Per-6-amino-β-cyclodextrin as an efficient supramolecular ligand and host for Cu(I)-catalyzed *N*-arylation of imidazole with aryl bromides

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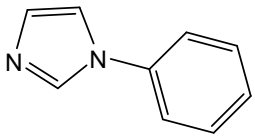
General informations: All NMR spectra were recorded on Advance Digital (400 MHz and 300 MHz for ^{1}H NMR, 100 MHz and 75 MHz for ^{13}C NMR) spectrometers. Chemical shifts are expressed in δ units relative to TMS signal as an internal reference in $CDCl_3$. Gas Chromatographic analysis was performed using 30 meter capillary column equipped with FID detector and high purity nitrogen as carrier gas. GC-MS analysis was performed using 30 meter capillary column and high purity helium as carrier gas.

Materials: Per-6-amino-β-cyclodextrin is synthesized and purified according to the procedure described in literature.[S1] The product is dried for 24 h in dryer under vacuum over phosphorous pentoxide at 60 ^{o}C and then is stored in the phosphorus pentoxide vacuum desicator. Imidazole, pyrrole, 2-methylimidazole, indole and all aryl bromides are purchased and used without further purification.

NMR and GC-MS data for products



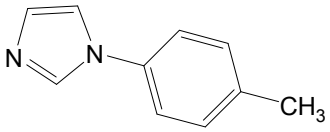
4a

1-Phenyl-1H-imidazole (4a) :

^{1}H NMR (300 MHz): 7.87(s, 1H), 7.51-7.46 (m, 2H), 7.40 -7.34 (m, 3H), 7.29 (bs, 1H), 7.21 (bs, 1H)

^{13}C NMR (75 MHz):137.1, 135.5, 130.1, 129.7, 127.4, 121.3, 118.2

GC-MS: *m/z* 144.0 (M^+)



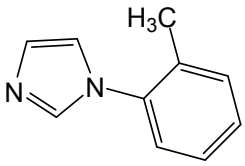
4b

1-*p*-Tolyl-1H-imidazole (4b):

^{1}H NMR (300 MHz): 7.81 (s, 1H), 7.27-7.18 (m, 6H), 2.39 (s, 3H)

^{13}C NMR (75 MHz): 137.4, 135.5, 134.8, 130.3, 130.0, 121.3, 118.3, 20.90

GC-MS: *m/z* 157.8 (M^+)



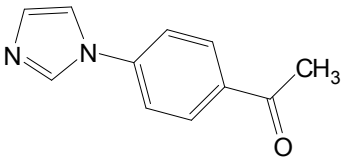
4c

1-*o*-Tolyl-1H-imidazole (4c):

^{1}H NMR (300 MHz): 7.59 (bs, 1H), 7.34 -7.27 (m, 3H), 7.23-7.20 (m, 2H), 7.06 (bs, 1H), 2.18 (s, 3H)

^{13}C NMR (75 MHz): 137.4, 136.5, 133.8, 131.2, 129.2, 128.7, 126.8, 126.4, 120.4, 17.5

GC-MS: *m/z*157.9 (M^+)



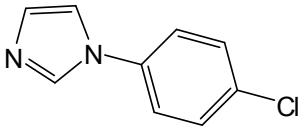
4d

1-(4-(1H-Imidazol-1-yl)phenyl)ethanone (4d)

^{1}H NMR (300 MHz): 8.08 (d, 2H), 7.95 (bs, 1H), 7.49 (d, 2H), 7.35 (bs, 1H), 7.24 (bs, 1H), 2.63 (s, 3H)

^{13}C NMR (75 MHz):196.4, 140.7, 135.7, 135.4, 131.0, 130.3, 120.6, 117.7, 26.5

GC-MS: *m/z* 185.9 (M^+)



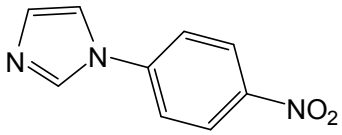
4e

1-(4-Chlorophenyl)-1H-imidazole (4e)

^{1}H NMR (300 MHz): 7.85 (bs, 1H), 7.46 – 7.42 (m, 2H), 7.35-7.26 (m, 4H)

^{13}C NMR (75 MHz): 135.7, 133.0, 131.9, 130.5, 129.9, 122.6, 118.1

GC-MS: *m/z* 177.8 (M^+)



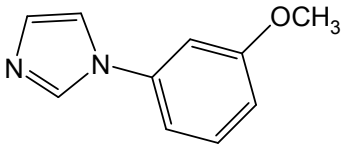
4f

1-(4-Nitrophenyl)-1H-imidazole (4f)

^{1}H NMR (400 MHz): 8.39 (d, 2H), 7.99 (bs, 1H), 7.58 (d, 2H), 7.38 (bs, 1H), 7.28 (bs, 1H)

^{13}C NMR (100 MHz): 146.3, 141.9, 135.4, 131.7, 125.7, 121.0, 117.6

GC-MS: *m/z* 188.9 (M^+)



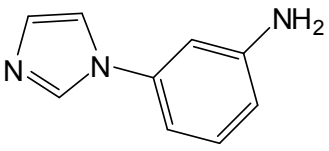
4g

1-(3-Methoxyphenyl)-1H-imidazole (4g)

^{1}H NMR (400 MHz): 7.94 (bs, 1H), 7.39 (t, 1H), 7.28 (d, 1H), 7.22 (bs, 1H), 6.99 (d, 1H), 6.93 -6.90 (m, 2H), 3.86 (s, 3H)

^{13}C NMR (100 MHz): 160.7, 138.2, 135.5, 130.7, 129.7, 118.4, 113.7, 112.8, 107.7, 55.5

GC-MS: *m/z* 173.9 (M^+)



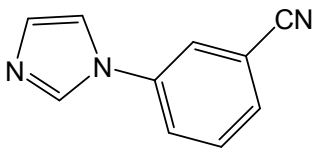
4h

3-(1H-Imidazol-1-yl)aniline (4h)

^{1}H NMR (300 MHz): 7.86 (bs, 1H), 7.29-7.15 (m, 3H), 6.81-6.64 (m, 3H), 4.05 (bs, 2H)

^{13}C NMR (75 MHz): 147.5, 137.9, 135.6, 130.2, 129.5, 118.4, 113.5, 110.8, 107.2

GC-MS: *m/z* 158.9 (M^+)



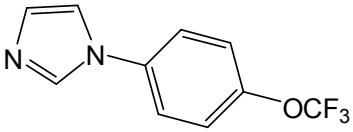
4i

3-(1H-Imidazol-1-yl)benzonitrile (4i)

^{1}H NMR (400 MHz): 7.90 (s, 1H), 7.83-7.42 (m, 4H), 7.31 (bs, 1H), 7.27 (bs, 1H)

^{13}C NMR (100 MHz): 138.0, 135.4, 131.3, 131.0, 128.5, 127.3, 125.5, 124.5, 117.4, 114.3

GC-MS: *m/z* 168.9 (M^+)



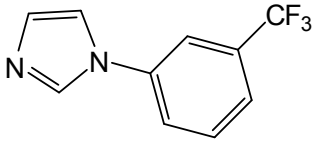
4j

1-(4-(Trifluoromethoxy)phenyl)-1H-imidazole (4j)

^{1}H NMR (400 MHz): 7.86 (bs, 1H), 7.39 (d, 2H), 7.24 (d, 2H), 6.73-6.36 (m, 2H)

^{13}C NMR (100 MHz): 149.9, 134.7, 132.0, 130.4, 128.5, 123.0, 121.2, 118.1, 115.5, 112.9

GC-MS: *m/z* 209.9 (M^+)



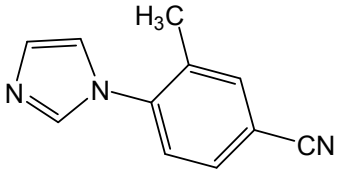
4k

1-(3-(Trifluoromethyl)phenyl)-1H-imidazole (4k)

^{1}H NMR (300 MHz): 7.82 (bs, 1H), 7.39 (d, 2H), 7.28-7.21 (m, 3H), 6.80-6.31 (m, 1H)

^{13}C NMR (75 MHz): 149.7, 135.5, 134.5, 130.4, 122.2, 121.1, 118.8, 118.2, 115.4, 111.9

GC-MS: *m/z* 221.7 (M^+)



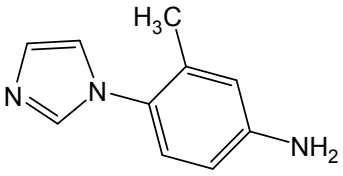
4l

4-(1H-Imidazol-1-yl)-3-methylbenzonitrile (4l)

^{1}H NMR (400 MHz): 7.92 (s, 1H), 7.71 (s, 1H), 7.37-7.31 (m,3H), 7.22 (s, 1H), 2.62 (s, 3H)

^{13}C NMR (100MHz): 144.5, 140.3, 135.3, 134.3, 132.0, 128.4, 122.3, 118.6, 117.6, 111.5

GC-MS: *m/z* 182.9 (M^+)



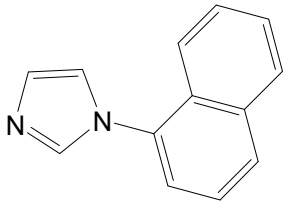
4m

4-(1H-Imidazol-1-yl)-3-methylaniline (4m)

^{1}H NMR (400 MHz): 7.78 (bs, 1H), 7.19 (bs, 2H), 7.21-7.07 (m, 2H), 6.72 (d, 1H), 3.75 (bs, 2H), 2.21 (s, 3H)

^{13}C NMR (100 MHz): 144.4, 129.3, 128.6, 124.3, 123.3, 120.8, 115.2, 17.4

GC-MS: *m/z* 172.9 (M^+)

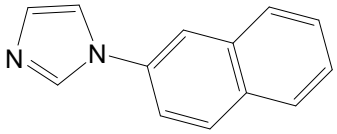


4n

1-(Naphthalen-1-yl)-1H-imidazole (4n)

^{1}H NMR (300 MHz): 7.93 (d, 2H), 7.77 (s, 1H), 7.77 (s, 1H), 7.61-7.38 (m, 3H), 7.31 (s, 2H), 7.24 (s, 1H)

GC-MS: *m/z* 193.9 (M^+)



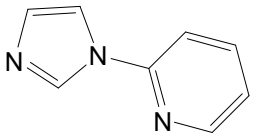
4o

1-(Naphthalen-2-yl)-1H-imidazole (4o)

^{1}H NMR (400 MHz): 7.96-7.81 (m, 5H), 7.59 -7.51 (m, 3H), 7.46 (bs, 1H), 7.27 (s, 1H)

^{13}C NMR (100 MHz): 134.8, 133.5, 132.2, 130.0, 127.8, 127.8, 127.3, 126.5, 120.2, 119.1

GC-MS: *m/z* 193.9 (M^+)



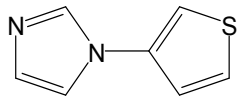
4p

2-(1H-Imidazol-1-yl)pyridine (4p)

^{1}H NMR (400 MHz): 8.47 (bs, 1H), 8.36 (bs, 1H), 7.83-7.79 (m,1H), 7.64 – 7.63 (t, 1H), 7.36-7.34 (m, 1H), 7.26-7.19 (m, 1H)

^{13}C NMR (100 MHz): 149.1, 139.0, 135.0, 130.4, 121.4, 116.1, 112.3

GC-MS: *m/z* 144.9 (M^+)



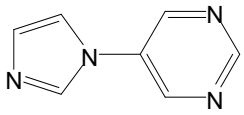
4q

1-(Thiophen-3-yl)-1H-imidazole (4q)

^{1}H NMR (300 MHz): 7.99 (bs, 1H), 7.44 (m, 1H), 7.31-7.19 (m, 4H)

^{13}C NMR (75 MHz): 136.2, 135.7, 129.8, 127.1, 121.2, 118.4, 113.0

GC-MS: *m/z* 150.0 (M^+)



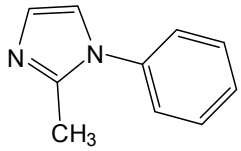
4r

5-(1H-Imidazol-1-yl)pyrimidine (4r)

^{1}H NMR (300 MHz): 9.25 (s, 1H), 8.90 (s, 2H), 7.45-7.84 (m, 2H), 7.33 (s, 1H)

^{13}C NMR (75 MHz): 157.4, 149.4, 135.1, 131.8, 128.3, 117.5

GC-MS: *m/z* 146.0 (M^+)

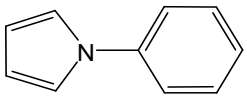


2-Methyl-1-phenyl-1H-imidazole

^{1}H NMR (400 MHz): 7.51-7.41 (m, 3H), 7.30-7.28 (m,2H), 7.08 (bs, 2H), 2.36 (s, 3H)

^{13}C NMR (100 MHz): 137.9, 132.0, 129.5, 128.2, 127.2, 125.5, 13.6

GC-MS: *m/z* 157.9 (M^+)

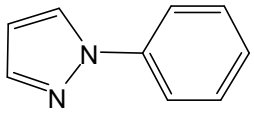


1-Phenyl-1H-pyrrole

^{1}H NMR (300 MHz) : 7.45-4.43 (m, 4H), 7.32-7.24 (m, 1H), 7.13 (s, 2H), 6.38 (s, 2H)

^{13}C NMR (75 MHz): 141.1, 129.9, 126.0, 120.9, 119.3, 110.8

GC-MS: *m/z* 142.9 (M^+)

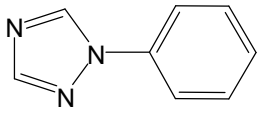


1-Phenyl-1H-pyrazole

^{1}H NMR (300 MHz): 7.89 (bs, 1H), 7.68-7.64 (m, 3H), 7.40 (t, 2H), 7.25 (m, 1H), 6.42 (bs, 1H)

^{13}C NMR (75 MHz):140.9, 140.0, 129.3, 126.7, 126.3, 119.1, 107.5

GC-MS: *m/z* 144.0 (M^+)

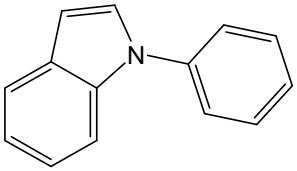


1-Phenyl-1H-1,2,4-triazole

^{1}H NMR (300 MHz) : 8.49 (s, 1H), 8.02 (s, 1H), 7.61-7.58 (d, 2H), 7.42 (t, 2H), 7.33-7.29 (t, 1H)

^{13}C NMR (75 MHz):152.4, 140.8, 136.8, 129.7, 128.1, 119.6

GC-MS: *m/z* 145.0 (M^+)

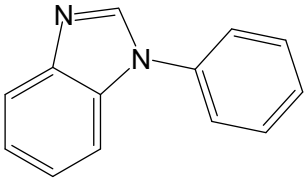


1-Phenyl-1H-indole

^{1}H NMR (300 MHz) : 7.69 (d, 1H), 7.57 (d, 1H), 7.52-7.50 (m, 4H), 7.41-7.32 (m, 2H), 7.23-7.14 (m, 2H), 6.68 (d, 1H)

^{13}C NMR (75 MHz): 139.8, 135.4, 129.5, 129.2, 127.9, 126.3, 124.3, 122.2, 121.0, 120.0, 110.4, 103.4

GC-MS: *m/z* 192.9 (M^+)



1-Phenyl-1H-benzo[*d*]imidazole

^{1}H NMR (300 MHz) : 8.10 (s, 1H), 7.88-7.85 (m, 1H), 7.68-7.41 (m, 6H), 7.33-7.22 (m, 2H)

^{13}C NMR (75 MHz): 143.7, 142.2, 136.1, 133.5, 130.5, 128.0, 123.7, 122.8, 120.3, 110.5

GC-MS: *m/z* 194.0 (M_+)

Reference:

S1. Ashton P. R.; Koniger, R.; Stoddart, J. F. *J. Org. Chem.* **1996**, *61*, 903.

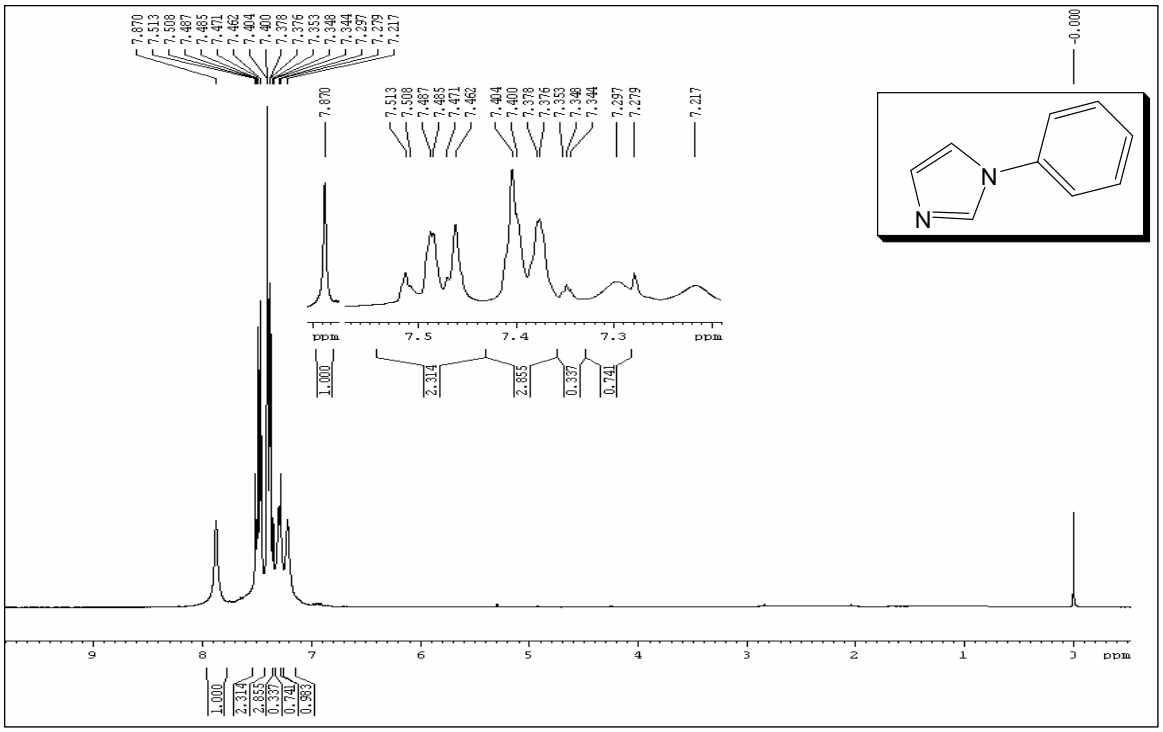


Fig. 1 ^{1}H-NMR spectrum of 1-phenyl-1H-imidazole **4a** (300 MHz, $CDCl_3$)

