

Electronic supplementary information

Article

Nickel Nanowires: Synthesis, Characterization and Application as Effective Catalysts for the Reduction of Nitroarenes

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1. General information

General methods Reactions were carried out in flame dried glassware under a dry nitrogen atmosphere using Schlenk technique.

Reagents were purchased from *Acros Organics, Alfa Aesar GmbH&Co., Merck KGAA and Sigma Aldrich GmbH.*

¹H, ¹³C NMR spectra were recorded at 298 K using Agilent-MR NMR (400 MHz for ¹H and at 100.5 MHz for ¹³C). Spectra were calibrated relative to solvents residual proton and carbon chemical shifts: DMSO ($\delta = 2.50$ ppm for ¹H NMR and $\delta = 39.50$ ppm for ¹³C NMR) and CH₃CN ($\delta = 1.94$ ppm for ¹H NMR and $\delta = 1.39$ ppm for ¹³C NMR). Coupling constants (*J*) are reported in Hertz (Hz). The multiplicity of the signals are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad signal), vbs (very broad signal).

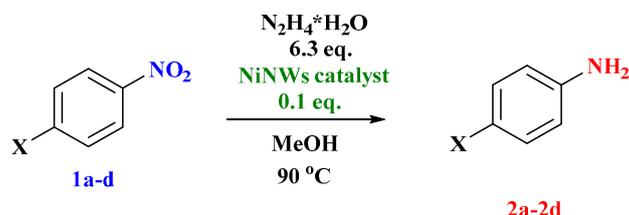
Thin layer chromatography (TLC) The progress of reaction was monitored by TLC using silica-gel-coated aluminum plates with a fluorescence indicator (Merck, SiO₂ 60, F254) and visualized by UV light (254 nm and 365 nm) or dipping into iodine chamber (well-closed chamber with a few crystals of elemental iodine and 10 g of silica gel).

Melting points (m.p.) were determined with a Boetius apparatus and are uncorrected.

Mass spectrometry were determined with API 4000Q TRAP tandem mass spectrometer detector equipped with an electrospray ionization (ESI) source (Applied Biosystems/MDS SCIEX, Foster City, CA).

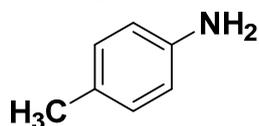
2. Experimental procedures

2.1. General Procedure for reduction of nitroarenes using nickel nanowires as effective catalyst



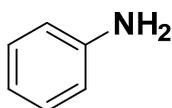
The appropriate nitrobenzene derivative (1.000 eq.) was added to Schlenk tube and was dissolved in methanol (each 1 ml per 1 mmol of nitrobenzene derivative). Next was loaded nickel nanowires catalyst (0.10 eq.) and reaction mixture was stirred at 50 °C. Then hydrazine hydrate (100%) was added slowly with a syringe and subsequently the temperature was raised to 90 °C (vigorous hydrogen gas evolution was observed). The resulting mixture was stirred for additional 3 to 4 hours and cooled to room temperature. Then, it was diluted with ethyl acetate (each 15 ml per 1 mmol of substrate) and washed with saturated sodium carbonate (each 5 ml per 1 mmol of substrate) and twice time with distilled water (each 5 ml per 1 mmol of substrate). The organic solution was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give pure aniline derivatives. The purity of product was sufficient as indicated by NMR spectra analysis.

4-Methylaniline (2a)



Following the general procedure above, the title compound (503 mg, 94%) was isolated as white solid. **Yield: 94%; M.p. 42-43°C;** (lit. mp = 42-43°C¹); **¹H NMR** (400 MHz, DMSO-d₆) δ 2.12 (s, 3H), 4.75 (bs, 2H), 6.46 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H); **¹³C NMR** (151 MHz, CDCl₃) δ 20.11, 114.06, 123.96, 129.22, 146.04; **MS (EI) m/z:** 108.08 [M+H]⁺.

Aniline (2b)

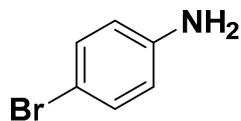


Following the general procedure above, the title compound (172 mg, 92%) was isolated as colorless oil. **Yield: 92%; B.p. 84°C** (lit. bp = 84°C²); **¹H NMR** (400 MHz, DMSO-d₆) δ 4.97 (bs, 2H), 6.49 (tt, J = 7.3, 1.1 Hz, 1H), 6.56 (dd, J = 8.5, 1.1 Hz, 2H), 7.00 (dd, J = 8.5, 7.3 Hz, 2H); **¹³C NMR** (101 MHz, DMSO-d₆) δ 113.87, 115.65, 128.78, 148.56; **MS (EI) m/z:** 93.13 [M+H]⁺.

