Electronic Supplementary Material (ESI) for RSC Advances.

Hydromagnesite Sheets Impregnated with Cobalt-Ferrite Magnetic Nanoparticles as Heterogeneous Catalytic System Leading to the Synthesis of Imidazo[1,2-*a*]pyridine Scaffolds

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❖ **Correlation between catalytic activity and reaction efficiency for the synthesis of 3-benzyl-2-phenyl imidazo[1,2-*a*]pyridine (4*a*)**

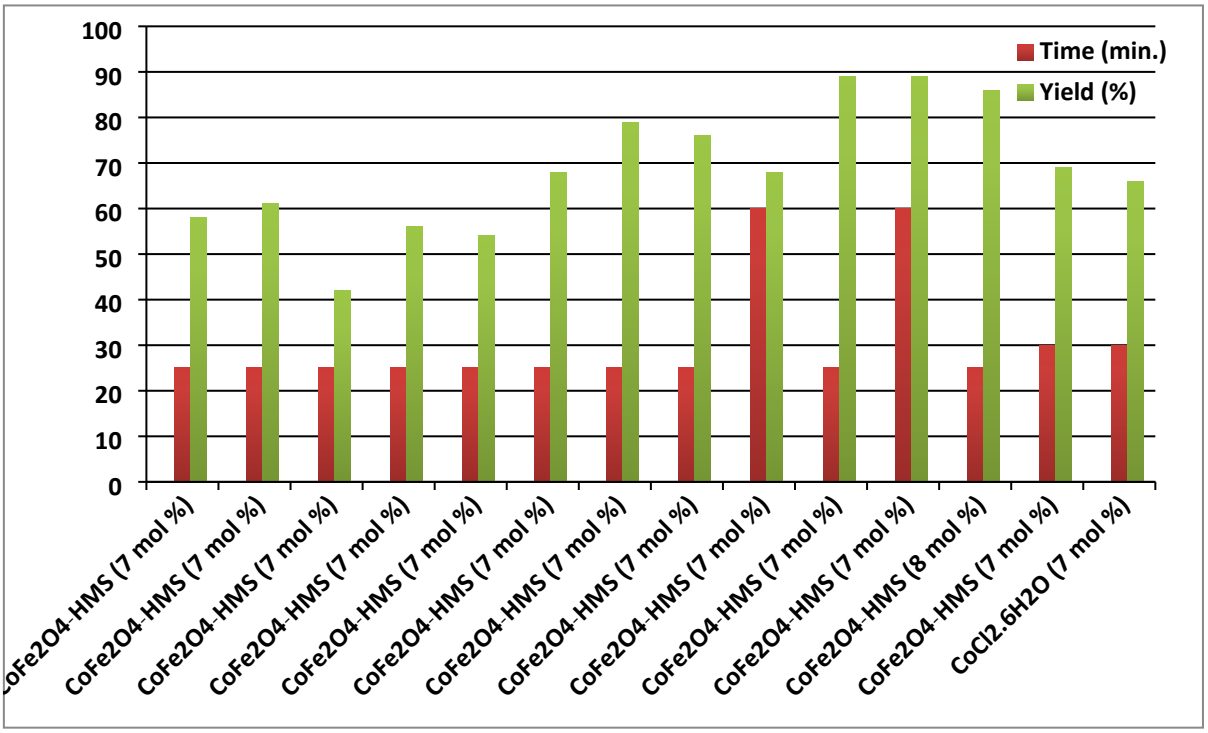
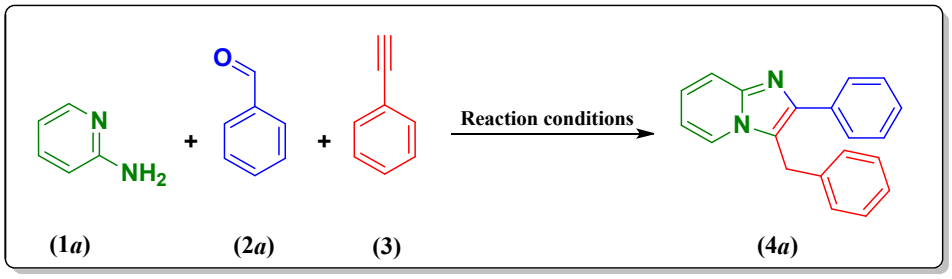


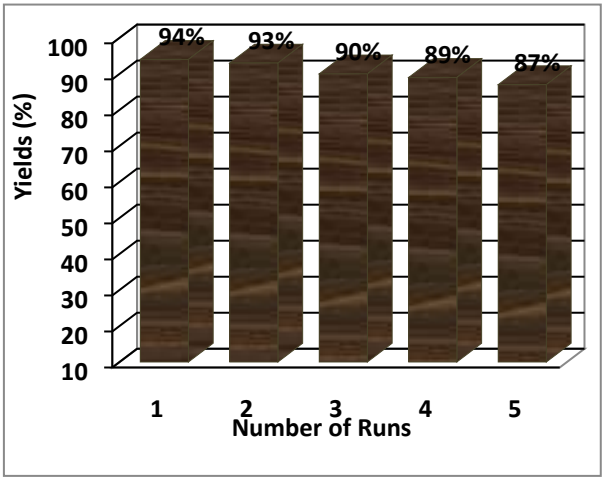
Figure 1. Correlation between catalytic activity and reaction efficiency for the synthesis of 3-benzyl-2-phenyl imidazo[1,2-*a*]pyridine (4*a*)

Table 1. Comparison of catalytic activity of different catalysts on the model reaction for the synthesis of 3-benzyl-2-phenylimidazo[1,2-*a*]pyridine (4*a*)

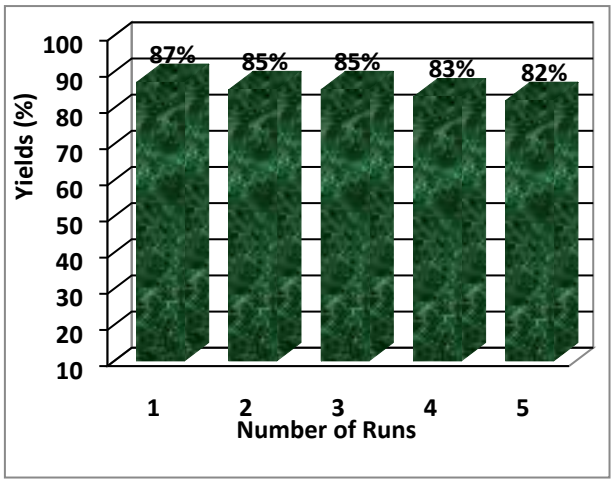


Entry	Reaction conditions	Solvent	Temperature/ Time	Yield (%)	Recyclability	Ref.
1	$CuSO_4.5H_2O$ (10 mol %) / Sodium ascorbate (20 mol %) / SDS (10 mol %)	H_2O	50 °C / 6 h	88	No	[1]
2	Fe_3O_4@SiO_2 NPs (5 mol %) / K_2CO_3	EtOH	Reflux / 3 h	86	Yes	[2]
3	PW-CIS500 (0.9 mol %)	-	100 °C / 2.5 h	95	Yes	[3]
4	Cu (1):Mn (0.25) (10 mol %)	H_2O	100 °C / 4 h	85	Yes	[4]
5	$InBr_3$ (10 mol %)	Dry toluene	120 °C / 12 h	82	No	[5]
6	CuCl (5 mol %), $Cu(OTf)_2$ (5mol %)	toulene	120 °C / 16 h	93	No	[6]
7	$CoFe_2O_4$-HMS (7 mol %)	PEG 400	r.t. / 0.42 h (25 min.)	89	Yes	Our work

❖ Recycling and reusability of magnetic nanocomposite and solvent



(i). $CoFe_2O_4$-HMS



(ii). PEG 400

Figure 2. The reusability of $CoFe_2O_4$-HMS (i) and PEG 400 (ii) in the synthesis of 3-benzyl-2-(4-chlorophenyl)-7-methylimidazo[1,2-*a*]pyridine (4*g*)

❖ Characterization of recovered $CoFe_2O_4$-HMS magnetic nanocatalyst

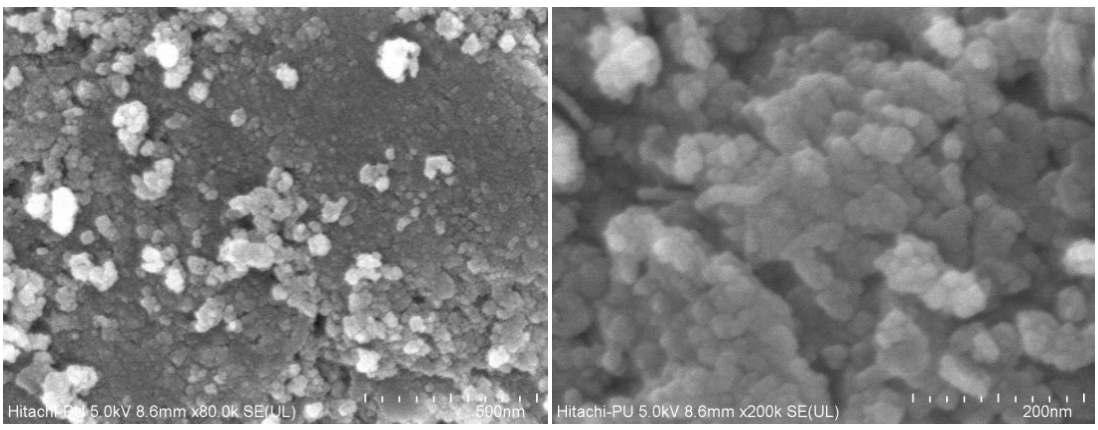


Figure 3. The field-emission scanning electron microscopy (FE-SEM) images of recovered $CoFe_2O_4$-HMS after fifth cycle

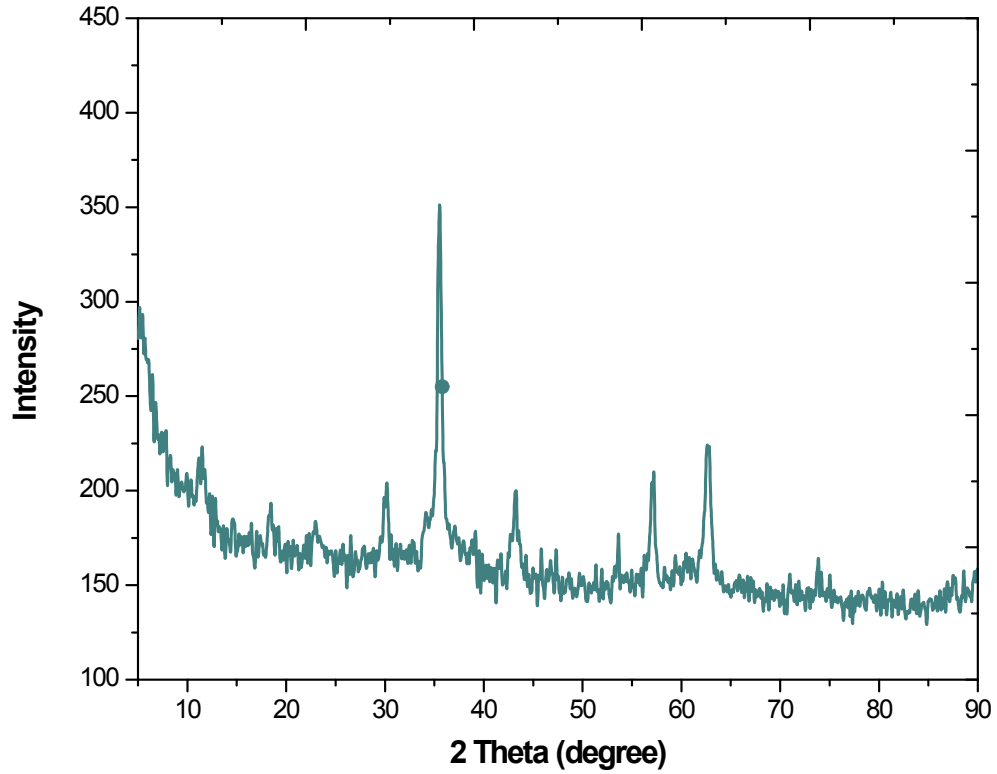


Figure 4. The PXRD diffraction pattern of $CoFe_2O_4$-HMS after fifth cycle of recovery of the catalyst

❖ Heterogeneous nature of $CoFe_2O_4$-HMS magnetic nanocatalyst

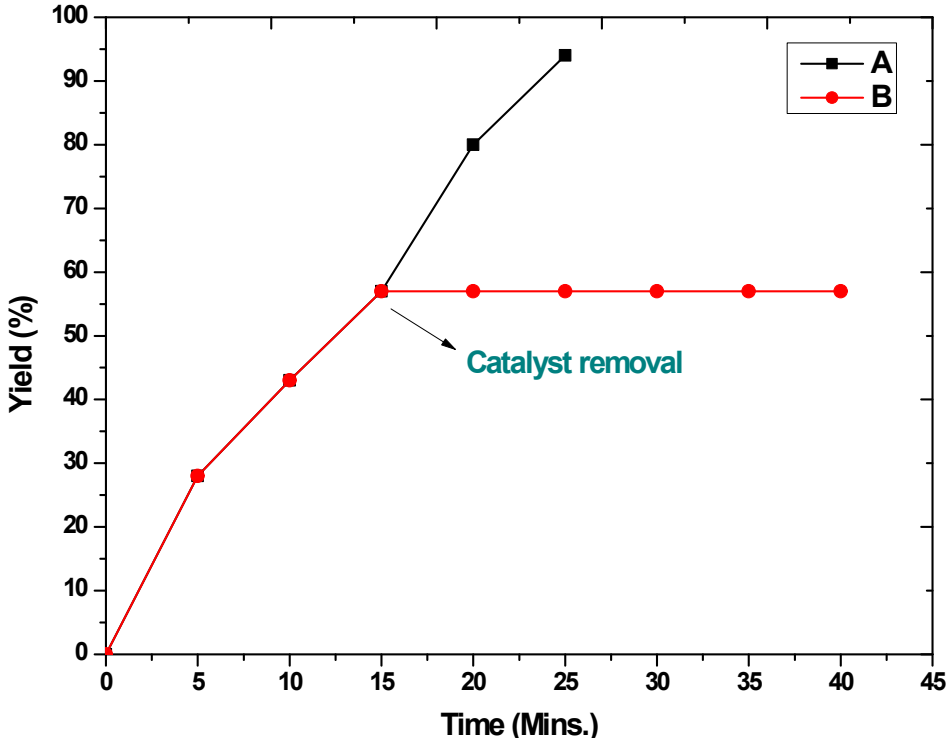


Figure 5. Hot filtration test and leaching effect of $CoFe_2O_4$-HMS for the ultrasonic-assisted synthesis of 2-benzyl-3-(4-chlorophenyl)-7-methylimidazo[1,2-*a*]pyridine (4*g*).

