

Weak Ag \cdots Ag and Ag \cdots π Interactions in Templating Regio Selective Single and Double [2+2] Reactions of N,N'-bis(3-(4-pyridyl)acryloyl)-hydrazine: Synthesis of Unprecedented Tricyclohexadecane Ring System

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Supporting Information

Experimental and characterization of the compounds by NMR and IR spectra, Powder XRD patterns; table for geometrical parameters for the alignment of double bonds; figures for ^1H NMR spectra recorded at various stages of irradiation;

Experimental

General

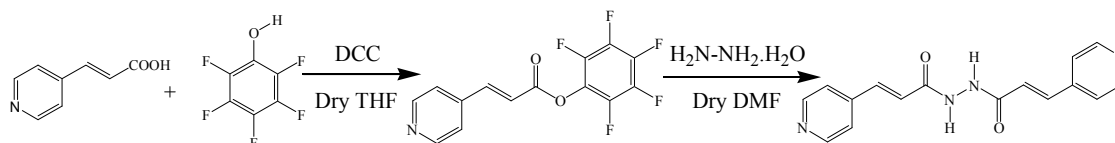
FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Powder XRD patterns were recorded with a PHILIPS Holland PW-1710 diffractometer. ^1H NMR and ^{13}C NMR (200/400 MHz) spectra were recorded on a BRUKER-AC 200/400 MHz spectrometer. UV-vis absorption was recorded using Shimadzu UV-1601 spectrophotometer. Elemental analyses were carried out by Perkin Elmer Series II 2400 and melting points were recorded using a Fisher Scientific melting point apparatus cat. No.12-144-1.

Synthesis of pentafluorophenyl ester of 4-pyridyl acrylic acid:

Dry THF (30 mL) solution of 4-pyridyl acrylic acid (1.192g, 8mmol), pentafluorophenol (1.62g, 8.8mmol) and DCC (1.816g, 8.8mmol) was stirred for a day under inert atmosphere. The resulting solution was filtered and the solvent has been removed from the filtrate under reduced pressure. The recrystallization of residue from petroleum ether resulted in colourless crystalline product in 67% yield. Mp 48-50°C; (Found C, 52.74; H, 1.78; N, 4.21. Calc. for $\text{C}_{14}\text{H}_6\text{F}_5\text{NO}_2$ (315.19): C, 53.35; H, 1.92; N, 4.44). δ_{H} (200 MHz; CDCl_3) 6.854 (d, $J = 16$ Hz, 1H, Olefin proton); 7.560 (d, $J = 6$ Hz, 2H, Py- β H); 7.887 (d, $J = 16$ Hz, 1H, Olefin proton); 8.700 (d, $J = 6$ Hz, 2H, Py- α H); δ_{C} (200 MHz; CDCl_3) 161.73 (1C, carbonyl), 149.65 (2C, Py $\text{C}^{2/6}$), 145.63 (1C, alkene C β to carbonyl), 142.29 (1C, Py C^4), 140.87 (2C, $\text{C}_6\text{F}_5\text{-C}^{2/6}$), 138.84 (1C, $\text{C}_6\text{F}_5\text{-C}^4$), 135.84 (2C, $\text{C}_6\text{F}_5\text{-C}^{3/5}$), 133.08 (2C, $\text{C}_6\text{F}_5\text{-C}^1$), 122.91 (2C, Py $\text{C}^{3/5}$), 120.38 (1C, alkene C α to carbonyl).

Synthesis of 4-PAH:

The above ester (2g, 6.36mmol) was taken in dry DMF (12mL) and hydrazine hydrate (154 μL , 3.18mmol) was added under inert atmosphere. The mixture was stirred for 12 hours during which light yellow coloured solid separated out. The resulted solution was filtered and the residue was washed with acetone. The crude product on recrystallization from MeOH produced the pure compound 4-PAH in 62.8% yield. Mp 277-279°C; (Found C, 64.94; H, 4.53; N, 18.76. Calc. for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_2$ (294.31): C, 65.30; H, 4.79; N, 19.04); λ_{max} (DMSO)/nm 267; ν_{max} / cm^{-1} 2966-3401 (brd & med: hydrogen bonded -NH stretch), 1605-1655 (shp & str: amide I & II band), 1482-1560 (shp & med to wk: olefin and pyridine ring C-C and C-N stretch), 1419, 1342, 1324, 1212, 1190, 978-1002 (shp & med to wk: N-H in plane rocking), 811, 596, 536, 508; δ_{H} (200 MHz; D_6DMSO) 6.977 (d, $J = 16$ Hz, 2H, Olefin proton); 7.527 (d, $J = 16$ Hz, 2H, Olefin proton); 7.549 (d, $J = 6$ Hz, 4H, Py- β H); 8.622 (d, $J = 6$ Hz, 4H, Py- α H); 10.753 (s, 2H, NH); δ_{C} (200 MHz; D_6DMSO) 162.72 (2C, carbonyl), 151.06 (4C, Py $\text{C}^{2/6}$), 142.42 (2C, alkene C β to carbonyl), 138.39 (2C, Py C^4), 124.41 (2C, alkene C α to carbonyl), 122.38 (4C, Py $\text{C}^{3/5}$).



Synthesis of complex 1:

Complex **1** was prepared by layering technique, methanolic solution (4mL) of $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (0.0113g; 0.05 mmol) was layered on top of blank solution of MeOH-DCM (8mL, in 4:1 ratio) which was layered on top of MeOH-DCM solution (8mL, in 2:1 ratio) of 4-PAH (0.0149g; 0.05 mmol) in a test tube. After 15 days light yellow coloured crystals of complex **1** were isolated by filtration in ~57% yield. (Found C 38.13, H 2.53, N 11.08. Calc. for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_6\text{ClAg}$ (501.63): C 38.31, H 2.81, N 11.17). $\nu_{\text{max}}/\text{cm}^{-1}$ 3252 (brd & med: hydrogen bonded -NH stretch), 1608-1652 (shp & str: amide I & II band and olefin C=C stretch), 1427-1556 (shp & med to wk: olefin and pyridine ring C-C and C-N stretch), 1086 (br & str: perchlorate Cl-O stretch), 962-975 (shp & med N-H in plane rocking), 621 (shp & str: perchlorate Cl-O stretch).

Synthesis of complex 2:

Complex **2** was prepared following the above layering technique in similar conditions using AgNO_3 in place of AgClO_4 . Light yellow coloured crystals of complex **2** were isolated by filtration in ~55% yield. (Found C 41.53, H 2.83, N 14.98. Calc. for $\text{C}_{16}\text{H}_{14}\text{N}_5\text{O}_5\text{Ag}$ (464.18): C 41.40, H 3.04, N 15.09). $\nu_{\text{max}}/\text{cm}^{-1}$ 3199-3400 (brd & med: hydrogen bonded -NH stretch), 1604-1651 (shp & str: amide I & II band), 1430-1557 (shp & med to wk: olefin and pyridine ring C-C and C-N stretch), 1339-1384 (shp & str: nitrate N-O stretch), 964-977 (shp & med N-H in plane rocking).

