Selective Reduction of Nitroarenes using Ru/C and CaH_2.

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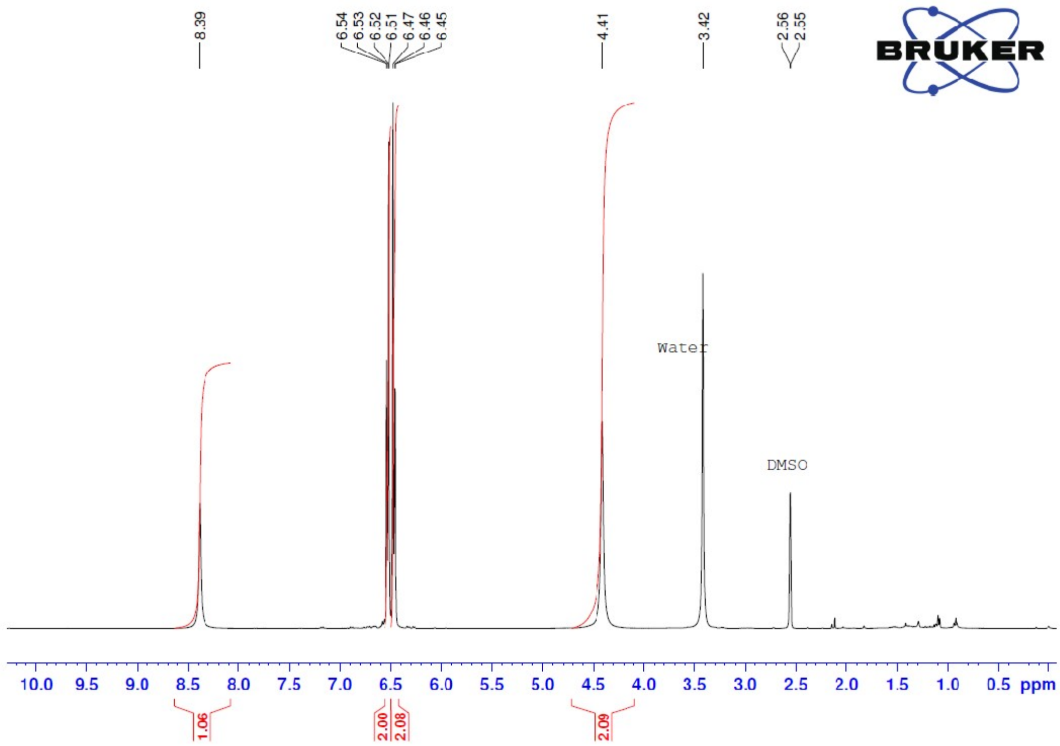
General Procedures: NMR spectra were obtained on a Bruker Advance III^{TM} 400Hz (400.13 MHz), chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of quartets (dq), triplet (t), triplet of doublets (td), quartet (q), quintet (quin), and multiplet (m). Gas chromatography was carried out on a GC-2014 Shimadzu with flame ionization detector using a 30 meter, 0.25 mmID, 0.25 µm df Rtx®-5 column.

GC-FID Method Parameters: The carrier gas used was N2, with a constant pressure of 96.3 kPa. The method ramp used starts at 40.00º C for 4 minutes, and then the temperature rises at a rate of 15.00º C per minute until it reaches 300.00º C, then it holds for 5 minutes.

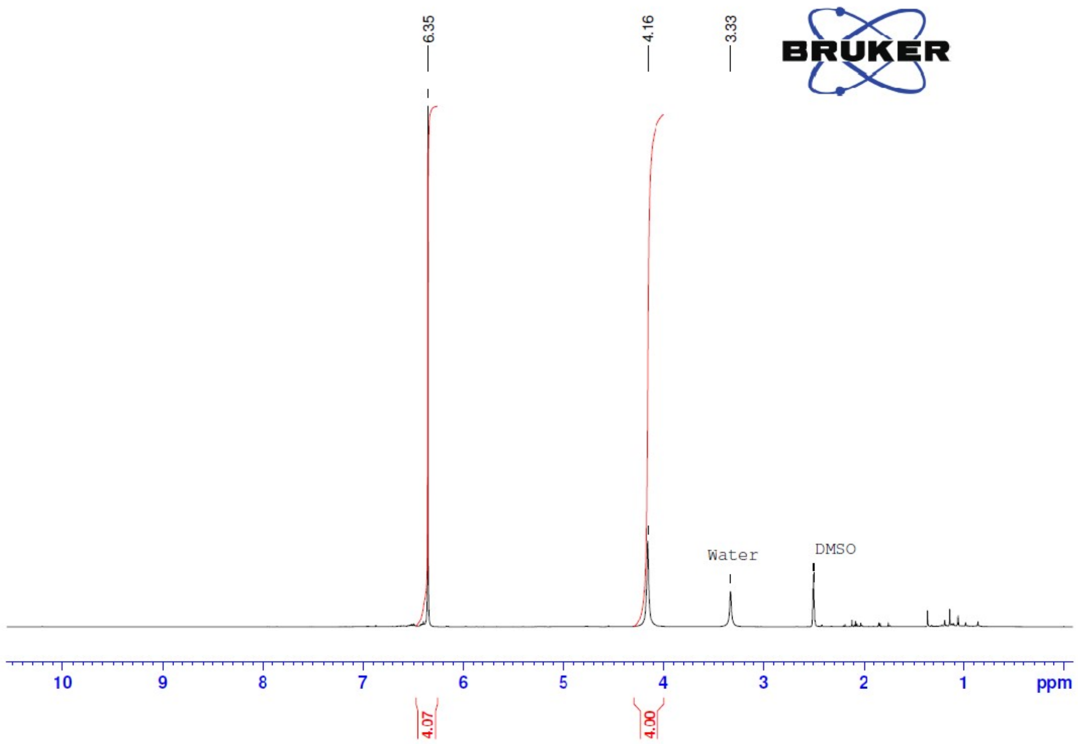
	Rate (ºC/min)	Temperature (ºC)	Hold Time (min)
1	-	40.00	4.00
2	15.00	300.00	5.00

Experimental procedures: Nitroarene (0.5 mmoL), Ru/C (5%) (5-10 mol%), were weighed into a 15 mL sealed tube, 4 mL of 2-Methyltetrahydrofuran was added and then CaH_2 (10 equiv) was added. The reaction mixture was allowed to stir at 100 ºC for 24 h. The reaction was then filtered with a millipore syringe filter (Durapore (PVDF) with graduated multilayer glass prefilter. 25 mm diameter, 0.45 µm). 0.5 µL of the filtrated reaction was extracted and added to a vial with 0.5 µL of 2-Methyltetrahydrofuran for gas chromatography analysis. The rest of the solution was concentrated.

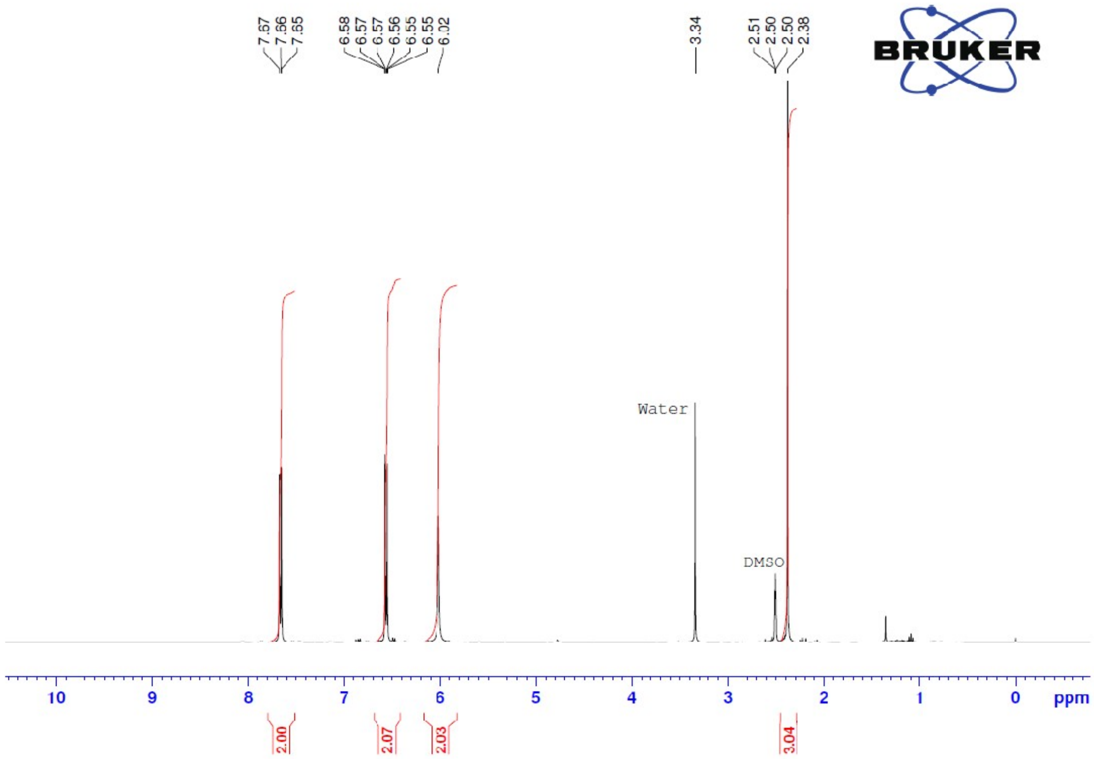
4-Aminophenol (2a): [1]H-NMR (400 MHz, DMSO):δ 8.38 H_{OH} (s, 1H), 6.86 H_{CAr}(dd, J = 8.5 Hz, 1.19 Hz, 4H), 4.40 H_{NH2} (s, 2H).



