Further Evidence on the Importance of Fluorous-Fluorous Interactions in Supramolecular Chemistry: A Combined Structural and Computational Study

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Supplementary Information

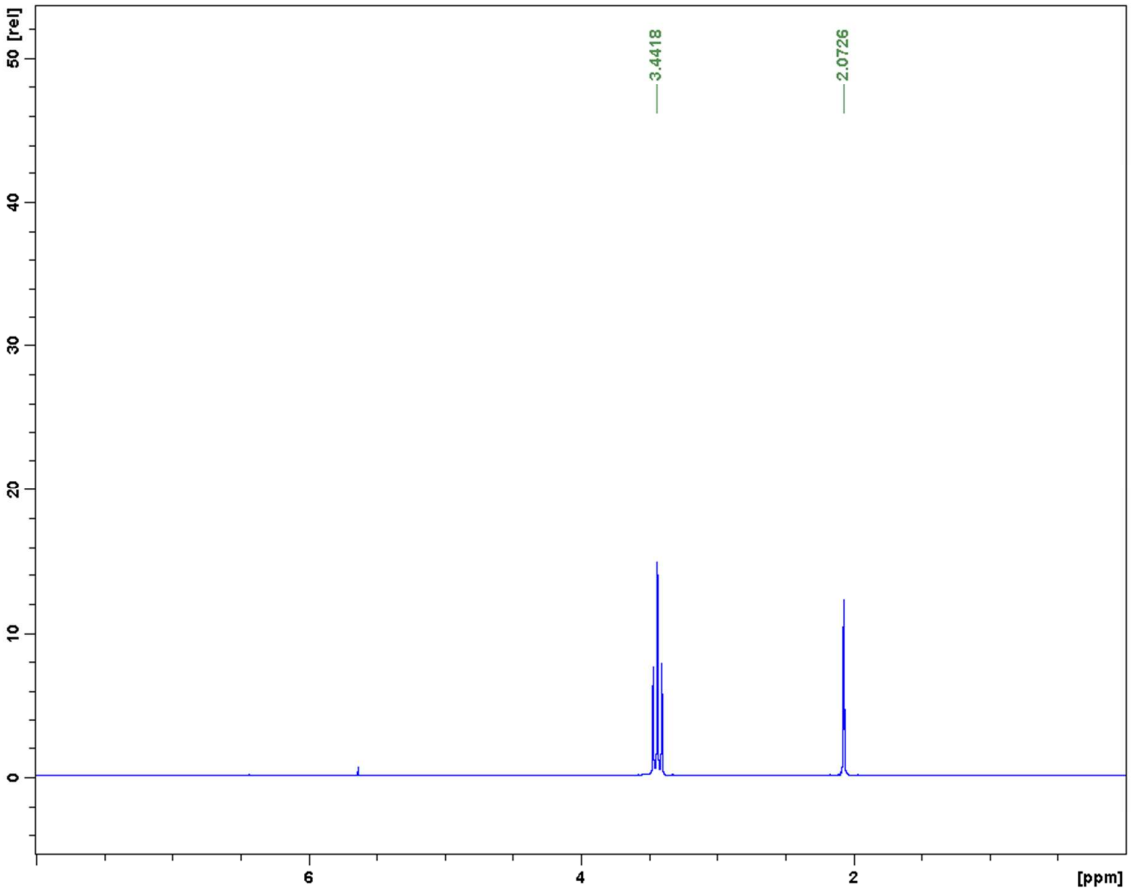

Figure S1. ^{1}H NMR spectrum of **2** in acetone-d_6.

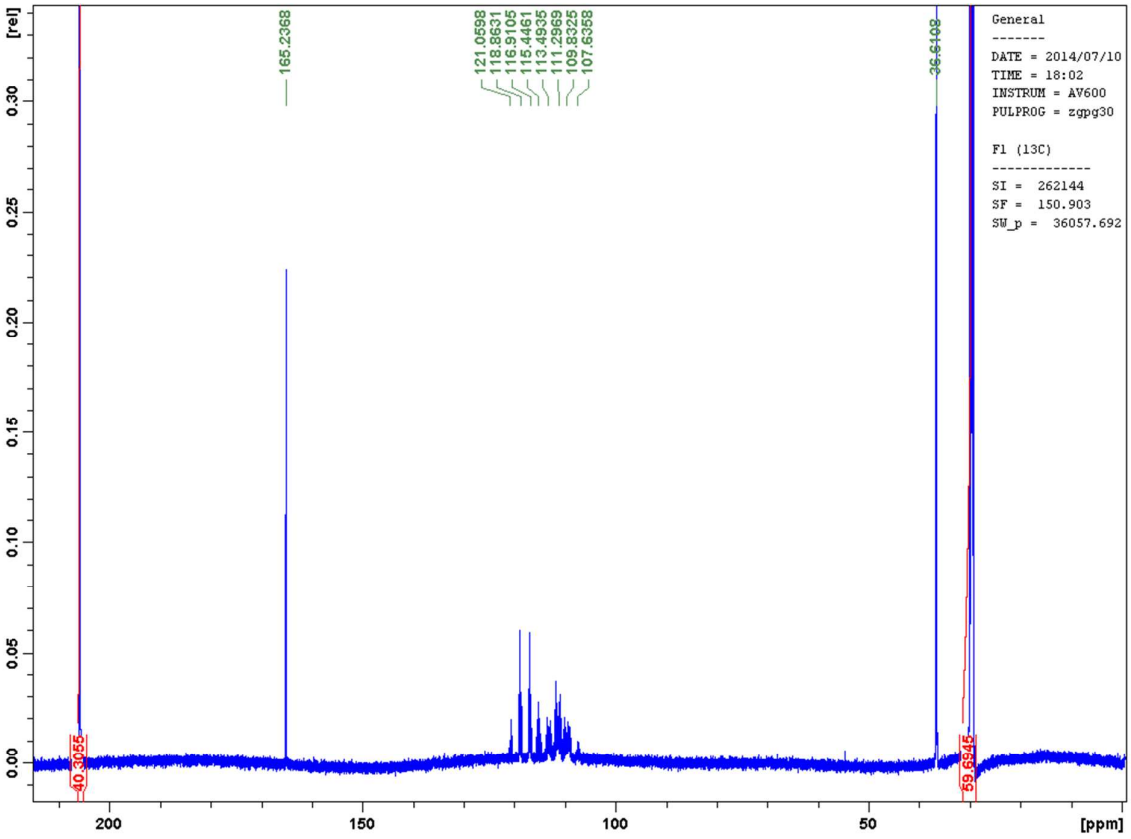

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in acetone-d_6.