Irradiation process:

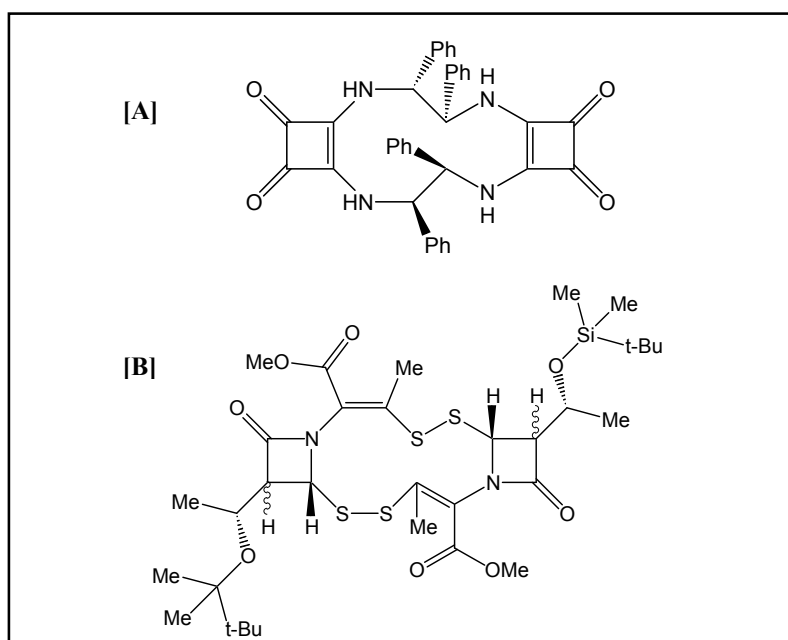
Irradiations were carried out in sunlight placing the materials between two thin glass plates. The photodimerization reactions in either complex **1** or **2** were found to be completed after continuous irradiation of 7-8 hours as supported by ^1H NMR spectroscopy. On the other hand no change in ^1H NMR spectra was observed for compound 4-PAH·4H₂O even after irradiation for 4-5 days in sunlight.

Separation of TCHD:

About 1g of irradiated complex **1** was taken in 5 mL of water and then acidified with dilute HCL up to pH 2-3. The resulted precipitate of AgCl was removed by filtration; the filtrate was carefully neutralized by drop wise addition of dilute NaOH. The resulted solid product (TCHD) was isolated by filtering and dried in oven. The crude TCHD was crystallized as the block shaped crystals from DMSO. Yield 96%. Mp 296-298°C; (Found C, 65.09; H, 4.48; N, 18.85. Calc. for $\text{C}_{32}\text{H}_{28}\text{N}_8\text{O}_4$ (588.62): C, 65.30; H, 4.79; N, 19.04); $\lambda_{\text{max}}(\text{DMSO})/\text{nm}$ 266. $\nu_{\text{max}}/\text{cm}^{-1}$ 2891-3260 (brd & med: hydrogen bonded -NH stretch), 1605-1696 (shp & str: amide I & II band), 1421, 1396, 1346, 1490, 1309, 1234, 1006 (shp & wk N-H in plane rocking), 798-821 (shp & wk: N-H out of plane wagging), 544-565 (shp & wk: N-H out of plane wagging); $\delta_{\text{H}}(200 \text{ MHz}; \text{D}_6\text{DMSO})$ 4.201 (4H, cyclobutane proton); δ 4.332 (4H, cyclobutane proton); δ 7.010 (d, 8H, $J = 5.2 \text{ Hz}$, Py- βH); δ 8.313 (d, 8H, $J = 5.2 \text{ Hz}$, Py- αH); δ 9.592 (s, 4H, NH proton); $\delta_{\text{C}}(200 \text{ MHz}; \text{D}_6\text{DMSO})$ 174.67 (4C, carbonyl), 149.76 (8C, Py $\text{C}^{2/6}$), 148.64 (4C, Py C^4), 123.54 (8C, Py $\text{C}^{3/5}$), 44.65 (4C, Cyclobutane C- α to keto).

Separation of MCB:

Similar procedure was followed for the separation of MCB. The crystallization of isolated crude solid from H₂O-MeOH formed plate like crystals. Yield 94%. Mp 324-326°C; (Found C, 64.87; H, 4.52; N, 18.67. Calc. for C₃₂H₂₈N₈O₄ (588.62): C, 65.30; H, 4.79; N, 19.04). $\nu_{\max}/\text{cm}^{-1}$ 3194-3518 (brd &str: hydrogen bonded -NH stretch), 1602-1678 (shp &str: amide I & II band), 1413, 1346, 1286, 1228, 1206, 1066, 970-993 (shp & med N-H in plane rocking), 812 (shp & med: N-H out of plane wagging), 551 (shp & med: N-H out of plane wagging); δ_{H} (200 MHz; D₆DMSO) 4.104/4.215 (AA'BB', 4H, cyclobutane proton); δ 6.802 (d, J = 16.2 Hz, 2H, olefin proton); δ 7.272 (d, 4H, J = 4.4 Hz, Py- β H); δ 7.421 (d, J = 16.2 Hz, 2H, olefin proton); δ 7.453 (d, 4H, J = 4.4 Hz, Py- β H); δ 8.467 (d, 4H, J = 4.4 Hz, Py- α H); δ 8.562 (d, 4H, J = 4.4 Hz, Py- α H); δ 10.261 (s, 2H, NH proton); δ 10.426 (s, 2H, NH proton); δ_{C} (200 MHz; D₆DMSO) 168.68 (2C, carbonyl- α to cyclobutane), 162.74 (2C, carbonyl- α to olefin), 150.84 (4C, Py C^{2/6}-attached to cyclobutane), 149.82 (4C, Py C^{2/6}-attached to olefin), 148.55 (2C, Py C⁴-attached to cyclobutane), 142.22 (2C, Py C⁴-attached to olefin), 137.98 (2C, alkene C β to carbonyl), 124.26 (2C, alkene C α to carbonyl), 123.54 (4C, Py C^{3/5}-attached to cyclobutane), 122.10 (4C, Py C^{3/5}-attached to olefin), 44.05 (2C, Cyclobutane C- α to keto).



Scheme S1. Schematic drawing for molecules (A and B) with four-twelve-four fused ring systems as resulted from the scifinder search.

Table S1. Geometrical parameters for different sets of align double bonds in 4-PAH·4H₂O, complex 1 and complex 2.