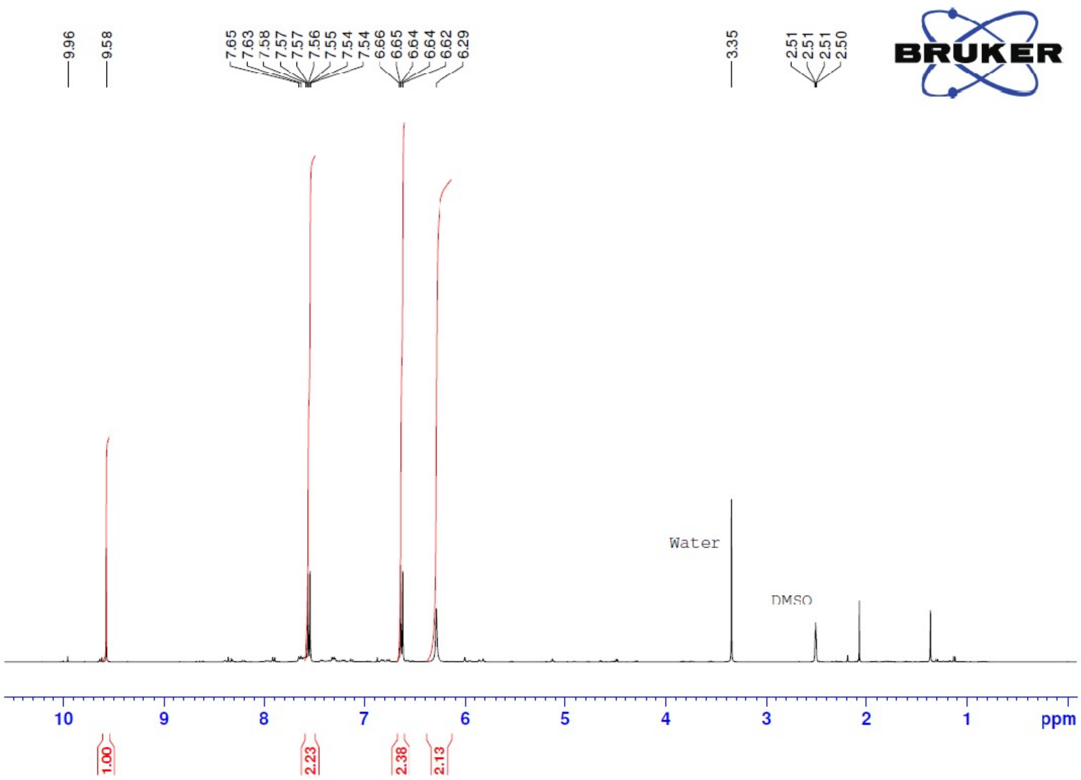
4-Phenylenediamine (2b): [1]H-NMR (400 MHz, DMSO):δ 6.35 H_{CAr} (s, 4H), 4.16 H_{NH2} (s, 4H).



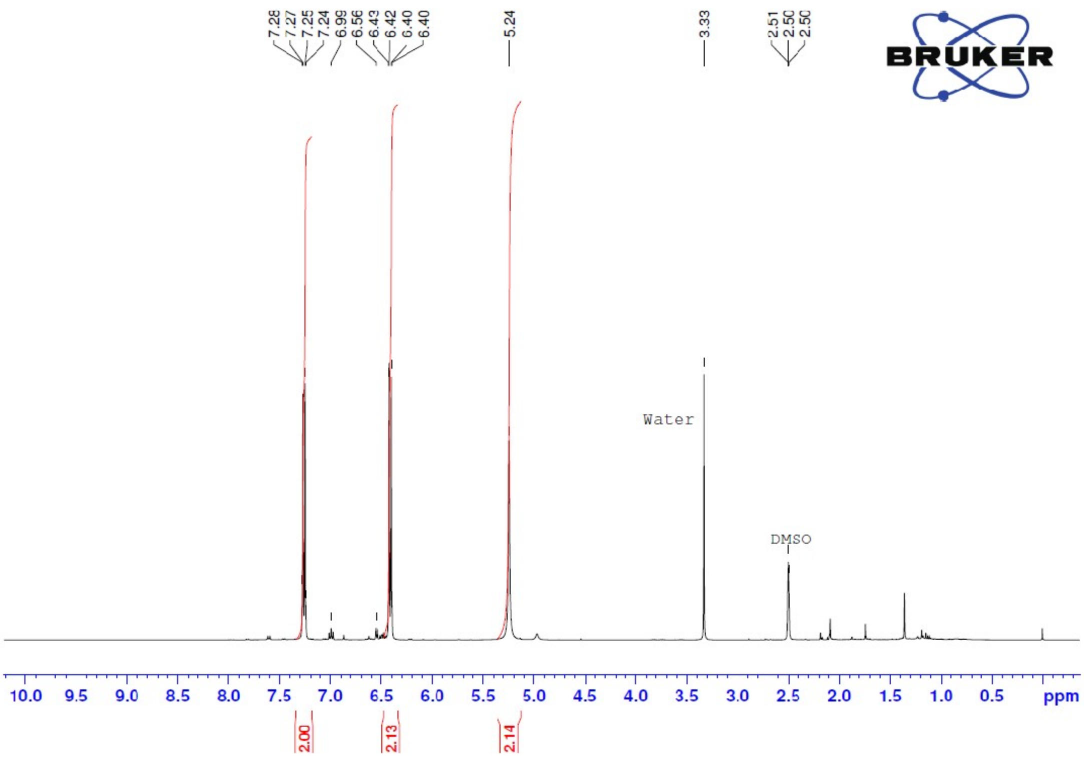
4-Aminoacetophenone (2c): ^{1}H-NMR (400 MHz, DMSO):δ 7.66 H_{CAr} (d, J=8.65, 2H), 6.56 H_{CAr} (d, J = 8.61 Hz, 2H), 6.01 H_{NH2} (s, 2H), 2.38 H_{C} (s, J = 2.99, 3H).



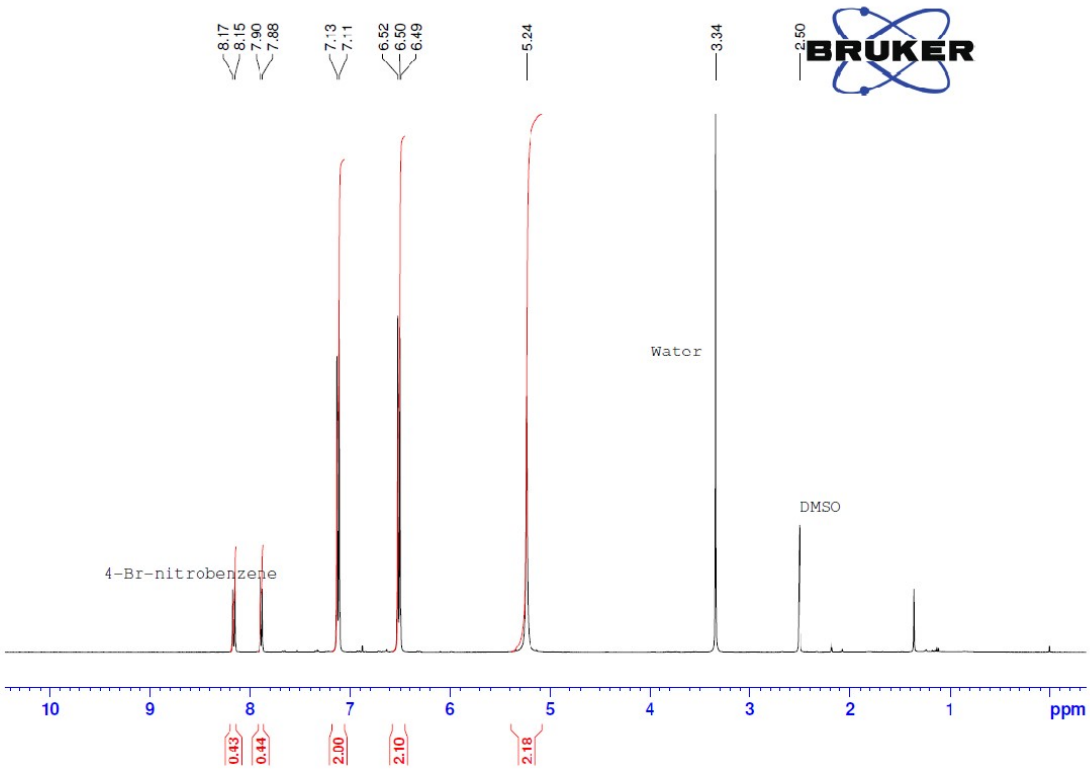
4-Aminobenzaldehyde (2d) : [1]H-NMR (400 MHz, DMSO):δ 9.52 H_{CHO} (s, 1H), 7.56 H_{CAr} (d, *J* = 7.89 Hz, 2H), 6.64 H_{CAr} (d, *J* = 7.88, 2H), 6.29 (s, 2H).



