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Supporting Information

Selective Reduction of Nitro-Compounds to Primary Amines by Nickel-Catalyzed Hydrosilylative reduction

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General comments

^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 instrument unless otherwise specified. $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. Chemical shift for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.6 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin -layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Mass-spectra (EI and ESI) were recorded on an Esquire 6000 and TRACE DSQ instrument. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

Typical experimental procedure

General Procedure for the Reduction of Aromatic Nitro Compounds with PMHS Catalyzed by Ni(acac)2: A solution of nitro-compound (1 mmol), catalyst (10 mol %), and PMHS (150 mol %) in dioxane (5 mL) was stirred at 80 ℃ under air atmosphere for the indicated time. And the progress of the reaction was monitored by thin-layer chromatography (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, and purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent gave the corresponding aromatic amines.

Analytical data

Aniline 2a:[16] colorless oil (45 mg, 0.48 mmol, 81%), R_f(Ethyl acetate/ Petroleum ether=1:5)=0.41. ^{1}H NMR (400MHz, $CDCl_3$) δ=3.52 (s, 2H), 6.60-6.75 (m, 3H), 7.12 ppm (t, J=8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=114.9, 118.2, 129.1, 146.3 ppm.

4-Chloroaniline 2b:[20] whrite solid (41 mg, 0.33 mmol, 78%) m.p.=66-68 ℃, R_f (Ethyl acetate/ Petroleum ether=1:5)=0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.61 (s, 2H), 6.59 (d, J=8.4 Hz, 2H), 7.09 ppm (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=116.2, 123.1, 129.0, 144.9 ppm.

2-Chloroaniline 2c:[16] colorless oil (38 mg, 0.30 mmol, 71%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.96 (s, 2H), 6.62-6.69 (m, 2H), 6.99-7.01 (m, 1H), 7.01-7.21 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=115.8, 118.9, 119.1, 127.5, 129.3, 142.8 ppm.

3-Chloro-phenylamine 2d:[16] colorless oil (41 mg, 0.33 mmol, 74%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.38. ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.06 (t, J=7.8 Hz, 1H), 6.72-6.74 (m, 1H), 6.65 (t, J=1.8 Hz, 1H), 6.52-6.54 (M, 1H), 3.66 ppm (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ=147.8, 147.8, 134.8, 130.4, 118.4, 114.9, 113.3, 113.3 ppm.

4-Bromoaniline 2e:[20] yellow solid (63 mg, 0.37 mmol, 78%) m.p.=63-65 ℃, R_f (Ethyl acetate/ Petroleum ether=1:5)=0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.64 (s, 2H), 6.56 (d, J=8.8 Hz, 2H), 7.23 ppm (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=110.1, 116.6, 131.9, 145.4 ppm.

4-Toluidine 2f: white solid (52 mg, 0.49 mmol, 73%) m.p.=41-43 ℃ (40-44 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:5)=0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.23 (s, 3H), 3.48 (s, 2H), 6.59 (d, J=8.4 Hz, 2H), 6.96 ppm (d, J=8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.4, 115.2, 127.6, 129.7, 143.8 ppm.

3-Toluidine 2g:[16] colorless oil (48 mg, 0.45 mmol, 81%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.37. ^{1}H NMR (400MHz, $CDCl_3$) δ=2.25 (s, 3H), 3.56 (s, 2H), 6.46-6.49 (m, 2H), 6.56-6.58 (m, 1H), 7.03 ppm (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.3, 112.1, 115.8, 119.3, 129.1, 139.0, 146.3 ppm.

2,4-Dimethyl-phenylamine 2h:[34] yellow oil (36 mg, 0.29 mmol, 82%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.82-6.87 (m, 2H), 6.57 (d, J=7.6 Hz, 1H), 3.43 (s, 2H), 2.22 (s, 3H), 2.13 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=144.1, 133.1, 129.8, 129.3, 124.3, 116.9, 20.8, 17.7 ppm.

5-Chloro-2-methyl-phenylamine 2i:[33] colorless oil (32 mg, 0.27 mmol, 76%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.94-6.96 (m, 1H), 6.65-6.68 (m, 2H), 3.73 (s, 2H), 2.12 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=149.2, 134.1, 133.3, 122.4, 120.2, 116.3, 17.2 ppm.

4-Amino-phenol 2j: white solid (67 mg, 0.61 mmol, 72%) m.p.=167-168 ℃ (166-168 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:3)=0.40. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.34 (s, 1H), 6.48-6.50 (m, 2H), 6.42-6.44 (m, 2H), 4.25 ppm (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ=148.8, 140.9, 116.0, 115.9 ppm.

2-Amino-phenol 2k: white solid (58 mg, 0.53 mmol, 73%) m.p.=186-188 ℃ (205 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:3)=0.38. ^{1}H NMR (600 MHz, DMSO-d6) δ: 8.89 (s, 1H), 6.61-6.62 (m, 1H), 6.55-6.57 (m, 1H), 6.50-6.53 (m, 1H), 6.36-6.38 (m, 1H), 4.43 ppm (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ=144.4, 136.9, 119.9, 116.9, 114.9, 114.8 ppm.

4-Amino-benzoic acid 2l: yellow solid (26 mg, 0.19 mmol, 67%) m.p.=184-186 ℃ (259-262 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:3)=0.37. ^{1}H NMR (600 MHz, DMSO-d_6) δ=11.91 (s, 1H), 7.58-7.61 (m, 2H), 6.51-6.53 (m, 2H), 5.82 ppm (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ=167.9, 153.5, 131.7, 117.3, 113.0 ppm.

3-Amino-benzoic acid 2m:[31] yellow solid (23 mg, 0.178 mmol, 63%) m.p.=169-171 ℃, R_f (Ethyl acetate/ Petroleum ether=1:3)=0.34. ^{1}H NMR (600 MHz, DMSO-d_6) δ=12.45 (s, 1H), 7.15 (t, J=1.8 Hz, 1H), 7.04-7.09 (m, 2H), 6.73-6.75 (m, 1H), 5.29 ppm (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ=168.3, 149.2, 131.7, 129.3, 118.4, 117.1, 114.9 ppm.

4-Methoxyaniline 2n:[11] white solid (85 mg, 0.669 mmol, 79%) m.p.=57-59 ℃, R_f (Ethyl acetate/ Petroleum ether=1:5)=0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.73 (s, 3H), 3.34 (s, 2H), 6.62-6.65 (m, 2H), 6.73-6.75 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=55.7, 114.7, 116.4, 139.9, 152.7 ppm.

4-Ethoxy-phenylamine 2o:[32] colorless oil (48 mg, 0.350 mmol, 82%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.71-6.75 (m, 2H), 6.59-6.63 (m, 2H), 3.94 (q, J=6.8 Hz, 2H), 3.37 (s, 2H), 1.36 ppm (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=143.3, 118.4, 117.7, 63.4, 11.9 ppm.

4-Nitroaniline 2p: yellow solid (27 mg, 0.176 mmol, 68%) m.p.=144-146 ℃ (147-148 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:4)=0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (s, 2H), 6.59-6.61 (m, 2H), 7.09-7.10 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=116.2, 123.0, 129.0, 144.9 ppm.

4-Phenylenediamine 2q: white solid (62 mg, 0.574 mmol, 83%) m.p.=133-135 ℃ (141 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:5)=0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.33 (s, 4H), 6.56 ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=116.6, 138.5 ppm.

4-Aminobenzaldehyde 2r: yellow solid (25 mg, 0.207 mmol, 67%) m.p.=71-73 ℃ (71-72 ℃),[30] R_f (Ethyl acetate/ Petroleum ether=1:3)=0.24. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.74 (s, 1H), 7.68 (d, J=8.6 Hz, 2H), 6.69 (d, J=8.5 Hz, 2H), 4.22 ppm (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ=190.4, 152.3, 132.3, 127.6, 114.0 ppm.

3-Vinylaniline 2s:[20] yellow liquid (29 mg, 0.244 mmol, 81%), R_f (Ethyl acetate/ Petroleum ether=1:5)=0.36. ^{1}H NMR (400 MHz, DMSO-d_6) δ=6.87-6.98 (m, 4H),

6.63-6.68 (m, 1H), 5.96 (d, *J*=7.3 Hz, 1H), 5.72 (d, *J*=11.2 Hz, 1H), 5.11 ppm (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*=146.1, 140.4, 137.2, 130.8, 116.7, 114.3, 112.7, 112.4 ppm.

4-Aminobenzamide 2t:[36] white solid (28 mg, 0.203 mmol, 67%) m.p.=178-179 ℃, R_f(Ethyl acetate/ Petroleum ether=1:1)=0.31. ^{1}H NMR (400 MHz, DMSO-d_6) *δ*=7.49 (d, *J*=5.2 Hz, 2H), 7.00 (s, 2H), 6.54 (d, *J*=5.6 Hz, 2H), 5.35 ppm (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*=168.8, 151.4, 129.4, 120.8, 110.8 ppm.

4,4'-Disulfanediyldianiline 2u:[37] yellow oil (32 mg, 0.129 mmol, 88%), R_f (Ethyl acetate/ Petroleum ether=2:1)=0.26. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*=7.22-7.28 (m, 4H), 6.54-6.62 (m, 4H), 3.77 ppm (s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ*=147.0, 133.9, 125.8, 115.3 ppm.

2-Phenylethen-1-amine 2v: brown liquid (45 mg, 0.378 mmol, 66%), R_f (Ethyl acetate/ Petroleum ether=1:7)=0.28. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*=7.88 (s, 2H), 7.30 (d, *J*=15.2 Hz, 1H), 7.20-7.23 (m, 5H), 5.03 ppm (d, *J*=15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*=143.2, 136.9, 129.5, 128.1, 126.2, 105.6 ppm.

2-(4-Bromophenyl)ethen-1-amine 2w: brown liquid (34 mg, 0.173 mmol, 61%), R_f (Ethyl acetate/ Petroleum ether=1:7)=0.31. ^{1}H NMR (400 MHz, CDCl3) *δ*=8.20 (s, 2H), 7.50 (d, *J*=7.6 Hz, 2H), 7.22 (d, *J*=15.2 Hz, 1H), 7.04 (t, *J*=8.4 Hz, 2H), 5.08 ppm (d, *J*=15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*=143.5, 132.6, 131.5, 128.7, 121.9, 105.8 ppm.

2-(p-Tolyl)ethen-1-amine 2x: yellow liquid (39 mg, 0.293 mmol, 68%), R_f (Ethyl acetate/ Petroleum ether=1:7)=0.33. ^{1}H NMR (400 MHz, CDCl3) *δ*=8.14 (s, 2H), 7.22

(d, *J*=15.2 Hz, 1H), 7.06-6.99 (m, 4H), 5.01 (d, *J*=15.2 Hz, 1H), 2.23 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*=143.5, 138.7, 132.1, 128.7, 124.8, 105.5, 21.6 ppm.

2-(4-Methoxyphenyl)ethen-1-amine 2y: yellow liquid (42 mg, 0.282 mmol, 71%), R_f(Ethyl acetate/ Petroleum ether=1:7)=0.36. ^{1}H NMR (400 MHz, CDCl3) *δ*=7.92 (s, 2H), 7.27-7.17 (m, 3H), 6.87-6.84 (m, 2H), 4.97 (d, *J*=15.2 Hz, 1H), 3.73 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*=160.7, 143.2, 129.9, 127.6, 115.3, 106.1, 55.2 ppm.

3-(2-Aminovinyl)aniline 2z: brown liquid (26 mg, 0.194 mmol, 54%), R_f (Ethyl acetate/ Petroleum ether=1:4)=0.38. ^{1}H NMR (400 MHz, CDCl3) *δ*=7.87 (s, 2H), 7.28 (d, *J*=15.2 Hz, 1H), 6.93-6.89 (m, 1H), 6.81 (d, *J*=7.2 Hz, 1H), 6.65 (d, *J*=7.6 Hz, 1H), 6.46 (s, 1H), 5.03 (d, *J*=15.2 Hz, 1H), 3.76 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*=146.3, 144.7, 133.4, 128.8, 118.5, 115.6, 114.2, 105.8 ppm.

4-(3-Amino-phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4a: yellow solid (104 mg, 0.378 mmol, 78%) m.p.=203-205 ℃, R_f (Ethyl acetate/ Petroleum ether=1:1)=0.37. ^{1}H NMR (400 MHz, DMSO-d_6) *δ*=9.01 (s, 1H), 7.53 (s, 1H), 6.82 (t, *J*=8.0 Hz, 1H), 6.28-6.40 (m, 3H), 4.95 (s, 2H), 4.89 (s, 1H), 3.88 (q, *J*=7.3 Hz, 2H), 2.12 (s, 3H), 1.01 ppm (t, *J*=6.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*=165.5, 152.2, 148.6, 147.7, 145.4, 128.7, 113.9, 112.9, 111.7, 99.5, 59.1, 54.1, 17.8, 14.1 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_3$ 276.1343; Found 276.1339.

4-(3-Amino-phenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4b: yellow solid (112 mg, 0.385 mmol, 76%) m.p.=216-218 ℃, R_f (Ethyl acetate/ Petroleum ether=1:1)=0.34. ^{1}H NMR (400 MHz, DMSO-d_6) *δ*=10.23

(s, 1H), 9.55 (s, 1H), 6.95 (t, *J*=8.0 Hz, 1H), 6.36-6.45 (m, 3H), 5.10 (s, 2H), 5.02 (s, 1H), 4.01 (q, *J*=7.2 Hz, 2H), 2.28 (s, 3H), 1.12 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=174.4, 165.7, 149.1, 144.9, 144.5, 129.4, 114.4, 113.7, 112.2, 101.3, 59.9, 54.7, 17.6, 14.5 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_2S$ 292.1114; Found 292.1118.

4-(4-Amino-phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4c: yellow solid (85 mg, 0.309 mmol, 84%) m.p.=207-209 ℃, R_f (Ethyl acetate/ Petroleum ether=1:1)=0.40. ^{1}H NMR (400 MHz, DMSO-d_6) δ=9.07 (s, 1H), 7.55 (s, 1H), 6.88 (d, *J*=8.0 Hz, 2H), 6.47 (d, *J*=8.0 Hz, 2H), 5.01 (s, 2H), 4.97 (s, 1H), 3.97 (q, *J*=6.8 Hz, 2H), 2.22 (s, 3H), 1.10 ppm (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=170.7, 157.4, 153.0, 152.5, 137.5, 132.1, 118.7, 105.2, 64.2, 58.7, 22.9, 19.3 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_3$ 276.1343; Found 276.1340.

4-(4-Amino-phenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4d: yellow solid (128 mg, 0.440 mmol, 83%) m.p.=221-223 ℃, R_f (Ethyl acetate/ Petroleum ether=1:1)=0.37. ^{1}H NMR (400 MHz, DMSO-d_6) δ=10.19 (s, 1H), 9.49 (s, 1H), 6.83 (d, *J*=8.0 Hz, 2H), 6.47 (d, *J*=8.0 Hz, 2H), 5.08 (s, 2H), 4.95 (s, 1H), 3.98 (q, *J*=7.2 Hz, 2H), 2.25 (s, 3H), 1.09 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=174.1, 165.7, 148.6, 144.5, 131.4, 127.7, 114.0, 101.8, 79.6, 59.9, 54.2, 17.5, 14.5 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_2S$ 292.1114; Found 292.1110.

4-(3-Amino-phenyl)-3-(2-cyano-ethyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4e: yellow oil (45 mg, 0.137 mmol, 84%), R_f (Ethyl acetate/ Petroleum ether=1:2): 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.08 (s, 1H), 7.07 (t, *J*=5.2 Hz, 1H), 6.70 (d, *J*=1.2 Hz, 1H), 6.57-6.60 (m, 2H), 5.25 (s, 1H), 4.19-4.25 (m, 2H), 3.93 (s, 2H), 3.81-3.85 (m, 1H), 3.47-3.52 (m, 1H), 2.83-2.88 (m, 1H), 2.66 (s, 3H), 2.42-2.47 (m, 1H), 1.18 ppm (t, *J*=4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=164.9, 151.7, 148.1, 147.2, 144.9, 128.2, 115.7, 113.4, 112.3, 111.1, 99.5, 59.2, 54.2, 41.5, 19.7, 17.7, 14.1 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}N_4O_3$ 329.1608; Found 329.1605.

4-(3-Amino-phenyl)-1,3-bis-(2-cyano-ethyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4f: yellow oil (62 mg 0.128 mmol, 92%), R_f (Ethyl acetate/ Petroleum ether=1:2)=0.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ=7.06 (t, *J*=7.8 Hz, 1H), 6.70 (t, *J*=1.8 Hz, 1H), 6.57-6.60 (m, 2H), 5.26 (s, 1H), 4.19-4.23 (m, 1H), 4.08-4.14 (m, 2H), 3.90-3.95 (m, 1H), 3.81 (s, 2H), 3.70-3.74 (m, 1H), 3.35-3.40 (m, 1H), 2.89-2.94 (m, 1H), 2.66-2.71 (m, 1H), 2.60-2.64 (m, 1H), 2.54 (s, 3H), 2.30-2.35 (m, 1H), 1.21 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ=164.4, 151.1, 147.5, 146.6, 144.4, 127.6, 115.3, 115.1, 112.8, 111.8, 110.6, 99.0, 59.4, 54.5, 42.6, 42.3, 19.9, 18.3, 18.0, 14.3 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_5O_3$ 382.1874; Found 382.1870.

4-(3-Amino-phenyl)-3-(2-methoxycarbonyl-ethyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4g: yellow oil (34 mg, 0.098 mmol, 86%), R_f (Ethyl acetate/ Petroleum ether=1:2)=0.37. ^{1}H NMR (400 MHz, $CDCl_3$)

δ=9.17 (s, 1H), 8.24 (s, 1H), 8.14 (d, *J*=8.0 Hz, 1H), 7.74 (d, *J*=7.6 Hz, 1H), 7.50 (t, *J*=8.0 Hz, 1H), 5.61 (s, 1H), 5.16 (d, *J*=10.8 Hz, 1H), 4.48 (d, *J*=10.4 Hz, 1H), 4.07-4.16 (m, 2H), 3.87 (s, 2H), 3.51-3.59 (m, 1H), 3.47 (s, 3H), 3.35-3.43 (m, 1H), 2.38 (s, 3H), 1.08 ppm (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.1, 164.8, 153.2, 147.5, 145.6, 141.1, 138.7, 127.8, 116.2, 115.7, 102.1, 62.9, 59.2, 51.6, 42.3, 32.4, 17.5, 13.9 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_3O_5$ 362.1710; Found 362.1713.

4-(3-Amino-phenyl)-1,3-bis-(2-methoxycarbonyl-ethyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4h: yellow oil (52 mg, 0.101 mmol, 88%), R_f (Ethyl acetate/ Petroleum ether=1:2)=0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.41 (s, 1H), 8.31 (d, *J*=8.0 Hz, 1H), 7.91 (d, *J*=7.6 Hz, 1H), 7.67 (t, *J*=7.6 Hz, 1H), 5.78 (s, 1H), 5.32 (d, *J*=10.4 Hz, 1H), 4.90-4.98 (m, 1H), 4.80-4.87 (m, 1H), 4.71 (d, *J*=10.8 Hz, 1H), 4.64 (d, *J*=10.8 Hz, 1H), 4.22-4.34 (m, 2H), 4.03 (s, 2H), 3.82 (d, *J*=10.4 Hz, 1H), 3.68-3.75 (m, 1H), 3.63 (d, *J*=1.6 Hz, 6H), 3.52-3.59 (m, 1H), 2.55 (s, 3H), 1.25 ppm (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=172.4, 172.1, 164.8, 153.3, 147.5, 145.4, 141.2, 138.8, 127.8, 116.3, 115.7, 102.1, 62.9, 59.2, 51.4, 51.2, 42.3, 42.0, 41.9, 32.6, 32.4, 17.5, 13.9 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{29}N_3O_7$ 448.2078; Found 448.2076.

4-(3-Amino-phenyl)-3-ethoxymethyl-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4i: yellow oil (32 mg, 0.096 mmol, 88%), R_f (Ethyl acetate/ Petroleum ether=1:2)=0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.77 (s, 1H), 7.03 (t, *J*=6.0 Hz, 1H), 6.95 (d, *J*=6.0 Hz, 1H), 6.89-6.91 (m, 1H), 6.84 (s, 1H), 5.72 (s,

1H), 5.25 (d, *J*=10.0 Hz, 1H), 4.67 (d, *J*=9.6 Hz, 1H), 4.02 (s, 1H), 3.58-3.65 (m, 1H), 3.42-3.49 (m, 1H), 2.20 (s, 3H), 0.98-1.04 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=176.3, 165.2, 142.2, 140.3, 133.8, 126.7, 124.1, 121.7, 120.5, 103.9, 79.2, 64.6, 60.4, 57.1, 18.2, 14.9, 14.3 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}N_3O_4$ 334.1761; Found 334.1761.

3-Acetoxymethyl-4-(3-amino-phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4j: yellow oil (48 mg, 0.146 mmol, 93%), R_f(Ethyl acetate/ Petroleum ether=1:2)=0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.87 (s, 1H), 7.11 (t, *J*=6.0 Hz, 1H), 7.04 (d, *J*=5.6 Hz, 1H), 6.97-6.99 (m, 1H), 6.90 (s, 1H), 5.69 (s, 1H), 5.64 (d, *J*=10.0 Hz, 1H), 5.17 (d, *J*=9.6 Hz, 1H), 4.15-4.27 (m, 2H), 3.98 (s, 2H), 2.42 (s, 3H), 1.92 (s, 3H), 1.22 ppm (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=170.5, 165.2, 153.3, 146.4, 137.9, 129.7, 127.6, 125.6, 123.0, 120.8, 106.1, 101.0, 69.5, 60.7, 20.7, 18.5, 14.2 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}N_3O_5$ 348.1554; Found 348.1550.

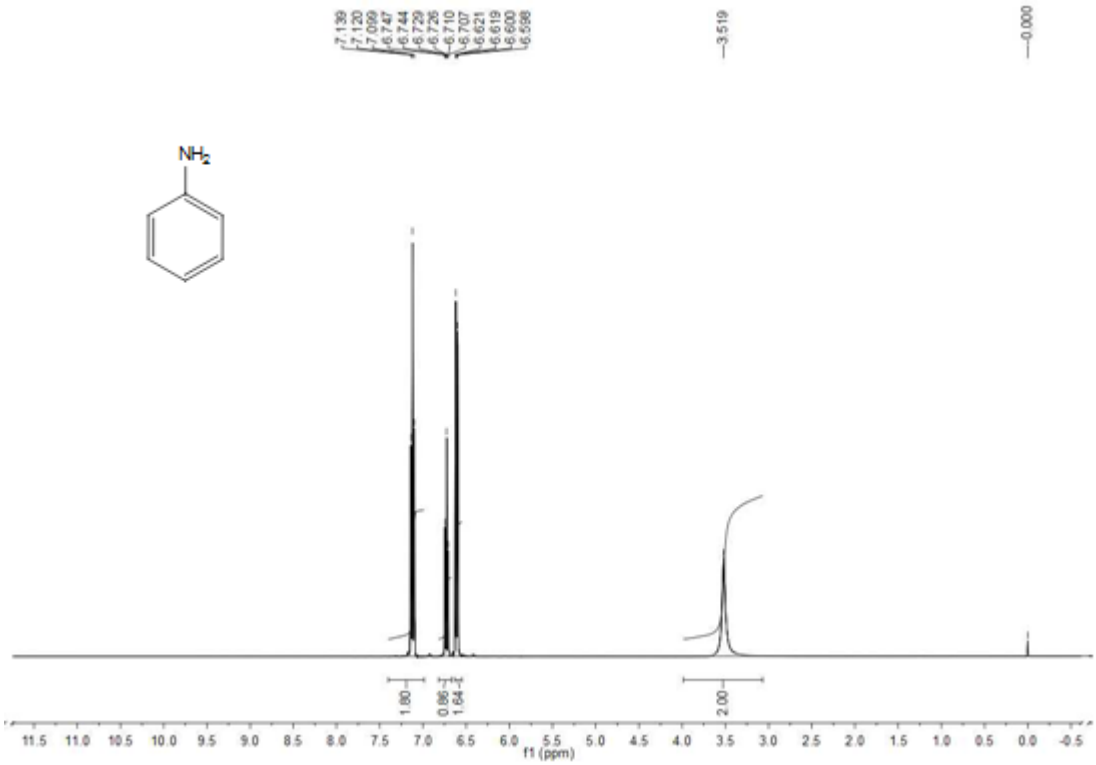
4-(3-Amino-phenyl)-6-methyl-2-morpholin-4-yl-pyrimidine-5-carboxylic acid ethyl ester 4k: yellow oil (46 mg, 0.136 mmol, 92%), R_f(Ethyl acetate/ Petroleum ether=1:3)=0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.09 (t, *J*=6.0 Hz, 1H), 7.02-7.04 (m, 1H), 6.97-6.99 (m, 1H), 6.93 (t, *J*=1.6 Hz, 1H), 4.02 (q, *J*=6.4 Hz, 2H), 3.95 (s, 2H), 3.90 (t, *J*=3.6 Hz, 4H), 3.74 (t, *J*=4.0 Hz, 4H), 2.49 (s, 3H), 1.14 ppm (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=168.3, 167.0, 165.5, 160.3, 142.4, 138.0, 127.9, 123.5, 121.8, 120.7, 114.4, 66.9, 60.8, 44.1, 23.0, 13.6 ppm; HRMS (ESI$^+$) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}N_4O_3$ 343.1765; Found 343.1766.

