

Supplementary Information

**Tailoring the charge transport characteristics in ordered small-molecule organic semiconductors by side-chain engineering and fluorine substitution**

Ilya E. Kuznetsov <sup>a</sup>, Denis V. Anokhin <sup>a,b,c</sup>, Alexey A. Piryazev <sup>a,b,c</sup>, Maxim E. Sideltsev <sup>a</sup>, Azaliia F. Akhkiamova <sup>a,b</sup>, Artyom V. Novikov <sup>d</sup>, Vladimir G. Kurbatov <sup>a,e</sup>, Dimitri A. Ivanov <sup>a,b,c,f</sup> and Alexander V. Akkuratov <sup>\*a</sup>

<sup>a</sup> Institute for Problems of Chemical Physics of the Russian Academy of Sciences (IPCP RAS), Academician Semenov avenue 1, Chernogolovka, Moscow 142432, Russian Federation.

<sup>b</sup> Sirius University of Science and Technology, 1 Olympic Ave, 354340, Sochi, Russian Federation.

<sup>c</sup> Moscow State University, Moscow, Russia, 119991, Moscow, GSP-1, 1 Leninskiye Gory.

<sup>d</sup> Skolkovo Institute of Science and Technology, Bolshoi blvd., 30, b. 1, Moscow, 121205, Russian Federation.

<sup>e</sup> Yaroslavl State Technical University, Moscow avenue 88, Yaroslavl, 150023, Russian Federation.

<sup>f</sup> Institut de Sciences des Matériaux de Mulhouse (CNRS UMR 7361), Université de Haute Alsace, France.

