Supporting information for publication

Sulfonated graphene as highly efficient and reusable acid carbocatalyst for the synthesis of ester plasticizers

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Contents:

Tributyl citrate (TBC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 4.58 (*bs*, 1H, -OH), 4.02 (*t*, 2H), 3.96 (*t*, 4H), 2.84(*d*, 2H, *J* = 15.2 Hz, -CH_2), 2.70 (*d*, 2H, *J* = 15.3 Hz, -CH_2), 1.48-1.54 (*m*, 6H), 1.26-1.37 (*m*, 6H), and 0.85(*t*, 9H); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 172.50, 169.27 (C=O), 72.91 (C), 64.53, 63.78 (-O-CH_2), 43.05, 34.74, 30.14, 18.62 (-CH_2), and 13.51 (-CH_3).

Triethyl citrate (TEC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 6.01 (*bs*, 1H, -OH), 4.09 (*t*, 2H), 3.99 (*t*, 4H), 2.80 (*d*, 2H, *J* = 15.2 Hz, -CH_2), 2.66 (*d*, 2H, *J* = 15.2 Hz, -CH_2), and 1.11 (*t*, 9H); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 173.02, 169.75 (C=O), 73.40 (C), 61.24, 60.49 (-O-CH_2), 43.38 (-CH_2), and 14.14 (-CH_3).

Trimethyl citrate (TMC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 5.88 (*bs*, 1H, -OH), 3.76 (*s*, 3H, -OCH_3), 3.65 (*s*, 3H, -OCH_3), 2.78 (*d*, 2H, *J* = 15.3 Hz, -CH_2), and 2.91 (*d*, 2H, *J* = 15.3 Hz, -CH_2); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 175.52, 170.05 (C=O), 73.39 (C), 55.02, 53.50 (-OCH_3), and 43.40 (-CH_3).

Tri-n-octyl citrate (TOC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 4.04 (*t*, 2H), 3.96 (*t*, 4H), 2.81 (*d*, 2H, *J* = 15.6 Hz, -CH_2), 2.70 (*d*, 2H, *J* = 15.6 Hz, -CH_2), 1.46-1.51 (*m*, 12H), 1.29 (*br*, 24H), and 0.85 (*t*, 9H); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 174.25, 172.44 (C=O), 72.46 (C), 64.75, 60.79 (-O-CH_2), 42.67, 32.56, 31.31, 28.05, 27.94, 25.25, 25.07, 22.22 (-CH_2), and 13.77 (-CH_3).

Tri-n-hexyl citrate (THC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 4.01 (*t*, 2H), 3.95 (*t*, 4H), 2.83 (*d*, 2H, *J* = 15.5 Hz, -CH_2), 2.69 (*d*, 2H, *J* = 15.6 Hz, -CH_2), 1.50-1.55 (*m*, 6H), 1.24 (*br*, 18H), and 0.84 (*t*, 9H); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 172.44, 169.41 (C=O), 72.86 (C), 64.76, 64.03 (-O-CH_2), 43.01, 32.56, 30.96, 28.06, 25.08, 22.05 (-CH_2), and 13.77 (-CH_3).

Triisobutyl citrate (TIBC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 5.11 (*bs*, 1H, -OH), 3.8 (*d*, 2H, *J* = 6.4 Hz, -O-CH_2), 3.7 (*d*, 4H, *J* = 6.4 Hz, -O-CH_2), 2.87 (*d*, 2H, *J* = 15.2 Hz, -CH_2), 2.76 (*d*, 2H, *J* = 15.1 Hz, -CH_2), 1.79-1.87 (*m*, 2H, -CH-), 1.56-1.61 (*m*, 1H, -CH-), 0.84 (*d*, 12H, *J* = 6.6 Hz, -CH_3), and 0.79 (*d*, 6H, *J* = 6.6 Hz, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 172.74, 169.61 (C=O), 73.20 (C), 71.13, 70.31 (-O-CH_2), 43.05 (-CH_2), 30.74, 27.53 (-CH-), 19.22 and 19.00 (-CH_3).

Triisopropyl citrate (TIPC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 4.88-4.91 (*m*, 1H, -O-CH-), 4.81-4.85 (*m*, 2H, -O-CH-), 2.85 (*d*, 2H, *J* = 15.5 Hz, -CH_2), 2.79 (*d*, 2H, *J* = 15.5 Hz, -CH_2), 1.18 (*d*, 6H, *J* = 6.4 Hz, -CH_3), and 1.14 (*d*, 12H, *J* = 6.4 Hz, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 174.64, 172.33 (C=O), 72.91 (C), 68.43, 67.40 (-O-CH-), 42.87 (-CH_2), 21.62 and 21.57 (-CH_3).

Tri-n-active amyl citrate (TAAC)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 4.32 (*bs*, 1H, -OH), 3.8 (*br*, 2H, -O-CH_2), 3.7 (*br*, 4H, -O-CH_2), 2.86 (*d*, 2H, *J* = 15.3 Hz, -CH_2), 2.74 (*d*, 2H, *J* = 15.3 Hz, -CH_2), 1.58-1.65 (*m*, 2H, -CH-), 1.35-1.39 (*m*, 6H, -CH_2-), 1.00-1.02 (*m*, 1H, -CH-), 0.83 (*t*, 9H, -CH_3), and 0.78 (*d*, 9H, *J* = 4.9 Hz, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 172.51, 169.48 (C=O), 72.95 (C), 68.51, 66.04 (-O-CH_2), 42.95, (-CH_2), 37.13, 33.69 (-CH-), 25.59 (-CH_2), 16.09 and 10.99 (-CH_3).

Dibutyl phthalate (DBP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.6 (*dd*, 2H, *J* = 8.7, 3.2 Hz), 7.5 (*dd*, 2H, *J* = 8.7, 3.2 Hz), 4.18 (*t*, 4H, -O-CH_2), 1.55-1.58 (*m*, 4H, -CH_2), 1.28-1.32 (*m*, 4H, -CH_2), 0.82 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 166.97 (C=O), 131.94 (C), 131.27, 128.63 (CH, Aromatic), 64.96 (-O-CH_2), 30.13, 18.74 (-CH_2), 13.37 (-CH_3).

Diethyl phthalate (DEP)

^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.6 (*dd*, 2H, *J* = 8.5, 2.9 Hz), 7.5 (*dd*, 2H, *J* = 8.5, 2.9 Hz), 4.27 (*t*, 4H, -O-CH_2), 1.23 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 167.09 (C=O), 132.35 (C), 131.45, 128.75 (CH, Aromatic), 61.41 (-O-CH_2), 13.87 (-CH_3).

Dimethyl phthalate (DMP)
^{1}H NMR (600 MHz, DMSO-*d6*, 298K): δ = 8.1 (*dd*, 2H, *J* = 8.6, 3.1 Hz), 7.7 (*dd*, 2H, *J* = 8.6, 3.1 Hz), 3.87 (*s*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-*d6*, 298K): δ = 168.32 (C=O), 132.87 (C), 131.97, 128.31 (CH, Aromatic), 13.81 (-OCH_3).

