Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Triphenylsulfonium topophotochemistry

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Contents:

1. Emission spectrum for the irradiation sources.

a) ***193-nm irradiation*** (30 W D_2-lamp with a 193 nm bandpass (20+/–5 nm FWHM) filter (flux through 1" aperture at 10 cm = 4.3 x 10^{-10} Einsteins s^{-1}) and a water filter.

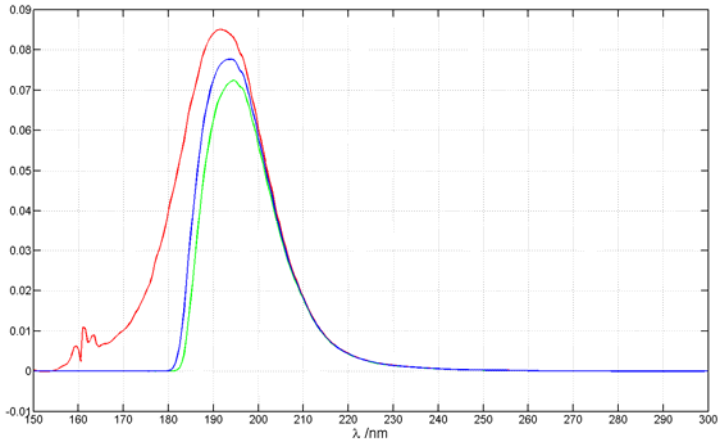


Fig S1. Calculated emission spectrum of the D_2-lamp. Red line: 193-nm bandpass filter; blue line: 193-nm bandpass filter + 0.5-cm-water filter; green light: 193-nm bandpass filter + 1-cm-water filter.

b) ***254-nm irradiation*** provided by a Xe-lamp with a krypton fluoride (KrF) excimer mirror coupled with two 1-cm-water filters and a 254-nm interference filter.

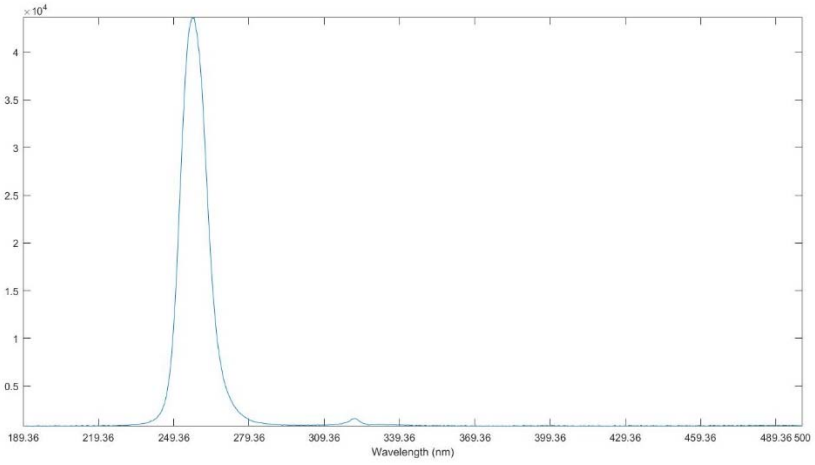


Fig S2. Emission spectrum of the Xe-lamp set-up (maximum band at 254 nm).

2. Monitoring over time the formation of photoproducts under 193-nm irradiation.

A PMMA/TPS film was irradiated at 193 nm and UV-Vis spectra were recorded every 15 minutes the first 8 hours then 12 and 24 hours.

