SUPPORTING INFORMATION

Stereoselective Pd(0) Catalysed Five Component Cascade Synthesis of Complex *Z,Z*-Bisallylamines.

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General technical data.

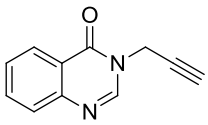
Thin layer chromatography (TLC) was carried out on a pre-coated aluminium plates with silica gel 60 F254 (Merck), and was visualised using ultraviolet light and/or aqueous $KMnO_4/I_2$. Flash column chromatography employed silica gel 60 (Merck, 230-400mesh). Meting points were determined on a Reichert hot-stage microscope and are uncorrected. Optical rotations were calculated using Polartronic H 532 (Schmidt + Haensch) instrument. Infrared spectra were recorded using a Perkin-Elmer Spectrum FT-IR spectrometer either as a thin film on sodium chloride discs or as a solid using golden gate apparatus. Proton nuclear magnetic resonance spectra were recorded at 500 and 300MHz on a Bruker DRX500 and DPX300 instruments, respectively. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (δ = 0.00) and coupling constants are given in hertz (Hz). The following abbreviations are used: s = singlet, br = broad, d = doublet, dd = doublet of doublets, ddd = doublet of double doublets, dt = doublet of triplets, m = multiplet, t = triplet, td = triplet of doublets. ^{13}C-NMR spectra were recorded at 75 MHz on a Bruker DPX300 instrument and chemical shifts are reported in parts per million (ppm). Mass spectral data were determined at 70 eV on a Micromass ZMD 2000 electrospray (ES) machine. Accurate masses were obtained using a Bruker Daltonics micrOTOF spectrometer. The m/z data mentioned in case of 9-component cascades are the result of two runs using the auto sampler technique and by injecting the sample directly to the machine using a syringe pump.

^{1}H-NMR peak assignments are mainly based on DEPT135, COSY, HMQC and HMBC spectral data.

All compounds were named according to the IUPAC system using the ACD/ILAB (ACD/IUPAC v.12.0 program) web service (http:/www.acdlabs.com).

Allenes **1**, **4** and **5** were prepared according to our previous work.[1]

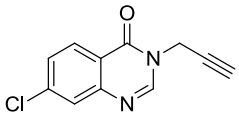
3-(Prop-2-yn-1-yl)quinazolin-4(3H)-one



Prepared by general procedure A[1] from quinazolin-4(3*H*)-one. Crystallisation of the residue from hexane-dichloromethane yielded the product (82%) as light yellow needles, mp 107-109; ^{1}H-NMR ($CDCl_3$, 300MHz) 8.33 (dm, 1H, ArH), 8.31 (s, 1H, N=CH_2), 7.82-7.71 (m, 2H, ArH),

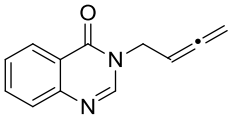
7.53 (dd, 1H, ArH, *J*= 1.5, 6.8, 8.2 Hz), 4.83 (d, 2H, NCH_2, *J*= 2.6Hz), 2.50 (t, 1H, C≡CH, *J*= 2.6 Hz); 13C-NMR (CDCl3, 75MHz) 160.4 (C=O), 147.9 (C), 145.0 (N=CH), 134.6 (CH), 127.6 (2) (CH), 126.8 (CH), 121.8 (C), 76.4 (*C*≡CH), 75.2 (C≡*C*H), 35.2 (NCH_2); ν_{max} (film) 1668 (C=O), 1607 (C=C) cm^{-1}; ESI-HRMS calculated for $C_{11}H_9N_2O$ $[M+H]^+$ 185.0709 found 185.0717.

7-Chloro-3-(prop-2-yn-1-yl)quinazolin-4(3H)-one



Prepared by general procedure A[1] from 7-chloroquinazolin-4(3H)-one. Crystallization of the residue from methanol yielded the product (88%) as colourless needles, mp 140-142 °C; ^{1}H-NMR ($CDCl_3$, 300MHz) 8.32 (s, 1H, N=CH), 8.23 (d, 1H, ArH, *J*= 8.6 Hz), 7.71 (d, 1H, ArH, *J*= 2.0 Hz), 7.46 (dd, 1H, ArH, *J*= 2.0, 8.6 Hz), 4.81 (d, 2H, NCH_2, *J*= 2.6 Hz), 2.54 (t, 1H, C≡CH, *J*= 2.6 Hz); 13C-NMR (CDCl3, 75MHz) 159.8 (C=O), 148.9 (C), 146.2 (N=CH), 140.8 (C), 128.2(2) (CH), 127.2 (CH), 120.2 (C), 76.1 (*C*≡CH), 75.5 (C≡*C*H), 35.3 (NCH_2); ν_{max} (film) 1669 (C=O), 1603 (C=C) cm^{-1}; ESI-HRMS calculated for $C_{11}H_8ClN_2O$ $[M+H]^+$ 219.0320 found 219.0313.

