

*Supplementary Materials:*

# Stimuli responsive materials supported by orthogonal hydrogen and halogen bonding or I···alkene interaction

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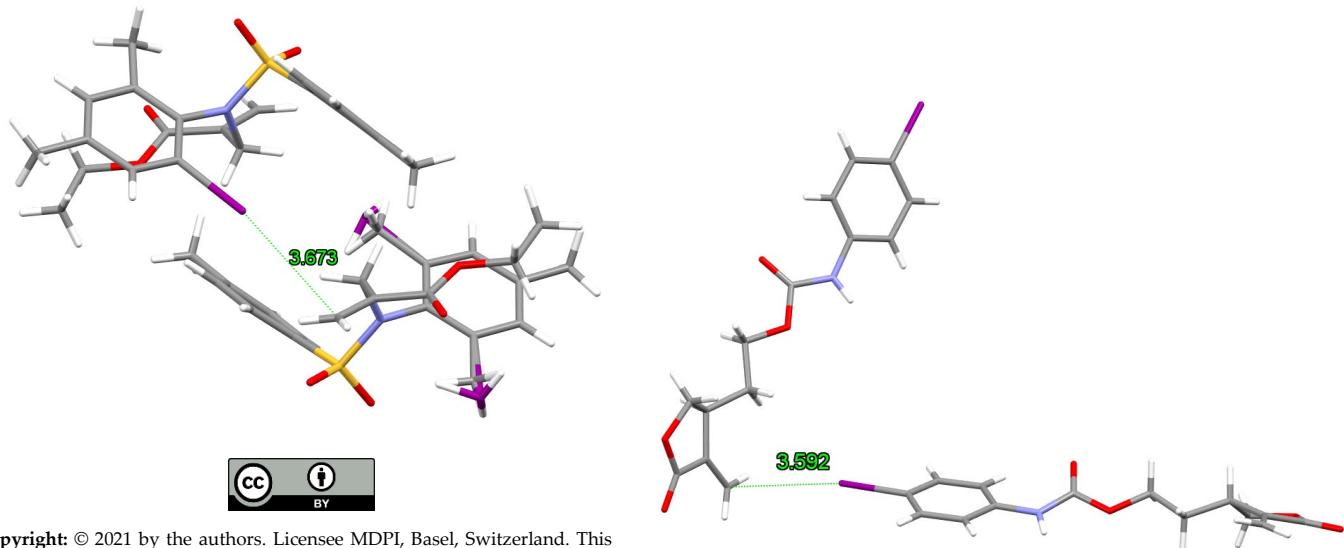
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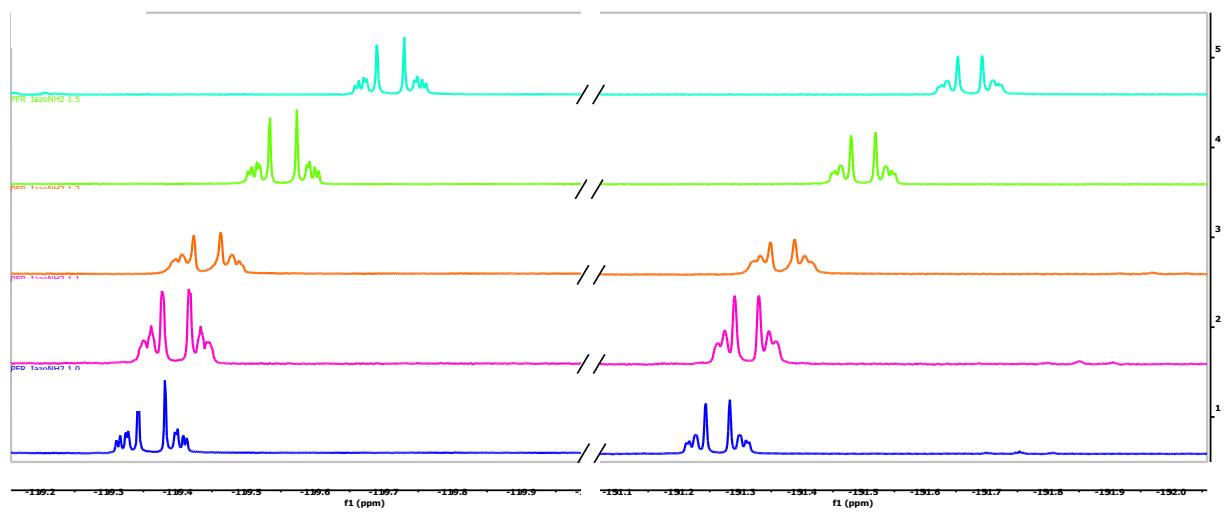
**X ray structures of compounds showing the I···CH<sub>2</sub>=C halogen bonds found in the Cambridge Structural Data base**



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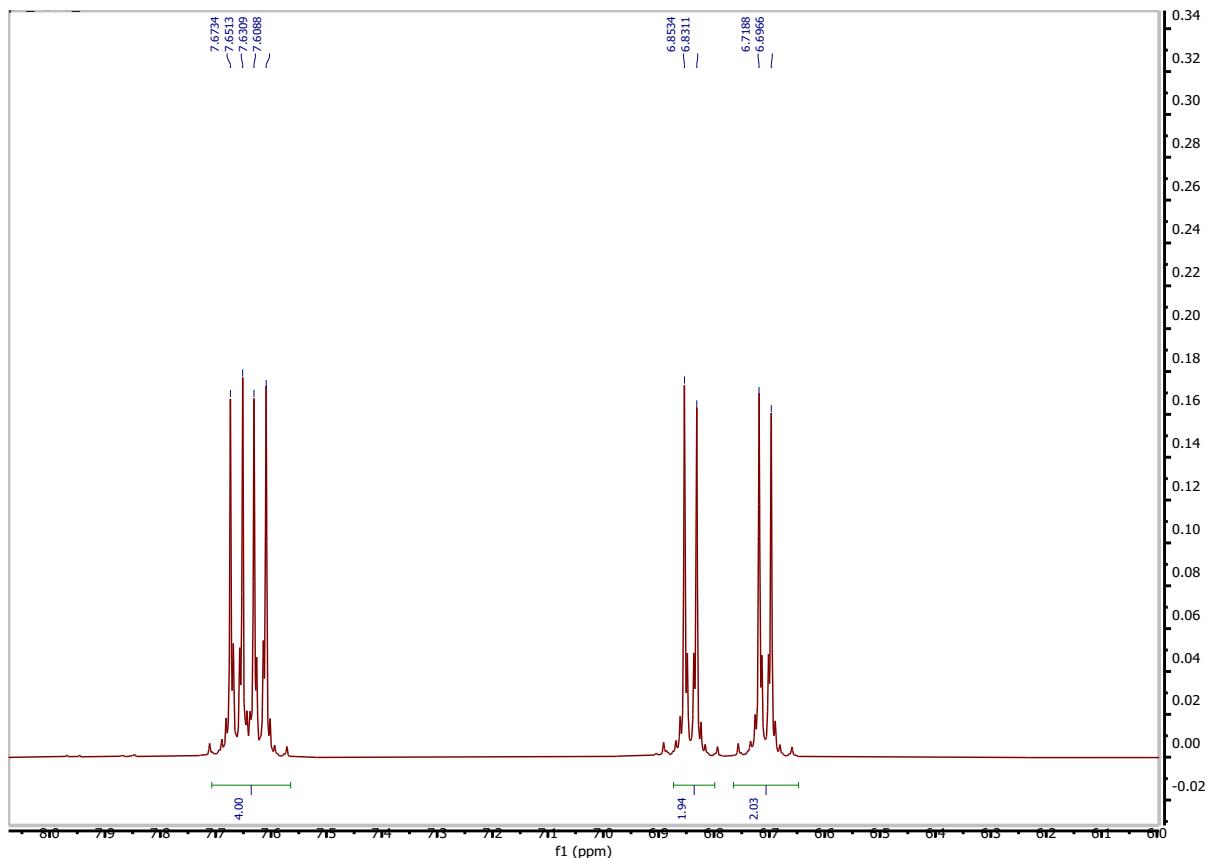
**Figure S1.** X ray structures of HOQKAC (A), HOTZOH (B), PEQVOZ (C) and USAJIK (D) showing the I···CH<sub>2</sub>=C halogen bonds found in the Cambridge Structural Data base (CSD version 5.42 updates, Sep 2021). Colors are as follows: grey, C; blue, N; red, oxygen; white, H; orange, S; purple, I.

