ELECTRONIC SUPPLEMENTARY INFORMATION

Pyrrolidinium herbicidal ionic liquids

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The following abbreviations were used to explain the multiplicities:
s = singlet, d = doublet, t = triplet, quart = quartet, q = quintet, m = multiplet

1-Decyl-1-methylpyrrolidinium bromide ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 14H, $N^+CH_2CH_2(C\underline{H_2})_7CH_3$), 1.79 (q, *J* = 7.9 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_7CH_3$), 2.31 (q, *J* = 5.5 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.30 (s, 3H, $C\underline{H_3}N^+$), 3.66 (t, *J* = 8.5 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_7CH_3$), 3.85 (t, *J* = 8.6 Hz, 4H, $C\underline{H_2}CH_2CH_2C\underline{H_2}$); ^{13}C NMR (75 MHz, 298 K,$CDCl_3$) δ ppm = 13.67, 21.25, 22.18, 23.70, 25.99, 28.77, 28.94, 31.37, 48.28, 63.82, 64.04. Elemental analysis calcd (%) for $C_{15}H_{32}NBr$ (M = 306.38) C 58.80, H 10.55, N 4.57; found: C 59.08, H 10.23, N 4.42.

1-Dodecyl-1-methylpyrrolidinium bromide ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 18H, $N^+CH_2CH_2(C\underline{H_2})_9CH_3$), 1.78 (q, *J* = 7.9 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_9CH_3$), 2.31 (q, *J* = 5.6 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.30 (s, 3H, $C\underline{H_3}N^+$), 3.66 (t, *J* = 8.5 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_9CH_3$), 3.86 (t, *J* = 8.5 Hz, 4H, $C\underline{H_2}CH_2CH_2C\underline{H_2}$); ^{13}C NMR (75 MHz, 298 K,$CDCl_3$) δ ppm = 13.66, 21.24, 22.19, 23.71, 26.01, 28.70 28,82, 28.92, 31.39, 48.29, 63.80, 64.0. Elemental analysis calcd (%) for $C_{17}H_{36}NBr$ (M = 334.44) C 61.05, H 10.87, N 4.19; found: C 61.47, H 10.73, N 4.00.

1-Decyloxymethyl-1-methylpyrrolidinium chloride ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 14H, $OCH_2CH_2(C\underline{H_2})_7CH_3$), 1.62 (q, *J* = 6.8 Hz, 2H, $OCH_2C\underline{H_2}(CH_2)_7CH_3$), 2.29 (q, *J* = 6.2 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.37 (s, 3H, $C\underline{H_3}N^+$), 3.76 (t, *J* = 8.6 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.89 (t, *J* = 8.6 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$) 3.85 (t, *J* = 8.5 Hz, 2H, $OC\underline{H_2}CH_2(CH_2)_7CH_3$), 5.07 (s, 2H, $N^+C\underline{H_2}O$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.58, 21.62, 22.12, 25.27, 28.72, 28.77, 28.95, 29.11, 31.31, 46.90, 60.27, 72.72, 88.65. Elemental analysis calcd (%) for $C_{16}H_{34}NOCl$ (M = 291.96) C65.82, H 11.76, N 4.80; found: C 65.48, H 11.97, N 5.00.

1-Dodecyloxymethyl-1-methylpyrrolidinium chloride ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.6 Hz, 3H,$CH_2C\underline{H_3}$), 1.25 (m, 18H, $OCH_2CH_2(C\underline{H_2})_9CH_3$), 1.61 (q, *J* = 6.8 Hz, 2H, $OCH_2C\underline{H_2}(CH_2)_9CH_3$), 2.29 (q, *J* = 6.2 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.37 (s, 3H, $C\underline{H_3}N^+$), 3.76 (t, *J* = 8.5 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.91 (t, *J* = 8.6 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$) 3.85 (t, *J* = 8.5 Hz, 2H, $OC\underline{H_2}CH_2(CH_2)_9CH_3$), 5.07 (s, 2H, $N^+C\underline{H_2}O$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.59, 21.60, 22.14, 25.29, 28.70, 28.75, 28.99, 29.01, 29.02, 29.15, 31.30, 46.91, 60.29, 72.70, 88.66. Elemental analysis calcd (%) for $C_{18}H_{38}NOCl$ (M = 320,02) C 67.55, H 11.99, N 4.38; found: C 67.06, H 12.11, N 4.21.