Reaction conditions: 2-amino-4methyl pyridine (1 mmol), 4-chlorobenzaldehyde (1 mmol), phenyl acetylene (1 mmol) in the presence of PEG 400 with catalyst **(A)** and catalyst removal **(B)** after 15 minutes.

❖ FTIR Analyses

Table 2. Functional groups with their wave number values

S.No.	Wave numbers (cm^{-1})	Functional groups
1.	3649, 3648, 3386, 3235	Stretching vibration of O-H group
2.	2981, 2891	Stretching vibration of C-H group
3.	1644,1634	Stretching vibration of C=O group
4.	1353, 1251	Bending vibration of –CH group
5.	1476, 1470, 1462, 1417, 1381, 955, 954, 880	Bending vibration of O-H group
6.	1155, 1116, 1095, 1070	Stretching vibration of C-O group
7.	723, 717, 588, 538, 534	Deformation vibration of Fe-OH group
8.	493	Deformation vibration of Co-O group

❖ Raman Analyses

Table 3. Measured Raman shift, Peak position, and vibrational modes of the samples

S.No.	Peak Position (cm^{-1})	Raman Shift	Peak Position (cm^{-1})	Raman Shift	Peak Position (cm^{-1})	Raman Shift	Vibrational Mode	Assignment
	$CoFe_2O_4$-HMS		**$CoFe_2O_4$ MNPs**		**HMS**			
1.	213.238	165	200.995	147	-	-	A_{1g} (1)	Symmetric stretching Fe-O
2.	243.767	210	243.767	210	-	-	A_{1g} (2)	Symmetric stretching Fe(Co)-O
3.	472.060	552	477.323	560	-	-	T_{2g} (2)	Asymmetric stretching Fe-O
4.	564.942	693	571.442	705	-	-	T_{2g} (3)	Asymmetric bending Fe(Co)-O
5.	613.556	769	618.078	776	-	-	E_g	Symmetric bending Fe(Co)-O
6.	686.863	883	702.847	908	-	-	T_{2g} (1)	Translation motion of the whole tetrahedron
7.	1125.05	1583	-	-	1125.05	1583	ν_1	Hydromagnesite band

❖ Surface Basic Property (Temperature Programmed Desorption of CO_2 (CO_2-TPD))

Table 4. The numbers of the weak and medium basic sites on the surface of HMS and $CoFe_2O_4$-HMS

Sample	Weak Basic sites ($a.u./m^2$)	Medium Basic sites ($a.u./m^2$)	Weak Basic sites/Medium Basic sites	Weak Basic sites/(Weak + Medium) Basic sites
HMS	4.8	22.5	0.21	0.18
$CoFe_2O_4$-HMS	5.5	12.9	0.43	0.30

Figure S1. The ^{1}H NMR Spectrum of *3-benzyl-2-phenylimidazo[1,2-a]pyridine* **(4a)**:

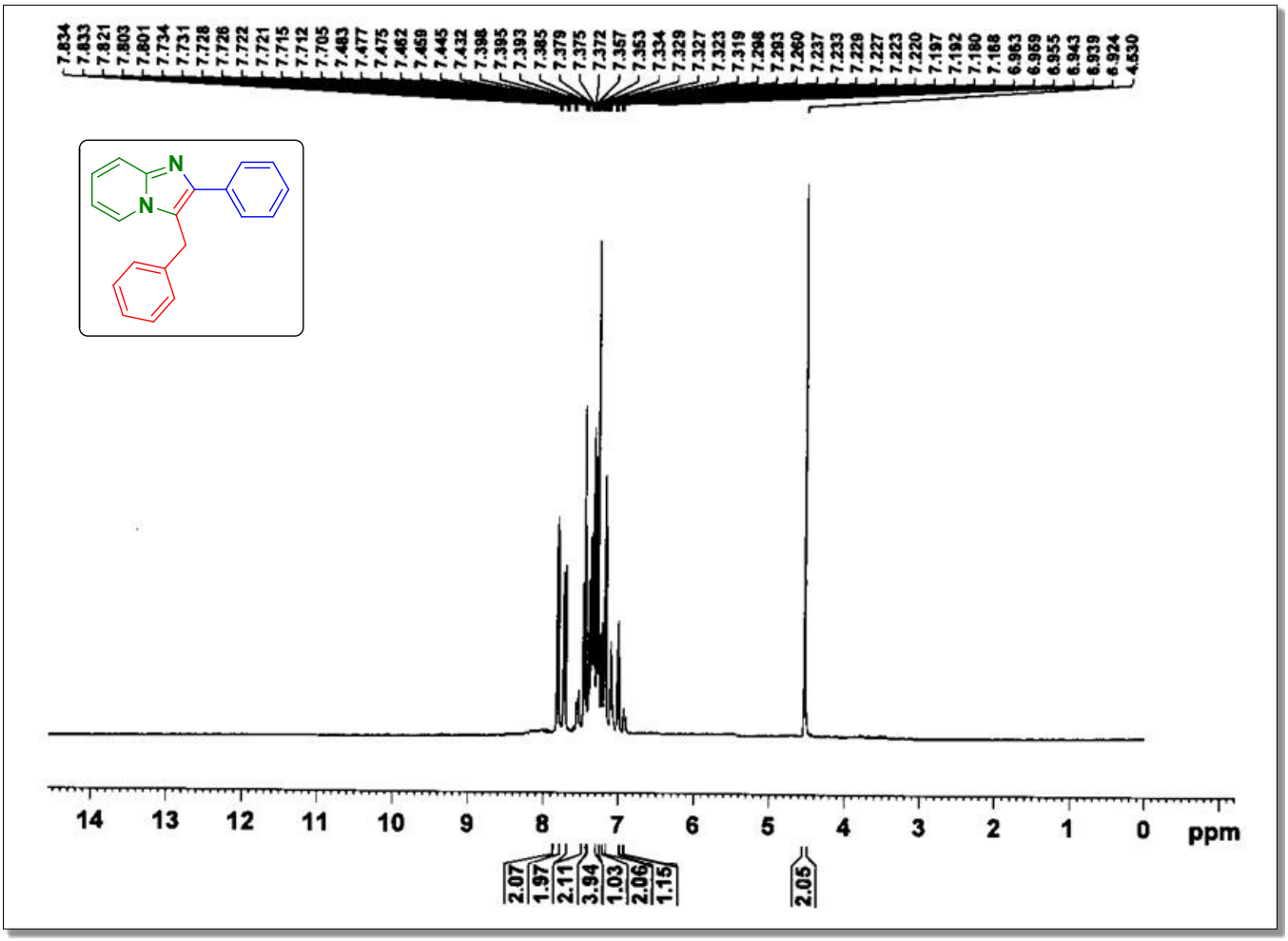


Figure S2. The ^{13}C NMR Spectrum of *3-benzyl-2-phenylimidazo[1,2-a]pyridine* **(4a)**:

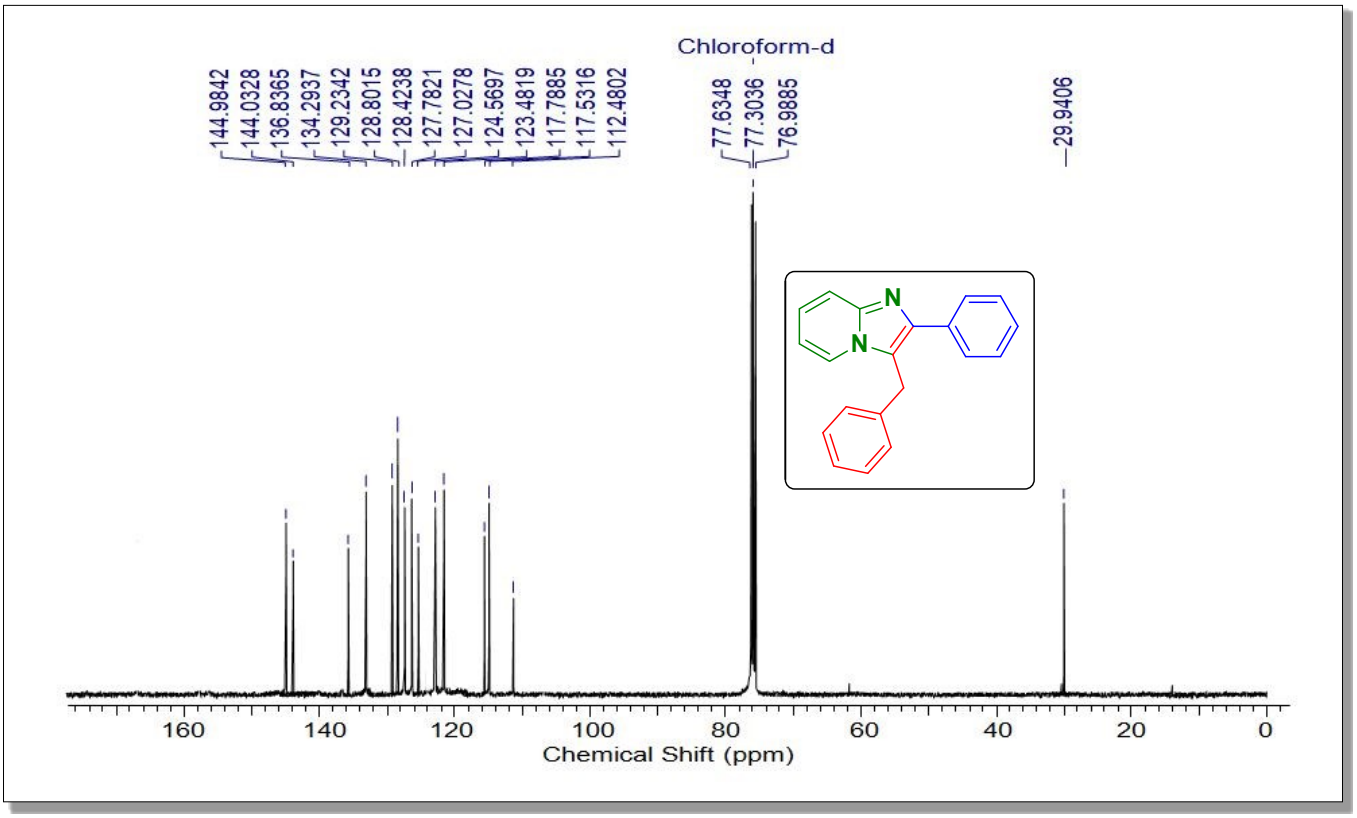


Figure S3. The ^{1}H NMR Spectrum of *3-benzyl-2-(4-chlorophenyl)imidazo[1,2-a]pyridine* **(4*b*)**:

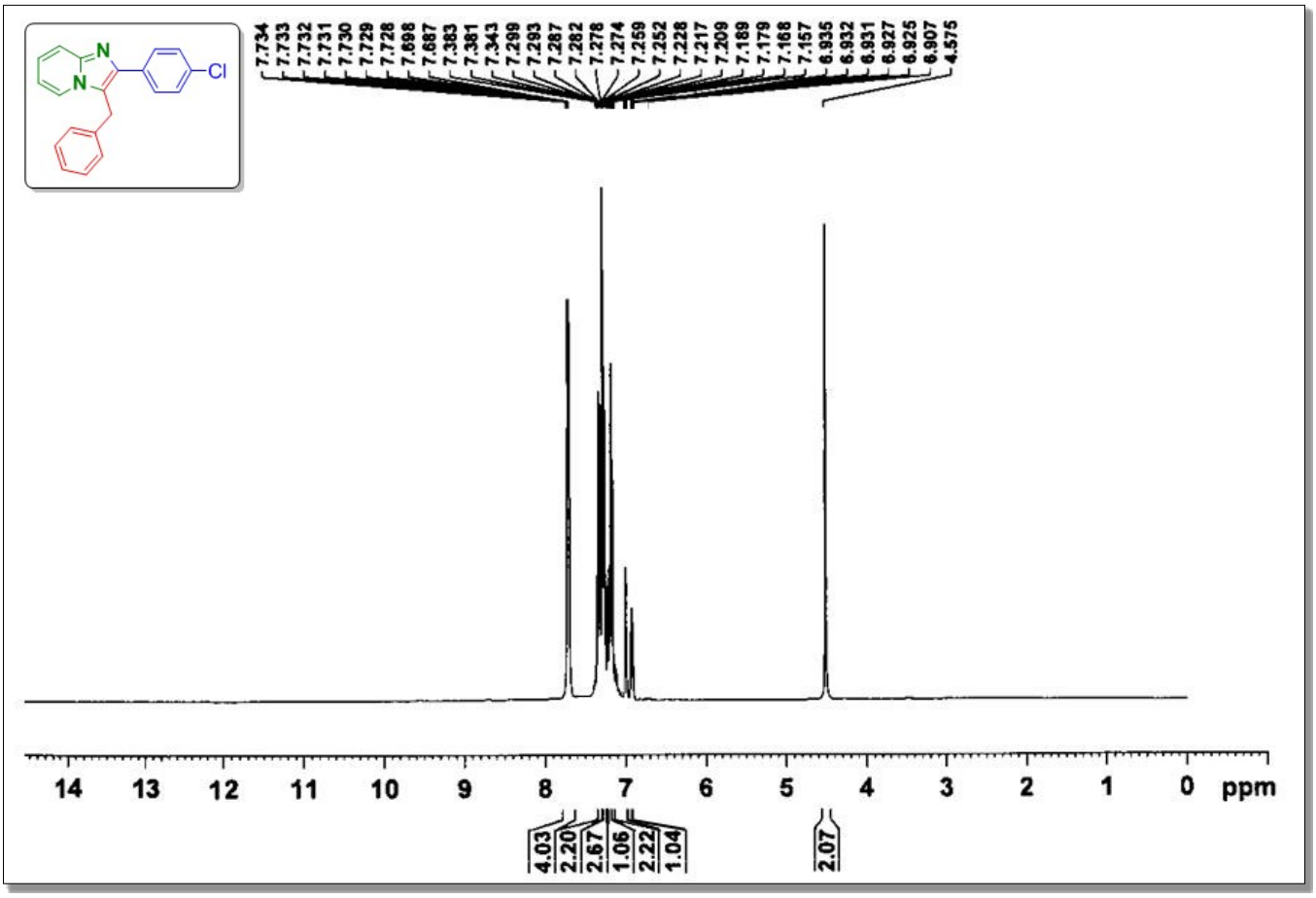


Figure S4. The ^{13}C NMR Spectrum of *3-benzyl-2-(4-chlorophenyl)imidazo[1,2-a]pyridine* **(4*b*)**:

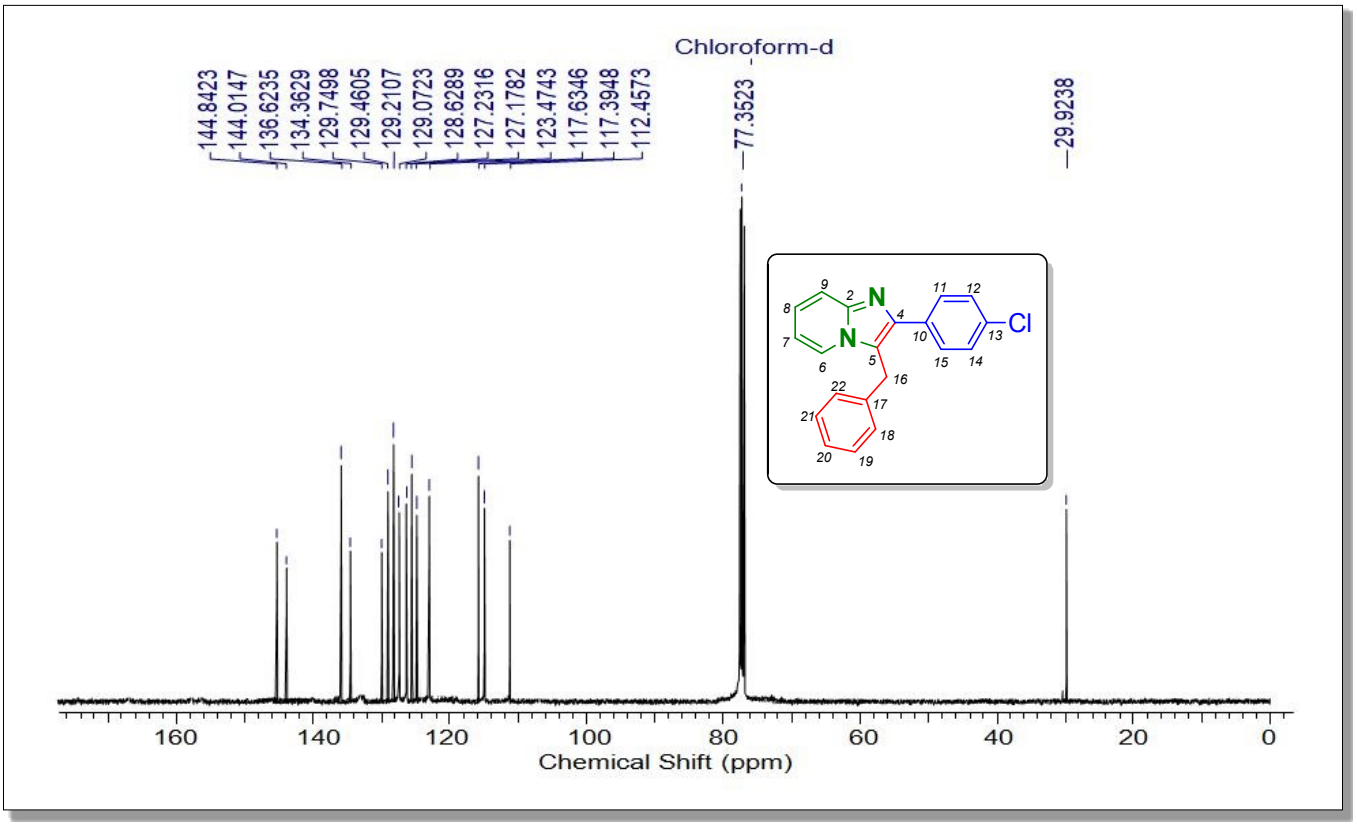


Figure S5. The IR Spectrum of ***4-(3-benzylimidazo[1,2-a]pyridin-2-yl)phenol*** (**4*c***):

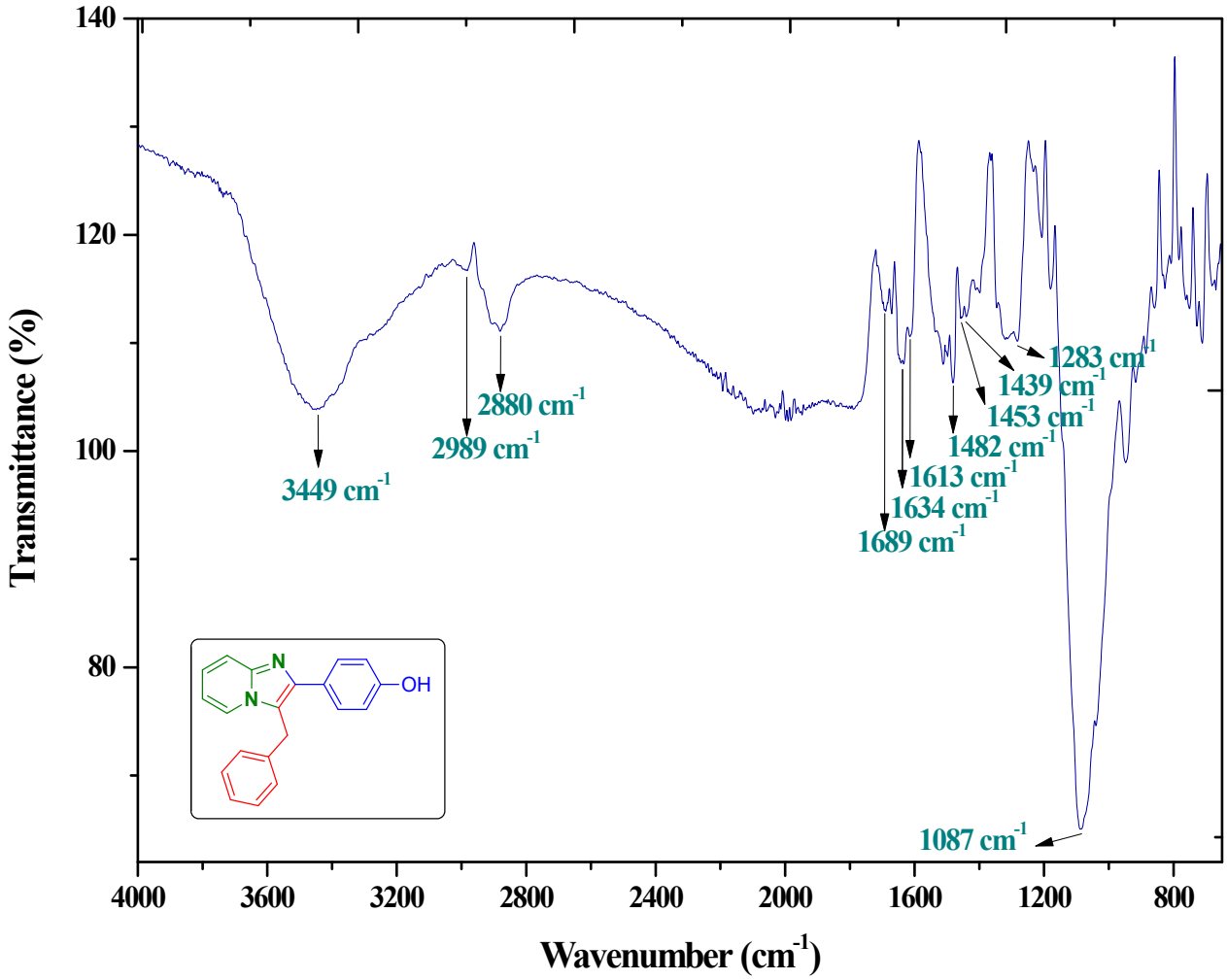


Figure S6. The ^{1}H NMR Spectrum of *4-(3-benzylimidazo[1,2-a]pyridin-2-yl)phenol* **(4*c*)**:

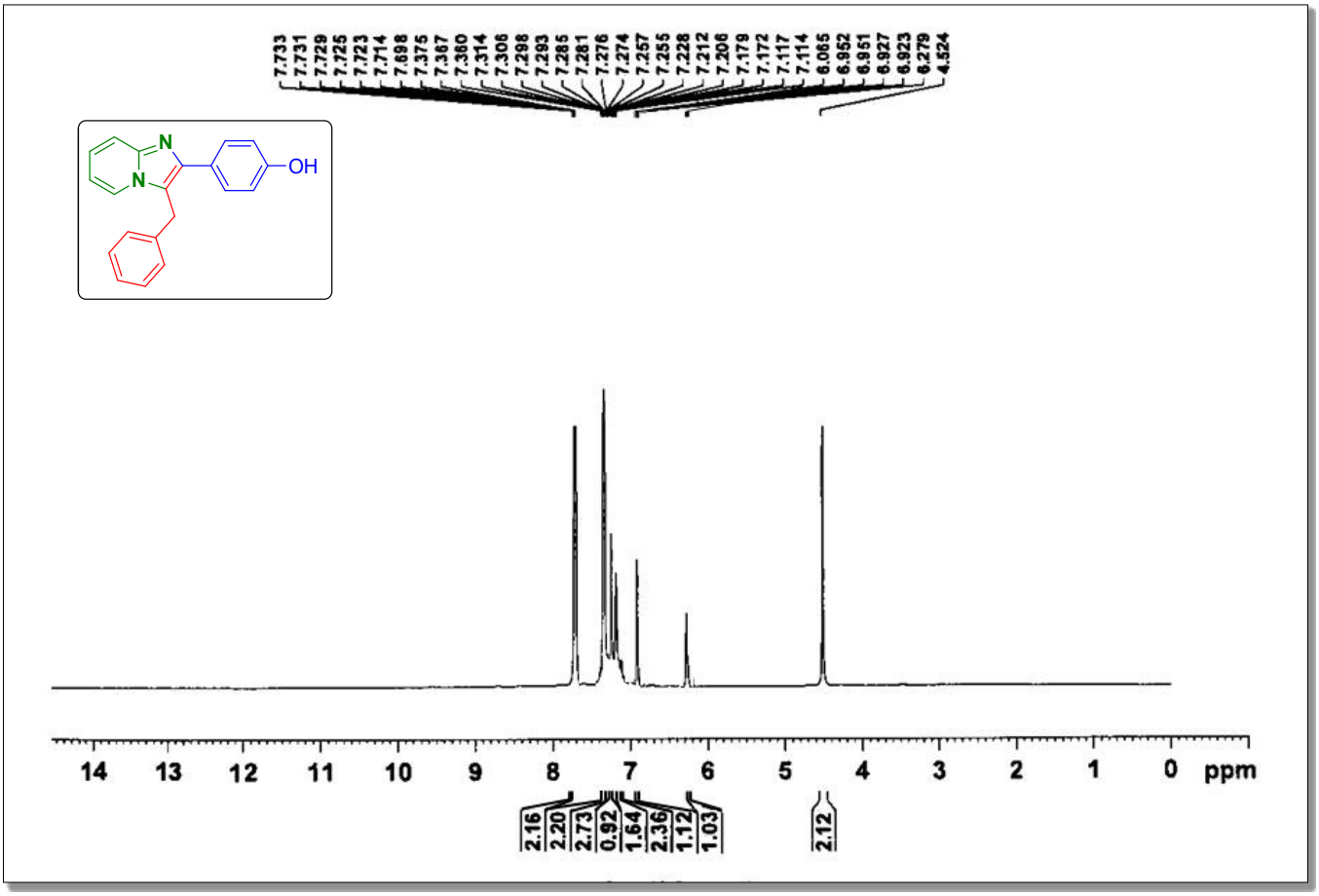


Figure S7. The ^{13}C NMR Spectrum of *4-(3-benzylimidazo[1,2-a]pyridin-2-yl)phenol* **(4*c*)**:

