

Supporting information

Terpyridine-Ru Complexes Non-Covalently Supported on Cobalt Magnetic Nanoparticles for Nitroarene Transfer Hydrogenation

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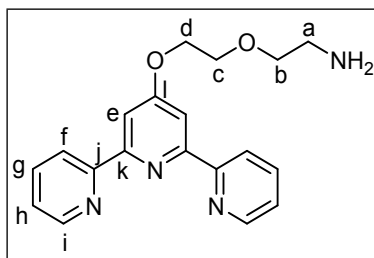
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1. Synthesis and characterization of terpyridine ligands

Compound **2**: (2-(2-([2, 2':6',2''-terpyridin]-4'-yloxy)ethoxy-1-amine



This procedure was adapted from a previously reported procedure.¹ In a Schlenk equipped with a magnetic stirring bar, potassium hydroxide (589 mg, 10.485 mmol), DMSO (5 mL) and 2- (2-aminoethoxy) ethanol (230 μ L, 2.307 mmol) were added successively. After 2 hours at 50 $^{\circ}$ C, 4-chloro-2,2',6',2''-terpyridine (600 mg, 2.241 mmol) and DMSO (3 mL) were added. After 24 hours of stirring, the obtained solution was then added to dichloromethane (80 mL) and washed with water (3x30 mL). The organic phase was dried over magnesium sulfate (MgSO_4) and then evaporated to dryness. The product **2** was obtained in the form of a light yellow solid with a yield of 97% (652 mg).

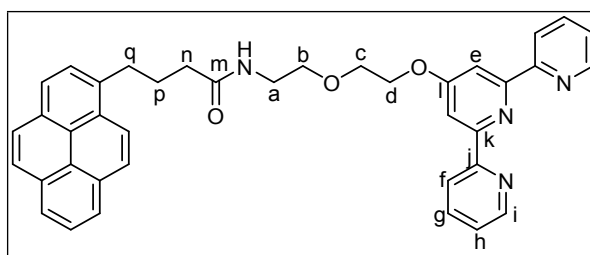
^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}$ C) δ (ppm): 2.92 (t, $^3J_{\text{H-H}} = 5.2$ Hz, 2H, $\text{C}^{\text{a}}\text{-H}$), 3.63 (t, $^3J_{\text{H-H}} = 5.2$ Hz, 2H, $\text{C}^{\text{b}}\text{-H}$), 3.91 (m, 2H, $\text{C}^{\text{c}}\text{-H}$), 4.41 (m, 2H, $\text{C}^{\text{d}}\text{-H}$), 7.32 (m, 2H, $\text{C}^{\text{h}}\text{-H}$), 7.84 (ddd, $^3J_{\text{H-H}} = 7.8$ Hz, $^3J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz, 2H, $\text{C}^{\text{g}}\text{-H}$), 8.07 (s, 2H, $\text{C}^{\text{e}}\text{-H}$), 8.61 (m, 2H, $\text{C}^{\text{f}}\text{-H}$), 8.70 (ddd, $^3J_{\text{H-H}} = 4.8$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz, $^5J_{\text{H-H}} = 0.9$ Hz, 2H, $\text{C}^{\text{i}}\text{-H}$)

$^{13}\text{C}\{-^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 $^{\circ}$ C) δ (ppm) : 41.87 (s, C^{a}), 67.74 (s, C^{b}), 69.28 (s, C^{c}), 73.76 (s, C^{d}), 107.48 (s, C^{e}), 121.31 (s, C^{f}), 123.83 (s, C^{h}), 136.77 (s, C^{g}), 149.03 (s, C^{i}), 156.05 (s, C^{j}), 157.12 (s, C^{k}), 167.03 (s, C^{l}).

ESI-HRMS m/z : found: 337,1680 $[\text{M}+\text{H}]^+$ (theoretical: 337,1659 $[\text{M}+\text{H}]^+$)

¹ Schubert, U. S. ; Eschbaumer, C.; Hien, O.; Andres, P. R. 4-functionalized 2,2':6',2''-terpyridines as building blocks for supramolecular chemistry and nanoscience. *Tetrahedron Lett.* **2001**, 42, 4705-4707.

Compound 3: N-(2-(2-([2,2':6',2''-terpyridin]-4'-yloxy)ethoxy)ethyl)-4-(pyrene-2-yl)butanamide



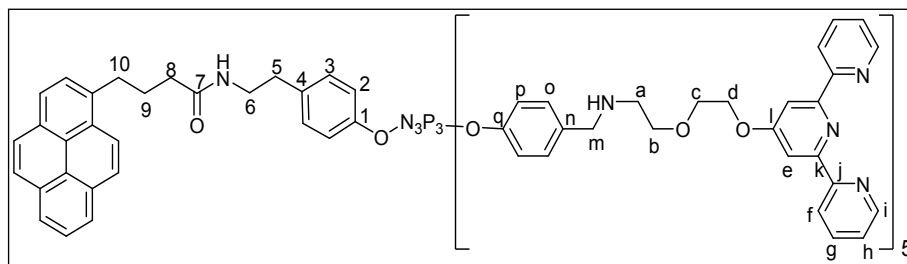
A Schlenk tube equipped with a magnetic stirring bar was charged with a solution of pyrenebutyric acid **1** (256 mg, 0.892 mmol, 1eq) in DMF (8 mL). At 0°C, were successively added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC-HCl) (205 mg, 1.068 mmol, 1.2eq), triethylamine (Et₃N) (149 µL, 1.068 mmol, 1.2eq) and HOBT (96 mg, 1.068, 1.2eq). After one hour at 0°C, a solution of **2** (300 mg, 0.892 mmol, 1 eq) in DMF (4 mL) was added. After another hour at 0°C the mixture was warmed up to room temperature and stirred for 6 days (monitoring by TLC). The DMF was removed under vacuum with toluene co-addition (3x5 mL). The solid obtained was recrystallized in ethanol to yield **3** as a yellow powder in a yield of 74% (399 mg).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 2.13 (m, 2H, C^p-H), 2.25 (m, 2H, Cⁿ-H), 3.31 (m, 2H, C^a-H), 3.56 (m, 2H, C^q-H), 3.67 (m, 2H, C^b-H), 3.89(m, 2H, C^c-H), 4.44 (m, 2H, C^d-H), 6.42 (s, 1H, NH), 7.30-7.31 (ddd, ³J_{H-H}= 4.8 Hz, ³J_{H-H}= 7.5 Hz, ⁴J_{H-H}= 1.1 Hz, 2H, C^h-H), 7.77 (d, ³J_{H-H}= 7.8 Hz, 1H, pyr), 7.83 (ddd, ³J_{H-H}= 7.5 Hz, ³J_{H-H}= 7.9 Hz, ⁴J_{H-H}= 1.8 Hz, 2H, C^g-H), 7.59-8.05 (m, 5H, pyr), 8.11 (s, 2H, C^e-H), 8.12-8.15 (m, 2H, pyr), 8.23 (d, 1H, ³J_{H-H}= 9.2 Hz, pyr), 8.57 (ddd, ³J_{H-H}= 7.9 Hz, ⁴J_{H-H}= 1.1 Hz, ⁵J_{H-H}= 0.9 Hz, 2H, C^f-H), 8.66 (ddd, ³J_{H-H}= 4.8 Hz, ⁴J_{H-H}= 1.8 Hz, ⁵J_{H-H}= 0.9 Hz, 2H, Cⁱ-H)

¹³C-{¹H} NMR (100 MHz, DMSO-d₆, 25 °C) δ (ppm) : 27.57 (s, C^p), 32.71 (s, C^q), 34.93 (s, Cⁿ), 39.05 (s, C^a), 67.71 (s, C^b), 69.14 (s, C^c), 70.36 (s, C^d), 107.01 (s, C^e), 120.70(s, C^f), 123.66 (s, C^h), 123.63 (s, pyr), 124.43 (s, pyr), 124.48 (s, pyr), 124.59 (s, pyr), 124.94 (s, pyr), 124.98 (s, pyr), 125.51 (s, pyr), 126.25 (s, pyr), 126.92 (s, pyr), 127.27 (s, pyr), 127.29 (s, pyr), 128.79 (s, pyr), 129.87 (s, pyr), 131.07 (s, pyr), 131.48 (s, pyr), 136.39 (s, pyr), 136.75 (s, C^g), 148.90 (s, Cⁱ), 155.91 (s, C^j), 157.06 (s, C^k), 167.09 (s, C^l), 171.43 (C=O).

ESI-HRMS m/z: found: 607.2714 [M+H]⁺ (theoretical: 607.2709 [M+H]⁺)

Compound **5**: Dendron with 5 terpyridine moieties



In a Schlenk tube equipped with a magnetic stirring bar, **2** (106 mg, 0.314 mmol) is dissolved in THF (2 mL). A solution of **9** (60 mg, 0.052 mmol) in THF (2 mL) was then added. After 48h of stirring at room temperature, sodium borohydride NaBH₄ (19 mg, 0.502 mmol) and methanol (2 mL) were added at 0°C. The mixture was warmed up to room temperature, stirred for 24 h and then quenched with a solution sodium carbonate Na₂CO₃ (77 mg in 1 mL H₂O) and extracted with ethyl acetate (3x3 mL), then with dichloromethane (3x3 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated to dryness under vacuum to yield **5** as a white powder in 79 % yield (113 mg, 79 %).

