Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information
For

Structural Influence on Stimuli-Responsive Halogen-Bonded Luminescent Supramolecular Polymers from Heteroditopic Isomers

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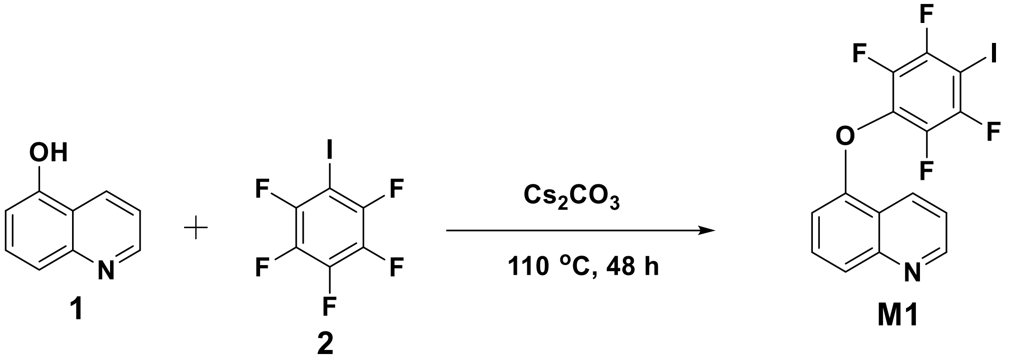
Materials and methods: All reagents were obtained from commercial suppliers and used without further purification unless otherwise mentioned. 5-Hydroxyquinoline was purchased from TCI Chemical Co. and 8-Hydroxyquinoline was purchased from Avra Synthesis Pvt. Ltd. Solvents were dried properly following standard procedures before setting up the reactions.^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 500 MHz, 400 MHz and 300 MHz spectrometer using $CDCl_3$ solvent. Chemical shifts (δ) are in ppm unit with TMS as the internal standard. The coupling constant (*J*) is reported in hertz (Hz). HRMS were done on XEVO G2-XS Q Tof and Micromass Q-Tof Micro machine. Column chromatography was carried out on silica gel (60-120 mesh). For UV-Vis absorption spectroscopy studies, spectroscopic grade solvents were used and spectra were recorded in a JASCO V-750 spectrophotometer. Transmission Electron Microscopy (TEM) was performed in JEOL-2010EX machine and JEOL-JEM-2100F machine operating at an accelerating voltage of 200KV. AFM images were captured with an Asylum Research MFP-3D AFM in tapping mode. Confocal laser scanning microscope (CLSM) was performed in Carl Zeiss-LSM880 machine. Fluorescence spectra were recorded in a FluoroMax-3 spectrophotometer from Horiba Jobin Yvon. FTIR spectra were obtained in a Perkin Elmer Spectrum 100 FT-IR Spectrometer. Dynamic Light Scattering (DLS) measurement was obtained from Malvern instrument (model: Malvern Zetasizer ZEN3500). SCXRD was done by Bruker Apex-III D8 venture instrument with CMOS detector. WAXRD in thin film state were measured in Bruker AXS D8 advance instrument with Cu-Kα tube ($\alpha = 0.15406$ nm).

Synthesis and characterization:

Synthetic strategies for **M1**, **M2** and **M3** were adopted from similar literature reports.[1]

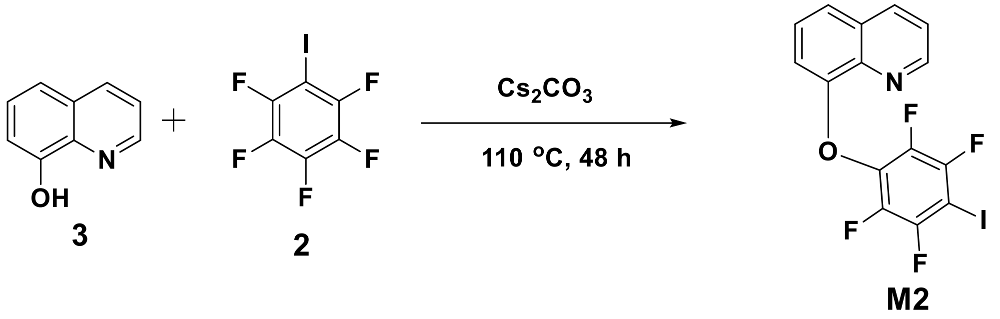
Synthesis of 5-(2,3,5,6-tetrafluoro-4-iodophenoxy)quinoline (M1): In a 25 mL round-bottomed flask, 5-hydroxyquinoline (**1**) (500 mg, 3.45 mmol), cesium carbonate (2.81 gm, 8.63 mmol) and pentafluoroiodobenzene (**2**) (6.8 mL, 51 mmol) were taken and the reaction mixture was heating at 110 °C for 96 hours under N_2 atmosphere. The reaction mixture was cooled and work-up was done using water and dichloromethane. The organic part was dried over Na_2SO_4 and the crude obtained was purified using a silica gel column (100-200 mesh). Initially the column was packed and eluted with hexane to remove the excess pentafluoroiodobenzene. The desired product was collected using dichloromethane as an eluent to obtain a white crystalline solid as a pure product

(295 mg, yield = 20%). M.P. = 234 °C-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.70 (dd, *J* = 9.4, 1.6 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 6.75 (d, *J* = 7.8 Hz, 1H).^{13}C-NMR (101MHz, $CDCl_3$, ppm): δ 152.5, 151.6, 149.3, 130.4, 128.8, 125.5, 121.5, 120.4, 108.4, 67.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.13 (d, *J* = 18.8 Hz), -151.51 (d, *J* = 18.8 Hz). HRMS (ESI): m/z calculated for $C_{15}H_6F_4INOH$ [**M1**+ H]$^+$: 419.9503; experimentally found : 419.9504.



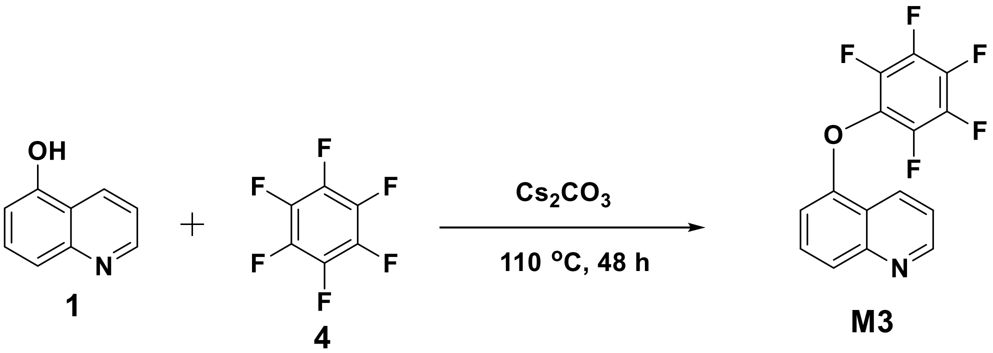
Scheme S1: Synthetic scheme for preparation of **M1**.

Synthesis of 8-(2,3,5,6-tetrafluoro-4-iodophenoxy)quinoline (M2): In a 25 mL round-bottomed flask, 8-hydroxyquinoline (**3**) (500 mg, 3.45 mmol), cesium carbonate (2.81 gm, 8.63 mmol) and pentafluoroiodobenzene (**2**) (6.8 mL, 51 mmol) were taken and the reaction mixture was heated at 110 ºC for 96 hours under N_2 atmosphere. The reaction mixture was cooled and work-up was done using water and dichloromethane. The dichloromethane part was dried over Na_2SO_4. Thereafter the product was purified by chromatography using a silica gel (100-200 mesh) column. Initially the column was packed and eluted with hexane to remove the excess pentafluoroiodobenzene. The desired product was collected using dichloromethane as an eluent to obtain an off-white crystalline solid (280 mg, yield = 19%). M.P. = 158 °C-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 5.9 Hz, 1H), 8.22 (d, *J* = 10.1 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.51 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H).^{13}C-NMR (101 MHz, $CDCl_3$, ppm): δ 152.8, 150.5, 148.8-146.3 (m, C-F coupling), 142.4-139.8 (m, C-F coupling), 139.8, 136.4,135.3-135.2 (m, C-F coupling), 130.2, 126.1, 123.6, 122.3, 112.9, 67.0 (t, C-F coupling, *J* = 28.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -120.09 (d, *J* = 18.8 Hz), -151.65 (d, *J* = 18.8 Hz). HRMS (ESI): m/z calculated for $C_{15}H_6F_4INOH$ [**M2** + H]$^+$: 419.9503; experimentally found : 419.9506.



Scheme S2: Synthetic scheme for preparation of **M2**.

Synthesis of 5-(perfluorophenoxy)quinoline (M3): In a 10 mL sealed tube, 5-hydroxyquinoline (**1**) (145 mg, 1.0 mmol), cesium carbonate (650 mg, 2.0 mmol) and hexafluorobenzene (**4**) (1.0 mL, 8.6 mmol) were taken and the reaction mixture was heated at 110 °C for 144 hours. The reaction mixture was cooled and work up was done using water and dichloromethane. The dichloromethane part was dried over Na_2SO_4 and the crude product was purified by column chromatography using a silica gel column (100-200 mesh). Initially the column was packed and eluted with hexane to remove the excess hexafluorobenzene. The desired product was collected using dichloromethane as an eluent to obtain a white crystalline solid (145 mg, yield = 47 %). M.P. = 109 °C-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.48 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H).^{13}C-NMR (75 MHz, $CDCl_3$, ppm): δ 152.8, 151.7, 149.4, 144.2-140.8 (m, C-F coupling), 141.1-137.5 (m, C-F coupling), 140.3-136.9 (m, C-F coupling), 130.5, 130.0-129.6 (m, C-F coupling), 128.9, 125.5, 121.6, 120.5, 108.1, ^{19}F NMR (377 MHz, $CDCl_3$) δ -153.68 (d, *J* = 21.2 Hz), -158.81 (t, *J* = 21.9 Hz), -161.41 (t, *J* = 21.4 Hz). HRMS (ESI): m/z calculated for $C_{15}H_6F_5NOH$ [**M3** + H]$^+$: 312.0442; experimentally found : 312.0447.



Scheme S3: Synthetic scheme for preparation of **M3**.

