Supporting Information

Nano Fe_3O_4 supported Biimidazole Cu(I) Complex as a retrievable catalyst for the synthesis of imidazo[1,2-a]pyridines in aqueous medium

Mahmood Tajbakhsh,* Maryam Farhang, Rahman Hosseinzadeh, Yaghoub Sarrafi

Faculty of Chemistry, Mazandaran University, Babolsar, 47415, Iran

Fax: (+98)1125242002, E-mail: Tajbaksh@umz.ac.ir

Email: Tajbaksh@iauamol.ac.ir

1. General Information:

The MNP@BiimCu catalyst was characterized by various techniques such as elemental analyzed (CHN), NMR, FT-IR, TG, SEM, TEM, EDS, XRD, AAS, ICP- OES and vibrating sample magnetometer (VSM) which revealed the superparamagnetic nature of the particles. All chemicals were purchased and used without any further purification. NMR spectra were recorded at 400 MHz for proton and at 100 MHz for carbon nuclei in ($CDCl_3$).

2. Characterizations of Catalyst:

The FT-IR spectra of MNPs (a), MNP@SiO_2 (b), MNP@CPS (c), Bim (d) and MNP@BiimCu (e) were shown in Fig. 1.

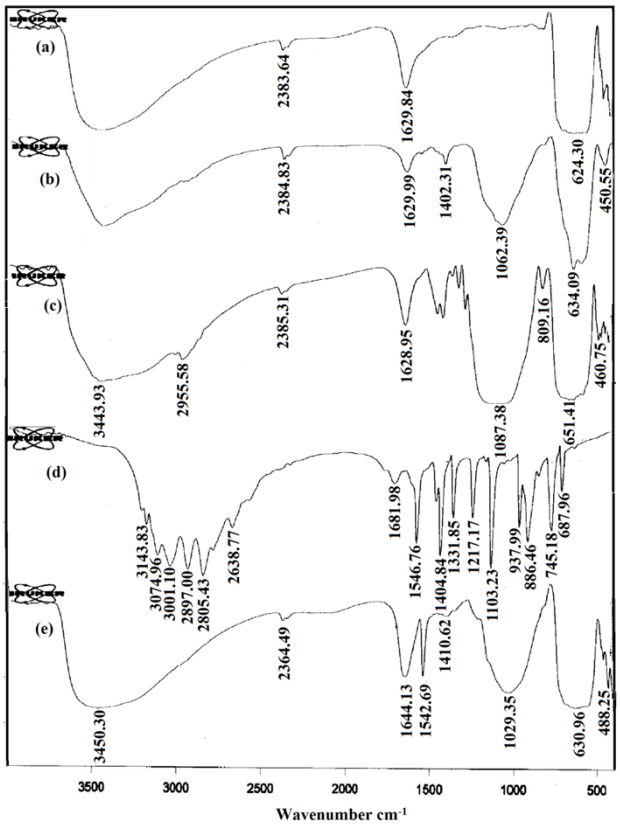


Fig 1. FTIR spectra of MNPs (a), MNP@SiO_2 (b), MNP@CPS (c), Bim (d), MNP@BiimCu (e).

XRD pattern: The X-ray diffraction analysis was done in a Philips PW 1830 X-ray diffractometer with CuKα source.

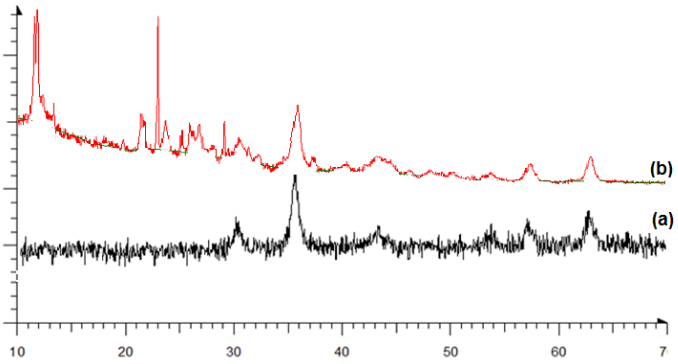


Fig. 2. XRD patterns of MNPs (2a) and MNP@BiimCu (2b)

Thermo gravimetric analysis (TG) results indicate the loading amount of functionalized organic groups on magnetic were 1.4 mmol/g.

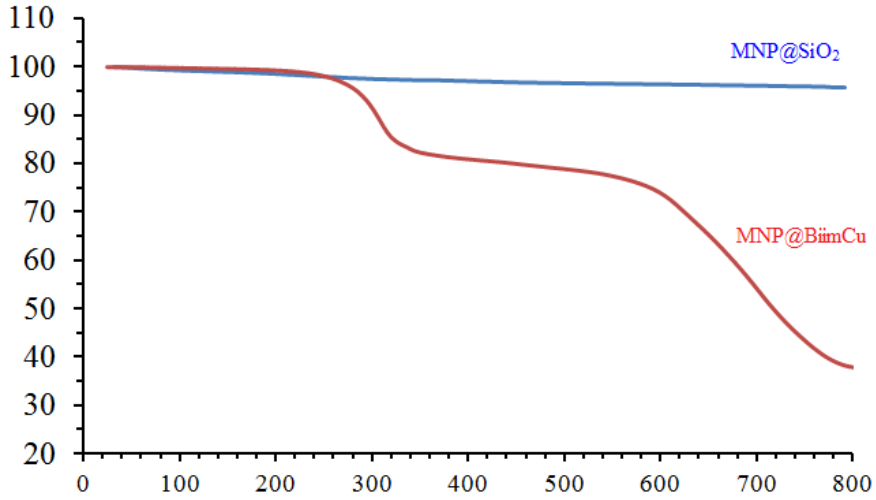


Fig. 3.The TGA thermogram of (a) MNP@SiO_2 (b) MNP@BiimCu 10 °C/min under N_2 atmosphere

The morphology of the powders was investigated by scanning electron microscopy (SEM). SEM analysis (Fig. 5) of the Nano-magnetic catalyst showed uniform-sized particles with spherical morphology with an average size range of 20–25 nm. Fig. 6 displays HRTEM image of MNP@BiimCu nanoparticles. As may be seen in the TEM image, the size of particles is around 15 nm and the particles are spherical in shape with some agglomeration, which is obvious because of the magnetic nature of the particles.

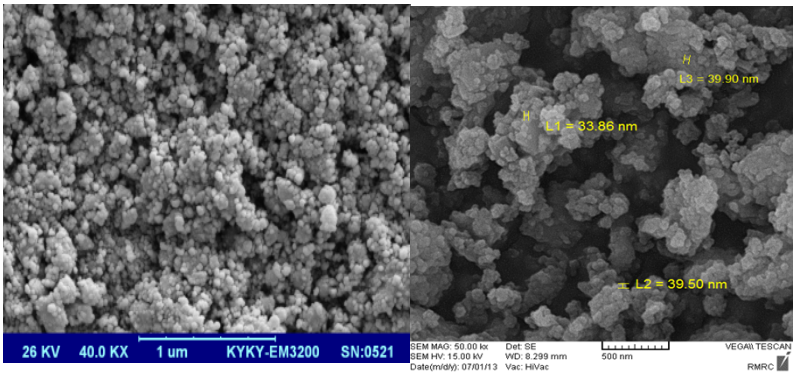


Fig. 5. SEM images of synthesized MNP@BiimCu (left) used (right)

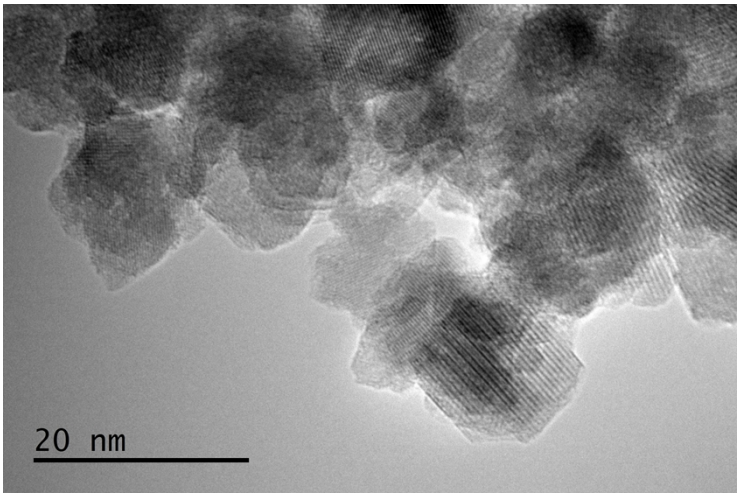


Fig. 6. Transmis sion elect ron microscopy (TEM) image of MNP@BiimCu.

Elemental analysis for $MNP@SiO_2$, MNP@CPS and MNP@BiimCu were carried out and the data were tabulated in Table 1 which is shown to be in good agreement with the result obtained from TGA (Fig. 3). Further to support the above observation, the EDX analysis of magnetic nanocatalyst indicates that CuI was chelated on the surface of MNP@Biim nanoparticles (Fig. 4).

Table1. Elemental analysis for $MNP@SiO_2$, MNP@CPS and MNP@BiimCu

Samples	C%	H%	N%	Cu%
$MNP@SiO_2$	0.10	0.21	-	-
MNP@CPS	5.85	1.50	-	-
MNP@BiimCu	14.59	2.17	8.21	7.3[a], 7.97[b],7.92[b.c]

[a, b] The amount of copper was determined using [a]AAS and [b]ICP,

[c] Recycled after ten times

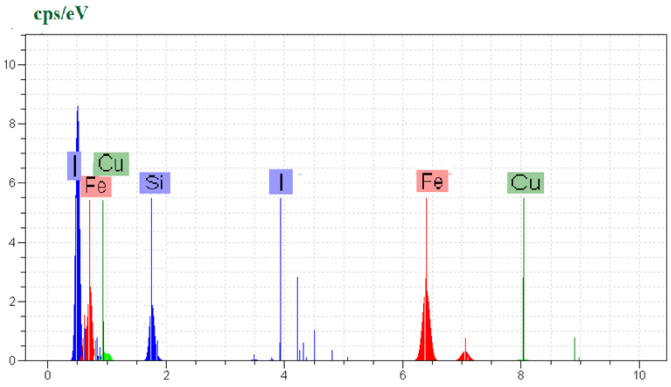


Fig. 4. EDS pattern of MNP@Biim Cu

The magnetic hysteresis measurements of both MNP@SiO_2 and MNP@BiimCu nanocrystallites obtained by VSM at 300 K, with the field sweeping from −8000 to +8000 Oe. As shown in Fig. 7 the relatively high saturation magnetization of synthesized nanoparticles is sufficient for magnetic separation with a conventional magnet (Fig. 7c).

