Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of naphthalene amino esters and arylnaphthalene lactone lignans through tandem reactions of 2-alkynylbenzonitriles

I. General Experimental Information

Commercial reagents were used without further purification, and the solvents were dried before using. 2-Alkyneylbenzonitriles (**1** and **4**) were prepared according to published method.[1] Melting points were recorded with a micro melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. High-resolution mass spectra (HRMS) were obtained by using a MicrOTOF mass spectrometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the preparation of 2-(phenylethynyl)benzonitrile (1a)

To a flask containing 2-bromobenzonitrile (2 mmol) and ethynylbenzene (2.4 mmol) in Et_3N (8 mL) was added $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.02 mmol). After the mixture was stirred at 50 ºC under N_2 atmosphere for 2 h, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford **1a** in 90% yield. Other 2-alkynylbenzonitriles (**1b-1m**) were prepared in a similar manner.

2-(Phenylethynyl)benzonitrile (1a)[2]

Eluent: ethyl acetate/hexanes (5%); yellow liquid (365 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.41 (m, 4H), 7.51-7.63 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 85.8, 96.0, 115.2, 117.6, 122.0, 127.7, 128.4, 129.3, 132.1, 132.5, 132.6, 133.2, 134.3. MS: m/z 204 $[MH]^+$.

2-(*m*-Tolylethynyl)benzonitrile (1b)

Eluent: ethyl acetate/hexanes (5%); yellow liquid (382 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.38-7.44 (m, 3H), 7.54-7.58 (m, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 85.3, 96.3, 115.2, 117.7, 121.8, 127.3, 128.2, 128.4, 129.2, 130.2, 132.1, 132.4, 132.5, 132.7, 138.2. MS: m/z 218 $[MH]^+$. HRMS calcd for $C_{16}H_{12}N$: 218.0970 [M+H], found: 218.0974.

2-((4-Methoxyphenyl)ethynyl)benzonitrile (1c)

Eluent: ethyl acetate/hexanes (5%); yellow solid (387 mg, 83%), mp 77-79 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 6.87-6.90 (m, 2H), 7.33-7.37 (m, 1H), 7.50-7.58 (4H), 7.63 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.4, 84.7, 96.4, 114.08, 114.15, 114.9, 117.8, 127.6, 127.9, 131.8, 132.4,

132.6, 133.6, 160.4. MS: m/z 234 $[MH]^+$. HRMS calcd for $C_{16}H_{12}NO$: 234.0919 [M+H], found: 234.0921.

2-(*p*-Tolylethynyl)benzonitrile (1d)

Eluent: ethyl acetate/hexanes (5%); yellow liquid (373 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (s, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.30-7.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 85.3, 96.3, 115.0, 117.7, 119.0, 127.8, 128.2, 129.3, 132.0, 132.5, 134.1, 134.3, 139.6. MS: m/z 218 $[MH]^+$. HRMS calcd for $C_{16}H_{12}N$: 218.0970 [M+H], found: 218.0978.

2-((4-Fluorophenyl)ethynyl)benzonitrile (1e)

Eluent: ethyl acetate/hexanes (5%); yellow solid (398 mg, 90%), mp 86-88 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05-7.10 (m, 2H), 7.39-7.44 (m, 1H), 7.55-7.62 (m, 4H), 7.68 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 85.4, 94.9, 115.3, 115.8, 116.0, 117.6, 118.1, 118.2, 127.1, 128.3, 132.0, 132.5, 132.7, 134.0, 134.1, 161.9, 164.4. MS: m/z 222 $[MH]^+$. HRMS calcd for $C_{15}H_9FN$: 222.0719 [M+H], found: 222.0725.

2-((4-Chlorophenyl)ethynyl)benzonitrile (1f)

Eluent: ethyl acetate/hexanes (5%); yellow solid (436 mg, 92%), mp 60-61 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.4 Hz, 2H), 7.41-7.45 (m, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.58-7.63 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.5, 94.8, 115.3, 117.6, 120.5, 126.9, 128.5, 128.9, 132.1, 132.5, 132.7, 133.2, 135.4. MS: m/z 238 $[MH]^+$. HRMS calcd for $C_{15}H_9ClN$: 238.0424 [M+H], found: 238.0430.

2-Ethynylbenzonitrile (1g)

Eluent: ethyl acetate/hexanes (5%); yellow solid (234 mg, 92%), mp 65-66 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.48 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.55-7.62 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 79.5, 83.8, 115.8, 117.2, 125.9, 129.0, 132.4, 132.7, 133.0. MS: m/z 128 $[MH]^+$. HRMS calcd for C_9H_6N: 128.0500 [M+H], found: 128.0507.

2-(Dec-1-ynyl)benzonitrile (1h)

Eluent: ethyl acetate/hexanes (5%); yellow liquid (392 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, *J* = 6.8 Hz, 3H), 1.28-1.30 (m, 8H), 1.45-1.49 (m, 2H), 1.63 (q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H), 7.31-7.35 (m, 1H), 7.46-7.49 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 19.6, 22.7, 28.4, 28.9, 29.1, 29.2, 31.8, 98.1, 115.3, 117.8, 127.5, 128.1, 132.2, 132.3, 132.5. MS: m/z 240 $[MH]^+$. HRMS calcd for $C_{17}H_{22}N$: 240.1752 [M+H], found: 240.1757.

5-Methoxy-2-((4-methoxyphenyl)ethynyl)benzonitrile (1i)

Eluent: ethyl acetate/hexanes (5%); yellow solid (458 mg, 87%), mp 103-105 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 3.82 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.47-7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.3, 55.7, 84.4, 94.4, 114.1, 114.5, 115.9, 117.2, 117.6, 119.2, 119.8, 133.30, 133.33, 158.8, 160.1. MS: m/z 264 $[MH]^+$. HRMS calcd for $C_{17}H_{14}NO_2$: 264.1025 [M+H], found: 264.1029.

5-Fluoro-2-((4-methoxyphenyl)ethynyl)benzonitrile (1j)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (462 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 6.88 (d, *J* = 7.6 Hz, 2H), 7.23-7.28 (m, 1H), 7.34 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.51-7.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.4, 83.6, 96.1, 113.9, 114.2, 116.4, 116.5, 116.56, 116.59, 119.5, 119.7, 120.3, 120.5, 124.15, 124.19, 133.5, 133.8, 133.9, 159.8, 160.5, 162.3. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{16}H_{11}FNO$: 252.0825 [M+H], found: 252.0831.

5-Fluoro-2-(*p*-tolylethynyl)benzonitrile (1k)

Eluent: ethyl acetate/hexanes (5%); yellow solid (428 mg, 91%), mp 55-57 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 7.16-7.34 (m, 4H), 7.45-7.48 (m, 2H), 7.54-7.59 (m, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ: 21.6, 84.2, 96.1, 116.5, 116.6, 118.8, 119.5, 119.7, 120.3, 120.6, 123.9, 124.0, 129.3, 131.9, 134.0, 134.1, 139.7, 159.9, 162.4. MS: m/z 236 $[MH]^+$. HRMS calcd for $C_{16}H_{11}FN$: 236.0876 [M+H], found: 236.0882.

2-((4-Chlorophenyl)ethynyl)-5-fluorobenzonitrile (1l)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (434 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.17-7.21 (m, 1H), 7.26-7.37 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.57-7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 85.5, 94.5, 116.9, 117.0, 119.9, 120.3, 121.2, 121.4, 121.8, 122.0, 128.9, 133.1, 134.1, 134.9, 135.5, 159.8, 162.3. MS: m/z 256 $[MH]^+$. HRMS calcd for $C_{15}H_8ClFN$: 256.0329 [M+H], found: 256.0333.

5-Chloro-2-((4-methoxyphenyl)ethynyl)benzonitrile (1m)

Eluent: ethyl acetate/hexanes (5%); yellow solid (497 mg, 93%), mp 118-120 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.49-7.53 (m, 4H), 7.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.4, 83.9, 97.5, 113.7, 114.2, 116.2, 116.5, 126.2, 132.3, 132.88, 132.91, 133.66, 133.70, 160.6. MS: m/z 268 $[MH]^+$. HRMS calcd for $C_{16}H_{11}ClNO$: 268.0529 [M+H], found: 268.0534.

2. Typical procedure for the preparation of 2-(3-hydroxyprop-1-ynyl)benzonitrile (4a)

To a flask containing 2-bromobenzonitrile (2 mmol) and prop-2-yn-1-ol (2.4 mmol) in Et_3N (8 mL) was added $Pd(PPh_3)_2Cl_2$ (0.04 mmol) and CuI (0.02 mmol). After the mixture was stirred at 50 ºC under N_2 atmosphere for 2 h, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford **4a** in 81% yield. Other 2-(3-hydroxyprop-1-ynyl)benzonitriles (**4b-4k**) were prepared in a similar manner.

2-(3-Hydroxyprop-1-ynyl)benzonitrile (4a)

Eluent: ethyl acetate/hexanes (20%); yellow solid (254 mg, 81%), mp 57-59 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.68 (s, 1H), 4.51 (s, 2H), 7.28-7.33 (m, 1H), 7.43 (d, J = 4.8 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.0, 81.3, 94.4, 114.8, 117.7, 126.6, 128.5, 132.5, 132.6. MS: m/z 158 $[MH]^+$. HRMS calcd for $C_{10}H_8NO$: 158.0606 [M+H], found: 158.0610.

2-(3-Hydroxyprop-1-ynyl)-5-methoxybenzonitrile (4b)

Eluent: ethyl acetate/hexanes (20%); yellow liquid (318 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.83 (s, 3H), 4.53 (s, 2H), 7.05 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.10 (d, J = 2.8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.4, 55.8, 81.5, 92.3, 116.3, 117.3, 117.4, 118.7, 119.2, 134.0, 159.3. MS: m/z 188 $[MH]^+$. HRMS calcd for $C_{11}H_{10}NO_2$: 188.0712 [M+H], found: 188.0718.

4-Fluoro-2-(3-hydroxyprop-1-ynyl)benzonitrile (4c)

Eluent: ethyl acetate/hexanes (20%); yellow solid (305 mg, 87%), mp 45-47 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.23 (s, 1H), 4.55 (s, 2H), 7.07-7.12 (m, 1H), 7.19 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.61 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.1, 80.37, 80.41, 95.6, 111.3, 111.4, 116.5, 116.8, 117.0, 119.7, 119.9, 129.2, 129.4, 134.9, 135.0, 163.1, 165.7. MS: m/z 176 $[MH]^+$. HRMS calcd for $C_{10}H_7FNO$: 176.0512 [M+H], found: 176.0517.

5-Fluoro-2-(3-hydroxyprop-1-ynyl)benzonitrile (4d)

Eluent: ethyl acetate/hexanes (20%); yellow solid (280 mg, 80%), mp 88-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.88 (s, 1H), 4.54 (s, 2H), 7.22-7.27 (m, 1H), 7.32 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.52 (dd, J_1 = 8.4 Hz, J_2 = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.2, 80.5, 94.1, 116.4, 116.5, 116.6, 116.7, 119.5, 119.8, 120.5, 120.7, 123.08, 123.12, 134.6, 134.7, 160.1, 162.7. MS: m/z 176 $[MH]^+$. HRMS calcd for $C_{10}H_7FNO$: 176.0512 [M+H], found: 176.0518.

5-Chloro-2-(3-hydroxyprop-1-ynyl)benzonitrile (4e)

Eluent: ethyl acetate/hexanes (20%); yellow solid (317 mg, 83%), mp 80-82 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.31 (s, 1H), 4.54 (s, 2H), 7.42-7.48 (m, 2H), 7.55 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 51.2, 80.5, 95.4, 116.4, 125.1, 132.2, 133.1, 133.7, 134.6. MS: m/z 192 $[MH]^+$. HRMS calcd for $C_{10}H_7ClNO$: 192.0216 [M+H], found: 192.0219.

2-(3-Hydroxypent-1-ynyl)benzonitrile (4f)

Eluent: ethyl acetate/hexanes (20%); yellow liquid (326 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07-1.11 (m, 3H), 1.84-1.87 (m, 2H), 2.81 (d, *J* = 3.6 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 7.36-7.40 (m, 1H), 7.51 (d, *J* = 3.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.4, 30.7, 64.0, 80.9, 96.9, 115.2, 126.7, 128.4, 132.36, 132.41, 132.5. MS: m/z 186 $[MH]^+$. HRMS calcd for $C_{12}H_{12}NO$: 186.0919 [M+H], found: 186.0925.

6-(3-Hydroxypent-1-ynyl)benzo[*d*][1,3]dioxole-5-carbonitrile (4g)

Eluent: ethyl acetate/hexanes (20%); yellow solid (412 mg, 90%), mp 63-64 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03-1.07 (m, 3H), 1.80-1.83 (m, 2H), 3.00 (s, 1H), 4.55 (s, 1H), 6.05 (s, 2H), 6.86 (d, *J* = 0.8 Hz, 1H), 6.93 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.4, 30.6, 63.9, 80.7, 95.5, 102.8, 108.5, 111.3, 112.0, 117.7, 122.5, 147.8, 151.2. MS: m/z 230 $[MH]^+$. HRMS calcd for $C_{13}H_{12}NO_3$: 230.0817 [M+H], found: 230.0822.

2-(3-Hydroxy-3-phenylprop-1-ynyl)benzonitrile (4h)

Eluent: ethyl acetate/hexanes (20%); yellow solid (410 mg, 88%), mp 182-184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.46 (s, 1H), 5.74 (s, 1H), 7.33-7.42 (m, 4H), 7.48-7.54 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 64.8, 82.5, 95.7, 115.2, 117.7, 126.5, 126.7, 126.9, 128.6, 128.7, 128.8, 132.5, 132.58, 132.60, 139.9. MS: m/z 234 $[MH]^+$. HRMS calcd for $C_{16}H_{12}NO$: 234.0919 [M+H], found: 234.0923.

2-(3-Hydroxy-3-phenylprop-1-ynyl)-5-methoxybenzonitrile (4i)

Eluent: ethyl acetate/hexanes (20%); yellow solid (447 mg, 85%), mp 192-194 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.59 (s, 1H), 3.77 (s, 3H), 5.71 (s, 1H), 7.00 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.39-7.42 (m, 3H), 7.65 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.8, 64.8, 82.4, 93.9, 116.2, 117.4, 117.6, 118.6, 119.1, 126.7, 127.0, 128.5, 128.7, 134.1, 140.2, 159.3. MS: m/z 264 $[MH]^+$. HRMS calcd for $C_{17}H_{14}NO_2$: 264.1025 [M+H], found: 264.1027.

5-Fluoro-2-(3-hydroxy-3-phenylprop-1-ynyl)benzonitrile (4j)

Eluent: ethyl acetate/hexanes (20%); yellow liquid (457 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.47 (s, 1H), 5.72 (d, J = 3.2 Hz, 1H), 7.21-7.40 (m, 5H), 7.50-7.55 (m, 1H), 7.64 (d, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 64.8, 81.4, 95.5, 116.5, 116.8, 116.9, 119.6, 119.8, 120.4, 120.6, 123.0, 126.9, 128.6, 128.8, 134.7, 134.8, 139.8, 160.2, 162.8. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{16}H_{11}FNO$: 252.0825 [M+H], found: 252.0831.

6-(3-Hydroxyprop-1-ynyl)benzo[*d*][1,3]dioxole-5-carbonitrile (4k)

Eluent: ethyl acetate/hexanes (20%); white solid (306 mg, 76%), mp 139-141 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ: 4.45 (s, 2H), 4.53 (s, 1H), 6.21 (s, 2H), 7.03 (s, 1H), 7.22 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ: 49.9, 80.0, 93.7, 103.3, 108.2, 111.3, 111.9, 117.1, 122.0, 148.4, 151.6. MS: m/z 202 $[MH]^+$. HRMS calcd for $C_{11}H_8NO_3$: 202.0504 [M+H], found: 202.0509.

3. Typical procedure for the preparation of ethyl 1-amino-3-phenyl-2-naphthoate (3a)

To a flask containing 2-(phenylethynyl)benzonitrile (**1a**, 1 mmol), THF (3 mL), and ethyl 2-bromo-acetate (**2**, 2 mmol) were added activated zinc dust (3 mmol) portion-wise with stirring. The mixture was then stirred at 80 ºC. Upon completion, it was diluted with saturated aqueous NH_4Cl (10 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with

EtOAc/hexane (5%) to give **3a** in 75% yield. Other 1-aminonaphthalene-2-carboxylates (**3b**-**3m**) were obtained in a similar manner from **1b**-**1m**. 9-Aminonaphtho[2,3-*c*]furan-1(3*H*)-ones (**5a**-**5k**) were obtained in a similar manner from **4a**-**4k**, respectively.

Ethyl 1-amino-3-phenyl-2-naphthoate (3a)[3]

Eluent: ethyl acetate/hexanes (5%); yellow syrup (218 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.72 (t, *J* = 7.6 Hz, 3H), 3.94 (q, *J* = 7.2 Hz, 2H), 7.14 (s, 1H), 7.26-7.35 (m, 5H), 7.45-7.49 (m, 1H), 7.53-7.57 (m, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.1, 60.3, 107.8, 119.1, 121.5, 122.5, 125.5, 126.5, 128.1, 128.4, 130.5, 133.4, 134.8, 140.1, 144.0, 146.3, 170.1. MS: m/z 292 $[MH]^+$.

Ethyl 1-amino-3-*m*-tolyl-2-naphthoate (3b)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (223 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 6.8 Hz, 3H), 2.46 (s, 3H), 4.02 (q, *J* = 6.8 Hz, 2H), 6.13 (s, 2H), 7.19-7.36 (m, 5H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.3, 21.5, 60.4, 107.8, 119.0, 121.6, 122.5, 125.3, 125.5, 127.3, 128.0, 128.4, 128.7, 128.9, 134.9, 137.5, 140.2, 144.0, 146.5, 170.3. MS: m/z 306 $[MH]^+$. HRMS calcd for $C_{20}H_{20}NO_2$: 306.1494 [M+H], found: 306.1498.

Ethyl 1-amino-3-(4-methoxyphenyl)-2-naphthoate (3c)

Eluent: ethyl acetate/hexanes (5%); yellow solid (221 mg, 69%), mp 128-130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.12 (s, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.43-7.47 (m, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 55.4, 60.4, 108.2, 113.4, 118.9, 121.5, 122.3, 125.3, 128.3, 128.6, 129.1, 134.9, 136.5, 139.6, 146.1, 158.6, 170.3. MS: m/z 322 $[MH]^+$. HRMS calcd for $C_{20}H_{20}NO_3$: 322.1443 [M+H], found: 322.1450.

Ethyl 1-amino-3-*p*-tolyl-2-naphthoate (3d)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (217 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.75 (t, *J* = 6.8 Hz, 3H), 2.40 (s, 3H), 3.95 (q, *J* = 7.6 Hz, 2H), 7.16-7.28 (m, 5H), 7.46-7.50 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.2, 21.1, 60.5, 119.5, 121.5, 125.5, 122.5, 127.9, 128.3, 128.6, 130.0, 130.5, 133.4, 134.9, 136.1, 140.0, 140.9, 145.4, 170.1. MS: m/z 306 $[MH]^+$. HRMS calcd for $C_{20}H_{20}NO_2$: 306.1494 [M+H], found: 306.1498.

Ethyl 1-amino-3-(4-fluorophenyl)-2-naphthoate (3e)

Eluent: ethyl acetate/hexanes (5%); yellow solid (238 mg, 77%), mp 68-69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 3.97 (q, *J* = 7.6 Hz, 2H), 6.20 (s, 2H), 7.06-7.12 (m, 3H), 7.32-7.35 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.3, 60.4, 107.2, 114.6, 114.8, 119.0, 121.6, 122.5, 125.6, 128.5, 128.6, 129.5, 129.6, 134.8, 139.0, 140.18, 140.21, 146.9, 160.4, 163.2, 170.0. MS: m/z 310 $[MH]^+$. HRMS calcd for $C_{19}H_{17}FNO_2$: 310.1243 [M+H], found: 310.1247.

Ethyl 1-amino-3-(4-chlorophenyl)-2-naphthoate (3f)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (244 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.76 (t, *J* = 7.6 Hz, 3H), 3.93 (q, *J* = 7.2 Hz, 2H), 6.19 (s, 2H), 7.03 (s, 1H), 7.19-7.30 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.3, 60.4, 106.1, 122.5, 125.7, 128.56, 128.64, 129.4, 132.4, 134.8, 138.8, 142.7, 147.0, 159.9, 169.8. MS: m/z 326 $[MH]^+$. HRMS calcd for $C_{19}H_{17}ClNO_2$: 326.0948 [M+H], found: 326.0952.

Ethyl 1-amino-2-naphthoate (3g)[4]

Eluent: ethyl acetate/hexanes (5%); white solid (146 mg, 68%), mp 103-105 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 (t, *J* = 7.2 Hz, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 6.82 (s, 2H), 7.08 (d, *J* = 8.8 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.89-7.91 (m, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ: 14.4, 60.3, 104.3, 115.8, 121.5, 125.2, 126.6, 128.3, 128.5, 136.4, 148.9, 169.0. MS: m/z 216 $[MH]^+$.

Ethyl 1-amino-3-octyl-2-naphthoate (3h)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (213 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, *J* = 7.6 Hz, 3H), 1.31-1.47 (m, 13H), 1.60-1.65 (m, 2H), 2.97 (t, *J* =8.0 Hz, 2H), 4.45 (q, *J* = 7.6 Hz, 2H), 5.73 (s, 2H), 7.03 (s, 1H), 7.36-7.40 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 14.3, 22.7, 29.4, 29.6, 29.9, 31.9, 32.0, 36.6, 60.8, 108.6, 118.5, 121.4, 122.1, 124.7, 127.90, 127.94, 135.2, 140.0, 146.3, 170.2. MS: m/z 328 $[MH]^+$. HRMS calcd for $C_{21}H_{30}NO_2$: 328.2277 [M+H], found: 328.2282.

Ethyl 1-amino-7-methoxy-3-(4-methoxyphenyl)-2-naphthoate (3i)

Eluent: ethyl acetate/hexanes (5%); yellow solid (239 mg, 68%), mp 153-154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, *J* = 7.6 Hz, 3H), 3.85 (s, 3H), 3.92 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 5.79 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 1H), 7.13 (s, 1H), 7.20-7.22 (m, 1H), 7.31 (d, *J* = 9.2 Hz, 2H), 7.66 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 55.38, 55.40, 60.5, 100.9, 109.2, 113.4, 119.0, 120.0, 123.3, 129.0, 130.0, 130.2, 136.4, 137.1, 144.7, 157.6, 158.5, 170.4. MS: m/z 352 $[MH]^+$. HRMS calcd for $C_{21}H_{22}NO_4$: 352.1549 [M+H], found: 352.1556.

Ethyl 1-amino-7-fluoro-3-(4-methoxyphenyl)-2-naphthoate (3j)

Eluent: ethyl acetate/hexanes (5%); yellow solid (285 mg, 84%), mp 139-141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, *J* = 6.8 Hz, 3H), 3.86 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 6.94 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 2H), 6.95 (s, 1H), 7.28-7.33 (m, 3H), 7.50 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H), 7.71-7.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 55.4, 60.6, 105.8, 106.0, 109.6, 113.5, 118.0, 118.3, 118.9, 123.1, 129.1, 130.9, 131.0, 131.7, 136.0, 138.8, 144.9, 158.7, 159.3, 161.7, 170.0. MS: m/z 340 $[MH]^+$. HRMS calcd for $C_{20}H_{19}FNO_3$: 340.1349 [M+H], found: 340.1353.

Ethyl 1-amino-7-fluoro-3-*p*-tolyl-2-naphthoate (3k)

Eluent: ethyl acetate/hexanes (5%); yellow solid (268 mg, 83%), mp 124-126 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.75-0.80 (m, 3H), 2.42 (s, 3H), 3.95-4.01 (m, 2H), 5.56 (s, 2H), 7.14 (d, *J* = 2.8 Hz, 1H), 7.20-7.33 (m, 5H), 7.51 (d, *J* = 10.8 Hz, 1H), 7.71-7.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.2, 21.1, 60.6, 105.8, 106.0, 109.3, 118.0, 118.3, 118.9, 123.1, 123.2, 127.9, 128.7, 130.9, 131.0, 131.7, 136.3, 139.3, 140.6, 145.1, 145.2, 159.3, 161.8, 170.1. MS: m/z 324 $[MH]^+$. HRMS calcd for $C_{20}H_{19}FNO_2$: 324.1400 [M+H], found: 324.1408.

Ethyl 1-amino-3-(4-chlorophenyl)-7-fluoro-2-naphthoate (3l)

Eluent: ethyl acetate/hexanes (5%); yellow syrup (295 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 3.97 (q, *J* = 7.2 Hz, 2H), 7.07 (s, 1H), 7.27-7.37 (m, 5H), 7.49-7.56 (m, 1H), 7.72 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.3, 60.6, 105.9, 106.1, 108.3, 118.3, 118.5, 118.9, 123.38, 123.45, 128.1, 129.3, 131.0, 131.1, 131.6, 132.6, 138.08, 138.11, 142.2, 145.7, 159.5, 162.0, 169.6. MS: m/z 344 $[MH]^+$. HRMS calcd for $C_{19}H_{16}ClFNO_2$: 344.0854 [M+H], found: 344.0859.

Ethyl 1-amino-7-chloro-3-(4-methoxyphenyl)-2-naphthoate (3m)

Eluent: ethyl acetate/hexanes (5%); yellow solid (312 mg, 88%), mp 133-135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 3.85 (s, 3H), 3.98 (q, *J* = 7.6 Hz, 2H), 5.89 (s, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.06 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 55.4, 60.6, 109.2, 113.5, 118.5, 121.0, 123.0, 128.9, 129.0, 130.1, 131.0, 133.1, 136.0, 139.9, 145.1, 158.7, 170.0. MS: m/z 356 $[MH]^+$. HRMS calcd for $C_{20}H_{19}ClNO_3$: 356.1053 [M+H], found: 356.1060.

9-Aminonaphtho[2,3-*c*]furan-1(3*H*)-one (5a)

Eluent: ethyl acetate/hexanes (20%); yellow solid (139 mg, 70%), mp 178-180 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.35 (s, 2H), 6.10 (s, 2H), 7.06 (s, 1H), 7.26-7.52 (m, 1H), 7.57-7.61 (m, 1H), 7.79 (d, *J* = 8.4

Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.6, 108.1, 121.69, 121.73, 125.0, 128.9, 129.0, 137.8, 140.9, 145.0, 145.6, 173.1. MS: m/z 200 $[MH]^+$. HRMS calcd for $C_{12}H_{10}NO_2$: 200.0712 [M+H], found: 200.0716.

9-Amino-7-methoxynaphtho[2,3-*c*]furan-1(3*H*)-one (5b)

Eluent: ethyl acetate/hexanes (20%); yellow solid (142 mg, 62%), mp 191-193 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.95 (s, 3H), 5.33 (s, 2H), 7.03 (s, 1H), 7.11 (d, J = 2.0 Hz, 1H), 7.26 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.5, 69.5, 100.9, 102.8, 108.3, 121.2, 122.7, 130.3, 133.0, 138.6, 144.4, 157.3, 174.1. MS: m/z 230 $[MH]^+$. HRMS calcd for $C_{13}H_{12}NO_3$: 230.0817 [M+H], found: 230.0828.

9-Amino-6-fluoronaphtho[2,3-*c*]furan-1(3*H*)-one (5c)

Eluent: ethyl acetate/hexanes (5%); brown solid (167 mg, 77%), mp 185-187 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.32 (s, 2H), 7.00 (s, 1H), 7.30-7.35 (m, 3H), 7.57 (d, J = 10.0 Hz, 1H), 8.42 (dd, J_1 = 9.6 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 69.3, 100.2, 106.29, 106.33, 111.8, 112.0, 114.2, 114.4, 118.9, 127.3, 127.4, 139.8, 139.9, 143.7, 147.3, 161.3, 163.7, 172.6. MS: m/z 218 $[MH]^+$. HRMS calcd for $C_{12}H_9FNO_2$: 218.0617 [M+H], found: 218.0623.

9-Amino-7-fluoronaphtho[2,3-*c*]furan-1(3*H*)-one (5d)

Eluent: ethyl acetate/hexanes (20%); brown solid (163 mg, 75%), mp 250-251 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.35 (s, 2H), 5.98 (s, 2H), 7.09 (s, 1H), 7.35-7.40 (m, 1H), 7.51 (dd, J_1 = 10.0 Hz, J_2 = 2.4 Hz, 1H), 7.79 (dd, J_1 = 9.2 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.5, 102.9, 105.9, 106.1, 108.2, 119.0, 119.3, 131.1, 131.2, 134.6, 140.3, 144.86, 144.92, 172.8. MS: m/z 218 $[MH]^+$. HRMS calcd for $C_{12}H_9FNO_2$: 218.0617 [M+H], found: 218.0624.

9-Amino-7-chloronaphtho[2,3-*c*]furan-1(3*H*)-one (5e)

Eluent: ethyl acetate/hexanes (5%); brown solid (182 mg, 78%), mp 177-179 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.35 (s, 2H),7.08 (s, 1H), 7.31 (s, 2H), 7.59 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 8.50 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 69.5, 106.8, 122.6, 123.4, 129.5, 129.7, 130.8, 136.4, 142.8, 146.4, 172.5. MS: m/z 234 $[MH]^+$. HRMS calcd for $C_{12}H_9ClNO_2$: 234.0322 [M+H], found: 234.0328.

9-Amino-3-ethylnaphtho[2,3-*c*]furan-1(3*H*)-one (5f)

Eluent: ethyl acetate/hexanes (5%); brown solid (163 mg, 72%), mp 111-113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01 (t, J = 7.6 Hz, 3H), 1.80-2.13 (m, 2H), 5.42-5.44 (m, 1H), 6.19 (s, 2H), 6.96 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.8, 28.2, 82.2, 102.4, 107.8, 121.7, 121.9, 124.9, 128.8, 128.9, 137.7, 144.4, 145.6, 172.7. MS: m/z 228 $[MH]^+$. HRMS calcd for $C_{14}H_{14}NO_2$: 228.1025 [M+H], found: 228.1036.

9-Amino-6,7-methylenedioxy-3-ethylnaphtho[2,3-*c*]furan-1(3*H*)-one (5g)

Eluent: ethyl acetate/hexanes (5%); brown solid (179 mg, 66%), mp 195-197 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.04 (m, 3H), 1.82-2.12 (m, 2H), 5.41-5.43 (m, 1H), 5.80 (s, 2H), 6.09 (s, 2H), 6.87 (s, 1H), 7.07 (s, 1H), 7.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.9, 28.2, 82.0, 98.4, 101.7, 102.9, 105.1, 107.9, 117.7, 135.7, 143.8, 144.3, 147.4, 150.0, 172.6. MS: m/z 272 $[MH]^+$. HRMS calcd for $C_{15}H_{14}NO_4$: 272.0923 [M+H], found: 272.0929.

9-Amino-3-phenylnaphtho[2,3-*c*]furan-1(3*H*)-one (5h)

Eluent: ethyl acetate/hexanes (20%); brown solid (226 mg, 82%), mp 200-202 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.41 (d, J = 0.4 Hz, 1H), 6.90 (s, 1H), 7.35-7.38 (m, 5H), 7.45-7.49 (m, 1H), 7.54-7.58 (m, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 82.5, 101.8, 109.3, 121.8, 125.2, 127.1, 128.9, 129.05, 129.08, 129.12, 137.7, 137.9, 144.3, 145.6, 172.4. MS: m/z 276 $[MH]^+$. HRMS calcd for $C_{18}H_{14}NO_2$: 276.1025 [M+H], found: 276.1033.

9-Amino-7-methoxy-3-phenylnaphtho[2,3-*c*]furan-1(3*H*)-one (5i)

Eluent: ethyl acetate/hexanes (20%); brown solid (226 mg, 74%), mp 222-224 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.94 (s, 3H), 6.40 (s, 1H), 6.88 (s, 1H), 7.15 (d, J = 1.6 Hz, 1H), 7.23-7.26 (m, 1H), 7.36 (s, 5H), 7.62 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.5, 82.5, 100.9, 102.6, 109.5, 121.2, 122.9, 127.1, 128.8, 129.0, 130.5, 133.0, 137.9, 142.0, 144.3, 157.5, 172.6. MS: m/z 306 $[MH]^+$. HRMS calcd for $C_{19}H_{16}NO_3$: 306.1130 [M+H], found: 306.1132.

9-Amino-7-fluoro-3-phenylnaphtho[2,3-*c*]furan-1(3*H*)-one (5j)

Eluent: ethyl acetate/hexanes (20%); brown solid (258 mg, 88%), mp 213-215 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.08 (s, 2H), 6.42 (s, 1H), 6.92 (s, 1H), 7.32-7.41 (m, 6H), 7.55 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H), 7.71 (dd, J_1 = 9.6 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 82.5, 102.6, 106.0, 106.2, 109.3, 119.0, 119.3, 122.5, 122.6, 127.1, 128.9, 129.1, 131.27, 131.34, 134.7, 137.6, 143.7, 144.8, 144.9, 159.0, 161.5, 172.2. MS: m/z 294 $[MH]^+$. HRMS calcd for $C_{18}H_{13}FNO_2$: 294.0930 [M+H], found: 294.0938.

9-Amino-6,7-methylenedioxynaphtho[2,3-*c*]furan-1(3*H*)-one (5k)

Eluent: ethyl acetate/hexanes (33.3%); white solid (170 mg, 70%), mp 233-235 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.29 (s, 2H), 5.80 (s, 2H), 6.09 (s, 2H), 6.93 (s, 1H), 7.06 (s, 1H), 7.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.3, 98.4, 101.7, 104.9, 108.0, 117.6, 134.6, 144.5, 147.4, 150.0, 155.0, 161.0, 171.6. MS: m/z 244 $[MH]^+$. HRMS calcd for $C_{13}H_{10}NO_4$: 244.0610 [M+H], found: 244.0613.

4. Procedure for the preparation of 9-iodo-6,7-methylenedioxynaphtho[2,3-*c*]furan-1(3*H*)-one (6)

To a flask containing 9-amino-6,7-methylenedioxynaphtho[2,3-*c*]furan-1(3*H*)-one (**5k**, 1 mmol) and hydrochloric acid (w/w = 25%, 0.2 mL) were added $NaNO_2$ (1.1 mmol) with stirring at 0 ºC. The mixture was then stirred at 5 ºC for 30 minutes. To the resulting mixture was added aqueous KI (w/w = 40%, 0.5 mL) at room temperature. Upon completion, it was diluted with saturated aqueous NH_4Cl (10 mL). The

filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give **6** in 85% yield.

9-Iodo-6,7-methylenedioxynaphtho[2,3-*c*]furan- 1(3*H*)-one (6)

Eluent: ethyl acetate/hexanes (20%); white solid (301 mg, 85%), mp 238-240 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.29 (s, 2H), 6.17 (s, 2H), 7.12 (s, 1H), 7.66 (s, 1H), 7.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 66.7, 66.8, 98.5, 102.3, 103.7, 110.0, 124.2, 133.4, 134.4, 141.0, 150.4, 150.6, 169.7. MS: m/z 355 $[MH]^+$. HRMS calcd for $C_{13}H_8IO_4$: 354.9467 [M+H], found: 354.9471.

5. Typical procedure for the preparation of taiwanin C and chinensin

To a flask containing 9-iodo-6,7-methylenedioxynaphtho[2,3-*c*]furan-1(3*H*)-one (**6**, 0.2 mmol), $Pd(OAc)_2$ (0.002 mmol), PPh_3 (0.006 mmol) and benzo[*d*][1,3]dioxol-5-ylboronic acid (**7a**, 0.22 mmol) in 1,4-dioxane (2 mL) was added Cs_2CO_3 (0.6 mmol). Then, the mixture was stirred at 80 ^{o}C under N_2 atmosphere for 8 h. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with ethyl acetate (3 mL × 3). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford taiwanin C. Chinensin was prepared in a similar manner through the coupling of **6** with 3,4-dimethoxyphenylboronic acid (**7b**).

Taiwanin C[5]

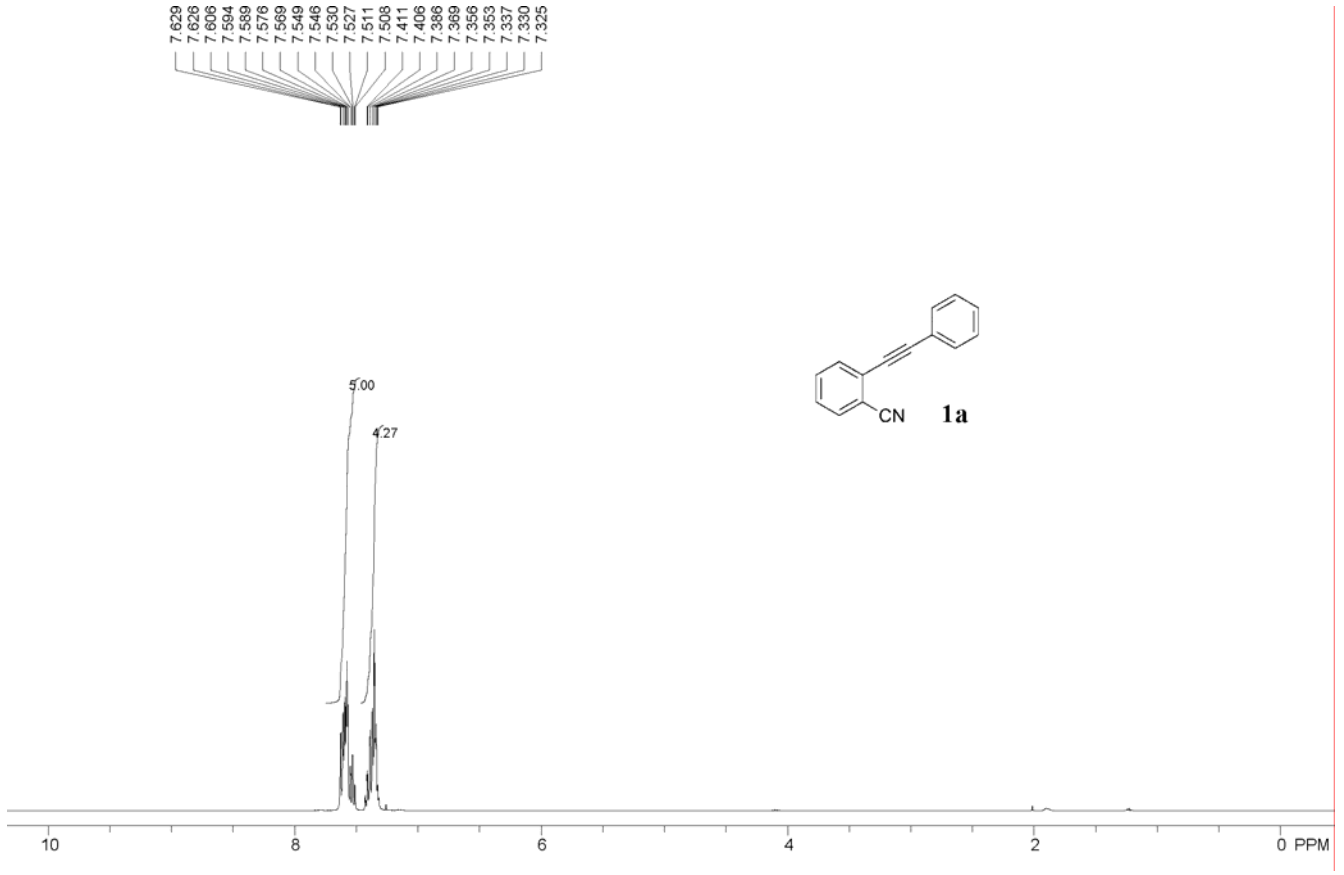
Eluent: ethyl acetate/hexanes (20%); white solid (65 mg, 93%), mp 272-273 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.37 (s, 2H), 6.06-6.09 (m, 4H), 6.78-6.81 (m, 2H), 6.79 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H), 7.11 (s, 1H), 7.20 (s, 1H), 7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 68.0, 101.3, 101.8, 103.7, 108.3,

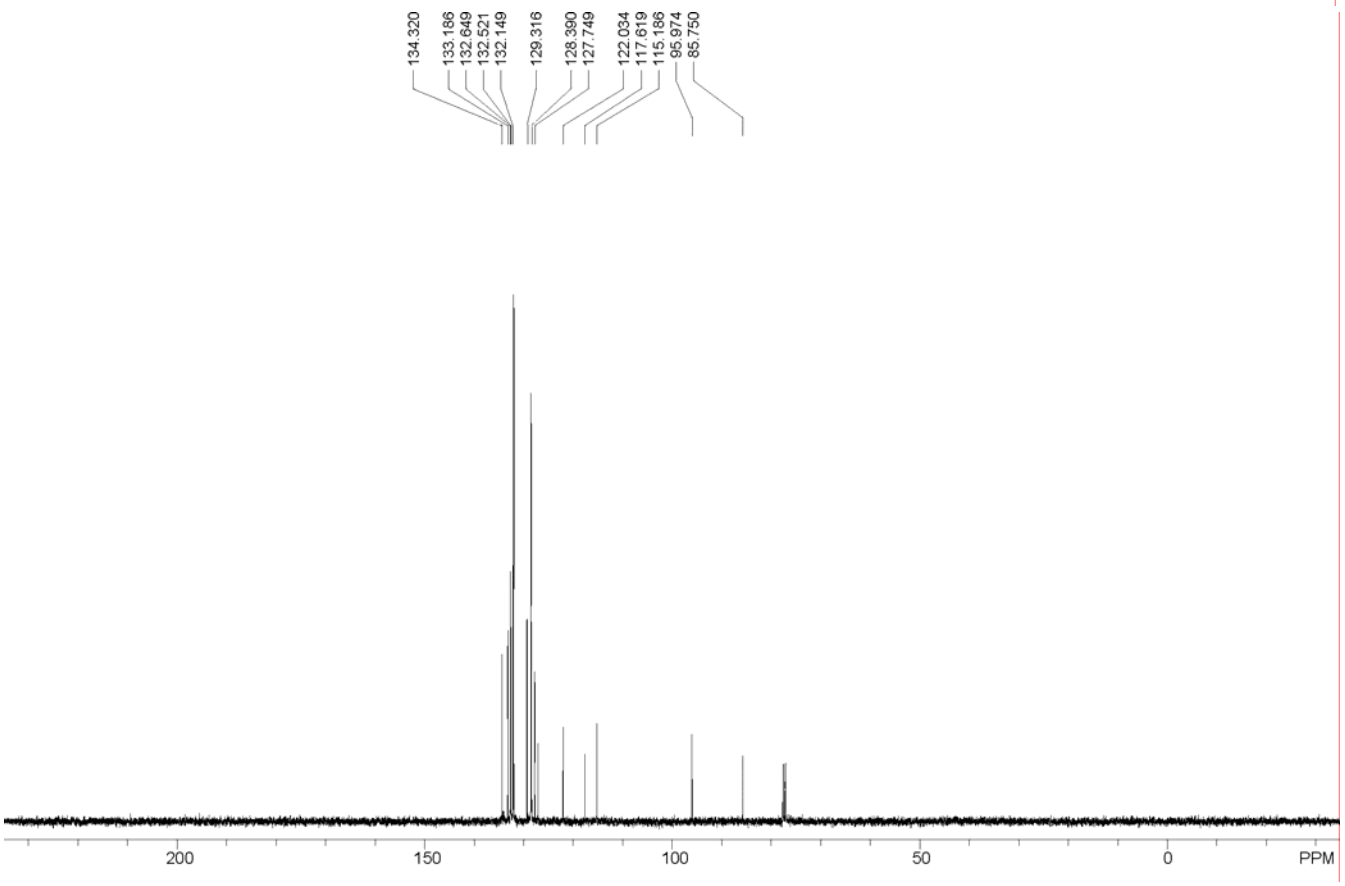
110.6, 118.9, 119.1, 123.5, 128.4, 130.5, 134.6, 139.8, 140.1, 147.5, 147.6, 148.7, 150.0, 169.9. MS: m/z 349 $[MH]^+$.

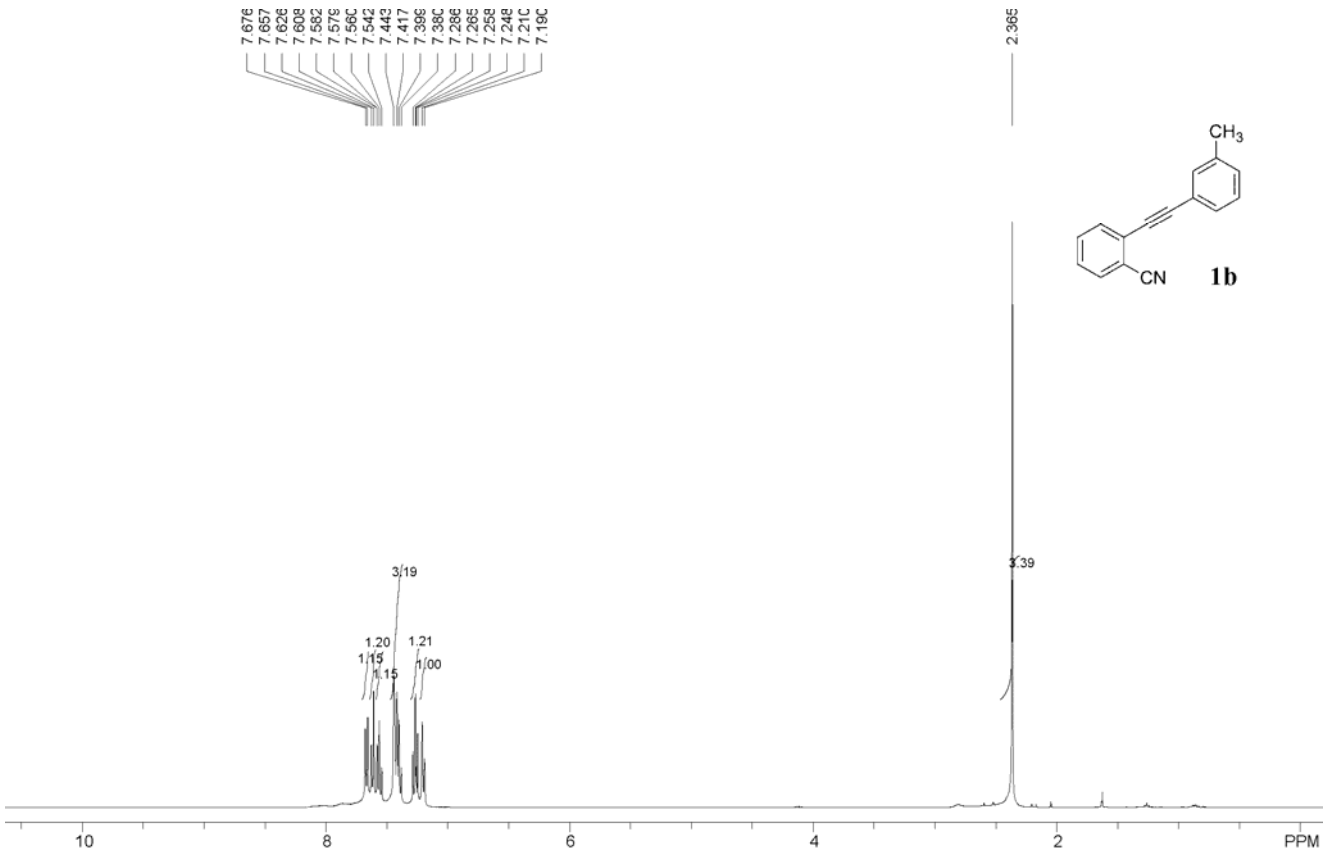
Chinensin[6]

Eluent: ethyl acetate/hexanes (33.3%); white solid (69 mg, 95%), mp 224-226 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 3H), 3.98 (s, 3H), 5.38 (s, 2H), 6.08 (s, 2H), 6.86 (d, J = 2.0 Hz, 1H), 6.91 (dd, J_1 = 9.6 Hz, J_2 = 1.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.12 (s, 1H), 7.20 (s, 1H), 7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.85, 55.95, 68.0, 101.8, 103.7, 103.8, 110.8, 113.4, 118.8, 119.0, 122.4, 127.2, 130.5, 134.6, 139.9, 140.5, 148.5, 148.6, 148.9, 149.9, 169.9. MS: m/z 365 $[MH]^+$.