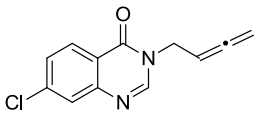
***3-(Buta-2,3-dien-1-yl)quinazolin-4(3H)-one* (2)**



Prepared by general procedure B[1] from 3-(Prop-2-yn-1-yl)quinazolin-4(3H)-one. Purification by flash column chromatography eluting with 1:1 (hexane: ethyl acetate) and then crystallization from hexane/chloroform yielded the product product **2** (68%) as light brown flat, mp 66-67°C; ^{1}H-NMR ($CDCl_3$, 300MHz) 8.32 (dm, 1H ArH), 8.06 (s, 1H, N=CH), 7.80-7.69 (m, 2H, ArH), 7.52 (ddd, 1H, ArH, *J*= 1.5, 6.8, 8.2 Hz), 5.43 (p, 1H, C=C*H*, *J*= 6.4 Hz), 4.88 (dt, 2H, $C=CH_2$, *J*= 3.0, 6.6 Hz), 4.62 (dt, 2H, NCH_2, *J*= 3.0, 6.2 Hz); 13C-NMR (CDCl3, 75MHz) 208.9 (C=*C*=C), 160.7 (C=O), 148.0 (C), 146.3 (N=CH), 134.2 (CH), 127.5 (CH), 127.3 (CH), 126.7 (CH), 122.0 (C), 86.6 (C=*C*H), 78.2 (C=*C*H_2), 44.5 (NCH_2); ν_{max} (film) 3053 (C=C-H), 1956

(C=C=C),1677 (C=O), 1611 (C=C) cm^{-1}; ESI-HRMS calculated for $C_{12}H_{11}N_2O$ $[M+H]^+$ 199.0866 found 199.0868.

3-(Buta-2,3-dien-1-yl)-7-chloroquinazolin-4(3*H*)-one (3)

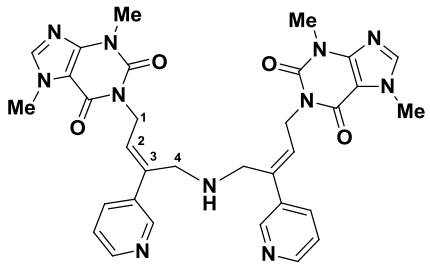


Prepared by general procedure B[1] from 7-Chloro-3-(prop-2-yn-1-yl)quinazolin-4(3*H*)-one. Purification by flash column chromatography eluting with 1:1 (hexane : ethyl acetate) and then crystallization with hexane/chloroform yielded the product (72%) as a light brown rods, mp 60-62°C; ^{1}H-NMR ($CDCl_3$, 300MHz) 8.23 (d, 1H, ArH, *J*= 8.6 Hz), 8.07 (s, 1H, N=CH), 7.70 (d, 1H, ArH, *J*= 2.0 Hz), 7.46 (dd, 1H, ArH, *J*= 2.0, 8.6 Hz), 5.42 (p, 1H, C=CH, *J*= 6.3 Hz), 4.88 (dt, 2H, $C=CH_2$, *J*= 2.9, 6.6 Hz), 4.60 (dt, 2H, NCH_2, *J*= 2.9, 6.1 Hz); 13C-NMR (CDCl3, 75MHz) 209.0 (C=*C*=C), 160.1 (C=O), 149.0 (C), 147.4 (N=CH), 140.5 (C), 128.3 (CH), 127.9 (CH), 127.1 (CH), 120.5 (ArCl), 86.5 (C=*C*H), 78.4 ($C=CH_2$), 44.5 (NCH_2); ν_{max} (film) 3066 (C=C-H), 1957(C=C=C), 1673 (C=O), 1603 (C=C) cm^{-1}; ESI-HRMS calculated for $C_{12}H_{10}ClN_2O$ $[M+H]^+$ 233.0476 found 233.0467.

General procedure for cascade synthesis of diallylamines.