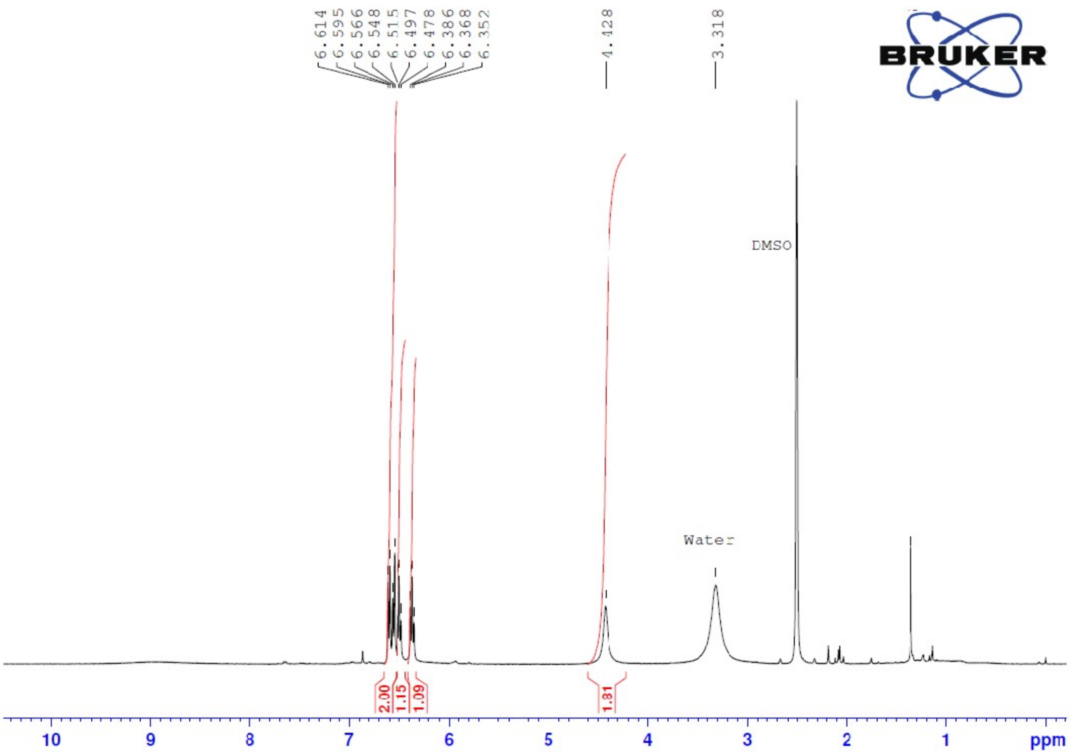
4-Iodoaniline (2e): [1]H-NMR (400 MHz, DMSO):δ 7.26 H_{CAr} (d, *J*=7.97, 1H), 6.42 H_{CAr} (d, *J* = 2.07 Hz, 1H), 5.24 (s, 2H).



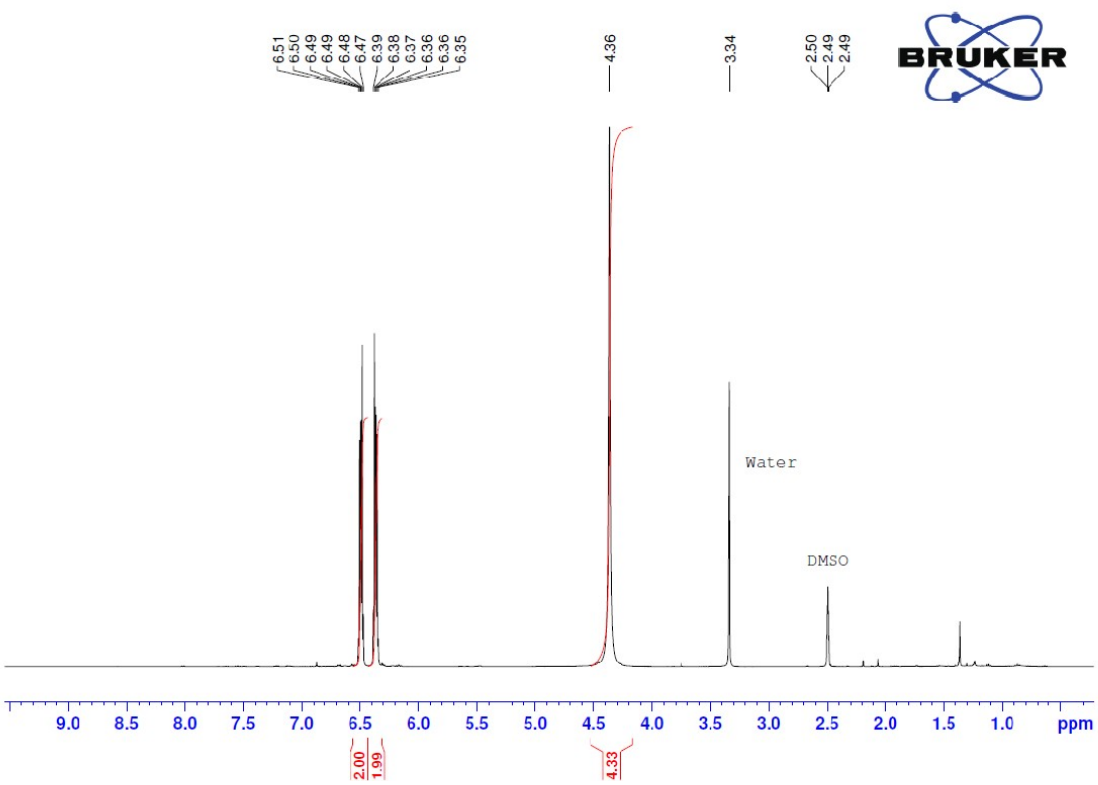
4-Bromoaniline (2f): ^{1}H-NMR (400 MHz, DMSO):δ 7.12 H_{CAr} (d, J = 8.65 Hz, 2H), 6.51 H_{CAr} (d, J = 8.65, 2H), 5.23 H_{NH2} (s, 2H). Starting material signals: ^{1}H NMR (400 MHz, DMSO): δ 8.16 H_{CAr} (d, J = 8.95 Hz, 2H), 8.13 H_{CAr} (d, J = 8.95, 2H).



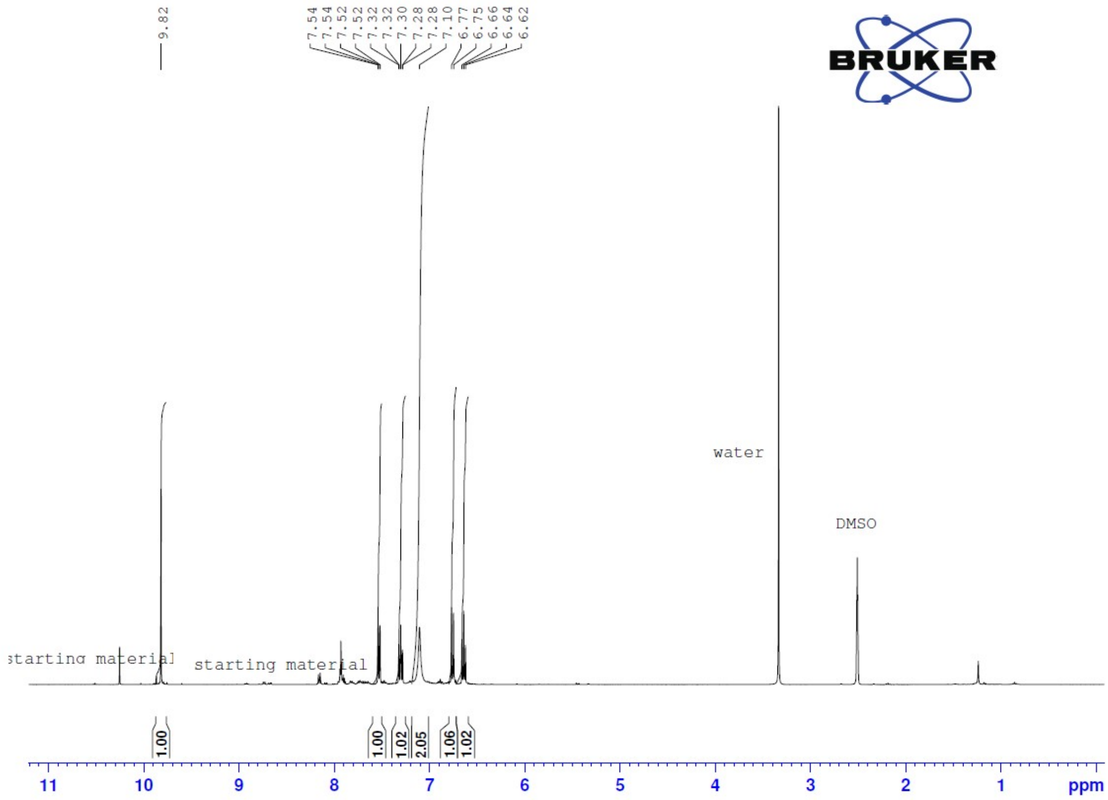
2-Nitrophenol (2g): ^{1}H-NMR (400 MHz, DMSO):δ 6.61 H_{CAr} (d, J = 7.56 Hz, 1H), 6.56 H_{CAr} (d, J = 7.56 Hz, 2H), 6.49 H_{CAr} (t, J = 7.31, 1H), 6.37 H_{CAr} (t, J = 7.31, 1H), 4.42 H_{NH2} (s, 2H).