Experimental procedures:

Solution Preparation: Measured quantity of M1, M2 and M3 were dissolved in chloroform to prepare 1.0 mM stock solution. For performing various experiments in chloroform, the stock solution was diluted 10 times to obtain a final concentration of 0.1mM. For various experiments in MCH, measured aliquot from the stock solution in chloroform was taken in a vial and the solvent was allowed to evaporate completely by slow heating. The thin film obtained was dissolved in known volume of MCH and was heated to ensure complete dissolution. The clear solution was slowly cooled to room temperature and equilibrated for few hours before taking any measurement. The final concentration was adjusted to 0.1 mM in MCH.

UV-visible studies: For all the three monomers, **M1, M2** and **M3**, solutions were prepared as mentioned above. These solutions were transferred into 0.1 cm pathlength quartz cuvette and the UV-Vis measurements were recorded at 25 ^{o}C. For variable temperature experiment with **M1**, 0.1 mM solution in MCH was transferred in a quartz cell (pathlength 0.1 cm) which was heated to higher temperature and spectra were recorded at 10 ^{o}C interval, once the desired temperature was reached.

Photoluminescence studies: Spectra of all the three monomers were recorded at a concentration of 0.1 mM each in $CHCl_3$ and MCH. Excitation and emission band width were maintained at 5 nm each, pathlength = 10 mm.

FTIR studies: Same protocol was followed as mentioned earlier for solution preparation. FTIR spectra were recorded in the solid state and in MCH (Conc. = 10 mM).

Dynamic Light Scattering (DLS) studies: DLS data were recorded from the solutions of **M1**, **M2** and **M3** in MCH. The concentration was maintained at 0.1 mM in each case. For DLS experiment at 90 ^{o}C, the solution of **M1** in MCH was heated to 90 ^{o}C using an inbuilt Peltier of instrument and was equilibrated for 5 minutes at that temperature before collecting the data.

Transmission Electron Microscopy (TEM) studies: 10.0 μL solutions of **M1**, **M2** and **M3** (Concentration = 0.1 mM) in MCH was drop casted on carbon coated copper grid (Ted Pella, Inc.) and were left open to air for 48 h for complete drying prior to imaging. For imaging at higher temperature (85 ^{o}C), a solution of **M1** in MCH was transferred to a preheated water bath at 85 ^{o}C for 5 minutes. The hot solution was immediately drop casted on the TEM grid, which was left open to air for 48 h prior to measurement.

Confocal laser scanning microscope (CLSM) studies: MCH solution of all the three samples **M1**, **M2** and **M3** were drop casted on microscopic cover glass and allowed to dry in a desiccator for 48 h and images were captured from a confocal laser scanning microscope Carl Zeiss LSM880 at 10X magnification. Nile red was used as a dye for staining. Nile Red concentration was kept at 1x 10^{-5} mM. For red emission, 561 nm laser light were used.

AFM studies: 10 μL MCH solutions of **M1** was drop casted on mica surface and air-dried for 48 h before capturing the images.

Additional figures:

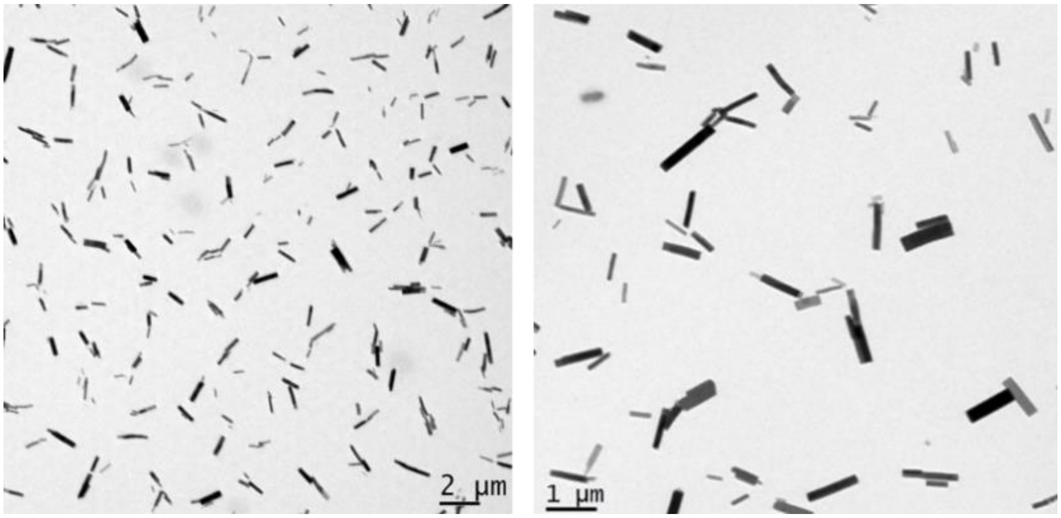


Figure S1: TEM images of **M1** in MCH. Concentration = 0.1 mM.

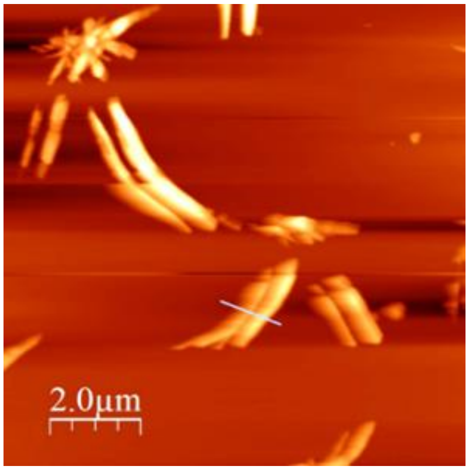


Figure S2: AFM images of **M1** in MCH, Concentration = 0.1 mM.

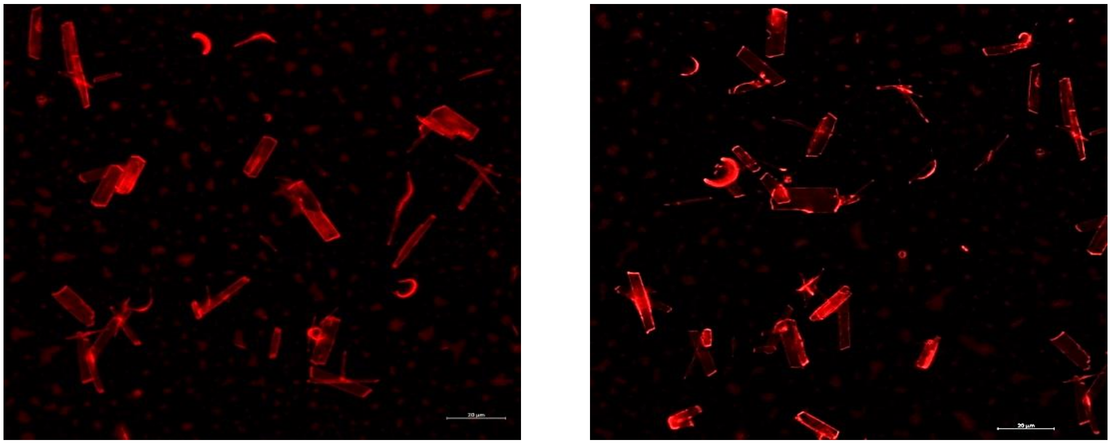


Figure S3: CLSM images of **M1** in MCH. Concentration = 0.1 mM, Nile red was used as a staining agent.

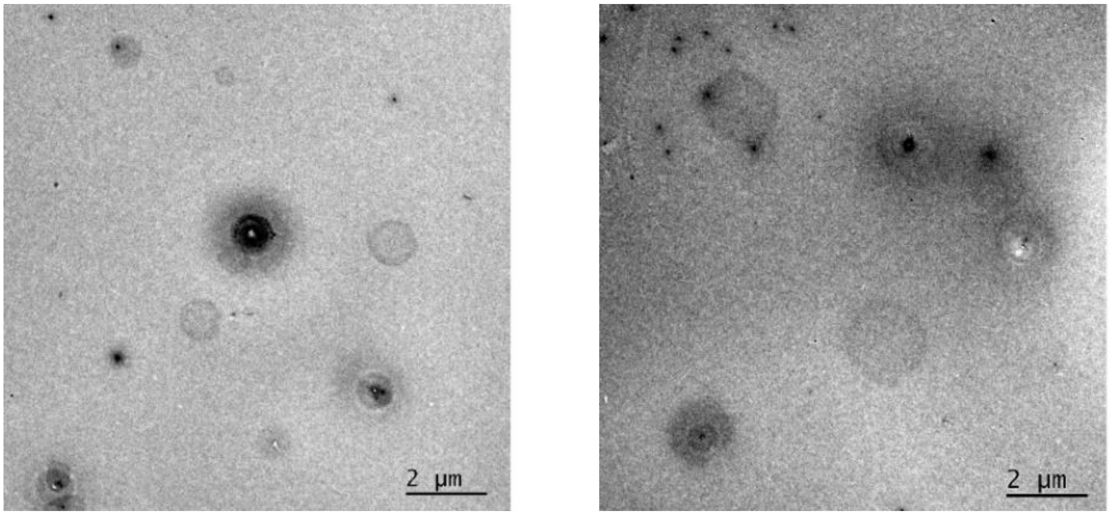


Figure S4: TEM images of **M3** in MCH. Concentration = 0.1 mM.

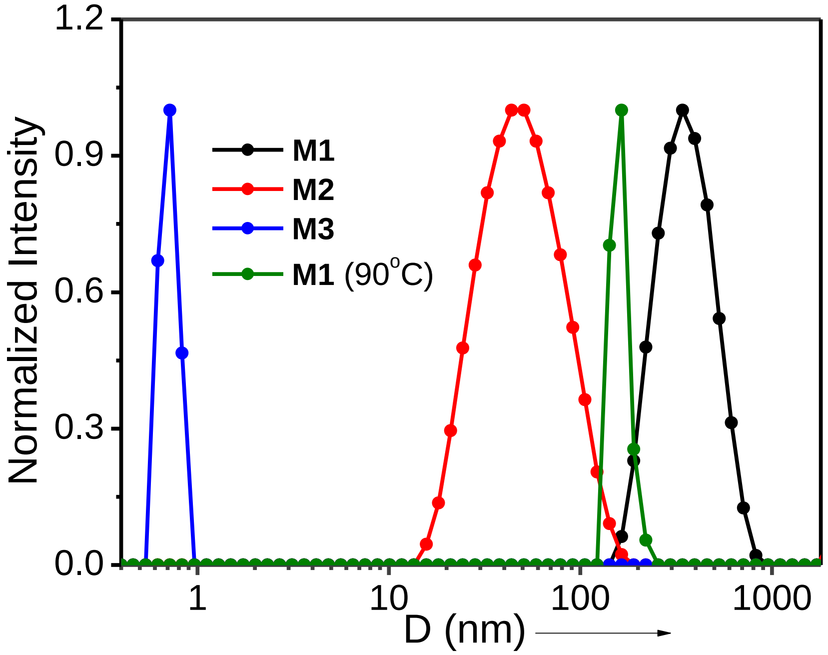


Figure S5: DLS data of **M1**, **M2** and **M3** in MCH. Y-axis is Intensity % normalized to 1. Conc. = 0.1 mM.