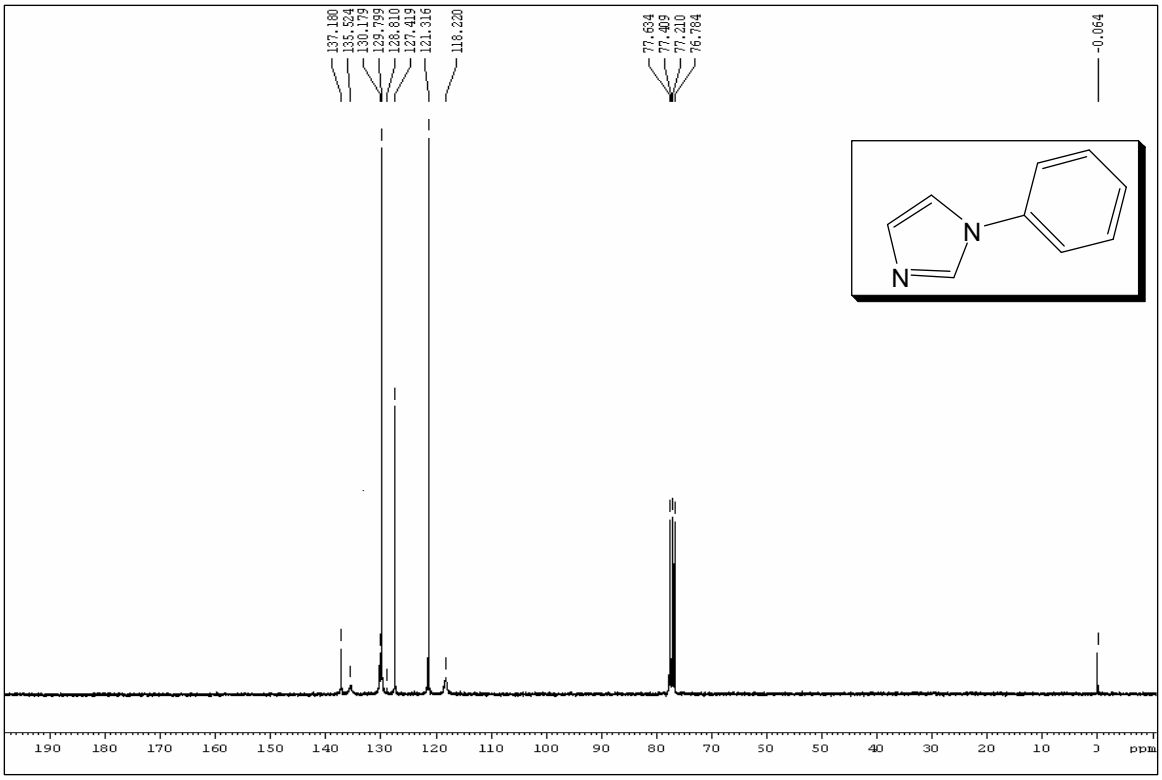


Fig. 2 ^{13}C-NMR spectrum of 1-phenyl-1H-imidazole **4a** (75 MHz, $CDCl_3$)

Fig. 3 ^{1}H-NMR spectrum of 1-*p*-tolyl-1H-imidazole **4b** (300 MHz, $CDCl_3$)

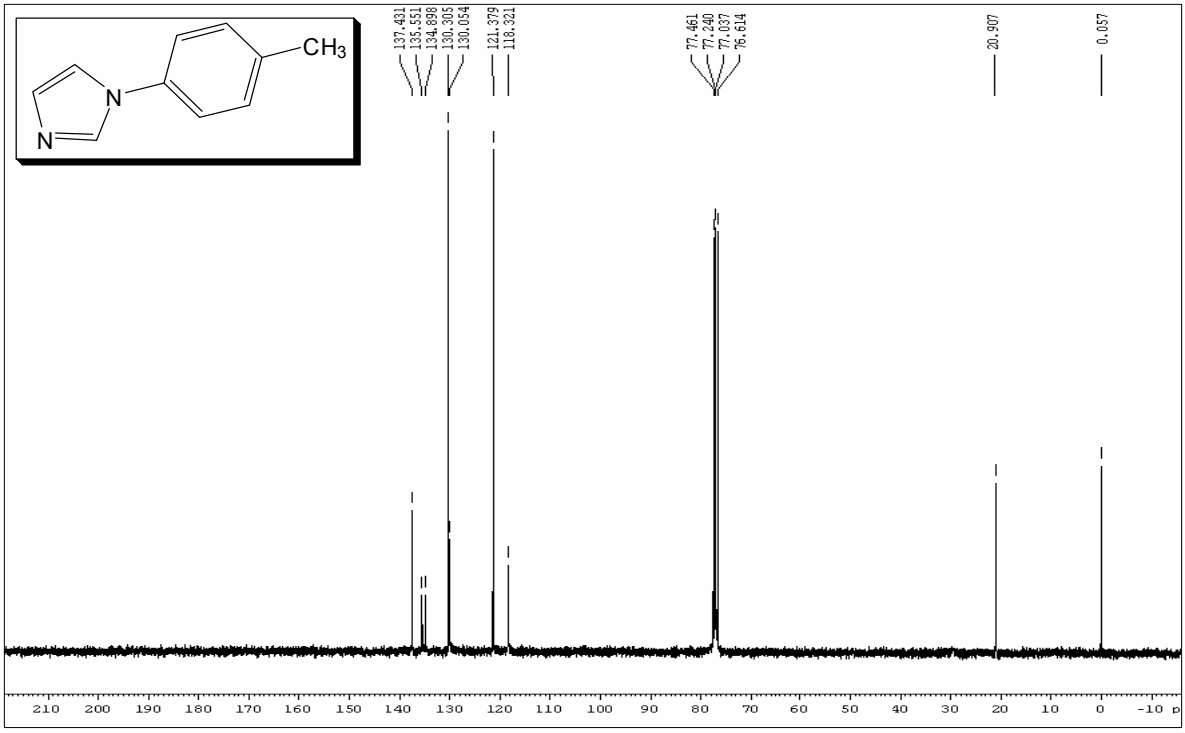


Fig. 4 ^{13} C-NMR spectrum of 1-*p*-tolyl-1H-imidazole **4b** (75 MHz, $CDCl_3$)

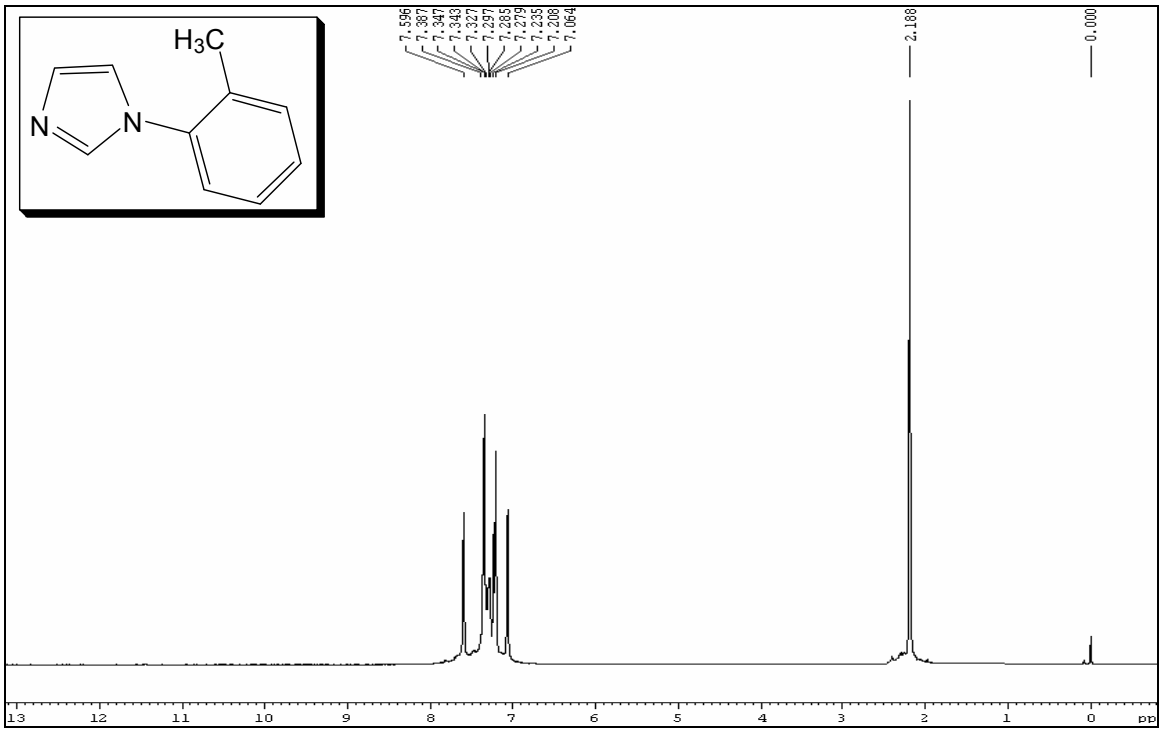


Fig. 5 ^{1}H-NMR spectrum of 1-*o*-tolyl-1H-imidazole **4c** (300 MHz, $CDCl_3$)

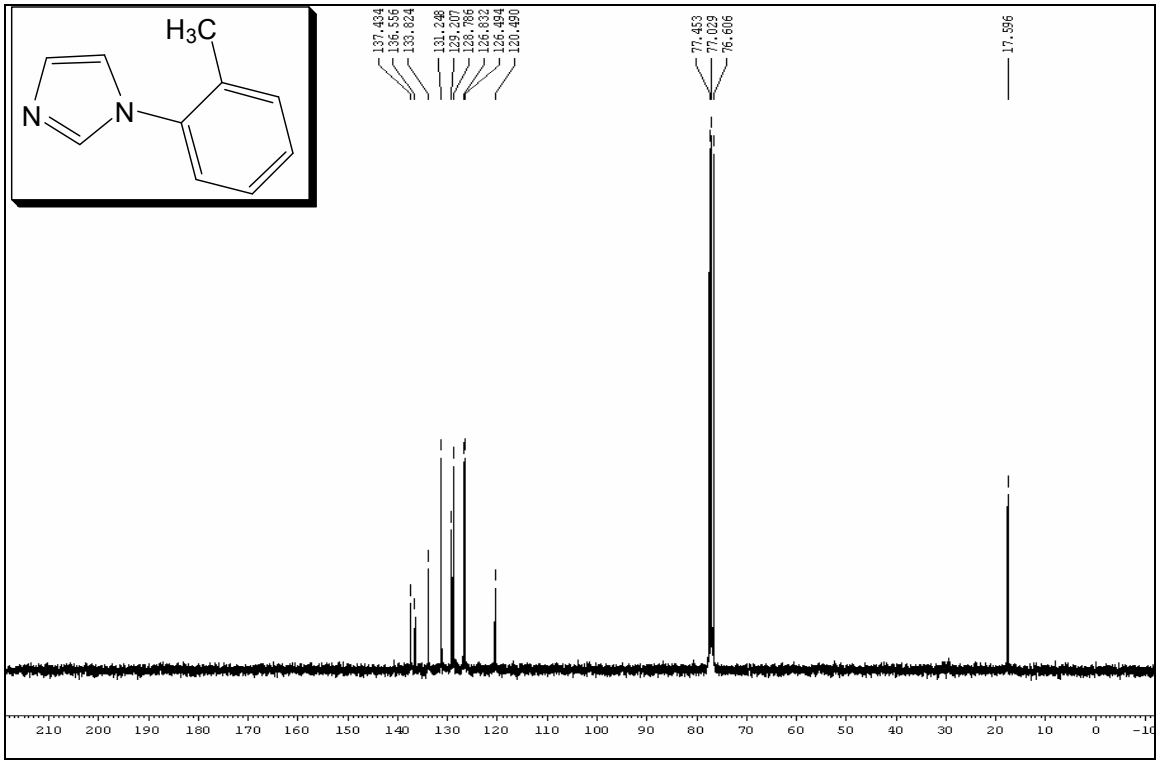


Fig. 6 ^{13} C-NMR spectrum of 1-*o*-tolyl-1H-imidazole **4c** (75 MHz, $CDCl_3$)

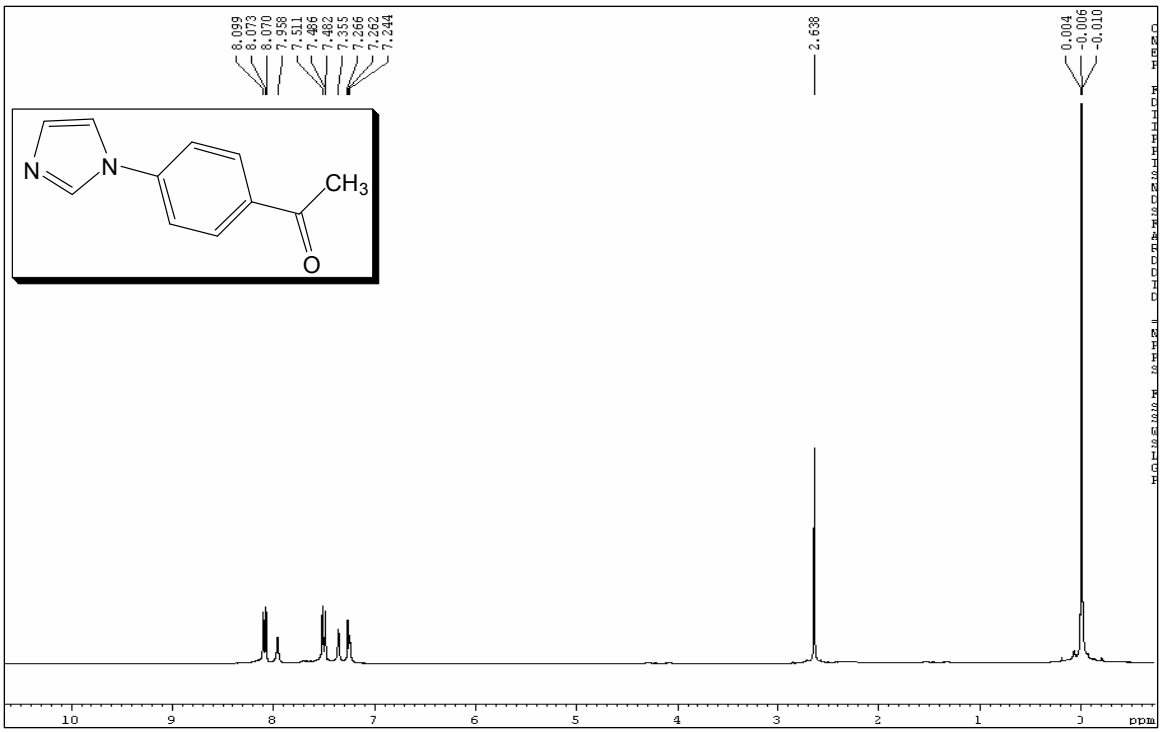


Fig. 7 [1] H-NMR spectrum of 1-(4-(1H-imidazol-1-yl)phenyl)ethanone **4d** (300 MHz, $CDCl_3$)

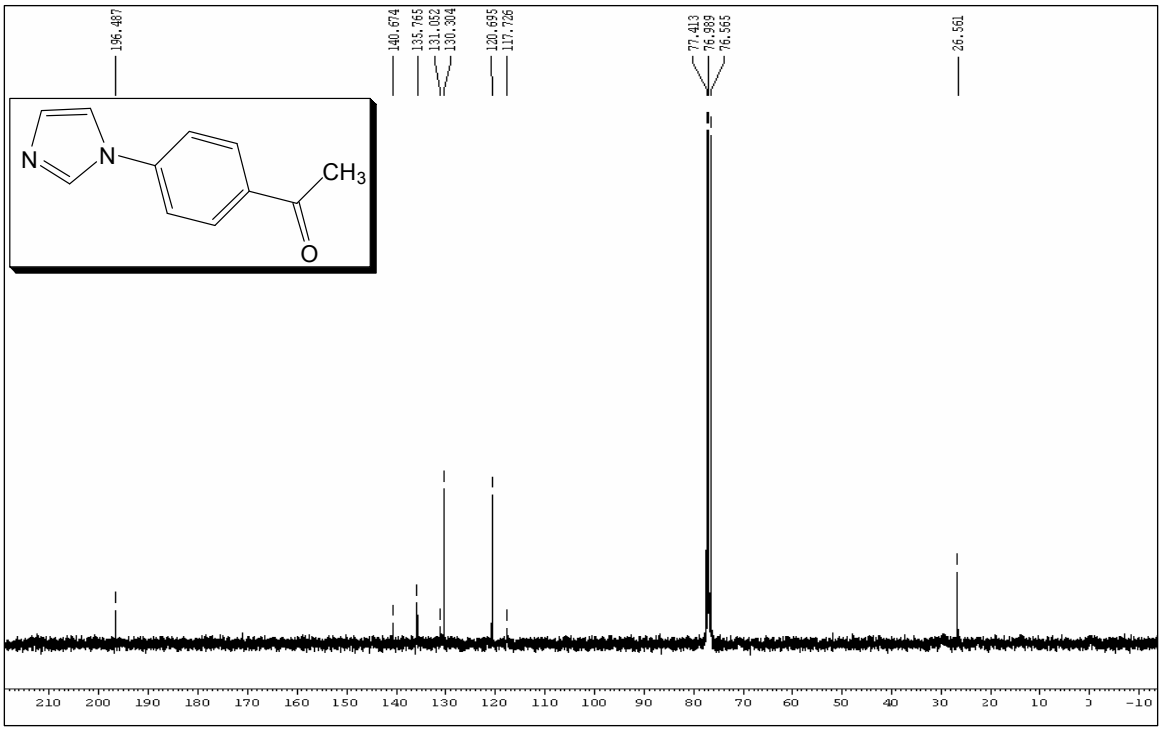


Fig. 8 [13] C-NMR spectrum of 1-(4-(1H-imidazol-1-yl)phenyl)ethanone **4d** (75 MHz, $CDCl_3$)

