

Electronic Supplementary Information (ESI) for:

Synthesis of Photoresponsive Main-Chain Oligomers with Azobenzene Moieties via ADMET Oligomerization and Their Micellization Properties.

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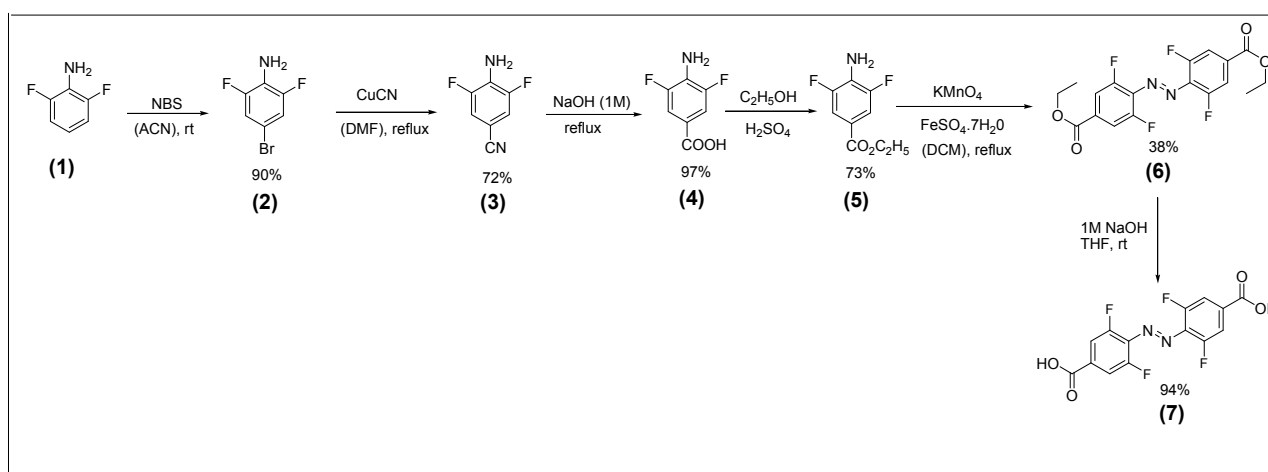
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Characterization

Transmission electron microscopy (TEM) measurements were conducted with an EM 900 transmission electron microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). The samples were dissolved in THF with concentration of 1 mg/mL and spread onto a Cu grid coated with a Carbon-film. After 1 min, excess solution was blotted off with filter paper, afterwards 5 μ L of 1% aqueous uranyl acetate solution were deposited onto the grid and drained off after 1 min. TEM images were obtained from negatively stained samples. Micrographs were taken with a SSCCD SM-1k-120 camera (TRS, Moorenweis, Germany).

Thermogravimetric analysis (TGA) was performed on a Netzsch TG tarsus 209 instrument. The samples were heated in a Pt pan under a nitrogen atmosphere, over a temperature range of 25–900 $^{\circ}$ C, with a heating rate of 10 $^{\circ}$ C min⁻¹.

Experimental part



Scheme S1: Synthetic scheme of the fluorinated and non-fluorinated azo-monomers

Synthesis of 2,6-difluoro-4-bromoaniline (2)

A solution of 2,6-difluoroaniline (12.9 g, 100 mmol) in acetonitrile (200 mL) was charged with N-bromosuccinimide (17.8 g, 100 mmol). The mixture was stirred for 24 h at room temperature, and then diluted with water and hexanes. The two phases were separated and the

organic phase was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (DCM/hexanes:1/1) to give compound (**2**, 92%).

^1H -NMR (**2**, CDCl_3): δ ppm 6.99 (dd, $J = 6.3$ Hz, 1.4 Hz, 2H, m-**ArH**-N), 3.73 (s, 2H, **NH**₂). ^{13}C -NMR (**2**, CDCl_3): δ ppm 152.7 (d, $J = 8.7$ Hz), 150.8 (d, $J = 7.7$ Hz), 123.5, 114.8, 107.1. ^{19}F -NMR (**2**, CDCl_3): δ ppm -132 (m). HRMS (ESI) calcd for $\text{C}_6\text{H}_5\text{BrF}_2\text{N}$ ($[\text{M}+\text{H}]^+$) 207.9568, found 207.9563

Synthesis of 4-amino-3,5-difluorobenzonitrile (**3**)

A solution of compound (**2**) (10 g, 48mmol) in DMF (100 mL) was added CuCN (12.8 g, 144 mmol) and refluxed for 24 h. Afterwards, the mixture was poured into a NH_3 12% aqueous solution and extracted with ethyl acetate. The two phases were separated and the organic phase was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (DCM/hexanes:2/1) to give compound (**3**, 72%).

^1H -NMR (**3**, CDCl_3): δ ppm 7.16 (dd, $J = 6.3$ Hz, 1.8 Hz, 2H, m-**ArH**-N), 4.15 (s, 2H, **NH**₂). ^{19}F -NMR (**3**, CDCl_3): δ ppm -130 (m). HRMS (ESI) calcd for $\text{C}_7\text{H}_3\text{F}_2\text{N}_2$ ($[\text{M}-\text{H}]^-$) 153.0439, found 153.0424

Synthesis of 4-amino-3,5-difluorobenzoic acid (**4**)

Compound (**3**) (5.3 g, 35 mmol) was suspended in NaOH 1M (160 mL) and heated to reflux for 24 h. The reaction was then cooled down to room temperature, and 1M HCl added to it, until the product precipitates as its hydrochloric salt. The salt was then dissolved in ethyl acetate, dried over MgSO_4 , filtered, concentrated under reduced pressure, to give compound (**4**, quantitative).

^1H -NMR (**4**, CDCl_3): δ ppm 12.73 (s, 1H, **COOH**), 7.69 (dd, $J = 5.1$ Hz, 1.6 Hz, 2H, m-**ArH**), 3.31 (s, 2H, **NH**₂). ^{13}C -NMR (**4**, CDCl_3): δ ppm 165.5, 150.6 (d, $J = 9.3$ Hz), 148.4 (d, $J = 9.3$ Hz), 129.6, 117.5, 112.2. ^{19}F -NMR (**4**, CDCl_3): δ ppm -130 (m). HRMS (ESI) calcd for $\text{C}_7\text{H}_4\text{F}_2\text{NO}_2$ ($[\text{M}-\text{H}]^-$) 172.0245, found 172.0241

Synthesis of ethyl 4-amino-3,5-difluorobenzoate (**5**)

Compound (**4**) (5.3 g, 30 mmol) was dissolved in ethanol (100 mL) and H₂SO₄ (2 mL), and refluxed for 10 h. The mixture was neutralized with saturated NaHCO₃, extracted with DCM, the two phases were separated and the organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure to give compound (**5**, 73%).

¹H-NMR (**5**, CDCl₃): δ ppm 7.52 (dd, J = 7.3 Hz, 2.1 Hz, 2H, m-ArH), 4.18 (q, J = 7.4 Hz, 2H, CH₂-CH₃), 3.97 (s, 2H, NH₂), 1.36 (t, J = 7.2 Hz, 3H, CH₂-CH₃). ¹³C-NMR (**5**, CDCl₃): δ ppm 169.5, 152.2 (d, J = 8.5 Hz), 149.3 (d, J = 8.5 Hz), 128.8, 118.3, 112.5, 61.4, 14.2. ¹⁹F-NMR (**5**, CDCl₃): δ ppm -130 (m). HRMS (ESI) calcd for C₉H₁₀F₂NO₂ ([M+H]⁺) 202.0614, found 202.0612

Synthesis of diethyl-4,4'-(2,2',6,6'-tetrafluoro)azobenzene dicarboxylate (**6**)

A one-neck flask was charged with compound (**5**) (1 g, 5 mmol) and a freshly ground mixture of KMnO₄ (8.5 g) and FeSO₄·7H₂O (8.5 g) dissolved in DCM (150 mL). The solution was refluxed 24 h, filtered through celite, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (DCM/hexanes: 1/1) to give compound (**6**, 38%).