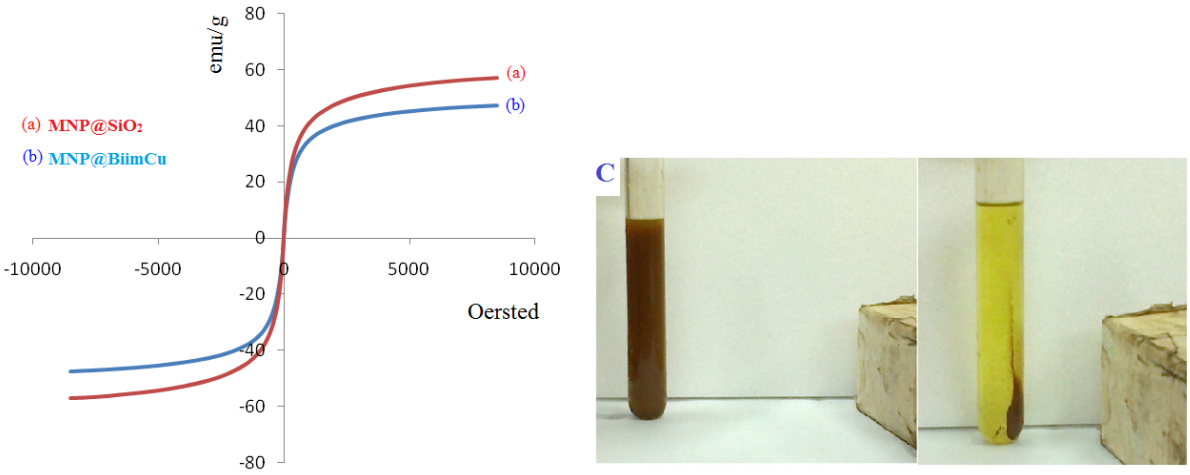


Fig. 7. VSM curve of MNP@SiO2 (a) vs. MNP@BiimCu (b),

(c) MNP@BiimCu ability to effective recovery at the end of reaction

3. Synthesis of Catalyst:

3.1 General details

Chemical materials were purchased from Merck and Aldrich Chemical Company in high purity. All the solvents were distilled, dried and purified by standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. The samples were analyzed using FT-IR spectroscopy (Bruker Vector 22Perkin Elmer 65 in KBr matrix). The X-ray powder diffraction (XRD) of the catalyst was carried out on a Philips PW 1830 X-ray diffractometer with CuKα source (λ=1.5418 Å) in a range of Bragg's angle (5-80°) at room temperature. Scanning electron microscope (SEM) pictures-EDS analyses were taken using VEGA//TESCAN KYKY-EM3200 microscope (acceleration voltage 26 kV). Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. The samples for TEM measurements were suspended in ethanol by sonication and then drop drying on a copper grid (400 mesh) coated with carbon film. ^{1}H, ^{13}C NMR spectra were recorded on a BRUKER DRX-400 AVANCE spectrometer. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 20 eV.Magnetic measurements were performed using vibration sample magnetometry (VSM, (MDK Co. Kashan, Iran) analysis**.** A simultaneous ICP-OES (Varian Vista-Pro, Springvale, Australia) coupled to a V-groove nebulizer and equipped with a charge cou-pled device (CCD) was applied for determination of the trace.

3.2. Preparation of 2,2'-biimidazole(Biim)I

To a mixture of ammonium acetate (0.46 mol, 35.4 g) and H_2O (6.5 mL) was added dropwise glyoxal (0.173 mol, 10.0 g) solution (20%) at 40 °C over a period of 3 h then the mixture was allowed to stir for an additional 5h at room temperature. The reaction mixture was filtered and then washed with distilled water (3 ×20 mL) and acetone (3 ×20 mL) to give a crude product. The brown solid was dissolved in 130 ml of hot ethylene glycol, and decolorized with activated carbon. After hot filtration, the product precipitated instantly to provide 3.2 g (42%) of white crystalline **I**[1].

3.3. Preparation of 3-chloropropyl-functionalized magnetic nanoparticles (MNP@CPS)

A mixture of $FeCl_3 \cdot 6H_2O$ (2.35 g, 8.7 mmol) and $FeCl_2 \cdot 4H_2O$ (0.86 g, 4.3 mmol) were dissolved in 40 ml deionized water. The resultant solution was left to be stirred for 30 min at 80 ºC. Then 5 mL of NH_4OH solution was added with vigorous stirring to produce a black solid and the reaction was continued for another 30 min. The black magnetite nanoparticles were isolated by magnetic decantation, washed several times with deionized water and then dried at 80 ºC for 10 h.

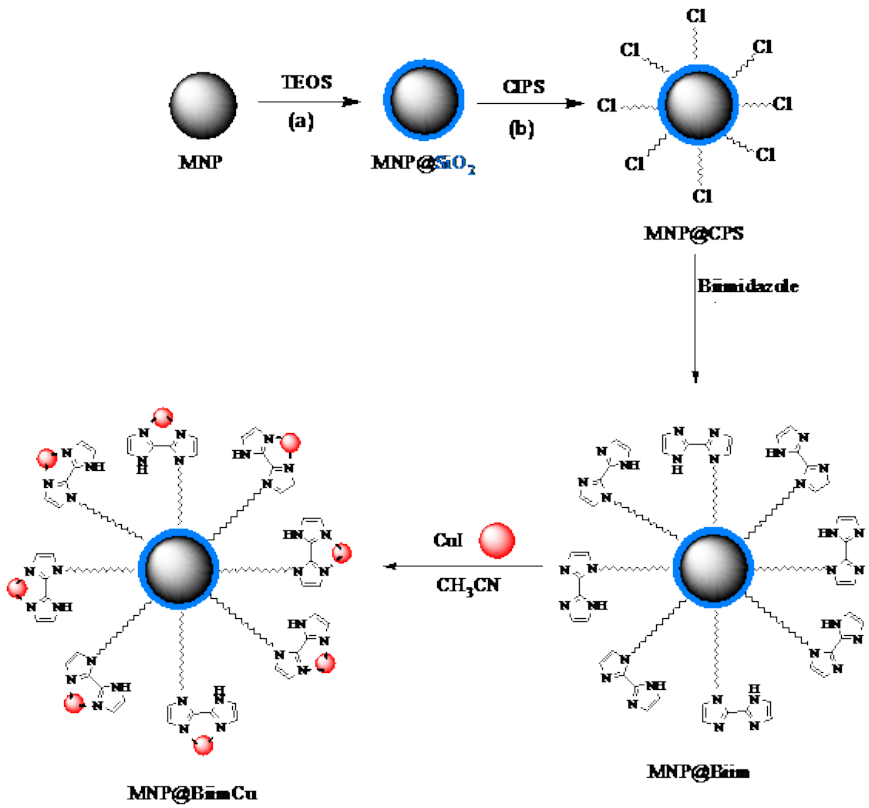
0.5 g of dried Fe_3O_4 nanoparticles were suspended in a mixture of 50 mL ethanol and 5 mL of $NH_3 \cdot H_2O$. Then, 0.2 mL of tetraethoxysilane (TEOS) was added to solution and the mixture was ultrasonicated for 2 h. Afterward silica coated MNP (MNP@SiO_2) was magnetically separated, washed three times with ethanol and dried at 80 ºC for 10 h.

MNP@SiO_2 (100mg) was dispersed in 15 ml of dry toluene by ultrasonication under nitrogen atmosphere. Next, 3-chloropropyltriethoxysilane (0.2 mL, 0.8mml) was dropwise added into the MNP@SiO_2 solution under reflux condition for 48 h[25].The CPS functionalized magnetic nanoparticles (MNP@CPS) was washed with 30 mL of toluene and ethanol before being dried at 60 ºC for 12 h.

3.4. Preparation of MNP@BiimCu catalyst

Sodium hydride 2.4 g (0.06 mol) was suspended in 5 mL of dry DMF under inert atmosphere. To this suspension, 6.7 g of Biimidazole (0.05 mol) was added and stirred for 30 more minutes at room temperature. The MNP@CPS (1.8 gr) was then added to this suspension and mixture was stirred at 65 ºC for 2 days. The dark brown precipitate formed was filtered, washed with water and methanol and then soxhlet extraction by hot methanol to remove no reacted specie and dried under vacuum at 70 ºC.

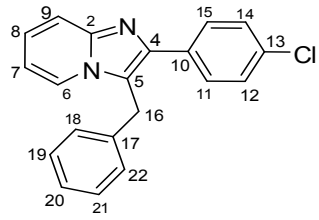
A mixture of MNP@Biim (2 g), copper iodide (500 mg) and dry acetonitrile (30 ml) was stirred at room temperature under nitrogen atmosphere for 48 h. The resulting solid was then separated by an external magnet and washed with acetonitrile and acetone for several times. The residue was dried for 24 h in air to afford the Nano Fe_3O_4 supported Biimidazole Cu(I) Complex (MNP@BiimCu).



