Supporting information

H-BOND SELF-ASSEMBLY: FOLDING VERSUS DUPLEX FORMATION

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NMR binding studies.

C8-PO, C8-N, C8-NO, N8-PO, N7-PO and C9-PO A•D and AA•DD complexes.

Binding constants for C8-PO, C8-N, C8-NO, N8-PO, N7-PO and C9-PO A•D and AA•DD complexes have been previously reported.

C7-PO A•D and AA•DD complexes.

Binding constants were measured by $^{31}$P NMR titrations in a Bruker 500 MHz AVIII HD Smart Probe spectrometer. The host (phosphine oxide derivatives S11 or 41) was dissolved in toluene-$d_8$ at a known concentration. The guest (phenol derivatives S10 or 40) was dissolved in the host solution and made to a known concentration. A known volume of host was added to an NMR tube and the spectrum was recorded. Known volumes of guest in host solution were added to the NMR tube, and the spectra were recorded after each addition. The chemical shifts of the host spectra were monitored as a function of guest concentration and analysed using a purpose written software in Microsoft Excel. Errors were calculated as two times the standard deviation from the average value (95% confidence limit).

Figure S1. C7-PO A•D 1-mer complex (a) 202 MHz $^{31}$P NMR data for titration of S10 into S11 (18.4 mM) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift of the $^{31}$P signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).
**Figure S2.** C7-PO AA•DD 2-mer complex (a) 202 MHz $^{31}$P NMR data for titration of 40 into 41 (3.68 mM) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift of the $^{31}$P signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).

**NMR dilutions of AD 2-mers.**

$^{31}$P NMR dilution experiments for C8-PO (16), N8-PO (26), N7-PO (29), C9-PO (33) and C7-PO (44) AD 2-mers were performed in a Bruker 400 MHz AVIII or Bruker 500 MHz AVIII HD Smart Probe spectrometer.

$^1$H NMR dilution experiments for C8-N (21) and C8-NO (13) were performed in a Bruker 400 MHz AVIII or Bruker 500 MHz Avance TCI Cryoprobe spectrometer.

**Figure S3.** a) 162 MHz $^{31}$P NMR data for dilution of C8-PO AD-2 mer (16) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).
Figure S4. a) 400 MHz $^1$H NMR data for dilution of C8-N AD-2 mer (21) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm). The red signal corresponds to the protons ortho to the pyridine nitrogen; the blue signal corresponds to the protons ortho to the phenol oxygen; the green signal corresponds to the benzylic methylene protons of the pyridine recognition unit.

Figure S5. a) 400 MHz $^1$H NMR data for dilution of C8-NO AD-2 mer (13) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm). The yellow signal corresponds to the protons ortho to the N-oxide nitrogen; the red signal corresponds to the protons meta to the phenol oxygen; the pink signal corresponds to the protons ortho to the phenol oxygen; the blue and green signals correspond to the benzylic methylene protons of the backbone.
Figure S6. a) 162 MHz $^{31}$P NMR data for dilution of N8-PO AD-2 mer (26) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

Figure S7. a) 162 MHz $^{31}$P NMR data for dilution of N7-PO AD-2 mer (29) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).
Figure S8. a) 202 MHz $^{31}$P NMR data for dilution of C9-PO AD-2 mer (33) at 298 K in toluene-$d_8$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).

Figure S9. a) 202 MHz $^{31}$P NMR data for dilution of C7-PO AD-2 mer (44) at 298 K in CDCl$_3$. (b) Plot of the change in chemical shift as a function of concentration (the line represents the best fit to a dimerisation isotherm).
Molecular mechanics calculations.  

Molecular mechanics calculations were performed using MacroModel version 9.8 (Schrödinger Inc.) on simplified AD 2-mers in which the solubilising groups were changed to methyl groups in order to reduce the computational cost. All structures were minimized first and the minimized structures were then used as the starting molecular structures for all MacroModel conformational searches. The force field used was MMFFs as implemented in this software. The charges were defined by the force field library and no cut off were used for non-covalent interaction. A Polak-Ribiere Conjugate Gradient (PRCG) was used and each structure was subjected to 10000 iterations. The minima converged on a gradient with a threshold of 0.01. Conformational search was performed from previously minimized structures using 10000 steps. Only the structures in a 5 kJ·mol$^{-1}$ window from the global minimum were analysed. Images shown in Fig. 6 were created using PyMOL.\textsuperscript{55}
**X-ray crystallography.**

**X-ray structure of compound 12.**

Pure compound 12 (4 mg) was dissolved in CHCl₃ (1 mL), and the mixture was filtered to a vial and sealed with a plastic cap, resulting in crystallization after 14 days at room temperature. Crystals suitable for X-ray crystallography were selected using an optical microscope and examined at 100 K on a Bruker SMART APEX-II CCD diffractometer operating with a Cu Kα sealed tube X-ray source. The structures were solved using SHELXL-97 and refined using WinGX V1.64.05.23.24. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised position.

| Formula      | C₃₉H₄₀N₄O₉  |
|--------------|-------------|
| Temperature / K | 100        |
| Space Group  | P-1         |
| Cell Lengths/ Å | 8.2839 (0.0005) | 12.3644 (0.0008) | 17.9163 (0.0012) |
| Cell Angles/ ° | 102.994 (0.0042) | 103.082 (0.0045) | 91.085 (0.0047) |
| Cell Volume/ Å³ | 1736.97    |
| Z            | 2           |
| R factor     | 0.1135      |

*Figure S10. X-ray structure of derivative 12 in ORTEP view (ellipsoids are drawn at 50% probability level).*
X-ray structure of compound 47.

Pure compound 47 (4 mg) was dissolved in toluene (0.5 mL), and the mixture was filtered to a vial and sealed with a plastic cap, resulting in crystallization after 10 days at room temperature. Crystals suitable for X-ray crystallography were selected using an optical microscope and examined at 180 K on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.7107 Å). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized position.

| Formula     | C₃₀H₳₁O₂P |
|-------------|-----------|
| Temperature / K | 180       |
| Space Group | P 2₁/n    |
| Cell Lengths/ Å | a 9.0540 (0.0004) b 25.6599 (0.0011) c 11.7725 (0.0005) |
| Cell Angles/ ° | α 90 β 111.578 (0.002) γ 90 |
| Cell Volume/ Å³ | 2543.37 |
| Z            | 4         |
| R factor    | 0.0686    |

Figure S11. X-ray structure of derivative 47 in ORTEP view (ellipsoids are drawn at 50% probability level).
Synthesis and characterization of described compounds

General experimental details

All the reagents and materials used in the synthesis of the compounds described below were bought from commercial sources, without prior purification. UV irradiations were performed using an UVP lamp model UVL-28 (2x365 nm tubes, 8 watt). Thin layer chromatography was carried out using with silica gel 60F (Merck) on aluminium. Flash chromatography was carried out on an automated system (Combiflash Companion, Combiflash Rf+ or Combiflash Rf Lumen) using prepacked cartridges of silica (25μ or 50μ PuriFlash® Columns). All NMR spectroscopy was carried out on a Bruker AVI250, AVI400, DPX400, AVIII400 spectrometer using the residual solvent as the internal standard. All chemical shifts (δ) are quoted in ppm and coupling constants given in Hz. Splitting patterns are given as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). FT-IR spectra were measured on a PerkinElmer Spectrum 100 or One spectrometer equipped with an ATR cell. Melting points were measured in a Mettler Toledo MP50 Melting Point System. Optical activity was measured in an AA-10 or an Anton Paar (MCP 100) at 589 nm. ES+ was carried out on a Waters LCT-TOF spectrometer or a Waters Xevo G2-S bench top QTOF machine.

Compounds 6, 8, 9, 14, 17, 18, 20, 23, 24, 27, 30, 32, 34 have been previously described.
Synthesis of 2-methoxy-5-nitrobenzaldehyde (S1).

![Chemical Structure](image)

5-Hydroxy-2-nitrobenzaldehyde (10.0 g, 59.8 mmol), K₂CO₃ (18.6 g, 135 mmol), methyl iodide (3.2 mL, 134.8 mmol) and DMF (100 mL) were stirred at room temperature for 16 h. The suspension was then poured into water (100 mL) and washed with EtOAc (3 x 200 mL). The combined organic extracts were subsequently washed with water (5 x 100 mL) then brine (100 mL), dried with MgSO₄, filtered and the solvent was removed on a rotary evaporator to yield the product as a yellow solid, which required no further purification (10.1 g, 92%). The spectroscopic data matches previously reported literature.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta_H = 10.45\) (s, 1H), 8.69 (d, 1H, \(J = 2.0\)), 8.45 (dd, 1H, \(J = 9.5, 2.0\)), 7.15 (d, 1H, \(J = 9.5\)), 4.09 (s, 3H).

\(^13\)C NMR (100.6 MHz, CDCl₃): \(\delta_C = 187.5, 141.6, 130.7, 124.6, 114.0, 112.3, 56.8\).
$^1$H NMR (400 MHz, CDCl$_3$) 2-methoxy-5-nitrobenzaldehyde (S1)
$^{13}$C NMR (100.6 MHz, CDCl$_3$) 2-methoxy-5-nitrobenzaldehyde (S1)
Synthesis of 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2).

![Chemical Structure](image)

2-Methoxy-5-nitrobenzaldehyde (S1, 8.72 g, 48.2 mmol), p-toluenesulfonic acid monohydrate (4.58 g, 24.1 mmol), ethylene glycol (13.4 mL, 241 mmol), toluene (50 mL) and 1,4-dioxane (200 mL) were stirred at reflux for 3 days. The solvent was removed on a rotary evaporator, and the residue was dissolved in ethyl acetate (200 mL). The solution was filtered, washed with water (3 x 100 mL) then brine (100 mL), dried with MgSO₄, filtered and the solvent was removed on a rotary evaporator, to yield the product as a yellow solid, which required no further purification (10.8 g, 99 %).

Mpt: 77-79 °C.

^1H NMR (400 MHz, CDCl₃): δ_H = 8.46 (d, 1H, J = 3.0), 8.29 (dd, 1H, J = 9.0, 3.0), 7.00 (d, 1H, J = 9.0), 6.05 (s, 1H); 4.23-4.05 (m, 4H), 4.01 (s, 3H).

^13C NMR (100.6 MHz, CDCl₃): δ_C = 162.5, 141.3, 127.4, 126.5, 123.2, 110.6, 98.2, 65.5, 65.5.

MS (ES+): m/z (%) = 226.1 [M+H]^+.

HRMS (ES+): calcd for C_{10}H_{12}NO₅ 226.0715, found 226.0715.

FT-IR (ATR): ν_{max} 2945, 2907, 2884, 1733, 1616, 1506, 1496, 1334, 1265 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2)
$^{13}$C NMR (100.6 MHz, CDCl$_3$) 2-(2-methoxy-5-nitrophenyl)-1,3-dioxolane (2)
Synthesis of 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3).

![Chemical Structure](image)

Compound 2 (9.84 g, 38.5 mmol), 10% Pd/C (0.750 g, 7.00 mmol) and degassed EtOAc (195 mL) was stirred under a H\textsubscript{2} atmosphere at room temperature for 2 days. Filtration through a celite plug and removal of the solvent on a rotary evaporator yielded the product as an orange oil, which required no further purification (7.51 g, quant.).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta_H = 6.94 \text{ (d, 1H, } J = 3.0), 6.76 \text{ (d, 1H, } J = 8.5), 6.68 \text{ (dd, 1H, } J = 8.5, 3.0), 6.12 \text{ (s, 1H), 4.16-4.10 (m, 2H), 4.08-4.02 (m, 2H), 3.81 (s, 3H), 3.50-3.30 (bs, 2H).}\)

\textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}): \(\delta_C = 151.0, 139.9, 126.6, 116.7, 114.1, 112.4, 99.3, 65.3, 56.4.\)

MS (ES\textsuperscript{+}): m/z (%) = 237.1 [M+MeCN+H]\textsuperscript{+}, 196.1 [M+H]\textsuperscript{+}.

HRMS (ES\textsuperscript{+}): calcd for C\textsubscript{10}H\textsubscript{14}NO\textsubscript{3} 196.0974, found 196.0966.

FT-IR (ATR): \(\nu_{\text{max}}\) 3354, 2949, 2887, 2834, 1626, 1500, 1464, 1225, 1063 cm\textsuperscript{-1}. 


$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$ 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3)
$^{13}$C NMR (100.6 MHz, CDCl$_3$) 3-(1,3-dioxolan-2-yl)-4-methoxyaniline (3)
Synthesis of 4.