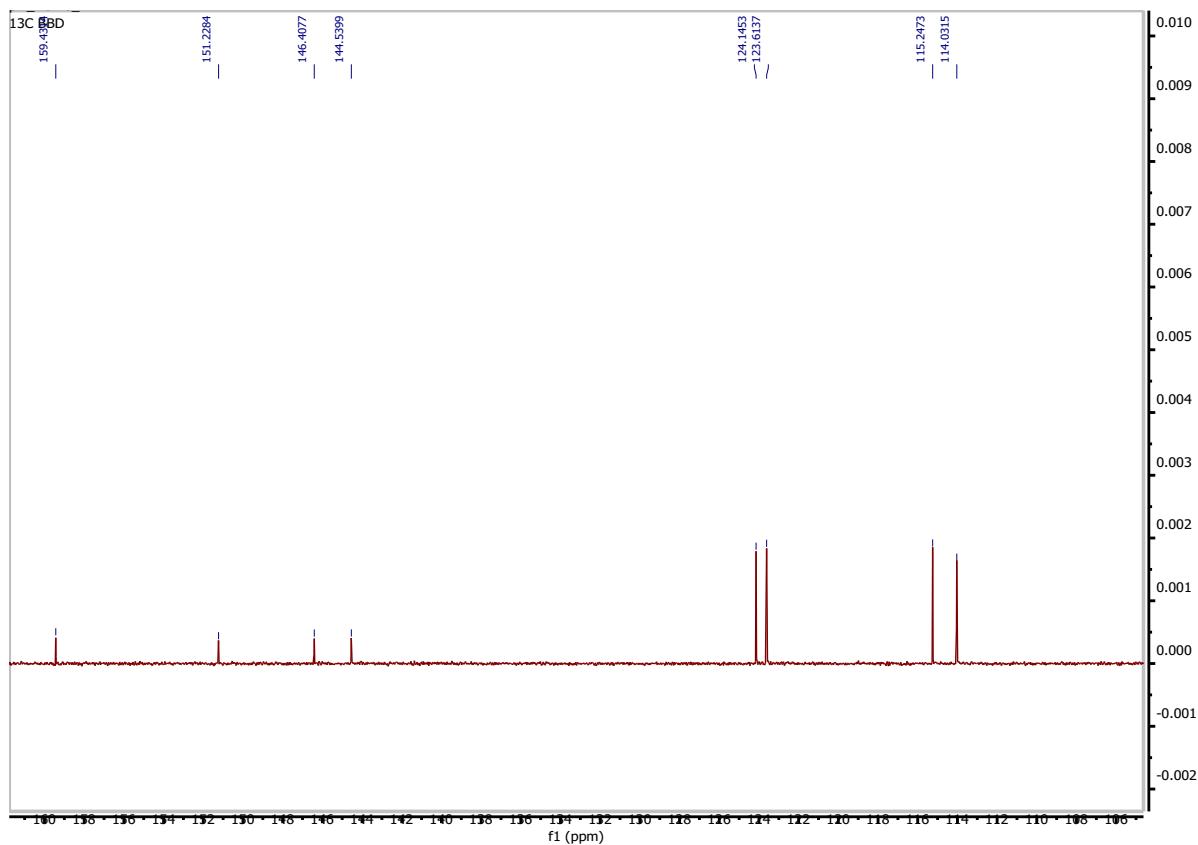
**Stack plot of <sup>19</sup>F NMR spectra at different molar ratios of I-azo-NH<sub>2</sub>/TBACl**



