Cuboidal $[Ni_4O_4]$ cluster as a precursor to recyclable, carbon-supported nickel nanoparticle reduction catalysts

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1. Synthetic procedures of the ligand and compounds 1 − 4

Materials

The ligand (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol (H**L**) was prepared according to the literature method.[1] Other chemicals and regents were obtained from commercial sources and used without further purification. IR spectra (KBr disk, 400−4000 cm^{-1}) were recorded on a Perkin-Elmer 1320 spectrometer. Elemental analyses for C, H and N were carried out on a Carlo-Erba CHNO-S microanalyzer. A BTF-1200C-S quartz tube furnace was employed for carbonization. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo Star system (heating rate of 5 °C·min^{-1}). The powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical X'Pert PRO MPD system (PW3040/60). UV-vis absorption spectra were obtained on a Varian Cary-50 UV-visible spectrophotometer. ^{1}H and ^{13}C NMR spectra in DMSO were recorded at r.t. on a Varian UNITY plus-400 spectrometer and chemical shifts are referenced to residual DMSO (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C). High-resolution mass spectra (HRMS-ESI) were obtained on a Micro™ or a Micro YA263 Q-TOF mass spectrometer. Melting points were recorded on a Mel-Temp II apparatus. Transmission electron microscopy (TEM) was carried out on a HITACHI HT-7700 electron microscope operated at 120 kV. High-resolution transmission electron microscopy (HRTEM) was performed on an FEI Tecnai G20 electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was accomplished using an SSI S-Probe XPS spectrometer. Raman spectra were obtained on a Confocal LabRAM HR800 spectrometer with a laser excitation wavelength of 632.8 nm. Magnetic measurements were performed on an MPMS-SQUID-VSM system at 300 K. The porosity measurements were performed on Belsorp surface area and porosity analysis instrument at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. All samples were degassed at 150 °C for 12 h before the measurement.

Synthesis of methyl 5-(4-(tert-butyl)phenyl)picolinate

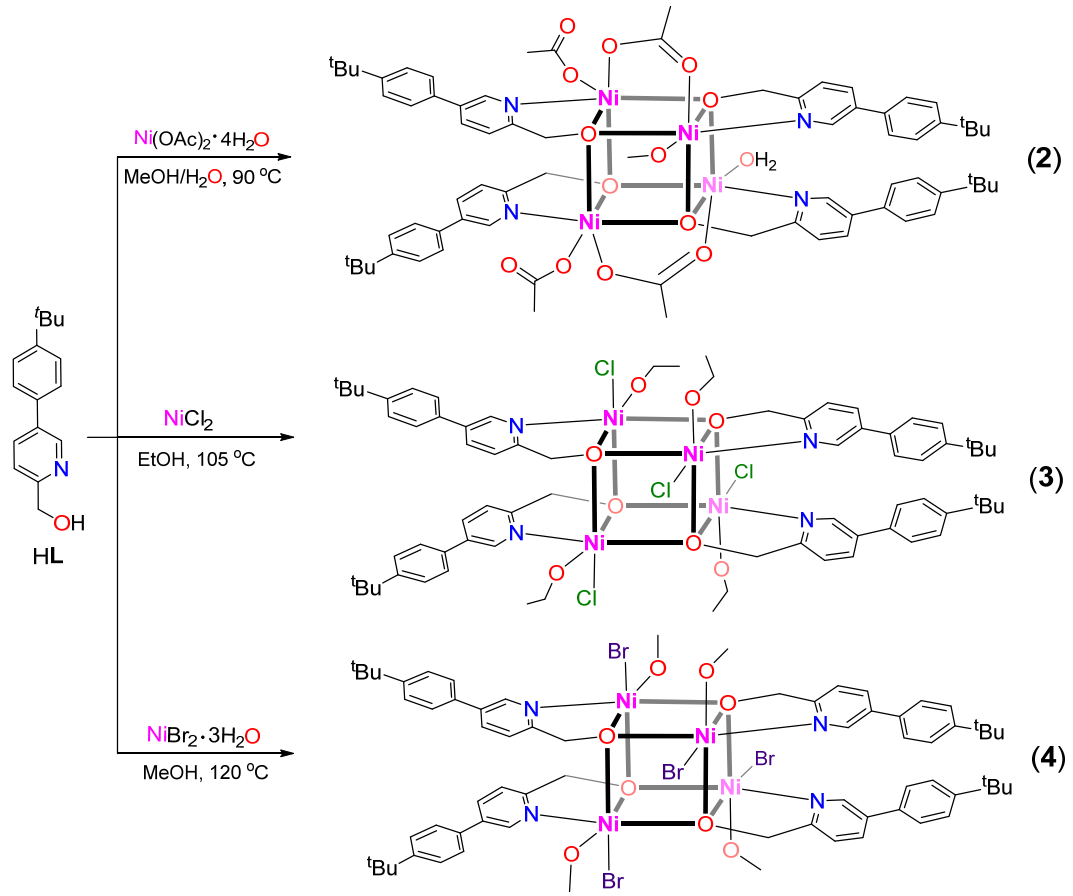
4-tert-Butylphenylboronic acid (534 mg, 3 mmol), 5-bromopyridine-2-carboxylic acid

methylester (432 mg, 2 mmol) and K_2CO_3 (552 mg, 4 mmol) were mixed together in a 50 mL double-necked flask and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol, 2 mol %) was then quickly added. The air in the flask was exchanged with N_2 three times followed by addition of 10 mL degassed toluene. The resulting mixture was heated at 110 °C for 48 h under an N_2 atmosphere. Toluene was then removed under reduced pressure. The resulting dark brown mixture was extracted with brine and ethyl acetate 3 times and the organic layers combined and dried over anhydrous Na_2SO_4. The solvent was evaporated and the resulting brown residue purified on a silica column with n-hexane/ethyl acetate (v / v = 6 : 1, R_f = 0.33) to yield the title compound as a fine yellow powder. Yield: 510 mg (94 %). Anal. calcd (%) for $C_{17}H_{19}NO_2$: C 75.79, H 7.06, N 5.20; found: C 75.63, H 7.16, N 5.07. m.p.: 135.5 − 136.2 °C. HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{20}NO_2$ $[M + H]^+$: 270.1416, found: 270.1498. IR (KBr disc): 2955(s), 1739(s), 1515(m), 1398(w), 1372(s), 1236(m), 1190(m), 1140(s), 1515(m), 1116(s), 832(s), 797(s), 770(w), 743(w). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.12 (s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 3.99 (s, 3H), 1.41 (s, 9H) ppm. ^{13}C NMR (DMSO-d_6, 101 MHz): δ 165.1, 151.6, 147.7, 145.9, 138.4, 134.8, 133.0, 126.9, 126.1, 125.0, 52.4, 34.4, 31.0 ppm.

Synthesis of (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol (HL)

Absolute EtOH (100 mL) was added to a 150 mL triple-necked flask in an ice bath and degassed with N_2 for 30 minutes. Methyl 5-(4-(tert-butyl)phenyl)picolinate (807 mg, 3 mmol) and $NaBH_4$ (91 mg, 2.4 mmol) were then added in sequence with stirring, followed by portion-wise addition of $CaCl_2$ (333 mg, 3 mmol) over 5 minutes. The reaction was placed in ice bath for 5 h and monitored with thin-layer chromatography. The reaction was quenched with concentrated H_2SO_4 by adjusting the pH value to 3 − 4 and left to stand overnight at r.t. before filtration. The solid residue was extracted with absolute EtOH. The combined EtOH extracts were evaporated to obtain a white solid that was dissolved in brine and further extracted three time with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4. Evaporation of the solvent

provided a white powder that was purified by silica gel column chromatography with petroleum ether/ethyl acetate (v / v = 2 : 1, R_f = 0.41) to yield the title compound as a fine white powder. Yield: 300 mg (41 %). Anal. calcd (%) for $C_{16}H_{19}NO$: C 79.62, H 7.88, N 5.81; found: C 78.59, H 7.86, N 5.67. m.p.:142.9 − 143.5 °C. HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{20}NO$ $[M + H]^+$: 242.1467, found: 242.1550. IR (KBr disc): 3372(w), 2920(w), 1524(w), 1456(m), 1336(s), 1259(m), 1215(m), 848(w), 826(s), 747(w), 718(w). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.77 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.52 (t, 3H, J = 9.2 Hz), 5.45 (t, J = 5.8 Hz, 1H), 4.60 (d, J = 5.8 Hz, 2H), 1.31 (s, 9H) ppm. ^{13}C NMR (DMSO-d_6, 101 MHz): δ 160.6, 150.4, 146.4, 134.3, 134.3, 133.6, 126.4, 125.9, 120.2, 64.1, 34.3, 31.1 ppm.



Scheme S1. Synthesis of compounds **2** − **4** from Ni salts and H**L**.

Synthesis of $[Ni_4L_4(\mu\text{-}HCOO)_2(HCOO)_2(H_2O)_2]\cdot H_2O$ (1)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (60 mg, 0.2 mmol) and H**L** (24 mg, 0.1 mmol) in 10 mL DMF/H_2O (v / v = 1 : 1) solvent was placed in a pressure tube. The tube was sealed

and heated at 120 °C for 72 h, followed by smooth cooling to r.t. over 48 h. Green block crystals of **1** were collected by filtration, washed with Et_2O and dried in air. Yield: 24 mg (67.13 % based on H**L**). Anal. calcd (%) for $C_{68}H_{84}N_4Ni_4O_{14}$: C 57.05, H 5.87, N 3.91; found: C 57.04, H 5.95, N 4.10. IR (KBr disc, cm^{-1}): 3412(s), 3030(w), 1615(s), 1578(s), 1447(w), 1382(m), 1270(w), 1231(w), 1201(w), 1043(w), 815(m), 777(w), 742(w). ESI-MS m/z: Calcd. for $[Ni_4\mathbf{L}_4(HCOO)_3]^+$: 1329.29, found: 1329.15 (Fig. S4a). Correct assignment of the protons from the ^1H NMR (Fig. S21) cannot be done due the paramagnetic nature of the product.

Synthesis of $[Ni_4L_4(\mu\text{-}OAc)_2(OAc)_2(H_2O)(MeOH)]\cdot 2H_2O\cdot 2MeOH$ (2)

$Ni(OAc)_2\cdot 4H_2O$ (25 mg, 0.1 mmol) and H**L** (24 mg, 0.1 mmol) were dissolved in a 10 mL MeOH/H_2O mixed solvent (*v* / *v* = 1 : 1). The reactants were sealed in a pressure tube, heated at 90 ºC for 72 h, followed by smooth cooling to r.t. over 48 h. Green block crystals were washed with cold MeOH/H_2O (*v* / *v* = 1 : 1) and dried overnight in air. Yield: 20 mg (50.55 % based on Ni). Anal. calcd (%) for $C_{150}H_{204}N_8Ni_8O_{36}$: C 56.87, H 6.45, N 3.54; found: C 56.55, H 6.48, N 3.87. IR (KBr disk, cm^{-1}): 3424(s), 2964(m), 1571(s), 1414(s), 1384(s), 1293(m), 1270(w), 1114(s), 1045(m), 820(m), 760(w), 728(w). ESI-MS m/z: Calcd. for $[Ni_4\mathbf{L}_4(OAc)_2(OH)]^+$: 1329.32, found: 1329.16 (Fig. S4b). Correct assignment of the protons from the ^1H NMR (Fig. S22) cannot be done due the paramagnetic nature of the product.

Synthesis of $[Ni_4L_4(EtOH)_4Cl_4]$ (3)

$NiCl_2$ (26 mg, 0.1 mmol), H**L** (48 mg, 0.2 mmol) and sodium butyrate (22 mg, 0.2 mmol) were dissolved in 10 mL EtOH. The clear green liquid was sealed in a pressure tube, heated at 105 °C for 72 h followed by smooth cooling to r.t. over 48 h. Green crystals were collected by filtration, washed with a small quantity of EtOH and dried in air. Yield: 12 mg (31.37 % based on Ni). Anal. calcd (%) for $C_{72}H_{96}Cl_4N_4Ni_4O_8$: C 56.76, H 6.31, N 3.68; found: C 56.25, H 6.45, N 3.60. IR (KBr disk, cm^{-1}): 3424(s), 2962(s), 1613(m), 1399(s), 1384(s), 1293(w), 1270(w), 1045(s), 821(m), 729(w), 728(w). ESI-MS m/z: Calcd. for $\{[Ni_4\mathbf{L}_4Cl_4(EtOH)_5(H_2O)_3] + 2H^+\}^{2+}$: 811.71, found:

811.73 (Fig. S4c). Correct assignment of the protons from the ^{1}H NMR (Fig. S23) cannot be done due the paramagnetic nature of the product.

Synthesis of [$Ni_4L_4(MeOH)_4Br_4$] (4)

$NiBr_2 \cdot 3H_2O$ (55 mg, 0.2 mmol) and H**L** (48 mg, 0.2 mmol) was dissolved in 10 mL of MeOH. The green clear solution was sealed in a pressure tube, heated at 120 °C for 72 h before smooth cooling to r.t. over 48 h. Green crystals were collected by filtration, washed with a small quantity of MeOH and dried in air. Yield: 31 mg (37.80 % based on Ni). Anal. calcd (%) for $C_{63}H_{88}N_4Ni_4O_8$: C 46.10, H 5.35, N 3.42; found: C 45.90, H 5.31, N 3.44. IR (KBr disk, cm^{-1}): 3423(s), 3031(w), 1610(m), 1447(w), 1384(m), 1363(m), 1236(w), 1236(w), 1045(s), 821(m), 743(w), 728(w). ESI-MS m/z: Calcd. for $\{[Ni_2\mathbf{L}_2Br_3(MeOH)(DMF)_2(H_2O)] + 2H^+\}^+$: 1033.06, found: 1032.83 (Fig. S4d). Correct assignment of the protons from the ^{1}H NMR (Fig. S24) cannot be done due the paramagnetic nature of the product.

Synthetic procedure for NiNPs/C

In a typical experiment, compound **1** was added to a ceramic boat and carefully loaded into a quartz tube furnace. The sample was subjected to a smooth flow of N_2 for 30 minutes to remove O_2 and moisture. This N_2 flow was turned down during heating. The sample was heated from r.t. to T (T = 450 °C, 500 °C, 550 °C and 600 °C) at a heating rate of 1 °C·min^{-1} and maintained at T for 3 h before evenly cooling to r.t. in a flow of N_2. The black sample obtained was denoted as NiNPs/C-T.

2. **X-ray structure determination for 1 - 4**

All measurements were made on a Bruker D8-Quest (**2**, **3** and **4**) and an Agilent Xcalibur (**1**) CCD X-ray diffractometer using an enhanced X-ray source Mo Kα (λ = 0.71073 Å). Each single crystal was mounted at the top of a glass fiber with grease in a stream of N_2. Cell parameters were refined using the programs Bruker SAINT (for **2**, **3** and **4**) and *CrysAlisPro* (Agilent Technologies, Ver. 1.171.35.21, 2012) (for **1**). Absorption corrections (multi-scan) were applied.[2] All crystal structures were solved

by direct methods and refined on F_2 by full-matrix least-squares methods with the SHELXTL-2013 program.[3] The tert-butyl groups in the **L** ligands of **1** displayed rotational disorder with the relative ratios of 0.70/0.30, 0.62/0.38, 0.29/0.71 and 0.30/0.70 refined for the two components. The locations of the hydrogen atoms on the water molecules were suggested by the Calc-OH program in the WinGX suite[4] and their O–H distances further restrained to O–H = 0.83 Å with thermal parameters constrained to U_{iso}(H) = 1.2U_{eq}(O). The location of the two hydrogen atoms on the coordinated EtOH in **3** were suggested by the Calc-OH program in the WinGX suite.[4] Their coordinates were subsequently fixed and thermal parameters constrained to U_{iso}(H) = 1.2U_{eq}(O). For **4**, part of the two **L** ligands displayed conformational disorder with the relative ratios of 0.42/0.58 and 0.62/0.38 for the two components. Some amount of spatially delocalized electron density in the lattice of **2** – **4** was found but acceptable refinement results could not be obtained. The solvent contribution was then modeled using SQUEEZE in the Platon program suite.[5] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC) (1536067 − 1536070). These data can be either obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif or from the Electronic Supplementary Information (ESI). A summary of crystal data and structure refinement parameters of **1** − **4** are given in Table S1 and the selected bond lengths and angles are listed in Table S2.

3. Structural discussion of 2 − 4

The cuboidal [Ni_4O_4] skeleton, the ralative arrangement of the four **L** ligands, as well as the bridging acetate of **2** (Fig. S1a) resemble that of **1**. There are, however, notable differences of the two structures. For example, although there are two additional monodentate acetate ligands in **2** (versus formate in **1**), these acetate ligands locate within the side plane of the cubane which supports two staggered **L** ligands (versus two monodentate formates in **1** located at the base plane of the cubane). As a consequence, one additional aqua ligand and MeOH ligand coordinated to the two Ni centers within the other side plane of the cubane (versus two aqua ligands in **1**

coordinated to the two Ni centers at the upper plane of the cubane).