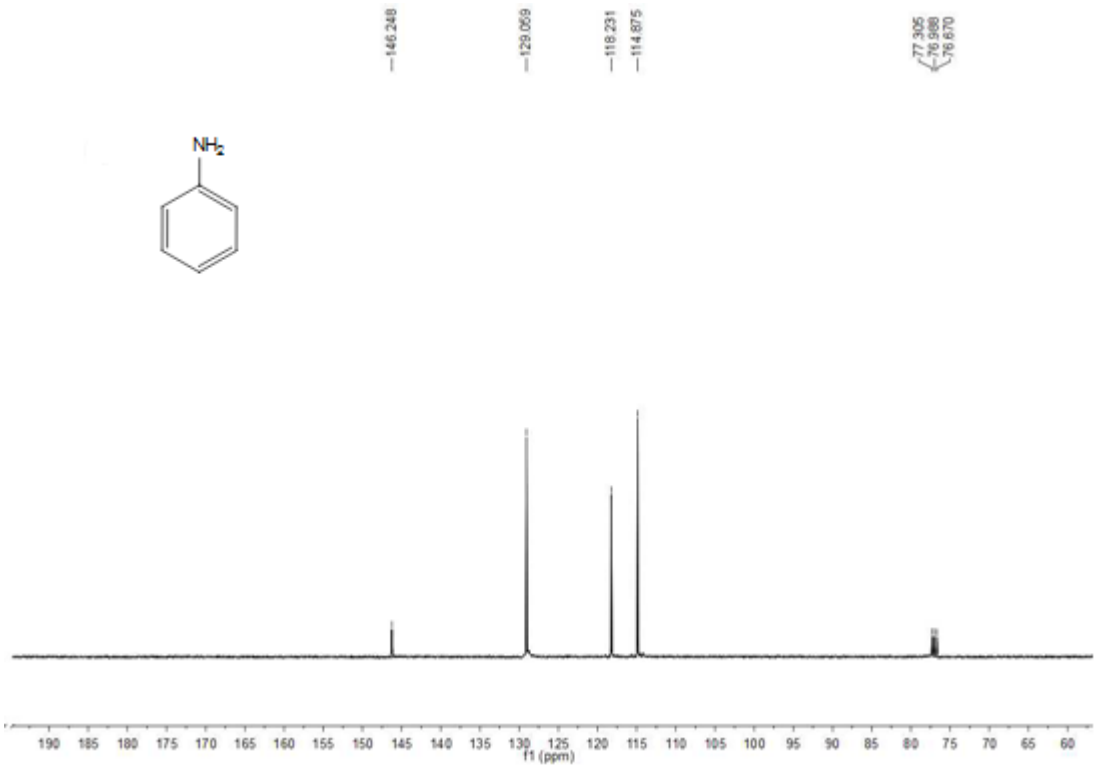
4-(4-Amino-phenyl)-6-methyl-3-morpholin-4-ylmethyl-2-oxo-1,2,3,4-tetrahydro-pyimidine-5-carboxylic acid ethyl ester 4l: yellow oil (78 mg, 0.219 mmol, 82%), R_f(Ethyl acetate/ Petroleum ether=1:2)=0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.83 (s, 1H), 7.02-7.08 (m, 4H), 5.58 (s, 1H), 4.50 (d, *J*=10.0 Hz, 1H), 4.09-4.19 (m, 2H), 3.98 (s, 2H), 3.63-3.67 (m, 4H), 3.39 (d, *J*=10.0 Hz, 1H), 2.55-2.61 (m, 2H), 2.40-2.46 (m, 2H), 2.37 (s, 3H), 1.27 ppm (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=165.2, 153.6, 146.1, 140.3, 133.8, 128.6, 128.3, 101.6, 66.9, 65.3, 60.1, 58.1, 50.9, 18.5, 14.3 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}N_4O_4$ 375.2027; Found 375.2021.

4-(4-Amino-phenyl)-3-azidomethyl-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester 4m: yellow oil (58 mg, 0.176 mmol, 86%), R_f(Ethyl acetate/ Petroleum ether=1:2)=0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.31 (s, 1H), 7.26-7.33 (m, 4H), 5.42 (s, 1H), 5.07 (d, *J*=10.0 Hz, 1H), 4.28 (d, *J*=10.0 Hz, 1H), 4.03-4.08 (m, 2H), 3.83 (s, 2H), 2.33 (s, 3H), 1.21 ppm (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=164.9, 152.9, 146.1, 140.3, 134.7, 129.2, 128.3, 102.3, 61.0, 60.4, 59.8, 18.5, 14.3 ppm; HRMS (ESI^+) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N_6O_3$ 331.1513; Found 331.1508.

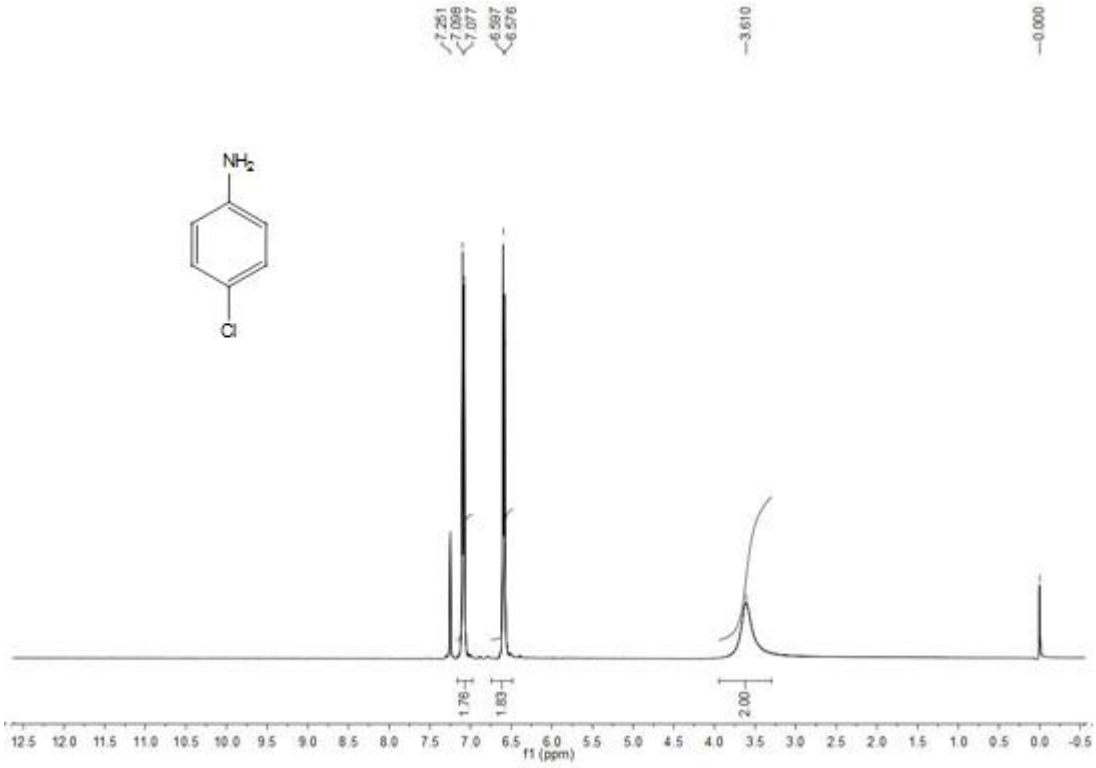
Copies of the NMR Spectra

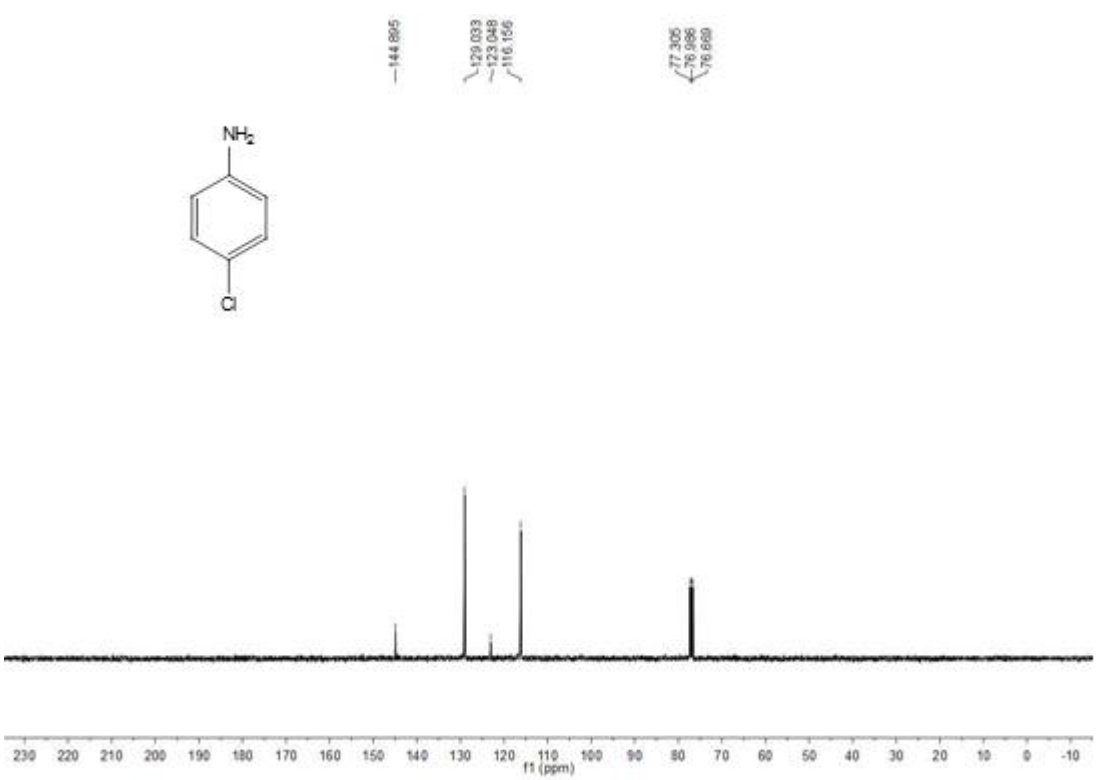
Aniline (2a)



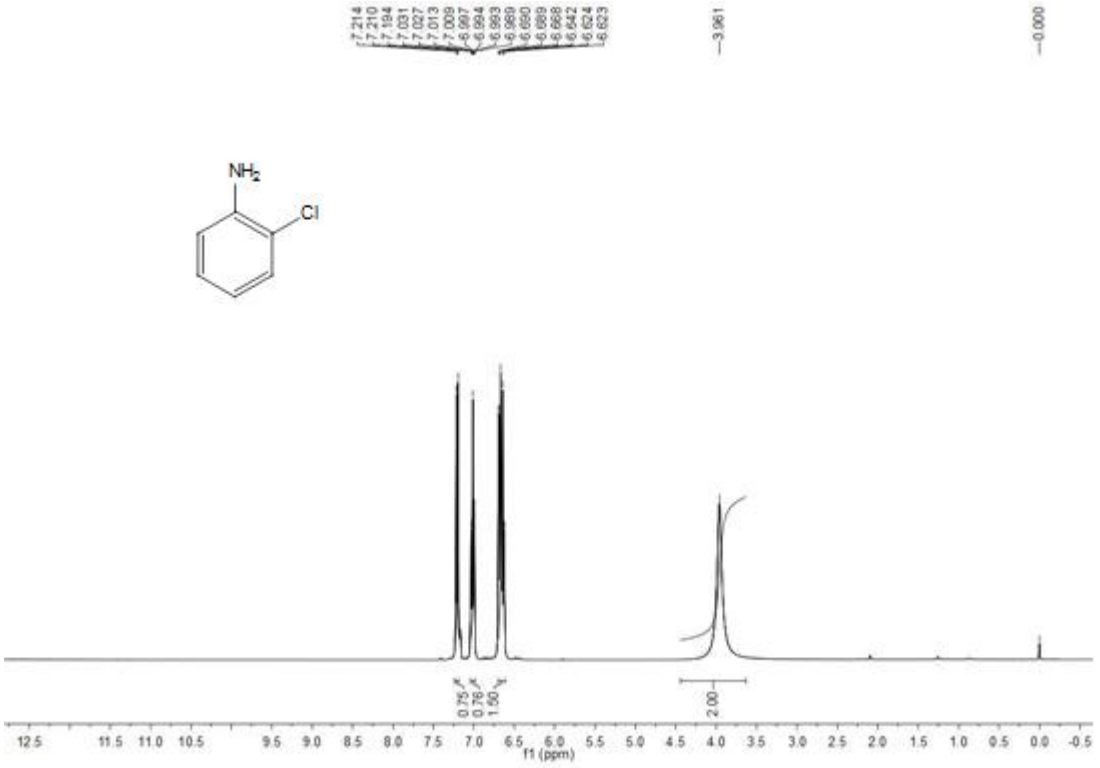


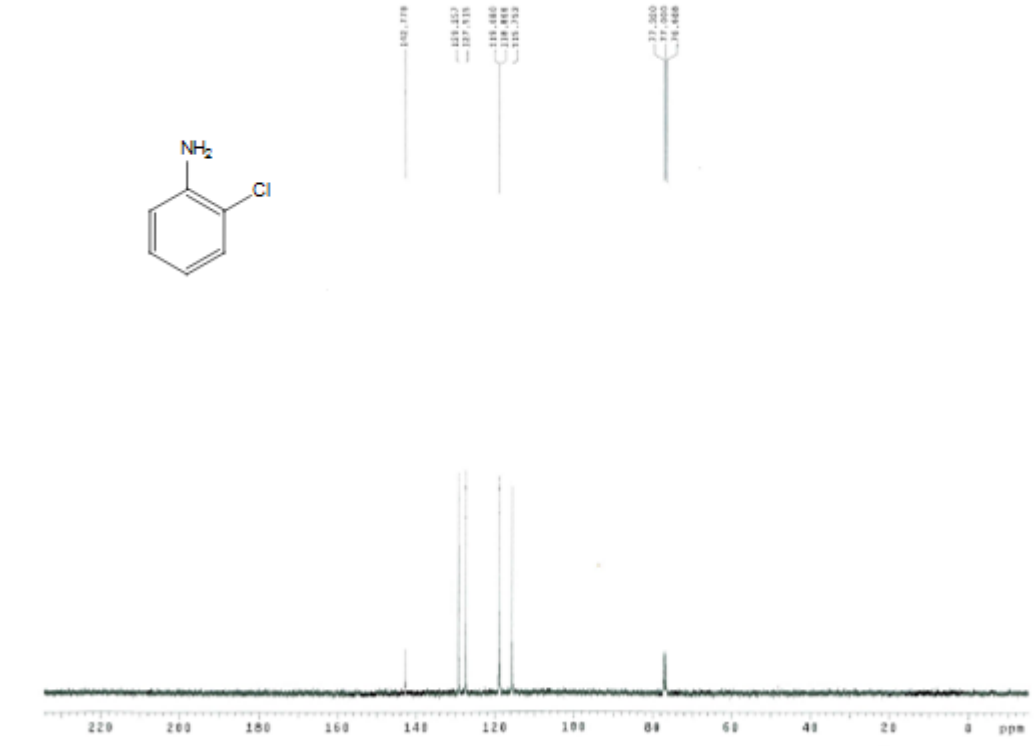
4-Chloroaniline (2b)



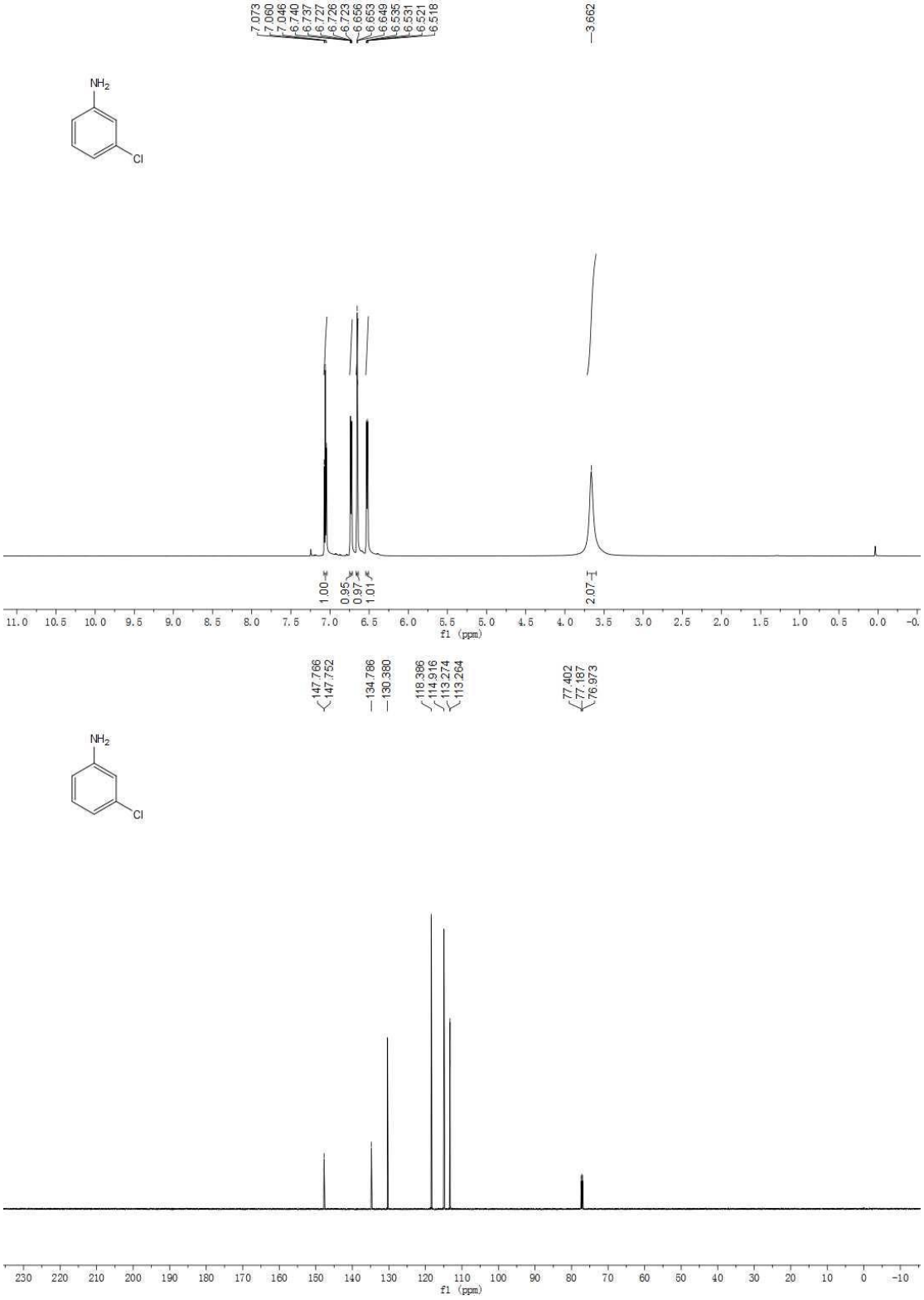


2-Chloroaniline (2c)

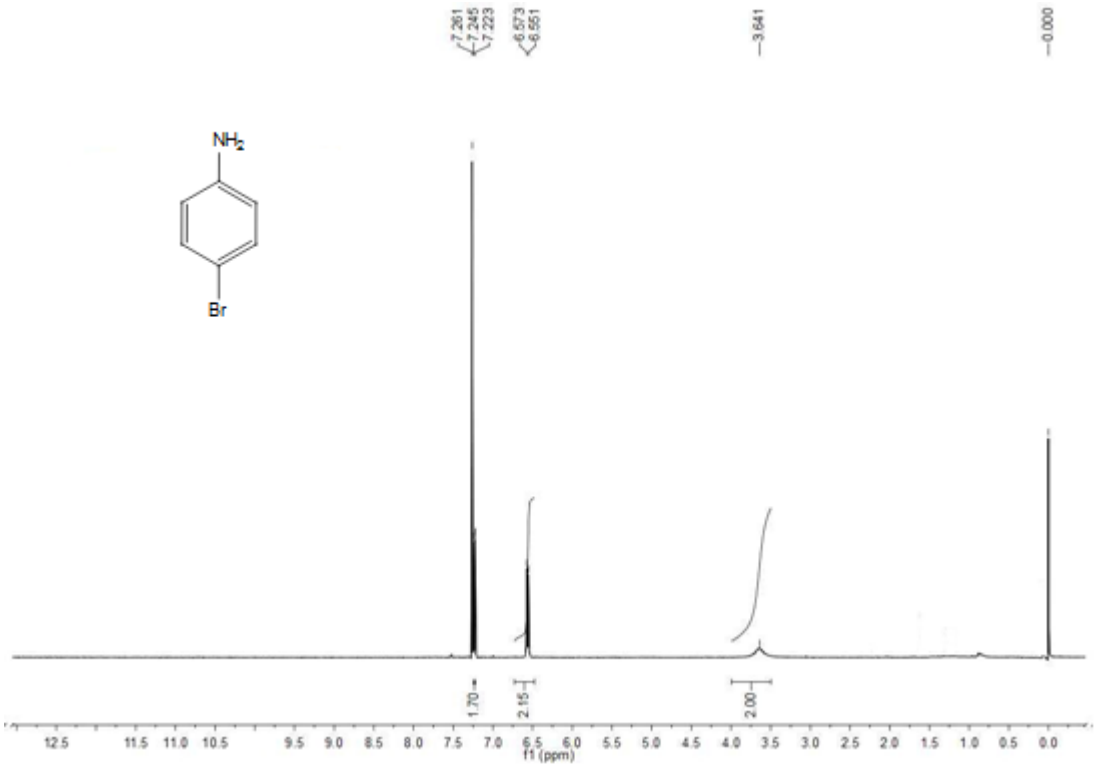


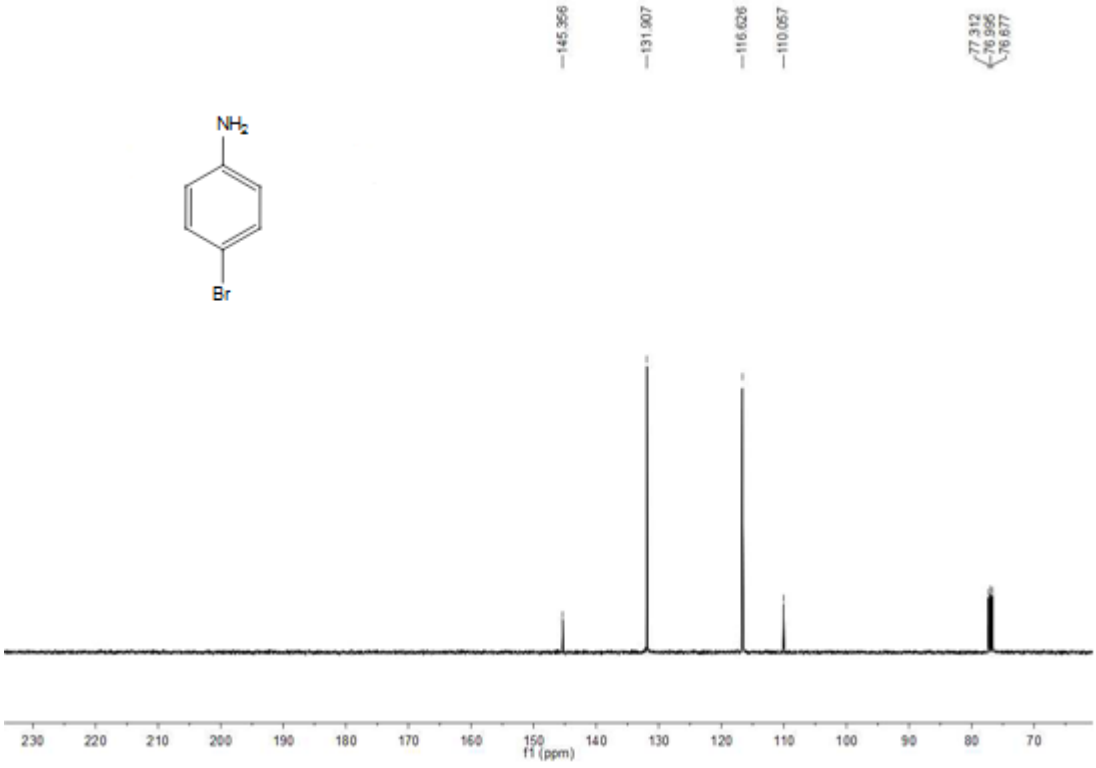


3-Chloro-phenylamine (2d)

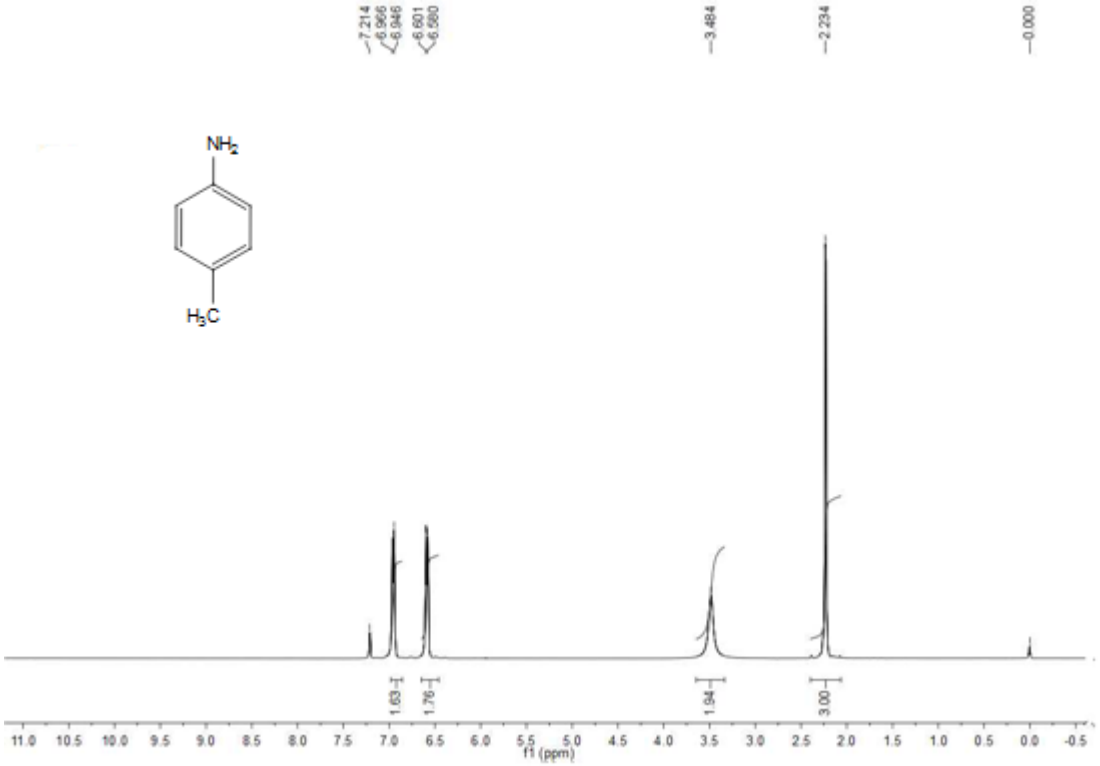


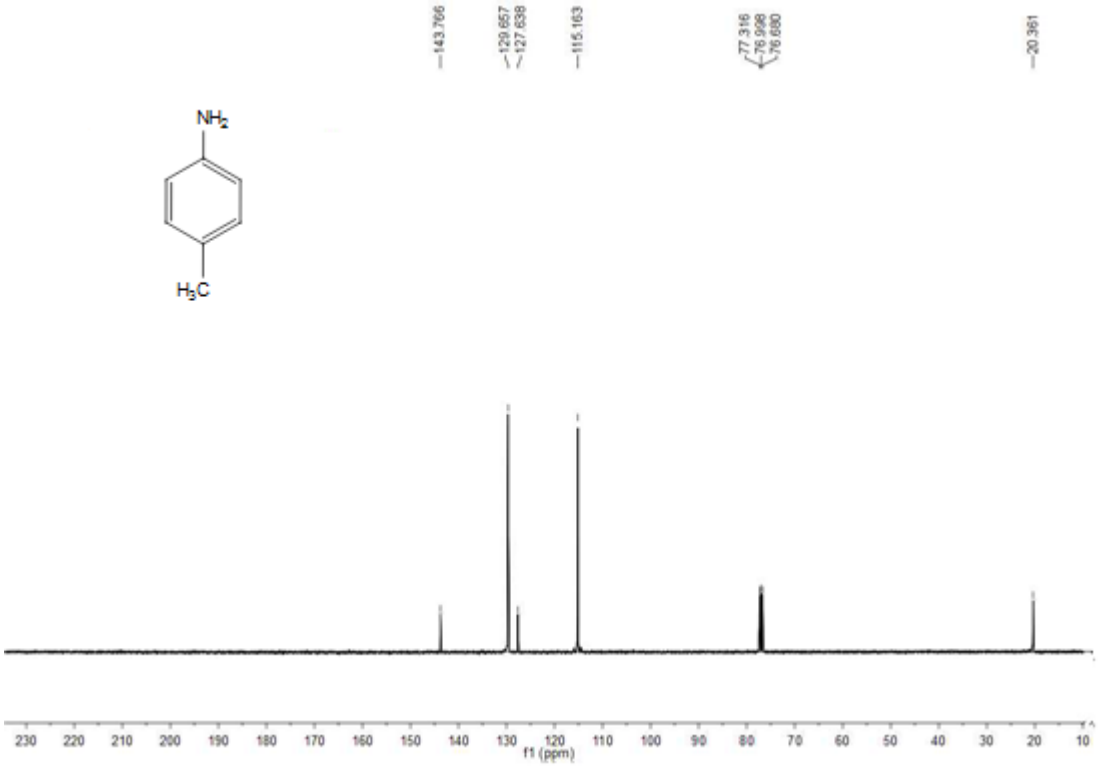
4-Bromoaniline (2e)



