Supplementary Materials: Reduction of Nitroarenes into Aryl Amines and *N*-Aryl hydroxylamines via Activation of $NaBH_4$ and Ammonia-Borane Complexes by Ag/TiO_2 Catalyst

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Table S1. Textural properties of mesoporous mesoporous TiO_2 nanoparticle assemblies (MTA) and Ag/MTA catalysts.

Sample	Ag loading [a] (wt %)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
MTA		149	0.27	7.1
2% Ag/MTA	2.1	126	0.23	7.1
3% Ag/MTA	2.9	128	0.23	5.6, 7.3
4% Ag/MTA	4.0	125	0.22	5.5, 7.4
7% Ag/MTA	6.8	119	0.21	5.4, 7.4

[a] Weight percent of Ag loading according to the Energy dispersive X-ray spectroscopy (EDS) data.

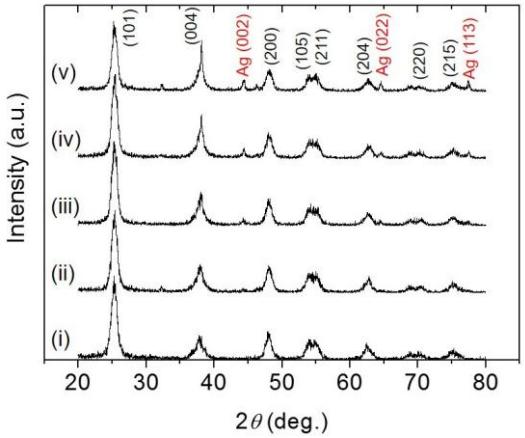


Figure S1. X-ray diffraction (XRD) patters of mesoporous samples: (**i**) MTA; (**ii**) 2% Ag/MTA; (**iii**) 3% Ag/MTA; (**iv**) 4% Ag/MTA; and (**v**) 7% Ag/MTA.

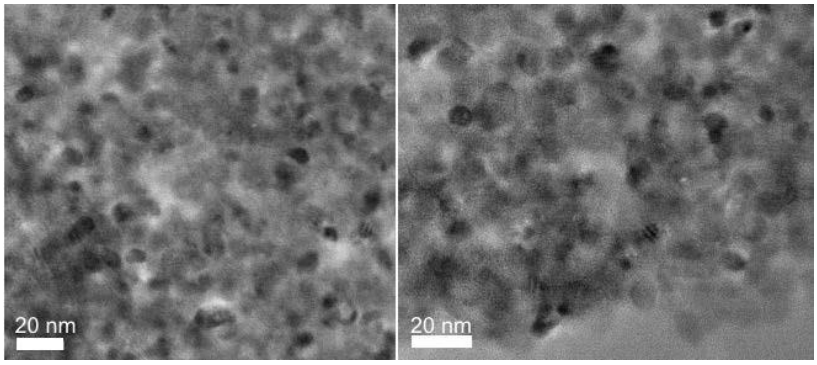


Figure S2. Typical transmission electron microscopy (TEM) images of mesoporous 4% Ag/MTA sample, showing that individual AgNPs (appeared as dark spots as evidenced by high resolution TEM (HRTEM) and fast Fourier transformation (FFT) analysis (see Figure 1c in the text)) are uniformly dispersed on the surface of TiO_2.

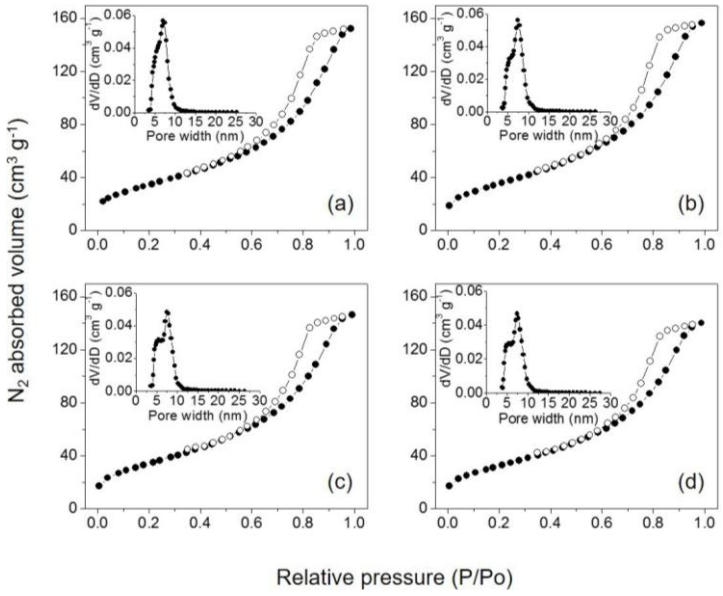


Figure S3. N_2 adsorption-desorption isotherms at 77 K and the corresponding non-local density functional theory (NLDFT) pore size distributions (insets) for the mesoporous: (**a**) 2% Ag/MTA; (**b**) 3% Ag/MTA; (**c**) 4% Ag/MTA; and (**d**) 7% Ag/MTA materials.

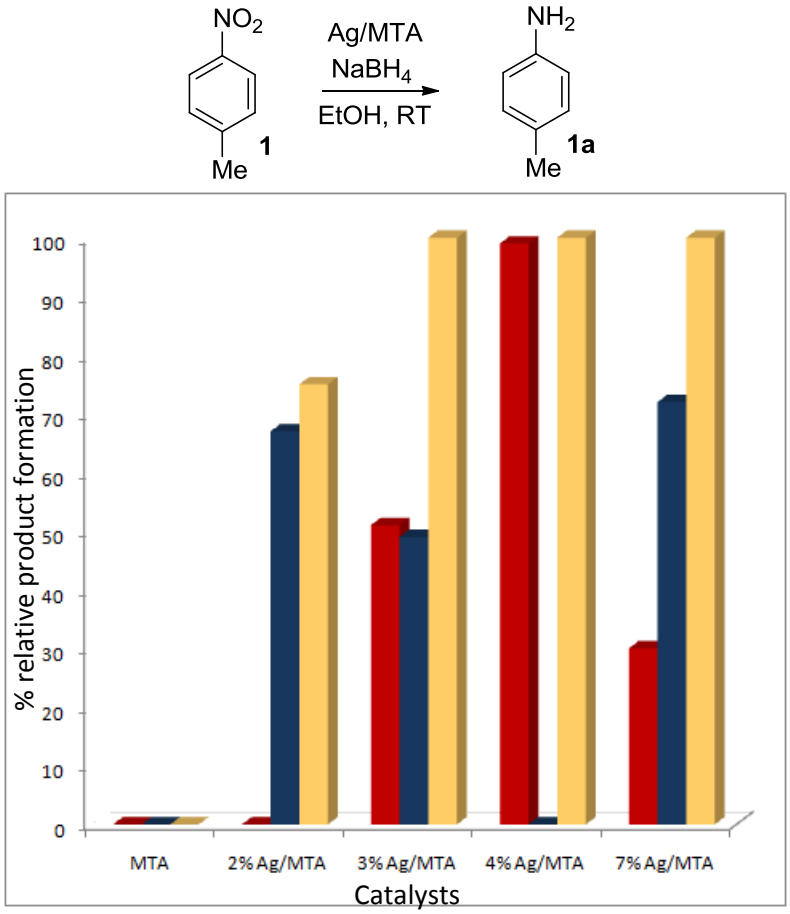


Figure S4. Catalysts evaluation based on the relative conversions of (**1**) to amine or to the condensation products azo, azoxy and hydrazo arenes, after 4 h. First (red) columns correspond to the relative yield of amine (**1a**); second (blue) columns correspond to the summary of the relative yields of the dimeric products; and third (yellow) columns correspond to the reaction conversion based on the consumption of **1**.

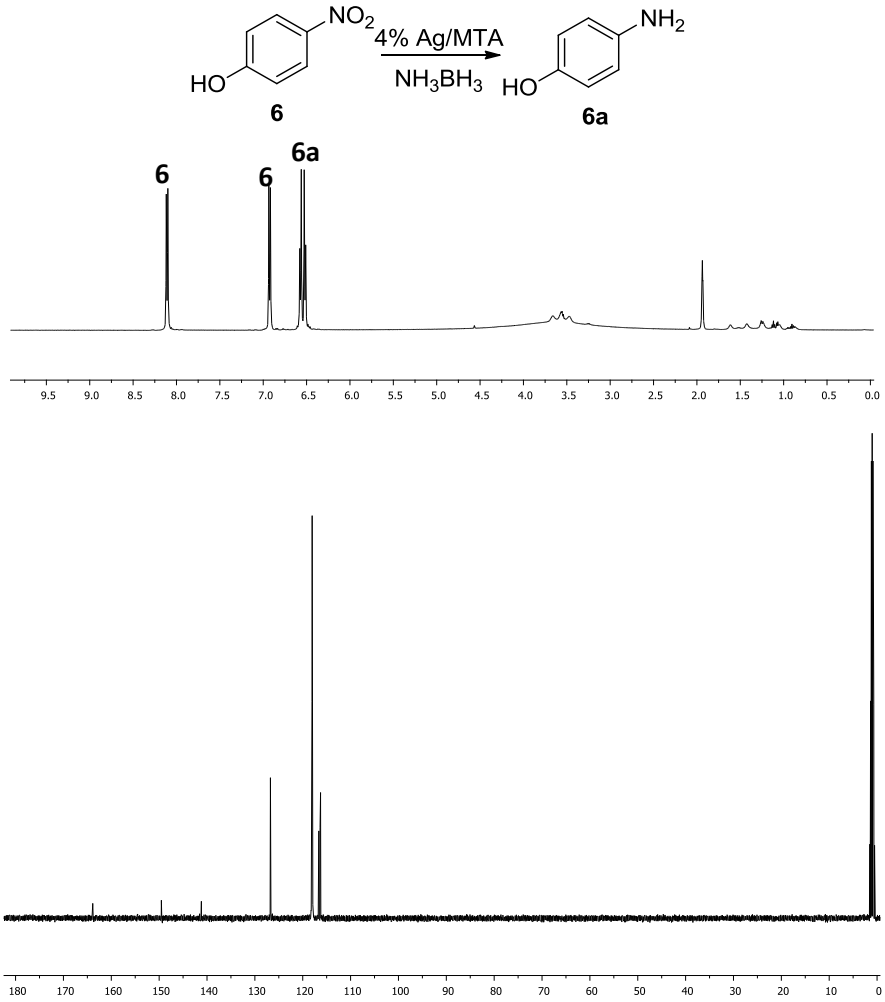


Figure S5. ^{1}H-NMR and ^{13}C-NMR of the crude mixture of the reduction of 6 in the presence of NH_3BH_3 catalyzed by 4% Ag/MTA.

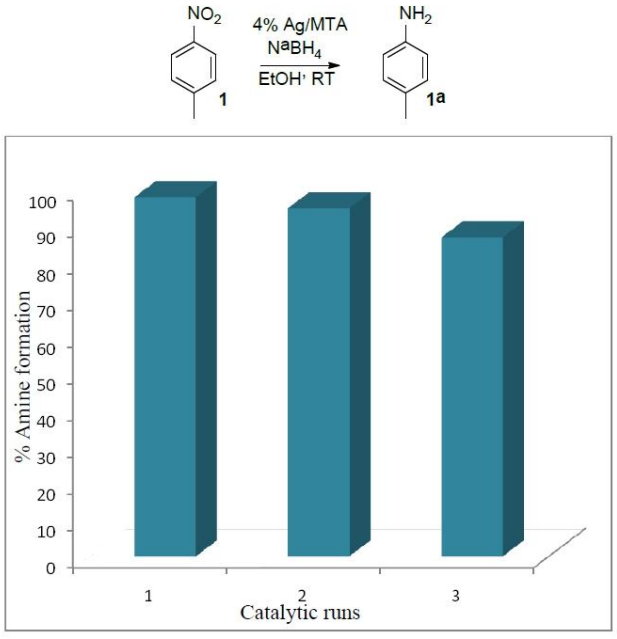


Figure S6. Recycling study of the mesoporous 4% Ag/MTA catalyst (Experimental conditions: 0.2 mmol of p-nitrotoluene, 20 mg of catalyst, 1.2 mmol of $NaBH_4$, 2 mL of ethanol, room temperature, t = 6 h).