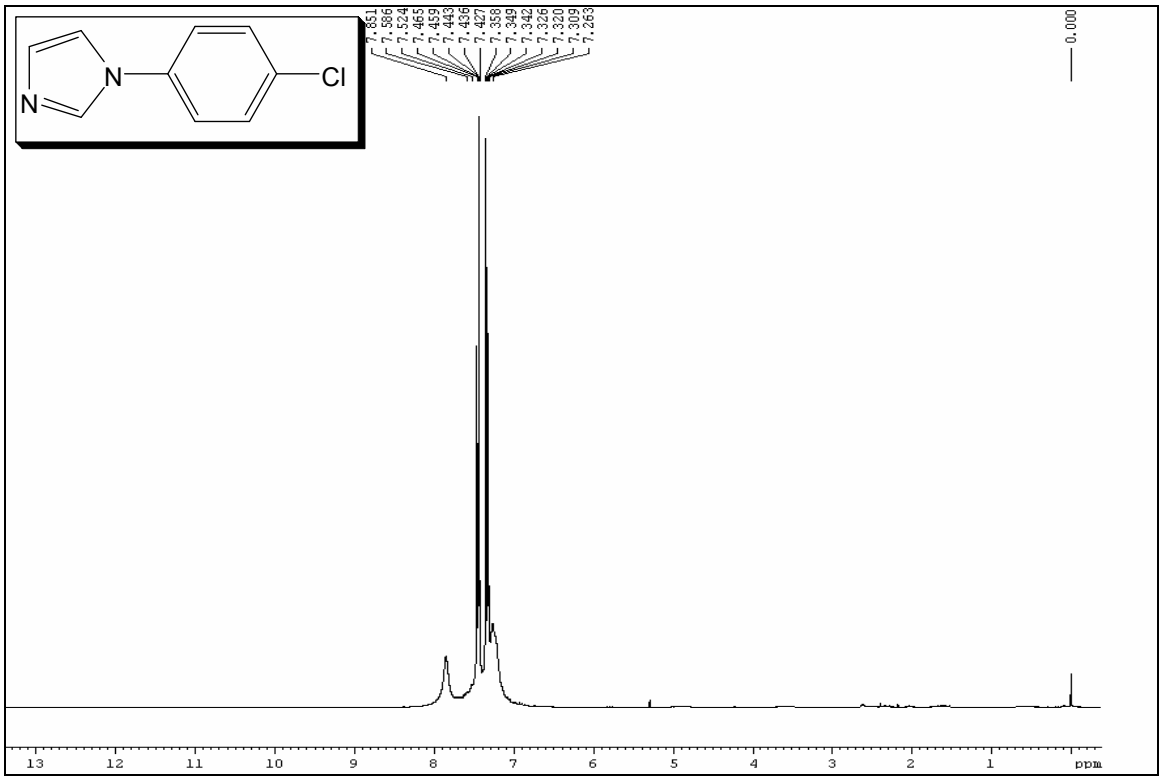


Fig. 9 ^{1}H-NMR spectrum of 1-(4-chlorophenyl)-1H-imidazole **4e** (300 MHz, $CDCl_3$)

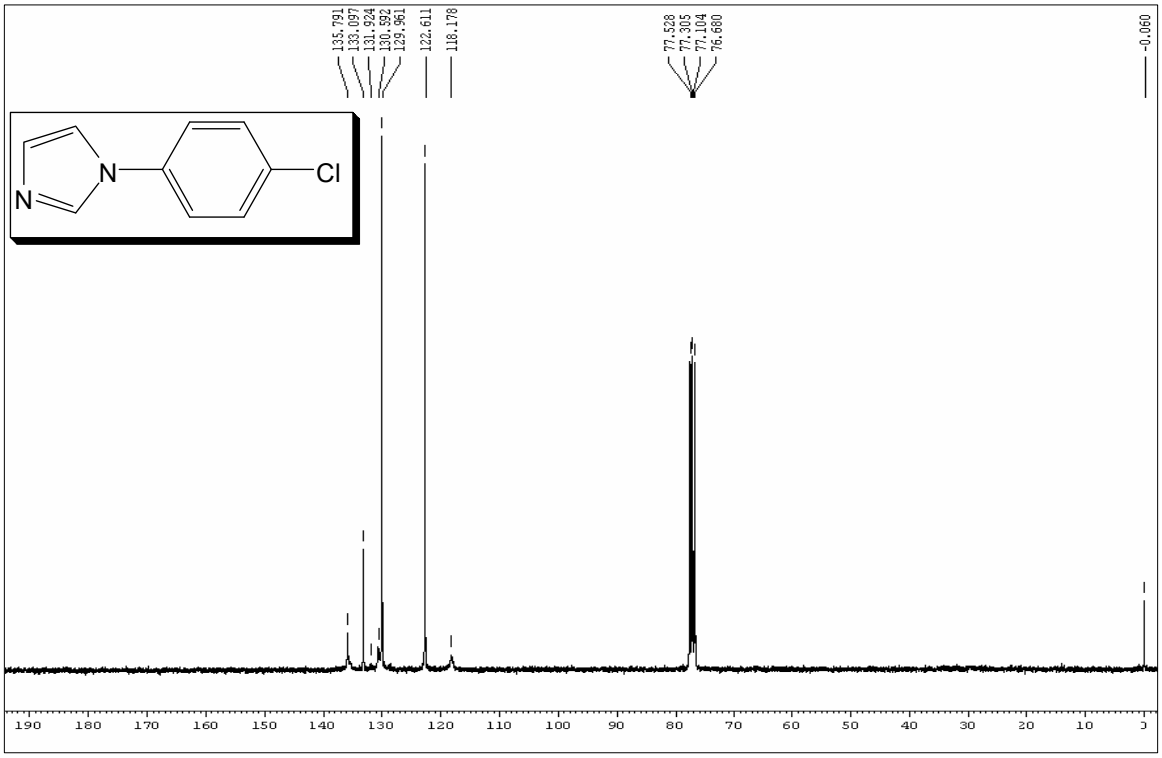


Fig. 10 ^{13}C-NMR spectrum of 1-(4-chlorophenyl)-1H-imidazole **4e** (75 MHz, $CDCl_3$)

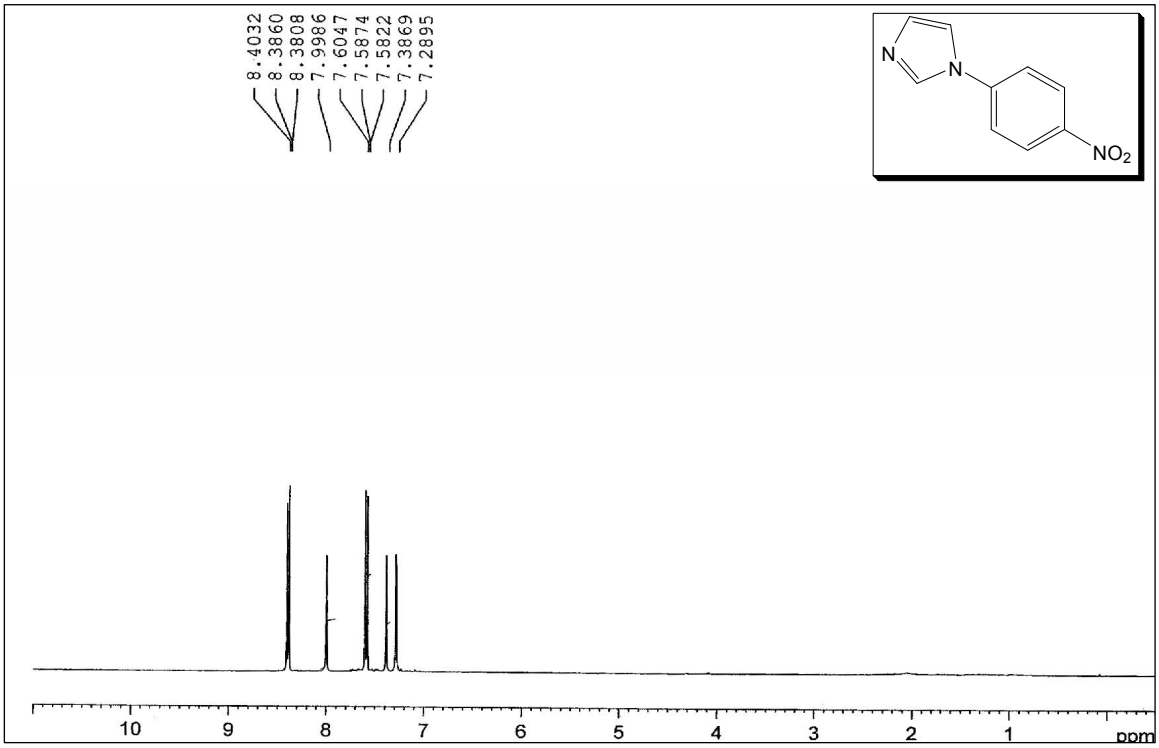


Fig. 11 ^{1}H-NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole **4f** (400 MHz, $CDCl_3$)

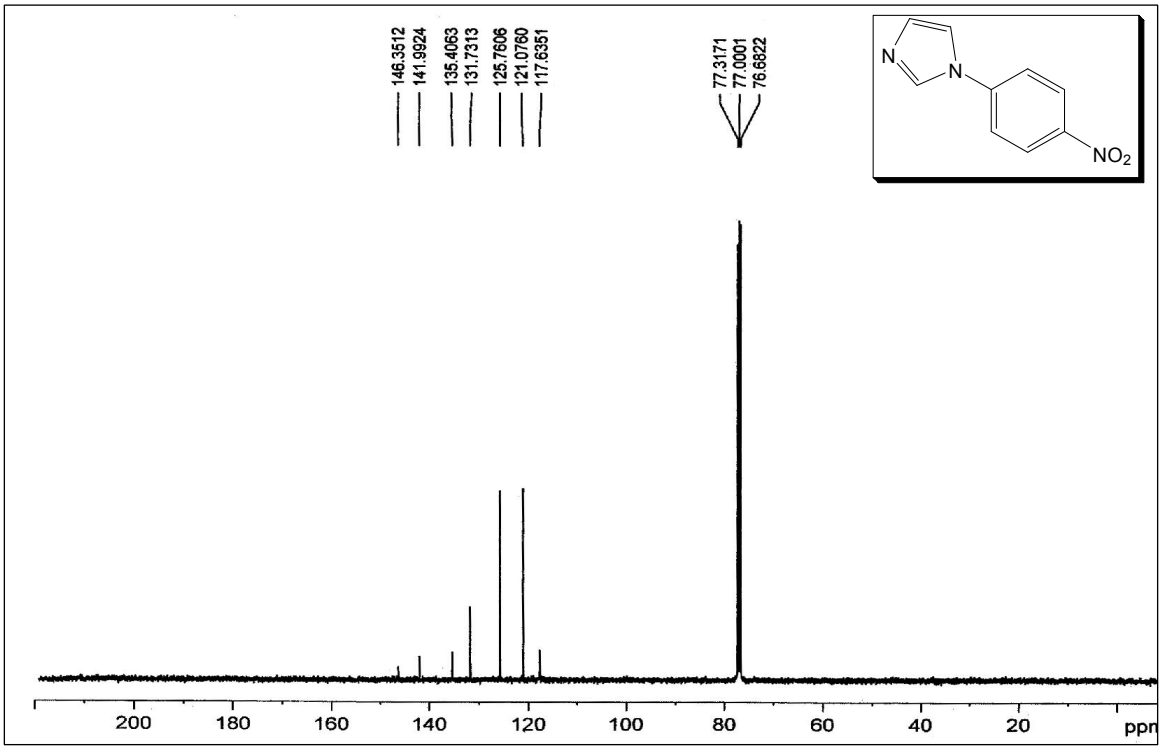


Fig. 12 ^{13}C-NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole **4f** (100 MHz, $CDCl_3$)

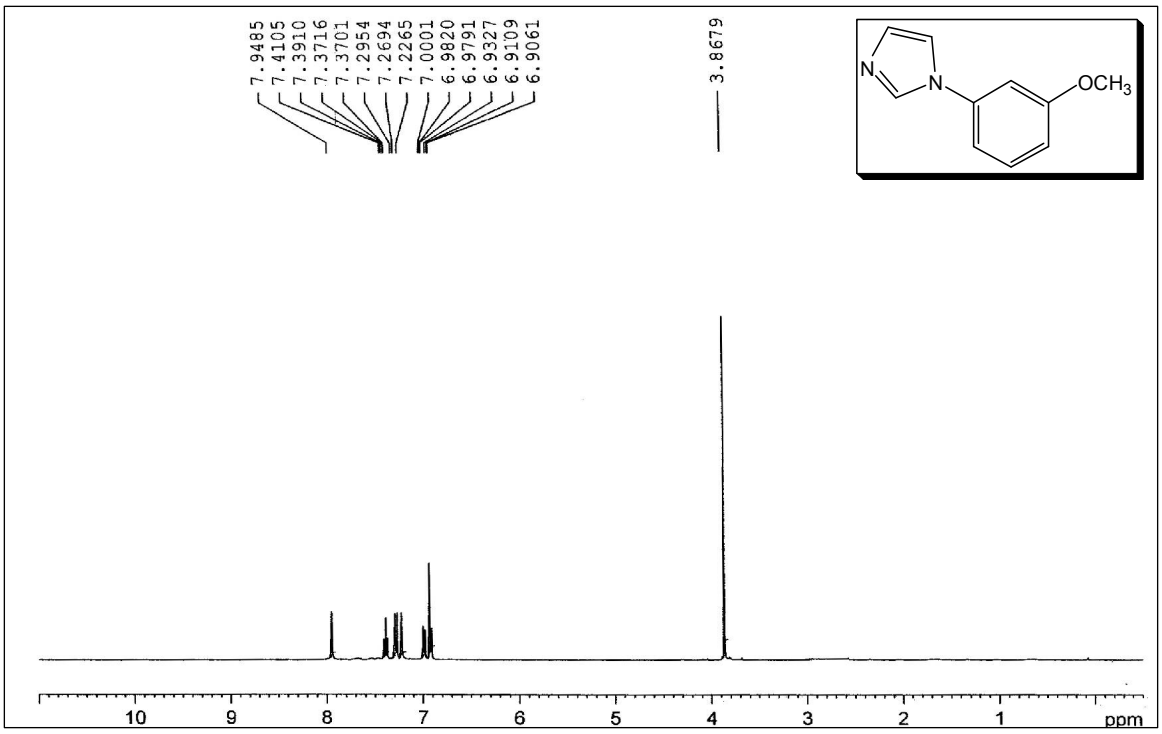


Fig. 13 ^{1}H-NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole **4g** (400 MHz, $CDCl_3$)

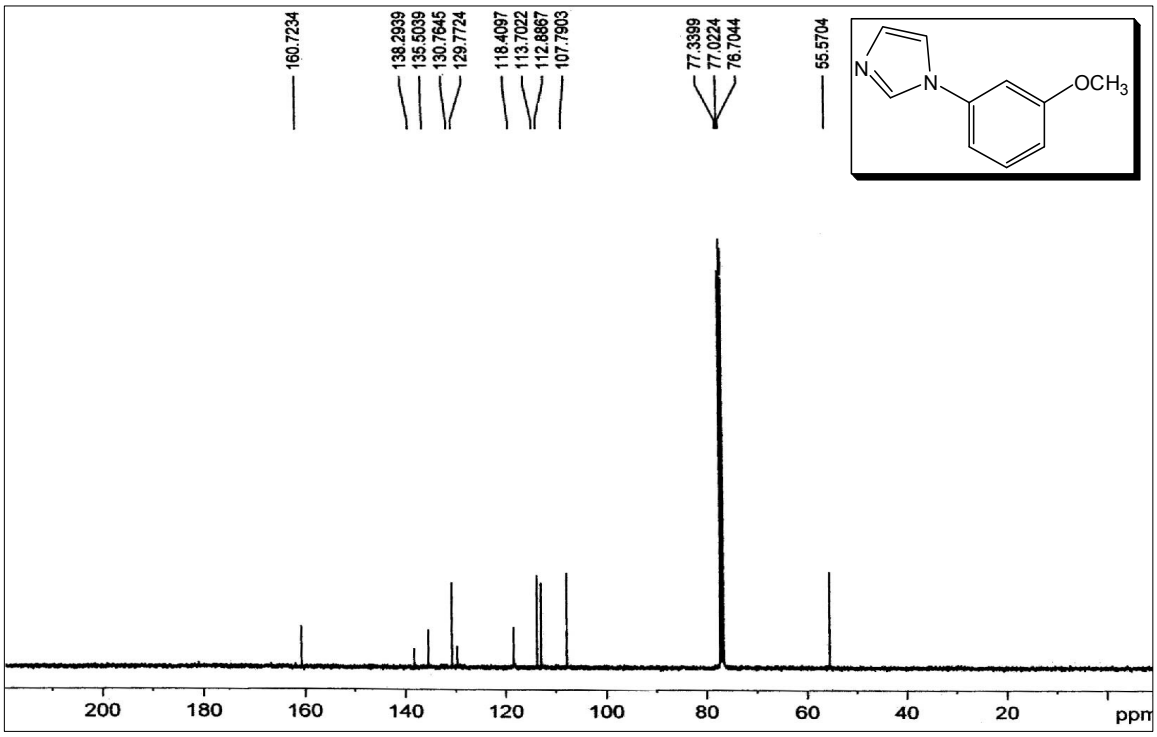


Fig. 14 ^{13}C-NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole **4g** (100 MHz, $CDCl_3$)

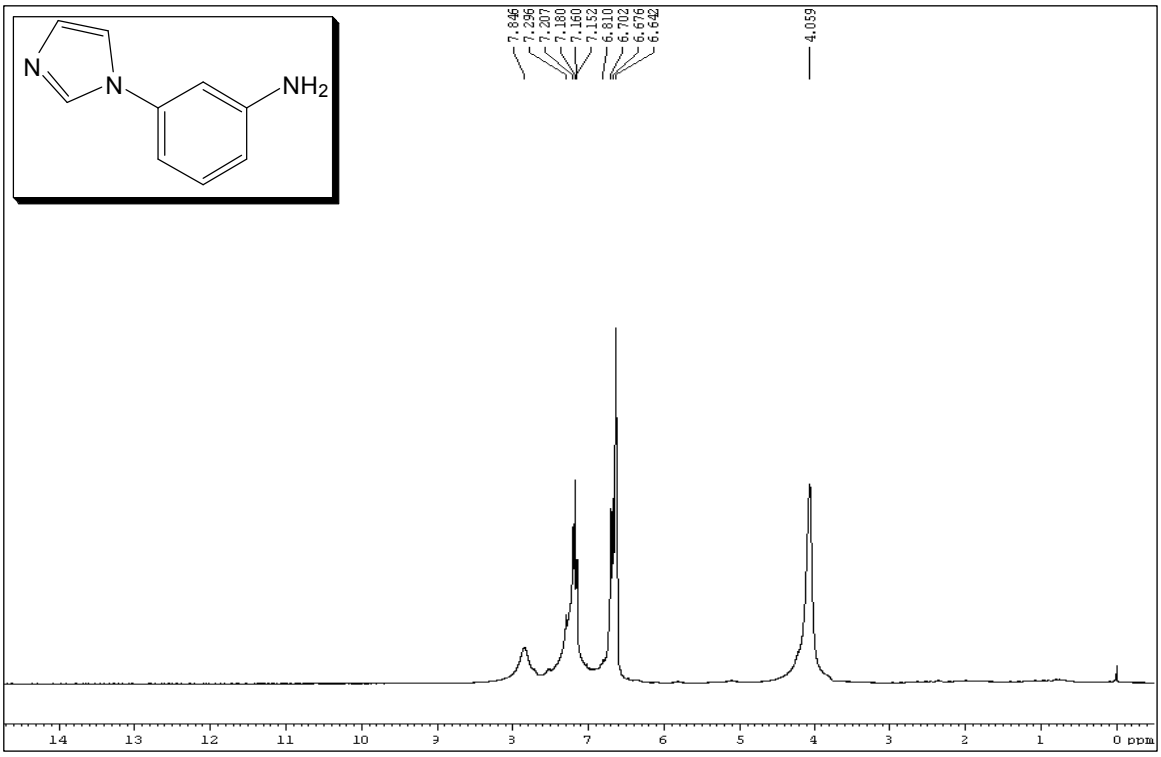


Fig. 15 ^{1}H-NMR spectrum of 3-(1H-imidazol-1-yl)aniline **4h** (300 MHz, $CDCl_3$)