1-Decyl-1-methylpyrrolidinium (4-chlorophenoxy)acetate (**1**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.24 (m, 14H, $N^+CH_2CH_2(C\underline{H_2})_7CH_3$), 1.70 (q, *J* = 5.9 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_7CH_3$), 2.23 (q, *J* = 6.4 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.16 (s, 3H, $C\underline{H_3}N^+$), 3.42 (t, *J* = 8.5 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_7CH_3$), 3.62 (t, *J* = 6.2 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.68 (t, *J* = 6.2 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$), 4.36 (s, 2H, $OC\underline{H_2}COO^-$), 6.89 (d, *J* = 9.1 Hz, 2H, $\underline{H}CCH{=}CClCH{=}C\underline{H}$), 7.19 (d, *J* = 9.1 Hz, 2H, $HCC\underline{H}{=}CClC\underline{H}{=}CH$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.89, 21.43, 22.39, 23.72, 26.19, 29.00, 29.19, 31.59, 48.41, 63.83, 64.12, 67.79, 115.90, 124.66, 128.82, 157.45, 172.78. Elemental analysis calcd (%) for $C_{23}H_{38}NO_3Cl$ (M = 412.07) C67.03, H 9.31, N 3.40; found: C 67.39, H 9.15, N 3.65.

1-Dodecyl-1-methylpyrrolidinium (4-chlorophenoxy)acetate (**2**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.25 (m, 18H, $N^+CH_2CH_2(C\underline{H_2})_9CH_3$), 1.70 (q, *J* = 5.9 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_9CH_3$), 2.22 (q, *J* = 6.3 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.16 (s, 3H, $C\underline{H_3}N^+$), 3.42 (t, *J* = 8.6 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_9CH_3$), 3.62 (t, *J* = 6.2 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.67 (t, *J*= 6.2 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$), 4.36 (s, 2H, $OC\underline{H_2}COO^-$), 6.89 (d, *J* = 9.0 Hz, 2H, $\underline{H}CCH{=}CClCH{=}C\underline{H}$), 7.19 (d, *J* = 9.0 Hz, 2H, $HCC\underline{H}{=}CClC\underline{H}{=}CH$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.90, 21.42, 22.40, 23.70, 26.22, 29.03, 29.04, 29.23, 31.61, 48.45, 63.85, 64.15, 67.82, 115.91, 124.66, 128.80, 157.44, 172.79. Elemental analysis calcd (%) for $C_{25}H_{42}NO_3Cl$ (M = 440.13) C68.22, H 9.64, N 3.18; found: C 68.69, H 9.48, N 2.99.

1-Decyloxymethyl-1-methylpyrrolidinium (4-chlorophenoxy)acetate (**3**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.8 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 14H, $OCH_2CH_2(C\underline{H_2})_7CH_3$), 1.57 (q, *J* = 5.0 Hz, 2H, $OCH_2C\underline{H_2}(CH_2)_7CH_3$), 2.15 (q, *J* = 5.4 Hz,4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.17 (s, 3H, $C\underline{H_3}N^+$), 3.50 (t, *J* = 6.2 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.69 (t, *J* = 6.2 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$) 3.73 (t, *J* = 6.6 Hz, 2H, $OC\underline{H_2}CH_2(CH_2)_7CH_3$), 4.37 (s, 2H, $OC\underline{H_2}COO^-$), 4.83 (s, 2H, $N^+C\underline{H_2}O$) 6.87 (d, *J* = 9.1 Hz, 2H, $\underline{H}CCH{=}CClCH{=}C\underline{H}$), 7.17 (d, *J* = 9.1 Hz, 2H, $HCC\underline{H}{=}CClC\underline{H}{=}CH$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.91, 21.96, 22.46, 25.61, 29.07, 29.14, 29.31, 29.40, 31.64, 47.18, 60.51, 68.09, 72.95, 89.05, 115.88, 124.55, 128.78, 157.65, 172.59. Elemental analysis calcd (%) for $C_{24}H_{40}NO_4Cl$ (M = 442.10) C 65.20, H 9.14, N 3.17; found: C 65.58, H 9.22, N 3.30.

1-Dodecyloxymethyl-1-methylpyrrolidinium (4-chlorophenoxy)acetate (**4**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.25 (m, 18H, $OCH_2CH_2(C\underline{H_2})_9CH_3$), 1.57 (q, *J* = 5.0 Hz, 2H, $OCH_2C\underline{H_2}(CH_2)_9CH_3$), 2.15 (q, *J* = 5.4 Hz, 4H, $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.17 (s, 3H, $C\underline{H_3}N^+$), 3.49 (t, *J* = 6.2 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.69 (t, *J* = 6.2 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$) 3.73 (t, *J* = 6.6 Hz, 2H, $OC\underline{H_2}CH_2(CH_2)_9CH_3$), 4.36 (s, 2H, $OC\underline{H_2}COO^-$), 4.83 (s, 2H, $N^+C\underline{H_2}O$) 6.87 (d, *J* = 9.1 Hz, 2H, $\underline{H}CCH{=}CClCH{=}C\underline{H}$), 7.17 (d, *J* = 9.1 Hz, 2H, $HCC\underline{H}{=}CClC\underline{H}{=}CH$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.90, 21.95, 22.45, 25.60, 29.09, 29.16, 29.30, 29.33, 29.42, 31.66, 47.19, 60.50, 68.11, 72.97, 89.07, 115.92, 124.57, 128.80, 157.66, 172.60. Elemental analysis calcd (%) for $C_{26}H_{44}NO_4Cl$ (M = 470.16) C 66.42, H 9.45, N 2.98; found: C 66.07, H 9.65, N 2.79.