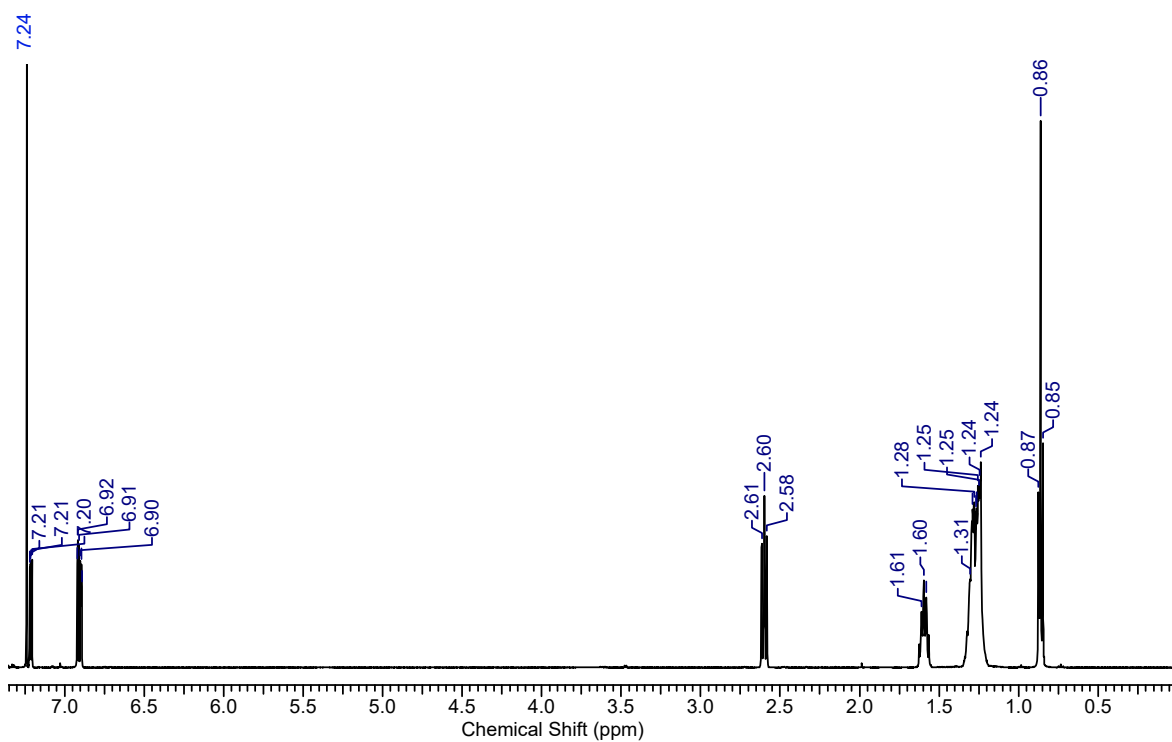


Figure S1. <sup>1</sup>H NMR spectrum of compound **1a**

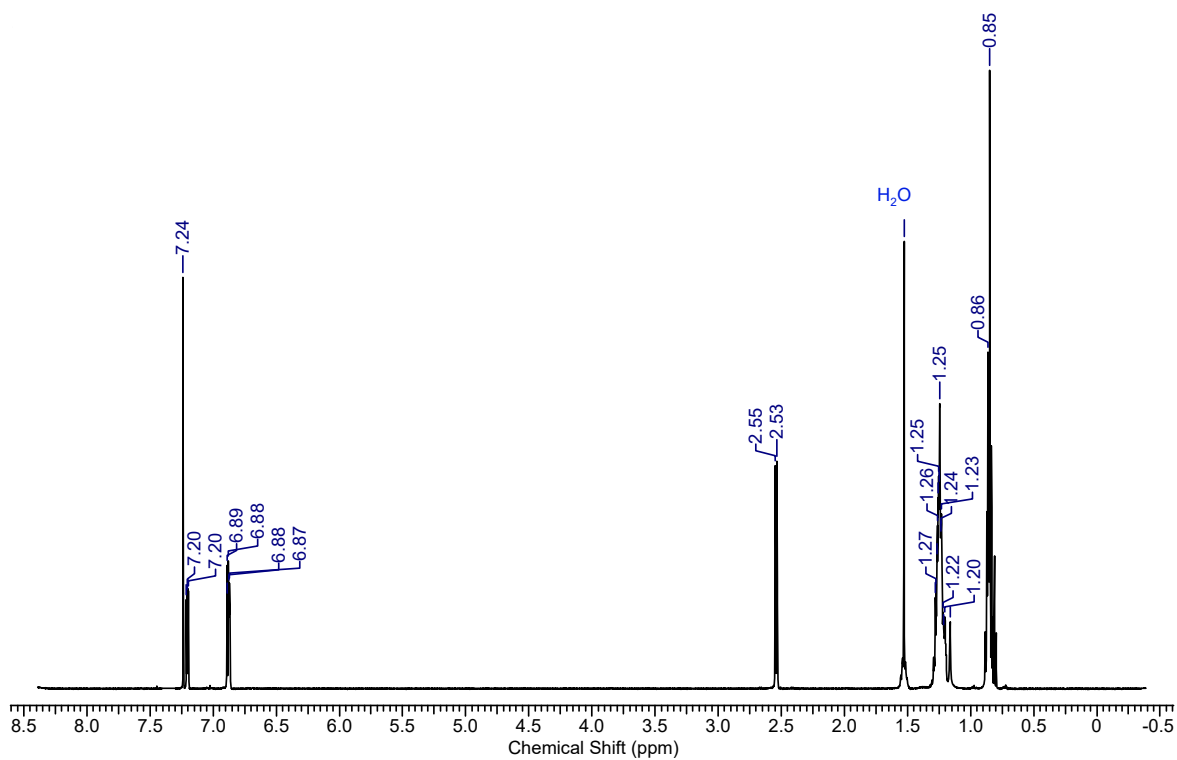


Figure S2. <sup>1</sup>H NMR spectrum of compound **1b**

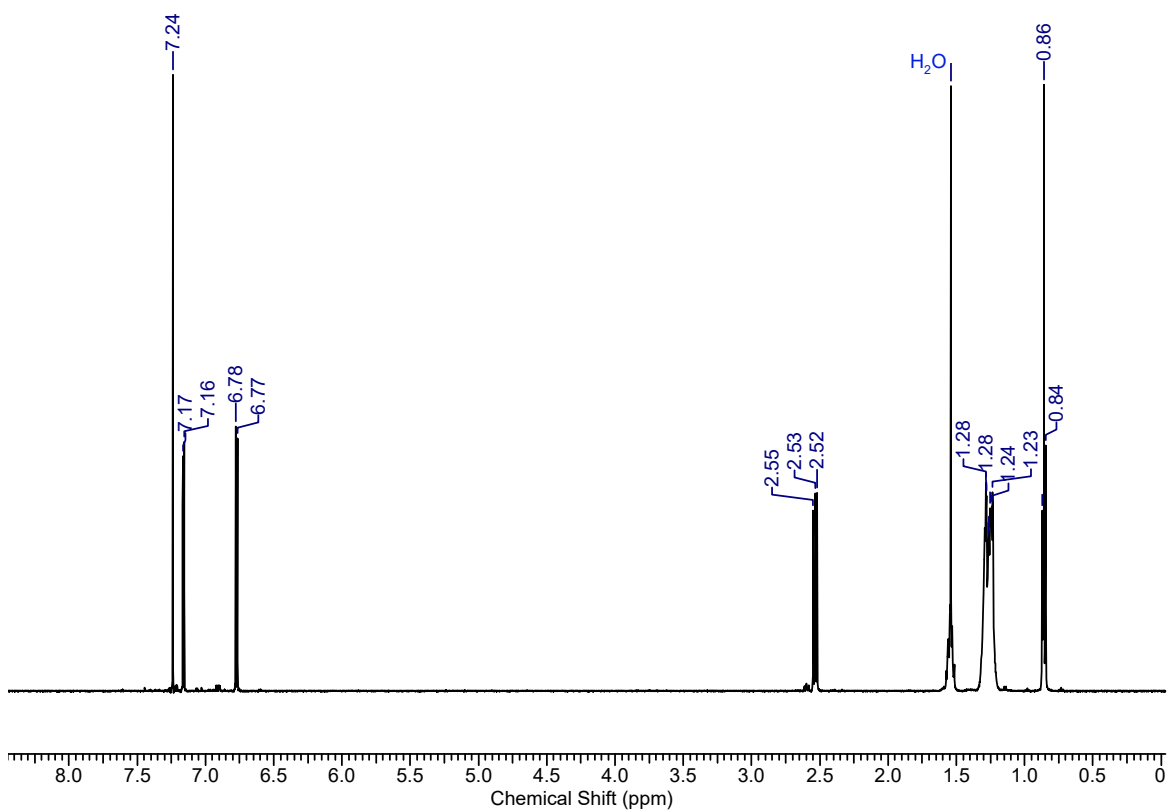


Figure S3. <sup>1</sup>H NMR spectrum of compound **2a**

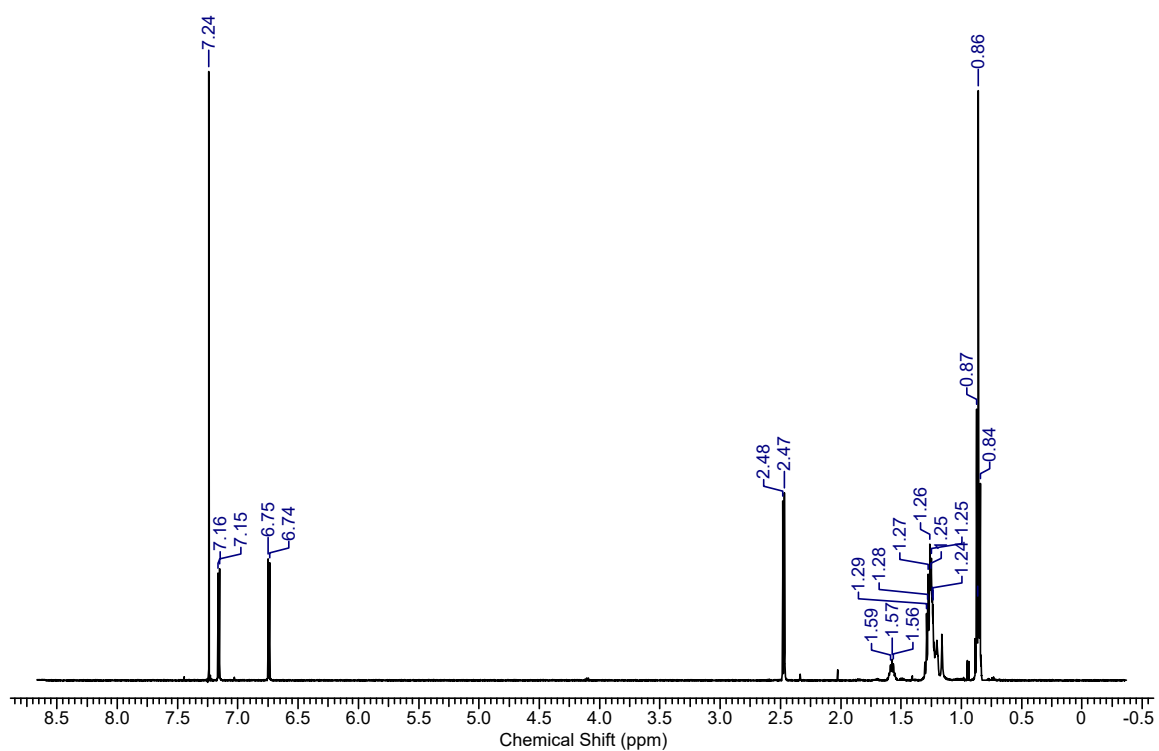


Figure S4. <sup>1</sup>H NMR spectrum of compound **2b**

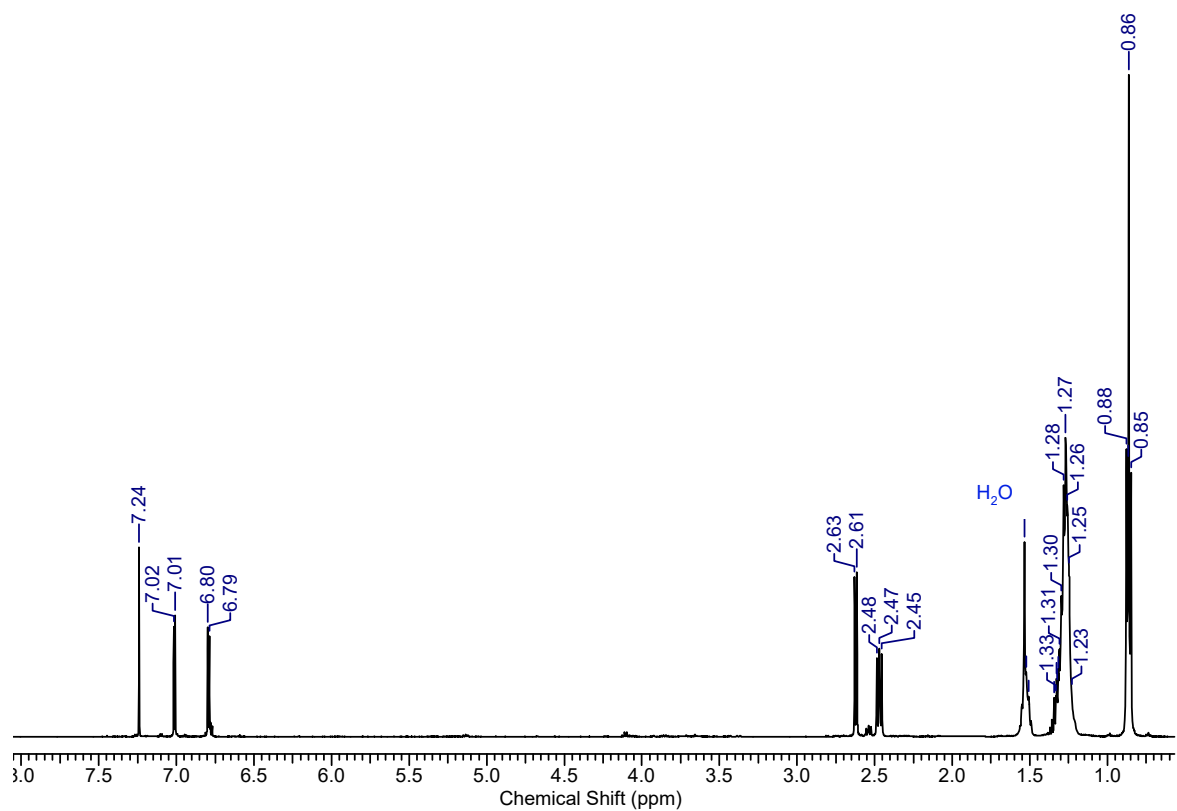