¹H NMR (400 MHz, CD₂Cl₂, 25°C) δ (ppm): 2.14 (m, 4H, C⁸-H, C⁹-H), 2.84 (m, 12H, C^a-H, C⁵-H), 3.30 (t, ³J_{H-H} = 7.6 Hz, 2H, C⁶-H), 3.42 (m, 2H, C¹⁰-H), 3.68 (m, 20H, C^b-H, C^m-H), 3.83 (m, 10H, C^c-H), 4.82 (m, 10H, C^d-H), 6.85 (m, 12H, C²-H, C^p-H), 7.00 (m, 2H, C³-H), 7.15 (m, 10H, C^o-H), 7.32 (m, 10H, C^h-H), 7.84 (m, 11H, C^g-H, pyrene), 8.03 (m, 15H, C^e-H, pyrene), 8.16 (m, 2H, pyrene), 8.28 (d, 1H, pyrene), 8.60 (m, 10H, C^f-H), 8.65 (m, 10H, Cⁱ-H).

³¹P-{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C) δ (ppm): 8.69-8.88 (m, N₃P₃)

¹³C-{¹H} NMR (100 MHz, CD₂Cl₂, 25°C) δ (ppm): 27.41 (s, C⁹), 32.69 (s, C¹⁰), 34.90 (m, C⁵, C⁸), 35.78 (s, C^m), 40.43 (s, C^a), 41.07 (s, C⁶), 67.72 (M, C^b), 69.22 (m, C^c), 70.79 (m, C^d), 107.19 (m, C^e), 120.62 (s br, C², C^p), 121.04 (m, C^f), 123.45 (s, pyr), 123.85 (m, C^h), 124.69 (s, pyr), 124.76 (s, pyr), 124.78 (s, pyr), 124.83 (s, pyr), 124.89 (s, pyr), 125.82 (s, pyr), 126.51 (s, pyr), 127.17 (s, pyr), 127.34 (s, pyr), 127.43 (s, pyr), 128.66 (s br, Cⁿ), 129.01 (C³), 129.12 (C^o), 129.60 (s, pyr), 129.79 (s, pyr), 130.87 (s, pyr), 131.36 (s, pyr), 135.90 (s, C⁴), 136.25 (s, pyr), 136.69 (m, C^g), 149.01 (m, Cⁱ), 149.38 (m, C^q, C^l), 155.83 (m, C^j), 157.08 (m, C^k), 166.97 (m, C^l), 172.30 (C=O),

ESI-HRMS m/z : found: 550.4202 [M+5H]⁵⁺ (theoretical: 550.4227 [M+5H]⁵⁺).

2. Grafting Measurements

The Co/C nanoparticles (20 mg) were added excess of pyrene-tagged ligands (0.01 mmol, 6.1 mg for **3**; 0.004 mmol, 11.0 mg for **5**) in 2-propanol (5 ml) and the suspensions were sonicated for 1 hour at 20°C (see Fig. S1).² Magnetic decantation was performed with magnet and MNPs were washed with 2-propanol (10 x 5 ml; the analysis of all washing solutions by UV spectroscopy showed that no more organic ligands was released from the fifth washing for **5** and from the seventh washing for **3**). The nanoparticles were then dried under vacuum and grafting was determined by elemental analysis.

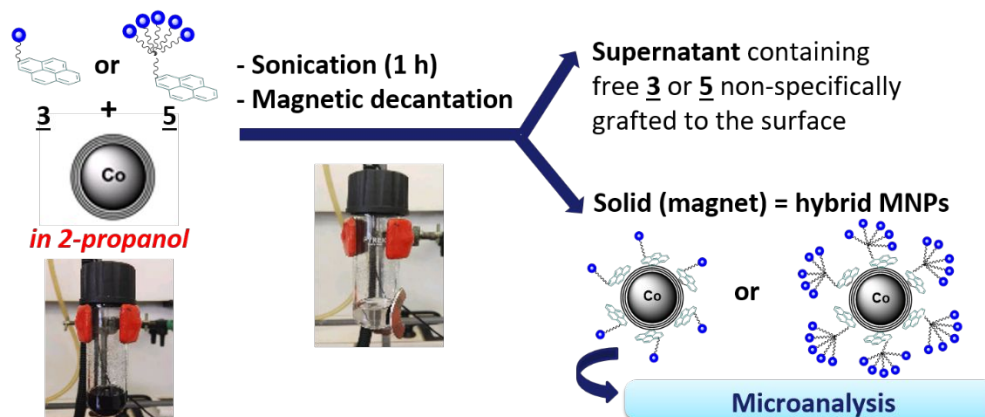


Figure S1: Procedure to prepare the hybrid MNPs decorated with terpyridine ligands

Naked NP: C: 6.056%; H: 0.086%; N: 0%; Hybrid NPs from **3**: C: 7.332%; H: 0.035%; N: 0.135%; Hybrid NPs from **5**: C: 11.184%; H: 0.292%; N: 0.972%

3. Catalytic reactions, recycling experiments, Ru leaching

General procedure for recycling experiments: In a Schlenk tube equipped with magnetic stirring bar, under nitrogen atmosphere, the catalyst was generated in situ from [$\{\text{RuCl}_2(\text{p-cymene})\}_2$] (12.0 mg, 0.0125 mmol) and ligand (0.025 mmol of terpyridine moieties: 0.025 mmol = 15.2 mg for **3**, 0.005 mmol = 13.7 mg for **5**) in 2-propanol (5 ml) for 30 min at 60°C. MNPs (500 mg for **3**, 100 mg for **5**) were introduced and the mixture sonicated for 30 minutes at 20 °C. The nitroarene (0.5 mmol: 51 μL for nitrobenzene (Figure 4) or 68.6 mg for 4-nitrotoluene (Figure 6)), KOH (0.075 mmol, 4.2 mg), and 2-propanol (5 ml) were next added. After 15 hours at reflux (temperature of the oil bath: 100 °C), the reaction mixture was cooled to room temperature, sonicated for 30 minutes at 20 °C and magnetic decantation was

² According to previous reports involving pyrene-tagged phosphines: Keller, M; Collière, V.; Reiser, O.; Caminade, A.-M.; Majoral, J.-P.; Ouali, A. Pyrene-Tagged Dendritic Catalysts Noncovalently Grafted onto Magnetic Co/C Nanoparticles: An Efficient and Recyclable System for Drug Synthesis. *Angew. Chem. Int. Ed.* **2013**, 52, 3626-3629. Loading of monovalent pyrene-tagged phosphines: 0.15 mmol/g of MNPs. Loading of pentavalent pyrene-tagged phosphines: 0.10 mmol/g of MNPs.

performed thanks to the magnet. The MNPs were rinsed twice with 2-propanol (1 mL). The standard 1,3,5-trimethoxybenzene was added to the joined solutions and the mixture obtained analyzed by ^1H NMR (after evaporation of the solvent) and GC-MS. To the hybrid MNPs dried under vacuum, nitroarene chosen for the next run (0.5 mmol: 51 μL for nitrobenzene (Figure 4, cycles 2 to 8); 78.8 mg for 4-chloronitrobenzene (Figure 6, cycle 2); 86.6 mg for 1-nitronaphtalene (Figure 6, cycle 3); 76.6 for 4-nitroanisole (Figure 6, cycle 4); 68.6 mg for 4-nitrotoluene (Figure 6, cycle 5)), KOH and 2-propanol (10 mL) were added and the same procedure was repeated at each run.

