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ELECTRONIC SUPPLEMENTARY INFORMATION

Esterquat Herbicidal Ionic Liquids (HILs) with two different herbicides: evaluation of activity and phytotoxicity

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Scheme S1 Synthesis of phenoxy-acid chlorides.

Table S1 Phenoxy-acid chlorides according to Scheme S1

Abbreviation of	R^1	R ²	Destillation		Yield
phenoxy-acid			р	Т	[%]
chloride			[hPa]	[°C]	
2,4-D-Cl	Cl	Н	7 – 8	141	80
MCPA-Cl	CH₃	Н	3 – 4	125	94
MCPP-Cl	CH₃	CH₃	29 – 30	149	88
4-CPA-Cl	Н	Н	22 – 23	144	94



Scheme S2 Synthesis of aminoester hydrochlorides.

Abbreviation of	R^1	R ²	Melting point	Yield	
aminoester			[°C]	[%]	
hydrochloride					
[2,4-D-DAE-H][Cl]	Cl	Н	155.5 – 158.3	94	
[MCPA-DAE-H][Cl]	CH₃	Н	154.0 – 155.8	98	
[MCPP-DAE-H][Cl]	CH₃	CH₃	65.7 – 67.2	99	
[4-CPA-DAE-H][Cl]	Н	Н	132.1 – 133.0	90	

 Table S2
 Aminoester hydrochlorides according to Scheme S2



Scheme S3 Synthesis of aminoesters.

Table S3 Aminoesters according to Scheme S3

Abbreviation of	R1	R ²	Yield [%]	
aminoester				
2,4-D-DAE	Cl	Н	75	
MCPA-DAE	CH₃	Н	81	
MCPP-DAE	CH₃	CH₃	80	
4-CPA-DAE	Н	Н	78	



Scheme S4 Synthesis of herbicidal esterguats.

Table S4 Herbicidal esterquats according to Scheme S4

Abbreviation of	R^1	R ²	Melting point	Surfactant	Yield
estrequat			[°C]	content [%]	[%]
[2,4-D-DAE-C ₁₀][Br]	Cl	Н	127.8 – 128.8	97.0	78
[MCPA-DAE-C ₁₀][Br]	CH₃	Н	126.8 – 127.3	97.5	73
[MCPP-DAE-C ₁₀][Br]	CH₃	CH₃	119.6 – 121.0	99.5	71
[4-CPA-DAE-C ₁₀][Br]	Н	Н	100.6 - 101.6	98.0	81

The following abbreviations were used to explain the multiplicities:

s = singlet, d = doublet, dd = doublet of doublets, t = triplet, quart = quartet, q = quintet, m = multiplet

2,4-D-Cl (2,4-dichlorophenoxy)acethyl chloride ¹H NMR (DMSO– d_6) δ ppm = 4.85 (s, 2H), 7.08 (d, J=8.9 Hz, 1H), 7.34 (dd, $J^{1,2}$ =2.6 Hz, $J^{1,3}$ =8.8 Hz, 1H), 7.55 (d, J=2.5 Hz, 1H); ¹³C NMR δ ppm = 65.29, 114.93, 122.40, 124.40, 127.91, 129.42, 152.41, 169.39. Anal. Calcd for C₈H₅O₂Cl₃: C 40.12, H 2.11; Found: C 39.75, H 2.01.

MCPA-Cl (4-chloro-2-methylphenoxy)acethyl chloride¹H NMR (DMSO– d_6) δ ppm = 2.19 (s, 3H), 4.72 (s, 2H), 6.84 (d, J=8.7 Hz, 1H), 7.16 (dd, J^{1,2}=2.7 Hz, J^{1,3}= 8.6 Hz, 1H), 7.21 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 15.93, 65.05, 112.97, 124.41, 126.39, 128.57, 130.14, 154.91, 170.12. Anal. Calcd for C₉H₈O₂Cl₂: C 49.34, H 3.69; Found: C 49.02, H 3.77.

MCPP-Cl (\pm)-2-(4-chloro-2-methylphenoxy)propionyl chloride ¹H NMR (DMSO– d_6) δ ppm = 1.54 (d, J=6.9 Hz, 3H), 2.19 (s, 3H), 4.83 (quart, J=6.8 Hz, 1H), 6.78 (d, J=8.8 Hz, 1H), 7.15 (dd, J^{1,2}=0.5 Hz, J^{1,3}=9.0 Hz, 1H), 7.20 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 15.96, 18.44, 72.19, 113.49, 124.43, 126.39, 128.88, 130.23, 154.69, 172.98. Anal. Calcd for C₁₀H₁₀O₂Cl₂: C 51.52, H 4.33; Found: C 51.23, H 4.47.

4-CPA-Cl (4-chlorophenoxy)acethyl chloride ¹H NMR (DMSO– d_6) δ ppm = 4.71 (s, 2H), 6.95 (d, J=9.0 Hz, 2H), 7.32 (d, J=9.0 Hz, 1H); ¹³C NMR δ ppm = 64.78, 116.30, 124.88, 129.26, 156.70, 169.88. Anal. Calcd for C₈H₆O₂Cl₂: C 46.86, H 2,96; Found: C 47.03, H 3.13.

[2,4-D-DAE-H][CI] (2,4-dichlorophenoxy)-2-acetoxyethyldimethylammonium hydrochloride ¹H NMR (DMSO– d_6) δ ppm = 2.78 (s, 6H), 3.49 (t, J=4.9 Hz, 2H), 4.52 (t, J=5.0 Hz, 2H), 5.10 (s, 2H), 7.32 (d, J=9.1 Hz, 1H), 7.33 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.8 Hz, 1H), 7.60 (d, J=2.7 Hz, 1H), 11.31 (s, 1H); ¹³C NMR δ ppm = 42.28, 54.55, 58.94, 65.44, 115.37, 122.22, 125.09, 127.91, 129.35, 152.10, 167.81. Anal. Calcd for C₁₂H₁₆NO₃Cl₃: C 43.85, H 4.92, N 4.26; Found: C 44.22, H 4.87, N 4.08.

[MCPADAE-H][CI] (4-chloro-2-methylphenoxy)-2-acetoxyethyldimethylammonium hydrochloride ¹H NMR (DMSO– d_6) δ ppm = 2.19 (s, 3H), 2.77 (s, 6H), 3.42 (t, J=5.0 Hz, 2H), 4.50 (t, J=5.0 Hz, 2H), 4.96 (s, 2H), 7.00 (d, J=8.8 Hz, 1H), 7.16 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.24 (d, J=2.7 Hz, 1H), 11.22 (s,

1H); ^{13}C NMR δ ppm = 15.78, 42.29, 54.58, 58.86, 65.08, 113.30, 124.48, 126.33, 128.42, 130.06, 154.58, 168.37. Anal. Calcd for $C_{13}H_{19}NO_3Cl_2$: C 50.65, H 6.23, N 4.55; Found: C 50.24, H 6.00, N 4.66.

