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# Supporting Information

## Metal-free synthesis of imidazopyridine from nitroalkene and 2-aminopyridine in the presence of catalytic iodine and aqueous hydrogen peroxide

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**1. General Information.**

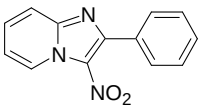
All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Tokyo Kasei Kogyo Co., Ltd., Sigma-Aldrich Co., Ltd., Wako Pure Chemical Industries, Ltd., Kishida Chemical Co., Ltd., and Nacalai Tesque. $^{1}$H NMR and $^{13}$C NMR spectra were obtained on a JEOL ECA 500 (500 MHz for $^{1}$H NMR and 125 MHz for $^{13}$C NMR). Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal $Me_4Si$. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254, YMC-GEL (8 nm S-25μm)).

**2. General Procedure**

**Synthesis of 3-Nitro-2-phenylimidazo[1,2-*a*]pyridine (3a) (Table 2)**:

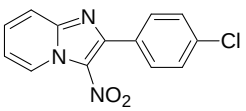
A solution of *trans*-β-nitrostyrene (**1a**)(44.7 mg, 0.3 mmol), 2-aminopyridine (**2a**)(33.9 mg, 1.2 equiv), iodine (7.6 mg, 0.1 equiv), and 35% aq. $H_2O_2$ (106 μl, 4 equiv) in DMSO (3 mL) in a pyrex test tube was stirred under air at 70 °C for 20 h. The reaction mixture was washed with aq. $Na_2S_2O_3$ and $H_2O$, and extracted with EtOAc. Organic layer was dried over $MgSO_4$, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (hexane : EtOAc = 2 : 1) provided 3-nitro-2-phenylimidazo[1,2-*a*]pyridine (**3a**) (54 mg, 75%).

**3-Nitro-2-phenylimidazo[1,2-*a*]pyridine (3a)[1] (Table 2)**



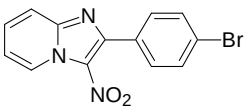
yellow solid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.49 (d, *J* = 7.5Hz, 1 H), 7.91−7.88 (m, 2 H),7.82 (d, *J* = 9.2 Hz, 1 H), 7.65−7.62 (m, 1 H), 7.50 (t, *J* = 3.2 Hz, 3 H), 7.28 (t, *J* = 6.9 Hz, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 150.2, 145.0, 131.8, 130.8, 130.1, 129.9, 128.0, 118.2, 116.4; CAS Registry Number: 67292-98-2

**2-(4-Chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3b)[1] (Table 2)**



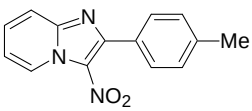
yellow solid; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.51 (d, *J* = 6.9 Hz, 1H), 7.88−7.83 (m, 3 H), 7.68 (t, *J* = 8.1 Hz, 1 H), 7.48 (d, *J* = 8.6 Hz, 2 H), 7.31−7.27 (m, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 149.0, 145.1, 136.4, 131.5, 131.0, 130.2, 128.4, 128.2, 118.3, 116.7; CAS Registry Number: 34165-02-1

**2-(4-Bromophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3c)[1] (Table 2)**



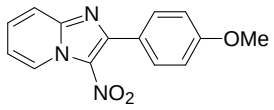
yellow solid; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 6.9 Hz, 1 H), 7.85−7.79 (m, 3 H), 7.69−7.63 (m, 3 H), 7.32−7.29 (m, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.0, 145.1, 131.7, 131.4, 131.1, 130.7, 128.2, 124.8, 118.3, 116.7; CAS Registry Number: 1312318-90-3

**3-Nitro-2-p-tolylimidazo[1,2-*a*]pyridine (3d)[1] (Table 2)**



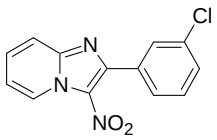
yellow solid; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J* = 6.9 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 3 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.32−7.24 (m, 3 H), 2.44 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 150.4, 145.1, 140.5, 130.8, 130.0, 129.0, 128.9, 128.2, 118.2, 116.3, 21.5; CAS Registry Number: 1355334-02-9

**2-(4-Methoxyphenyl)-3-nitroimidazo[1,2-*a*]pyridine (3e)[1] (Table 2)**



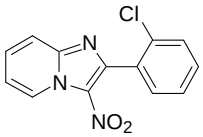
yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 6.9 Hz, 1 H), 7.94 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 9.1 Hz, 1 H), 7.64 (t, *J* = 8.1 Hz, 1 H), 7.25 (dd, *J* = 18.3, 6.6 Hz, 1 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 3.89 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 161.2,150.2, 145.2, 131.8, 130.9, 128.2, 124.0, 118.0, 116.2, 113.5, 55.3; CAS Registry Number: 956077-87-5

**2-(3-Chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3f)[1] (Table 2)**



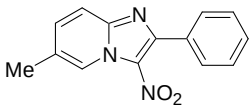
yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.4 Hz, 1 H), 7.91−7.80 (m, 3 H), 7.70−7.67 (m, 1 H), 7.49−7.43 (m, 2 H), 7.33−7.30 (m, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 148.6, 145.1, 134.1, 133.6, 131.1, 130.2, 130.0, 129.4, 128.3, 128.1, 118.4, 116.8; CAS Registry Number: 1355334-06-3

**2-(2-Chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3g)[1] (Table 2)**



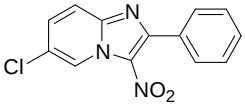
yellow viscous oil; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 6.9 Hz, 1 H), 7.88 (d, *J* = 9.2 Hz, 1 H), 7.69 (t, *J* = 7.8 Hz, 1 H), 7.55−7.53 (m, 2 H), 7.47−7.39 (m, 2 H), 7.34 (t, *J* = 6.9 Hz, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.0, 134.0, 131.9, 130.9, 130.8, 130.7, 129.5, 127.8, 126.7, 118.5, 116.8; CAS Registry Number: 1355334-05-2

**6-Methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3h)[1] (Table 2)**



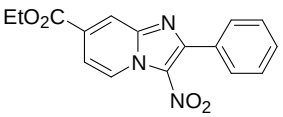
yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1 H), 7.89−7.87 (m, 2 H), 7.70 (d, *J* = 9.2 Hz, 1 H), 7.49−7.46 (m, 4H), 2.48 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 150.0, 144.0, 133.6, 132.0, 129.9, 129.8, 128.0, 126.8, 126.0, 117.3, 18.6; CAS Registry Number: 1355334-14-3

**6-Chloro-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3i)[1] (Table 2)**



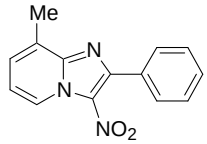
yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.55 (d, *J* = 1.7, 1 H), 7.89−7.86 (m, 2 H), 7.76 (d, *J* = 9.2, 1 H), 7.60 (dd, *J* = 9.5, 2.2 Hz, 1 H), 7.51-7.48 (m, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 150.2, 143.2, 132.0, 131.3, 130.3, 130.0, 128.1, 126.0, 124.9, 118.4; CAS Registry Number: 1355334-16-5

**Ethyl 3-nitro-2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (3j)[1] (Table 2)**



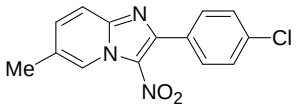
yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.5 Hz, 1 H), 8.48 (s, 1 H), 7.92−7.89 (m, 2 H), 7.82 (dd, *J* = 7.5, 1.7 Hz, 1 H), 7.53−7.51 (m, 3 H), 4.48 (q, *J* = 7.5 Hz, 2 H), 1.46 (t, *J* = 7.5 Hz, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.7, 150.8, 144.2, 132.1, 131.4, 130.4, 130.0, 128.2, 127.8, 120.0, 115.4, 62.4, 14.2; CAS Registry Number: 1355334-17-6

**8-Methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3k)[1] (Table 2)**



yellow solid; $^1$H NMR (500 MHz, $CDCl_3$) δ 9.34 (d, *J* = 6.9 Hz, 1 H), 7.91-7.89 (m, 2 H), 7.51−7.48 (m, 3 H), 7.43 (d, *J* = 6.9 Hz, 1 H), 7.16 (t, *J* = 6.9 Hz, 1 H), 2.71 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.6, 145.1, 132.1, 130.0, 129.9, 129.8, 128.5, 128.0, 125.8, 116.4, 16.5; CAS Registry Number: 1355334-10-9

**6-Methyl-2-(4-Chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3l) (Table 2)**




yellow solid; mp 187-188 $^{o}$C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1 H), 7.85 (d, J = 8.6 Hz, 2 H), 7.72 (d, J = 9.2 Hz, 1 H), 7.51 (d, J = 9.2 Hz, 1 H), 7.45 (d, J = 8.6 Hz, 2 H), 2.51 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 148.8, 144.1, 136.1, 133.8, 131.3, 130.4, 128.3, 127.1, 126.1, 117.4, 18.6; HRMS (DART, positive) calcd for $C_{14}H_{10}ClN_3O_2$ $[M + H]^+$ 288.05398, Found 288.05225.

**Reference**

(1) Yan, R.; Yan, H.; Ma, C.; Ren, Z.; Gao, X.; Huang, G.; Liang, Y. *J. Org. Chem.* **2012**, *77*, 2024.

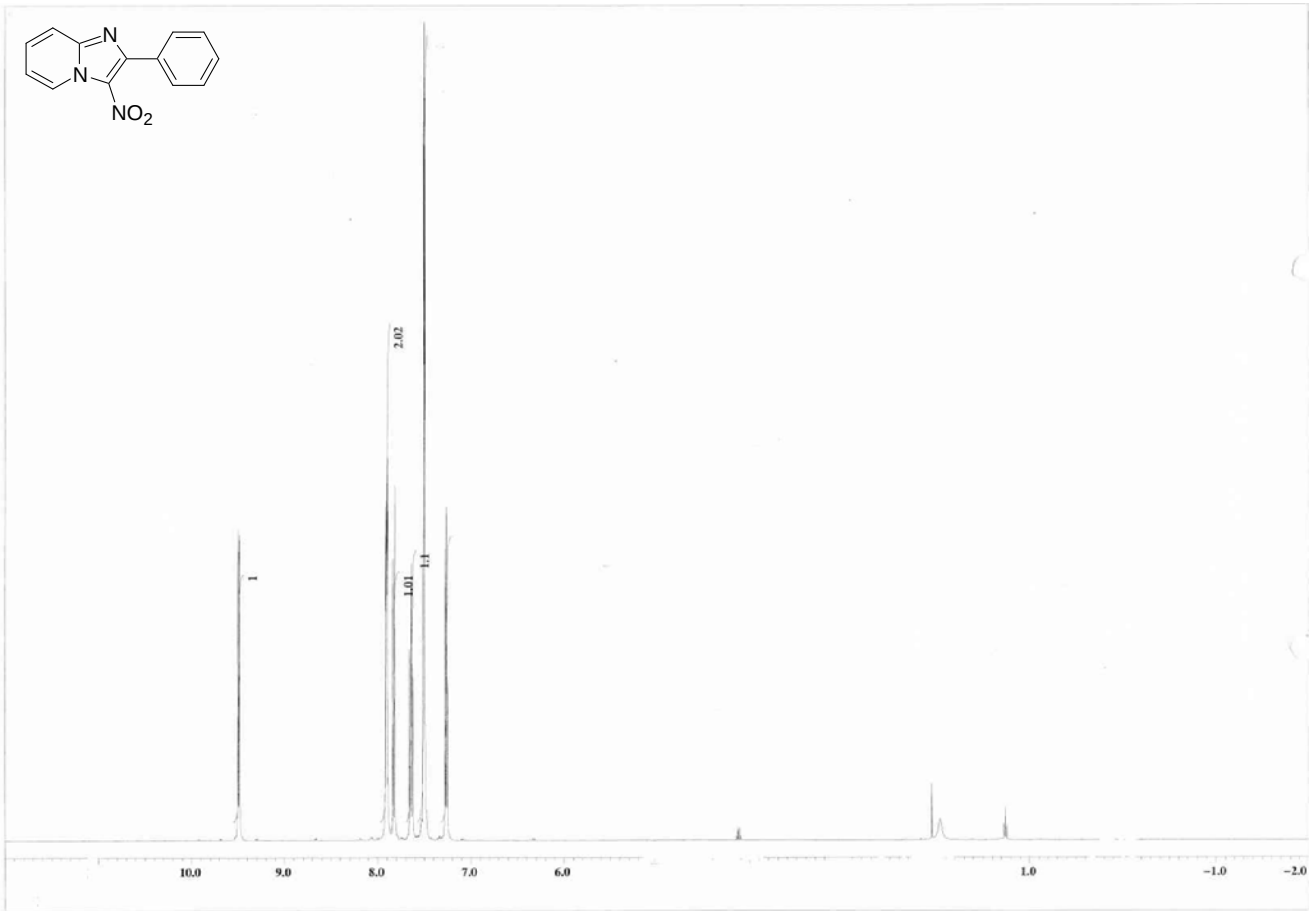



Fig. 1: $^{1}$H NMR of **3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3a)**