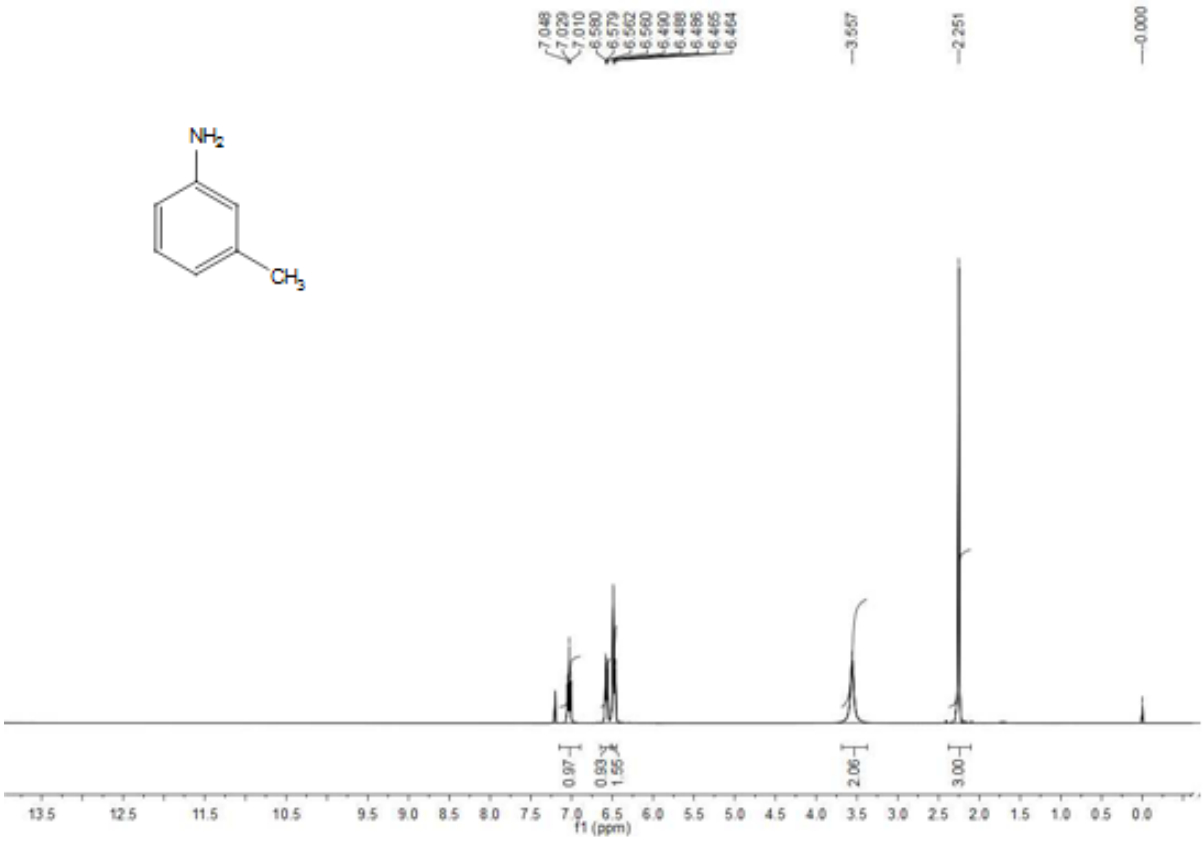


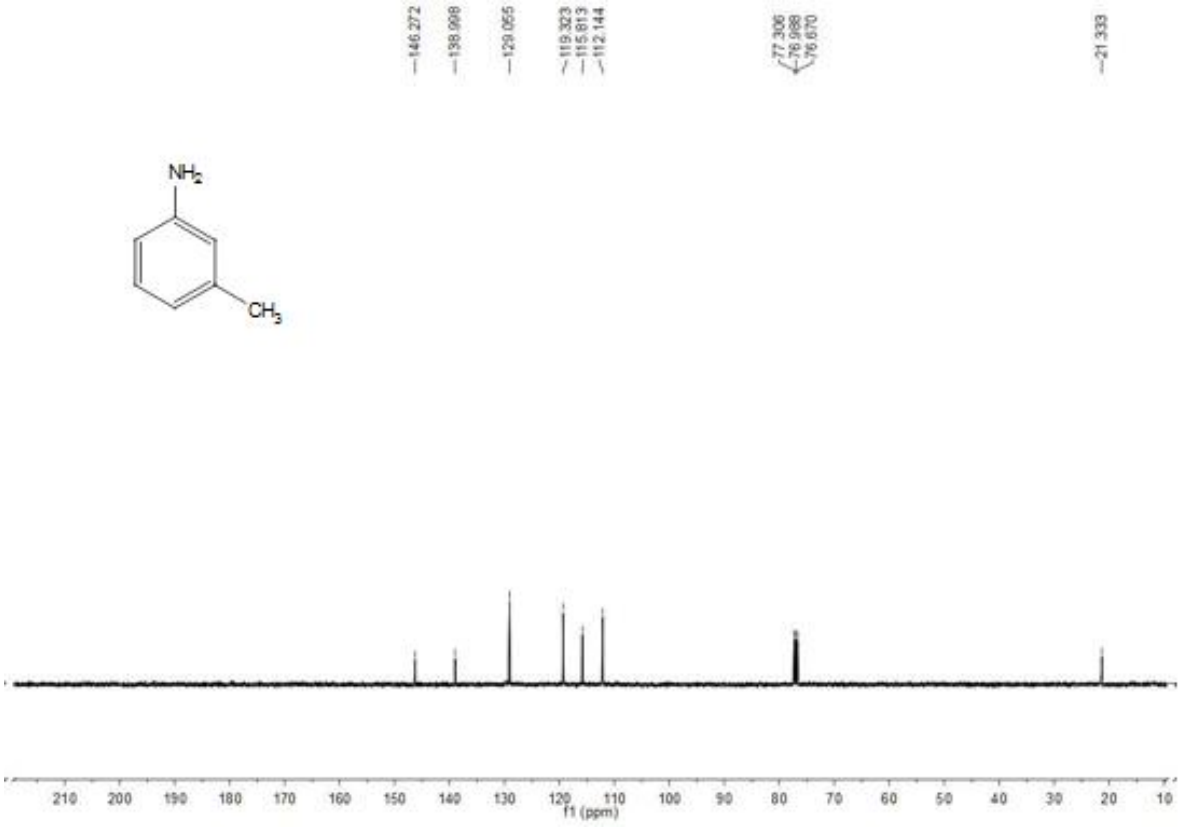
4-Toluidine (2f)



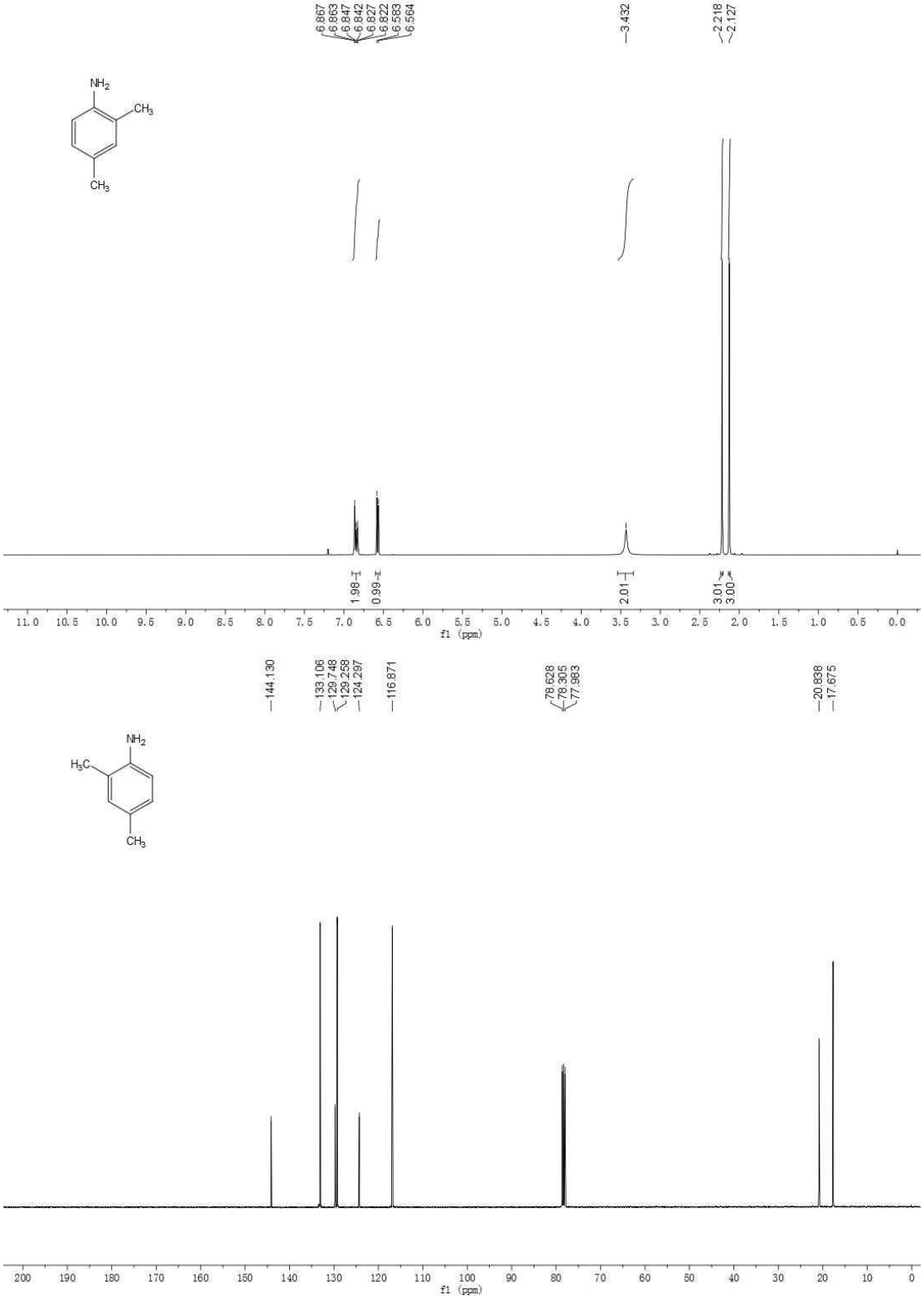


3-Toluidine (2g)

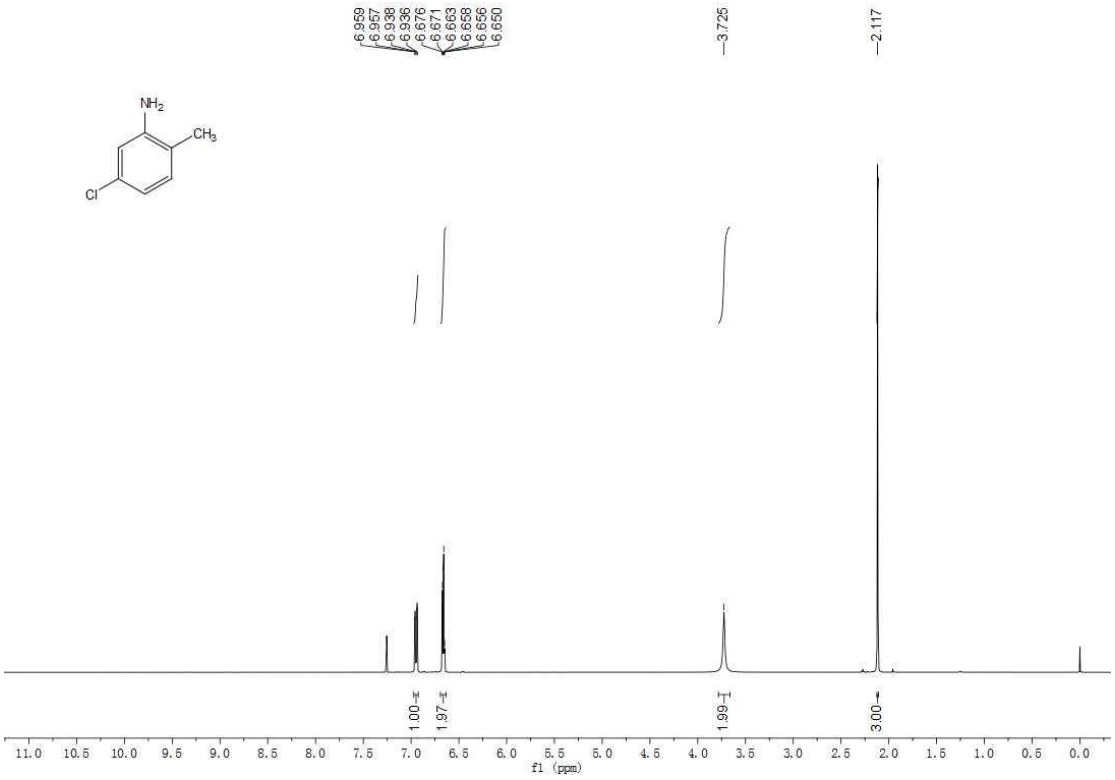


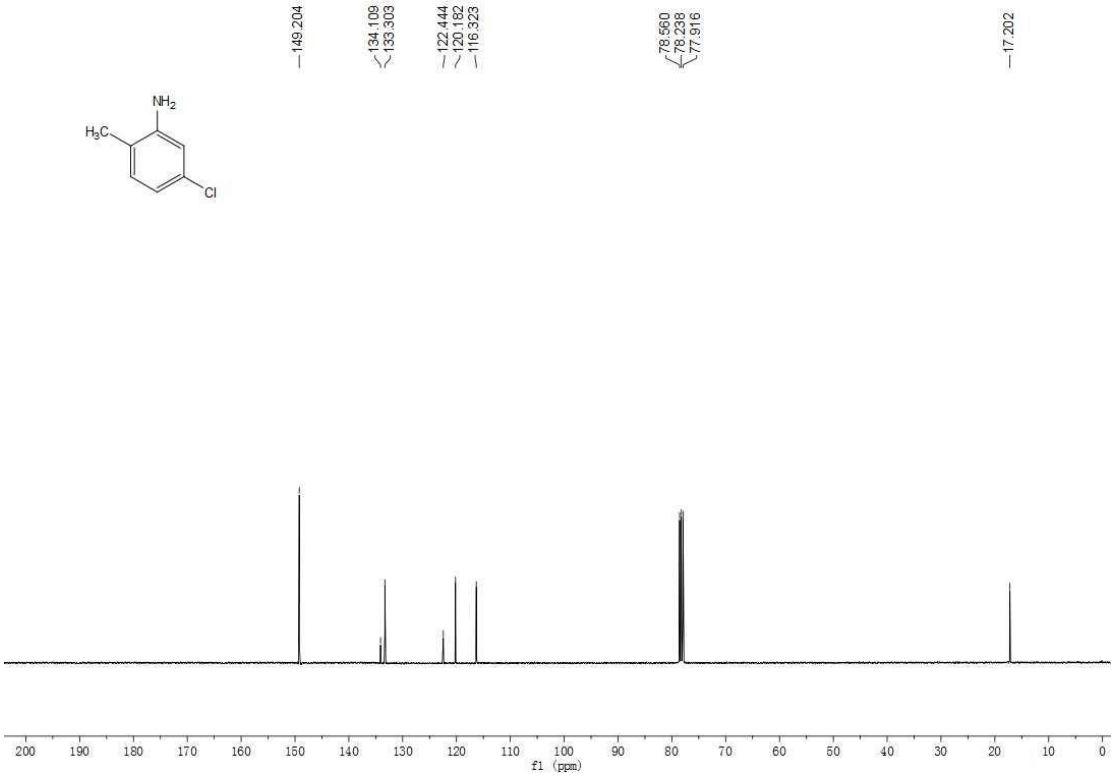


2,4-Dimethyl-phenylamine (2h)

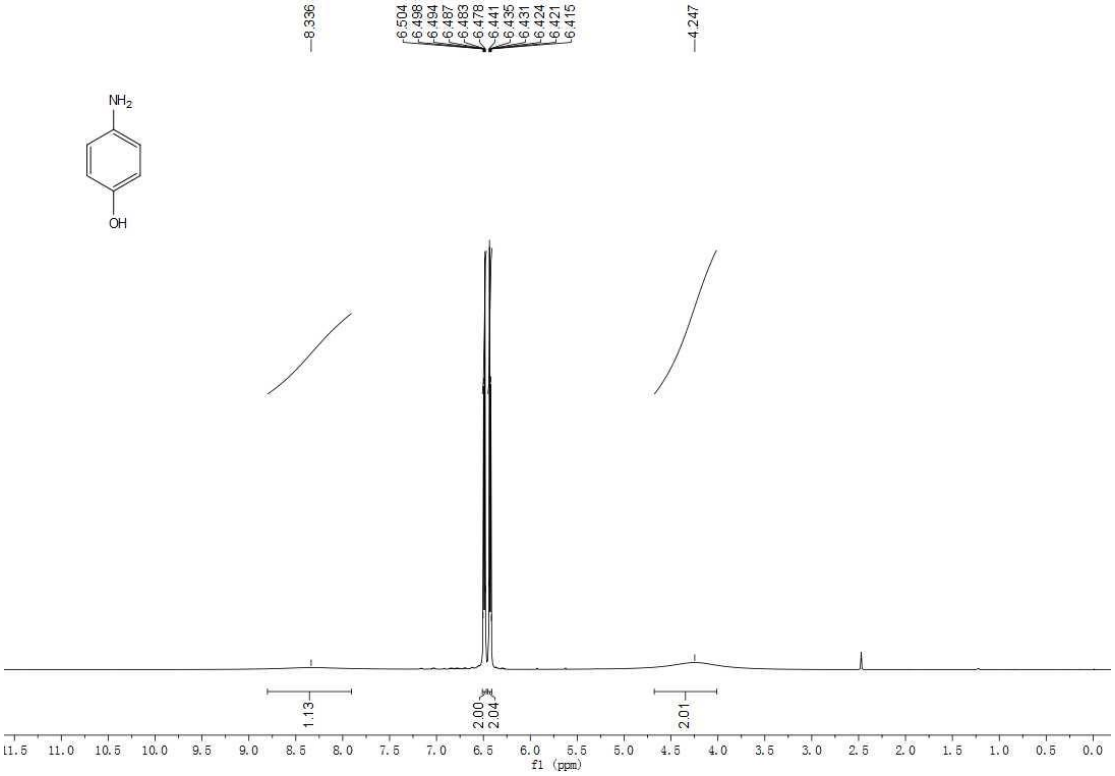


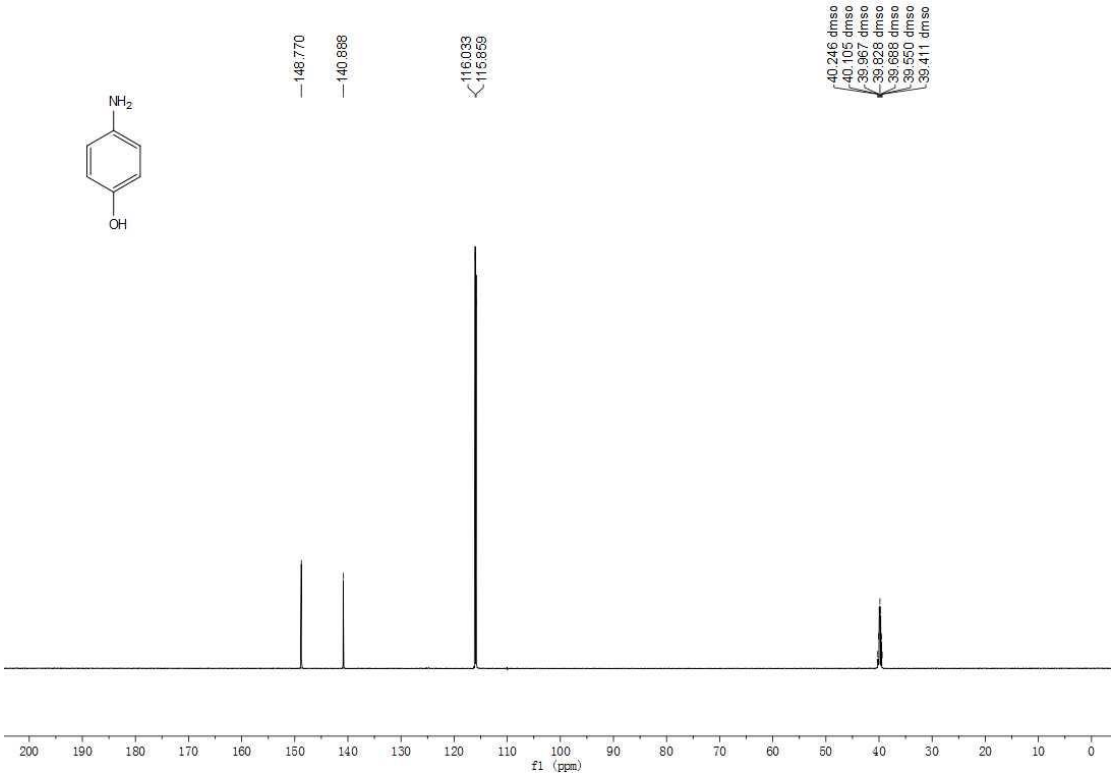
5-Chloro-2-methyl-phenylamine (2i)



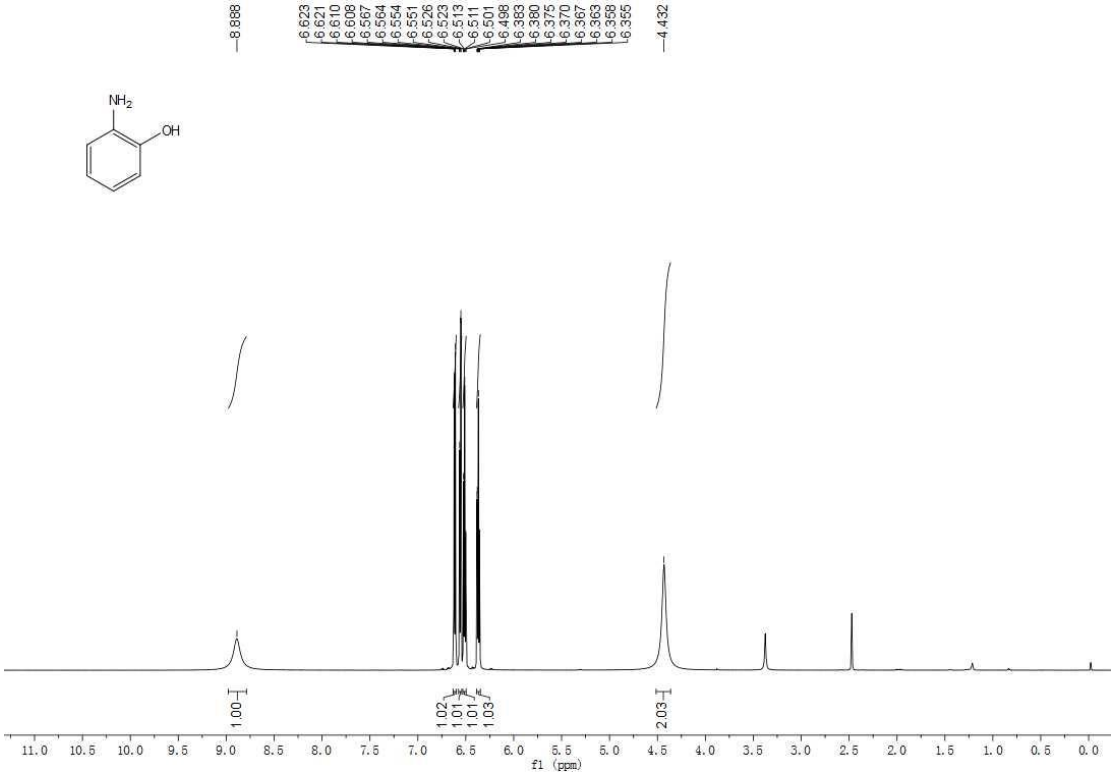


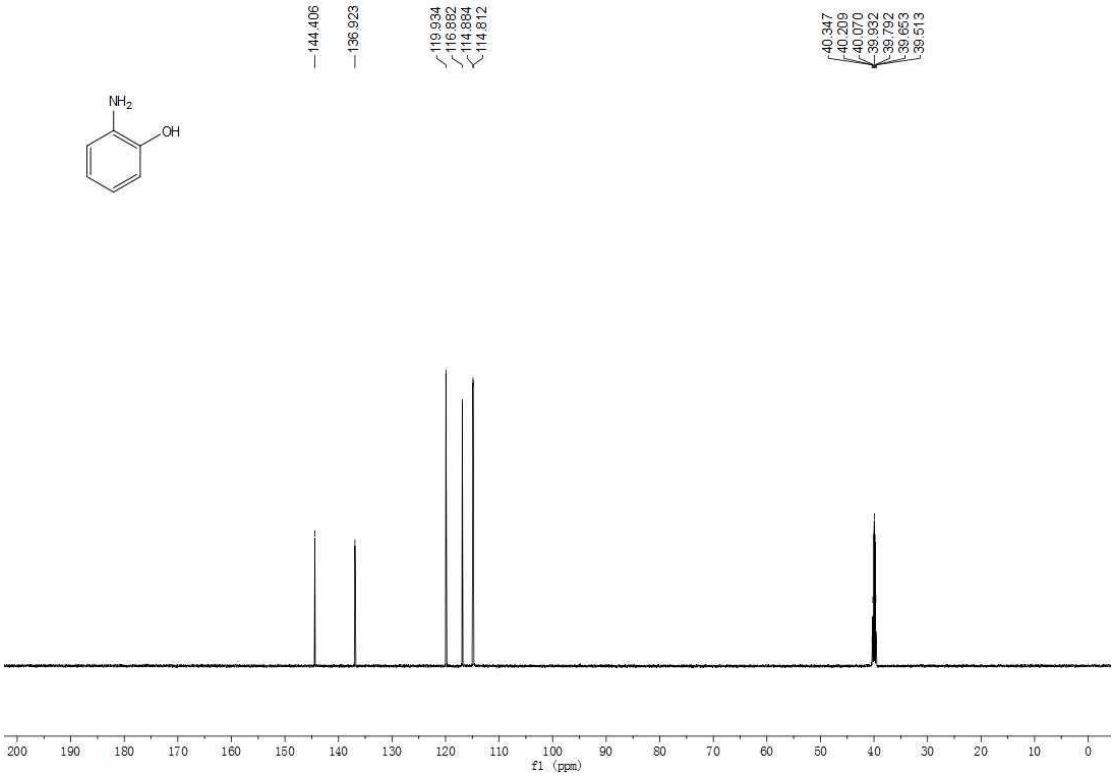
4-Amino-phenol (2j)



