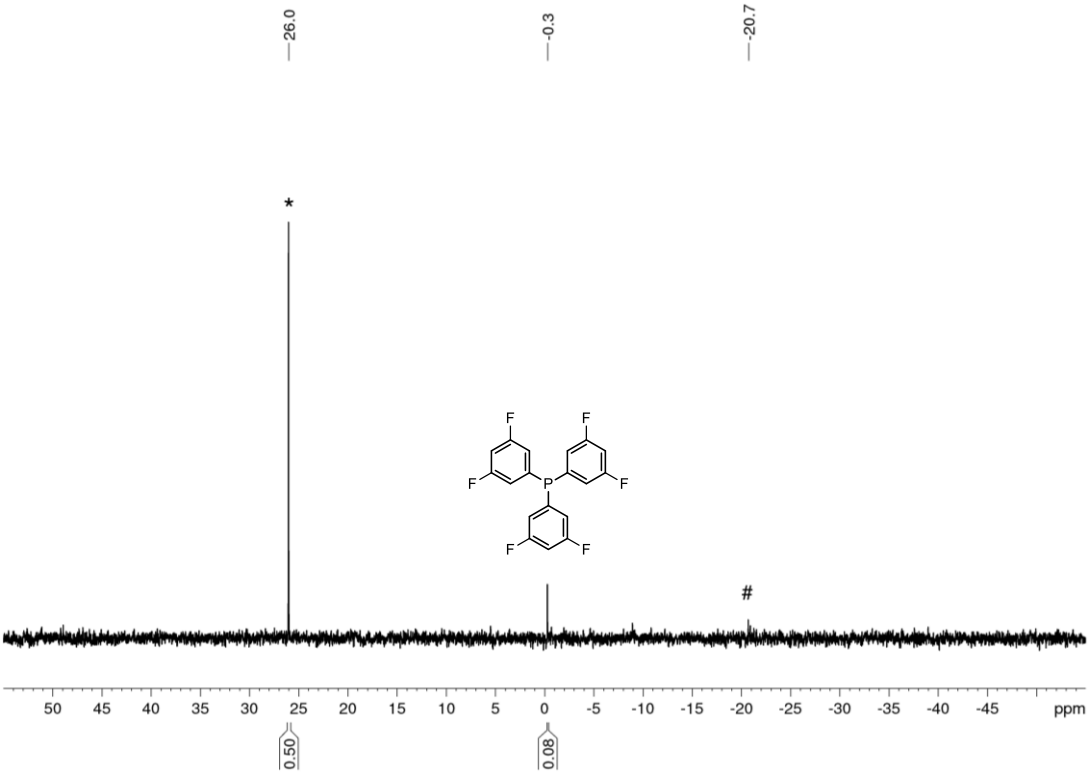


Figure S13. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-chloro-3,5-difluorobenzene (Table S8, Entry 10). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.11. Tris(4-(trifluoromethyl)phenyl)phosphine

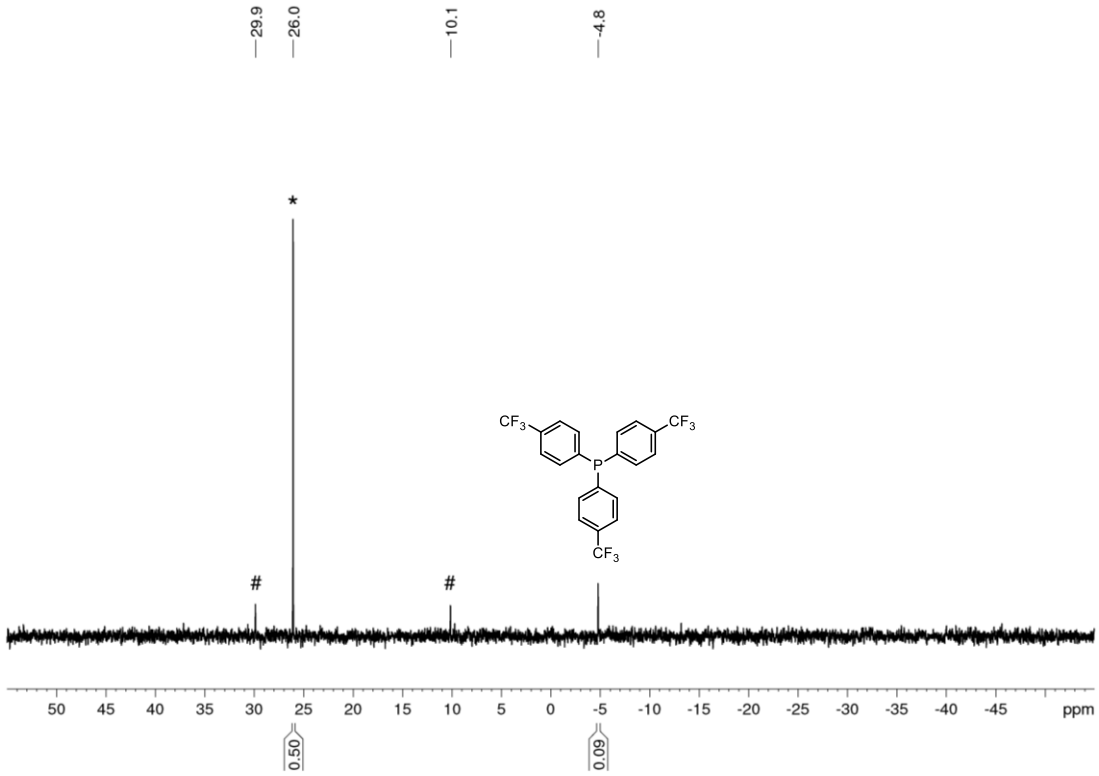


Figure S14. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-chloro-4-(trifluoromethyl)benzene (Table S8, Entry 11). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signals of unknown by-product.

S4.12. Tetrakis(4-(*tert*-butyl)phenyl)phosphonium chloride & Tris(4-(*tert*-butyl)phenyl)phosphine

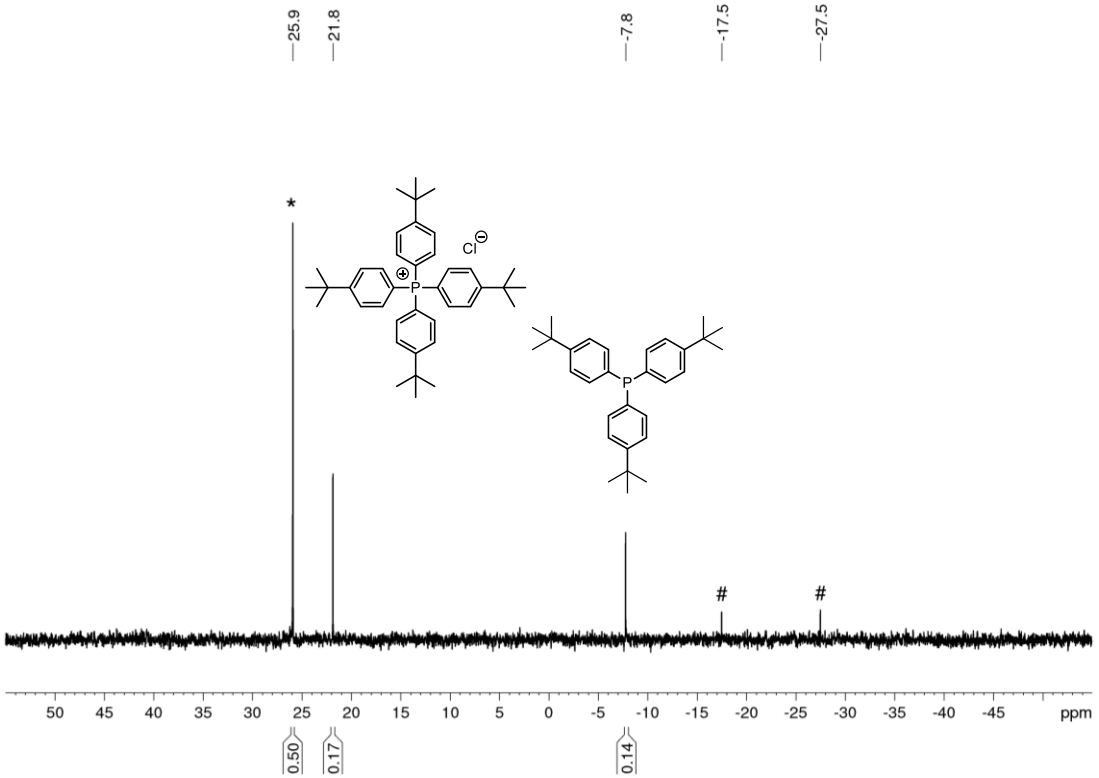


Figure S15. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-(*tert*-butyl)-4-chlorobenzene (Table S8, Entry 12). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signals of unknown by-products.

S4.13. Tetrakis(4-ethylphenyl)phosphonium chloride & Tris(4-ethylphenyl)phosphine

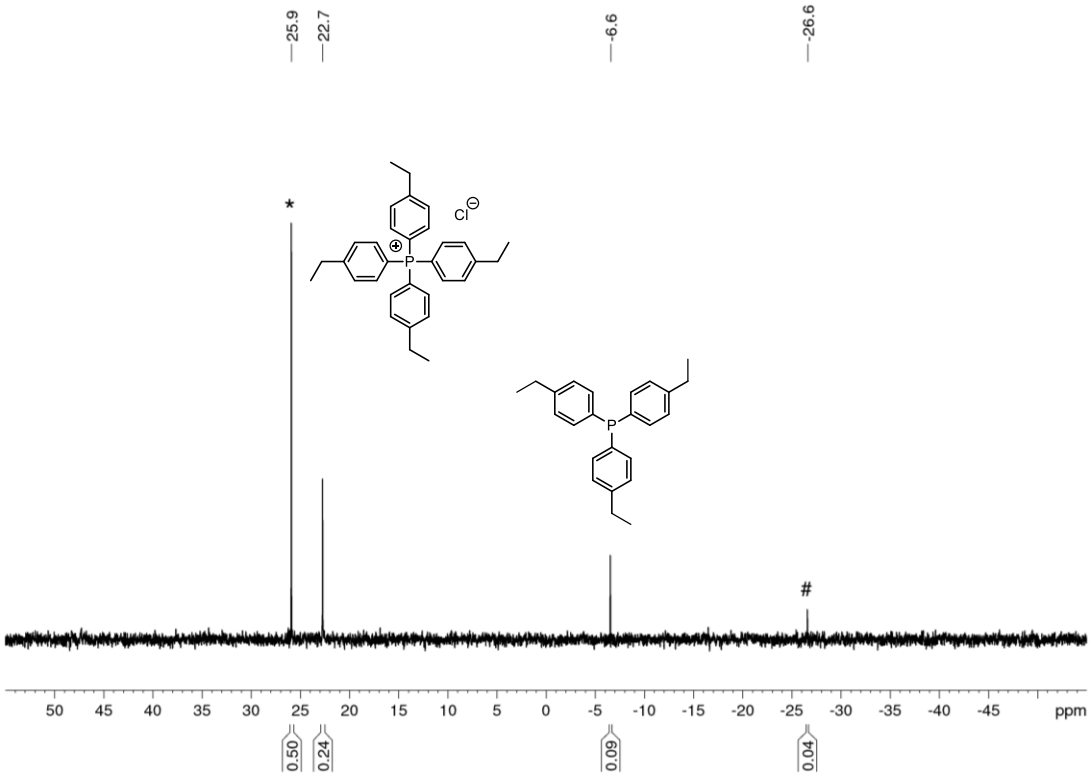


Figure S16. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-chloro-4-ethylbenzene (Table S8, Entry 13). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.14. Tribenzylphosphine

