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Fluorinated phthalonitrile resins with improved thermal oxidative stability

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Materials and methods. All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. Dimethylacetamide (DMAA), dichloromethane (DCM), petroleum ether and methyl ethyl ketone (MEK) were purchased from Alfa Aesar Company and were used as received. THF (HPLC grade), silica gel (0.04–0.065mm seed), potassium carbonate, hydroquinone, 4-nitrophthalonitrile, 3,4,5,6-tetrafluorophthalonitrile, 4-aminophenol, 3-aminophenol, copper(II) 2-ethylhexanoate, $ZnCl_2$, $SnCl_2$, CuI and 1,3-bis(4-aminophenoxy)benzene (APB) were obtained from Sigma-Aldrich and used as received. Hexafluorobenzene, tetrafluorohydroquinone, 4-amino-2,3,5,6-tetrafluorophenol, potassium fluoride were purchased from Perm Chemical Company LLC (Perm, Russia) and were used without further purification.

NMR spectra were run on a Bruker Advance 600 at 600 MHz for ^{1}H, 151 MHz for ^{13}C and 565 MHz for ^{19}F with DMSO-d$_6$ as solvents. Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix, at a heating rate of 10 °C min^{-1} and an Ar purge rate of 50 ml min^{-1} and was applied for the determination of melting points of the monomers and the curing study. Thermal stability was evaluated by thermogravimetric analysis (TGA) on Netzsch TG 209 P3 Tarsus at a heating rate of 10 °C min^{-1} in range 40–1000 °C and Ar or air purge rate of 50 ml min^{-1}. Glass transition temperature (T_g) was measured by the 3 point bending method on Netzsch TMA 402 with 1.82 MPa load. Melt viscosity was measured with MCR 302 rheometer with cone 7 at 40 rpm.

Tin(II) chloride dehydration was performed at 300 °C and reduced pressure to exclude the possibility of pore formation during polymerization due to dehydration.

4,4'-(1,4-Phenylenebis(oxy))diphthalonitrile (1) was obtained as reported [D.A. Erzunov, A.S. Vashurin and O.I. Koifman, *Russ. Chem. Bull.*, 2018, **67**, 2250].

5,5'-(1,4-Phenylenebis(oxy))bis(3,4,6-trifluorophthalonitrile) (2). 3,4,5,6-Tetrafluorophthalononitrile (20.00 g, 0.1 mol), hydroquinone (5.51 g, 0.05 mol), potassium fluoride (13.07 g, 0.225 mol) and methyl ethyl ketone (250 ml) were placed under argon flow into a one-necked flask equipped with a reflux condenser with a stopcock. The mixture was stirred at room temperature for 24 hours. The process was monitored by TLC (eluent CH_2Cl_2). After finishing of the reaction, the solution was filtered and evaporated on a rotary evaporator. To achieve a purity above 99%, flash chromatography (eluent: CH_2Cl_2/petroleum ether, 1:1) was performed. After evaporating of the solvent, a white substance was isolated (14.28 g). The yield was 61%.

^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 7.31 (s, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ ppm 154.58, 152.86, 152.67, 151.07, 149.35, 148.78, 147.05, 137.73, 117.83, 109.98, 100.91, 100.36.

^{19}F NMR (565 MHz, DMSO-d_6) δ ppm -120.33 (t, 1F), -128.26 (dd, J = 21.9, 9.5 Hz, 1F), -135.45 (dd, J = 21.9, 9.5 Hz, 1F).

Anal. Calcd. for $C_{22}H_4F_6N_4O_2$: C, 56.19; H, 0.86; F, 24.24; N, 11.91. Found: C, 56.05; H, 0.97; F, 24.22; N, 11.70.

5,5'-[(Perfluoro-1,4-phenylene)bis(oxy)]bis(3,4,6-trifluorophthalonitrile) (3). Tetrafluorohydroquinone (3.64 g, 0.02 mol), potassium fluoride (5.24 g, 0.09 mol) and THF (100 ml) were placed under argon in a pre-dried two-necked flask equipped with a reflux condenser with a stopper plug. The mixture was stirred for 30 min at room temperature, then 3,4,5,6-tetrafluorophthalonitrile (8.00 g, 0.04 mol) was added. The mixture was boiled for 24 hours, controlling the process using TLC (eluent CH_2Cl_2). After completion of the reaction, the solution was filtered and evaporated on a rotary evaporator. Flash chromatography (eluent: CH_2Cl_2/petroleum ether, 1:1) was performed to purify the substance. Yield: 2.25 g (21%), white substance.
^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ ppm 153.34, 151.62, 150.53, 148.81, 147.74, 146.00, 141.43, 139.73, 137.75, 131.26, 109.68, 101.67, 100.93.
^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ ppm -122.16 (s, 2F), -127.76 (dd, J = 22.0, 9.5 Hz, 2F), -136.86 (dd, J = 22.3, 8.3 Hz, 2F), -155.01 (s, 2F).
Anal. Calcd. for $C_{22}F_{10}N_4O_2$: C, 48.73; F, 35.04; N, 10.33. Found: C, 48.49; F, 34.93; N, 10.31.

4,4'-[(Perfluoro-1,4-phenylene)bis(oxy)]dianiline (5a). In a three-necked flask equipped with a reflux condenser with a stopper plug, 4-aminophenol (64.5 g, 0.59 mol) and DMAA (500 ml) were placed under argon. The mixture was stirred until 4-aminophenol was completely dissolved, then K_2CO_3 (89.1 g, 0.65 mol) was added, and this was stirred for another hour. After that, hexafluorobenzene (50 g, 0.27 mol) was added, the temperature was raised to 60 °C, and the mixture was stirred for 24 hours. The temperature was then raised to 110 °C, and stirring was continued for more 24 hours. The mixture was poured into water (2.5 L) and left for 2 hours, which caused precipitation. The precipitate was filtered off and oven-dried. Flash chromatography (eluent CH_2Cl_2) afforded a brownish substance in a yield of 86.7 g (89%).
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ ppm 6.86 (d, *J* = 6.2 Hz, 2H), 6.55 (d, *J* = 10.4 Hz, 2H), 4.96 (s, 2H).
^{13}C NMR (151 MHz, DMSO- *d*$_6$) δ ppm 148.27, 145.21, 142.78, 141.15, 130.42, 116.27, 114.63.
^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ ppm -156.26 (s, 4F).
Anal. Calcd. for $C_{18}H_{12}F_4N_2O_2$: C, 59.35; H, 3.32; F, 20.86; N, 7.69. Found: C, 59.14; H, 3.34; F, 20.77; N, 7.65.

