Calculation method for ^{1}H NMR spectroscopy.

The acid composition can be calculated from NMR spectrum. An area per proton (U) can be determined [1].

$$U = \frac{1}{3} \times \left[\frac{c}{2} + \frac{e}{2} + \frac{g}{3} \right] \quad [1]$$

Often, the e peak had a bad resolution because of the signal of methylene protons of remaining PhosIL overlapping with this signal.

So in order to have a good area per proton (U'), e integrals will be deleted giving formula [2].

$$U' = \frac{1}{2} \times \left[\frac{c}{2} + \frac{g}{3} \right] \quad [2]$$

The products of linoleic acid hydrogenation in ILs were saturated acid (X), mono-unsaturated acid (Y) and poly-unsaturated acid (Z). The hypothesis that only these compounds were formed was made and gave relation [3].

$$X + Y + Z = 1 \quad [3]$$

The proportion of unsaturated compounds Y and Z can be determined from olefenic protons area, divinyl methylene protons area, and allyl methylene protons area (a, b and d respectively).

$$\frac{a}{2 \times U'} = 2 \times Z + Y \quad [4]$$

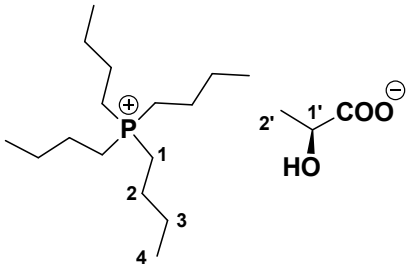
$$\frac{b}{2 \times U'} = Z \quad [5]$$

$$\frac{d}{4 \times U'} = Y + Z \quad [6]$$

The saturated acid proportion X can be calculated from [3] and [6].

$$X = 1 - \frac{d}{4 \times U'} \quad [7]$$

Tetrabutylphosphonium L-lactate **1**



The general procedure (pathway **A**) was followed with 0.9 mL L-lactic acid. A colourless oil was obtained (3.20 g, 87 %).

$[\alpha]_D^{20}$ = -3 (C 0.49, H_2O)

IR (film) cm^{-1}: 3386, 2963, 2925, 1601, 1458, 1229, 1089, 970, 837, 700 cm^{-1}

NMR ^{1}H (500.1 MHz, $CDCl_3$) δ: 0.9 (12H, t, J= 6.8 Hz, H4), 1.27 (3H, d, J= 6.7 Hz, H2'), 1.45 (16H, m, H3, H2), 2.24 (8H, m, H1), 3.88 (1H, q, J= 6.7 Hz, H1')

NMR ^{13}C (125.7 MHz, $CDCl_3$) δ: 13.4 (C4), 18.9 (C1), 21.6 (C2'), 23.7 (C2), 23.9 (C3), 68.2 (C1'), 180.0 (C=O)

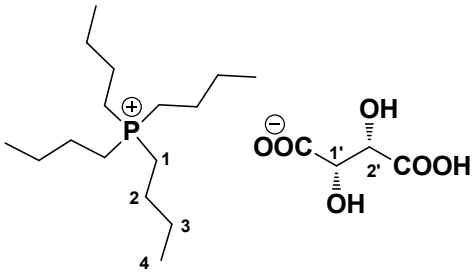
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 33.08 (s)

MS: (+) 259 (-) 89

Calculated for $C_{19}H_{41}PO_3$. H_2O, C: 62.26 %; H: 11.82 %

Found C: 62.38 %; H: 12.09 %

Tetrabutylphosphonium L-tartrate **2**



The general procedure (pathway **A**) was followed with 1.8 g L-tartaric acid. A viscous oil was obtained (3.50 g, 81 %).