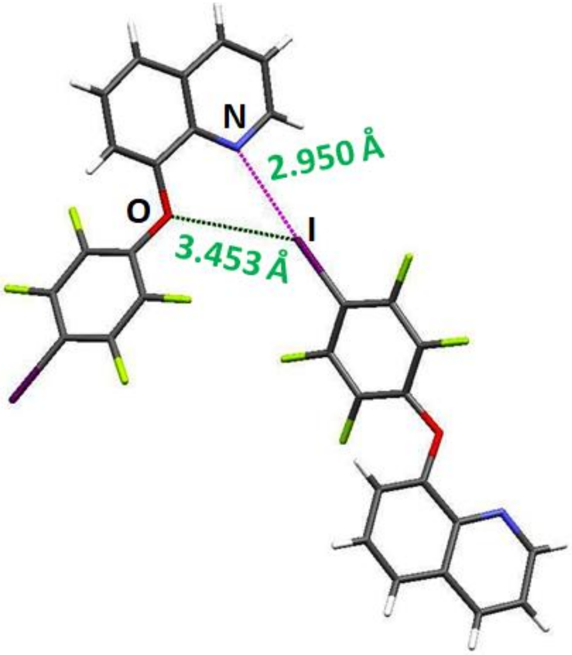


Figure S6: Single crystal structure of **M2** showing O···I contact = 3.453Å, which is slightly shorter than the sum of their van der Waals radii (3.5 Å). This suggests the possibility of very weak X-bonding between O-atom and I-atom that probably elongates the N···I distance in **M2**, compared to **M1**.

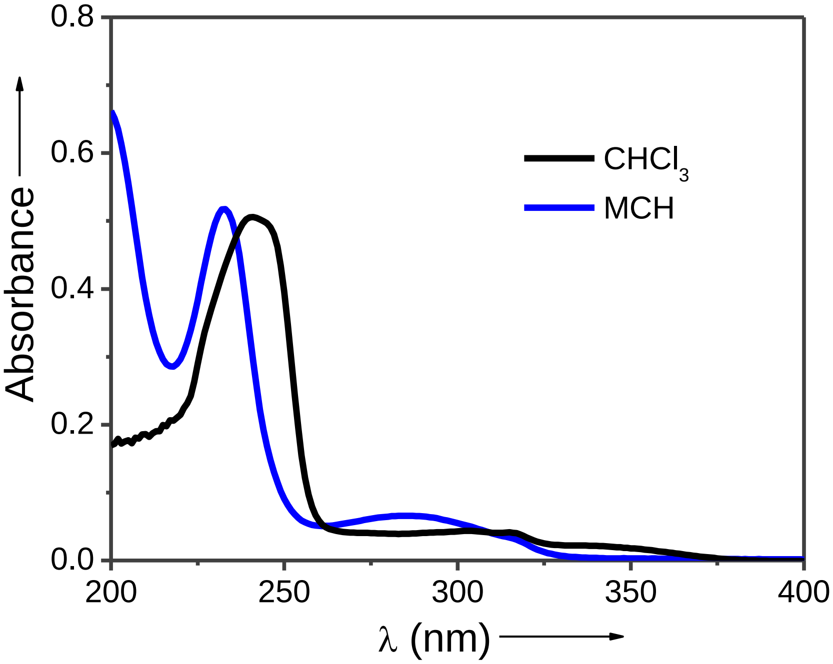


Figure S7: UV-Vis spectrum for **M2** in chloroform and MCH. Concentration = 0.1 mM.

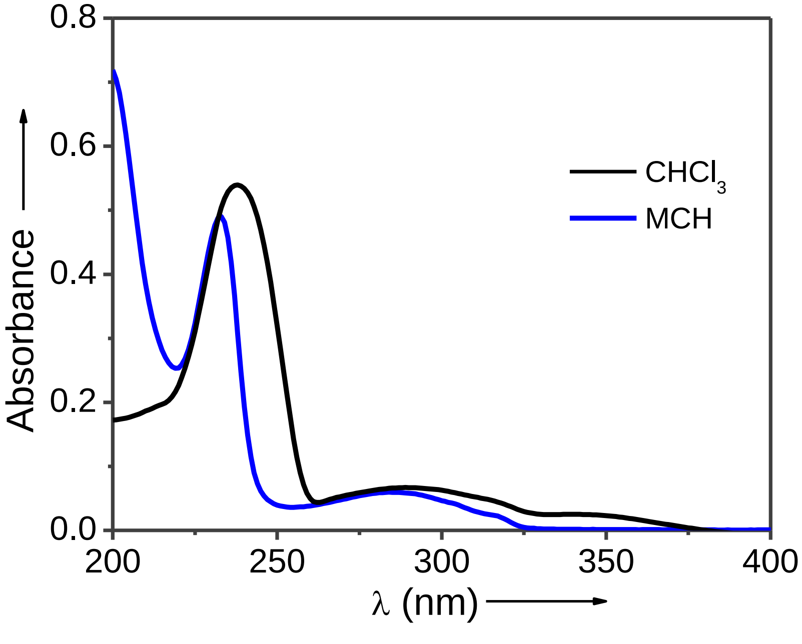


Figure S8: UV-Vis spectrum for **M3** in chloroform and MCH. Concentration = 0.1 mM.

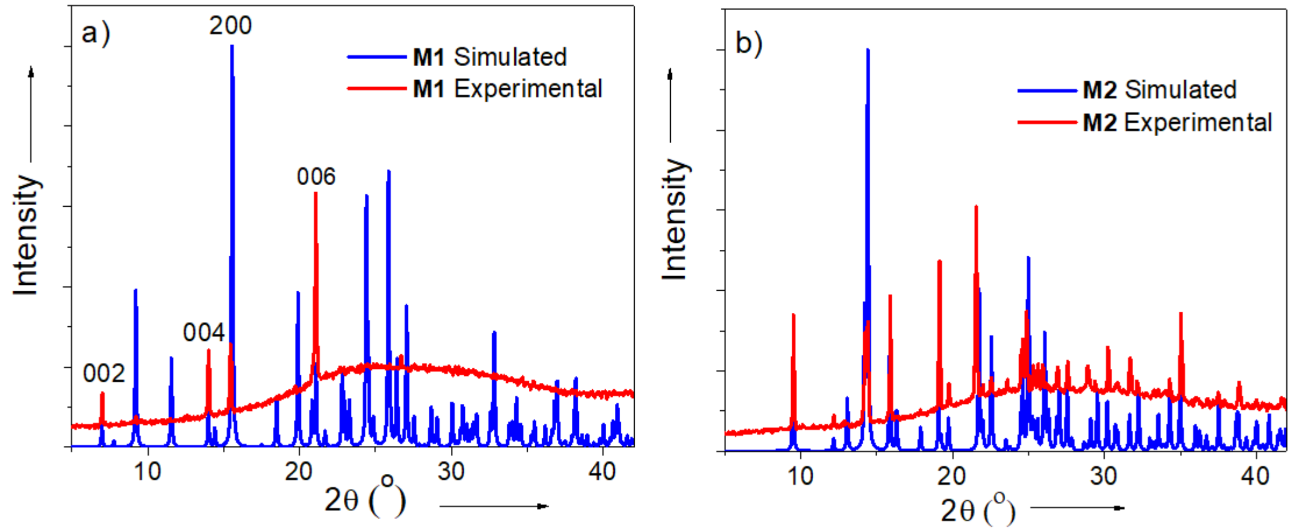


Figure S9: Comparison of the simulated XRD pattern from the single crystals with the WAXRD data in the film state obtained from a solution of a) **M1** and b) **M2** in MCH.

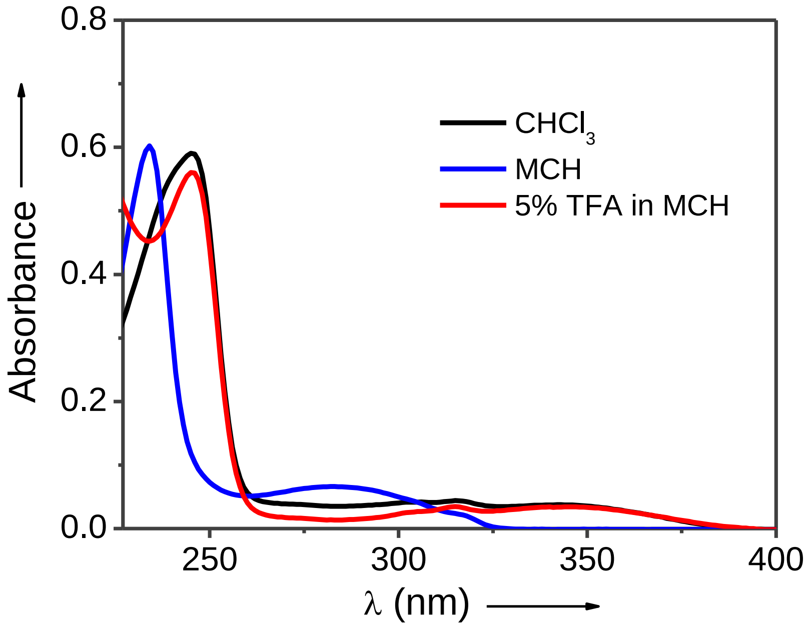


Figure S10: Red-shifted UV-Vis spectrum of **M1** in presence of 5% trifluoroacetic acid (TFA) in MCH.