Preparation of MNP@BiimCu a) 50 ml EtOH (50mL), $NH_3 \cdot H_2O$ (5 ml), TEOS (0.2 ml) for 2h; b) dry toluene (15 mL), CPTES (0.2 ml), reflux for 48h; c) Bim (6.7 g), NaH (2.4g) in DMF (15 ml) in 65 ºC for 48 h, d) CuI (0.5g) and dry CH_3CN (30 ml) under N_2 for 48h

5. General procedure for the synthesis of imidazo[1,2-a]pyridine derivatives

In a 10 mL round bottomed flask, a mixture of 2-aminopyridine (1 mmol) and benzaldehyde (1 mmol) was stirred. After 20 min, phenylacetylene (1.1 mmol), MNP@Bim Cu (0.01 g, 1.4 mol %), 0.005g CTAB and 2mL H_2O were added to the above mixture and the resulting mixture was allowed to stir under reflux conditions for specified period of time. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction the catalyst was magnetically separated. The residue was extracted with EtOAc (2×10 mL) followed by drying with anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography to afford the desired product.



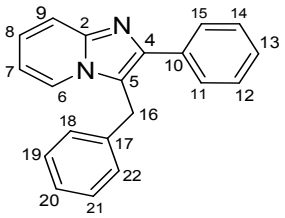
3-Benzyl-2-(4-chlorophenyl)imidazo[1,2-a]pyridine (Table 2,Entry 1) [2,3,4,5 and 6].

White solid, mp 146°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69−7.73 (m, 4H), 7.31-7.35 (m, 2H), 7.25−7.29 (m, 3H), 7.19−7.22 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.73 (dt, *J* = 6.60 Hz, *J* = 1.2 Hz, 1H), 4.51 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8(C2), 144.1(C4), 137.6(C13), 131.5(C13),130.1(C18 and 22), 129.6(C10), 129.4(C11 and 15), 129.0(C21 and 19), 127.7(C5), 126.9(C20), 124.1(C12 and 14), 123.4(C6), 117.5(C8), 117.4(C9), 112.2(C7), 29.9(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{15}ClN_2$: 318.0925, found: 318.0913.



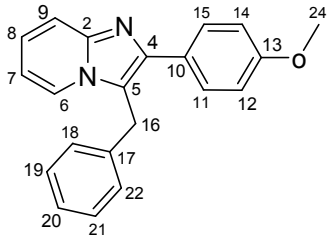
3-Benzyl-2-phenylimidazo[1,2-a]pyridine (Table 2, Entry2). [2,3,4,5 and 6]

White crystalline solid, mp 119-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80−7.82 (m, 2H), 7.70−7.74 (m, 2H), 7.43 (td, *J* = 6.0 Hz, *J* = 1.2 Hz, 2H), 7.29-7.39 (m, 4H), 7.19−7.23 (m, 1H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.71 (dt, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 4.53 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.9(C2), 144.2(C4), 136.8(C17), 134.4(C10), 129.0(C18, 22), 128.7(C19, 21), 128.2(C11,15), 127.75(C12, 14), 127.73(C13) 126.9(C2), 124.2(C5), 123.4(C6), 117.9(C8), 117.3(C9), 112.2(C7), 29.9(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{16}N_2$: 284.1315, found: 284.1302.



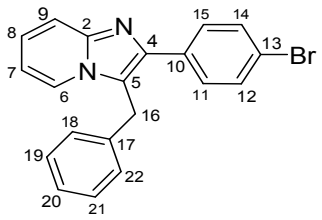
3-Benzyl-2-(4-methoxyphenyl)imidazo[1,2-a]pyridine (Table 2, Entry3).[5,6]

White crystalline solid; mp 130-132°C.

^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.73 (m, 4H), 7.31–7.26 (m, 4H), 7.16 (m, 2H), 7.07 (d, *J* = 6.8 Hz, 2H), 6.79 (m, 1H), 4.50 (s, 2H, CH_2), 3.89 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.3(C13), 145.1(C2), 144.1(C4), 136.8(C17), 129.8(C18, 22), 129.3(C11,15), 128.2(C19, 21), 127.6(C10), 127.2(C5), 124.5(C20), 123.1(C6), 117.6(C8), 117.1(C9), 114.4(C7), 112.2(C12, 14), 54.2(C24), 30.8(C16).

HRMS (ESI) [M+H] calcd for $C_{21}H_{18}N_2O$: 315.1491, found: 315.1483.



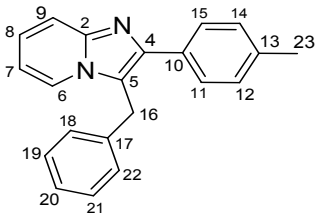
3-Benzyl-2-(4-bromophenyl)imidazo[1,2-a]pyridine (Table2, Entry4).[2,4 and 5]

Yellow crystals: decomposes at 160°-162C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73−7.67 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.33−7.26 (m, 3H), 7.18 (t, *J* = 8.4 Hz, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.72 (t, *J* = 6.9 Hz, 1H), 4.43 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.1(C2), 143.2(C17), 136.8(C4), 133.5(C11,15), 131.7(C18, 22), 130.1(C10), 129.3(C19, 21), 127.9(C5), 127.3(C20), 124.8(C12, 14), 123.5(C6), 122.1(C8), 117.7(C13), 117.6(C9), 112.3(C7), 29.7(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{15}BrN_2$: 363.2543, found: 363.2536.



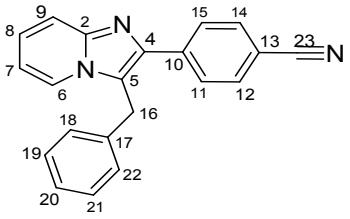
3-Benzyl-2-p-tolylimidazo[1,2-a]pyridine (Table 2,Entry 5).[5,6 and 7]

Light yellow solid; mp 160 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (m, 4 H), 7.31-7.34 (m, 4H), 7.25-7.27 (m, 1H), 7.16 - 7.22 (m, 3H), 6.72 (t, *J* = 7.6 Hz, 1H), 4.52 (s, 2H, CH_2), 2.41 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl3) δ = 144.9(C2), 144.2(C4), 137.5(C17), 136.8(C13), 131.4(C18, 22), 129.1(C10), 128.9(C19, 21), 128.3(C12, 14), 127.7(C11, 15), 126.9(C5), 124.2(C20), 123.4(C6), 117.7(C8), 117.4(C9), 112.0(C7), 29.9(C16), 21.3. (C23).

HRMS (ESI) [M+H] calcd for $C_{21}H_{18}N_2$: 298.1473, found: 298.1466.



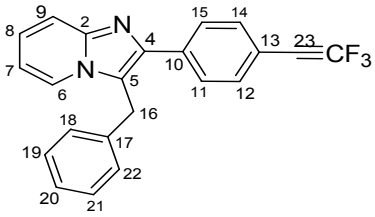
4-(3-Benzylimidazo[1,2-a]pyridin-2-yl)benzonitrile (Table 2,Entry 6).[2,4 and 5]

Light yellow solid; mp 135−136 °C.

1H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 6.6 Hz, 2H), 7.72 (d, *J* = 6.7 Hz, 1H), 7.70−7.64 (m, 3H), 7.36−7.27 (m, 3H), 7.24−7.20 (m, 1H), 7.10 (d, *J*= 6.8 Hz, 2H), 6.72 (m, 1H), 4.49 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.4(C2), 141.9(C10), 138.7(C17), 136.3(C18, 22), 132.2(C4), 129.2(C12, 14), 128.5(C19, 21), 127.4(C11, 15), 127.1(C5), 125.0(C20), 123.6(C6), 120.1(C8), 118.1(C23), 117.9(C9), 112.8(C7), 112.4(C13), 29.6(C16).

HRMS (ESI) [M+H] calcd for $C_{21}H_{15}N_3$: 309.3645, found: 309.3649.



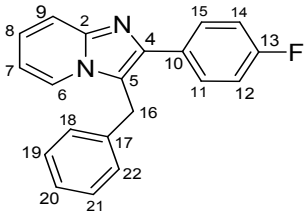
3-Benzyl-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (Table 2,Entry 7).[6]

White solid; mp 138-141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.2 Hz, 2H), 7.68-7.78 (m, 4 H), 7.24 - 7.36 (m, 3H), 7.19 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2 H), 6.76 (t, J = 7.2 Hz, 1 H), 4.49 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.6(C2), 143.5(C4), 137.6(C10), 136.2(C17), 129.1(C23), 128.3(C18, 22), 127.6(C13), 127.2(C11, 15), 125.8(C19, 21), 125.7(C5), 125.5(C20), 124.8(C12, 14), 124.2(C6), 118.8(C8), 116.7(C9), 112.6(C7), 29.8(C16).

HRMS (ESI) [M+H] calcd for $C_{21}H_{15}F_3N_2$: 352.1289, found: 352.1278.



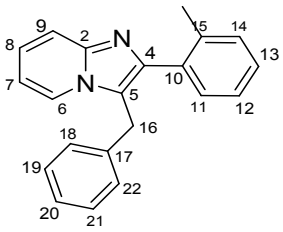
3-Benzyl-2-(4-fluorophenyl)imidazo[1,2-a]pyridine (Table 2,Entry 8).[2,4 and 6]

Light yellow oil; mp 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68-7.82 (m, 4H), 7.25−7.34 (m, 3H), 7.19-7.23 (m, 1H), 7.11−7.15 (m, 4H), 6.74 (t, J = 6.8 Hz 1H), 4.49 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6 (d, J_{C-F} = 245.4 Hz) (C13), 144.9(C2), 143.3(C4), 138.5(C17), 129.8(C18, 22), 129.5 (d, $J_{C-C-C-F}$ = 11.3 Hz) (C11, 15), 129.1(C10), 127.6(C19, 21), 127.0(C5), 123.9 (d, J_{C-C-F} = 94.9 Hz) (C12, 14), 117.6(C6), 115.7(C8), 115.5(C9), 112.3(C7), 29.8(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{15}FN_2$: 302.3412, found: 302.3414.