¹ Kim, J.; Chang, S. *Chem. Commun.* 2008, 3052.

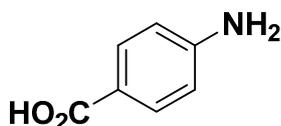
² Li, J.; Shi, X.Y.; Bi, Y.-Y.; Wei, J.-F.; Chen, Z.-G. *ACS Catal.*, 2011, 657.

4-Bromoaniline (2c)



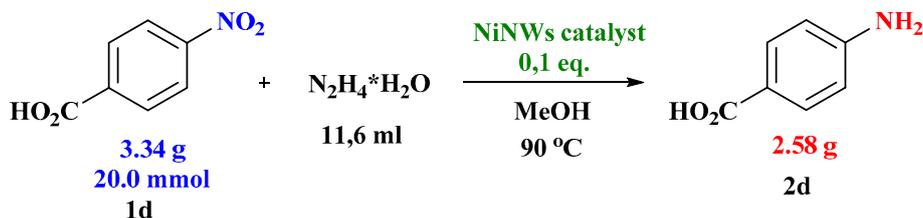
Following the general procedure above, the title compound (495 mg, 96%) was isolated as white-yellow solid. **Yield: 96%; M.p. 62-63°C;** (lit. mp = 62-64°C³); **¹H NMR** (400 MHz, DMSO-d₆) δ 5.23 (bs, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H); **¹³C NMR** (101 MHz, DMSO-d₆) δ 106.00, 115.75, 131.28, 148.03; **MS (EI) *m/z*:** 172.02 [M+H]⁺, 174.02 [M+2+H]⁺.

4-Aminobenzoic acid (2d)



Following the general procedure above, the title compound (386 mg, 94%) was isolated as white solid. **Yield: 94%; M.p. 188-189°C;** (lit. mp = 186-189°C⁴); **¹H NMR** (400 MHz, DMSO-d₆) δ 5.84 (bs, 2H), 6.54 (d, *J* = 6.6 Hz, 2H), 7.61 (d, *J* = 6.7 Hz, 2H), 11.39 (vbs, 1H); **¹³C NMR** (101 MHz, DMSO-d₆) δ 112.59, 116.93, 131.21, 153.10, 167.48; **MS (EI) *m/z*:** 159.12 [M+Na]⁺.

2.2. Gram-scale synthesis



4-Nitrobenzoic acid (3.34 g, 20.0 mmol) was added to Schlenk tube and was dissolved in anhydrous methanol (20 ml) under N₂ atmosphere (Schlenk line). Next was loaded nickel nanowires catalyst (118 mg, 2.0 mmol) and reaction mixture was stirred at 50 °C. Then hydrazine hydrate (64% aqueous solution, 11.6 ml, 200.0 mmol) was added slowly with a syringe and subsequently the temperature was raised to 90 °C (vigorous hydrogen gas evolution was observed). The resulting mixture was stirred for additional 3 to 4 hours and cooled to room temperature. Then it was diluted with ethyl acetate (300 ml) and washed with saturated sodium carbonate (50 ml) and twice time with distilled water (50 ml). The organic solution was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give pure 4-aminobenzoic acid (2.58 g, 18.8 mmol, 94%). The purity of product was sufficient as indicated by NMR spectra analysis.

³ Keith C. Brown, K.C.; Corbett, J.F. *J. Org. Chem.*, 1979, 25.

⁴ Li, J.; Shi, X.Y.; Bi, Y.-Y.; Wei, J.-F.; Chen, Z.-G. *ACS Catal.*, 2011, 657.

