

Supporting information

Copper bromide-decorated magnetic oyster shell biosupport as a sustainable catalyst for heterogeneous synthesis of imidazo[1,2-a]pyridines in glycerol

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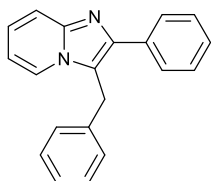
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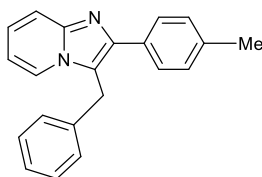
Characterization data of compounds

3-Benzyl-2-phenylimidazo[1,2-*a*]pyridine¹



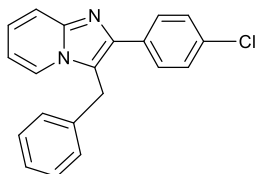
Yield: 93%. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 4.50 (2H, s, CH₂), 6.70 (1H, t, *J* = 6.6 Hz, CH_{Ar}), 7.15 (2H, d, *J* = 7.4 Hz, 2CH_{ortho} of ph), 7.18 (1H, t, *J* = 7.5 Hz, CH_{para} of ph), 7.23-7.27 (1H, m, CH_{Ar}), 7.30 (2H, t, *J* = 7.5 Hz, 2CH_{meta} of Ph), 7.32 (1H, t, *J* = 7.7 Hz, CH_{para} of ph), 7.36 (1H, d, *J* = 7.4 Hz, CH_{Ar}), 7.43 (2H, t, *J* = 7.6 Hz, 2CH_{meta} of Ph), 7.67-7.69 (2H, m, CH_{Ar}), 7.80 (1H, d, *J* = 7.3 Hz, 2CH_{ortho} of Ph). ¹³C NMR (125.77 MHz, CDCl₃) δ: 30.0 (CH₂), 112.3, 117.7, 117.8, 123.5, 124.2, 127.0, 127.8, 128.3, 128.7, 129.2, 134.7, 136.9, 144.4, 145.0.

3-Benzyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine²



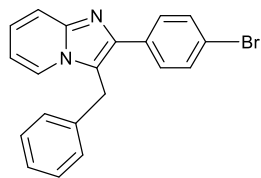
Yield: 87%. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 2.40 (3H, s, CH₃), 4.50 (2H, s, CH₂), 6.70 (1H, t, *J* = 6.5 Hz, CH_{Ar}), 7.16 (2H, d, *J* = 7.5 Hz, 2CH of Ar), 7.18 (1H, t, *J* = 8 Hz, CH_{Ar}), 7.25-7.27 (3H, m, CH_{Ar}), 7.30-7.33 (2H, m, 2CH_{meta} of Ph), 7.68-7.70 (3H, m, CH_{Ar}), 7.71 (1H, d, *J* = 7.9 Hz, CH_{Ar}).

3-Benzyl-2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine¹



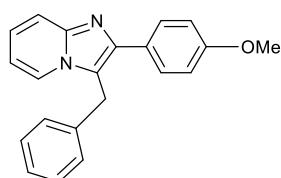
Yield: 85 %. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 4.48 (2H, s, CH₂), 6.73 (1H, t, *J* = 6.7 Hz, CH_{Ar}), 7.14 (2H, d, *J* = 7.3 Hz, 2CH of Ar), 7.21 (1H, t, *J* = 8.0 Hz, CH_{Ar}), 7.25-7.33 (3H, m, 3CH_{Ar}), 7.41 (2H, d, *J* = 8.2 Hz, 2CH of Ar), 7.67-7.74 (4H, m, 4CH_{Ar}).

3-Benzyl-2-(4-bromophenyl)imidazo[1,2-*a*]pyridine^{1, 3}



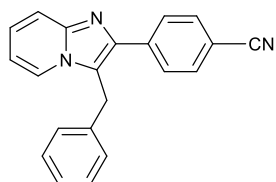
Yield: 83%. ^1H NMR (500.13 MHz, CDCl_3) δ (ppm): 4.48 (2H, s, CH_2), 6.74 (1H, t, $J = 6.7$ Hz, CH_{Ar}), 7.13 (2H, d, $J = 7.5$ Hz, 2CH of Ar), 7.21 (1H, t, $J = 8.1$ Hz, CH_{Ar}), 7.25-7.34 (3H, m, 3CH_{Ar}), 7.56 (2H, d, $J = 8.0$ Hz, CH_{Ar}), 7.66 (2H, d, $J = 8.4$ Hz, CH_{Ar}), 7.69-7.72 (2H, m, CH_{Ar}).

3-Benzyl-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine²



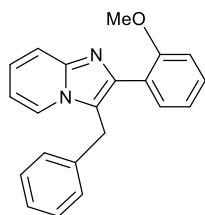
Yield: 90%. ^1H NMR (500.13 MHz, CDCl_3) δ (ppm): 3.83 (3H, s, OCH_3), 4.47 (2H, s, CH_2), 6.69 (1H, t, $J = 6.7$ Hz, CH_{Ar}), 6.97 (2H, d, $J = 8.7$ Hz, 2CH of Ar), 7.14 (2H, d, $J = 7.0$ Hz, 2CH of Ar), 7.16 (1H, t, $J = 7.7$ Hz, CH_{Ar}), 7.23-7.32 (3H, m, 3CH_{Ar}), 7.67 (2H, t, $J = 7.3$ Hz, 2CH_{meta} of Ph), 7.72 (2H, d, $J = 8.7$ Hz, 2CH of Ar).

4-(3-Benzylimidazo[1,2-*a*]pyridin-2-yl)benzonitrile⁴



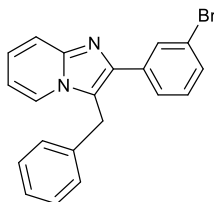
Yield: 65%. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.53 (2H, s, CH_2), 6.96 (1H, t, $J = 6.6$ Hz, CH_{Ar}), 7.13 (2H, d, $J = 6.1$ Hz, $2\text{CH}_{\text{ortho}}$ of ph), 7.30-7.40 (3H, m, 3CH_{Ar}), 7.45 (1H, t, $J = 7.9$ Hz, CH_{para} of ph), 7.76 (2H, d, $J = 8.6$ Hz, 2CH_{Ar}), 7.84 (1H, d, $J = 6.9$ Hz, CH_{Ar}), 7.92-8.02 (3H, m, 3CH_{Ar}).