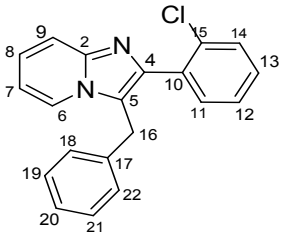
3-Benzyl-2-(2-methylphenyl)imidazo[1,2-a]pyridine (Table 2,Entry 9).[8]

Semisolid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67–7.72 (m, 2H), 7.46-7.53 (m, 4H), 7.19–7.38 (m, 4H), 7.15 (d, J = 7.2 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 4.29 (s, 2H, CH_2), 2.28 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2(C2), 144.5(C4), 138.6(C11), 137.3(C17), 134.1(C10), 130.8(C18, 22), 130.2(C13), 128.8(C15), 128.1(C19, 21), 126.7(C12), 125.5(C20, 5), 124.2(C6), 119.1(C14), 117.2(C8, 9), 112.4(C7), 29.8(C16), 21.3(C23).

HRMS (ESI) [M+H] calcd for $C_{21}H_{19}N_2$: 299.1549, found: 299.1556.



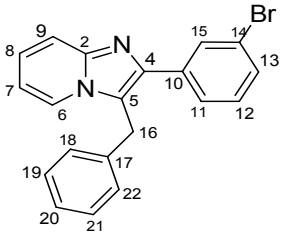
3-Benzyl-2-(2-chlorophenyl)imidazo[1,2-a]pyridine (Table 2,Entry 10).[5,6]

Brown crystalline solid; mp 116 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73–7.69 (m, 2H), 7.58–7.54 (m, 1H) 7.56–7.49 (m, 1H), 7.38–7.30 (m, 2H) 7.26 (d, *J* = 8.0 Hz, 2H), 7.25–7.12 (m, 2H), 7.03 (d, *J* = 5.3 Hz, 2H), 6.76 (t, *J* = 8.0 Hz, 1H), 4.32 (s, 2H, CH_2).

13CNMR (CDCl3, 125 MHz) δ = 145.3(C2), 141.9(C10), 136.5(C4), 133.2(C17), 132.8(C11), 130.1(C18, 22), 129.6(C15), 128.4(C13), 127.6(C12), 126.9(C19, 21), 126.6(C5), 124.1(C20), 122.8(C14), 120.4(C6), 117.6(C8, 9), 112.1(C7), 29.9(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{15}ClN_2$: 318.8019, found: 318.8025.



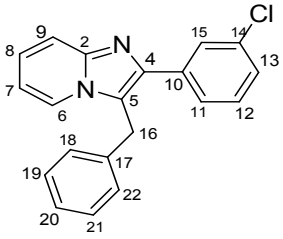
3-Benzyl-2-(3-bromophenyl)imidazo[1,2-a]pyridine (Table 2,Entry 11).[3]

White solid; mp = 154-156 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.03 (t, *J* = 2 Hz, 1H), 7.67-7.75 (m, 3H), 7.49–7.51 (m, 1H), 7.30–7.34 (m, 4H), 7.21–7.26 (m, 1H), 7.15 (d, *J* = 6.80 Hz, 2H), 6.76 (td, *J* = 6.8 Hz, *J* = 6.80 Hz, *J* = 1.2 Hz, 1H), 4.51 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 144.7(C2), 144.2(C4), 136.4(C17), 136.3(C10), 134.6 (C18, 22), 129.8(C11), 129.4(C14), 128.1(C19, 21), 127.9(C15), 127.3(C13), 126.9(C5), 126.7(C20), 124.2(C6), 123.4(C8), 118.1(C12), 117.6(C9), 112.3(C7), 29.8(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{16}BrN_2$: 363.1243, found: 363.1237



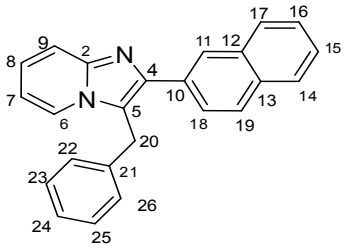
3-Benzyl-2-(3-chlorophenyl)imidazo[1,2-a]pyridine (Table 2,Entry 12).[2,5,6 and 7]

White solid; mp = 141-142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (s, 1H), 7.65-7.76 (m, 2H), 7.61- 7.65 (m, 1H), 7.21-7.35 (m, 5H), 7.19 - 7.22 (m, 1 H), 7.05 (d, *J* = 7.2 Hz, 2 H), 6.78 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 4.52 (s, 2 H, CH_2).

^{13}C NMR (100 MHz, CDCl3): 145.1(C2), 142.5(C17), 136.6(C4), 136.1(C18, 22), 135.1(C10), 129.8(C12), 129.1(C11), 128.4 (C15), 127.6(C19, 21), 127.3(C5), 127.1(C10), 126.2(C20), 125.4(C13), 123.2(C6), 117.8(C8), 117.3(C9), 112.2(C7), 29.8(C16).

HRMS (ESI) [M+H] calcd for $C_{20}H_{15}ClN_2$: 318.0932, found: 318.0939.



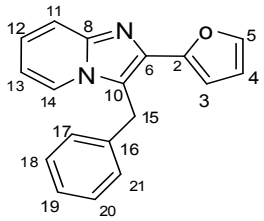
3-Benzyl-2-(naphthalen-1-yl)-imidazo[1,2-a]pyridine (Table2,Entry13).[3]

White solid; mp = 162-165 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.21 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.68 (d, J = 7.8 Hz, 2H), 7.38–7.56 (m, 4H), 7.14–7.28 (m, 4H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.75 (t, *J* = 6.8 Hz, 1H), 4.32 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3(C2), 138.7(C21), 135.6(C12), 133.8(C26, 22), 132.1(C14), 131.5(C10), 129.1(C25, 23),128.7(C16), 128.1(C16), 127.4(C4), 127.3(C5), 126.2(C19), 125.8(C18), 125.9(C15), 125.3(C13), 124.1(C6), 123.6(C8), 122.5(C9), 117.2(C11), 112.4(C7), 29.7(C20).

HRMS (ESI) [M+H] calcd for $C_{24}H_{19}N_2$: 335.1558, found: 335.1568.



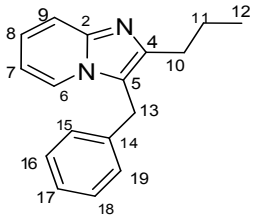
3-Benzyl-2-(furan-2-yl)imidazo[1,2-a]pyridine (Table2,Entry14).[2,5]

Brown crystalline solid; mp= 99-101 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.76 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.45 (s, 1H), 7.22–7.16 (m, 6H), 7.03 (d, *J* = 4.5 Hz, 1H), 6.64 (t, *J* = 8.2 Hz,1H), 6.50–6.54 (m, 1H), 4,34 (s, 2H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz) δ = 152.3(C2), 146.0(C8), 144.1(C10), 136.7(C5), 134.3(C16), 128.8(C17, 21), 128.1(C18, 20), 125.6(C19), 122.3(C14), 121.8(C6), 117.1(C12), 116.5(C11), 112.2(C14), 111.6(C13), 107.5(C3), 29.8(C15).

HRMS (ESI) [M+H] calcd for $C_{18}H_{14}N_2O$: 275.1170, found: 275.1186.



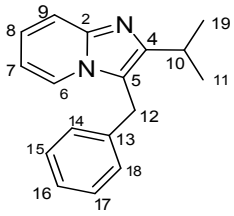
3-Benzyl-2-(propyl)imidazo[1,2-a]pyridine (Table2,Entry15).[2]

Yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (t, J= 8.20 Hz, 2H), 7.26–7.30 (m, 2H), 7.12–7.19 (m, 4H), 6.69 (t, J= 7.20 Hz, 1H), 4.29 (s, 2H, CH_2), 2.38 (t, J= 6.8 Hz, 2H, $C^{10}H$), 1.84–1.86 (m, 2H, $C^{11}H$), 1.8 (t, J= 6.8 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.5(C2), 128.2(C14), 127.3(C4), 123.4(C15, 19), 123.1(C16, 18), 129.3(C17), 118.7(C6), 117.4(C5), 111.2(C9, 8), 110.5(C7), 29.9(C13), 29.2(C10), 24.3(C11), 14.6(C12).

HRMS (ESI) [M+H] calcd for $C_{17}H_{18}N_2$: 250.1489, found: 250.1476.



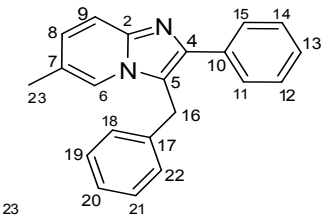
3-Benzyl-2-(isopropyl)imidazo[1,2-a]pyridine (Table2,Entry16).[2,4]

Yellow crystals; mp= 82-83 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (t, J = 8.5 Hz, 2H), 7.26 -7.30 (m, 2H), 7.24 (s, 1H), 7.12 (s, 3H), 6.61 (t, J = 7.2 Hz, 1H), 4.36 (s, 2H, CH_2), 3.19 -3.34 (m, 1H, $C^{10}H$), 1.49 (d, J= 6.53 Hz, 6H, $2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2(C2), 129.3(C13), 127.7(C4), 126.9(C14, 18), 126.5(C6), 123.6(C15, 17), 123.1(C16), 117.2(C5), 116.9(C8, 9), 111.6(C7), 29.7(C12), 27.1(C10), 24.2(C11, 19).

HRMS (ESI) [M+H] calcd for $C_{17}H_{18}N_2$: 250.1468, found: 250.1472.



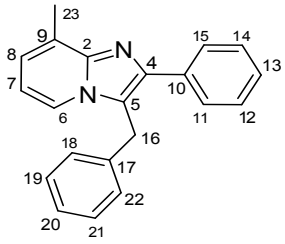
3-Benzyl-(6-methyl-2-phenyl)imidazo[1,2-a]pyridine(Table 2, Entry 17).[5,6]

White solid; mp= 207-209º C.

