Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Supramolecular organization of perfluorinated 1*H*-indazoles in the solid state using X-ray crystallography, SSNMR and sensitive (VCD) and non sensitive (MIR, FIR and Raman) to chirality vibrational spectroscopies

María Mar Quesada-Moreno,[a] Juan Ramón Avilés-Moreno,[b] Juan Jesús López-González,*[a] Kane Jacob,[c,d] Laure Vendier,[c,d] Michel Etienne,[c,d] Ibon Alkorta,[e] José Elguero[e] and Rosa Mª Claramunt[f]

[a] Grupo de Investigación Química Física Teórica y Experimental (FQM-173), Departamento de Química Física y Analítica, Facultad de Ciencias Experimentales, Universidad de Jaén, Campus de Las Lagunillas, E-23071 Jaén, Spain.

[b] Departamento de Sistemas Físicos, Químicos y Naturales, Facultad de Ciencias Experimentales, Universidad Pablo de Olavide, Carretera de Utrera Km 1, E-41013 Sevilla, Spain

[c] Laboratoire de Chimie de Coordination du CNRS (LCC), 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4, France.

[d] Université de Toulouse, UPS, INPT, LCC, 31077 Toulouse Cedex 4, France.

[e] Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain

[f] Grupo de Investigación Sistemas Supramoleculares Bioorgánicos, Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, Senda del Rey, 4, E-28040 Madrid, Spain

*Author to whom correspondence should be addressed.

