Supporting Information

Stable hybrid catalyst (POM-PPPh$_3$/L/Ni) for reduction of toxic nitroarene compounds in water

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Experimental

Materials and Methods

Nickel (II) acetate tetrahydrate, molybdenum trioxide, phosphoric acid, nitric acid, (3-bromopropyl)triphenylphosphonium bromide, diethylenetriamine, and salicylaldehyde were purchased from Sigma-Aldrich, Merck, or Fluka in analytical grade and used as received. Nitrobenzene, 1-bromo-4-nitrobenzene, 1-chloro-4-nitrobenzene, 1-fluoro-4-nitrobenzene, 1-chloro-3-nitrobenzene, 1-chloro-2-nitrobenzene, 4-nitrophenol (4-NP), 3-nitrophenol, 4-nitroacetophenone, 1,2-dinitrobenzene, 4-nitroanilin, 1-nitronaphthalen, 4-nitrobenzoicacid, 2-nitrobenzaldehyde, 1-methoxy-4-nitrobenzene, and 4-nitroacetophenone were purchased from Sigma-Aldrich and used without further purification.

Thermogravimetric analysis (TGA) of the samples was performed using a Netzsch-TGA 209 F1 thermogravimeter heated from 25 to 700 °C at a heating rate of 10 °C.min^{-1} under static air. Fourier transform infrared (FT-IR) spectra from solid samples were carried on a Perkin-Elmer-RXI FT-IR spectrometer, using KBr disks. Inductively coupled plasma-optical emission spectrometry (ICP-OES) results for depicting the molar ratio of Mo and Ni were obtained on a SPECTRO ARCOS

analyzer. In order to investigate the crystal structure, the Powder X-ray diffraction (XRD) analyses were used on a Rigaku D-max CIII X-ray diffractometer with Cu Kα radiation. Field emission scanning electron microscopy (FESEM) and elemental mapping analyses were executed in a high-resolution MIRA3-TSCAN microscope. X-ray photoelectron spectroscopy (XPS) was performed using a vacuum generator Thermo ESCALAB 250 XI with Mg X-ray sources. Transmission electron microscopy (TEM) images were carried out on the TEM Philips EM 208S (accelerating voltage:100 kV) instrument. The ^{1}H NMR spectra of products were recorded on Bruker AMX 300 MHz NMR spectrometers using $CDCl_3$ or DMSO-d^6 as the solvent. The electronic absorption spectra (UV–visible) of the nitroarenes were carried out on a Perkin Elmer Lambda 25 UV-vis spectrophotometer in the wavelength range of 200-800 nm in a quartz cuvette. Gas chromatography-mass spectrometry (GC-MS) experiment was carried out with Agilent 7890A-MSD 5975 to specify the mechanism.