Para meters	4-PAH·4H ₂ O	Complex 1				Complex 2	
		Set-A ₁	Set-A ₂	Set-B ₁	Set-B ₂	Set-A	Set-B
d (Å) ^[a]	3.765	3.765	3.862	4.088	3.716	4.115	3.919
d ₁ (Å) ^[b]	1.805	1.415	1.209	1.376	0.669	2.302	0.891
d ₂ (Å) ^[b]	3.384	3.762	3.734	3.873	3.663	3.823	3.827
θ (°) ^[c]	0.00	2.26	13.42	0.00	0.00	8.59	0.00
θ ₁ (°) ^[d]	116.8	111.5	108.6	109.4	99.7	124.7	102.1
θ ₂ (°) ^[d]	87.5	81.7	85.7	84.5	72.1	78.2	73.3

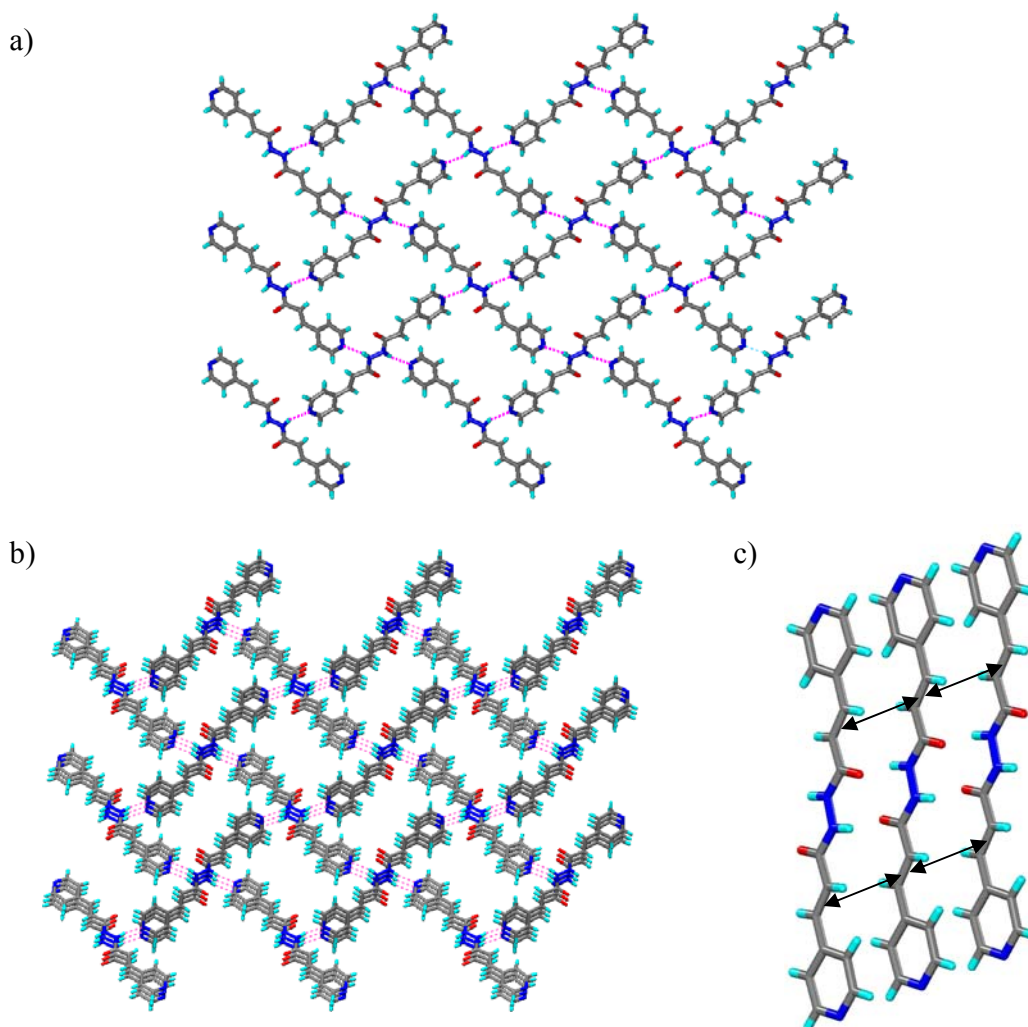
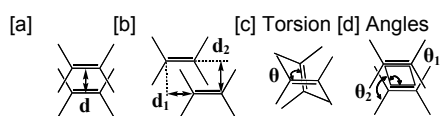


Fig. S1. Illustrations for crystal structure of 4-PAH·4H₂O: a) 2D-herringbone layer through N-H···N(Py) hydrogen bond; b) packing of such 2D layers; c) molecular stacking with alignment of both double bonds.

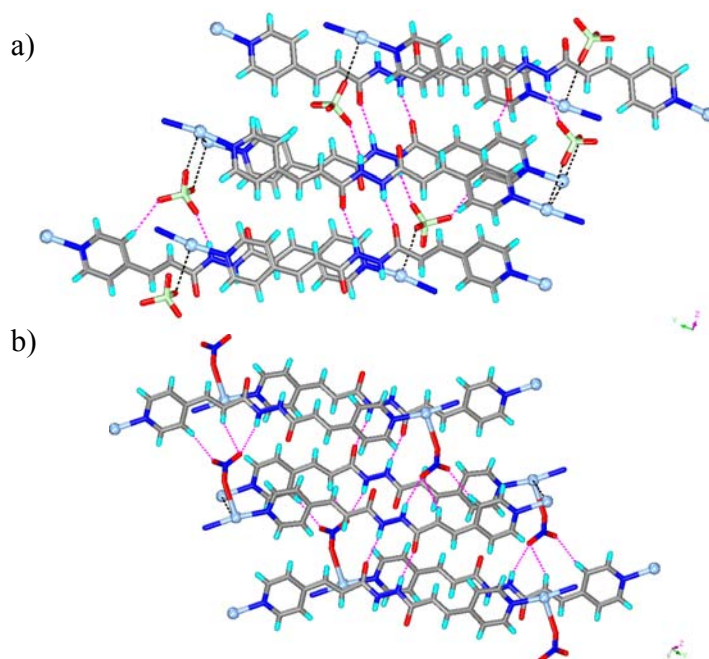


Fig. S2. Illustrations for crystal structures of complexes **1** and **2**: hydrogen bonding interactions of the double chain unit with the adjacent chains; a) in complex **1**; b) in complex **2**.