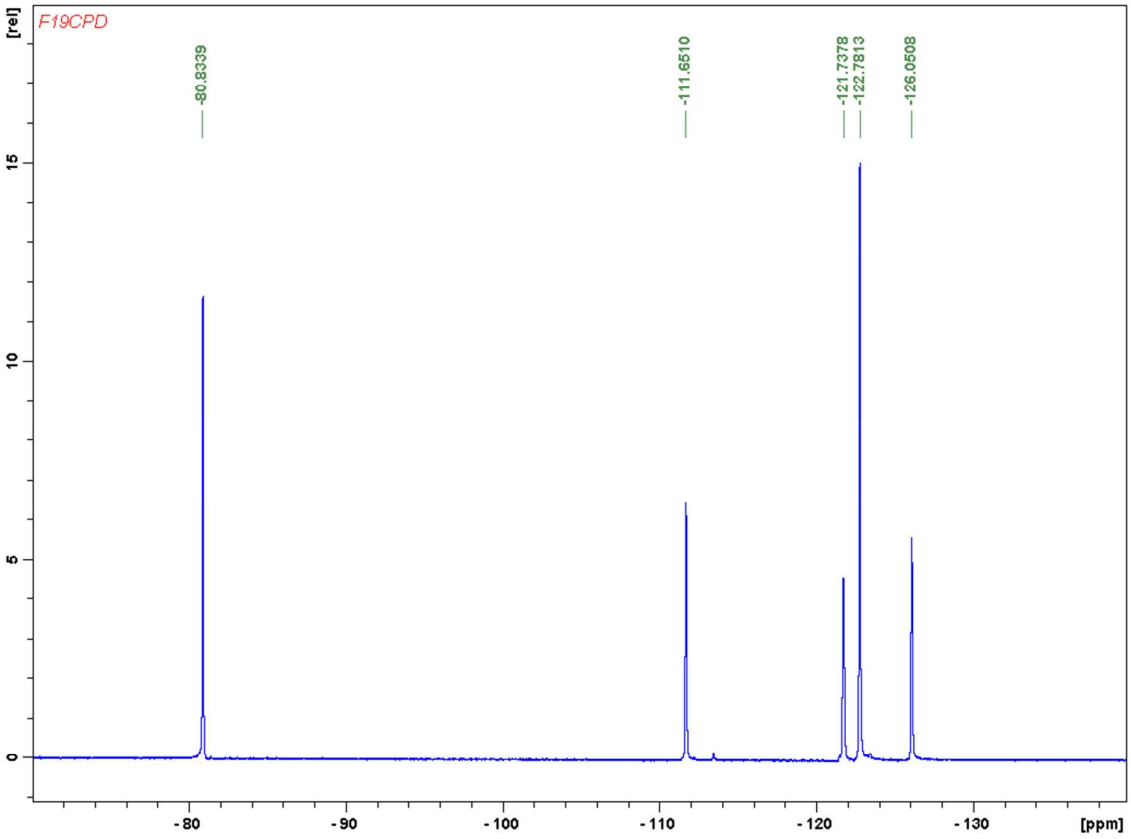

Figure S3. ^{19}F NMR spectrum of **2** in acetone-d_6.

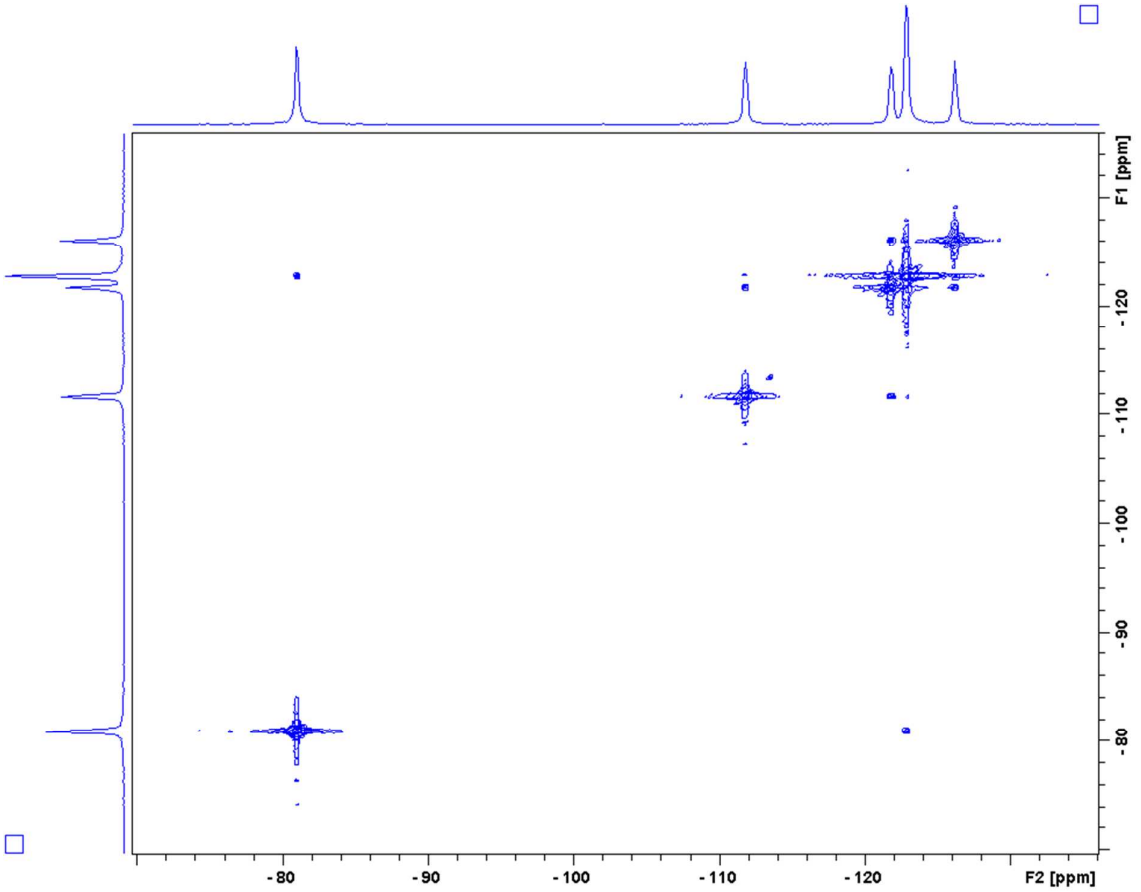

Figure S4. ^{19}F-^{19}F COSY NMR spectrum of **2** in acetone-d_6.