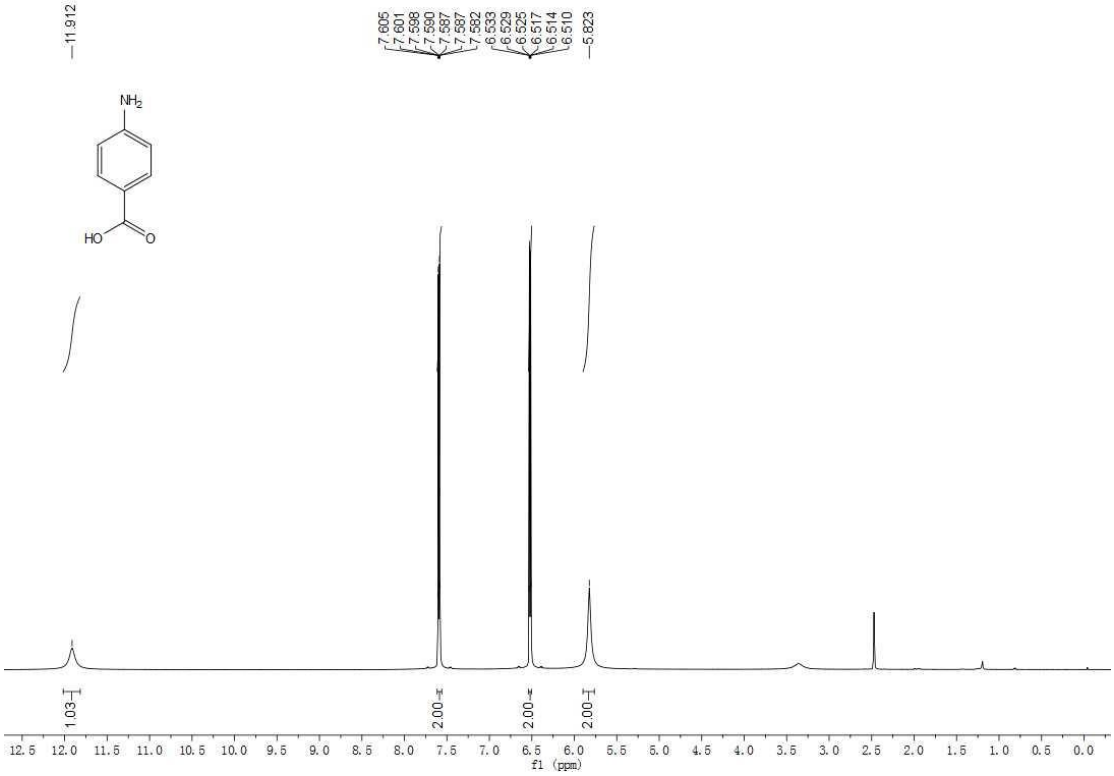


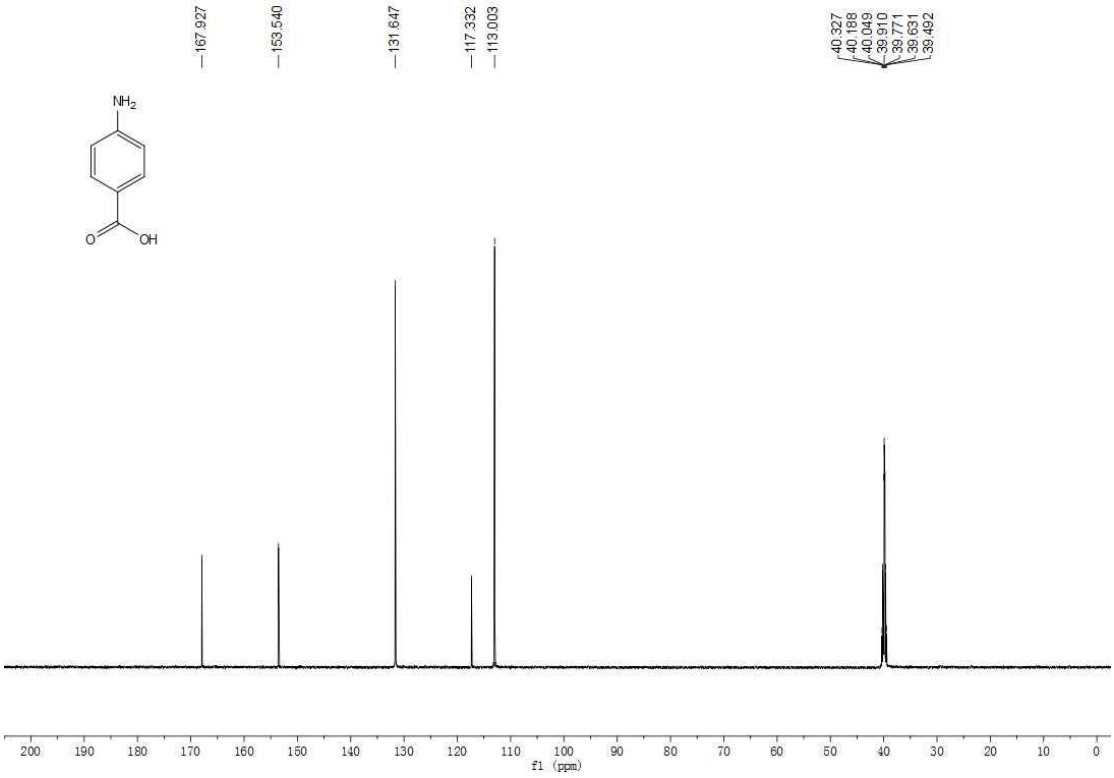
2-Amino-phenol (2k)



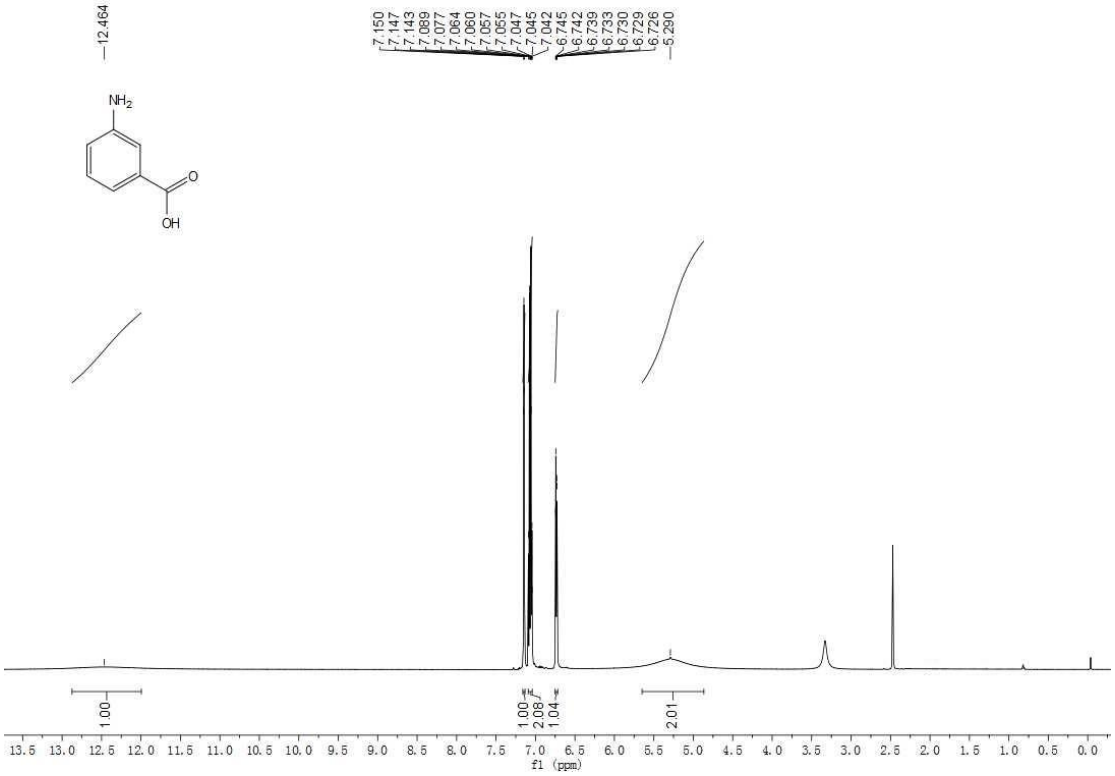


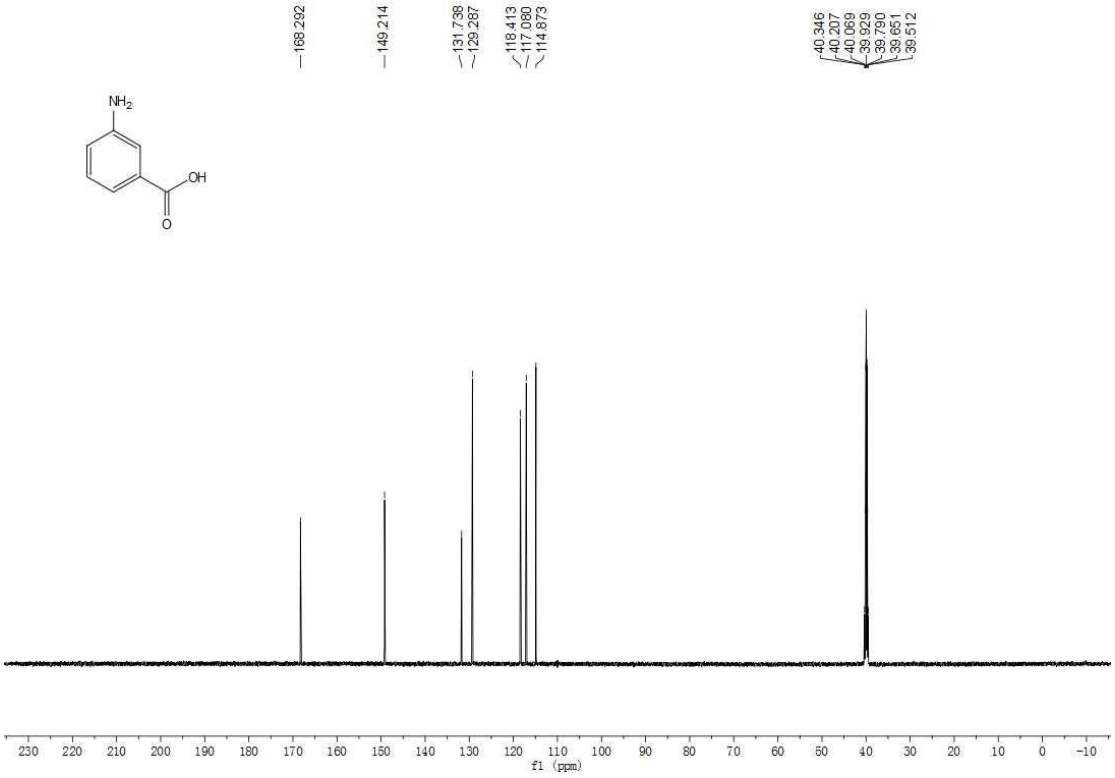
4-Amino-benzoic acid (2l)



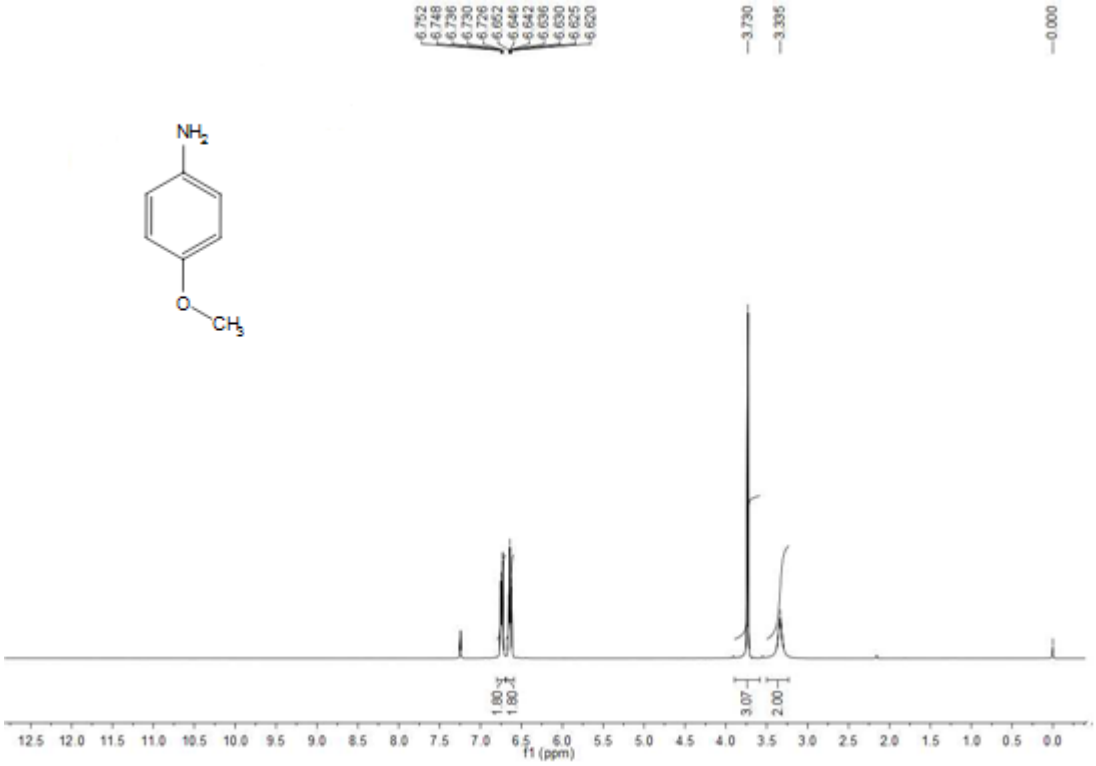


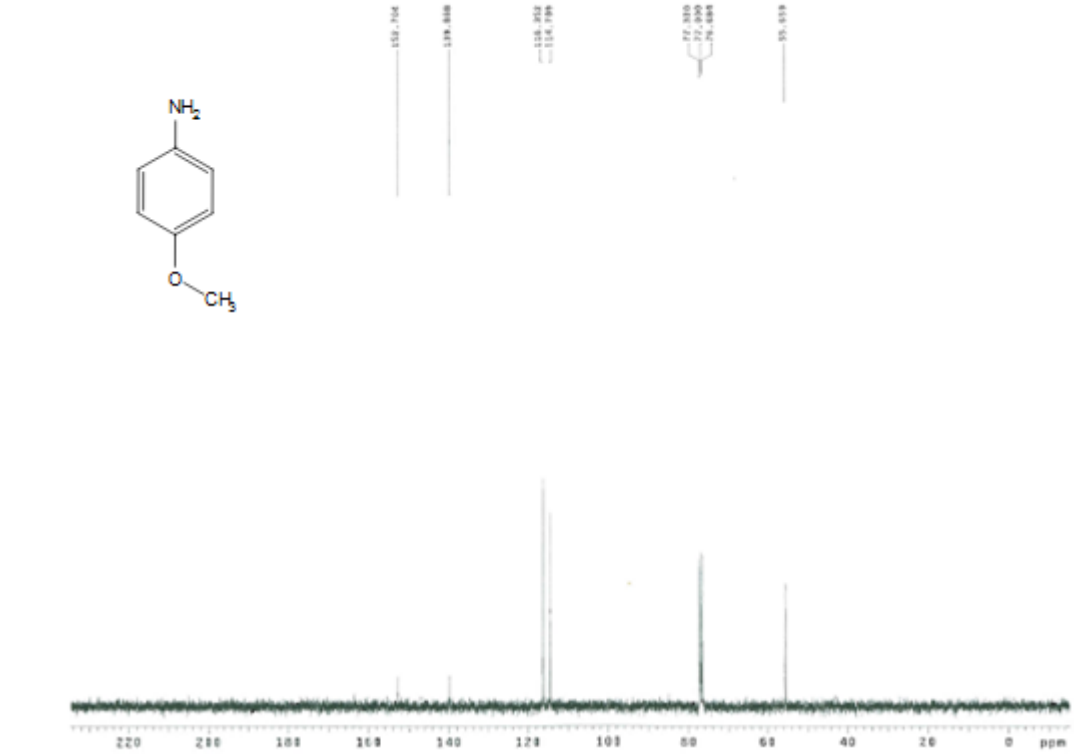
3-Amino-benzoic acid (2m)



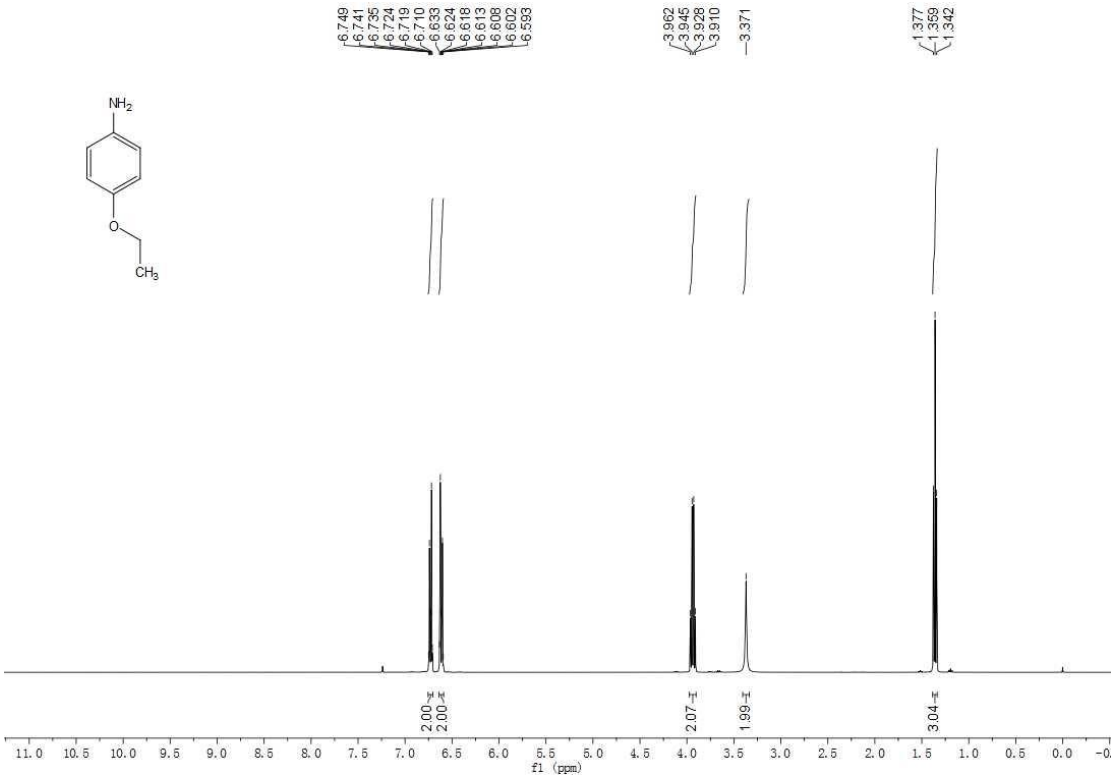


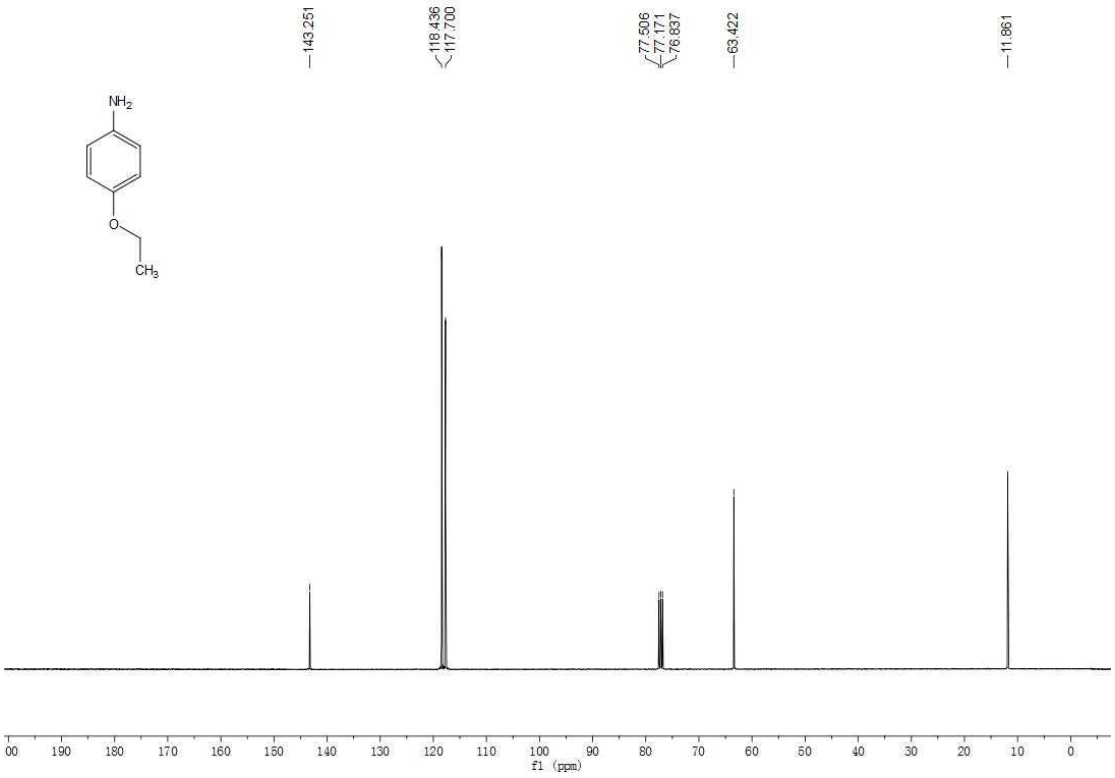
4-Methoxyaniline (2n)



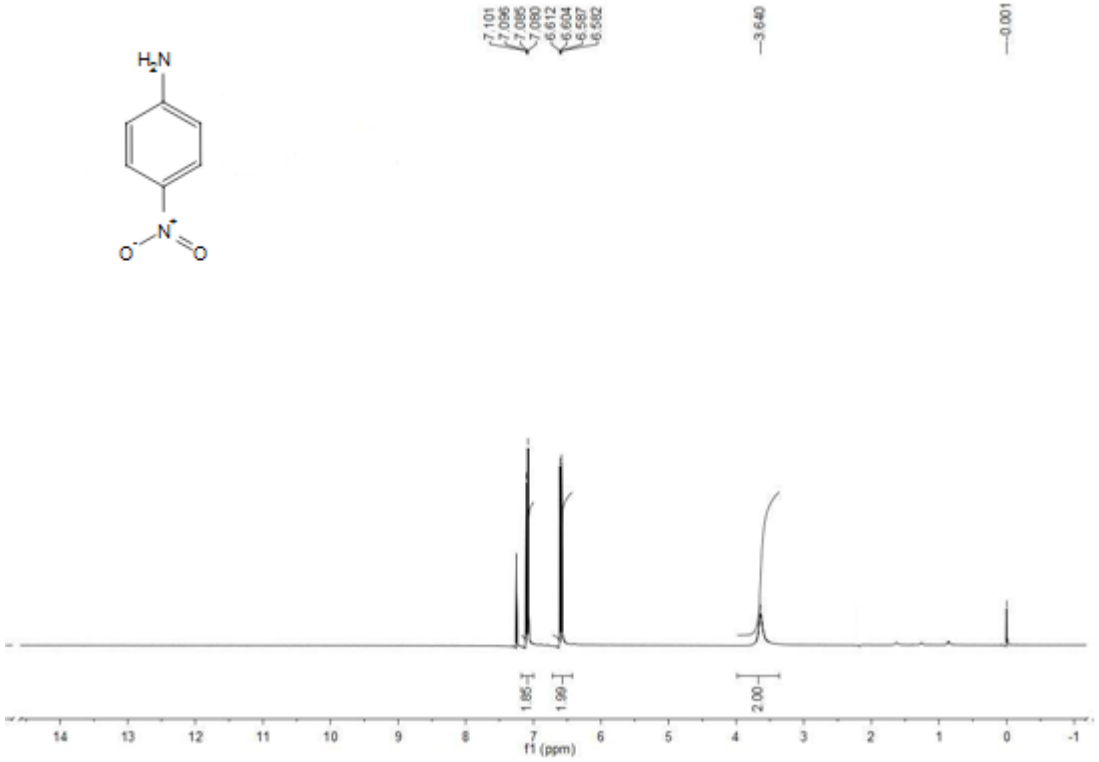


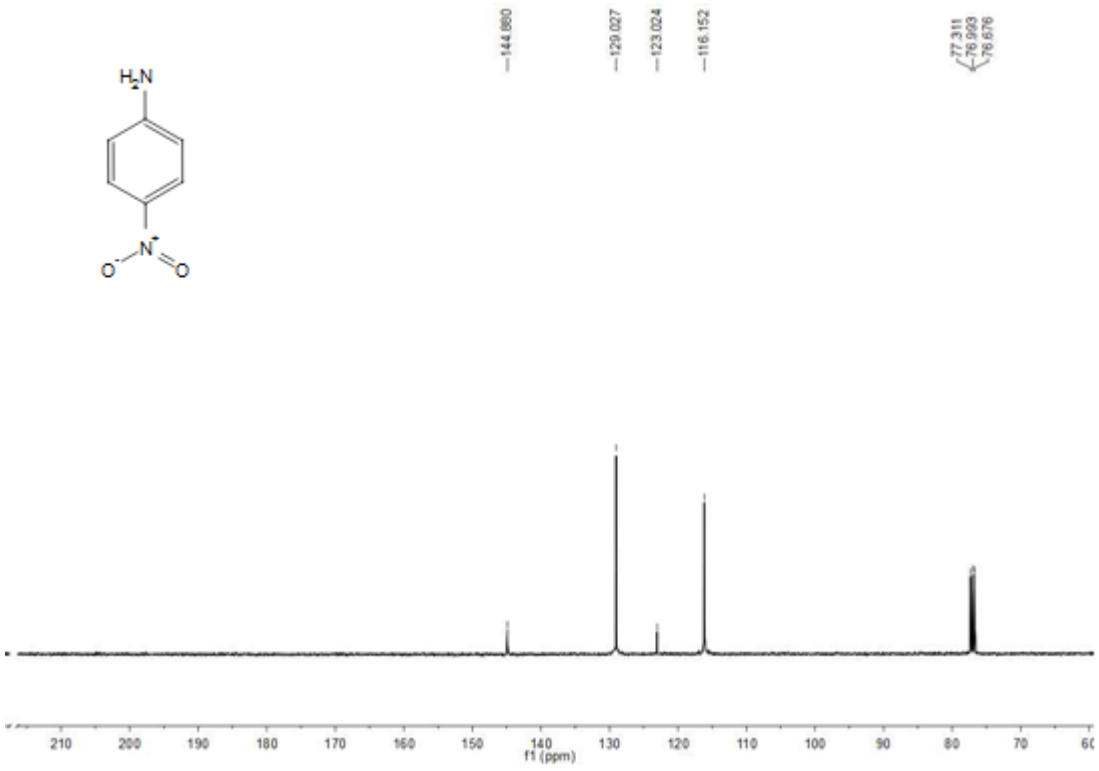
4-Ethoxy-phenylamine (2o)