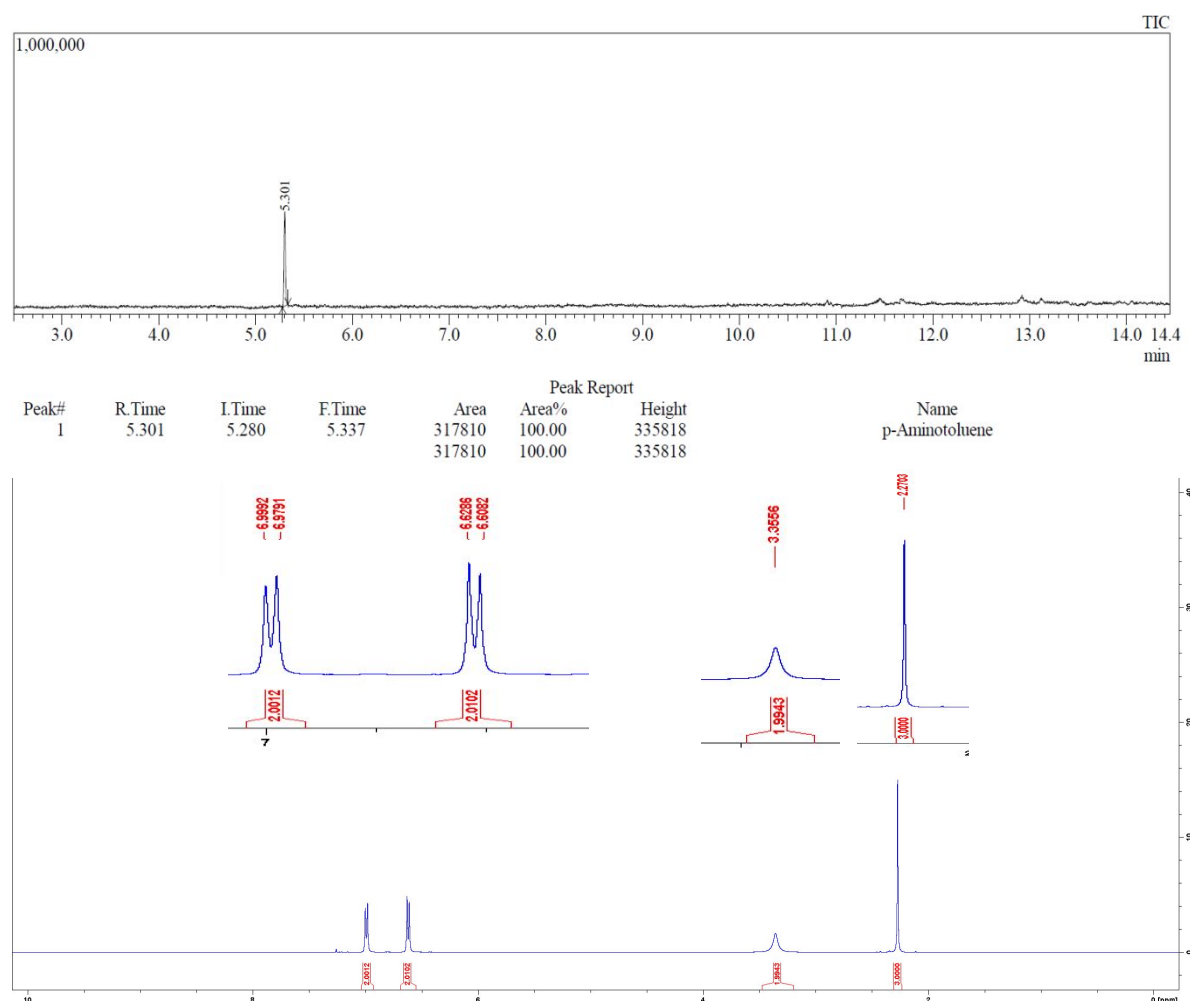


Figure S2: ^1H NMR and GC-MS spectra of the crude obtained after magnetic decantation, washings of MNPs and removing of 2-propanol: *p*-toluidine is isolated in 90% yield (50 mg) (5th run of recycling experiments, see main manuscript Figure 6).

Table S1: Determination by ICP-MS of the Ru amounts present in the crude obtained at each run after magnetic decantation (cases of ligands **3** and **5**).

Entry	1	2	3	4	5	6
Run	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Ru (ppm) Ligand 3	34	19	7	4	2	2
Ru (ppm) Ligand 5	18	14	4	3	2	1

4. HRTEM / STEM images and EDX spectra of the hybrid MNPs before and after catalysis

The catalyst was prepared as described above from [$\{\text{RuCl}_2(\text{p-cymene})\}_2$] (12.0 mg, 0.0125 mmol) and ligand (0.025 mmol of terpyridine moieties: 15.2 mg for **3**, 13.7 mg for **5**) in 2-propanol (5 ml) for 30 min at 60°C. Next MNPs were added, the mixture allowed to sonicated for 30 minutes at 20 °C and the MNPs separated and washed twice with 2-propanol. To improve image quality and limit MNPs agglomeration, ultramicrotomy permitting the preparation of thin sections to observe the actual structure in a bulk material was achieved. Samples of MNPs prepared were first embedded in a resin and the resulting sample were sectioned with an ultra-microtome to be analyzed by HRTEM.

Table S2: STEM images of the MNPs decorated with Ru complexes involving ligands **3** (a) or **5** (b) before catalysis and corresponding EDX spectra

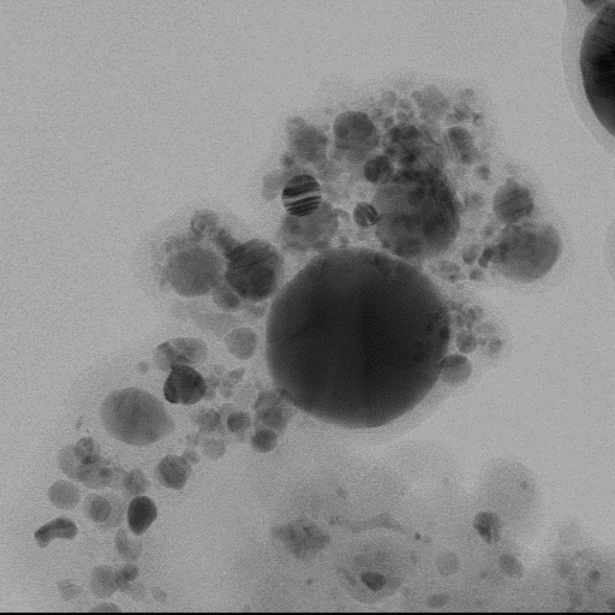
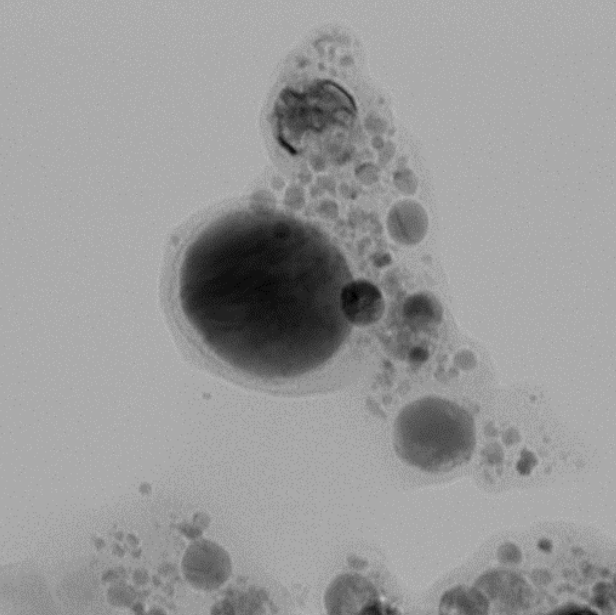
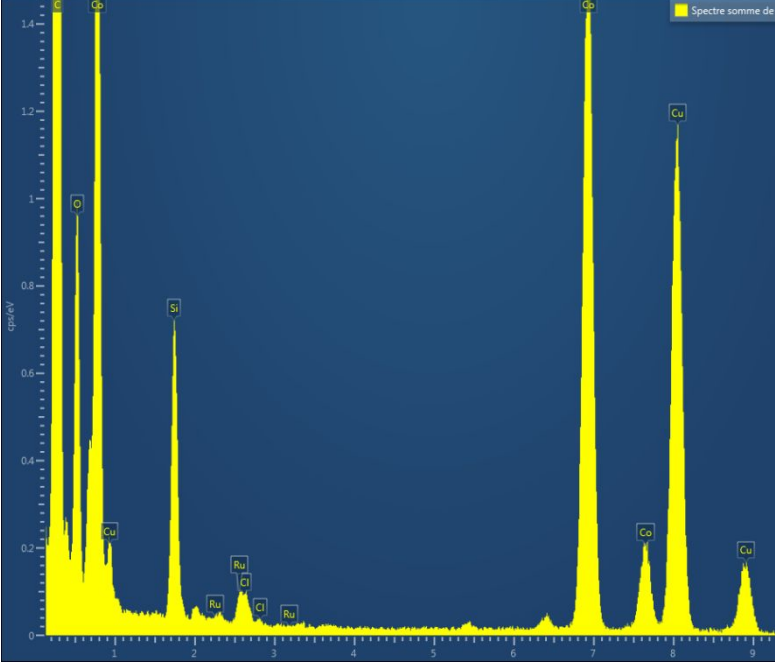
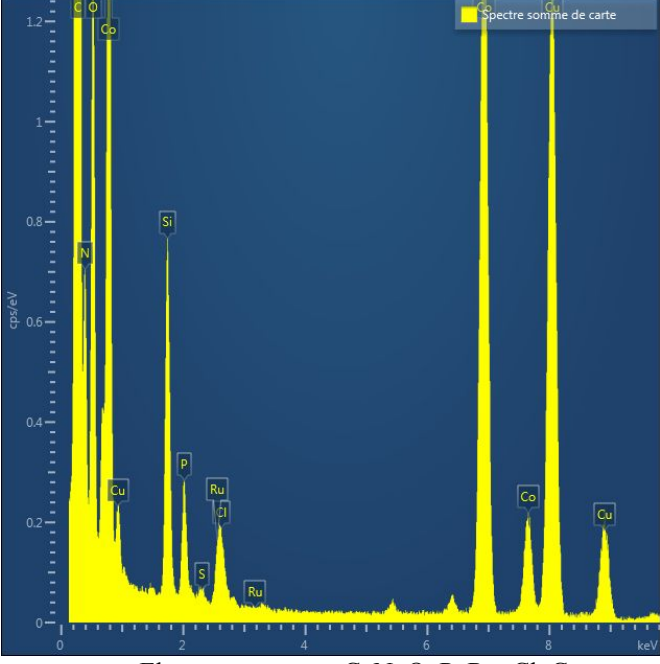
a) Catalytic materials made from $[\{\text{RuCl}_2(\text{p-cymene})\}_2]$ and 3	b) Catalytic materials made from $[\{\text{RuCl}_2(\text{p-cymene})\}_2]$ and 5
 <p>Specimen [STEM BF] TEM 2200FS 200kV x500k 100% Comment: 50.0nm 1/15/2020 11:58:45 Operator:</p>	 <p>Specimen [STEM BF] TEM 2200FS 200kV x500k 100% Comment: 50.0nm 1/15/2020 11:22:51 Operator:</p>
 <p>Elements present : C, N, O, Ru, Cl, Co Cu corresponds to the signal of the grid used for analysis. Si included in the resin used for sample preparation</p>	 <p>Elements present : C, N, O, P, Ru, Cl, Co Cu corresponds to the signal of the grid used for analysis. Si included in the resin used for sample preparation</p>