¹H-NMR (**6**, CDCl₃): (80% *trans*-isomer) δ ppm 7.26 (m, 4H, m-ArH-N=N-ArH), 4.19 (q, J = 7.2 Hz, 4H, CH₂-CH₃), 1.42 (t, J = 7.1 Hz, 6H, CH₂-CH₃). ¹³C-NMR (**6**, CDCl₃): (80% *trans*-isomer) δ ppm 164.6, 154.5 (d, J = 5.2 Hz), 153.2 (d, J = 5.2 Hz), 133.8, 113.0, 62.1, 14.0. ¹⁹F-NMR (**6**, CDCl₃): δ ppm -118 (d, J = 6.1 Hz), -119 (d, J = 8.5 Hz). HRMS (ESI) calcd for C₁₈H₁₅F₄N₂O₄ ([M+H]⁺) 399.0962, found 399.0966

Synthesis of 2,2',6,6'-tetrafluoro-4,4'-dicarboxyazobenzene (**7**)

Compound (**6**) (350 mg, 0.9 mmol) was dissolved in 15 mL THF and 4 mL 1 M NaOH was added, the solution was stirred for 2 h at room temperature. In the meantime, the solution was adjusted to pH = 4 with 1 M HCl, extracted with ethyl acetate and the organic phase concentrated under reduced

pressure to give compound (**7**, 94%).

^1H -NMR (**7**, DMSO): (80% *trans*-isomer) δ ppm 12.75 (s, 2H, **COOH**), 7.26 (d, $J = 8.2$ Hz, 2H, m-**ArH-N=N-ArH**). ^{13}C -NMR (**7**, DMSO): (80% *trans*-isomer) δ ppm 165.9, 155.8 (d, $J = 5.2$ Hz), 153.6 (d, $J = 5.2$ Hz), 135.6, 133.4. ^{19}F -NMR (**7**, DMSO): δ ppm -118 (d, $J = 6.1$ Hz), -119 (d, $J = 8.5$ Hz). HRMS (ESI) calcd for $\text{C}_{14}\text{H}_7\text{F}_4\text{N}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$) 343.0336, found 343.0333

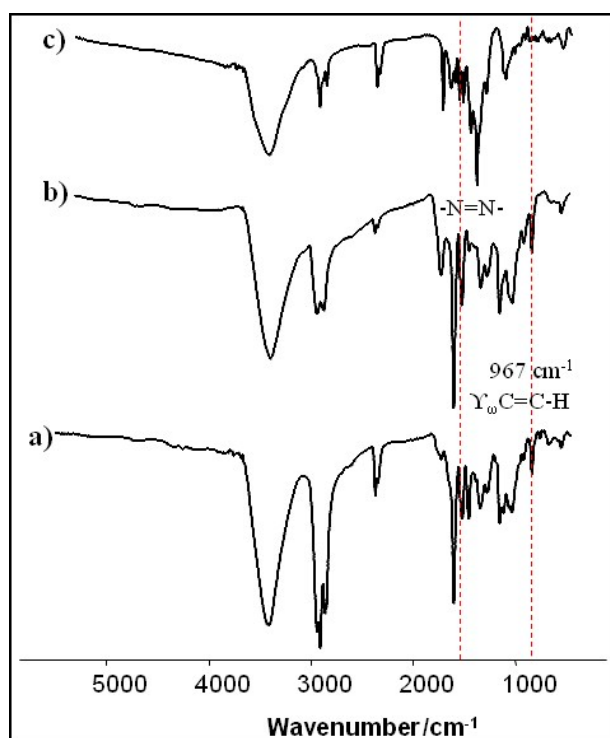


Figure S1. FTIR spectra of the non-fluorinated azobenzene compounds. (a) shows the spectrum of the azo-monomer used for the oligomerization reactions, (b) shows the spectrum of the unsaturated oligomers and (c) Shows the spectrum of the saturated oligomers after hydrogenation

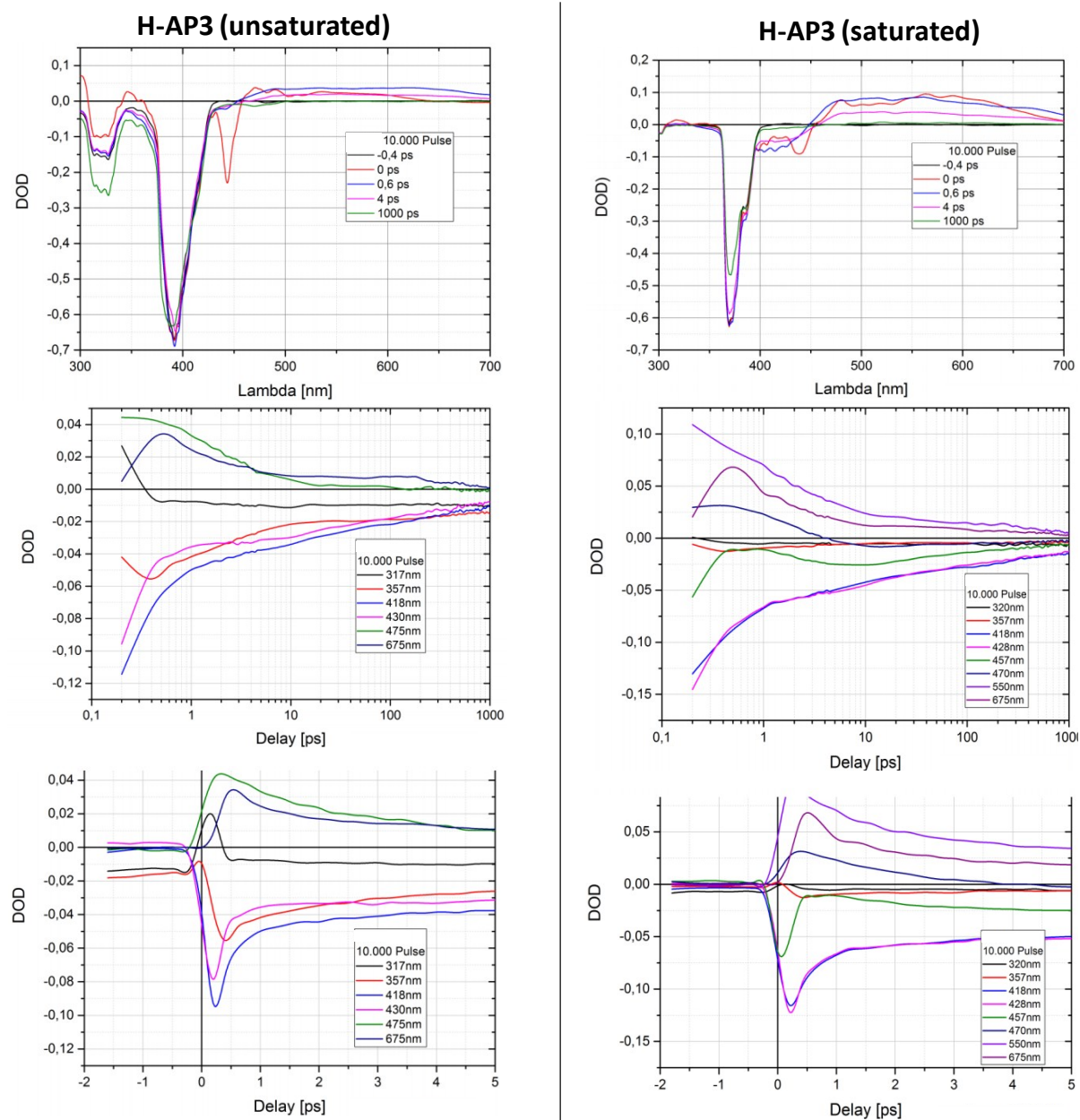


Figure S2. UV-VIS and Ultrafast dynamics measurements of the non-fluorinated azo- compounds, showing the full delay time range of transient, upon 338 nm excitation.