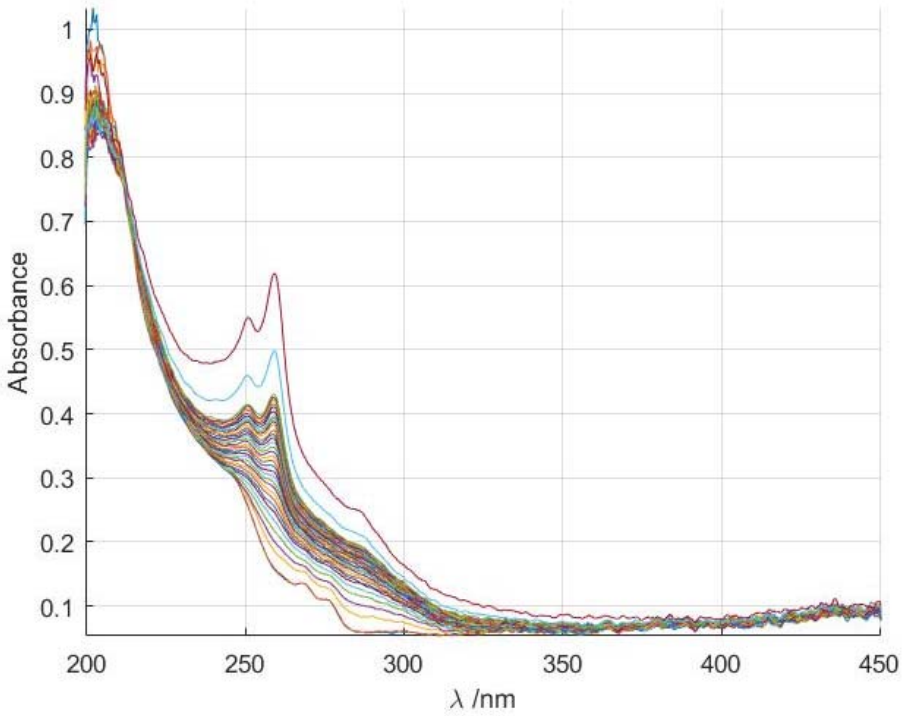


Fig S3. UV-Vis spectra of the photoproducts obtained over time at 193-nm irradiation.

3. 193-nm irradiation of TPS films with different polymer matrixes.

a) Poly(ethyleneglycol) methyl ether (M_w = 2,000) film (10% w/v PGME, 1% w/v TPS).

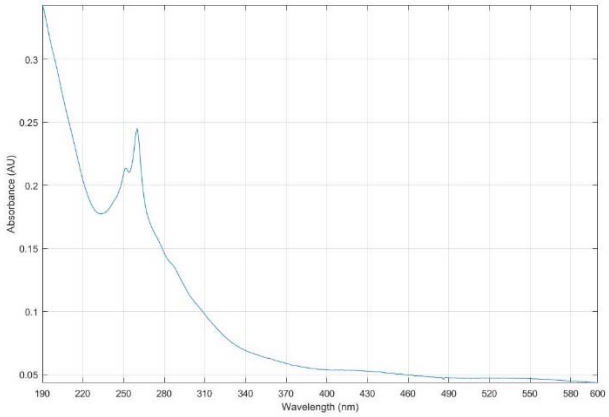


Figure S4. UV-Vis spectrum after 3 days of 193-nm irradiation of a PGME/TPS film.

b) Poly(tBMA-co-HEMA-co-GBLMA).