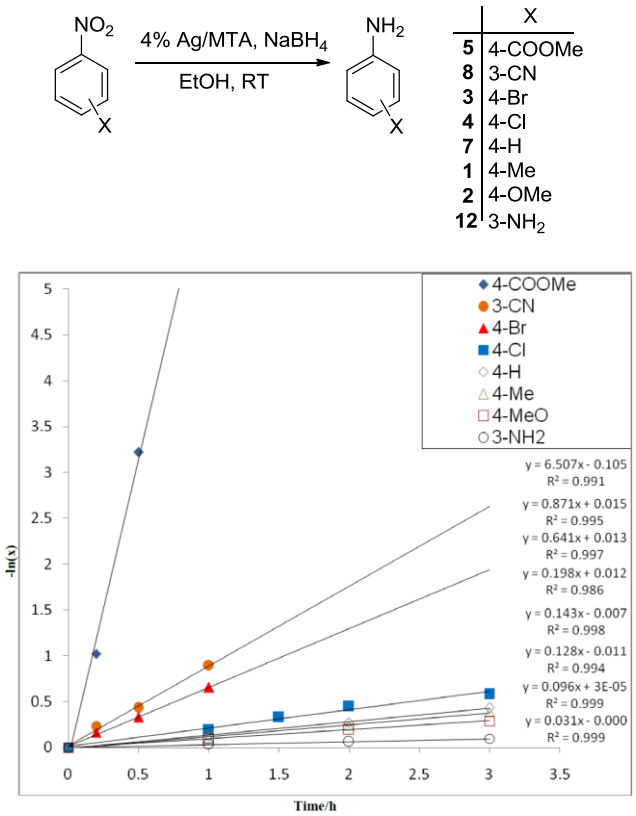


Figure S7. Kinetic plots for the nitroarenes **1**, **2**, **3**, **4**, **5**, **7**, **8** and **12** consumptions catalyzed by 4% Ag/MTA using $NaBH_4$ (4 mol-excess) as reducing agent.

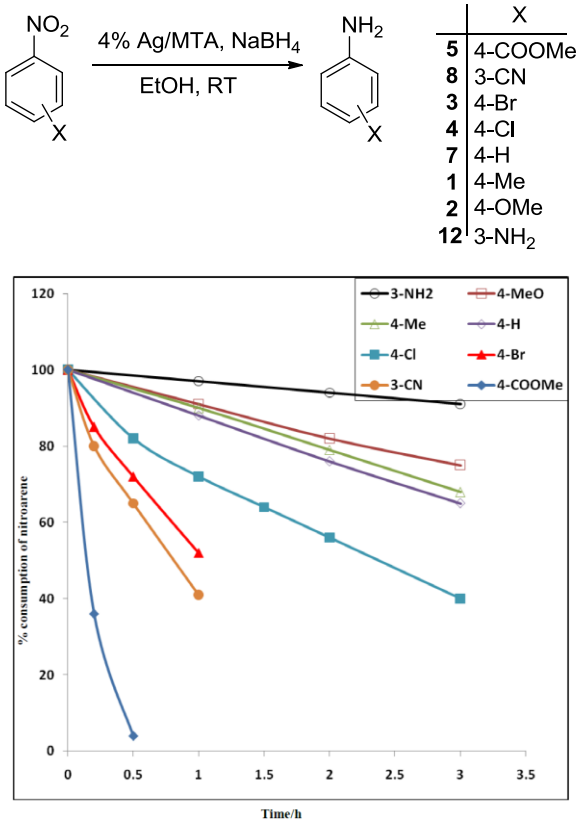


Figure S8. Profile of the nitroarenes **1**, **2**, **3**, **4**, **5**, **7**, **8** and **12** consumptions catalyzed by 4% Ag/MTA using $NaBH_4$ (4 mol-excess) as reducing agent.

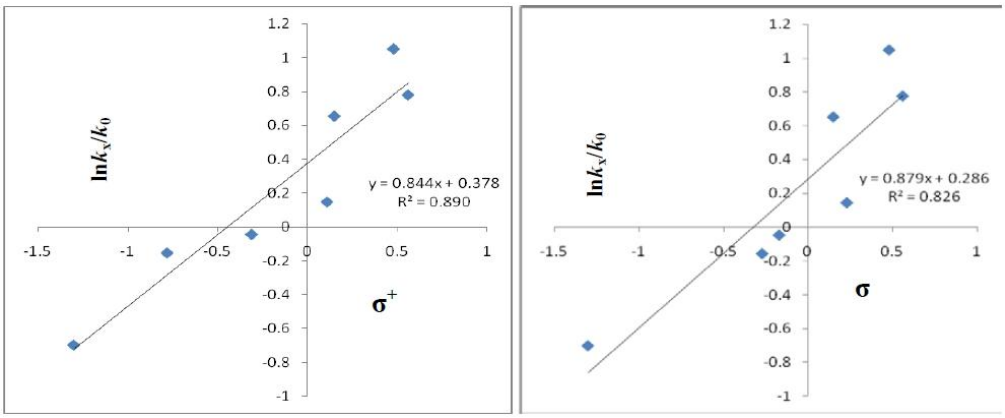


Figure S9. Hammett-type kinetic plots for the nitroarenes **1**, **2**, **3**, **4**, **5**, **8** and **12** reductions catalyzed by 4% Ag/MTA using $NaBH_4$ as reducing agent. The values for σ^+ and σ were taken from the textbook [1].

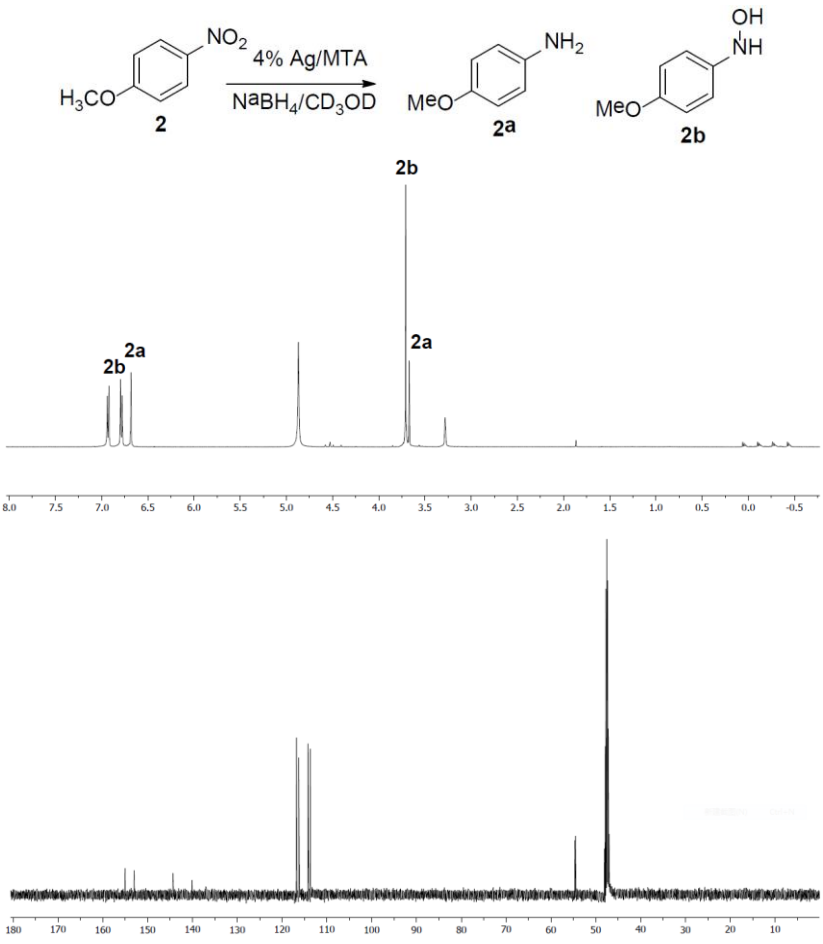


Figure S10. ^{1}H-NMR and ^{13}C-NMR of the crude mixture of the reduction of **2** in the presence of $NaBH_4$ in CD_3OD, catalyzed by 4% Ag/MTA, at initial reaction time (<1 h).

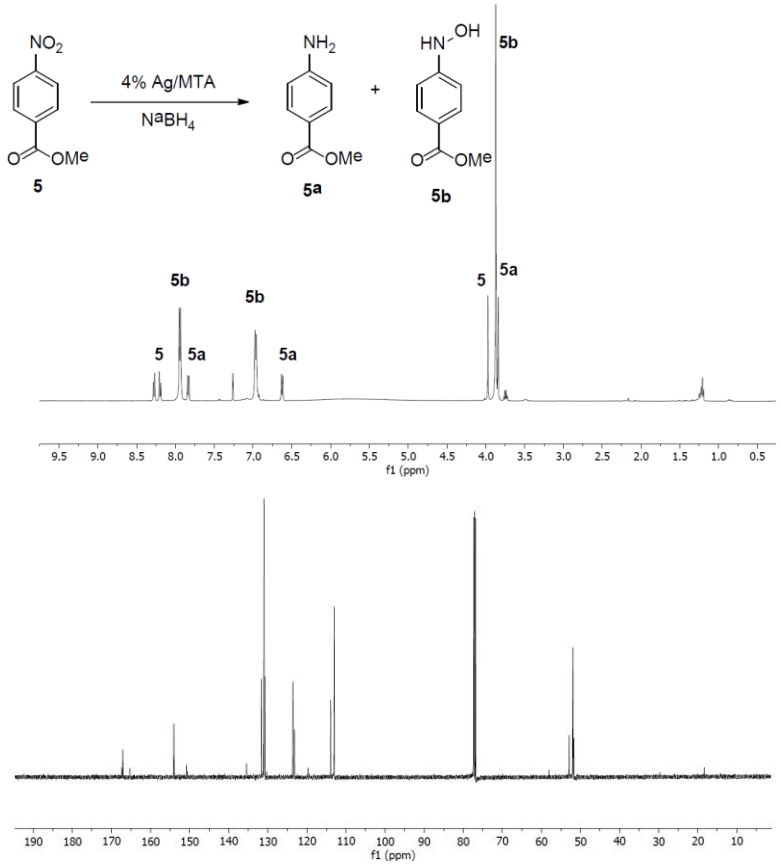


Figure S11. ^{1}H-NMR and ^{13}C-NMR of the crude mixture of the reduction of **5** in the presence of $NaBH_4$, catalyzed by 4% Ag/MTA, at initial reaction time (<0.5 h).

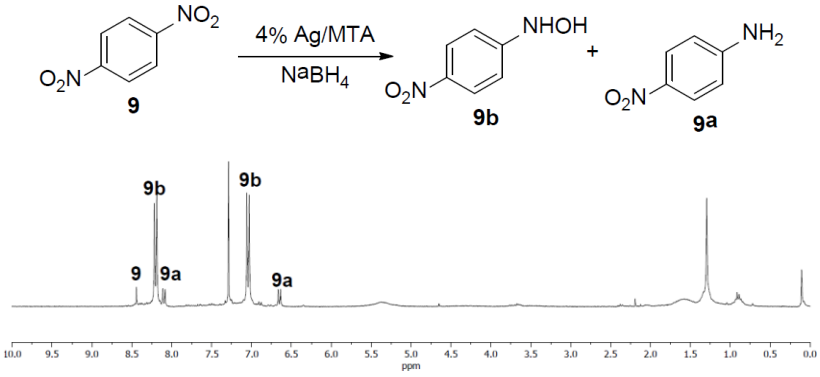
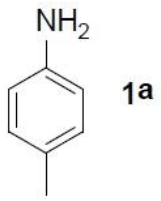


Figure S12. ^{1}H-NMR of the crude mixture of the reduction of **9** in the presence of $NaBH_4$, catalyzed by 4% Ag/MTA, at initial reaction time (<0.5 h).

^{1}H-NMR and ^{13}C-NMR Data

Toluidine [2,3]

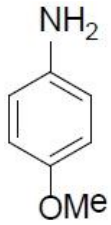


1a

^{1}H-NMR (300 MHz, $CDCl_3$): 6.91 (d, 2H, *J* = 8.5 Hz), 6.56 (d, 2H, *J* = 8.5 Hz), 3.49 (br, 2H, -NH_2), 2.19

(s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 143.6, 129.5, 127.6, 115.1, 20.2.