Di-n-octyl phthalate (DOP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.6 (*dd*, 2H, *J* = 8.8, 3.1 Hz), 7.5 (*dd*, 2H, *J* = 8.8, 3.1 Hz), 4.15 (*t*, 4H, -O-CH_2), 1.57-1.61 (*m*, 4H, -CH_2), 1.17-1.28 (*m*, 20H, -CH_2), 0.78 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 168.68 (C=O), 131.84 (C), 131.00, 128.47 (CH, Aromatic), 65.01 (-O- CH_2), 31.30, 28.77, 28.72, 28.04, 25.60, 22.11 (-CH_2), 13.61 (-CH_3).

Di-n-hexyl phthalate (DHP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.6 (*dd*, 2H, *J* = 8.6, 3.1 Hz), 7.5 (*dd*, 2H, *J* = 8.6, 3.1 Hz), 4.13 (*t*, 4H, -O-CH_2), 1.50-1.55 (*m*, 4H, -CH_2), 1.15-1.18 (*m*, 12H, -CH_2), 0.79 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 168.69 (C=O), 131.97 (C), 131.65, 128.32 (CH, Aromatic), 64.89 (-O-CH_2), 31.38, 28.89, 25.60, 22.03 (-CH_2), 13.70 (-CH_3).

Diisobutyl phthalate (DIBP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.7 (*dd*, 2H, *J* = 8.9, 3.2 Hz), 7.6 (*dd*, 2H, *J* = 8.9, 3.2 Hz), 3.99 (*d*, *J* = 6.6 Hz, 4H, -O-CH_2), 1.90-1.95 (*m*, 2H, -CH-), 0.88 (*d*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 166.80 (C=O), 131.87 (C), 131.22, 128.57 (CH, Aromatic), 71.02 (-O-CH_2), 27.20 (CH, Aliphatic), 18.82 (-CH_3).

Di-n-active amyl phthalate (DAAP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.7 (*dd*, 2H, *J* = 8.8, 3.0 Hz), 7.6 (*dd*, 2H, *J* = 8.8, 3.0 Hz), 4.07-4.10 (*m*, 2H, -O-CH_2), 3.99-4.02 (*m*, 2H, -O-CH_2), 1.68-1.73 (*m*, 2H, -CH), 1.37-1.43 (*m*, 4H, -CH_2), 0.88 (*d*, 6H, -CH_3), 0.84 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 166.90 (C=O), 131.96 (C), 131.27, 128.62 (CH, Aromatic), 69.59 (-O-CH_2), 37.12 (CH, Aliphatic), 25.55 (-CH_2), 16.04, 10.90 (-CH_3).

Di(2-ethylhexyl) phthalate (DEHP)
^{1}H NMR (600 MHz, DMSO-d_6, 298K): δ = 7.7 (*dd*, 2H, *J* = 8.8, 3.1 Hz), 7.5 (*dd*, 2H, *J* = 8.8, 3.1 Hz), 4.21-4.23 (*m*, 4H, -O-CH_2), 1.61-1.65 (*m*, 2H, -CH), 1.32-1.34 (*q*, 4H, -CH_2), 1.23-1.32 (*m*, 12H, -CH_2), 0.85 (*t*, 6H, -CH_3), 0.80 (*t*, 6H, -CH_3); ^{13}C NMR (150 MHz, DMSO-d_6, 298K): δ = 167.81 (C=O), 132.65 (C), 132.23, 128.32 (CH, Aromatic), 66.91 (-O-CH_2), 39.55 (CH, Aliphatic), 29.35, 28.62, 23.91, 23.05 (-CH_2), 14.22, 12.36 (-CH_3).

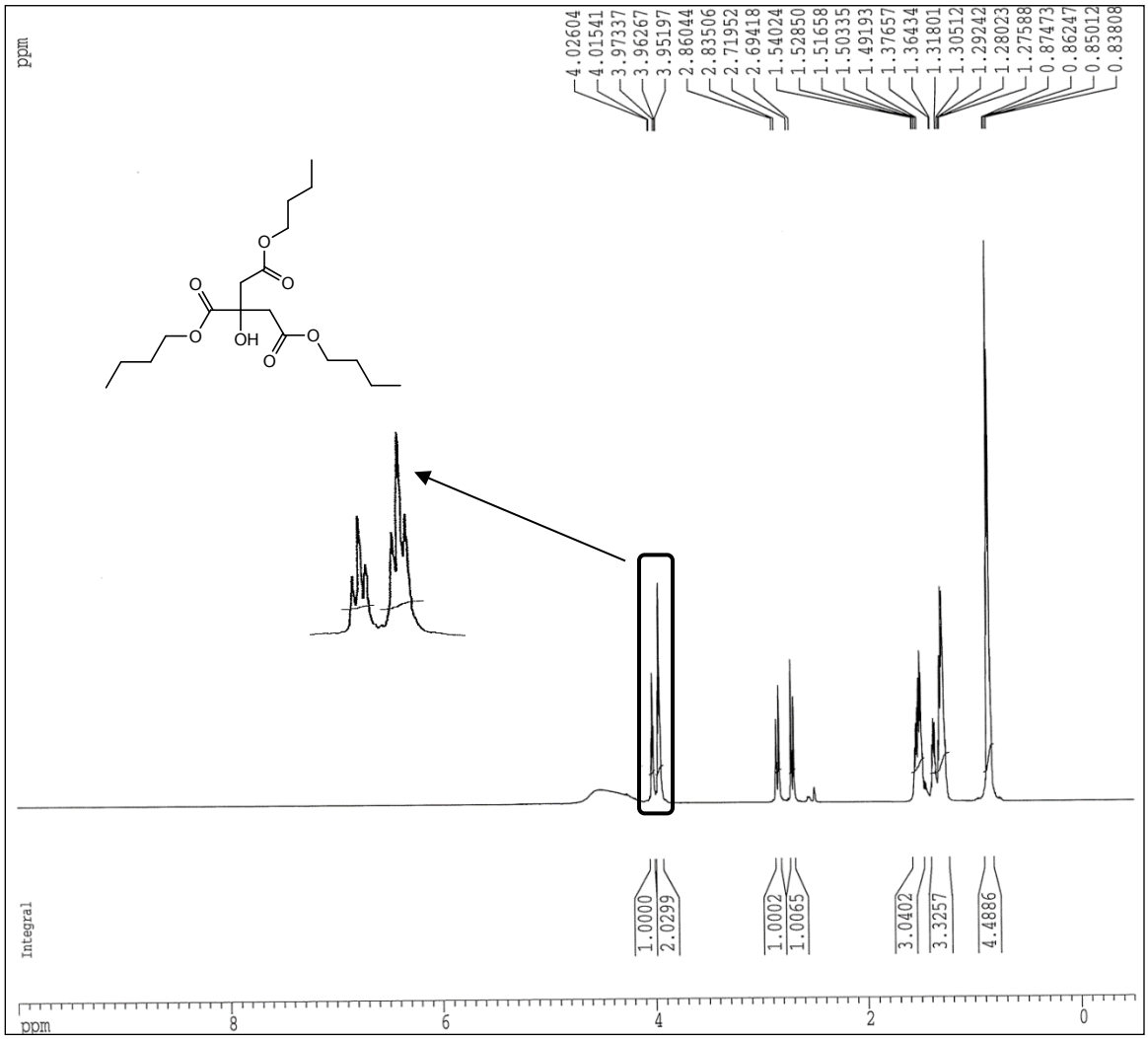

Figure S1. ^{1}H NMR spectrum of tributyl citrate (TBC)