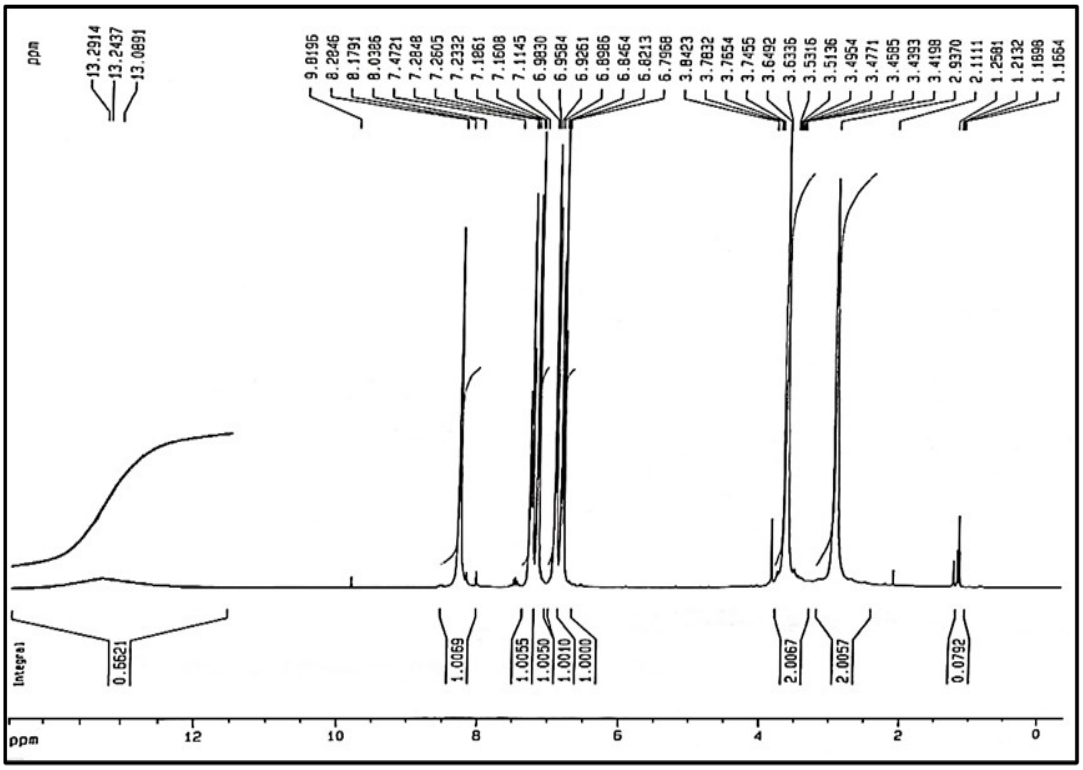

Figure S1. ^{1}H NMR spectrum of the prepared Schiff base.

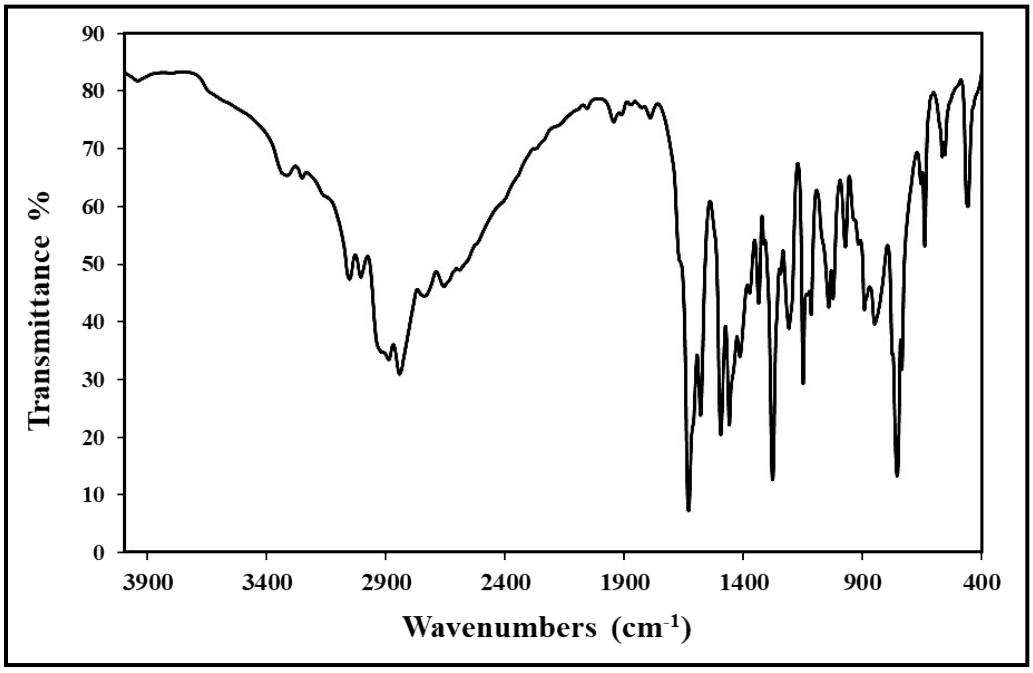

Figure S2. FT-IR spectrum of the prepared Schiff base.