Compounds **3** (Fig. S1b) and **4** (Fig. S1c) are structurally similar and only differ in coordination solvates (EtOH in **3** and MeOH in **4**) and outside donor (Cl in **3** and Br in **4**). Take the structure of **3** as an example, all the four Ni centers adopt the same coordination environment and are associated by three μ_3-O atoms in three orthogonal vectors from three **L** ligands. Its octahedral coordination is filled by one N atom (from one of the three **L** ligands), one terminal Cl^- and one EtOH solvate. It is notable that although compounds **1** and **2**, **3** and **4** share similar Ni_4O_4 cluster skeletons, they represent two structural types. A pair of **L** ligands on each of the opposite cuboidal faces exhibit a staggered conformation and these **L** pairs have different orientations. In **1** and **2**, the two **L** ligand pairs are nearly parallel while in **3** and **4**, the two **L** ligand pairs are roughly orthogonal. The Ni···Ni separations for **2** (2.9251(4) – 3.2081(4) Å), **3** (3.0804(11) – 3.1818(11) Å) and **4** (3.1048(17) – 3.1628(16) Å) are comparable to those found in **1** (2.8896(7) – 3.1982(7) Å). While the Ni-μ_3-O distances for **2** (2.0352(13) – 2.0820(13) Å), **3** (2.039(3) – 2.116(5) Å) and **4** (2.037(7) – 2.119(7) Å) are also similar to those found in **1** (2.043(2) – 2.090(2) Å). Further structural analysis revealed intramolecular hydrogen bonding between coordinated water and monodenate carboxylate (**1**), MeOH and monodenate carboxylate (**2**), EtOH and Cl (**3**), and MeOH and Br (**4**) (Table S3), which may partly explain the formation of such different cuboidal structural types.

4. Procedure for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) monitored by UV-vis

NiNPs/C-T (2 mg) and water (2.05 mL) were added into in a 4.5 mL glass vial and ultra-sonicated for a few minutes to form a suspension. 4-NP (0.3 mL, 1 mM) was added and the light yellow mixture stirred for several minutes (800 rpm) at 20 °C. This light yellow solution immediately became deep yellow upon introducing an aqueous $NaBH_4$ solution (0.65 mL, 0.2 M) and then gradually became colorless. The conversion process was monitored by UV-vis spectroscopy. The catalyst was separated with a magnet and rinsed with water for subsequent runs.

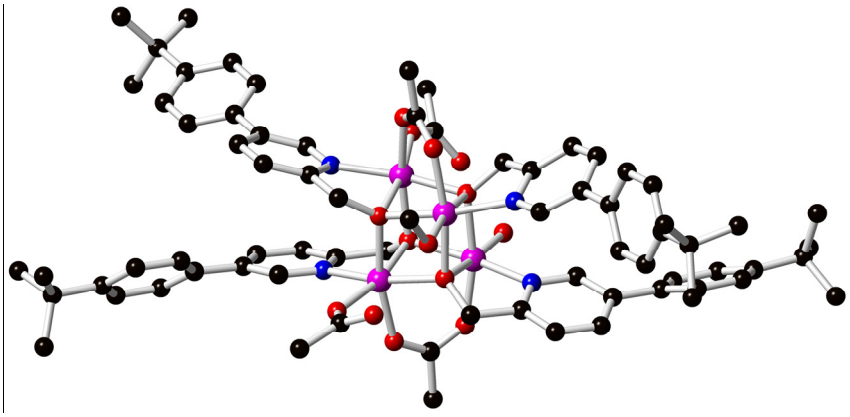
5. Procedure for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in 1 mmol scale

4-NP (139 mg, 1 mmol) was slowly dissolved in 4 mL of water, and an additional 2 mL water solution containing $NaBH_4$ (227 mg, 6 mmol) solution was added before adding solid NiNPs/C-450 (10 mg). The mixture stirred for 2 h (800 rpm) at 20 ºC. The conversion process was monitored by thin layer chromatography (TLC) and the resulting dark brown mixture extracted with ethyl acetate for 3 times. The organic layer was combined and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v* / *v* = 1 : 1, R_f = 0.53) yielded 4-AP. Yield: 104.20 mg (95.60 %).

6. Preparation of Ni-free carbon nanoparticles from NiNPs/C-450

40 mg NiNPs/C-450 was mixed with 40 mL HCl (10 M) and the mixture kept stirring overnight at 90 ºC. The black solid was filtered off, repeatedly washed with H_2O and EtOH before finally dried in an oven.

7. Figures S1 − S11



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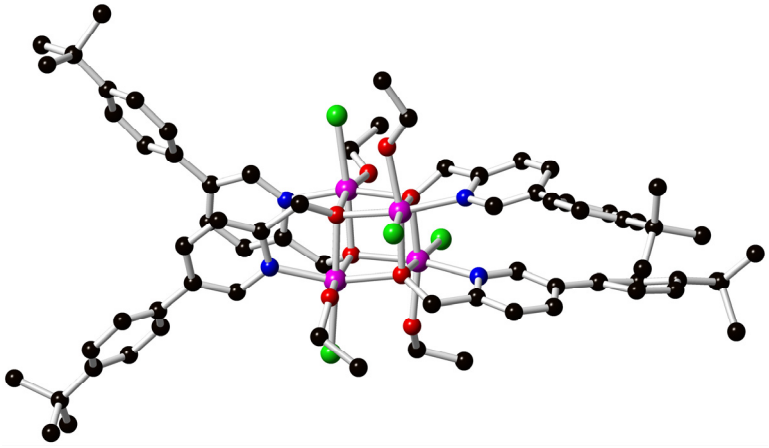

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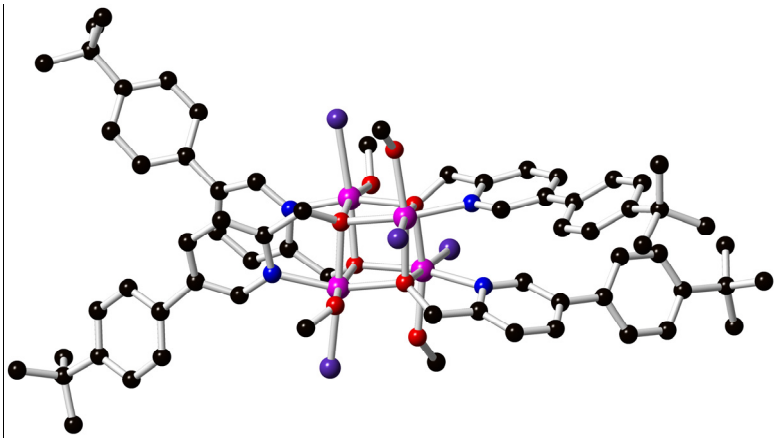


(c)

Fig. S1 Structures of **2** (a), **3** (b), and **4** (c) with the disordered components, lattice solvates and hydrogen atoms omitted. Color codes: Ni (magenta), O (red), N (blue), C (black), Cl (green), Br (indigo).

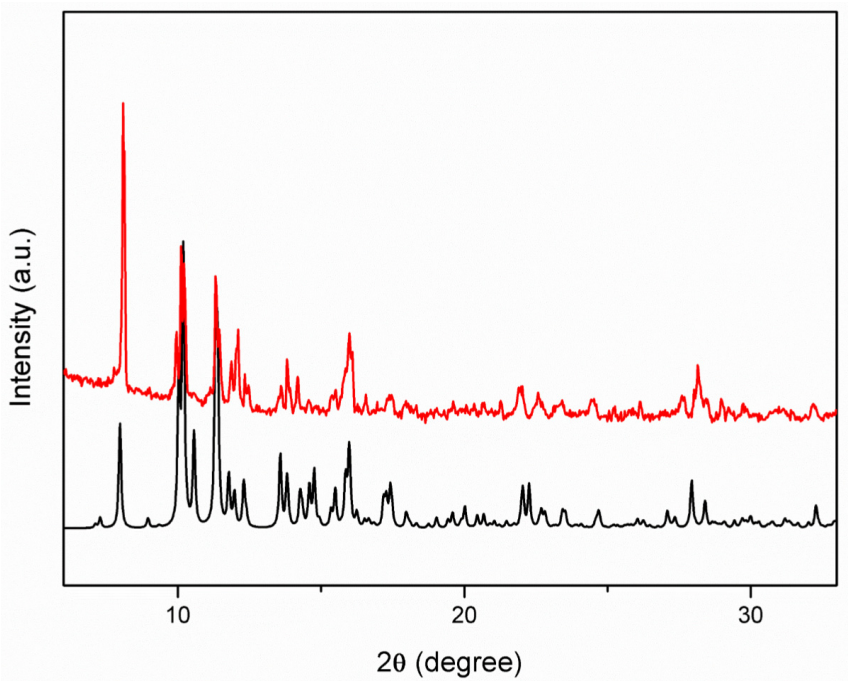
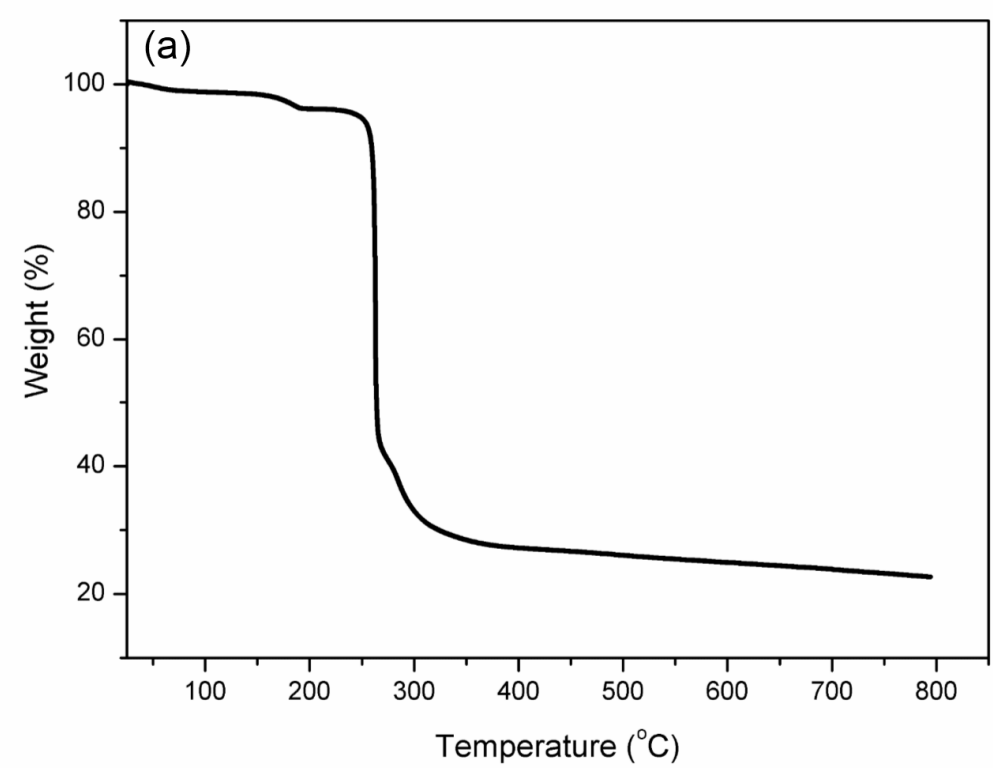
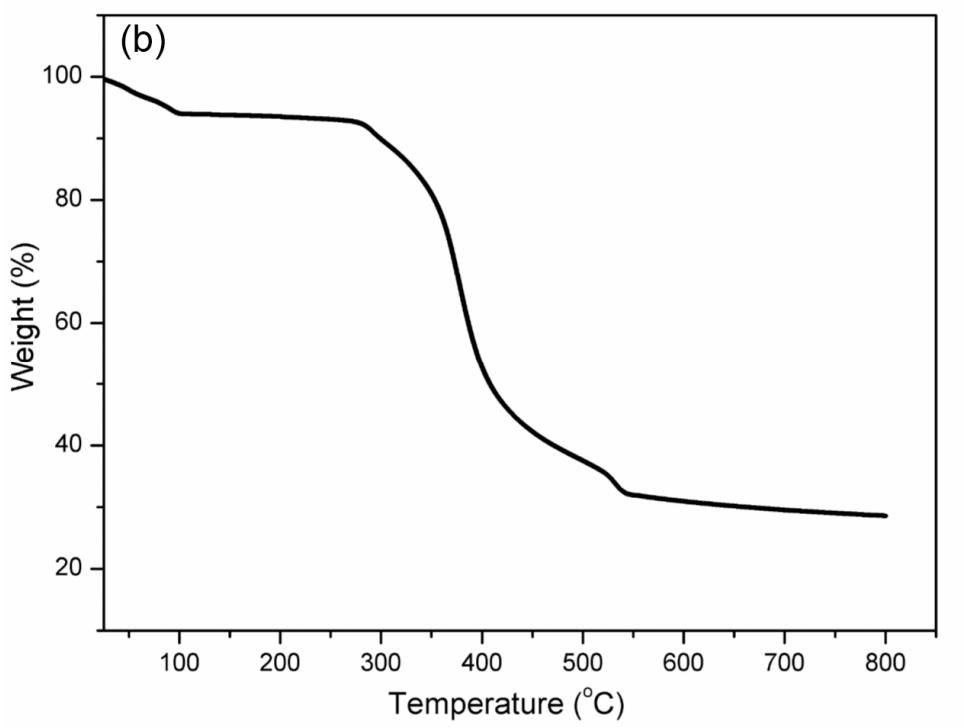


Fig. S2 PXRD pattern of compound **1** (red) and the simulated PXRD pattern (black).

