Electronic Supplementary Material (ESI) for Chemical Science.

Chemoselective Nitro Reduction and Hydroamination Using a Single Iron Catalyst

Supporting Information

Kailong Zhu, Michael P. Shaver* and Stephen P. Thomas*

School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, United Kingdom.
Email: michael.shaver@ed.ac.uk; stephen.thomas@ed.ac.uk

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General Considerations

All ^{1}H, $^{13}C\{^{1}H\}$ spectra were obtained on Bruker Avance III 400 and 500 MHz spectrometers or on a Bruker Avance I 600 MHz spectrometer. $^{13}C\{^{1}H\}$ denotes proton-decoupled ^{13}C spectra. All spectra were obtained at ambient temperature. The chemical shifts (δ) and coupling constants (*J*) were recorded in parts per million (ppm) and Hertz (Hz) respectively. ^{1}H and $^{13}C\{^{1}H\}$ multiplicities and coupling constants are reported where applicable. Spectra were recorded relative to the residual solvent residual peak ($CDCl_3$, 7.27 ppm, 77.00 ppm).

Amine-bis(phenolate) iron(III) complexes **4a, 4b** used in this work were synthesised according to established literature procedures.[1] Triethoxysilane, methyldiphenylsilane and 1,1,1,3,5,5,5-heptamethyltrisiloxane were purchased from Alfa Aesar. Phenylsilane and diphenylsilane were purchased from Sigma-Aldrich. Iron (III) chloride was purchased from Sigma-Aldrich. Nitro substrates **1g**, **1h**, **1i**, **1j**, **1k** and **1s** were synthesised according to literature process.[2] All other nitro substrates were purchased from various commercial vendors. All chemicals were used without further purification.

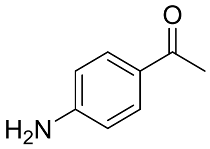
Flash chromatography was performed on silica gel (Merck Geduran Si 60). Petroleum spirit refers to petroleum ether distillate obtained at 40-60 °C. Thin layer chromatography was performed on aluminium backed silica plates (Merck 60 F_{254}).

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

General Procedure for the Reduction of Nitro Compounds:

A mixture of catalyst **4b** (0.012 mmol, 5.5 mg), nitro compound **1** (0.6 mmol), triethoxysilane (2.4 mmol, 393.6 mg) and acetonitrile (0.6 mL) were stirred in a preheated oil bath (80 °C) for a specified time. After full consumption of the starting material, as determined by TLC, the solvents were removed under vacuum. The crude product was then dissolved in a minimal amount of CH_2Cl_2 and purified by flash column chromatography using petroleum spirit/ethyl acetate.

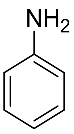
4-Aminoacetophenone 2a:



Using 4-nitroacetophenone (0.6 mmol, 99.0 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 4h. The amine **2a** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a pale yellow powder (73.7 mg, 91%). Melting point: 104-105 °C. (Petroleum Spirit/EtOAc); Lit.[3] 105-106 °C (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.81 (m, 2H), 6.68-6.64 (m, 2H), 4.18 (br, 2H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 196.5, 151.2, 130.8, 127.9, 113.7, 26.1.

Data obtained were in accordance with those previously reported.[3]

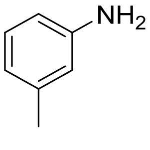
Aniline 2b:



Using nitrobenzene (0.6 mmol, 73.8 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 4h. The amine **2b** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a brown oil (46.9 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22-7.17 (m, 2H), 6.82-6.77 (m, 1H), 6.74-6.70 (m, 2H), 3.66 (br, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.4, 129.3, 118.6, 115.1.

Data obtained are in accordance with those previously reported.[4]

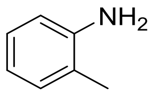
3-Aminotoluene 2c:



Using 3-nitrotoluene (0.6 mmol, 82.2 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2c** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a pale yellow oil (53.9 mg, 84%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10-7.07 (m, 1H), 6.64-6.62 (m, 2H), 6.56-6.53 (m, 1H), 3.62 (br, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 146.4, 139.1, 129.2, 119.5, 115.9, 112.3, 21.4.

Data obtained are in accordance with those previously reported.[4]

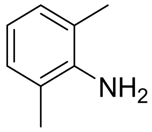
2-Aminotoluene 2d:



Using 2-nitrotoluene (0.6 mmol, 82.2 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2d** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a light yellow oil (45.0 mg, 70%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.08-7.05 (m, 2H), 6.75-6.72 (m, 1H), 6.70 (d, $J = 6.0$ Hz, 1H), 3.61 (br, 2H), 2.20 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): 144.6, 130.4, 127.0, 122.3, 118.6, 114.9, 17.3.

Data obtained are in accordance with those previously reported.[4]

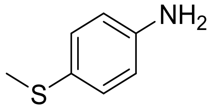
2,6-Dimethylaniline 2e:



Using 1, 3-dimethyl-2-nitrobenzene (0.6 mmol, 90.7 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2e** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (5:1 v/v) as a pale yellow oil (59.5 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.99 (d, $J = 10.0$ Hz, 2H), 6.71-6.68 (m, 1H), 3.61 (br, 2H), 2.23 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 142.7, 128.3, 121.7, 118.0, 17.6.

Data obtained are in accordance with those previously reported.[5]

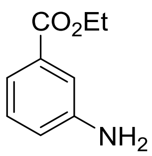
4-(Methylthio)aniline 2f:



Using 4-nitrothioanisole (0.6 mmol, 101 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 8h. The amine **2f** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a pale yellow oil (77.6 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22-7.19 (m, 2H), 6.67-6.63 (m, 2H), 3.68 (br, 2H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 145.2, 131.1, 125.8, 115.8, 18.8.

Data obtained are in accordance with those previously reported.[5]

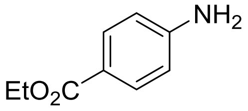
Ethyl 3-aminobenzoate 2g:



Using ethyl 4-nitrobenzoate (0.6 mmol, 117 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 5h. The amine **2g** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a pale yellow oil (90.1 mg, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (m, 1H), 7.38-7.37 (m, 1H), 7.22 (t, $J = 8.0$ Hz, 1H), 6.88-6.85 (m, 1H), 4.37 (q, $J = 8.0$ Hz, 2H), 3.81 (br, 2H), 1.40 (t, $J = 8.0$ Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 166.8, 146.5, 131.5, 129.2, 119.7, 119.3, 115.8, 60.9, 14.3.

Data obtained are in accordance with those previously reported.[6]

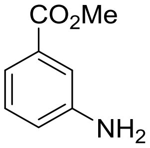
Ethyl 4-aminobenzoate 2h:



Using ethyl 4-nitrobenzoate (0.6 mmol, 117 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 5h. The amine **2h** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a white powder (97.1 mg, 98%). Melting point: 88-89 °C. (Petroleum Spirit/EtOAc); Lit.[3] 89-90 °C (hexane/EtOAc). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.89-7.86 (m, 2H), 6.66-6.63 (m, 2H), 4.34 (q, *J* = 10.0 Hz, 2H), 4.14 (br, 2H), 1.38 (t, *J* = 10.0 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 166.8, 150.9, 131.6, 119.9, 113.8, 60.3, 14.4.

Data obtained are in accordance with those previously reported.[3]

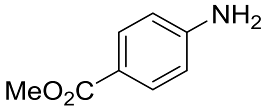
Methyl 3-aminobenzoate 2i:



Using methyl 4-nitrobenzoate (0.6 mmol, 109 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 5h. The amine **2i** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a light yellow oil (85.2 mg, 94%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.45-7.43 (m, 1H), 7.37 (s, 1H), 7.24-7.21 (m, 1H), 6.88-6.86 (m, 1H), 3.90 (s, 3H), 3.83 (br, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 167.3, 146.6, 131.1, 129.3, 119.7, 119.4, 115.8, 52.0.

Data obtained are in accordance with those previously reported.[6]

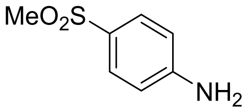
Methyl 4-aminobenzoate 2j:



Using methyl 4-nitrobenzoate (0.6 mmol, 109 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 5h. The amine **2j** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a white powder (84.2 mg, 93%). Melting point: 109-111 °C. (Petroleum Spirit/EtOAc); Lit.[7] 108 °C (hexanes/EtOAc). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.89-7.85 (m, 2H), 6.67-6.64 (m, 2H), 4.08 (br, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 167.2, 150.8, 131.6, 119.8, 113.8, 51.6.

Data obtained are in accordance with those previously reported.[7]

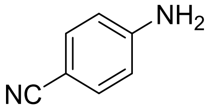
4-(Methylsulfonyl)aniline 2k:



Using 1-Methylsulfonyl-4-nitrobenzene (0.6 mmol, 121 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 4h. The amine **2k** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (1:2 v/v) as a pale yellow powder (82.1 mg, 80%). Melting point: 130-133 °C (Petroleum Spirit/EtOAc); Lit.[8] 134 ºC (water). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71-7.68 (m, 2H), 6.74-6.71 (m, 2H), 4.26 (br, 2H), 3.02 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 151.4, 129.4, 128.8, 114.1, 45.0.

NMR data obtained are in accordance with those previously reported.[2]

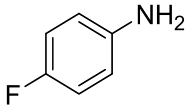
4-Aminobenzonitrile 2l:



Using 4-nitrobenzonitrile (0.6 mmol, 88.8 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2l** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as a pale yellow powder (46.0 mg, 65%). Melting point: 83-84°C (Petroleum Spirit/EtOAc); Lit.[3] 85-86 ºC (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.41 (m, 2H), 6.68-6.65 (m, 2H), 4.22 (br, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 150.5, 133.8, 120.2, 114.5, 100.1.

Data obtained are in accordance with those previously reported.[3]

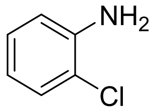
4-Fluoroaniline 2m:



Using 1-fluoro-4-nitrobenzene (0.6 mmol, 84.6 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 5h. The amine **2m** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a colourless oil (54.6 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90-6.85 (m, 2H), 6.66-6.62 (m, 2H), 3.55 (br, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 156.5 (d, $J_{C\text{-}F}$ = 235 Hz) 142.4, 116.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.7 (d, $J_{C\text{-}F}$ = 25.0 Hz).

Data obtained are in accordance with those of an authentic sample (Aldrich Cat. No. F3800).

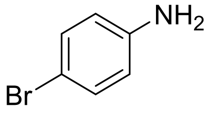
2-Chloroaniline 2n:



Using 1-chloro-2-nitrobenzene (0.6 mmol, 94.2 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 8h. Solvents were removed under vacuum and the residue was purified isolated *by* flash column chromatography using petroleum spirit/ethyl acetate (6:1 v/v) to give an inseperable mixture of the starting material and the aniline product. The yield of amine **2n** was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (87%).

Data obtained are in accordance with those of an authentic sample (Aldrich Cat. No. 23310).

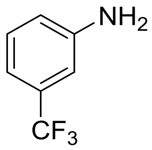
4-Bromoaniline 2o:



Using 1-bromo-4-nitrobenzene (0.6 mmol, 121 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 8h. The amine **2o** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (3:1 v/v) as a pale yellow powder (92.0 mg, 90%). Melting point: 58-60°C (Petroleum Spirit/EtOAc); Lit.[3] 61-62 ºC (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 500 MHz): δ; 7.27-7.24 (m, 2H), 6.59-6.56 (m, 2H), 3.68 (br, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 145.5, 132.0, 116.7, 110.2.

Data obtained are in accordance with those previously reported.[3]

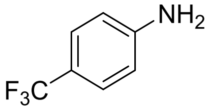
3-(Trifluoromethyl)aniline 2p:



Using 3-nitrobenzotrifluoride (0.6 mmol, 115 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 3h. The amine **2p** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (4:1 v/v) as a colourless oil (86.9 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.25 (m, 1H), 7.02-7.00 (m, 1H), 6.92 (s, 1H), 6.85-6.83 (m, 1H), 3.86 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 146.7, 131.6 (q, $J_{\text{C-F}}$ = 31.2 Hz), 129.7, 124.2 (q, $J_{\text{C-F}}$ = 271.2 Hz), 118.0, 115.0 (q, $J_{\text{C-F}}$ = 3.8 Hz), 111.3 (q, $J_{\text{C-F}}$ = 3.8 Hz). ^{19}F NMR ($CDCl_3$, 471 MHz): δ -63.0.

Data obtained are in accordance with those previously reported.[2]

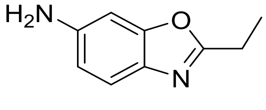
4-(Trifluoromethyl)aniline 2q:



Using 4-nitrobenzotrifluoride (0.6 mmol, 115 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 3h. The amine **2q** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (4:1 v/v) as a colourless oil (82.1 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, J = 8.0, 2H) 6.71 (d, J = 8.0 Hz, 2H), 3.96 (br, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 149.4, 126.7 (q, $J_{\text{C-F}}$ = 3.8 Hz), 124.8 (q, $J_{\text{C-F}}$ = 268.8 Hz), 120.2 (q, $J_{\text{C-F}}$ = 32.5 Hz), 114.2; ^{19}F NMR ($CDCl_3$, 471 MHz): δ -61.2.

Data obtained are in accordance with those previously reported.[7]

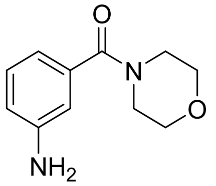
2-Ethyl-6-benzoxazolamine 2r:



Using 2-ethyl-6-nitrobenzoxazole (0.6 mmol, 115 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2r** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (1:1 v/v) as an orange powder (85.6 mg, 88%). Melting point: 57-58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, J = 12.0 Hz, 1H), 6.78 (s, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.79 (br, 2H), 2.89 (q, J = 8.0 Hz, 2H), 1.42 (t, J = 8.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 166.1, 152.0, 144.3, 133.8, 119.6, 112.5, 96.5, 22.0, 11.0.

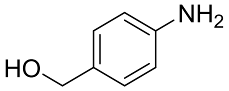
Data obtained are in accordance with those previously reported.[9]

4-(3-Aminobenzoyl)morpholine 2s:



Using morpholin-4-yl(3-nitrophenyl)methanone (0.6 mmol, 142 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (11.0 mg, 0.024 mmol) in MeCN (0.6 ml) at 80 °C for 4h. The amine **2s** was isolated by flash column chromatography using ethyl acetate as a yellow oil (121 mg, 98%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18-7.14 (m, 1H), 6.73-6.70 (m, 3H), 3.89-3.45 (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 170.6, 146.8, 136.4, 129.4, 116.7, 116.3, 113.4, 66.9. HRMS (EI) Exact mass calcd for $C_{11}H_{14}N_2O_2$ $[M]^+$: 206.1055, found: 206.1061.

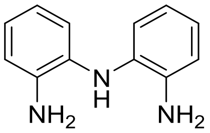
4-(Hydroxymethyl)aniline 2t:



Using 4-nitrobenzyl alcohol (0.6 mmol, 91.8 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (0.6 ml) at 80 °C for 6h. The amine **2t** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as colourless solid (40.8 mg, 55%). Melting point: 60-61 °C. (Petroleum Spirit/EtOAc); Lit.[10] 60-63 °C (EtOAc) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.20-7.17 (m, 2H), 6.69-6.66 (m, 2H), 4.76 (s, 2H) 3.65 (br, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 145.7, 130.3, 128.5, 114.9, 65.3.

Data obtained are in accordance with those previously reported.[10]

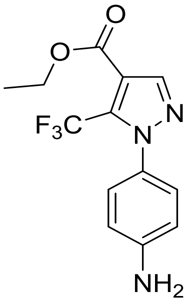
Bis(2-aminophenyl)amine 2u:



Using 2-nitro-*N*-(2'-nitrophenyl)aniline (0.6 mmol, 155 mg), triethoxysilane (4.8 mmol, 787 mg) and **4b** (5.5 mg, 0.012 mmol) in MeCN (1.2 ml) at 80 °C for 4h. The amine **2u** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (2:1 v/v) as an orange powder (110 mg, 80%). Melting point: 100-102 °C. (Petroleum Spirit/EtOAc); Lit.[11] 101 °C (petroleum). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.99-6.93 (m, 2H), 6.83-6.77 (m, 6H), 5.08 (br, 1H), 3.67 (br, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 138.4, 131.2, 123.3, 120.3, 119.8, 116.5.

NMR data obtained are in accordance with those previously reported.[12]

Ethyl 1-(4-aminophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate 2v:



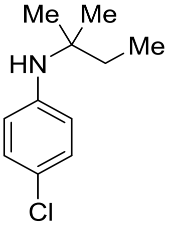
Using ethyl 1-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (0.6 mmol, 197 mg), triethoxysilane (2.4 mmol, 394 mg) and **4b** (8.2 mg, 0.018 mmol) in MeCN (0.6 ml) at 80 °C for 3h. The amine **2v** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (1:1 v/v) as a white powder (162 mg, 90%). Melting point: 107-108 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (s, 1H), 7.20-7.18 (m, 2H), 6.74-6.71 (m, 2H), 4.38 (q, J = 10.0 Hz, 2H), 3.94 (br, 2H), 1.40 (t, J = 10.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 161.2, 148.1, 142.0, 132.5 (q, $J_{\text{C-F}}$ = 40.0 Hz), 130.0, 126.9, 119.2 (q, $J_{\text{C-F}}$ = 270 Hz), 116.1, 114.6, 61.2, 14.0.

Data obtained are in accordance with those previously reported.[13]

General Procedure for the Formal Hydroamination of Olefin with Nitro Compounds:

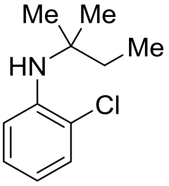
To a solution of the nitro compound (0.3 mmol, 1.0 equiv) and catalyst **4b** (2.8 mg, 0.006 mmol, 2.0 mol%) in EtOH (1.5 mL) was added donor olefin (0.9 mmol, 3.0 equiv), and $PhSiH_3$ (1.0 or 2.0 equiv). The resulting mixture was stirred at room temperature until full consumption of the staring nitro compound was observed as indicated by TLC. Zinc (390 mg, 6.0 mmol, 20 equiv) and aqueous HCl (2N, 3.0 ml) was added to the reaction mixture. After stirring at 60 °C for another 1h, the reaction mixture was cooled to room temperature and filtered through Celite and the filter cake washed with EtOAc. The filtrate was collected and saturated aqueous $NaHCO_3$ solution added until strongly basic and then extracted with EtOAc three times. The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product purified by flash column chromatography using petroleum spirit/ethyl acetate.

4-Chloro-*N*-(*tert*-pentyl)aniline 6a:



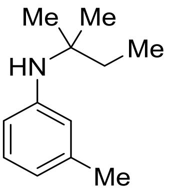
General procedure was followed by using 1-chloro-4-nitrobenzene (0.3 mmol, 47.1 mg), phenylsilane (0.6 mmol, 64.8 mg, 75.0 µl), 2-methyl-2-butene (0.9 mmol, 63.0 mg, 95.0 µl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 2h. The amine **6a** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (50:1~30:1 v/v) as a colourless oil (44.3 mg, 75%). ^1H NMR ($CDCl_3$, 600 MHz): δ 7.12-7.09 (m, 2H), 6.67-6.64 (m, 2H), 1.67(q, J = 8.0 Hz, 2H), 1.29 (s, 6H), 0.91 (t, J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 145.6, 128.8, 122.6, 117.8, 54.0, 33.9, 27.8, 8.4. HRMS (EI) Exact mass calcd for $C_{11}H_{16}ClN$ $[M]^+$: 197.0971, found: 197.0968.

2-Chloro-*N*-(*tert*-pentyl)aniline 6b:



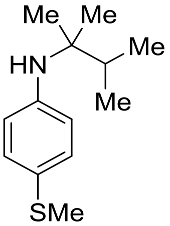
General procedure was followed by using 1-chloro-2-nitrobenzene (0.3 mmol, 47.1 mg), phenylsilane (0.6 mmol, 64.8 mg, 75.0 µl), 2-methyl-2-butene (0.9 mmol, 63.0 mg, 95.0 µl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 2h. The amine **6b** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (100:1~50:1 v/v) as a colourless oil (23.8 mg, 40%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.27 (dd, J = 7.9, 1.6 Hz, 1H), 7.11-7.08 (m, 1H), 6.97-6.95 (m, 1H), 6.64-6.61 (m, 1H), 1.76 (q, J = 7.5 Hz, 2H), 1.37 (s, 6H), 0.92 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 143.0, 129.3, 127.2, 120.6, 117.0, 114.4, 54.0, 33.8, 27.7, 8.4. HRMS (EI) Exact mass calcd for $C_{11}H_{16}ClN$ $[M]^+$: 197.0971, found: 197.0970.

3-Methyl-*N*-(*tert*-pentyl)aniline 6c:



General procedure was followed by using 3-nitrotoluene (0.3 mmol, 41.1 mg), phenylsilane (0.6 mmol, 64.8 mg, 75.0 μl), 2-methyl-2-butene (0.9 mmol, 63.0 mg, 95.0 μl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 2h. The amine **6c** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (50:1~30:1 v/v) as a colourless oil (30.3 mg, 57%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.06 (t, J = 7.8 Hz, 1H), 6.59-6.57 (m, 3H), 2.30 (s, 3H), 1.70 (q, J = 7.4 Hz, 2H), 1.31 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 147.0, 138.6, 128.8, 118.8, 117.8, 113.8, 53.8, 34.1, 27.9, 21.6, 8.5. HRMS (EI) Exact mass calcd for $C_{11}H_{16}ClN$ [M]$^+$: 177.1517, found: 177.1520.

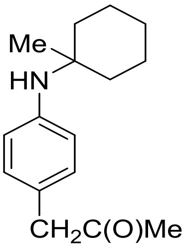
***N*-(2,3-dimethylbutan-2-yl)-4-(methylthio)aniline 6d:**



General procedure was followed by using 4-nitrothioanisole (0.3 mmol, 50.1 mg), phenylsilane (0.3 mmol, 32.4 mg, 38.0 μl), 2,3-dimethyl-1-butene (0.9 mmol, 75.6 mg, 111 μl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 1h. The amine **6d** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (50:1~30:1 v/v) as a colourless oil (26.8 mg, 60%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.20-7.17 (m, 2H), 6.70-6.67 (m, 2H), 2.44 (s, 3H), 2.17-2.08 (m, 1H), 1.27 (s, 6H), 0.95 (d, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 145.7, 130.9, 124.6, 117.3, 56.7, 35.5, 24.9, 18.9, 17.6.

Data obtained are in accordance with those previously reported.[14]

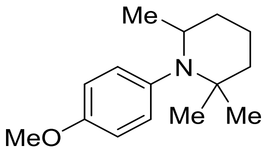
1-(4-((1-Methylcyclohexyl)amino)phenyl)propan-2-one 6e:



General procedure was followed by using 4-nitrophenylacetone (0.3 mmol, 53.7 mg), phenylsilane (0.6 mmol, 64.8 mg, 75.0 μl), 1-methyl-1-cyclohexene (0.9 mmol, 86.4 mg, 106 μl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 2h. The amine **6e** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (20:1~5:1 v/v) as a colourless oil (29.5 mg, 40%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.01-6.98 (m, 2H), 6.73-6.71 (m, 2H), 3.57 (s, 2H), 2.15 (s, 3H), 1.87-1.82 (m, 2H), 1.60-1.49 (m, 7H), 1.43-1.36 (m, 1H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): δ 207.5, 145.7, 129.8, 123.2, 117.2, 53.2, 50.3, 38.3, 29.0, 26.9, 25.8, 22.2.

Data obtained are in accordance with those previously reported.[14]

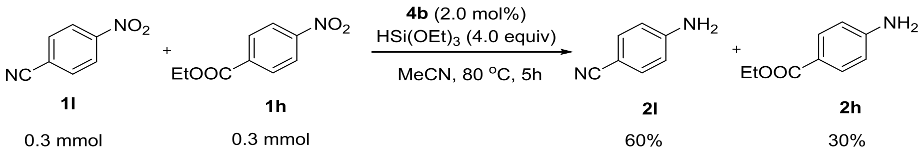
1-(4-Methoxyphenyl)-2,2,6-trimethylpiperidine 7a:



General procedure was followed by using 4-nitroanisole (0.3 mmol, 45.9 mg), phenylsilane (0.3 mmol, 32.4 mg, 37.0 µl), 6-methyl-5-hepten-2-one (0.9 mmol, 113 mg, 132 µl) and **4b** (2.8 mg, 0.006 mmol) in EtOH (1.5 ml) at room temperature for 1h. The amine **7a** was isolated by flash column chromatography using petroleum spirit/ethyl acetate (50:1~20:1 v/v) as a colourless oil (31.5 mg, 45%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.05 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 8.2 Hz, 2H), 3.81 (s, 3H), 3.33-3.26 (m, 1H), 1.78-1.70 (m, 2H), 1.67-1.54 (m, 3H), 1.36-1.28 (m, 1H), 1.06 (s, 3H), 0.9 (s, 3H), 0.74 (d, J = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz): δ 156.7, 140.7, 131.0, 112.7, 55.3, 54.7, 50.2, 41.1, 36.2, 32.6, 22.9, 21.0, 17.5.