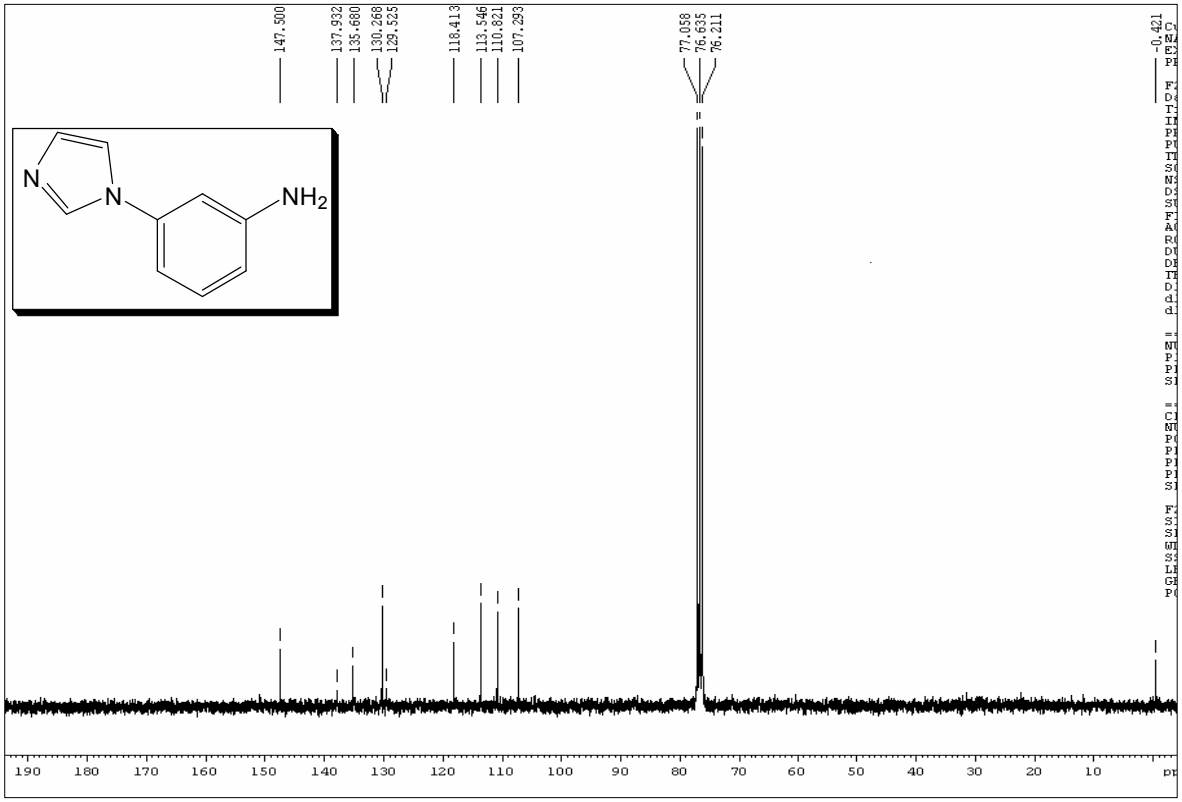


Fig. 16 ^{13}C-NMR spectrum of 3-(1H-imidazol-1-yl)aniline **4h** (75 MHz, $CDCl_3$)

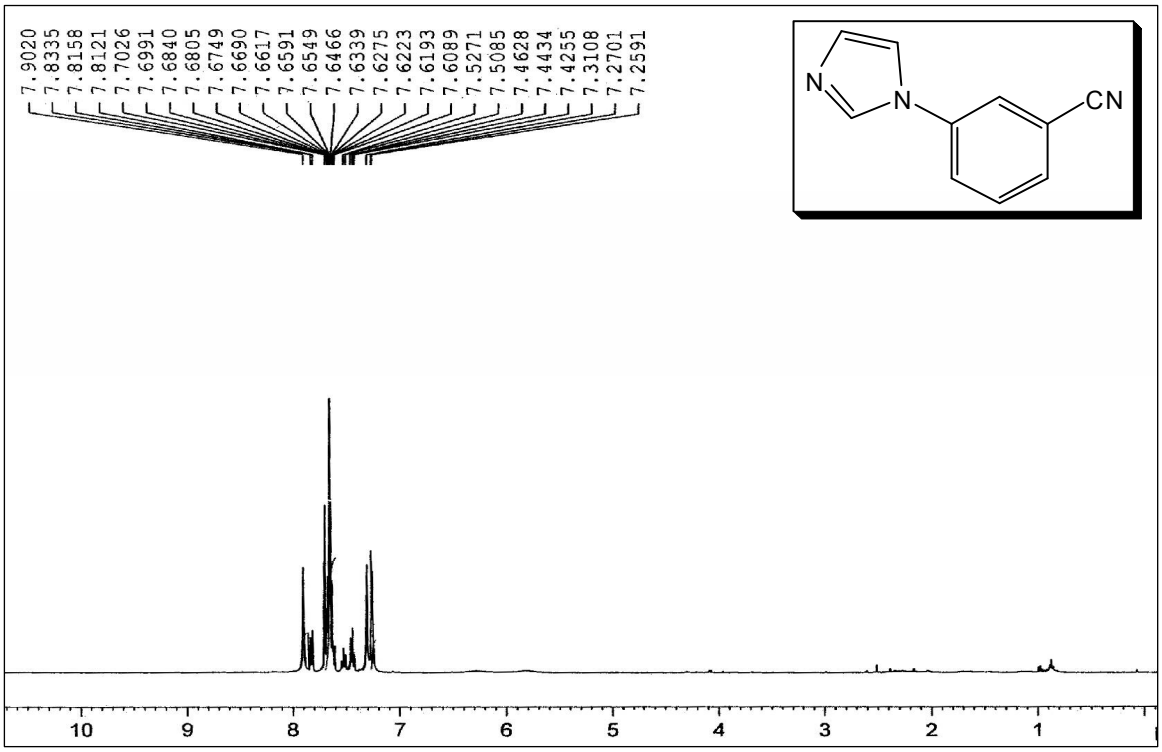


Fig. 17 ^{1}H-NMR spectrum of 3-(1H-imidazol-1-yl)benzonitrile **4i** (400 MHz, $CDCl_3$)

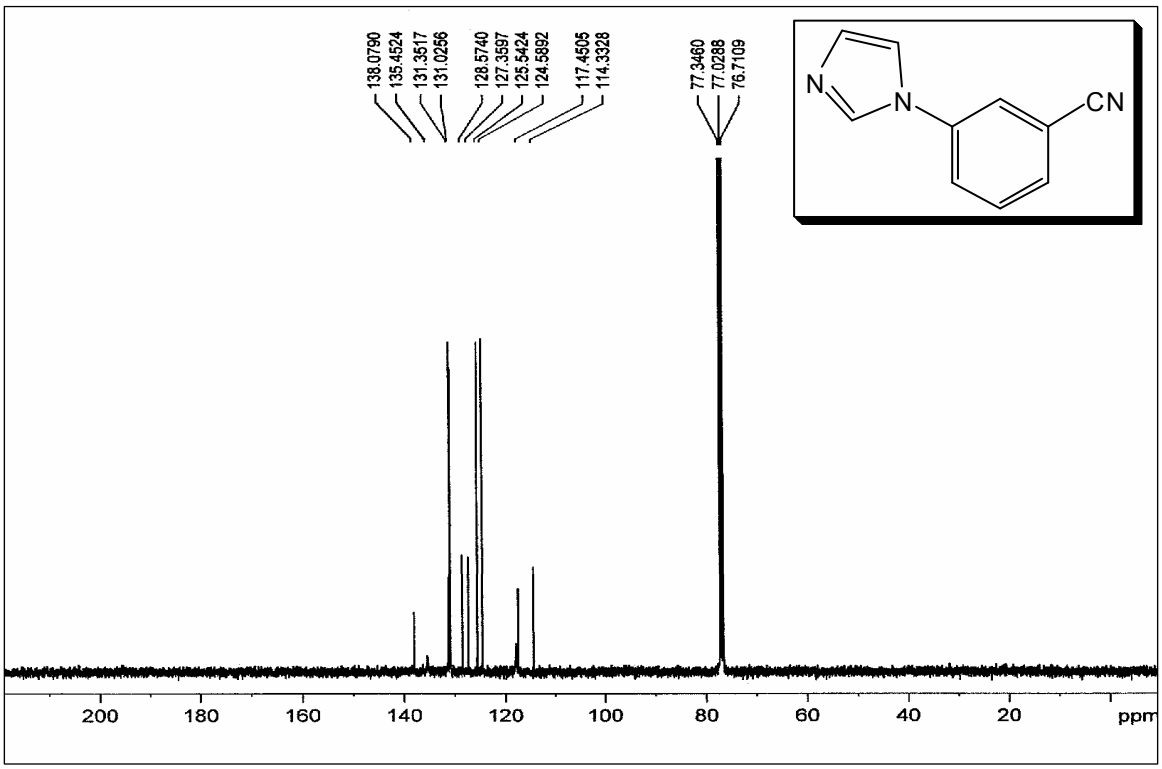


Fig. 18 ^{13}C-NMR spectrum of 3-(1H-imidazol-1-yl)benzonitrile **4i** (100 MHz, $CDCl_3$)

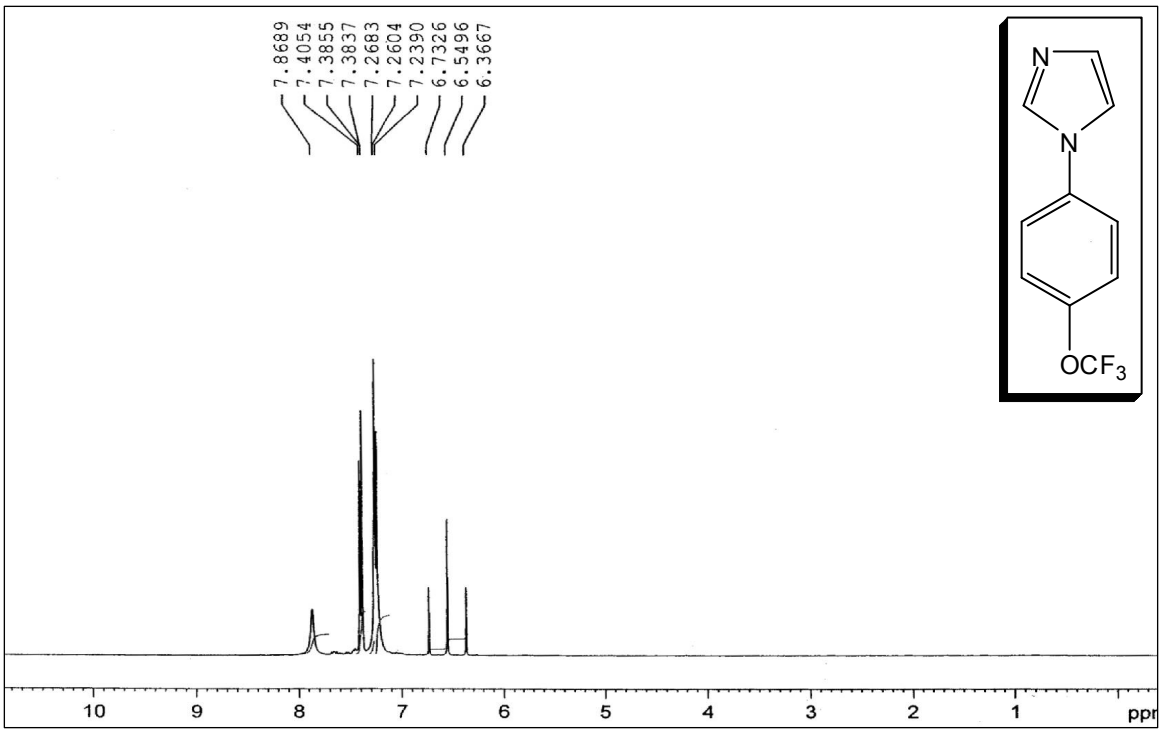


Fig. 19 ^{1}H-NMR spectrum of 1-(4-(trifluoromethoxy)phenyl)-1H-imidazole **4j** (400 MHz, $CDCl_3$)

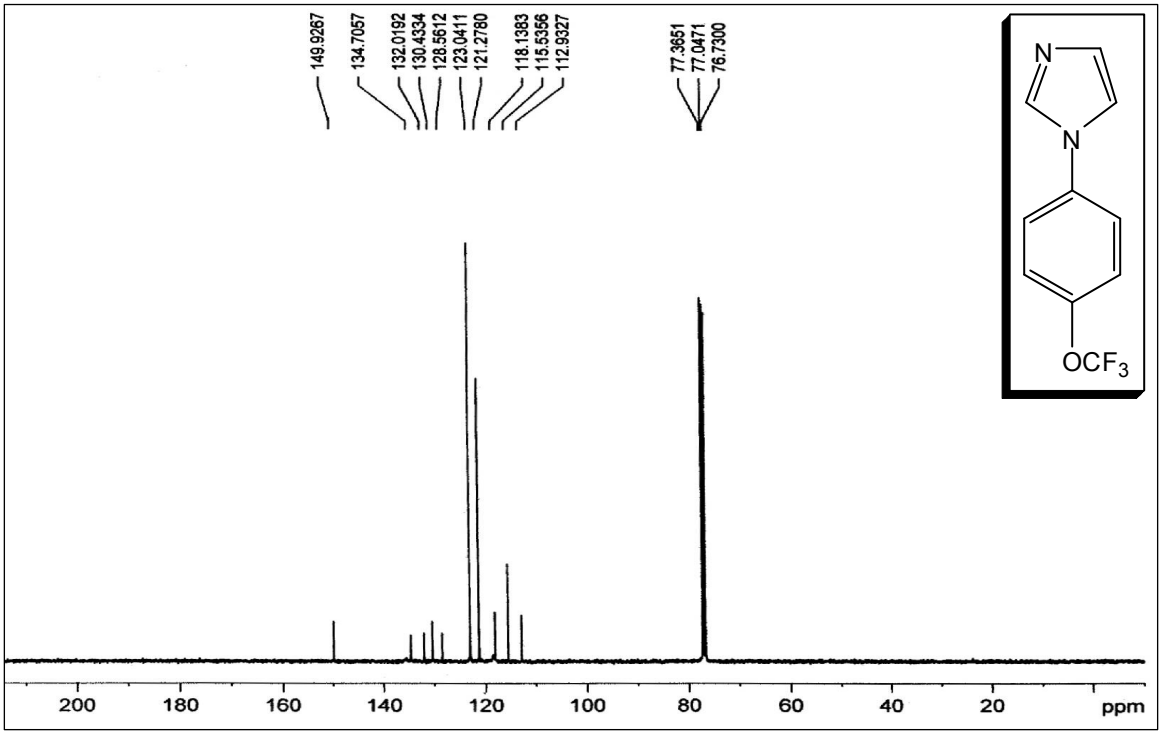


Fig. 20 ^{13}C-NMR spectrum of 1-(4-(trifluoromethoxy)phenyl)-1H-imidazole **4j** (100 MHz, $CDCl_3$)

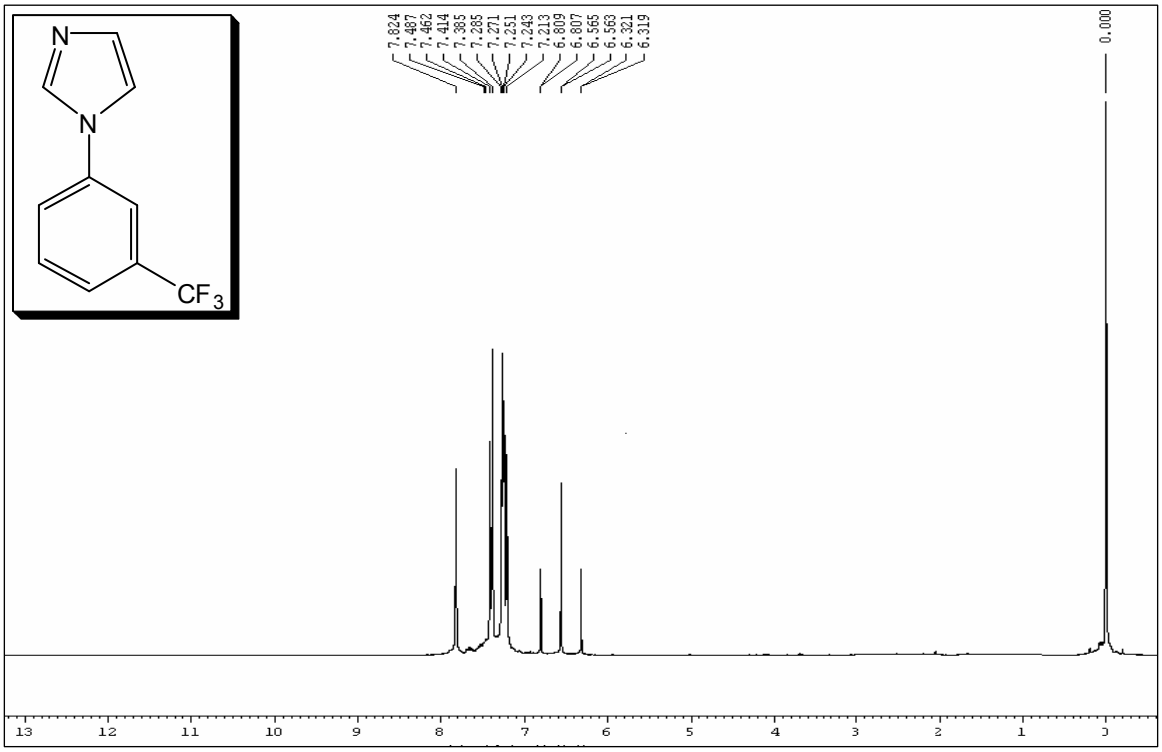


Fig. 21 ^{1}H-NMR spectrum of 1-(3-(trifluoromethyl)phenyl)-1H-imidazole **4k** (300 MHz, $CDCl_3$)