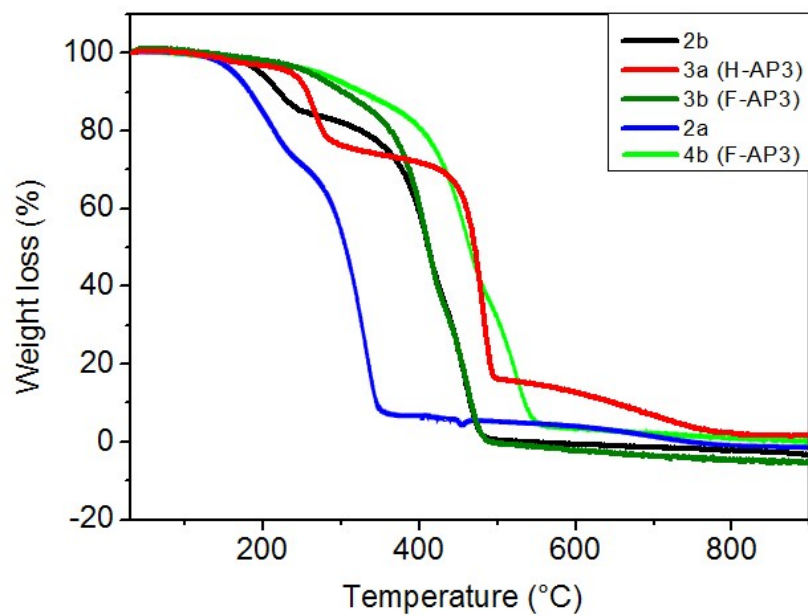


Figure S3. Thermal decomposition of the azo-monomers and oligomers

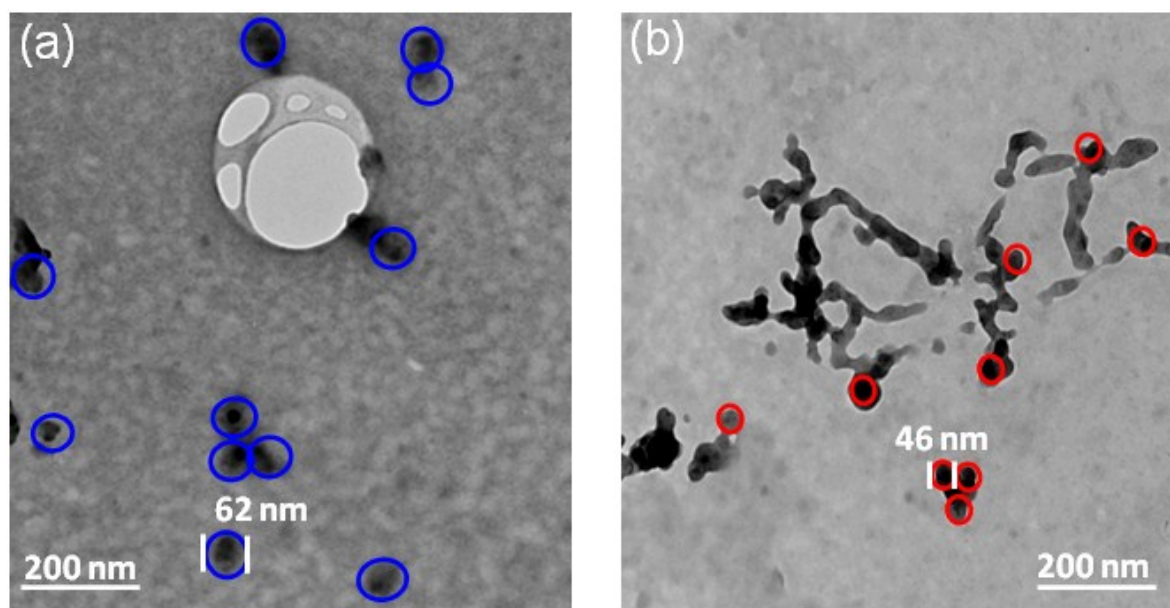


Figure S4. TEM images of the fluorinated azo-oligomers (**4b**) before (a) and after (b) photo-irradiation

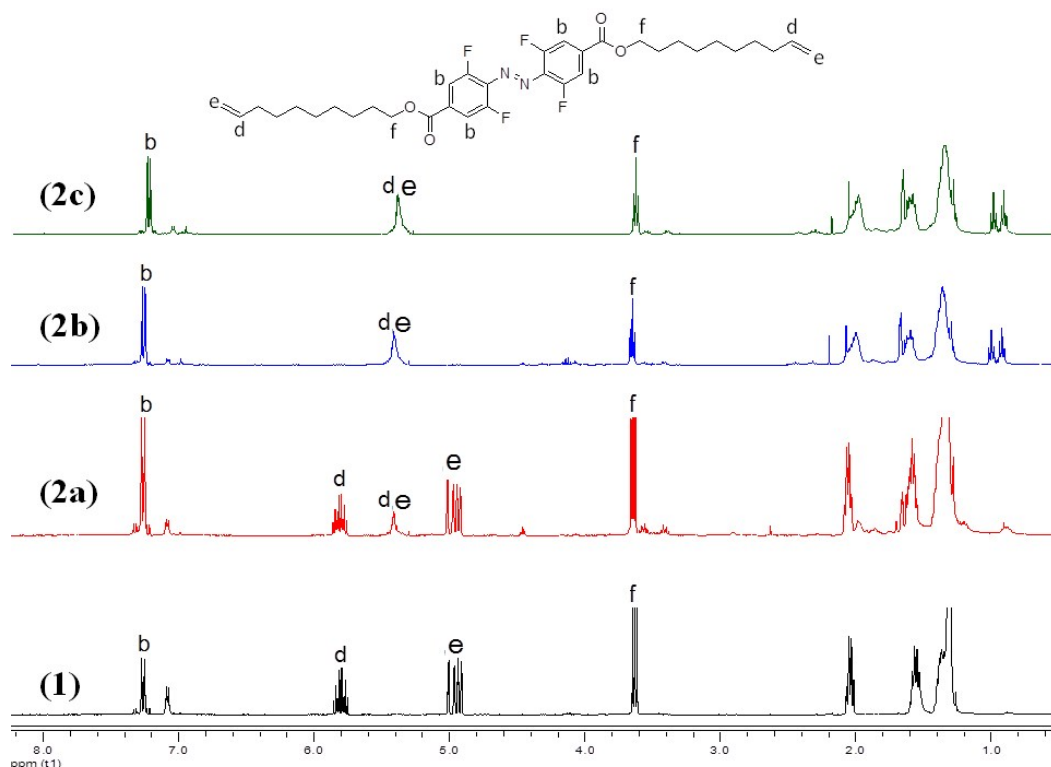


Figure S5: ^1H -NMR of the fluorinated azobenzenes. The numbers (1) shows the azo-monomers before oligomerization, (2) shows the azo-oligomers after oligomerization, a, b and c shows 24 h, 72 h and 120 h oligomerization time respectively.