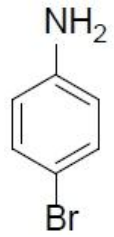
4-Methoxyaniline [2]



2a

^{1}H-NMR (300 MHz, $CDCl_3$): 6.75 (d, 2H, *J* = 9 Hz), 6.65 (d, 2H, *J* = 9 Hz), 3.74 (s, 3H), 3.48 (br, 2H, -NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): 152.8, 139.9, 116.4, 114.7, 55.7.

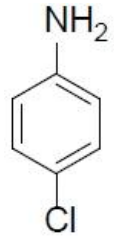
4-Bromoaniline [3]



3a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.22 (d, 2H, *J* = 8.5 Hz), 6.53 (d, 2H, *J* = 8.5 Hz), 3.65 (br, 2H, -NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): 145.4, 132.0, 116.7, 110.2.

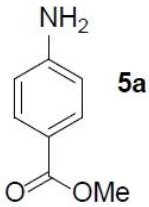
4-Chloroaniline [3]



4a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.04 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.5 Hz), 3.62 (br, 2H, -NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): 144.8, 128.9, 123.0, 116.0.

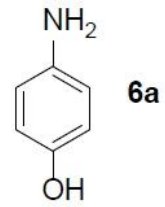
Methyl 4-aminobenzoate [4]



5a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.83 (d, 2H, *J* = 8.5 Hz), 6.62 (d, 2H, *J* = 8.5 Hz), 4.09 (br, 2H, -NH_2), 3.84 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 167.2, 150.8, 131.5, 119.8, 113.7, 51.5.

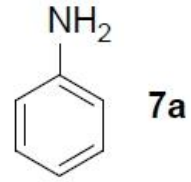
4-Aminophenol [3]



6a

^{1}H-NMR (300 MHz, CD_3OD): 6.56 (d, 2H, *J* =9 Hz), 6.51 (d, 2H, *J* = 9 Hz), 3.40 (br, 2H, -NH_2); ^{13}C-NMR (75 MHz, CD_3OD): 149.7, 141.7, 116.8, 116.7.

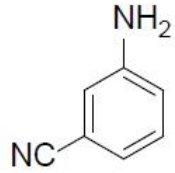
Aniline [2]



7a

^{1}H-NMR: (300 MHz, $CDCl_3$): 7.13 (t, 2H, *J* = 8.5 Hz), 6.73 (t, 1H, *J* = 8.5 Hz), 6.65 (d, 2H, *J* = 8.5 Hz), 3.42 (br, 2H, -NH_2); ^{13}C-NMR: (75 MHz, $CDCl_3$): 146.2, 129.0, 118.3, 114.9.

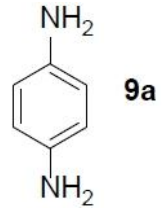
3-Aminobenzonitrile [5]



8a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.18 (t, 1H, *J* = 7.5 Hz), 6.96 (d, 1H, *J* = 7.5 Hz), 6.89 (s, 1H), 6.85 (d, 1H, *J* = 7.5 Hz), 3.86 (br, 2H, -NH_2); ^{13}C-NMR (75 MHz, CDCl3): 146.9, 129.9, 121.8, 119.2, 119.1, 117.5, 112.9.

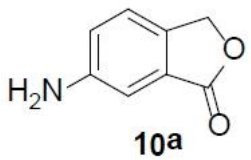
4-Aminoaniline [2]



9a

^{1}H-NMR (300 MHz, $CDCl_3$): 6.56 (s, 4H), 3.19 (br, 4H, -NH_2); ^{13}C-NMR (75 MHz, $CDCl_3$): 138.6, 116.7.

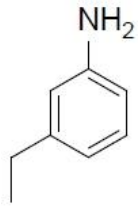
6-aminoisobenzofuran-1(3*H*)-one [6]



10a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.21 (d, 1H, *J* = 8.0 Hz), 7.13 (d, 1H, *J* = 2.0 Hz), 6.95 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 5.20 (s, 2H), 3.92 (s, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): 171.4, 147.5, 136.4, 127.0, 122.7, 121.6, 109.8, 69.6.

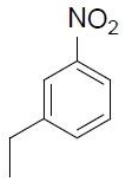
3-Ethylaniline [2,3]



11a

^{1}H-NMR (300 MHz, $CDCl_3$): 7.07 (t, 1H, *J* = 7.5 Hz), 6.61 (d, 1H, *J* = 7.5 Hz), 6.54 (s, 1H), 6.51 (d, 1H, *J* = 7.5 Hz), 3.56 (s, 2H), 2.56 (q, 2H, *J* = 7 Hz), 1.21 (t, 3H, *J* = 7 Hz).

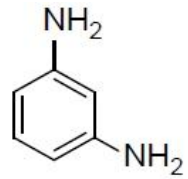
1-Ethyl-3-nitrobenzene



11c

^{1}H-NMR (300 MHz, $CDCl_3$): 7.76-7.72 (m, 1H), 7.43 (t, 1H, *J* =7.7 Hz), 7.31 (d, 2H, *J* = 7.7 Hz), 2,77 (q, 2H, *J* = 7.5 Hz). 1.32 (t, 3H, *J* = 7.5 Hz).

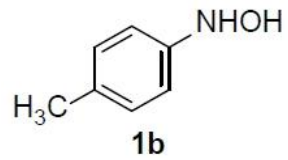
3-amino aniline [3,4]



12a

^{1}H-NMR (500 MHz, $CDCl_3$): 6.94 (t, 1H, *J* = 7.9 Hz), 6.12 (dd, 2H, J_1 = 7.9 Hz, J_2 = 2.0 Hz), 6.04 (t, 1H, *J* = 2.0 Hz), 3.56 (br, 4H, -NH_2); ^{13}C-NMR (125 MHz, $CDCl_3$): 147.5, 130.2, 106.0, 101.9.

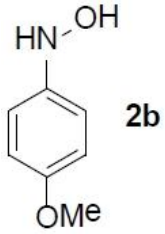
N-(p-tolyl)hydroxylamine [7,8]



1b

^{1}H-NMR (300 MHz, $CDCl_3$): 7.09 (d, 2H, *J* = 8.4 Hz), 6.92 (d, 2H, *J* = 8.4 Hz), 2.30. ^{13}C-NMR (75 MHz, $CDCl_3$): 147.3, 132.0, 129.5, 115.2, 20.6.

N-(4-methoxyphenyl)hydroxylamine [7,8]

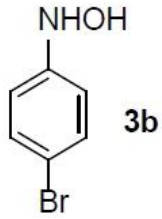


2b

^{1}H-NMR (300 MHz, CD_3OD): 6.94 (d, 2H, *J* = 9 Hz), 6.80 (d, 2H, *J* = 9 Hz), 3.72 (s, 3H); ^{13}C-NMR (125 MHz, CD_3OD): 156.5, 145.8, 118.3, 115.7, 56.1; MS *m*/*z* (ESI) calcd for $C_7H_9NO_2$ $(M-H)^+$ 138.06,

found 137.85.

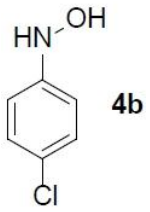
N-(4–bromophenyl)hydroxylamine [7]



3b

^{1}H-NMR (300 MHz, $CDCl_3$): 7.38 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 5.51 (br, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.9, 131.9, 116.2, 114.5.

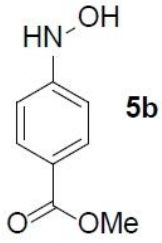
N-(4-chlorophenyl)hydroxylamine [7]



4b

^{1}H-NMR (300 MHz, $CDCl_3$): 7.24 (d, 2H, *J* = 8.8 Hz), 6.93(d, 2H, *J* = 8.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): 148.3, 128.9, 127.2, 115.9. ^{1}H-NMR (500 MHz, CD_3OD): 7.17 (d, 2H, *J* = 8.5 Hz), 6.93 (d, 2H, *J* = 8.5 Hz); ^{13}C-NMR (125 MHz, CD_3OD): 151.8, 129.5, 126.2, 116.2. MS *m*/*z* (ESI) calcd for C_6H_6NOCl $(M-H)^+$ 142.56, found 142.41.

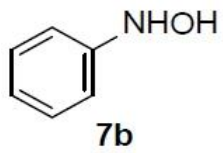
Methyl 4-(hydroxyamino)benzoate [7]



5b

^{1}H-NMR (300 MHz, $CDCl_3$): 7.96 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 3.88. ^{13}C-NMR (75 MHz, $CDCl_3$): 167.0, 154.0, 131.0, 123.5, 113.0, 51.8. ^{1}H-NMR (300 MHz, CD_3OD): 7.85 (d, 2H, *J* = 8.5 Hz), 6.93 (d, 2H, *J* = 8.5 Hz), 3.87 (s, 3H). MS *m*/*z* (ESI) calcd for $C_8H_9NO_3$ $(M-H)^+$ 166.05, found 165.90.

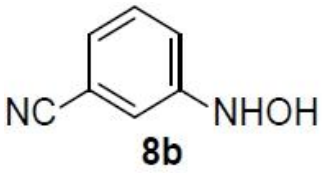
N-phenylhydroxylamine [7]



7b

^{1}H-NMR (300 MHz, $CDCl_3$): 7.31–7.28 (m, 2H), 7.02–6.97 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.7, 128.9, 122.4, 114.8.

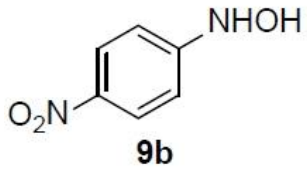
3–(Hydroxyamino)benzonitrile [7,8]



8b

^{1}H-NMR (500 MHz, $CDCl_3$): 7.34 (t, 1H, *J* = 8.0 Hz), 7.29 (s, 1H), 7.23 (d, 1H, *J* = 8.0 Hz), 7.15 (d, 1H, *J* = 8.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): 150.4, 129.6, 125.5, 118.9, 118.3, 117.1, 112.7. MS *m*/*z* (ESI) calcd for $C_7H_6N_2O$ $(M-H)^+$ 133.04, found 132.95.

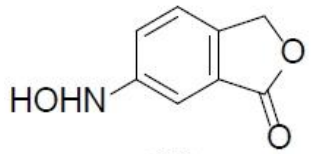
N-(4-nitrophenyl)hydroxylamine [7]



9b

^{1}H-NMR (300 MHz, Acetone-d_6): 8.11 (d, 2H, *J* = 9.2 Hz), 7.03 (d, 2H, *J* = 9.2 Hz). ^{13}C-NMR (75 MHz, Acetone-d_6): 157.9, 140.7, 126.0, 112.0.

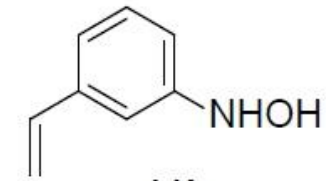
6-(hydroxyamino)isobenzofuran-1(3H)-one [7,8]



10b

^{1}H-NMR (500 MHz, Acetone-d_6): 8.15 (br, 1H), 7.46 (d, 1H, *J* = 8.3 Hz), 7.39 (s, 1H, *J* = 2.0 Hz), 7.31 (dd, 1H, J_1 = 8.3 Hz, J_2 = 1.7 Hz), 5.27 (s, 2H). ^{13}C-NMR (125 MHz, Acetone-d_6): 171.7, 148.6, 139.7, 127.2, 123.5, 120.9, 108.7, 70.3.

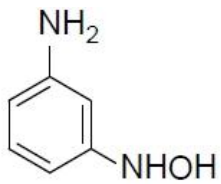
N-(3−Vinylphenyl)hydroxylamine [7]



11b

^{1}H-NMR (500 MHz, CD_3OD): 7.16 (t, 1H, *J* = 7.5 Hz), 7.05 (s, 1H), 6.93 (d, 1H, *J* = 7.5 Hz), 6.84 (d, 1H, *J* = 7.5 Hz), 6.67 (dd, 1H, J_1 = 18 Hz, J_2 = 12 Hz), 5.69 (d, 1H, *J* = 18 Hz), 5.15 (d, 1H, *J* = 12 Hz); ^{13}C-NMR (125 MHz, CD_3OD): 153.0, 139.8, 138.6, 130.2, 120.2, 116.4, 114.2, 113.3; MS *m*/*z* (ESI) calcd for C_8H_9NO $(M-H)^+$ 134.06, found 133.95.