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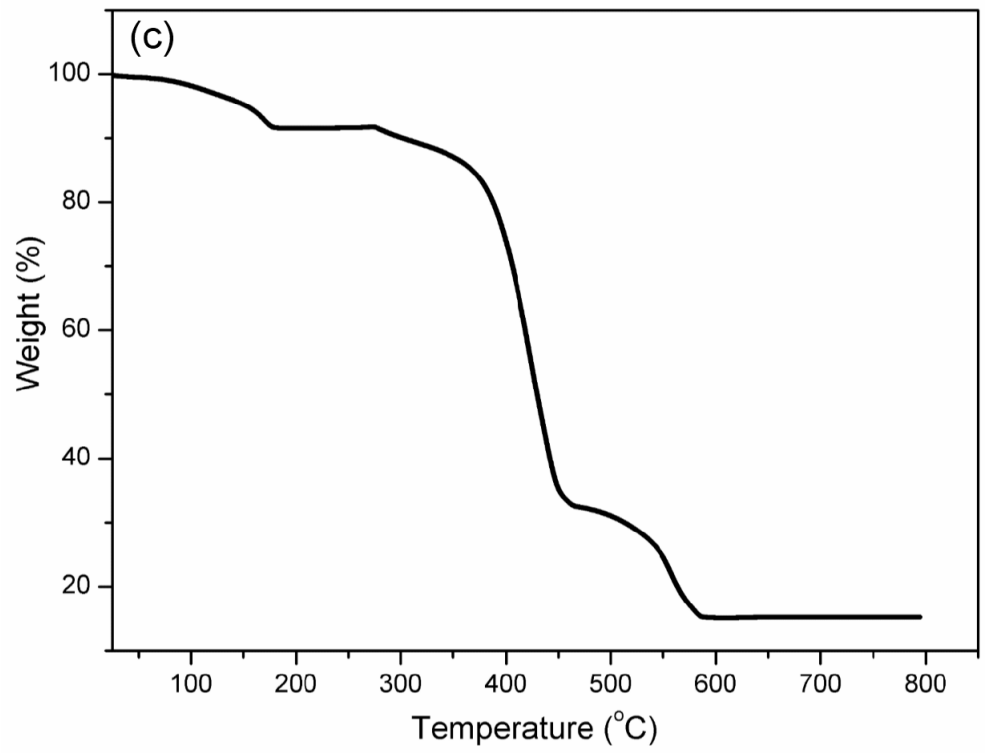
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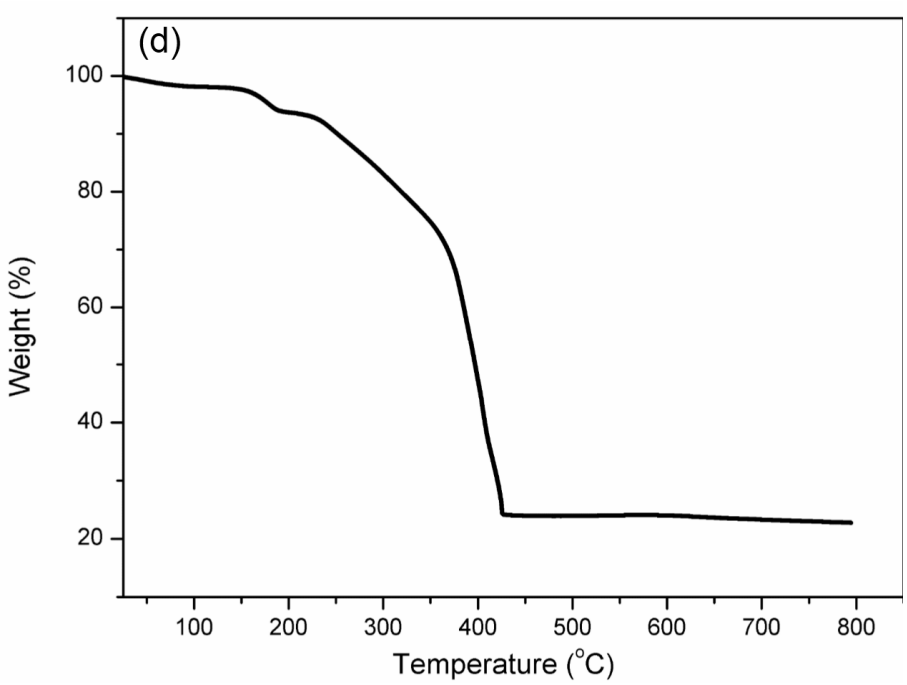
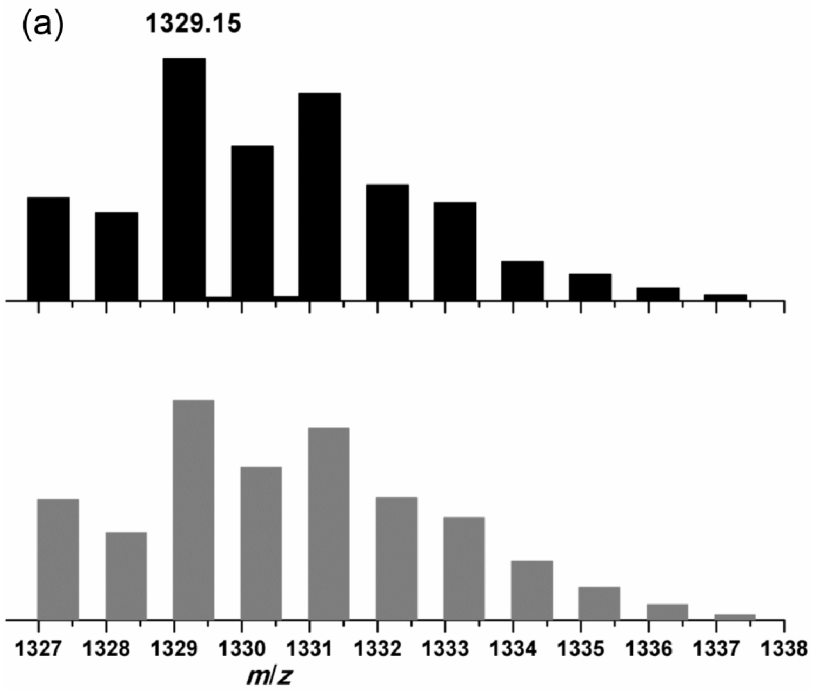
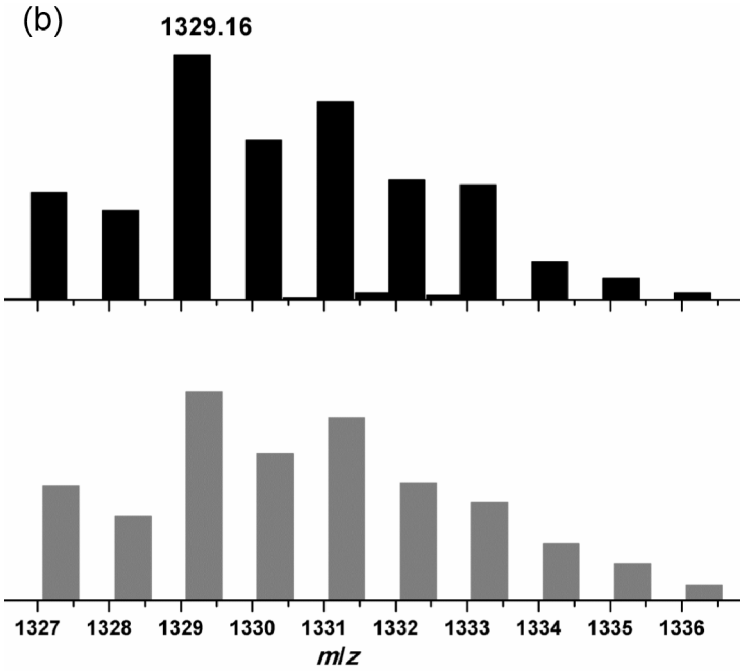


Fig. S3 TGA of compound **1** (a), **2** (b), **3** (c) and **4** (d) collected under an N_2 atmosphere.

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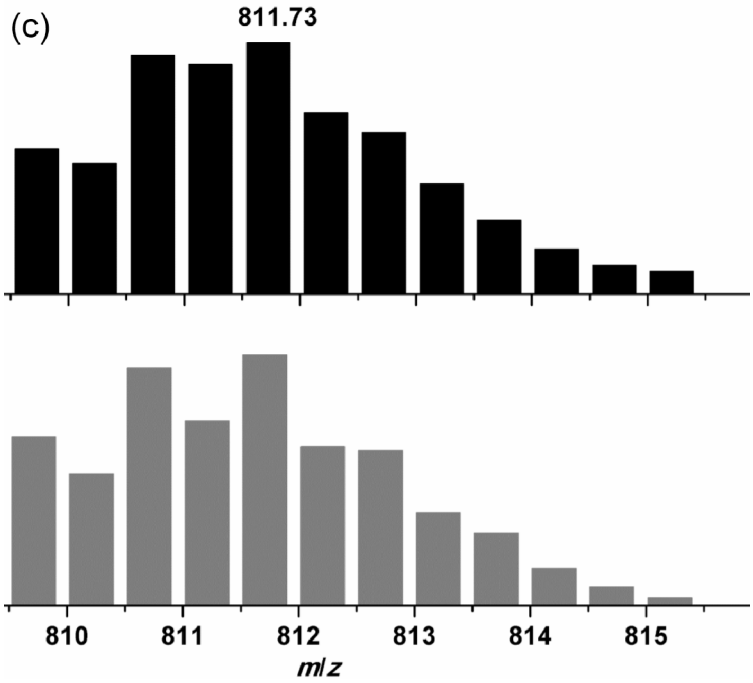
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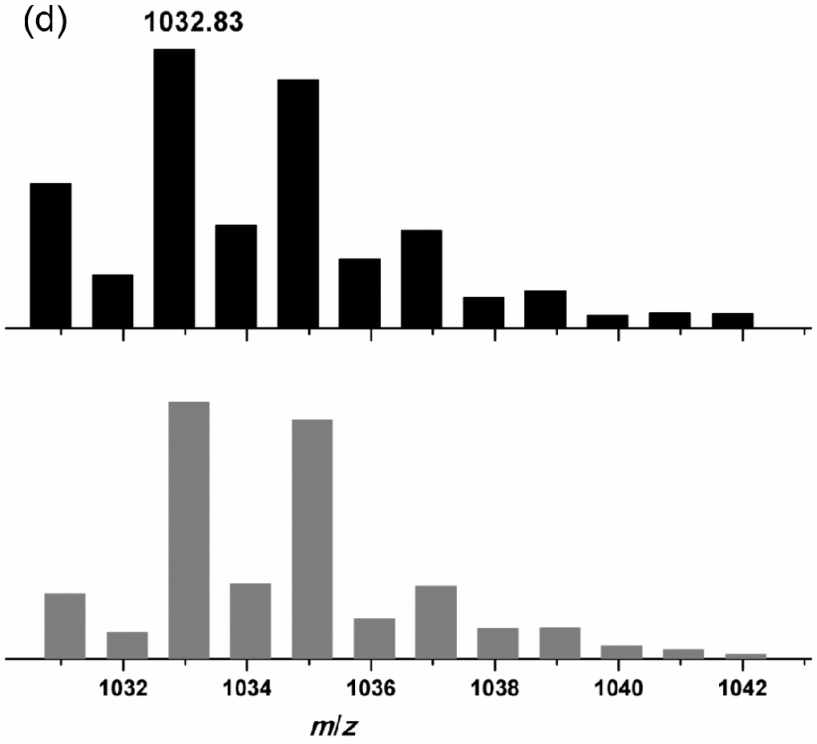


Fig. S4 The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of the $[Ni_4\mathbf{L}_4(HCOO)_3]^+$ cation of **1** (a). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of the $[Ni_4\mathbf{L}_4(OAc)_2(OH)]^+$ cation of **2** (b). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of the $\{[Ni_4\mathbf{L}_4Cl_4(EtOH)_5(H_2O)_3] + 2H^+\}^{2+}$ cation of **3** (c). The positive-ion ESI mass spectrum (black) and the calculated isotope pattern (gray) of the $\{[Ni_2\mathbf{L}_2Br_3(MeOH)(DMF)_2(H_2O)] + 2H^+\}^+$ cation of **4** (d).

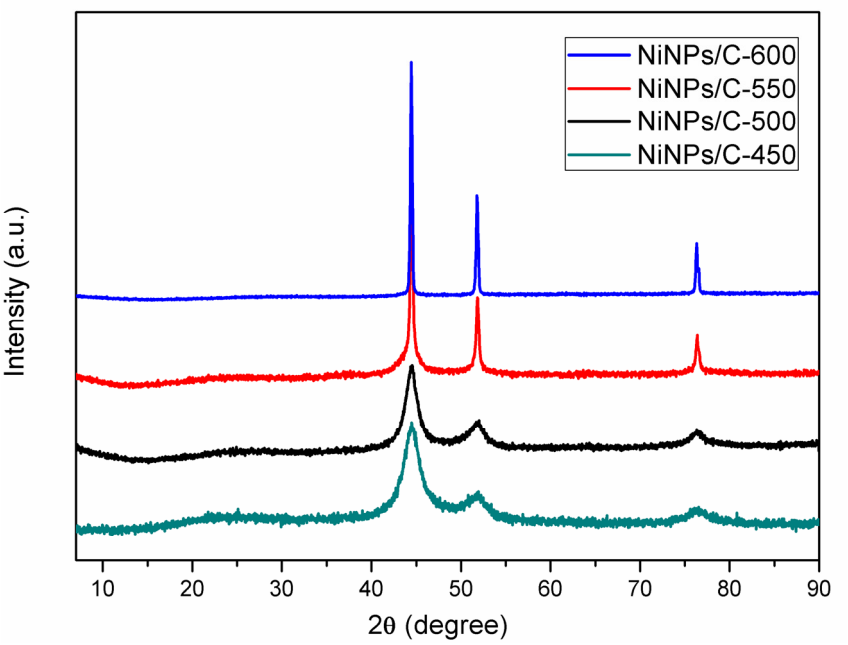


Fig. S5 PXRD patterns of NiNPs/C-450, NiNPs/C-500, NiNPs/C-550, NiNPs/C-600.

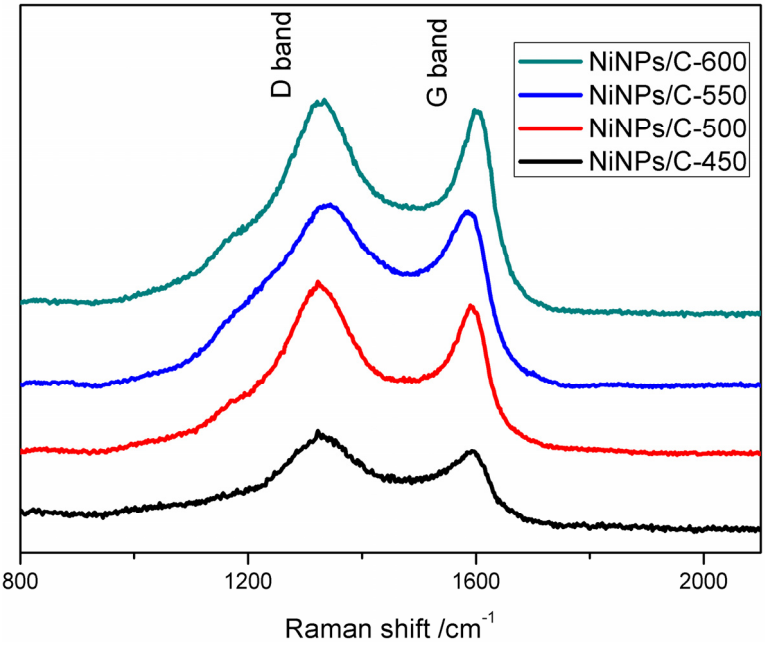


Fig. S6 Raman spectra of the obtained NiNPs/C-450, NiNPs/C-500, NiNPs/C-550, NiNPs/C-600.

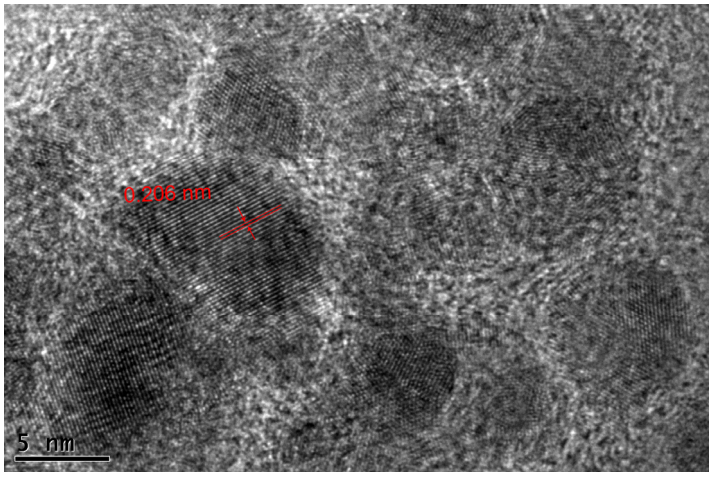
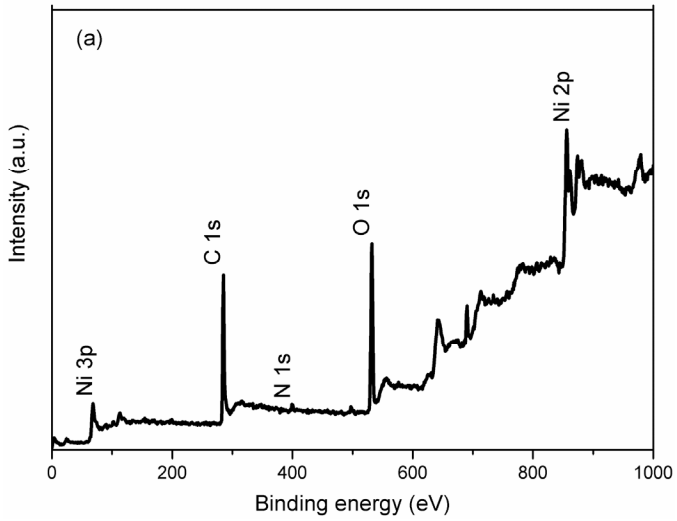
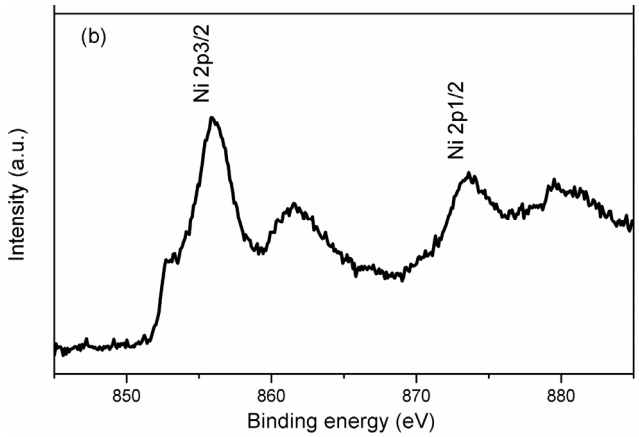


Fig. S7 HRTEM image of the obtained NiNPs/C-450.





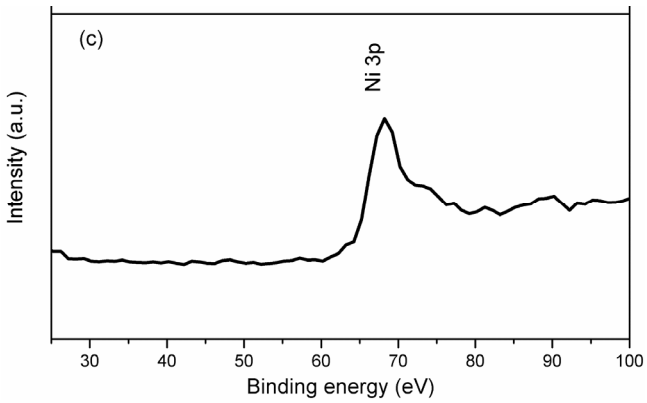


Fig. S8 XPS spectra of NiNPs/C-450 (a), Ni 2p (b), and Ni 3p (c).

