Supporting Information

Chemoselective *N*-deacetylation under mild conditions

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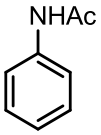
Table of Contents

General: Unless otherwise noted, all reactions have been carried out with distilled and dried solvents under an atmosphere of dry N_2, argon and oven-dried glassware. All reagents were purchased from commercial sources and used as received, unless otherwise indicated. Thin-layer chromatography (TLC) was performed using silica gel 60 GF_{254} pre-coated aluminum backed plates (2.5 mm) with detection by UV light. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ and DMSO-d_6. Chemical shifts in ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard, *J* values are given in Hz. ^{13}C NMR are reported as δ in ppm downfield from tetramethylsilane and relative to the signal of chloroform-d and DMSO-d_6. ^{13}C NMR spectra were recorded with complete proton decoupling. Mass samples were analyzed by High resolution mass spectrometry using ESI TOF. FT-IR spectra were obtained using a FT-IR spectrophotometer as thin films on sodium chloride or KBr discs and reported in cm^{-1}. Optical rotations were measured on a polarimeter. Melting points were measured in open glass capillary and values are uncorrected.

General procedure A for Acetylation of amines:[1]

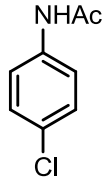
***N*-phenylacetamide (1a):**



To a stirred solution of aniline (0.5 mL, 5.3 mmol 1 equiv) in dry DCM (10 mL) under argon was added acetic anhydride (0.66 mL, 6.4 mmol, 1.2 equiv) and the reaction was stirred at room temperature and monitored by TLC. Upon completion the reaction mixture was washed with a saturated solution of sodium carbonate and the combined organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to afford the desired product **1a** in yield (0.72 g) as a white crystalline solid.

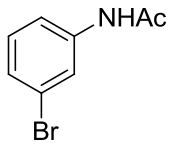
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 2.17 (s, 3H). (Data is in accordance with the literature value[2])

***N*-(4-chlorophenyl) acetamide (1b):**



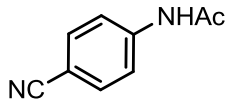
Compound **1b** was prepared following the general procedure A, starting from 4-chloroaniline in 55% yield. Spectral data was consistent with that previously reported.[3] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 2.04 (s, 3H).

***N*-(3-bromophenyl) acetamide (1c):**



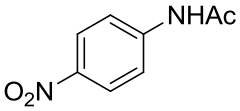
Compound **1c** was prepared following the general procedure A,, from 3-bromoaniline in 65% yield. Spectral data was consistent with that previously reported[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 2H), 2.18 (s, 3H)

***N*-(4-cyanophenyl)acetamide (1d):**



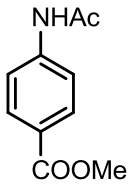
Compound **1d** was prepared following the general procedure A, from 4-cyanoaniline in 88% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 7.75 (s, 4H), 2.09 (s, 3H).

***N*-(4-nitrophenyl)acetamide (1e):**



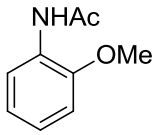
Compound **1e** was prepared following the general procedure A, from 4-nitroaniline in 91% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 8.21 (d, *J* = 9.4 Hz, 2H), 7.82 (d, *J* = 9.3 Hz, 2H), 2.11 (s, 3H).

Methyl 4-acetamidobenzoate (1f):



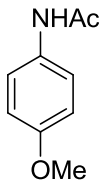
Compound **1f** was prepared following the general procedure A, from methyl 4-aminobenzoate in 83% yield. Spectral data was consistent with that previously reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 2.19 (s, 4H).

***N*-(2-methoxyphenyl)acetamide (1g):**



Compound **1g** was prepared following the general procedure A, from 2-methoxyaniline in 78% yield. Spectral data was consistent with that previously reported.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.01 (td, *J* = 7.9, 1.4 Hz, 1H), 6.98 – 6.89 (m, *J* = 7.7, 6.7 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 2.18 (s, 3H).

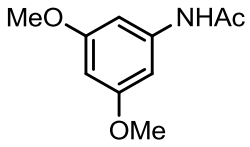
***N*-(4-methoxyphenyl)acetamide (1h):**



Compound **1h** was prepared following the general procedure A, from 4-methoxyaniline in 84% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz,

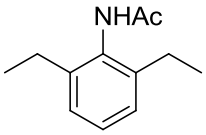
$CDCl_3$) δ 7.39 (dd, *J* = 13.9, 6.4 Hz, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.78 (d, *J* = 1.4 Hz, 3H), 2.15 (d, *J* = 1.4 Hz, 3H).

***N*-(3, 5-dimethoxyphenyl)acetamide (1i):**



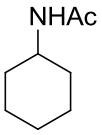
Compound **1i** was prepared following the general procedure A, from 3, 4-dimethoxyaniline in 73% yield. Spectral data was consistent with that previously reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.9 Hz, 1H), 6.71 (s, 2H), 6.19 (s, 1H), 3.73 (s, 6H), 2.12 (s, 3H).

***N*-(2, 6-diethylphenyl)acetamide (1j):**



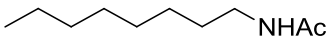
Compound **1j** was prepared following the general procedure A, from 2, 6 diethylaniline in 70% yield. Spectral data was consistent with that previously reported.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.07 (m, 3H), 6.96 (bs, 1H), 2.60 (dq, *J* = 13.8, 7.6, 6.8 Hz, 4H), 1.17 (dt, *J* = 13.8, 6.8 Hz, 6H).

***N*-cyclohexylacetamide (1k):**



Compound **1k** was prepared following the general procedure A, from cyclohexylamine in 85% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 3.82 – 3.68 (m, 1H), 1.99 (s, 3H), 1.96 – 1.87 (m, 2H), 1.75 – 1.67 (m, 2H), 1.66 – 1.57 (m, 1H), 1.42 – 1.29 (m, 2H), 1.21 – 1.06 (m, 3H)

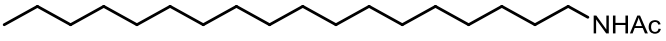
***N*-octylacetamide (1l):**



Compound **1l** was prepared following the general procedure A, from octylamine 90% yield. Spectral data was consistent with that previously reported.[7]

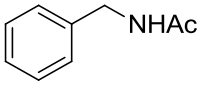
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, 1H), 3.25 – 3.16 (m, 2H), 1.95 (d, *J* = 6.9 Hz, 3H), 1.52 – 1.40 (m, 2H), 1.34 – 1.18 (m, 10H), 0.89 – 0.81 (m, 3H).

***N*-octadecylacetamide (1m):**



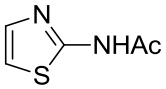
Compound **1m** was prepared following the general procedure A, from octadecan-1-amine 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (s, 1H), 3.20 (dd, *J* = 12.8, 7.0 Hz, 2H), 1.96 (s, 3H), 1.51 – 1.40 (m, 2H), 1.31 – 1.16 (m, 30H), 0.84 (t, *J* = 6.9 Hz, 3H).

***N*-benzylacetamide (1n):**



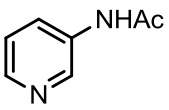
Compound **1n** was prepared following the general procedure A, from benzylamine in 84% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.06 (m, 5H), 5.93 (s, 1H), 4.26 (d, *J* = 3.4 Hz, 2H), 1.86 (s, 3H).

***N*-(thiazol-2-yl)acetamide (1o):**



Compound **1o** was prepared following the general procedure A, from 2-aminothiazole in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 3.6 Hz, 1H), 7.01 (d, *J* = 3.7 Hz, 1H), 2.35 (s, 3H).

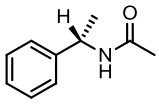
***N*-(pyridin-3-yl) acetamide (1p):**



Compound **1p** was prepared following the general procedure A, from 3-aminopyridine in 72% yield. Spectral data was consistent with that previously reported.[8] ^{1}H NMR (400 MHz,

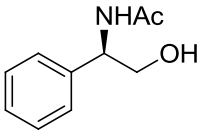
$CDCl_3$) δ 8.68 (s, 1H), 8.59 (s, 1H), 8.30 (d, *J* = 4.6 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 2.20 (s, 3H).

(*S*)-*N*-(1-phenylethyl)acetamide (1q):



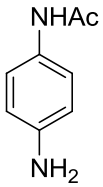
Compound **1q** was prepared following the general procedure A, from (*s*)-alpha methyl benzylamine in 90% yield. Spectral data was consistent with that previously reported.[9]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 5.95 (s, 1H), 5.16 – 5.07 (m, 1H), 1.98 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H).

(*R*)-*N*-(2-hydroxy-1-phenylethyl) acetamide (1r):



Compound **1r** was prepared following the general procedure A, from (*R*)-phenylglycinol in 65% yield. Spectral data was consistent with that previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 6.35 (s, 1H), 5.07 (dd, *J* = 10.8, 6.1 Hz, 1H), 3.94 – 3.85 (m, 2H), 2.07 (s, 3H), 2.02 (s, 1H).

***N*-(4-aminophenyl) acetamide (1s):**

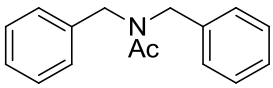


To a stirred solution of *N*-(4-nitrophenyl) acetamide **1e** (1 g, 5.55 mmol) in EtOH/water (25:5 ml) was added iron powder (3.09 g, 55.5 mmol) and 2 drops of conc.HCl. The resulting mixture was refluxed for 2 h. Then 10% $NaHCO_3$ solution was added and the suspension was stirred for 10 min. After which EtOH was evaporated in vacuuo and then EtOAc was added. The aqueous layer was washed with EtOAc (2 X 20 mL) and combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated in vacuuo to afford crude product **1s,** which was purified by silica gel column chromatography using

EtOAc:Hexane (20:80) to give pure compound **1s** (0.79 g, 95% yield). Spectral data was consistent with that previously reported.[10]

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.43 (bs, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 8.7 Hz, 2H), 4.77 (bs, 2H), 1.89 (s, 3H).

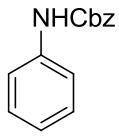
***N, N*-dibenzylacetamide (1t):**



Compound **1t** was prepared following the general procedure A, from dibenzylamine. Spectral data was consistent with that previously reported.[11]

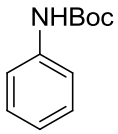
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 6.97 (m, 10H), 4.52 (s, 2H), 4.36 (s, 2H), 2.14 (S, 3H).

Benzyl phenylcarbamate (3):



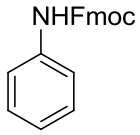
The compound **4** was prepared following the literature procedure.[12]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 9H), 7.10 – 7.04 (m, 1H), 6.72 (s, 1H), 5.21 (s, 2H).

tert-butyl phenylcarbamate (4):



The compound **5** was prepared following the literature procedure.[13]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.48 (bs, 1H), 1.49 (s, 9H)

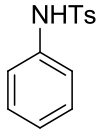
(9H-fluoren-9-yl) methyl phenylcarbamate (5):



To a stirred solution of aniline (0.2 g, 2.14 mmol) and pyridine (0.2 mL, 2.57 mmol) in dry DCM at 0^{o}C was added solution of Fmoc-Cl (0.61g, 2.36 mmol) in dry DCM and the resulting reaction mixture was stirred at room temperature for 1 h. After which the solution was acidified with dil.HCl. The aqueous layer was extracted with DCM (2 X 10 mL). Combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford **5** (0.54 g, 80%). Spectral data was consistent with that previously reported.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.27 (m, 8H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.65 (bs, 1H), 4.55 (d, *J* = 6.6 Hz, 2H), 4.28 (t, *J* = 6.6 Hz, 1H)

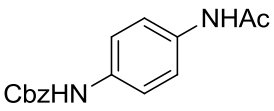
4-methyl-N-phenylbenzenesulfonamide (6):



To a stirred solution of aniline (0.2 g, 2.14 mmol) and Et_3N (0.448 mL, 3.22 mmol) in dry DCM at 0 ^{o}C was added p-toluenesulfonyl chloride (TsCl) (0.49 g, 2.57 mmol) portion wise and reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was acidified by the addition of dilute HCl and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford **6** in quantitative yield. Spectral data was consistent with that previously reported.[15]

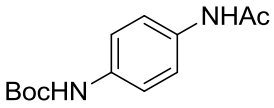
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.08 – 7.01 (m, 3H), 2.32 (s, 4H)

Benzyl (4-acetamidophenyl) carbamate (7):



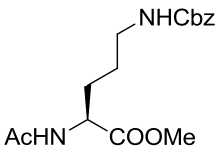
The compound **7** was prepared following the literature procedure[12] starting from compound **1s.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.83 (s, 1H), 9.66 (s, 1H), 7.50 – 7.28 (m, 9H), 5.13 (s, 2H), 2.00 (s, 3H)

tert-butyl (4-acetamidophenyl)carbamate (8):



The compound **8** was prepared following the literature procedure[13] starting from compound **1s.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 6.48 (bs, 1H), 2.13 (s, 3H), 1.49 (s, 9H).

(S)-methyl 2-acetamido-5-(((benzyloxy)carbonyl)amino)pentanoate (11):



L-Ornithine hydrochloride (2.0 g, 11.86 mmol) and copper (II) acetate (1.19 g, 5.93 mmol) were dissolved in 9 mL of 10% aq. sodium carbonate, and the solution was vigorously stirred for 45 minutes. To the stirred solution were added 20 mL of water and 20 mL of 1,4-dioxane, followed by slow addition of solution of CbzCl (1.86 mL, 13.05 mmol) in 10 mL of 1,4-dioxane. After 6 h, $NaBH_4$ (0.54 g, 14.23 mmol) was added portionwise. After 15 min, the copper(I) oxide precipitate formed was filtered. The clear, colourless filtrate on neutralization with dilute HCl in cold condition gave white precipitated. The precipitate was filtered and washed with water to afford crude L- N^{δ}-Cbz ornithine. Acetic anhydride (1.45 g, 14.23 mmol) was added to the solution of L- N^{δ}-Cbz ornithine in 1N NaOH and stirred for 3 h at room temperature. Afterwhich, ethyl acetate was added and the aqueous layer was extracted with EtOAc and washed with brine, dried over anhydrous sodium sulphate and evaporated in vaccuo to afford L- N^{δ}-Cbz-N^{α}-acyl ornithine. Which on treatment with MeI (1.47 mL, 23.72mmol) and K_2CO_3 (3.27 g, 23.72 mmol) in dry DMF under N_2 atmosphere for 2 h. After which water and EtOAc were added and organic layer was separated. Aqueous

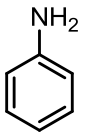
layer was extracted with EtOAc and combined organic layers were washed with brine, sodium thiosulphate, and dried over anhydrous $NaSO_4$. Solvent was evaporated reduced pressure to afford crude L- N^{δ}-Cbz-N^{α}-acyl ornithine methyl ester **11**. This was purified over silica gel using EtOAc:n-Hexane (20:80) as an eluent to afford pure **11** in 85 % yield (3.25 g).

$[\alpha]_D^{25}$ = +26 (c 1.0, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 6.22 (s, 1H), 5.08 (s, 2H), 4.96 (bs, 1H), 4.60 (dd, *J* = 12.9, 7.5 Hz, 1H), 3.73 (s, 3H), 3.21 (dd, *J* = 12.9, 6.5 Hz, 2H), 2.02 (s, 3H), 1.94 – 1.79 (m, *J* = 14.4, 5.8 Hz, 1H), 1.77 – 1.68 (m, *J* = 14.1 Hz, 1H), 1.61 – 1.49 (m, *J* = 6.8 Hz, 2H); HRMS (ESI): Calcd. For $C_{16}H_{22}N_2O_5Na$ $(M + Na)^+$: 345.1426 found 345.1434.

General procedure B for the deacetylation of amine:

To a stirred solution of *N*-acetyl amine (0.2 g) in anhydrous THF (2 mL) was added Schwartz reagent (1.5-2 equiv) at room temperature and the reaction mixture was stirred for 2-5 min. After which, water was added to quench the reaction. Then the resulting solution was extracted with EtOAc (10 mL X 2). The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the corresponding crude amine which was purified by silica gel column chromatography to afford pure amine.