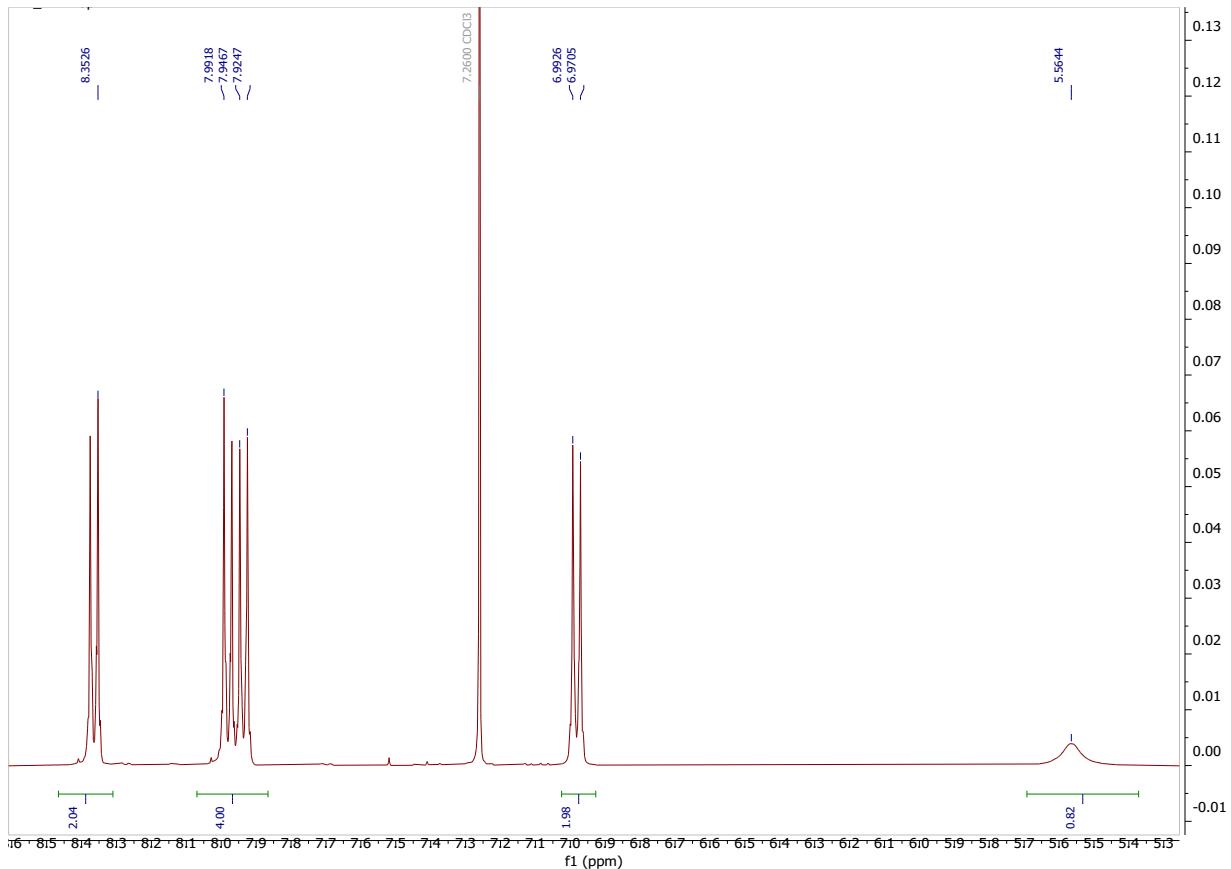
**Figure S2.** Stack plot of  $^{19}\text{F}$ -NMR spectra of I-azo-NH<sub>2</sub> (CDCl<sub>3</sub>), at different molar ratios of I-azo-NH<sub>2</sub>/TBACl. Molar ratios: a) 1:0; b) 1:1; c) 1:2; d) 1:5; e) 1:10.

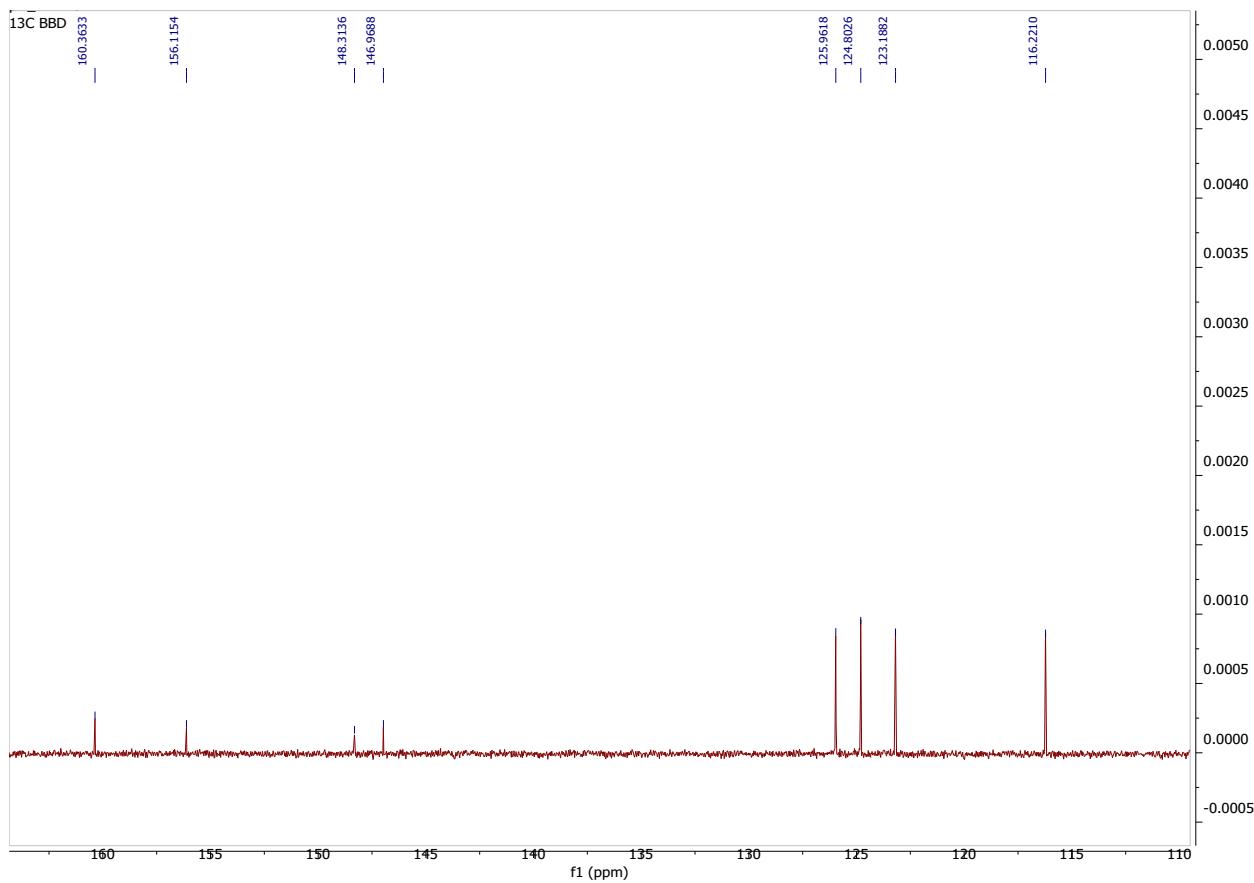
#### $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ -NMR spectra for all compounds