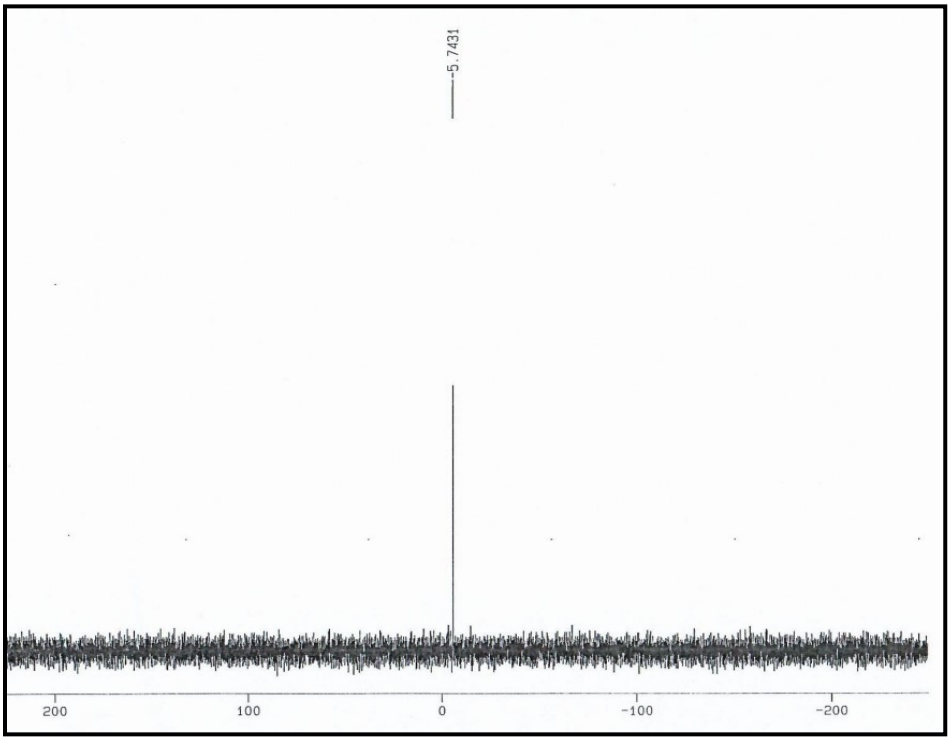

Figure S3. ^{31}P NMR spectrum of the POM.