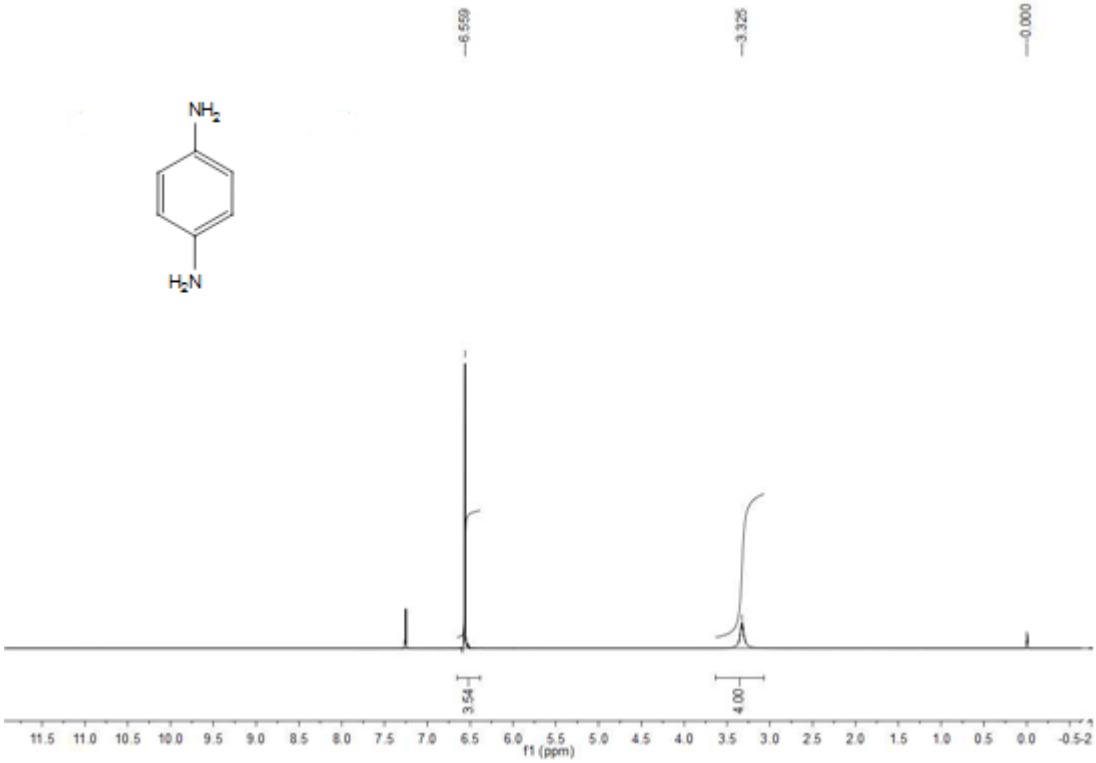


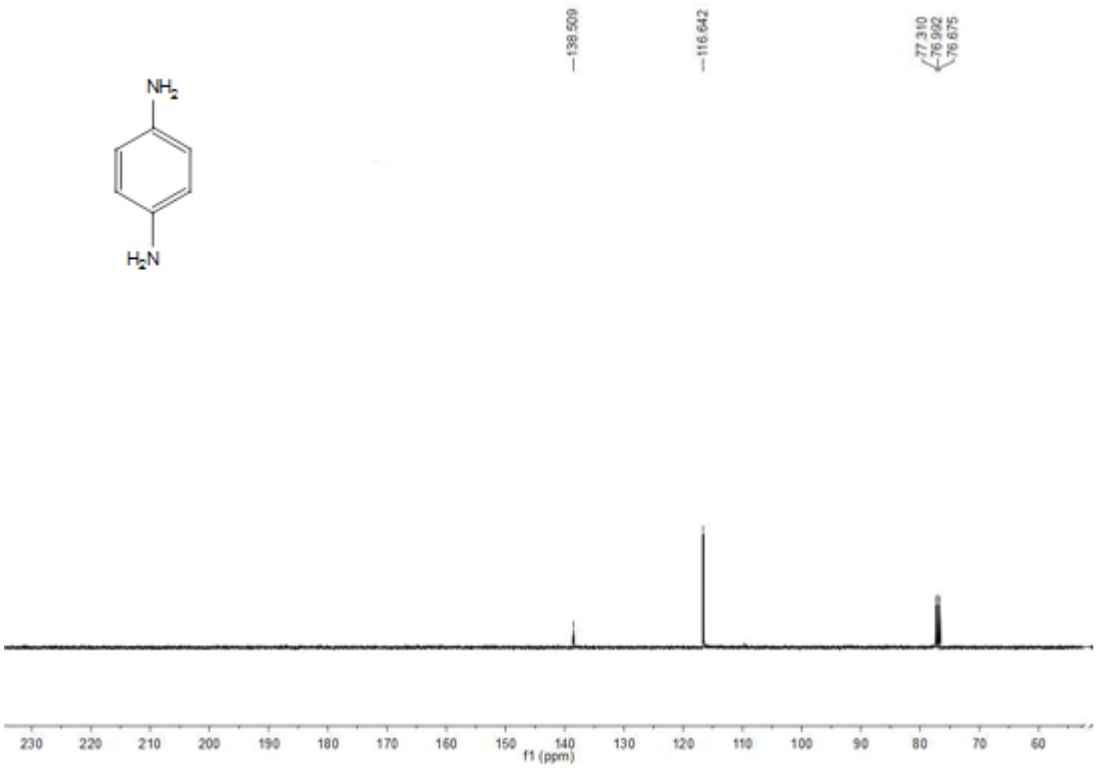
4-Nitroaniline (2p)



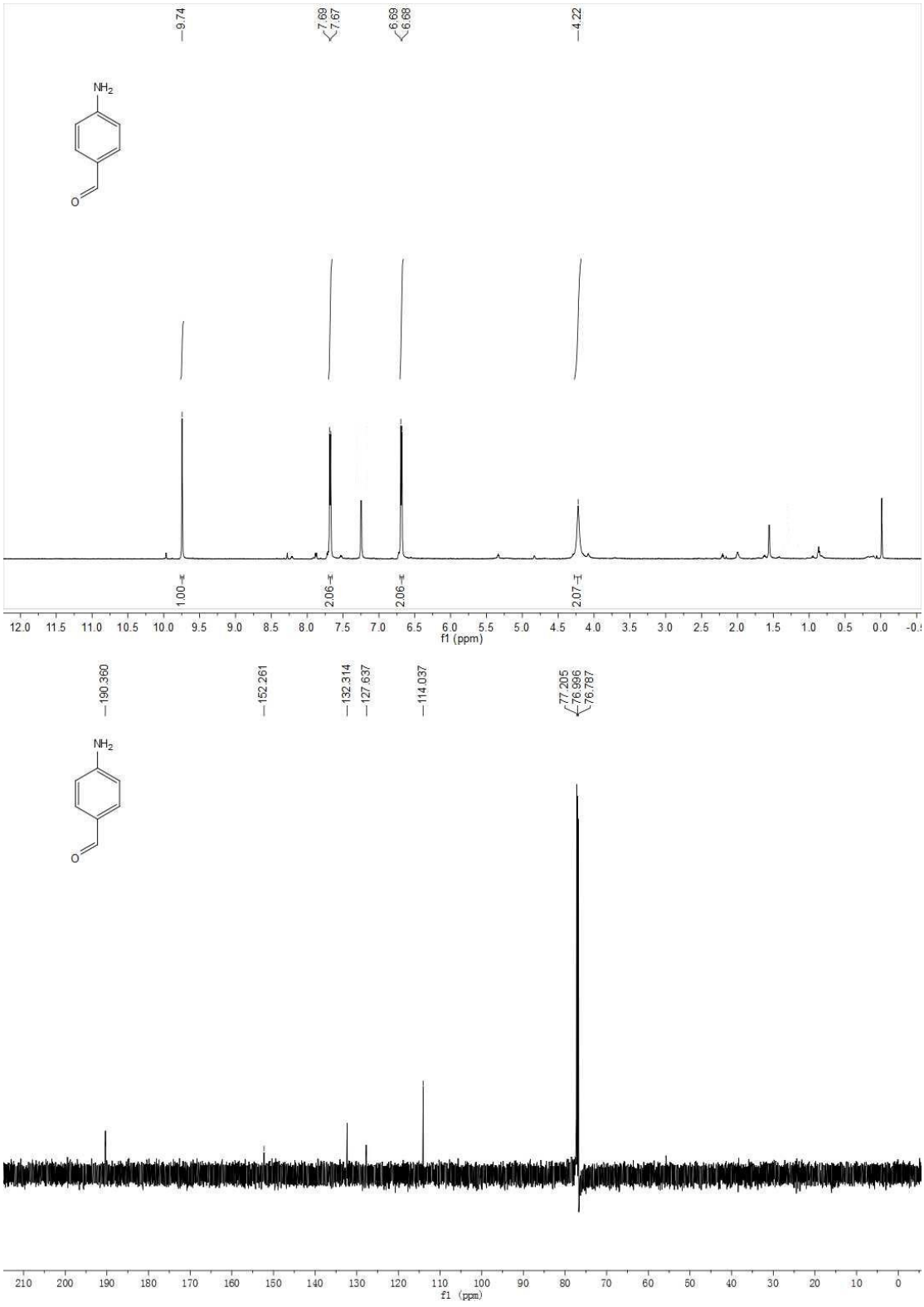


4-Phenylenediamine (2q)

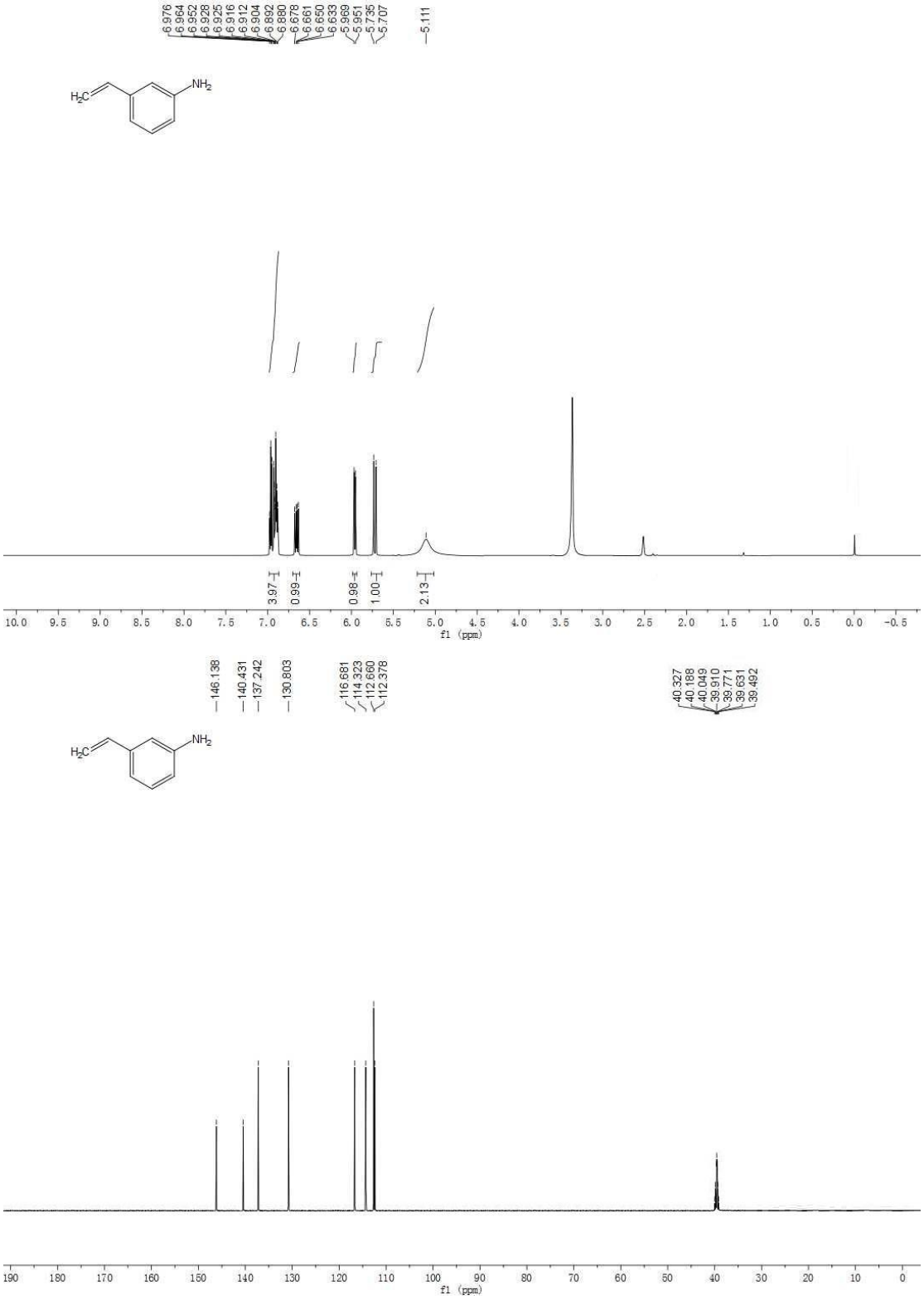




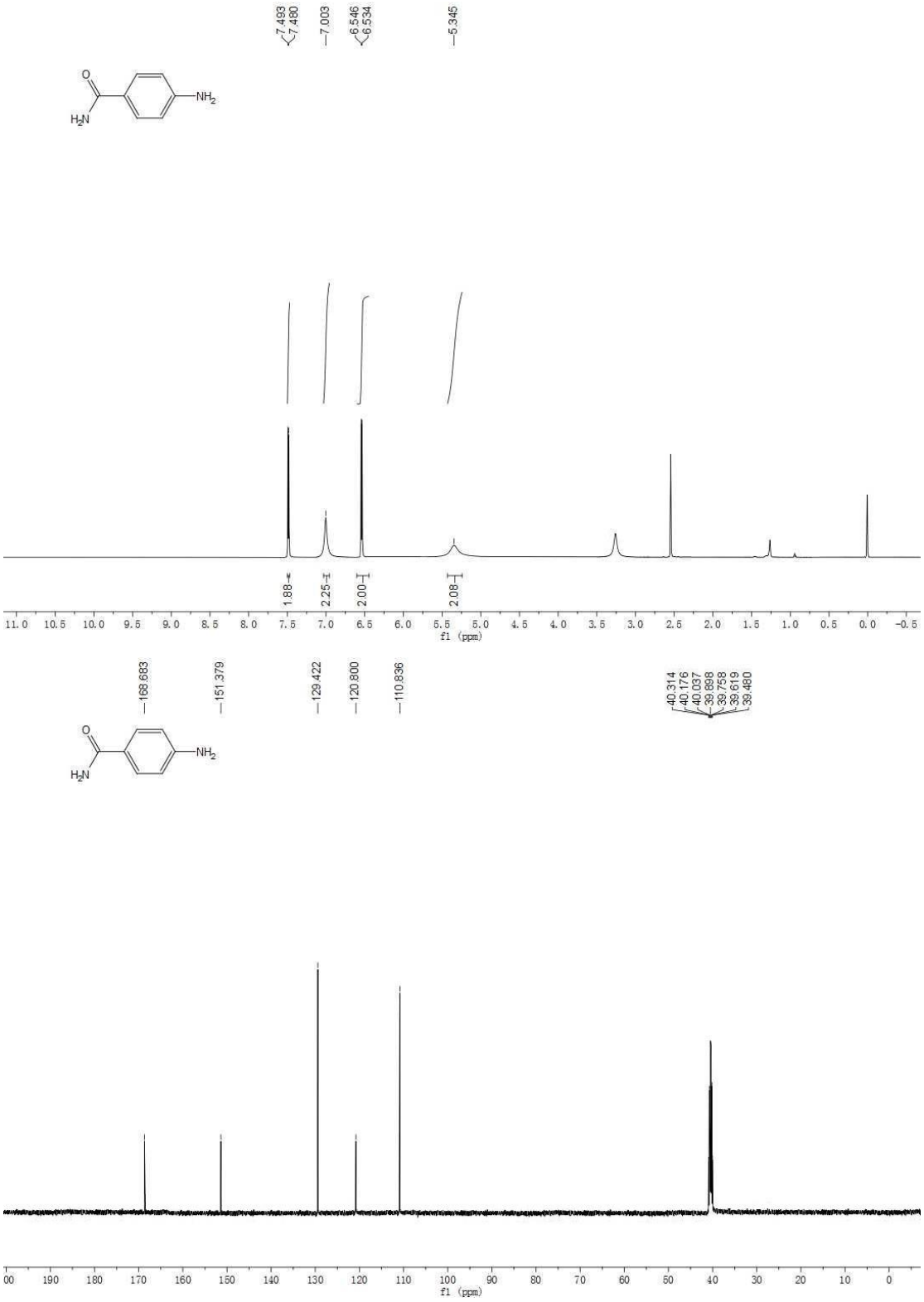
4-Aminobenzaldehyde (2r)



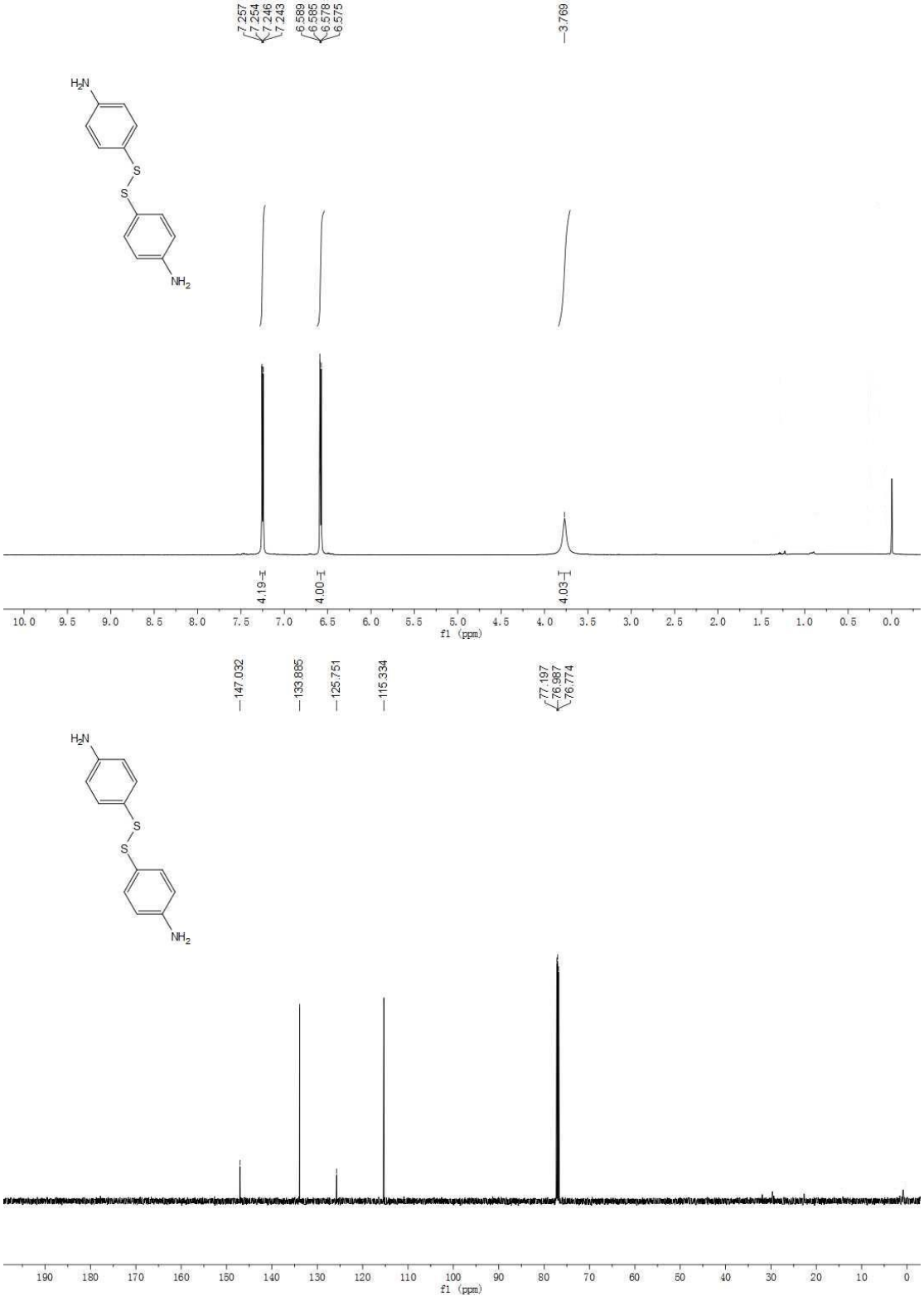
3-vinylaniline (2s)



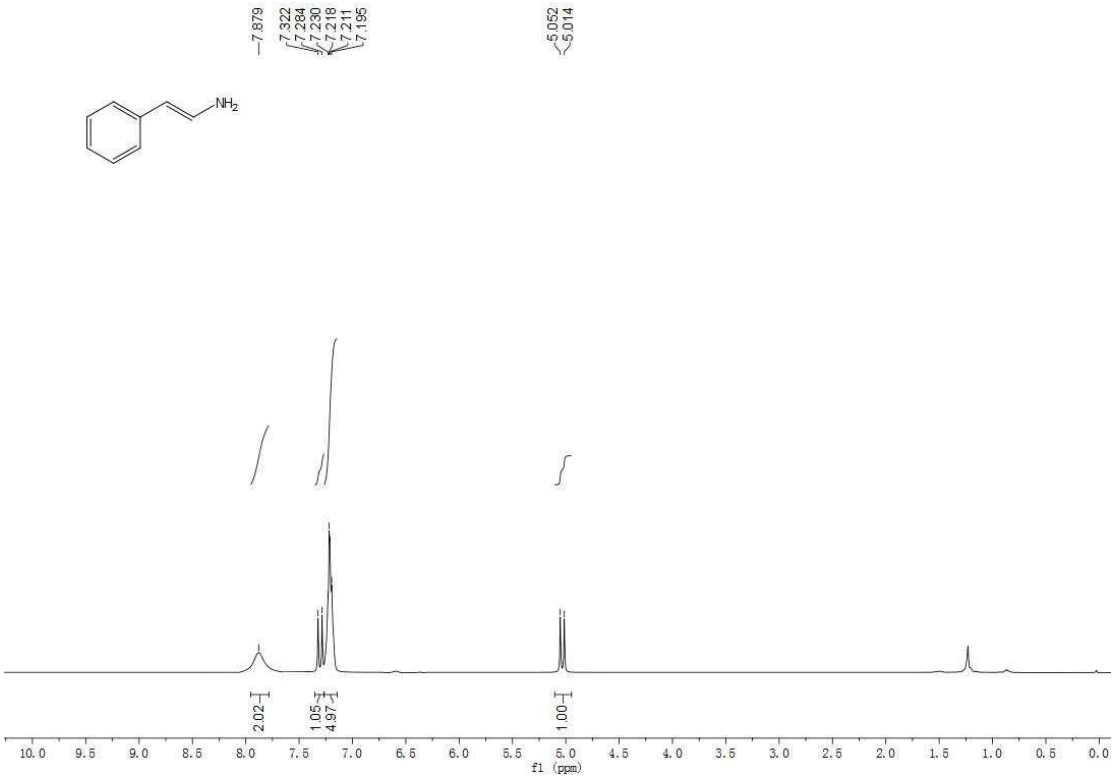
4-aminobenzamide (2t)

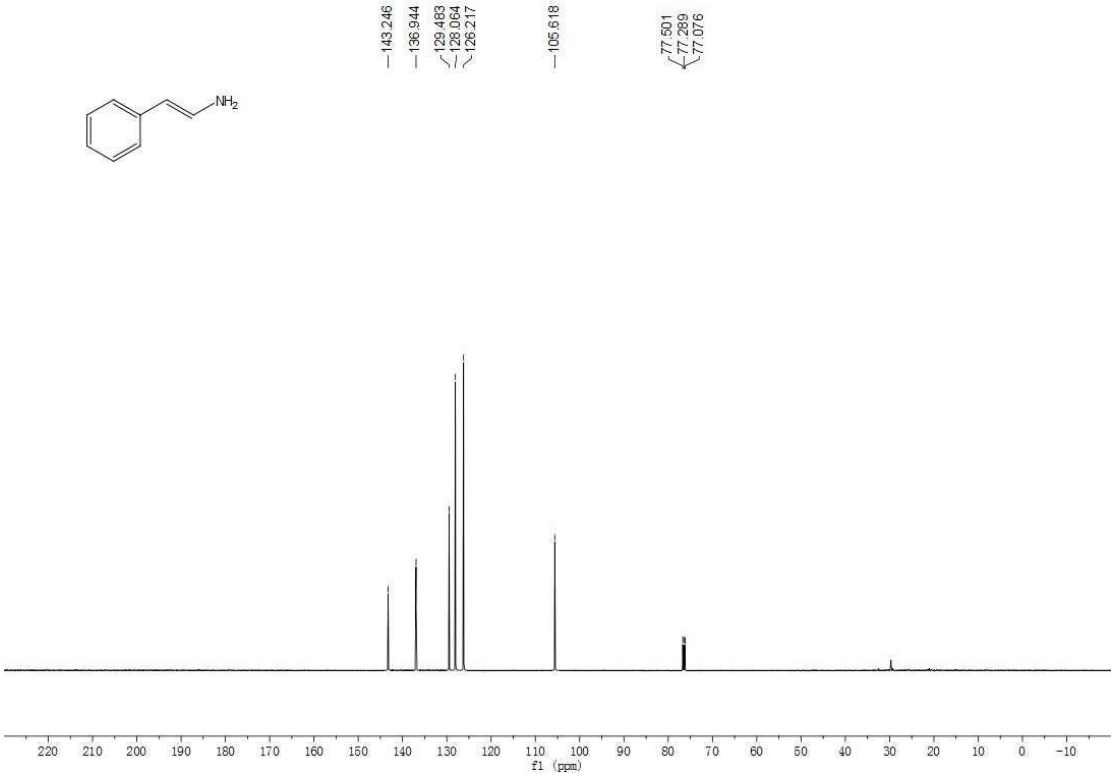


4,4'-disulfanediyldianiline (2u)