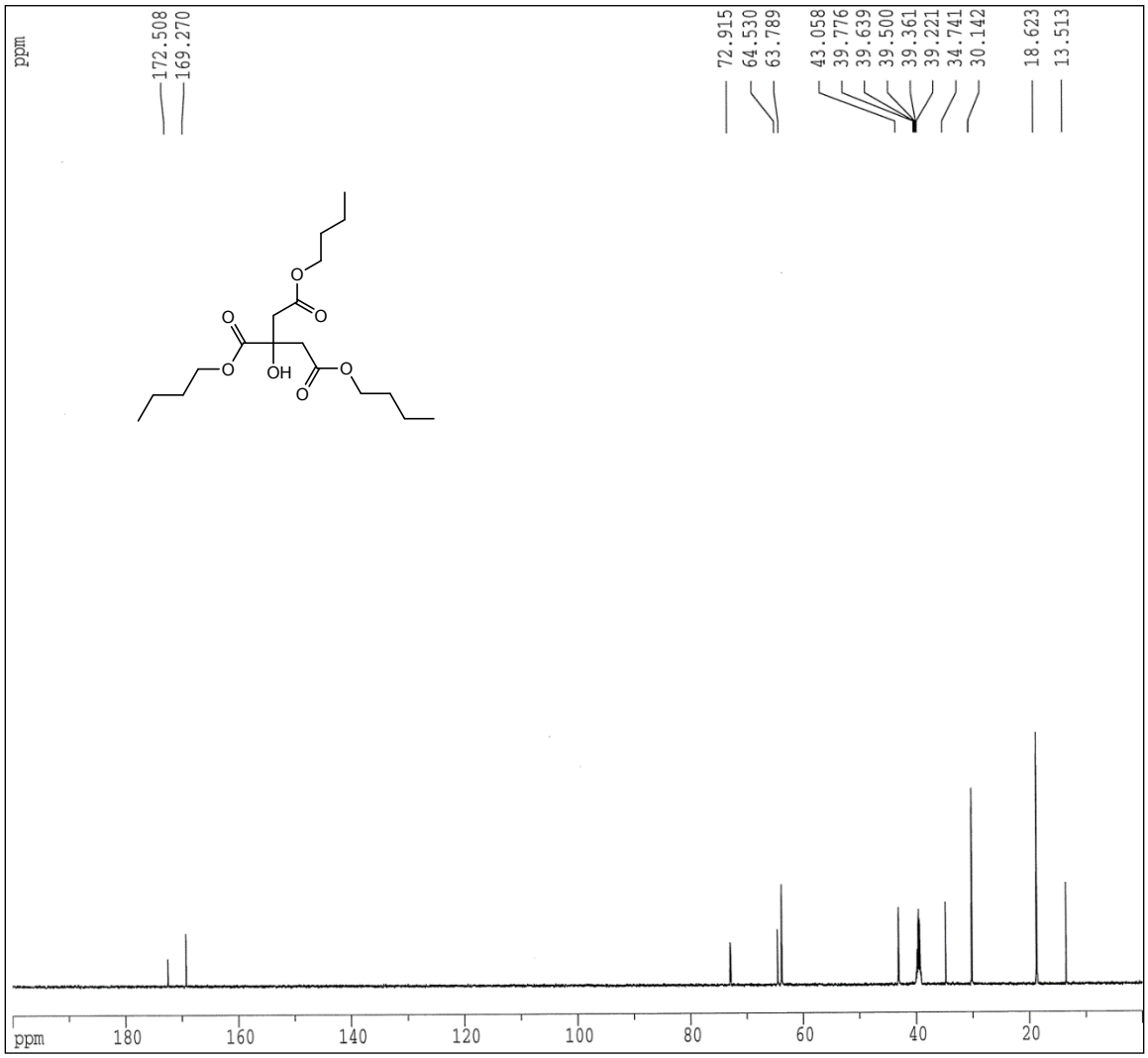

Figure S2. ^{13}C NMR spectrum of tributyl citrate (TBC)

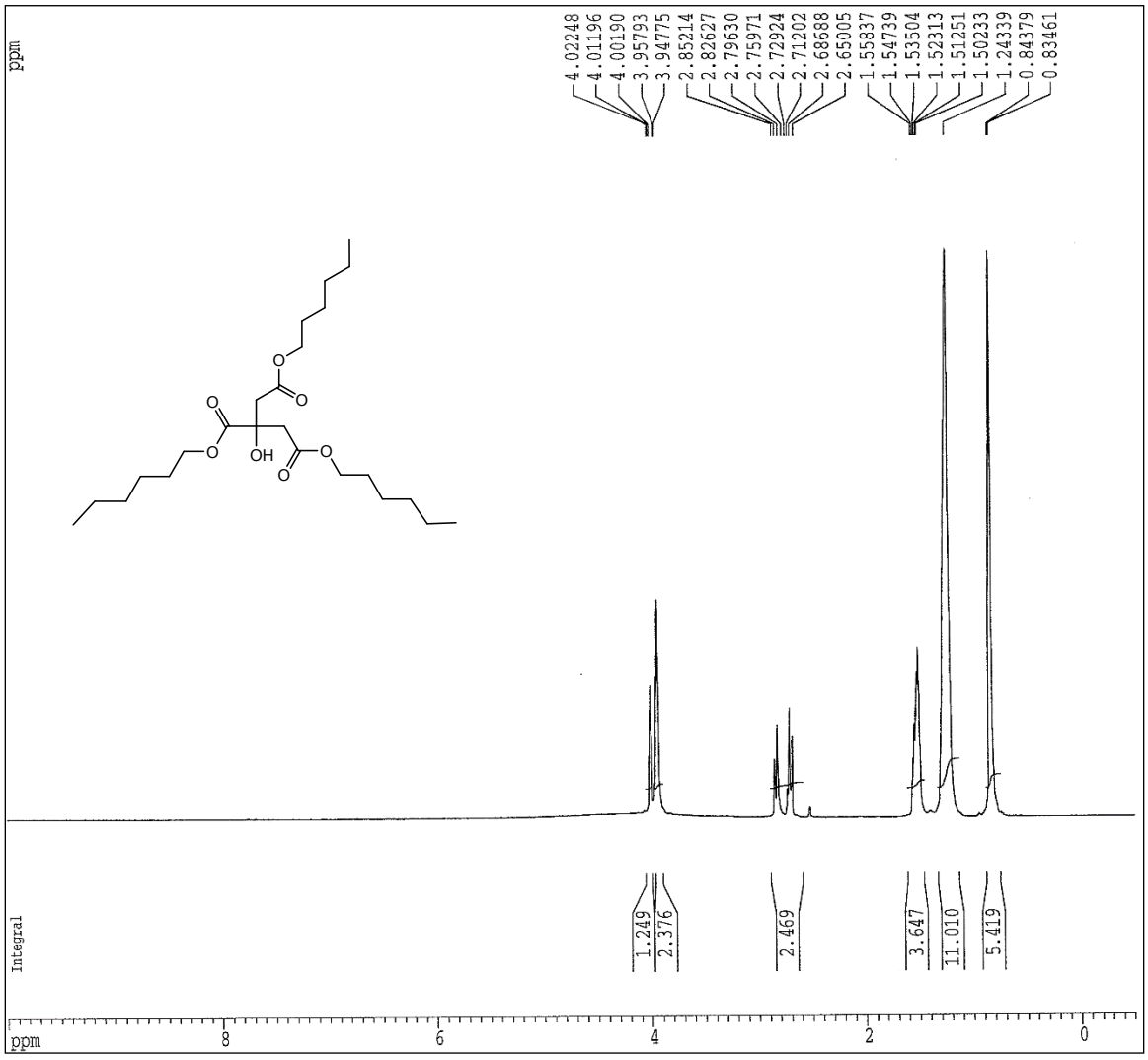

Figure S3. ^{1}H NMR spectrum of trihexyl citrate (THC)