3,3'-[(Perfluoro-1,4-phenylene)bis(oxy)]dianiline (5b) was obtained in 86% yield as above from 3-aminophenol.
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ ppm 7.00 (m, 2H), 6.37 (dd, J = 6.2 Hz, 2H), 6.30 (t, 2H), 6.24 (dd, J = 8.1 Hz, 2H), 5.29 (s, 4H).
^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ ppm 157.98, 150.57, 142.73, 141.07, 130.14, 129.72, 109.57, 102.00, 100.08.
Anal. Calcd. for $C_{18}H_{12}F_4N_2O_2$: C, 59.35; H, 3.32; F, 20.86; N, 7.69. Found: C, 59.33; H, 3.35; F, 20.79; N, 7.59.

Curing. The polymerization was carried out in glass vials, where monomer-curing agent mixture (300-400 mg) was placed. The vials were connected to a Schlenk line, evacuated, and heated to 150-160 °C to melt and degas the mixture. The system was filled with argon (several evacuation – argon filling iterations), and the vials were heated at specified temperature. After completion of the curing program, the vials were cooled under argon. Samples were prepared from the obtained polymers for further studies.

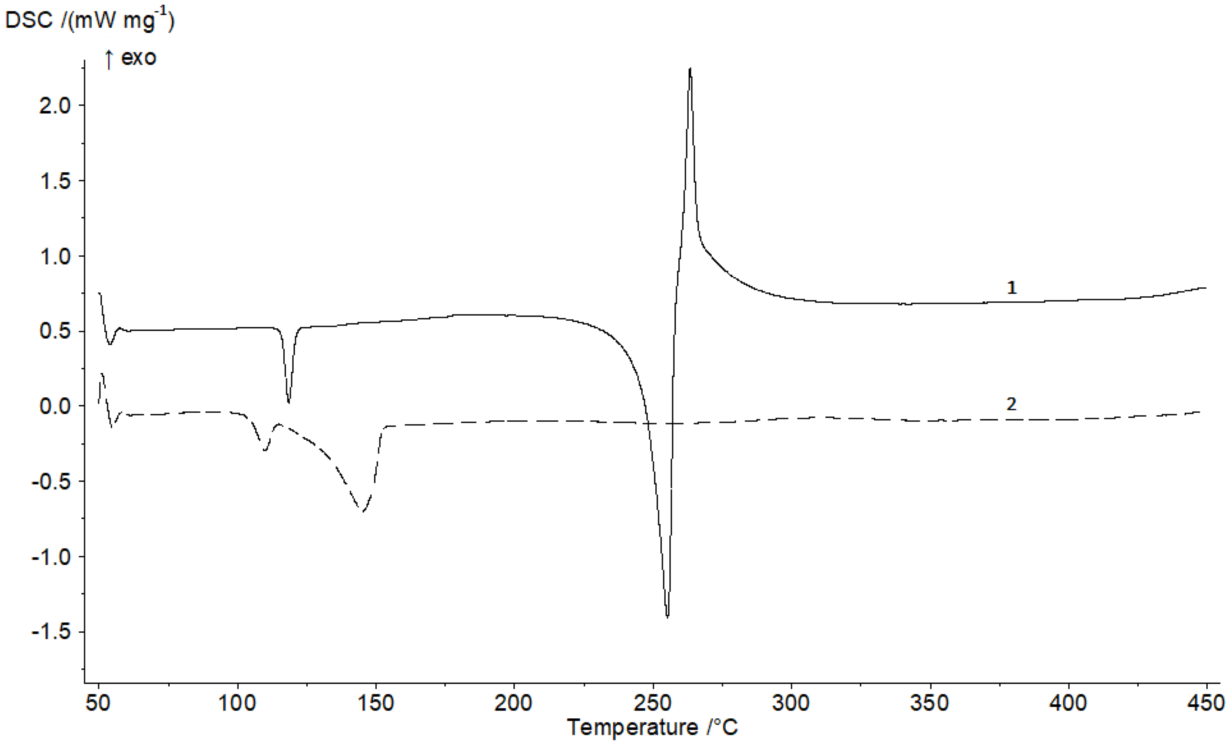


Figure S1 DSC curves of mixtures of the studied monomers with APB: (*1*) monomer **1** and APB; (*2*) monomer **2** and APB.

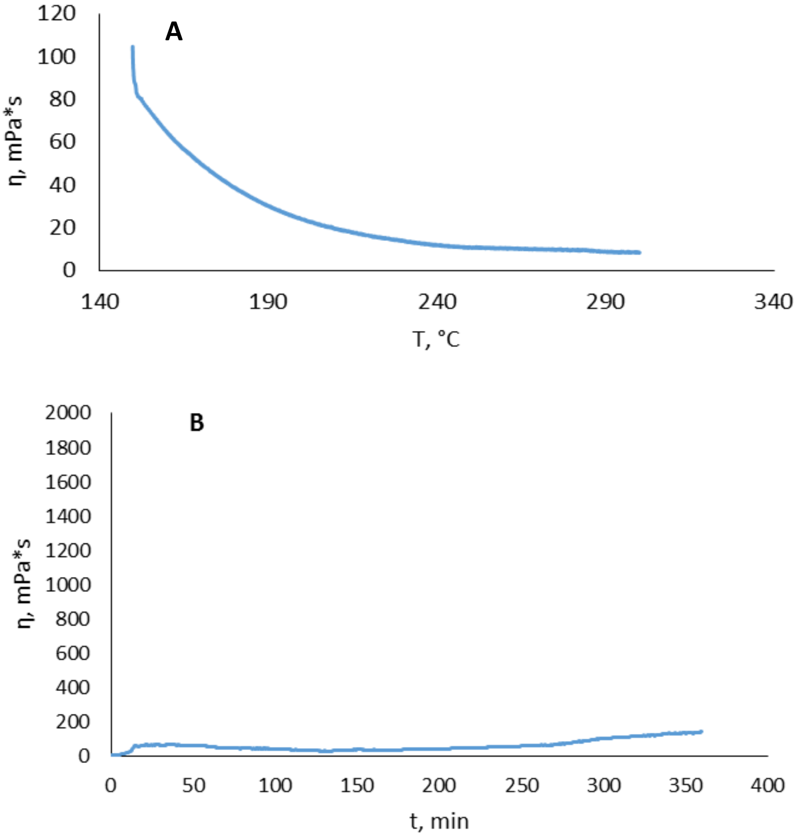
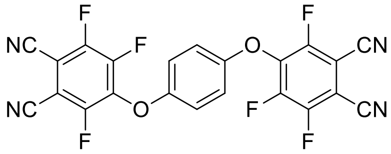


