Electronic Supplementary Material for Organic & Biomolecular Chemistry

SUPPLEMENTARY INFORMATION

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Experimental Procedure

Melting points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as the internal reference) unless specified otherwise. X-ray Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces. The X-ray structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. Column chromatography was performed on silica gel. All the reactions were performed under a nitrogen atmosphere and in oven dried glassware.

General method of preparation of nitropyridines :

Method A: Trifluoroacetic anhydride [10mL] was chilled in an ice bath and the pyridine or substituted pyridines [17mmol] were slowly added and stirred at chilled conditions for 2 h followed by the drop wise addition of concentrated nitric acid [1.9 mL]. After stirring for 9–10 h, the solution was dripped slowly into chilled aqueous solution of sodium metabisulfite. After 24 h, the solution was brought to pH= 6-7 from pH=2-3 by addition of 25% NaOH solution and extracted with methylene chloride to give the nitropyridines which were further purified by column chromatography using hexane : ethyl acetate (1:1).

Method B: Potassium nitrate (20 mmol) was taken in a flask, evacuated of air and purged with nitrogen gas. TFA (20 mmol) was then added to sodium nitrate. Stirred for 10 mins. and TFAA (10 mmol) was added to the mixture. Stirred for 15 mins. Pyridine (10mmol)

was added very slowly dropwise with a syringe. Stirred for 6 hours. Sodium metabisufite solution [2.0 g in 15 ml of water] was added slowly under cooling to the mixture. Stirred for 12 hrs. The pH was then brought to 6-7 with conc. NaOH under cooling and extracted with chloroform. The chloroform layer was dried with magnesium sulphate and the solvent removed to give the nitropyridines which were further purified by column chromatography using hexane : ethyl acetate (1:1).

3-Nitropyridine (6a): yellow prisms (83 %); ^{1}H NMR: δ 7.60 (dd, *J* = 8.4, 4.8 Hz, 1H), 8.53 (ddd, *J* = 8.4, 2.6, 1.5 Hz, 1H), 8.96 (dd, *J* = 4.8, 1.5 Hz, 1H), 9.46 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR: δ 123.7, 130.9, 144.1, 144.9, 154.7. Anal. Calcd for $C_5H_4N_2O_2$: C, 48.39; H, 3.25; N, 22.57. Found C, 48.44; H, 3.10; N, 22.14.

2-Methyl-5-nitropyridine (6b): white prisms (68 %); ^{1}H NMR: δ 2.71 (s, 3H), 7.36 (d, *J* = 8.5 Hz, 1H), 8.37 (dd, *J* = 8.5, 2.6 Hz, 1H), 9.33 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR: δ 24.8, 123.3, 131.2, 142.4, 144.6, 165.4. Anal. Calcd for $C_6H_6N_2O_2$: C, 52.17; H, 4.38; N, 20.28. Found C, 52.38; H, 4.28; N, 20.05.

3-Methyl-5-nitropyridine (6c): yellow prisms (62 %); ^{1}H NMR: δ 2.51 (s, 3H), 8.30 (br s, 1H), 8.75 (br s, 1H), 9.27 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR: δ 18.1, 131.0, 134.4, 142.2, 144.0, 155.4. Anal. Calcd for $C_6H_6N_2O_2$: C, 52.17; H, 4.38; N, 20.28. Found C, 52.24; H, 4.26; N, 20.03.

4-Methyl-3-nitropyridine (6d): yellow oil (86 %); ^{1}H NMR: δ 2.67 (s, 3H), 7.36 (d, *J* = 4.9 Hz, 1H), 8.67 (d, *J* = 5.0 Hz, 1H), 9.15 (s, 1H); ^{13}C NMR: δ 19.9, 127.0, 142.9, 145.8, 147.0,152.9. Anal. Calcd for $C_6H_6N_2O_2$: C, 52.17; H, 4.38; N, 20.28. Found C, 51.80; H, 4.28; N, 19.98.

3-Ethyl-5-nitropyridine (6e): yellow oil (64 %); ^{1}H NMR: δ 1.37 (t, *J* = 7.6 Hz, 3H), 2.87 (q, *J* = 7.6 Hz, 2H), 8.34 (br s, 1H), 8.79 (br s, 1H), 9.25 (d, *J* = 2.3 Hz, 1H); ^{13}C

NMR: δ 14.5, 25.4, 129.6, 140.2, 142.1, 144.0, 154.5. Anal. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41. Found C, 55.24; H, 5.20; N, 18.72.

4-Ethyl-5-nitropyridine (6f): yellow oil (25 %); ^{1}H NMR: δ 1.34 (t, *J* = 7.6 Hz, 3H), 2.99 (q, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 5.1 Hz, 1H), 8.71 (d, *J* = 5.1 Hz, 1H), 9.09 (s, 1H); ^{13}C NMR: δ 13.4, 25.2, 124.9, 145.4, 145.5, 147.6, 152.9. Anal. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41. Found C, 55.37; H, 5.18; N, 18.20.