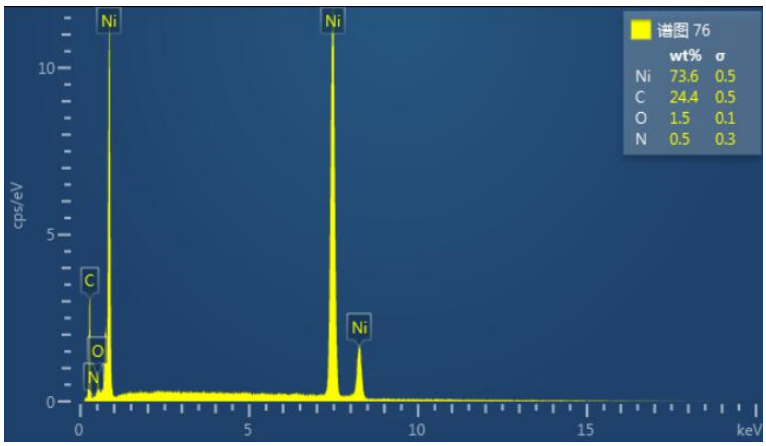


Fig. S9 The EDX spectrum of NiNPs/C-450.

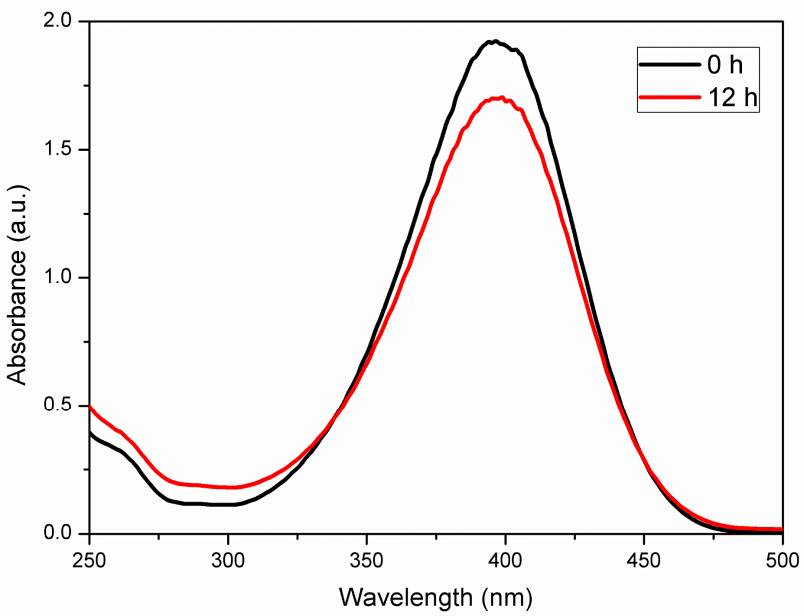


Fig. S10 UV-vis absorption spectra for the catalytic reduction of 4-NP without adding any catalysts at time zero and after 12 h.

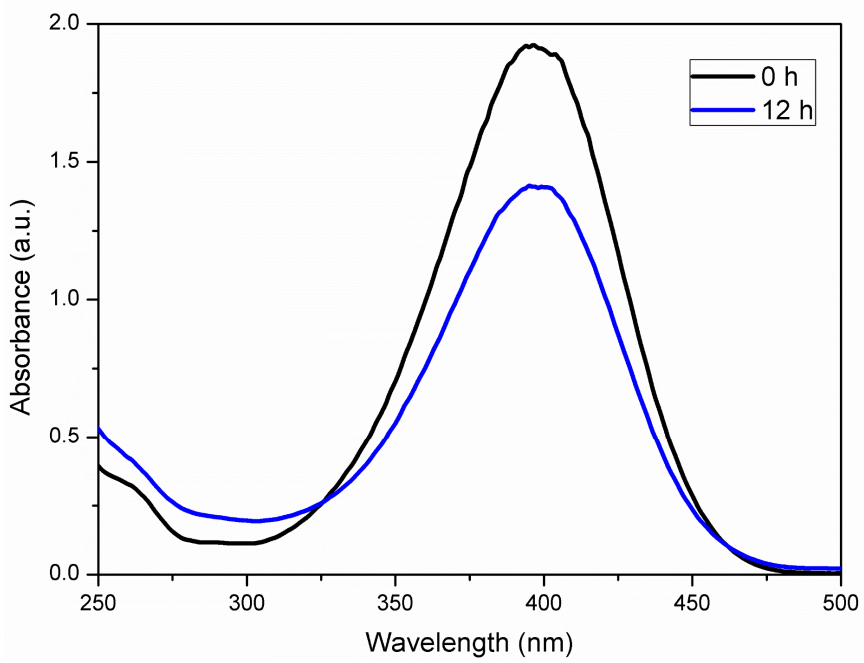


Fig. S11 UV-vis absorption spectra for the catalytic reduction of 4-NP with compound **1** as a catalyst at time zero and after 12 h.

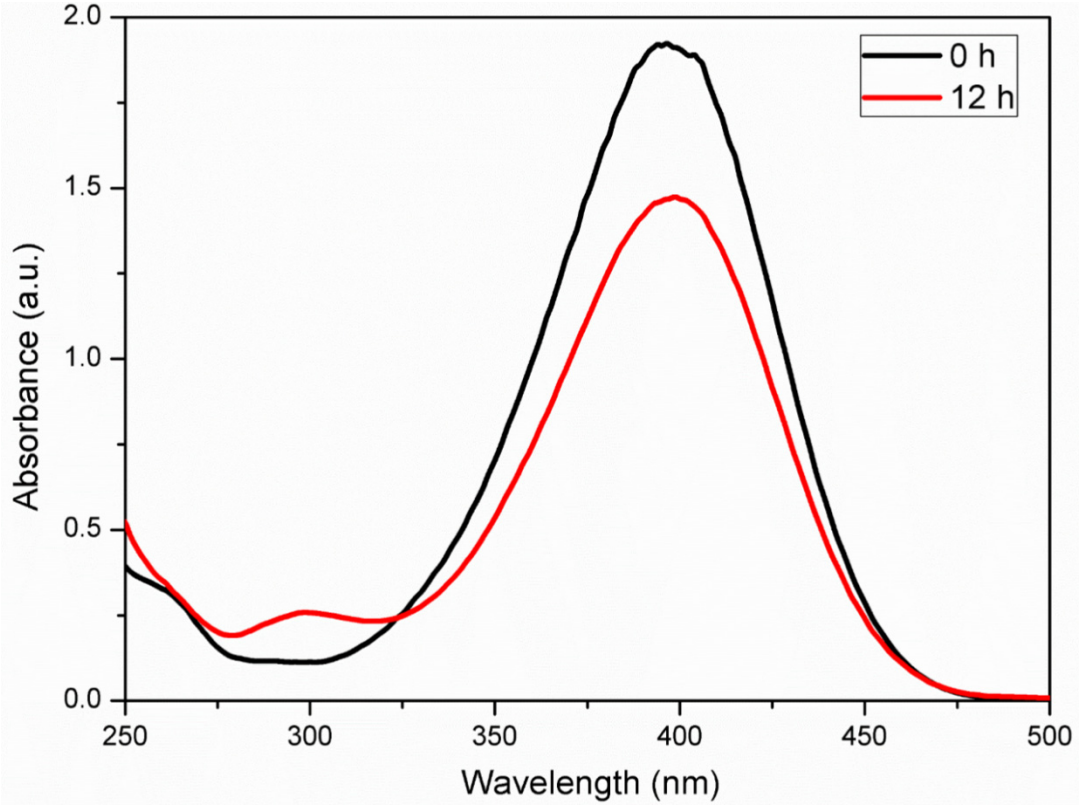
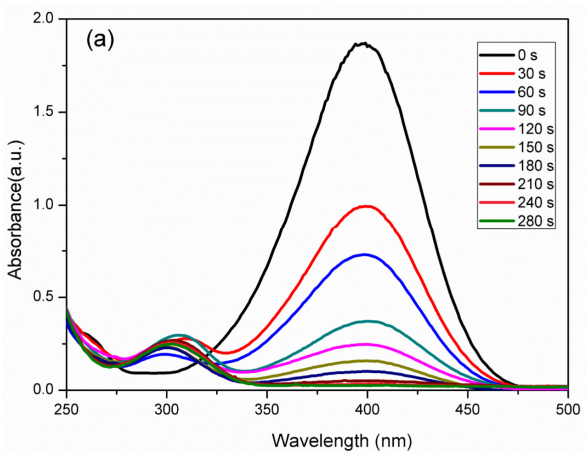
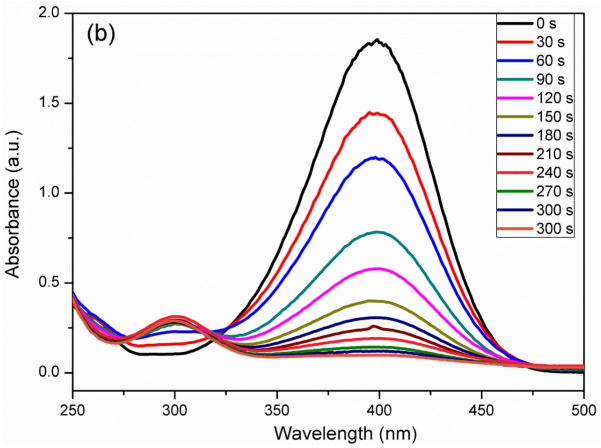


Fig. S12 UV-vis absorption spectra for the catalytic reduction of 4-NP with metal-free host material as a catalyst at time zero and after 12 h.





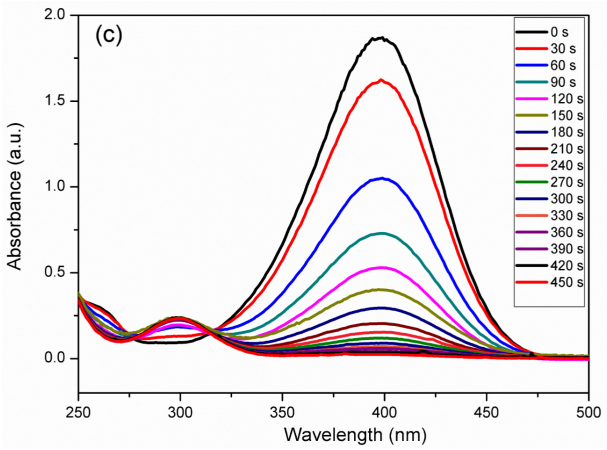


Fig. S13 UV-vis absorption spectra for the catalytic reduction of 4-NP with NiNPs/C-500 (a), NiNPs/C-550 (b), and NiNPs/C-600 (c).

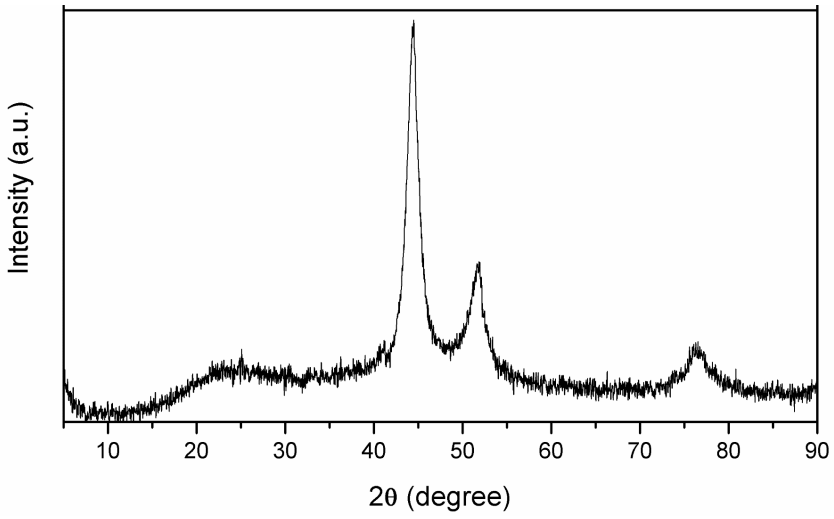
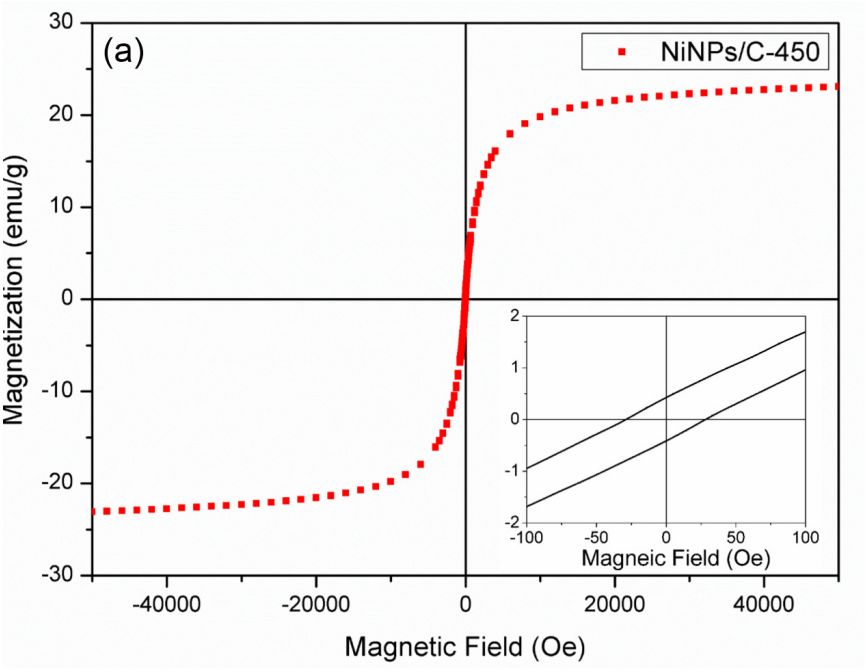


Fig. S14 PXRD spectrum of NiNPs/C-450 after 10 catalytic cycles.



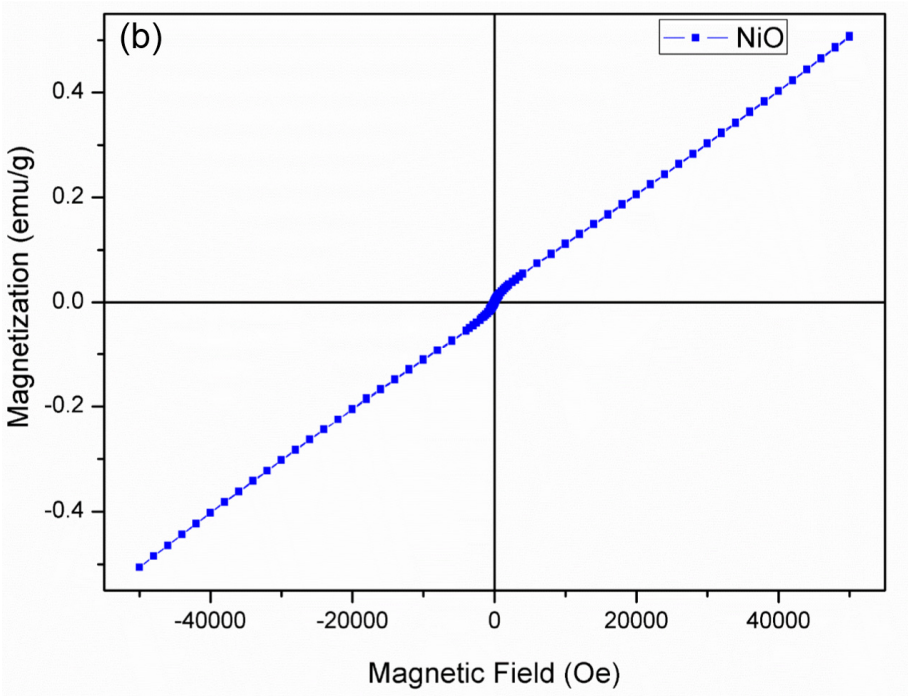


Fig. S15 The hysteresis loops obtained for NiNPs/C-450 with inset of shows the width of the hysteresis loop near the zero filed (a). The hysteresis loops obtained for NiO (b).

