Indium-based metal-organic frameworks as catalysts: Synthesis of 2-nitro-3-arylimidazo[1,2-a]pyridines via oxidative amination under air using MIL-68(In) as an effective heterogeneous catalyst

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Supporting Information

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 ^{o}C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 ^{o}C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400

Transmission Electron Microscope (TEM) at 100 kV. The MIL-68(In) sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 ^{o}C for 1 min; heated them from 100 to 280 ^{o}C at 40 ^{o}C/min; and held them at 280 ^{o}C for 1.5 min. Inlet and detector temperatures were set constant at 280 ^{o}C. 4-Bromoanisole was used as an internal standard to calculate GC yield. GC-MS analyses were performed using a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 50 ^{o}C for 2 min; heated samples from 50 to 280^{o}C at 10 ^{o}C/min and held them at 280 ^{o}C for 10 min. Inlet temperature was set constant at 280 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library. The ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

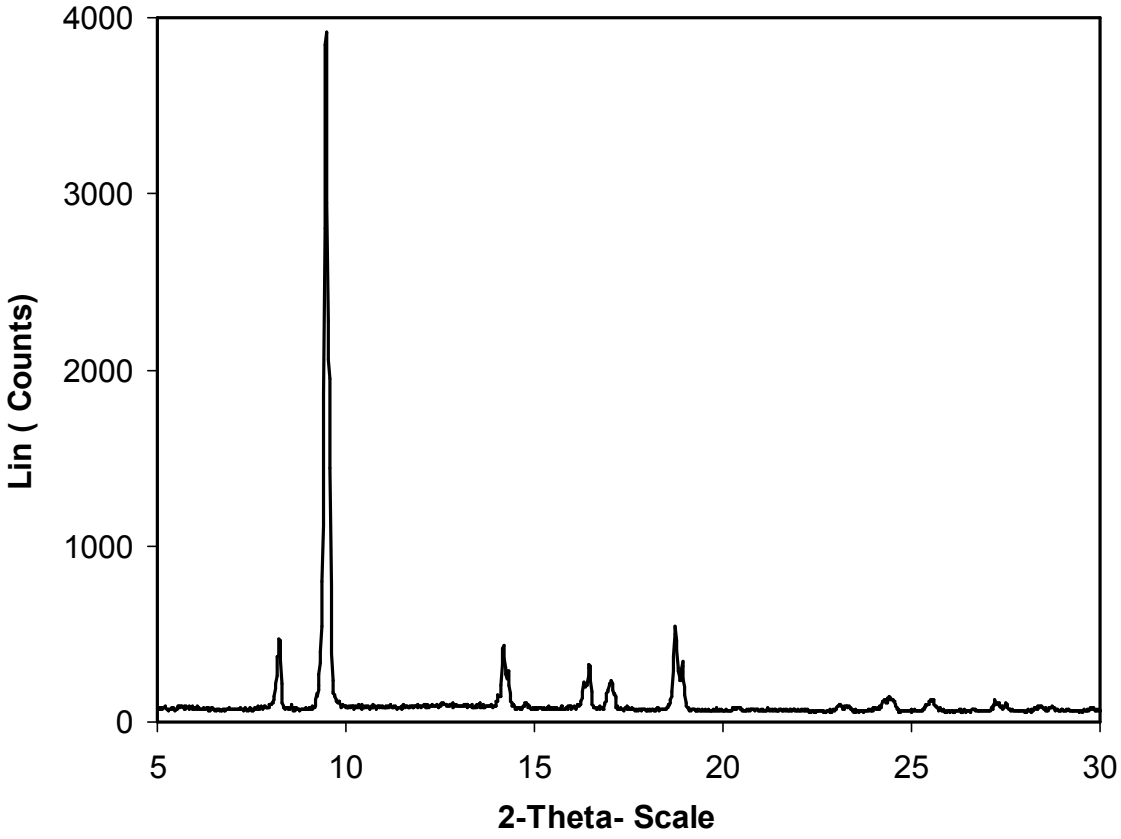

Fig. S1. X-ray powder diffractograms of the MIL-68(In).

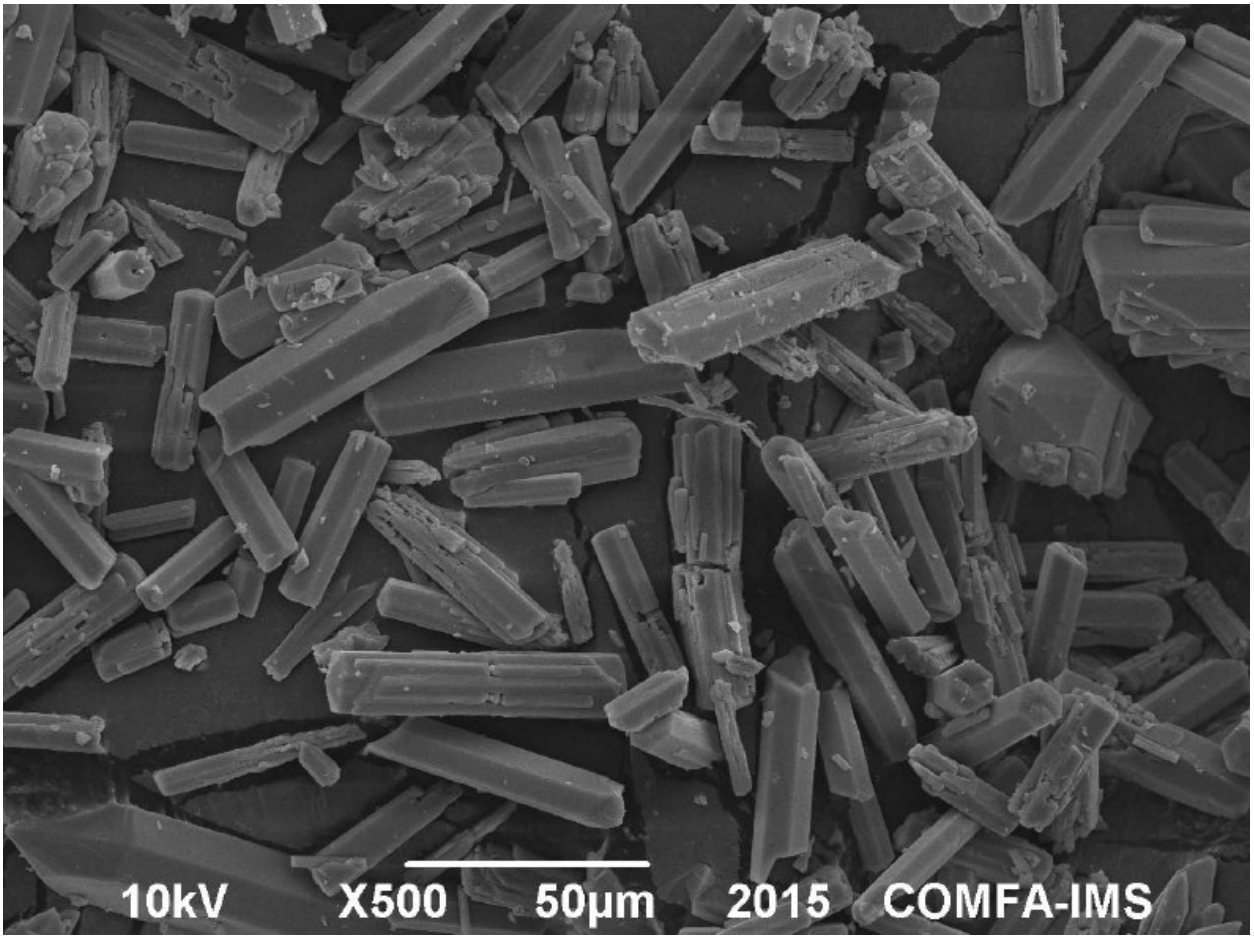

Fig. S2. SEM micrograph of the MIL-68(In).

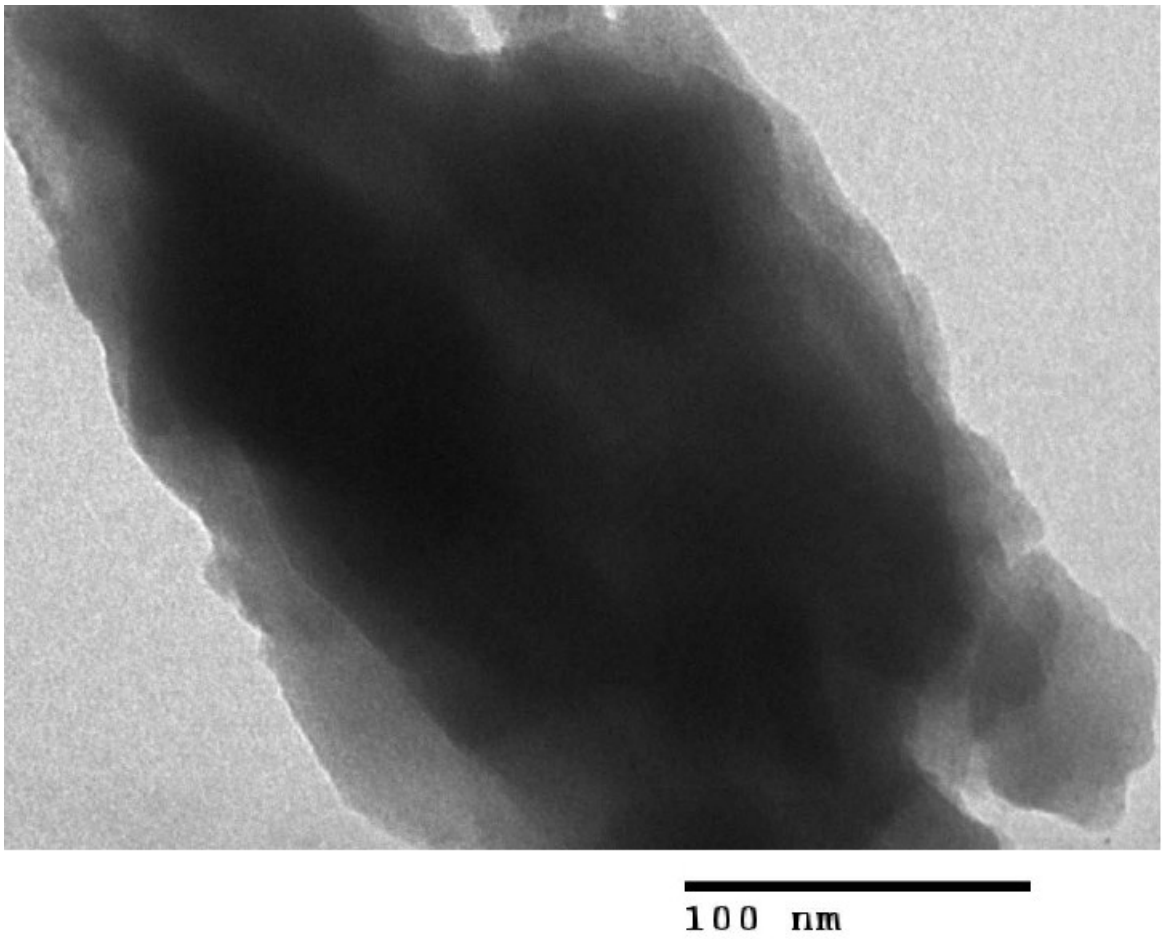

Fig. S3. TEM micrograph of the MIL-68(In).