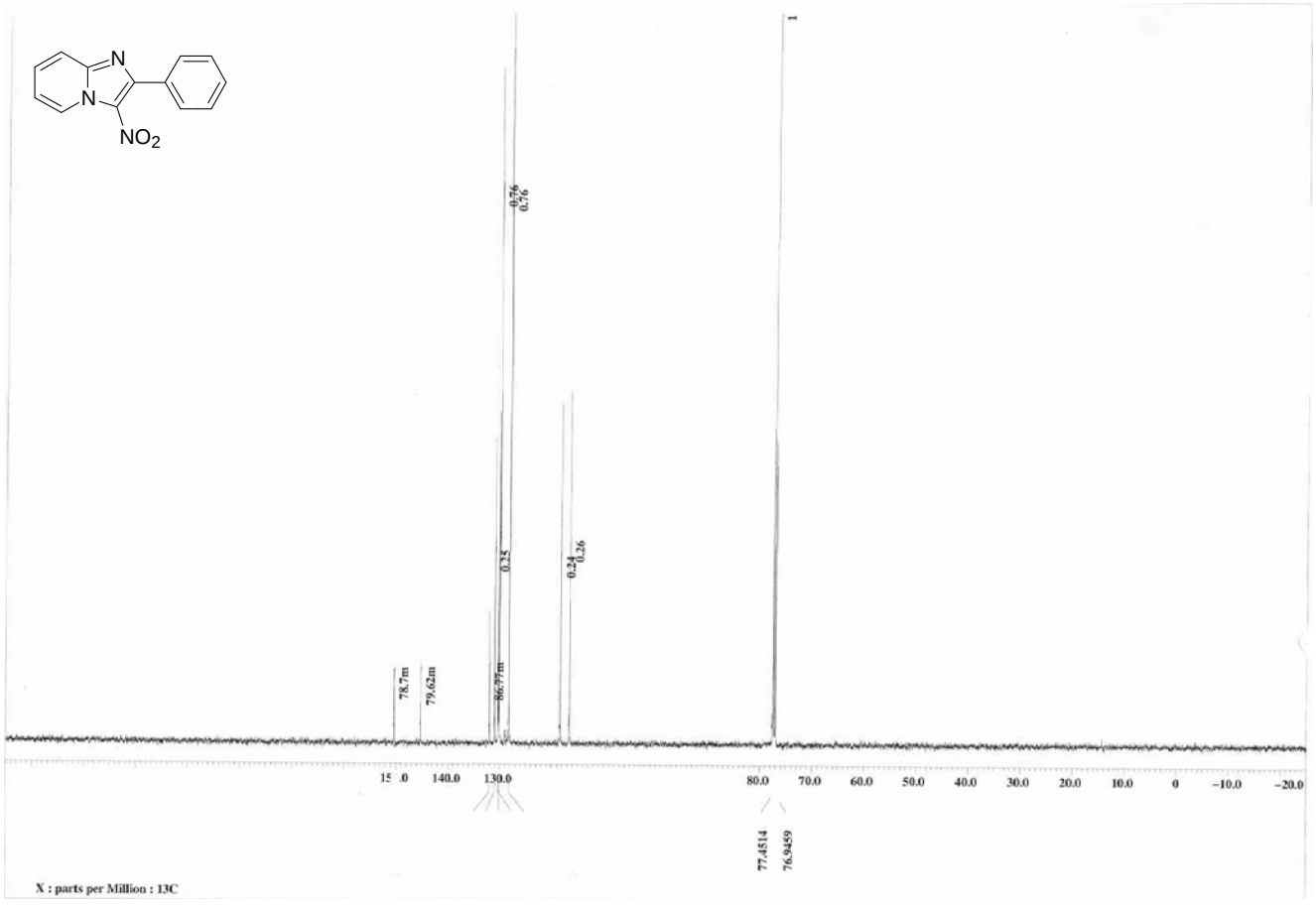



Fig. 2: $^{13}$C NMR of **3-Nitro-2-phenylimidazo[1,2-*a*]pyridine (3a)**

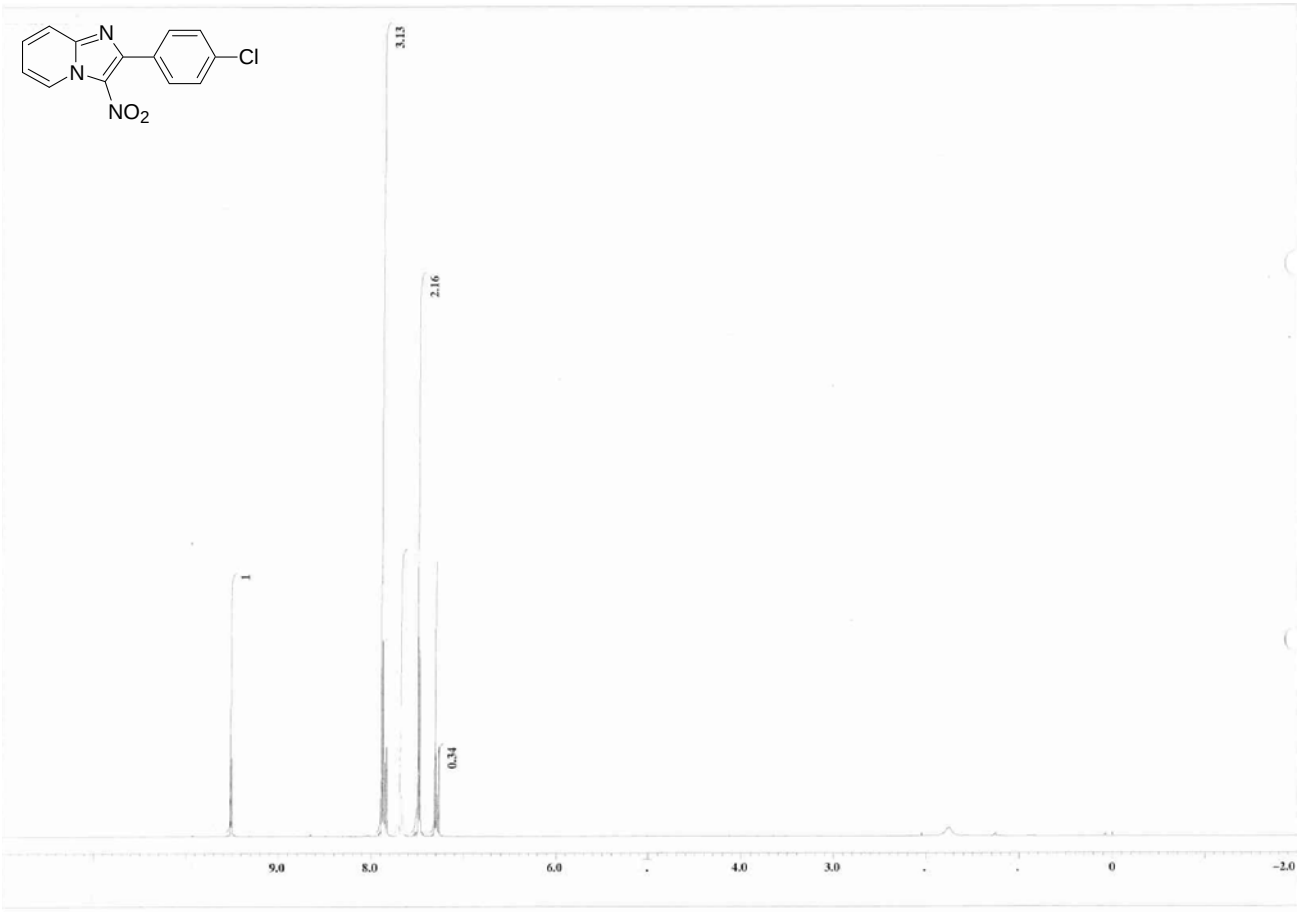



Fig. 3: $^{1}$H NMR of **2-(4-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3b)**

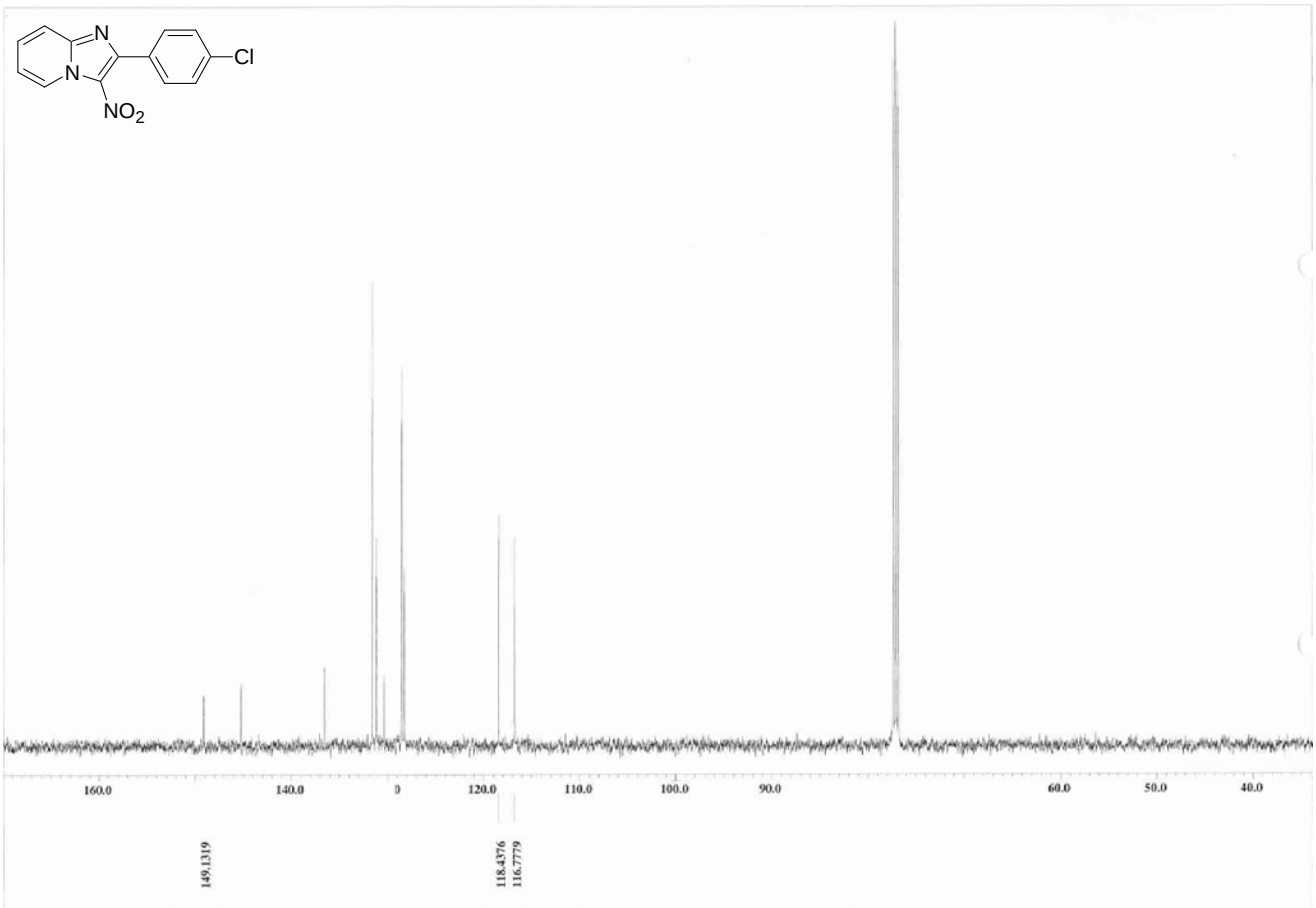



Fig. 4: $^{13}$C NMR of **2-(4-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3b)**