Figure S5. <sup>1</sup>H NMR spectrum of compound **3a**

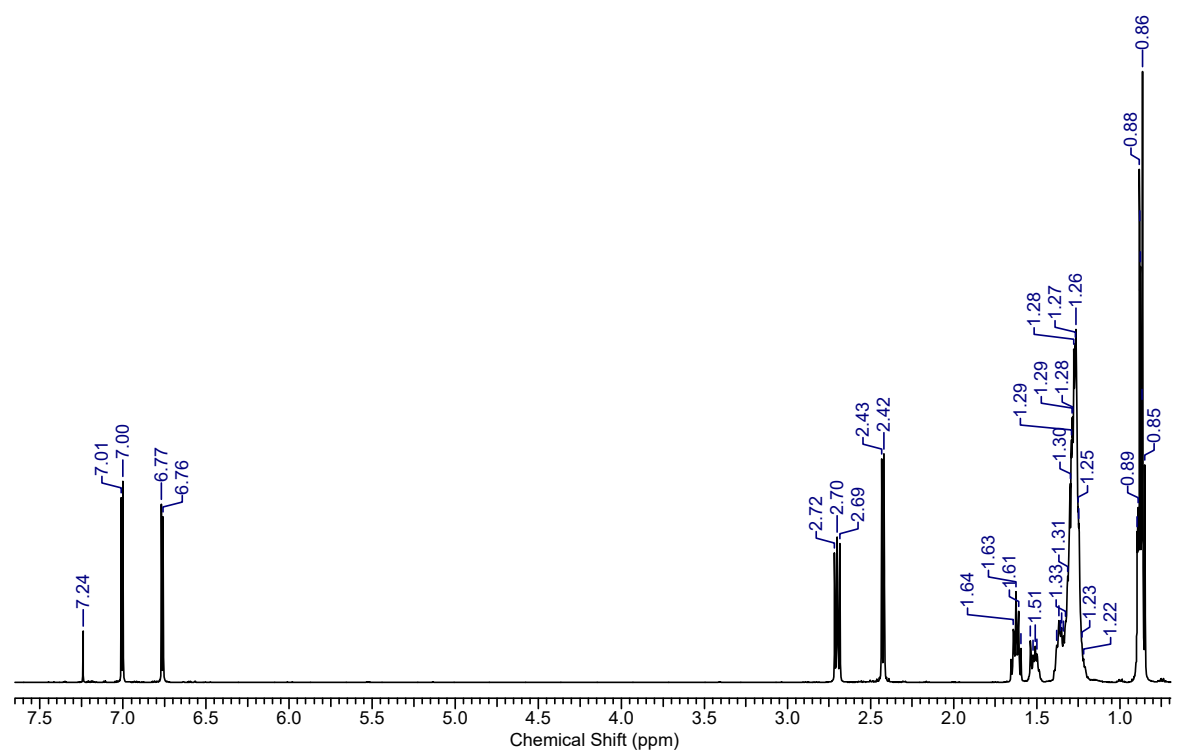


Figure S6. <sup>1</sup>H NMR spectrum of compound **3b**

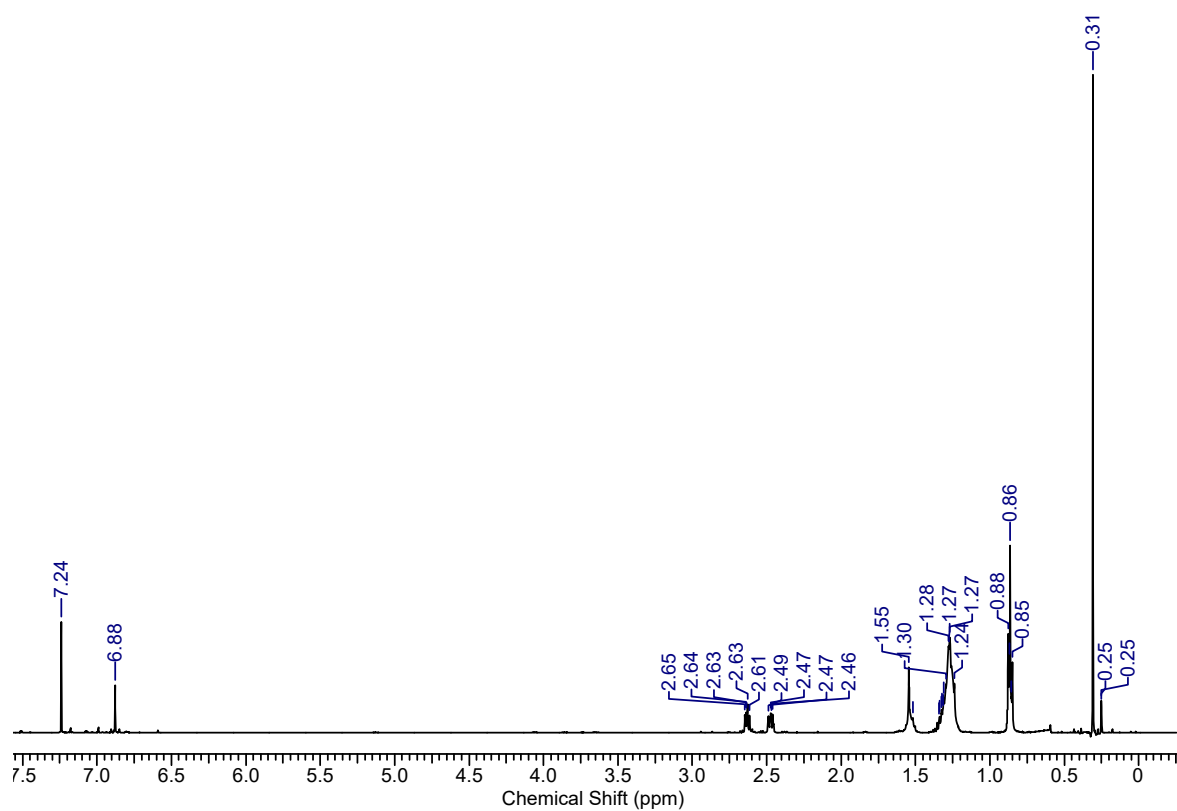


Figure S7.  $^1\text{H}$  NMR spectrum of compound **4a**

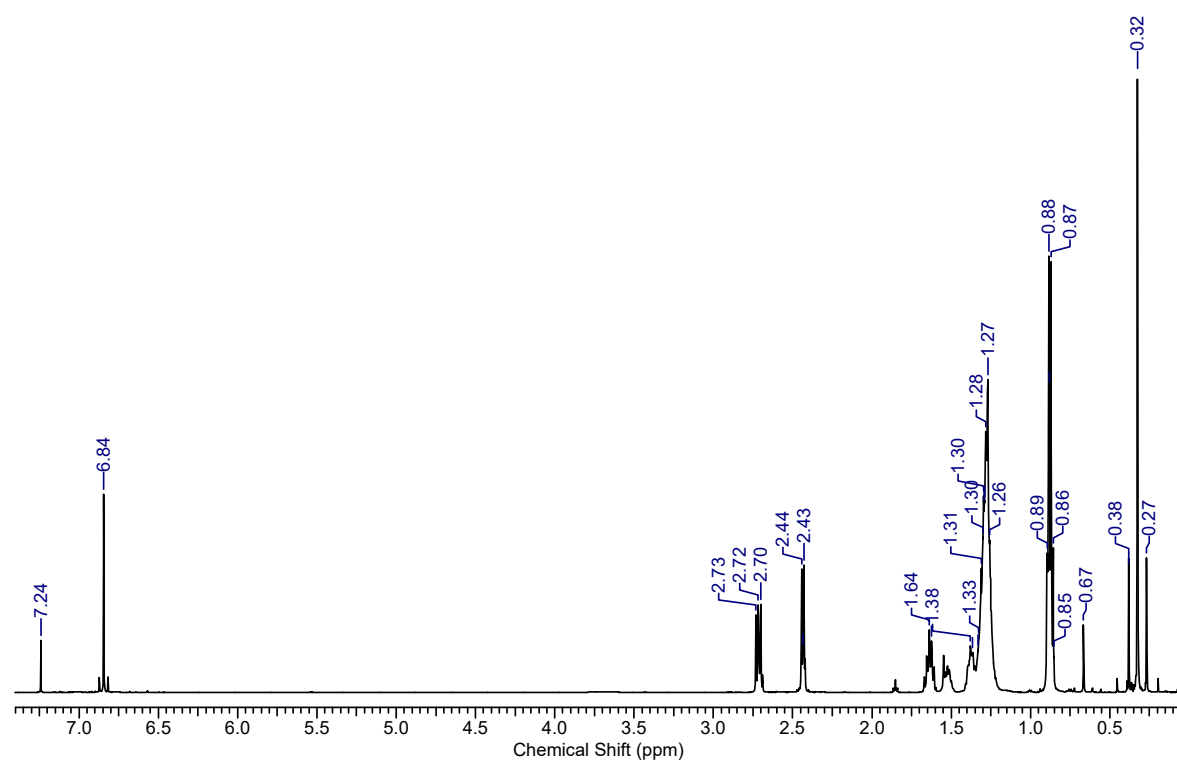


Figure S8.  $^1\text{H}$  NMR spectrum of compound **4b**

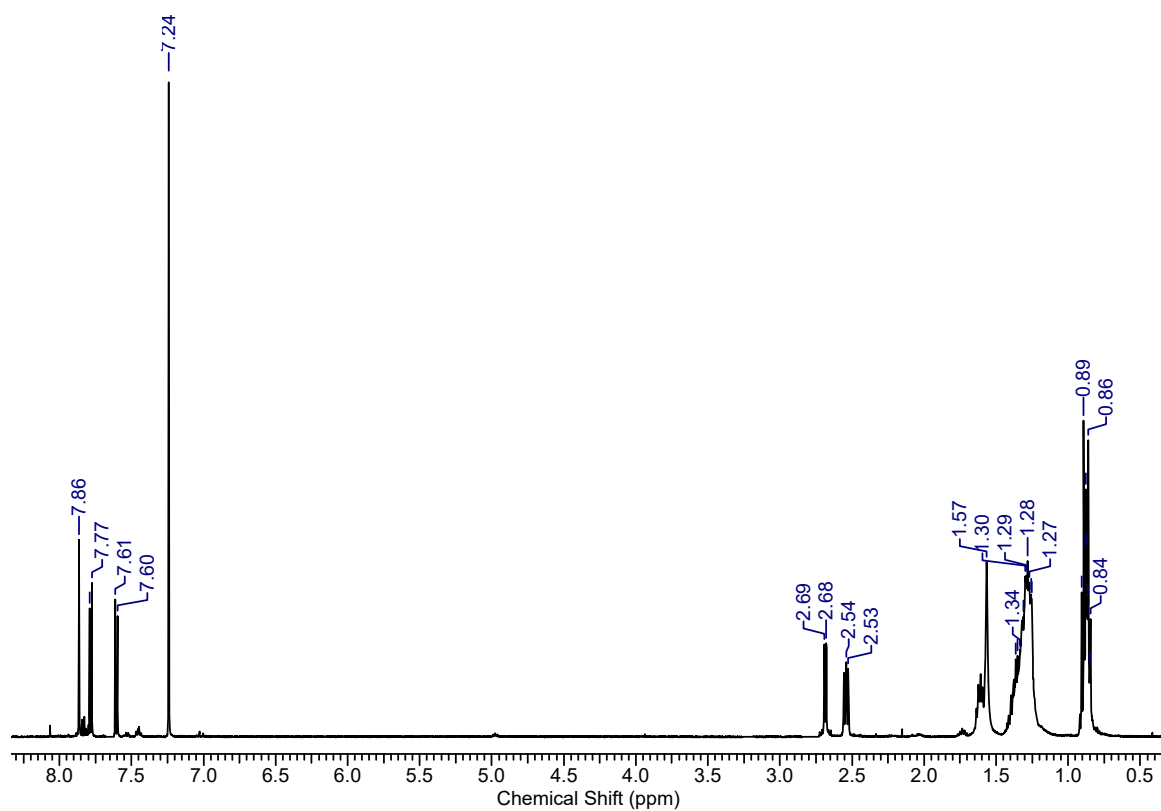


Figure S9. <sup>1</sup>H NMR spectrum of compound **5a**

