Light driven release of acids for technological applications

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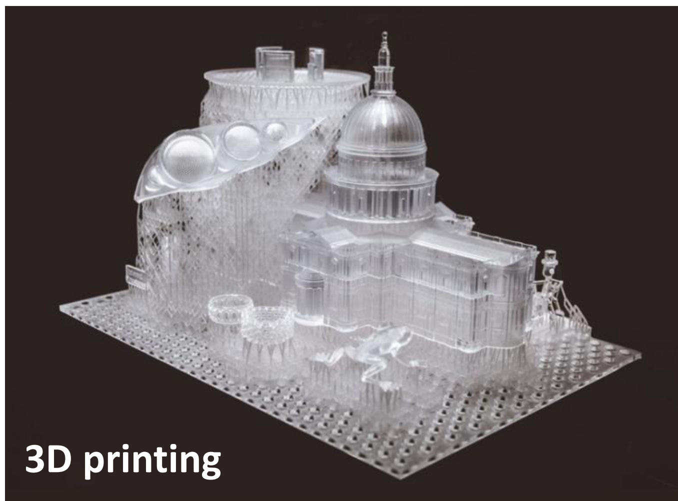
PhotoAcid Generators (*PAGs*): Compounds able to release acid upon light absorption

Applications:



Coating

Photoresist

Semiconductor

hν

Exposure

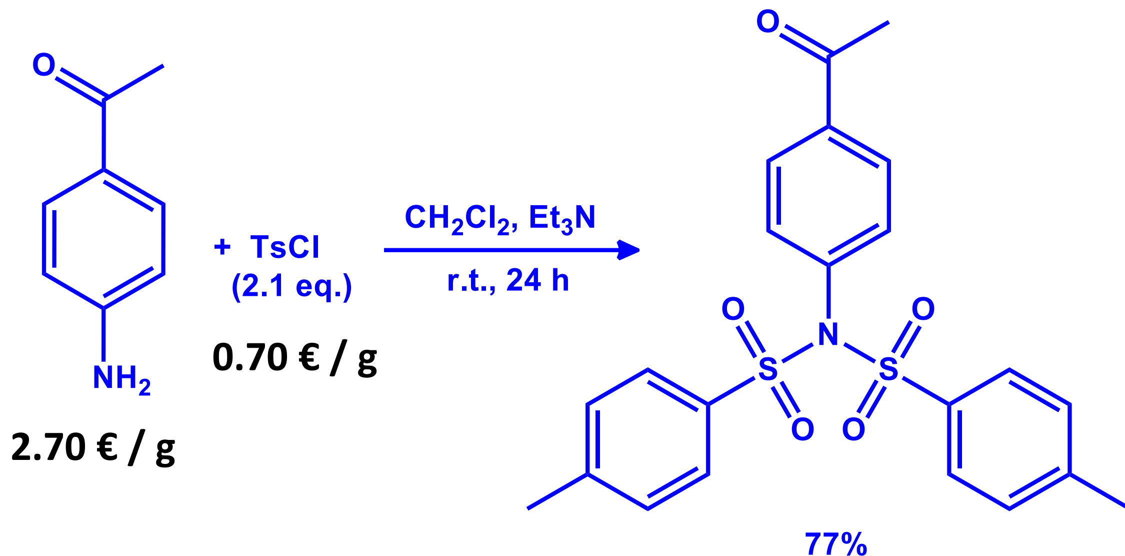
Positive development

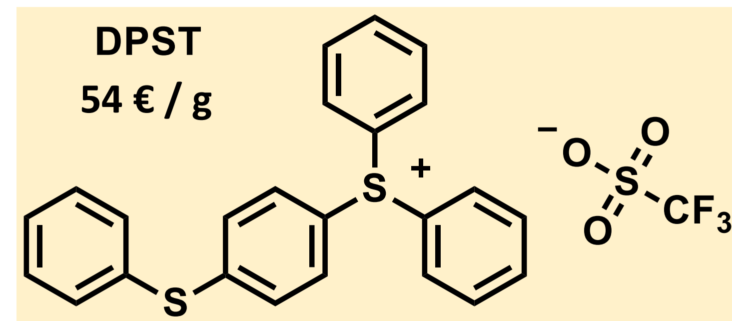
Negative development

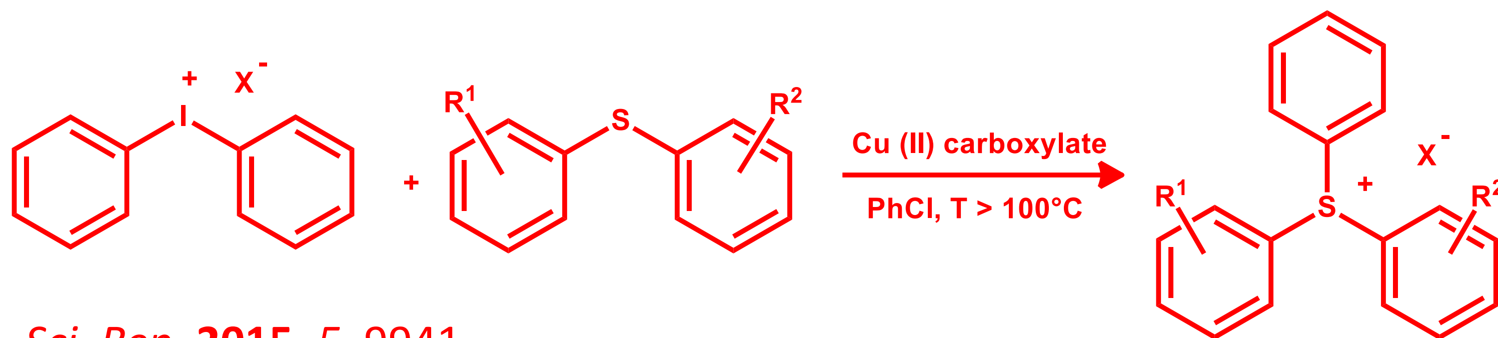
Etching

Cleaning

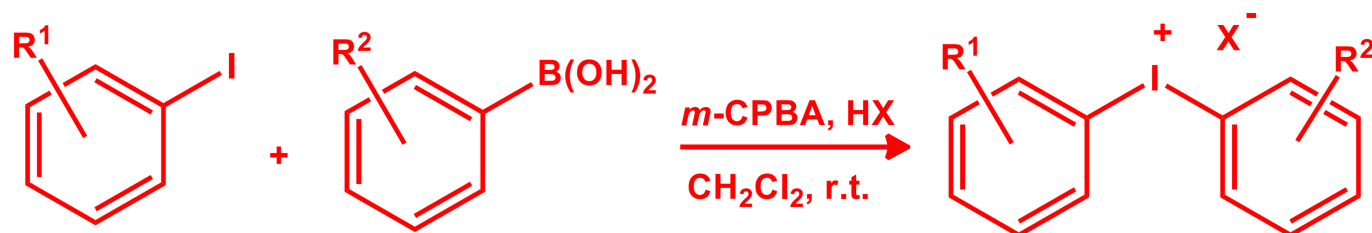
J. Photochem. Photobiol. C **2007**, *8*, 157-173