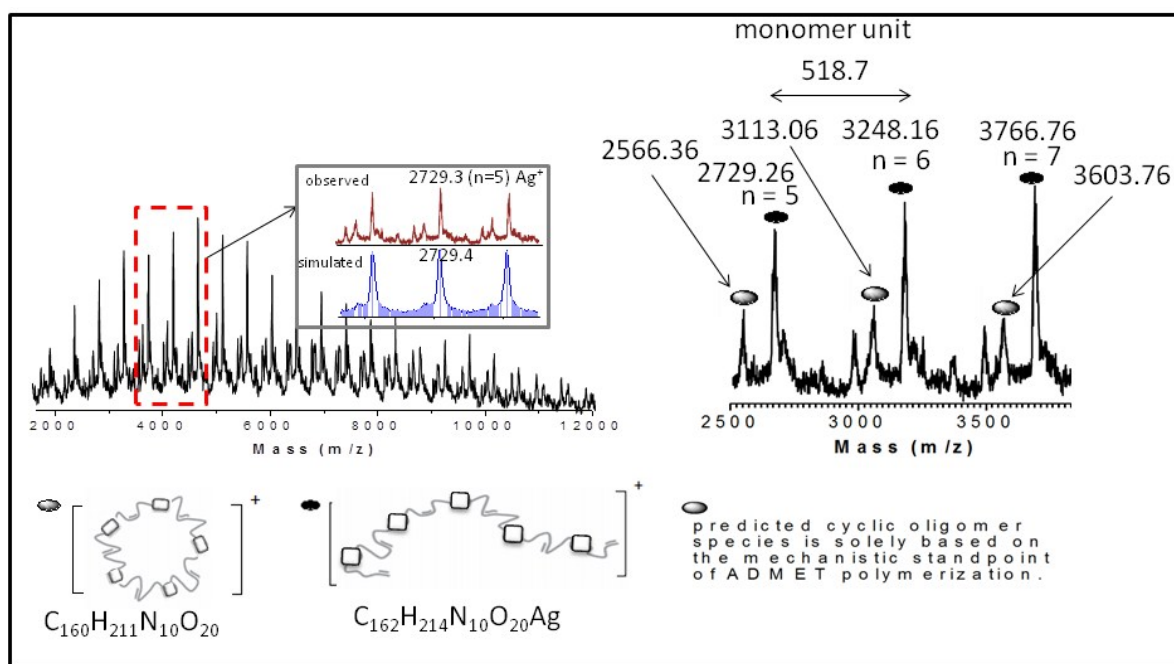


Figure S6. MALDI-ToF MS spectra of the unsaturated azo-oligomer (**3a**, run 4)

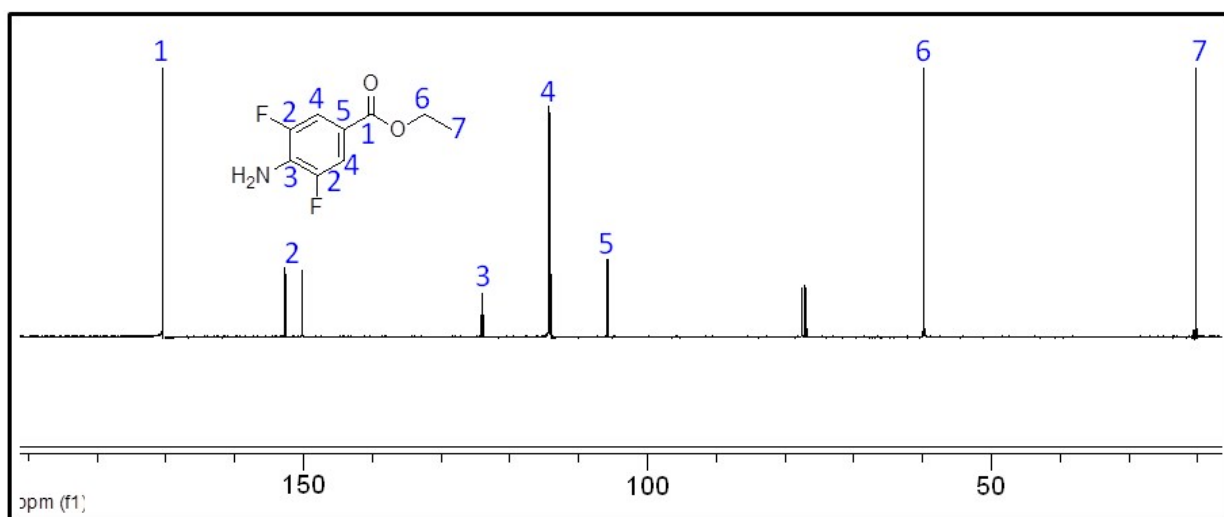


Figure S7. ^{13}C -NMR of ethyl 4-amino-3,5-difluorobenzoate (5)

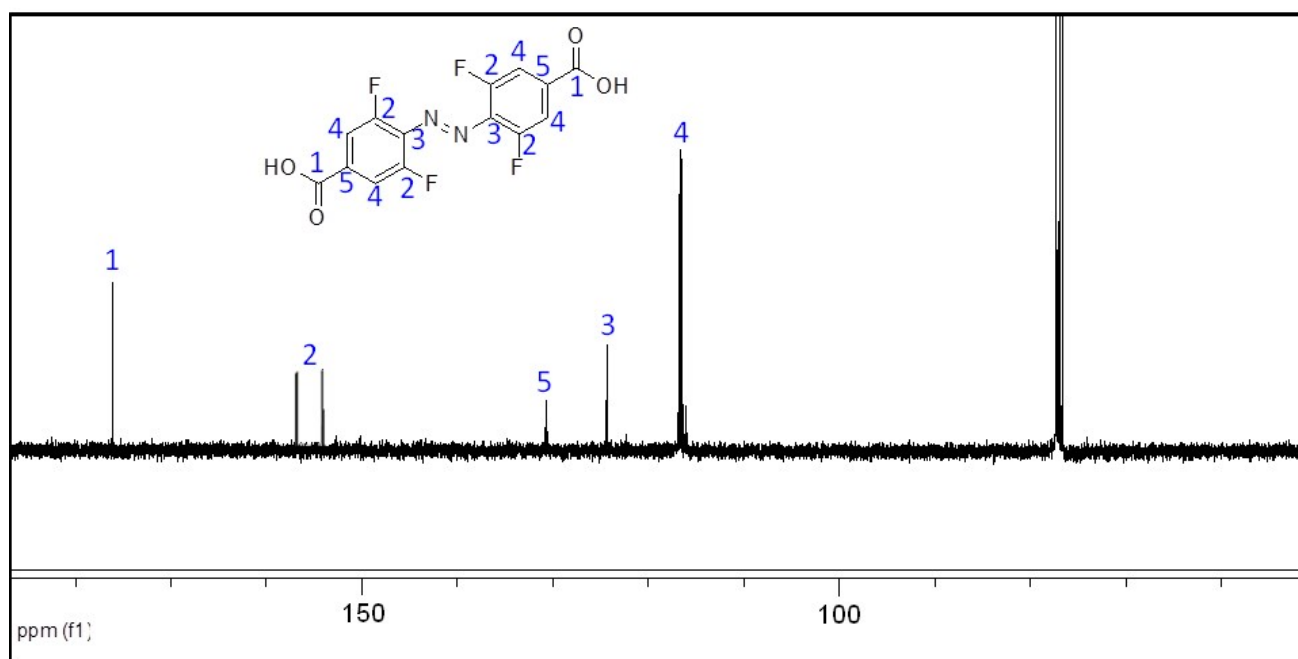


Figure S8. ^{13}C -NMR of 2,2',6,6'-tetrafluoro-4,4'-dicarboxyazobenzene (7)