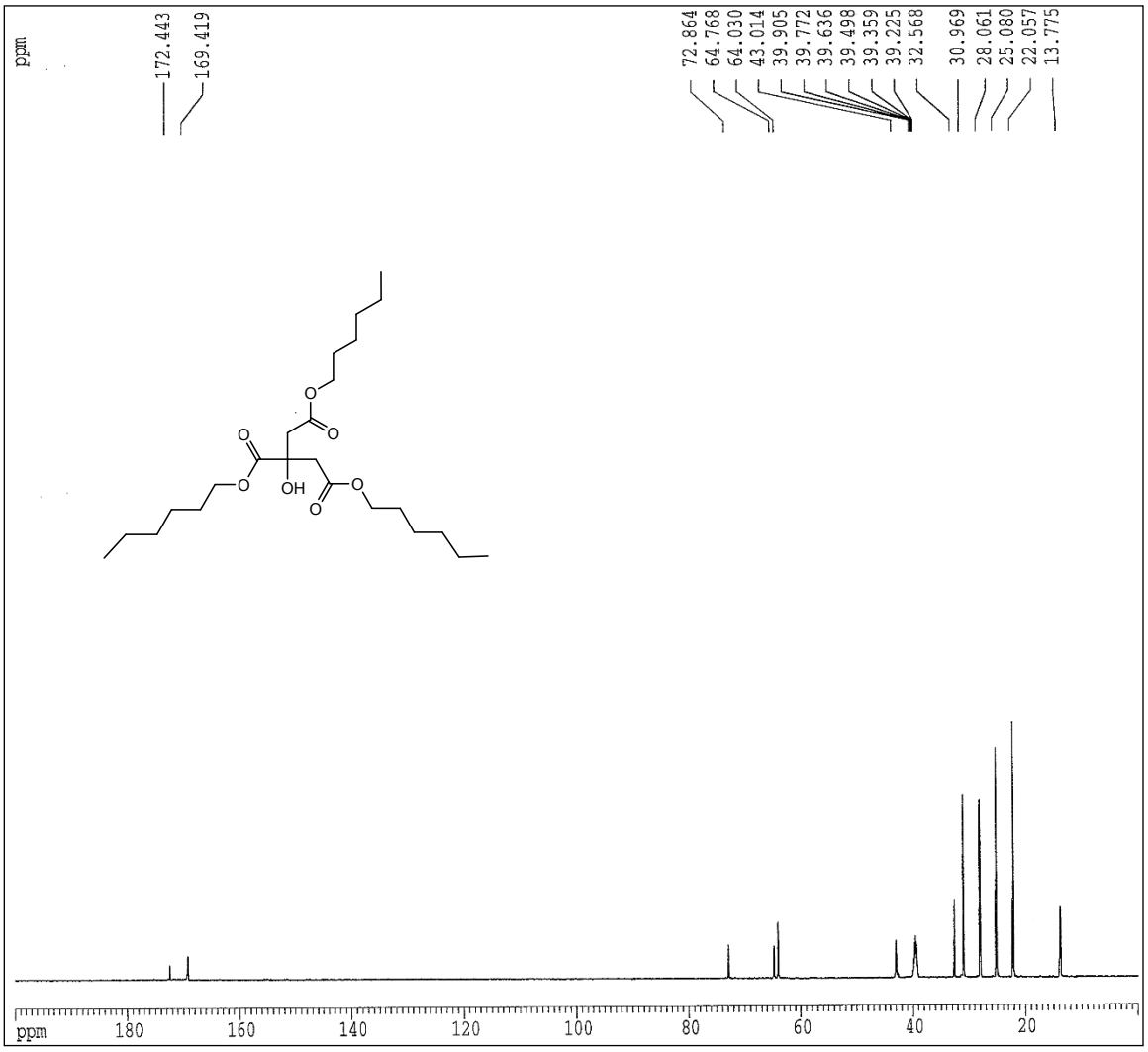

Figure S4. ^{13}C NMR spectrum of trihexyl citrate (THC)