A mixture of allene (0.5 mmol), aryliodide (0.6 mmol), ammonium tartrate (1.5-3 mmol), Pd_2dba_3 (2.5 mol%), TFP (0.1 mol%) and potassium carbonate (1 mmol) in 5:1 v/v dioxane:DMF (12 mL) was heated and stirred at 100°C (oil bath temperature) until the reaction completed (monitored by TLC). The reaction mixture was cooled to room temperature and the solvent evaporated. Dichloromethane was then added and the solution extracted with 30% NH_4OH then water. The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate concentrated *in vacuo*. The residue was purified by flash column chromatography.

1,1'-{Iminobis[(2*Z*)-3-(pyridin-3-yl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12a)

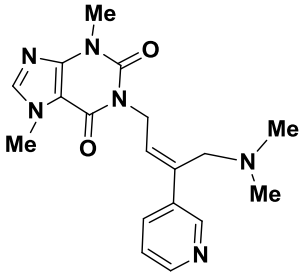


Flash chromatography gradient elution with 20:1 $CHCl_3$/MeOH and then 18:1:1 ($CHCl_3$: MeOH: NH_4OH) gave colourless amorphous product (80%), mp 148-149 °C; δ_H (300 MHz, $CDCl_3$) 8.70 (d, *J*=1.7 Hz, 1H, ArH), 8.44 (dd, *J*= 4.7, 1.3 Hz, 1H, ArH), 7.76 (dt, *J*= 8.0, 1.8 Hz, 1H, ArH), 7.53 (s, 1H, N=CH), 7.15 (dd, *J*= 8.0, 4.8 Hz, 1H, ArH), 5.92 (t, *J*= 7.0 Hz, 1H, C=CH), 4.90 (d, *J*= 7.0 Hz, 2H, NCH_2), 3.98 (s, 3H, NCH_3), 3.94 (s, 2H, CH_2NH), 3.60 (s, 3H, NCH_3); δ_c (75 MHz,$CDCl_3$) 155.0, 151.3, 148.9, 148.3, 147.8, 141.6, 138.7, 137.1, 133.9, 126.6, 123.0, 107.6, 48.0, 39.5, 33.6, 29.8; ν_{max} /cm^{-1} (film); 3312, 3113, 3051, 2949, 1704, 1666, 1604, 1550; ESI-HRMS calculated for $C_{32}H_{34}N_{11}O_4$ $[M+H]^+$ 636.2790 found 636.2780.

NOE data ($CDCl_3$) for **12a**.

	% Enhancement				
Irradiated proton	1-H	2-H	4-H	pyridyl-H (δ 8.70)	pyridyl-H (δ 7.76)
1-H		5.20	3.54	-	-
2-H	3.25		-	6.62	3.79
4-H	3.66	-		3.12	3.19

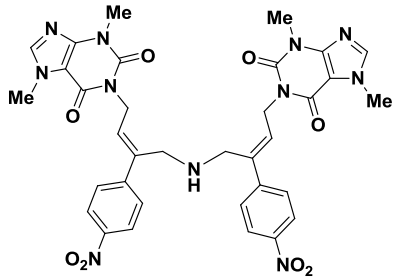
1-[(2*Z*)-4-(dimethylamino)-3-(pyridin-3-yl)but-2-en-1-yl]-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dionen (12aa).



A mixture of allene (0.116 g, 0.50 mmol), 3-iodopyridine (0.123 g, 0.60 mmol), urea (0.36 g, 6.00 mmol), $Pd_2(dba)_3$ (0.011 g, 2.5 mol%), TFP (0.012 g, 10 mol%) and K_2CO_3 (0.207 g, 1.50 mmol) in 2:1 v/v DMF/water (3 mL) was stirred and heated at 80 ºC for 4h (oil bath