Aniline (2a):[16]



Compound **2a** was obtained following the general procedure B starting from **1a** as light yellow liquid (0.129 g, 94%)**.** IR (cm^{-1}) 3350, 3033, 2873, 1601, 1496; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 6.79 – 6.74 (m, 1H), 6.72 – 6.68 (m, 2H), 3.63 (bs, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 129.4, 118.7, 115.2, HRMS (ESI): Calcd. For C_6H_7N $(M + H)^+$: 94.0656 found 94.0659

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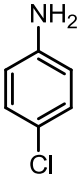
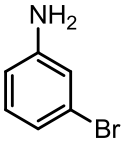
4-Chloroaniline (2b):[17]



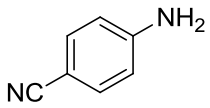
Compound **2b** was obtained following the general procedure B starting from **1b** as a white solid (0.138 g, 92%)**.** mp = 68-70 ^{o}C; IR (cm^{-1}): 3472, 3364, 3156, 1614, 1492; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 3.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 129.2, 123.3, 116.4, HRMS (ESI): Calcd. For C_6H_7ClN $(M+H)^+$:128.0267 found 128.0269

3-Bromoaniline (2c):[18]



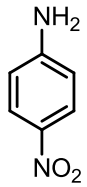
Compound **2c** was obtained following the general procedure B starting from **1c** as a light yellow liquid (0.144 g, 90%). IR (cm^{-1}): 3454, 3371, 3217, 2963, 1580. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, *J* = 8.0 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.59 (ddd, *J* = 7.8, 2.2, 0.9 Hz, 1H), 3.70 (bs, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 130.7, 123.2, 121.5, 117.9, 113.7, HRMS (ESI): Calcd. For C_6H_7BrN $(M+H)^+$:171.9762 found 171.9767

4-aminobenzonitrile (2d):[16]



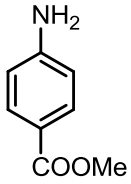
Compound **2d** was obtained following the general procedure B starting from **1d** as a white solid (0.123 g, 84%)**.** mp=84-85^{o}C; IR KBr (cm^{-1}): 3466, 2220; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 6.13 (bs, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.5, 133.9, 121.2, 113.9, 96.0, HRMS (ESI): Calcd. For $C_7H_7N_2$ $(M+H)^+$: 119.0609 found 119.0611

4-Nitroaniline (2e): [16]



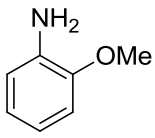
Compound **2e** was obtained following the general procedure B starting from **1e** as a yellow solid (0.136 g, 89%)**.** mp = 147-149 ^{o}C; IR KBr (cm^{-1}): 3470, 3373, 1583, 1285; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 9.1 Hz, 1H), 6.62 (d, *J* = 9.1 Hz, 1H), 4.38 (bs, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 129.2, 123.3, 116.4, HRMS (ESI): Calcd. For $C_6H_7N_2O_2$ $(M+H)^+$: 139.0507 found 139.0512

Methyl 4-aminobenzoate (2f): [16]



Compound **2f** was obtained following the general procedure B starting from **1f** as a light yellow solid (0.138 g, 87%). mp =109-111 ^{o}C; IR KBr (cm^{-1}): 3430, 3334, 1680, 1629; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 6.64–6.6 (m, 2H), 4.06 (bs, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 150.9, 131.7, 119.9, 113.9, 51.7; HRMS (ESI): Calcd. For $C_8H_{10}NO_2$ $(M+H)^+$: 152.0711 found 152.0711

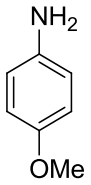
2-methoxyaniline (2g):[19]



Compound **2g** was obtained following the general procedure B starting from **1g** as a light yellow liquid (0.128 g, 86%). IR (cm^{-1}): 3466, 3356, 2973, 2866, 1620, 1506; ^{1}H NMR (400

MHz, $CDCl_3$) δ 6.84 – 6.68 (m, 4H), 3.85 (s, 3H), 3.56 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 136.0, 121.2, 118.8, 115.3, 110.6, 55.6**,** HRMS (ESI): Calcd. For $C_7H_{10}NO$ $(M+H)^+$:124.0762 found 124.762

4-methoxyaniline (2h):[17]



Compound **2h** was obtained following the general procedure B starting from **1h** as white solid (0.131g, 88%)**.** mp = 54-57 ^oC; IR (cm^{-1}): 3422, 3332; ^1H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.9 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)) δ 152.9, 140.0, 116.5, 114.9, 55.9, HRMS (ESI): Calcd. For $C_7H_{10}NO$ $(M+H)^+$: 124.0762 found 124.0764

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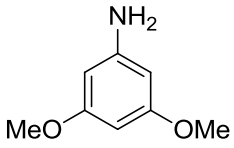
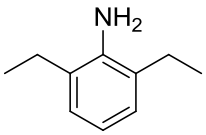
3, 5-dimethoxyaniline (2i):[20]



Compound **2i** was obtained following the general procedure B starting from **1i** as a light brown solid (0.135g, 86%). mp = 53-56 ^oC; IR (cm^{-1}): 3440, 3345, 2920, 1595**;** ^1H NMR (400 MHz, $CDCl_3$) δ 5.93 (t, *J* = 2.1 Hz, 1H), 5.87 (d, *J* = 2.1 Hz, 2H), 3.74 (2s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 148.5, 93.9, 91.1, 55.3, HRMS (ESI): Calcd. For $C_8H_{12}NO_2$ $(M+H)^+$:154.0868 found 154.0868

2, 6-diethylaniline (2j):

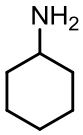


Compound **2i** was obtained following the general procedure B starting from **1j** as colorless oil (0.135g, 87%). IR (cm^{-1}) neat: 3389, 3022, 2967, 1620, 1448**;** ^1H NMR (400 MHz,

$CDCl_3$) δ 6.95 (d, *J* = 7.5 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 1H), 3.88 (bs, 2H), 2.53 (q, *J* = 7.5 Hz, 4H), 1.24 (t, *J* = 7.5 Hz, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.1, 126.2, 118.7, 24.4, 13.2

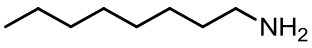
HRMS (ESI): Calcd. For $C_5H_7N_2$ $(M+H)^+$: 150.1282 found 150.1284

Cyclohexanamine (1k): [21]



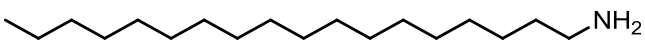
Compound **2k** was obtained following the general procedure B starting from **1k** as light yellow liquid (0.128 g, 91%). IR (cm^{-1}) neat: 3486, 2975, 2928, 2855, 1646, 1594; ^{1}H NMR (400 MHz $CDCl_3$) δ 2.61 (m, 1H), 1.85 – 1.77 (m, 2H), 1.75 – 1.65 (m, 2H), 1.63 – 1.55 (m, 1H), 1.39 – 1.18 (m, 4H), 1.17 – 0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.6, 37.0, 25.8, 25.3; HRMS (ESI): Calcd. For $C_6H_{14}N$ $(M+H)^+$:100.1126 found 100.1126

Octan-1-amine (2l):[22]



Compound **2l** was obtained following the general procedure B starting from **1l** as colorless liquid (0.140 g, 93%)**.** IR (cm^{-1}) neat: 3370, 3210, 1605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J* = 7.0 Hz, 2H), 1.48 – 1.38 (m, 2H), 1.35 – 1.17 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.4, 34.0, 32.0, 29.6, 29.4, 27.0, 22.8, 14.2, HRMS (ESI): Calcd. For $C_8H_{19}N$ $(M+H)^+$:130.1595 found 130.1599

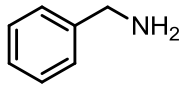
Octadecan-1-amine (2m):[23]



Compound **2m** was obtained following the general procedure B starting from **1m** as white solid (0.157g, 91%). mp = 49-51^{o}C; IR (cm^{-1}) KBr: 3410, 3230 1635; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (t, *J* = 7 Hz, 2H), 1.42 (dd, *J* = 13.8, 6.8 Hz, 2H), 1.33 – 1.20 (m, 32H), 0.87

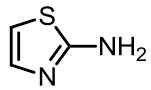
(t, *J* = 6.9 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.4, 34.1, 32.1, 29.9, 29.7, 29.5, 27.1, 22.8, 14.3, HRMS (ESI): Calcd. For $C_{18}H_{40}N$ $(M+H)^+$: 270.3161 found 270.3163

Benzylamine (2n):[24]



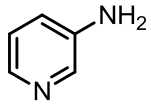
Compound **2n** was obtained following the general procedure B starting from **1n** as pale yellow liquid (0.13 g, 91%). IR (cm^{-1}) neat: 3361, 2953, 1642, 1576; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 3.87 (s, 2H), 1.50 (bs, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 128.7, 127.2, 126.9, 46.6, HRMS (ESI): Calcd. For $C_7H_{10}N$ $(M+H)^+$: 108.0813 found 108.0811

Thiazol-2-amine (2o):[25]



Compound **2o** was obtained following the general procedure B starting from **1o** as light yellow color solid (0.124g, 89%). mp = 90-92 ^{o}C; IR (cm^{-1}): 3416, 3278, 3109, 3094, 1632, 1526, 1470; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.92 (d, *J* = 3.7 Hz, 1H), 6.89 (bs, 2H), 6.53 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.3, 138.1, 106.0; HRMS (ESI): Calcd. For $C_3H_5N_2S$ $(M+H)^+$: 101.0173 found 101.0178

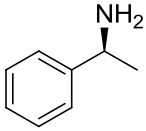
3-aminopyridine (2p):[19]



Compound **2p** was obtained following the general procedure B starting from **1p** as a light brown solid (0.123 g, 89%). mp = 63-66 ^{o}C; IR (cm^{-1}): 3360, 3145, 3045, 1627, 1565, 1430;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.8 Hz, 1H), 8.02 (dd, *J* = 4.7, 1.1 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.97 (ddd, *J* = 8.3, 2.6, 1.3 Hz, 1H), 3.57 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.0, 137.5, 123.8, 121.5, HRMS (ESI): Calcd. For $C_5H_7N_2$ $(M+H)^+$: 95.0609 found 95.0611

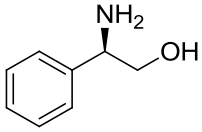
(*S*)-1-phenylethanamine (2q):[26]



Compound **2q** was obtained following the general procedure B starting from **1q** as pale yellow oil (0.138 g, 93%). $[\alpha]_D^{25}$ = –34.2 (c 1.0, $CHCl_3$)(lit[14]. $[\alpha]_D^{25}$ = – 35.1 (*c* 1.0, $CHCl_3$);

IR (cm^{-1}): 3363, 3027, 2966, 1598, 1492; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 4H), 7.26–7.21 (m, 1H), 4.12 (q, *J* = 6.6 Hz, 1H), 1.54 (bs, 2H), 1.39 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 128.6, 126.9, 125.8, 51.5, 25.8; HRMS (ESI): Calcd. For $C_8H_{12}N$ $(M+H)^+$: 122.0969 found 122.0973

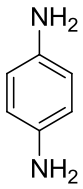
(*R*)-2-amino-2-phenylethanol (2r):[27]



Compound **2r** was obtained following the general procedure B starting from **1r** as yellow solid.

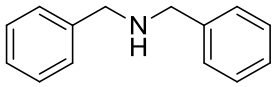
(0.136 g, 89%). mp = 74-77 °C; $[\alpha]_D^{25}$ = -30.1 (*c* 0.76, 1N HCl) (lit.[15] $[\alpha]_D^{25}$ = -31 (*c* 0.76,1NHCl); IR (cm^{-1}): 3200, 2835, 1604, 1497, 1453; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5H), 3.98 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.69 – 3.63 (m, 1H), 3.53 – 3.46 (m, 1H), 2.38 (bs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.8, 127.7, 126.6, 68.0, 57.4; HRMS (ESI): Calcd. For $C_8H_{12}NO$ $(M+H)^+$: 138.0919 found 138.0920

Benzene-1, 4-diamine (2s):[28]



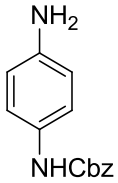
Compound **2s** was obtained following the general procedure B starting from **1s** as light brown solid (0.129 g, 90%)**.** mp = 140-143^{o}C; IR (cm^{-1}): 3360, 3281, 3174; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.36 (s, 4H), 4.18 (bs, 4H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.4, 115.9, HRMS (ESI): Calcd. For $C_6H_9N_2$ (M+H)$^{+}$: 109.0765 found 109.0766

Dibenzylamine (2t):[29]



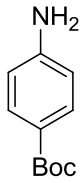
Compound **2t** was obtained following the general procedure B starting from **1t** as colorless liquid (0.151g, 94%). IR (cm^{-1}): 3061, 3027, 2835, 1643, 1604, 1495 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 10H), 3.73 (S, 4H), 1.86 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.6, 128.4, 127.2, 53.2, HRMS (ESI): Calcd. For $C_{14}H_{16}N$ (M+H)$^{+}$: 198.1283 found 198.1289

Benzyl (4-aminophenyl)carbamate (9):[30]



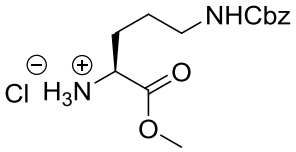
Compound **9** was obtained following the general procedure B starting from **7** as light brown solid (0.155 g, 91%)**.** mp = 90-95 ^{o}C; IR (cm^{-1}): ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.22 (s, 1H), 7.43 –7.28 (m, 5H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 5.09 (s, 2H), 4.79 (bs, 2H). ^{13}C NMR (100 MHz, DMSO-9) δ 154.1, 137.5, 128.9, 128.4, 128.4, 120.7, 114.49, 65.8; HRMS (ESI): Calcd. For $C_{14}H_{15}N_2O_2$ (M+H)$^{+}$: 243.1134 found 243.1135

Tert-butyl 4-aminobenzoate (10):[31]



Compound **10** was obtained following the general procedure B starting from **8** in (0.154g, 93%)**.** mp= 112-115 ^{o}C**;** ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 4.73 (bs, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6, 144.4, 129.1, 120.6, 114.5, 78.6, 28.8; HRMS (ESI): Calcd. For $C_{11}H_{17}N_2O_2$ $(M+H)^+$: 209.1290 found 209.1292

(*S*)-5-(((benzyloxy)carbonyl)amino)-1-methoxy-1-oxopentan-2-aminium chloride (12):



To a stirred solution of L- N^{δ}-Cbz-N^{α}-acyl ornithine methyl ester **11** (0.2 g, 0.62 mmol) in anhydrous THF (2 mL) was added Schwartz reagent (0.32 g, 1.2 mmol) at room temperature and the reaction mixture was stirred for 5 min. After which, HCl in dioxane was added to quench the reaction. Excess solvent was evaporated in vaccuo and anhydrous Et_2O was added to precipitate the hydrochloride salt. The hydrochloride salt was washed with cold n-hexane to afford pure compound **12** (0.157 g, 80%).

$[\alpha]_D^{19}$ = + 13.8 (*c* 4.0, MeOH) (*lit*[32]. $[\alpha]_D^{19}$ = + 14 (*c* 4.0, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 3H), 7.38 – 7.22 (m, 5H), 5.70 (s, 1H), 5.04 (s, 2H), 4.17 (s, 1H), 3.76 – 3.63 (m, 3H), 3.14 (d, *J* = 53.2 Hz, 2H), 2.06 (s, 2H), 1.72 (d, *J* = 48.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 156.9, 136.9, 128.6, 128.1, 66.7, 53.4, 53.0, 40.3, 27.6, 25.4; HRMS (ESI): Calcd. For $C_{14}H_{22}N_2O_4$ $(M)^+$: 281.1496 found 281.1503

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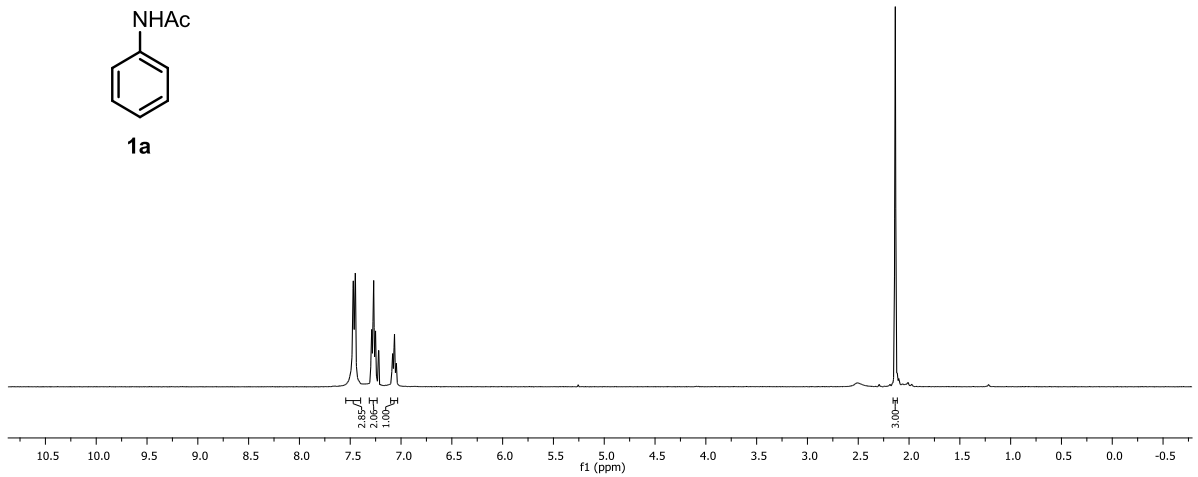