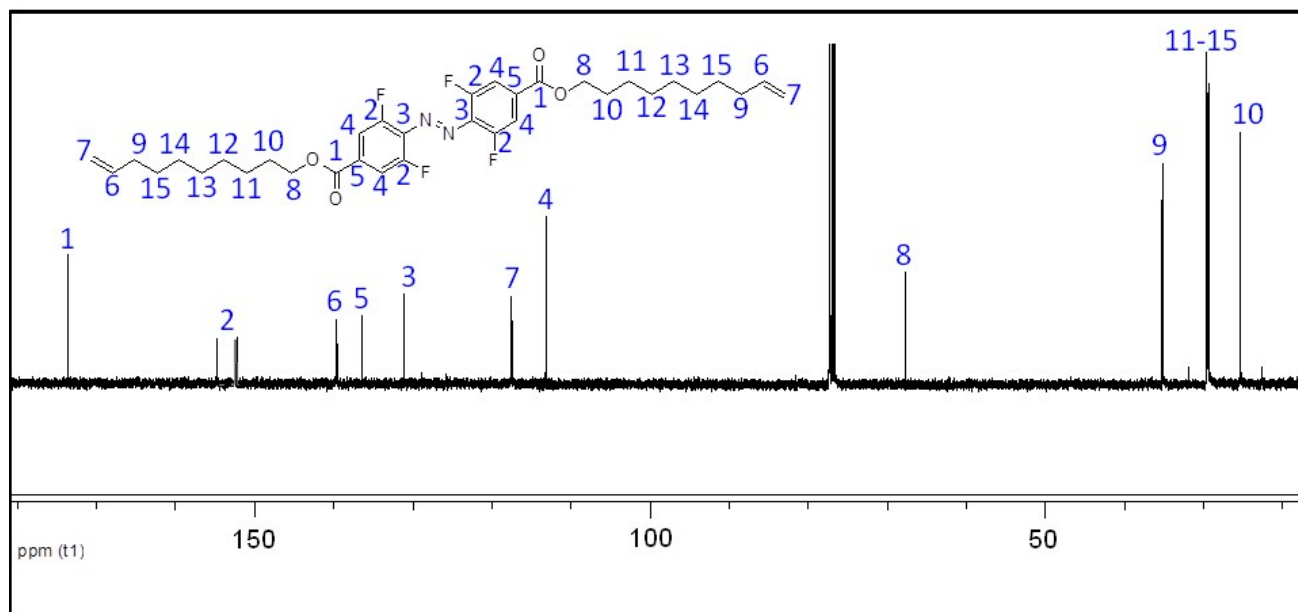


Figure S9. ^{13}C -NMR of the symmetric fluorinated azobenzene diene monomer (**2b**)

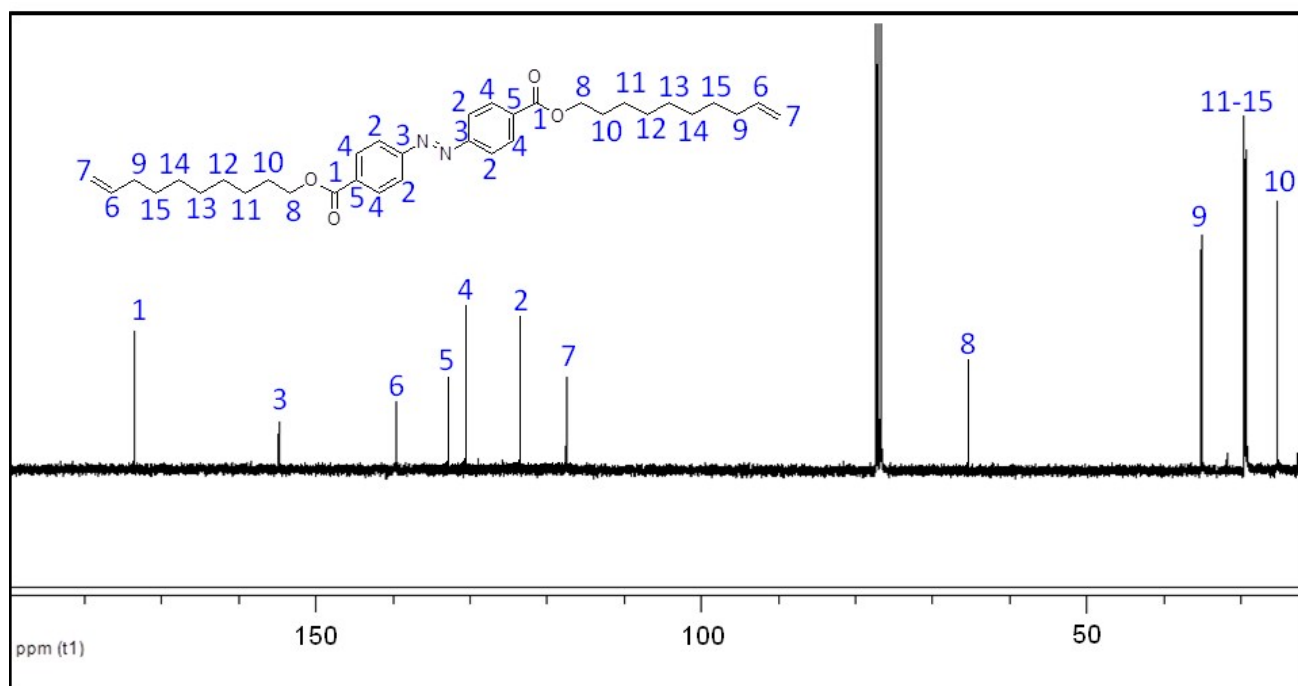


Figure S10. ^{13}C -NMR of the symmetric non-fluorinated azobenzene diene monomer (**2a**)