Figure S2 Rheology study of mixture consisting of monomer **2** and APB: (*A*) viscosity-temperature curve; (*B*) isothermal plot of viscosity at 250 °C as a function of time.

Table S1 Curing parameters of monomer **2** in the presence of different metals salts

Monomer	Curing agent	Curing agent content, mol. %	ΔH, kJ mol^{-1}
	$ZnCl_2$	3	12.12
	CuI	3	-
	$Cu(C_8H_{15}O_2)_2$	3	3.96
	$SnCl_2$	3	7.65

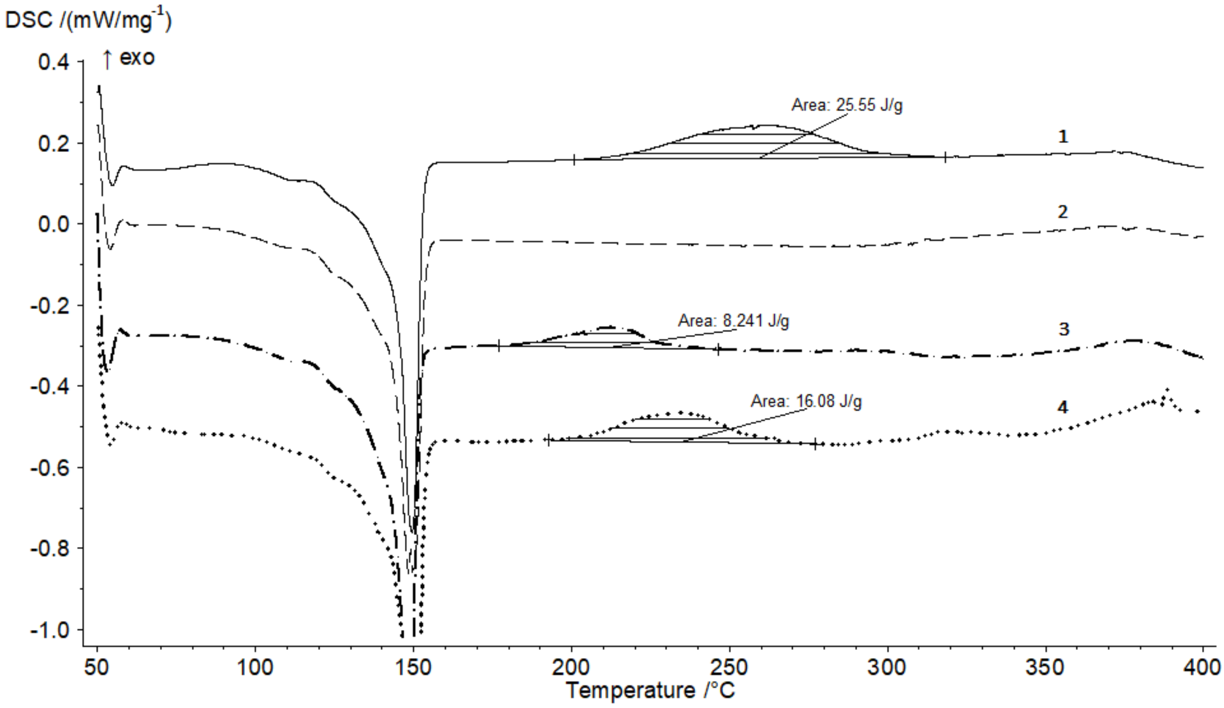


Figure S3 DSC curves of mixtures of the monomer **2** and different inorganic salts: (*1*) $ZnCl_2$; (*2*) CuI; (*3*) $Cu(C_8H_{15}O_2)_2$; (*4*) $SnCl_2$.