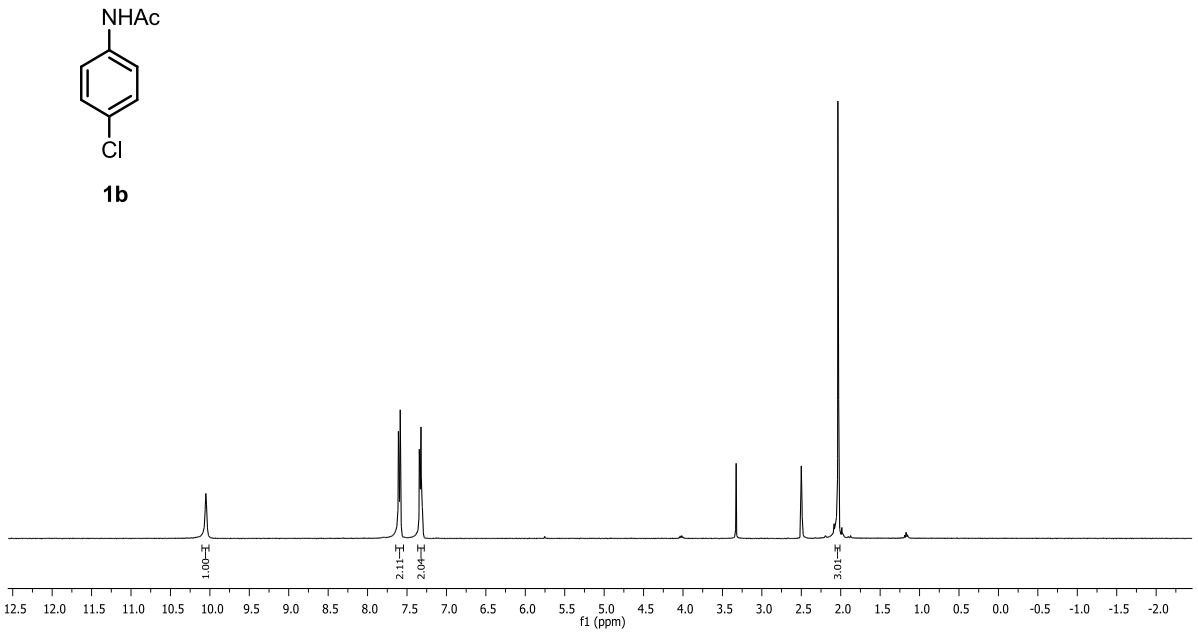

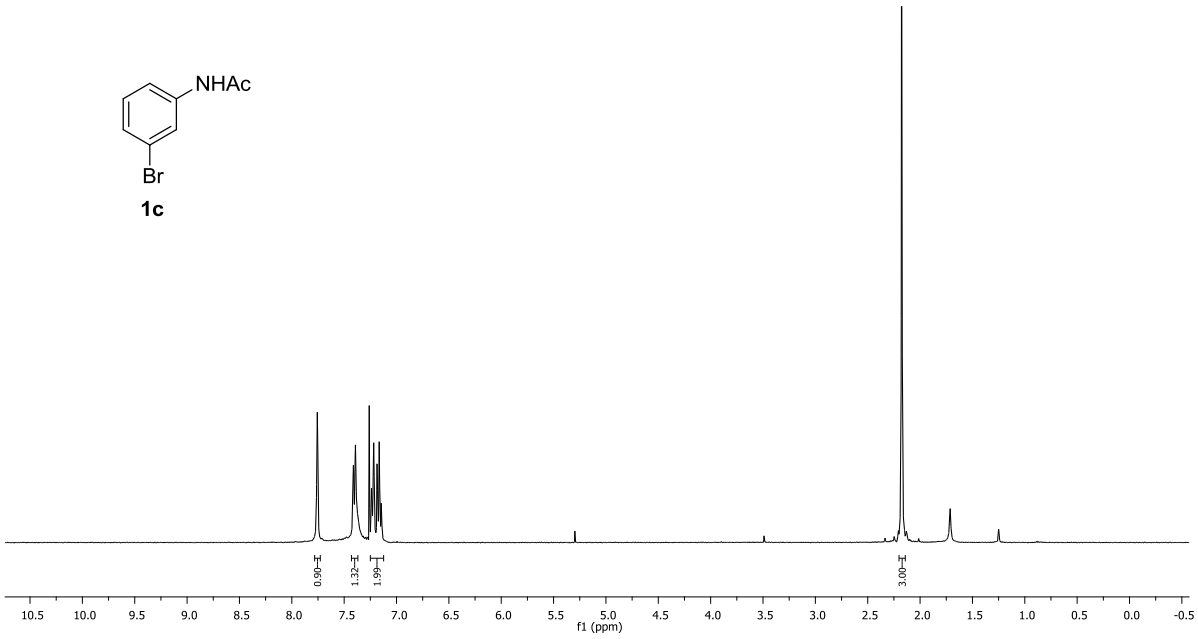

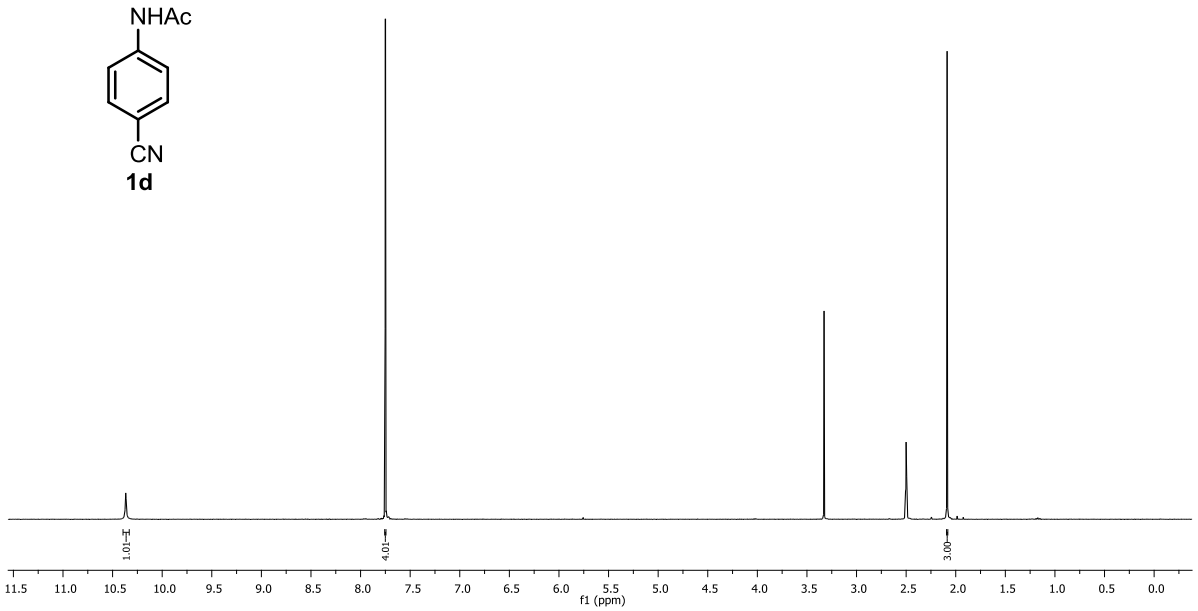

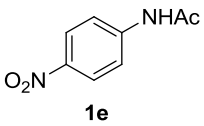

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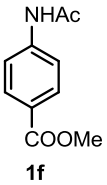

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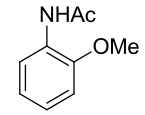

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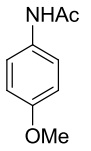

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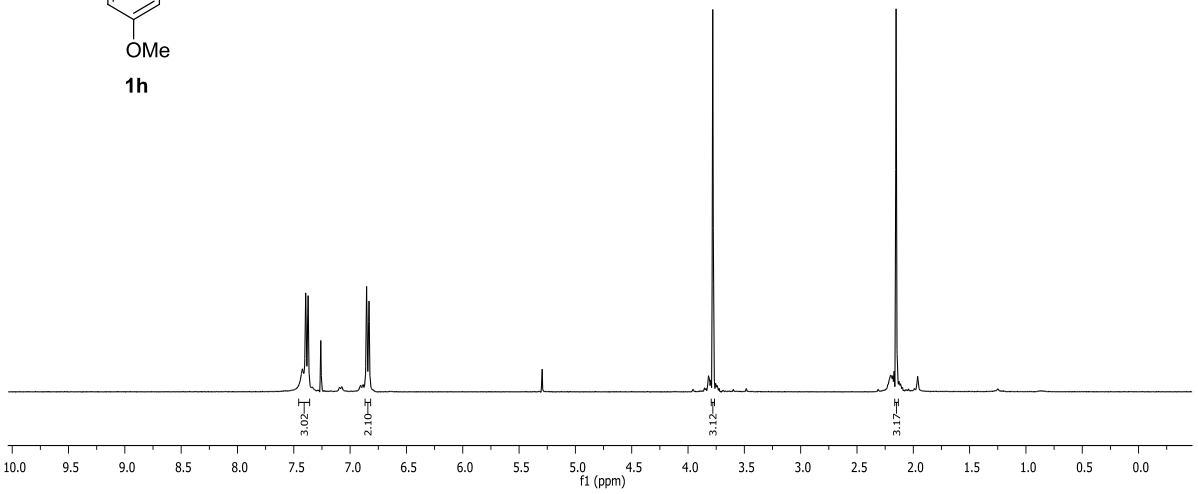

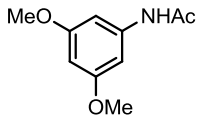

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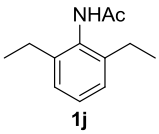

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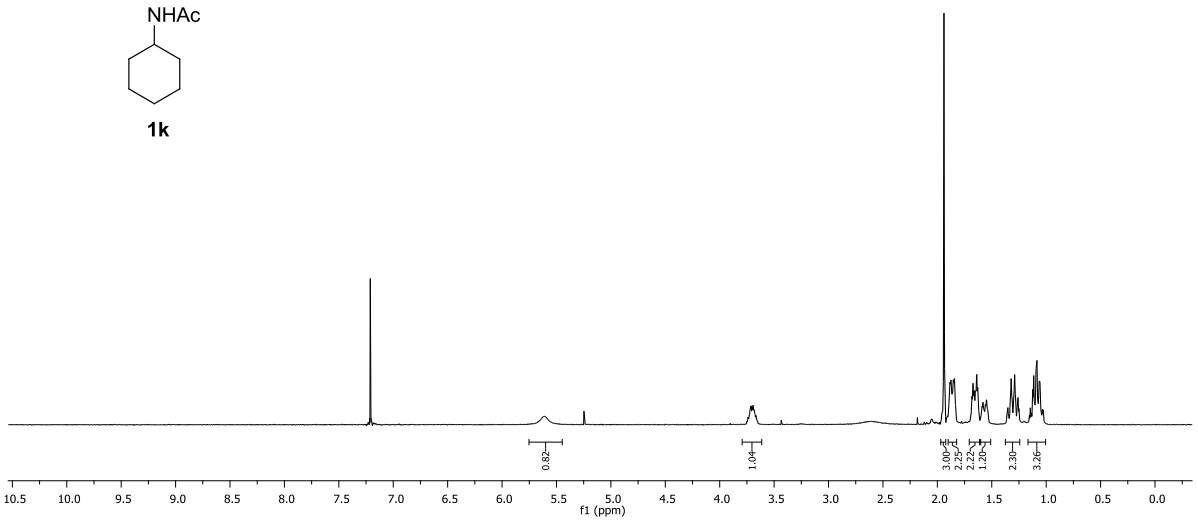

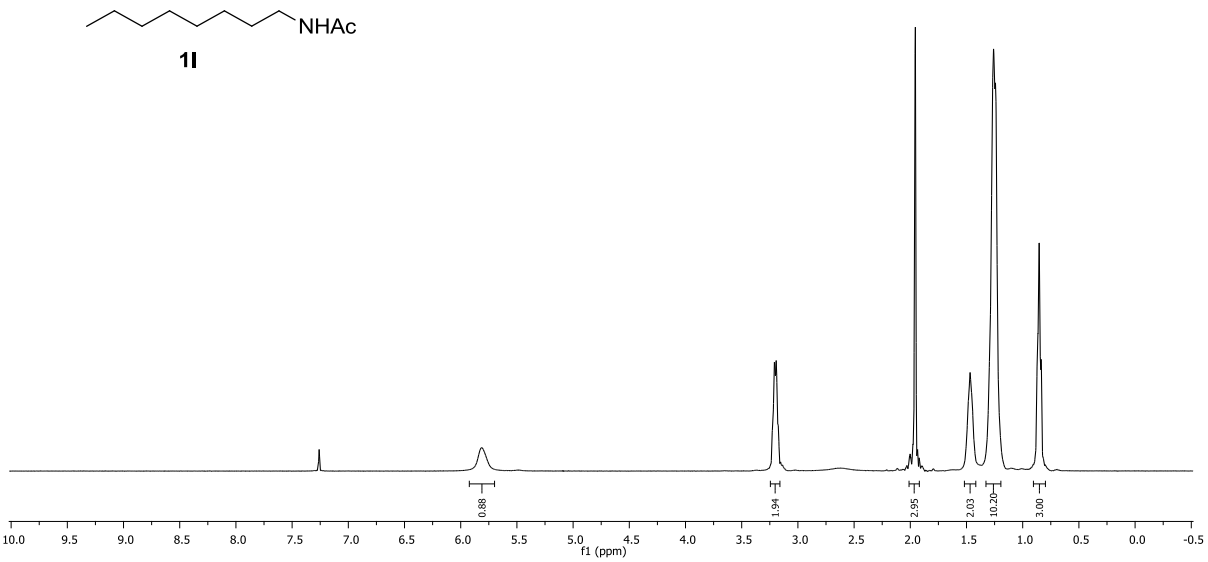

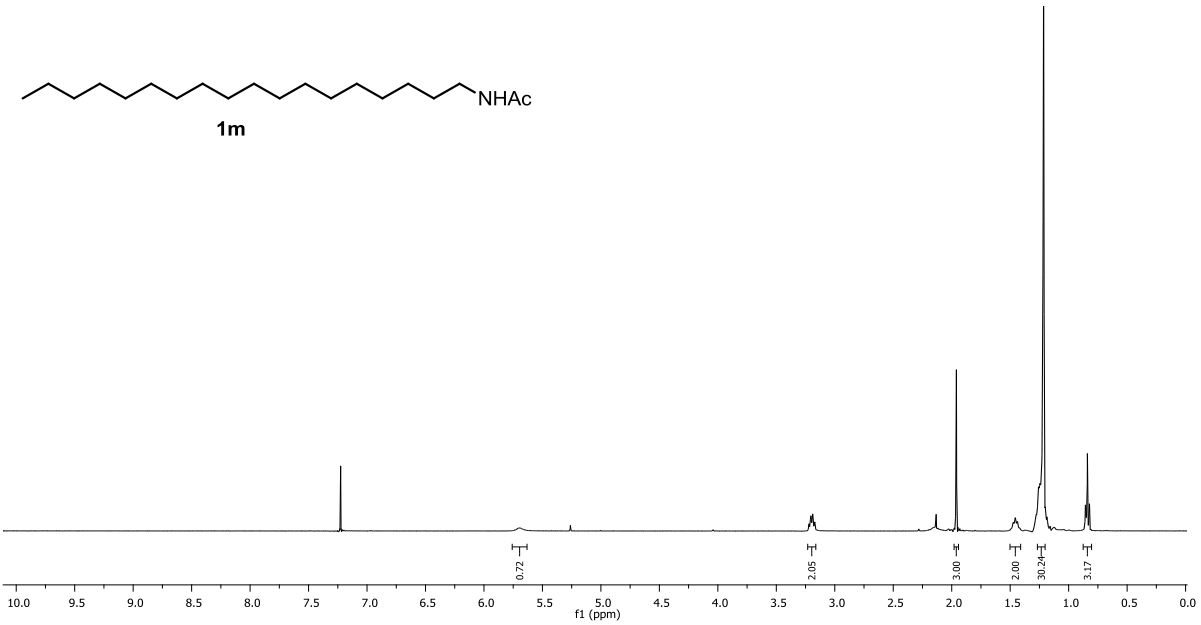

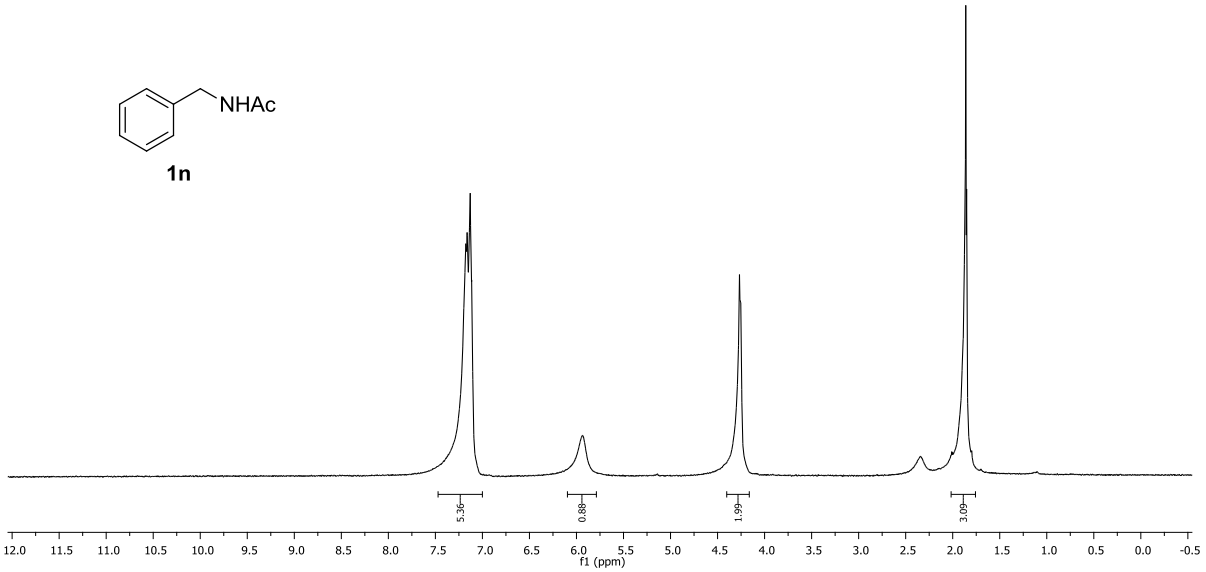

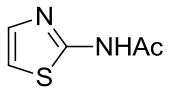

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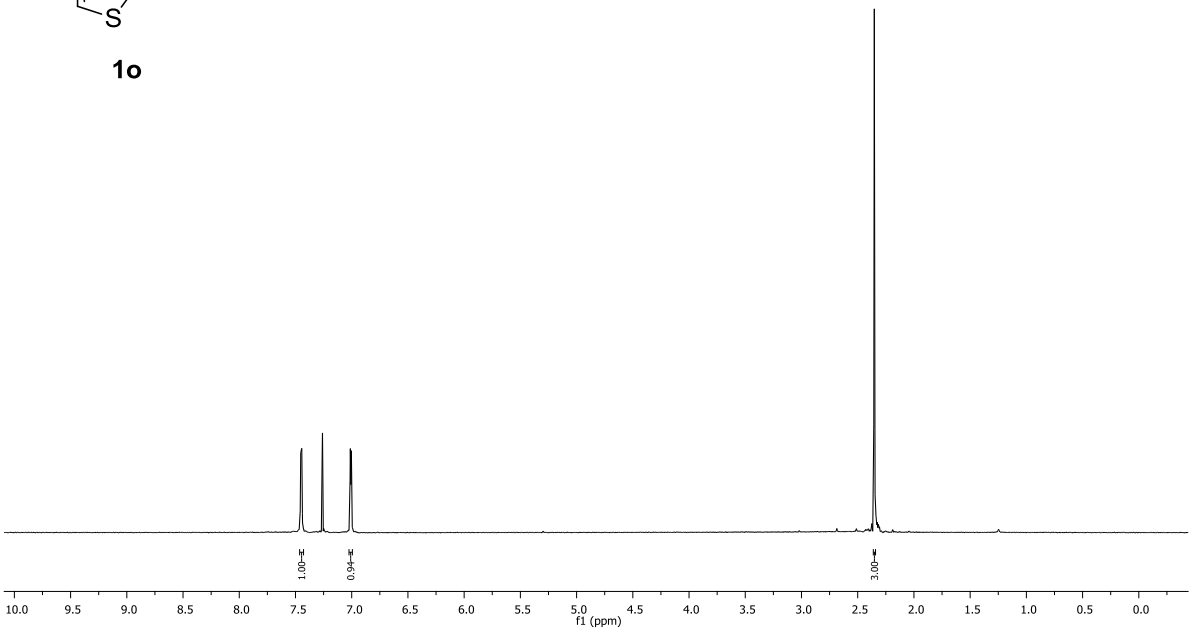