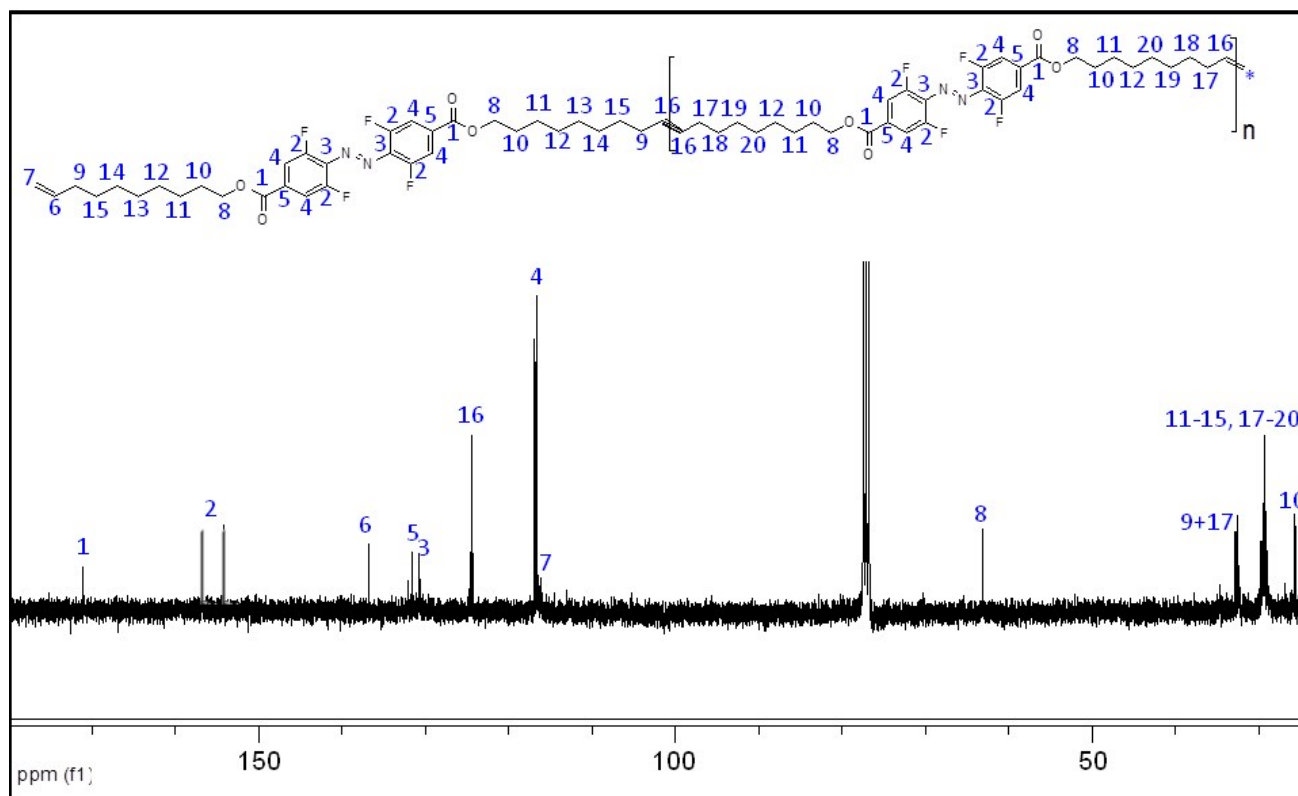


Figure S11. ^{13}C -NMR of the of the unsaturated azo-oligomer (**3b**)

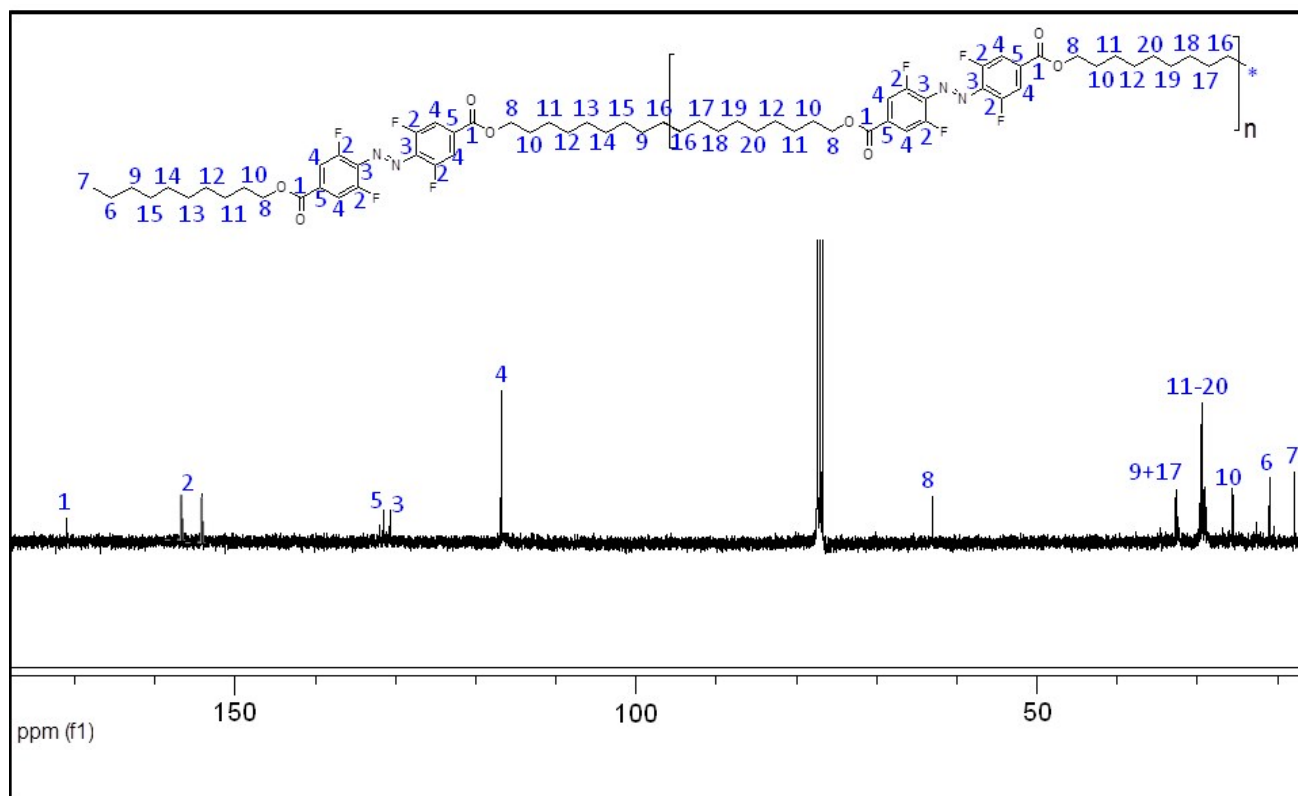


Figure S12. ^{13}C -NMR of the of the saturated azo-oligomer (**4b**)

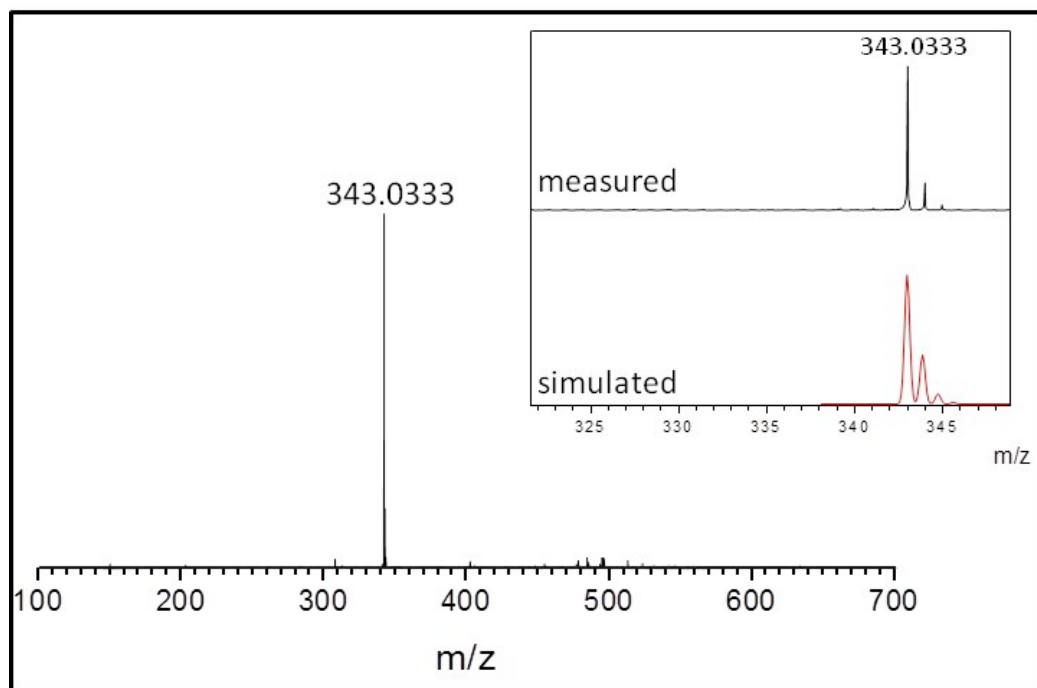


Figure S13. HRMS (ESI) of the 2,2',6,6'-tetrafluoro-4,4'-dicarboxyazobenzene (**7**)