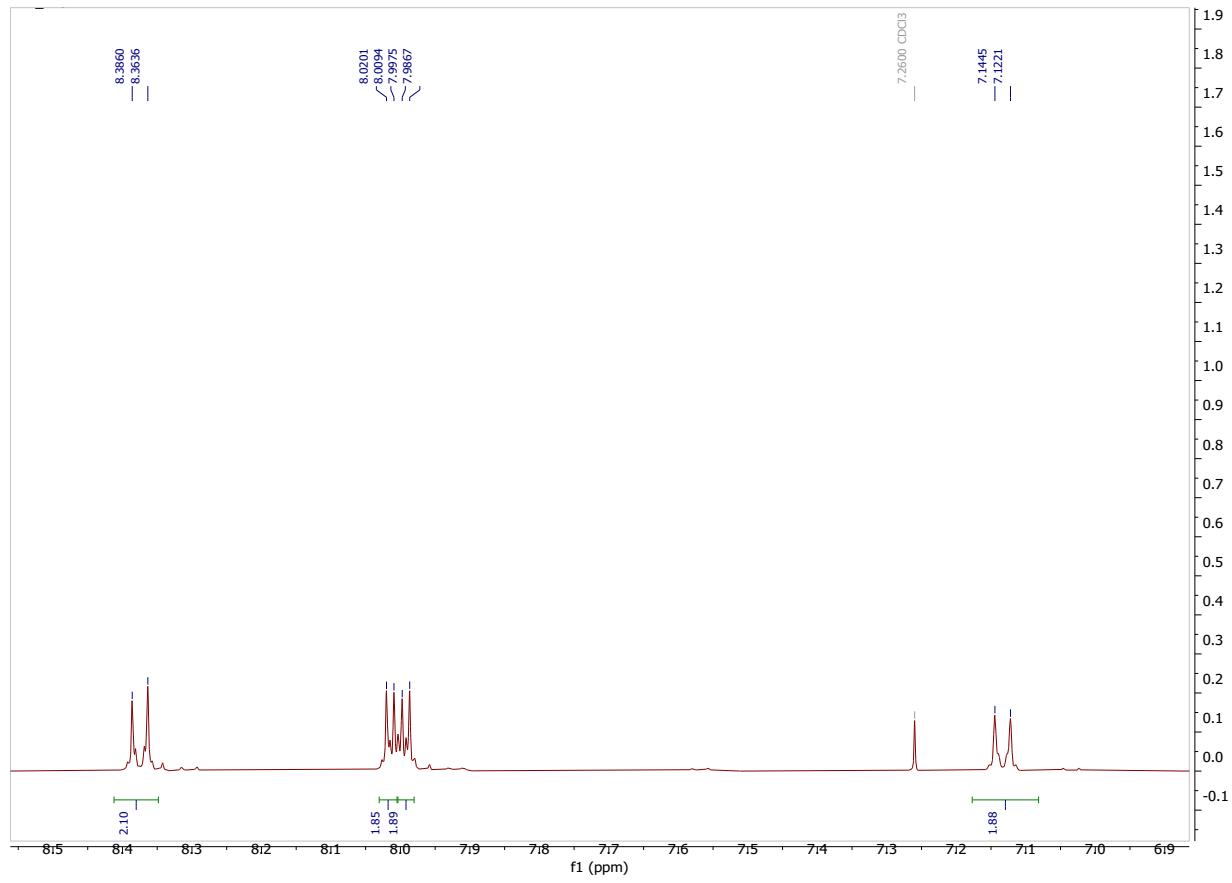


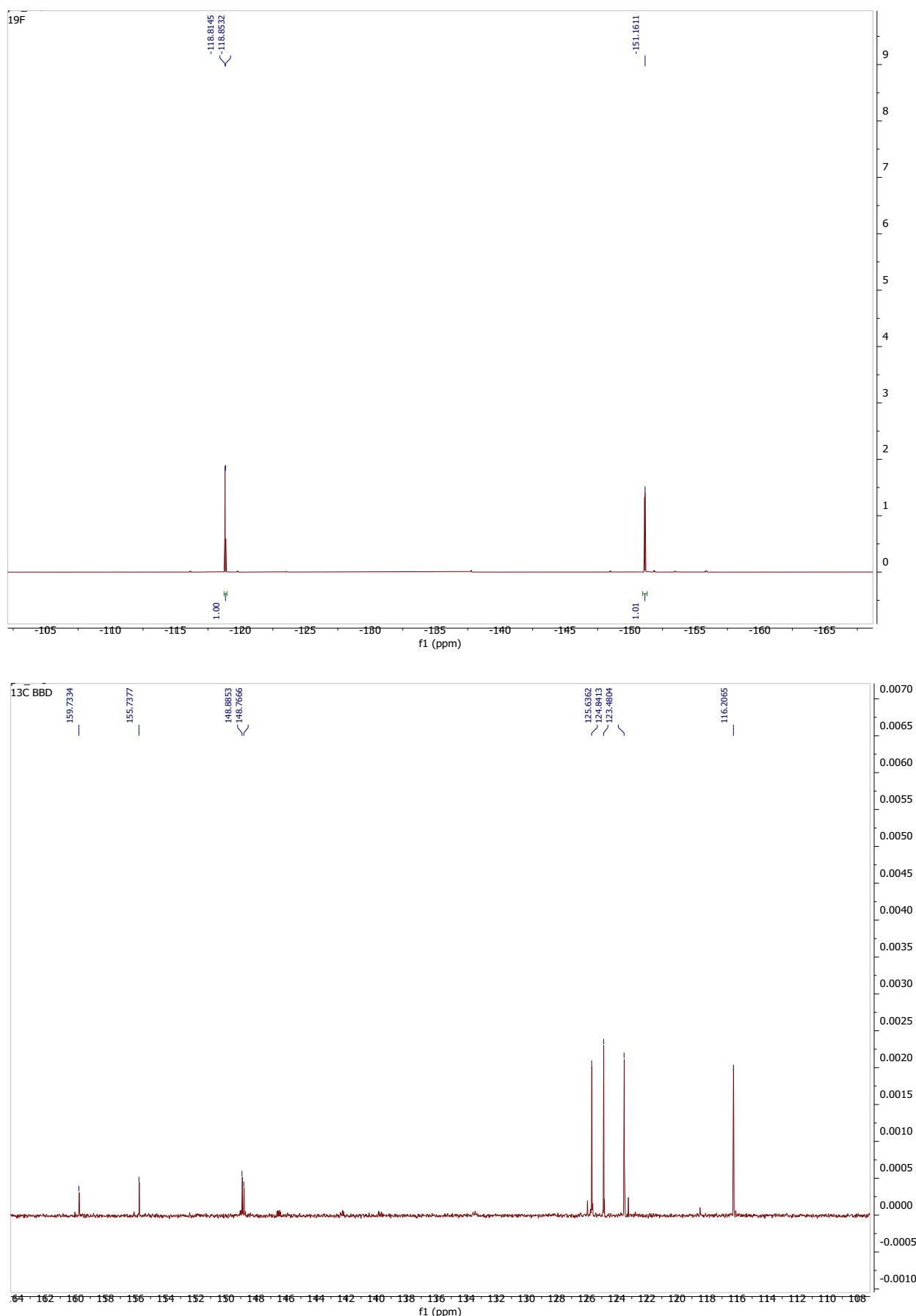
**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra for compound OH-azo-NH<sub>2</sub> (CD<sub>3</sub>OD).