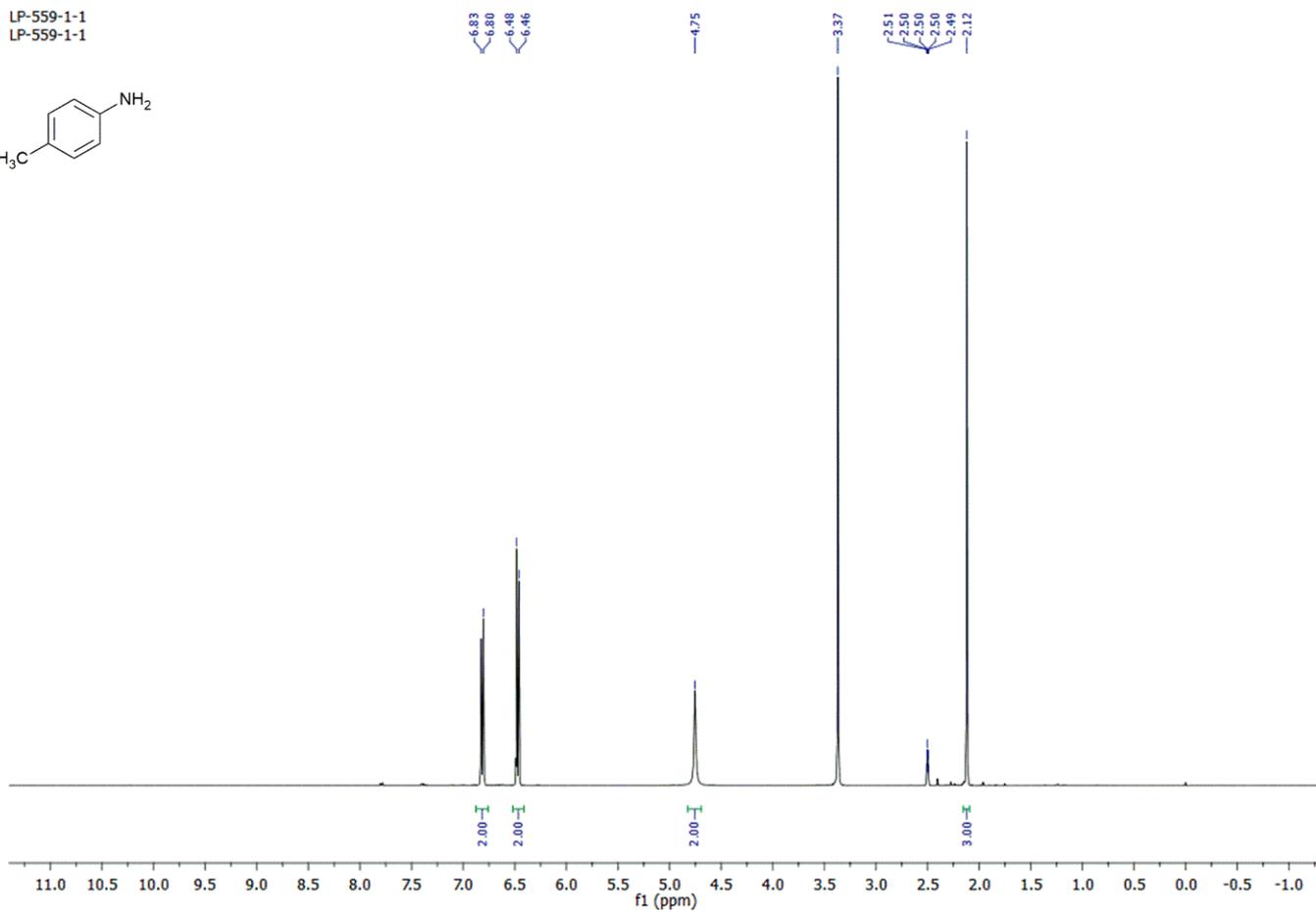
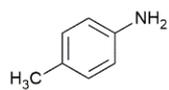


Figure S1. Progress of the reaction reduction of 4-nitrobenzoic acid: (a) 4-Nitrobenzoic acid and NiNWs in methanol, (b) After addition of hydrazine hydrate, (c) Reaction mixture upon completion and (d) Isolated pure 4-aminobenzoic acid after simple work up.