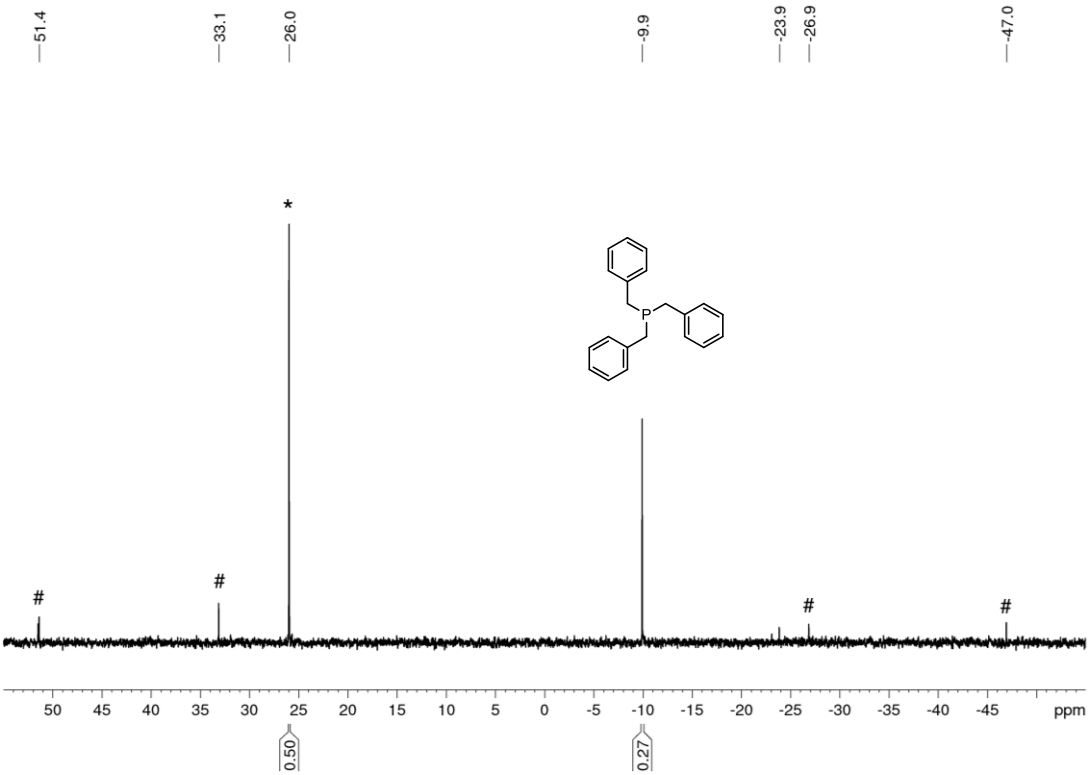


Figure S17. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using benzyl chloride (Table S8, Entry 14). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signals of unknown by-products.

S4.15. Tri(*tert*-butyl)phosphine

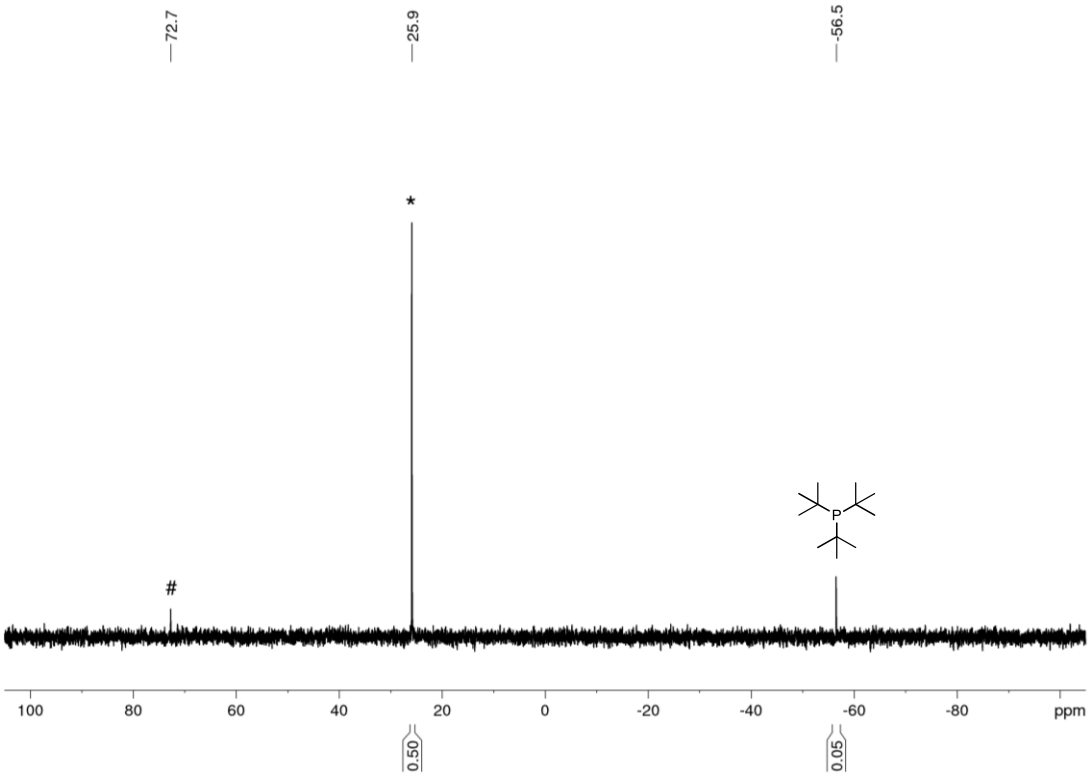


Figure S18. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using tert-butyl chloride (Table S8, Entry 15). * marks the internal standard Ph_3PO (0.02 mmol). # marks the signal of an unknown by-product.

S4.16. Tris(phenylethyl)phosphine

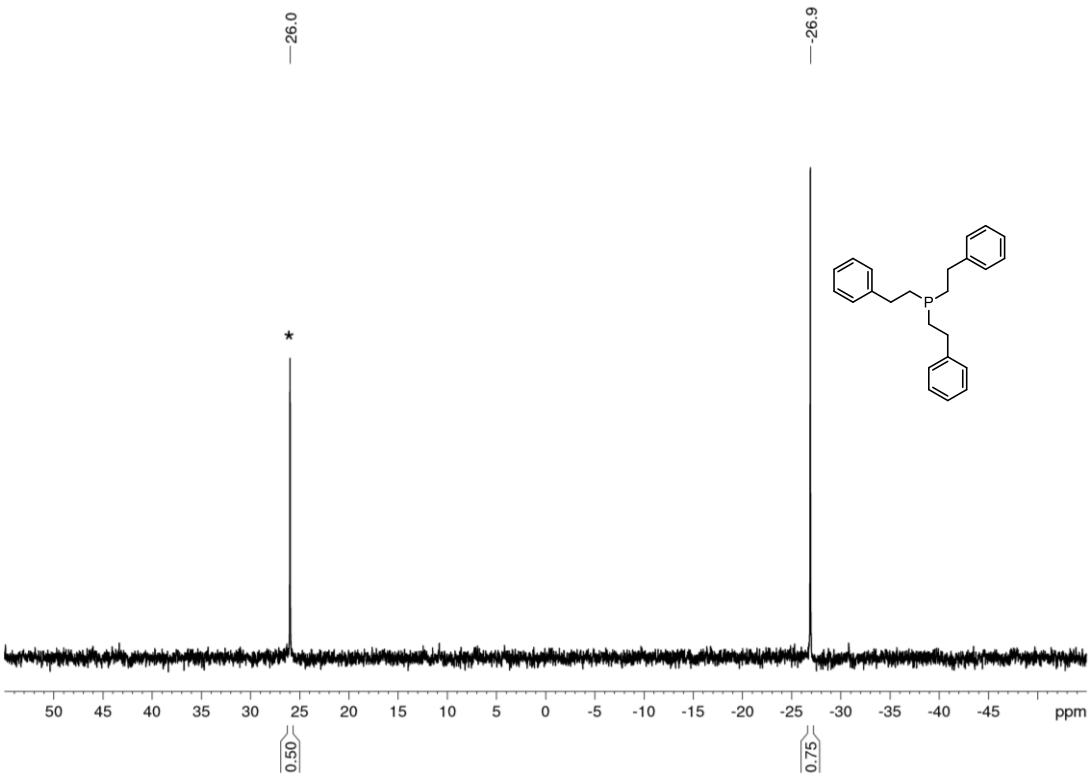


Figure S19. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using (2-chloroethyl)benzene (Table S8, Entry 16). * marks the internal standard Ph_3PO (0.02 mmol).