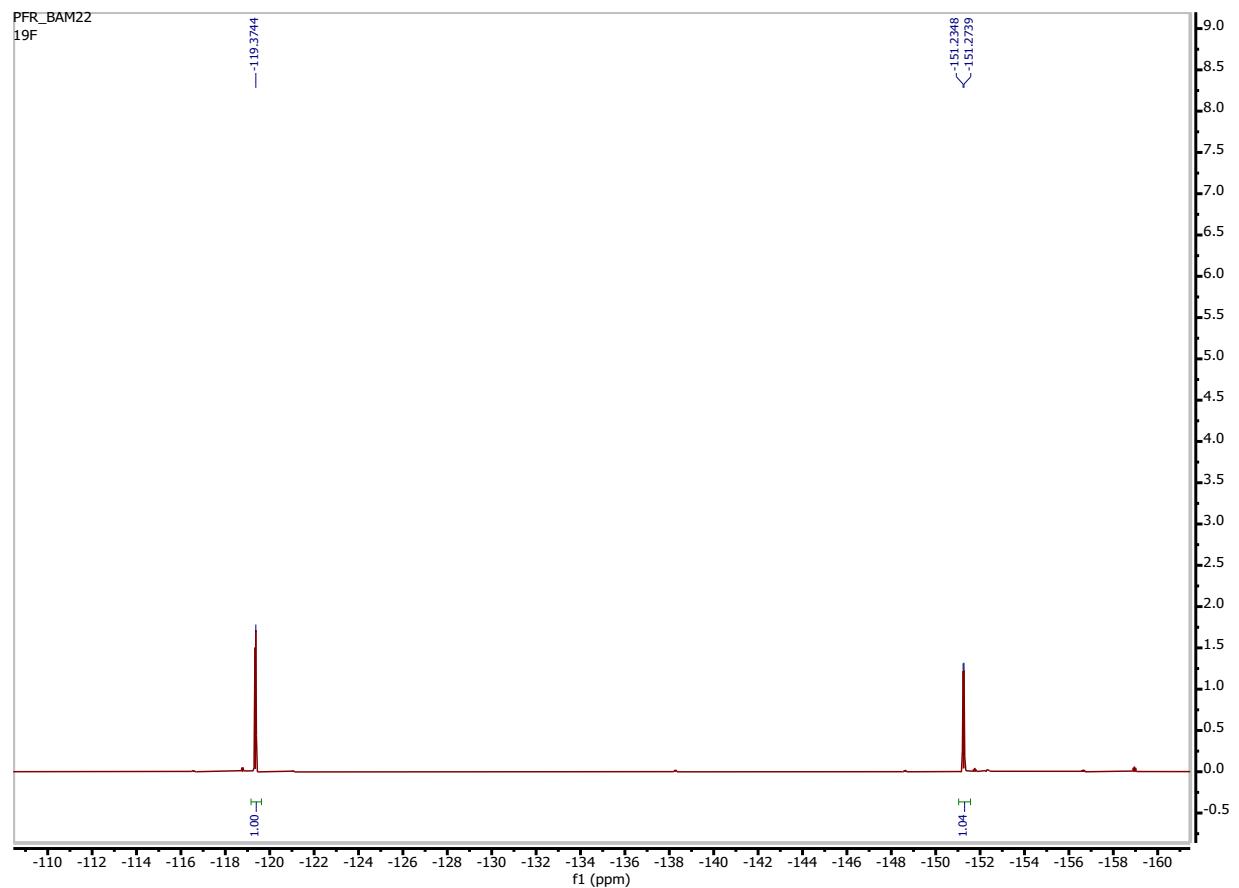
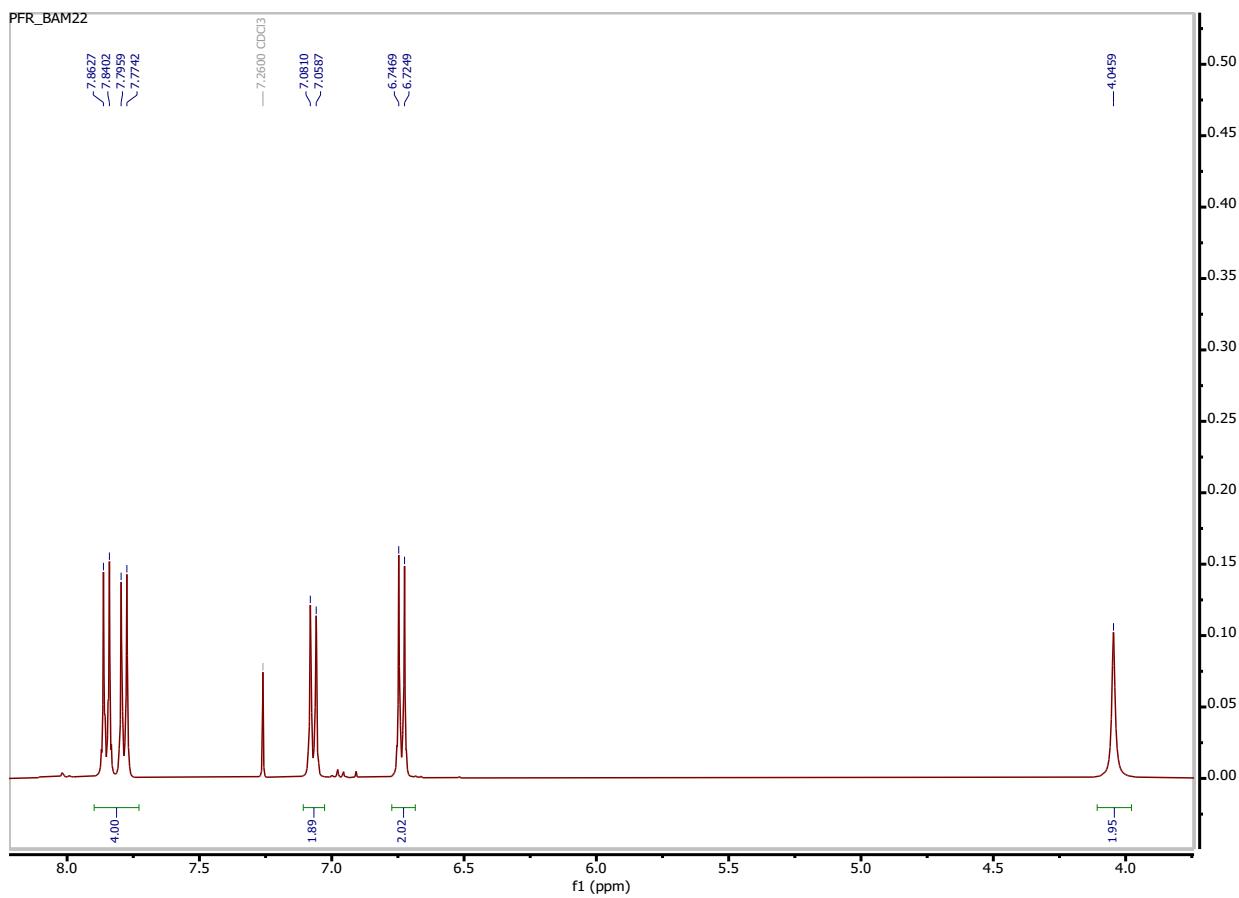