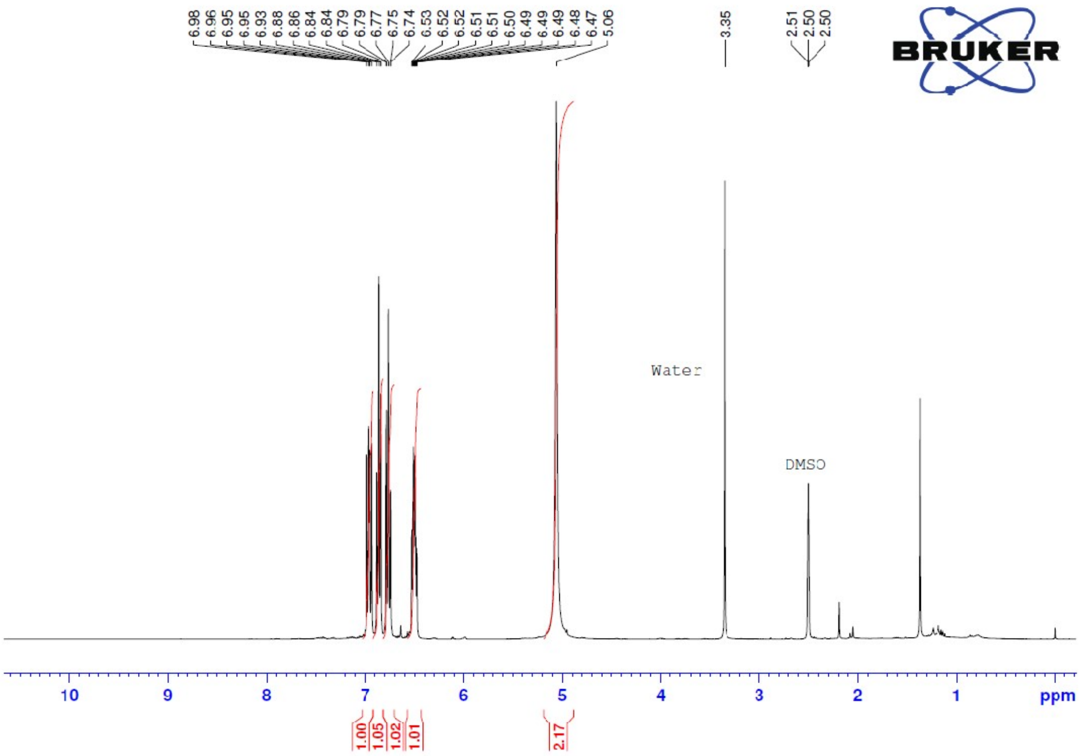
2-Phenylenediamine (2h): ^{1}H-NMR (400 MHz, DMSO):δ 6.49 H_{CAr} (m, 2H), 6.37 H_{CAr} (m, 2H), 4.35 H_{NH2} (s, 4H).



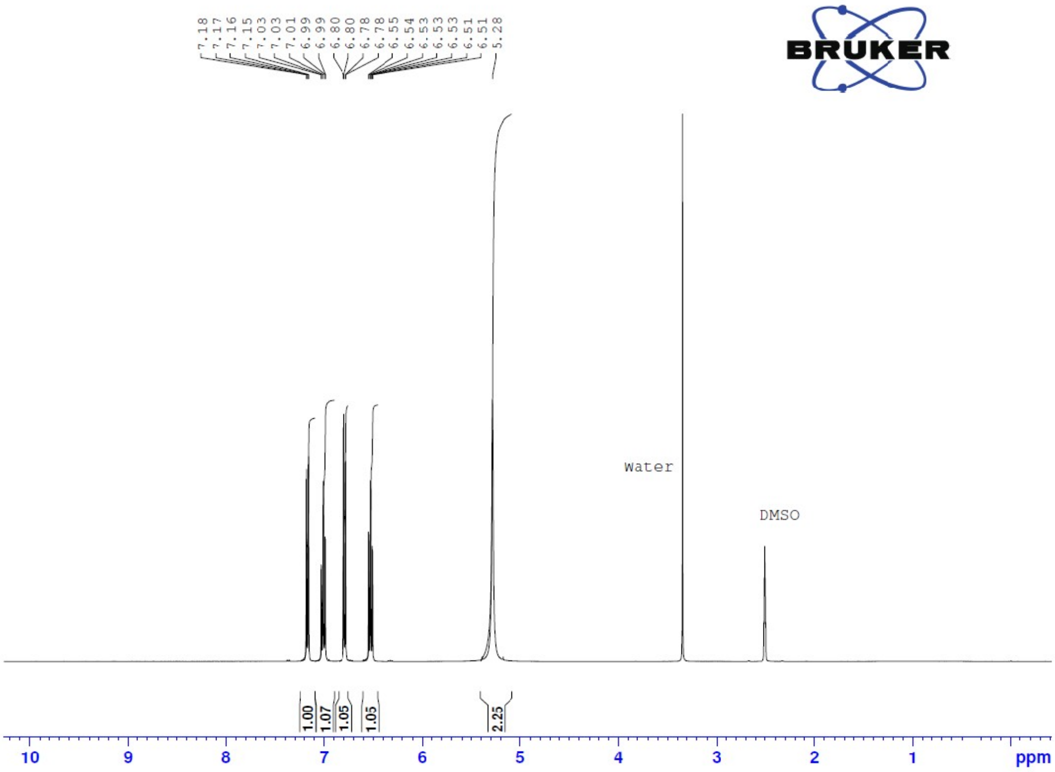
2-Aminobenzaldehyde (2i): [1]H-NMR (400 MHz, DMSO):δ 9.82 H_{CHO} (s, 1H), 7.52 H_{CAr} (d, J = 7.79 Hz, 1H), 7.29 H_{CAr} (t, J = 7.83, 1H), 7.10 H_{NH2} (s, 2H), 6.76 H_{CAr} (d, J = 8.38 Hz, 1H), 6.64 H_{CAr} (t, J = 7.36, 1H).



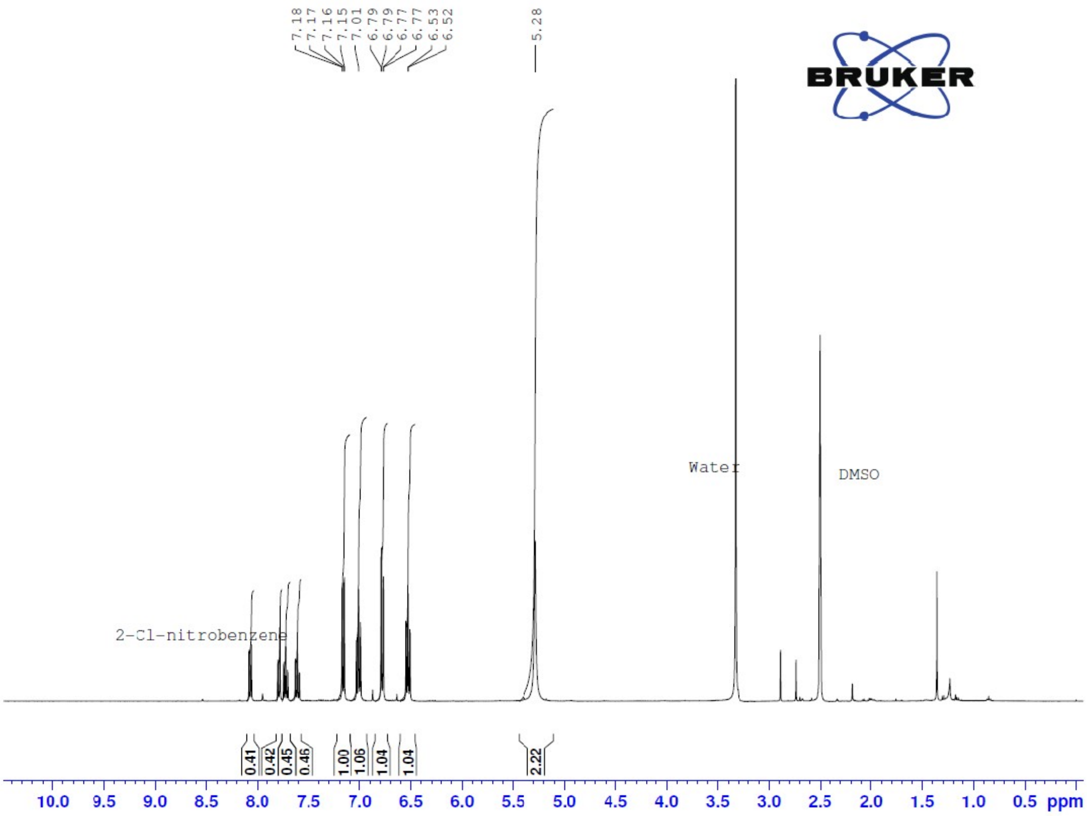
2-Fluoroaniline (2j): ^{1}H-NMR (400 MHz, DMSO):δ 6.96 H_{CAr} (q, J=9.77, 1H), 6.86 H_{CAr} (t, J = 8.05 Hz, 1H), 6.77 H_{CAr} (quin, J = 8.33, 2H), 6.50 H_{CAr} (m, 1H), 5.05 H_{NH2} (s, 2H).