JJLG) email: jjlopez@ujaen.es

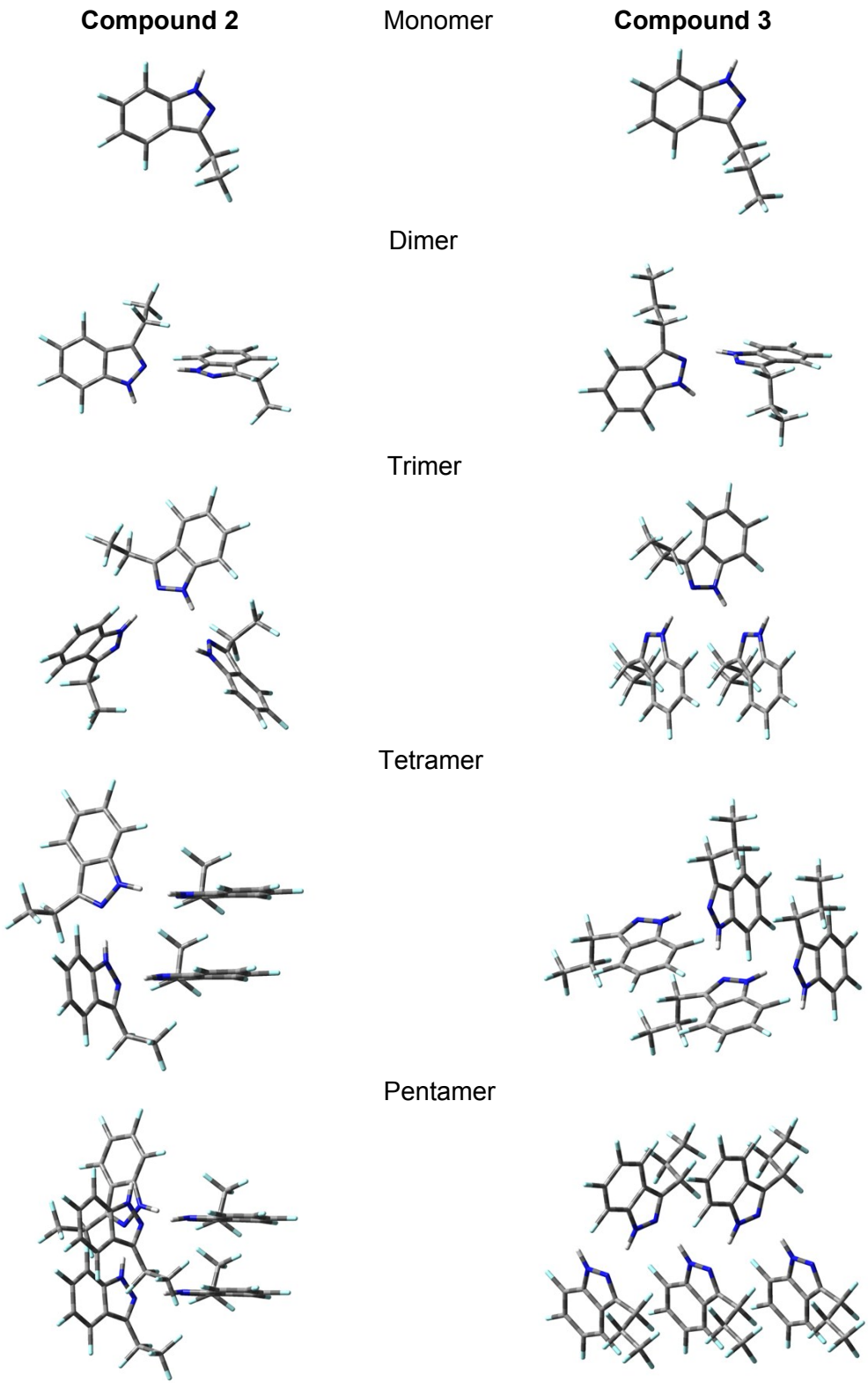

Figure 1S. Molecular structures of the monomers, dimers, trimers, tetramers and pentamers of compounds **2** and **3**.

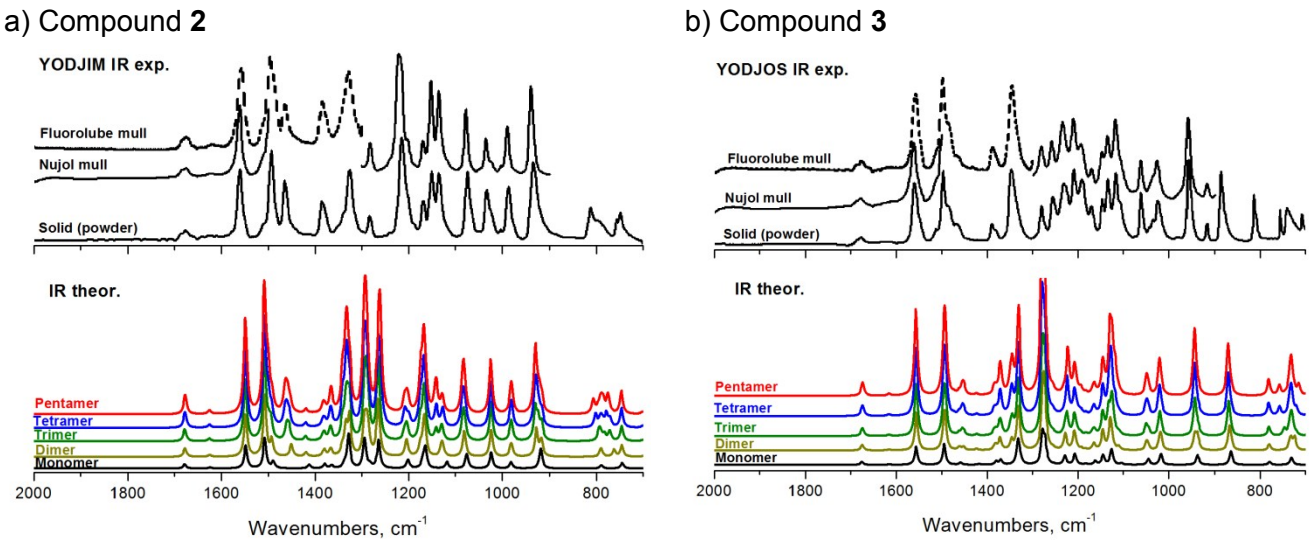

Figure 2S. Experimental (top) and scaled predicted (bottom) IR spectra of compounds **2** (panel a) and **3** (panel b) in the 2000-700 cm^{-1} spectral region. Scaling frequency factor of 0.96. Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}.