[MCPP-DAE-H][Cl] (±)-(4-chloro-2-methylphenoxy)-2-(2'-propionyloxyethyl)dimethylammonium hydrochloride ¹H NMR (DMSO- d_6) δ ppm = 1.58 (d, J=6.7 Hz, 3H), 2.19 (s, 3H), 2.75 (s, 6H), 3.41 (t, J=4.8 Hz, 2H), 4.49 (t, J=4.7 Hz, 2H), 5.13 (quart, J=6.8 Hz, 1H), 6.99 (d, J=8.8 Hz, 1H), 7.15 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.6 Hz, 1H), 7.24 (d, J=2.7 Hz, 1H), 11.43 (s, 1H); ¹³C NMR δ ppm = 15.78, 18.08, 42.22, 54.46, 59.36, 71.99 114.04, 124.48, 126.39, 128.75, 130.08, 154.23, 170.79. Anal. Calcd for C₁₄H₂₁NO₃Cl₂: C 52.18, H 6,58, N 4.35; Found: C 52.41, H 6.23, N 4.20.

[4-CPA-DAE-H][Cl] (4-chlorophenoxy)-2-acetoxyethyldimethylammonium hydrochloride ¹H NMR (DMSO– d_6) δ ppm = 2.78 (s, 6H), 3.42 (t, J=5.0 Hz, 2H), 4.51 (t, J=5.0 Hz, 2H), 4.96 (s, 2H), 7.05 (d, J=9.1 Hz, 2H), 7.34 (dd, J=9.1 Hz, 2H), 11.25 (s, 1H); ¹³C NMR δ ppm = 42.29, 54.57, 58.82, 64.89, 116.44, 124.94, 129.22, 156.42, 168.30. Anal. Calcd for C₁₂H₁₇NO₃Cl₂: C 48.99, H 5.84, N 4.76; Found: C 49.39, H 6.00, N 4.83.

2,4-D-DAE (2-dimethylamino)ethyl (2,4-dichlorophenoxy)acetate ¹H NMR (DMSO– d_6) δ ppm = 2.19 (s, 6H), 2.53 (t, J=5.7 Hz, 2H), 4.23 (t, J=5.7 Hz, 2H), 4.96 (s, 2H), 7.12 (d, J=9.1 Hz, 1H), 7.35 (dd, $J^{1,2}$ =2.6 Hz, $J^{1,3}$ =8.8 Hz, 1H), 7.58 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 45.0, 56.9, 62.27, 65.4, 115.1, 122.3, 125.1, 127.9, 129.4, 152.2, 168.0. Anal. Calcd for C₁₂H₁₅NO₃Cl₂: C 49.33, H 5.19, N 4.80; Found: C 49.65, H 5.09, N 4.96.

MCPA-DAE (2-dimethylamino)ethyl (4-chloro-2-methylphenoxy)acetate ¹H NMR (DMSO– d_6) δ ppm = 2.16 (s, 6H), 2.19 (s, 3H), 2.49 (t, J=5.7 Hz, 2H), 4.20 (t, J=5.7 Hz, 2H), 4.82 (s, 2H), 6.89 (d, J=8.8 Hz, 1H), 7.16 (dd, $J^{1,2}$ =2.7 Hz, $J^{1,3}$ =8.6 Hz, 1H), 7.23 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 15.74, 45.16, 57.03, 62.26, 65.07, 113.08, 124.47, 126.26, 128.50, 130.03, 154.65, 168.58. Anal. Calcd for C₁₃H₁₈NO₃Cl: C 57.45, H 6.69, N 5.16; Found: C 57.09, H 6.83, N 5.38.

MCPP-DAE (2-dimethylamino)ethyl (\pm)-2-(4-chloro-2-methylphenoxy)propionate ¹H NMR (DMSOd₆) δ ppm = 1.53 (d, J=6.7 Hz, 3H), 2.14 (s, 6H), 2.19 (s, 3H), 2.45 (t, J=5.6 Hz, 2H), 4.18 (t, J=5.6 Hz, 2H), 4.93 (quart, J=6.8 Hz, 1H), 6.83 (d, J=8.8 Hz, 1H), 7.13 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.22 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 15.74, 18.25, 45.13, 57.07, 62.38, 72.21, 113.66, 124.52, 126.21, 128.83, 130.08, 154.35, 171.23. Anal. Calcd for C₁₄H₂₀NO₃Cl: C 58.83, H 7.07, N 4.90; Found: C 58.49, H 6.98, N 4.99

4-CPA-DAE (2-dimethylamino)ethyl (4-chlorophenoxy)acetate ¹H NMR (DMSO– d_6) δ ppm = 2.18 (s, 6H), 2.51 (t, J=5.7 Hz, 2H), 4.21 (t, J=5.7 Hz, 2H), 4.81 (s, 2H), 6.97 (d, J=9.1 Hz, 2H), 7.33 (d, J=9.1 Hz, 1H); ¹³C NMR δ ppm = 45.07, 56.96, 62.15, 64.83, 116.33, 124.92, 129.16, 156.47, 168,46. Anal. Calcd for C₁₂H₁₆NO₃Cl: C 55.92, H 6.27, N 5.44; Found: C 56.27, H 6.12, N 5.26.

[2,4-D-DAE-C₁₀][Br] (2,4-dichlorophenoxy)-2-acetoxyethyldecyldimethylammonium bromide ¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.68 (q, J=3.9 Hz, 2H), 3.14 (s, 6H), 3.37 (t, J=8.5 Hz, 2H), 3.76 (t, J=4.2 Hz, 2H), 4.59 (t, J=2.3 Hz, 2H), 5.01 (s, 2H), 7.26 (d, J=9.0 Hz, 1H), 7.37 (dd, J^{1,2}=2.5 Hz, J^{1,3}=8.9 Hz, 1H), 7.59 (d, J=2.5 Hz, 1H); ¹³C NMR δ ppm = 13.87, 21.75, 22.03, 25.72, 28.50, 28.62, 28.81, 28.86, 31.23, 50.49, 58.46, 61.24, 63.87, 65.52, 115.42, 122.24, 125.18, 127.94, 129.33, 152.01, 167.48. Anal. Calcd for C₂₂H₃₆NO₃Cl₂Br: C 51.47, H 7.08, N 2.73; Found: C 51.58, H 7.23, N 2.66.