3-Benzyl-2-(2-methoxyphenyl)imidazo[1,2-*a*]pyridine⁵



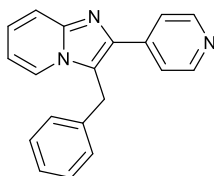
Yield: 76%. ^1H NMR (500.13 MHz, CDCl_3) δ (ppm): 3.83 (3H, s, OCH_3), 4.47 (2H, s, CH_2), 6.69 (1H, t, $J = 6.5$ Hz, CH_{Ar}), 6.97 (1H, d, $J = 8.0$ Hz, CH_{Ar}), 7.06 (1H, t, $J = 6.9$ Hz, CH_{Ar}), 7.13 (2H, d, $J = 6.9$ Hz, 2CH of Ar), 7.17 (1H, t, $J = 6.8$ Hz, CH_{Ar}), 7.22 (1H, d, $J = 6.7$ Hz, CH_{Ar}), 7.26-7.32 (2H, m, 2 CH_{Ar}), 7.37 (1H, t, $J = 7.3$ Hz, CH_{Ar}), 7.62-7.71 (3H, m, 3 CH_{Ar}).

3-Benzyl-2-(3-bromophenyl)imidazo[1,2-a]pyridine³



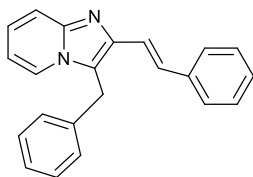
Yield: 81%. ^1H NMR (500.13 MHz, CDCl_3) δ (ppm): 4.50 (2H, s, CH_2), 6.74 (1H, t, $J = 6.8$ Hz, CH_{Ar}), 7.14 (2H, d, $J = 7.2$ Hz, 2CH of Ar), 7.21 (1H, t, $J = 7.4$, CH_{Ar}), 7.27-7.35 (4H, m, 4 CH_{Ar}), 7.49 (1H, d, $J = 8.0$ Hz, CH_{Ar}), 7.66-7.70 (2H, m, 2 CH_{meta} of Ph), 7.73 (1H, d, $J = 6.9$ Hz, CH_{Ar}), 8.03 (1H, t, $J = 1.6$ Hz, CH_{Ar}). ^{13}C NMR (125.77 MHz, CDCl_3) δ : 29.8 (CH_2), 112.4, 117.7, 118.2, 122.9, 123.5, 124.5, 126.5, 127.0, 127.7, 129.1, 130.1, 130.7, 131.2, 136.5, 136.7, 142.6, 144.9.

3-Benzyl-2-(pyridin-4-yl)imidazo[1,2-a]pyridine⁴



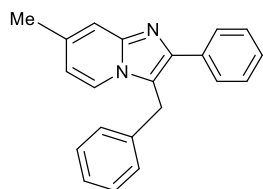
Yield: 74%. ^1H NMR (400.20 MHz, CDCl_3) δ (ppm): 4.68 (2H, s, CH_2), 6.95 (1H, t, $J = 6.5$ Hz, CH_{Ar}), 7.11 (2H, d, $J = 7.5$ Hz, 2 CH_{ortho} of Ph), 7.22-7.24 (1H, m, CH_{Ar}), 7.28-7.30 (2H, m, 2 CH_{Ar}), 7.32-7.35 (1H, m, CH_{Ar}), 7.67 (1H, d, $J = 9$ Hz, CH_{Ar}), 7.79 (2H, d, $J = 5$ Hz, 2 CH_{Ar}), 8.26 (1H, d, $J = 6.9$ Hz, CH_{Ar}), 8.62 (2H, d, $J = 4.8$ Hz, 2 CH_{Ar}).

(E)-3-Benzyl-2-styrylimidazo[1,2-a]pyridine^{1, 3}



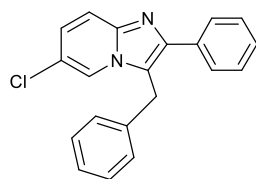
Yield: 72%. ^1H NMR (500.13 MHz, CDCl_3) δ : 4.42 (2H, s, CH_2), 6.68 (1H, t, $J = 6.8$ Hz, CH_{Ar}), 7.15-7.18 (3H, m, 2 CH_{ortho} of Ph), 7.23-7.32 (5H, m, CH_{Ar}), 7.37 (2H, t, $J = 7.8$ Hz, 2 CH_{meta} of Ph), 7.58 (2H, d, $J = 7.4$ Hz, CH_{ortho} of Ph), 7.62 (1H, d, $J = 9.1$ Hz, CH_{Ar}), 7.70 (1H, d, $J = 4.1$ Hz, CH_{Ar}), 7.72 (1H, d, $J = 13.0$ Hz, CH_{Ar}).

3-Benzyl-7-methyl-2-phenylimidazo[1,2-a]pyridine¹



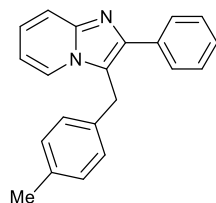
Yield: 85%. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 2.40 (3H, s, CH₃), 4.48 (2H, s, CH₂), 6.54 (1H, d, *J* = 7.0 Hz, CH_{Ar}), 7.16 (2H, d, *J* = 7.1 Hz, 2CH_{ortho} of Ph), 7.25-7.36 (4H, m, 4CH_{Ar}), 7.41-7.46 (3H, m, 3CH_{Ar}), 7.58 (1H, d, *J* = 6.9 Hz, CH_{Ar}), 7.78-7.80 (2H, m, 2CH_{ortho} of Ph).

3-Benzyl-6-chloro-2-phenylimidazo[1,2-a]pyridine¹



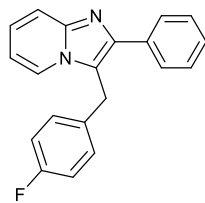
Yield: 75%. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 4.47 (2H, s, CH₂), 7.12-7.16 (3H, m, CH_{Ar}), 7.27-7.33 (3H, m, CH_{Ar}), 7.34-7.38 (1H, m, CH_{Ar}), 7.43 (2H, t, *J* = 7.9 Hz, CH_{Ar}), 7.62 (1H, d, *J* = 9.5 Hz, CH_{Ar}), 7.73 (1H, d, *J* = 2.0 Hz, CH_{Ar}), 7.75-7.78 (2H, m, CH_{Ar}). ¹³CNMR (125.77 MHz, CDCl₃) δ: 30.0 (CH₂), 118.1, 118.5, 120.6, 121.3, 125.6, 127.3, 127.8, 128.1, 128.3, 128.8, 129.3, 134.2, 136.3, 143.4, 145.4.