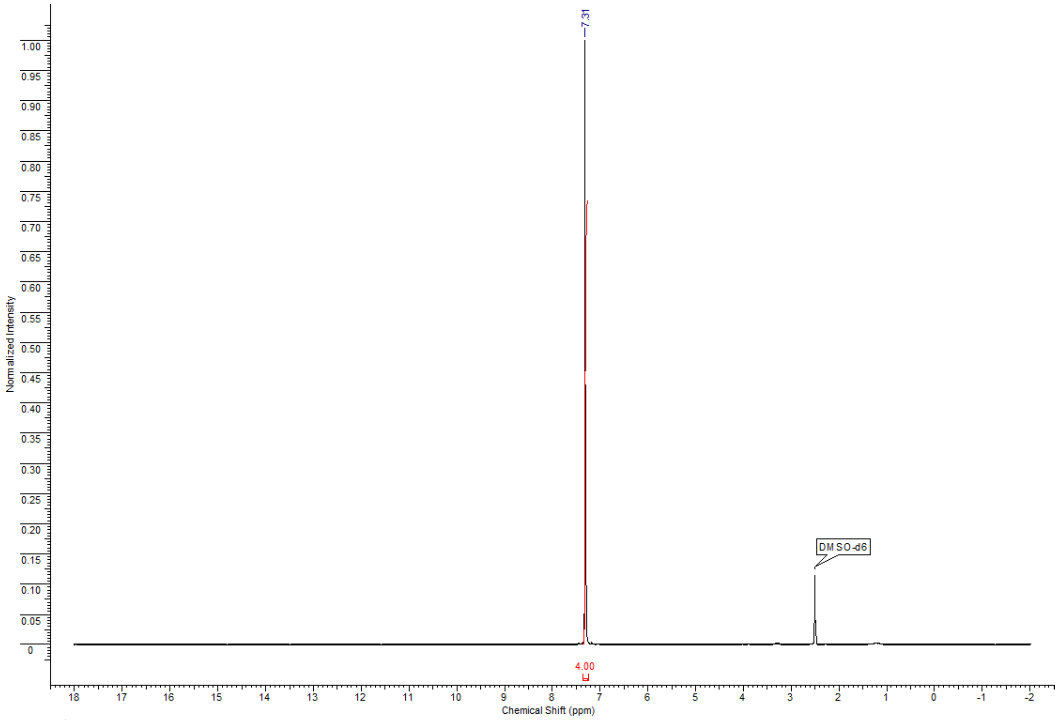


Figure S4 ^{1}H NMR spectrum of monomer **2**

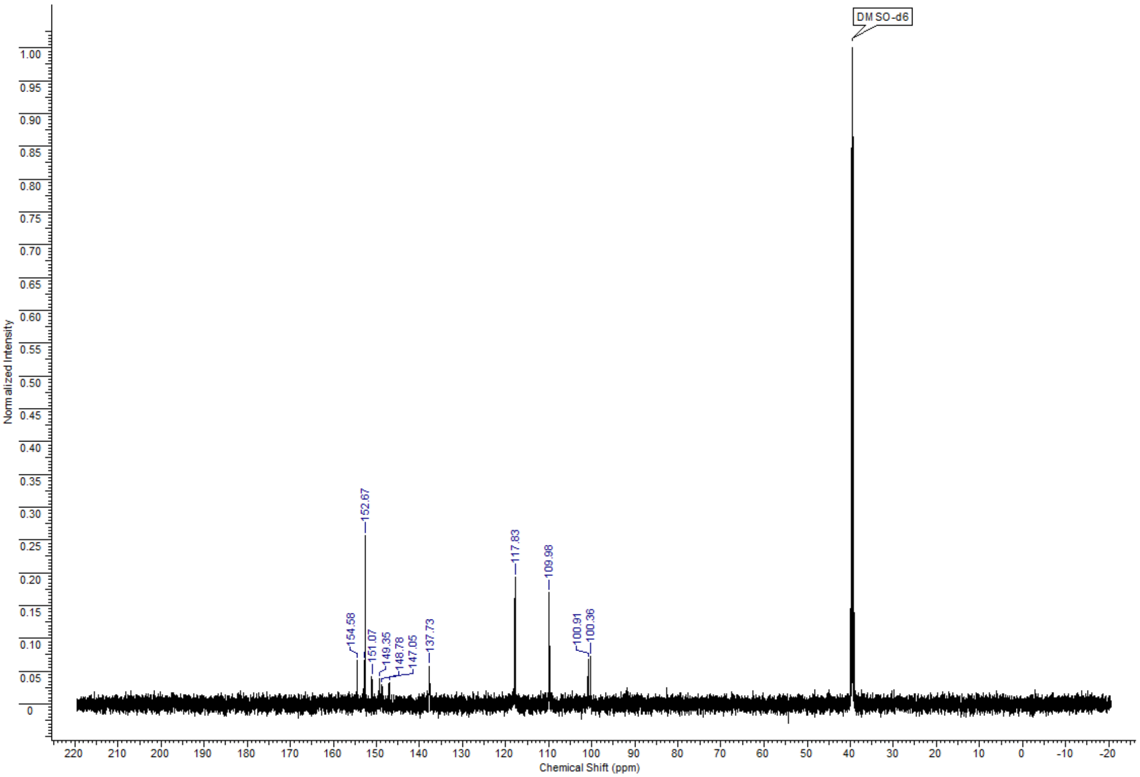


Figure S5 ^{13}C NMR spectrum of monomer **2**