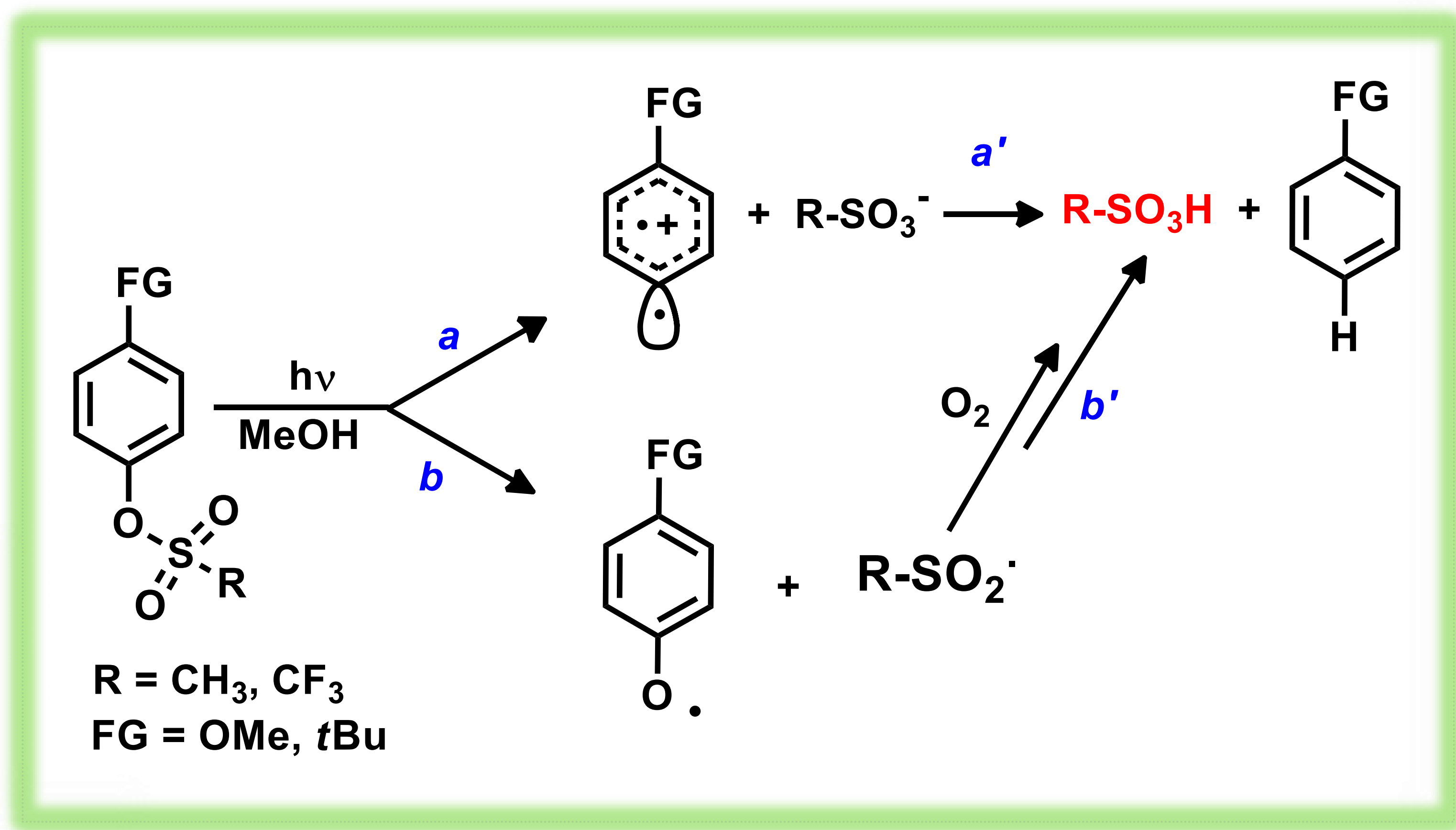


Sci. Rep. **2015**, *5*, 9941



J. Org. Chem. **2008**, *73*, 4602-4607

Aryl sulfonates as non-ionic PAGs

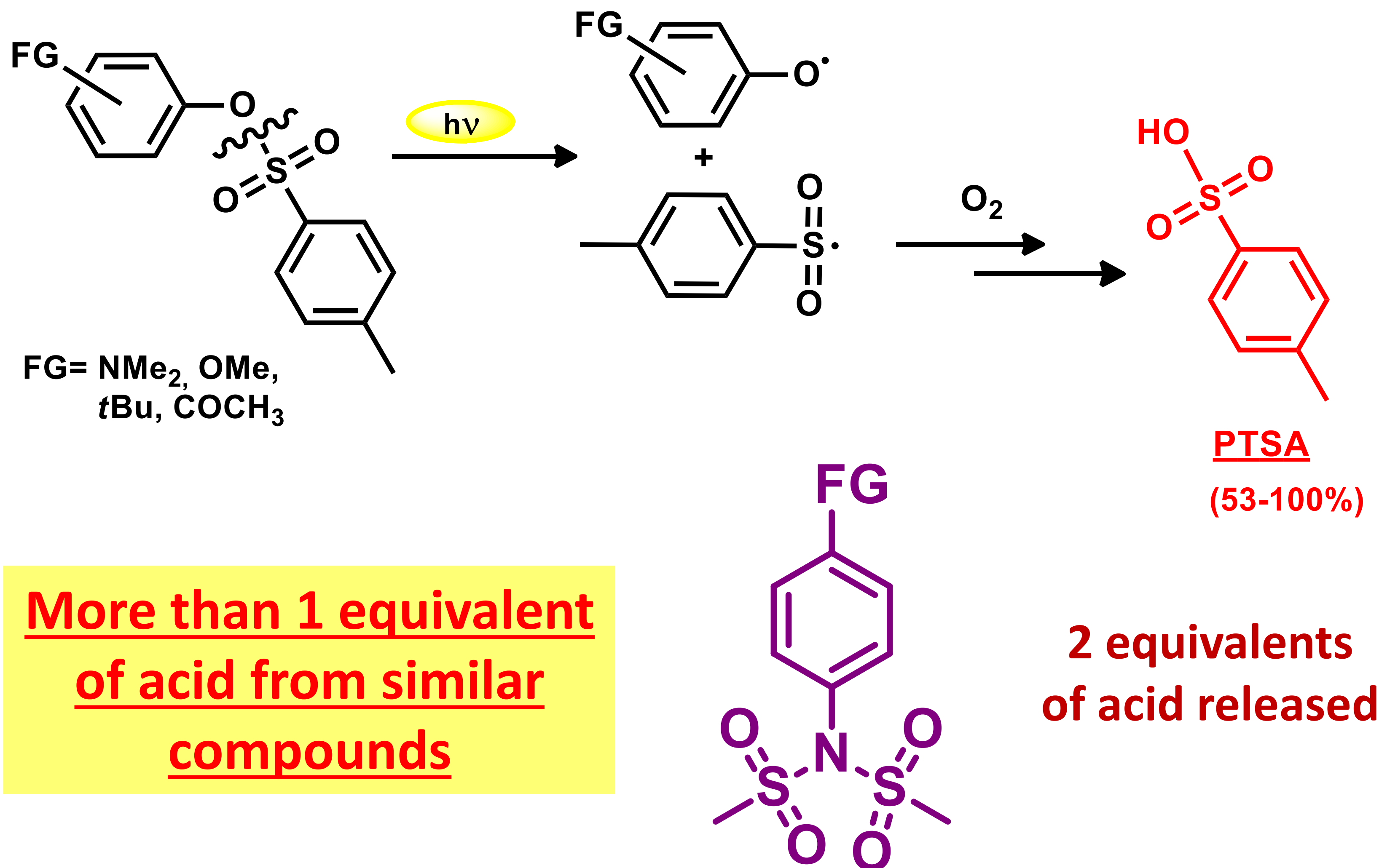


New PAGs based on simple molecules

Applications in polymerization and photolithography

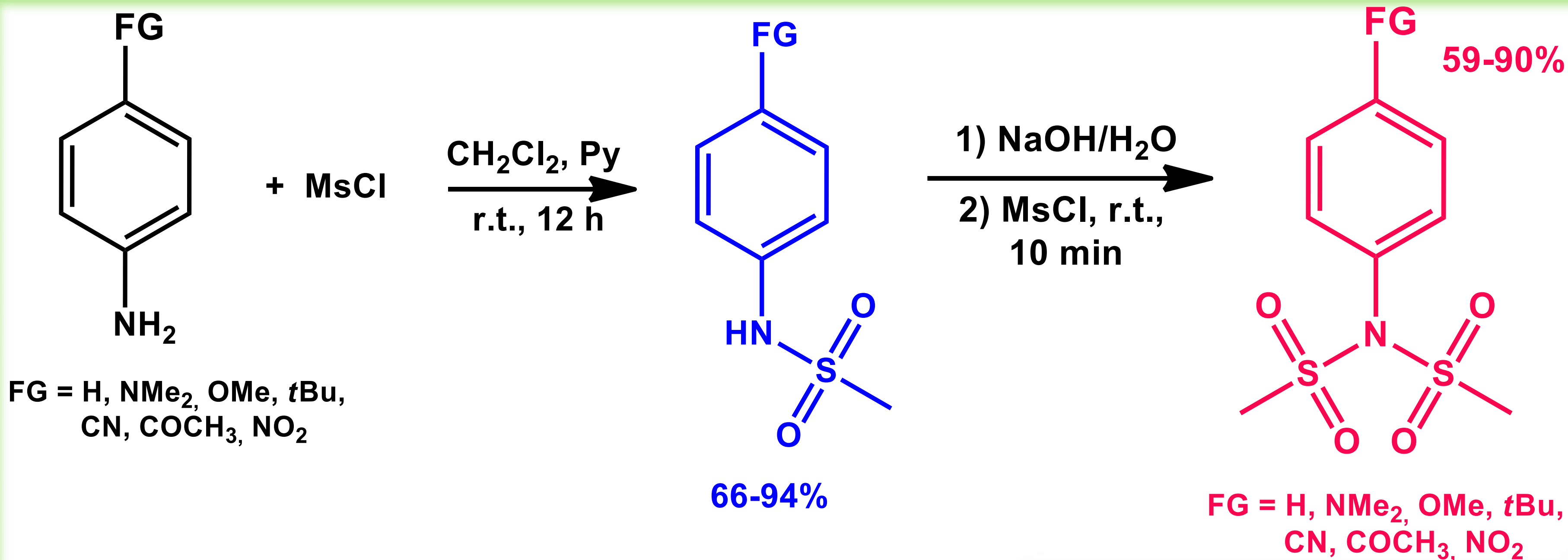
Photochem. Photobiol. Sci. **2011**, *10*, 123-127

Aryl tosylates as non-ionic PAGs



RSC Adv. **2015**, *5*, 33239-33248.

