Halloysite catalyzed esterification of bio-mass derived acids

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Supporting Information

Halloysite clay was purchased from Sigma Aldrich (Source: Applied Minerals, Inc. Dragon Mine, Utah USA) and was used without modification. All other chemicals were purchased from Alfa Aesar, Sigma Aldrich and VWR. All chemicals were used as received without further purification or modification. Reaction mixtures were filtered prior to work-up using Fisherbrand™ filter paper, P2-grade [Porosity: Fine (particle retention: 1-5 µm)]. ^{1}H NMR spectra were recorded at r.t. in DMSO-d_6 or $CDCl_3$ on a Bruker 400 MHz instrument operating at a frequency of 300 MHz for ^{1}H NMR. ^{1}H chemical shifts were referenced to the DMSO solvent signal (2.50 ppm) or the $CHCl_3$ solvent signal (7.26 ppm).

All the products are known compounds. ^{1}H NMR are shown below for each entry to illustrate the purity of the sample. ^{1}H NMR spectra were identical to spectra in the Spectral Database for organic compounds. SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 8/18/2019)

Figure S1. methyl levulinate [624-45-3]

^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.55 (s, 3H), 2.70 (t, J = 6.0 Hz, 2H), 2.42 (t, J = 6.0 Hz, 2H) 2.08 (s, 3H).

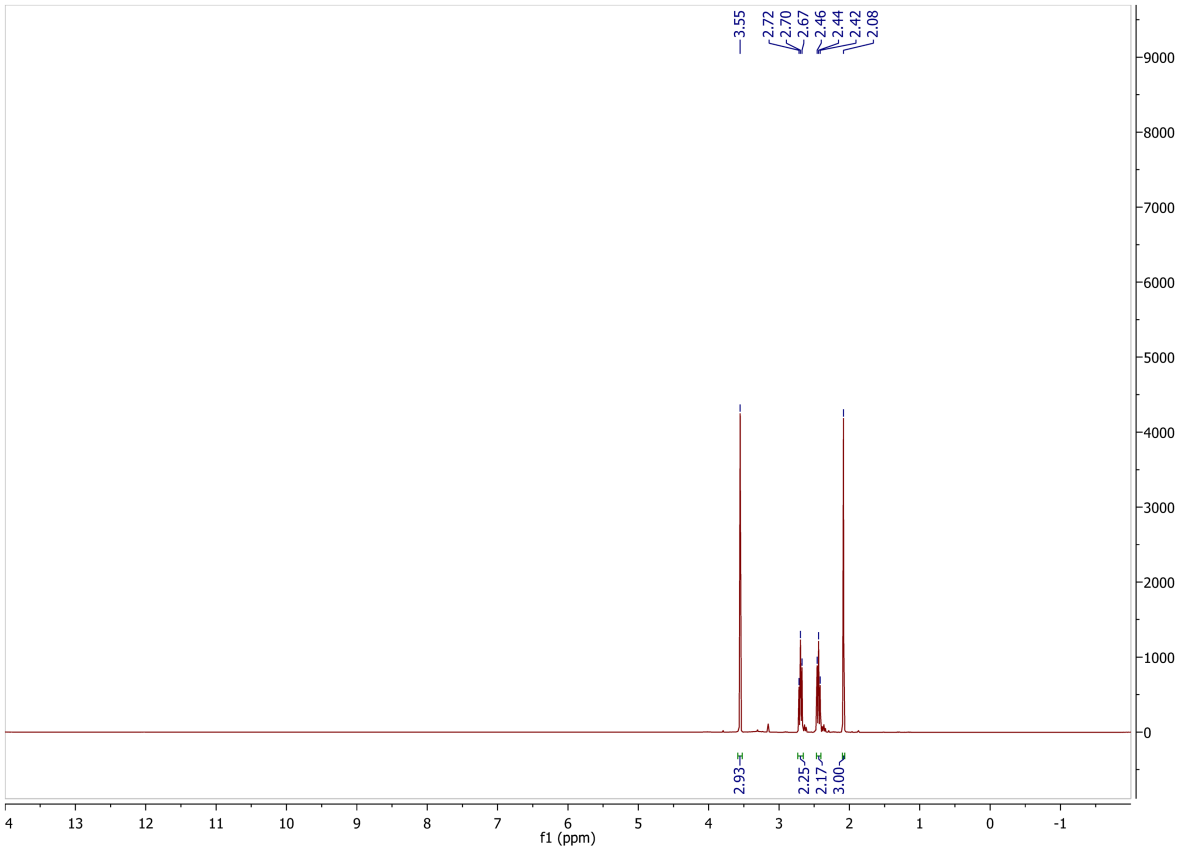

Figure S2. ethyl levulinate [539-88-8]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.12 (q, J = 6.6 Hz, 2H), 2.74 (t, J = 6.6 Hz, 2H), 2.54 (t, J = 6.6 Hz, 2H) 2.19 (s, 3H), 1.25 (t, J = 6.6 Hz, 3H).