III. Copies of ^{1}H and ^{13}C NMR spectra of 1a-1m



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7.286
7.265
7.258
7.248
7.210
7.190
2.365
CH3
CN
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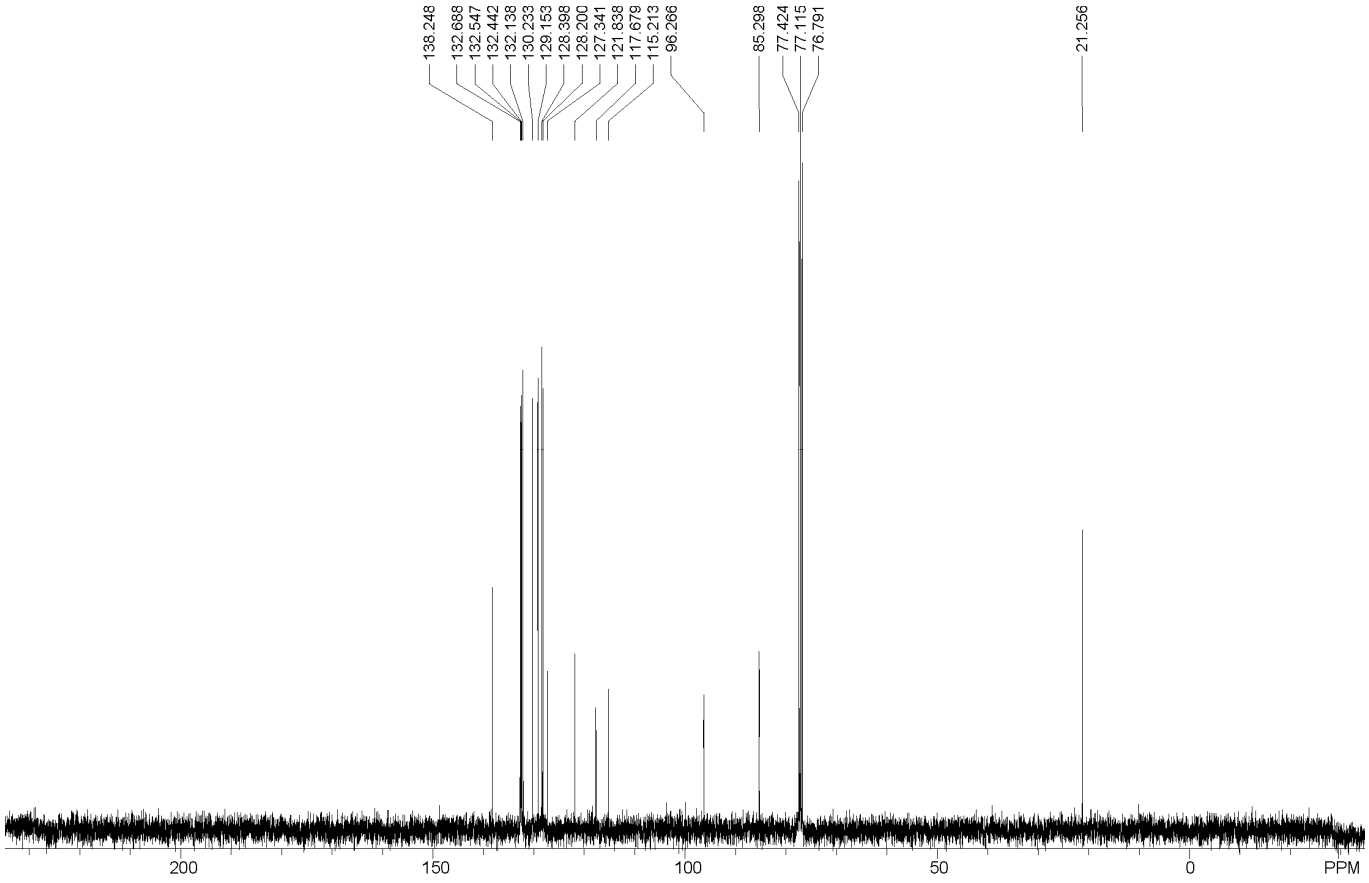
1.15
1.15
1.21
1.00
3.39
10
8
6
4
2
PPM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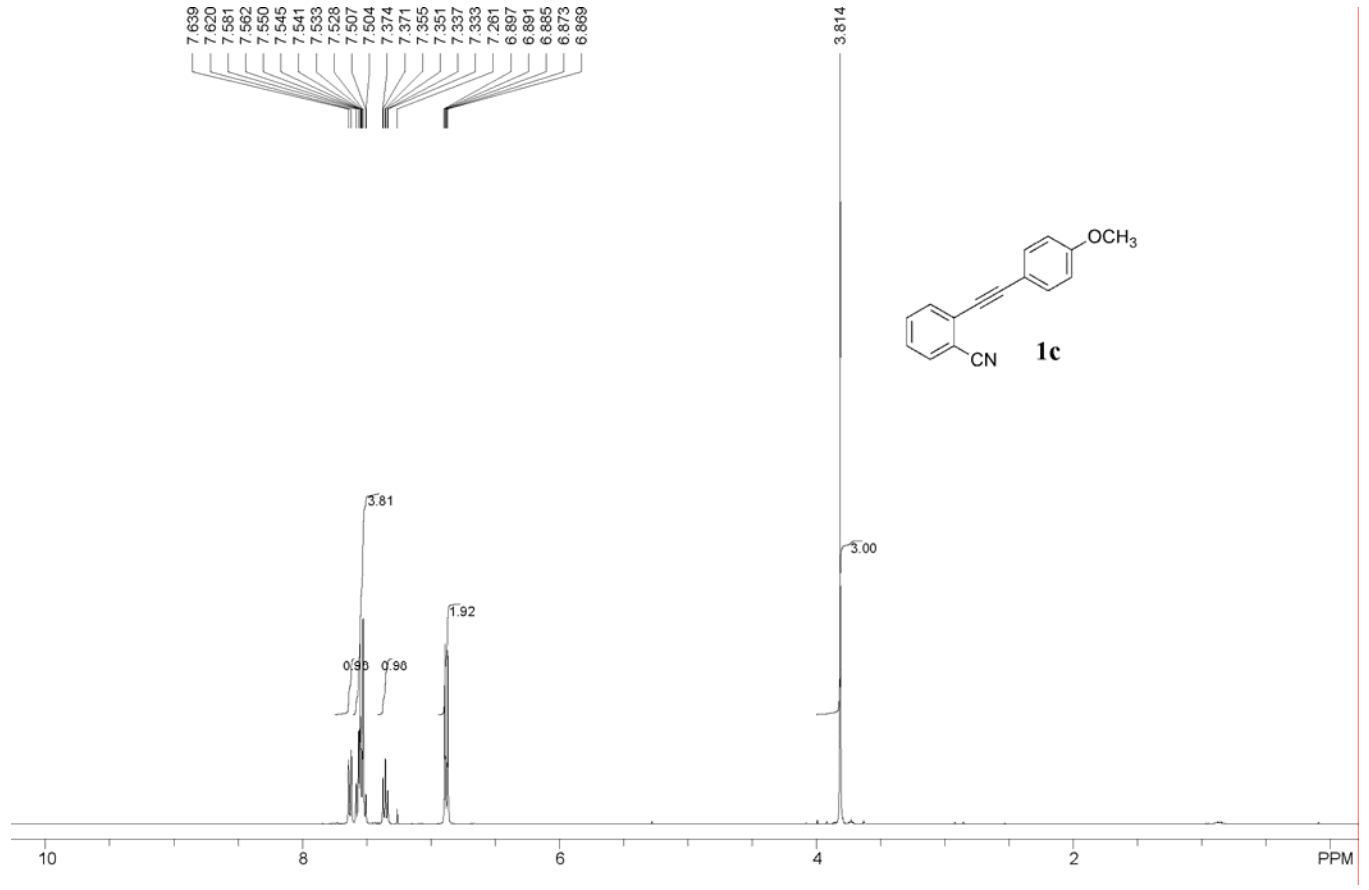
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7.355
7.351
7.337
7.333
7.261
6.897
6.891
6.885
6.873
6.869
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10
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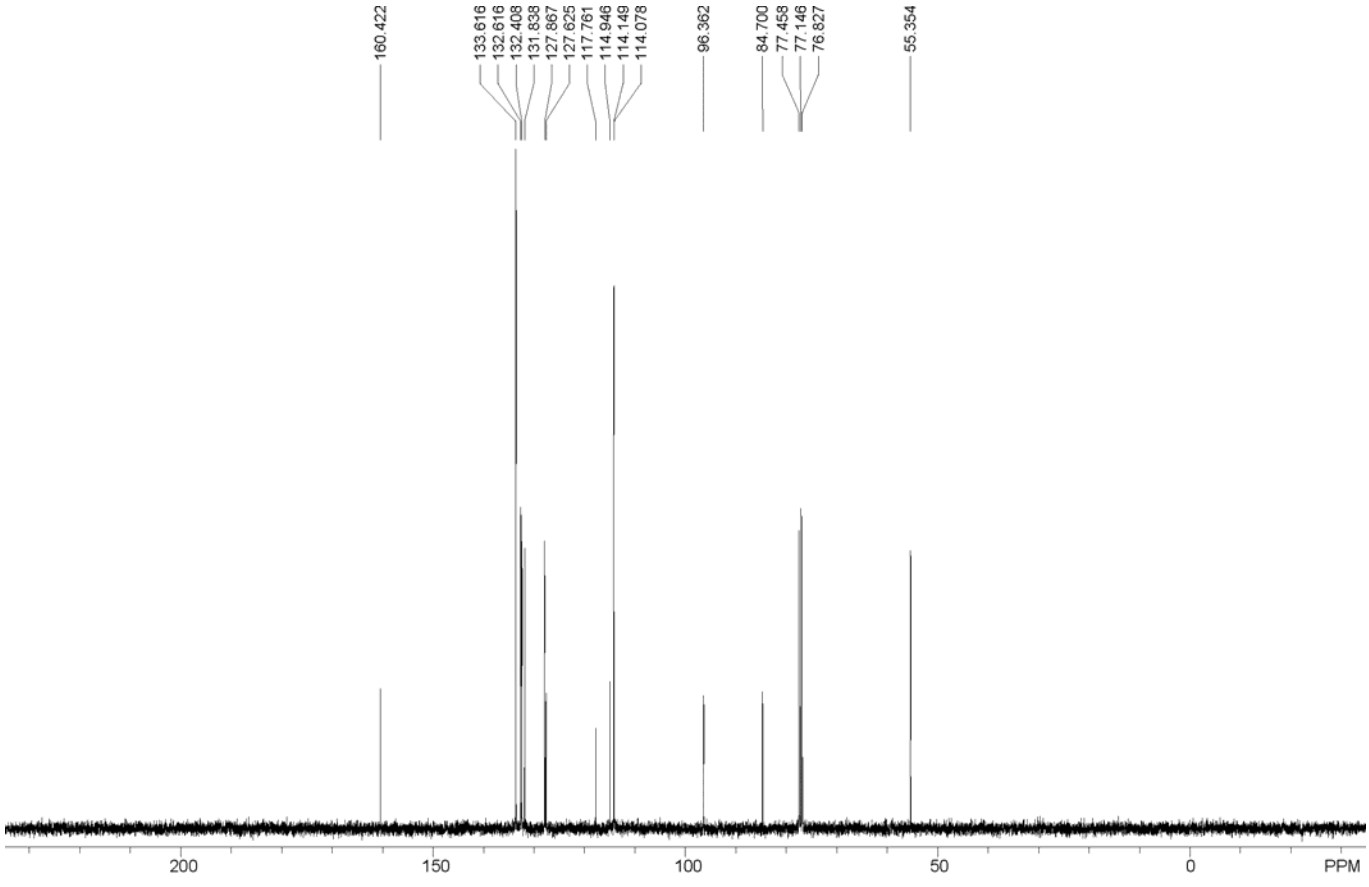
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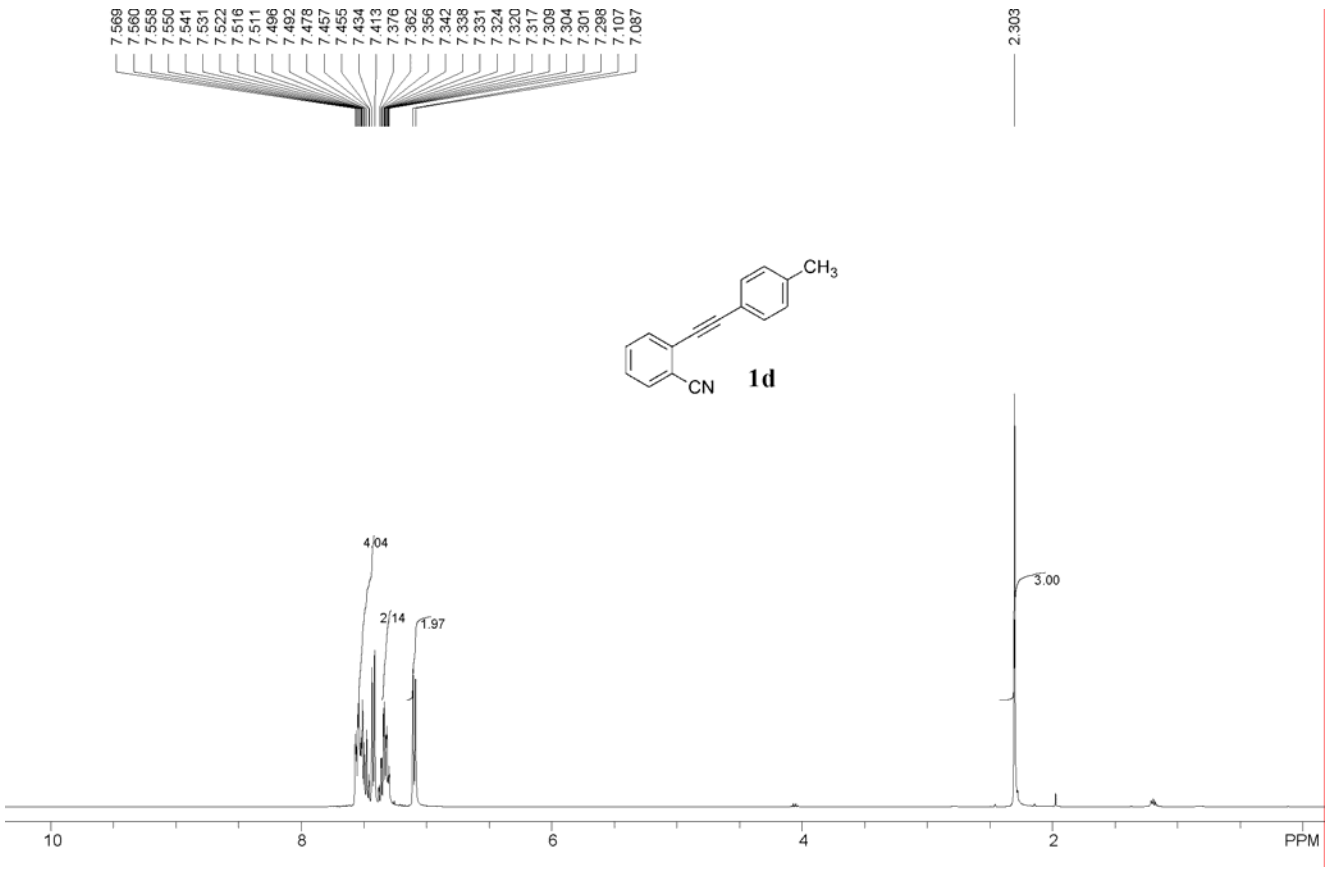
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7.455
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7.331
7.324
7.320
7.317
7.309
7.304
7.301
7.298
7.107
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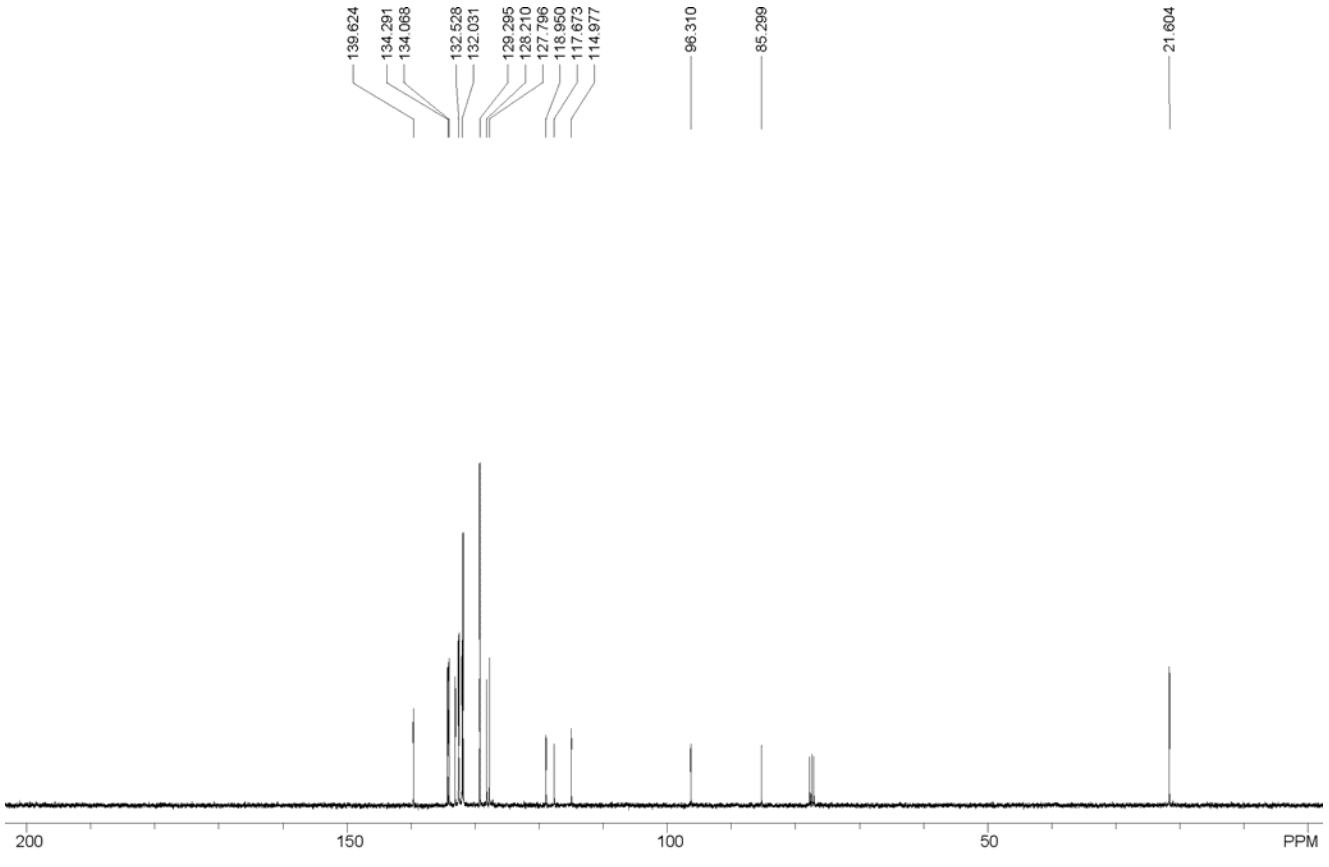
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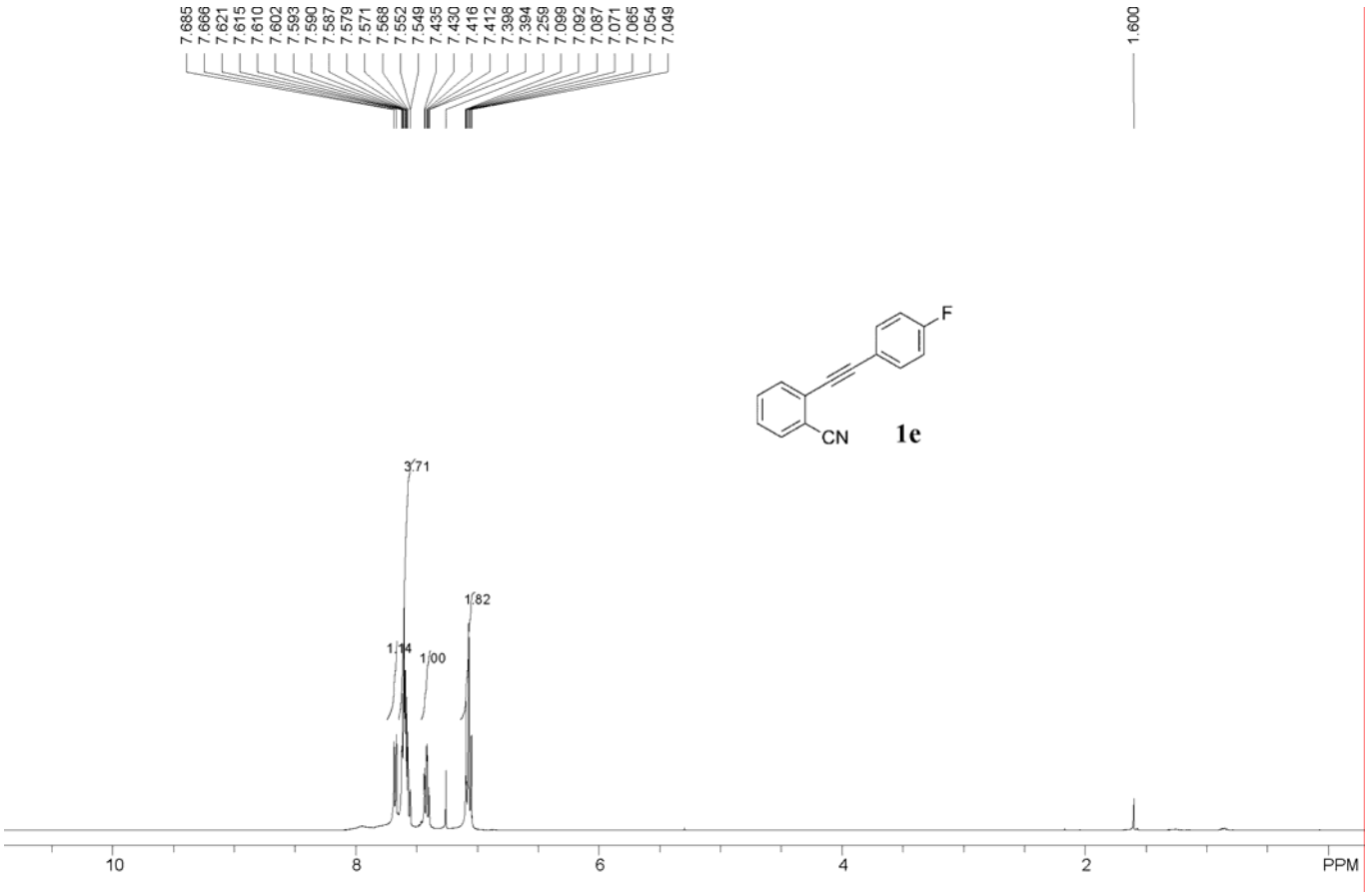
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7.549
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7.416
7.412
7.398
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7.259
7.099
7.092
7.087
7.071
7.065
7.054
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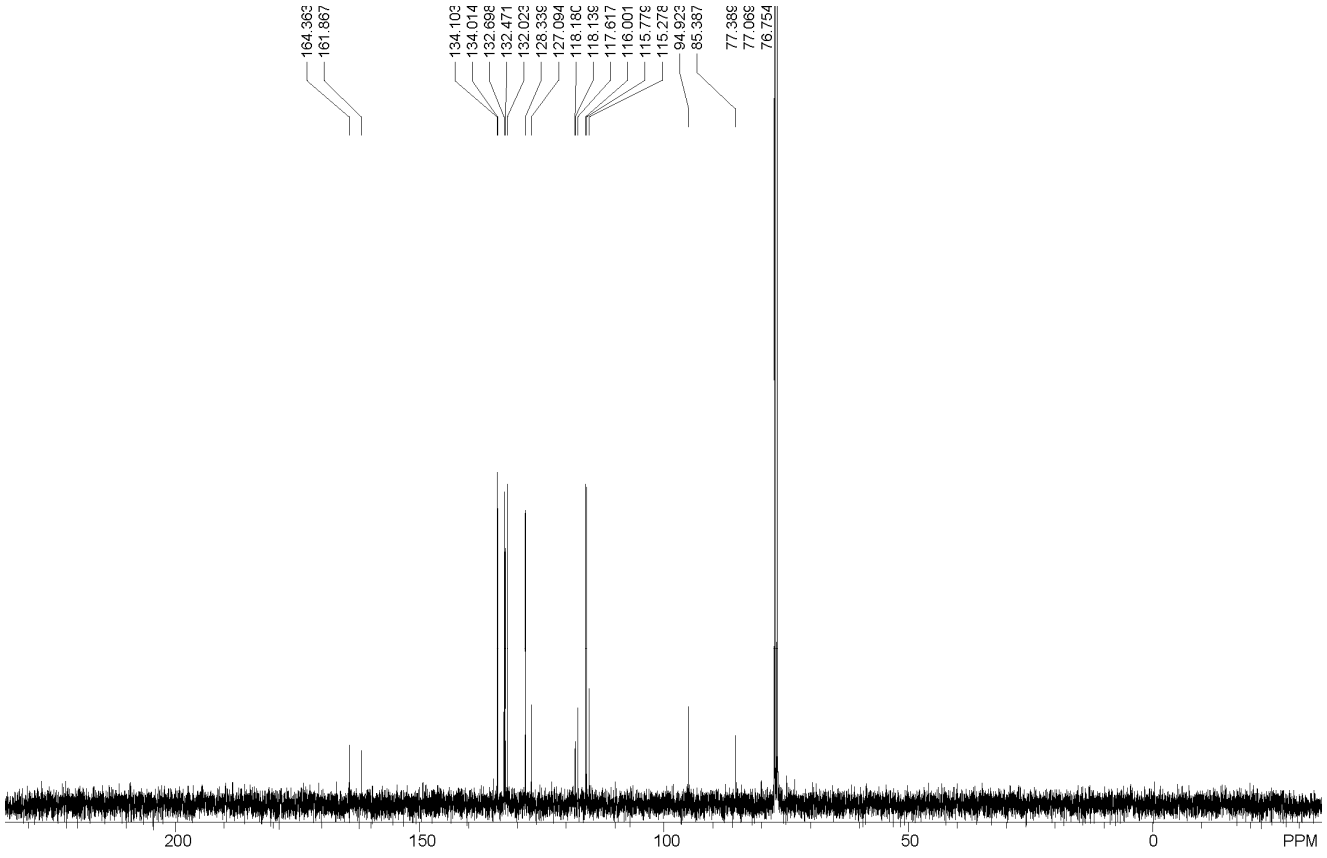
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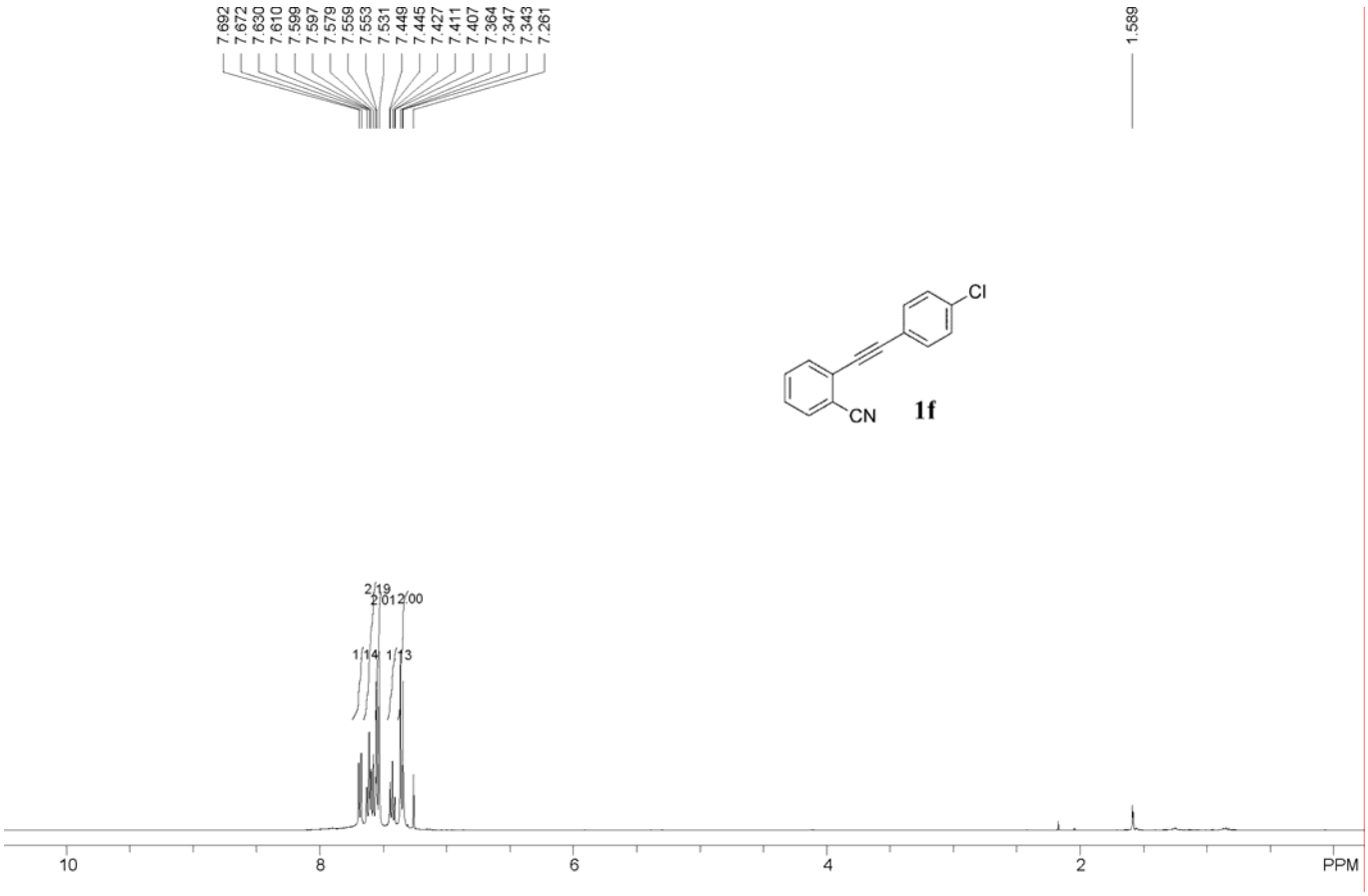
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7.411
7.407
7.364
7.347
7.343
7.261
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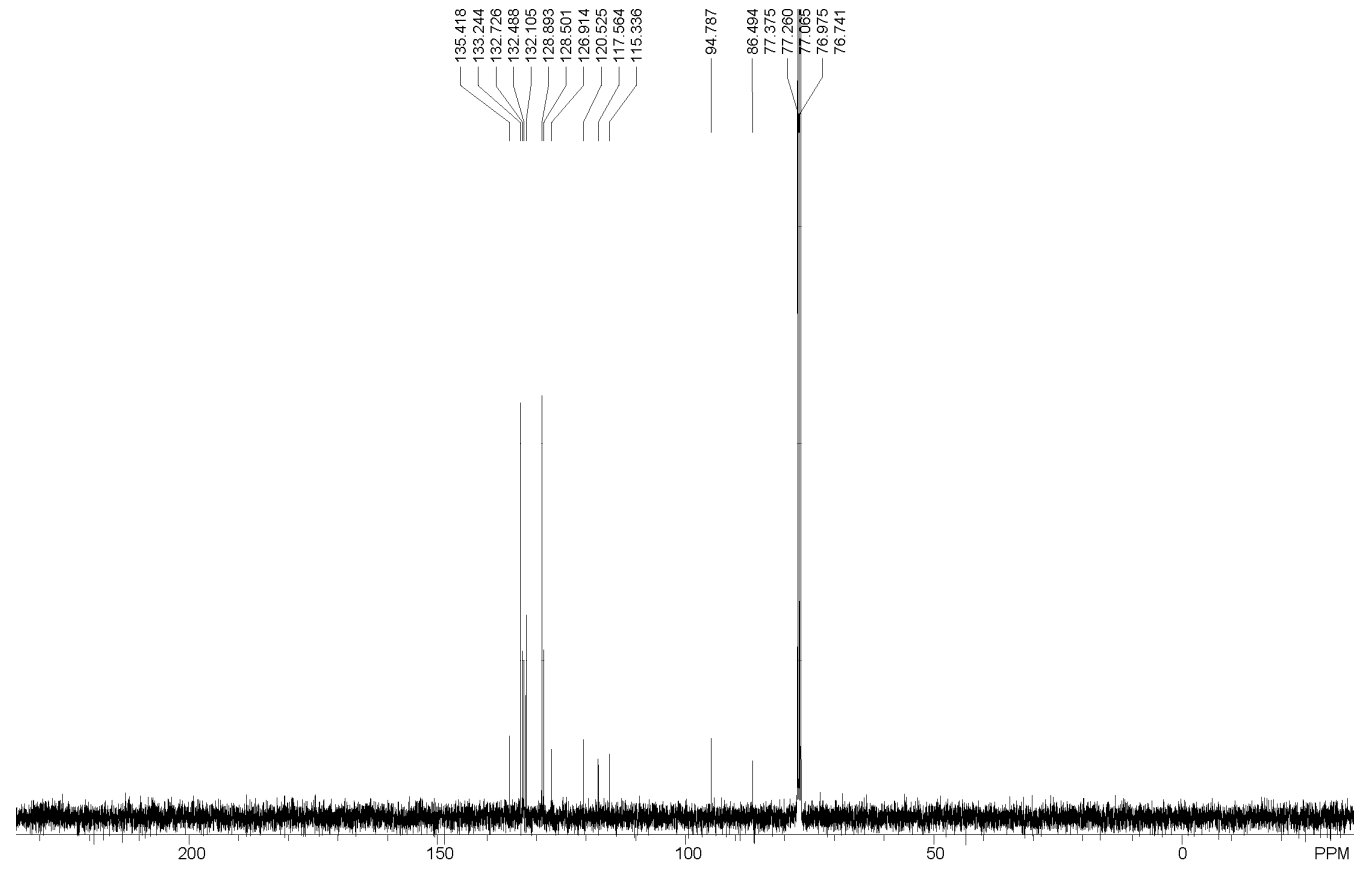
2.00
1.14
1.13
10
8
6
4
2
PPM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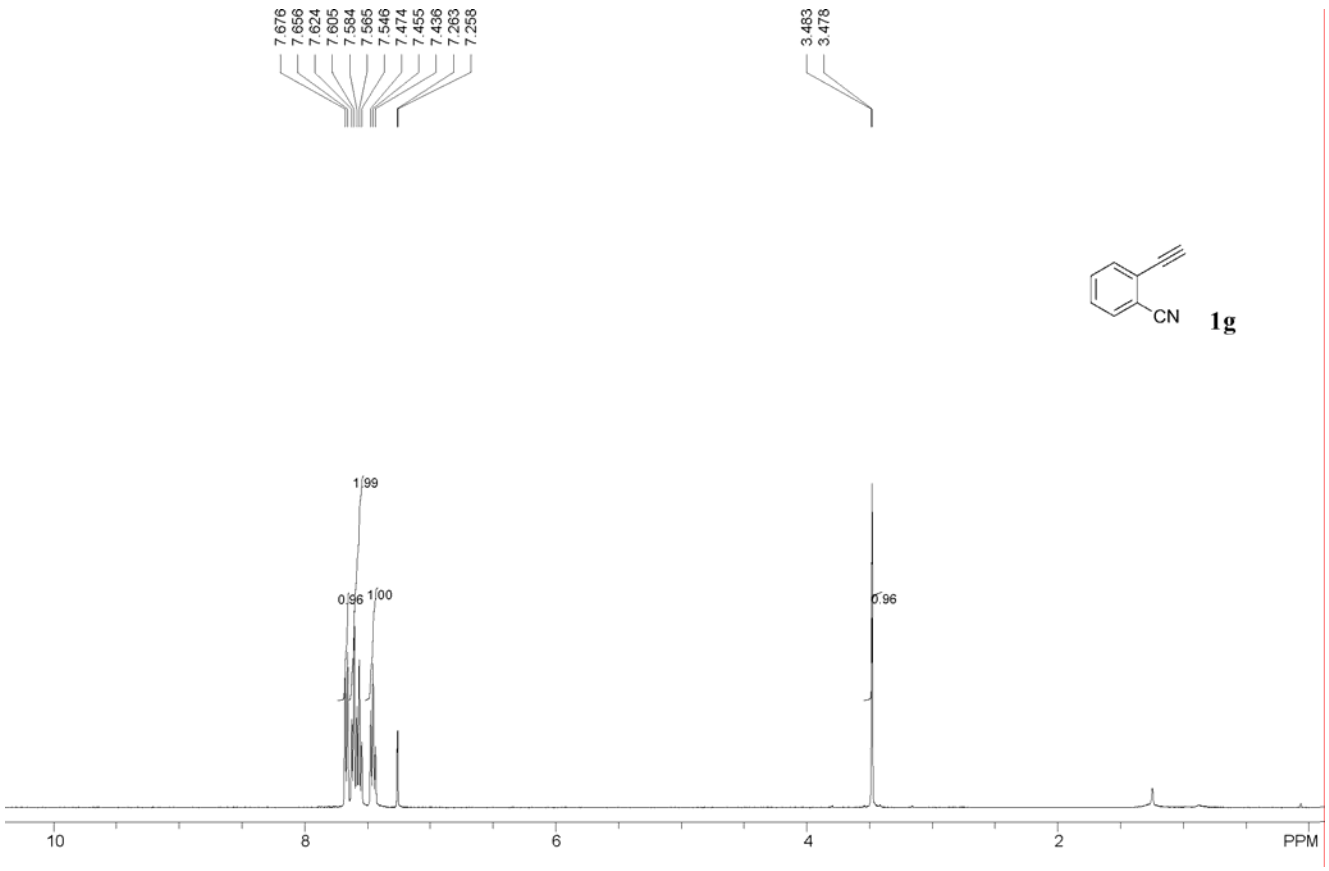
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CN
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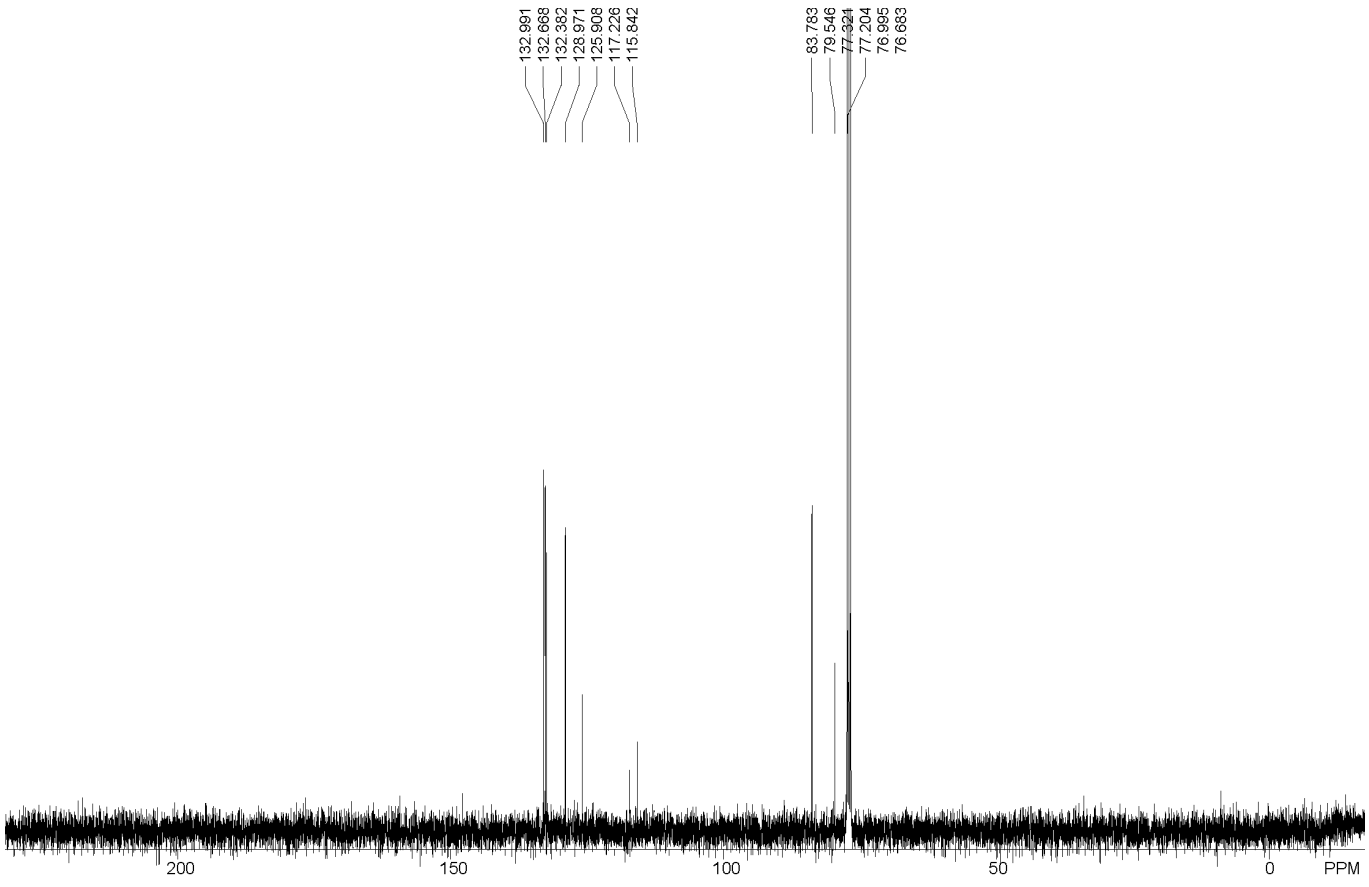
1.00
0.96
10
8
6
4
2
PPM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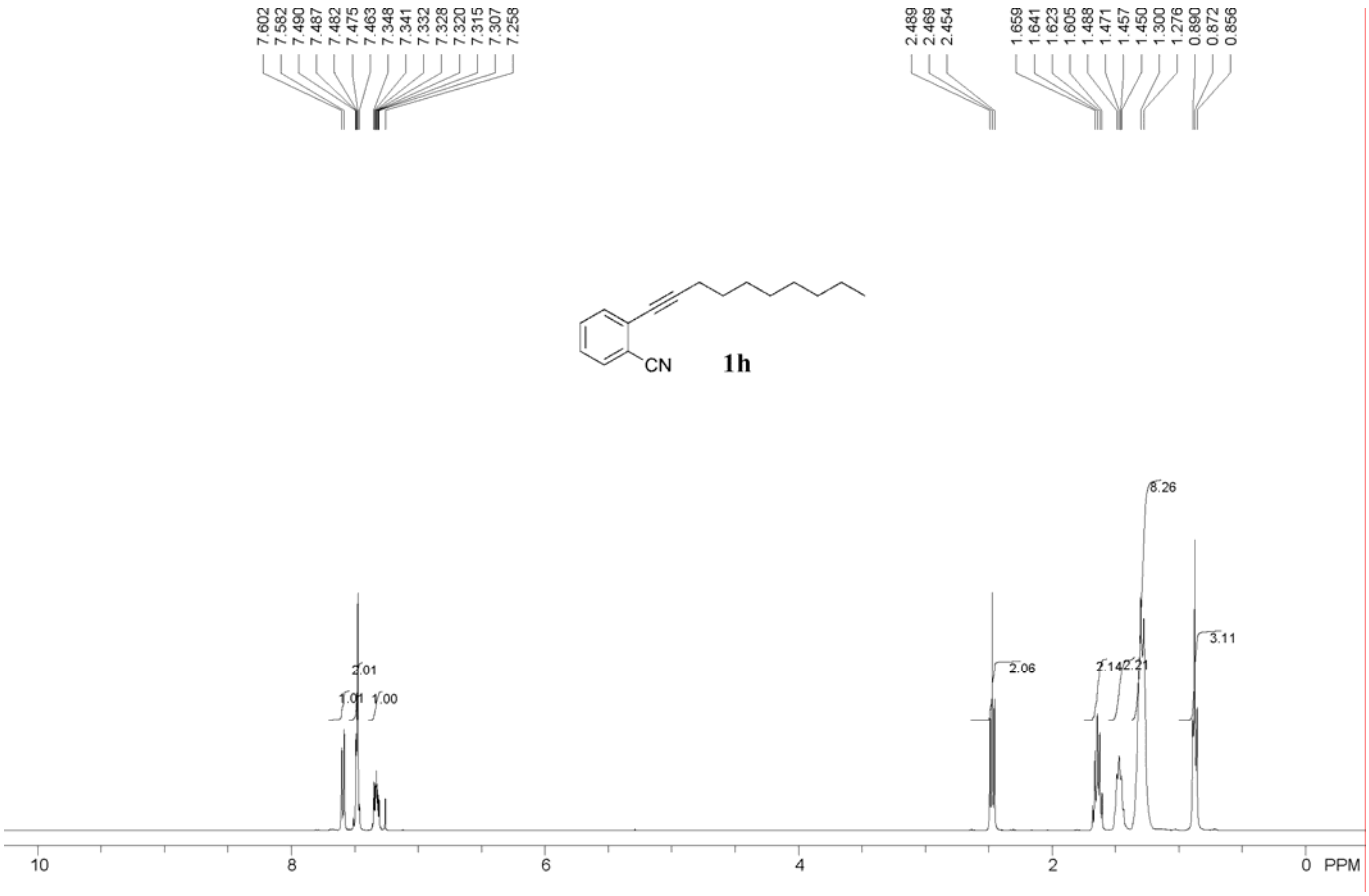
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7.315
7.307
7.258
2.489
2.469
2.454
1.659
1.641
1.623
1.605
1.488
1.471
1.457
1.450
1.300
1.276
0.890
0.872
0.856
CN
1h
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4
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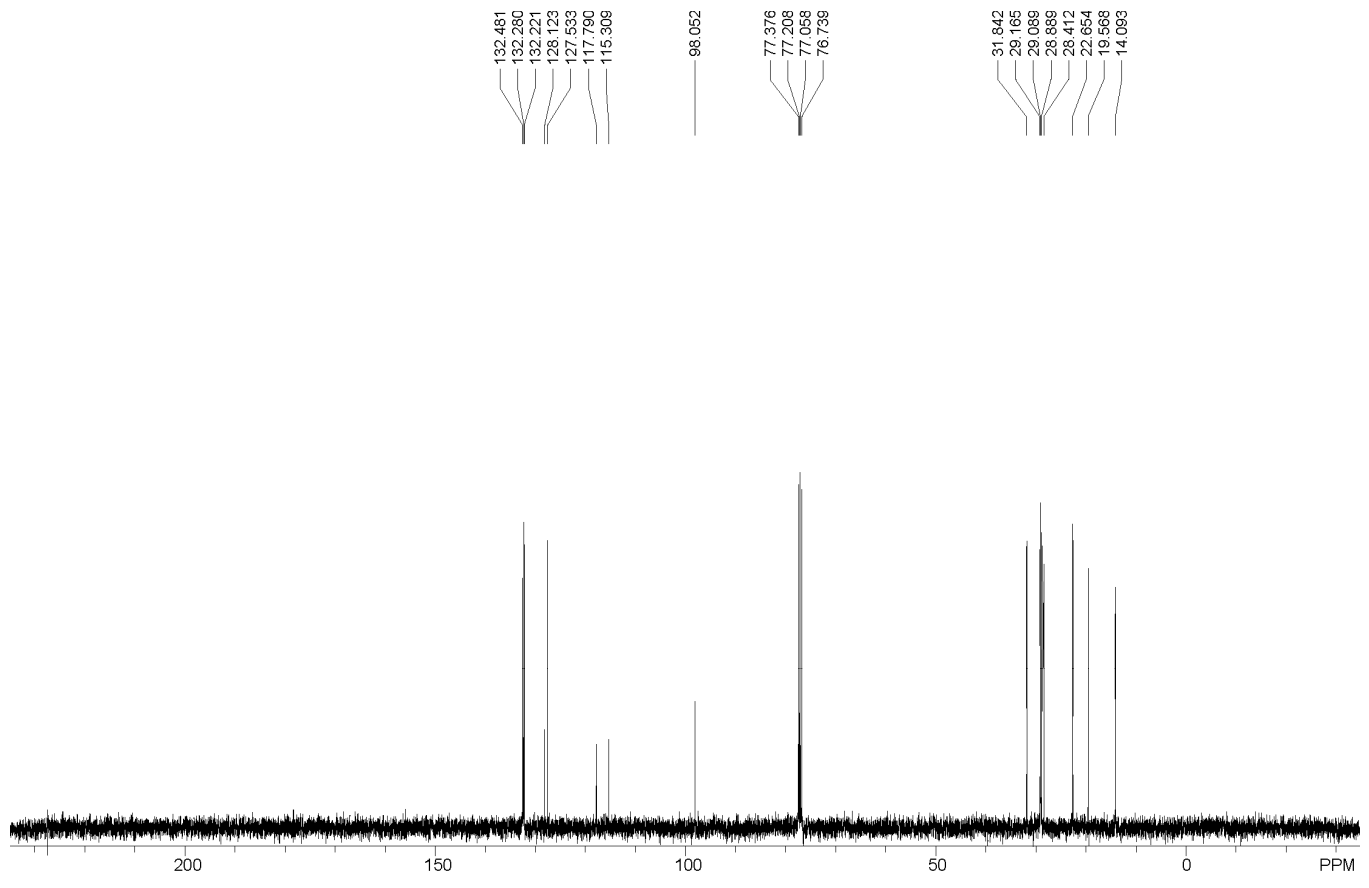
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28.889
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22.654
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14.093
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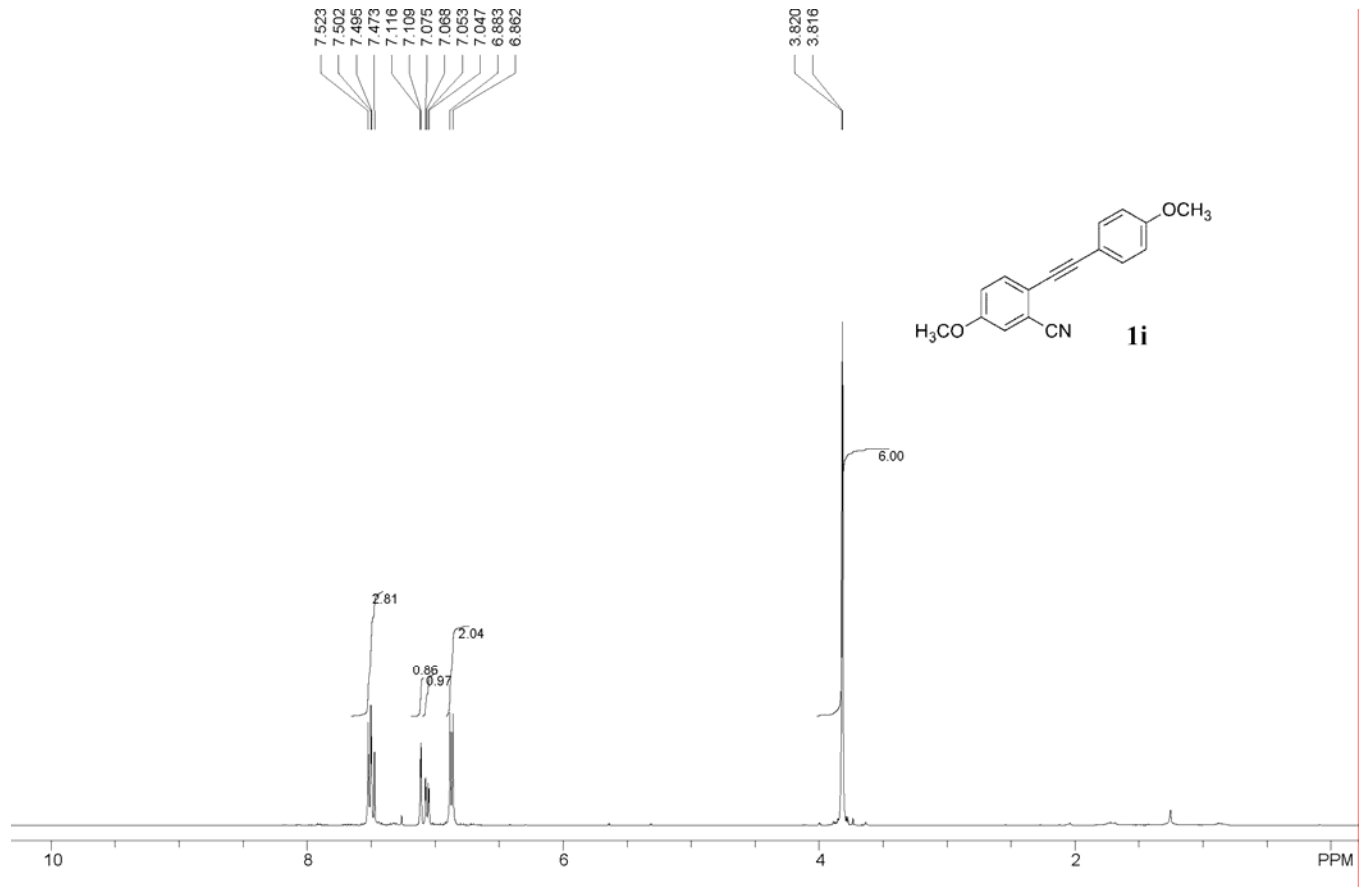
PPM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7.047
6.883
6.862
3.820
3.816
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CN
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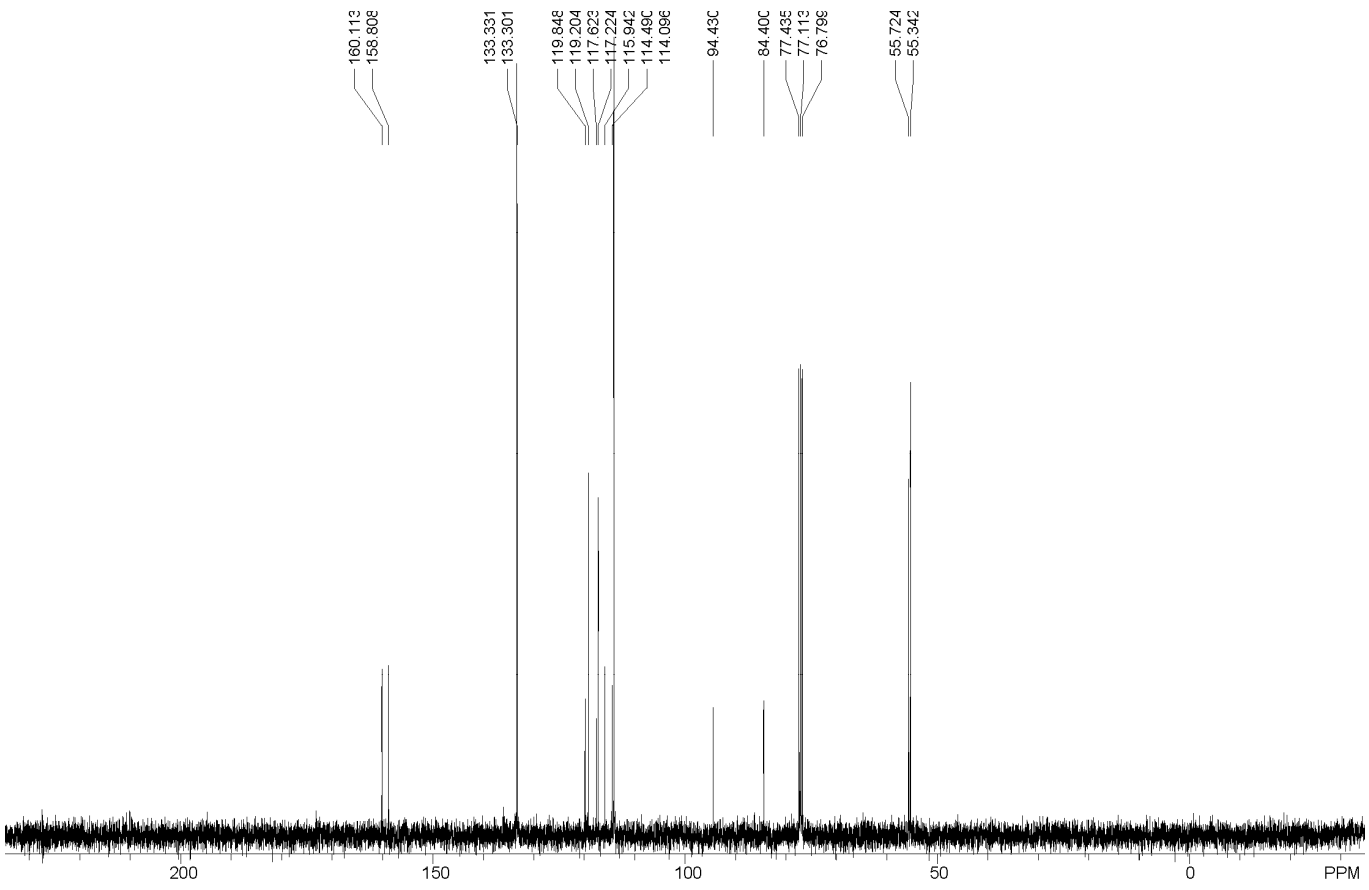
2.04
0.86
0.97
10
8
6
4
2
PPM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150
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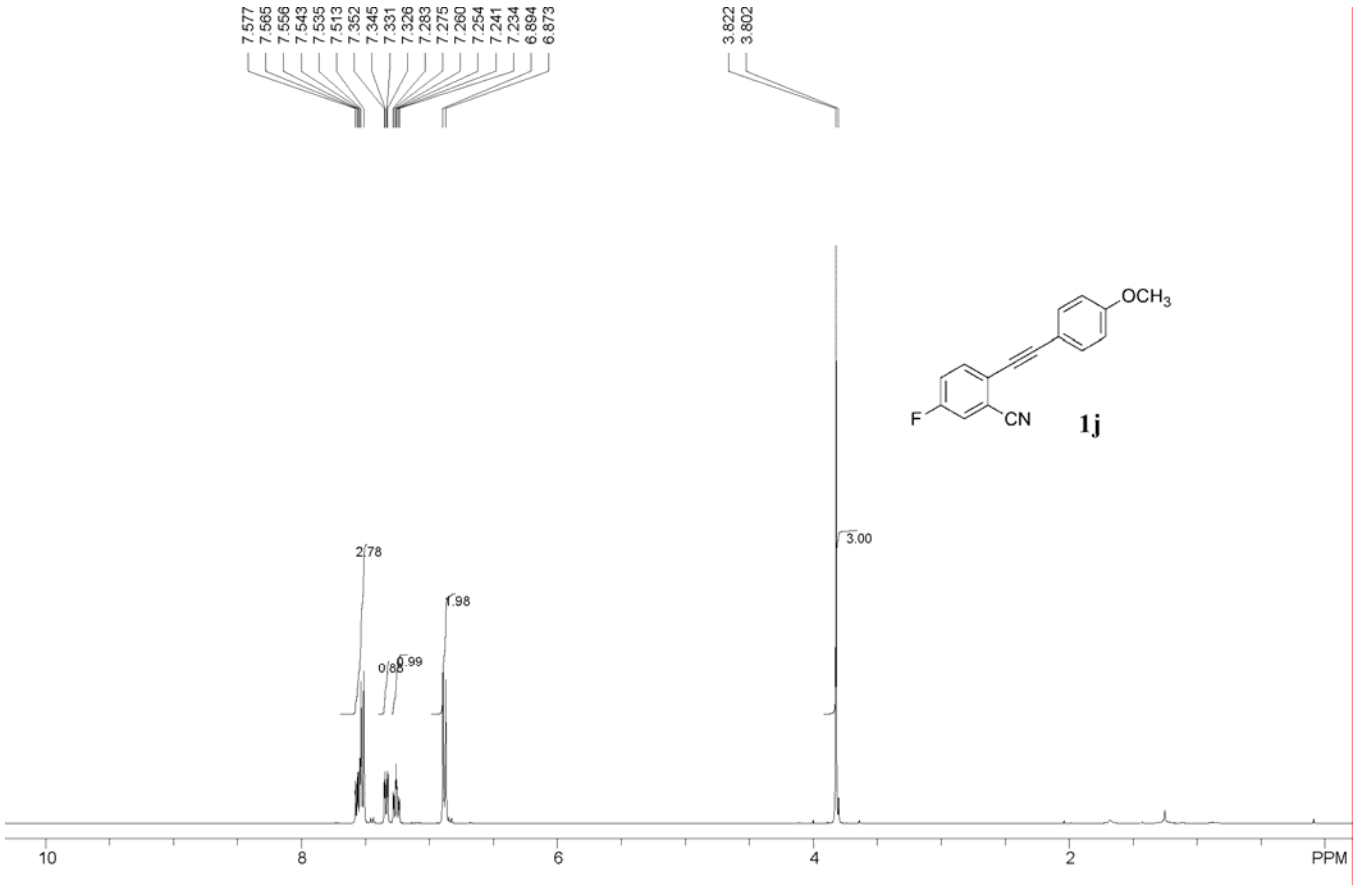
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7.241
7.234
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6.873
3.822
3.802
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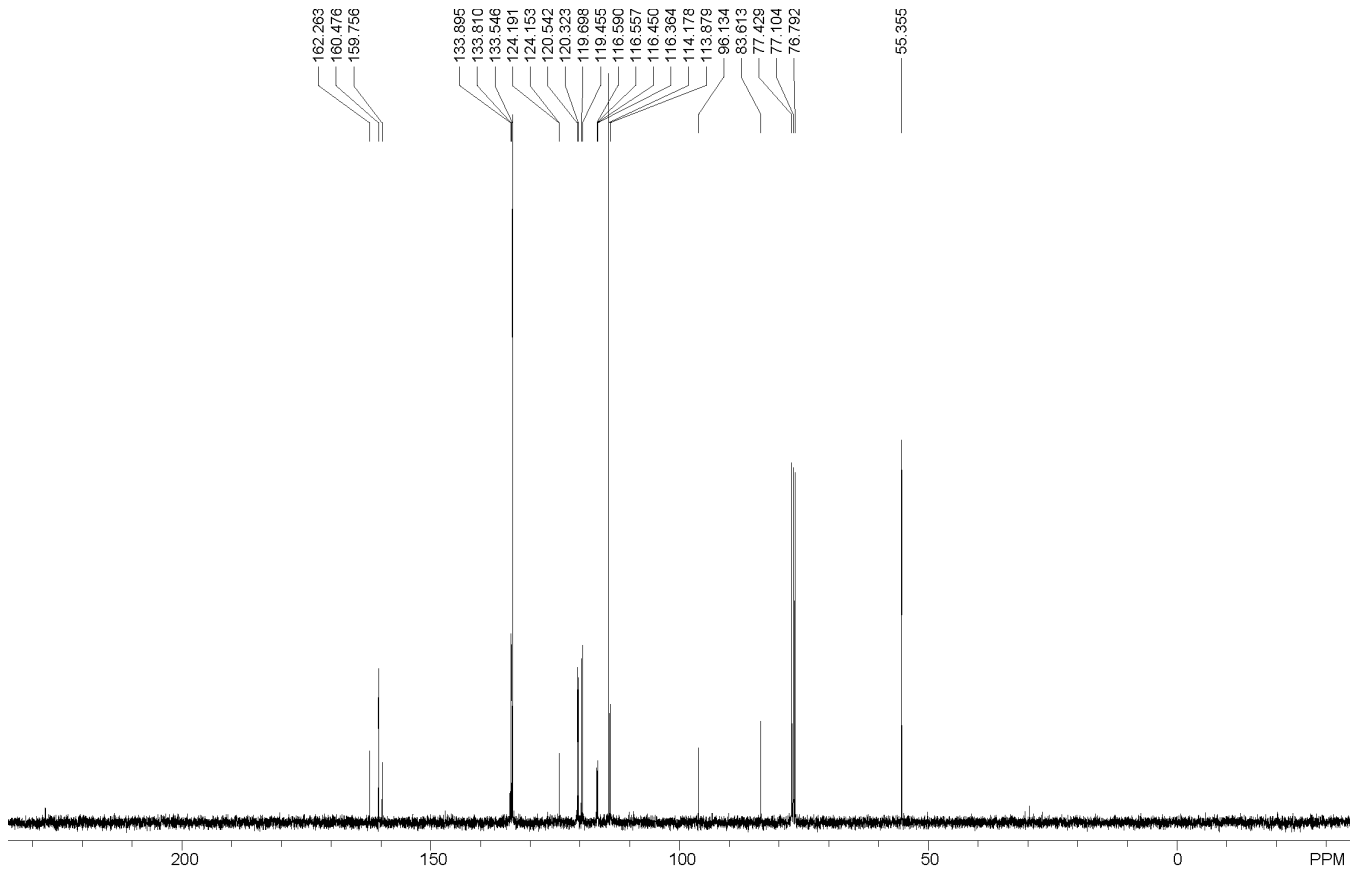
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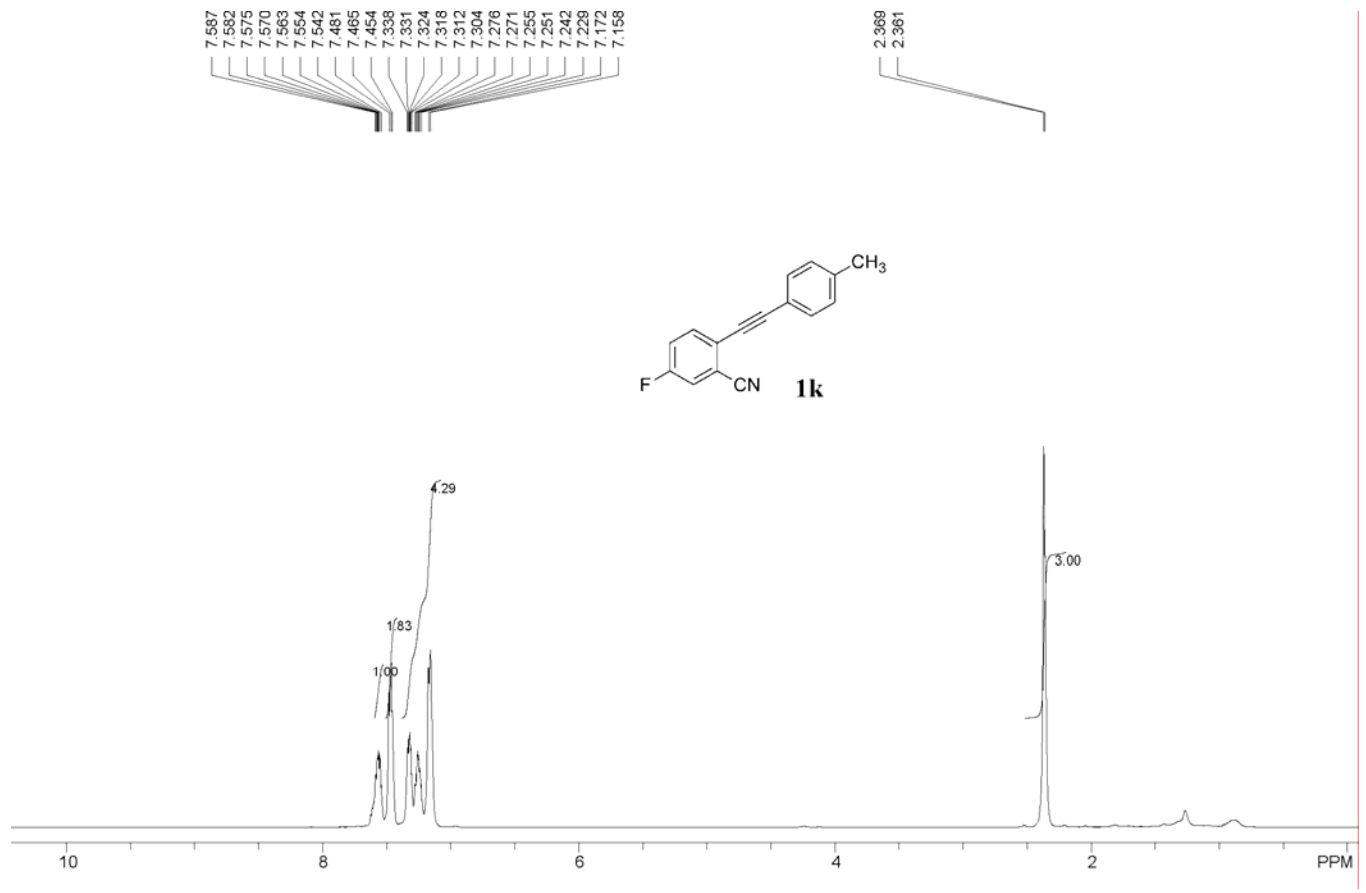
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7.276
7.271
7.255
7.251
7.242
7.229
7.172
7.158
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CN
1k
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3.00
10
8
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4
2
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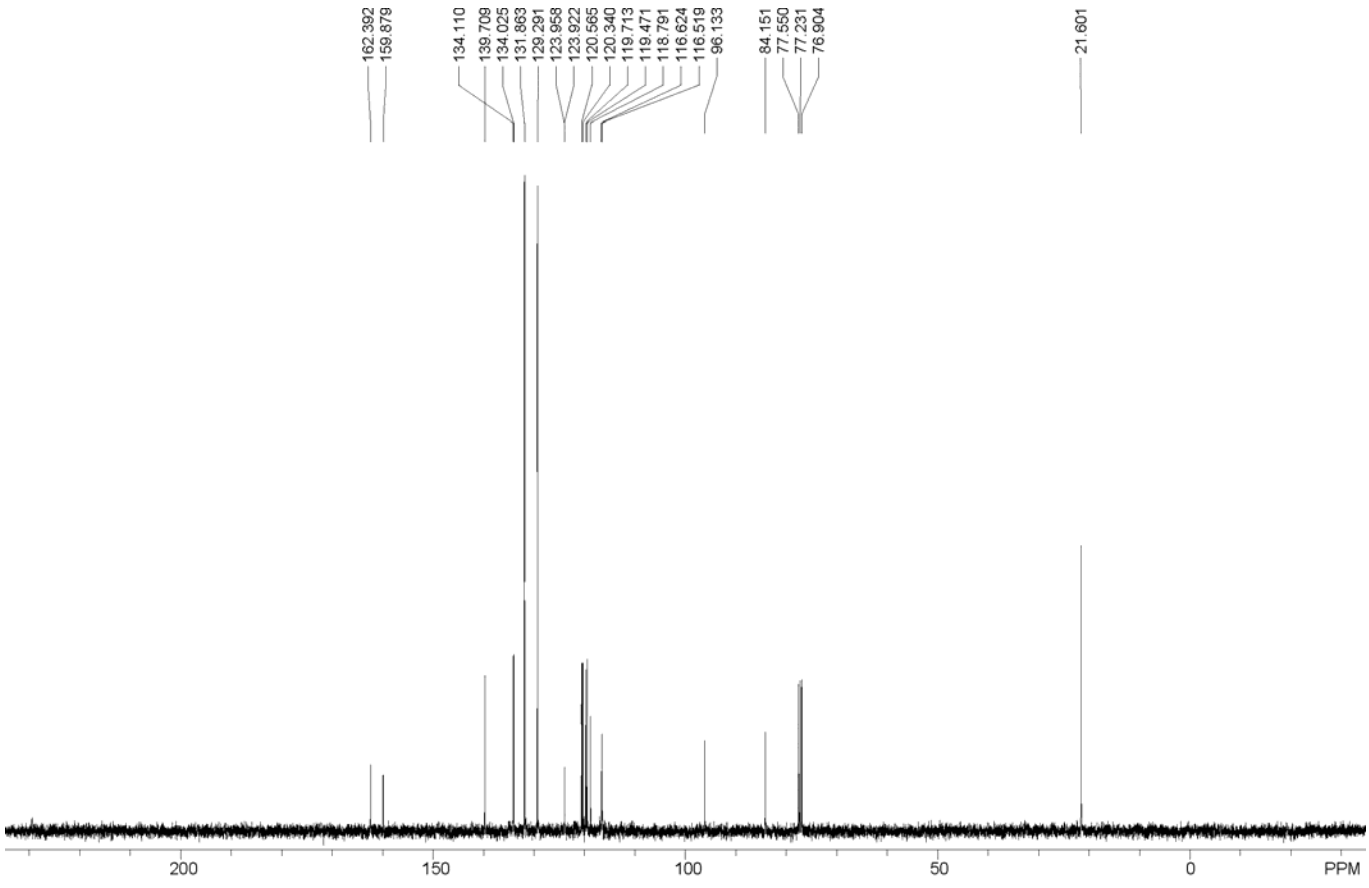
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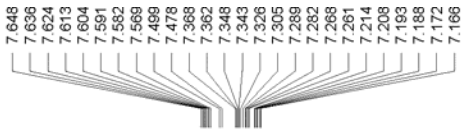
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7.343
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7.208
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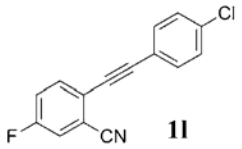
7.188
7.172
7.166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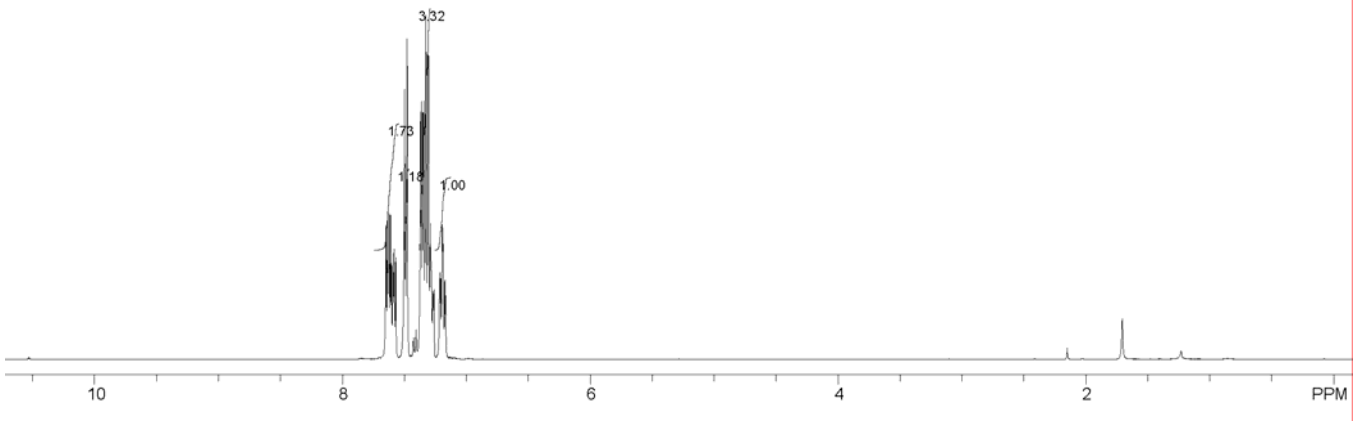
F
CN

