Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Green Light Enabled Staudinger-Bertozzi Ligation

Kubra Kalayci, Hendrik Frisch, Christopher Barner-Kowollik,* Vinh X. Truong*

Table of Contents

1. Additional Data

Table S1. LC-MS Data of the identified photo-release products with calculated and measured mass values. P

Compound	Calculated Mass (*m/z*)	Experimental Mass (*m/z*)
A	676.1108	676.1108
B	337.0988	337.0990
C	550.2142	550.2142
D	246.1125	246.1124
E	248.1282	248.1281

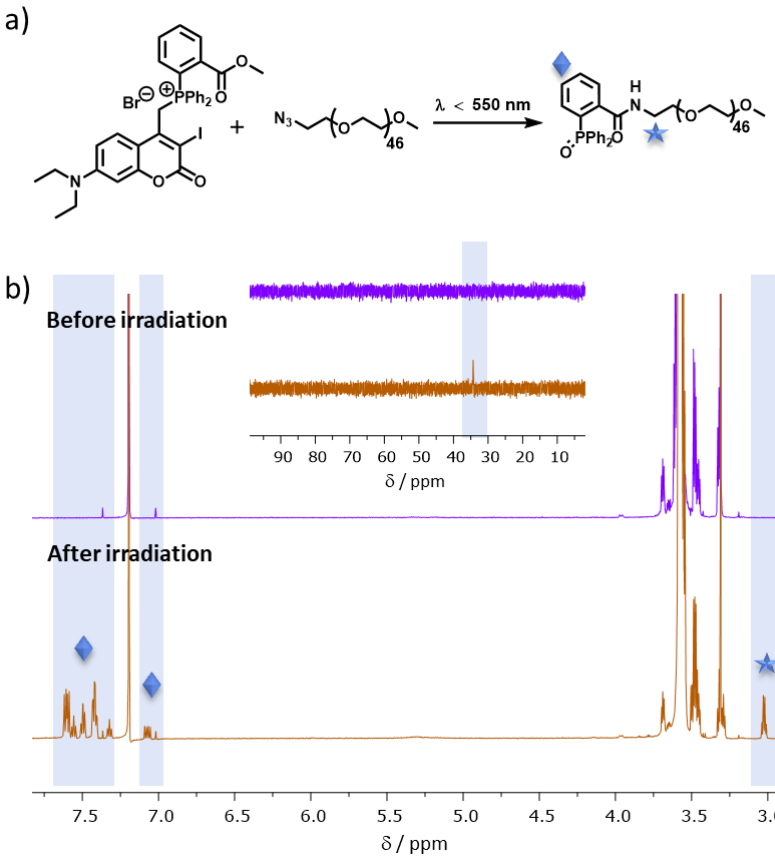


Figure S1. ^{1}H and ^{31}P NMR spectra ($CDCl_3$, 600 MHz) of the PEG-azide before and after irradiation at λ_{max} = 445 nm with excess of **S4** (refer to Figure S8).

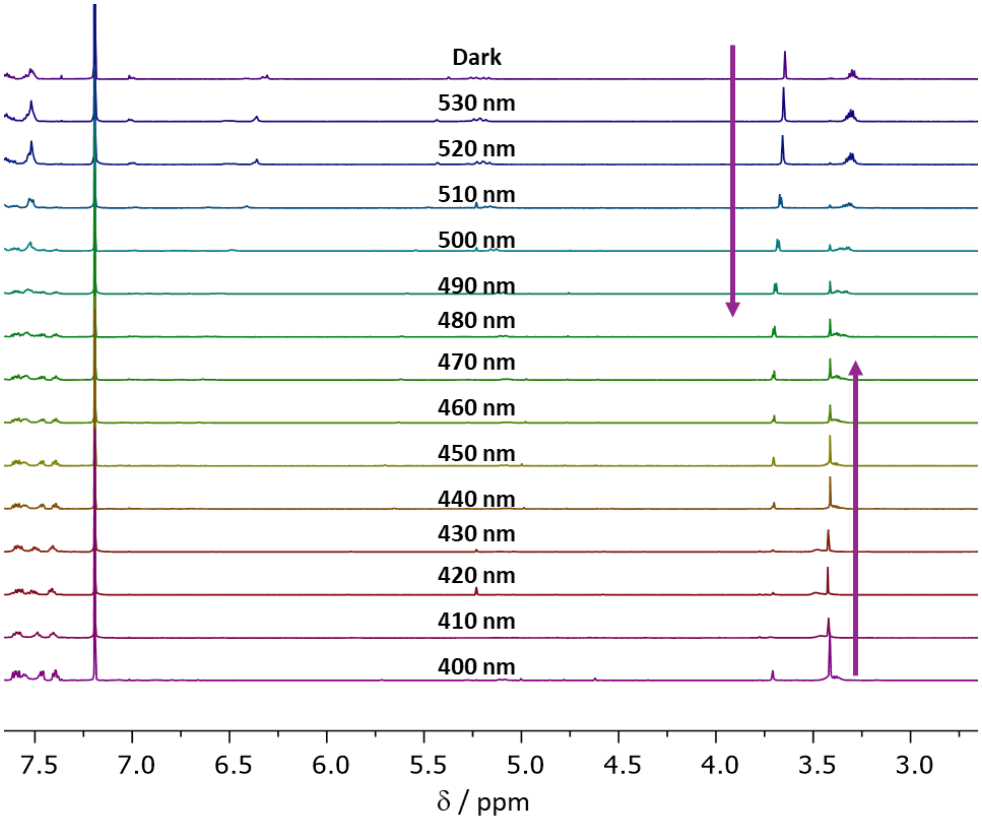


Figure S2. [1]H NMR spectra of caged MPPB solutions before and after each irradiation between λ = 400-530 nm at a constant photon count. For each experiment a new sample solution was used.

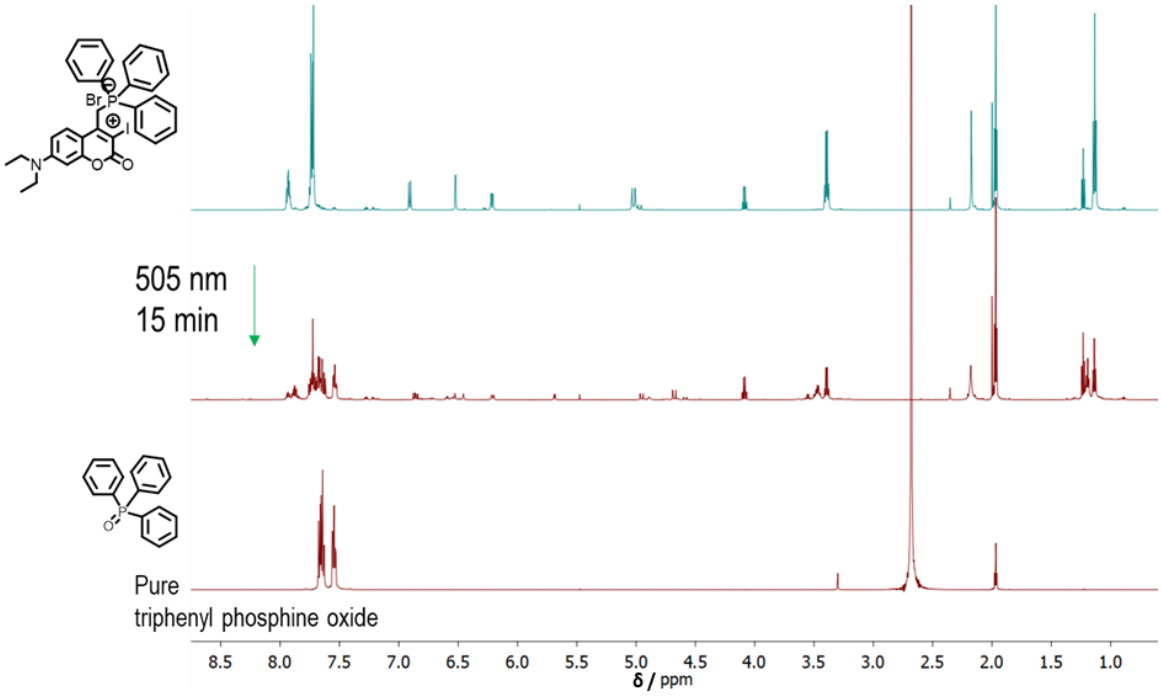


Figure S3. [1]H NMR spectra of caged triphenyl phosphine and the product after green light irradiation (505 nm, 15 min, LED light source), refer to **Figure S17** for complete assignment of the resonances within the NMR spectrum of caged triphenylphosphine.

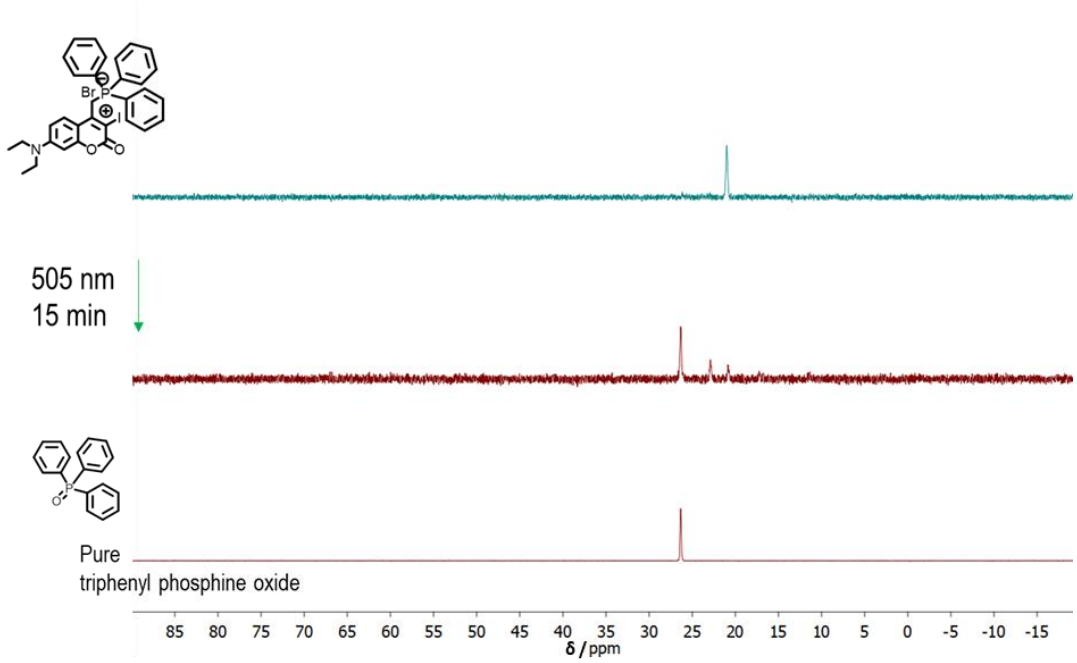


Figure S4. ^{31}P NMR spectra of caged triphenyl phosphine and the product after green light irradiation (505 nm, 15 min, LED light source).

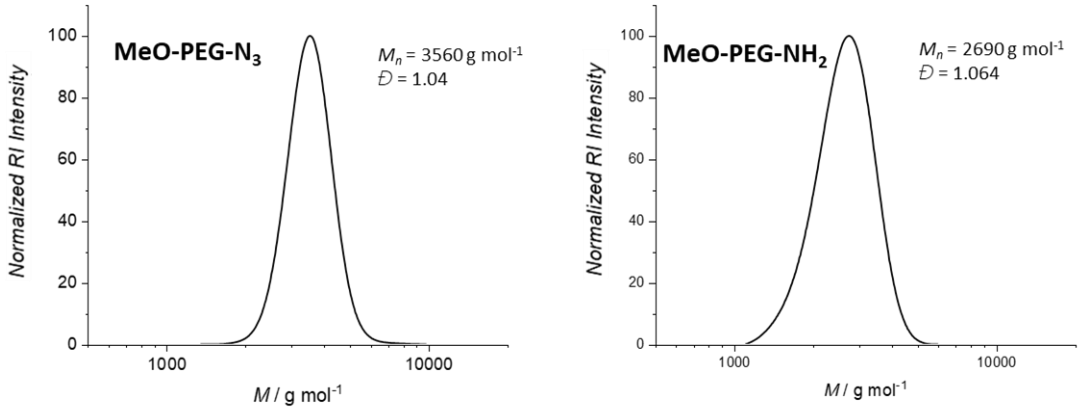


Figure S5. SEC (THF, polystyrene calibration) trace of MeO-PEG-N_3 and MeO-PEG-NH_2 from green light-induced (λ_{max} =505 nm) Staudinger reaction of caged triphenylphosphine and MeO-PEG-N_3.

