

Synthesis of Primary Amides via Copper-Catalyzed Aerobic Decarboxylative Ammonoxidation of Phenylacetic Acids and α -Hydroxyphenylacetic Acids with Ammonia in Water

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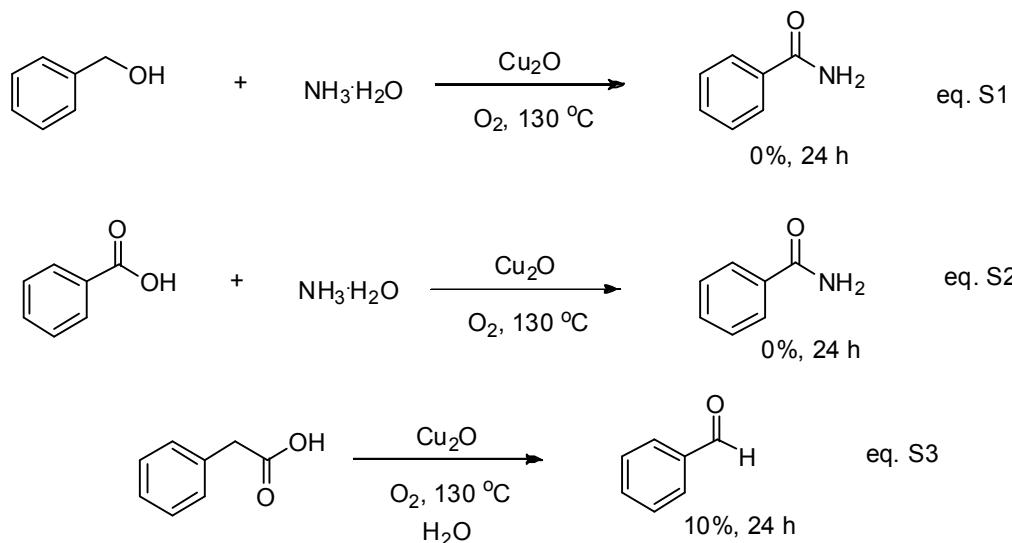
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General information

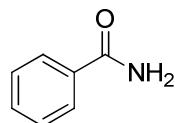
All experiments were conducted with a sealed pressure vessel. Flash column chromatography was performed over silica gel (200-300 mesh). ^1H NMR spectra were recorded on a Bruker AVIII-400M spectrometers, Chemical shifts (in ppm) were referenced to DMSO-d₆ (δ = 2.50 ppm) as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with DMSO-d₆ (δ = 39.6 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and the most materials was purchased from adamas.

Control Experiments



Procedure and characterization data for products

Benzamide (**2**, CAS: 55-21-0)¹

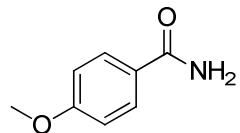


A sealed pressure vessel was charged with phenylacetic acid **1** (68.0 mg, 0.5 mmol), Cu₂O (14 mg, 0.1 mol), and aqueous ammonia solution (28

wt% in H₂O; 1.5 mL). The resulting solution was stirred at 130 °C under O₂ (monitored by TLC and GC) for 24 hours. Upon completion of the reaction, ethyl acetate (20 mL) was added, the organic layer was washed with saturate NaHCO₃ (20 mL) solution twice, brine (20 mL) once, the combined aqueous layers was extracted with EtOAc (20 mL) twice. The combine organic layers were dried over anhydrous Na₂SO₄. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, ethyl acetate: petroleum ether=2:1) to gave 50.3 mg of **2** in 83% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.99 (1H, s), 7.89 (2H, d, *J*=7.2 Hz), 7.53-7.37 (4H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 168.1, 134.4, 131.3, 128.3, 127.6. mp 125-128 °C.

The same procedure was used for α -hydroxyphenylacetic acid **24** and gave 39.3 mg of **2** in 65% isolated yield.

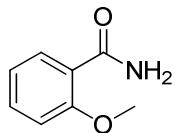
4-methoxybenzamide (**3**, CAS: 3424-93-9)¹



The same procedure was used for 2-(4-methoxyphenyl) acetic acid. The reaction gave 60.5 mg of **3** in 80% yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.85 (3H, d, *J*=8.4 Hz), 7.16 (1H, s), 6.96 (2H, d, *J*=8.4 Hz), 3.79 (3H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 167.5, 161.6, 129.3, 126.5, 113.4, 55.3. mp 164-166 °C.

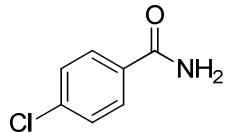
The same procedure was used for 2-hydroxy-2-(4-methoxyphenyl)acetic acid **25** and gave 60.1 mg of **3** in 70% isolated yield .

2-methoxybenzamide (**4**, CAS: 2439-77-2)²



The same procedure was used for 2-(2-methoxyphenyl)acetic acid except that the reaction was carried out at 150°C. The reaction gave 36.2 mg of **4** in 48% yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.81 (1H, d, *J*=7.6 Hz), 7.63 (1H, s), 7.50-7.45 (2H, m), 7.12 (1H, d, 8 Hz), 7.02 (1H, t, *J*=7.2 Hz), 3.88 (3H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.4, 157.3, 132.5, 130.8, 122.8, 120.5, 55.9. mp 127-128 °C.

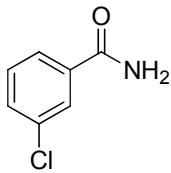
4-chlorobenzamide (**5**, CAS: 619-56-7)¹



The same procedure was used for 2-(4-chlorophenyl)acetic acid. The reaction gave 50.6 mg of **5** in 65% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.04 (1H, s), 7.89 (2H, d, *J*=8.4 Hz), 7.50 (2H, d, *J*=8.4 Hz), 7.44 (1H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.9, 136.1, 133.0, 129.4, 128.3. mp 173-176 °C.

The same procedure was used as for 2-(4-chlorophenyl)-2-hydroxyacetic acid **26** and gave 46.6 mg of **5** in 60% isolated yield .

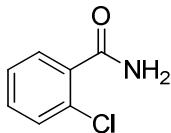
3-chlorobenzamide (**6**, CAS: 618-48-4)¹



The same procedure was used for 2-(3-chlorophenyl)acetic acid. The reaction gave 58.3 mg of **6** in 75% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.08 (1H, s), 7.90 (1H, t, *J*=1.6 Hz), 7.83 (1H, dd, *J*=7.6, 1.3 Hz), 7.58 (1H, t, *J*=8.0 Hz), 7.50-7.46 (2H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.5, 136.3, 133.1, 131.1, 130.2, 127.3, 126.2. mp 134-137 °C.

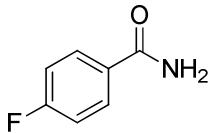
The same procedure was used for 2-(3-chlorophenyl)-2-hydroxyacetic acid **27** and gave 35.0 mg of **6** in 45% isolated yield.

2-chlorobenzamide (**7**, CAS: 609-66-5)¹



The same procedure was used for 2-(2-chlorophenyl)acetic acid. The reaction gave 70.0 mg of **7** in 90% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.85 (1H, s), 7.56 (1H, s), 7.48-7.35 (4H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 168.2, 137.1, 130.6, 129.6 (2C), 128.6, 127.0. mp 142-143 °C.

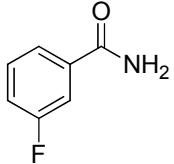
4-fluorobenzamide (**8**, CAS: 824-75-9)¹



The same procedure was used as for 2-(4-fluorophenyl)acetic acid. The reaction gave 38.3 mg of **8** in 55% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.98-7.92 (3H, m), 7.37 (1H, s), 7.27 (2H, t, *J*=9.2 Hz). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.8, 163.9 (d, *J*=246.8 Hz), 130.7 (d, *J*=2.7 Hz), 130.1 (d, *J*=8.9 Hz), 115.1 (d, *J*=21.6 Hz). mp 154-157 °C.

The same procedure was used for 2-(4-fluorophenyl)-2-hydroxyacetic acid **28** and gave 34.8 mg of **8** in 50% isolated yield.

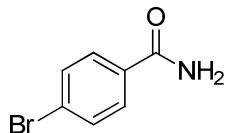
3-fluorobenzamide (**9**, CAS: 455-37-8)¹



The same procedure was used for 2-(3-fluorophenyl)acetic acid. The reaction gave 41.6 mg of **9** in 60% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.05 (1H, s), 7.72 (1H, d, *J*=7.6 Hz), 7.66 (1H, d, *J*=10 Hz), 7.51 (2H, t, *J*=7.6 Hz), 7.36 (1H, t, *J*=8 Hz). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.5, 161.9 (d, *J*_{CF}=242.2 Hz), 136.7 (d, *J*_{3CF}=8.6 Hz), 130.3 (d, *J*_{3CF}=7.8 Hz), 123.6 (d, *J*_{4CF}=2.1 Hz), 118.1 (d, *J*_{3CF}=21 Hz), 114.2 (d, *J*_{3CF}=22.4 Hz). mp 129-133 °C.

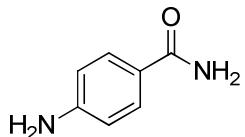
The same procedure was used for 2-(3-fluorophenyl)-2-hydroxyacetic acid **30** and gave 41.5 mg of **9** in 60% isolated yield.

4-bromobenzamide (**10**, CAS: 698-67-9)¹



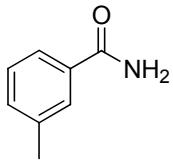
The same procedure was used for 2-(4-bromophenyl)acetic acid except that the reaction was carried out at 95 °C. The reaction gave 40 mg of **10** in 40% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.03 (1H, s), 8.80 (2H, d, *J*=8.4 Hz), 7.65 (2H, d, *J*=8.4 Hz), 7.44 (1H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 161.0, 133.5, 131.3, 129.7, 125.1. mp 191-194 °C.

4-aminobenzamide (**11**, CAS: 2835-68-9)⁸



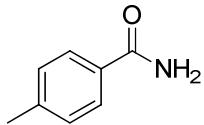
The same procedure was used for 2-(4-bromophenyl)acetic acid. The reaction gave 24.5 mg of **11** in 36% isolated yield as a light yellow solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.58 (2H, d, *J*=8.4 Hz), 7.50 (1H, s), 6.81 (1H, s), 6.52 (2H, d, *J*=8.8 Hz), 5.57 (2H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 168.1, 151.6, 129.1, 120.9, 122.5. mp 180-183 °C.

3-methylbenzamide (**12**, CAS: 618-47-3)¹



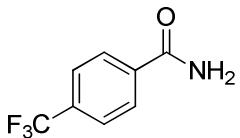
The same procedure was used for 2-(m-tolyl)acetic acid except that the reaction was carried out at 110 °C. The reaction gave 44.0 mg of **12** in 65% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.68 (1H, s), 7.36-7.28 (3H, m), 7.23-7.19 (2H, m), 2.37 (3H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 171.1, 137.0, 135.1, 130.4, 129.2, 127.0, 125.4, 19.5. mp 94-96 °C.

4-methylbenzamide (**13**, CAS: 619-55-6)¹



The same procedure was used for 2-(p-tolyl)acetic acid. The reaction gave 40.5 mg of **13** in 60% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.88 (1H, s), 7.77 (2H, d, *J*=8 Hz), 7.24 (3H, d, *J*=7.6 Hz), 2.34 (3H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 167.8, 141.0, 131.5, 128.7, 127.5, 20.9. mp 160-162 °C.

4-(trifluoromethyl)benzamide (**14**, CAS: 1891-90-3)¹

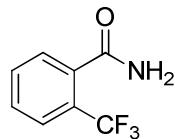


The same procedure was used for 2-(4-(trifluoromethyl)phenyl)acetic

acid except that the reaction was carried out at 100 °C. The reaction gave 53.0 mg of **14** in 56% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.19 (1H, s), 8.06 (2H, d, *J*=8.4 Hz), 7.81 (2H, d, *J*=8.0 Hz), 7.61 (1H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.9, 138.2, 131.3 (d, *J*=31.6 Hz), 128.4, 125.3 (d, *J*=3.7 Hz), 122.7. mp 184-186 °C.

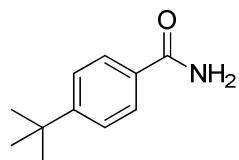
The same procedure was used for 2-hydroxy-2-(4-(trifluoromethyl)phenyl)acetic acid **31** and gave 48.2 mg of **14** in 38% isolated yield.

2-(trifluoromethyl)benzamide (**15**, CAS: 360-64-5)³



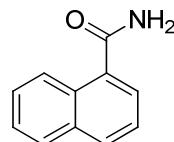
The same procedure was used for 2-(2-(trifluoromethyl)phenyl)acetic acid except that the reaction was carried out at 110 °C. The reaction gave 46.3 mg of **15** in 49% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.93 (1H, s), 7.77-7.68 (2H, m), 7.64-7.52 (3H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 169.1, 136.8, 132.3, 129.4, 128.2, 126.2-125.2 (m, CF₃), 122.4. mp 160-164 °C.