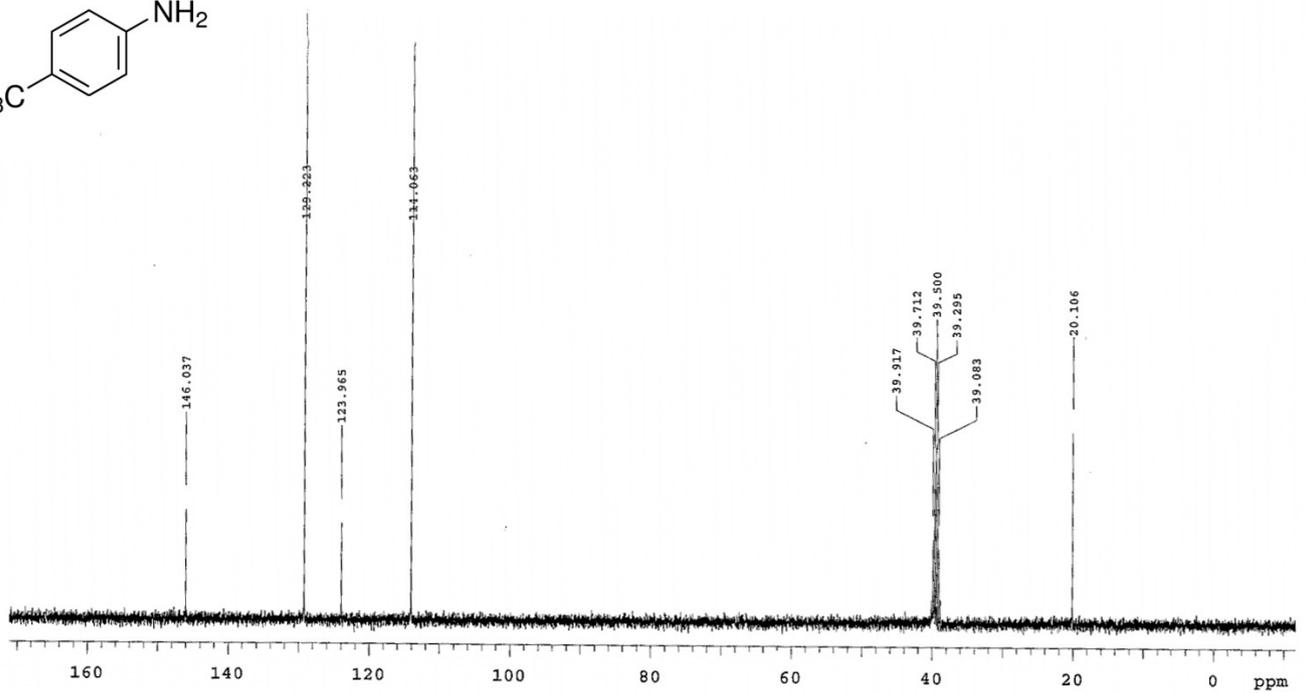
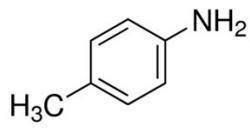
3. Data from NMR spectroscopy

3.1. ¹H NMR 4-methylaniline

LP-559-1-1
LP-559-1-1

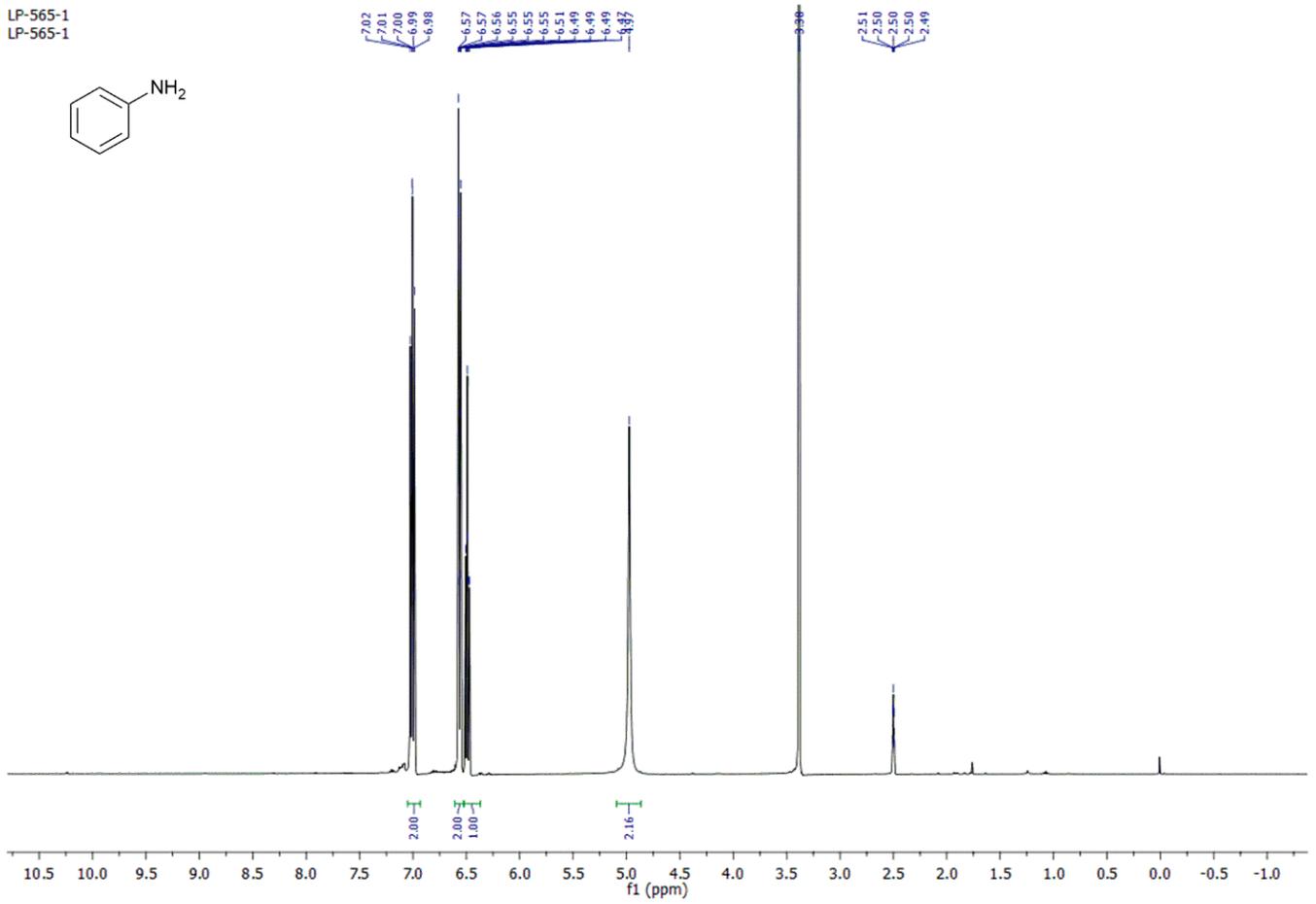
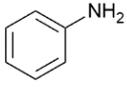