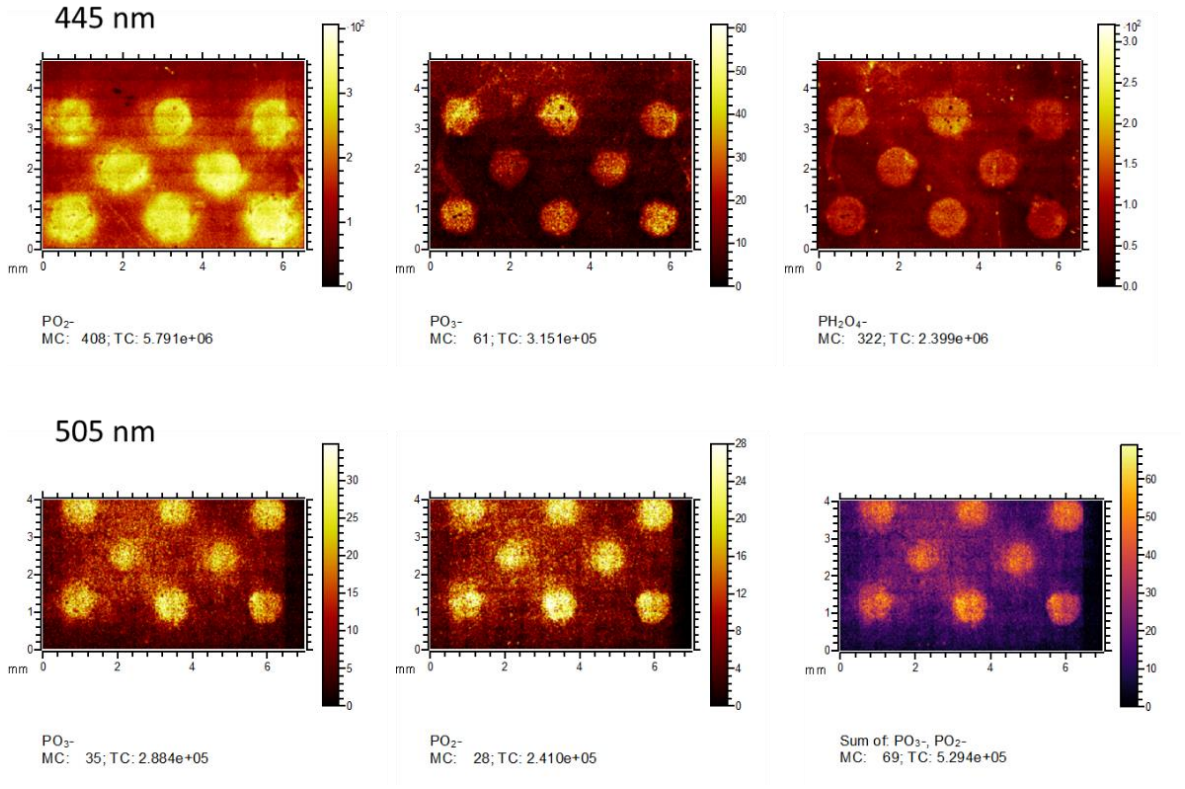


Figure S6. ToF-SIMS images of the solid surfaces in negative mode after irradiation with λ_{max} = 445 and 505 nm LEDs. Fragments related to MPPB (PO_2^-, PO_3-, $PH_2O_4^-$) were observed only in the dotted patterns (yellow color).

2. Experimental Details

2.1. ^{1}H and ^{31}P NMR

NMR spectra were recorded on a Bruker Avance III 600 MHz with a 5 mm broadband auto-tunable probe with Z-gradients at 293 K. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances ($CDCl_3$ δ = 7.26 ppm), couplings are shown as s: singlet, d: doublet, t: triplet, m: multiplet. In most spectra trace of water appears as a broad singlet at around 1.5-2.5 ppm. NMR spectra were processed using MestReNova software.

2.2. LC-MS

LC-MS measurements were performed on an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SZ), autosampler (WPS 3000TSL) and a temperature controlled column compartment (TCC 3000). Separation was performed on a C18 HPLC column (Phenomenex Luna 5µm, 100 Å, 250 × 2.0 mm) operating at 40 °C. Water (containing 5 mmol L^{-1} ammonium acetate) and acetonitrile were used as eluents. A gradient of acetonitrile: H_2O 5:95 to 100:0 (v/v) in 7 min at a flow rate of 0.40 mL·min^{-1} was applied. The flow was split in a 9:1 ratio, where 90 % of the eluent was directed through a DAD UV-detector (VWD 3400, Dionex) and 10 % was infused into the electrospray source. Spectra were recorded on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the *m/z* range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 2 were applied, respectively. The capillary temperature and was set to 300 °C, the S-lens RF level was set to 68, and the aux gas heater temperature was set to 100 °C.

2.3. SEC-ESI-MS

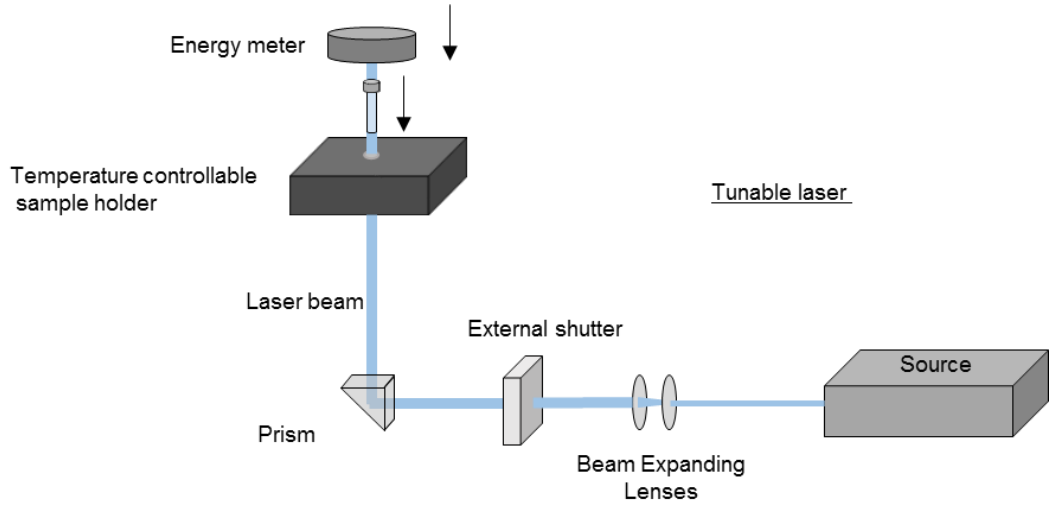
Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150 and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature-controlled column department (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV-detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[1] 0.27 mL·min^{-1} of the eluent were directed through the UV- and RI-detector and 30 µL·min^{-1} were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 200 µL aliquot of a polymer solution with a concentration of 2 mg·mL^{-1} was injected into the SEC system.

2.4. UV-VIS Spectroscopy

UV/vis spectra were recorded on a *Shimadzu* UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were prepared in ACN and measured in *Hellma Analytics* quartz high precision cells with a path length of 10 mm at ambient temperature.

2.5. Experiments using laser irradiation

The incident light used for laser experiments was a Coherent Opolette 355 tunable OPO operated at 350-550 nm with a full width half maximum of 7 ns and a repetition rate of 20 Hz. The emitted pulse, which has a flat-top spatial profile, was expanded to 6mm diameter using focusing lenses and directed upwards using a prism. The beam was then centered on a glass laser vial which is positioned in a 6mm diameter slot in a temperature-controlled sample holder. The energy transmitted through the sample holder was measured using a Coherent Energy Max PC power meter.



Scheme S1. Experimental setup for tunable laser experiments.

2.5.1 Control over the constant number of photons [2]

The number of photons n_p ([n_p] = mol) that a monochromatic laser pulse contains can be calculated by application of the Planck-Einstein relation from the energy of the pulse E_{pulse}, the incident wavelength λ, Planck's constant h and the speed of light c:

$$n_p = \frac{E_{pulse}\ \lambda}{h\ c\ N_A}$$

If the absorption of the glass vial and the extent of reflection and scattering at the vial at the respectively relevant wavelength is known, a target energy value can be calculated that must be reached during the above described measurement to guarantee that the desired number of photons penetrates the sample solution during the subsequent irradiation. The wavelength dependent transmittance of the glass vials was determined experimentally using the above setup. Three glass vials were randomly selected as calibration vials. For varying wavelengths and in each case at a constant power output of the laser the energy was measured both with and without the calibration vials fitted into the sample holder. The top parts of these vials were cut off to minimize errors in the procedure, since only the bottom and sides of the glass vials would contribute significantly to the reduction of the photon flux that enters the solution.

The measured energy per pulse without a calibration vial in the sample holder is denoted as E_0 and the measured energy per pulse with a calibration vial in the sample holder as E_n. The transmittance was calculated as the ratio of E_n to E_0. The average transmittance over the measurements of the three vials (T_λ) was plotted together with the respective error:

$$T_\lambda = \frac{E_n}{E_0}$$

The target energy per pulse E_0 can be calculated directly from the wavelength λ, the number of pulses k, the transmittance of the glass vial at the respective wavelength T_λ and the desired total photon count n_p:

$$E_0 = \frac{n_\mathrm{p}\ \mathrm{N_A}\ \mathrm{h}\ \mathrm{c}}{k\ T_\lambda\ \lambda}$$

By controlling the target E_0 at the respective wavelength, the number of photons that penetrate each sample solution of one set of experiments as described in the following subsections was guaranteed to be identical despite irradiation at different wavelengths.

An example calculation (λ = 300 nm) is shown below:

$$E^0 = \frac{2.5 \cdot 10^{-7}\ \mathrm{mol} \cdot 6.022141 \cdot 10^{23}\ \mathrm{mol^{-1}} \cdot 6.62607 \cdot 10^{-34}\ \mathrm{kg}\frac{\mathrm{m^2}}{\mathrm{s}} \cdot 2.99792 \cdot 10^{8}\ \frac{\mathrm{m}}{\mathrm{s}}}{1000 \cdot 0.377 \cdot 3 \cdot 10^{-7}\ \mathrm{m}}$$
$$= 2.64 \cdot 10^{-4}\ \mathrm{J}$$

2.5.2 Transmittance of the glass vials

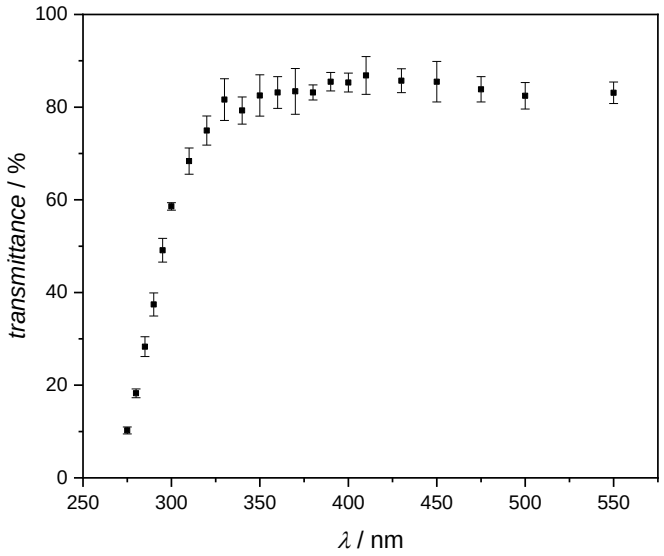


Figure S7: Transmittance of glass vials in dependence of irradiation wavelength, refer to Table S2.

Table S2: Transmittance of the bottom of the glass vials used in this study. The transmittance values shown and used here were obtained analogously to a method reported previously.[2] The glass vials were cut at a height of 3 mm. Thus, the number of photons delivered into the sample solution can be determined more precisely, than in initial attempts to estimate the number of photons.[3] The values are in agreement to the previously found transmittance at 285 nm, which was determined with the same glass vials as used here. [4]

λ / nm	T_λ / %	Standard deviation
275	10.23419	0.74982
280	18.25024	0.94703
285	28.31044	2.14137
290	37.43074	2.49132

295	49.11881	2.55629
300	58.57746	0.79725
310	68.34923	2.82282
320	74.95204	3.14492
330	81.62937	4.49571
340	79.27099	2.93382
350	82.52063	4.45387
360	83.15709	3.42489
370	83.40189	4.93431
380	83.17113	1.63659
390	85.48502	1.99615
400	85.31216	2.03069
410	86.83816	4.06669
430	85.71046	2.57226
450	85.49291	4.38069
475	83.84506	2.73637
500	82.44994	2.85985
550	83.10058	2.33119

2.5.3 Calculation of the Action Plot

The conversion of the photo-release was calculated by the equation:

$$X = \frac{Area_{product}}{Area_{Product} + Area_{Reactant}}$$

Where $Area_{product}$ is the integral of the ^{1}H-NMR peak of methoxy group after photo-release (Refer to Figure 2 in the main article) and $Area_{Reactant}$ is the integral of the ^{1}H-NMR peak of methoxy group before irradiation.