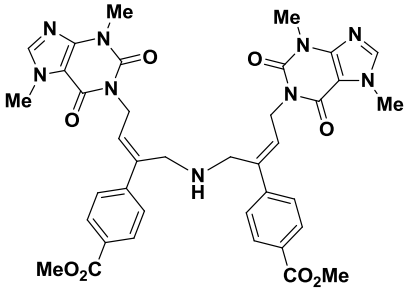
temperature). The mixture was cooled, evaporated under reduced pressure and the resulting residue dissolved in $CHCl_3$ and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate evaporated under reduced pressure. Flash chromatography eluting with 5:1 EtOAc/MeOH gave colourless amorphous product (79%), mp 172-174 °C; δ_H (300 MHz, $CDCl_3$); 8.68 (d, *J*= 1.6 Hz, 1H, ArH), 8.45 (dd, *J*= 4.9, 1.6 Hz, 1H, ArH), 7.76 (dt, *J*= 7.7, 1.6 Hz, 1H, ArH), 7.54 (s, 1H, N=CH), 7.21 (dd, *J*= 7.7, 4.9 Hz, 1H, ArH), 5.92 (t, *J*= 6.6, 1H, C=C*H*), 4.93 (d, *J*= 6.6 Hz, 2H, N*CH*$_2$), 4.00 (s, 3H, NCH_3), 3.59 (s, 3H, NCH_3), 3.56 (s, 2H, CH_3NCH_2), 2.27 (6H, s, 2xNCH_3); δ_c (75 MHz, $CDCl_3$); 155.0, 151.4, 148.9, 148.3, 147.8, 141.6, 137.6, 137.1, 133.8, 128.1, 122.9, 107.6, 57.6, 45.3, 39.5, 33.6, 29.8; ν_{max}/cm^{-1} (film); 2943, 2818, 2766, 1704, 1660, 1603, 1549, 1455, 1414, 1366, 1315, 1286, 1234; ESI-HRMS calculated for $C_{18}H_{23}N_6O_2$ $[M+H]^+$ 355.1877 found 355.1886.

1,1'-{Iminobis[(2*Z*)-3-(4-nitrophenyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12b)



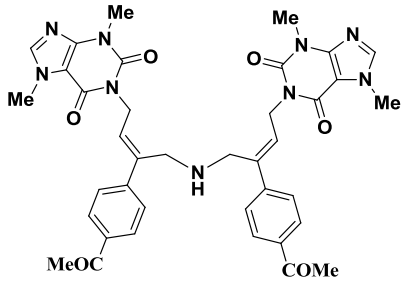
Flash chromatography gradient elution with 20:1 $CHCl_3$/MeOH and then 9:1 $CHCl_3$/MeOH gave colourless amorphous product (82%), mp 228-230 °C; δ_H (300 MHz, $CDCl_3$) 8.10 (d, *J*= 8.8 Hz, 2H, ArH), 7.65 (d, *J*= 8.8 Hz, 2H, ArH), 7.53 (s, 1H, N=CH), 6.00 (t, *J*= 6.8 Hz, 1H, C=CH), 4.89 (d, *J*= 6.8 Hz, 2H, NCH_2), 3.97 (s, 3H, NCH_3), 3.94 (s, 2H, C*H*$_2$NH), 3.57 (s, 3H, NCH_3); δ_c (75 MHz,$CDCl_3$) 155.0 , 151.4, 149.0, 148.2, 146.9, 141.7, 139.7, 128.7, 127.2, 123.5, 107.6, 48.2, 39.6, 33.6, 29.8; ν_{max} /cm^{-1} (solid); 3122, 1702, 1655, 1591, 1342; ESI-HRMS calculated for $C_{34}H_{34}N_{11}O_8$ $[M+H]^+$ 724.2586 found 724.2588.

Dimethyl 4,4'-{iminobis[(2*Z*)-4-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-1-yl)but-2-ene-1,2-diyl]}dibenzoate (12c)



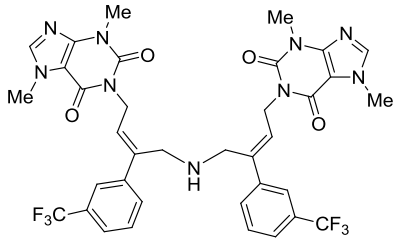
Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave a colourless amorphous product (80%), mp 212-214 °C; δ_H (300 MHz, $CDCl_3$) 7.89 (d, *J*= 8.5 Hz, 2H, ArH), 7.52 (s, 1H, N=CH), 7.51 (d, *J*= 8.5 Hz, 2H, ArH), 5.96 (t, *J*= 7.0 Hz, 1H, C=CH), 4.88 (d, *J*= 7.0 Hz, 2H, NCH_2), 3.97 (s, 3H, NCH_3), 3.95 (s, 2H, C*H*$_2$NH), 3.89 (s, 3H, CO_2Me), 3.57 (s, 3H, NCH_3); δ_c (75MHz, $CDCl_3$) 166.9, 154.9, 151.3, 148.9, 146.0, 141.6, 140.7, 129.5, 128.6, 126.9, 126.4, 107.6, 52.0, 47.9, 39.6, 33.6, 29.7; ν_{max}/cm^{-1} (film); 1703, 1658, 1605, 1549, 1280; ESI-HRMS calculated for $C_{38}H_{40}N_9O_8$ $[M+H]^+$ 750.2994 found 750.3029.