3.2. ^{13}C NMR 4-methylaniline



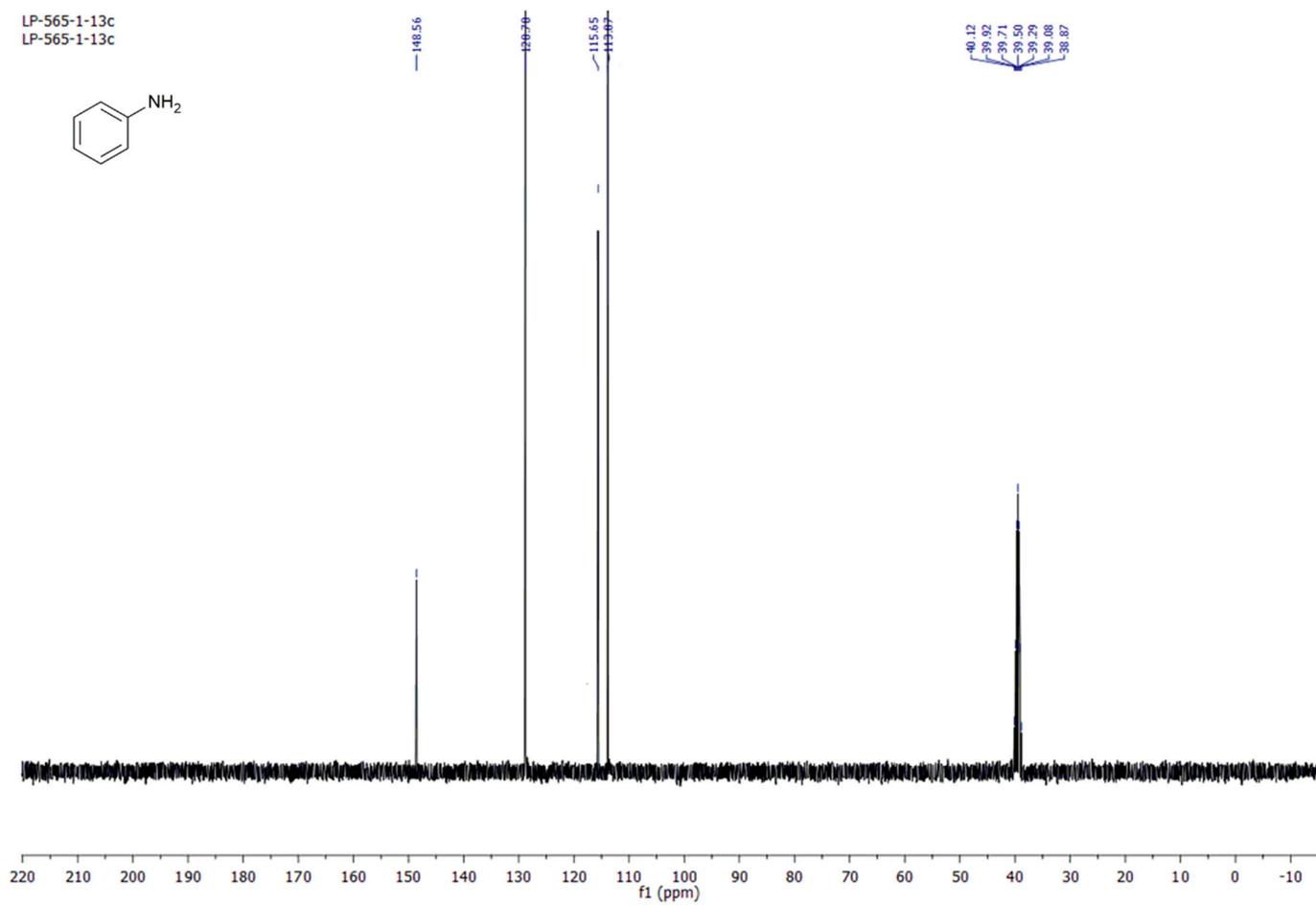
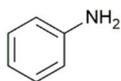
3.3. ¹H NMR aniline