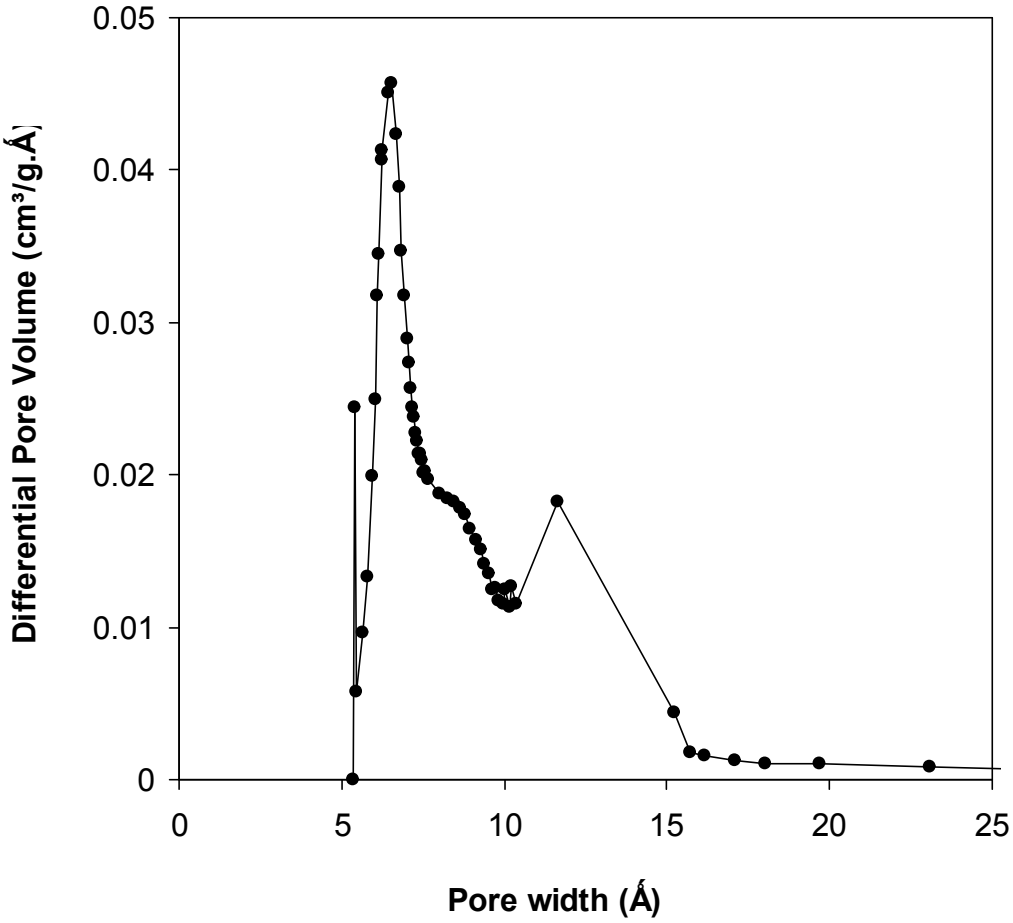

Fig. S4. Pore size distribution of the MIL-68(In).

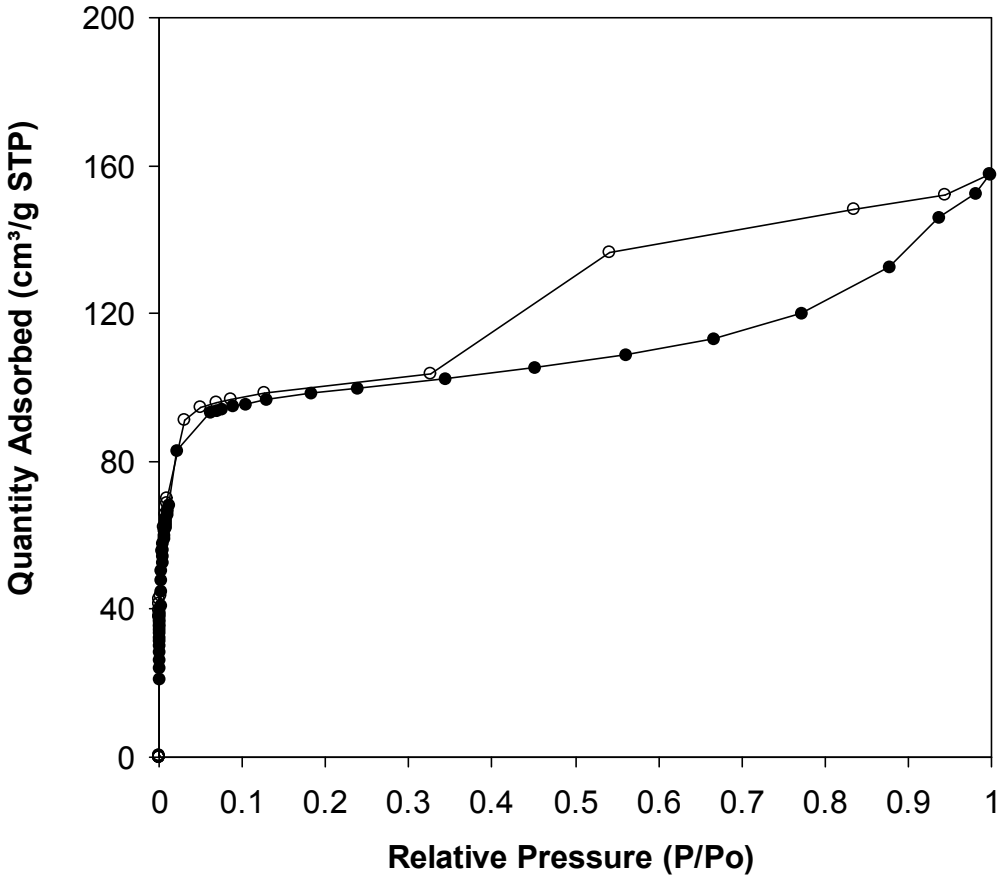

Fig. S5. Nitrogen adsorption/desorption isotherm of the MIL-68(In). Adsorption data are shown as closed circles and desorption data as open circles.

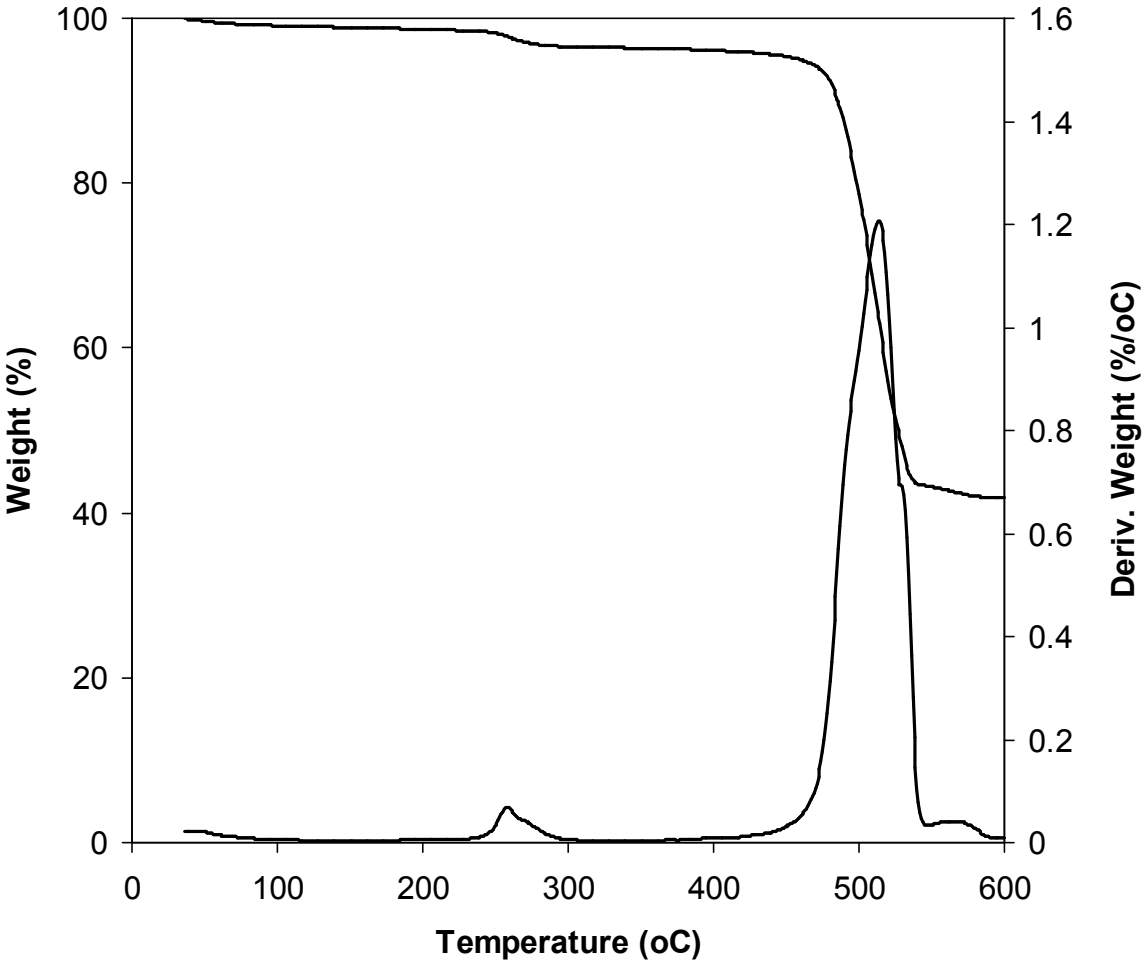

Fig. S6. TGA analysis of the MIL-68(In).

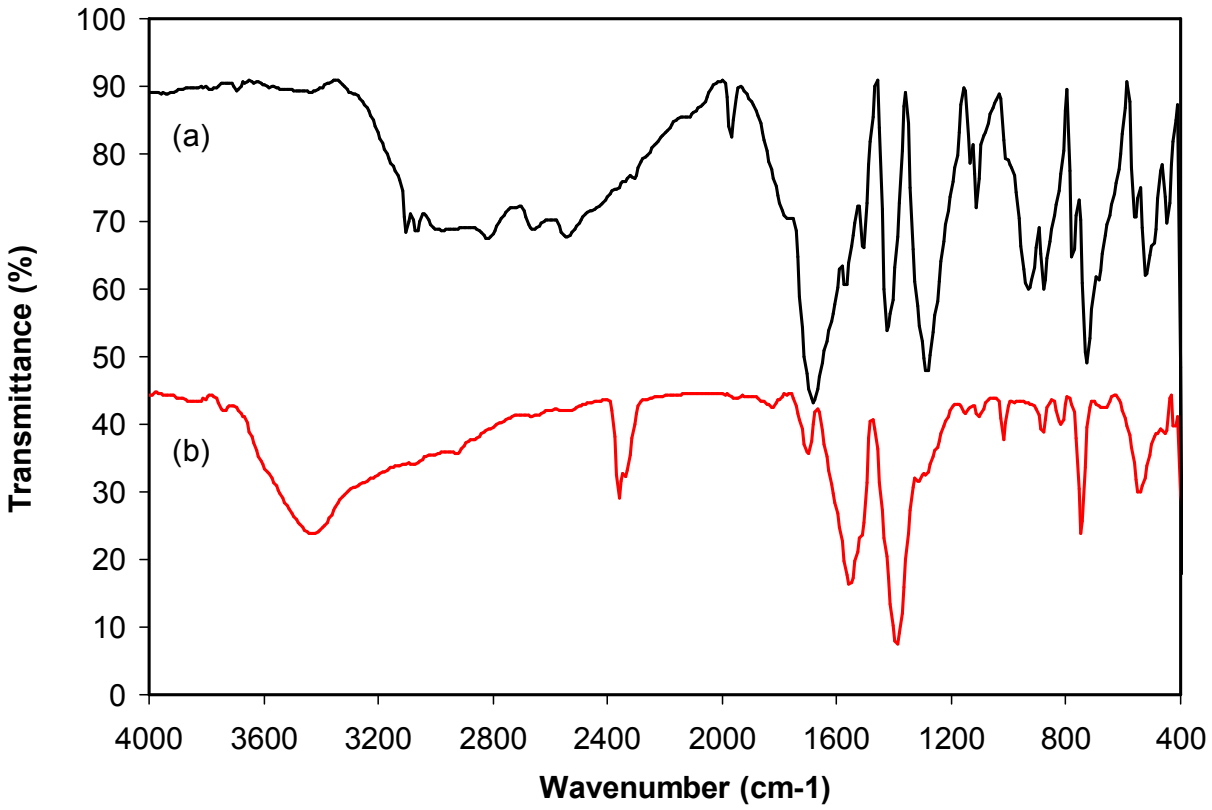

Fig. S7. FT-IR spectra of terephthalic acid (a), and the MIL-68(In) (b).