[MCPA-DAE-C₁₀][Br] (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium bromide ¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.5 Hz, 3H), 1.25 (m, 14H), 1.67 (q, J=4.2 Hz, 2H), 2.20 (s, 3H), 3.13 (s, 6H), 3.40 (t, J=8.5 Hz, 2H), 3.75 (t, J=4.9 Hz, 2H), 4.58 (t, J=4.9 Hz, 2H), 4.89 (s, 2H), 6.98 (d, J=8.8 Hz, 1H), 7.18 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.6 Hz, 1H), 7.25 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.90, 15.71, 21.77, 22.06, 25.74, 28.53, 28.65, 28.84, 28.89, 31.25, 50.48, 58.33, 61.25, 63.83, 65.14, 113.28, 124.54, 126.30, 128.36, 130.02, 154.48, 168.05. Anal. Calcd for C₂₃H₃₉NO₃ClBr: C 56.03, H 7.99, N 2.84; Found: C 56.35, H 8.12, N 2.77.

[MCPP-DAE-C₁₀][Br] (4-chloro-2-methylphenoxy)-2-(2'-propionoxyethyl)decyldimethylammonium bromide ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.25 (m, 14H), 1.56 (d, J=6.8 Hz, 3H), 1.65 (q, J=4.9 Hz, 2H), 2.19 (s, 3H), 3.10 (s, 6H), 3.39 (t, J=4.3 Hz, 2H), 3.75 (t, J=1.8 Hz, 2H), 4.56 (t, J=2.3 Hz, 2H), 5.04 (quart, J=6.8 Hz, 1H), 6.93 (d, J=8.8 Hz, 1H), 7.17 (dd, J^{1,2}=2.8 Hz, J^{1,3}=8.8 Hz, 1H), 7.24 (d, J=2.3 Hz, 1H); ¹³C NMR δ ppm = 13.89, 15.72, 18.02, 21.75, 22.04, 25.71, 28.49, 28.61, 28.80, 28.85, 31.22, 50.38, 58.55, 61.40, 63.76, 72.13, 114.03, 124.54, 126.34, 128.75, 130.06, 154.17, 170.51. Anal. Calcd for C₂₄H₄₁NO₃ClBr: C 56.85, H 8.17, N 2.76; Found: C 56.52, H 7,99, N 2.57.

[4-CPA-DAE-C₁₀][Br] (4-chlorophenoxy)-2-acetoxyethyldecyldimethylammonium bromide ¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.25 (m, 14H), 1.67 (q, J=4.5 Hz, 2H), 3.11 (s, 6H), 3.39 (t, J=8.4 Hz, 2H), 3.73 (t, J=5.0 Hz, 2H), 4.56 (t, J=5.0 Hz, 2H), 4.87 (s, 2H), 7.03 (d, J=9.1 Hz, 2H), 7.35 (d, J=9.1 Hz, 2H); ¹³C NMR δ ppm = 13.89, 21.75, 22.04, 25.73, 28.51, 28.62, 28.81, 28.87, 31.23, 50.49, 58.32, 61.23, 63.87, 64.93, 116.42, 125.01, 129.20, 156.32, 167.96. Anal. Calcd for C₂₂H₃₇NO₃ClBr: C 55.17, H 7.80, N 2.93; Found: C 55.46, H 7.97, N 2.77.

[2,4-D-DAE-C₁₀**][MCPA]** (2,4-dichlorophenoxy)-2-acetoxyethyldecyldimethylammonium (4-chloro-2methylphenoxy)acetate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.8 Hz, 3H), 1.24 (m, 14H), 1.65 (q, J=5.7 Hz, 2H), 2.17 (s, 3H), 3.06 (s, 6H), 3.31 (t, J=8.5 Hz, 2H), 3.38 (t, J=5.1 Hz, 2H), 3.82 (t, J=2.4 Hz, 2H), 4.49 (s, 2H), 4.53 (s, 2H), 6.75 (d, J=8.8 Hz, 1H), 6.93 (d, J=8.8 Hz, 1H), 7.11 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.6 Hz, 1H), 7.18 (d, J=2.7 Hz, 1H), 7.29 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.8 Hz, 1H), 7.50 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.92, 15.87, 21.78, 22.09, 25.80, 28.52, 28.67, 28.84, 28.91, 31.28, 50.75, 54.87, 64.09, 64.65, 66.38, 67.03, 112.78, 114.86, 121.95, 123.47, 123.81, 126.07, 127.65, 128.14, 128.98, 129.70, 153.13, 155.40, 169.79, 170.47. Anal. Calcd for C₃₁H₄₄NO₆Cl₃: C 58.81, H 7.02, N 2.21; Found: C 58.44, H 7.17, N 2.03.

[2,4-D-DAE-C₁₀][MCPP] (2,4-dichlorophenoxy)-2-acetoxyethyldecyldimethylammonium (\pm)-2-(4chloro-2-methylphenoxy)propionate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.46 (d, J=6.8 Hz; 3H), 1.65 (q, J=5.7 Hz, 2H), 2.16 (s, 3H), 3.05 (s, 6H); 3.30 (t, J=8.4 Hz, 2H), 3.38 (t, J=5.0 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.53 (s, 2H), 4.62 (quart, J=6.8 Hz, 1H), 6.73 (d, J=8,8 Hz, 1H), 6.92 (d, J=8.8 Hz, 1H), 7.09 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.6 Hz, 1H), 7.17 (d, J=2.7 Hz, 1H), 7.28 (dd, J^{1,2}=2.8 Hz, J^{1,3}=9.0 Hz, 1H), 7.50 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.92, 15.87, 18.62, 21.78, 22.09, 25.80, 28.52, 28.68, 28.84, 28.91, 31.28, 50.74, 54.88, 64.09, 64.63, 66.98, 73.34, 113.25, 114.85, 121.95, 123.43, 123.83, 126.04, 127.65, 128.31, 128.99, 129.72, 153.12, 155.08, 169.77, 173.58. Anal. Calcd for C₃₂H₄₆NO₆Cl₃: C 59.39, H 7.18, N 2.16; Found: C 59.02, H 7.01, N 2.02.

[2,4-D-DAE-C₁₀][4-CPA] (2,4-dichlorophenoxy)-2-acetoxyethyldecyldimethylammonium (4-chlorophenoxy)acetate ¹H NMR (DMSO- d_6) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.3 Hz; 2H), 3.06 (s, 6H), 3.31 (t, J=8.4 Hz, 2H), 3.38 (t, J=5.0 Hz, 2H), 3.83 (t, J=2.3 Hz, 2H), 4.49 (s, 2H), 4.58 (s, 2H), 6.88 (d, J=9.1 Hz, 2H), 6.95 (d, J=8.8 Hz, 1H), 7.29 (d, J=9.1 Hz, 2H), 7.30 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.8 Hz, 1H), 7.52 (d, J=2.8 Hz, 1H); ¹³C NMR δ ppm = 13.92, 21.78, 22.09, 25.79, 28.51, 28.66, 28.83, 28.90, 31.28, 50.75, 54.88, 64.10, 64.63, 65.92, 66.75, 114.85, 116.14, 121.99, 123.96, 127.68, 128.97, 153.02, 157.15, 169.80, 170.31. Anal. Calcd for C₃₀H₄₂NO₆Cl₃: C 58.20, H 6.85, N 2.26; Found: C 58.57, H 7.03, N 2.01.

