Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tuning Porosity and Activity of Microporous Polymer Network Organocatalysts by Co-Polymerisation

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Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Chloroform used in reaction was HPLC grade. 1,3,5-tris(2-thienyl)benzene was purchased from Sigma-Aldrich and *(R)*-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phosphoric acid was synthesised according to the literature.[1]

Inert reactions were carried out using standard schlenk technique or in an *MBraun* glove box type MB 120 BG. Analytical thin-layer chromatography (TLC) was performed on *Merck* or *Macherey-Nagel* silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel *Merck 60* (particle size 0.03-0.06 mm). Solvent mixtures are understood as volume/volume. 1H-NMR, 13C-NMR were recorded on a *Bruker* DRX 400 or DRX 500 spectrometer in the given solvent. Data are reported in the following order: chemical shift (δ) in ppm; number of protons; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) are in Hertz (Hz).

Nitrogen sorption isotherms were measured using an Autosorb-1 porosimetry device manufactured by Quantachrome, samples were degassed at 100 °C for 24 h at reduced pressure before measurement. ICP-OES measurements were performed at Fraunhofer-Institute of Applied Polymer Research on a Perkin-Elmer® Optima 2100 DV device after exposing the samples to microwaves under acidic conditions for decomposition.

Synthesis of 2-phenyl quinoline

Under nitrogen atmosphere a two neck round bottom flask was charged with phenyl boronic acid (120 mg, 1 mmol, 1 eq.), 2-Chloroquinoline (164 mg, 1 mmol, 1 eq.) tetrakis-(triphenylphophine)-palladium (57.5 mg, 5 mol%) and potassium carbonate (414 mg, 3 mmol, 3 eq.). The flask was protected against light. Degassed benzene (2.5 mL), degassed ethanol

(2.5 mL) were added via syringe. The mixture was heated at 80°C for 24 h and then diluted with CH_2Cl_2. After separation the aqueous phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with water and dried over sodium sulfate. After removal of solvent the crude product was recrystallised dissolving in ethanol to give 2-phenyl quinolone as a light pink solid (184.72 mg, 0.9 mmol, 90%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] **=** 8.23 (1H, d, J = 8 Hz), 8.18-8.16 (3H), 7.89 (1H, d, J = 8 Hz), 7.84 (1H, dd, J = 8 Hz, J = 4 Hz), 7.73 (1H), 7.55-7.52 (3H), 7.48-7.45(1H)

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 157.4 (1C, C_q), 148.29 (1C, C_q), 139.69 (1C, C_q), 136.84 (1C, CH), 129.75 (1C, CH), 129.71 (1C, CH), 129.37 (1C, CH), 128.88 (2C, CH), 127.62 (2C, CH), 127.50 (1C, CH), 127.21 (1C, C_q), 126.33 (1C, CH), 119.06 (1C, CH).

Synthesis of polymer networks

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phoshoric acid polymer network

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phoshoric acid chloride (50 mg, 0.055 mmol, 1 eq.) was dissolved in 25 mL dry toluene and heated to 60 °C. Under vigorous stirring $FeCl_3$ (72 mg, 0.44 mmol, 8 eq.), dissolved in 5 mL dry acetonitrile, was added to the solution. The reaction mixture was stirred for 4 h at 60 °C and quenched with ethanol. The resulting polymer network was separated by centrifugation (4000 rpm), washed several times with ethanol, a mixture (1:1) of aqueous HCl (c = 2 mol/L) and THF, and CH_2Cl_2 to remove residues of the monomer and reactants. The product was dried in high vacuum for 24 h. (Yield 24 mg, 48%)

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phoshoric acid - 1,3,5-Tris(2-thienyl)benzene copolymer network (here ratio 1:5)

(R)-3,3'-bis(10-(thiophen-3-yl)anthracen-9-yl)-1,1'-binaphthalen-2,2'-diyl-phoshoric acid chloride (30 mg, 0.034 mmol, 1 eq.) and 1,3,5-tris(2-thienyl)benzene (55 mg, 0.17 mmol, 5 eq.) were dissolved in 40 mL dry toluene and heated to 60 °C. Under vigorous stirring $FeCl_3$ (270 mg, 1.70 mmol, 50 eq.), dissolved in 10 mL dry acetonitrile, was added to the solution. The reaction mixture was stirred for 4 h at 60 °C and quenched with ethanol. The resulting polymer network was separated by filtration, washed several times with ethanol, a mixture

(1:1) of aqueous HCl (c = 2 mol/L) and THF, and CH_2Cl_2 to remove residues of the monomers and reactants. The product was dried in high vacuum for 24 h. (Yield 55 mg, 64%) The ratio of the monomers in the resulting network structure was determined by ICP-OES. The amount of phosphor in the sample was 1.16 wt% which corresponds to a monomer ratio of 1: 5,4 (phosphoric acid : TTB) in the polymer network.