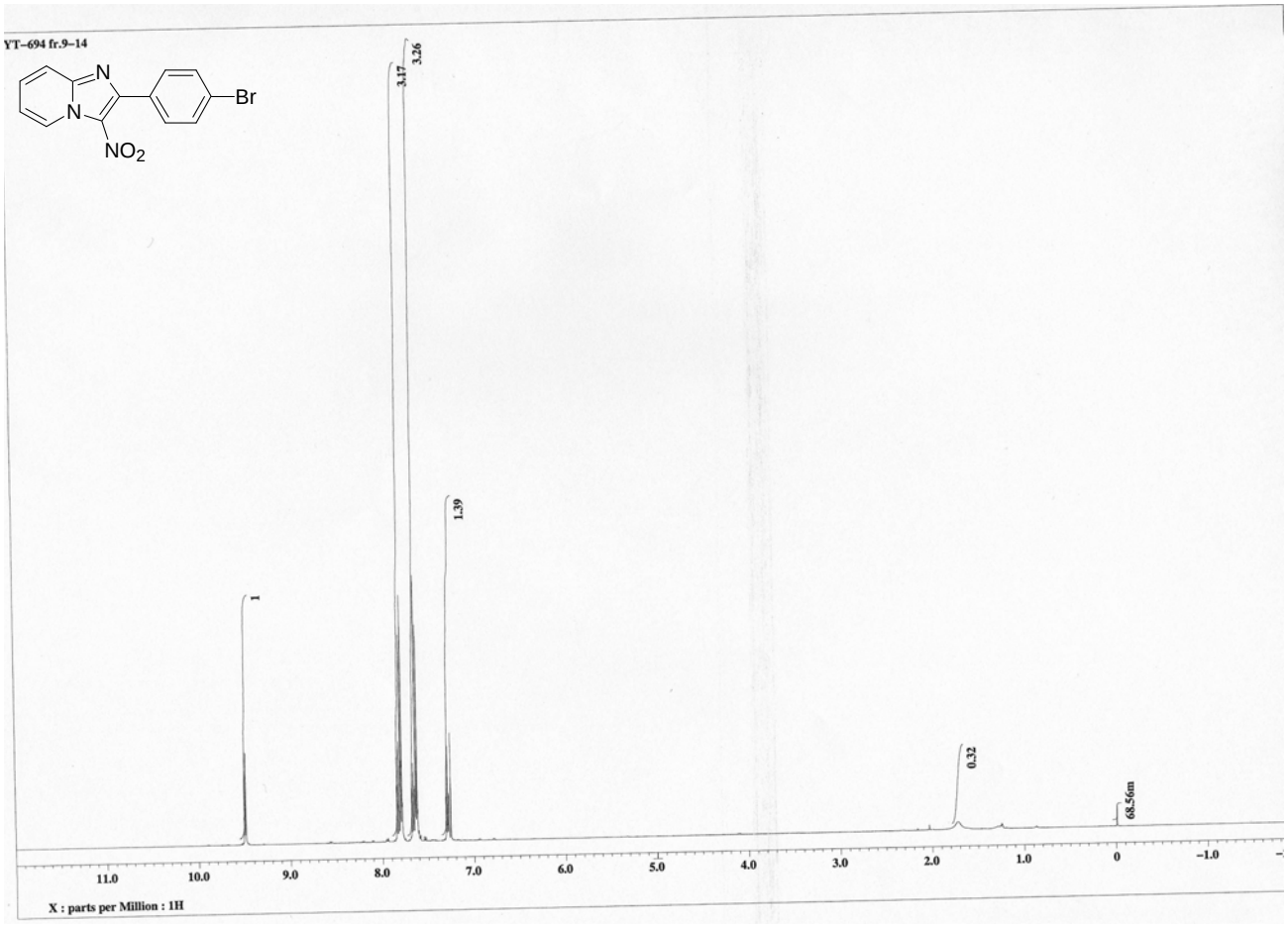



Fig. 5: $^{1}$H NMR of **2-(4-bromophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3c)**

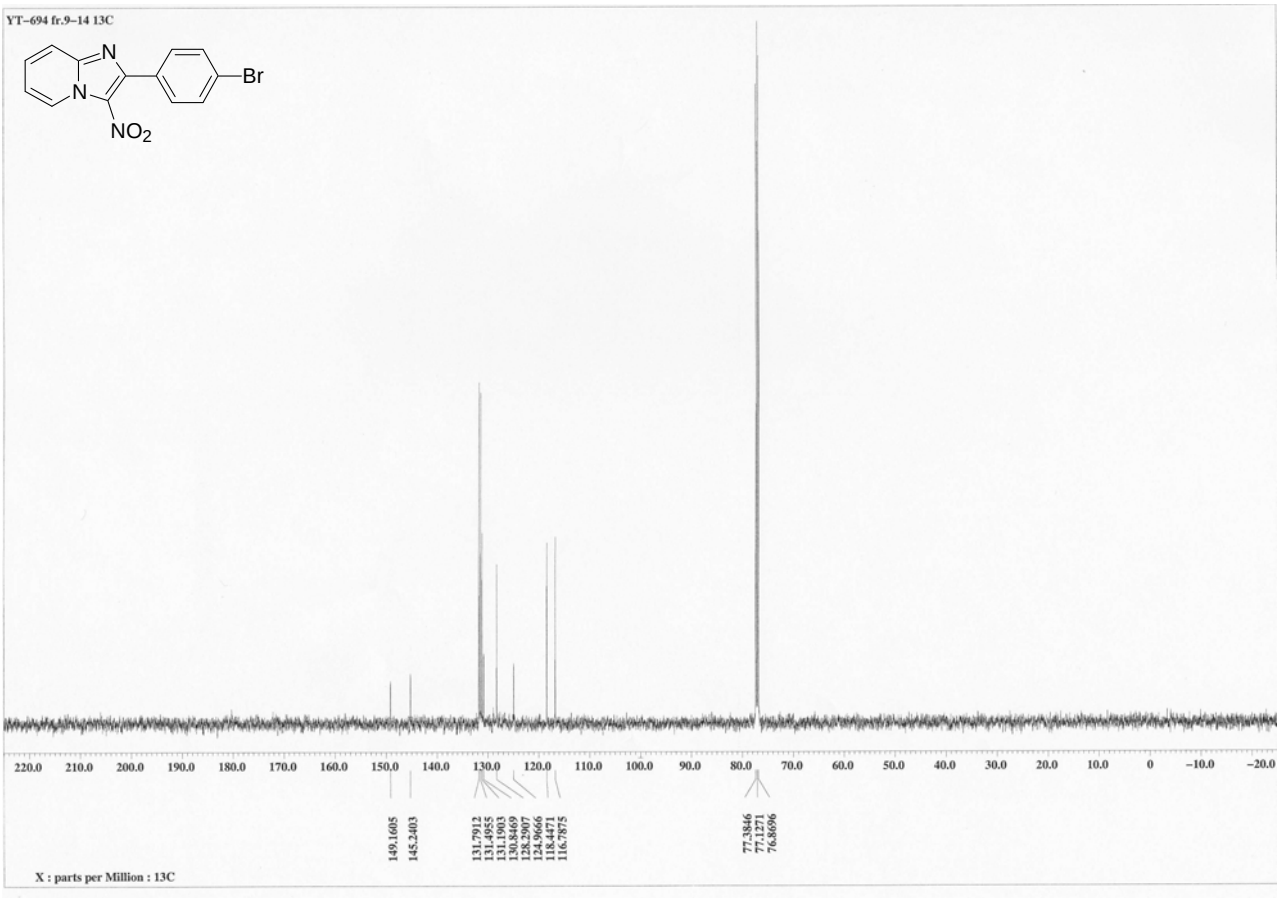



Fig. 6: $^{13}$C NMR of **2-(4-bromophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3c)**