3-(4-Methylbenzyl)-2-phenylimidazo[1,2-a]pyridine²



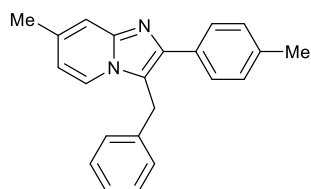
Yield: 80%. ¹H NMR (500.13 MHz, CDCl₃) δ (ppm): 2.33 (3H, s, CH₃), 4.46 (2H, s, CH₂), 6.72 (1H, t, *J* = 6.7 Hz, CH_{Ar}), 7.04 (2H, d, *J* = 7.8 Hz, 2CH_{Ar}), 7.12 (2H, d, *J* = 7.8 Hz, 2CH_{Ar}), 7.19 (1H, t, *J* = 7.5 Hz, CH_{Ar}), 7.35 (1H, t, *J* = 7.5 Hz, CH_{para} of Ph), 7.43 (2H, t, *J* = 7.5 Hz, 2CH_{meta} of Ph), 7.70-7.72 (2H, m, 2CH_{Ar}), 7.78 (2H, d, *J* = 7.5 Hz, 2CH_{ortho} of Ph).

3-(4-Fluorobenzyl)-2-phenylimidazo[1,2-a]pyridine^{2, 6}



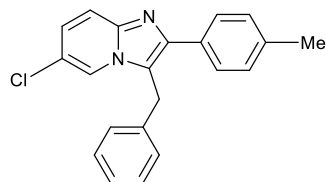
Yield: 85%. ^1H NMR (500.13 MHz, CDCl_3) δ (ppm): 4.46 (2H, s, CH_2), 6.74 (1H, t, $J = 6.8$ Hz, CH_{Ar}), 7.00 (2H, t, $J = 8.6$ Hz, 2CH_{ortho} of ph), 7.08-7.11 (2H, m, CH_{Ar}), 7.20 (1H, t, $J = 8.0$ Hz, CH_{Ar}), 7.36 (1H, t, $J = 6.5$ Hz, CH_{Ar}), 7.44 (2H, t, $J = 8.0$ Hz, CH_{Ar}), 7.67-7.72 (2H, m, CH_{Ar}), 7.76 (2H, d, $J = 7.2$ Hz, CH_{Ar}).

3-Benzyl-7-methyl-2-(4-methylphenyl)imidazo[1,2-*a*]pyridine



Yield: 60%. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 2.39 (3H, s, CH_3), 2.41 (3H, s, CH_3), 4.47 (2H, s, CH_2), 6.60 (1H, d, $J = 8.6$ Hz, CH_{Ar}), 7.14 (2H, d, $J = 6.7$ Hz, 2CH_{Ar}), 7.22-7.32 (5H, m, 5CH_{Ar}), 7.54-7.62 (2H, m, 2CH_{Ar}), 7.68 (2H, d, $J = 7.9$ Hz, 2CH_{Ar}).

3-Benzyl-6-chloro-2-(4-methylphenyl)imidazo[1,2-*a*]pyridine



Yield: 63%. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 2.39 (3H, s, CH_3), 4.48 (2H, s, CH_2), 7.14 (2H, d, $J = 7.5$ Hz, 2CH_{Ar}), 7.20-7.40 (6H, m, 6CH_{Ar}), 7.68 (2H, d, $J = 7.8$ Hz, 2CH_{Ar}), 7.77 (2H, d, $J = 6.6$ Hz, 2CH_{Ar}).