3-Acetyl-5-nitropyridine (6g): white prisms (20%); ^{1}H NMR: δ 2.76 (s, 3H), 8.97 (t, *J* = 2.4 Hz, 1H), 9.44 (d, *J* = 2.4 Hz, 1H), 9.60 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR: δ 27.0, 130.3, 132.4, 144.3, 148.1, 154.2, 194.3. Anal. Calcd for $C_7H_6N_2O_3$: C, 50.61; H, 3.64; N, 16.87. Found C, 50.67; H, 3.53; N, 16.84.

4-Acetyl-5-nitropyridine (6h): yellow oil (83 %); ^{1}H NMR: δ 2.60 (s, 3H), 7.36 (dd, J=4.9, 0.7 Hz, 1H), 8.97 (dd, *J* = 4.9, 0.7 Hz, 1H), 9.37 (s, 1H); ^{13}C NMR: δ 29.9, 120.6, 144.7, 145.7, 150.9, 155.1, 197.8. Anal. Calcd for $C_7H_6N_2O_3$: C, 50.61; H, 3.64; N, 16.87. Found C, 50.67; H, 3.52; N, 16.74.

2-Flouro-5-nitropyridine (6i): yellow oil (10 %); ^{1}H NMR: δ 7.14 (ddd, *J* = 8.9, 3.2, 0.6 Hz, 1H), 8.62 (ddd, *J* = 8.9, 6.4, 2.9 Hz, 1H), 9.15 (ddd, *J* = 2.9, 1.1, 0.6 Hz, 1H); ^{13}C NMR: δ 110.5 (J_{CF} = 16.6), 136.8 (J_{CF} = 10.6), 142.6, 144.8 (J_{CF} = 17.4), 165.7 (J_{CF} = 249.7).

3-Chloro-5-nitropyridine (6j): white prisms (76 %); ^{1}H NMR: δ 8.50 (t, *J* = 1.7Hz, 1H), 8.89 (d, *J* = 1.7 Hz, 1H), 9.34 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR: δ 130.8, 132.5, 142.7, 144.2, 154.0. Anal. Calcd for $C_5H_3ClN_2O_2$: C, 37.89; H, 1.91; N, 17.68. Found C, 38.33; H, 1.87; N, 17.39.

4-Nitroisoquinoline (6k): orange needles (37%); ^{1}H NMR: δ 7.79 (ddd, *J* = 8.1, 7.8, 1.0 Hz, 1H), 7.96 (ddd, *J* = 8.1, 8.1, 1.4 Hz, 1H), 8.13 (dddd, *J* = 8.1, 1.4, 0.7, 0.5 Hz, 1H),

8.62 (ddd, J = 8.7, 1.0, 0.7, 0.7 Hz, 1H), 9.26 (s, 1H), 9.43 (d, J = 0.8 Hz, 1H); ^{13}C NMR: δ 122.5, 127.8, 128.4, 128.9, 129.0, 134.0, 141.1, 158.0. Anal. Calcd for $C_9H_6N_2O_2$: C, 62.05; H, 3.47; N, 16.08. Found C, 62.03; H, 3.41; N, 15.96.

3-Nitro-4-(N,N-dimethyl)pyridine (6l): yellow microcrystals (32%); ^{1}H NMR: δ 3.00 (s, 6H), 6.79 (d, J = 6.2 Hz, 1H), 8.27 (d, J = 6.2 Hz, 1H), 8.77 (s, 1H). ^{13}C NMR: δ 41.5, 110.6, 148.0, 149.1, 151.3, 153.0. Anal. Calcd for $C_7H_9N_3O_2$: C, 50.28; H, 5.43; N, 25.14. Found C, 50.25; H, 5.40; N, 24.95.

2,4-Dimethyl-5-nitropyridine (6m): yellow oil (52%); ^{1}H NMR: δ 2.61 (s, 3H), 2.63 (s, 3H), 7.26 (br s, 1H), 9.10 (s, 1H); ^{13}C NMR: δ 20.2, 24.3, 126.6, 143.2, 143.8, 145.7, 163.3. Anal. Calcd for $C_7H_8N_2O_2$: C, 55.24; H, 5.30; N, 18.41. Found C, 55.46; H, 5.35; N, 18.24.

3,4-Dimethyl-5-nitropyridine (6n): yellow prisms (30 %); ^{1}H NMR: δ 2.39 (s, 3H), 2.47 (s, 3H), 8.54 (s, 1H), 8.87 (s, 1H); ^{13}C NMR: δ 15.0, 17.0, 134.2, 140.2, 143.1, 153.1, 166.7. Anal. Calcd for $C_7H_8N_2O_2$: C, 55.24; H, 5.30; N, 18.41. Found C, 55.54; H, 5.34; N, 18.29.

5-methyl-2-(trinitromethyl)pyridine (6o): white prisms (10 %); ^{1}H NMR: δ 2.50 (s, 3H), 7.78 (dd, J = 8.2, 1.4 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 8.59 (br s, 1H); ^{13}C NMR: δ 18.6, 124.5, 127.8, 138.0, 139.1, 139.8, 150.8.

X-ray experimental for compound 6o': Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to

monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 155 parameters were refined in the final cycle of refinement using 1656 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.58% and 10.20%, respectively. Refinement was done using F^2.

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.