[MCPA-DAE-C₁₀**][2,4-D]** (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (2,4-dichlorophenoxy)acetate ¹H NMR (DMSO–d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1,64 (q, J=5.7 Hz, 2H), 2.17 (s, 3H), 3.05 (s, 6H), 3.30 (t, J=8.4 Hz, 2H), 3.38 (t, J=5.0 Hz, 2H), 3.83 (t, J=2.3 Hz, 2H), 4.51 (s, 2H), 4.55 (s, 2H), 6.75 (d, J=8.8 Hz, 1H), 6.94 (d, J=8.8 Hz, 1H), 7.12 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.3 Hz, 1H), 7.18 (d, J=2.7 Hz, 1H), 7.29 (dd, J^{1,2}=2.8 Hz, J^{1,3}=9.0 Hz, 1H), 7.50 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.91, 15.87, 21.78, 22.09, 25.80, 28.53, 28.68, 28.84, 28.91, 31.28, 50.74, 54.89, 64.11, 64.64, 66.29, 66.93, 112.78, 114.85, 121.97, 123.52, 123.88, 126.07, 127.66, 128.16, 129.00, 129.71, 153.09, 155.36, 169.83, 170.48. Anal. Calcd for C₃₁H₄₄NO₆Cl₃: C 58.81, H 7.02, N 2.21; Found: C 58.53, H 6.85, N 2.03.

[MCPA-DAE-C₁₀**][MCPP]** (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (\pm)-2-(4-chloro-2-methylphenoxy)propionate ¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.25 (m, 14H), 1.44 (d, J=6.8 Hz, 3H), 1.65 (q, J=4.8 Hz, 2H), 2.15 (s, 3H); 2.16 (s, 3H), 3.04 (s, 6H), 3.29 (t, J=6.8 Hz, 3H), 3.29 (t, J=6.8 Hz), 3.29 (t, J=6.8

J=8.5 Hz, 2H), 3.36 (t, J=5.1 Hz, 2H), 3.81 (t, J=2.3 Hz, 2H), 4.43 (s, 2H), 4.57 (quart, J=6.8 Hz, 1H), 6.71 (d, J=8.7 Hz, 1H), 6.72 (d, J=8.8 Hz, 1H), 7.08 (dd, $J^{1,2}$ =2.8 Hz, $J^{1,3}$ =8.2 Hz, 1H), 7.10 (dd, $J^{1,2}$ =2.8 Hz, $J^{1,3}$ =8.7 Hz, 1H), 7.16 (d, J=2.8 Hz, 1H), 7.17 (d, J=2.8 Hz, 1H); ¹³C NMR δ ppm = 13.96, 15.91, 15.93, 18.71, 21.77, 22.11, 25.80, 28.52, 28.68, 28.84, 28.92, 31.29, 50.76, 54.87, 64.07, 64.65, 66.55, 73.57, 112.78, 113.26, 123.28, 123.32, 126.04, 126.06, 128.10, 128.25, 129.68, 129.69, 155.19, 155.49, 170.34, 173.56. Anal. Calcd for C₃₃H₄₉NO₆Cl₂: C 63.24, H 7.90, N 2.24; Found: C 63.62, H 8.01, N 2.09.

[MCPA-DAE-C₁₀][4-CPA] (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (4-chlorophenoxy)acetate ¹H NMR (DMSO- d_6) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.3 Hz, 2H), 2.17 (s, 3H), 3.05 (s, 6H), 3.30 (t, J=8.5 Hz, 2H), 3.38 (t, J=5.0 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.45 (s, 2H), 4.49 (s, 3H), 6.75 (d, J=8.8 Hz, 1H), 6.87 (d, J=9.1 Hz, 2H), 7.11 (dd, J^{1,2}=2.3 Hz, J^{1,3}=8.3 Hz, 1H), 7.18 (d, J=2.7 Hz, 1H), 7.28 (d, J=9.1 Hz, 2H); ¹³C NMR δ ppm = 13.92, 15.88, 21.78, 22.09, 25.80, 28.52, 28.68, 28.84, 28.91, 31.28, 50.75, 54.89, 64.11, 64.66, 66.20, 66.40, 112.78, 116.14, 123.47, 123.92, 126.07, 128.15, 128.94, 129.71, 155.41, 157.27, 170.37, 170.50. Anal. Calcd for C₃₁H₄₅NO₆Cl₂: C 62.19, H 7.59, N 2.34; Found: C 62.58, H 7.78, N 2.22.

[MCPP-DAE-C₁₀][2,4-D] (4-chloro-2-methylphenoxy)-2-(2'-propionoxyethyl)decyldimethylammonium (2,4-dichlorophenoxy)acetate¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.46 (d, J=6.7 Hz, 3H), 1.65 (q, J=3.8 Hz, 2H), 2.16 (s, 3H), 3.05 (s, 6H); 3.30 (t, J=8.4 Hz, 2H), 3.37 (t, J=5.0 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.53 (s, 2H), 4.62 (quart, J=6.8 Hz, 1H), 6.72 (d, J=8.8 Hz, 1H), 6.92 (d, J=8.8 Hz, 1H), 7.09 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.6 Hz, 1H), 7.16 (d, J=2.7 Hz, 1H), 7.28 (dd, J^{1,2}=2.8 Hz, J^{1,3}=9.0 Hz, 1H), 7.50 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.91, 15.86, 18.61, 21.78, 22.09, 25.79, 28.52, 28.66, 28.83, 31.28, 50.74, 54.87, 64.10, 64.63, 66.96, 73.33, 113.26, 114.84, 121.94, 123.42, 123.83, 126.02, 127.63, 128.31, 128.98, 129.72, 153.10, 155.07, 169.76, 173.56. Anal. Calcd for C₃₂H₄₆NO₆Cl₃: C 59.39, H 7.18, N 2.16; Found: C 59.01, H 7.02, N 2.36.