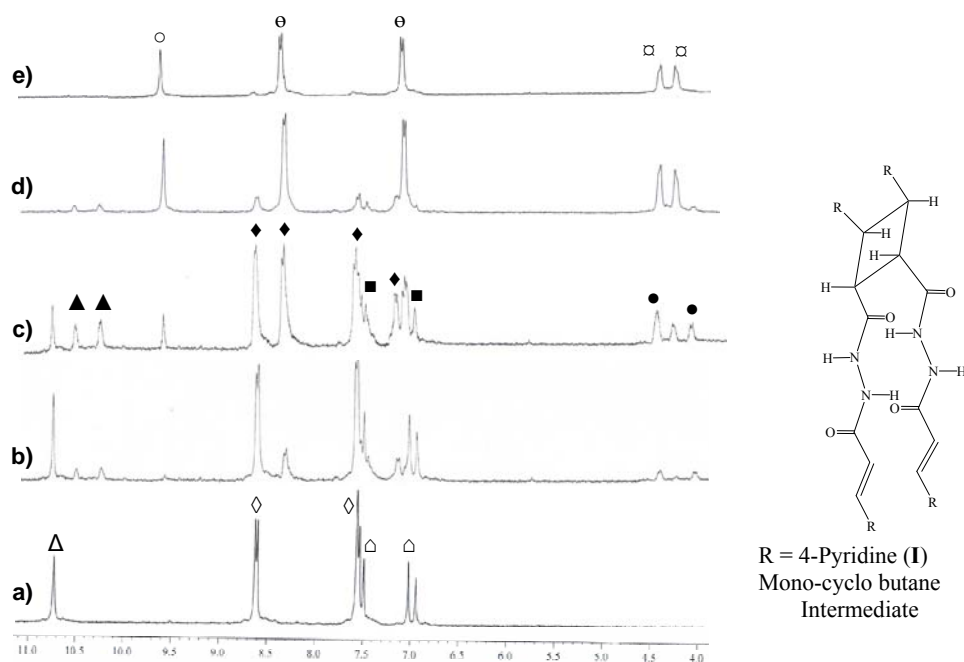
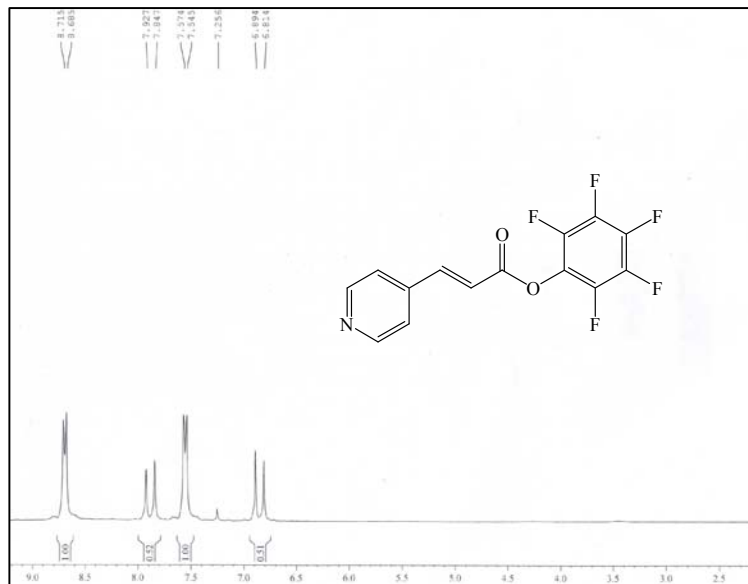


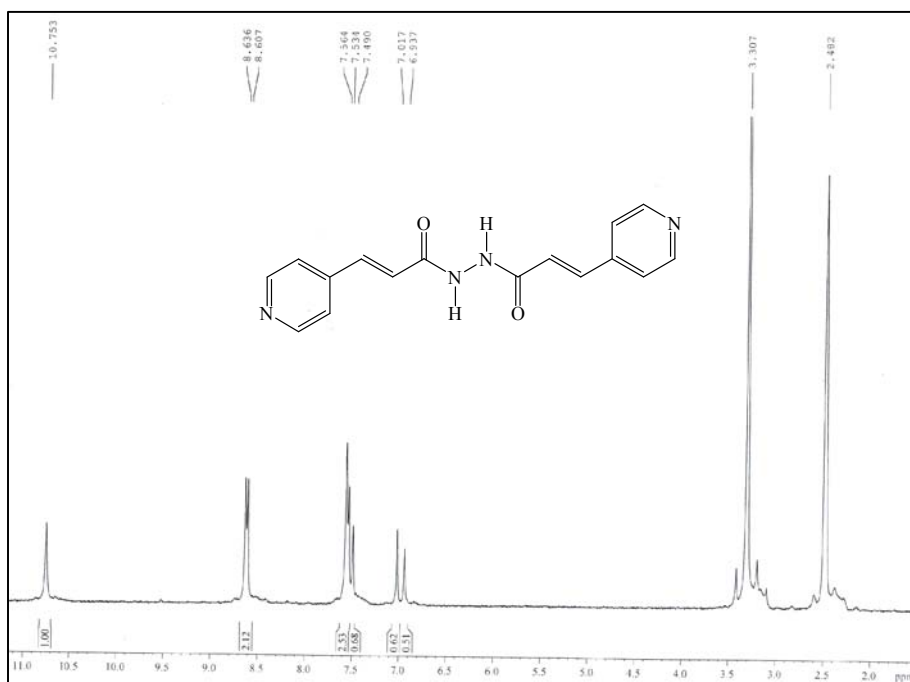
Fig.S3. ^1H NMR spectra of complex **1** in d^6 DMSO recorded at various stages of reaction: a) before irradiation; b) after half day; c) after two days; d) after 10 days of exposure to room light; e) after 100% reaction: Δ (NH of 4-PAH), \diamond (Py-H of 4-PAH), \triangle (alkene-H of 4-PAH), \blacktriangle (NH of **I**), \blacklozenge (Py-H of **I**), \blacksquare (alkene-H of **I**), \bullet (cyclobutane-H of **I**), \circ (NH of TCHD), Θ (Py-H of TCHD), \square (cyclobutane-H of TCHD).

¹H NMR Spectra

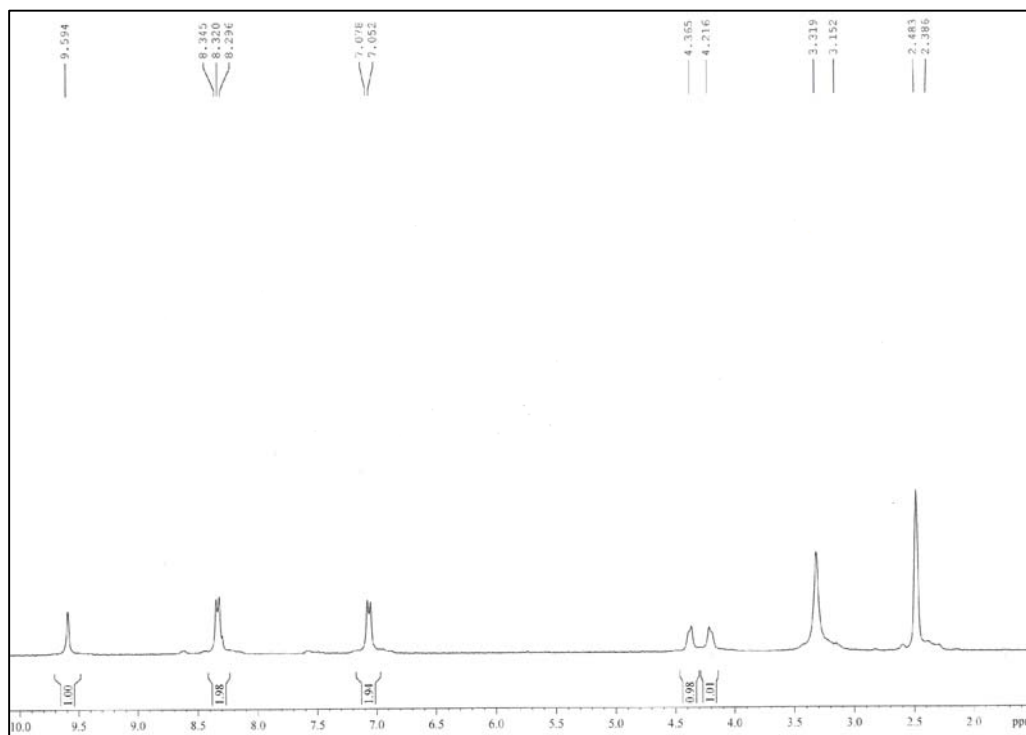
1) Pentafluorophenyl ester of 4-pyridylacrylic acid.