Table S3: Mapping of the elements on hybrid MNPs obtained from **5** before catalysis

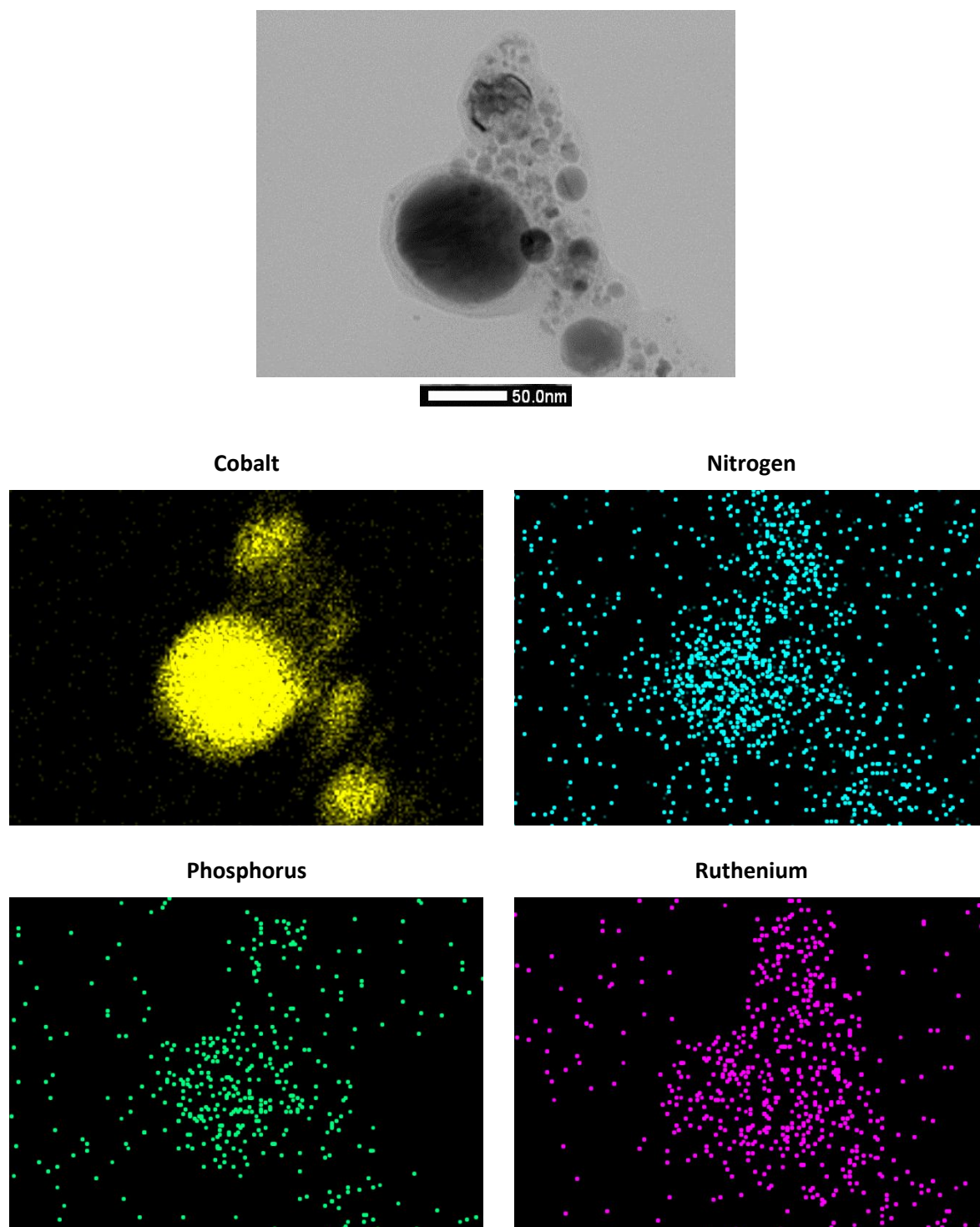


Table S4: STEM images of the MNPs decorated with Ru complexes involving ligand **5** after catalysis and corresponding EDX spectra (elements present: C, N, O, P, Ru, Co)

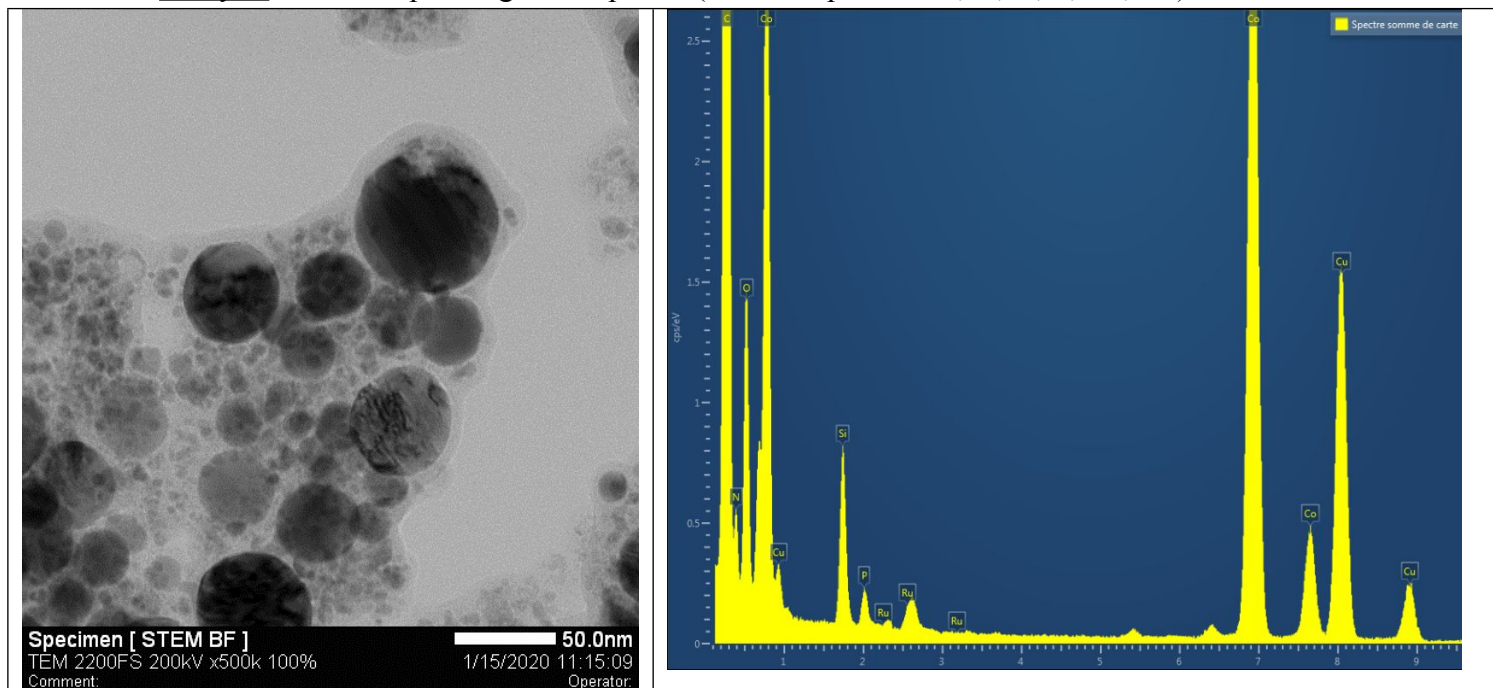
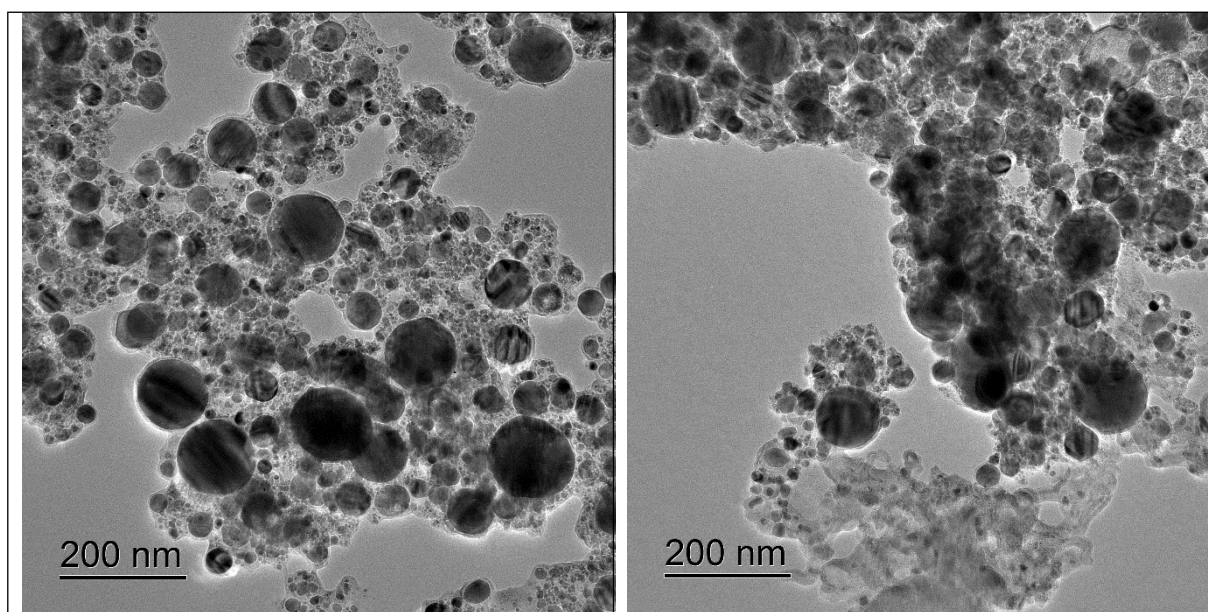