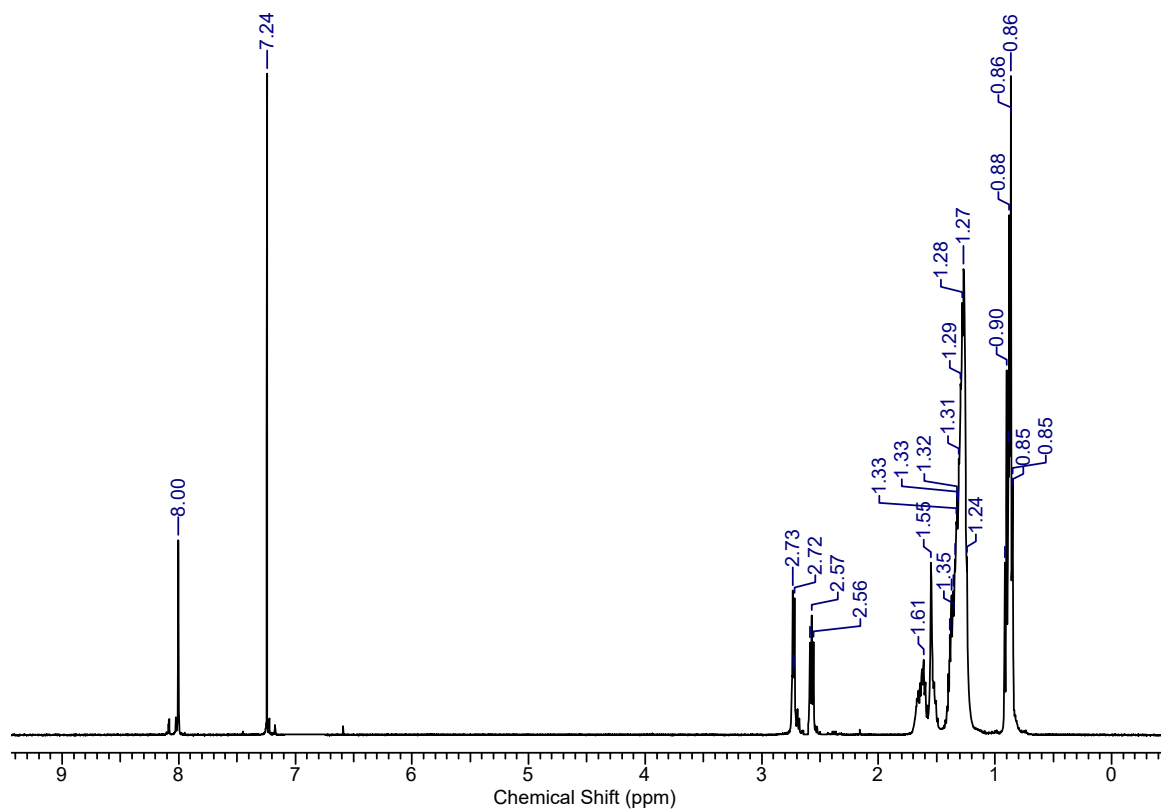


Figure S10. <sup>1</sup>H NMR spectrum of compound **5b**

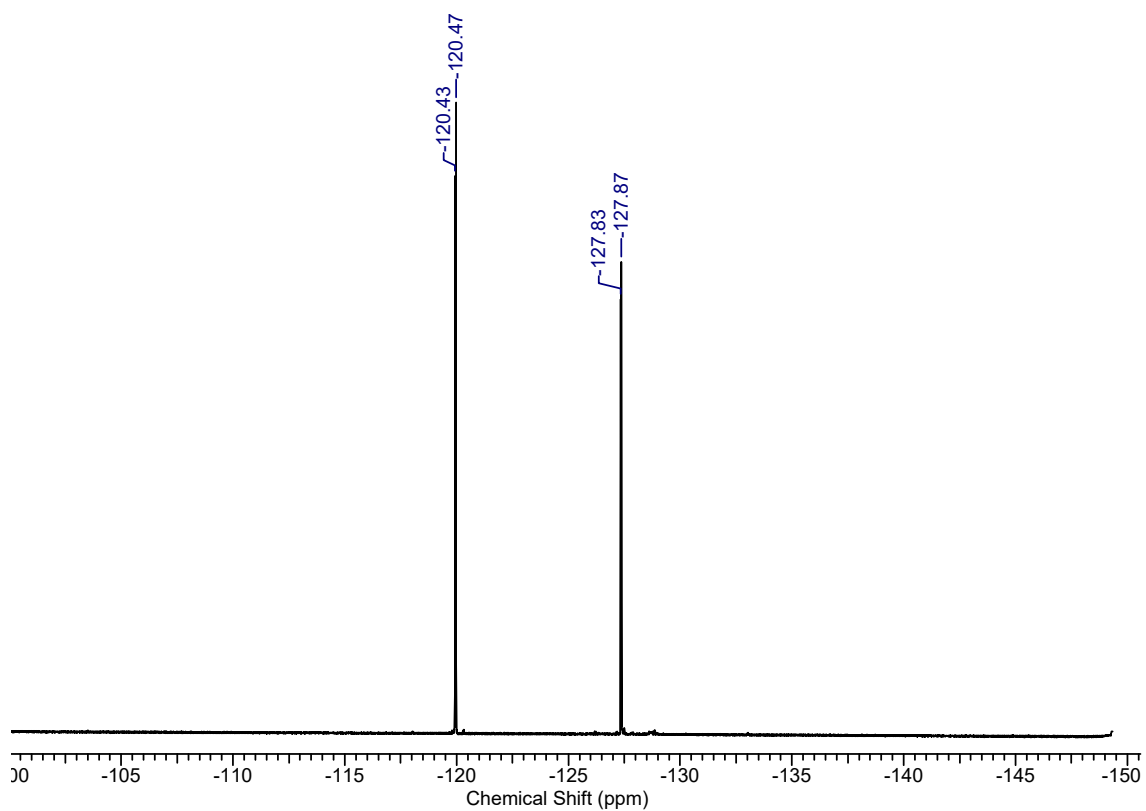


Figure S11.  $^{19}\text{F}$  NMR spectrum of compound **5b**

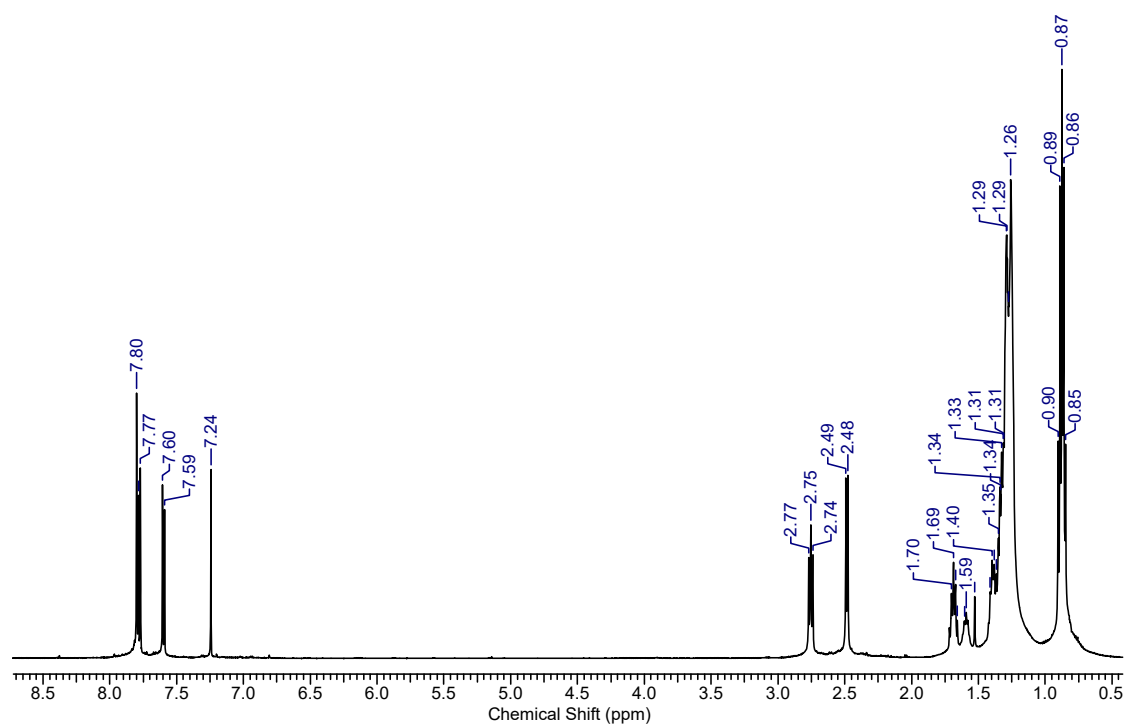


Figure S12.  $^1\text{H}$  NMR spectrum of compound **5c**

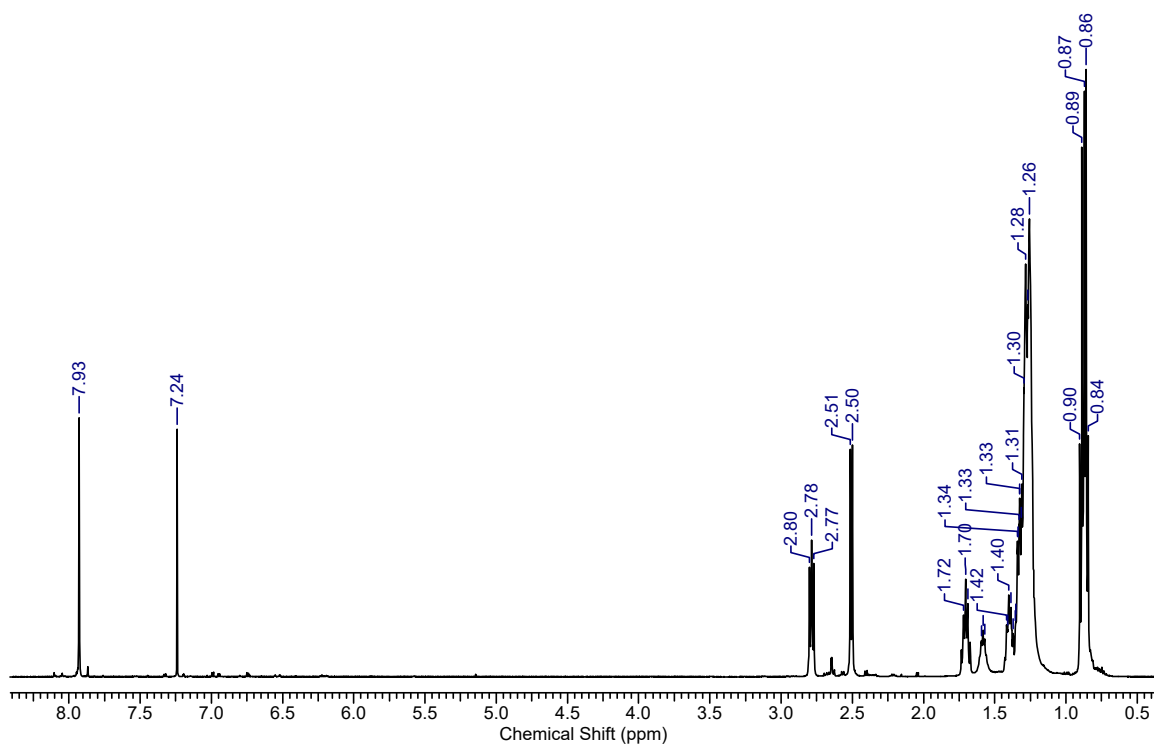


Figure S13. <sup>1</sup>H NMR spectrum of compound **5d**

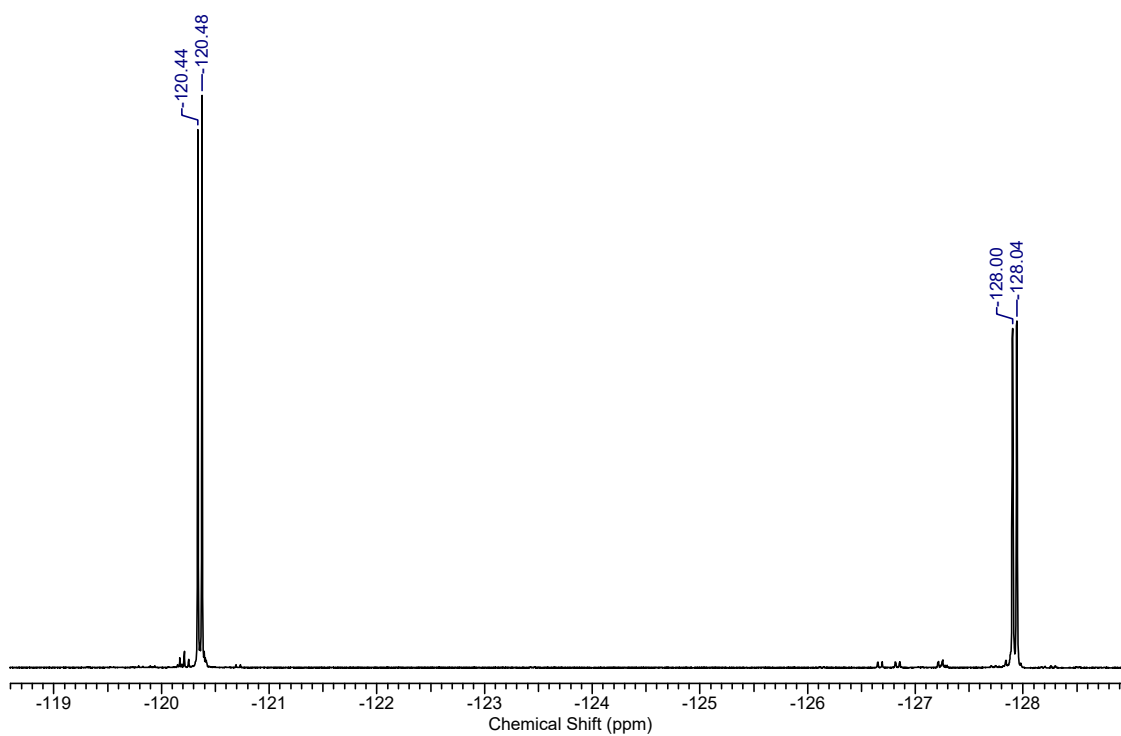