Catalysis:

General procedure for organocatalytic transfer hydrogenation of 2-aryl quinoline:

The reaction was performed in a NMR tube and monitored by in-situ NMR spectroscopy. 2-phenyl quinoline (35 micro mol, 1 eq.) and Hantzsch-Ester (87.5 micro mol, 2.5 eq.) were dissolved in 0.6 mL $CDCl_3$ and 2 mol% (calculated on the amount of phosphoric acid) of the catalyst was added. NMR spectra were measured every 20 min.

Literature:

[1] D. S. Kundu, J. Schmidt, C. Bleschke, A. Thomas and S. Blechert, *Angewandte Chemie-International Edition*, **2012**, 51, 5456-5459.

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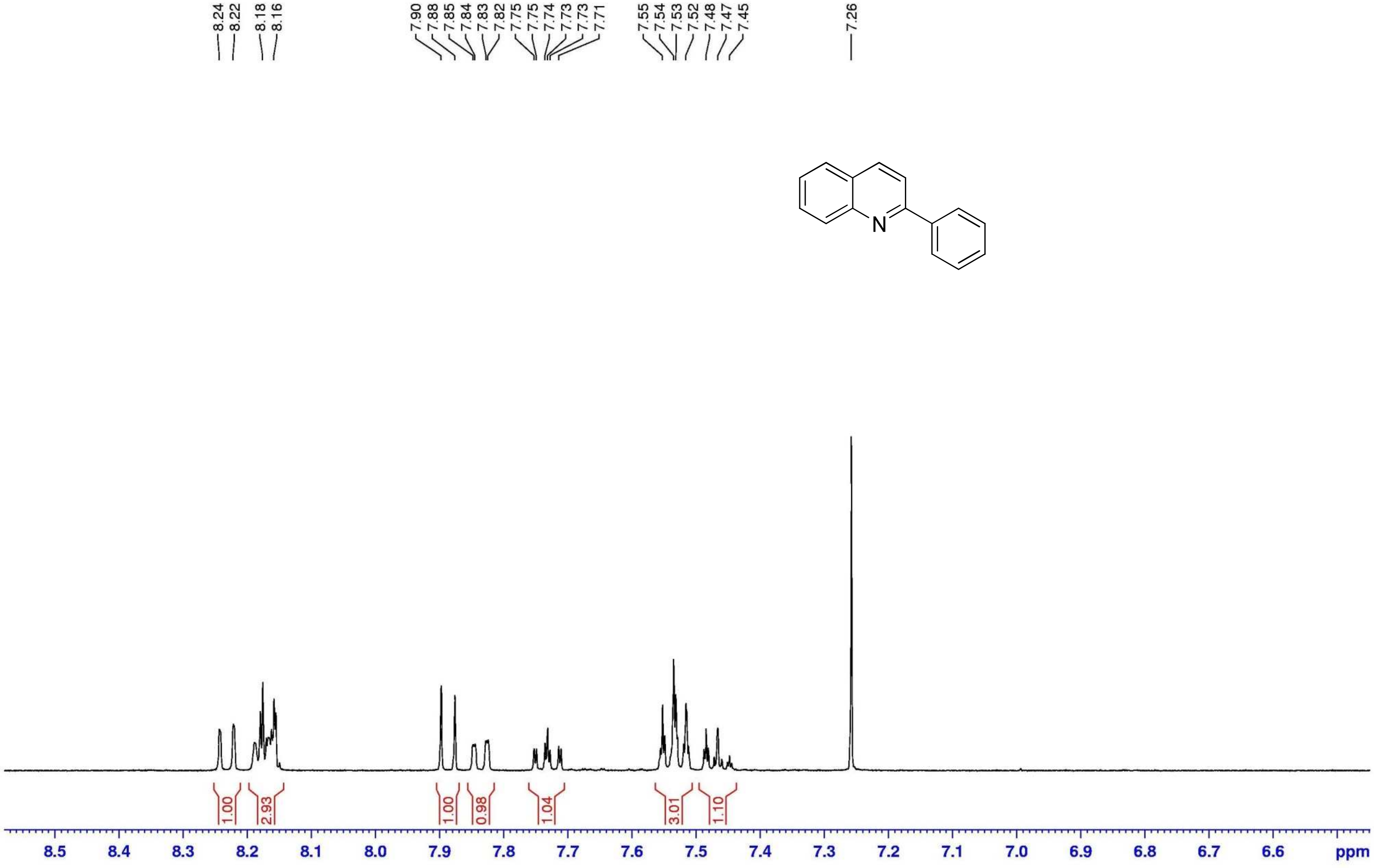