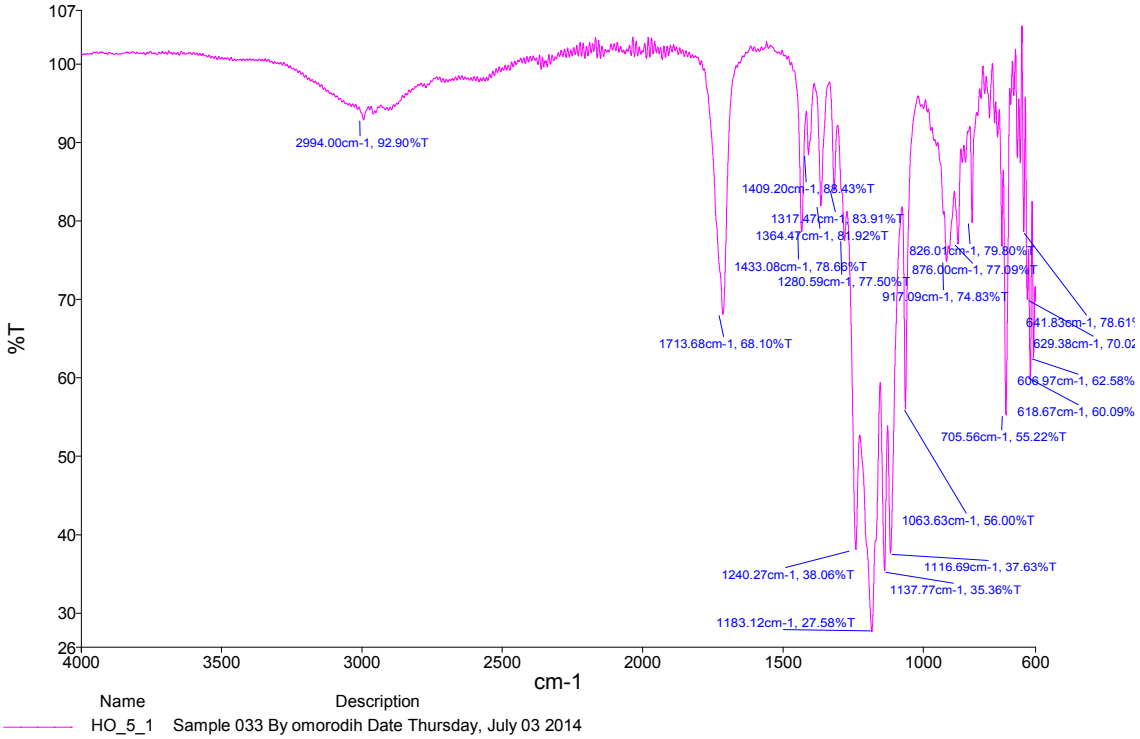

Figure S5. Infrared spectrum of **2**.

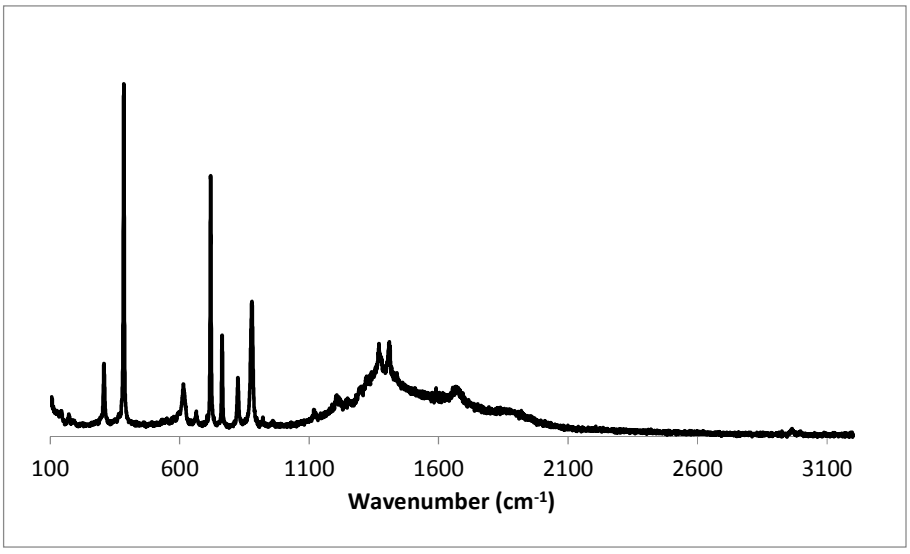

Figure S6. Raman Spectrum of **2**.