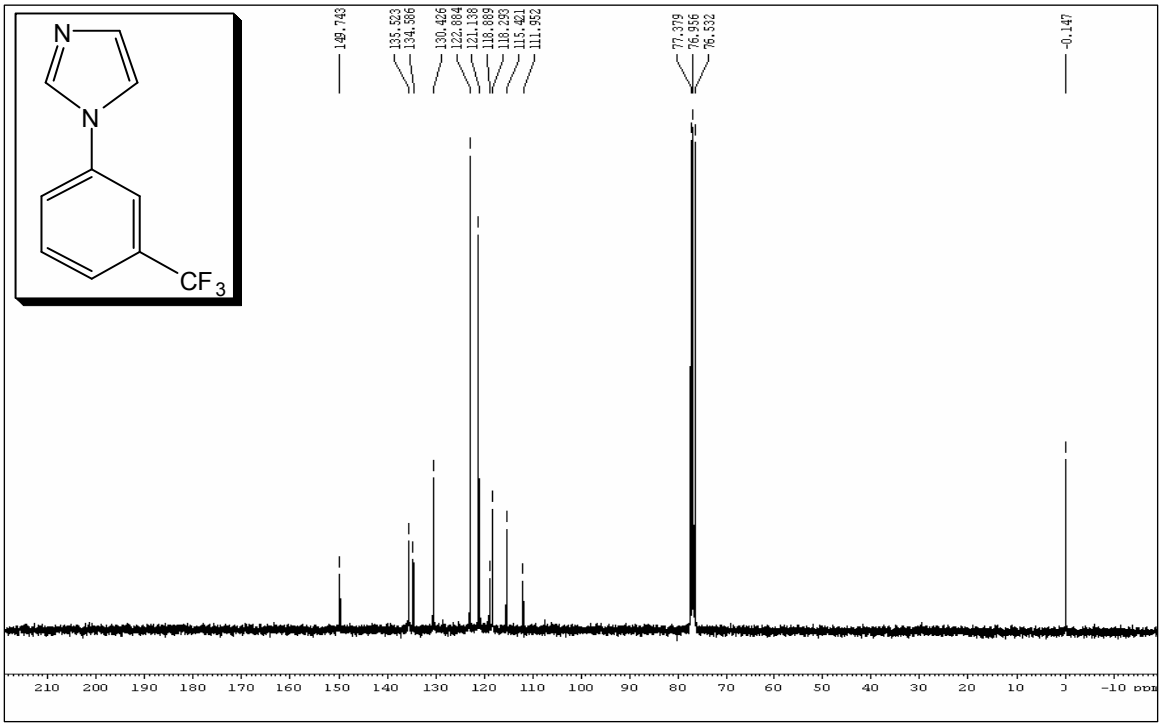


Fig. 22 ^{13}C-NMR spectrum of 1-(3-(trifluoromethyl)phenyl)-1H-imidazole **4k** (75 MHz, $CDCl_3$)

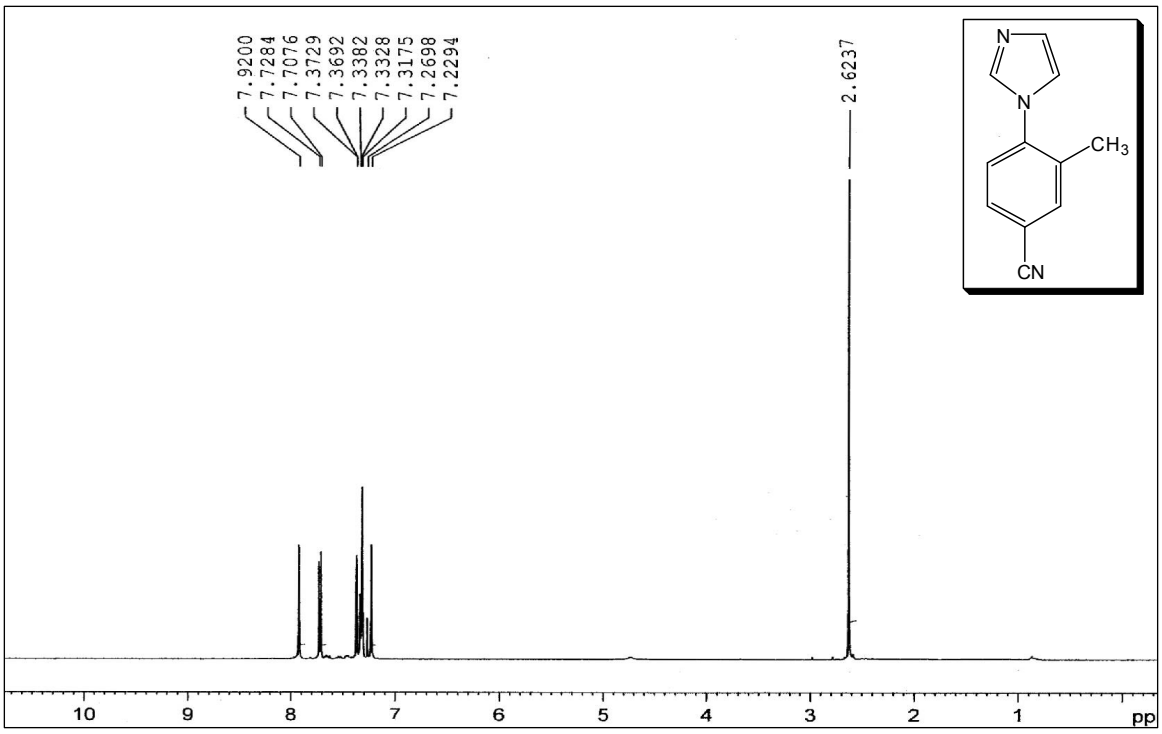


Fig. 23 ^{1}H-NMR spectrum of 4-(1H-imidazol-1-yl)-3-methylbenzonitrile **4l** (400 MHz, $CDCl_3$)

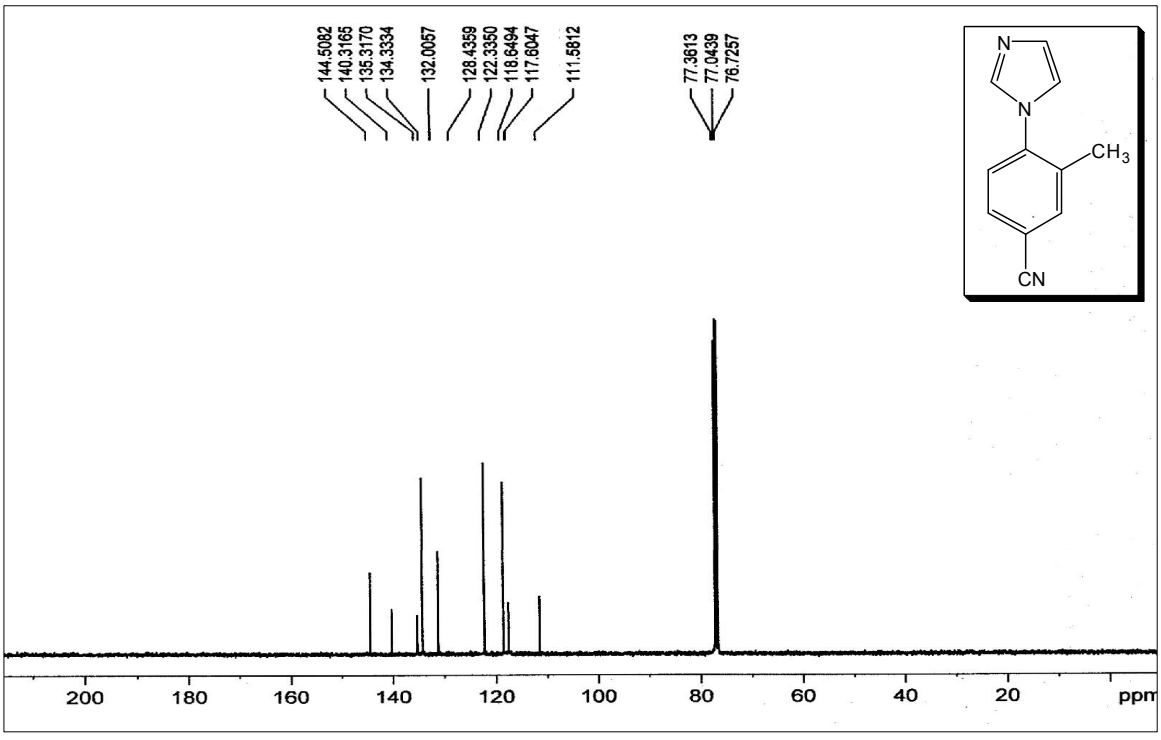


Fig. 24 ^{1}C-NMR spectrum of 4-(1H-imidazol-1-yl)-3-methylbenzonitrile **4l** (75 MHz, $CDCl_3$)

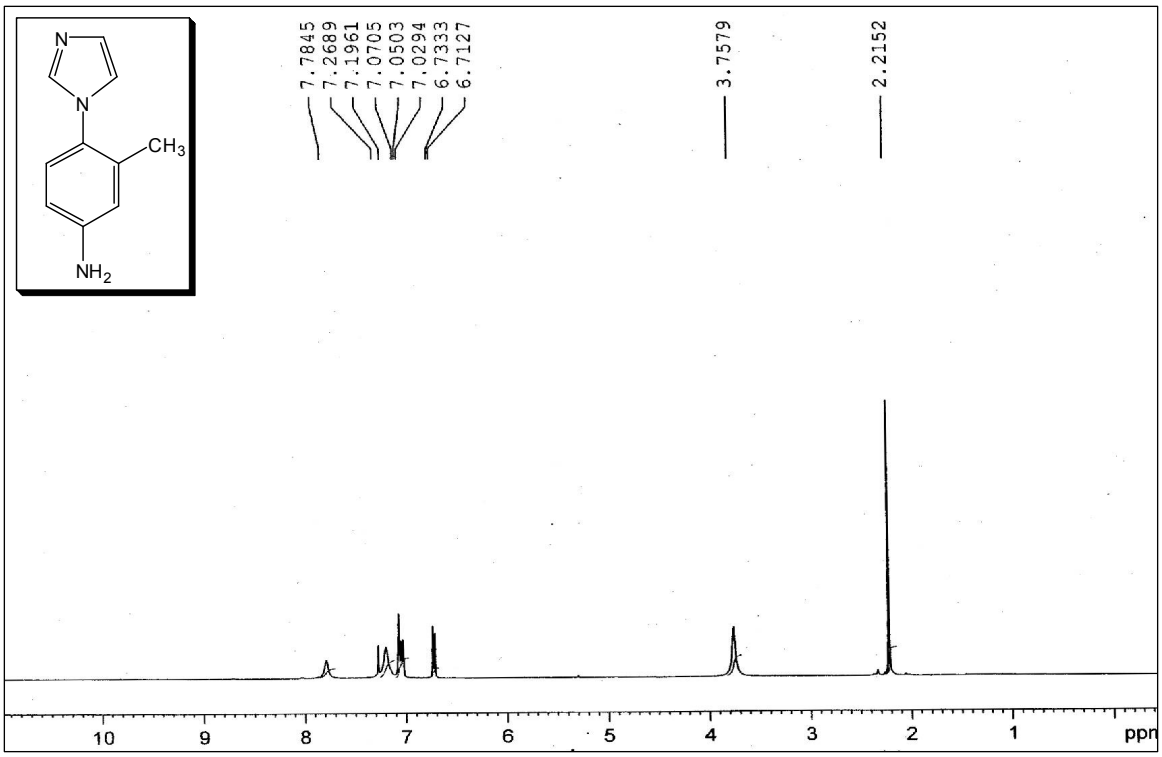


Fig. 25 ^{1}H-NMR spectrum of 4-(1H-imidazol-1-yl)-3-methylaniline **4m** (400 MHz, $CDCl_3$)

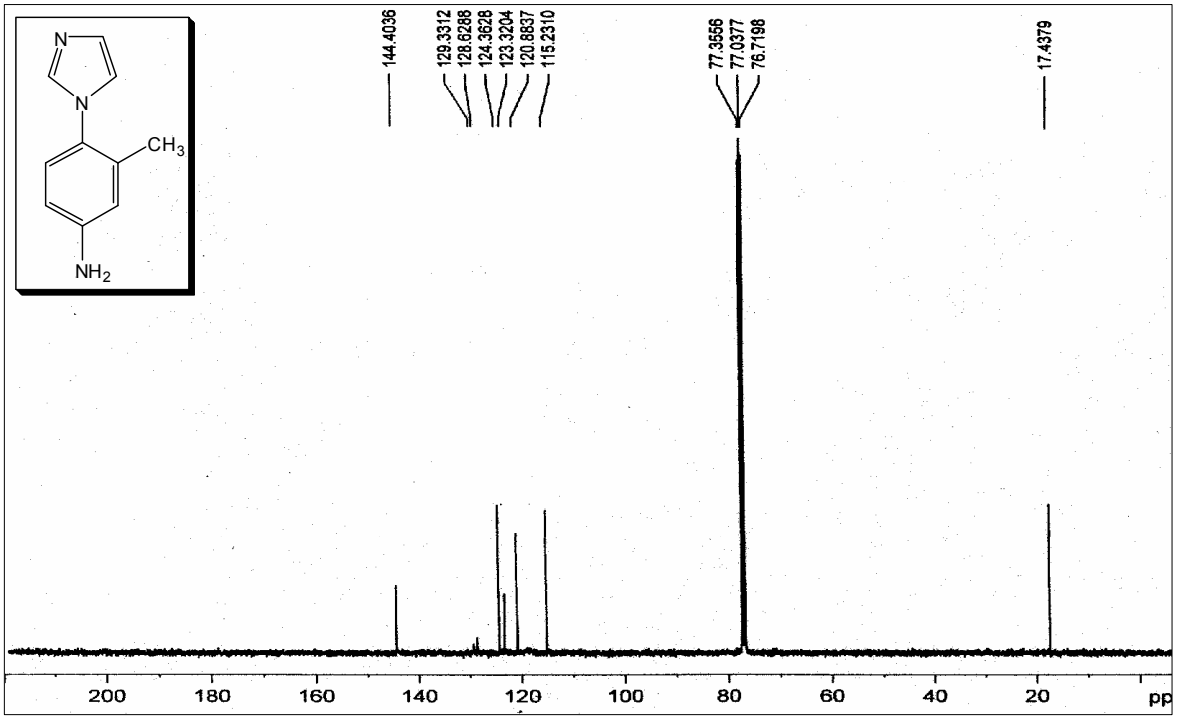


Fig. 26 ^{13}C-NMR spectrum of 4-(1H-imidazol-1-yl)-3-methylaniline **4m** (100 MHz, $CDCl_3$)

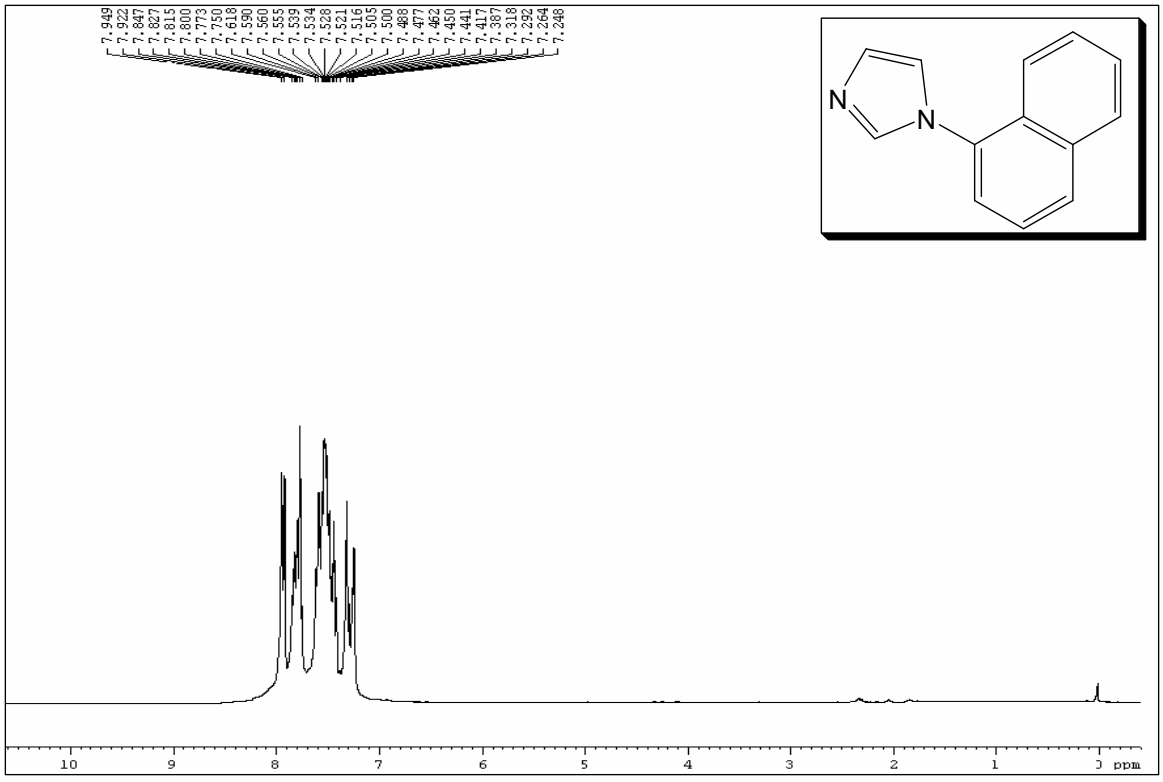


Fig. 27 ^{1}H-NMR spectrum 1-(naphthalen-1-yl)-1H-imidazole **4n** (300 MHz, $CDCl_3$)

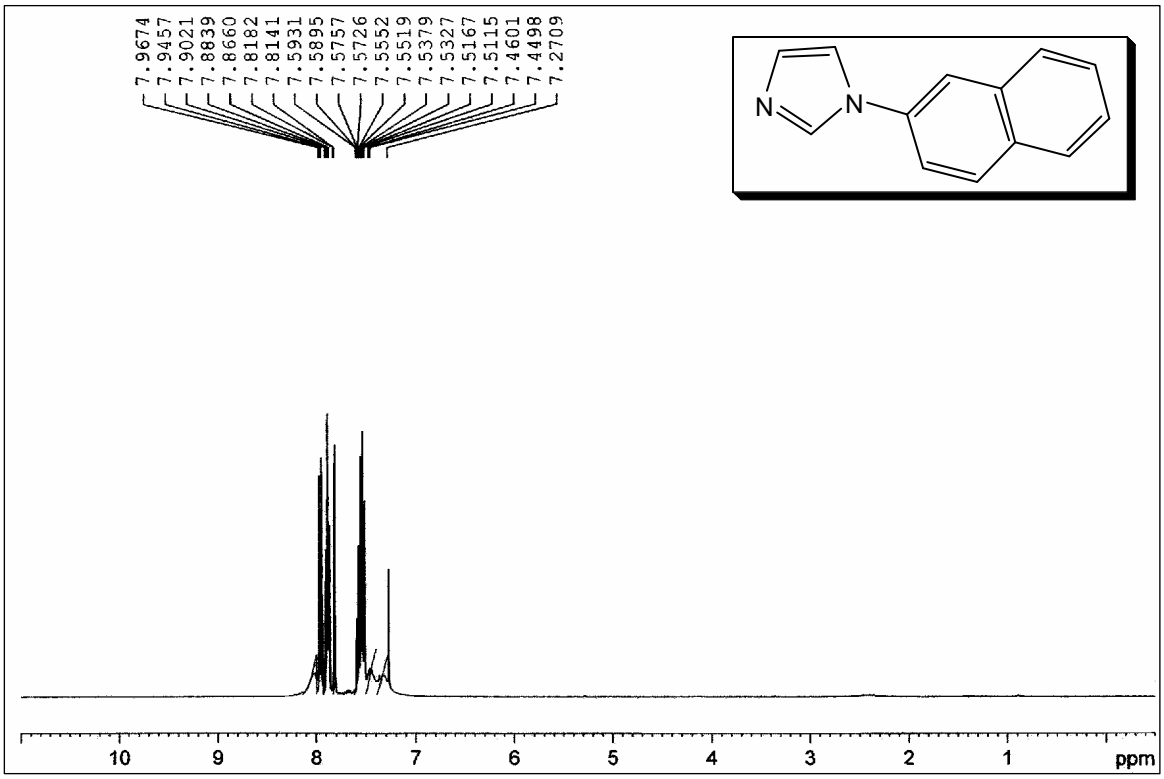


Fig. 28 ^{1}H-NMR spectrum of 1-(naphthalen-2-yl)-1H-imidazole **4o** (400 MHz, $CDCl_3$)