1-Decyl-1-methylpyrrolidinium (2,4-dichlorophenoxy)acetate (**5**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 14H, $N^+CH_2CH_2(C\underline{H_2})_7CH_3$), 1.67 (q, *J* = 4.1 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_7CH_3$), 2.19 (q, *J* = 4.1 Hz, 4H,$CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.13 (s, 3H, $C\underline{H_3}N^+$), 3.39 (t, *J* = 8.5 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_7CH_3$), 3.60 (t, *J* = 6.1 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.66 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$), 4.46 (s, 2H, $OC\underline{H_2}COO^-$), 6.90 (d, *J* = 8.9 Hz, 1H, $HCC\underline{H}{=}C{-}O$), 7.11 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.9 Hz, 1H,$C\underline{H}{=}CClCH{=}CCl$), 7.30 (d, *J* = 2.4 Hz,1H, $ClCC\underline{H}{=}CCl$); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.89, 21.42, 22.43, 23.73, 26.20, 29.01, 29.18, 29.21, 31.59, 48.18, 63.79, 63.97, 68.87, 114.56, 122.37, 124.46, 127.31, 129.15, 153.56, 171.68. Elemental analysis calcd (%) for $C_{23}H_{37}NO_3Cl_2$(M = 446.54) C 61.86, H 8.40, N 3.14; found: C 61.51, H 8.28, N 3.01.

1-Dodecyl-1-methylpyrrolidinium (2,4-dichlorophenoxy)acetate (**6**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δppm = 0.88 (t, *J* = 6.7 Hz, 3H,$CH_2C\underline{H_3}$), 1.26 (m, 18H, $N^+CH_2CH_2(C\underline{H_2})_9CH_3$), 1.67 (q, *J* = 5.0 Hz, 2H, $N^+CH_2C\underline{H_2}(CH_2)_9CH_3$), 2.19 (q, *J* = 5.0 Hz, 4H,$CH_2C\underline{H_2}C\underline{H_2}CH_2$), 3.13 (s, 3H, $C\underline{H_3}N^+$), 3.39 (t, *J* = 8.5 Hz, 2H, $N^+C\underline{H_2}CH_2(CH_2)_9CH_3$), 3.60 (t, *J* = 6.1 Hz, 2H, $C\underline{H_2}CH_2CH_2CH_2$), 3.65 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2C\underline{H_2}$), 4.46 (s, 2H, $OC\underline{H_2}COO^-$), 6.90 (d, *J* = 8.9 Hz, 1H, $HCC\underline{H}{=}C{-}O$), 7.11 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.9 Hz, 1H,$C\underline{H}{=}CClCH{=}CCl$), 7.30 (d, *J* = 2.5 Hz,1H, $ClCC\underline{H}{=}CCl$); ^{13}C NMR

(75 MHz, 298 K, $CDCl_3$) δ ppm = 13.90, 21.44, 22.45, 23.71, 26.23, 29.02, 29.19, 29.20, 29. 22, 29.23, 31.61, 48.19, 63.80, 63.99, 68.88, 114.54, 122.33, 124.45, 127.30, 129.16, 153.57, 171.69. Elemental analysis calcd (%) for $C_{25}H_{41}NO_3Cl_2$(M = 474.57) C 63.27, H 8.73, N 2.95; found: C 63.69, H 8.91, N 2.77.

1-Decyloxymethyl-1-methylpyrrolidinium (2,4-dichlorophenoxy)acetate (**7**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,CH_2CH_3), 1.26 (m, 14H, $OCH_2CH_2(CH_2)_7CH_3$), 1.57 (q, *J* = 6.9 Hz, 2H, $OCH_2CH_2(CH_2)_7CH_3$), 2.13 (q, *J* = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2$), 3.14 (s, 3H, CH_3N^+), 3.47 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2CH_2$), 3.66 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2CH_2$) 3.70 (t, *J* = 6.6 Hz, 2H, $OCH_2CH_2(CH_2)_7CH_3$), 4.46 (s, 2H, OCH_2COO^-), 4.77 (s, 2H, N^+CH_2O), 6.90 (d,*J* = 8.8 Hz, 1H, HCCH=C-O), 7.10 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.9 Hz, 1H,CH=CClCH=CCl), 7.30 (d, *J* = 2.4 Hz,1H, ClCCH=CCl); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.92, 21.98, 22.46, 25.61, 29.09, 29.14, 29.32, 29.37, 31.66, 47.16, 60.48, 68.80, 72.95, 89.03, 114.49, 122.43, 124.53, 127.30, 129.20, 153.50, 171.85. Elemental analysis calcd (%) for $C_{24}H_{39}NO_4Cl_2$ (M = 476.54) C 60.49, H 8.27, N 2.94; found: C 60.77, H 8.41, N 3.11.