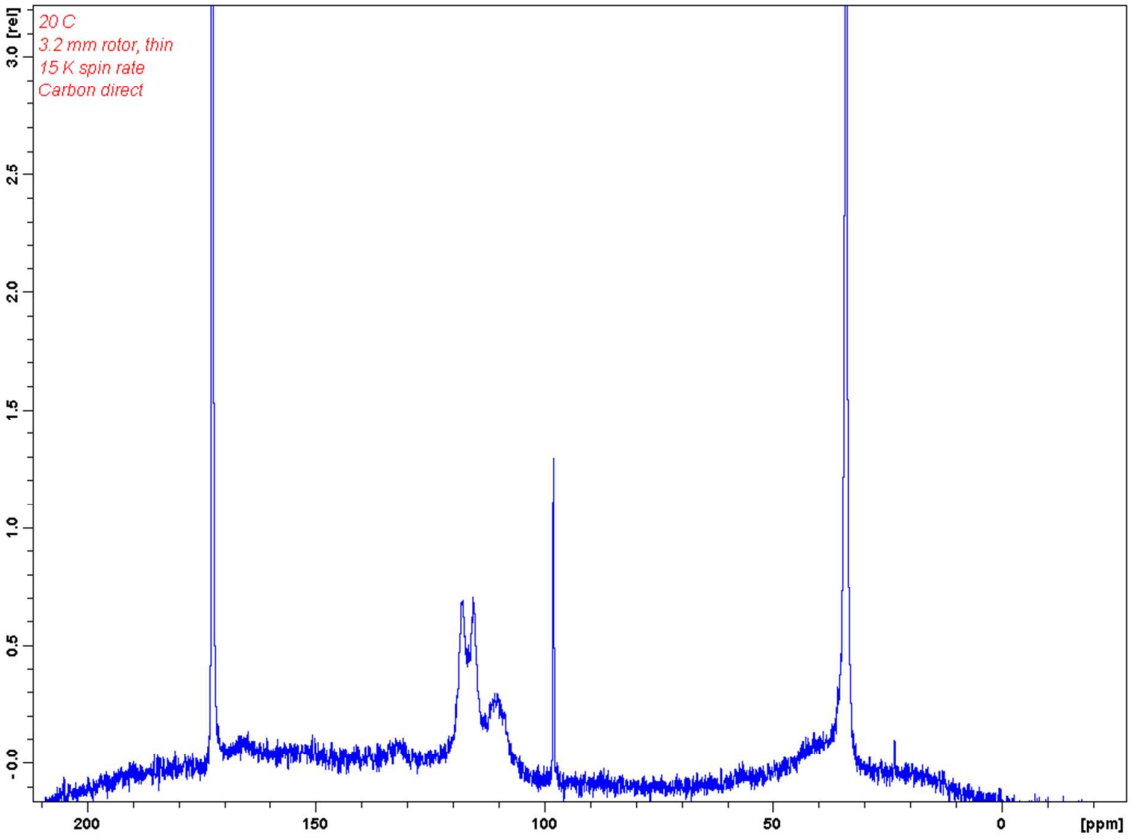

Figure S7. Solid-State $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

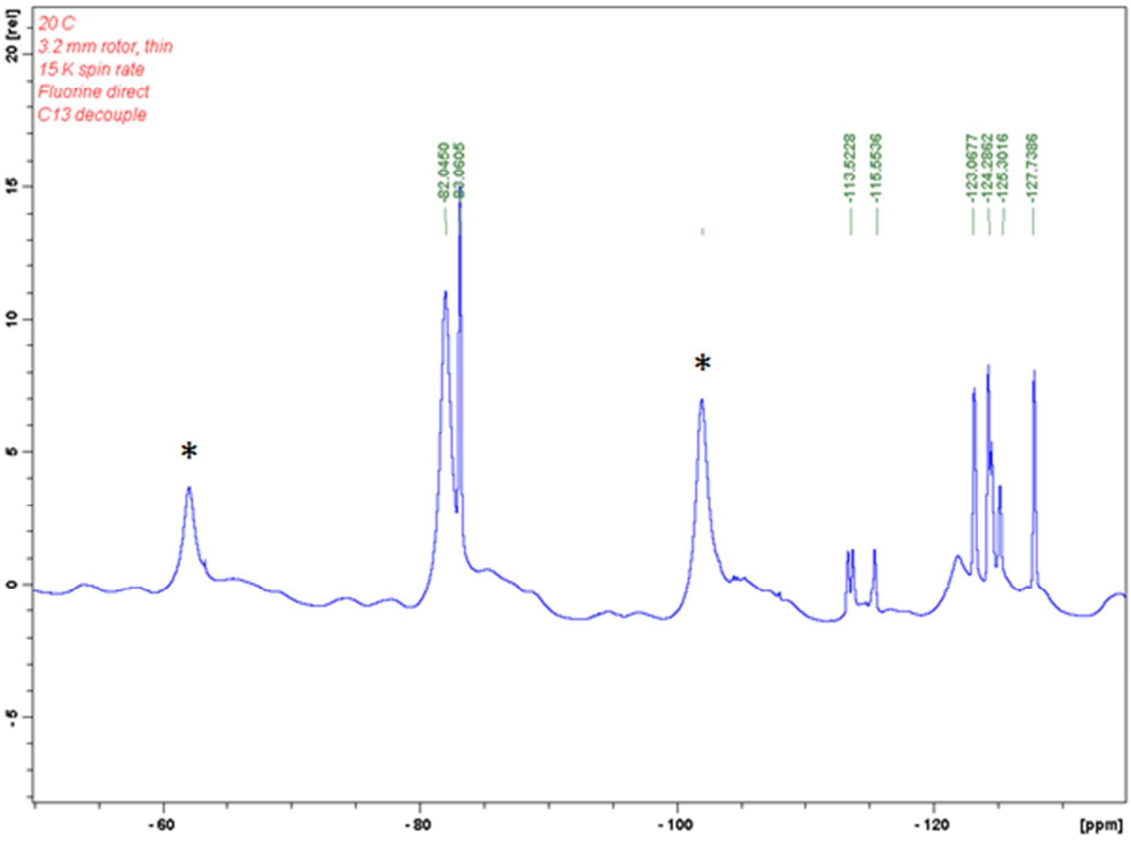

Figure S8. Solid-State ^{19}F NMR spectrum of **2** (* indicates spinning side bands).

Full characterisation data for **2**

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 3.4 (t, 2H, $^{3}J_{HF}$ = 17.8 Hz, CH_2); ^{13}C NMR (600 MHz, $(CD_3)_2CO$): δ 166.6 (s, CO); 118.7 (tt, $^{1}J_{C\text{-}F}$ = 257 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, CF_2); 117.8 (tt, $^{1}J_{C\text{-}F}$ = 288 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, $CF_2CF_2CH_2$); 116.9 (tt, $^{1}J_{C\text{-}F}$ = 257 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, $CF_2CF_2CH_2$); 111.7 (tt, $^{1}J_{C\text{-}F}$ = 270 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, $CF_3CF_2CF_2CF_2$); 110.9 (tt, $^{1}J_{C\text{-}F}$ = 270 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, $CF_3CF_2CF_2$); 109.9 (tt, $^{1}J_{C\text{-}F}$ = 270 Hz, $^{2}J_{C\text{-}F}$ = 32.9 Hz, CF_3CF_2); 36.5 (tt, $^{2}J_{C\text{-}F}$ = 22.8 Hz, $^{1}J_{C\text{-}H}$ = 21.5 Hz; CH_2); ^{19}F NMR [376.6 MHz, C6D6]: δ -80.9 (CF_3); -111.7 (CF_2CH_2); -121.9 ($CF_3CF_2CF_2$); 122.8 ($CF_3CF_2CF_2CF_2$, $CF_2CF_2CH_2$); 126.1 (CF_3CF_2); IR (cm^{-1}) $\tilde{\nu}$: 2994 (w, OH), 1714 (s, C=O), 1433, 1409 (w), 1364 (s), 1317 (s), 1240 (s, C–F), 1183 (w, C–F), 1138 (s, C–F), 1117 (s, C–F), 1066 (s, C–F), 917 (w C–F), 876

(s), 826 (s), 706 (s), 618 (m), 606 (m). MS (ESI-) m/z: 391.1 [M-H, 100%]; HRMS (ESI-) calculated for $C_8H_2F_{13}O_2$: 376.985739, found: 376.985270.