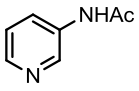

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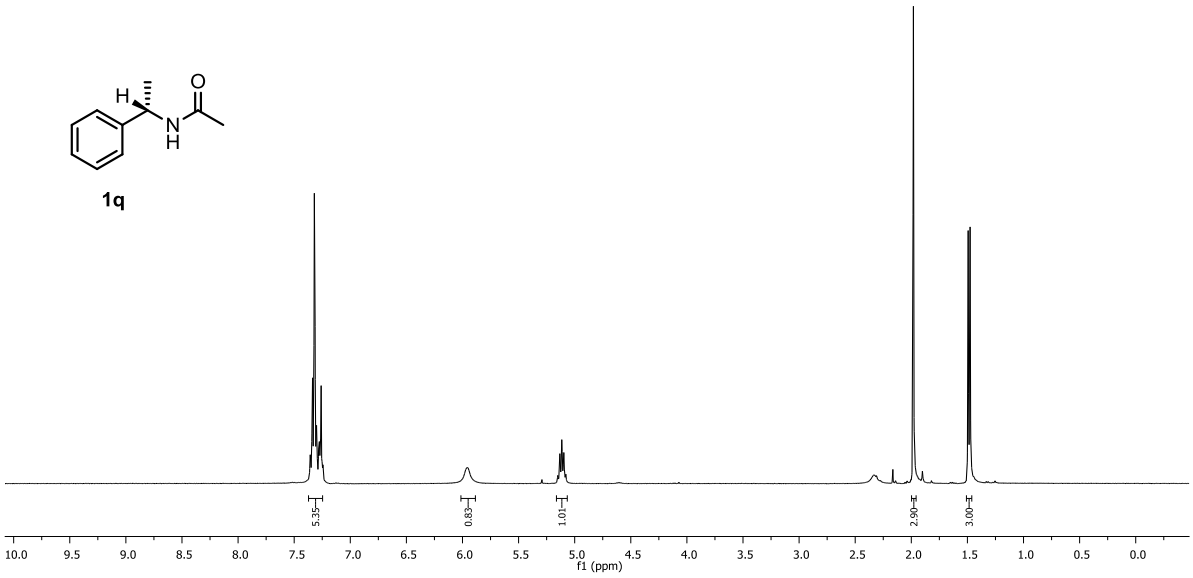

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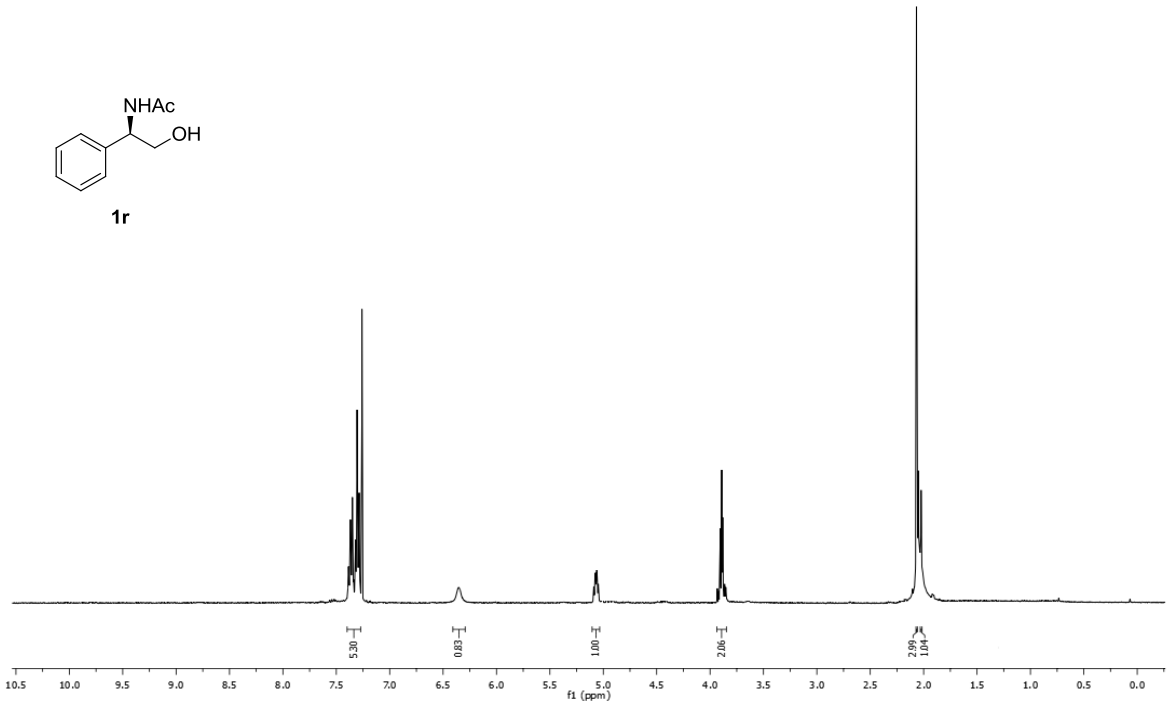

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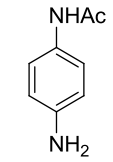

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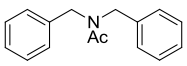

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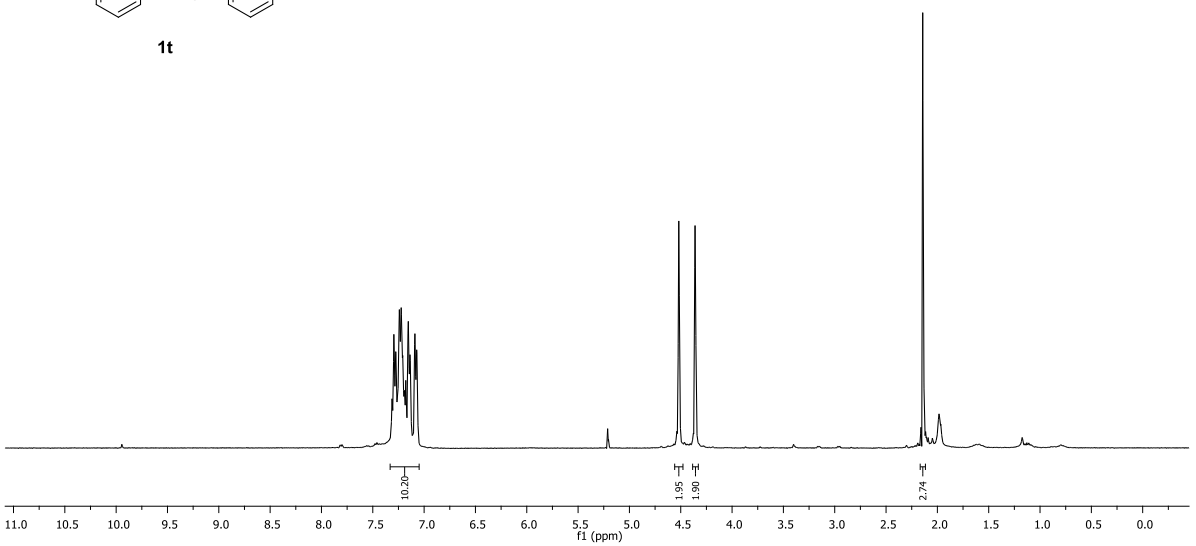

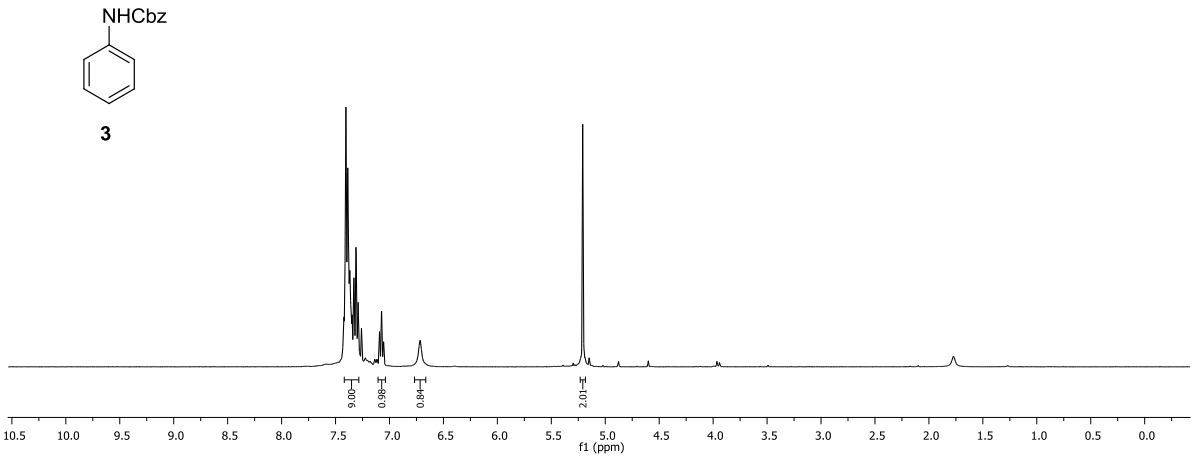

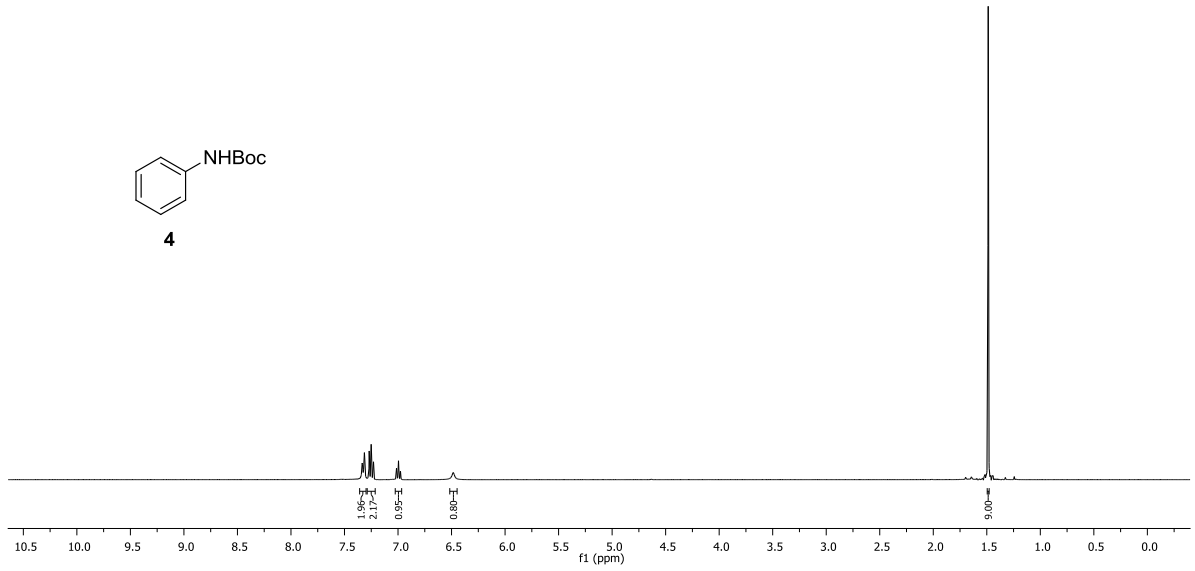

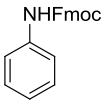

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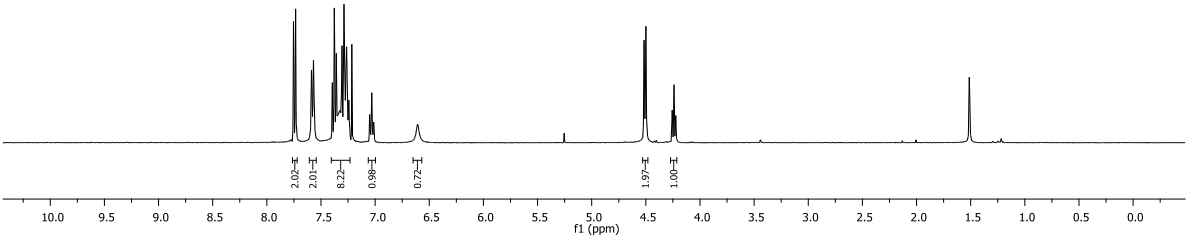

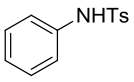

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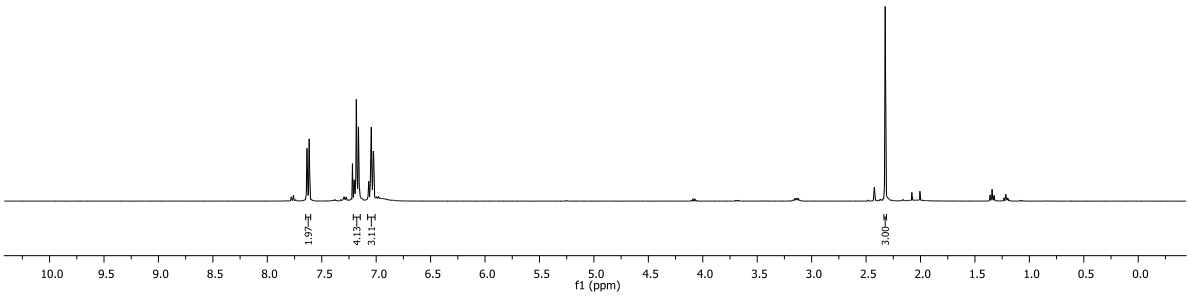

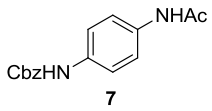

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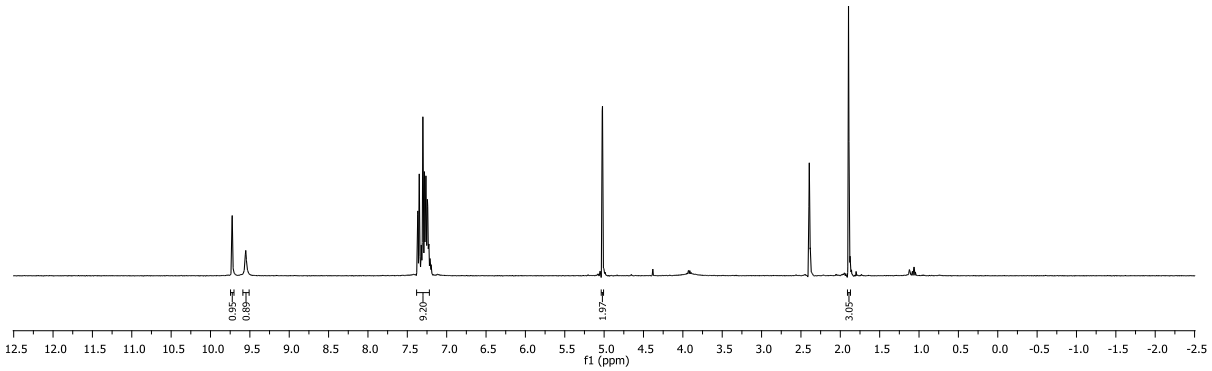

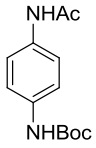

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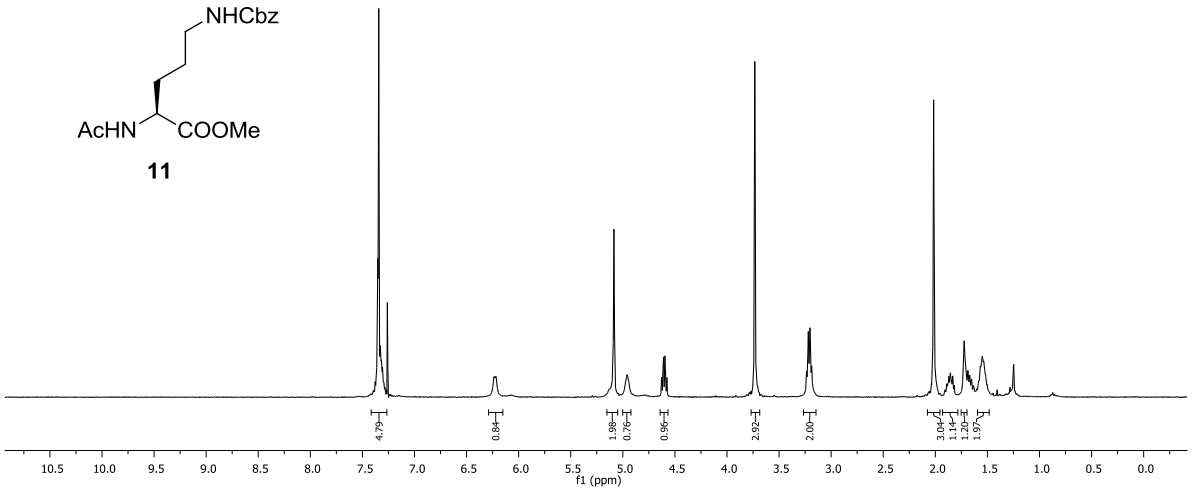