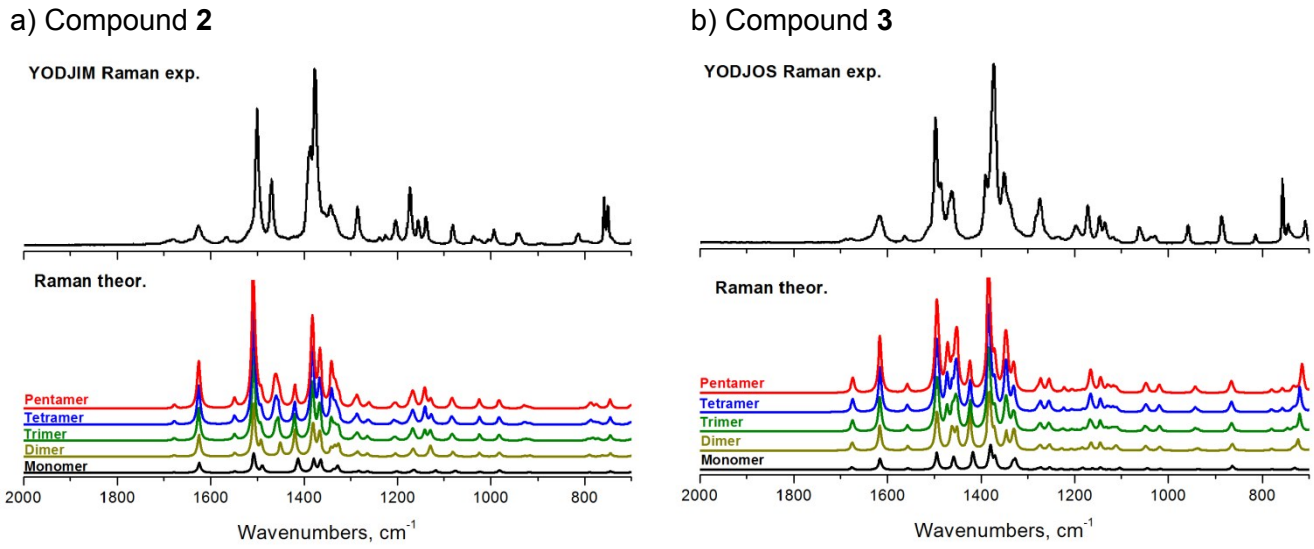

Figure 3S. Experimental (top) and scaled predicted (bottom) Raman spectra of compounds **2** (panel a) and **3** (panel b) in the 2000-700 cm^{-1} spectral region. Scaling frequency factor of 0.96. Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}.