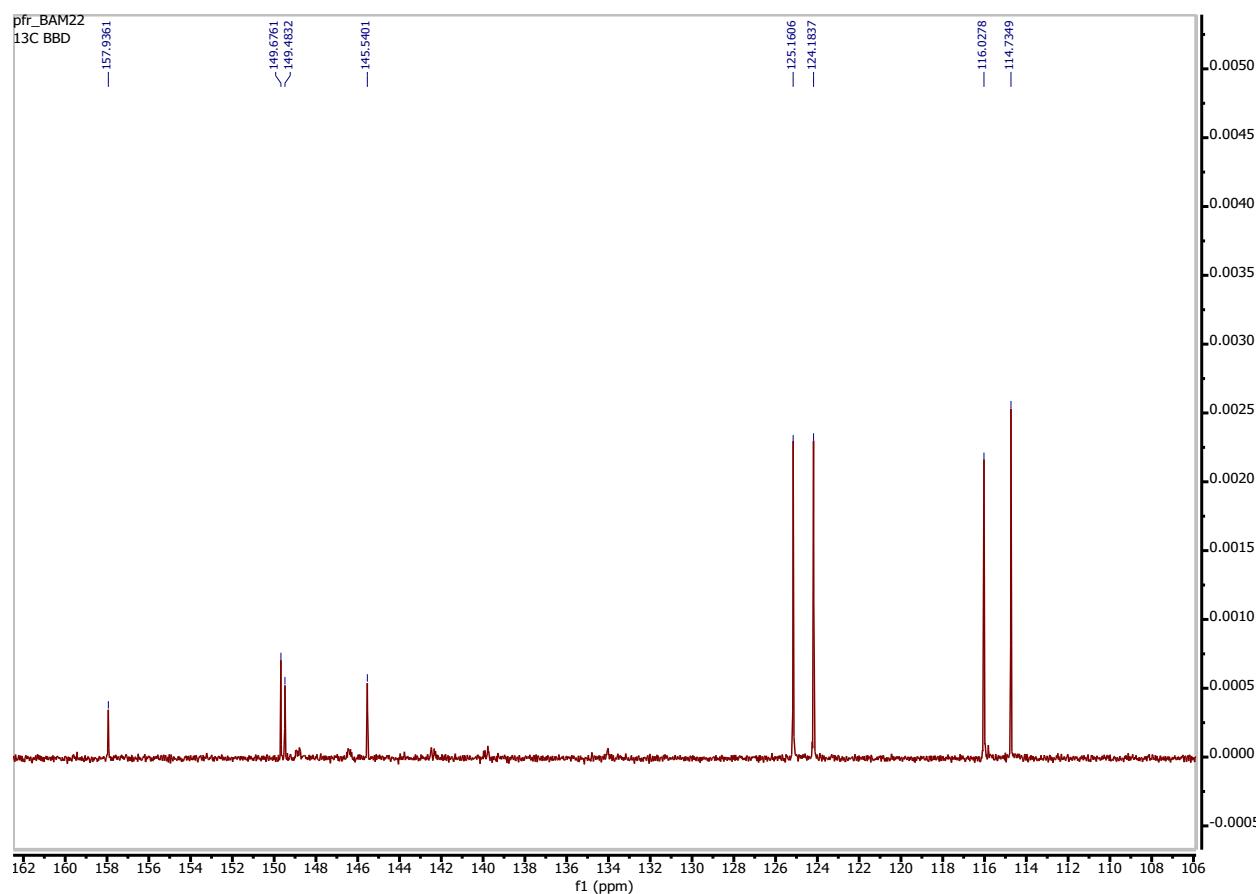
**Figure S4.**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra for compound OH-azo-NO<sub>2</sub> ( $\text{CDCl}_3$ ).