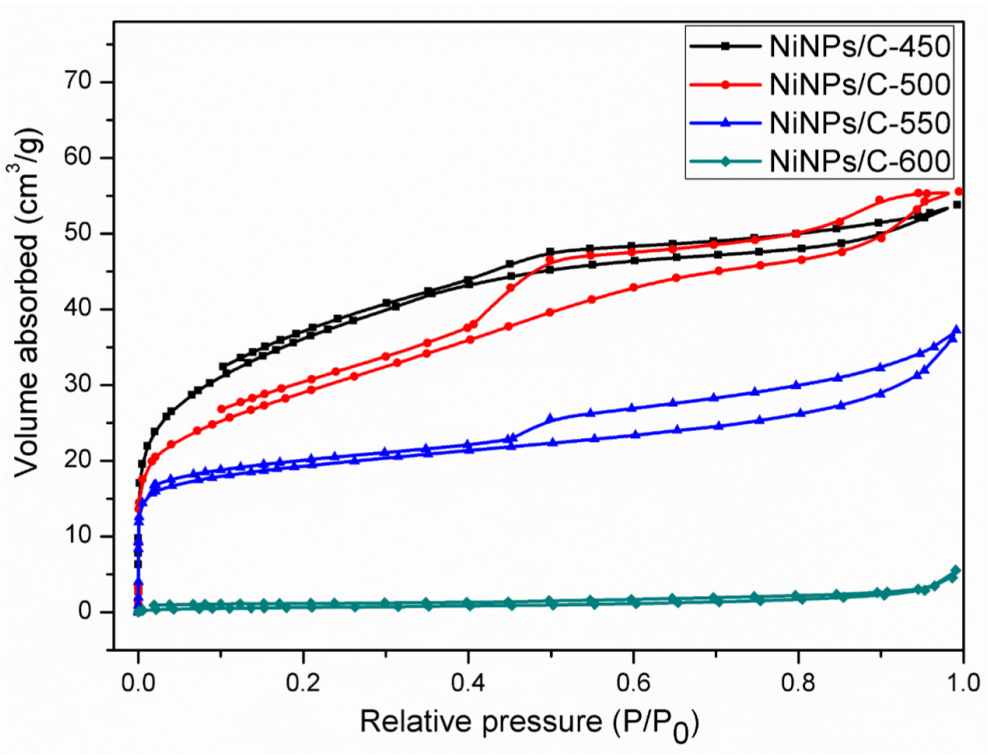


Fig. S16 N_2 adsorption-desorption isotherms of NiNPs/C-450 (black), NiNPs/C-500 (red), NiNPs/C-550 (blue) and NiNPs/C-600 (olive).

8. Tables S1 − S5

Table S1 Crystal data and structure refinement parameters for 1 – 4

Compounds	**1**	**2**	**3**	**4**
Formula	$C_{68}H_{82}N_4Ni_4O_{15}$	$C_{150}H_{204}N_8Ni_8O_{36}$	$C_{72}H_{96}Cl_4N_4Ni_4O_8$	$C_{68}H_{84}Br_4N_4Ni_4O_8$
Formula weight	1430.21	3164.88	1522.16	1639.87
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$
a/Å	12.2603(4)	12.3023(11)	30.848(4)	27.418(3)
b/Å	12.8921(4)	16.2603(14)	16.941(2)	17.6175 (18)
c/Å	23.0008(8)	22.3585(18)	33.157(4)	30.949(3)
α/°	76.203(3)	102.451(2)	90	90
β/°	84.493(3)	100.521(2)	104.778(3)	101.688(2)
γ/°	88.665	109.527(2)	90	90
V/Å^3	3514.3(2)	3955.5(6)	16755(4)	14640 (2)
D_c/(g cm^{-3})	1.352	1.329	1.207	1.488
Z	2	1	8	8
μ (Mo–Kα)/mm^{-1}	1.120	1.005	1.061	3.249
F(000)	1500	1672	6400	6688
Total reflections	40873	193877	248890	136657
Unique reflections	18299	19637	20796	16135
No observations	12527	14822	15044	9629
No parameters	850	956	945	837
R_{int}	0.0406	0.0556	0.0659	0.1101
R^a	0.0624	0.0363	0.0955	0.0869
wR^b	0.1638	0.0777	0.2224	0.1908
GOF^c	1.071	1.021	1.106	1.065

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. ^{c}GOF = $\{\Sigma w((F_o^2-F_c^2)^2)]/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Table S2 Selected bond lengths (Å) and angles (°) for 1 − 4

Compound 1

Ni(1)-Ni(3)	2.9557(7)	Ni(2)-Ni(4)	2.8895(6)
Ni(1)-Ni(2)	3.1717(6)	Ni(1)-Ni(4)	3.1789(7)
Ni(2)-Ni(3)	3.1989(6)	Ni(3)-Ni(4)	3.1519(6)
Ni(1)-O(1)	2.090(2)	Ni(1)-O(2)	2.086(2)
Ni(1)-O(3)	2.043(2)	Ni(1)-O(6)	2.016(3)
Ni(1)-N(1)	2.086(3)	Ni(1)-O(8)	2.076(3)
Ni(2)-O(1W)	2.023(3)	Ni(2)-O(1)	2.058(2)
Ni(2)-O(2)	2.055(2)	Ni(2)-O(4)	2.077(3)
Ni(2)-O(11)	2.071(3)	Ni(2)-N(2)	2.066(3)
Ni(3)-O(10)	2.039(3)	Ni(3)-O(1)	2.064(3)

Ni(3)-O(7)	2.062(3)	Ni(3)-O(3)	2.080(2)
Ni(3)-N(3)	2.065(3)	Ni(3)-O(4)	2.085(2)
Ni(4)-O(2W)	2.001(3)	Ni(4)-O(2)	2.051(3)
Ni(4)-O(3)	2.050(2)	Ni(4)-O(4)	2.069(2)
Ni(4)-N(4)	2.065(3)	Ni(4)-O(12)	2.092(3)
O(6)-Ni(1)-O(3)	103.40(11)	O(3)-Ni(1)-O(8)	91.43(11)
O(6)-Ni(1)-O(8)	88.34(11)	O(3)-Ni(1)-N(1)	164.00(11)
O(6)-Ni(1)-N(1)	92.58(12)	O(6)-Ni(1)-O(2)	100.23(10)
O(8)-Ni(1)-N(1)	88.21(12)	O(8)-Ni(1)-O(2)	168.04(11)
O(3)-Ni(1)-O(2)	78.53(10)	O(6)-Ni(1)-O(1)	170.80(12)
N(1)-Ni(1)-O(2)	99.62(11)	O(8)-Ni(1)-O(1)	93.55(10)
O(3)-Ni(1)-O(1)	85.57(10)	O(2)-Ni(1)-O(1)	79.32(9)
N(1)-Ni(1)-O(1)	78.49(11)	O(1W)-Ni(2)-O(1)	91.39(10)
O(1W)-Ni(2)-O(2)	170.05(12)	O(1W)-Ni(2)-N(2)	96.19(12)
O(2)-Ni(2)-O(1)	80.80(9)	O(1)-Ni(2)-N(2)	100.87(11)
O(2)-Ni(2)-N(2)	79.40(11)	O(2)-Ni(2)-O(11)	95.90(10)
O(1W)-Ni(2)-O(11)	92.89(11)	N(2)-Ni(2)-O(11)	88.61(12)
O(1)-Ni(2)-O(11)	169.12(11)	O(2)-Ni(2)-O(4)	88.09(9)
O(1W)-Ni(2)-O(4)	96.51(11)	N(2)-Ni(2)-O(4)	167.30(11)
O(1)-Ni(2)-O(4)	79.04(10)	O(11)-Ni(2)-O(4)	90.53(11)
O(10)-Ni(3)-O(7)	89.47(12)	O(7)-Ni(3)-O(1)	92.04(11)
O(10)-Ni(3)-O(1)	105.27(11)	O(7)-Ni(3)-N(3)	86.13(13)
O(10)-Ni(3)-N(3)	89.97(12)	O(10)-Ni(3)-O(3)	168.49(12)
O(1)-Ni(3)-N(3)	164.65(11)	O(1)-Ni(3)-O(3)	85.30(9)
O(7)-Ni(3)-O(3)	94.77(10)	O(10)-Ni(3)-O(4)	97.08(11)
N(3)-Ni(3)-O(3)	79.67(11)	O(7)-Ni(3)-O(4)	169.80(11)
O(1)-Ni(3)-O(4)	78.72(10)	N(3)-Ni(3)-O(4)	101.63(12)
O(3)-Ni(3)-O(4)	80.30(9)	N(4)-Ni(4)-O(12)	89.03(12)
O(2W)-Ni(4)-O(3)	93.79(11)	O(3)-Ni(4)-O(2)	79.17(9)
O(2W)-Ni(4)-O(2)	94.63(12)	O(3)-Ni(4)-N(4)	98.88(11)
O(2W)-Ni(4)-N(4)	97.57(13)	O(2W)-Ni(4)-O(4)	173.72(12)
O(2)-Ni(4)-N(4)	167.75(11)	O(2)-Ni(4)-O(4)	88.40(9)
O(3)-Ni(4)-O(4)	81.35(9)	O(2W)-Ni(4)-O(12)	92.04(12)
N(4)-Ni(4)-O(4)	79.36(11)	O(2)-Ni(4)-O(12)	91.62(11)
O(3)-Ni(4)-O(12)	169.46(10)	O(4)-Ni(4)-O(12)	93.38(10)
Compound 2			
Ni(1)-Ni(3)	3.1987(4)	Ni(2)-Ni(4)	3.2081(4)
Ni(1)-Ni(2)	2.9251(4)	Ni(1)-Ni(4)	3.1538(5)

Ni(2)-Ni(3)	3.0959(4)	Ni(3)-Ni(4)	2.9384(4)
Ni(1)-O(6)	2.0178(14)	Ni(1)-N(1)	2.0727(16)
Ni(1)-O(4)	2.0653(14)	Ni(1)-O(1)	2.0797(13)
Ni(1)-O(7)	2.0729(15)	Ni(1)-O(2)	2.0352(13)
Ni(2)-O(2)	2.0379(13)	Ni(2)-O(13)	2.0450(14)
Ni(2)-O(8)	2.0409(15)	Ni(2)-O(1)	2.0674(13)
Ni(2)-O(3)	2.0619(14)	Ni(2)-N(2)	2.0864(16)
Ni(3)-O(1W)	2.0083(15)	Ni(3)-O(3)	2.0595(13)
Ni(3)-O(4)	2.0441(13)	Ni(3)-O(12)	2.0736(15)
Ni(3)-N(3)	2.0687(16)	Ni(3)-O(2)	2.0778(14)
Ni(4)-O(4)	2.0820(13)	Ni(4)-O(11)	2.0489(15)
Ni(4)-O(9)	2.0280(14)	Ni(4)-O(3)	2.0786(13)
Ni(4)-N(4)	2.0899(16)	Ni(4)-O(1)	2.0616(14)
O(6)-Ni(1)-O(4)	103.19(6)	O(7)-Ni(1)-O(1)	91.00(5)
O(6)-Ni(1)-O(2)	103.52(6)	O(6)-Ni(1)-N(1)	91.15(6)
O(2)-Ni(1)-O(4)	78.07(5)	O(4)-Ni(1)-N(1)	101.79(6)
O(2)-Ni(1)-N(1)	165.02(6)	O(2)-Ni(1)-O(7)	91.04(6)
O(6)-Ni(1)-O(7)	86.84(6)	N(1)-Ni(1)-O(7)	86.70(6)
O(4)-Ni(1)-O(7)	166.58(5)	O(2)-Ni(1)-O(1)	86.27(5)
O(6)-Ni(1)-O(1)	170.00(6)	N(1)-Ni(1)-O(1)	78.98(6)
O(4)-Ni(1)-O(1)	80.59(5)	O(2)-Ni(2)-O(8)	95.78(6)
O(2)-Ni(2)-O(13)	170.48(6)	O(8)-Ni(2)-O(13)	93.29(6)
O(2)-Ni(2)-O(3)	82.70(5)	O(8)-Ni(2)-O(3)	169.12(5)
O(13)-Ni(2)-O(3)	88.93(6)	O(2)-Ni(2)-O(1)	86.52(5)
O(8)-Ni(2)-O(1)	90.83(6)	O(13)-Ni(2)-O(1)	96.26(5)
O(3)-Ni(2)-O(1)	78.33(5)	O(2)-Ni(2)-N(2)	79.29(6)
O(8)-Ni(2)-N(2)	86.71(6)	O(13)-Ni(2)-N(2)	98.37(6)
O(3)-Ni(2)-N(2)	103.52(6)	O(1)-Ni(2)-N(2)	165.27(6)
O(1W)-Ni(3)-O(4)	93.61(6)	O(1W)-Ni(3)-O(3)	172.61(7)
O(4)-Ni(3)-O(3)	87.18(5)	O(1W)-Ni(3)-N(3)	99.23(7)
O(4)-Ni(3)-N(3)	167.08(6)	O(3)-Ni(3)-N(3)	79.91(6)
O(1W)-Ni(3)-O(12)	95.43(7)	O(4)-Ni(3)-O(12)	91.92(6)
O(3)-Ni(3)-O(12)	91.88(6)	N(3)-Ni(3)-O(12)	88.27(6)
O(1W)-Ni(3)-O(2)	91.20(6)	O(4)-Ni(3)-O(2)	77.59(5)
O(3)-Ni(3)-O(2)	81.79(5)	N(3)-Ni(3)-O(2)	100.63(6)
O(12)-Ni(3)-O(2)	167.94(5)	O(9)-Ni(4)-O(11)	91.66(6)
O(9)-Ni(4)-O(1)	96.06(6)	O(11)-Ni(4)-O(1)	168.07(5)
O(9)-Ni(4)-O(3)	106.92(5)	O(11)-Ni(4)-O(3)	90.99(6)

O(1)-Ni(4)-O(3)	78.08(5)	O(9)-Ni(4)-O(4)	166.13(6)
O(11)-Ni(4)-O(4)	93.93(6)	O(1)-Ni(4)-O(4)	80.63(5)
O(3)-Ni(4)-O(4)	85.69(5)	O(9)-Ni(4)-N(4)	89.68(6)
O(11)-Ni(4)-N(4)	90.18(6)	O(1)-Ni(4)-N(4)	98.92(6)
O(3)-Ni(4)-N(4)	163.32(6)	O(4)-Ni(4)-N(4)	77.63(6)
Compound 3			
Ni(1)-Ni(3)	3.0804(11)	Ni(2)-Ni(4)	3.1104(11)
Ni(1)-Ni(2)	3.1803(12)	Ni(1)-Ni(4)	3.0965(10)
Ni(2)-Ni(3)	3.0832(11)	Ni(3)-Ni(4)	3.1818(11)
Ni(1)-N(1)	2.037(5)	Ni(1)-O(5)	2.091(5)
Ni(1)-O(3)	2.049(3)	Ni(1)-Cl(1)	2.3492(15)
Ni(1)-O(1)	2.063(4)	Ni(1)-O(2)	2.107(4)
Ni(2)-N(2)	2.054(5)	Ni(2)-O(6)	2.110(5)
Ni(2)-O(2)	2.053(4)	Ni(2)-Cl(2)	2.3623(18)
Ni(2)-O(4)	2.057(4)	Ni(2)-O(1)	2.116(5)
Ni(3)-N(3)	2.043(4)	Ni(3)-O(4)	2.087(4)
Ni(3)-O(2)	2.039(3)	Ni(3)-Cl(3)	2.3729(17)
Ni(3)-O(3)	2.054(4)	Ni(3)-O(7)	2.089(4)
Ni(4)-O(1)	2.058(4)	Ni(4)-O(3)	2.099(4)
Ni(4)-N(4)	2.056(5)	Ni(4)-Cl(4)	2.3588(18)
Ni(4)-O(4)	2.066(4)	Ni(4)-O(8)	2.107(5)
N(1)-Ni(1)-O(1)	79.81(18)	N(1)-Ni(1)-O(5)	89.2(2)
N(1)-Ni(1)-O(3)	162.28(18)	O(1)-Ni(1)-O(5)	90.95(19)
O(3)-Ni(1)-O(1)	82.70(15)	O(3)-Ni(1)-O(2)	81.71(14)
O(3)-Ni(1)-O(5)	88.28(17)	O(5)-Ni(1)-O(2)	167.47(16)
N(1)-Ni(1)-O(2)	98.08(18)	O(3)-Ni(1)-Cl(1)	100.19(11)
O(1)-Ni(1)-O(2)	80.36(17)	O(5)-Ni(1)-Cl(1)	92.98(14)
N(1)-Ni(1)-Cl(1)	97.46(15)	O(1)-Ni(1)-Cl(1)	175.18(12)
O(2)-Ni(1)-Cl(1)	96.18(11)	O(2)-Ni(2)-N(2)	79.61(16)
N(2)-Ni(2)-O(4)	161.20(18)	N(2)-Ni(2)-O(6)	86.4(2)
O(2)-Ni(2)-O(4)	82.38(15)	O(2)-Ni(2)-O(1)	80.38(16)
O(2)-Ni(2)-O(6)	91.99(17)	O(4)-Ni(2)-O(1)	81.40(16)
O(4)-Ni(2)-O(6)	88.93(18)	O(2)-Ni(2)-Cl(2)	175.01(14)
N(2)-Ni(2)-O(1)	100.7(2)	O(4)-Ni(2)-Cl(2)	100.17(13)
O(6)-Ni(2)-O(1)	168.36(17)	O(1)-Ni(2)-Cl(2)	95.70(12)
N(2)-Ni(2)-Cl(2)	98.20(14)	O(6)-Ni(2)-Cl(2)	92.35(14)
O(2)-Ni(3)-O(3)	83.26(15)	O(2)-Ni(3)-O(4)	81.99(15)
O(2)-Ni(3)-N(3)	162.18(17)	O(3)-Ni(3)-O(4)	80.06(16)

