Chlorosulfonic acid coated on porous organic polymer as a bifunctional catalyst for one-pot three-component synthesis of 1,8-naphthyridines

Supporting Information

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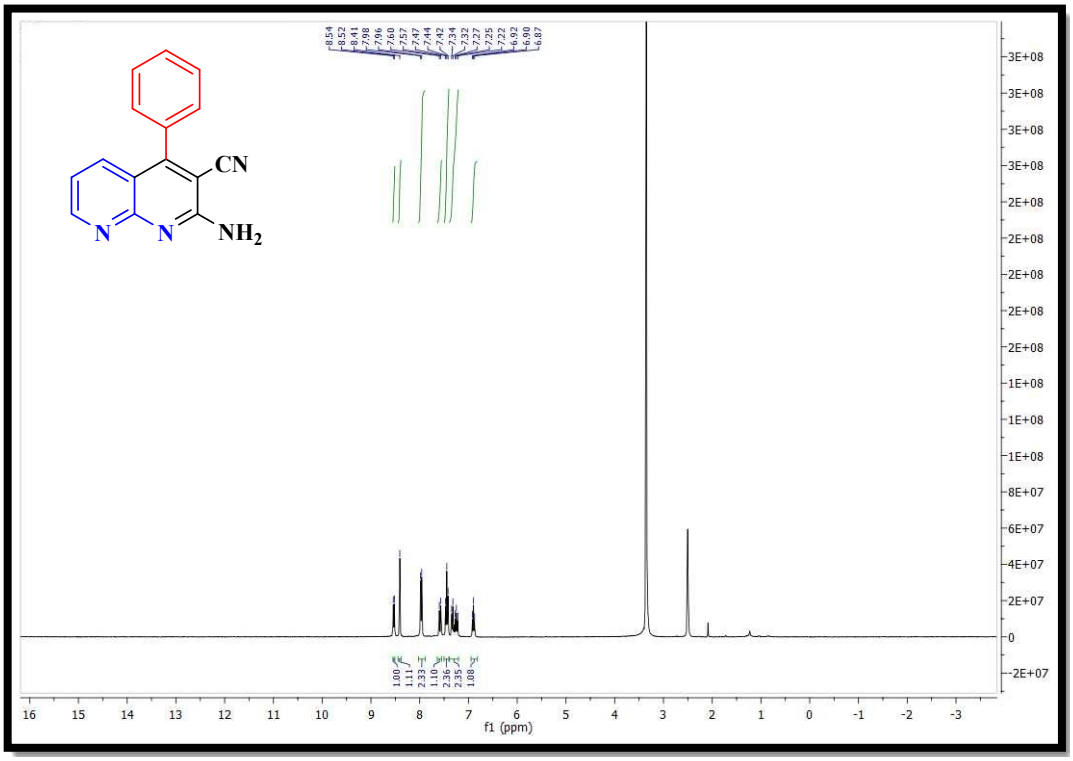
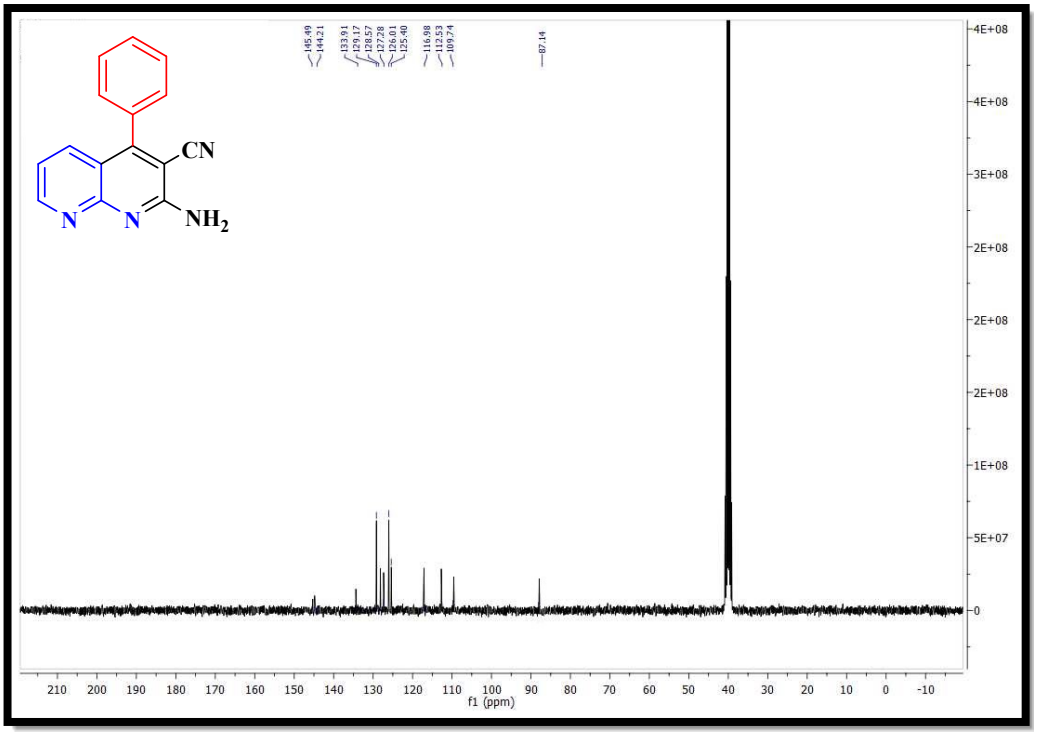
Spectral data for products.

2-Amino-4-phenyl-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.52 (d, J = 7.9 Hz, 1H), 8.35 (s, 1H), 8.10–7.88 (m, 3H), 7.65 (d, J = 9.1 Hz, 1H), 7.58 (dd, J = 8.5, 6.5 Hz, 2H), 7.38–7.32 (m, 1H), 7.15 (ddd, J = 9.1, 6.5, 2.5 Hz, 1H), 6.80 (d, J = 6.8, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 145.49, 144.21, 134.38, 133.91, 129.17, 128.16, 127.28, 126.01, 125.40, 116.98, 112.53, 109.74, 87.14.