4-Pyridinecarboxaldehyde N-oxide (1.01 g, 8.20 mmol), compound 3 (1.69 g, 8.67 mmol) and CHCl₃ (50 mL), over 4 Å molecular sieves, were allowed to stand at room temperature for 16 h. The solution was filtered and had the solvent removed on a rotary evaporator to yield the crude imine (2.69 g), which was used without further purification. The crude imine was dissolved in MeOH (60 mL). NaBH₄ (0.93 g, 36.0 mmol) was added at 0 °C, protected by a N₂ atmosphere, and the solution stirred at room temperature for 30 minutes. Acetone (60 mL) was added and the solvent was removed on a rotary evaporator. The solid residue was dissolved in CH₂Cl₂ (100 mL), which was washed with water (3 x 40 mL) and brine (40 mL). The organic extracts were dried with Na₂SO₄, filtered and the solvent removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 0 to 10% of MeOH in CH₂Cl₂) to yield compound 4 as an off white solid (2.07 g, 84%).

Mpt: 181-184 °C.

¹H NMR (400 MHz, 9:1 CD₃OD-CDCl₃): δH = 8.22 (d, 2H, J = 7.0), 7.50 (d, 2H, J = 7.0), 6.83-6.77 (m, 2H), 6.55 (dd, 1H, J = 8.5, 3.0), 6.01 (s, 1H), 4.36 (s, 2H), 4.08-4.01 (m, 2H), 4.01-3.94 (m, 2H), 3.75 (s, 3H).

¹³C NMR (100.6 MHz, 9:1 CD₃OD-CDCl₃): δC = 150.5, 145.1, 141.6, 138.64, 126.5, 125.2, 114.1, 112.6, 112.0, 99.1, 64.9, 55.7, 46.2.

MS (ES+): m/z (%) = 303.1 [M+H]+;

HRMS (ES+): calcd for C₁₆H₁₉N₂O₄ 303.1345, found 303.1354.

FT-IR (ATR): νmax 3293, 2923, 1535, 1507, 1484, 1439, 1391, 1289, 1228, 1604, 960 cm⁻¹.
$^1$H NMR (400 MHz, 9:1 CD$_3$OD-CDCl$_3$) compound 4

View the image for the detailed NMR spectrum information.
$^{13}$C NMR (100.6 MHz, 9:1 CD$_3$OD-CDCl$_3$) compound 4
Synthesis of 5.

2-Methoxy-5-nitrobenzaldehyde (0.735 g, 4.60 mmol), compound 3 (0.959 g, 4.87 mmol) and CHCl₃ (50 mL), over 4 Å molecular sieves, were allowed to stand at room temperature for 16 h. The solution was filtered and had the solvent removed on a rotary evaporator to yield the crude imine (2.71 g), which was used without further purification. The crude imine was dissolved in MeOH (60 mL). NaBH₄ (0.70 g, 20.3 mmol) was added at 0 °C, protected by a N₂ atmosphere, and the solution stirred at room temperature for 30 minutes. Acetone (60 mL) was added and the solvent was removed on a rotary evaporator. The solid residue was dissolved in CH₂Cl₂ (100 mL), which was washed with water (3 x 40 mL) and brine (40 mL). The organic extracts were dried with Na₂SO₄, filtered and the solvent removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 0 to 100% EtOAc in hexane) to yield compound 5 as a yellow solid (0.900 g, 62 %).

Mpt: 118-119 °C.

¹H NMR (400 MHz, CD₃CN): δ H = 8.19-8.15 (m, 2H), 7.12 (dt, 1H, J = 9.0, 1.5), 6.83-6.89 (m, 2H), 6.59 (dd, 1H, J = 9.0, 3.0), 5.97 (s, 1H), 4.83-4.35 (bs, 1H), 4.33 (d, 2H, J = 5.0), 4.05-4.01 (m, 2H), 4.01 (s, 3H), 3.96-3.92 (m, 2H), 3.72 (s, 3H).

¹³C NMR (100.6 MHz, CD₃CN): δ C = 163.6, 151.1, 143.1, 142.3, 130.7, 128.1, 125.4, 124.4, 114.9, 113.8, 112.7, 111.6, 99.7, 65.9, 57.2, 56.9, 43.2.

MS (ES+): m/z (%) = 361.1 [M+H]⁺.

HRMS (ES+): calcd for C₁₈H₂₁N₂O₆ 361.1400, found 361.1399.

FT-IR (ATR): ν max 3363, 3064, 3029, 2921, 2844, 1590, 1511, 1494, 1335, 1295, 1054 cm⁻¹.
$^{1}H$ NMR (400 MHz, CD$_3$CN) compound 5
$^{13}$C NMR (100.6 MHz, CD$_3$CN) compound 5
Synthesis of 7.

Benzaldehyde derivative 6 (2.14 g, 3.40 mmol), aniline 5 (0.820 g, 1.52 mmol), NaBH(AcO)$_3$ (0.902 g, 4.26 mmol) and degassed CHCl$_3$ (15 mL) were stirred at room temperature for 24 h. Na$_2$CO$_3$ (10 mL of a 1M solution) was added and the aqueous layer was extracted with CHCl$_3$ (3 x 30 mL). The organic extract was dried with MgSO$_4$, filtered and the solvent removed on a rotary evaporator to yield the yellow solid, which was partially purified by flash chromatography (a gradient from 0 to 100% EtOAc in hexane) to yield a mixture of the acetal and the aldehyde (1.51 g), which was immediately dissolved in CHCl$_3$ (10 mL) and HCl (3 mL of a 10 M solution), which was vigorously stirred at room temperature for 16 h. The reaction mixture was neutralized with NaHCO$_3$ (20 mL of a 1 M solution), and the aqueous layer was extracted with CHCl$_3$ (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried with MgSO$_4$ and filtered. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography on silica (gradient from 0 to 100% EtOAc in hexane) to yield compound 7 as a yellow foam (0.950 g, 95%).

Mpt: 57-59 °C.

$^1$H NMR (400 MHz, CD$_3$CN): $\delta_H = 10.32$ (s, 1H), 8.16 (dd, 1H, $J = 9.0$, 3.0), 7.88 (d, 1H, $J = 3.0$), 7.72 (dt, 4H, $J = 6.5$, 1.5), 7.48-7.39 (m, 6H), 7.10 (d, 1H, $J = 9.0$), 7.02 (d, 2H, $J = 9.0$), 7.00-6.95 (m, 3H), 6.73 (d, 2H, $J = 8.5$), 4.56 (s, 2H), 4.54 (s, 2H), 3.95 (s, 3H), 3.83 (s, 3H), 1.08 (s, 9H).

$^{13}$C NMR (100.6 MHz, CD$_3$CN): $\delta_C = 190.0$, 163.4, 155.5, 143.4, 142.2, 136.3, 133.6, 132.1, 131.1, 128.9, 128.8, 128.7, 125.7, 125.5, 123.6, 122.1, 120.6, 118.2, 114.7, 111.6, 111.4, 57.1, 56.8, 55.3, 50.7, 26.2, 19.9.

MS (ES+): m/z (%) = 661.3 [M+H]$^+$. 

HRMS (ES+): calcd for C$_{39}$H$_{43}$N$_2$O$_6$Si 661.2743, found 661.2725.

FT-IR (ATR): $\nu_{max}$ 2931, 2857, 1677, 1608, 1591, 1500, 1337, 1251, 913 cm$^{-1}$. 

S26
$^{13}$C NMR (100.6 MHz, CD$_3$CN) compound 7
Synthesis of 10.

![Chemical Structure]

Aldehyde 7 (0.423 g, 0.640 mmol), aniline derivative 4 (0.093 g, 0.307 mmol), NaBH(AcO)$_3$ (0.182 g, 0.860 mmol) and degassed CHCl$_3$ (2 mL) were stirred at room temperature for 24 h. Na$_2$CO$_3$ (2 mL of a 1M solution) was added, and the aqueous layer was extracted with CHCl$_3$ (5 x 10 mL). The organic extract was dried with MgSO$_4$, filtered and the solvent removed on a rotary. The obtained residue was purified by flash chromatography on silica (gradient from 0:1:0 to 1:9:0 to 0:9:1 MeOH:EtOAc:CH$_2$Cl$_2$) to yield compound 10 as a yellow foam (0.219 g, 75%).

**Mpt:** 85-88 °C.

**$^1$H NMR (400 MHz, CD$_3$CN):** $\delta_H$ = 8.06 (dd, 1H, $J = 9.0$, 3.0), 7.97 (dt, 2H, $J = 7.0$, 1.5), 7.76-7.70 (m, 5H), 7.50-7.45 (m, 2H), 7.40 (m, 4H), 7.07 (d, 2H, $J = 7.0$), 6.97 (d, 1H, $J = 9.5$), 6.94, (d, 2H, $J = 9.5$), 6.78 (d, 1H, $J = 9.0$), 6.72 (dt, 2H, $J = 8.5$, 2.0), 6.68 (d, 1H, $J = 3.0$), 6.63 (d, 1H, $J = 9.0$), 6.55 (dd, 1H, $J = 9.0$, 3.0), 6.35 (dd, 1H, $J = 9.0$, 3.0), 6.31 (d, 1H, $J = 3.0$), 5.90 (s, 1H), 4.45 (s, 2H), 4.42 (s, 2H), 4.40 (s, 2H), 4.19 (s, 2H), 3.89 (s, 3H), 3.88-3.85 (m, 4H), 3.73 (s, 3H), 3.71 (s, 3H), 1.09 (s, 9H).

**$^{13}$C NMR (100.6 MHz, CD$_3$CN):** $\delta_C$ = 163.1, 155.4, 155.4, 150.9, 150.4, 143.2, 143.1, 139.5, 139.3, 136.4, 133.7, 133.7, 133.0, 131.1, 129.1, 128.9, 127.4, 125.5, 125.2, 123.4, 120.6, 115.2, 114.1, 113.1, 112.8, 112.7, 112.6, 111.6, 99.7, 65.8, 57.1, 56.6, 56.4, 55.8, 54.5, 51.2, 51.1, 26.9, 19.9.

**MS (ES+):** m/z (%) = 474.2 [M+2H]$^+$, 947.4 [M+H]$^+$.

**HRMS (ES+):** calcld for C$_{55}$H$_{59}$N$_4$O$_9$Si 947.4051, found 947.4033.

**FT-IR (ATR):** $\nu_{max}$ 2931, 2898, 2858, 1609, 1591, 1504, 1464, 1428, 1337, 1260, 1227, 1021 cm$^{-1}$. 
$^1$H NMR (400 MHz, CD$_3$CN) compound 10
$^{13}\text{C NMR (100.6 MHz, CD}_3\text{CN)}$ compound 10
Synthesis of 11.

Aldehyde 8 (2.02 g, 2.60 mmol) and aniline derivative 9 (2.09 g, 5.21 mmol) were dissolved in CHCl₃ (9 mL) and NaBH(OAc)₃ (1.55 g, 7.29 mmol, 2.8 equiv.) was added with stirring. After 2 days of stirring more NaBH(OAc)₃ was added (1.0 g) and then after 2 more days the reaction was quenched with saturated aqueous NaHCO₃ solution and extracted into CHCl₃ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO₄) before the solvent removed with a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 5 to 10% of EtOAc in hexane and then 10 to 100% MeOH in a 1:1 mixture of CH₃CN and CHCl₃) to yield compound 11 as a pale yellow oil (2.24 g, 74%).

**¹H NMR (400 MHz, CDCl₃):** δ_H = 8.06-7.99 (m, 3H), 7.92 (d, 1H, J = 3.0), 7.08-6.96 (m, 4H), 6.82-6.76 (m, 3H), 6.02 (s, 1H), 4.46-4.37 (m, 6H), 4.05 (s, 2H), 3.99-3.87 (m, 6H), 3.77 (d, 2H, J = 9.0), 3.73 (d, 2H, J = 5.5), 1.77-1.57 (m, 3H), 1.55-1.15 (m, 27H), 0.94-0.79 (m, 18H).

**¹³C NMR (100.6 MHz, CDCl₃):** δ_C = 161.7, 155.1, 150.2, 149.4, 142.6, 142.5, 141.5, 140.0, 139.1, 131.3, 128.6, 128.2, 126.8, 126.3, 124.5, 124.4, 123.2, 120.2, 114.7, 113.7, 113.4, 112.6, 112.0, 111.7, 110.6, 99.5, 71.9, 71.6, 70.9, 65.3, 55.7, 53.0, 50.6, 50.4, 39.7, 39.7, 39.4, 30.8, 30.7, 30.7, 29.3, 29.3, 29.3, 24.2, 24.1, 23.3, 23.2, 23.2, 18.1, 14.3, 14.3, 12.8, 11.4.