The error in conversion X, ΔX, was estimated according to a simple error propagation method:

$$\Delta X = \sqrt{\left[\frac{\partial X}{\partial Area_{Dimer}}\right]^2 \cdot \Delta Area_{Dimer}{}^2 + \left[\frac{\partial X}{\partial Area_{Monomer}}\right]^2 \cdot \Delta Area_{Monomer}{}^2}$$

$$\Delta X = \sqrt{\left[\frac{Area_{Monomer}}{(Area_{Dimer} + Area_{Monomer})^2}\right]^2 \cdot [0.1 Area_{Dimer}]^2 + \left[\frac{-Area_{Dimer}}{(Area_{Monomer} + Area_{Dimer})^2}\right]^2 \cdot [0.1 Area_{Monomer}]^2}$$

2.5.4. Kinetics Measurements and Quantum Yield Calculations

Assuming the photo-cleavage of the caged phosphine **S4** follows first order kinetics, its disappearance rate is:

$d[c]/dt = -k[c]$

in which *c* is the concentration of the photolabile compound and *k* is the photolysis coefficient, which is dependent on the photo-physical properties of **S4** and incident photon flux. The above equation can be converted[7] to:

$\ln[c_0/c] = (10^3 \ln(1/10)\varepsilon I\Phi)t = (2303\varepsilon I\Phi)t$

in which I is the incident photon flux, which was determined by ferrioxalate actinometry[8] to be $2.22 \cdot 10^{-9}$ mol·s^{-1}cm^{-2} for blue LED light (445 nm) and $1.61 \cdot 10^{-11}$ mol·s^{-1}cm^{-2} for green LED light (505 nm), ε is the molar absorptivity of **S4**, determined by Beer-Lambert's law to be $1.069 \cdot 10^{4}$ mol^{-1}cm^{2} at λ = 445 nm and 32. 4 mol^{-1}cm^{2} at λ = 505 nm, Φ is the quantum yield of the photolysis.

The consumption of the caged compound **S4** was determined by ^{1}H NMR spectroscopy. Specifically, a solution of **S4** (7.56 mg, 0.1 mmol) in $CDCl_3$ (1 mL, containing trimethylsilane as internal standard for calibration) was irradiated with either blue (445 nm) or green (505 nm) LED light. After each time interval, an ^{1}H NMR measurement was undertaken and the conversion of **S4** was determined by integration of the OCH_3 resonance at 3.4 ppm (refer to **Figure S2**).

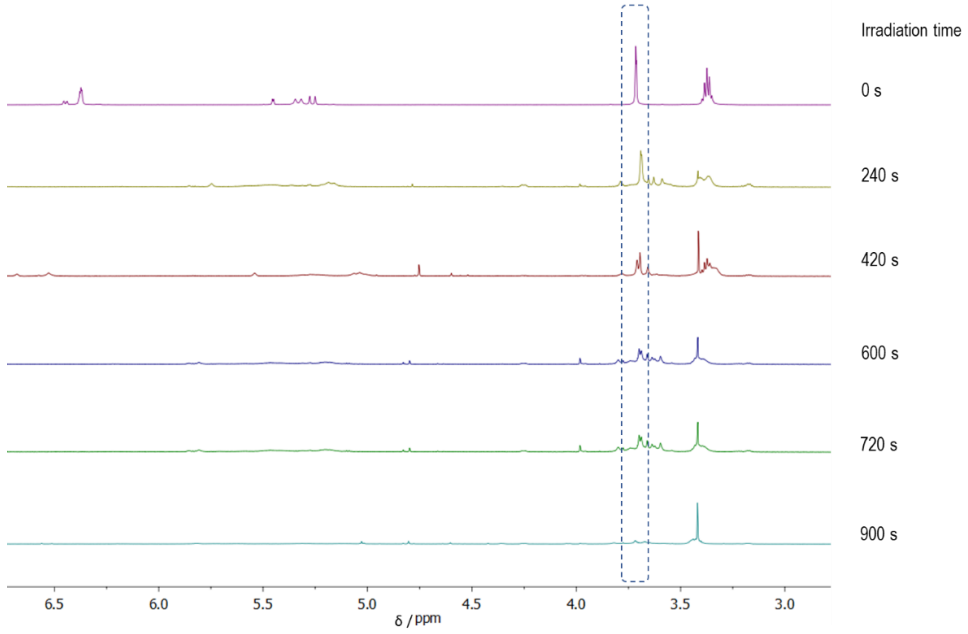
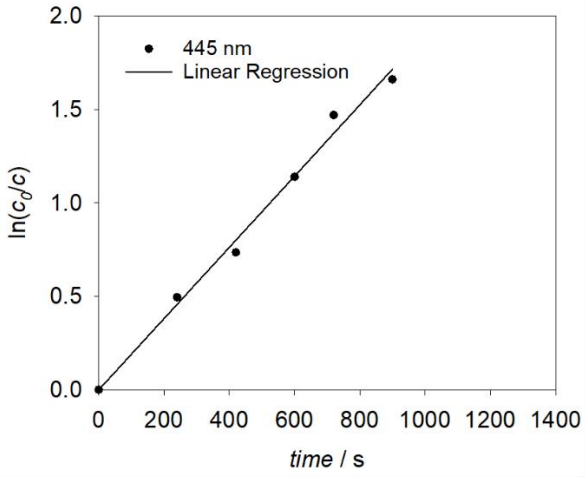


Figure S8. The photolysis of **S4** by blue (445 nm) light irradiation followed by ^{1}HNMR (in $CDCl^{3}$, 600 MHz) showing the disappearance of the resonance at 3.4 ppm.

The photolysis efficiency under irradiation at 445 nm and 505 nm was analysed as below:



Equation: Polynomial, Linear
f = y0+a*x

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9953	0.9907	0.9907	0.0605

	Coefficient	Std. Error	t	P
y0	-0.0000	0.0000	(+inf)	<0.0001
a	0.0019	4.3599E-005	43.7079	<0.0001

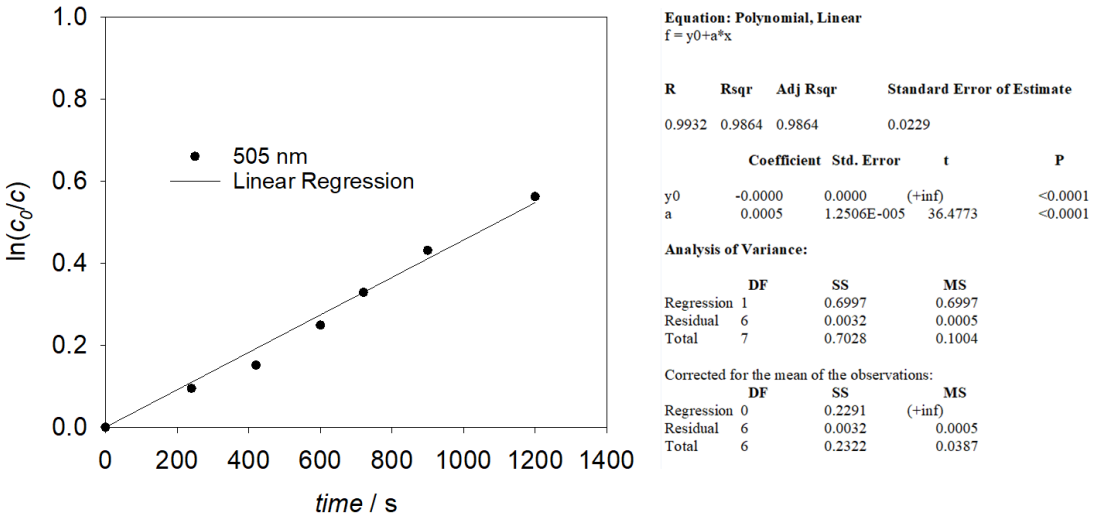
Analysis of Variance:

	DF	SS	MS
Regression	1	6.9811	6.9811
Residual	5	0.0183	0.0037
Total	6	6.9993	1.1666

Corrected for the mean of the observations:

	DF	SS	MS
Regression	0	1.9429	(+inf)
Residual	5	0.0183	0.0037
Total	5	1.9611	0.3922

Figure S9. Consumption of **S4** under irradiation of blue light (445 nm) as a function of time and linear regression fit (using SigmaPlot 14.0 software) to extract a slope value of $1.9 \cdot 10^{-3}$, which is the photolysis coefficient ($2303\varepsilon I\Phi$). Thus, the quantum yield of the photolysis is close to Φ = 0.035.



Equation: Polynomial, Linear
f = y0+a*x

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9932	0.9864	0.9864	0.0229

	Coefficient	Std. Error	t	P
y0	-0.0000	0.0000	(+inf)	<0.0001
a	0.0005	1.2506E-005	36.4773	<0.0001

Analysis of Variance:

	DF	SS	MS
Regression	1	0.6997	0.6997
Residual	6	0.0032	0.0005
Total	7	0.7028	0.1004

Corrected for the mean of the observations:

	DF	SS	MS
Regression	0	0.2291	(+inf)
Residual	6	0.0032	0.0005
Total	6	0.2322	0.0387

Figure S10. Consumption of **S4** under irradiation of green light (505 nm) as a function of time and linear regression fit (using SigmaPlot 14.0 software) to extract a slope value of $5 \cdot 10^{-4}$ which is the photolysis coefficient ($2303 \varepsilon I \Phi$). Thus the quantum yield of the photolysis is close to $\Phi = 2.4 \cdot 10^{-3}$

2.6. ToF-SIMS

ToF-SIMS data were acquired using an IONTOF M6 instrument (IONTOF GmbH, Münster, Germany) equipped with a reflectron time-of-flight analyser and Bi/Mn primary-ion source. Bi^{3+} cluster ions were selected from the 30 keV pulsed primary-ion beam for the analysis and the pulses 'bunched' for optimum mass resolution ($m/\Delta m > 8000$). Primary ions were limited to 1.14×10^{10} ions cm^{-2}, which is well below that required for static conditions. During data acquisition, the pressure in the analysis chamber was maintained at, or below, 1.5×10^{-9} mbar. Due to the required large fields of view, the stage raster mode was used and individual patches of 2000 μm^2 were stitched by moving the sample. Each patch consists of 5 scans, rastered in random mode, with 1000 pixels/mm^2. Spectra were calibrated on the omnipresent C^-, CH^-, CH_2^-, C_2^-, C_3^-, C_4^-, C_5H^-, C_6H^- for negative polarity or on the C^+, CH^+, CH_2^+, $C_2H_2^+$, $C_3H_2^+$, $C_4H_4^+$, $C_5H_4^+$ peaks for positive polarity. Based on these datasets the chemical assignments for characteristic fragments were determined.

2.7. Surface Patterning

Silicon substrates were cleaned in plasma cleaner prior to treatment. Subsequently, they were functionalized with compound **S6** at 50°C for 5 hours by placing them in the solution (1 mg/mL) in acetonitrile. The substrates were washed with excess acetonitrile and sonicated. For the photo-patterning experiments, the substrates were placed in a photomask and the photomask was dipped into a solution of caged MPPB (1 mg/mL) in a vial (**Figure S11**). The vial was covered with a glass slid and the substrate irradiated from the top with LEDs (**Figure S12**).

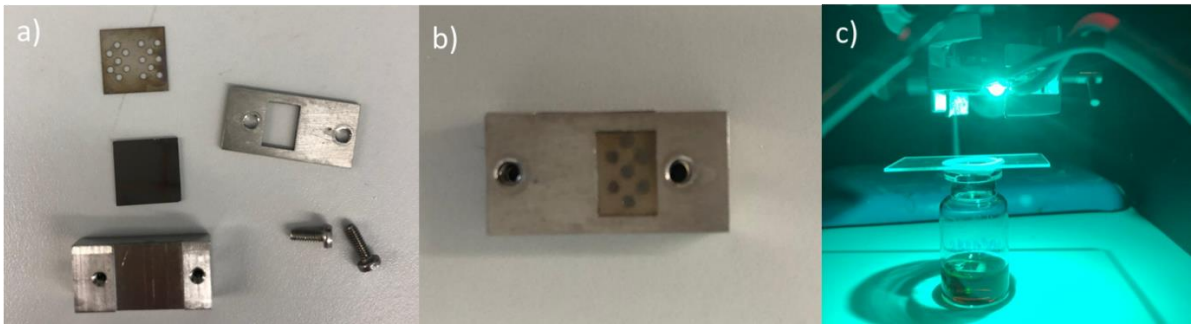


Figure S11. Set-up for surface patterning. **a)** Photomask components and silicon surface. **b)** Assembled set-up. **c)** Patterning set-up with an LED light source and the photomask placed in a MPPB solution.