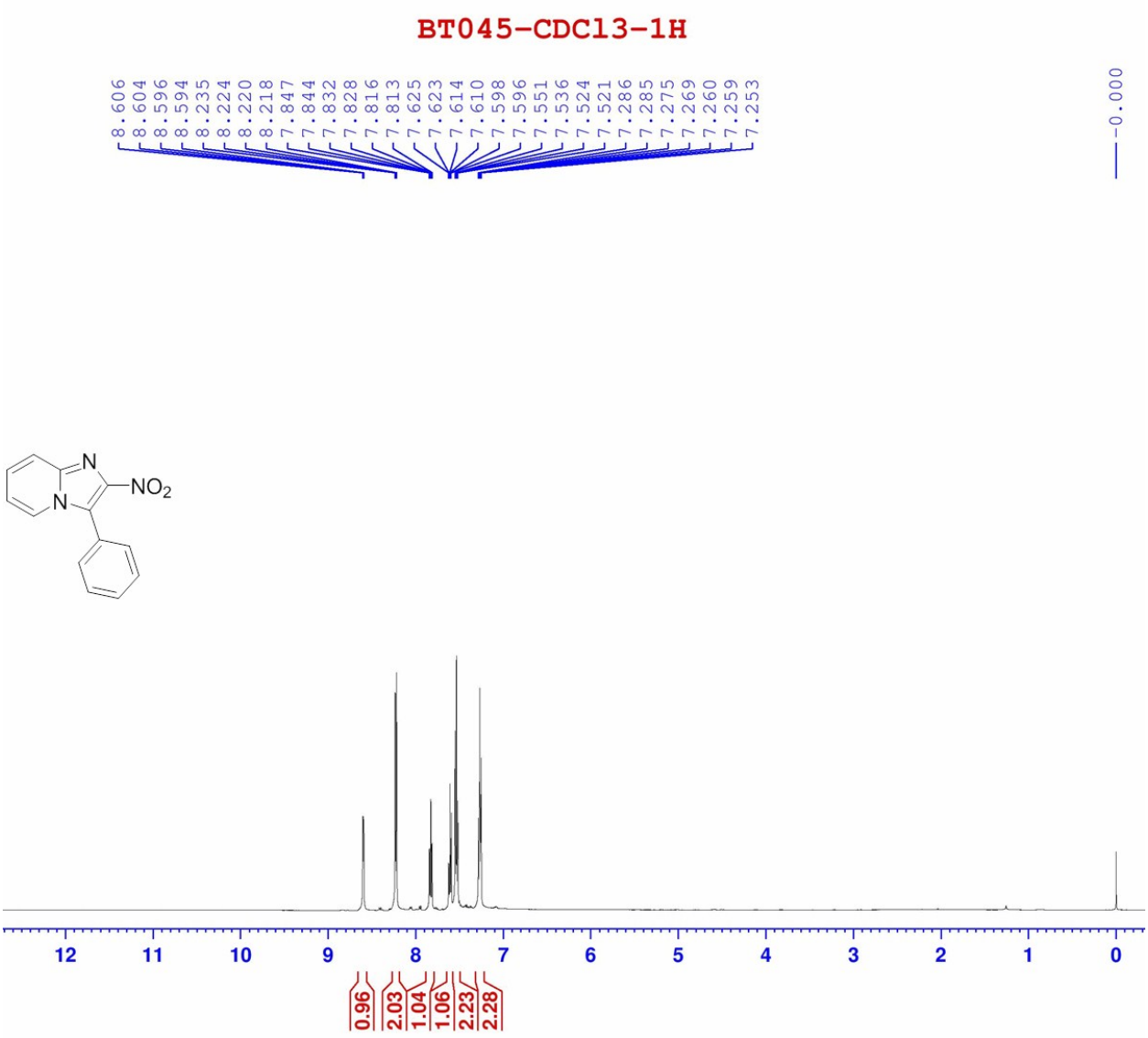

Fig.S8. ^{1}H-NMR spectra of 2-nitro-3-phenylimidazo[1,2-a]pyridine

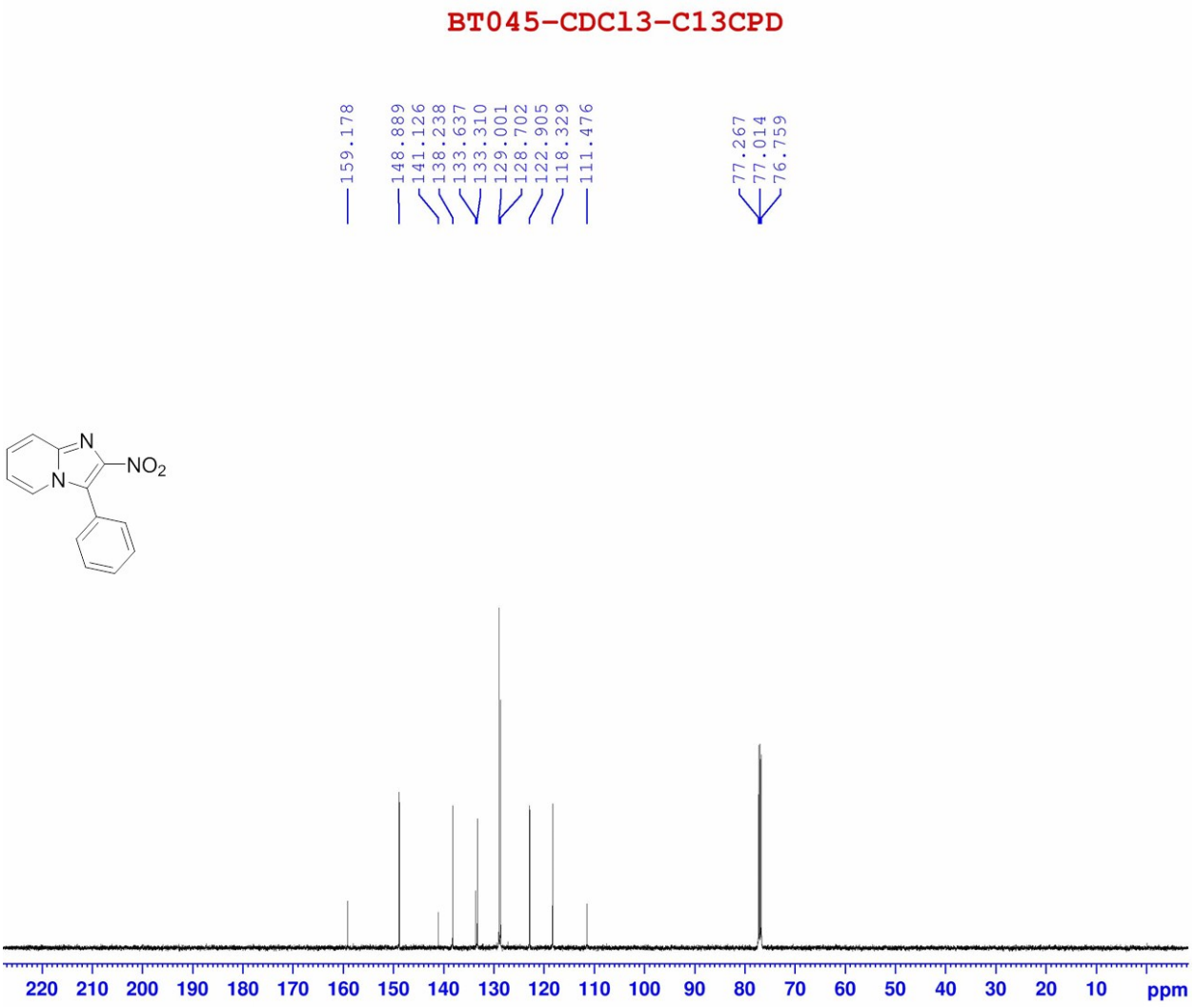

Fig.S9. ^{13}C-NMR spectra of 2-nitro-3-phenylimidazo[1,2-a]pyridine

Characterization data for 2-nitro-3-phenylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 77% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 7.253-7.286 (m, 2H), 7.521-7.551 (m, 2H), 7.596-7.625 (m, 1H), 7.813-7.847 (m ,1H), 8.218-8.235 (m, 2H), 8.594-8.606 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 111.476, 118.329, 122.905, 128.702, 129.001, 133.310, 133.637, 138.238, 141.126, 148.889, 159.178.