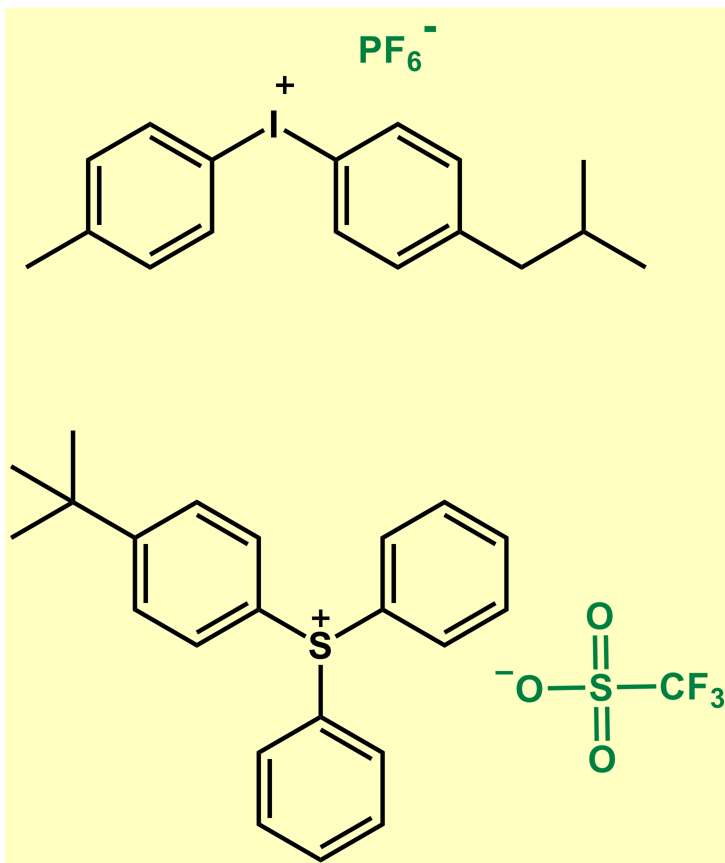
Synthesis of *N*-arylmethanesulfonimides



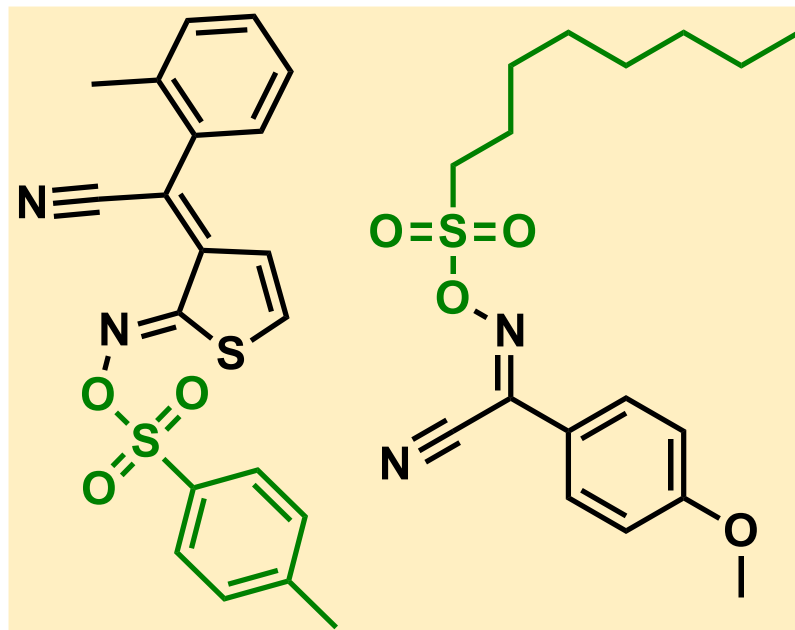
λ_{MAX} = 250-310 nm

- **Irradiation** (254 nm, 4 Hg lamps 15 W)
- Determination/Quantification **photoproducts** (GC-FID; HPLC)
- **Acidity released** (potentiometric titration with NaOH 0.1 M)
- Determination/Quantification **acid species** (ion exchange HPLC)

Photoacid Generators (*PAGs*)



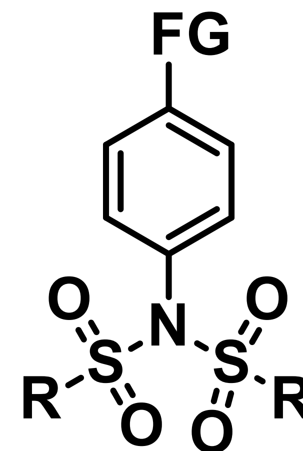
Ionic PAGs



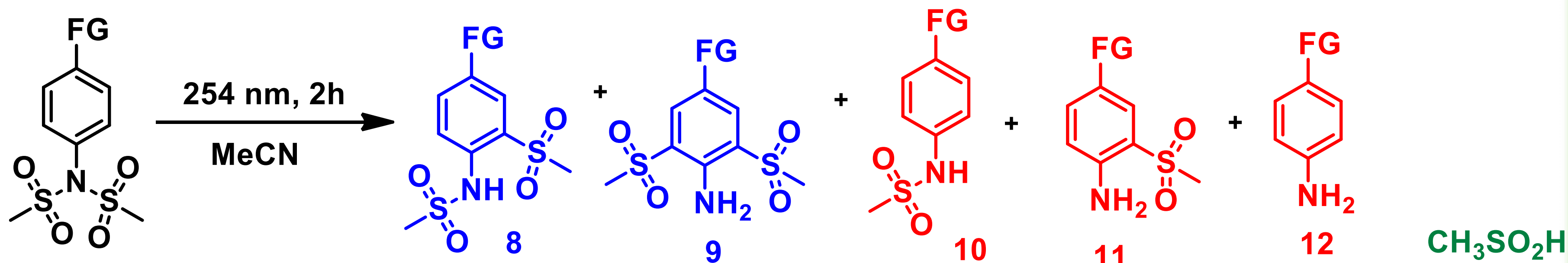
Non-ionic PAGs

J. Photochem. Photobiol. C **2007**, *8*, 157-173.

Compound	λ_{max} [nm], ε [M^{-1} cm^{-1}]	λ_{em}, $\Phi_F \times 10^{-2}$
1 (FG = NMe_2, R = CH_3)	273, 26988 305, 3771	364, 1.42
2 (FG = OMe, R = CH_3)	233, 16260 272, 2249	298, 1.15
3 (FG = *t*Bu, R = CH_3)	222, 14894 254, 3342	283, 0.29
4 (FG = H, R = CH_3)	210, 8493 262, 621	283, 0.21
5 (FG = CN, R = CH_3)	232, 18730 274, 1509	298, 12.0
6 (FG = Ac, R = CH_3)	242, 14061 288, 2498	-
7 (FG = NO_2, R = CH_3)	214, 6084 260, 11513	-
13 (FG = Ac, R = $CH_3C_6H_4$)	240, 32496	-
14 (FG = Ac, R = CF_3)	239, 18151 280, 1655	-



Photochemistry (deaerated 0.01 M solutions):