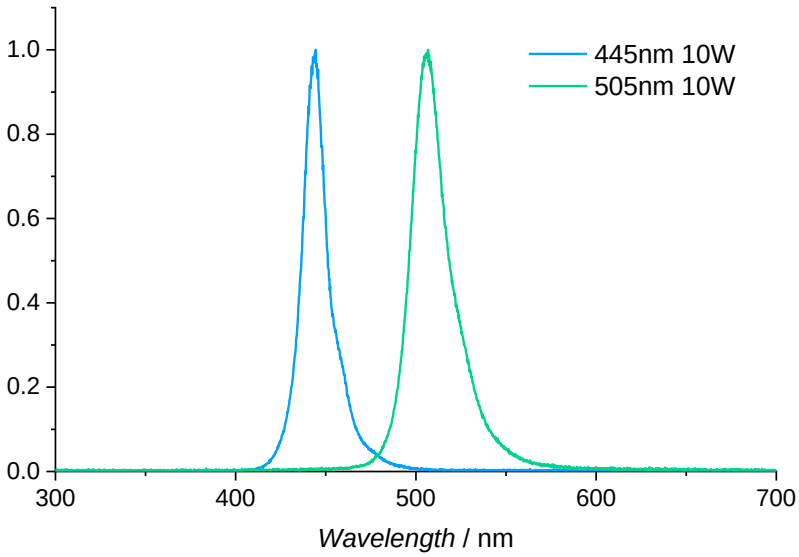


Figure S12. Emission spectra of 445 and 505 nm LEDs used for irradiation experiments.

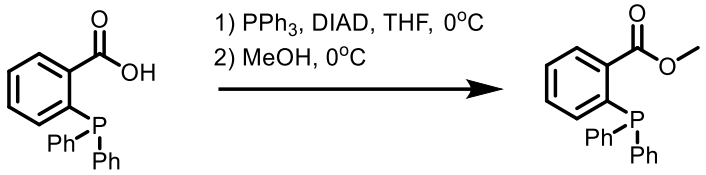
3. Synthetic procedures

3.1. Materials

Solvents (dichloromethane, hexane, petroleum ether, ether, ethyl acetate, dioxane, acetone, acetonitrile, tetrahydrofuran, and methanol) were purchased from Thermo Fisher Scientific in HPLC grade and used directly. All other chemicals used as received from the supplier without further purification.

Thin-layer chromatography (TLC) was performed on silica gel 60 F254 alumina sheets (Merck) and visualized by UV light or potassium permanganate solution. Column chromatography was run on silica gel 60 (0.04-0.06 mm, 230-400 mesh ASTM, Merck).

3.2. Synthesis of Methyl 2-(diphenylphosphino)benzoate (S1)[6]



To a solution of triphenylphosphine (2.6 g, 9.8 mmol) in anhydrous tetrahydrofuran (45 mL) was added diethylazodicarboxylate (1.71 g, 9.8 mmol) at 0°C, and the reaction was stirred for 15 minutes. Methanol (0.27 mL, 6.5 mmol) was subsequently added and after 5 min, a solution of 2-(diphenylphosphino)benzoic acid (2 g, 6.5 mmol) in anhydrous THF (40 mL) was added. The reaction was stirred an additional 5 minutes at 0°C and then, warmed to ambient temperature. The residue was purified via flash chromatography with eluent (hexane: ethylacetate = 4: 1) to afford pure product as a white solid (Yield:1.26 g, 61%). ^{1}H NMR (600 MHz, Acetonitrile-d_3) δ 7.97 – 7.85 (m, 1H), 7.41 – 7.11 (m, 12H), 6.90 – 6.79 (m, 1H), 3.59 (s, 3H). The NMR spectral data are similar to the previously reported values.[6]

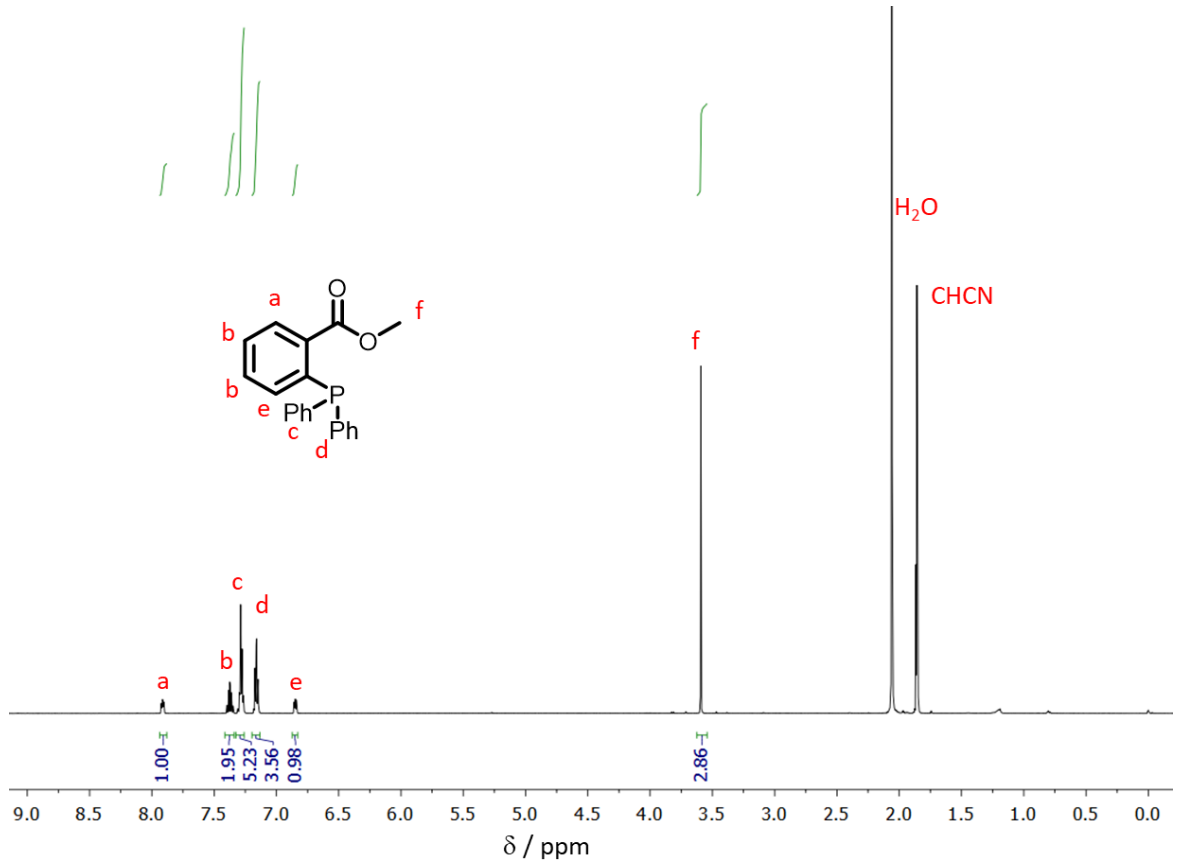


Figure S13. ^{1}H NMR spectrum of **S1** (CD_3CN, 600 MHz).

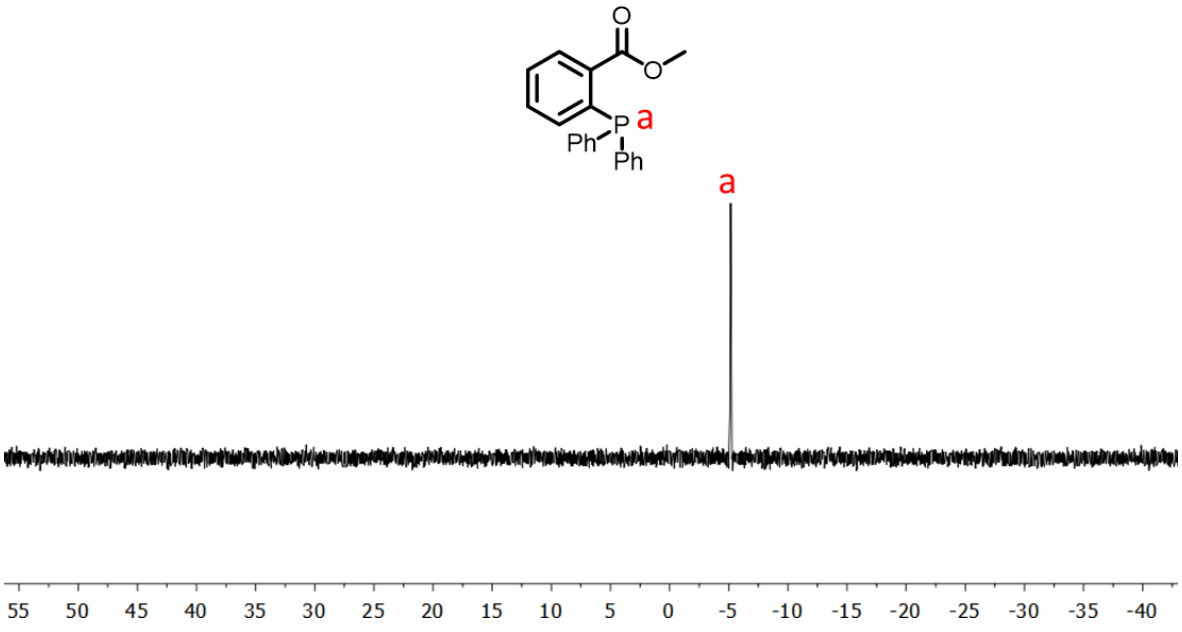
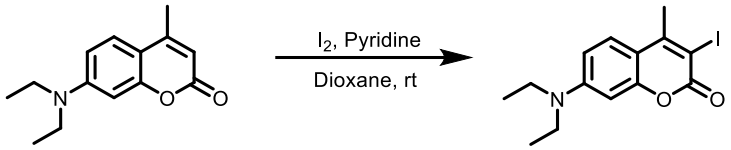


Figure S14. ^{31}P NMR spectrum of **S2** ($CDCl_3$).

3.3. Synthesis of 7-(diethylamino)-3-iodo-4-methyl-2H-chromen-2-one (S2)[7]



To a solution iodine (30 mmol, 7.62 g, 3 equiv.) in a mixture of 100 ml dioxane and 5 ml pyridine, 7-(diethylamino)-4-methyl-2H-chromen-2-one (10 mmol, 2.31 g, 1 equiv.) was added. The mixture was stirred at ambient temperature overnight. A 50 mL saturated solution of sodium thiosulfate was poured into the reaction mixture and extracted with DCM (3 x 100 ml). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was separated by flash chromatography with eluent (ethyl acetate: hexane = 1: 4), and the title compound was afforded as a yellow solid (Yield: 2.93 g, 80%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 9.1 Hz, 1H), 6.51 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.43 (d, *J* = 2.6 Hz, 1H), 3.34 (q, *J* = 7.1 Hz, 4H), 2.53 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H). The NMR spectral data are similar to the previously reported values.[7]