$[\alpha]_D^{20}$ = +11 (C 0.53, H_2O)

IR (film) ν: 3376, 2959, 2874, 1710, 1605, 1410, 1315, 1069, 915, 813 cm^{-1}

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.95 (12H, t, J= 7.2 Hz, H4), 1.5 (16H, m, H3, H2), 2.2 (8H, m, H1), 4.1 (2H, s, H1', H2')

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.4 (C4), 18.5 (C1), 23.6 (C2), 23.7 (C3), 71.3 (C1',C2'), 175.3 (C=O)

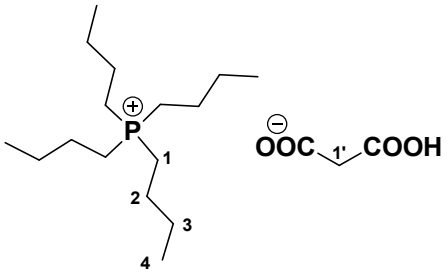
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 33.17 (s)

MS: (+) 259 (-) 149

Calculated for $C_{20}H_{41}PO_6$. 1,3 H_2O C: 55.62%; H: 10.17 %

Found C: 55.56%; H: 9.81 %

Tetrabutylphosphonium malonate **3**



The general procedure (pathway **A**) was followed with 1.24 g of malonic acid. A white wax was obtained (3.58 g, 92 %).

IR (film) ν: 3437, 2966, 2929, 2867, 2232, 1707, 1628, 1355, 1192, 1096, 751 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.95 (12H, t, J= 6.9 Hz, H4), 1.52 (16H, m, H3, H2), 2.29 (8H, m, H1), 3.06 (2H, s, H1')

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.4 (C4), 18.5 (C1), 23.6 (C2), 23.9 (C3), 38.6 (C1'), 173.3 (C=O)

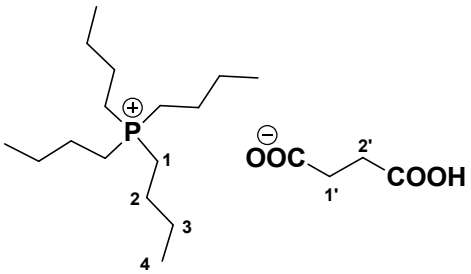
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 33.17 (s)

MS: (+) 259 (-) 103

Calculated for $C_{19}H_{39}PO_4$. 1.5 H_2O, C: 58.59%; H: 10.87 %

Found C: 55.78%; H: 10.43 %

Tetrabutylphosphonium succinate **4**



The general procedure (pathway **A**) was followed with 1.42 g of succinic acid. A colourless oil was obtained (3.50 g, 91 %).

IR (film) ν: 3457, 2963, 2932, 2871, 2737, 1929, 1413, 1315, 1096, 915, 799, 704 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.96 (12H, t, J= 7.0 Hz, H4), 1.51 (16H, m, H3, H2), 2.26 (8H, m, H1), 2.53 (4H, s, H1', H2')

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.4 (C4), 18.5 (C1), 23.6 (C2), 23.9 (C3), 32.5 (C1', C2'), 177.4 (C=O)

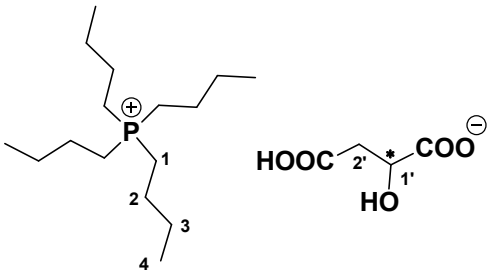
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 32.95 (s)

MS: (+) 259 (-) 117

Calculated for $C_{20}H_{41}PO_4$. 0.75 H_2O, C: 61.59%; H: 10.98 %

Found C: 61.59%; H: 10.92 %

Tetrabutylphosphonium L-malate **5**



The general procedure (pathway A) was followed with 1.62 g of L-malic acid. A white wax was obtained (3.76 g, 92 %).