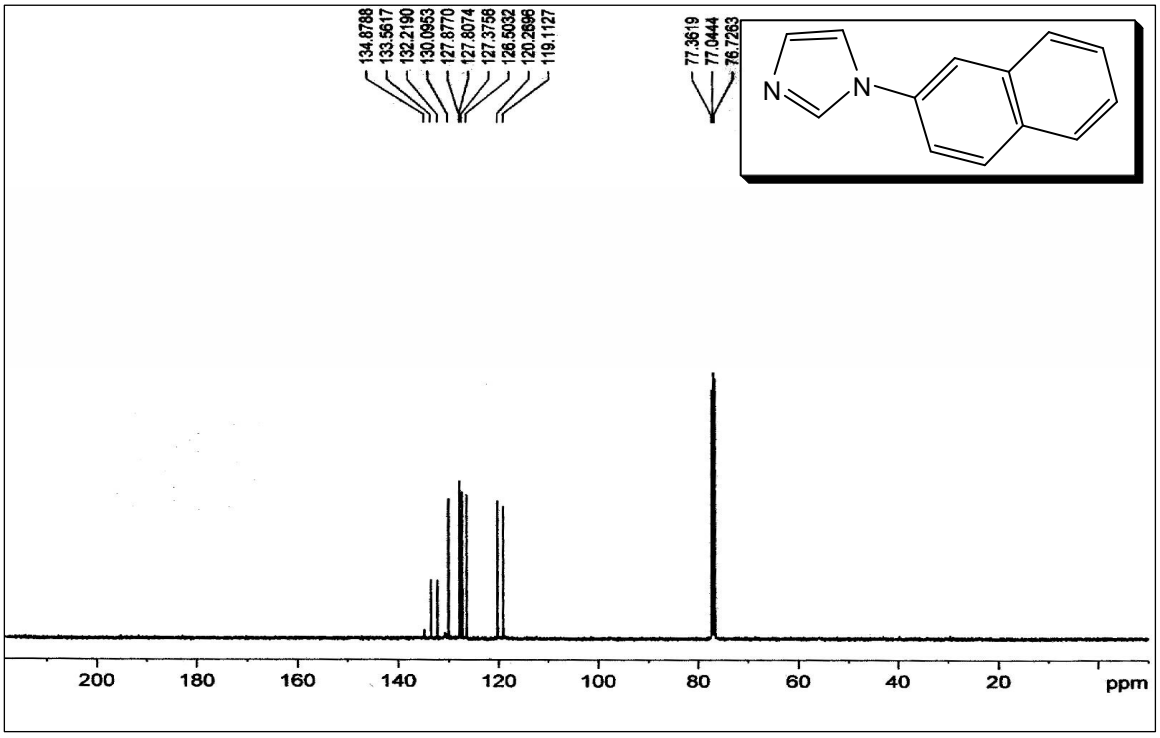


Fig. 29 ^{13}C-NMR spectrum of 1-(naphthalen-2-yl)-1H-imidazole **4o** (100 MHz, $CDCl_3$)

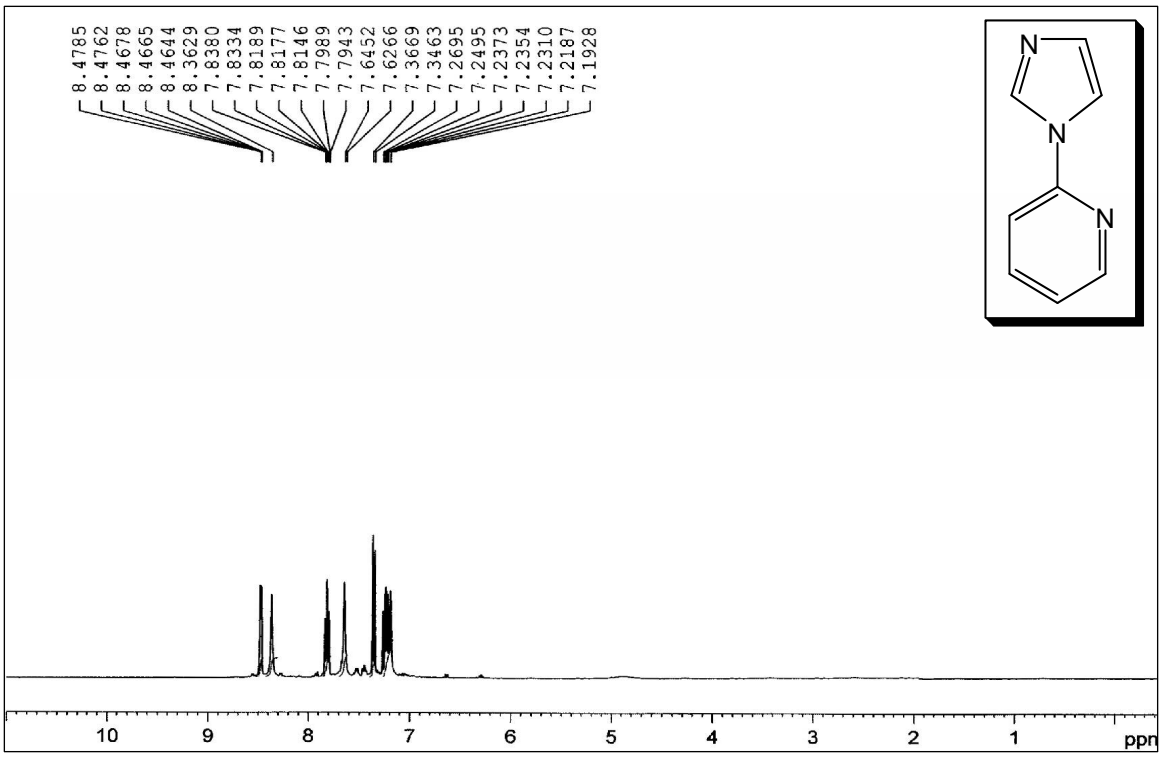


Fig. 30 ^{1}H-NMR spectrum of 2-(1H-imidazol-1-yl)pyridine **4p** (400 MHz, $CDCl_3$)

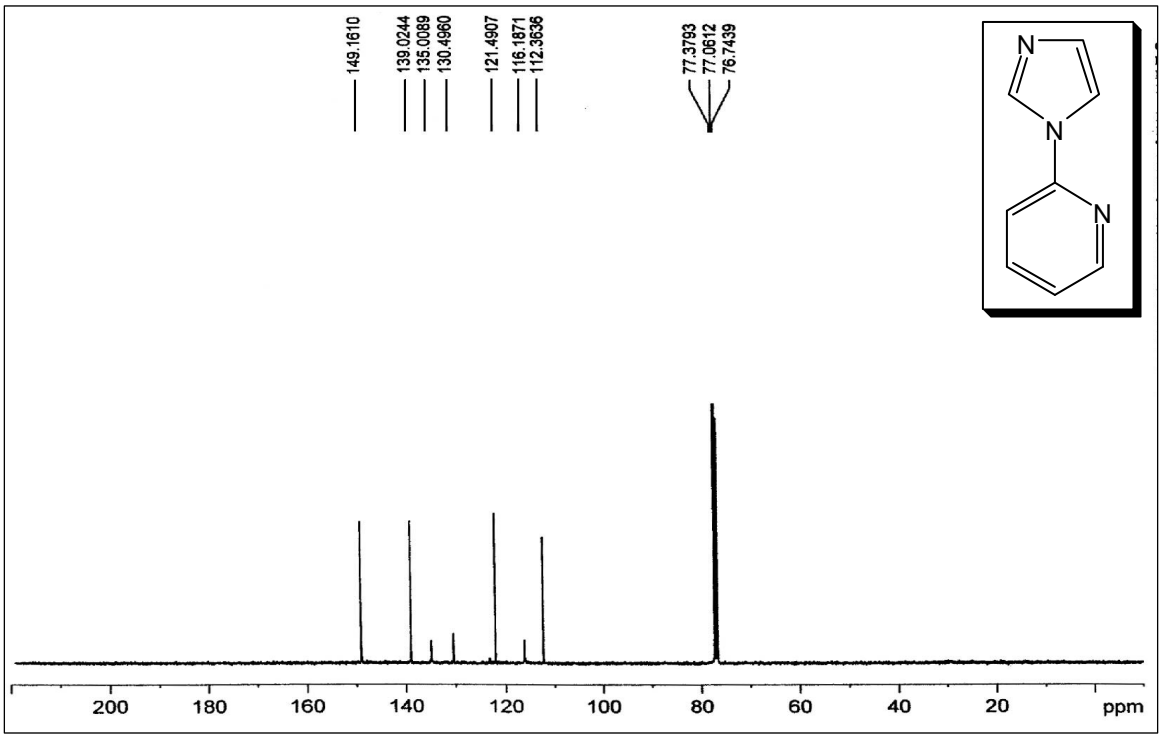


Fig. 31 ^{13}C-NMR spectrum of 2-(1H-imidazol-1-yl)pyridine **4p** (100 MHz, $CDCl_3$)

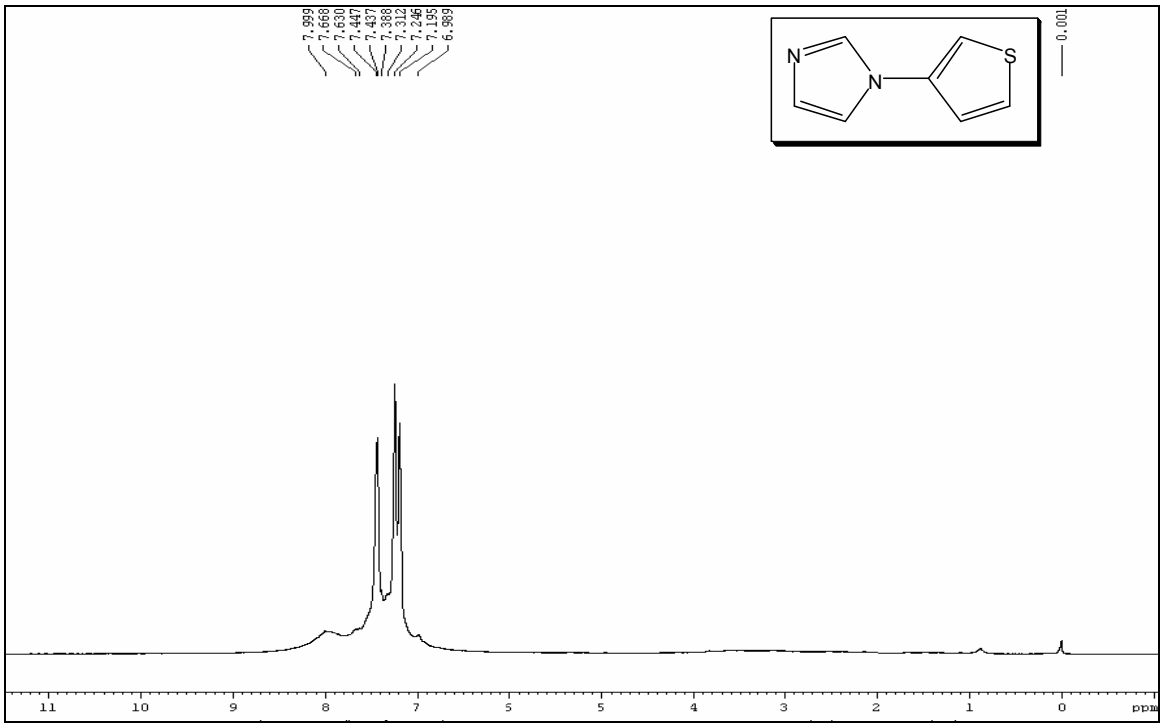


Fig. 32 ^{1}H-NMR spectrum of 1-(thiophen-3-yl)-1H-imidazole **4q** (300 MHz, $CDCl_3$)

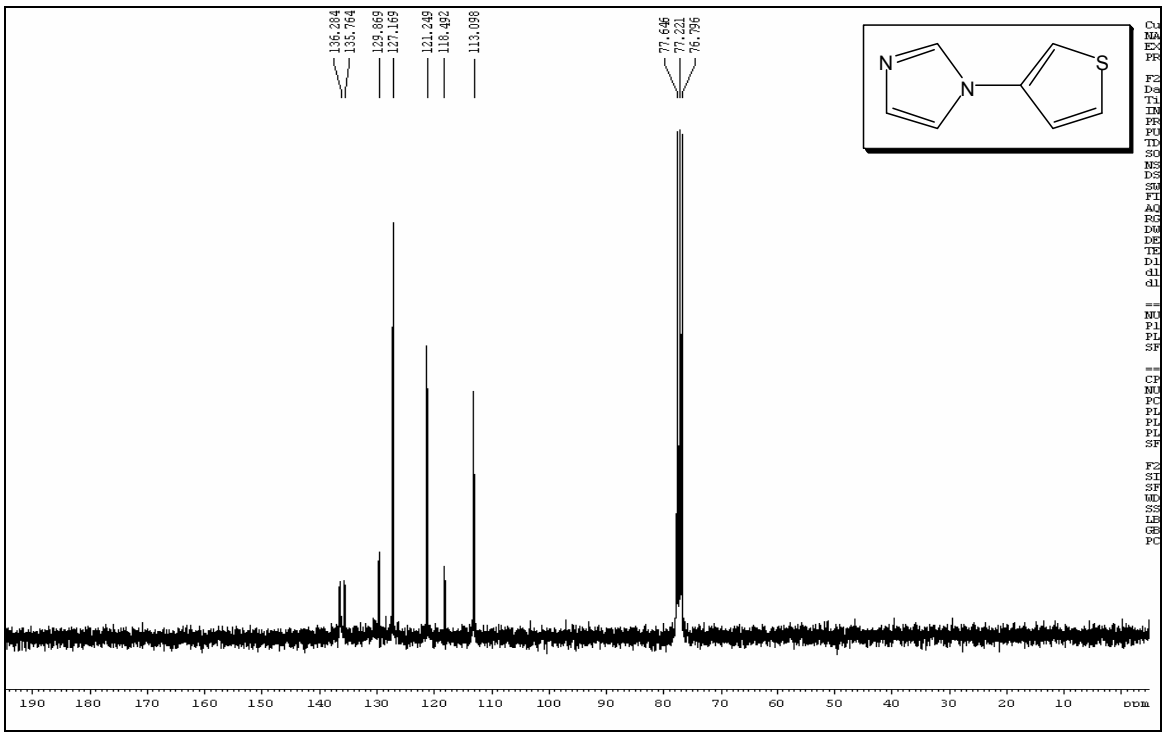


Fig. 33 ^{13}C-NMR spectrum of 1-(thiophen-3-yl)-1H-imidazole **4q** (75 MHz, $CDCl_3$)

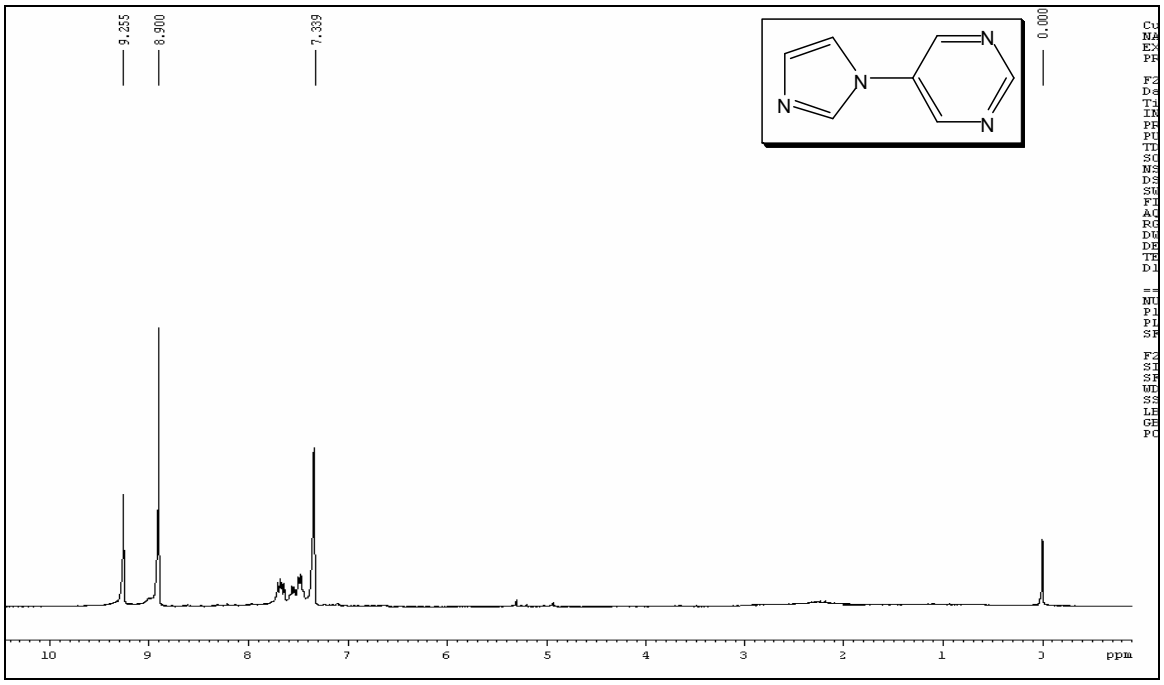


Fig. 34 ^{1}H-NMR spectrum of 5-(1H-imidazol-1-yl)pyrimidine **4r** (300 MHz, $CDCl_3$)