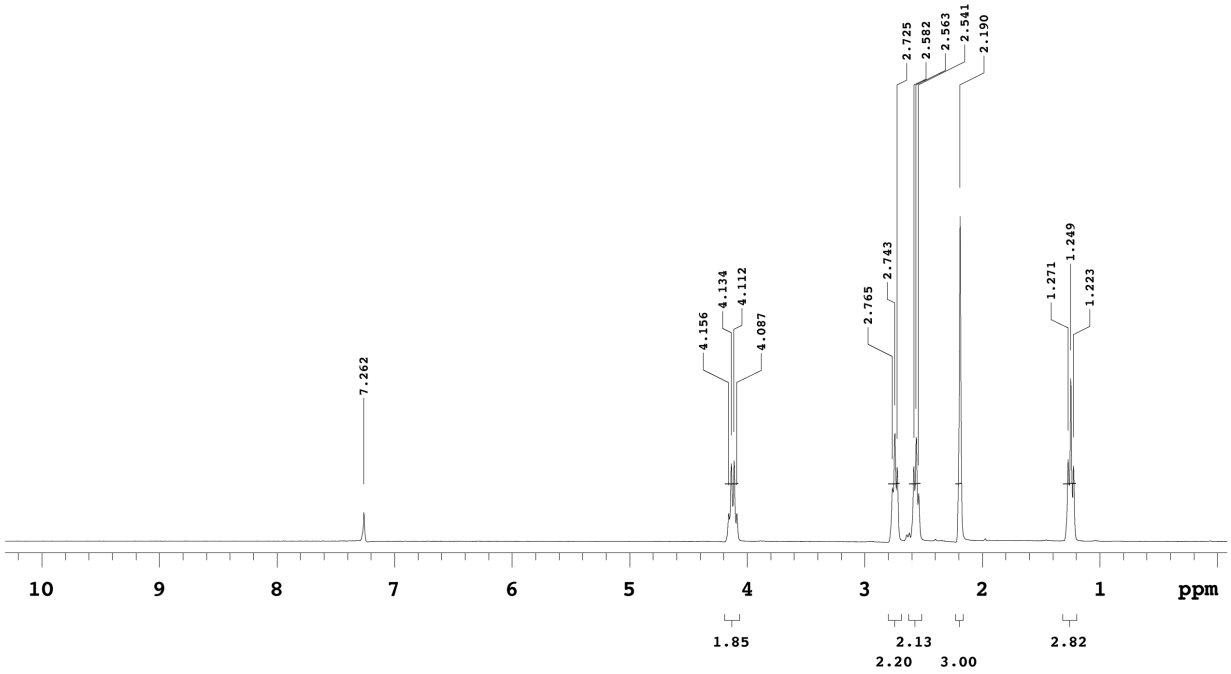

Figure S3. n-propyl levulinate [645-67-0]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.03 (t, J = 6.6 Hz, 2H), 2.76 (t, J = 6.6 Hz, 2H), 2.57 (t, J = 6.6 Hz, 2H) 2.19 (s, 3H), 1.63 (m, 2H), 0.93 (t, J = 6.6 Hz, 3H).

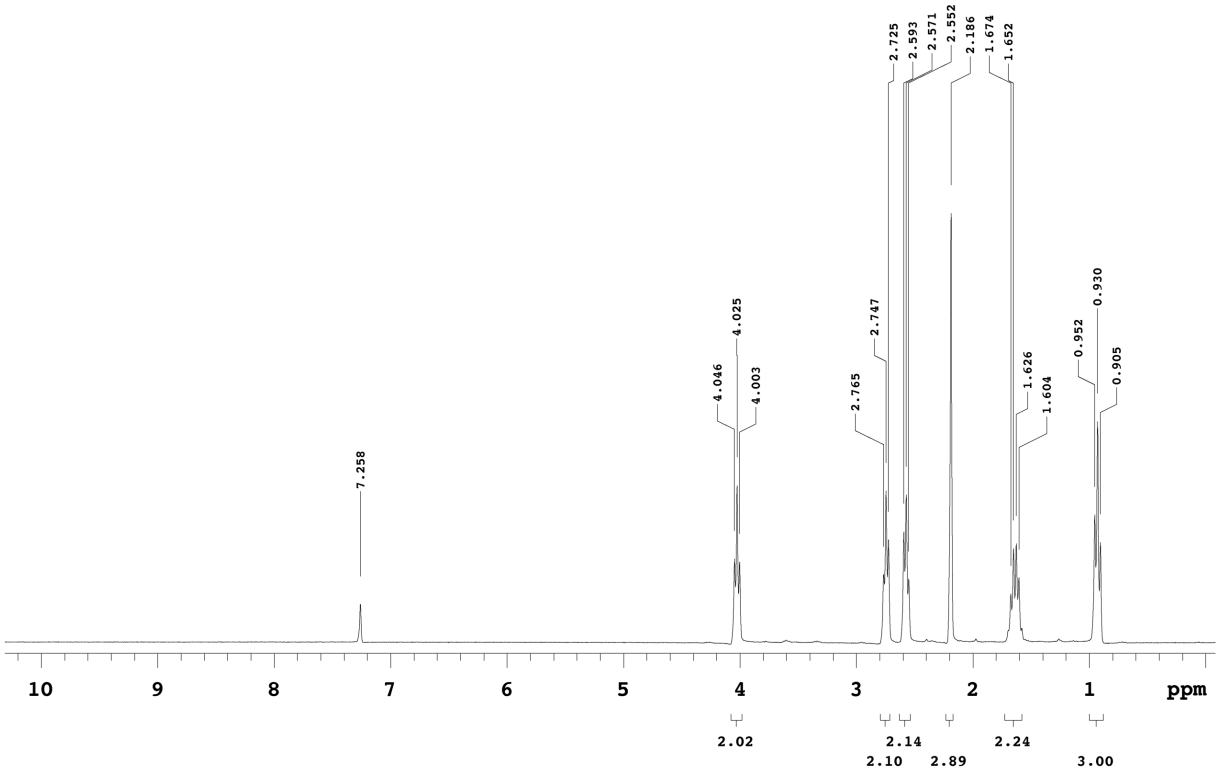

Figure S4. n-butyl levulinate [2052-15-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.07 (t, J = 6.6 Hz, 2H), 2.74 (t, J = 6.6 Hz, 2H), 2.56 (t, J = 6.6 Hz, 2H) 2.19 (s, 3H), 1.60 (m, 2H), 1.36 (m, 2H), 0.92 (t, J = 6.6 Hz, 3H).

