Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Fluorine Substituted Organic Dyes For Efficient Dye Sensitized Solar Cells

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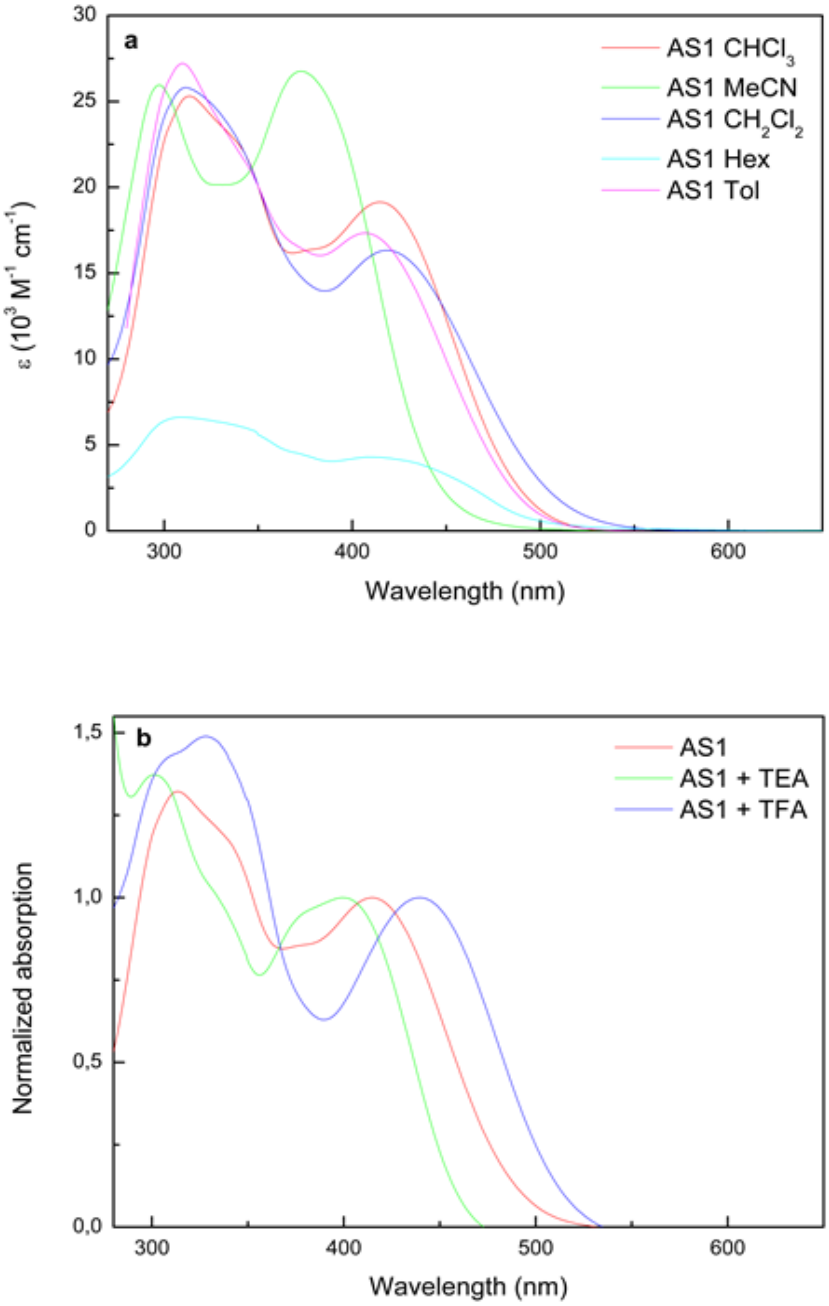


Fig. S1 Absorption spectra of the dyes **AS1** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS1** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

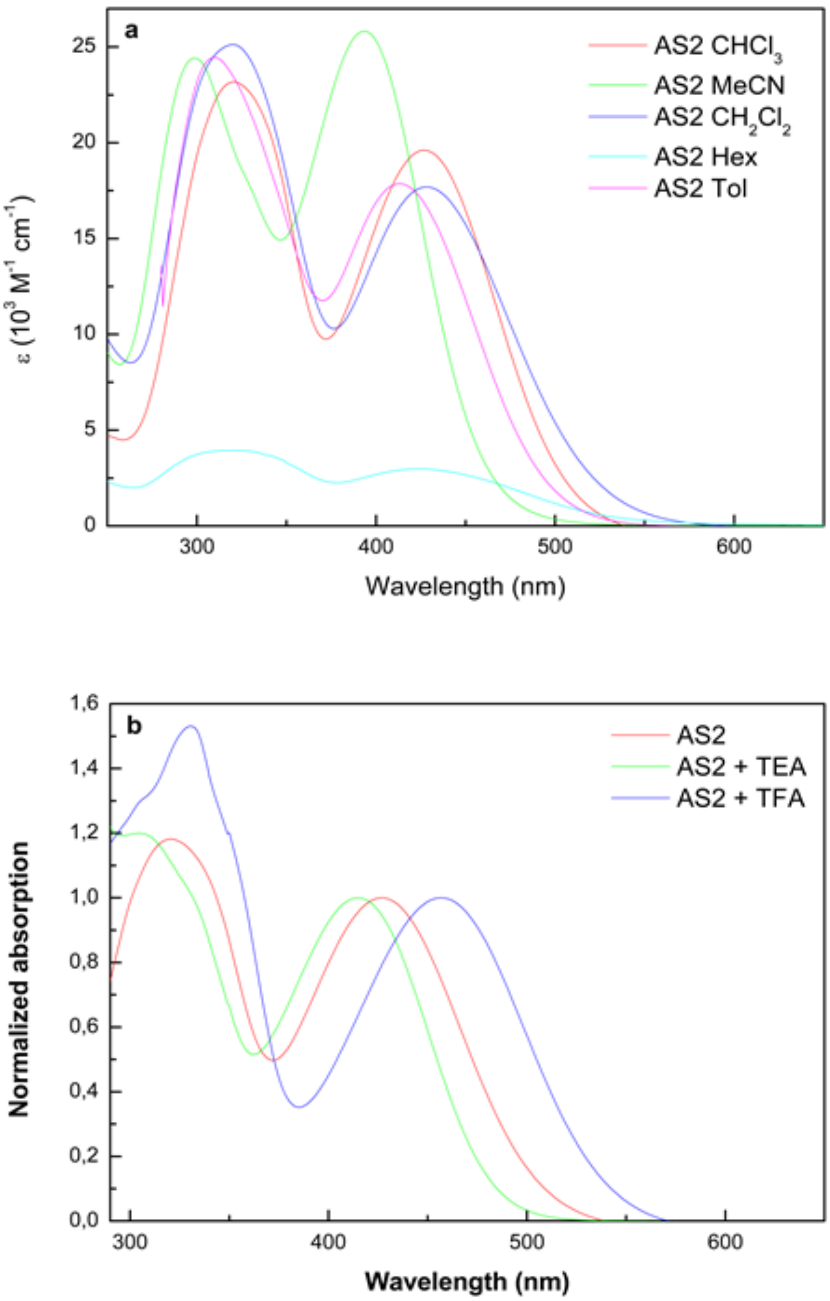


Fig. S2 Absorption spectra of the dyes **AS2** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS2** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