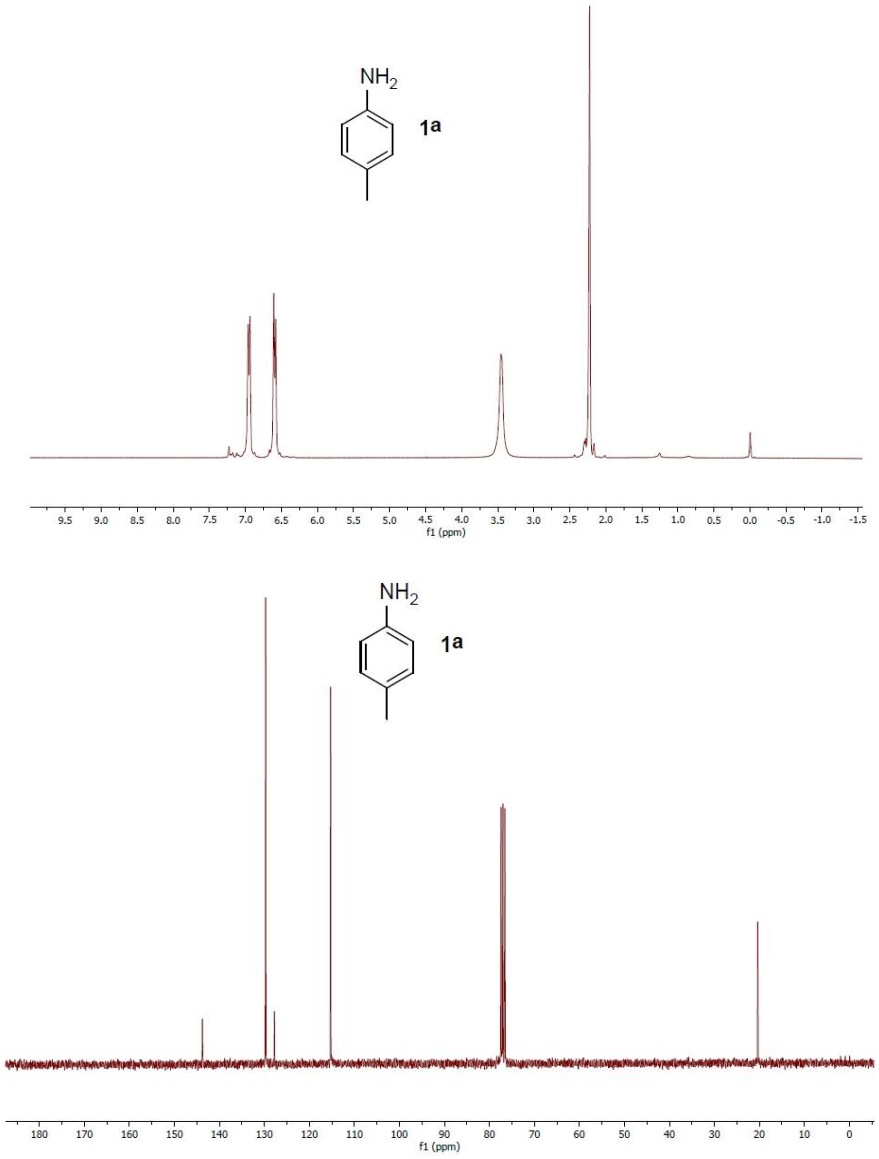
3-N-hydroxyl-aniline [7,8]

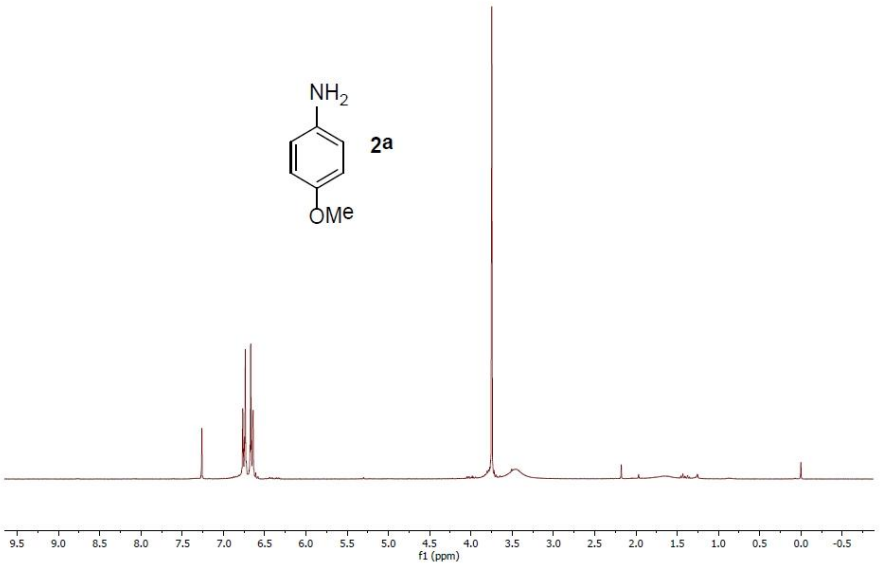


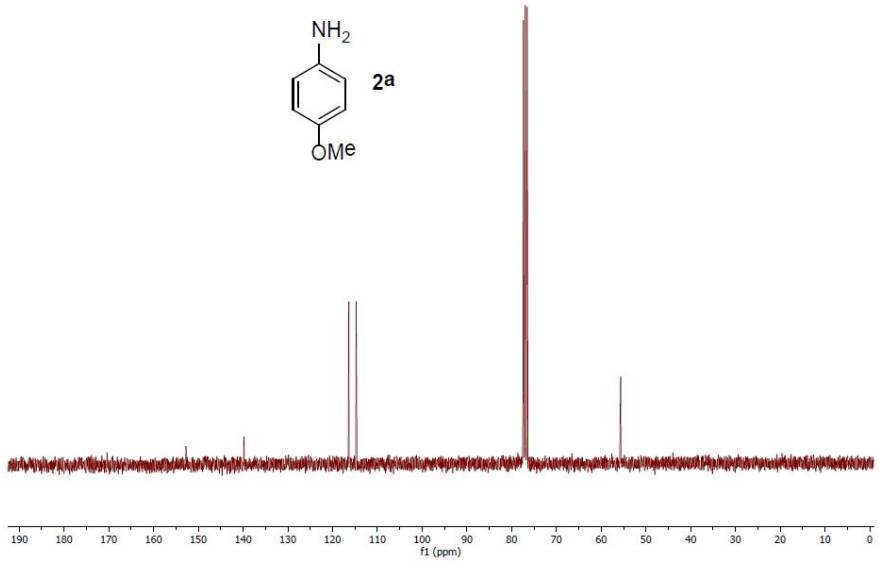
12b

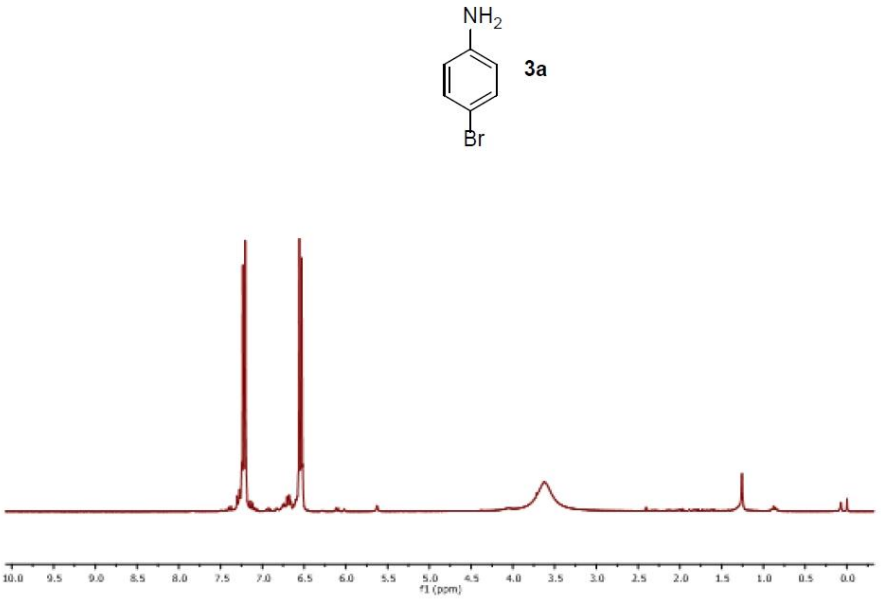
^{1}H-NMR (500 MHz, $CDCl_3$): 7.04 (t, 1H, *J* = 8.0 Hz), 6.38 (s, 1H), 6.36 (d, 1H, *J* = 8.0 Hz), 6.31 (d, *J* = 8.0 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$): 151.0, 147.2, 129.8, 109.2, 104.9, 101.4

