Supporting Information

Experimental

Chemicals and solvents were obtained from various commercial sources and used without further purification unless otherwise stated. Thin layer chromatography was performed on glass-backed silica-gel 60 F_{254} and/or neutral aluminium oxide plates. Column chromatography was performed on silica gel 60A. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ unless otherwise stated on either a Jeol JNM FX 200 MHz or a 400 MHz Bruker DMX 400 spectrometer. All chemical shifts are reported in δ (ppm) using the residual proton impurities of the NMR solvent as an internal reference and *J* values are reported in Hz. Mass spectra EI, FAB and MALDI mass spectra were obtained by the chemistry department at Imperial College London. UV-absorption spectra were measured on a HP 8453 diode-array spectrometer using spectroscopic grade chloroform or dichloromethane. Infrared spectra were measured as KBr discs or as thin-films between NaCl plates using a Perkin Elmer FTIR 1720 spectrometer.

Dodecyrylmethylenetriphenylphosphane, ***8***

To a stirred solution of acetylmethyltriphenylphosphane **7** (19 g, 0.06 mol) in dry THF (450 ml) under nitrogen at -78^{o}C was added *n*-butyllithium (37.5 ml, of 1.6M solution in hexanes). The resultant red solution was then stirred for 20 min. before the slow addition of 1-bromodecane (13.27 g, 0.06 mol) maintaining the temperature at -78^{o}C. On complete addition the reaction mixture was slowly allowed to reach room temperature overnight. The THF was removed *in vacuo* and the residue dissolved in DCM (100 ml) this was then washed with water (2 x 100 ml), dried over anhydrous $MgSO_4$, filtered and concentrated to afford the desired product as a clear oil; yield 27.1 g (99%). ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.67-7.40 (m, 15H, Ar-H), 3.75 (d, 1H, P=CH), 2.31 (t, 2H, $COCH_3CH_2R$), 1.70-1.63 m, 2H, $COCH_2CH_2R$), 1.35-1.24 (m,16H, CH_2), 0.89 (t, 3H, CH_3CH_2R); MS (EI) found m/z = 458 (M^+, 39%) requires m/z = 458; FTIR (NaCl) ν_{max} : 3056, 2924, 2852, 1536 (carbonyl), 1583, 1482 (aromatic), , 1435, 1158, 1106 (phenyl-P) cm^{-1}.

*Decyrylmethylenetriphenylphosphane **9***

This was synthesised following the same procedure for compound **8**. Quantities: acetylmethyltriphenylphosphane **7** (19.0 g, 0.016 mol), *n*-butyllithium (37.5 ml of a 1.6 M solution in hexanes), 1-bromooctane (11.59 g, 0.06 mol) and anhydrous THF (450 ml); yield 25.41 g (99%). ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.66-7.40 (m, 15H, Ar-H), 3.75 (d, 1H, P=CH), 2.31 (t, 2H, $COCH_3CH_2R$); 1.70-1.64 m, 2H, $COCH_2CH_2R$), 1.31-1.23 (m,16H, CH_2), 0.89 (t, 3H, CH_3CH_2R); MS (EI) found m/z = 430 (M^+, 14%) requires m/z = 430; FTIR (NaCl) ν_{max} : 3056, 3000-2840, 1560 (carbonyl), 1498, 1450 (aromatic), 1405, 1115, 1110 (phenyl-P) cm^{-1}.

*Octyrylmethylenetriphenylphospharane **10***

This was synthesised following the same procedure for compound **8**. Quantities: acetylmethyltriphenylphosphane **7** compound (15.0 g, 0.047 mol), *n*-butyllithium (29.4 ml of a 1.6 M solution in hexanes), 1-bromohexane (7.80 g, 0.047 mol) and anhydrous THF (450 ml); yield 17.10 g (91%). ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.77-7.40 (m, 15H, Ar-H), 3.75 (d, 1H, P=CH), 2.31 (t, 2H, $COCH_3CH_2R$), 1.67-1.60 m, 2H, $COCH_2CH_2R$), 1.33-1.20 (m,16H, CH_2), 0.88 (t, 3H, CH_3CH_2R); MS (EI) found m/z = 402 (M^+, 39%) requires m/z = 402; FTIR (NaCl) ν_{max} : 3070, 2924, 2852, 1536 (carbonyl), 1583, 1482 (aromatic), , 1435, 1158, 1106 (phenyl-P) cm^{-1}.