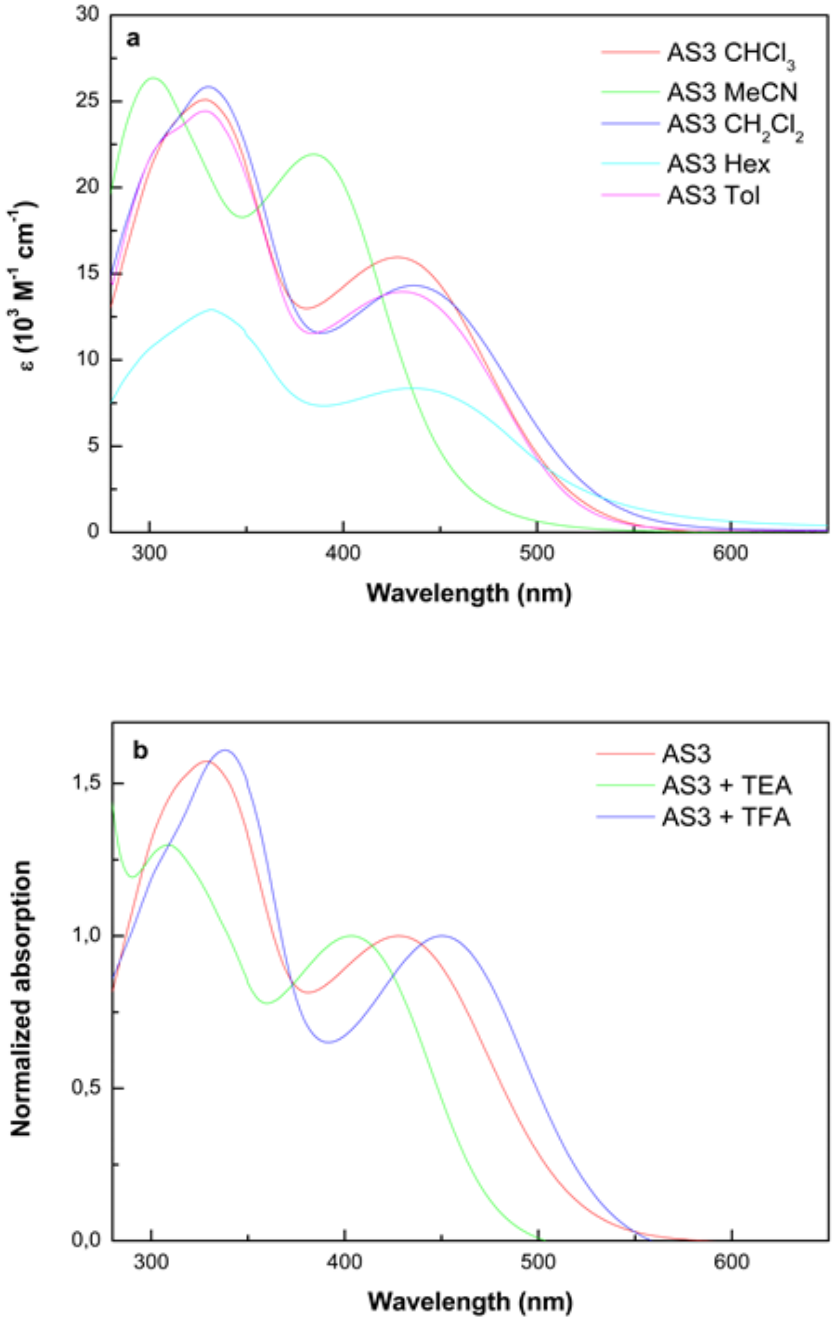


Fig. S3 Absorption spectra of the dyes **AS3** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS3** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

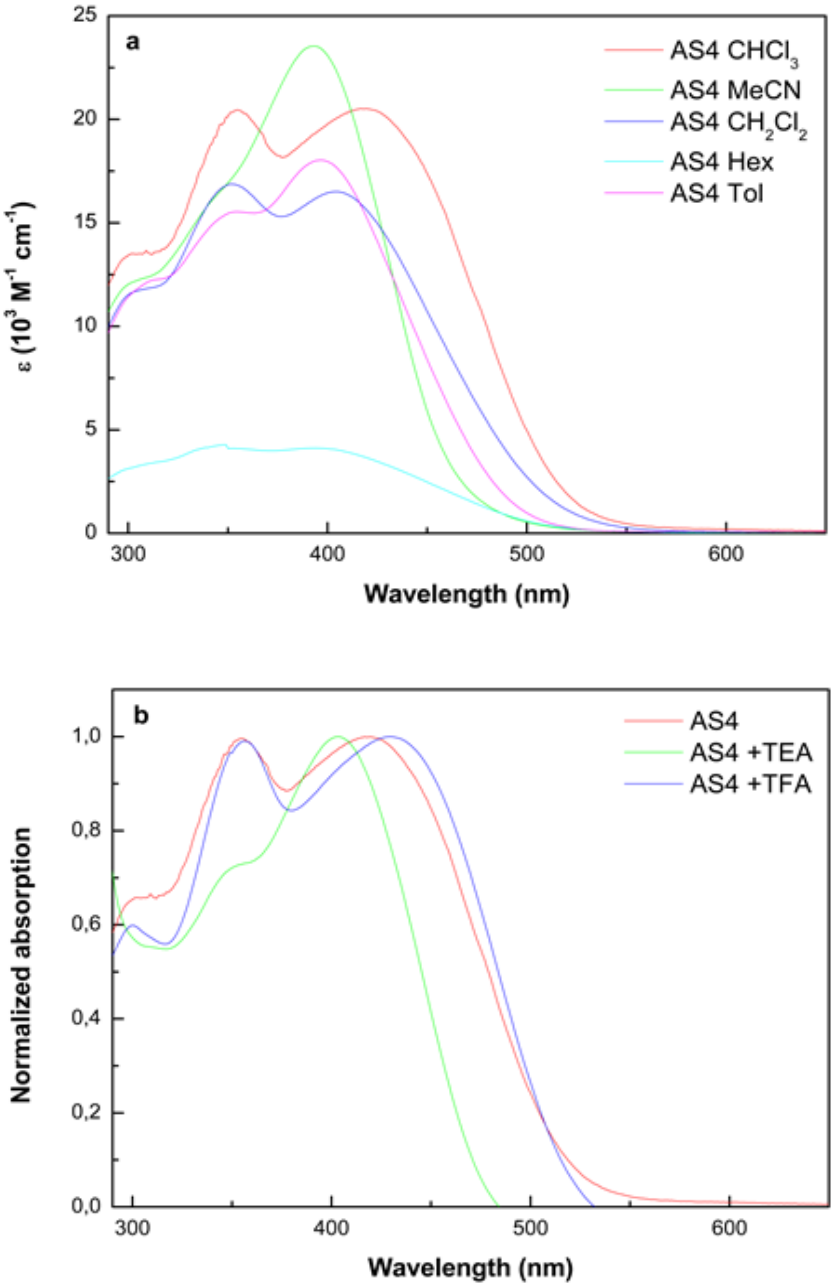


Fig. S4 Absorption spectra of the dyes **AS4** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS4** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