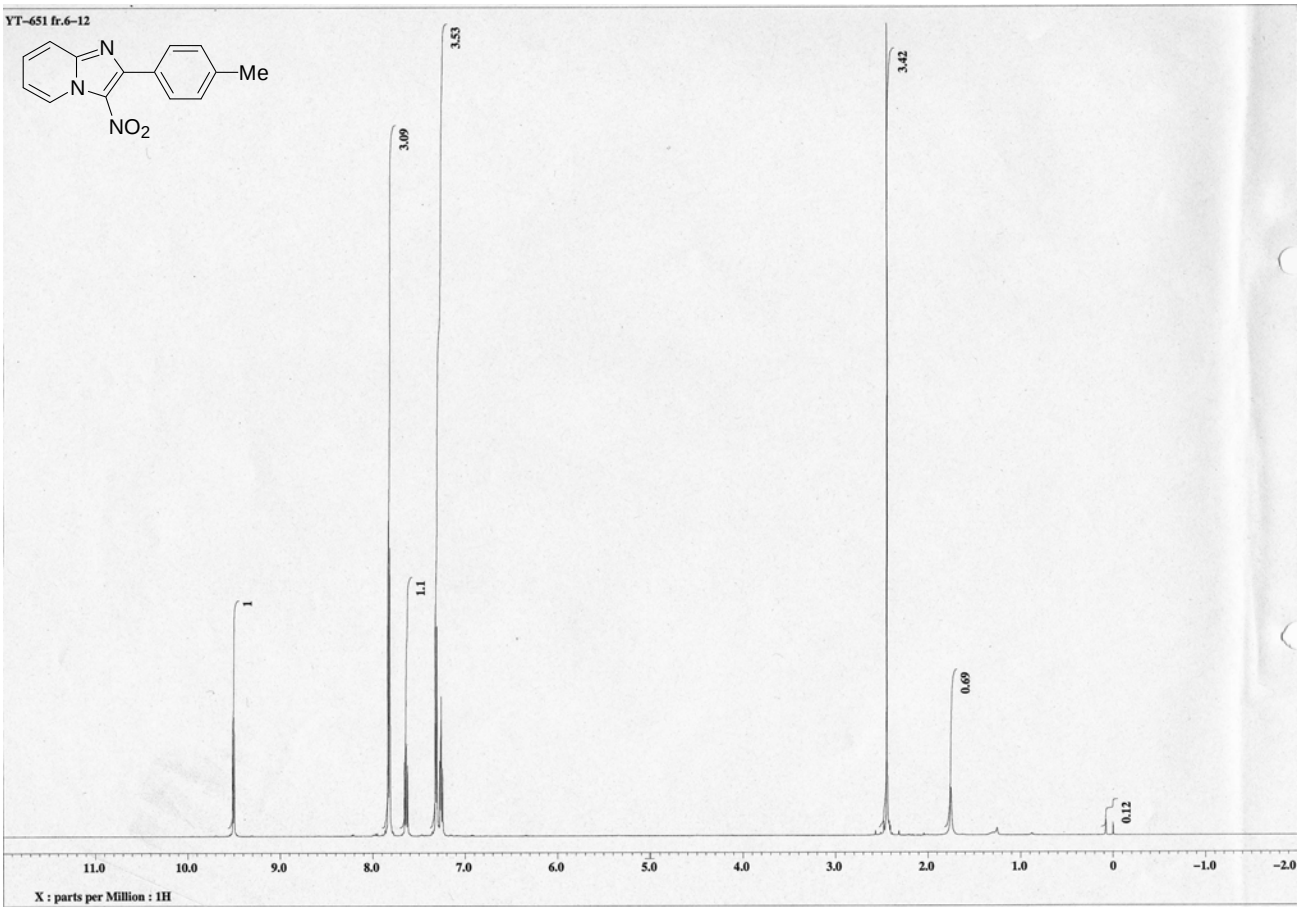



Fig. 7: [1]H NMR of **3-nitro-2-p-tolylimidazo[1,2-*a*]pyridine (3d)**

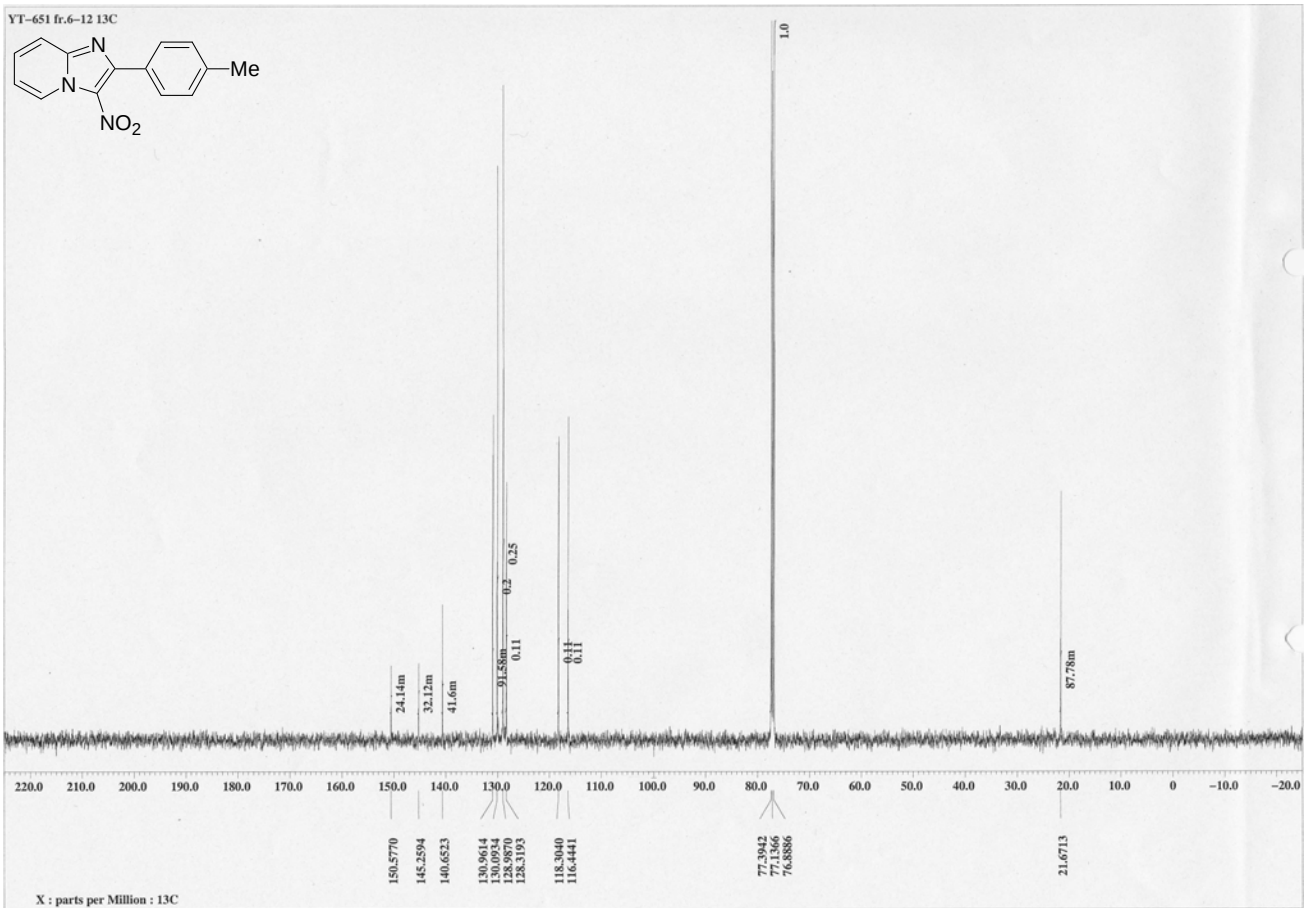



Fig. 8: [13]C NMR of **3-nitro-2-p-tolylimidazo[1,2-*a*]pyridine (3d)**

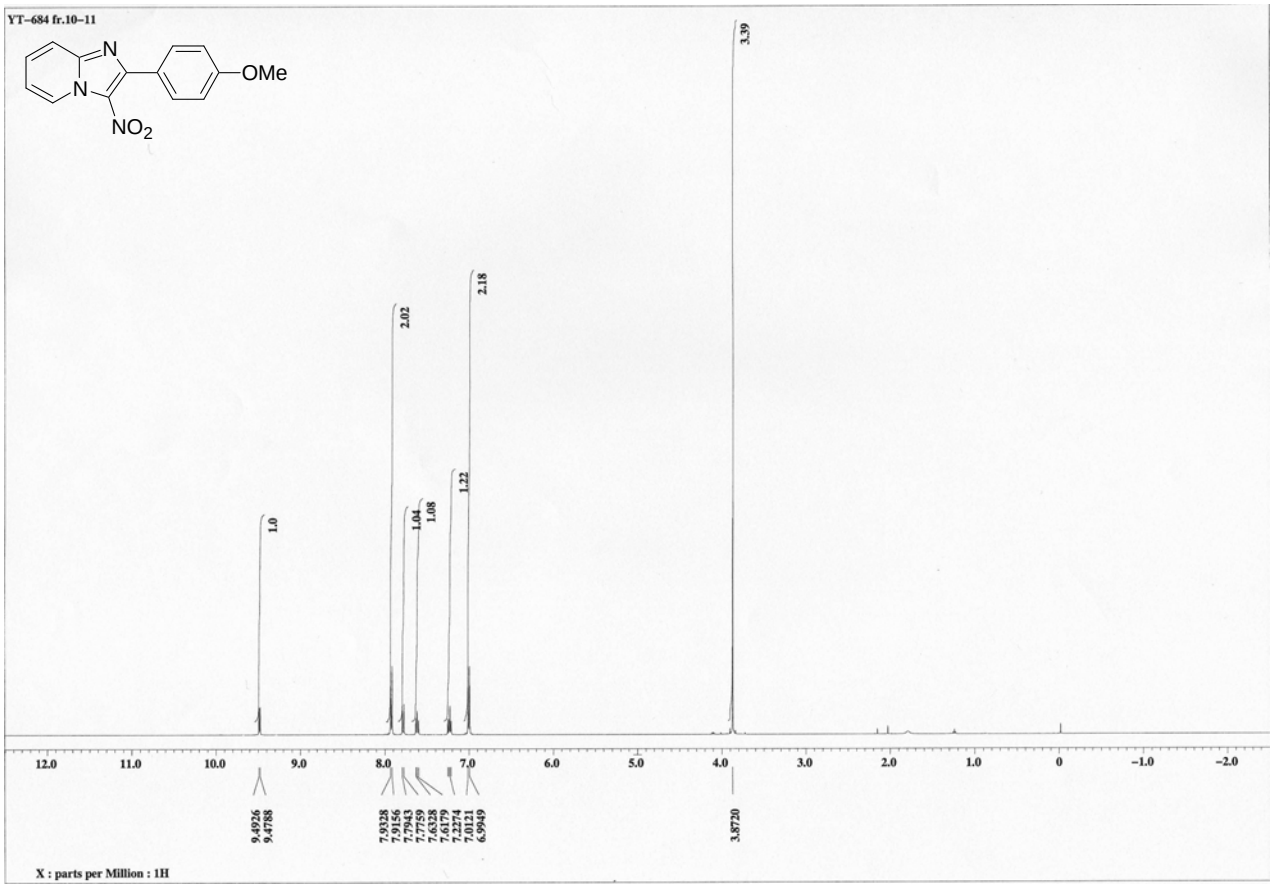



Fig. 9: $^{1}$H NMR of **2-(4-methoxyphenyl)-3-nitroimidazo[1,2-*a*]pyridine (3e)**

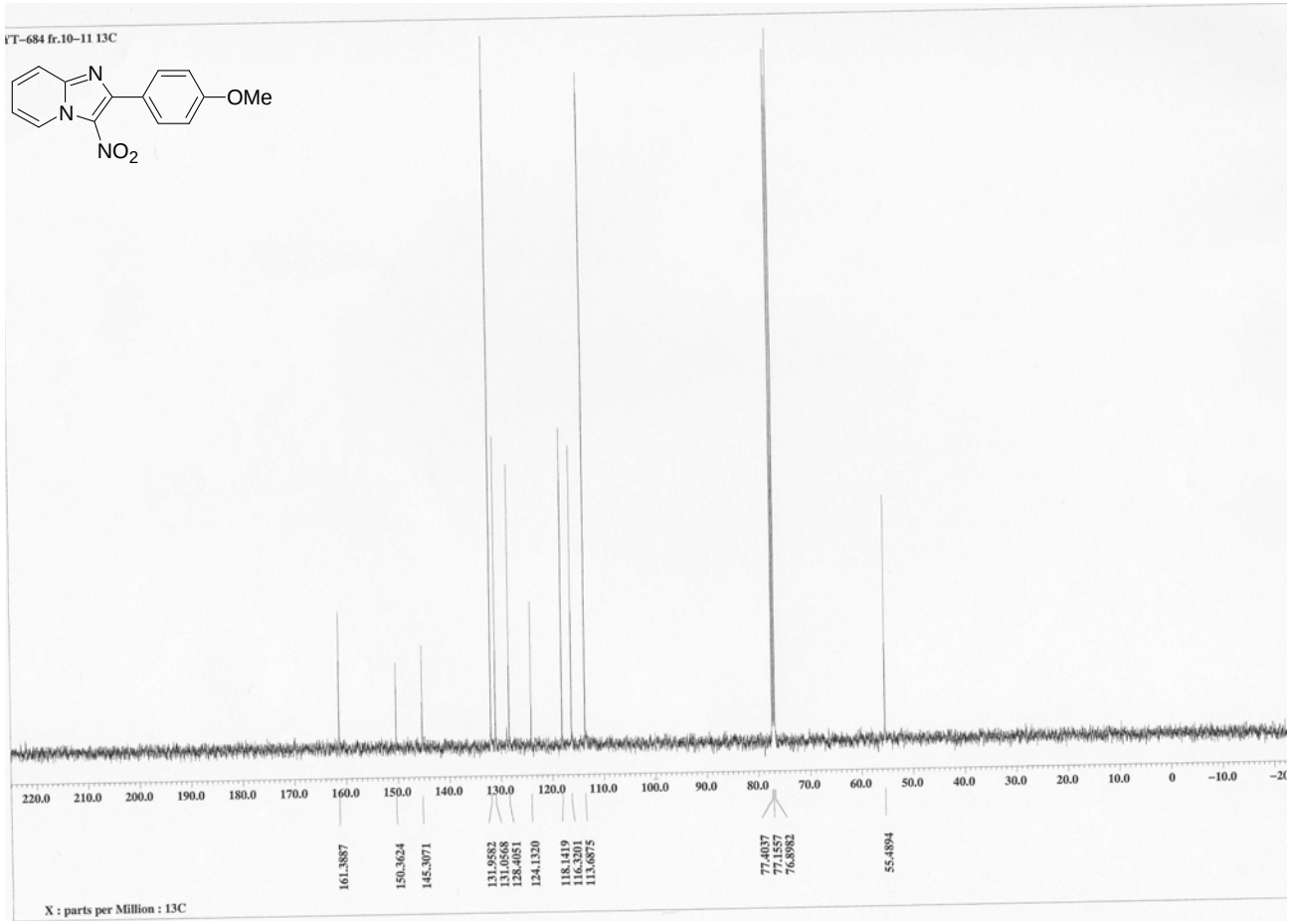



Fig. 10: $^{13}$C NMR of **2-(4-methoxyphenyl)-3-nitroimidazo[1,2-*a*]pyridine (3e)**

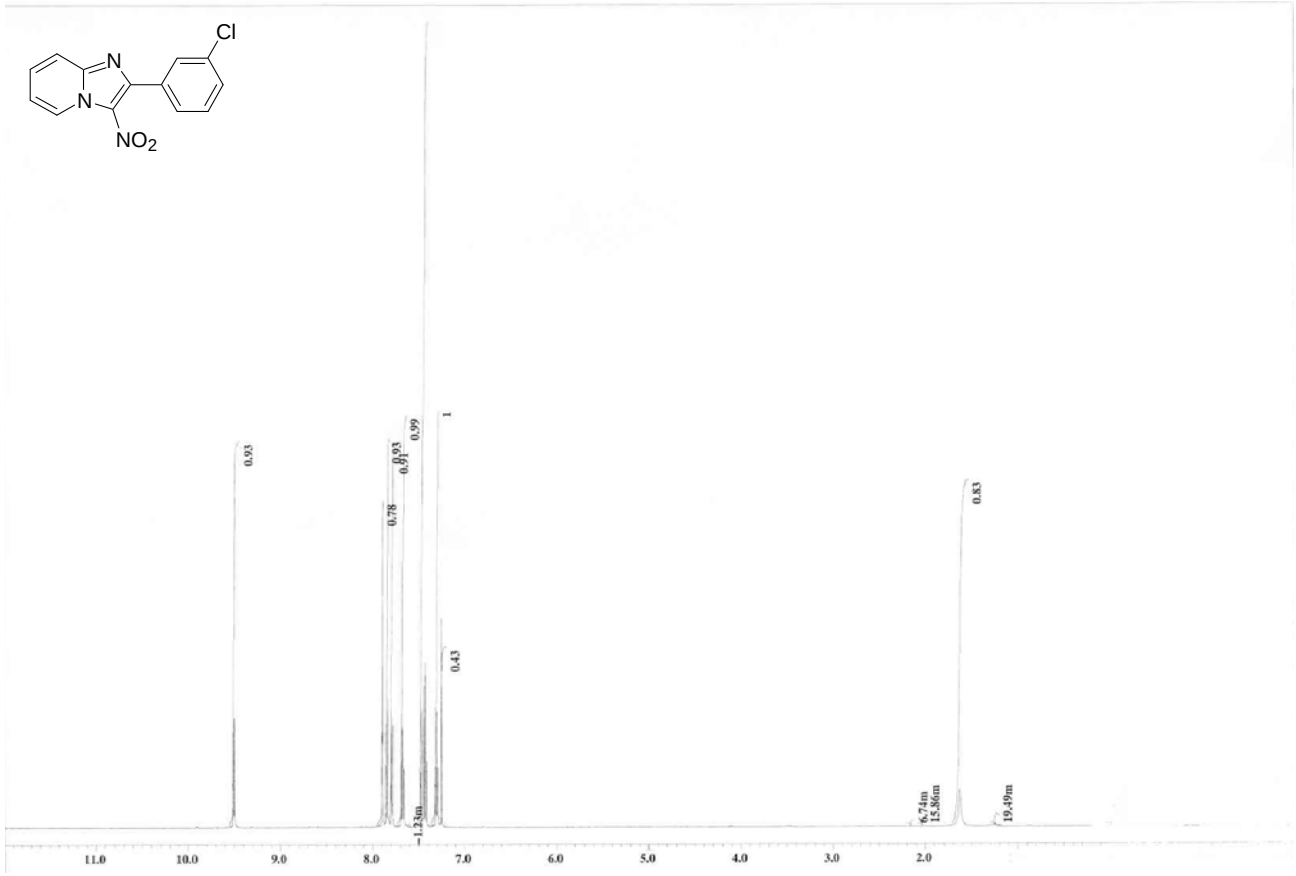



Fig. 11: $^{1}$H NMR of **2-(3-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3f)**