Figure S14. <sup>19</sup>F NMR spectrum of compound **5d**



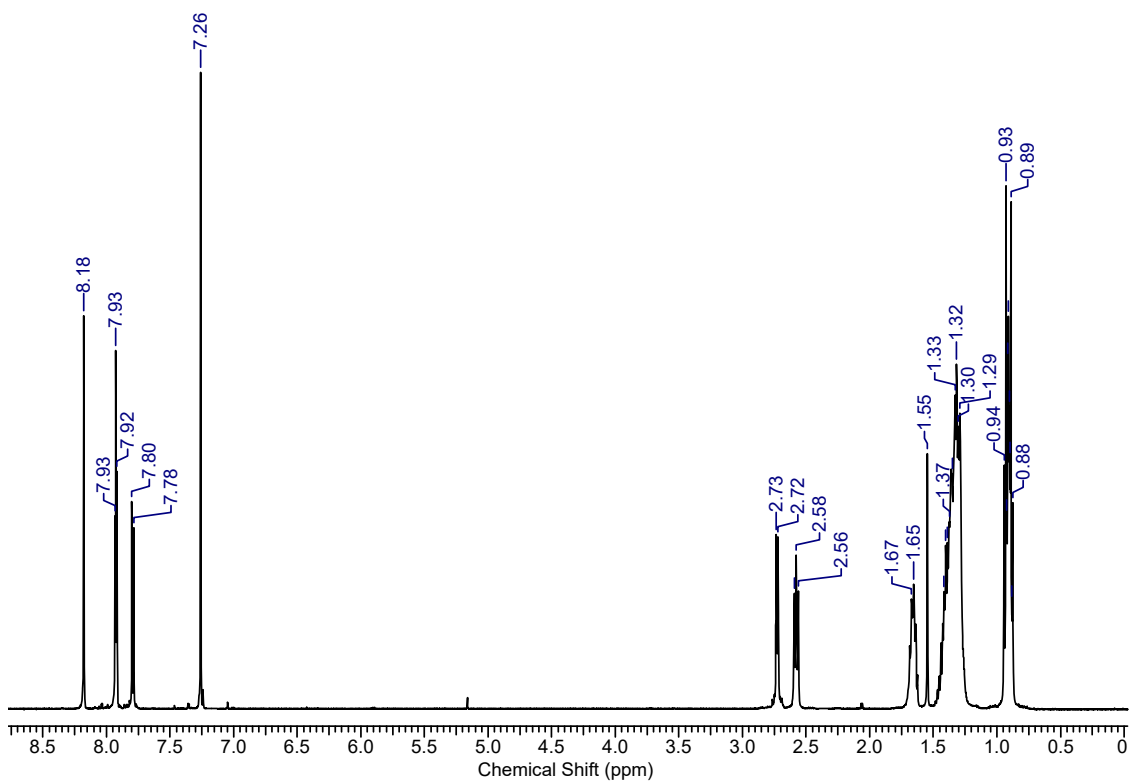


Figure S15. <sup>1</sup>H NMR spectrum of compound M1

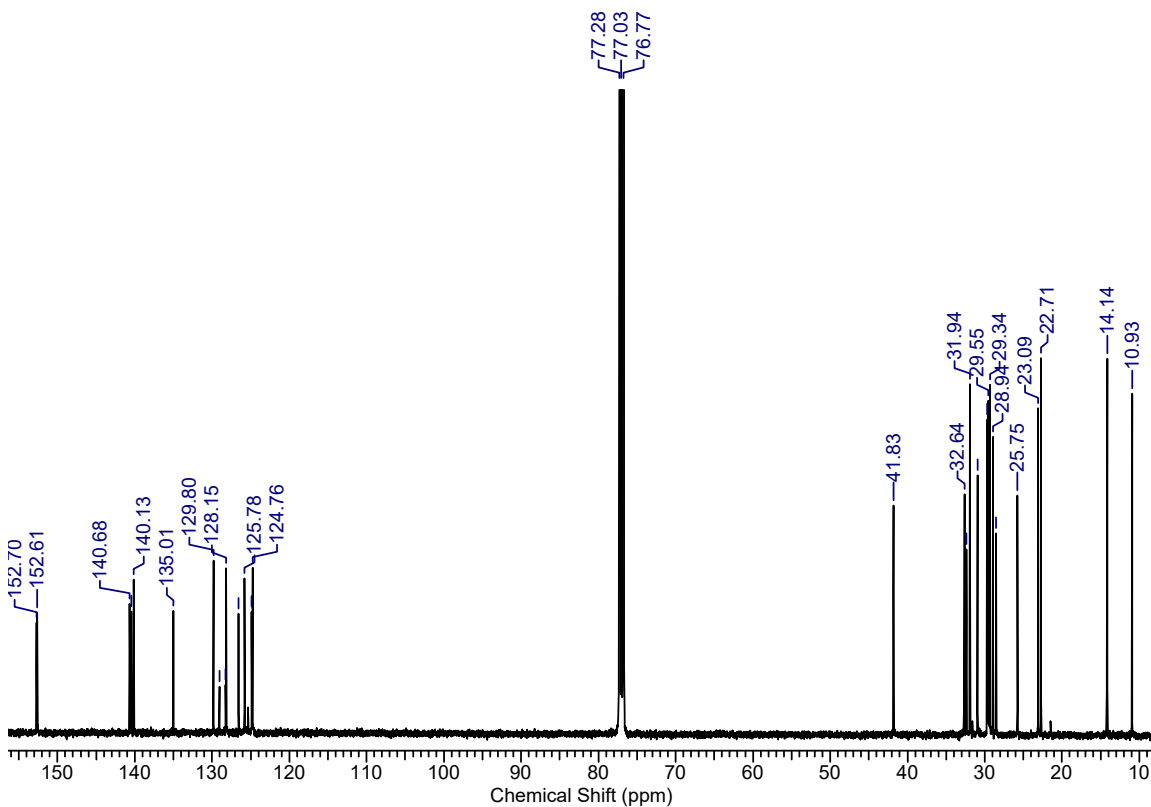


Figure S16. <sup>13</sup>C NMR spectrum of compound M1

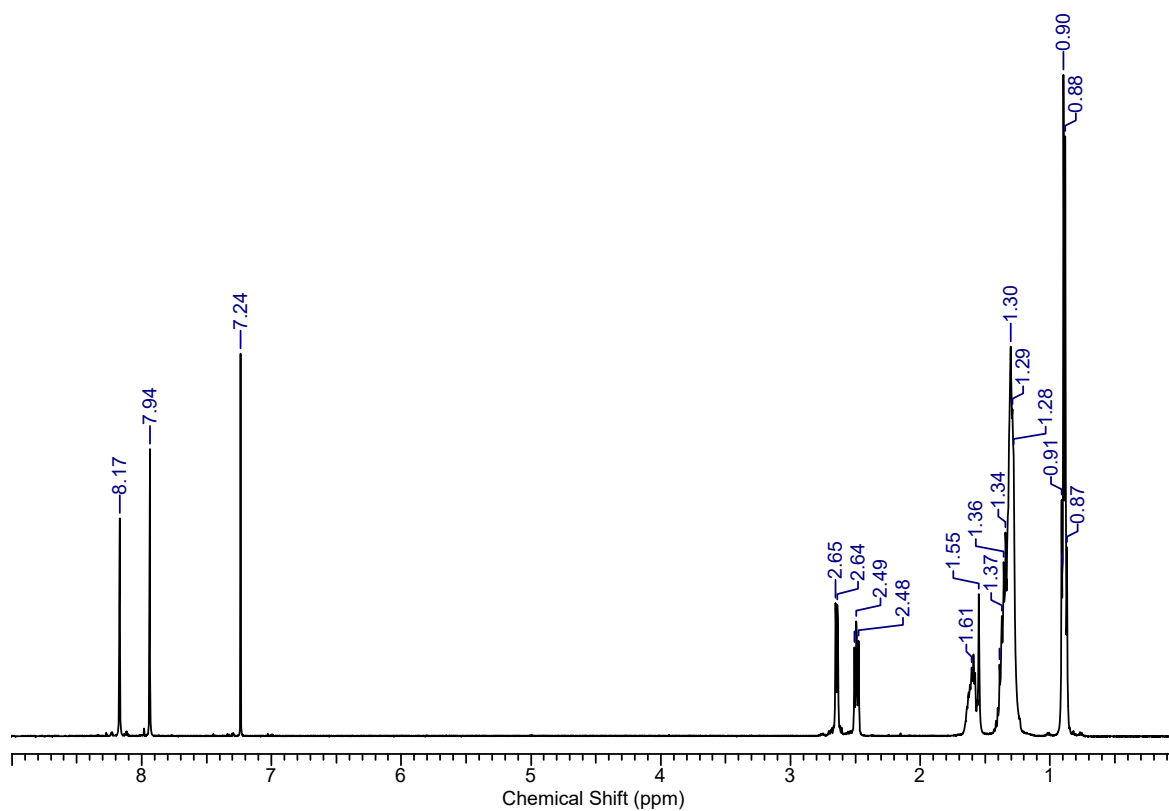


Figure S17. <sup>1</sup>H NMR spectrum of compound M2

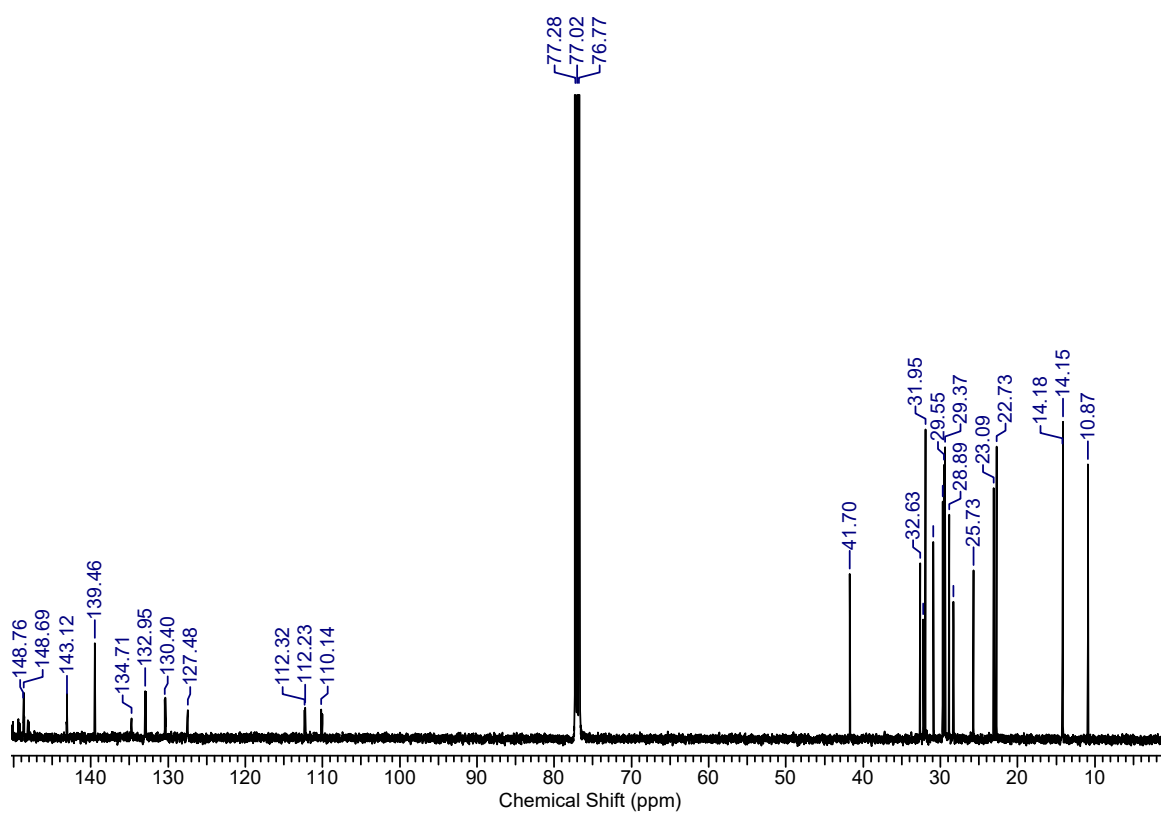


Figure S18. <sup>13</sup>C NMR spectrum of compound M2

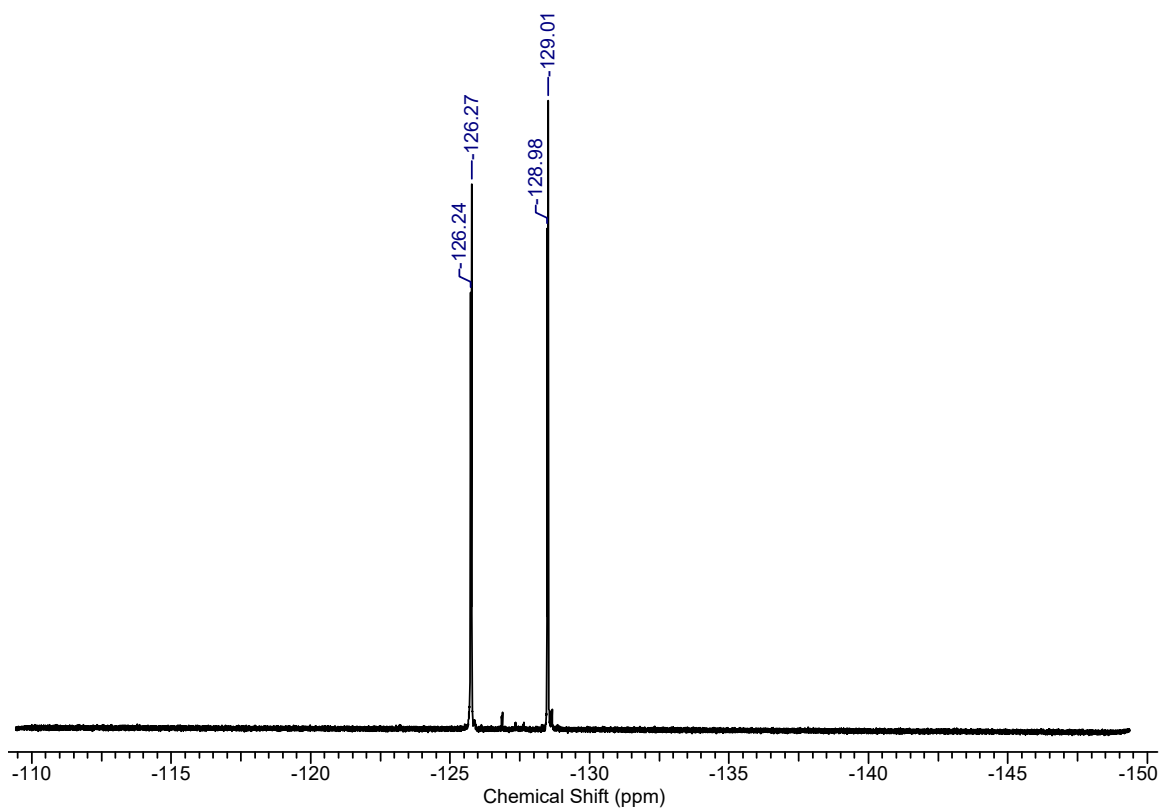