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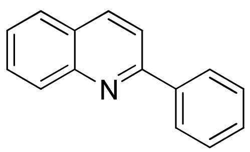

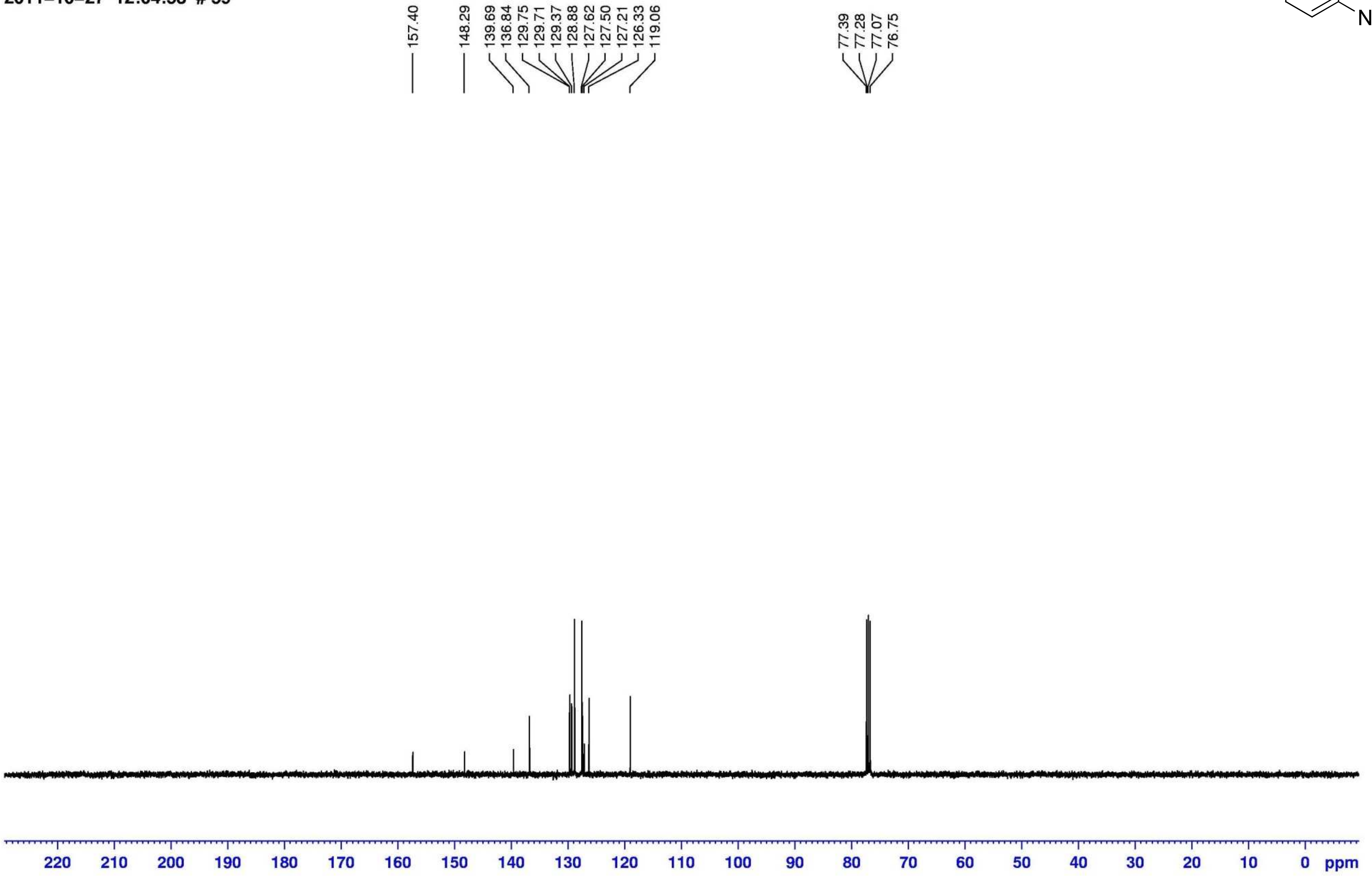