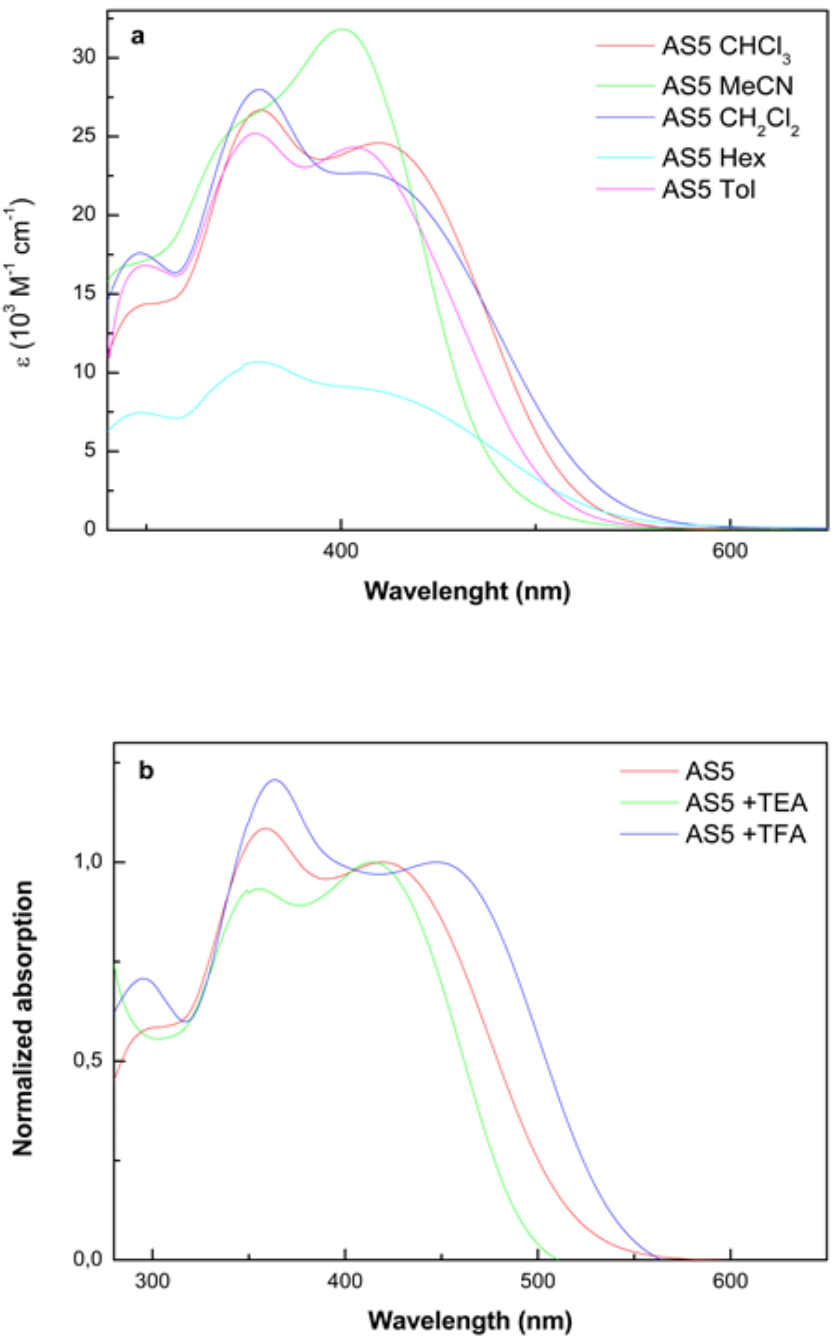


Fig. S5 Absorption spectra of the dyes **AS5** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS5** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

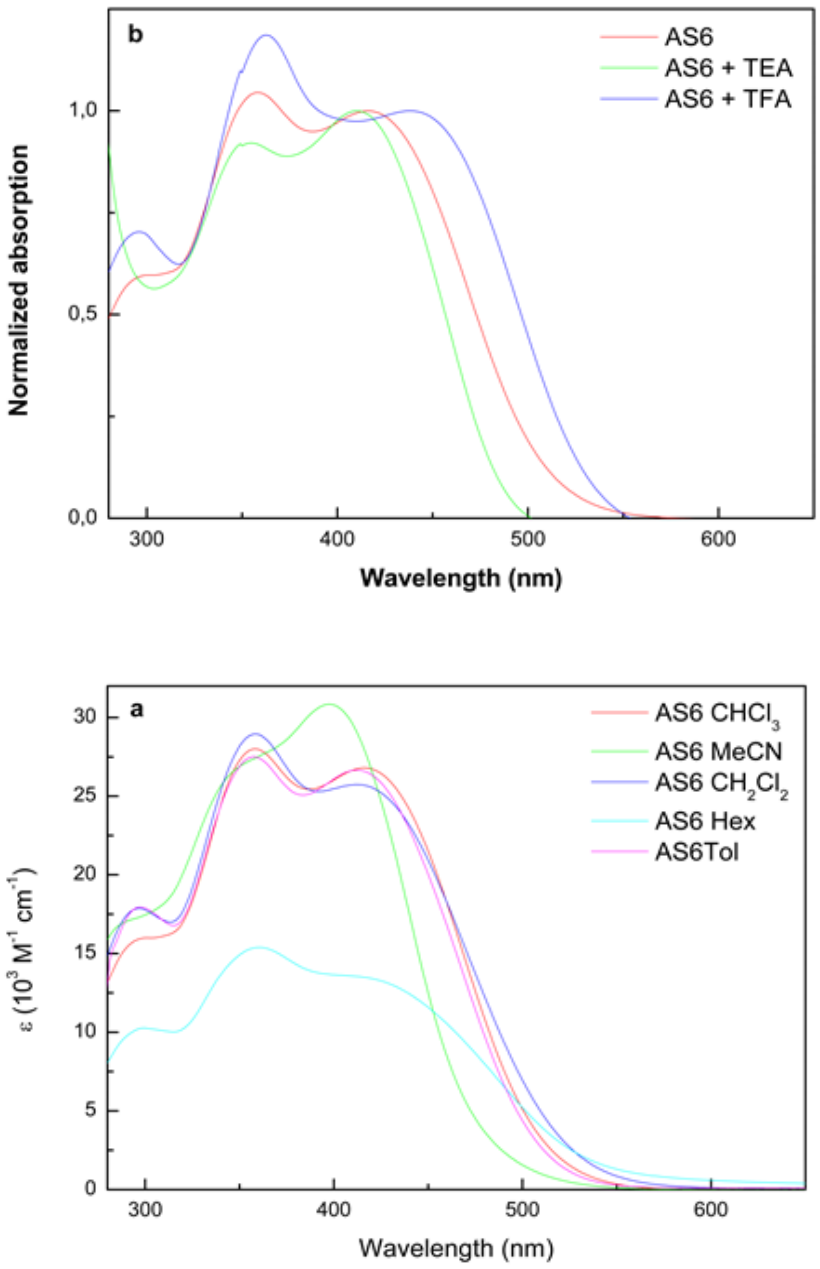


Fig. S6 Absorption spectra of the dyes **AS6** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS6** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