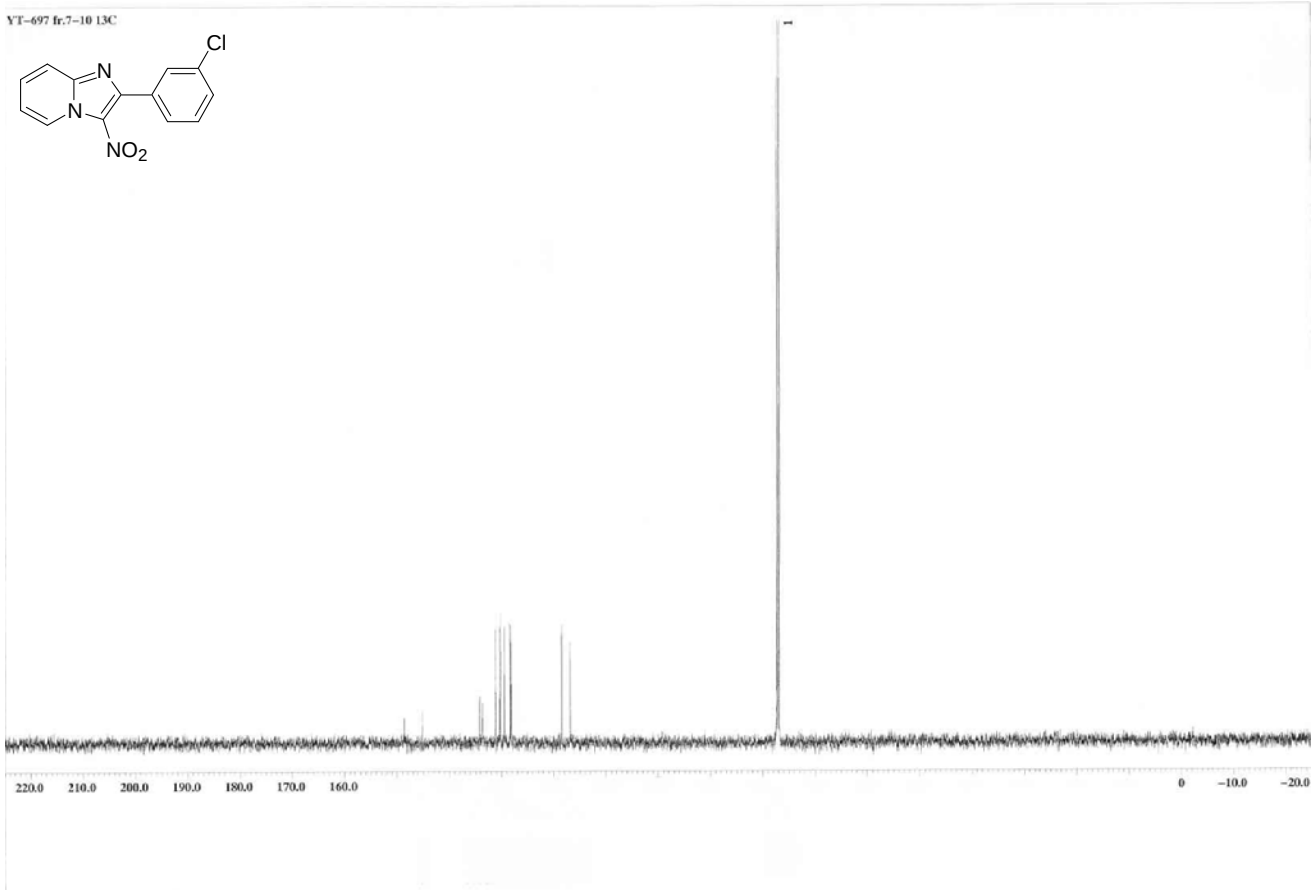



Fig. 12: $^{13}$C NMR of **2-(3-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3f)**

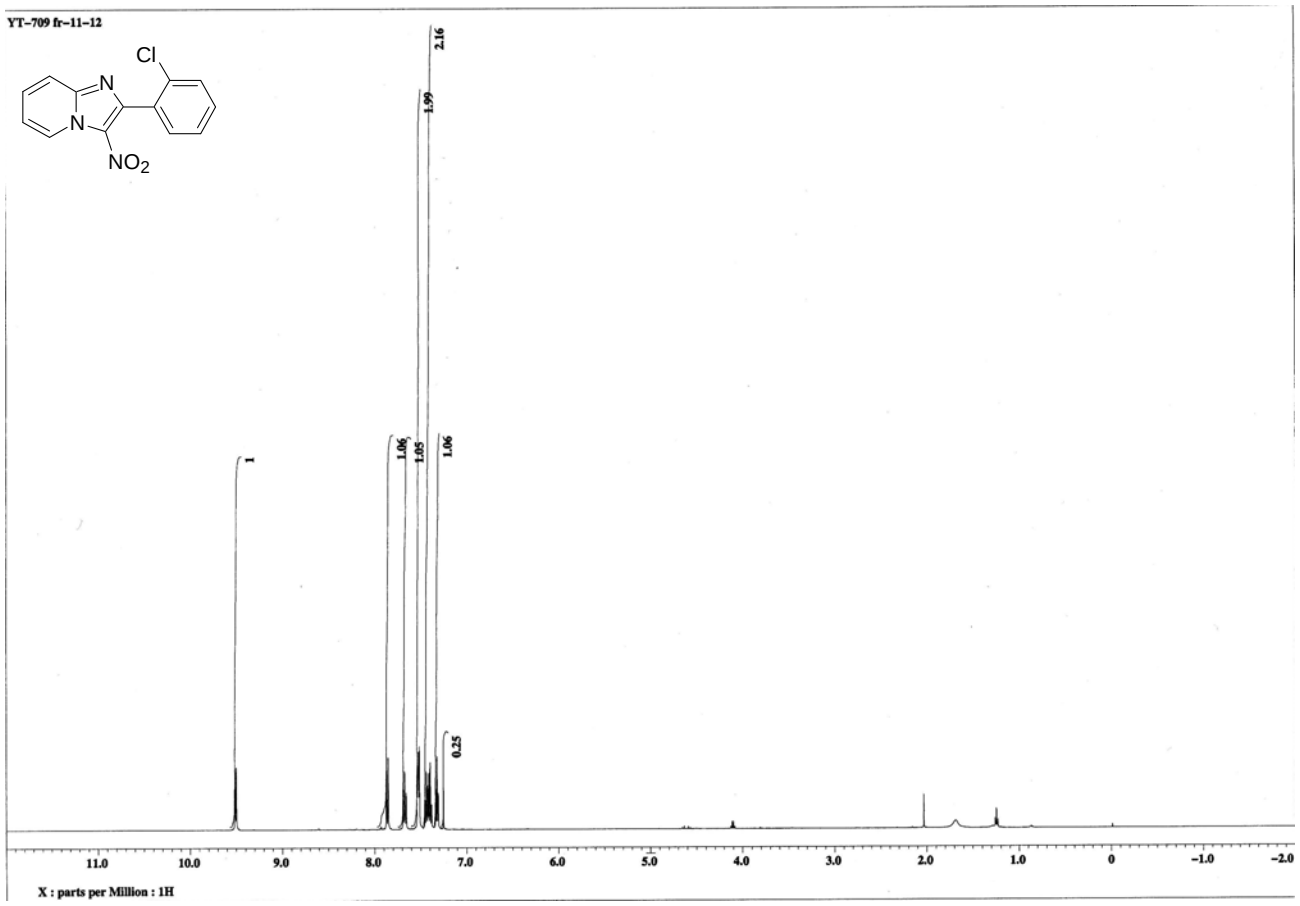



Fig. 13: $^{1}$H NMR of **2-(2-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3g)**

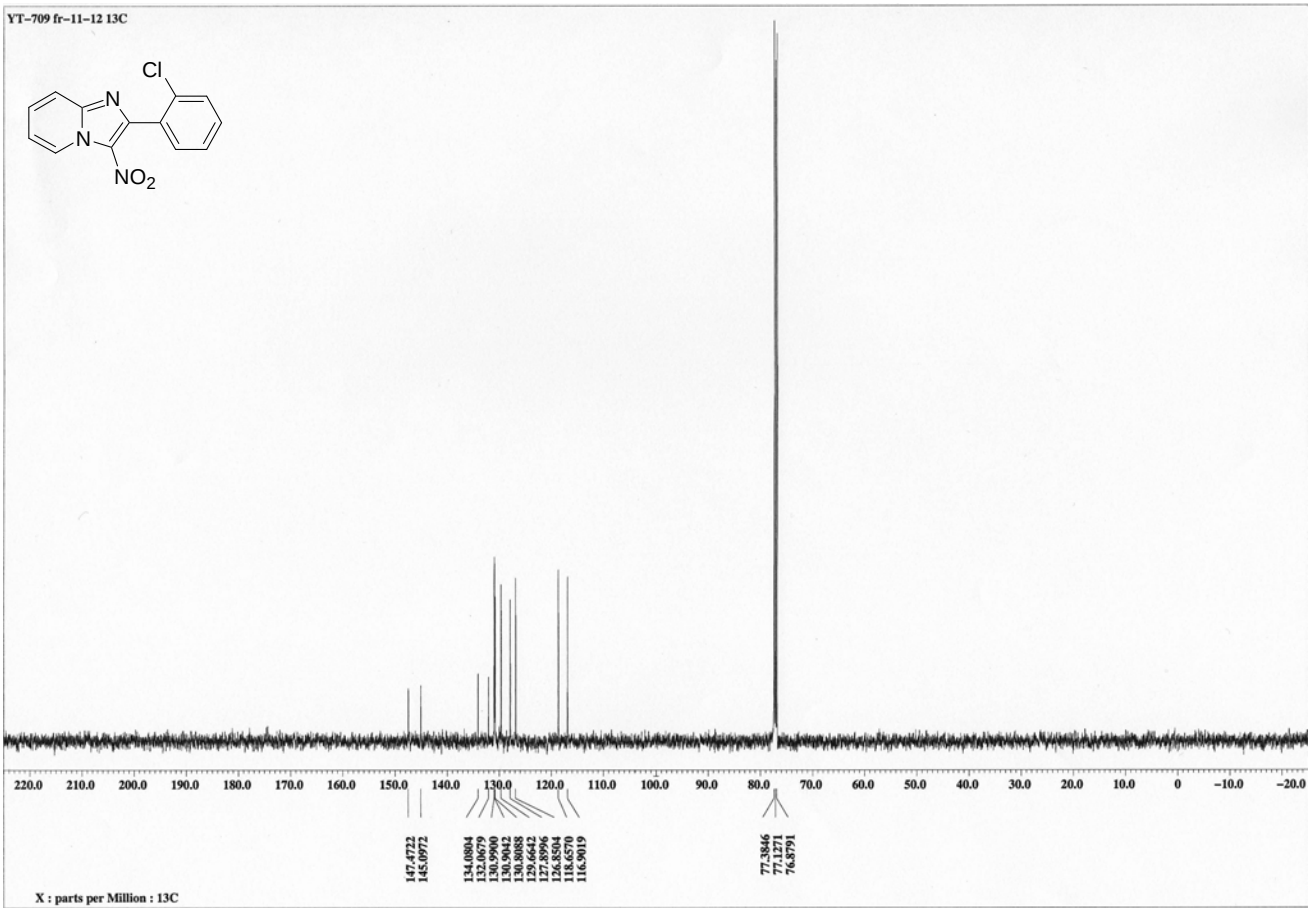



Fig. 14: $^{13}$C NMR of **2-(2-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3g)**