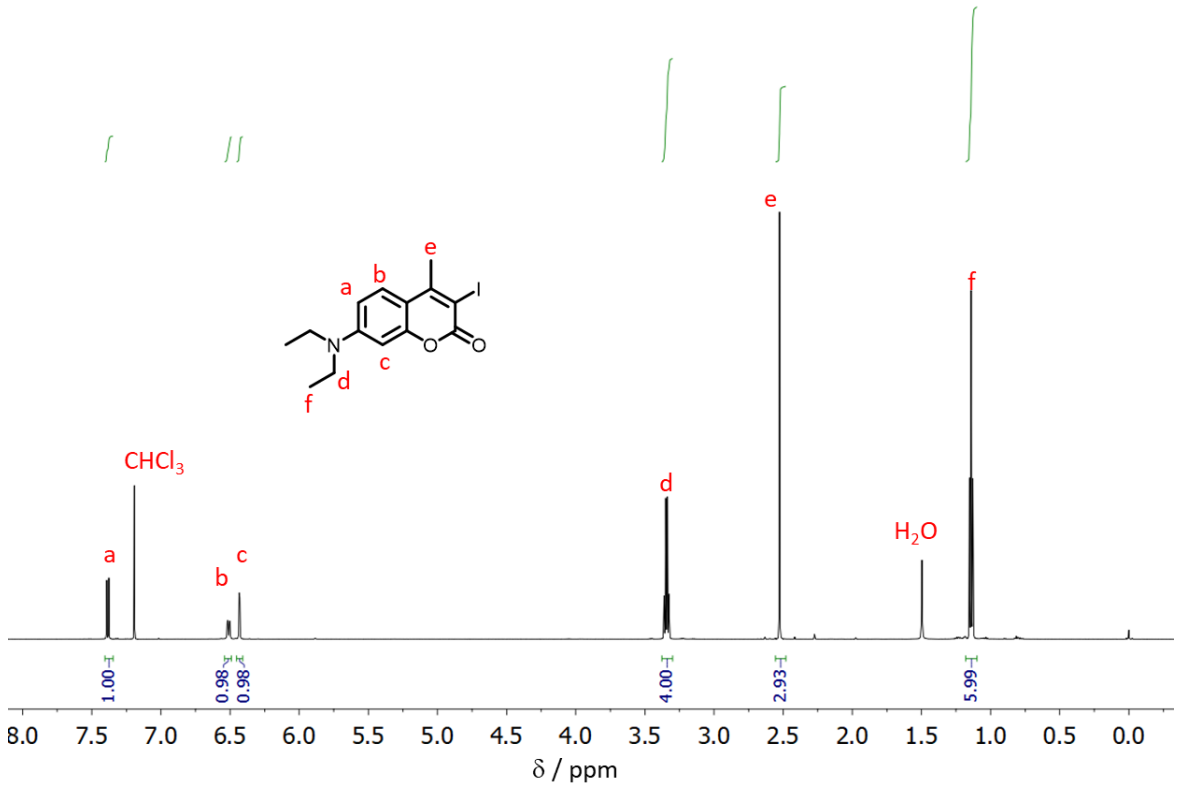
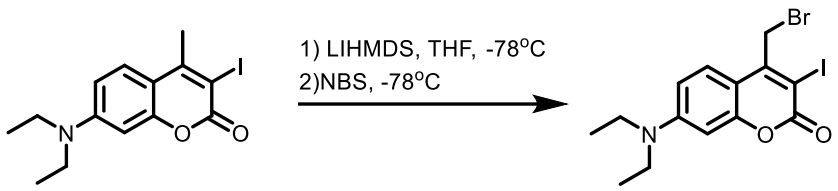


Figure S15. ^{1}H NMR spectrum of **S2** ($CDCl_3$, 600 MHz).

3.4. Synthesis of 4-(bromomethyl)-7-(diethylamino)-3-iodo-2H-chromen-2-one (S3)[7]



To a solution of **S2** (5 mmol, 1.785 g, 1 equiv.) in anhydrous THF (45 mL) cooled to – 30 °C, LiHMDS (1 M in THF, 6.5 mL, 1.3 equiv.) was added dropwise. The solution was stirred for 1 hour, followed by cooling to –78 °C. A solution of N-bromosuccinimide (979 mg, 5.5 mmol, 1.1 equiv.) in anhydrous THF (5 mL) was added dropwise, and the mixture was stirred at –78 °C for 2 h. The mixture was treated with HCl (0.1 M) and extracted three times with DCM (3×100 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether: ethyl acetate: DCM = 4: 1: 1) to yield the product as orange solid (Yield: 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 9.1 Hz, 1H), 6.6 (dd, *J* = 9.1, 2.5 Hz), 6.48 (s), 4.62 (s), 3.39 (t, J = 7.1 Hz), 1.15 (t, J = 7.1Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 155.8, 153.6, 151.3, 125.9, 109.3, 106.7, 97.4, 84.4, 45.0, 32.9, 12.5; $[M]^+_{calculated}$= 435.9403, $[M]^+_{experimental}$ = 435.9402.

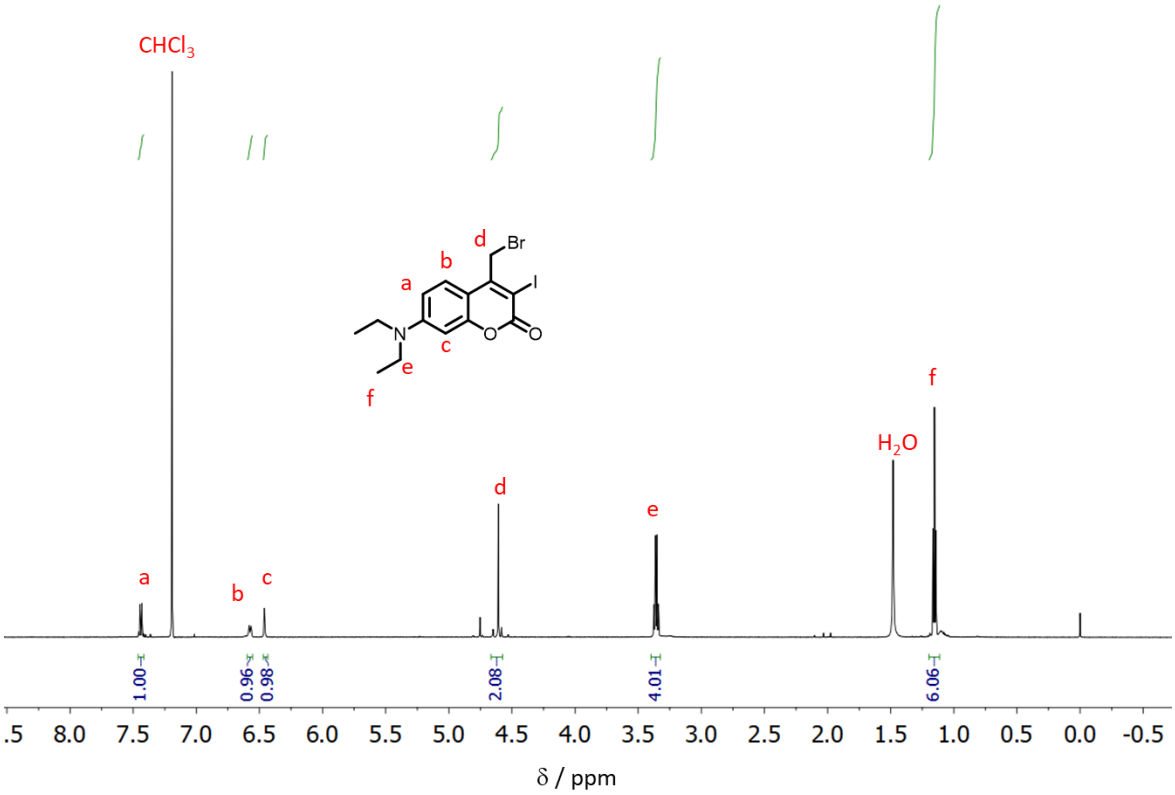
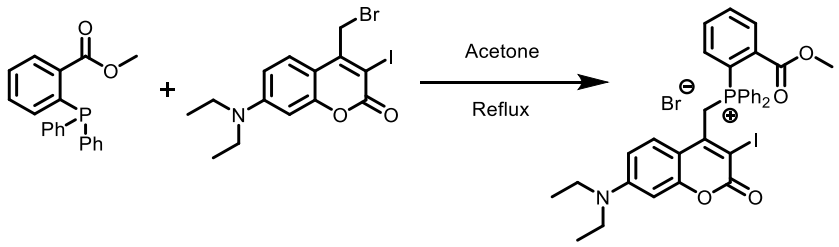


Figure S16. ^{1}H NMR spectrum of **S3** ($CDCl_3$, 600 MHz).

3.5. Synthesis of ((7-(diethylamino)-3-iodo-2-oxo-2H-chromen-4-yl)methyl)(2-(methoxycarbonyl)phenyl)diphenylphosphonium (S4)



To a solution of **S3** (39 mg, 0.1 mmol, 1 equiv.) in 1 mL acetone, **S1** (48 mg, 0.15 mmol, 1.5 equiv.) was added. The solution was stirred under reflux for 2 h, and subsequently cooled to ambient temperature. The resulting precipitate was purified by centrifugation in petroleum ether: ethyl acetate (1: 1) for several times, followed by in ether for three times. The product was collected as yellow solid (yield: 78%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 (t, *J* = 6.5 Hz, 1H), 8.41 – 8.25 (m, 2H), 8.09 – 7.99 (m, 2H), 7.94 (d, *J* = 4.1 Hz, 1H), 7.64 (td, *J* = 13.5, 7.5 Hz, 4H), 7.59 – 7.46 (m, 6H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.41 (d, *J* = 8.7 Hz, 1H), 6.36 – 6.28 (m, 1H), 5.21 (dd, *J* = 39.2, 16.4 Hz, 2H), 3.64 (d, *J* = 1.1 Hz, 3H), 3.35 – 3.26 (m, 4H), 1.11 (td, *J* = 7.1, 4.0 Hz, 6H); ^{13}C NMR (145 MHz): 156.01, 154.27, 151.32 (d), 144.3, 137.87, 136.35, 134.97 (d), 135.63 (d), 133.41 (d), 130.05 (d), 129.86 (d), 127.32 (d), 119.51, 118.91 (d), 118.16, 110.7, 110.23, 109.41, 107.52, 97.25, 97.86, 53. 88(d), 45.01 (d), 31.53, 12.48; $[M]^{+}_{calculated}$= 676.1108, $[M]^{+}_{experimental}$= 676.1102

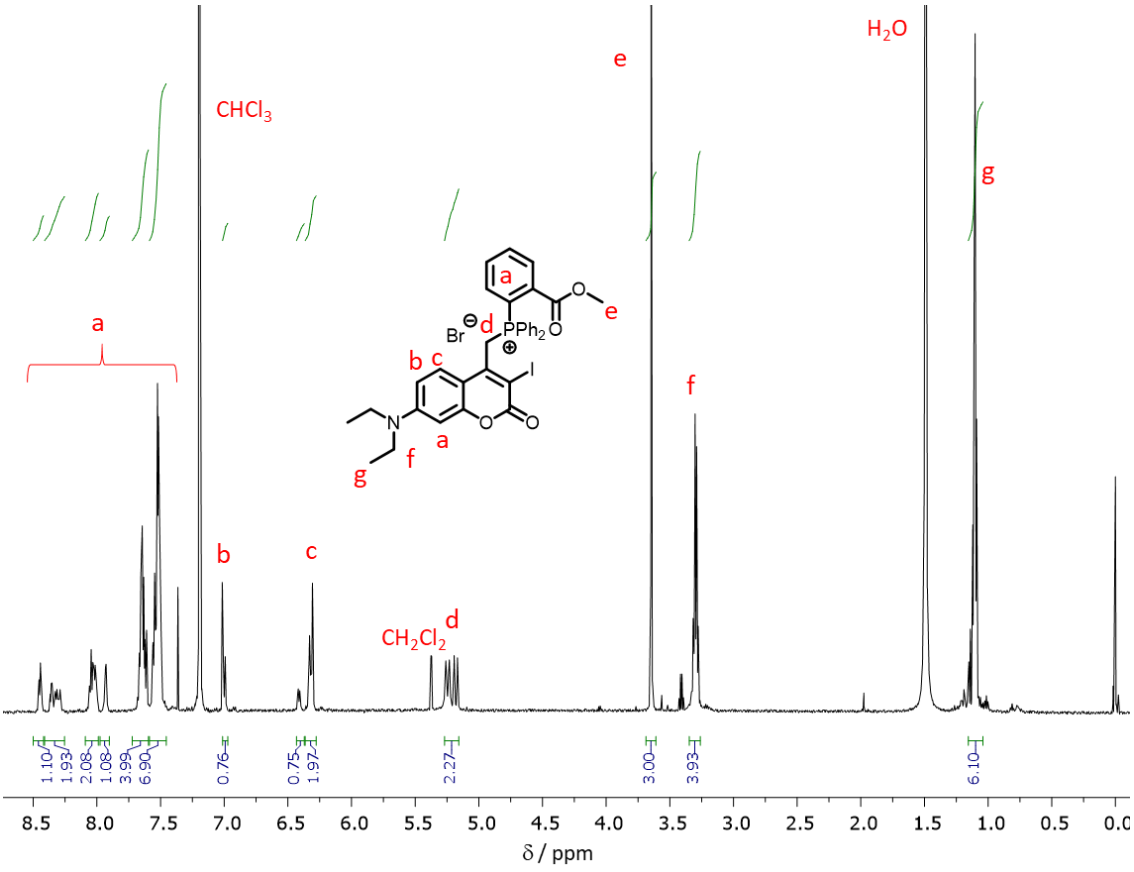


Figure S17. ^{1}H NMR spectrum of **S4** ($CDCl_3$, 600 MHz).