1,1'-{Iminobis[(2*Z*)-3-(4-acetylphenyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12d)



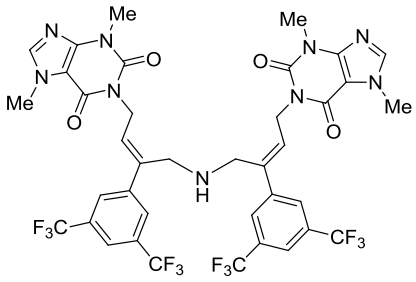
Flash chromatography eluting with 40:1 $CHCl_3$/MeOH gave the product as a colourless froth (67%), mp 110-112 °C; δ_H (300 MHz, $CDCl_3$); 7.82 (d, *J*= 8.2 Hz, 4H, 4 × ArH), 7.56 (s, 2H, 2xN=CH), 7.54 (d, *J*= 8.2 Hz, 4H, 4 × ArH), 5.83 (t, *J*= 7.1 Hz, 2H, 2 × C=CH), 4.91 (d, *J*= 7.1 Hz, 4H, 2 × N*CH*$_2$), 3.99 (s, 6H, 2 × NCH_3), 3.97 (s, 4H, 2 ×*CH*$_2$NH), 3.58 (s, 6H, 2 × NCH_3), 2.58 (6H, s, 3 × $COCH_3$), 2.23 (1H, br s, NH); δ_c (75 MHz, $CDCl_3$); 197.7, 154.9, 151.3, 148.8, 146.2, 141.7, 140.6, 135.7, 128.3, 127.1, 126.6, 107.6, 47.8, 39.6, 33.6, 29.7, 26.6; ν_{max}/cm^{-1} (film); 3320, 3114, 3012, 2945, 1704, 1659, 1602, 1549, 1487, 1455, 1428, 1412, 1358, 1312, 1270, 1234; ESI-HRMS calculated for $C_{38}H_{40}N_9O_6$ $[M+H]^+$ 718.3096 found 718.3111.

1,1'-(Iminobis{(2*Z*)-3-[3-(trifluoromethyl)phenyl]but-2-ene-4,1-diyl})bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12e)



Flash column chromatography eluting with gradient 20:1 $CHCl_3$/MeOH gave colourless amorphous product (63%), mp 193-195 °C; δ_H (300 MHz, $CDCl_3$) 7.76 (s, 1H, ArH), 7.65 (d, *J*= 7.7 Hz, 1H, ArH), 7.51 (s, 1H, N=CH), 7.44 (d, *J*= 7.7 Hz, 1H, ArH), 7.33 (t, *J*= 7.7 Hz, 1H, ArH), 5.91 (t, *J*= 7.1 Hz, 1H, C=CH), 4.89 (d, *J*= 7.1 Hz, 2H, NCH_2), 3.96 (s, 3H, NCH_3), 3.95 (s, 2H, CH_2NH), 3.56 (s, 3H, NCH_3); δ_c (75 MHz, $CDCl_3$) 155.0, 151.4, 148.9, 142.3, 141.6, 140.3, 130.4 (q, *J*= 31.9 Hz), 129.8, 128.6, 126.5, 126.0–122.4 (br d, *J*= 272.8 Hz), 123.8 (q, *J*= 3.7 Hz), 123.2 (q, *J*= 3.9 Hz), 107.6, 48.3, 39.6, 33. 6, 29.7; ν_{max}/cm^{-1} (film); 3524, 3113, 2955, 1704, 1659, 1604, 1550, 1123, 1334; ESI-HRMS calculated for $C_{36}H_{34}F_6N_9O_4$ $[M+H]^+$ 770.2632 found 770.2657.

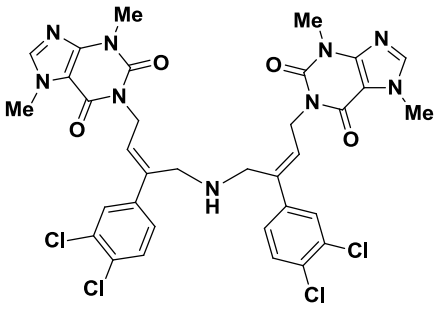
1,1'-(Iminobis{(2*Z*)-3-[3,5-bis(trifluoromethyl)phenyl]but-2-ene-4,1-diyl})bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12f)