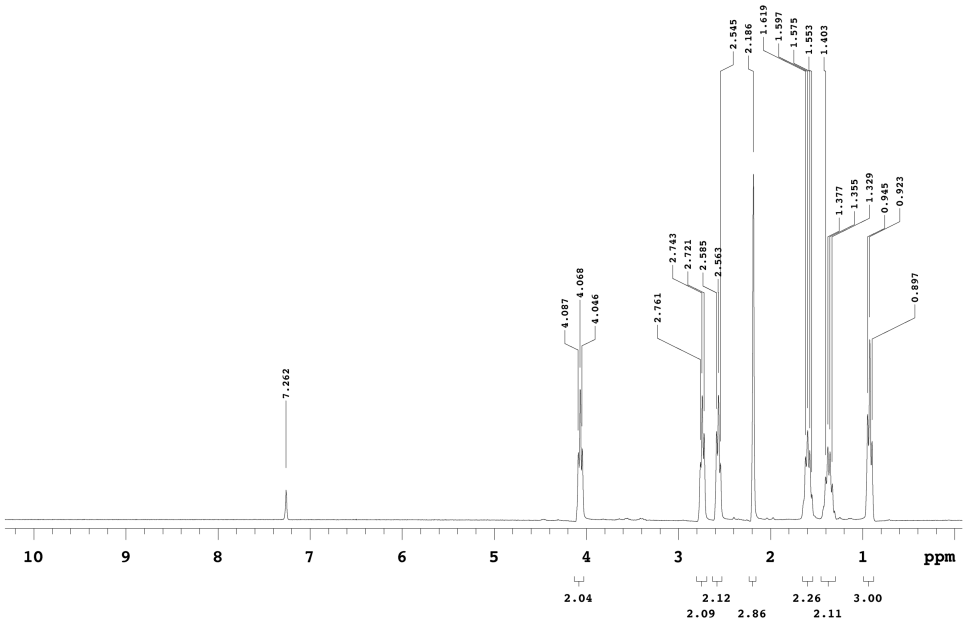

Figure S5. dimethyl succinate [106-65-0]
^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.49 (s, 6H), 2.63 (s, 4H).

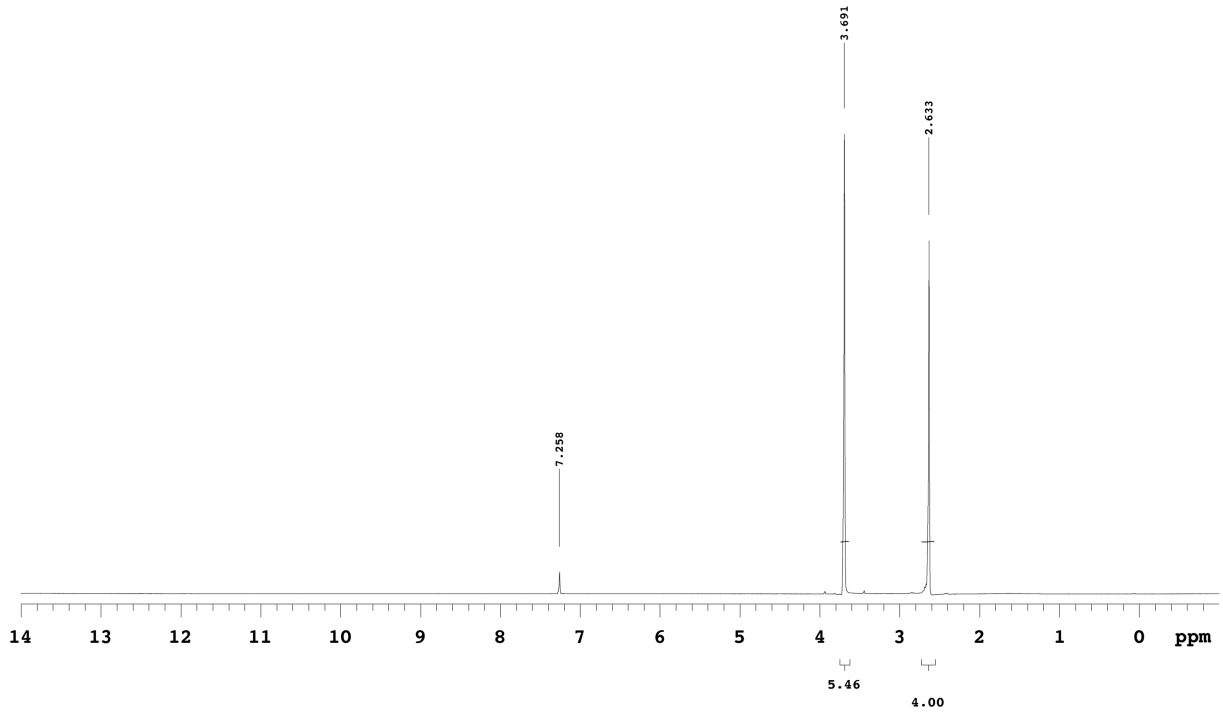

Figure S6. diethyl succinate [123-25-1]
^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.14 (q, J = 6.6 Hz, 4H), 2.62 (s, 4H), 1.25 (t J = 6.6 Hz, 6H).