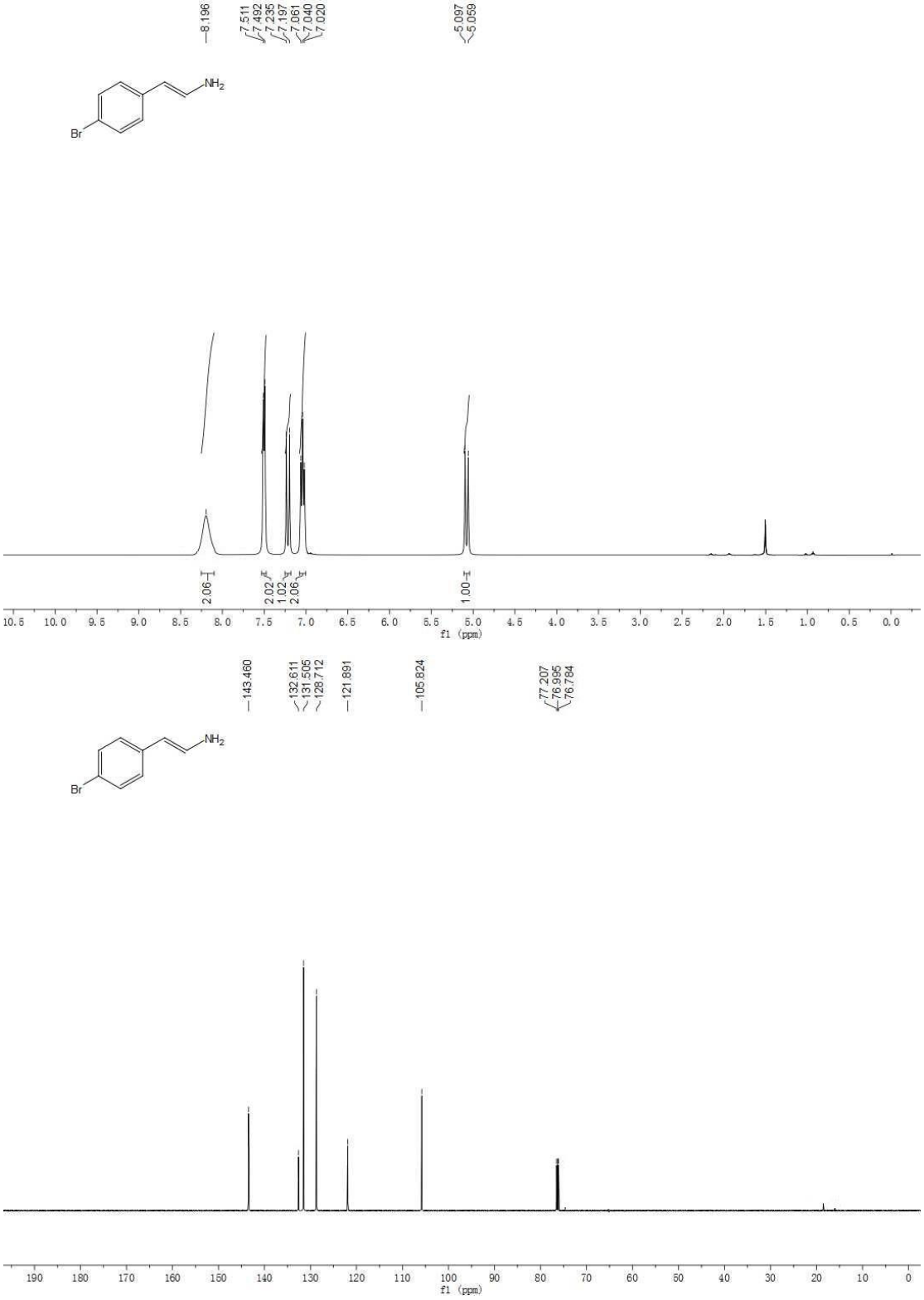


2-phenylethen-1-amine (2v)





2-(4-bromophenyl)ethen-1-amine (2w)



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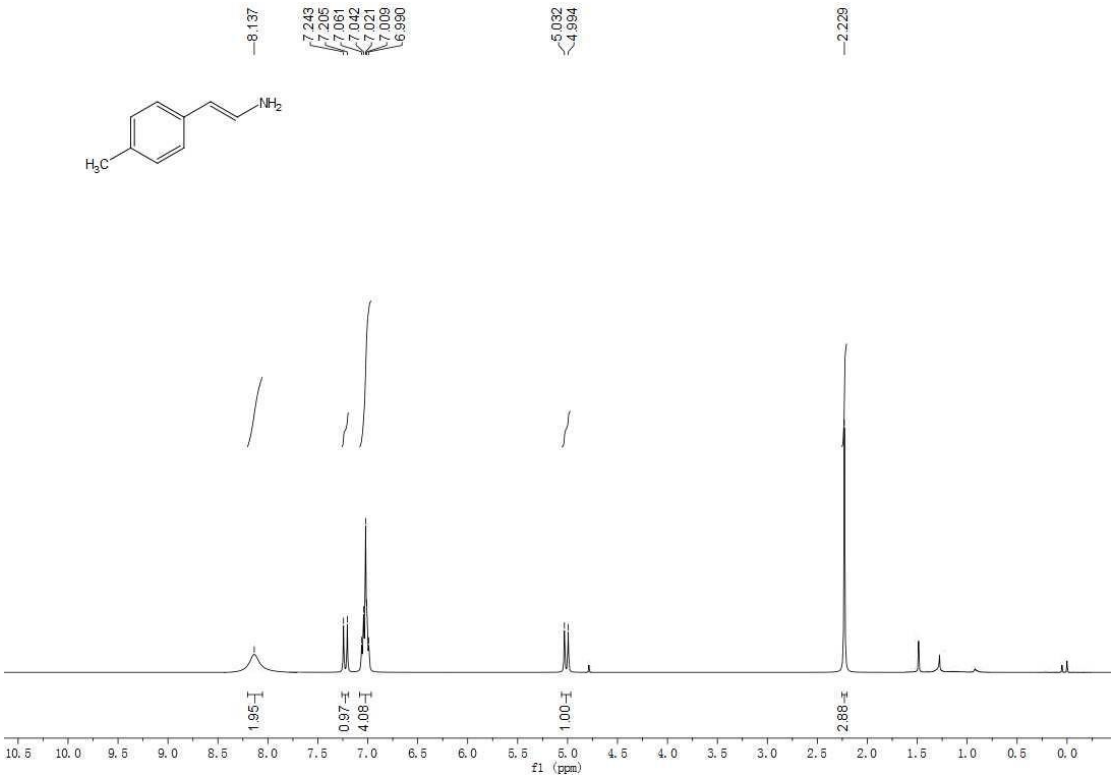

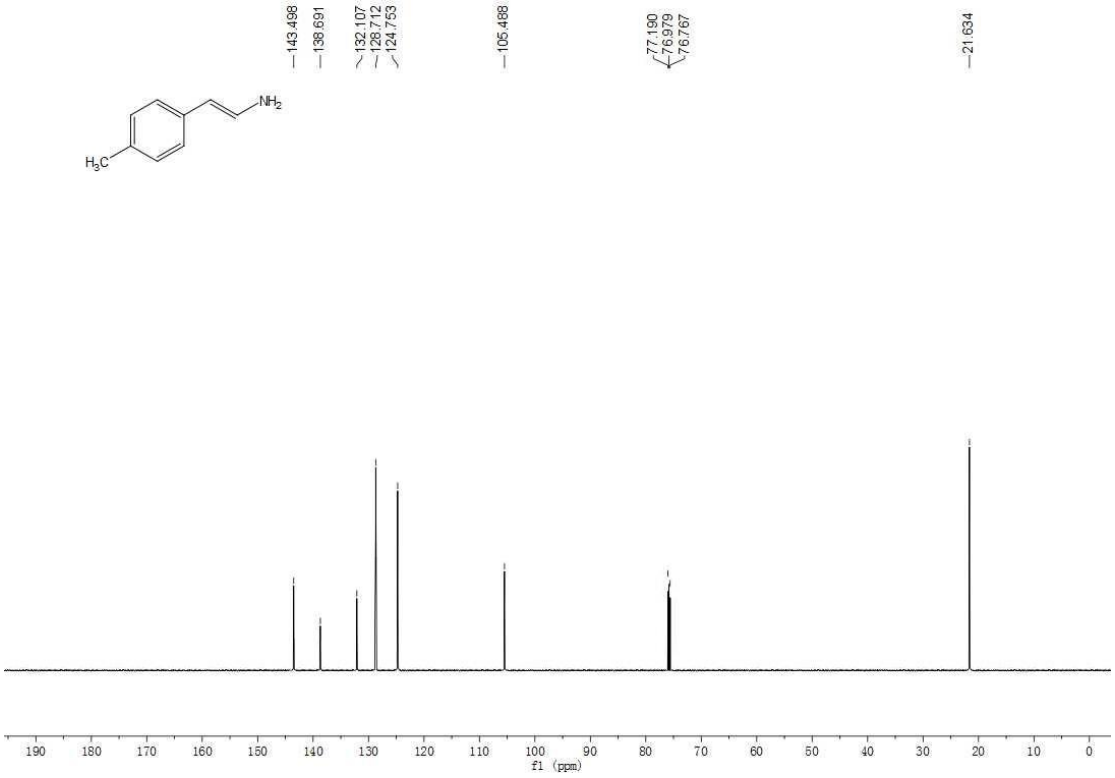

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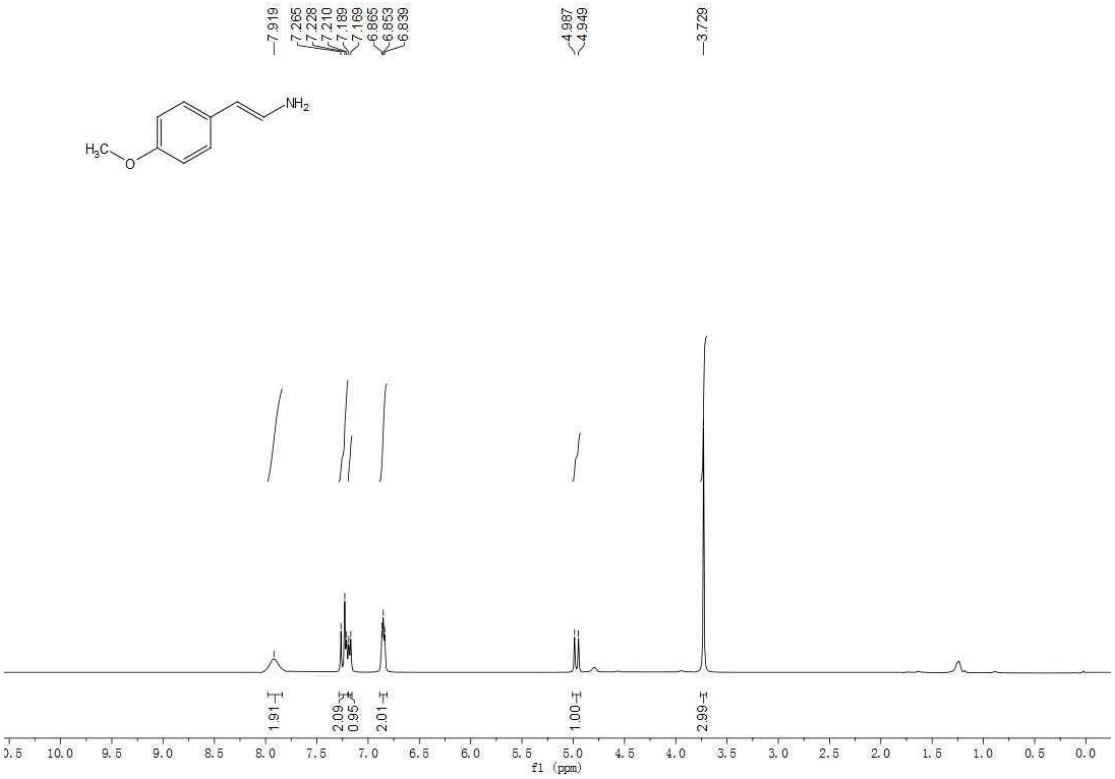
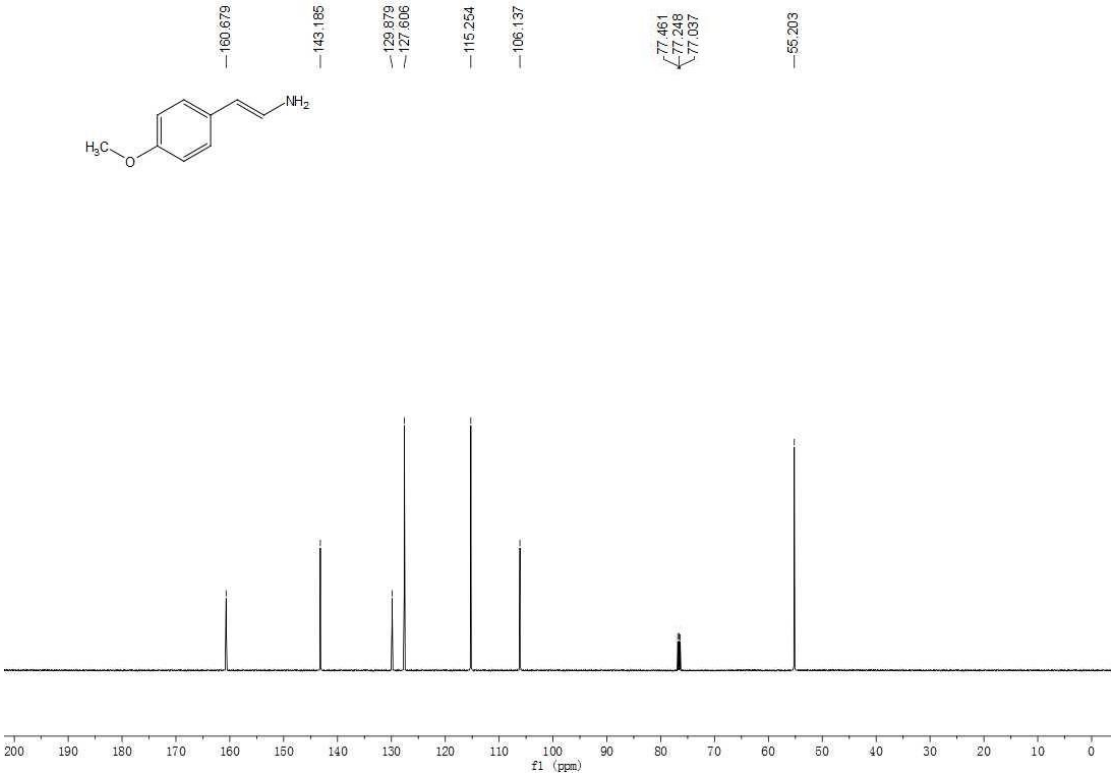
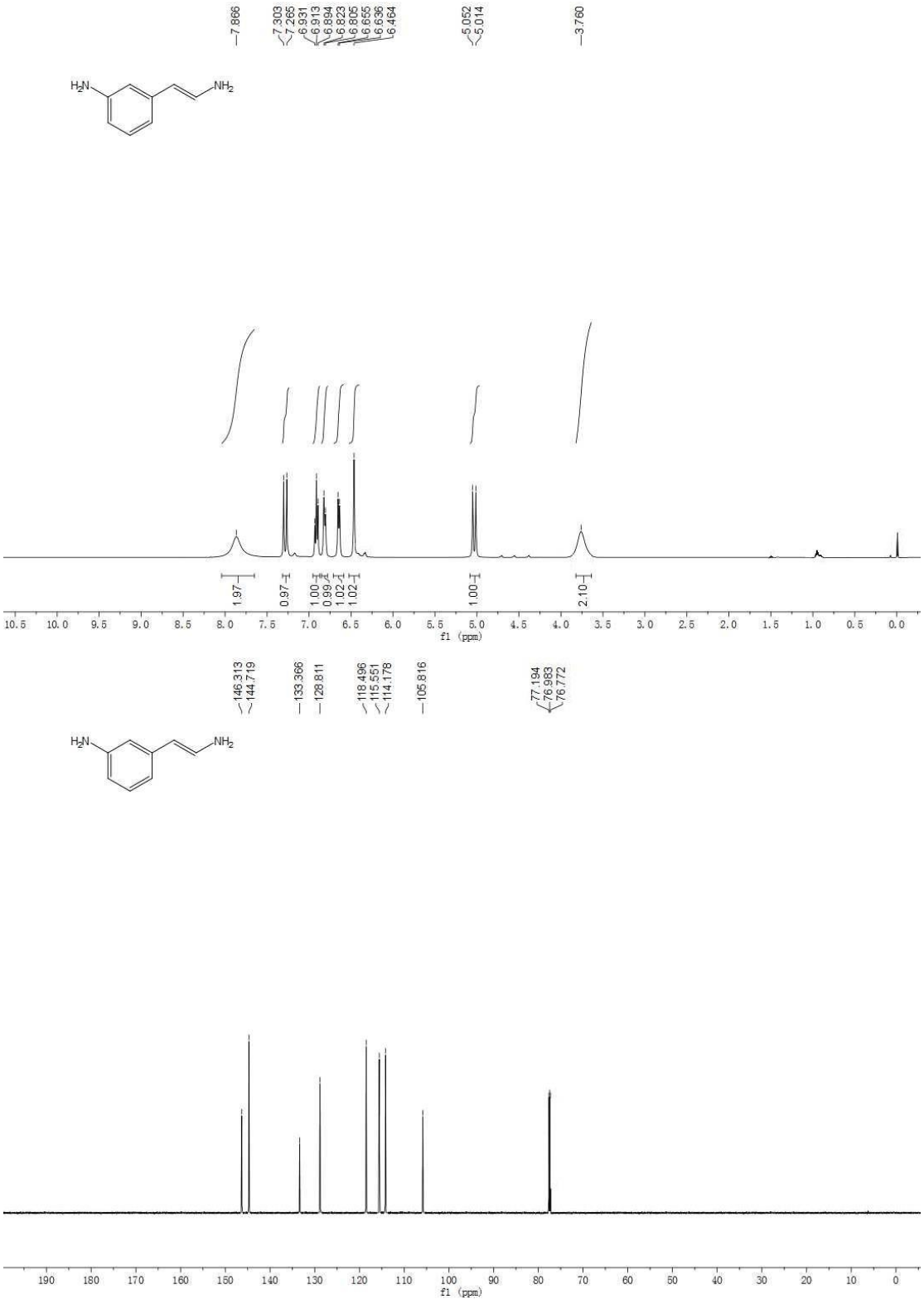
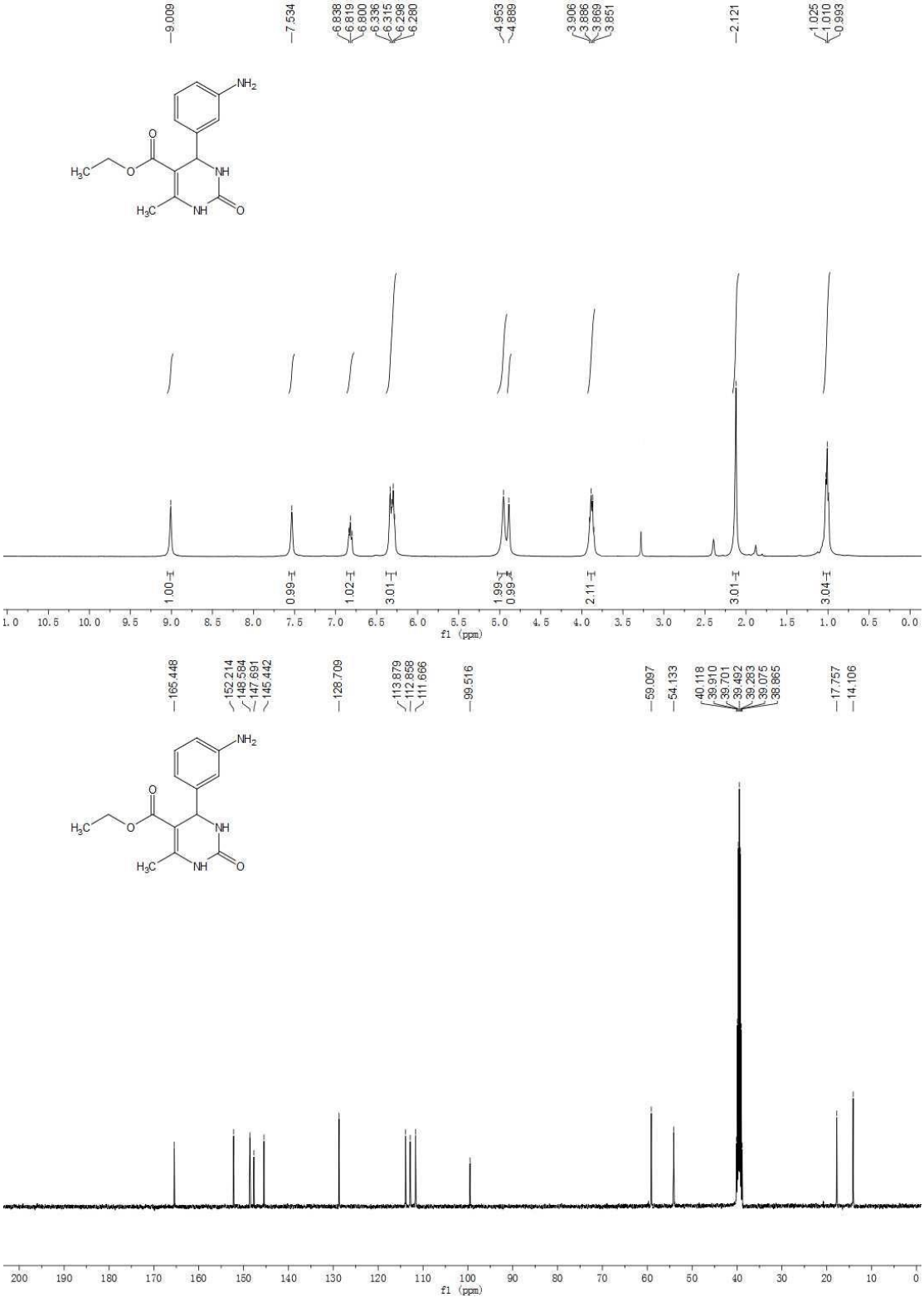




3-(2-aminovinyl)aniline (2z)



4-(3-Amino-phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester (4a)



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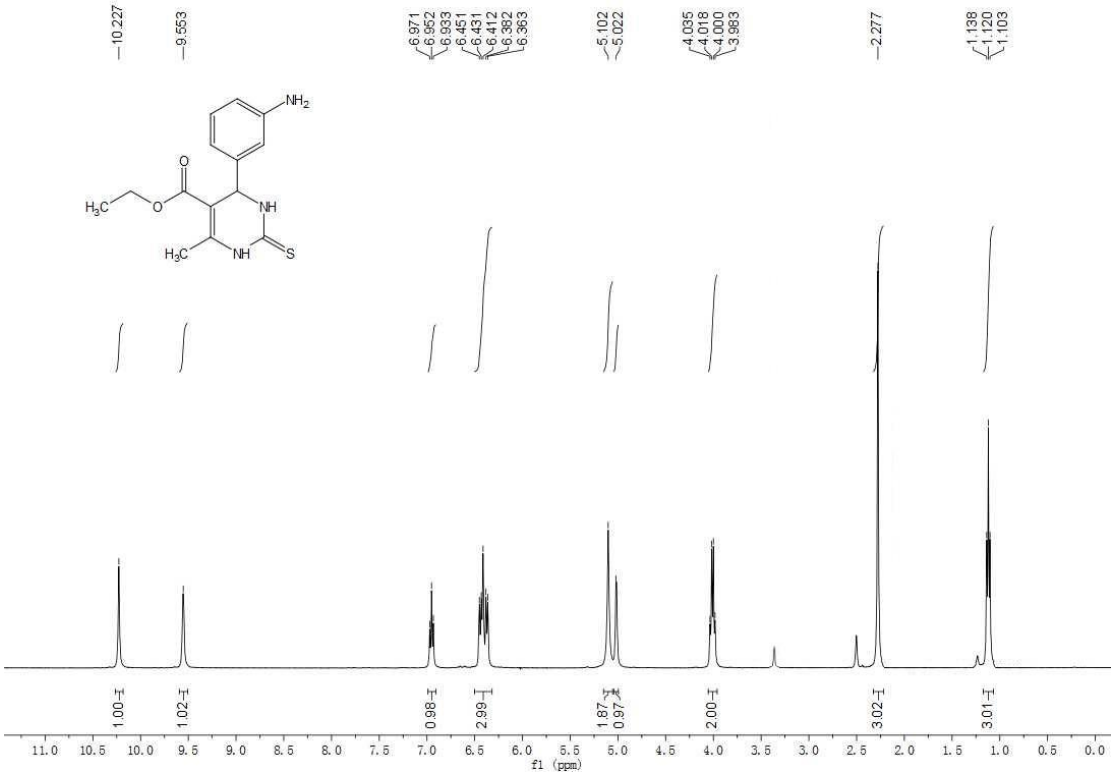