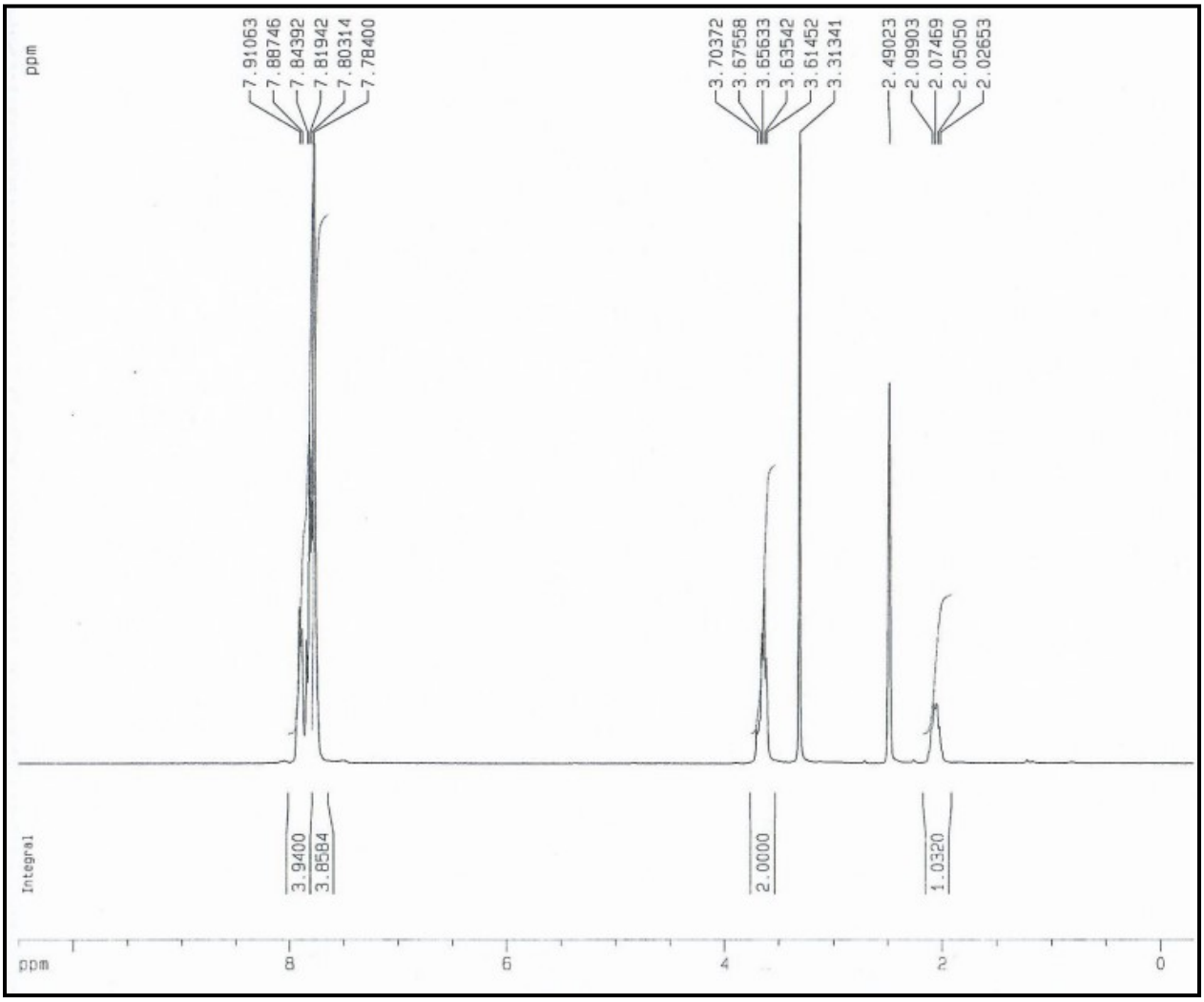

Figure S4. ^{1}H NMR spectrum of the prepared POM-PPPh$_3$.

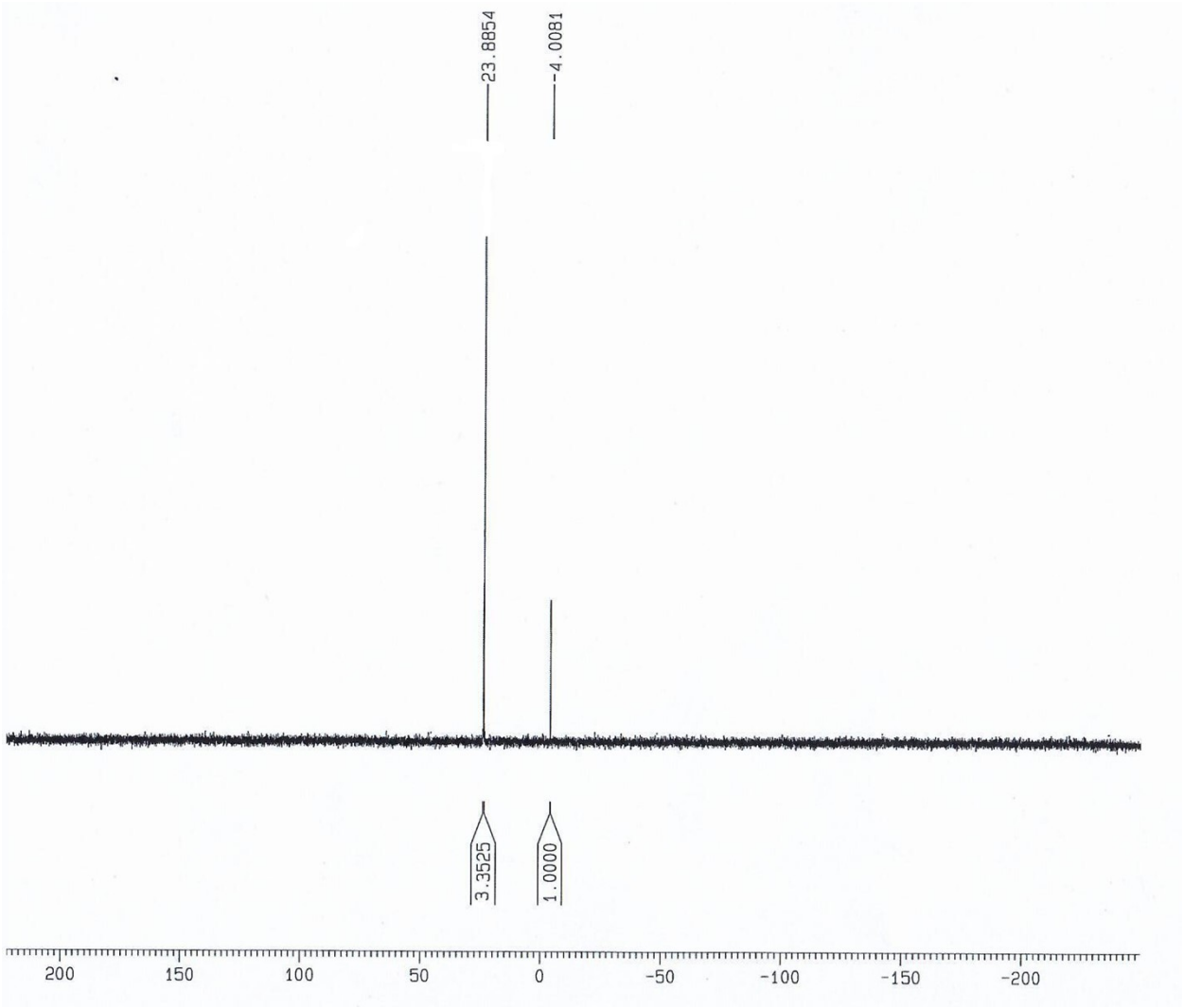

Figure S5. ^{31}P NMR spectrum of the prepared POM-PPh_3.