4-(tert-butyl)benzamide (**16**, CAS: 56108-12-4)⁴



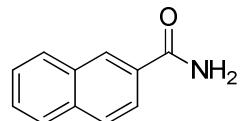
The same procedure was used for 2-(4-(tert-butyl)phenyl)acetic acid except that the reaction was carried out at 140 °C. The reaction gave 71.7 mg of **16** in 81% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.88 (1H, s), 7.80 (2H, d, *J*=8 Hz), 7.44 (2H, d, *J*=8.4 Hz), 7.24 (1H, s), 1.28 (9H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 167.8, 153.9, 131.5, 127.3, 124.9, 34.5, 30.9. mp 185-187 °C.

1-naphthamide (**17**, CAS: 2243-81-4)¹



The same procedure was used for 2-(naphthalen-1-yl)acetic acid except that the reaction was carried out at 140 °C. The reaction gave 60.7 mg of **17** in 71% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.36 (1H, d, *J*=7.6 Hz), 8.04-7.96 (3H, m), 7.69-7.52 (5H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 170.7, 134.6, 133.2, 129.8, 129.7, 128.2, 126.6, 126.1, 125.6, 125.2, 125.0. mp 197-199 °C.

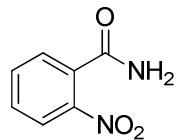
2-naphthamide (**18**, CAS: 2243-82-5)¹



The same procedure was used for 2-(naphthalen-2-yl)acetic acid. The reaction gave 68 mg of **18** in 80% isolated yield as a white solid. ¹H

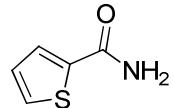
NMR: (400 MHz, DMSO-d₆, ppm) δ 8.51 (1H, s), 8.16 (1H, s), 8.01-7.95 (4H, m), 7.60 (d, *J*=11.6 Hz), 7.52 (d, *J*=2.8 Hz). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 168.0, 134.2, 132.1, 131.6, 128.8, 127.8 (2C), 127.5, 126.6, 124.4. mp 192-194 °C.

2-nitrobenzamide (**19**, CAS: 610-15-1)⁵



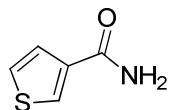
The same procedure was used for 2-(2-nitrophenyl)acetic acid. The reaction gave 53.1 mg of **19** in 64% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.13 (1H, s), 7.98 (1H, d, *J*=8.0 Hz), 7.76 (1H, t, *J*=7.6 Hz), 7.68 (3H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 167.2, 147.2, 133.3, 132.6, 130.6, 128.8, 123.9. mp 175-179 °C.

Thiophene-2-carboxamide (**20**, CAS: 5813-89-8)¹



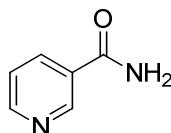
The same procedure was used for 2-(thiophen-2-yl)acetic acid. The reaction gave 45.1 mg of **20** in 71% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.95 (1H, s), 7.74-7.18 (2H, m), 7.35 (1H, s), 7.13-7.11 (1H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 163.0, 140.4, 131.0, 128.8, 128.0. mp 181-183 °C.

thiophene-3-carboxamide (**21**, CAS: 51460-47-0)¹



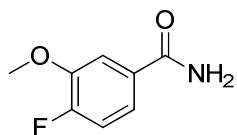
The same procedure was used for 2-(thiophen-3-yl)acetic acid. The reaction gave 54.0 mg of **21** in 71% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 8.13-8.12 (1H, m), 7.78 (1H, s), 7.53(2H, d, *J*=2.8 Hz), 7.49 (1H, s), 7.21 (1H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 163.0, 140.4, 131.0, 128.8, 128.0. mp 182-184 °C.

Nicotinamide (**22**, CAS: 98-92-0)¹



The same procedure was used for 2-(pyridin-3-yl)acetic acid. The reaction gave 42.4 mg of **22** in 62% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 9.03 (1H, s), 8.69 (1H, d, *J* = 3.2 Hz), 8.21-8.16 (2H, m), 7.59 (1H, s), 7.48 (1H, t, *J* = 2.8 Hz). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.6, 152.0, 148.8, 135.3, 129.8, 123.5. mp 128-131 °C.

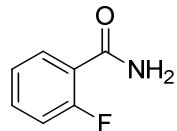
4-fluoro-3-methoxybenzamide (**23**, CAS: 874804-32-7)⁶



The same procedure was used for 2-(4-fluoro-3-methoxyphenyl)acetic

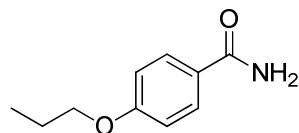
acid except that the reaction was carried out at 95 °C. The reaction gave 27.0 mg of **23** in 32% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.99 (1H, s), 7.64 (1H, dd, *J*=8.4, 2.0 Hz), 7.51-7.47 (1H, m), 7.38 (1H, s), 7.27 (1H, dd, *J*=11.2, 8.4 Hz), 3.88 (3H, s). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 166.8, 153.3 (d, *J*=247.5 Hz), 152.1, 146.8 (d, *J*=10.9 Hz), 131.0 (d, *J*=3.2 Hz), 120.5 (d, *J*= 7.7 Hz), 115.5 (d, *J*=18.4 Hz), 113.1, 56.0.

2-fluorobenzamide (**33**, CAS: 445-28-3)⁹



The same procedure was used for 2-(2-fluorophenyl)-2-hydroxyacetic acid **29**. The reaction gave 43.7 mg of **33** in 53% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.68-7.61 (3H, m), 7.54-7.49 (1H, m), 7.28-7.23 (2H, m). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 165.3, 159.3 (d, *J*=247.5 Hz), 132.4 (d, *J*=8.5 Hz), 130.2 (d, *J*=2.7 Hz), 124.4 (d, *J*=3.1 Hz), 123.8 (d, *J*=14.0 Hz), 116.1 (d, *J*=22.5 Hz). mp 116-119 °C.

4-propoxybenzamide (**34**, CAS: 350988-71-5)



The same procedure was used for 2-hydroxy-2-(4-propoxyphenyl)acetic acid **32**. The reaction gave 64.4 mg of **34** in 72% isolated yield as a white solid. ¹H NMR: (400 MHz, DMSO-d₆, ppm) δ 7.85-7.82 (3H, m), 7.15 (1H, s), 6.97-6.93 (2H, m), 3.96 (2H, t, *J*=6.4 Hz), 1.72 (2H, dd, *J*=14, 6.8 Hz), 0.96 (3H, t, *J*=7.6 Hz). ¹³C NMR: (100 MHz, DMSO-d₆, ppm) δ 168.0, 161.5, 129.8, 126.8, 114.3, 69.6, 22.4, 10.8. mp 154-156 °C.

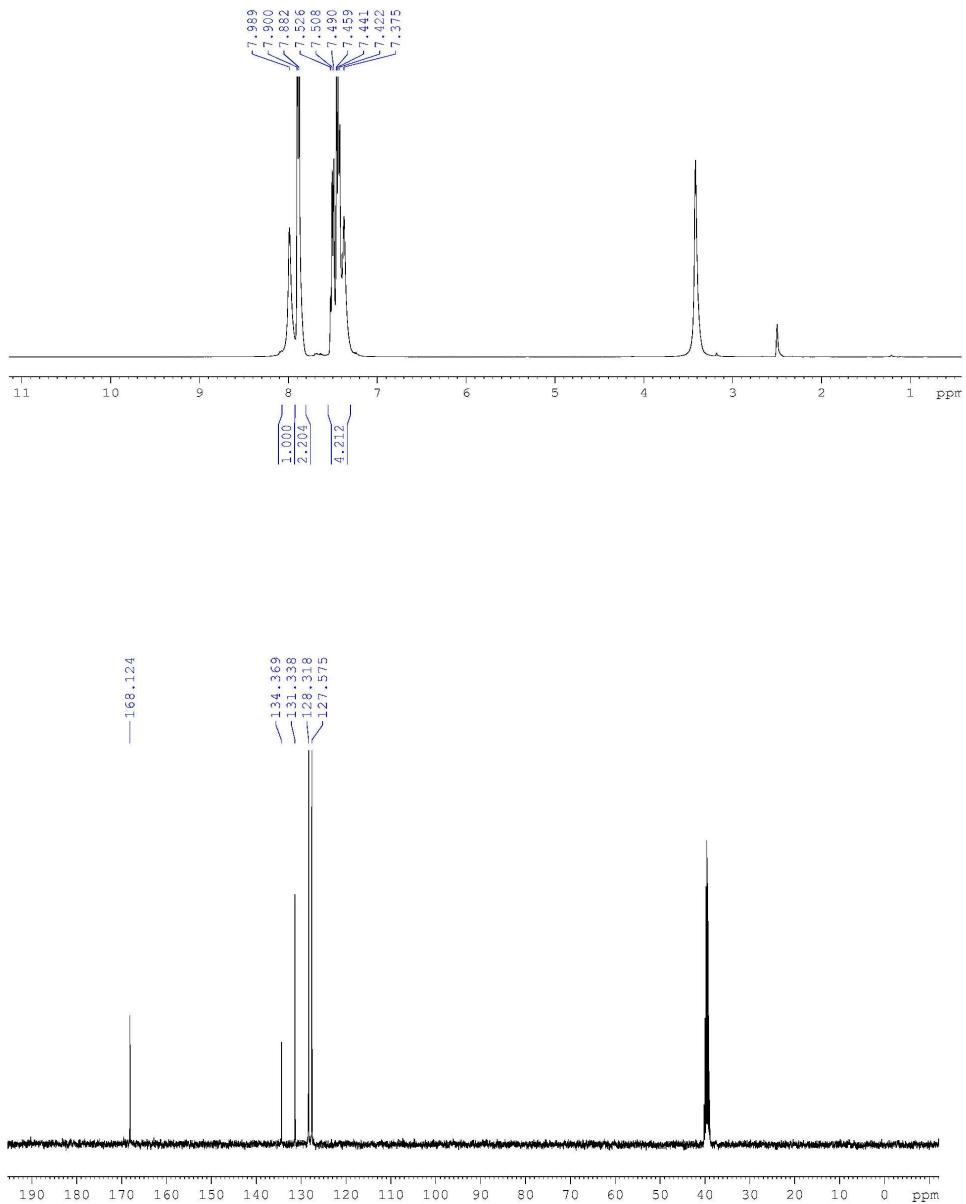
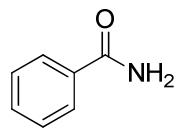
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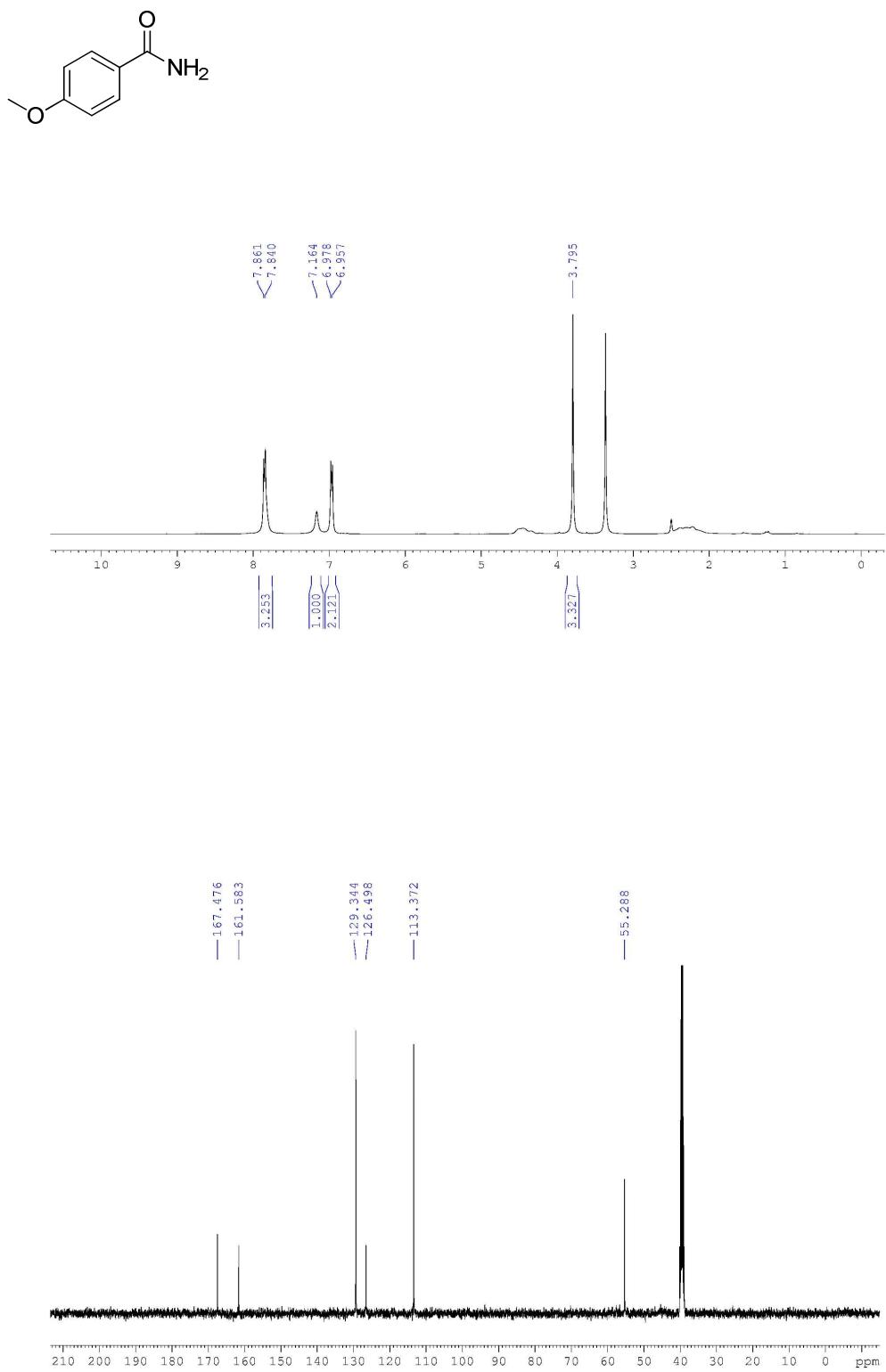
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Spectroscopic data