IR (film) ν: 3396, 2959, 2929, 2871, 1717, 1598, 1461, 1413, 1355, 1089, 912, 809, 775, 707 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.93 (12H, t, J= 6.9 Hz, H4), 1.48 (16H, m, H3, H2), 2.21 (8H, m, H1), 2.7 (2H, m, H2'), 4.1 (1H, dd, J= 5.3, J= 8.99 Hz, H1')

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.4 (C4), 18.5 (C1), 23.6 (C2), 23.9 (C3), 41.5 (C2'), 66.2 (C1'), 173.9 (C=O), 78.2 (C=O)

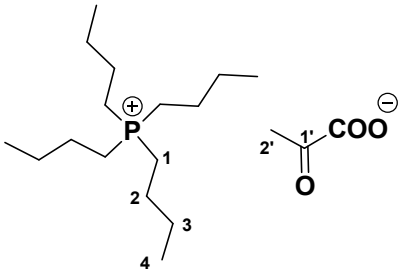
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 33.18 (s)

MS: (+) 259 (-) 117

Calculated for $C_{20}H_{41}PO_5$. 0.8 H_2O, C: 59.03%; H: 10.55 %

Found C: 59.09%; H: 10.55 %

Tetrabutylphosphonium pyruvate **6**



The general procedure (pathway **A**) was followed with 0.83 mL of pyruvic acid. A yellow oil was obtained (3.30 g, 87 %).

IR (film) ν: 2935, 2871, 1725, 1461, 1375, 1338, 1059 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.89 (12H, t, J= 7.0 Hz, H4), 1.44 (16H, m, H3, H2), 2.24 (8H, m, H1), 2.26 (3H, s, H2')

^{13}C NMR (63 MHz, $CDCl_3$) δ: 13.0 (C4), 18.4 (C1), 23.9 (C2), 23.8 (C3), 27.3 (C2'), 169.0 (C=O ketone), 205.0 (C=O carboxylate)

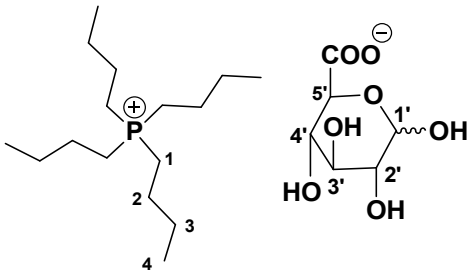
^{31}P NMR (202 MHz, $CDCl_3$) δ: 33.18 (s)

MS: (+) 259 (-) 87

Calculated for $C_{19}H_{39}PO_3$. 1.75 H_2O, C: 60.37%; H: 11.33 %

Found C: C: 60.45%; H: 10.43 %

Tetrabutylphosphonium D-glucuronate **7**



The general procedure (pathway **B**) was followed with 2.30 g of D-glucuronic acid. A white wax was obtained (3.1 g, 80 %).

$[\alpha]_D^{20}$ = +11 (C 0.49, H_2O)

IR (film) ν: 3410, 2959, 2867, 2512, 1605, 1420, 1158, 1055, 908, 789 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.93 (12H, t, J= 6.6 Hz, H4), 1.48 (16H, m, H3, H2), 2.25 (8H, m, H1), 3.31 (0.5H, m, H2'β), 3.46 (1H, m, H3'β, H4'α), 3.55 (0.5H, m, H5'β), 3.80 (0.5, m, H2'α), 4.11 (1H, m, H3'α, H4'β), 4.47 (0.5H, m, H5'α), 5.2 (0.5H, m, H1'β), 5.4 (0.5H, m, H1'α)

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.0 (C4), 18.0 (C1), 23.1 (C2), 23.8 (C3), 71.6 (C2'α), 71.8 (C5'α), 72.1 (C5'β), 72.4 (C3'β), 72.9 (C3'α), 74.3 (C2'β), 75.9 (C4'α), 76.2 (C4'β), 96.6 (C1'α), 97.5 (C1'β), 174 (C=O α),175 (C=O β)