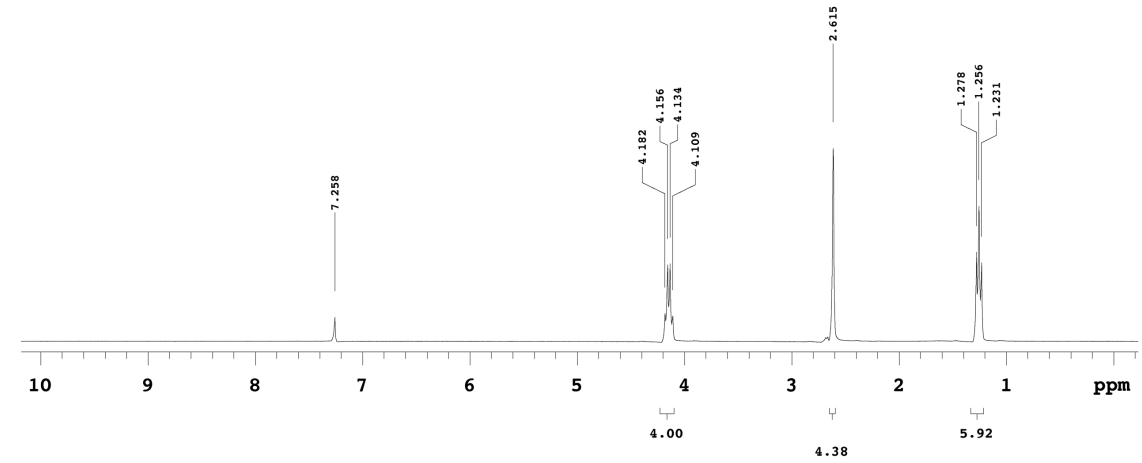

Figure S7. di-*n*-propyl succinate [925-15-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.05 (t, J = 6.6 Hz, 4H), 2.63 (s, 4H), 1.65 (m, 4H), 0.93 (t, J = 7.8 Hz, 6H).

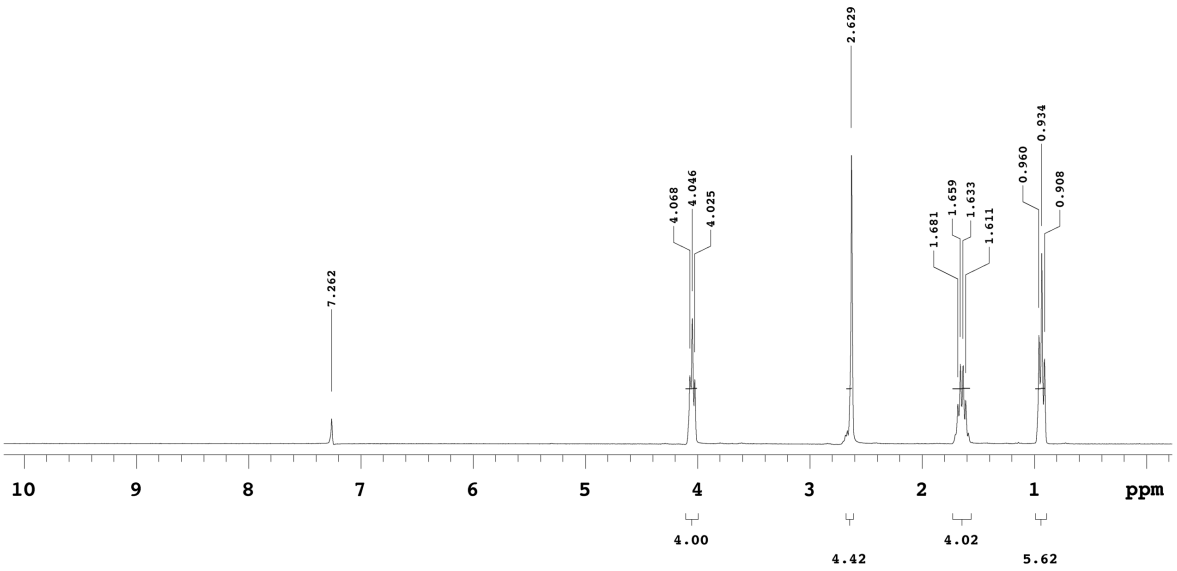

Figure S8. di-n-butyl succinate [141-03-7]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.09 (t, J = 6.6 Hz, 4H), 2.62 (s, 4H), 1.60 (m, 4H), 1.37 (m 4H), 0.93 (t, J = 7.8 Hz, 6H).