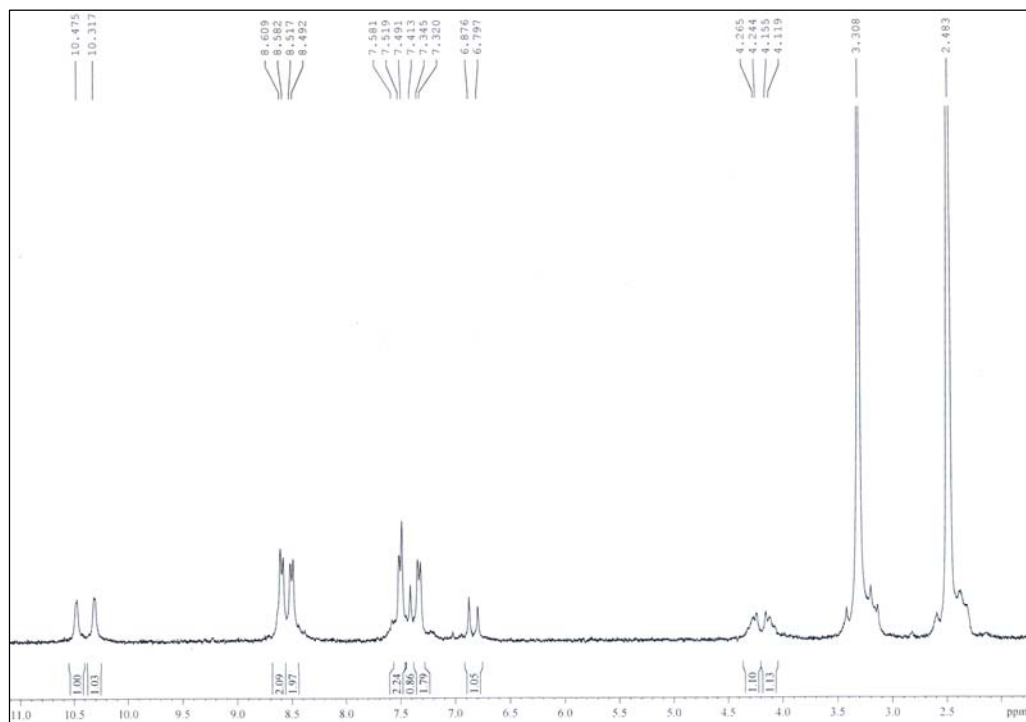
2) 4-PAH.



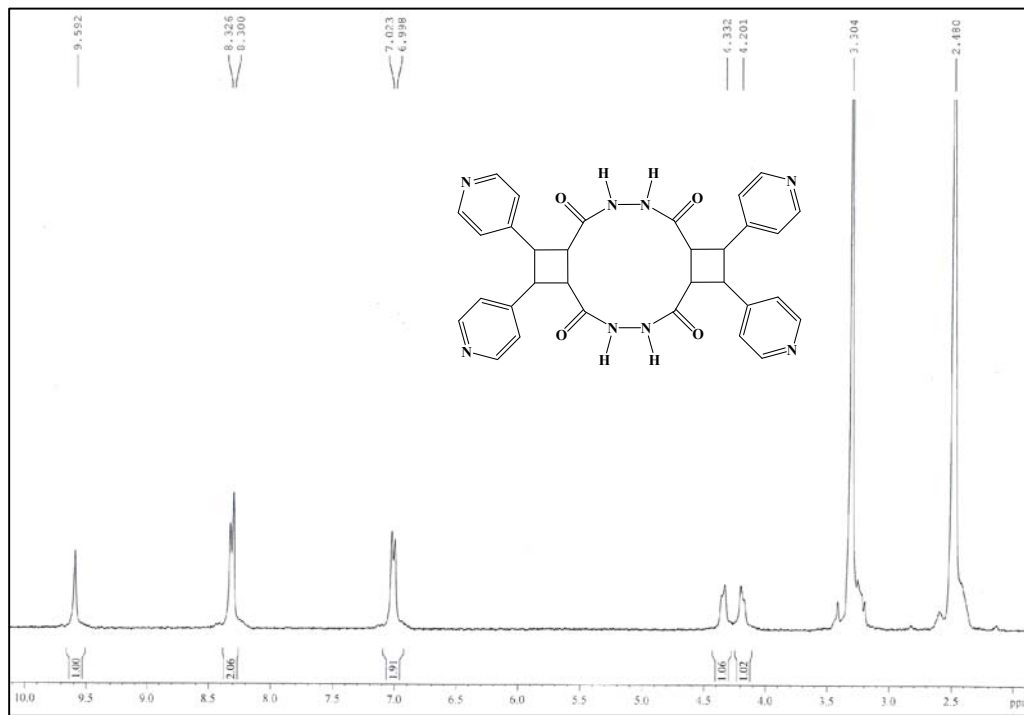
3) Irradiated Complex 1.



4) Irradiated Complex 2.



5) TCDH.