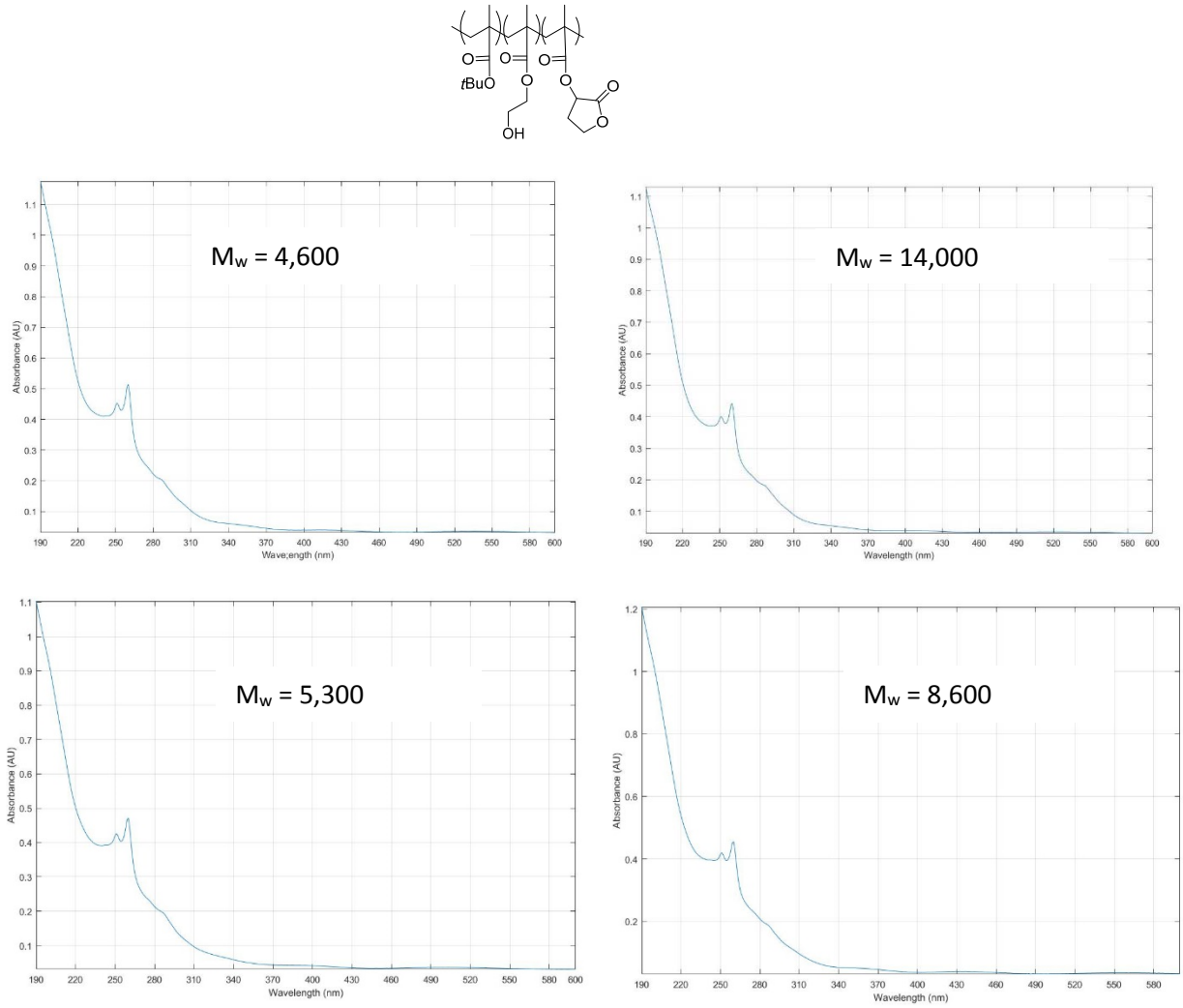


Figure S5. UV-Vis spectra of poly(tBMA-co-HEMA-co-GBLMA)/TPS films after 3 days of 193-nm irradiation.

4. Monitoring over time the formation of photoproducts at 254-nm irradiation.

A PMMA/TPS film was irradiated at 254 nm and UV-Vis spectra were recorded every hour during 20h.

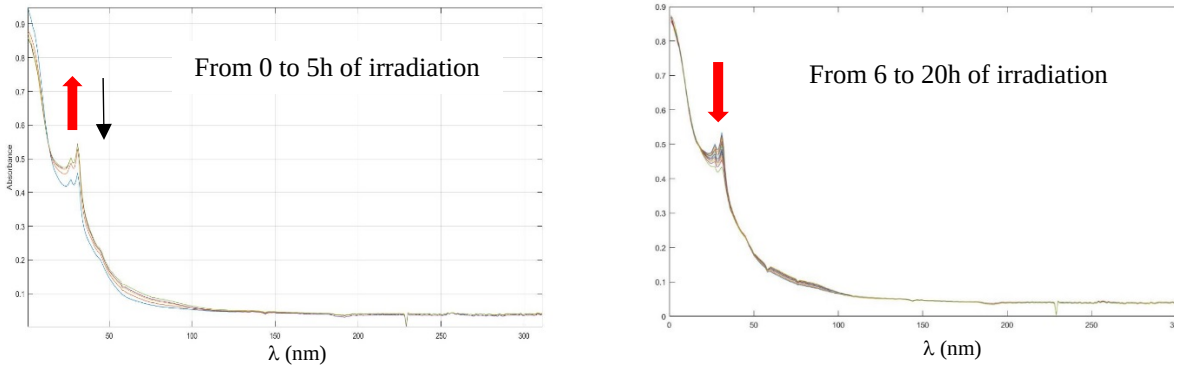
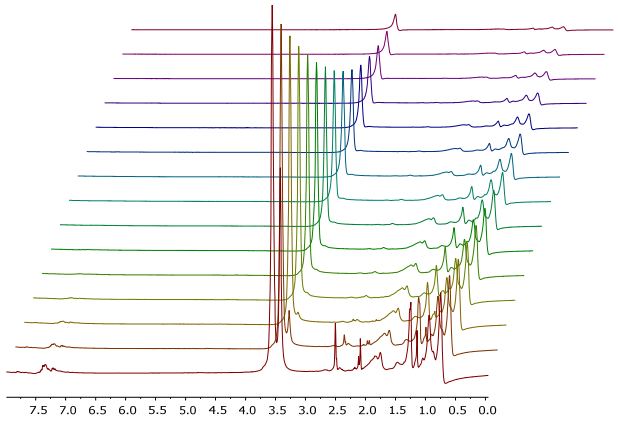