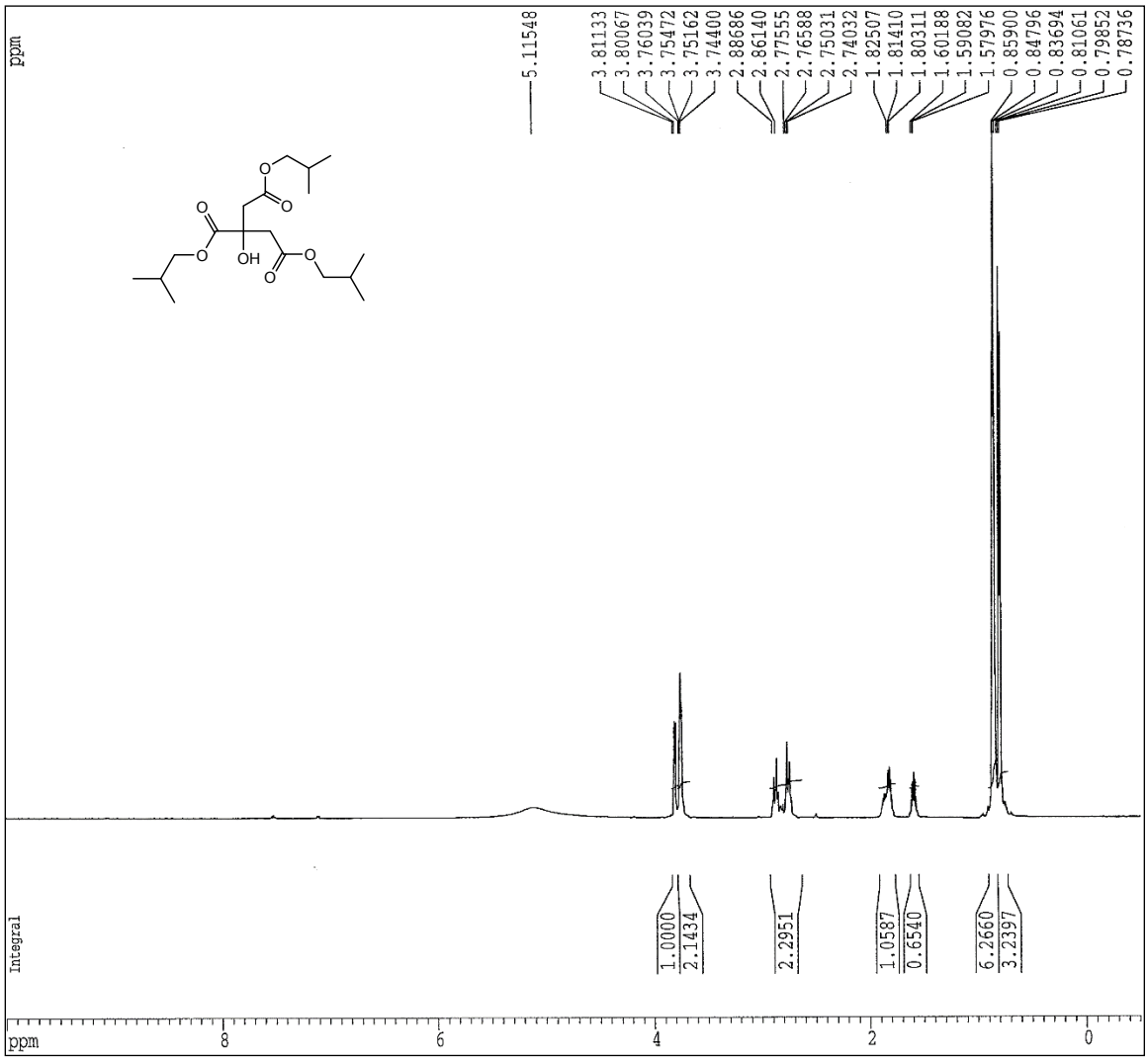

Figure S5. ^{1}H NMR spectrum of triisobutyl citrate (TIBC)

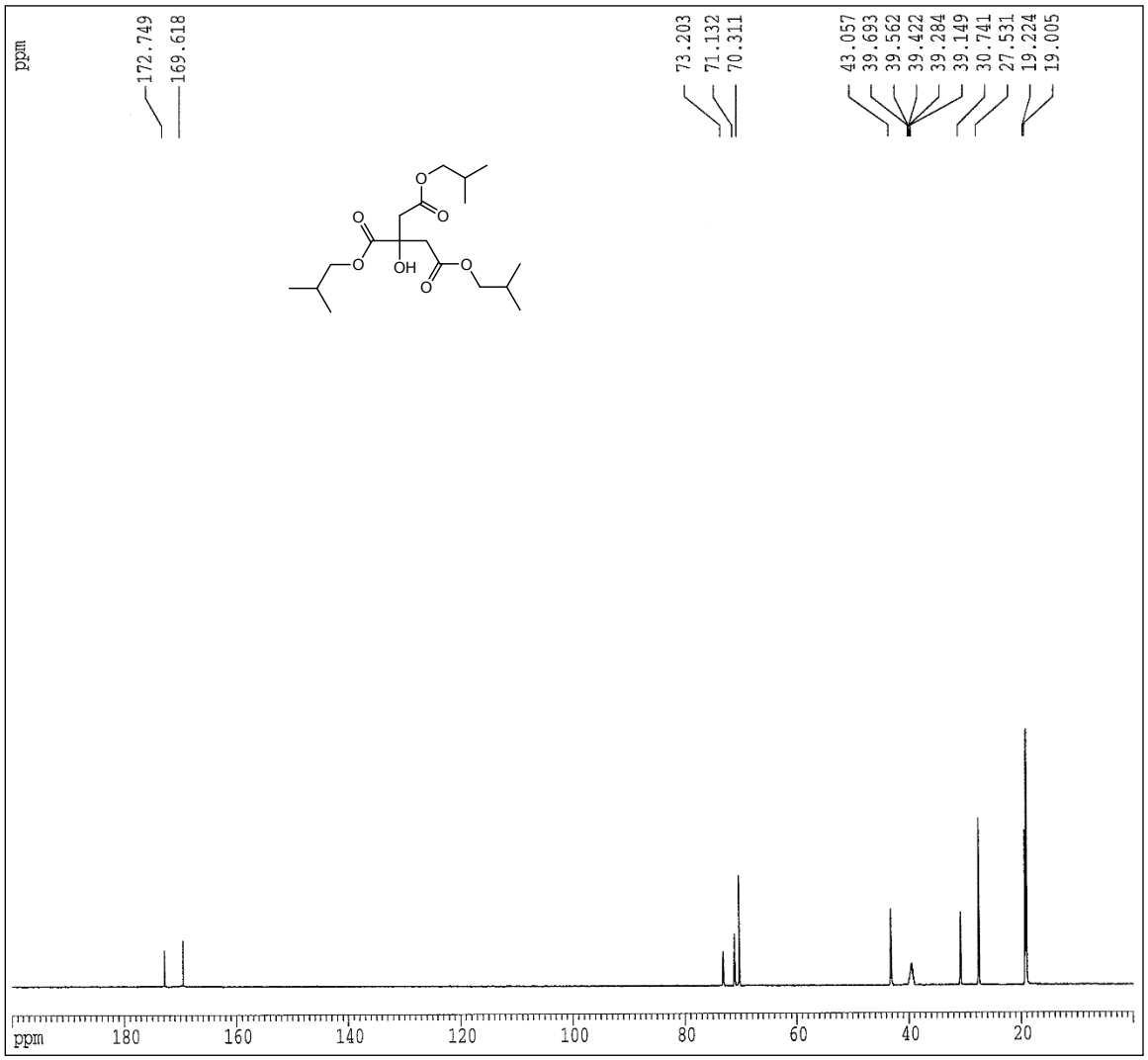

Figure S6. ^{13}C NMR spectrum of triisobutyl citrate (TIBC)