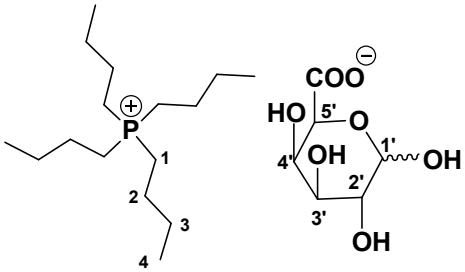
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 32.95 (s)

MS: (+) 259 (-) 193

Calculated for $C_{22}H_{45}PO_7$. 1.75 H_2O, C: 54.59%; H: 10.10%

Found C: 54.59%; H: 9.55%

Tetrabutylphosphonium D-galacturonate **8**



The general procedure (pathway **B**) was followed with 2.64 g of D-galacturonic acid. A white wax was obtained (2.99 g, 77 %).

$[\alpha]_D^{20}$ = +19 (C 0.55, H_2O)

IR (film) ν: 3396, 2956, 2935, 2864, 2499, 1601, 1465, 1407, 1308, 1226, 1147, 1082, 1038, 970, 908, 796 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.97 (12H, t, J= 6.4 Hz, H4), 1.51 (16H, m, H3, H2), 2.27 (8H, m, H1), 3.92 (1.5H, m, H2'α, H3'β, H2'β), 4.01(0.5H, m, H3'α), 4.14 (0.5H, m, H5'β), 4.1 (0.5H, m, H4'β), 4.24 (0.5H, m, H4'α), 4.3 (0.5H,m, H5'α), 4.68 (0.5H, m, H1'β), 5.2 (0.5H, m, H1'α)

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.0 (C4), 17.6 (C1), 23.1 (C2), 23.7 (C3), 68.4 (C2'α), 69.6 (C3'α), 70.6 (C4'β), 71.2 (C4'α), 71.8 (C5'α), 71.9 (C2'β), 73.2 (C3'β), 75.6 (C5'β), 92.6 (C1'α), 101.4 (C1'β), 175.4 (C=O α), 176.2 (C=O β)

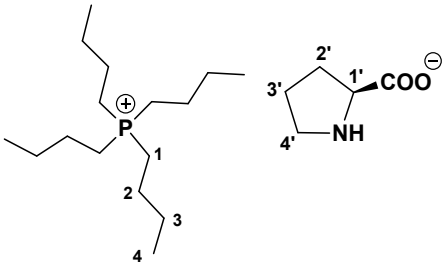
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 32.93 (s)

MS: (+) 259 (-) 193

Calculated for $C_{22}H_{45}PO_7$. 1.9 H_2O, C: 54.28%; H: 10.10%

Found C: 54.28%; H: 9.68%

Tetrabutylphosphonium S-prolinate **9**



The general procedure (pathway **A**) was followed with 1.69 g of *S*-proline. A yellow oil was obtained (3.6 g, 87 %).

$[\alpha]_D^{20}$ = -21 (C 0.55, H_2O)

IR (film) ν: 3396, 2956, 2935, 2864, 2499, 1601, 1465, 1407, 1308, 1226, 1147, 1082, 1038, 970, 908, 796 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 0.97 (12H, t, J= 6.4 Hz, H4), 1.51 (16H, m, H3, H2), 2.27 (8H, m, H1), 3.92 (1.5H, m, H2'α, H3'β, H2'β), 4.01(0.5H, m, H3'α), 4.14 (0.5H, m, H5'β), 4.1 (0.5H, m, H4'β), 4.24 (0.5H, m, H4'α), 4.3 (0.5H,m, H5'α), 4.68 (0.5H, m, H1'β), 5.2 (0.5H, m, H1'α)

^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.0, 17.6, 23.1, 23.7, 68.4, 69.6, 70.6, 71.2, 71.8, 71.9, 73.2, 75.6, 92.6, 101.4, 175.4 (C=O),1176.2 (C=O)