Figure S6. UV-Vis spectra of the photoproducts obtained over time at 254-nm irradiation.

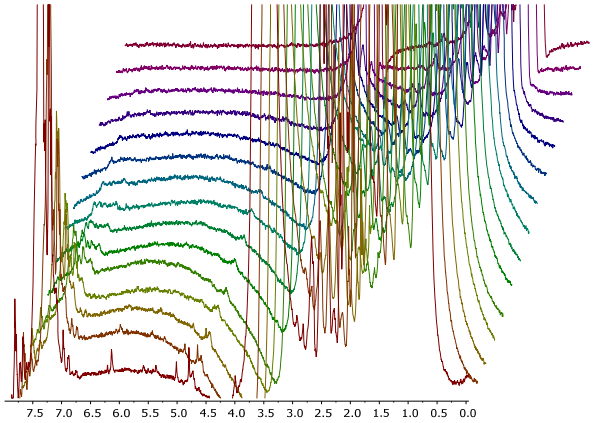
5. DOSY-NMR experiment.

After irradiation of a 10% PMMA/ 1% TPS wafer at an exposure of 50 mJ/cm^2 (information on the preparation of the wafer: Coating solvent = PGMEA, Si substrate, HMDS primed and baked at 120 °C for 30 s., No BARC used, Formulation coated at 1500 rpm; soft-baked at 95 °C for 60 s., Film thickness determination ~ 3200 Å, Center dose ladder: 0, 10, 20, 30, 40 and 50 mJ/cm^2, ASM-L/1100; Dipole 35y), the film was wiped off with acetone. After evaporation of the solution under vacuum, the solid was dissolved in DMSO-d_6 and a DOSY-NMR experiment was performed. The DOSY-NMR experiment performed was a DgcsteSL (DOSY gradient compensated stimulated echo Spin Lock) with a diffusion delay of 50 ms, a difference in gradient pulse of 5 ms and an array of 15 gradient values.

(a)



(b)



(c)

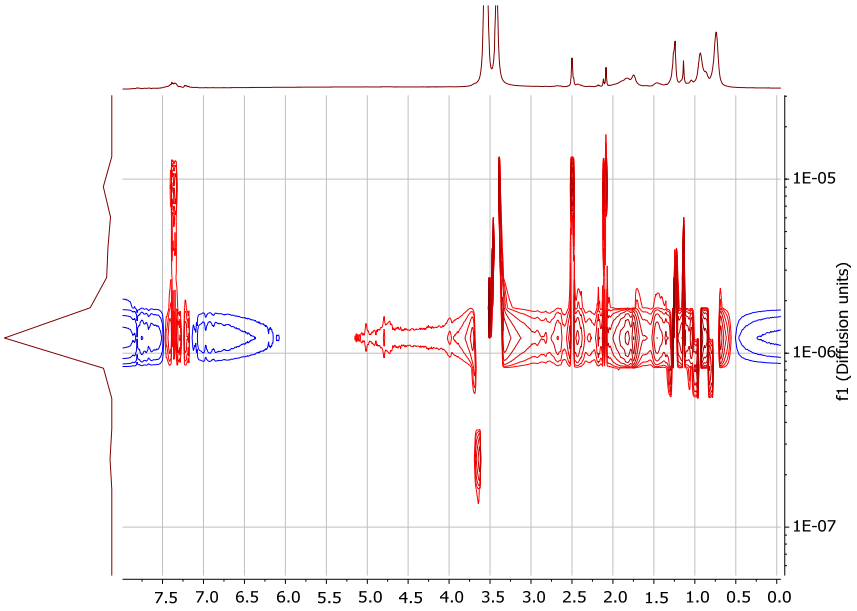


Figure S7. DOSY-NMR spectrum of an irradiated film a) DOSY-NMR spectrum, b) zoomed-in spectrum, and c) 2D-DOSY view.