[MCPP-DAE-C₁₀][MCPA] (4-chloro-2-methylphenoxy)-2-(2'-propionoxyethyl)decyldimethylammonium (4-chloro-2-methylphenoxy)acetate ¹H NMR (DMSO-*d*₆) δ ppm = 0.85 (t, *J*=6.9 Hz, 3H), 1.24 (m, 14H), 1.43 (d, *J*=6.8 Hz, 3H), 1.64 (q, *J*=5.1 Hz, 2H), 2.16 (s, 3H), 2.16 (s, 3H), 3.04 (s, 6H), 3.30 (t, *J*=8.5 Hz, 2H), 3.37 (t, *J*=5.1 Hz, 2H), 3.81 (t, *J*=5.1 Hz, 2H), 4.44 (s, 2H), 4,57 (quart, *J*=6.8 Hz, 1H), 6.70 (d, *J*=8.8 Hz, 1H), 6.73 (d, *J*=8.8 Hz, 1H), 7.06 (dd, *J*^{1,2}=2.6 Hz, *J*^{1,3}=9.2 Hz, 1H), 7.09 (dd, *J*^{1,2}=2.6 Hz, *J*^{1,3}=9.2 Hz, 1H), 7.15 (dd, *J*^{1,2}=2.8 Hz, *J*^{1,3}=9.1 Hz, 1H), 7.16 (d, *J*=3.0 Hz, 1H); ¹³C NMR δ ppm = 13.90, 15.87, 15.87, 18.66, 21.75, 22.07, 25.77, 28.49, 28.64, 28.88, 28.92, 31.25, 50.71, 54.84, 64.06, 64.63, 66.52, 73.57, 112.73, 113.21, 123.26, 123.32, 126.01, 128.08, 128.09, 128.21, 129.64, 155.16, 155.45, 170.42, 173.61. Anal. Calcd for C₃₃H₄₉NO₆Cl₂: C 63.24, H 7.90, N 2.24; Found: C 63.63, H 8.02, N 2.07.

[MCPP-DAE-C₁₀][4-CPA] (4-chloro-2-methylphenoxy)-2-(2'-propionoxyethyl)decyldimethylammonium (4-chlorophenoxy)acetate¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.25 (m, 14H), 1.45 (d, J=6.6 Hz, 3H), 1.65 (q, J=3.9 Hz, 2H), 2.16 (s, 3H), 3.05 (s, 6H), 3,29 (t, J=8.5 Hz, 2H), 3.38 (t, J=5.1 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.43 (s, 2H), 4.60 (quart, J=6.8 Hz, 1H), 6.72 (d, J=8.7 Hz, 1H), 6.86 (d, J=9.1 Hz, 2H), 7.09 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.16 (d, J=2.6 Hz, 1H), 7.27 (d, J=9.0 Hz, 1H); ¹³C NMR δ ppm = 13.94, 15.89, 18.65, 21.77, 22.10, 25.79, 28.52, 28.68, 28.91, 31.29, 50.74, 54.87, 64.05, 64.62, 66.19, 73.40, 113.23, 116.11, 123.36, 123.87, 126.03, 128.27, 128.93, 129.71, 155.10, 157.26, 170.29, 173.58. Anal. Calcd for C₃₂H₄₇NO₆Cl₂: C 62.73, H 7.75, N 2.29; Found: C 63.06, H 7.59, N 2.44.

[4-CPA-DAE-C₁₀][2,4-D] (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (2,4-dichlorophenoxy)acetate¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.24 (m, 14H), 1.65 (q, J=3.8 Hz; 2H), 3.05 (s, 6H), 3.30 (t, J=8.5 Hz, 2H), 3.38 (t, J=5.1 Hz, 2H), 3.83 (t, J=2.3 Hz, 2H), 4.48 (s, 2H), 4.56 (s, 2H), 6.88 (d, J=9.1 Hz, 2H), 6.94 (d, J=9.0 Hz, 1H), 7.28 (d, J=9.1 Hz, 2H), 7.29 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.9 Hz, 1H), 7.51 (d, J=2.6 Hz, 1H); ¹³C NMR δ ppm = 13.97, 21.81, 22.14, 25.83, 28.57, 28.72, 28.89, 28.95, 31.33, 50.77, 54.91, 64.10, 64.65, 66.04, 66.86, 114.85, 116.15, 121.98, 123.92, 124.02, 127.71, 128.99, 129.05, 153.07, 157.21, 169.91, 170.42. Anal. Calcd for C₃₀H₄₂NO₆Cl₃: C 58.20, H 6.85, N 2.26; Found: C 58.58, H 6.66, N 2.09.

[4-CPA-DAE-C₁₀][MCPA] (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (4-chloro-2-methylphenoxy)acetate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.8 Hz, 3H), 1.24 (m, 14H), 1.65 (q, J=3.8 Hz, 2H), 2.17 (s, 3H), 3.05 (s, 6H), 3.30 (t, J=8.5 Hz, 2H), 3.37 (t, J=5.1 Hz, 2H), 3.82 (t, J=2.4 Hz, 2H), 4.44 (s, 2H), 4.48 (s, 2H), 6.75 (d, J=8.7 Hz, 1H), 6.87 (d, J=9.1 Hz, 2H), 7.11 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.18 (d, J=2.3 Hz, 1H), 7.28 (d, J=9.1 Hz, 1H); ¹³C NMR δ ppm = 13.96, 15.92, 21.80, 22.13, 25.82, 28.55, 28.71, 28.87, 28.94, 31.31, 50.76, 54.90, 64.08, 64.64, 66.19, 66.38, 112.77, 116.14, 123.46, 123.92, 126.10, 128.15, 128.96, 129.73, 155.42, 157.28, 170.40, 170.52. Anal. Calcd for C₃₁H₄₅NO₆Cl₂: C 62.19, H 7.59, N 2.34; Found: C 62.58, H 7.76, N 2.18.

[4-CPA-DAE-C₁₀]**[MCPP]** (4-chlorophenoxy)-2-acetoxyethyldecyldimethylammonium (±)-2-(4-chloro-2-methylphenoxy)propionate ¹H NMR (DMSO–d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.45 (d, J=6.8 Hz, 3H), 1.64 (q, J=3.9 Hz, 2H), 2.16 (s, 3H), 3.04 (s, 6H), 3,30 (t, J=8,5 Hz, 2H), 3.37 (t, J=3.2 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.42 (s, 2H), 4.59 (quart, J=6.8 Hz, 1H), 6.72 (d, J=8.8 Hz, 1H), 6.86 (d, J=9.1 Hz, 2H), 7.09 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.6 Hz, 1H), 7.16 (d, J=2.7 Hz, 1H), 7.27 (d, J=9.1 Hz, 1H); ¹³C NMR δ ppm = 13.98, 15.93, 18.72, 21.80, 22.14, 25.87, 28.57, 28.72, 28.88, 29.95, 31.33, 50.75, 54.90, 64.07, 64.64, 66.28, 73.52, 113.22, 116.13, 123.34, 123.87, 126.06, 128.26, 128.95, 129.72, 155.18, 157.32, 170.40, 173.72. Anal. Calcd for C₃₂H₄₇NO₆Cl₂: C 62.73, H 7.75, N 2.29; Found: C 62.41, H 7.91, N 2.09.