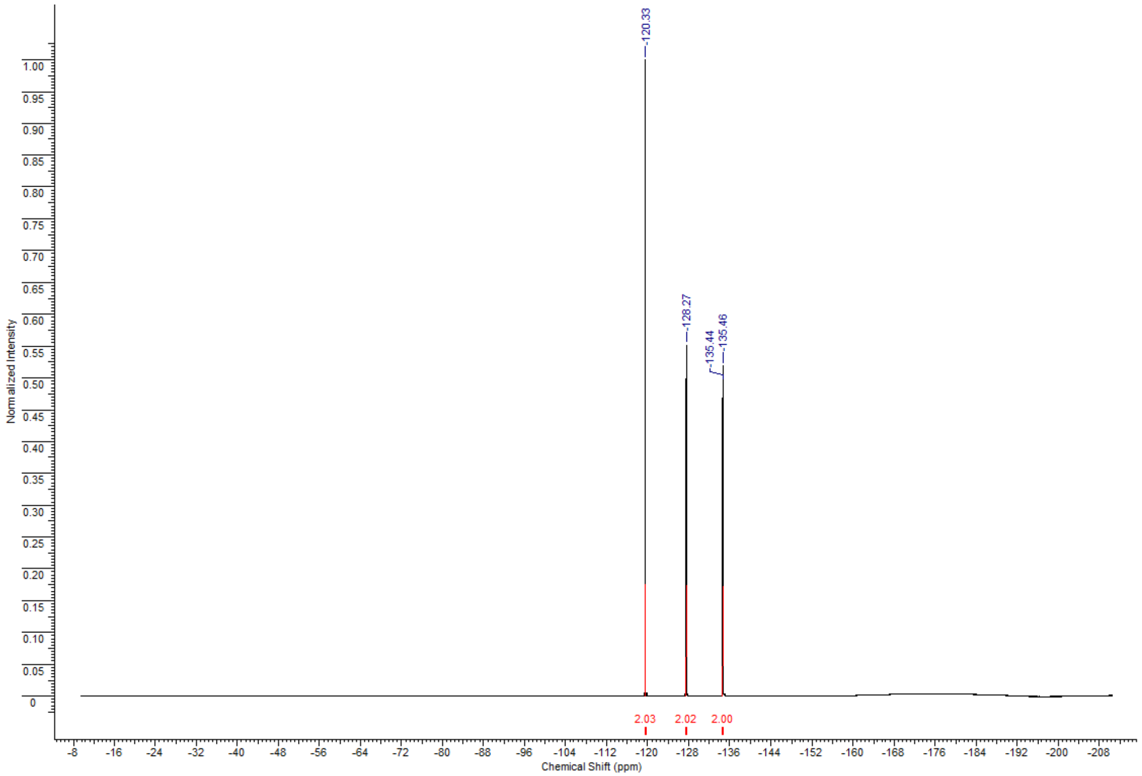


Figure S6 ^{19}F NMR spectrum of monomer **2**

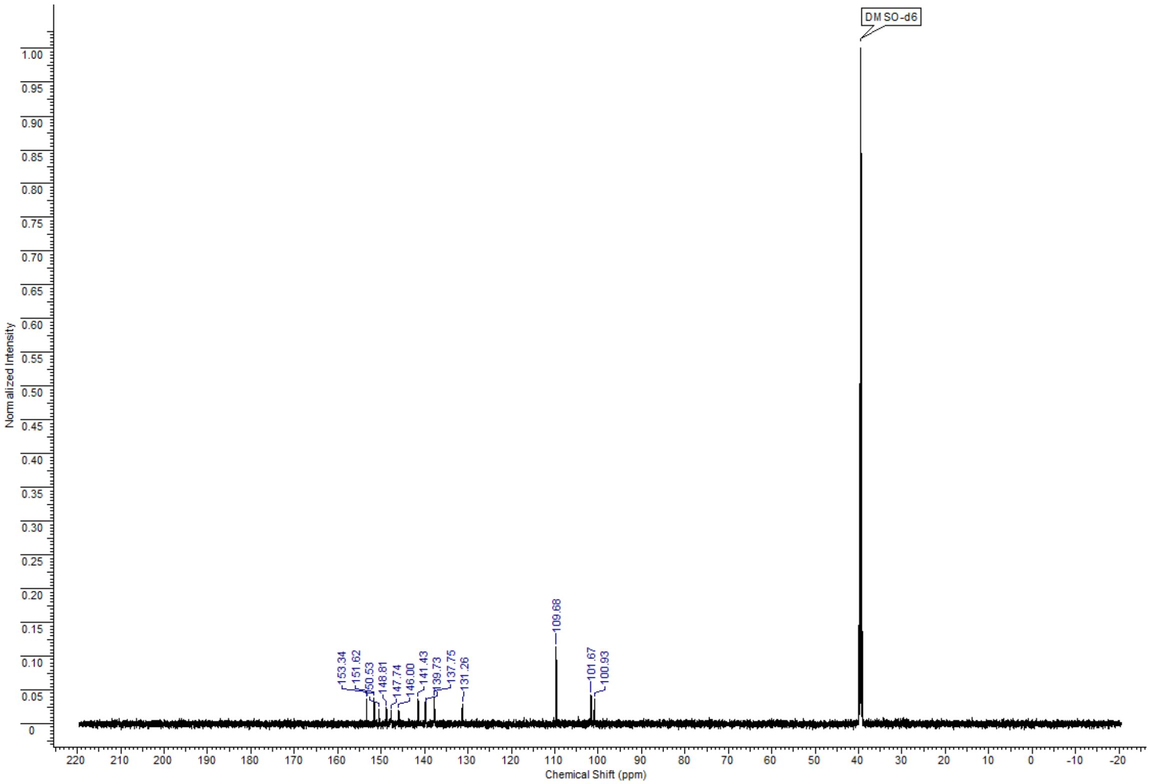


Figure S7 ^{13}C NMR spectrum of monomer **3**