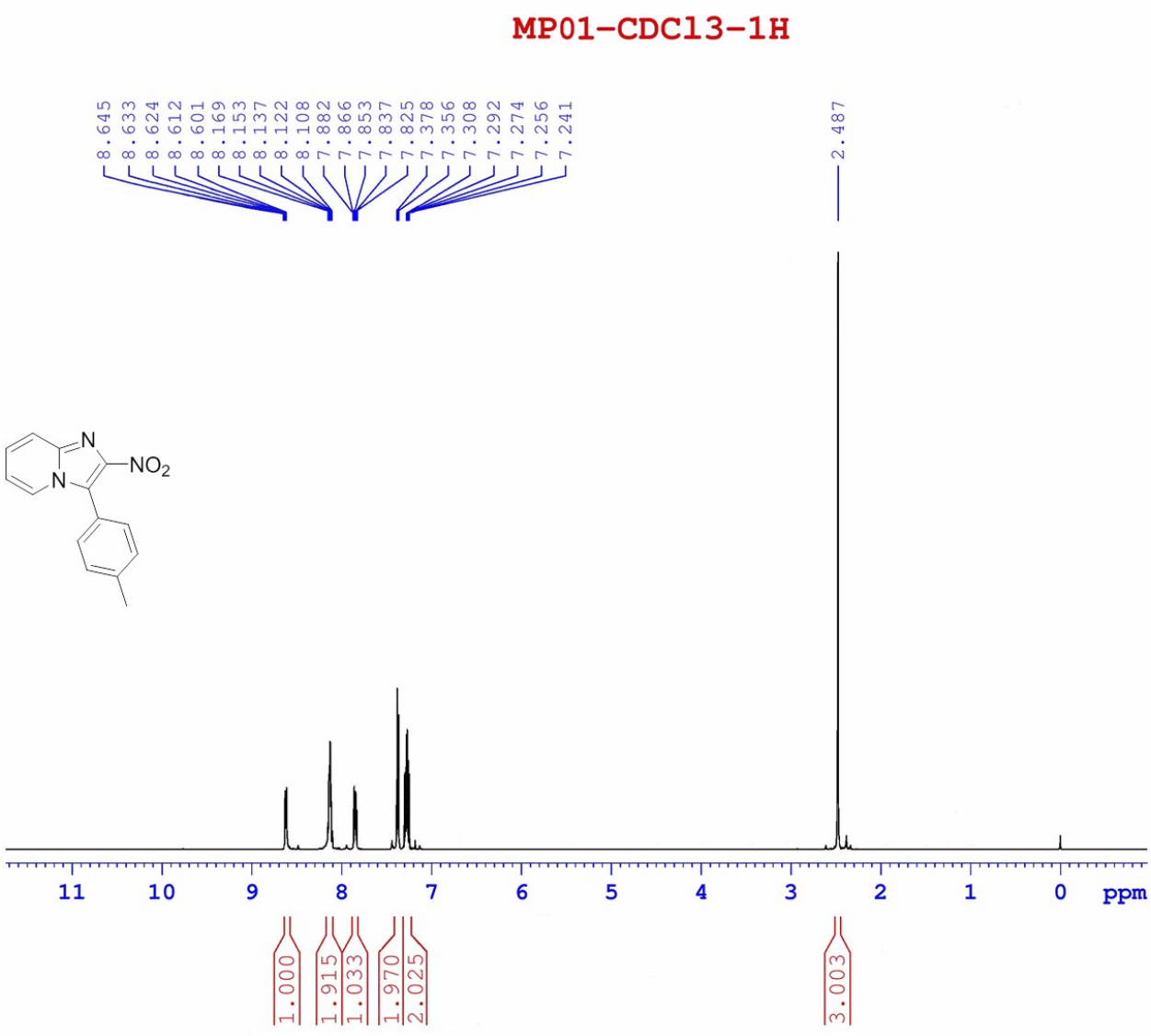

Fig.S10. ^{1}H-NMR spectra of 2-nitro-3-p-tolylimidazo[1,2-a]pyridine

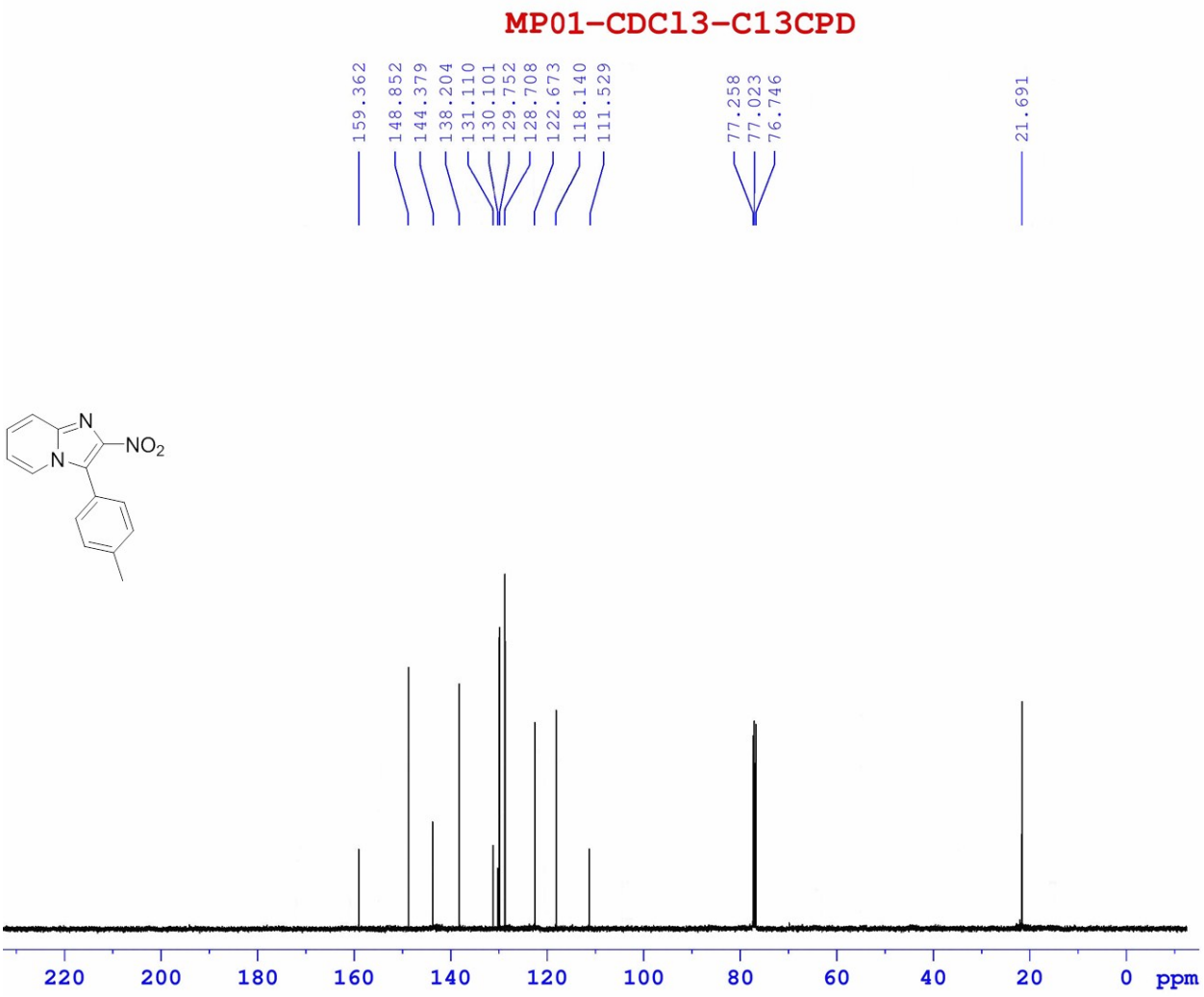

Fig.S11. ^{13}C-NMR spectra of 2-nitro-3-p-tolylimidazo[1,2-a]pyridine

Characterization data for 2-nitro-3-p-tolylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 74% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.487 (s, 3H), 7.241-7.308 (m, 2H), 7.356 (d, 2H), 7.825-7.882 (m ,1H), 8.108-8.169 (m, 2H), 8.601-8.645 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.691, 111.529, 118.140, 122.673, 128.708, 129.752, 130.101, 131.110, 138.204, 144.379, 148.852, 159.362.

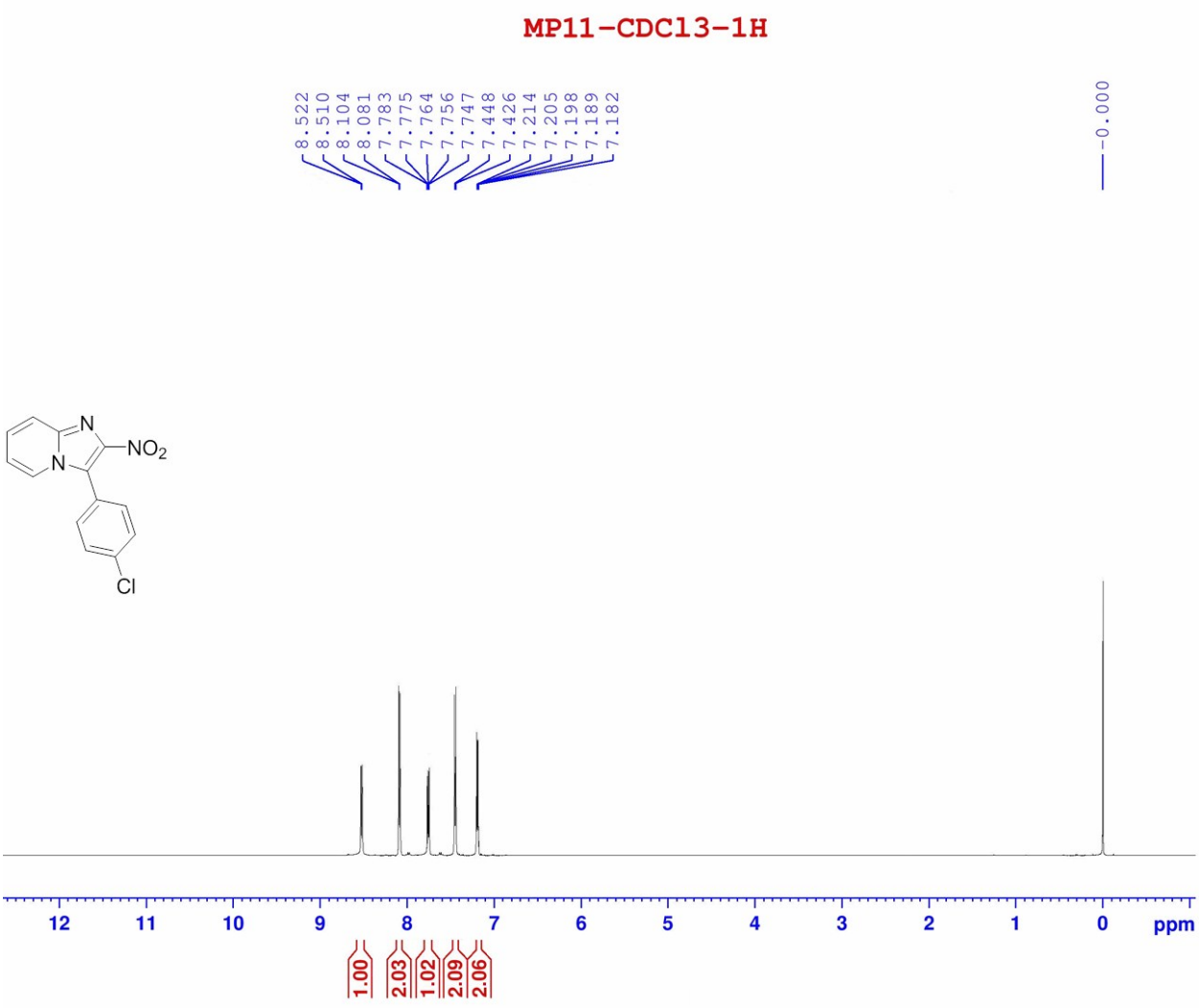

Fig.S12. [1]H-NMR spectra of 3-(4-chlorophenyl)-2-nitroimidazo[1,2-a]pyridine

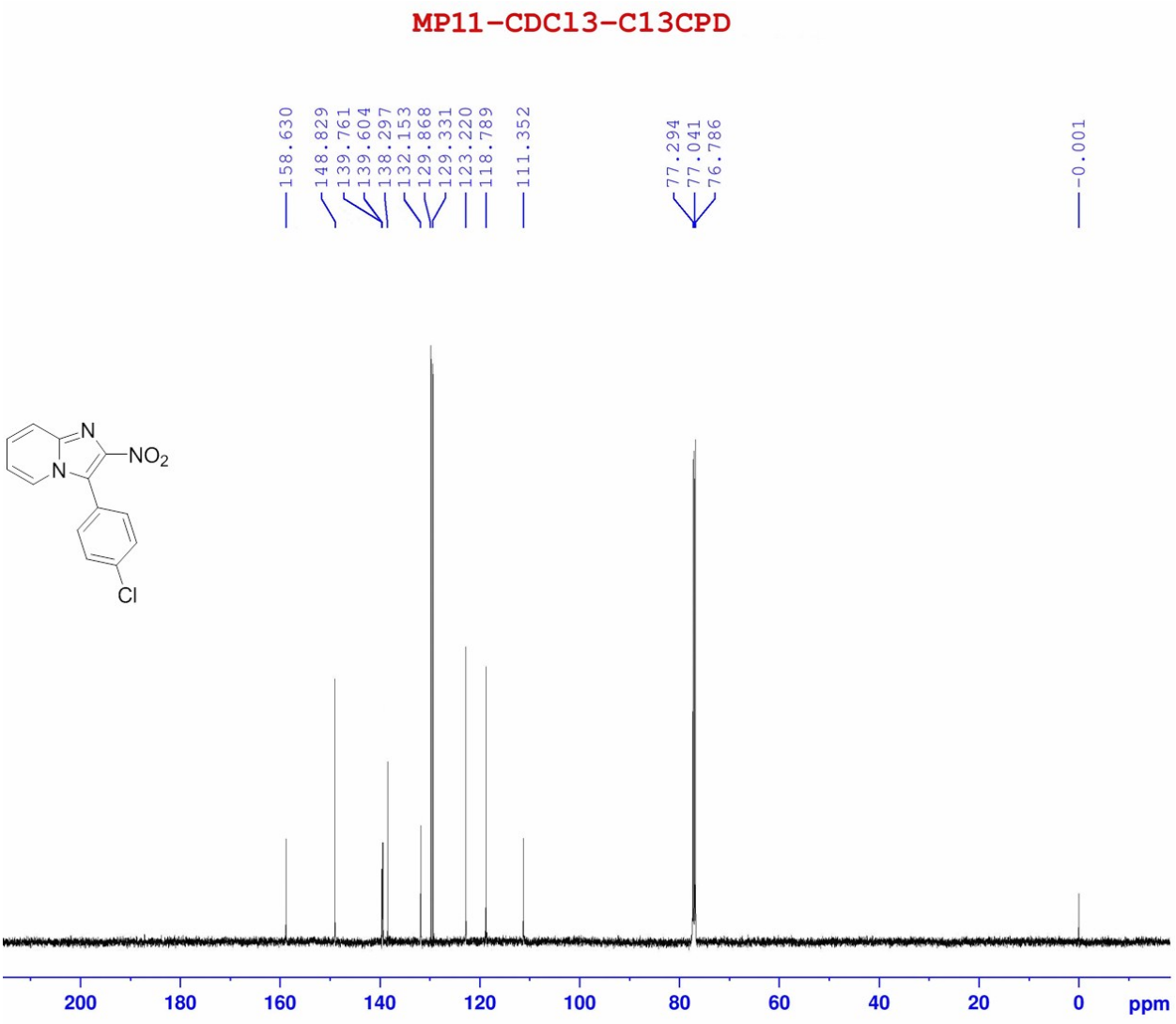

Fig.S13. ^{13}C-NMR spectra of 3-(4-chlorophenyl)-2-nitroimidazo[1,2-a]pyridine

Characterization data for 3-(4-chlorophenyl)-2-nitroimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 72% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 7.182-7.214 (m, 2H), 7.426 (d, 2H), 7.747-7.783 (m, 1H), 8.081 (d, 2H), 8.510 (d, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 111.352, 118.789, 123.220, 129.331, 129.868, 132.153, 138.297, 139.604, 139.761, 148.829, 158.630.