S4.17 Reactivity of 1,4-hetero-halogenated benzene derivatives

S4.17.1 Tetrakis(4-chlorophenyl)phosphonium iodide & Tris(4-chlorophenyl)phosphine[2]

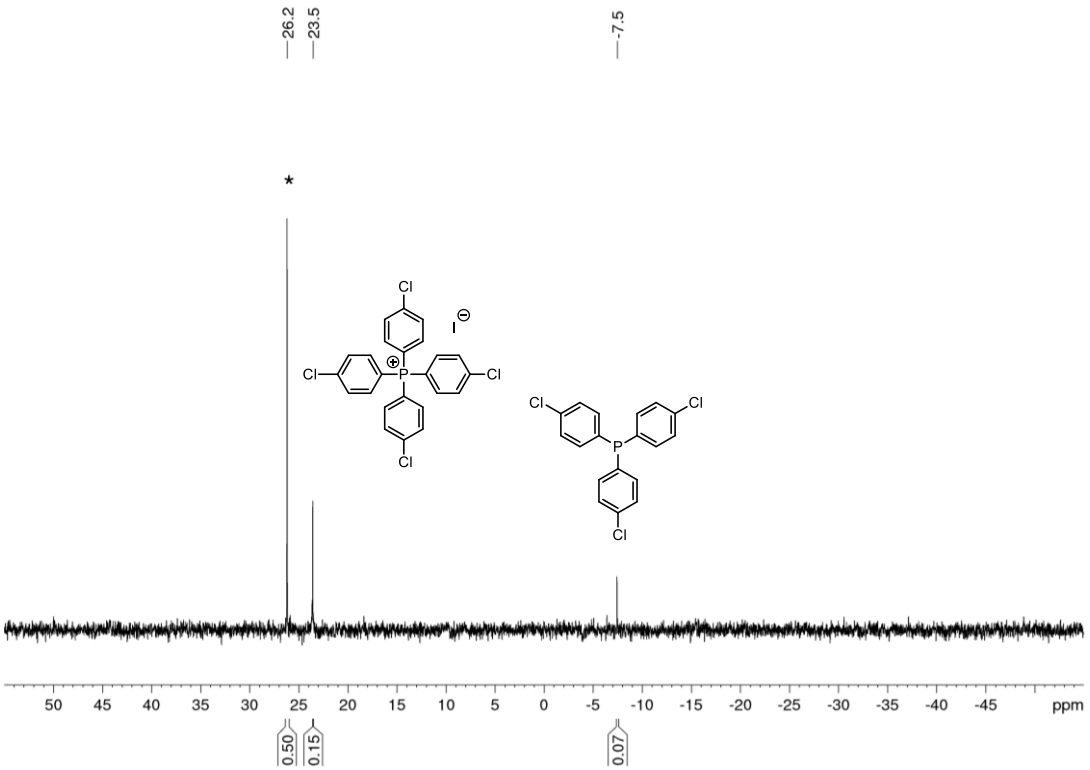


Figure S20. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-chloro-4-iodobenzene. * marks the internal standard Ph_3PO (0.02 mmol). The signals were assigned to the stated products based on the chemical shifts found in the literature.[2]

S4.17.2 Mixed activation of the C-X bonds by using 1-bromo-4-chlorobenzene

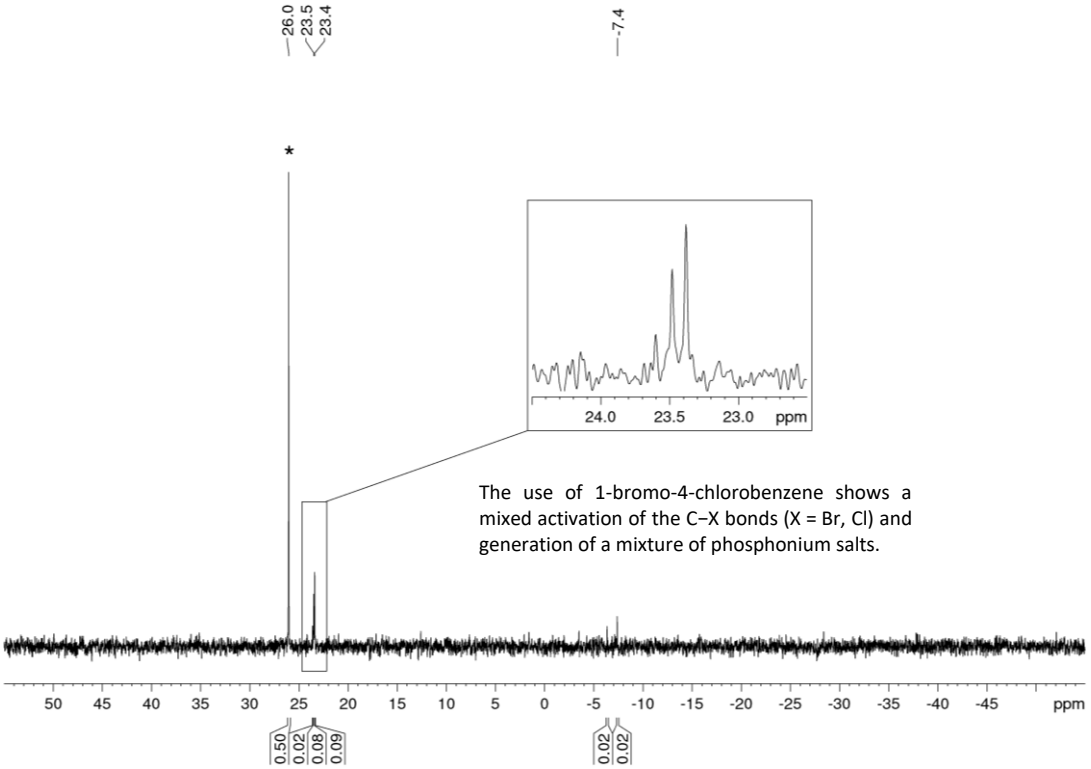


Figure S21. Quantitative single scan $^{31}P\{^{1}H\}$ (zgig) NMR spectrum for the photochemical functionalization of P_4 using 1-bromo-4-chlorobenzene. * marks the internal standard Ph_3PO (0.02 mmol).

S4.18. Unsuccessful substrate scope

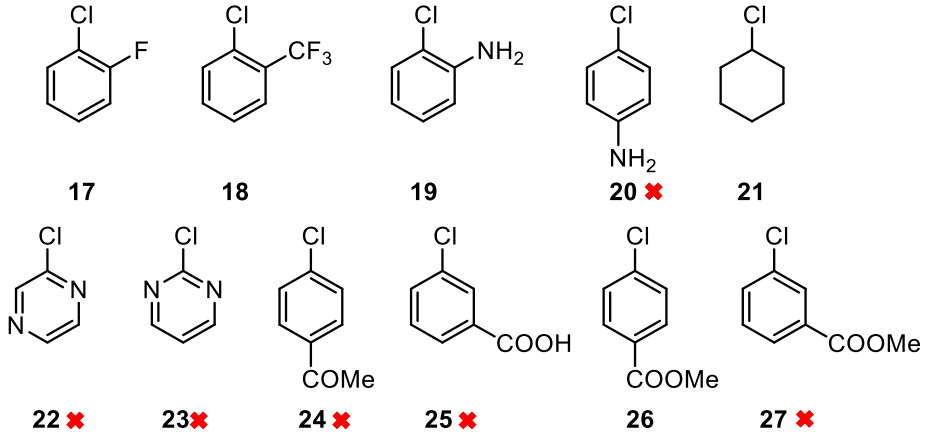


Figure S22. Further substrate scope for photochemical P_4 functionalization. These substrates were not able to generate the corresponding phosphonium salts and phosphines. The reactions with the substrates highlighted with a red sign did not show full conversion of P_4 by $^{31}P\{^1H\}$ NMR. Substrates **17**, **19**, **20** and **22-25** showed no signal beside the internal standard PPh_3O and P_4 (see red signs above, no P_4 in the reactions with **17** and **19**). Using substrates **18**, **21**, **26** and **27** (P_4 still left) the $^{31}P\{^1H\}$ NMR showed very unselective reactions with a lot of unknown side-products, but no product formation.

S5. Isolation and characterization of selected products (reactions at 0.8 mmol scale)

Figure S23. Illustration of the equipment setup used for photochemical reactions at 0.8 mmol scale.

S5.1. Photochemical preparation of tetraphenylphosphonium chloride from P_4 (0.8 mmol scale)

To a 100 mL stoppered tube equipped with a stirring bar were added chlorobenzene (8.0 mmol, 10 equiv. based on the phosphorus atom), organic photoreductant TDAE[1] (4.0 mmol, 5 equiv. based on the phosphorus atom), and P_4 (0.2 mmol, 1 equiv., as a stock solution in 1.426 mL benzene). The mixture was dissolved in acetone (5 mL). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S21), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 20 h. Quantitative $^{31}P\{^1H\}$ (zgig) NMR spectroscopy (Ph_3PO as internal standard) showed 54% tetraphenylphosphonium chloride and 8% triphenylphosphine (see Figure S24).

The reaction mixture was filtered to remove the side product $[TDAE]Cl_2$ which was formed during the reaction. The solvent was evaporated *in vacuo* and the red orange waxy residue was washed with diethyl ether (4 x 3 mL) to separate the unreacted chlorobenzene, TDAE and the intermediate triphenylphosphine (Ph_3P) and tetraphenyldiphosphine (Ph_4P_2) from the tetraphenylphosphonium chloride. The residue was dissolved in H_2O (8 mL) and filtered. Subsequently, aqueous HCl (1 M, 10 mL) was added to the filtrate, and the solution was extracted with DCM (3 x 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Subsequently, the light yellow residue was redissolved in DCM. Addition of *n*-hexane to the DCM solution afforded NMR-spectroscopically pure tetraphenylphosphonium chloride as a white solid after filtration (57.2 mg, 19%).

The characterization data of the product are consistent with the data found in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm]: 7.94-7.90 (m, 4H), 7.81 (dt, *J* = 7.8, 3.5 Hz, 8H), 7.64 (dd, *J* = 12.9, 7.6 Hz, 8H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ[ppm]: 135.8 (d, *J* = 3.0 Hz), 134.5 (d, *J* = 10.3 Hz), 130.9 (d, *J* = 12.9 Hz), 117.5 (d, *J* = 89.5 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ[ppm]: 23.8