**HRMS (ES⁺):** calculated for C₄₀H₆₀N₆O₈Si 1159.7494, found 1159.7439.

**FT-IR (thin film):** ν_max 2958, 2926, 2863, 1681, 1609, 1592, 1504, 1463, 1338, 1262, 1227, 1166 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) compound 11
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 11
Synthesis of 12.

Compound 10 (0.082 g, 0.086 mmol) was dissolved in THF (1 mL) and a solution of TBAF in THF (1M, 0.300 mL, 0.300 mmol) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 30 minutes and the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography on silica (gradient from 10 to 100% of MeOH in CH₂Cl₂) to yield compound 12 as a yellow solid, which was recrystallized from chloroform (0.056 g, 91%).

Mpt: 181 °C (CHCl₃).

¹H NMR (400 MHz, DMSO-d₆): δH = 9.26 (s, 1H), 8.11-8.04 (m, 3H), 7.73 (d, 1H, J = 2.5), 7.12-7.07 (m, 3H), 6.98 (d, 2H, J = 8.5), 6.81 (d, 1H, J = 9.0), 6.69-6.64 (m, 3H), 6.61 (d, 1H, J = 3.0), 6.55 (dd, 1H, J = 9.0, 3.0), 6.34 (d, 1H, J = 3.5), 6.33-6.29, (m, 1H), 5.85 (s, 1H), 4.46 (s, 2H), 4.39 (s, 4H), 4.21 (s, 2H), 3.90 (s, 3H), 3.86-3.82 (m, 4H), 3.68 (s, 3H), 3.67 (s, 3H).

¹³C NMR (100.6 MHz, DMSO-d₆): δC = 161.8, 156.2, 149.3, 148.7, 142.0, 141.6, 140.6, 138.4, 137.7, 128.9, 128.2, 127.9, 126.0, 125.9, 124.5, 124.2, 121.9, 115.2, 113.9, 112.7, 112.1, 111.9, 111.5, 111.2, 111.0, 98.3, 64.4, 56.4, 56.0, 55.7, 55.5, 54.5, 52.8, 50.3, 49.6.

MS (ES+): m/z (%) = 709.3 [M+H]+, 375.7 [M+CH₃CN+2H]²⁺, 355.1 [M+2H]²⁺.

HRMS (ES+): calcd for C₃₉H₃₅N₅O₇ 709.2874, found 947.4033.

FTIR (ATR): v_max 3115, 2936, 2832, 1591, 1502, 1336, 1261, 1224, 1020 cm⁻¹.
$^1$H NMR (400 MHz, DMSO-$d_6$) compound 12
$^{13}$C NMR (100.6 MHz, DMSO-$d_6$) compound 12
Synthesis of 13.

Compound 11 (0.082 g, 0.070 mmol) was dissolved in THF (2 mL) and a solution of TBAF in THF (1M, 0.140 mL, 0.140 mmol) was added dropwise at 0 °C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et₂O (4 × 10 mL). All organic fractions were combined and washed with brine (1 × 10 mL) dried (MgSO₄) and the solvent removed on a rotary evaporator. The crude mixture was then purified by flash chromatography on silica (gradient from 0 to 5% of MeOH in CH₂Cl₂) to yield compound 13 as a yellow oil (0.048 g, 66%).

$^1$H NMR (400 MHz, CDCl₃): $\delta_H = 8.08$ (dd, 1H, $J = 9.0, 3.0$), 8.04 (d, 2H, $J = 6.5$), 7.98 (d, 1H, $J = 9.0, 3.0$), 7.05 (d, 2H, $J = 6.5$), 6.92 (d, 2H, $J = 8.5$), 6.86 (d, 1H, $J = 9.0$), 6.77-6.72 (m, 3H), 6.68 (d, 1H, $J = 9.0$), 6.66 (d, 1H, $J = 9.0$), 6.46-6.38 (m, 3H), 6.05 (s, 1H), 4.54 (s, 2H), 4.40 (s, 4H), 4.04 (s, 2H), 4.03-3.92 (m, 6H) 3.80 (d, 2H, $J = 5.5$), 3.72 (d, 2H, $J = 5.5$), 1.81-1.57 (m, 3H), 1.55-1.18 (m, 24H), 0.94-0.79 (m, 18H).

$^{13}$C NMR (100.6 MHz, CDCl₃): $\delta_C = \delta 161.9, 156.0, 150.5, 149.2, 142.5, 142.4, 141.6, 139.0, 129.7, 128.8, 127.9, 126.6, 126.3, 124.6, 124.5, 123.3, 116.2, 115.4, 113.9, 113.7, 112.6, 112.5, 111.9, 110.6, 99.7, 71.9, 71.6, 70.8, 65.3, 55.9, 53.5, 51.4, 51.1, 39.7, 39.4, 30.8, 30.7, 29.3, 29.2, 24.3, 24.2, 24.1, 23.4, 23.2, 23.1, 14.3, 11.3.

HRMS (ES+): calculated for C₆₀H₆₂N₄O₂²⁺Na 1025.5974, found 1025.5943.

FT-IR (thin film): $\nu_{max}$ 2956, 2925, 2857, 1681, 1613, 1592, 1500, 1463, 1338, 1263, 1221, 1167 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) compound 13

![NMR spectrum of compound 13](image)

The spectrum shows various peaks at different ppm values, indicating the presence of different functional groups and chemical shifts in the molecule.
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 13
Synthesis of 15.

Aldehyde 8 (0.158 g, 0.20 mmol) and aniline 14 (0.175 g, 0.31 mmol) were dissolved in DCE (0.700 mL) and NaBH(OAc)$_3$ (0.121 g, 0.57 mmol) was added. After 2 days of stirring at room temperature the reaction was quenched with saturated aqueous NaHCO$_3$ solution, and extracted into CHCl$_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO$_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 0 to 10% of MeOH in Et$_2$O) to yield compound 15 a pale yellow oil (0.217 g, 80%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 8.00$ (dd, 1H, $J = 9.0, 3.0$), 7.94 (d, 1H, $J = 9.0$), 7.11 (d, 2H, $J = 8.5$), 7.07 (d, 2H, $J = 8.5$), 6.79-6.85 (m, 4H), 6.76 (d, 1H, $J = 9.0$), 6.74 (d, 1H, $J = 9.0$) 6.72 (dd, 1H, $J = 9.0, 3.0$), 6.51-6.58 (m, 2H), 6.41 (d, 1H, $J = 3.0$), 6.34 (dd, 1H, $J = 9.0, 3.0$), 6.08 (s, 1H), 4.49 (s, 2H), 4.41-4.45 (m, 4H), 4.36 (d, 2H, $J = 7.5$), 4.21 (s, 2H), 3.90-3.93 (m, 6H), 3.79 (d, 2H, $J = 5.5$), 3.76 (d, 2H, $J = 5.5$), 1.60-1.79 (m, 3H), 1.18-1.58 (m, 45H), 1.09 (d, 18H, $J = 7.5$), 0.81-0.98 (m, 17H).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C =$ 161.6, 157.4 (d, $J = 11.1$), 155.1, 149.3, 149.3, 143.3, 142.8, 141.5, 132.9, 131.4, 128.6, 128.4, 128.3, 127.3, 126.6, 124.4, 123.2, 120.1, 114.2, 113.9, 113.5, 113.2, 112.5, 111.6, 111.2, 110.6, 99.9, 71.9, 71.5, 71.0, 65.2, 62.8 (d, $J = 70.5$), 55.8, 54.0, 50.4, 49.8, 39.9, 39.7, 39.5, 35.7 (d, $J = 57.5$), 30.9, 30.8, 30.8, 29.3, 29.3, 29.3, 26.7, 24.3, 24.2, 24.2, 23.3, 23.2, 18.2, 14.3, 14.3, 12.9, 11.4.

MS (MALDI+): m/z (%) = 1332.2 [M+H]+.

HRMS (ES+): calculated for C$_{79}$H$_{123}$N$_{10}$O$_{10}$P$_{28}$Si 1332.8710, found 1332.8678.

FT-IR (thin film): $\nu_{\text{max}}$ 2953, 2929, 2867, 1609, 1507, 1464, 1339, 1263, 1226 cm$^{-1}$. 
\( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) compound 15
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 15
Synthesis of 16.

Compound 15 (0.101 g, 0.08 mmol) was dissolved in THF (2 mL) and a solution of TBAF in THF (1M, 0.080 mL, 0.08 mmol) was added at 0 °C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et₂O (3 × 10 mL). All organic fractions were combined and washed with brine (3 × 10 mL) dried (MgSO₄) and the solvent removed on a rotary evaporator. The crude mixture was then purified by flash chromatography on silica (gradient from 50 to 100% of EtOAc in hexane) to yield compound 16 as a light yellow oil (0.030 g, 34%).

^1H NMR (400 MHz, CDCl₃): δ_H = 8.03 (dd, 1H, J = 9.0, 3.0), 7.97 (d, 1H, J = 3.0), 7.09 (d, 2H, J = 8.5), 6.93 (d, 2H, J = 7.0), 6.82 (d, 1H, J = 3.0), 6.80 (d, 1H, J = 9.0), 6.72 (d, 2H, J = 7.0), 6.70 (d, 2H, J = 7.0), 6.63 (d, 1H, J = 9.0), 6.61-6.56 (m, 2H), 6.44-6.35 (m, 2H), 6.07 (s, 1H), 4.44 (s, 4H), 4.37 (s, 2H), 4.33 (d, 2H, J = 6.5), 4.28 (s, 2H), 4.01-3.89 (m, 4H), 6.82 (d, 1H, J = 3.0), 7.09 (d, 2H, J = 8.5), 6.93 (d, 2H, J = 7.0), 6.82 (d, 1H, J = 3.0), 6.80 (d, 1H, J = 9.0), 6.72 (d, 2H, J = 7.0), 6.70 (d, 2H, J = 7.0), 6.63 (d, 1H, J = 9.0), 6.61-6.56 (m, 2H), 6.44-6.35 (m, 2H), 6.07 (s, 1H), 4.44 (s, 4H), 4.37 (s, 2H), 4.33 (d, 2H, J = 6.5), 4.28 (s, 2H), 4.01-3.89 (m, 4H), 3.91 (d, 2H, J = 6.0), 3.78 (d, 2H, J = 5.5), 3.72 (d, 2H, J = 5.5), 1.79-1.57 (m, 3H), 1.56-1.15 (m, 42H), 0.97 0.77 (18H, m).

^13C NMR (100.6 MHz, CDCl₃): δ_C = 161. 8, 157.3 (d, J = 10.5), 155.9, 149.6, 148.9, 143.7, 142.7, 141.5, 133.2, 129.7, 128.8, 128.5, 127.9, 127.8, 126.1, 124.4, 123.2, 116.1, 114.9, 114.2, 113.9, 113.5, 112.2, 111.5, 110.5, 100.1, 71.8, 71.5, 70.8, 65.2, 62.6 (d, J = 70.0), 55.7, 55.5, 50.9, 50.3, 39.7, 39.3, 35.5 (d, J = 57.5), 30.8, 30.7, 29.2, 26.6, 24.2, 24.1, 23.2 23.1, 14.2, 11.3.

^31P NMR (161.3 MHz, CDCl₃): δ_P = 58.4.

HRMS (ES+): calculated for C_{70}H_{103}N_{10}O_{10}P 1176.7381, found 1176.7355.

FT-IR (thin film): ν_max 2956, 2921, 2853, 1679, 1609, 1592, 1502, 1467, 1336, 1263, 1225, 1175, 1124 cm^{-1}.
$^1$H NMR (400 MHz, CDCl$_3$) compound 16
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 16
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 16
Synthesis of S2.

Derivative 17 (3.66 g, 6.58 mmol) was dissolved in THF (20 mL) and a solution of TBAF in THF (1M, 13.2 mL, 13.2 mmol) was added at 0 °C. After 1 h of stirring at room temperature, water (5 mL) was added and the aqueous mixture washed with Et₂O (4 × 10 mL). All organic fractions were combined and washed with brine (1 × 10 mL) dried (MgSO₄) and the solvent removed on a rotary evaporator. The crude mixture was then purified by recrystallization from hot CH₂Cl₂ and hexane to yield compound S2 as a yellow solid (1.80 g, 69%).

Mpt: 110-114 °C.

¹H NMR (250 MHz, CDCl₃): δ_H = 7.23 (d, 2H, J = 8.5), 6.90 (d, 1H, J = 3.0), 6.81-6.73 (m, 3H), 6.61 (dd, 1H, J = 9.0, 3.0), 6.15 (s, 1H), 4.20 (s, 2H), 4.17-3.98 (m, 4H), 3.82 (d, 2H), 1.80-1.66 (m, 1H), 1.62-1.22 (m, 8H), 0.99-0.86 (m, 6H).