1l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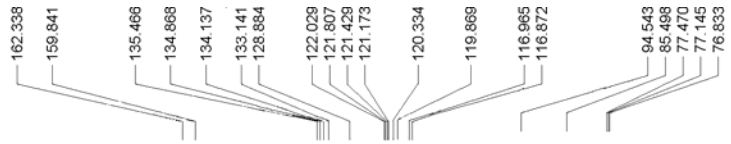
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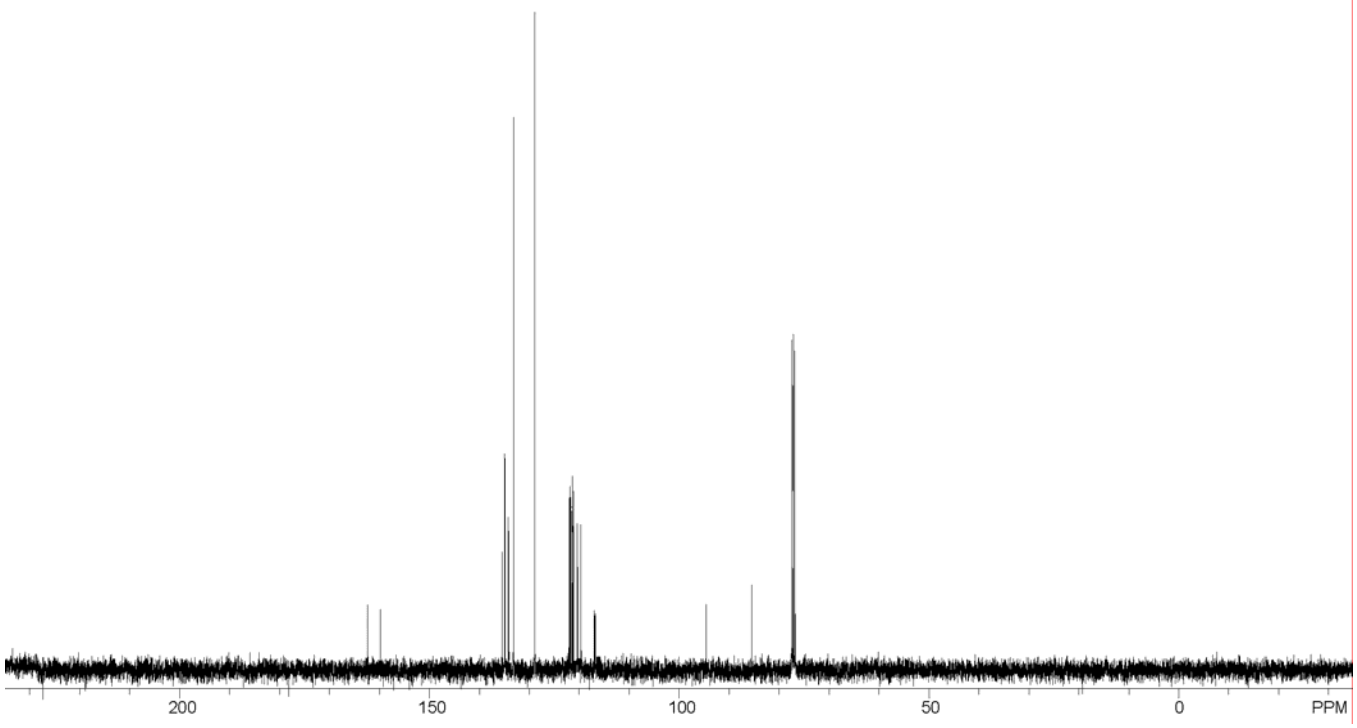
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150
100
50
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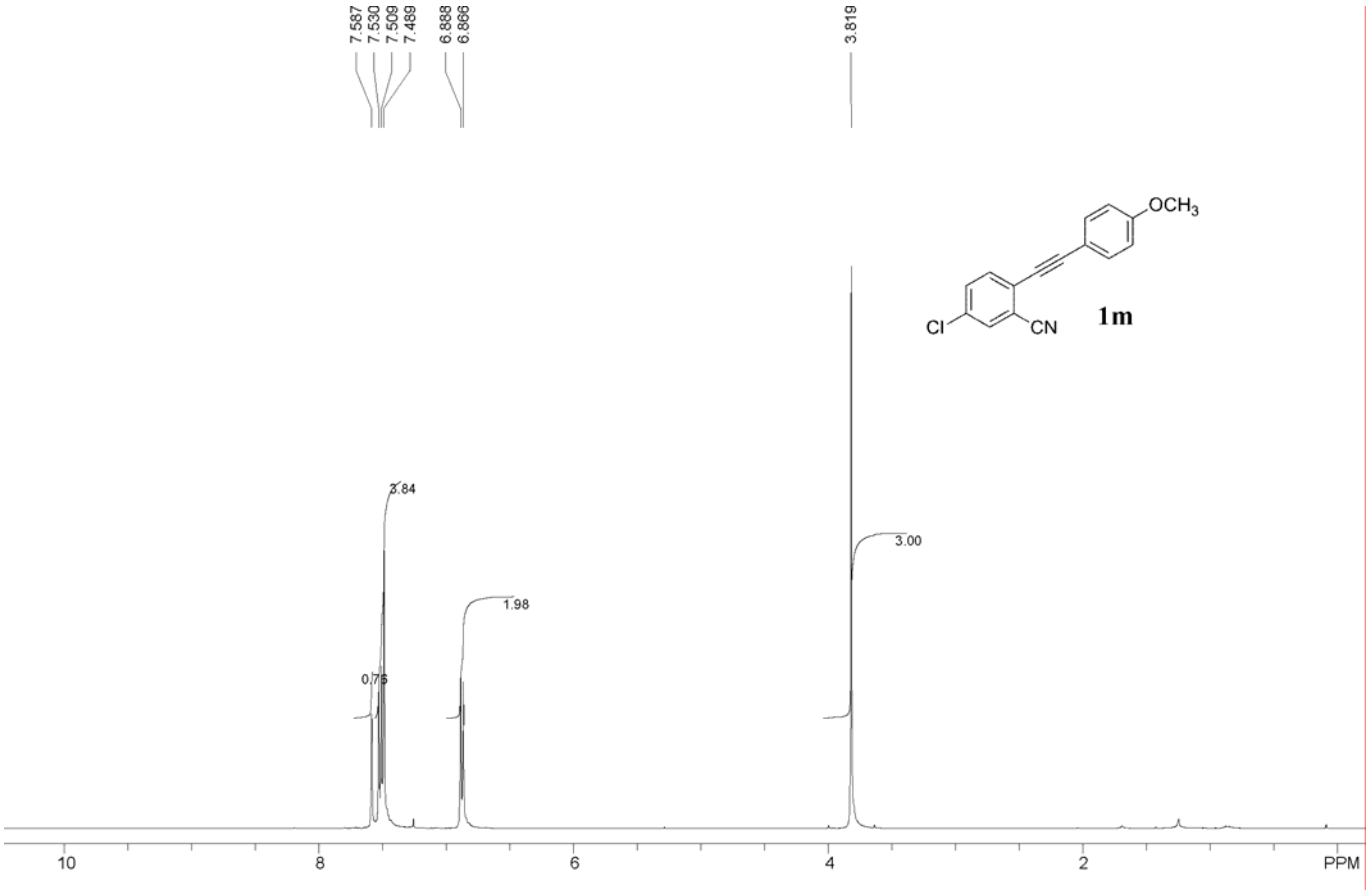
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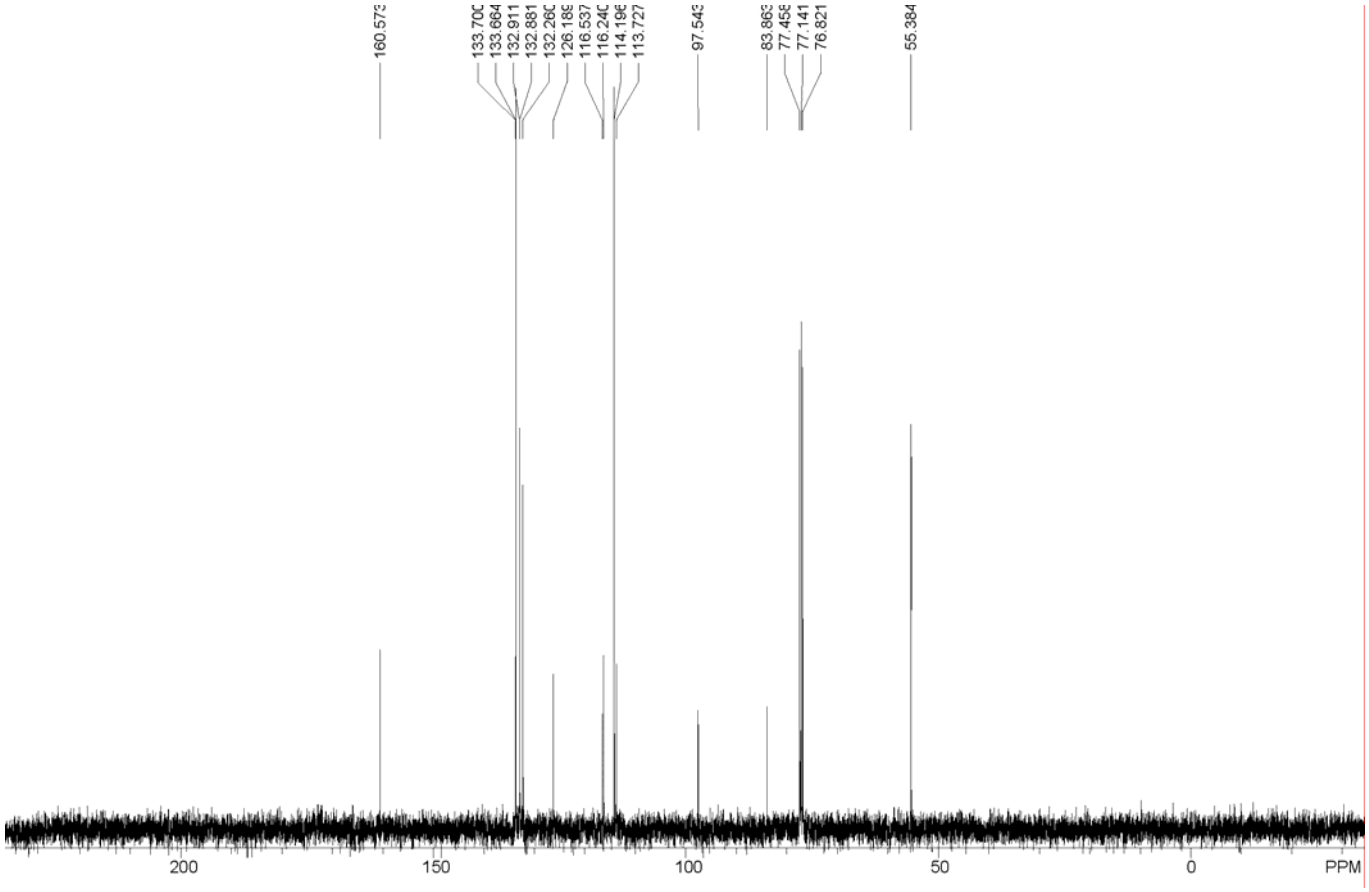
2
PPM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113.727
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83.863
77.458
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55.384
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100
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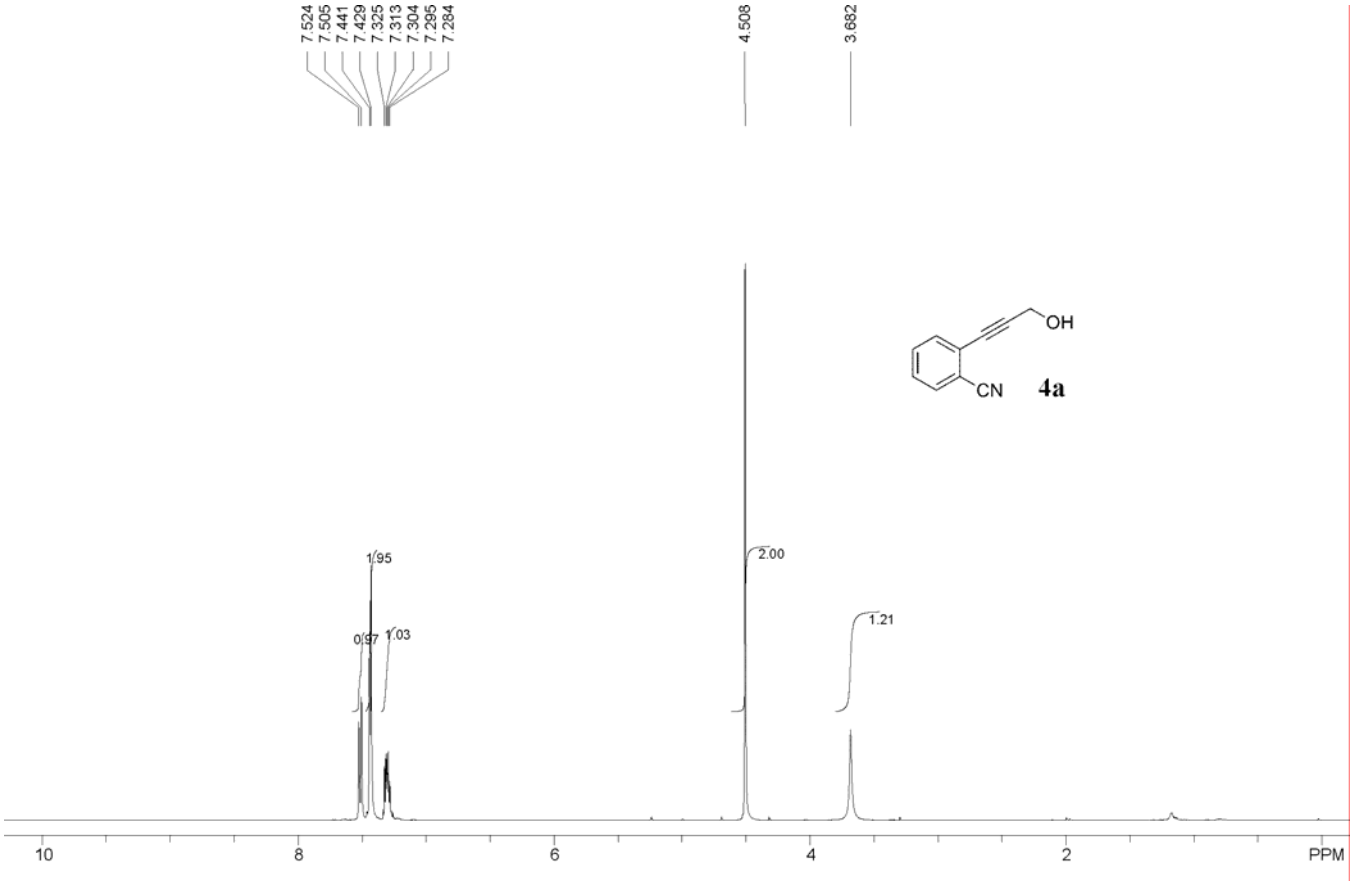
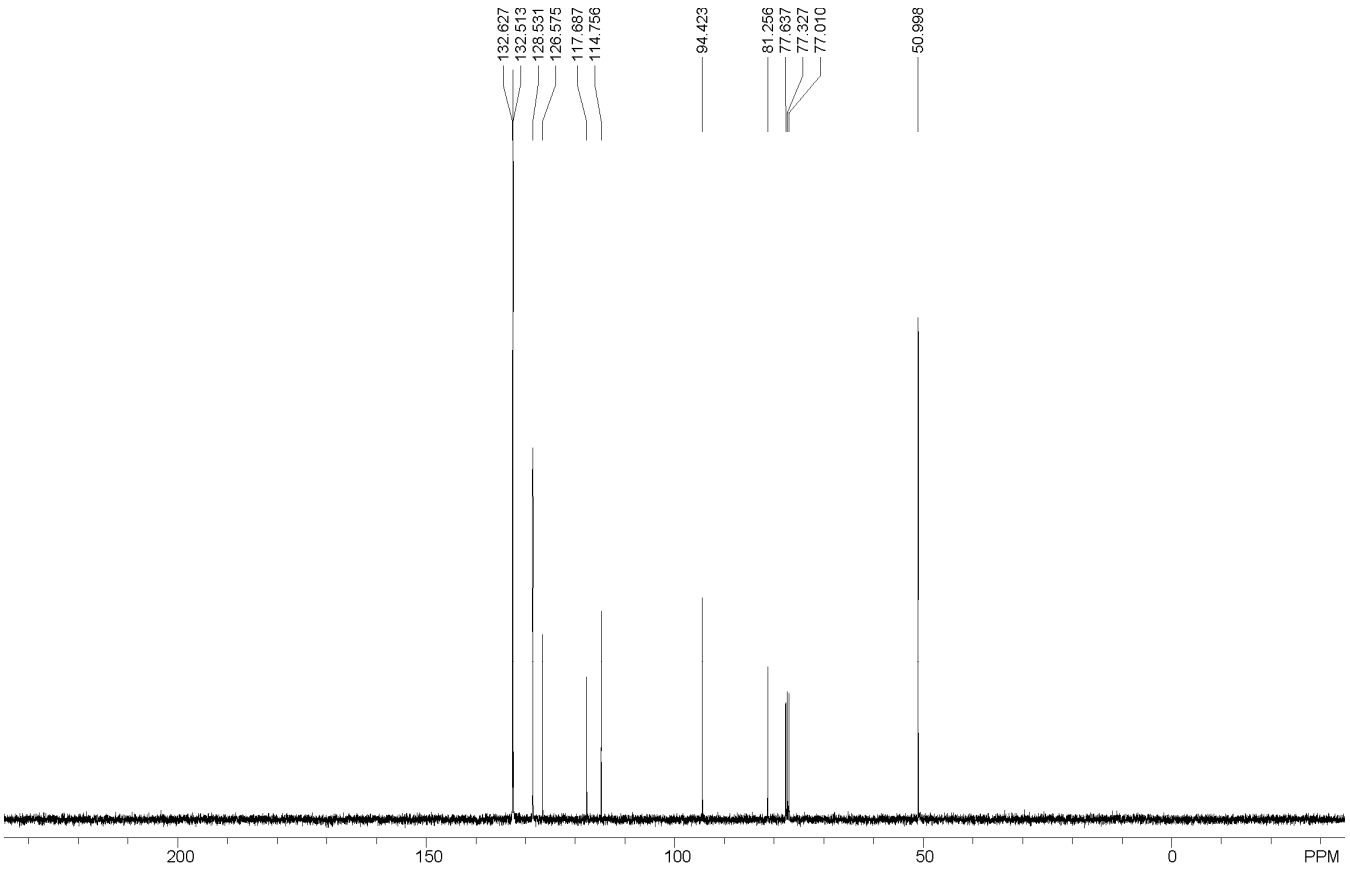
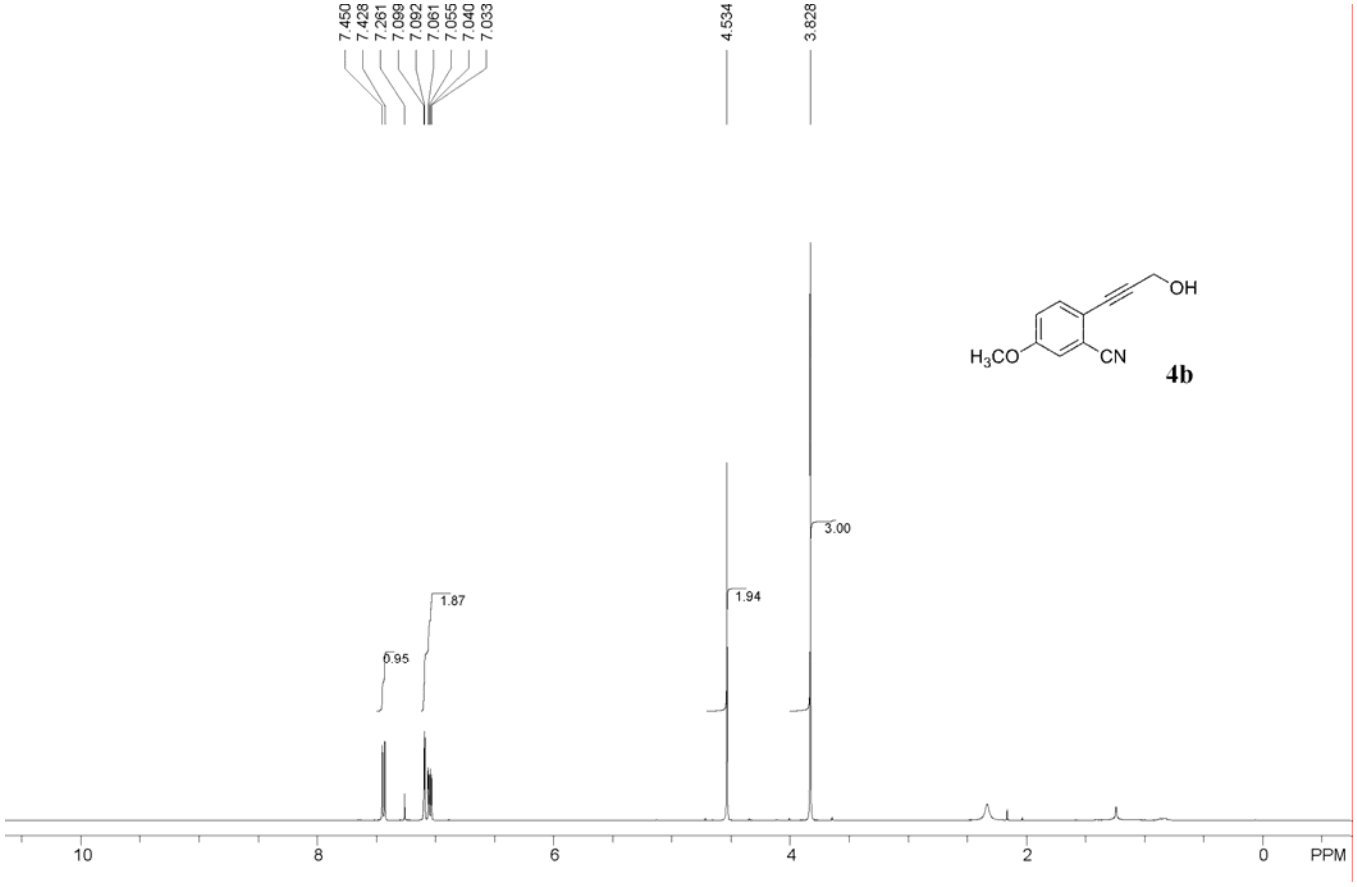
IV. Copies of ^{1}H and ^{13}C NMR spectra of 4a-4k