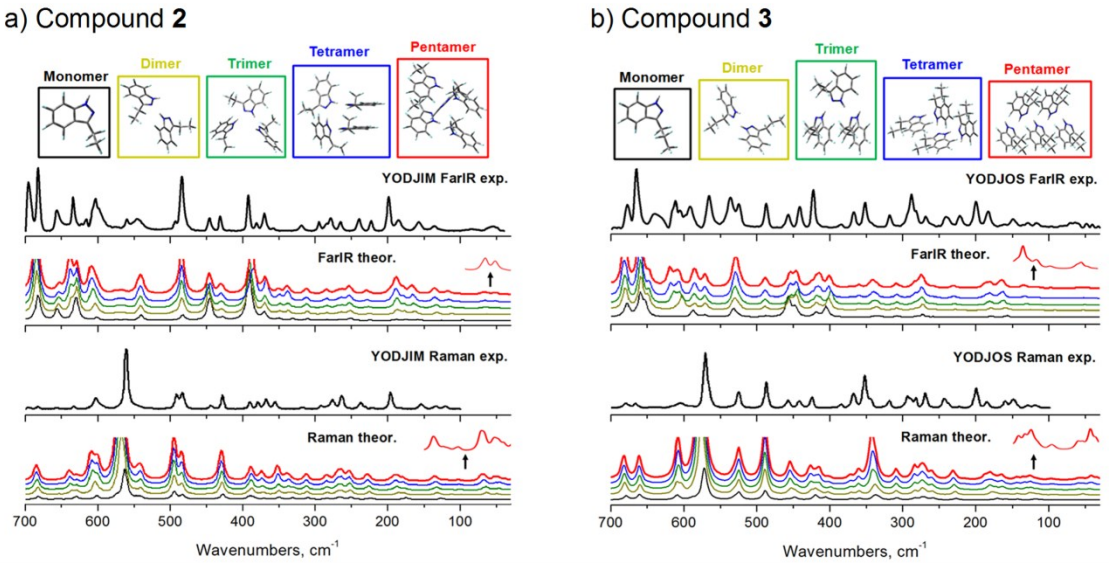

Figure 4S. Experimental and scaled predicted FarIR and Raman spectra of the monomers, dimers, trimers, tetramers and pentamers of compounds **2** (panel a) and **3** (panel b) in the solid phase (powder) in the 700-30 cm^{-1} spectral region. Scaling frequency factor of 0.99. Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}.

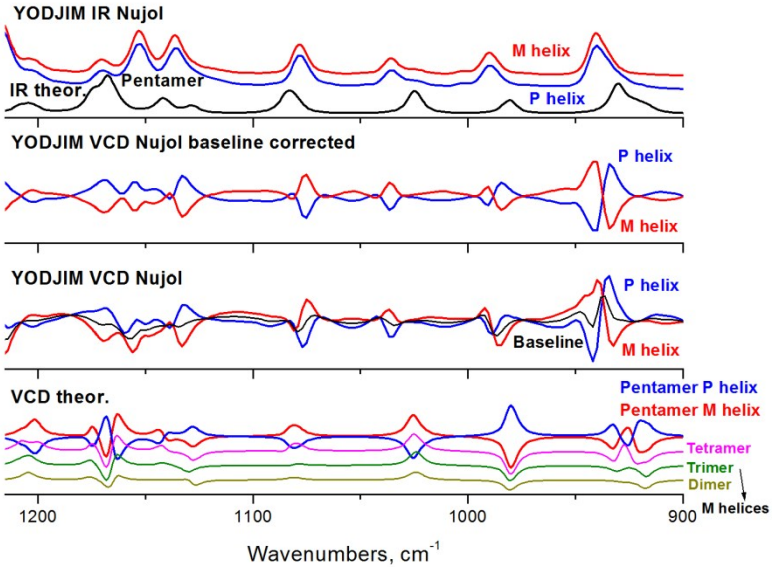

Figure 5S. Experimental and theoretical IR spectra (top) and experimental (top and bottom middle) and theoretical (bottom) VCD spectra of compound **2** in nujol mull in the 1215-900 cm^{-1} spectral region. In the bottom middle graphic, the raw VCD spectra were corrected by subtracting nujol signals. The average of these two VCD spectra provides the baseline, which was subtracted from them giving the baseline corrected VCD spectra shown in the top middle graphic. Theoretical VCD spectra of the dimers, trimers, tetramers and pentamers are shown in the bottom graphic. Scaling frequency factor of 0.96. Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}.