^{1}H NMR(400 MHz, $CDCl_3$) δ = 7.78–7.82 (m, 2H), 7.58 (d, J = 8.3 Hz, 1H), 7.52 (s, 1H), 7.41–7.46 (m, 2H), 7.25–7.38 (m, 4H), 7.18 (d, J = 7.2 Hz, 2H), 6.98 (dd, J= 8.9, 1.7 Hz, 1H), 4.52 (s, 2H, CH_2), 2.27 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.1(C2), 143.4(C4), 136.9(C17), 135.1(C10), 129.3(C18, 22), 128.5(C8), 128.2(C19, 21), 127.6(C7), 127.5(C6), 127.3(C11, 15), 127.1(C12, 14), 120.9(C5), 120.6(C13), 118.3(C20), 117.1(C9), 29.8(C16), 18.7(C23).

HRMS (ESI) [M+H] calcd for $C_{21}H_{18}N_2$**:** 299.1537, found: 299.1539.



3-Benzyl-(8-methyl-2-phenyl)imidazo[1,2-a]pyridine (Table 2, Entry 18). [2]

light yellow crystals; mp= 126-127 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (s, 2H), 7.63 (d, J = 7.20 Hz, 1H), 7.53 (s, 2H), 7.25 - 7.32 (m, 4H), 7.12 (d, J = 7.20 Hz, 2H), 7.03 (d, J = 7.10 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 4.48 (s, 2H, CH_2), 2.75 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ =146.3(C2), 144.1(C4), 136.9(C17), 135.4(C10), 129.2(C18, 22), 128.6(C8), 128.4(C9), 127.9(C19, 21),127.5(C11, 15), 127.1(C12,14), 125.4(C5), 124.2(C13), 120.6(C20), 118.4(C6), 113.2(C7), 29.4(C16), 17.6(C23).

HRMS (ESI) [M+H] calcd for $C_{21}H_{18}N_2$: 298.1475, found: 298.1472.

Reference

[1] J-C. Xiao, B. Twamley, and J-M. Shreeve, *Org. Lett*. 2004, **6**, 3845–3847.

[2] N.Chernyak, and V. Gevorgyan, *Angew. Chem., Int. Ed*. 2010, **49**, 2743−2746.

[3] B.V.S. Reddy, P.S. Reddy, Y.J. Reddy and J.S. Yadav, *Tetrahedron Lett*. 2011, **52**, 5789−5793.

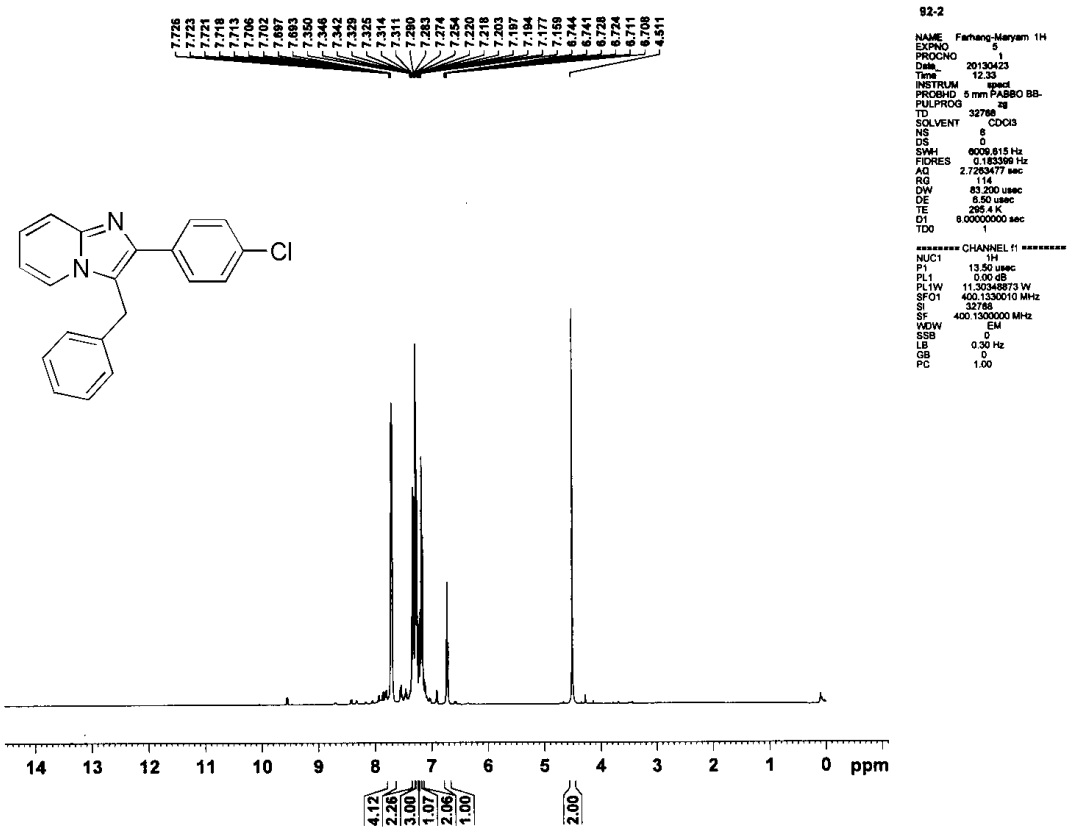
[4] S.K. Guchhait, A.L. Chandgude and G. Priyadarshani, *J. Org. Chem.* 2012, **77**, 4438–4444.

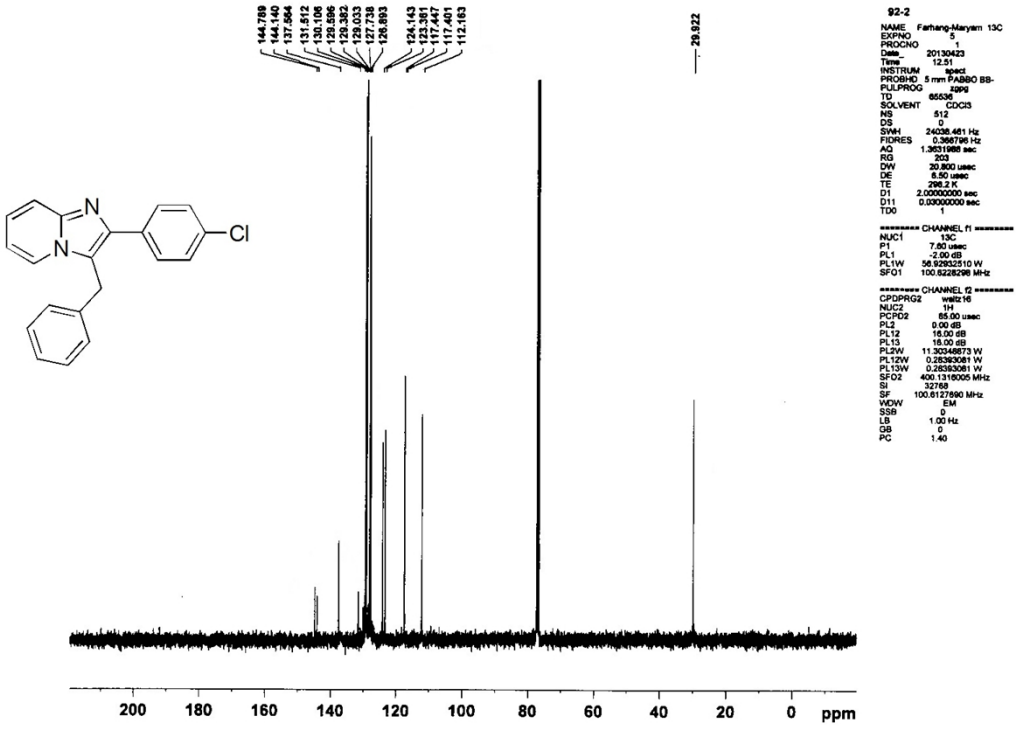
[5] P. Liu, C-L. Deng, X. Lei, G.-q. Lin, *Eur. J. Org. Chem*. 2011, 7308–7316.

[6] P. Liu, L.S. Fang, X. Lei and G.Q. Lin, *Tetrahedron Lett.* 2010, **51**, 4605−4608.

[7] T. Guntreddi, B.K. Allam and K.N. Singh, *Synlet,t* 2012, **23**, 2635–2638.

[8] S. Mishra and R.Ghosh, *Synthesis* 2011, 3463−3470.





92-2

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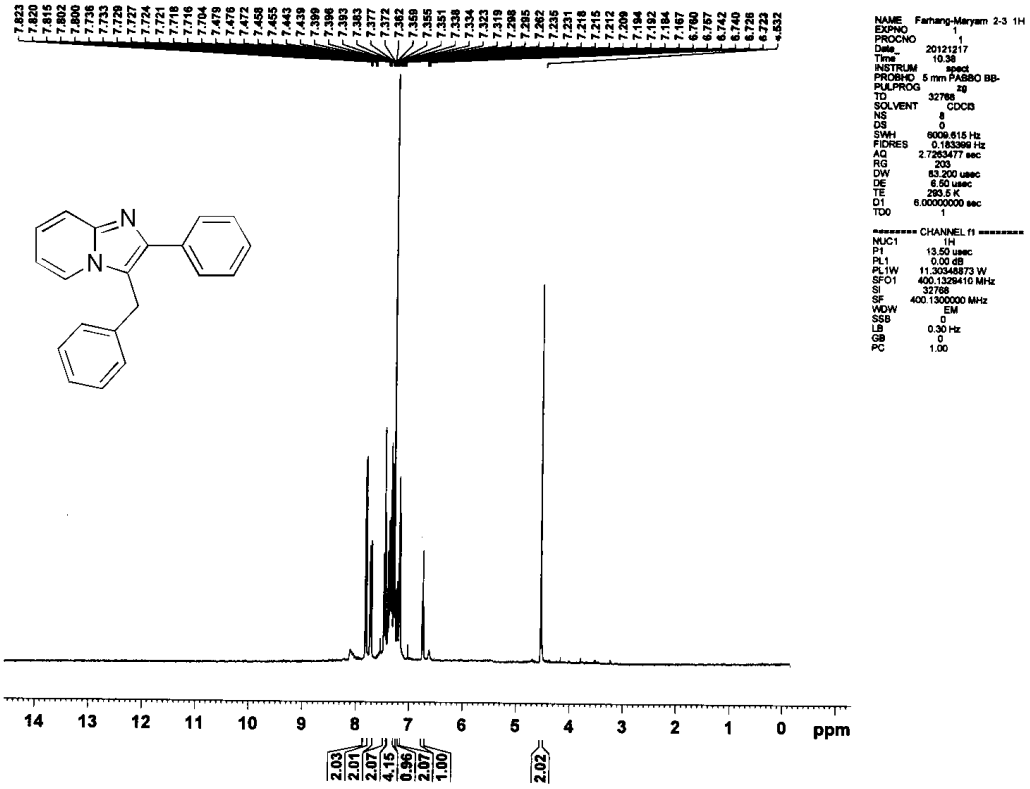