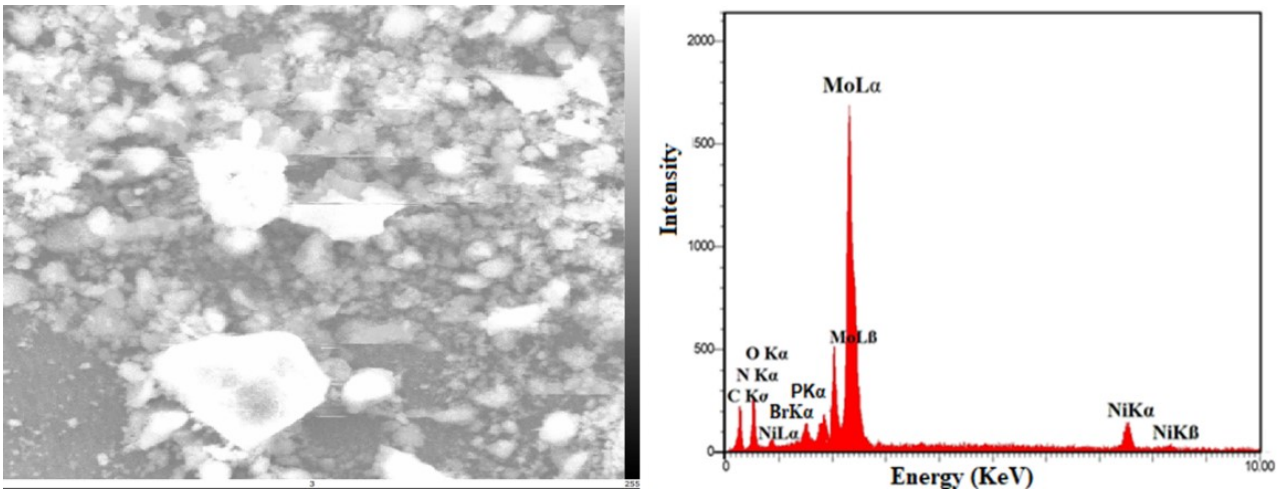

Figure S6. EDX spectrum of POM-PPPh$_3$/L/Ni nanocatalyst.