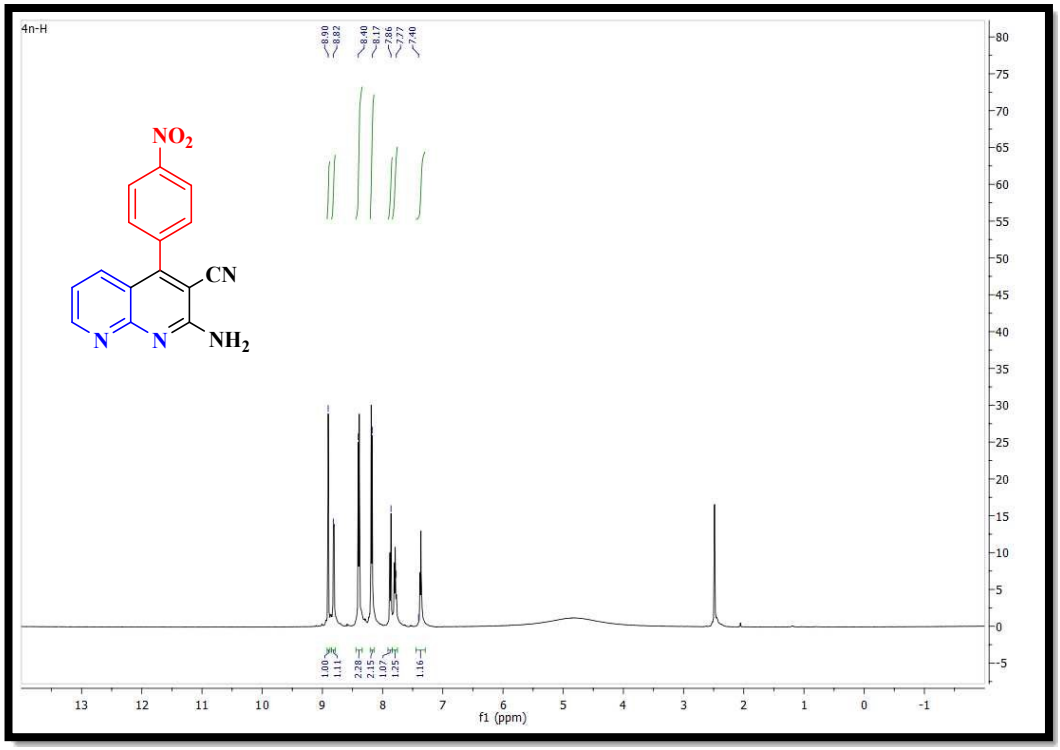




2-Amino-4-(4-nitrophenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 (s, 2H), 8.82 (d, J = 8.8 Hz, 2H), 8.51 (d, J = 8.6 Hz, 2H), 8.19 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.58, 156.60, 148.02, 142.43, 136.29, 135.40, 132.33, 128.70, 127.37, 124.77, 116.88, 114.15, 113.96, 112.94, 87.33.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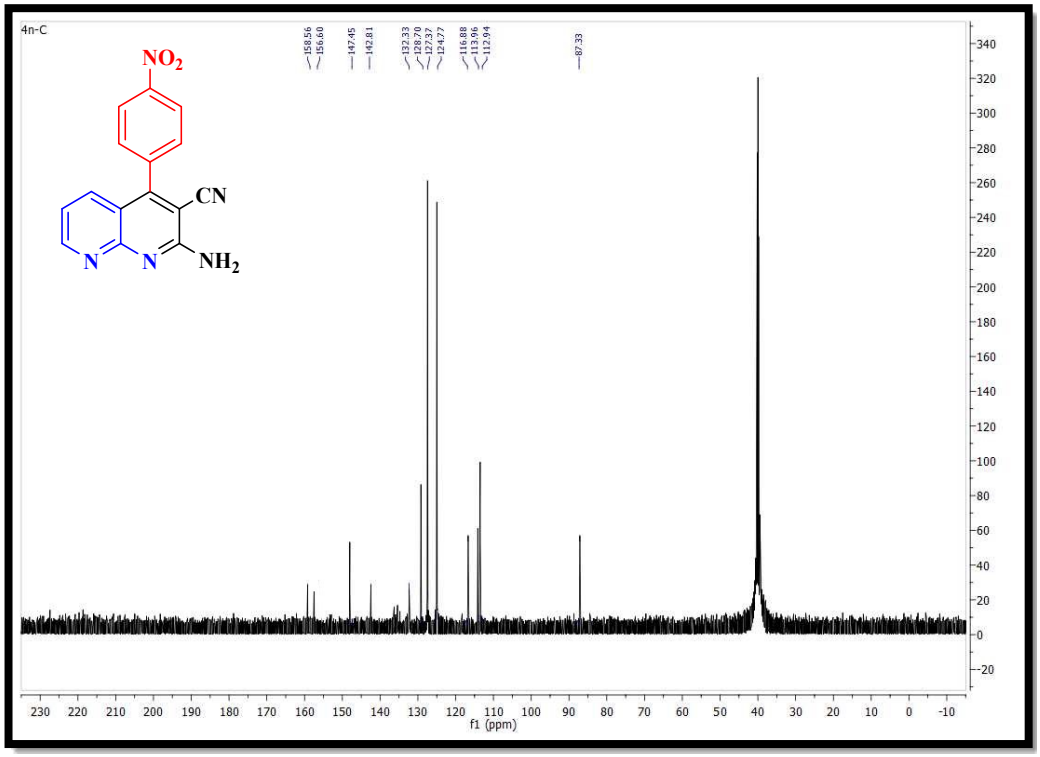
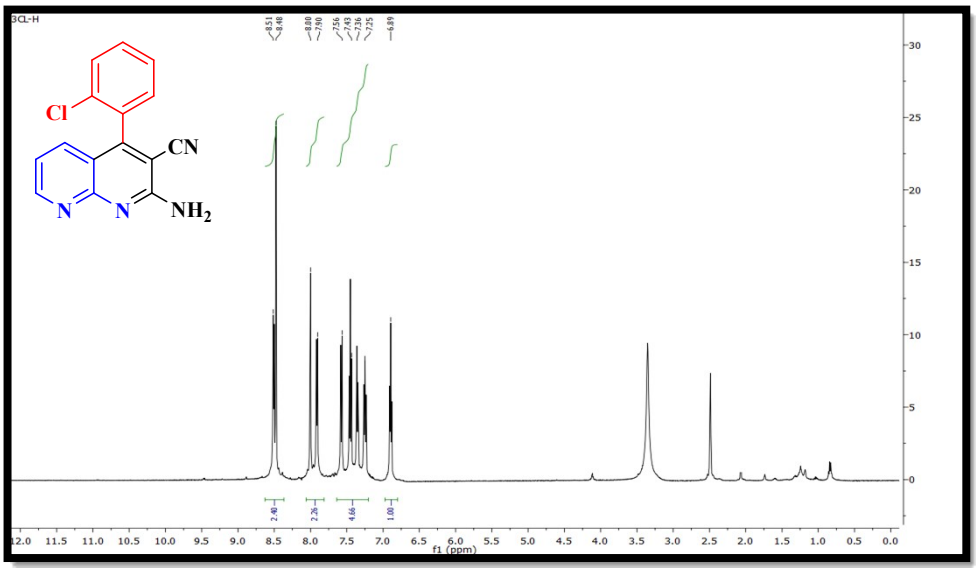
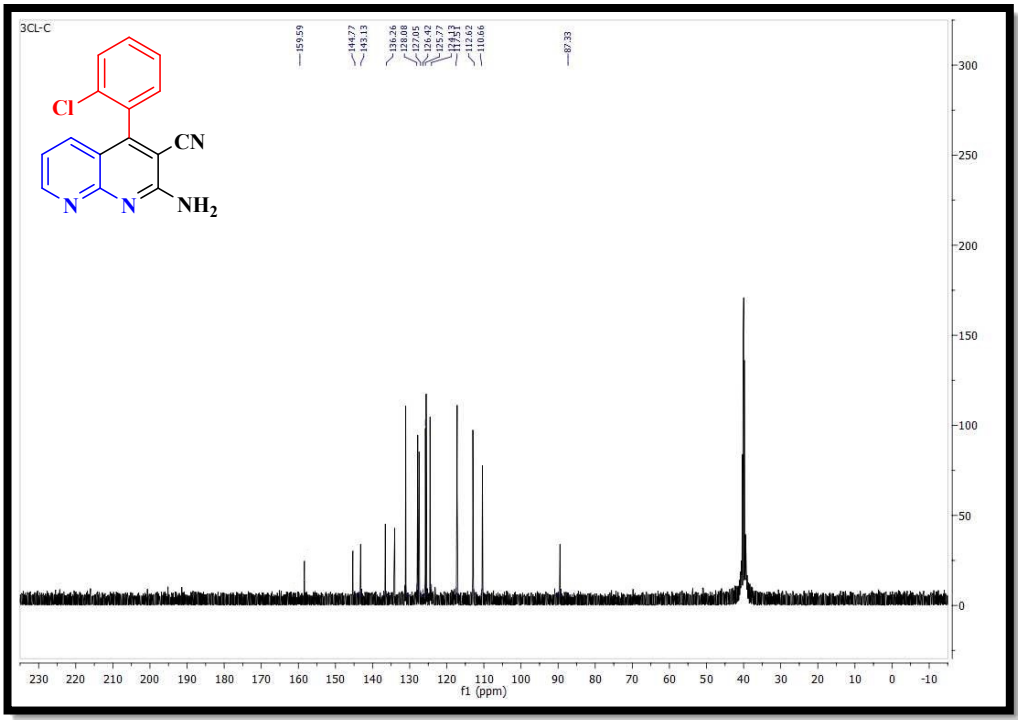
NH2
N
N
f1 (ppm)


4n-C
NO2
CN
NH2
N
N
f1 (ppm)

2-Amino-4-(2-chlorophenyl)-1,8-naphthyridine-3-carbonitrile

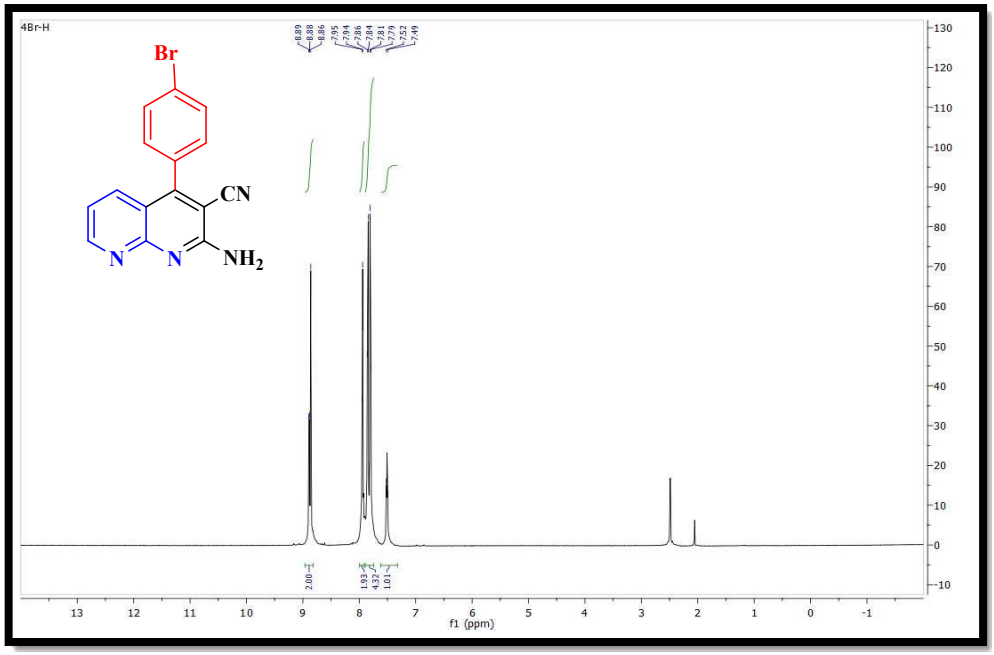
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (d, J = 7.7 Hz, 1H), 8.49 (s, 1H), 8.00 (t, J = 2.9 Hz, 1H), 7.95–7.89 (m, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.46 (t, J = 8.8 Hz, 1H), 7.36 (dd, J = 8.9, 2.5 Hz, 1H), 7.31–7.22 (m, 1H), 6.90 (t, J = 6.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.59, 144.77, 143.13, 136.26, 128.08, 127.05, 126.42, 125.77, 124.13, 117.51, 112.62, 110.66, 87.33.