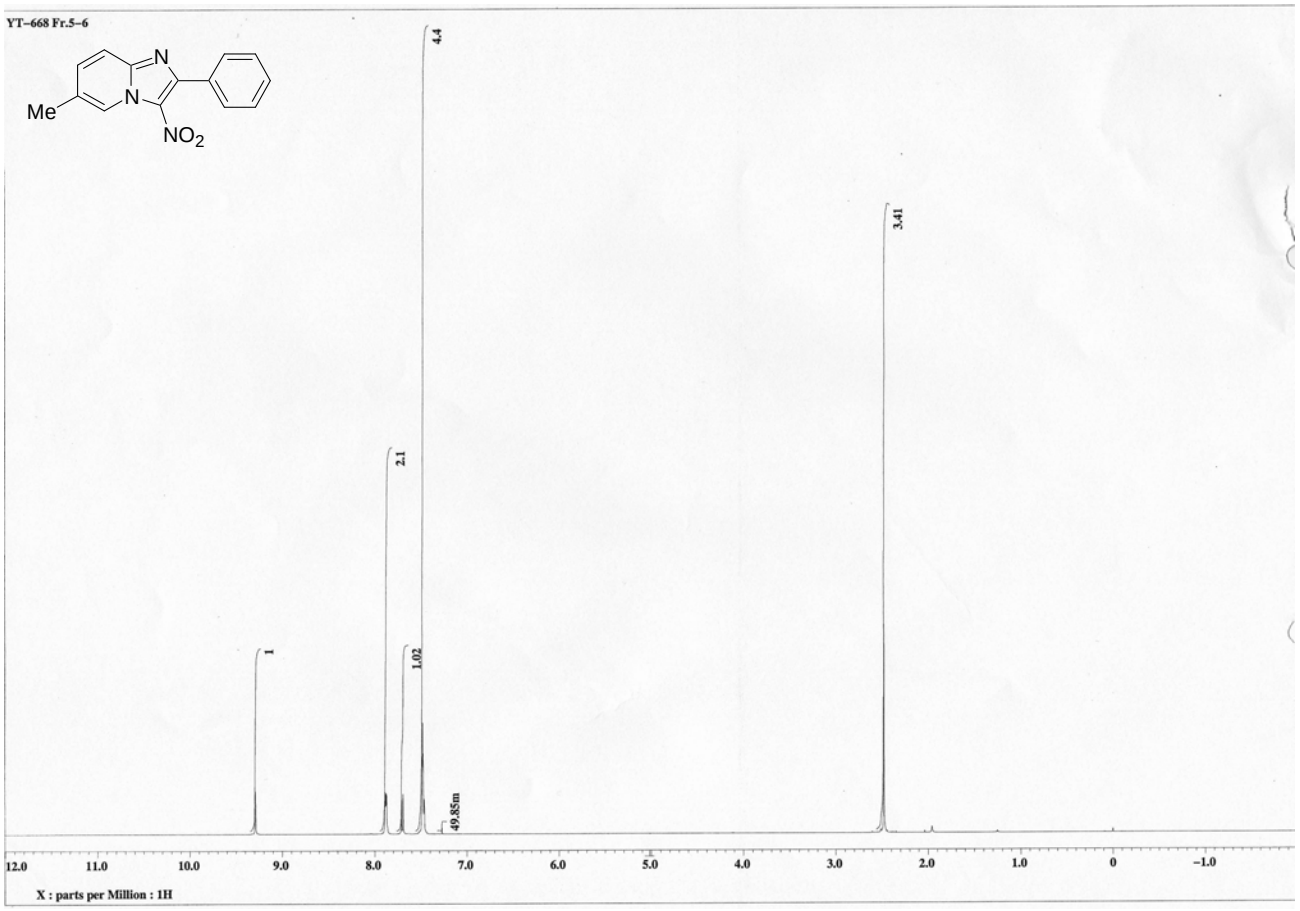



Fig. 15: $^{1}$H NMR of **6-methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3h)**

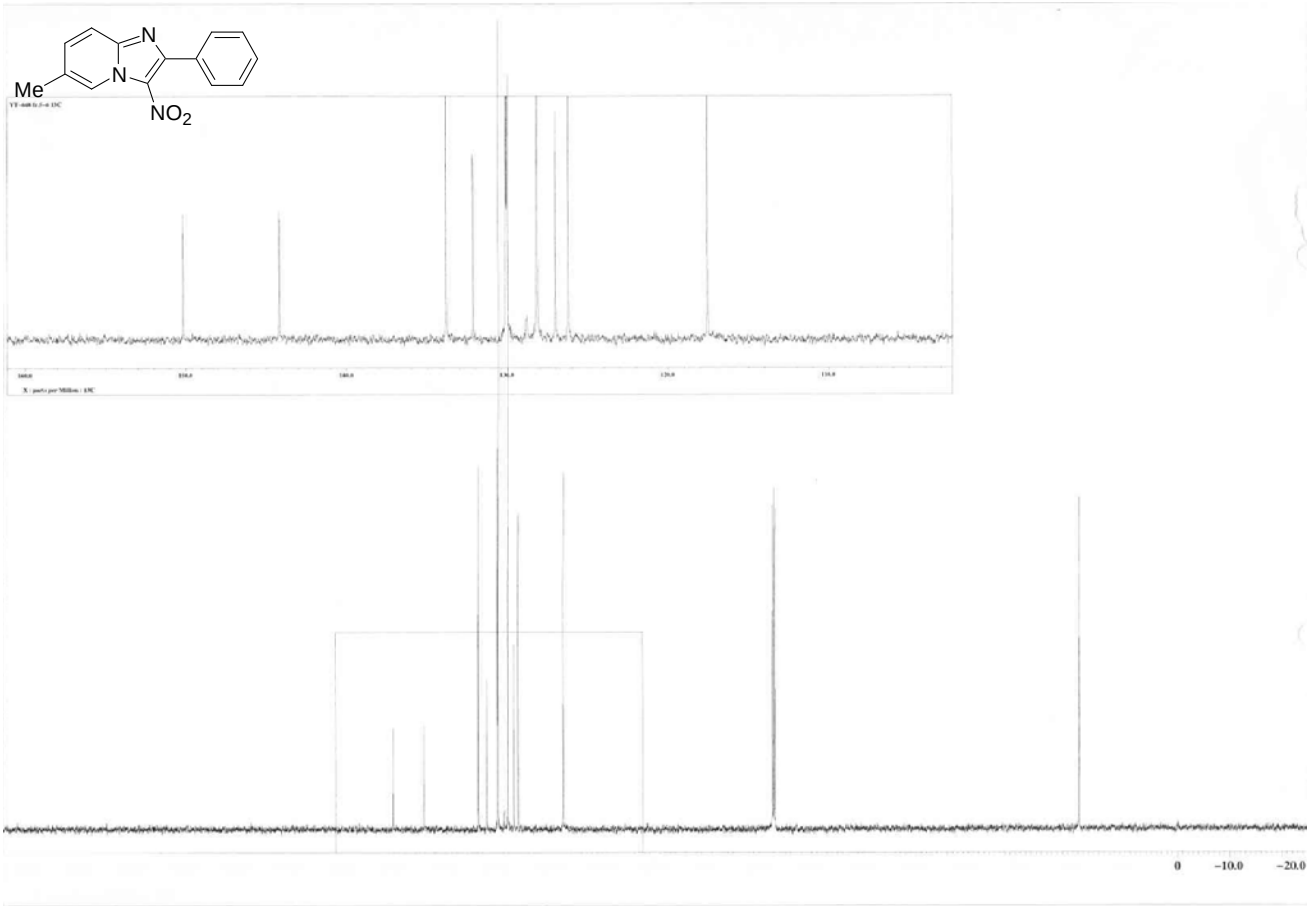



Fig. 16: $^{13}$C NMR of **6-methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3h)**

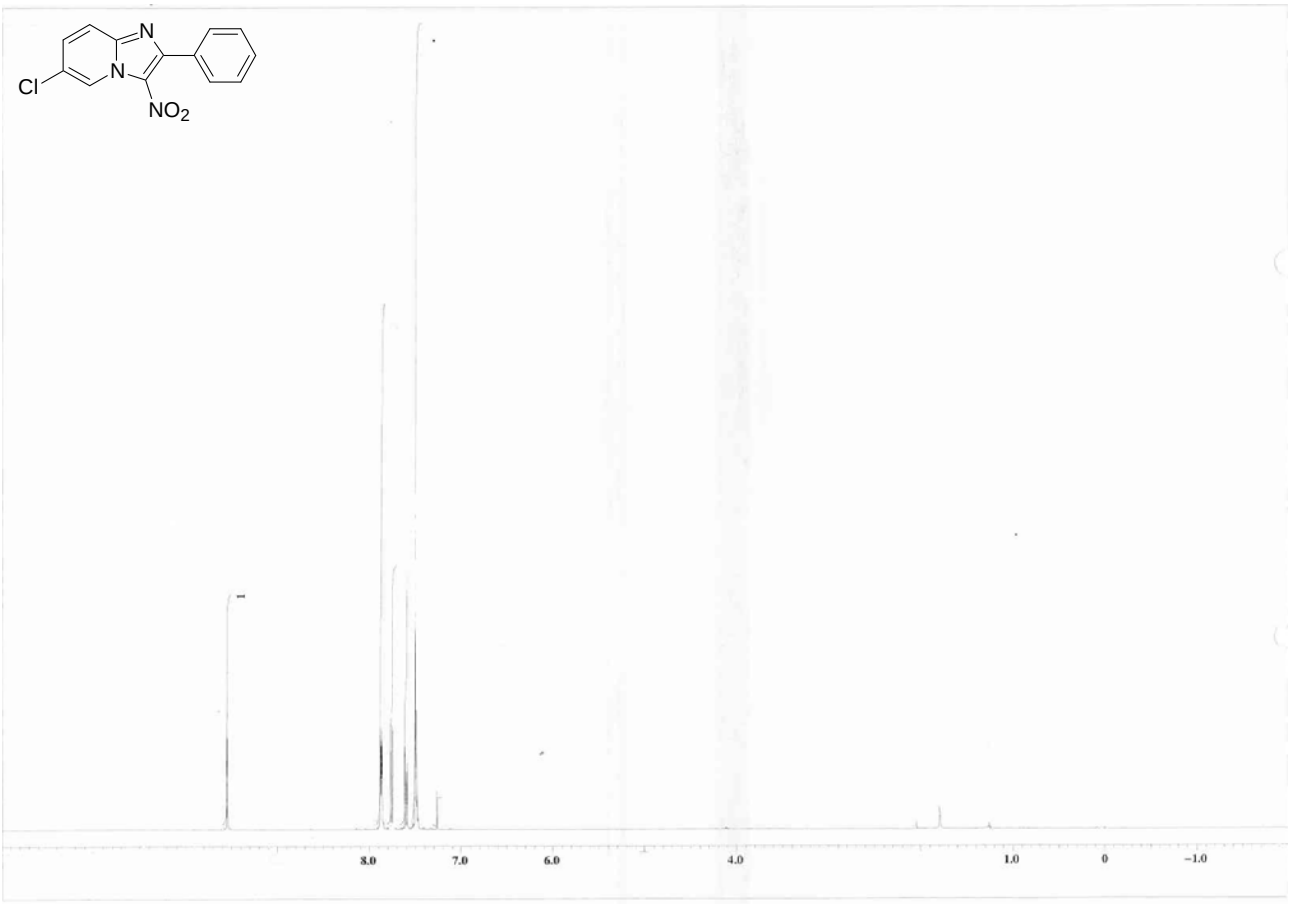



Fig. 17: $^{1}$H NMR of **6-chloro-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3i)**