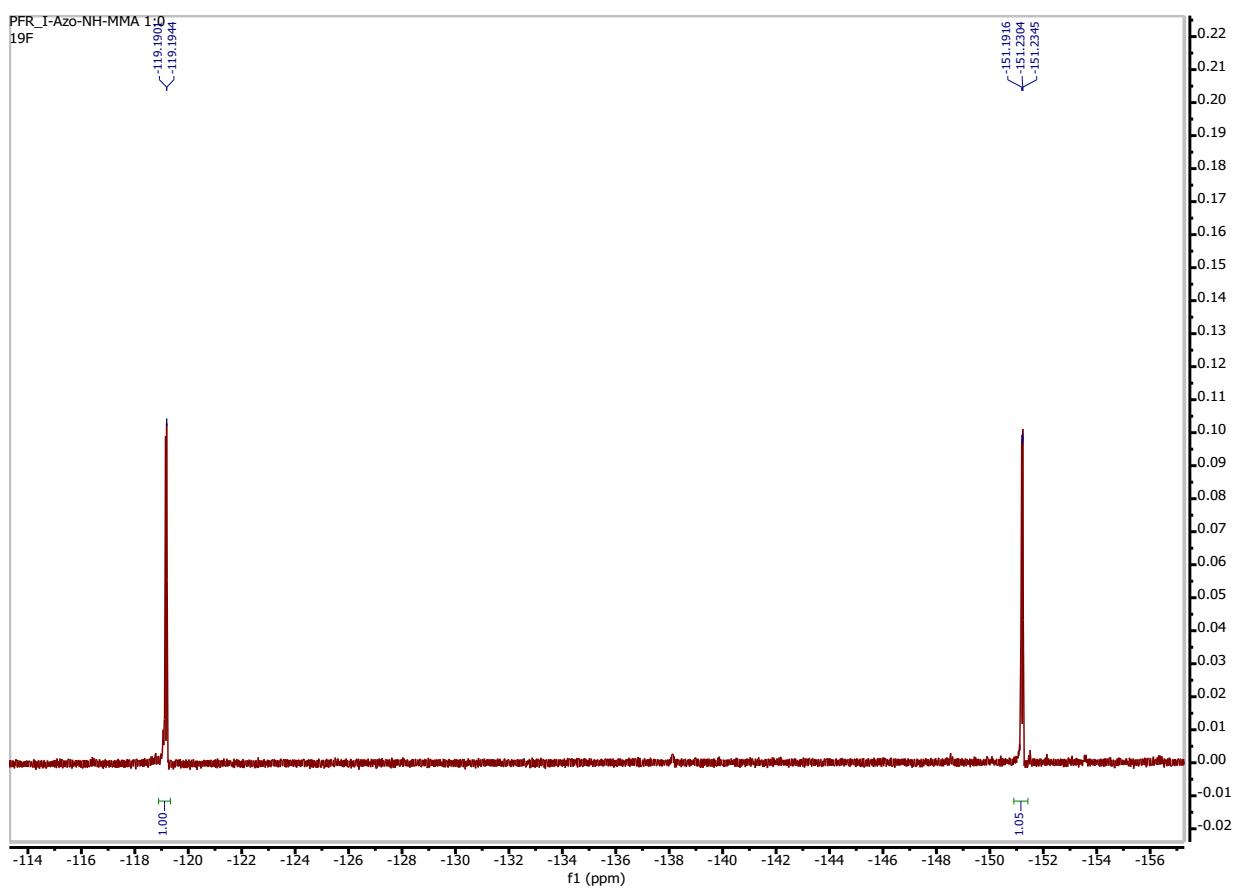
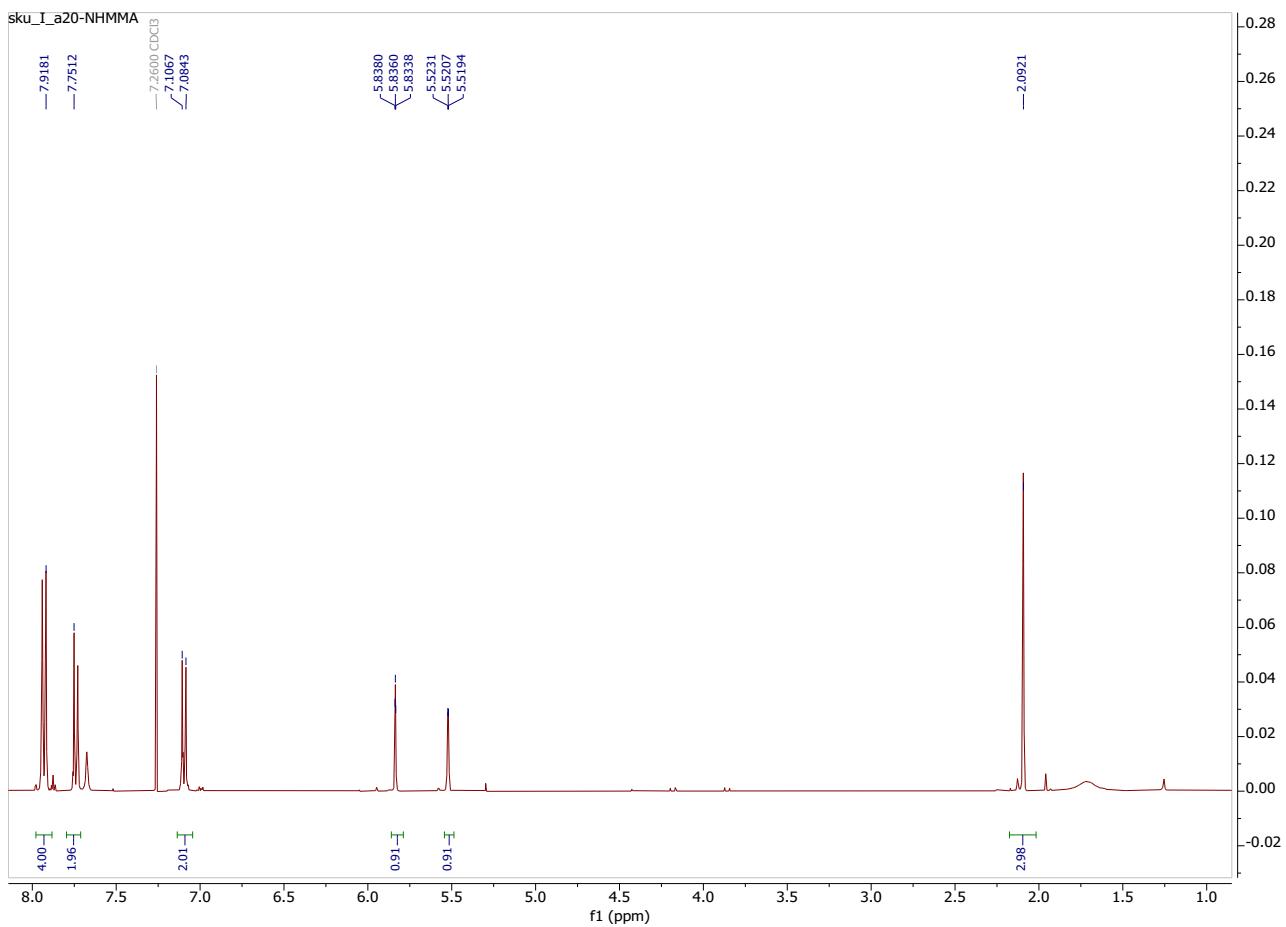