The ^1H and ^{13}C NMR spectra of compounds

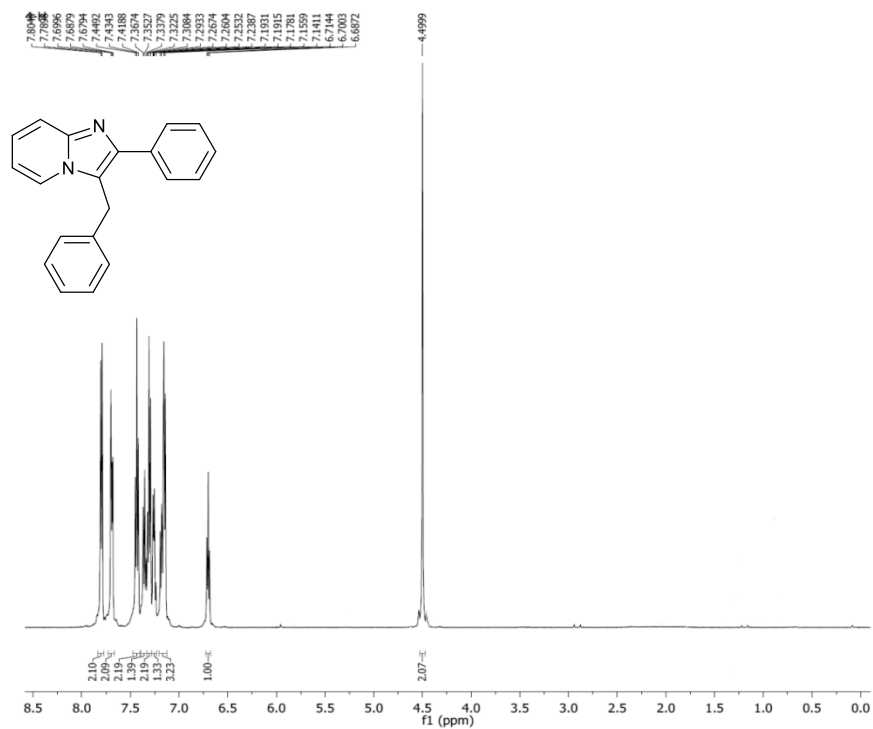


Figure 1. The ^1H NMR spectrum of 3-Benzyl-2-phenylimidazo[1,2-a]pyridine

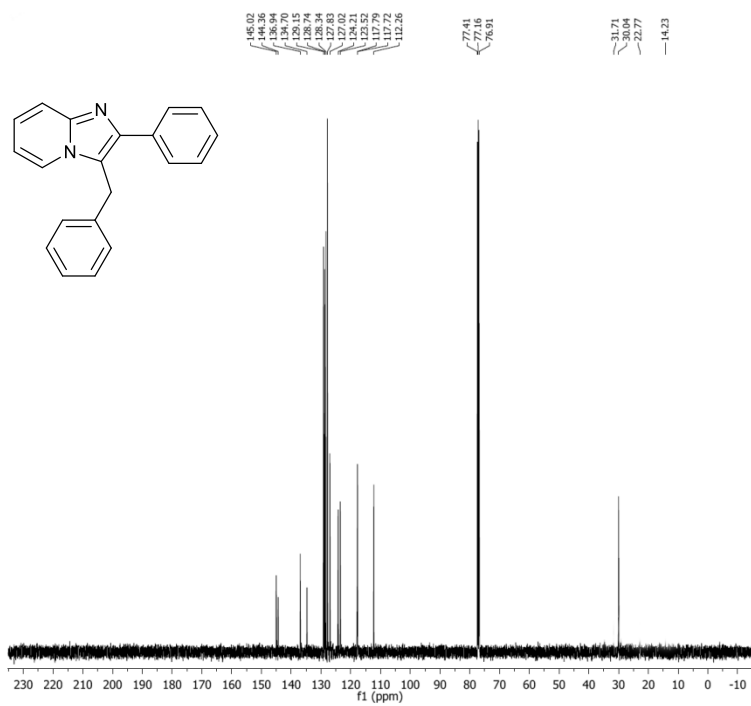


Figure 2. The ^{13}C NMR spectrum of 3-Benzyl-2-phenylimidazo[1,2-a]pyridine

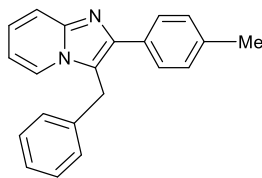


Figure 3. The ^1H NMR spectrum of 3-Benzyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine

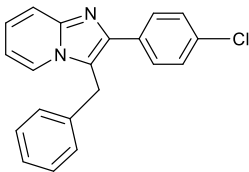


Figure 4. The ^1H NMR spectrum of 3-Benzyl-2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine

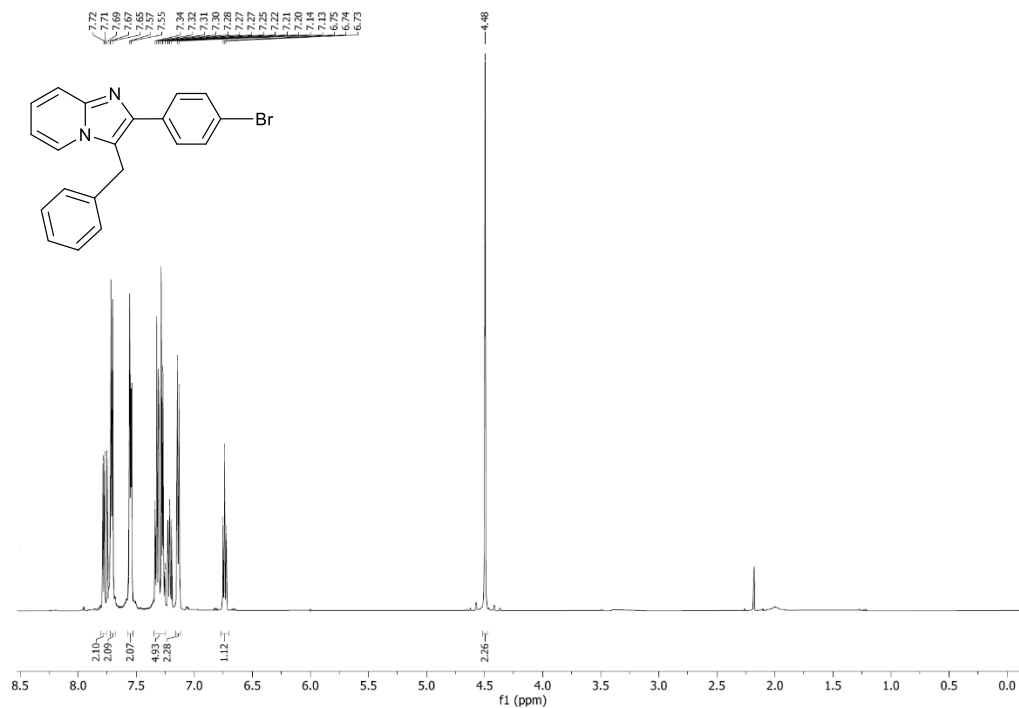


Figure 5. The ¹H NMR spectrum of 3-Benzyl-2-(4-bromophenyl)imidazo[1,2-*a*]pyridine

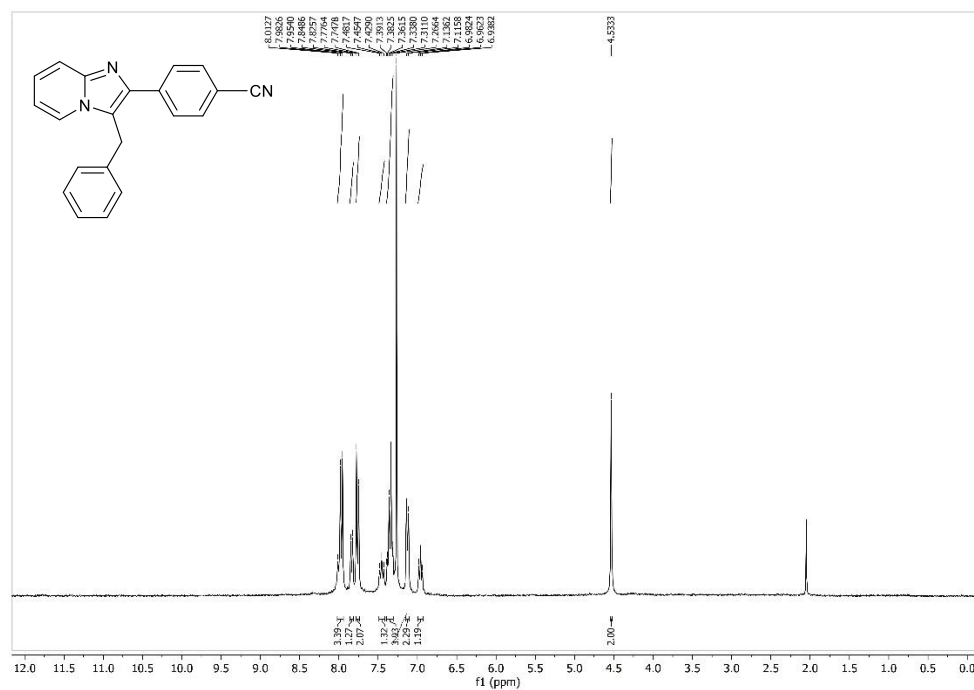


Figure 6. The ¹H NMR spectrum of 4-(3-Benzylimidazo[1,2-*a*]pyridin-2-yl)benzonitrile