Table S5: Hybrid MNPs obtained from **3** before catalysis (left) and after 5 cycles (right) :
some agglomeration of MNPs after catalytic cycles



5. NMR and mass spectra

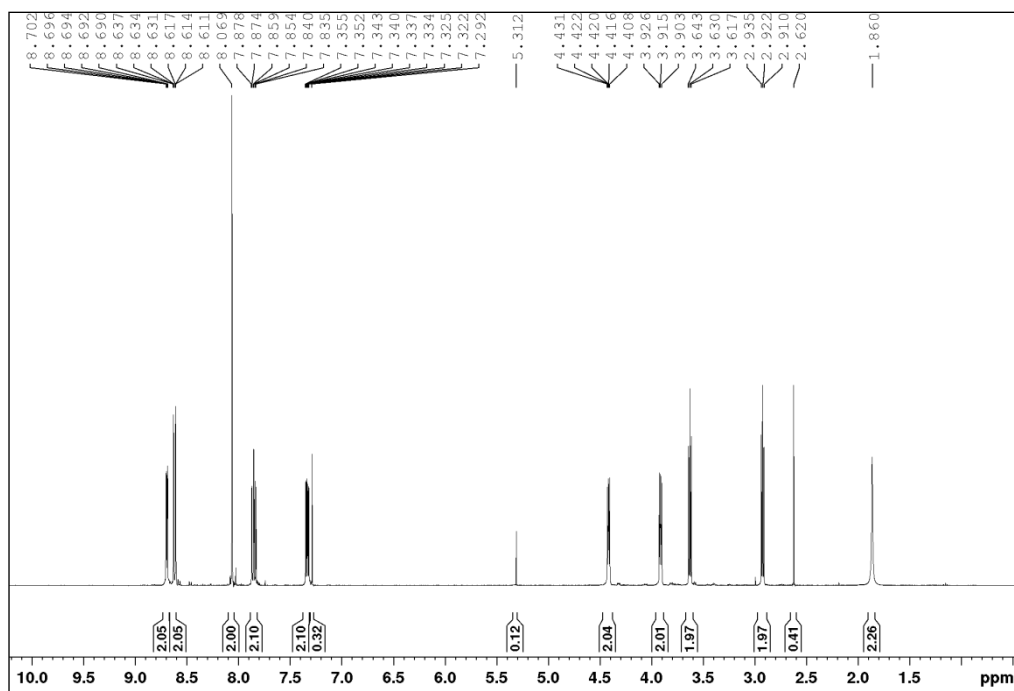


Figure S3. Compound **2** : ¹H NMR spectrum in CDCl₃

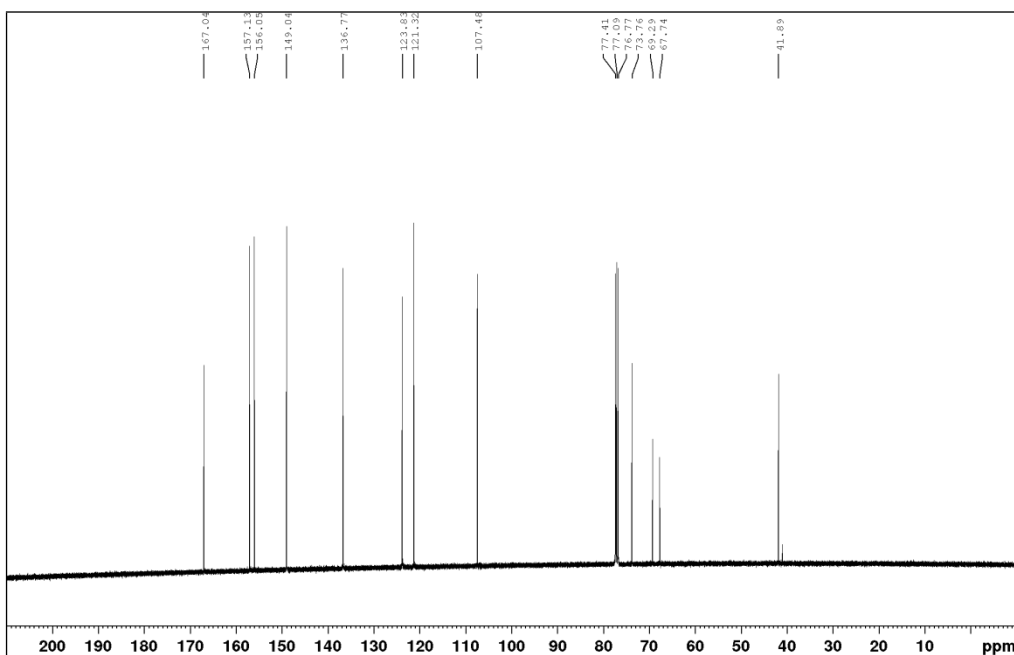
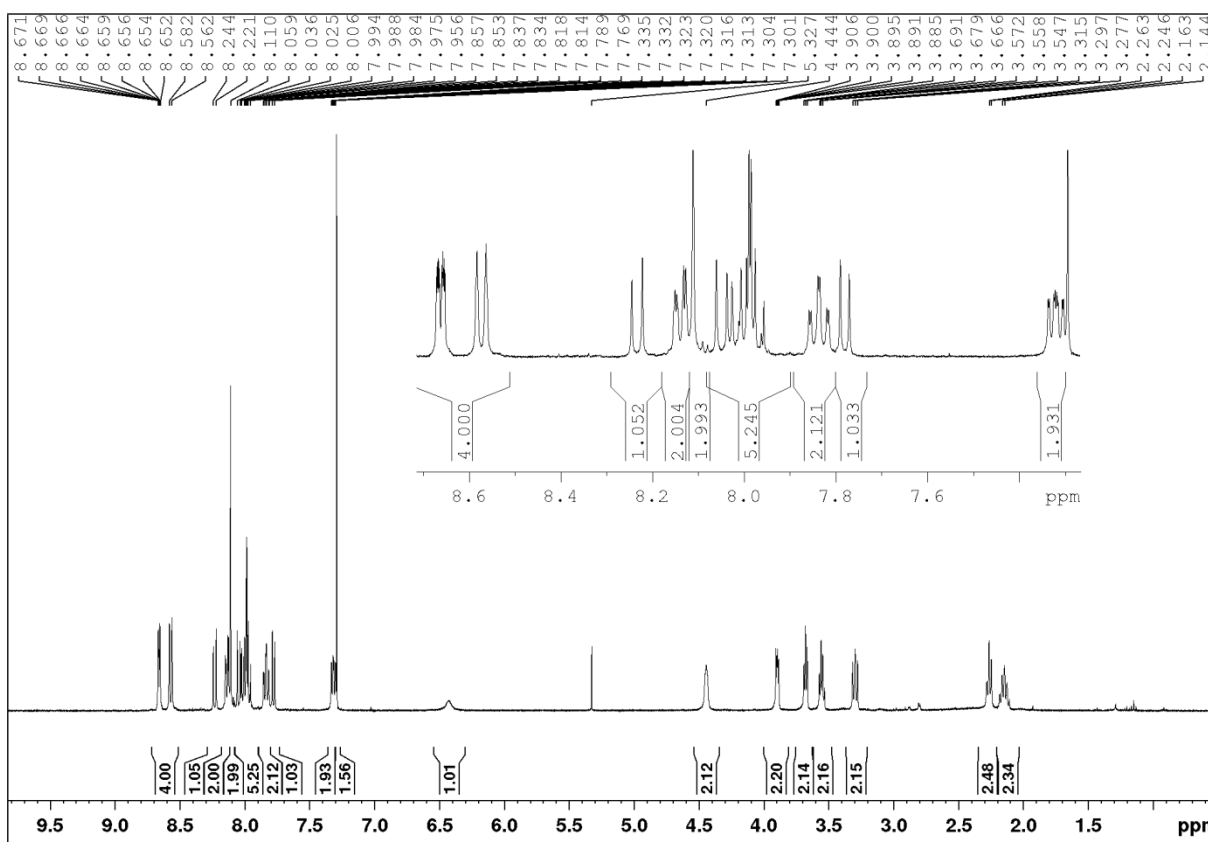
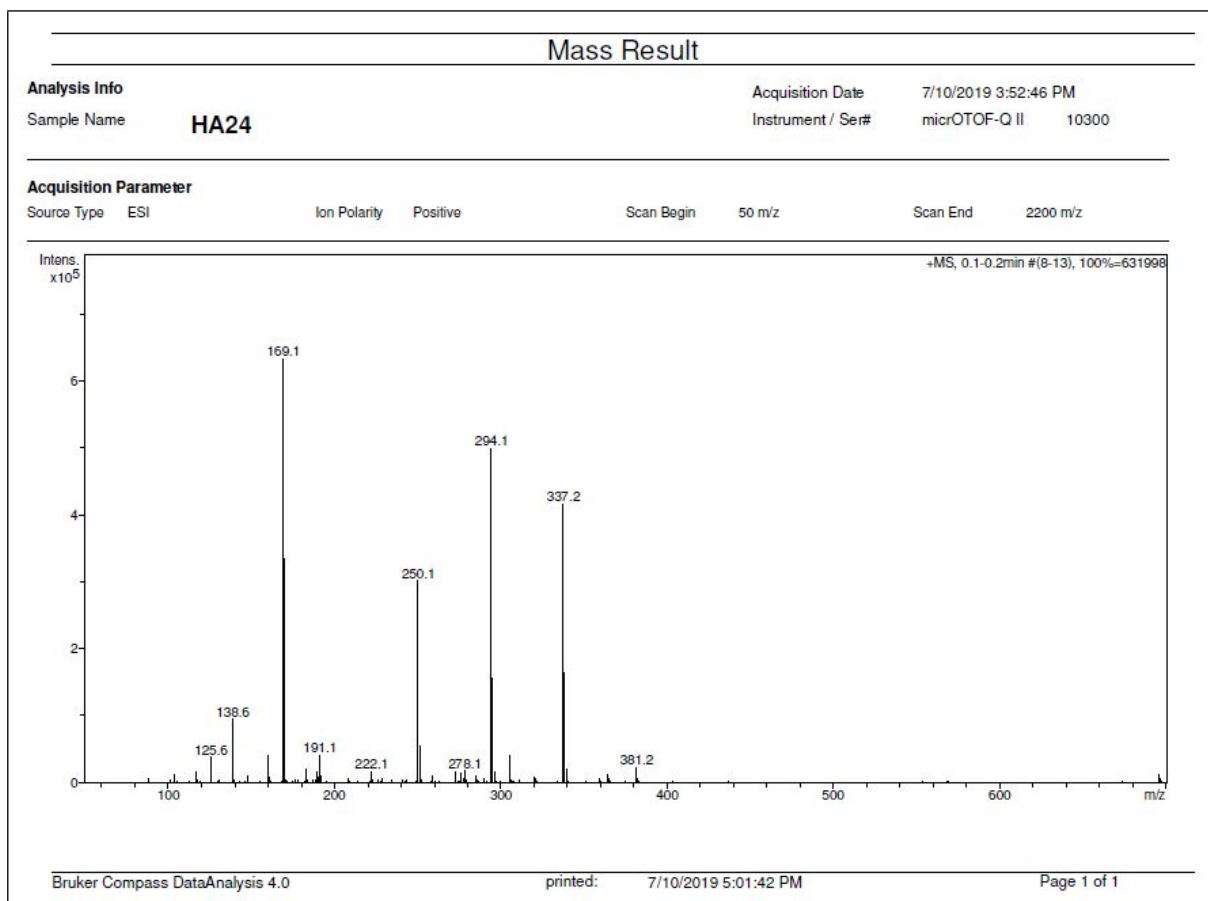