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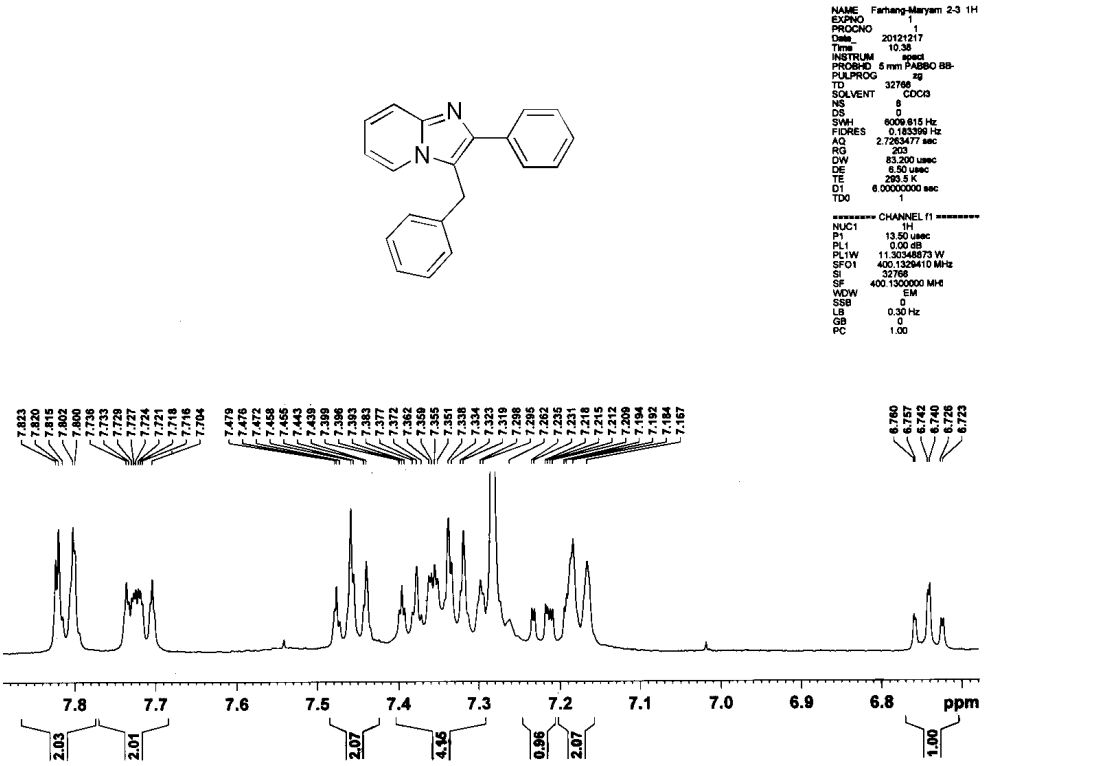
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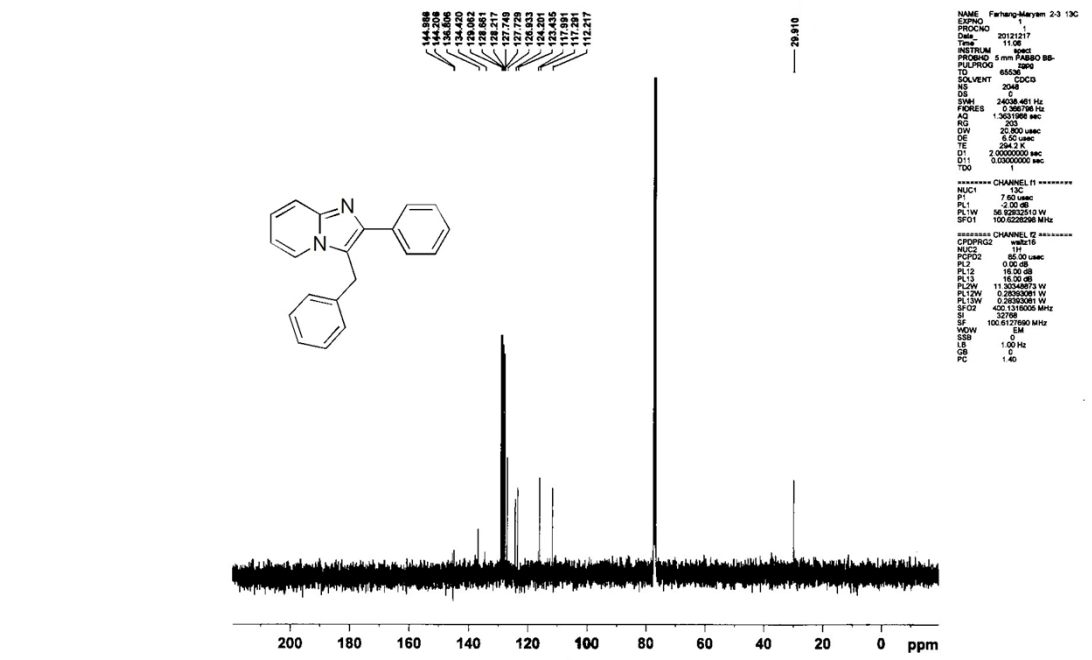
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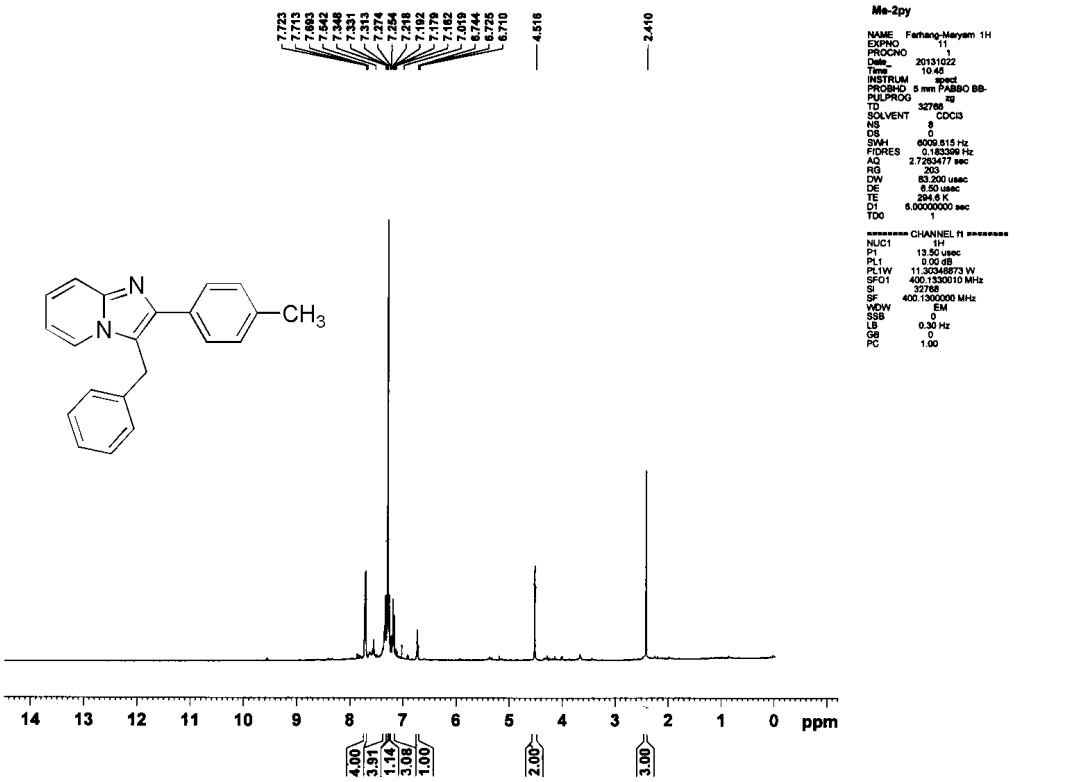