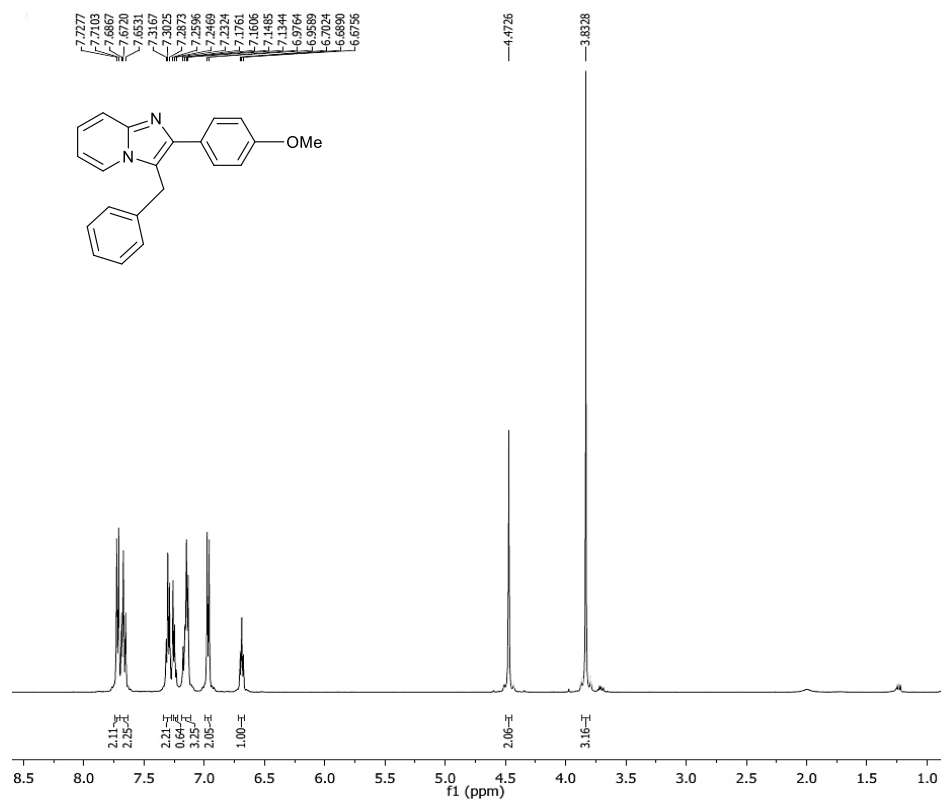


Figure 7. The ¹H NMR spectrum of 3-Benzyl-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine

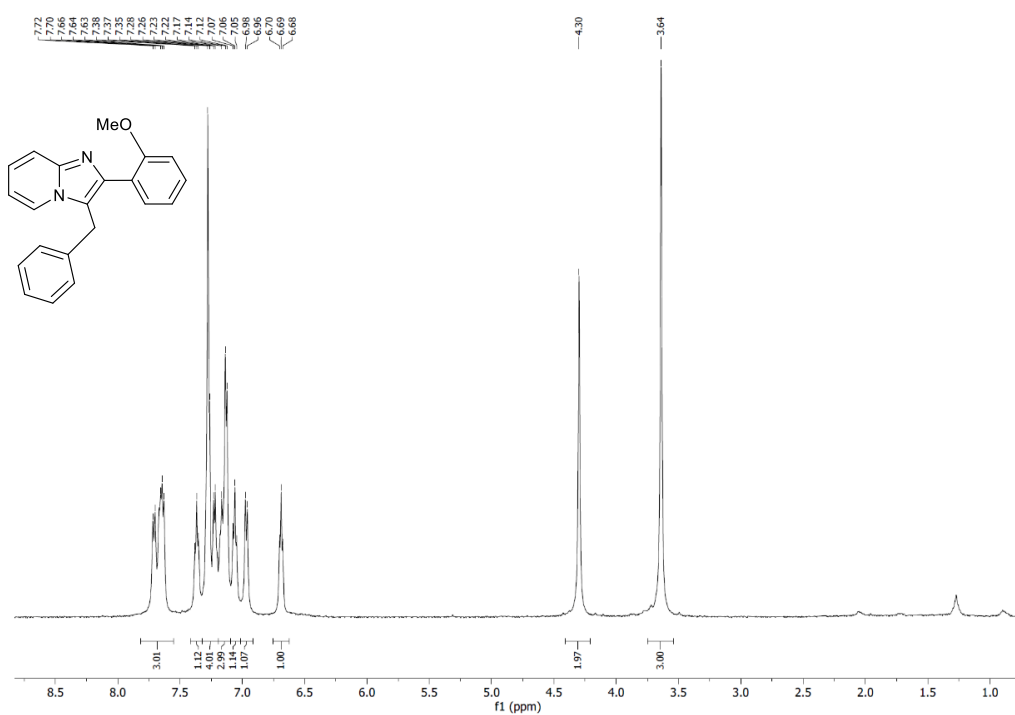


Figure 8. The ¹H NMR spectrum of 3-Benzyl-2-(2-methoxyphenyl)imidazo[1,2-*a*]pyridine

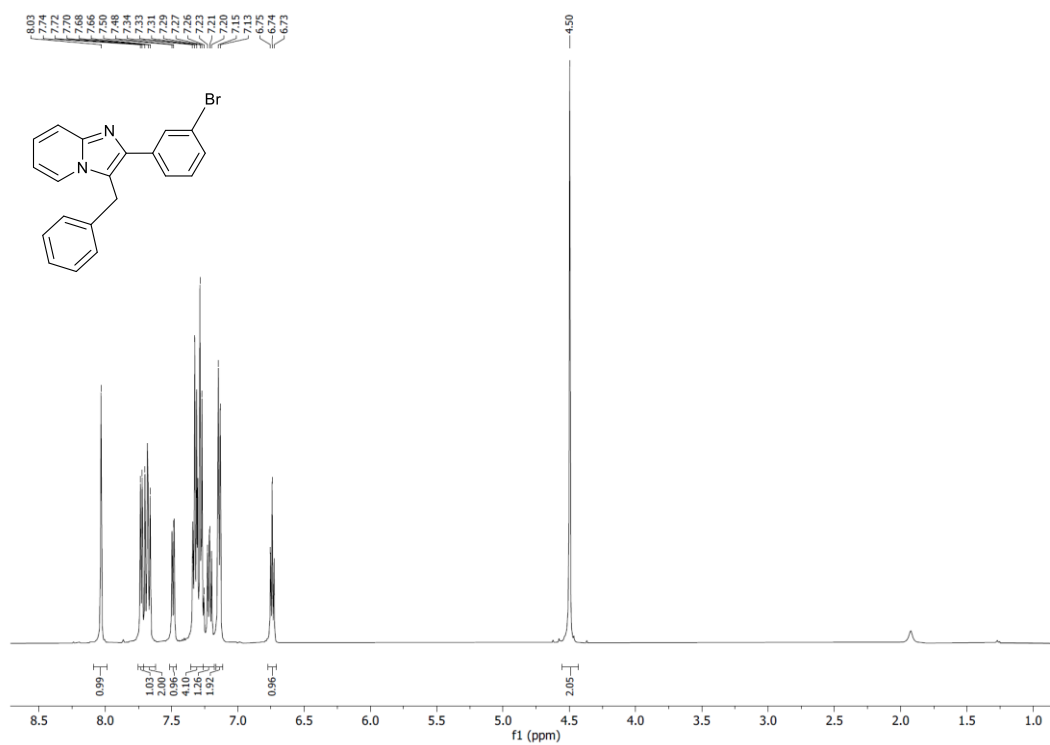


Figure 9. The ¹H NMR spectrum of 3-benzyl-2-(3-bromophenyl)imidazo[1,2-*a*]pyridine