N(3)-Ni(3)-O(3)	79.91(16)	N(3)-Ni(3)-O(7)	88.95(18)
N(3)-Ni(3)-O(4)	100.71(17)	O(4)-Ni(3)-O(7)	167.06(17)
O(2)-Ni(3)-O(7)	86.21(16)	N(3)-Ni(3)-Cl(3)	96.95(14)
O(3)-Ni(3)-O(7)	93.33(16)	O(4)-Ni(3)-Cl(3)	95.60(13)
O(2)-Ni(3)-Cl(3)	100.33(12)	O(3)-Ni(3)-Cl(3)	173.99(11)
O(7)-Ni(3)-Cl(3)	91.72(13)	N(4)-Ni(4)-O(1)	162.1(2)
O(1)-Ni(4)-O(4)	82.59(17)	O(1)-Ni(4)-O(3)	81.63(14)
N(4)-Ni(4)-O(4)	80.34(17)	N(4)-Ni(4)-O(8)	86.7(2)
N(4)-Ni(4)-O(3)	100.28(17)	O(4)-Ni(4)-O(8)	91.3(2)
O(4)-Ni(4)-O(3)	79.53(16)	N(4)-Ni(4)-Cl(4)	96.83(14)
O(1)-Ni(4)-O(8)	88.56(18)	O(4)-Ni(4)-Cl(4)	174.40(13)
O(3)-Ni(4)-O(8)	167.33(17)	O(8)-Ni(4)-Cl(4)	93.34(18)
O(1)-Ni(4)-Cl(4)	100.62(14)	O(3)-Ni(4)-Cl(4)	96.32(12)
Compound 4			
Ni(1)-Ni(3)	3.1628(16)	Ni(2)-Ni(4)	3.150(2)
Ni(1)-Ni(2)	3.1238(17)	Ni(1)-Ni(4)	3.1196(19)
Ni(2)-Ni(3)	3.1081(15)	Ni(3)-Ni(4)	3.1048(17)
Ni(1)-O(4)	2.041(6)	Ni(1)-O(5)	2.105(11)
Ni(1)-O(1)	2.045(7)	Ni(1)-Br(1)	2.506(2)
Ni(1)-N(1)	2.073(9)	Ni(1)-O(3)	2.119(7)
Ni(2)-O(1)	2.052(5)	Ni(2)-O(4)	2.106(8)
Ni(2)-N(2)	2.045(6)	Ni(2)-Br(2)	2.5061(16)
Ni(2)-O(2)	2.055(6)	Ni(2)-O(6)	2.124(9)
Ni(3)-O(7)	2.093(6)	Ni(3)-N(3)	2.071(6)
Ni(3)-O(3)	2.037(7)	Ni(3)-Br(3)	2.5133(16)
Ni(3)-O(2)	2.071(5)	Ni(3)-O(1)	2.105(6)
Ni(4)-O(3)	2.050(6)	Ni(4)-O(2)	2.077(6)
Ni(4)-O(4)	2.050(7)	Ni(4)-Br(4)	2.5325(18)
Ni(4)-N(4)	2.059(7)	Ni(4)-O(8)	2.087(10)
O(4)-Ni(1)-N(1)	160.4(4)	O(4)-Ni(1)-O(5)	88.5(3)
O(4)-Ni(1)-O(1)	81.6(3)	N(1)-Ni(1)-O(5)	87.2(4)
O(1)-Ni(1)-N(1)	79.4(4)	O(1)-Ni(1)-O(3)	80.1(3)
O(1)-Ni(1)-O(5)	91.6(5)	O(5)-Ni(1)-O(3)	167.0(3)
O(4)-Ni(1)-O(3)	80.4(2)	O(1)-Ni(1)-Br(1)	174.90(17)
N(1)-Ni(1)-O(3)	101.0(3)	O(5)-Ni(1)-Br(1)	92.9(4)
O(4)-Ni(1)-Br(1)	100.8(2)	O(3)-Ni(1)-Br(1)	95.8(2)
N(1)-Ni(1)-Br(1)	98.5(3)	O(1)-Ni(2)-O(2)	82.7(2)
N(2)-Ni(2)-O(1)	161.8(3)	O(1)-Ni(2)-O(4)	79.9(3)

N(2)-Ni(2)-O(2)	80.5(2)	N(2)-Ni(2)-O(6)	83.4(3)
N(2)-Ni(2)-O(4)	104.0(3)	O(2)-Ni(2)-O(6)	91.2(3)
O(2)-Ni(2)-O(4)	80.2(2)	N(2)-Ni(2)-Br(2)	96.78(19)
O(1)-Ni(2)-O(6)	90.0(3)	O(2)-Ni(2)-Br(2)	174.92(18)
O(4)-Ni(2)-O(6)	167.4(2)	O(6)-Ni(2)-Br(2)	92.8(2)
O(1)-Ni(2)-Br(2)	100.47(18)	O(4)-Ni(2)-Br(2)	96.37(19)
O(3)-Ni(3)-O(2)	81.7(2)	O(3)-Ni(3)-O(7)	91.5(3)
O(3)-Ni(3)-N(3)	79.8(3)	O(2)-Ni(3)-O(7)	88.5(2)
N(3)-Ni(3)-O(2)	160.4(3)	N(3)-Ni(3)-O(1)	102.2(2)
N(3)-Ni(3)-O(7)	85.6(3)	O(7)-Ni(3)-O(1)	167.6(3)
O(3)-Ni(3)-O(1)	80.6(3)	N(3)-Ni(3)-Br(3)	97.3(2)
O(2)-Ni(3)-O(1)	81.0(2)	O(7)-Ni(3)-Br(3)	92.57(18)
O(3)-Ni(3)-Br(3)	174.89(19)	O(2)-Ni(3)-Br(3)	101.56(17)
O(1)-Ni(3)-Br(3)	95.9(2)	O(4)-Ni(4)-O(3)	81.8(2)
O(4)-Ni(4)-N(4)	80.5(3)	O(3)-Ni(4)-N(4)	161.8(3)
O(4)-Ni(4)-O(2)	81.0(3)	O(3)-Ni(4)-O(2)	81.2(2)
N(4)-Ni(4)-O(2)	100.0(3)	O(4)-Ni(4)-O(8)	94.1(4)
O(3)-Ni(4)-O(8)	87.0(3)	N(4)-Ni(4)-O(8)	90.2(3)
O(2)-Ni(4)-O(8)	167.7(3)	O(4)-Ni(4)-Br(4)	174.51(17)
O(3)-Ni(4)-Br(4)	102.02(19)	N(4)-Ni(4)-Br(4)	95.9(3)
O(2)-Ni(4)-Br(4)	95.64(16)	O(8)-Ni(4)-Br(4)	90.1(4)

Table S3 Hydrogen bonding parameters for 1 − 4

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
Compound 1				
O1W-H1W1···O9	0.832(18)	1.76(2)	2.585(4)	70(4)
O1W-H2W1···O11#1	0.836(18)	1.93(2)	2.729(4)	159(4)
O2W-H1W2···O5	0.829(19)	1.762(19)	2.590(5)	175(5)
O2W-H2W2···O12#2	0.832(19)	1.90(2)	2.721(4)	172(5)
O3W-H1W3···O8	0.857(19)	2.03(3)	2.837(5)	157(6)
O3W-H2W3···O9	0.849(19)	1.92(2)	2.766(5)	176(6)
Symmetry codes for generating equivalent atoms: #1 *–x* + 1, *–y*, *–z*; #2 *–x*, *–y*, *–z*; #3 *–x* + 1, *–y* + 1, *–z*.				
Compound 2				
O1W-H1W1···O5	0.813(17)	1.836(17)	2.647(2)	174(3)
O2W-H1W2···O15	0.903(17)	1.863(17)	2.765(3)	176(3)
O13-H1O3···O10	0.814(16)	1.786(16)	2.597(2)	175(3)
O14-H1O4···O2W	0.883(18)	1.90(2)	2.770(3)	166(4)
O15-H1O5···O10	0.875(18)	1.854(19)	2.725(3)	173(4)

O2W-H2W2···O6#1	0.849(17)	2.52(3)	3.121(3)	129(3)
O2W-H2W2···O7#1	0.849(17)	2.21(2)	2.996(2)	153(3)
O1W-H2W1···O3W#2	0.864(17)	1.835(18)	2.664(2)	160(3)
O3W-H2W3···O5	0.834(17)	1.878(17)	2.710(2)	176(3)

Symmetry codes for generating equivalent atoms: #1 $x + 1, y, z$; #2 $–x + 1, –y + 1, –z$; #3 $x + 1, y – 1, z$.

Compound 3				
O5-H1O5···Cl4	0.833(4)	2.2510(16)	3.047(5)	160.2(3)
O6-H1O6···Cl3	0.839(5)	2.2432(17)	3.046(5)	160.4(3)
O7-H1O7···Cl1	0.841(4)	2.2059(14)	3.017(4)	162.0(3)
O8-H1O8···Cl2	0.853(6)	2.3204(18)	3.042(5)	142.5(4)
Compound 4				
O6-H1O6···Br3	0.82(2)	2.32(3)	3.135(6)	172(11)
O7-H1O7···Br4	0.83(2)	2.41(4)	3.190(6)	157(9)
O5-H1O5···Br2	0.82(2)	2.36(7)	3.151(11)	162(20)
O8-H1O8···Br1	0.83(2)	2.34(3)	3.157(12)	174(17)

Table S4 Comparison of different catalysts with NiNPs/C-450 for the reduction of 4-nitrophenol to 4-aminophenol

Sample	Type	k ($\times 10^{-3}$ s^{-1})	κ ($\times 10^{-3}$ $mg^{-1}\cdot s^{-1}$)	Converse (%)	Reference
Fe_3O_4@SiO_2 -Au@mSiO_2	microsphere	5.8	1.93	90(8)	6
Ni/SiO_2@Au	microsphere	10	2.5	73(8)	7
p(AMPS)-Ni	hydrogel	0.9	0.15	75(5)	8
Au@C	nanocomposite	3.6	1.8	32(10)	9
Ni(modified)	nanoparticles	2.4	0.80	/	10
NiNPs/C-450	nanocomposite	19	9.5	97(10)	this work

Table S5 The BET surface area, total pore volume, and average pore size of NiNPs/C-450, NiNPs/C-500, NiNPs/C-550, NiNPs/C-600.

Sample	BET surface area ($m^2\cdot g^{-1}$)	Pore volume ($cm^3\cdot g^{-1}$)	Average size (nm)
NiNPs/C-450	125	0.08	2.65
NiNPs/C-500	101	0.08	3.40
NiNPs/C-550	52	0.06	4.40
NiNPs/C-600	2	0.01	14.96

9. Original ^{1}H NMR, ^{13}C NMR, TOF-Mass, ESI-Mass and IR spectra of HL and compounds 1 – 4.

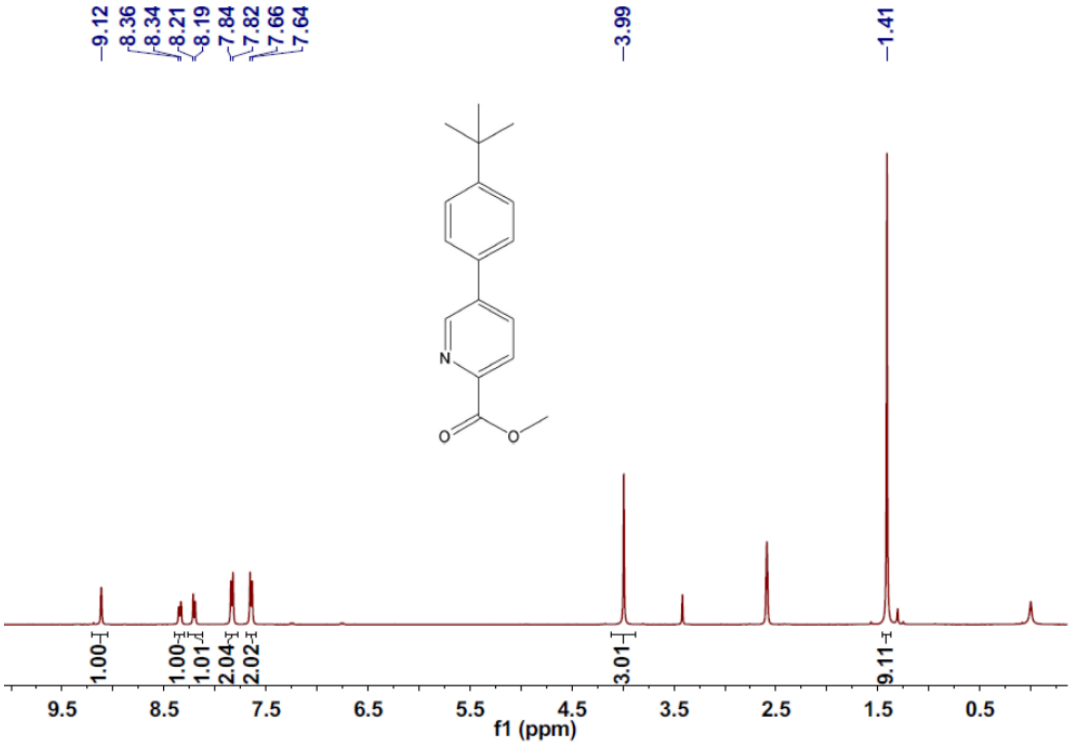


Fig. S17 The ^{1}H NMR spectrum of methyl 5-(4-(tert-butyl)phenyl)picolinate.

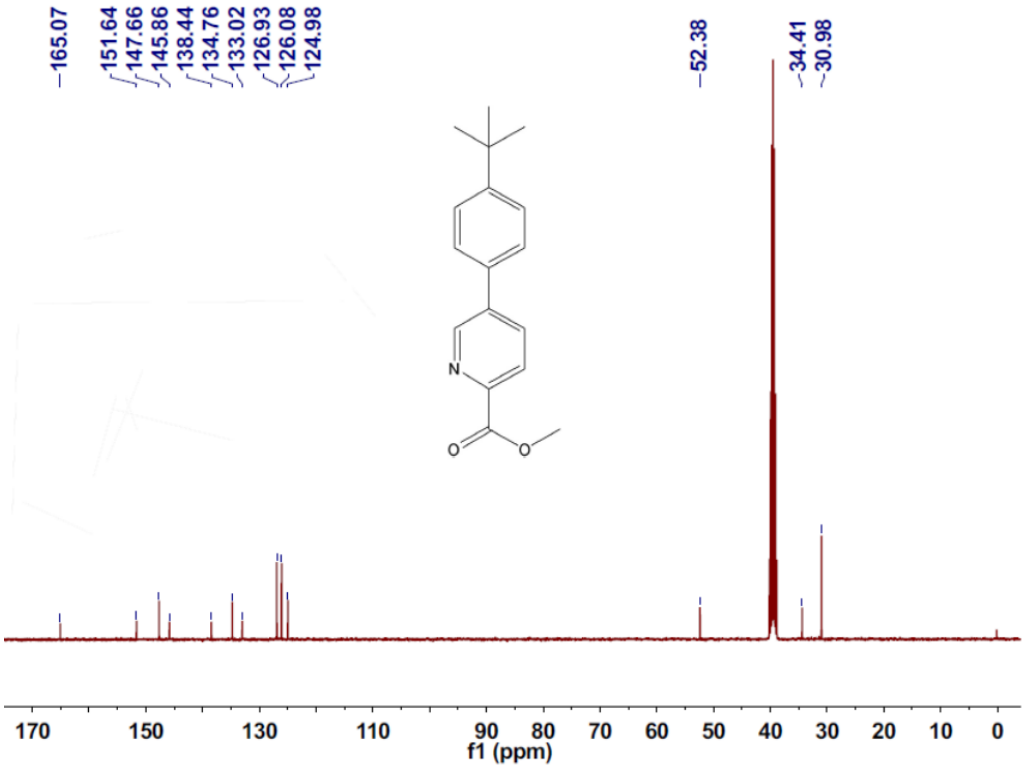


Fig. S18 The ^{13}C NMR spectrum of methyl 5-(4-(tert-butyl)phenyl)picolinate.