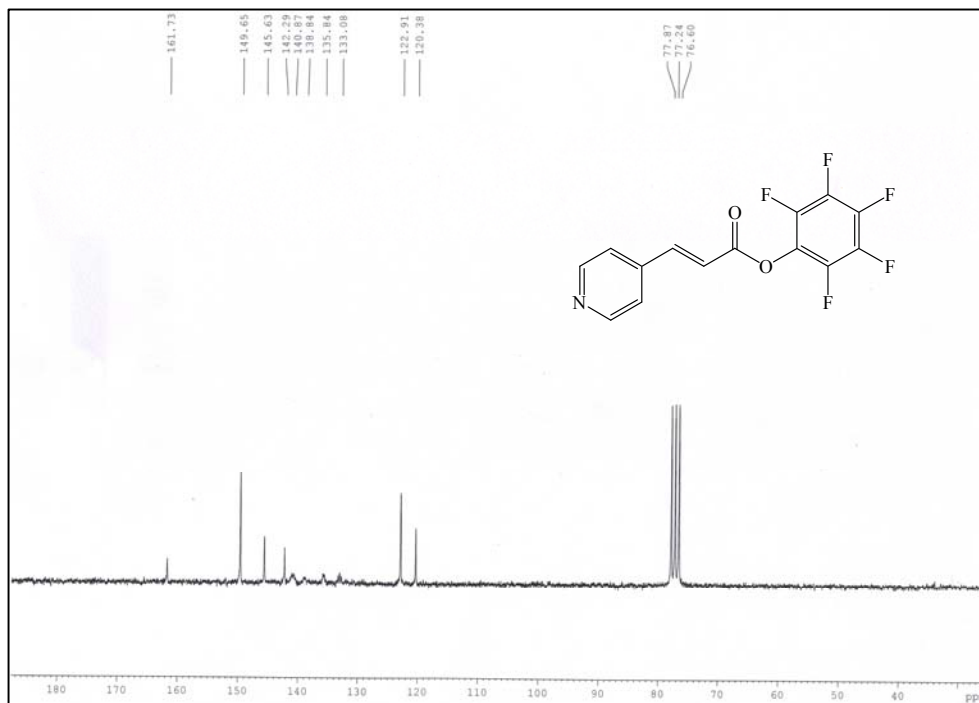


6) MCB.

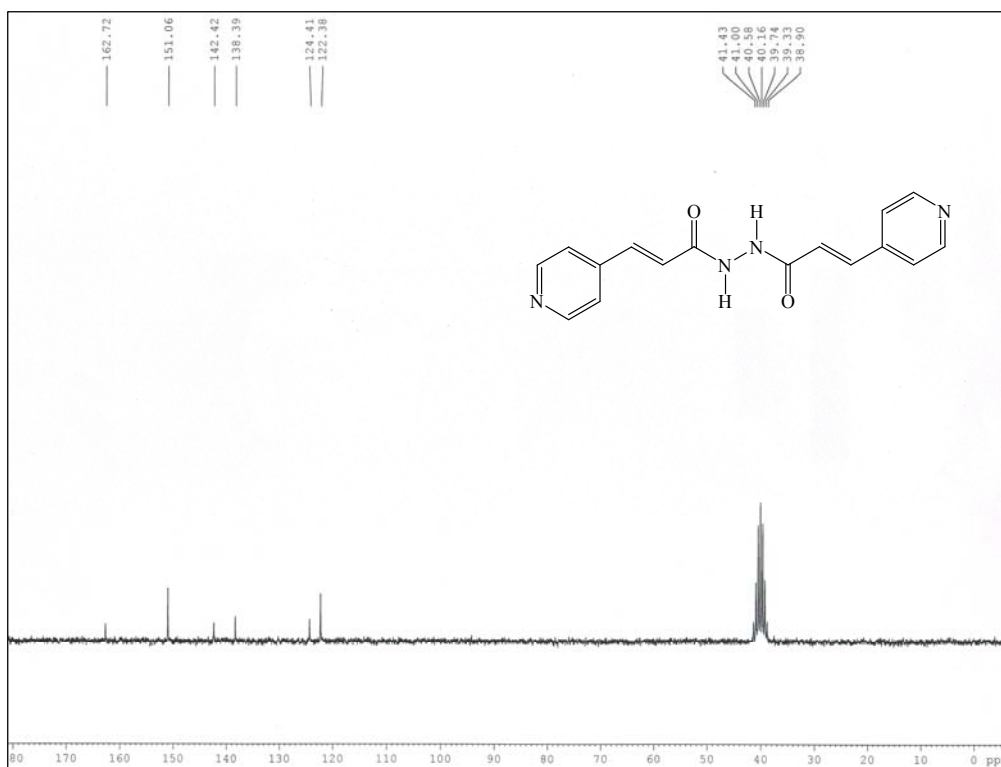


¹³C NMR Spectra

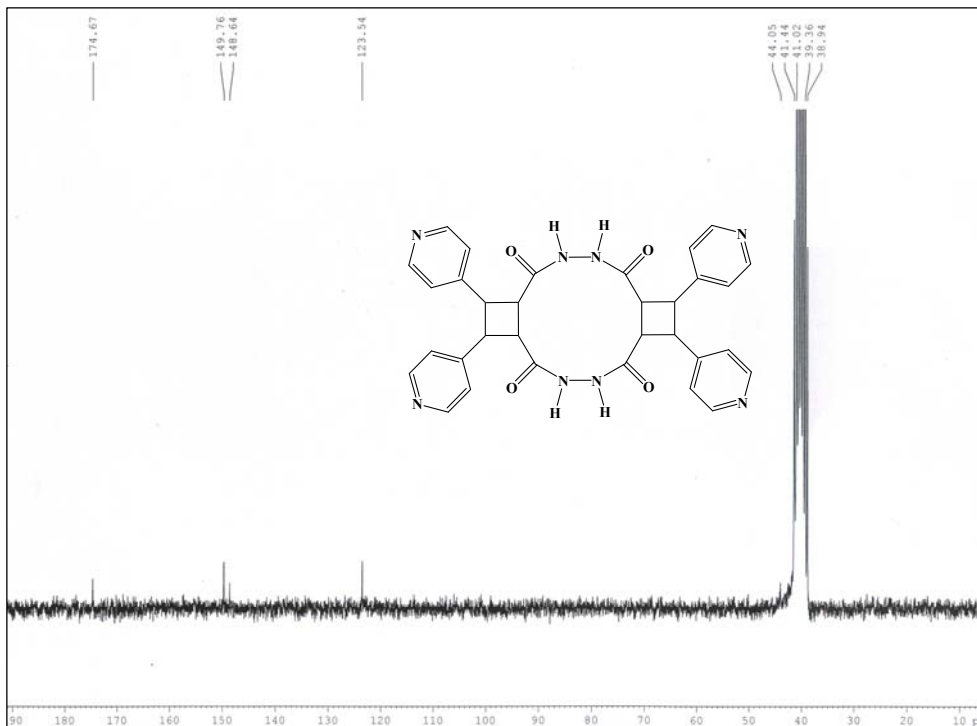
1) Pentafluorophenyl ester of 4-pyridylacrylic acid.