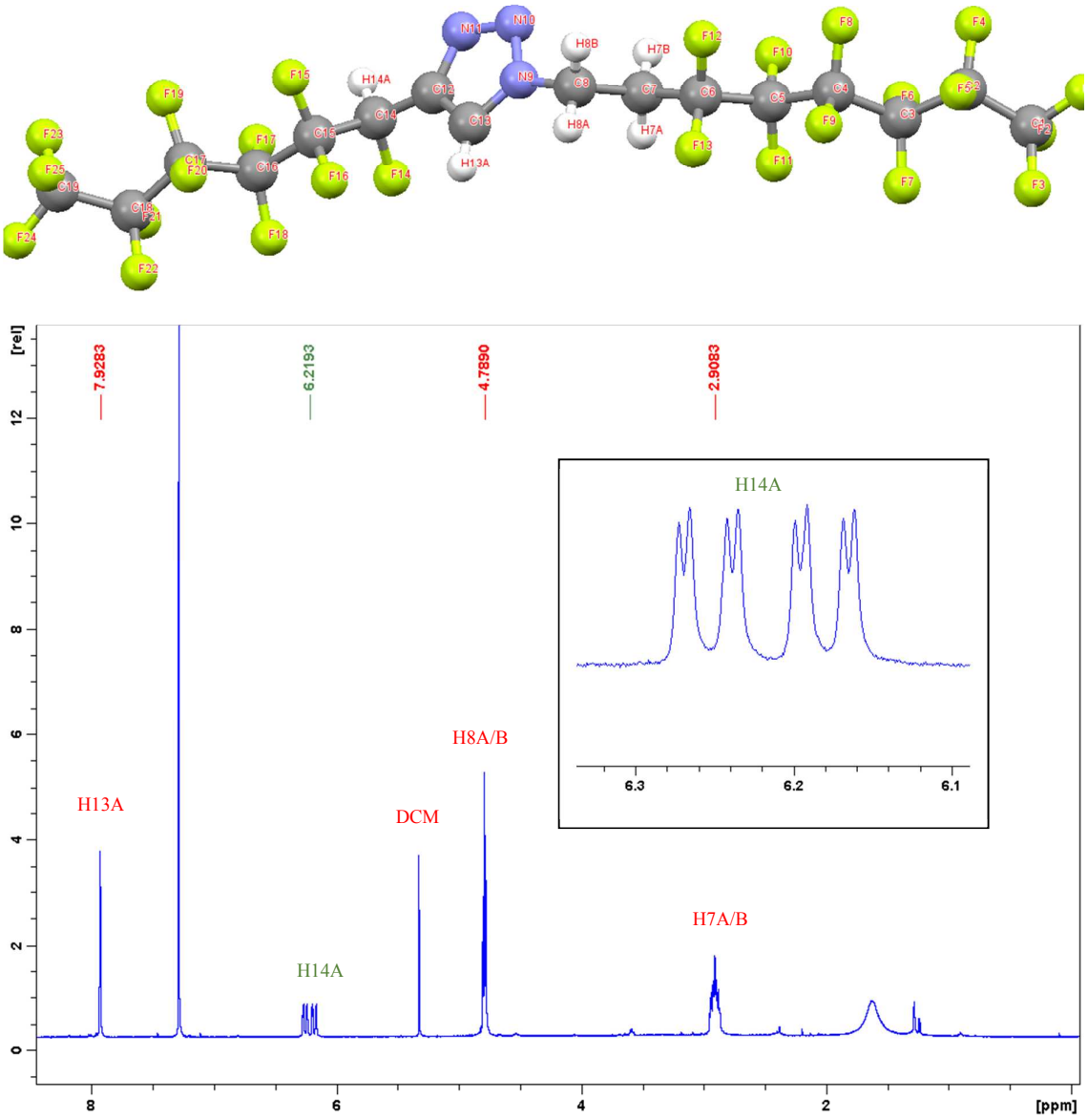

Figure S9. ^{1}H NMR spectrum of **3** in $CDCl_3$. Insert shows zoom in of the peak at 6.2 ppm.

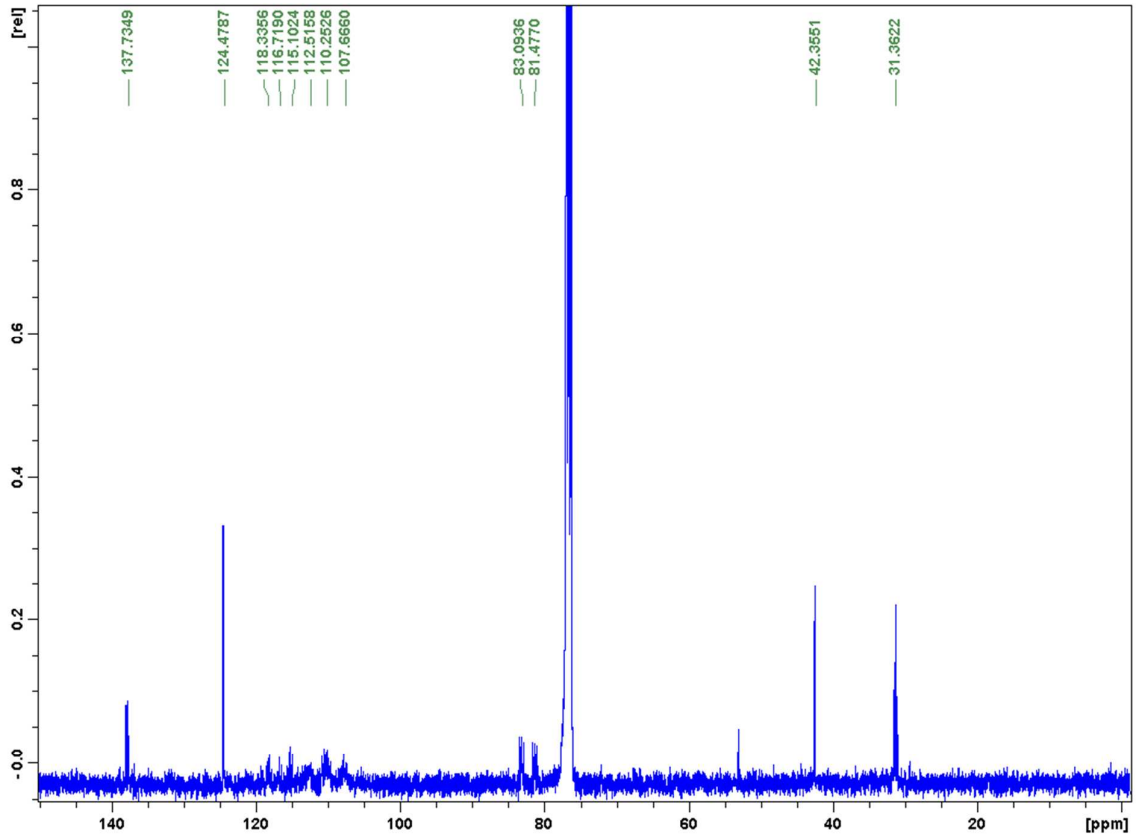

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

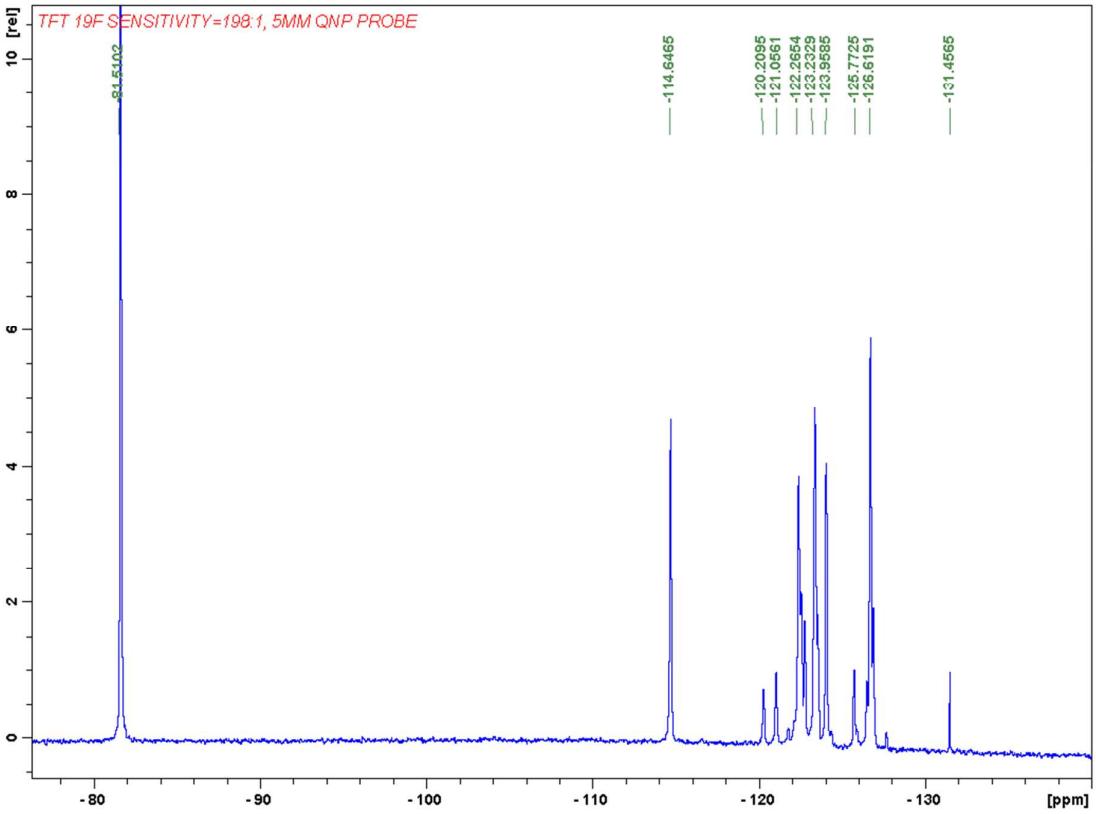

Figure S11. ^{19}F NMR spectrum of **3** in $CDCl_3$.