*13-Hexaeicsene-12-one **11***

A solution of **8** (27.0 g, 0.059 mol) and tridecanal (11.68 g, 0.059 mol) was refluxed in anhydrous DCM (250 ml) under nitrogen for 24 h. The DCM was then reduced in volume and pentane added until precipitation was complete. This was filtered and the filtrate concentrated to afford an oil which was purified by chromatography on silica gel with hexane containing diethyl ether (20%) as eluant. The ketone **11** was obtained as a white solid; yield 14.82 g (65%), M.p 44-46^{o}C. ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 6.86-6.78 (dt, 1H, CH_A=C$\underline{H}_B$$CH_{2C}$, J_{AB} =15.68 Hz and J_{BC} =6.89 Hz), 6.11-6.05 (dt, 1H, C$\underline{H}_A$=$CH_B$$CH_{2C}$, J_{AB} =16.02 Hz and J_{AC} =1.45 Hz), 2.52

(t, 2H, $RCH_2C\underline{H}_2CO$), 2.23-2.17 (m, 2H, $CH_2C\underline{H}_2CHC$=), 1.64-1.57 (m, 2H, $RC\underline{H}_2CH_2CO$), 1.47-1.42 (m, 2H, $RC\underline{H}_2CH_2CH$=), 1.40-1.22 (m, 34H, alkyl-H), 0.88 (t, 6H, 2x -CH_3). MS (EI) found m/z 378 (M^+, 85%) requires m/z 378; FTIR ν_{max}: 2912, 2850, 1678 (carbonyl), 1640 (alkene) cm^{-1}.

*11-Doeicosene-10-one **12***

This was synthesised following the same procedure for compound **11**. Quantities: compound **9** (25.80 g, 0.06 mol), undecyclic aldehyde (10.20 g, 0.06 mol) and anhydrous DCM (250 ml). Purified by chromatography on silica gel with hexane containing diethyl ether (20%) as eluant. The ketone **12** was obtained as a viscous oil which solidified on standing; yield 12.03 g (62%), M.p 30-33^oC. ^1H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 6.86-6.78 (dt, 1H, CH_A=$C\underline{H}_BCH_{2C}$, J_{AB} =15.84 Hz and J_{BC} =6.91 Hz), 6.11-6.04 (dt, 1H, $C\underline{H}_A$=CH_BCH_{2C}, J_{AB} =15.89Hz and J_{AC} =1.42 Hz), 2.52 (t, 2H, $RCH_2C\underline{H}_2CO$), 2.23-2.17 (m, 2H, $CH_2C\underline{H}_2CHC$=), 1.62-1.54 (m, 2H, $RC\underline{H}_2CH_2CO$), 1.47-1.42 (m, 2H, $RC\underline{H}_2CH_2CH$=), 1.40-1.23 (m, 34H, alkyl-H), 0.88 (t, 6H, 2x -CH_3). MS (EI) found m/z 322 (M^+, 77%) requires m/z 322 FTIR ν_{max}: 2920, 2852, 1674 (carbonyl), 1628 (alkene) cm^{-1}.

*9-Octadecene-8-one **13***

This was synthesised following the same procedure for compound **11**. Quantities: compound **10** (19.0 g, 0.047 mol), nonyl aldehyde (6.68 g, 0.047 mol) and anhydrous DCM (200 ml). Purified by chromatography on silica gel with hexane containing diethyl ether (10%) as eluant. The ketone **13** was obtained as a clear oil; yield 9.0 g (72%). ^1H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 6.86-6.78 (dt, 1H, CH_A=$C\underline{H}_BCH_{2C}$, J_{AB} =16.11 Hz and J_{BC} =7.14 Hz), 6.13-6.04 (dt, 1H, $C\underline{H}_A$=CH_BCH_{2C}, J_{AB} =16.11Hz and J_{AC} =1.47 Hz), 2.52 (t, 2H, $RCH_2C\underline{H}_2CO$), 2.19 (m, 2H, $CH_2C\underline{H}_2CHC$=), 1.67-1.54 (m, 2H, $RC\underline{H}_2CH_2CO$), 1.47-1.42 (m, 2H, $RC\underline{H}_2CH_2CH$=), 1.41-1.23 (m, 34H, alkyl-H), 0.88 (t, 6H, 2x -CH_3). MS (EI) found m/z 266 (M^+, 26%) requires m/z 266; FTIR ν_{max}: 2920, 2852, 1688 (carbonyl), 1638 (alkene) cm^{-1}.