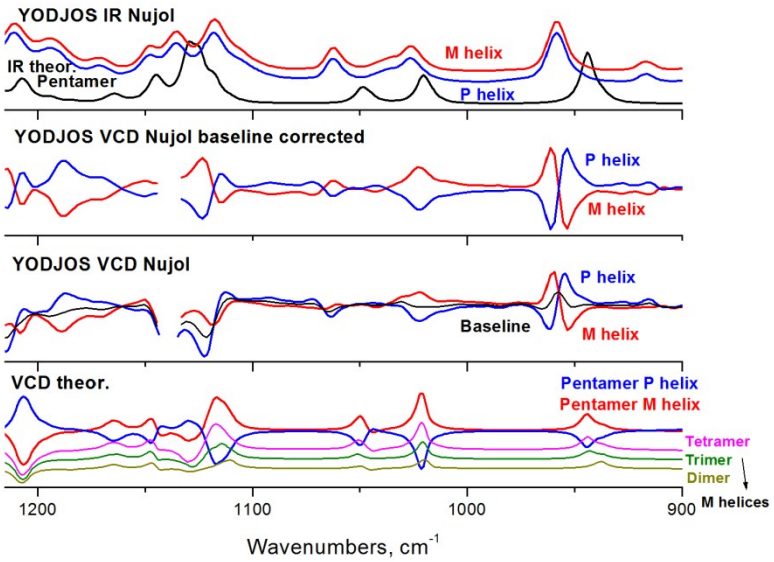

Figure 6S. Experimental and theoretical IR spectra (top) and experimental (top and bottom middle) and theoretical (bottom) VCD spectra of compound **3** in nujol mull in the 1215-900 cm^{-1} spectral region. In the bottom middle graphic, the raw VCD spectra were corrected by subtracting nujol signals. The average of these two VCD spectra provides the baseline, which was subtracted from them giving the baseline corrected VCD spectra shown in the top middle graphic. Theoretical VCD spectra of the dimers, trimers, tetramers and pentamers are shown in the bottom graphic. Scaling frequency factor of 0.96. Lorentzian function, pitch = 1 cm^{-1}, FWHM (Full Width Half Maximum) = 4 cm^{-1}.

Mol	Atom	Exp	Calc	dummy N2	dummy N1H
1	C3	136.2	136.8	0	0
	C3a	106.3	108.1	0	0
	C4	139.0	142.0	0	0
	C5	139.0	139.9	0	0
	C6	139.0	143.4	0	0
	C7	133.0	135.0	0	0
	C7a	128.1	127.2	0	0
	CF3	120.0	124.9	0	0
	N1H	–200.0	–216.9	0	1
	N2	–81.9	–60.9	1	0
	F4	–141.2	–136.7	0	0
	F5	–160.5	–159.9	0	0
	F6	–154.5	–151.4	0	0
	F7	–156.7	–161.9	0	0
	CF3	–62.7	–60.8	0	0
2	C3	129.3	136.2	0	0
	C3a	108.1	109.2	0	0
	C4	133.7	142.2	0	0
	C5	133.7	140.2	0	0
	C6	133.7	143.3	0	0
	C7	129.3	133.9	0	0
	C7a	129.3	127.0	0	0
	CF2	108.1	114.0	0	0
	CF3	129.3	123.4	0	0
	N1H	–195.6	–213.4	0	1
	N2	–76.9	–56.2	1	0
	F4	–138.6	–134.1	0	0
	F5	–155.7	–159.4	0	0
	F6	–151.9	–151.9	0	0
	F7	–159.4	–161.6	0	0
	CF2 a1	–111.5	–109.3	0	0
	CF2 a2	–118.4	–116.0	0	0
	CF3	–84.2	–84.1	0	0
3	C3	134.0	135.9	0	0
	C3a	108.4	109.8	0	0
	C4	134.0	141.4	0	0
	C5	134.0	140.1	0	0
	C6	134.0	143.0	0	0
	C7	127.8	134.1	0	0
	C7a	127.8	126.7	0	0
	CF2	109.7	116.4	0	0
	CF2	108.4	112.5	0	0
	CF3	127.8	122.6	0	0
	N1H	–195.9	–213.0	0	1
	N2	–71.6	–55.8	1	0
	CF2 a1	–111.7	–107.7	0	0
	CF2 a2	–113.8	–111.0	0	0
	CF2 b	–123.9	–123.6	0	0
	CF3	–79.4	–78.4	0	0

Table 1S. Comparison of experimental and calculated chemical shifts (ppm) and presence (1)/absence (0) data matrix.