2-Amino-4-(4-bromoophenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 (d, *J* = 7.8 Hz, 1H), 8.85 (s, 2H), 7.93 (d, *J* = 6.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 6.5, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.31, 154.63, 140.72, 134.89, 134.09, 133.93, 129.43, 128.46, 126.34, 124.18, 117.72, 112.69, 112.18, 109.99, 85.68.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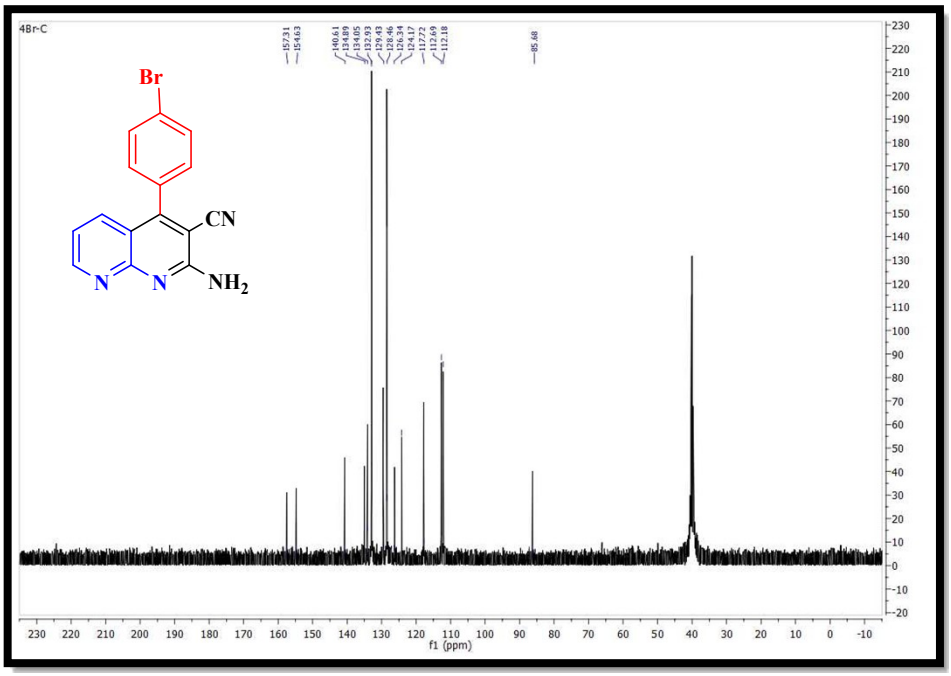
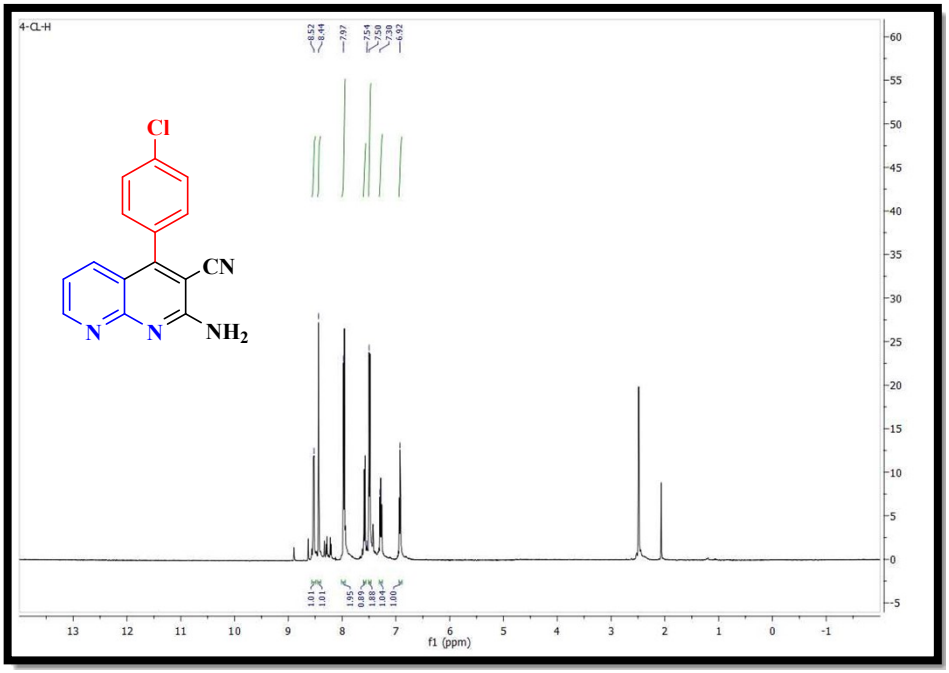
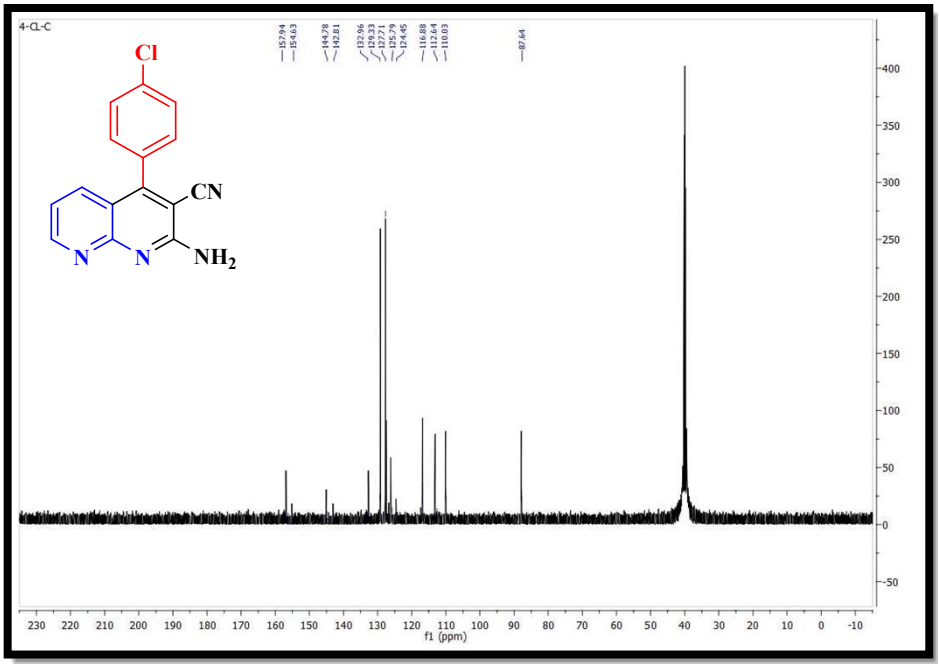
CN
N
N
NH2
f1 (ppm)


4Br-C
Br
CN
N
N
NH2
f1 (ppm)

2-Amino-4-(4-chlorophenyl)-1,8-naphthyridine-3-carbonitrile

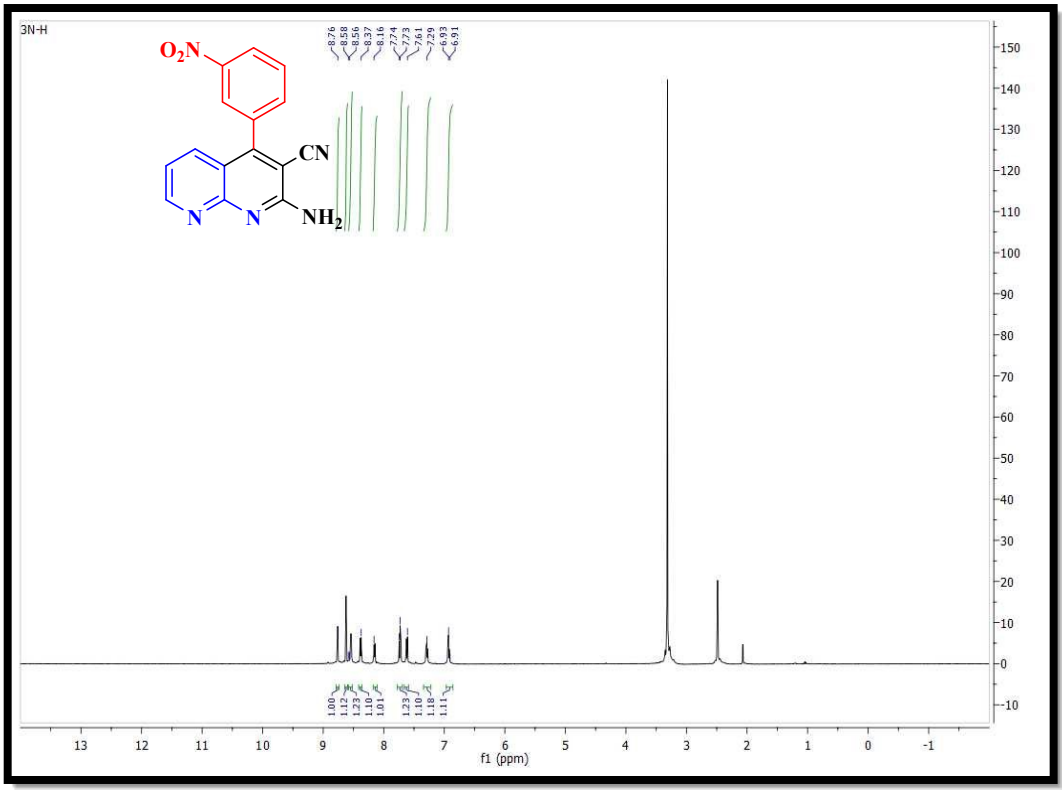
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (d, J = 6.8 Hz, 1H), 8.34 (s, 2H), 7.98 –7.95 (m, 1H), 7.64 (d, J = 9.3 Hz, 1H), 7.55–7.48 (m, 1H), 7.34-7.22 (m, 1H), 6.91 (t, J = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.94, 154.63, 144.78, 142.81, 132.96, 129.33, 127. 71, 125.79, 124.45, 116.88, 112.64, 110.03, 87.64.