6. Photoproducts of TPS in solution (cuvette set-up).

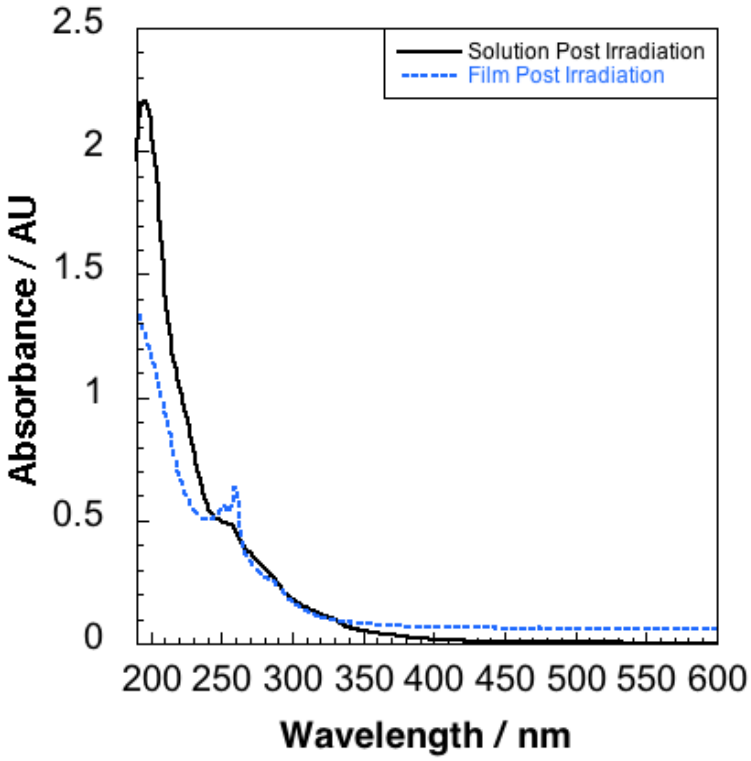


Figure S8. UV-Vis spectra of PMMA-TPS in acetonitrile and in film after irradiation.