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CN
4b
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1.87
0.95
10
8
6
4
2
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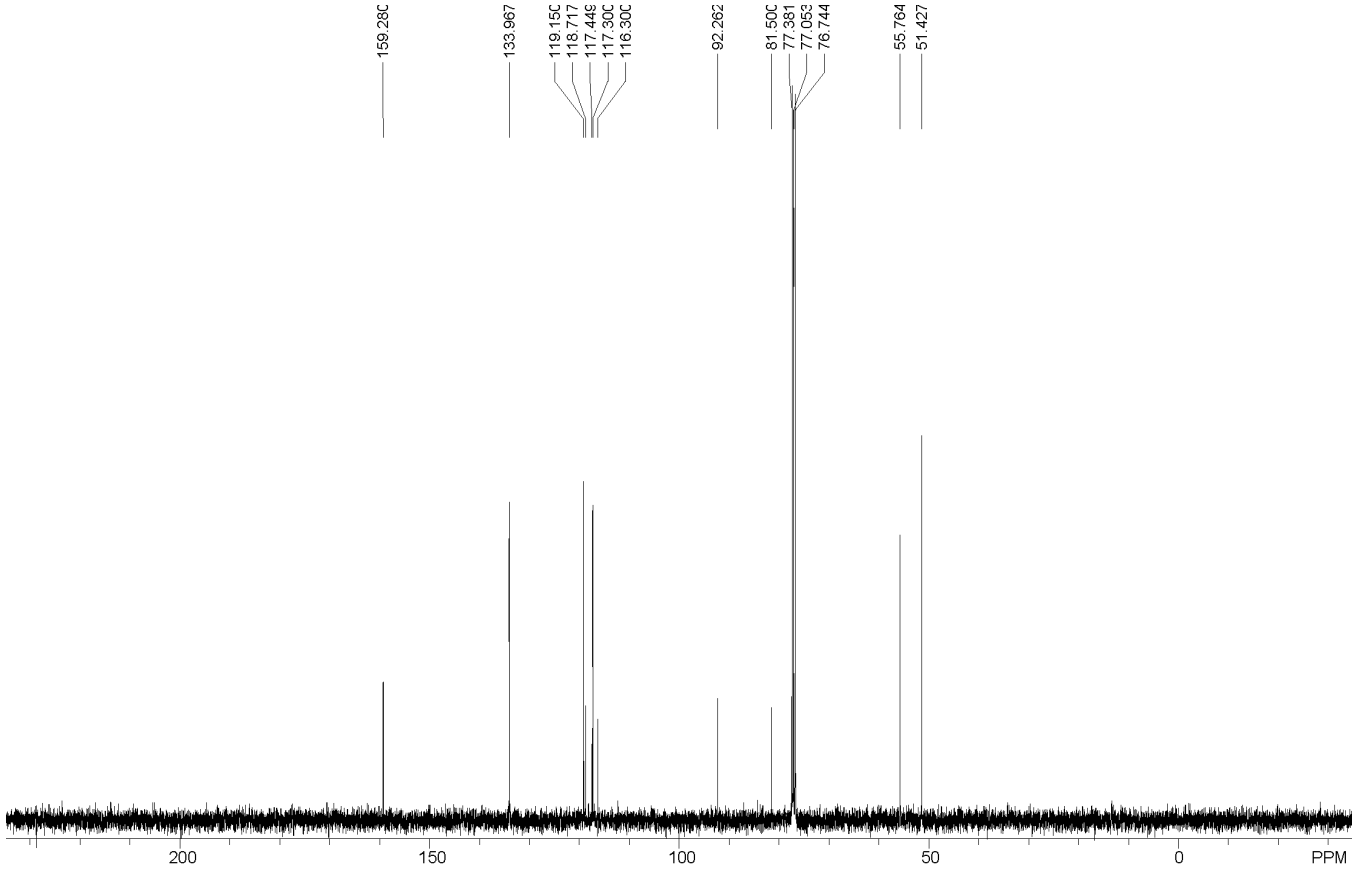
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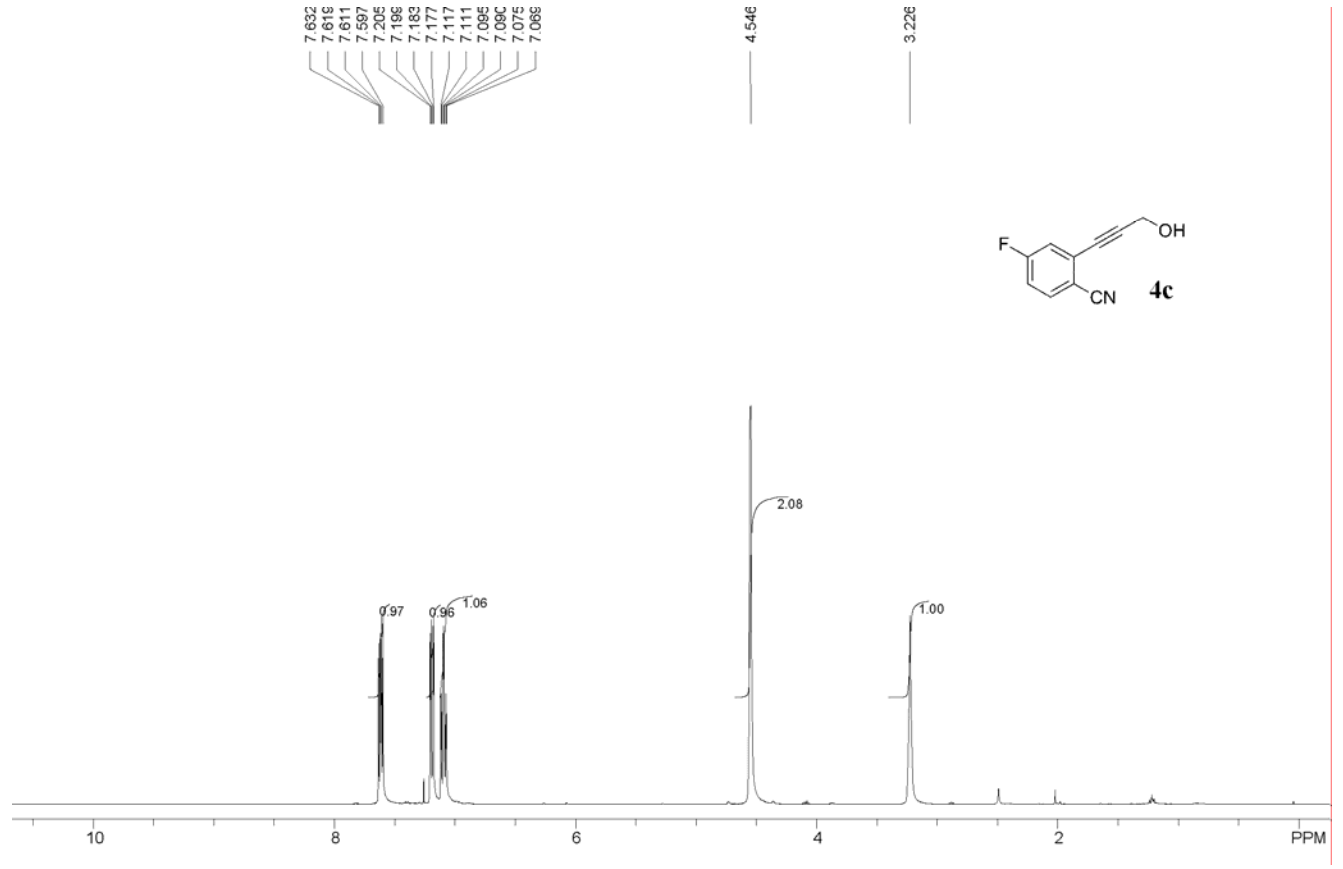
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7.095
7.090
7.075
7.069
4.546
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1.00
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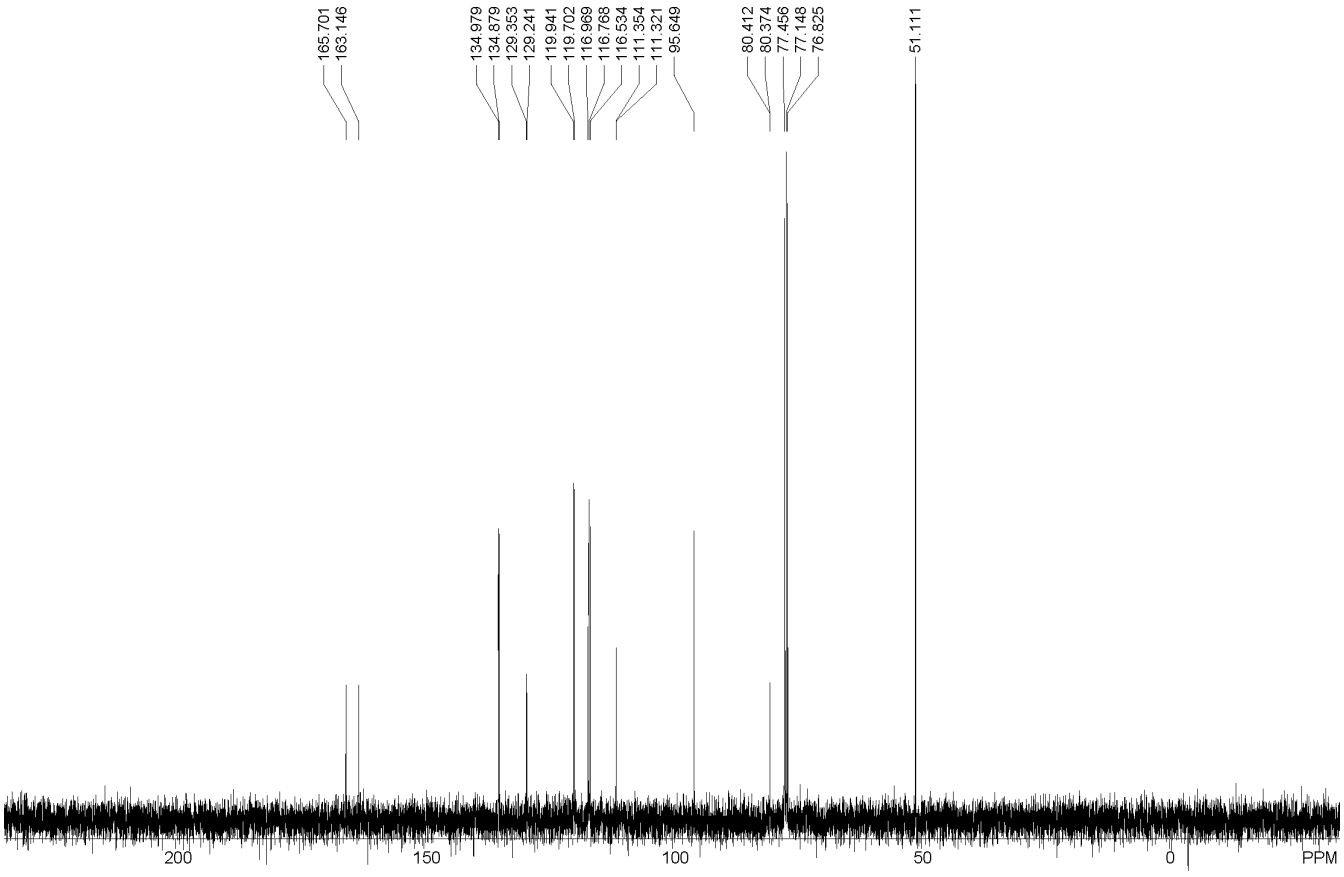
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119.702
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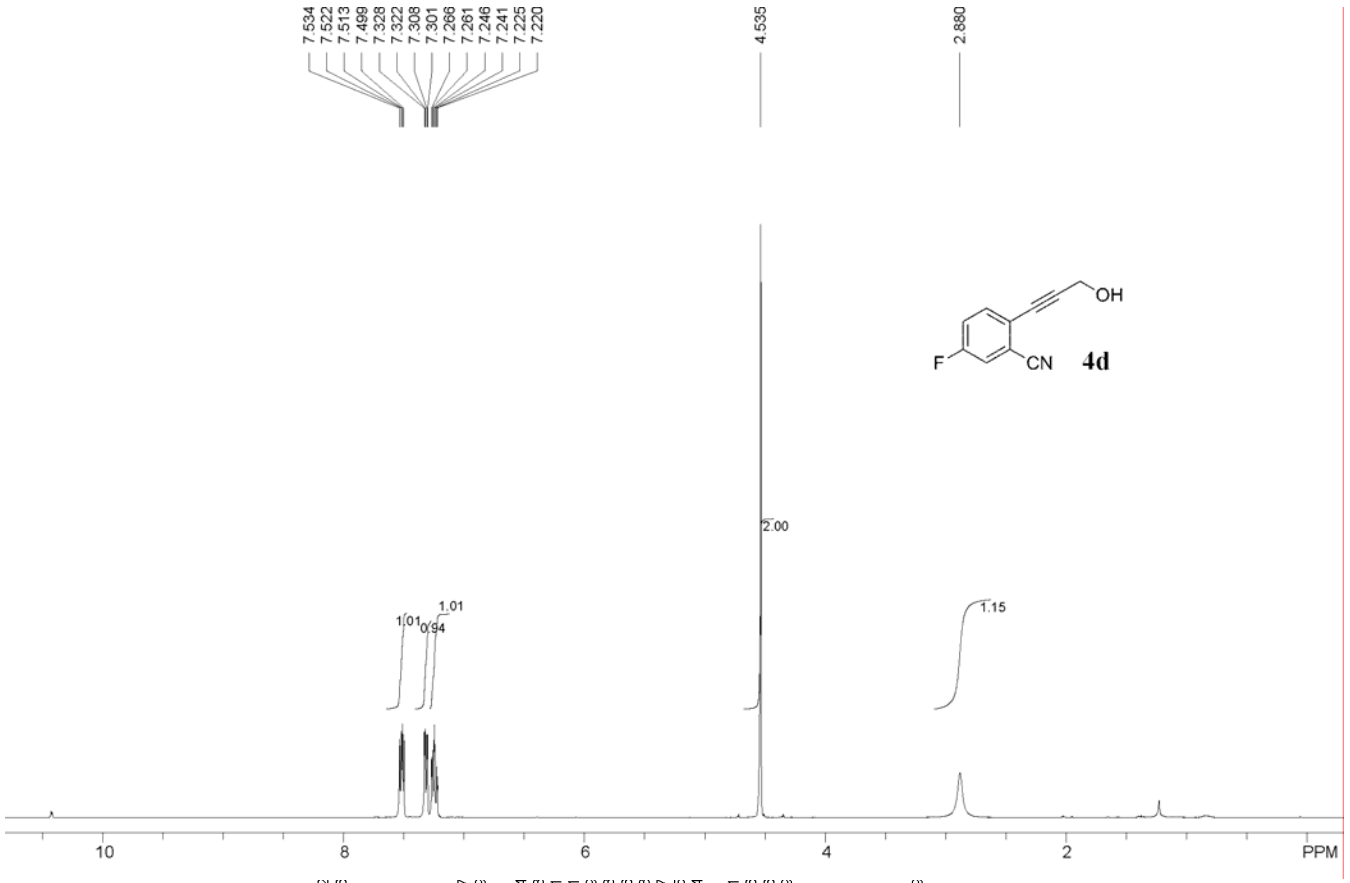
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7.513
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7.301
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7.261
7.246
7.241
7.225
7.220
4.535
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1.01
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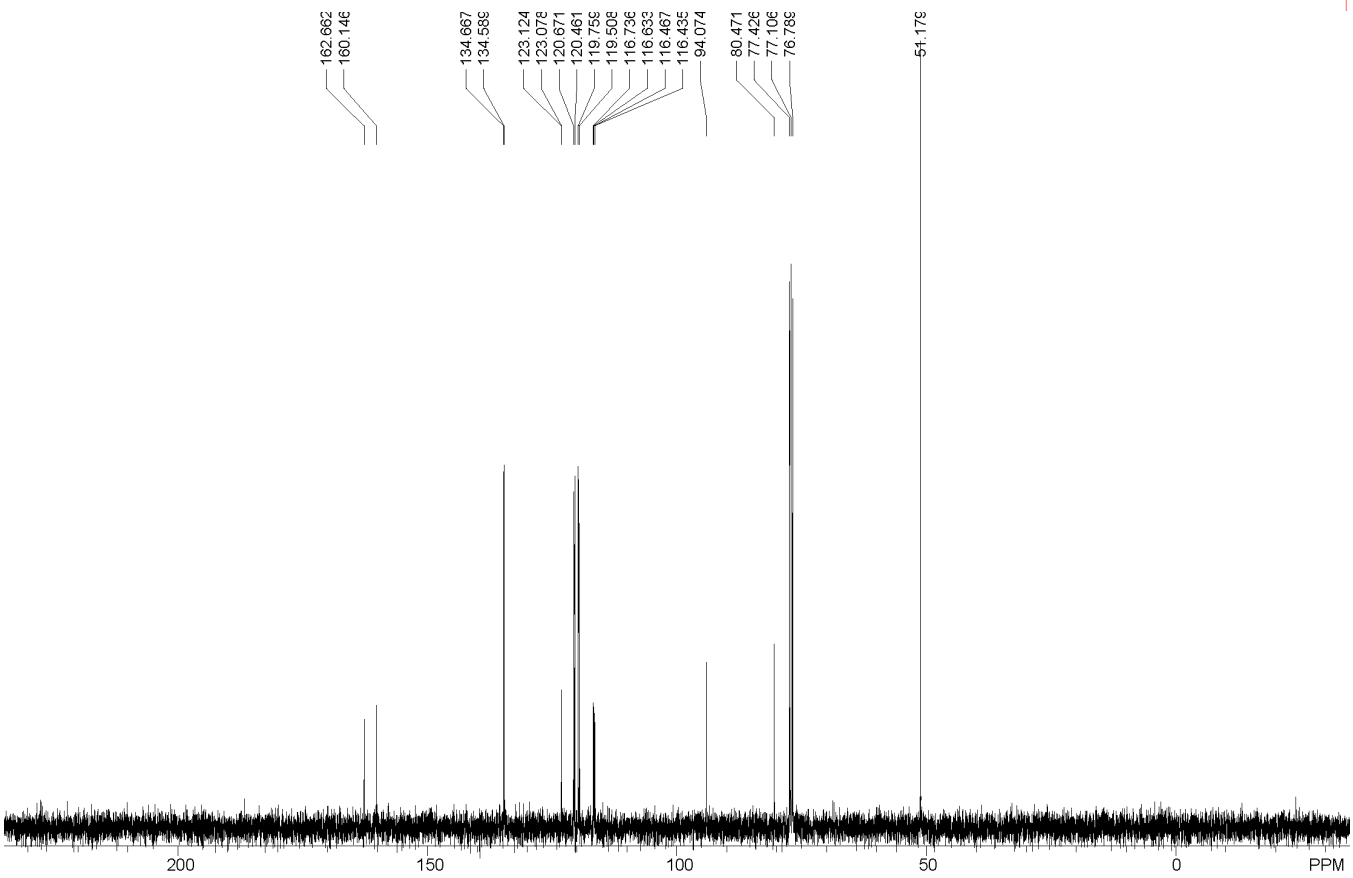
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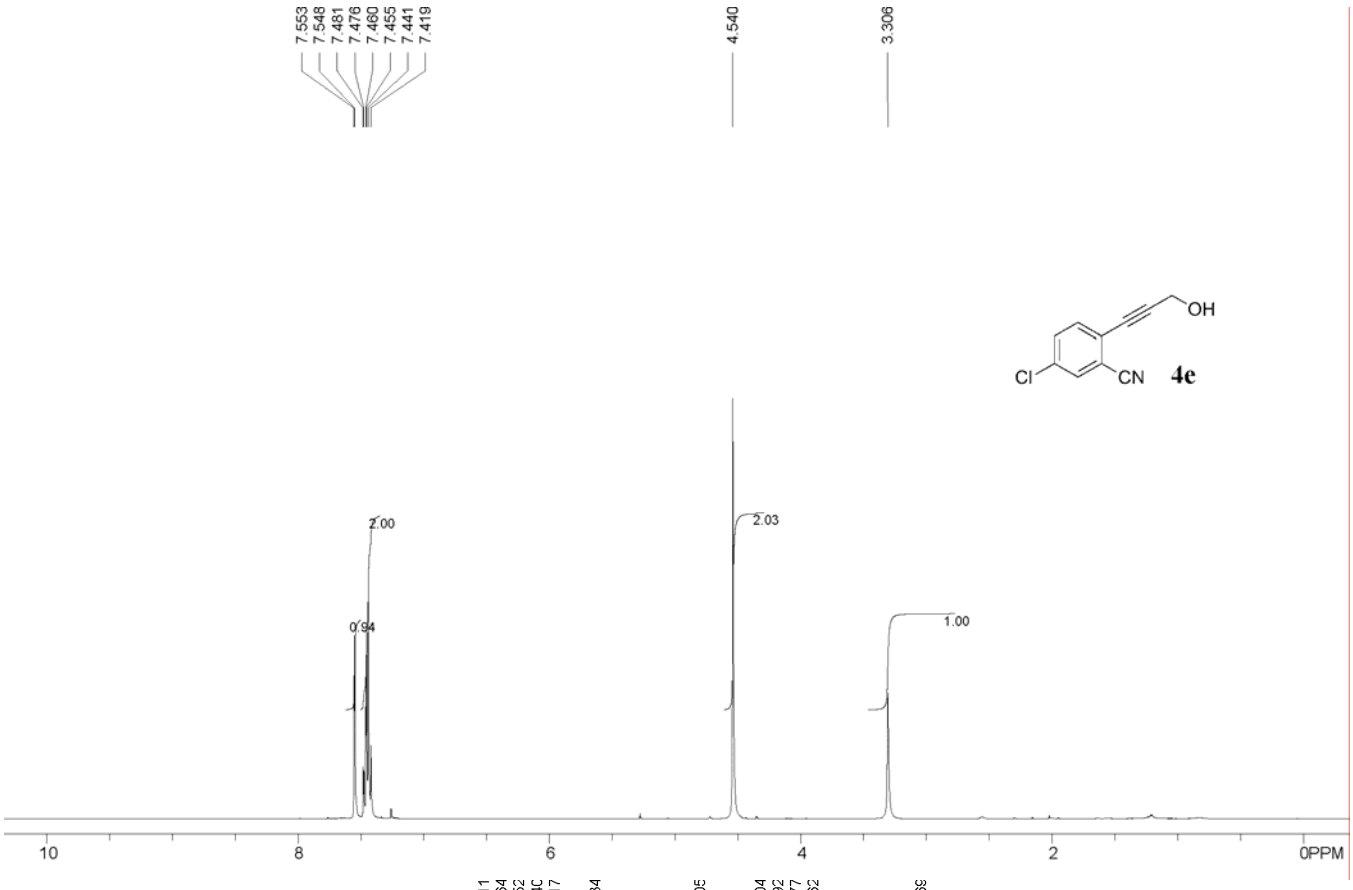
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7.419
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Cl
CN
4e
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1.00
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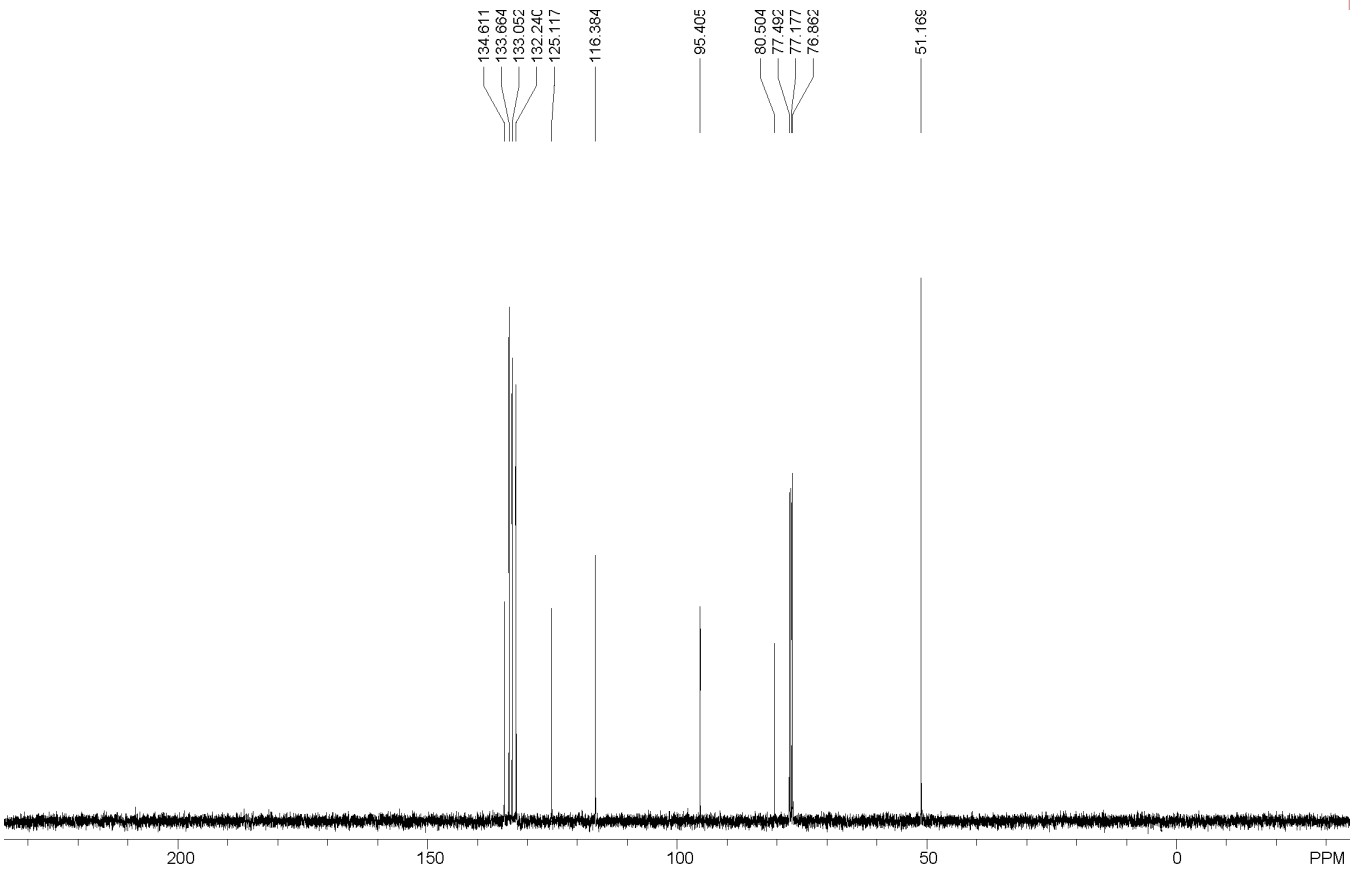
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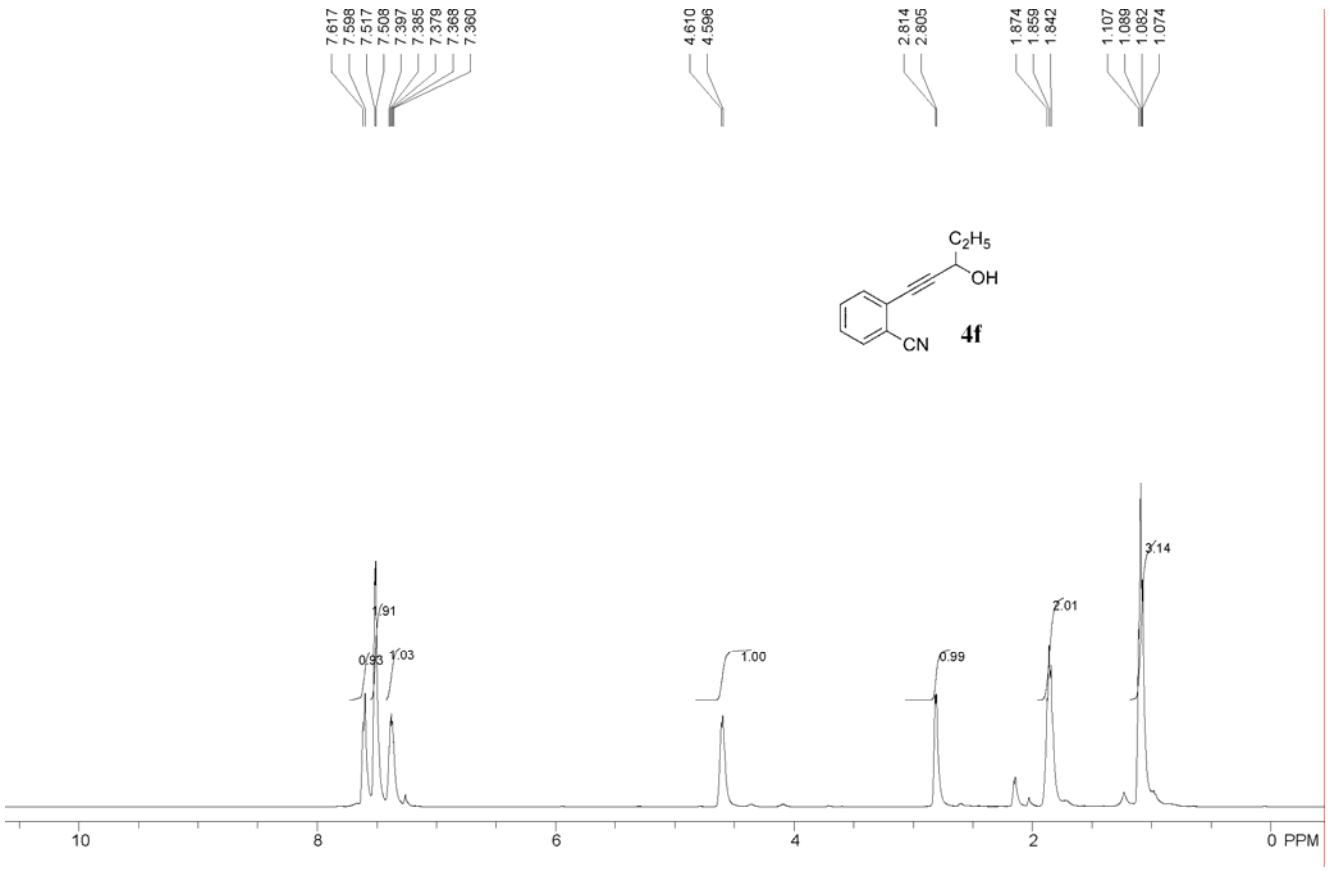
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7.368
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4.610
4.596
2.814
2.805
1.874
1.859
1.842
1.107
1.089
1.082
1.074
C_2H_5
OH
CN
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0.93
1.03
1.00
0.99
2.01
3.14
10
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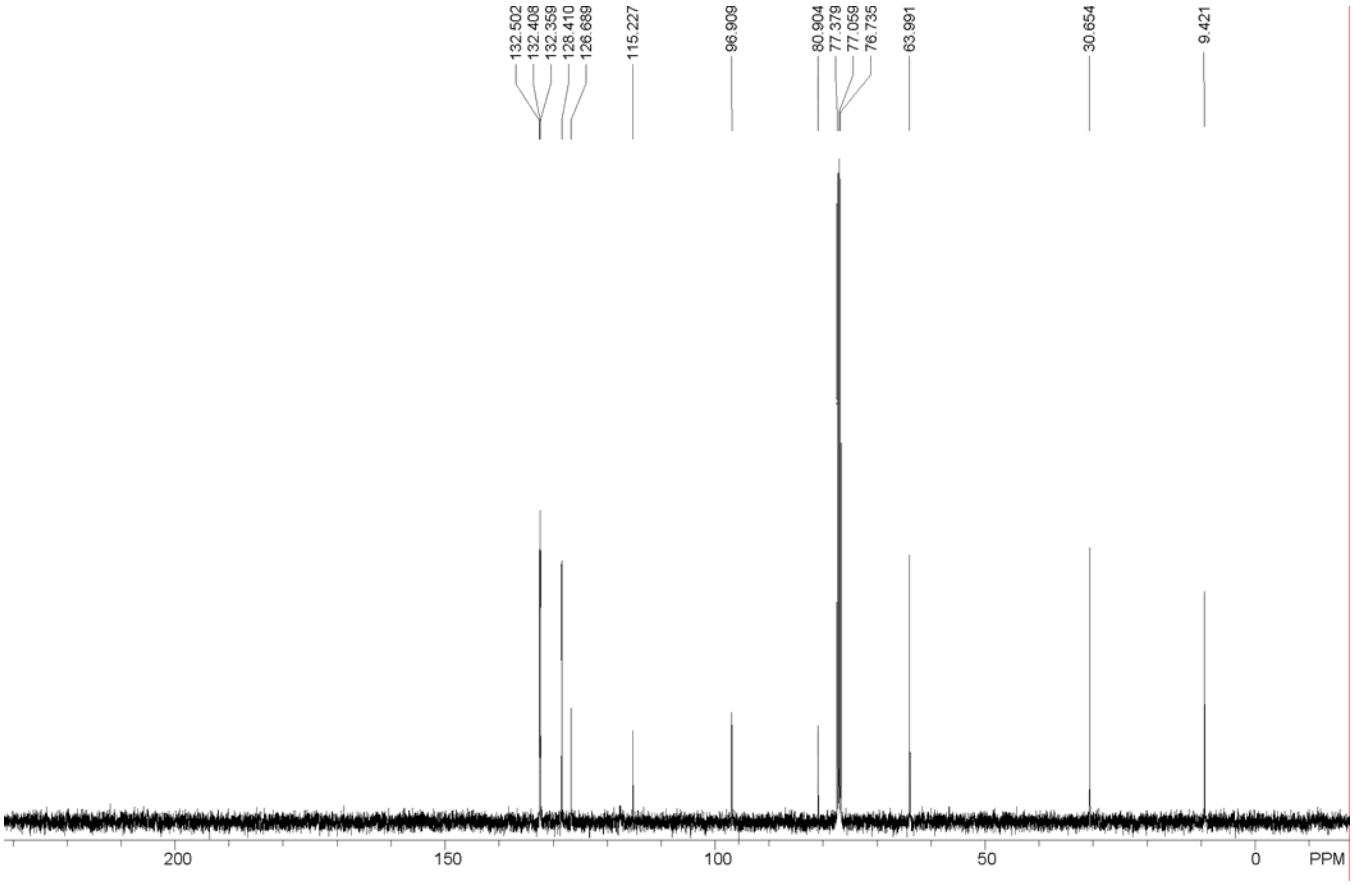
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132.359
128.410
126.689
115.227
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80.904
77.379
77.059
76.735
63.991
30.654
9.421
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150
100
50
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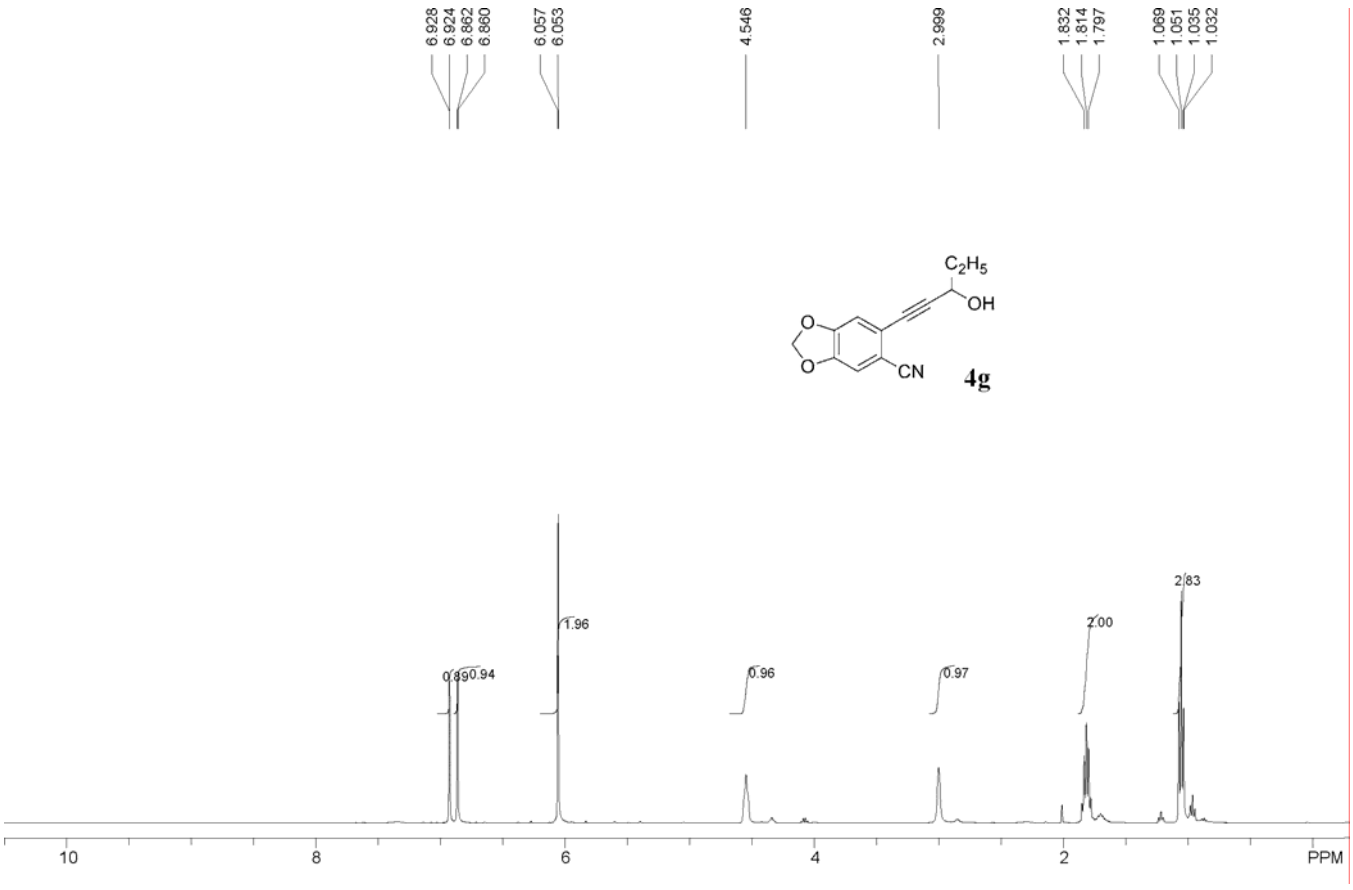
PPM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6.924
6.862
6.860
6.057
6.053
4.546
2.999
1.832
1.814
1.797
1.069
1.051
1.035
1.032
C_2H_5
OH
O
O
CN
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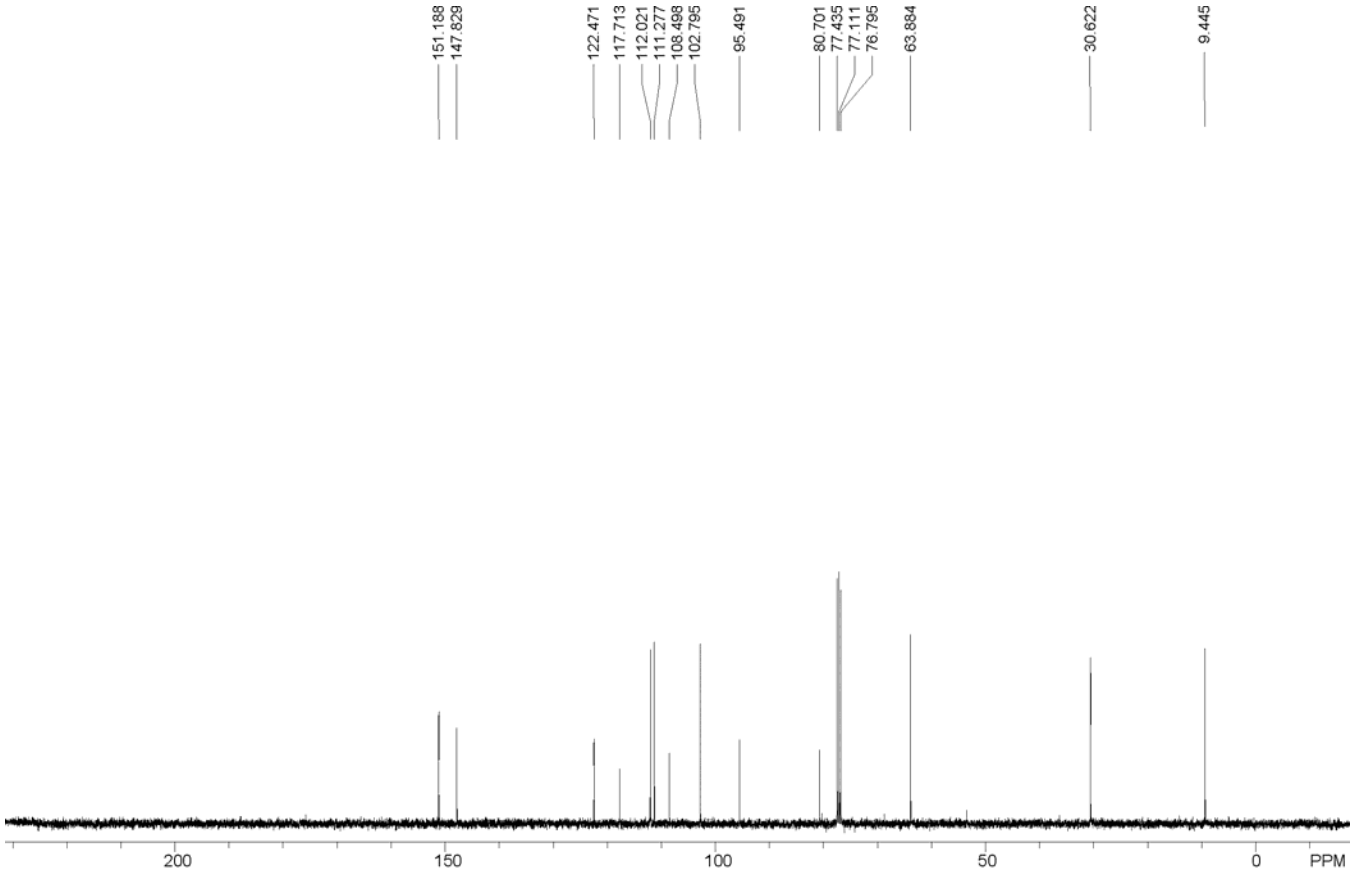
1.96
0.96
0.97
2.00
2.83
10
8
6
4
2
PPM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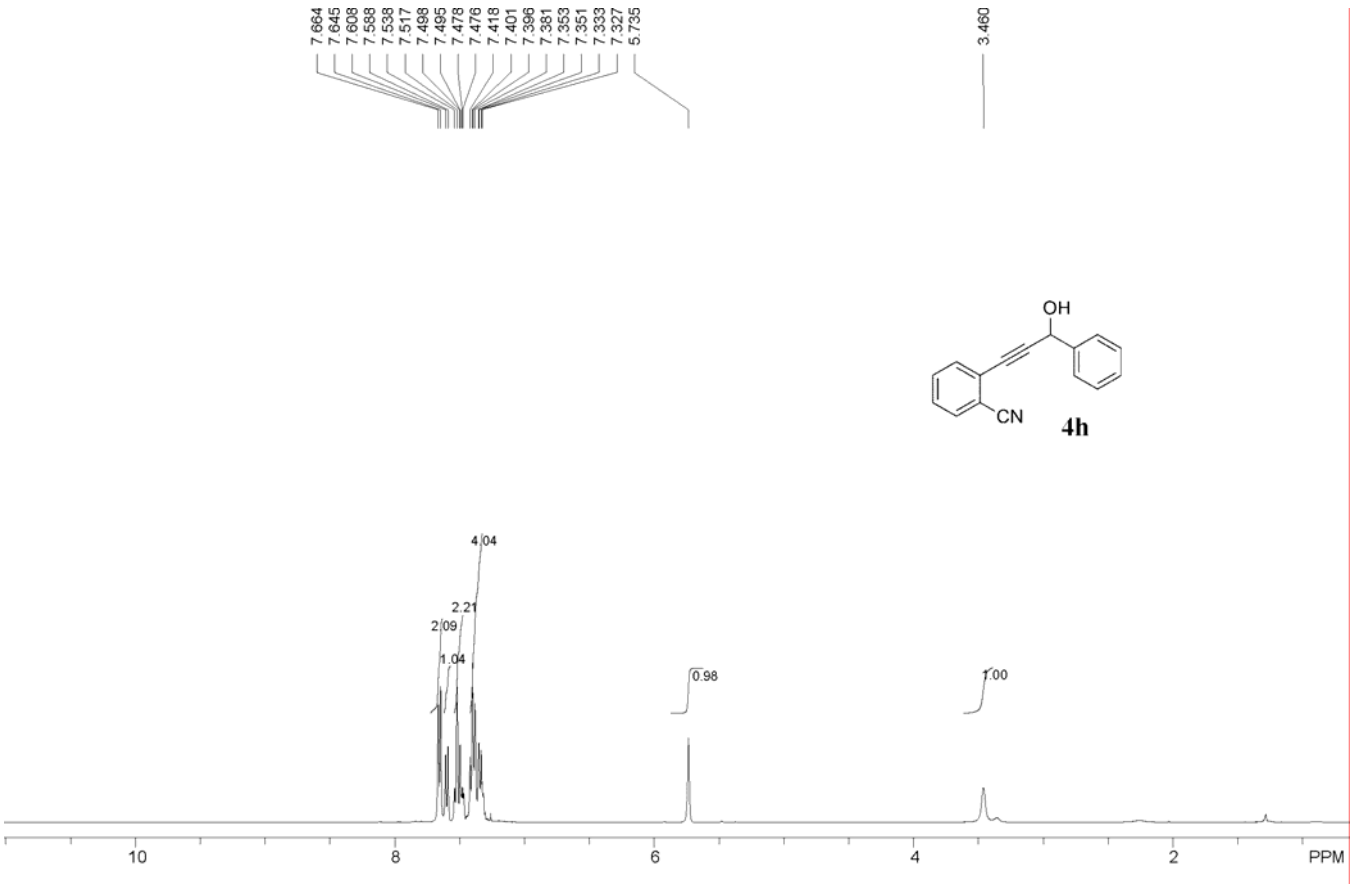
PPM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7.608
7.588
7.538
7.517
7.498
7.495
7.478
7.476
7.418
7.401
7.396
7.381
7.353
7.351
7.333
7.327
5.735
3.460
OH
CN
4h
4.04
2.21
2.09
1.04
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1.00
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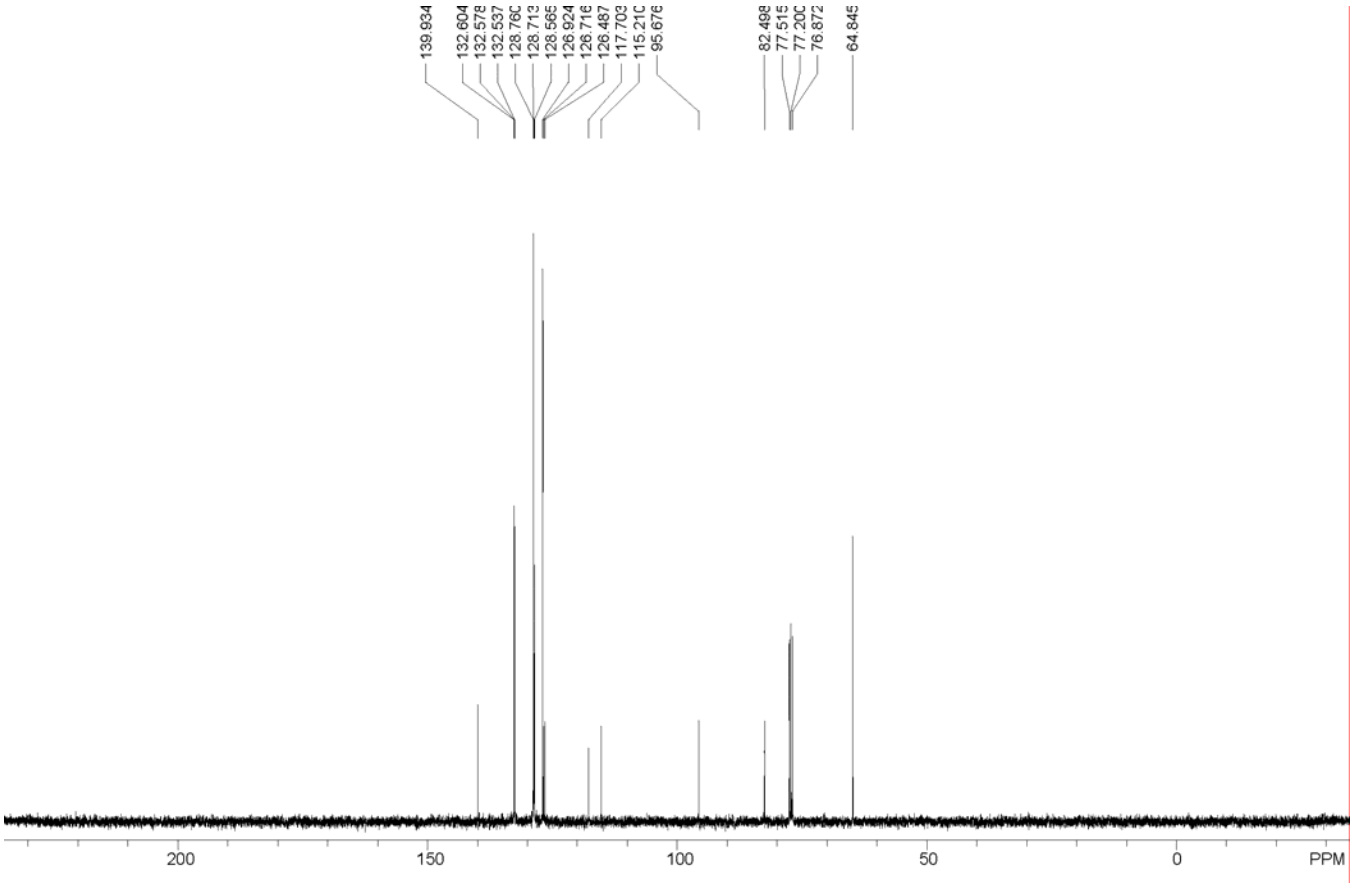
6
4
2
PPM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128.713
128.565
126.924
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126.487
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95.678
82.498
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76.872
64.845
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100
50
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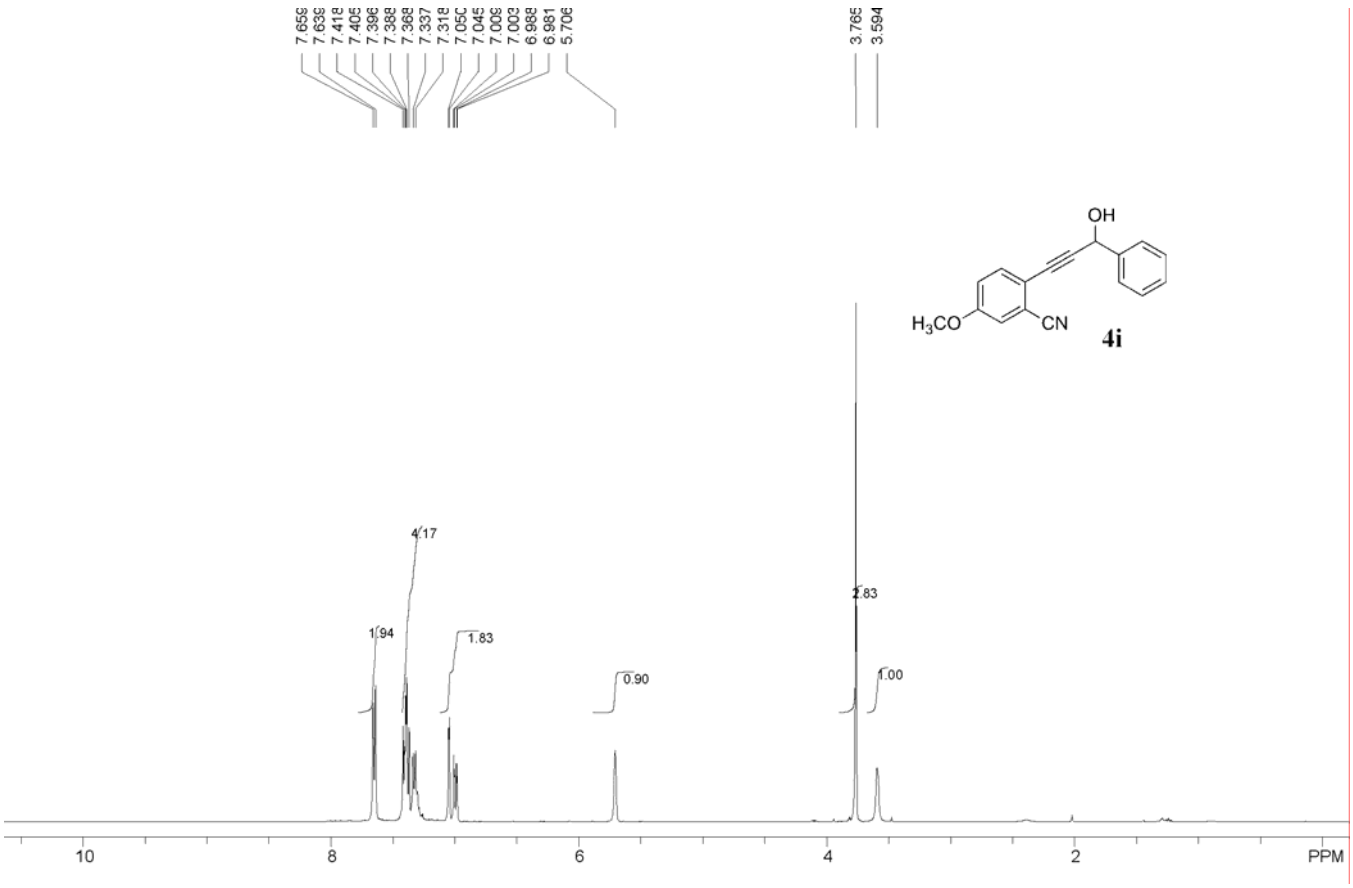
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7.045
7.009
7.003
6.988
6.981
5.706
3.765
3.594
OH
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CN
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4
2
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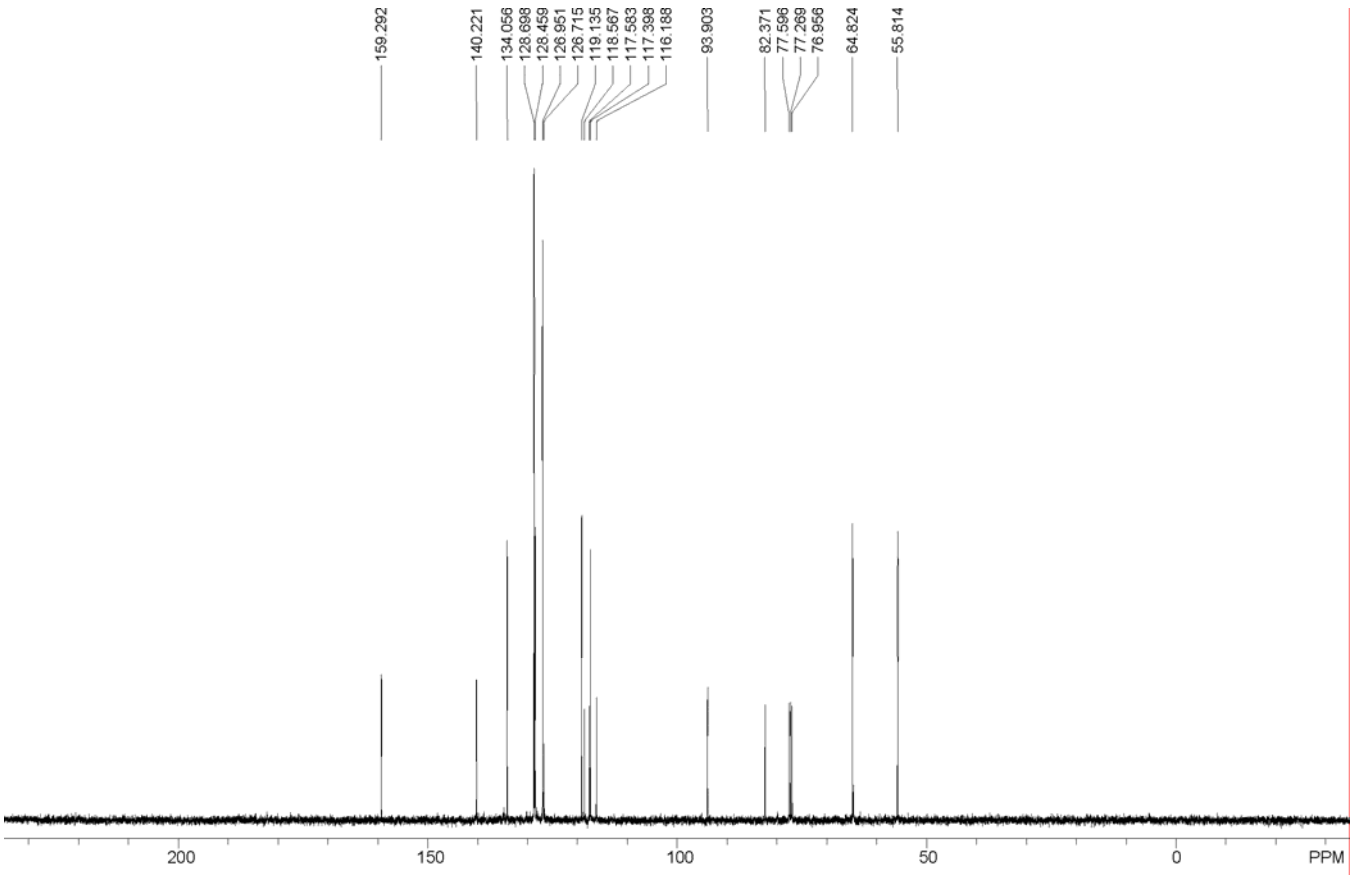
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126.715
119.135
118.567
117.583
117.398
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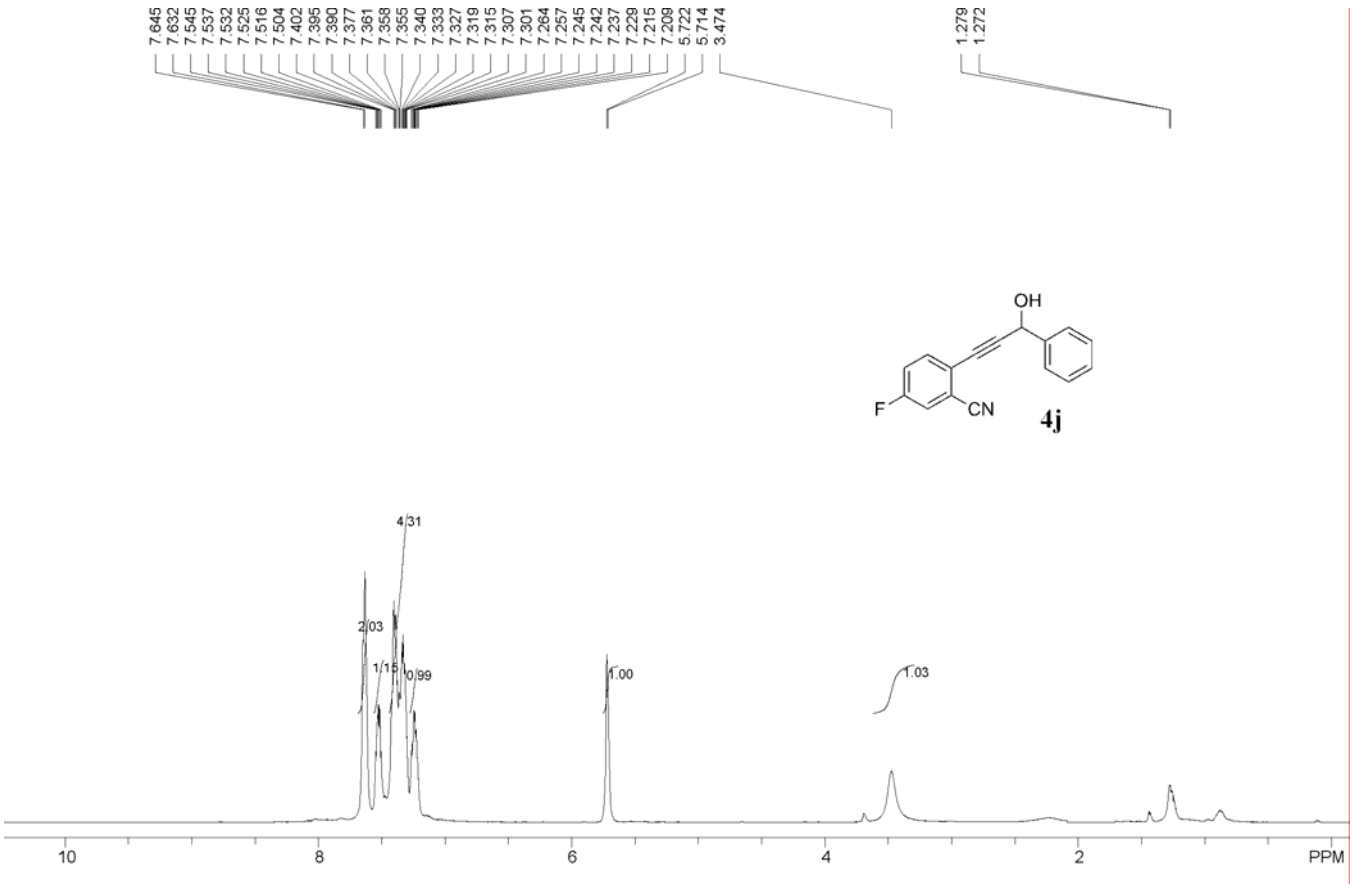
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7.532
7.525
7.516
7.504
7.402
7.395
7.390
7.377
7.361
7.358
7.355
7.340
7.333
7.327
7.319
7.315
7.307
7.301
7.264
7.257
7.245
7.242
7.237
7.229
7.215
7.209
5.722
5.714
3.474
1.279
1.272
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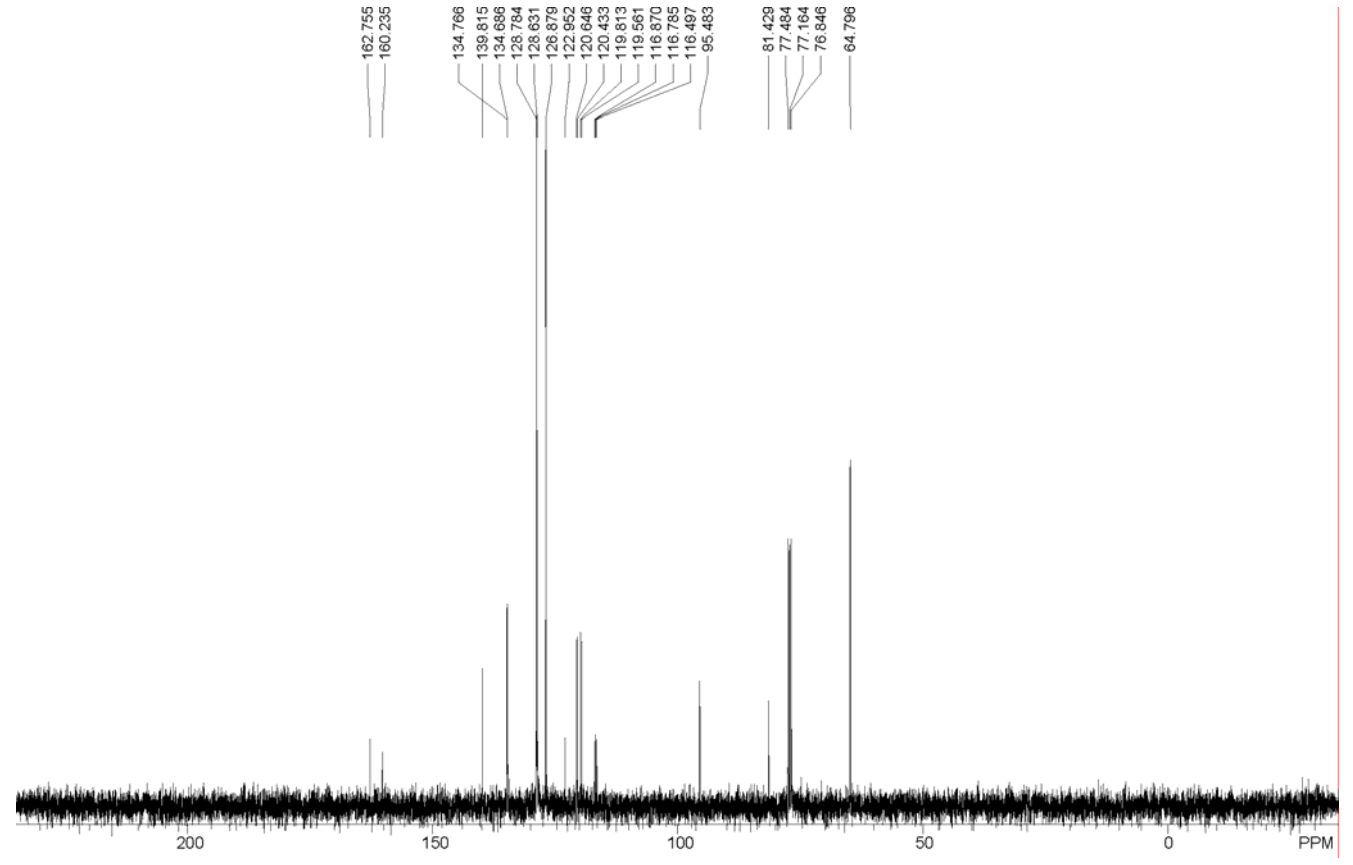
4
2
PPM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122.952
120.646
120.433
119.813
119.561
116.870
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95.483
81.429
77.484
77.164
76.846
64.796
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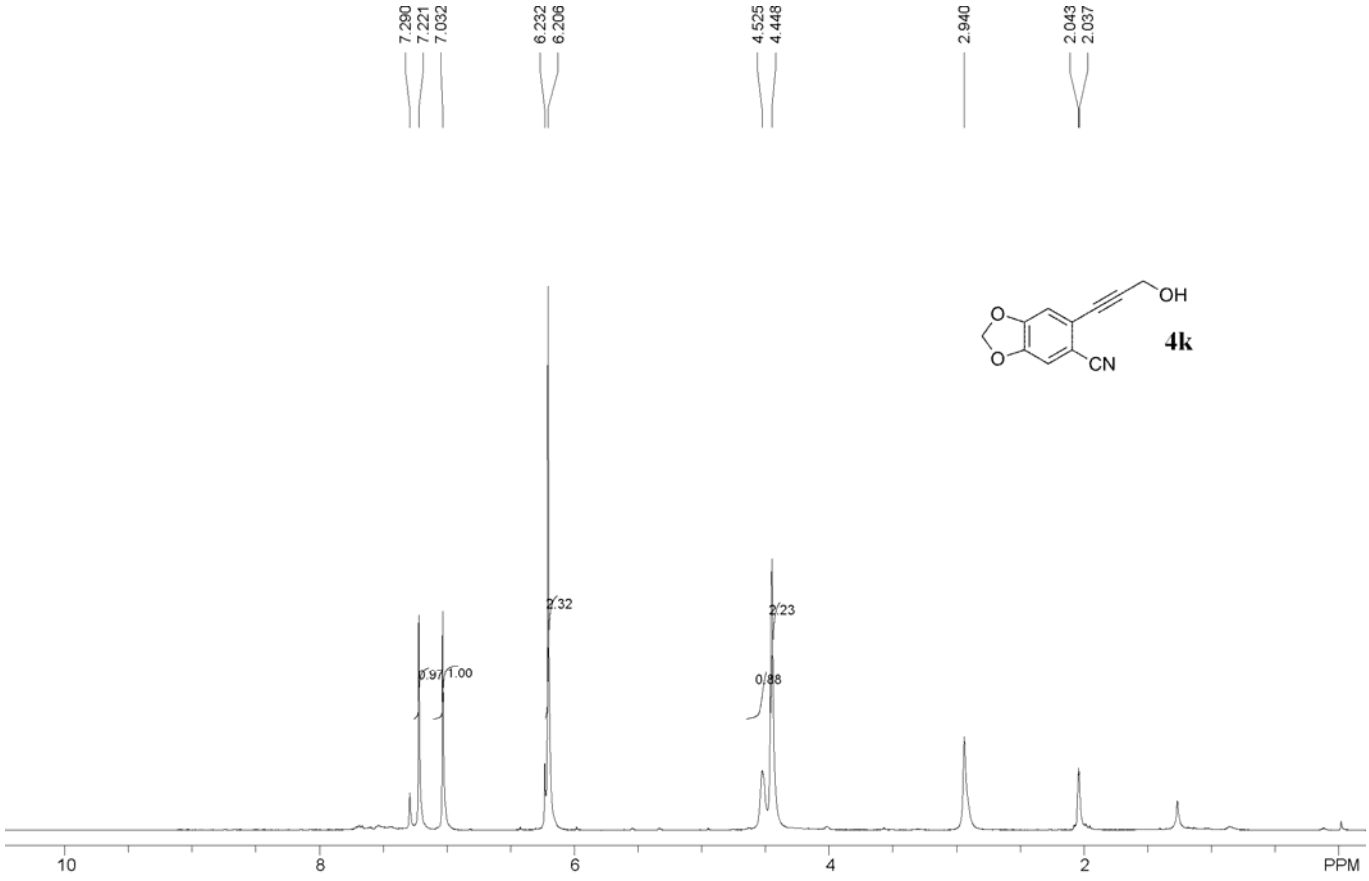
150
100
50
0
PPM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6.232
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4.448
2.940
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2.037
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O
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CN
4k
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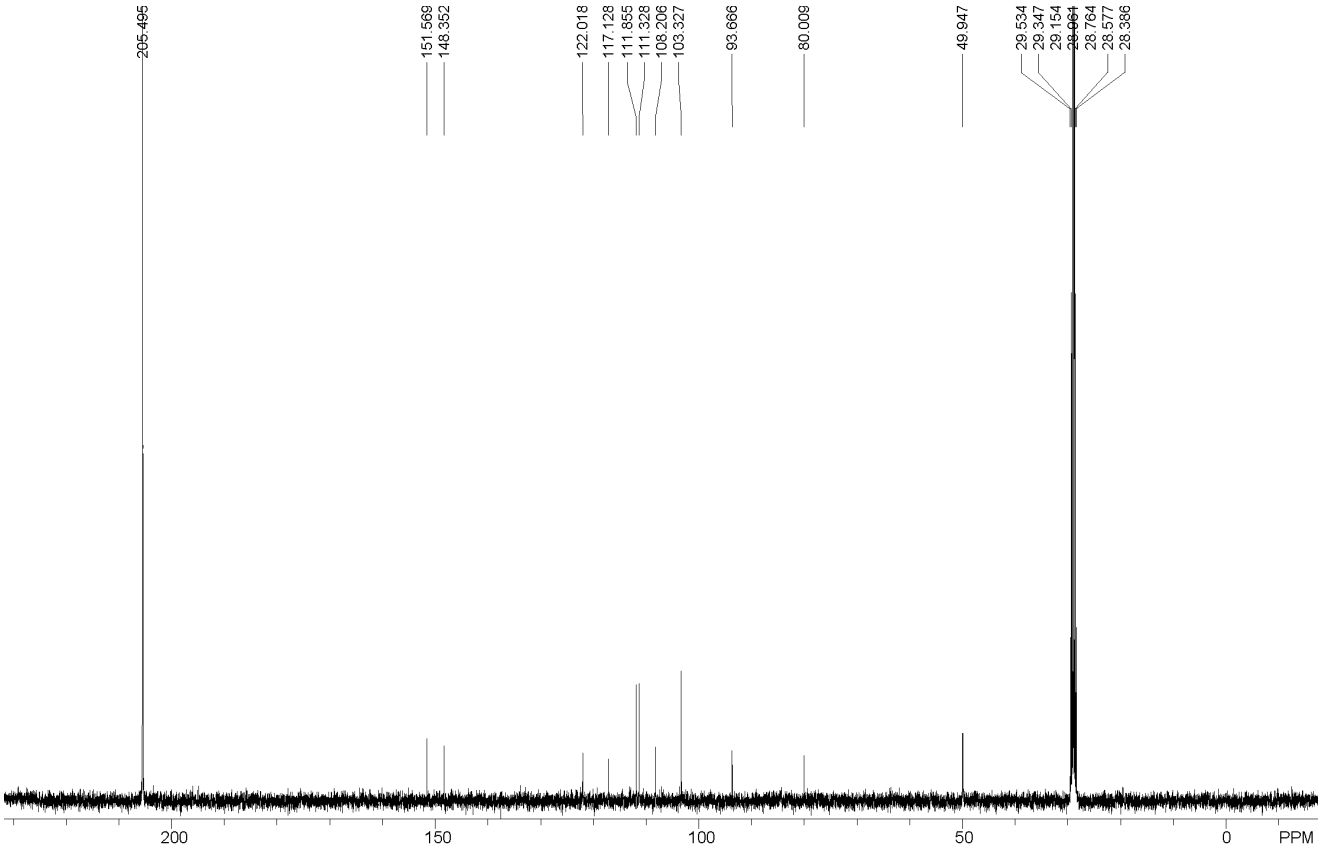
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29.347
29.154
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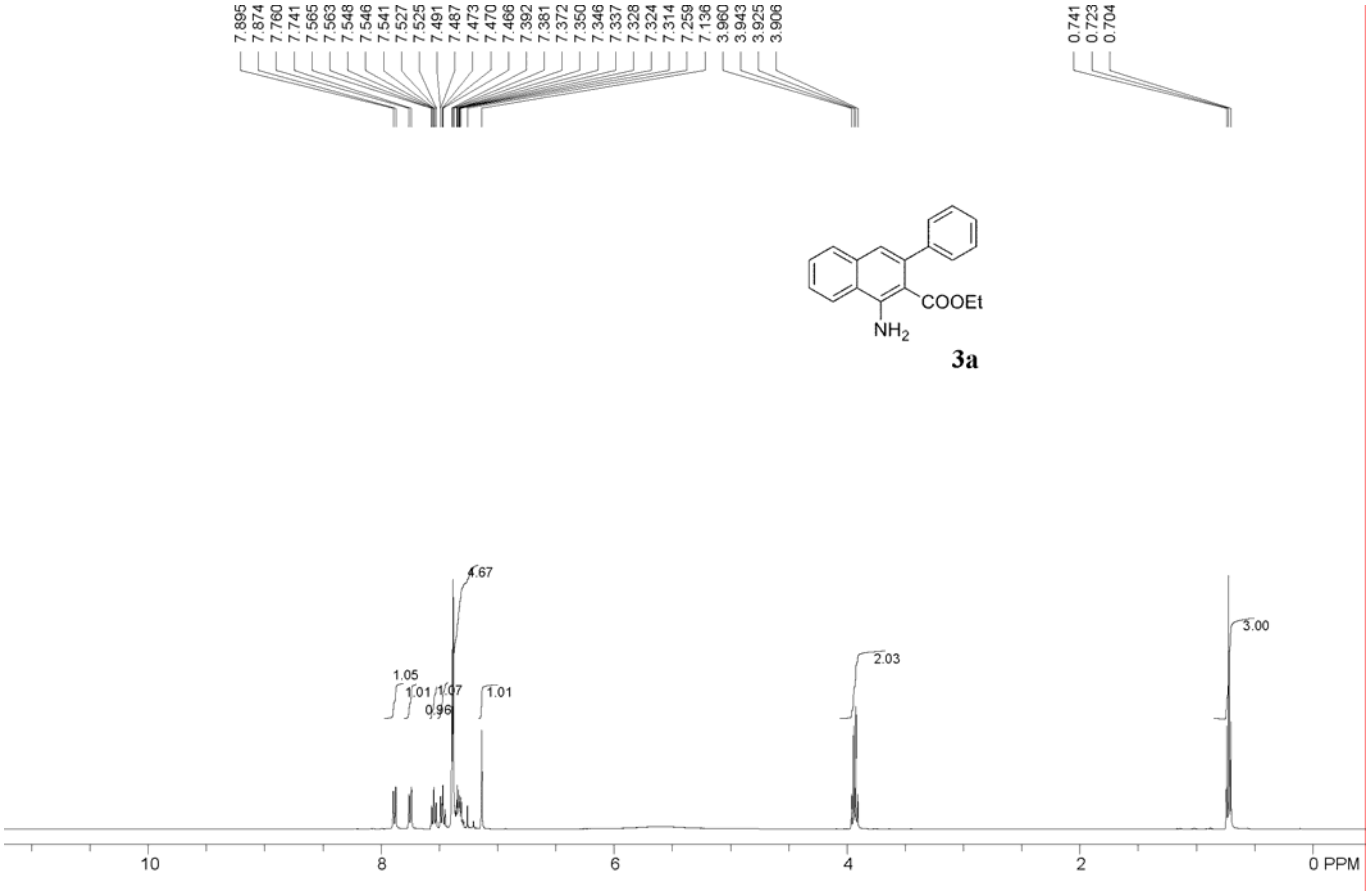
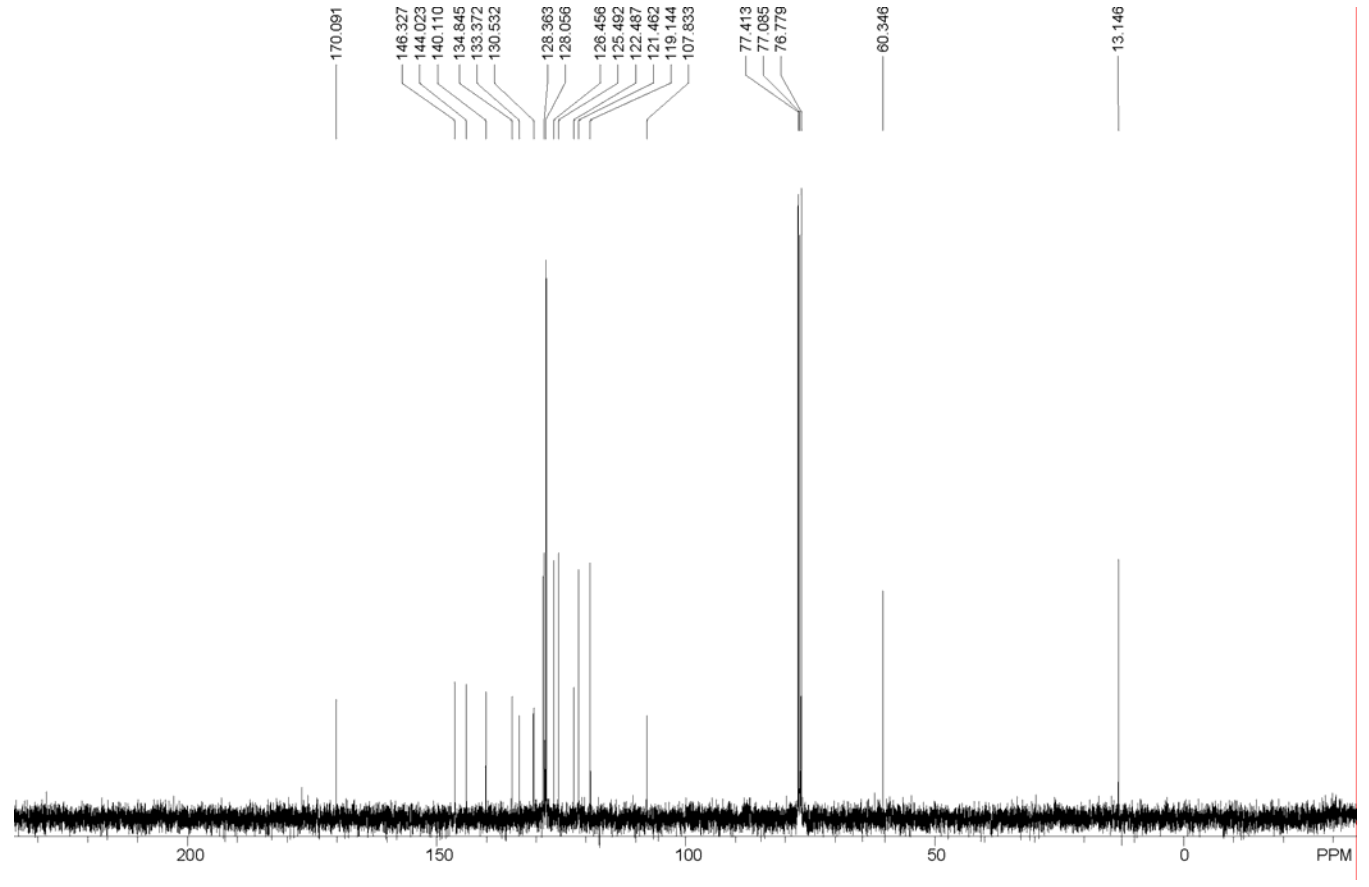
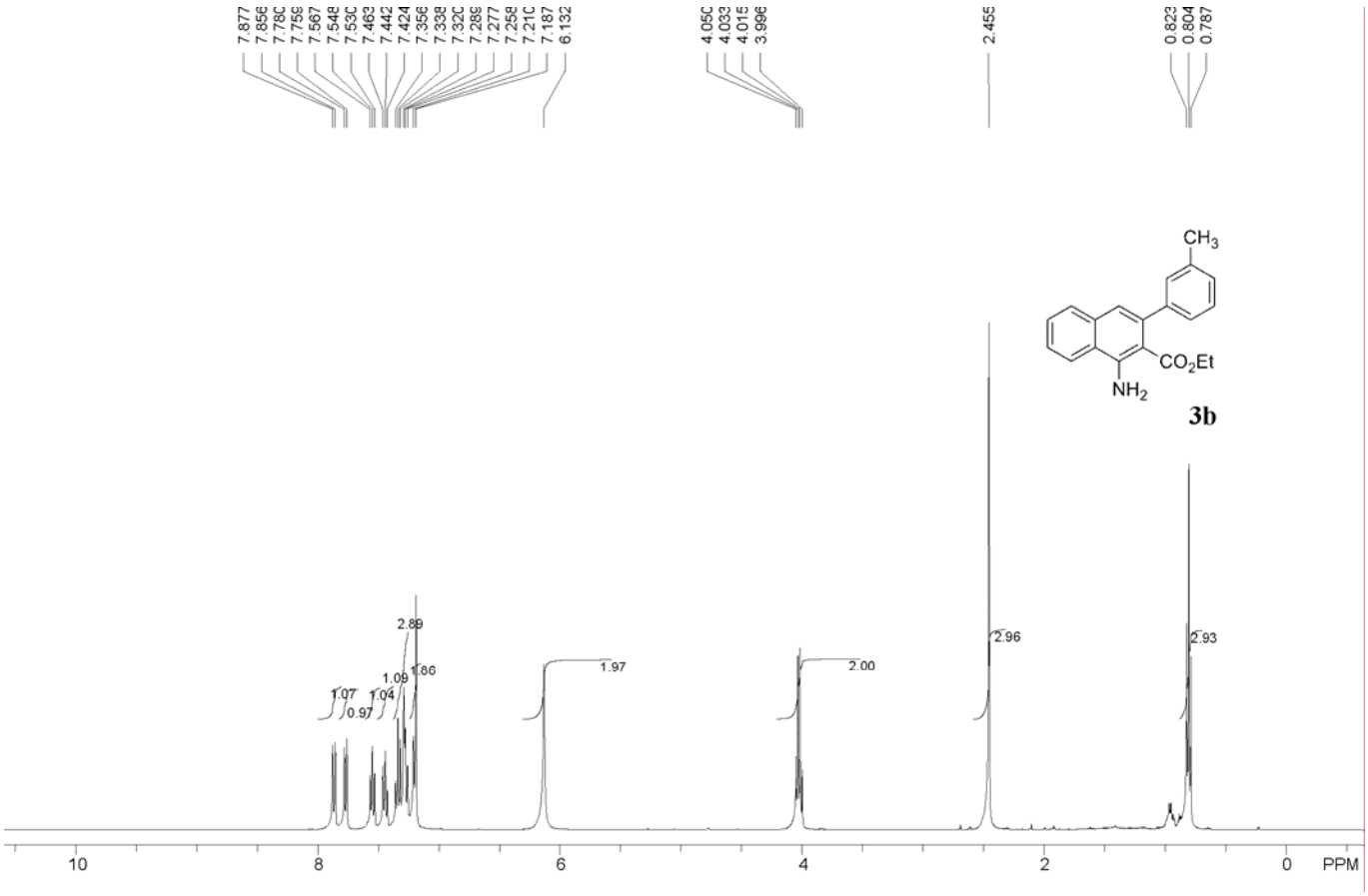
V. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3m