1-Dodecyloxymethyl-1-methylpyrrolidinium (2,4-dichlorophenoxy)acetate (**8**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,CH_2CH_3), 1.25 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$), 1.57 (q, *J* = 6.9 Hz, 2H, $OCH_2CH_2(CH_2)_9CH_3$), 2.13 (q, *J* = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2$), 3.15 (s, 3H, CH_3N^+), 3.47 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2CH_2$), 3.66 (t, *J* = 6.1 Hz, 2H, $CH_2CH_2CH_2CH_2$) 3.70 (t, *J* = 6.6 Hz, 2H, $OCH_2CH_2(CH_2)_9CH_3$), 4.46 (s, 2H, OCH_2COO^-), 4.76 (s, 2H, N^+CH_2O), 6.90 (d, *J* = 8.9 Hz, 1H, HCCH=C-O), 7.10 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.9 Hz, 1H,CH=CClCH=CCl), 7.30 (d, *J* = 2.5 Hz,1H, ClCCH=CCl); ^{13}C NMR (75MHz, 298 K, $CDCl_3$) δ ppm = 13.91, 21.99, 22.48, 25.59, 29.06, 29.08, 29.12, 29.31, 29.39, 31.69, 47.19, 60.42, 68.82, 72.97, 89.03, 114.53, 122.45, 124.51, 127.33, 129.21, 153.50, 171.85. Elemental analysis calcd (%) for $C_{26}H_{43}NO_4Cl_2$(M = 504.60) C 61.88, H 8.61, N 2.78; found: C 61.44, H 8.77, N 2.97.

1-Decyl-1-methylpyrrolidinium (4-chloro-2-methylphenoxy)acetate (**9**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,CH_2CH_3), 1.26 (m, 14H, $N^+CH_2CH_2(CH_2)_7CH_3$), 1.63 (q, *J* = 4.0 Hz, 2H, $N^+CH_2CH_2(CH_2)_7CH_3$), 2.15 (q, *J* = 4.1 Hz, 4H, $CH_2CH_2CH_2CH_2$), 2.21 (s, 3H, ClC=CHCCH_3) 3.08 (s, 3H, CH_3N^+), 3.33 (t, *J* = 8.5 Hz, 2H, $N^+CH_2CH_2(CH_2)_7CH_3$), 3.52 (t, *J* = 8.8 Hz, 2H, $CH_2CH_2CH_2CH_2$), 3.62 (t, *J* = 8.8 Hz,2H, $CH_2CH_2CH_2CH_2$), 4.37 (s, 2H, OCH_2COO^-), 6.73 (d, *J* = 8.8 Hz, 1H, HCCH=C-O), 6.99 (dd, $J^{1,2}$ = 2.7 Hz, $J^{1,3}$ = 8.6 Hz, 1H,CH=CClCH=CCH_3), 7.02 (d, *J* = 2.7 Hz,1H, ClCCH=CCH_3); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.89, 16.21, 21.40, 22.44, 23.70, 26.23, 29.03, 29.19, 29.23, 31.61, 48.18, 63.70, 63.93, 68.39, 112.78, 123.98, 125.93, 128.29, 129.72, 155.94, 173.41. Elemental analysis calcd (%) for $C_{24}H_{40}NO_3Cl$ (M = 426.10) C67.65, H 9.48, N 3.29; found: C 67.98, H 9.29, N 3.41.

1-Dodecyl-1-methylpyrrolidinium (4-chloro-2-methylphenoxy)acetate (**10**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,CH_2CH_3), 1.25 (m, 18H, $N^+CH_2CH_2(CH_2)_9CH_3$), 1.63 (q, *J*= 4.1 Hz, 2H, $N^+CH_2CH_2(CH_2)_9CH_3$), 2.15 (q, *J* = 4.1 Hz, 4H, $CH_2CH_2CH_2CH_2$), 2.21 (s, 3H, ClC=CHCCH_3) 3.08 (s, 3H, CH_3N^+), 3.33 (t, *J* = 8.5 Hz, 2H, $N^+CH_2CH_2(CH_2)_9CH_3$), 3.51 (t, *J* = 8.8 Hz, 2H, $CH_2CH_2CH_2CH_2$), 3.61 (t, *J* = 8.8 Hz,2H, $CH_2CH_2CH_2CH_2$), 4.37 (s, 2H, OCH_2COO^-), 6.73 (d, *J* = 8.8 Hz, 1H, HCCH=C-O), 6.99 (dd, $J^{1,2}$ = 2.6 Hz, $J^{1,3}$ = 8.6 Hz, 1H, CH=CClCH=CCH_3), 7.02 (d, *J* = 2.6 Hz,1H, ClCCH=CCH_3); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.93, 16.25, 21.47, 22.48, 23.72, 26.28, 29.09, 29.23, 29.24, 29.29, 29.32, 31.67, 48.19, 63.72, 63.95, 68.42, 112.79, 123.98, 125.91, 128.30, 129.70, 155.94, 173.41. Elemental analysis calcd (%) for $C_{26}H_{44}NO_3Cl$ (M = 454.16) C68.76, H 9.79, N 3.08; found: C 68.35, H 9.67, N 3.27.