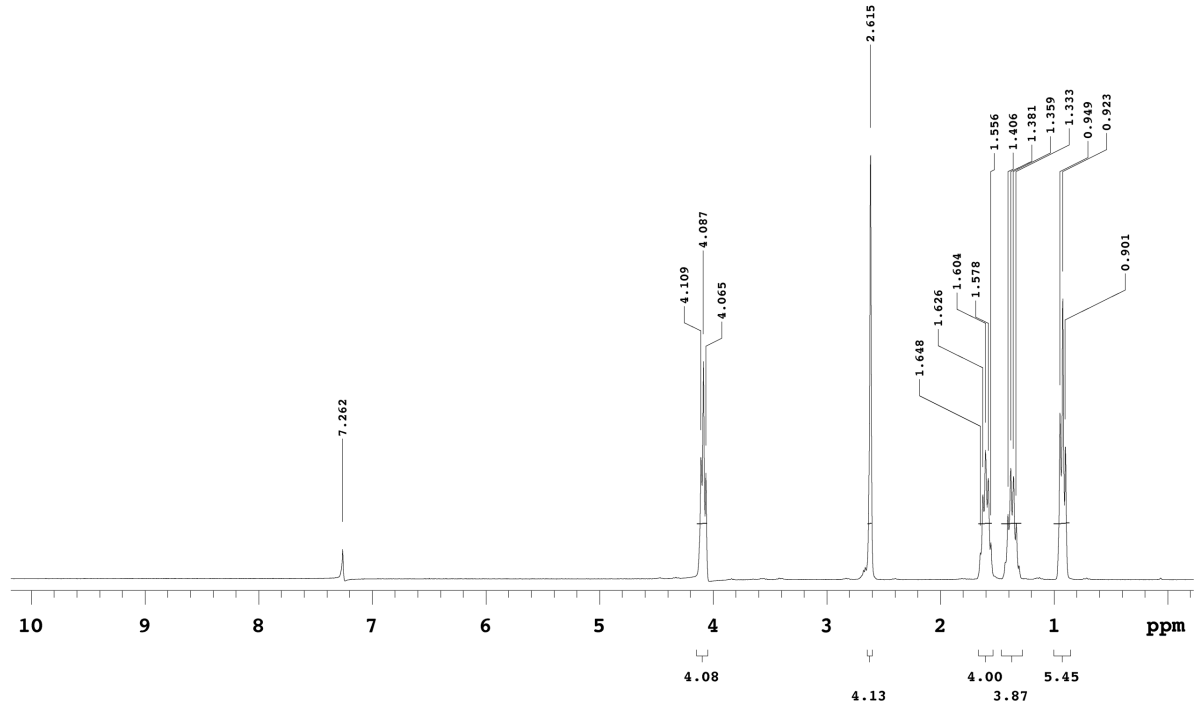

Figure S9. dimethyl fumarate [624-49-7]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.86 (s, 2H), 3.81 (s, 6H).

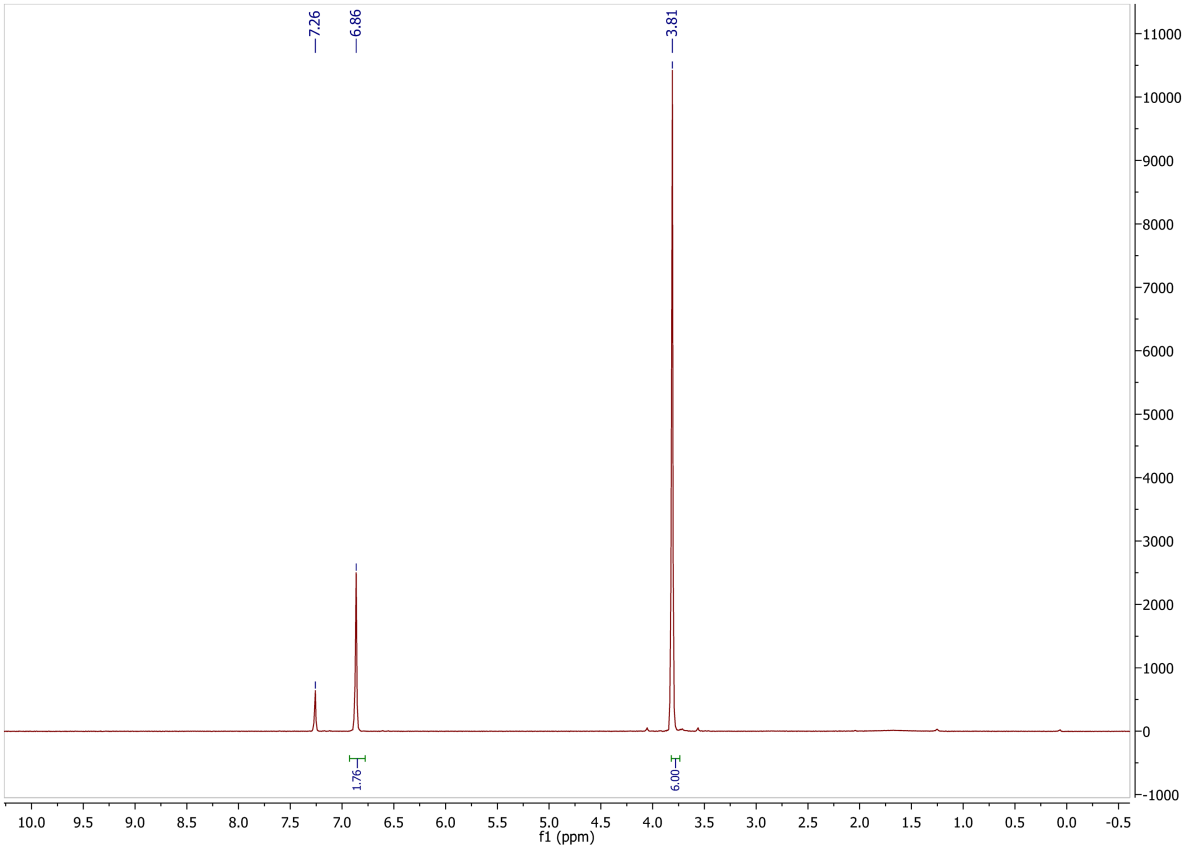

Figure S10. diethyl fumarate [623-91-6]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.85 (s, 2H), 4.26 (q, J = 6.0 Hz, 4H), 1.31 (t, J = 6.0 Hz, 6H).