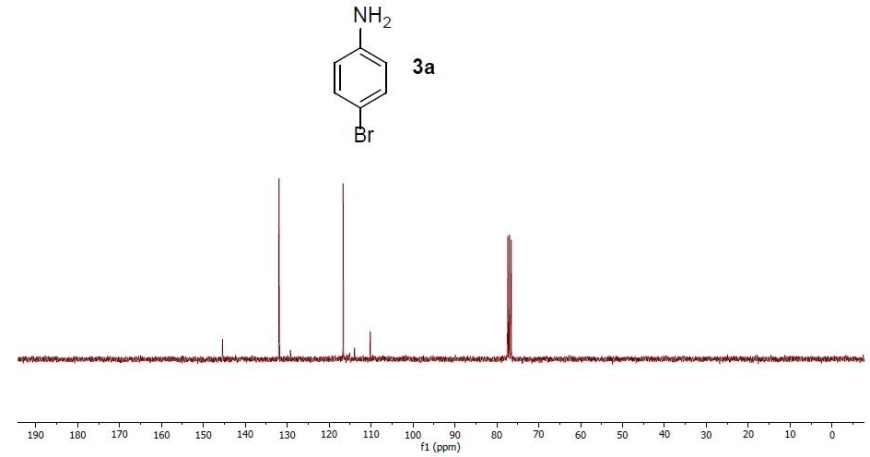
^{1}H-NMR and ^{13}C-NMR Spectra

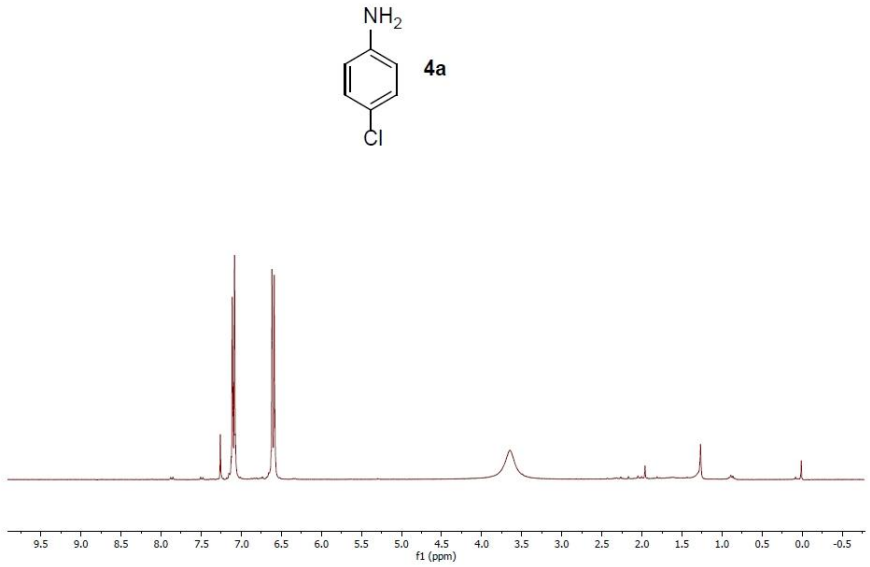


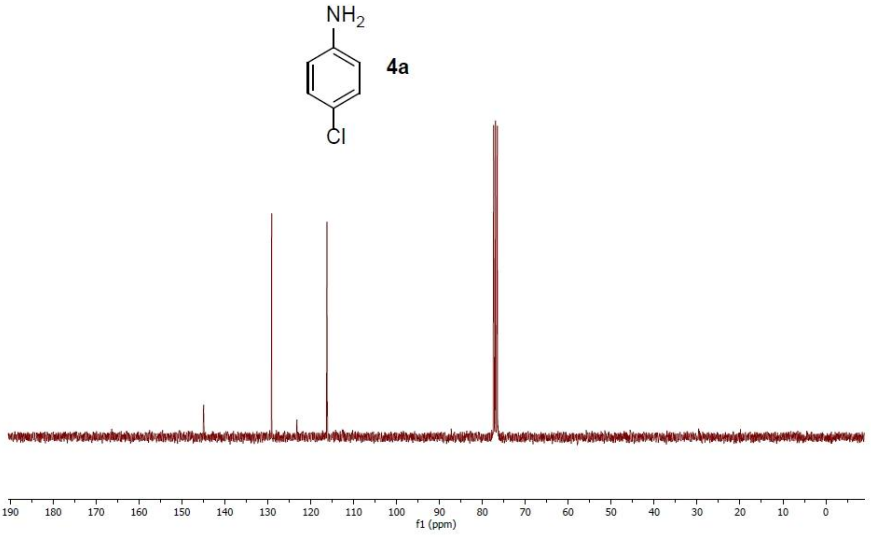

NH2
2a
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

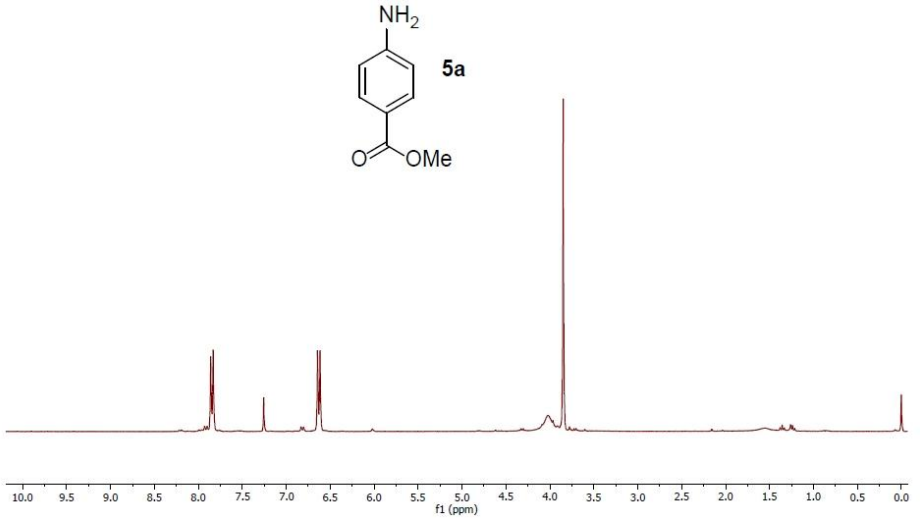

NH2
2a
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

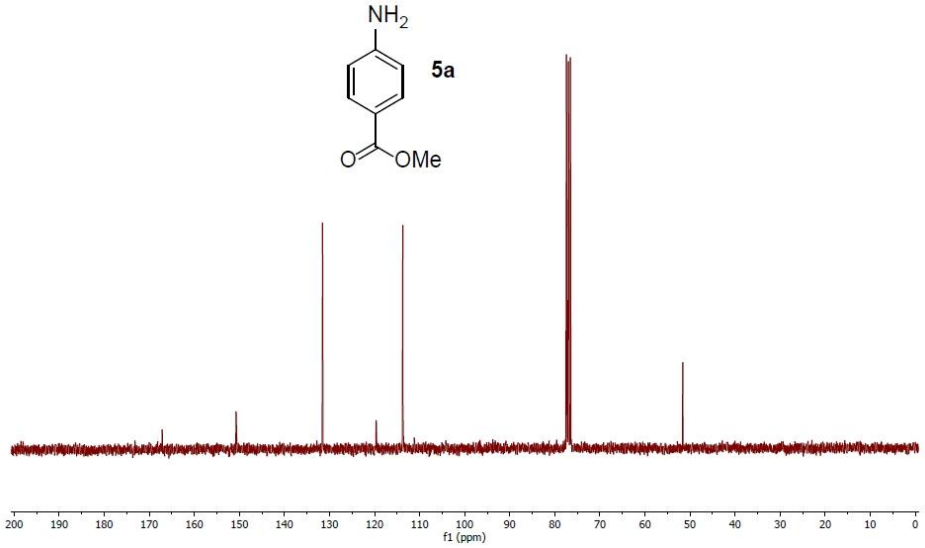

NH2
3a
Br
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

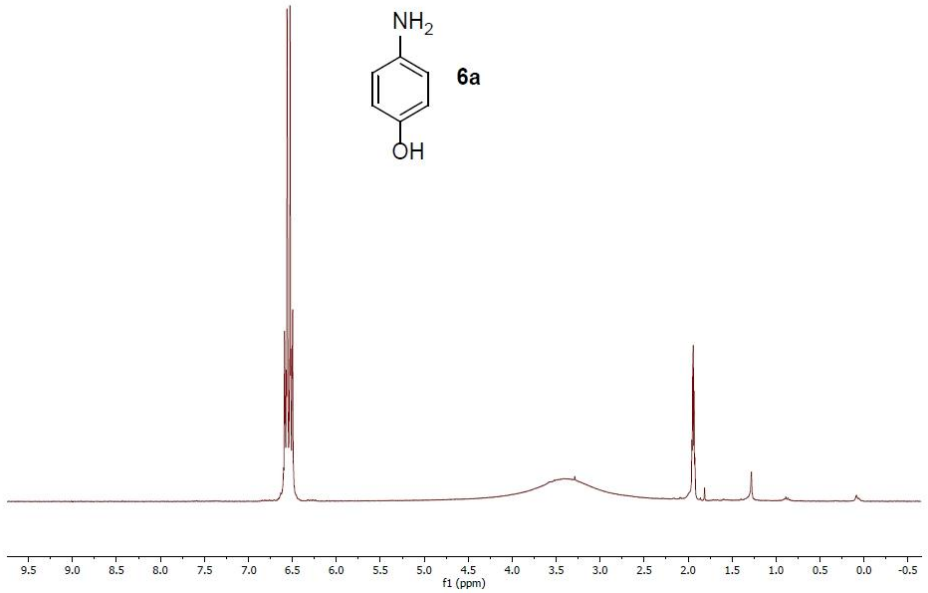

NH2
Br
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

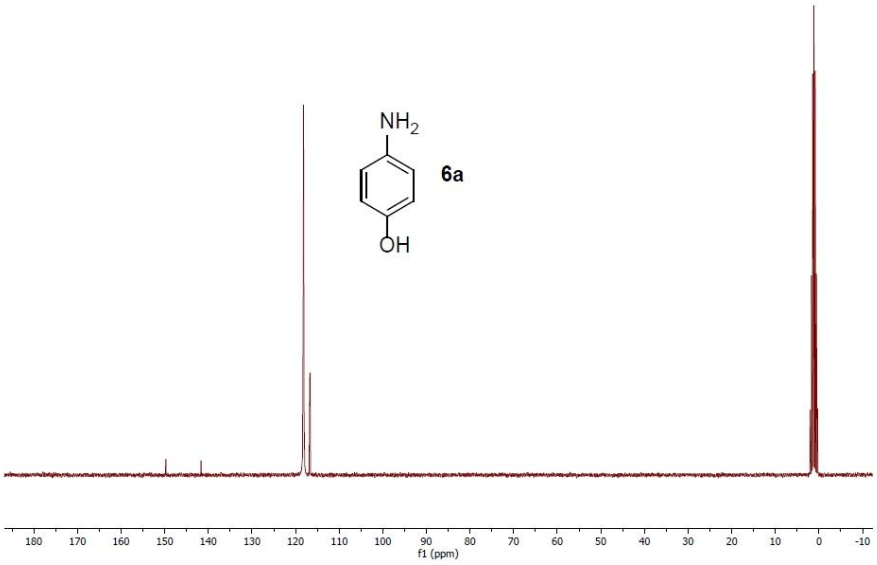

NH2
Cl
4a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

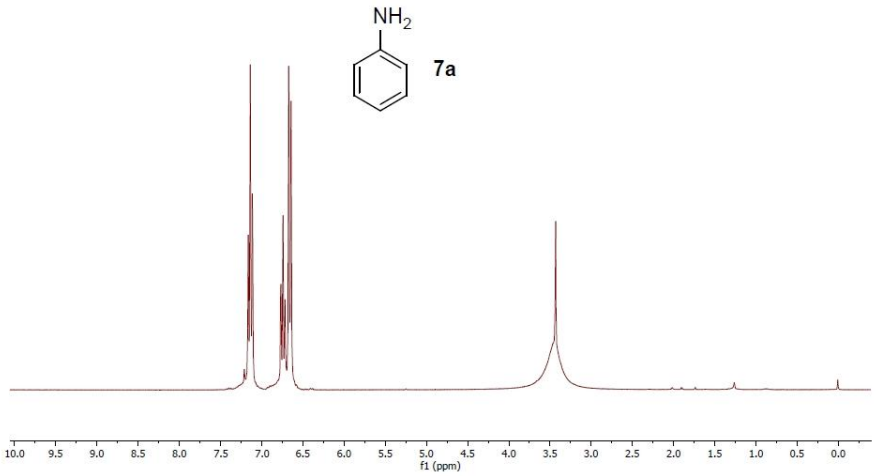

NH2
Cl
4a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

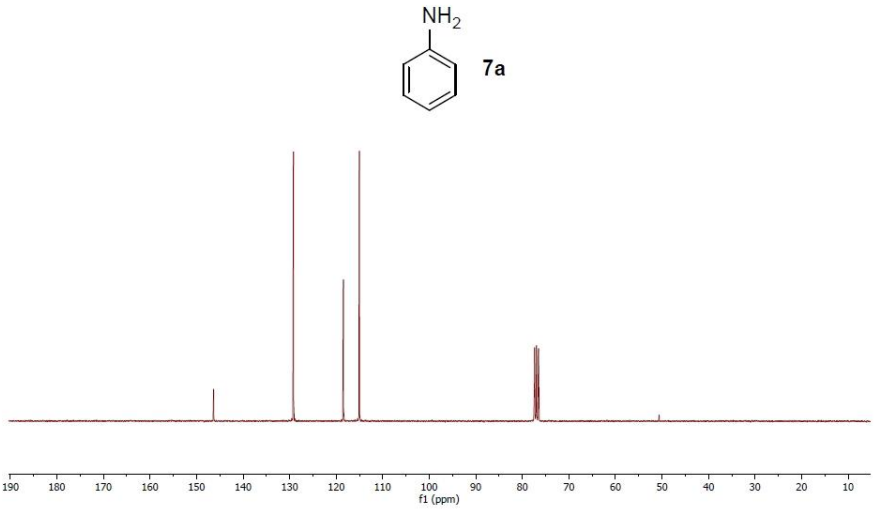

NH2
5a
O
OMe