1-Decyloxymethyl-1-methylpyrrolidinium (4-chloro-2-methylphenoxy)acetate (**11**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,CH_2CH_3), 1.26 (m, 14H, $OCH_2CH_2(CH_2)_7CH_3$), 1.56 (q, *J* = 5.1 Hz, 2H, $OCH_2CH_2(CH_2)_7CH_3$), 2.11 (q, *J* = 5.0 Hz, 4H, $CH_2CH_2CH_2CH_2$), 2.23 (s, 3H, ClC=CHCCH_3), 3.12 (s, 3H, CH_3N^+), 3.43 (t, *J* = 8.8 Hz, 2H, $CH_2CH_2CH_2CH_2$), 3.43 (t, *J* = 9.0 Hz, 2H, $CH_2CH_2CH_2CH_2$) 3.67 (t, *J* = 6.5 Hz, 2H, $OCH_2CH_2(CH_2)_7CH_3$), 4.39 (s, 2H, OCH_2COO^-), 4.75 (s, 2H, N^+CH_2O), 6.74 (d, *J* = 8.6 Hz, 1H, HCCH=C-O), 7.01 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.7 Hz, 1H, CH=CClCH=CCH_3), 7.05 (d, *J* = 2.5 Hz,1H, ClCCH=CCH_3); ^{13}C NMR (75 MHz, 298 K,$CDCl_3$) δ ppm = 13.92, 16.22, 21.96, 22.47, 25.63, 29.06, 29.10, 29.34, 29.40, 31.67, 47.15, 60.47, 68.47, 72.93, 89.01, 112.62, 123.95, 125.88,

128.29, 129.77, 156.00, 173.11. Elemental analysis calcd (%) for $C_{25}H_{42}NO_4Cl$ (M = 456.13) C 65.83, H 9.30, N 3.07; found: C 65.49, H 9.42, N 3.25.

1-Dodecyloxymethyl-1-methylpyrrolidinium (4-chloro-2-methylphenoxy)acetate (**12**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.9 Hz, 3H,$CH_2C\underline{H}_3$), 1.26 (m, 18H, $OCH_2CH_2(C\underline{H}_2)_9CH_3$), 1.56 (q, *J* = 5.0 Hz, 2H, $OCH_2C\underline{H}_2(CH_2)_9CH_3$), 2.11 (q, *J* = 5.0 Hz, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.23 (s, 3H, ClC=CHCC$\underline{H}_3$), 3.12 (s, 3H, $C\underline{H}_3N^+$), 3.42 (t, *J* = 8.8 Hz, 2H, $C\underline{H}_2CH_2CH_2CH_2$), 3.43 (t, *J* = 9.0 Hz, 2H, $CH_2CH_2CH_2C\underline{H}_2$) 3.66 (t, *J* = 6.5 Hz, 2H, $OC\underline{H}_2CH_2(CH_2)_9CH_3$), 4.39 (s, 2H, $OC\underline{H}_2COO^-$), 4.75 (s, 2H, $N^+C\underline{H}_2O$), 6.74 (d, *J* = 8.6 Hz, 1H, HCC$\underline{H}$=C-O), 7.01 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.7 Hz, 1H,C$\underline{H}$=CClCH=CCH_3), 7.05 (d, *J* = 2.5 Hz,1H, ClCC$\underline{H}$=CCH_3); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.90, 16.25, 21.91, 22.48, 25.67, 29.08, 29.15, 29.20, 29.22, 29.36, 29.42, 31.68, 47.16, 60.47, 68.46, 72.91, 89.03, 112.61, 123.96, 125.89, 128.29, 129.83, 156.05, 173.12. Elemental analysis calcd (%) for $C_{27}H_{46}NO_4Cl$ (M = 484.19) C 66.97, H 9.60, N 2.89; found: C 66.68, H 9.51, N 2.93.