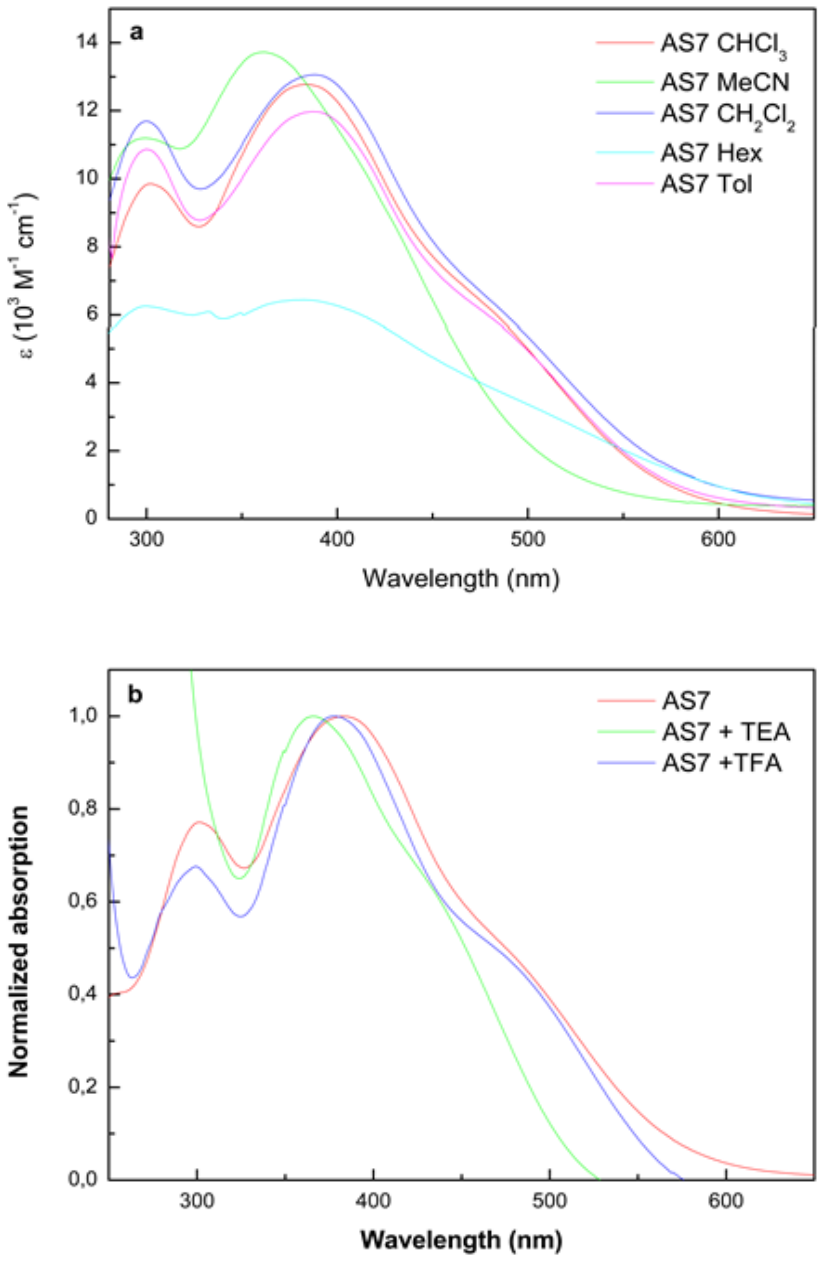


Fig. S7 Absorption spectra of the dyes **AS7** in different solvents (3×10^{-5} M) (a), absorption spectra of the dyes **AS7** in $CHCl_3$ (3×10^{-5} M) before (red line) and after the addition of Triethylamine (TEA) (green line) and of Trifluoroacetic Acid (TFA) (blue line) (b).

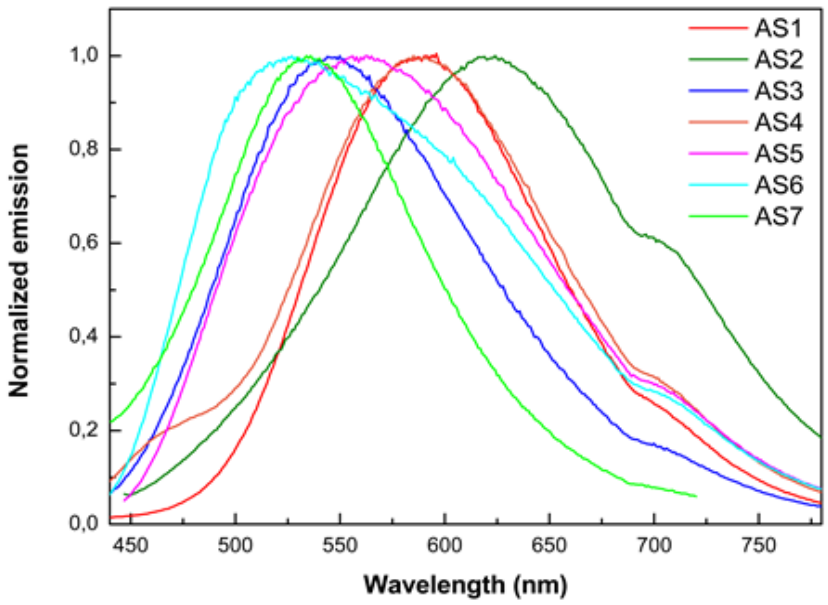


Fig. S8 Normalized Emission Spectra of the dyes **AS1-7** in different $CHCl_3$.

Table S1. Absorption spectra for the Dyes before and after the addition of Trifluoroacetic Acid (TFA) and Triethylamine (TEA) and emission data.