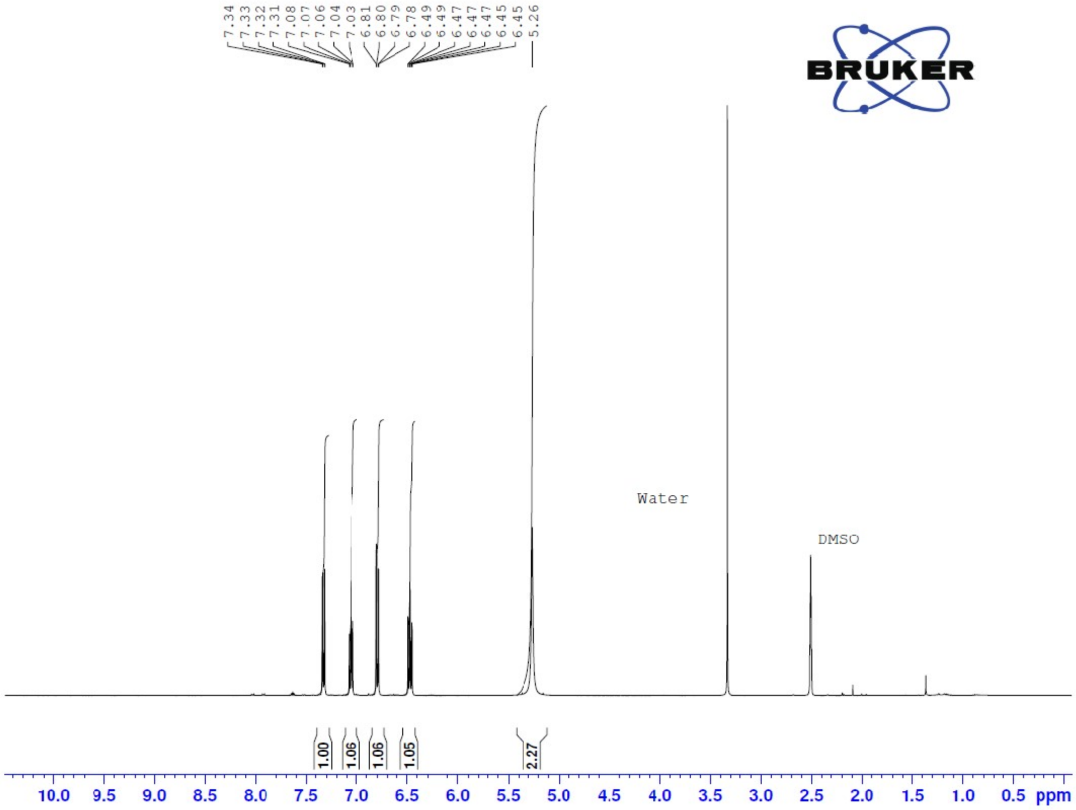
2-Chloroaniline (2k): [1]H-NMR (400 MHz, DMSO): δ 7.16 H_{CAr} (dd, $J1$ = 7.96 Hz, $J2$=1.40 Hz, 1H), 7.00 H_{CAr} (t, J = 7.73, 1H), 6.78 H_{CAr} (dd, $J1$ = 8.01 Hz, J2= 1.59 Hz, 1H) , 6.53 H_{CAr} (t, J = 7.69 Hz, 1H), 5.28 H_{NH2} (s, 2H).



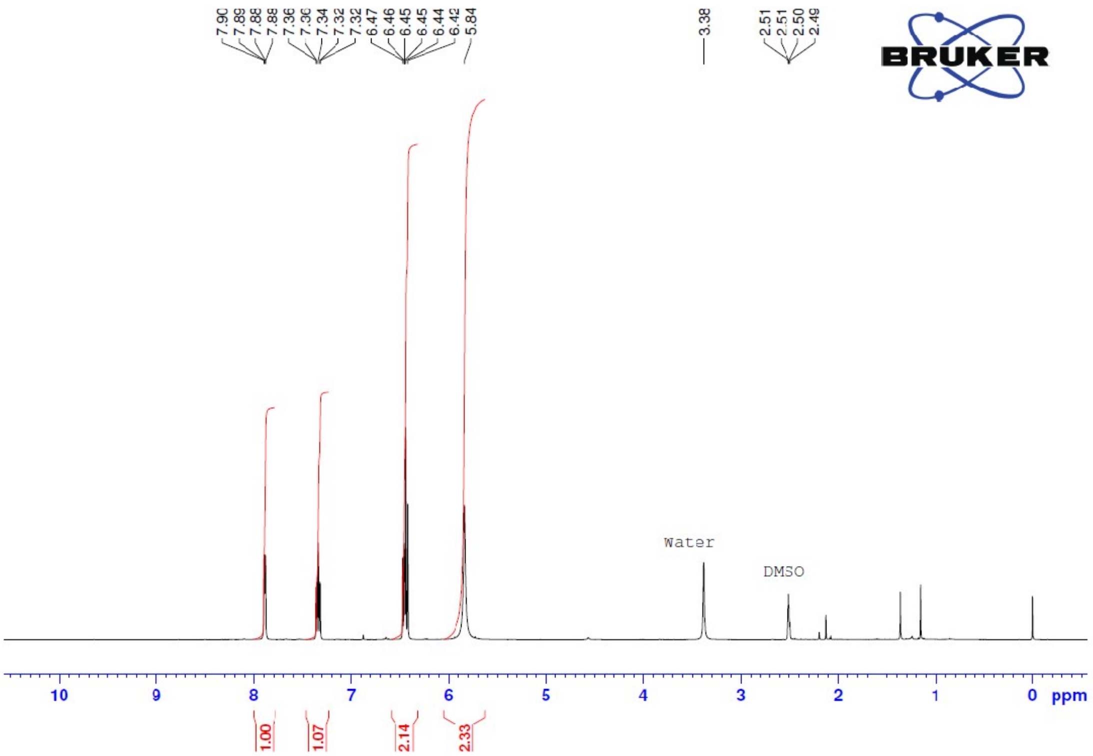
2-Chloroaniline without purification



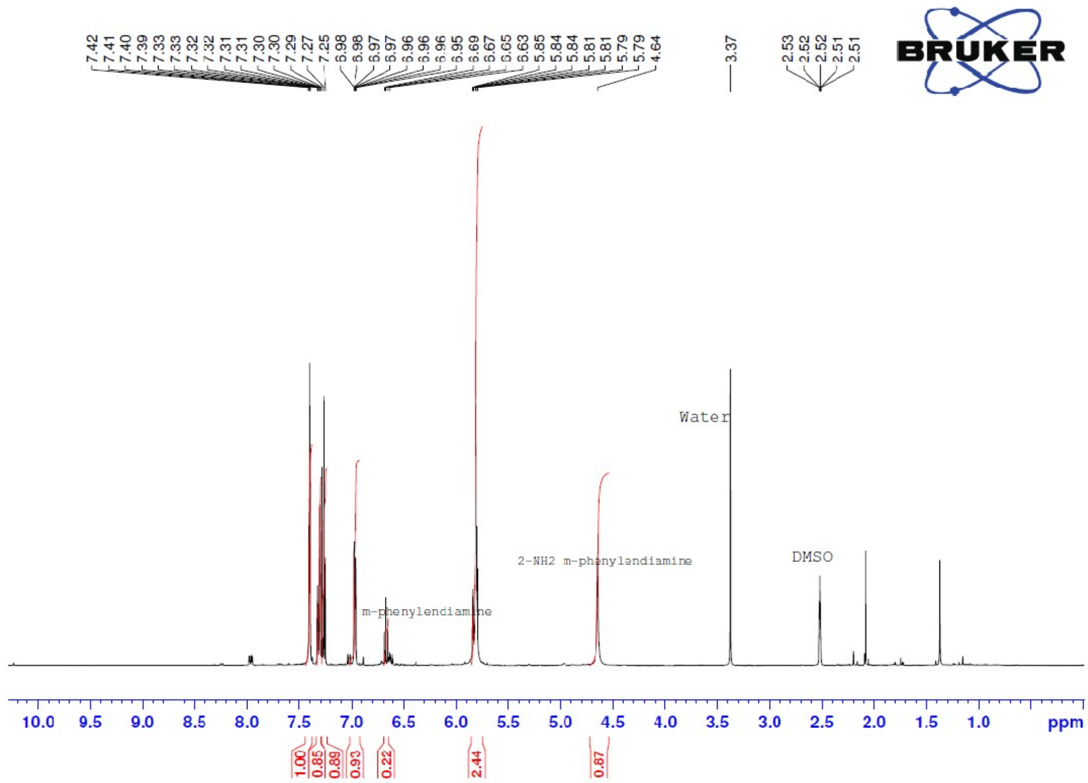
2-Bromoaniline (2l): [1]H-NMR (400 MHz, DMSO):δ 7.33 H_{CAr} (dd, *J1* = 8.01 Hz, *J2*=1.41 Hz, 1H), 7.06 H_{CAr} (t, *J* = 7.76, 1H), 6.79 H_{CAr} (dd, J1= 8.01 Hz, J2=1.41 Hz, 1H) , 6.47 H_{CAr} (t, *J* = 7.62 Hz, 1H), 5.27 H_{NH2} (s, 2H).