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

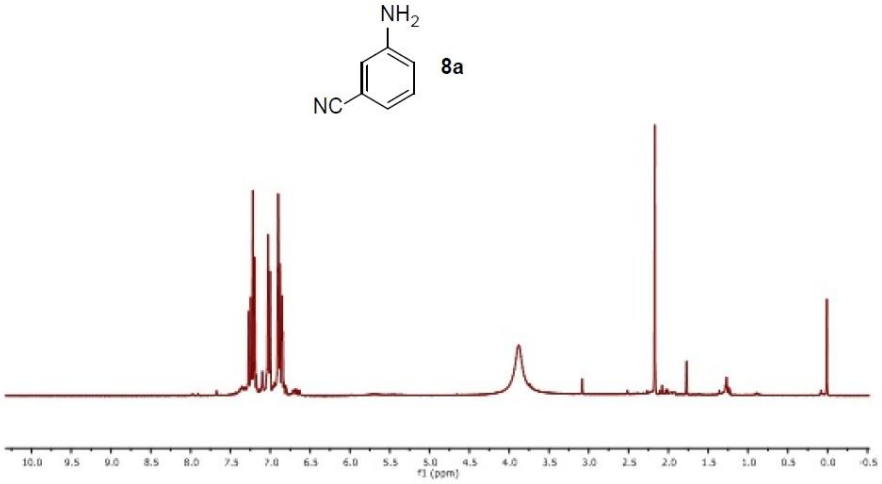

NH2
5a
O
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

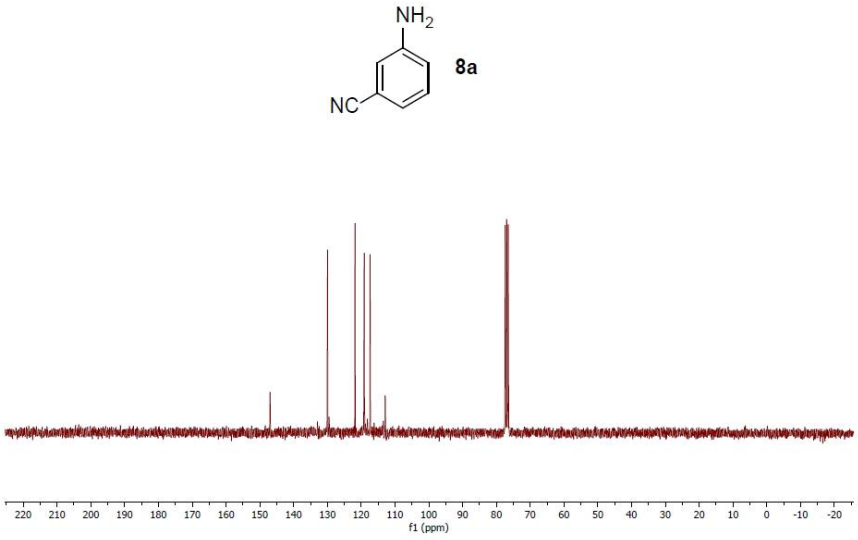

NH2
6a
OH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

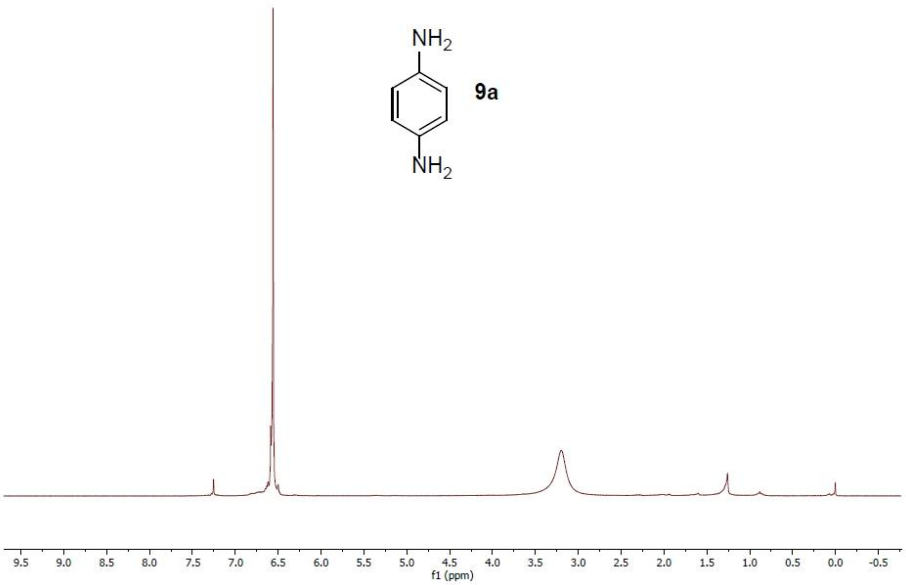

NH2
OH
6a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

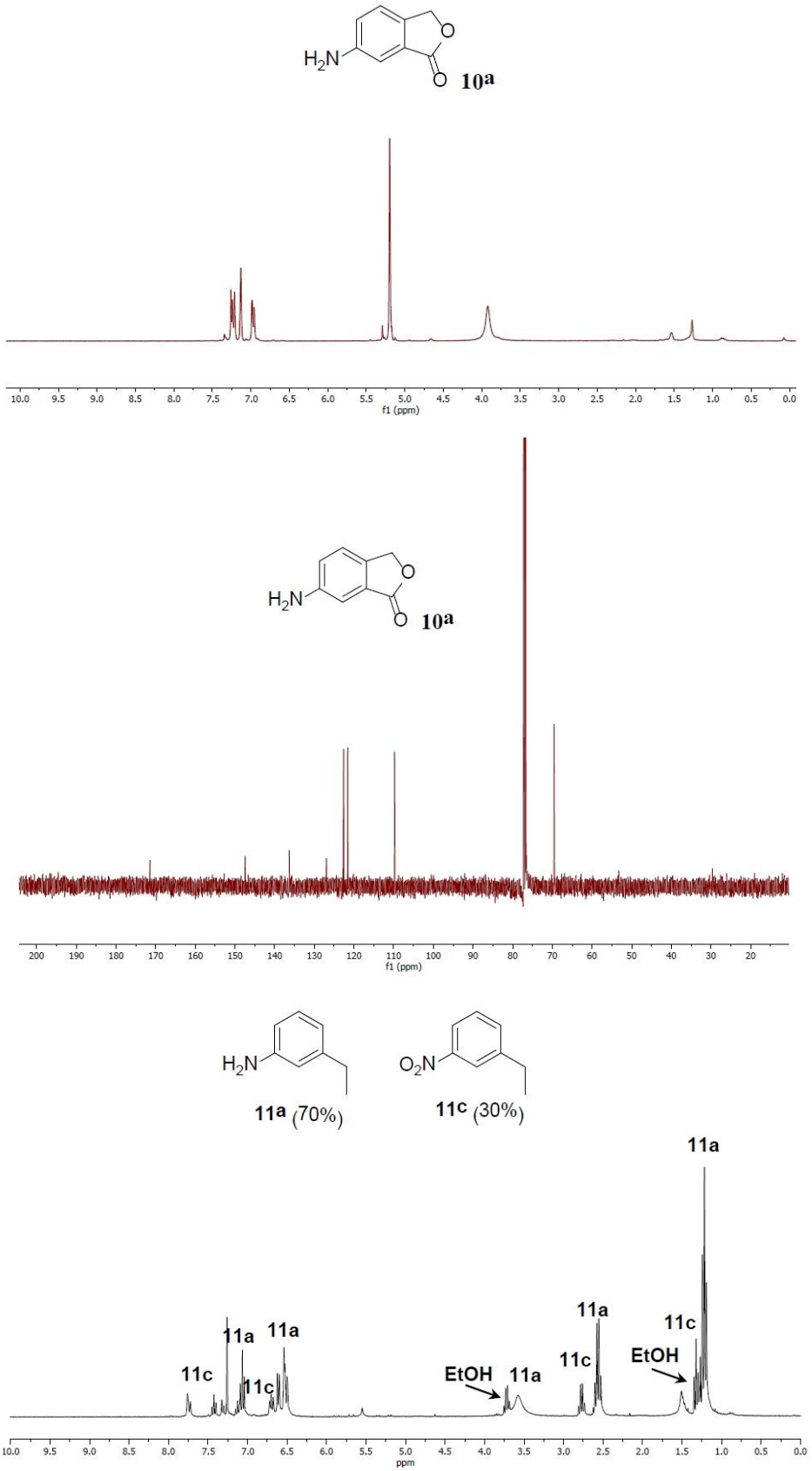

NH2
7a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

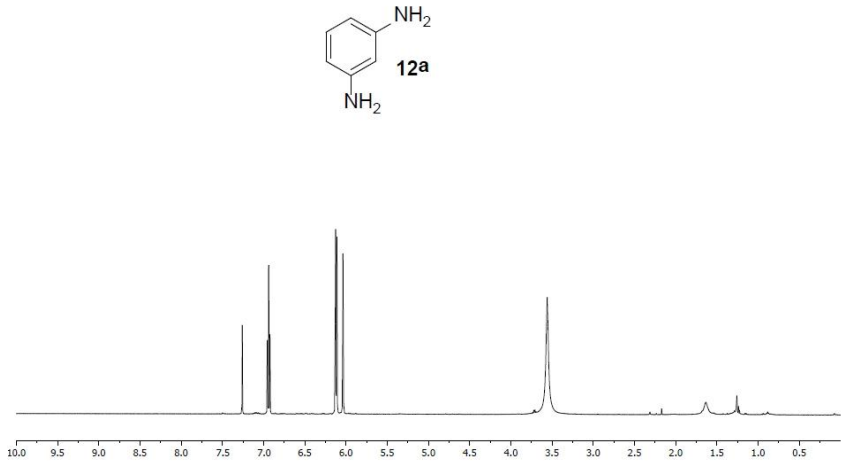

NH2
7a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

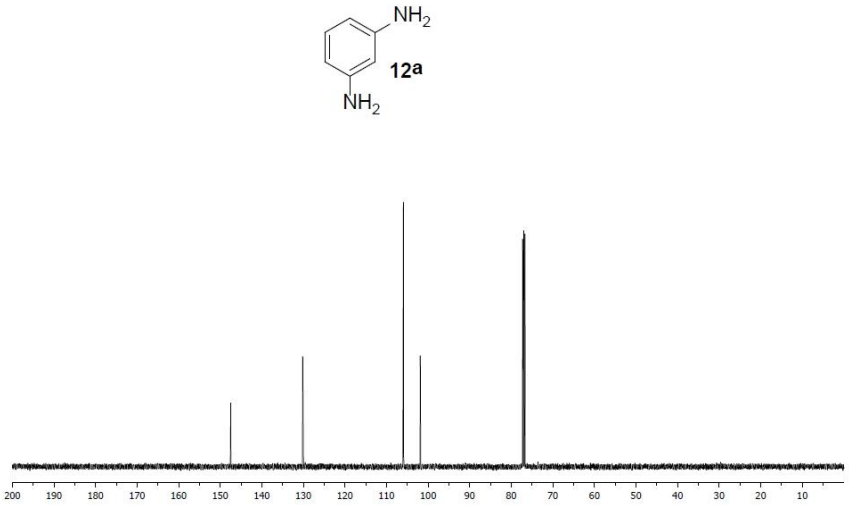

NH2
NC
8a
f1 (ppm)

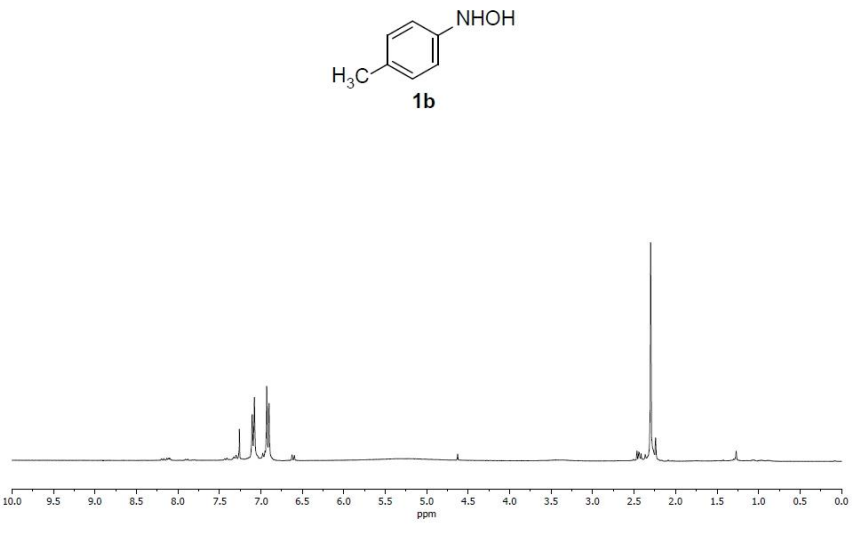

NH2
NC
8a
f1 (ppm)


NH2
NH2
9a
f1 (ppm)


H2N
O
O
10a
f1 (ppm)
H2N
O
O
10a
f1 (ppm)
H2N
11a (70%)
O2N
11c (30%)
11a
11c
11a
11a
11c
EtOH
11a
11a
11c
EtOH
11c
ppm