Me-2py

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TD0 1

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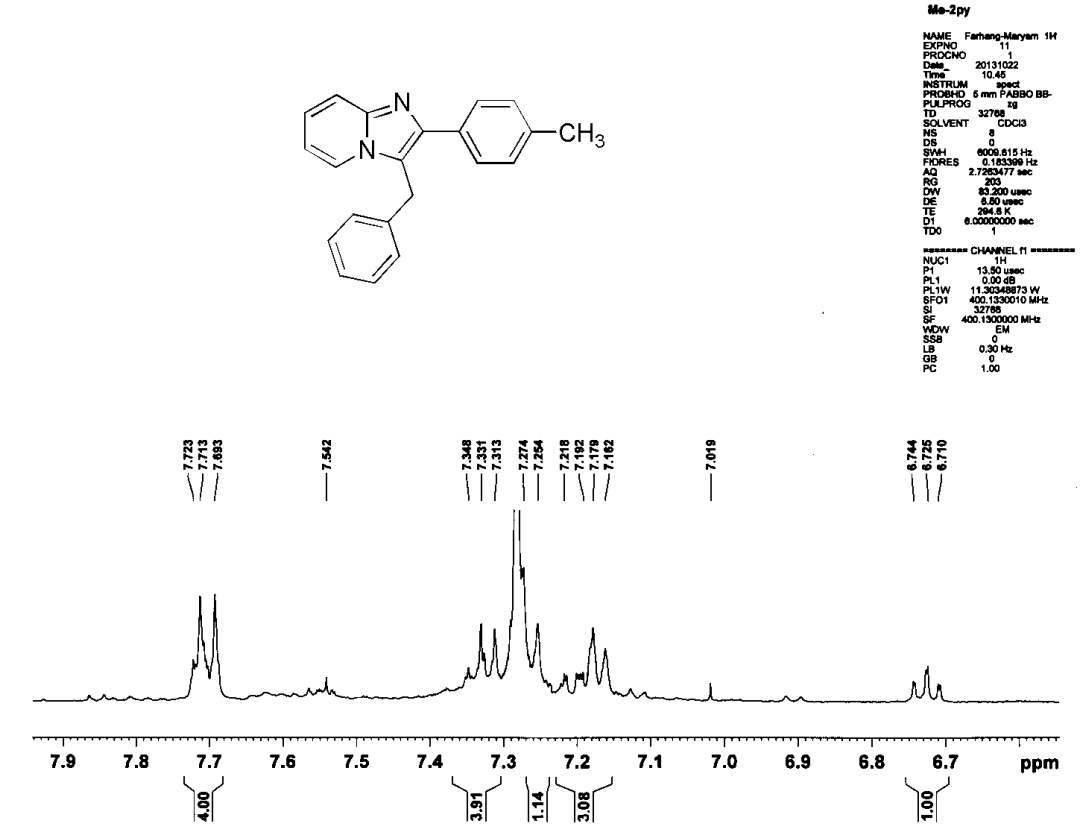

Me-2py

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DW 83.200 usec
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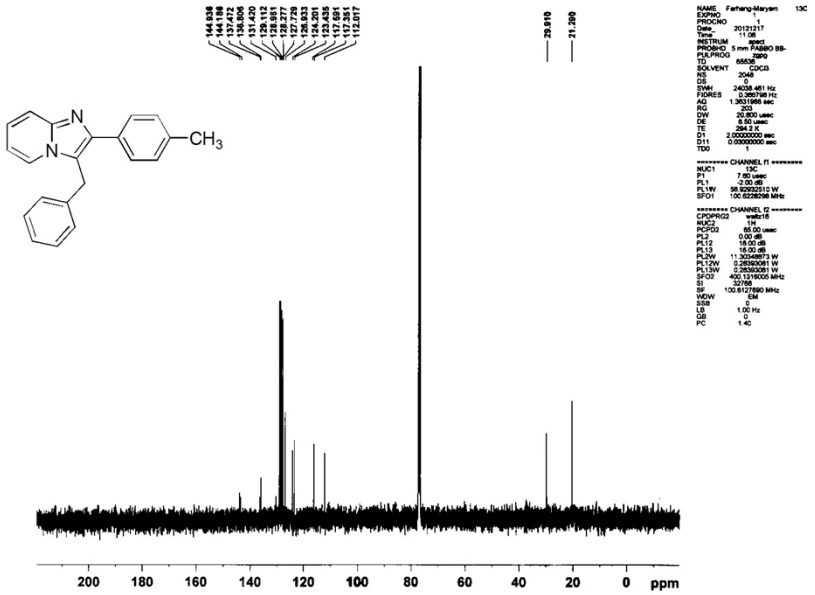
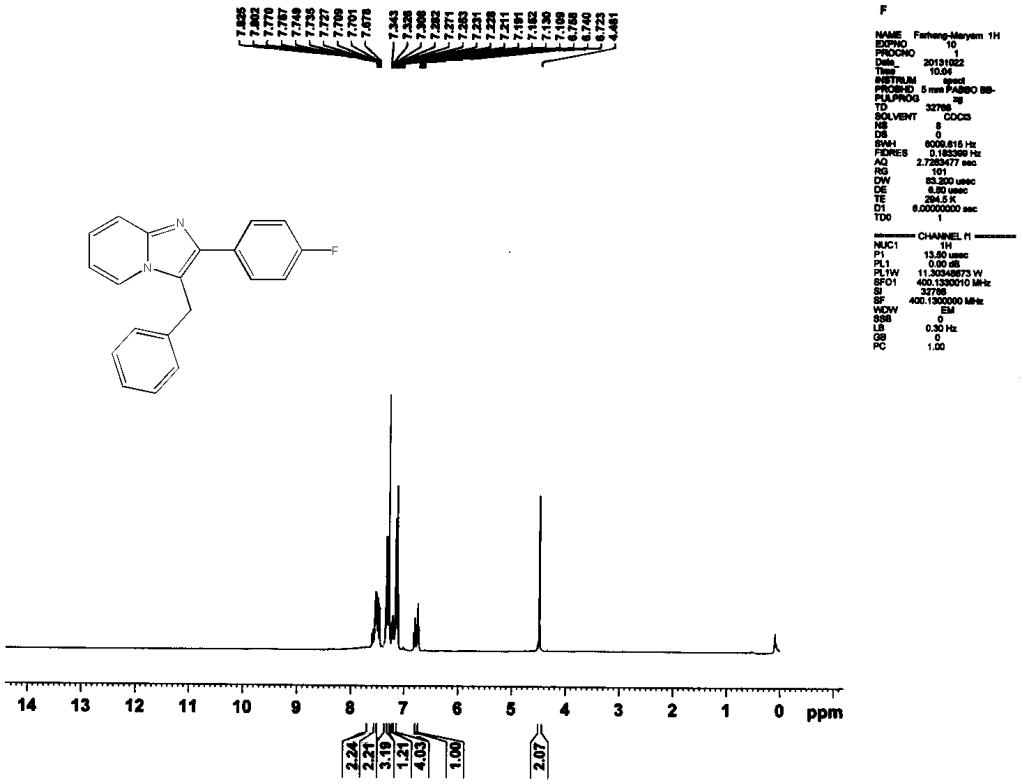
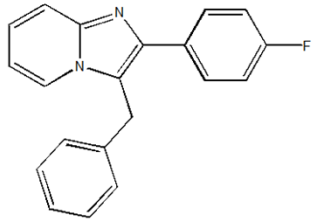
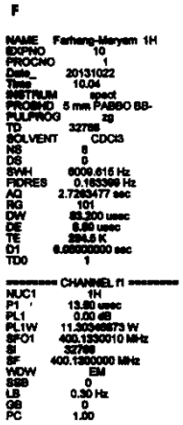
TE 294.6 K
D1 6.00000000 sec
TD0 1

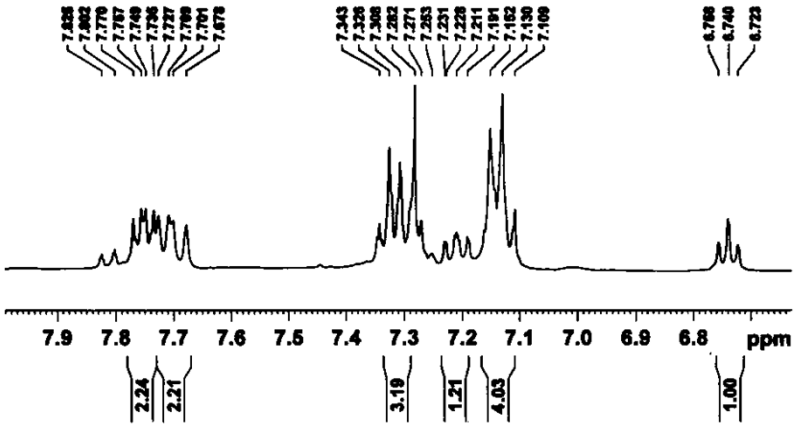
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 0.00 dB
PL1W 11.30348873 W
SFO1 400.1330010 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

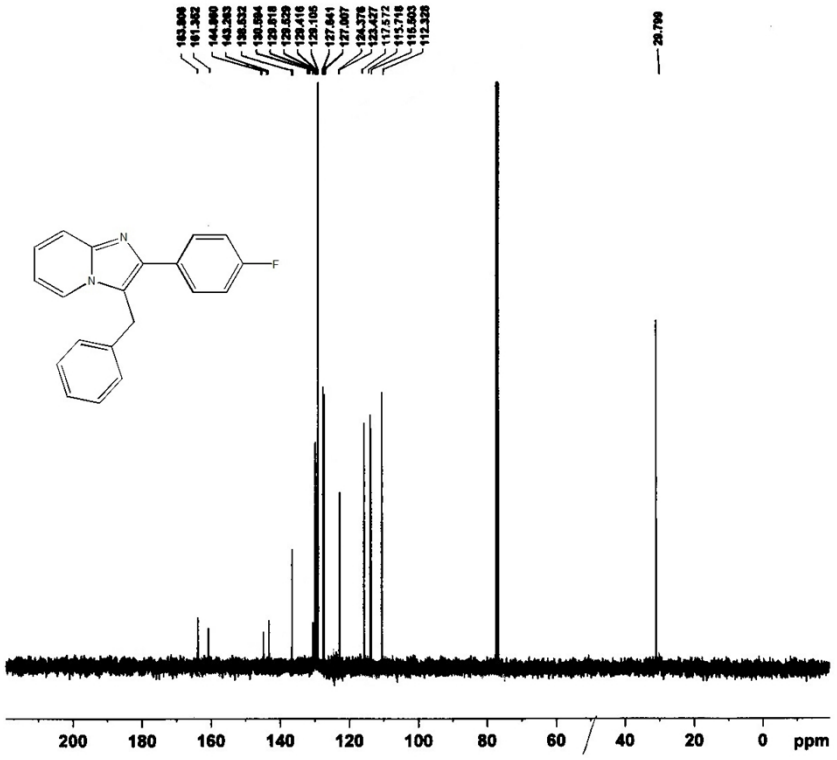

144.539
144.186
137.472
136.906
131.420
129.112
128.951
128.777
127.729
126.533
124.201
121.454
117.591
112.351
112.017
29.910
21.290
N
N
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm

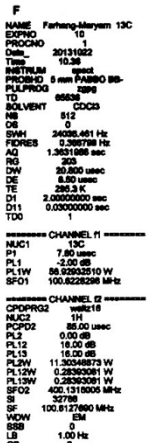

7.825
7.802
7.770
7.767
7.749
7.735
7.727
7.709
7.701
7.678
7.343
7.338
7.308
7.282
7.271
7.263
7.231
7.228
7.211
7.191
7.182
7.139
7.109
6.788
6.740
6.723
4.461
F
N
N
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.24
2.21
3.19
1.21
4.03
1.00
2.07

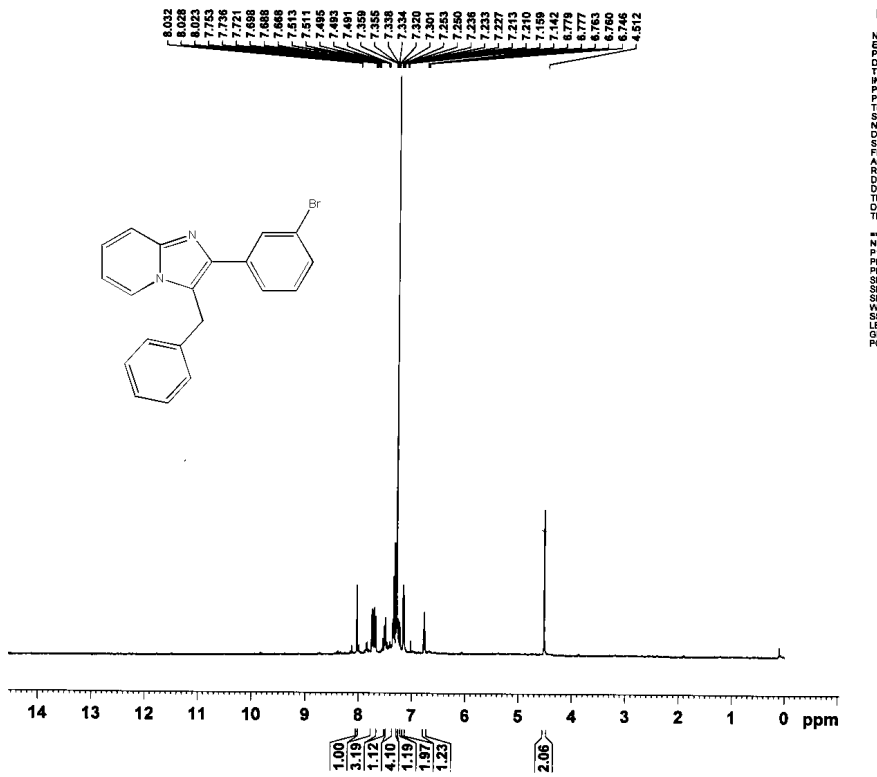

N
N
F


F
NAME Farhang-Maryam 1H
EXPNO 10
PROCNO 1
Date_ 20131022
Time 10.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8009.615 Hz
FIDRES 0.183369 Hz
AQ 2.7263477 sec
RG 101
DW 83.200 usec
DE 6.50 usec
TE 294.5 K
D1 6.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 0.00 dB
PL1W 11.30346873 W
SFO1 400.1330010 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


7.838
7.802
7.770
7.767
7.749
7.736
7.727
7.709
7.701
7.678
7.343
7.326
7.308
7.282
7.271
7.253
7.231
7.228
7.211
7.191
7.152
7.130
7.109
6.766
6.740
6.723
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm
2.24
2.21
3.19
1.21
4.03
1.00


163.809
161.352
144.999
140.353
136.532
130.884
129.818
129.529
129.416
129.105
127.841
127.007
124.378
123.427
117.572
115.716
115.503
112.328
29.799
N
N
F
200 180 160 140 120 100 80 60 40 20 0 ppm


F
NAME Farhang-Maryam 13C
EXPNO 10
PROCNO 1
Date_ 20131022
Time 10.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631986 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.90 usec
PL1 -2.00 dB
PL1W 59.92932510 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 85.00 usec
PL2 0.00 dB
PL12 16.00 dB
PL13 16.00 dB
PL2W 11.30346873 W
PL12W 0.28393081 W
PL13W 0.28393081 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

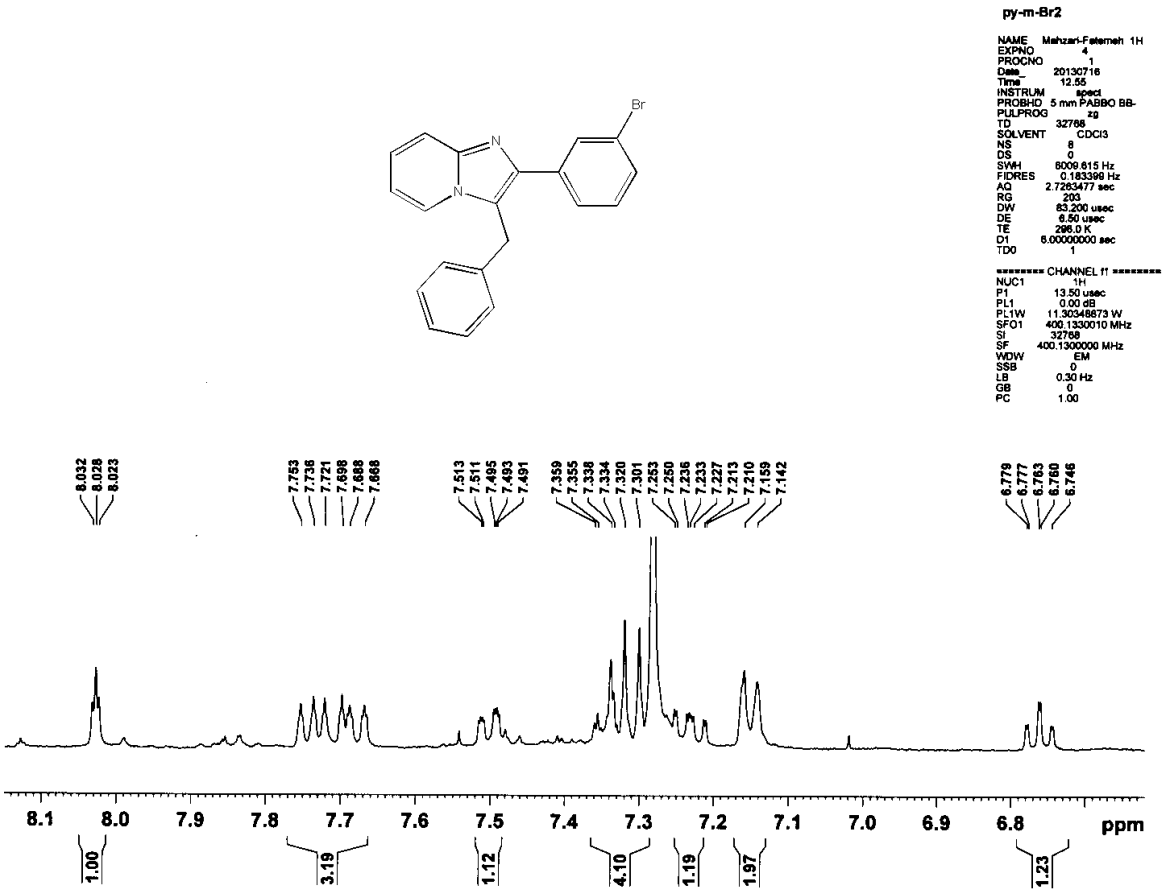


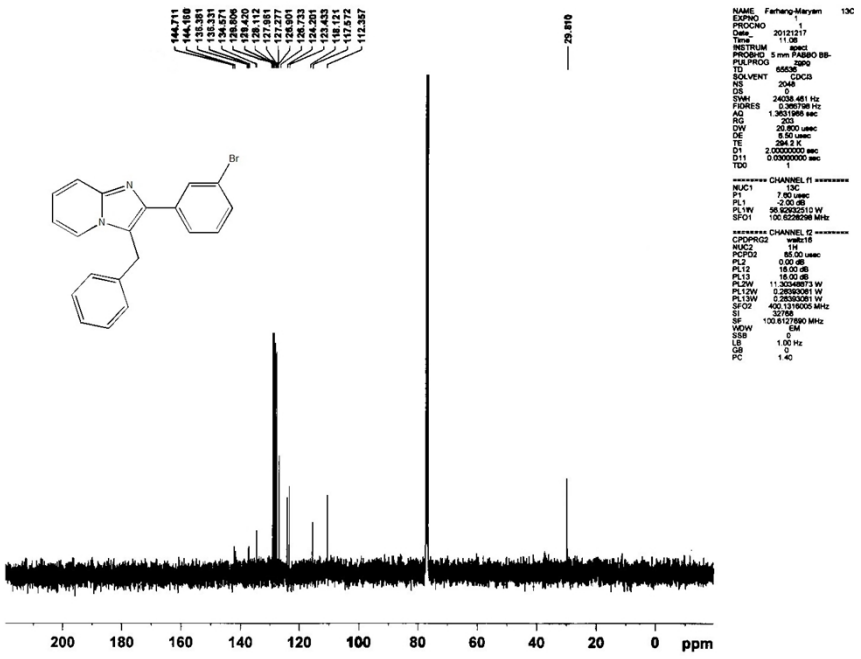
py-m-Br2

NAME	Mahzari-Fatemeh 1H
EXPNO	4
PROCNO	1
Date_	20130716
Time	12.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	8
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	203
DW	83.200 usec
DE	6.50 usec
TE	298.0 K
D1	6.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	13.50 usec
PL1	0.00 dB
PL1W	11.30348673 W
SFO1	400.1330010 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00




144.711
144.169
135.381
135.331
134.571
129.806
129.450
128.112
127.277
127.081
126.901
126.733
124.201
123.433
118.121
117.572
112.357
29.819
Br
N
N
200
180
160
140
120
100
80
60
40
20
0
ppm