LP-565-1
LP-565-1



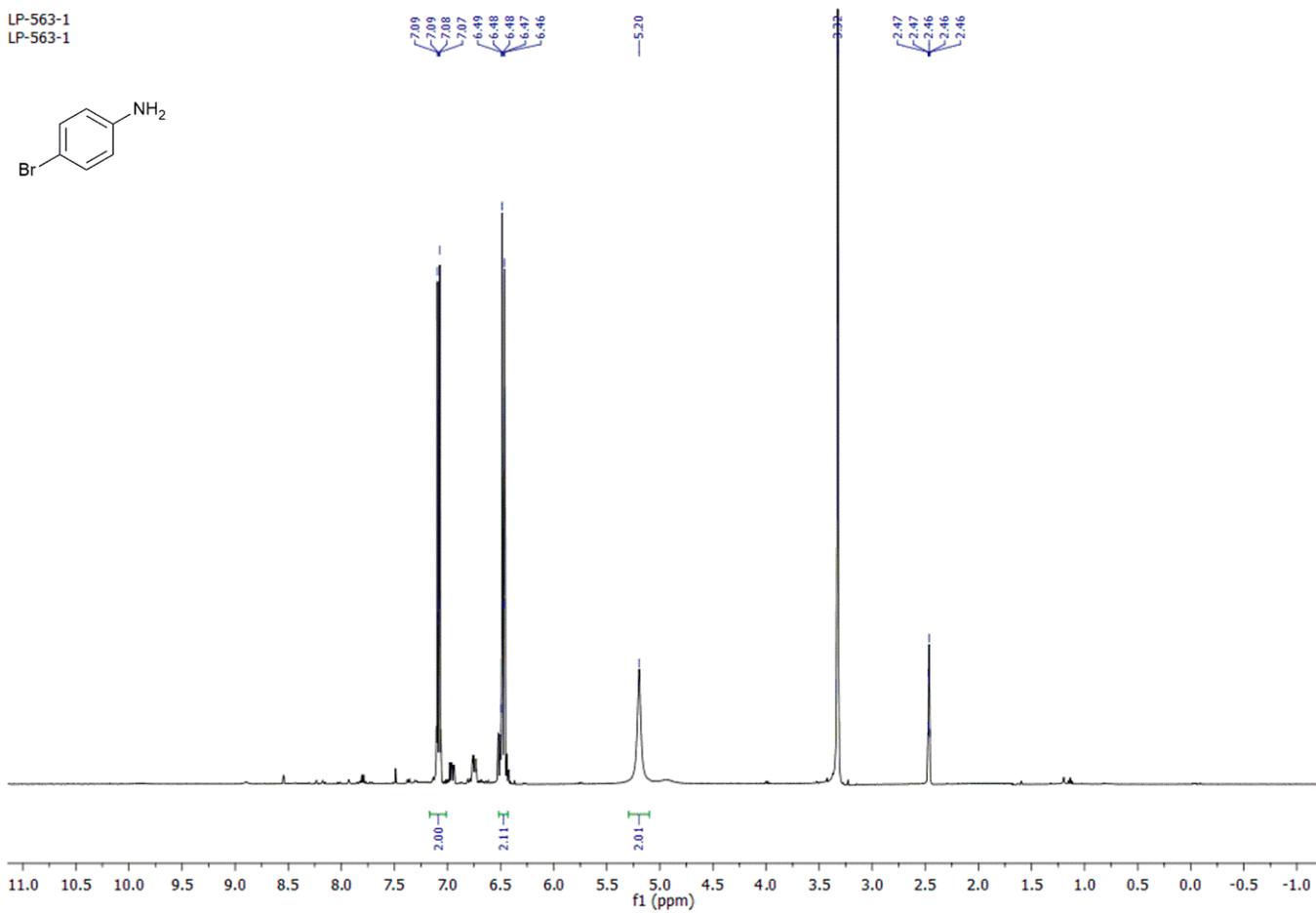
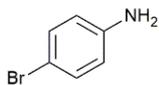
3.4. ^{13}C NMR aniline