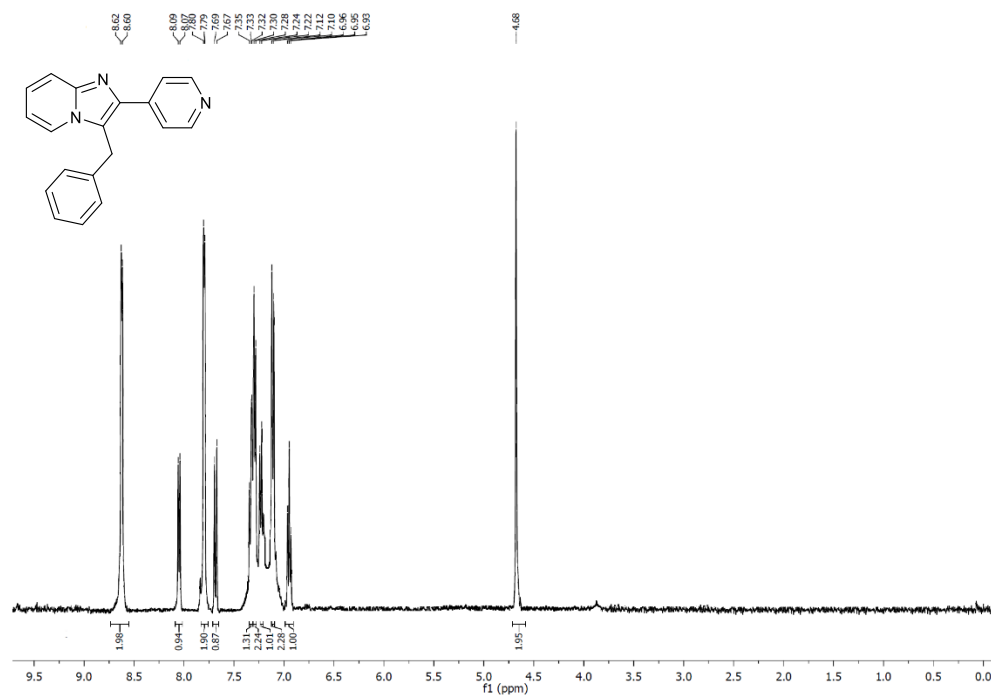


Figure 10. The ¹H NMR spectrum of 3-benzyl-2-(pyridin-4-yl)imidazo[1,2-*a*]pyridine

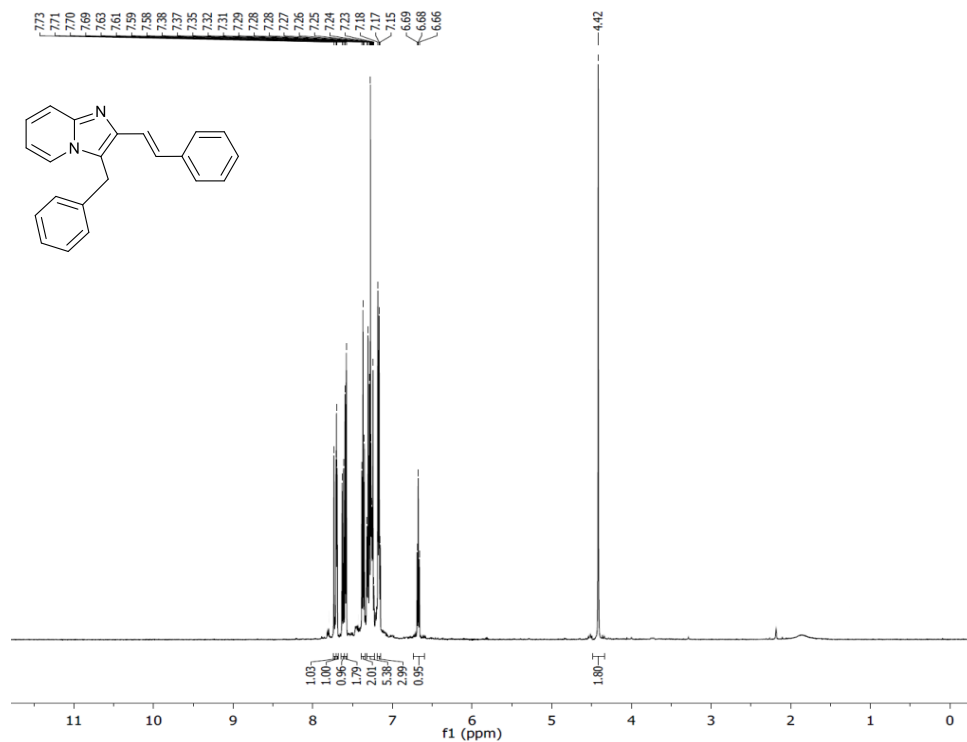


Figure 11. The ¹H NMR spectrum of (*E*)-3-Benzyl-2-styrylimidazo[1,2-*a*]pyridine