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7.286
7.277
7.258
7.210
7.187
6.132
4.050
4.033
4.015
3.996
2.455
0.823
0.804
0.787
CH3
CO2Et
NH2
3b
2.89
1.86
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0.97
1.97
2.00
2.96
2.93
10
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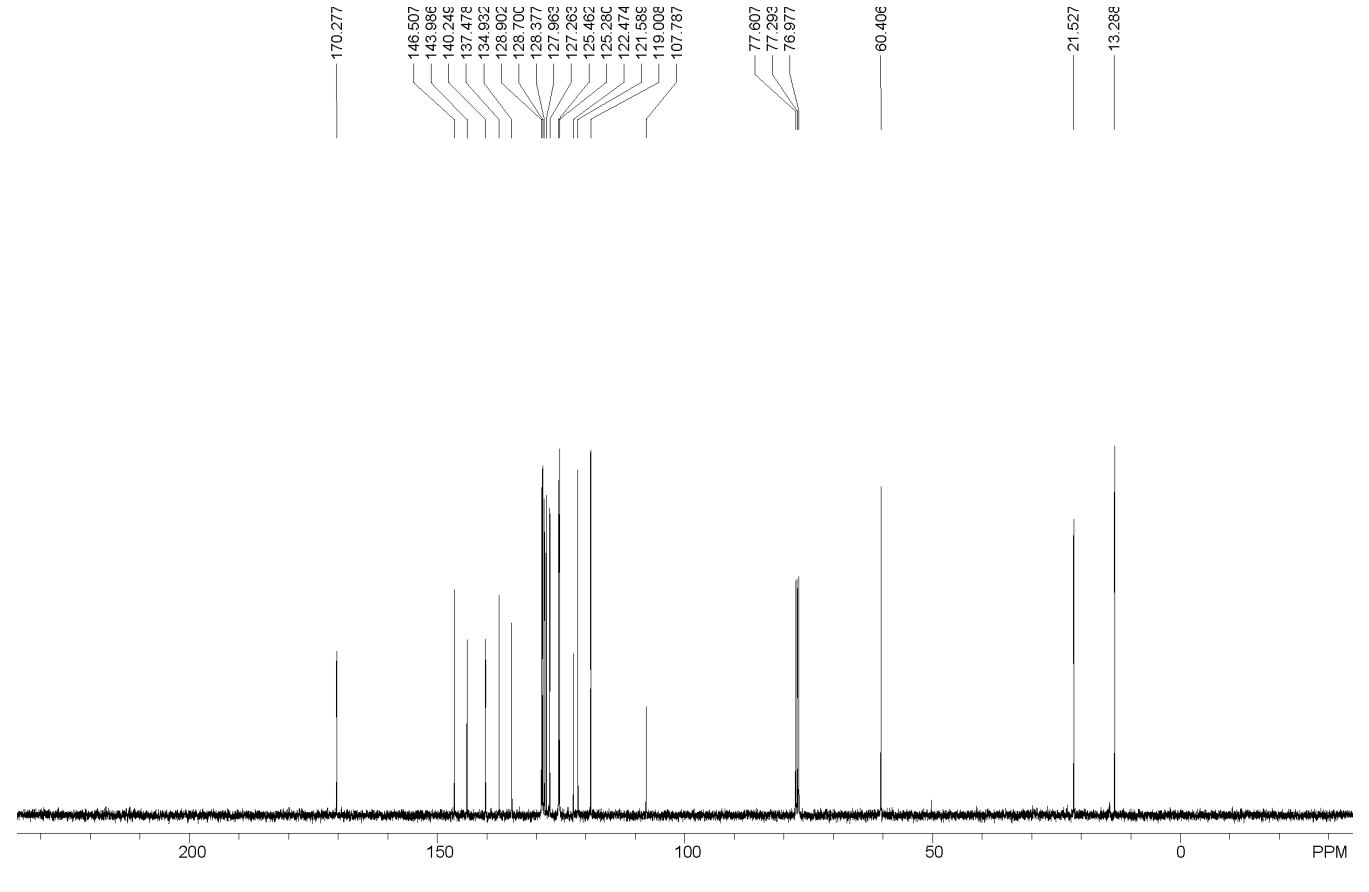
6
4
2
0
PPM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127.963
127.263
125.462
125.280
122.474
121.588
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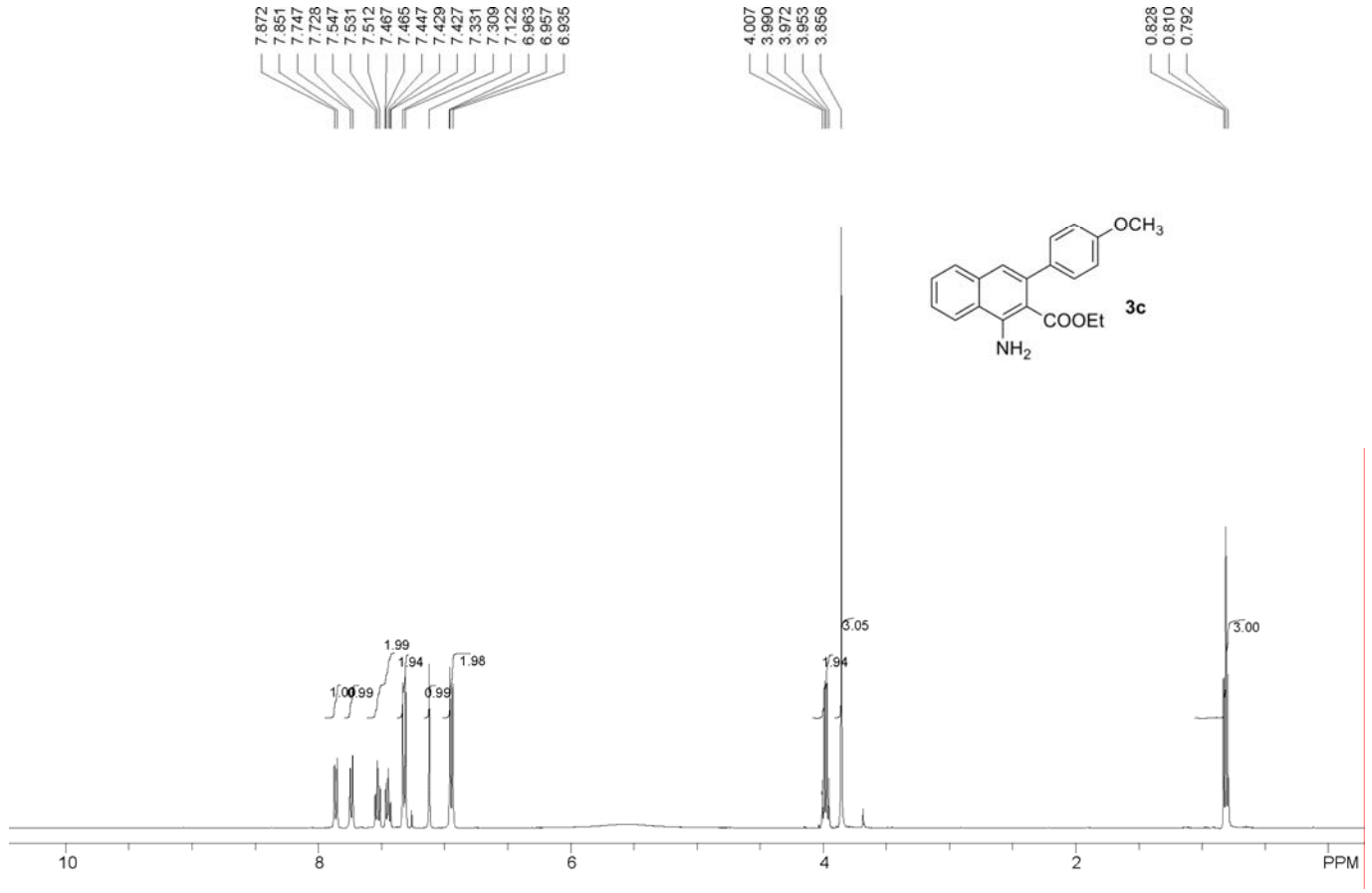
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7.331
7.309
7.122
6.963
6.957
6.935
4.007
3.990
3.972
3.953
3.856
0.828
0.810
0.792
OCH3
COOEt
NH2
3c
1.99
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3.00
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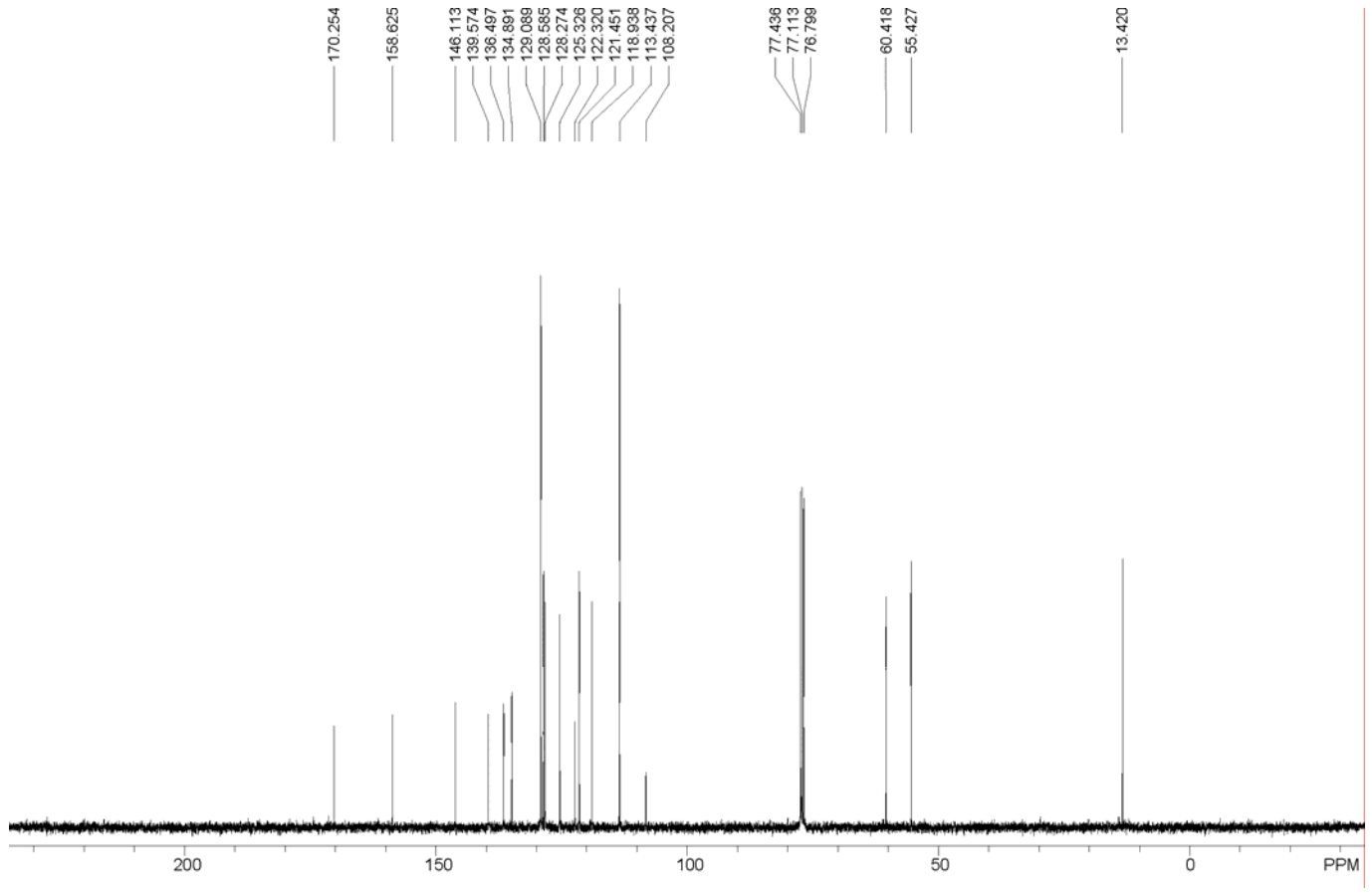
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125.326
122.320
121.451
118.938
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77.113
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13.420
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100
50
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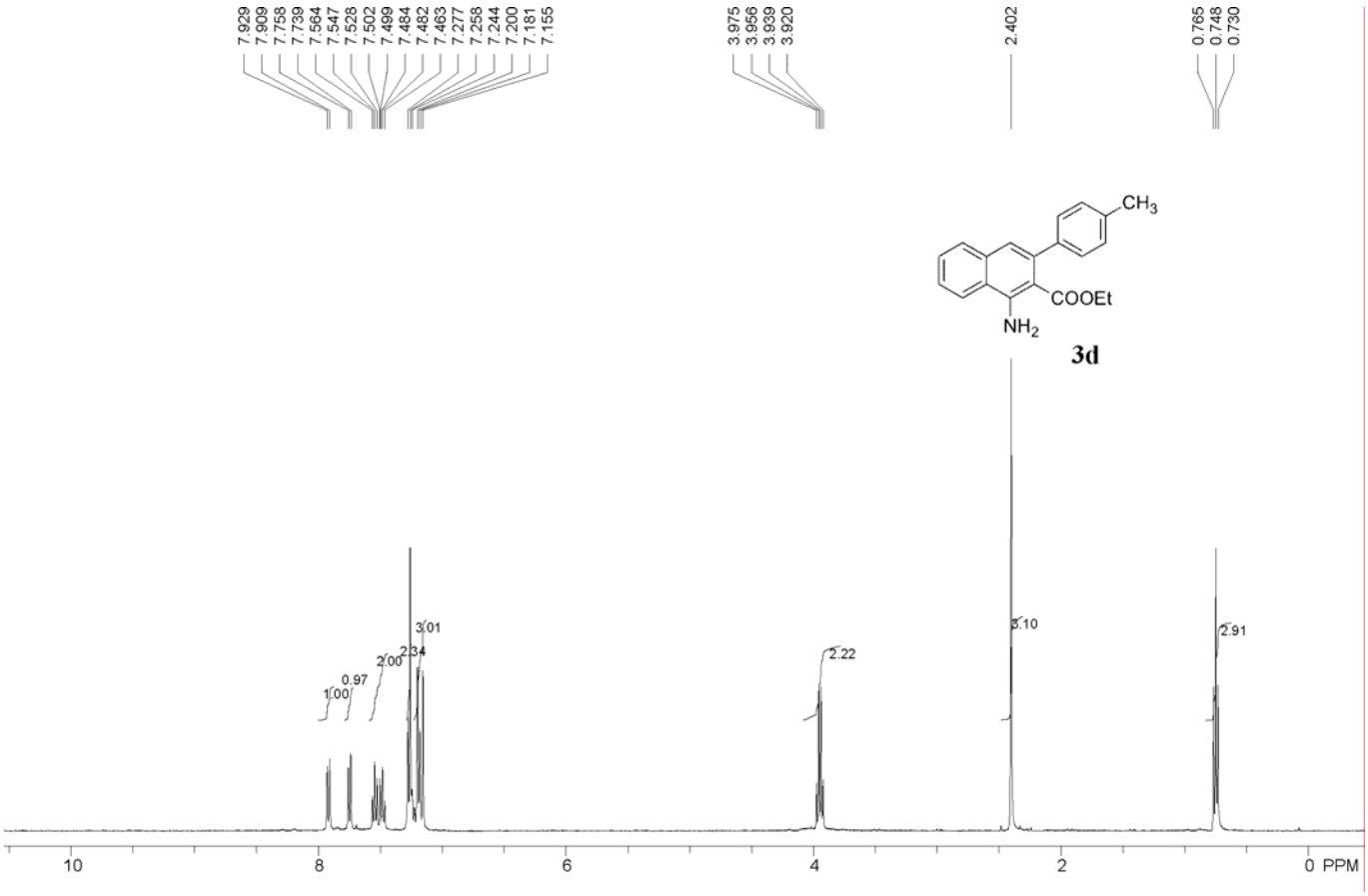
PPM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7.277
7.258
7.244
7.200
7.181
7.155
3.975
3.956
3.939
3.920
2.402
0.765
0.748
0.730
CH3
COOEt
NH2
3d
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2.00
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2.22
3.10
2.91
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4
2
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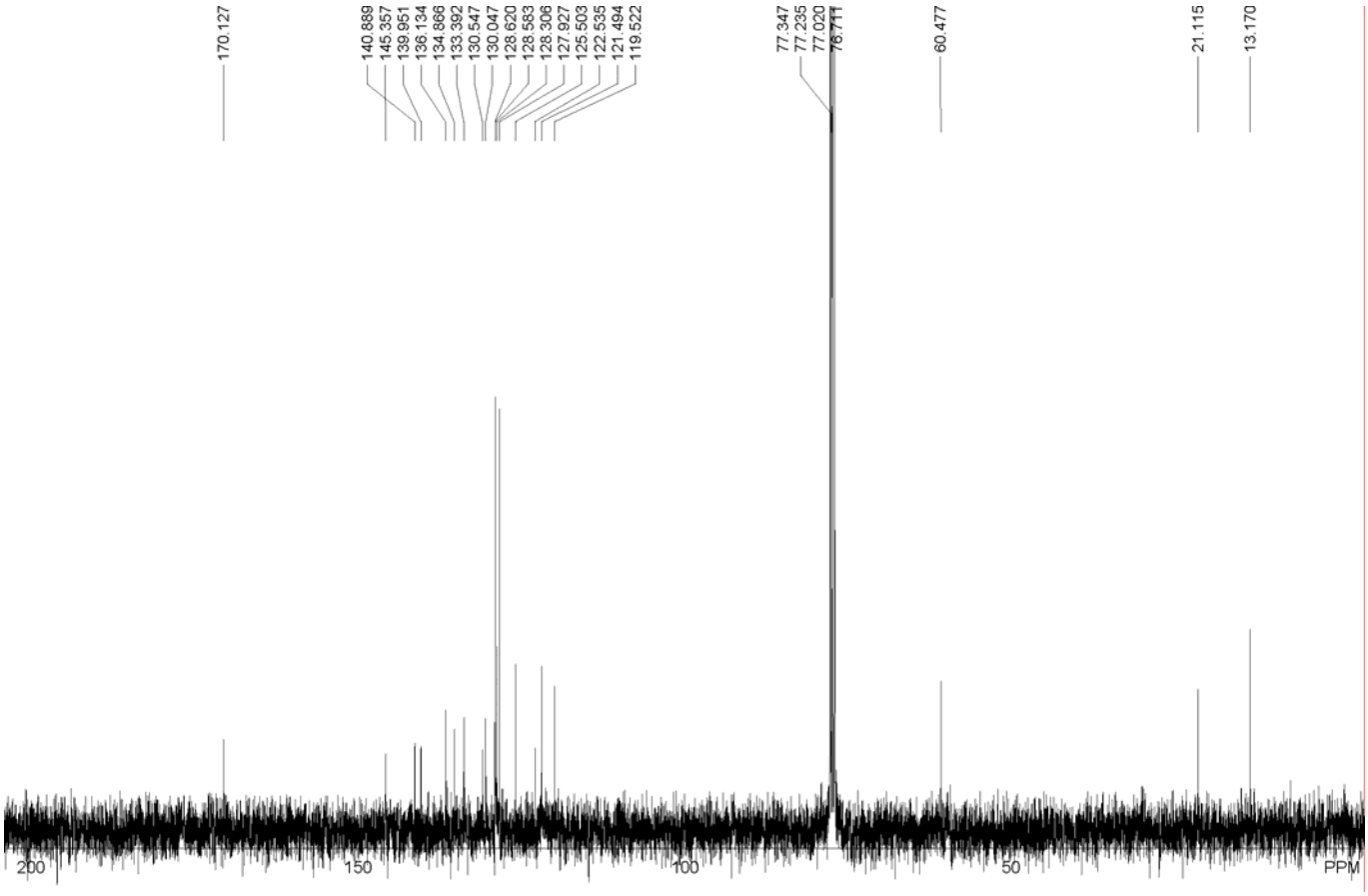
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128.620
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125.503
122.535
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77.235
77.020
76.711
60.477
21.115
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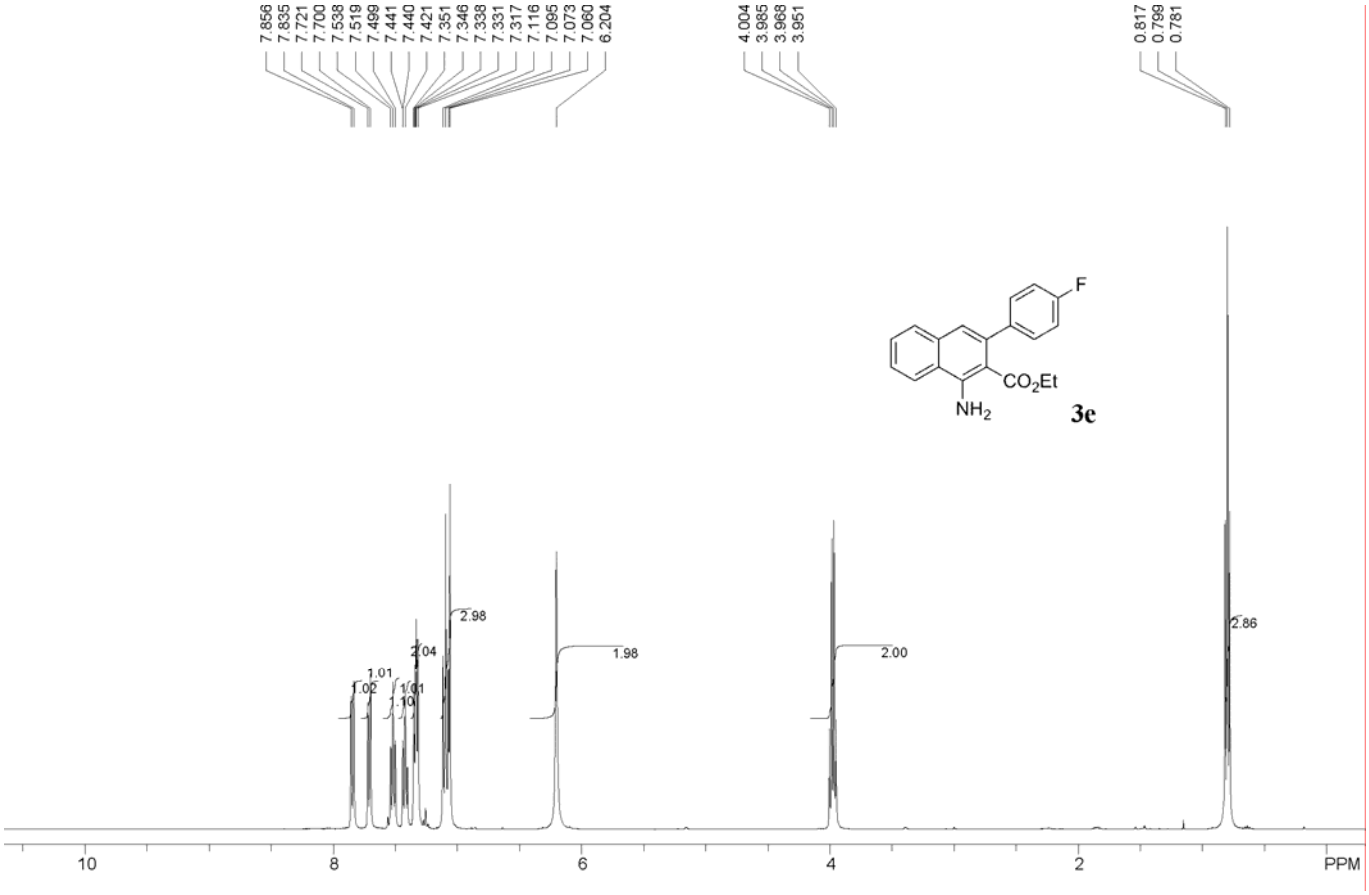
150
100
50
PPM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7.519
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7.441
7.440
7.421
7.351
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7.331
7.317
7.116
7.095
7.073
7.060
6.204
4.004
3.985
3.968
3.951
0.817
0.799
0.781
F
CO2Et
NH2
3e
2.98
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1.01
1.02
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1.10
2.04
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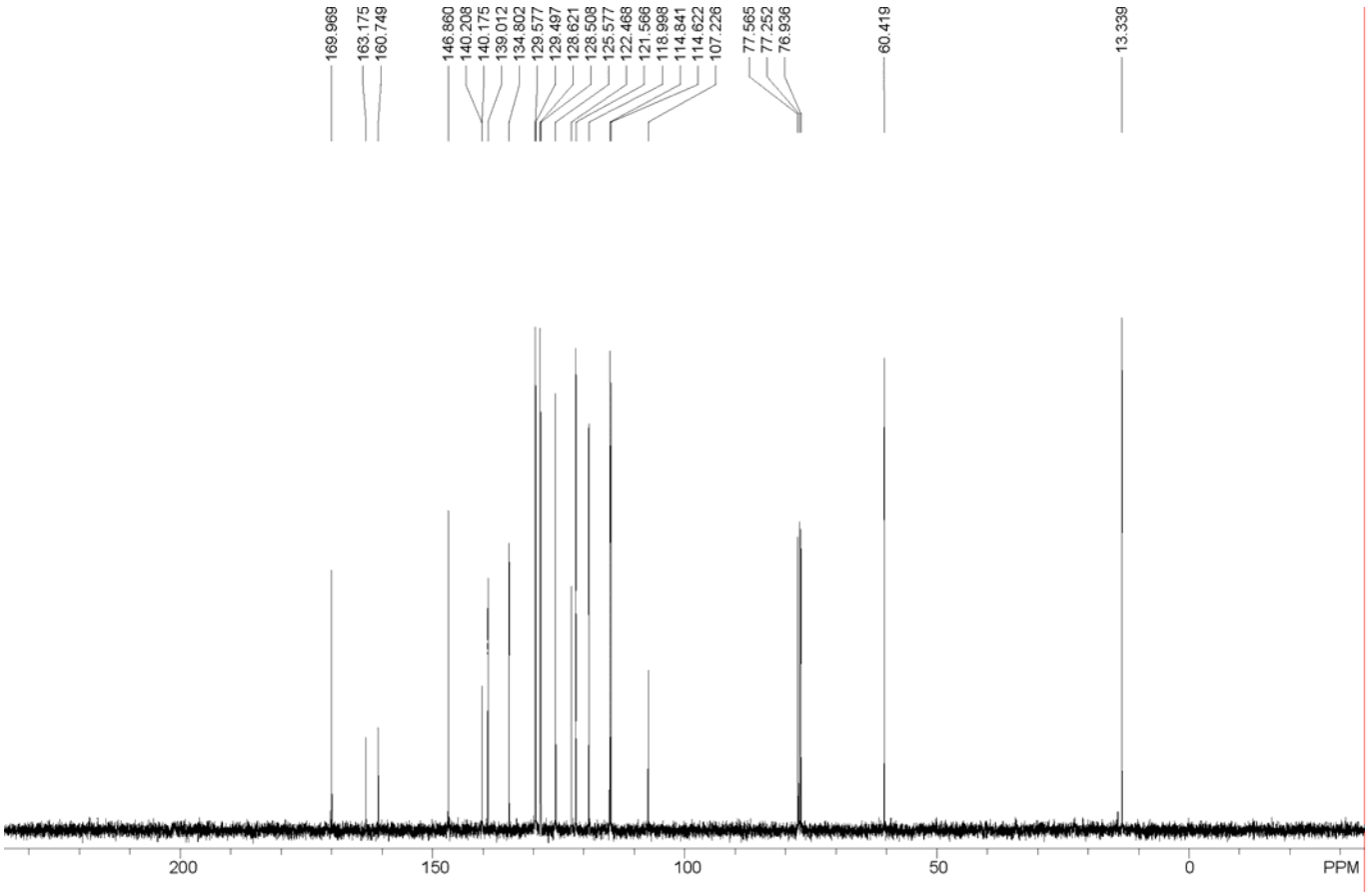
PPM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125.577
122.468
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118.998
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77.565
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13.339
200
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50
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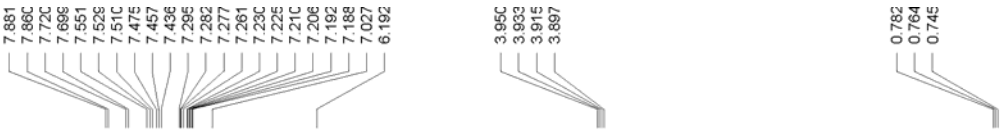
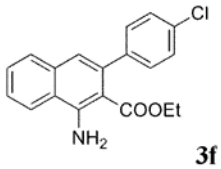
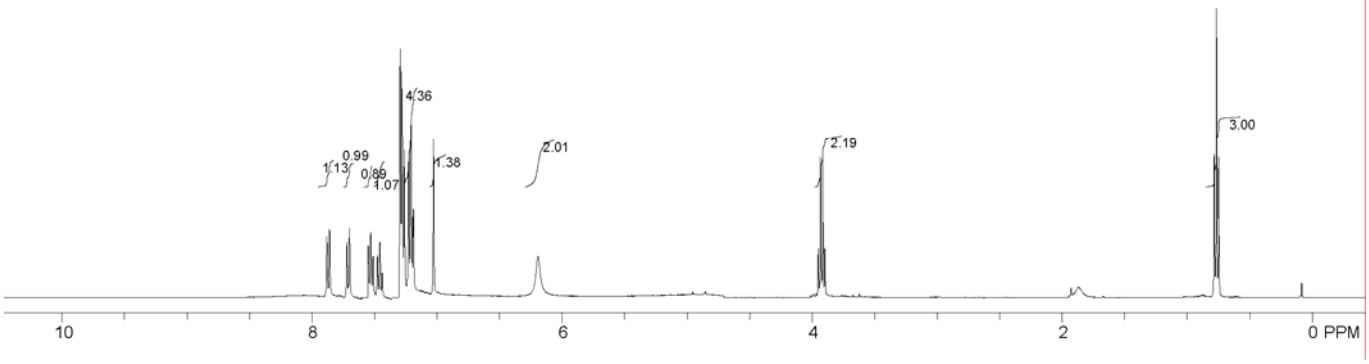



Cl
COOEt
NH2

3f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1.38
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2.19
3.00
10
8
6
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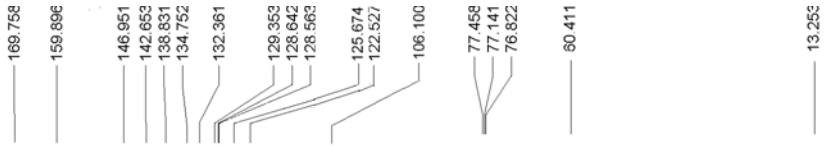