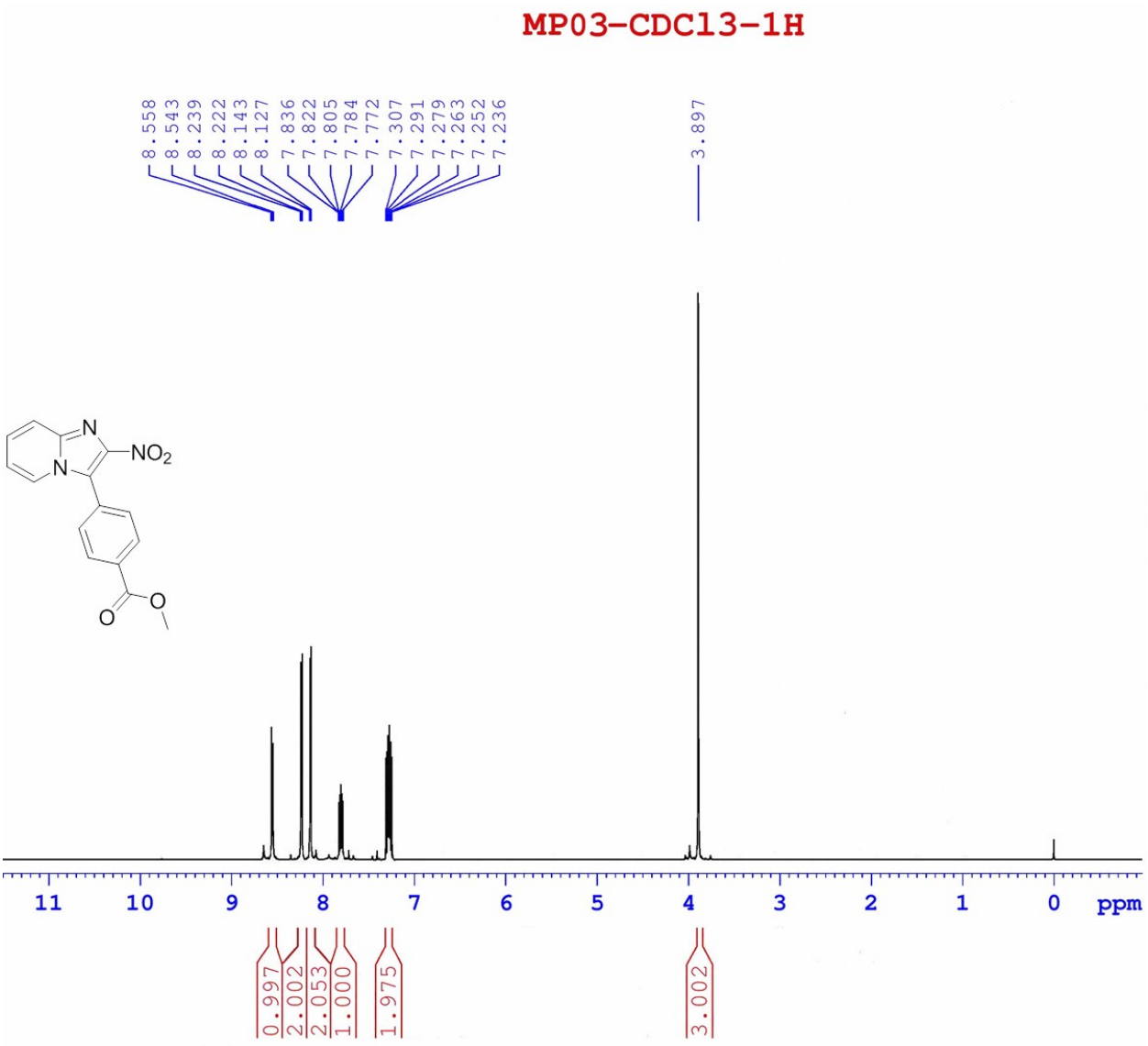

Fig.S14. ^{1}H-NMR spectra of methyl 4-(2-nitroimidazo[1,2-a]pyridin-3-yl)benzoate

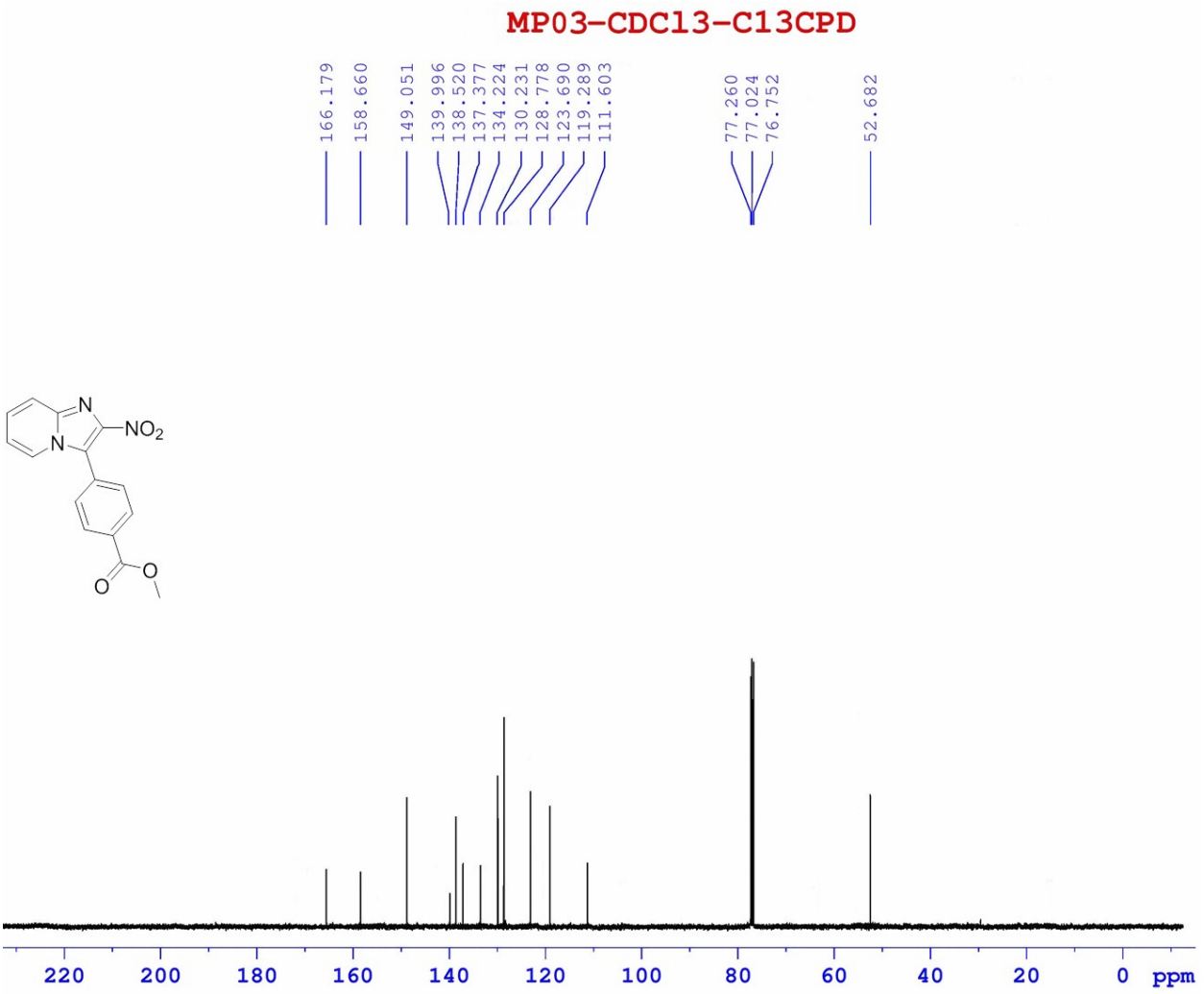

Fig.S15. ^{13}C-NMR spectra of methyl 4-(2-nitroimidazo[1,2-a]pyridin-3-yl)benzoate

Characterization data for methyl 4-(2-nitroimidazo[1,2-a]pyridin-3-yl)benzoate

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 75% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 3.897 (s, 3H), 7.236-7.307 (m, 2H), 7.772-7.836 (m, 1H), 8.127 (d, 2H), 8.222 (d ,2H), 8.543 (d, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 52.682, 111.603, 119.289, 123.690, 128.778, 130.231, 134.224, 137.377, 138.520, 139.996, 149.051, 158.660, 166.179.

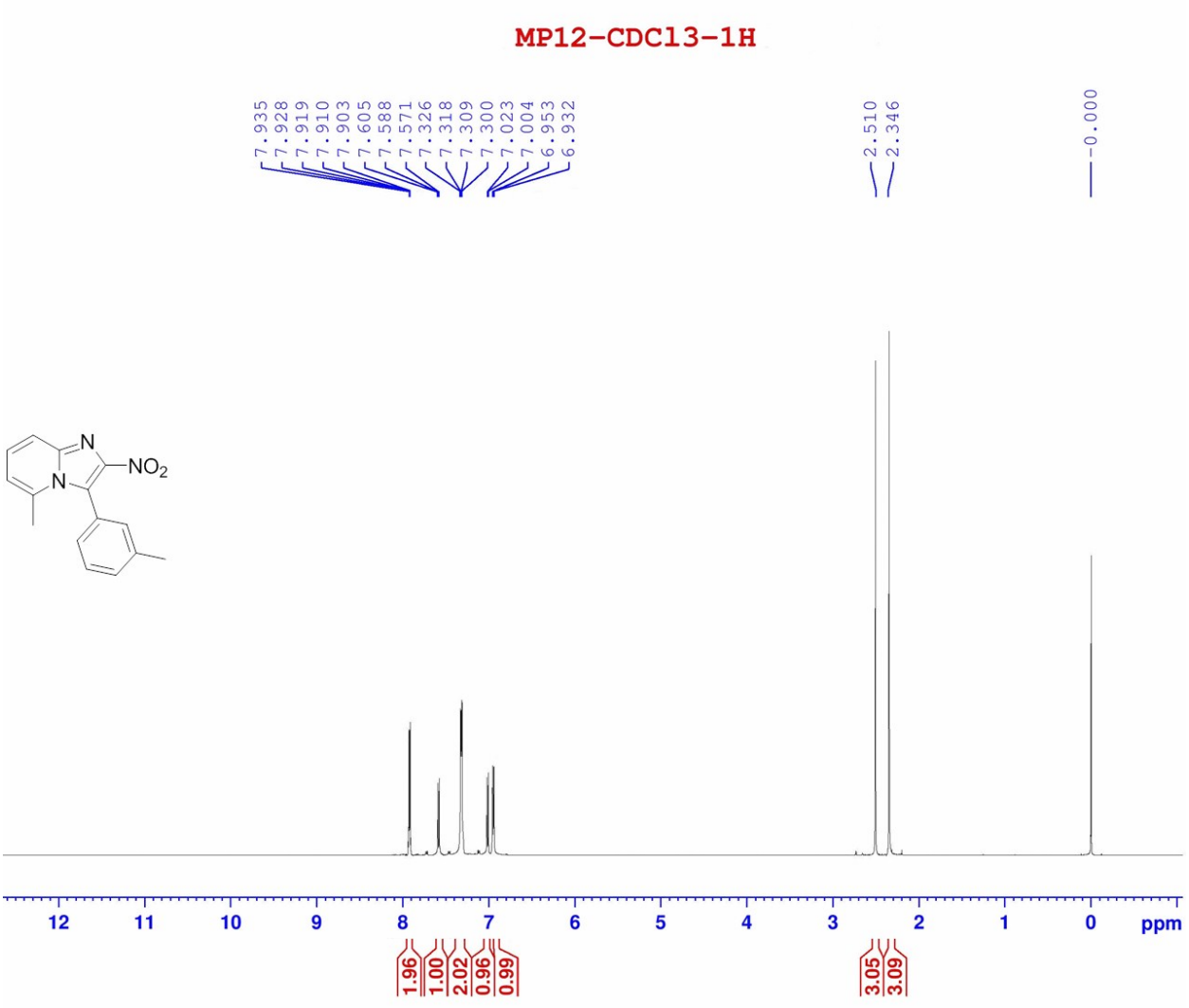

Fig.S16. ^{1}H-NMR spectra of 5-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

