Supplementary Material (ESI) for Green Chemistry

Eco-Friendly Hydrodehalogenation of Electron-rich Aryl Chlorides and Fluorides by Photochemical Reaction.†

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1) Experimental details
2) ^{1}H NMR and ^{13}C NMR spectra of 8

1) Experimental details

General

NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15 W phosphor coated lamps (maximum of emission 310 nm, overall flux ~ 2×10^{-6} Einstein min^{-1} cm^{-2}) or with four low pressure Hg lamps (maximum of emission at 254 nm, overall flux ~ 6×10^{-6} Einstein min^{-1} cm^{-2}) for the irradiation.

4-Chloro-3,5-dimethylanisole (**7**) was obtained in 92% yield from the corresponding phenol (**2**), by methylation with methyl iodide[S1] and purified by distillation under reduced pressure. **7**: ^{1}H NMR (CDCl$_3$), δ: 2.40 (s, 6H), 3.80 (s, 3H), 6.65 (s, 2H). IR (neat), ν/cm^{-1}: 1162, 1324, 1474, 1591, 2947. Anal. Calcd for $C_9H_{11}ClO$: C 63.35, H 6.50. Found: C 63.1, H 6.8.

Synthesis of 2-chloro-benzo-4,5-diox-1-ol (**9**): SO_2Cl_2 (160 μL, 2.2 mmol) was added slowly to a stirred solution of sesamol (300 mg, 2.2 mmol) in CH_2Cl_2 (20 mL). After 1 hour, the solvent was removed in vacuo and the solid residue was purified by column chromatography (cyclohexane/ethyl acetate 9:1, as eluant), affording 260 mg (68% yield) of **9** (colorless solid, m.p. 87-88°C). Spectroscopic data were in accordance with literature data.[S2] Anal. Calcd for $C_7H_5ClO_3$: C 48.72, H 2.92. Found: C 48.7, H 3.0.

4-Chloro- and 4-fluoro-*N*,*N*-dimethylaniline (**10** and **17**) were prepared by methylation of 4-chloro- and 4-fluoroaniline, respectively, following a literature procedure[S3] and crystallized from ethanol just before use. All the other aryl chlorides and fluorides along with the reduction products are commercially available and were distilled or crystallized before use.

General procedure for the photochemical reduction of aryl chlorides and fluorides: A solution of compound ArX (0.05 or 0.1 M, 0.25 or 0.5 mmol respectively), the reducing agent (0.5 M H_3PO_2 or 0.5 M Et_3SiH) in the chosen solvent (5 ml) was poured in quartz tubes, purged with nitrogen, serum capped and irradiated at 254 or 310 nm. The end mixtures were analyzed by GC and the yields were determined by comparison with authentic samples of ArH. When hypophosphorous acid was used, the irradiated solutions were neutralized with solid potassium carbonate and filtered before analysis. In the experiments in neat *i*-PrOH, compounds ArX were dissolved in this solvent, treated as above and irradiated.

Preparative photoreduction of 4-chloro-*N*,*N*-dimethylaniline (10): A solution of 4-chloro-*N*,*N*-dimethylaniline (2.3 g, 15 mmol, 0.1 M) in *i*-PrOH (150 ml) was placed in an immersion-well apparatus and irradiated by a 125 W high-pressure mercury arc through quartz for 2 hours, while maintaining a nitrogen flux. After removing the solvent in vacuo, the crude residue was purified by bulb to bulb distillation affording 1.4 g of *N*,*N*-dimethyl aniline (colorless oil, 77% yield).

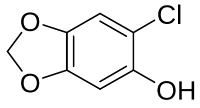
(S1) F. B. Mallory, D. S. Amenta, C. W. Mallory and J. J. Chiang Cheung, *J. Org. Chem.* 1996, **61**, 1551-1554.

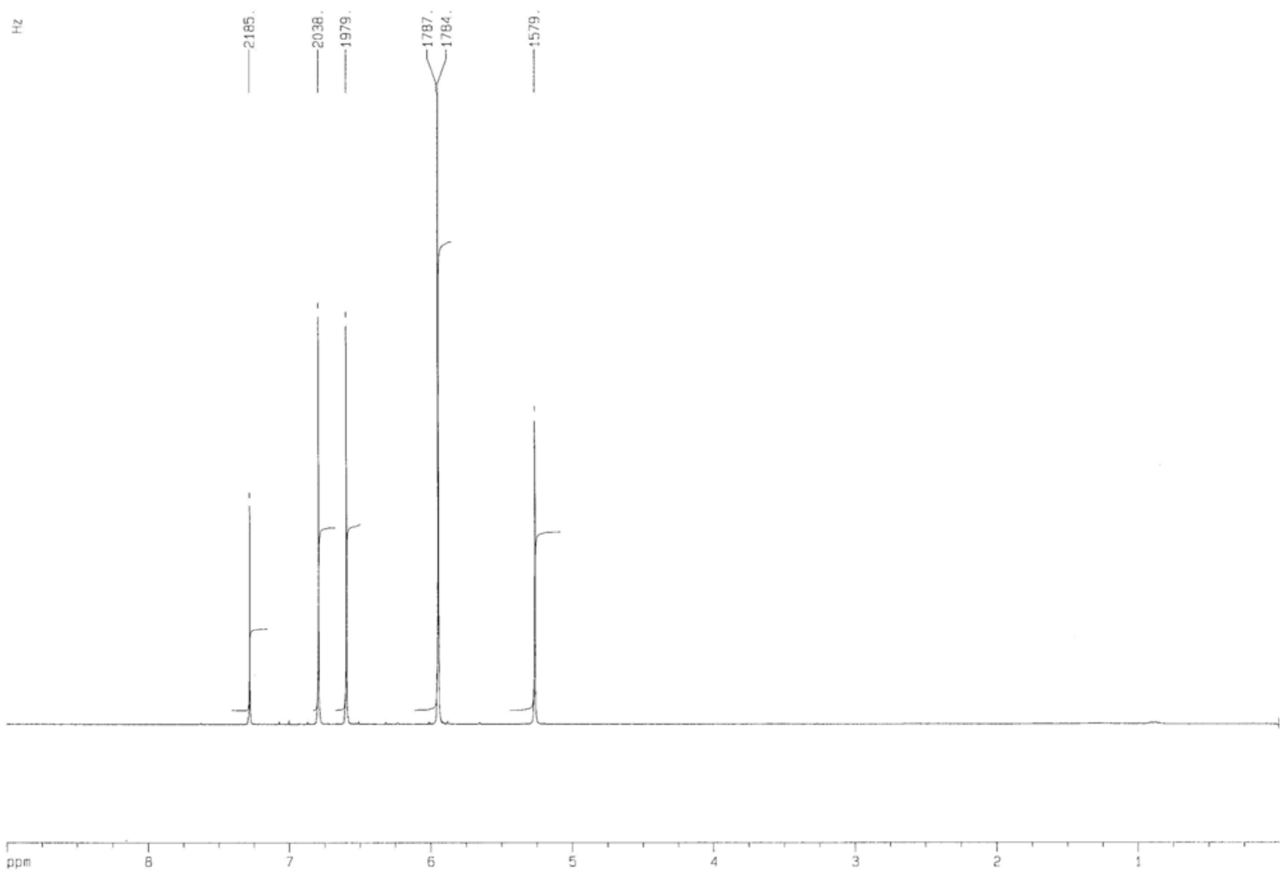
(S2) J. S. Yadav, B. V. S. Reddy, P. S. R. Reddy, A. K. Basak and A. V. Narsaiah, *Adv. Synth. Catal.* 2004, **346**, 77-82.