3-Dodecyl-4-dodecanoylpyrrole ***14***

A solution of toluenesulphonylmethyl isocyanide TosMIC (7.48 g, 0.038 mol) and compound **11** (14.50 g, 0.038 mol) in 2:1 anhydrous ether/anhydrous DMSO (270 ml) was slowly added to a stirred suspension of sodium hydride (1.84 g of a 60% dispersion in mineral oil, 0.077 mol) in anhydrous ether (100 ml) under nitrogen. After addition the reaction was stirred for 30 min. before being quenched by the careful addition of water (60 ml). The ether layer was separated and the aqueous layer back extracted with ether (3 x 150 ml). The combined ether extracts was dried over $MgSO_4$, filtered and evaporated to give an oil. Purification by chromatography on silica gel with a 1:1 mixture of hexane and ether as eluant gave the pyrrole as a white solid; yield 3.98 g (25%), M.p 66-68^oC. ^1H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 8.31 (broad s, 1H, pyrrole-N$\underline{H}$, exchangeable with D_2O), 7.36 (m, 1H, pyrrole-$C_2\underline{H}$), 6.56 (m, 1H, pyrrole-$C_5\underline{H}$), 2.78-2.69 (overlapping t, 4H, pyrrole-C_4-C$\underline{H}_2$ and COC$\underline{H}_2$), 173-1.65 (m, 2H, $COCH_2C\underline{H}_2$), 1.58-1.52 (m, 2H, pyrrole-$C_4CH_2C\underline{H}_2$), 1.32-1.24 (m, 34H, alkyl-H), 0.88 (t, 6H, -C$\underline{H}_3$). MS (EI) found m/z 417 (M^+, 78 %) requires m/z 417; FTIR ν_{max}: 3210 (pyrrole NH), 2920, 2848, 2848, 1622 (carbonyl) cm^{-1}.

3-Decyl-4-decanoylpyrrole ***15***

This was synthesised following the same procedure for compound **14**. Quantities: TosMIC (7.27 g, 0.037 mol), compound **12** (12.0 g, 0.037 mol), and NaH (1.80 g, 0.075 mol) in 2:1 ether/DMSO (260 ml). Purified by chromatography on silica gel with a 1:1 mixture of hexane and ether as eluant to give the pyrrole as a white solid; yield 3.43 g (25%), M.p 51-53^oC. ^1H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 8.32 (broad s, 1H, pyrrole-N$\underline{H}$, exchangeable with D_2O), 7.36 (m, 1H, pyrrole-$C_2\underline{H}$), 6.56 (m, 1H, pyrrole-$C_5\underline{H}$), 2.78-2.67 (overlapping t, 4H, pyrrole-C_4-C$\underline{H}_2$ and COC$\underline{H}_2$), 1.71-1.62 (m, 2H, $COCH_2C\underline{H}_2$), 1.58-1.52 (m, 2H, pyrrole-$C_4CH_2C\underline{H}_2$), 1.32-1.23 (m, 26H, alkyl-H), 0.88 (t, 6H, -C$\underline{H}_3$). MS (EI) found m/z 361 (M^+, 100 %) requires m/z 361; FTIR ν_{max}: 3280 (pyrrole NH), 2920, 2852, 1632 (carbonyl) cm^{-1}.