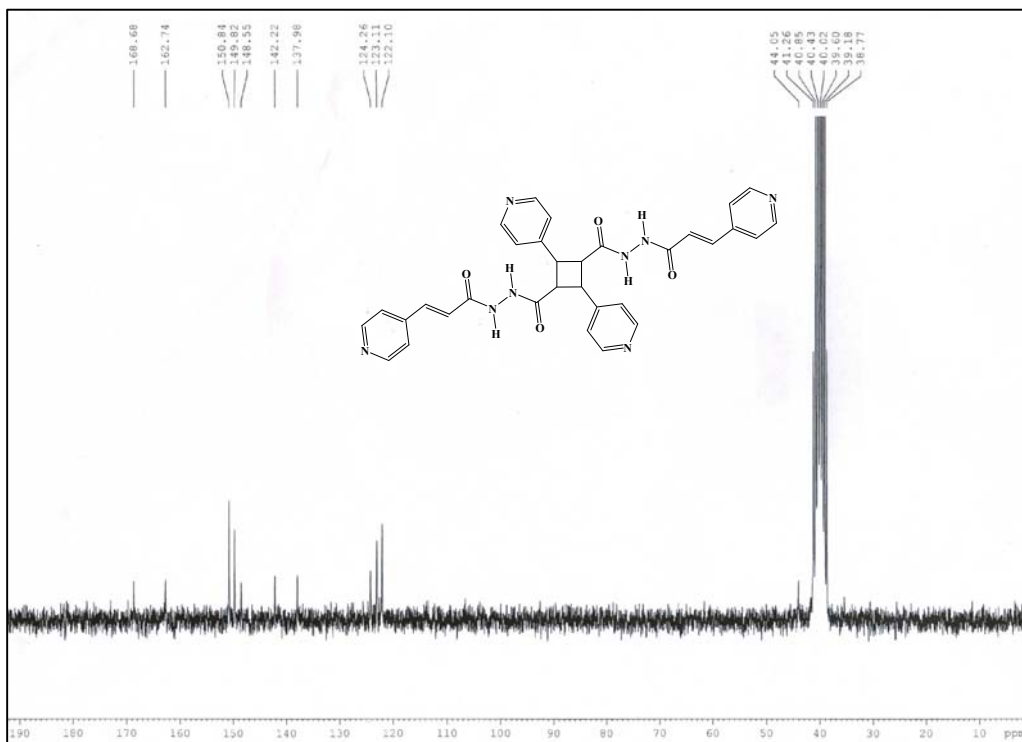
2) 4-PAH.



3) TCDH.

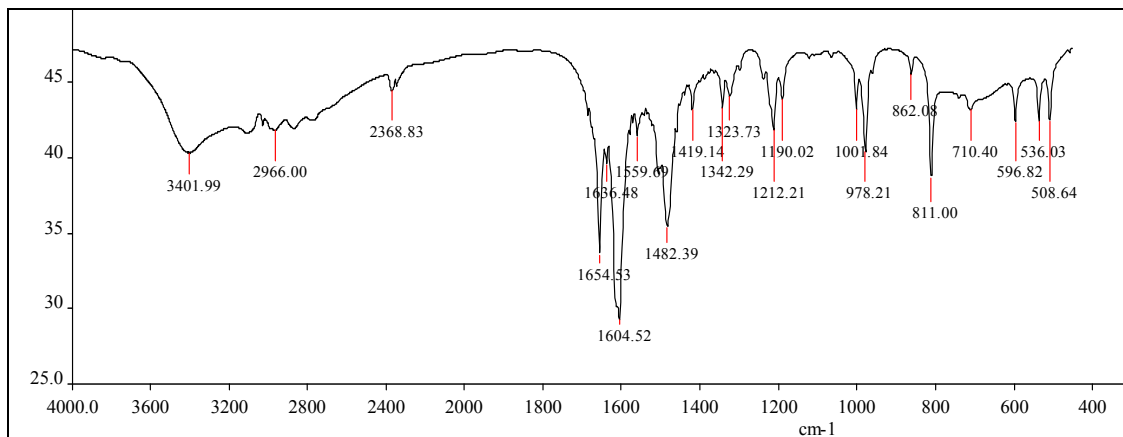


4) MCB.

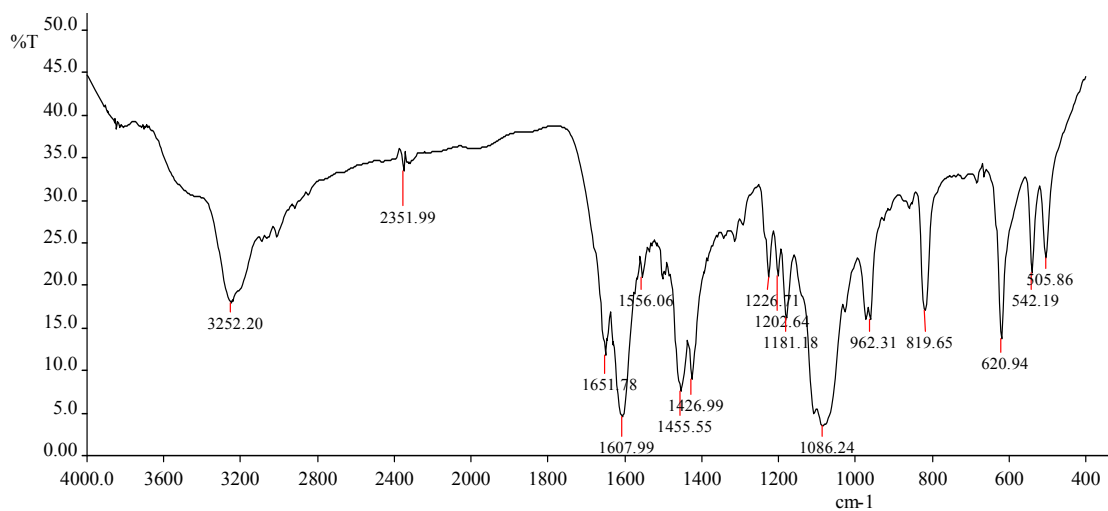


IR Spectra

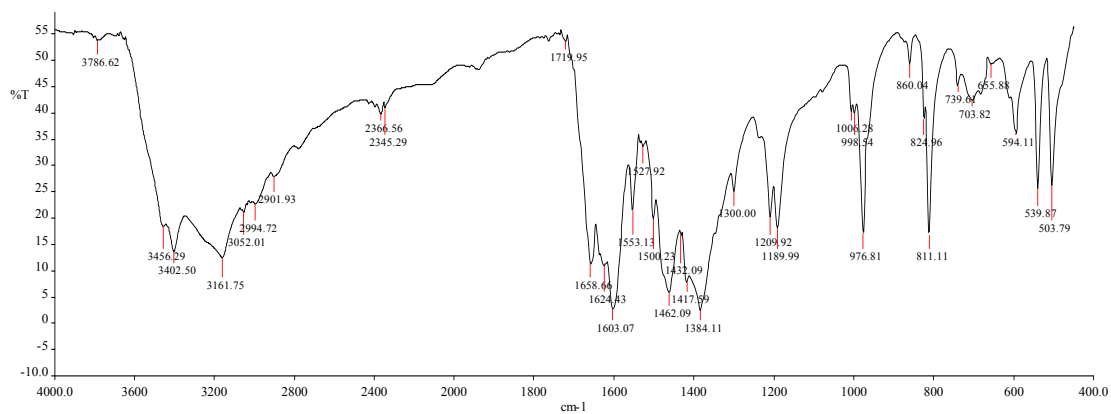
1) 4-PAH.