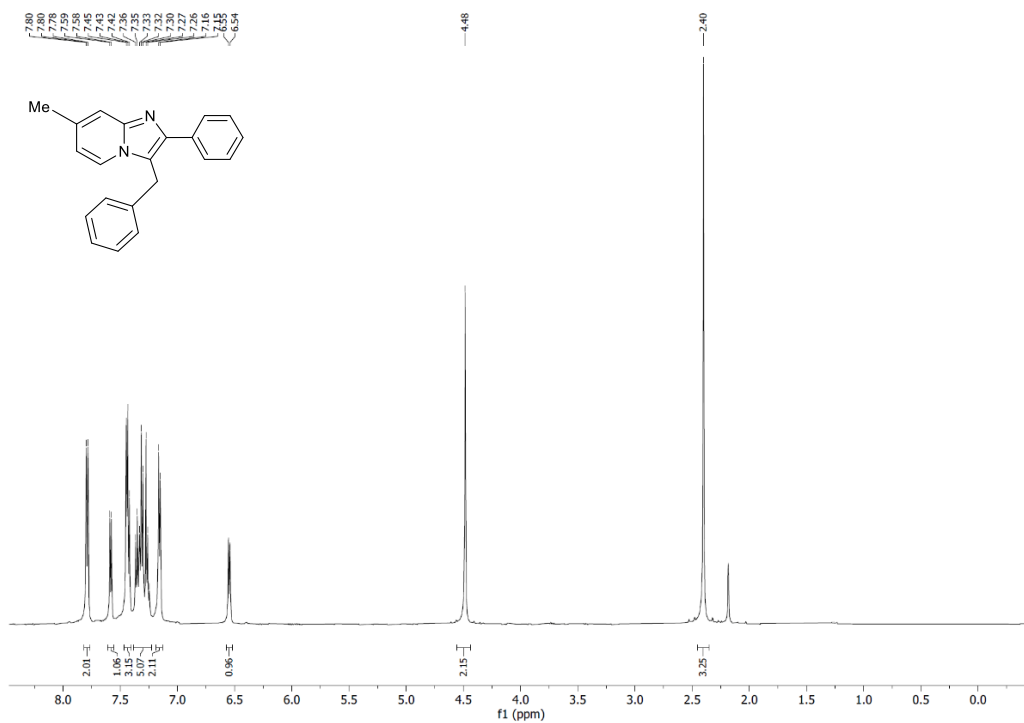


Figure 12. The ¹H NMR spectrum of 3-Benzyl-7-methyl-2-phenylimidazo[1,2-*a*]pyridine

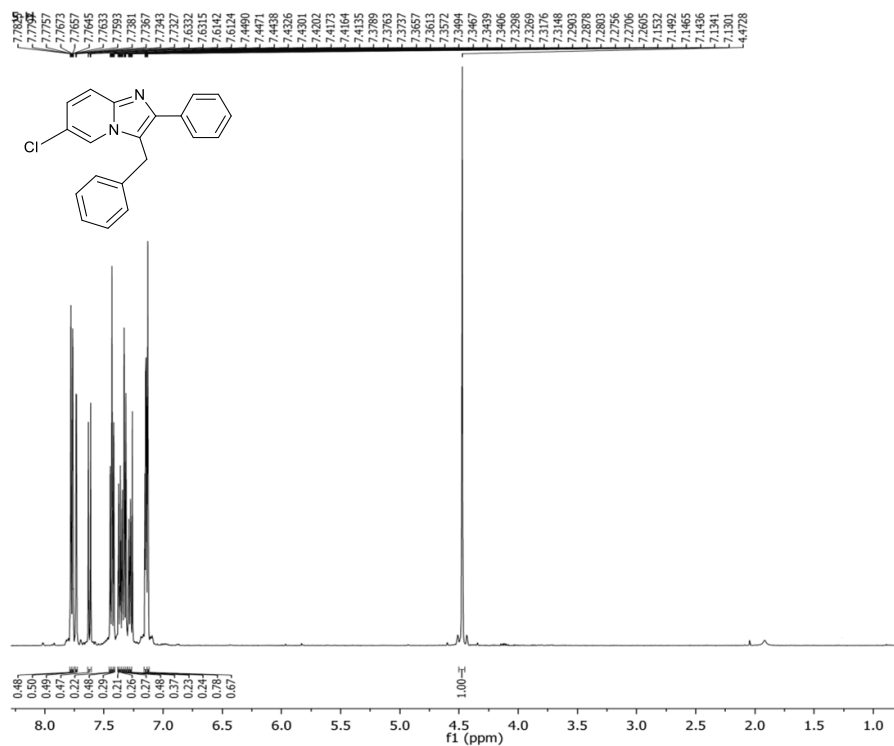


Figure 13. The ¹H NMR spectrum of 3-Benzyl-6-chloro-2-phenylimidazo[1,2-*a*]pyridine

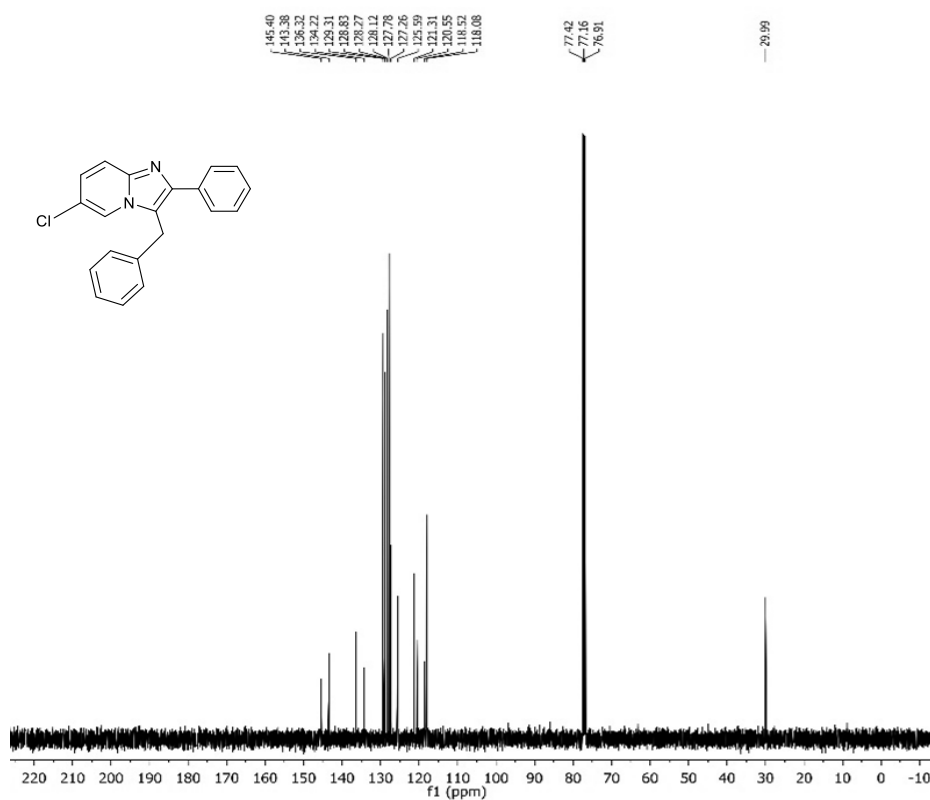


Figure 14. The ¹³C NMR spectrum of 3-Benzyl-6-chloro-2-phenylimidazo[1,2-*a*]pyridine