Data obtained are in accordance with those previously reported.[14]

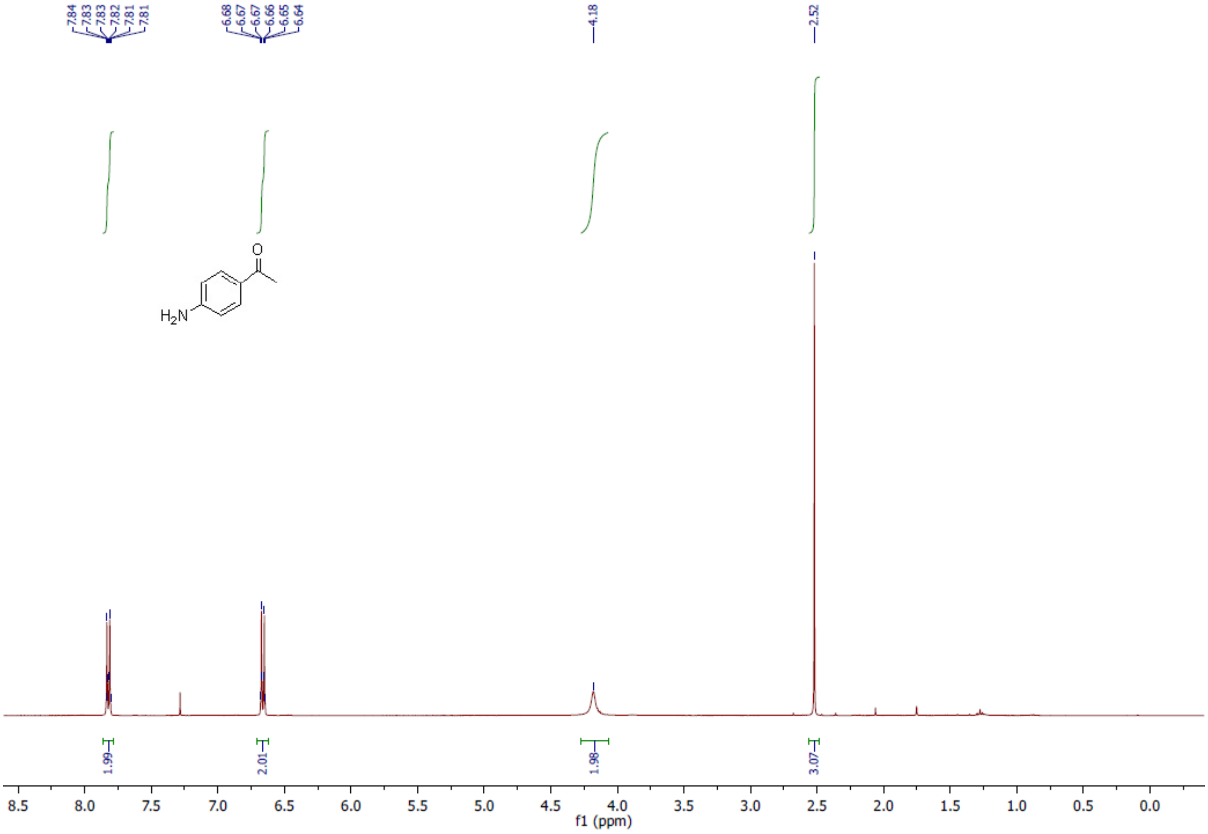
Procedure for the Reduction of Mixed Substrates:

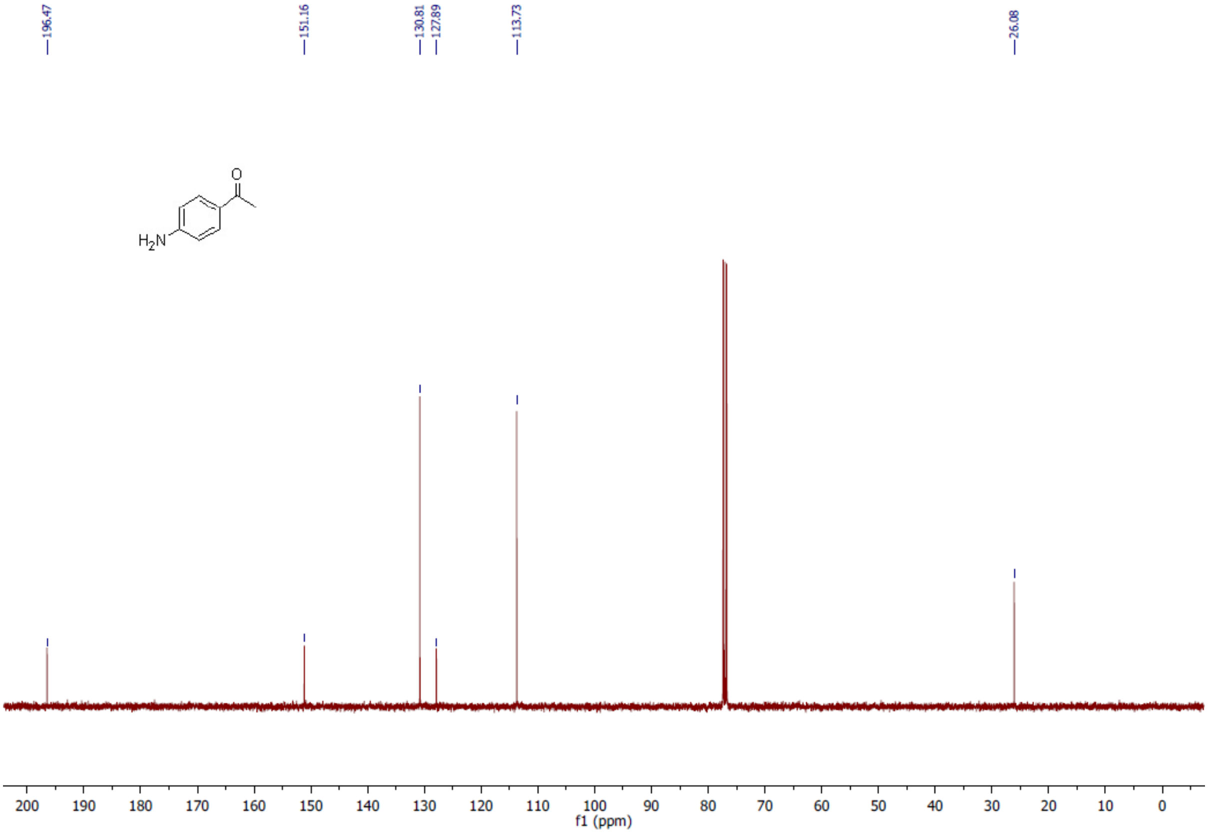


A mixture of catalyst **4b** (0.012 mmol, 5.5 mg), 4-nitrobenzonitrile **1l** (0.3 mmol, 44.4 mg), ethyl 4-nitrobenzoate **1h** (0.3 mmol, 58.5 mg), triethoxysilane (2.4 mmol, 393.6 mg) and acetonitrile (0.6 mL) were stirred in a preheated oil bath (80 °C) for 5h. The solvents were removed under vacuum. The crude product was then dissolved in a minimal amount of CH_2Cl_2 and purified by flash column chromatography using petroleum spirit/ethyl acetate (4:1-2:1, v/v) to give a mixture of **2l** and **2h**. The yield was analysed by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard.

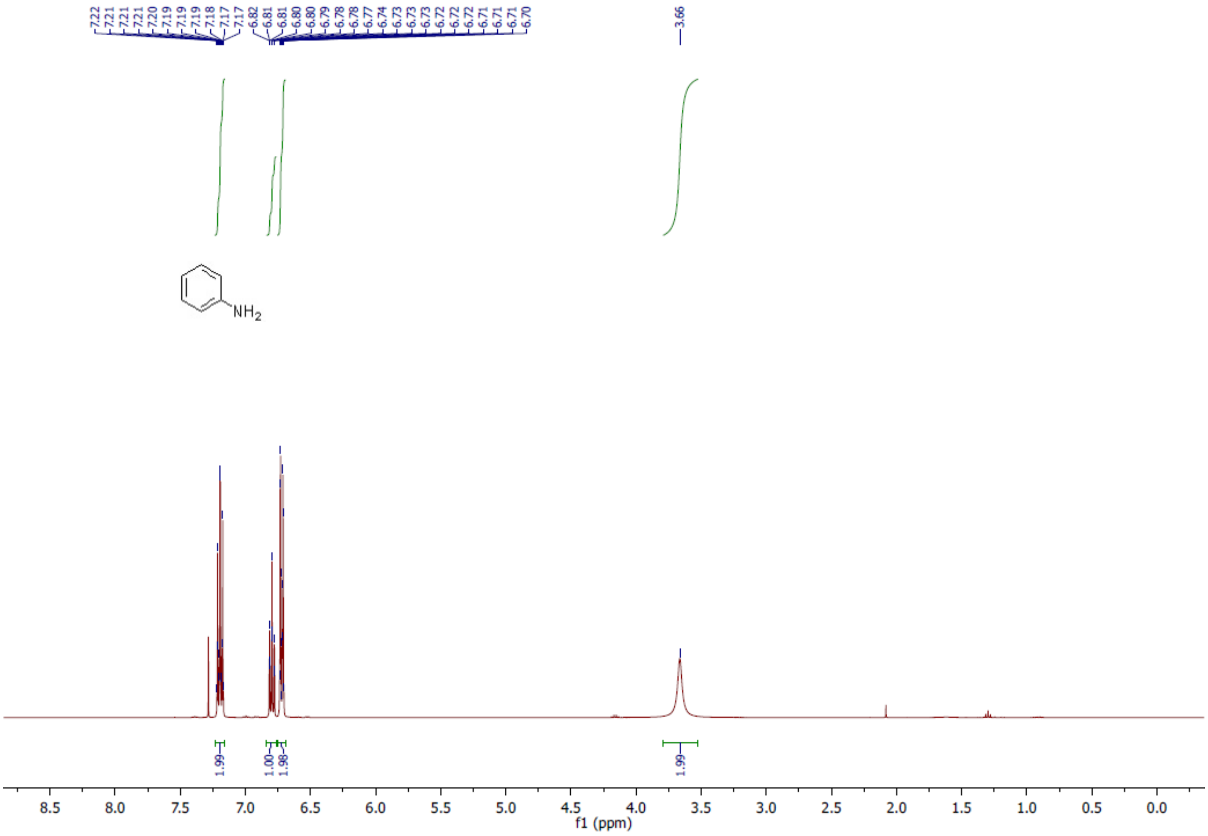
NMR Spectrum of Compounds

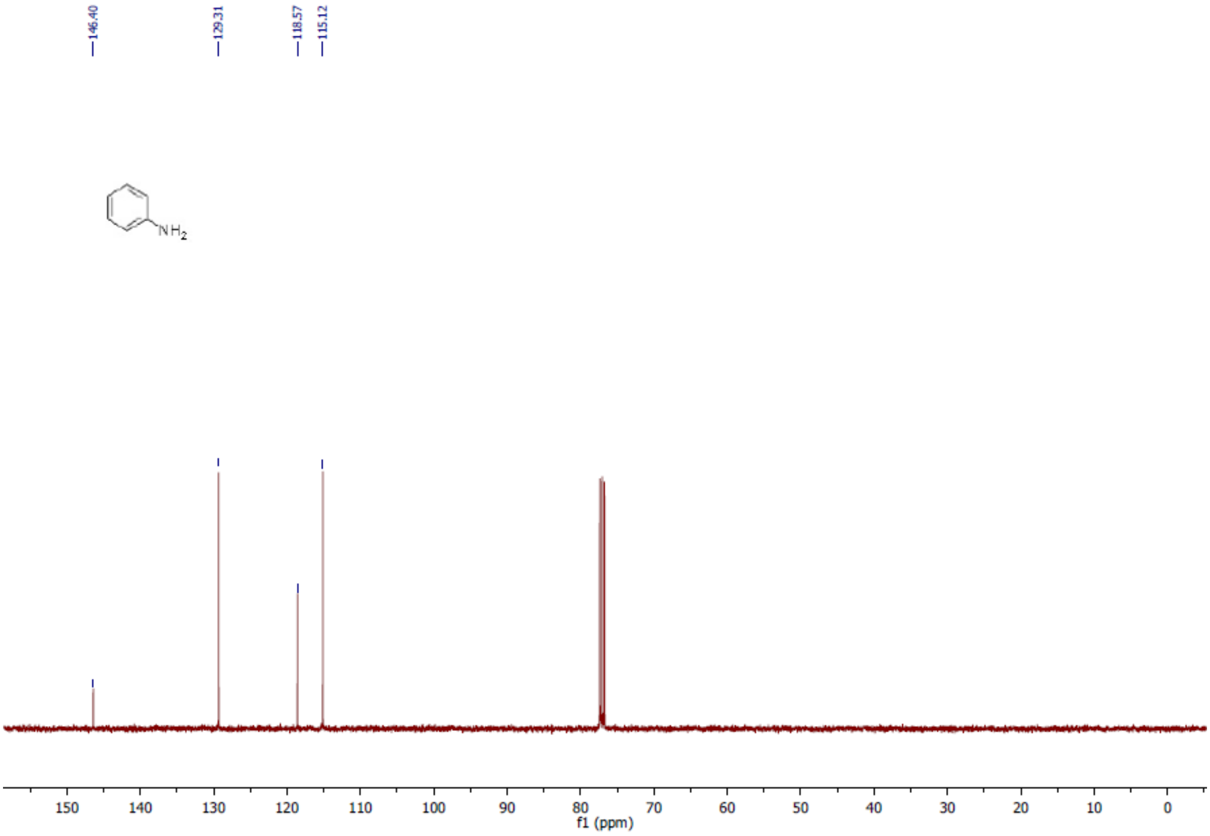
4-Aminoacetophenone 2a:



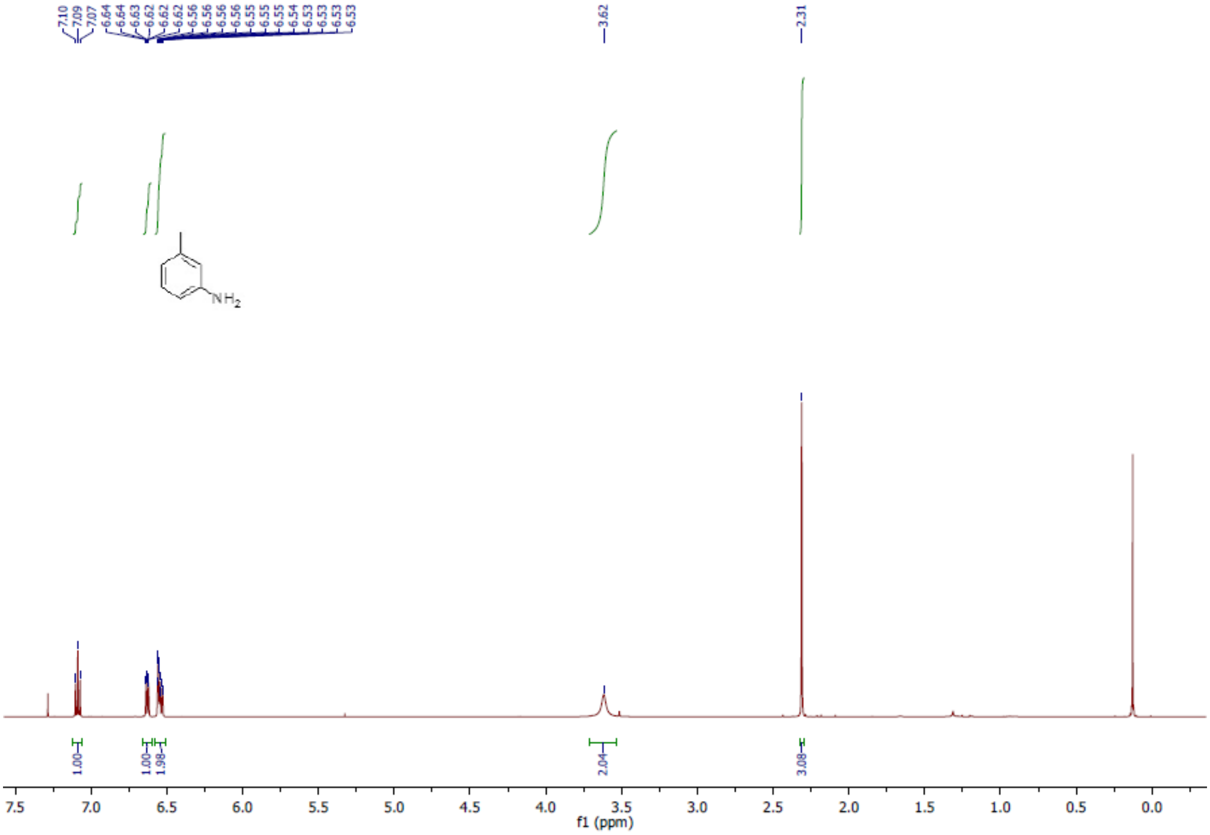


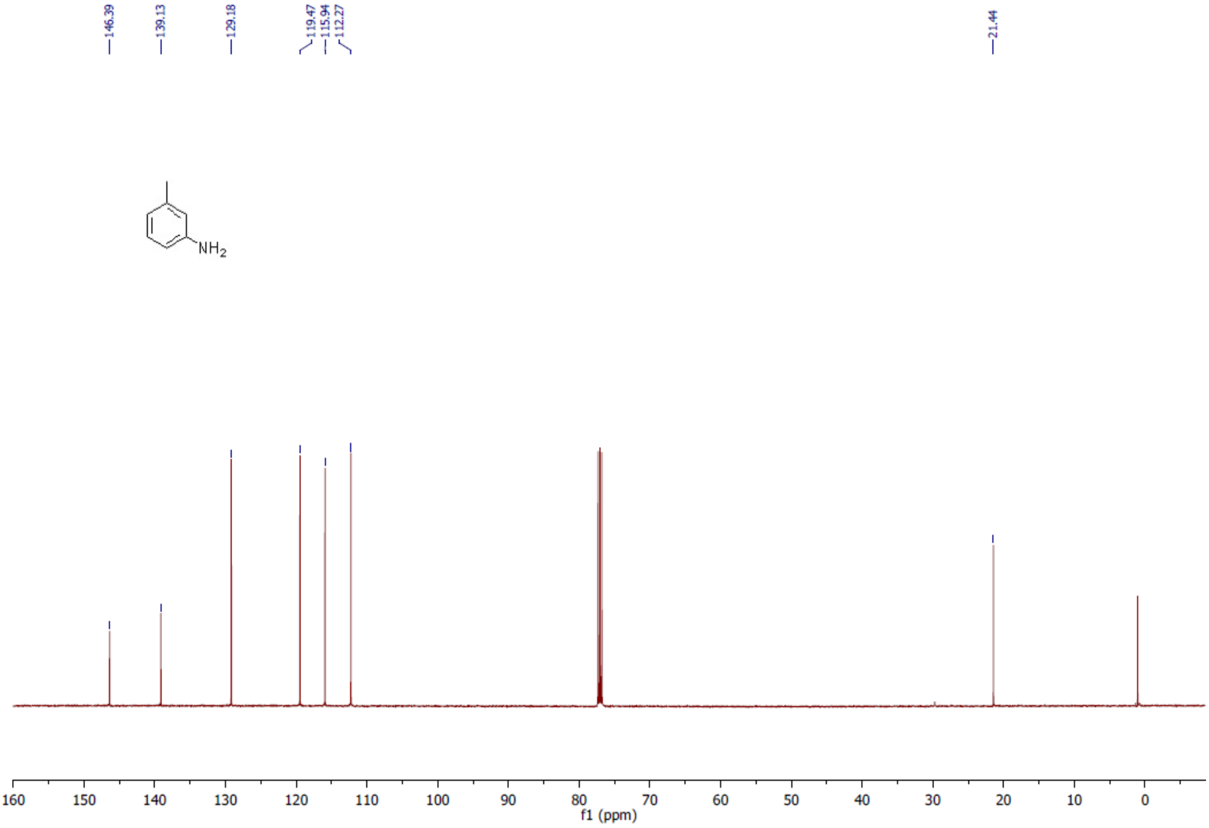
Aniline 2b:


7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.17
7.17
6.82
6.81
6.81
6.80
6.80
6.79
6.78
6.78
6.77
6.74
6.73
6.73
6.73
6.72
6.72
6.72
6.71
6.71
6.71
6.70
3.66
NH2
1.99
1.00
1.98
1.99
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)

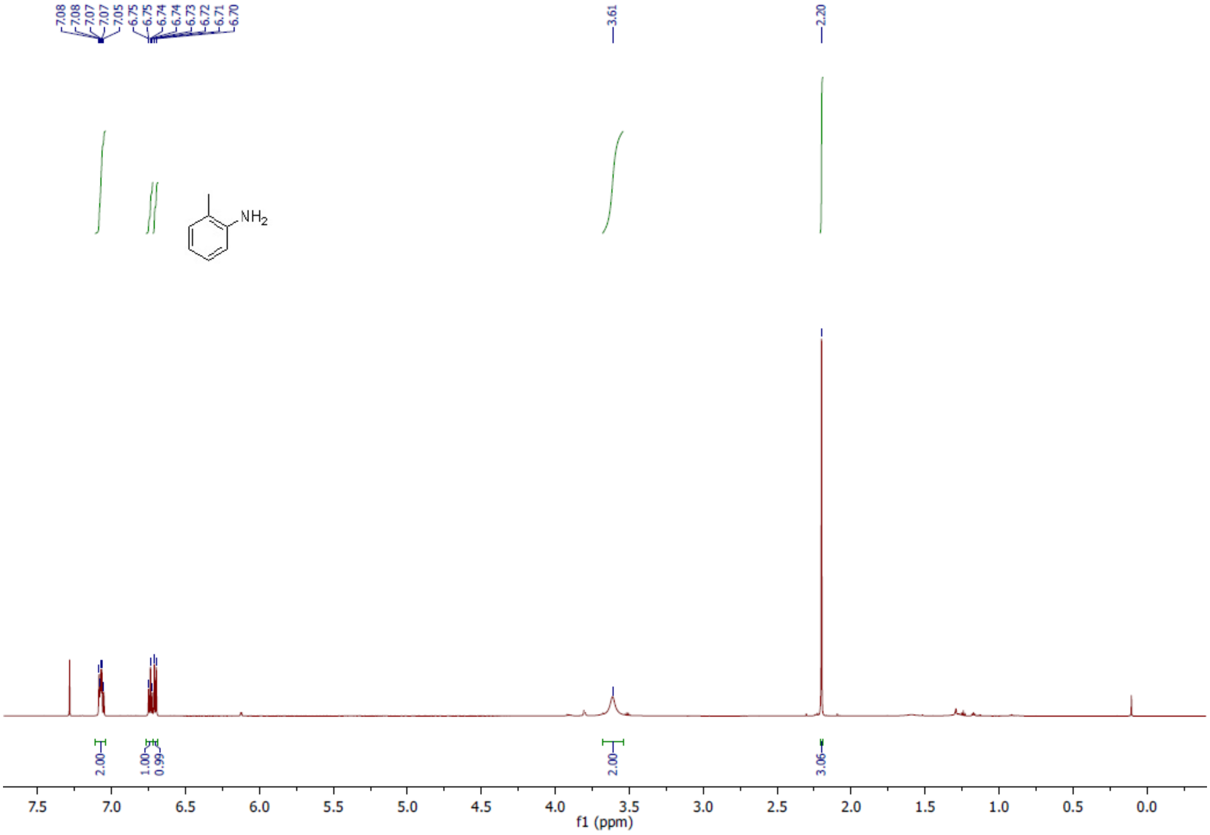

146.40
129.31
118.57
115.12
NH2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

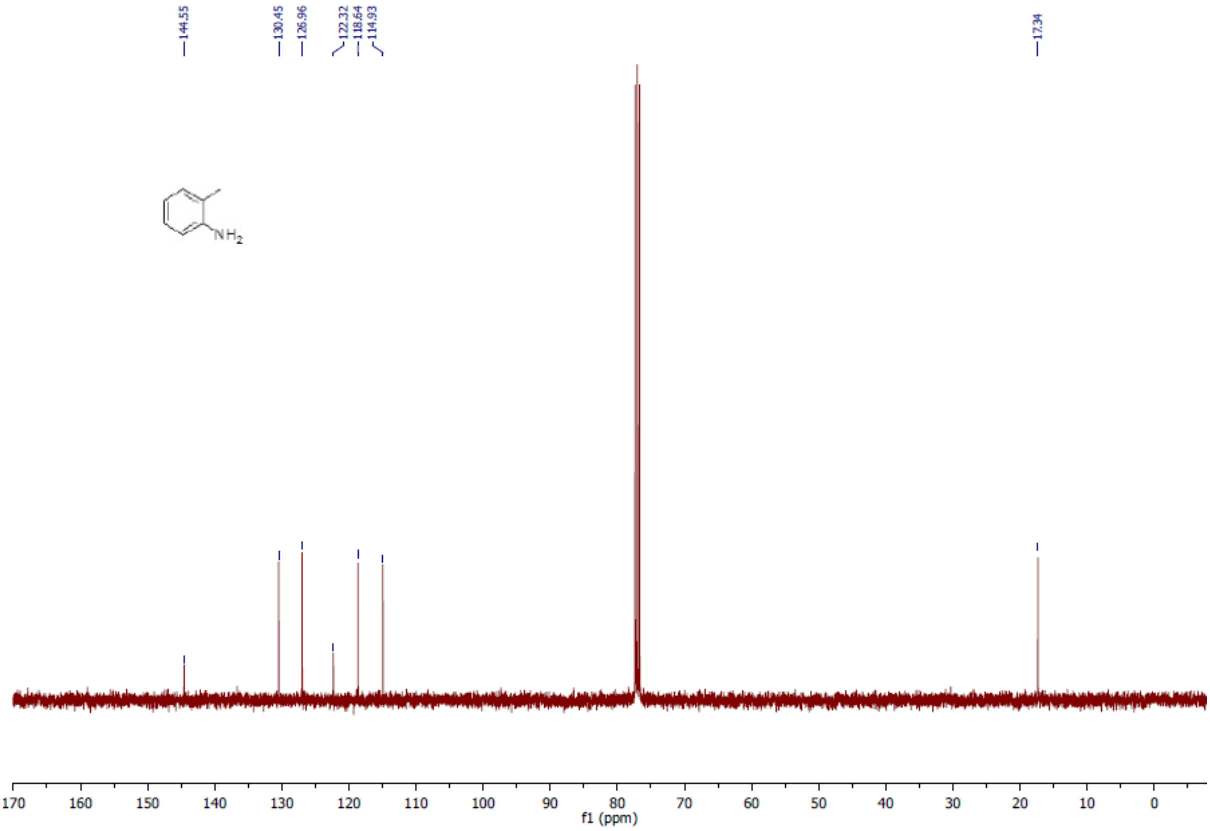
3-Aminotoluene 2c:



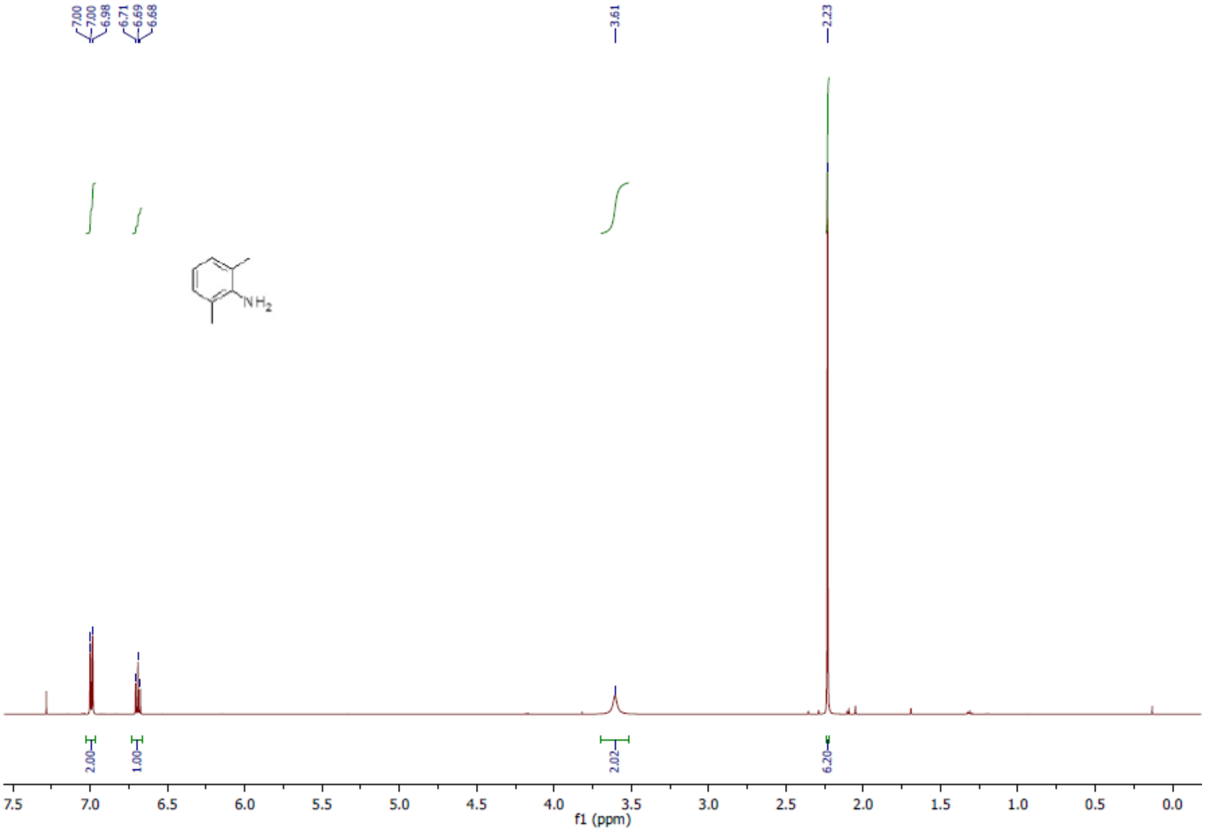


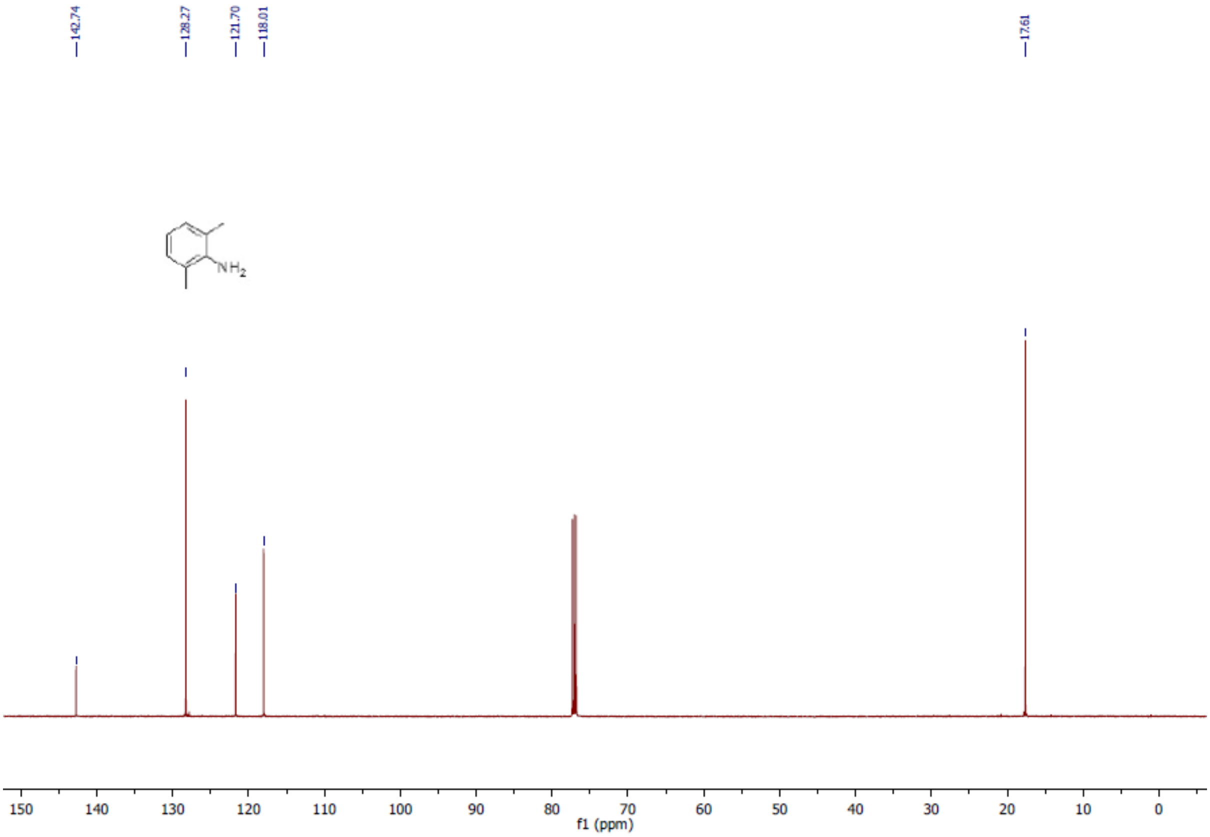
2-Aminotoluene 2d:



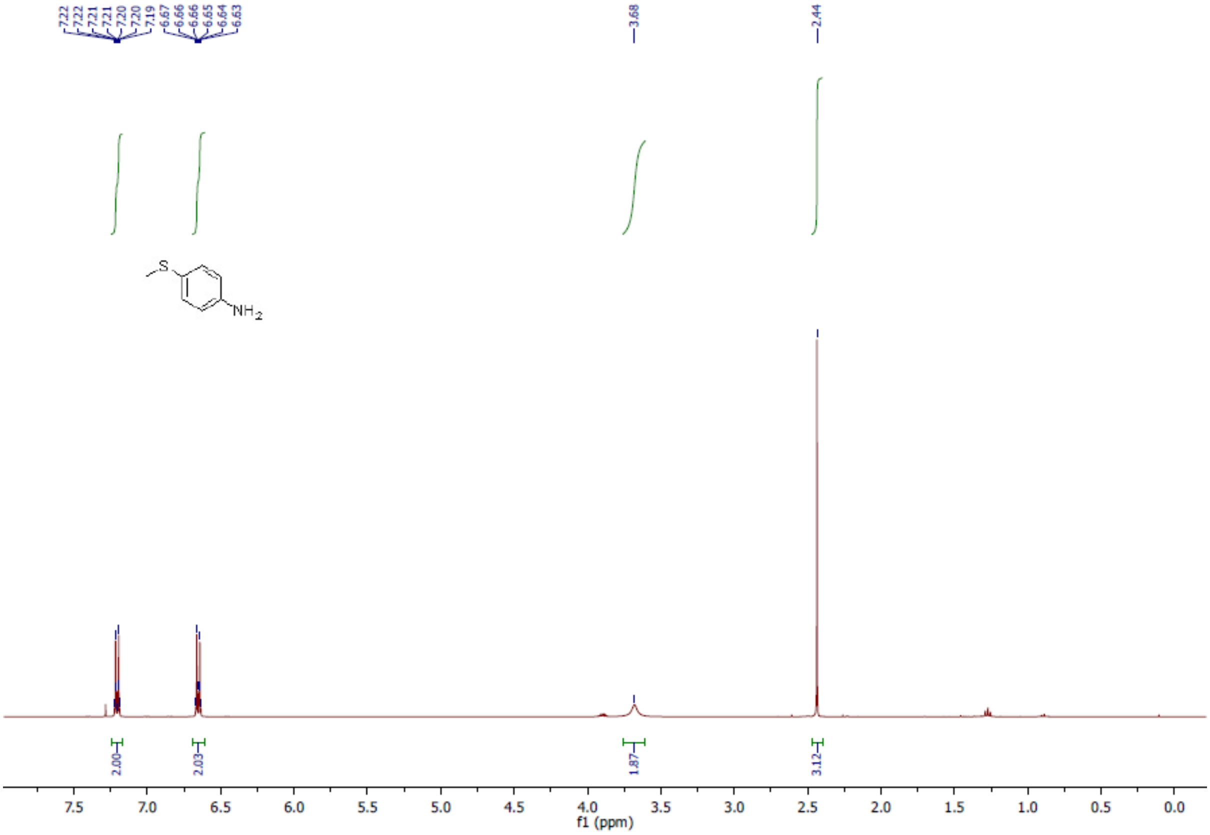


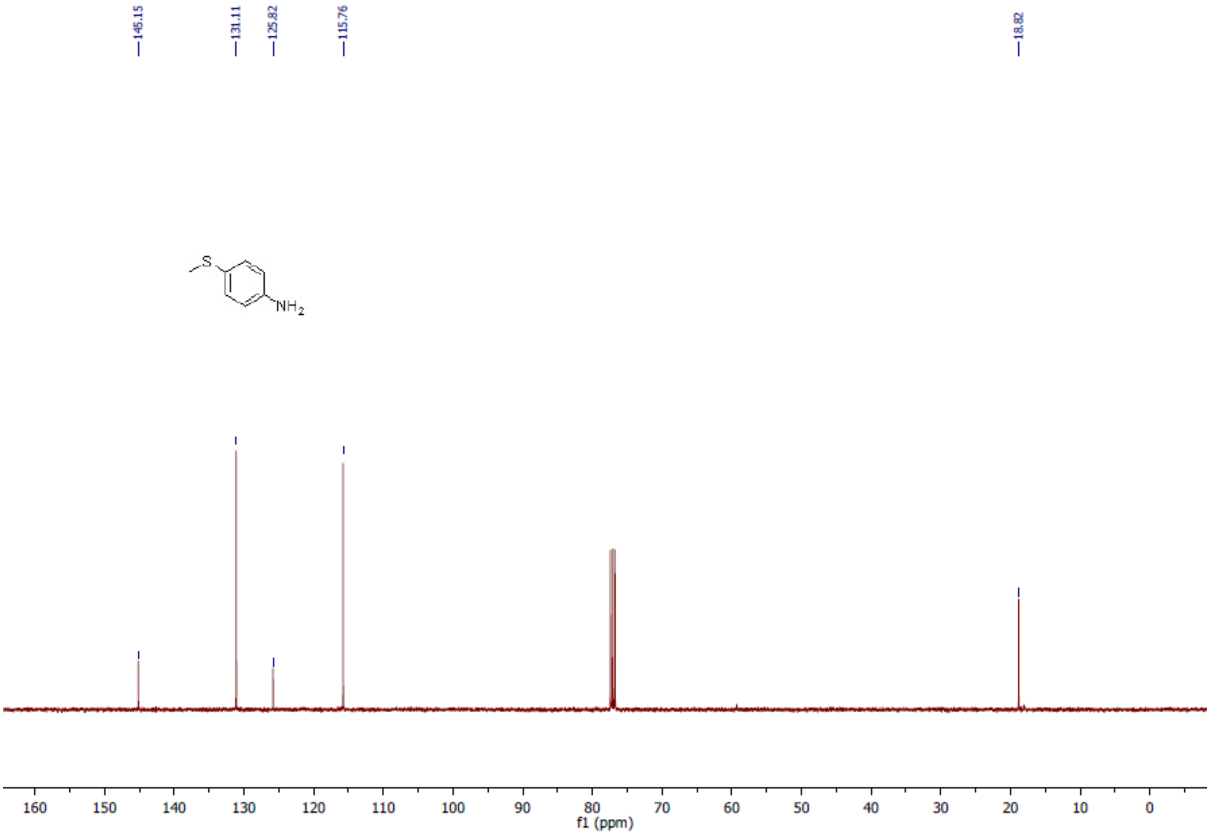
2, 6-Dimethylaniline 2e:



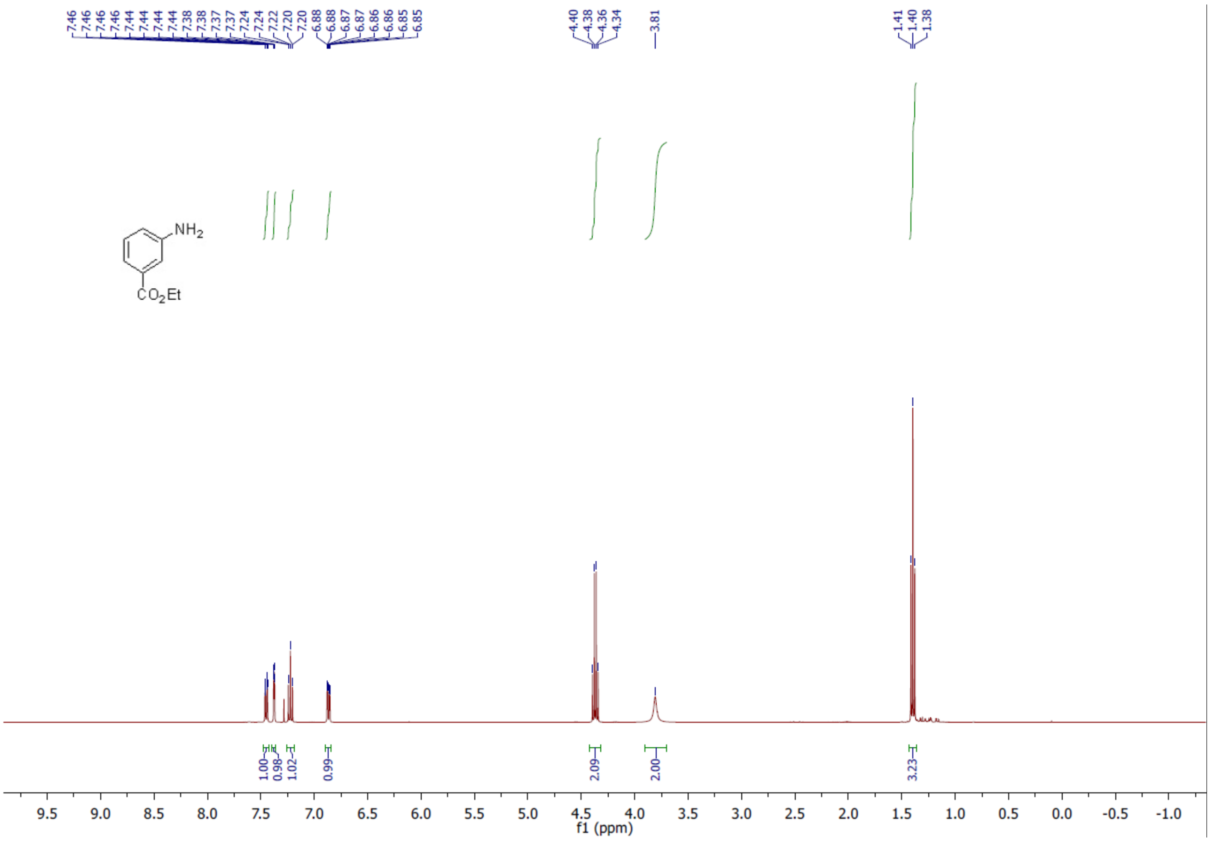


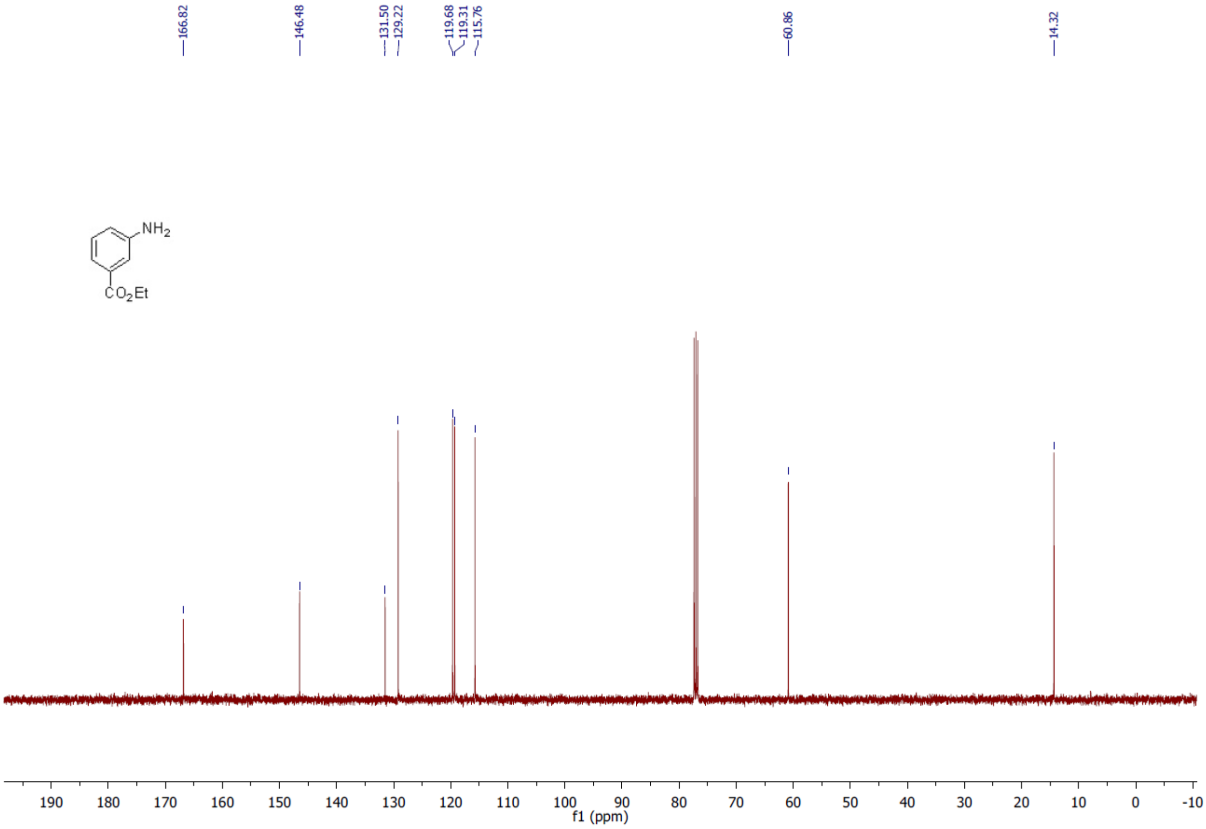
4-(Methylthio)aniline 2f:



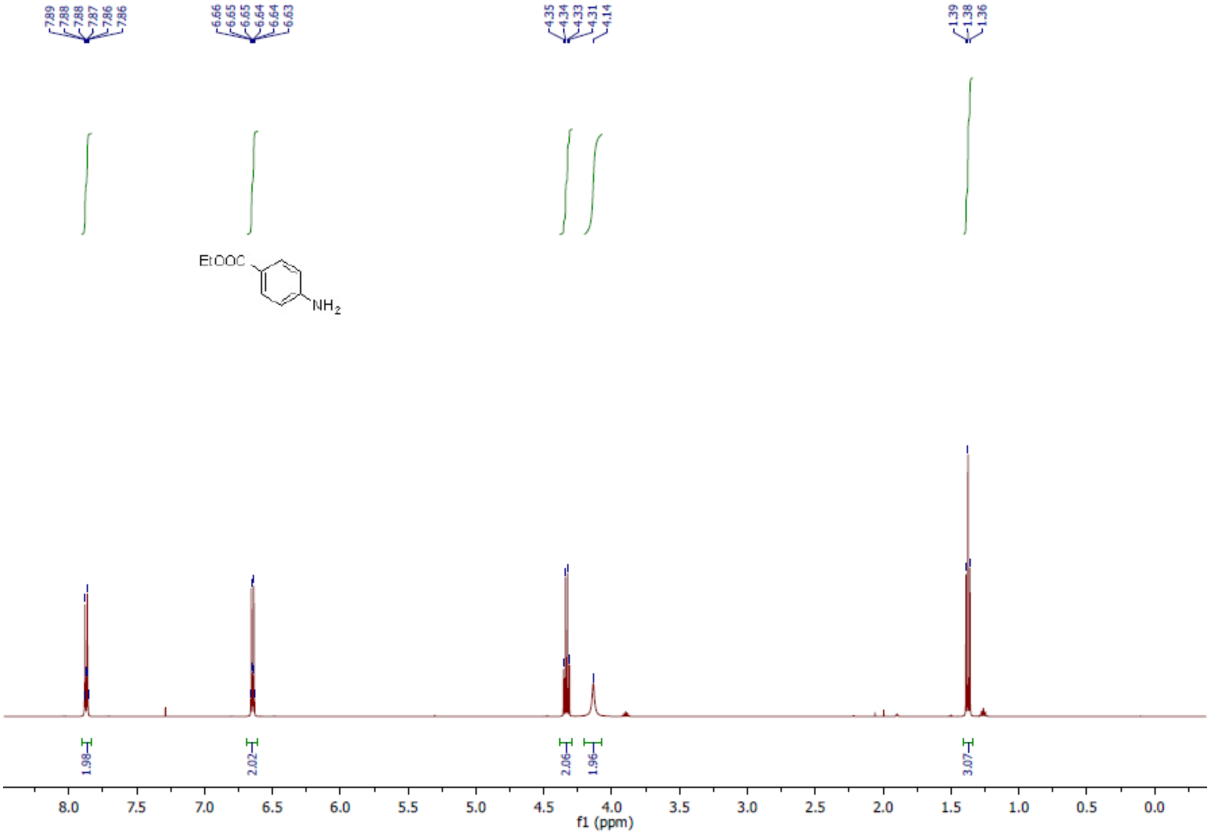


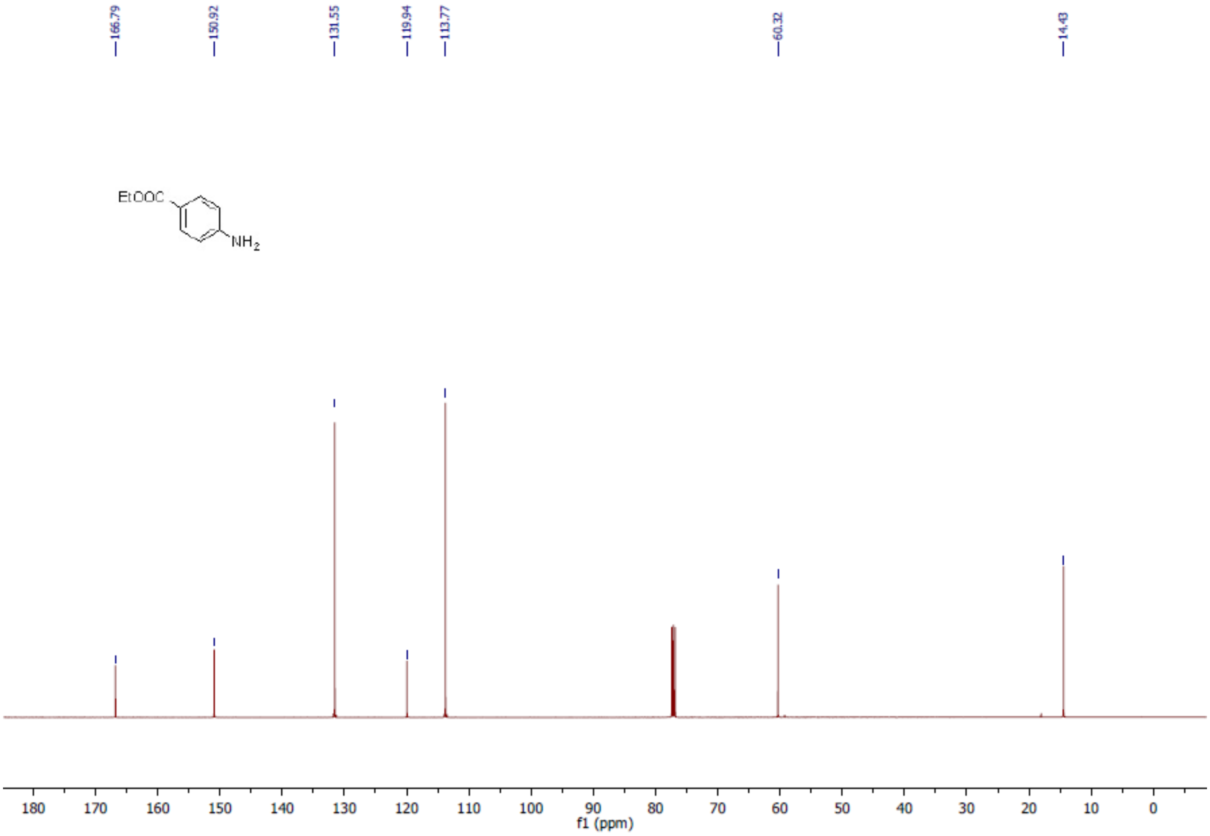
Ethyl 3-aminobenzoate 2g:



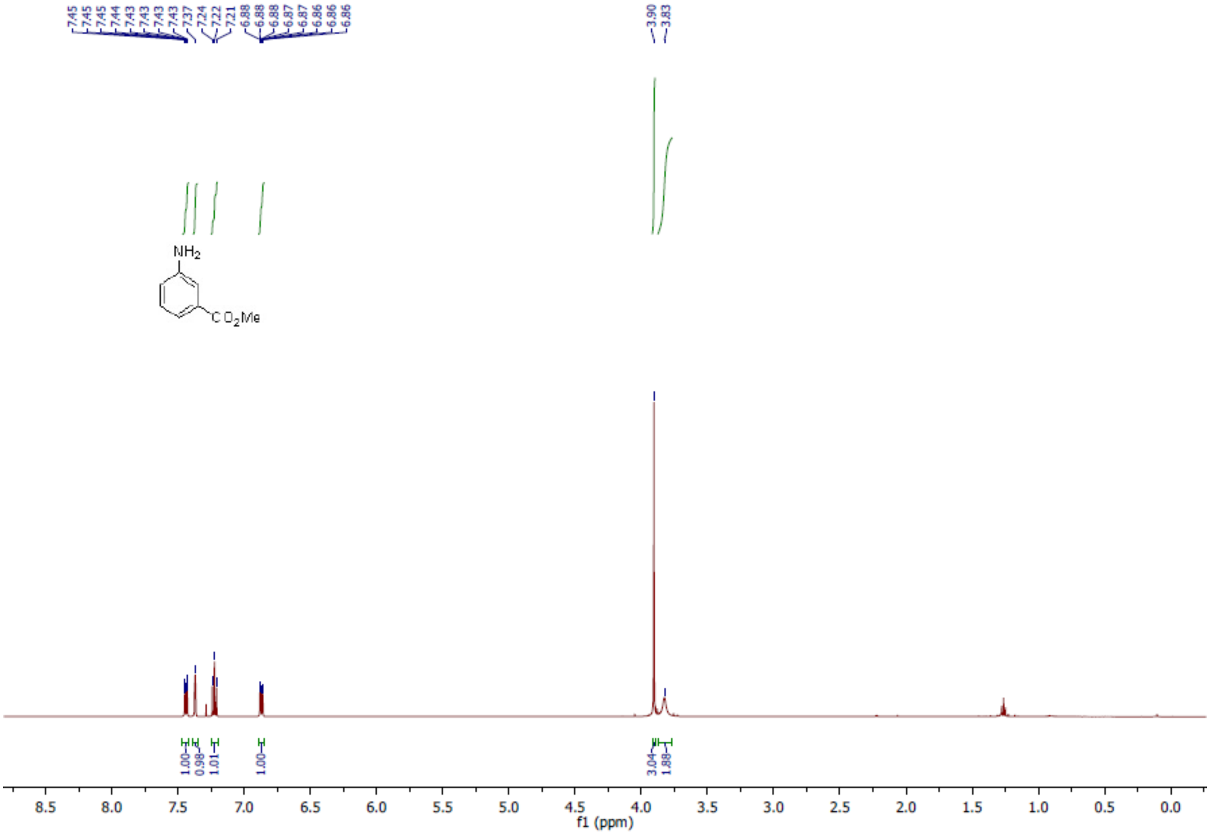


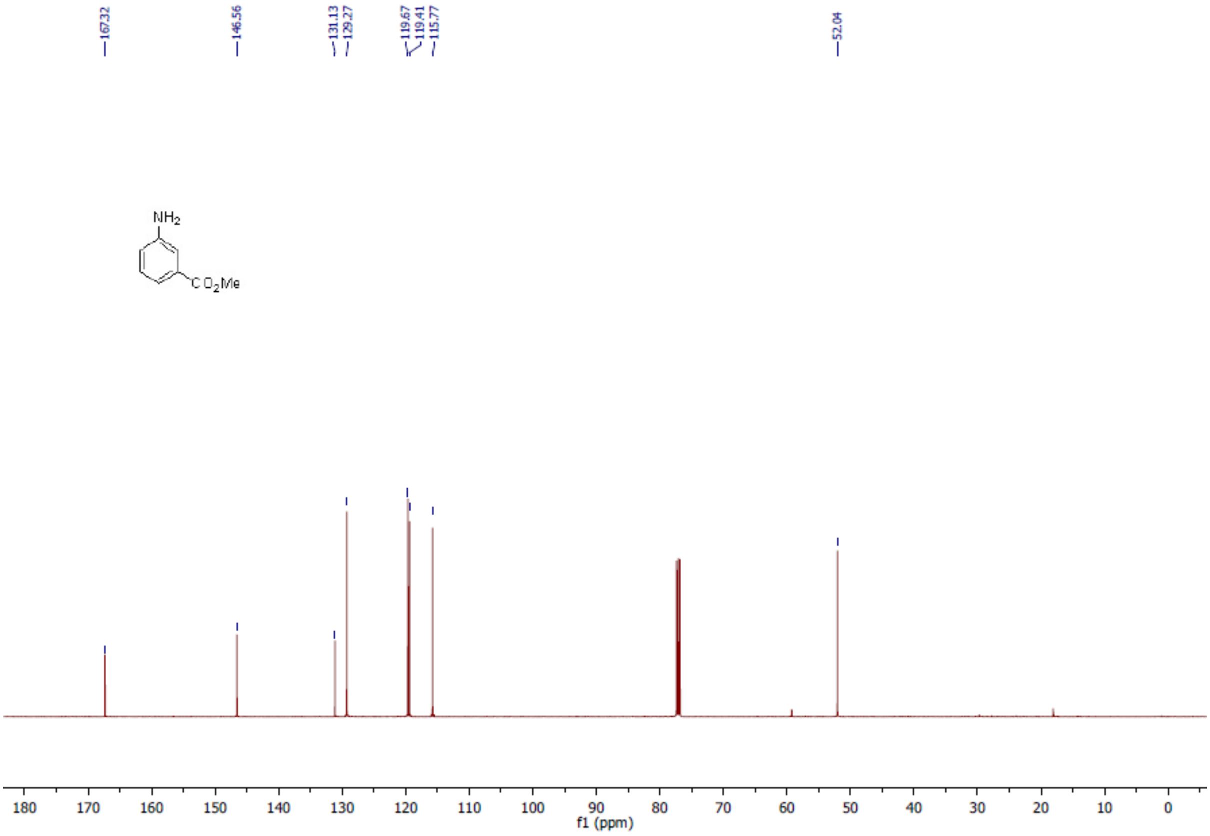
Ethyl 4-aminobenzoate 2h:



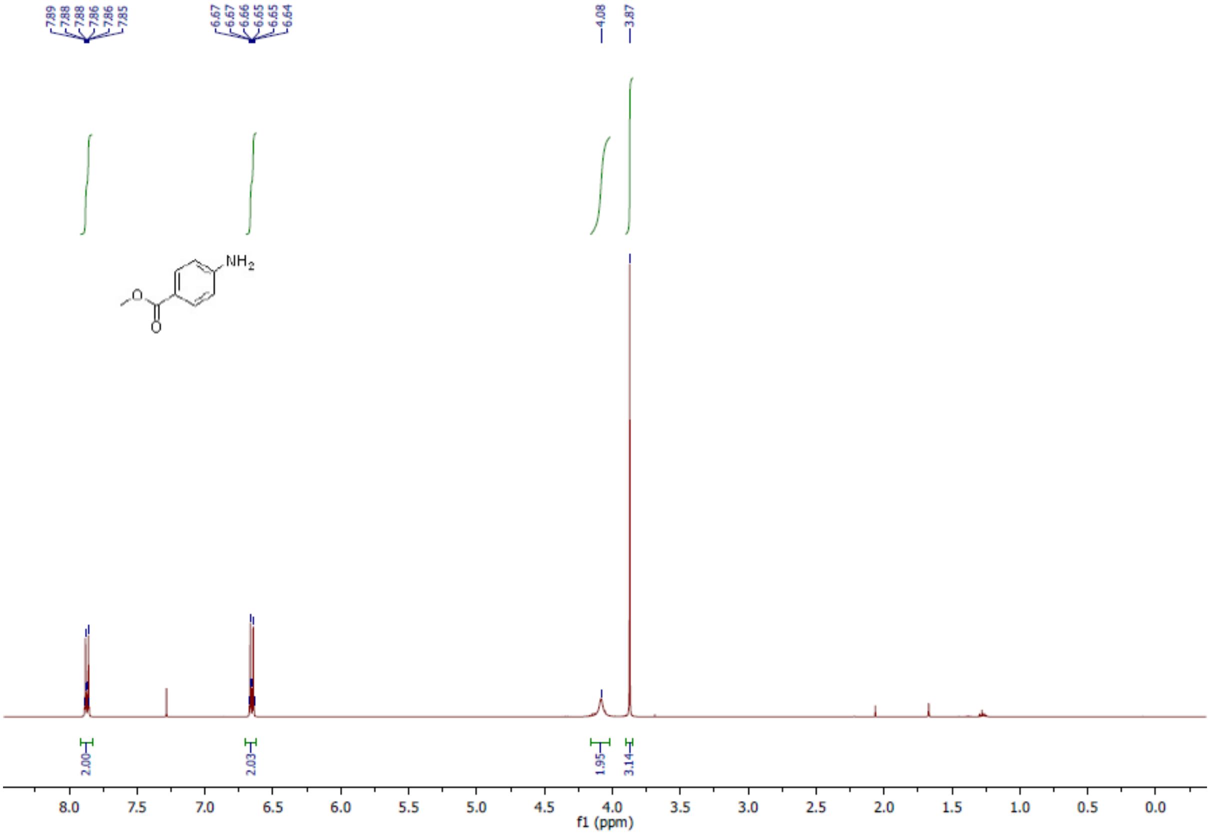


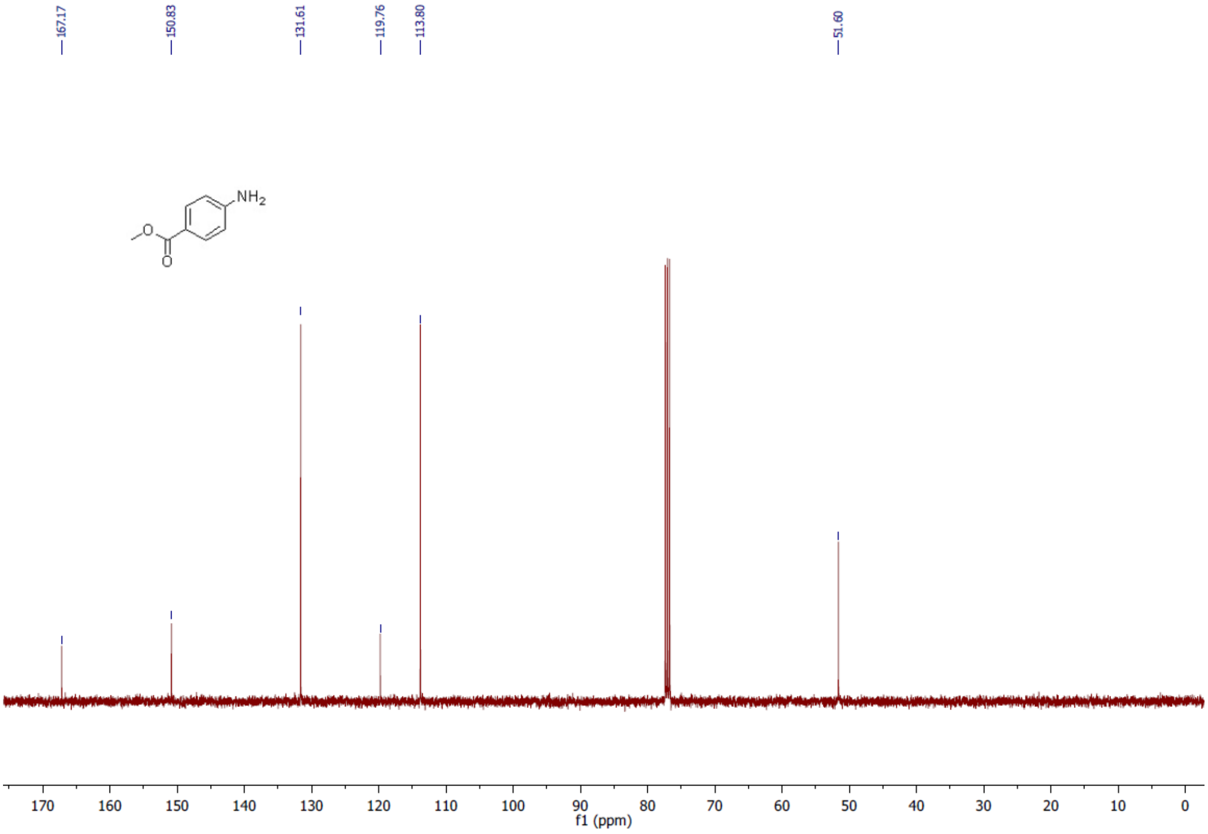
Methyl 3-aminobenzoate 2i:



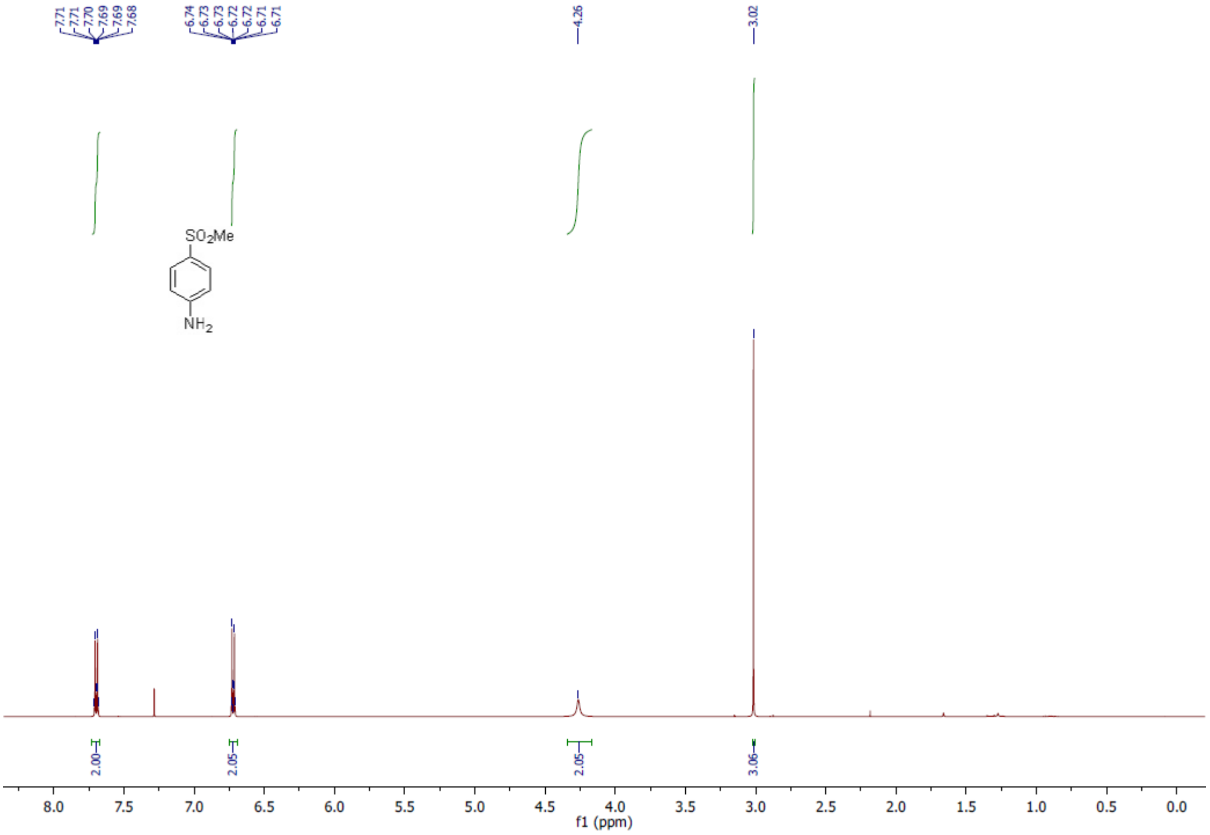


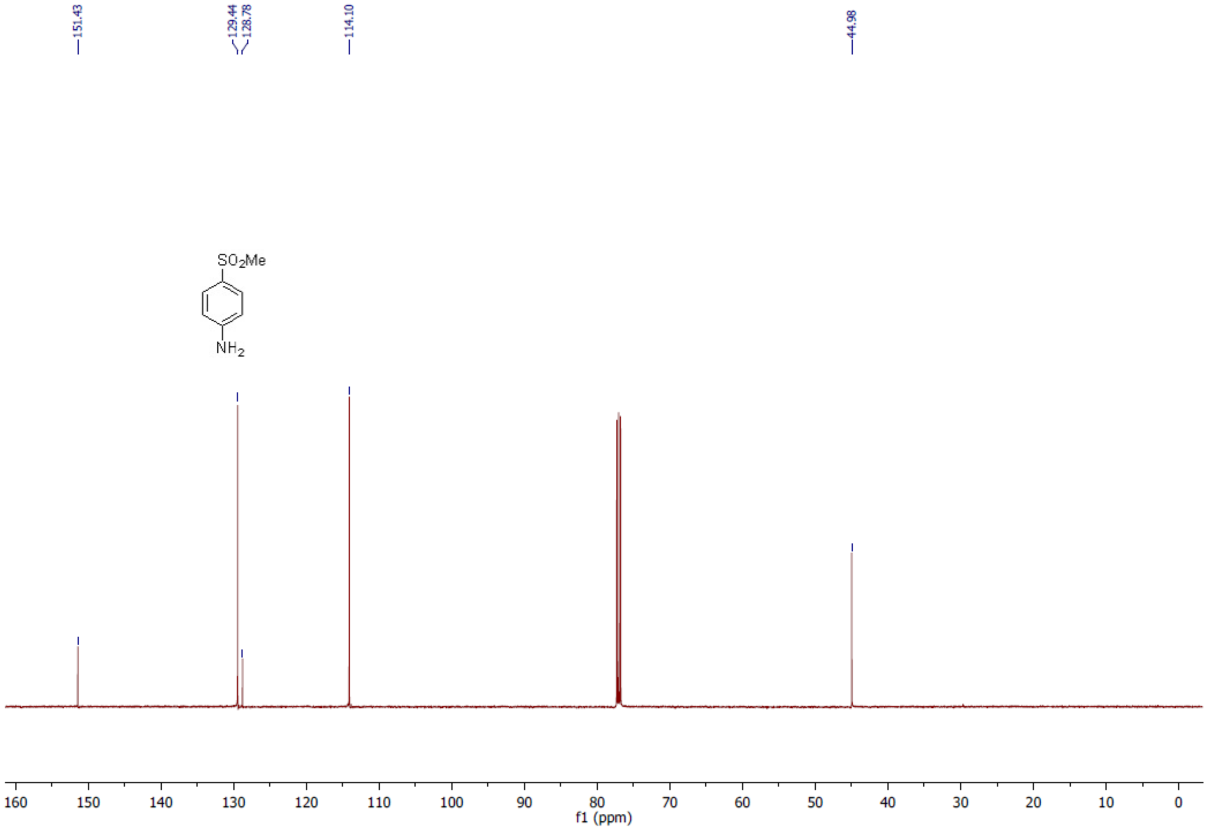
Methyl 4-aminobenzoate 2j:



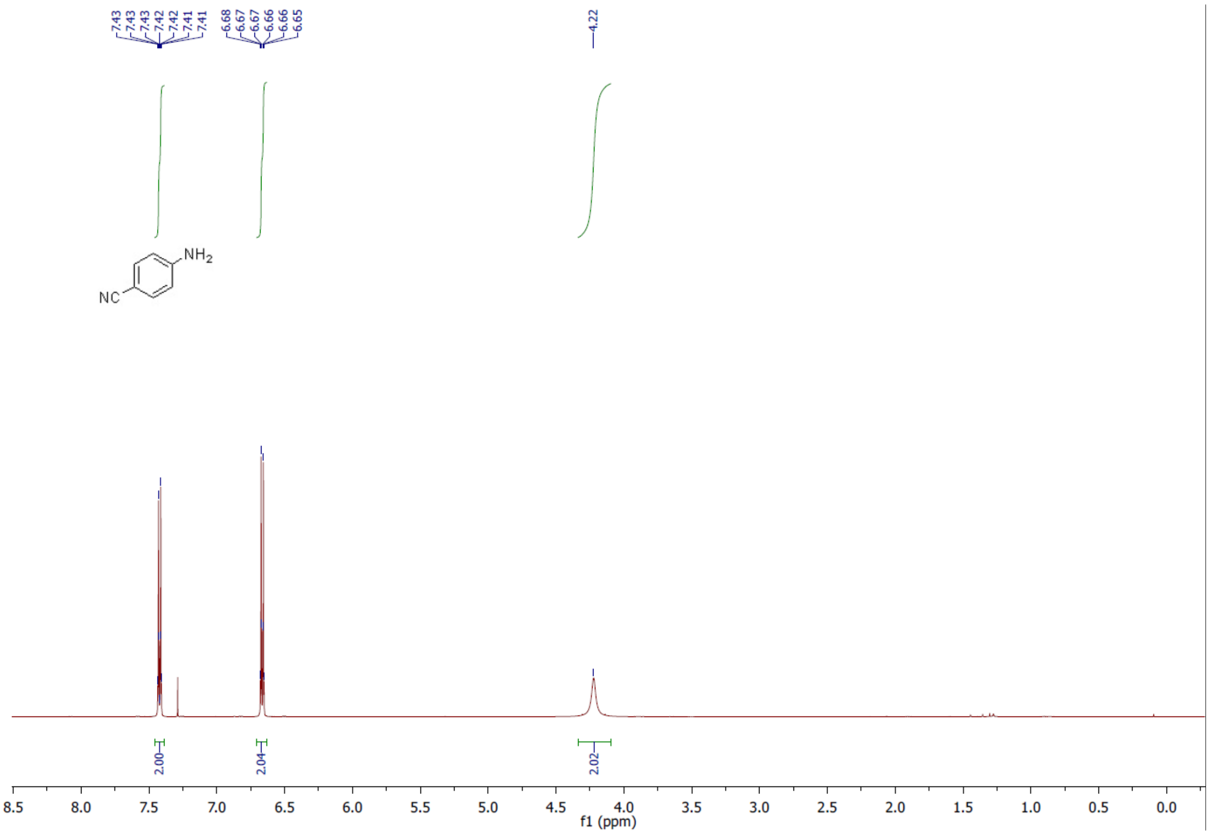


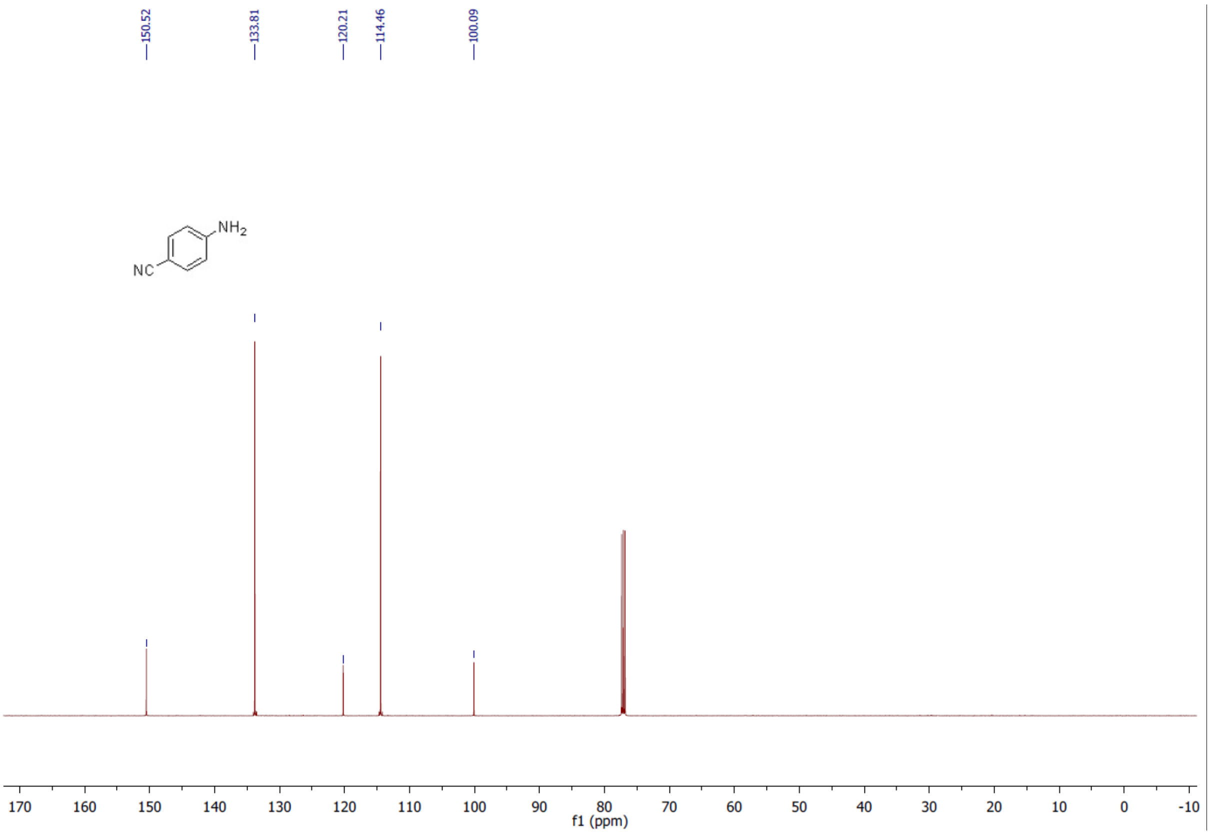
4-(Methylsulfonyl)-aniline 2k:



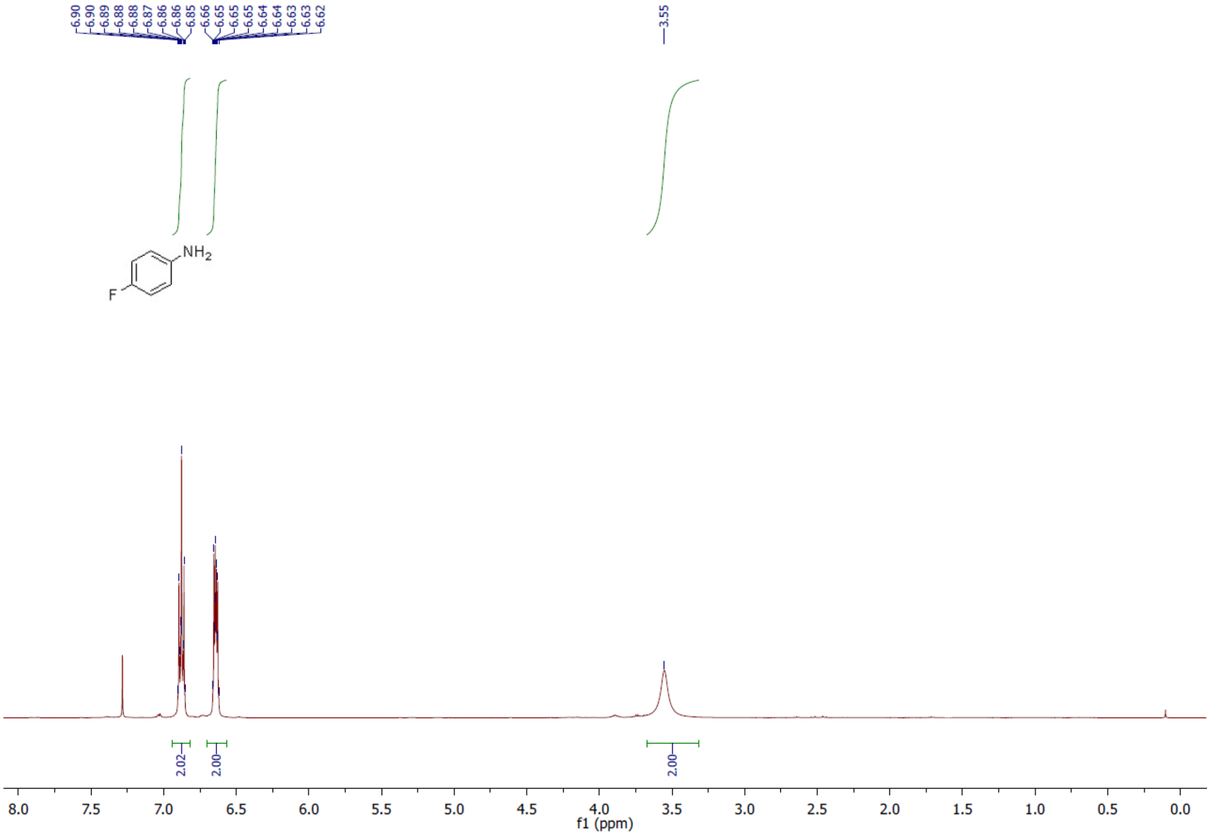


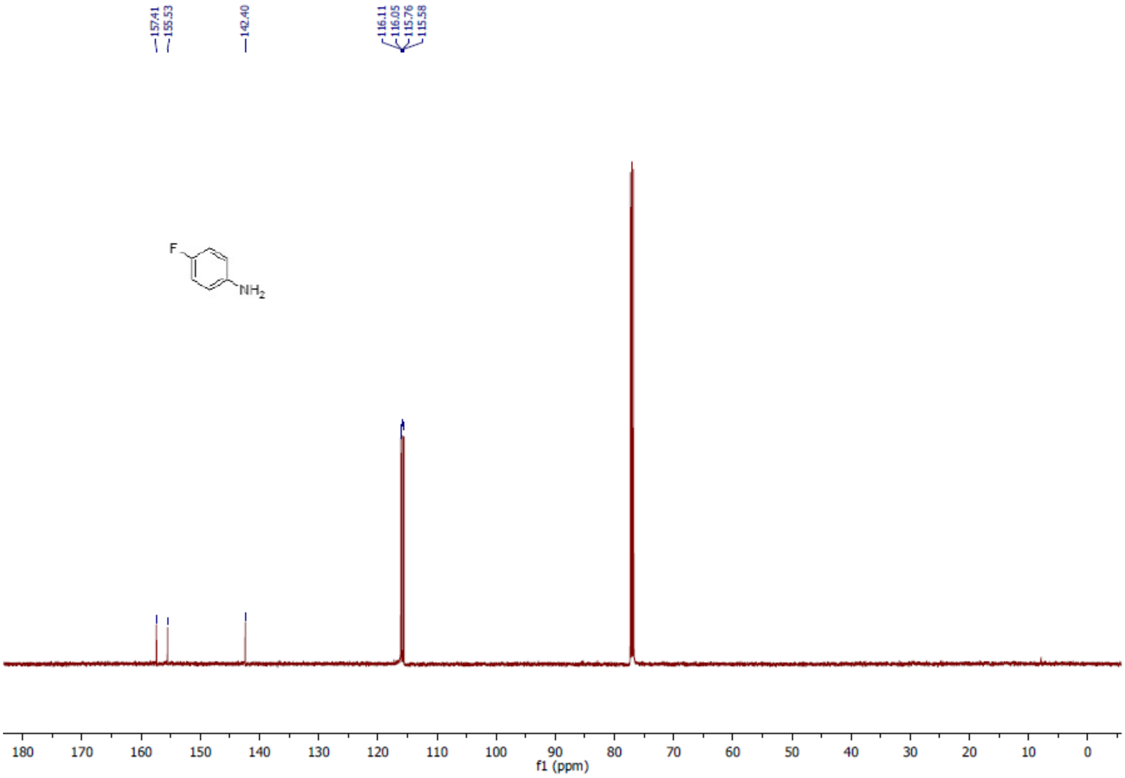
4-Aminobenzonitrile 2l:



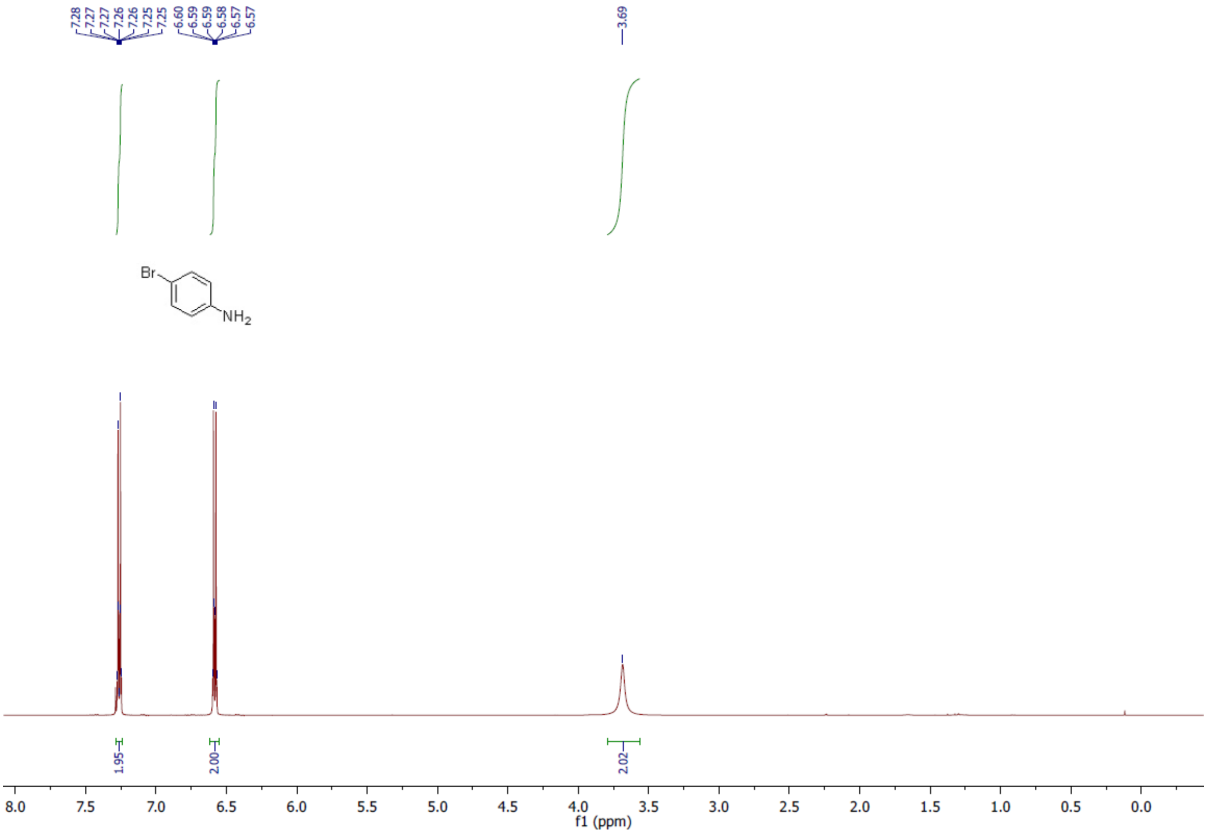


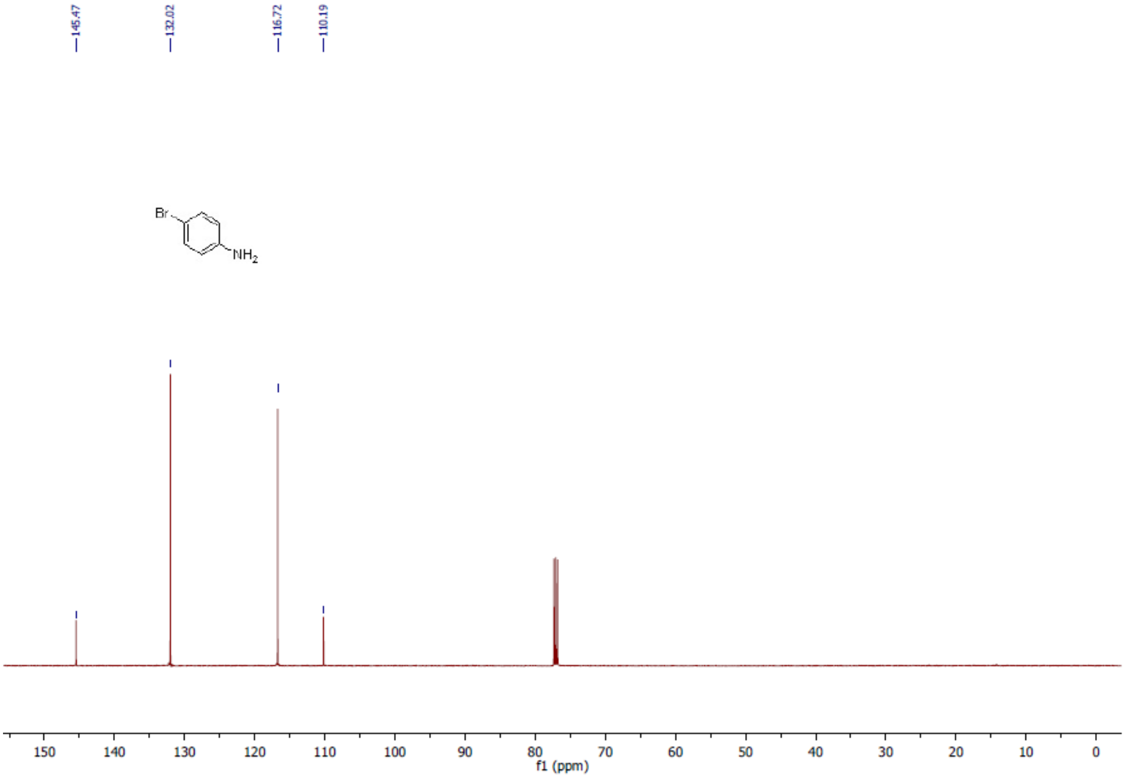
4-Fluoroaniline 2m:



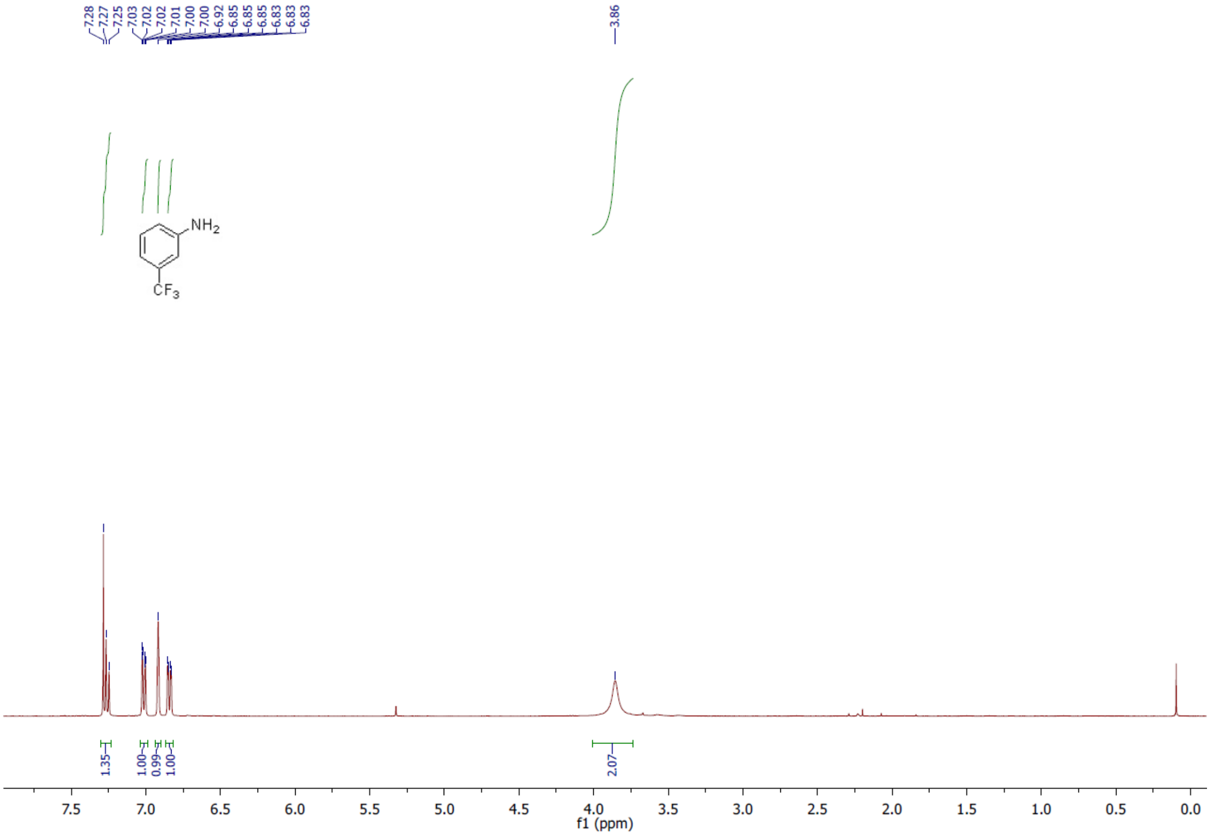


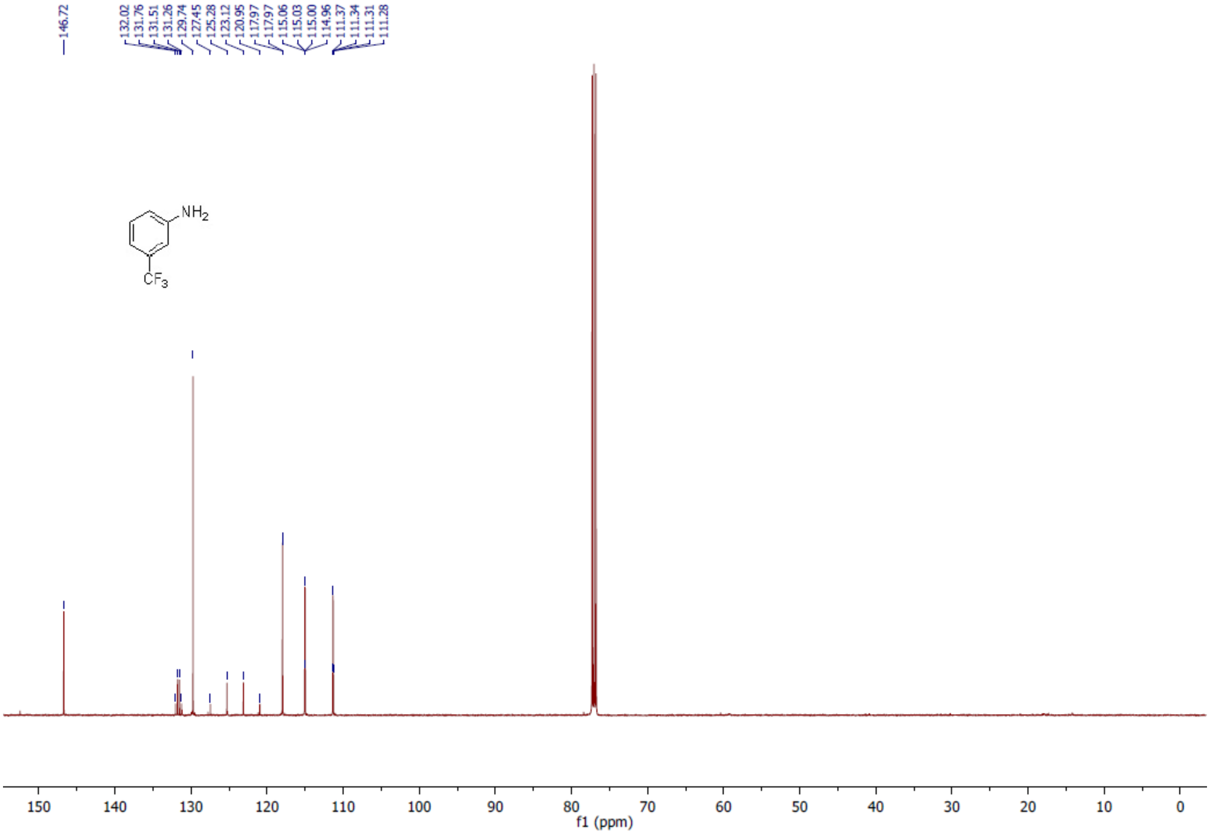
4-Bromoaniline 2o:

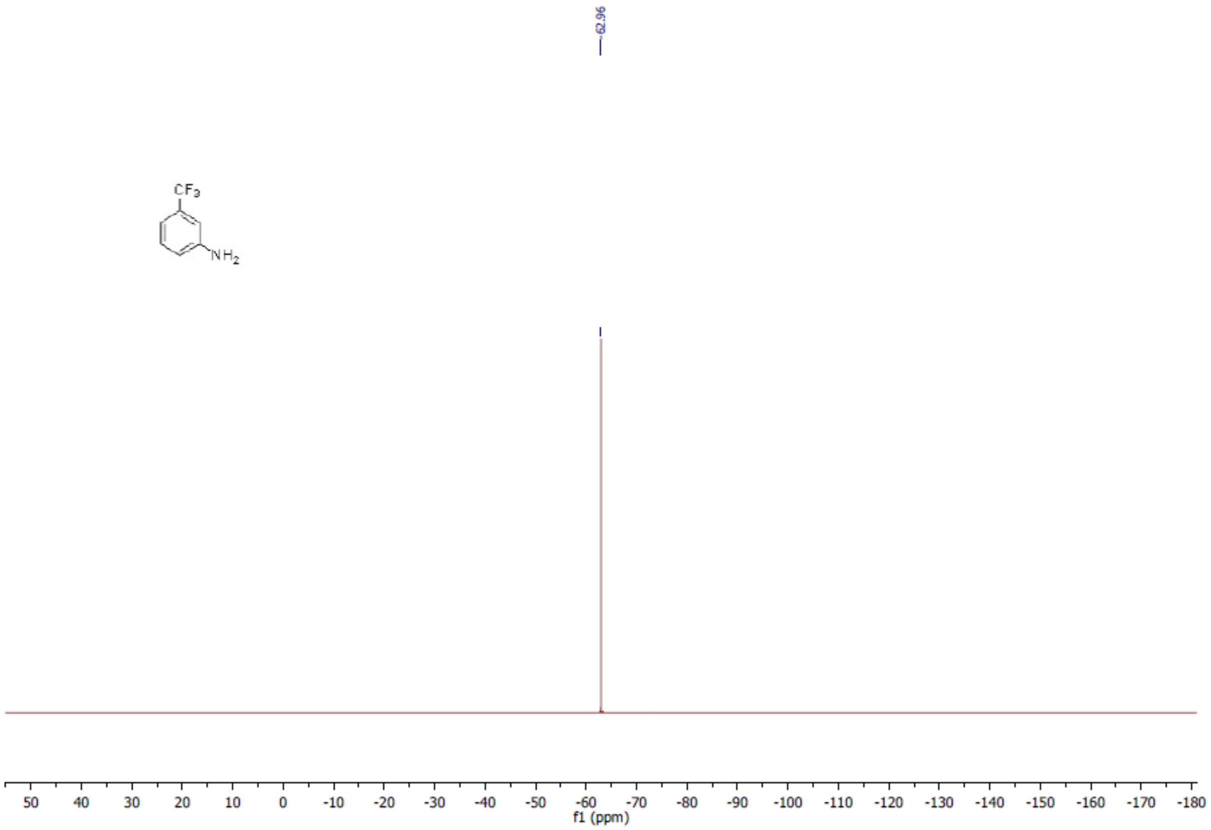




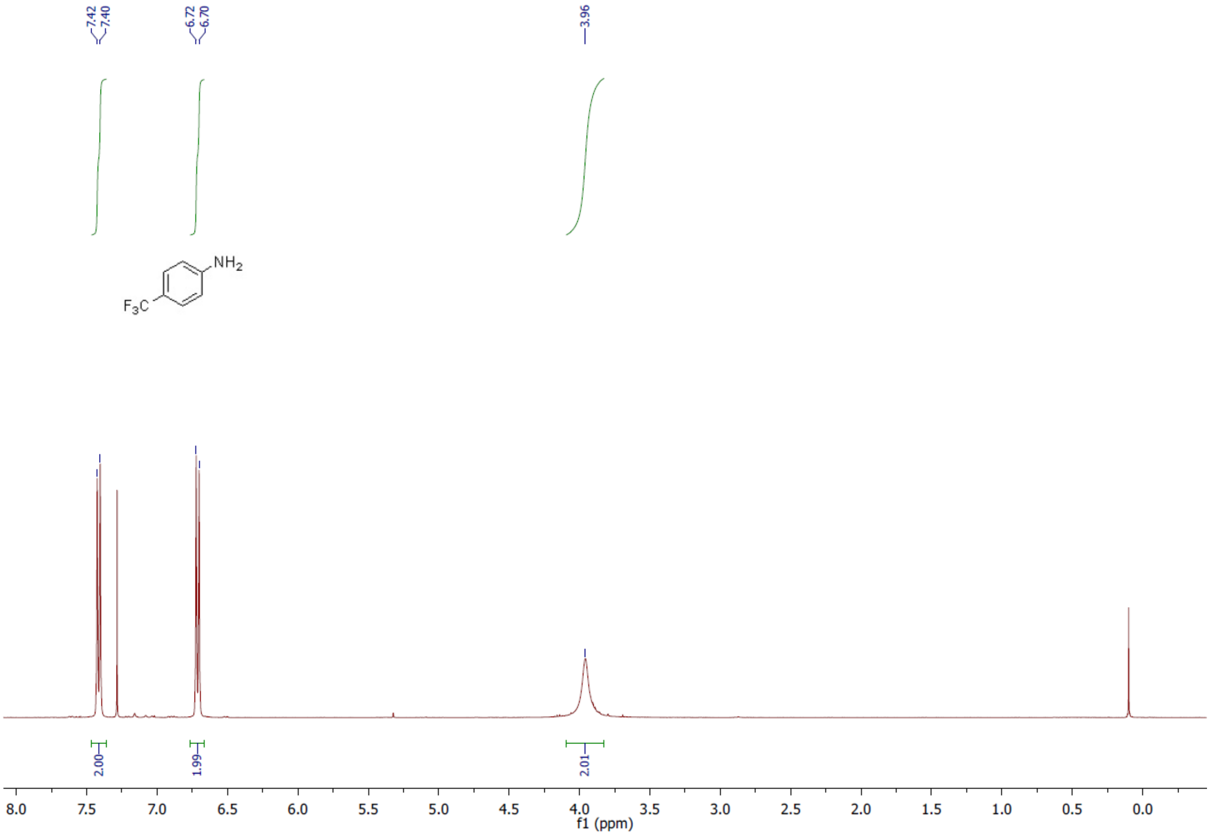
3-(Trifluoromethyl)aniline 2p:

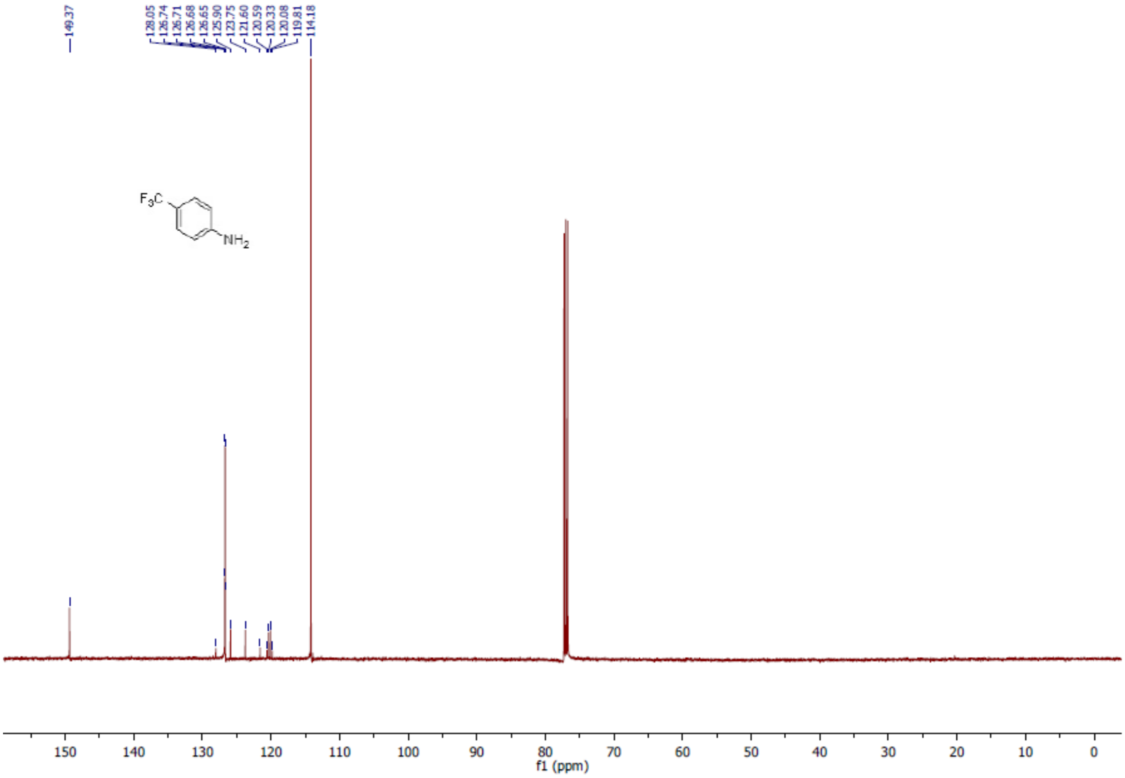


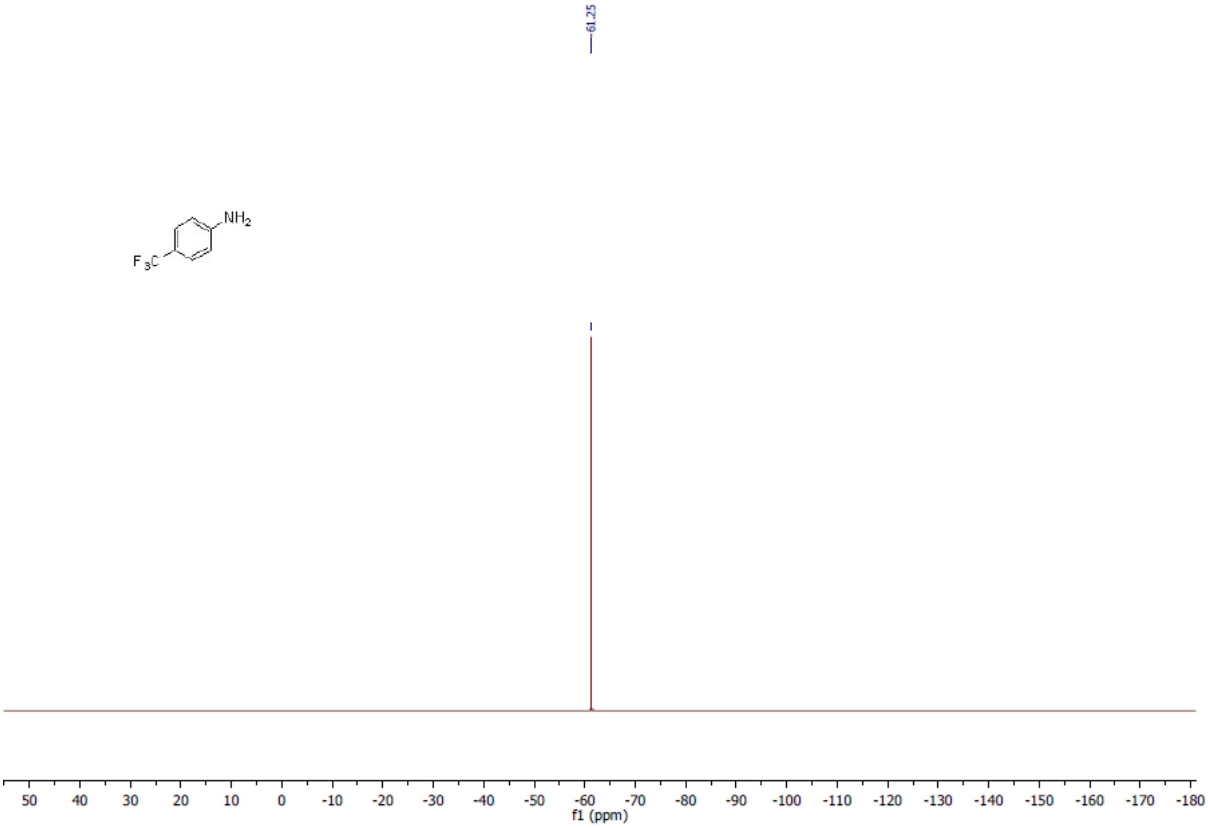



-62.96
CF3
NH2
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

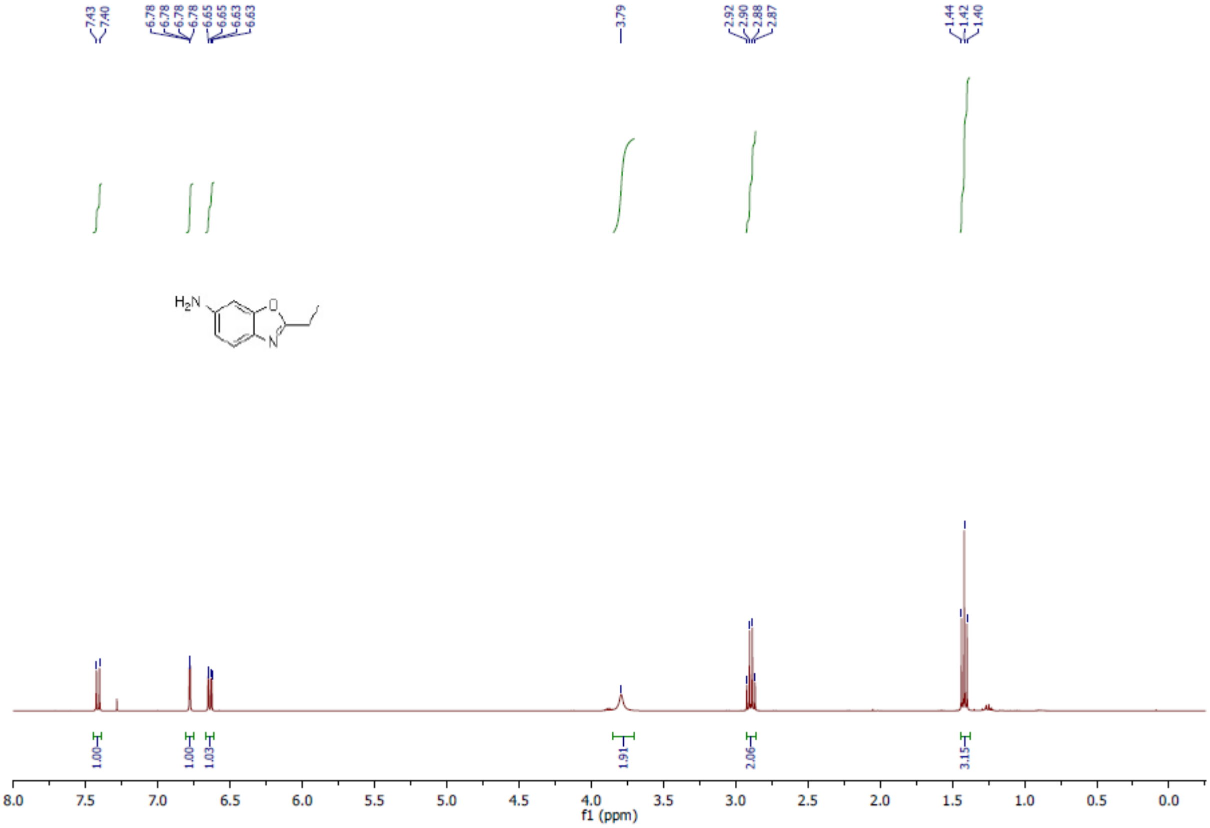
4-(Trifluoromethyl)aniline 2q:

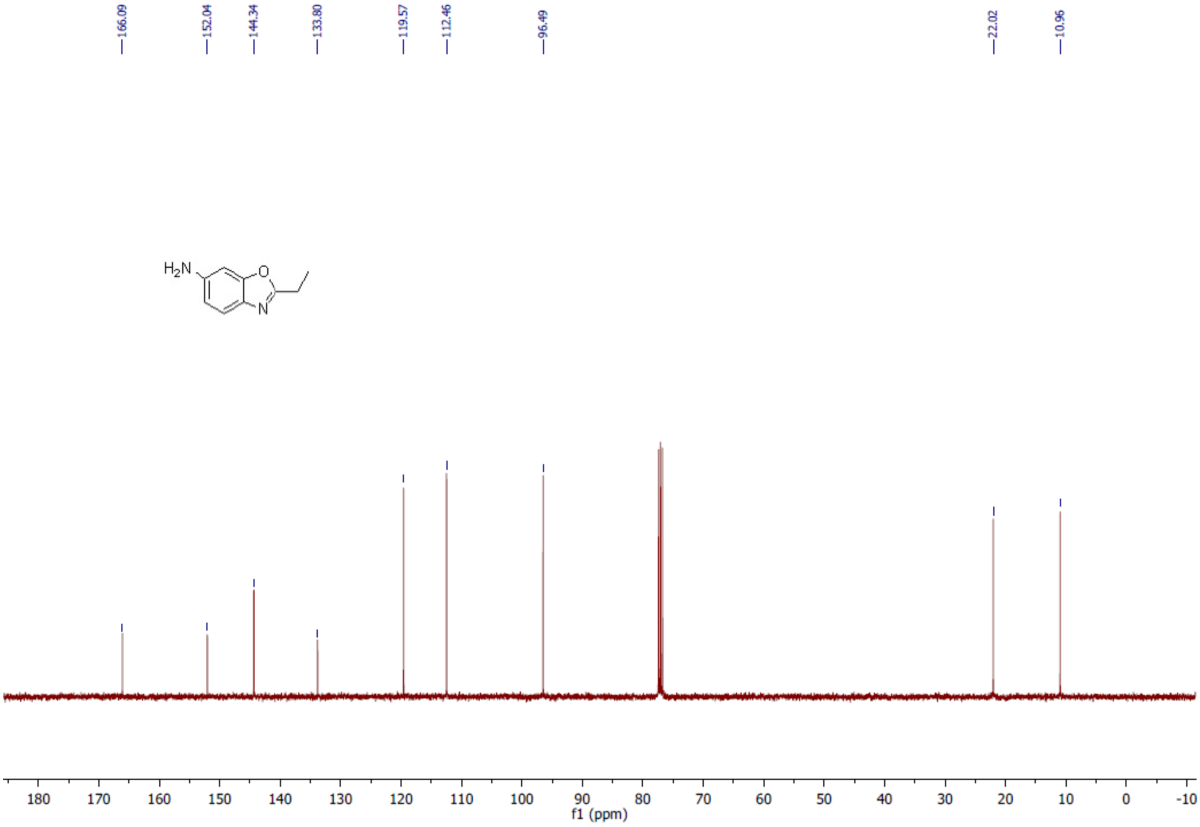




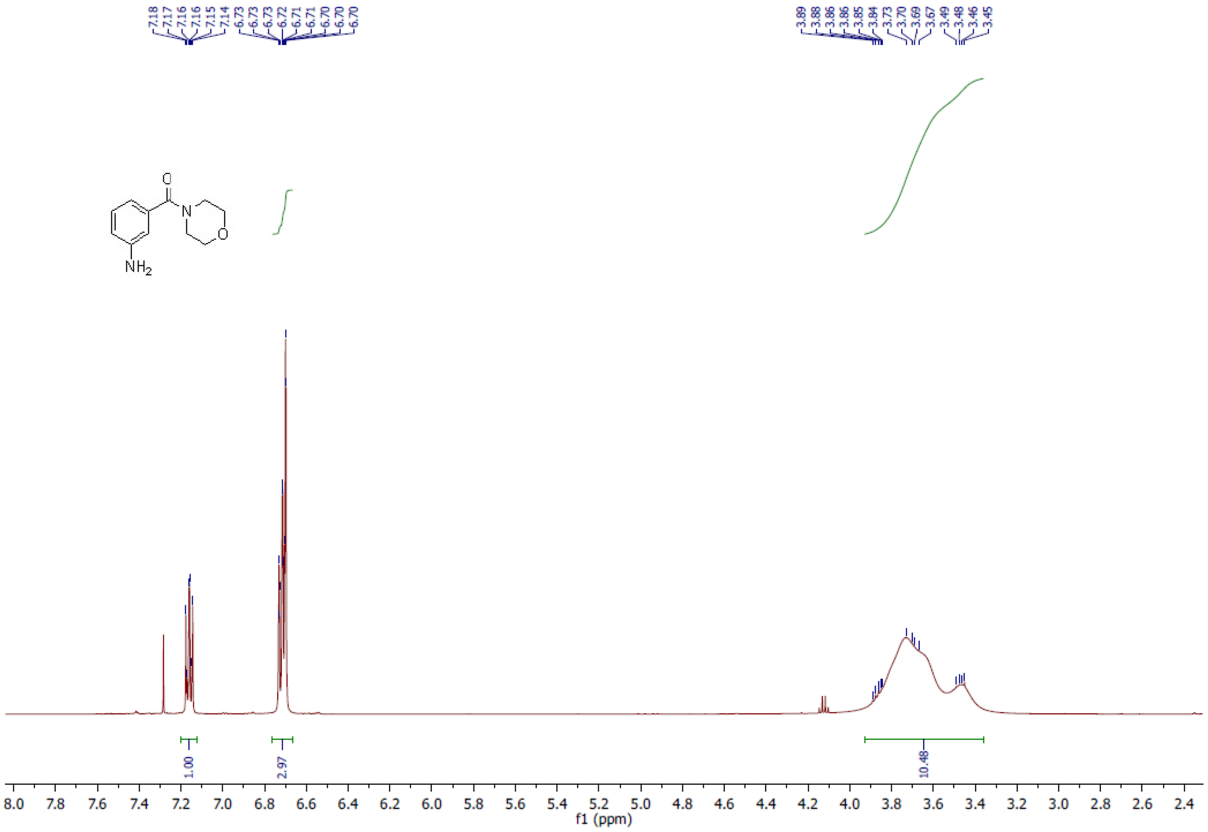

-61.25
NH2
F3C
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

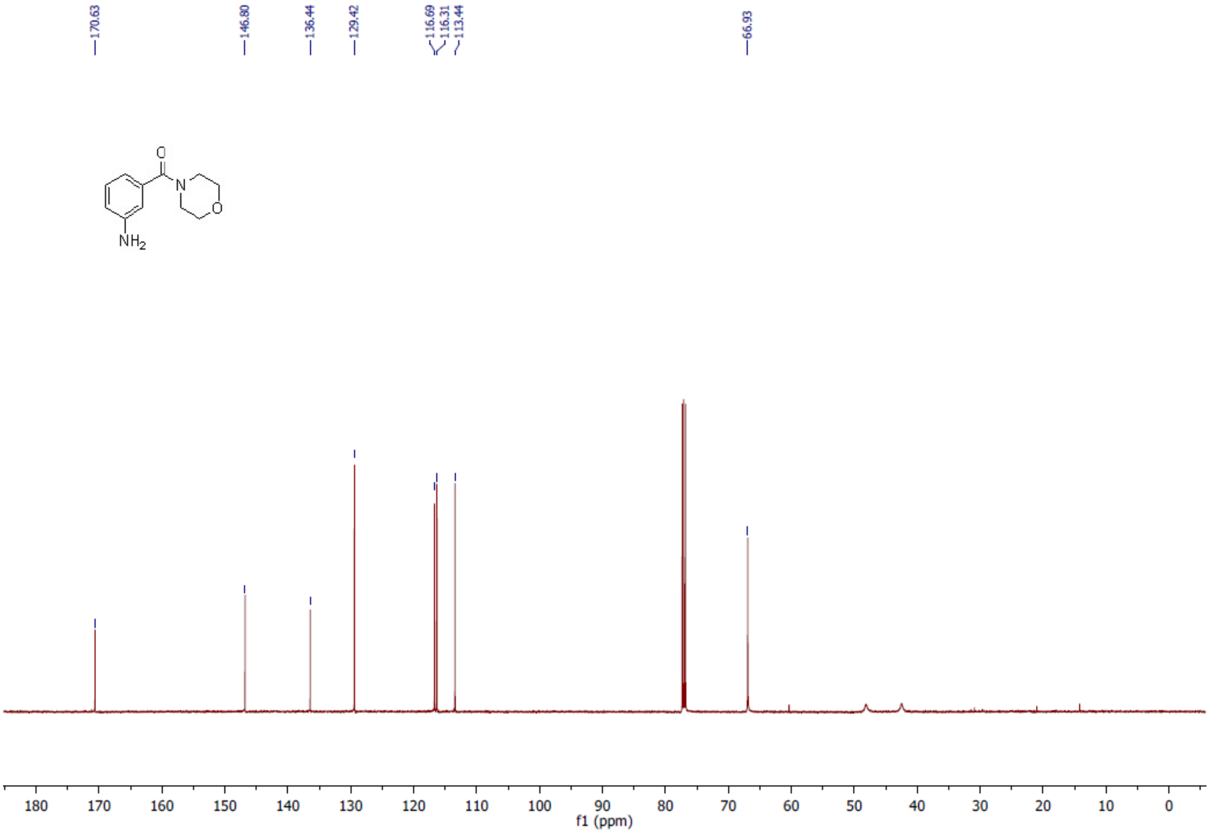
2-Ethyl-6-benzoxazolamine 2r:



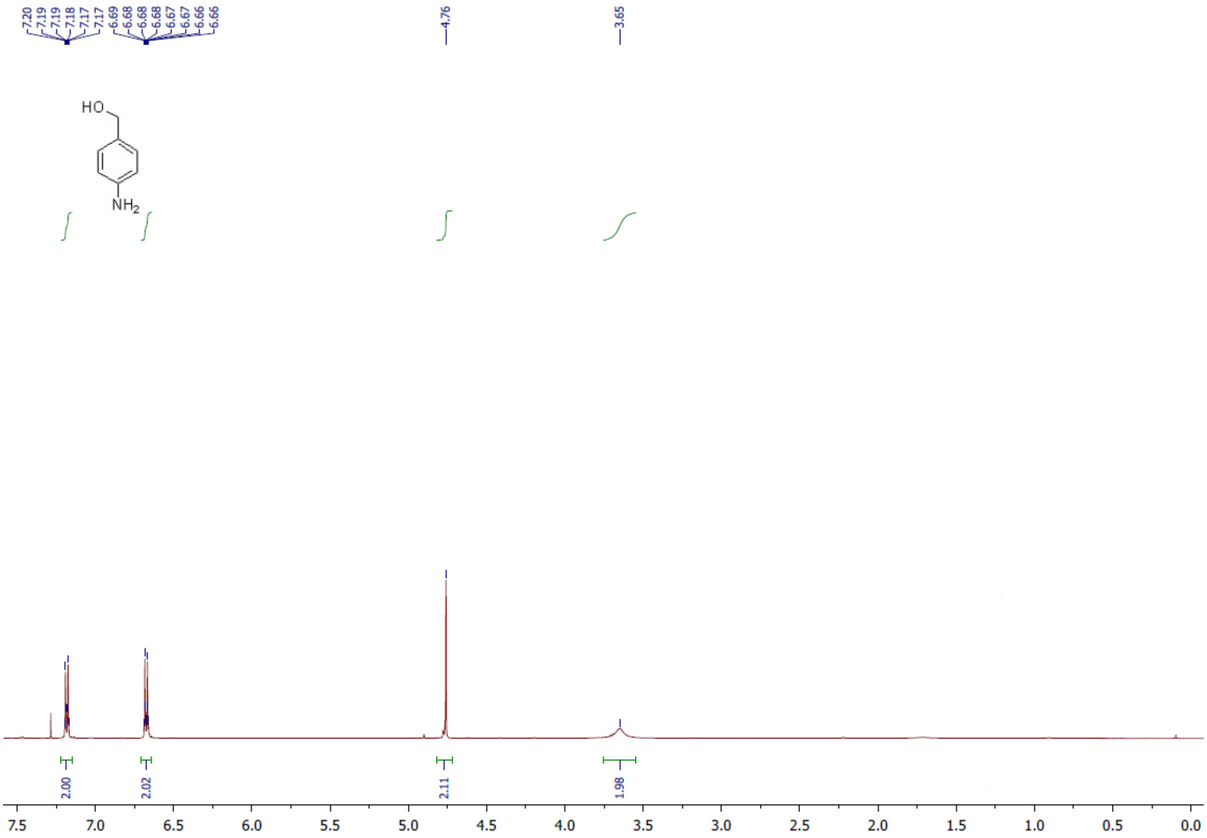


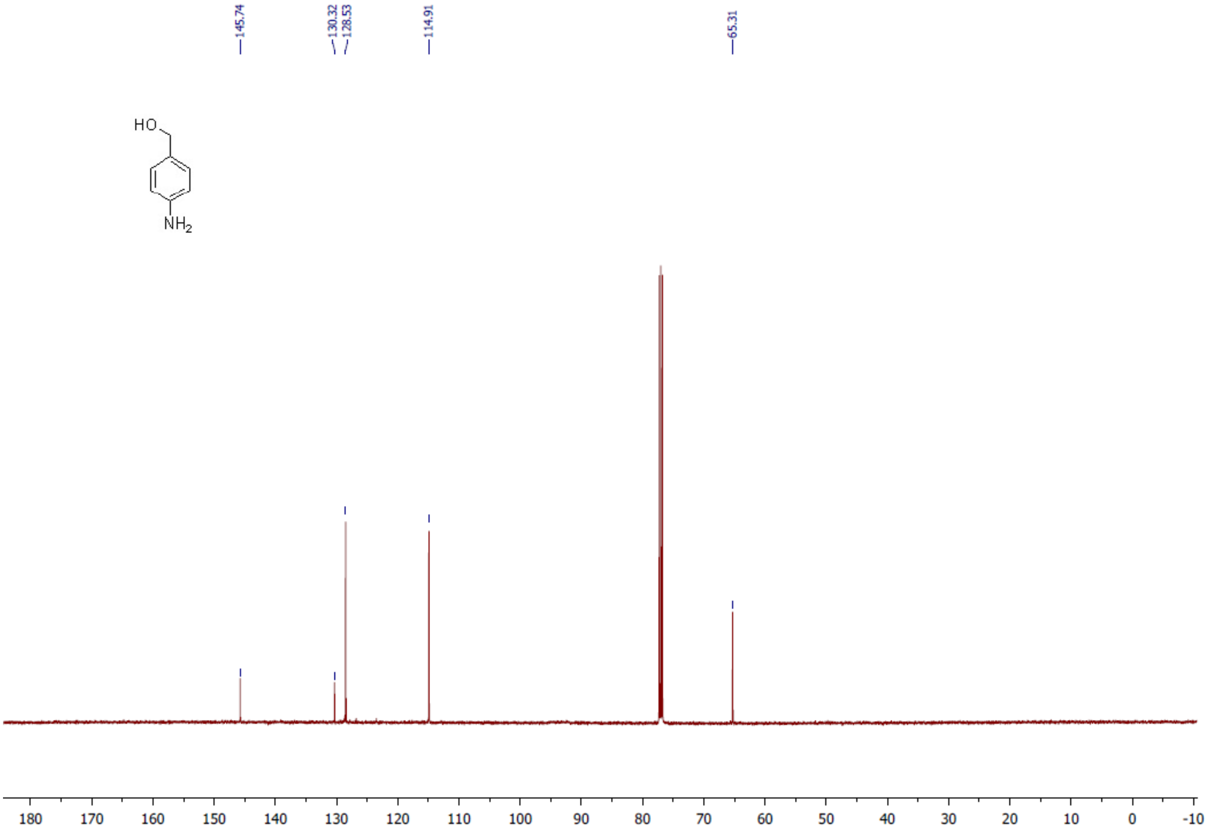
4-(3-Aminobenzoyl)morpholine 2s:



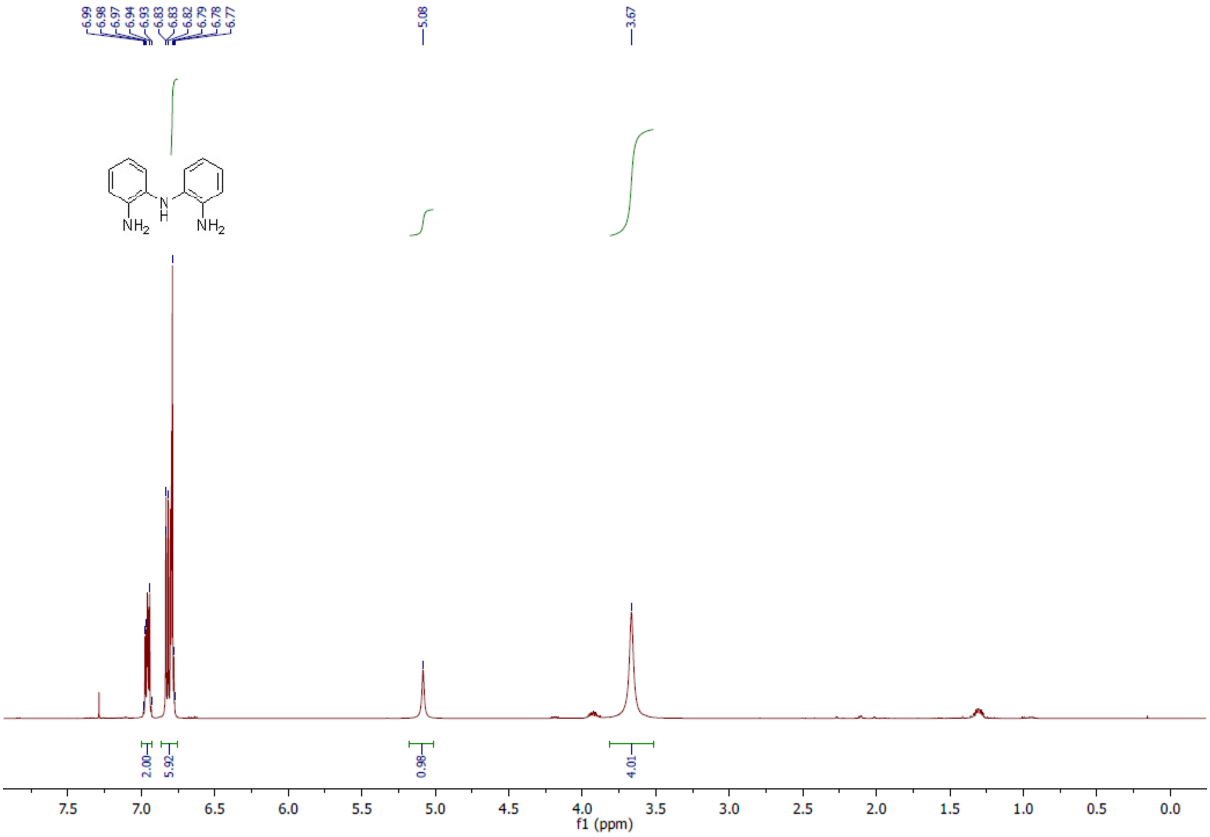


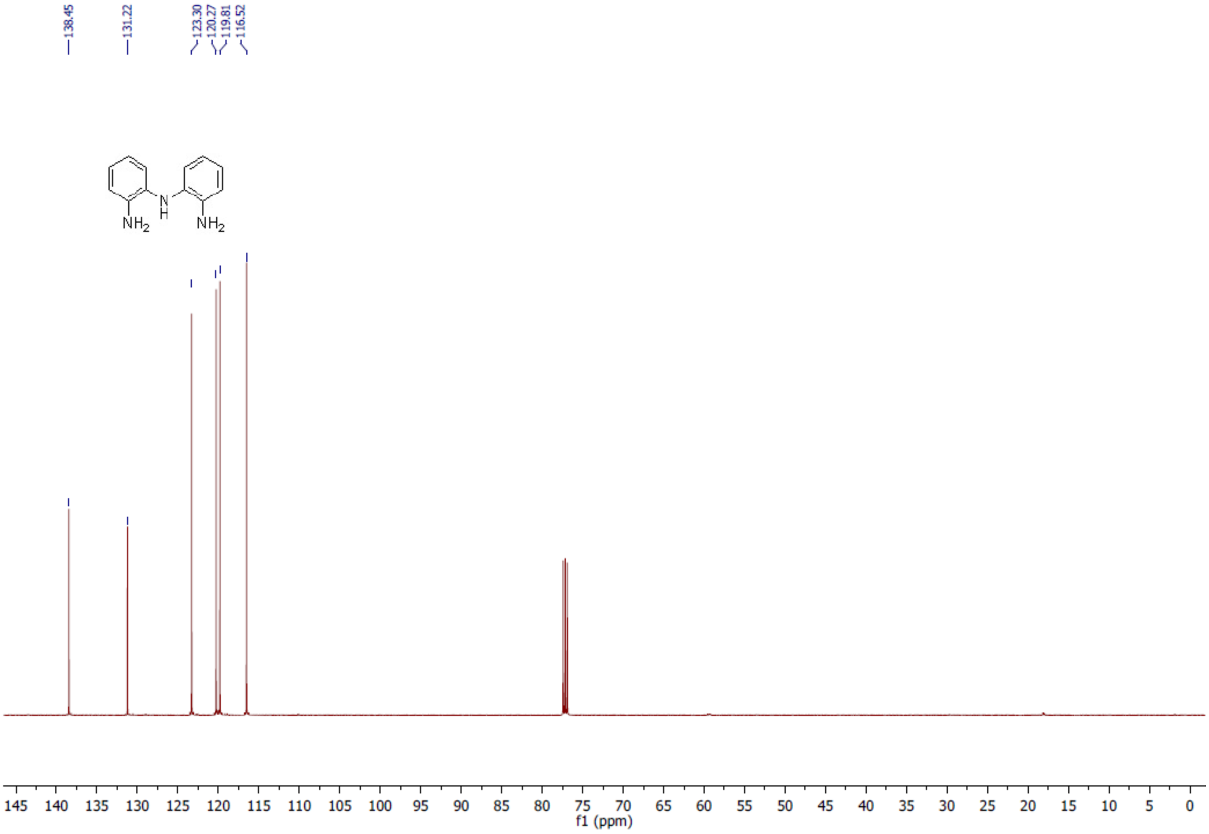
4-(Hydroxymethyl)aniline 2t:



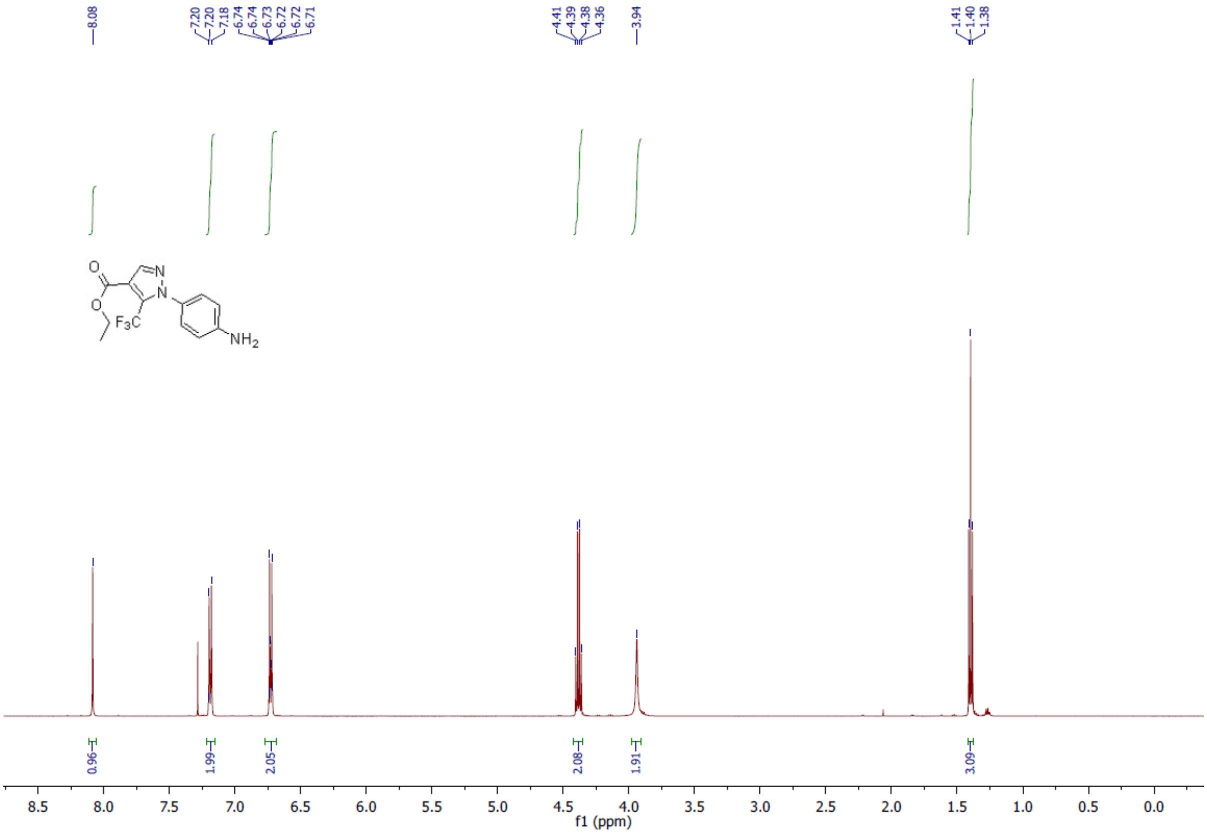


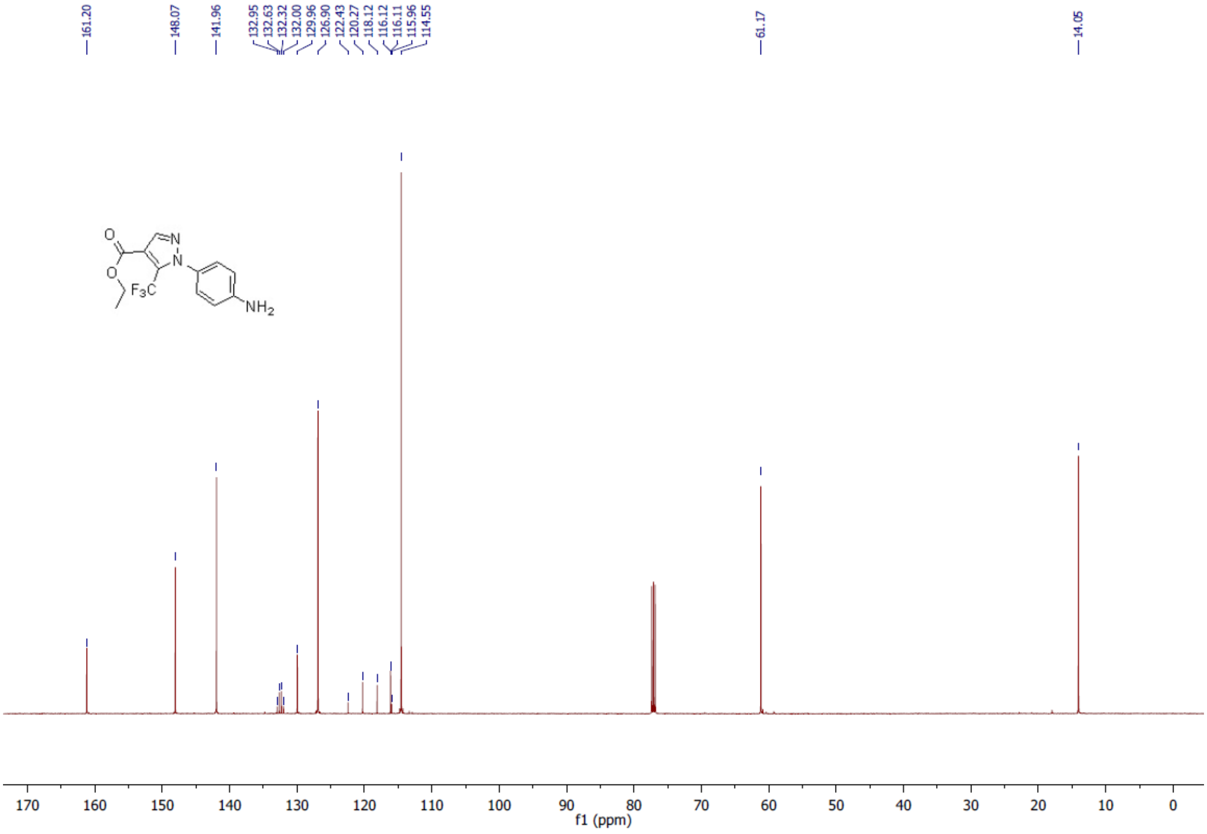
Bis(2-aminophenyl)amine 2u:



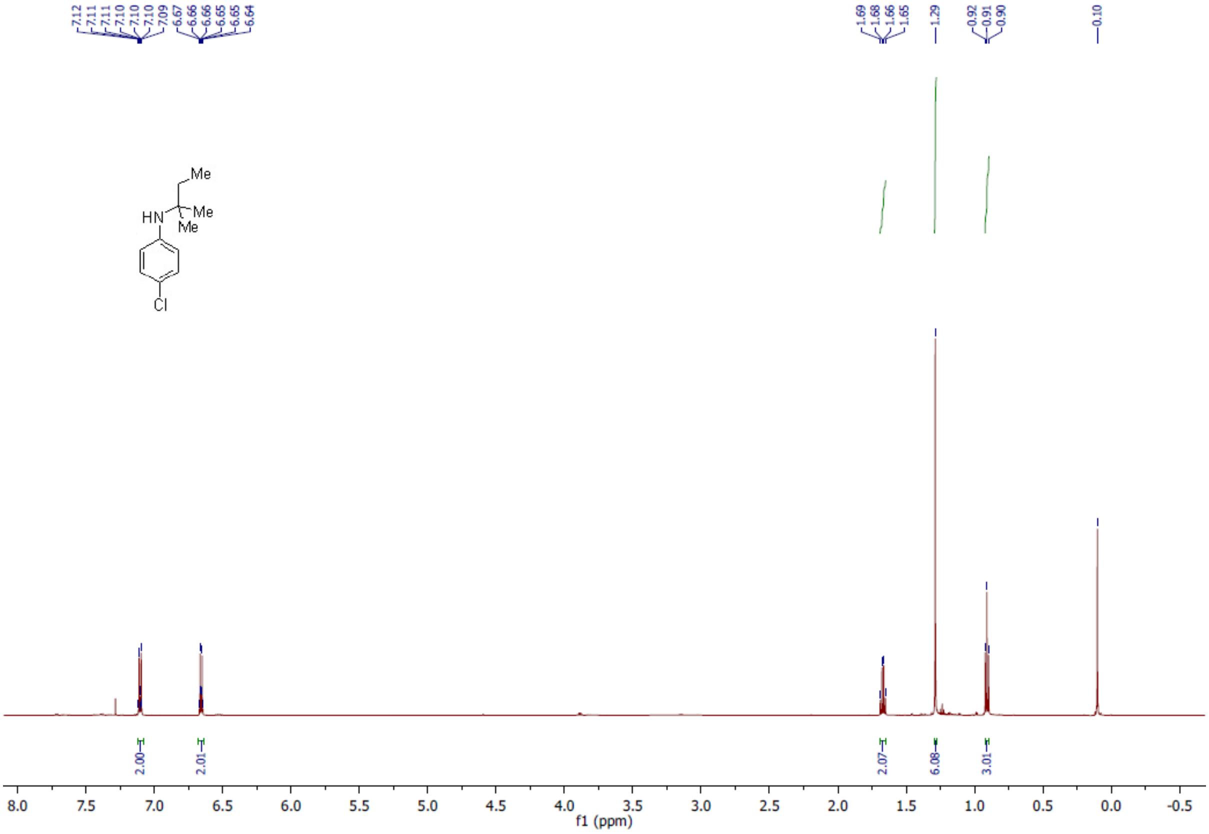


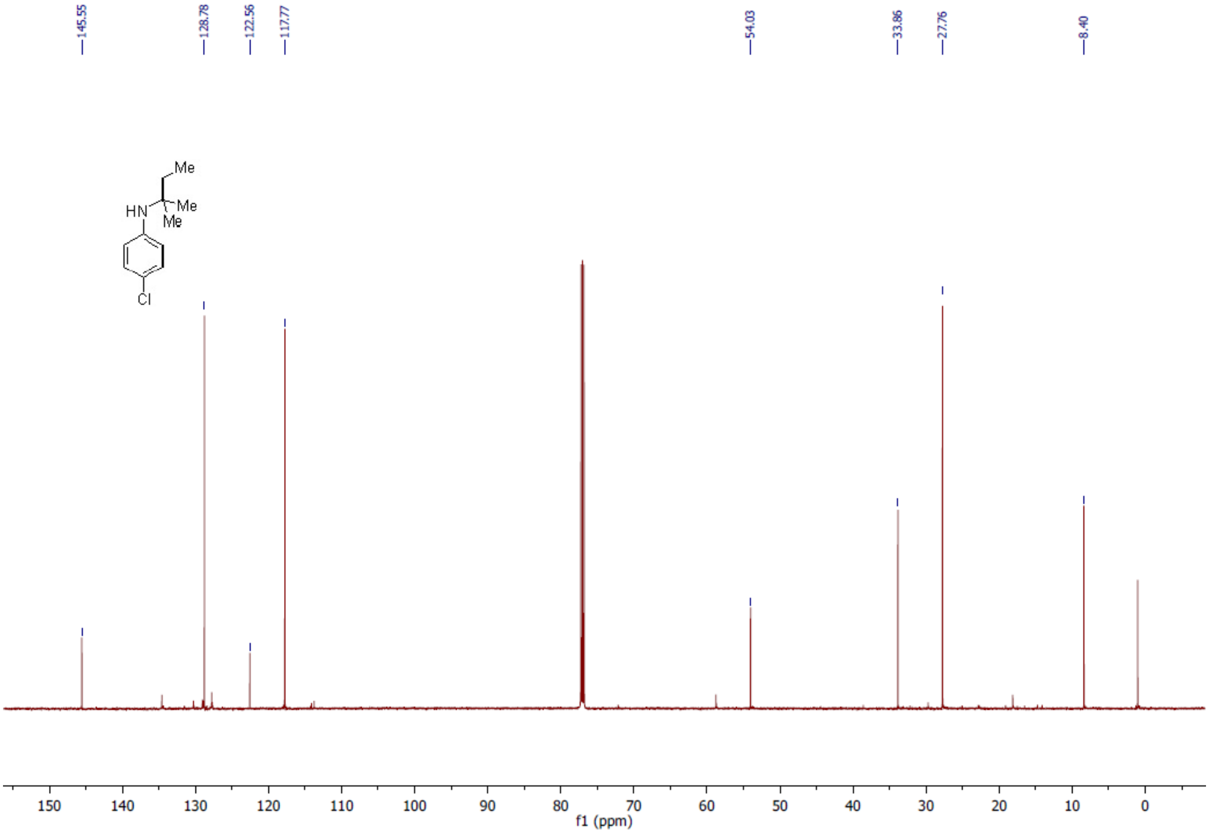
Ethyl 1-(4-aminophenyl)-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate 2v:



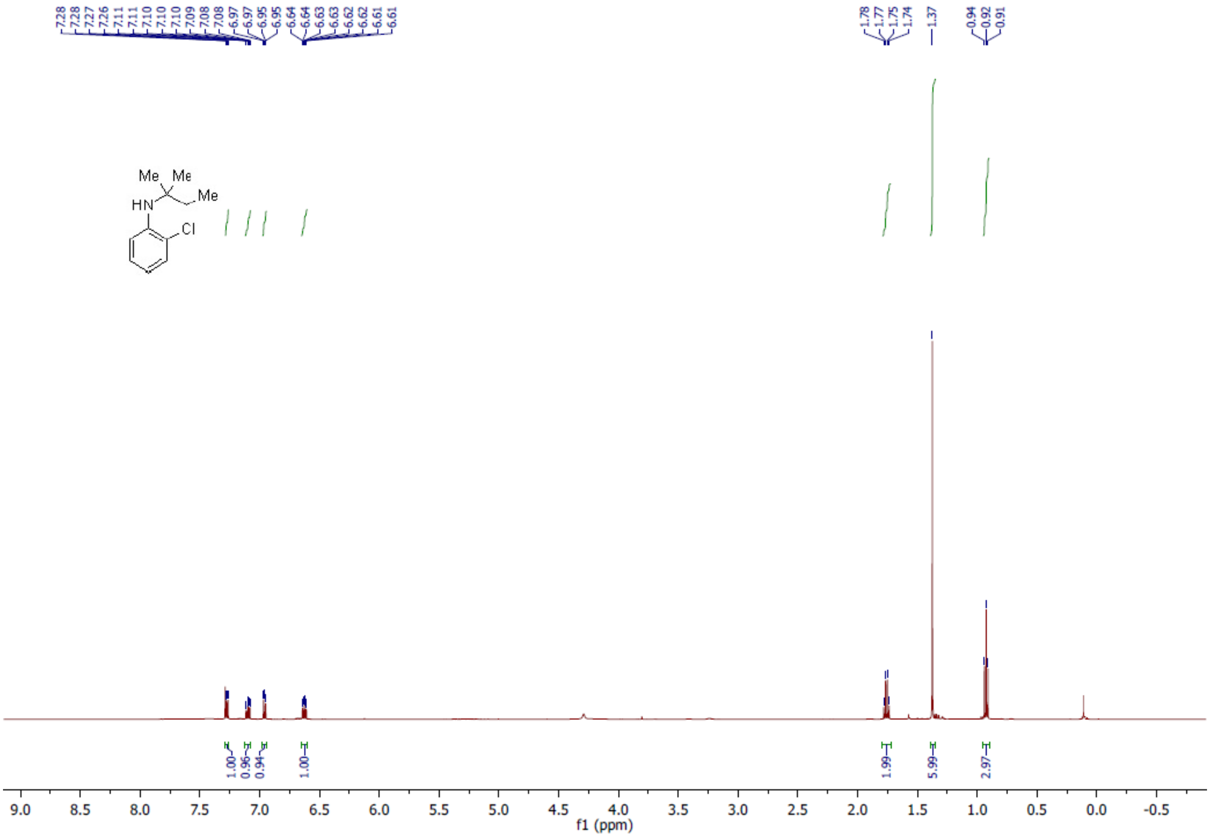


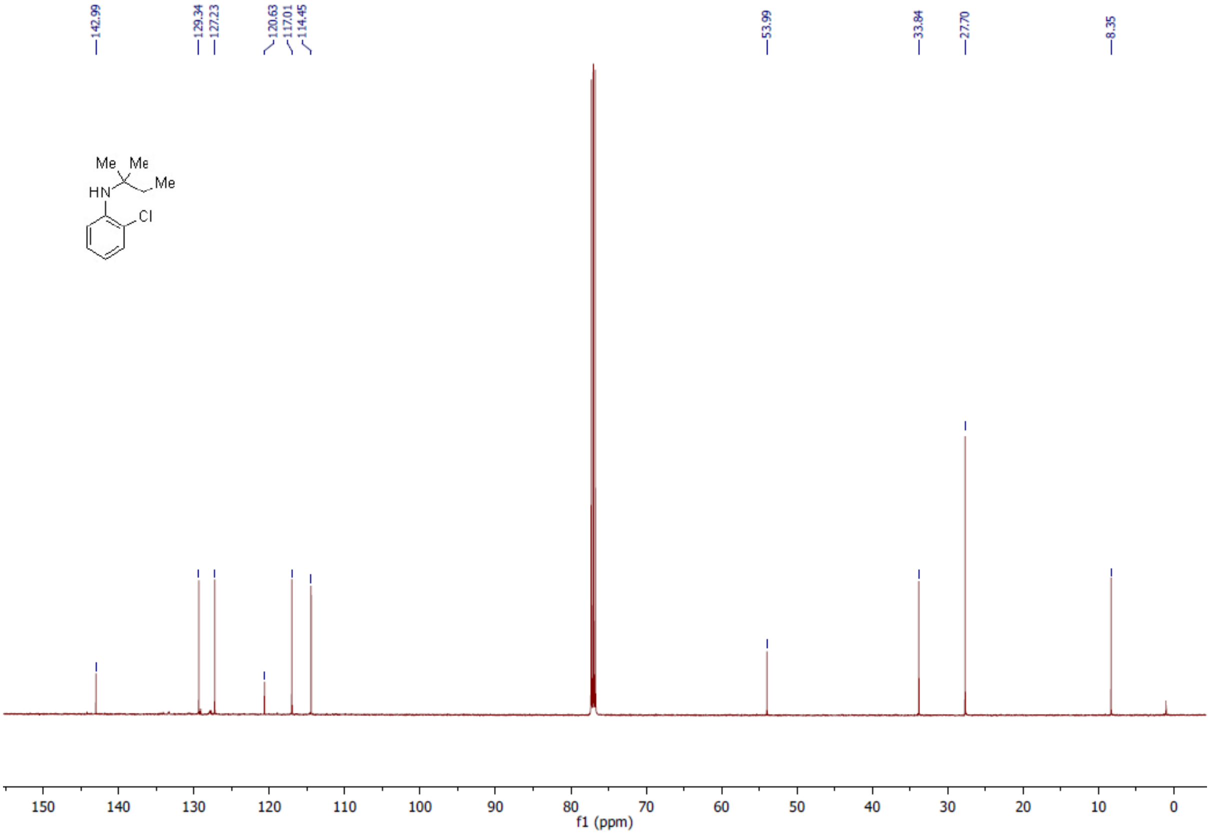
4-Chloro-*N*-(*tert*-pentyl)aniline 6a



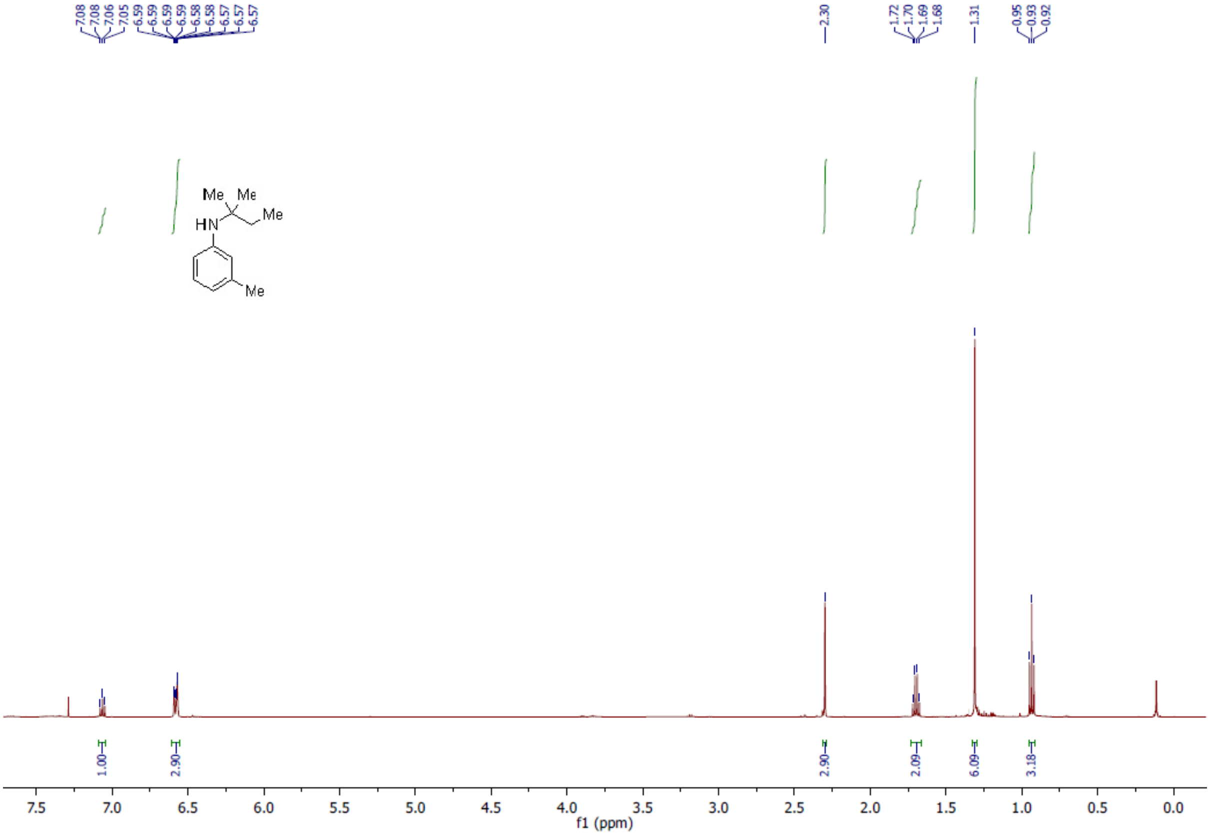


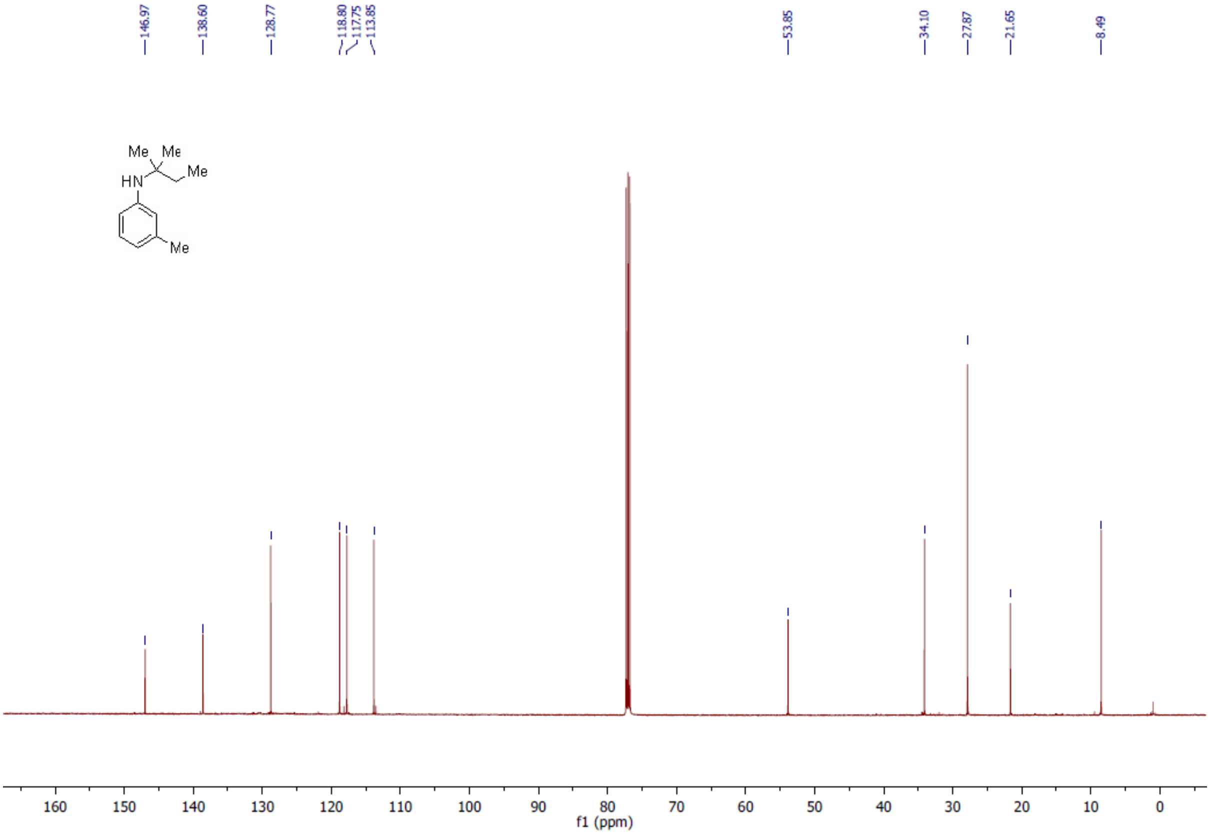
2-Chloro-*N*-(*tert*-pentyl)aniline 6b:



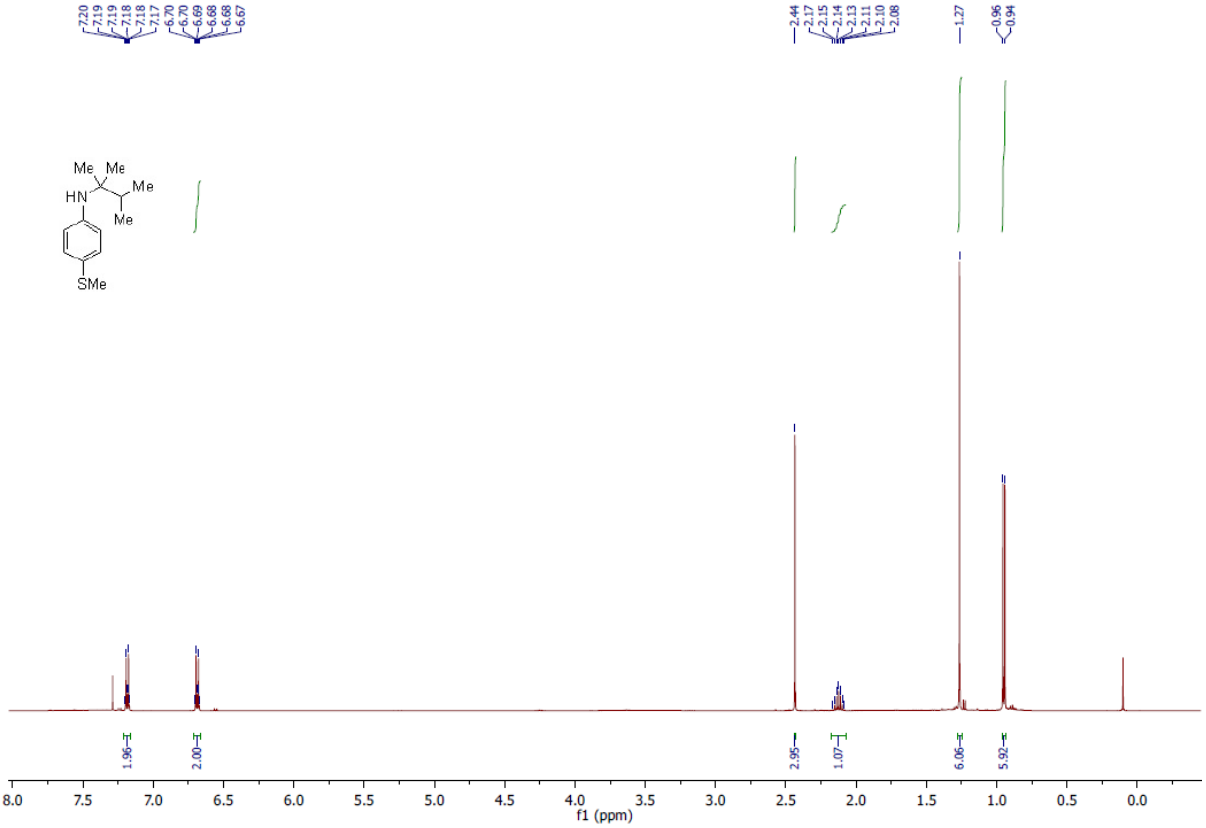


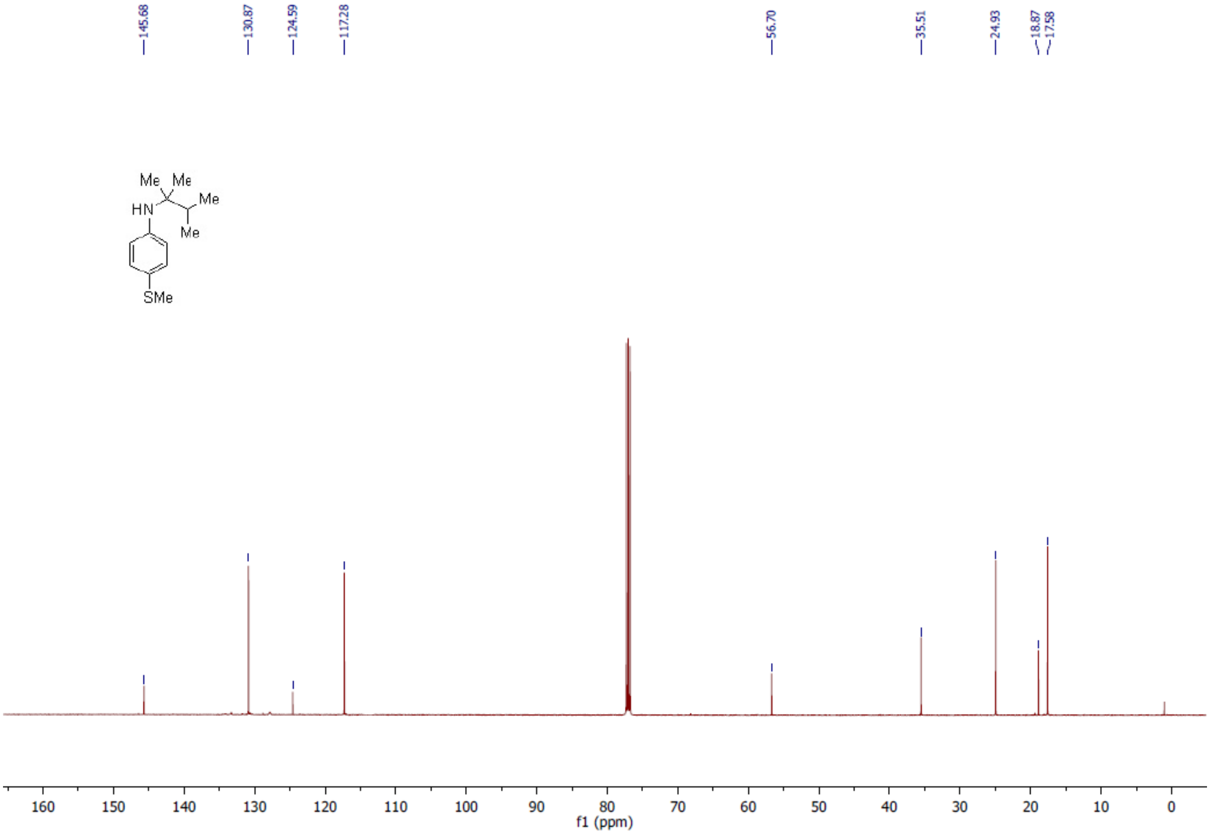
3-Methyl-*N*-(*tert*-pentyl)aniline 6c:



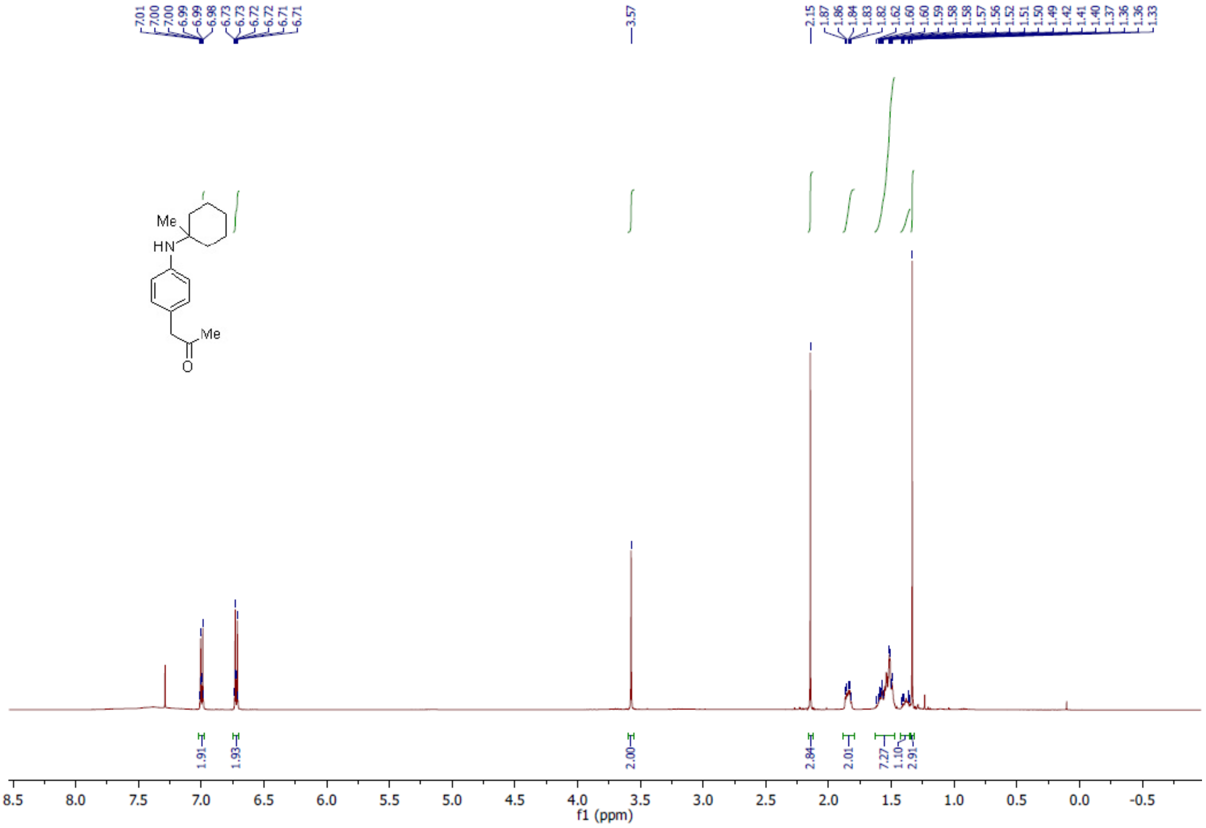


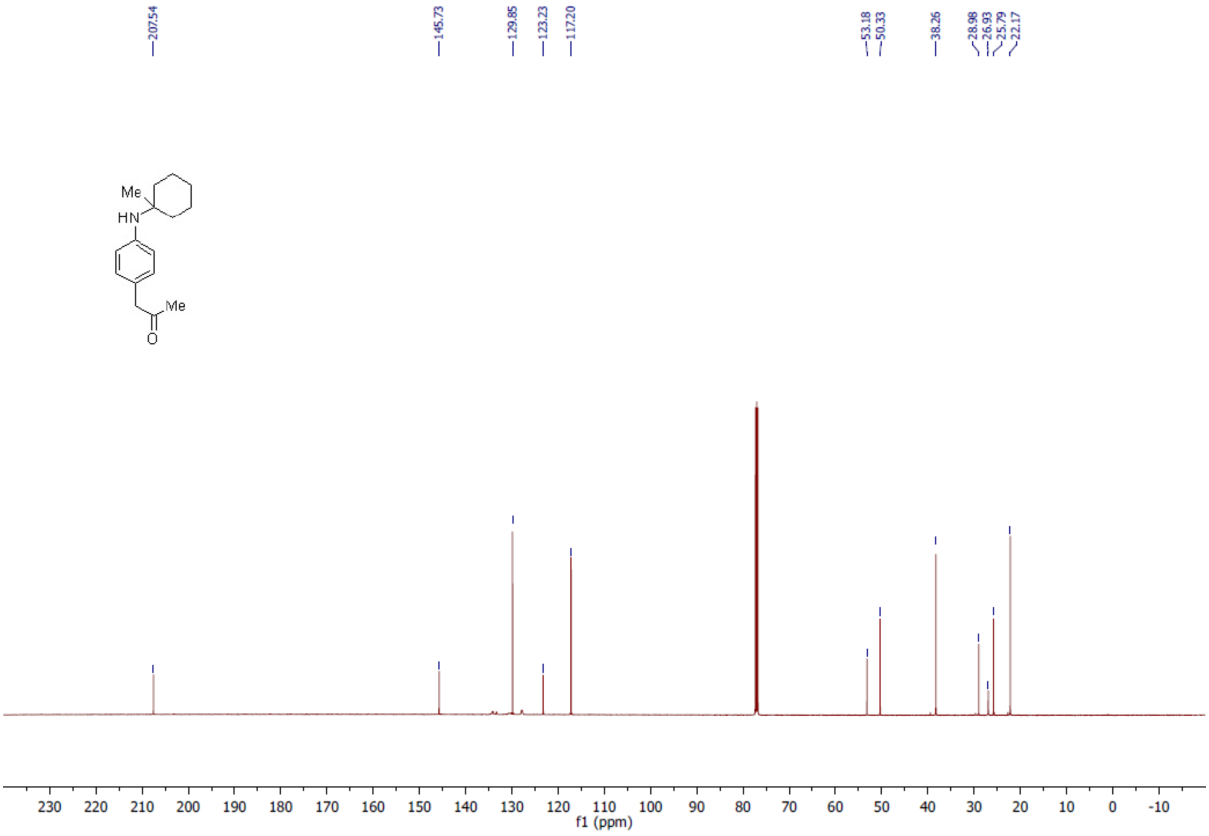
_N_-(2,3-dimethylbutan-2-yl)-4-(methylthio)aniline 6d:



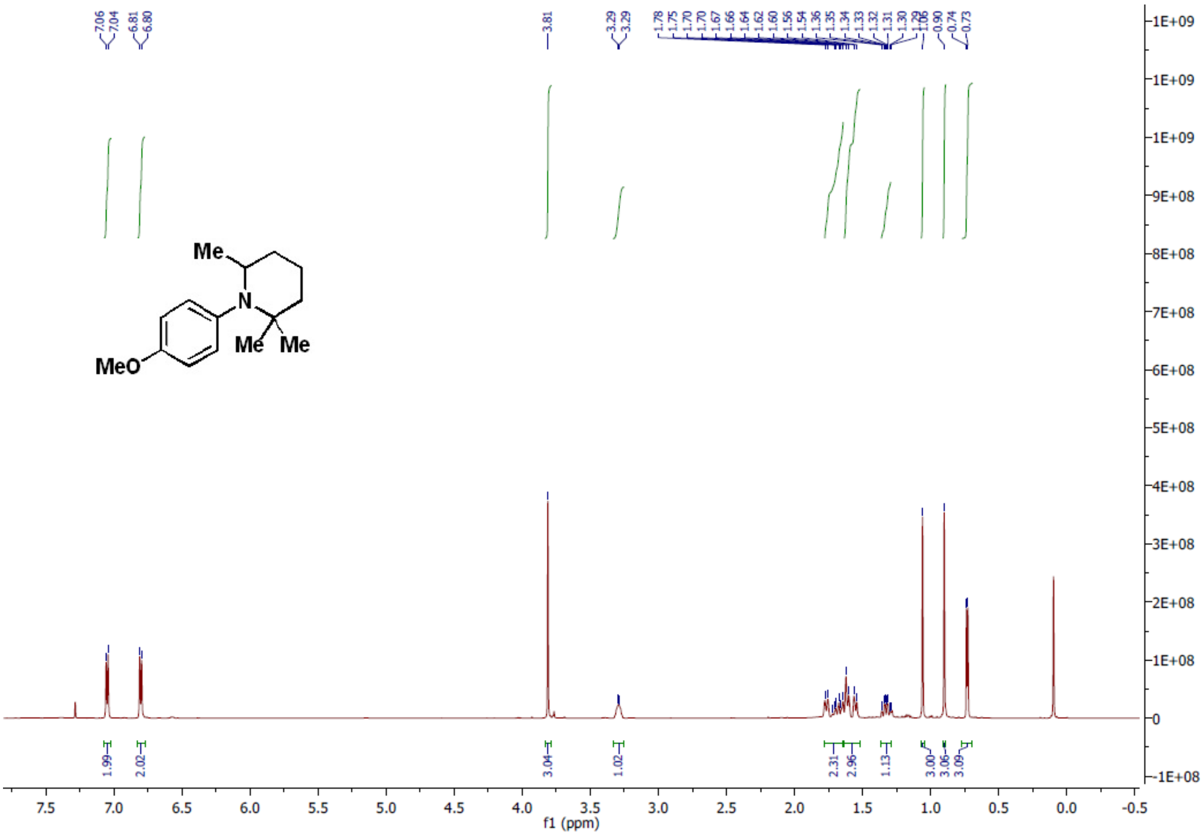


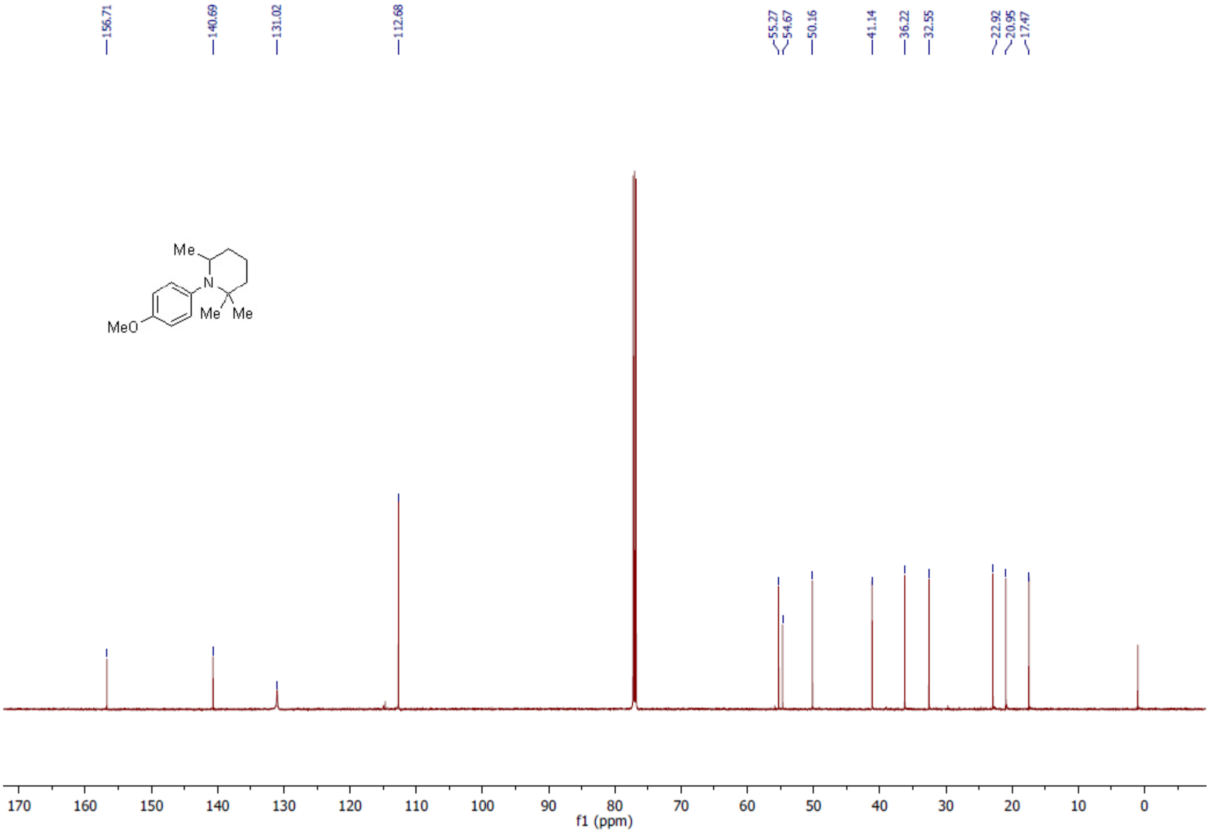
1-(4-((1-Methylcyclohexyl)amino)phenyl)propan-2-one 6e:





1-(4-Methoxyphenyl)-2,2,6-trimethylpiperidine 7a:





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