2-Amino-4-(3-nitrophenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.79 – 8.74 (m, 1H), 8.62 (s, 1H), 8.56 (d, J = 6.8 Hz, 1H), 8.39 (d, J = 7.5 Hz, 1H), 8.15 (ddd, J = 8.5, 2.5, 1.5 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.65–7.59 (m, 1H), 7.30 (ddd, J = 9.2, 7.7, 2.5 Hz, 1H), 6.94 (d, J = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.26, 153.37, 148.85, 145.47, 142.43, 136.19, 132.64, 130.99, 127.05, 126.41, 122.78, 119.88, 117.50, 113.26, 110.99, 84.02.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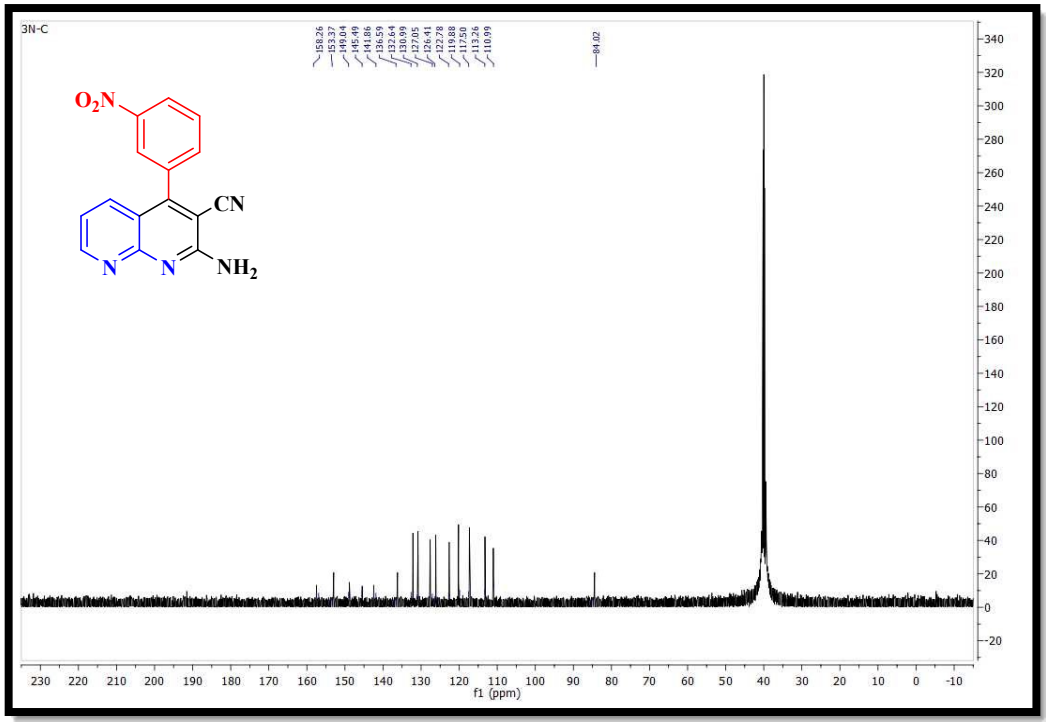
O_2N
CN
NH_2
N
N
f1 (ppm)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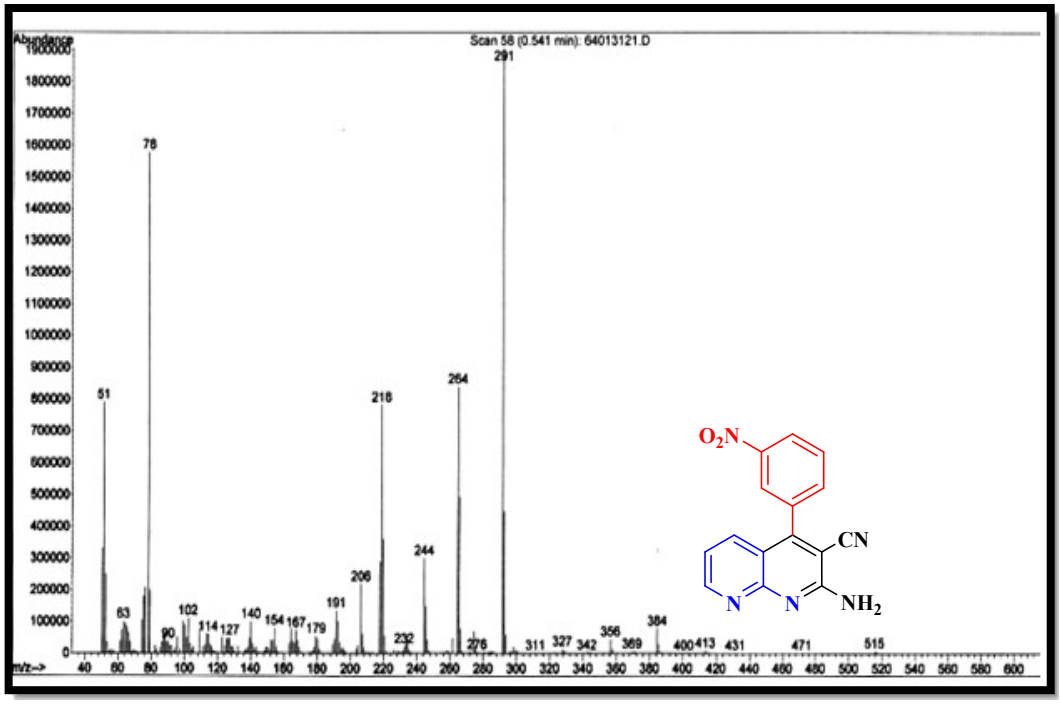
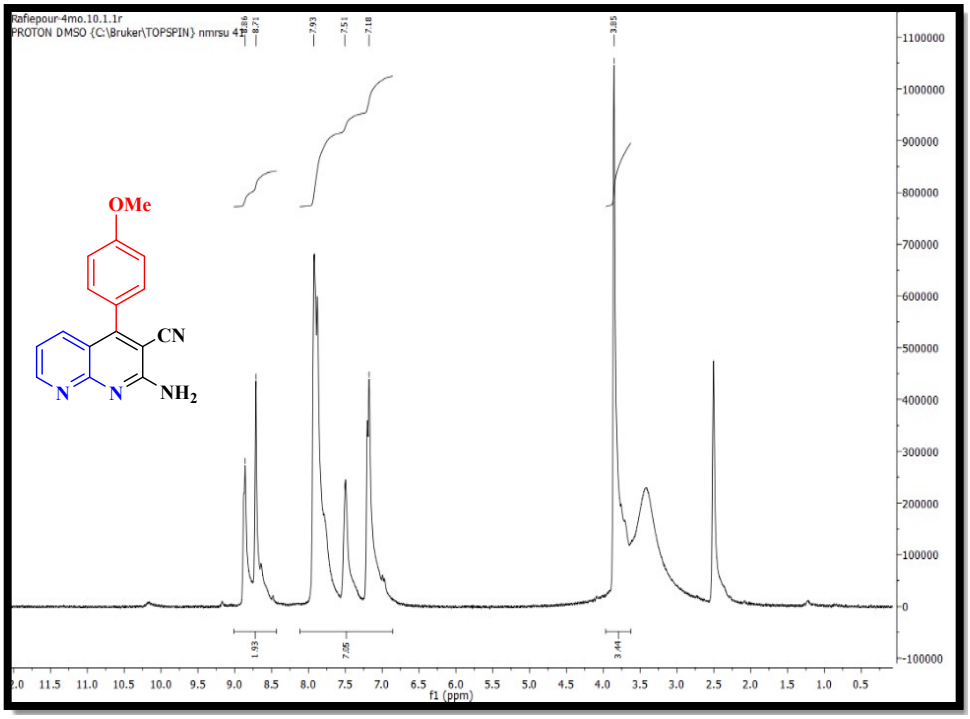
O_2N
CN
NH_2
N
N
f1 (ppm)