Figure S19.  $^{19}\text{F}$  NMR spectrum of compound **M2**

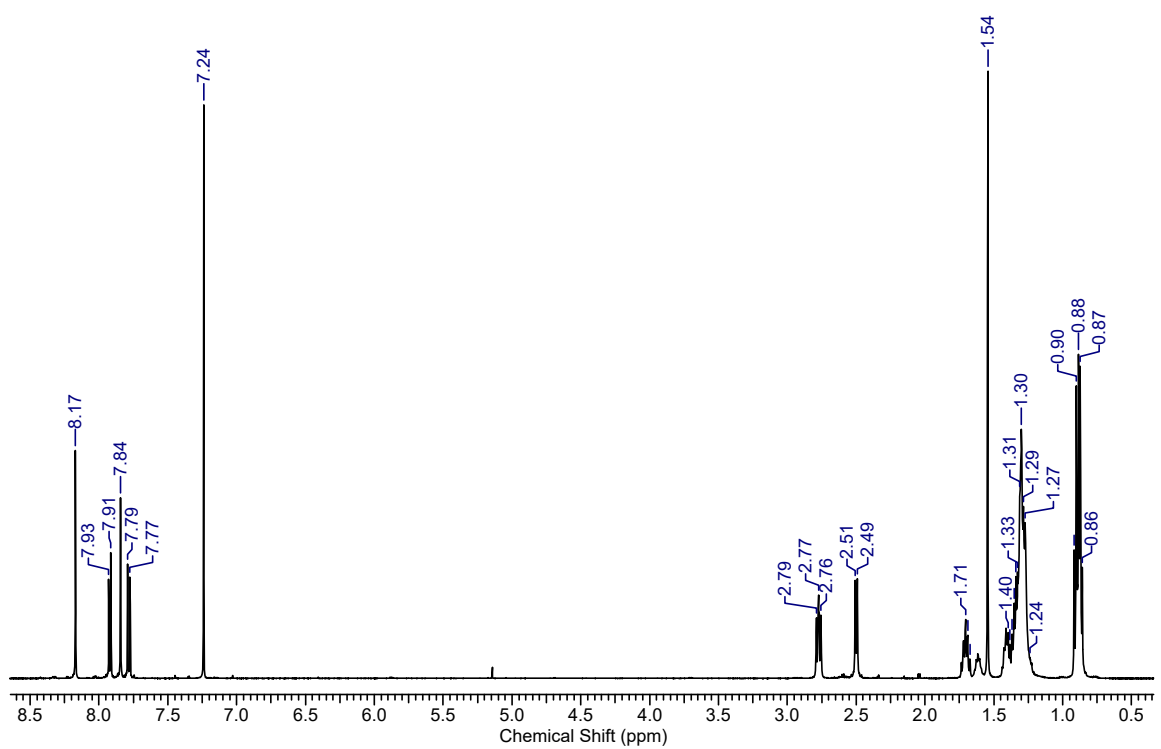


Figure S20.  $^1\text{H}$  NMR spectrum of compound **M3**

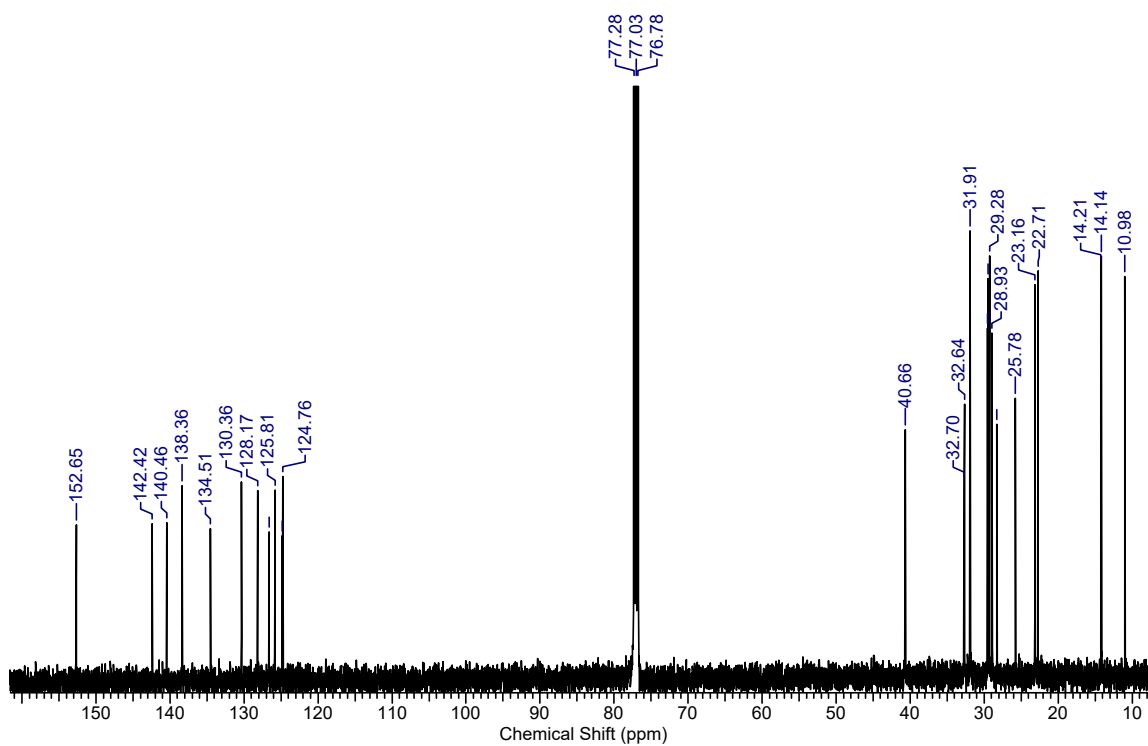


Figure S21.  $^{13}\text{C}$  NMR spectrum of compound **M3**

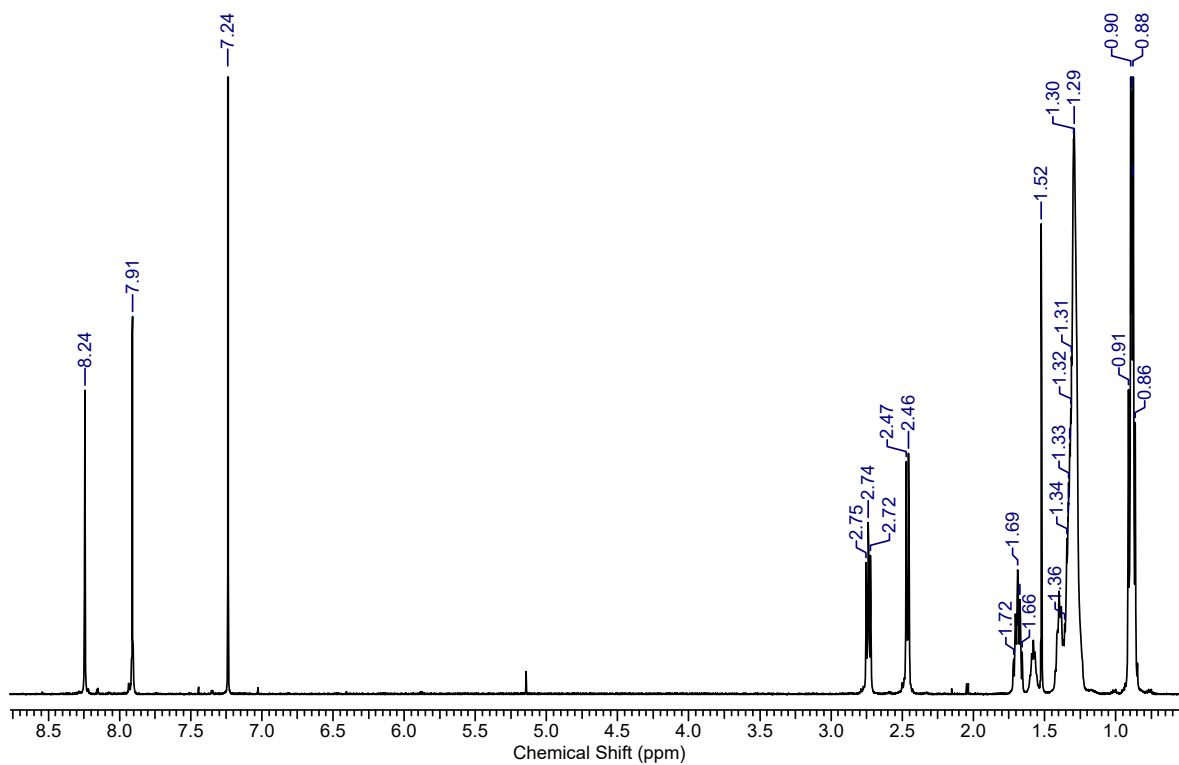


Figure S22.  $^1\text{H}$  NMR spectrum of compound **M4**

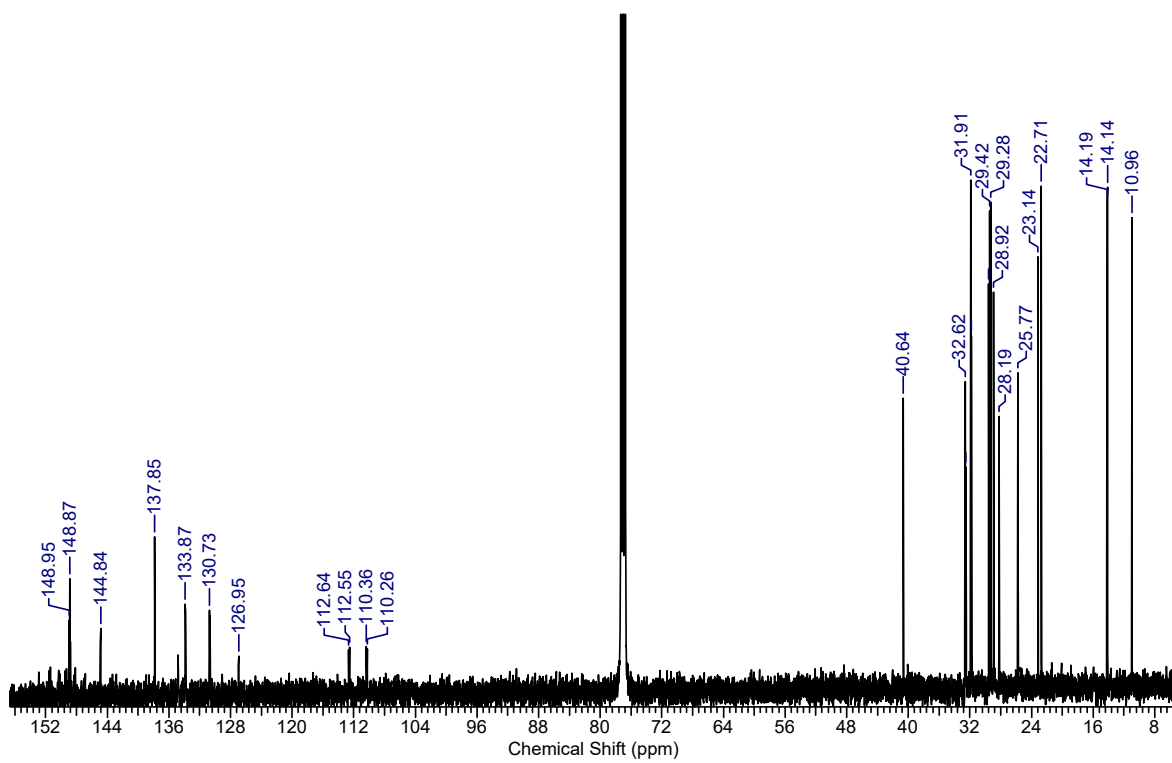