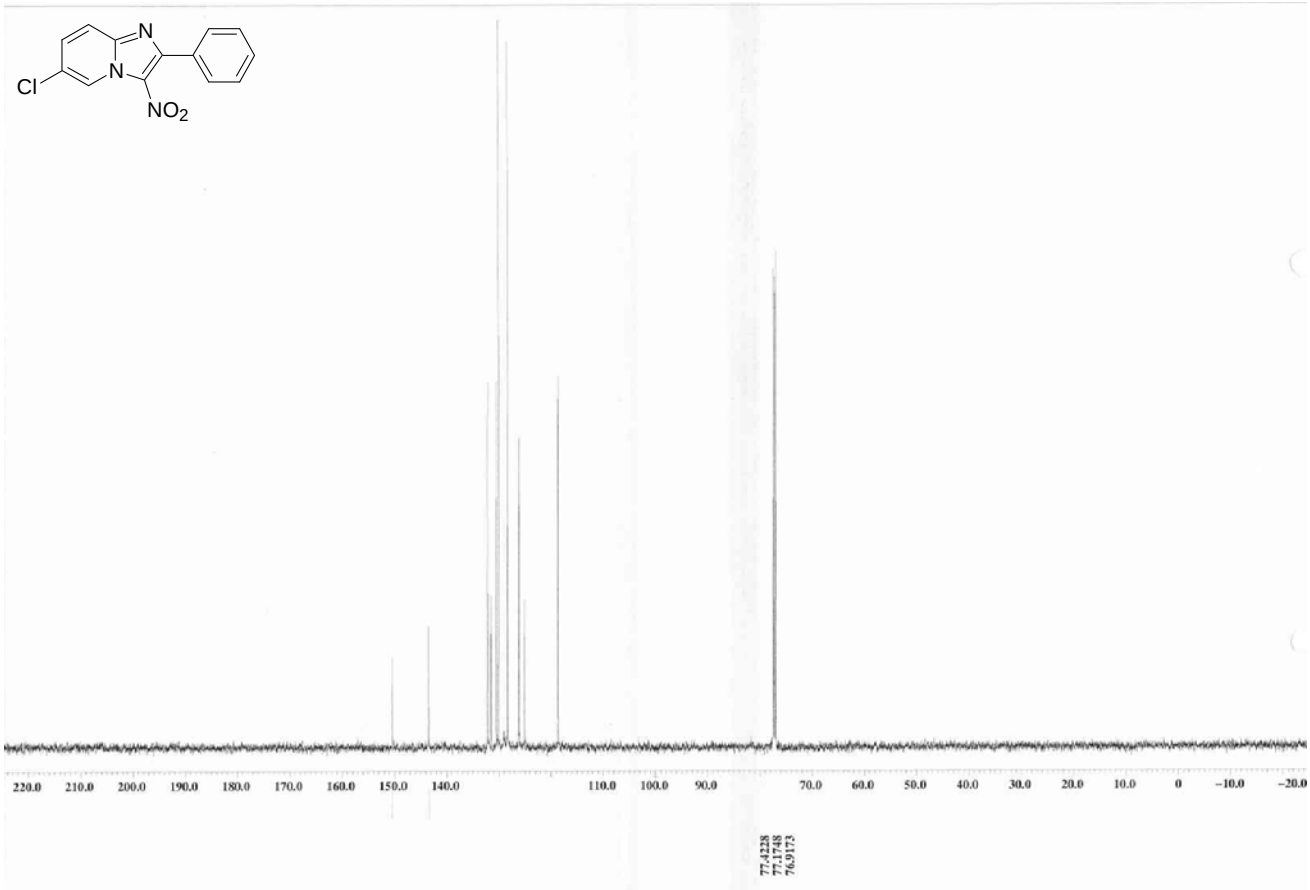



Fig. 18: $^{13}$C NMR of **6-chloro-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3i)**

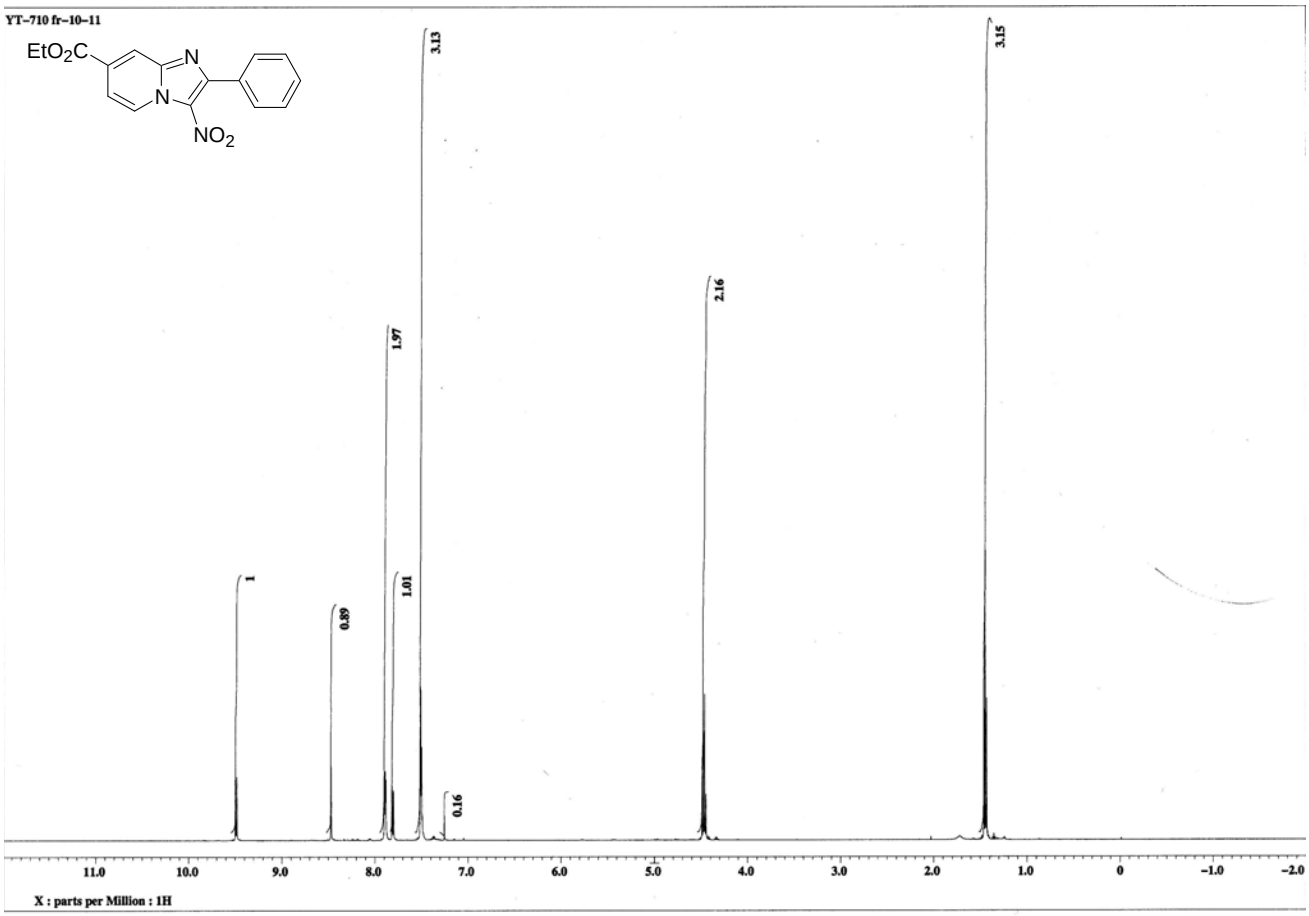



Fig. 19: $^{1}$H NMR of **ethyl 3-nitro-2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (3j)**

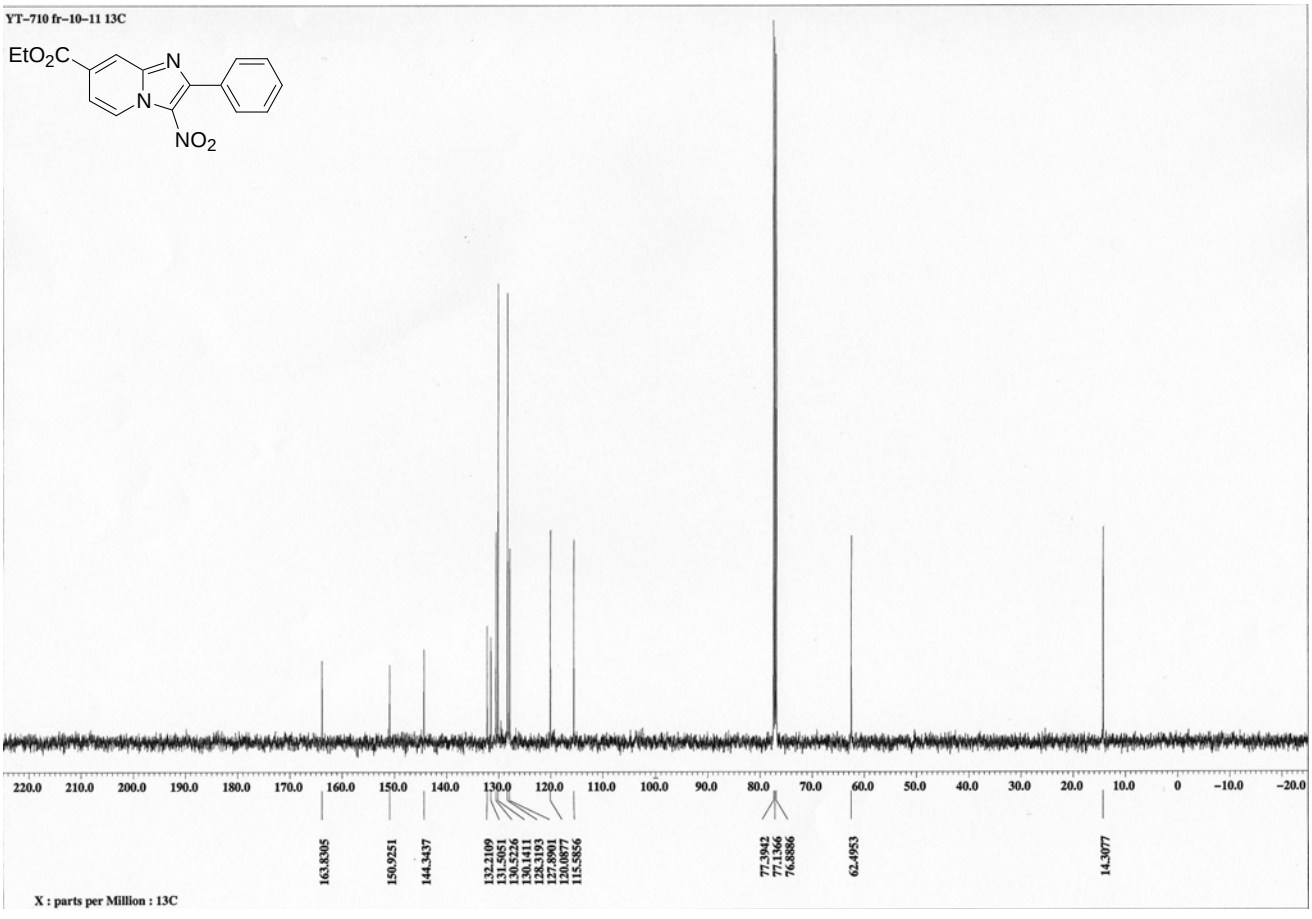



Fig. 20: $^{13}$C NMR of **ethyl 3-nitro-2-phenylimidazo[1,2-*a*]pyridine-7-carboxylate (3j)**

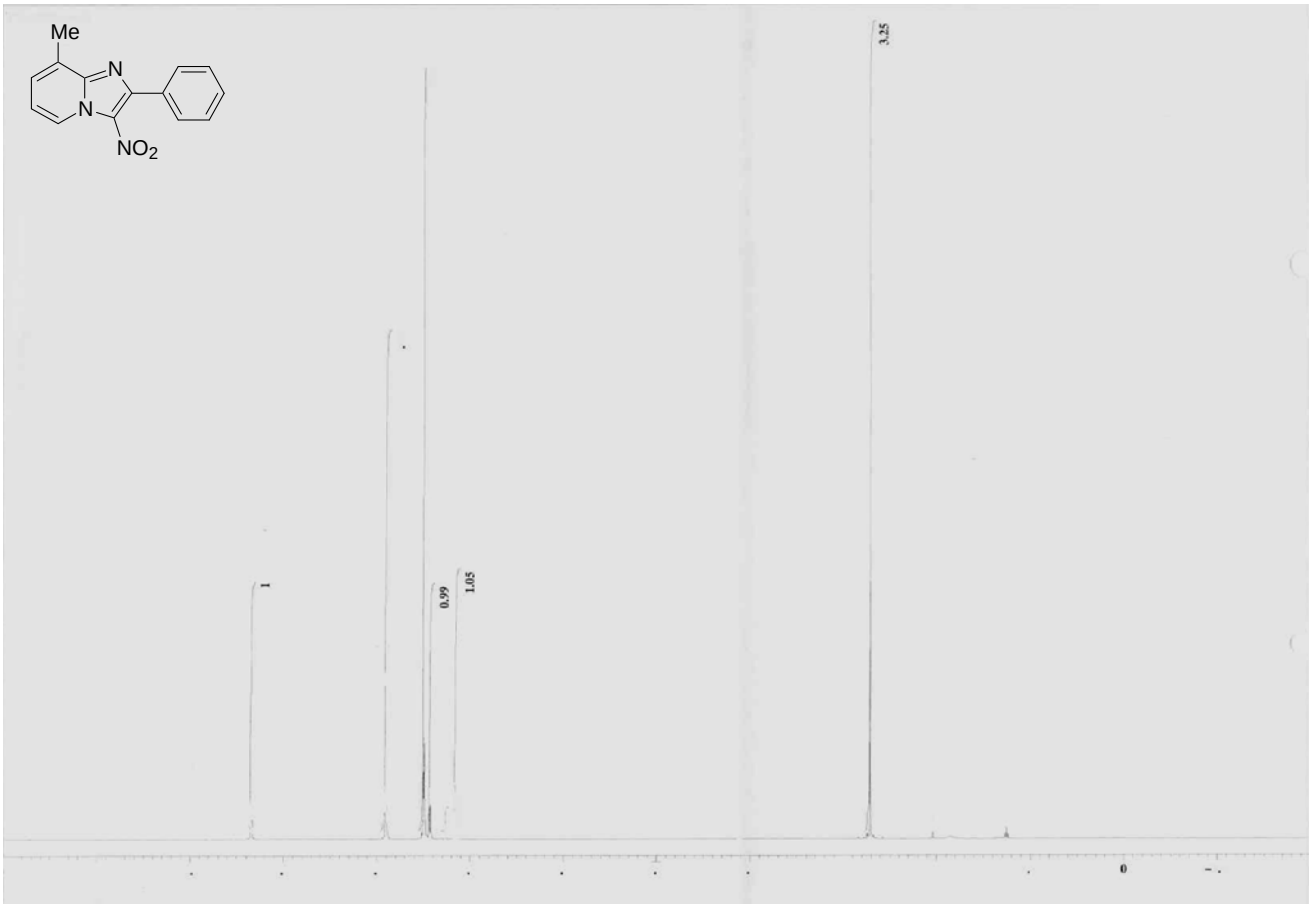



Fig. 21: $^{1}$H NMR of **8-methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3k)**