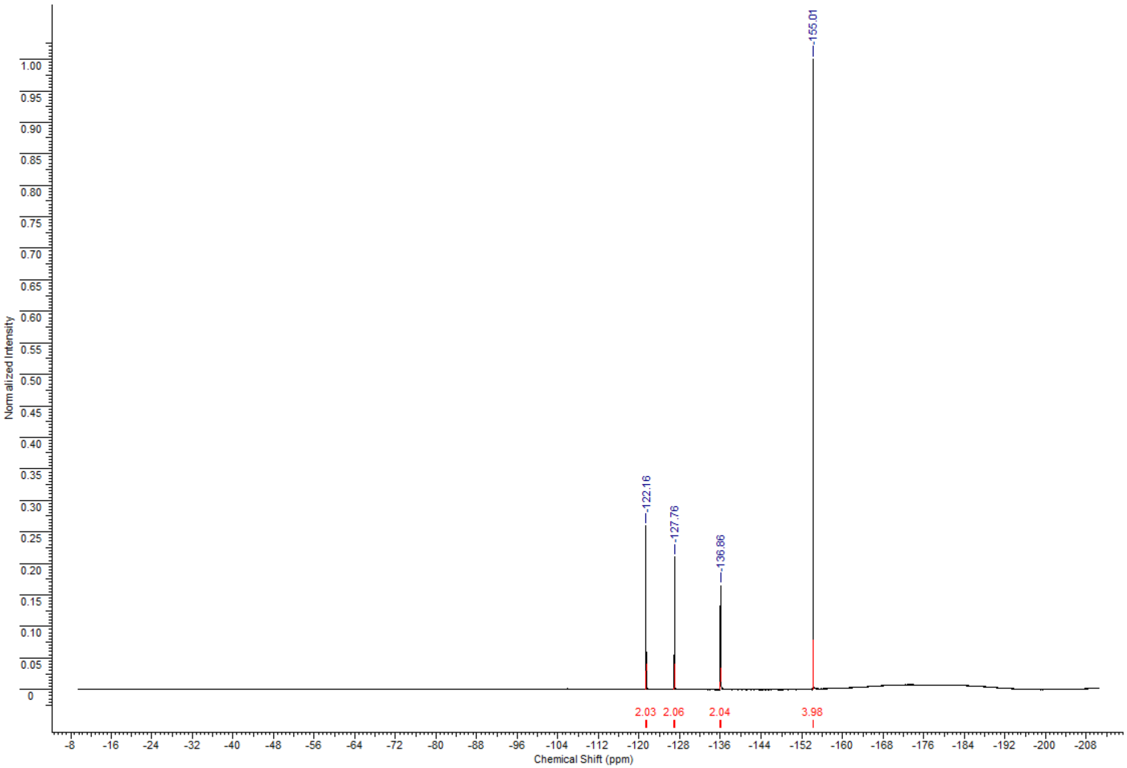


Figure S8 ^{19}F NMR spectrum of monomer **3**

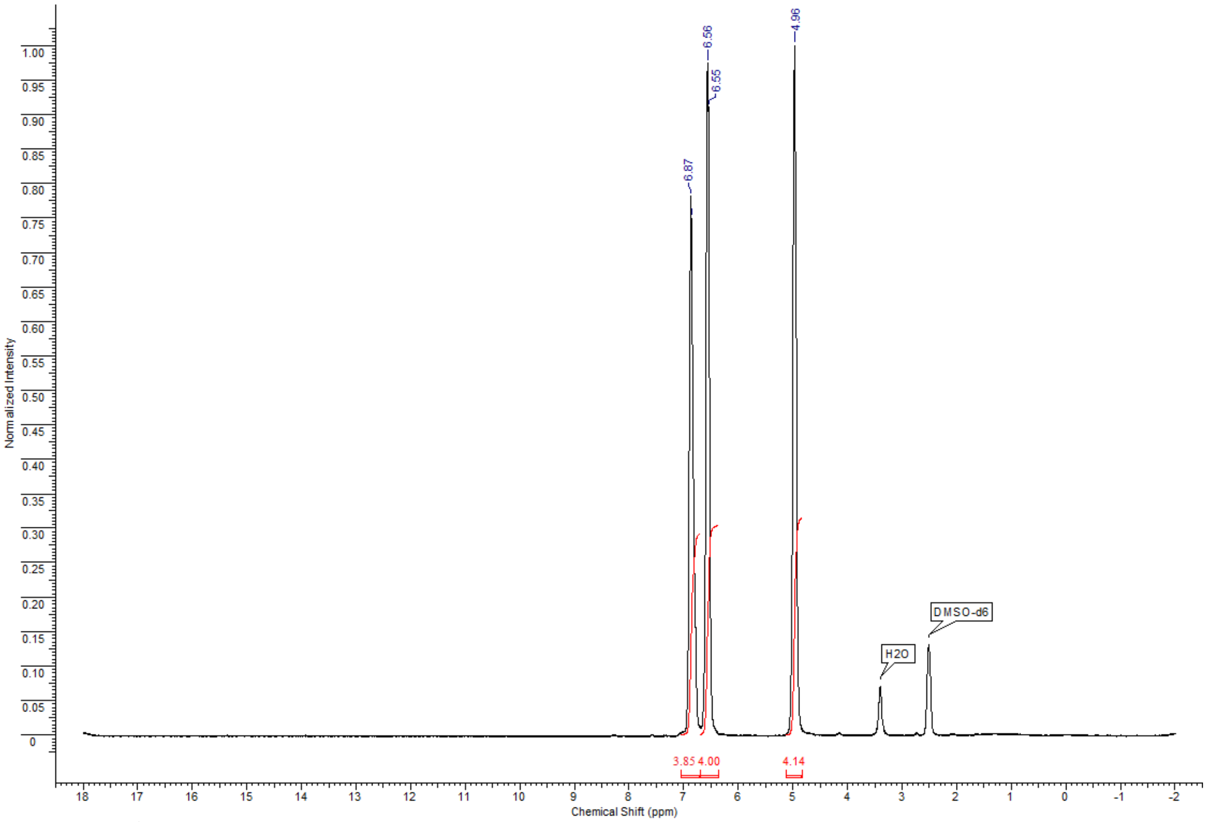


Figure S9 ^{1}H NMR spectrum of diamine **4**

