H_3PO_4/metal halide induces an one pot solvent-free esterification-halogenation of glycerol and diols

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Suporting information

NMR spectra of the synthesised compounds

1,3-Dichloro-2-propyl hexadecanoate [CAS: 72165-62-9]:. ^{1}H NMR ($CDCl_3$) δ: 5.18 (quin, *J*=5.2 Hz, 1H, O-C*H*), 3.73 (m, 4H, 2 CH_2-Cl), 2.37 (t, *J*=7 Hz, 2H, C$H_{2\ (\alpha)}$ (C=O)), 1.65 (m, 2H, C$H_{2\ (\beta)}$ (C=O)), 1.26 (m, 24H, CH_2), 0.88 (t, *J*=7 Hz, 3H, CH_3). ^{13}C-RMN ($CDCl_3$), δ: 172.7 (*C*=O), 71.5 (O-*C*H), 42.5 (*C*H_2-Cl), 34.1 (*C*$H_{2\ (\alpha)}$ (C=O)), 31.9 (*C*H_2-CH$_2$-CH$_3$), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0 (*C*H_2), 24.8 (*C*$H_{2\ (\beta)}$ (C=O)), 22.7 (*C*H_2-CH$_3$), 14.1 (*C*H_3).

1,3-Dibromo-2-propyl hexadecanoate (A) [CAS: 7739-59-5] and 2,3-dibromo-1-propyl hexadecanoate (B) [CAS: 858835-01-5]: *A Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 5.12 (quin, *J*=5.3 Hz, 1H, O-C*H*), 3.57 (d, *J*=5.3 Hz, 4H, CH_2-Br), 2.37 (t, 2H, C$H_{2\ (\alpha)}$ (C=O)), 1.65 (m, 2H, C$H_{2\ (\beta)}$ (C=O)), 1.26 (m, 24H, CH_2), 0.88 (t, *J*=7 Hz, 3H, CH_3). ^{13}C-RMN ($CDCl_3$), δ: 172.3 (*C*=O), 70.9 (O-*C*H), 42.5 (*C*H_2-Br), 34.1 (*C*$H_{2\ (\alpha)}$ (C=O)), 32.0 (*C*H_2-CH$_2$-CH$_3$), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0 (*C*H_2), 24.5 (*C*$H_{2\ (\beta)}$ (C=O)), 22.1 (*C*H_2-CH$_3$), 14.0 (*C*H_3). *B Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 4.45 (m, 2H, O–CH_2), 4.18 (m. 1H, C*H*–Br), 3.75 (m, 2H, CH_2–Br). ^{13}C-RMN ($CDCl_3$), δ: 173.0 (*C*=O), 64.6 (O-*C*H$_2$), 46.9 (CH$_2$-*C*HBr-CH$_2$), 32.3 (CHBr-*C*H$_2$Br). All other NMR signals are hidden by the signals of A. m.p.: 31-33ºC.

1,3-Dichloro-2-propyl octanaote [CAS: 88606-77-3]: ^{1}H NMR ($CDCl_3$), δ: 5.12 (quin, *J*=5.2 Hz, 1H, O-C*H*), 3.68 (dd, *J*=5.7 Hz, *J*=2.2 Hz, 4H, 2 CH_2-Cl), 2.31 (t, *J*=7.6 Hz, 2H, C$H_{2\ (\alpha)}$ (C=O)), 1.58 (quin, *J*=7.4 Hz, 2H, C$H_{2\ (\beta)}$ (C=O)), 1.24 (m, 8H, CH_2), 0.82 (t, *J*=7.2 Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 173 (*C*=O), 72 (O-*C*H), 42 (*C*H_2-Cl), 34.4 (*C*$H_{2\ (\alpha)}$ (C=O)), 32.1 (*C*H_2-CH$_2$-CH$_3$), 29.5 (*C*H_2), 25 (*C*$H_{2\ (\beta)}$ (C=O)), 22.5 (*C*H_2-CH$_3$), 14.5 (*C*H_3).