1-Decyl-1-methylpyrrolidinium 2-(4-chloro-2-methylphenoxy)propionate (**13**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.8 Hz, 3H,$CH_2C\underline{H}_3$), 1.26 (m, 14H, $N^+CH_2CH_2(C\underline{H}_2)_7CH_3$), 1.53 (d, *J* = 6.7, 3H, OCH(C$\underline{H}_3$)COO^-), 1.61 (q, *J* = 4.0 Hz, 2H, $N^+CH_2C\underline{H}_2(CH_2)_7CH_3$), 2.12 (q, *J* = 5.2 Hz, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.21 (s, 3H, ClC=CHCC$\underline{H}_3$) 3.03 (s, 3H, $C\underline{H}_3N^+$), 3.30 (t, *J* = 8.6 Hz, 2H, $N^+C\underline{H}_2CH_2(CH_2)_7CH_3$), 3.48 (t, *J* = 5.5 Hz, 2H, $C\underline{H}_2CH_2CH_2CH_2$), 3.56 (t, *J* = 5.5 Hz, 2H, $CH_2CH_2CH_2C\underline{H}_2$), 4.40 (quart, *J* = 6.8, 2H, OC$\underline{H}$(CH_3)COO^-), 6.77 (d, *J* = 8.6 Hz, 1H, HCC$\underline{H}$=C-O), 6.97 (dd, $J^{1,2}$ = 2.4 Hz, $J^{1,3}$ = 8.5 Hz, 1H, C$\underline{H}$=CClCH=CCH_3), 7.02 (d, *J* = 2.6 Hz,1H, ClCC$\underline{H}$=CCH_3); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$) δ ppm = 13.89, 16.26, 19.31, 21.36, 22.43, 23.70, 26.22, 29.01, 29.18, 29.22, 31.60, 48.10, 63.63, 63.86, 76.33, 113.49, 123.56, 125.83, 128.45, 129.57, 155.88, 176.90. Elemental analysis calcd (%) for $C_{25}H_{42}NO_3Cl$ (M = 440.13) C 68.22, H 9.64, N 3.18; found: C 68.60, H 9.75, N 3.29.

1-Dodecyl-1-methylpyrrolidinium 2-(4-chloro-2-methylphenoxy)propionate (**14**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δppm = 0.88 (t, *J* = 6.8 Hz, 3H,$CH_2C\underline{H}_3$), 1.26 (m, 18H, $N^+CH_2CH_2(C\underline{H}_2)_9CH_3$), 1.53 (d, *J* = 6.7, 3H, OCH(C$\underline{H}_3$)COO^-), 1.61 (q, *J* = 5.2 Hz, 2H, $N^+CH_2C\underline{H}_2(CH_2)_9CH_3$), 2.12 (q, *J* = 5.2 Hz, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.21 (s, 3H, ClC=CHCC$\underline{H}_3$) 3.03 (s, 3H, $C\underline{H}_3N^+$), 3.29 (t, *J* = 8.6 Hz, 2H, $N^+C\underline{H}_2CH_2(CH_2)_9CH_3$), 3.48 (t, *J* = 5.5 Hz, 2H, $C\underline{H}_2CH_2CH_2CH_2$), 3.56 (t, *J* = 5.5 Hz, 2H, $CH_2CH_2CH_2C\underline{H}_2$), 4.40 (quart, *J* = 6.8, 2H, OC$\underline{H}$(CH_3)COO^-), 6.77 (d, *J* = 8.5 Hz, 1H, HCC$\underline{H}$=C-O), 6.97 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.5 Hz, 1H,C$\underline{H}$=CClCH=CCH_3), 7.02 (d, *J* = 2.5 Hz,1H, ClCC$\underline{H}$=CCH_3); ^{13}C NMR (75MHz, 298 K, $CDCl_3$) δ ppm = 13.91, 16.28, 19.30, 21.39, 22.46, 23.71, 26.25, 29.07, 29.19, 29.22, 29.24, 31.61, 48.11, 63.60, 63.88, 76.30, 113.49, 123.55, 125.82, 128.38, 129.55, 155.89, 176.91. Elemental analysis calcd (%) for $C_{27}H_{46}NO_3Cl$ (M = 468.19) C 69.26, H 9.92, N 2.99; found: C 69.57, H 10.08, N 2.79.

1-Decyloxymethyl-1-methylpyrrolidinium 2-(4-chloro-2-methylphenoxy)propionate (**15**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.8 Hz, 3H,$CH_2C\underline{H}_3$), 1.26 (m, 14H, $OCH_2CH_2(C\underline{H}_2)_7CH_3$), 1.55 (d, *J* = 6.8, 3H, OCH(C$\underline{H}_3$)COO^-), 1.64 (q, *J* = 6.8 Hz, 2H, $OCH_2C\underline{H}_2(CH_2)_7CH_3$), 2.07 (q, *J* = 4.7 Hz, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.23 (s, 3H, ClC=CHCC$\underline{H}_3$), 3.07 (s, 3H, $C\underline{H}_3N^+$), 3.38 (t, *J* = 5.5 Hz, 2H, $C\underline{H}_2CH_2CH_2CH_2$), 3.58 (t, *J* = 5.5 Hz, 2H, $CH_2CH_2CH_2C\underline{H}_2$) 3.64 (t, *J* = 6.5 Hz, 2H, $OC\underline{H}_2CH_2(CH_2)_7CH_3$), 4.43 (quart, *J* = 6.8, 2H, OC$\underline{H}$(CH_3)COO^-), 4.71 (s, 2H, $N^+C\underline{H}_2O$), 6.78 (d,*J* = 8.6 Hz, 1H, HCC$\underline{H}$=C-O), 6.98 (dd, $J^{1,2}$ = 2.4 Hz, $J^{1,3}$ = 8.6 Hz, 1H,C$\underline{H}$=CClCH=CCH_3), 7.03 (d, *J* = 2.5 Hz,1H, ClCC$\underline{H}$=CCH_3); ^{13}C NMR (75 MHz, 298 K,$CDCl_3$) δ ppm = 13.90, 16.26, 19.31, 21.91, 22.46, 25.63, 29.08, 29.14, 29.32, 29.40, 31.66, 47.90, 60.40, 72.90, 76.22, 88.96, 113.12, 123.51, 125.76, 128.37, 129.63, 155.90, 176.78. Elemental analysis calcd (%) for $C_{26}H_{44}NO_4Cl$ (M = 470.16) C 66.42, H 9.45, N 2.98; found: C 66.78, H 9.18, N 3.13.