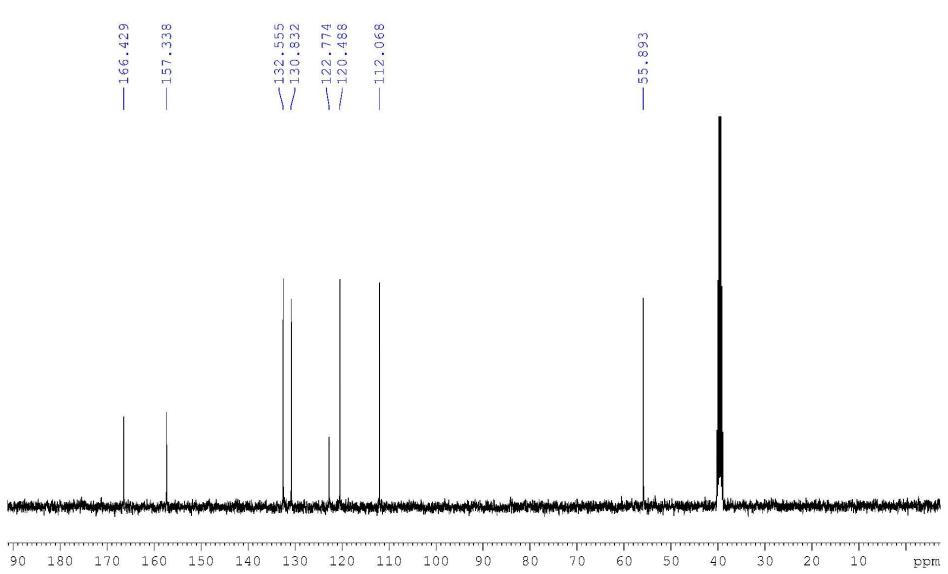
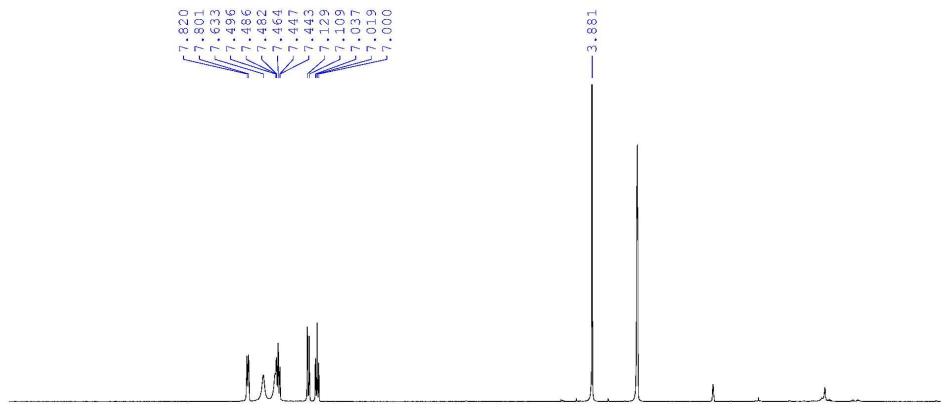
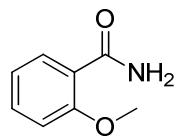
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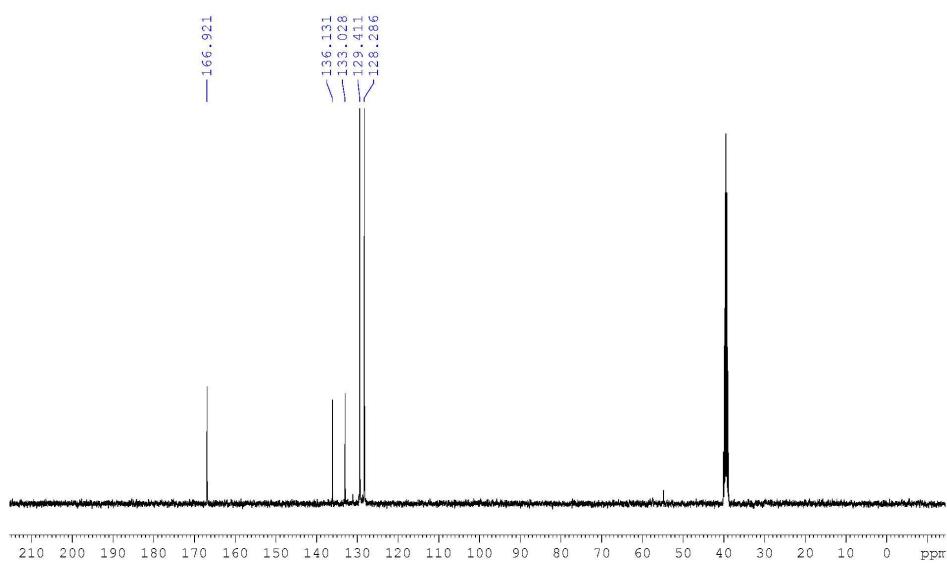
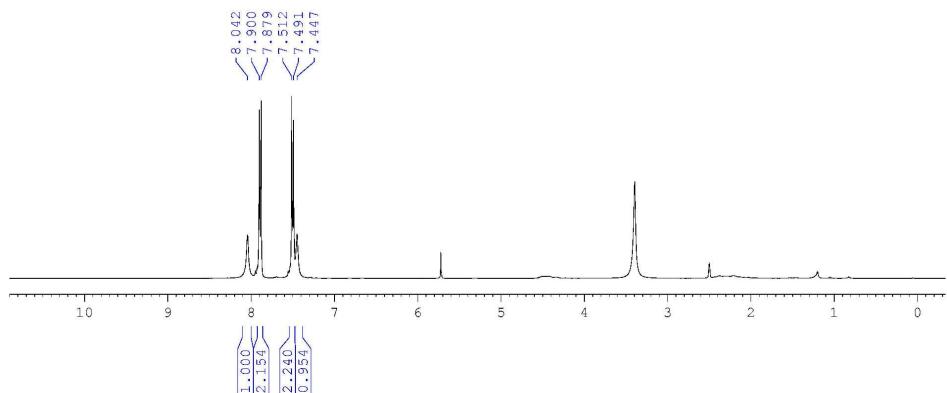
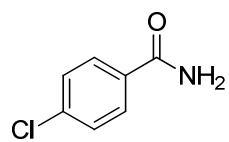
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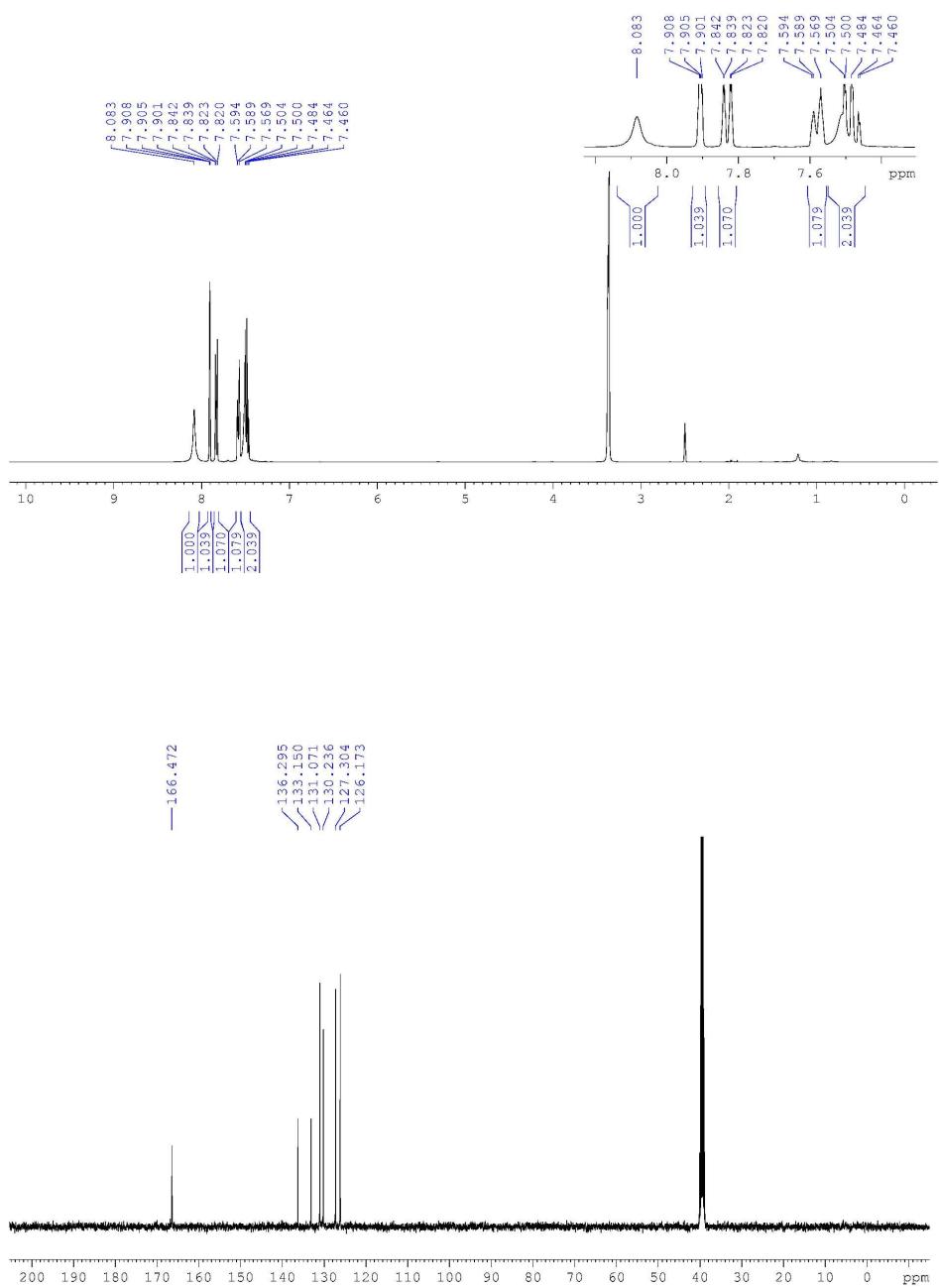
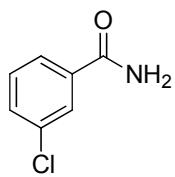