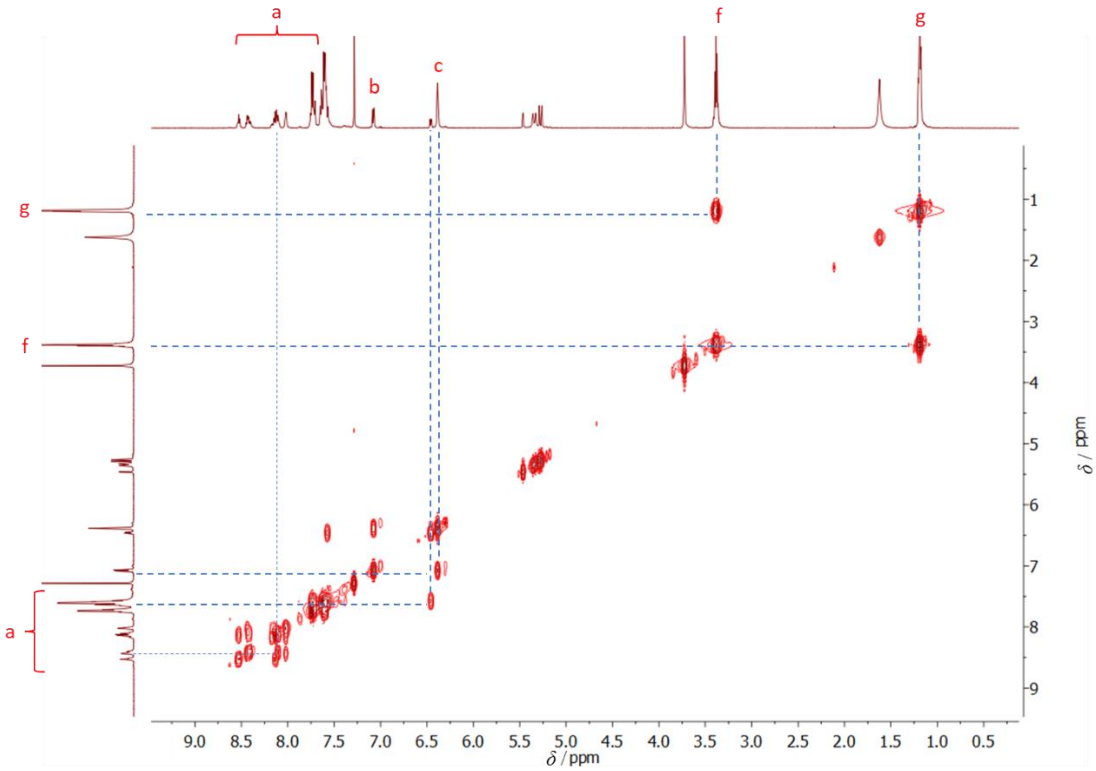


Figure S18. ^{1}H COSY NMR spectrum of S4 ($CDCl_3$). The relevant cross resonances (referred to Figure S13 for the chemical structure) are depicted as dashed lines.

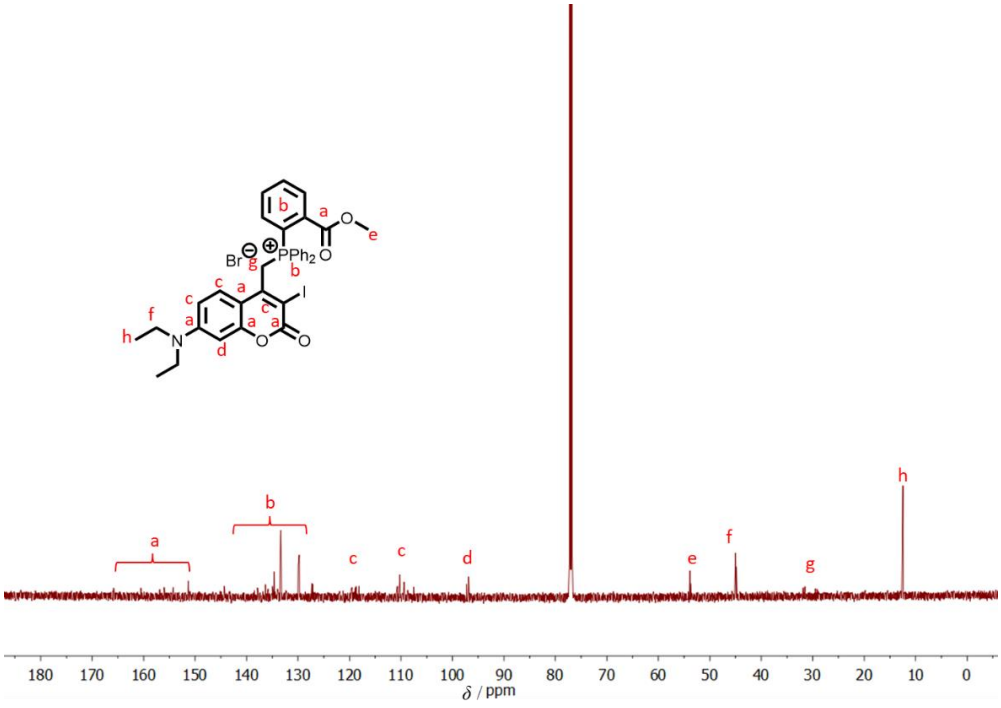
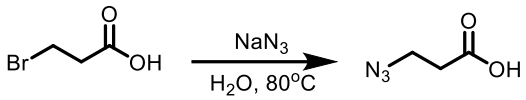


Figure S19. ^{13}C NMR spectrum of **S4** ($CDCl_3$, 145 MHz).

3.6. Synthesis of 3-azidopropanoic acid (S5)



3-Bromopropionic acid (0.76 g, 5.00 mmol, 1 equiv.) was dissolved in H_2O (10 mL). Sodium azide (0.65 g, 10.00 mmol, 2 equiv.) was added and stirred overnight at 80°C. The reaction mixture was acidified with concentrated HCl to pH = 1 and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine (30 mL). The solvent was dried over Na_2SO_4 and evaporated at 25 °C to obtain 3-azidopropanoic acid as light yellow oil, which was used without further purification (Yield:0.55 g, 94%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.53 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.5 Hz, 2H).

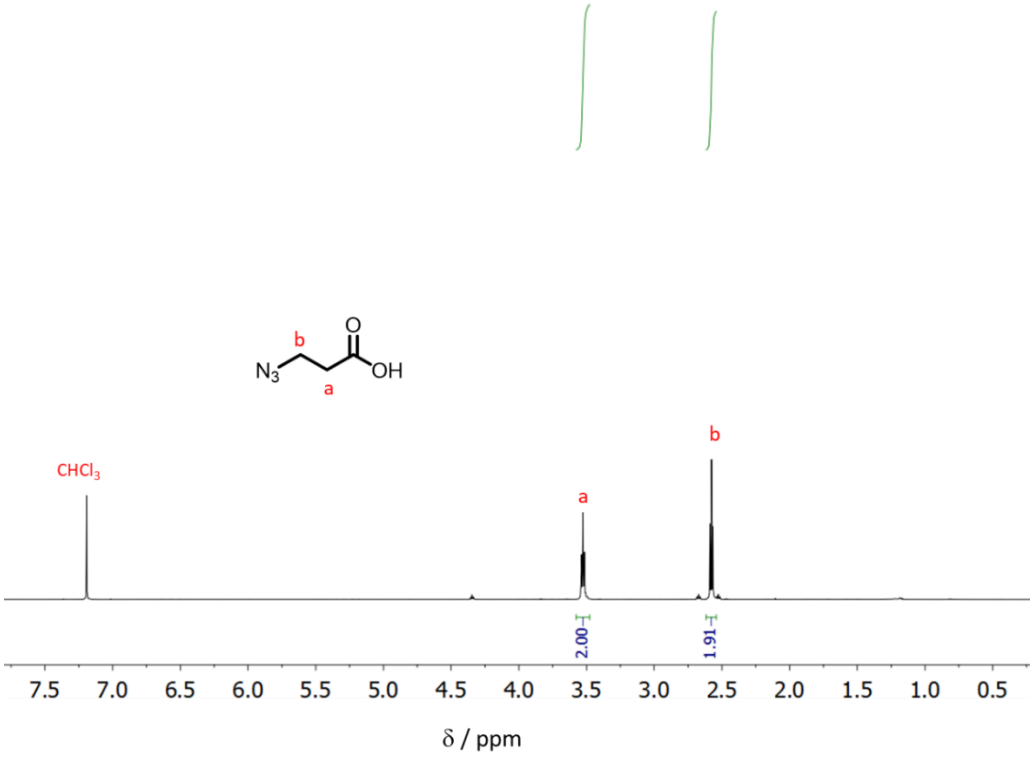
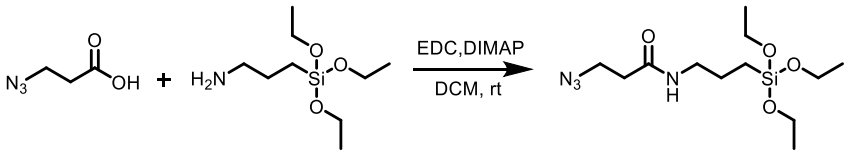


Figure S20. ^{1}H NMR spectrum of **S5** ($CDCl_3$, 600 MHz).

3.7. Synthesis of 3-azido-N-(3-(triethoxysilyl)propyl)propanamide (S6)



To a solution of **S5** (0.52 g, 4.6 mmol, 1 equiv) in 40 mL DCM, 3-{[(Ethylimino)methylidene]amino}-*N*,*N*-dimethylpropan-1-amine (1.31 g, 6.8 mmol, 1.5 equiv.) and *N*,*N*-Dimethylpyridin-4-amine (83 mg, 0.7 mmol, 0.15 equiv.) were added under stirring at ambient temperature. 3-(triethoxysilyl)propan-1-amine (1.51 g, 6.8 mmol, 1.5 equiv.) was subsequently added to this solution and reaction mixture

stirred overnight at ambient temperature. The reaction mixture was extracted with NaHCO3 (2 x 40 mL), water (2 x 40 mL) and brine (2 x 40 mL). Organic layers are combined and dried over Na_2SO_4. The solvent was evaporated via rotavap and the product was obtained as pale yellow oil (Yield: 1.23 g, 85%). This compound was used without further purification. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.87 (s, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 3.65 (qt, *J* = 7.0, 0.8 Hz, 2H), 3.21 (q, *J* = 6.6 Hz, 2H), 2.33 (t, *J* = 6.5 Hz, 2H), 2.17 (s, 1H), 1.61 – 1.54 (m, 2H), 1.17 (q, *J* = 7.0 Hz, 9H), 0.61 – 0.56 (m, 2H).

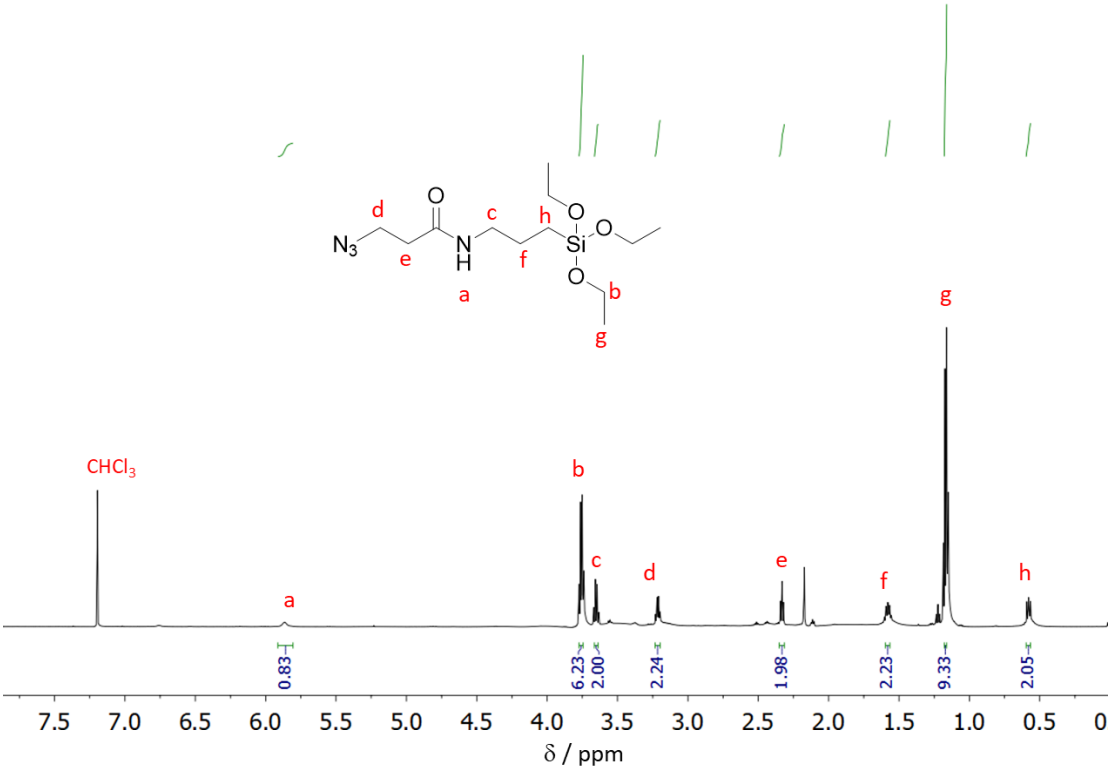


Figure S21. ^{1}H NMR spectrum of **S6** ($CDCl_3$, 600 MHz).