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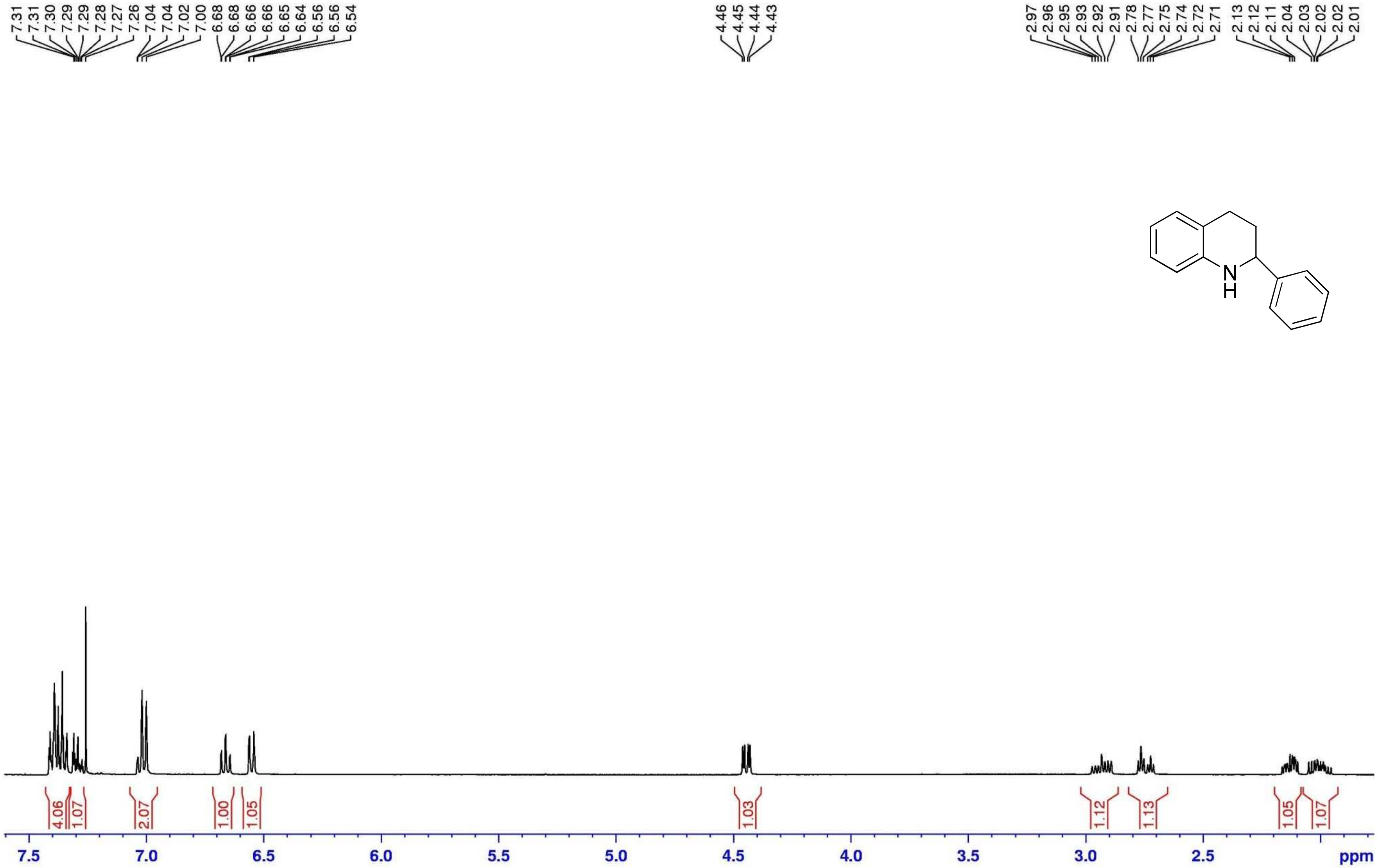

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