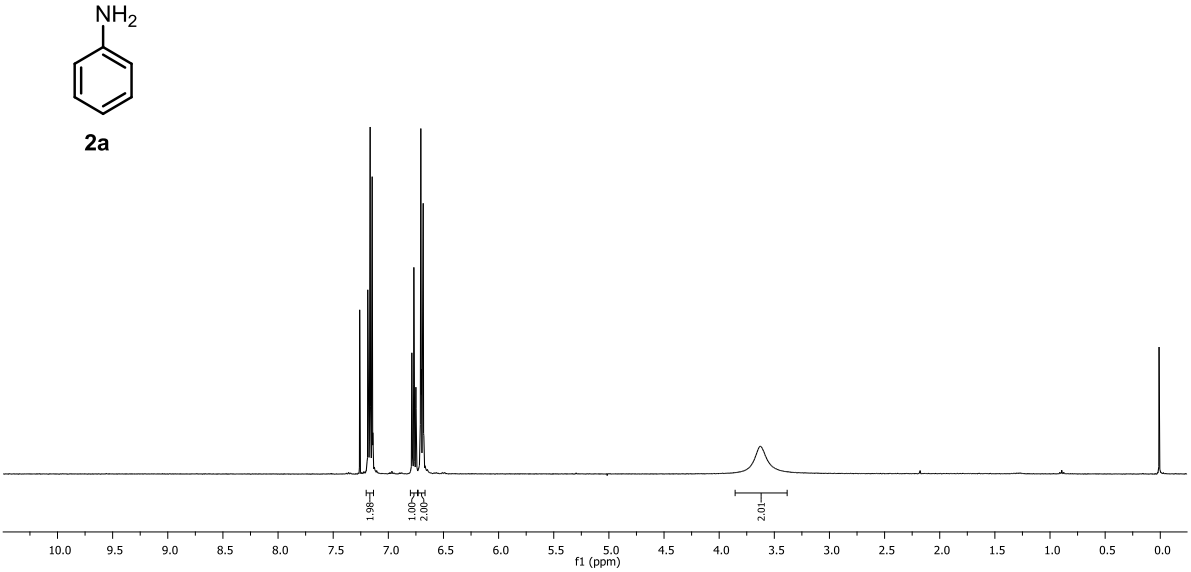

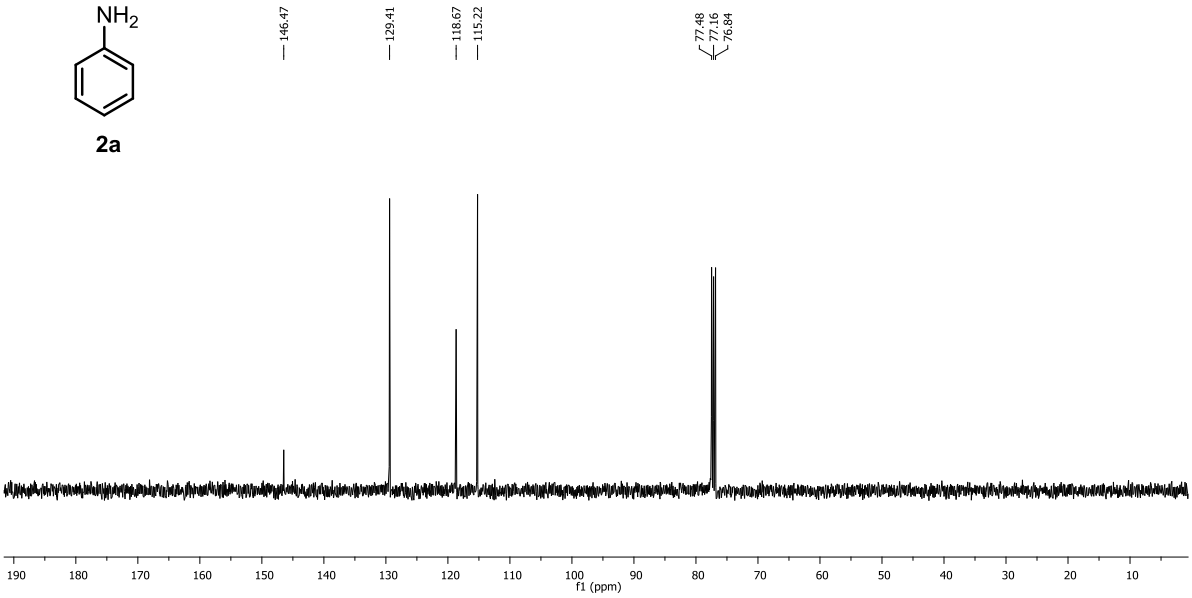

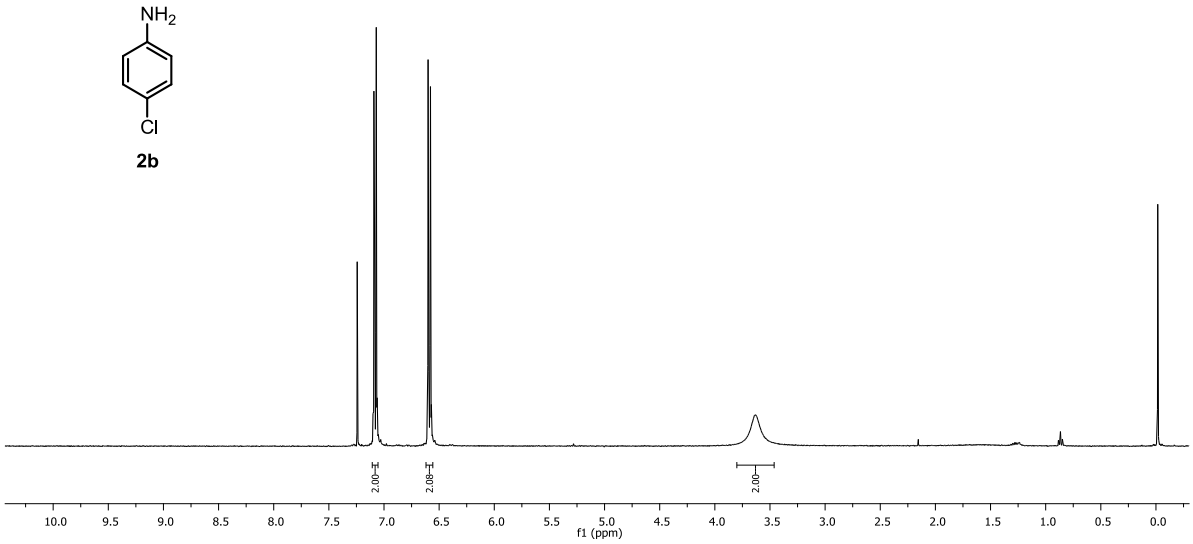

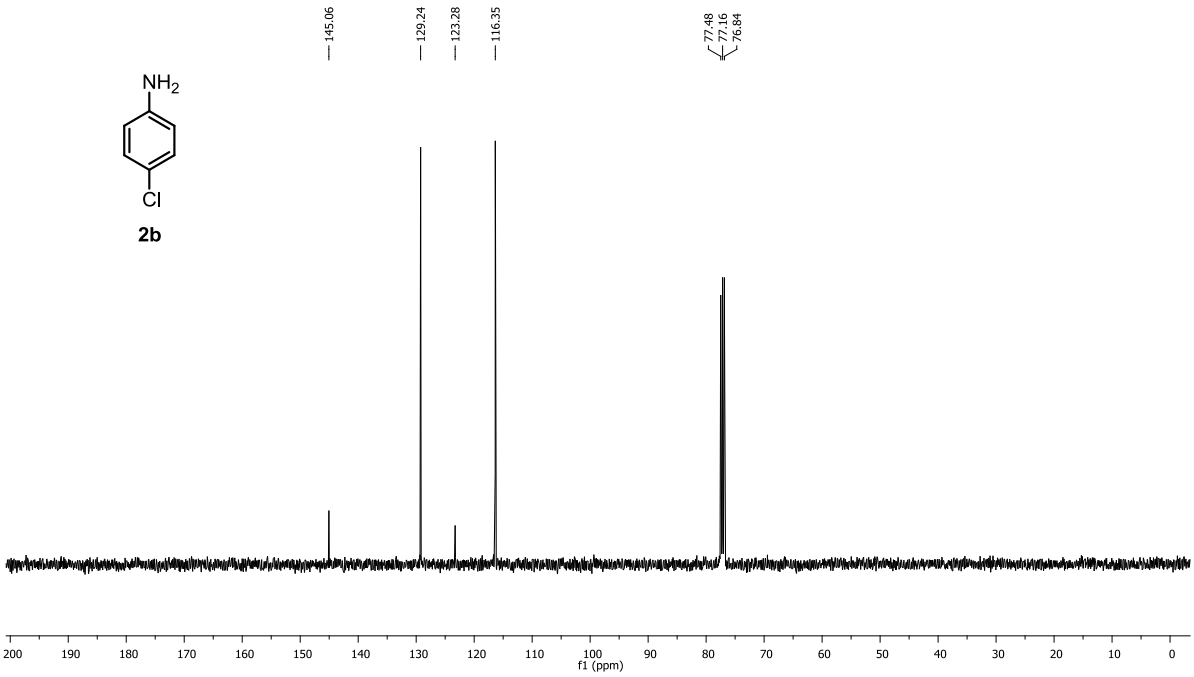

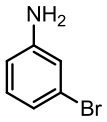
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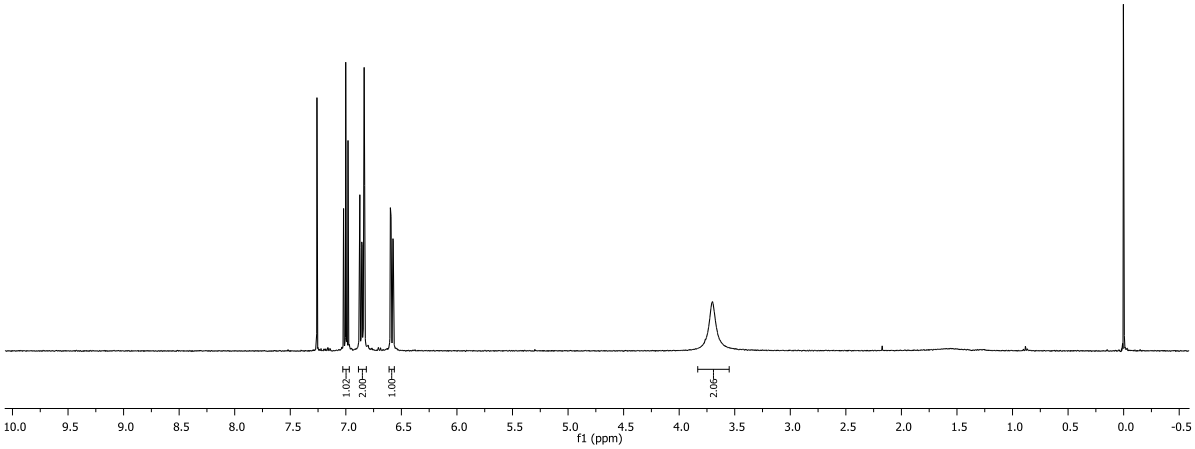
Br

2c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2.00
1.00
2.06
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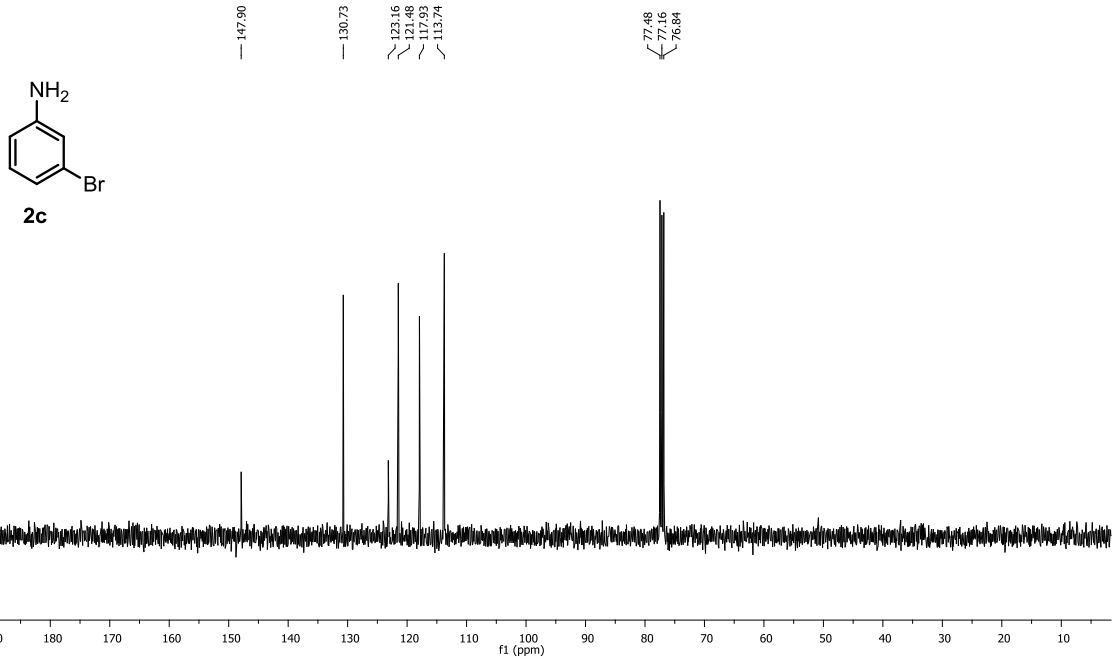
f1 (ppm)


147.90
130.73
123.16
121.48
117.93
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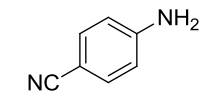
77.16
76.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

NH2
Br

2c



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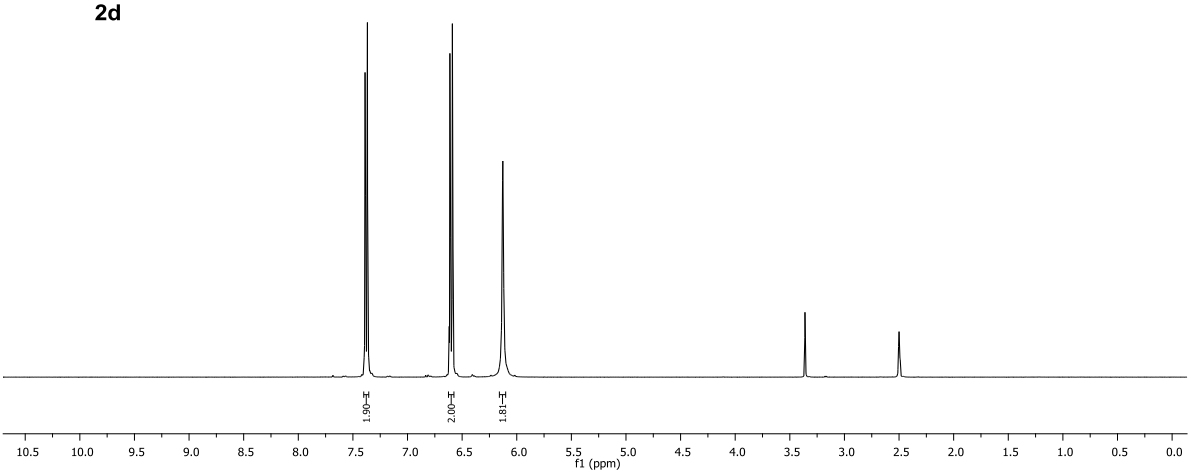

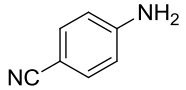

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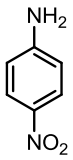

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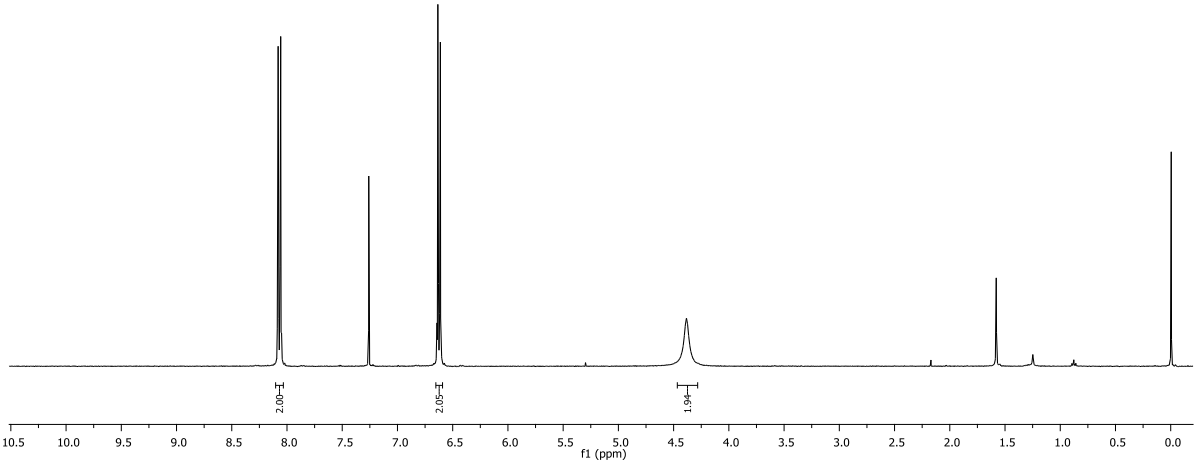