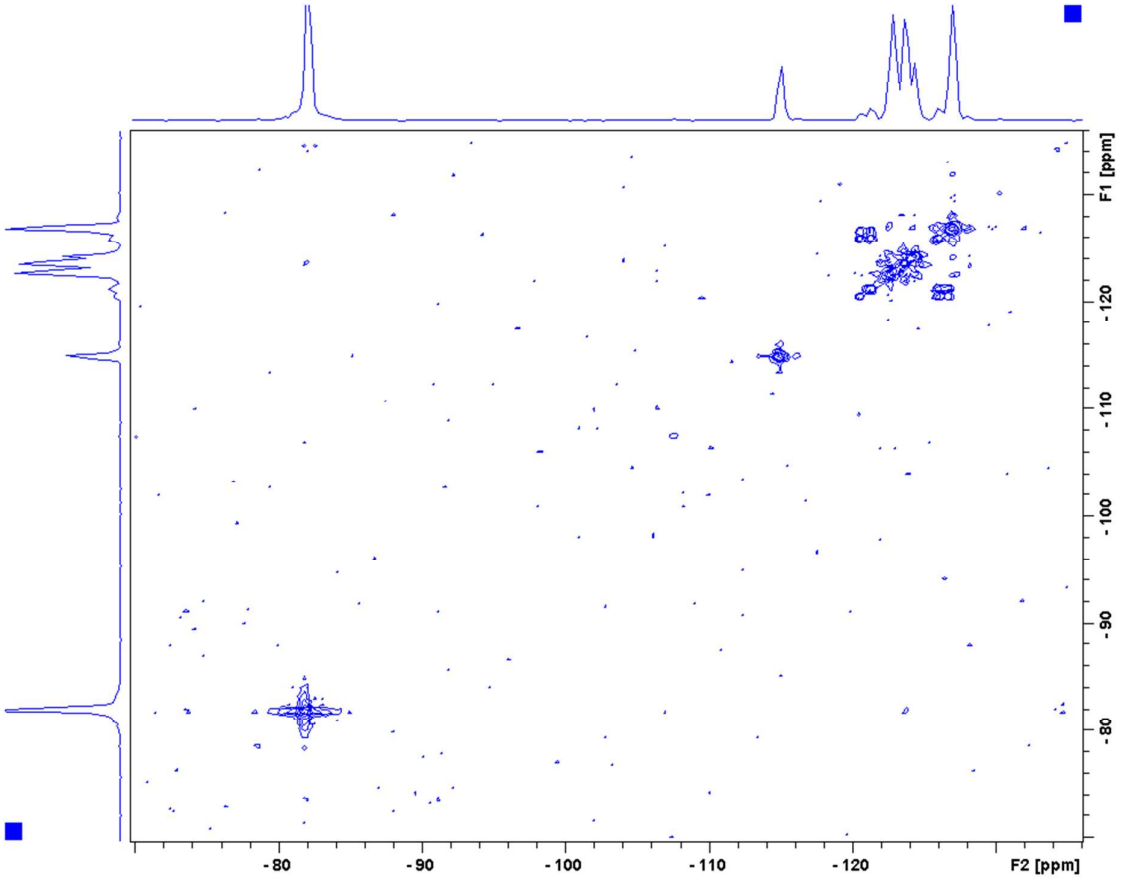

Figure S12. ^{19}F-^{19}F COSY NMR spectrum of **3** in acetone-d_6.

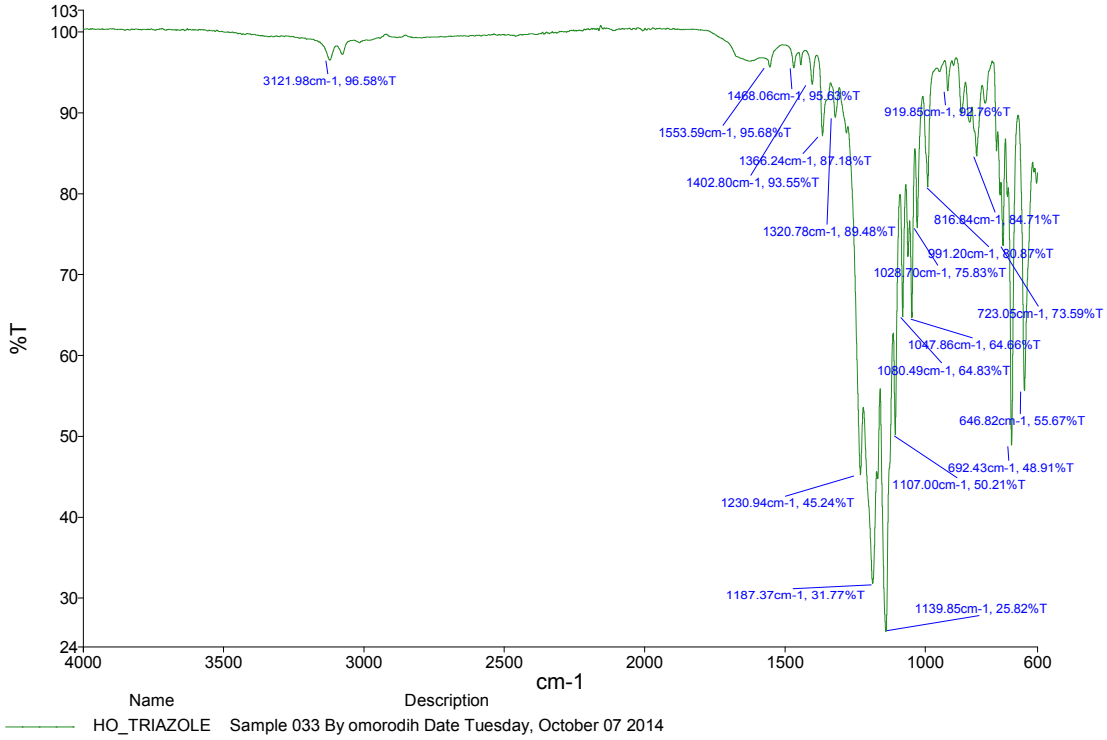

Figure S13. IR spectrum of **3**.