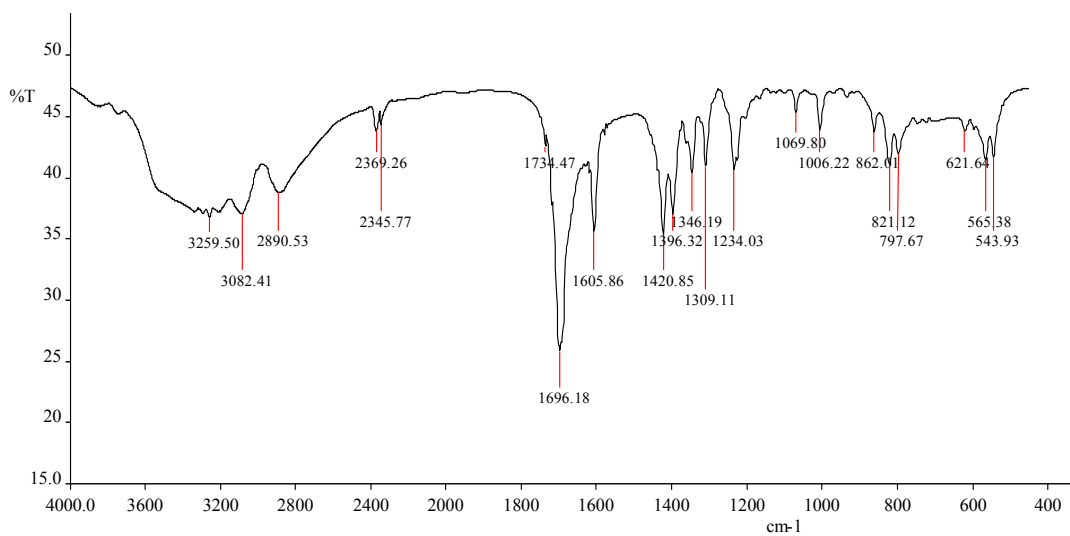
2) Complex 1.



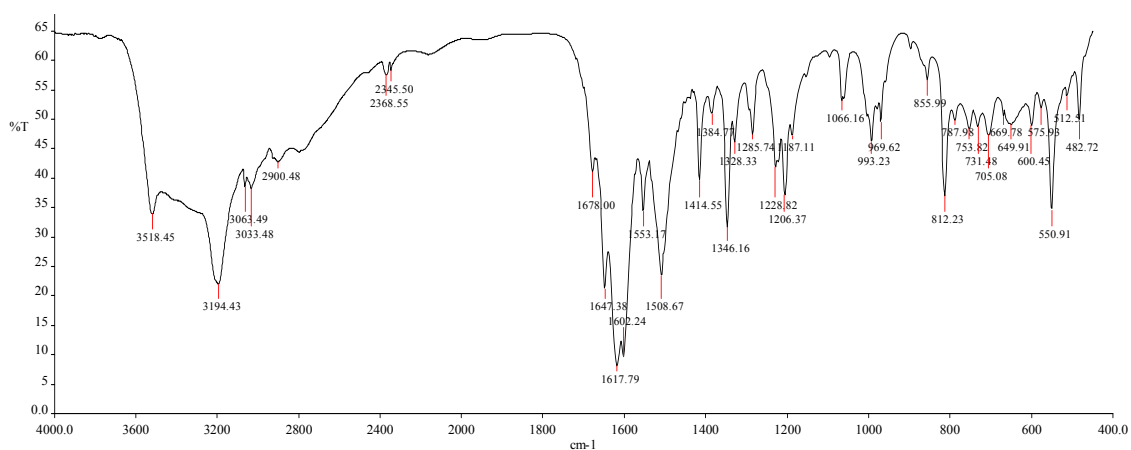
3) Complex 2.



4) TCHD.



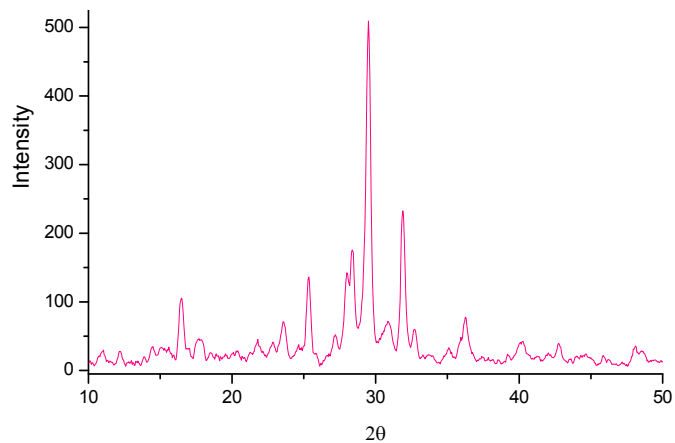
5) MCB.



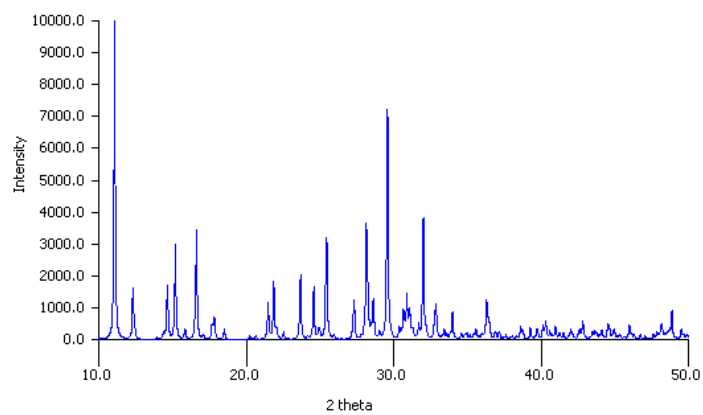
XRPD patterns

1) Complex 1.

(A) Experimental

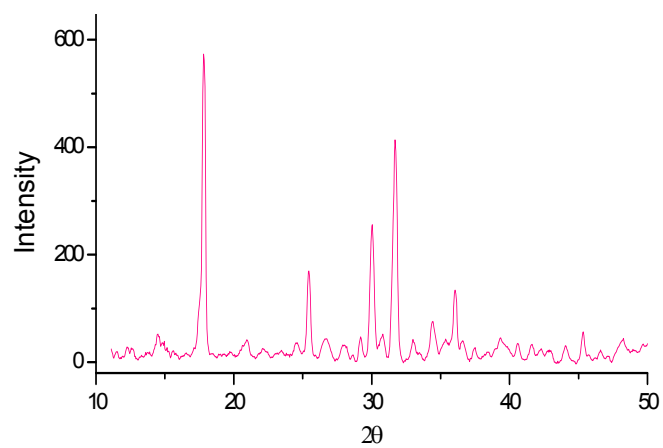


(B) Calculated



2) Complex 2.

(A) Experimental



(B) Calculated