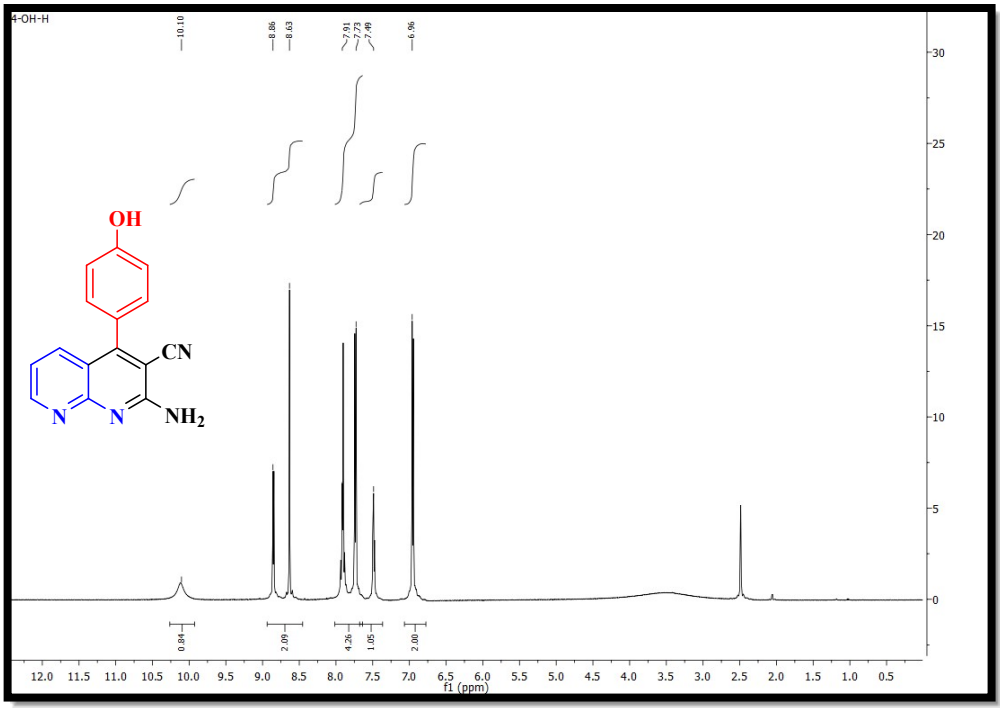
2-Amino-4-(4-methoxyphenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.78 (d, J = 7.7 Hz, 1H), 8.75 – 8.55 (m, 4H), 7.99–7.70 (m, 6H), 7.60 (d, J = 7.5, 4.6 Hz, 1H), 7.29 (d, J = 8.4 Hz, 3H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.32, 148.50, 138.20, 135.45, 128.37, 128.26, 120.30, 117.73, 115.16, 112.51, 110.95, 80.12, 56.98.



2-Amino-4-(4-hydroxyphenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.10 (s, 1H), 8.92 – 8.80 (m, 1H), 8.62 (s, 1H), 7.97–7.85 (t, 2H), 7.75–7.65 (m, 1H), 7.59 (d, J = 7.5, 2.5 Hz, 1H), 6.88 – 6.93 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.23, 139.90, 136.26, 133.28, 129.29, 128.70, 127.77, 117.73, 117.20, 111.99, 110.04, 86.39.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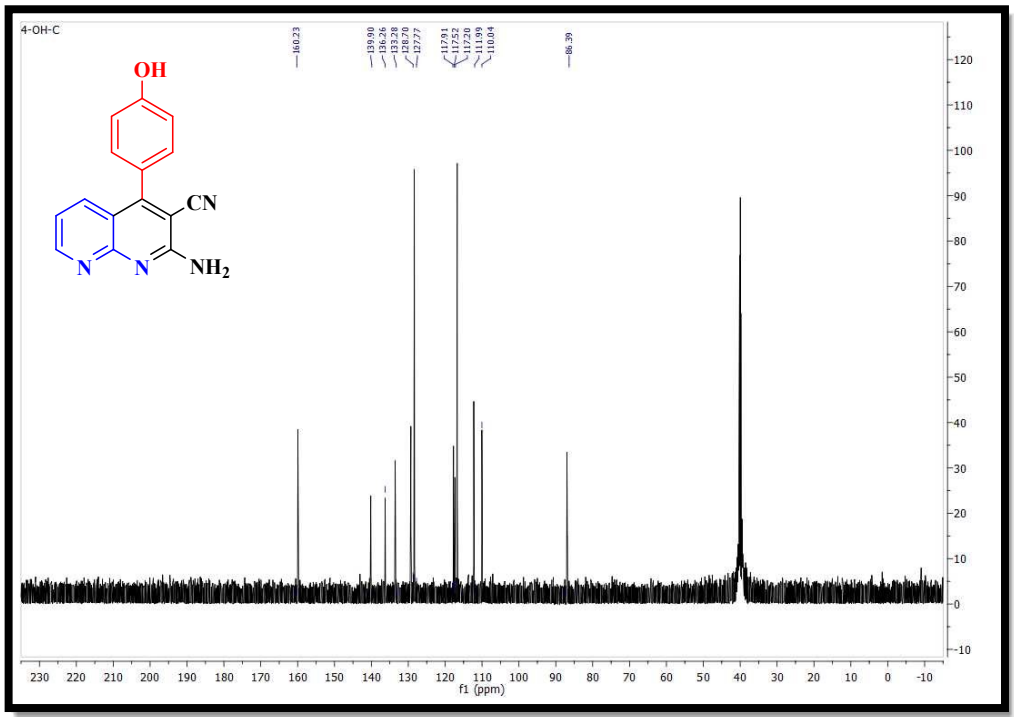
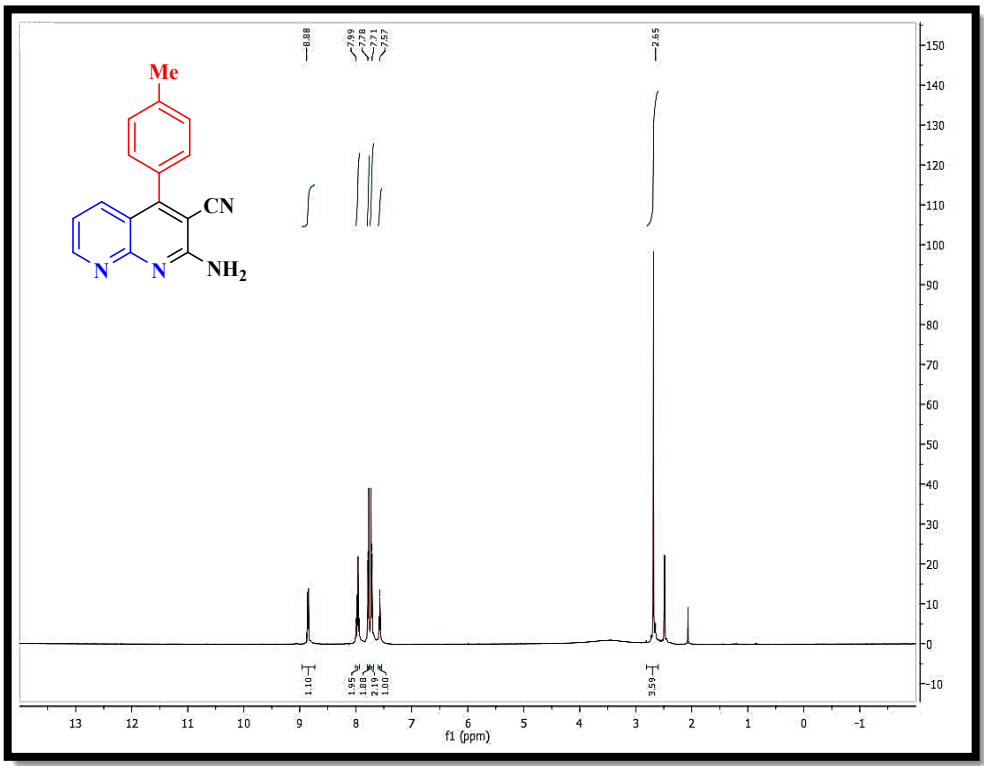
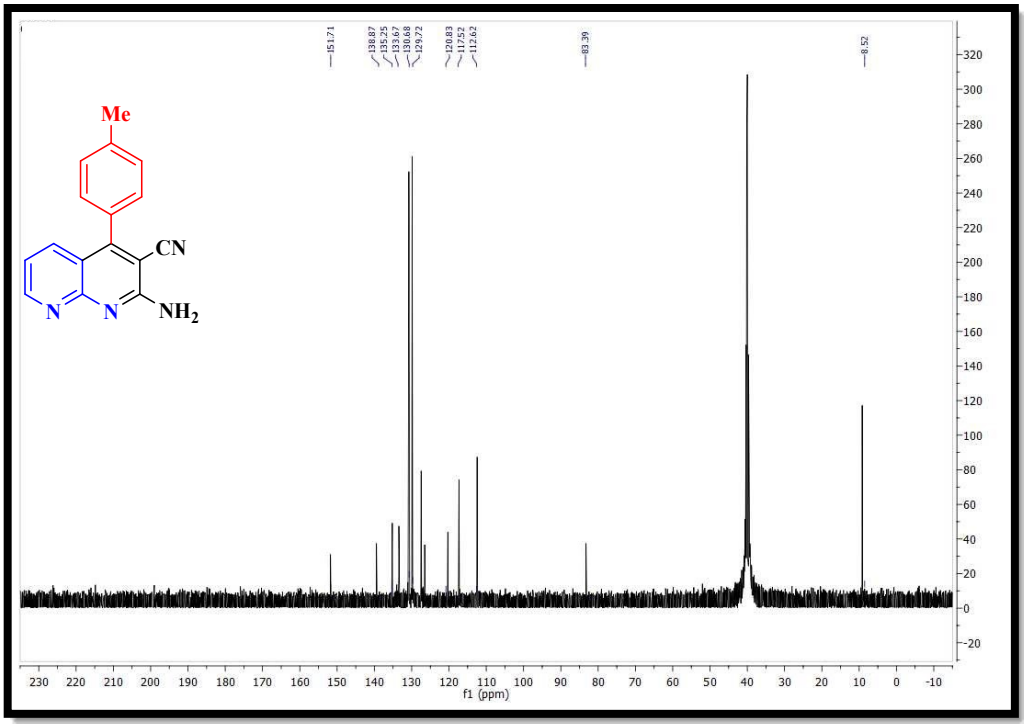
CN
N
N
NH2
f1 (ppm)


4-OH-C
OH
CN
N
N
NH2
f1 (ppm)