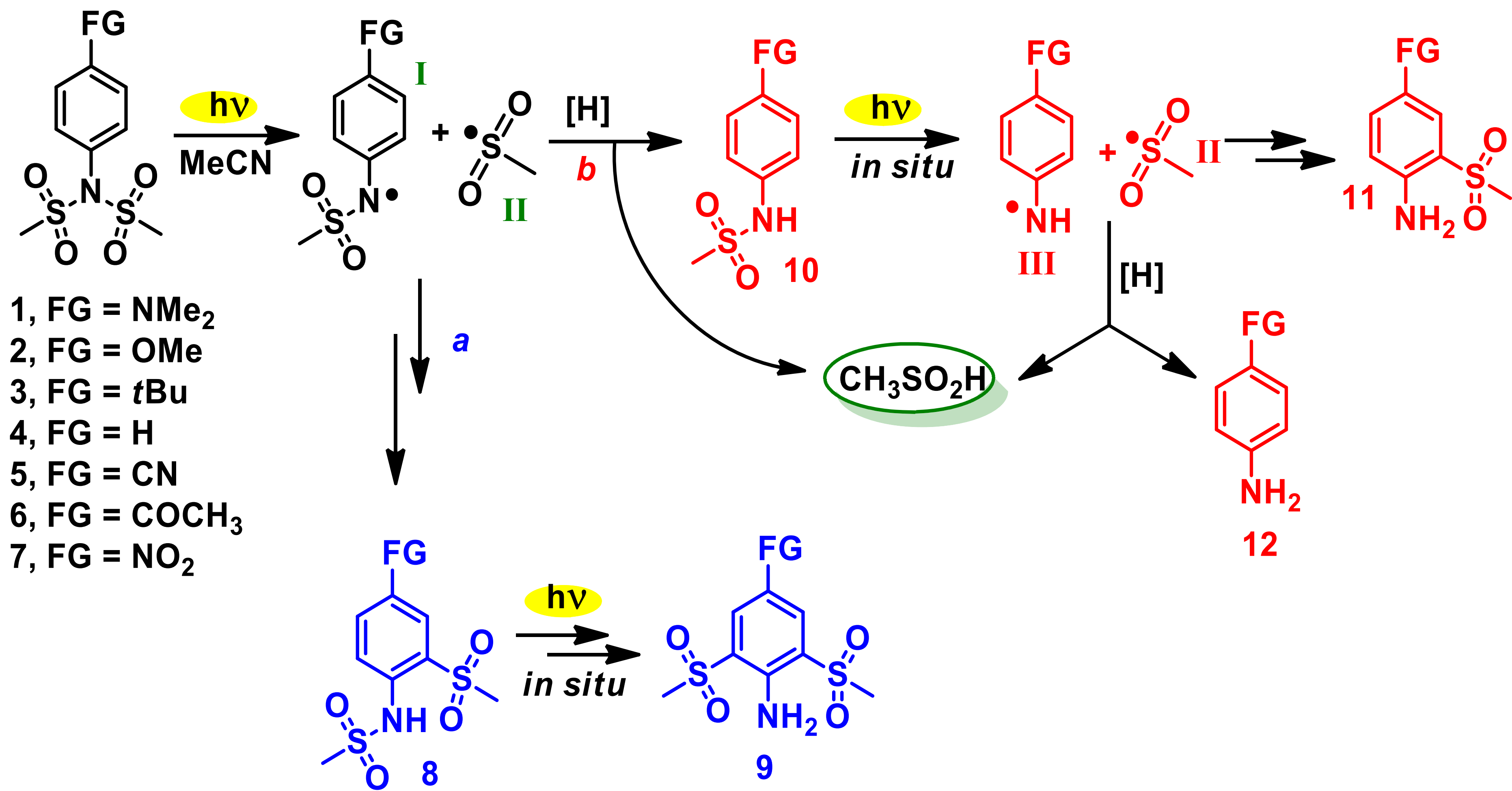
	Φ_{-1}	8	9	10	11	12	CH_3SO_2H
1, FG = NMe_2	0.31	82	10	0	0	0	0
2, FG = OMe	0.21	12	20	22	0	11	45
3, FG = *t*Bu	0.09	0	0	21	55	12	96
4, FG = H	0.10	0	0	32	0[a]	14	74
5, FG = CN	0.10	0	0	17	53	22	116
6, FG = $COCH_3$	0.28	0	0	36	18[b]	18	93
7, FG = NO_2	< 0.01	0	0	0	0	0	0

[a] ***4-methanesulfonylaniline*** *was found in a 9% yield.*

[b] ***4-methanesulfonylaniline*** *was found in a 4% yield.*

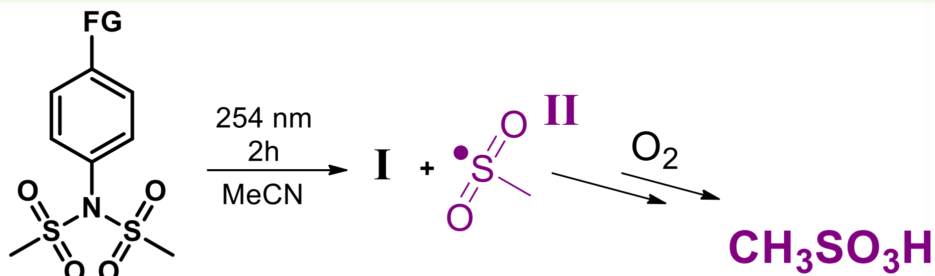
Chem. Eur. J. **2016**, 22, 16998-17005.

Mechanism:



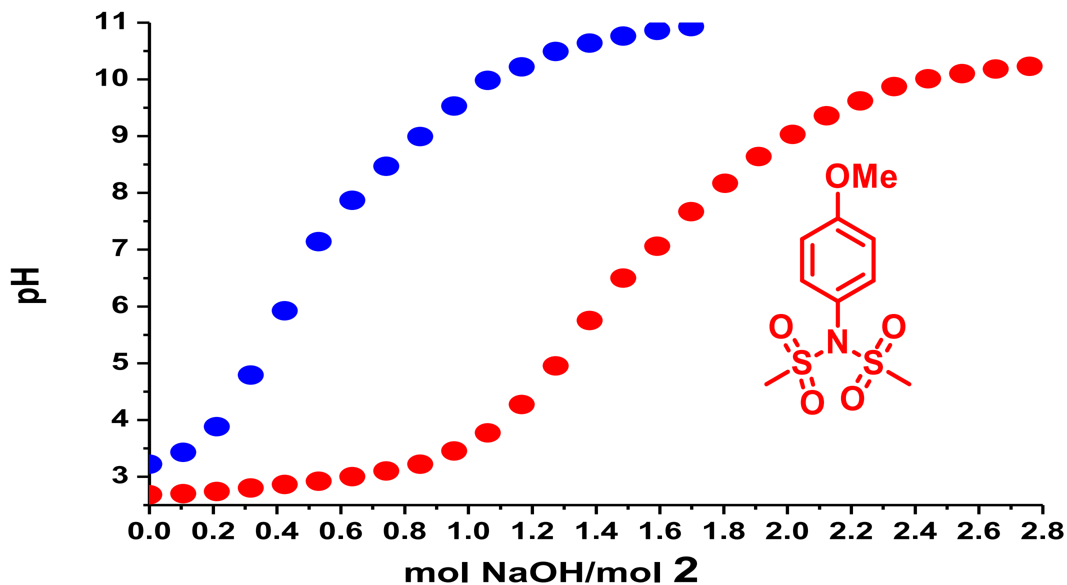
Chem. Eur. J. **2016**, *22*, 16998-17005

Photochemistry (oxygenated 0.01 M solutions):