Dye	λ_{max}/nm [a]	$\varepsilon/M^{-1}cm^{-1}$ [a]	λ_{max}/nm [b]	λ_{max}/nm [c]	λ_{em}/nm [a]
AS1	415 (313)	19143 (25300)	399	440	591
AS2	427 (321)	19614 (23180)	415	457	624
AS6	428 (329)	15958 (25100)	403	451	550
AS4	417 (355)	20529 (20460)	403	429	585
AS5	419 (358)	24529 (26675)	414	448	563
AS6	416 (358)	26798 (28009)	410	438	527
AS7	383 (383)	12776 (9855)	366	379	534

[a]Recorded in $CHCl_3$. [b]Recorded in $CHCl_3$ in the presence of triethylamine. [c]Recorded in $CHCl_3$ in the presence of trifluoroacetic acid.

2. Computational Characterization

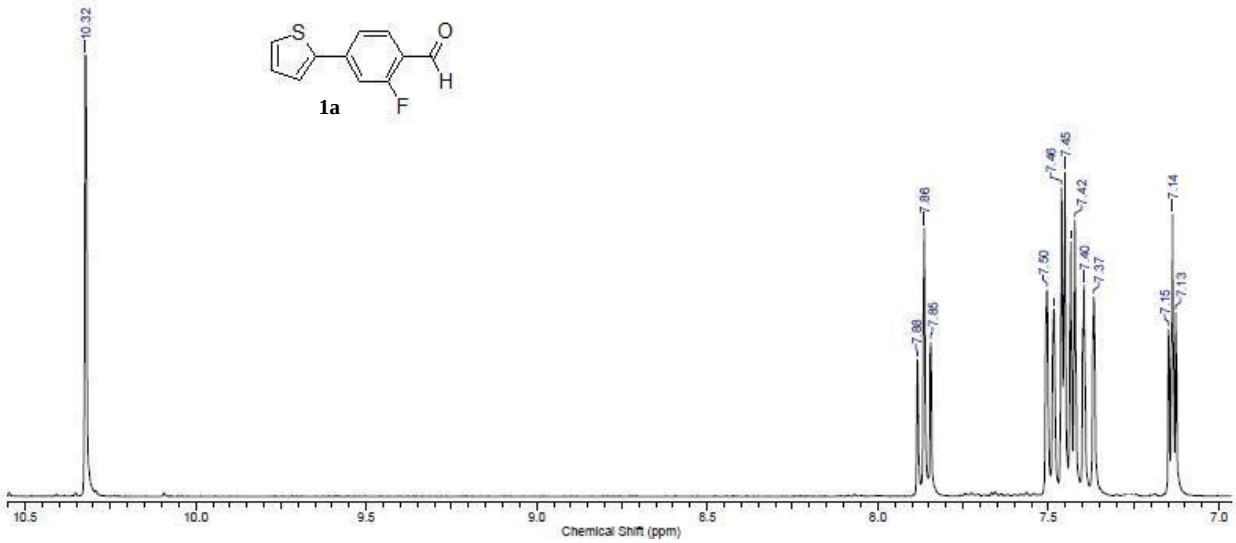
Table S2. Calculated details of electronic transitions with the relative oscillator strengths f_{osc} obtained by performing for the **AS1** dye, in gas phase, different TD-DFT and RI-CC2 calculations.

XC functional	Single excited state	λ (nm)	f_{osc}
BLYP	HOMO → LUMO (94.7%)	712.2448	0.5684
	HOMO -1 → LUMO (70.5%)	433.6638	1.0275
	HOMO → LUMO +1 (14.8%)		
	HOMO -2→ LUMO (48.7%)	401.1962	0.1832
	HOMO → LUMO +1 (43.9%)		
B3LYP	HOMO → LUMO (99.3%)	534.6866	0.8945
	HOMO -1 → LUMO (84.7%)	369.3075	1.0081
	HOMO → LUMO +1 (13.8%)		
	HOMO → LUMO +2 (93.8%)	337.7298	0.1182×10^{-1}
BHLYP	HOMO → LUMO (81.8%)	399.5729	1.6984
	HOMO -1 → LUMO (76.0%)	299.7153	0.2341
	HOMO → LUMO +2 (85.1%)	285.9950	0.1826×10^{-1}
RI-CC2	HOMO → LUMO (88.2%)	425.7028	-
	HOMO → LUMO +9 (43.8%)	320.0973	-
	HOMO -1 → LUMO (53.4%)	310.6229	-

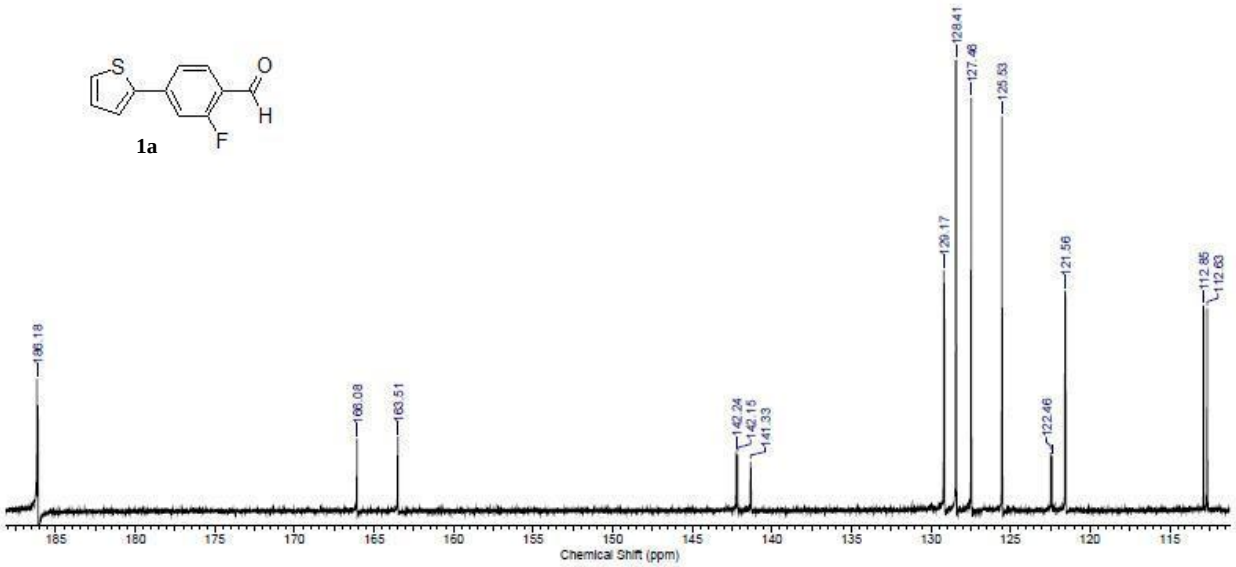
3. Fabrication of DSSCs and photovoltaic measurements