1-Dodecyloxymethyl-1-methylpyrrolidinium 2-(4-chloro-2-methylphenoxy)propionate (**16**) ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ ppm = 0.88 (t, *J* = 6.8 Hz, 3H,$CH_2C\underline{H}_3$), 1.26 (m, 18H, $OCH_2CH_2(C\underline{H}_2)_9CH_3$), 1.55 (d, *J* = 6.8, 3H, OCH(C$\underline{H}_3$)COO^-), 1.63 (q, *J* = 6.8 Hz, 2H, $OCH_2C\underline{H}_2(CH_2)_9CH_3$), 2.07 (q, *J* = 4.7 Hz, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.23 (s, 3H, ClC=CHCC$\underline{H}_3$), 3.07 (s,

3H, $C\underline{H}_3N^+$), 3.38 (t, *J* = 5.5 Hz, 2H, $C\underline{H}_2CH_2CH_2CH_2$), 3.58 (t, *J* = 5.5 Hz, 2H, $CH_2CH_2CH_2C\underline{H}_2$) 3.64 (t, *J* = 6.5 Hz, 2H, $OC\underline{H}_2CH_2(CH_2)_9CH_3$), 4.43 (quart, *J* = 6.8, 2H, $OC\underline{H}(CH_3)COO^-$), 4.70 (s, 2H, $N^+C\underline{H}_2O$), 6.78 (d,*J* = 8.6 Hz, 1H, $HCC\underline{H}$=C-O), 6.99 (dd, $J^{1,2}$ = 2.6 Hz, $J^{1,3}$ = 8.6 Hz, 1H,$C\underline{H}$=CClCH=CCH_3), 7.03 (d, *J* = 2.6 Hz,1H, $ClCC\underline{H}$=CCH_3); ^{13}C NMR (75 MHz, 298 K,$CDCl_3$) δ ppm = 13.92, 16.28, 19.30, 21.90, 22.47, 25.65, 29.09, 29.17, 29.20, 29.22, 29.30, 29.42, 31.68, 47.91, 60.42, 72.91, 76.25, 88.96, 113.10, 123.50, 125.77, 128.36, 129.65, 155.91, 176.78. Elemental analysis calcd (%) for $C_{28}H_{48}NO_4Cl$ (M = 498.22) C 67.50, H 9.73, N 2.81; found: C 67.92, H 9.58, N 2.92.