2 Total Energy= -1351.98649306 Hartree, NIMAG= 0 C,-1.1491969655,11.3708080723,0.6634079952 C,-2.2321520603,11.0243064868,1.5405748673 C,-3.109299187,9.9457545876,1.74240429 C,-4.0569287611,10.0276414676,2.7406883678 C,-4.1615924254,11.1727381716,3.5599786326 C,-3.3151013196,12.2441636593,3.3847623823 C,-2.3549671073,12.1598249532,2.375063315 C,-0.5279644684,10.5702484818,-0.4476698444 C,0.5276080651,9.5289124287,0.0338371241 N,-1.3939389839,13.0397246714,1.9682692432 H,-1.1988212192,13.9599240725,2.3304866726 N,-0.6716952674,12.5670359809,0.9408493333 F,-3.0470247512,8.8422067592,0.9957537702 F,-4.9034663228,9.01610056,2.9562644627 F,-5.0972346353,11.1980586616,4.5096329311 F,-3.4036912825,13.3390036578,4.1572339809 F,-1.4915103465,9.8801098144,-1.1203468611 F,0.0983947687,11.3845495892,-1.3302919702 F,-0.0248743896,8.6846046945,0.9204610091 F,0.9965672155,8.8179091925,-0.995010367 F,1.5540040485,10.1518848627,0.6283365114	2_b3lyp_giao ******** Atom Abs. Rel. 1C 40.99 136.23 2C 69.07 109.19 3C 34.82 142.16 4C 36.87 140.19 5C 33.68 143.27 6C 43.37 133.94 7C 50.57 127.00 8C 64.13 113.95 9C 54.26 123.45 10N 64.85 -213.35 11H 22.35 9.32 12N -101.25 -56.22 13F 308.84 -134.08 14F 335.25 -159.41 15F 327.43 -151.91 16F 337.55 -161.61 17F 282.99 -109.29 18F 289.96 -115.97 19F 253.75 -81.25 20F 262.51 -89.65 21F 254.06 -81.54
3 Total Energy= -1589.84212674 Hartree, NIMAG= 0 C,0.8535062524,5.7228349773,2.2734460588 C,0.1034027948,4.5019716089,2.3651504176 C,-0.0014300118,3.4036239934,3.2341475535 C,-0.8829864974,2.3878356857,2.9304149338 C,-1.6803459528,2.4333106664,1.7660607691 C,-1.6000241214,3.4990601602,0.8981656771 C,-0.7076376045,4.5270569435,1.2068167879 C,1.8894947716,6.2794423144,3.2116398543 C,1.2644185187,7.0475313035,4.4230812434 C,2.2481498859,7.5142678584,5.5421131533 N,-0.408342134,5.6889485709,0.5551466964 H,-0.7882313964,6.0316345438,-0.3133977792 N,0.5282588423,6.4057327257,1.1944974367 F,0.727916856,3.3189694281,4.3479812697 F,-1.0035614899,1.3310499528,3.739470825 F,-2.5162882768,1.4235910981,1.5215517431 F,-2.353706894,3.5551948686,-0.2116497719 F,2.7053537622,7.1392774888,2.5569389525 F,2.6567272601,5.265205043,3.7048252341 F,0.633873853,8.143784373,3.9454953675 F,0.3397844546,6.2462745249,5.0092592362 F,1.5702568636,8.2492251179,6.4342826306 F,3.2314839106,8.2641341437,5.0345769788 F,2.7835787639,6.4685418267,6.1770738748	3_b3lyp_giao ******** Atom Abs. Rel. 1C 41.30 135.93 2C 68.39 109.84 3C 35.62 141.39 4C 36.99 140.07 5C 34.01 142.95 6C 43.19 134.11 7C 50.90 126.68 8C 61.55 116.43 9C 65.64 112.49 10C 55.11 122.63 11N 64.50 -213.01 12H 22.34 9.33 13N -101.74 -55.76 14F 308.77 -134.01 15F 335.59 -159.73 16F 328.05 -152.50 17F 338.50 -162.52 18F 284.73 -110.96 19F 281.34 -107.70 20F 297.73 -123.42 21F 298.18 -123.85 22F 251.51 -79.10 23F 251.83 -79.40 24F 249.14 -76.83

Table 2S. Geometry, energy and NMR parameters for **2** and **3** calculated at B3LYP/6-311++G(d,p) computational level.