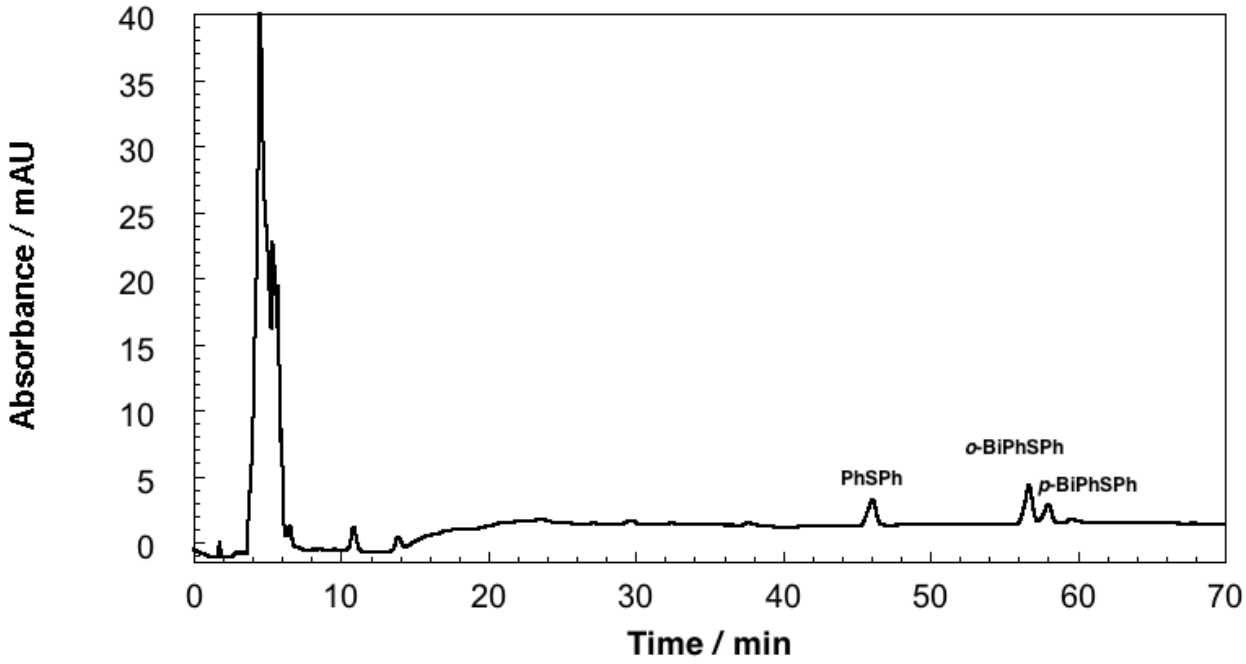


Figure S9. HPLC chromatogram of a PMMA-TPS solution after 3 d at 193 nm.

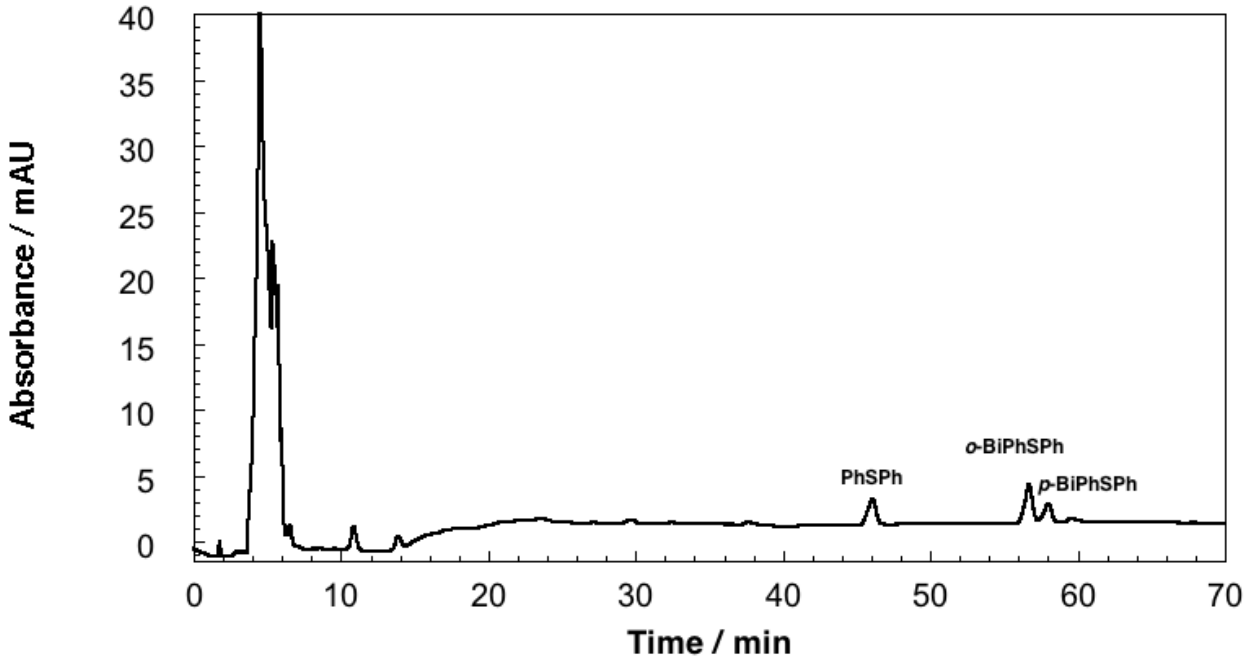


Figure S10. HPLC chromatogram of a PMMA-TPS solution (cuvette set-up) after 3 h at 254 nm.

hν (nm)	TPS conv. (%)	acetanilie	PhSPh	2-BiPhSPh	4-BiPhSPh	Products recovered (%)
193	6.7	1.4	1.6	2.0	1.0	99.3
254	25.2	3.9	4.5	5.0	1.8	86.1

Table S1. Photoproduct distribution (%) after 3 days of irradiation at 193 nm or 3 hours at 254 nm.