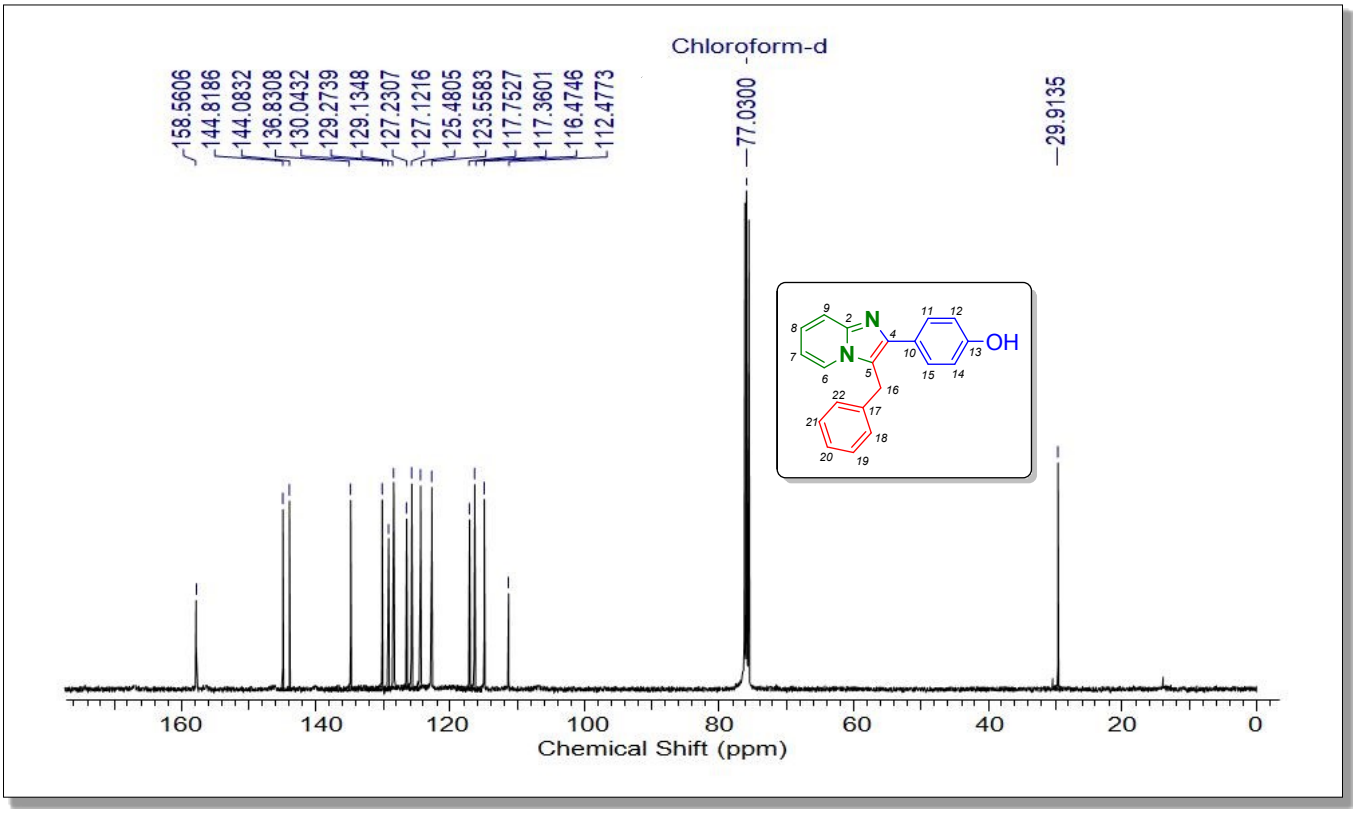


Figure S8. The ^{1}H NMR Spectrum of *3-benzyl-2-(2-nitrophenyl)imidazo[1,2-a]pyridine* (**4*d***):

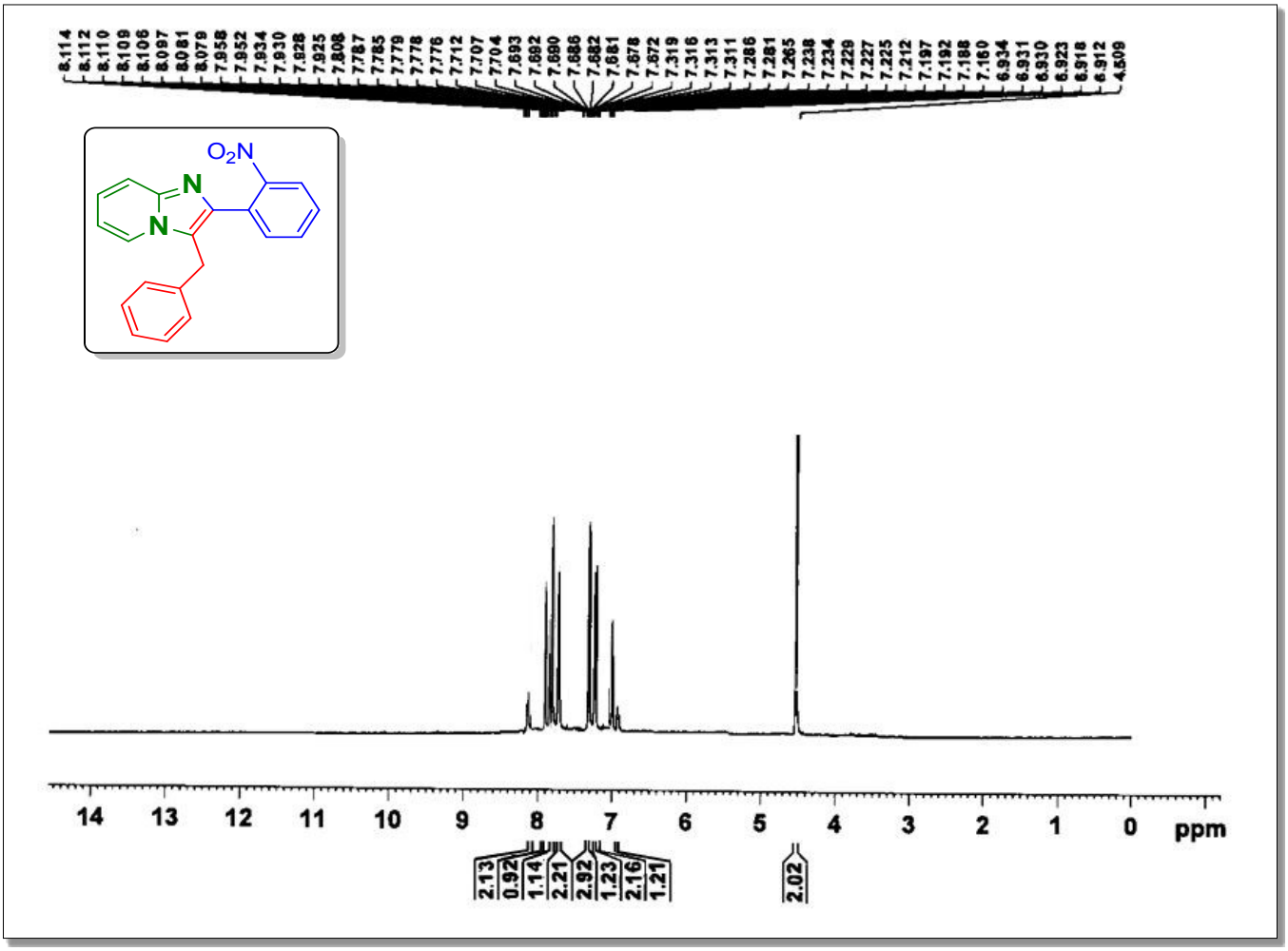


Figure S9. The ^{13}C NMR Spectrum of *3-benzyl-2-(2-nitrophenyl)imidazo[1,2-a]pyridine* **(4*d*)**:

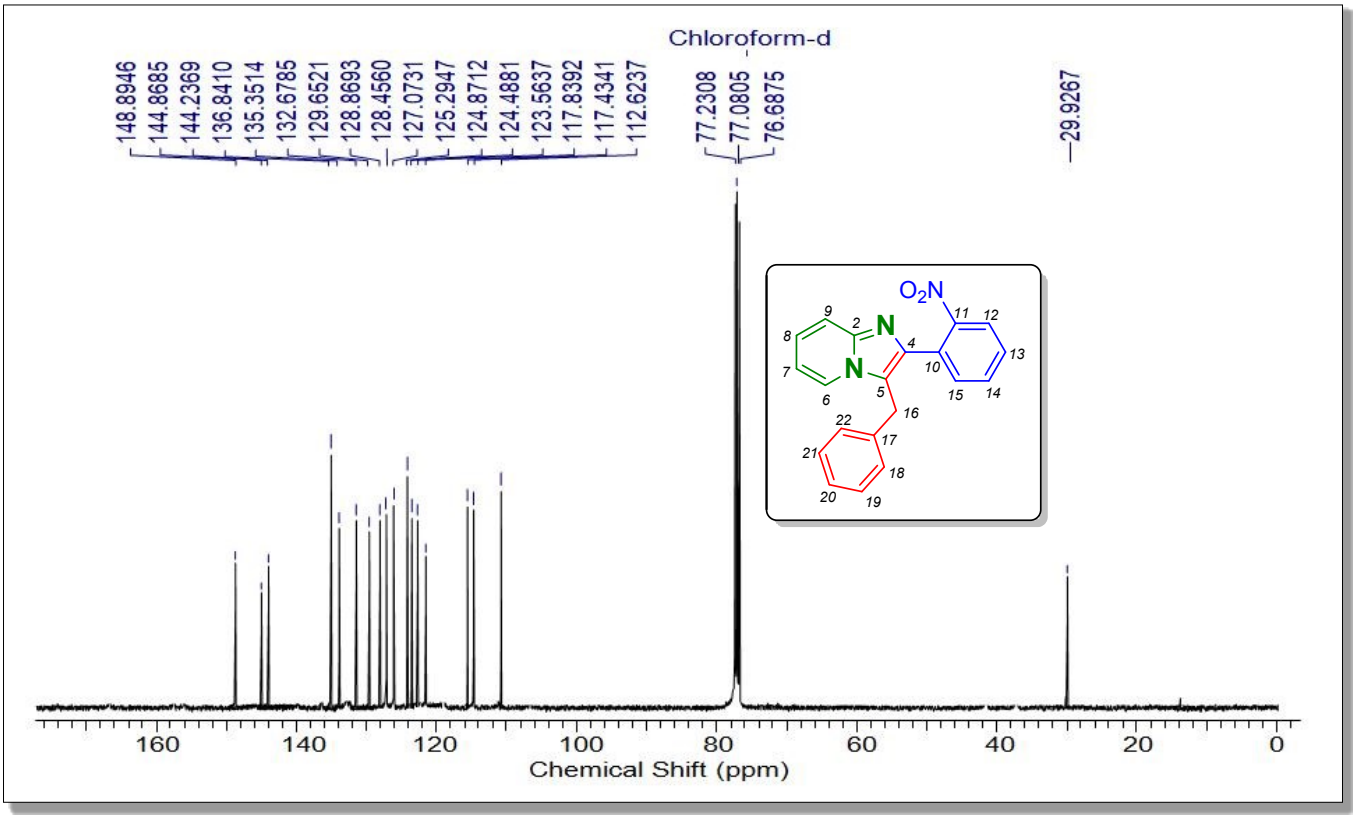


Figure S10. The IR Spectrum of ***4-(3-benzylimidazo[1,2-a]pyridin-2-yl)-3-methoxyphenol*** (**4*e***):