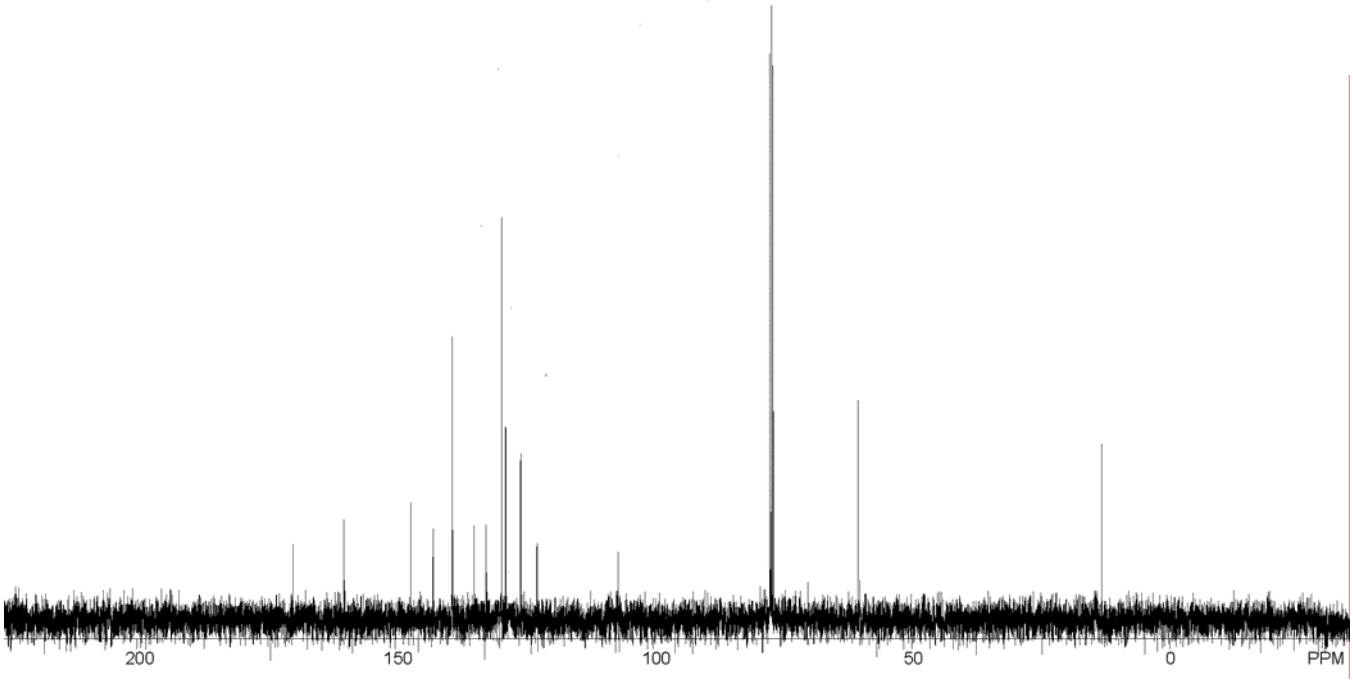
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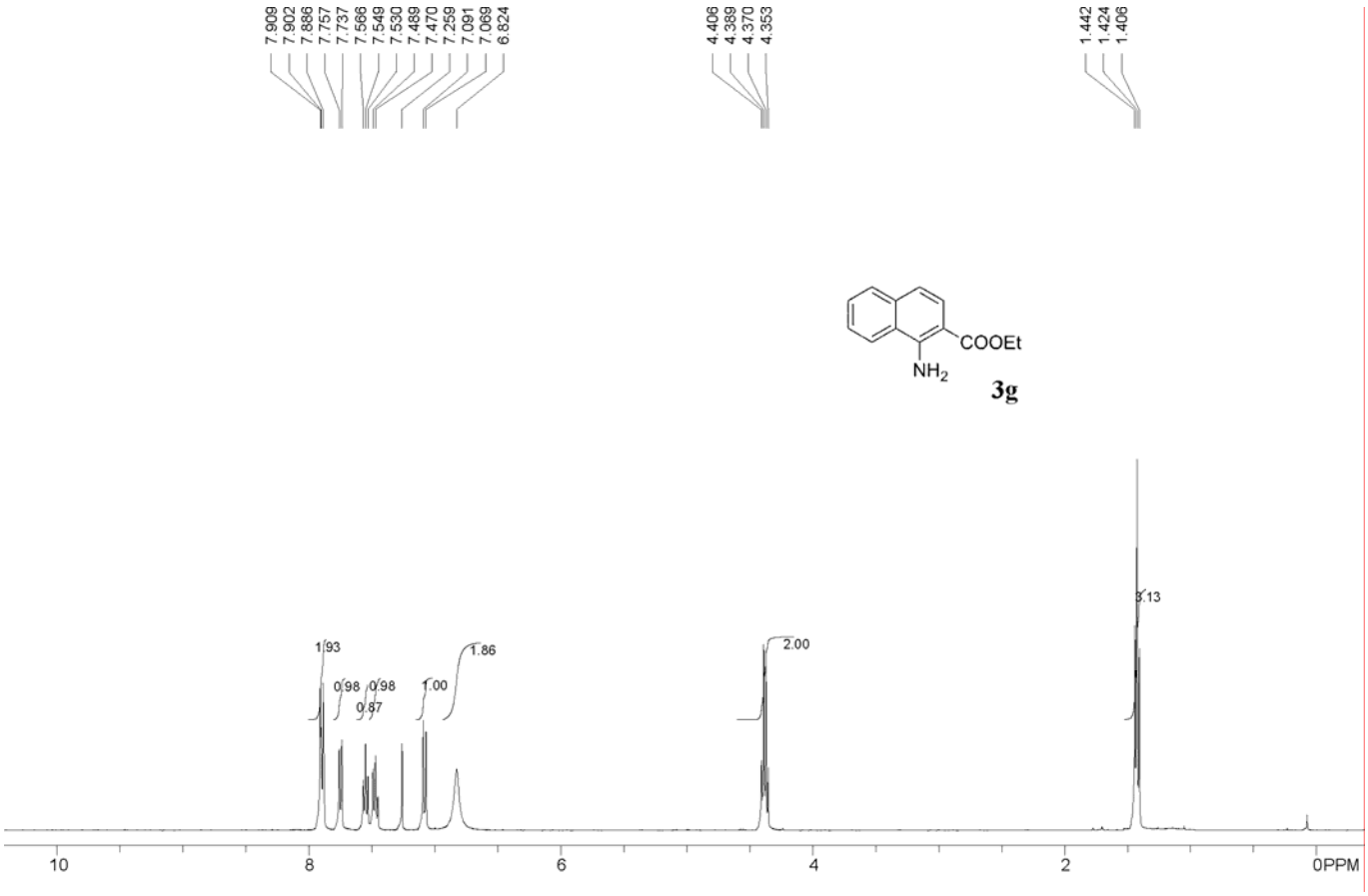
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7.530
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7.259
7.091
7.069
6.824
4.406
4.388
4.370
4.353
1.442
1.424
1.406
COOEt
NH2
3g
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0.98
0.87
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1.86
2.00
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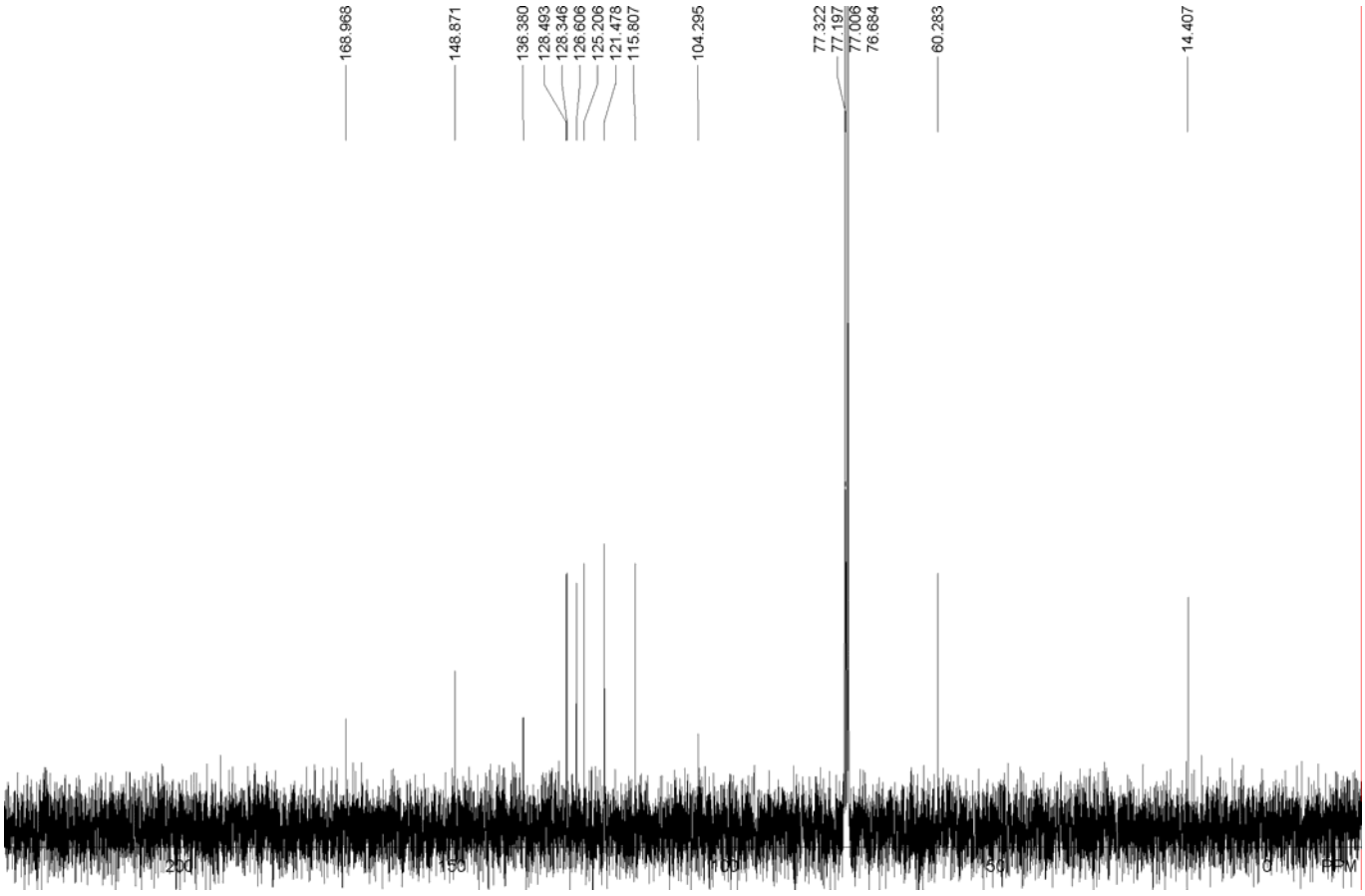
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126.606
125.206
121.478
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77.006
76.684
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14.407
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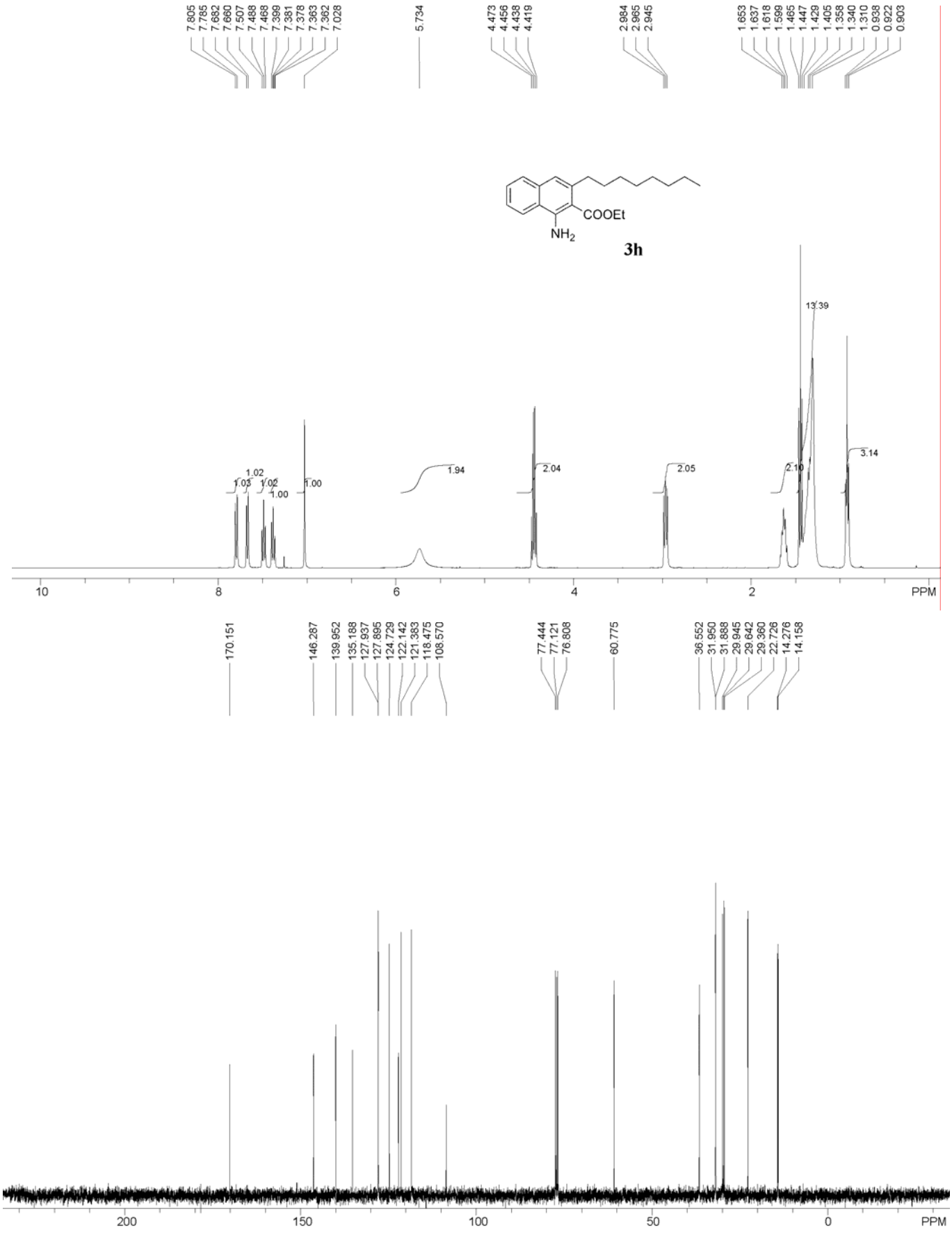
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7.682
7.660
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7.468
7.399
7.381
7.378
7.363
7.362
7.028
5.734
4.473
4.456
4.438
4.419
2.984
2.965
2.945
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1.637
1.618
1.599
1.465
1.447
1.429
1.405
1.358
1.340
1.310
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0.922
0.903
COOEt
NH2
3h
1.02
1.03
1.02
1.00
1.00
1.94
2.04
2.05
2.10
13.39
3.14
10
8
6
4
2
PPM
170.151
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139.952
135.188
127.937
127.895
124.729
122.142
121.383
118.475
108.570
77.444
77.121
76.808
60.775
36.552
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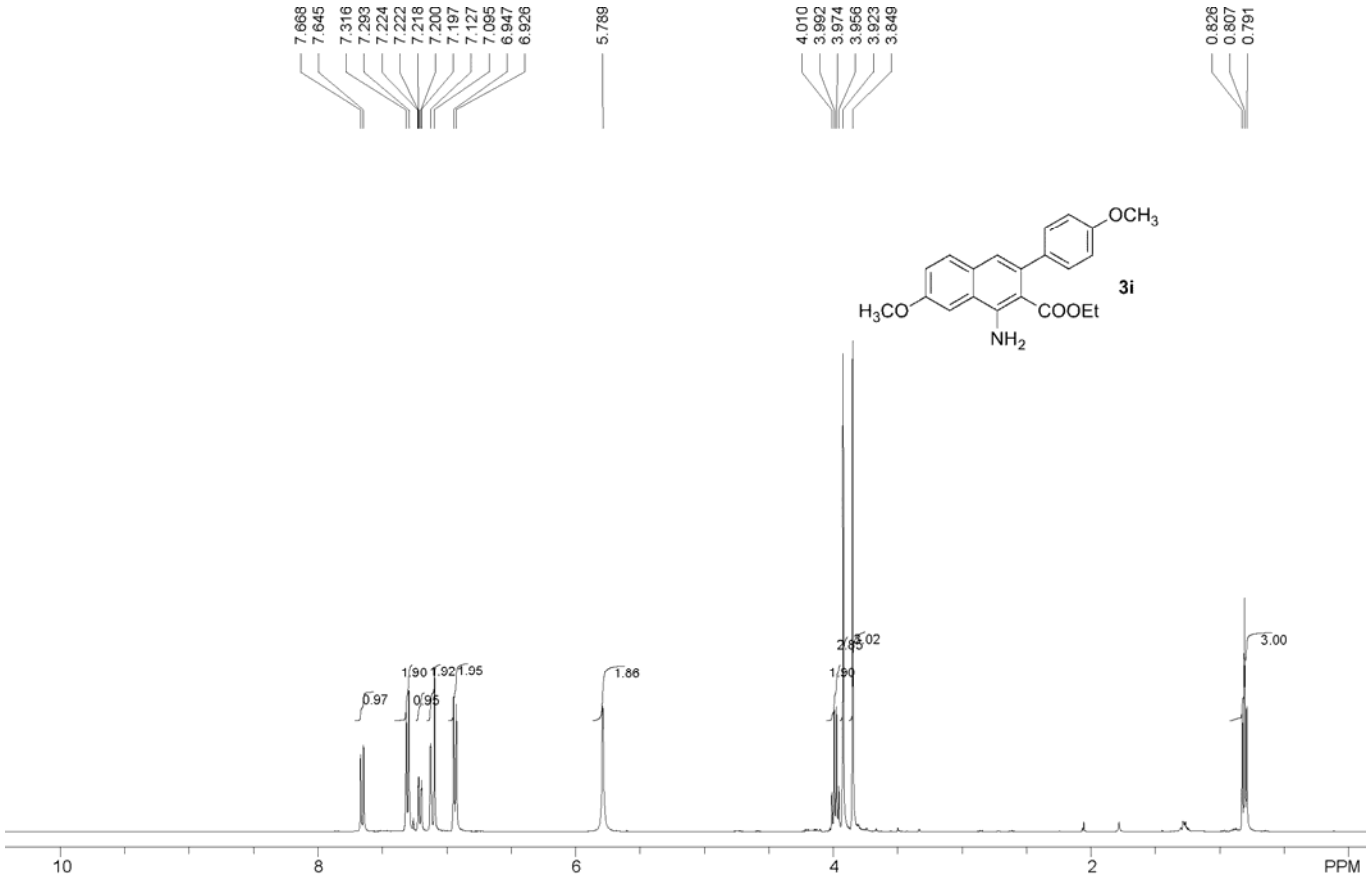
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7.293
7.224
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7.218
7.200
7.197
7.127
7.095
6.947
6.926
5.789
4.010
3.992
3.974
3.956
3.923
3.849
0.826
0.807
0.791
OCH3
H3CO
COOEt
NH2
3i
0.97
1.90
0.95
1.92
1.95
1.86
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1.90
3.00
10
8
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4
2
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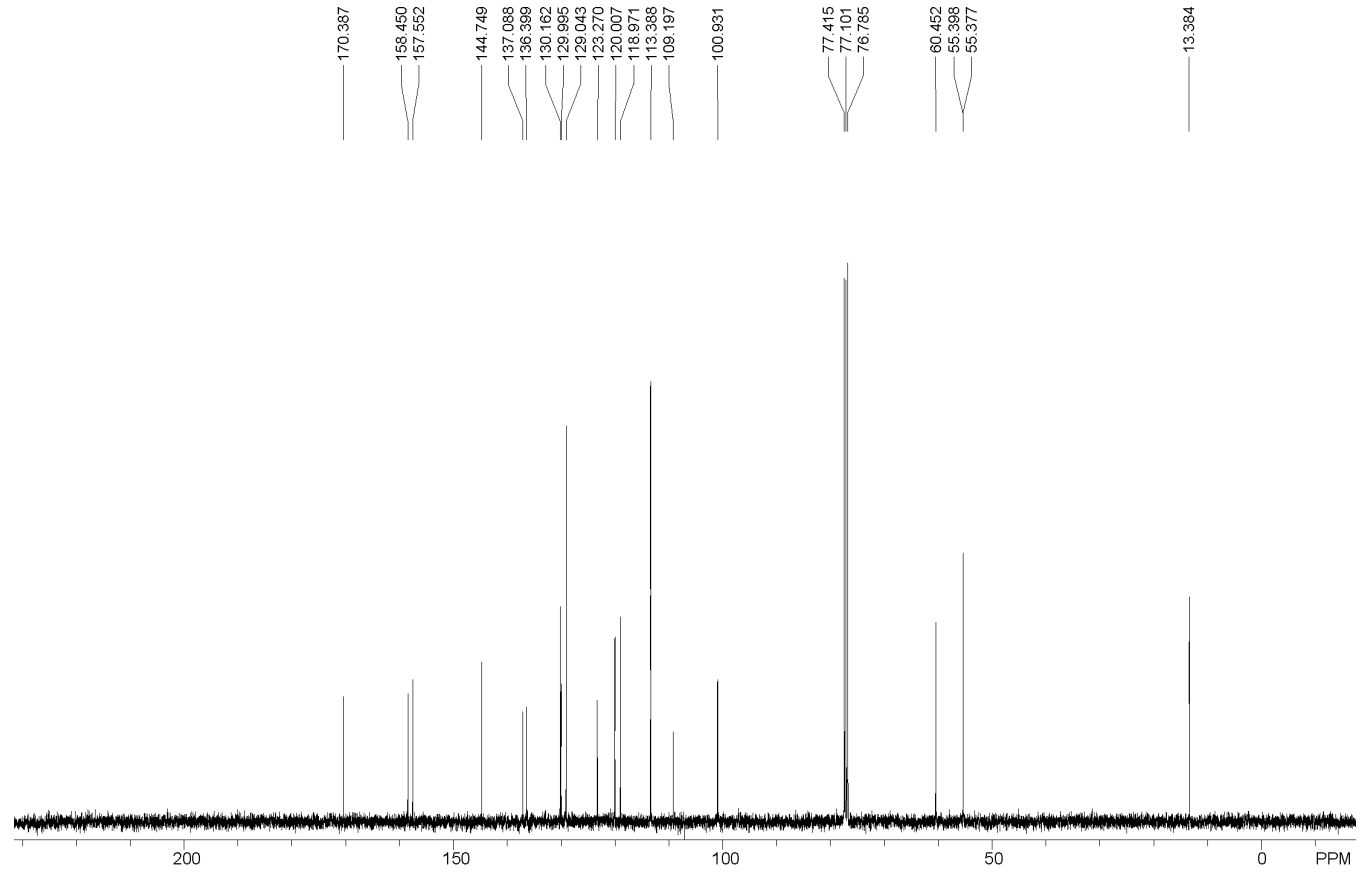
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130.162
129.995
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123.270
120.007
118.971
113.388
109.197
100.931
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77.101
76.785
60.452
55.398
55.377
13.384
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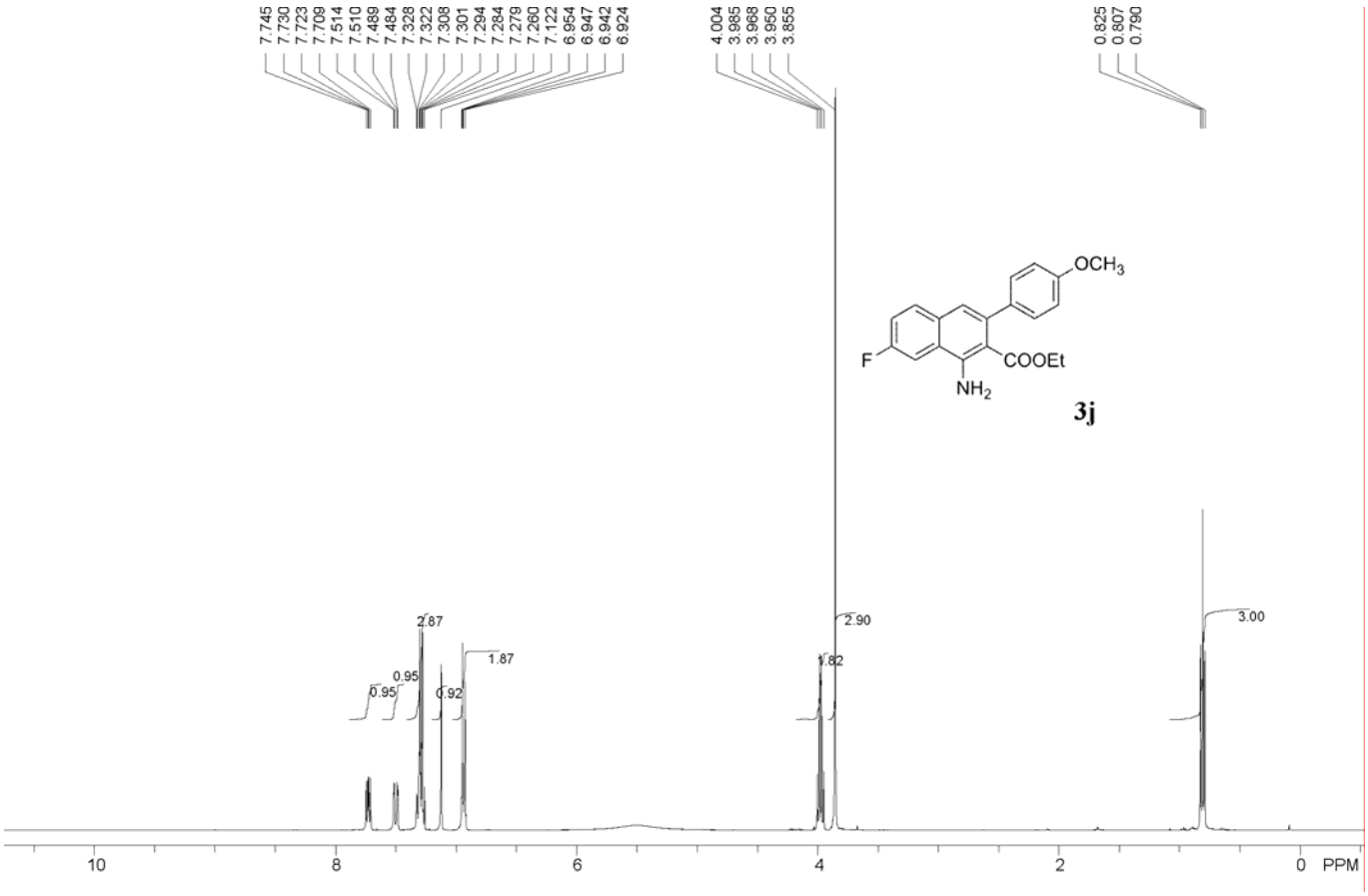
150
100
50
0
PPM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7.709
7.514
7.510
7.489
7.484
7.328
7.322
7.308
7.301
7.294
7.284
7.279
7.260
7.122
6.954
6.947
6.942
6.924
4.004
3.985
3.968
3.950
3.855
0.825
0.807
0.790
OCH3
F
COOEt
NH2
3j
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1.87
1.82
0.95
0.95
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10
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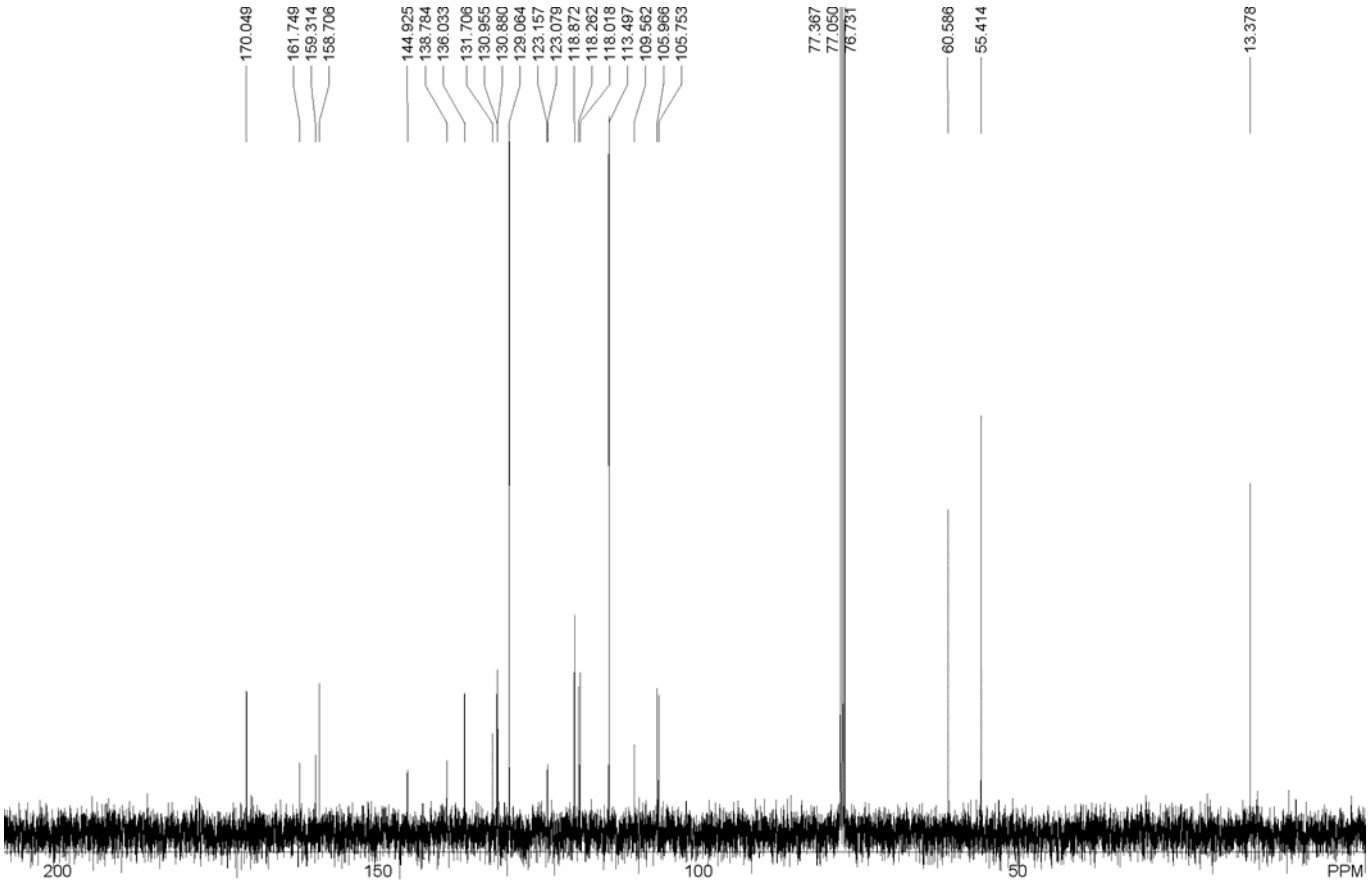
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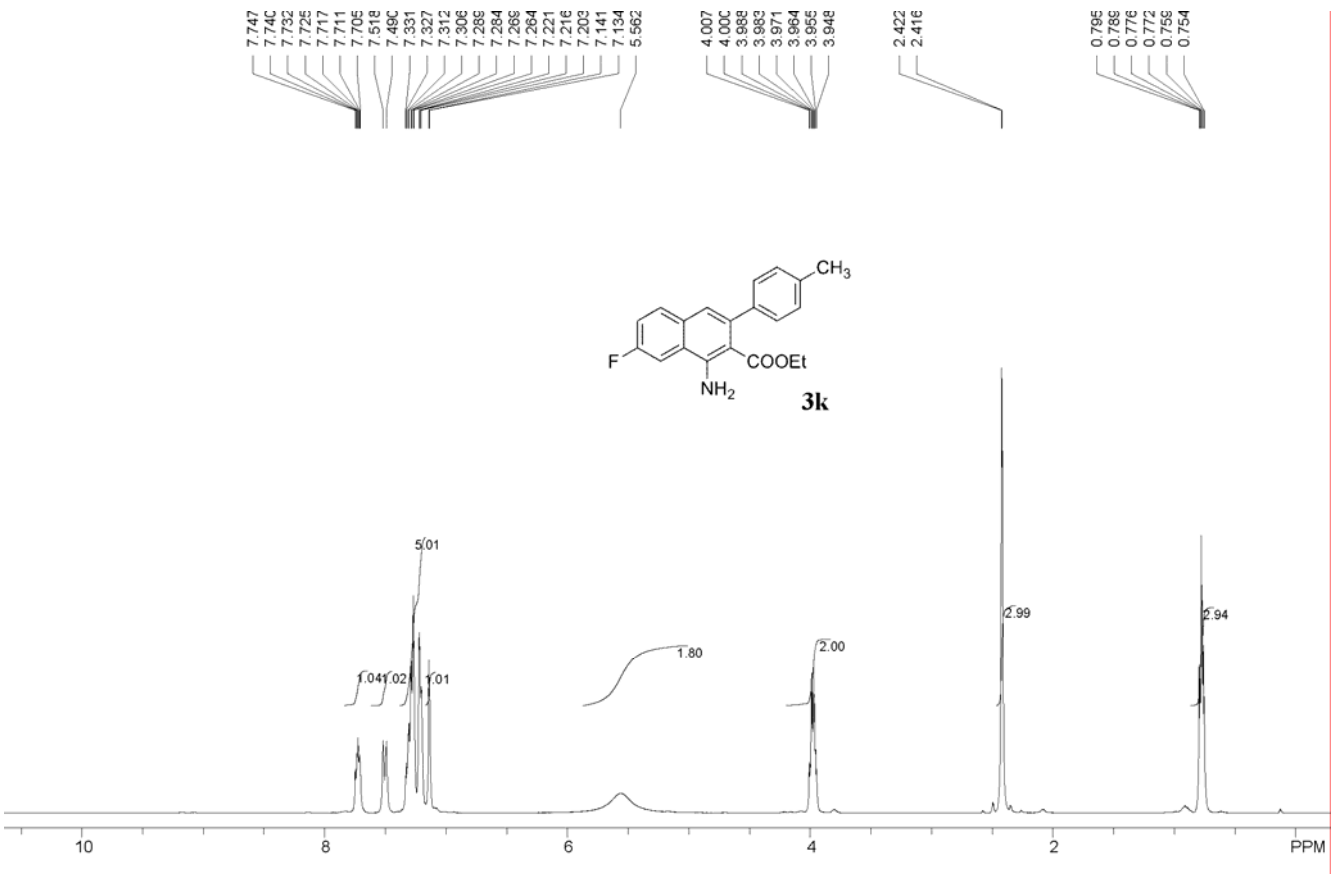
159.314
158.706
144.925
138.784
136.033
131.706
130.955
130.880
129.064
123.157
123.079
118.872
118.262
118.018
113.497
109.562
105.966
105.753
77.367
77.050
76.731
60.586
55.414
13.378
200
150
100
50
PPM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7.725
7.717
7.711
7.705
7.518
7.490
7.331
7.327
7.312
7.308
7.288
7.284
7.266
7.264
7.221
7.216
7.203
7.141
7.134
5.562
4.007
4.000
3.988
3.983
3.971
3.964
3.955
3.948
2.422
2.416
0.795
0.786
0.776
0.772
0.756
0.754
CH3
F
COOEt
NH2
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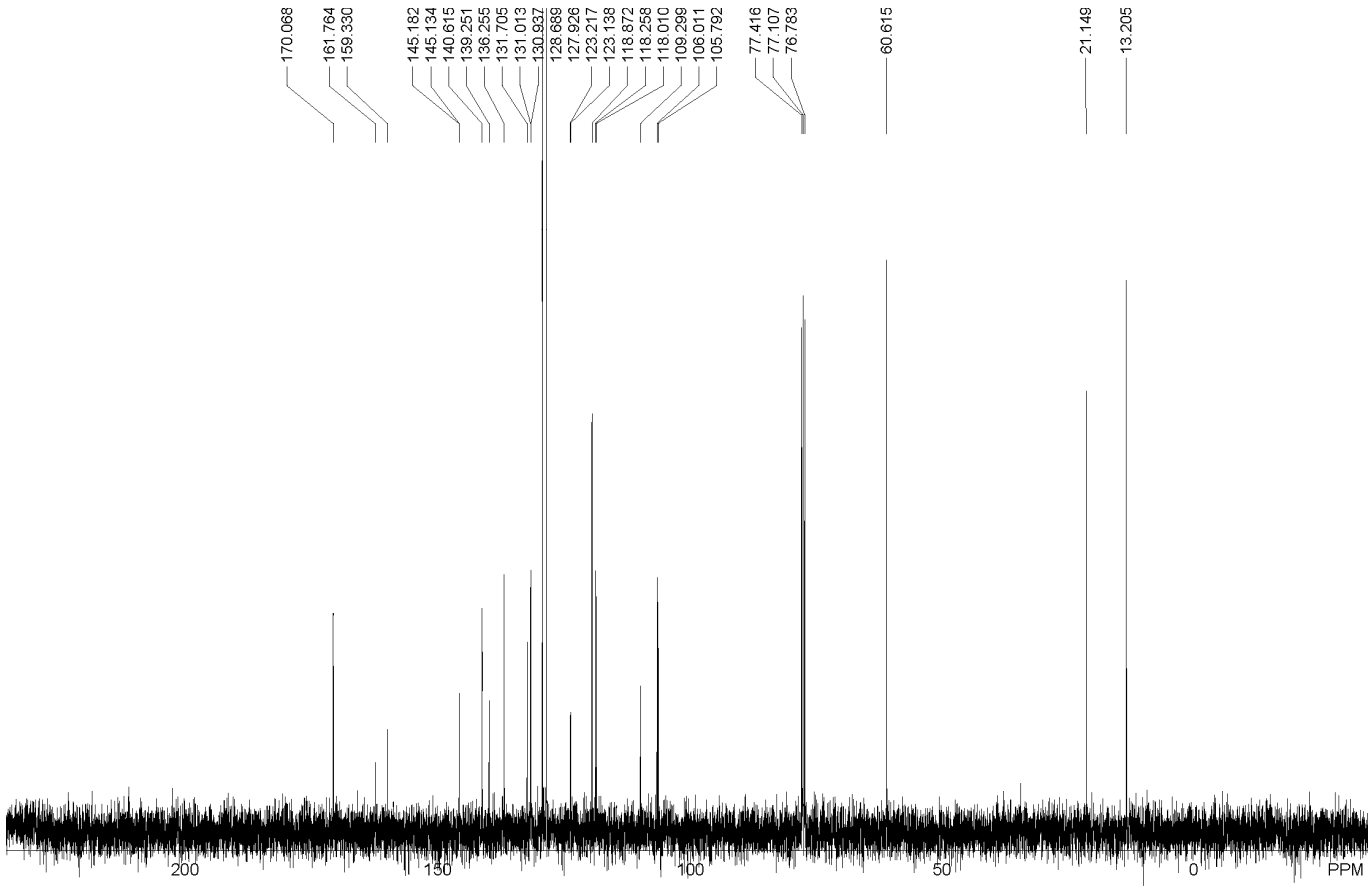
1.02
1.01
1.80
2.00
2.99
2.94
10
8
6
4
2
PPM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145.134
140.615
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136.255
131.705
131.013
130.937
128.689
127.926
123.217
123.138
118.872
118.258
118.010
109.299
106.011
105.792
77.416
77.107
76.783
60.615
21.149
13.205
200
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50
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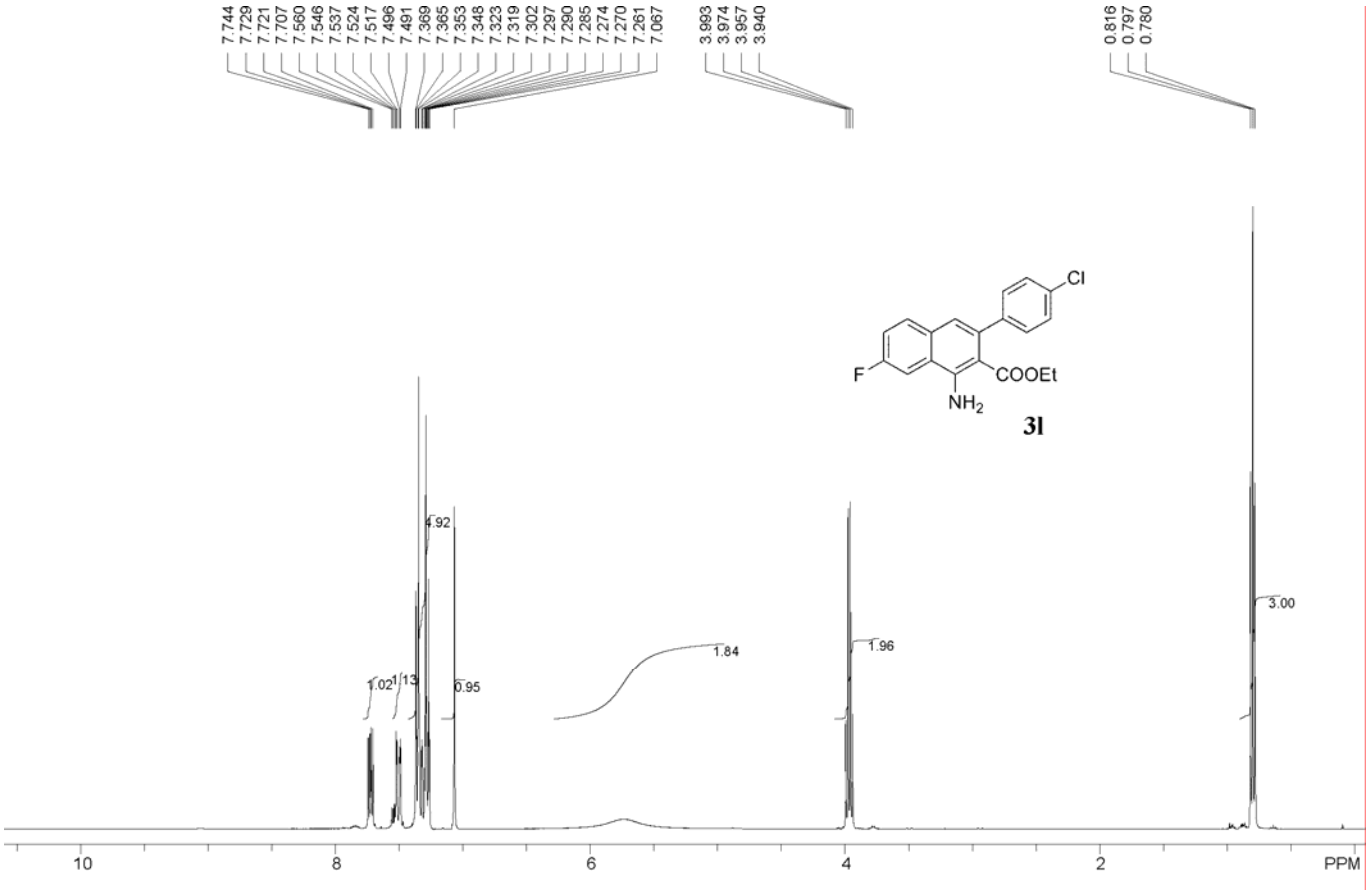
PPM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7.546
7.537
7.524
7.517
7.496
7.491
7.369
7.365
7.353
7.348
7.323
7.319
7.302
7.297
7.290
7.285
7.274
7.270
7.261
7.067
3.993
3.974
3.957
3.940
0.816
0.797
0.780
Cl
F
COOEt
NH2
3l
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1.84
1.96
3.00
1.02
1.13
0.95
10
8
6
4
2
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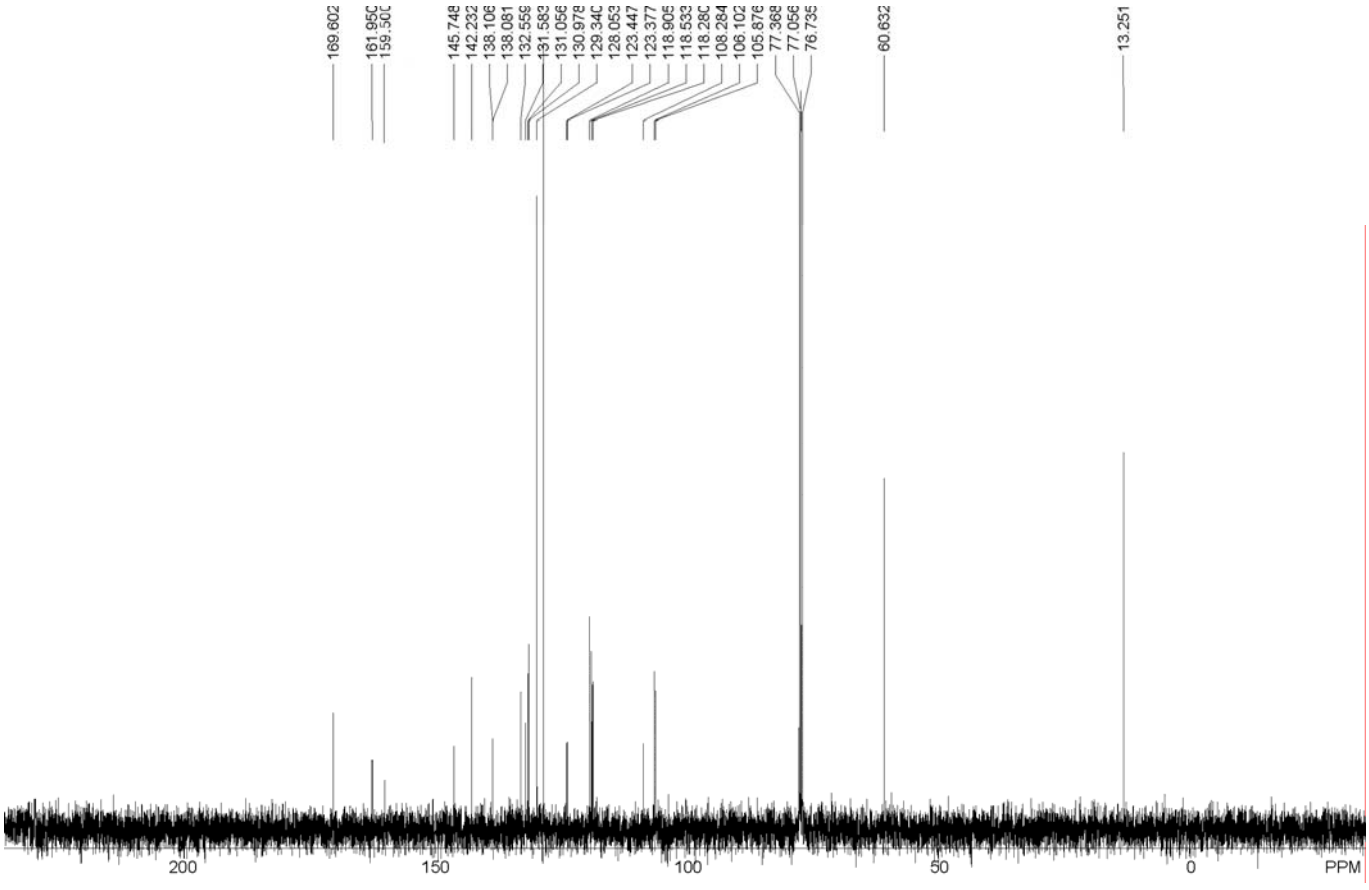
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123.447
123.377
118.905
118.533
118.280
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77.368
77.056
76.735
60.632
13.251
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100
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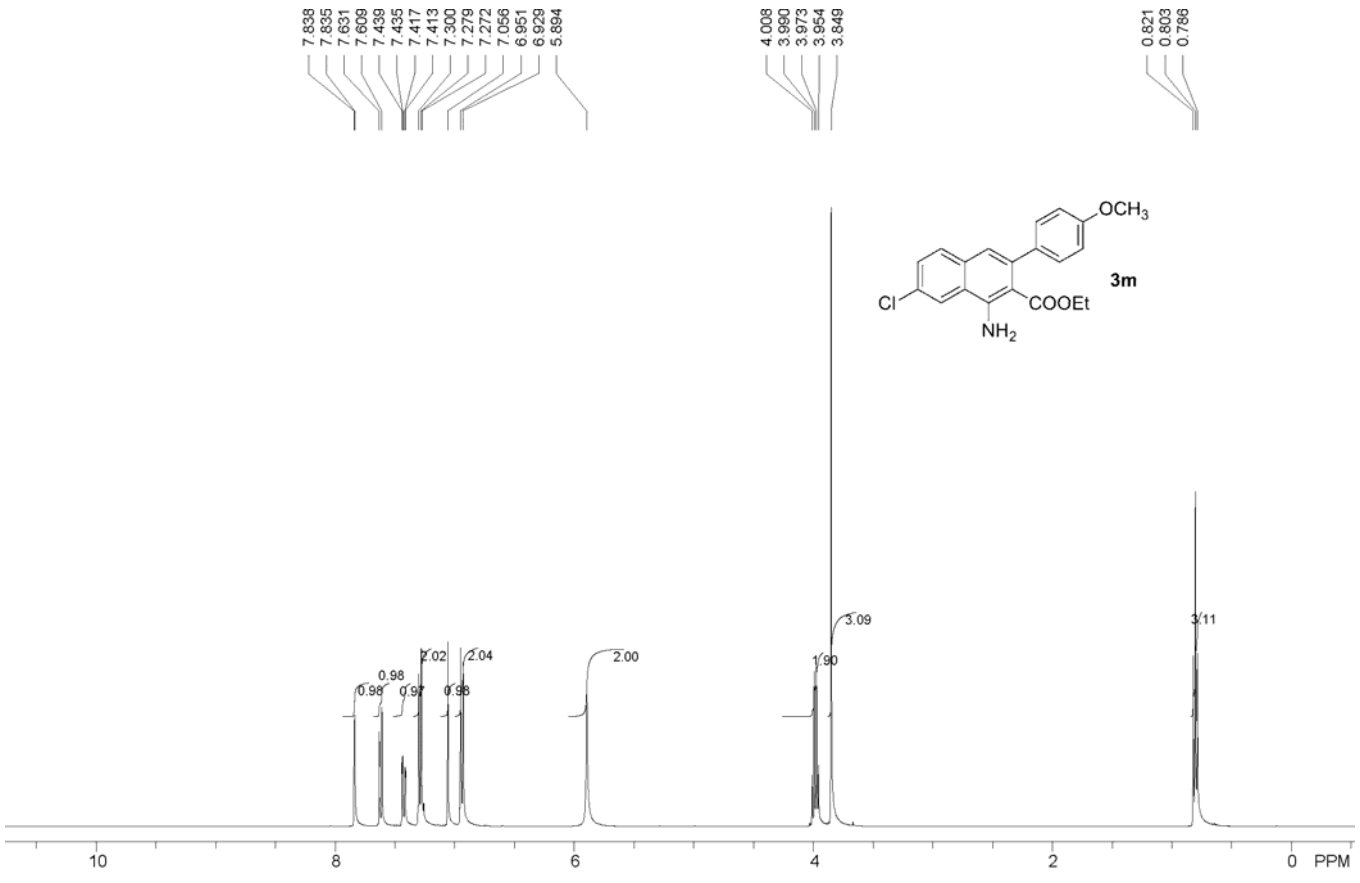
PPM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7.631
7.609
7.439
7.435
7.417
7.413
7.300
7.279
7.272
7.056
6.951
6.929
5.894
4.008
3.990
3.973
3.954
3.849
0.821
0.803
0.786
OCH3
Cl
COOEt
NH2
3m
0.98
0.98
0.97
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2.04
2.00
1.90
3.09
3.11
10
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6
4
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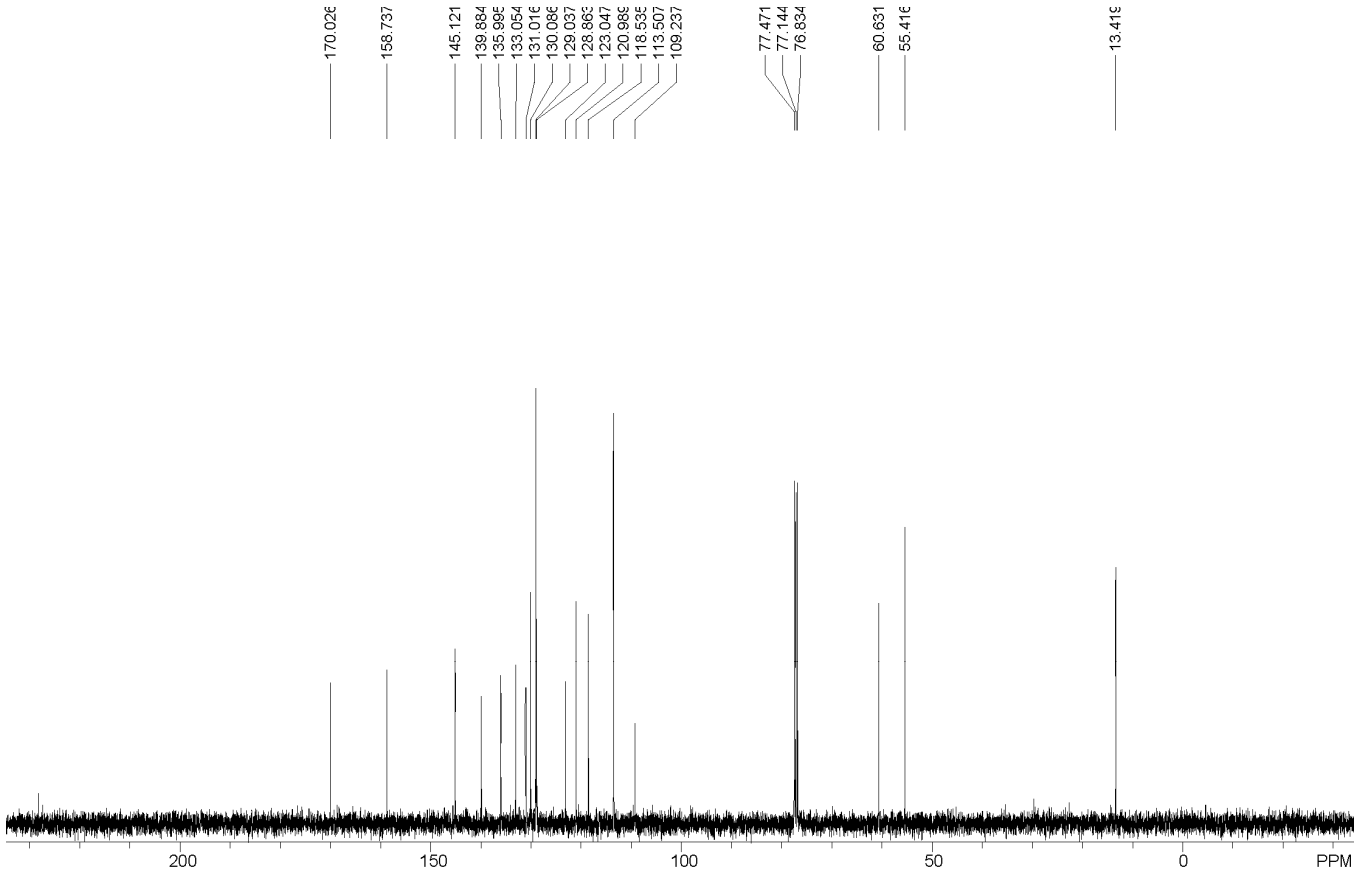
PPM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130.086
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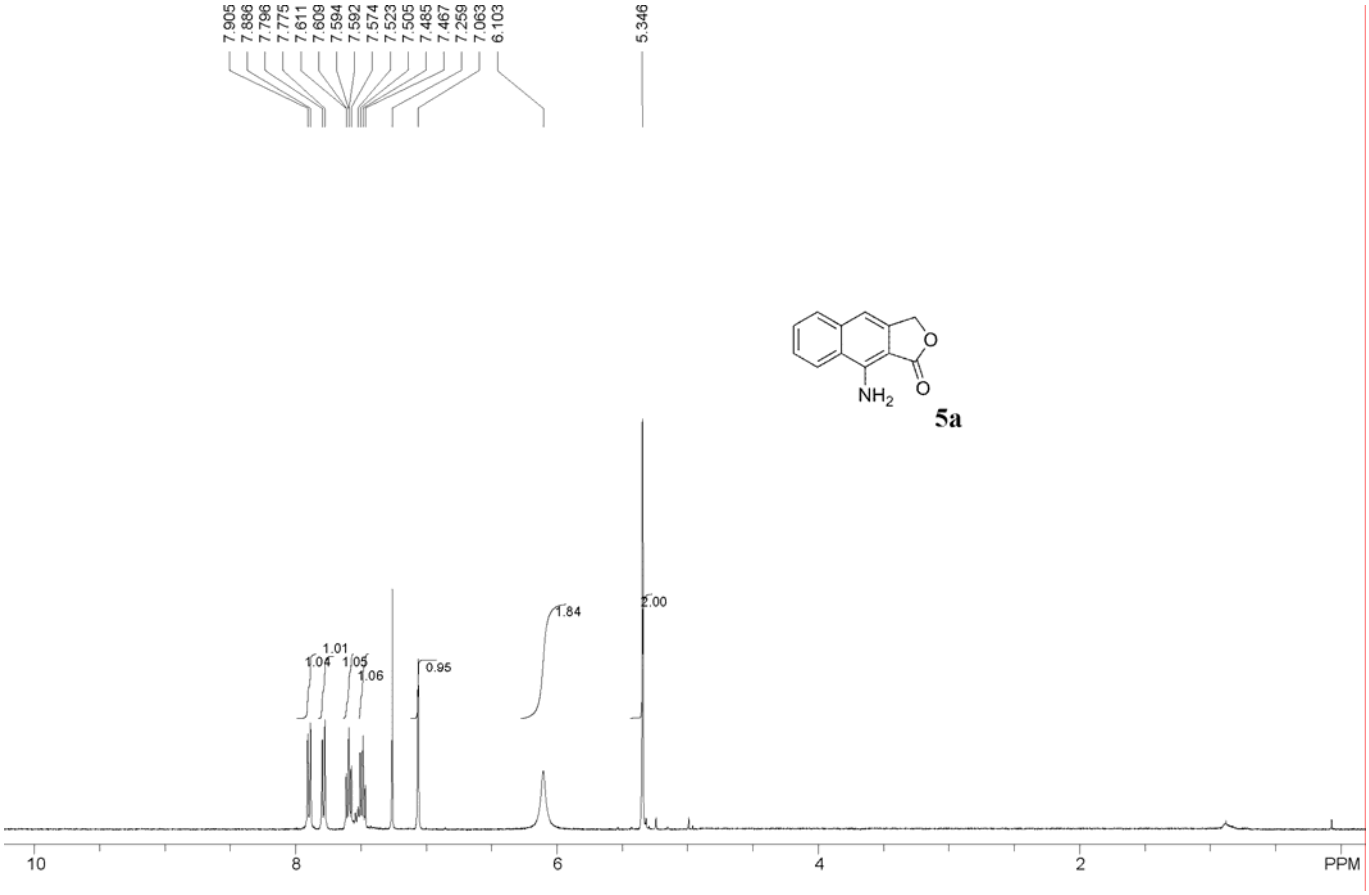
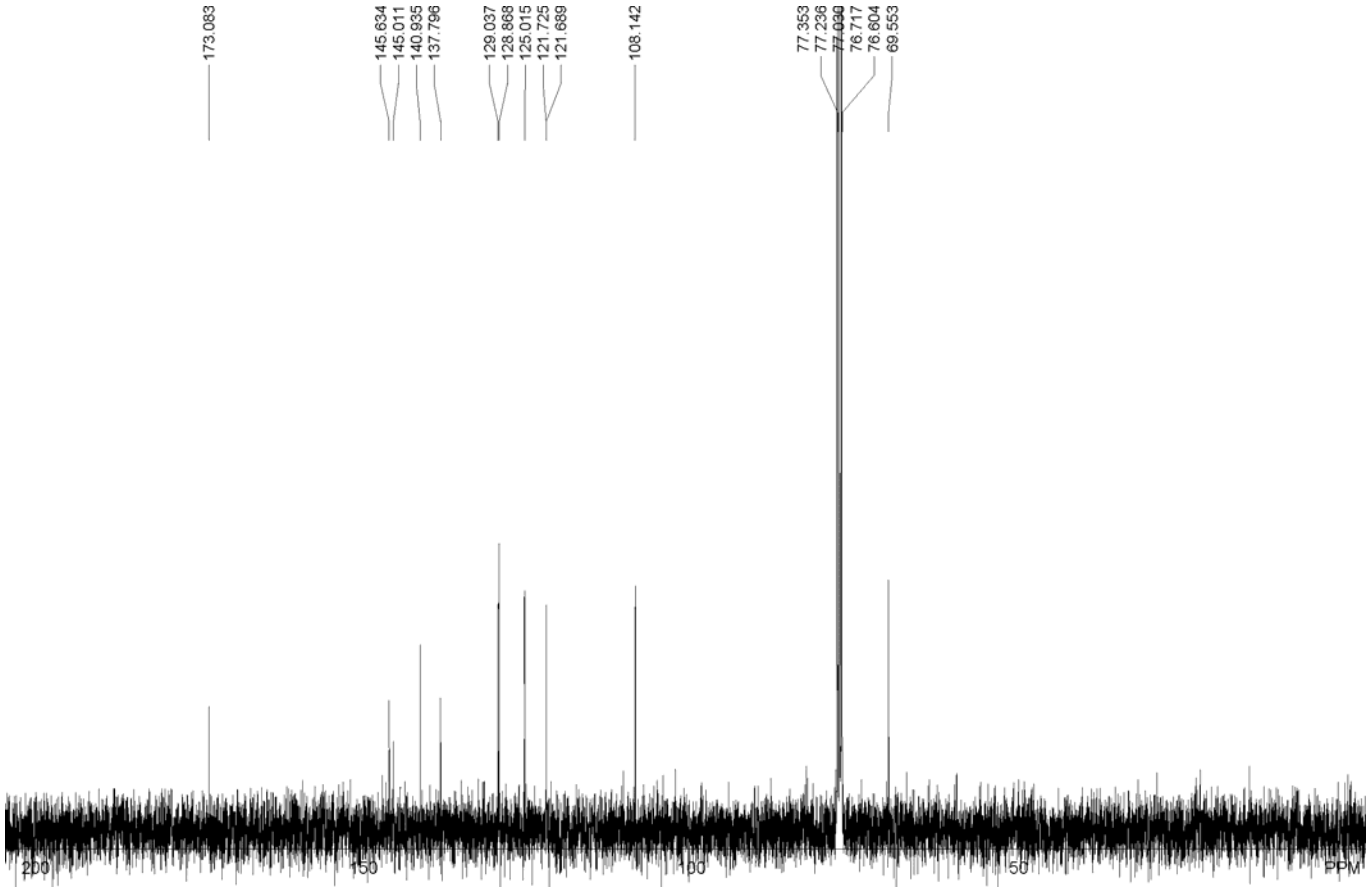
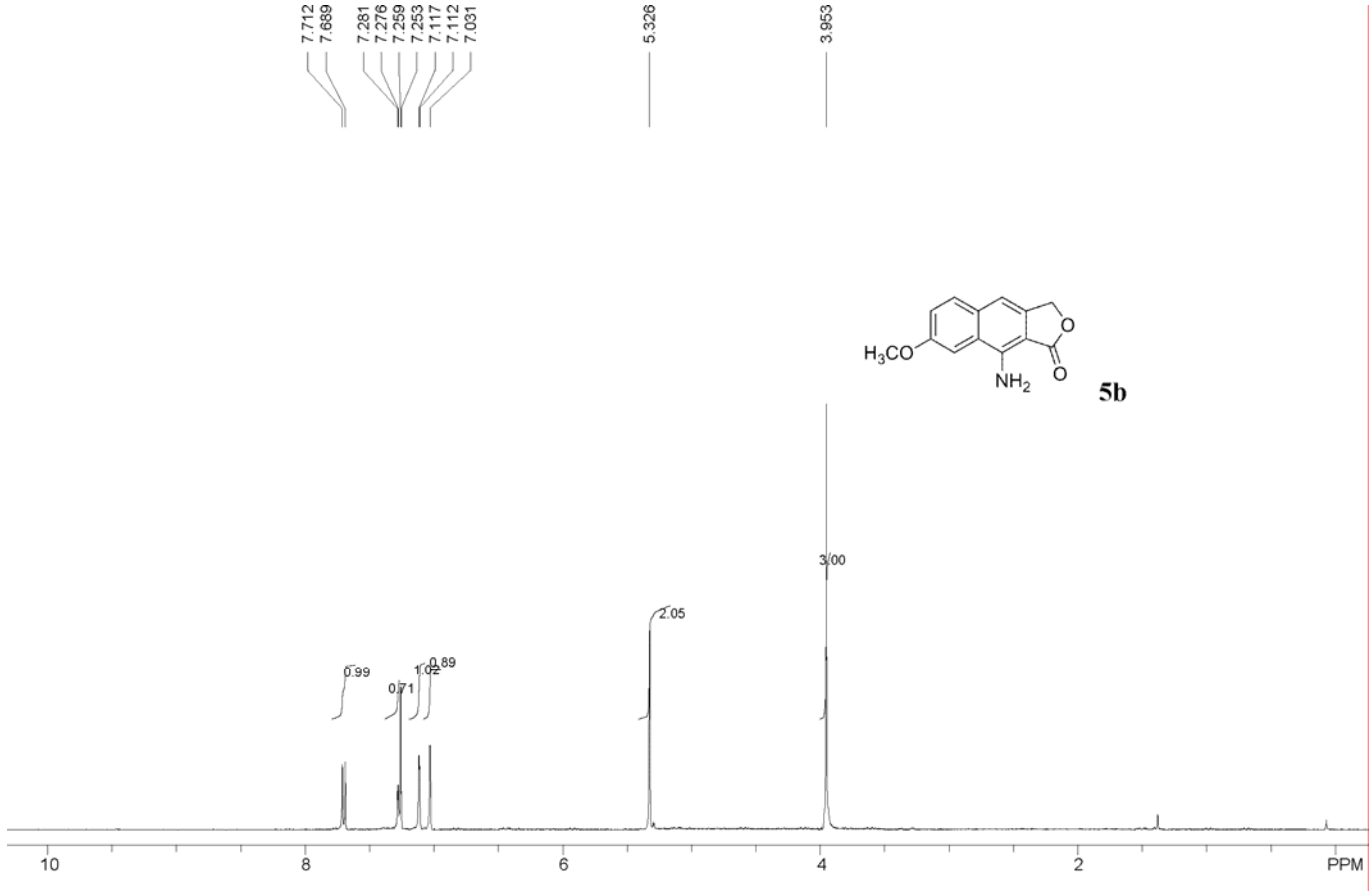
128.863
123.047
120.988
118.535
113.507
109.237
77.471
77.144
76.834
60.631
55.416
13.416
200
150
100
50
0
PPM