1,3-Dichloro-2-propyl pivaloate [CAS: 220499-01-4]: ^{1}H NMR ($CDCl_3$), δ: 5.14 (quin, *J*=5.2 Hz, 1H, O-C*H*), 3.76 (m, 4H, 2 CH_2-Cl), 1.24 (m, 9H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 177.9 (*C*=O), 71.6 (O-*C*H), 42.7 (*C*H_2-Cl), 39.2 (*C*-(CH$_3$)$_3$), 27.3 (3*C*H$_3$).

2-Chloro-1-ethyl hexadecanoate [CAS: 929-16-8]: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, *J*=6.6 Hz, 3 H) 1.20-1.40 (m, 24 H) 1.55-1.60 (m, 2 H) 2.35 (t, *J*=7.4 Hz, 2 H) 3.68 (t, *J*=5.8 Hz, 2 H) 4.33 (t, *J*=5.8 Hz, 2 H). ^{13}C-RMN ($CDCl_3$), δ: 173.5 (*C*=O), 63.8 (O-*C*H$_2$), 41.6 (*C*H$_2$-Cl), 34.1 (*C*H$_{2\ (\alpha)}$ (C=O)), 31.9 (*C*H$_2$-CH$_2$-CH$_3$), 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0 (*C*H$_2$), 24.9 (*C*H$_{2\ (\beta)}$ (C=O)), 22.7 (*C*H$_2$-CH$_3$), 14.1 (*C*H$_3$).

4-Chloro-1-butyl hexadecanoate [CAS: 72165-61-8]: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, *J*=6.56 Hz, 3 H) 1.20-1.37 (m, 24 H) 1.57-1.67 (m, 2 H) 1.74-1.91 (m, 4 H) 2.30 (t, *J*=7.5 Hz, 2 H) 3.57 (t, *J*=6.3 Hz, 2 H) 4.11 (t, *J*=6.1 Hz, 2 H). ^{13}C-RMN ($CDCl_3$), δ: 173.8 (*C*=O), 63.2 (O-*C*H$_2$), 44.4 (*C*H$_2$-Cl), 34.2 (*C*H$_{2\ (\alpha)}$ (C=O)), 31.8 (*C*H$_2$-CH$_2$-CH$_3$), 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0 (*C*H$_2$), 26.0 (O-CH$_2$-*C*H$_2$), 24.9 (*C*H$_{2\ (\beta)}$ (C=O)), 22.7 (*C*H$_2$-CH$_3$), 14.1 (*C*H$_3$).

6-Chloro-1-hexyl hexadecanoate [CAS: 486424-47-9]: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, *J*=6.6 Hz, 3 H) 1.20-1.52 (m, 28 H) 1.57-1.70 (m, 4 H) 1.77-1.83 (m, 2 H) 2.29 (t, *J*=7.3 Hz, 2 H) 3.54 (t, *J*=6.7 Hz, 2 H) 4.07 (t, *J*=6.6 Hz, 2 H). ^{13}C-RMN ($CDCl_3$), δ: 173.8 (*C*=O), 64.0 (O-*C*H$_2$), 44.8 (*C*H$_2$-Cl), 34.3 (*C*H$_{2\ (\alpha)}$ (C=O)), 32.4 (O-CH$_2$-*C*H$_2$), 31.9 (*C*H$_2$-CH$_2$-CH$_3$), 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.4, (*C*H$_2$), 26.4 (O-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$), 25.2 (O-CH$_2$-CH$_2$-*C*H$_2$), 24.9 (*C*H$_{2\ (\beta)}$ (C=O)), 22.6 (*C*H$_2$-CH$_3$), 14.0 (*C*H$_3$).

2-Chloro-1-propyl hexadecanoate (A) [CAS: 23290-41-7] and 1-chloro-2-propyl hexadecanoate (B) [CAS: 486424-48-0]: *B Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, J=6.56 Hz, 3 H) 1.20-1.35 (m, 24 H) 1.32 (d, J=6.4 Hz, 3 H) 1.60-1.75 (m, 2 H) 2.31 (t, J=7.2 Hz, 2 H) 3.55 (dd, J=11.4, 5.5 Hz, 1 H) 3.59 (dd, J=11.4, 5.1 Hz, 1 H) 5.05-5.16 (m, 1 H). ^{13}C-RMN ($CDCl_3$), δ: 173.0 (*C*=O), 69.3 (O-*C*H_2), 46.8 (*C*H_2-Cl), 34.4 (*C*$H_{2\ (\alpha)}$ (C=O)), 31.8 (*C*H_2-CH_2-CH_3), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0 (*C*H_2), 24.9 (*C*$H_{2\ (\beta)}$ (C=O)), 22.6 (*C*H_2-CH_3), 17.5 (O-CH-*C*H_3), 14.1 (*C*H_3). *A Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 1.52 (d, J=6.7 Hz, 3 H) 3.80-3.83 (m, 1 H) 4.15-4.21 (m, 2 H). ^{13}C-RMN ($CDCl_3$), δ: 72.0 (O-*C*H_2), 53.8 (*C*H_2-Cl), 21.6 (*C*H_2-CH_3). All other NMR signals are hidden by the signals of B.