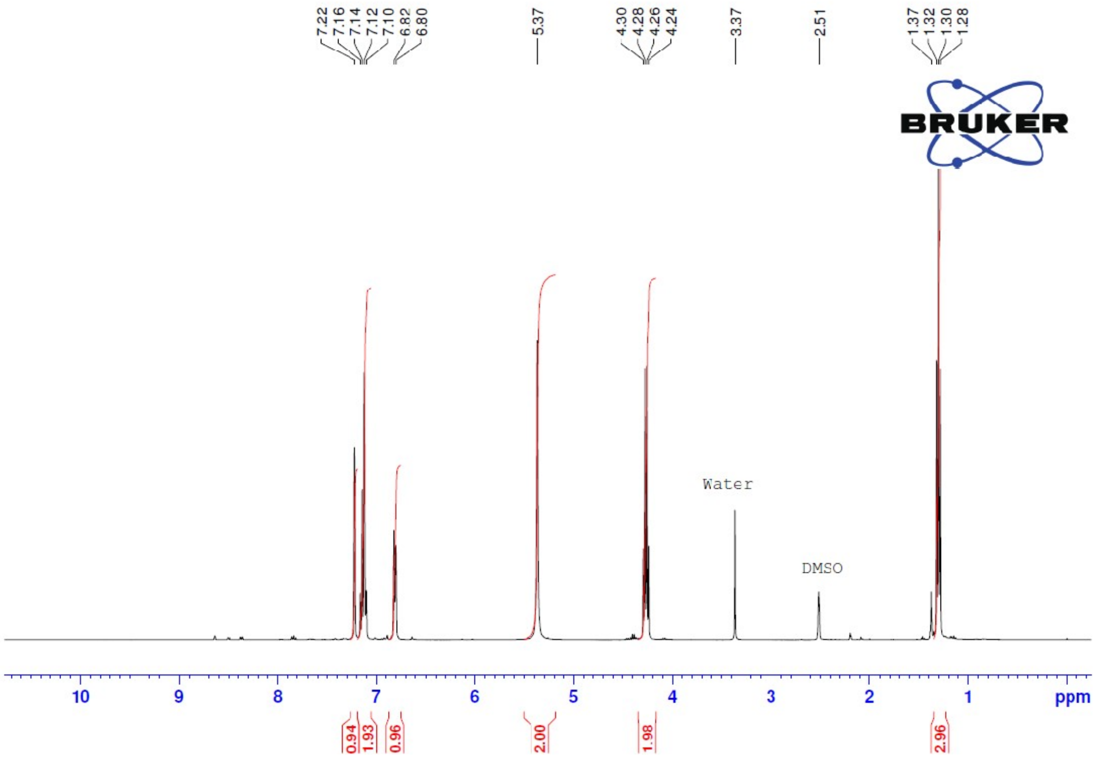
3-Chloroaniline (2m): [1]H-NMR (400 MHz, DMSO):δ 7.89 H_{CAr} (d, J = 4.95 Hz, 1H), 7.34 H_{CAr} (t, J = 7.65, 1H), 6.41-6.48 H_{CAr} (m, 2H), 5.83 H_{NH2} (s, 2H).



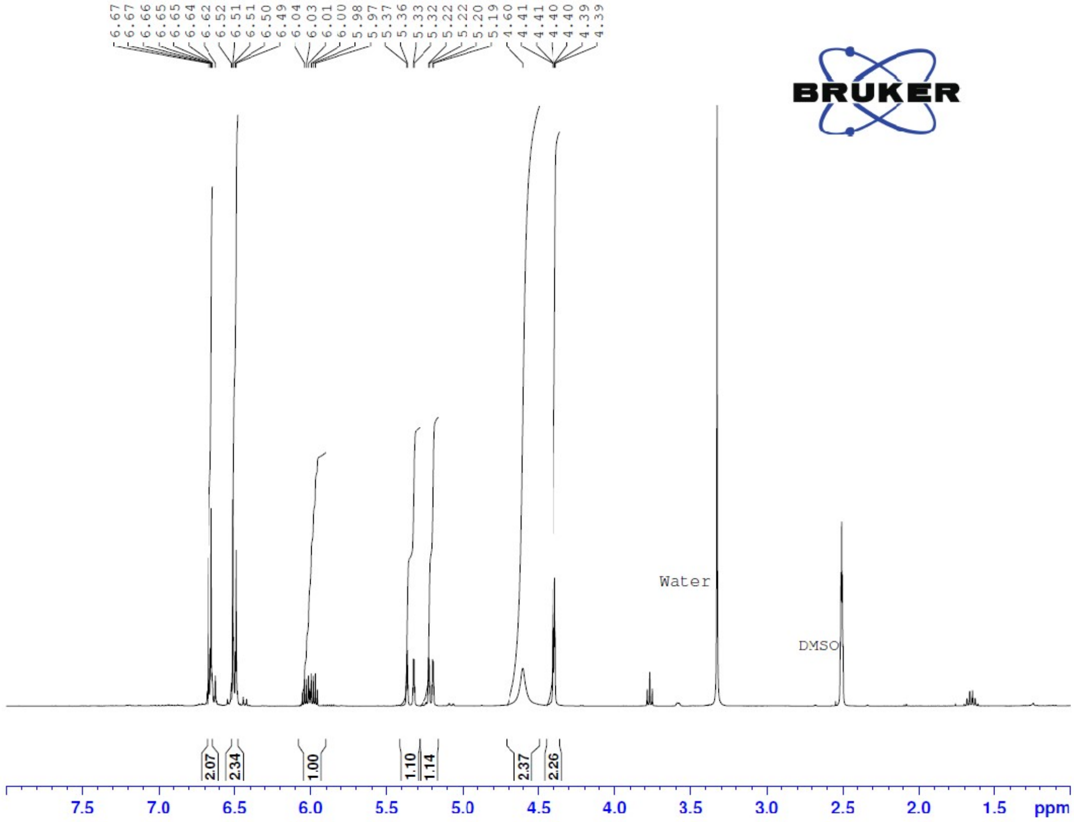
3-nitroaniline (2n): ^{1}H NMR (400 MHz, DMSO): δ 7.40 H_{CAr} (m, 1H), 7.31 H_{CAr} (m, 1H), 7.26 H_{CAr} (m, 1H), 6.96 H_{CAr} (m, 1H), 5.80 H_{NH2} (s, 2H).