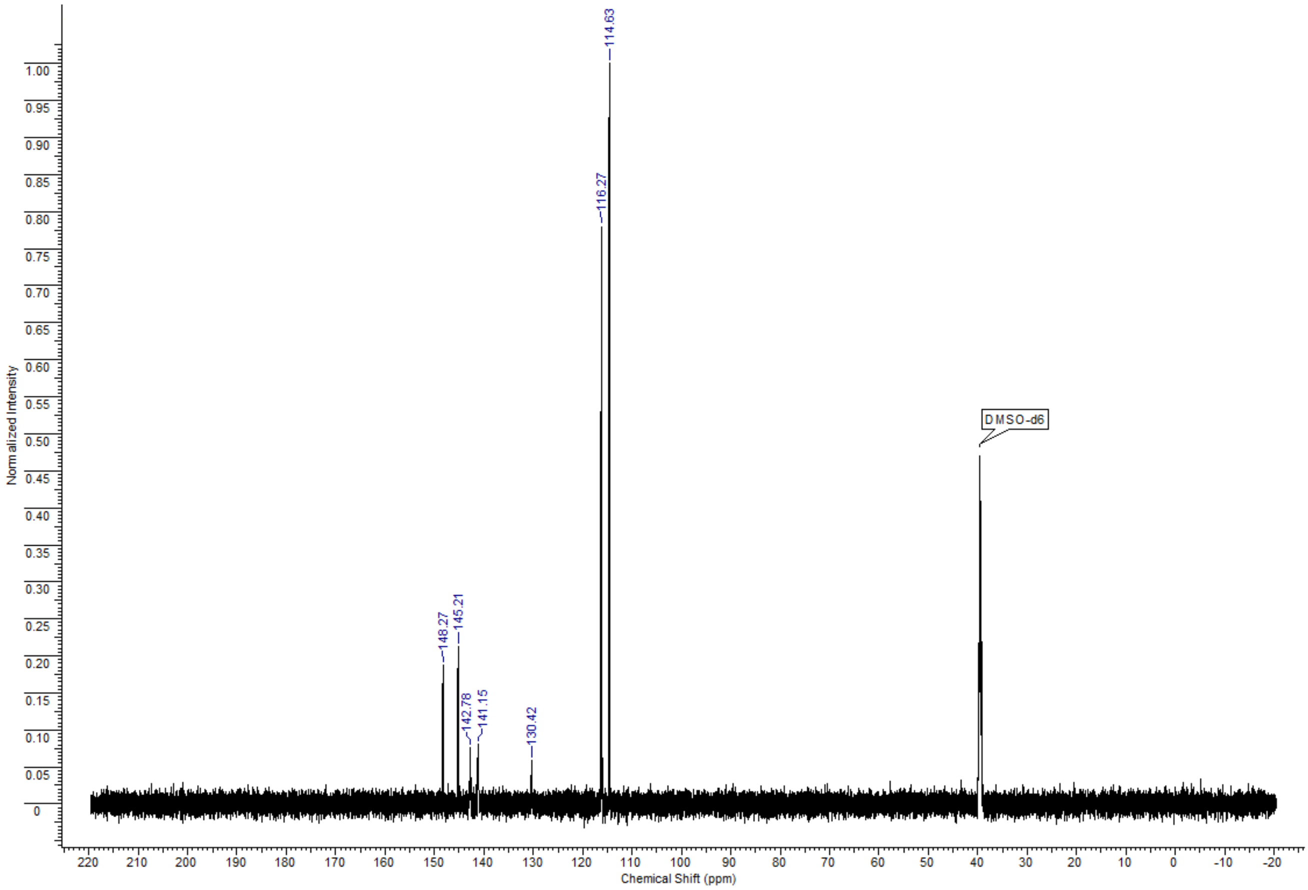


Figure S10 ^{13}C NMR spectrum of diamine **4**

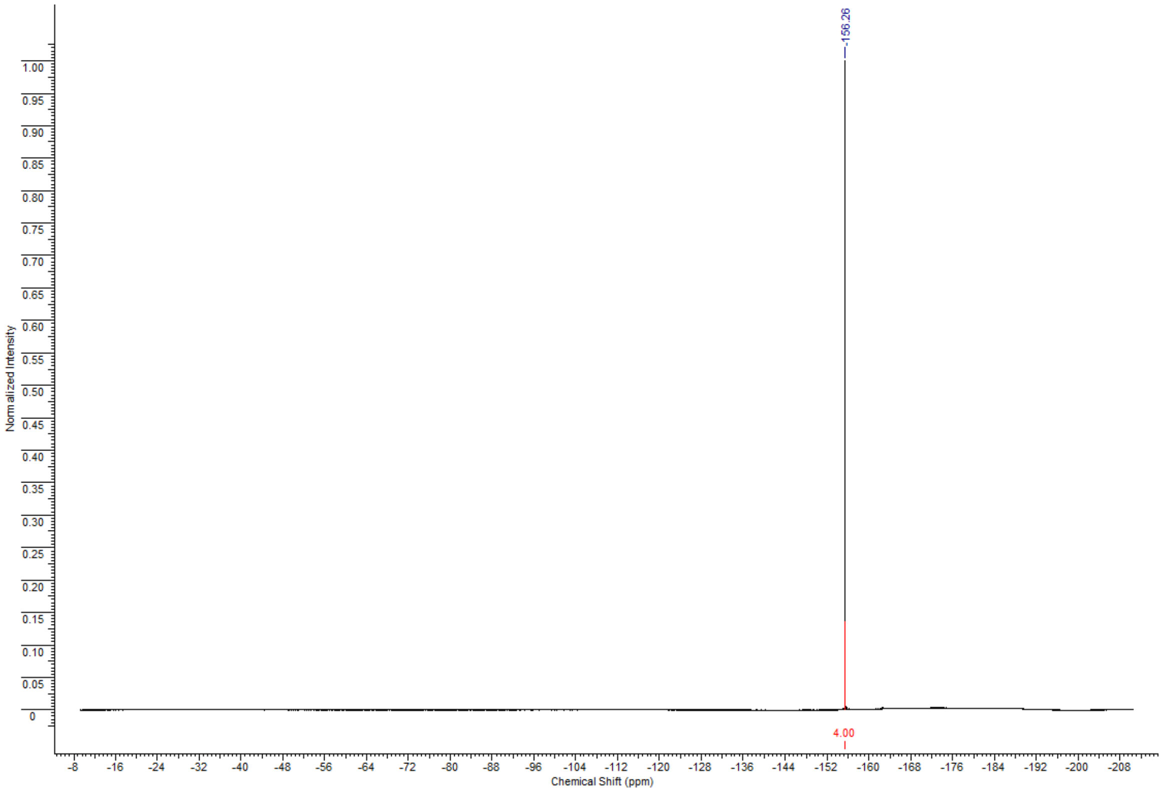


Figure S11 ^{19}F NMR spectrum of diamine **4**