Flash chromatography eluting with 20:1 EtOAc/MeOH gave the product as a colourless froth (86%), mp 94-96 °C; δ_H (300 MHz, $CDCl_3$); 7.94 (2H, s, ArH), 7.70 (1H, s, ArH), 7.54 (1H, s, N=CH), 5.95 (2H, t, *J*= 7.1 Hz, C=CH), 4.92 (2H, d, *J*=7.1 Hz, NCH_2), 3.98 (s, 5H, NCH_3+CH_2NH), 3.58 (3H, s, NCH_3); δ_c (75 MHz, $CDCl_3$);155.0, 151.3, 149.0, 143.8, 141.7, 139.3, 131.3 (q, *J*= 33.2 Hz), 128.3, 126.6 (d, *J*= 3.3 Hz), 123.3 (q, *J*= 273.1 Hz), 120.9 (t, *J*= 3.3 Hz), 107.6, 48.4, 39.5, 33.6, 29.8; ν_{max}/cm^{-1} (film); 3312, 3017, 2952, 1710, 1660, 1605,

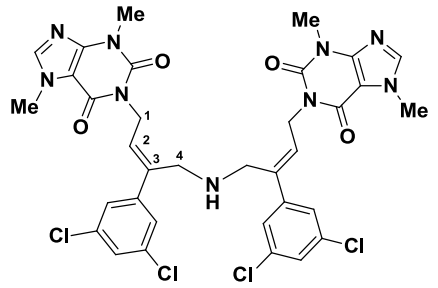
1550, 1456, 1430, 1415, 1382, 1312, 1279, 1235; ESI-HRMS calculated for $C_{38}H_{32}F_{12}N_9O_4[M+H]^+$ 906.2380 found 906.2366.

1,1'-{Iminobis[(2*Z*)-3-(3,4-dichlorophenyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12g)



Flash chromatography eluting with 32:1 $CHCl_3$/MeOH gave colourless amorphous product (81%), mp 128-130 °C; δ_H (300 MHz, $CDCl_3$) 7.60 (t, *J*= 1.0 Hz, 1H, ArH), 7.53 (s, 1H, N=CH), 7.31 (d, *J*= 1.0 Hz, 2H, ArH), 5.89 (d, *J*= 7.0 Hz, 2H, C=CH), 4.87 (d, *J*= 7.0 Hz, 2H, NCH_2), 3.98 (s, 3H, NCH_3), 3.89 (s, 2H, CH_2NH) , 3.58 (s, 3H, NCH_3); δ_c (75 MHz, $CDCl_3$) 154.9, 151.3, 148.9, 141.6 (2), 139.4, 132.2, 131.0, 130.0, 128.5, 126.5, 125.8, 107.6, 48.0 , 39.5, 33.6, 29.8; ν_{max}/cm^{-1} (film); 3505, 3115, 3054, 2949, 1704, 1666, 1604, 1549, 763, 737; ESI-HRMS calculated for $C_{34}H_{32}{}^{35}Cl_4N_9O_4$ 770.1326 $[M+H]^+$ found 770.1315.

1,1'-{Iminobis[(2*Z*)-3-(3,5-dichlorophenyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12h)



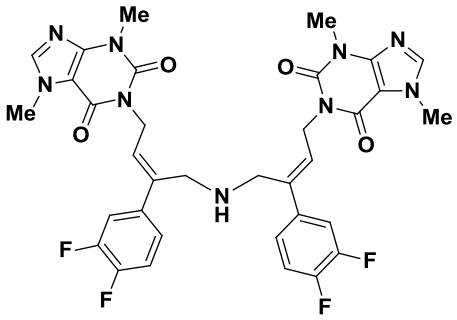
Flash chromatography eluting with 20:1 EtOAc/MeOH gave the product as a colourless froth (87%), mp 102-104 °C; δ_H (300 MHz, $CDCl_3$); 7.53 (s, 2H, 2 × N=CH), 7.39 (d, *J*= 1.6 Hz, 4H, 4 × ArH), 7.18 (t, *J*= 1.6 Hz, 2H, 2 × ArH), 5.89 (t, *J*= 7.1 Hz, 2H, 2 × C=CH), 4.88 (d, *J*= 7.1 Hz, 4H, 2 × NCH_2), 3.98 (s, 6H, 2 × NCH_3), 3.87 (s, 4H, 2 × CH_2NH), 3.58 (s, 6H, 2 × NCH_3), 2.17 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$); 154.9, 151.3, 148.9, 144.7, 141.6, 139.4, 134.6, 127.2,

127.1, 125.0, 107.6, 48.1, 39.5, 33.7, 29.8; ν_{max}/cm^{-1} (film); 3311, 3071, 3014, 2949, 1704, 1660, 1604, 1584, 1557, 1487, 1455, 1414, 1355, 1313, 1286, 1234; ESI-HRMS calculated for $C_{34}H_{32}{}^{35}Cl_4N_9O_4$ $[M+H]^+$ 770.1326 found 770.1328.