2-Amino-4-(*p*-tolyl)-1,8-naphthyridine-3-carbonitrile

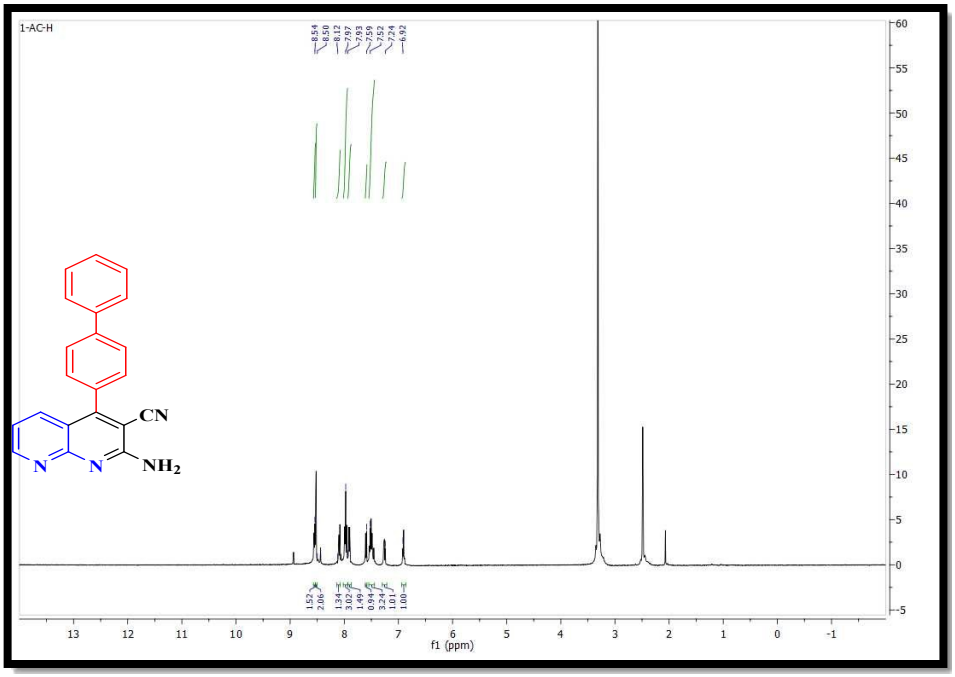
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 – 8.80 (m, 1H), 7.96 (ddd, J = 9.3, 6.8, 2.5 Hz, 2H), 7.77 (d, J = 9.5 Hz, 2H), 7.76 – 7.65 (m, 2H), 7.57 (dd, J = 6.5, 2.7 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.71, 139.45, 135.20, 133.42, 130.84, 130.85, 129.90, 127.45, 126.52, 120.30, 117.32, 112.46, 83.39, 9.19.





2-Amino-4-(biphenyl)-1,8-naphthyridine-3-carbonitrile

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.64 (d, *J* = 7.9 Hz, 1H), 8.50 (d, *J* = 4.9 Hz, 2H), 8.12 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.97 (t, *J* = 9.2 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 9.3 Hz, 1H), 7.51 (t, *J* = 15.0, 7.3, 3.9 Hz, 3H), 7.24 (t, *J* = 6.9 Hz, 1H), 6.80 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.31, 154.61, 147.45, 133.67, 132.64, 131.71, 128.39, 126.42, 125.39, 124.45, 117.19, 116.89, 112.95, 110.34, 80.48.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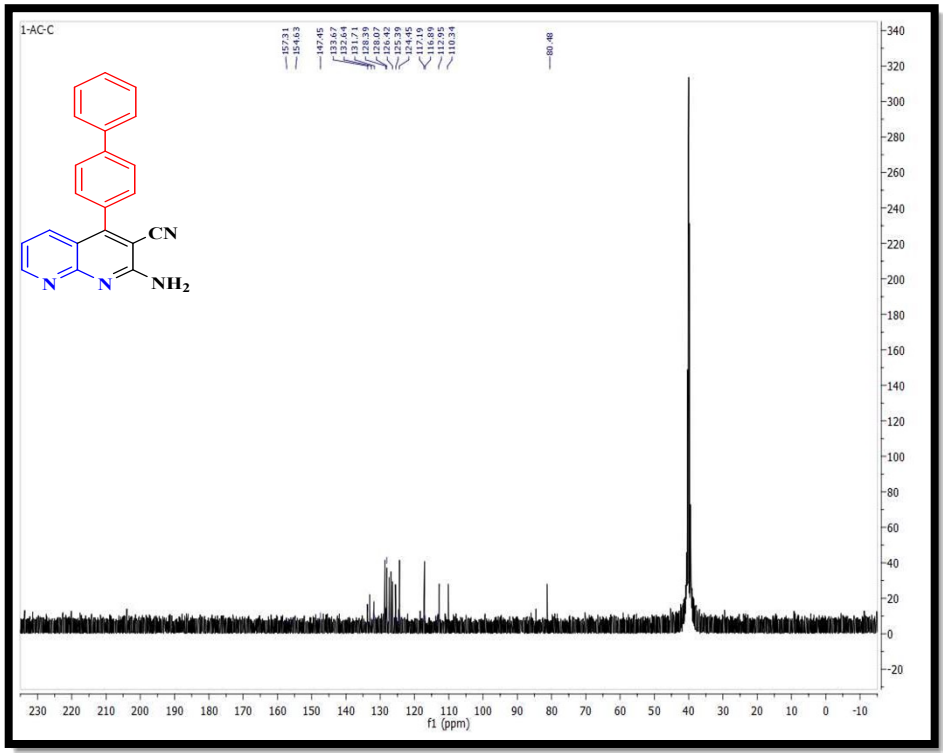
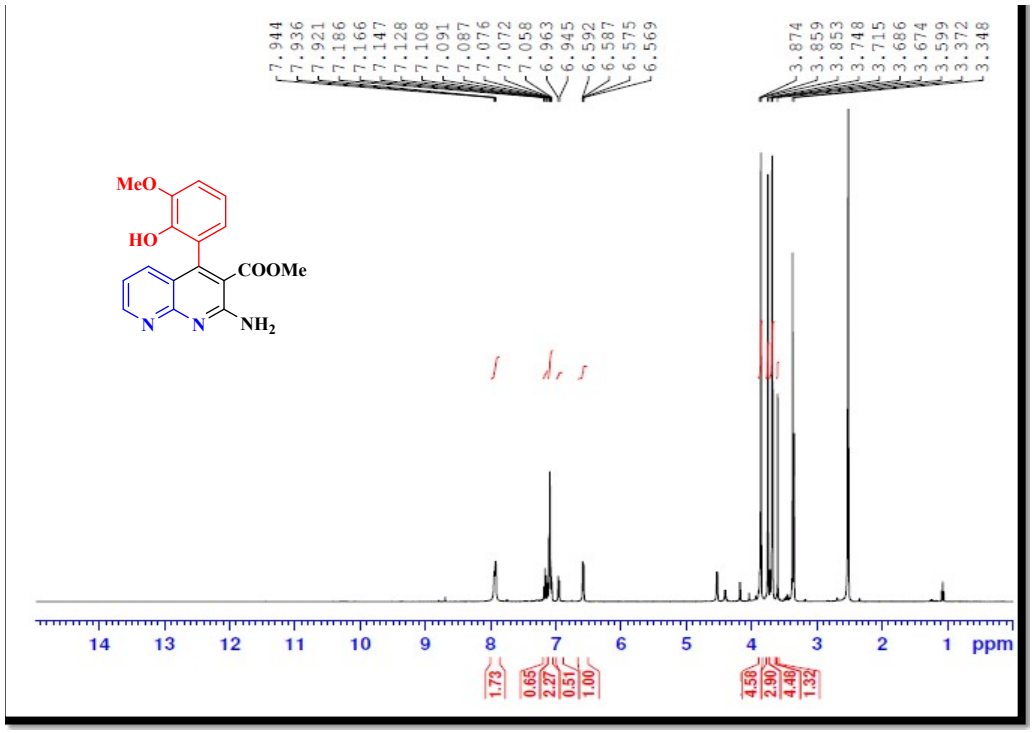
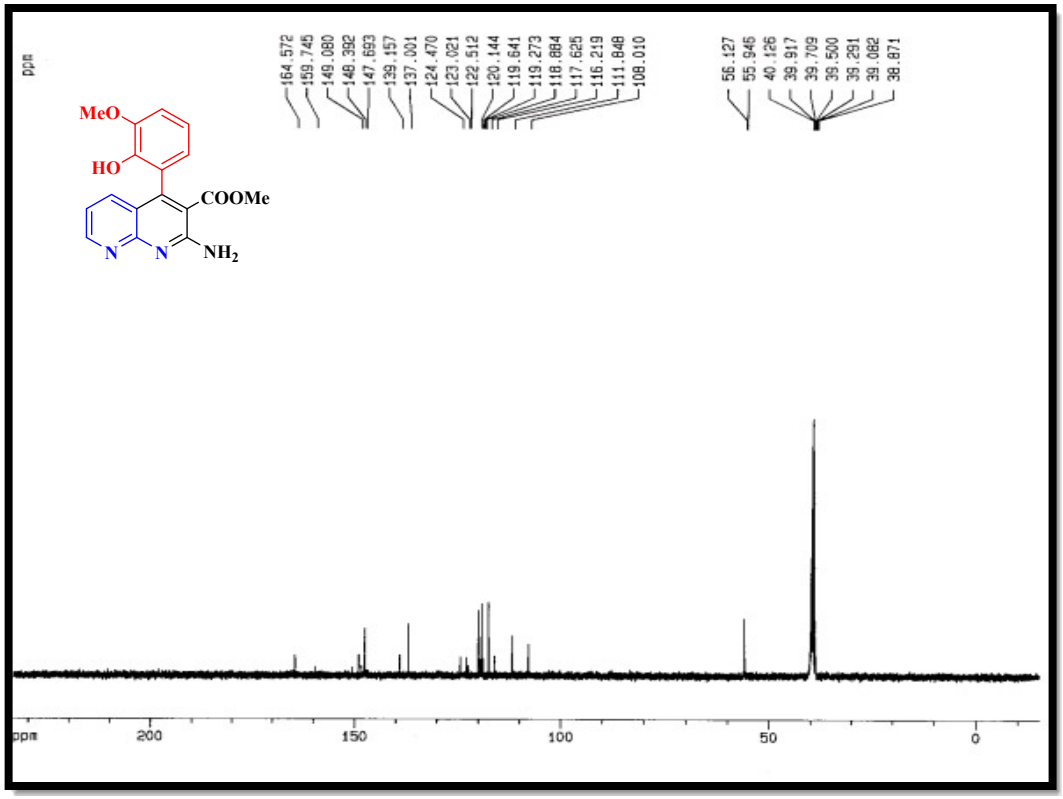
NH2
f1 (ppm)