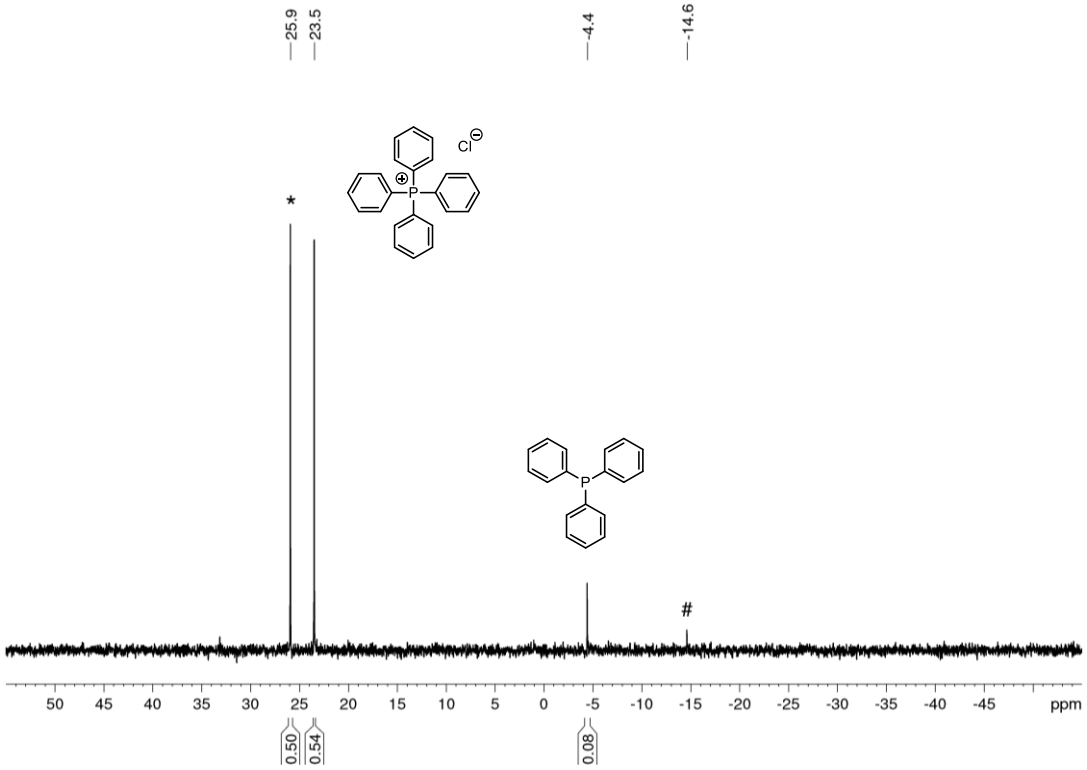


Figure S24. Quantitative single scan $^{31}P\{^1H\}$ (zgig) NMR spectrum for the scale-up photochemical functionalization of P_4 using chlorobenzene. * marks the internal standard Ph_3PO. # marks the intermediate Ph_4P_2.

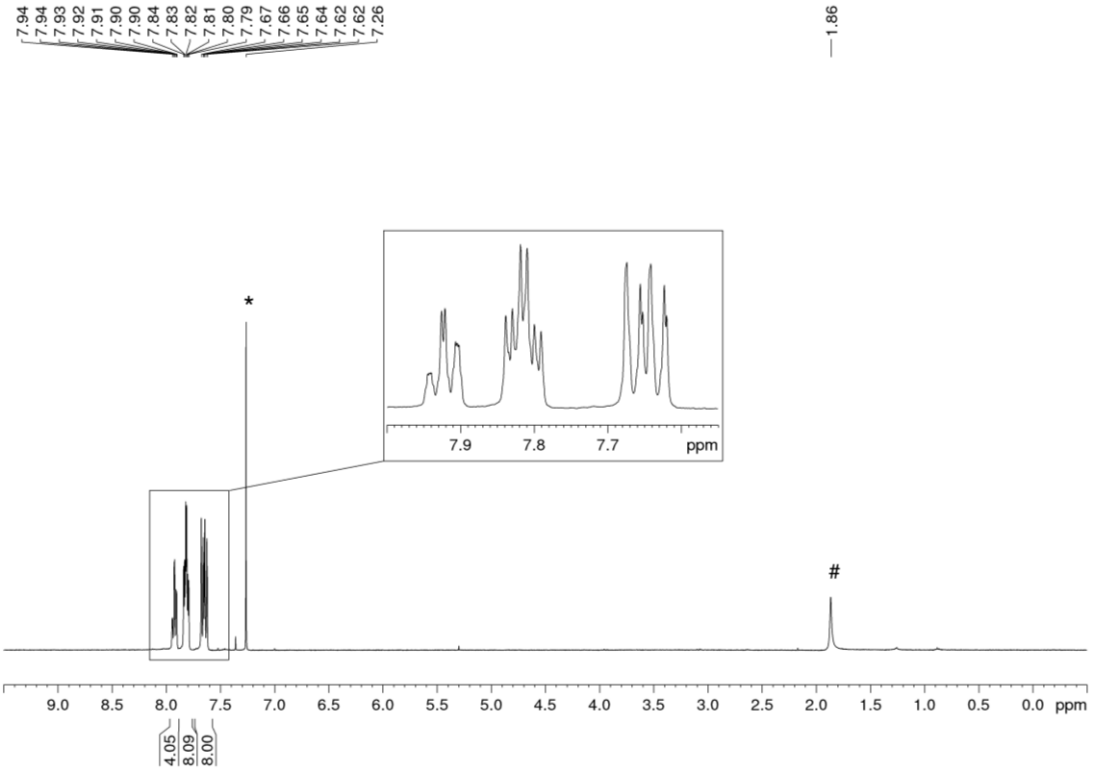


Figure S25. ^1H NMR spectrum of tetraphenylphosphonium chloride prepared photochemically from P_4 at 0.8 mmol scale. * marks $CDCl_3$. # marks adventitious H_2O.

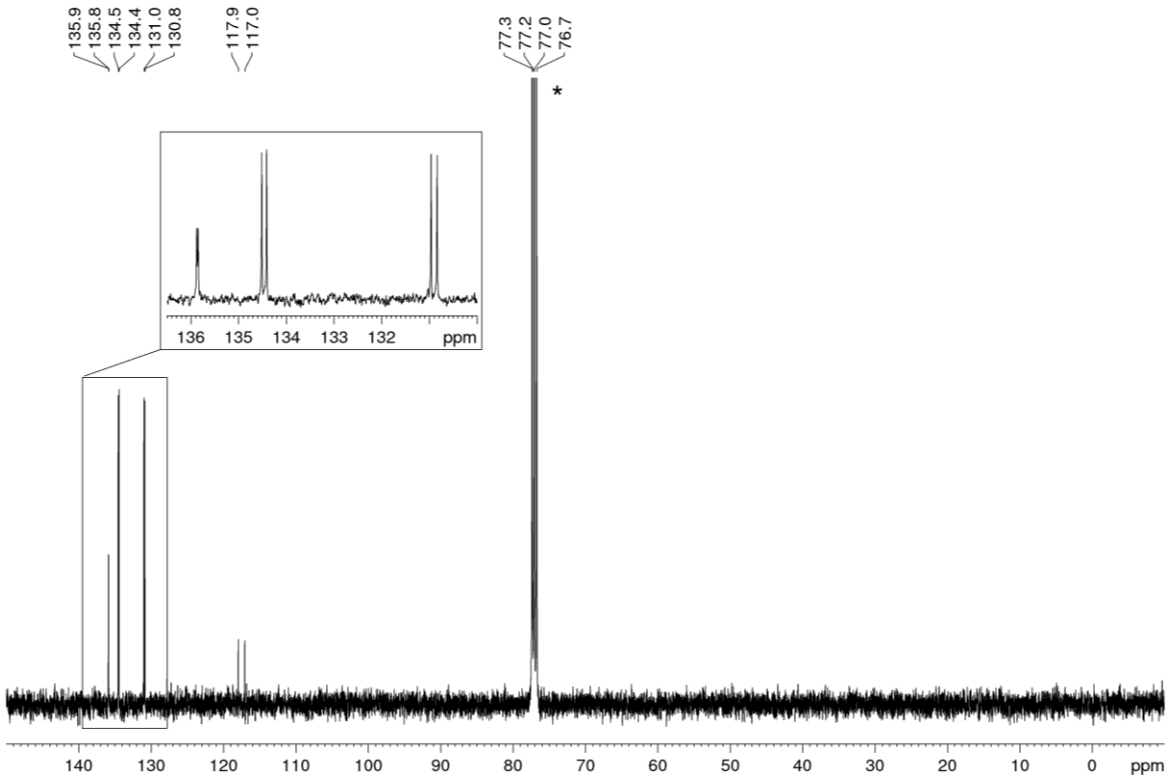


Figure S26. ^{13}C NMR spectrum of tetraphenylphosphonium chloride prepared photochemically from P_4 at 0.8 mmol scale. * marks $CDCl_3$.

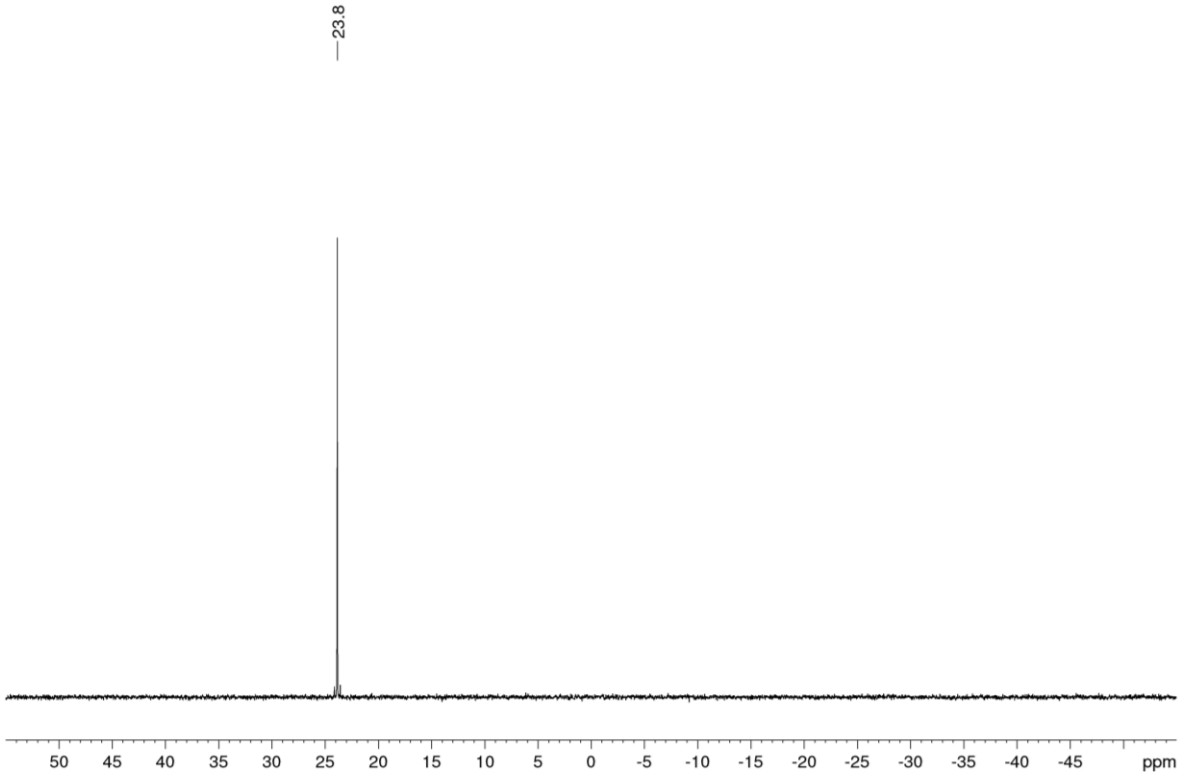


Figure S27. $^{31}P\{^1H\}$ NMR spectrum of tetraphenylphosphonium chloride prepared photochemically from P_4 at 0.8 mmol scale.