NOE data ($CDCl_3$) for **12h**.

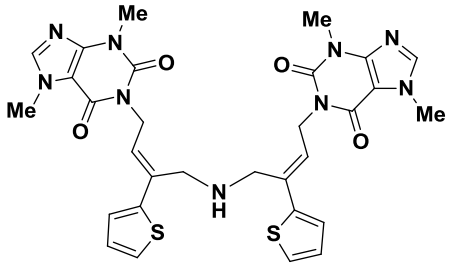
	% Enhancement			
Irradiated proton	1-H	2-H	4-H	phenyl-H (δ 7.39)
1-H		5.87	2.91	-
2-H	4.09		-	16.75
4-H	4.79	-		11.38

1,1'-{Iminobis[(2*Z*)-3-(3,4-difluorophenyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12i)



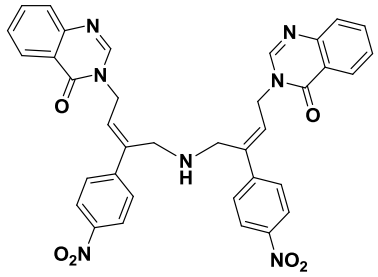
Flash chromatography eluting with 10:1 EtOAc/MeOH gave the product as a colourless froth (93%), mp 92-94 °C; δ_H (300 MHz, $CDCl_3$); 7.53 (s, 2H,2 x N=CH), 7.36-7.29 (m, 2H, 2 x ArH), 7.21–7.16 (m, 2H, 2 x ArH), 7.06-6.97 (m, 2H, 2 x ArH), 5.85 (t, *J*= 7.1 Hz, 2H, 2 x C=CH), 4.87 (d, *J*= 7.1 Hz, 4H, 2 x NCH_2), 3.98 (s, 6H, 2 x NCH_3), 3.87 (s, 4H, 2 x CH_2NH), 3.57 (s, 6H, 2 x NCH_3), 2.17 (1H, br s, NH); δ_c (75 MHz, $CDCl_3$); 154.9, 151.3, 150.0 (dd, *J*= 246.6 , 13.3 Hz), 149.6 (dd, *J*= 248.2, 12.7 Hz), 148.9, 141.6, 139.6, 138.6 (dd, *J*= 5.5, 4.4 Hz), 125.8, 122.5 (dd, *J*= 5.5, 3.3 Hz), 116.7 (d, *J*= 16.6 Hz), 115.5 (d, *J*= 17.7 Hz), 107.6, 48.1, 39.5, 33.6, 29.7;ν_{max}/cm^{-1} (film); 3313, 3015, 2950, 1704, 1660, 1602, 1549, 1515, 1487, 1455, 1415, 1357, 1287, 1234; ESI-HRMS calculated for $C_{34}H_{32}F_4N_9O_4$ $[M+H]^+$ 706.2508 found 706.2475.

1,1'-{Iminobis[(2*E*)-3-(2-thienyl)but-2-ene-4,1-diyl]}bis(3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) (12j)



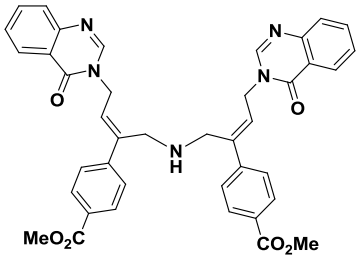
Flash chromatography eluting with gradient 95:5 $CHCl_3$/MeOH and then 93:5:2 ($CHCl_3$:MeOH:NH_4OH) gave colourless amorphous product (66%), mp 200-203 °C; δ_H (300 MHz, $CDCl_3$) 7.50 (s, 1H, N=CH), 7.15 (dd, *J*= 3.6, 0.7 Hz, 2H, 2 x ArH), 7.10 (dd, *J*= 5.1 ,0.7 Hz, 2H, 2 x ArH), 6.90 (dd, *J*= 5.1, 3.6 Hz, 2H, 2 x ArH), 6.03 (t, *J*= 7.3 Hz, 2H, 2 x C=CH), 4.90 (d, *J*= 7.3 Hz, 4H, 2 x NCH_2), 3.98 (s, 4H, 2 x *C*H_2NH), 3.96 (s, 6H, 2 x NCH_3), 3.56 (s, 6H, 2 x NCH_3) 2.18 (s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 155.0, 151.3, 148.8, 145.1, 141.5, 135.6, 127.3, 124.2, 124.1, 123.0, 107.7, 48.4, 39.5, 33.6, 29.7; ν_{max}/cm^{-1} (film); 1703, 1659, 1604, 1549, 734; ESI-HRMS calculated for $C_{30}H_{32}N_9O_4S_2$ $[M+H]^+$ 646.2013 found 646.2036.