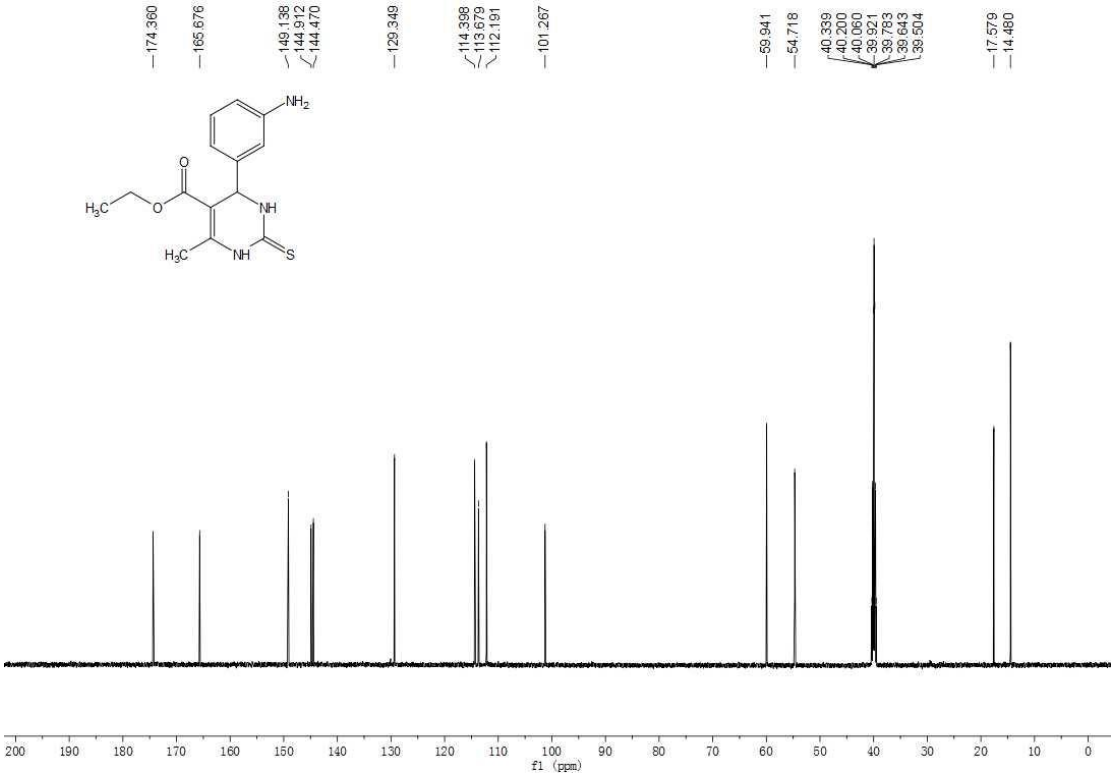

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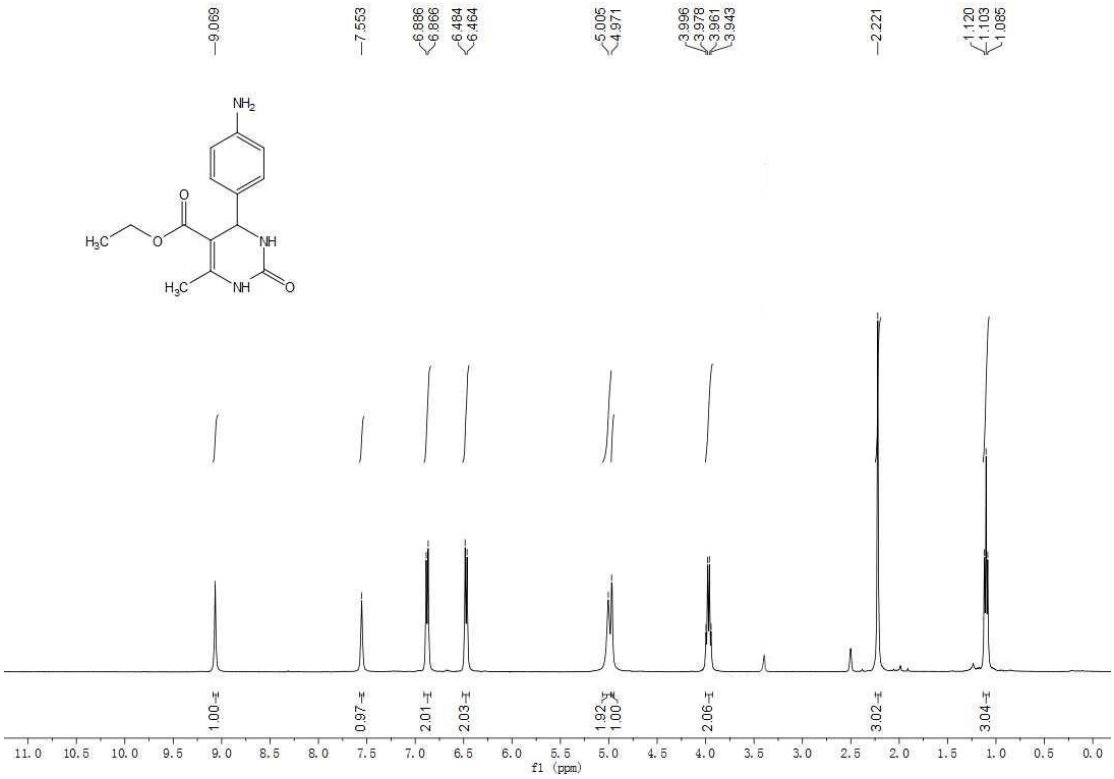

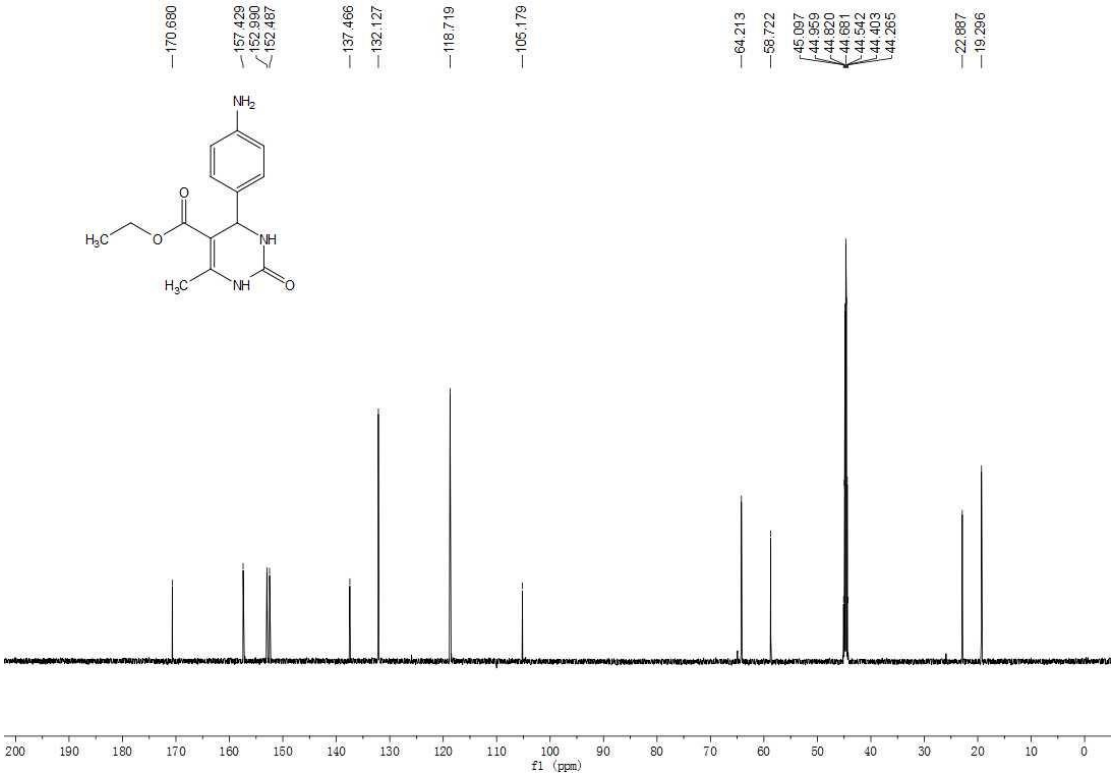

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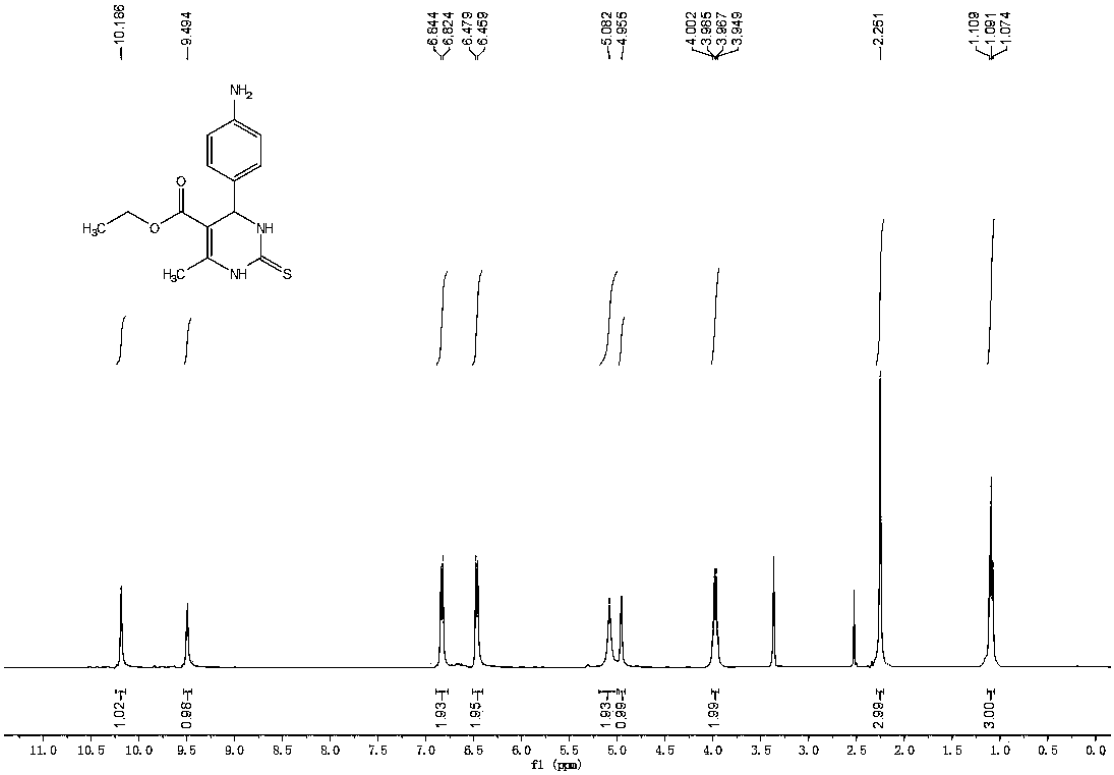

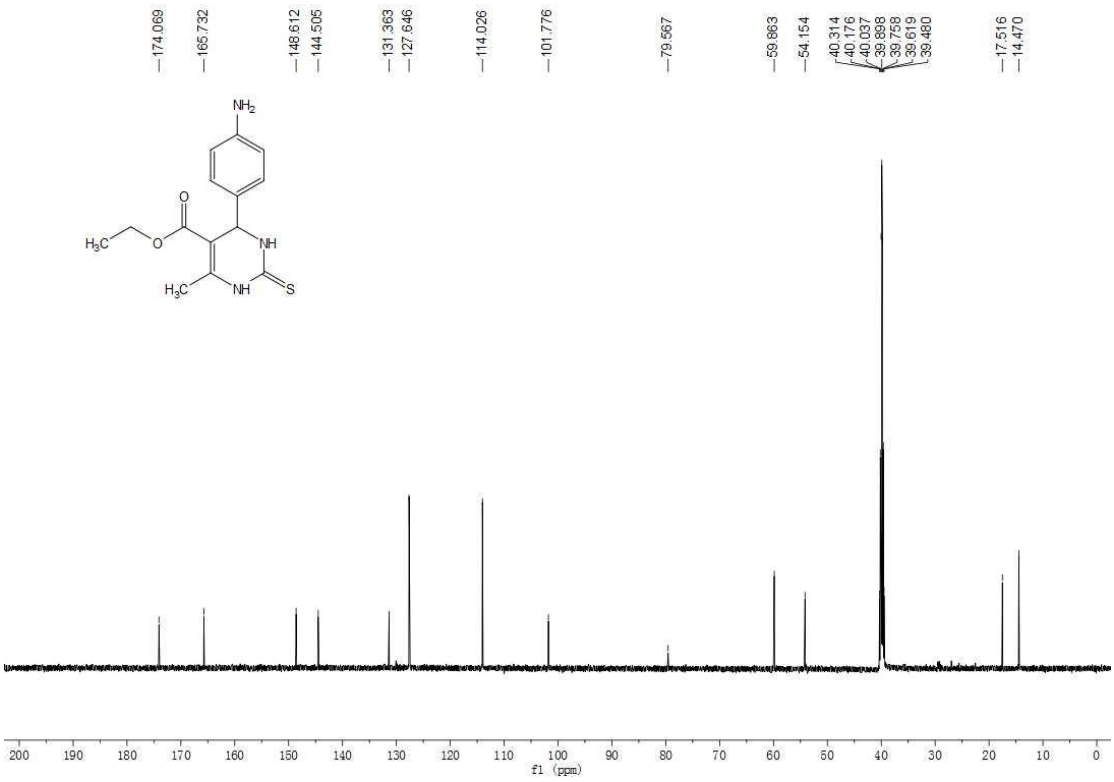

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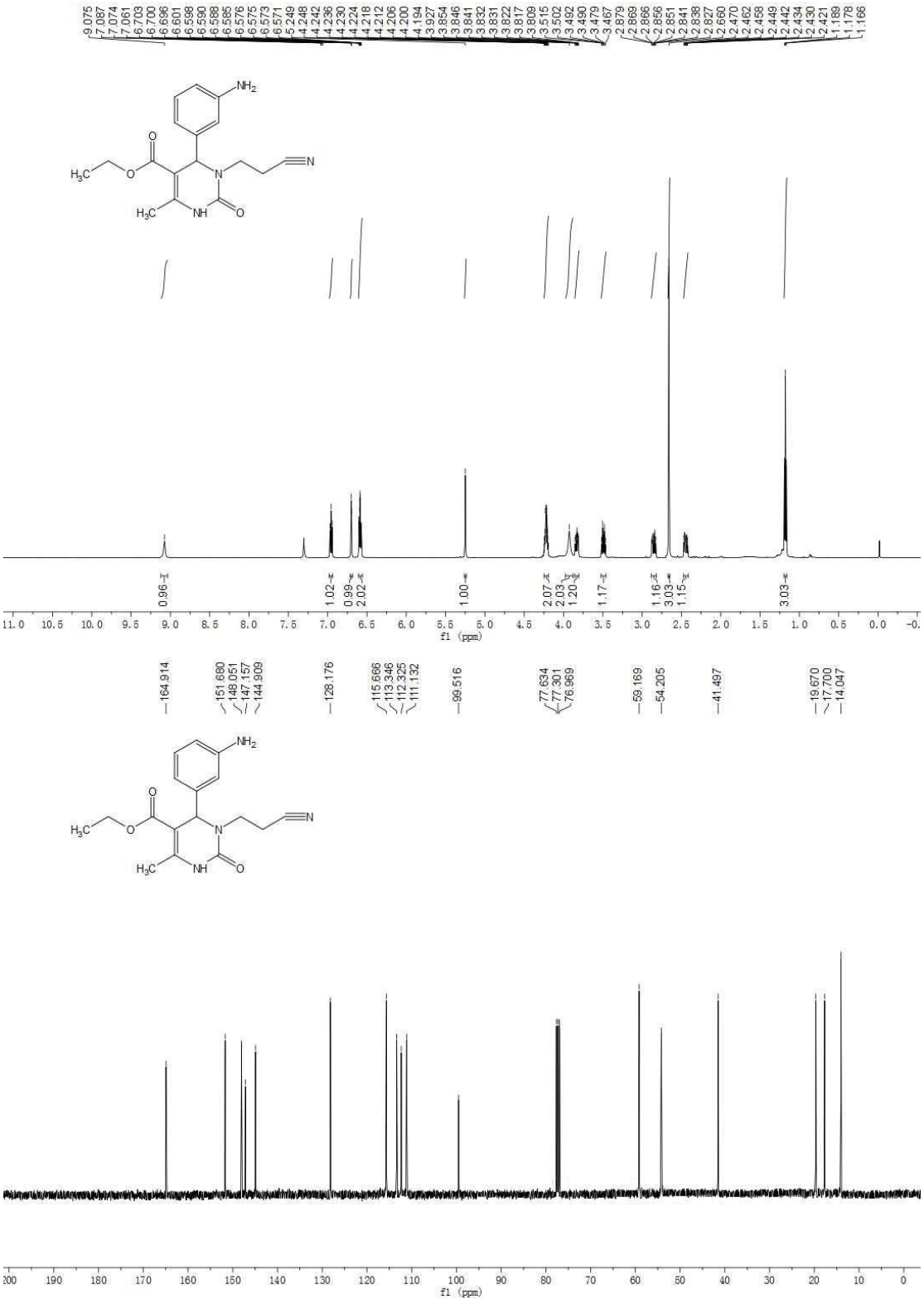

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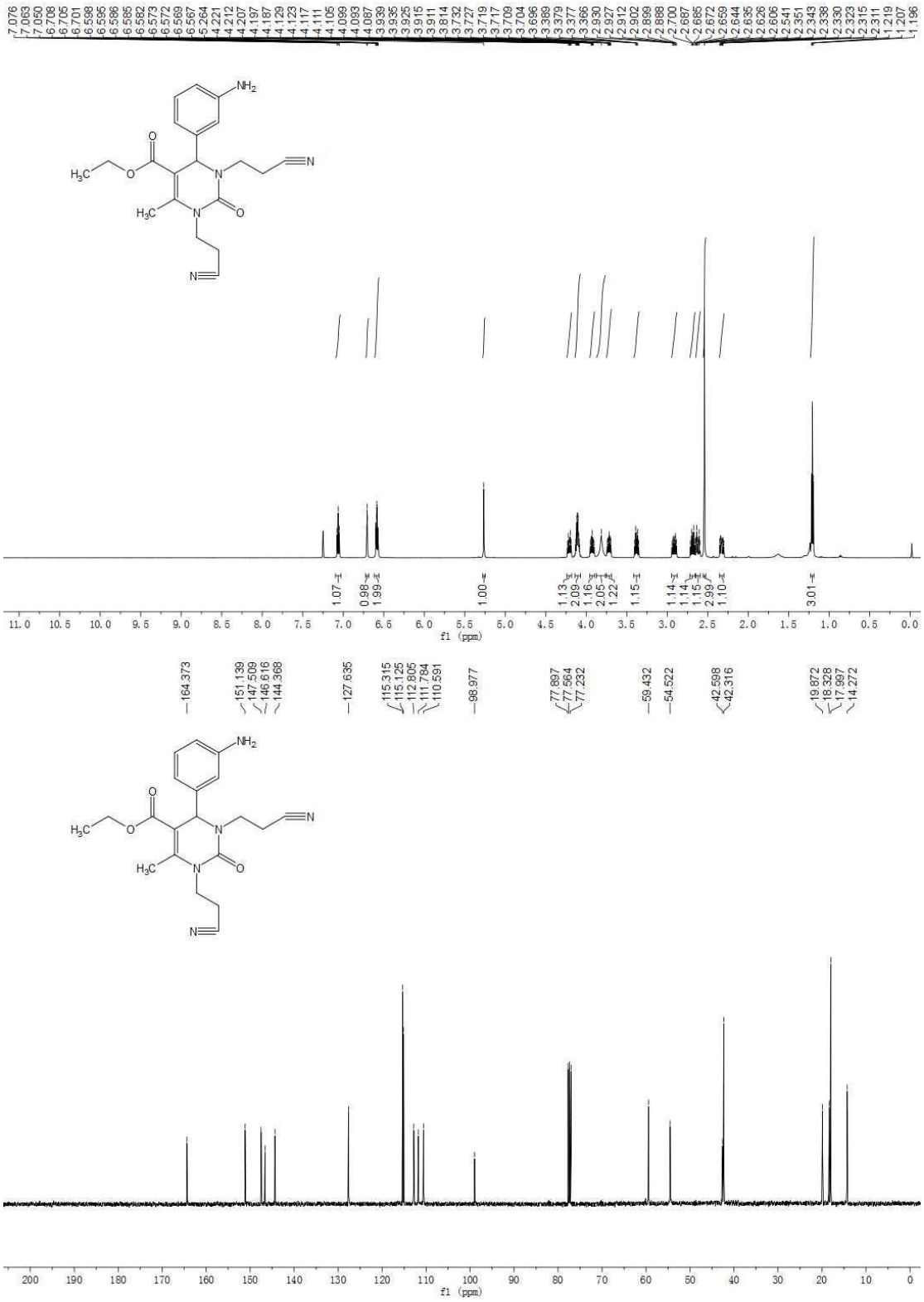

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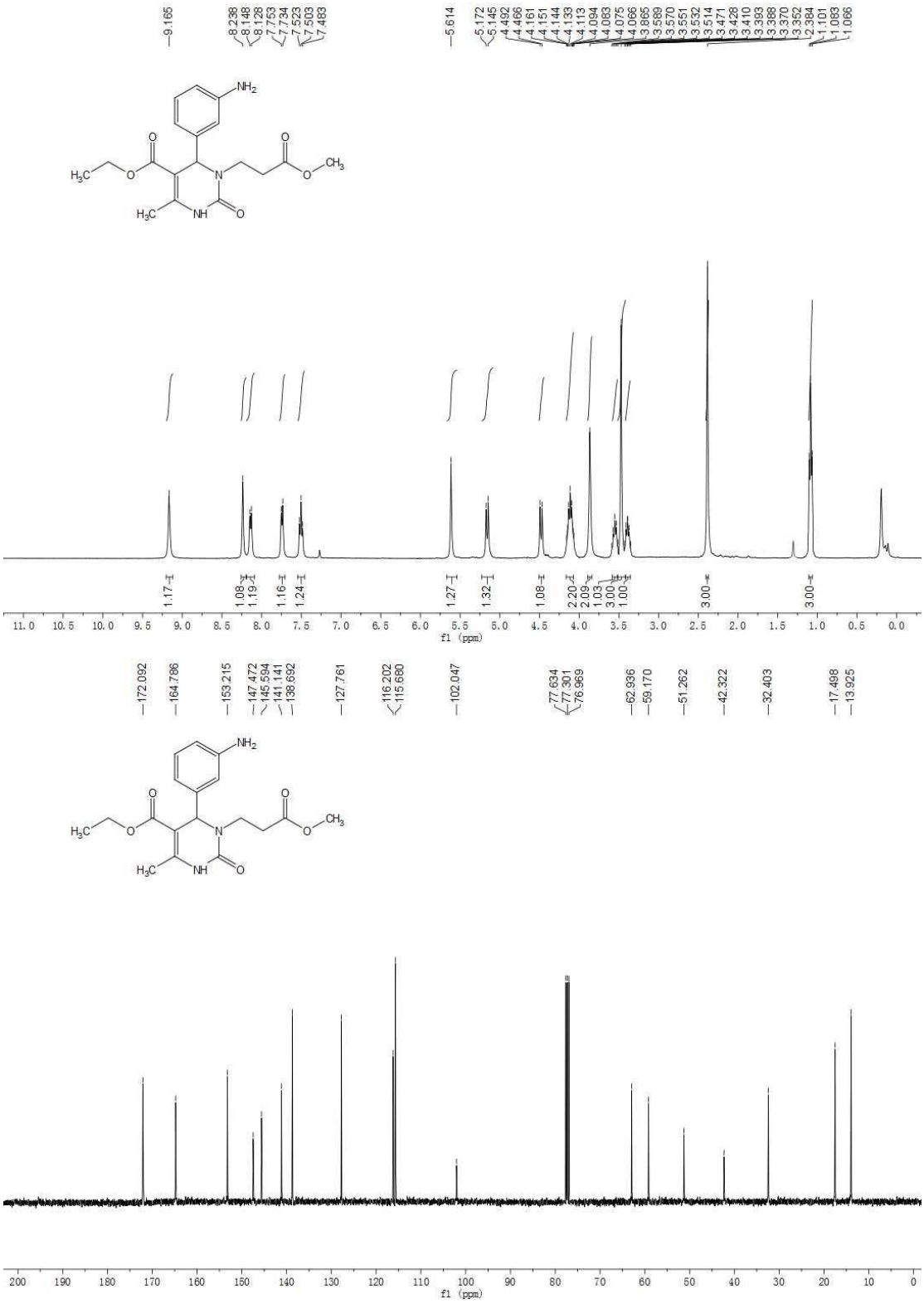

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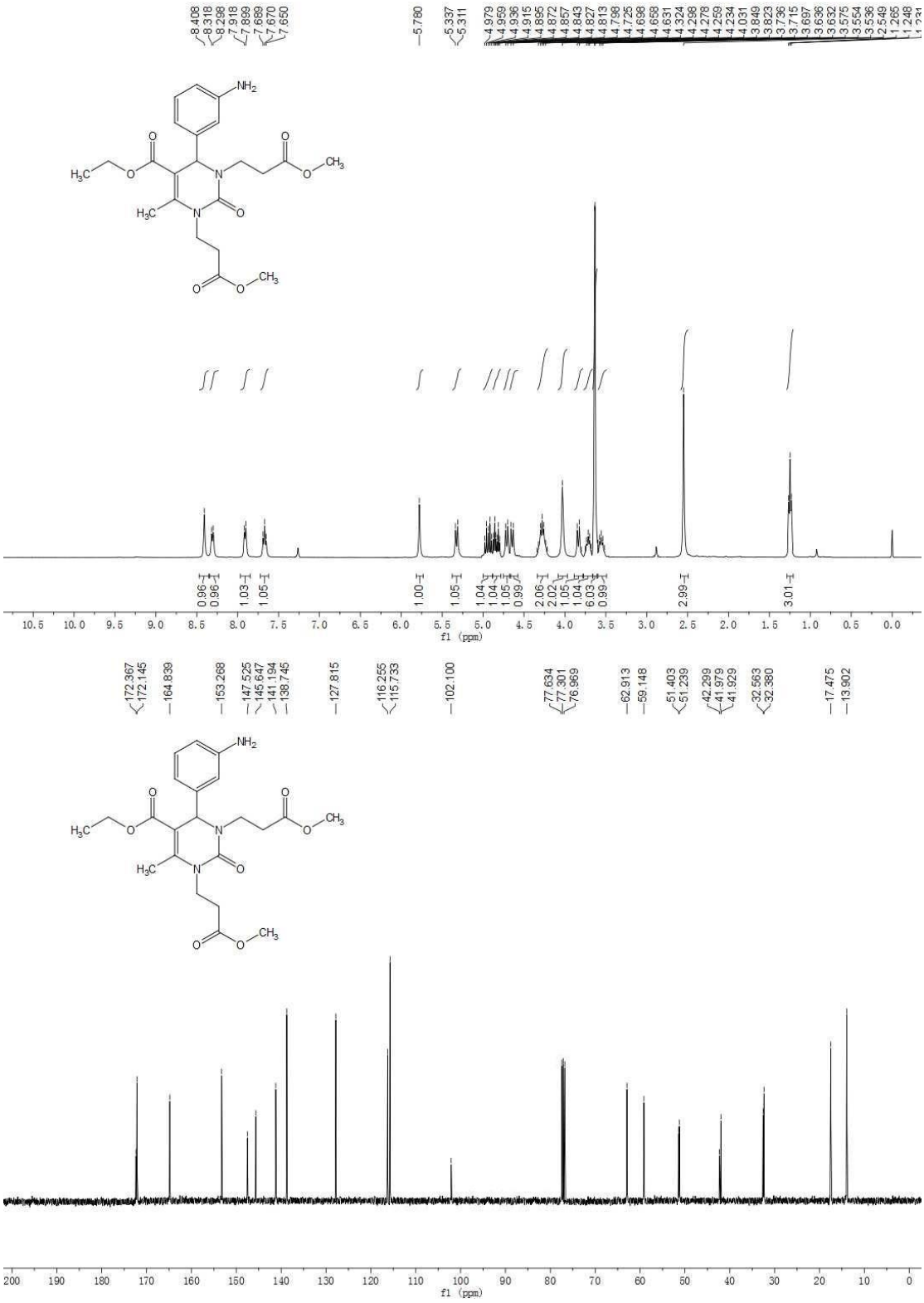