Figure S23. <sup>13</sup>C NMR spectrum of compound M4

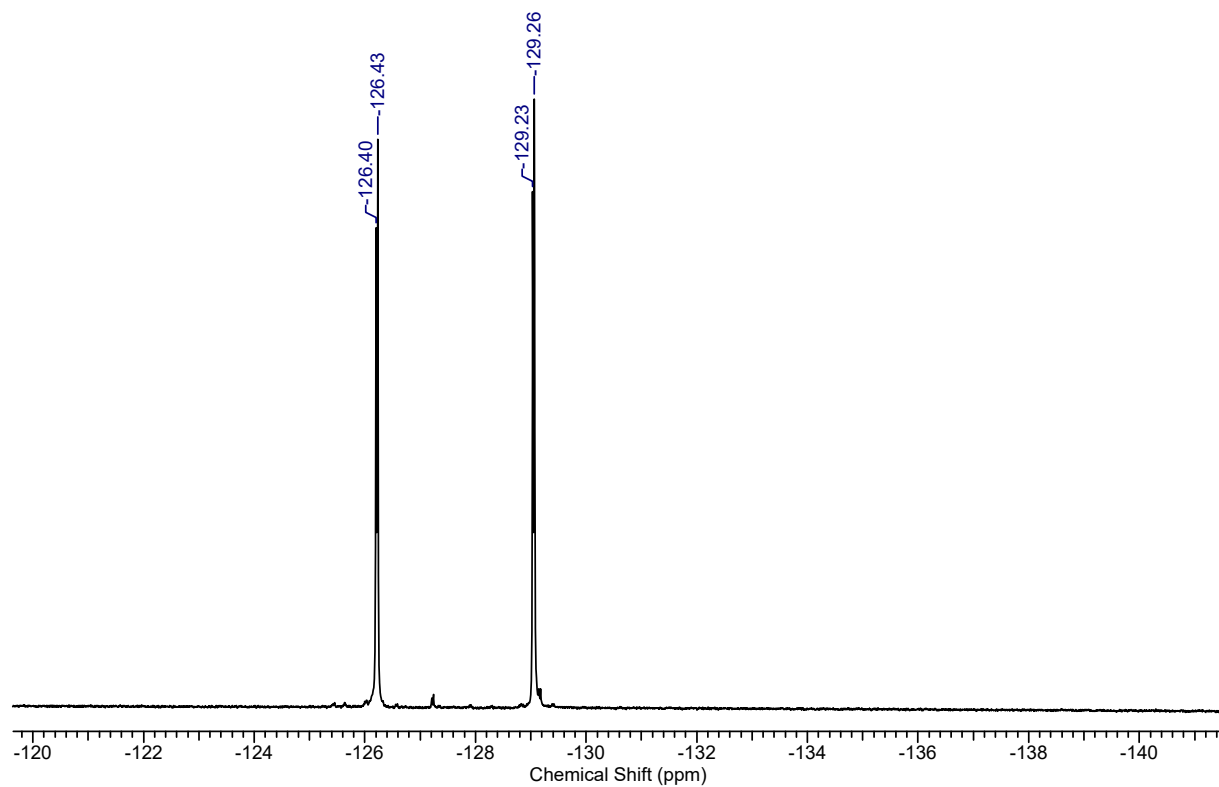


Figure S24. <sup>19</sup>F NMR spectrum of compound M4

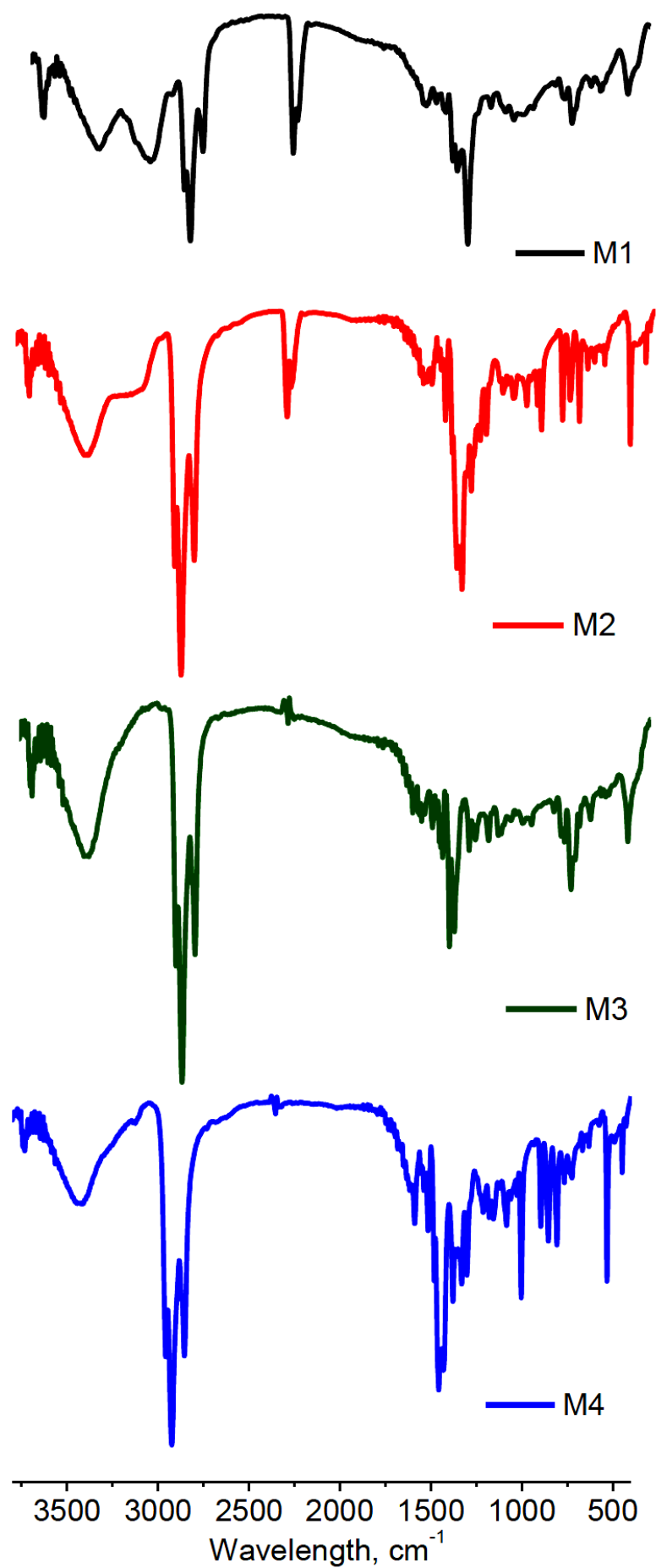


Figure S25. FT-IR spectrum of compounds **M1-M4**

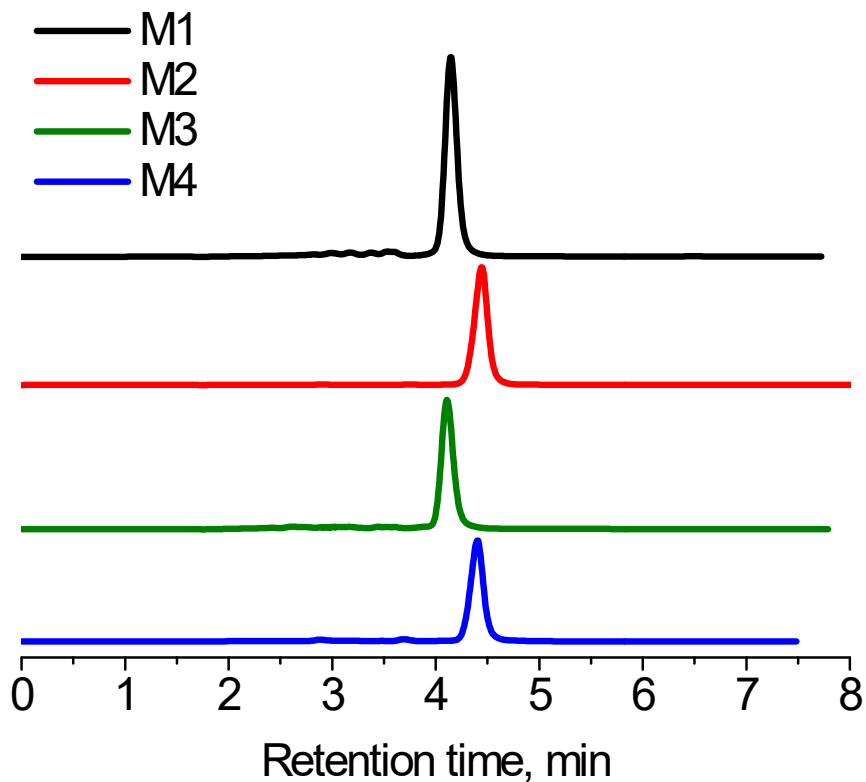


Figure S26. HPLC of compounds **M1-M4**. Conditions: eluent - acetonitrile:toluene (7:3); flow rate 1 mL/min; temperature 40°C; column - Phenomenex Luna C18, 5 $\mu$ m (4.6  $\times$  150 mm).