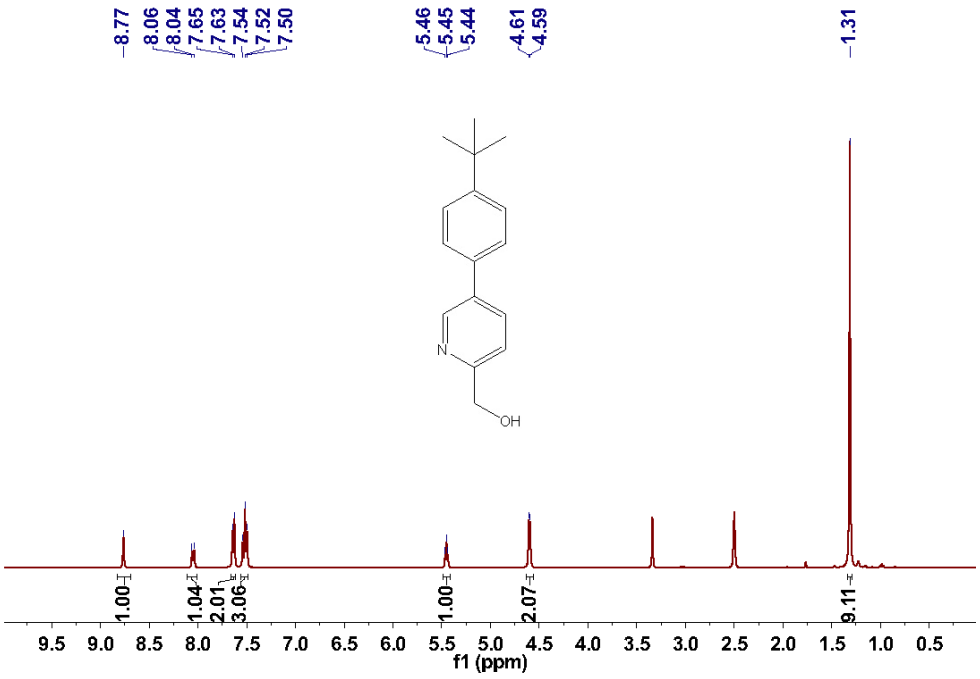


Fig. S19 The ^{1}H NMR spectrum of (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol.

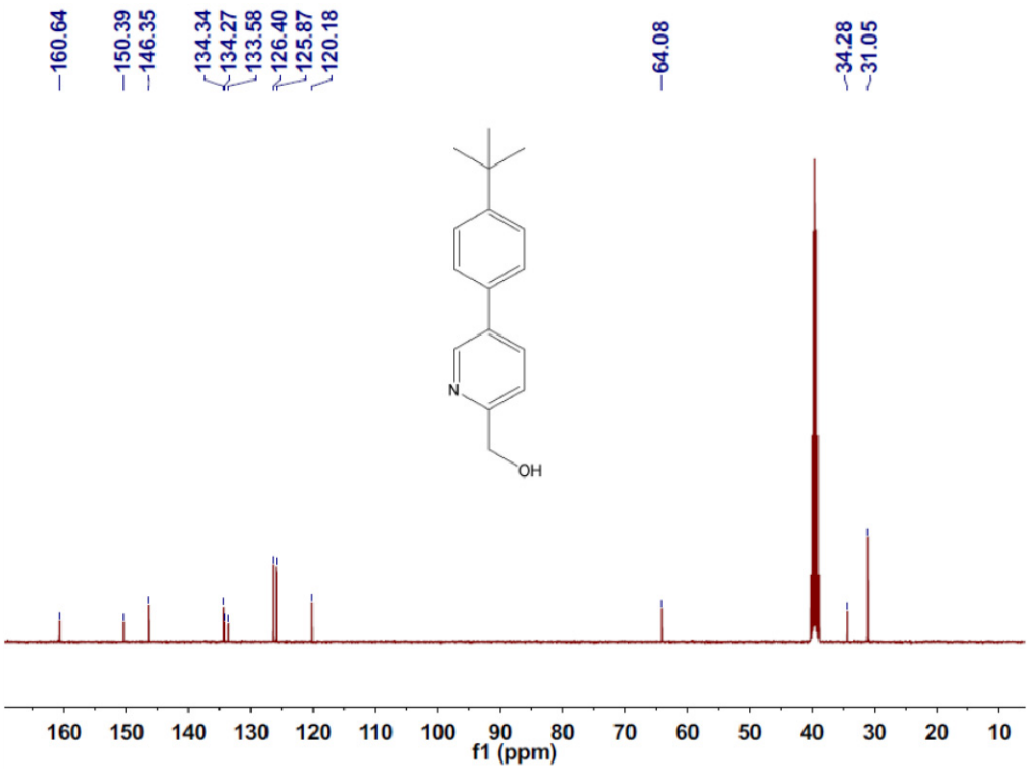


Fig. S20 The ^{13}C NMR spectrum of (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol.

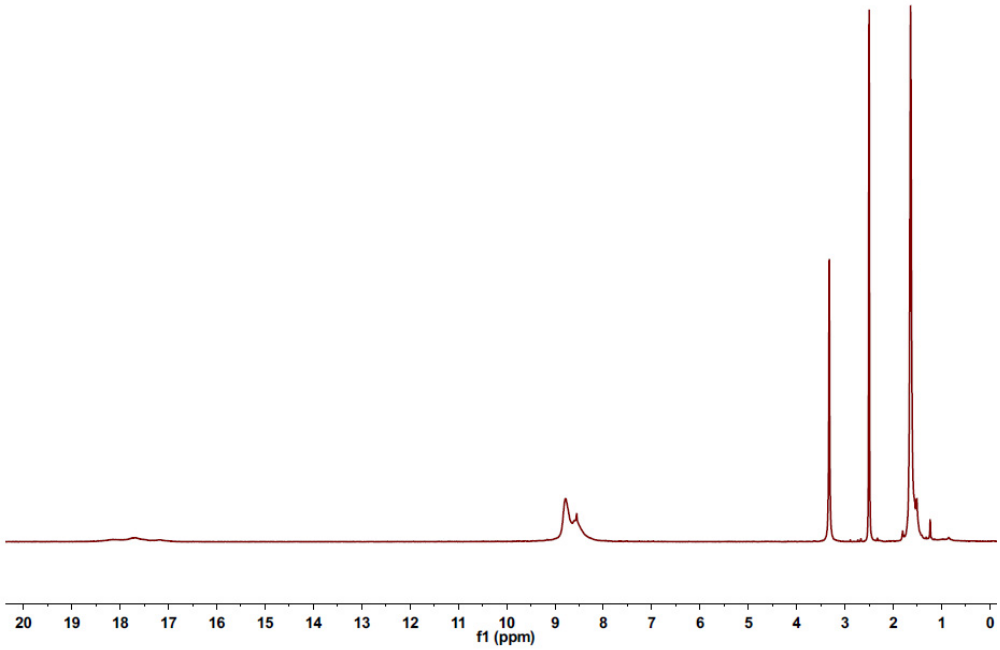


Fig. S21 The ^{1}H NMR spectrum of compound **1**.

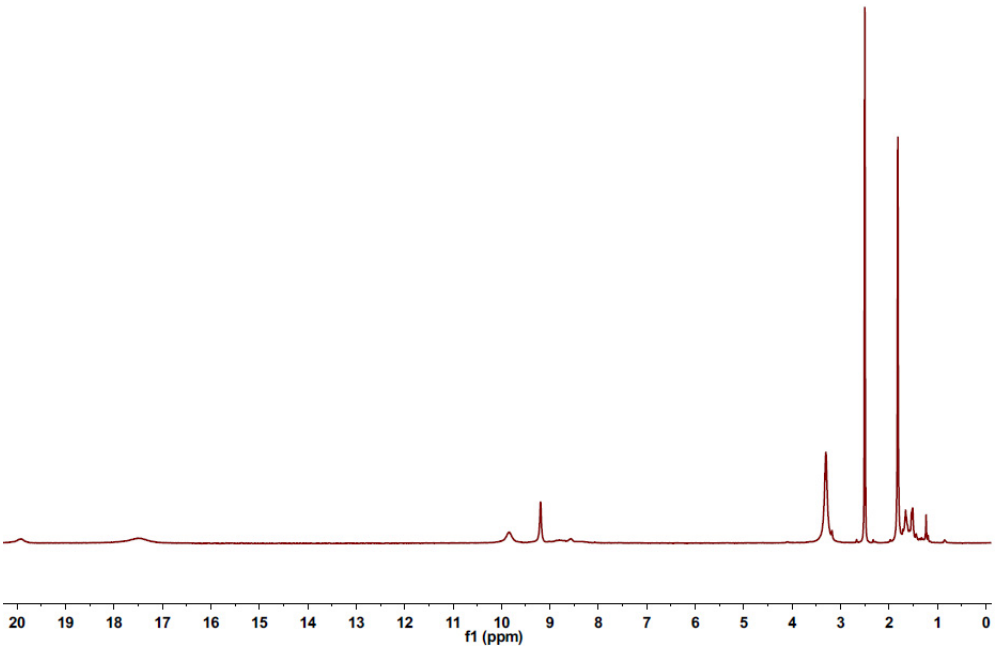


Fig. S22 The ^{1}H NMR spectrum of compound **2**.

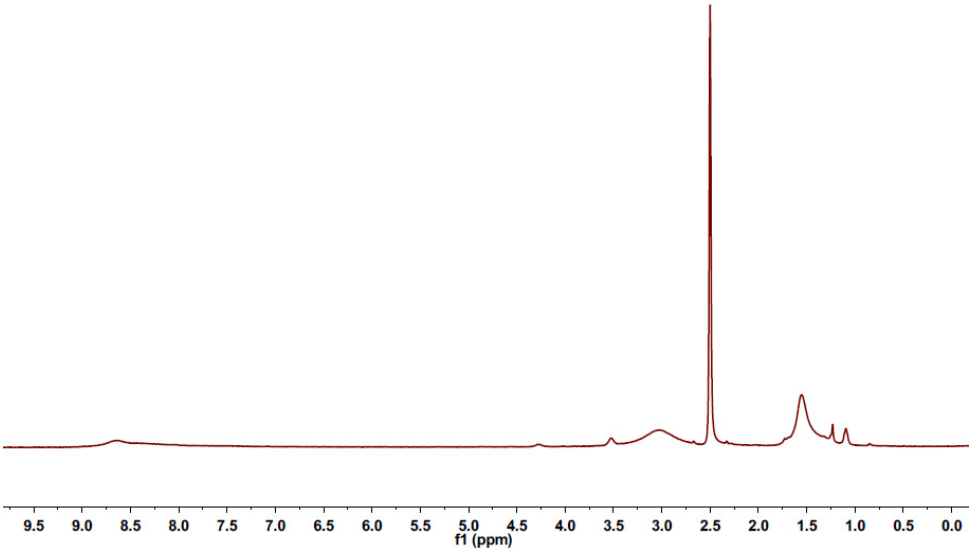


Fig. S23 The ^{1}H NMR spectrum of compound **3**.

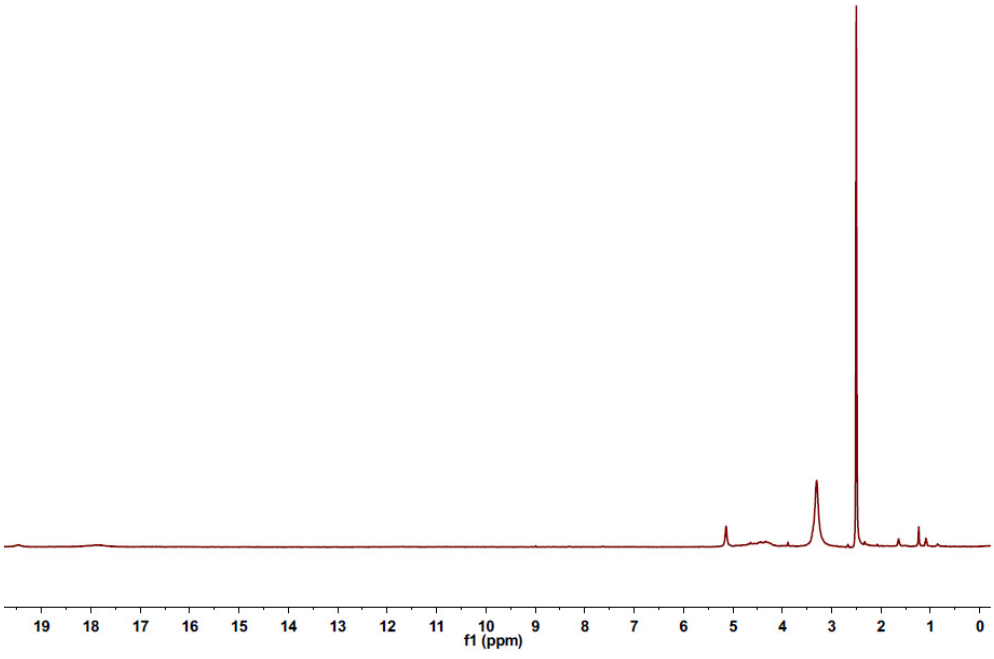


Fig. S24 The ^{1}H NMR spectrum of compound **4**.

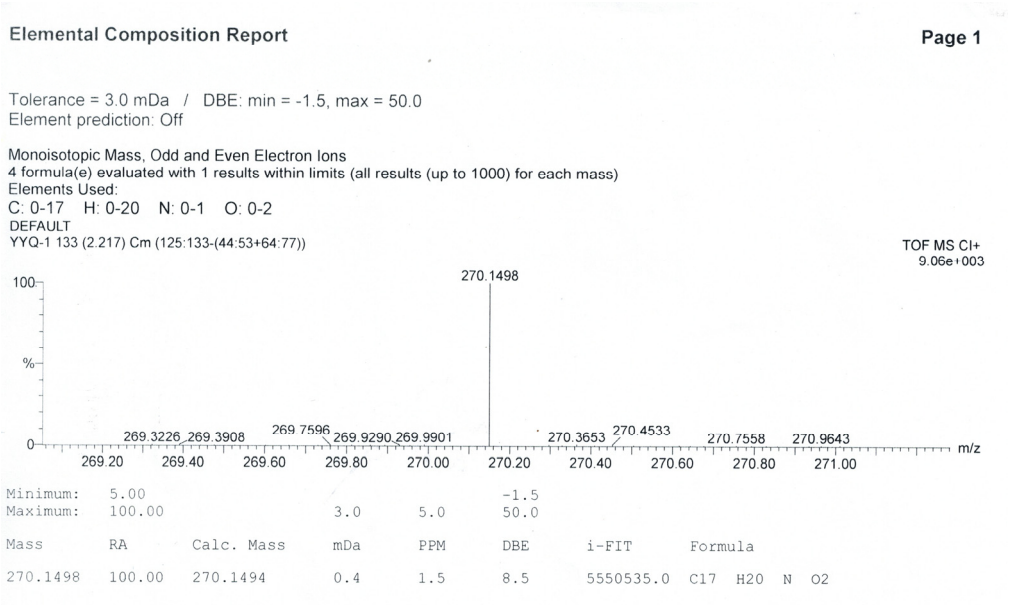


Fig. S25 The TOF-MS spectrum of methyl 5-(4-(tert-butyl)phenyl)picolinate.

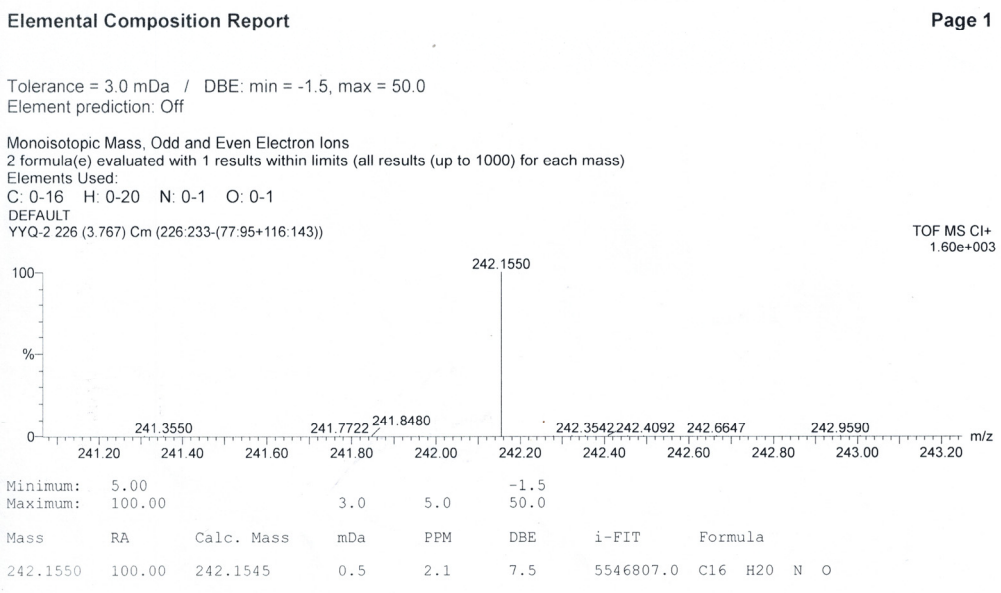


Fig. S26 The TOF-MS spectrum of (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol.