[MCPA-DAE-C₁₀][Clopyralid] (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (3,6-dichloro)-2-pikolinate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.3 Hz, 2H), 2.18 (s, 3H), 3.08 (s, 6H), 3.33 (t, J=8.5 Hz, 2H), 3.40 (t, J=5.1 Hz, 2H), 3.83 (t, J=5.1 Hz, 2H), 4.65 (s, 2H), 6.81 (d, J=8.7 Hz, 1H), 7.15 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.20 (d, J=2.7 Hz, 1H), 7.39 (d, J=8.4 Hz, 2H), 7.89 (d, J=8.4 Hz, 2H); ¹³C NMR δ ppm = 13.93, 15.81, 21.79, 22.10, 25.80, 28.52, 28.67, 28.84, 28.91, 31.29, 50.77, 54.91, 64.09, 64.59, 65.43, 112.83, 123.38, 123.95, 124.68, 126.19, 128.32, 129.88, 140.29, 147.32, 155.00, 157.82, 166.65, 170.13. Anal. Calcd for C₂₉H₄₁N₂O₅Cl₃: C 57.66, H 6.86, N 4.64; Found: C 58.03, H 6.69, N 4.78.

[MCPA-DAE-C₁₀**][Dicamba]** (4-chloro-2-methylphenoxy)-2-acetoxyethyldecyldimethylammonium (3,6-dichloro-2-metoxy)benzoate ¹H NMR (DMSO- d_6) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.3 Hz, 2H), 2.18 (s, 3H), 3.06 (s, 6H), 3.31 (t, J=8.5 Hz, 2H), 3.39 (t, J=5.1 Hz, 2H), 3.81 (s, 3H), 3.82 (t, J=5.1 Hz, 2H), 4.61 (s, 2H), 6.79 (d, J=8.8 Hz, 1H), 7.13 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.8 Hz, 1H), 7.14 (d, J=8.6 Hz, 1H), 7.19 (d, J=2.7 Hz, 1H), 7.31 (d, J=8.6 Hz, 1H); ¹³C NMR δ ppm = 13.95, 15.86, 21.80, 22.12, 25.80, 28.54, 28.69, 28.85, 28.93, 31.30, 50.76, 54.90, 61.25, 64.08, 64.60, 65.62, 112.79, 123.82, 125.34, 125.49, 126.16, 127.65, 128.21, 128.26, 129.85, 137.81, 151.58, 155.10, 165.94, 170.22. Anal. Calcd for C₃₁H₄₄NO₆Cl₃: C 58.81, H 7.02, N 2.21; Found: C 58.42, H 6.89, N 2.02.

[4-CPA-DAE-C₁₀][Clopyralid] (4-chlorophenoxy)-2-acetoxyethyldecyldimethylammonium (3,6-dichloro)-2-pikolinate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.4 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.6 Hz, 2H), 3.07 (s, 6H), 3.32 (t, J=8.5 Hz, 2H), 3.39 (t, J=5.0 Hz, 2H), 3.83 (t, J=5.0 Hz, 2H), 4.62 (s, 2H), 6.92 (d, J=9.1 Hz, 2H), 7.31 (d, J=9.0 Hz, 2H), 7.38 (d, J=8.6 Hz, 1H) 7.89 (d, J=8.5 Hz, 1H); ¹³C NMR δ ppm = 13.95, 21.79, 22.10, 25.80, 28.52, 28.68, 28.84, 28.91, 31.29, 50.78, 54.91, 64.09, 64.61, 65.22, 116.19, 123.30, 124.40, 124.64, 129.09, 140.27, 147.32, 156.85, 158.02, 166.63, 170,04. Anal. Calcd for C₂₈H₃₉N₂O₅Cl₃: C 56.90, H 6.68, N 4.75; Found: C 56,51, H 6.49, N 4.87.

[4-CPA-DAE-C₁₀][Dicamba] (4-chlorophenoxy)-2-acetoxyethyldecyldimethylammonium (3,6-dichloro-2-metoxy)benzoate ¹H NMR (DMSO-d₆) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.24 (m, 14H), 1.66 (q, J=4.5 Hz, 2H), 3.07 (s, 6H), 3.32 (t, J=8.5 Hz, 2H), 3.39 (t, J=5.0 Hz, 2H), 3.81 (s, 3H), 3.83 (t, J=5.0 Hz, 2H), 4.60 (s, 2H), 6.91 (d, J=9.1 Hz, 2H), 7.30 (d, J=9.0 Hz, 2H), 7.15 (d, J=8.6 Hz, 1H) 7.32 (d, J=8.5 Hz, 1H); ¹³C NMR δ ppm = 13.95, 21.79, 22.11, 25.80, 28.52, 28.68, 28.84, 28.91, 31.29, 50.76, 54.90, 61.27, 64.08, 64.60, 65.38, 116.17, 124.30, 125.36, 125.51, 127.66 128.33, 129.06, 137.58, 151.61, 156.93, 165.91, 170.09. Anal. Calcd for C₃₀H₄₂NO₆Cl₃: C 58.20, H 6.85, N 2.26; Found: C 58.58, H 7.01, N 2.08.



Fig. S1 ¹H NMR spectrum of **2,4-D-Cl**.



2,4-D-Cl (2,4-dichlorophenoxy)acethyl chloride

¹³C NMR (DMSO– d_6) δ ppm = 65.29, 114.93, 122.40, 124.40, 127.91, 129.42, 152.41, 169.39.



Fig. S2 ¹³C NMR spectrum of 2,4-D-Cl.



Fig. S3 ¹H NMR spectrum of MCPA-CI.



Fig. S4 ¹³C NMR spectrum of MCPA-CI.



Fig. S5 ¹H NMR spectrum of **MCPP-CI**.



Fig. S6 ¹³C NMR spectrum of MCPP-Cl.



Fig. S7 ¹H NMR spectrum of 4-CPA-CI.

4-CPA-Cl (4-chlorophenoxy)acethyl chloride

¹³C NMR (DMSO– d_6) δ ppm = 64.78, 116.30, 124.88, 129.26, 156.70, 169.88.

Fig. S8¹³C NMR spectrum of **4-CPA-CI**.

Fig. S9 ¹H NMR spectrum of [2,4-D-DAE-H][CI].

Fig. S10 ¹³C NMR spectrum of [2,4-D-DAE-H][Cl].

Fig. S11 ¹H NMR spectrum of [MCPA-DAE-H][Cl].

Fig. S12 ¹³C NMR spectrum of [MCPA-DAE-H][Cl].

Fig. S13 ¹H NMR spectrum of [MCPP-DAE-H][Cl].

Fig. S14 ¹³C NMR spectrum of [MCPP-DAE-H][Cl].

Fig. S15 ¹H NMR spectrum of [4-CPA-DAE-H][CI].

Fig. S16 ¹³C NMR spectrum of [4-CPA-DAE-H][CI].

Fig. S17 ¹H NMR spectrum of **2,4-D-DAE**.

Fig. S18 ¹³C NMR spectrum of 2,4-D-DAE.

Fig. S19 ¹H NMR spectrum of **MCPA-DAE**.

Fig. S20 ¹³C NMR spectrum of MCPA-DAE.

