**NHC-catalysed aerobic aldehyde-esterifications with alcohols: no additives or cocatalysts required**

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**Supporting Information**

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1 General Methods

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Melting points were determined using a standard melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker Avance III 400 MHz (400.23 MHz) spectrometer using the solvent peak as internal reference (CDCl₃: δ H 7.26; δ C 77.0 and DMSO-d₆: δ H 2.51; δ C 39.5). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet); coupling constants (J) are in Hertz (Hz). Carbon NMR were recorded on the previously mentioned instrument (100.61 Hz) with total proton decoupling. Fluorine NMR spectra were recorded on the previously mentioned instrument at 376.5 Hz. Mass spectra (MS ESI) were recorded using a Finnigan MAT 95 or Varian MAT 311A. Electron Impact mass spectra were recorded on the same machine in EI mode. TLC analysis was performed on precoated silica gel 60F254 slides, and visualised by KMnO₄ staining. Flash chromatography was carried out using silica gel, particle size 0.2-0.063 mm and using the indicated mobile phase as correlated with TLC analysis. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory.

Tetrahydrofuran was distilled from sodium/benzophenone under argon. Methanol, ethanol, isopropanol and allyl alcohol were distilled from sodium under argon. Benzyl alcohol was purified via flash chromatography using a gradual solvent gradient of CH₂Cl₂:MeOH to remove residual benzaldehyde and benzyl benzoate. All reactions were carried out using oven-dried 25 mL vials, equipped with a plastic lid perforated by 4 holes 2 mm in diameter, unless otherwise specified. Liquid aldehydes were distilled under vacuum prior to use. Solid aldehydes were washed acid-free with 10% aq. K₂CO₃-solution prior to use.

2 General Procedures

General Procedure 1 (Esterification of Aldehydes by Triazolium Precatalyst, Table 1 and 2)

To a 25 mL vial equipped with a magnetic stirring bar was charged the triazolium precatalyst 18 (36 mg, 0.15 mmol, 15 mol%). Dry THF (2.5 mL) and dry MeOH (2.5 mL) were added. DBU (170 µL, 1.1 mmol, 110 mol%) was added and the solution was stirred for 2 minutes. The relevant aldehyde (1 mmol) was then added. The vessel was sealed with a plastic lid perforated by 4 holes 2 mm in diameter and the reaction mixture was stirred for the indicated time at room temperature. The solvent was then removed in vacuo and the resulting residue subjected to flash chromatography to yield the ester product.

3 Synthesis of 4-Ethyl-1-methyl-4H-[1,2,4]triazol-1-ium iodide (18)
1-Methyl-1H-1,2,4-triazole (S1)

To a flame-dried 250 mL round-bottomed flask equipped with a magnetic stirring bar was charged MeOH (80 mL) and sodium (3.30 g). The solution was stirred for 5 minutes before 1,2,4-triazole (10 g, 1.55 mol, 1 equiv) was added and the mixture stirred at room temperature until the solid had dissolved. The vessel was then placed under a protective atmosphere of argon and cooled to 0 °C in a H2O/ice bath. Iodomethane (9.04 mL, 20.61 g, 1.55 mol, 1 equiv) was added dropwise via syringe. Stirring was continued for 5 minutes at 0 °C before warming to room temperature and stirring for a further 2 hours under argon before refluxing at 60 °C for 20 h. Upon cooling, the solvent was removed in vacuo and H2O (60 mL) was added. The product was extracted with CH2Cl2 (3 x 50 mL), the combined organic layers dried over MgSO4 and concentrated in vacuo to yield the title product as a yellow liquid (4.67 g, 39%) that was dried under vacuum for several hours. δH (400 MHz, CDCl3): 3.80 (s, 3H, CH3), 7.78 (s, 1H, CH), 7.93 (s, 1H, CH). HRMS (m/z –ESI+): Found 84.0564 (C3H6N3+ requires 84.0562).