(S3) A. G. Giumanini, G. Chiavari, M. M. Musini and P. Rossi, *Synthesis* 1980, 743-745.

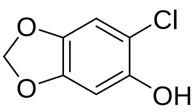
2) ^{1}H NMR and ^{13}C NMR spectra of compounds 8

Compound **8**





Compound **8**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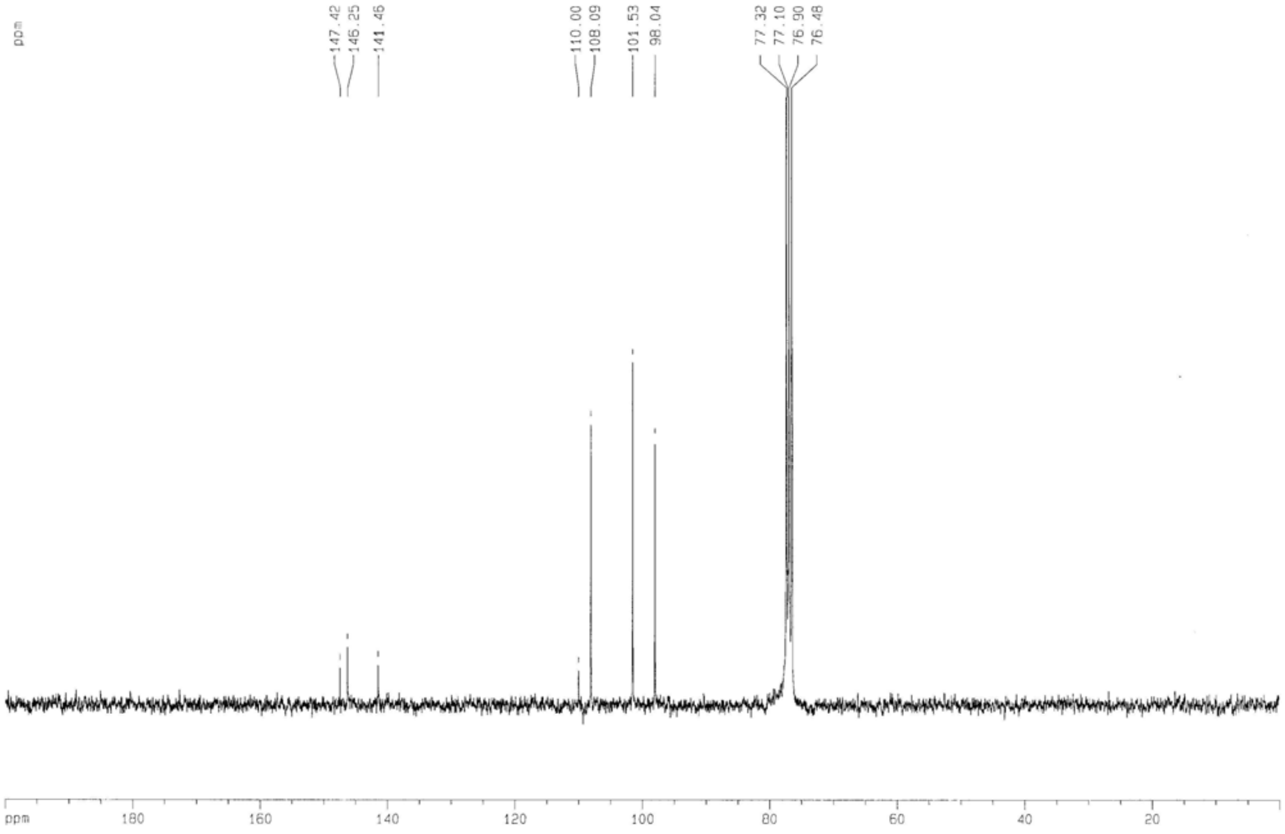
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