Figure S4. Compound **2** : ¹³C NMR spectrum in CDCl₃



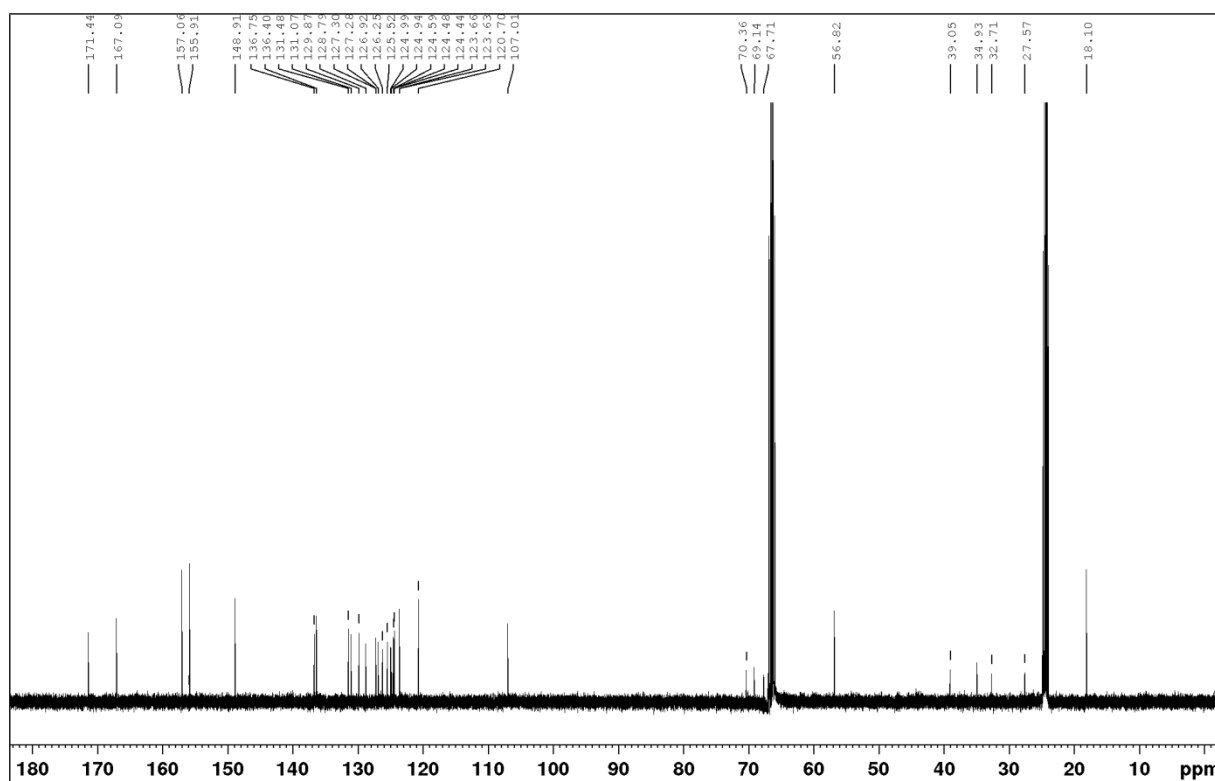


Figure S7. Compound **3** : ^{13}C NMR spectrum in CDCl_3

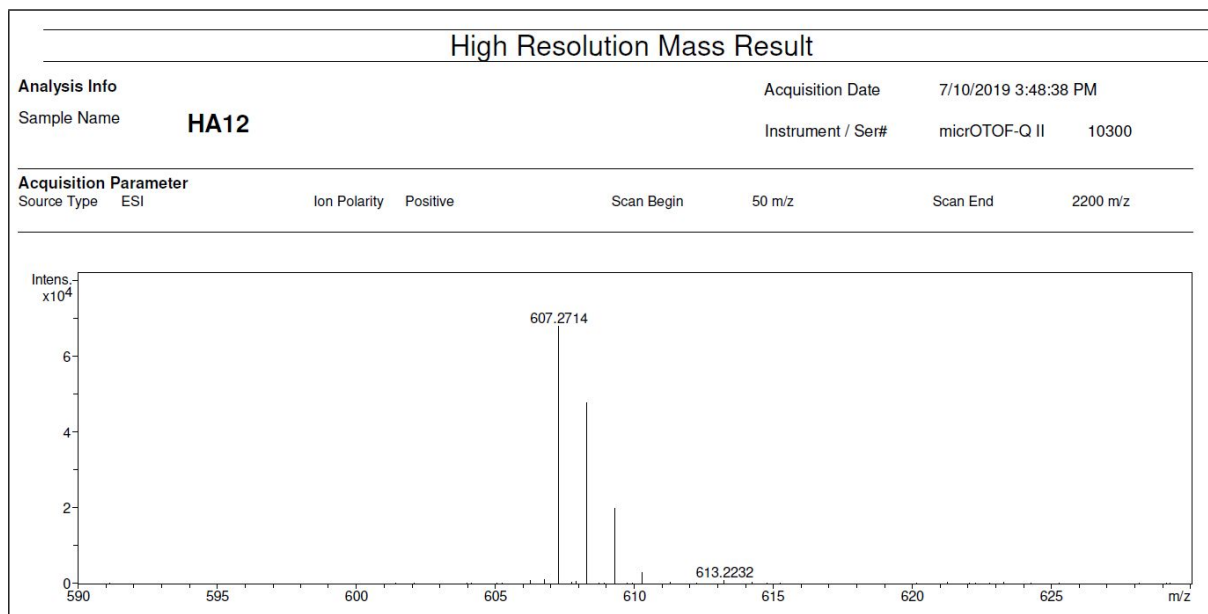


Figure S8. Compound **3** : Mass spectroscopy (ESI)