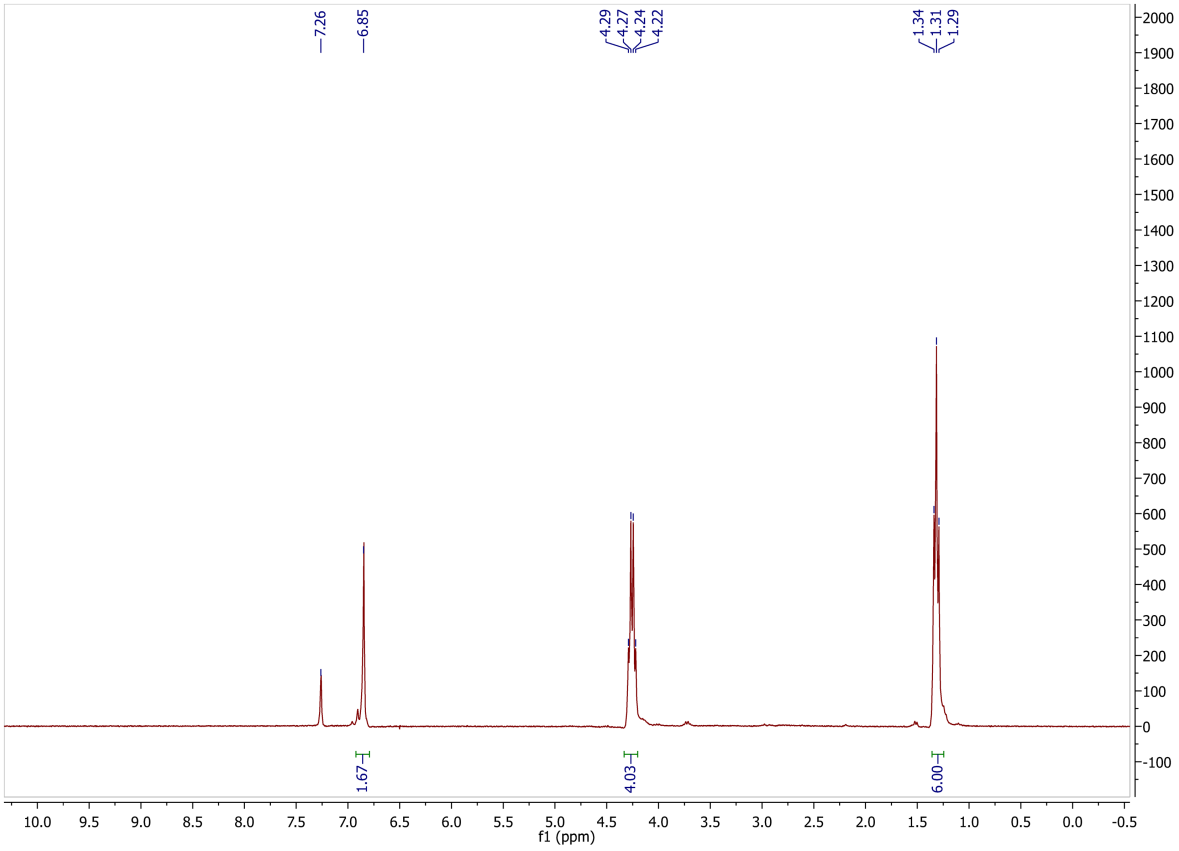

Figure S11. di-*n*-propyl fumarate [14595-35-8]
^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.86 (s, 2H), 4.16 (t, J = 6.6 Hz, 4H), 1.70 (m, 4H), 0.98 (t, J = 6.6 Hz, 6H).

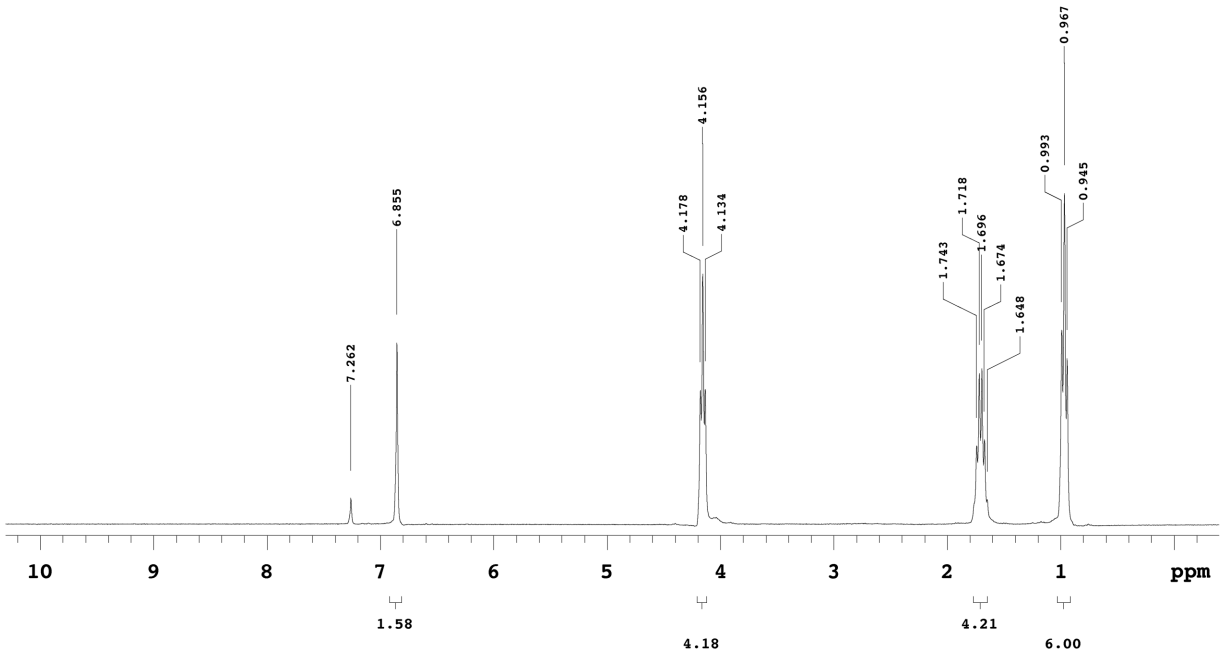

Figure S12. di-n-butyl fumarate [105-75-9]
^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.84 (s, 2H), 4.20 (t, J = 6.6 Hz, 4H), 1.67 (m, 4H), 1.42 (m, 4H), 0.97 (t, J = 6.6 Hz, 6H). Identical to ^{1}H NMR reported in the literature.[1]