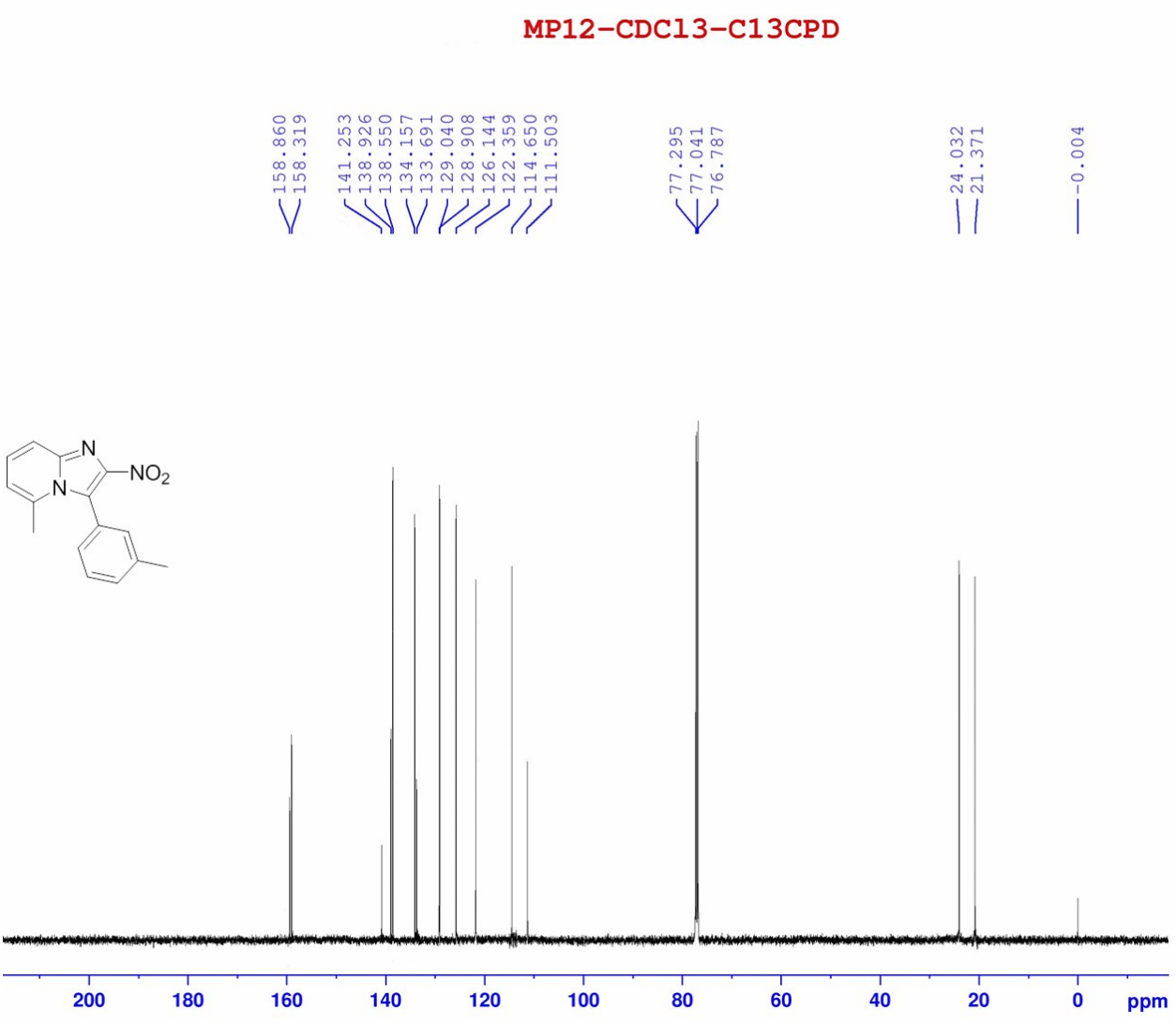

Fig.S17. ^{13}C-NMR spectra of 5-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

Characterization data for 5-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 76% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.346 (s, 3H), 2.510 (s, 3H), 6.932 (d, 1H), 7.004 (d ,1H), 7.300-7.326 (m, 2H), 7.571 (t, 1H), 7.903-7.935 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.371, 24.032, 111.503, 114.650, 122.359, 126.144, 128.908, 129.040, 133.691, 134.157, 138.550, 138.926, 141.253, 158.319, 158.860.

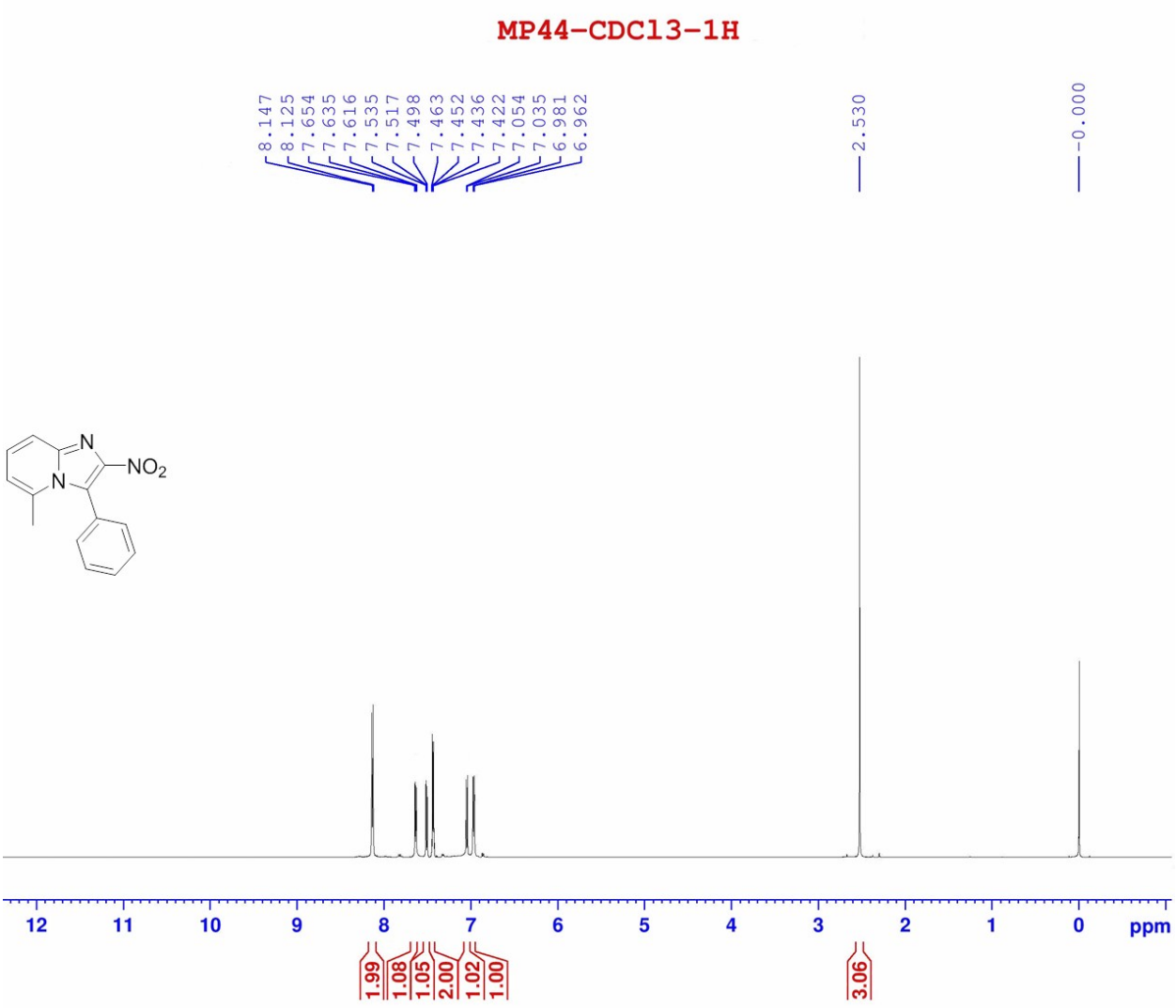

Fig.S18. ^{1}H-NMR spectra of 5-methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

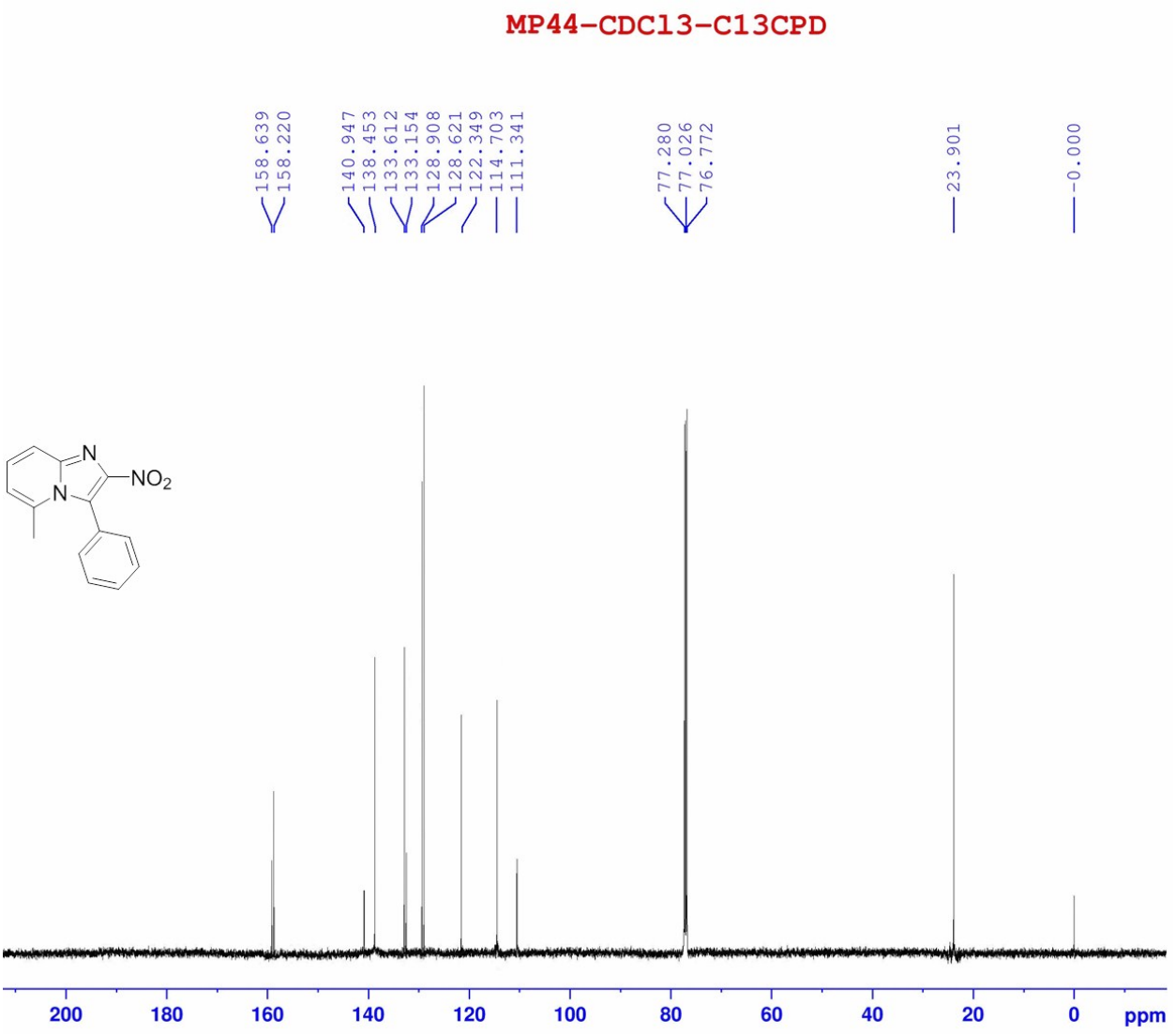

Fig.S19. ^{13}C-NMR spectra of 5-methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

Characterization data for 5-methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 70% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.530 (s, 3H), 6.962 (d, 1H), 7.035 (d, 1H), 7.422-7.463 (m, 2H), 7.498-7.535 (m, 1H), 7.616-7.654 (m, 1H), 8.125 (d, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 23.901, 111.341, 114.703, 122.349, 128.621, 128.908, 133.154, 133.612, 138.453, 140.947, 158.220, 158.639.