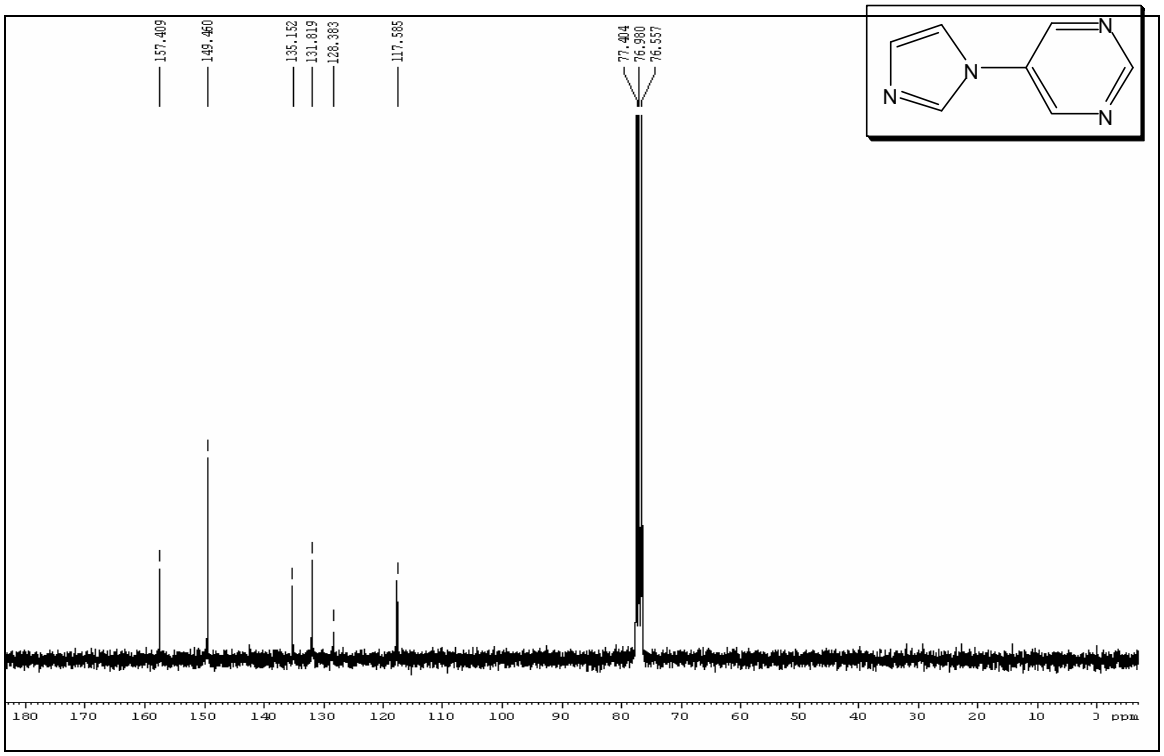


Fig. 35 ^{13}C-NMR spectrum of 5-(1H-imidazol-1-yl)pyrimidine **4r** (75 MHz, $CDCl_3$)

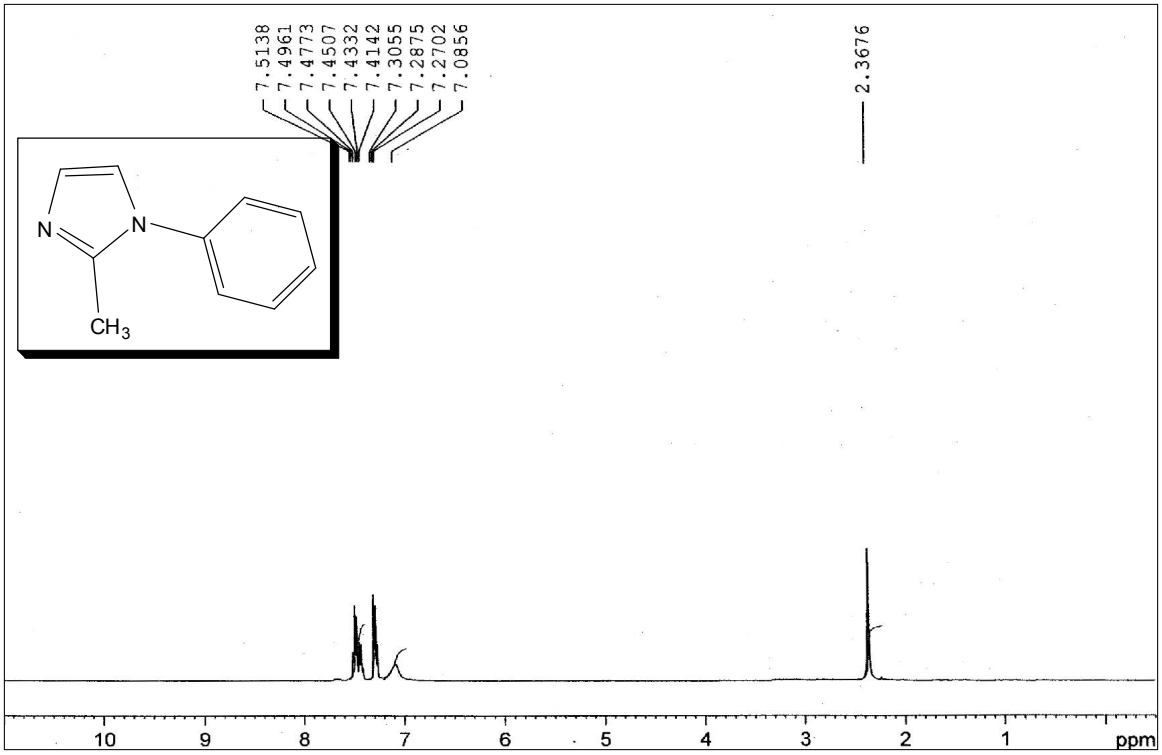


Fig. 36 ^{1}H-NMR spectrum of 2-methyl-1-phenyl-1H-imidazole (400 MHz, $CDCl_3$)

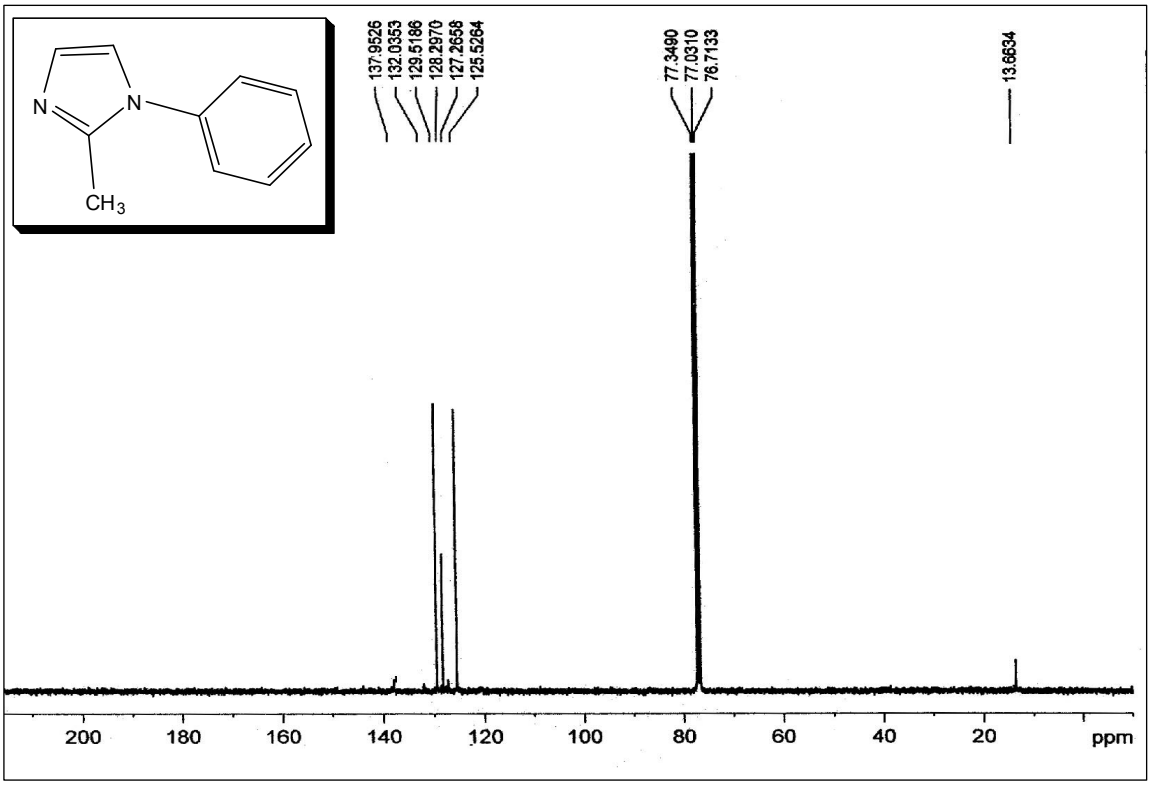


Fig. 37 ^{13}C-NMR spectrum of 2-methyl-1-phenyl-1H-imidazole (100 MHz, $CDCl_3$)

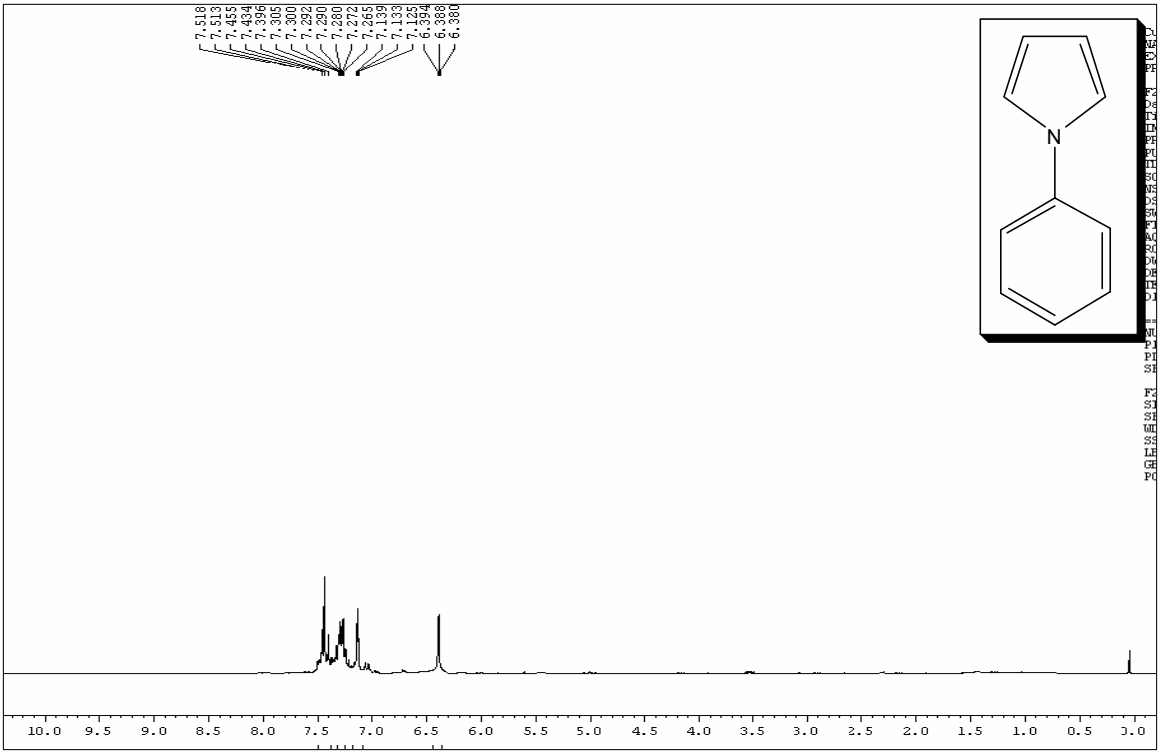


Fig. 38 ^{1}H-NMR spectrum of 1-phenyl-1H-pyrrole (300 MHz, $CDCl_3$)

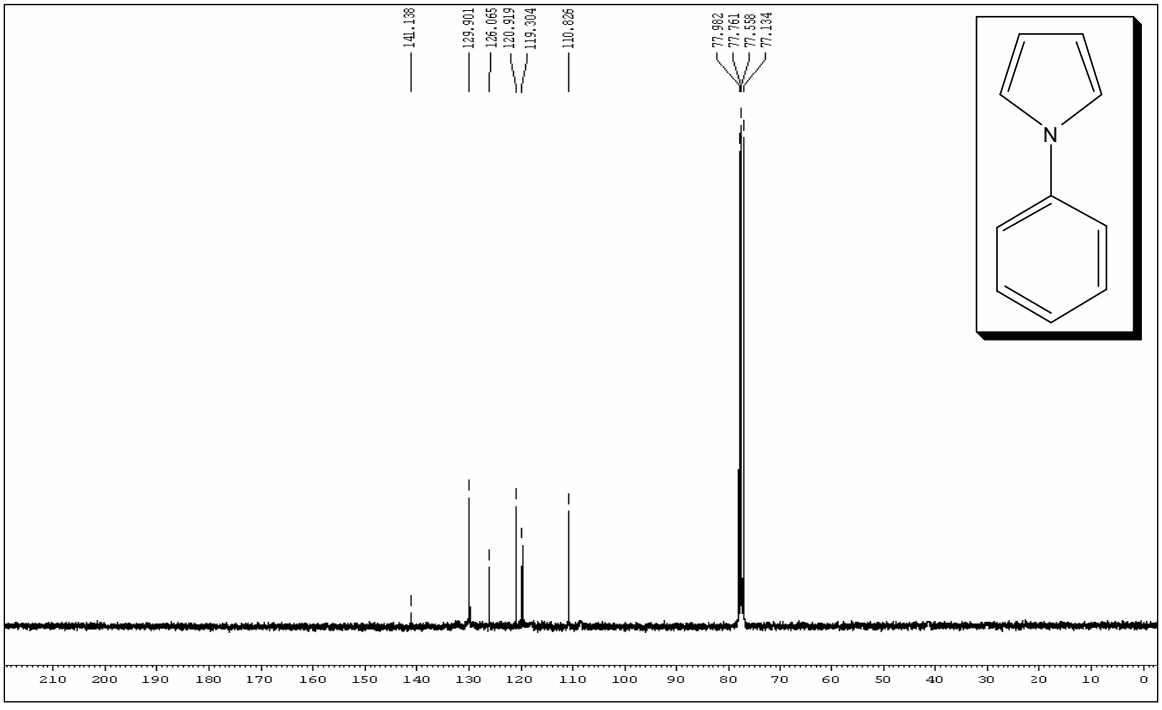


Fig. 39 ^{13}C-NMR spectrum of 1-phenyl-1H-pyrrole (75 MHz, $CDCl_3$)

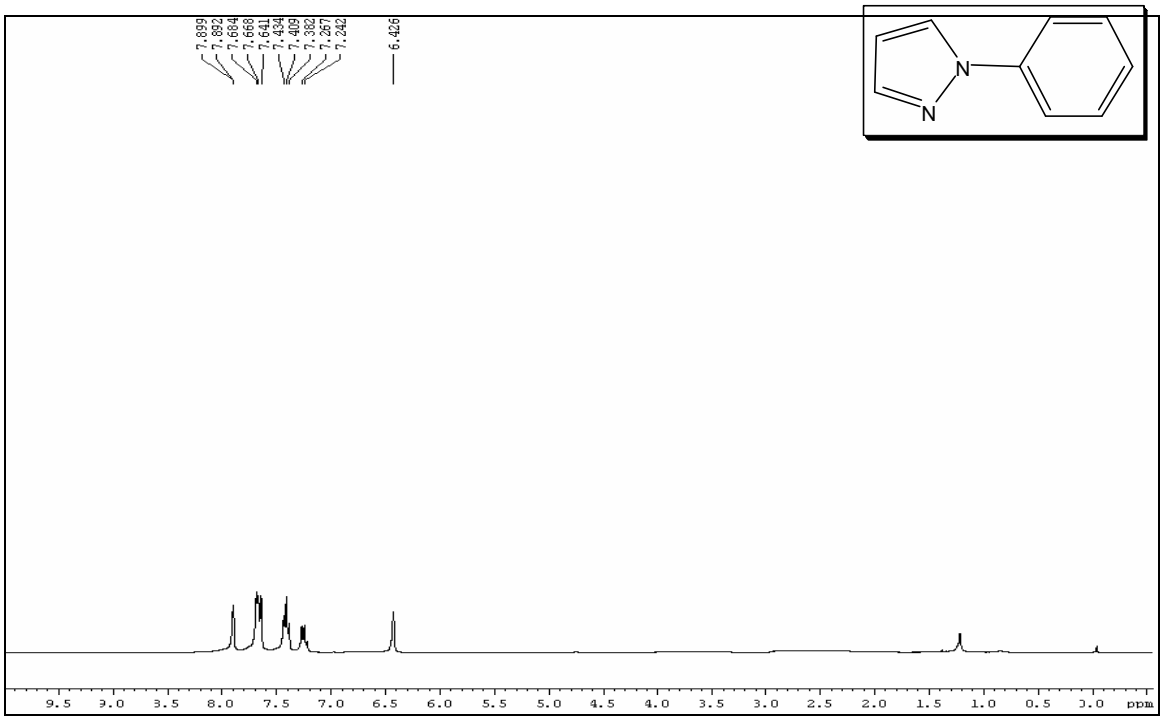


Fig. 40 ^{1}H-NMR spectrum of 1-phenyl-1H-pyrazole (300 MHz, $CDCl_3$)

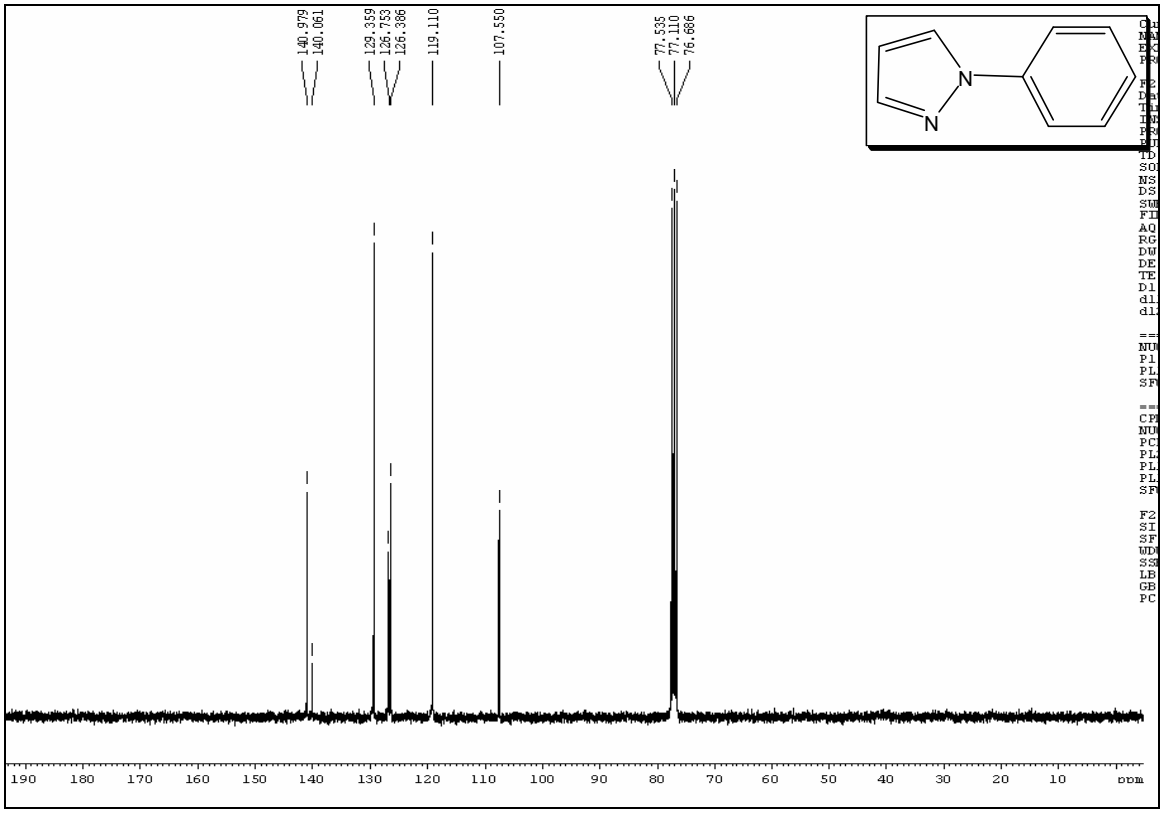


Fig. 41 ^{13}C-NMR spectrum of 1-phenyl-1H-pyrazole (75 MHz, $CDCl_3$)