¹³C NMR (100.6 MHz, CDCl₃): δ_C = 154.8, 150.2, 142.1, 131.6, 129.1, 126.9, 115.4, 114.5, 113.9, 112.2, 99.4, 72.0, 65.2, 48.8, 39.5, 30.5, 79.1, 23.9, 23.1, 14.1, 11.1.

HRMS (ES+): calculated for C_{24}H_{34}NO₄ 400.2488, found 400.2495.

FT-IR (thin film): ν_max 3290, 2952, 2921, 2873, 2853, 1611, 1598, 1493, 1469, 1243, 1074 cm⁻¹.
$^1$H NMR (250 MHz, CDCl$_3$) compound S2
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S2
Synthesis of 19.

Compounds S2 (1.30 g, 3.25 mmol) and 18 (1.82 g, 6.51 mmol) were dissolved in DCE (12 mL) and NaBH(OAc)$_3$ (1.93 g, 9.11 mmol) was added at room temperature with stirring. After 18 h of stirring at room temperature, the reaction was quenched with saturated aqueous NaHCO$_3$ solution and extracted into CHCl$_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO$_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (20% EtOAc in hexane) to yield compound 19 a waxy yellow solid (2.05 g, 95%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 8.17-8.10$ (m, 2H), 7.12 (d, 2H, $J = 8.0$), 7.01 (d, 1H, $J = 3.0$), 6.93 (d, 1H, $J = 10.0$), 6.77 (d, 1H, $J = 9.0$), 6.72 (d, 2H, $J = 8.0$), 6.55 (dd, 1H, $J = 9.0, 3.0$), 6.20 (s, 1H), 4.57 (s, 2H), 4.54 (s, 2H), 4.06-3.94 (m, 6H), 3.81 (d, 2H, $J = 6.0$), 1.86-1.68 (m, 1H), 1.58-1.25 (m, 16H), 1.02-0.86 (m, 12H).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C = 161.9, 154.9, 150.0, 143.0, 141.3, 130.2, 128.8, 128.4, 126.6, 124.4, 123.5, 115.4, 115.2, 113.6, 112.5, 110.4, 99.7, 71.7, 71.4, 65.0, 55.2, 50.0, 39.5, 39.2, 30.5, 29.1, 29.0, 24.0, 23.9, 23.1, 23.0, 14.1, 14.1, 11.1.

HRMS (ES+): calculated for C$_{39}$H$_{55}$N$_2$O$_7$ 663.4009, found 663.4008.

FT-IR (thin film): $\nu_{\text{max}}$ 3421, 2956, 2929, 2869, 1677, 1609, 1592, 1510, 1494, 1336, 1267, 1177 cm$^{-1}$. 
$^1$H NMR (400 MHz, CDCl$_3$) compound 19
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 19
Synthesis of S3.

Compound 19 (1.23 g, 1.85 mmol) was dissolved in CHCl₃ (10 mL) and concentrated aqueous HCl (10 mL) was added with stirring. After 2 days the mixture was neutralised using aqueous NaHCO₃ and the organic portion separated from the aqueous part. The aqueous layer was washed with CHCl₃ (3 × 10 mL) before all organic fractions were washed with brine (1 × 10 mL) dried (MgSO₄) and the solvent removed on a rotary evaporator to yield a yellow solid which was recrystallized from CH₂Cl₂ and hexane (1.15 g, 95%).

Mpt: 105-107 °C.

¹H NMR (500 MHz, CDCl₃): \( \delta_H = 10.42 \; (s, \; 1H), \; 8.11 \; (dd, \; 1H, \; J = 9.0, \; 3.0), \; 7.98 \; (d, \; 1H, \; J = 3.0), \; 7.17 \; (d, \; 1H, \; J = 3.0), \; 7.09 \; (d, \; 2H, \; J = 8.5), \; 6.93-6.88 \; (m, \; 2H), \; 6.84 \; (d, \; 1H, \; J = 9.0), \; 6.77 \; (d, \; 2H, \; J = 8.5), \; 4.55 \; (s, \; 2H), \; 4.54 \; (s, \; 2H), \; 3.98 \; (d, \; 2H, \; J = 5.5), \; 3.87 \; (dd, \; 2H, \; J = 5.5, \; 1.5), \; 1.83-1.68 \; (m, \; 2H), \; 0.96-0.82 \; (m, \; 12H).

¹³C NMR (125.7 MHz, CDCl₃): \( \delta_C = 190.4, \; 161.9, \; 155.0, \; 154.7, \; 142.7, \; 141.3, \; 129.7, \; 128.2, \; 127.8, \; 125.1, \; 124.5, \; 123.0, \; 121.4, \; 115.5, \; 114.2, \; 110.9, \; 110.5, \; 71.5, \; 71.2, \; 54.6, \; 49.6, \; 39.5, \; 39.1, \; 30.6, \; 30.5, \; 29.0, \; 28.9, \; 23.9, \; 23.9, \; 22.9, \; 14.0, \; 14.0, \; 11.1, \; 11.1.

HRMS (ES+): calculated for C₃₇H₅₁N₂O₆ 619.3747, found 619.3738.

FT-IR (thin film): \( \nu_{max} = 3433, \; 2956 \; 2925, \; 2861, \; 1677, \; 1610, \; 1592, \; 1510, \; 1493, \; 1465, \; 1439, \; 1338, \; 1269, \; 1245, \; 1207, \; 1177 \; \text{cm}^{-1}. \)
$^1$H NMR (500 MHz, CDCl$_3$) compound S3
$^{13}$C NMR (125.7 MHz, CDCl$_3$) compound S3

![Chemical structure of compound S3 with its NMR spectrum showing various chemical shifts.](S56.png)
Synthesis of 21.

Compounds S3 (0.100 g, 0.26 mmol) and 20 (0.242 g, 0.39 mmol) were dissolved in DCE (1 mL) and NaBH(OAc)$_3$ (0.155 g, 0.73 mmol) was added at room temperature with stirring. After 18 h of stirring at room temperature, the reaction was quenched with saturated aqueous NaHCO$_3$ solution, and extracted into CHCl$_3$ (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO$_4$) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica (gradient from 40 to 70% of EtOAc in hexane) to yield compound 21 as an orange oil (0.134 g, 52%).

$^1$H NMR (500 MHz, CDCl$_3$): δ$_H$ = 8.43 (d, 2H, $J$ = 5.5), 8.06 (dd, 1H, $J$ = 9.0, 3.0), 7.98 (d, 1H, $J$ = 3.0), 7.16 (d, 2H, $J$ = 5.5), 6.96 (d, 2H, $J$ = 8.5), 6.84 (d, 1H, $J$ = 9.0), 6.71 (d, 2H, $J$ = 8.5), 6.69 (d, 1H, $J$ = 9.0), 6.67 (d, 1H, $J$ = 3.0), 6.62 (d, 1H, $J$ = 9.0), 6.47 (dd, 1H, $J$ = 9.0, 3.0), 6.43 (d, 1H, $J$ = 3.0), 6.38 (dd, 1H, $J$ = 9.0, 3.0), 6.06 (s, 1H), 4.52 (s, 1H), 4.44 (m, 4H), 4.23 (s, 1H), 3.96-3.90 (m, 6H), 3.80 (d, 2H, $J$ = 6.0), 3.74 (d, 2H, $J$ = 6.0), 1.80-1.69 (m, 2H), 1.67-1.60 (m, 1H), 1.56-1.19 (m, 24H), 0.97-0.80 (m, 18H).

$^{13}$C NMR (125.7 MHz, CDCl$_3$): δ$_C$ = 161.6, 155.5, 151.1, 149.7, 149.0, 148.2, 142.4, 141.3, 129.8, 128.5, 127.7, 126.4, 126.1, 124.3, 123.0, 122.3, 115.8, 114.3, 113.4, 113.3, 112.3, 111.6, 111.5, 110.4, 99.6, 71.6, 71.3, 70.6, 65.0, 55.7, 53.9, 50.8, 50.4, 39.5, 39.4, 39.2, 30.6, 30.5, 29.0, 29.0, 24.0, 23.9, 23.9, 23.0, 23.0, 22.9, 14.0, 14.0, 11.1.

HRMS (ES+): calculated for C$_{60}$H$_{83}$N$_4$O$_9$ 987.6205, found 987.6201.

FT-IR (thin film): ν$_{max}$ 3671, 2988, 2901, 1405, 1336, 1225 cm$^{-1}$. 

S57
$^1$H NMR (500 MHz, CDCl$_3$) compound 21

[Chemical structure and NMR spectrum]
$^{13}$C NMR (125.7 MHz, CDCl$_3$) compound 21
Synthesis of 25.

A mixture of p-aminophenol (0.092 g, 0.85 mmol), terephthalaldehyde derivative 23 (0.333 g, 0.85 mmol) and compound 24 (0.240 g, 0.85 mmol) in CHCl₃ (10 mL) was stirred under N₂ atmosphere at room temperature for 48 h. The solvent was then removed under reduced pressure and the crude dissolved in MeOH. NaBH₄ (0.380 g, 9.50 mmol) was added at 0°C and the solution left stirring for 10 min. The solution was neutralized with 2M HCl (4 mL) and extracted with CH₂Cl₂ (3 x 10 mL). The organic layers were combined and washed with brine (1 x 10 mL). The solution was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was then purified by column chromatography on silica (EtOAc/MeOH 90:10). Compound 25 was isolated as a pink oil (0.130 g, 20%).

¹H NMR (400 MHz, CD₃CN): δ H = 6.94 (bs, 1H), 6.88 (d, 2H, J = 6.0), 6.76-6.74 (m, 2H), 3.77-3.75 (m, 4H), 1.64-1.62 (m, 2H), 1.44-1.34 (m, 8H), 1.34-1.23 (m, 26H), 0.89-0.83 (m, 12H).

¹³C NMR (100.6 MHz, CD₃CN): δ c = 151.0, 150.9, 150.9, 149.1, 144.0, 142.2, 127.9, 127.4, 115.9, 115.5, 114.5, 114.2, 113.2, 113.1, 71.1, 71.1, 63.4 (d, J = 70), 43.6, 43.1, 39.6, 39.5, 35.1 (d, J = 58), 30.7, 30.7, 29.1, 29.0, 26.0, 24.0, 23.0, 23.0, 13.7, 10.8.

³¹P NMR (161.3.0 MHz, CD₃CN): δ p = 56.7.

MS (ES+): m/z (%) =751.5 [M+H]^⁺.

HRMS (ES+): calcd for C₄₅H₇₂N₂O₅P 751.5179, found 751.5172.

FT-IR (thin film): ν max 3050, 2961, 2929, 2873, 1509 cm⁻¹.
$^1$H NMR (400 MHz, CD$_3$CN) compound 25
$^{31}$P NMR (161.3 MHz, CD$_3$CN) compound 25
Synthesis of 26.

A mixture of compound 25 (0.100 g, 0.14 mmol), 2-methoxybenzaldehyde (0.064 mL, 0.42 mmol) and NaBH(AcO)$_3$ (0.150 g, 0.71 mmol) in DCE (0.6 mL) was stirred under N$_2$ atmosphere at room temperature for 2 h. The solution was diluted with DCE and then washed with saturated aqueous NaHCO$_3$ (1 x 10 mL), water (1 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was then purified by column chromatograph on silica (CH$_2$Cl$_2$/EtOAc 90:10). The product was isolated as a pink oil (0.100 g, 76%).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta_H$ = 7.19-7.07 (m, 4H), 6.91-6.88 (m, 2H), 6.82-6.78 (m, 2H), 6.76-6.73 (m, 3H), 6.68 (s, 1H), 6.57-6.55 (m, 4H), 6.49-6.47 (m, 2H), 4.53 (s, 2H), 4.49 (s, 2H), 4.46 (s, 2H), 4.44 (s, 2H), 4.23 (d, 2H, $J = 6.0$), 3.76 (d, 6H, $J = 3.0$), 3.62-3.59 (m, 4H), 1.58-1.49 (m, 34H), 0.83-0.76 (m, 12H).

$^{13}$C NMR (100.6 MHz, CD$_3$CN): $\delta_c$ = 157.6, 157.6, 150.6 (d, $J = 8$), 150.4 (d, $J = 11$), 148.7, 144.3, 142.9, 128.1, 127.9, 127.7, 127.2, 126.9, 126.2, 120.3, 120.3, 115.8, 115.3, 114.4, 113.8, 112.2, 112.1, 110.6, 110.6, 71.1, 71.0, 63.4 (d, $J = 70$), 55.2, 55.2, 50.6, 50.6, 50.5, 50.4, 39.4, 39.3, 35.1 (d, $J = 58$), 30.6, 30.6, 29.0, 28.9, 26.0, 23.9, 23.9, 23.0, 23.0, 13.7, 10.8.