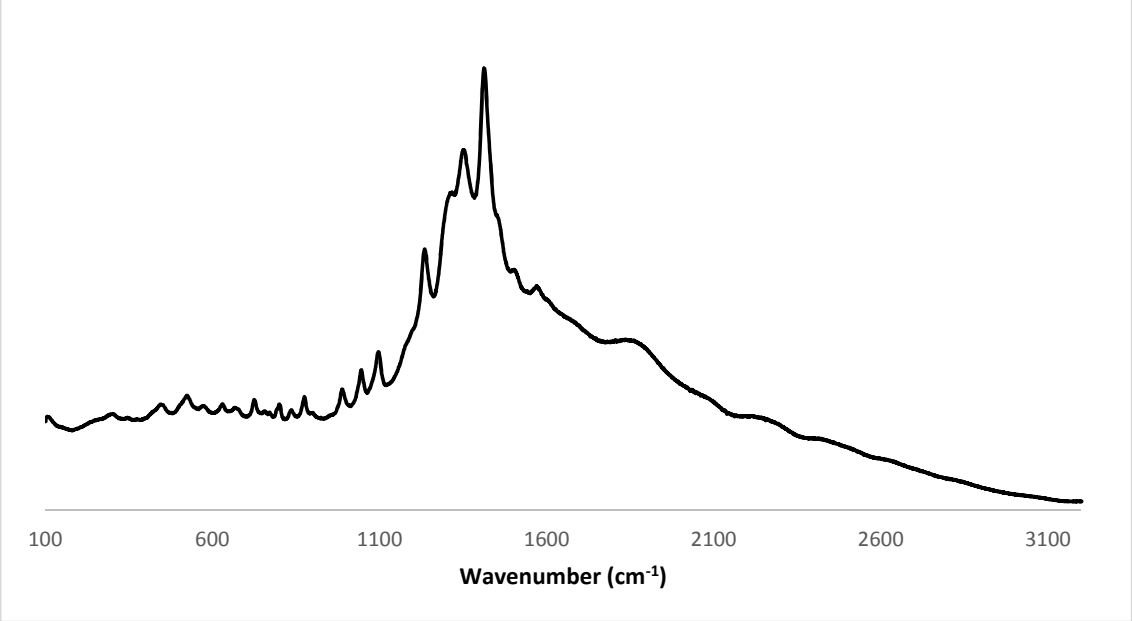

Figure S14. Raman spectrum of **3**.

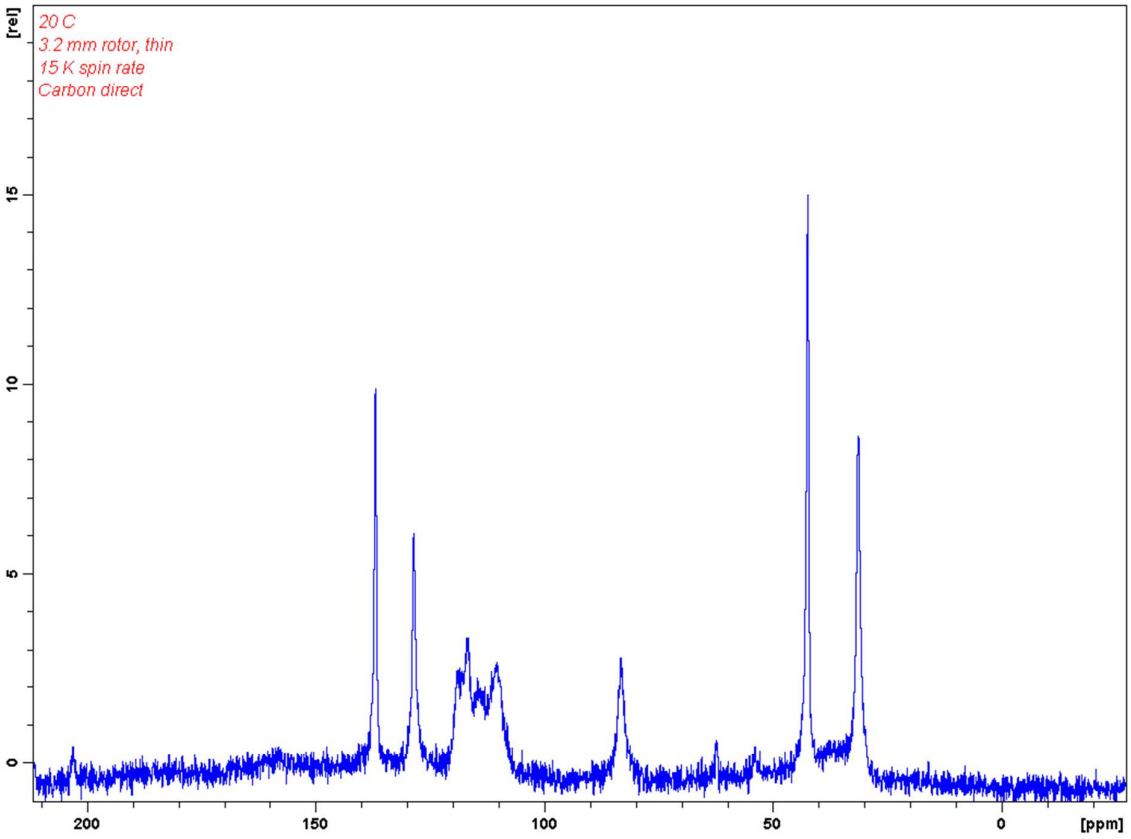

Figure S15. Solid State $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

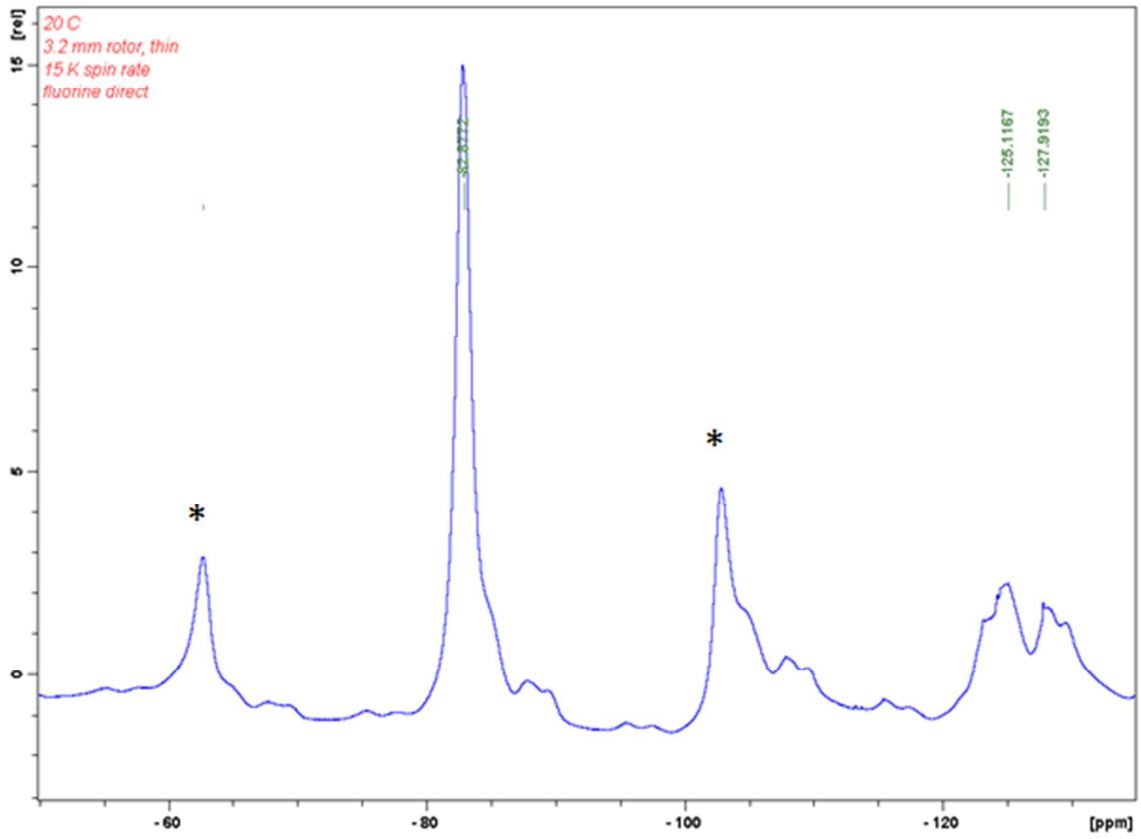

Figure S16. Solid-State ^{19}F NMR spectrum of **3**.