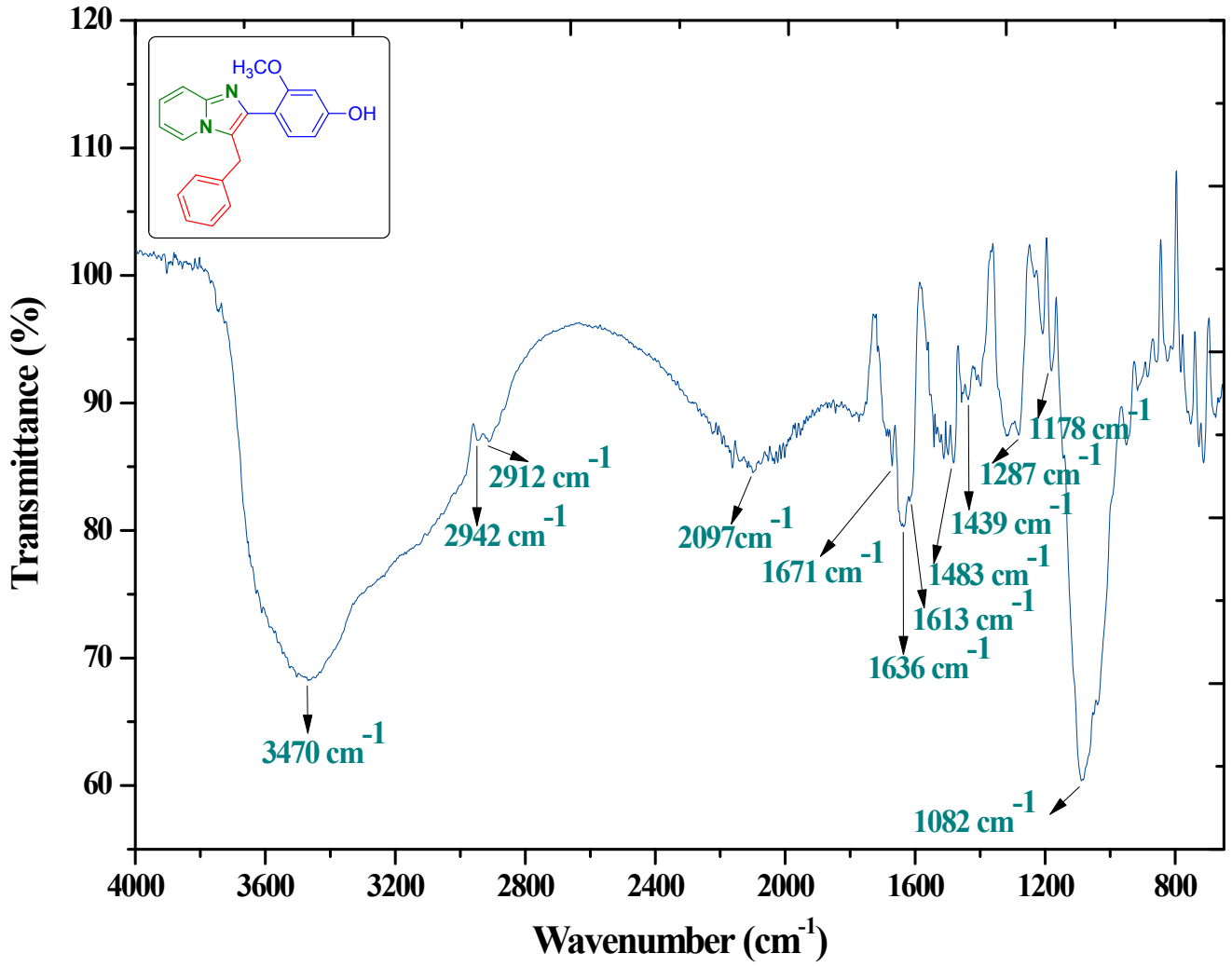


Figure S11. The ^{1}H NMR Spectrum of *4-(3-benzylimidazo[1,2-a]pyridin-2-yl)-3-methoxyphenol* **(4e)**:

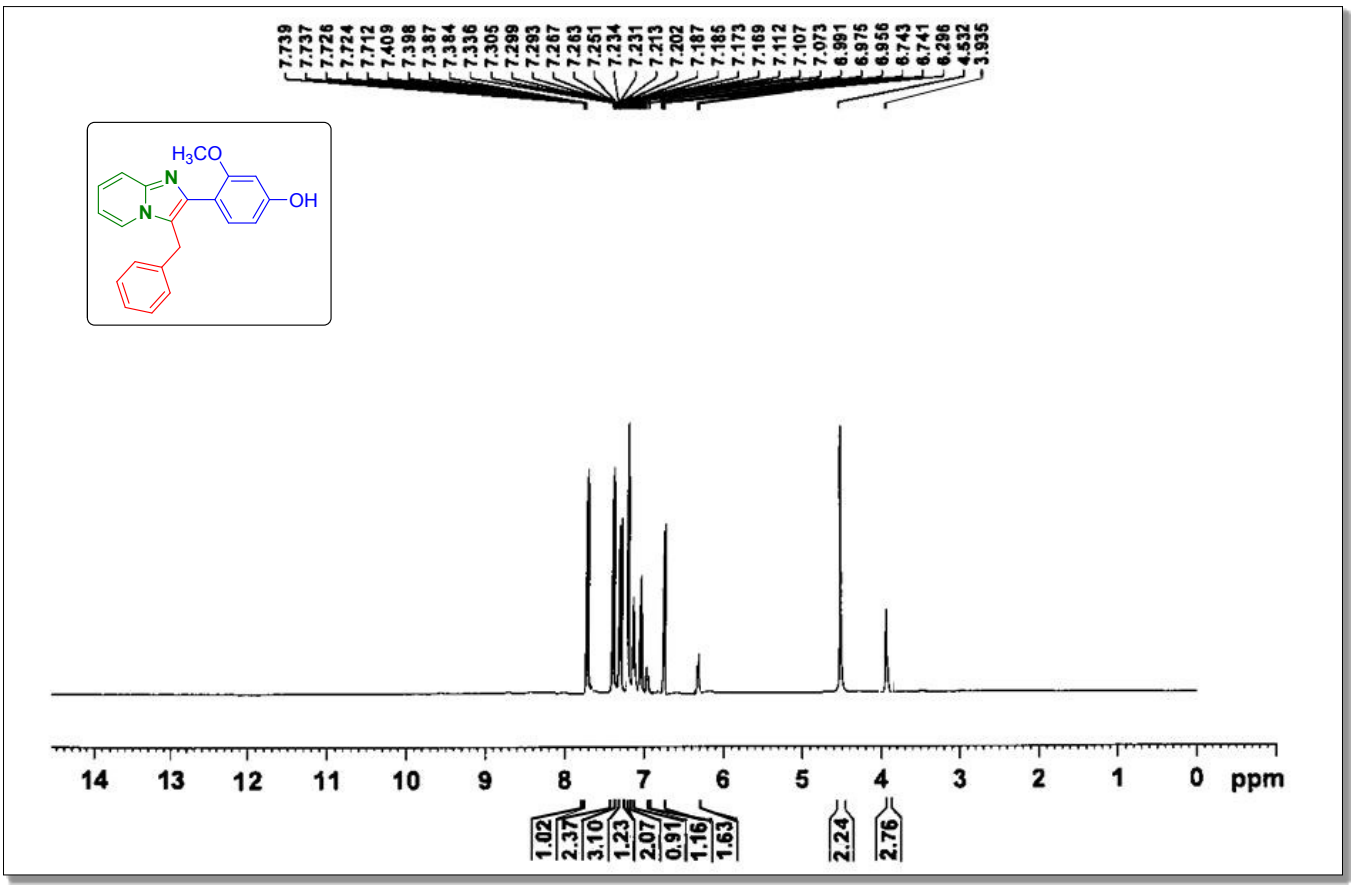


Figure S12. The ^{13}C NMR Spectrum of *4-(3-benzylimidazo[1,2-a]pyridin-2-yl)-3-methoxyphenol* **(4e)**:

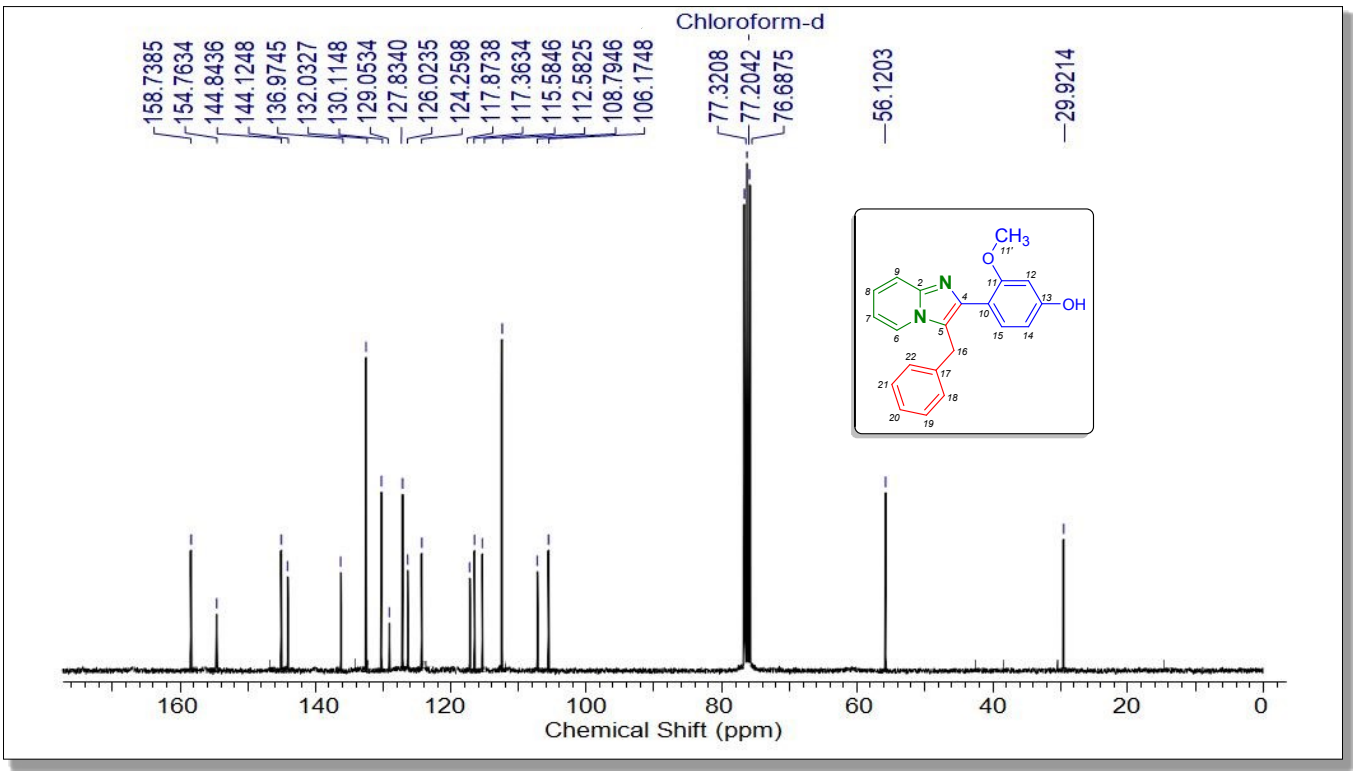


Figure S13. The [1]H NMR Spectrum of 3-*benzyl-7-methyl-2-phenylimidazo[1,2-a]pyridine* **(4f)**:

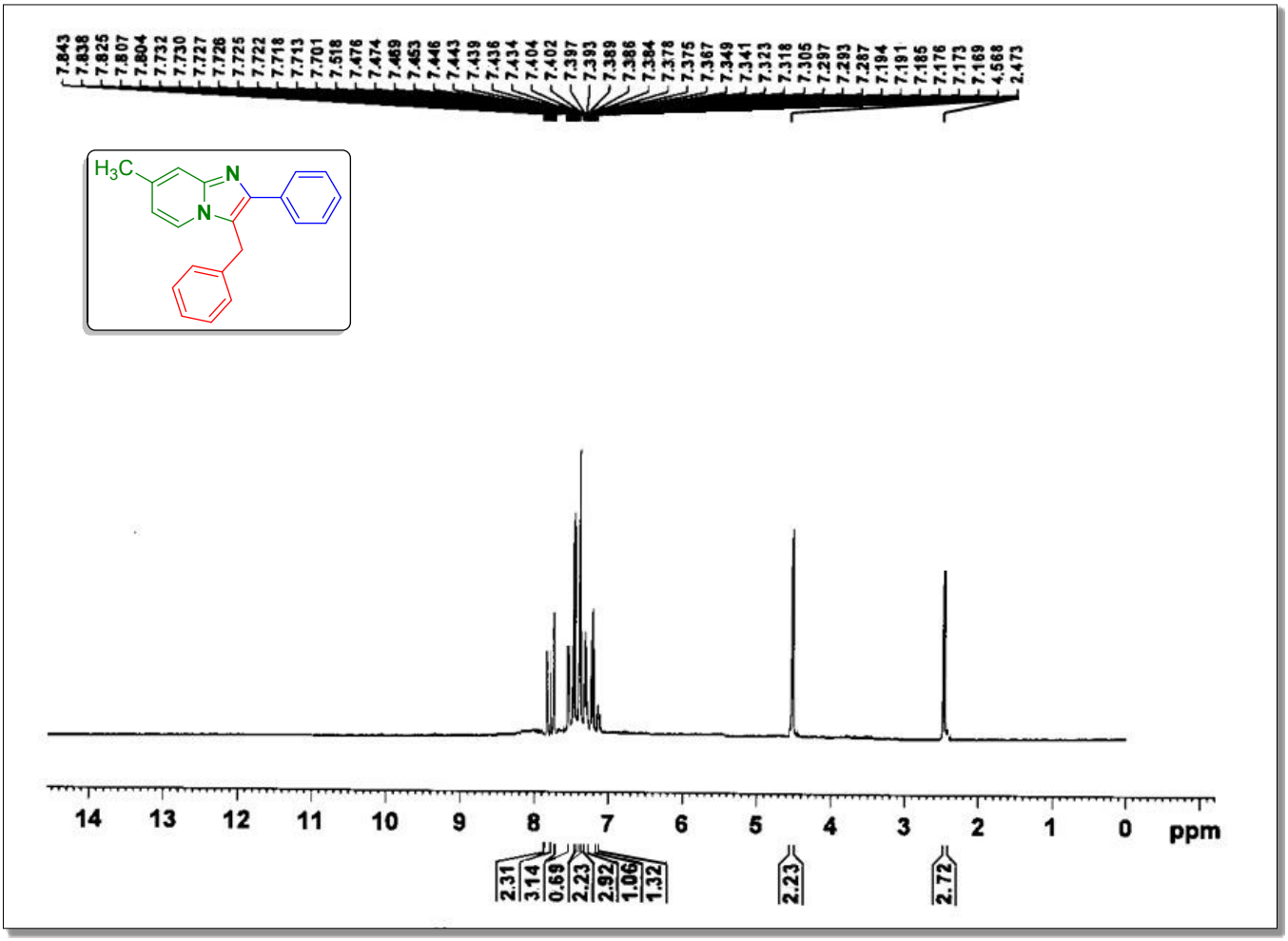


Figure S14. The ^{13}C NMR Spectrum of 3-*benzyl-7-methyl-2-phenylimidazo[1,2-a]pyridine* **(4f)**:

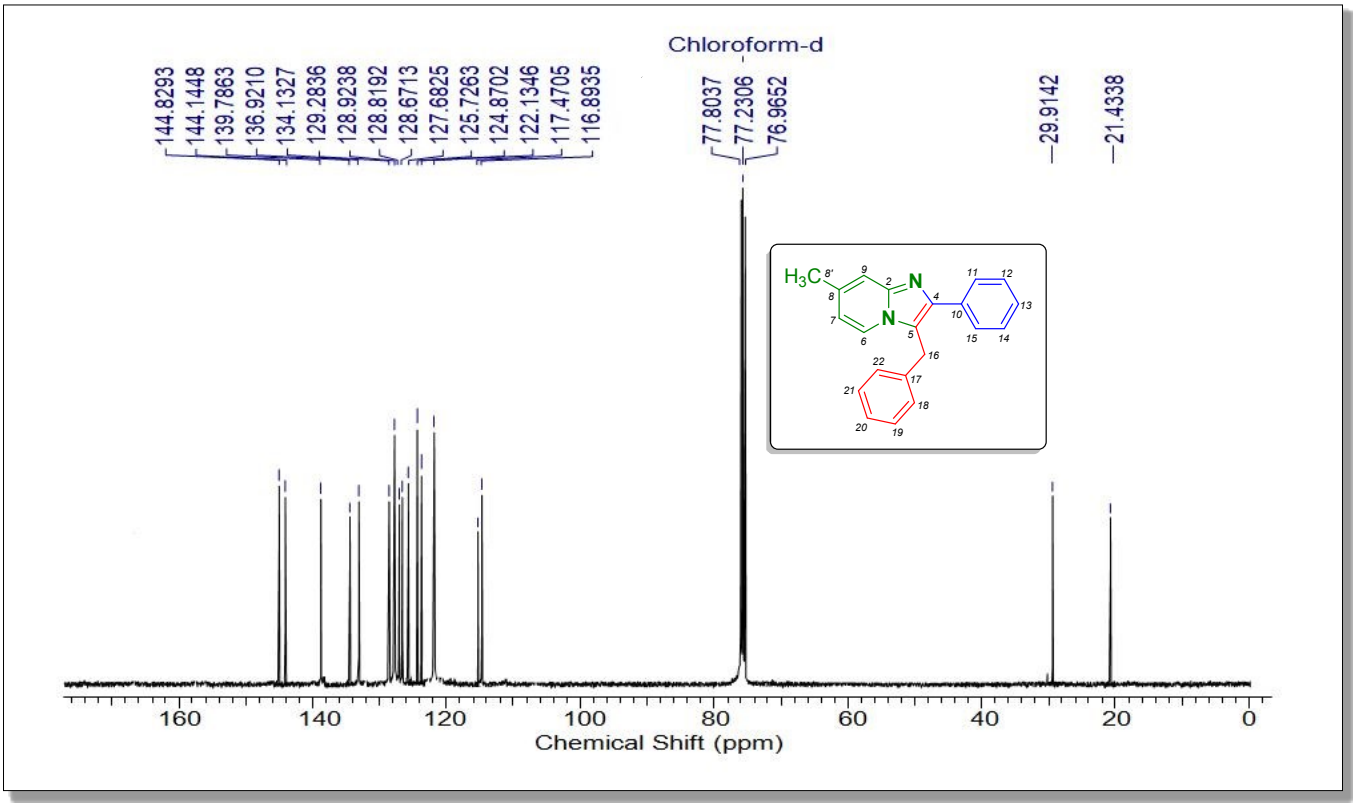


Figure S15. The ^{13}C NMR Spectrum of *3-benzyl-2-(4-chlorophenyl)-7-methylimidazo[1,2-a]pyridine* **(4g)**:

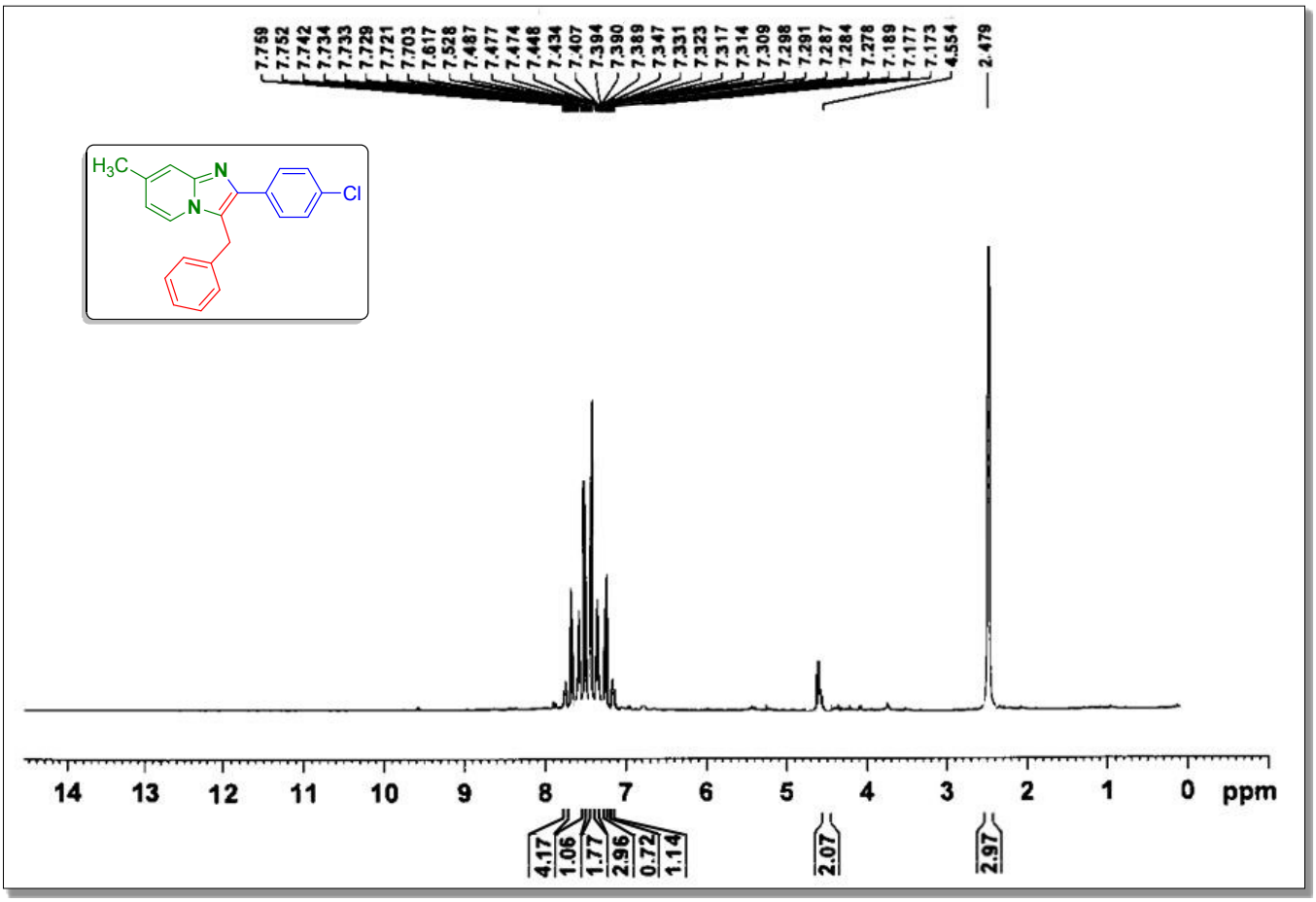


Figure S16. The ^{13}C NMR Spectrum of *3-benzyl-2-(4-chlorophenyl)-7-methylimidazo[1,2-a]pyridine* **(4g)**:

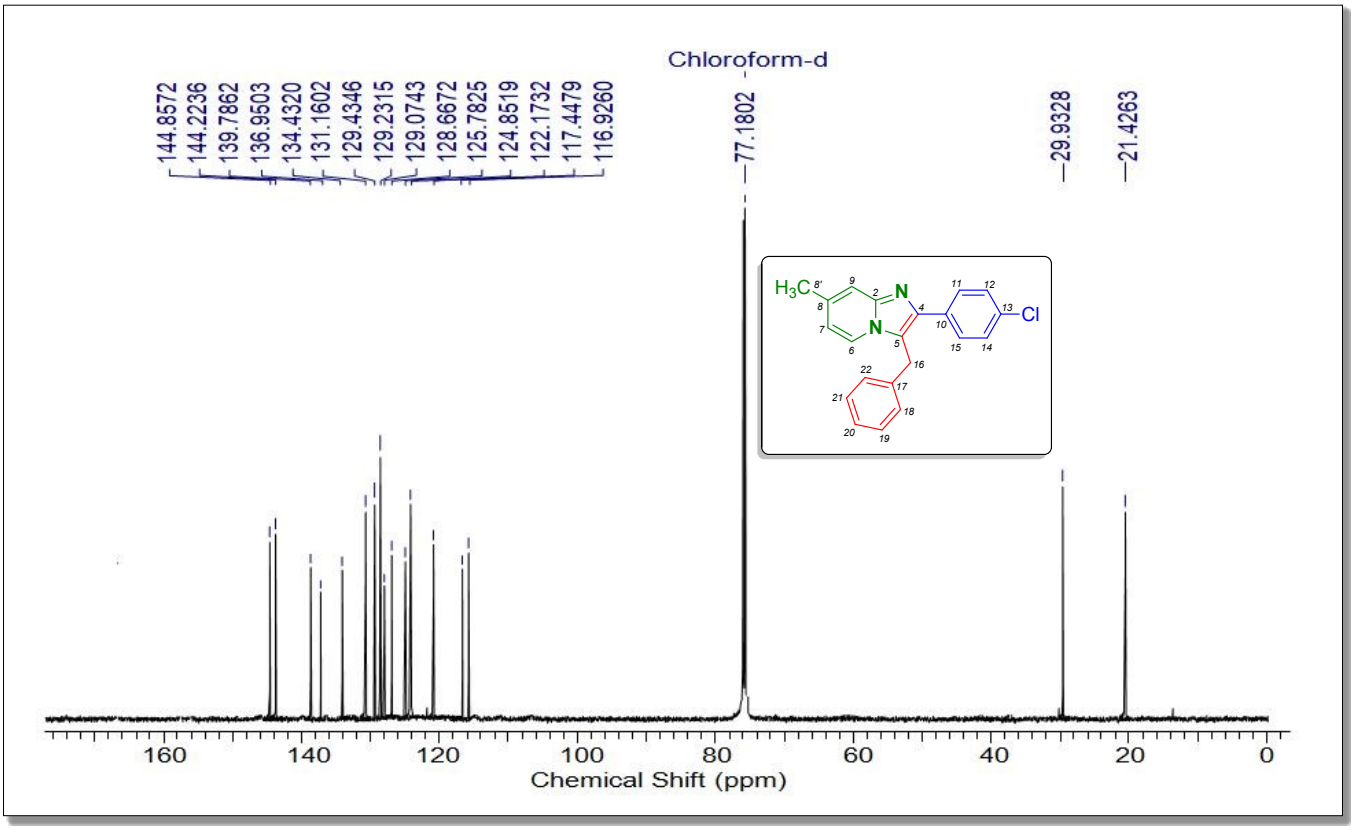


Figure S17. The ^{1}H NMR Spectrum of *4-(3-benzyl-7-methylimidazo[1,2-a]pyridin-2-yl)phenol* **(4h)**:

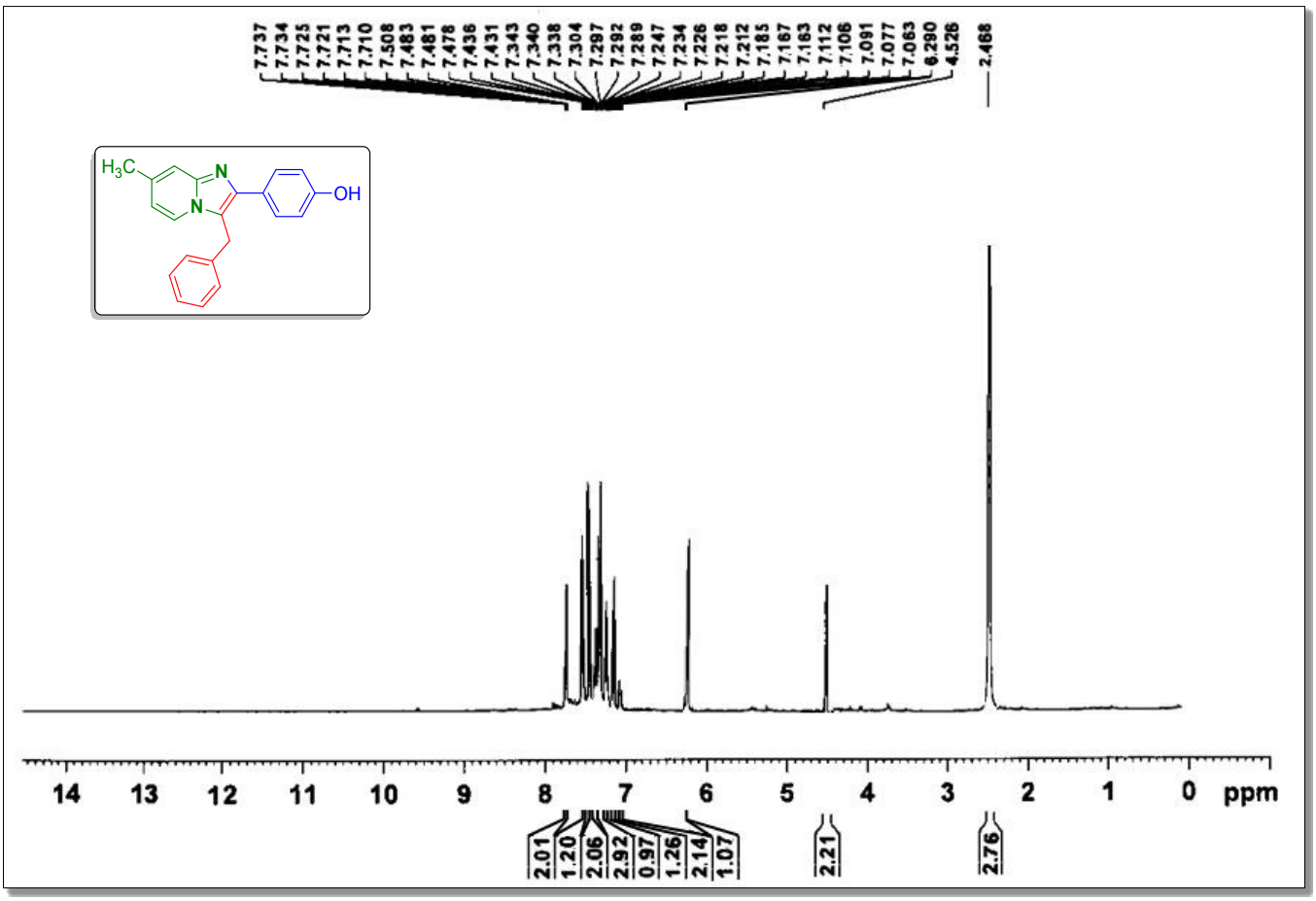


Figure S18. The ^{13}C NMR Spectrum of *4-(3-benzyl-7-methylimidazo[1,2-a]pyridin-2-yl)phenol* **(4h)**:

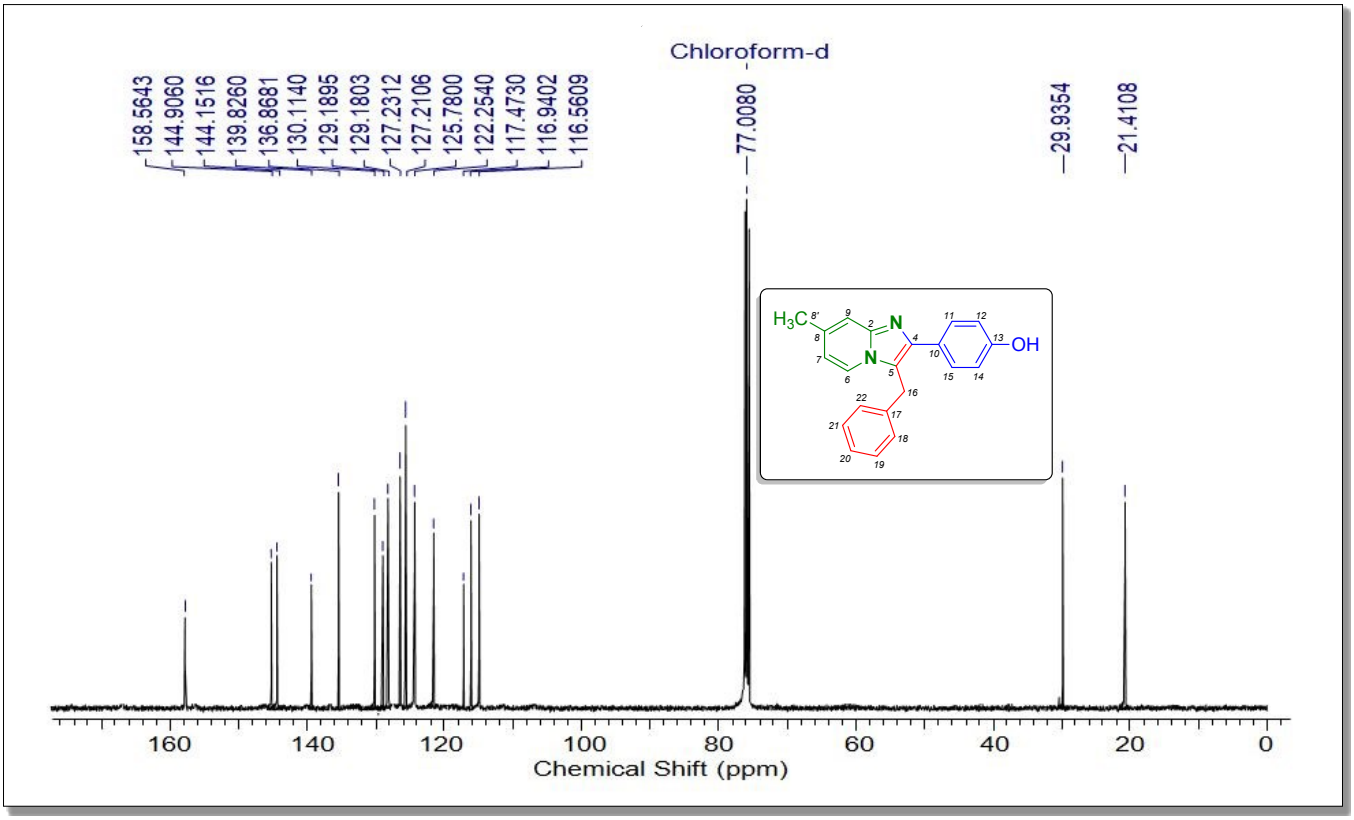


Figure S19. The ^{1}H NMR Spectrum of 3-*benzyl-7-methyl-2-(2-nitrophenyl)imidazo[1,2-a]pyridine* **(4i)**:

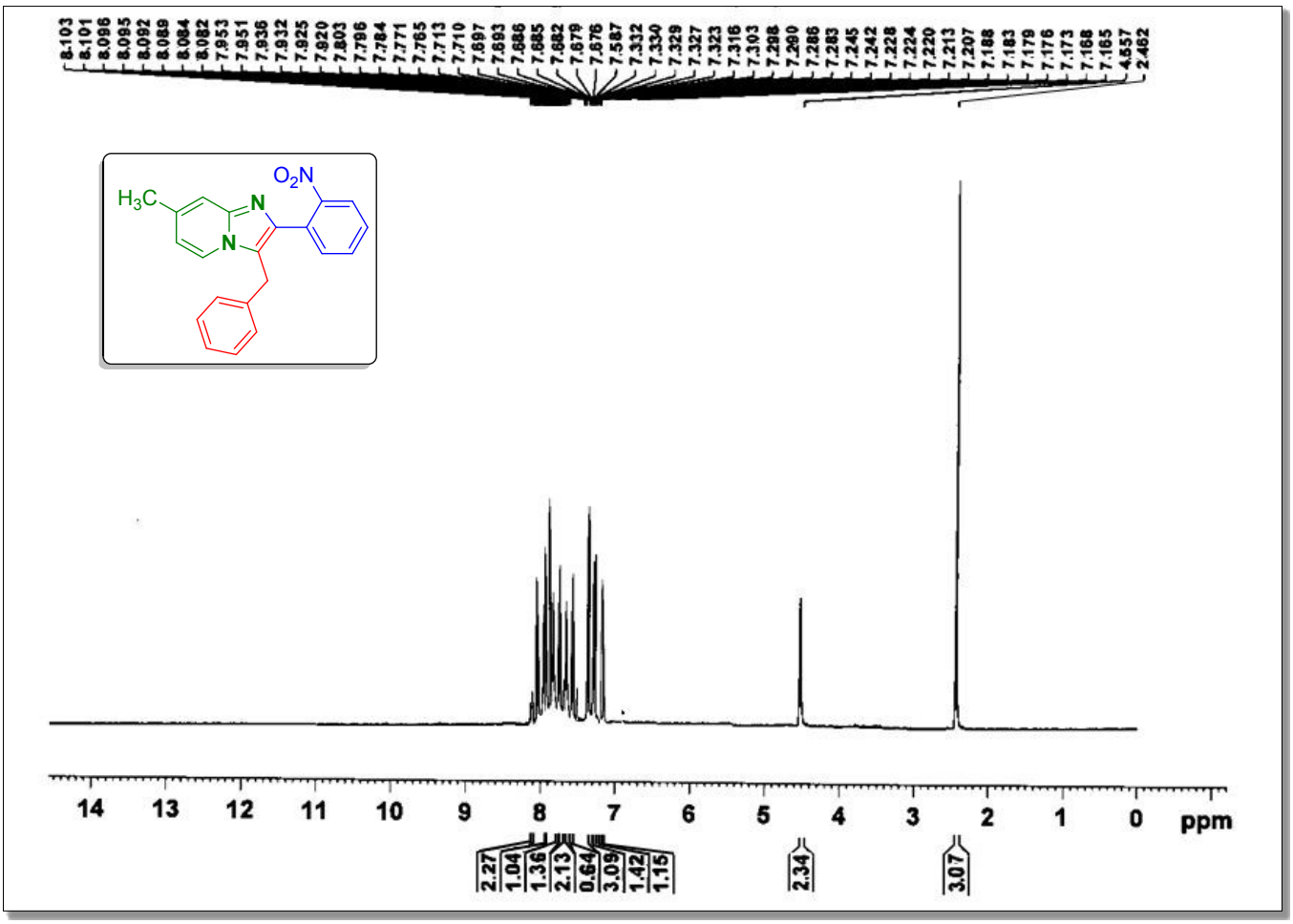


Figure S20. The ^{13}C NMR Spectrum of 3-*benzyl-7-methyl-2-(2-nitrophenyl)imidazo[1,2-a]pyridine* **(4i)**:

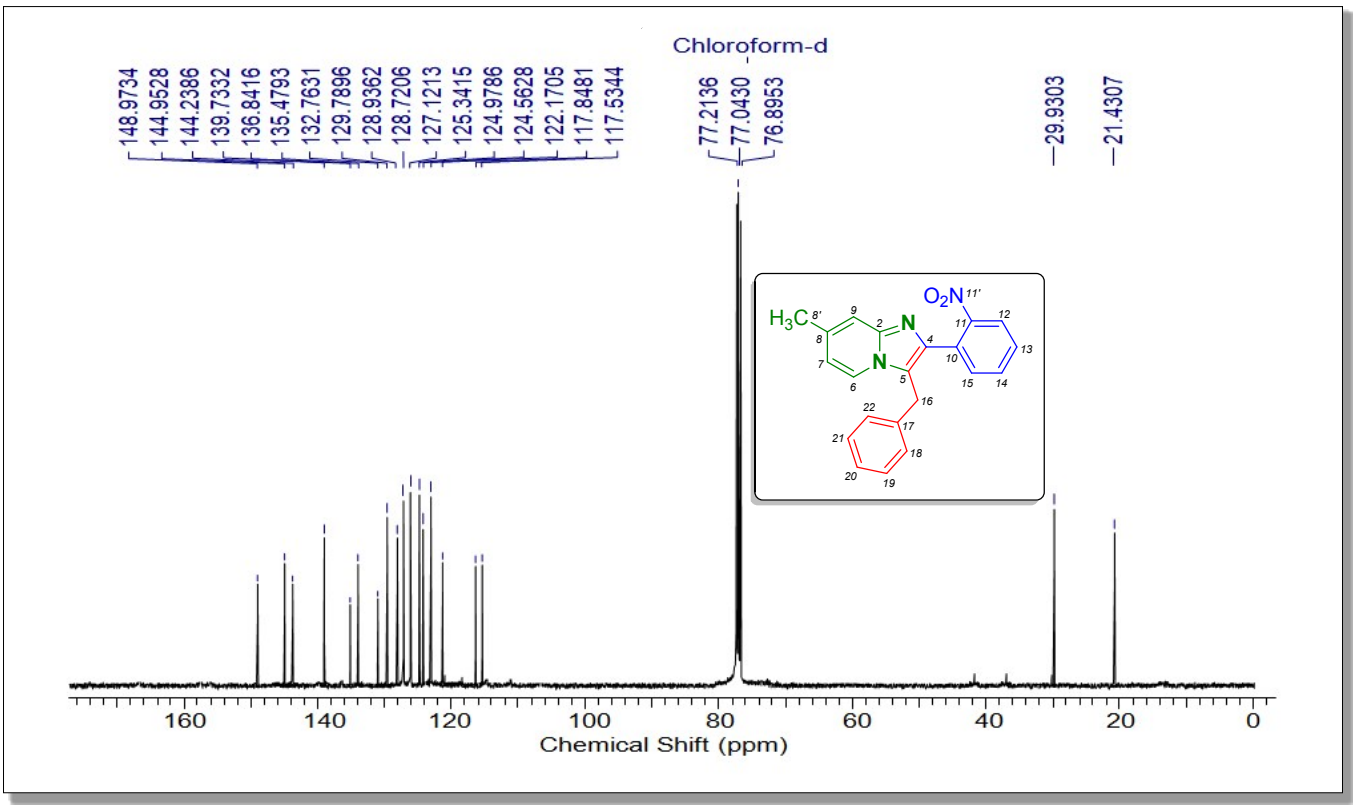


Figure S21. The ^{1}H NMR Spectrum of *4-(3-benzyl-7-methylimidazo[1,2-a]pyridin-2-yl)-3-methoxyphenol* **(4j)**:

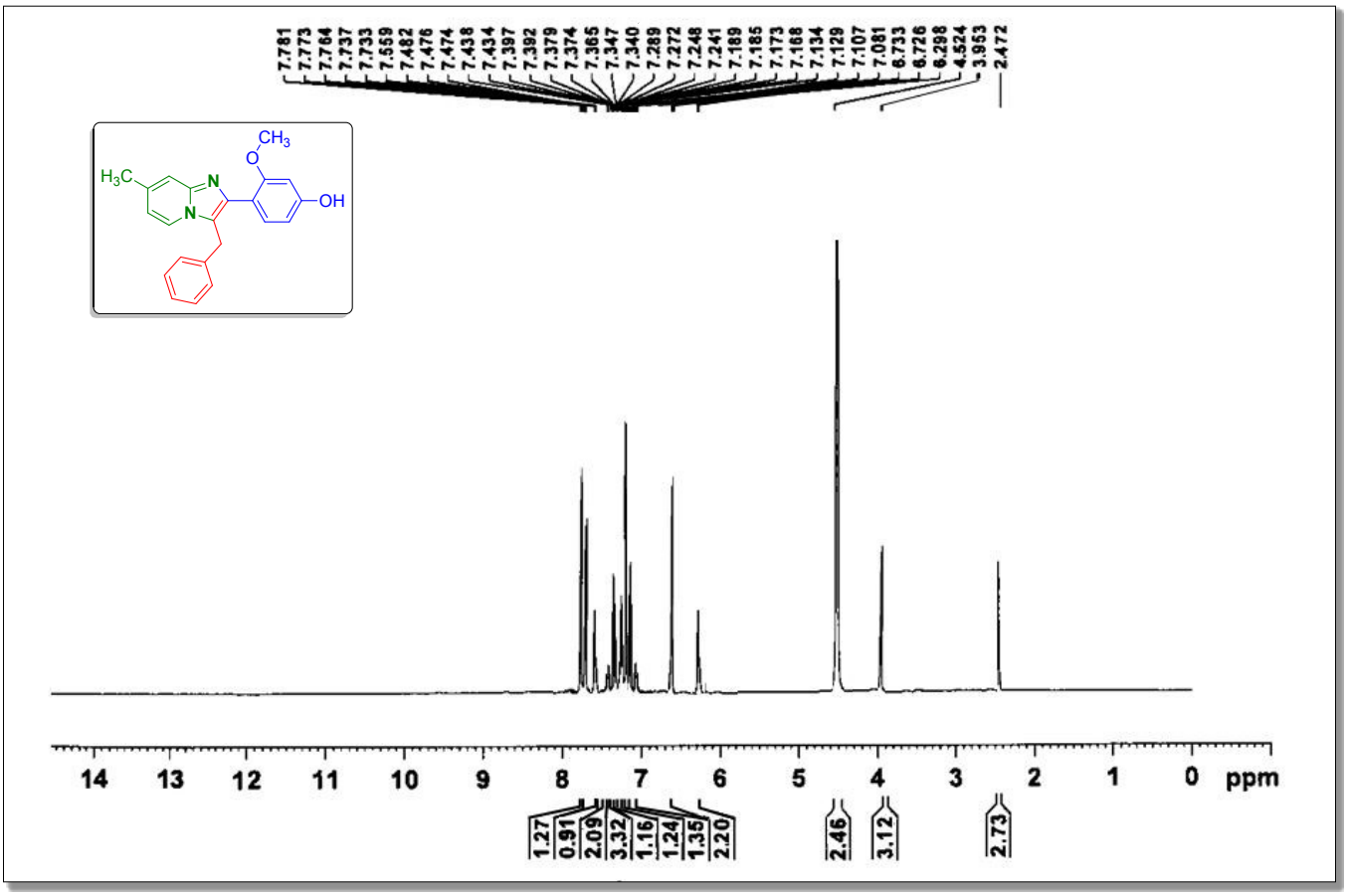


Figure S22. The ^{13}C NMR Spectrum of *4-(3-benzyl-7-methylimidazo[1,2-a]pyridin-2-yl)-3-methoxyphenol* **(4j)**:

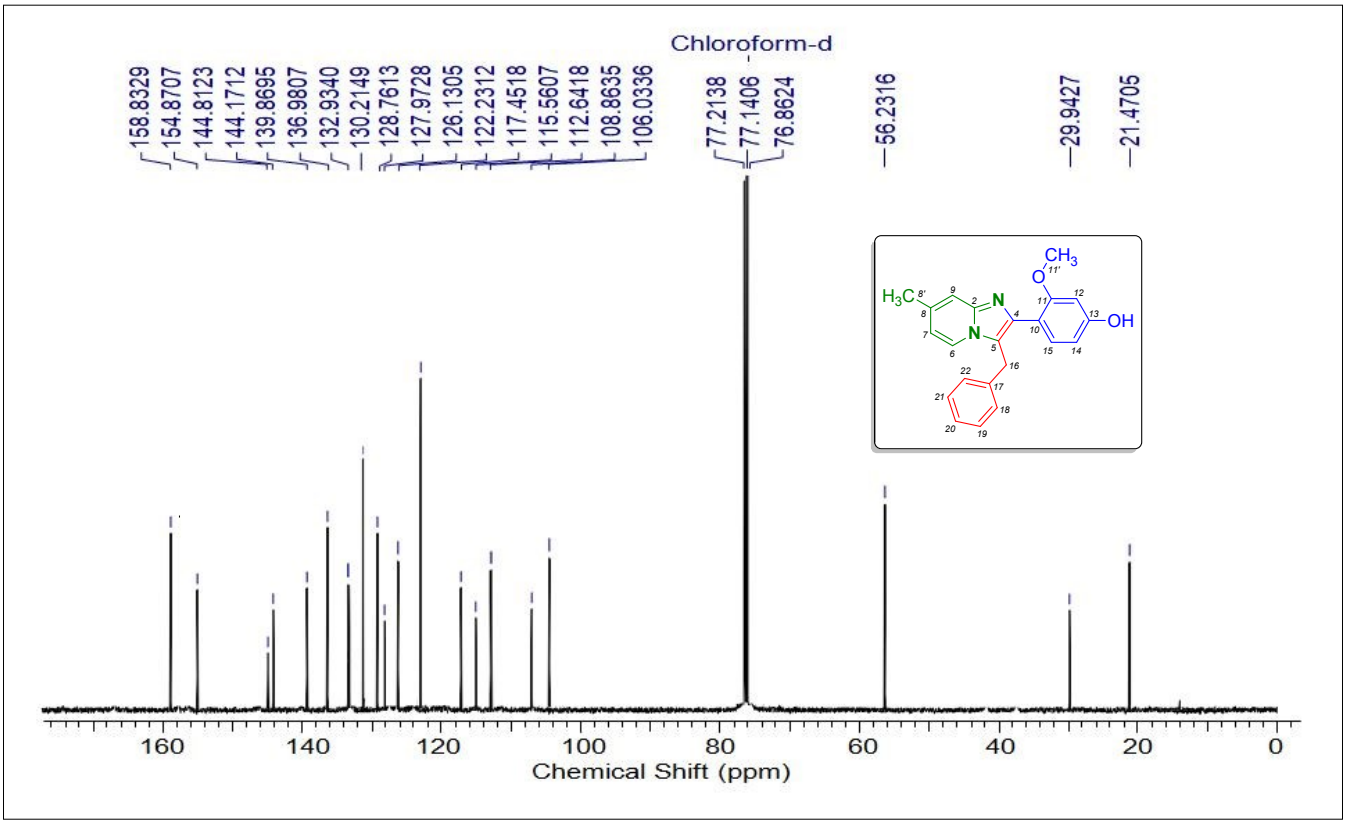


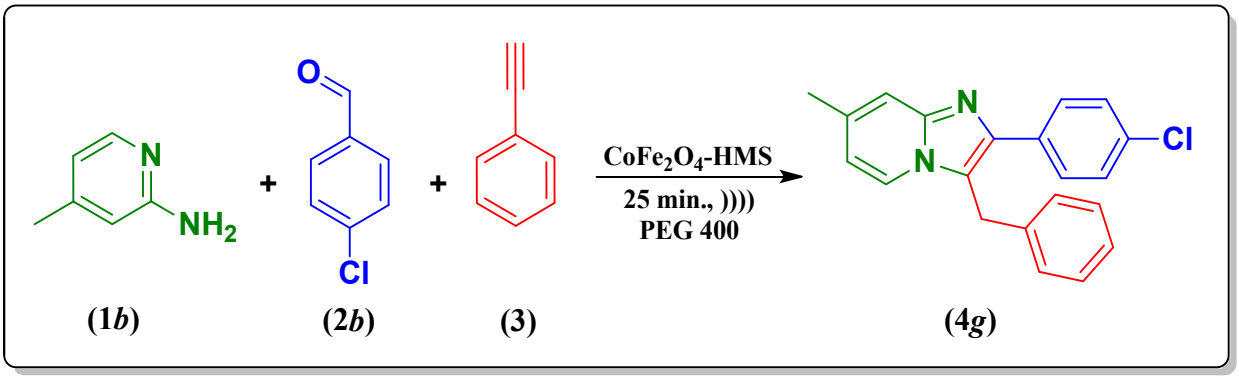
Table S1. Ecoscale calculation for the reaction of 2-amino-4-methyl pyridine, 4-chlorobenzaldehyde and phenylacetylene, in the presence of PEG 400.

EcoScale Penalty points	Details of Parameter	Penalty Points[b]
1. Yield		3
2. Cost of reactants	2-amino-4-methyl pyridine	0
	4-chlorobenzaldehyde	0
	Phenyl acetylene	0
	PEG 400	0
	$CoFe_2O_4$-HMS	0
3. Safety[a]	2-amino-4-methyl pyridine (T)	5
	4-chlorobenzaldehyde (T)	5
	Phenyl acetylene (F, T)	10
	PEG 400	0
	$CoFe_2O_4$-HMS	0
4. Technical setup	Unconventional activation technique (Ultrasound)	2
5. Temperature/time	Room temperature, < 1h	0
6. Workup and purification	Adding solvent	0
Total Penalty points		**25**

[a]Based on the hazard warning symbols.

[b]The total of all penalties was 25, which gave a score of **75** (100 - 25), which is indicative of an excellent green synthesis.

Table S2. Calculation of E-factor, mass intensity, atom economy, reaction mass efficiency and carbon efficiency for the reaction of 2-amino-4methyl pyridine, 4-chlorobenzaldehyde and phenyl acetylene, in the presenceof PEG 400.



(1*b*) (2*b*) (3) (4*g*)

- **Total amount of reactants**: Reactant (1*b*) + Reactant (2*b*) + Reactant (3)
  = 0.1081g + 0.1405 g + 0.1097 g = **0.3583 g**

- **Amount of final product (4*g*)**: **0.3354 g**

- **Amount of waste**: (0.3583 g – 0.3354 g) = **0.0229 g**

$$E\text{ - }Factor = \frac{Amount\ of\ Waste}{Amount\ of\ Product}$$

$$E\text{ - }Factor = \frac{0.0229g}{0.3583g}$$

$$E\text{ - }Factor = 0.0639$$

❖ **Process Mass Intensity (PMI)**

$$Process\ Mass\ Intensity = \frac{Amount\ of\ Waste + Amount\ of\ Product}{Amount\ of\ Product}$$

$$Process\ Mass\ Intensity = E\text{ - }Factor + 1$$

$$Process\ Mass\ Intensity = 1.0639$$

❖ **Atom Economy (AE)**

$$Atom\ Economy\ = \frac{MW\ of\ desired\ Product}{\Sigma\ of\ MW\ \ of\ stoichiometric\ rectants}\ x\ 100$$

$$Atom\ Economy\ = \frac{0.3354}{0.3583}\ x\ 100$$

$$Atom\ Economy\ = 93.60\ \%$$

❖ **Reaction Mass Efficiency**

$$Reaction\ Mass\ Efficiency\ = \frac{Mass\ of\ desired\ Product}{\Sigma\ of\ Mass\ of\ rectants}\ x\ 100$$

$$Reaction\ Mass\ Efficiency\ = \frac{332.8}{368.7}\ x\ 100$$

$$Reaction\ Mass\ Efficiency = 90.26\ \%$$

❖ **Carbon Efficiency (CE)**

$$Carbon\ Efficiency = \frac{Amount\ of\ carbon\ in\ product}{Total\ carbon\ present\ in\ reactants}\ x\ 100$$

$$Carbon\ Efficiency\ = \frac{1.974}{2.665}\ x\ 100$$

$$Carbon\ Efficiency = 74.07\ \%$$

References

1. Z. T. Bhutia, D. Das, A. Chatterjee, M. Banerjee, *ACS Omega*, 2019, **4**, 4481—4490.
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3. G. Purohit, A. Kharkwal, D.S. Rawat, *ACS Sustainable Chem. Eng.*, 2020, **8**, 5544—5557.
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