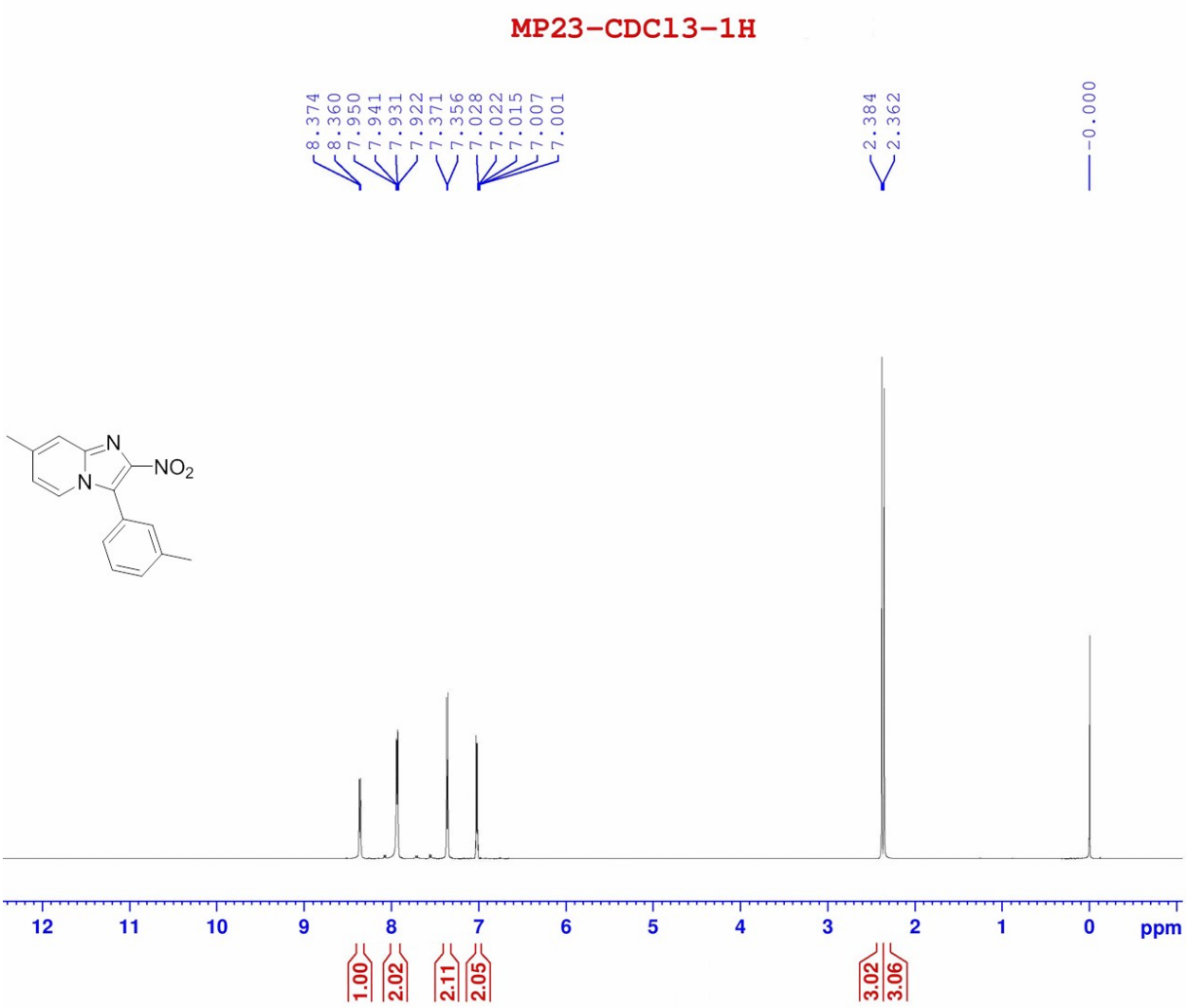

Fig.S20. ^{1}H-NMR spectra of 7-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

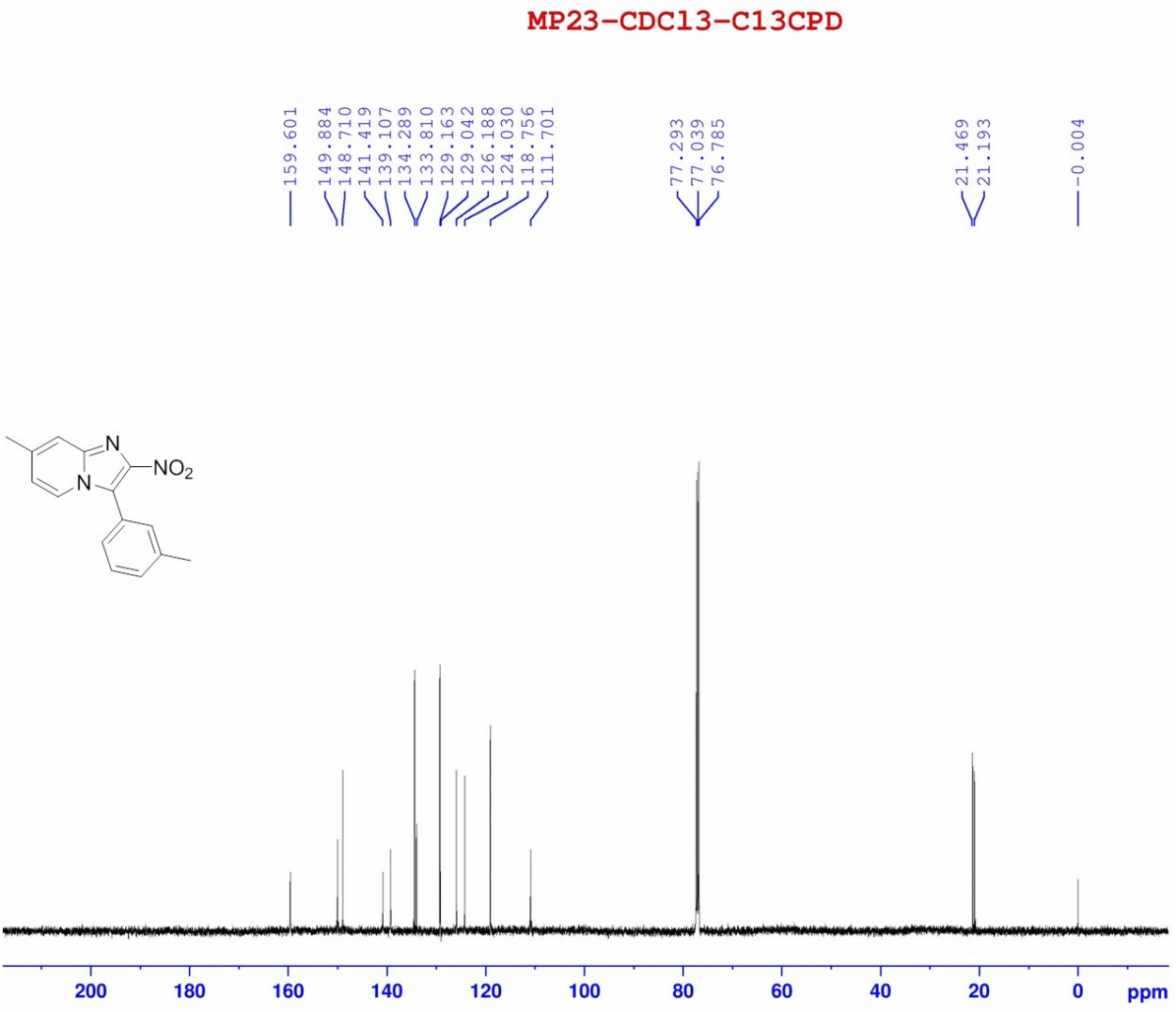

Fig.S21. ^{13}C-NMR spectra of 7-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

Characterization data for 7-methyl-2-nitro-3-m-tolylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 73% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.362 (s, 3H), 2.384 (s, 3H), 7.001-7.028 (m, 2H), 7.356 (d, 2H), 7.922-7.950 (m, 2H), 8.360 (d ,1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.193, 21.469, 111.701, 118.756, 124.030, 126.188, 129.042, 129.163, 133.810, 134.289, 139.107, 141.419, 148.710, 149.884, 159.601.

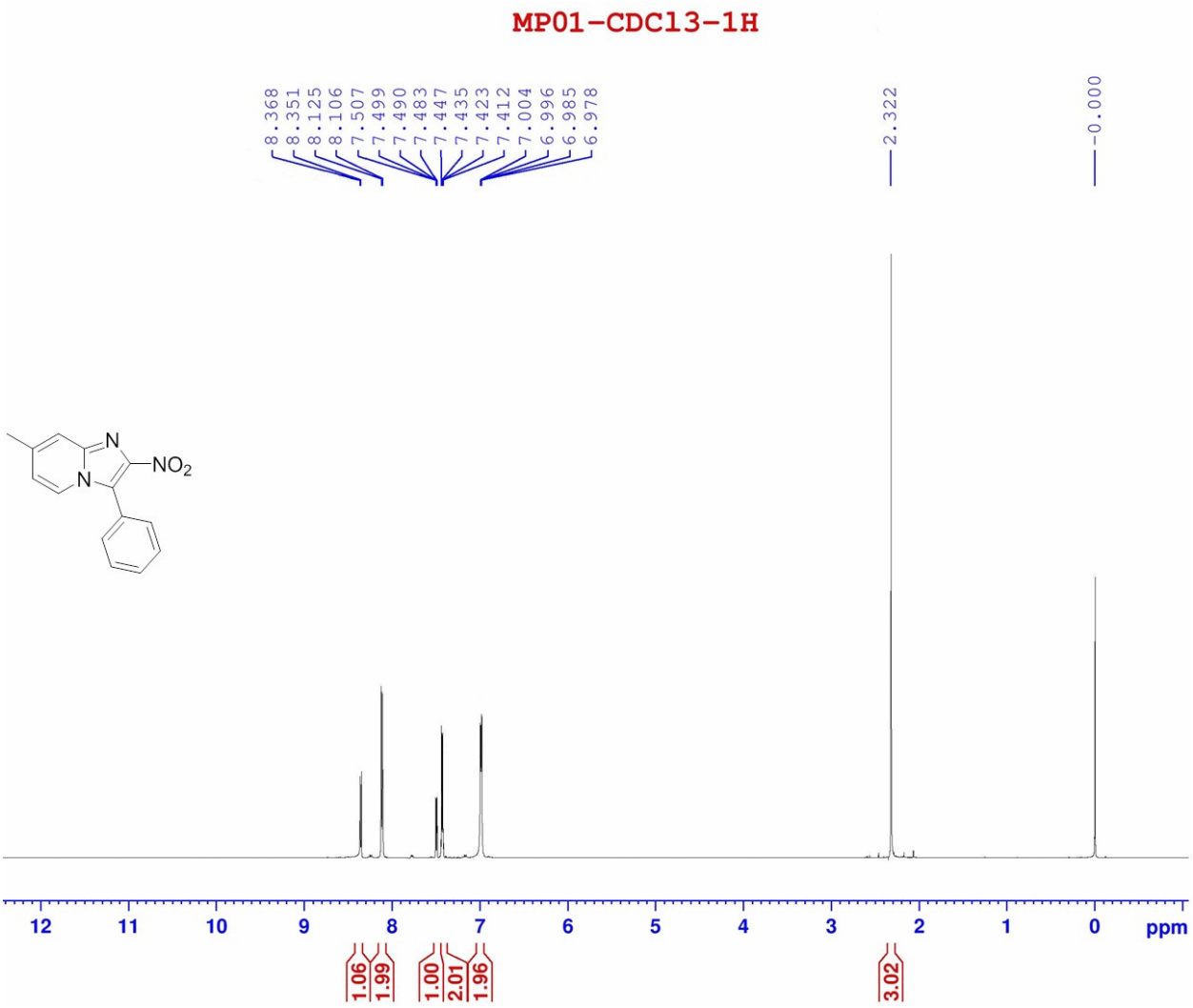

Fig.S22. [1]H-NMR spectra of 7-methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