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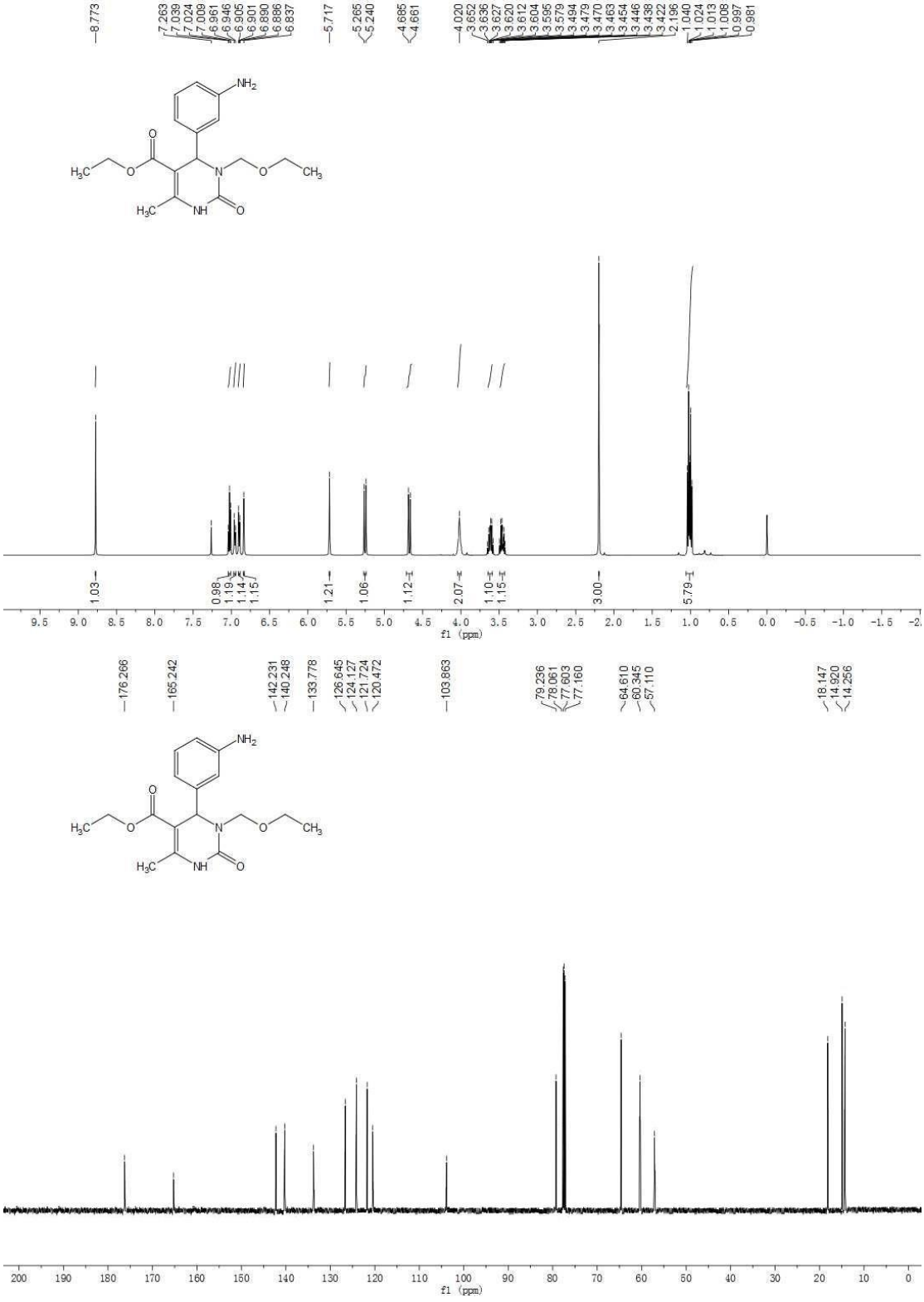

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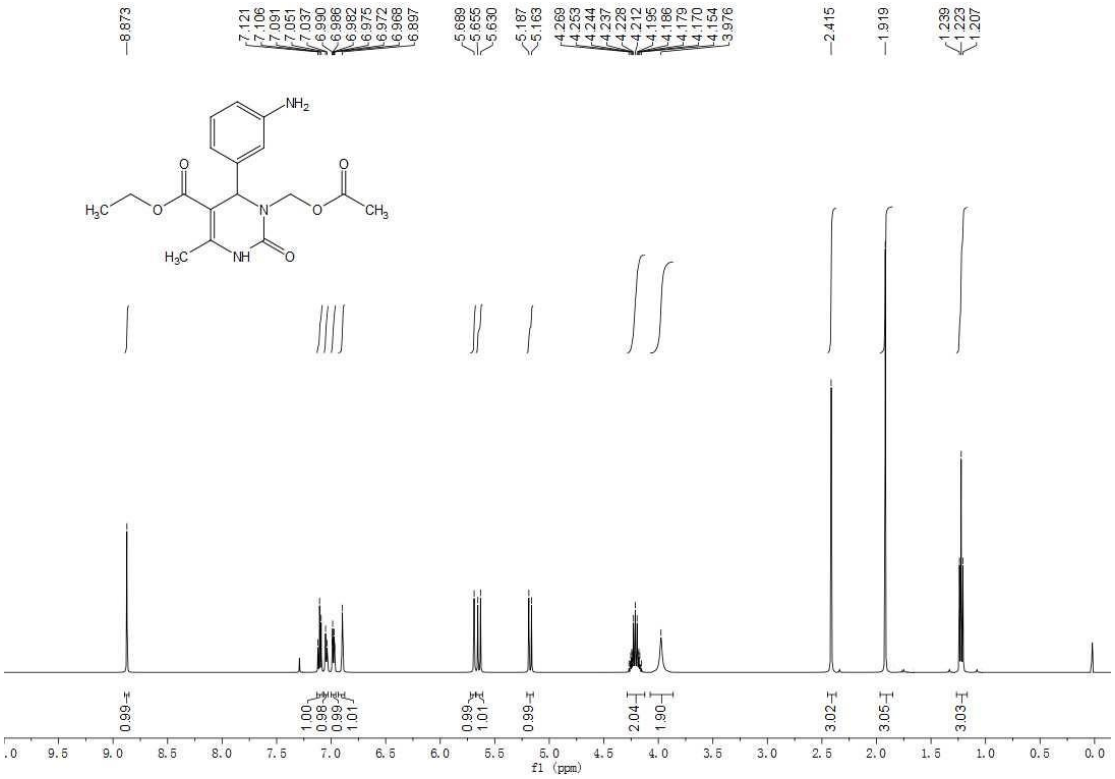
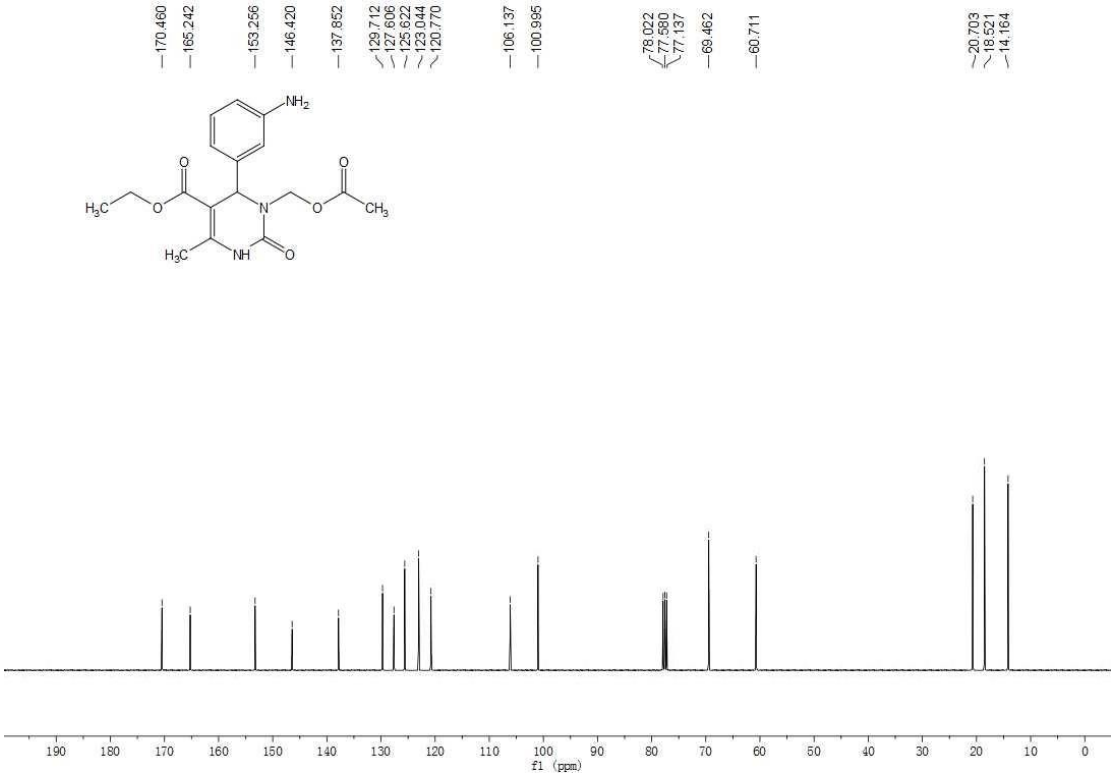
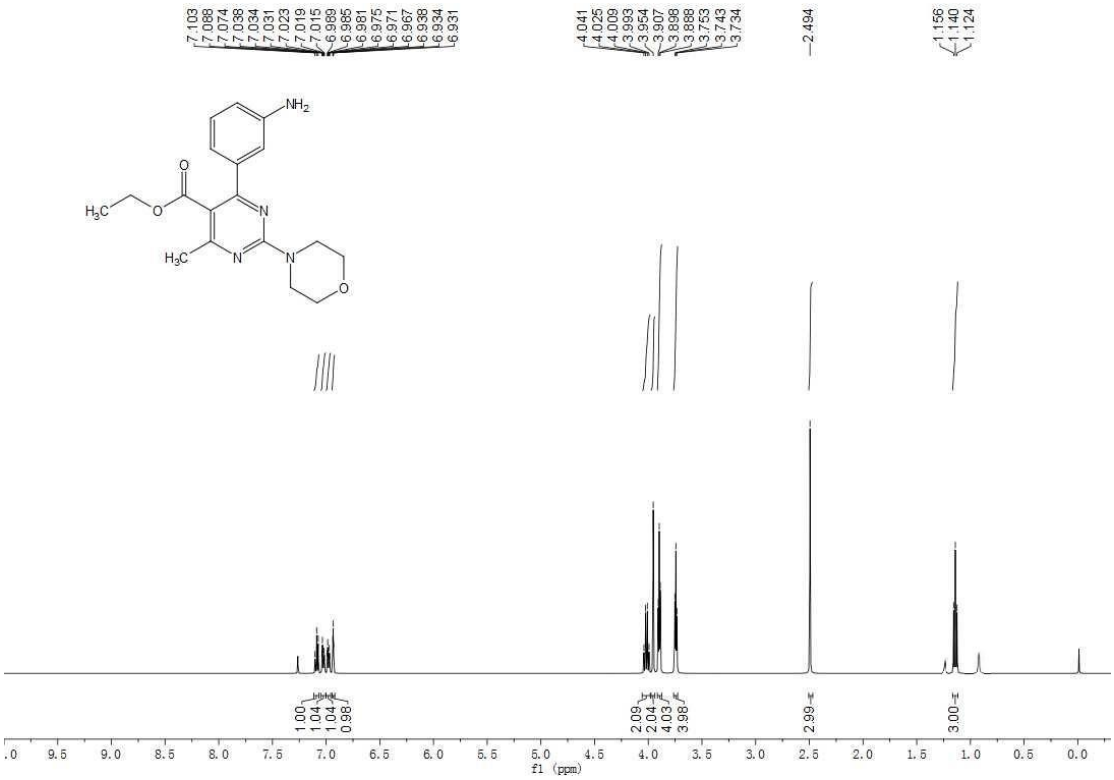
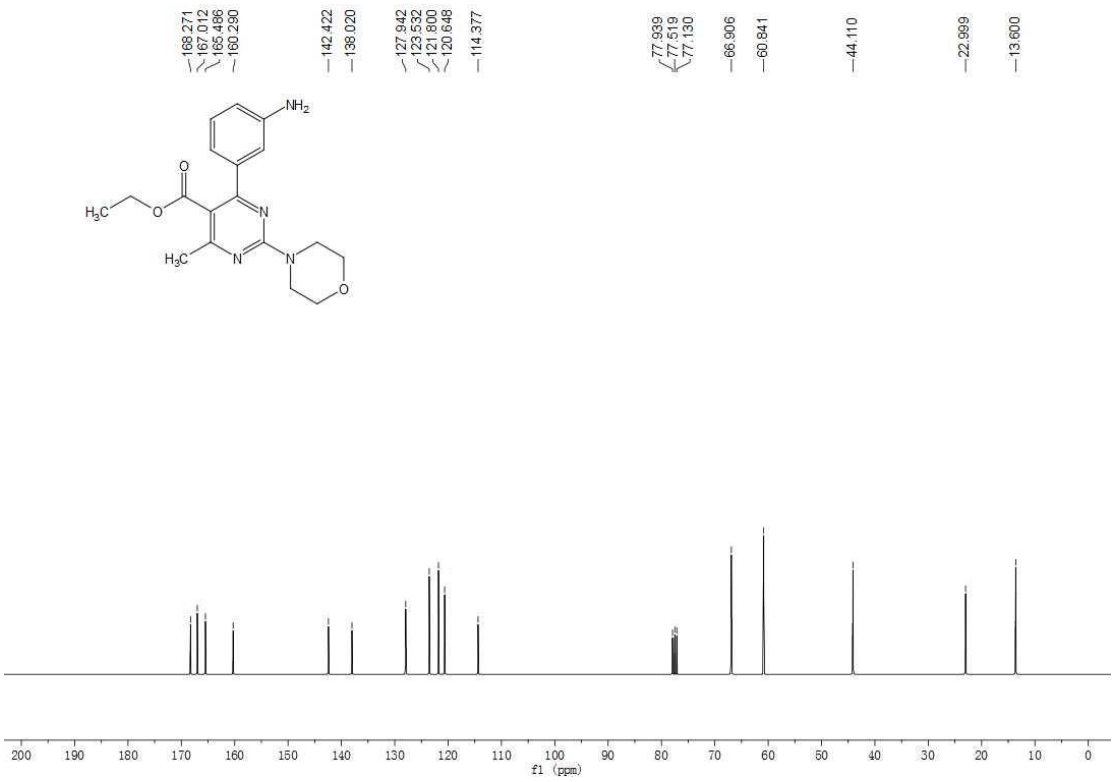




4-(3-Amino-phenyl)-6-methyl-2-morpholin-4-yl-pyrimidine-5-carboxylic acid ethyl ester (4k)





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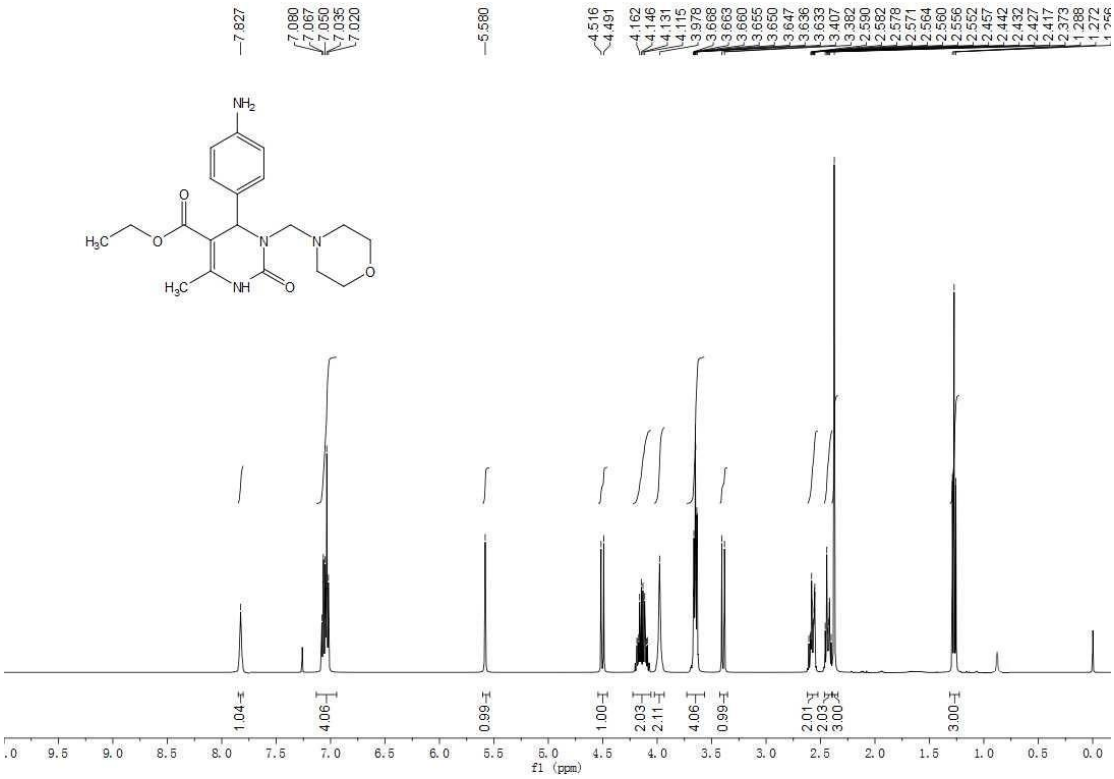
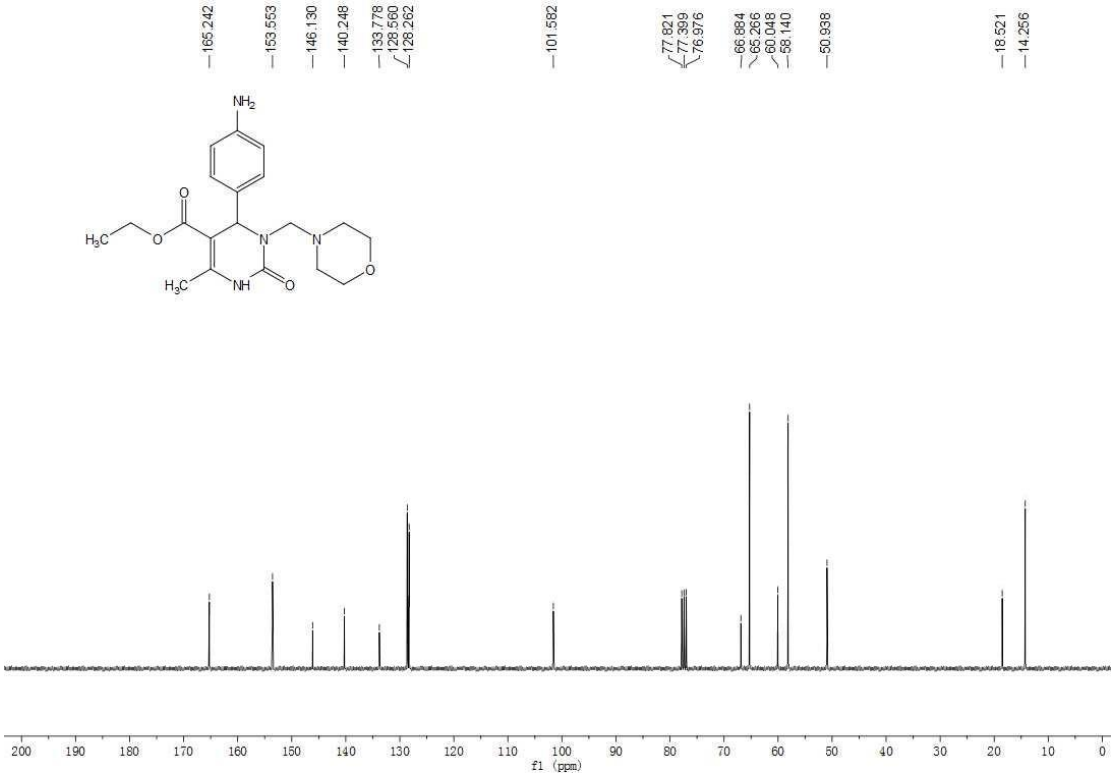
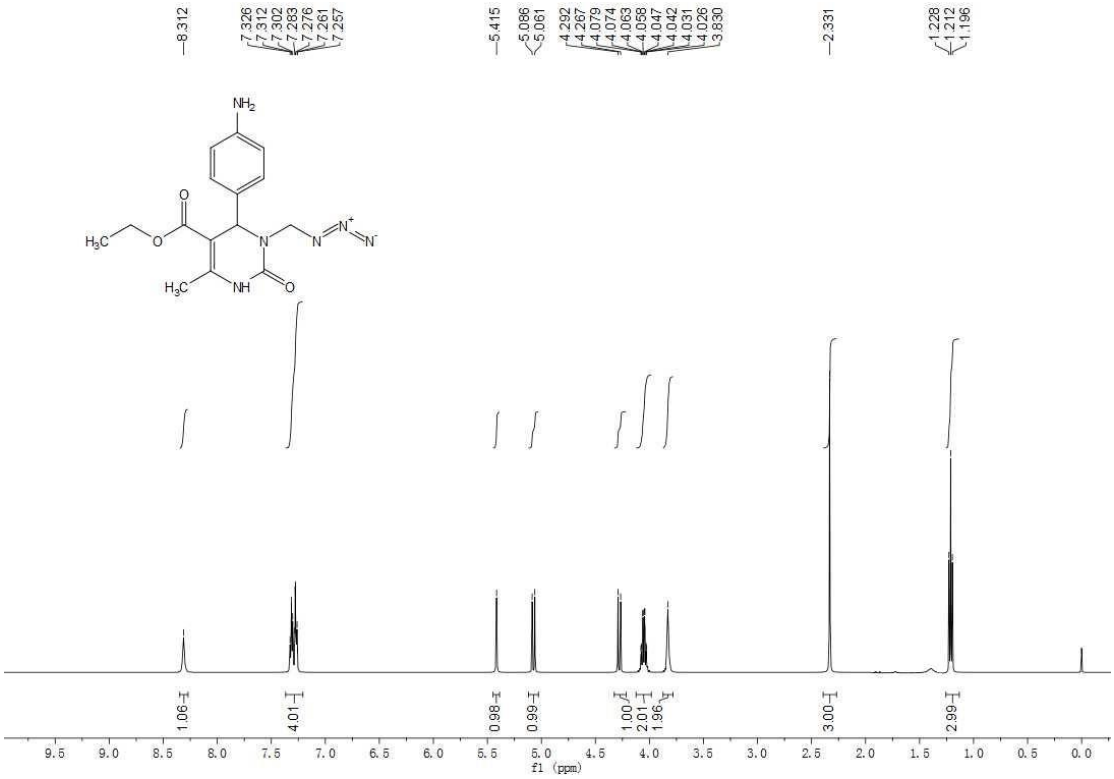
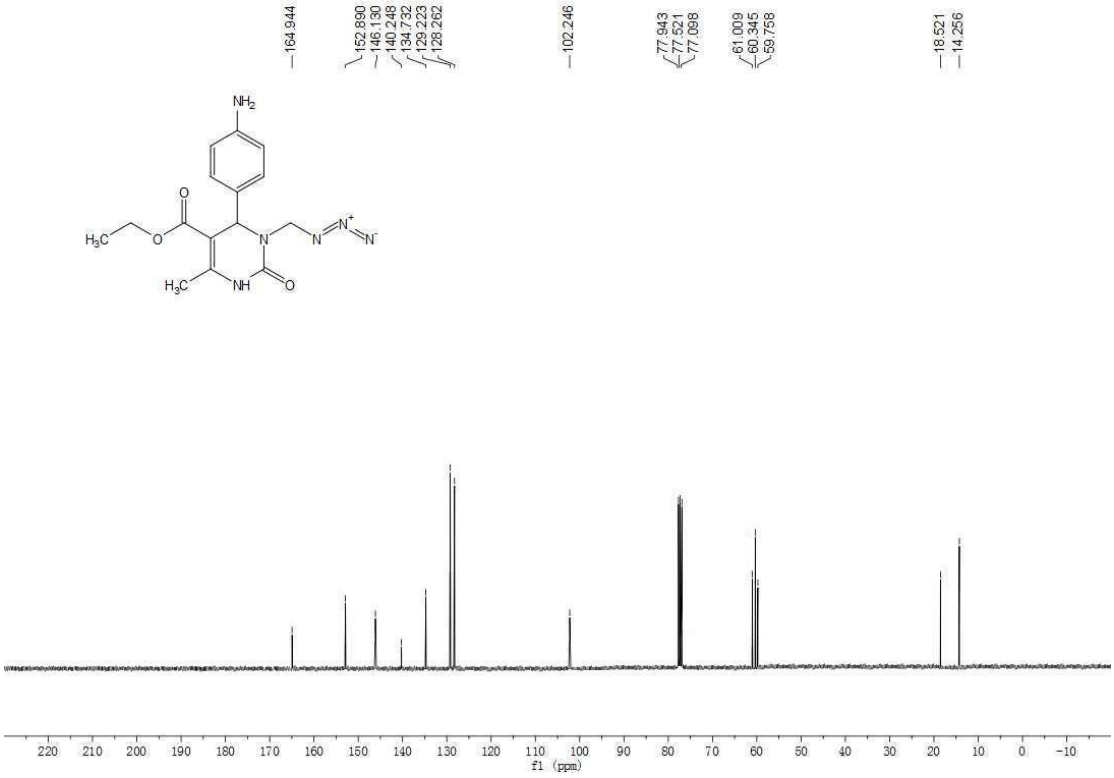




4-(4-Amino-phenyl)-3-azidomethyl-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidin e-5-carboxylic acid ethyl ester (4m)





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