NH2
12a
NH2
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


NH2
12a
NH2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


NHOH
H3C
1b
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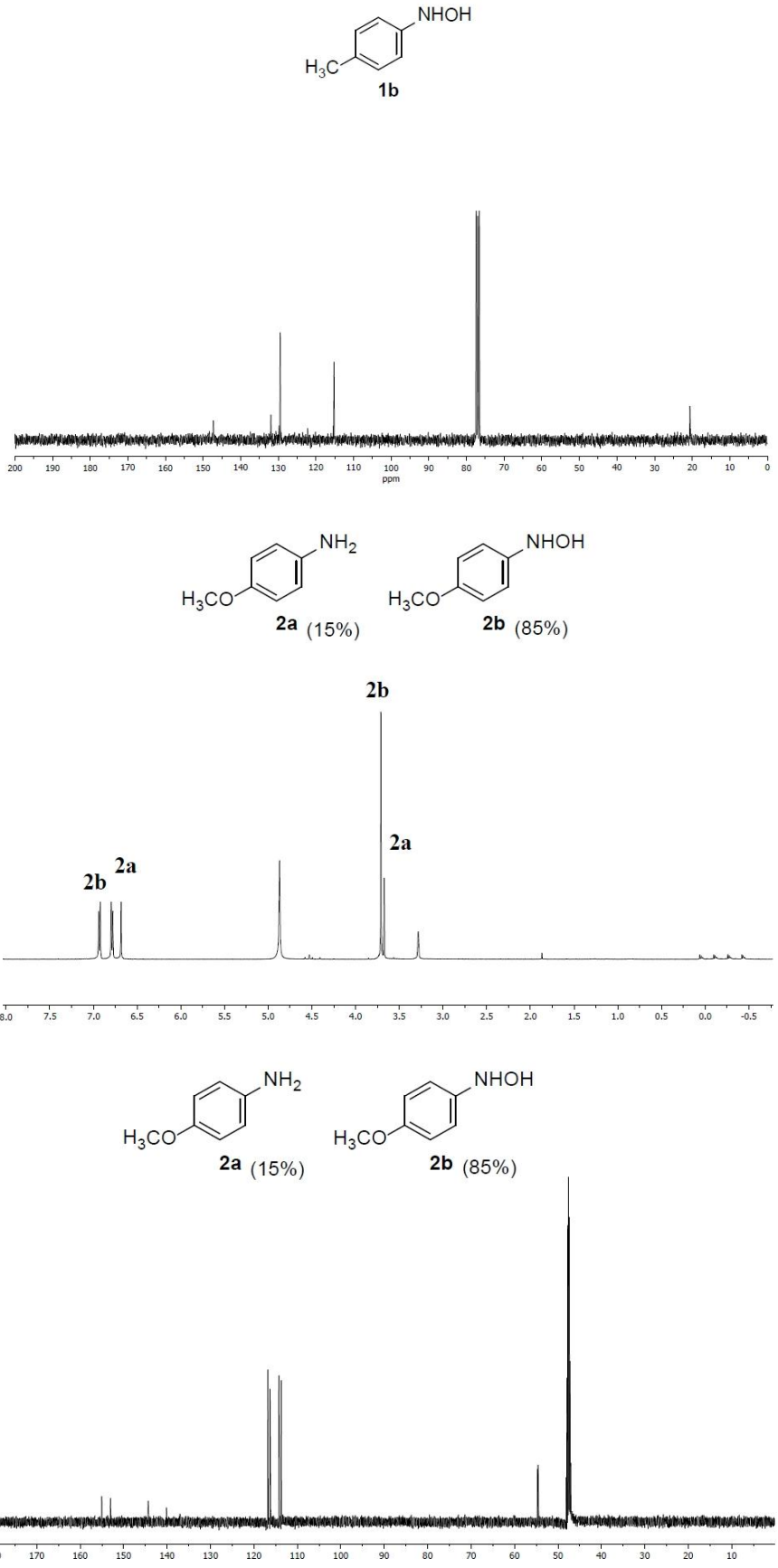
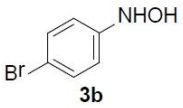
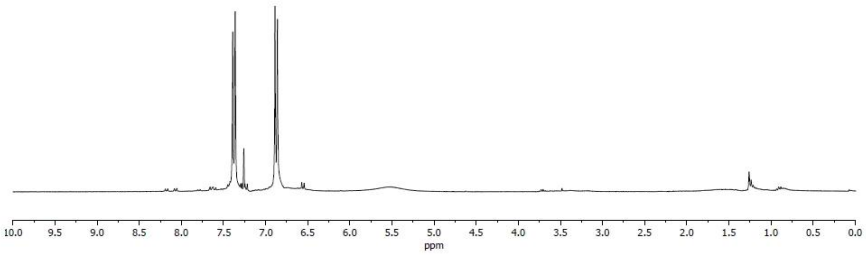
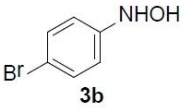
ppm


NHOH
H3C
1b
ppm
NH2
H3CO
2a (15%)
NHOH
H3CO
2b (85%)
2b
2a
2b
2a
NH2
H3CO
2a (15%)
NHOH
H3CO
2b (85%)

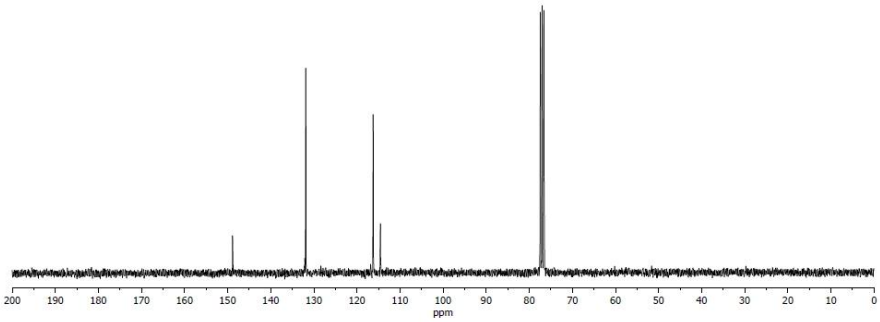

NHOH
Br

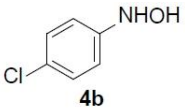
3b


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

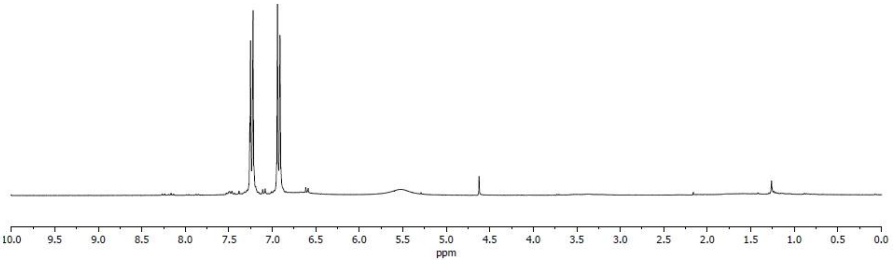

NHOH
Br

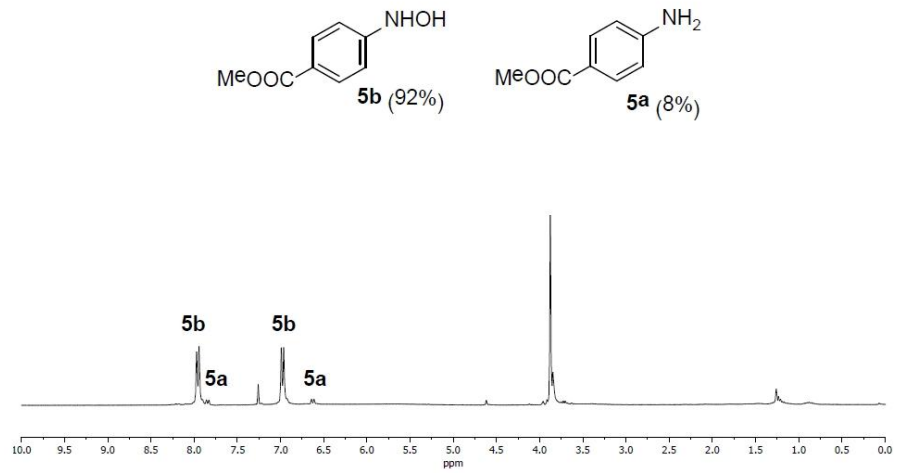
3b

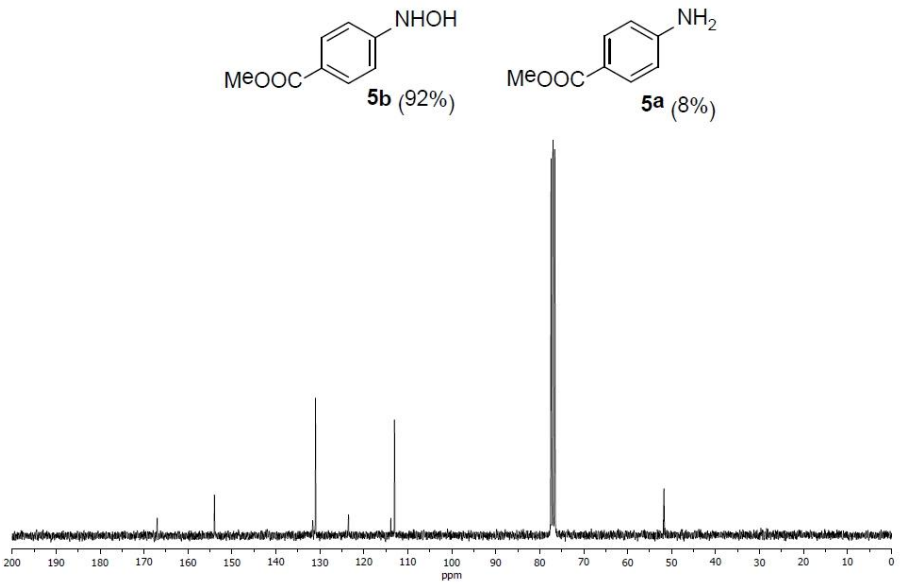

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

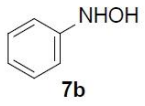

NHOH
Cl

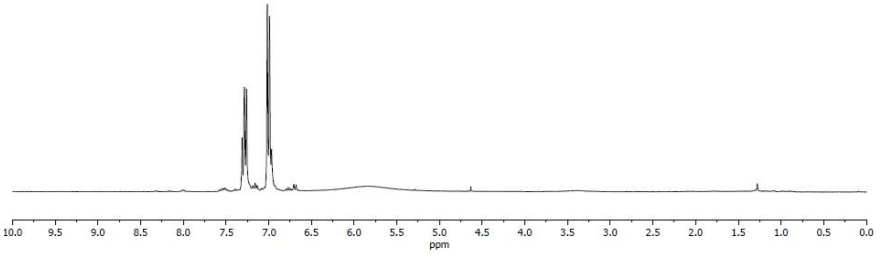
4b

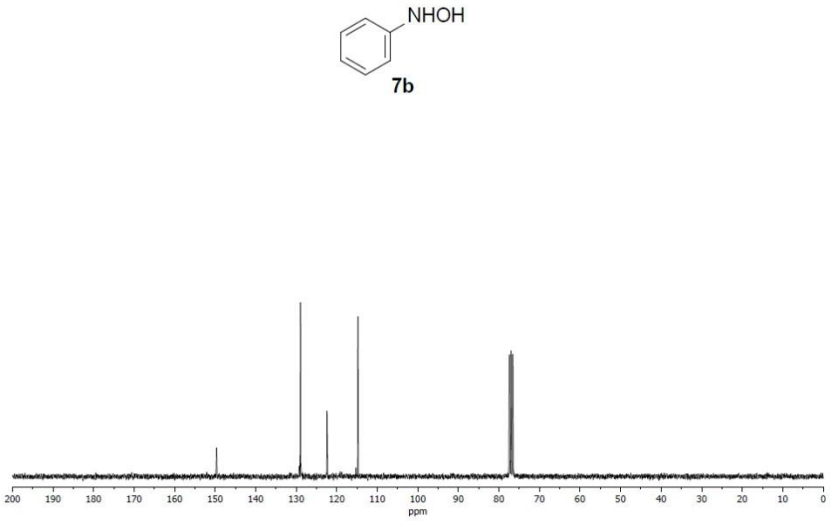

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

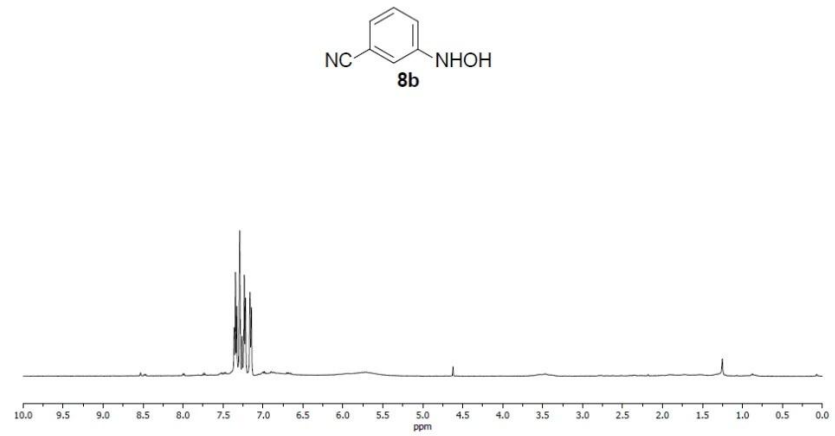

NHOH
MeOOC
5b (92%)
NH2
MeOOC
5a (8%)
5b
5b
5a
5a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