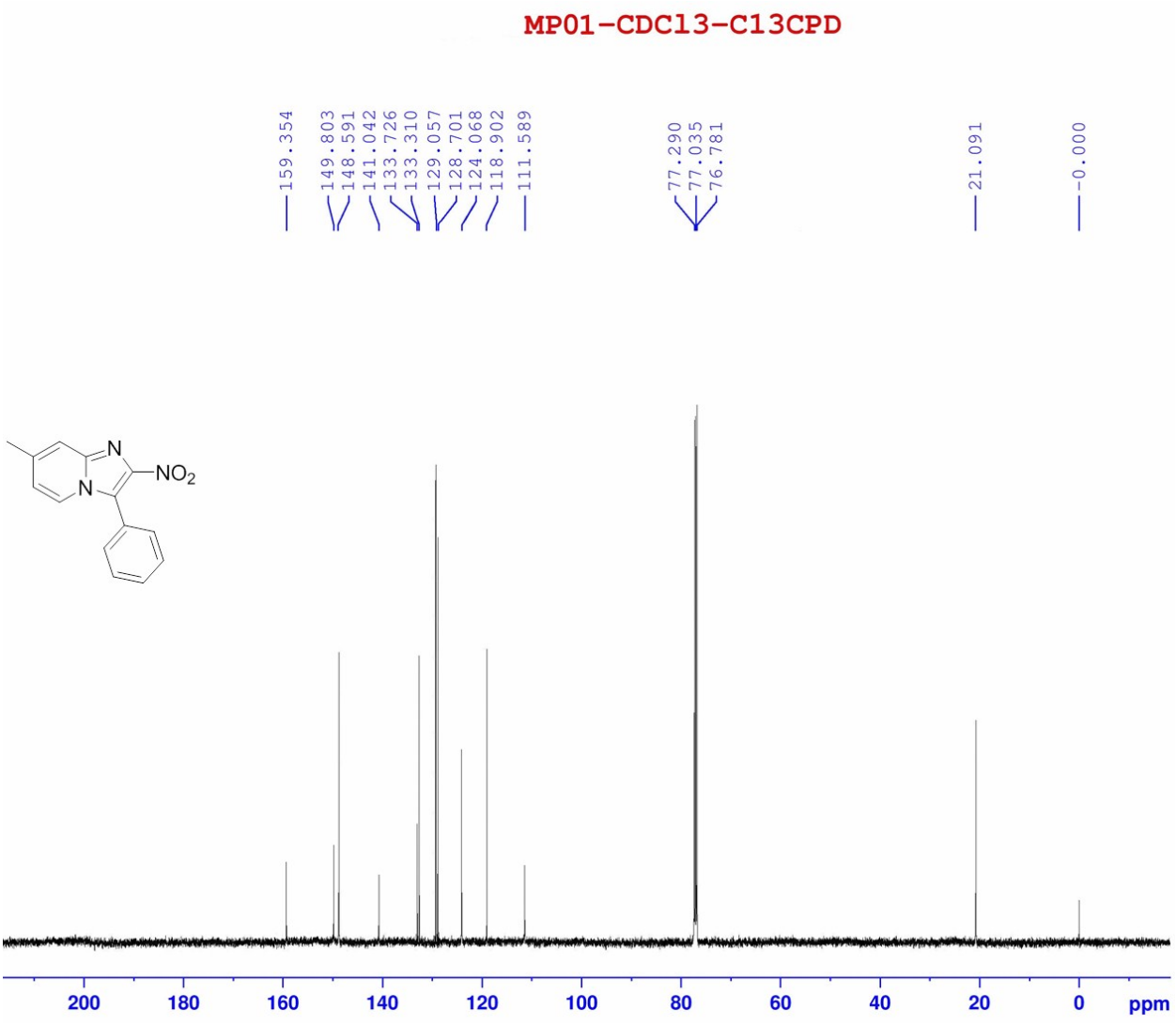

Fig.S23. ^{13}C-NMR spectra of 7-Methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

Characterization data for 7-methyl-2-nitro-3-phenylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 74% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.322 (s, 3H), 6.978-7.004 (m, 2H), 7.412-7.447 (m, 2H), 7.483-7.507 (m, 1H), 8.106 (d, 2H), 8.351 (d ,1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.091, 111.589, 118.902, 124.068, 128.701, 129.057, 133.310, 133.726, 141.042, 148.591, 149.803, 159.354.

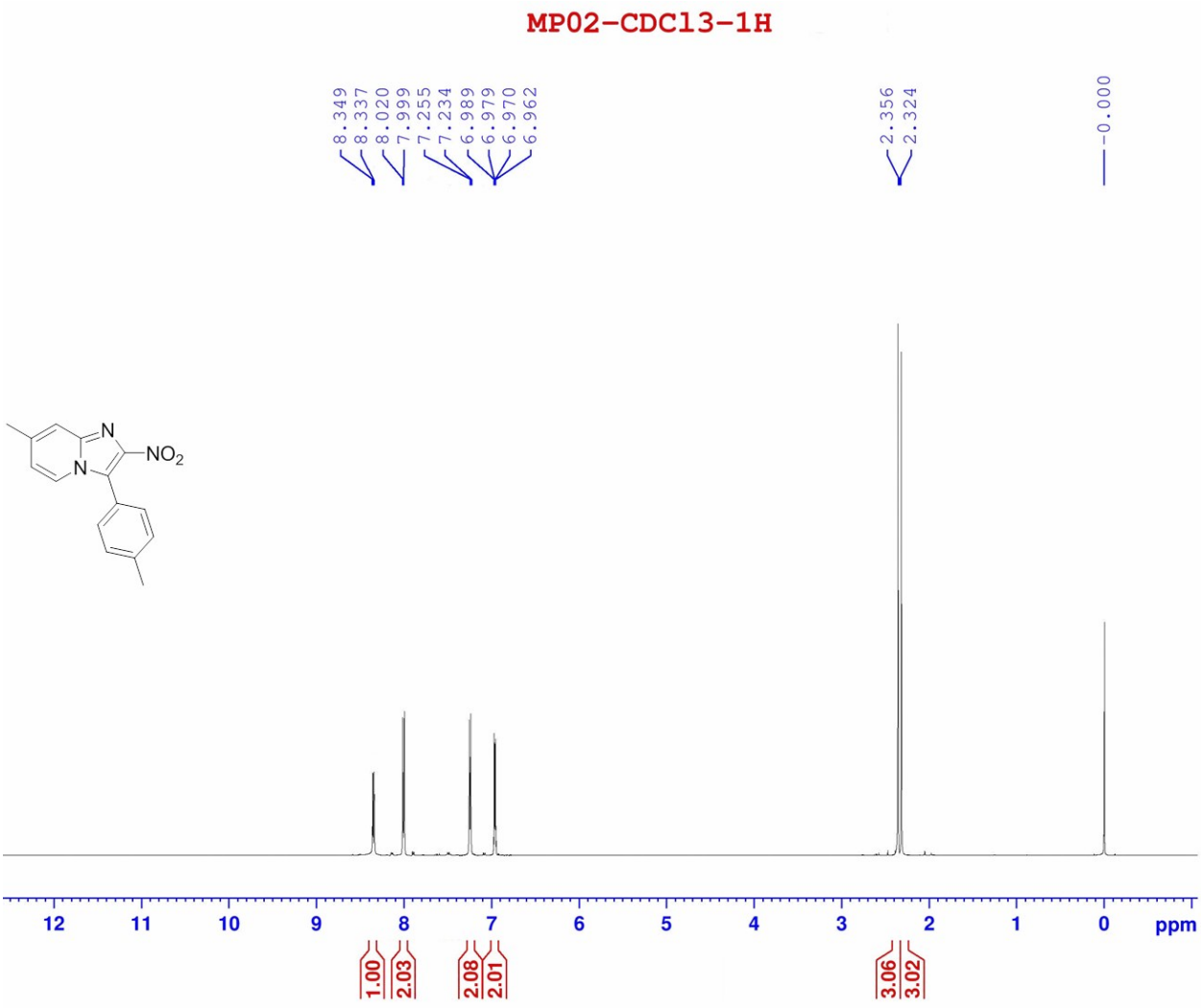

Fig.S24. ^{1}H-NMR spectra of 7-methyl-2-nitro-3-p-tolylimidazo[1,2-a]pyridine

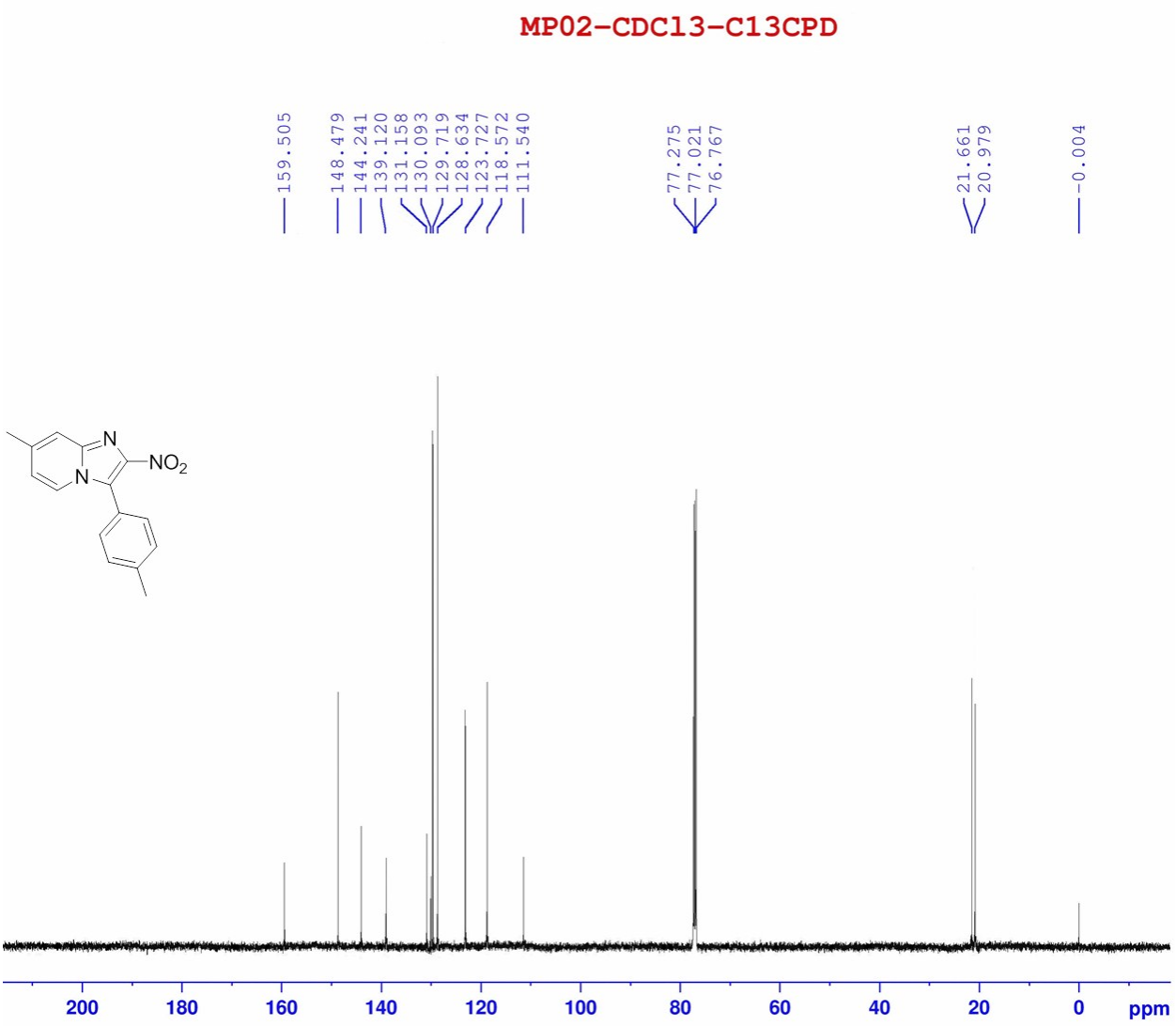

Fig.S25. ^{13}C-NMR spectra of 7-methyl-2-nitro-3-p-tolylimidazo[1,2-a]pyridine

Characterization data for 7-methyl-2-nitro-3-p-tolylimidazo[1,2-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate / hexane): Gummy mass, 69% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) 2.324 (s, 3H), 2.356 (s, 3H), 6.962-6.989 (m, 2H), 7.234 (d, 2H), 7.999 (d, 2H), 8.337 (d, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 20.979, 21.661, 111.540, 118.572, 123.727, 128.634, 129.719, 130.093, 131.158, 139.120, 144.241, 148.479, 159.505.