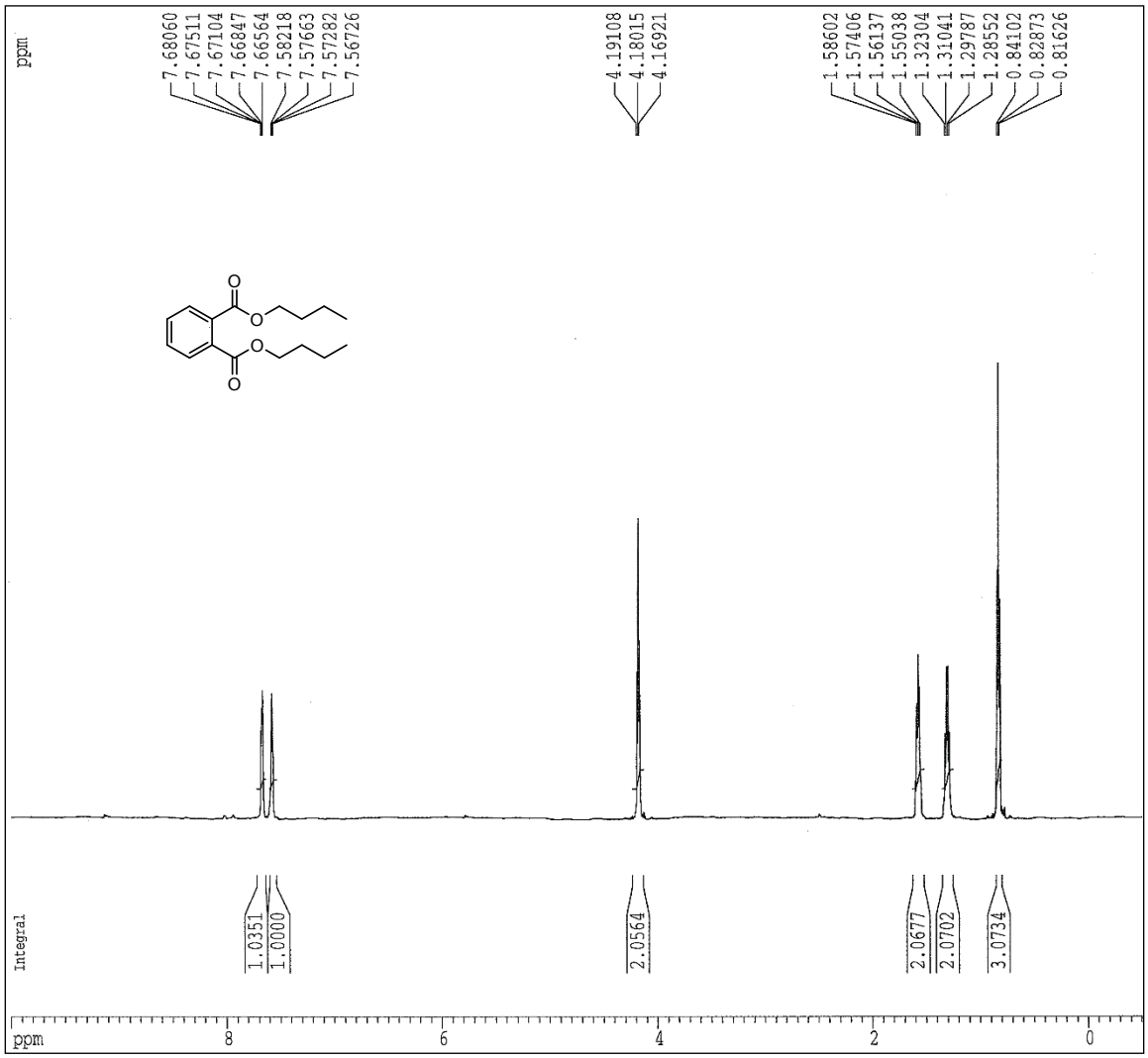

Figure S7. ^{1}H NMR spectrum of dibutyl phthalate (DBP)

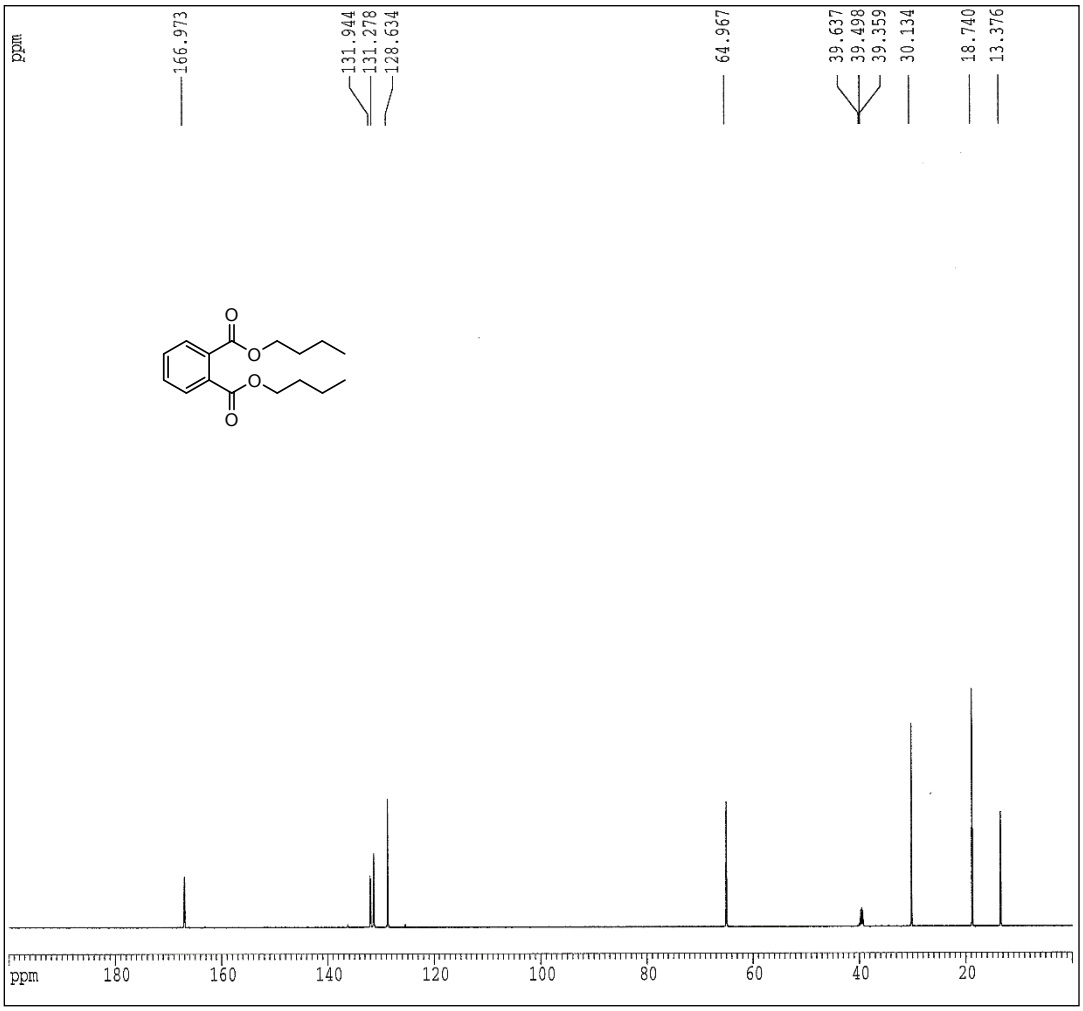

Figure S8. ^{13}C NMR spectrum of dibutyl phthalate (DBP)