S5.2. Photochemical preparation of tris(phenylethyl)phosphine from P_4 (0.8 mmol scale)

All operations were carried out under inert gas atmosphere. To a 100 mL stoppered tube equipped with a stirring bar were added (2-chloroethyl)benzene (8.0 mmol, 10 equiv. based on the phosphorus atom), organic photoreductant TDAE[1] (4.0 mmol, 5 equiv. based on the phosphorus atom), and P_4 (0.2 mmol, 1 equiv., as a stock solution in 1.426 mL benzene). The mixture was dissolved in acetone (5 mL). The tube was sealed, placed in a water-cooled block (to ensure a near-ambient temperature was maintained, Figure S21), and irradiated with UV light (365 nm, 14 V, 700 mA, Osram OSLON SSL 80) for 20 h. The reaction mixture was filtered to remove the side product $[TDAE]Cl_2$. The solvent, unreacted (2-chloroethyl)benzene and TDAE were evaporated *in vacuo* at 80°C (ca. $2 \cdot 10^{-2}$ mbar). The side product 1,4-diphenylbutane was removed by distillation at low pressure (ca $1 \cdot 10^{-2}$ mbar) by warming the flask with a heat gun. The product tris(phenylethyl)phosphine was distilled from the remaining orange oil on a high vacuum pump ($1 \cdot 10^{-5}$ mbar) while heating with a heat gun to 300°C (40.1 mg, 14%).

The characterization data of the product are consistent with the data found in the literature.[4]

^{1}H NMR (400 MHz, C_6D_6): δ[ppm]: 7.19-7.05 (m, 15H & C_6D_6), 2.66-2.60 (m, 6H), 1.59-1.55 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ[ppm]: 142.9 (d, *J* = 10.1 Hz), 128.4 (s), 128.2 (s), 125.9 (s), 32.4 (d, *J* = 15.2 Hz), 29.3 (d, *J* = 15.9 Hz).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ[ppm]: −27.7.

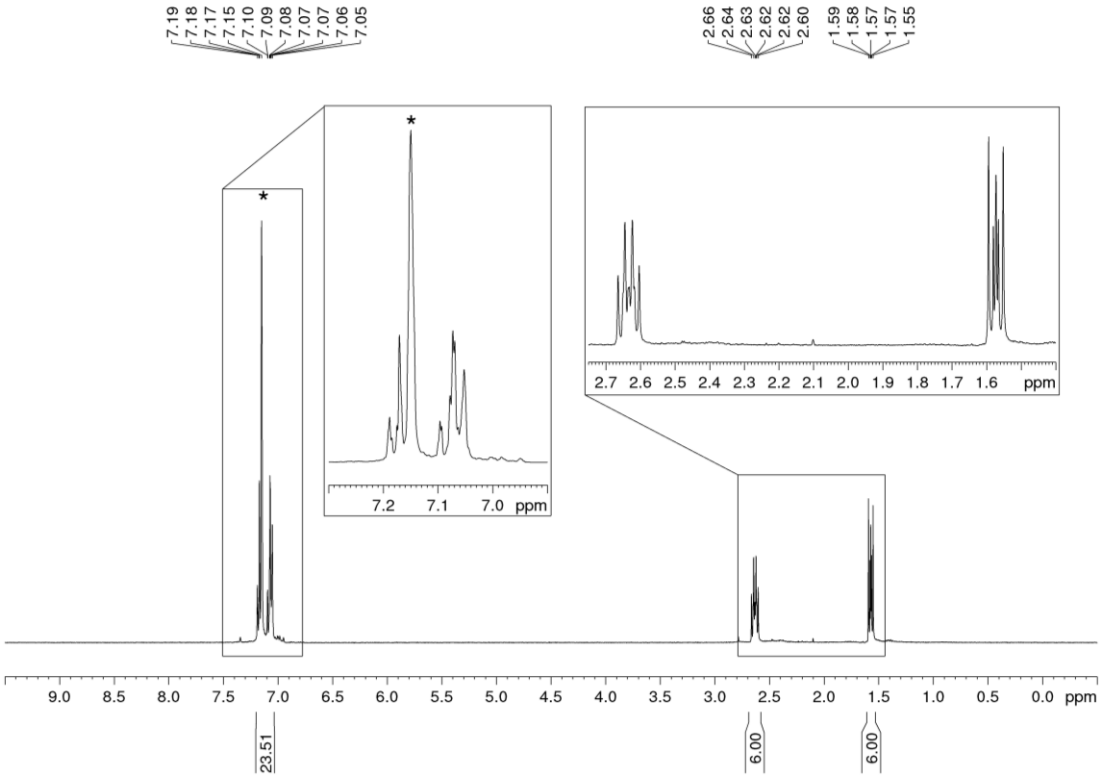


Figure S28. ^{1}H NMR spectrum of tris(phenylethyl)phosphine prepared photochemically from P_4 at 0.8 mmol scale. * marks C_6D_6.

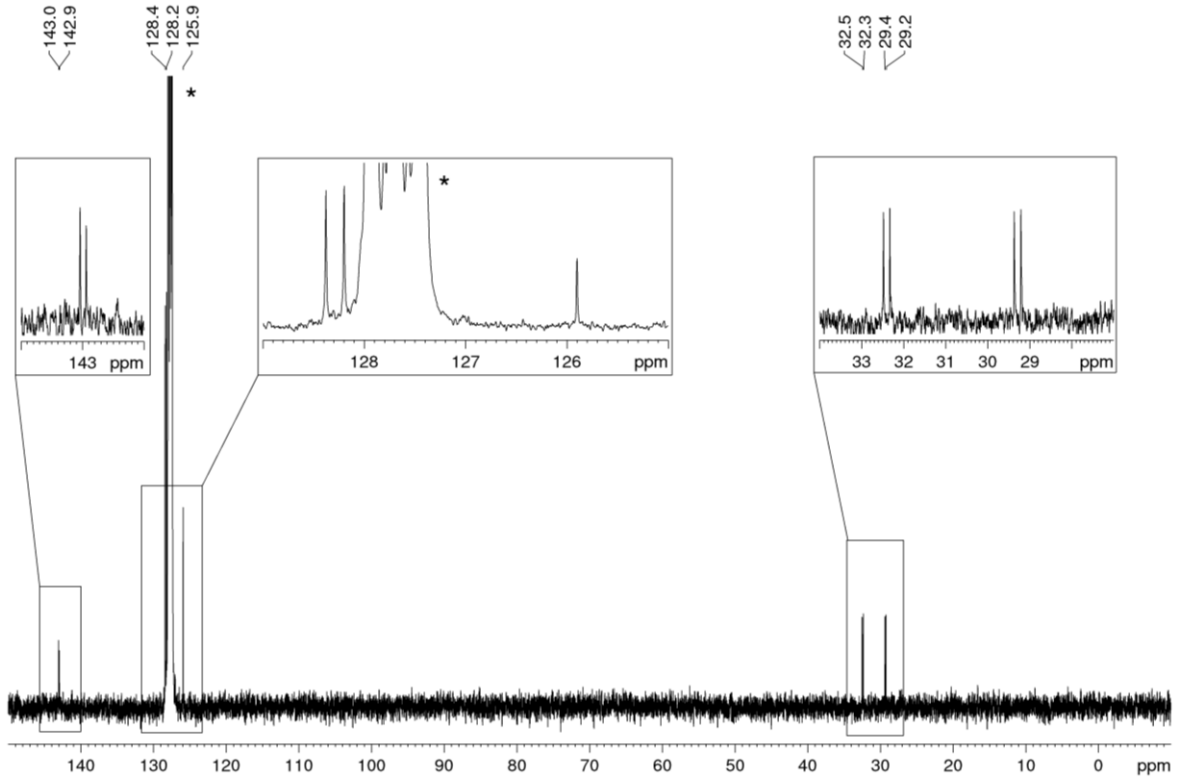


Figure S29. ^{13}C NMR spectrum of tris(phenylethyl)phosphine prepared photochemically from P_4 at 0.8 mmol scale. * marks C_6D_6.

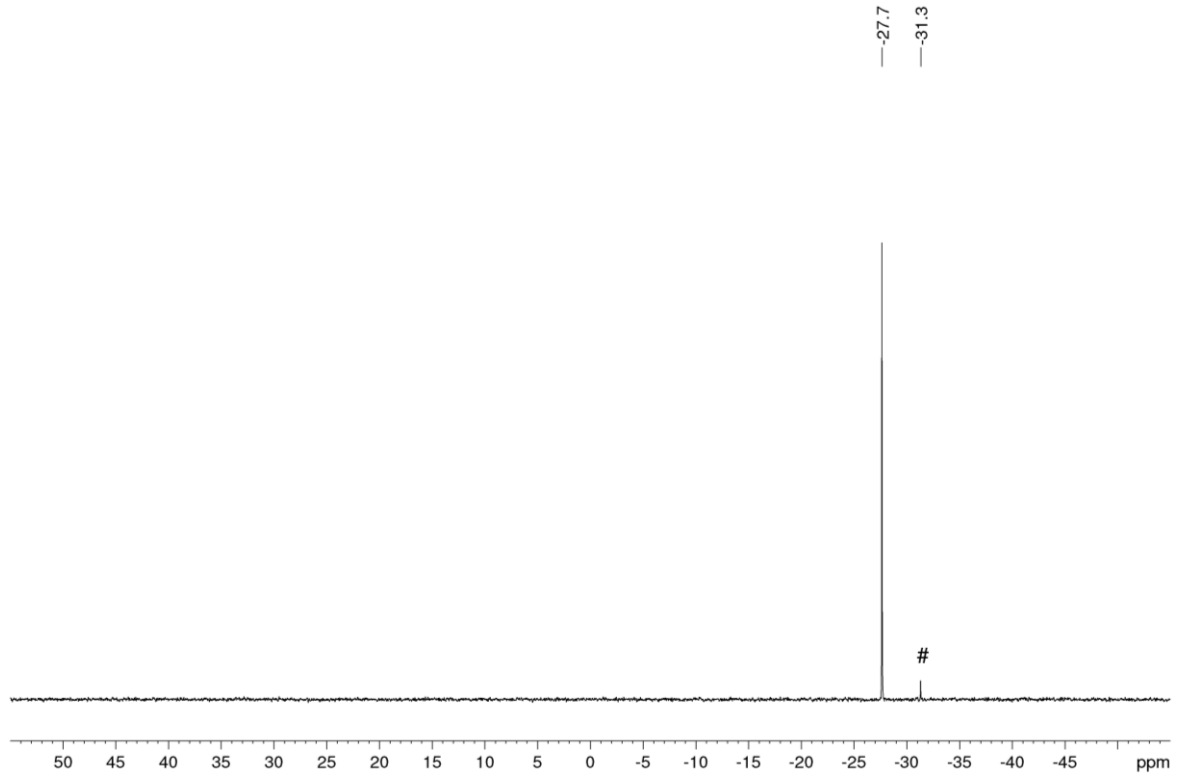


Figure S30. $^{31}P\{^1H\}$ NMR spectrum of tris(phenylethyl)phosphine prepared photochemically from P_4 at 0.8 mmol scale. # marks an unknown impurity.