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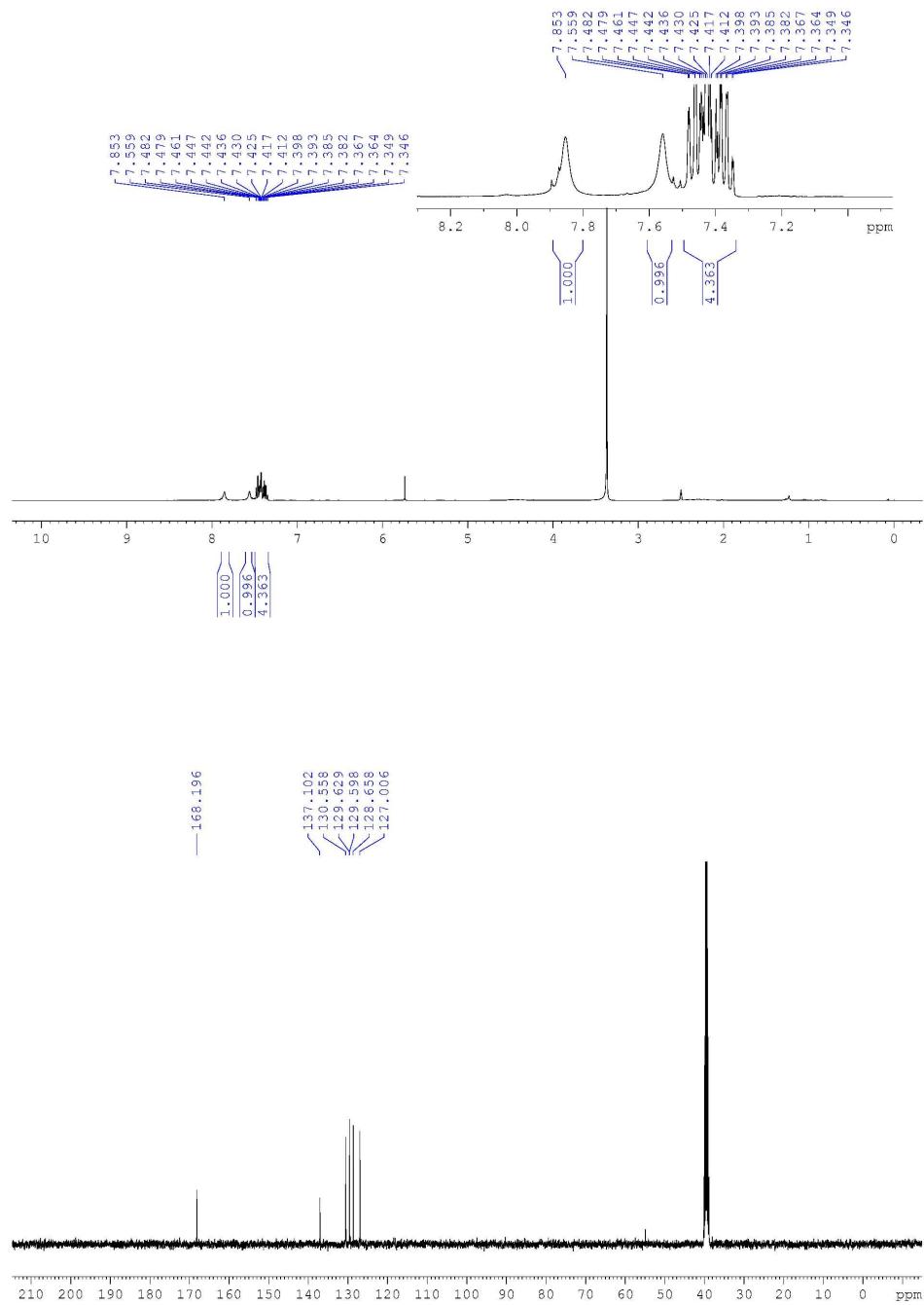
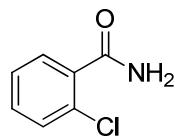
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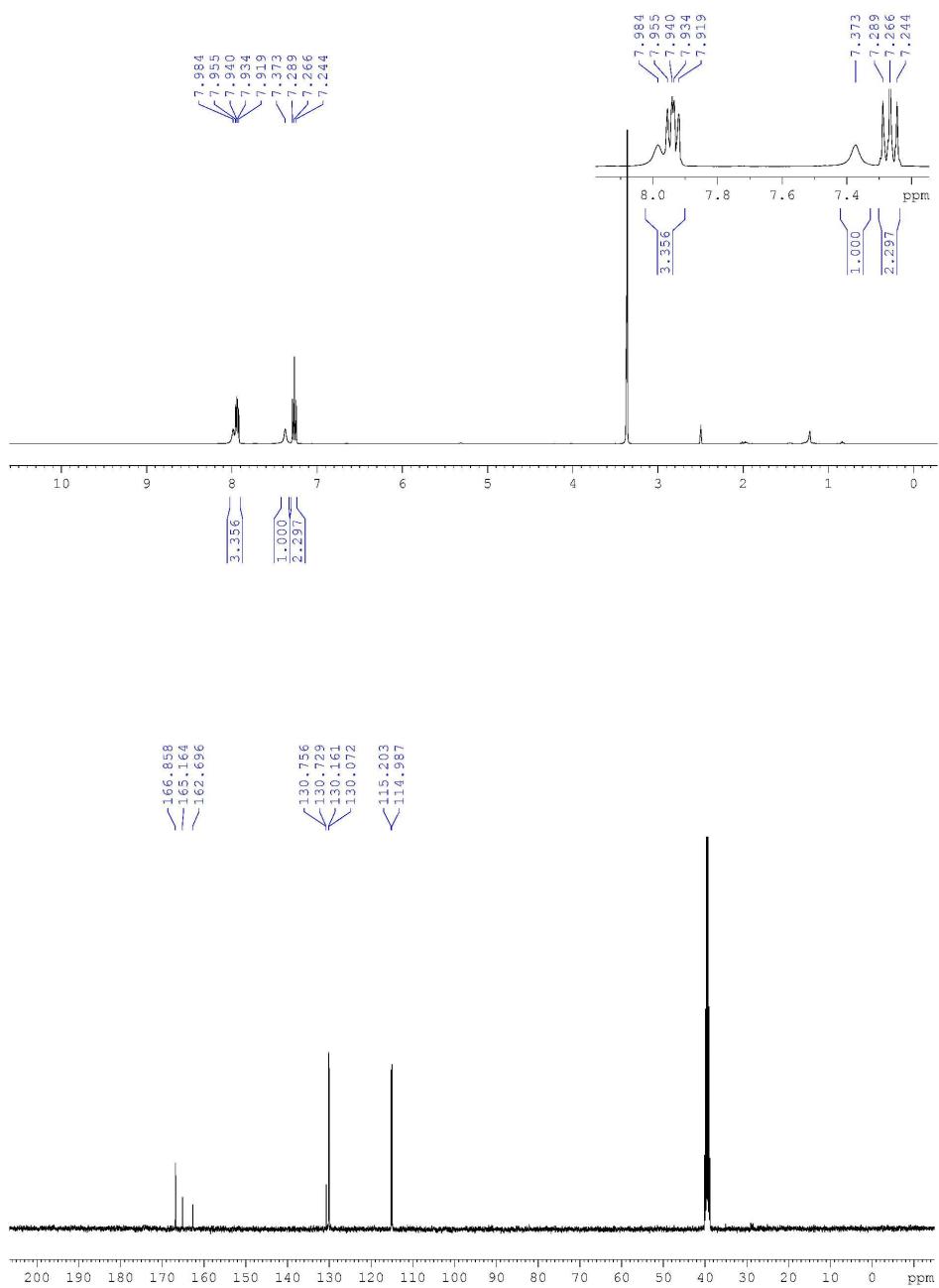
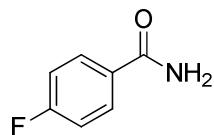
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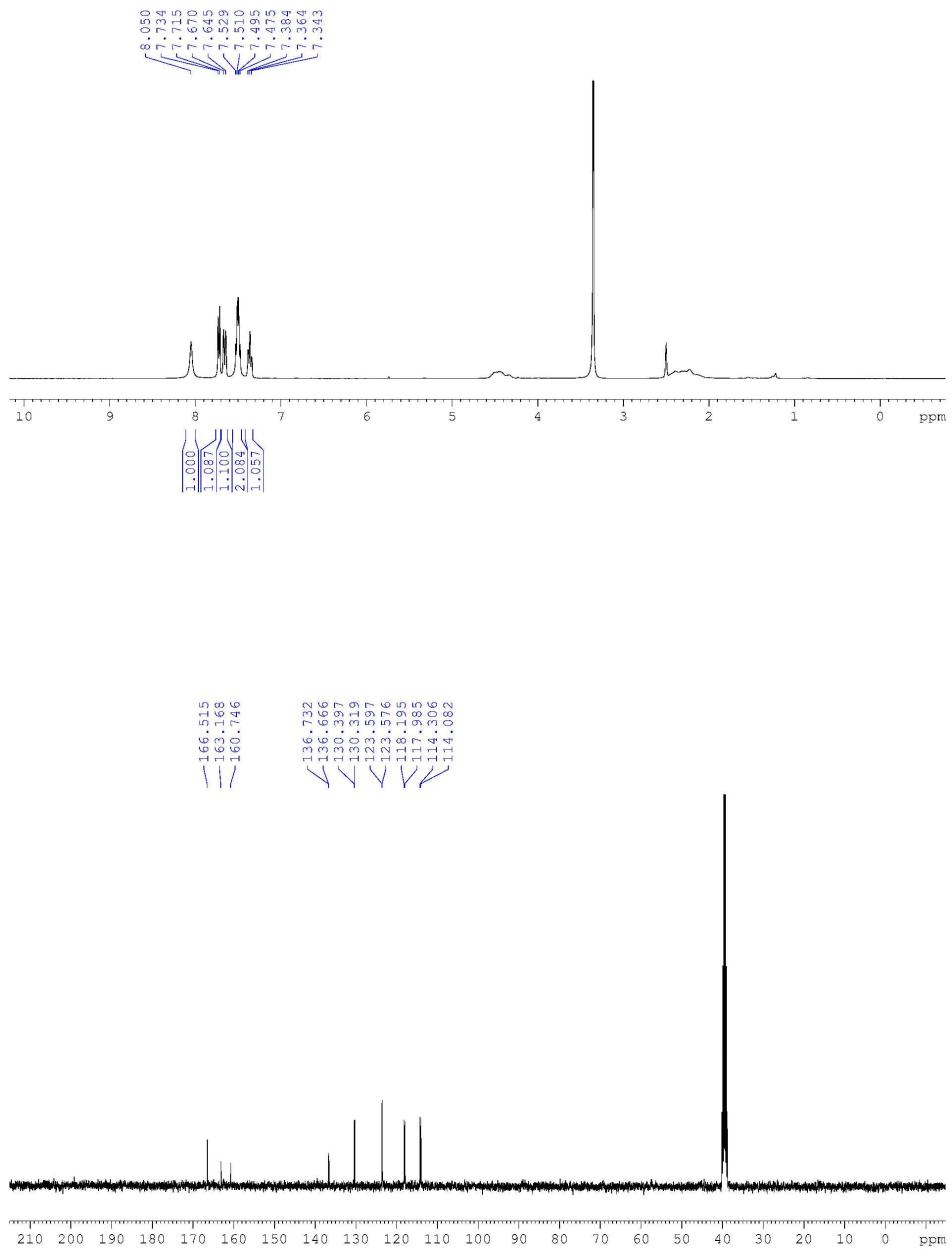
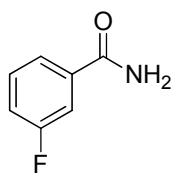
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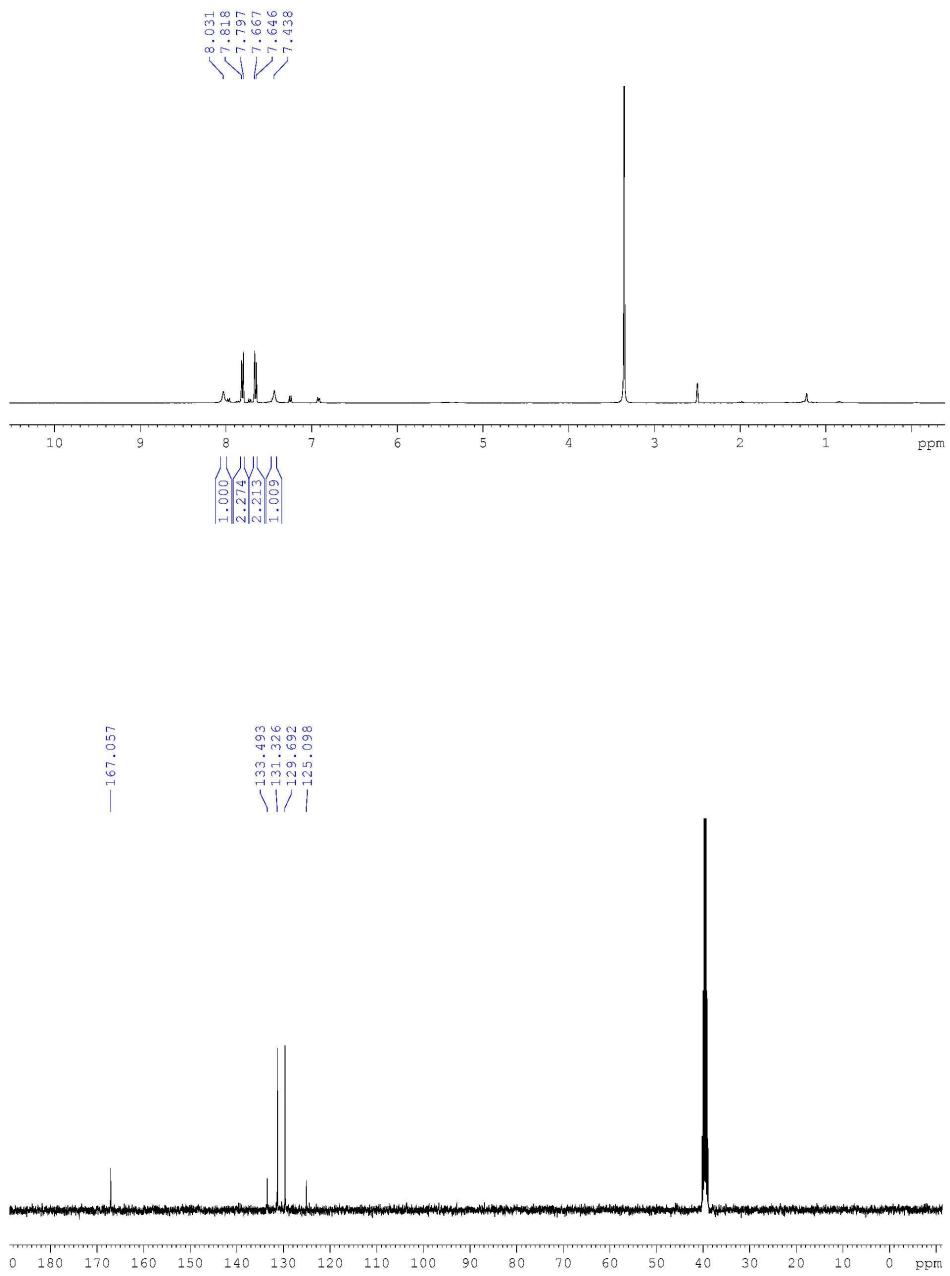