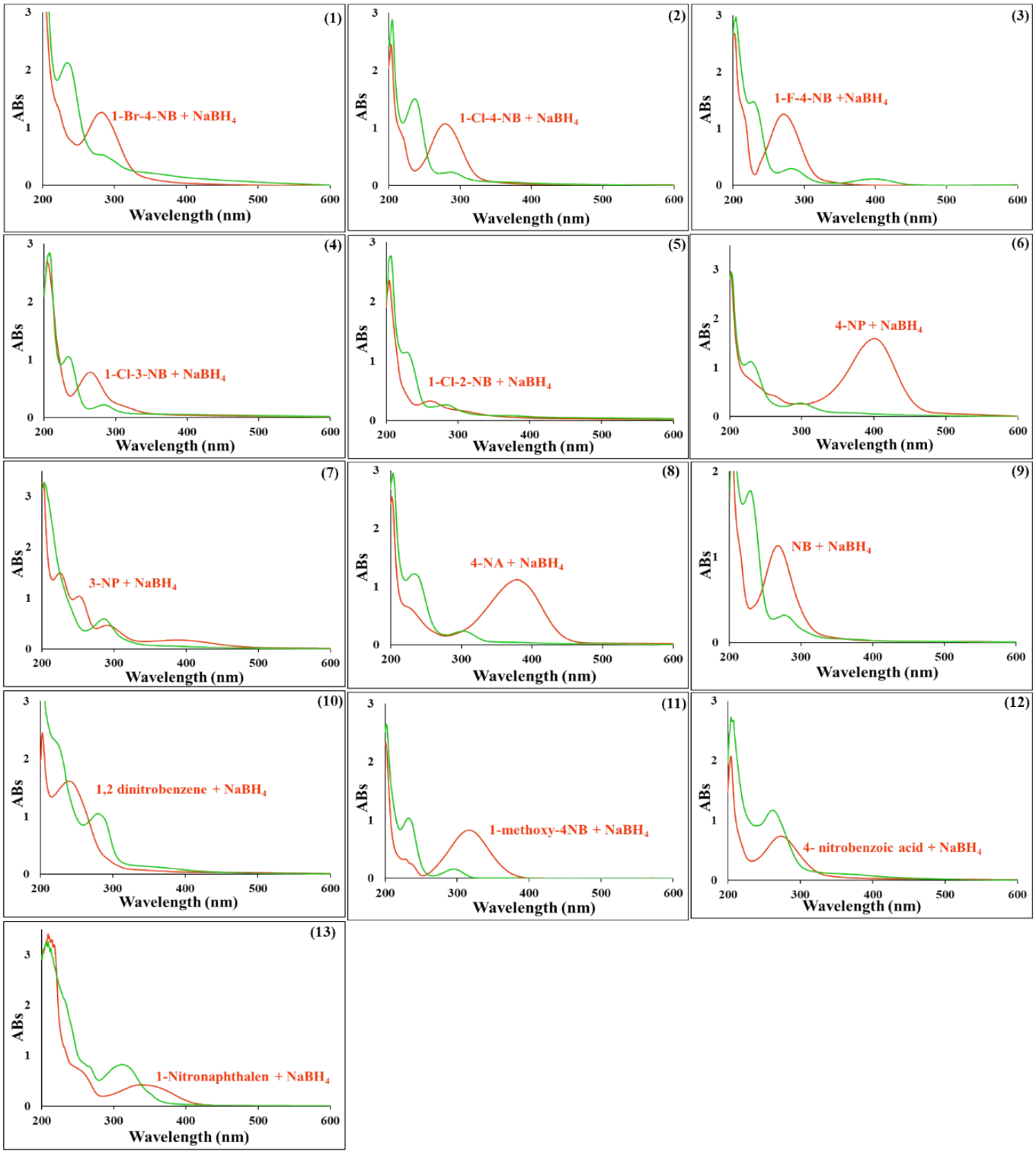

Figure S7. UV-Vis spectra of the reduction of various nitroaromatic compounds to the corresponding aminoarenes in the presence of POM-PPh_3/L/Ni nanocatalyst (Orange lines: before the addition of catalyst, Green lines: at the end of the reaction).

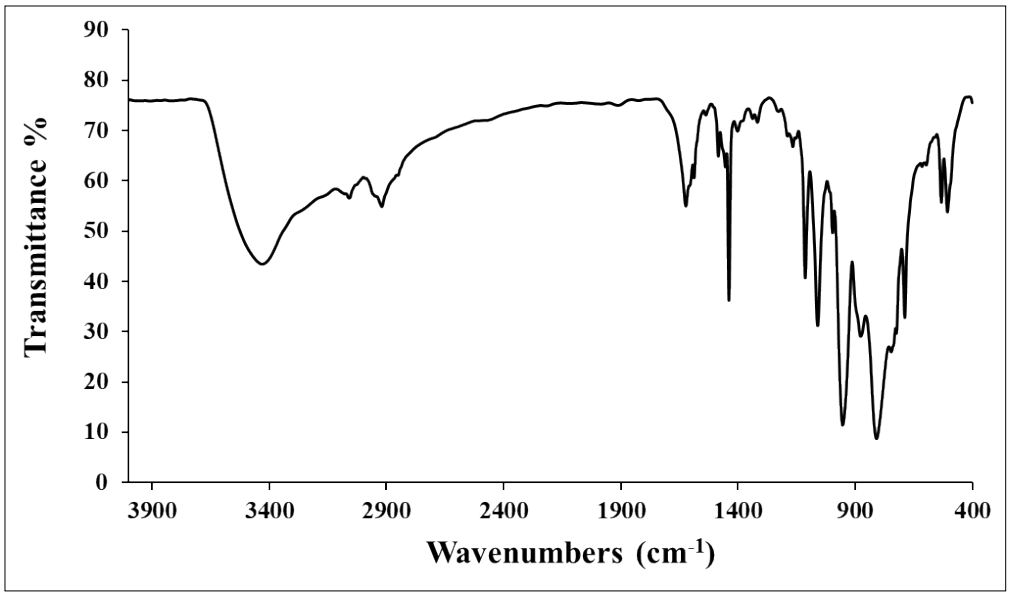

Figure S8. FT-IR spectrum of POM-PPPh$_3$/L/Ni nanocatalyst after the recyclability test.