$^{31}$P NMR (161.3.0 MHz, CD$_3$CN): $\delta_p$ = 56.3.

MS (ES+): m/z (%) =991.6 [M+H]$^+$.  
HRMS (ES+): calcd for C$_{61}$H$_{88}$N$_2$O$_7$P 991.6329, found 991.6309.

FT-IR (thin film): $\nu_{\text{max}}$ 2956, 2927, 2871, 1510 cm$^{-1}$.  

S64
$^1$H NMR (400 MHz, CD$_3$CN) compound 26
$^{13}$C NMR (100.6 MHz, CD$_3$CN) compound 26
$^{31}$P NMR (161.3 MHz, CD$_3$CN) compound 26
Synthesis of 28.

A mixture of \(p\)-aminophenol (0.225 g, 2.06 mmol), compound 24 (0.584 g, 2.06 mmol) and aldehyde derivative 27 (0.540 g, 2.06 mmol) in CHCl\(_3\) (1 mL) was stirred under N\(_2\) atmosphere at room temperature for 48 h. The solvent was then removed under reduced pressure and the crude dissolved in MeOH. NaBH\(_4\) (1.000 g, 26.43 mmol) was added at 0°C and the solution left stirring for 10 min. The solution was neutralized with 2M HCl (4 mL) and extracted with CH\(_2\)Cl\(_2\) (3x10 mL). The organic layers were combined and washed with brine (1 x 10 mL). The solution was dried over MgSO\(_4\) and the solvent was removed under reduced pressure. The crude material was then purified by column chromatography on silica (EtOAc/MeOH 95:5). Compound 28 was isolated as a pink oil (0.200 g, 16%).

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta_H = 6.94\) (s, 1H), 6.83-6.82 (m, 2H), 6.78-6.73 (m, 4H), 6.58-6.49 (m, 4H), 5.02 (bs, 2H), 4.37 (d, 2H, \(J = 7.0\)), 4.23 (d, 4H, \(J = 9.0\)), 3.83 (dd, 2H, \(J = 6.0, 1.0\)), 1.75-1.66 (m, 1H), 1.54-1.26 (m, 26H), 0.95-0.90 (m, 6H).

\(^{31}\)P NMR (161.3.0 MHz, CDCl\(_3\)): \(\delta_P = 58.8\).
$^1$H NMR (400 MHz, CDCl$_3$) compound 28
$^{31}$P NMR (161.30 MHz, CDCl$_3$) compound 28
Synthesis of 29.

A mixture of 28 (0.200 g, 0.32 mmol), 2-methoxybenzaldehyde (0.130 mL, 0.80 mmol) and NaBH(AcO)$_3$ (0.330 g, 1.56 mmol) in DCE (1 mL) was stirred under N$_2$ atmosphere at room temperature for 2 h. The solution was then diluted with DCE and washed with saturated aqueous NaHCO$_3$ (1 x 10 mL), water (1 x 10 mL) and brine (1 x 10 mL). The organic layer was dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was then purified by column chromatograph on silica (CH$_2$Cl$_2$/EtOAc 90:10). Compound 29 was isolated as a pink oil (0.190 g, 69%).

$^1$H NMR (500 MHz, CD$_3$CN): δ$_H$ = 7.86 (s, 1H), 7.21-7.16 (m, 2H), 7.10 (d, 2H, J = 7.0), 6.93 (t, 2H, J = 8), 6.84-6.81 (m, 2H), 6.73 (s, 2H), 6.71 (s, 1H) 6.61 (s, 2H), 6.53-6.49 (m, 4H), 6.39 (d, 2H, J = 8.0), 4.51 (s, 2H), 4.47 (s, 2H), 4.43 (s, 2H), 4.37 (s, 2H), 4.31 (d, 2H, J = 5.0), 3.80 (s, 3H), 3.79 (s, 3H), 3.72 (d, 2H, J = 6.0), 1.62-1.59 (m, 1H), 1.43-1.27 (m, 26H), 0.88-0.85 (m, 6H).

$^{13}$C NMR (125.7 MHz, CD$_3$CN): δ$_C$ = 160.7, 158.3, 151.4 (d, J = 10), 150.0, 144.7, 143.1, 142.8, 142.1, 128.8, 128.8, 128.5, 127.9, 127.6, 121.1, 121.1, 118.8, 116.5, 116.1, 115.6, 114.9, 112.2, 112.2, 111.4, 111.3, 71.1, 64.2 (d, J = 69), 56.6, 56.1, 55.9, 55.9, 51.9, 51.7, 40.1, 35.9 (d, J = 58), 31.2, 29.7, 26.8, 24.5, 23.7, 14.4, 11.4.

$^{31}$P NMR (202.4 MHz, CD$_3$CN): δ$_P$ = 57.3.

MS (ES+): m/z (%) =863.5 [M+H]$^+$. 

HRMS (ES+): calcd for C$_{53}$H$_{72}$N$_2$O$_6$P 863.5128, found 863.5163.

FT-IR (thin film): $\nu_{\max}$ 3151, 2956, 2932, 2870, 1593, 1512 cm$^{-1}$. 

S71
$^1$H NMR (500 MHz, CD$_3$CN) compound 29

![NMR spectrum image]

**Chemical shifts:**
- $7.86, 7.20, 7.18, 7.09, 6.93, 6.82, 6.73, 6.72, 6.61, 6.51, 6.40, 6.38, 4.51, 4.47, 4.43, 4.37, 4.31, 3.80, 3.79, 3.72$
- $2.20 \text{H}^1\text{O}, 1.93 \text{CD}_{3}\text{CN, 1.61, 1.38, 1.36, 1.30, 1.27, 0.87, 0.86, 0.85}$
$^{13}$C NMR (125.7 MHz, CD$_3$CN) compound 29
$^{31}$P NMR (202.4 MHz, CD$_3$CN) compound 29
Synthesis of 31.

To a solution of compound 30 (0.051 g, 0.13 mmol) in dry and degassed MeOH (0.5 mL) under N₂ atmosphere was added DMPA (0.003 g, 0.01 mmol) and tert-butyl mercaptan (0.044 mL, 0.39 mmol). The reaction was stirred at room temperature under UV irradiation (365 nm) for 45 min. Then, the solvent was removed under vacuum and the crude purified by flash chromatography on silica (CH₂Cl₂/MeOH 30:1) to yield compound 31 (0.056 g, 90%) as a syrup.

[^20]D = +4.0 (c 0.24, CHCl₃).

**¹H NMR (400 MHz, CDCl₃):** δ_H = 7.58 (dd, 2H, J = 10.5, 8.1), 7.27 (m, 2H), 2.85 (m, 2H), 2.63 (m, 2H), 2.50 (m, 2H), 2.29 (s, 3H), 1.92 (m, 3H), 1.81 (m, 2H), 1.55 (m, 6H), 1.36 (m, 6H), 1.26 (s, 9H), 0.85 (t, 3H, J = 7.0).

**¹³C NMR (100.6 MHz, CDCl₃):** δ_C = 195.6, 144.2 (d, J = 3), 130.5 (d, J = 9), 130.1 (d, J = 94), 129.4 (d, J = 11), 42.0, 40.0, 38.6, 33.2, 33.1, 31.0, 30.6, 29.7 (d, J = 69), 26.5, 25.7, 24.1 (d, J = 15), 23.5 (d, J = 4), 13.6.

**³¹P NMR (161.3 MHz, CDCl₃):** δ_P = 40.5.

**MS (ES⁺):** m/z (%) = 485.3 [M+H]⁺.

**HRMS (ES⁺):** calcd for C₂₆H₄₆O₂P₂ 485.2677, found 485.2676.

**FT-IR (ATR):** ν_max 2957, 2930, 2866, 1689, 1458, 1363, 1164, 1135, 1111, 796 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) compound 31
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 31
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 31
Synthesis of 33.

A solution of 31 (0.116 g, 0.24 mmol) in MeOH (4.5 mL) was treated with 2N NaOH solution (0.359 mL, 0.72 mmol). After stirring at room temperature for 30 min, the reaction was quenched with diluted HCl solution (2 mL) and extracted with EtOAc (3 x 10 mL). The organic phase was dried over MgSO₄, evaporated and dried in a high vacuum pump for 30 min. The obtained residue was dissolved in dry and degassed MeOH (1 mL) under N₂ atmosphere. DMPA (0.006 g, 0.02 mmol) and 32 (0.060 g, 0.24 mmol) were added and the reaction was stirred at room temperature under UV irradiation (365 nm) for 1.5 h. Then, the solvent was removed under vacuum and the crude purified by flash chromatography on silica (CH₂Cl₂:MeOH 25:1) to yield compound 33 (0.116 g, 70%) as a syrup.

\[ \alpha _{D}^{20} = +15.0 \text{ (c 0.16, CHCl}_3). \]

\(^1\text{H NMR (400 MHz, CDCl}_3): \delta_\text{H} = 7.64 \text{ (bs, 1H)}, 7.58 \text{ (dd, 2H, } J = 10.5, 8.0), 7.25 \text{ (m, 2H)}, 6.93 \text{ (d, 2H, } J = 8.5 \text{ Hz), 6.76 \text{ (d, 2H, } J = 8.5), 2.90 \text{ (t, 2H, } J = 7.5 \text{ Hz), 2.66 \text{ (m, 2H), 2.54 \text{ (m, 1H), 2.50 \text{ (m, 2H), 2.37 \text{ (m, 5H), 2.32 \text{ (s, 3H), 1.90 \text{ (m, 6H), 1.44 \text{ (m, 16H), 1.31 \text{ (s, 9H), 0.88 \text{ (td, 6H, } J = 7.2, 2.1 \text{ Hz).}}}}}}}

\(^{13}\text{C NMR (100.6 MHz, CDCl}_3): \delta_\text{C} = 196.0, 155.5, 144.9 \text{ (d, } J = 3), 130.9, 130.6, 130.5, 129.9, 129.7, 129.6, 129.0, 130.0, 115.7, 42.1, 40.1, 39.2, 38.7, 38.6, 33.6, 33.4, 33.2, 32.8, 31.1, 30.8, 29.7 \text{ (d, } J = 37), 29.3, 29.2, 26.9, 25.9, 24.2 \text{ (d, } J = 15), 23.6 \text{ (d, } J = 4), 13.7. \]

\(^{31}\text{P NMR (161.3 MHz, CDCl}_3): \delta_\text{P} = 42.4. \]

MS (ES+): m/z (%) = 693.4[M+H]

HRMS (ES+): calcd for C₃₈H₆₀O₃P₃ 693.3599, found 693.3602.

FT-IR (ATR): \( \nu_{\max} \) 2955, 2927, 2869, 1688, 1515, 1455, 1153, 1107, 797 cm\(^{-1}\).
$^1$H NMR (400 MHz, CDCl$_3$) compound 33
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 33
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 33
Synthesis of 35.

34 (0.250 g, 1.55 mmol) was added to a dried flask and the flask evacuated and back-filled with N\textsubscript{2} (3x). 3-Bromoiodobenzene (0.217 mL, 1.71 mmol) and 1,4-dioxane (deoxygenated by freeze-pump-thaw, 4 mL) were added. In a separate flask, Pd\textsubscript{2}(dba)\textsubscript{3} (0.031 g, 0.03 mmol) and Xantphos (0.020 g, 0.03 mmol) were placed in a flask and evacuated and back-filled with N\textsubscript{2} (3x). These were dissolved in 1,4-dioxane (3 mL) and the solution transferred to the initial flask. Et\textsubscript{3}N (0.230 mL, 1.55 mmol) was added and the reaction stirred at room temperature for 2 h. CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added and the reaction washed with NaHCO\textsubscript{3} (25 mL). The aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3x 10 mL) and combined organics dried (MgSO\textsubscript{4}) and solvent removed. The obtained brown solid was purified by flash chromatography on silica (CH\textsubscript{2}Cl\textsubscript{2}/MeOH 20:1) to yield the compound 35 as a yellow oil (0.459 g, 93%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.83\) (d, 1H, \(J = 10.4\)), 7.67-7.63 (m, 1H), 7.63-7.57 (m, 1H), 7.36 (td, 1H, \(J = 8.0, 2.8\)), 2.04-1.75 (m, 4H), 1.69-1.30 (m, 8H), 0.87 (t, 6H, \(J = 8.0\)).

\textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}): \(\delta = 135.6\) (d, \(J = 89\) Hz), 134.5 (d, \(J = 3\)), 133.2 (d, \(J = 9\) Hz), 130.3 (d, \(J = 12\)), 128.9 (d, \(J = 9\)), 123.3 (d, \(J = 14\)), 29.7 (d, \(J = 65\)), 24.1 (d, \(J = 14\)), 23.5 (d, \(J = 4\)), 13.6.

\textsuperscript{31}P NMR (161.3 MHz, CDCl\textsubscript{3}): \(\delta = 39.8\).

HRMS (ES\textsuperscript{+}): calcd for C\textsubscript{14}H\textsubscript{23}\textsuperscript{79}BrOP 317.0670, found 317.0668.

FT-IR (ATR): \(\nu_{\text{max}}\) 2956, 2932, 2871, 1465, 1398, 1169 cm\textsuperscript{-1}. 
$^1$H NMR (400 MHz, CDCl$_3$) compound 35

Chemical shifts in ppm:
\(^{13}\)C NMR (100.6 MHz, CDCl\(_3\)) compound 35
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 35

![NMR spectrum of compound 35](image)
Synthesis of \( S_4 \).

35 (0.317 g, 1.00 mmol), \( \text{Pd}_2\text{(dba)}_3 \) (0.018 g, 0.02), Cul (0.004 g, 0.02 mmol) and \( \text{PPh}_3 \) (0.026 g, 0.10 mmol) were added to a flask with \( \text{Et}_3\text{N} \) (5 mL) and DMF (5 mL). \( \text{N}_2 \) was bubbled through the reaction for 15 minutes. TMSA (0.170 mL, 1.20 mmol) was added and the reaction stirred at 50 °C for 4 h in the dark under \( \text{N}_2 \) atmosphere. The reaction was filtered through celite and washed through with \( \text{EtOAc} \) (30 mL). The solution was washed with 1M HCl (3x 30 mL) and 5% LiCl solution (2x 30mL), and then dried (\( \text{MgSO}_4 \)). The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by flash chromatography on silica (\( \text{CH}_2\text{Cl}_2/\text{MeOH} \) 19:1) to yield the desired compound \( S_4 \) as a brown oil (0.268 g, 90%).

\[ \begin{align*}
\text{[Chemical Structure Image]}
\end{align*} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta_\text{H} = 7.74 \text{ (dt, } 1\text{H, } J = 11.0, 1.5), 7.63 \text{ (ddt, } 1\text{H, } J = 10.5, 7.5, 1.5), 7.57 \text{ (dd, } 1\text{H, } J = 8.0, 1.5), 7.40 \text{ (td, } 1\text{H, } J = 8.0, 2.5), 2.06-1.88 \text{ (m, } 2\text{H}), 1.87-1.75 \text{ (m, } 2\text{H}), 1.70-1.44 \text{ (m, } 2\text{H), 1.45-1.27 \text{ (m, } 6\text{H), 0.84 (t, } 6\text{H, } J = 7.0), 0.23 (s, 9\text{H}).}
\]

\[ ^{13}\text{C NMR (100.6 MHz, CDCl}_3\text{): } \delta_\text{C} = 134.7 \text{ (d, } J = 3), 133.6 \text{ (d, } J = 10), 132.8 \text{ (d, } J = 91), 130.2 \text{ (d, } J = 8), 128.5 \text{ (d, } J = 12), 123.8 \text{ (d, } J = 12), 103.8, 95.9, 29.5 \text{ (d, } J = 69), 24.0 \text{ (d, } J = 14), 23.4 \text{ (d, } J = 4), 13.52, -0.17.
\]

\[ ^{31}\text{P NMR (161.3 MHz, CDCl}_3\text{): } \delta_\text{P} = 41.3.
\]

\( \text{HRMS (ES+): calcd for C}_{19}\text{H}_{32}\text{OPSi 335.1960, found 335.1956.} \)

\( \text{FT-IR (ATR): } \nu_{\text{max}} \text{ 2958, 2930, 2163, 1467, 1400, 1164, 842, 759, 693 cm}^{-1}. \)
$^1$H NMR (400 MHz, CDCl$_3$) compound S4
\(^{13}\text{C NMR (100.6 MHz, CDCl}_3\text{)}\) compound S4
$^{31}\text{P NMR (161.3 MHz, CDCl}_3\text{)}$ compound S4
Synthesis of 36.

Compound S4 (0.365 g, 0.86 mmol) was dissolved in dry THF (29 mL) and reaction purged with N₂. Reaction was cooled to 0 °C and TBAF (1M in THF, 1.89 mL, 1.89 mmol) added. The reaction was stirred for 10 min and then diluted with EtOAc (50 mL). This solution was washed with 1M HCl (3 x 50 mL) and then dried (MgSO₄). The solvent was removed by rotary evaporation under reduced pressure yielding 36 as a brown oil (0.230 g, 95%).

**¹H NMR (400 MHz, CDCl₃):** \( \delta_H = 7.80 \) (dt, 1H, \( J = 11.0, 1.5 \)), 7.73 (ddt, 1H, \( J = 10.5, 7.5, 1.5 \)), 7.65 (dd, 1H, \( J = 8.0, 1.5 \)), 7.48 (td, 1H, \( J = 8.0, 2.5 \)), 3.17 (s, 1H), 2.06-1.93 (m, 2H), 1.91-1.78 (m, 2H), 1.61-1.55 (m, 2H), 1.48-1.33 (m, 6H), 0.89 (t, 6H, \( J = 7.0 \)).

**¹³C NMR (100.6 MHz, CDCl₃):** \( \delta_C \) = 134.9 (d, \( J = 3 \)), 133.7 (d, \( J = 10 \)), 133.3 (d, \( J = 91 \)), 133.7 (d, \( J = 8 \)), 128.7 (d, \( J = 12 \)), 125.0 (d, \( J = 12 \)), 122.9, 78.5, 29.6 (d, \( J = 69 \)), 24.1 (d, \( J = 14 \)), 23.5 (d, \( J = 4 \)), 13.6.

**³¹P NMR (161.3 MHz, CDCl₃):** \( \delta_p = 40.2 \).

**HRMS (ES⁺):** calcd for C₁₉H₂₃OPSi 335.1960, found 335.1956.

**FT-IR (ATR):** \( \nu_{max} \) 2958, 2930, 2163, 1467, 1400, 1164, 842, 759, 693 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) compound 36
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 36
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 36
Synthesis of 38.

3,5-Dibromophenol (3.00 g, 11.90 mmol), S-(-)-β-citronellol (4.34 mL, 23.80 mmol) and PPh₃ (4.14 g, 15.8 mmol) were dissolved in dry THF (90 mL) under N₂. Diisopropyl azodicarboxylate (3.11 mL, 15.80 mmol) was added slowly at 0 °C. The reaction was allowed to warm to room temperature and was stirred overnight under N₂. The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid, which was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound 38 as a yellow oil (4.55 g, 98%).

\[\alpha\]₀^20 = -4.11 (c 1.31, CHCl₃).

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta_H = 7.23\) (t, 1H, \(J = 1.5\)), 6.98 (d, 2H, \(J = 1.5\)), 5.14-5.06 (m, 1H), 4.00-3.89 (m, 2H), 2.08-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, \(J = 6.5\)).

\(^13\)C NMR (100.6 MHz, CDCl₃): \(\delta_C = 160.3, 131.4, 126.2, 124.5, 123.1, 116.9, 66.9, 37.0, 35.9, 29.4, 25.7, 25.4, 19.5, 17.7.\)

HRMS (ES+): calcd for \(\text{C}_{16}\text{H}_{22}\text{Br}_2\text{O}\) 386.9954, found 386.9960.

FT-IR (ATR): \(\nu_{\text{max}}\) 2955, 2913, 1583, 1557, 1437, 1254, 828 cm\(^{-1}\).
$^1$H NMR (400 MHz, CDCl$_3$) compound 38
Synthesis of S5.

38 (1.00 g, 2.56 mmol), Pd₂dba₃ (0.094 g, 0.10 mmol), Cul (0.020 g, 0.10 mmol) and PPh₃ (0.134 g, 0.51 mmol) were added to a flask with Et₃N (8.5 mL) and DMF (8.5 mL), and N₂ bubbled through the reaction for 15 minutes. TMSA (0.87 mL, 6.15 mmol) was added and the reaction heated by microwave irradiation at 95 °C for 15 min. The reaction was filtered through celite and washed through with EtOAc (80 mL). The solution was washed with 1 M HCl (3 x 50 mL), 5% LiCl solution (2 x 50 mL) and then dried (MgSO₄). The solvent was removed by rotary evaporation under reduced pressure yielding the residue was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound S5 as a light yellow oil (1.07 g, 98%).

[α]₀ = -3.51 (c 1.03, CHCl₃).

¹H NMR (400 MHz, CDCl₃): δ_H = 7.18 (t, 1H, J = 1.5), 6.93 (d, 2H, J = 1.5), 5.13-5.07 (m, 1H), 3.99-3.92 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, J = 6.5), 0.24 (s, 18H).

¹³C NMR (100.6 MHz, CDCl₃): δ_C = 158.6, 131.3, 128.0, 124.6, 124.2, 118.3, 104.1, 94.5, 66.7, 37.0 (, 35.9, 29.7, 25.7, 25.4, 19.5, 17.7, -0.09.

HRMS (ES⁺): calcd for C₂₆H₄₁O₂Si₂ 425.2696, found 425.2698.

FT-IR (ATR): ν_max 2961, 2929, 1578, 1249, 1156, 837, 758 cm⁻¹.
$^{1}H$ NMR (400 MHz, CDCl$_3$) compound S5
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S5
Synthesis of 39.

SS (0.365 g, 0.86 mmol) was dissolved in dry THF (29 mL) and reaction purged with N₂. Reaction was cooled to 0 °C and TBAF (1M in THF, 1.89 mL, 1.89 mmol) added. Reaction was stirred for 10 min and filtered through a plug of silica, washing through with 40-60 pet. ether. The solvent was removed by rotary evaporation under reduced pressure yielding 39 as a brown oil (0.230 g, 95%).

\[ \alpha = -4.44 (c 0.70, \text{CHCl}_3) \]

\(^1\text{H NMR (400 MHz, CDCl}_3\text{)}\): \(\delta_H = 7.20 (t, 1H, J = 1.5), 7.00 (d, 2H, J = 1.5), 5.13-5.07 (m, 1H), 3.99-3.92 (m, 2H) 3.05 (s, 1H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, \(J = 6.5\)).

\(^{13}\text{C NMR (100.6 MHz, CDCl}_3\text{)}\): \(\delta_C = 158.7, 131.4, 128.1, 124.6, 123.3, 118.9, 82.64, 77.52, 66.6, 37.1, 35.9, 29.5, 25.7, 25.4, 19.5, 17.7.\)

HRMS (ES+): calcld for C\text{20}H\text{25}O 281.1905, found 281.1905.

FT-IR (ATR): \(\nu_{max} 3297, 2960, 2925, 1579, 1420, 1321, 1294, 1158 \text{ cm}^{-1}.\)
$^1$H NMR (400 MHz, CDCl$_3$) compound 39

![NMR spectrum graph]
\(^{13}\text{C}\) NMR (100.6 MHz, CDCl\(_3\)) compound 39
Synthesis of 40.

Compound 39 (0.075 g, 0.27 mmol), 3-iodophenol (0.118 g, 0.54 mmol), Pd$_2$(dba)$_3$ (5 mg, 0.55 x 10$^{-2}$ mmol), Cul (1 mg, 0.55 x 10$^{-2}$ mmol) and PPh$_3$ (7 mg, 0.027) were added to a flask with Et$_3$N (1.5 mL) and DMF (1.5 mL), and N$_2$ bubbled through the reaction for 15 min. The reaction was stirred at room temperature for 4 h in the dark under N$_2$. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1 M HCl (3 x 10 mL), 5% LiCl solution (2 x 10 mL) and then dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure and the residue was purified by flash chromatography on silica (40-60 pet. ether/EtOAc 4:1) to yield the desired compound 40 as a brown solid (0.110 g, 88%).

Mpt: 65-68 °C.

$[\alpha]_D$ = -2.519 (c 0.68, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.28 (t, 1H, $J$ = 1.5), 7.22 (t, 2H, $J$ = 8.0), 7.07 (m, 2H), 7.05-6.96 (m, 4H), 6.84 (ddd, 2H, $J$ = 8.0, 2.5, 1.0), 5.17-5.09 (m, 1H), 5.06 (bs, 2H), 4.07-3.96 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.70 (s, 3H), 1.60-1.63 (m, 1H), 1.62 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.96 (d, 3H, $J$ = 6.5).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C$ = 158.8, 155.3, 131.4, 129.7, 127.3, 124.6, 124.4, 124.3, 124.2, 118.3, 117.9, 116.0, 89.2, 88.6, 66.6, 37.1, 36.0, 29.5, 25.8, 25.5, 19.6.