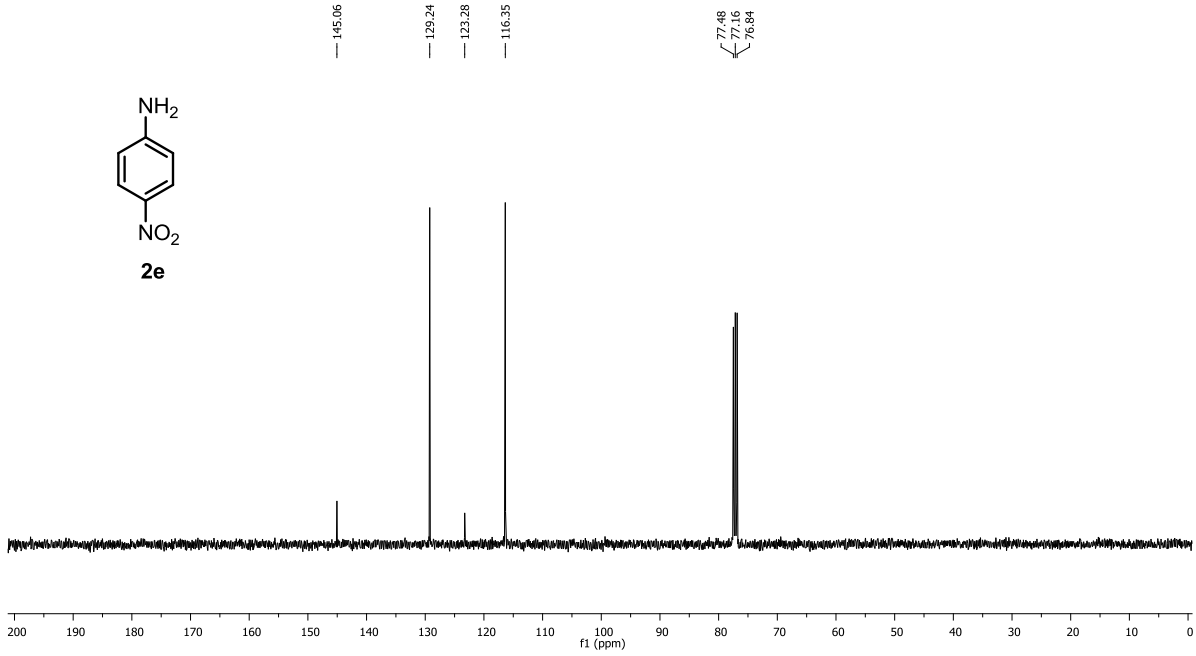

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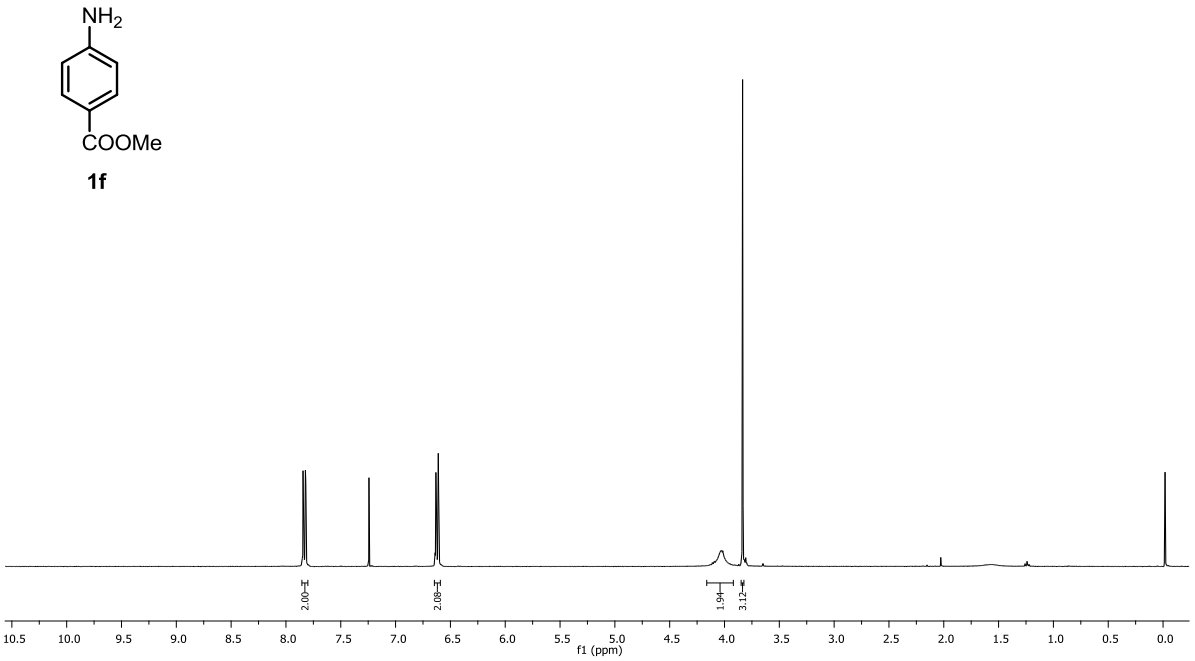