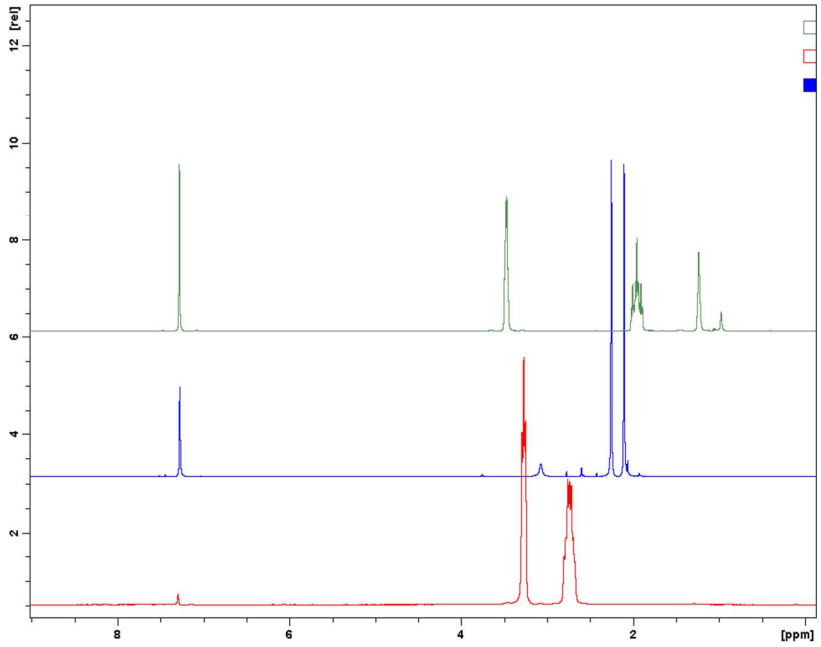

Figure S17. ^{1}H NMR spectra of the reaction of $CF_3(CF_2)_5CH_2CH_2I$ with DMF in $CDCl_3$; red $CF_3(CF_2)_5CH_2CH_2I$; blue $CF_3(CF_2)_5CH_2CH_2I$ + DMF; green $CF_3(CF_2)_5CH_2CH_2OH$.

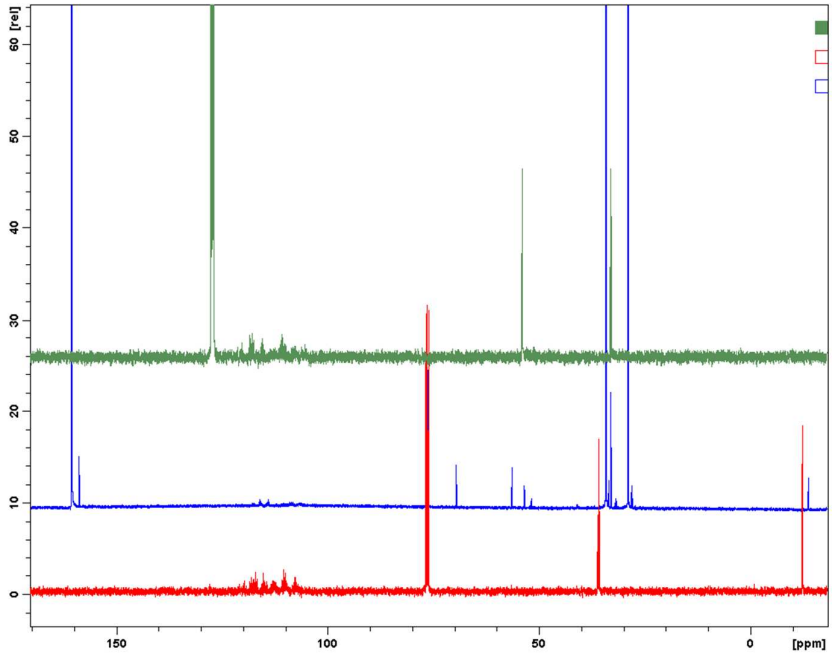

Figure S18. $^{13}C\{^{1}H\}$ NMR spectra of the reaction of $CF_3(CF_2)_5CH_2CH_2I$ with DMF in $CDCl_3$; red $CF_3(CF_2)_5CH_2CH_2I$; blue $CF_3(CF_2)_5CH_2CH_2I$ + DMF; green $CF_3(CF_2)_5CH_2CH_2OH$.

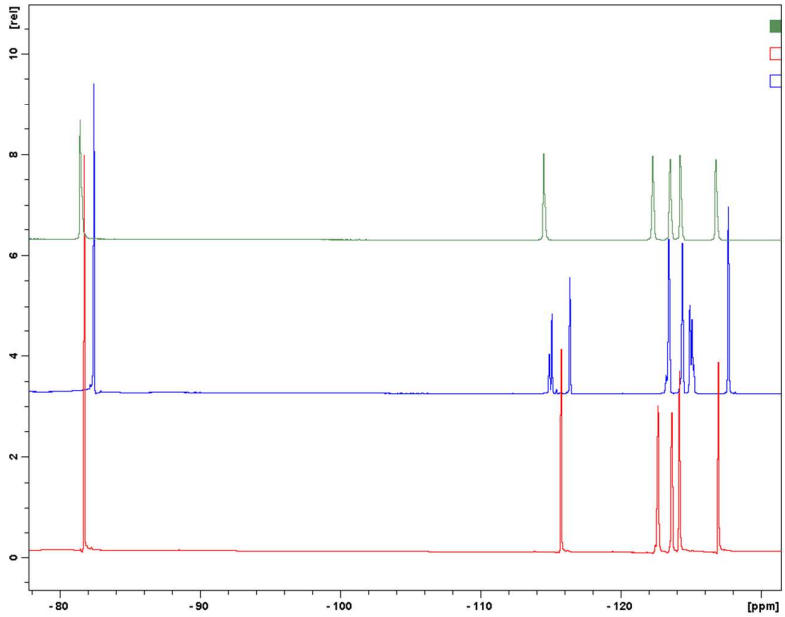

Figure S19. ^{19}F NMR spectra of the reaction of $CF_3(CF_2)_5CH_2CH_2I$ with DMF in $CDCl_3$; red $CF_3(CF_2)_5CH_2CH_2I$; blue $CF_3(CF_2)_5CH_2CH_2I$ + DMF; green $CF_3(CF_2)_5CH_2CH_2OH$.

Table S1 Basis set superposition error and dispersion contribution to interaction energy (in kcal/mol).

Complex	BSSE	Disp
2a	0.58	-3.75
2b	0.48	-5.04
2c	1.16	-9.85
2d	0.14	-1.05
2e	0.35	-2.51
3a	1.83	-15.67
3b	0.33	-2.09
3c	1.89	-14.96
3d	2.05	-17.30
3e	1.42	-14.85

Interaction energy calculated as IE = E(dimer) – E(monomer1, CP) – E(monomer2, CP), where CP indicates that the monomer energy has been counterpoise corrected. All geometries were extracted from crystal structure without further modification.