LP-565-1-13c
LP-565-1-13c



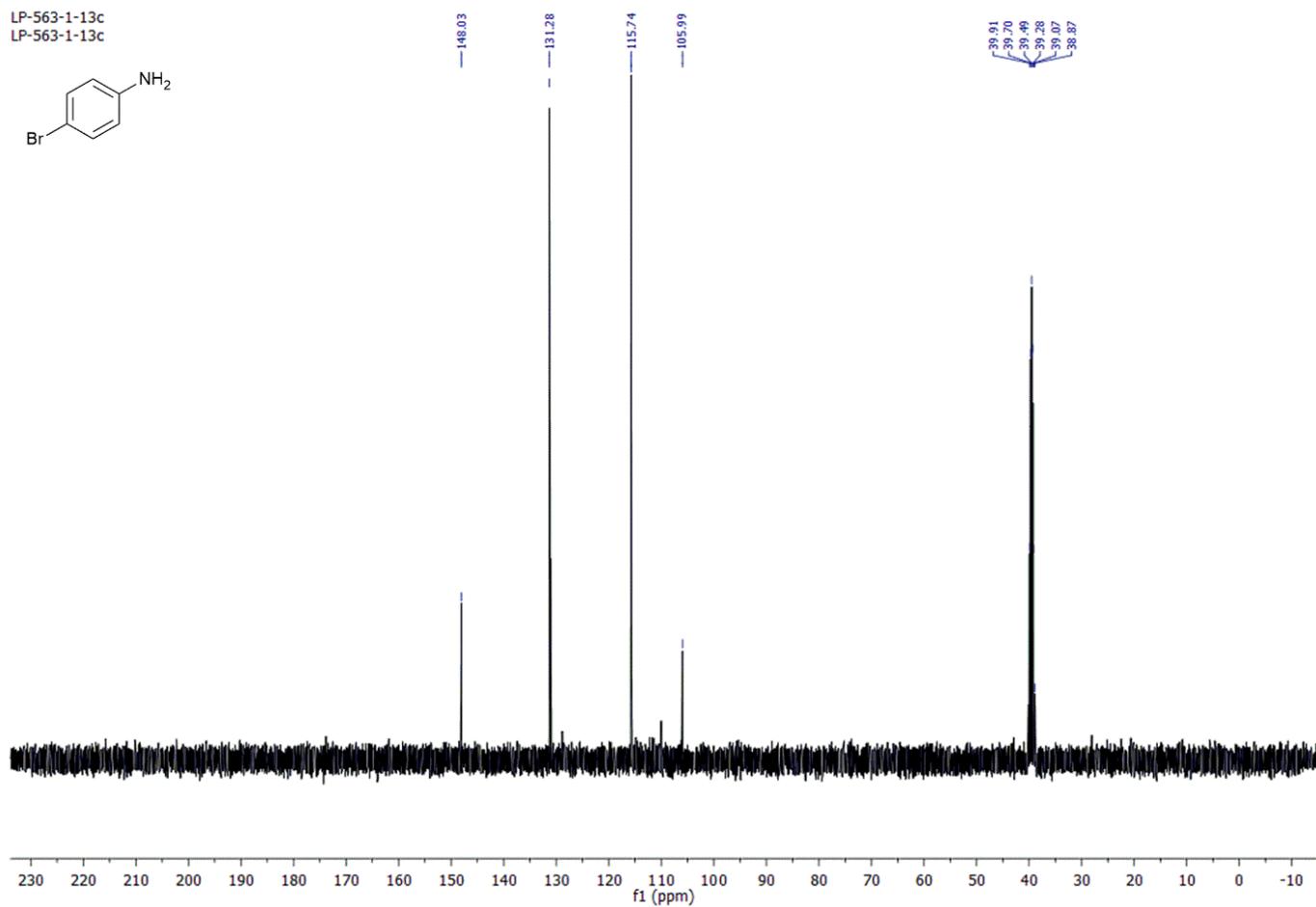
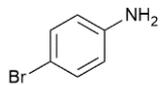
3.5. ¹H NMR 4-bromoaniline