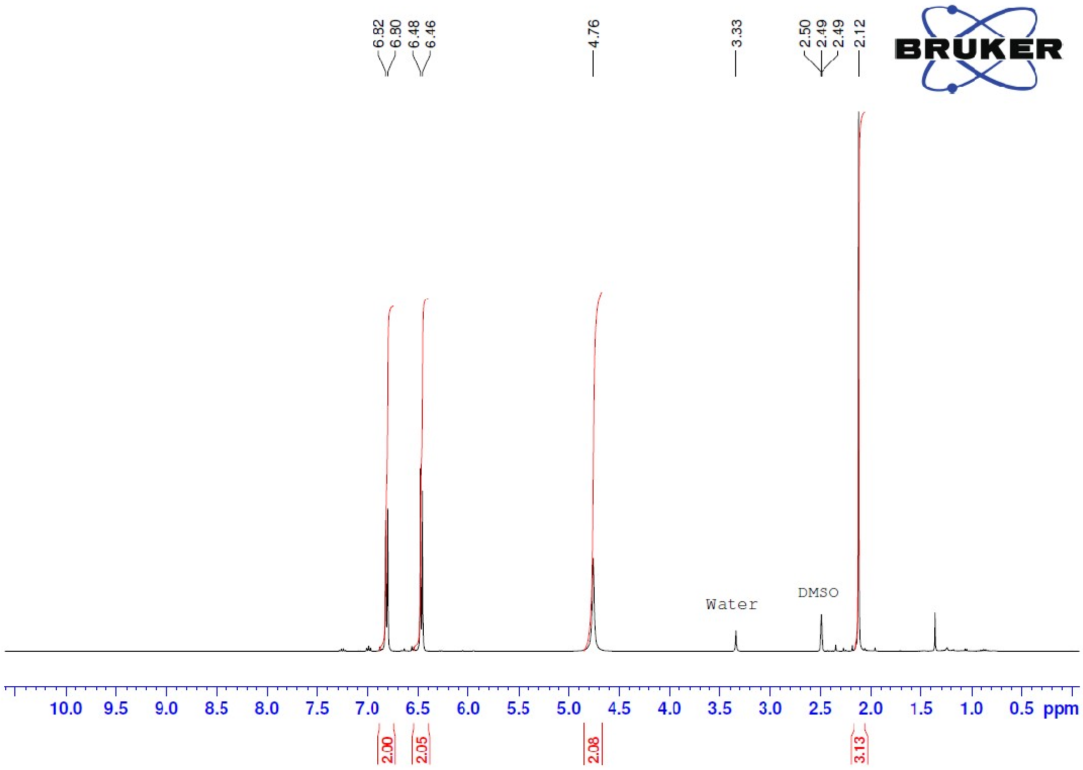
Ethyl 3-aminobenzoate (2o): ^{1}H NMR (400 MHz, DMSO):δ 7.22 H_{CAr} (s, 1H), 7.14 H_{CAr} (m, 1H), 6.82 H_{CAr} (m, 1H), 5.37 H_{NH2} (s, 2H), 4.28 (q, 2H), 1.32 (t, 3H)



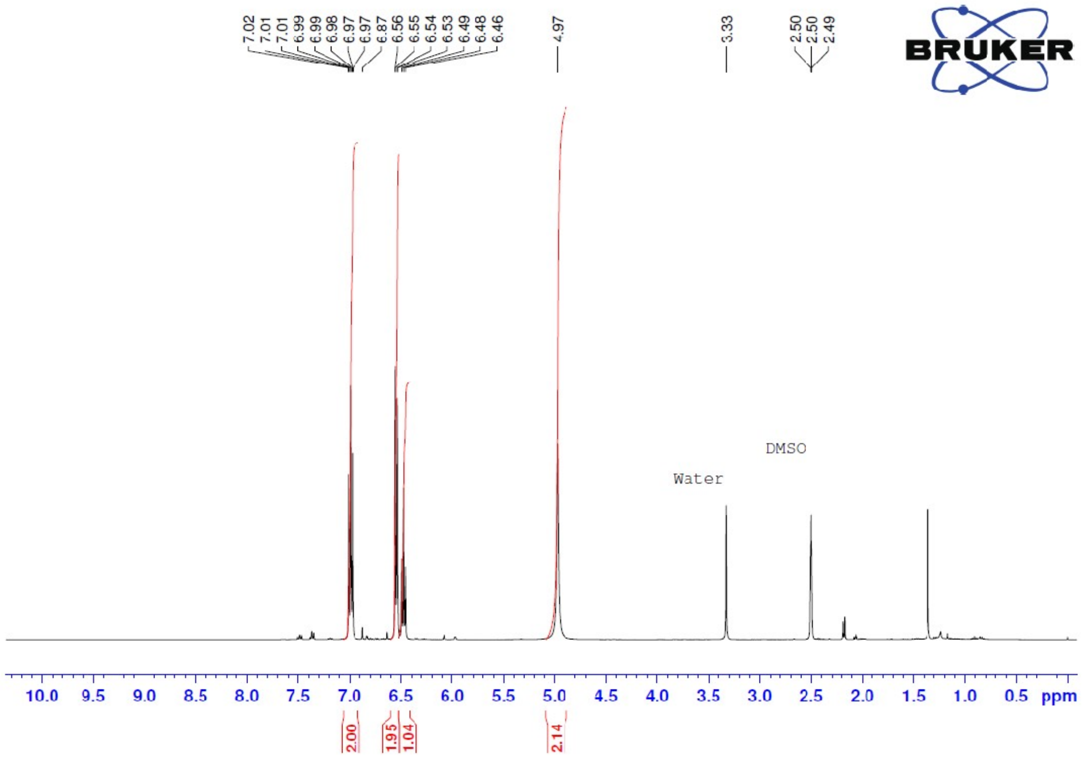
4-(Allyloxy)aniline (2q): [1]H-NMR (400 MHz, DMSO):δ 6.67-6.60 H_{CAr} (m, 2H), 6.52-647 H_{CAr} (m, 2H), 6.05-5.94 H_C (m, 1H), 5.36 H_C (q, J=1.68, 1H), 5.36 H_C (dq, J_1=17.28, J_2=1.77 , 1H), 5.19 H_C (dq, J_1=10.51, J_2=1.61 , 1H), 4.60 H_{NH2} (s, 2H), 4.39 H_C (dt, J_1=5.16, J_2=1.45, 2H)



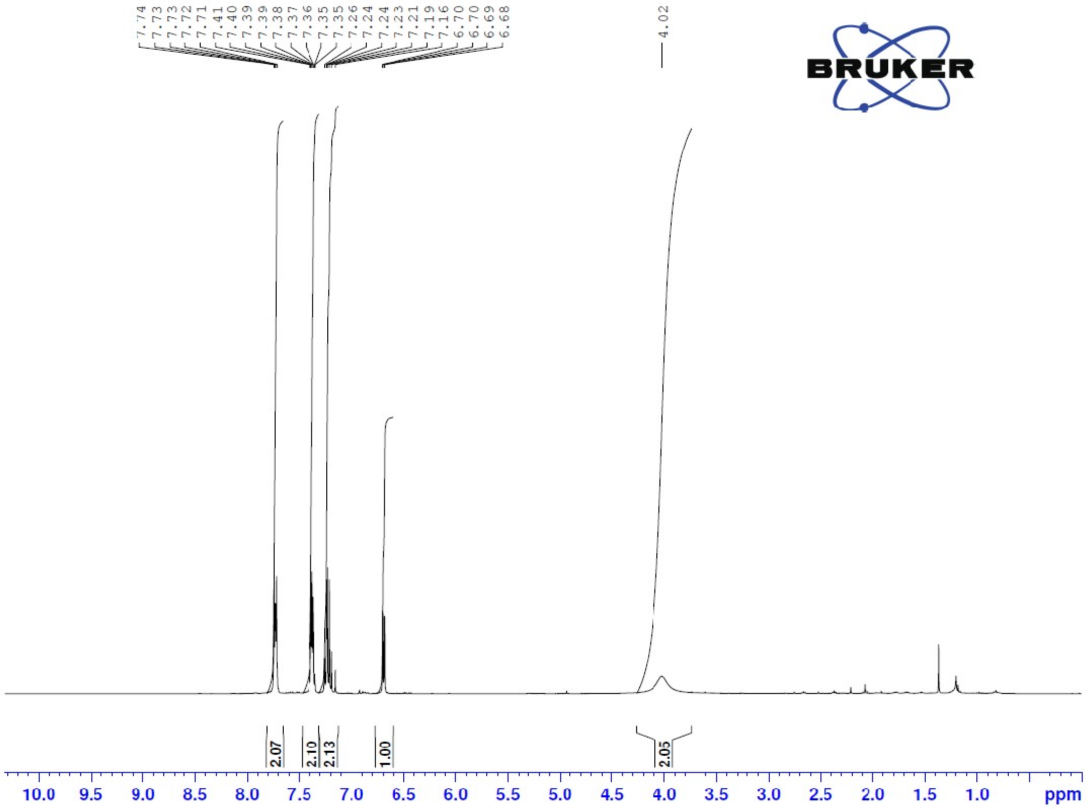
4-Toluidine (2r): ^{1}H-NMR (400 MHz, DMSO):δ 6.81 H_{CAr} (d, J=8.14, 2H), 6.46 H_{CAr} (d, J = 8.30 Hz, 2H), 4.75 H_{NH2} (s, 2H), 2.11 H_{C} (s, J = 2.11, 3H).



