Electronic Supplementary Information for

Practical Catalytic Nitration Directly with Commercial Nitric Acid for Preparation of Aliphatic Nitroesters

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(A) General Remarks

All starting materials and catalysts were purchased from commercial sources and used without further treatment unless noted.

N-2-Hydroxyethyl-nicotinamide was synthesized as the follow procedure: the mixture of ethyl nicotinate (0.1 mol) and ethanolamine (0.15 mol) was stirred at 55 °C for 3 h, and then at room temperature for 15 h. 100 mL Ethylether was added into the mixture under stirring. Filtration and ether-washing gave the crude product. The white crystalline *N*-2-hydroxyethyl-nicotinamide was obtained by recrystallization of the crude product with *iso*-propanol-chloroform (v:v = 1:1) in 61 % yield, mp 88 °C.

Gas chromatography measurements were conducted using a SHIMADZU 2010 plus gas chromatograph with a flame ionization detector. A SHIMADZU SH-Rtx-1701 capillary column ($30m \times 0.25mm \times 0.25um$) was used to separate products for the *O*-nitration of 2-ethylhexanol. Quantitation of components was performed by the internal standard method using *n*-dodecane as an internal standard.

¹H NMR and ¹³C NMR spectra were recorded on 400 MHz Bruker spectrometers. The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The mass spectra were performed on the SHIMADZU GCMS-QP 2010 Plus mass spectrometer by means of EI technique. The pH values were determined by a REX PHS-3C pH meter of Shanghai Rex Instrument Factory.

(B) Typical experimental procedure

The catalytic nitrations were performed in a 25-mL Schlenk tube and the general procedure is described typically with the *O*-nitration of 2-ethylhexanol to 2-ethylhexyl nitrate (**EHN**) as follows: Into the solution of 2-ethylhexanol (2.5 mmol) in 2 mL cyclohexane, $Eu(OTf)_3$ (10 mol%), HNO₃ (1.02 eq.), and urea (3 mol%, based on HNO₃) were added. The reaction mixture was stirred at 95 °C for 10 h. After the reaction was completed, the mixture was cooled to room temperature and extracted three times with DCM. The organic phases were combined and washed with saturated aqueous NaHCO₃ solution and water, dried over Na₂SO₄, filtered. The filtrate was concentrated under reduced pressure to give the product **EHN**.

(C) Characterization Data of the Products

2-ethylhexyl nitrate : ¹H NMR (400 MHz, CDCl3) δ (ppm) : 4.38 – 4.31 (m, 2H),1.71 – 1.63 (m, 1H), 1.44 – 1.21 (m, 8H), 0.92 – 0.85 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) : 76.2, 37.9, 30.6, 29.1, 24.0, 23.2, 14.3, 11.2.

n-nonyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.44 (t, J = 6.8 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.43 – 1.27 (m, 12H), 0.88 (t, J = 7.2 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.8, 32.2, 29.7, 29.50, 29.46, 27.1, 26.0, 23.0, 14.4.

n-octyl nitrate:

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.44 (t, J = 6.4 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.43 – 1.28 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.8, 32.0, 29.41, 29.39, 27.1, 26.0, 23.0, 14.4.

n-heptyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.43 (t, J = 6.8 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.44 – 1.19 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.8, 31.9, 29.1, 27.0, 25.9, 22.8, 14.3.

n-hexyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.43 (t, J = 6.8 Hz, 2H), 1.74 – 1.67(m, 2H), 1.43 – 1.28 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.8, 31.6, 27.0, 25.6, 22.7, 14.2.

n-pentyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.44 (t, J = 6.8 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.39 – 1.33 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.8, 28.1, 26.7, 22.5, 14.1.

n-butyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm): 4.45 (t, J = 6.8 Hz, 2H), 1.74 – 1.67 (m 2H), 1.48 – 1.39 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 73.5, 29.0, 19.2, 13.9.

n-propyl nitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.40 (t, J = 6.8 Hz, 2H), 1.79 – 1.70 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 75.1, 20.5, 10.4.

2-cyclohexylethyl nitrate:

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.48 (t, J = 6.8 Hz, 2H), 1.73 – 1.70 (m, 5H), 1.63 – 1.57 (m, 2H), 1.45 – 1.36 (m, 1H), 1.30 – 1.13 (m, 3H), 0.99 – 0.90 (m, 2H). ¹³**C NMR** (101 MHz, CDCl3) δ (ppm) : 72.1, 34.7, 34.3, 33.4, 26.6, 26.4.

tert-butyl nitrate : **¹H NMR** (400 MHz, CDCl₃) δ (ppm) : 1.54 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ (ppm) : 90.3, 27.0.

ethane-1,2-diyl dinitrate : **¹H NMR** (400 MHz, CDCl₃) δ (ppm) : 4.75 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) : 68.5.

propane-1,2-diyl dinitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 5.42 – 5.35 (m, 1H), 4.69 (dd, J = 13.2, 3.2 Hz, 1H), 4.48 (dd, J = 13.2, 6.8 Hz, 1H), 1.44 (d, J = 6.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 76.2, 72.1, 15.2.

propane-1,2,3-triyl trinitrate :

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) : 5.55 – 5.50 (m, 1H), 4.83 (dd, J = 12.8, 4.0 Hz, 2H), 4.67 (dd, J = 12.8, 6.0 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) : 74.9, 68.3.

hexahydrofuran [3,2-*b*] furan-3,6-diethyl dinitrate: ¹H NMR (400 MHz, CDCl₃) δ (ppm) : 5.40 – 5.37 (m, 2H), 5.01 (t, *J* = 5.2 Hz, 1H), 4.58 (d, *J* = 5.2 Hz, 1H), 4.17 – 4.06 (m, 3H), 3.93 (dd, *J* = 11.2, 5.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) : 85.5, 85.1, 81.8, 81.0, 71.9, 69.7.

N-(2-hydroxyethyl) nicotinamide:

¹**H NMR** (400 MHz, DMSO-*d*₆) δ (ppm) : 9.01 (dd, *J* = 2.0, 0.4 Hz, 1H), 8.70 – 8.65 (m, 2H), 8.19 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.51-7.47 (m, 1H), 4.77 (s, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 3.35 (q, *J* = 6.0 Hz, 2H). ¹³**C NMR** (101 MHz, DMSO) δ (ppm) : 164.9, 151.8, 148.4, 135.0, 130.0, 123.4, 59.6, 42.2.

m.p. 88°C

2-(nicotinamido)ethyl nitrate(15b) :

¹**H NMR** (400 MHz, DMSO- d_6) δ (ppm) : 9.00 (d, J = 1.6 Hz, 1H), 8.94 (t, J = 5.2 Hz, 1H), 8.72 (dd, J = 4.8, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 4.67 (t, J = 5.2 Hz, 2H), 3.64 (q, J = 5.6 Hz, 2H).

¹³**C NMR** (101 MHz, DMSO) δ (ppm) : 165.2, 152.0, 148.3, 135.1, 129.5, 123.6, 72.2, 36.8.

m.p. 91-92°C

(D) Copies of all spectra

2-ethylhexyl nitrate:



n-nonyl nitrate:



n-octyl nitrate :



n-heptyl nitrate:







n-butyl nitrate:



n-propyl nitrate :



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2-cyclohexylethyl nitrate :



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propane-1,2-diyl dinitrate :







hexahydrofuran [3,2-*b*] furan-3,6-diethyl dinitrate :



N-(2-hydroxyethyl)nicotinamide:



2-(nicotinamido)ethyl nitrate :