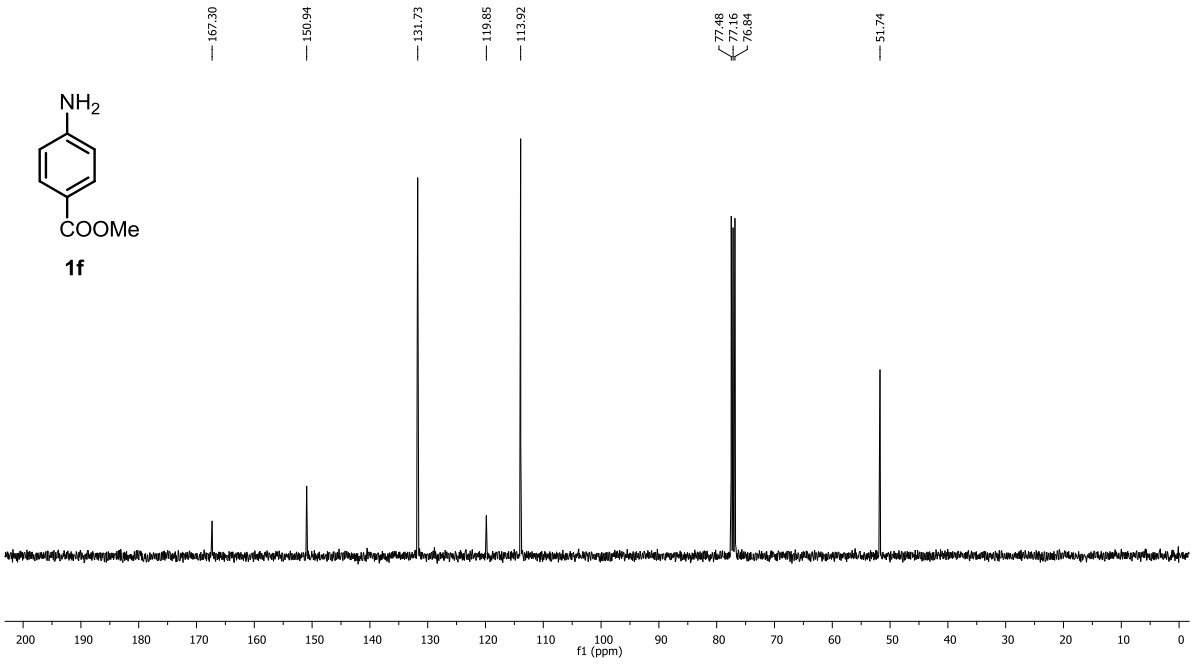

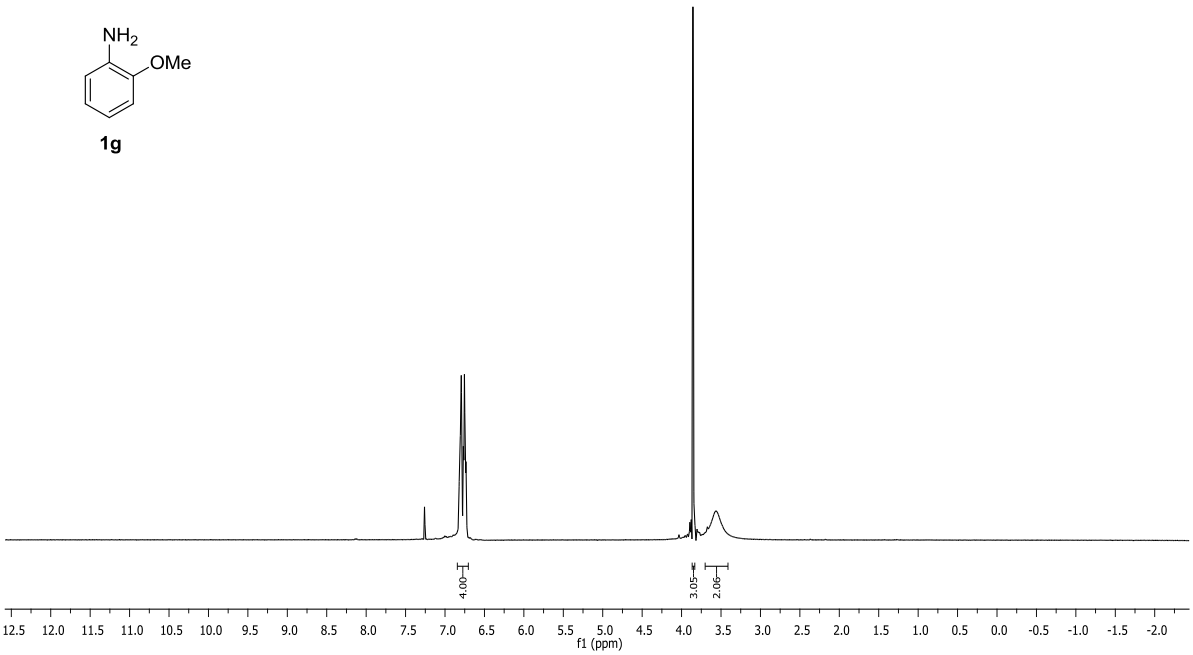

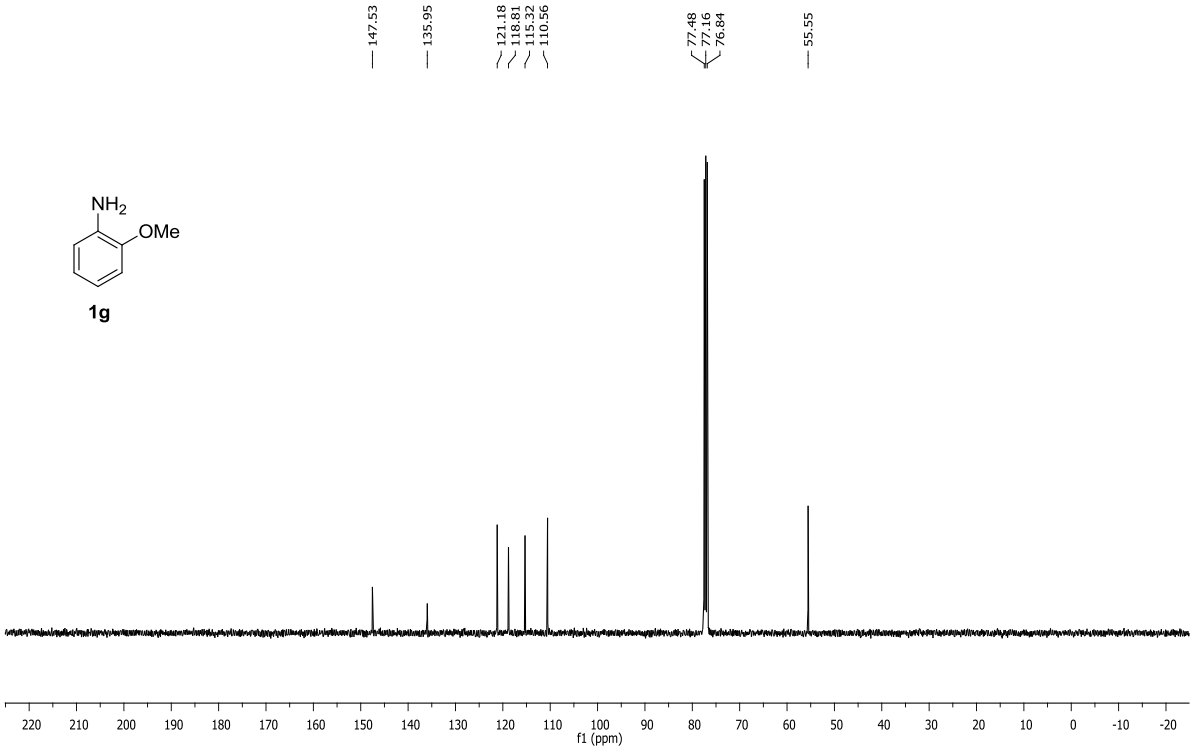

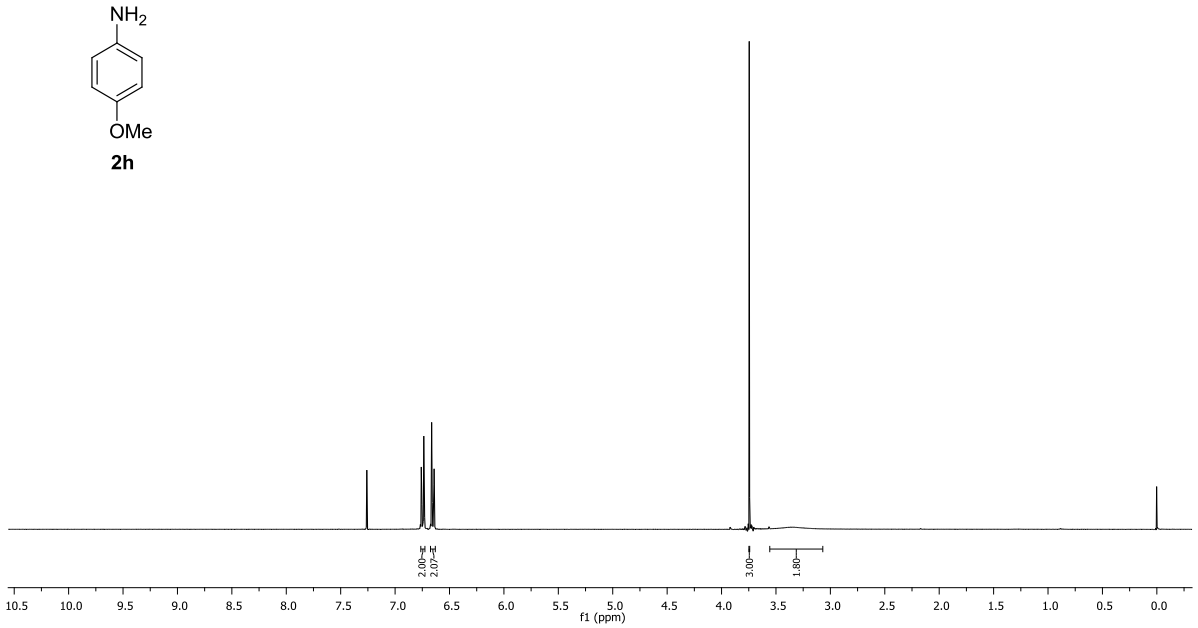

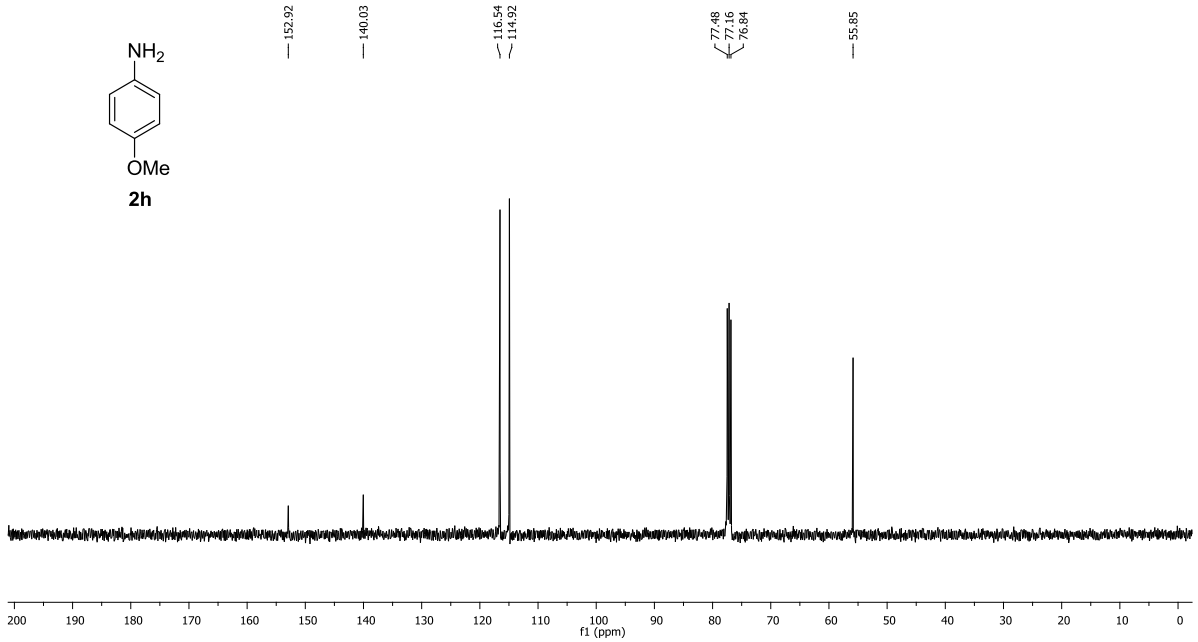

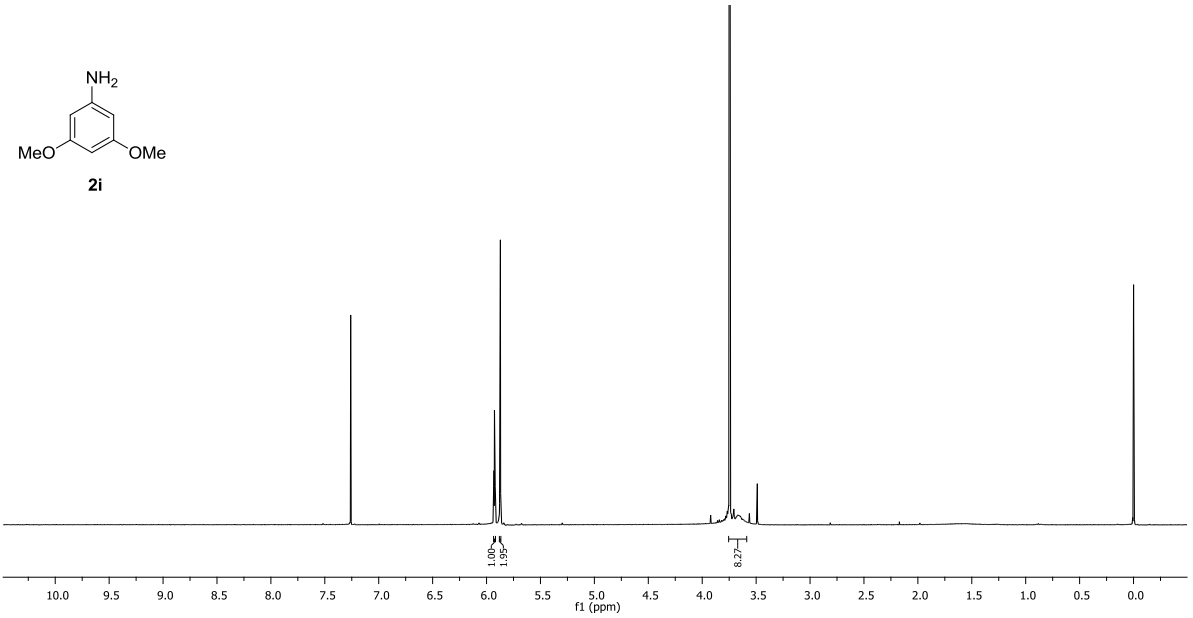

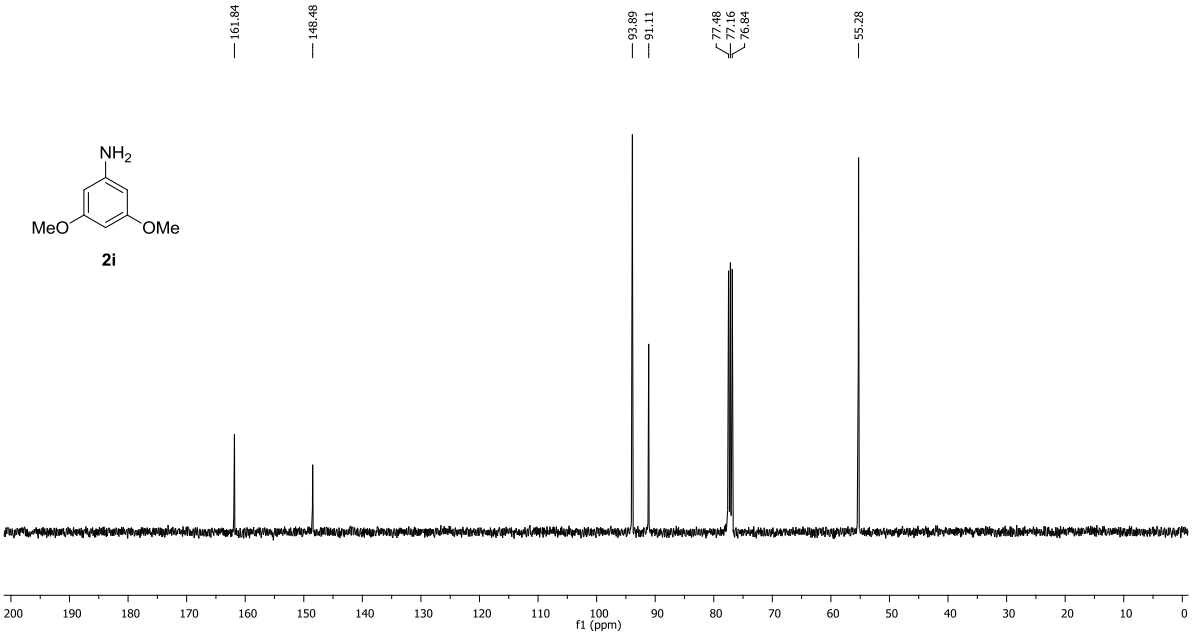

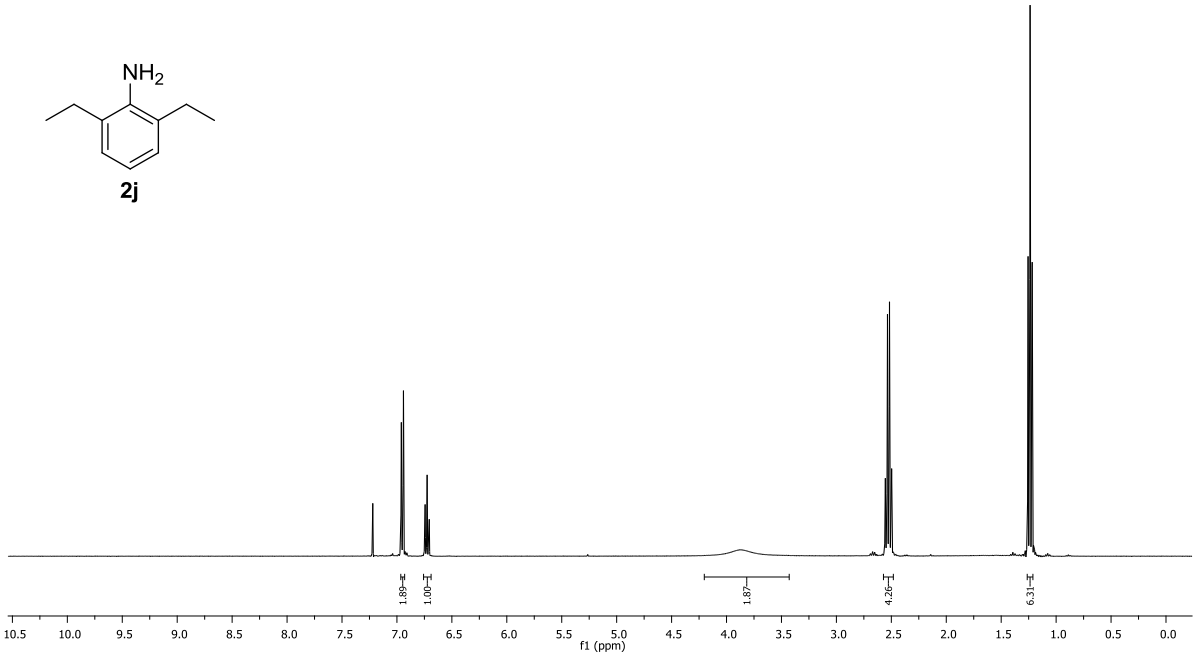

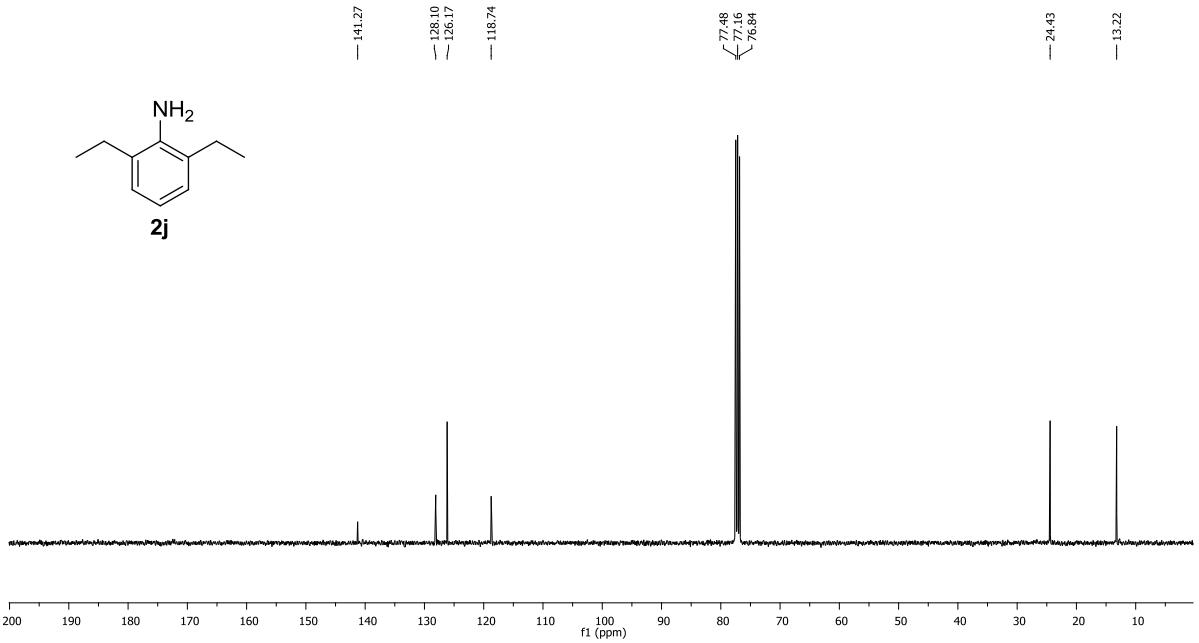

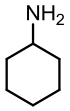

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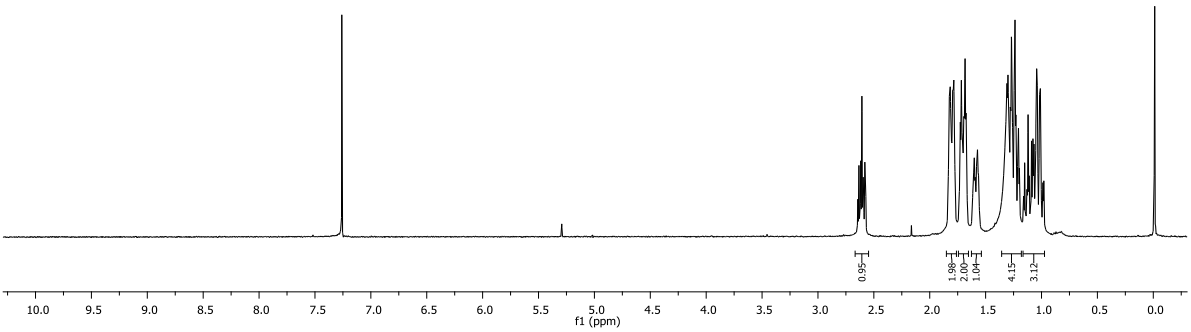

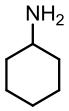

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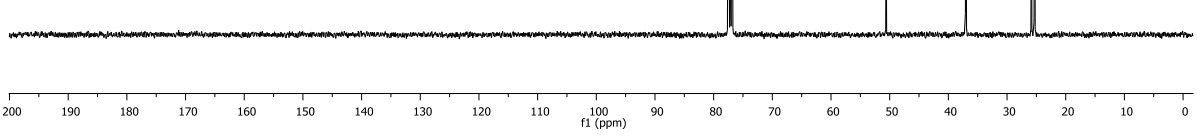

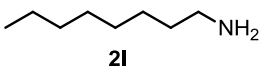

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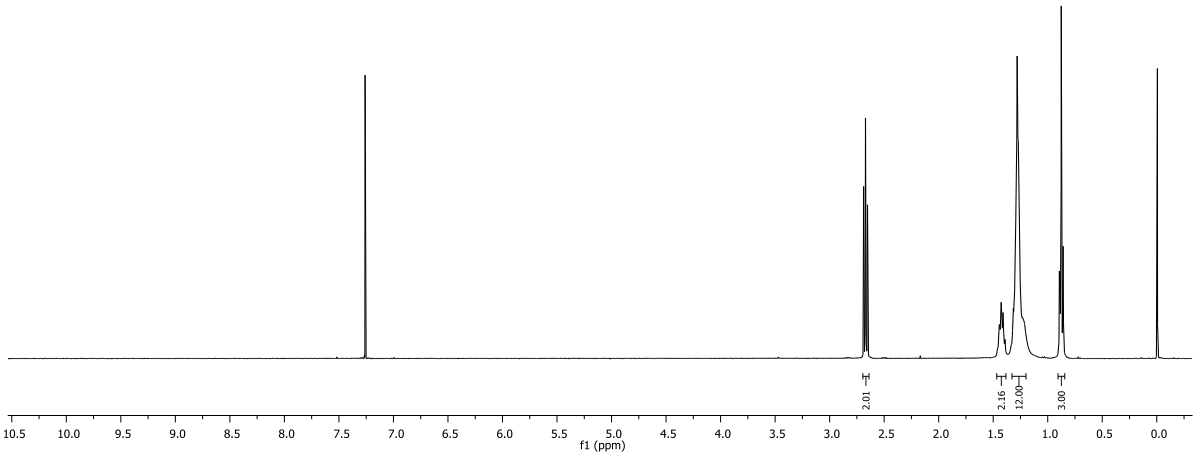

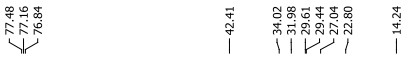

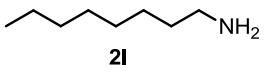

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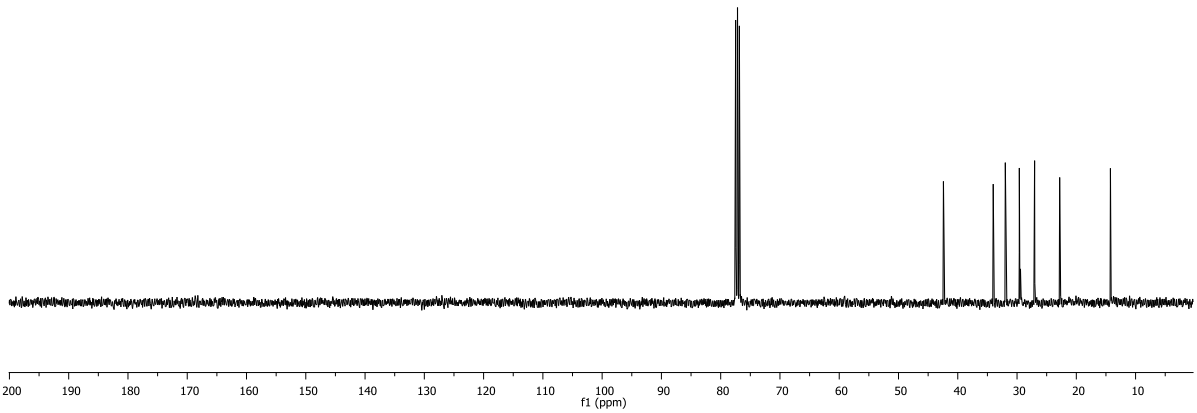

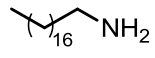

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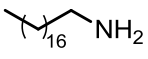

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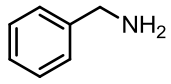

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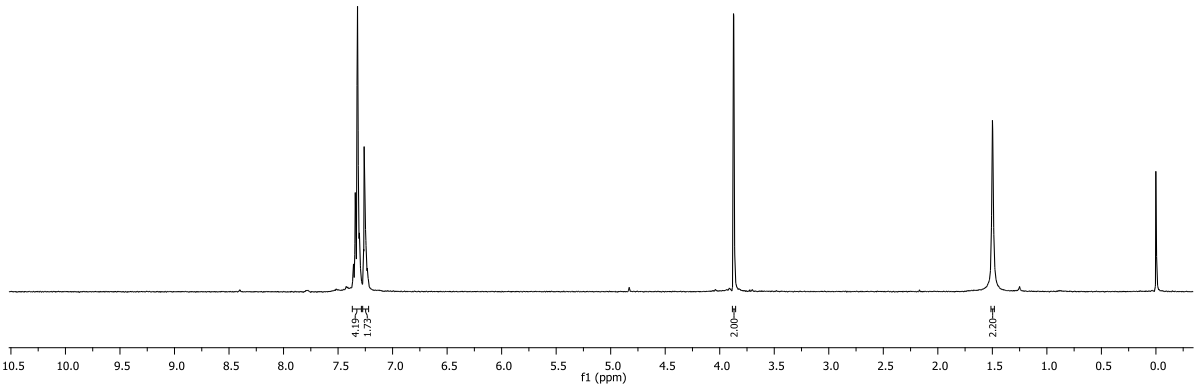

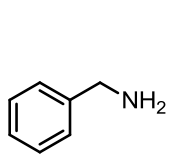

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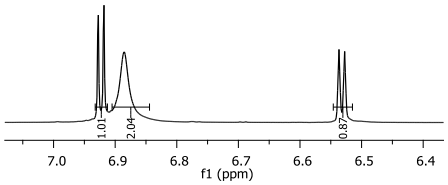

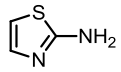

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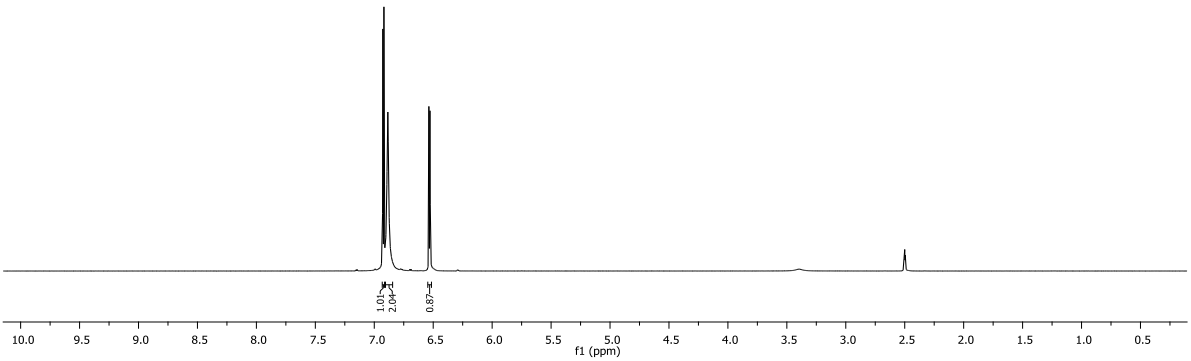

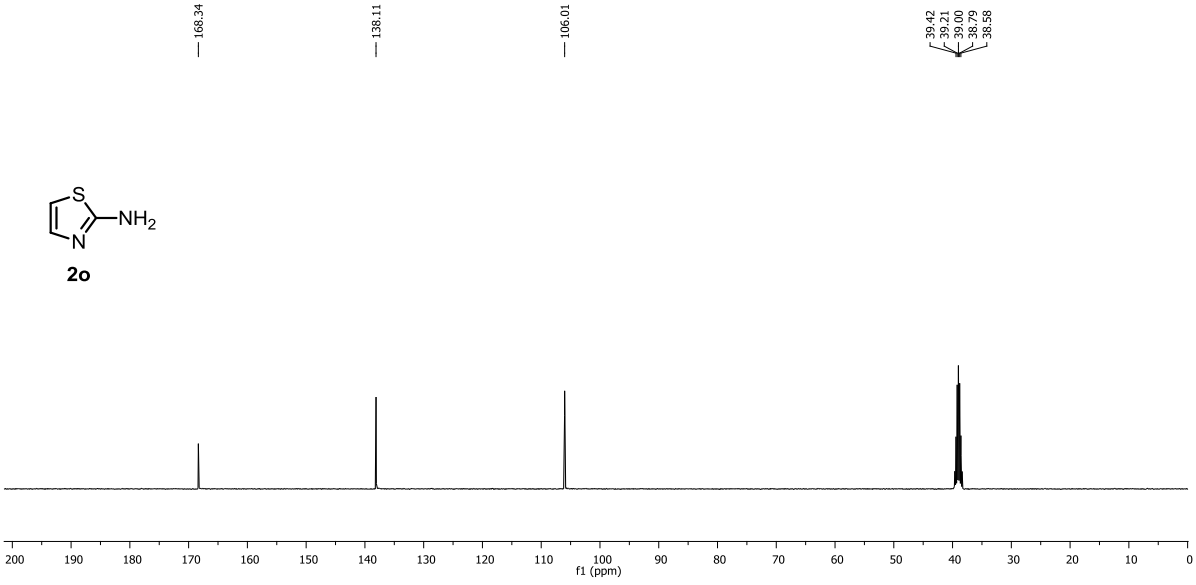

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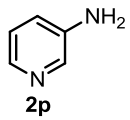