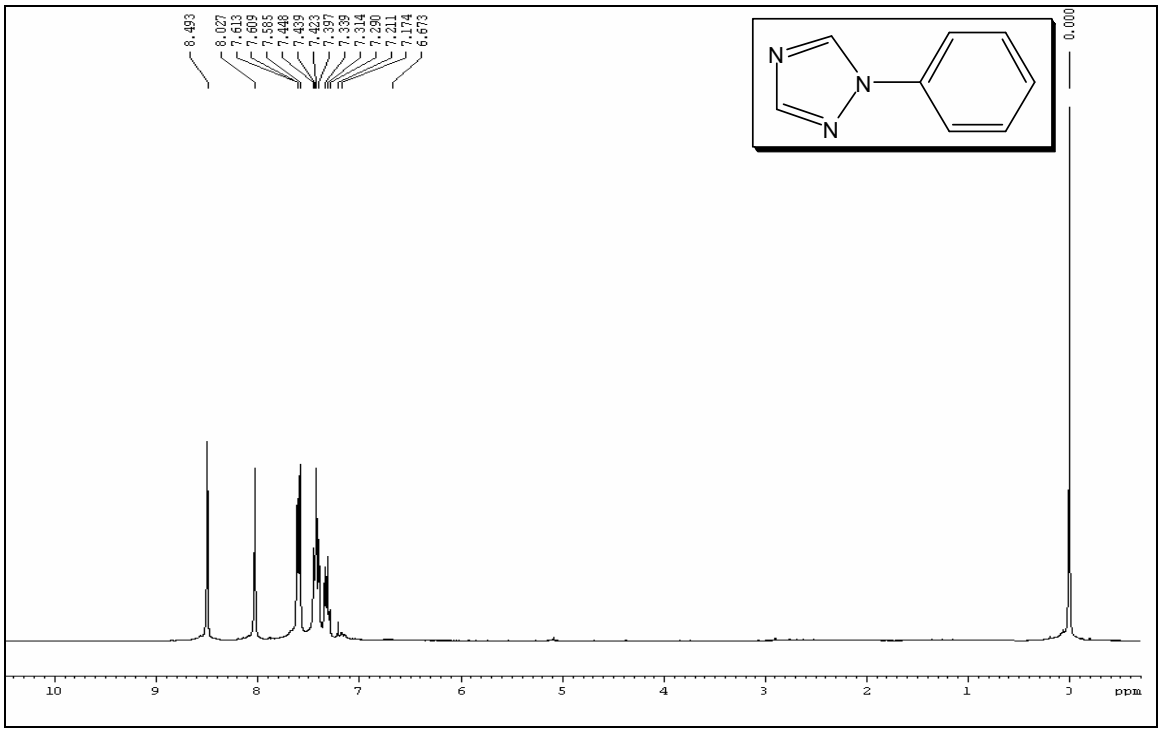


Fig. 42 ^{1}H-NMR spectrum of 1-phenyl-1H-1,2,4-triazole (300 MHz, $CDCl_3$)

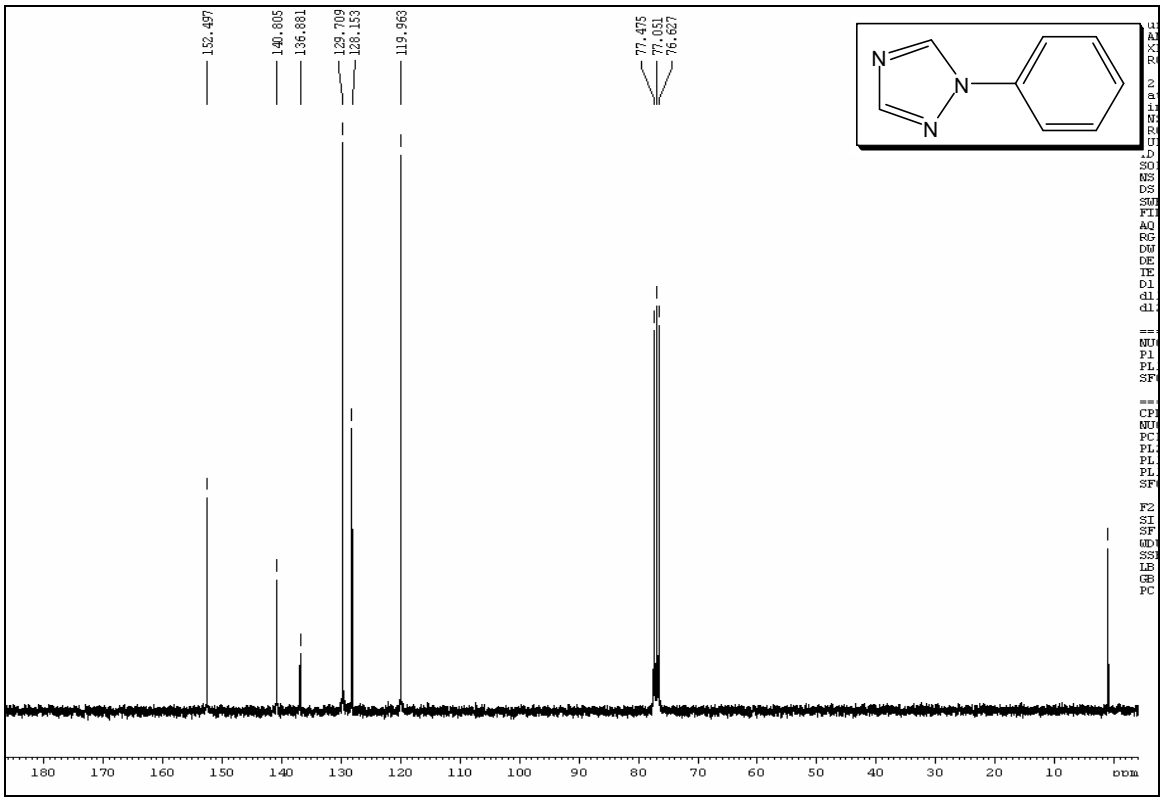


Fig. 43 ^{13}C-NMR spectrum of 1-phenyl-1H-1,2,4-triazole (75 MHz, $CDCl_3$)

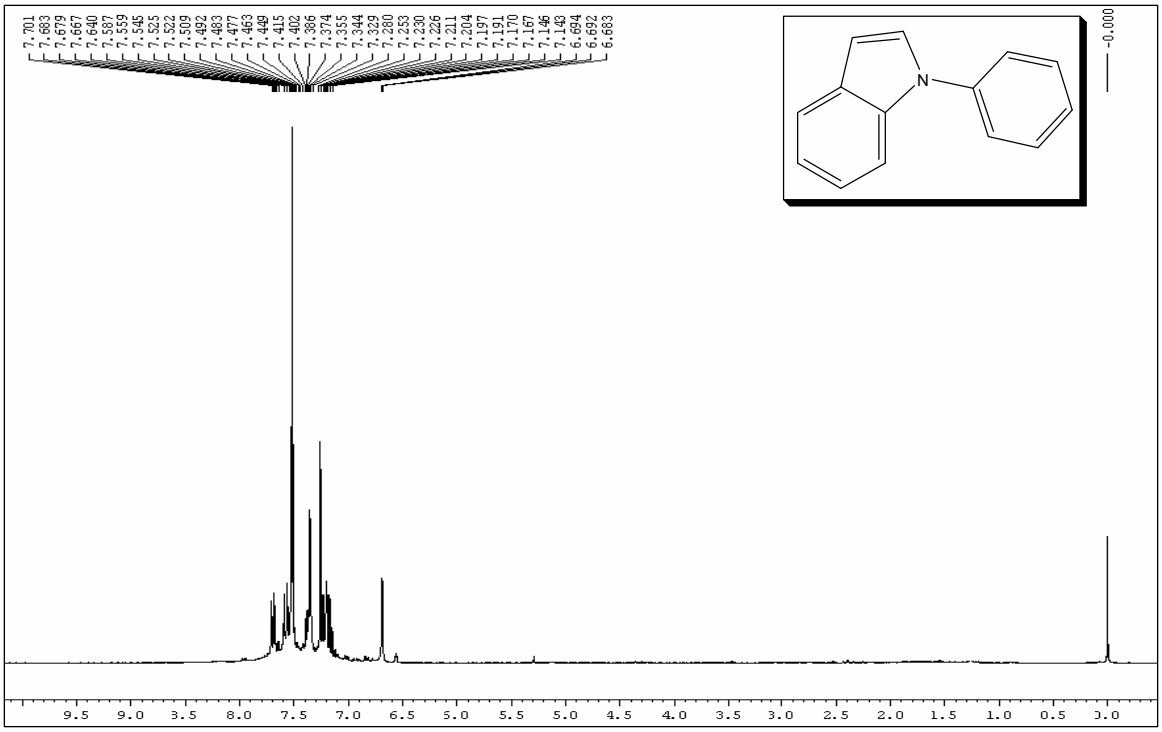


Fig. 44 ^{1}H-NMR spectrum of 1-phenyl-1H-indole (300 MHz, $CDCl_3$)

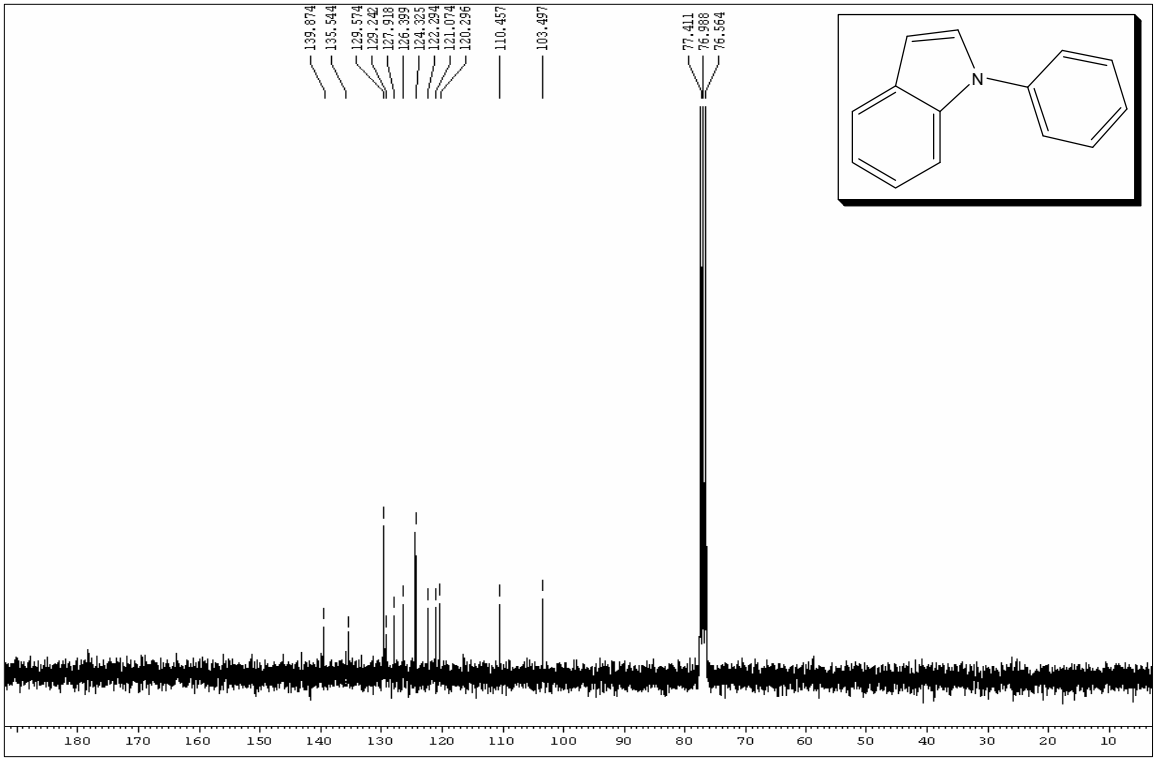


Fig. 45 ^{13}C-NMR spectrum of 1-phenyl-1H-indole (75 MHz, $CDCl_3$)

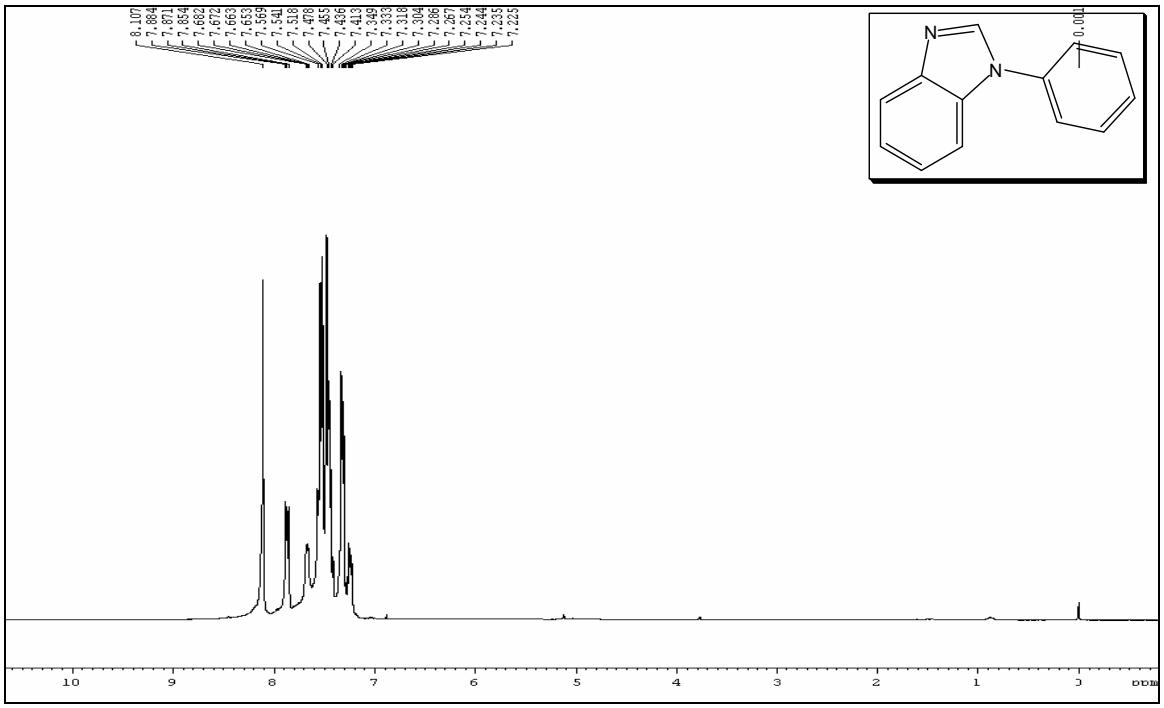


Fig. 46 ^{1}H-NMR spectrum of 1-phenyl-1H-benzo[d]imidazole (300 MHz, $CDCl_3$)

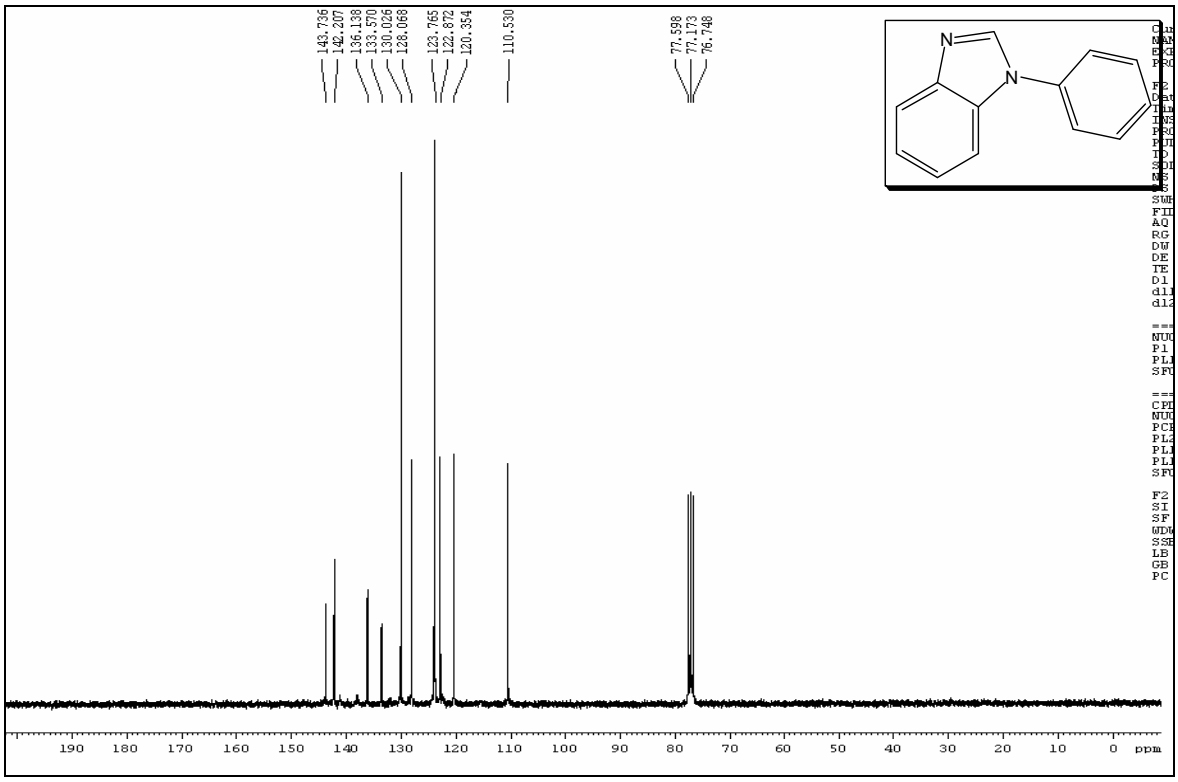


Fig. 47 ^{13}C-NMR spectrum of 1-phenyl-1H-benzo[*d*]imidazole (75 MHz, $CDCl_3$)