DSSC devices were prepared according to the reported literature[64-66] as follows: fluorine-doped tin oxide (FTO, 10 ohm/sq., provided by Solaronix S.A.) glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Double-layer photoanodes (thickness 13 μm) were prepared as follows: a layer of Dyesol 18NR-T paste was deposited onto FTO glass and dried at 125°C for 15 min to obtain a transparent nanocrystalline film of thickness around 8 μm; a scattering layer, 5 μm, made by Dyesol 18-NR-AO colloidal paste was coated onto the transparent layer and the sintering process at 500°C for 30 min was performed. The active area of photoanodes was 0.16 cm^2. The electrodes coated with the TiO_2 pastes were gradually heated under an air flow and sintered at 450 °C for 30 min. The substrate temperature was then allowed to slowly decrease. Once cooled down at about 80°C, the electrodes were immersed into 0.2 mM solutions of dyes **AS1**, **AS2**, **AS3** and **AS4** in AcCN with 3mM chenodeoxycholic acid and kept for 12 h in dark at room temperature. The reference photoanodes were prepared by dyeing into a solution 0.2 mM of (bis(tetrabutylammonium)-cis-di(thiocyanato)-N,N'-bis (4 - carboxylato - 4' - carboxylic acid-2, 2 -bipyridine) ruthenium(II) (N719, provided by Solaronix S.A.) in a mixture of acetonitrile and tert-butyl alcohol (v/v, 1:1) at room temperature for 14 h. The counter electrodes were prepared by sputtering a 50 nm Pt layer on a hole drilled cleaned FTO plate. The two plates were faced and assembled by means of a gasket of 50μm-thick Surlyn® foil (Dyesol Ltd) interposed between them. The redox electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 1-methyl-3-propylimidazolium iodide, and 0.5 M tert-butylpyridine in dry acetonitrile) was vacuum-injected into the space between the electrodes. Photocurrent-voltage I-V measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 300W Xenon Arc Lamp) serving as a light source. The light intensity (or radiant power) was calibrated to 100 mW/cm^2 using as reference a Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measurement by a DC method. IPCE measurements were carried out with a computerized setup consisting of a xenon arc lamp (140 W, Newport, 67005) coupled to a monochromator (Cornerstore 260 Oriel 74125). Light intensity was measured by a calibrated UV silicon photodetector (Oriel 71675) and the short circuit currents of the DSSCs were measured by using an optical power/energy meter, dual channel (Newport 2936-C).

4. NMR Spectra



1a



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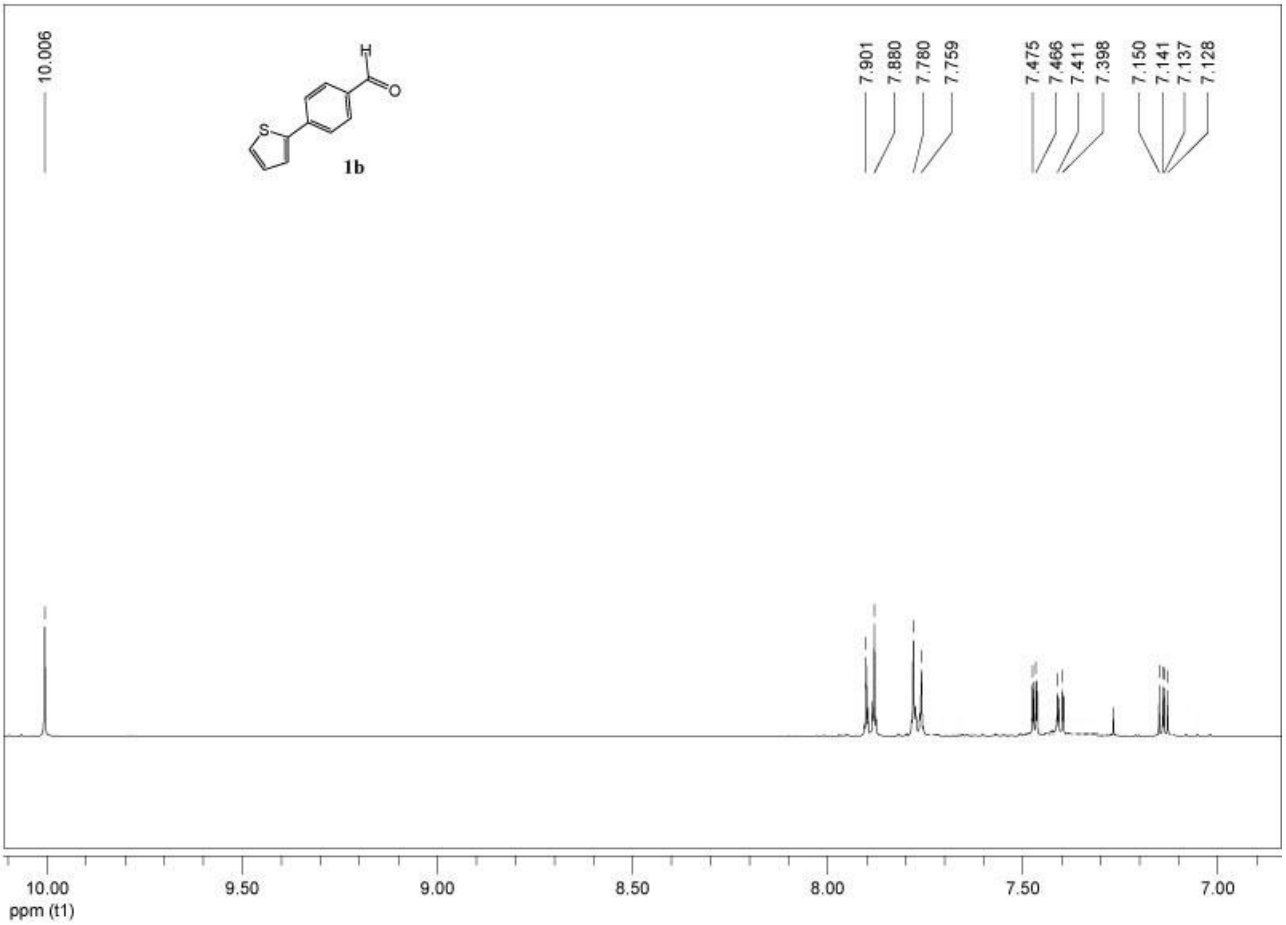