7. Photoproducts of TPS in wafers (lithography set-up).

UV-vis spectra obtained at a retention time of 15.1 minutes, corresponding to the elution of 2-BiPhSPh.

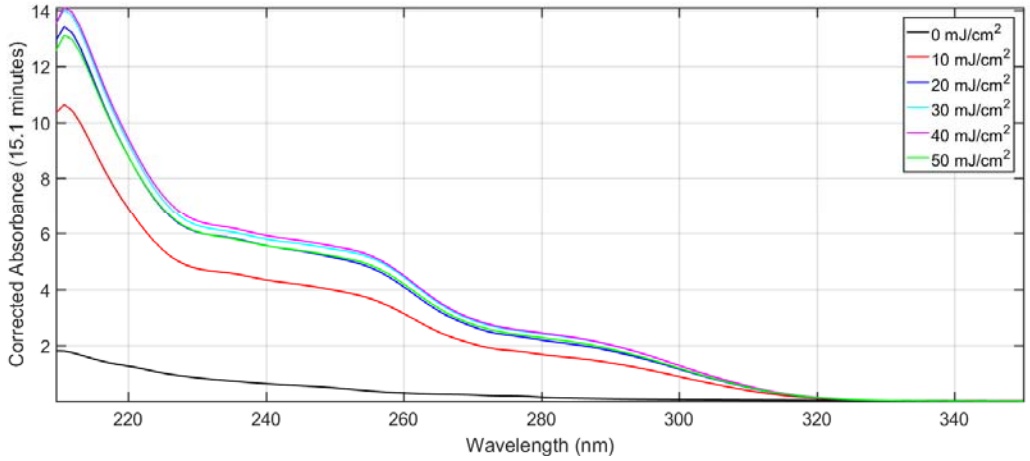


Figure S11. UV-vis spectra taken at 15.1 minutes retention time from GPC trace, corresponding to 2-BiPhSPh fraction.

8. Cross-experiment by irradiation of a 10 % w/v PMMA/ 0.5% w/v TPS/ 0.5% w/v tBu-TPS film.

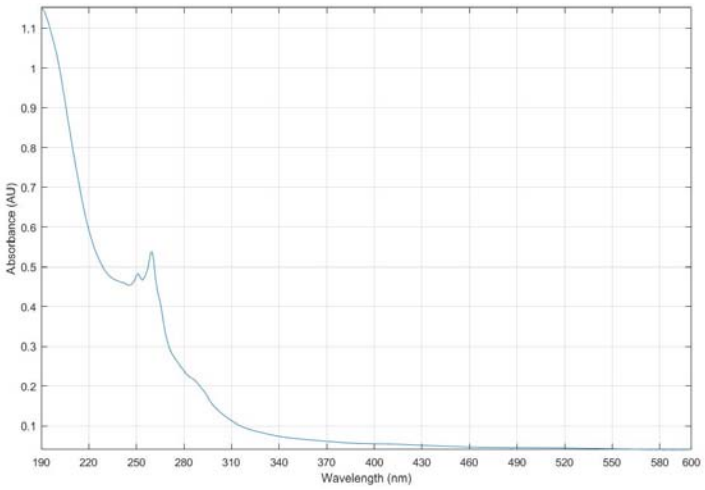


Figure S12. UV-Vis spectrum of PMMA/TPS/tBuTPS films after 3 days of 193-nm irradiation.