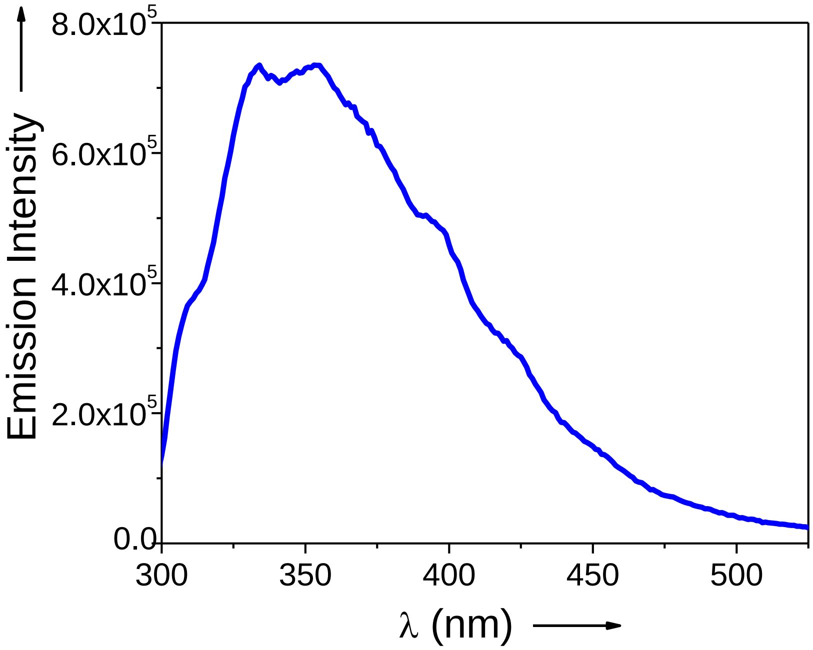


Figure S11: Emission spectra of **M1** in MCH. Conc. = 0.1 mM, λ_{ex} = 280 nm.

X-ray structure determinations:

The molecular structure of **M1**, **M2** and **M3** was determined by single crystal X-ray structure determination technique. Diffraction-quality crystals were obtained from dichloromethane. Single crystal for the samples were coated with Parabar oil and was mounted under a nitrogen cold stream. Data collections was performed at 151K on a Bruker D8VENTURE Microfocus diffractometer equipped with PHOTON II Detector, with Mo Kα radiation (λ = 0.71073Å), controlled by the APEX3 (v2017.3-0) software package. Space group was assigned by systematic absences (determined by XPREP) and analysis of metric symmetry and was further checked by PLATON.[2] Structure was solved by direct method and refined against all data in the reported 2θ ranges by full-matrix least squares on F^2 using the SHELXL program suite[3] in the WinGX[4] interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The details of crystal data collection and refinement of compound **M1**, **M2** and **M3** are summarized in Table **S1, S2** and **S3** respectively

Table S1

Compound	**M1**
Empirical formula	$C_{15} H_6 F_4 I N O$
FW	419.11
T, K	161(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.6686(18)
b, Å	4.5292(7)
c, Å	25.933(4)
α, deg	90.00°
β, deg	102.908°(5)
γ, deg	90.00°
V, Å^3	1335.9(14)
Z, ρ, Mg m^{-3}	4, 2.084
μ, mm^{-1}	2.084
F(000)	800
Refln. collected	12588
Ind. Reflen	2953
Data/restn./param	2953 / 0 / 199
GOF on F^2	1.249
Final R indices [I>2σ(I)]	0.0930, 0.1034

Table S2

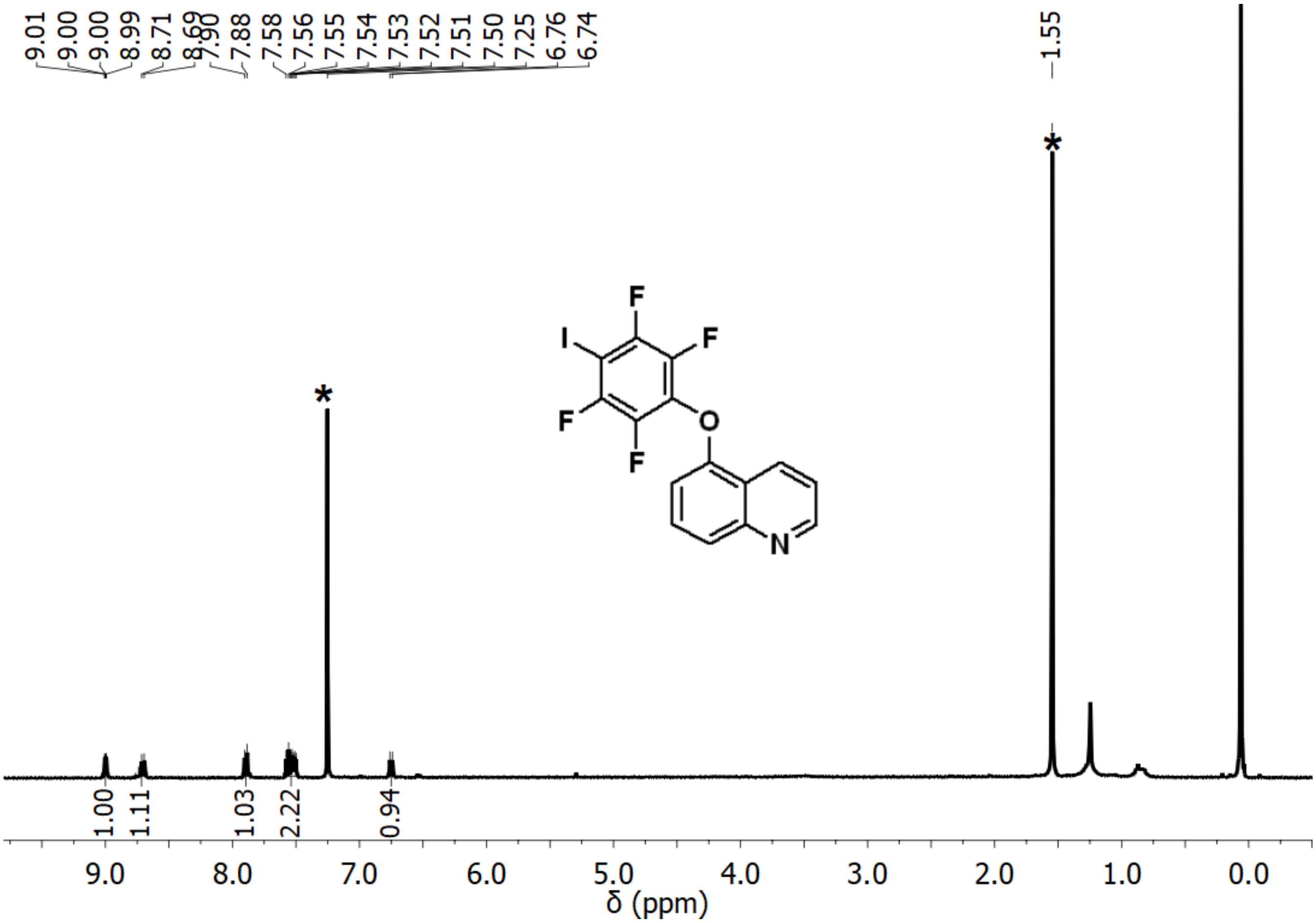
Compound	**M2**
Empirical formula	$C_{15}H_{6}F_{4}INO$
FW	419.11
T, K	293(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
a, Å	14.522(3)
b, Å	12.084(3)
c, Å	8.162(2)
α, deg	90.00°
β, deg	90.00°
γ, deg	90.00°
V, $Å^3$	1432.3(6)
Z, ρ, Mg m^{-3}	4, 1.944
μ, mm^{-1}	2.280
F(000)	800
Refln. collected	11866
Ind. Reflen	3104
Data/restn./param	3104 / 0 / 200
GOF on F^2	1.087
Final R indices [I>2σ(I)]	0.0444, 0.0477

Table S3

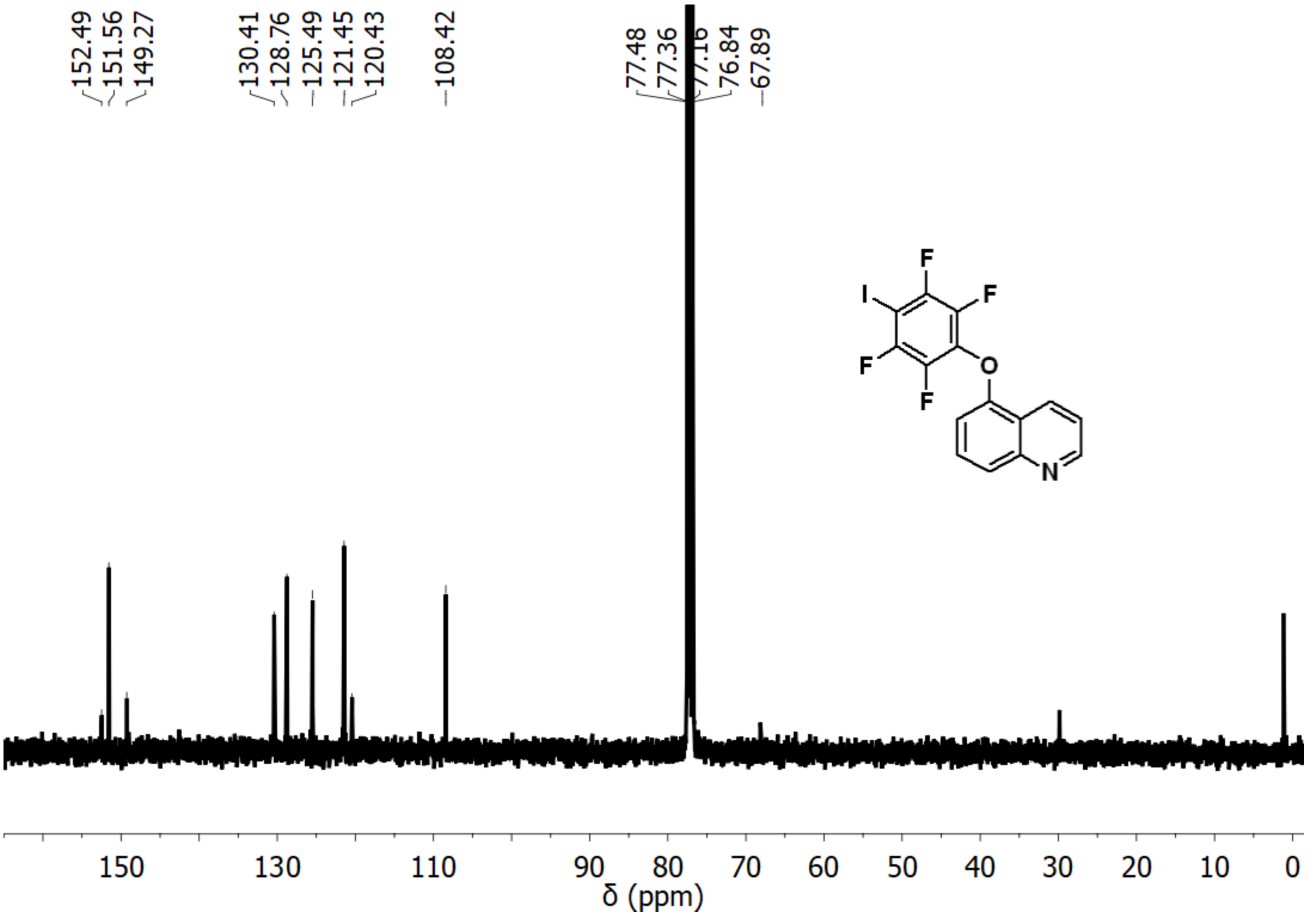
Compound	**M3**
Empirical formula	C_{15} H_6 F_5 N O
FW	311.21
T, K	102(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	14.424(9)
b, Å	7.211(5)
c, Å	24.193(15)
α, deg	90.00°
β, deg	91.950(17)
γ, deg	90.00°
V, $Å^3$	2515(3)
Z, ρ, Mg m^{-3}	8, 1.644
μ, mm^{-1}	2.826
F(000)	1248
Refln. collected	5288
Ind. Reflen	2676
Data/restn./param	2676 / 0 / 397
GOF on F^2	1.120
Final R indices [I>2σ(I)]	0.1178, 0.1520