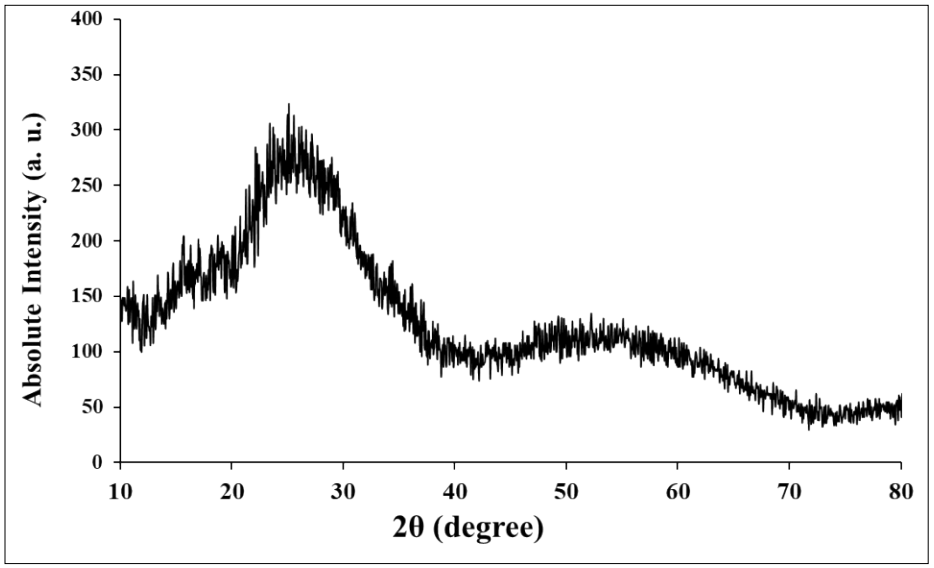

Figure S9. XRD pattern of POM-PPPh$_3$/L/Ni nanocatalyst after the recyclability test.

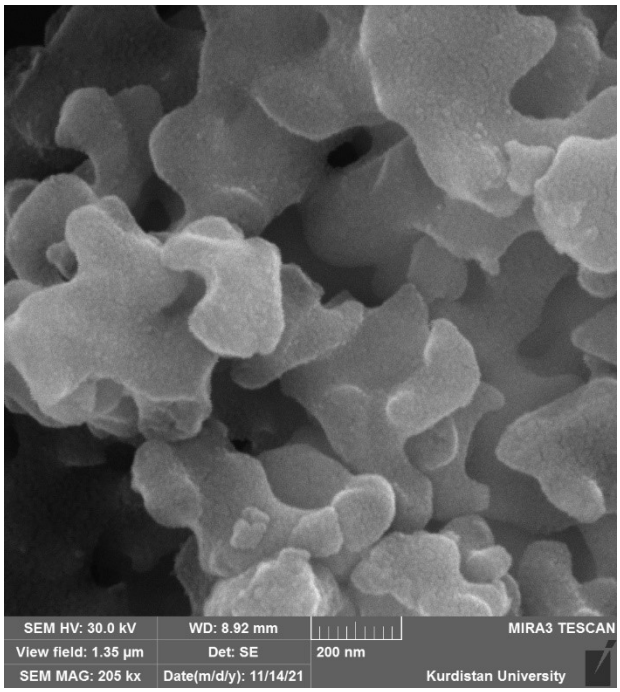

Figure S10. FESEM image of POM-PPPh$_3$/L/Ni nanocatalyst after the recyclability test.