HRMS (ES+): calcd for C$_{32}$H$_{32}$O$_3$ 465.2417, found 465.2424.

FT-IR (ATR): $\nu_{max}$ 3390 (br), 1577, 1184, 864, 781, 735 cm$^{-1}$. 

S104
$^1$H NMR (400 MHz, CDCl$_3$) compound 40
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 40
Synthesis of 41.

Compounds 39 (0.080 g, 0.29 mmol), 8 (0.217 g, 0.69 mmol), Pd$_2$(dba)$_3$ (13 mg, 1.37 x 10$^{-2}$ mmol), Cul (3 mg, 1.37 x 10$^{-2}$ mmol) and PPh$_3$ (0.018 g, 0.07 mmol) were added to a flask with Et$_3$N (2 mL) and DMF (2 mL), and N$_2$ bubbled through the reaction for 15 min. The reaction was heated by microwave irradiation at 95 °C for 10 min. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1M HCl (3x 10 mL), 5% LiCl solution (2x 10 mL) and then dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained residue was purified by flash chromatography in silica (CH$_2$Cl$_2$/MeOH 19:1) to yield the desired compound 41 as a brown oil (0.107 g, 50%).

Mpt: 40-43 °C.

[α]$_D$ = -1.16 (c 1.3, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$H = 7.83 (d, 1H, J = 11.0), 7.70-7.62 (m, 2H), 7.44 (td, 1H, J = 8, 2.5), 7.29 (t, 1H, J = 1.5), 7.04 (d, 2H, J = 2.5 Hz), 5.11-5.04 (m, 1H), 4.01-3.91 (m, 2H), 2.04-1.73 (m, 7H), 1.71-1.49 (m, 12H), 1.46-1.27 (m, 5H), 0.92 (d, 3H, J = 6.5), 0.84 (t, 6H, J = 7 Hz).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$C = 158.9, 134.3 (d, J = 2.5), 133.8 (d, J = 86), 133.5 (d, J = 10), 131.3, 130.2 (d, J = 6), 128.7 (d, J = 10), 127.2, 124.6, 124.1, 118.1, 89.8, 88.7, 66.4, 37.1, 36.1, 29.6 (d, J = 69), 29.5, 25.7, 25.4, 24.1 (d, J = 15), 23.4 (d, J = 2), 19.6, 17.7, 13.5 (d, J = 1).

$^{31}$P NMR (161.3 MHz, CDCl$_3$): $\delta$P = 35.3.

HRMS (ES+): calcd for C$_{24}$H$_{30}$O$_2$ 349.2155, found 349.2162.

FT-IR (ATR): $\nu$max 2958, 2929, 1578, 1221, 1170, 1046, 793, 692 cm$^{-1}$. 
$^1$H NMR (400 MHz, CDCl$_3$) compound 41
$^{13}$C NMR (100.6 MHz, CDCl₃) compound 41
$^{31}\text{P NMR (161.3 MHz, CDCl}_3\text{)}$ compound 41
Synthesis of 42.

Compound 38 (1.00 g, 2.56 mmol) was dissolved in dry Et₂O (30 mL) in a dried flask. The reaction was cooled to -78 °C. n-BuLi (1.6M in hexanes, 1.76 mL, 2.82 mmol) was added slowly over 1 h, and the reaction was stirred for 1 h at -78 °C. A solution of I₂ (1.30 g, 5.13 mmol) in dry Et₂O (5 mL) was added and reaction stirred at -78 °C for 1 hr before being allowed to warm to room temperature over 1 h. Saturated aqueous Na₂S₂O₃ solution (30 mL) was added and reaction stirred until colourless. The organic phase was separated and washed with water (2 x 30 mL), brine (30 mL) and then dried (MgSO₄). The solvent was removed by rotary evaporation under reduced pressure and the obtained oil was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound 42 as a light yellow oil (0.972 g, 87%).

\[ \alpha_{D}^{20} = -3.72 \ (c \ 1.26, \ CHCl₃) \].

\(^{1}H\) NMR (400 MHz, CDCl₃): \( \delta_H = 7.42 \ (dd, \ 1H, \ J = 1.5, 1.5), 7.17 \ (dd, \ 1H, \ J = 2.0, 1.5), 7.01 \ (dd, \ 1H, \ J = 2.0, 1.5), 5.15-5.04 \ (m, \ 1H), 3.99-3.88 \ (m, \ 2H), 2.10-1.90 \ (m, \ 2H), 1.87-1.75 \ (m, \ 1H), 1.69 \ (s, \ 3H), 1.68-1.63 \ (m, \ 1H), 1.61 \ (s, \ 3H), 1.60-1.55 \ (m, \ 1H), 1.42-1.33 \ (m, \ 1H), 1.28-1.18 \ (m, \ 1H), 0.95 \ (d, \ 3H, \ J = 6.5), 0.24 \ (s, \ 9H) \).

\(^{13}C\) NMR (100.6 MHz, CDCl₃): \( \delta_C = 160.1, 131.8, 131.4, 124.5, 123.1, 122.8, 117.6, 94.2, 66.9, 37.0, 35.9, 29.4, 25.8, 25.4, 19.5, 17.7 \).

HRMS (ES?): calcd for C₁₆H₂₁BrO 436.9977, found 436.9971.

FT-IR (ATR): \( \nu_{max} \) 2962, 2914, 1577, 1550, 1433, 1228, 829 cm⁻¹.
$^1$H NMR (400 MHz, CDCl$_3$) compound 42
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 42
Synthesis of 43.

Compounds 36 (0.226 g, 0.86 mmol), 42 (0.343 g, 0.78 mmol), Pd$_2$(dba)$_3$ (15 mg, 1.6 x 10$^{-2}$ mmol), Cul (3 mg, 1.6 x 10$^{-2}$ mmol) and PPh$_3$ (21 mg, 0.079 mmol) were added to a flask under N$_2$. Et$_3$N (5 mL) and DMF (5 mL) were added and the reaction purged with N$_2$ for 20 minutes, then stirred at room temperature overnight in the dark. The reaction was washed through celite with EtOAc (30 mL), and washed with 1M HCl (3 x 30 mL), 5% LiCl solution (2x 30 mL) and then dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained oil was purified by flash chromatography in silica (CH$_2$Cl$_2$/MeOH 19:1) to yield the desired compound 43 as a light brown oil (0.420 mg, 94%).

$[^{13}]$C NMR (100.6 MHz, CDCl$_3$): $\delta$ = 159.6, 134.3 (d, $J$ = 3), 133.5 (d, $J$ = 9), 133.4 (d, 91), 131.4, 130.4 (d, $J$ = 8), 128.7 (d, $J$ = 11), 126.6, 125.1, 124.6, 123.5 (d, $J$ = 12), 122.6, 118.9, 116.2, 89.2, 89.2, 66.8, 37.1, 35.9, 29.6 (d, $J$ = 69), 29.5, 25.7, 25.4, 24.1 (d, $J$ = 14), 23.5 (d, $J$ = 4), 19.5, 17.7, 13.6.

$[^{31}]$P NMR (161.3 MHz, CDCl$_3$): $\delta$ = 40.4.

HRMS (ES+): calcd for C$_{32}$H$_{45}$O$_2$BrP 571.2341, found 571.2331.

FT-IR (ATR): $\nu_{\text{max}}$ 2957, 2929, 2110, 1593, 1558, 1424, 1173, 796 cm$^{-1}$.
$^1$H NMR (400 MHz, CDCl$_3$) compound 43
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 43
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 43
Synthesis of 44.

[43 (0.390 g, 0.68 mmol), 3-hydroxyphenylacetylene (0.373 mL, 3.41 mmol), Pd$_2$(dba)$_3$ (13 mg, 1.4 x 10$^{-2}$ mmol), Cul (2.7 mg, 1.4 x 10$^{-2}$ mmol), and PPh$_3$ (19 mg, 7.1 x 10$^{-2}$ mmol) were placed in a flask under N$_2$. Degassed DMF (5 mL) and Et$_3$N (5 mL) were added and reaction stirred overnight at 50 °C in the dark. The reaction was washed through celite with EtOAc (30 mL), washed with 1M HCl (3x 30 mL) and then dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 19:1) to yield the desired compound 44 as a brown oil (0.149 g, 36%).

$[^{[\alpha]}]_D^{20} = -3.94$ (c 1.10, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 8.72$ (bs, 1H), 7.83 (dt, 1H, $J = 11.5, 1.5$), 7.75-7.63 (m, 2H), 7.50 (td, 1H, $J = 7.5, 2.5$), 7.25 (t, 1H, $J = 1.5$), 7.19 (t, 1H, $J = 8.0$), 7.13 (dd, 1H, $J = 2.5, 1.5$), 7.04 (dt, 1H, $J = 7.5, 1.0$), 7.01 (qd, 2H, $J = 2.5, 1.5$), 6.93 (ddd, 1H, $J = 8.0, 2.5, 1.0$), 5.14-5.07 (m, 1H), 4.05-3.95 (m, 2H), 2.10-1.77 (m, 7H), 1.73-1.54 (m, 8H), 1.50-1.33 (m, 6H), 1.28-1.16 (m, 1H), 0.96 (d, 3H, $J = 6.5$), 0.87 (t, 6H, $J = 7.0$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta_C = 158.8, 157.1, 134.6$ (d, $J = 2$), 133.3 (d, $J = 10$), 133.0 (d, $J = 2$), 131.4, 130.1 (d, $J = 8$), 129.5, 128.9 (d, $J = 11$), 127.3, 124.7, 124.6, 124.1, 124.0, 123.7 (d, $J = 3$), 123.1, 118.7, 118.1, 117.6, 116.5, 90.3, 90.1, 88.3, 87.9, 66.6, 37.1, 36.0, 29.5, 27.5 (d, $J = 51$), 25.7, 25.5, 24.1 (d, $J = 15$), 23.4 (d, $J = 4$), 19.5, 17.7, 13.6.

$^{31}$P NMR (161.3 MHz, CDCl$_3$): $\delta_P = 43.3$.

FT-IR (ATR): $\nu_{\text{max}}$ 2958, 2929, 2215, 1577, 1449, 1195, 1156 cm$^{-1}$.

HRMS (ES+): calcd for C$_{40}$H$_{50}$O$_3$P 609.3498, found 609.3492.
$^1$H NMR (400 MHz, CDCl$_3$) compound 44
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 44
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound 44
Synthesis of 47.

3-Hydroxyphenylacetylene (0.052 g, 0.44 mmol), 1,3-diiodobenzene (0.145 g, 0.44 mmol), compound 36 (0.115 g, 0.44 mmol), Pd$_2$(dba)$_3$ (8 mg, 8.8 x 10$^{-3}$ mmol), Cul (2 mg, 8.8 x 10$^{-3}$ mmol) and PPh$_3$ (12 mg, 4.4 x 10$^{-2}$ mmol) were added to a flask under N$_2$. Degassed Et$_3$N (2.2 mL) and DMF (2.2 mL) were added and the reaction stirred at room temperature overnight in the dark. The reaction was washed through celite with EtOAc (20 mL), washed with 1M HCl (3 x 20 mL), 5% LiCl solution (2 x 30 mL) and then dried (MgSO$_4$). The solvent was removed under reduced pressure and the obtained solid was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 19:1) to yield the desired compound 47 as a yellow crystalline solid (0.069 g, 35%).

**Mpt:** 146-149 °C (CHCl$_3$).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ$_H$ = 8.40 (bs, 1H), 7.85 (d, 1H, J = 11.0), 7.74-7.60 (m, 3H), 7.57-7.40 (m, 3H), 7.31 (t, 1H, J = 8.0), 7.19 (t, 1H J = 8.0 Hz), 7.12 (d, 1H, J = 1.0), 7.05 (d, 1H, J = 7.6), 6.92 (dd, 1H, J = 8.0, 1.5), 2.10-1.97 (m, 2H), 1.96-1.85 (m, 2H), 1.70-1.56 (m, 2H), 1.50-1.34 (m, 6H), 0.87 (t, 6H, J = 7.0 Hz).

**$^{13}$C NMR (100.6 MHz, CDCl$_3$):** δ$_C$ = 156.9, 134.7, 134.6 (d, J = 3), 133.4 (d, J = 10), 133.1, 132.2 (d, J = 4), 132.1, 132.1, 132.4 (d, J = 52), 130.1, 130.0, 129.5, 128.9 (d, J = 12), 128.6 (d, J = 17), 123.2, 122.9, 118.6, 116.5, 90.4, 90.1, 88.7, 87.8, 29.4 (d, J = 70), 24.1 (d, J = 15), 23.4 (d, J = 4), 13.6.