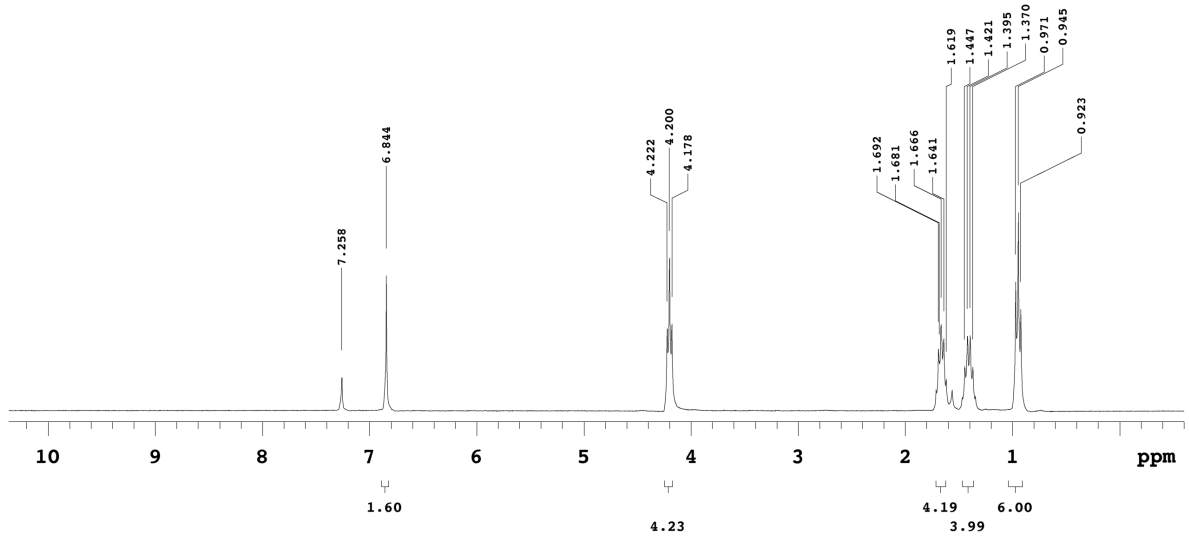

Figure S13. dimethyl maleate [624-48-6]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.86 (s, 2H), 3.81 (s, 6H).

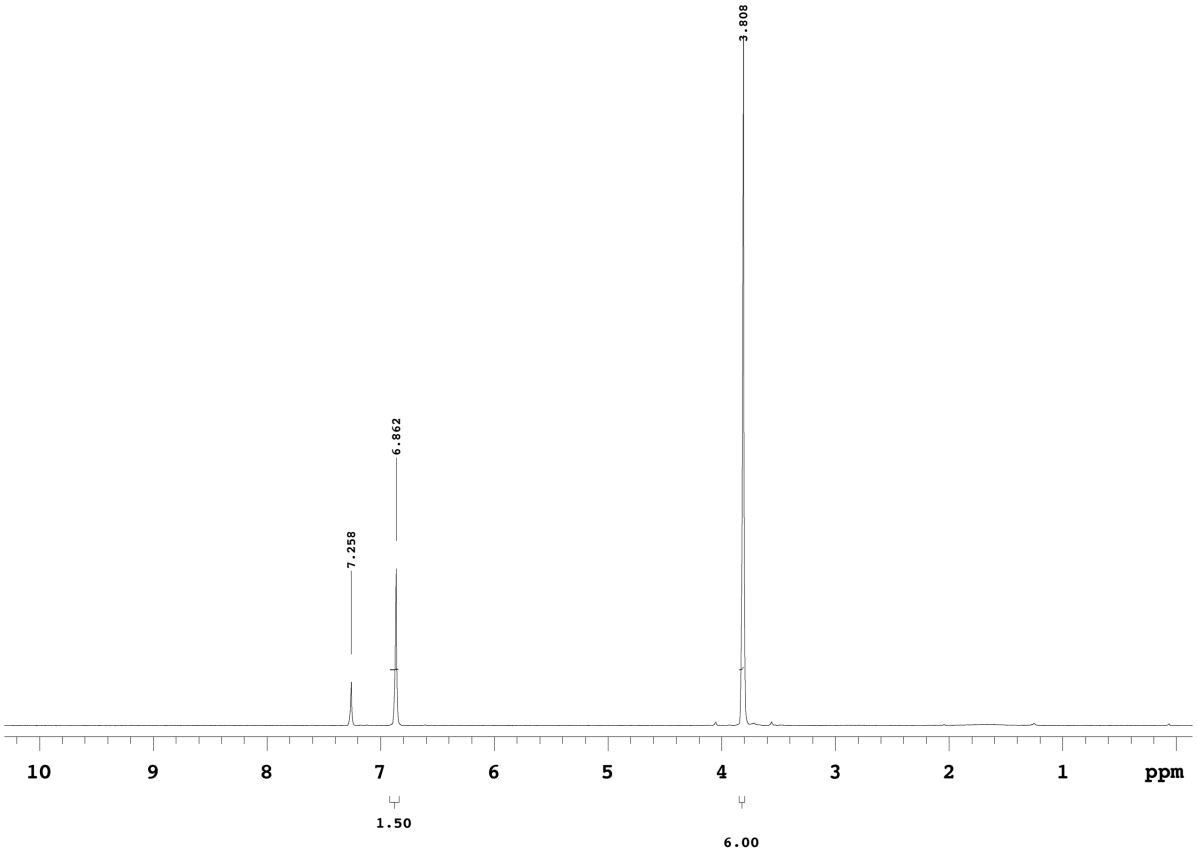

Figure S14. diethyl maleate [141-05-9]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.22 (s, 2H), 4.25 (q, J = 6.6 Hz, 4H), 1.30 (t, J = 6.6 Hz, 6H).