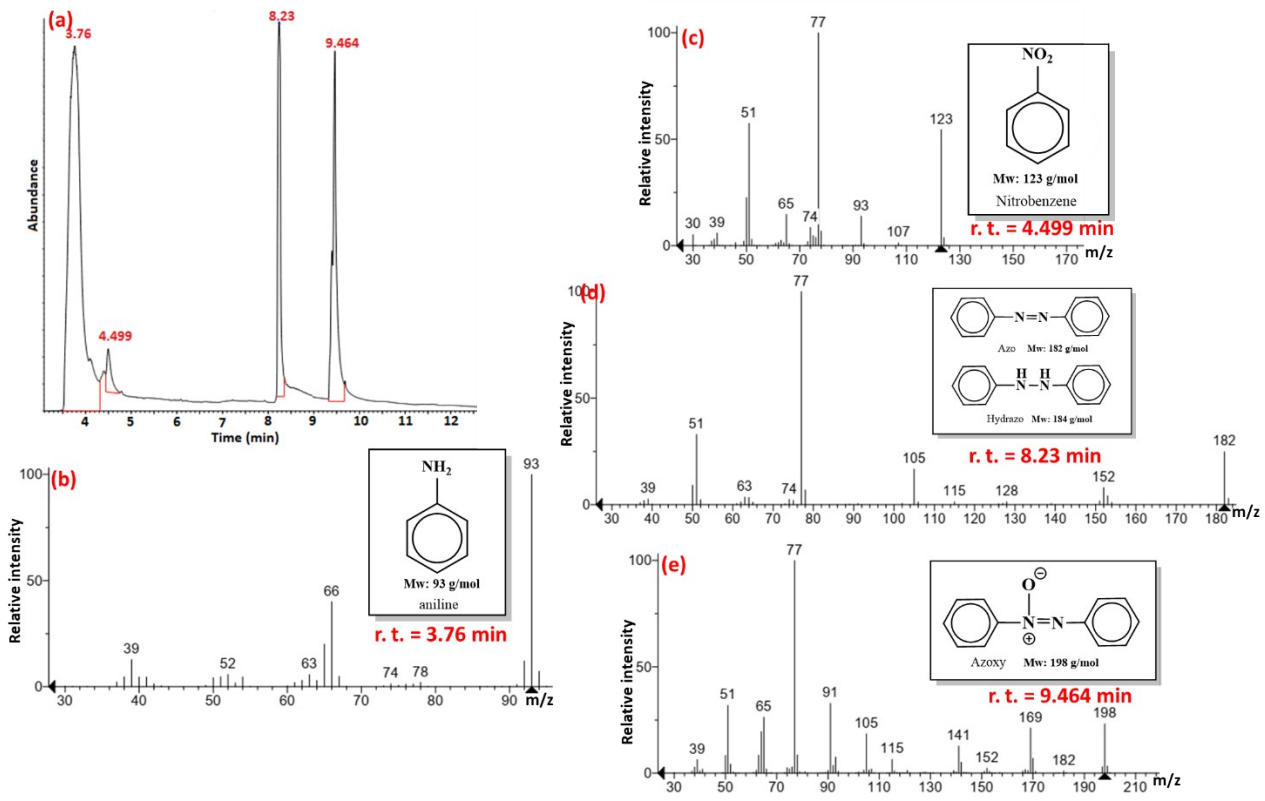

Figure S11. (a) GC and (b), (c), (d), and (e) the mass spectra of the products of NB reduction after 5 min in the presence of POM-$PPPh_3$/L/Ni nanocatalyst.

Table S1. FT-IR data of the POM, POM-$PPPh_3$, POM-$PPPh_3$/L, and POM-$PPPh_3$/L/Ni.

Compounds	**Bonds**	**Frequency (cm^{-1})**
POM	$M\text{-}O_{b/c}\text{-}M_{as}$	780
	$M\text{-}O_{b/c}\text{-}M_{as}$	870
	$M{=}O_{stret}$	960
	$P\text{-}O_{stret}$	1065
POM-$PPPh_3$	$M\text{-}O_{b/c}\text{-}M_{as}$	787
	$M\text{-}O_{b/c}\text{-}M_{as}$	875

	$M=O_{stret}$	957
	$P-O_{stret}$	1070
	$C-H_{OOP}$	650-1000
	$P-CH_2$	1438
	C=C	1400-1600
	$C-H_{aliphatic}$	2895
	$C-H_{aromatic}$	3050
POM-PPPh$_3$/L	$M-O_{b/c}-M_{as}$	778
	$M-O_{b/c}-M_{as}$	875
	$M=O_{stret}$	950
	$P-O_{stret}$	1080
	$C-H_{OOP}$	650-1000
	$P-CH_2$	1440
	C=C	1400-1600
	C=N	1629
	$C-H_{aliphatic}$	2902
	$C-H_{aromatic}$	3050
POM-PPPh$_3$/L/Ni	$M-O_{b/c}-M_{as}$	780
	$M-O_{b/c}-M_{as}$	880
	$M=O_{stret}$	950
	$P-O_{stret}$	1073
	$C-H_{OOP}$	650-1000
	$P-CH_2$	1440

C=C	1400-1600
C=N	1621
C-H $_{aliphatic}$	2898
C-H $_{aromatic}$	3046

Table S2. XPS data of the Mo 3d at POM-PPPh$_3$/L/Ni nanocatalyst.

Elements	**Binding Energy (eV)**
Mo $3d_{5/2}$	232.4, 232.6
Mo $3d_{3/2}$	235.6, 235.8