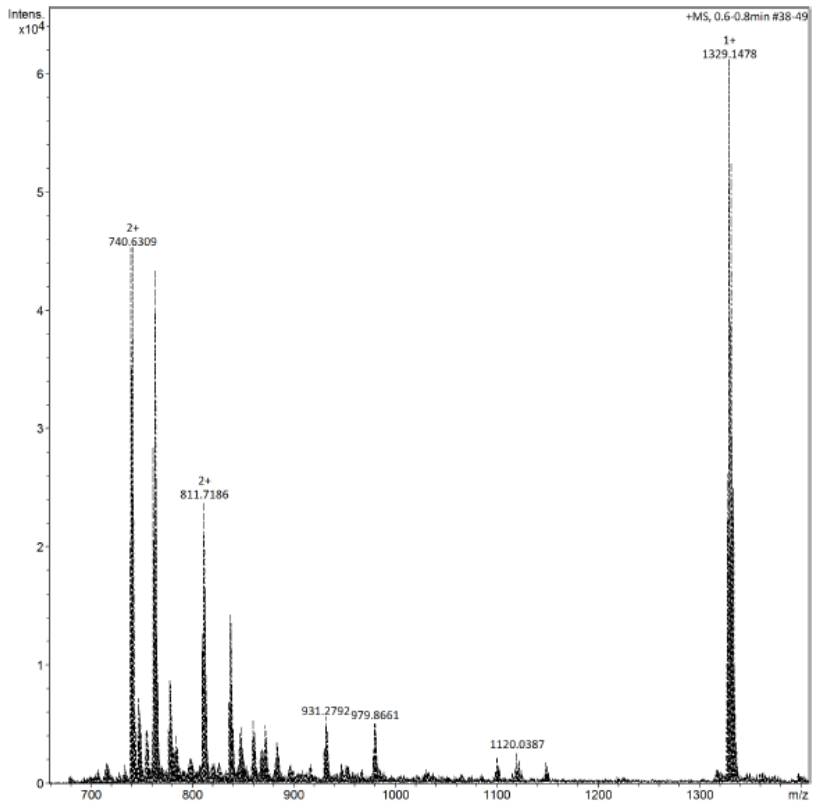


Fig. S27 The ESI-MS spectrum of compound **1**.

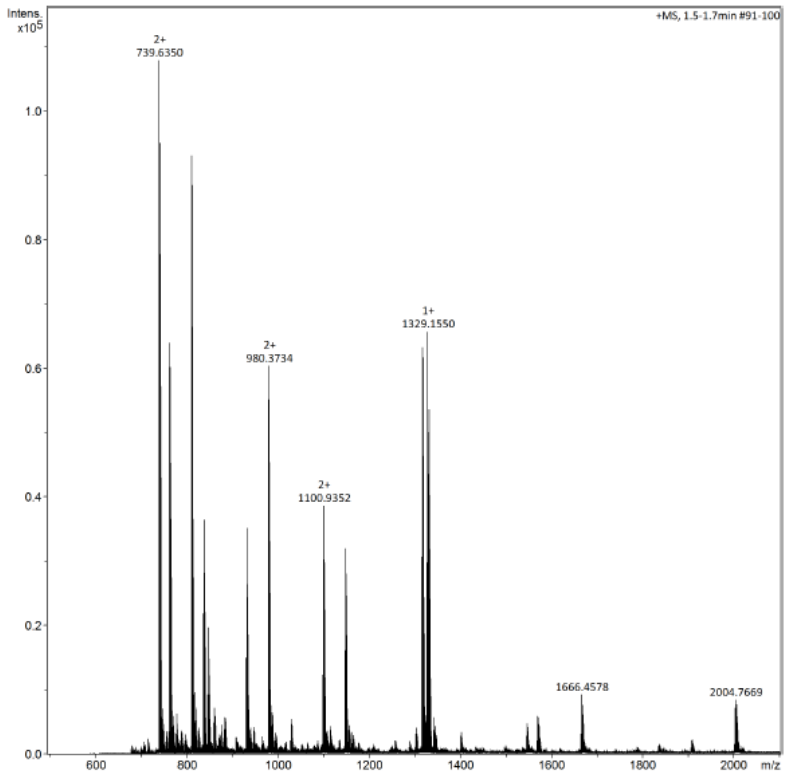


Fig. S28 The ESI-MS spectrum of compound **2**.

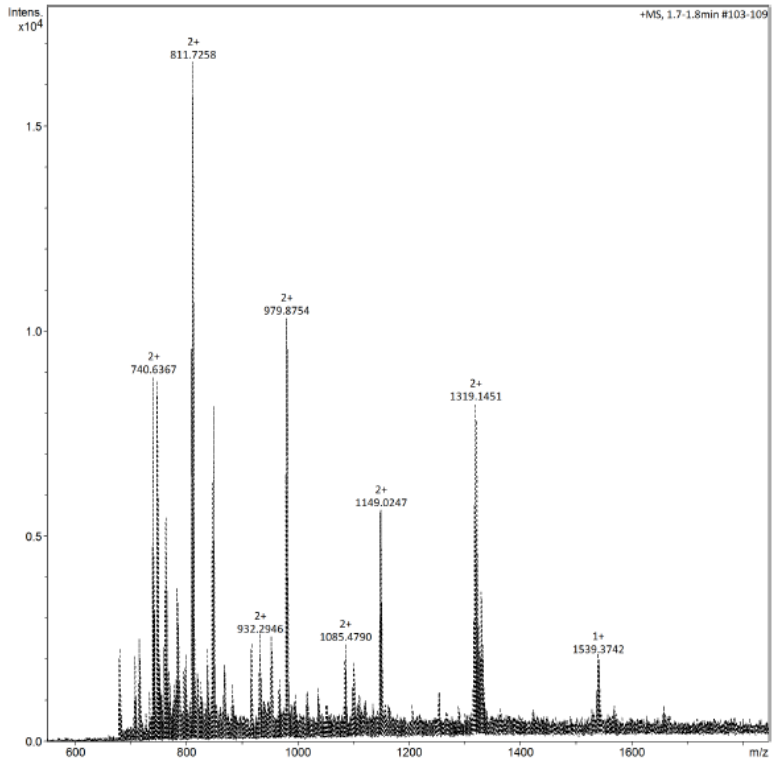


Fig. S29 The ESI-MS spectrum of compound **3**.

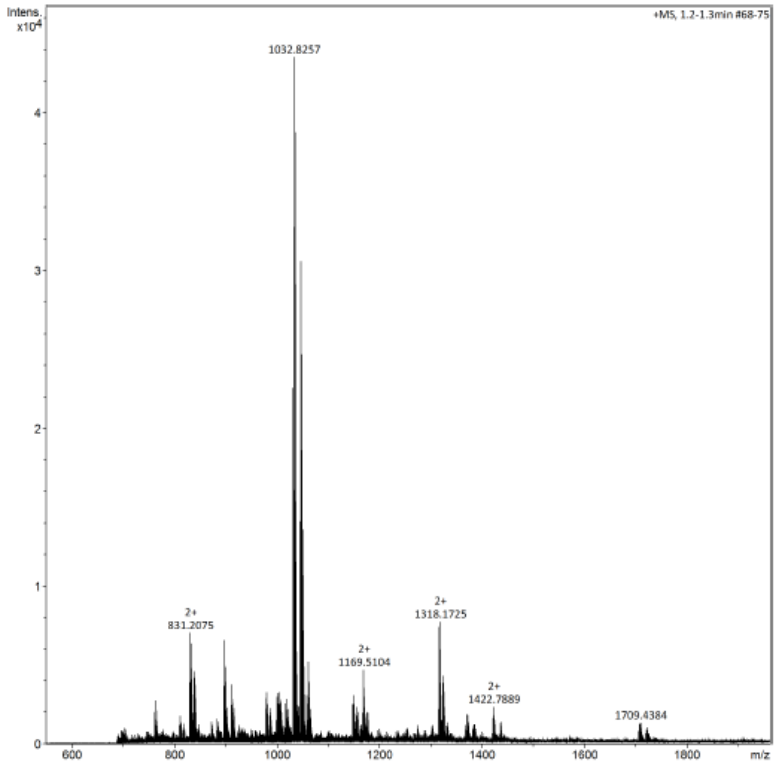


Fig. S30 The ESI-MS spectrum of compound **4**.

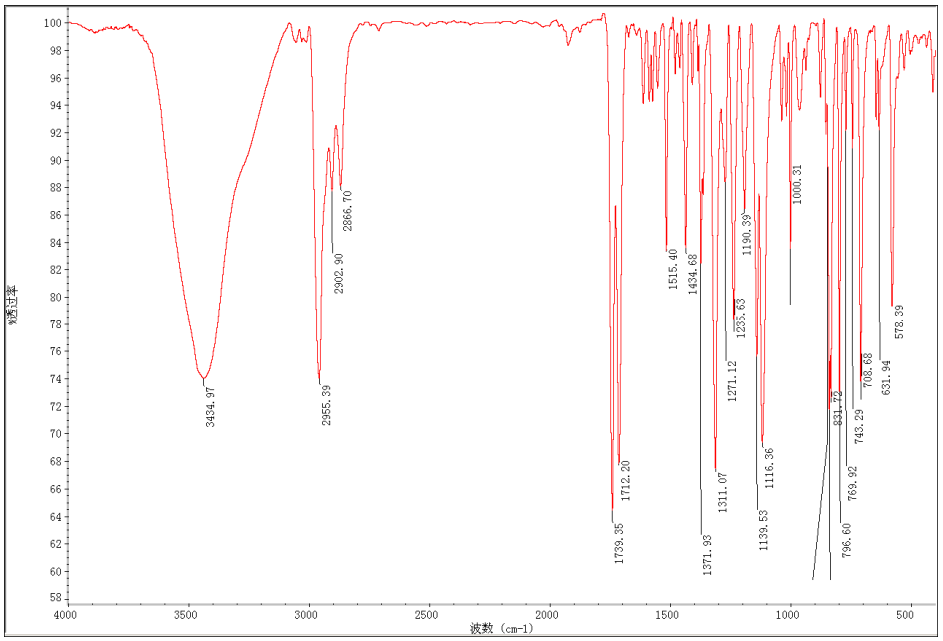


Fig. S31 The IR spectrum of methyl 5-(4-(tert-butyl)phenyl)picolinate.

Fig. S32 The IR spectrum of (5-(4-(tert-butyl)phenyl)pyridine-2-yl)methanol.

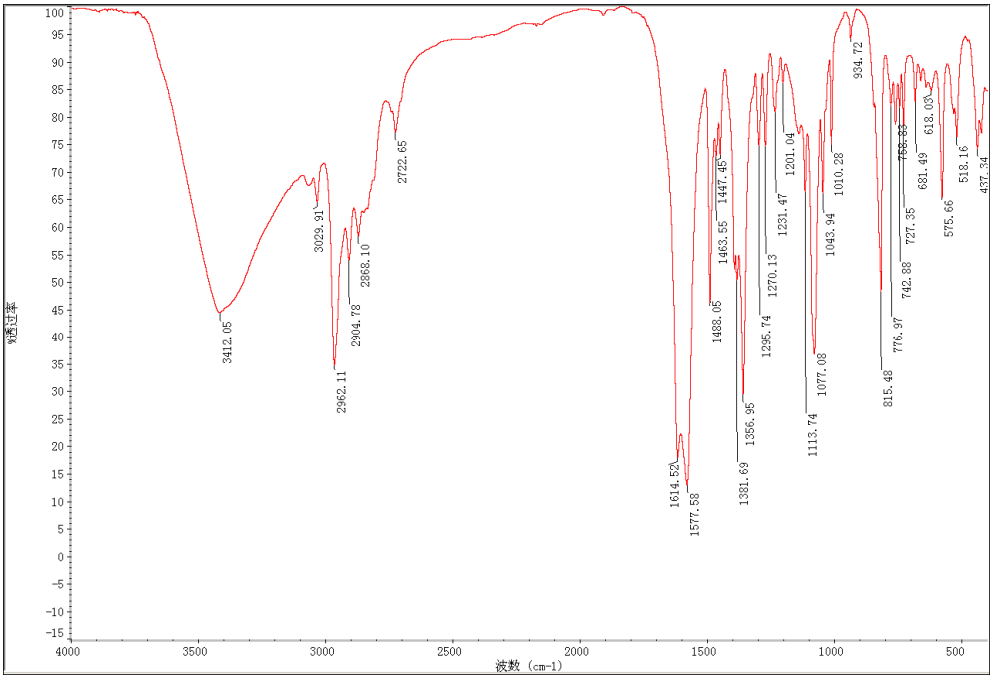


Fig. S33 The IR spectrum of compound **1**.

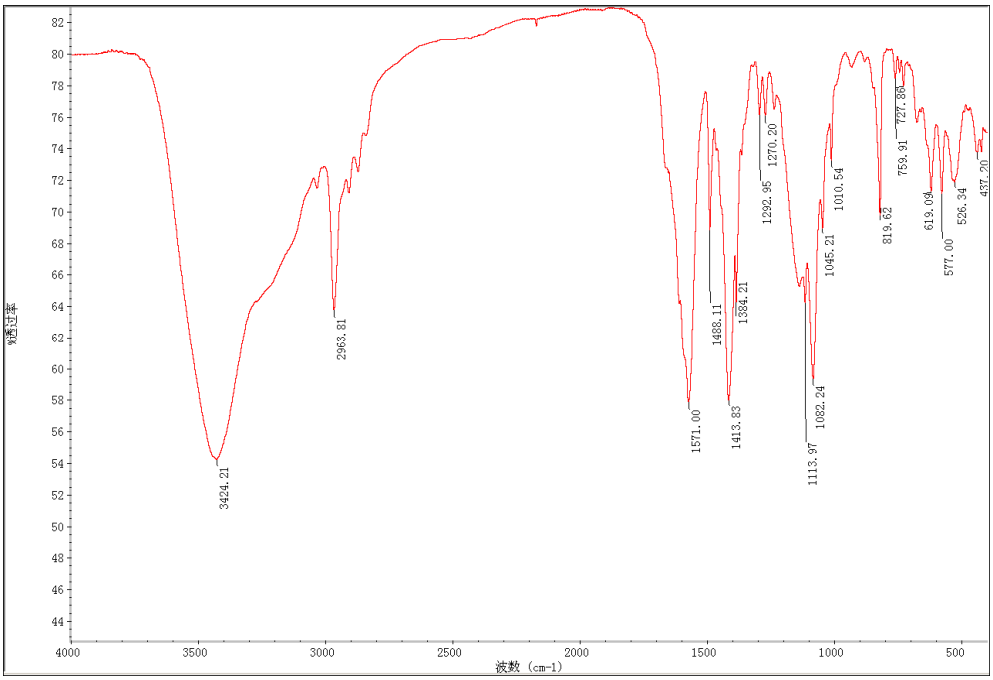


Fig. S34 The IR spectrum of compound **2**.

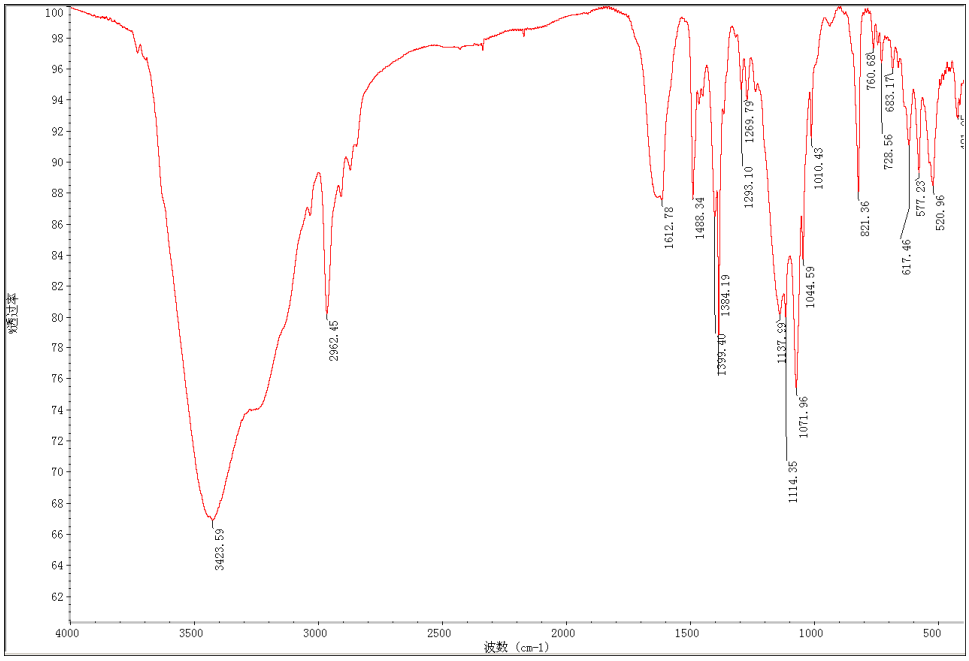


Fig. S35 The IR spectrum of compound **3**.

Fig. S36 The IR spectrum of compound **4**.

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