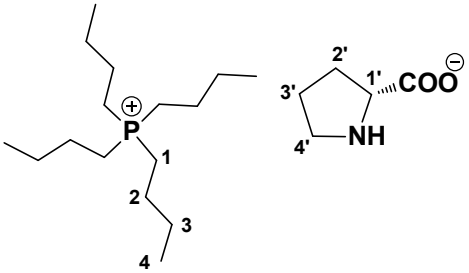
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 32.93 (s)

MS: (+) 259 (-) 114

Calculated for $C_{21}H_{44}NPO_2$. 2.25 H_2O, C: 60.91%; H: 11.80%; N: 3.38%

Found C: 61.05%; H: 11.51%; N: 3.64%

Tetrabutylphosphonium R-prolinate **10**



The general procedure (pathway **A**) was followed with 1.38 g of *R*-proline. A yellow oil was obtained (3.64 g, 94 %).

$[\alpha]_D^{20}$ = +21 (C 0.53, H_2O)

IR (film) ν: 3409, 2959, 2872, 1618, 1410, 1311, 1096, 1005, 916, 817, 719 cm^{-1}

^{1}H NMR (500 MHz, D_2O) δ: 0.91 (12H, t, J= 7.1 Hz, H4), 1.5 (16H, m, H3, H2), 1.92 (4H, m, H2'a, H2'b, H3'), 2.14 (8H, m, H1), 3.13 (1H, m, H4'b), 3.26 (1H, m, H4'a), 3.90 (1H, m, H1')

^{13}C NMR (125.7 MHz, D_2O) δ: 12.5 (C4), 17.2 (C1), 22.65 (C2), 23.1 (C3), 24.15 (C3'), 29.5 (C2'), 46.0 (C4'), 61.3 (C1'), 181.6 (C=O)

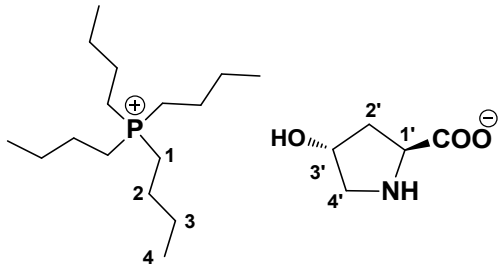
^{31}P NMR (202.4 MHz, D_2O) δ: 33.52 (s)

MS: (+) 259 (-) 114

Calculated for $C_{21}H_{44}NPO_2$. 0.75 H_2O, C: 65.16%; H: 11.85%; N: 3.62%

Found C: 61.21%; H: 11.90%; N: 3.63%

Tetrabutylphosphonium 4-hydroxy-S-prolinate **11**



The general procedure (pathway **A**) was followed with 1.60 g of 4-hydroxy-*S*-prolinate. A yellow oil was obtained (3.7 g, 90 %).

$[\alpha]_D^{20}$ = - 19 (C 0.53, H_2O)

IR (film) ν: 3382, 2870, 1583, 1416, 1232, 1091, 916, 821, 605 cm^{-1}.

^{1}H NMR (500.1 MHz, D_2O) δ: 0.94 (12H, t, J= 7.1 Hz, H4), 1.45 (8H, m, H3), 1.55 (8H, m, H2), 2.01(1H, m, H2'a), 2.16 (8H, m, H1), 2.24 (1H, m, H2'b), 2.99 (1H, m, H4'a), 3.35 (1H, m, H4'b), 3.96 (1H, m, H3'), 4.53 (1H, m, H1')

^{13}C NMR (125.7 MHz, D_2O) δ: 12.52 (C4), 17.43 (C1), 22.3 (C2), 23.3 (C3), 38.8 (C2'), 53.4 (C4'), 60.0 (C1'), 71.0 (C3'), 182 (C=O)