S6. *In situ* NMR experiments

The apparatus used for *in situ* NMR reaction monitoring with *in situ* illumination has been reported previously.[5] The insert and the NMR tube were connected with the screw cap of a recently published UVNMR-illumination device to enable measurements under inert conditions.[6] Two FEP (fluorinated ethylene propylene) coated rubber septa increased the attachment between the insert and the tube. (Figure S31). The same illumination apparatus was used for *in situ* NMR reaction monitoring with *in situ* illumination that was used in previous investigations of the light-driven arylation of P_4.[7]

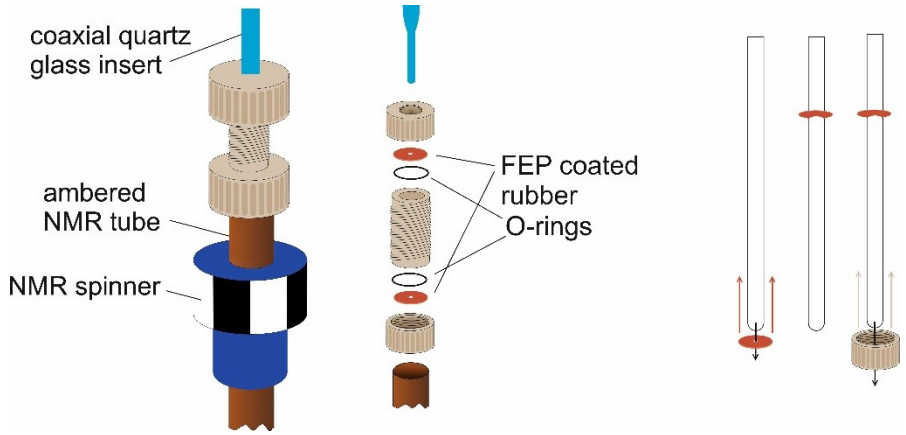


Figure S31. Schematic representation showing connection between the ambered NMR tube and illuminating insert used for *in situ* NMR reaction monitoring.

A 365 nm LED (LEUVA66 from Lasercomponents) was employed for sample illumination inside the NMR spectrometer. The spectra were recorded at 298 K and processed with Bruker TopSpin 4.0.3.

In order to cover the full chemical shift range of the ^{31}P-NMR signals occurring during the reaction monitoring within a single spectrum, the spectra were recorded with broadband excitation using the broadband pulse shapes “xyBEBOP” (excitation window of 500 kHz with a pulse duration of 500 ms) kindly provided to us by Prof. Dr. Burkhard Luy.[8]

The spectra were recorded with ^{1}H-decoupling (power gated decoupling) to increase the signal-to-noise ratio of potential intermediates. Therefore, the reaction monitoring gives no quantitative but qualitative information about the kind and sequence of phosphorus species. For integration, these spectra were processed with magnitude calculation (*mc*) and the baseline was corrected automatically with the command *absn*.

Measurements were conducted on a Bruker Avance NEO 600 MHz spectrometer equipped with a double resonance broad band probe (BBO). NMR frequencies were referenced externally and are given in parts per million (ppm). ^{1}H and ^{13}C frequencies are referenced to TMS (tetramethylsilane) and ^{31}P to H_3PO_4 (85 wt. % in H_2O). ^{1}H-NMR spectra were calibrated on the solvent residual peak of

acetone-d_6 (2.05 ppm). In case non-deuterated acetone was used as solvent, the ^{1}H-NMR of acetone was calibrated to 2.08 ppm (due to isotopic shift between acetone-d_2 to acetone-d_1 and probably further to acetone-d_0 of 10 Hz each on the 600 MHz spectrometer; see Figure S32). Heteronuclear spectra (^{13}C and ^{31}P) were then calibrated using the unified scaling procedure recommended by IUPAC.[9]

S6.1. Procedure for ^{31}P and ^{1}H monitoring of the model reaction

The reaction mixture was prepared in accordance with the general procedure for photochemical functionalization of P_4 in a 0.01 mmol scale (section S2) using chlorobenzene as the substrate, with the exception that deuterated acetone-d_6 $(CD_3)_2CO$ was used as solvent. A 300 μL aliquot of this reaction mixture was then taken for NMR reaction monitoring. The reaction mixture was prepared under inert atmosphere (N_2) in an ambered NMR-tube. The *in situ* illumination device was inserted into the tube and fastened with the screw cap.

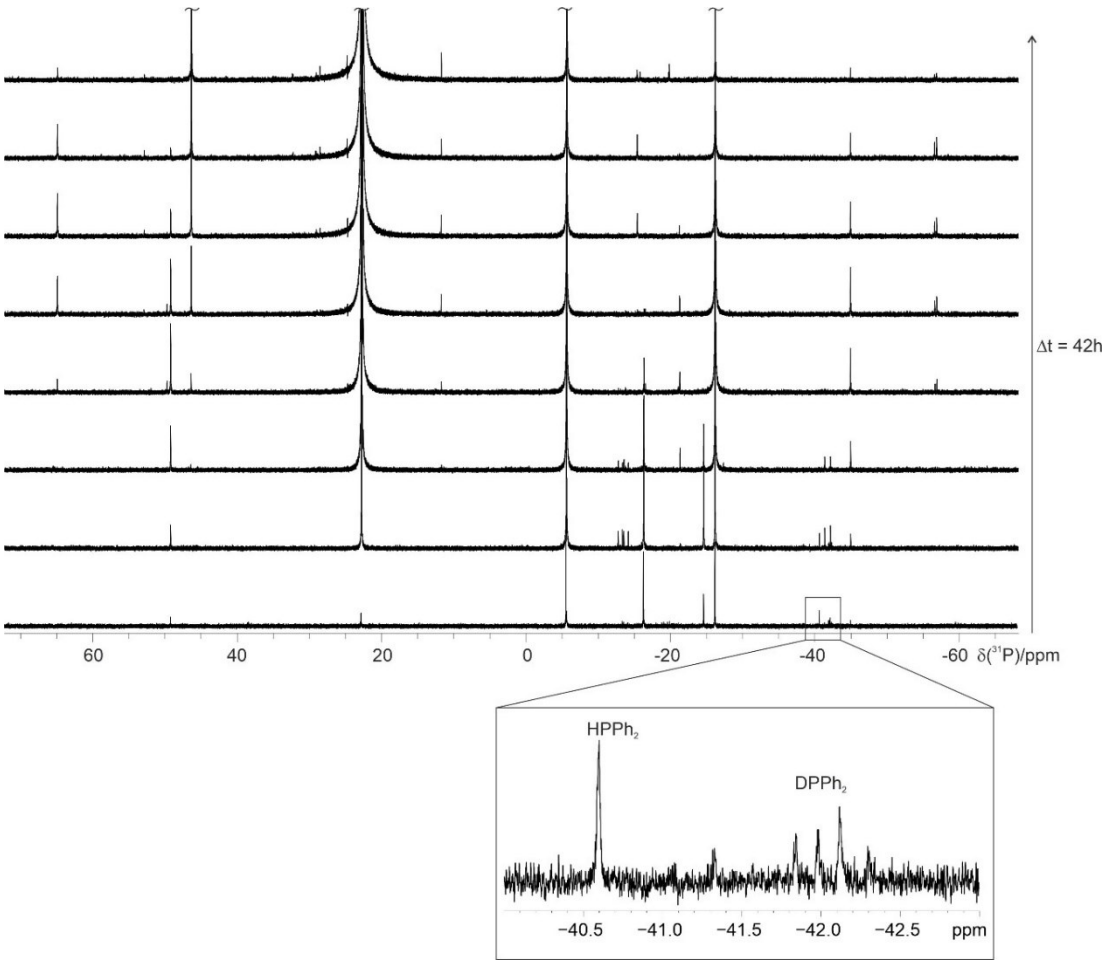


Figure 32. *In situ* ^{31}P{^{1}H} NMR monitoring of the model reaction (time = 42 h). Deuterium incorporation of deuterated acetone-d_6 into the arylated $HPPh_2$ forming a mixture of deuterated and non-deuterated intermediates.

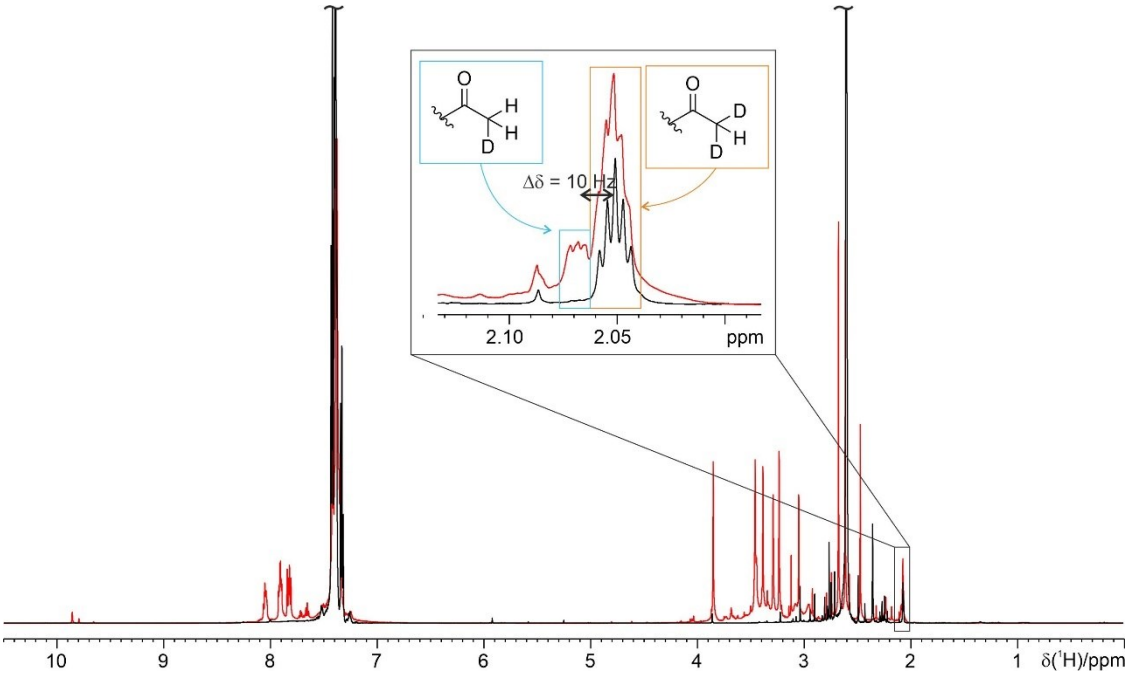


Figure S33. *In situ* ^{1}H NMR monitoring of the model reaction showed that monodeuterated acetone is generated indicating the presence of H/D exchange processes during the reaction.