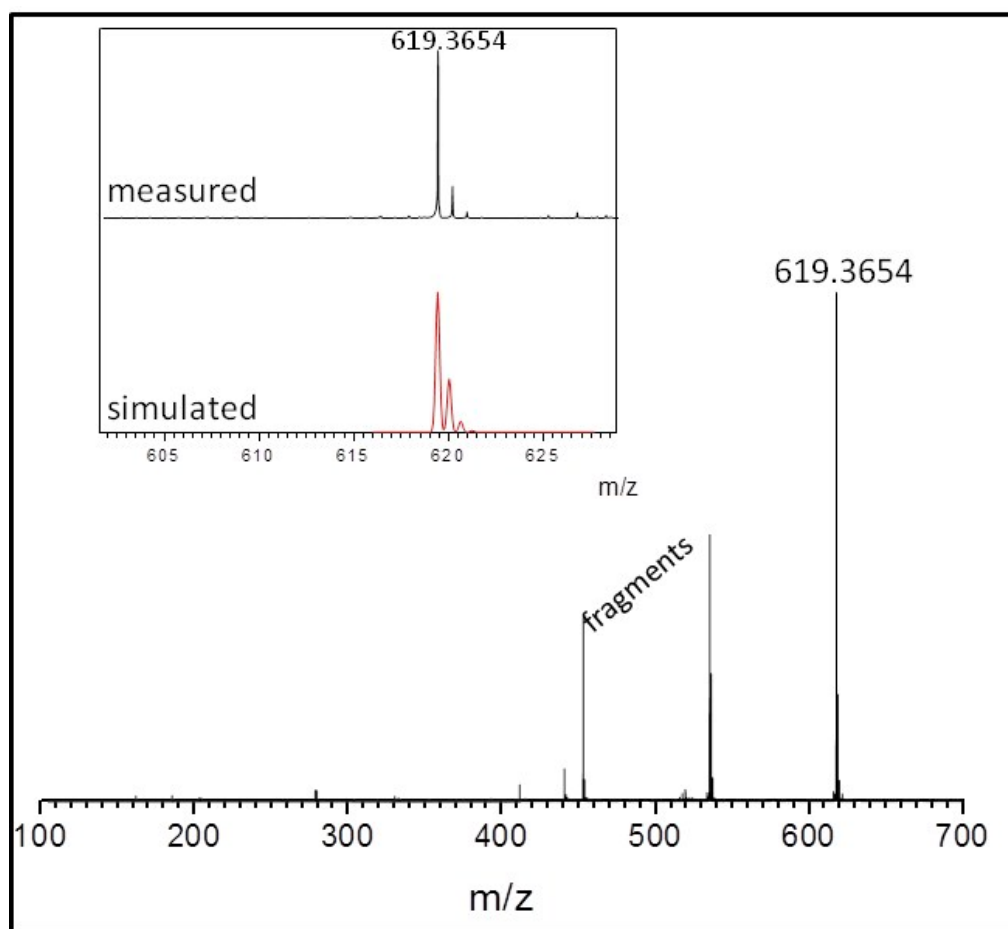


Figure S14. HRMS (ESI) of the fluorinated azo-monomer (**2b**)

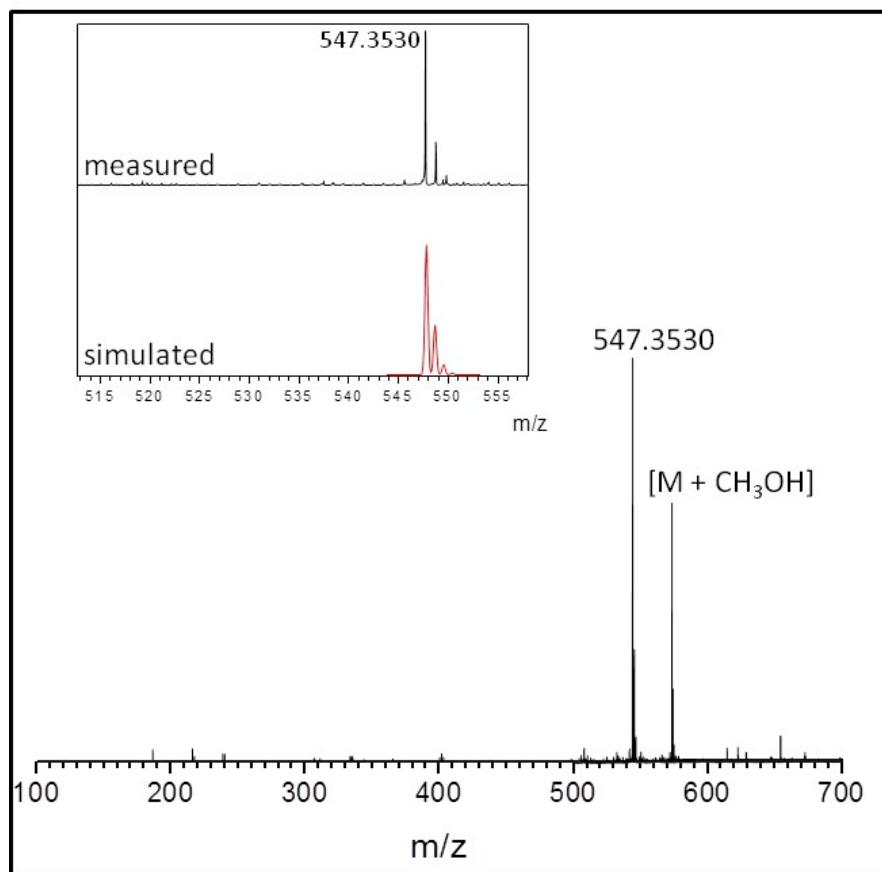


Figure S15. HRMS (ESI) of the non-fluorinated azo-monomer (**2a**)

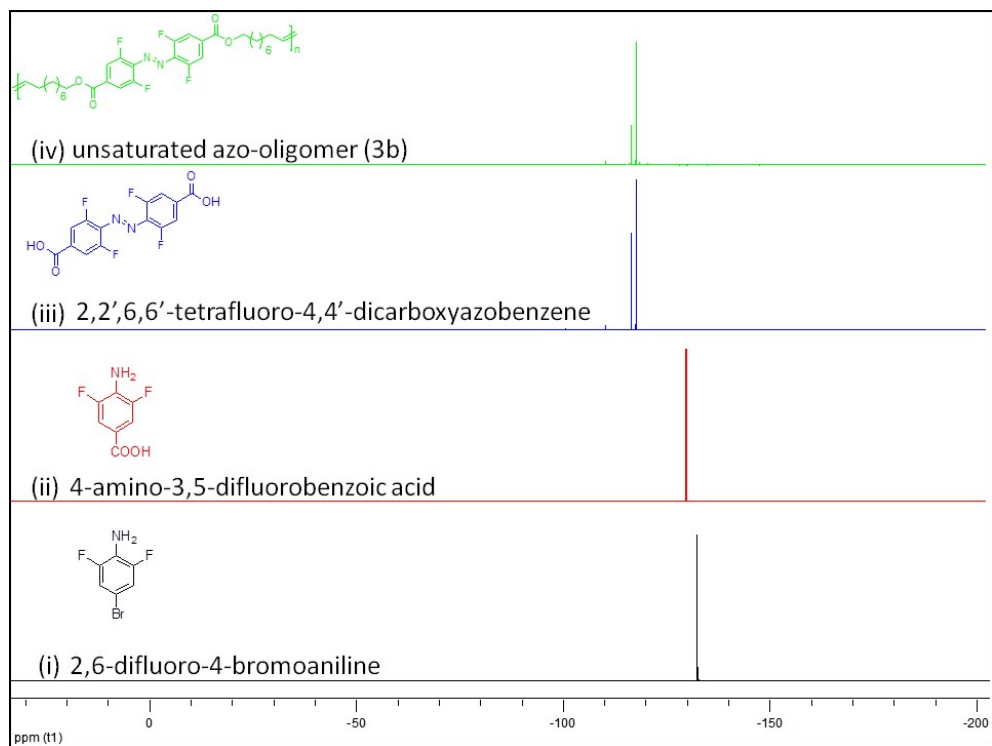


Figure S16. ^{19}F -NMR spectra of the fluorinated compounds.