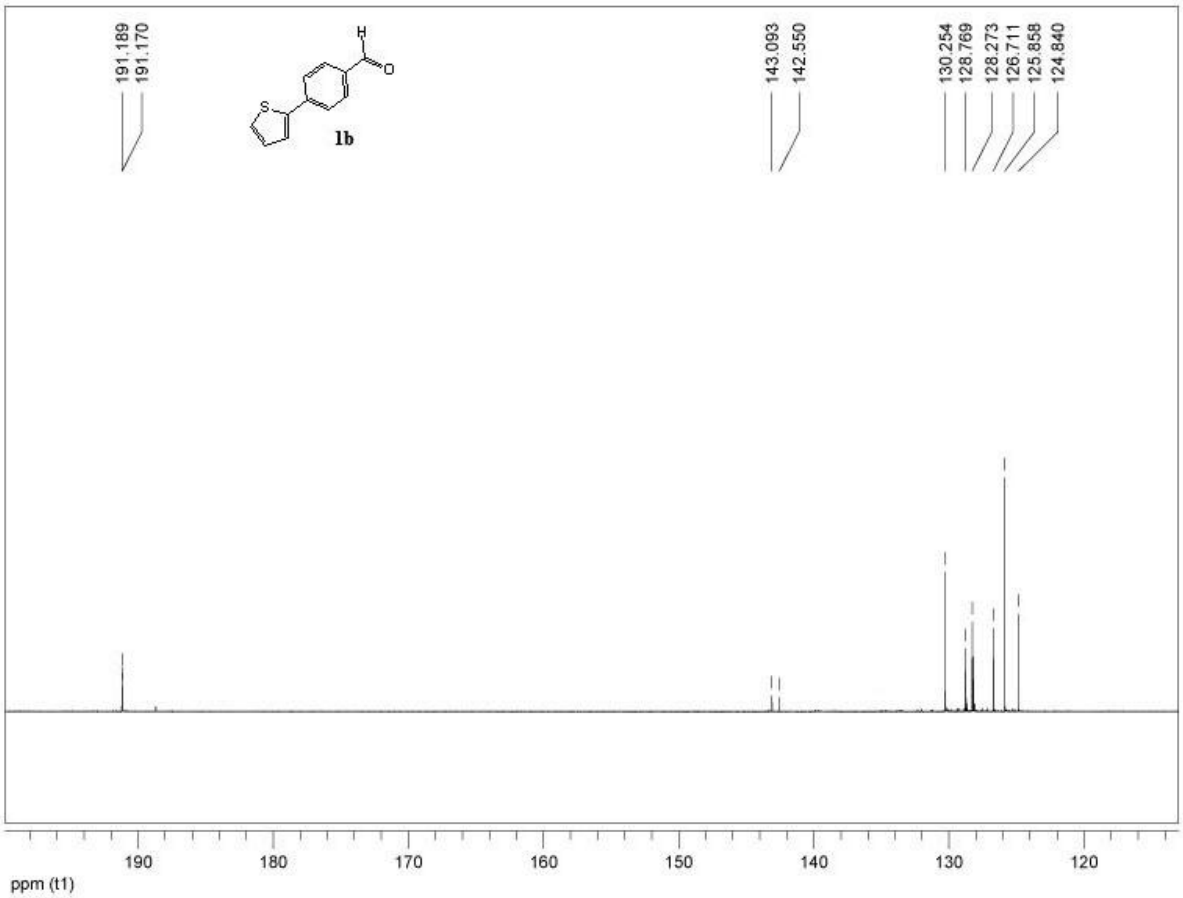

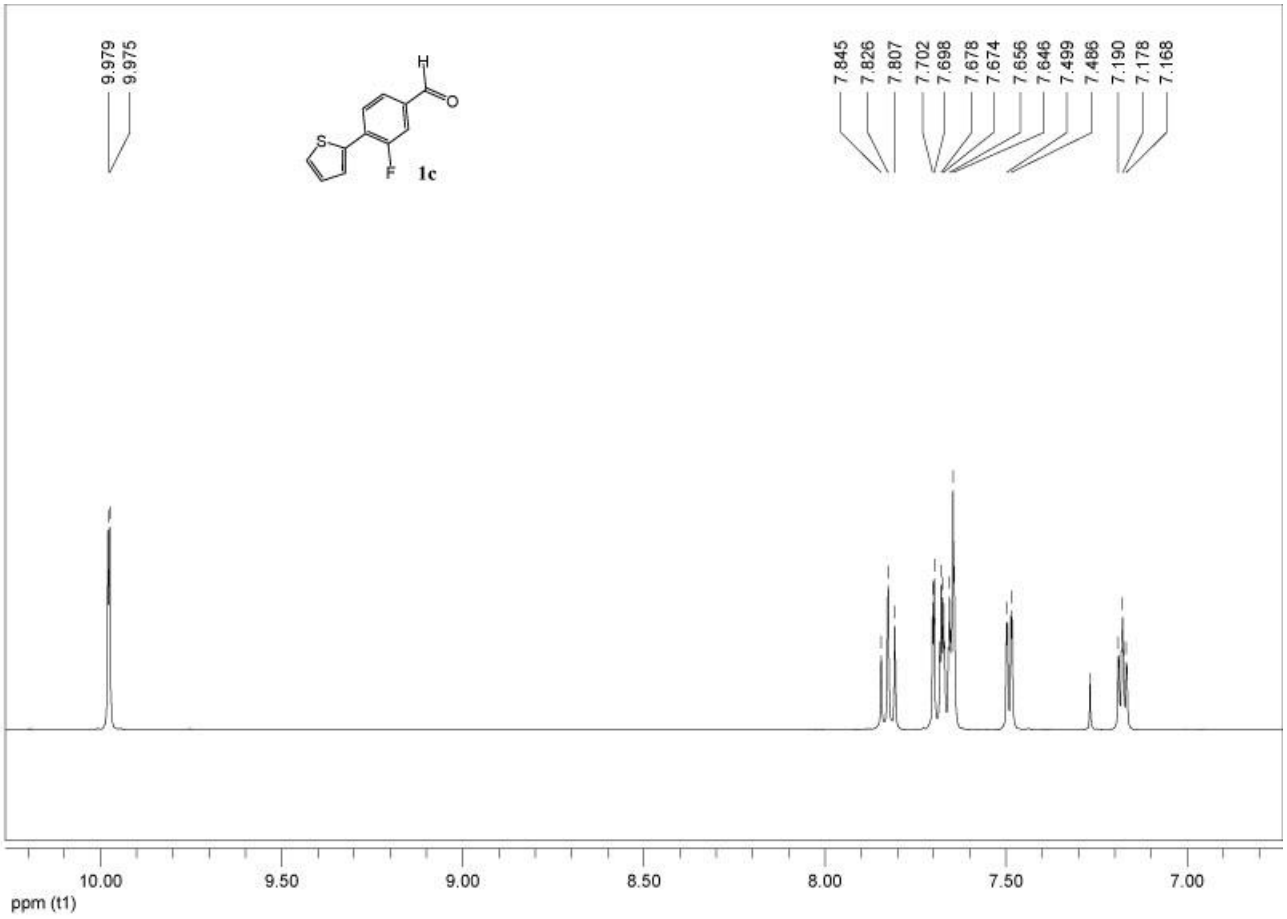

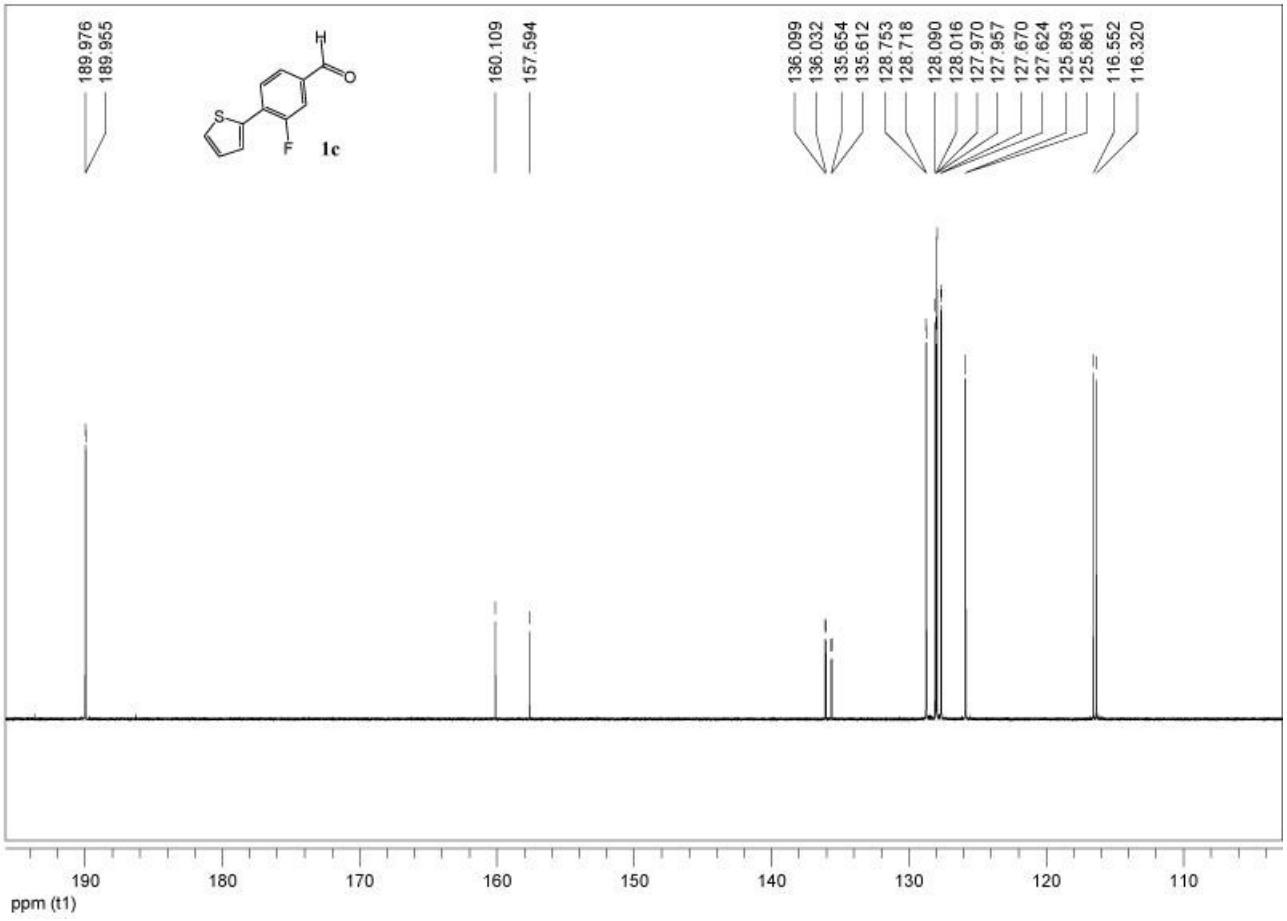

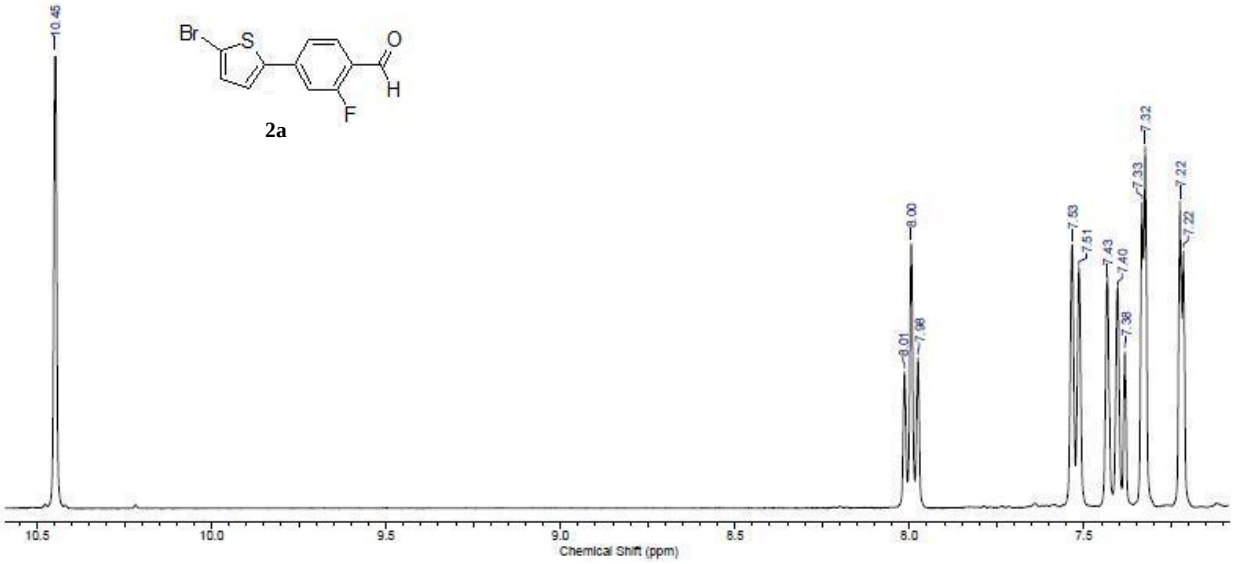

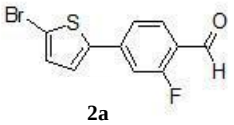

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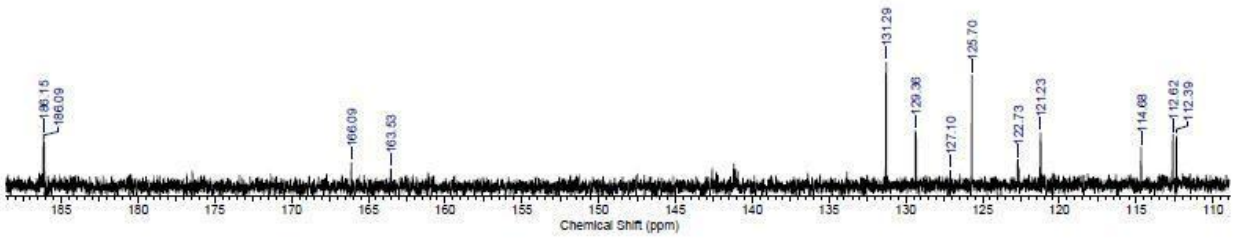

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