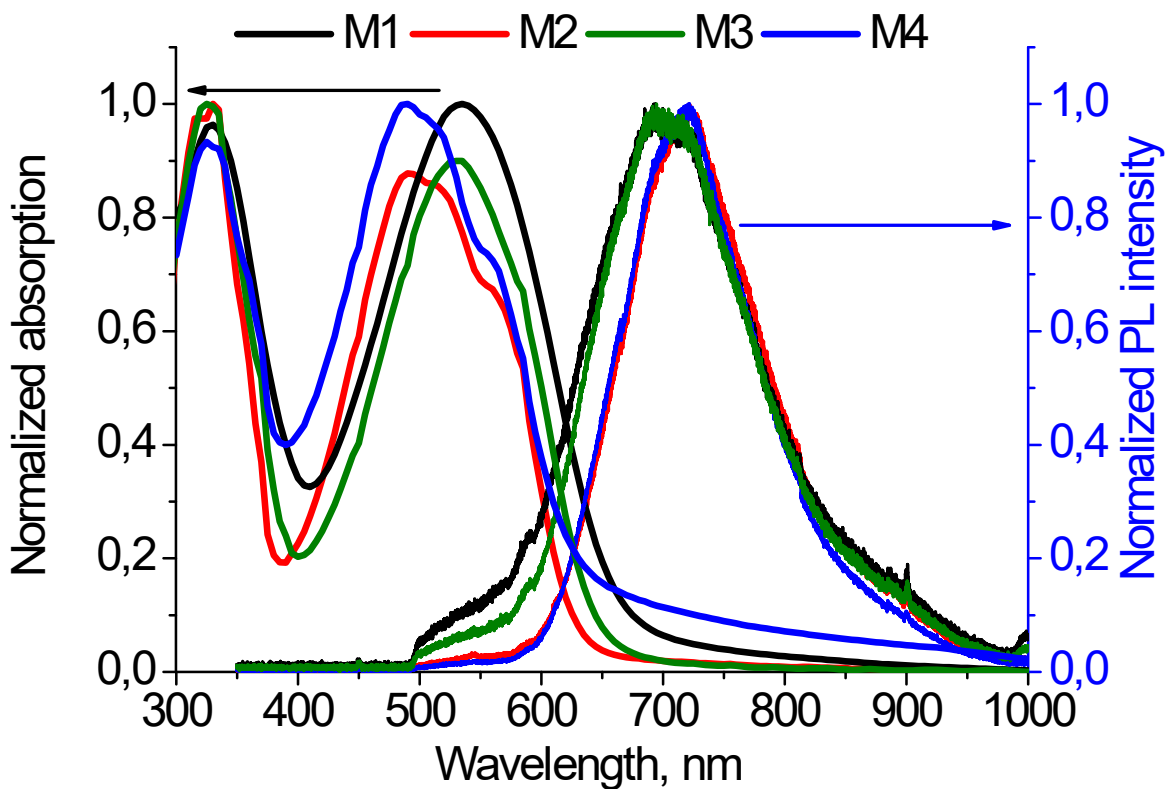


Figure S27. Absorption and fluorescence spectra of the compounds **M1-M4** in films normalized relative to their respective dominant bands.

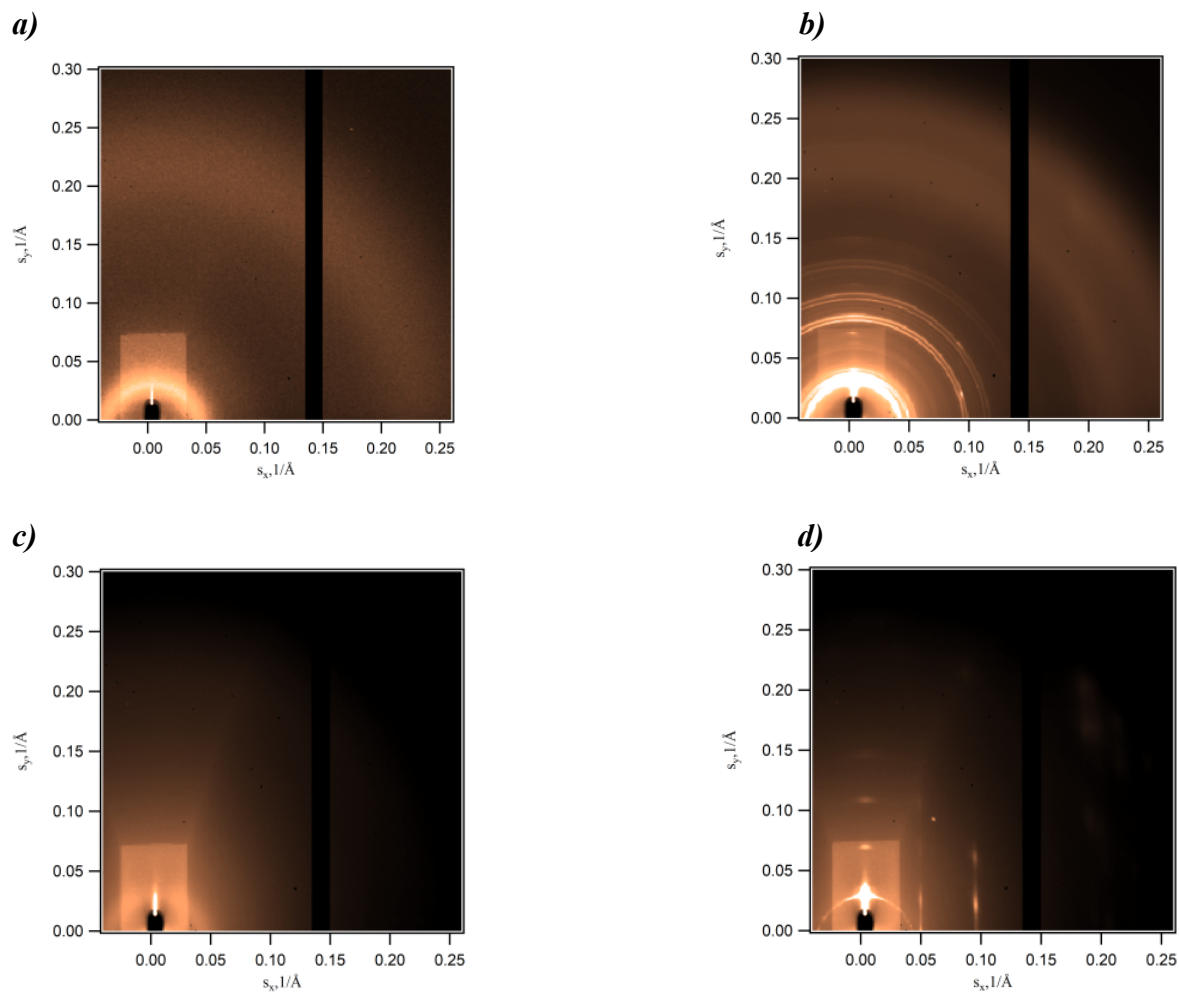


Figure S28. 2D GIWAXS patterns of M1 (a), M2 (b), M3 (c) and M4 (d) at 120°C

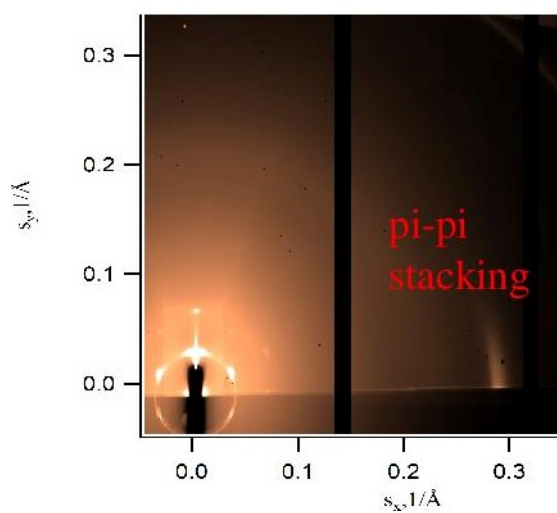


Figure S29. Full 2D GIWAXS pattern of M3



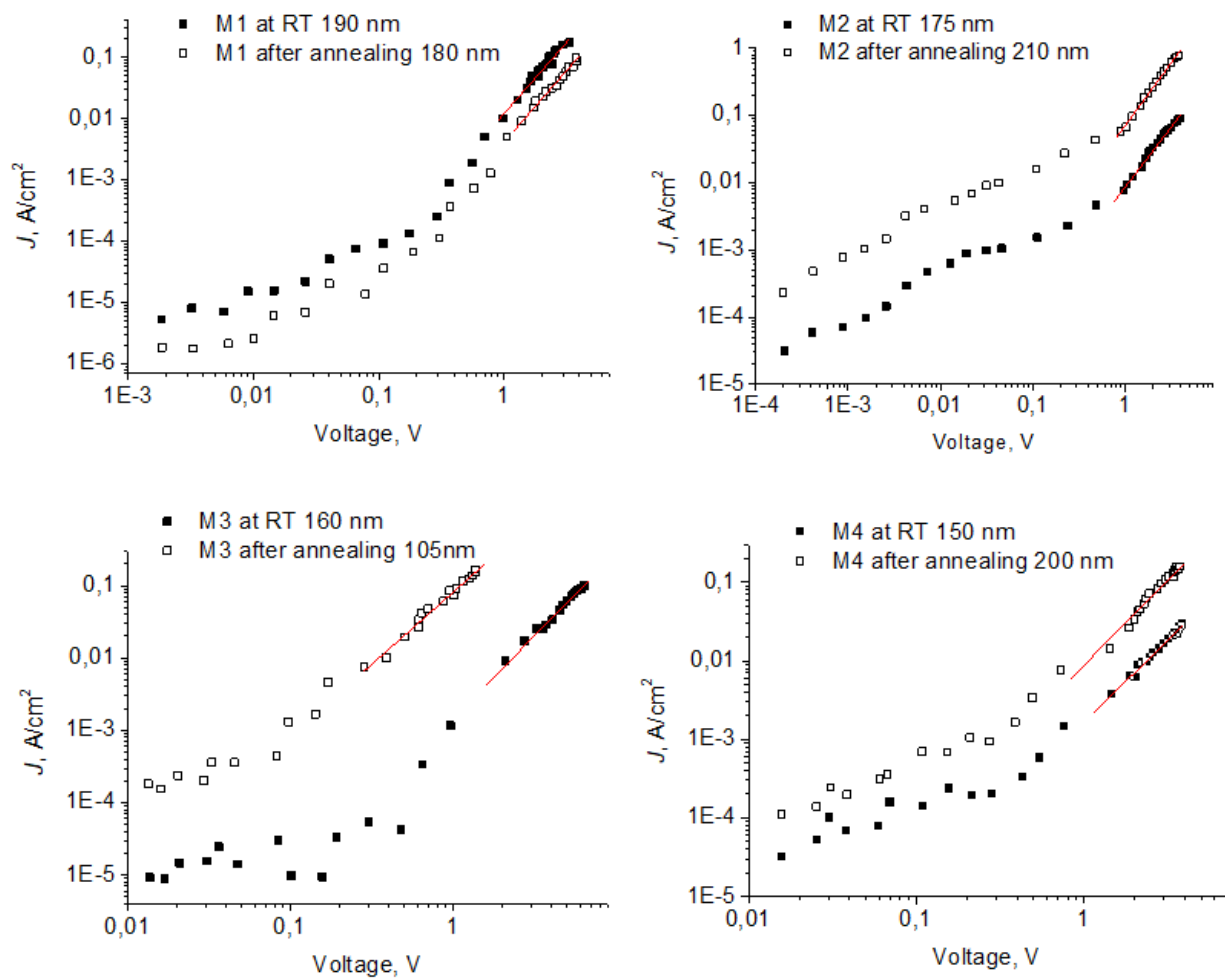


Figure S30.  $J$ - $V$  curves of hole-only devices based on compounds **M1-M4** (solid points for as-cast films and empty points for annealed films at  $120^\circ\text{C}$ ). The red lines represent the best fitting from space charge limited current model.