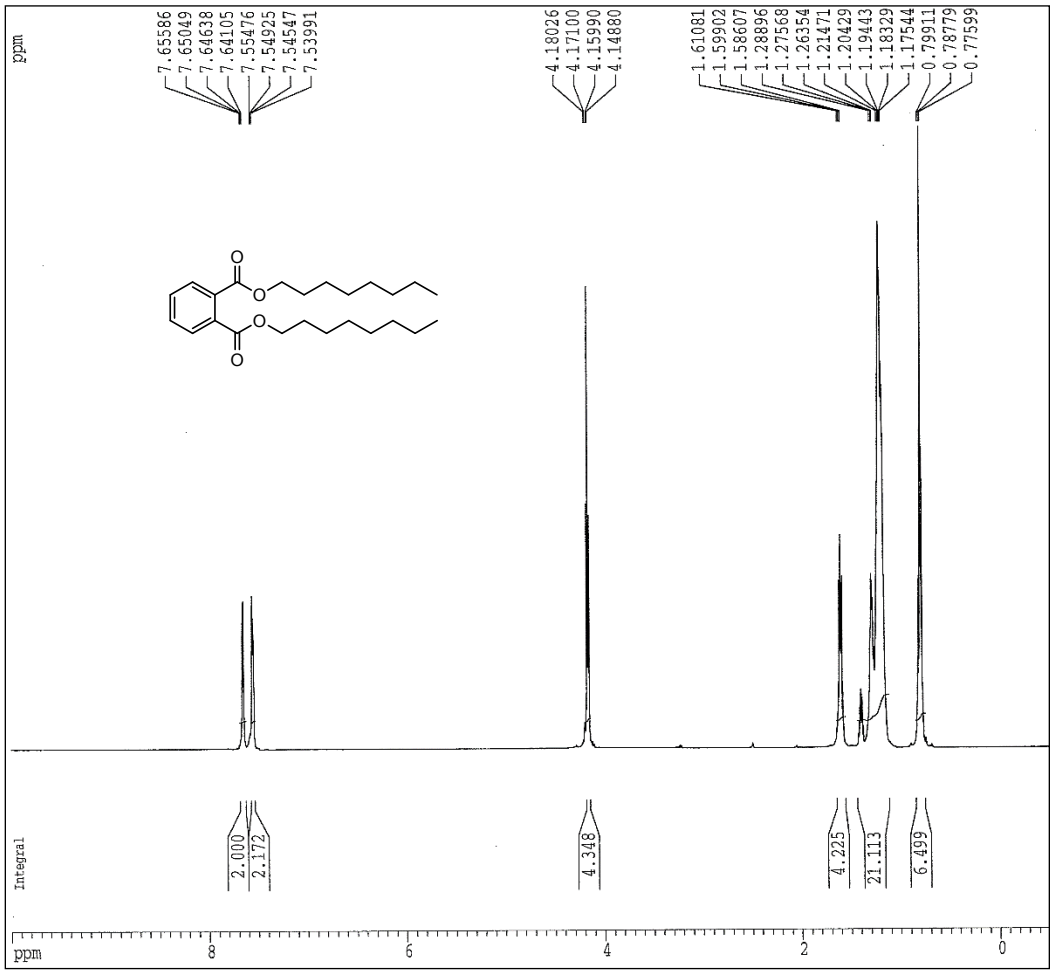

Figure S9. ^{1}H NMR spectrum of dioctyl phthalate (DOP)

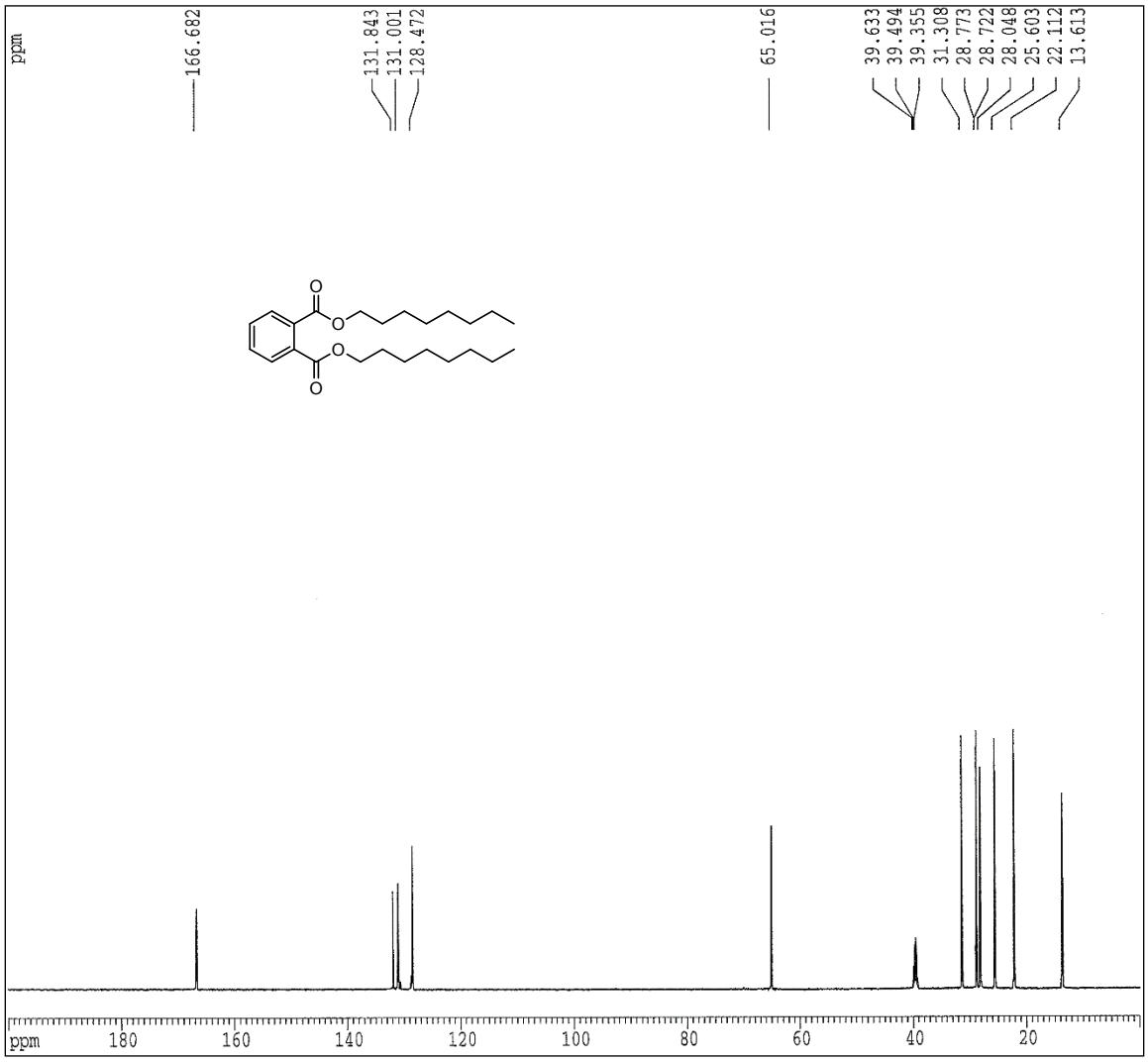

Figure S10. ^{13}C NMR spectrum of dioctyl phthalate (DOP)