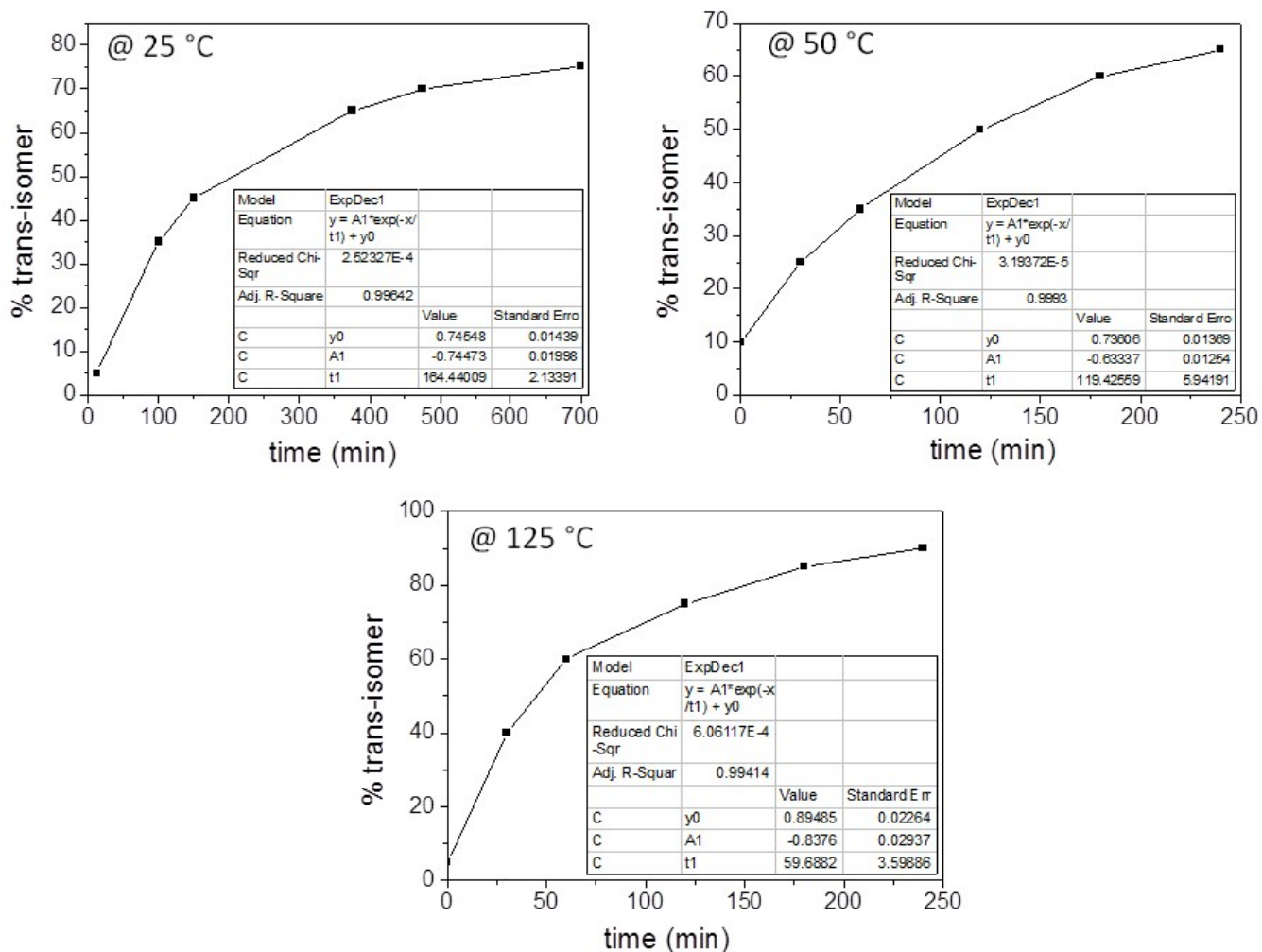


Figure S17. Estimated thermal *cis* to *trans* isomerisation kinetic studies of the fluorinated azobenzene monomer in DMSO. Plots of % *trans*-isomer (as determined by UV-VIS absorbance spectroscopy) versus time (min) at different temperatures.

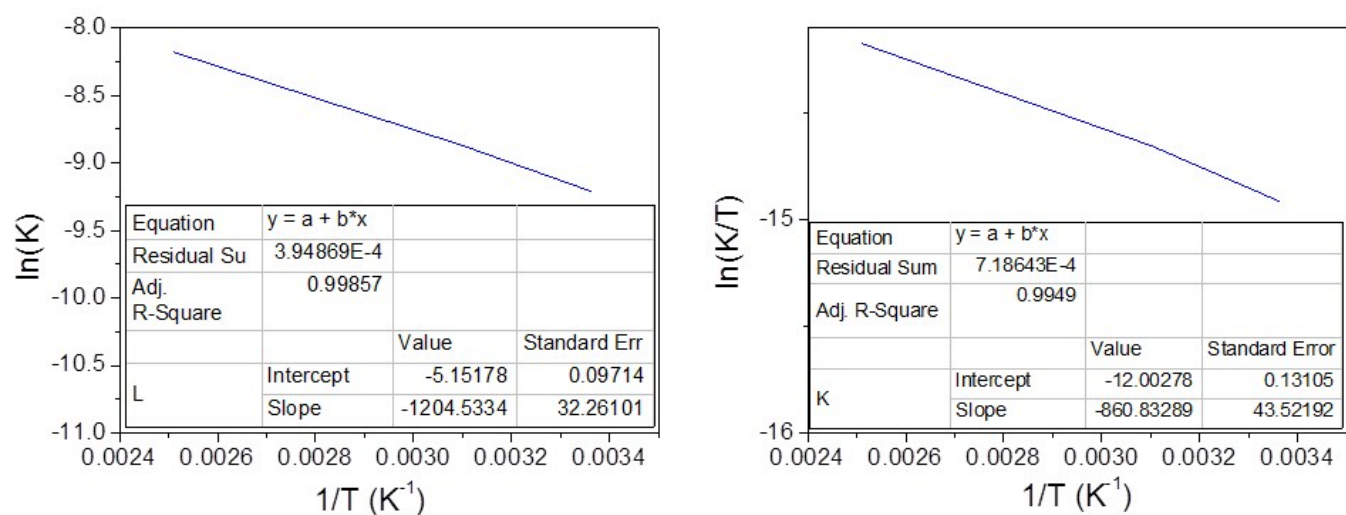


Figure S18. Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters at 298 K as calculated using the Arrhenius and Eyring equations.

T (K)	K (s^{-1})	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol)	$\Delta G^\ddagger$ (kJ/mol)
298	1.02×10^{-4}	72	-297	96
323	1.40×10^{-4}			103
398	2.79×10^{-4}			190