3-Octyl-4-octanoylpyrrole ***16***

This was synthesised following the same procedure for compound **14**. Quantities: TosMIC (2.93 g, 0.015 mol), compound **13** (4.0 g, 0.015 mol), and NaH (1.20 g, 0.030 mol) in 2:1 ether/DMSO (100 ml). Purified by chromatography on silica gel with a 1:1 mixture of hexane and ether as eluant to give the pyrrole as a white solid; yield 1.93 g (42%), M.p 62-65^{o}C. ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 9.0 (broad s, 1H, pyrrole-N<u>H</u>, exchangeable with D_2O), 7.35 (m, 1H, pyrrole-C_2<u>H</u>), 6.55 (m, 1H, pyrrole-C_5<u>H</u>), 2.79-2.67 (overlapping t, 4H, pyrrole-C_4-C<u>H</u>$_2$ and COC<u>H</u>$_2$), 1.73-1.62 (m, 2H, $COCH_2C$<u>H</u>$_2$), 1.58-1.49 (m, 2H, pyrrole-C_4CH_2C<u>H</u>$_2$), 1.30-1.26 (m, 18H, alkyl-H), 0.88 (t, 6H, -C<u>H</u>$_3$). MS (EI) found m/z 305 (M^+, 100 %) requires m/z 305; FTIR ν_{max} : 3240 (pyrrole NH), 3000-2820, 1642 (carbonyl) cm^{-1}.

*3,4-Didodecypyrrole **17***

A solution of 3-dodecyl-4-dodecanoylpyrrole **14** (3.90 g, 0.0094 mol) dissolved in anhydrous THF (40 ml) was slowly added to a slurry of lithium aluminium hydride (1.42 g,) in anhydrous ether (100 ml) at room temperature. The reaction was then refluxed for 3h, allowed to cool to room temperature and quenched by the careful addition of water (2 ml), aqueous sodium hydroxide (2 ml of a 15 % w/w solution), and then water again (2 ml). The inorganic solids were then filtered off and the THF removed to afford the pyrrole as a clear viscous oil which solidified on standing; yield 3.76 g (98%), M.p 24-27^{o}C. ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.80 (broad s, 1H, pyrrole-NH, exchangeable with D_2O), 6.51 (d, 2H, pyrrole-C_2H and pyrrole –C_5H), 2.41 (t, 4H, pyrrole-CH_2), 1.60-1.51 (m, 4H, pyrrole-CH_2CH_2), 1.32-1.25 (m, 36H, alkyl-H), 0.88 (t, 6H, -CH_3). MS (EI) found m/z 403 (M^+, 52 %) requires m/z 403; FTIR ν_{max} : 3394 (pyrrole NH), 2924, 2852 cm^{-1}.

*3,4-Didecylpyrrole **18***

This was synthesised following the same procedure for compound **17**. Quantities: 3-decyl-4-decanoylpyrrole **15** (3.4 g, 0.0094 mol) dissolved in dry THF (40 ml) and $LiAlH_4$ (1.43 g) in dry ether (100 ml). A clear oil was obtained; yield 3.0 g (92 %). ^{1}H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.80 (broad s, 1H, pyrrole-NH, exchangeable with D_2O), 6.51 (d, 2H, pyrrole-C_2H and

pyrrole –C_5H), 2.40 (t, 4H, pyrrole-CH_2), 1.60-1.53 (m, 4H, pyrrole-CH_2CH_2), 1.32-1.27 (m, 20H, alkyl-H), 0.88 (t, 6H, -CH_3). MS (EI) found m/z 347 (M^+, 12 %) requires m/z 347; FTIR ν_{max} : 3394 (pyrrole NH), , 2922, 2852 cm^{-1}.

*3,4-Dioctylpyrrole **19***

This was synthesised following the same procedure for compound **17**. Quantities: 3-octyl-4-octanoylpyrrole **16** (3.87 g, 0.013 mol) dissolved in dry THF (40 ml) and $LiAlH_4$ (1.94 g) in dry ether (100 ml). A clear oil was obtained; yield 3.65 g (96 %). ^1H NMR ($CDCl_3$, 270 MHz) ∂ (ppm): 7.81 (broad s, 1H, pyrrole-NH, exchangeable with D_2O), 6.50 (d, 2H, pyrrole-C_2H and pyrrole –C_5H), 2.41 (t, 4H, pyrrole-CH_2), 1.60-1.44 (m, 4H, pyrrole-CH_2CH_2), 1.41-1.25 (m, 28H, alkyl-H), 0.88 (t, 6H, -CH_3). MS (EI) found m/z 291 (M^+, 57 %) requires m/z 291; FTIR ν_{max} : 3392 (pyrrole NH), 3000-2840 cm^{-1}.