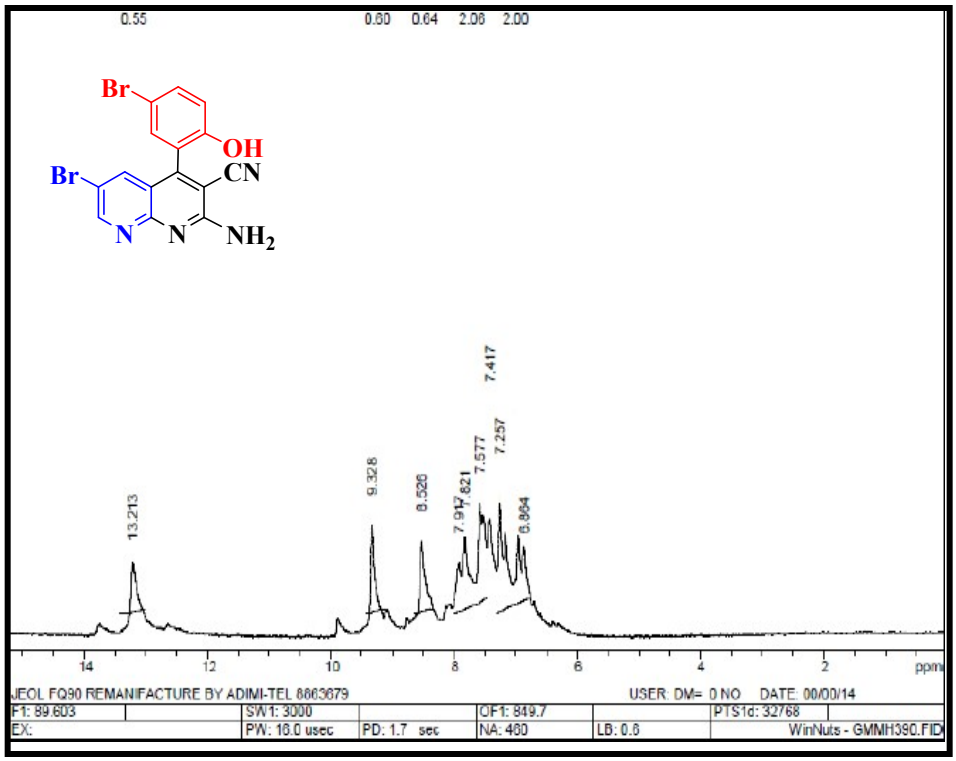

1-AC-C
CN
NH2
f1 (ppm)

2-Amino-4-(2-hydroxy-3-methoxyphenyl)-1,8-naphthyridine-3-carboxylate: ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.34 (s, 1H, OH), 3.67 (s, 3H, OCH_3), 3.71 (s, 2H, NH_2), 3.85 (s, 3H, OCH_3), 6.56-6.59 (t, *J* = 4.8 Hz, 1H, ArH), 6.94-6.96 (d, *J* = 7.2 Hz, 1H, ArH), 7.05-7.18 (m, 3H, ArH), 7.92-7.94 (t, *J* = 3.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.9, 56.1, 108.0, 111.8, 116.2, 117.6, 119.2, 120.1, 122.5, 123.0, 124.4, 137.0, 139.1, 147.6, 148.3, 149.0, 159.7, 164.5.