3.8. Synthesis of PEG-azide (S7)

MeO-PEG-OH (MW: 2000 Da, 4 g, 2 mmol) and triethylamine (0.5 g, 5 mmol) were dissolved in dichloromethane (10 mL) and the solution was cooled on an ice bath. To this solution methanesulfonyl chloride (0.5 g, 4.6 mmol) was added and the solution was stirred at 0 ◦C for 1 h. The solution was allowed to reach ambient temperature and precipitated into diethyl ether (100 mL). The precipitate was collected and used directly in the next step.

The above solid was dissolved in DMF (10 mL) and sodium azide (0.35 g, 5 mmol) was added. The solution was stirred at 70 ºC for 10 h and DMF was evaporated *in vacuo.* The residue was redissolved in dichloromethane (50 mL), filtered, washed with water (100 mL x 2), brine (100 mL), and dried on $MgSO_4$. The solution was concentrated to ca. 5 mL and precipitated into diethyl ether (100 mL) to give polymer product was white solid (total yield: 87%). ^{1}H NMR (600 MHz, Chloroform-*d*): 3.89 (broad s), 3.41 (s), 3.2 (s). M_n = 3560 g mol^{-1}, $Đ$ = 1.04.

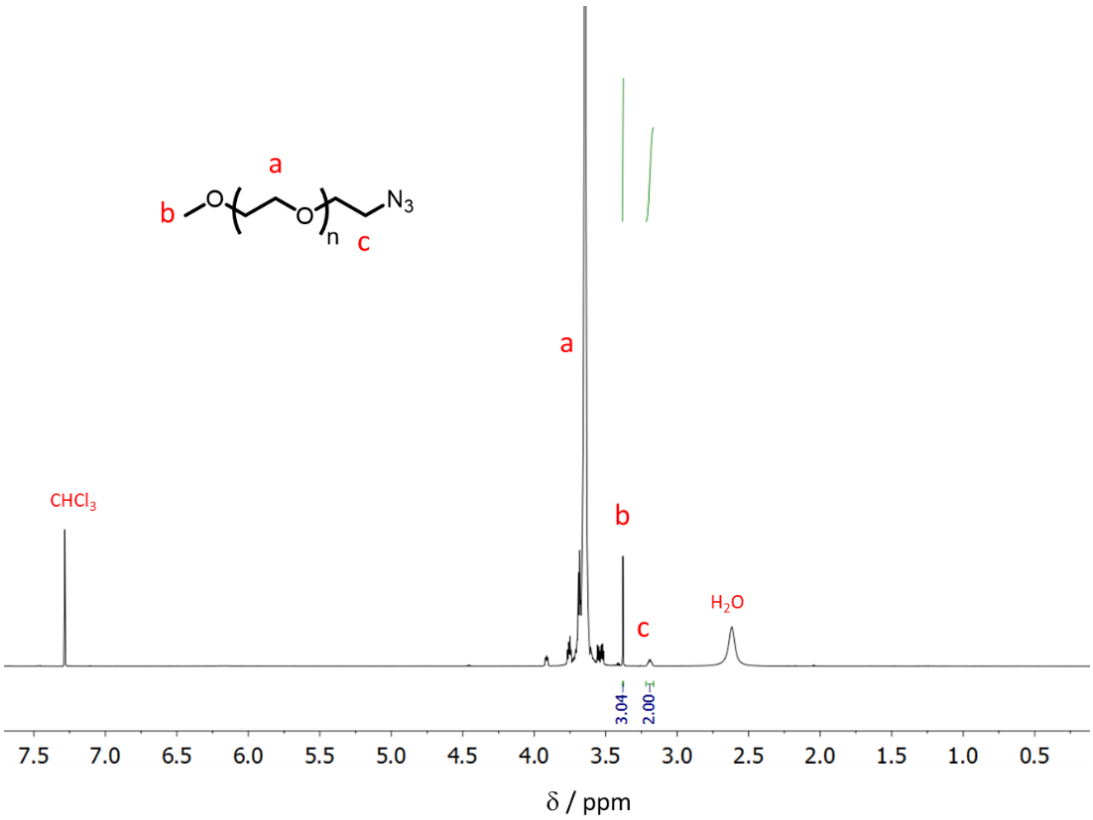
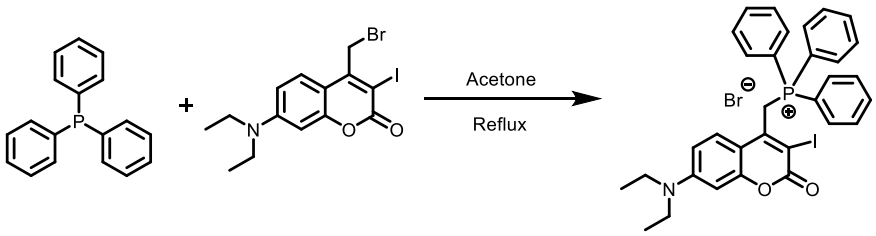


Figure S22. ^{1}H NMR spectrum of **S7** ($CDCl_3$, 600 MHz).

3.9. Synthesis of caged triphenyl phosphine (S8)



To a solution of S3 (390 mg, 1 mmol, 1 equiv.) in acetonitrile (10 mL) triphenylphosphine (480 mg, 0.15 mmol, 1.5 equiv.) was added. The solution was stirred under reflux for 2 h, and subsequently cooled to ambient temperature. The solid was purified by column chromatography running with hexane: ethylacetate: MeOH (v/v/v = 1/1/0.1) to give product as red solid (yield: 88%). ^{1}H NMR (600 MHz, Acetonitrile-d): 7.98 (m), 7.72 (m), 6.81 (d, *J* = 9.2 Hz), 6.5 (s), 6.24 (d, *J* = 9.1 Hz), 5.1 (d, *J* = 4.2 Hz), 3.39 (q, *J* = 7.1 Hz), 1.21 (t, *J* = 7.2 Hz). ^{13}C NMR (145 MHz): 171.2, 136.35 (d), 135.26 (d), 134.68 (d), 130.94 (d), 130.56 (d), 127.21, 117.86, 117.33, 116.76, 109.27, 97.32, 60.53, 45.02, 20.72, 14.09, 12.19. $[M]^{+}_{calculated}$= 618.1054, $[M]^{+}_{experimental}$= 618.1067.

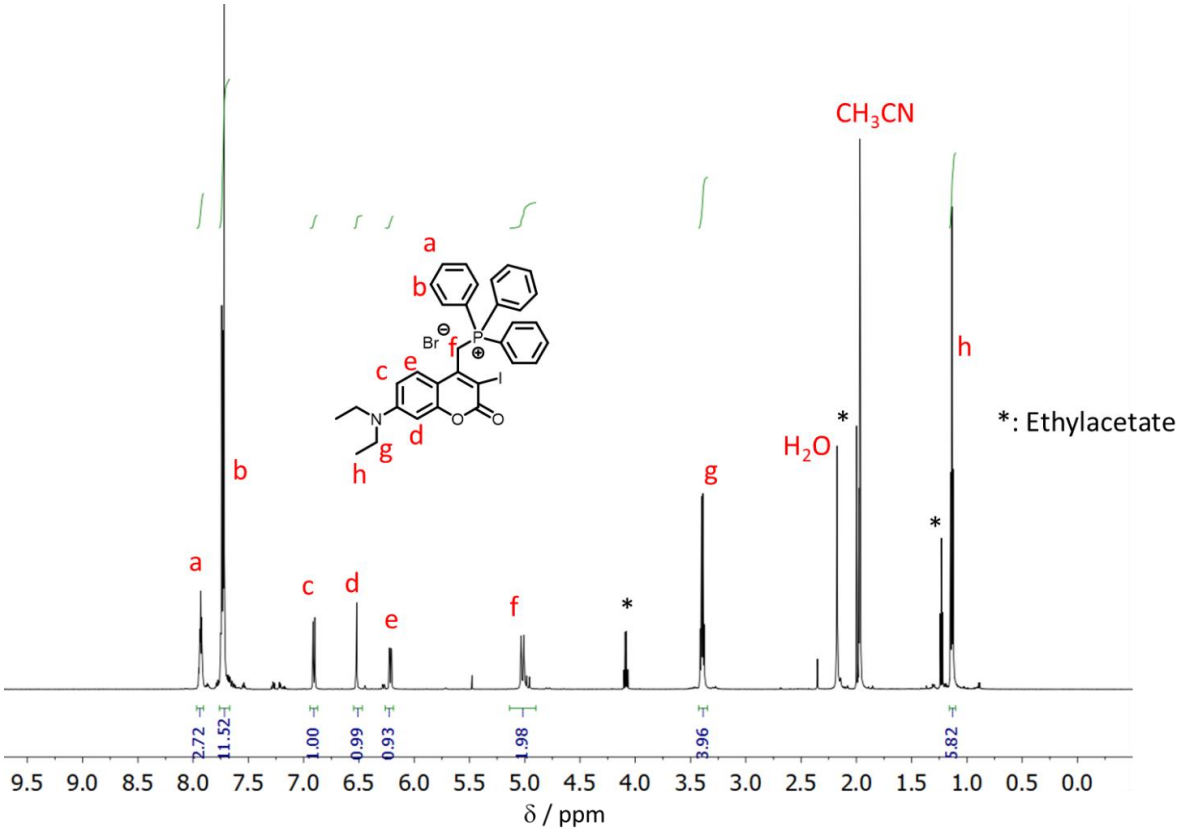


Figure S23. ^{1}H NMR spectrum of **S8** (CD_3CN, 600 MHz).

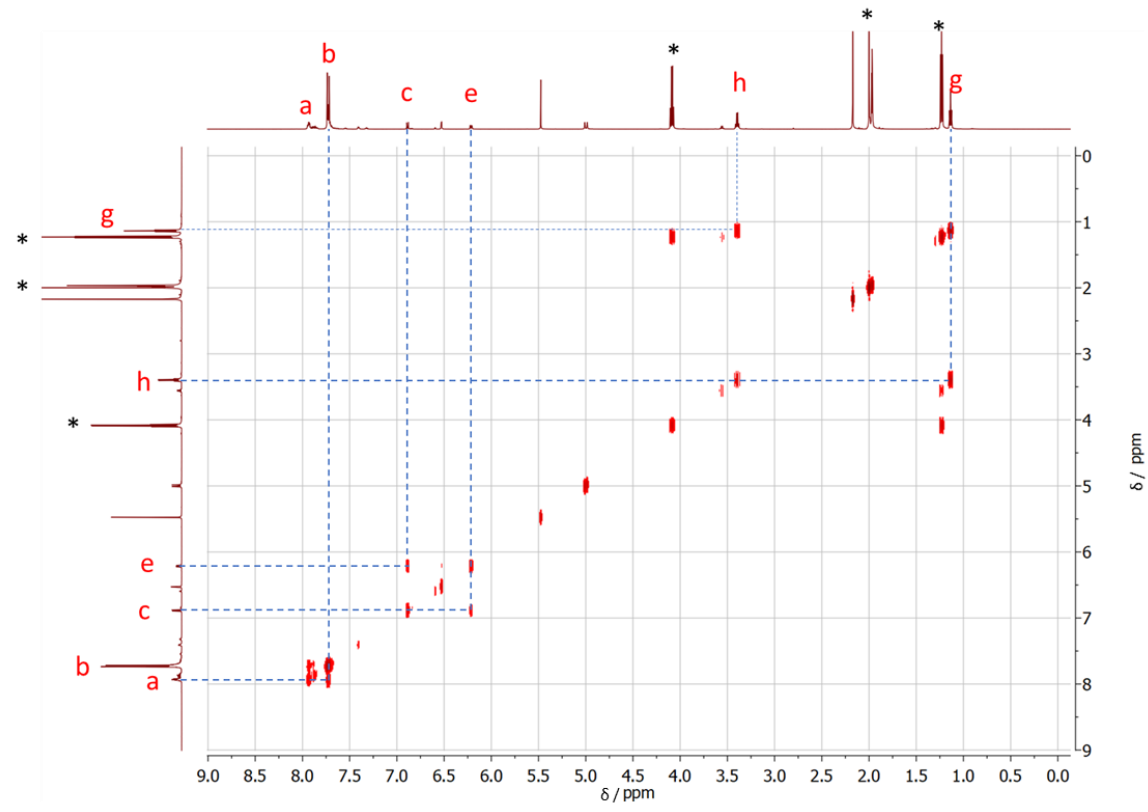


Figure S24. ^{1}H COSY NMR spectrum of S4 (CD_3CN). The relevant cross resonances (referred to Figure S13 for the chemical structure) are depicted as dashed lines.