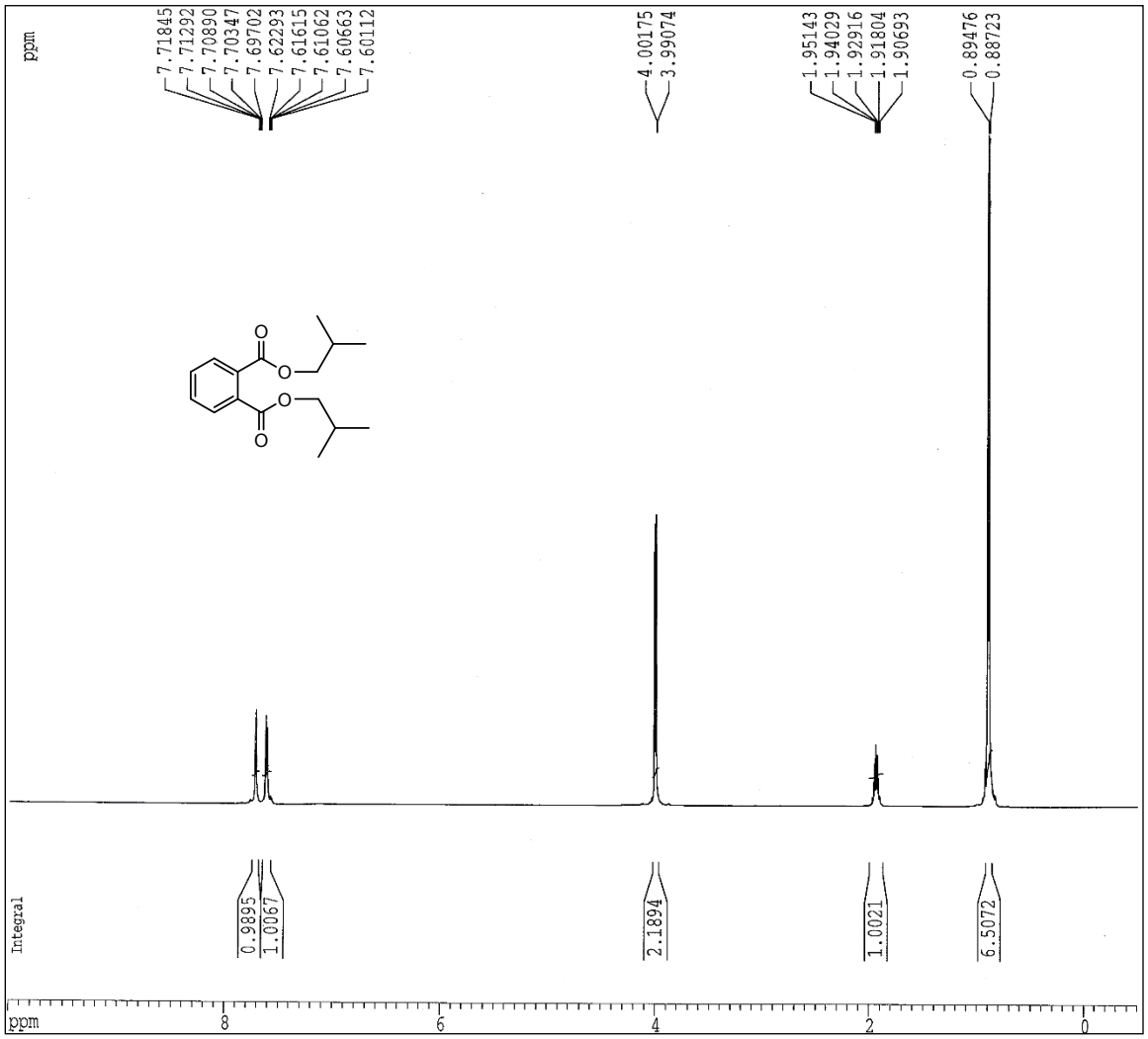

Figure S11. ^{1}H NMR spectrum of diisobtyl phthalate (DIBP)

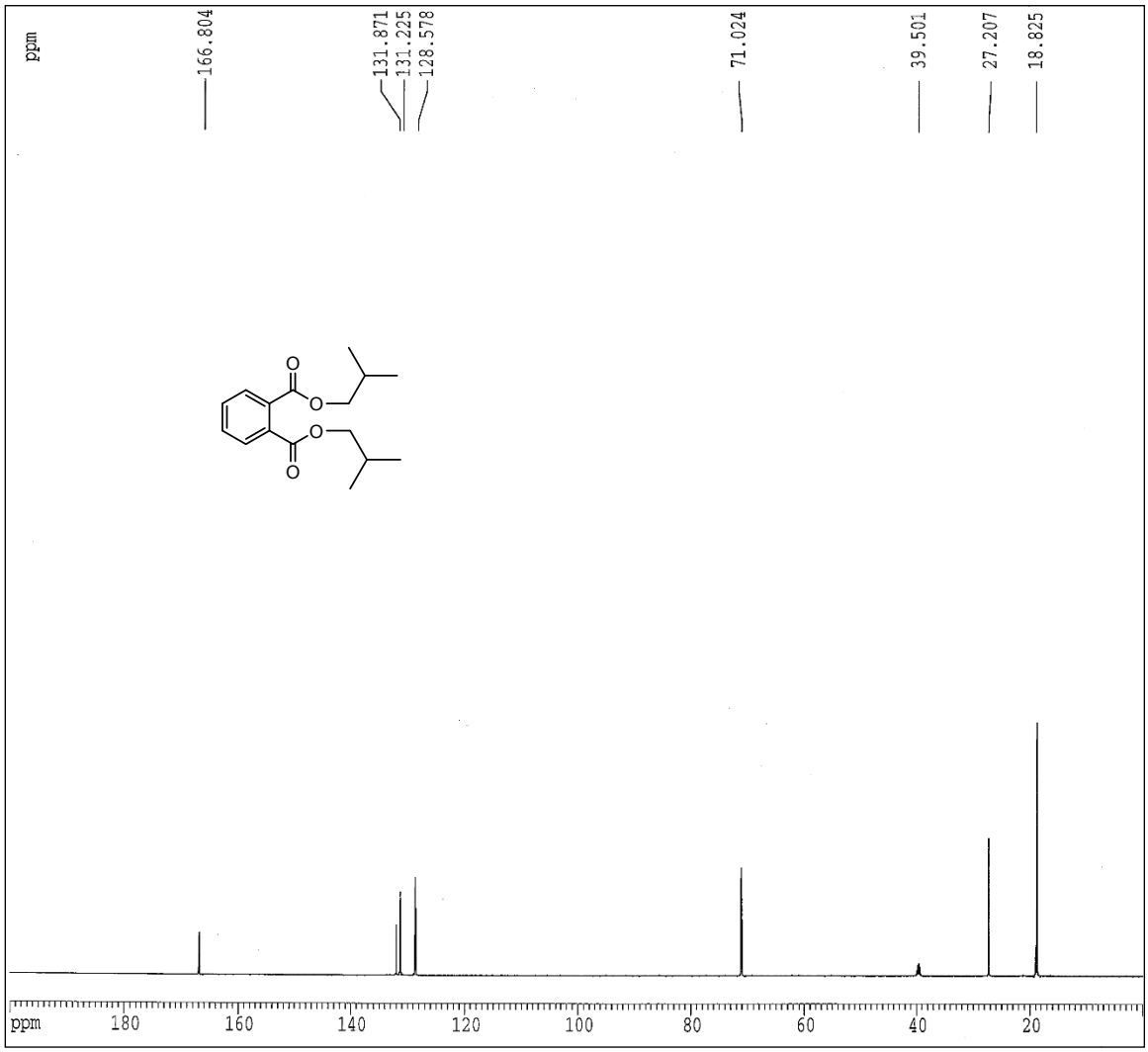

Figure S12. ^{13}C NMR spectrum of diisobtyl phthalate (DIBP)