2-Amino-6-bromo-4-(5-bromo-2-hydroxyphenyl)-1,8-naphthyridine-3-carbonitrile: ^{1}H NMR (90 MHz, $CDCl_3$): δ 6.86-7.49 (m, 5H, ArH, NH_2), 8.52 (s, 1H, ArH), 9.32 (s, 1H, ArH), 13.21 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_c: 109.7, 118.3, 119.2, 120.8, 134.4, 135.6, 140.0, 149.1, 154.7, 159.8, 162.8.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2.00
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OH
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Br
N
N
NH2
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7.821
7.577
7.417
7.257
6.864
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12
10
8
6
4
2
ppm
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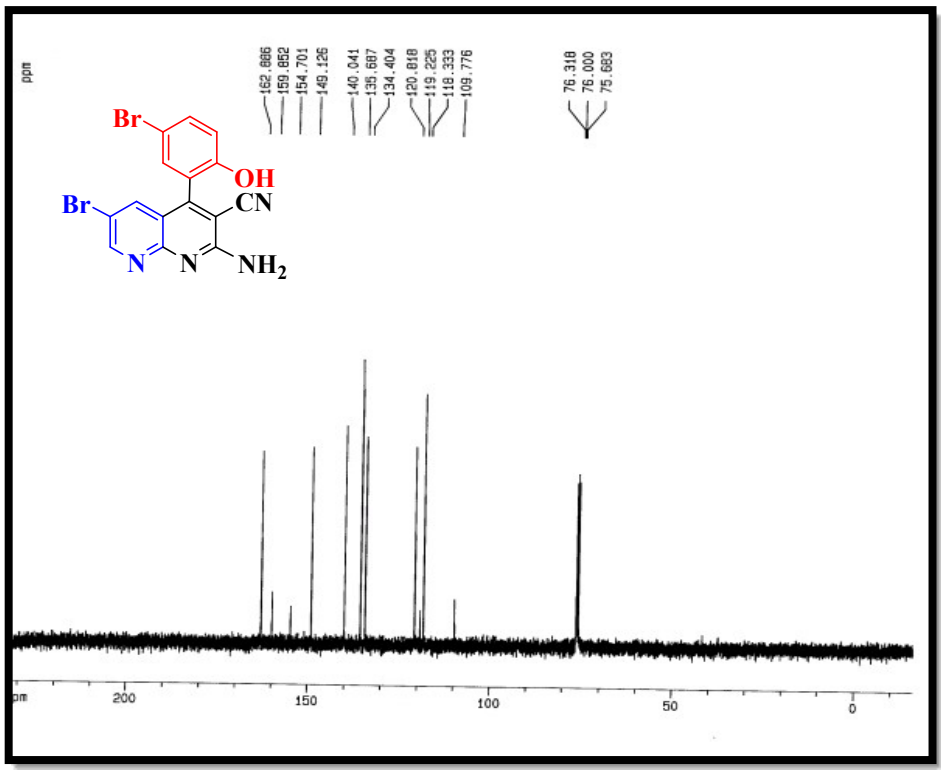
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119.225
118.333
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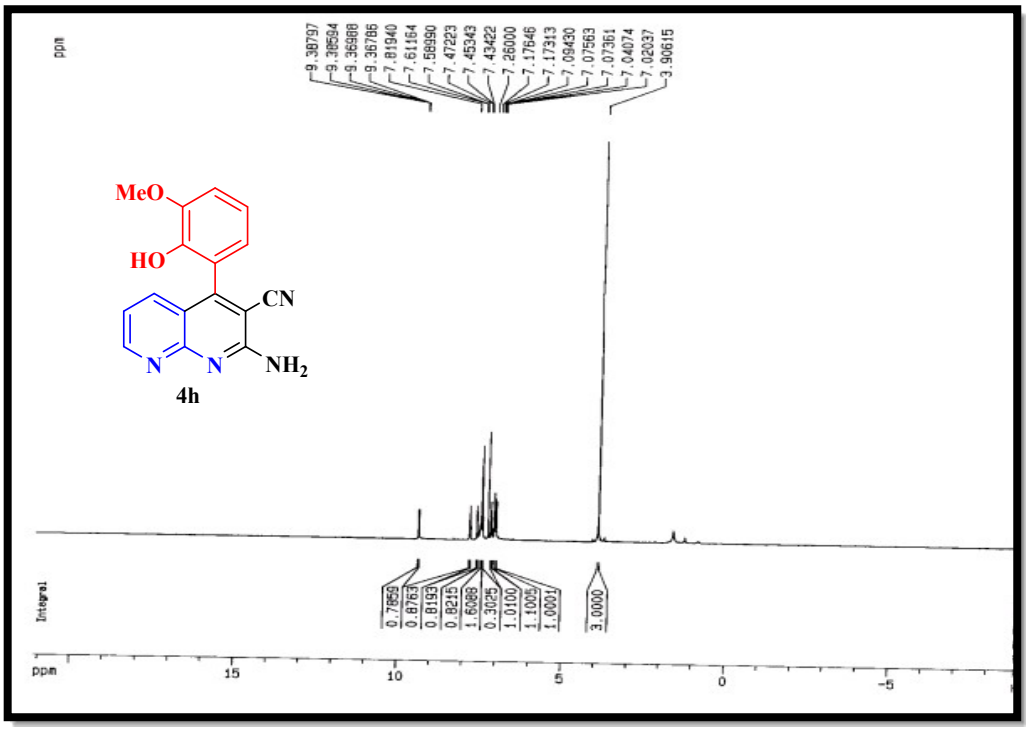
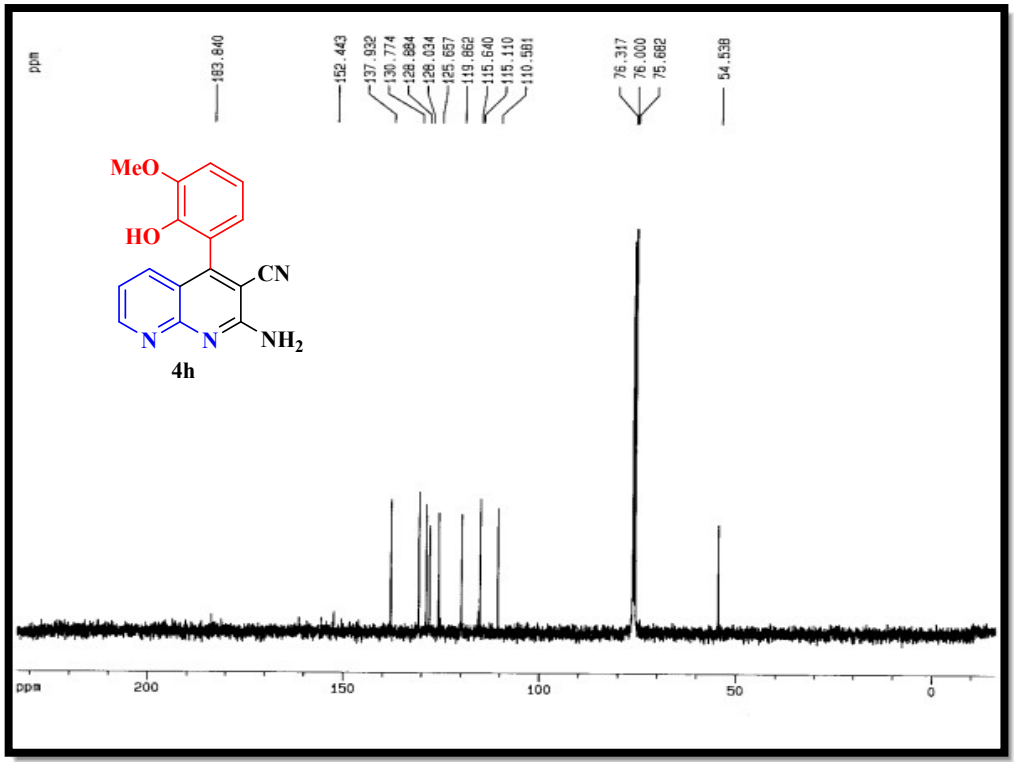
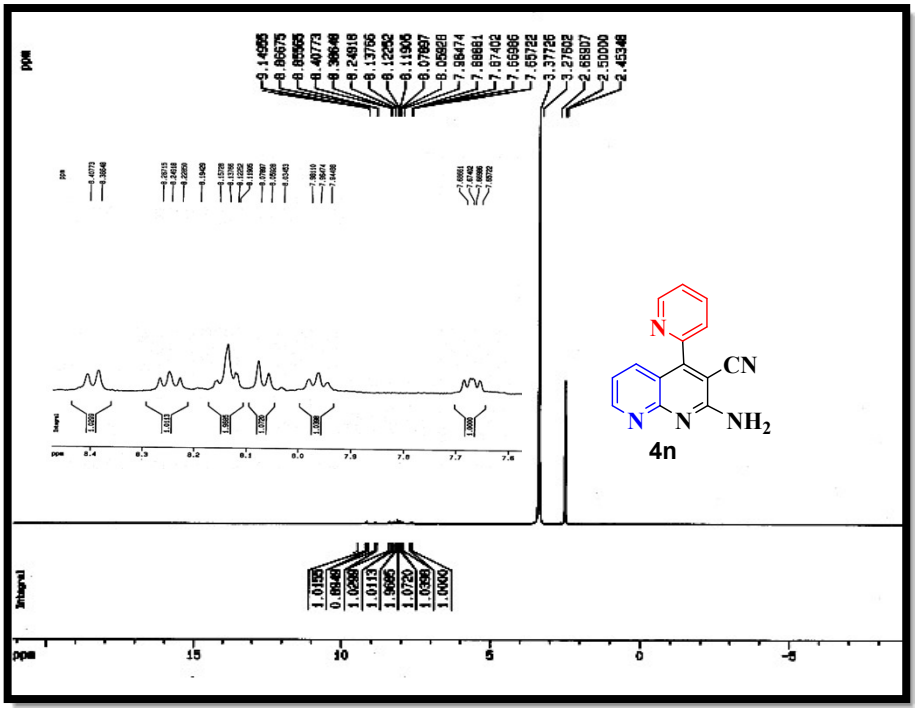
76.318
76.000
75.683
Br
OH
CN
Br
N
N
NH2
200
150
100
50
0

2-Amino-4-(2-hydroxy-3-methoxyphenyl)-1,8-naphthyridine-3-carbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H, OCH_3), 7.02-7.04 (d, *J* = 8.0 Hz, 1H, ArH), 7.05-7.09 (t, *J* = 6.8 Hz, 1H, ArH), 7.15-7.19 (t, *J* = 5.6 Hz, 1H, ArH), 7.45-7.47 (d, *J* = 7.6 Hz, 1H, ArH), 7.50 (br, 2H, NH_2), 7.58-7.61 (d, *J* = 8.8 Hz, 1H, ArH), 7.81-7.82 (t, *J* = 4.0 Hz, 1H, ArH), 9.37 (d, *J* = 7.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.5, 110.5, 115.1, 115.6, 119.8, 125.6, 128.0, 128.8, 130.7, 137.9, 150.4, 152.4, 159.1, 161.2, 183.8.





2-Amino-4-(pyridin-2-yl)-1,8-naphthyridine-3-carbonitrile:^{1}H NMR (400 MHz, DMSO-d_6): δ 7.65-7.68 (t, *J* = 6.8 Hz, 1H, ArH), 7.94-7.98 (t, 1H, *J* = 6.8 Hz, ArH), 8.03-8.07 (d, *J* = 10.0 Hz, 1H, ArH), 8.11-8.12 (d, 2H, NH_2), 8.38-8.40 (d, *J* = 8.4 Hz, 1H, ArH), 8.85-8.86 (d, *J* = 4.4 Hz, 1H, ArH), 9.14-9.16 (d, *J* = 7.2 Hz, 1H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 108.0, 110.9, 113.3, 117.2, 118.4, 122.8, 124.4, 128.5, 129.7, 130.0, 137.3, 138.4, 142.7, 150.4, 152.8, 157.5.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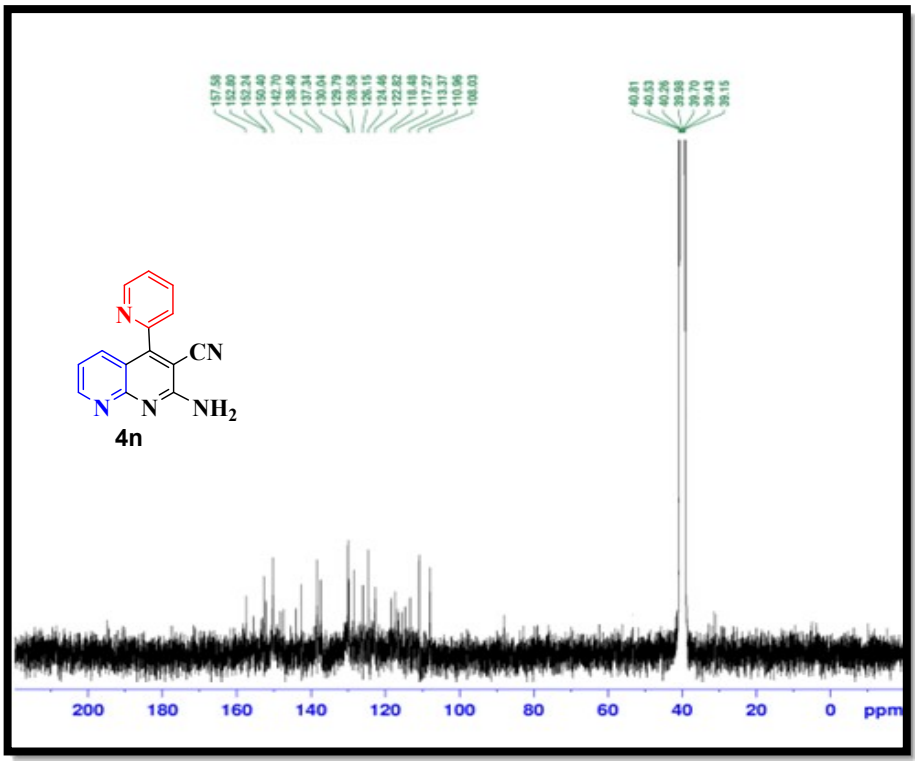
NH2
4n


CN
NH2
4n
200
180
160
140
120
100
80
60
40
20
0
ppm