S6.2 NMR Investigations of the Intermediate Int1

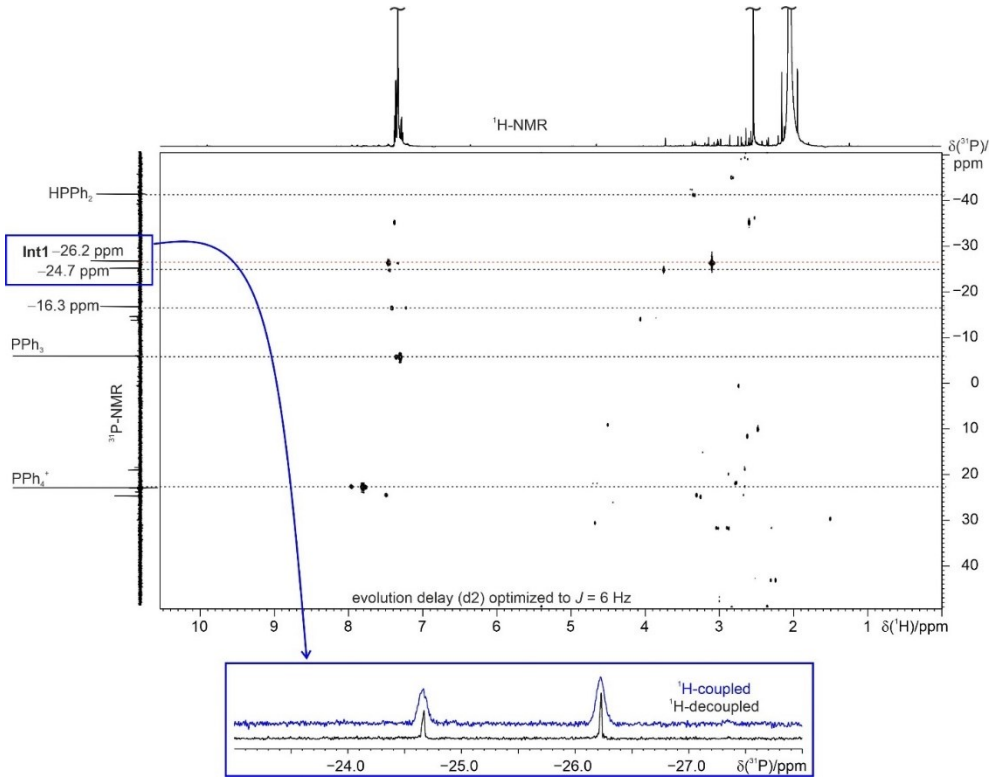


Figure S34. 2D ^{1}H-^{31}P-HMQC experiment recorded of the model reaction after irradiation for one hour. ^{31}P{^{1}H}-NMR experiments indicated only small couplings between ^{1}H and ^{31}P for the intermediate **Int1.**

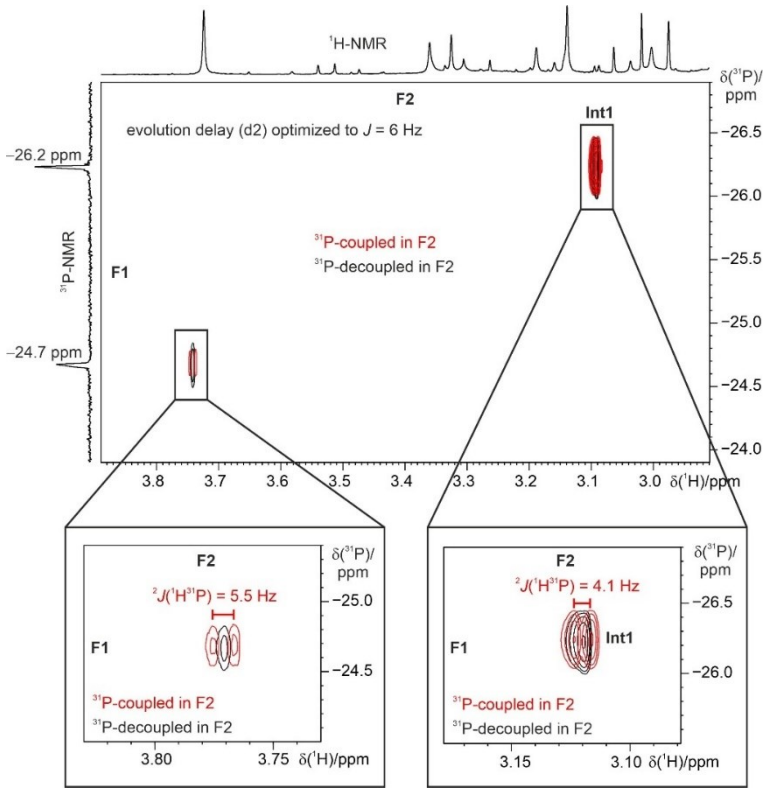


Figure S35. 2D ^{1}H-^{31}P-HMQC experiment recorded of the model reaction after irradiation for one hour.

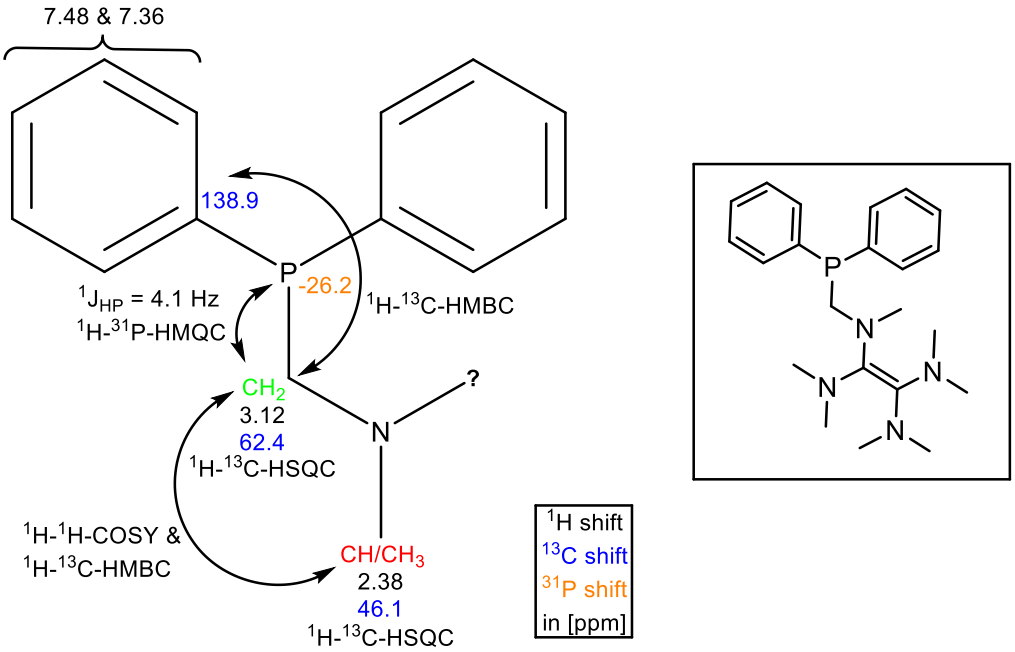
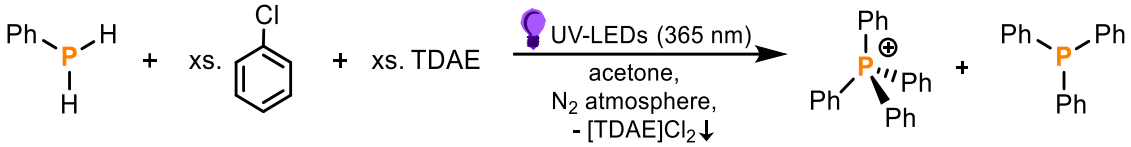


Figure S36. Left: Proposed structural core of the intermediate **Int1** based on combination of its ^{31}P chemical shift, ^{1}H-^{31}P-HMQC, ^{1}H-^{13}C-HSQC and -HMBC, ^{1}H-^{1}H-COSY experiments and comparison with literature data.[10] Right: Proposed structure fitting to the chemical context of the here investigated reactions.

S7. Photochemical phenylation of $PhPH_2$, Ph_2PH, Ph_4P_2 and Ph_3P

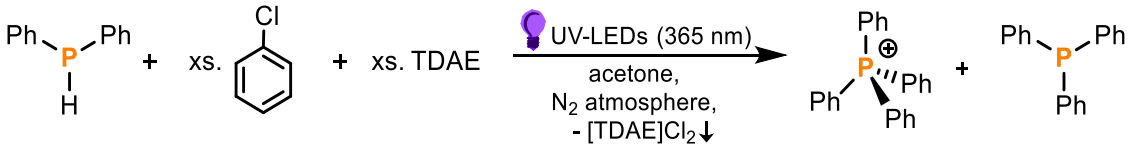
Table S9. Photochemical functionalization of $PhPH_2$ to $[Ph_4P]Cl$.[a][b]



Entry	Conditions[a][b] **TDAE:PhCl**	Conv. to **$[Ph_4P]Cl$ / %**	Conv. to **Ph_3P / %**	**Intermediates**	Consumption of **$PhPH_2$/ %**
1	3:6	52	24	Ph_4P_2 (4), Int1 (5)	100
2	TDAE (3 equiv.) no PhCl	–	–	unselective	92
3	5:10	68%	9	–	100

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with $PhPH_2$ (4.4 µL, 0.04 mmol). [b] Listed equivalents are defined per P atom.