3-Chloro-1-butyl hexadecanoate (A) [CAS: 23139-83-5] and 4-chloro-2-butyl hexadecanoate (B) [CAS: 486424-51-5]: *B Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, J=6.4 Hz, 3 H) 1.20-1.35 (m, 27 H) 1.1.58-1.66 (m, 2 H) 1.90-2.14 (m, 2 H) 2.29 (t, J=7.3 Hz, 2 H) 3.53 (dt, J=6.6, 1.1 Hz, 2 H) 5.05-5.58 (m, 1 H). ^{13}C-RMN ($CDCl_3$), δ: 173.3 (*C*=O), 67.9 (O-*C*H), 40.7 (O-CH-*C*H_2), 38.7 (*C*H_2-Cl), 34.5 (*C*$H_{2\ (\alpha)}$ (C=O)), 31.9 (*C*H_2-CH_2-CH_3), 29.7, 29.6, 29.4, 29.3, 29.2, 29.1 (*C*H_2), 25.0 (*C*$H_{2\ (\beta)}$ (C=O)), 22.7 (*C*H_2-CH_3), 19.9 (O-CH-*C*H_3), 14.1 (*C*H_3). *A Regioisomer:* ^{1}H NMR ($CDCl_3$) δ: 1.55 (d, J=6.6 Hz, 3H) 4.06-4.41 (m, 3 H). ^{13}C-RMN ($CDCl_3$), δ: 61.5 (O-*C*H), 54.2 (*C*H-Cl). All other NMR signals are hidden by the signals of B.

4-chloro-1-pentyl hexadecanoate (A) [CAS: 486424-52-6] and 5-chloro-2-pentyl hexadecanoate (B) [CAS: 486424-53-7]. *B Regioisomer*: ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, *J*=6.6 Hz, 3 H) 1.18-1.37 (m, 24 H) 1.23 (d, *J*=6.3 Hz, 3 H) 2.30 (t, *J*=7.6 Hz, 2 H) 3.54 (t, *J*=6.7 Hz, 2 H) 4.94 (tq, *J*=6.3, 6.3 Hz, 1 H). ^{13}C-RMN ($CDCl_3$), δ: 173.7 (*C*=O), 69.9 (O-*C*H), 44.9 (CH_2-*C*H_2Cl), 34.9 (*C*$H_{2\ (\alpha)}$ (C=O)), 33.5 (O-CH-*C*H_2), 32.1 (*C*H_2-CH_2-CH_3), 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3 (*C*H_2), 28.8 (O-CH-CH_2-*C*H_2), 26.2, 25.6 (*C*$H_{2\ (\beta)}$ (C=O)), 22.9 (*C*H_2-CH_3), 20.3 (O-CH-*C*H_3), 14.3 (*C*H_3)**.** *A Regioisomer:* ^{1}H NMR ($CDCl_3$) δ: 1.53 (d, *J*=6.6 Hz, 3 H) 2.27 (t, *J*=7.3 Hz, 2 H) 4.00-4.15 (m, 3 H) 1.57-1.88 (m, 6 H). ^{13}C-RMN ($CDCl_3$), δ: 174.1 (*C*=O), 63.8 (O-*C*H_2), 58.3 (CH_2-*C*HCl), 36.9 (O-CH_2-CH_2-*C*H_2), 25.2 (O-CH_2-*C*H_2), 25.3 (CH_2-CHCl*C*H_3). All other NMR signals are hidden by the signals of B.