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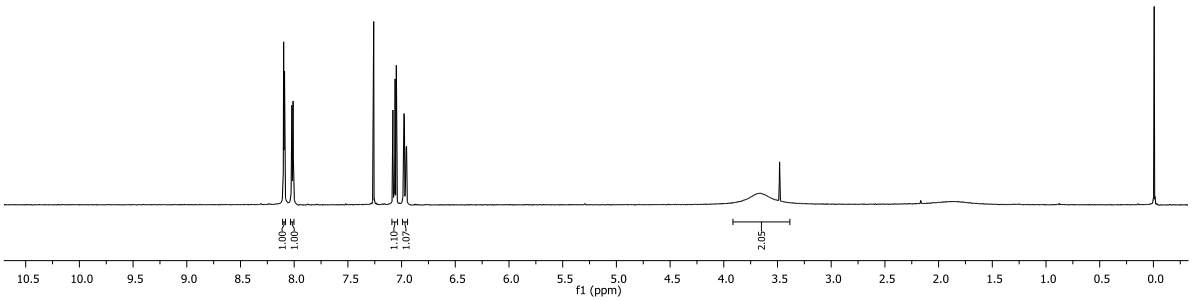

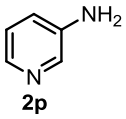

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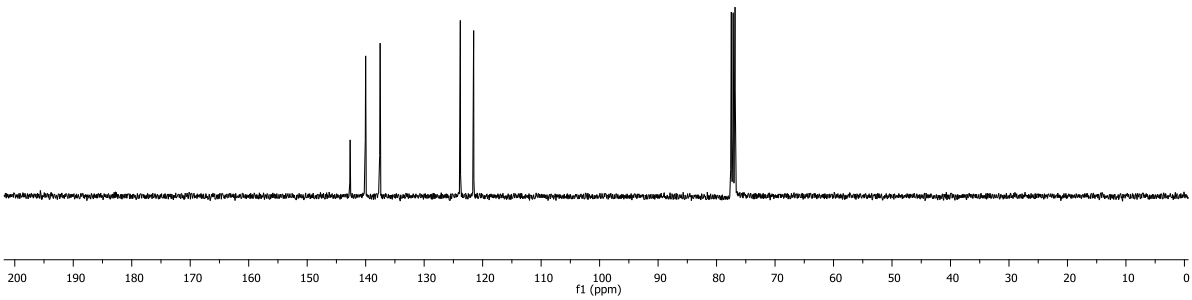

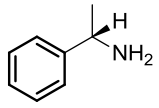

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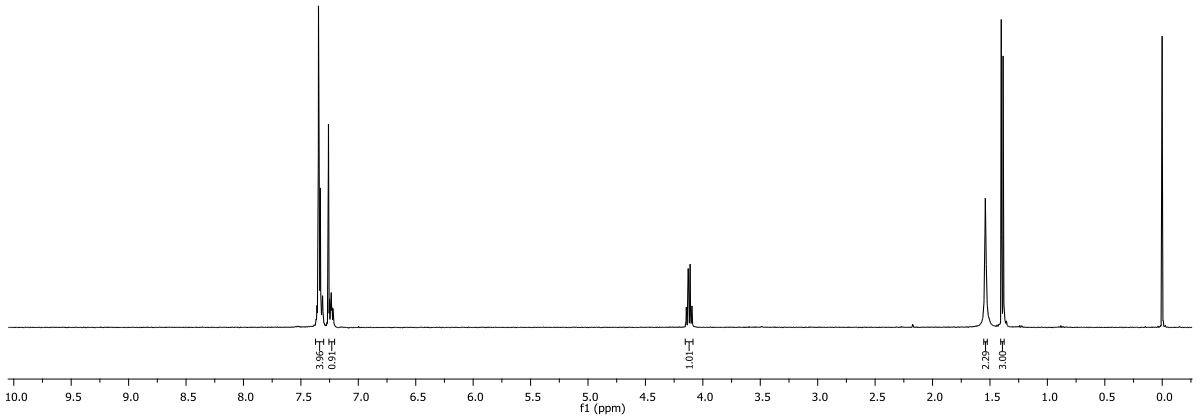

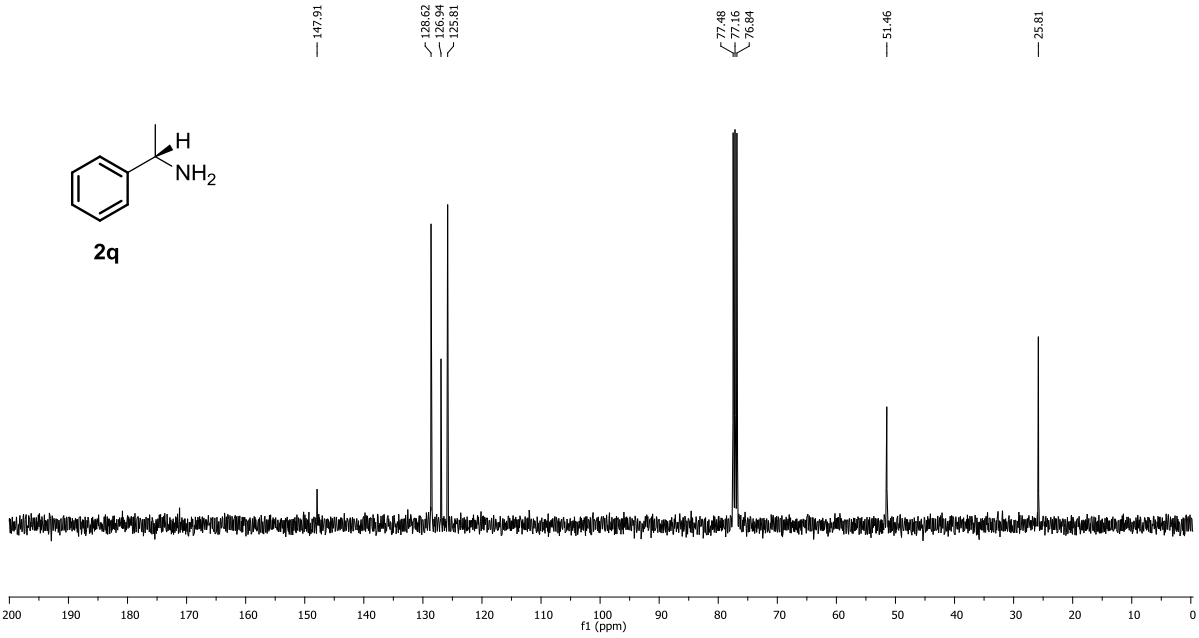

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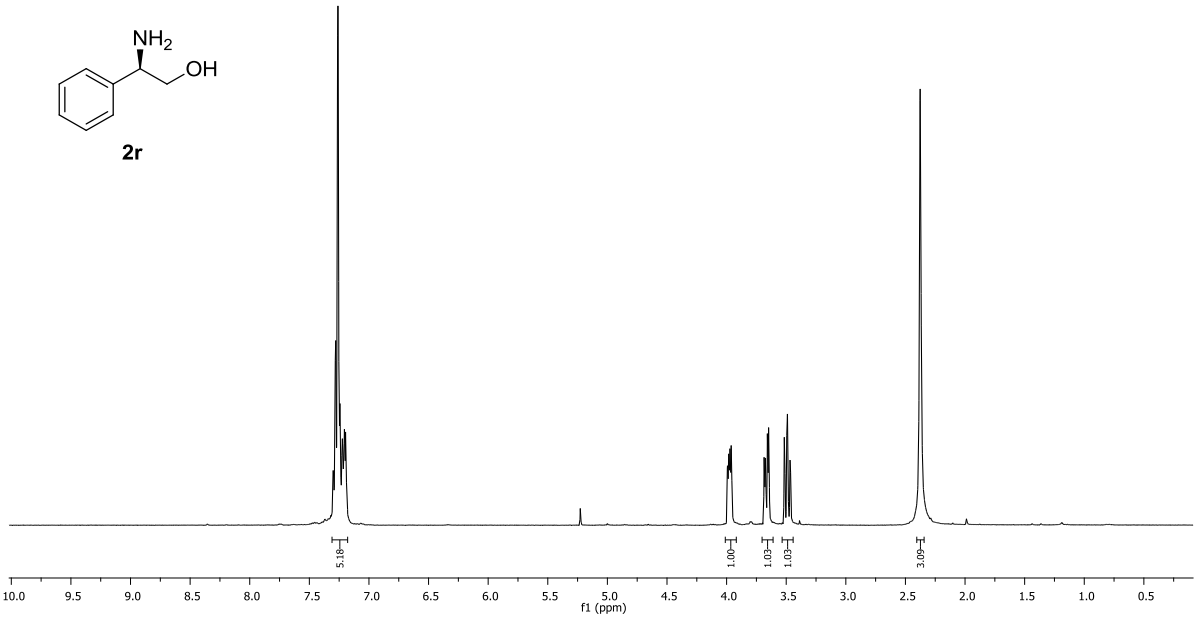

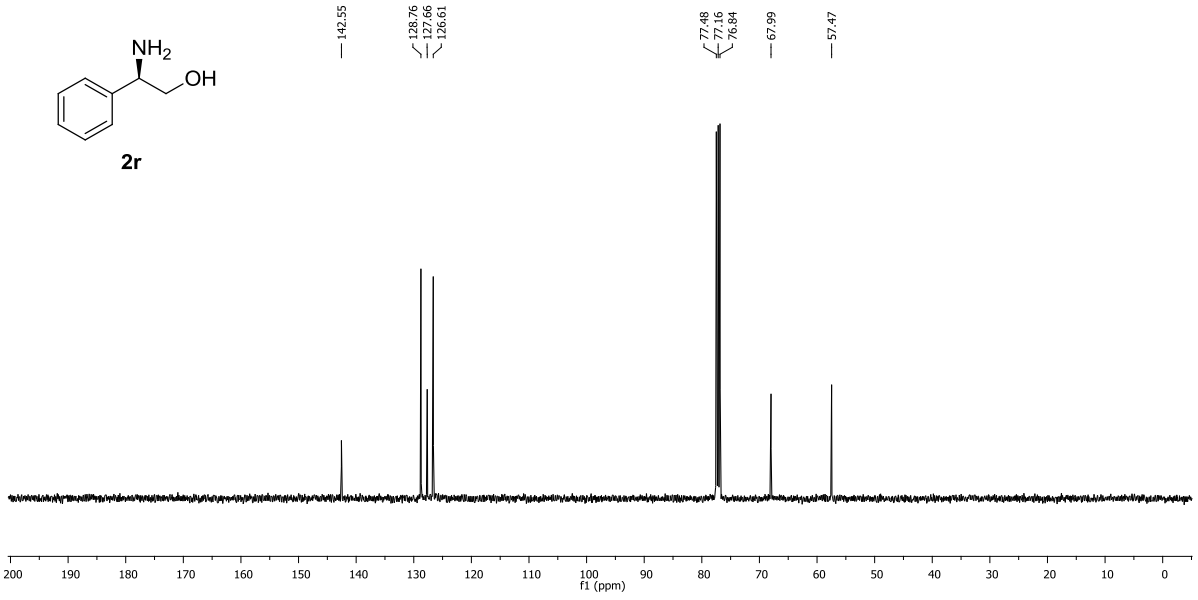

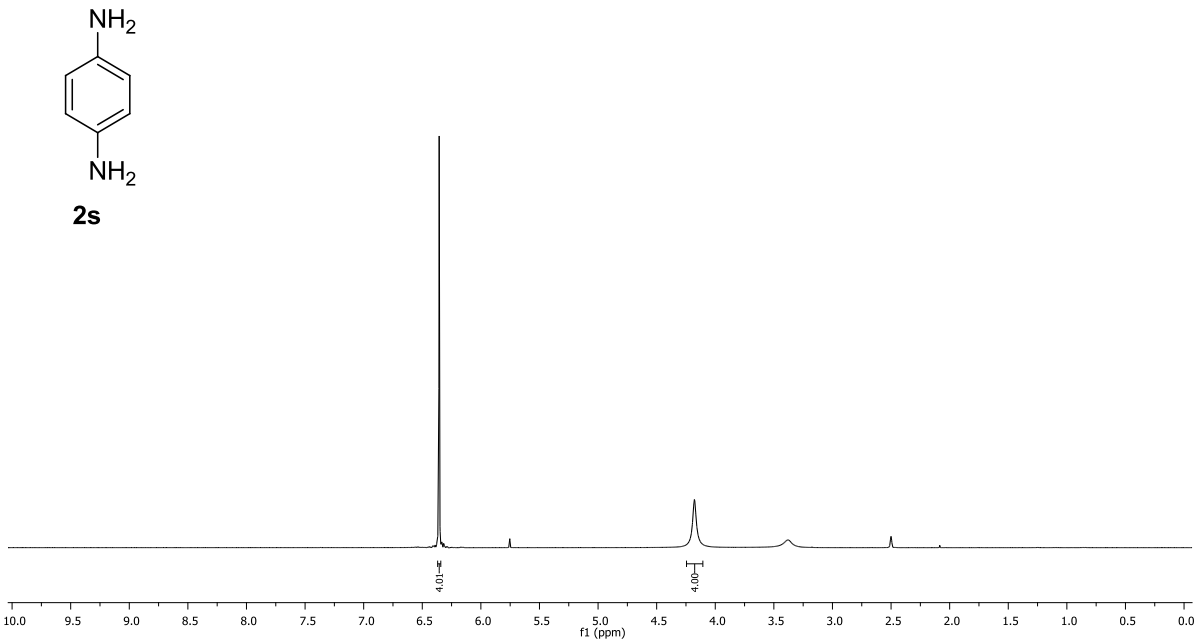

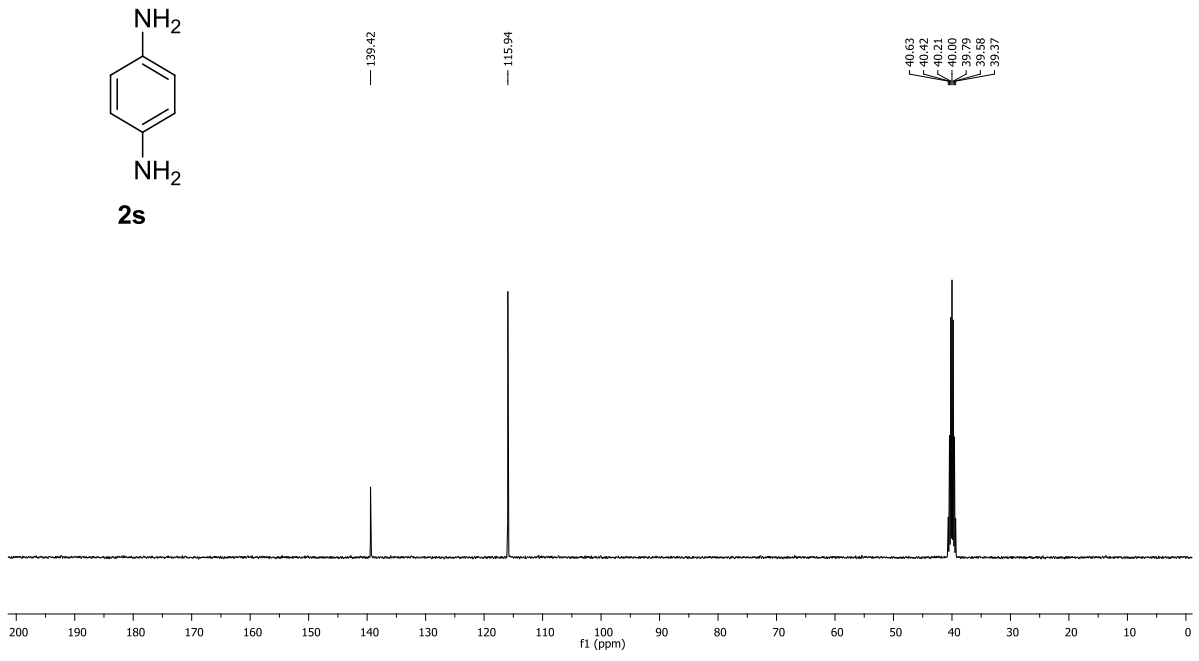

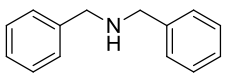

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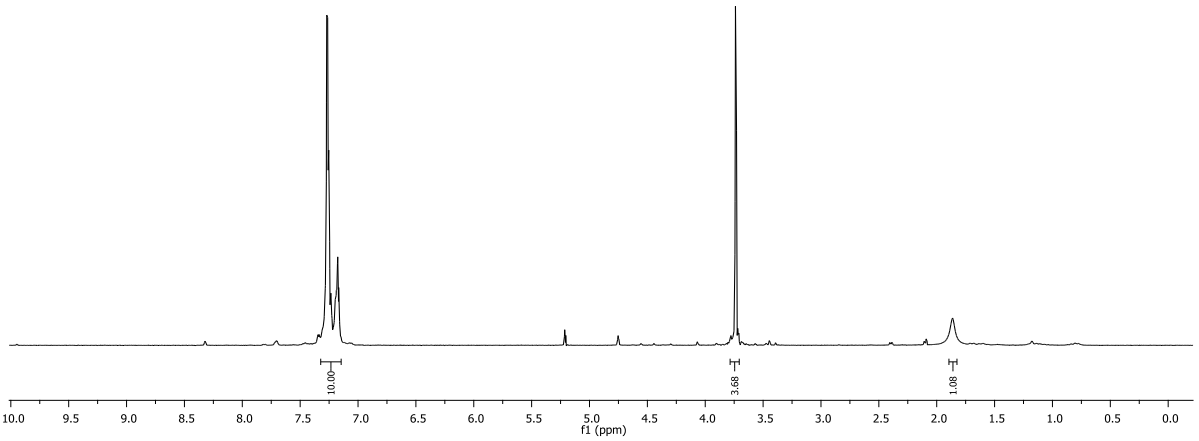

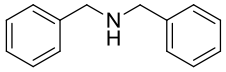

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