LP-563-1
LP-563-1



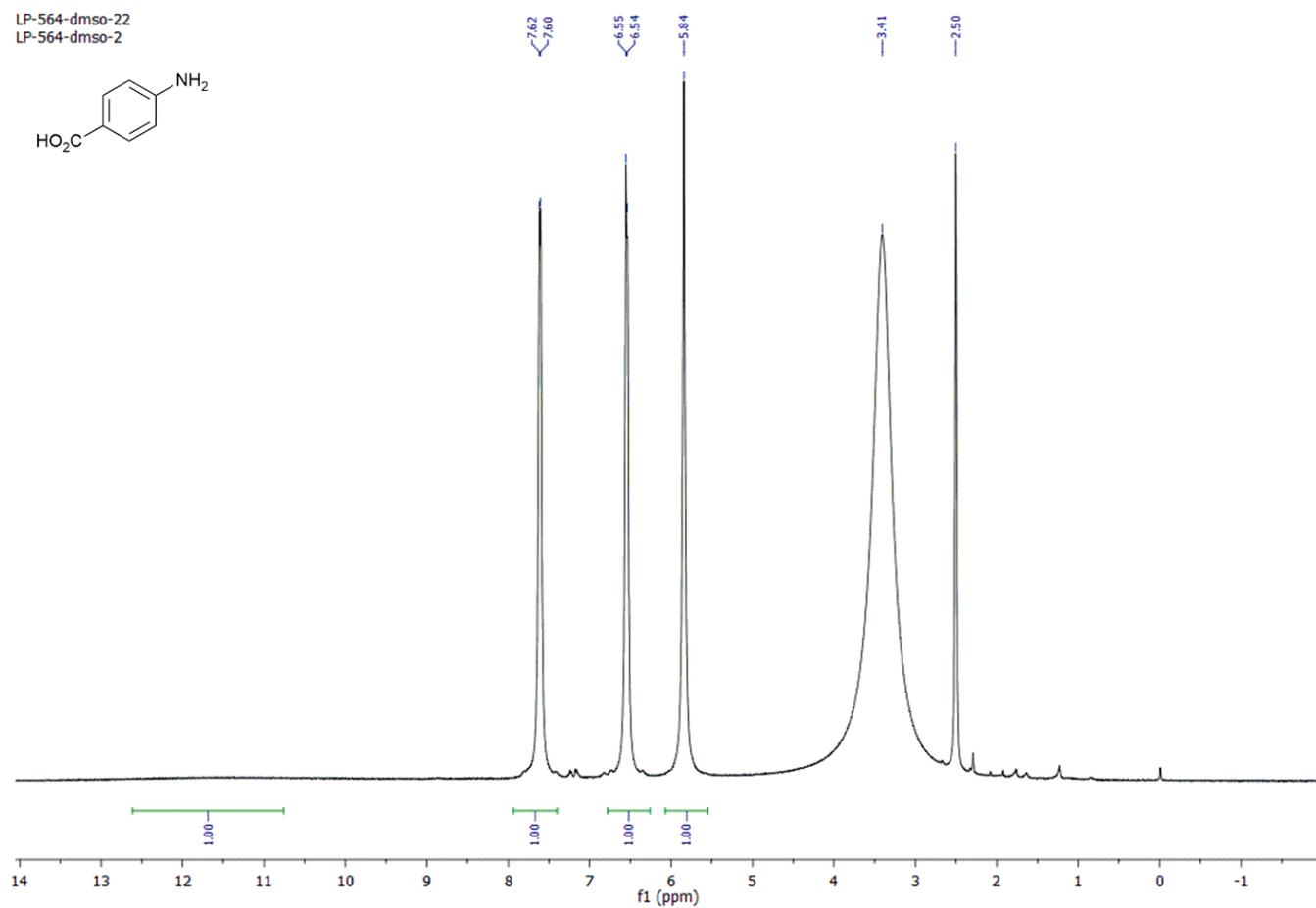
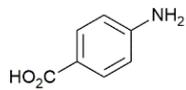
3.6. ^{13}C NMR 4-bromoaniline

LP-563-1-13c
LP-563-1-13c



3.7. ¹H NMR 4-aminobenzoic acid

LP-564-dms0-22
LP-564-dms0-2



3.8. ¹³C NMR 4-aminobenzoic acid

LP-564-dmso-2-13c
LP-564-dmso-2-13c