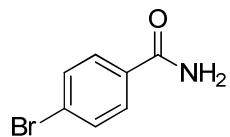
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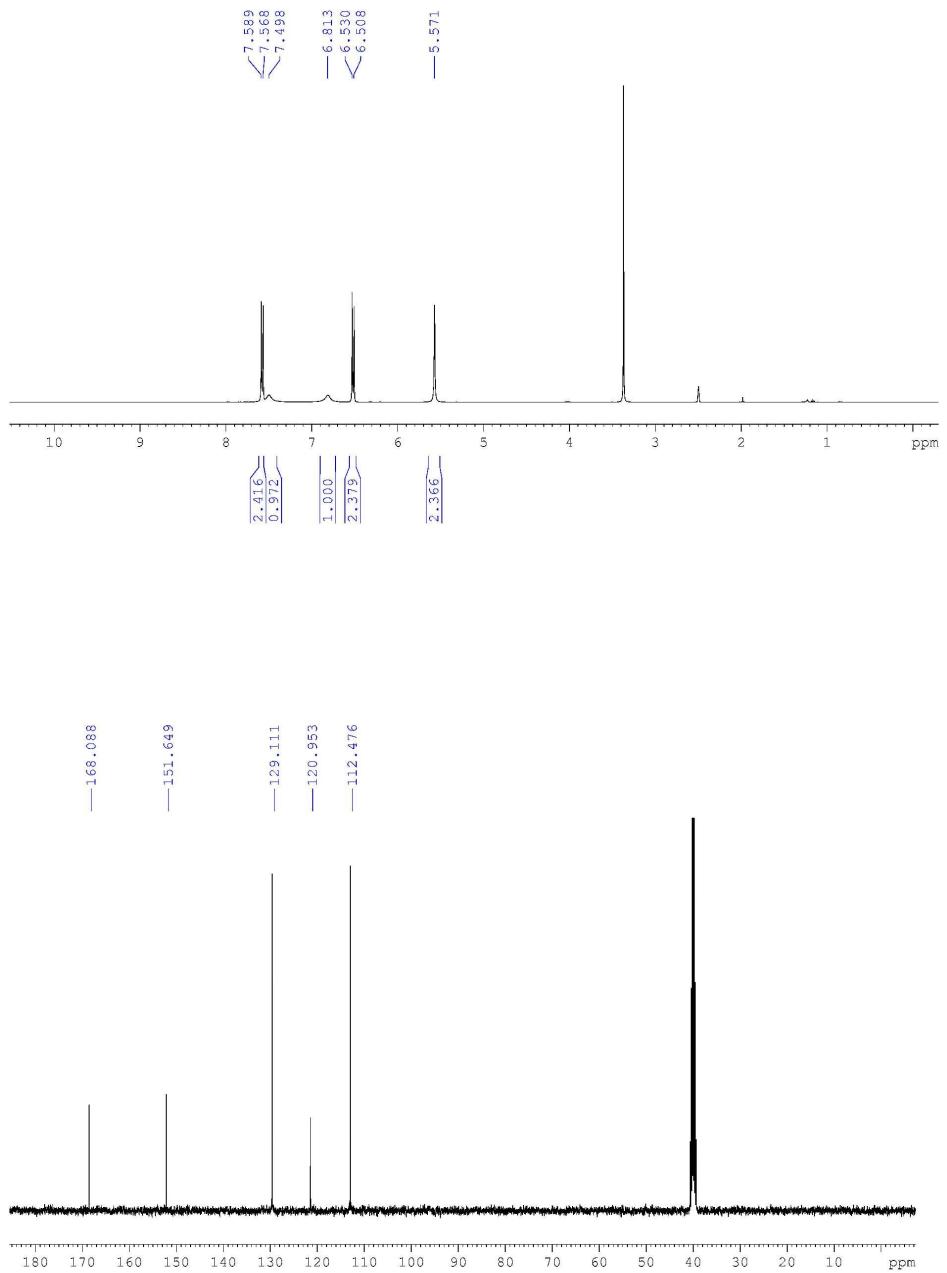
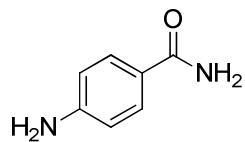
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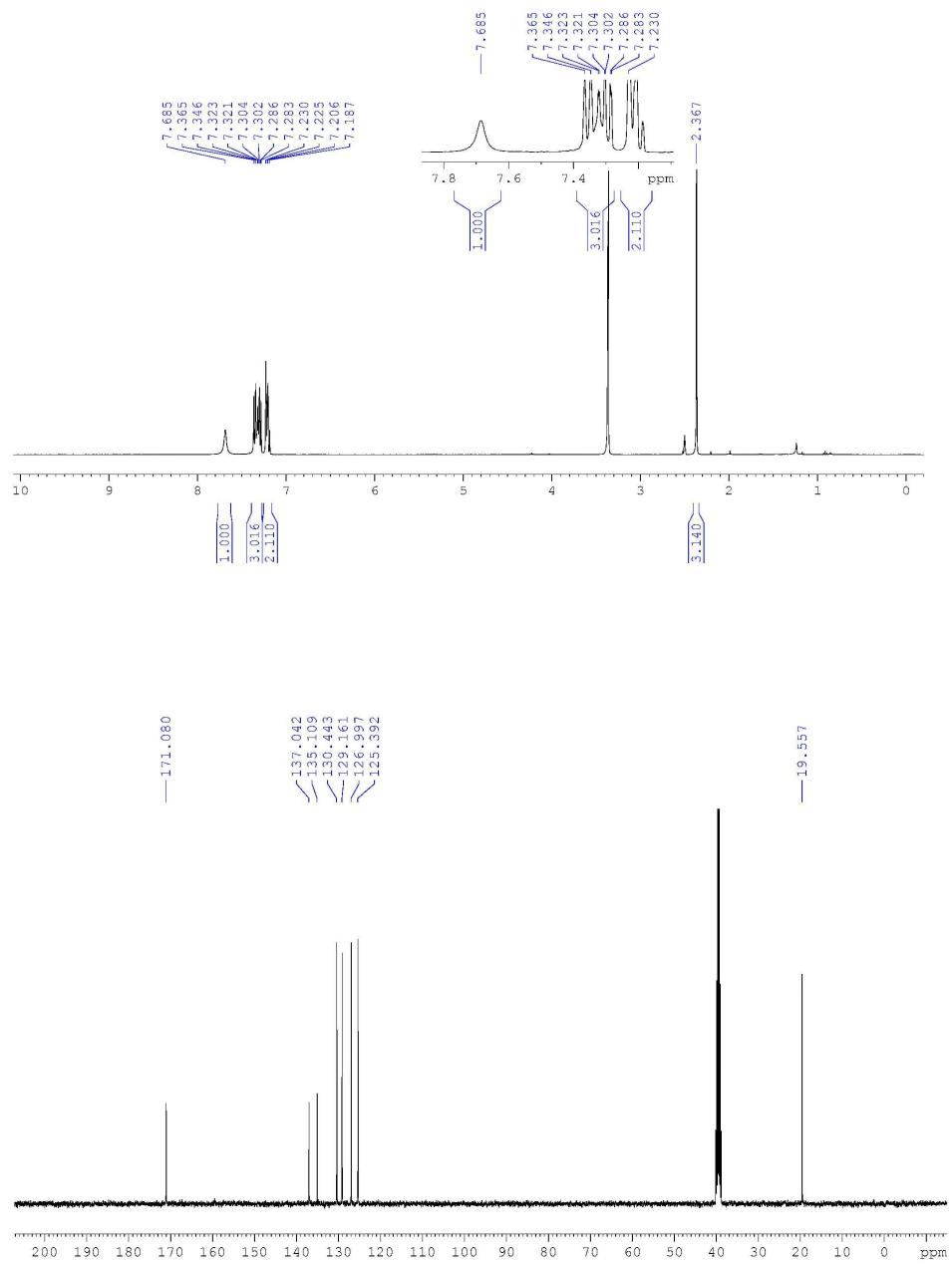
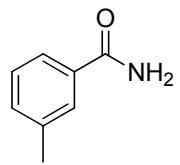
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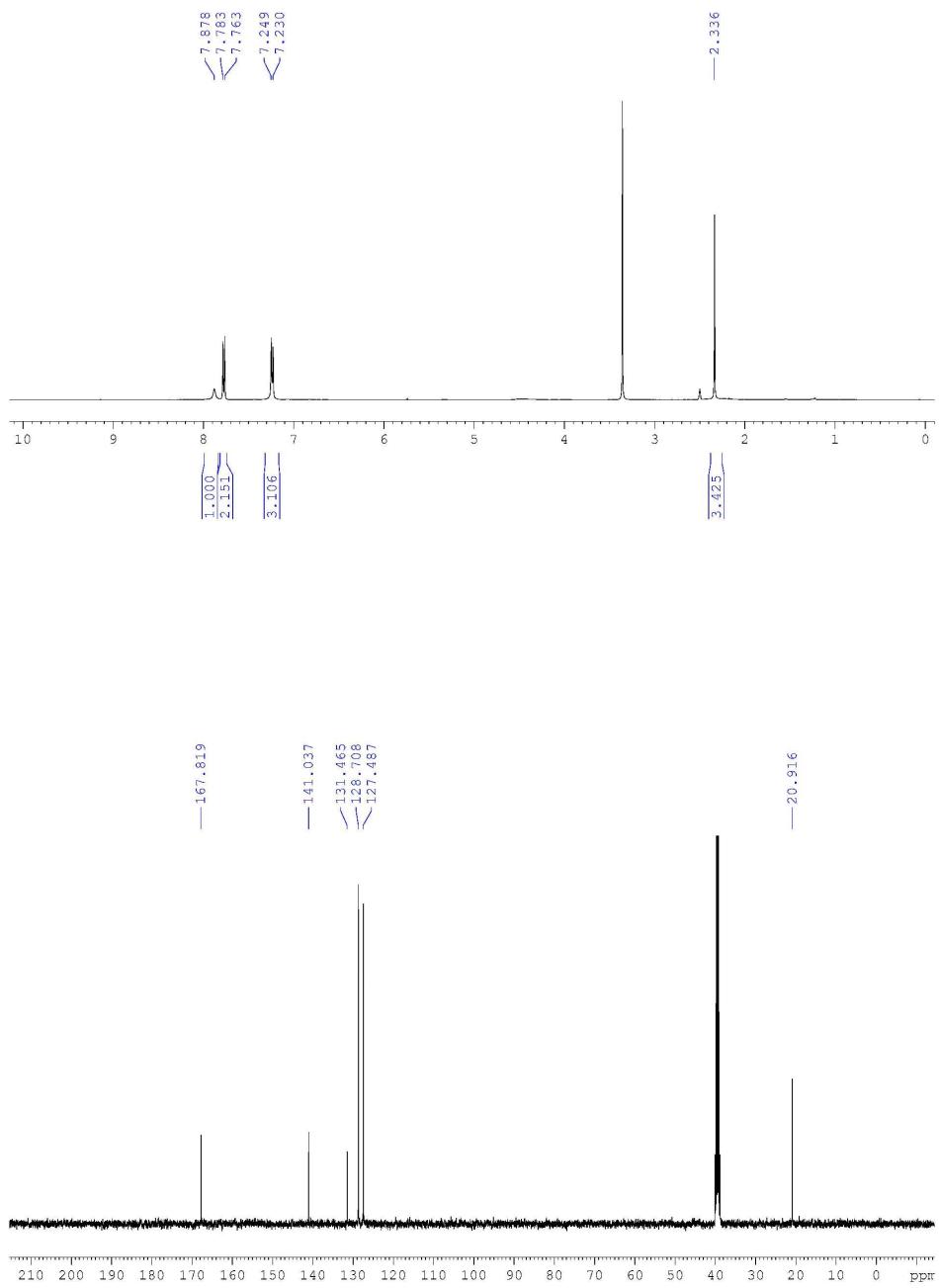
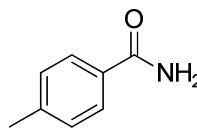