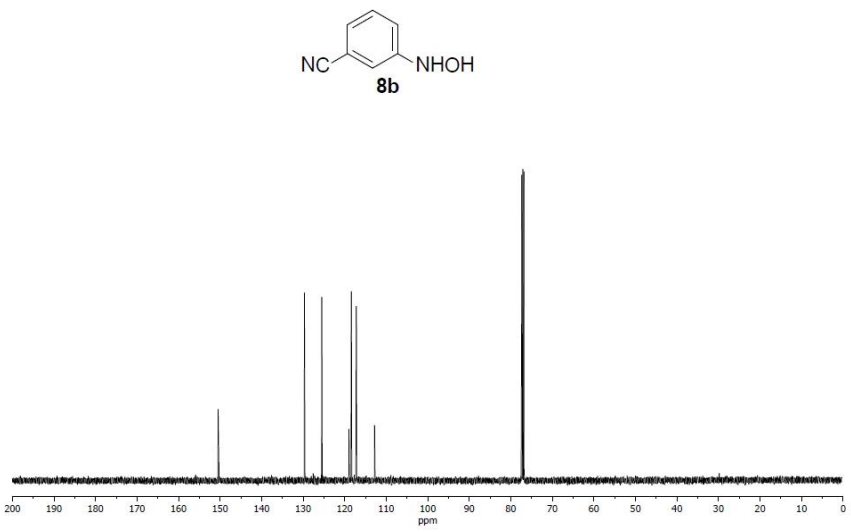

NHOH
MeOOC
5b (92%)
NH2
MeOOC
5a (8%)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NHOH
7b


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


NHOH
7b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


NC
NHOH
8b
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


NC
NHOH
8b
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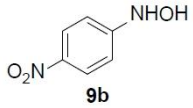
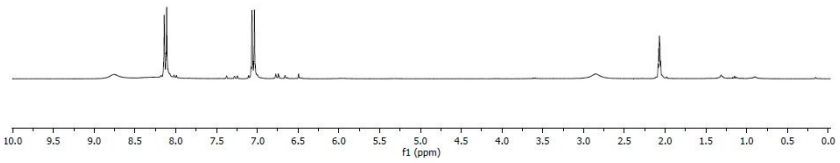
ppm


NHOH
O_2N

9b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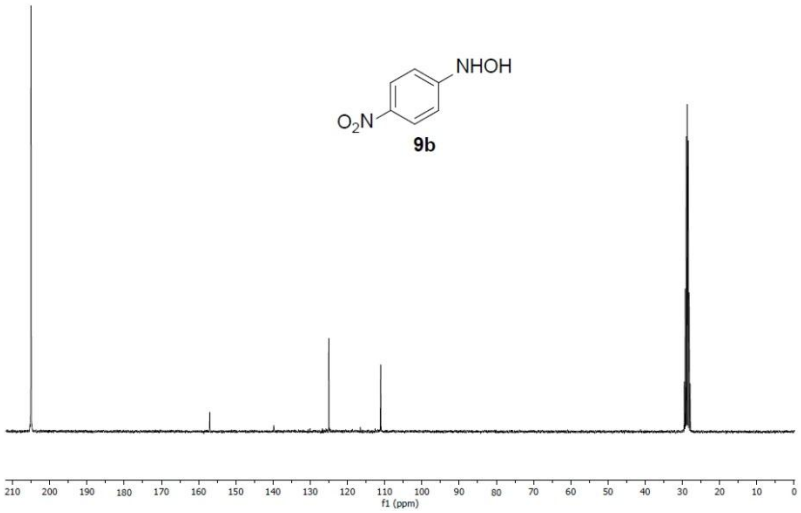
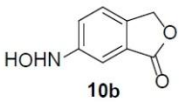
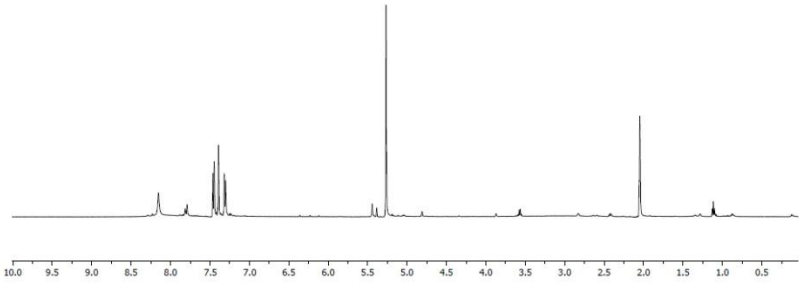
f1 (ppm)


NHOH
O_2N
9b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HOHN
O
O

10b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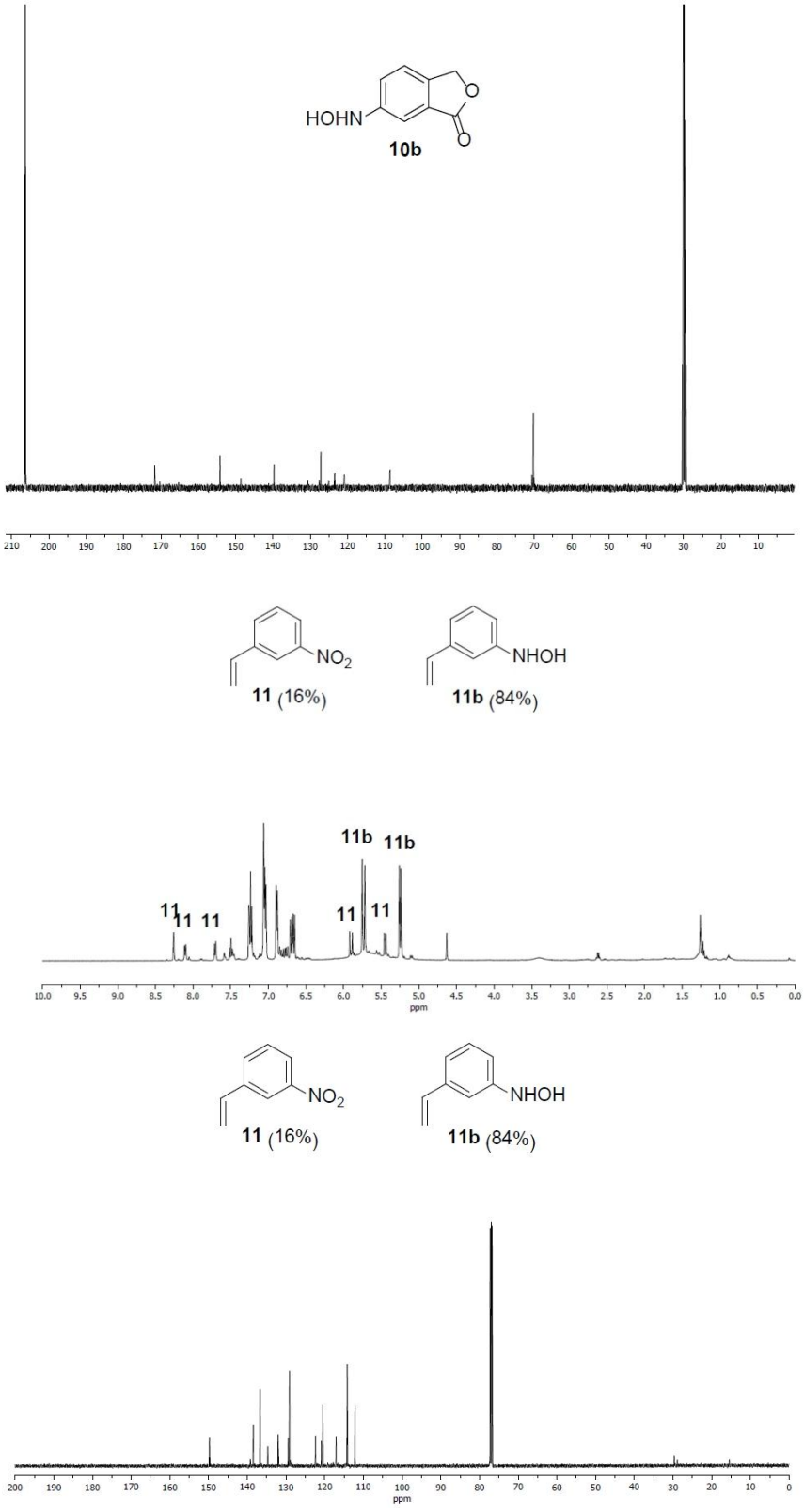
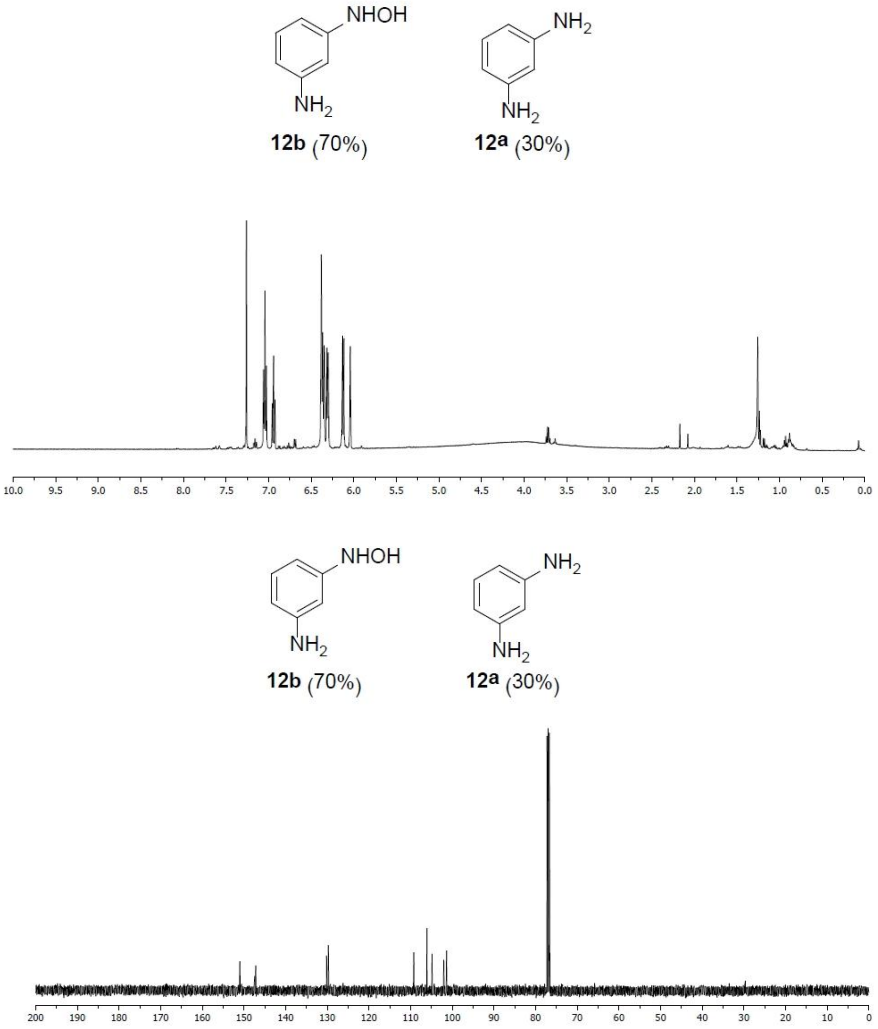

HOHN
O
O
10b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
NO2
11 (16%)
NHOH
11b (84%)
11b 11b
11 11 11 11 11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
NO2
11 (16%)
NHOH
11b (84%)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



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