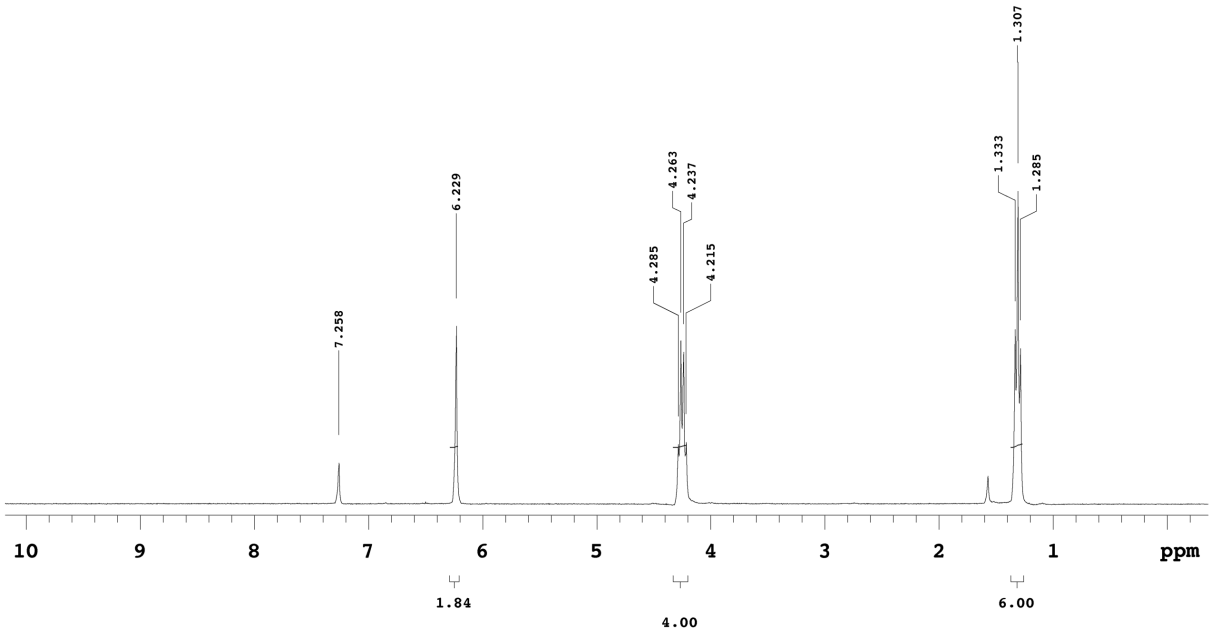

Figure S15. di-*n*-propyl maleate [2432-63-5]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.23 (s, 2H), 4.14 (t, J = 6.6 Hz, 4H), 1.69 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H).

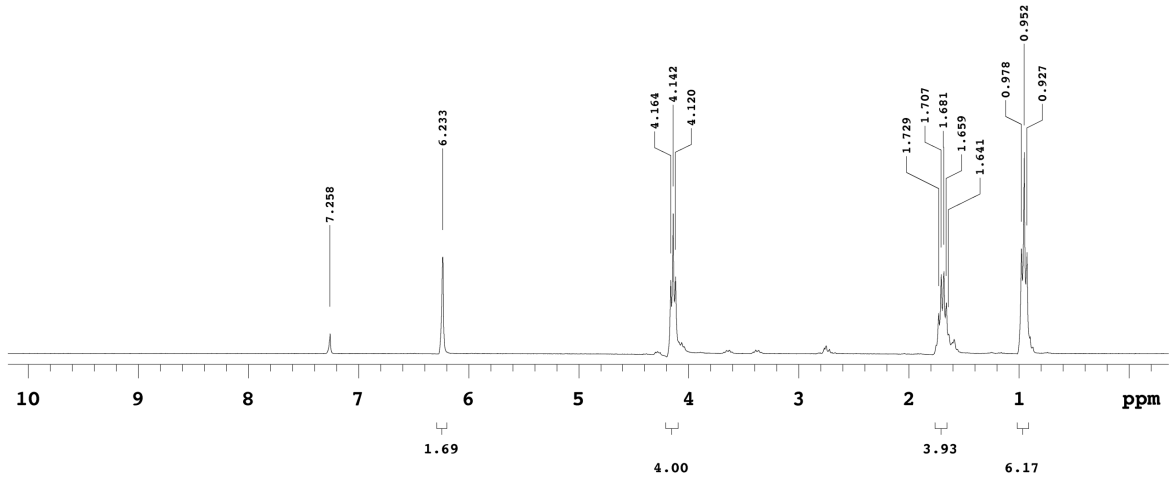

Figure S16. di-n-butyl maleate [105-75-0]

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.23 (s, 2H), 4.19 (t, J = 6.6 Hz, 4H), 1.65 (m, 4H), 1.39 (m, 4H), 0.94 (t, J = 6.6 Hz, 6H).