Fig. S21 ¹H NMR spectrum of **MCPP-DAE.**

Fig. S22 ¹³C NMR spectrum of MCPP-DAE.

Fig. S23 ¹H NMR spectrum of 4-CPA-DAE.

Fig. S24 ¹³C NMR spectrum of 4-CPA-DAE.

Fig. S25 ¹H NMR spectrum of [2,4-D-DAE-C₁₀][Br].

Fig. S26 ¹³C NMR spectrum of [2,4-D-DAE-C₁₀][Br].

Fig. S27 ¹H NMR spectrum of [MCPA-DAE-C₁₀][Br].

-0

ppm

[MCPA-DAE-C₁₀][Br] (4-chloro-2-methylphenoxy)-2acetoxyethyldecyldimethylammonium bromide

¹³C NMR (DMSO– d_6) δ ppm = 13.90, 15.71, 21.77, 22.06, 25.74, 28.53, 28.65, 28.84, 28.89, 31.25, 50.48, 58.33, 61.25, 63.83, 65.14, 113.28, 124.54, 126.30, 128.36, 130.02, 154.48, 168.05.

Fig. S28 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][Br].

Fig. S29 ¹H NMR spectrum of [MCPP-DAE-C₁₀][Br].


[MCPP-DAE-C₁₀][Br] (4-chloro-2-methylphenoxy)-2-(2'-propionoxyethyl)decyldimethylammonium bromide

¹³C NMR (DMSO– d_6) δ ppm = 13.89, 15.72, 18.02, 21.75, 22.04, 25.71, 28.49, 28.61, 28.80, 28.85, 31.22, 50.38, 58.55, 61.40, 63.76, 72.13, 114.03, 124.54, 126.34, 128.75, 130.06, 154.17, 170.51.



Fig. S30 ¹³C NMR spectrum of [MCPP-DAE-C₁₀][Br].



Fig. S31 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][Br].



Fig. S32 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][Br].



Fig. S33 ¹H NMR spectrum of [2,4-D-DAE-C₁₀][MCPA].



[2,4-D-DAE-C₁₀][MCPA] (2,4-dichlorophenoxy)-2acetoxyethyldecyldimethylammonium (4-chloro-2methylphenoxy)acetate

¹³C NMR (DMSO- d_6) δ ppm = 13.92, 15.87, 21.78, 22.09, 25.80, 28.52, 28.67, 28.84, 28.91, 31.28, 50.75, 54.87, 64.09, 64.65, 66.38, 67.03, 112.78, 114.86, 121.95, 123.47, 123.81, 126.07, 127.65, 128.14, 128.98, 129.70, 153.13, 155.40, 169.79, 170.47.



Fig. S34 ¹³C NMR spectrum of [2,4-D-DAE-C₁₀][MCPA].



Fig. S35 ¹H NMR spectrum of [2,4-D-DAE-C₁₀][MCPP].





¹³C NMR (DMSO–*d*₆) δ ppm = 13.92, 15.87, 18.62, 21.78, 22.09, 25.80, 28.52, 28.68, 28.84, 28.91, 31.28, 50.74, 54.88, 64.09, 64.63, 66.98, 73.34, 113.25, 114.85, 121.95, 123.43, 123.83, 126.04, 127.65, 128.31, 128.99, 129.72, 153.12, 155.08, 169.77, 173.58.



Fig. S36 ¹³C NMR spectrum of [2,4-D-DAE-C₁₀][MCPP].



Fig. S37 ¹H NMR spectrum of [2,4-D-DAE-C₁₀][4-CPA].



Fig. S38¹³C NMR spectrum of **[2,4-D-DAE-C**₁₀**][4-CPA]**.



Fig. S39 ¹H NMR spectrum of [MCPA-DAE-C₁₀][2,4-D].



Fig. S40 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][2,4-D].



[MCPA-DAE-C₁₀][MCPP] (4-chloro-2-methylphenoxy)-2acetoxyethyldecyldimethylammonium (±)-2-(4-chloro-2*methylphenoxy)propionate*

¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.25 (m, 14H), 1.44 (d, J=6.8 Hz, 3H), 1.65 (q, J=4.8 Hz, 2H), 2.15 (s, 3H); 2.16 (s, 3H), 3.04 (s, 6H), 3.29 (t, J=8.5 Hz, 2H), 3.36 (t, J=5.1 Hz, 2H), 3.81 (t, J=2.3 Hz, 2H), 4.43 (s, 2H), 4.57 (quart, J=6.8 Hz, 1H), 6.71 (d, J=8.7 Hz, 1H), 6.72 (d, J=8.8 Hz, 1H), 7.08 (dd, J^{1,2}=2.8 Hz, J^{1,3}=8.2 Hz, 1H), 7,10 (dd, J^{1,2}=2.8 Hz, J^{1,3}=8.7 Hz, 1H), 7.16 (d, J=2.8 Hz, 1H), 7.17 (d, J=2.8 Hz, 1H).



Fig. S41 ¹H NMR spectrum of [MCPA-DAE-C₁₀][MCPP].



Fig. S42 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][MCPP].



Fig. S43 ¹H NMR spectrum of [MCPA-DAE-C₁₀][4-CPA].



Fig. S44 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][4-CPA].





¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.7 Hz, 3H), 1.24 (m, 14H), 1.46 (d, J=6.7 Hz, 3H), 1.65 (q, J=3.8 Hz, 2H), 2.16 (s, 3H), 3.05 (s, 6H); 3.30 (t, J=8.4 Hz, 2H), 3.37 (t, J=5.0 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.53 (s, 2H), 4.62 (quart, J=6.8 Hz, 1H), 6.72 (d, J=8.8 Hz, 1H), 6.92 (d, J=8.8 Hz, 1H), 7.09 (dd, J^{1,2}=2.6 Hz, J^{1,3}=8.6 Hz, 1H), 7.16 (d, J=2.7 Hz, 1H), 7.28 (dd, J^{1,2}=2.8 Hz, J^{1,3}=9.0 Hz, 1H), 7.50 (d, J=2.6 Hz, 1H).



Fig. S45 ¹H NMR spectrum of [MCPP-DAE-C₁₀][2,4-D].



[MCPP-DAE-C₁₀][2,4-D] (4-chloro-2-methylphenoxy)-2-(2'propionoxyethyl)decyldimethylammonium (2,4-dichlorophenoxy)acetate

¹³C NMR (DMSO- d_6) δ ppm = 13.91, 15.86, 18.61, 21.78, 22.09, 25.79, 28.52, 28.66, 28.83, 31.28, 50.74, 54.87, 64.10, 64.63, 66.96, 73.33, 113.26, 114.84, 121.94, 123.42, 123.83, 126.02, 127.63, 128.31, 128.98, 129.72, 153.10, 155.07, 169.76, 173.56.



Fig. S46 ¹³C NMR spectrum of [MCPP-DAE-C₁₀][2,4-D].