VI. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5k



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7.112
7.031
5.326
3.953
H_3CO
NH_2
O
O
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2.05
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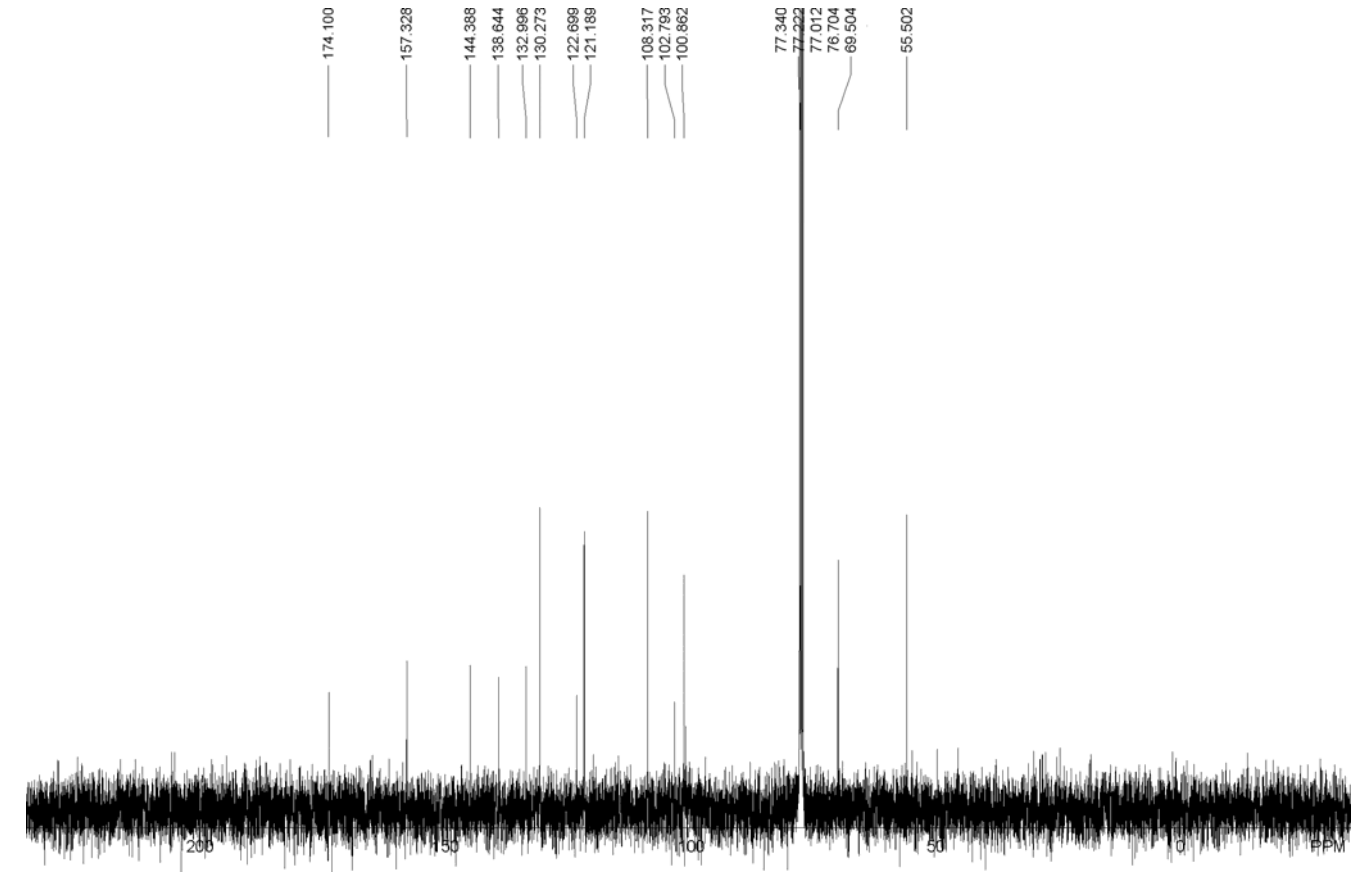
1.02
0.89
10
8
6
4
2
PPM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132.996
130.273
122.699
121.189
108.317
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77.340
77.222
77.012
76.704
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55.502
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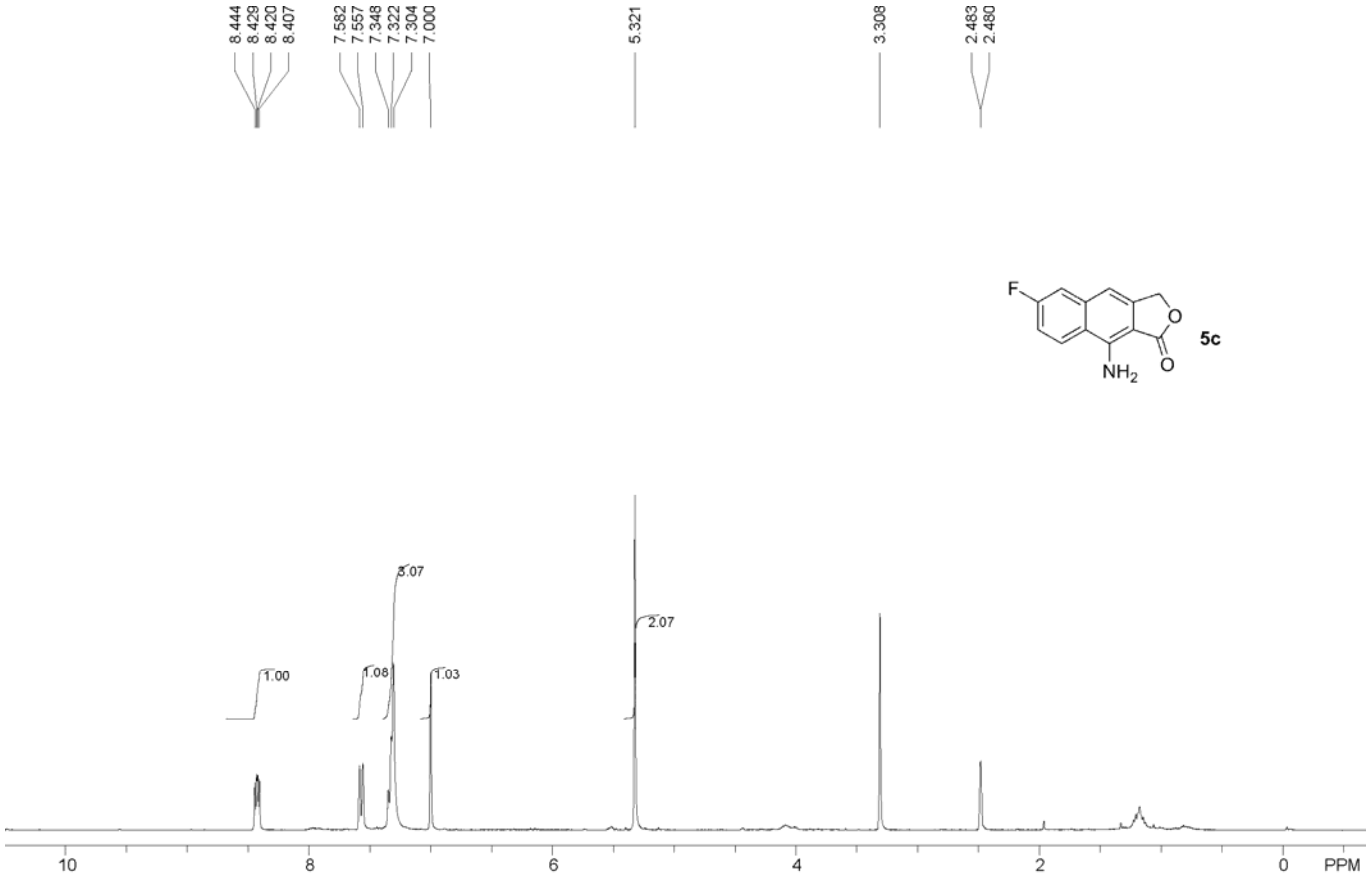
50
0
PPM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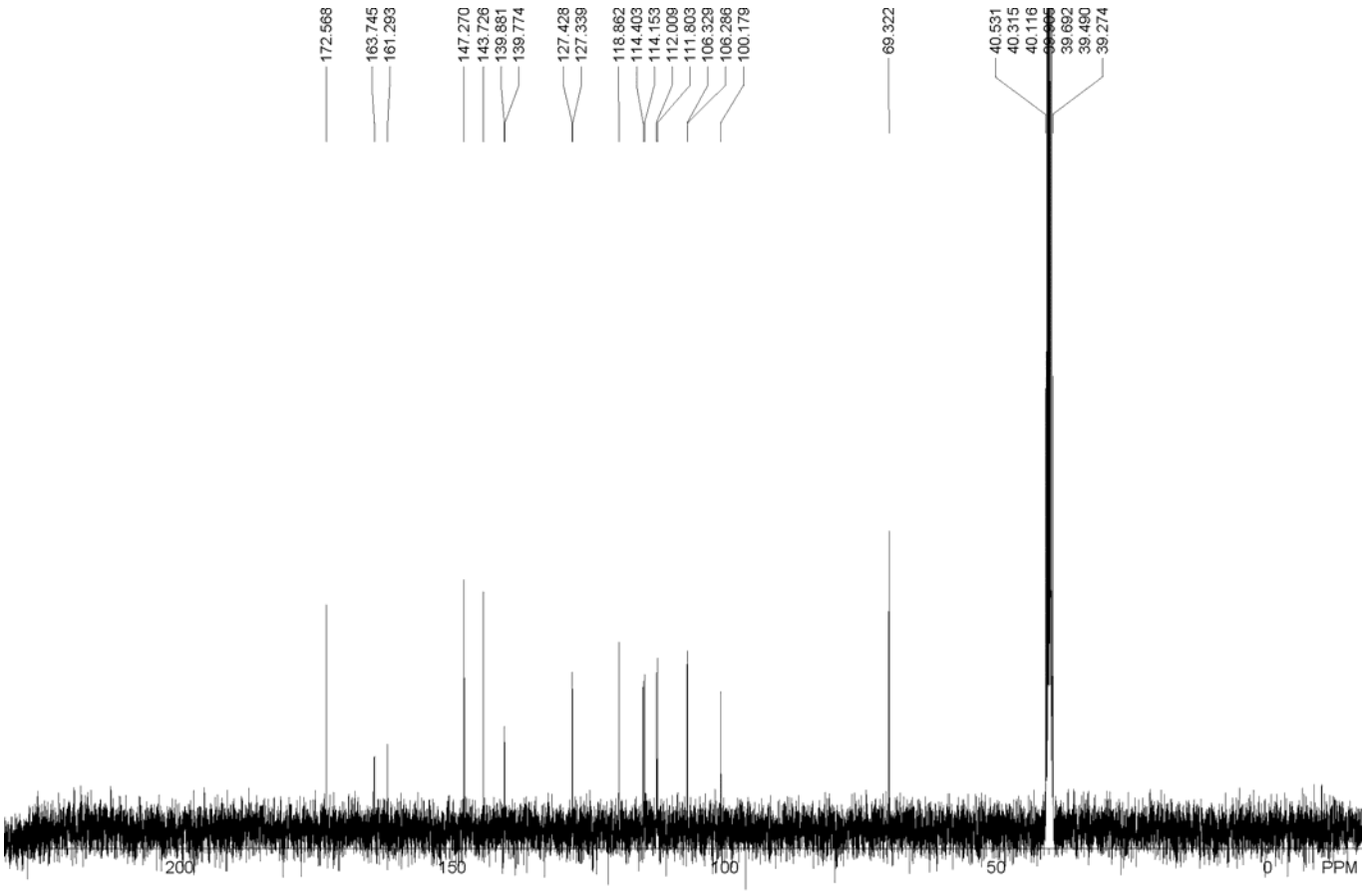
8.420
8.407
7.582
7.557
7.348
7.322
7.304
7.000
5.321
3.308
2.483
2.480
F
O
O
NH2
5c
3.07
2.07
1.00
1.08
1.03
10
8
6
4
2
0
PPM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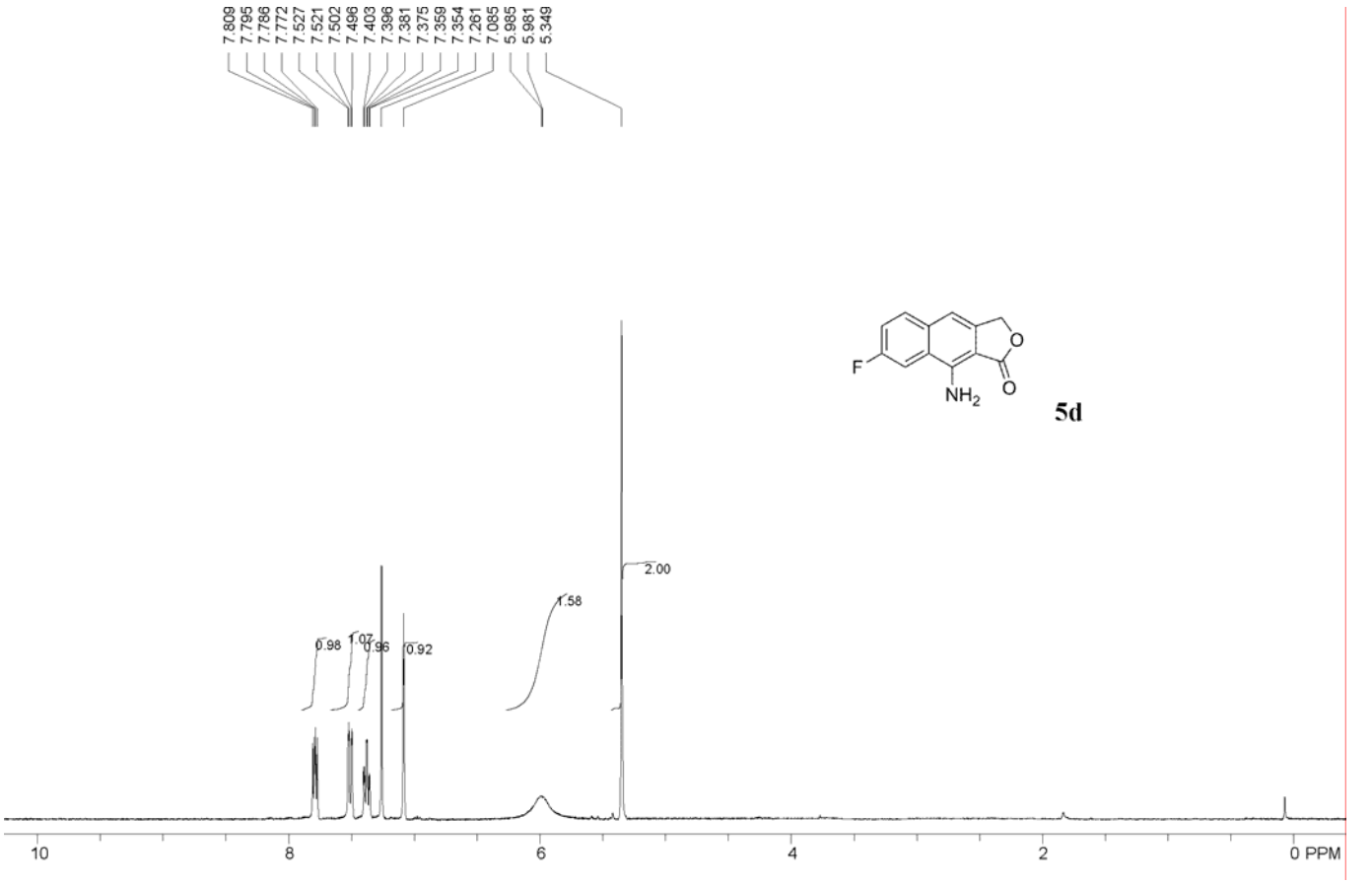
147.270
143.726
139.881
139.774
127.428
127.339
118.862
114.403
114.153
112.009
111.803
106.329
106.286
100.179
69.322
40.531
40.315
40.116
39.692
39.490
39.274
200
150
100
50
0
PPM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7.772
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7.521
7.502
7.496
7.403
7.396
7.381
7.375
7.359
7.354
7.261
7.085
5.985
5.981
5.349
F
O
O
NH2
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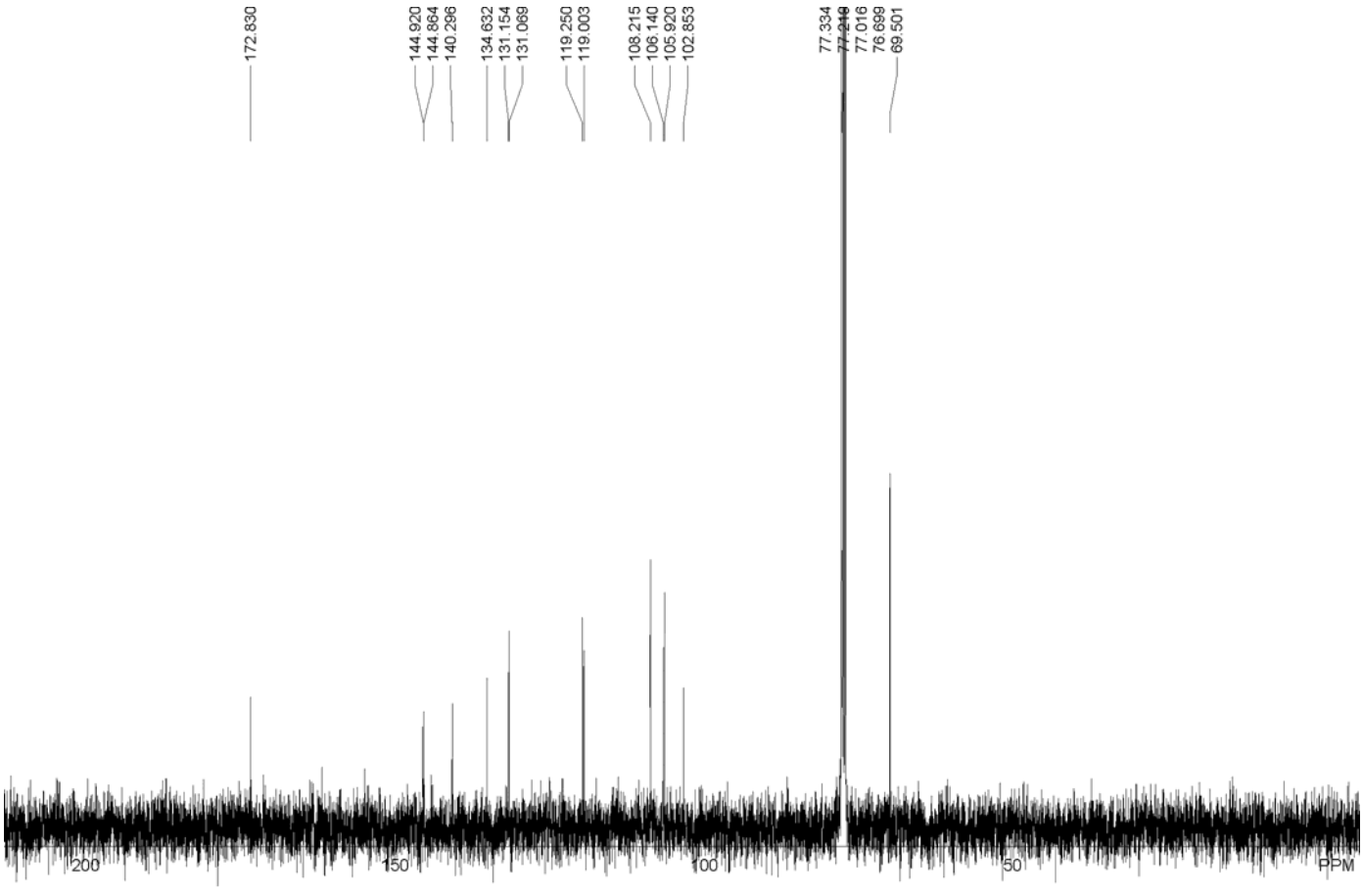
1.07
0.96
0.92
10
8
6
4
2
0 PPM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102.853
77.334
77.016
76.699
69.501
200
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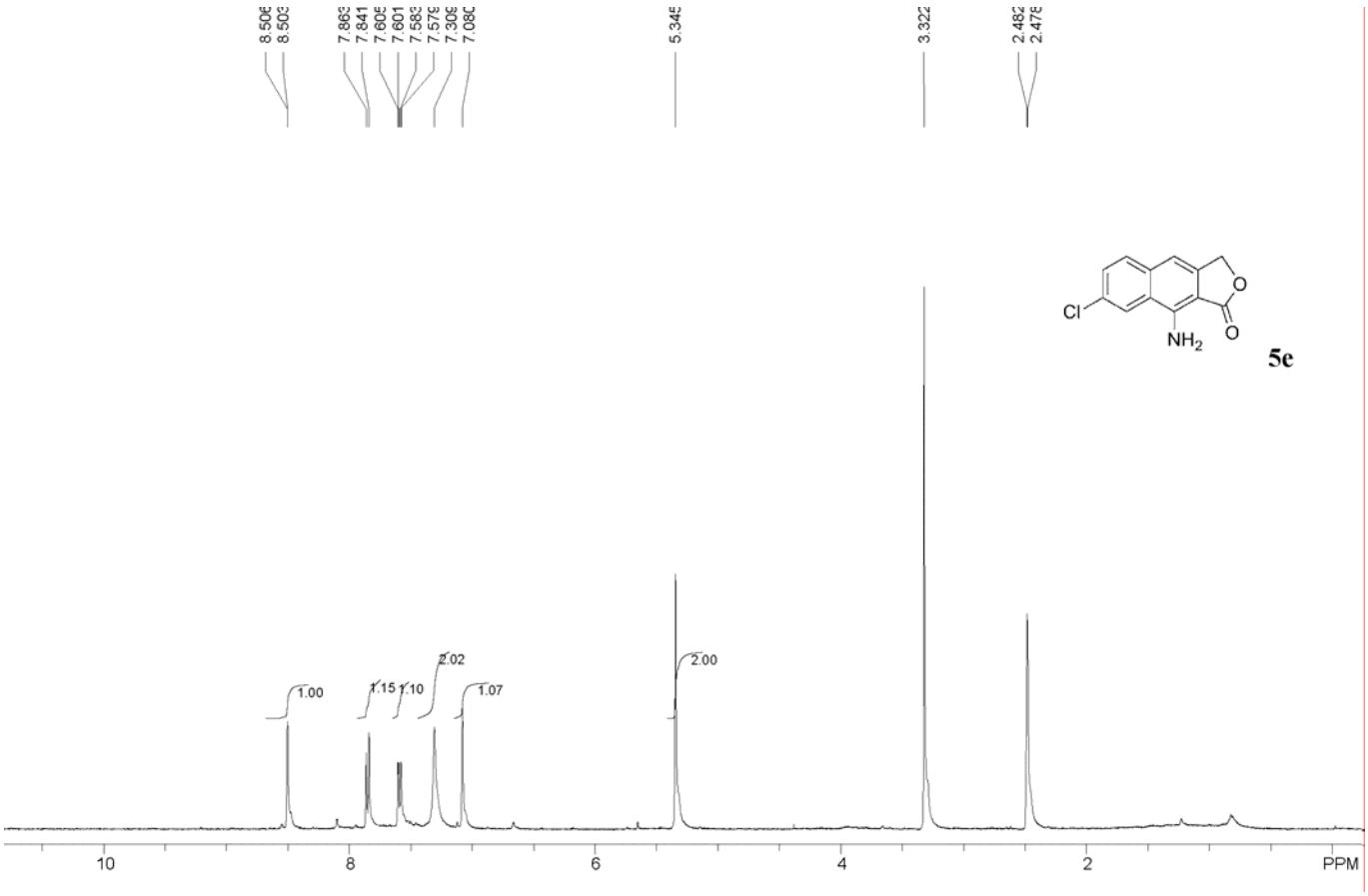
100
50
PPM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7.841
7.605
7.601
7.583
7.575
7.306
7.080
5.345
3.322
2.482
2.478
Cl
O
O
NH2
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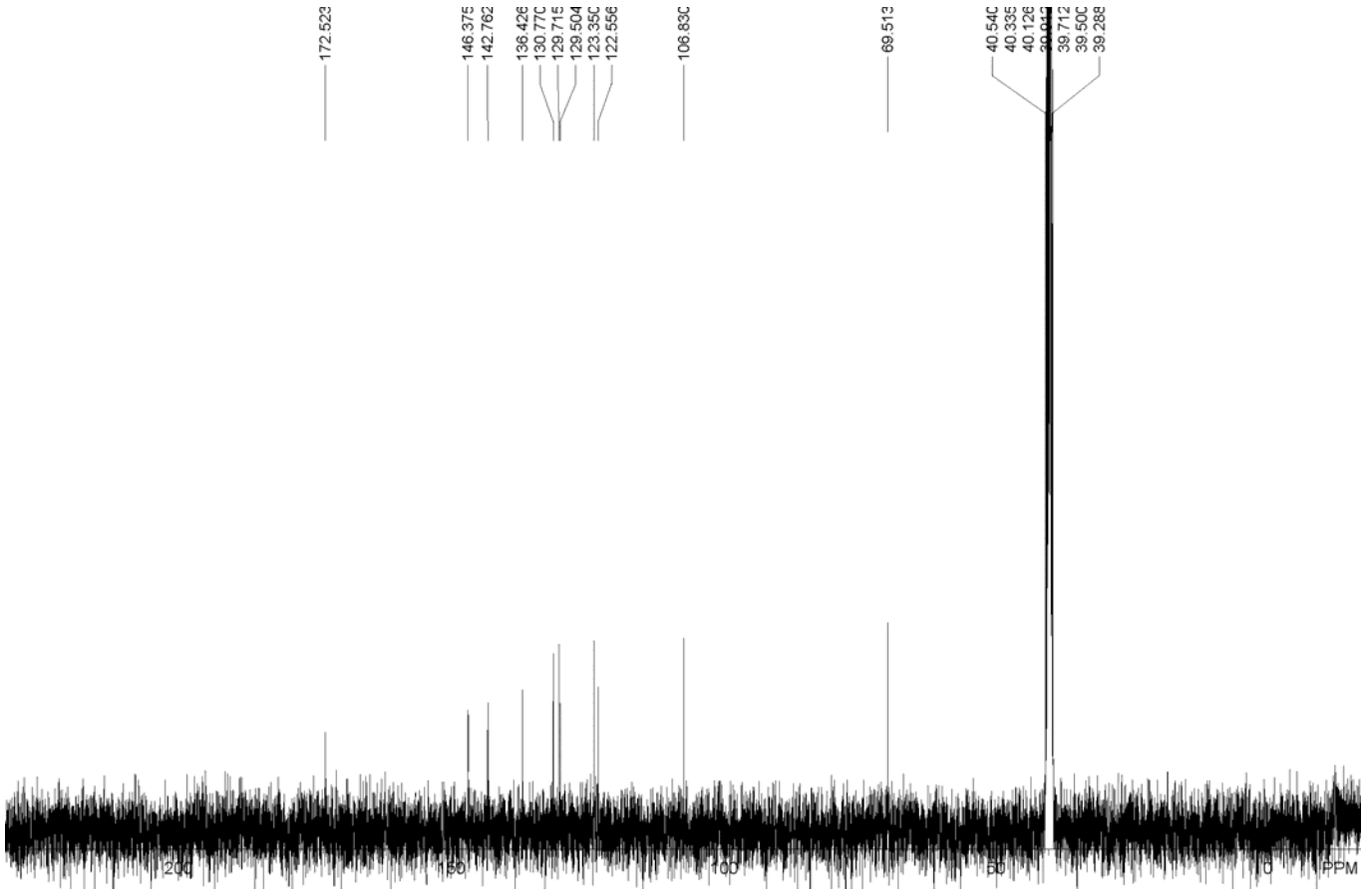
1.15
1.10
2.02
1.07
2.00
10
8
6
4
2
PPM