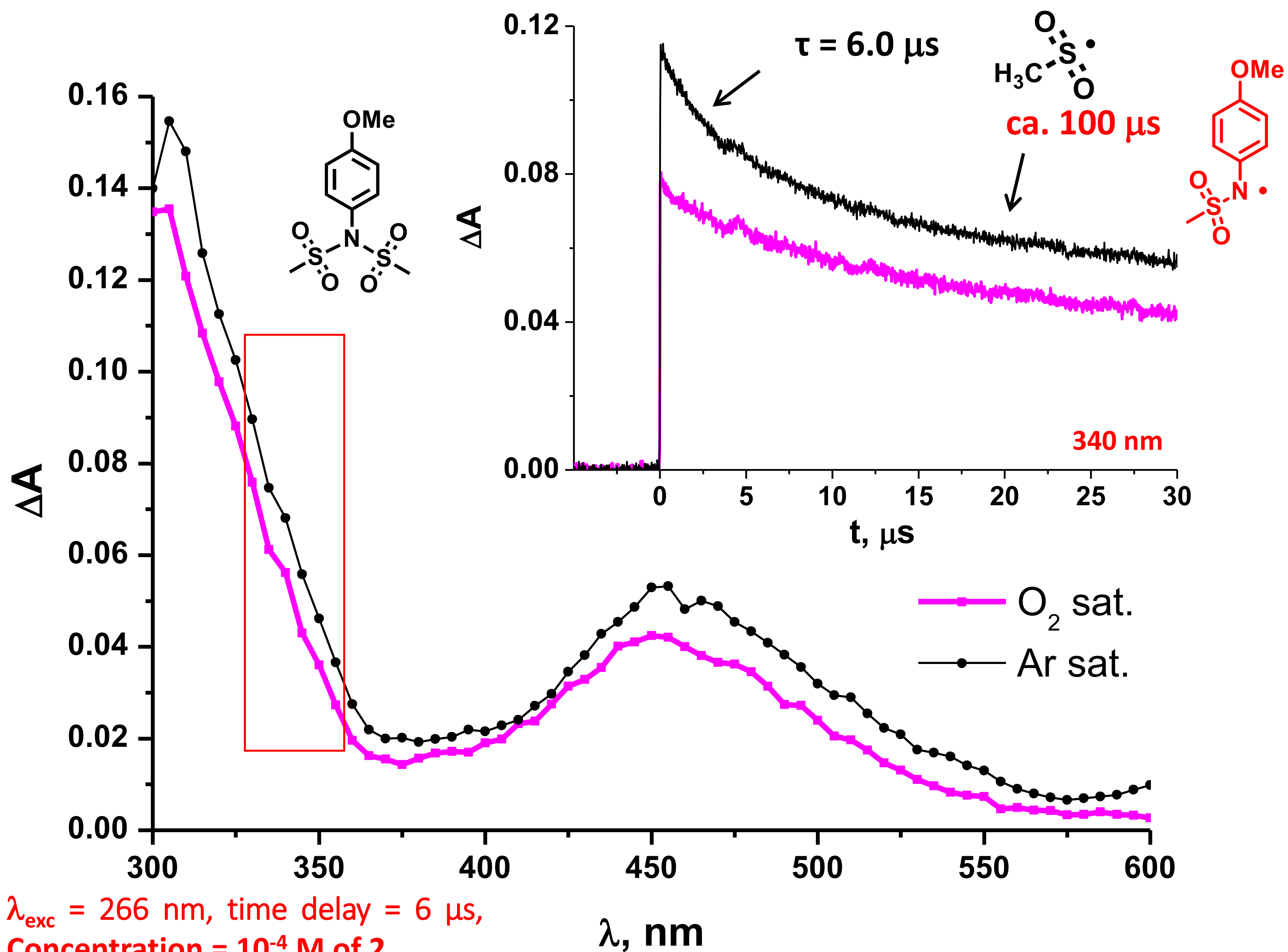


	Φ_{-1}	CH_3SO_3H
1, FG = NMe_2	0.29	66
2, FG = OMe	0.21	154
3, FG = *t*Bu	0.08	178
4, FG = H	0.08	154
5, FG = CN	0.10	182
6, FG = $COCH_3$	0.28	192
7, FG = NO_2	< 0.01	0

Up to 2 equiv. CH_3SO_3H



Laser flash photolysis experiments:

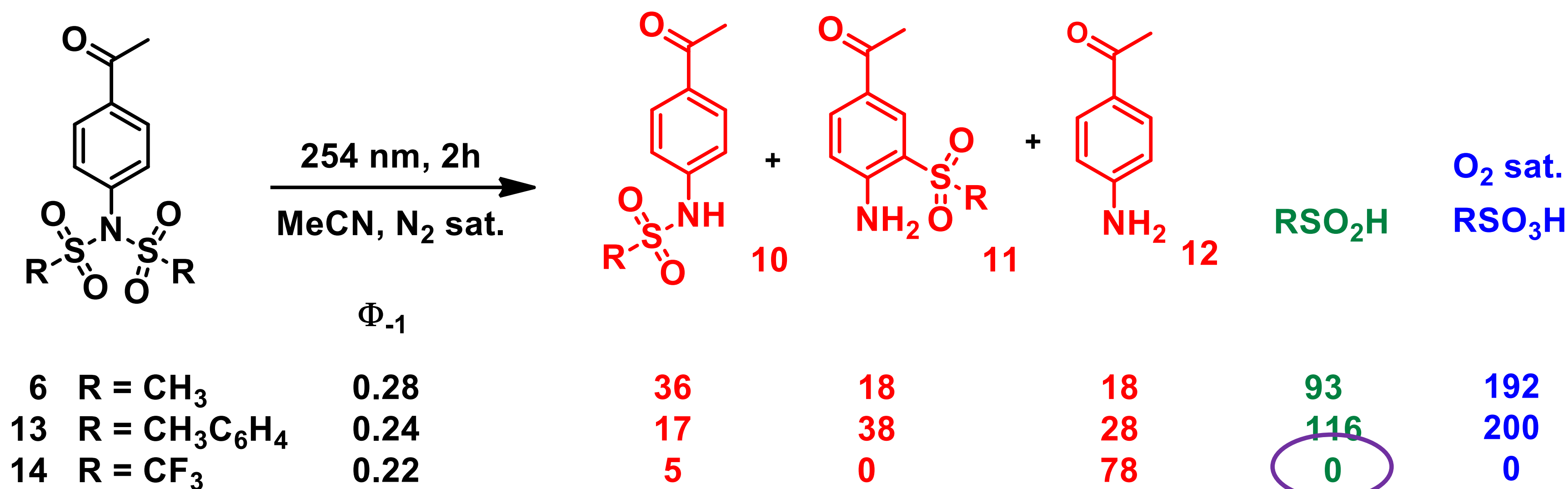


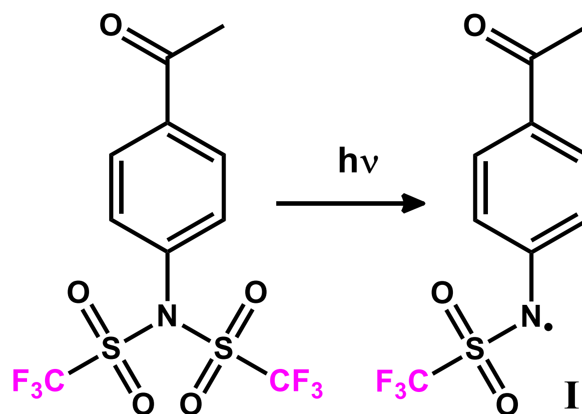
λ_{exc} = 266 nm, time delay = 6 μs,

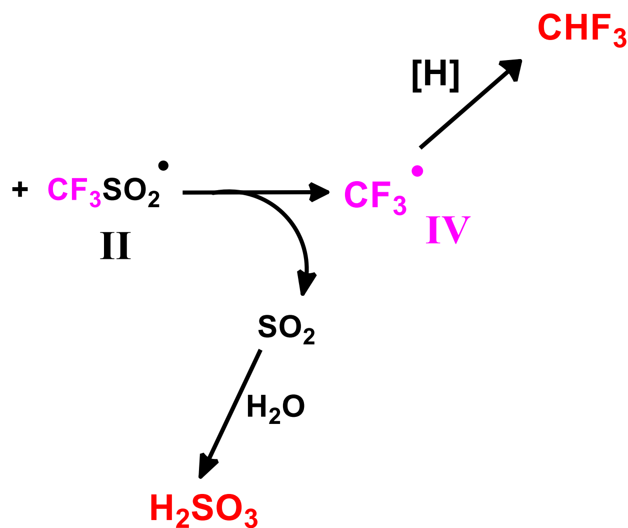
Concentration = 10^{-4} M of 2.

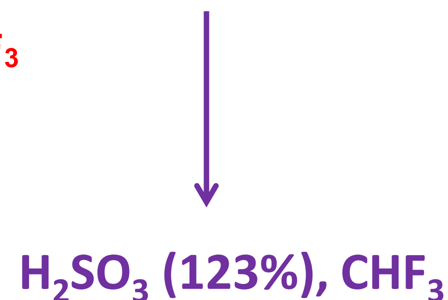
Chem. Eur. J. **2016**, 22, 16998-17005

Photochemistry of other *N*-arylsulfonimides (0.01 M):





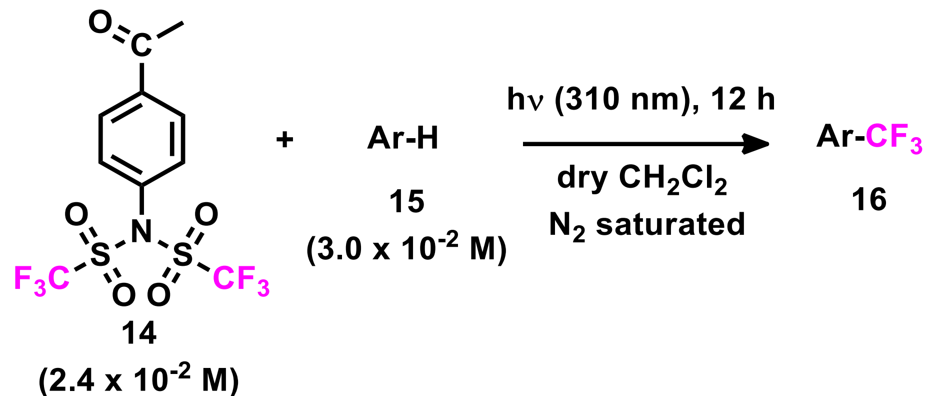




NOT SUITABLE AS PAG

Chem. Eur. J. **2016**, *22*, 16998-17005

N-aryltrifluoromethanesulfonimides for trifluoromethylation of aromatics:



CF_3
73%

R = H, 60%
R = CF_3, 12%

MeO OMe CF_3
81%

OMe MeO CF_3 OMe
85%

O CF_3
74%

O O F_3C S CF_3
59%

N CF_3
59%

MeO N OMe CF_3
64%

O N N O N N CF_3
58%

H_3C CH_3 CF_3 H_3C CH_3
61%

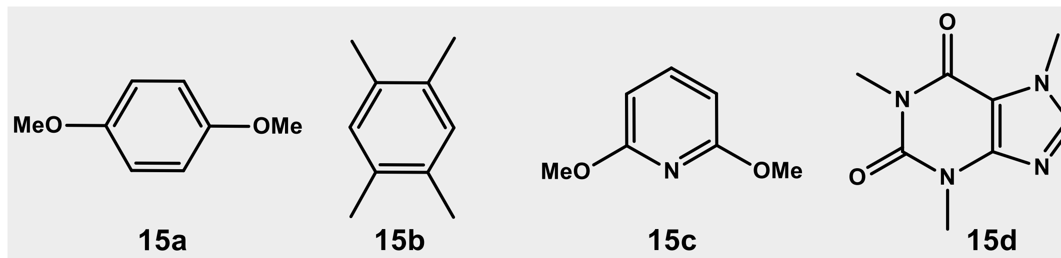
H_3C OMe F_3C OMe OMe
79%

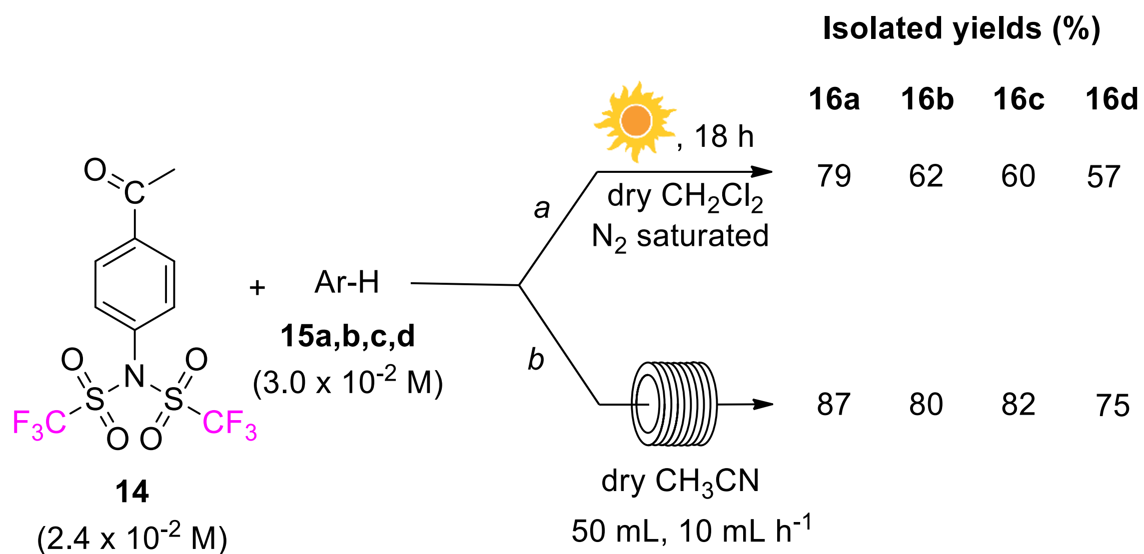
CF_3 N N CH_3
69%

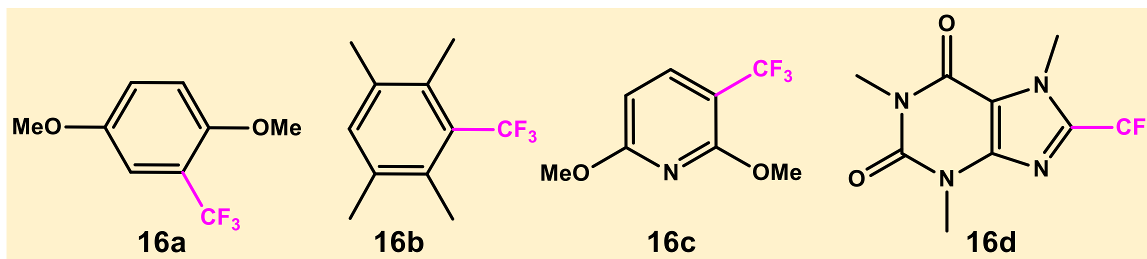
O H_3C N H N CF_3 O N N CH_3
67%

Chem. Commun. **2018**, *54*, 4144-4147.

Trifluoromethylation of aromatics: sunlight irradiation and flow conditions.

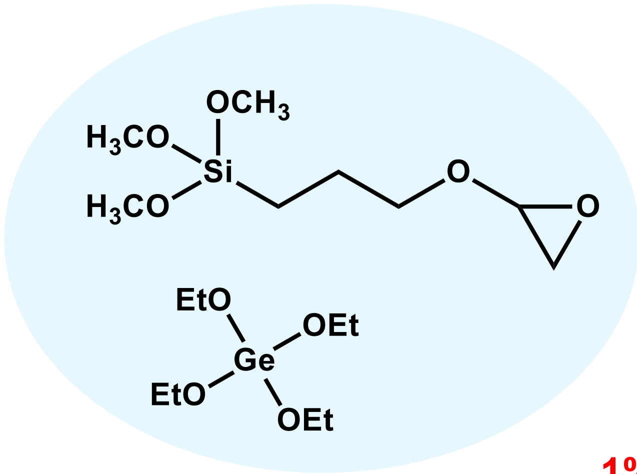


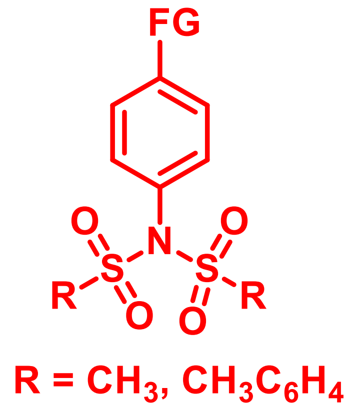




Chem. Commun. **2018**, *54*, 4144-4147.

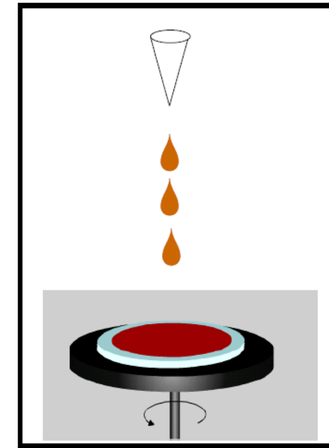
Application: photolithography **Photopolymerization experiments**