Fig. S47 ¹H NMR spectrum of [MCPP-DAE-C₁₀][MCPA].



Fig. S48 ¹³C NMR spectrum of [MCPP-DAE-C₁₀][MCPA].



[MCPP-DAE-C₁₀][4-CPA] (4-chloro-2-methylphenoxy)-2-(2'propionoxyethyl)decyldimethylammonium (4-chlorophenoxy)acetate

¹H NMR (DMSO– d_6) δ ppm = 0.86 (t, J=6.9 Hz, 3H), 1.25 (m, 14H), 1.45 (d, J=6.6 Hz, 3H), 1.65 (q, J=3.9 Hz, 2H), 2.16 (s, 3H), 3.05 (s, 6H), 3,29 (t, J=8.5 Hz, 2H), 3.38 (t, J=5.1 Hz, 2H), 3.82 (t, J=2.3 Hz, 2H), 4.43 (s, 2H), 4.60 (quart, J=6.8 Hz, 1H), 6.72 (d, J=8.7 Hz, 1H), 6.86 (d, J=9.1 Hz, 2H), 7.09 (dd, J^{1,2}=2.7 Hz, J^{1,3}=8.7 Hz, 1H), 7.16 (d, J=2.6 Hz, 1H), 7.27 (d, J=9.0 Hz, 1H).



Fig. S49 ¹H NMR spectrum of [MCPP-DAE-C₁₀][4-CPA].



Fig. S50 ¹³C NMR spectrum of [MCPP-DAE-C₁₀][4-CPA].



Fig. S51 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][2,4-D].



Fig. S52 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][2,4-D].



Fig. S53 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][MCPA].



Fig. S54 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][MCPA].



Fig. S55 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][MCPP].



Fig. S56 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][MCPP].



Fig. S57 ¹H NMR spectrum of [MCPA-DAE-C₁₀] [Clopyralid].



Fig. S58 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][Clopyralid].



Fig. S59 ¹H NMR spectrum of **[MCPA-DAE-C**₁₀]**[Dicamba]**.



Fig. S60 ¹³C NMR spectrum of [MCPA-DAE-C₁₀][Dicamba].



Fig. S61 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][Clopyralid].



Fig. S62 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][Clopyralid].



Fig. S63 ¹H NMR spectrum of [4-CPA-DAE-C₁₀][Dicamba].



Fig. S64 ¹³C NMR spectrum of [4-CPA-DAE-C₁₀][Dicamba].

Table	S5	Germination	Index	(GI)	values	for	seedlings	growing	in	soil	with	addition	of	HILs	(mean
value	s of	three replicat	es (±SI	D))											

	Abbreviation of sample	GI [%] ± SD				
	2,4-D + MCPA	6.65 ± 1.01				
	[2,4-D-DAE-C ₁₀][MCPA]	9.31 ± 1.96				
	[MCPA-DAE-C ₁₀][2,4-D]	7.49 ± 1.46				
	2,4-D + MCPP	4.82 ± 2.14				
	[2,4-D-DAE-C ₁₀][MCPP]	0				
S	[MCPP-DAE-C ₁₀][2,4-D]	4.82 ± 0.41				
suce	2,4-D + 4-CPA	14.81 ± 1.85				
ere	[2,4-D-DAE-C ₁₀][4-CPA]	7.98 ± 0.95				
ref	[4-CPA-DAE-C ₁₀][2,4-D]	6.32 ± 1.08				
pu	MCPA + MCPP	6.49 ± 1.87				
Ра	[MCPA-DAE-C ₁₀][MCPP]	10.19 ± 1.40				
ILS	[MCPP-DAE-C ₁₀][MCPA]	6.99 ± 0.84				
Т	MCPA + 4-CPA	8.98 ± 0.73				
	[MCPA-DAE-C ₁₀][4-CPA]	5.32 ± 0.66				
	[4-CPA-DAE-C ₁₀][MCPA]	15.48 ± 0.81				
	MCPP + 4-CPA	9.31 ± 1.86				
	[MCPP-DAE-C ₁₀][4-CPA]	19.46 ± 1.34				
	[4-CPA- DAE-C ₁₀][MCPP]	23.45 ± 2.73				
S	MCPA + Clopyralid	4.82 ± 0.90				
su ce	[MCPA-DAE-C ₁₀][Clopyralid]	3.16 ± 0.11				
ere	MCPA + Dicamba	13.64 ± 1.61				
ref	[MCPA-DAE-C ₁₀][Dicamba]	5.99 ± 0.45				
pu	4-CPA + Clopyralid	32.06 ± 1.17				
В	[4-CPA-DAE-C ₁₀][Clopyralid]	32.77 ± 1.59				
ILS	4-CPA + Dicamba	25.12 ± 1.56				
Ξ	[4-CPA-DAE-C ₁₀][Dicamba]	22.29 ± 1.51				
Table S6 Mutagenic activity expressed by the number of revertants and mutagenic index (*MI*) in strains TA98, TA100, TA1535 and TA1537 of *Salmonella typhimurium* exposed to HILs [2,4-D-DAE-C₁₀][MCPP] and [MCPA-DAE-C₁₀][Clopyralid] with (+S9) or without (-S9) metabolic activation. Data were presented as mean number of revertants (±SD) induced spontaneously in control cultures (*R*s) and in the cultures treated with reference mutagen or HCJ tested (*R*i). ^a*p*<0.05, ^b*p*<0.01, ^c*p*<0.001 significant differences in relation to spontaneous mutations determined in control cultures

Bacteria strain	Control	Mutagen		[2,4-D-DAE-C 10][MCPP] (10 μg/plate)		[MCPA-DAE-C ₁₀][Clopyralid] (10 µg/plate)	
	Rs	Ri	MI	Ri	MI	Ri	MI
TA98							
-S9	17 ± 3	87 ± 16 ^b	5.3	37 ± 7 ª	2.2	28 ± 7	1.6
+\$9	107 ± 4	215 ± 4 ^c	2.0	129 ± 10 ª	1.2	106 ± 13	1.0
TA100							
-S9	35 ± 9	316 ± 24 ^c	9.0	67 ± 12 ª	2.0	43 ± 7	1.2
+S9	128 ± 22	293 ± 10 ^c	2.3	193 ± 30 ª	1.5	201 ± 22 ^a	1.6
TA1535							
-S9	11 ± 5	395 ± 32 ^c	37.0	13 ± 5	1.4	18 ± 11	1.6
+S9	77 ± 11	189 ± 9 ^c	2.4	132 ± 5 ^b	1.7	102 ± 9 ^a	1.3
TA1537							
-S9	6 ±2	129 ± 5 ^c	24.5	3 ± 1	0.5	2 ± 2	0.3
+S9	34 ± 3	357 ± 25 ^c	10.7	64 ± 4 ^c	1.9	56 ± 3 ^c	1.6