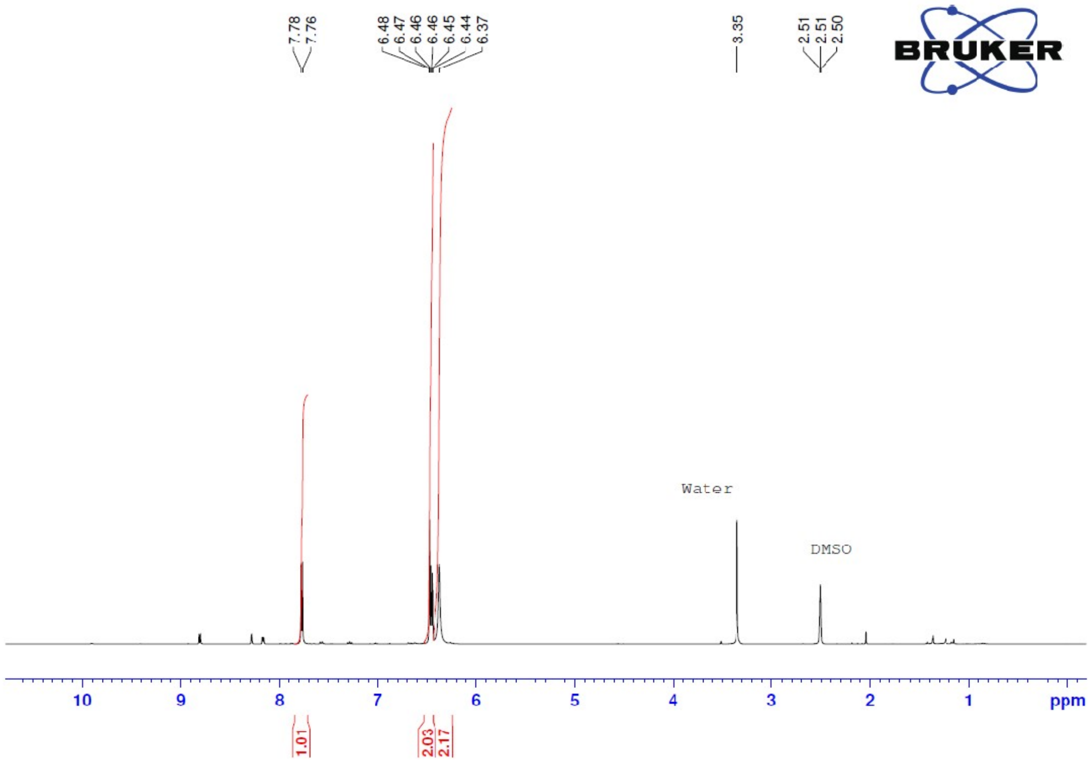
Aniline (2s): ^{1}H-NMR (400 MHz, DMSO):δ 6.99 H_{CAr} (t, *J*=7.75, 2H), 6.55 H_{CAr} (d, *J* = 3.99 Hz, 2H), 6.47 H_{CAr} (t, *J* = 7.21, 1H), 4.97 H_{NH2} (s, 2H).



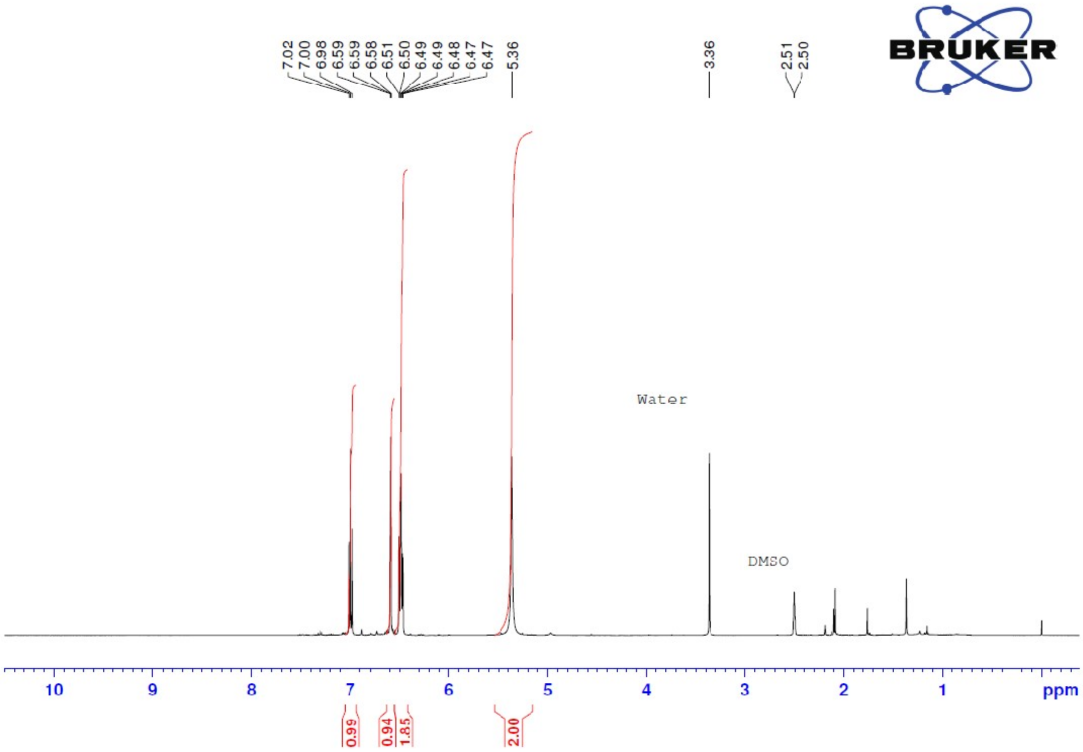
1-aminonaphtalene (2t): ^{1}H-NMR (400 MHz, DMSO):δ 7.73 H_{CAr} (m, 2H), 7.37 H_{CAr} (m, 2H), 7.23 H_{CAr} (m, 2H), 6.69 H_{CAr} (dd, *J1* =6.85, *J2* = 1.33, 1H), 4.06 H_{NH2} (s, 2H).



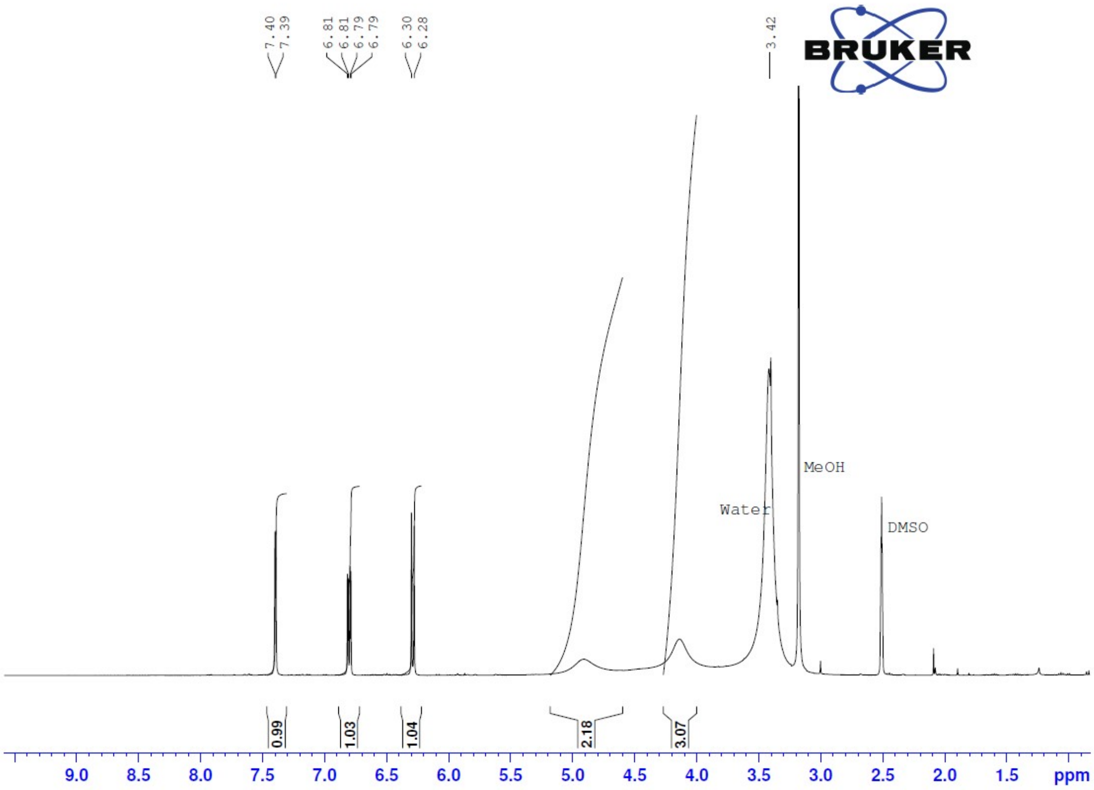
2-Chloro-4-aminopyridine (2u): ^{1}H-NMR (400 MHz, DMSO):δ 7.77 H_{CAr} (d, J = 5.50 Hz, 1H), 6.47 H_{CAr} (d, J = 1.86 Hz, 1H), 6.45 H_{CAr} (dd, $J1$ = 5.63, $J2$ = 1.97, 1H), 6.37 H_{NH2} (s, 2H).



2-Aminopyridine (2v): [1]H-NMR (400 MHz, DMSO):δ 6.99 H_{CAr} (t, *J*=7.99, 1H), 6.58 H_{CAr} (t, *J* = 2.06 Hz, 1H), 6.49 H_{CAr} (q, *J* = 6.16, 2H), 5.36 H_{NH2} (s, 2H).



2,5-Aminopyridine (2v): [1]H-NMR (400 MHz, DMSO):δ 7.39 H_{CAr} (t, *J*=2.45, 1H), 6.80 H_{CAr} (dd, *J1* = 2.45 Hz, *J2* = 9.18 Hz 1H), 6.28 H_{CAr} (d, *J* = 9.16, 1H), 4.93 H_{NH2} (br, s, 2H), 4.11 H_{NH2} (br, s, 2H).



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