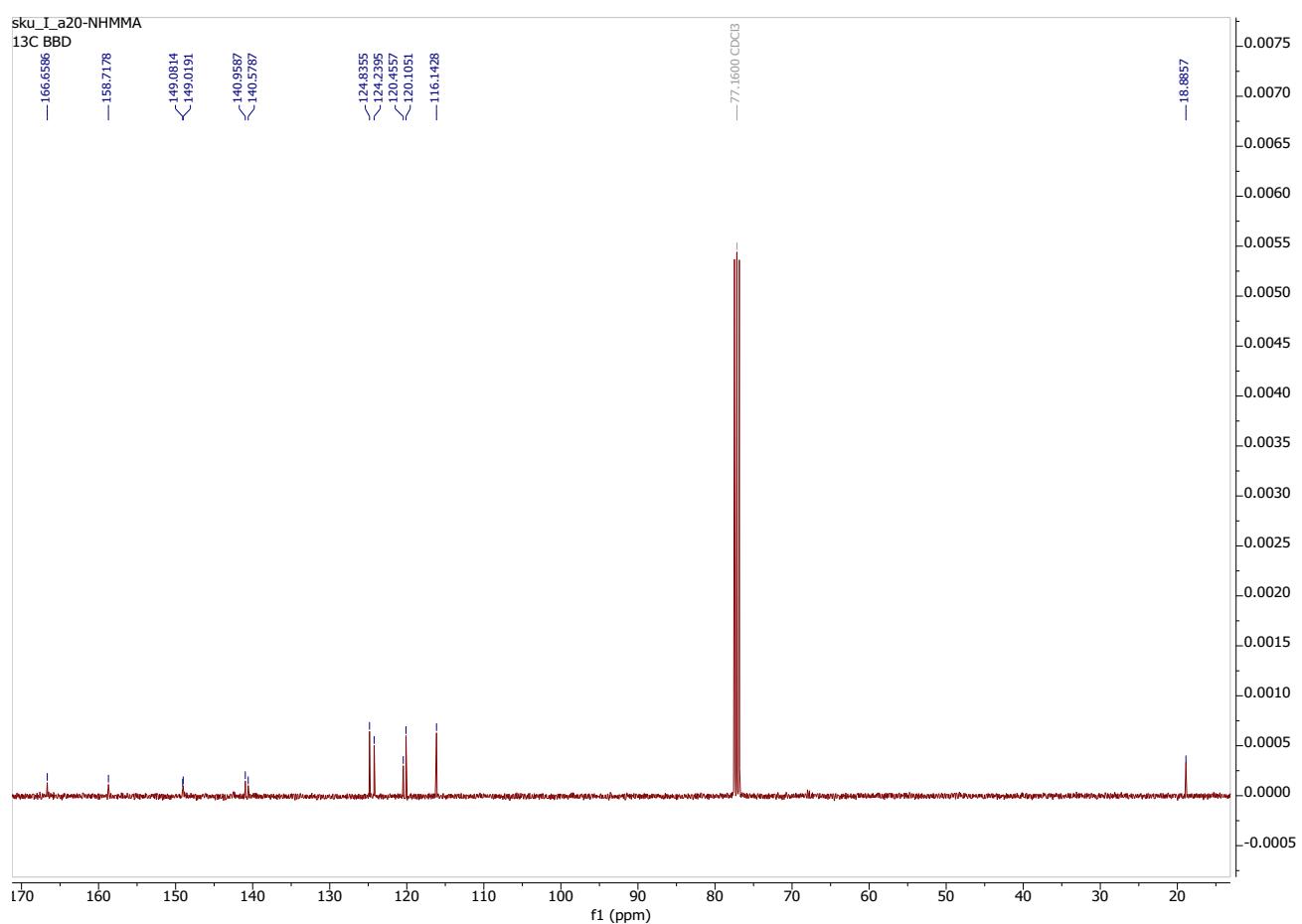
**Figure S5.** <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C-NMR spectra for compound I-azo-NO<sub>2</sub> (CDCl<sub>3</sub>).





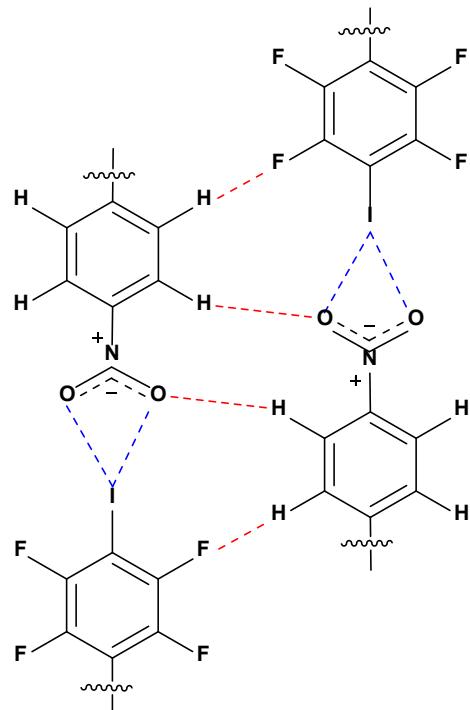
**Figure S6.** <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C-NMR spectra for compound I-azo-NH<sub>2</sub> (CDCl<sub>3</sub>).





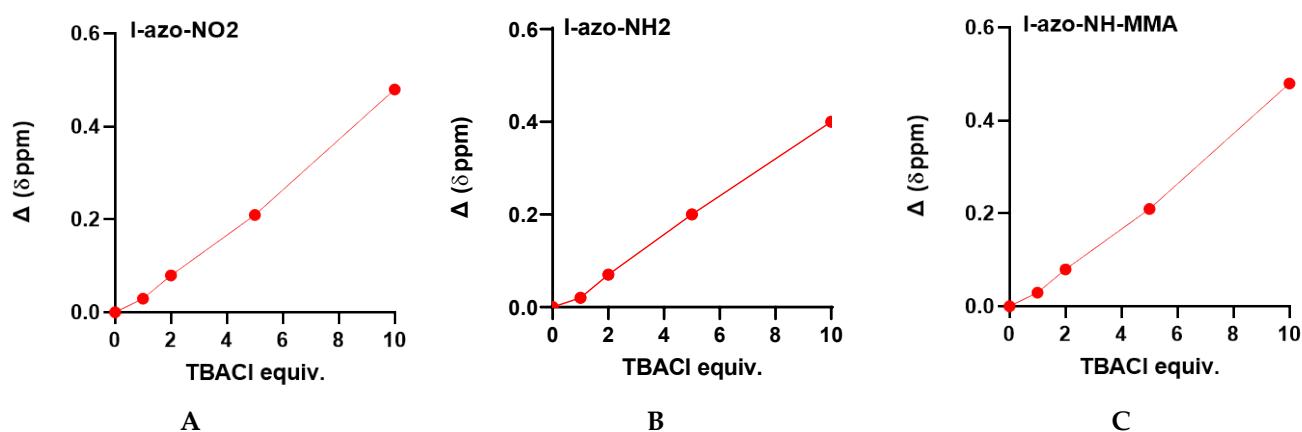
**Figure S7.**  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$ -NMR spectra for compound I-azo-NH-MMA ( $\text{CDCl}_3$ ).

Scheme representing the self-complementary Ar-I $\cdots$ O<sub>2</sub>N–Ar synthon



**Scheme 1.** Self-complementary Ar-I $\cdots$ O<sub>2</sub>N–Ar synthon. Halogen and hydrogen bonds are represented in blue and red dashed lines, respectively.

#### NMR titration of azo dyes with tetrabutylammonium chloride



**Figure S8.** <sup>19</sup>F-NMR titration curves of I-azo-NO<sub>2</sub> (A), I-azo-NH<sub>2</sub> (B) and I-azo-NH-MMA (C) with tetrabutylammonium chloride. Molar ratios (azo dyes/TBACl): 1:0; 1:1; 1:2; 1:5; 1:10.