5e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129.715
129.504
123.350
122.556
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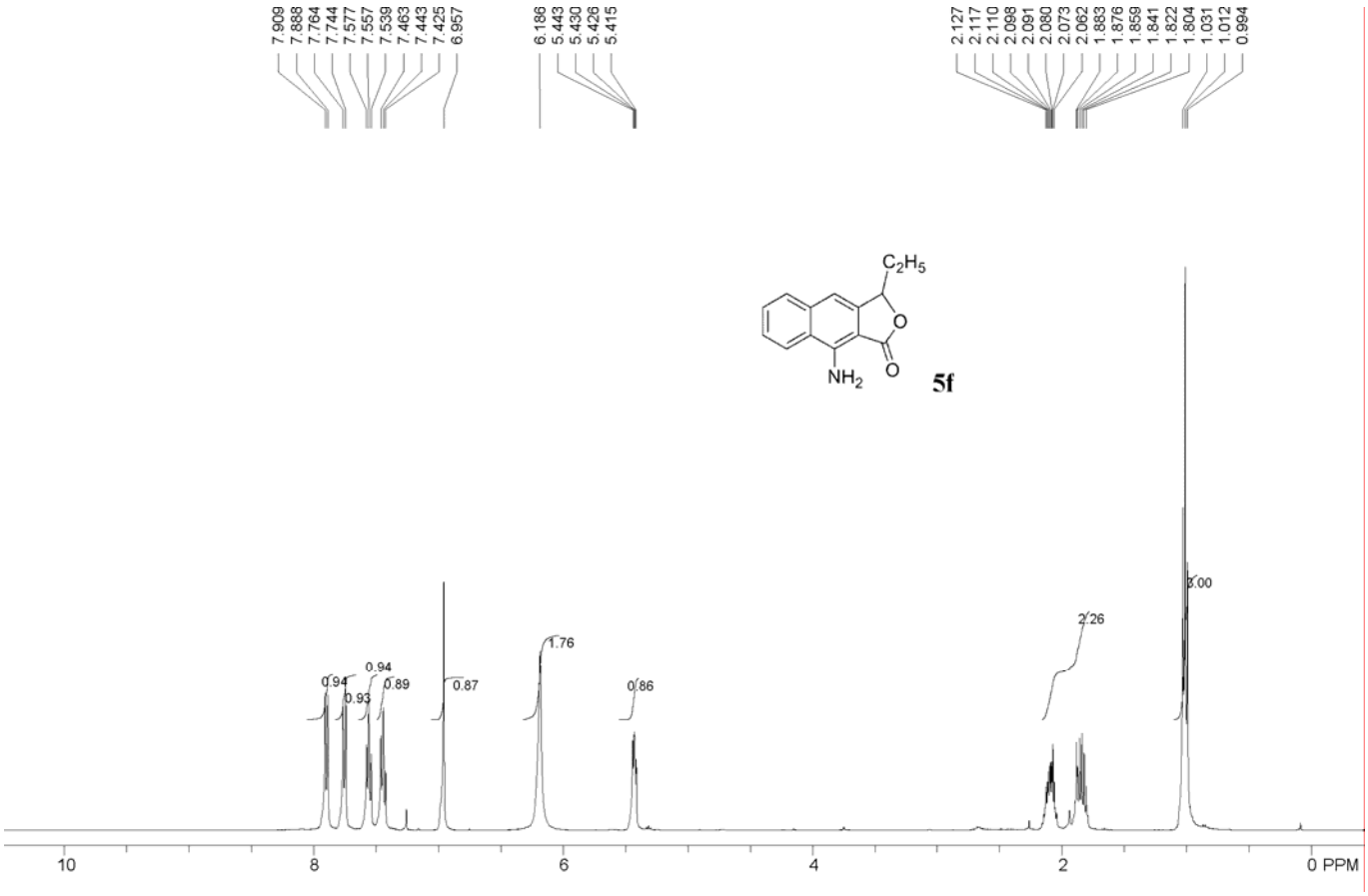
40.540
40.335
40.126
39.712
39.500
39.288
200
150
100
50
0
PPM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7.463
7.443
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6.957
6.186
5.443
5.430
5.426
5.415
2.127
2.117
2.110
2.098
2.091
2.080
2.073
2.062
1.883
1.876
1.859
1.841
1.822
1.804
1.031
1.012
0.994
C2H5
O
O
NH2
5f
0.94
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0.86
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4
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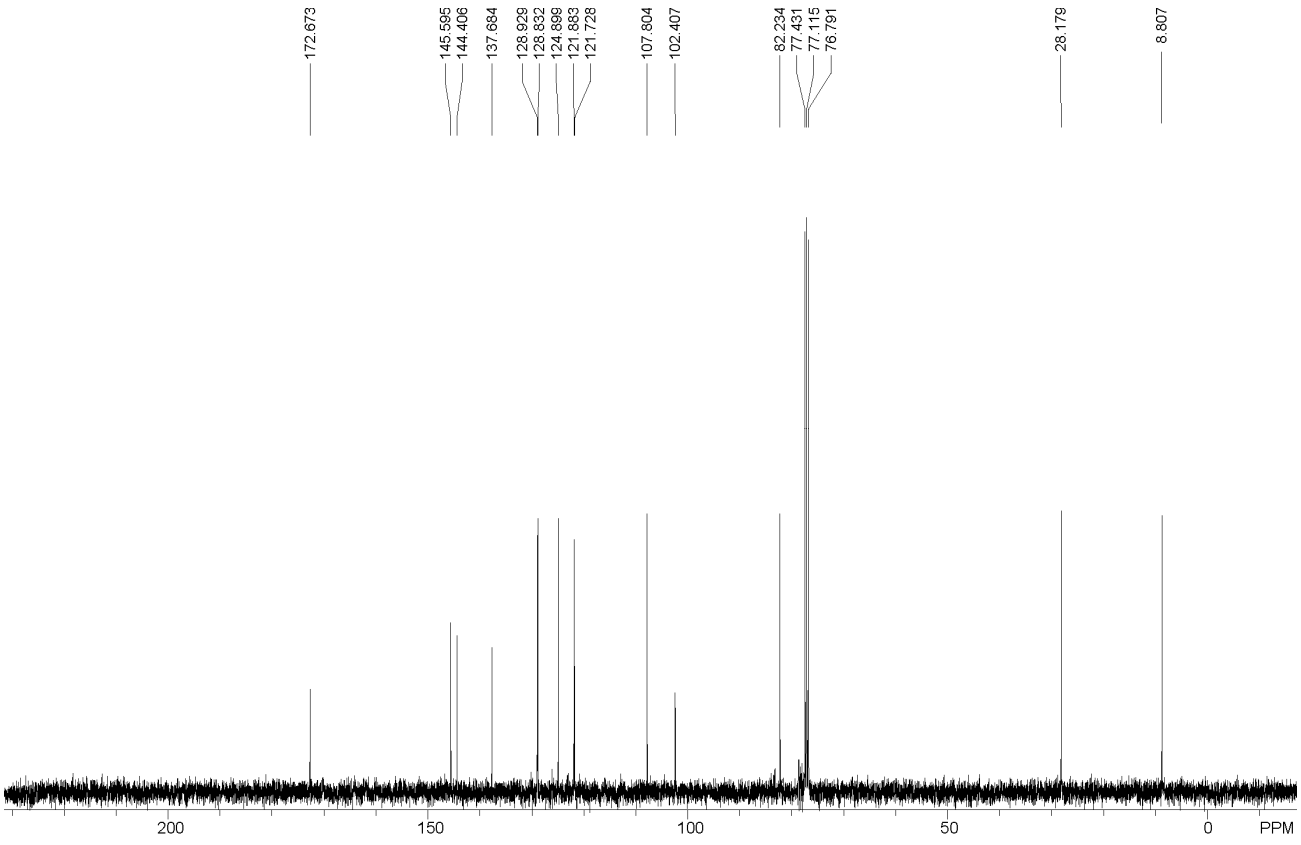
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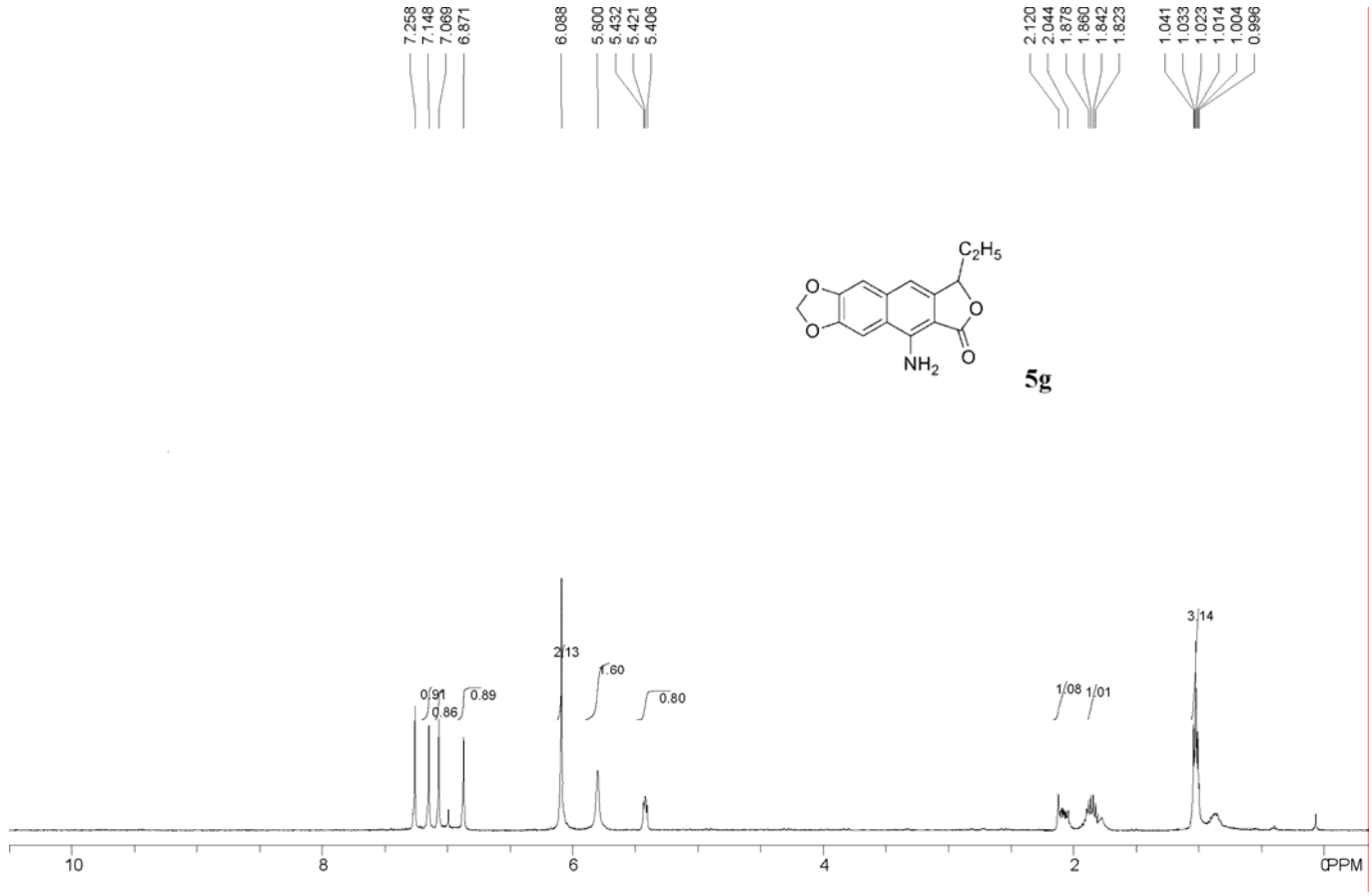
82.234
77.431
77.115
76.791
28.179
8.807
200
150
100
50
0
PPM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5.421
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2.044
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1.860
1.842
1.823
1.041
1.033
1.023
1.014
1.004
0.996
C_2H_5
O
O
O
O
NH_2
5g
0.91
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1.08
1.01
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10
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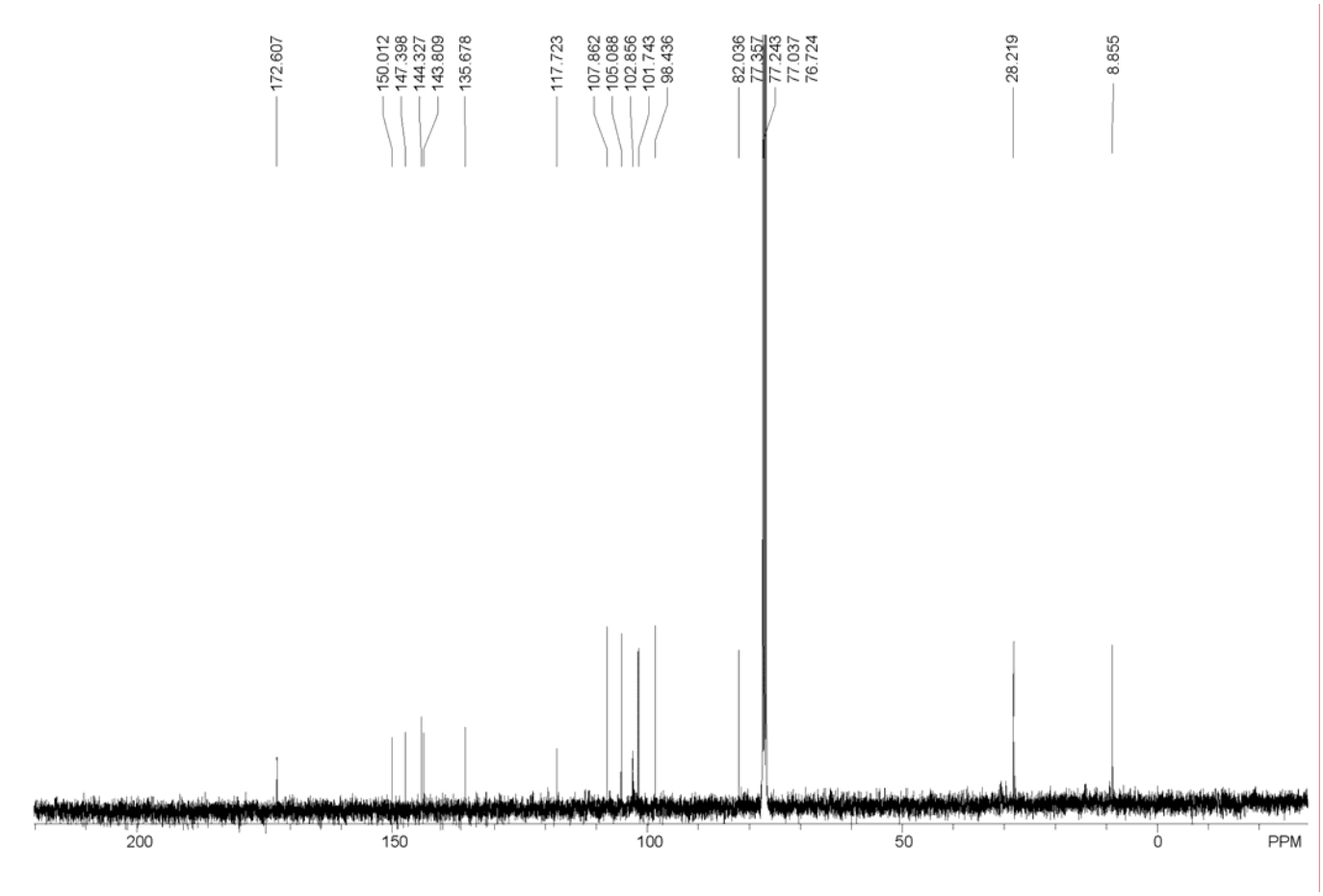
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101.743
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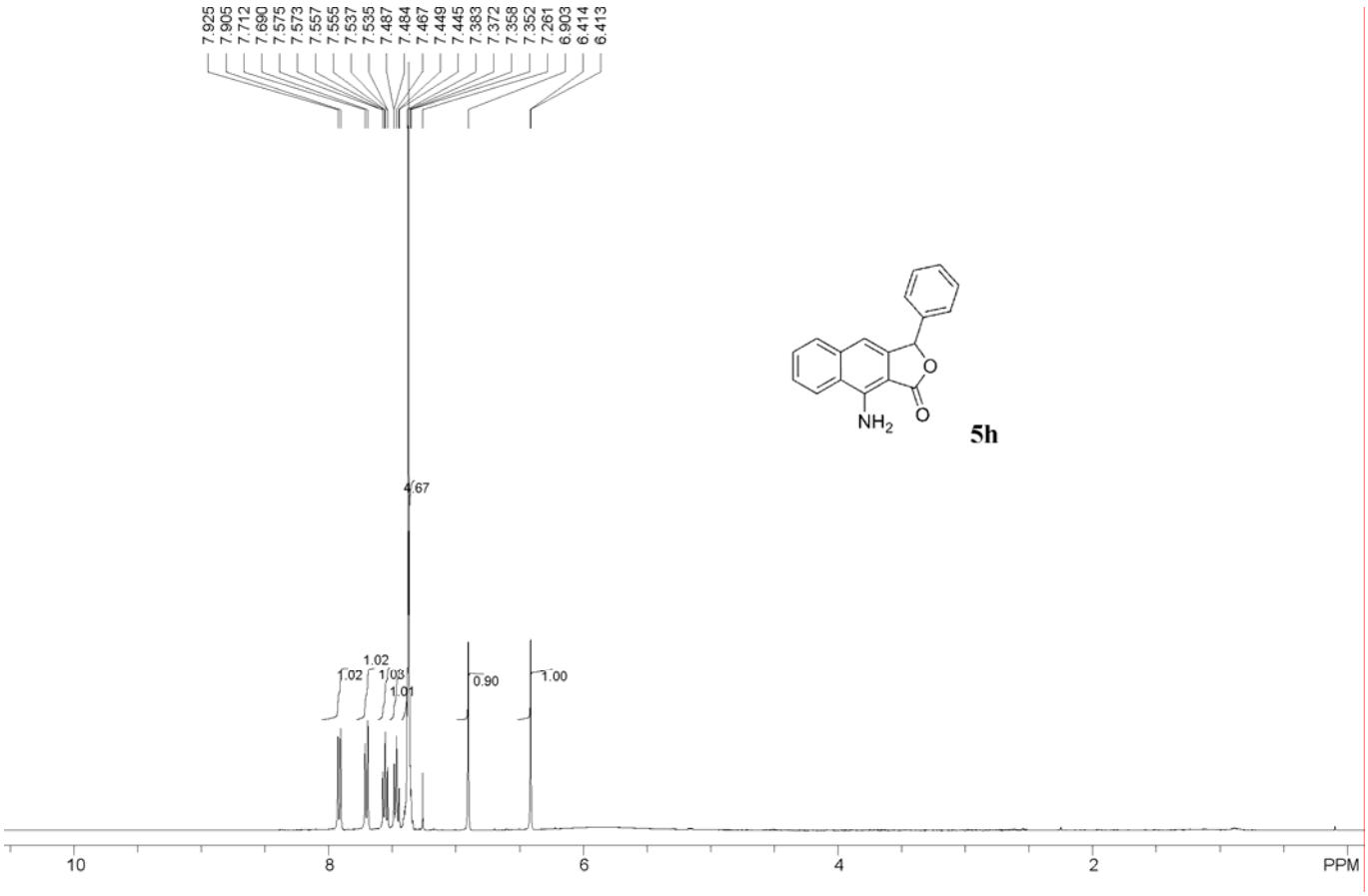
77.357
77.243
77.037
76.724
28.219
8.855
200
150
100
50
0
PPM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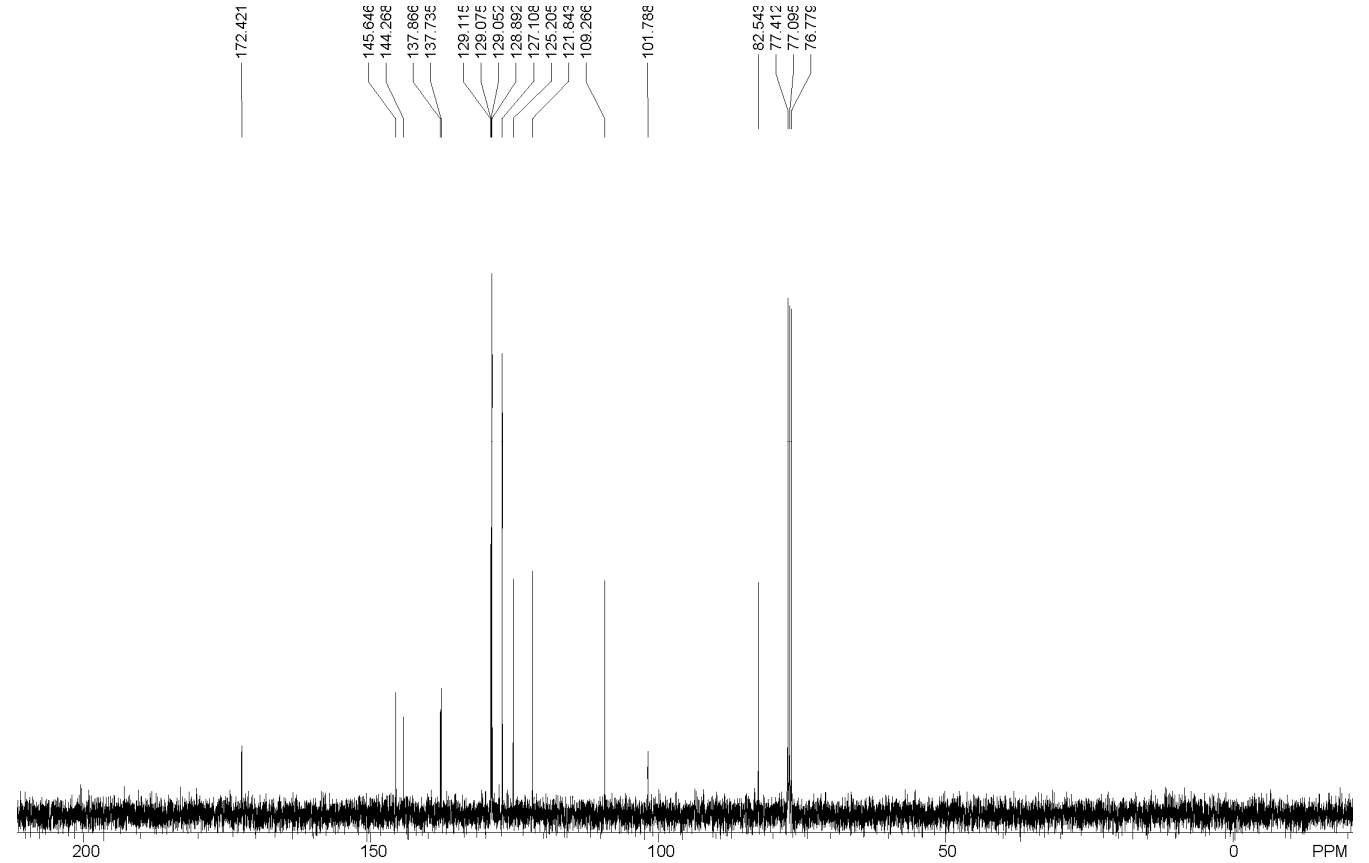
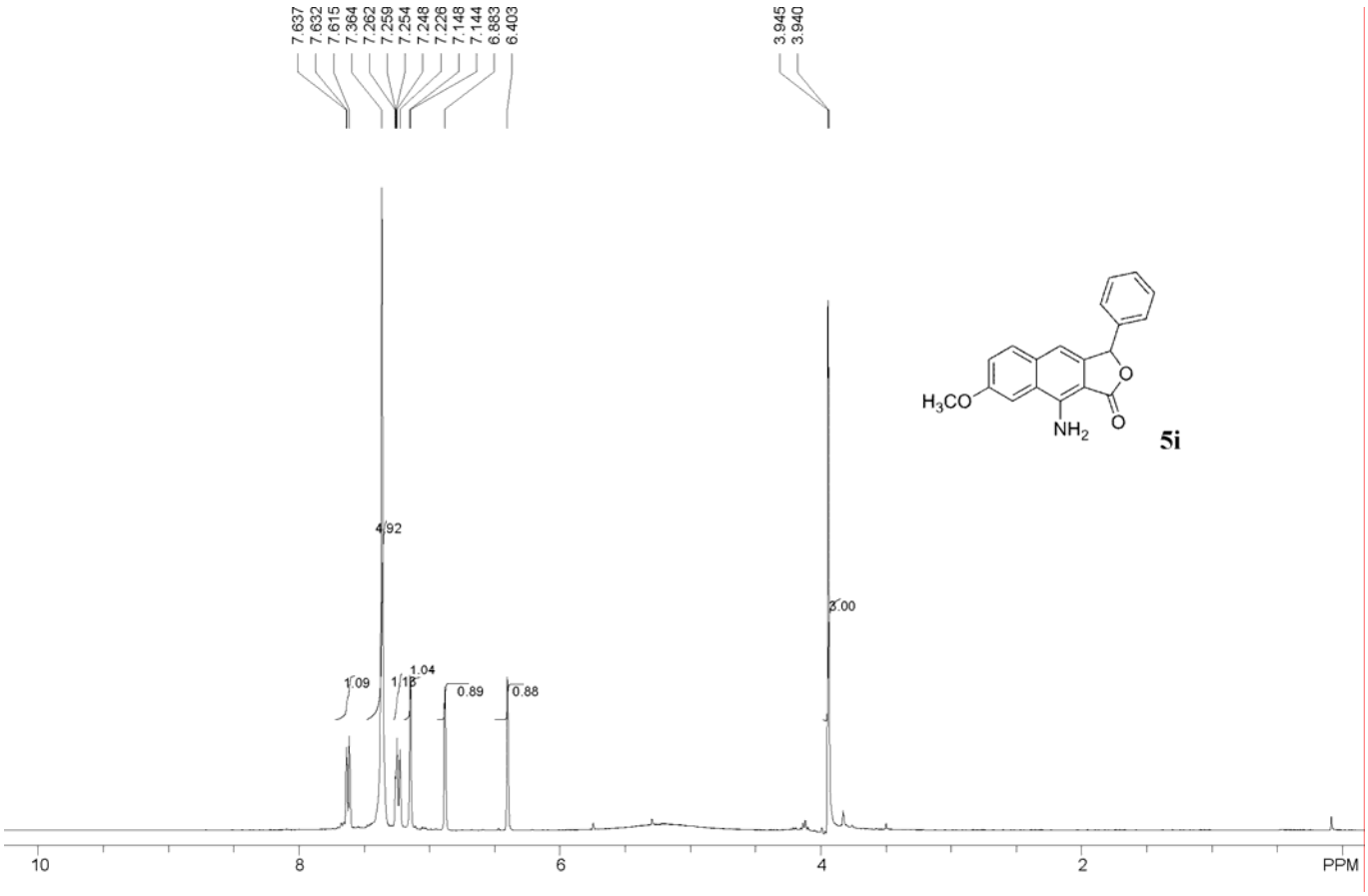
7.905
7.712
7.690
7.575
7.573
7.557
7.555
7.537
7.535
7.487
7.484
7.467
7.449
7.445
7.383
7.372
7.358
7.352
7.261
6.903
6.414
6.413
4.67
1.02
1.02
1.03
1.01
0.90
1.00
10
8
6
4
2
PPM

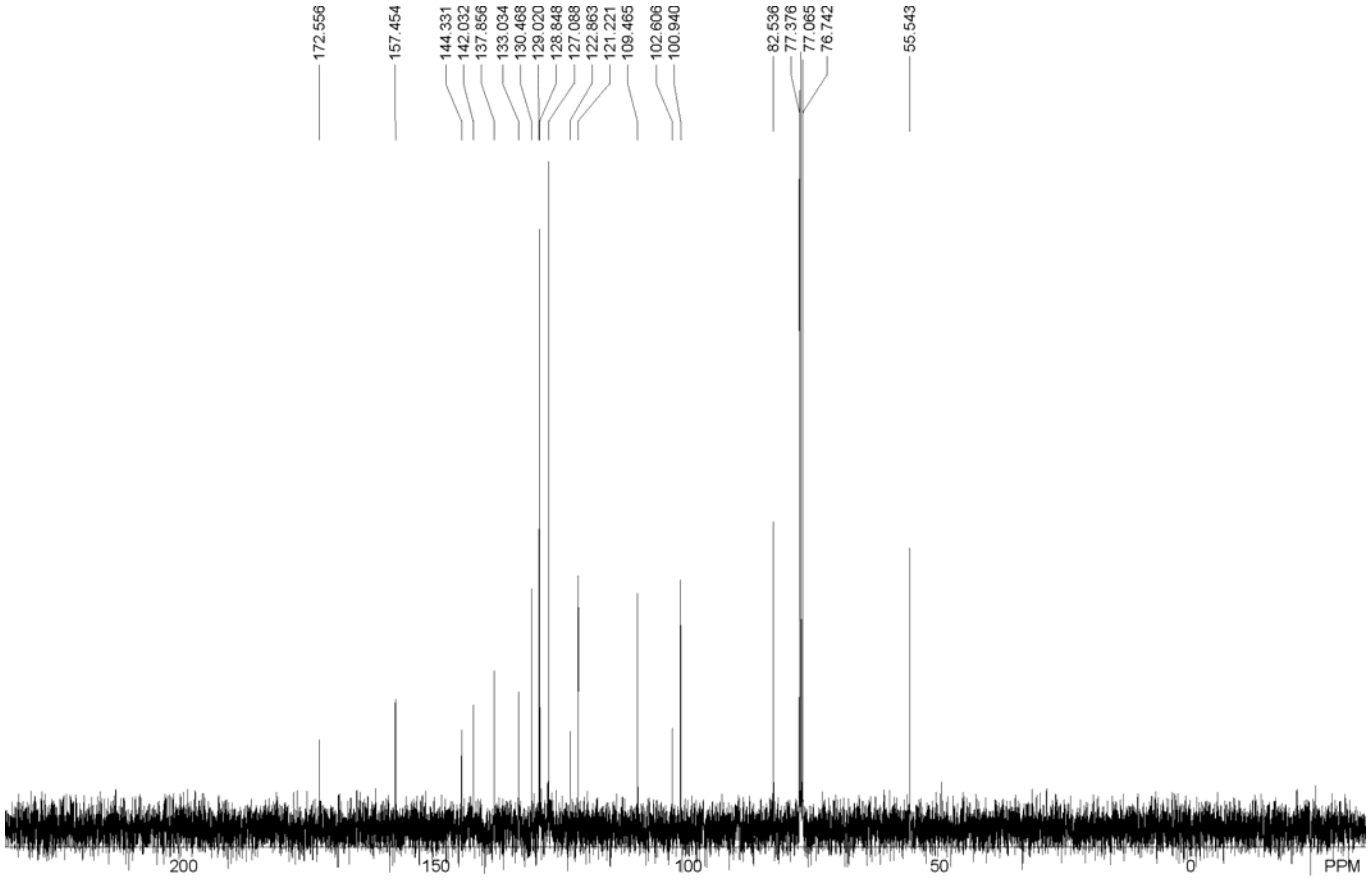
5h

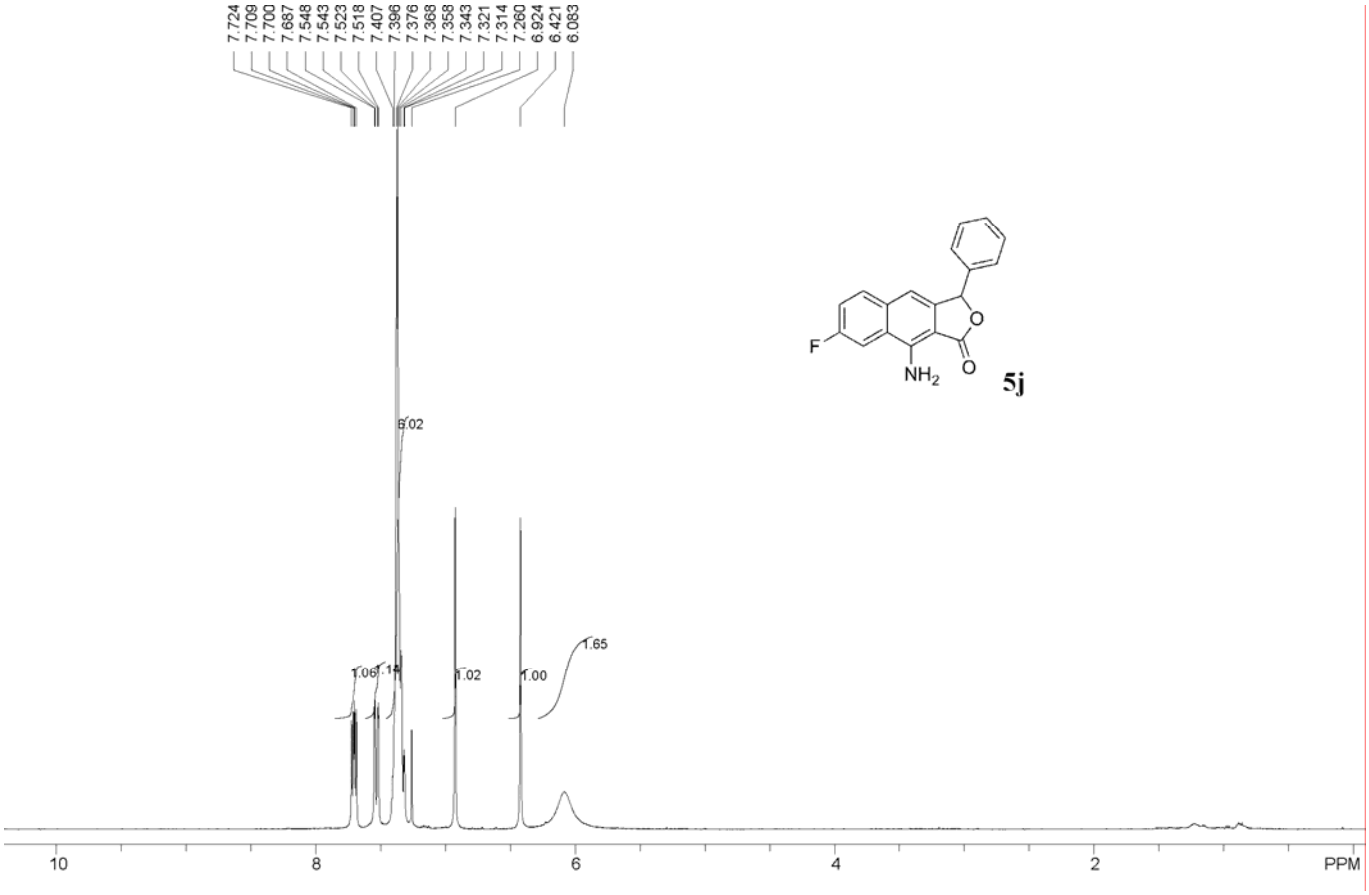

172.421
145.646
144.268
137.866
137.735
129.115
129.075
129.052
128.892
127.108
125.205
121.843
109.266
101.788
82.543
77.412
77.095
76.778
200
150
100
50
0
PPM


7.637
7.632
7.615
7.364
7.262
7.259
7.254
7.248
7.226
7.148
7.144
6.883
6.403
3.945
3.940
4.92
3.00
1.09
1.13
1.04
0.89
0.88
10
8
6
4
2
PPM

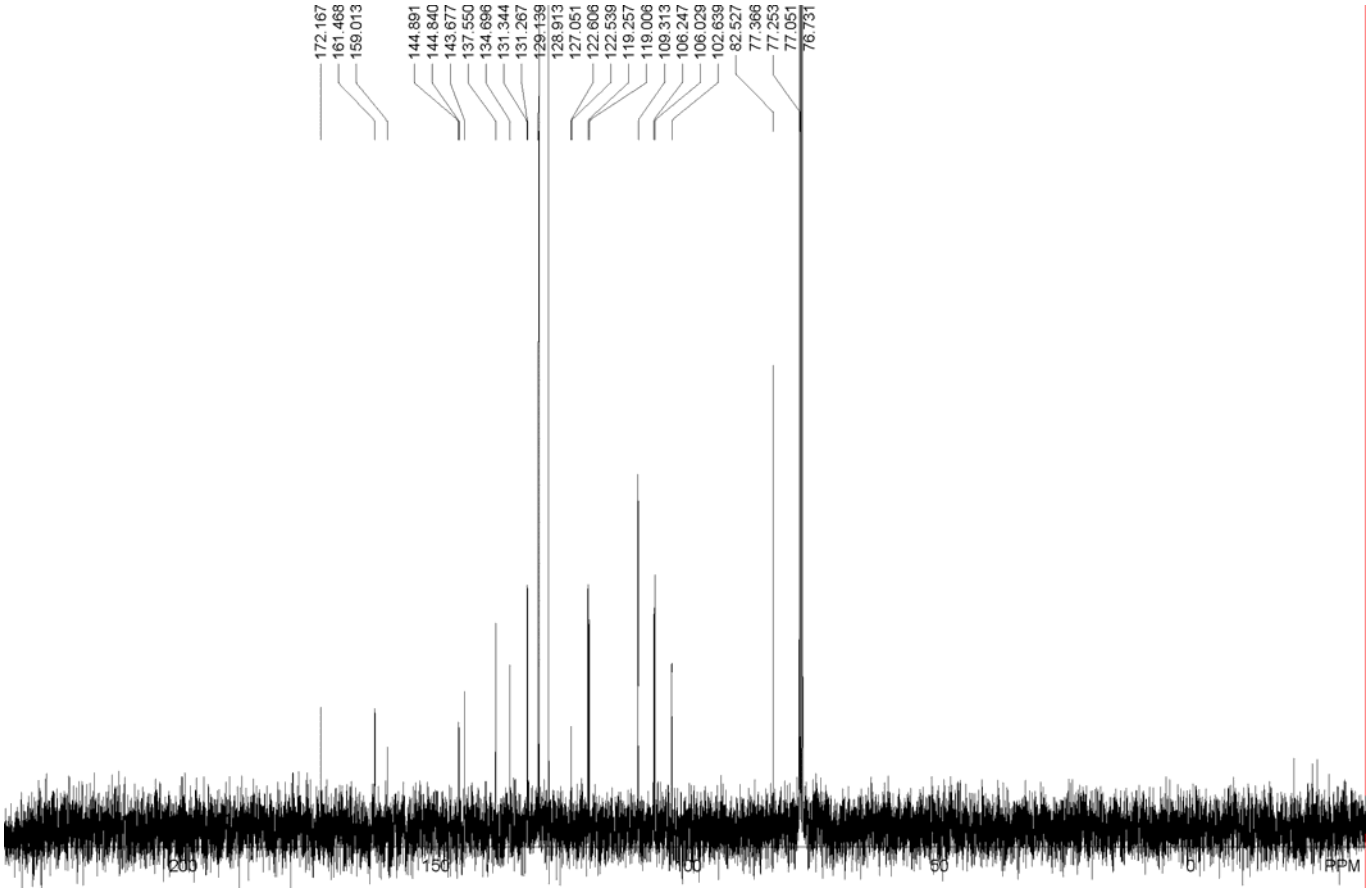
H3CO
NH2
O
O

5i

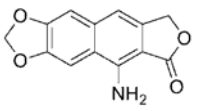

172.556
157.454
144.331
142.032
137.856
133.034
130.468
129.020
128.848
127.088
122.863
121.221
109.465
102.606
100.940
82.536
77.376
77.065
76.742
55.543
200
150
100
50
0
PPM


7.724
7.709
7.700
7.687
7.548
7.543
7.523
7.518
7.407
7.396
7.376
7.368
7.358
7.343
7.321
7.314
7.260
6.924
6.421
6.083
6.02
1.06
1.14
1.02
1.00
1.65
F
O
O
NH2
10
8
6
4
2
PPM

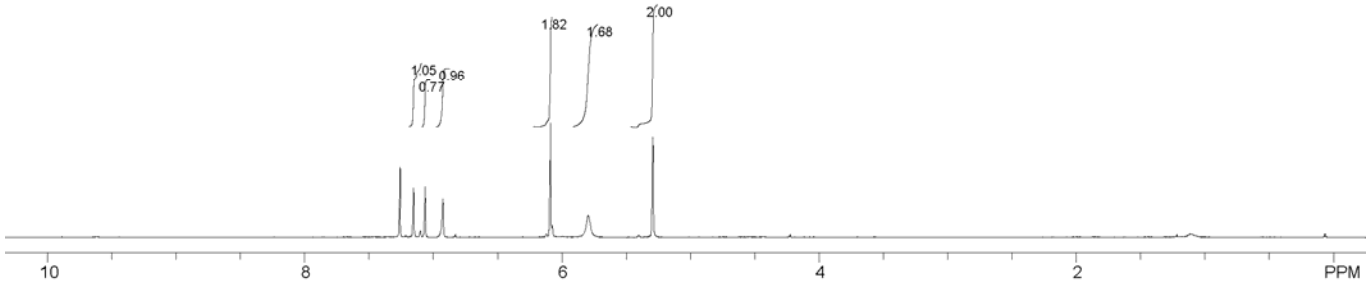
5j

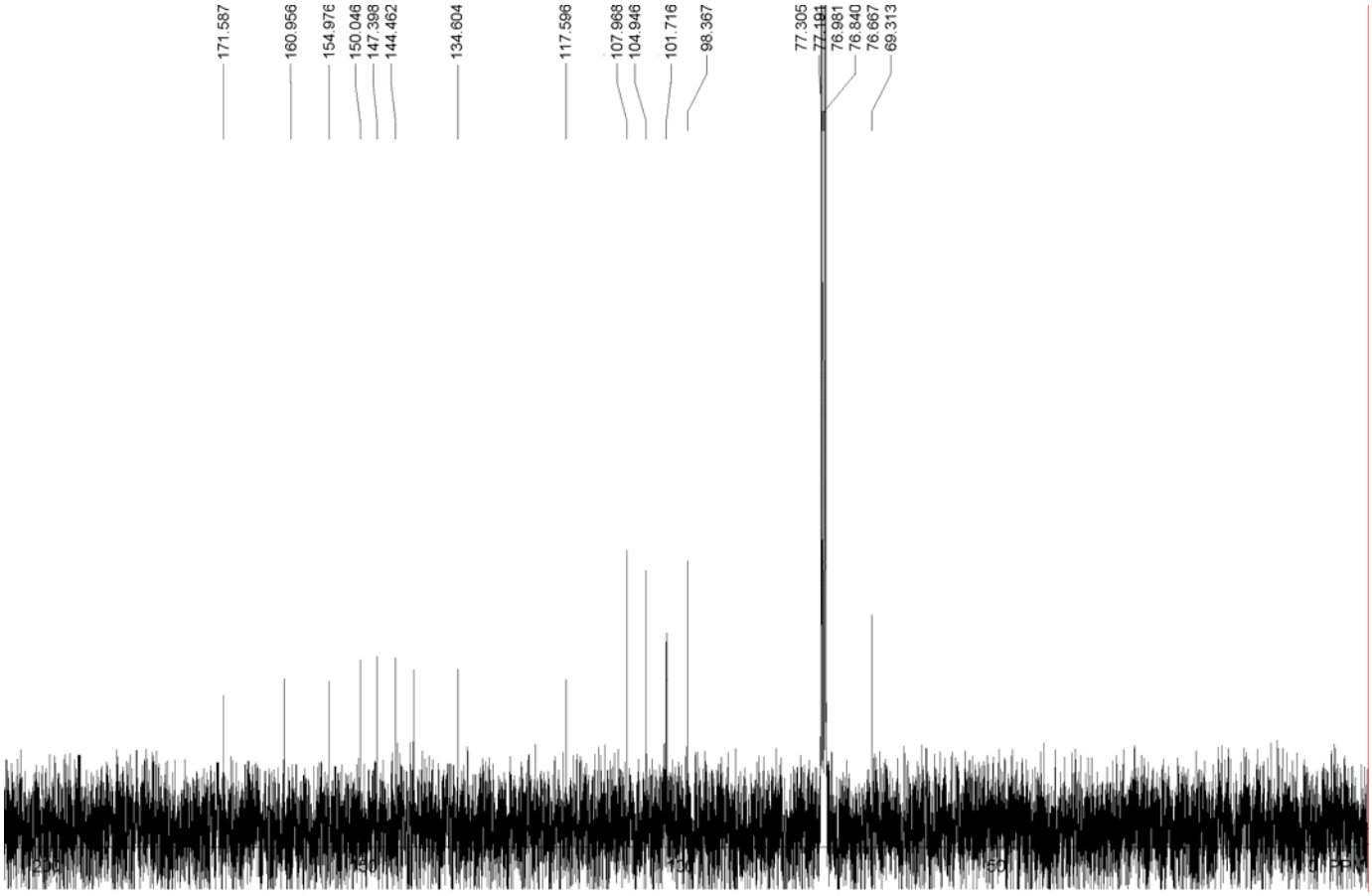

172.167
161.468
159.013
144.891
144.840
143.677
137.550
134.696
131.344
131.267
129.139
128.913
127.051
122.606
122.539
119.257
119.006
109.313
106.247
106.029
102.639
82.527
77.366
77.253
77.051
76.731
200
150
100
50
0
PPM


7.257
7.152
7.063
6.925
6.088
5.795
5.292

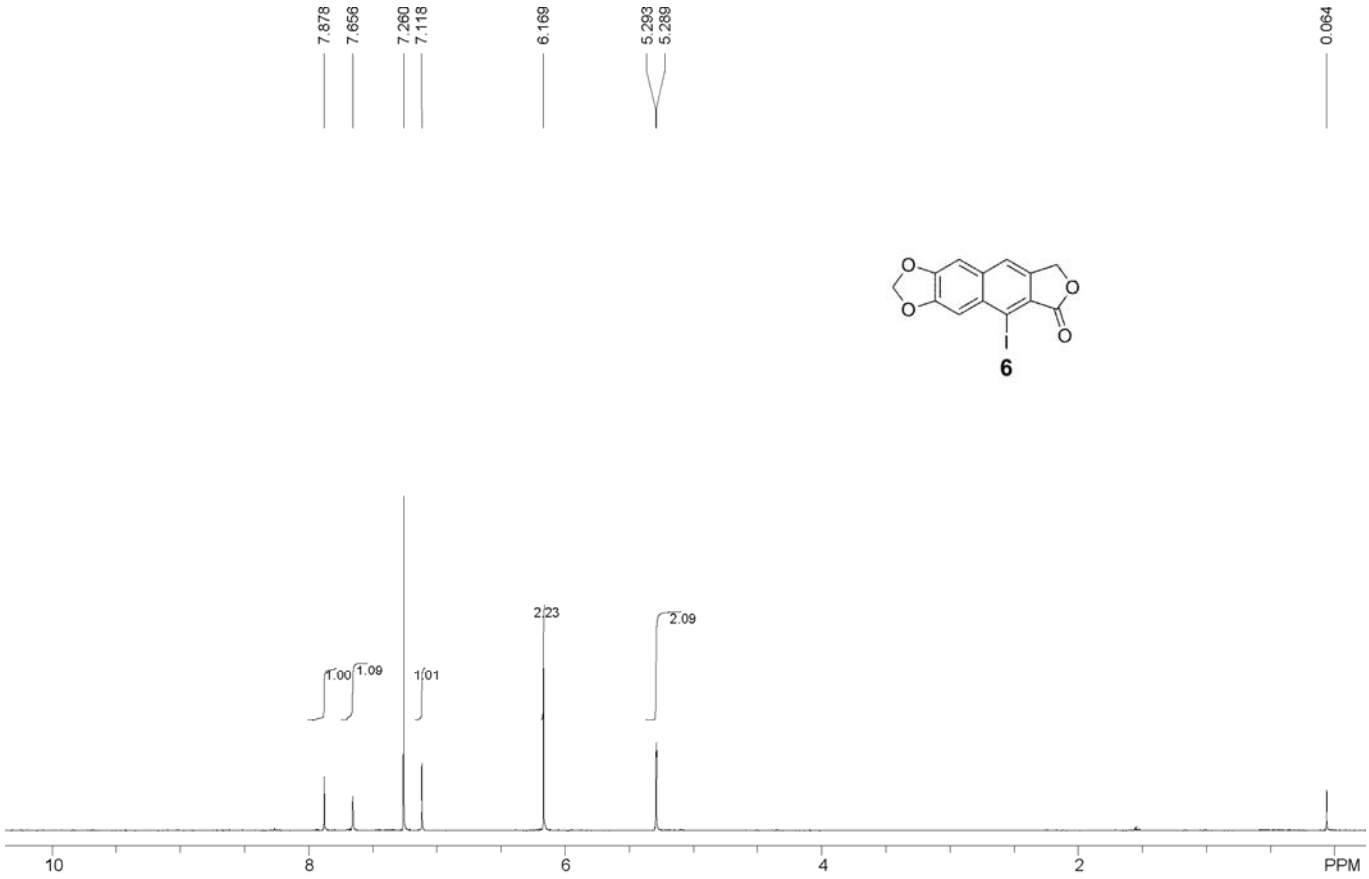

O
O
O
O
NH2

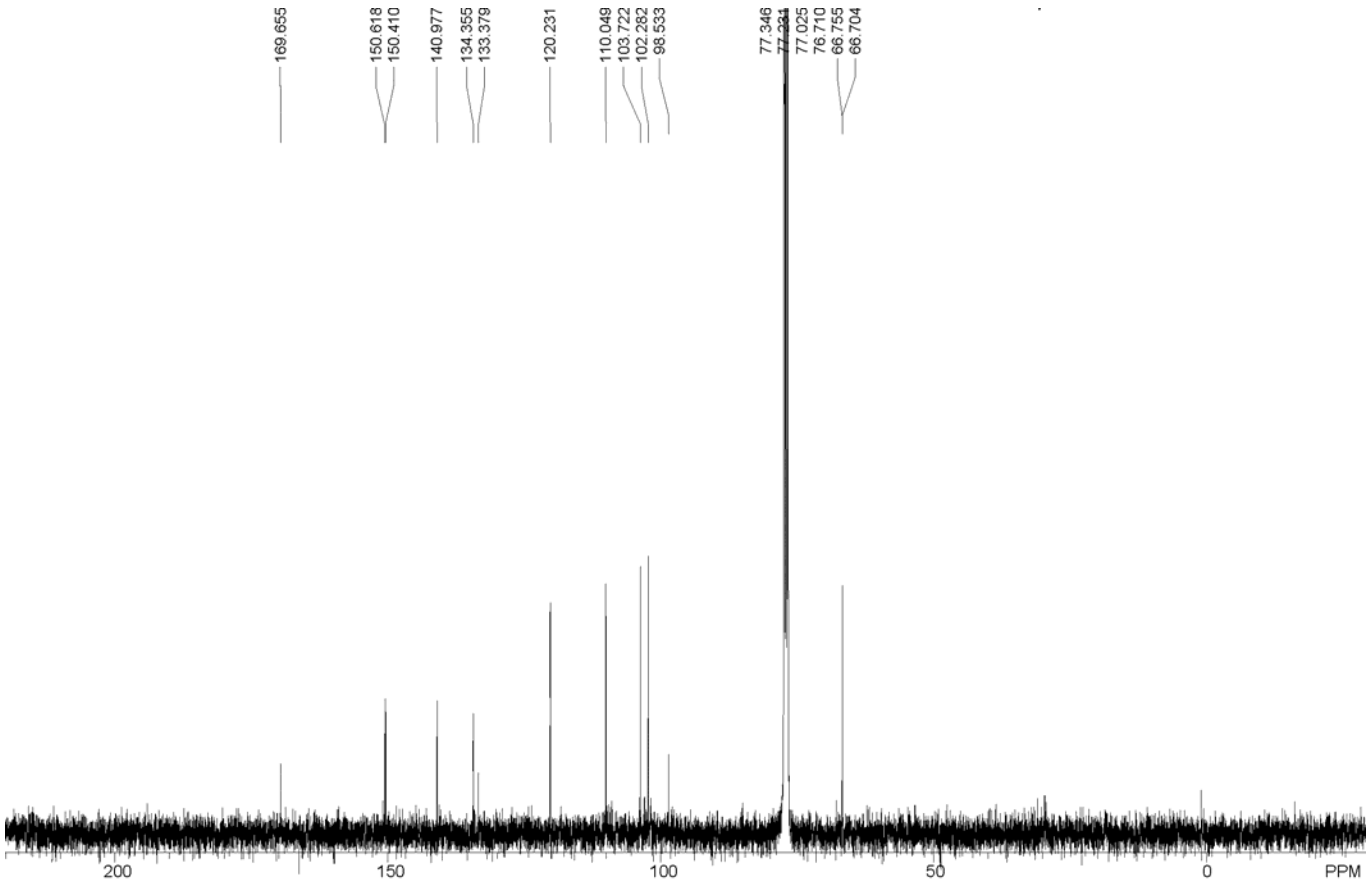
5k


1.82
1.68
2.00
1.05
0.77
0.96
10
8
6
4
2
PPM


171.587
160.956
154.976
150.046
147.398
144.462
134.604
117.596
107.968
104.946
101.716
98.367
77.305
76.981
76.840
76.667
69.313

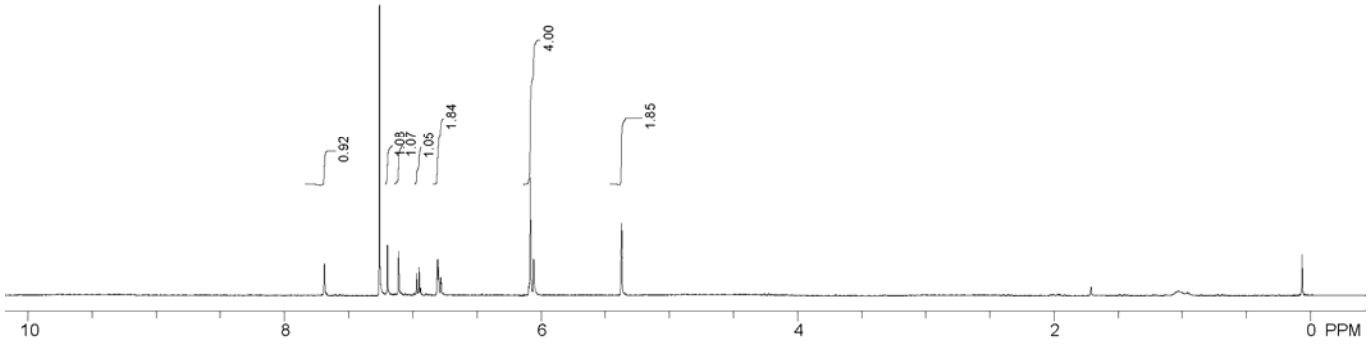
VII. Copies of ^{1}H and ^{13}C NMR spectra of 6

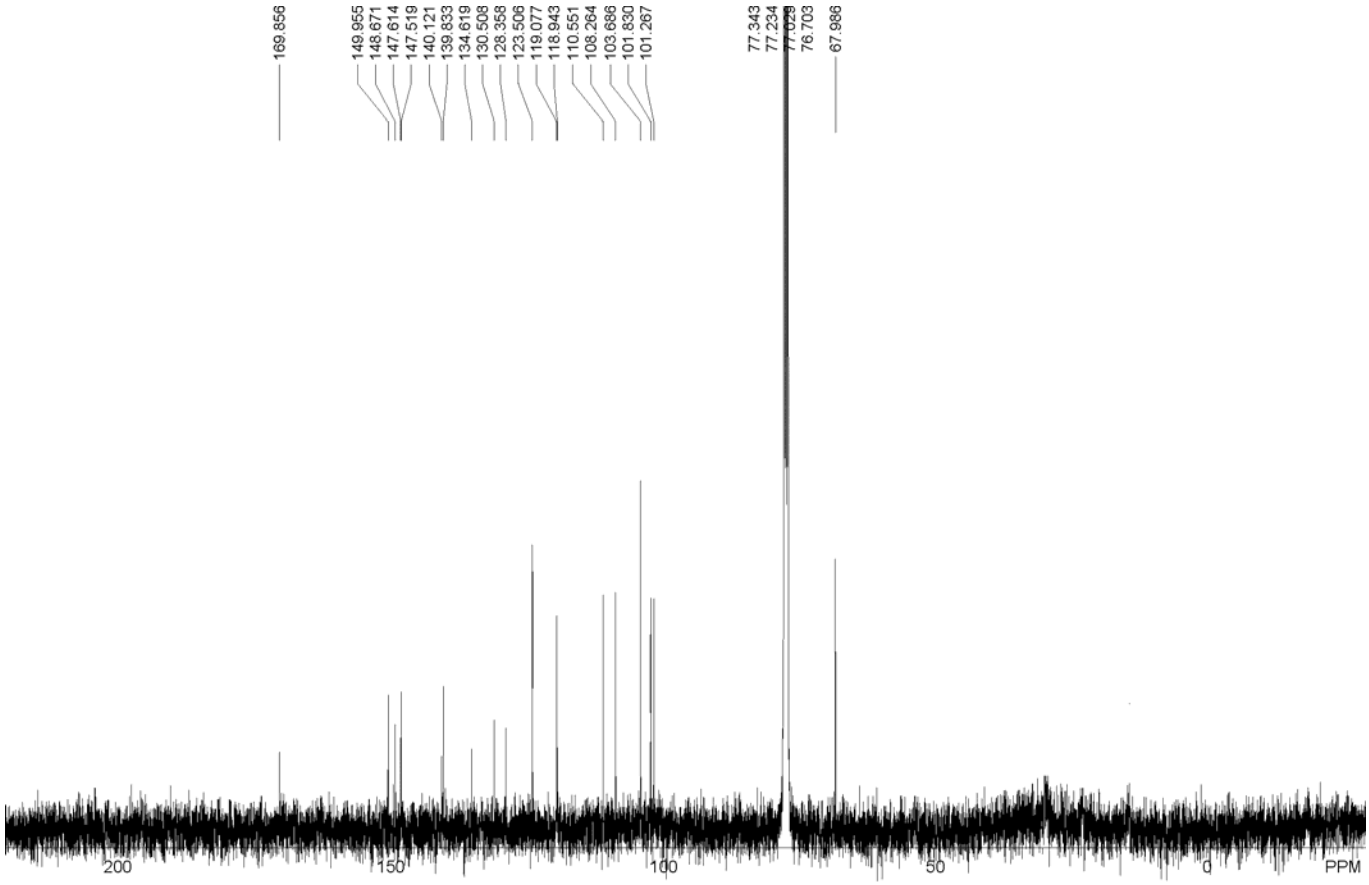




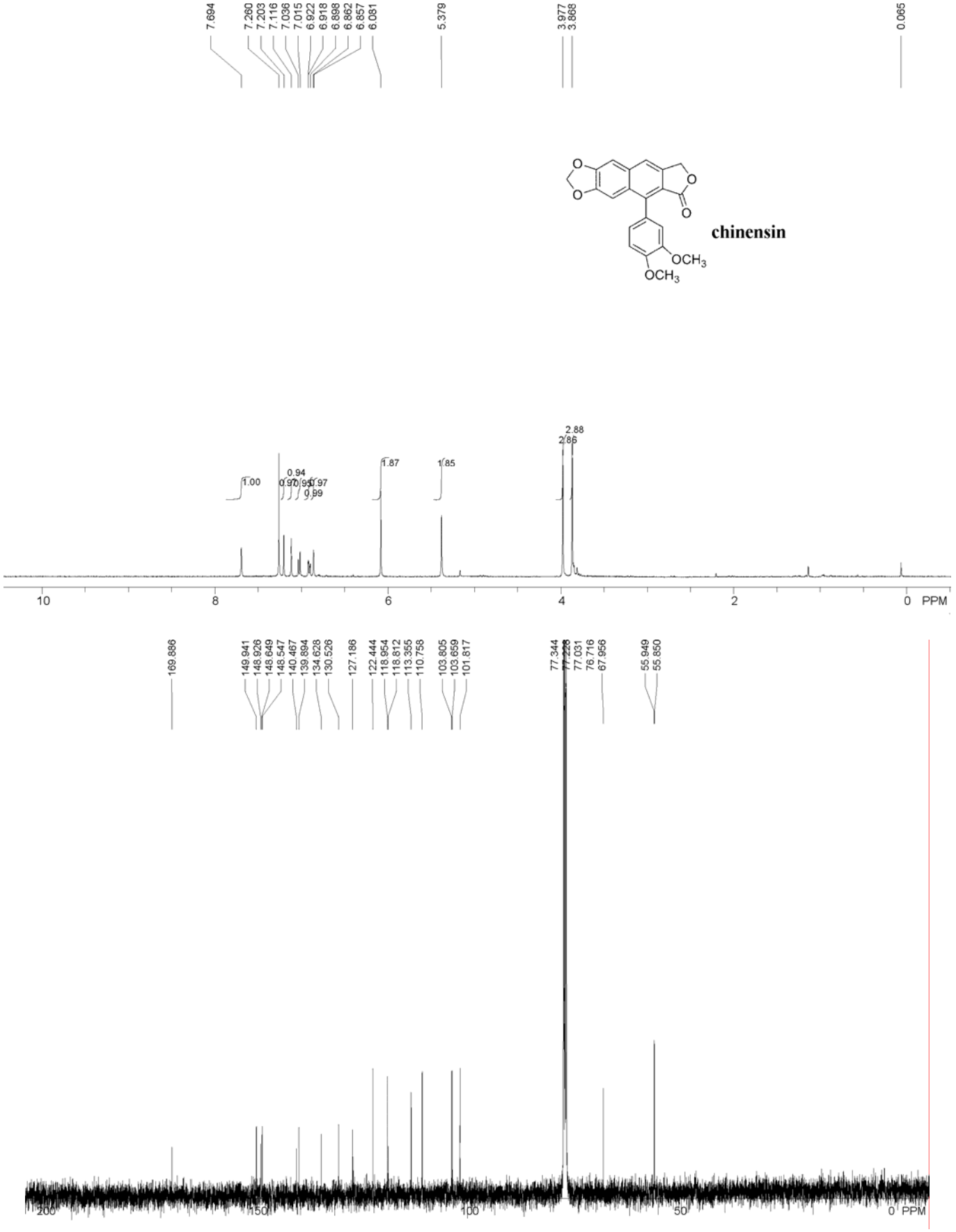
VIII. Copies of ^{1}H and ^{13}C NMR spectra of taiwanin C

taiwanin C





IX. Copies of ^{1}H and ^{13}C NMR spectra of chinensin



X. References

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