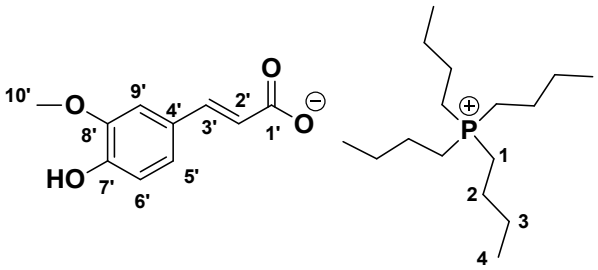
^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 32.95 (s)

MS: (+) 259 (-) 130

Calculated for $C_{21}H_{45}NPO_3$. 1.2 H_2O, C: 61.34%; H: 11.37%; N: 3.41%

Found C: 61.41%; H: 11.30%; N: 3.38%

Tetrabutylphosphonium ferulate **12**



The general procedure (pathway C) was followed with 2.30 g of ferulic acid. A white solid was obtained (4.06 g, 86 %).

Mp: 115°C

IR (film) ν: 3525, 2870, 1855, 1635, 1591, 1518, 1375, 1037, 705, 572 cm^{-1}.

^{1}H NMR (500.1 MHz, D_2O) δ: 0.79 (12H, t, J= 6.9 Hz, H4), 1.32 (16H, m, H3, H2), 1.89 (8H, m, H1), 3.76 (3H, s, H10'), 6.22 (1H, d, J= 16.1 Hz, H2'), 6.75 (1H, d, J= 8.6 Hz, H5'), 7.00 (1H, d, J= 8.6 Hz, H6'), 7.16 (2H, m, H9', H3')

^{13}C NMR (125.7 MHz, D_2O) δ: 12.53 (C4), 17.1 (C1), 22.6 (C2), 23.1 (C3), 55,9 (C10'), 110,9 (C9'), 115.7 (C6'), 121,9 (C5'), 122.1 (C4'), 123.0 (C2'), 127.7 (C7'), 127.8 (C8'), 140.7 (C3'), 175.0 (C=O)

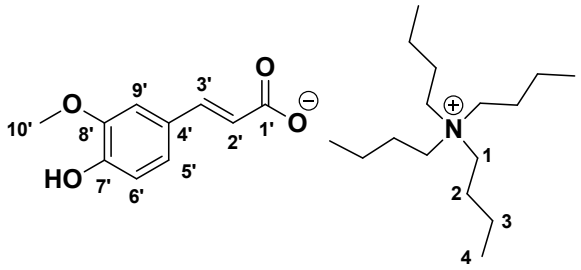
^{31}P NMR (202.4 MHz, D_2O) δ: 32.99 (s)

MS: (+) 259 (-) 193

Calculated for $C_{26}H_{45}PO_4$. 1.1 H_2O, C: 66.10%; H: 10.07%

Found C: 65.99%; H: 9.86%

Tetrabutylammonium ferulate **13**



The general procedure (pathway D') was followed with 2.30 g of ferulic acid. A white solid was obtained (4 g, 92 %).

Mp: 119°C

IR (film) ν: 3555, 2961, 2874, 1856, 1633, 1518, 1372, 1251, 1032, 704, 573 cm^{-1}.

^{1}H NMR (500.1 MHz, $CDCl_3$) δ: 1.00 (12H, t, J = 7.8 Hz, H4), 1.37 (8H, m, H3), 1.62 (8H, m, H2), 3.21 (8H, m, H1), 3.86 (3H, s, H10'), 6.28 (1H, d, J= 16.1 Hz, H2'), 6.73 (1H, d, J= 8.77 Hz, H5'), 6.95 (1H, d, J= 10.1 Hz, H6'), 7.10 (1H, s, H9'), 7.30 (1H, d, J= 16.1 Hz , H3')