**$^{31}$P NMR (161.3 MHz, CDCl$_3$):** δ$_P$ = 43.3.

**HRMS (ES+):** calcd for C$_{30}$H$_{32}$O$_2$P 455.2140, found 455.2144.

**FT-IR (ATR):** $\nu_{\text{max}}$ 3073 (br), 2957, 2930, 2217, 1593, 1144, 791, 731, 687 cm$^{-1}$. 

S122
$^1$H NMR (400 MHz, CDCl$_3$) compound 47
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound 47
$^{31}P$ NMR (161.3 MHz, CDCl$_3$) compound 47
Synthesis of C7-PO A and D 1-mers.

**Scheme S1:** Synthesis of C7-PO A and D 1-mers.

**Synthesis of S7.**

3-Iodophenol (1.00 g, 4.55 mmol), S(-)-β-citronellol (1.66 mL, 9.09 mmol) and PPh$_3$ (1.55 g, 5.91 mmol) were dissolved in dry THF (30 mL) under N$_2$. Diisopropyl azodicarboxylate (1.17 mL, 5.91 mmol) was added slowly at 0 °C. The reaction was allowed to warm to room temperature and was stirred overnight under N$_2$. The solvent was removed by rotary evaporation under reduced pressure and the obtained brown solid was purified by flash chromatography on silica (40-60 pet. ether) to yield the S7 as a light yellow oil (1.55 g, 95%).

$[\alpha]_D^{20}$ = -4.27 (c 1.02, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$): δ$_H$ = 7.27 (d, $J = 8.0$, 1H), 7.26 (s, 1H), 6.99 (t, $J = 8.0$, 1H), 6.86 (m, 1H), 5.14-5.06 (m, 1H), 4.00-3.89 (m, 2H), 2.08-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, $J = 6.5$ Hz).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): δ$_C$ = 159.7, 131.4, 130.7, 129.6, 124.6, 123.6, 114.2, 94.4, 66.5, 37.1, 36.0, 29.5, 25.8, 25.5, 19.6, 17.7.

HRMS (ES+): calcd for C$_{16}$H$_{24}$IO 359.0872, found 359.0861.

FT-IR (ATR): $\nu_{\text{max}}$ 2958, 2923, 2873, 1584, 1567, 1467, 1241, 1224 cm$^{-1}$. 

S126
$^1$H NMR (400 MHz, CDCl$_3$) compound S7
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S7
Synthesis of S8.

S7 (1.00 g, 2.79 mmol), Pd$_2$(dba)$_3$ (51 mg, 5.58 x 10$^{-2}$ mmol), CuI (10 mg, 5.58 x 10$^{-2}$ mmol) and PPh$_3$ (73 mg, 0.279 mmol) were added to a flask with Et$_3$N (9 mL) and DMF (9 mL), and N$_2$ bubbled through the reaction for 15 min. TMSA (0.44 mL, 3.07 mmol) was added and the reaction stirred at room temperature for 4 h in the dark under N$_2$ atmosphere. The reaction was filtered through celite and washed through with EtOAc (50 mL). The solution was washed with 1M HCl (2 x 50 mL), 5% LiCl solution (2 x 50 mL) and then dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure and the obtained brown solid was purified by flash chromatography on silica (40-60 pet. ether) to yield the desired compound S8 as a light yellow oil (0.860 g, 94%).

$[\alpha]_D^{20} = -5.48$ (c 0.91, CHCl$_3$).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.18 (t, 1H, $J = 8.0$), 7.04 (dt, 1H, $J = 8.0$, 1.0), 6.99 (dd, 1H, $J = 2.5$, 1.0), 6.86 (ddd, 1H, $J = 8.0$, 2.5, 1.0), 5.15-5.07 (m, 1H), 4.01-3.93 (m, 2H), 2.10-1.92 (m, 2H), 1.88-1.76 (m, 1H), 1.69 (s, 3H), 1.68-1.63 (m, 1H), 1.61 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.95 (d, 3H, $J = 6.5$), 0.25 (s, 9H).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C$ = 158.8, 131.3, 129.2, 124.6, 124.3, 124.0, 117.2, 115.9, 105.1, 93.8, 66.3, 37.1, 36.1, 29.5, 25.7, 25.5, 19.6, 17.7, -0.01.

HRMS (ES+): calcd for C$_{21}$H$_{33}$OSi 329.2301, found 329.2301.

FT-IR (ATR): $\nu_{\text{max}}$ 2959, 2925, 1596, 1574, 1249, 1156, 934 cm$^{-1}$. 

S129
$^1$H NMR (400 MHz, CDCl$_3$) compound S8
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S8
Synthesis of S9.

S8 (0.350 g, 1.07 mmol) was dissolved in dry THF (30 mL) and the reaction purged with \( \text{N}_2 \). The reaction was cooled to 0 °C and TBAF (1M in THF, 2.13 mL, 2.13 mmol) was added. The reaction was stirred for 10 min and filtered through a plug of silica, washing through 40-60 pet. ether:EtOAc (49:1). The solvent was removed by rotary evaporation under reduced pressure yielding S9 as a yellow oil (0.270 g, 99%).

\( \left[ \alpha \right]_{D}^{20} = -5.98 \) (c 0.93, CHCl₃).

\(^1\text{H NMR (400 MHz, CDCl₃)}: \delta_H = 7.21 \text{ (t, } 1\text{H, } J = 8.0 \text{ Hz}), 7.07 \text{ (dt, } 1\text{H, } J = 8.0, 1.0), 7.01 \text{ (dd, } 1\text{H, } J = 2.5, 1.0), 6.90 \text{ (ddd, } 1\text{H, } J = 8.0, 2.5, 1.0), 5.14-5.07 \text{ (m, } 1\text{H}), 4.03-3.93 \text{ (m, } 2\text{H}), 3.05 \text{ (s, } 1\text{H}), 2.10-1.92 \text{ (m, } 2\text{H}), 1.88-1.76 \text{ (m, } 1\text{H}), 1.69 \text{ (s, } 3\text{H}), 1.68-1.63 \text{ (m, } 1\text{H}), 1.61 \text{ (s, } 3\text{H}), 1.60-1.55 \text{ (m, } 1\text{H}), 1.42-1.33 \text{ (m, } 1\text{H}), 1.28-1.18 \text{ (m, } 1\text{H}), 0.95 \text{ (d, } 3\text{H, } J = 6.5).\

\(^{13}\text{C NMR (100.6 MHz, CDCl₃)}: \delta_C = 158.8, 131.3, 129.3, 124.6, 124.4, 123.0, 117.6, 116.0, 83.7, 76.8, 66.5, 37.1, 36.1, 29.5, 25.7, 25.5, 19.5, 17.7.\

\( \text{HRMS (ES+)}: \text{calcd for } C_{18}H_{24}O \text{H} 257.1905, \text{found } 257.1905.\

\( \text{FT-IR (ATR): } \nu_{\text{max}} 3299, 2961, 2915, 1975, 1575, 1474, 1257, 1145 \text{ cm}^{-1}.\)
$^1$H NMR (400 MHz, CDCl$_3$) compound S9
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S9

[Spectroscopic data and chemical structure]
Synthesis of S10.

S9 (0.350 g, 1.37 mmol), 3-iodophenol (0.301 g, 1.37 mmol), Pd2(dba)3 (25 mg, 2.70 x 10^{-2} mmol), CuI (5 mg, 2.70 x 10^{-2} mmol) and PPh3 (36 mg, 0.14 mmol) were added to a flask with Et3N (5 mL) and DMF (5 mL), and N2 bubbled through the reaction for 15 min. The reaction was stirred at room temperature for 4 h in the dark under N2 atmosphere. The reaction was filtered through celite and washed through with EtOAc (30 mL). The solution was washed with 1M HCl (2 x 30 mL), 5% LiCl solution (2 x 50 mL) and then dried (MgSO4). The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid which was purified by flash chromatography on silica (40-60 pet. ether/EtOAc 4:1) to yield the desired compound S10 as a brown solid (0.442 g, 93%).

Mpt: 40-43 °C.

[α]D = -4.54 (c 0.48, CHCl3).

1H NMR (400 MHz, CDCl3): δH = 7.27-7.17 (m, 2H), 7.14-7.09 (m, 2H), 7.06 (dd, 1H, J = 2.5, 1.5), 7.00 (dd, 1H, J = 2.5, 1.5), 6.90 (ddd, 1H, J = 8.5, 2.5), 6.82 (dd, 1H, J = 8.0, 2.5, 1.0), 5.13-5.07 (m, 1H), 4.99 (bs, 1H), 4.01-3.91 (m, 2H), 2.09-1.92 (m, 2H), 1.85-1.76 (m, 1H), 1.70 (s, 3H), 1.60-1.63 (m, 1H), 1.62 (s, 3H), 1.60-1.55 (m, 1H), 1.42-1.33 (m, 1H), 1.28-1.18 (m, 1H), 0.96 (d, 3H, J = 6.5).

13C NMR (100.6 MHz, CDCl3): δC = 158.9, 155.3, 131.4, 129.7, 129.4, 124.7, 124.5, 124.4, 124.1, 124.0, 118.2, 117.0, 115.8, 115.6, 89.5, 88.7, 66.4, 37.1, 36.1, 29.5, 25.8, 25.5, 19.6, 17.7.

HRMS (ES+): calcd for C24H28O2 349.2155, found 349.2162.

FT-IR (ATR): νmax 3365 (br), 2911, 1612, 1574, 1496, 1324, 1189 cm^{-1}.
$^1$H NMR (400 MHz, CDCl$_3$) compound S10
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S10
Synthesis of S11.

Compounds S9 (103 mg, 0.40 mmol), 35 (152 mg, 0.48 mmol), Pd$_2$(dba)$_3$ (7.3 mg, 8.0 x 10$^{-3}$ mmol), Cul (1.5 mg, 8.0 x 10$^{-3}$ mmol) and PPh$_3$ (10.5 mg, 0.04 mmol) were added to a flask with Et$_3$N (2 mL) and DMF (2 mL). N$_2$ was bubbled through the reaction for 15 min. The reaction was heated by microwave irradiation at 95 °C for 10 min. The reaction was filtered through celite and washed through with EtOAc (10 mL). The solution was washed with 1M HCl (3 x 10 mL), 5% LiCl solution (2 x 10 mL) and the dried (MgSO$_4$). The solvent was removed by rotary evaporation under reduced pressure yielding a brown solid which was purified by flash chromatography on silica (CH$_2$Cl$_2$/MeOH 20:1) to yield the desired compound S11 as a brown waxy solid (0.169 g, 86%).

$[\alpha]_D$ = -4.48 (c 0.96, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 7.81 (d, 1H, $J$ = 10.0), 7.67-7.59 (m, 2H), 7.44 (t, 1H, $J$ = 8.0), 7.21 (t, 1H, $J$ = 8.0), 7.08 (d, 1H, $J$ = 8.0), 7.03 (t, 1H, $J$ = 2.0), 6.87 (dd, 1H, $J$ = 8.0, 2.0), 5.11-5.04 (m, 1H), 4.01-3.91 (m, 2H), 2.04-1.73 (m, 7H), 1.71-1.49 (m, 12H), 1.46-1.27 (m, 5H), 0.92 (d, 3H, $J$ = 6.5), 0.84 (t, 6H, $J$ = 7.0).

$^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta_C$ = 158.9, 134.3, 133.4 (d, $J$ = 9), 132.0 (d, $J$ = 10), 131.2, 130.0 (d, $J$ = 6), 129.4, 128.7 (d, $J$ = 10), 124.6, 124.0, 123.9 (d, $J$ = 10), 123.6, 117.0, 115.9, 90.8, 88.1, 66.4, 37.1, 36.1, 29.6 (d, $J$ = 69), 29.5, 25.7, 25.4, 24.1 (d, $J$ = 15), 23.4 (d, $J$ = 2), 19.6, 17.7, 13.5 (d, $J$ = 1).

$^{31}$P NMR (161.3 MHz, CDCl$_3$): $\delta_P$ = 40.3.

HRMS (ES+): calcd for C$_{24}$H$_{28}$O$_2$ 349.2155, found 349.2162.

FT-IR (ATR): $\nu_{\text{max}}$ 2957, 2929, 1596, 1574, 1466, 1222, 1170, 686 cm$^{-1}$. 
$^1$H NMR (400 MHz, CDCl$_3$) compound S11
$^{13}$C NMR (100.6 MHz, CDCl$_3$) compound S11
$^{31}$P NMR (161.3 MHz, CDCl$_3$) compound S11
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