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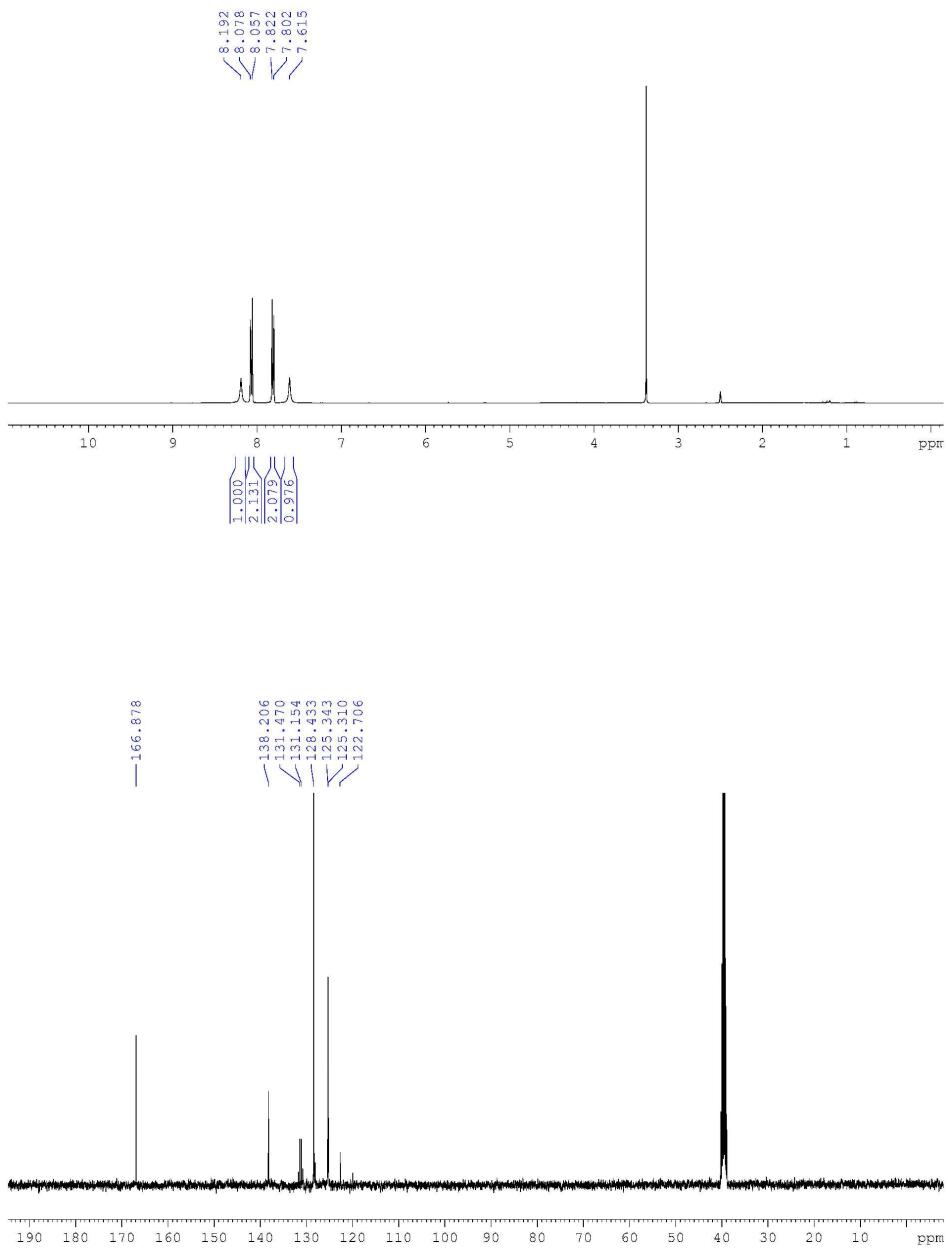
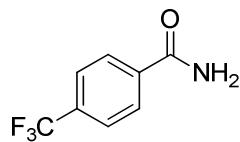
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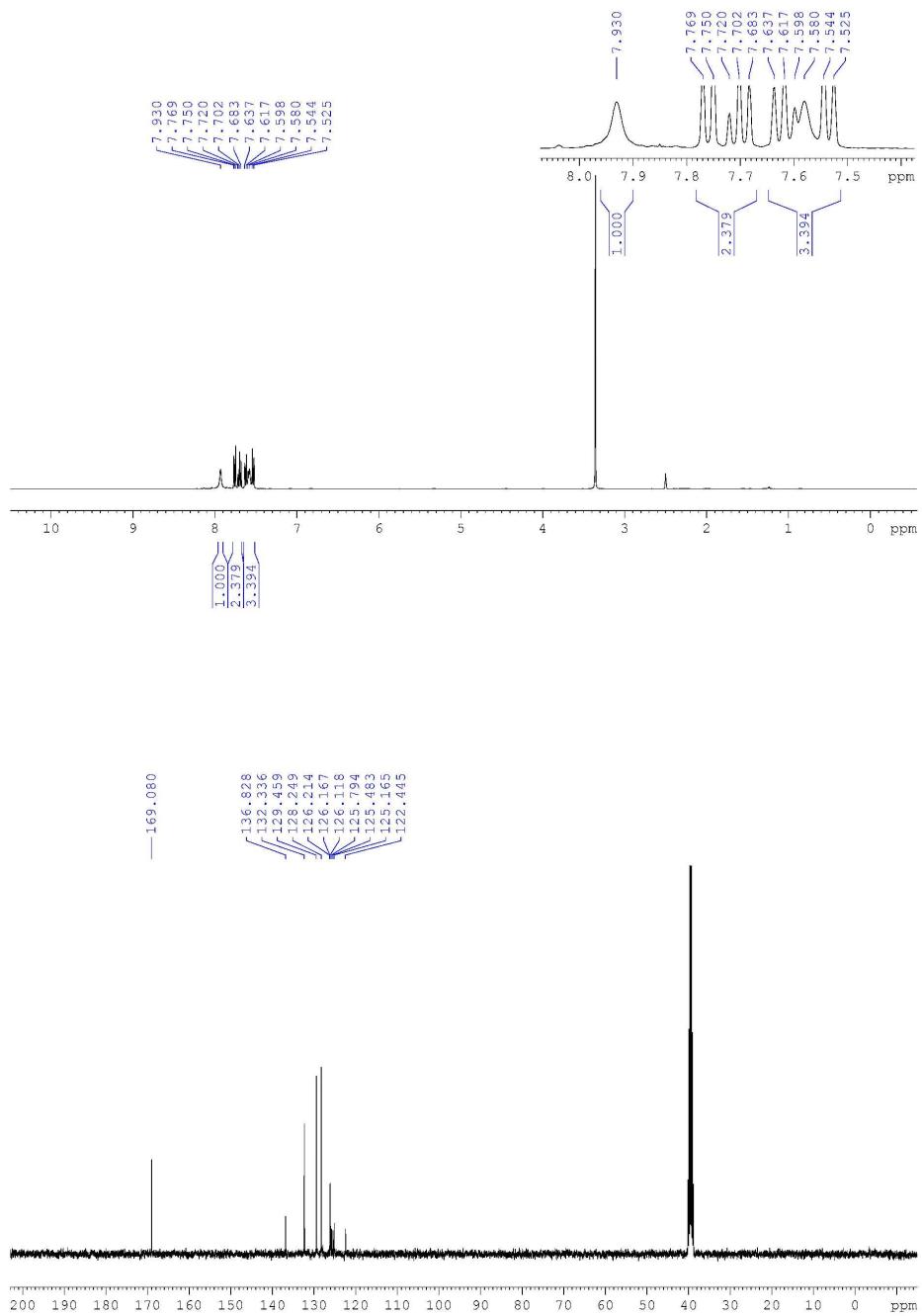
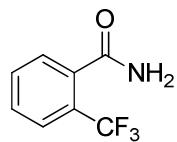
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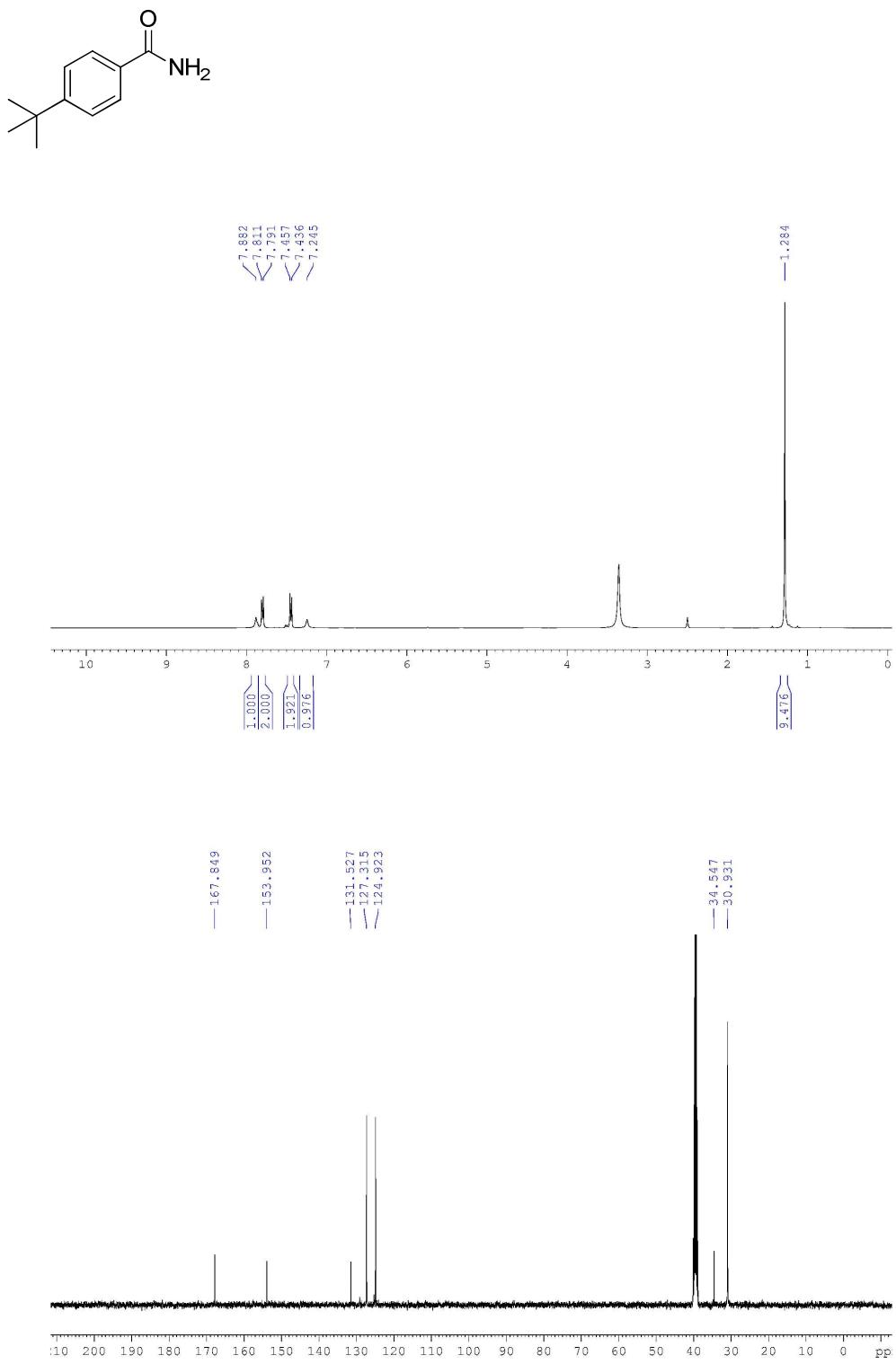
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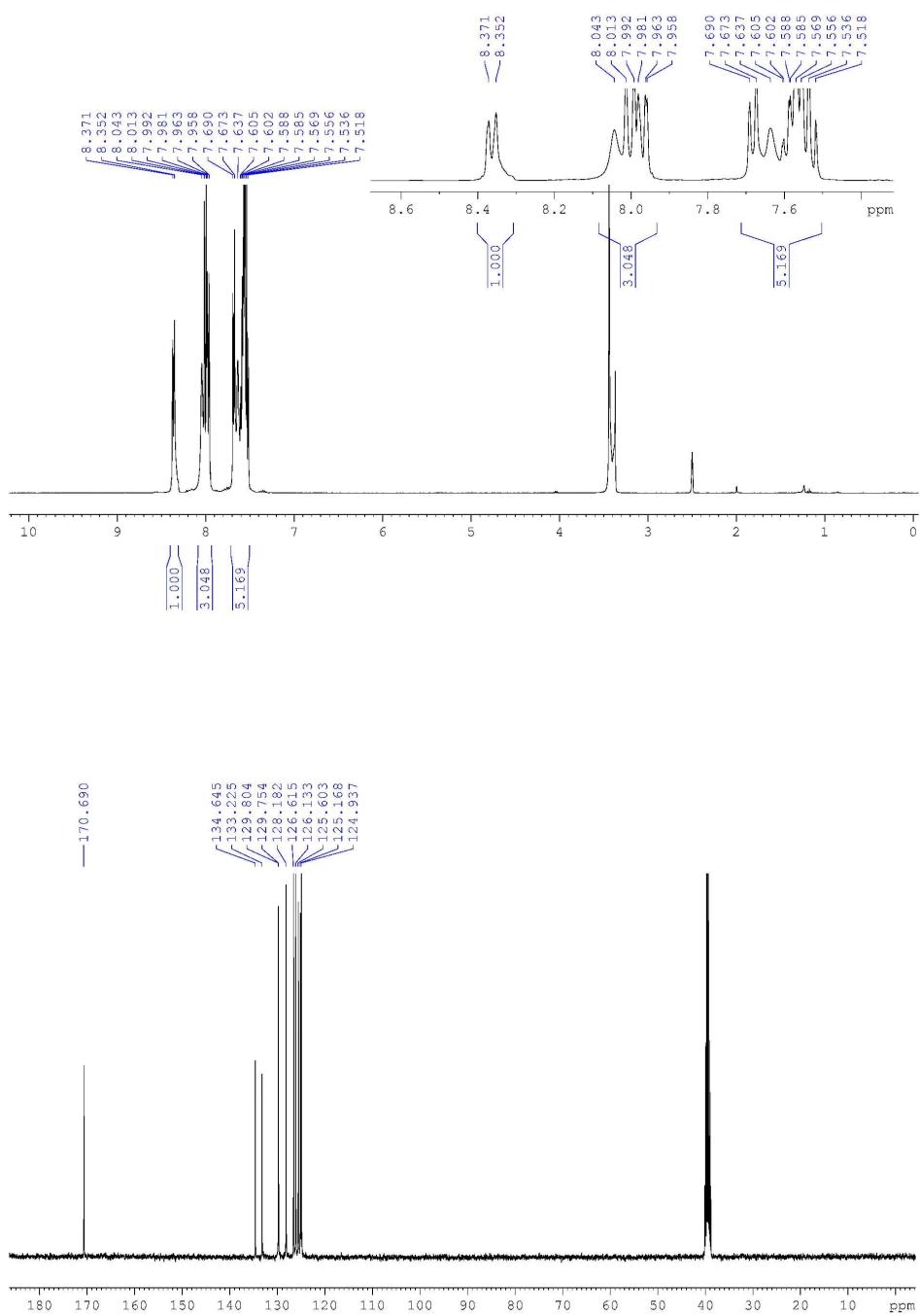