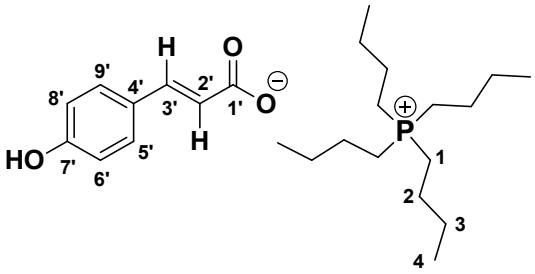
^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 13.3 (C4), 19.8 (C3), 25.0 (C2), 56.3 (C10'), 60.1 (C1), 111.8 (C9'), 117.2 (C6'), 120.6 (C5'), 123.9 (C4'), 130.2 (C2'), 137.5 (C7'), 142.3 (C8'), 150.8 (C3'), 172 (C=O)

MS: (+) 242 (-) 193

Calculated for $C_{26}H_{45}NO_4$. 0.75 H_2O, C: 69.53%; H: 10.43%, N: 3.12%

Found C: 69.34%; H: 10.10%, N: 3.10%

Tetrabutylphosphonium p-coumarate **14**



The general procedure (pathway D) was followed with 1.90 g of *p*-coumaric acid. A white solid was obtained (3.9 g, 89 %).

Mp: 145°C

IR (film) ν: 3412, 3020, 2465, 1865, 1630, 1589, 1554, 1350, 985, 708, 522 cm^{-1}.

^{1}H NMR (500.1 MHz, D_2O) δ: 0.9 (12H, t, J= 7.1 Hz, H4), 1.49 (16H, m, H3, H2), 2.10 (8H, m, H1), 6.3 (1H, d, J= 16.1 Hz, H2'), 6.91 (2H, m, H6', H8'), 7.33 (1H, d, J= 17.4 Hz H9'), 7.55 (2H, m, H3', H5')

^{13}C NMR (125.7 MHz, D_2O) δ: 12.5 (C4), 17.2 (C1), 22.6 (C2), 23.1 (C3), 115.7 (C6', C8'), 121.6 (C4'), 128.2 (C2'), 129.6 (C5', C9'), 138.0 (C3'), 140.5 (C7'), 181.6 (C=O)

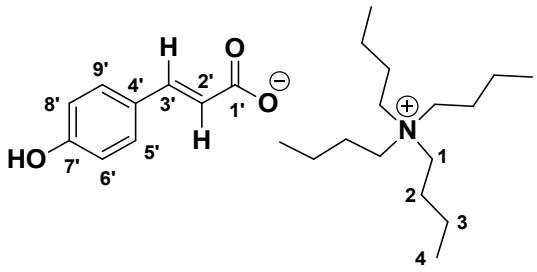
^{31}P NMR (202.4 MHz, D_2O) δ: 33.08 (s)

MS: (+) 249 (-) 163

Calculated for $C_{25}H_{43}PO_3$. 1 H_2O, C: 68.15%; H: 10.29%

Found C: 68.01%; H: 10.10%

Tetrabutylammonium p-coumarate **15**



The general procedure (pathway D') was followed with 1.90 g of p-coumaric acid. A white solid was obtained (3.8 g, 94 %).

Mp: 150°C

IR (film) ν: 3446, 3017, 2962, 2873, 1870, 1633, 1601, 1514, 1352, 988, 706, 521 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.00 (12H, t, J = 7.4 Hz, H4), 1.46 (16H, m, H3, H2), 3.35 (8H, m, H1), 6.20 (1H, d, J= 17.4 Hz, H2'), 6.64 (2H, m, H6', H8'), 7.25 (3H, m, H9', H5', H3')

^{13}C NMR (63 MHz, $CDCl_3$) δ: 13.4 (C4), 19.6 (C3), 23.4 (C2), 55.3 (C1), 114.9 (C6', C8'), 126.4 (C4'), 130.3 (C2'), 131.2 (C5', C9'), 145.5 (C3'), 158.0 (C7'), 174.8 (C=O)

MS: (+) 242 (-) 163

Calculated for $C_{26}H_{43}NO_3$. 0.3 H_2O, C: 73.06%; H: 10.69%, N: 3.41%

Found C: 73.06%; H: 10.63%, N: 3.34%