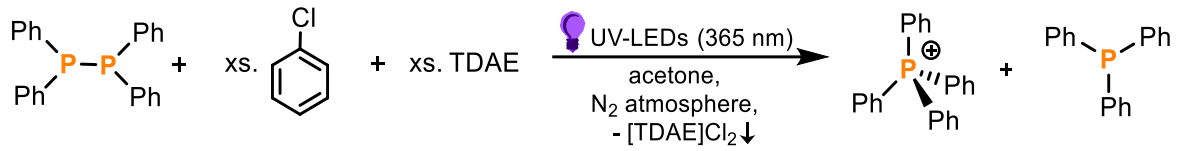
Table S10. Photochemical functionalization of Ph_2PH to $[Ph_4P]Cl$.[a][b]



Entry	Conditions[a][b] **TDAE:PhCl**	Conv. to **$[Ph_4P]Cl$ / %**	Conv. to **Ph_3P / %**	**Intermediates**	Consumption of **Ph_2PH/ %**
1	3:6	76	15	Int1 (16)	100
2	TDAE (3 equiv.) no PhCl	0	5	P_2Ph_4 (40)	78
3	5:10	41	4	3	100

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_2PH (7.0 µL, 0.04 mmol). [b] Listed equivalents are defined per P atom.

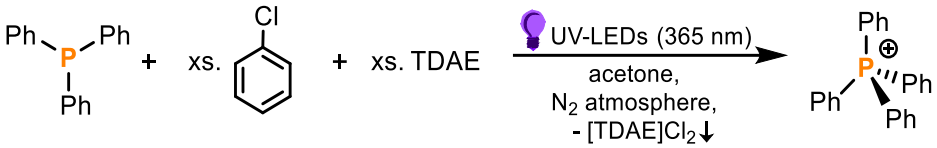
Table S11. Photochemical functionalization of Ph_4P_2 to $[Ph_4P]Cl$.[a][b]



Entry	Conditions[a][b] **TDAE:PhCl**	Conv. to **$[Ph_4P]Cl$ / %**	Conv. to **Ph_3P / %**	**Intermediates**	Consumption of **Ph_4P_2/ %**
1	1.5:3	55	28	Int1 (8)	100
2	TDAE (2 equiv.) no PhCl	0	6	PPh_2H (6)	68
3	3:3	39	28	Int1 (8), PPh_2H (3)	100
4	3:6	55	5	Int1	100
5	5:10	44	6	Int1	100

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_4P_2 (7.4 mg, 0.02 mmol). [b] Listed equivalents are defined per P atom.

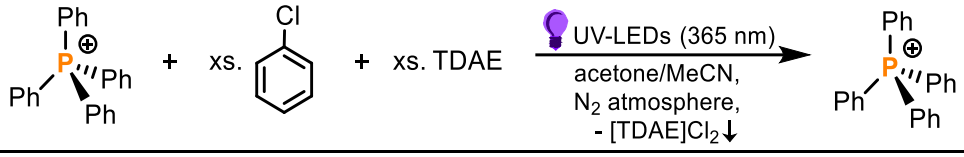
Table S12. Photochemical functionalization of Ph_3P to $[Ph_4P]Cl$.[a][b]



Entry	Conditions[a][b] **TDAE:PhCl**	Conv. to **$[Ph_4P]Cl$ / %**	Leftover **Ph_3P / %**	Consumption of **PPh_3 / %**
1	1.5:3	36	5	95
2	TDAE (1.5 equiv.) no PhCl	–	92	8
3	3:6	55	0[~]	100
4	5:10	43	0[~]	100

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with Ph_3P (10.5 mg, 0.04 mmol). [b] Listed equivalents are defined per P atom.). [~] Signal in the $^{31}P\{^1H\}$ NMR (NS 256), but too small to determine the yield in the quantitative $^{31}P\{^1H\}$ NMR (NS 1).

Table S13. Stability test of phosphonium salt [Ph_4P]Cl toward photochemical conditions.[a][b]



Entry	Conditions[a][b] **TDAE:PhCl**	Leftover **[Ph_4P]Cl / %**	Decomposition[c] of **[Ph_4P]Cl / %**
1	1.5:3	56	44[c]
2	TDAE (1.5 equiv) no PhCl	80	12 (8)[d]
3	5:10	37	63[c]

[a] The general procedure for reactions at 0.04 mmol scale (section S2) was modified by replacing P_4 with [Ph_4P]Cl (15.0 mg, 0.04 mmol) for stability check of the phosphonium salt under the photochemical conditions. For better solubility of the phosphonium salt a mixture of acetone (0.5 mL) and MeCN (0.2 mL) was used. [b] Listed equivalents are defined per P atom. [c] No decomposition or other signals appear in the $^{31}P\{^1H\}$ NMR. [d] Decomposition to the triphenylphosphine Ph_3P.

S8. Side product $[TDAE]Cl_2$

The side product $[TDAE]Cl_2$[11] can be recovered by simple filtration of the reaction mixture and recrystallization by slow diffusion of acetone into a DMSO solution which resulted in colorless crystals.

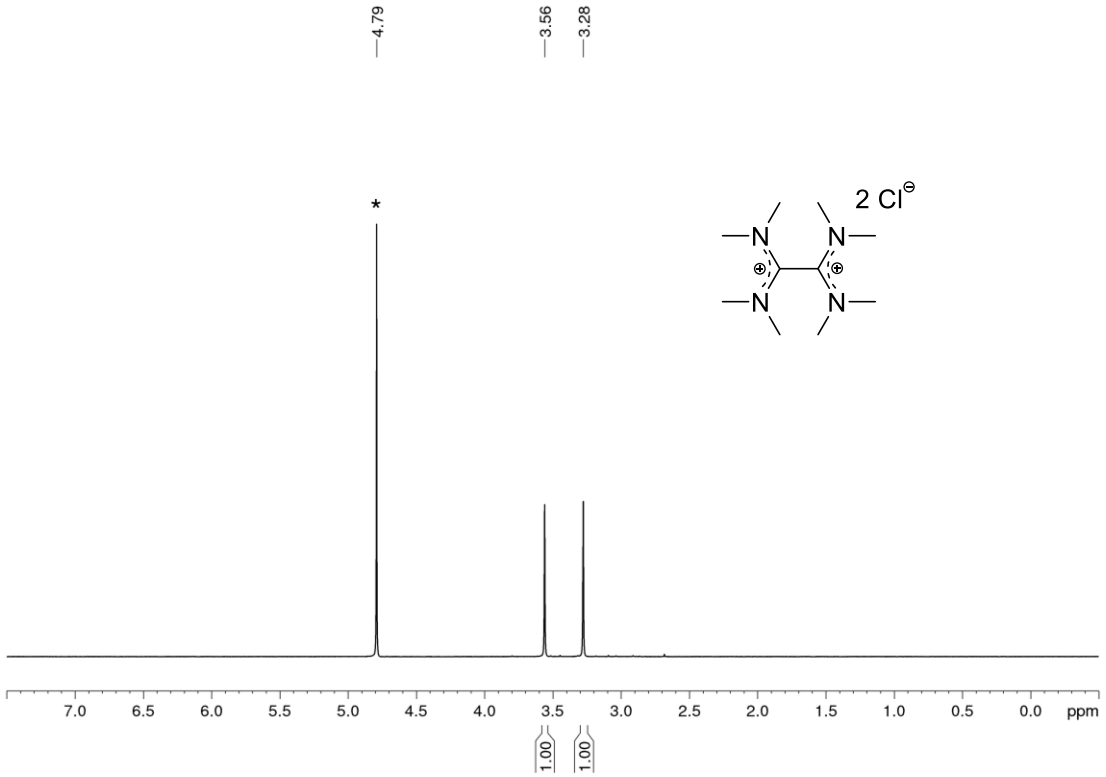


Figure S37. ^{1}H NMR spectrum (400.13 MHz, 300 K, D_2O) of byproduct $[TDAE]Cl_2$. * marks D_2O.

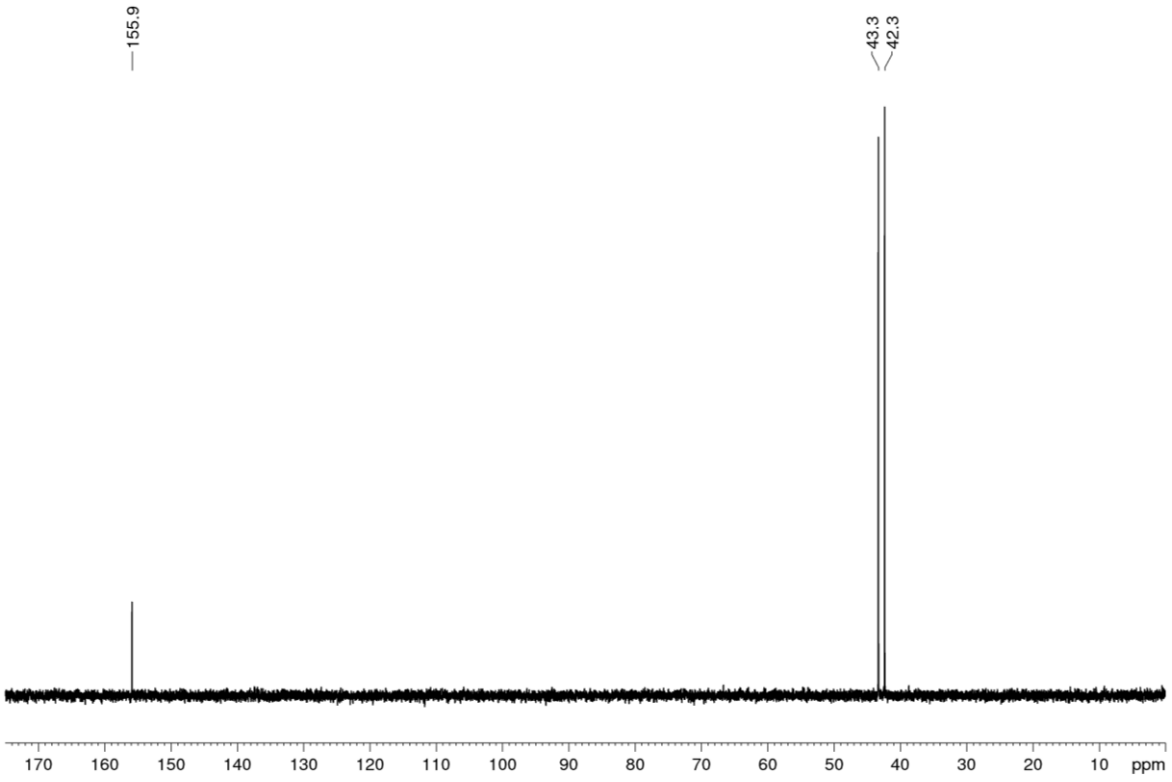


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, D_2O) of byproduct $[TDAE]Cl_2$.

S9. References

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