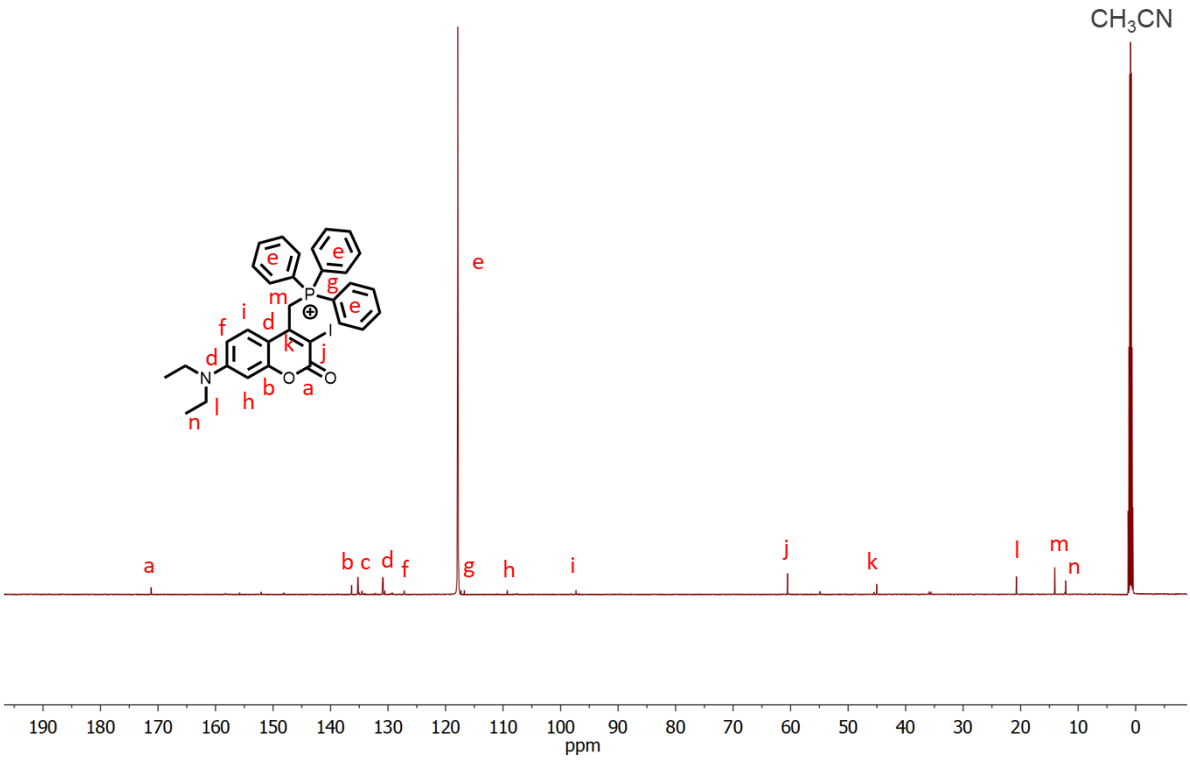


Figure S25. ^{13}C NMR spectrum of **S8** (CD_3CN, 145 MHz).

3.10. Green light-induced Staudinger reactions

To a solution of of MeO-PEG-N_3 (100 mg, 0.05 mmol) in acetonitrile/water (v/v = 8/2, 2 mL) x either caged methyl ester triphenylphosphine **S4** or caged triphenyl phosphine **S8** (2.5 mmol) were added. The glass vessel was sealed and the solution was purged with argon for 30 min, followed by irradiation with green light (505 nm, LED light source, Figure S8) for 1 h. The solution was then precipitated in ice cold diethyl ether (20 mL). The precipitate was collected, redissolved in dichloromethane (1 mL) and precipitated in ice cold diethyl ether (20 mL). This process was repeated twice to give products as off-white solids (yield: 61-65%).

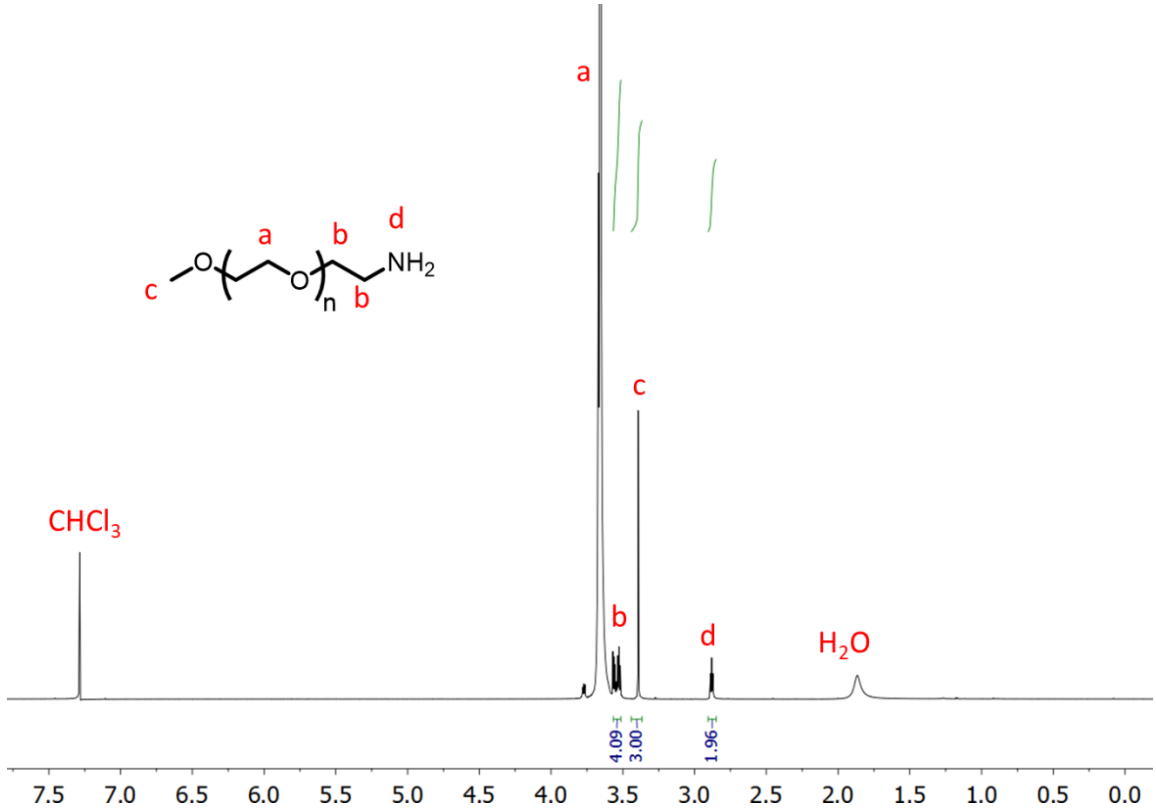


Figure S26. ^{1}H NMR spectrum of product from green light induced Staudinger reaction of MeO-PEG-N_3 with **S8** (CD_3Cl, 600 MHz).

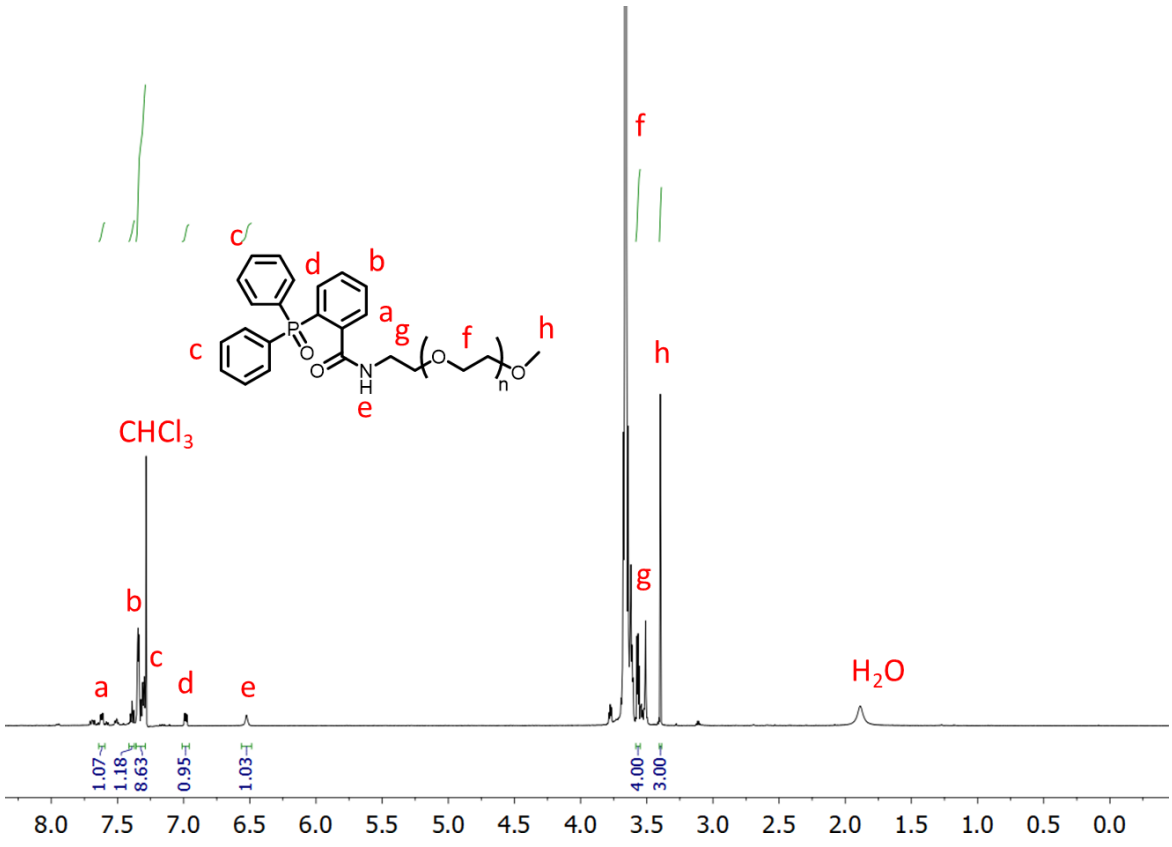


Figure S27. ^{1}H NMR spectrum of product from green light induced Staudinger reaction of MeO-PEG-N_3 with **S4** (CD_3Cl, 600 MHz).

4. References

[1] Gruendling, T.; Guilhaus, M.; Barner-Kowollik, C. *Macromolecules* **2009**, *42*, 6366.

[2] D. E. Marschner, H. Frisch, J. T. Offenloch, B. T. Tuten, C. R. Becer, A. Walther, A. S. Goldmann, P. Tzvetkova, C. Barner-Kowollik, *Macromolecules* **2018**, *51*, 3802–3807.

[3] J. P. Menzel, B. B. Noble, A. Lauer, M. L. Coote, J. P. Blinco, C. Barner-Kowollik, *J. Am. Chem. Soc.* **2017**, *139*, 15812-15820.

[4] D. E. Fast, A. Lauer, J. P. Menzel, A.-M. Kelterer, G. Gescheidt, C. Barner-Kowollik, *Macromolecules* **2017,** *50*, 1815-1823.

[5] J. P. Menzel, F. Feist, B. Tuten, T. Weil, J. P. Blinco, C. Barner-Kowollik, *Angew. Chem. Int. Ed.* **2019**, *58*, 7470-7474.

[6] J. A. Reisz, E. B. Klorig, M. W. Wright, S. B. King, *Org. Lett.* **2009,** *11*, 2719-2021.

[7] X. J. Tang, Y. Wu, R. Zhao, X. Kou, Z. Dong, W. Zhou, Z. Zhang, W. Tan, X. Fang, *Angew. Chem. Int. Ed.* **2020**, *59,* 18386-18389.

[8] a) C. G. Hatchard, C. A. Parker, *Proc. Math. Phys. Eng. Sci. P ROY SOC A-MATH PHY* **1956,** 235**,** 518-536; b) M. Li, A. P. Dove and V. X. Truong, *Angew Chem Int*, **2020**, 59, 2284-2288.