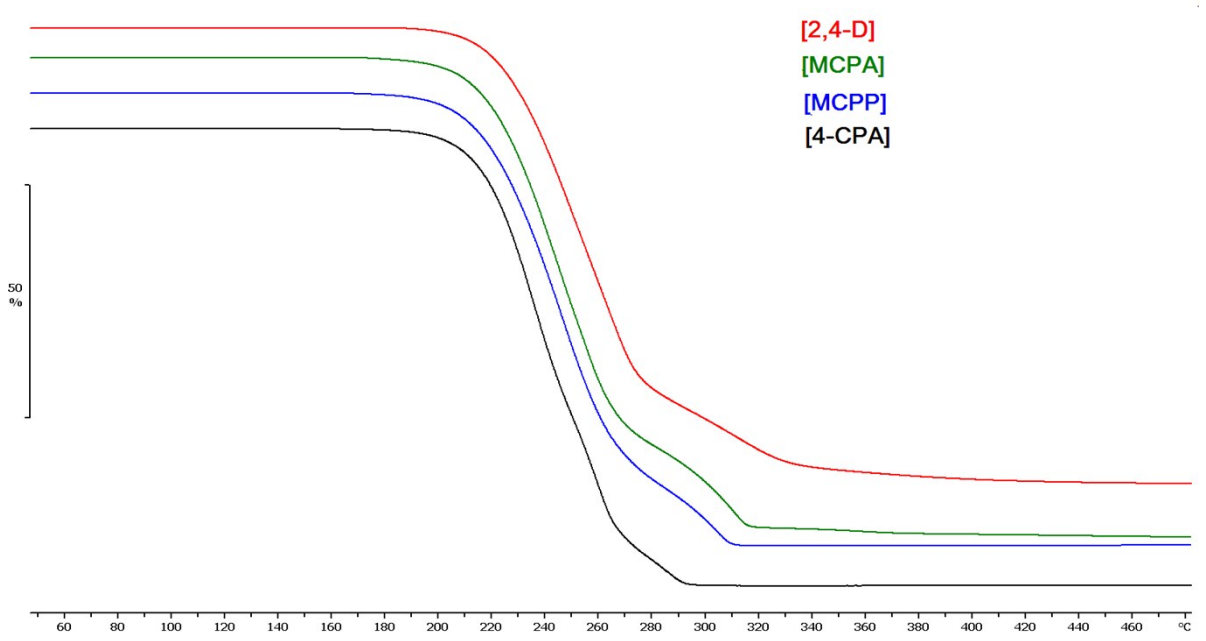

Fig. S1 TGA curve for 1-dodecyl-1-methylpyrrolidinium ILs

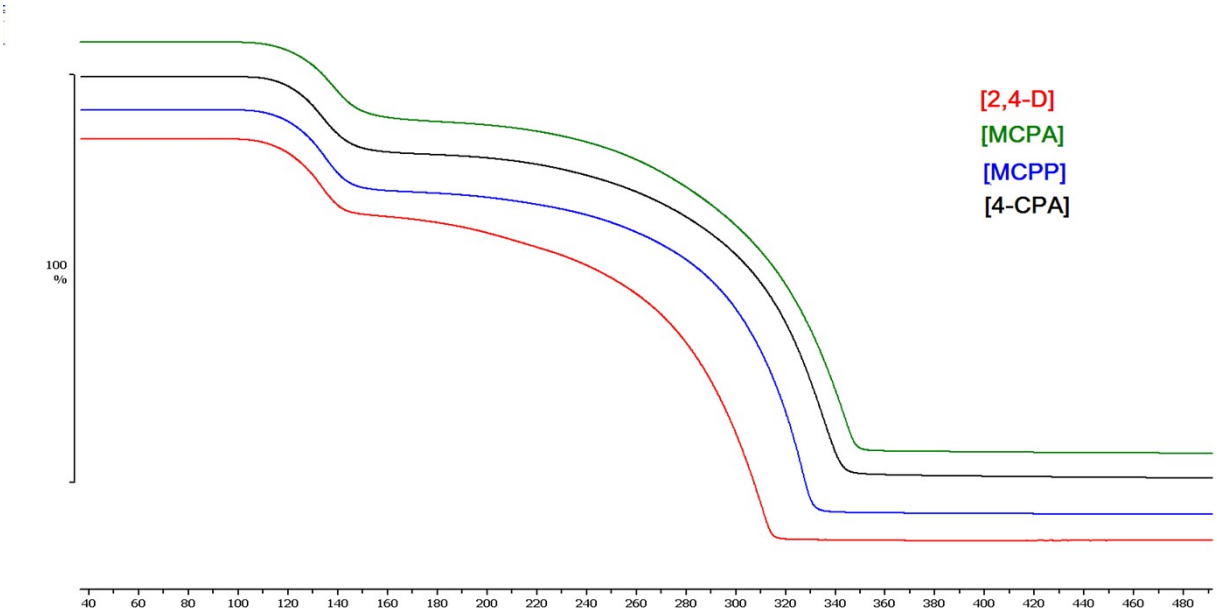

Fig. S2 TGA curve for 1-decyloxymethyl-1-methylpyrrolidinium ILs

Table S1 Viscosity, density and refractive index of synthesized ILs (at 25 °C)

ILs	Density (g cm^{-3})	Viscosity (Pa s)	Refractive index
3	1.1400	0.5066	1.4955
4	1.1224	0.6349	1.4933
5	1.2783	8.5087	1.5158
6	1.2400	8.7441	1.5133
7	1.2000	0.9326	1.5090
8	1.1720	1.0006	1.5043
9	1.1716	4.9590	1.5128
10	1.1388	5.2978	1.5101
11	1.1250	0.4049	1.5004
12	1.1124	0.5612	1.4984
13	1.1590	7.0425	1.5083
14	1.1356	7.0994	1.5051
15	1.1130	0.6398	1.4973
16	1.1086	0.6912	1.4943

Table S2 Efficacy of pyrrolidinium ILs with phenoxycarboxylate anions against lambsquarters (*Chenopodium album* L.*)* in growth chamber experiment

IL	Anion	Dose[a] (g ha^{-1})	Fresh weight reduction (%)
1	4-CPA	889	55
2		948	65
3		952	53
4		1013	54
5	2,4-D	811	58
6		862	57
7		866	54
8		917	59
9	MCPA	855	63
10		909	53
11		913	67
12		995	56
13	MCPP	825	47
14		877	54
15		881	53
16		932	63
[b]Aminopielik Standard 600 SL		667 mL	46
[c]Chwastox Extra 300 SL		1333 mL	36

[a]It contains the mass of the anhydrous IL, in all treatments the rate of fenoxycarboxylate anion was 400 g ha^{-1}, [b]600 g 2,4-D per 1 L, [c]300 g MCPA per 1 L.