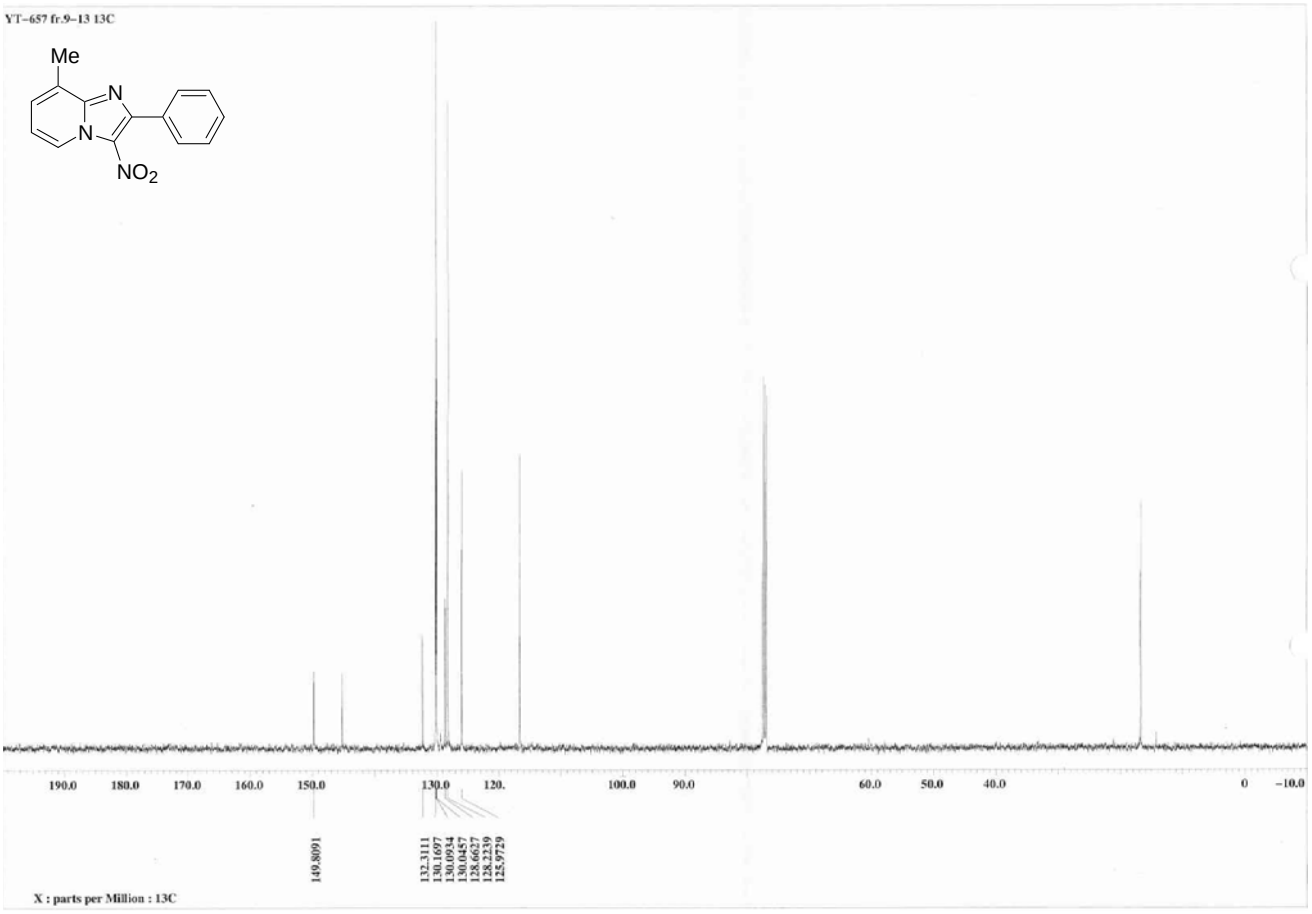



Fig. 22: $^{13}$C NMR of **8-methyl-3-nitro-2-phenylimidazo[1,2-*a*]pyridine (3k)**

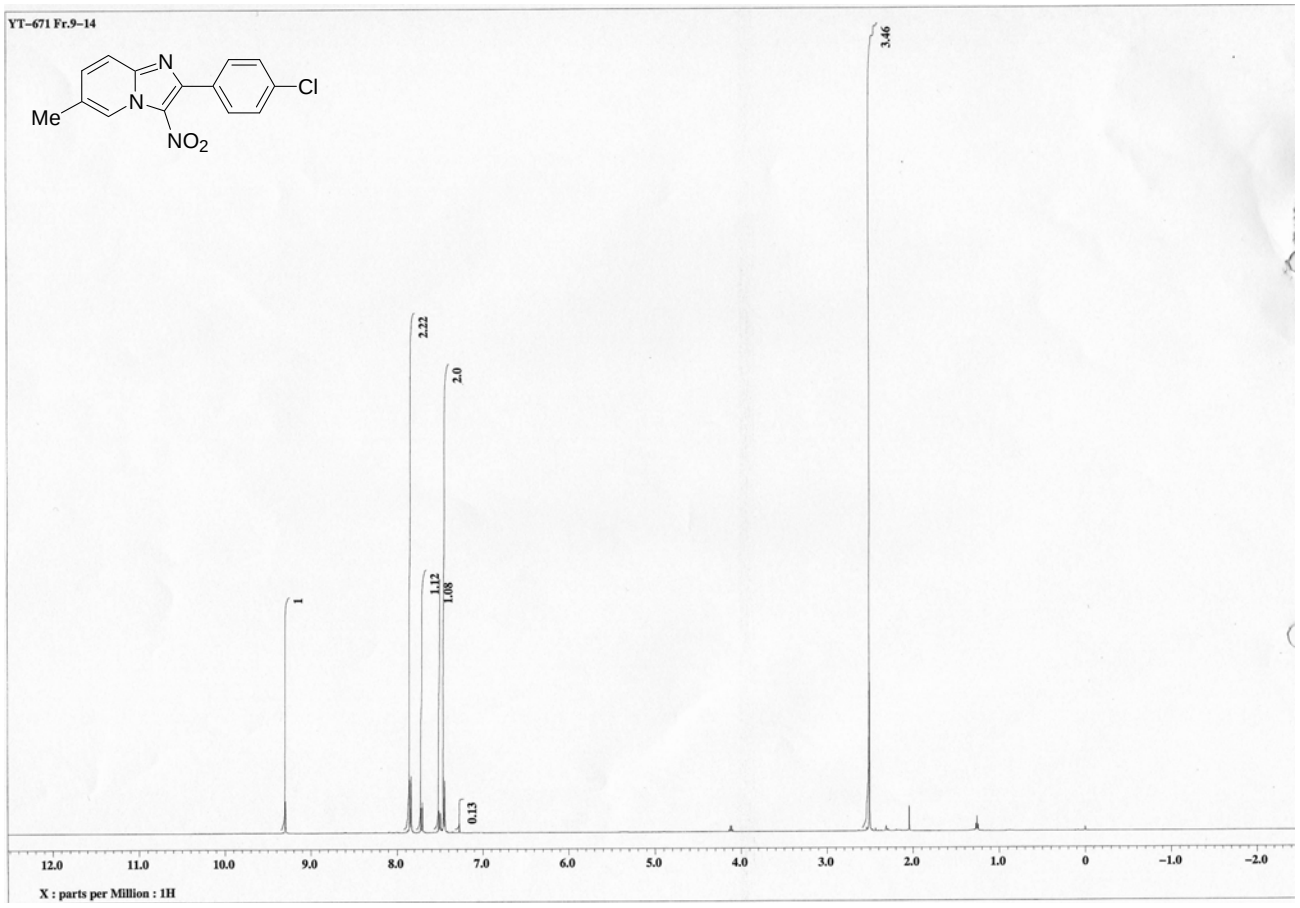



Fig. 23: $^{1}$H NMR of **6-methyl-2-(4-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3l)**

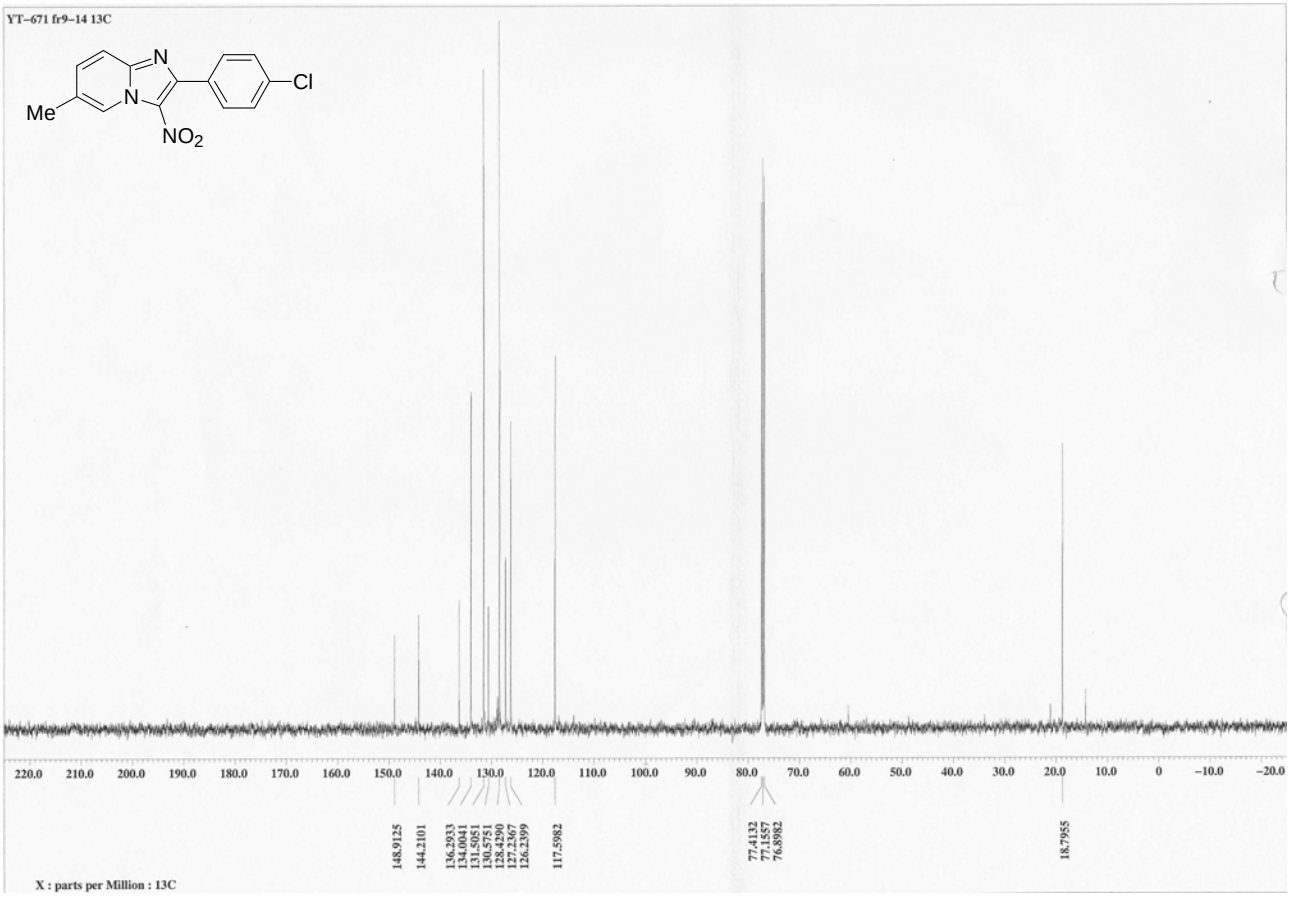



Fig. 24: $^{13}$C NMR of **6-methyl-2-(4-chlorophenyl)-3-nitroimidazo[1,2-*a*]pyridine (3l)**