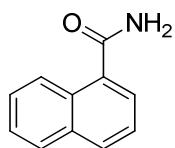
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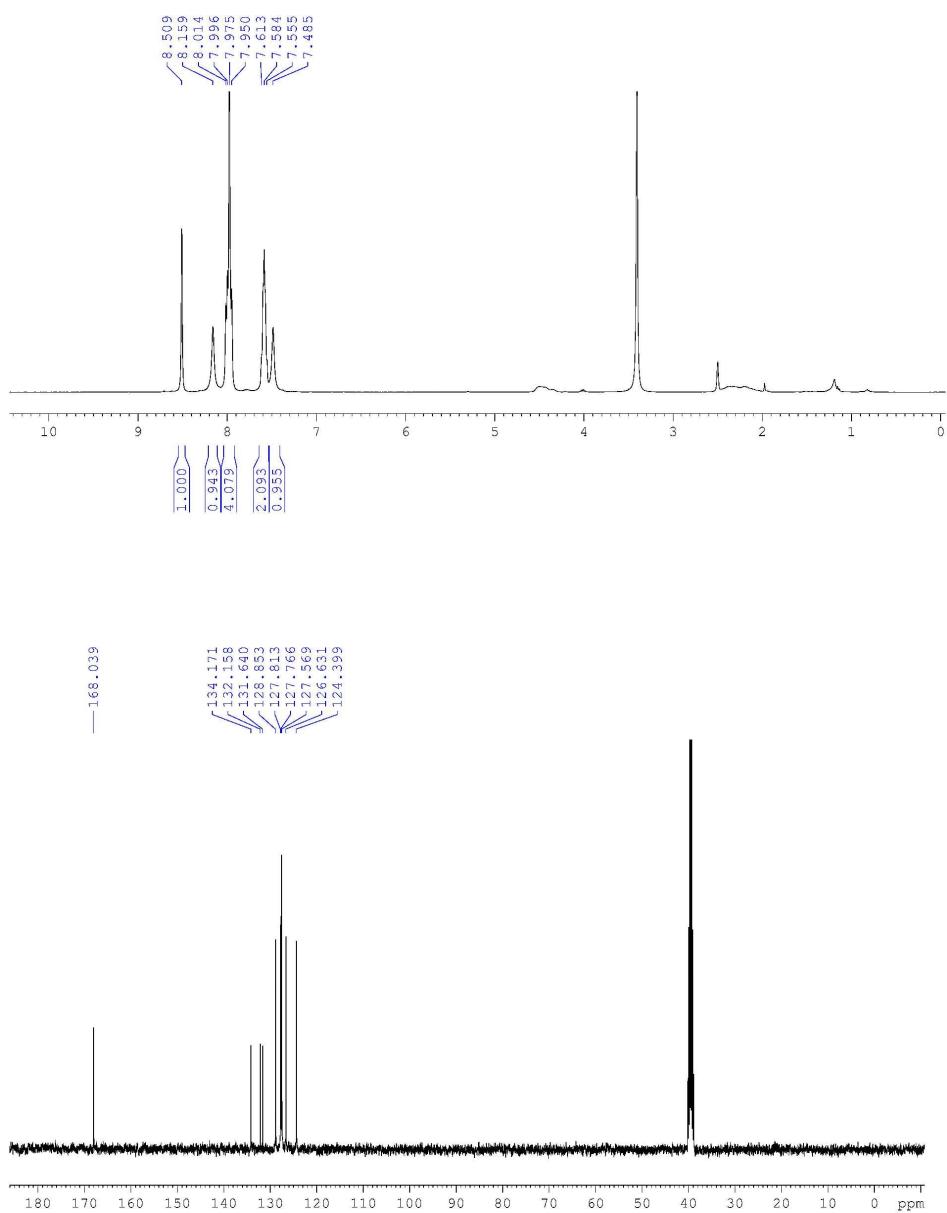
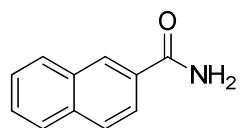
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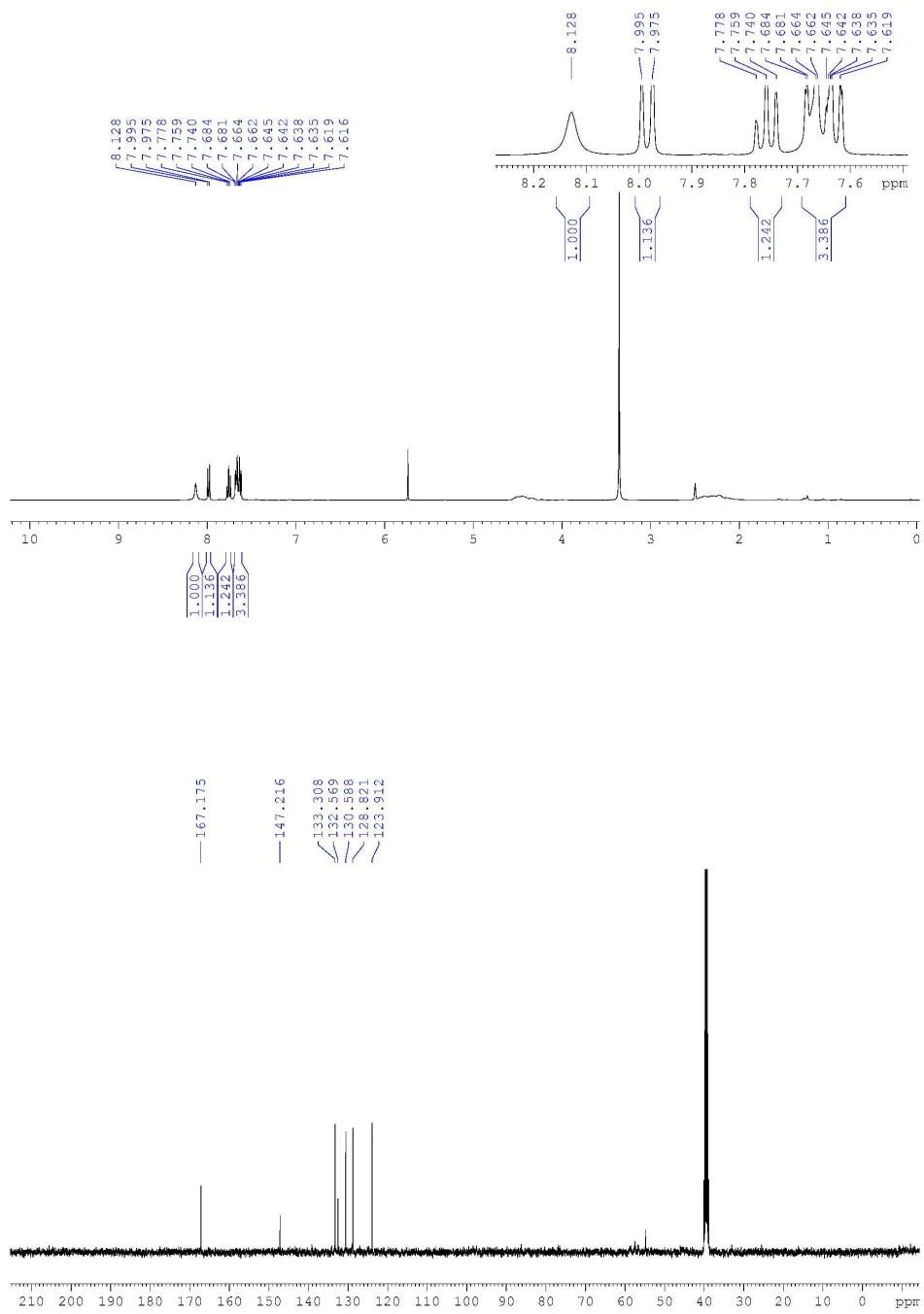
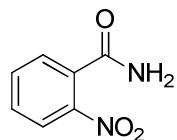
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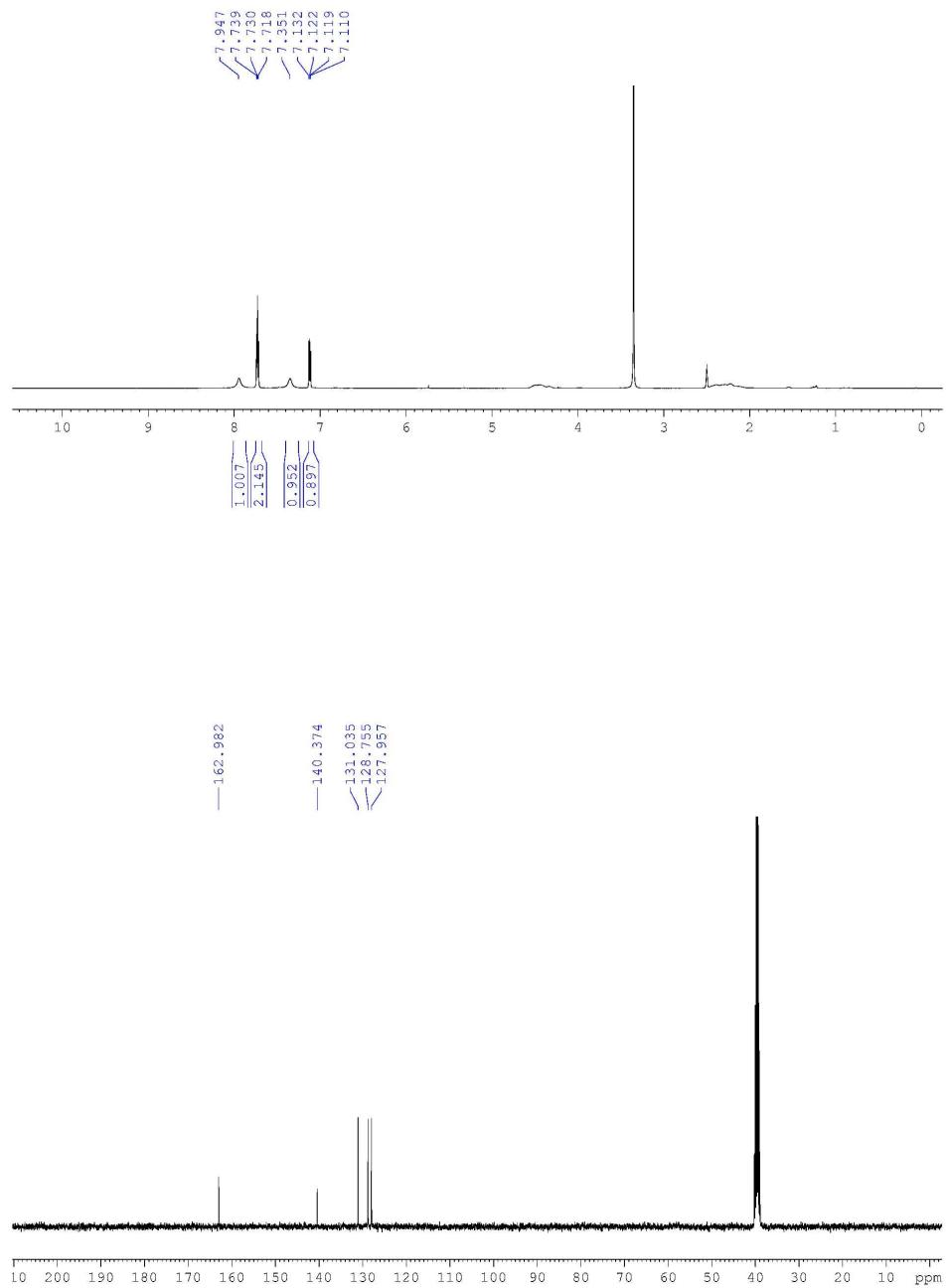
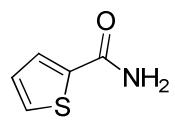