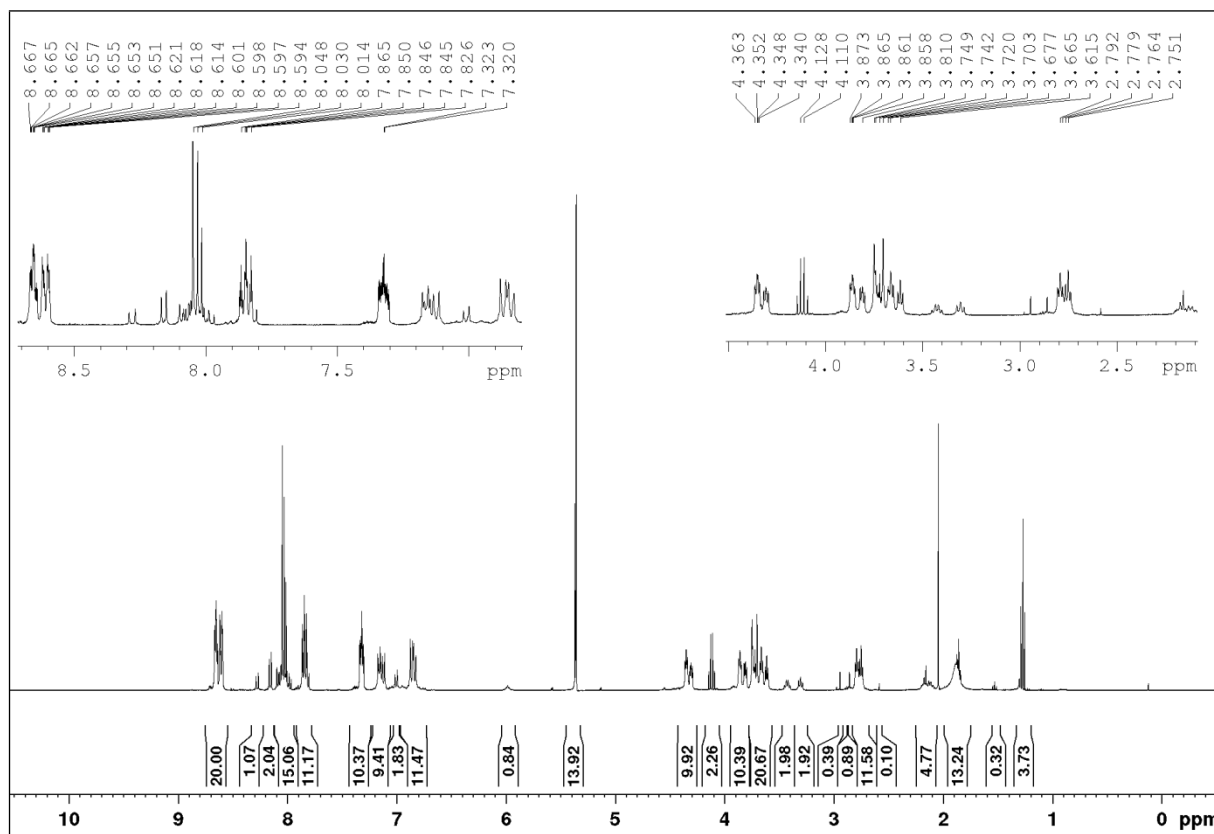


Figure S9. Compound **5** : ¹H NMR spectrum in CD₂Cl₂

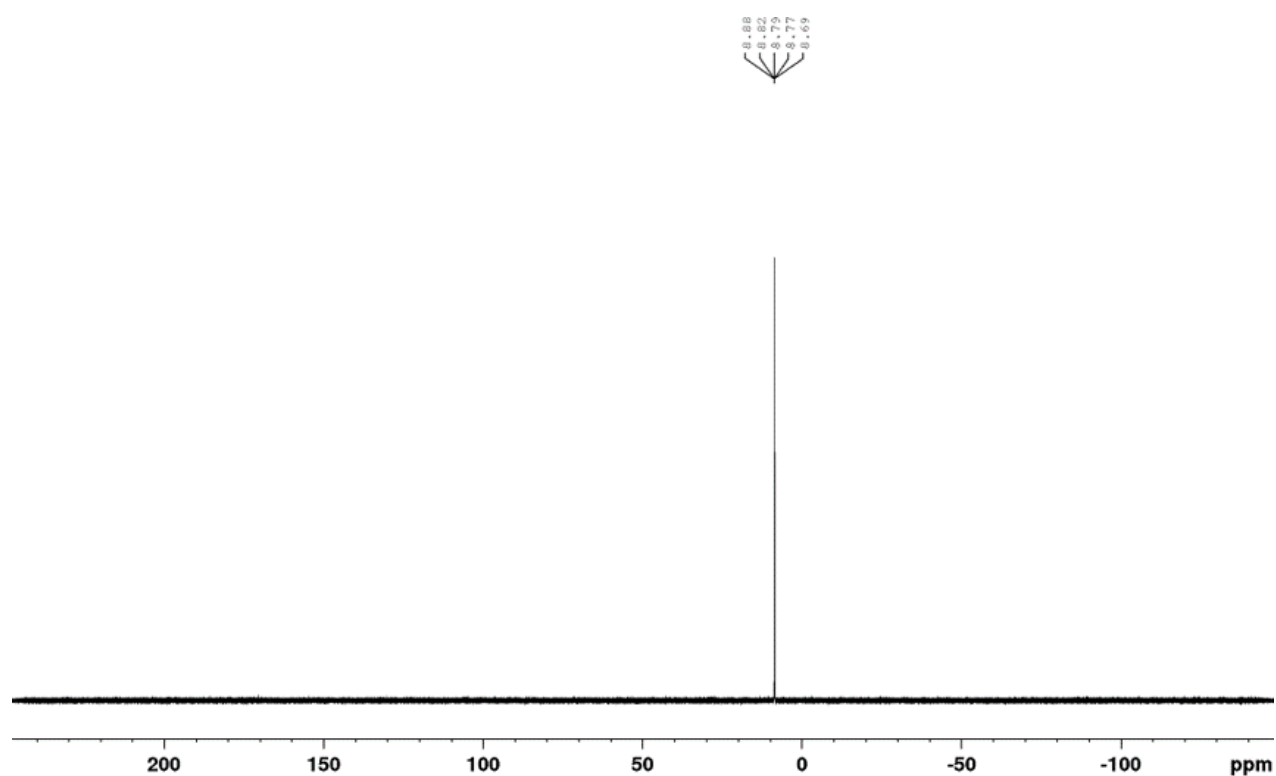


Figure S10. Compound **5** : ³¹P NMR spectrum in CD₂Cl₂

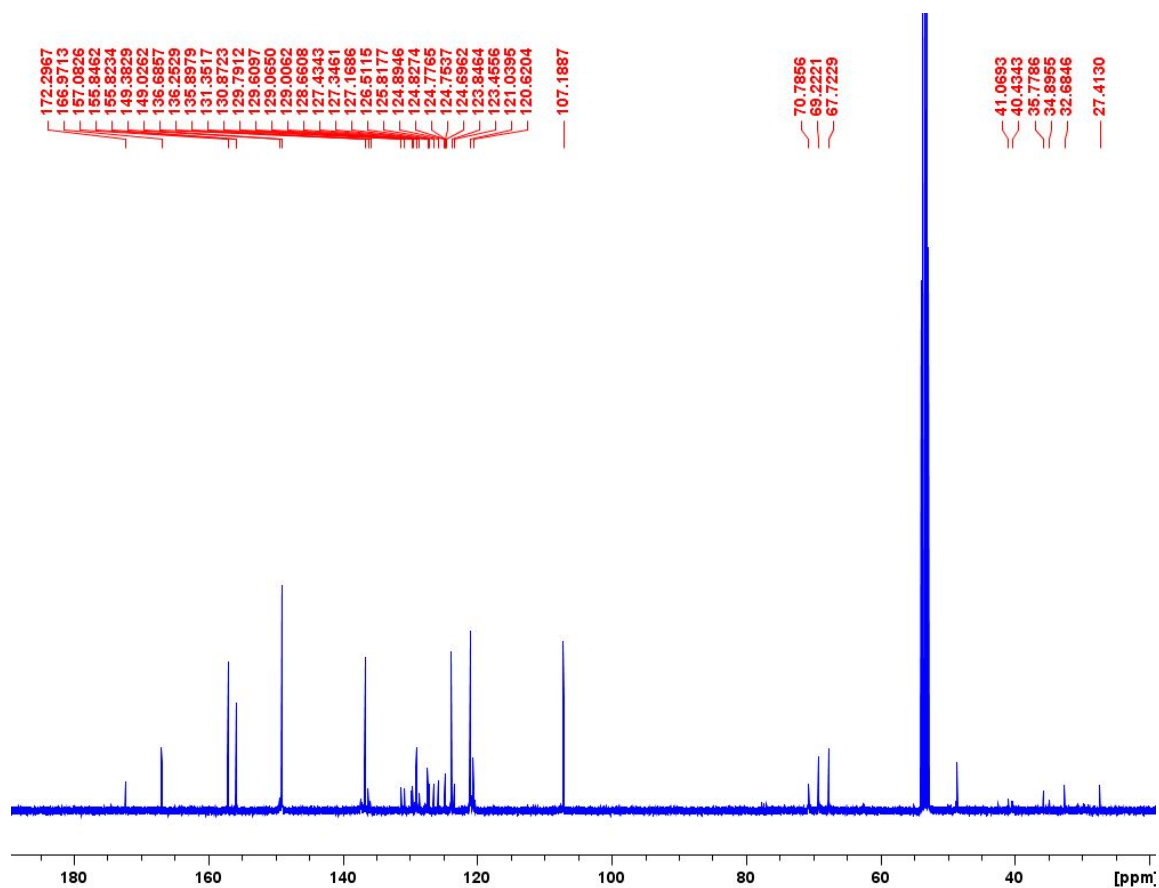


Figure S11. Compound **5** : ¹³C NMR spectrum in CD₂Cl₂

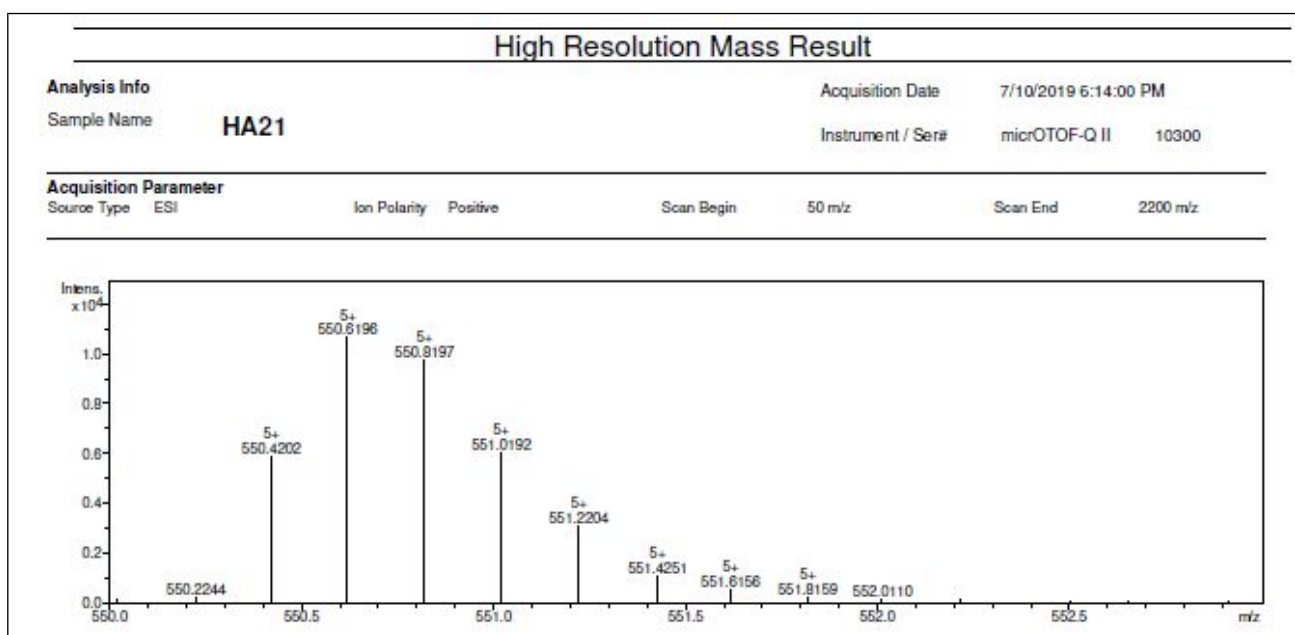