NMR and HRMS Spectra:

^{1}H NMR spectrum of M1: (*) denotes the residual solvent peak and associated water.

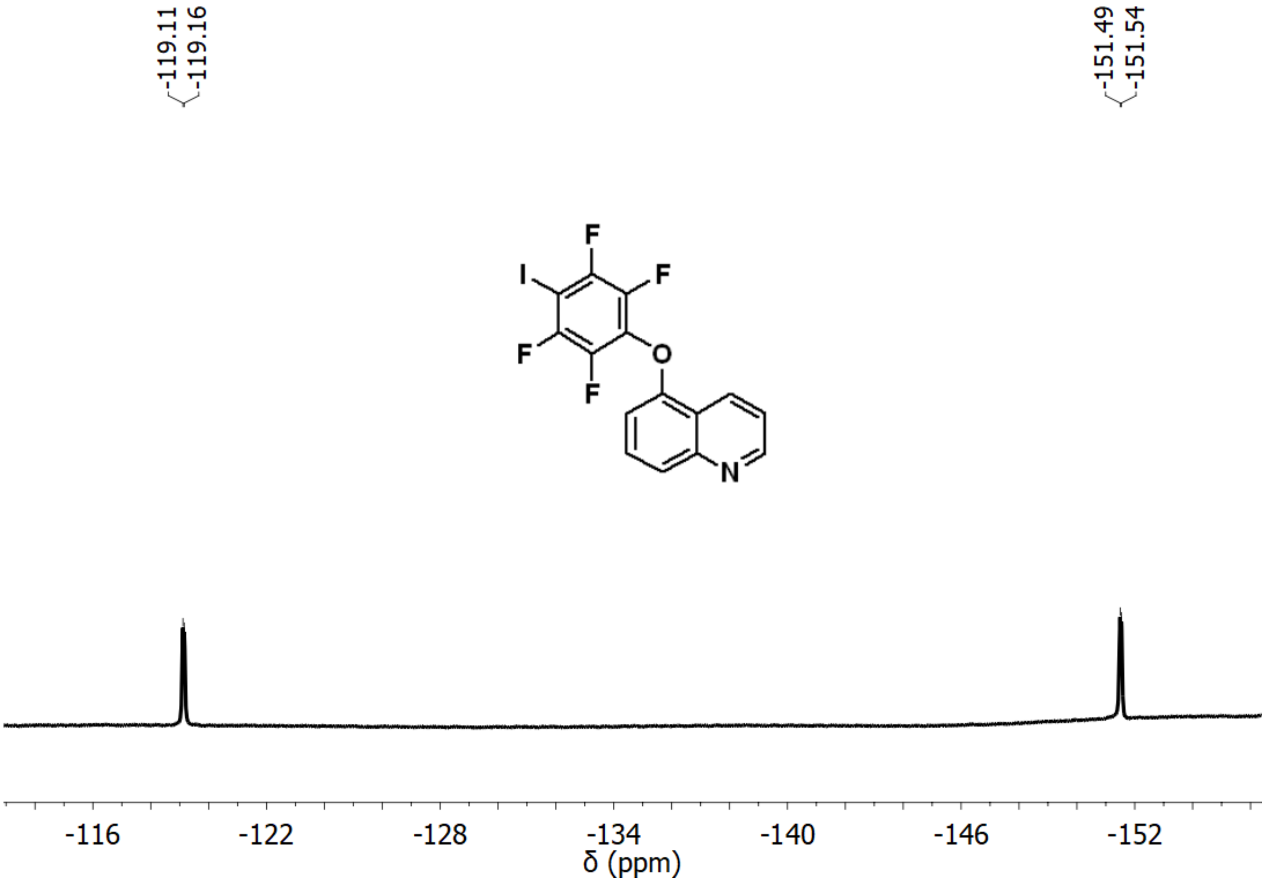


^{13}C NMR spectrum of M1:

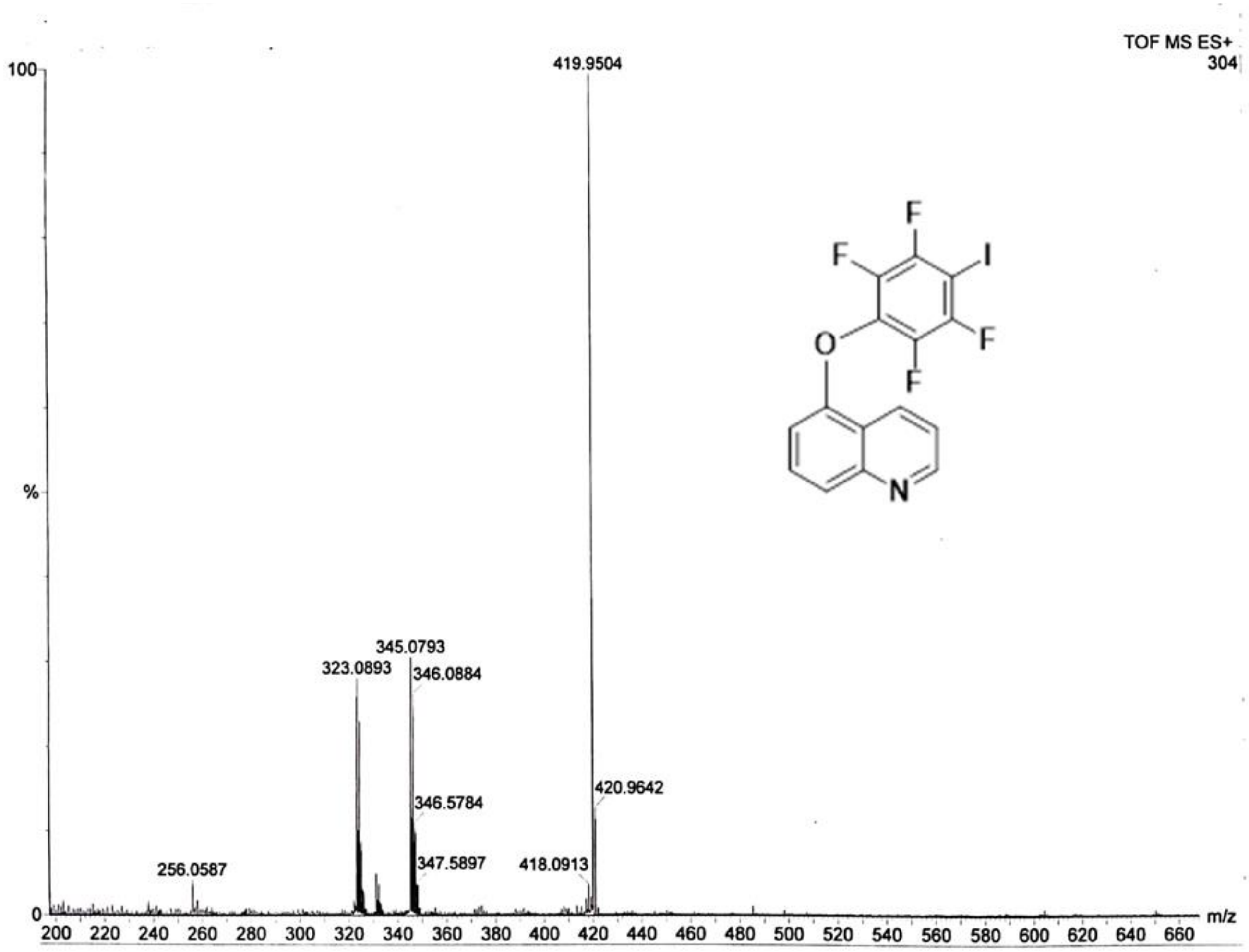


Note: Due to large number of fluorine-carbon couplings with very high coupling constants[5] (^{1}J C-F > 240 Hz), the ^{13}C peak intensities for the C-F carbons in tetrafluoroiodophenyl ring between 130-150 ppm could not be traced even after overnight scanning with 70 mg sample. Above this concentration, **M1** started crystallizing out. ^{19}F NMR spectroscopy was used to characterize the presence of tetrafluoroiodophenyl ring attached to 5-hydroxyquinoline.