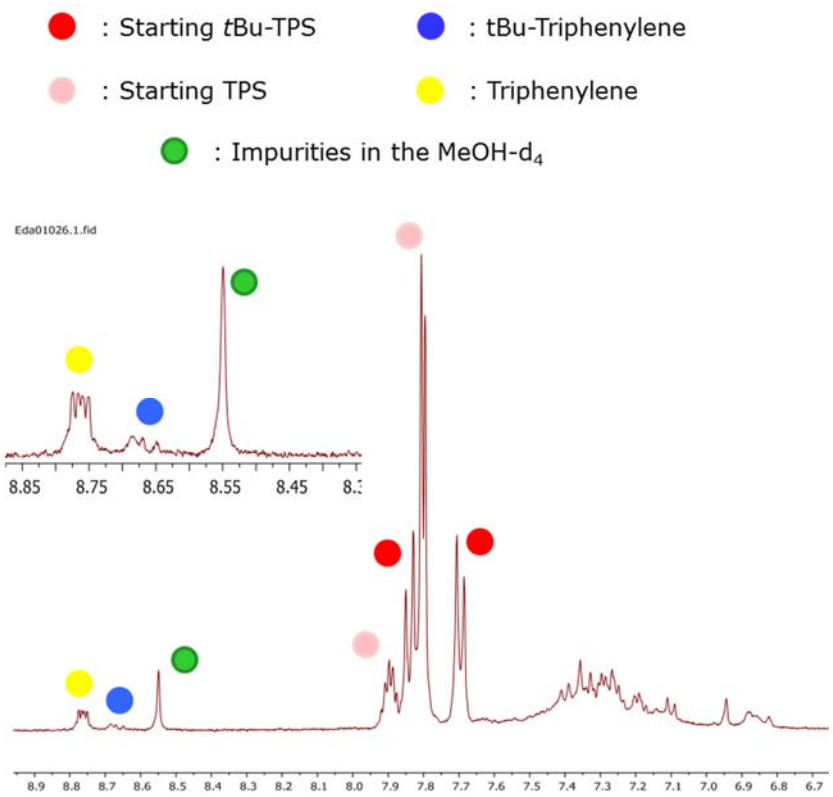


Figure S13. Selected range of the ^{1}H NMR spectrum after 193-nm irradiation of a 10 % w/v PMMA/ 0.5% w/v TPS/ 0.5% w/v tBu-TPS film.

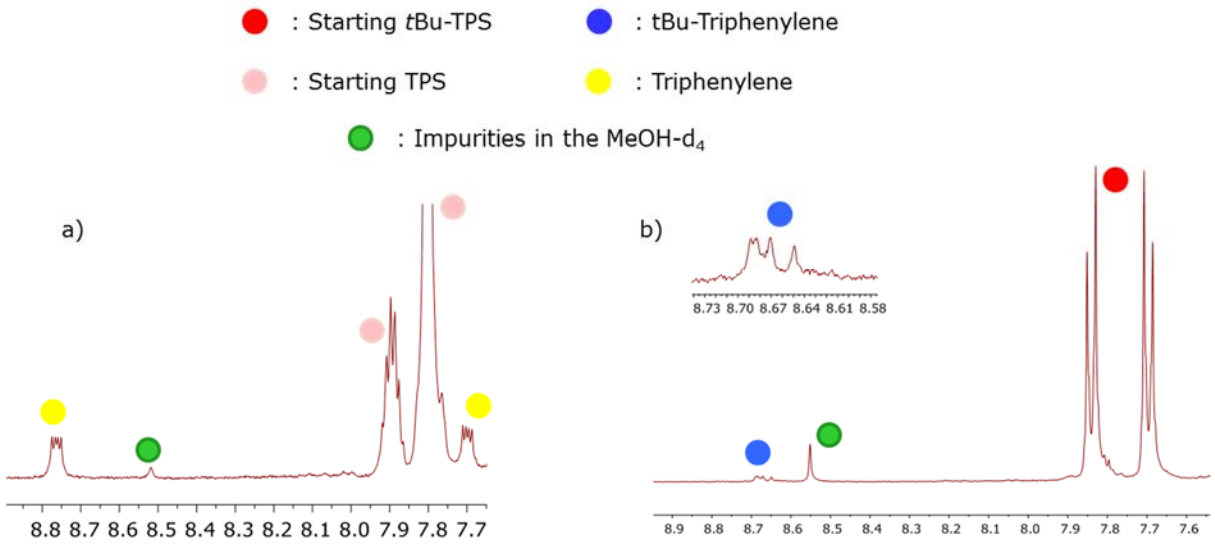


Figure S14. Selected range of the ^{1}H NMR spectrum after 193-nm irradiation of a) 10 % w/v PMMA/ 1% w/v TPS film, b) 10 % w/v PMMA/ 1% w/v tBu-TPS film.