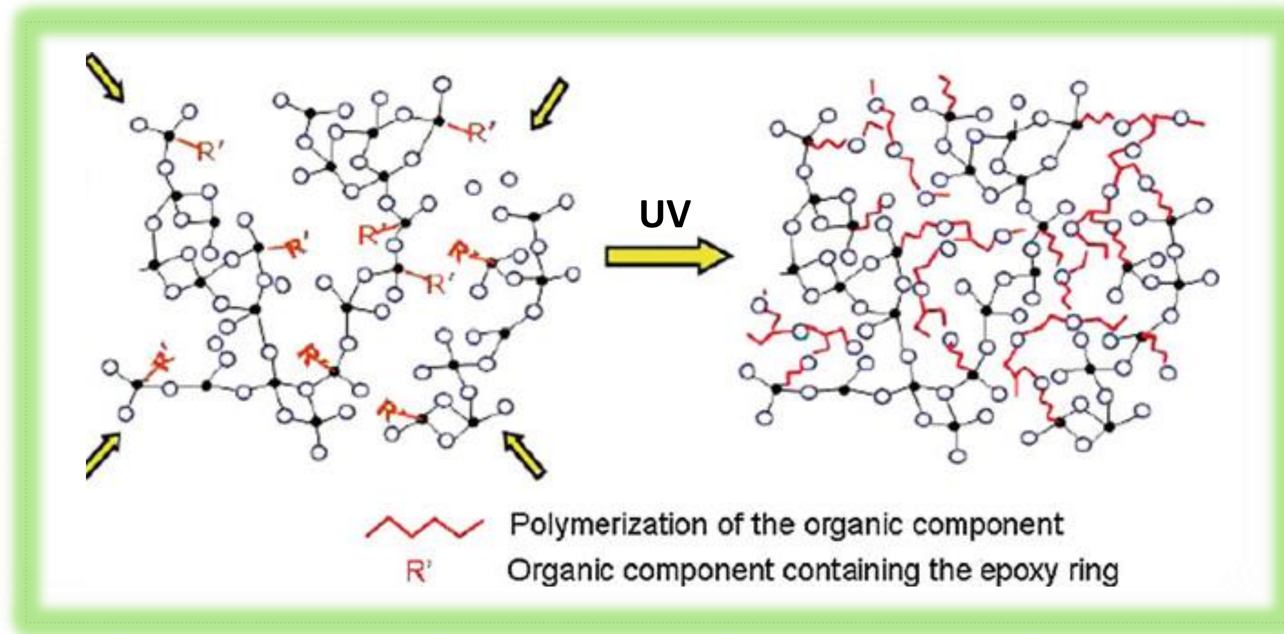




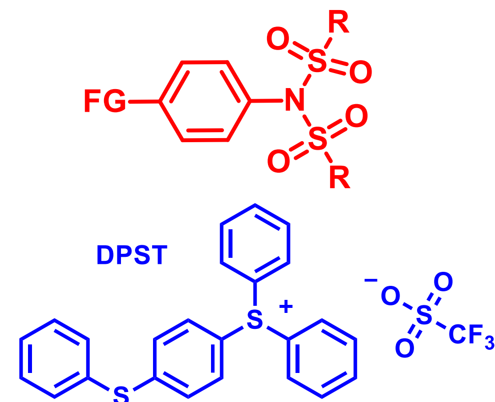
R = CH_3, $CH_3C_6H_4$

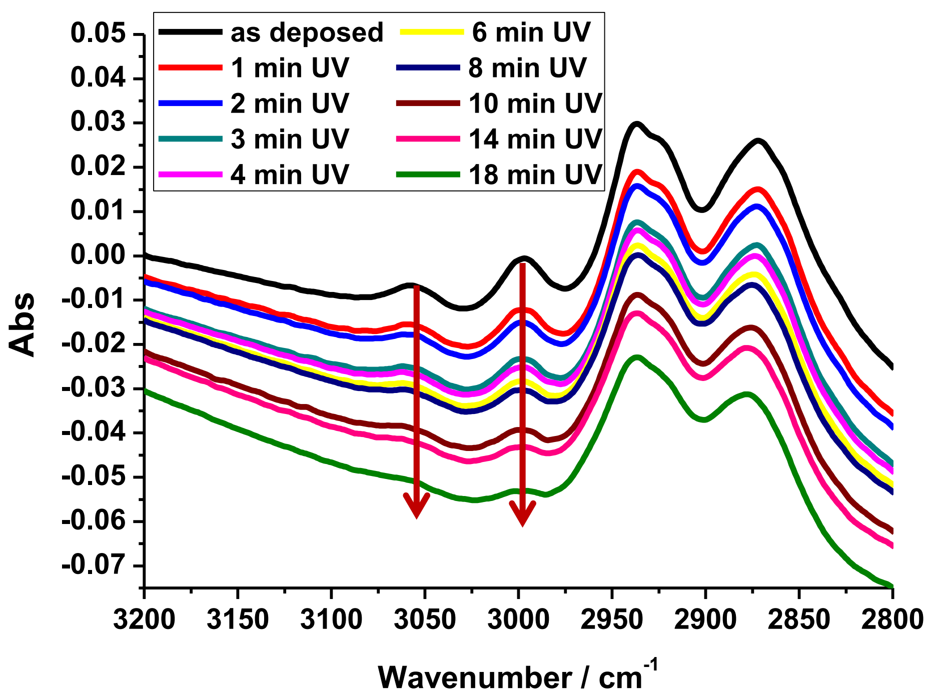
1% molar to epoxy group

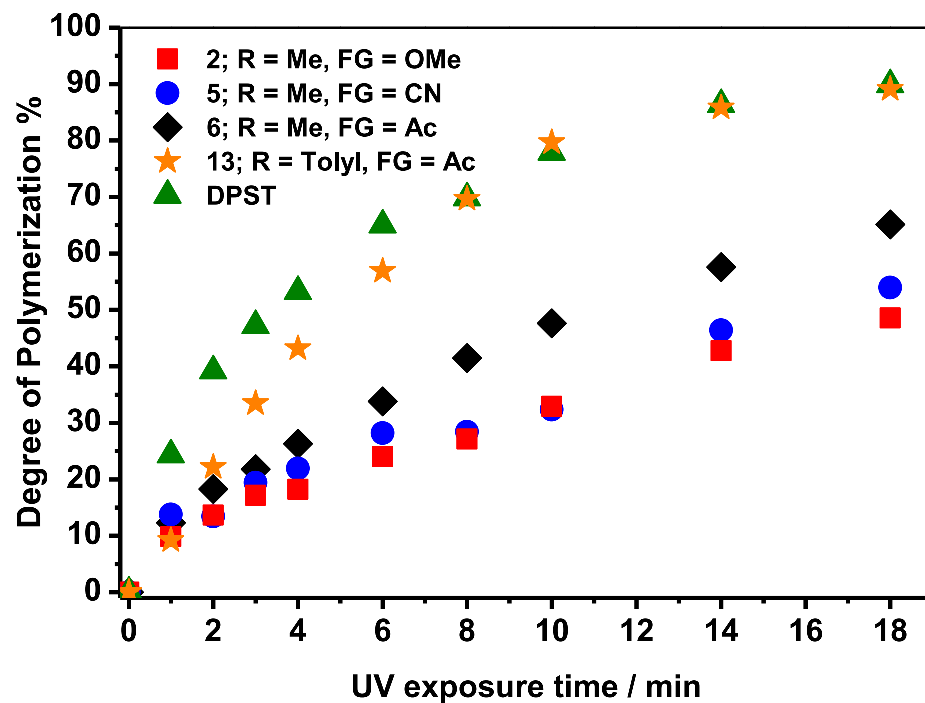




Wavenumber (cm-1)	3387	3060	3000	1255	1156	1092	945
Vibrational mode	OH stretching	Epoxide CH stretching	Epoxide CH stretching	C-0 (epoxide) asymmetric stretching	C-O-C asymmetric stretching	Si-O-Si asymmetric stretching	Si-OH stretching







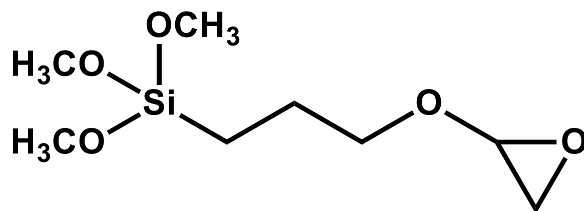
Peaks decrease after UV exposure ⇒ ring opening reaction

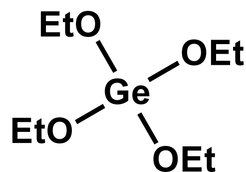
Degree of polymeriyation up to 90% (similar to DPST)

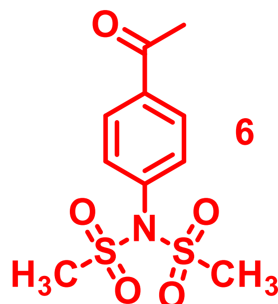
ChemistrySelect **2017**, 2, 3633-3636.

Photopolymerization experiments

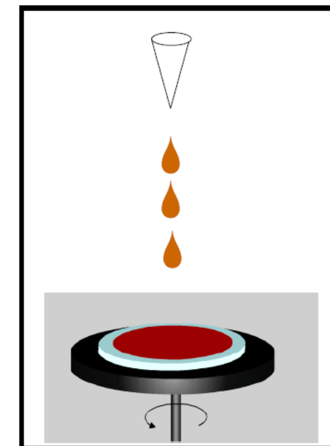
photolithography

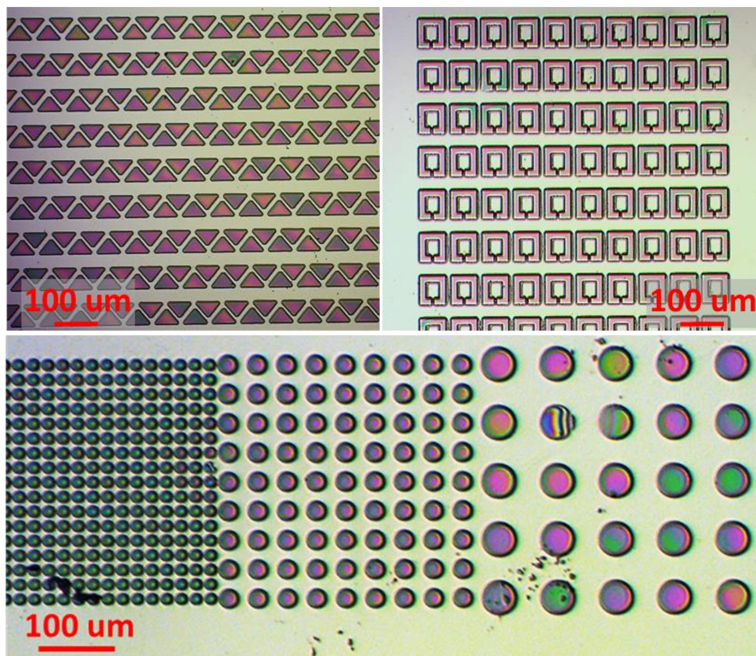






1% molar to epoxy groups



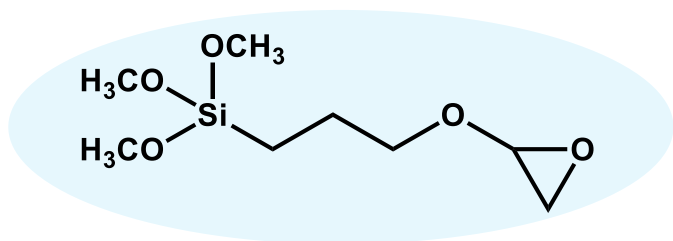


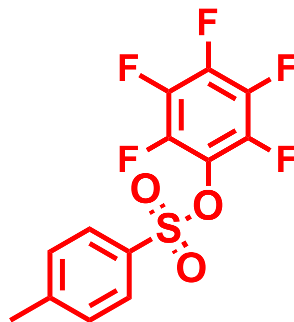
- UV irradiation for 1-3 min (Hg-Xe UV spot light source)
- Features resolutions between 10 and 100 μm can be achieved for compound 6 (development in EtOH/aqueous HCl 1:1 for 15-60 sec)

ChemistrySelect **2017**, *2*, 3633-3636.