4-Ethyl-1-methyl-4H-[1,2,4]triazol-1-ium iodide (18)

To a flame-dried 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged 1-methyl-1H-1,2,4-triazole (S1) (4.2 g, 0.051 mol, 1 equiv). The vessel was placed under a protective atmosphere of argon and ethyl iodide (17.3 g, 8.9 mL, 0.111 mol, 2.17 equiv) was added via syringe. The flask was covered with aluminium foil and the reaction mixture stirred for 96 h at room temperature under argon. The resulting precipitate was filtered, washed with Et2O (3 x 20 mL) and recrystallised from 1% CH2Cl2/MeOH to yield the title product as a white crystalline solid (3.07 g, 0.0128 mol, 23%).

m.p.: 137 – 139 °C. RF (CH2Cl2:MeOH, 4:1): 0.41. δ (cm⁻¹): 3423, 3028, 1773, 1583, 1164, 990, 730, 720, 653. δH (400 MHz, DMSO-d6): 10.03 (s, 1H, CH), 9.18 (s, 1H, CH), 4.20 (q, J = 7.32 Hz, 2H, CH2), 4.03 (s, 3H, CH3), 1.42 (t, J = 7.32 Hz, 3H, CH3). δC (100 MHz, DMSO-d6): 144.7, 143.1, 43.4, 39.0472, 15.0. HRMS (m/z –ESI+): Found 112.0874 (C5H10N3+ requires 112.0875).

4 Experimental Data for Ester Products (Table 1 and 2)

Methyl benzoate (13, Table 2, entry 1)
Prepared according to **general procedure 1** (24 h) using benzaldehyde (102 μL, 1 mmol). Purified via flash chromatography (*n*-hexane:Et₂O, 85:15): 128 mg (94%) as a colourless oil. All spectral data corresponds to previous literature characterisation.

**Methyl 2-naphthoate (31, Table 2, entry 2)**

Prepared according to **general procedure 1** (12 h) using 2-naphthaldehyde (156 mg, 1 mmol). Purified via flash chromatography (*n*-hexane:Et₂O, 9:1): 167 mg (90%) as a white solid. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 8.60 (s, 1H), 8.06 (d, J = 9.68 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.72 Hz, 2H), 7.58 – 7.49 (m, 2H), 3.97 (s, 3H). HRMS (*m/z*-EI): Found 186.0688 (C<sub>12</sub>H<sub>10</sub>O₂ requires 186.0681).

**Methyl 4-methylbenzoate (32, Table 2, entry 3)**

Prepared according to **general procedure 1** (30 h) using 4-tolualdehyde (118 μL, 1 mmol). Purified via flash chromatography (*n*-hexane:ethyl acetate, 9:1): 138 mg (92%) as a white solid. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 7.92 (d, J = 8.16 Hz, 2H), 7.24 (d, J = 8.0 Hz , 2H), 3.87 (s, 3H), 2.38 (s, 3H). HRMS (*m/z*-EI): Found 150.0680 (C<sub>9</sub>H<sub>10</sub>O₂ requires 150.0681)

**Methyl 4-(methoxy)benzoate (33, Table 2, entry 4)**

Prepared according to **general procedure 1** (92 h) using 4-anisaldehyde (122 μL, 1 mmol). Purified via flash chromatography (*n*-hexane:ethyl acetate, 9:1): 150 mg (90%) as a white solid. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 7.98 (d, J = 8.88 Hz, 2H), 6.90 (d, J = 8.88 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H). HRMS (*m/z*-EI): Found 166.0635 (C<sub>9</sub>H<sub>10</sub>O₃ requires 166.0630).

**Methyl 3-chlorobenzoate (34, Table 2, entry 5)**

Prepared according to **general procedure 1** (92 h) using 4-anisaldehyde (122 μL, 1 mmol). Purified via flash chromatography (*n*-hexane:ethyl acetate, 9:1): 150 mg (90%) as a white solid. δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 7.98 (d, J = 8.88 Hz, 2H), 6.90 (d, J = 8.88 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H). HRMS (*m/z*-EI): Found 166.0635 (C<sub>9</sub>H<sub>10</sub>O₃ requires 166.0630).
Prepared according to **general procedure 1** (24 h) using 3-chlorobenzaldehyde (113 µL, 1 mmol). Purified *via* flash chromatography (*n*-hexane : Et₂O, 85:15): 157 mg (92%) as a colourless oil. δₓ (400 MHz, CDCl₃): 7.99 (s, 1H), 7.95 (d, J = 7.80 Hz, 1H), 7.50 (d, J = 8.04 Hz, 1H), 7.38 (app. t, 1H), 3.90 (s, 3H). HRMS (m/z-EI): Found 170.0133 (C₈H₇O₂Cl requires 170.0135).