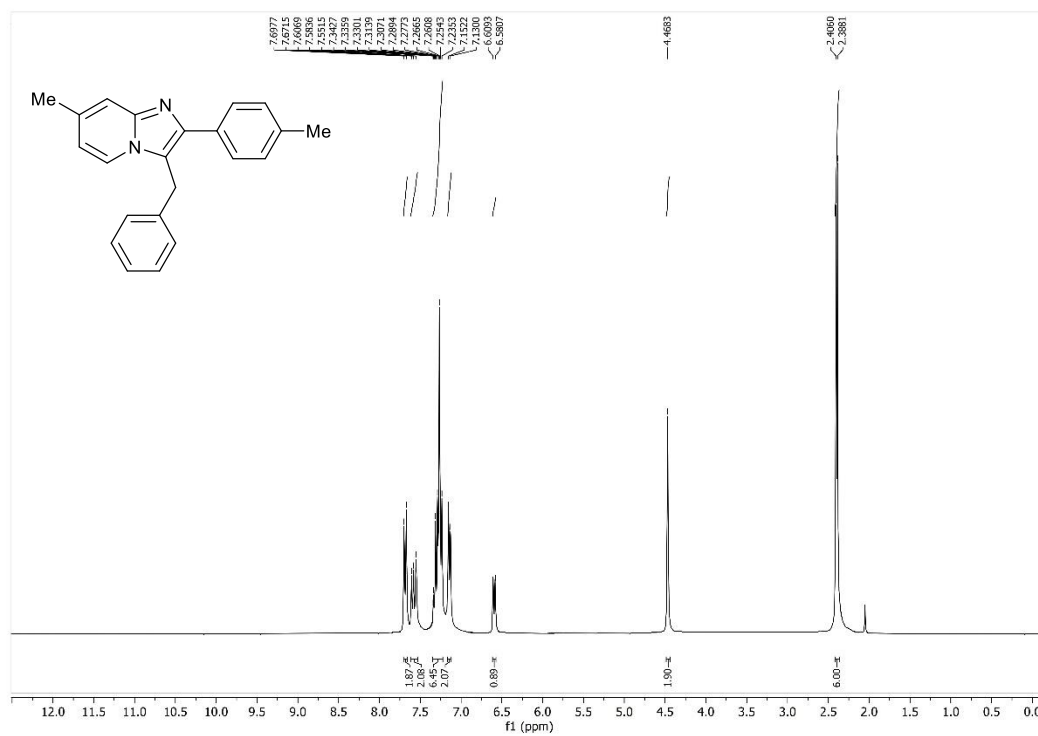


Figure 17. The ¹H NMR spectrum of 3-Benzyl-7-methyl-2-(4-methylphenyl)imidazo[1,2-a]pyridine

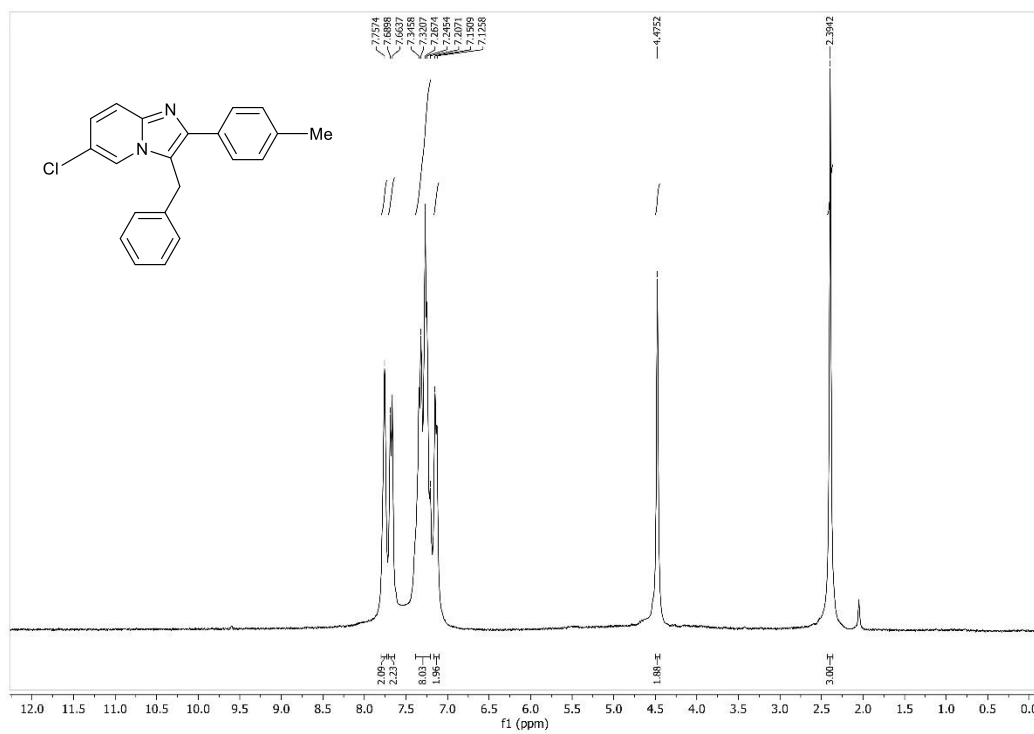


Figure 18. The ¹H NMR spectrum of 3-Benzyl-6-chloro-2-(4-methylphenyl)imidazo[1,2-a]pyridine

References:

1. S. K. Guchhait, A. L. Chandgude and G. Priyadarshani, *The Journal of organic chemistry*, 2012, **77**, 4438-4444.
2. P. Liu, C.-L. Deng, X. Lei and G.-q. Lin, *European Journal of Organic Chemistry*, 2011, **2011**, 7308-7316.
3. Z. T. Bhutia, D. Das, A. Chatterjee and M. Banerjee, *ACS Omega*, 2019, **4**, 4481-4490.
4. S. K. Guchhait, A. L. Chandgude and G. Priyadarshani, *The Journal of Organic Chemistry*, 2012, **77**, 4438-4444.
5. D. Firmansyah, A. I. Ciuciu, V. Hugues, M. Blanchard-Desce, L. Flamigni and D. T. Gryko, *Chemistry–An Asian Journal*, 2013, **8**, 1279-1294.
6. J. Lu, X.-T. Li, E.-Q. Ma, L.-P. Mo and Z.-H. Zhang, *ChemCatChem*, 2014, **6**, 2854-2859.