Figure S12. Compound **5** : mass spectrum

6. UV spectra of compounds 3 and 5

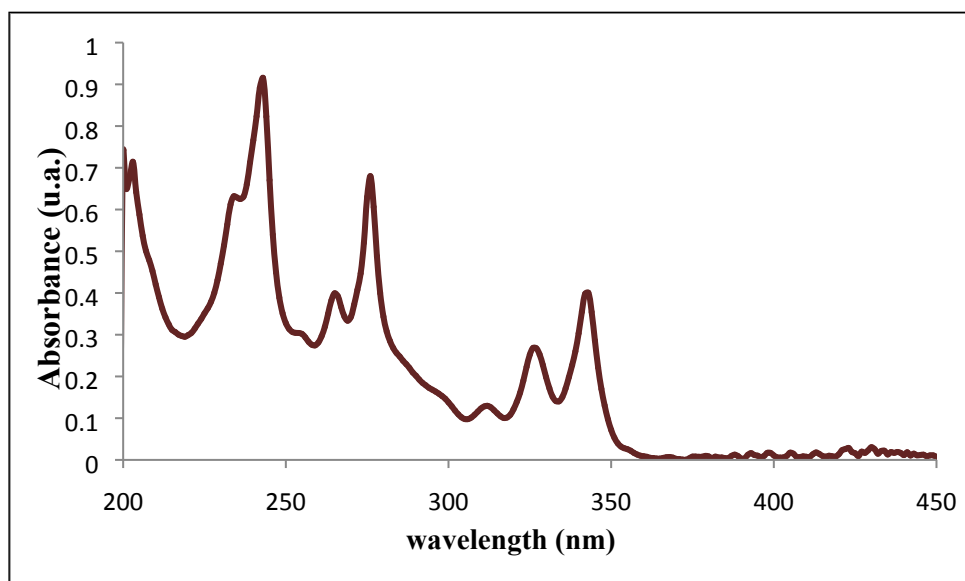


Figure S13. UV spectrum of 3 in 2-propanol

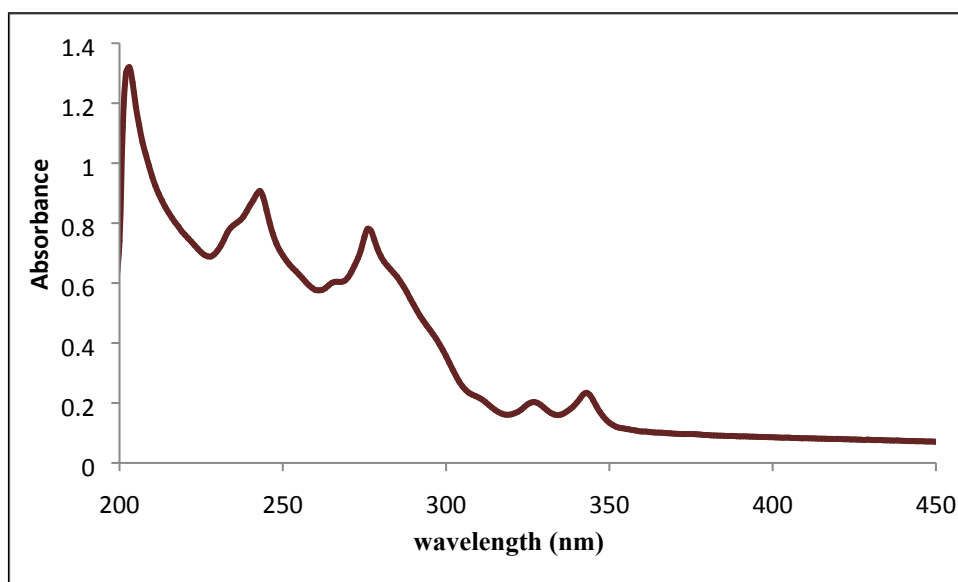


Figure S14. UV spectrum of 5 in 2-propanol

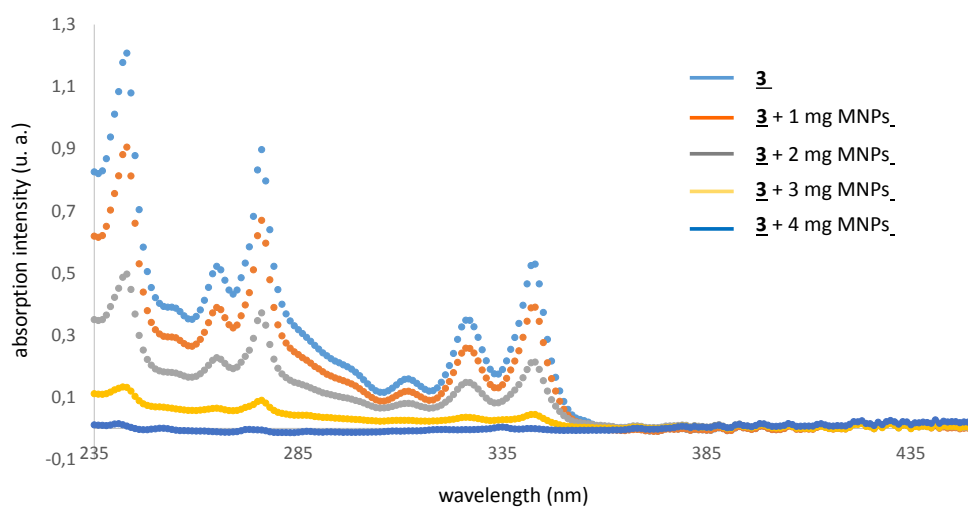


Figure S15. Effect of the addition of MNPs on the absorption spectrum of **3**