**Methyl 4-chlorobenzoate (35, Table 2, entry 6)**

Prepared according to **general procedure 1** (12 h) using 4-chlorobenzaldehyde (141 mg, 1 mmol). Purified *via* flash chromatography (*n*-hexane:Et₂O, 9:1): 123 mg (72%) as a white solid. δₓ (400 MHz, CDCl₃): 7.94 (d, J = 8.48 Hz, 2H), 7.38 (d, J = 8.52 Hz, 2H), 3.88 (s, 3H). HRMS (m/z-EI): Found 170.0141 (C₈H₇O₂Cl requires 170.0135).

**Methyl 3-(methoxy)benzoate (36, Table 2, entry 7)**

Prepared according to **general procedure 1** (68 h, 45 °C in 10 mL round-bottomed flask) using 3-anisaldehyde (122 µL, 1 mmol). Purified *via* flash chromatography (*n*-hexane:CH₂Cl₂, 3:1): 128 mg (77%) as a pale yellow oil. δₓ (400 MHz, CDCl₃): 7.61 (d, J = 7.68 Hz, 1H), 7.54 (s, 1H), 7.32 (app. t, 1H), 7.07 (d, J = 10.76 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H). HRMS (m/z-ESI): Found 165.0552 (C₉H₁₀O₃ requires 165.0552).
Methyl 2-chlorobenzoate (38, Table 2, entry 9)

Prepared according to general procedure 1 (24 h) using 2-chlorobenzaldehyde (113 μL, 1.0 mmol). Purified via flash chromatography (n-hexane:CH₂Cl₂, 3:1): 90 mg (53%) as a pale yellow oil. δH (400 MHz, CDCl₃): 7.81 (d, J = 7.76 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.30 (app t, 1H), 3.91 (s, 3H). HRMS (m/z-EI): Found 170.0135 (C₈H₇O₂Cl requires 170.0135).

Methyl 2-thiophene 2-carboxylate (40, Table 2, entry 11)

Prepared according to general procedure 1 (18 h) using thiophene-2-carbaldehyde (94 μL, 1 mmol). Purified via flash chromatography (n-hexane:ethyl acetate, 4:1): 92 mg (65%) as a pale yellow oil. δH (400 MHz, CDCl₃): 7.77 (d, J = 3.8 Hz, 1H), 7.52 (d, J = 4.96 Hz, 1H), 7.07 (t, J = 4.12 Hz, 1H), 3.87 (s, 3H). HRMS (m/z-EI): Found 142.0090 (C₆H₆O₂S requires 142.0089).

Methyl 3-nicotinate (41, Table 2, entry 12)

Prepared according to general procedure 1 (20 min) using 3-pyridinecarboxaldehyde (94 μL, 1 mmol). Purified via flash chromatography (n-hexane:ethyl acetate, 7:3): 126 mg (93%) as a white solid. M.p. 41-43 °C (lit.,¹ 39.5-41.5 °C). δH (400 MHz, CDCl₃): 9.19 (s, 1H), 8.74 (app. bs, 1H), 8.27 (d, J = 7.9, 1H), 7.38 (app. t, 1H), 3.92 (s, 3H). HRMS (m/z-ESI⁺, M+H): Found 138.0553 (C₇H₈NO₂ requires 138.0555).

5 $^1$H NMR Spectra of crude reaction mixtures

Table 1, entry 6 (96%)
6 $^1$H NMR Spectra of isolated ester products

Methyl 2-naphthoate (Table 2, entry 2)

![NMR Spectrum of Methyl 2-naphthoate](image)
Methyl 4-methylbenzoate (Table 2, entry 3)
Methyl 4-(methoxy)benzoate (Table 2, entry 4)
Methyl 3-chlorobenzoate (Table 2, entry 5)
Methyl 4-chlorobenzoate (Table 2, entry 6)
Methyl 3-(methoxy)benzoate (Table 2, entry 7)
Methyl 2-chlorobenzoate (Table 2, entry 9)
Methyl 2-thiophene carboxylate (Table 2, entry 11)
Methyl 3-nicotinate (Table 2, entry 12)
7 $^1$H and $^{13}$C NMR Spectra of the triazolium precatalyst 18

![NMR Spectra Image]