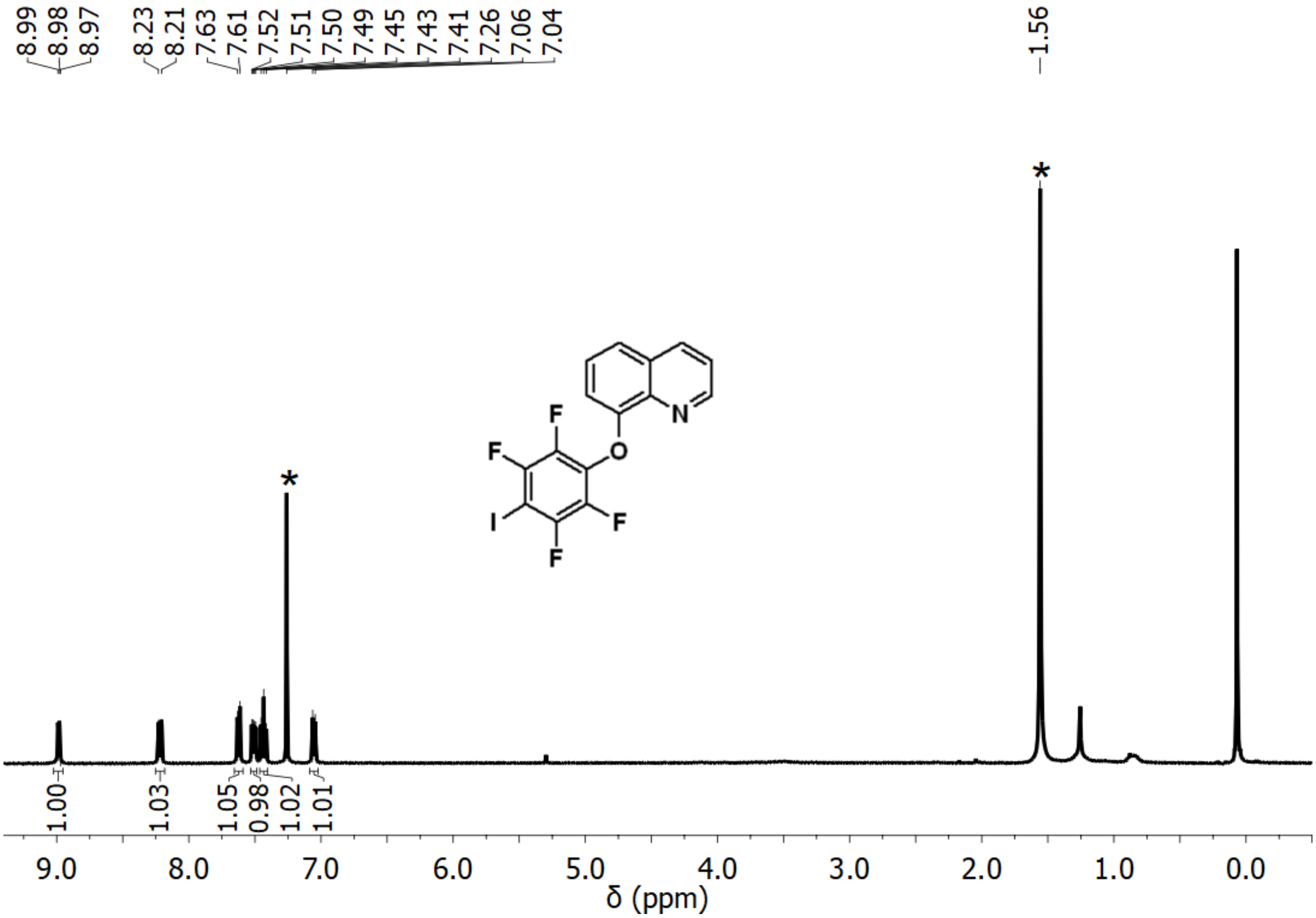
^{19}F NMR spectrum of M1:



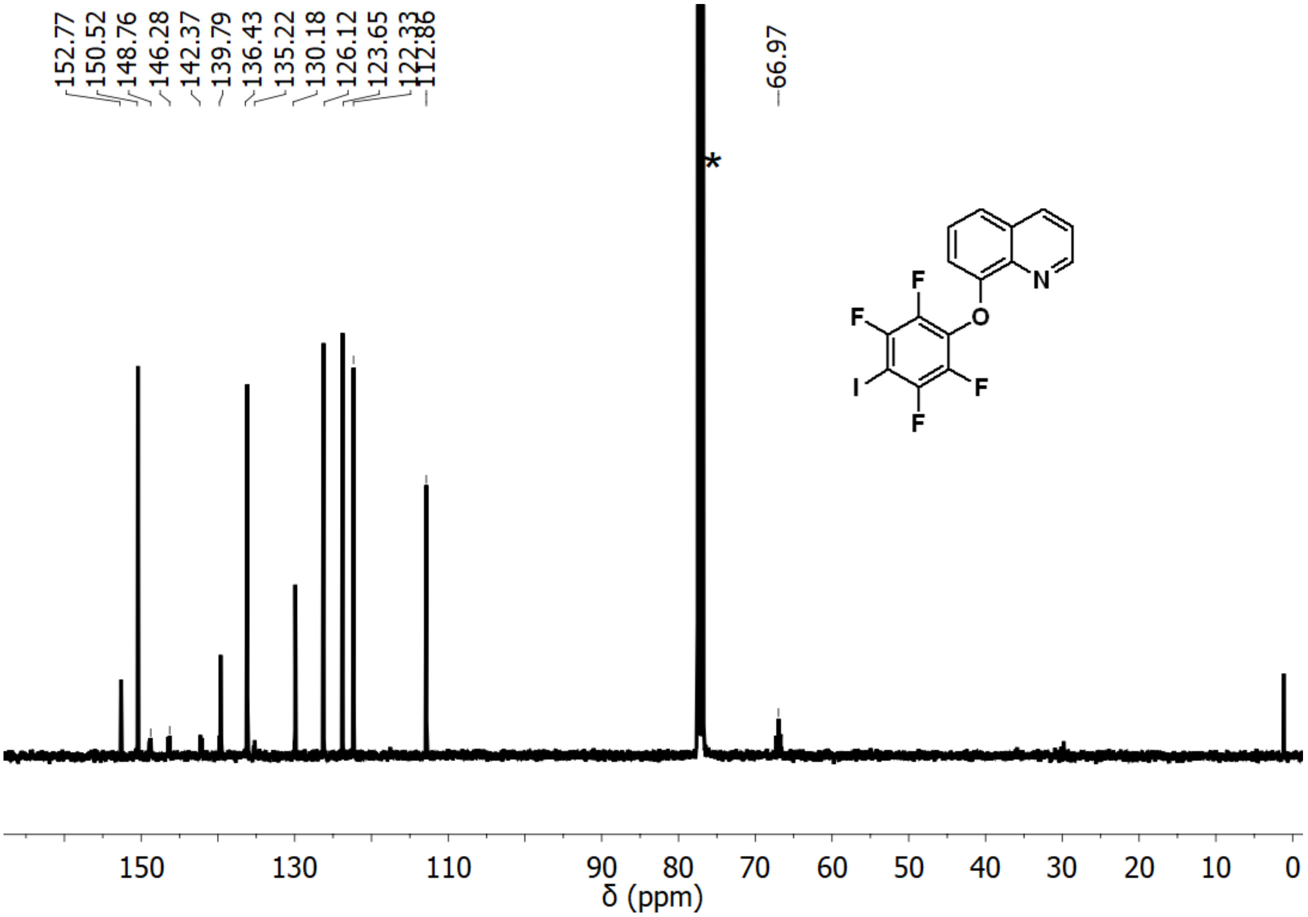
HRMS data of M1:



^{1}H NMR spectrum of M2: (*) denotes the residual solvent peak and associated water.

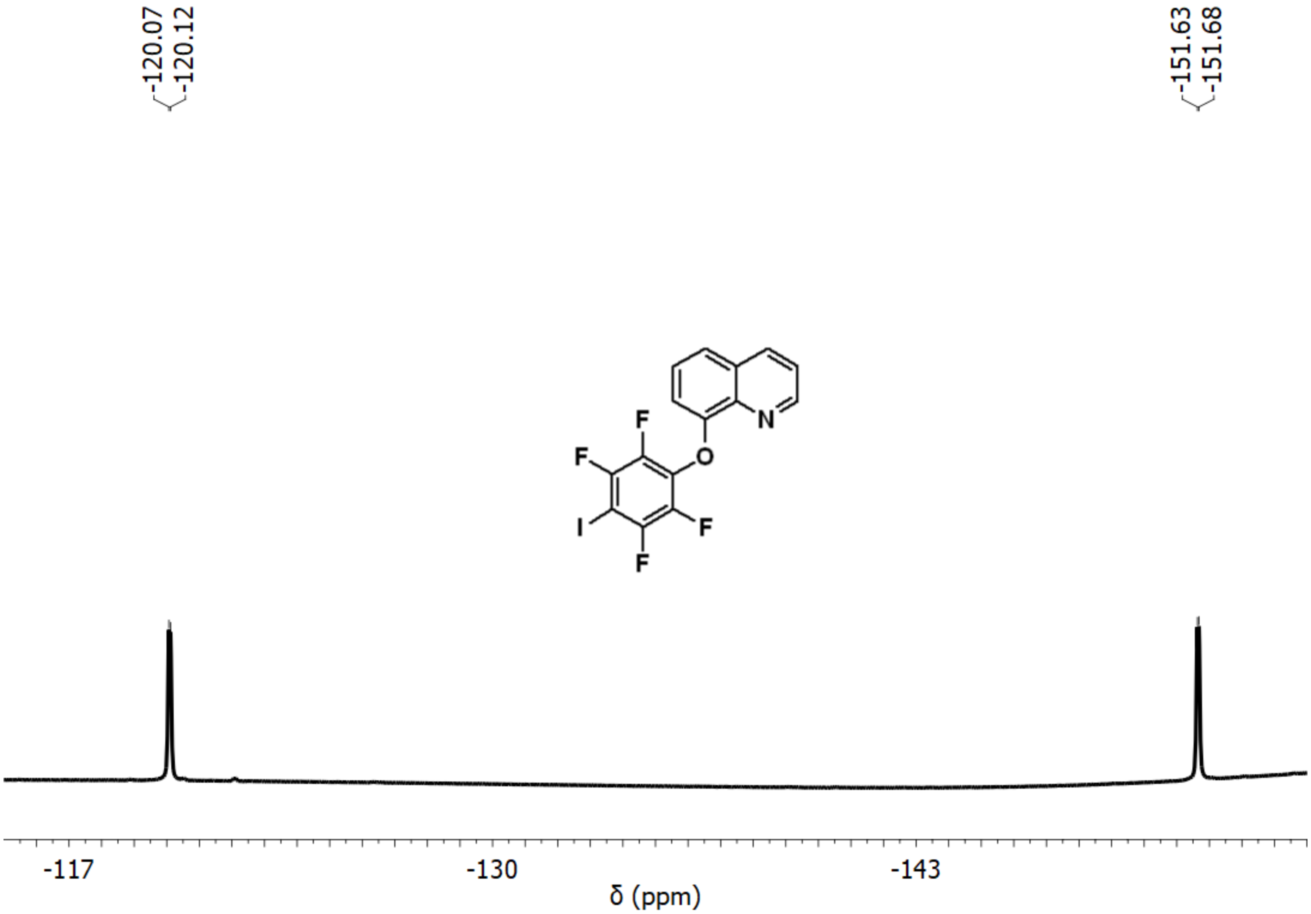


^{13}C NMR spectrum of M2:

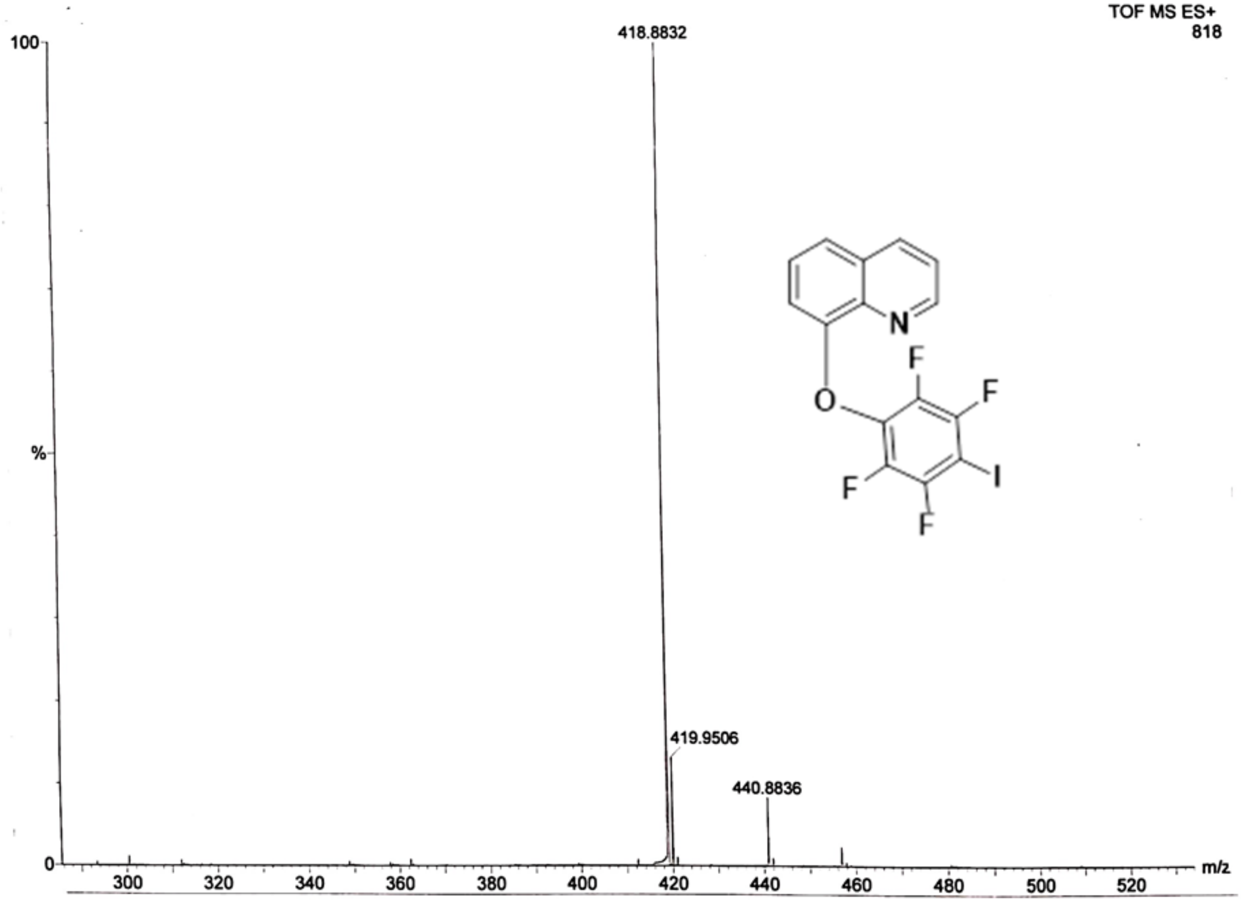


Note: Due to large number of fluorine-carbon couplings, the ^{13}C peak intensities for the tetrafluoroiodophenyl ring carbons drastically reduced and peak splitting was observed.[5]

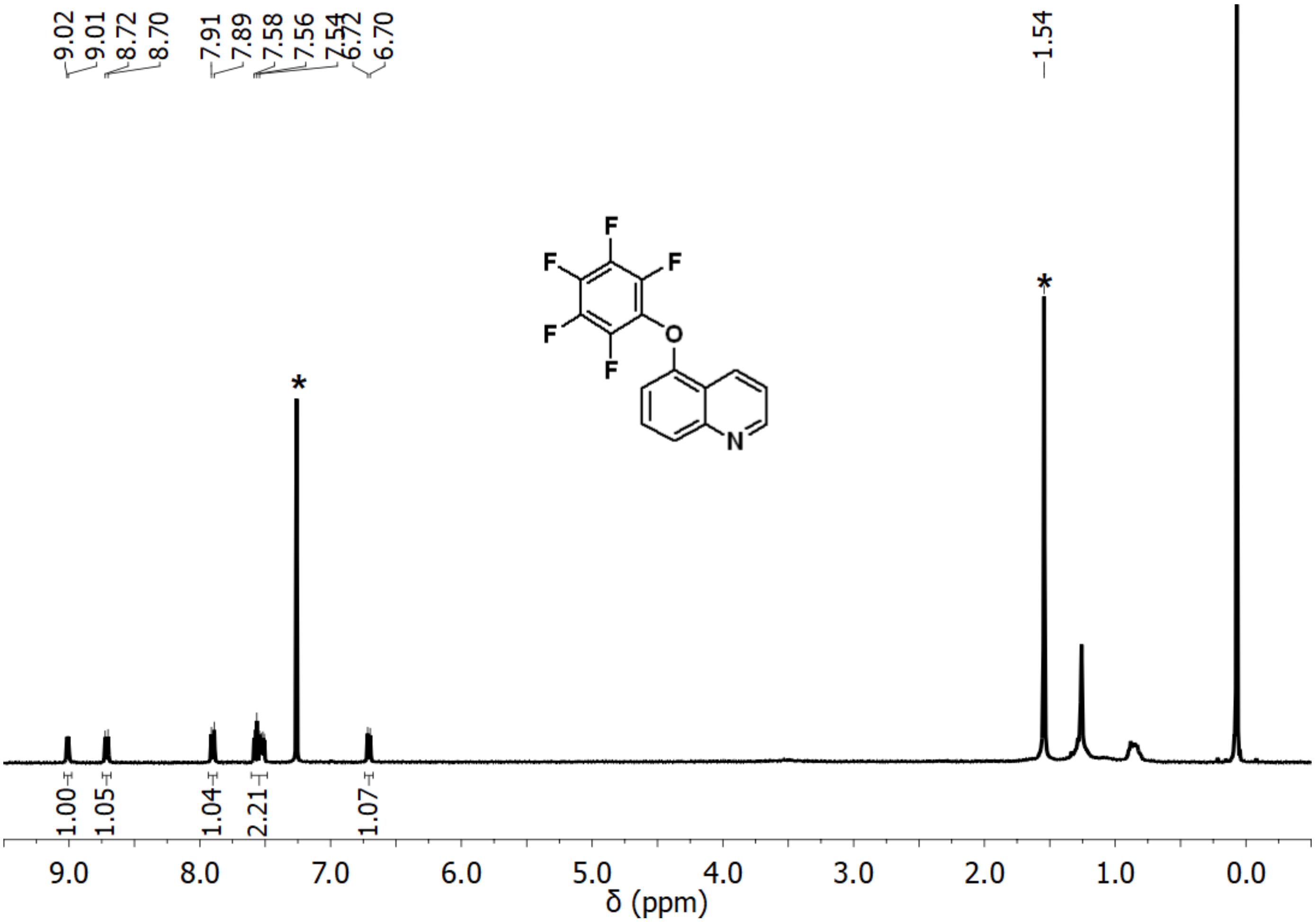
^{19}F NMR spectrum of M2:



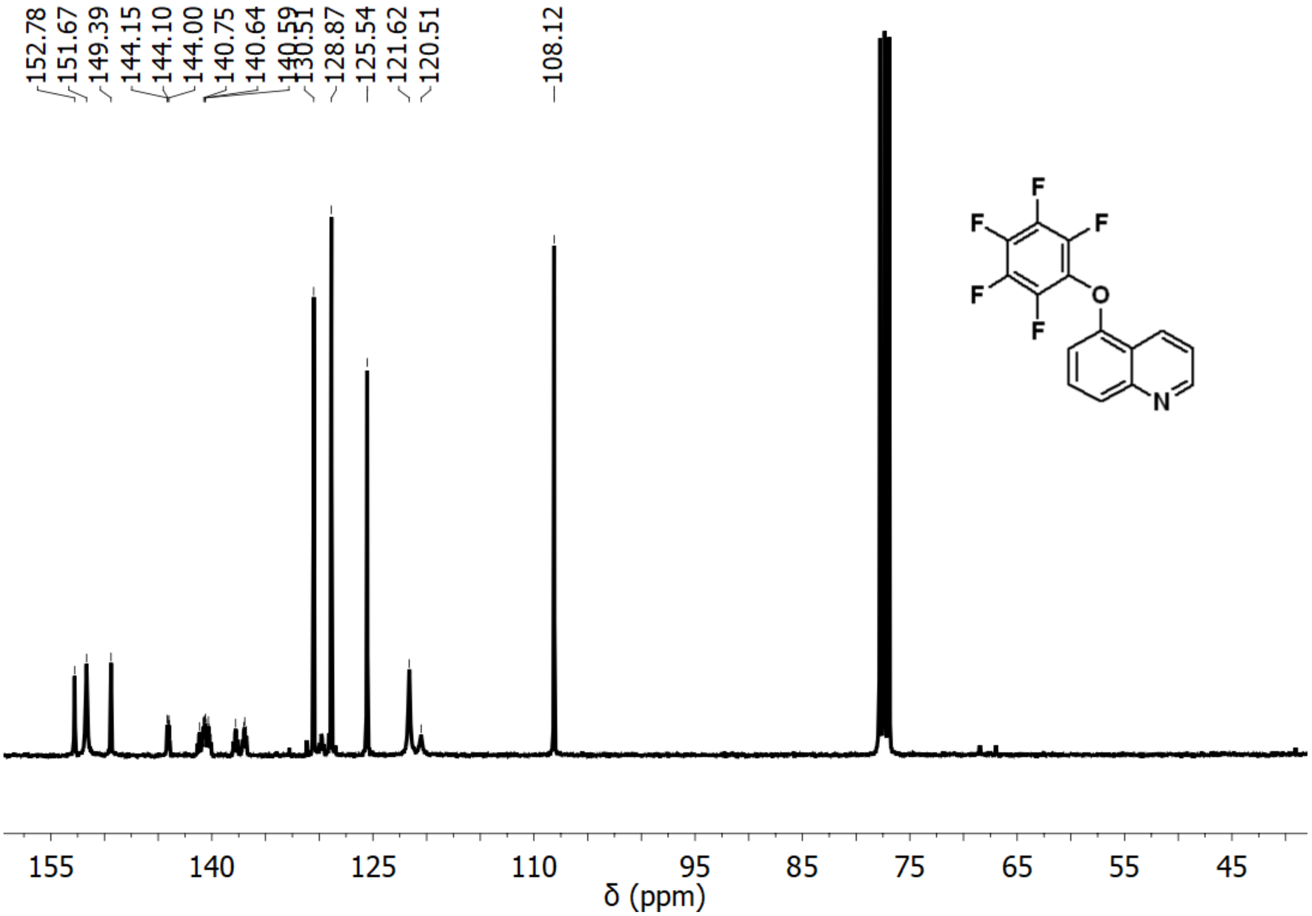
HRMS data of M2:



^{1}H NMR spectrum of M3:(*) denotes the residual solvent peak and associated water.

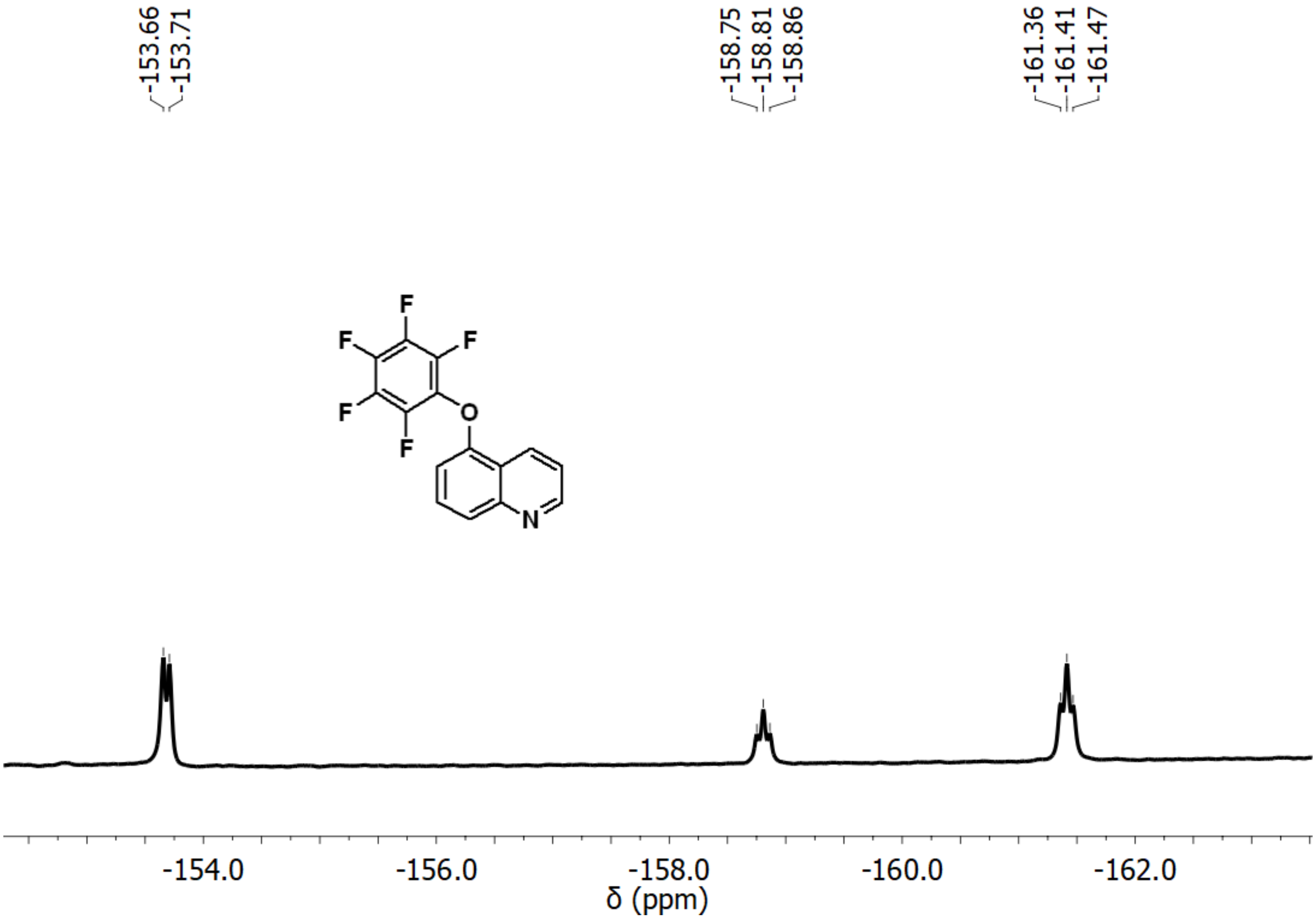


^{13}C NMR spectrum of M3:

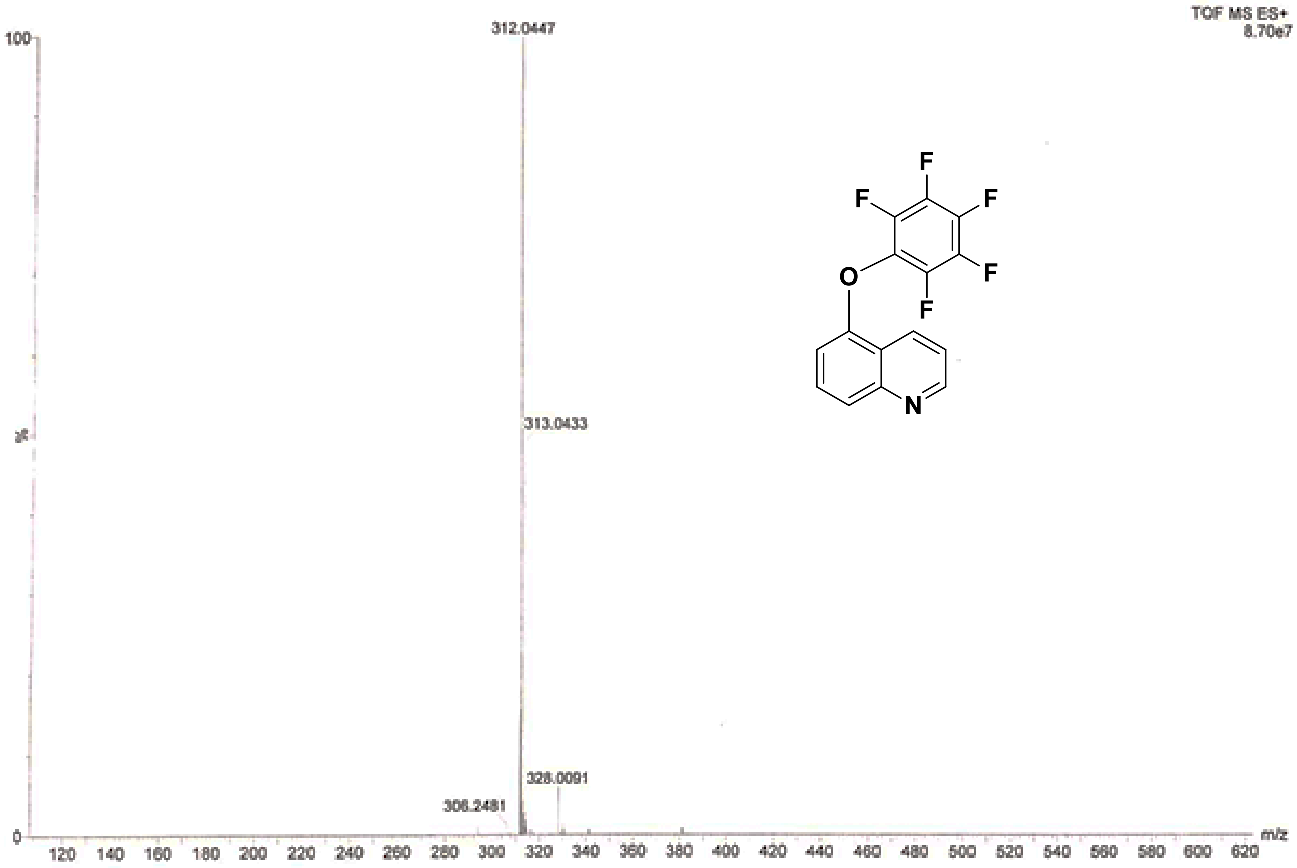


Note: Due to large number of fluorine-carbon couplings, the ^{13}C peak intensities for the pentafluorophenyl ring carbons drastically reduced and peak splitting was observed.[5]

^{19}F NMR spectrum of M3:



HRMS data of M3:



Reference:

1. A. Mele, P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *J. Am. Chem. Soc.*,2005, **127**,14972-14973.
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4. L. J. Farrugia, *J. Appl. Crystallogr.*,1999, **32**, 837−838.
5. V. Arun, L. Roy and S. De Sarkar, *Chem. Eur. J.*, 2020, **26**, 16649-16654.