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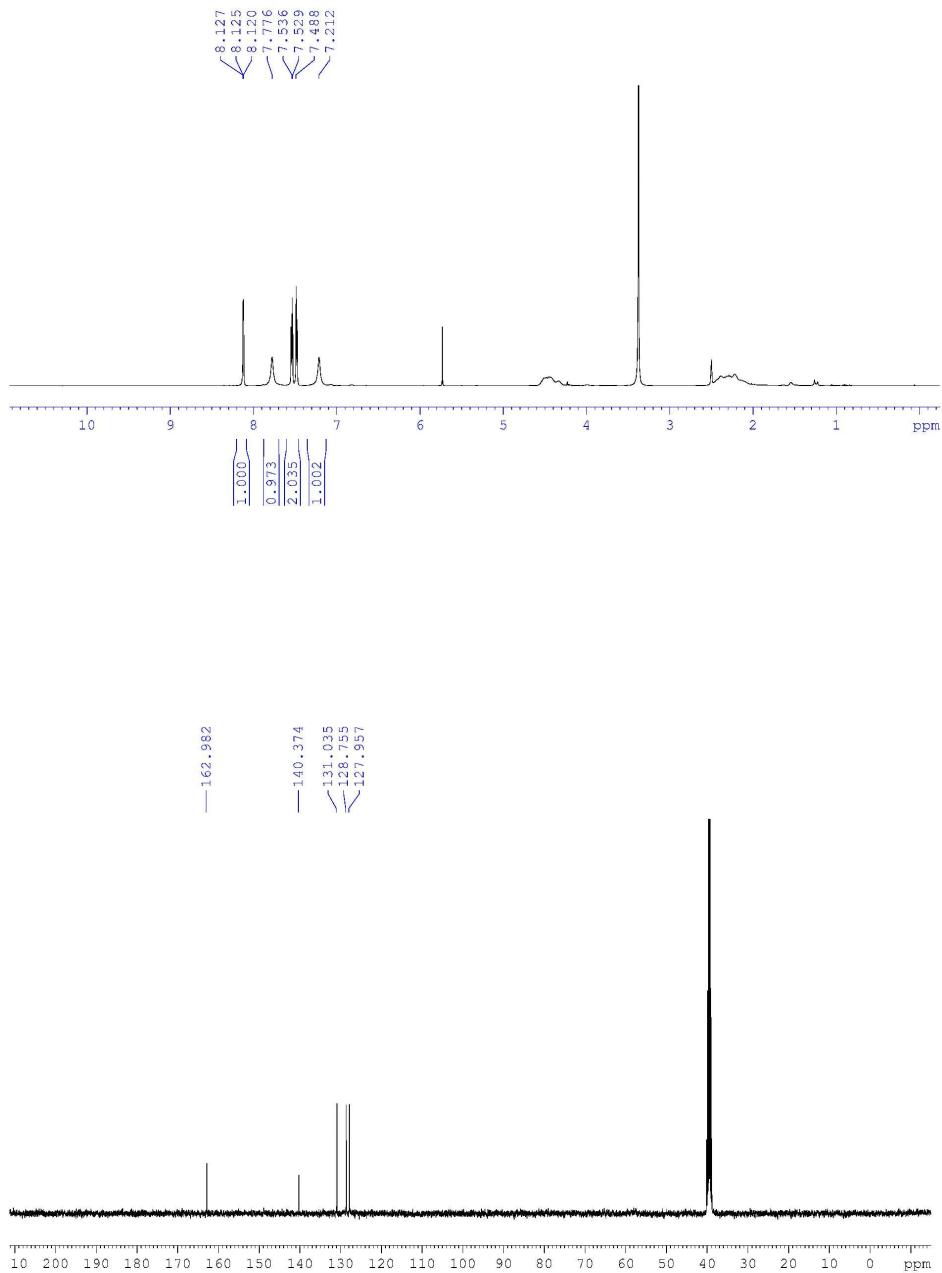
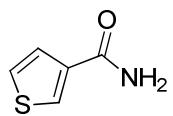
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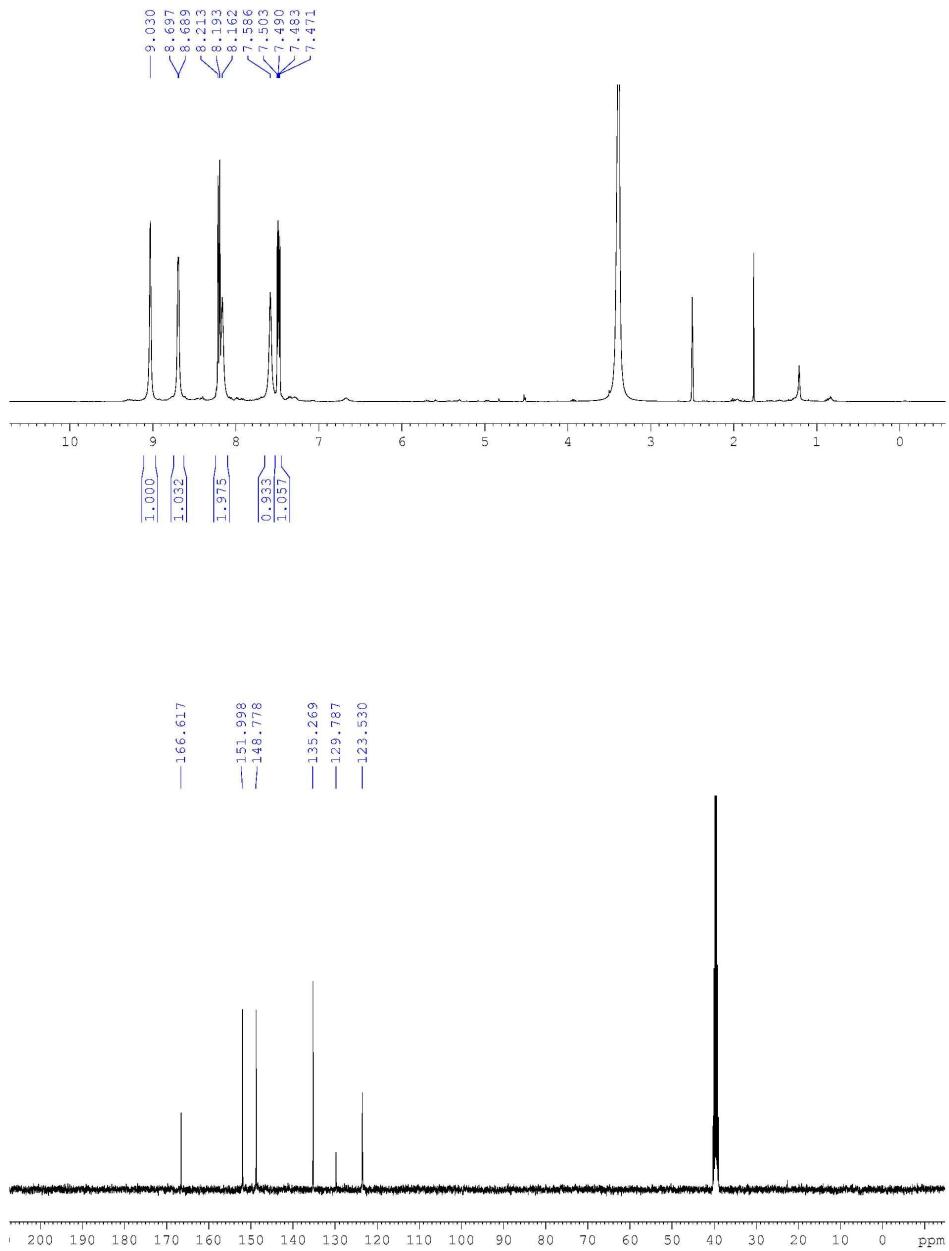
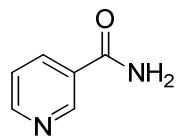
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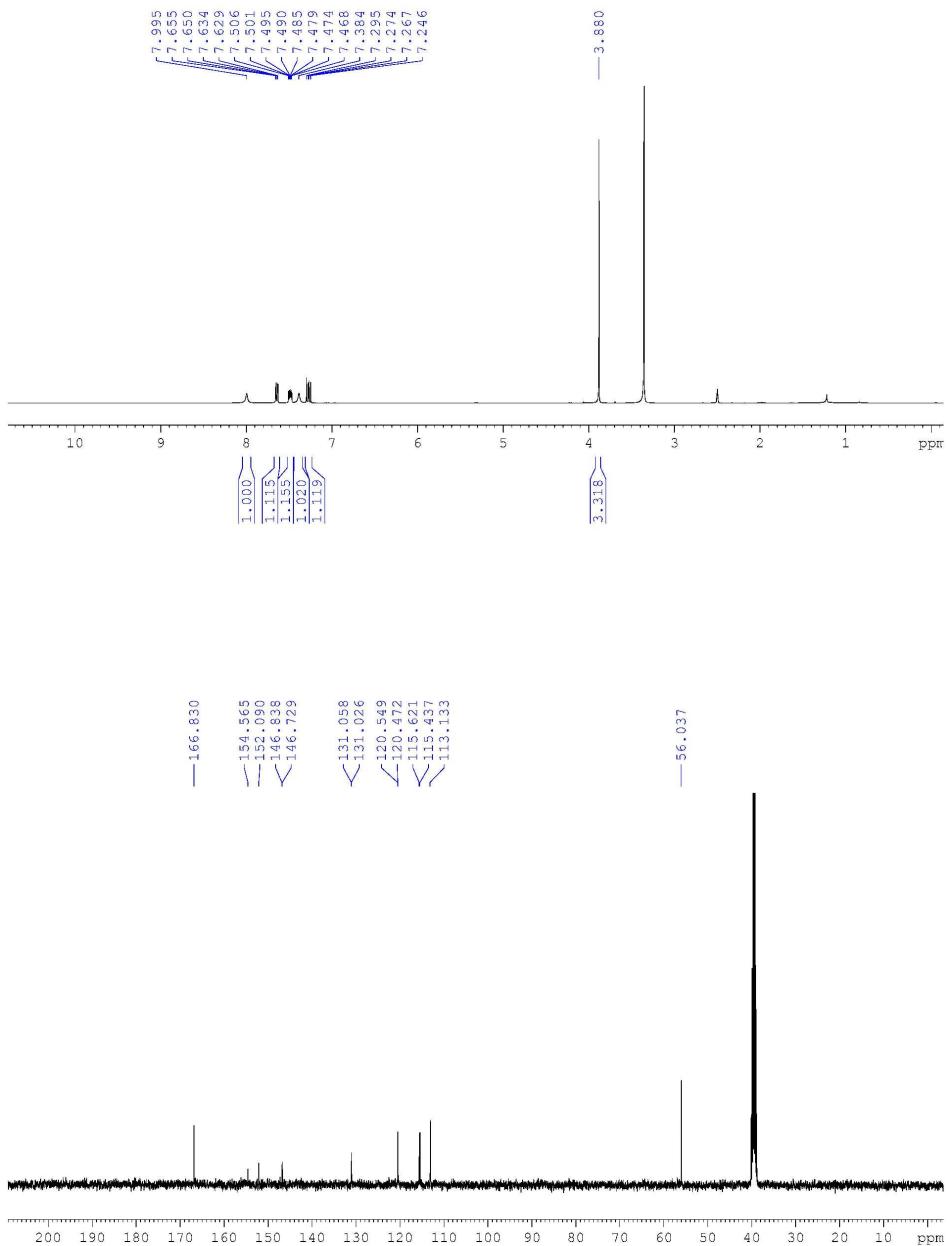
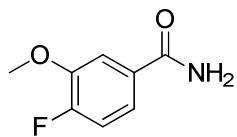
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