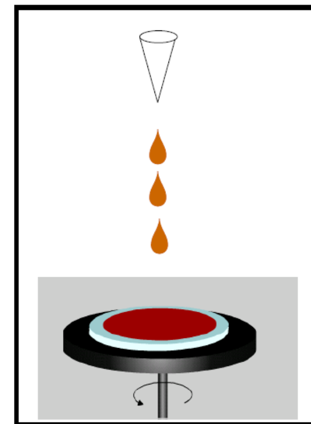
Application: contact EUV photolithography

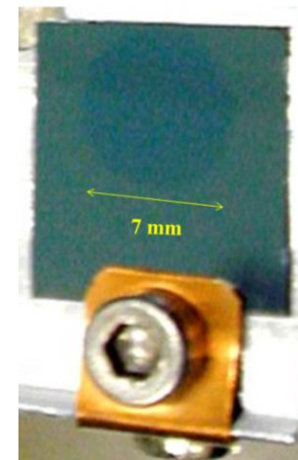
EUV (10-100 nm) lithography: better spatial resolution





1% molar to epoxy group

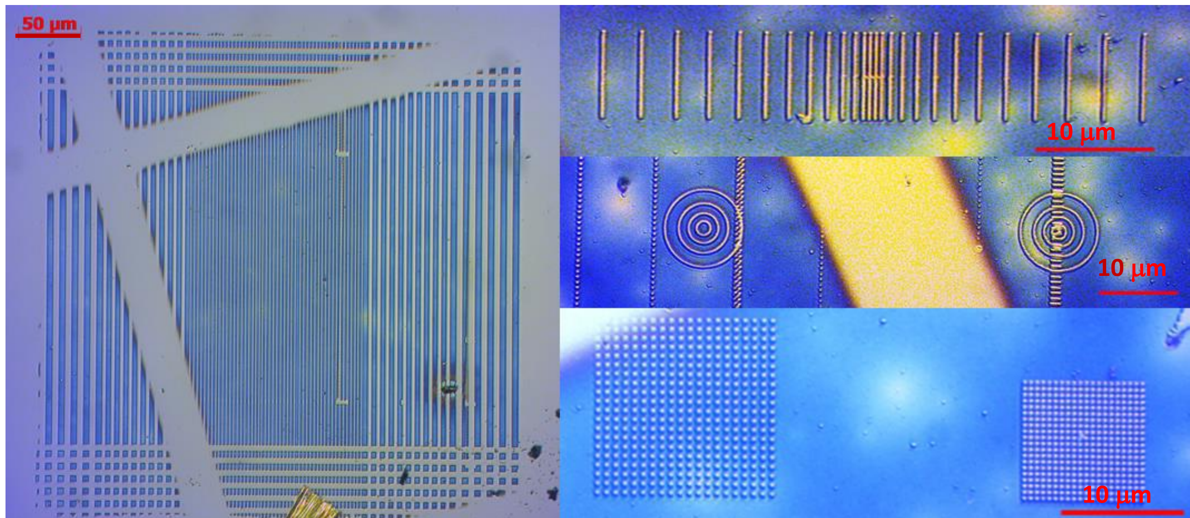


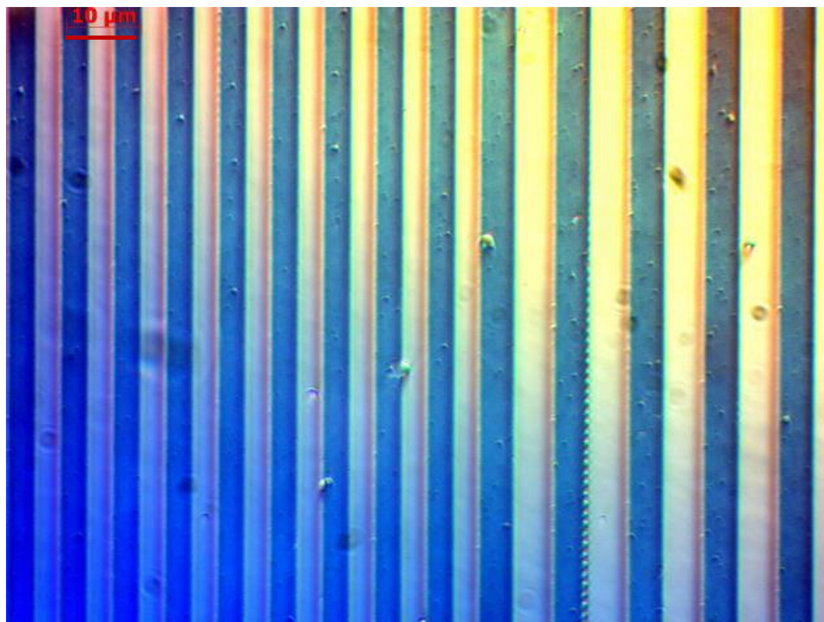


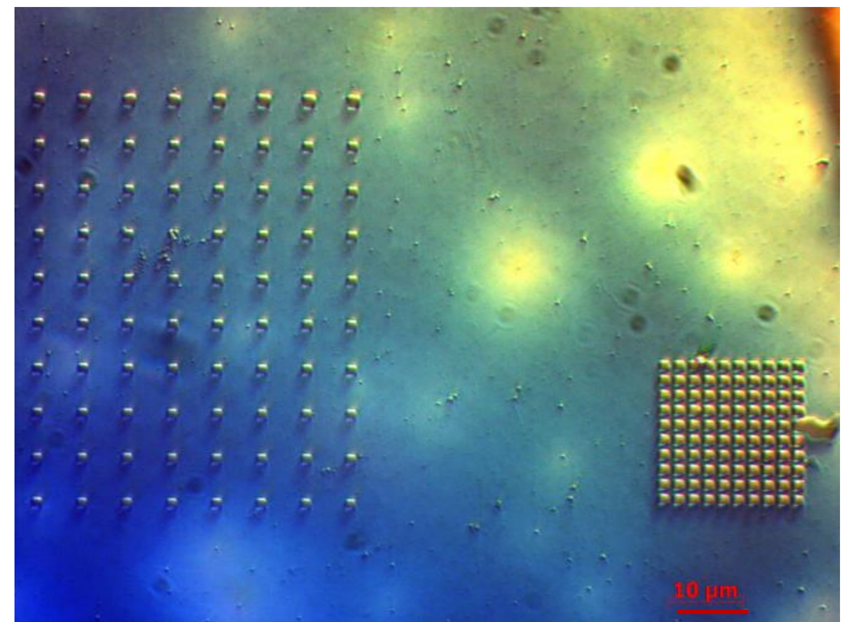
- Low pressure xenon Discharge Produced Plasma source (10-20 nm)
- Masks with gold patterns on a silicon nitride membrane
- Spatial resolution down to 100 nm
- Patterns obtained with a 5 mJ/cm^2 EUV dose

ChemPhotoChem **2018**, *2*, 425-432.

Application: contact EUV nanolithography







ChemPhotoChem **2018**, *2*, 425-432.

Conclusions:

- **Aryl tosylates** are good simple PAGs for the release of *p*-toluenesulfonic acid.
- ***N*-arylsulfonimides** are excellent PAGs, releasing very high amount of sulfonic acids (**up to 200% yield**) and behaving as photolithographic initiators.
- **Perfluoroaryl sulfonates** are very good initiators for **EUV lithography**.
- **Photoacid generators as phototriggers** for redox reactions.

Perspectives:

- Development of PAGs for EUV based on ***N*-arylsulfonimides**.
- Development of **visible light sensitive PAGs**.