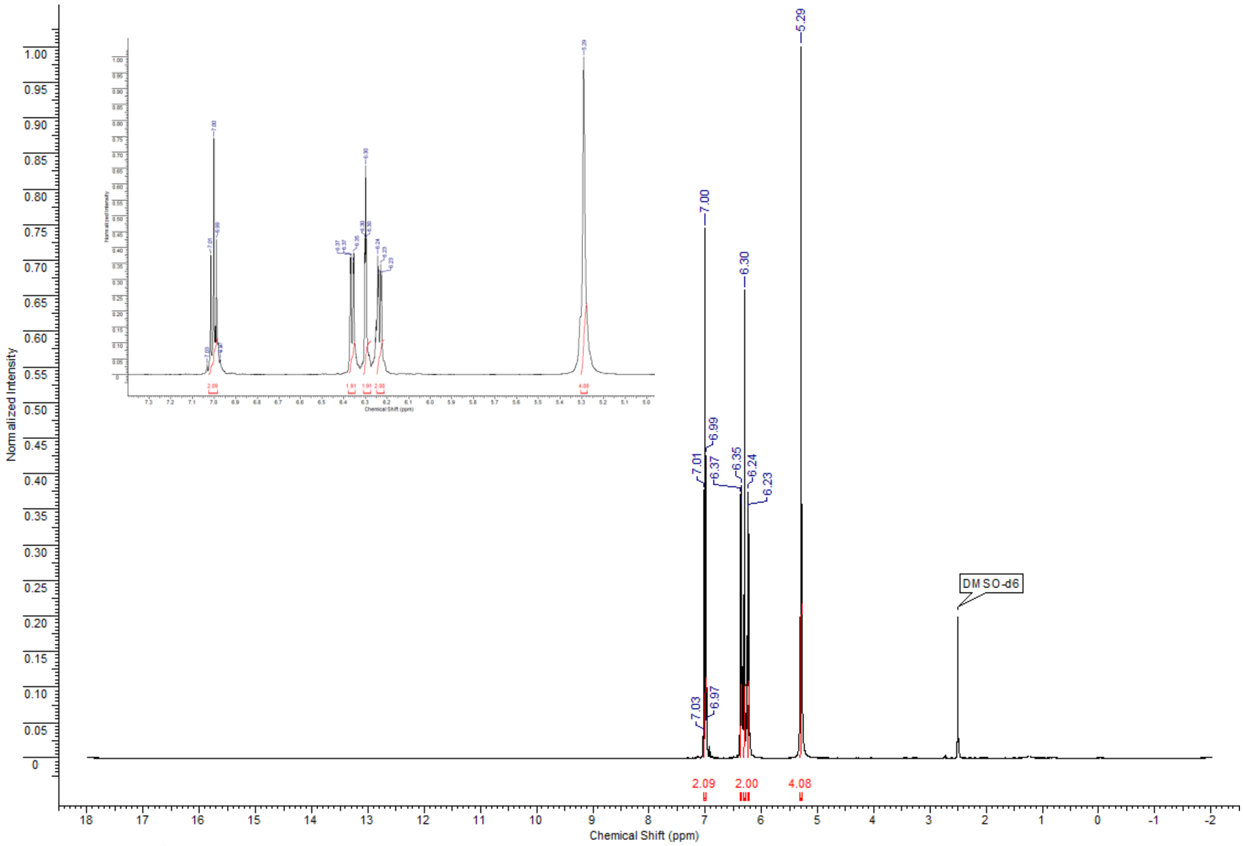


Figure S12 ^{1}H NMR spectrum of diamine **5**

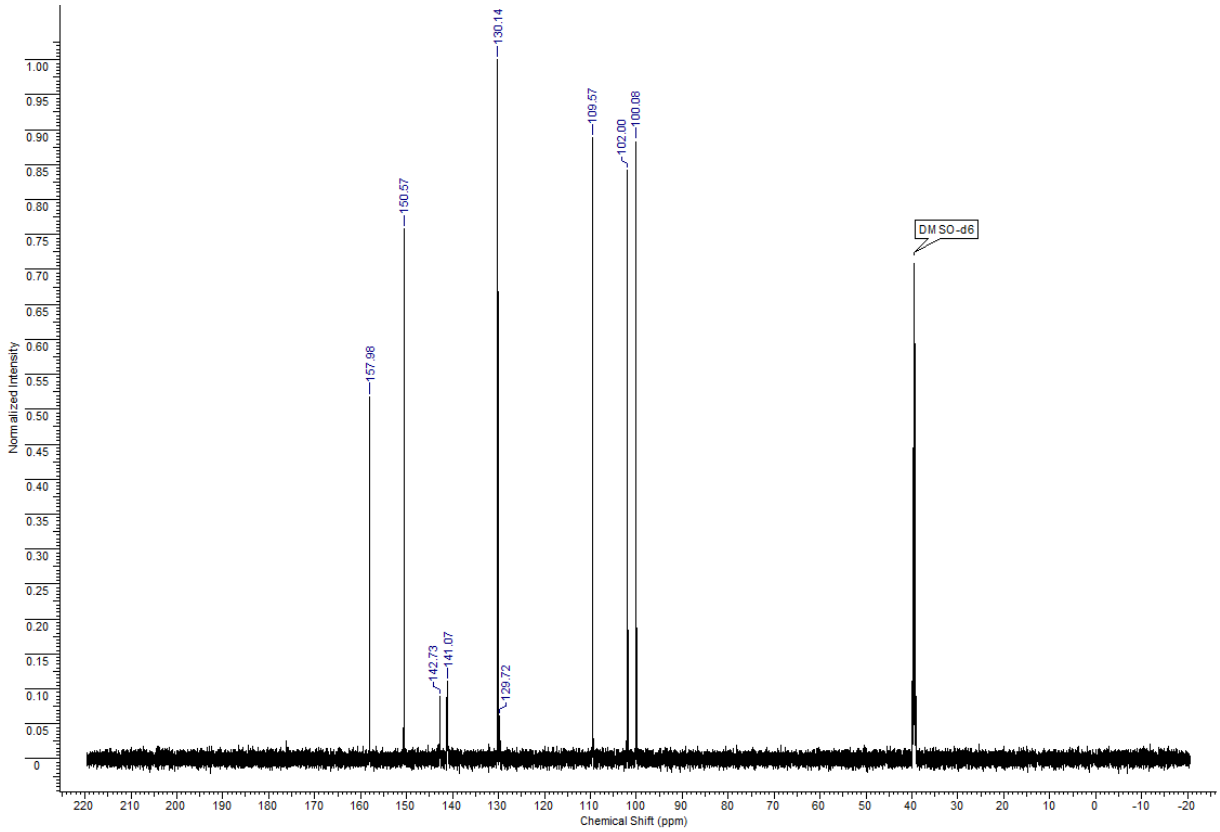


Figure S13 ^{13}C NMR spectrum of diamine **5**