3,3'-{Iminobis[(2*Z*)-3-(4-nitrophenyl)but-2-ene-4,1-diyl]}diquinazolin-4(3*H*)-one (13a)



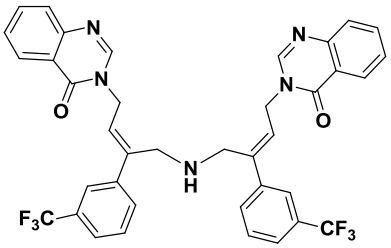
Precipitation from methanol gave a colourless amorphous product (57%), mp 190-192°C; δ_H (300 MHz, $CDCl_3$) 8.26 (dd, *J*= 8.0, 1.1 Hz, 2H, 2 x ArH), 8.17–8.10 (m, 4H, 4 x ArH), 8.14 (s, 2H, 2 x N=CH), 7.81–7.67 (m, 4H, 4 x ArH), 7.63–7.57 (m, 4H, 4 x ArH), 7.51 (ddd, *J*= 8.1, 7.0, 1.4 Hz, 2H, 2 x ArH), 6.01 (t, *J*= 7.2 Hz, 2H, 2 x C=CH), 4.90 (d, *J*= 7.2 Hz, 4H, 2 x NCH_2), 3.96 (s, 4H, 2 x *C*H_2NH), 1.60 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 161.0, 148.0, 147.3 (2), 145.9, 141.3, 134.5, 127.6, 127.5, 127.3, 126.6, 123.7, 122.0, 48.5, 44.6; ν_{max}/cm^{-1} (solid); 3298 , 3080, 2927, 2849, 1672, 1609, 1350; ESI-HRMS calculated for $C_{36}H_{30}N_7O_6$ $[M+H]^+$ 656.2252 found 656.2272.

Dimethyl 4,4'-{iminobis[(2*Z*)-4-(4-oxoquinazolin-3(4*H*)-yl)but-2-ene-1,2-diyl]}dibenzoate (13b)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (57%), mp 207-209 °C; δ_H (300 MHz, $CDCl_3$) 8.28 (dd, *J*= 8.1, 1.0 Hz, 4H, 4 x ArH), 8.15 (s, 2H, 2 x N=CH), 7.92 (d, *J*= 8.6 Hz, 4H, 4 x ArH), 7.78–7.67 (m, 4H, 4 x ArH), 7.49 (ddd, *J*= 8.1, 6.9, 1.5 Hz, 2H, 2 x ArH), 7.42 (d, *J*= 8.6 Hz, 4H, 4 x ArH), 5.96 (t, *J*= 7.1 Hz, 2H, 2 x C=CH), 4.85 (d, *J*= 7.1 Hz, 4H, 2 x CH_2N), 3.92 (s, 4H, 2 x *CH*$_2$NH), 3.87 (s, 6H, 2 x CO_2Me), 1.70 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 166.6, 161.0, 148.1, 146.2, 145.0, 142.2, 134.3, 129.8, 129.4, 127.5, 127.4, 126.7, 126.4, 126.1, 122.1, 52.1, 47.9, 44.4; ν_{max}/cm^{-1} (film); 3311, 3076, 2950, 2860, 1727, 1659, 1607, 1278; ESI-HRMS calculated for $C_{40}H_{36}N_5O_6$ $[M+H]^+$ 682.2660 found 682.2647.

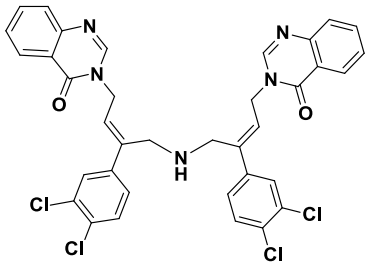
3,3'-{Iminobis[(2*Z*)-3[3-(trifluoromethyl)phenyl)]but-2-ene-4,1-diyl]}diquinazolin-4(3*H*)-one (13c)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (65%), mp 140-142 °C; δ_H (300 MHz, $CDCl_3$) 8.28 (dd, *J*= 8.0, 1.0 Hz, 2H, 2 x ArH), 8.18 (s, 2H, 2 x N=CH), 7.78–7.66 (m, 6H, 6 x ArH), 7.58 (d, *J*= 7.8 Hz, 2H, 2 x ArH), 7.52–7.45 (m, 4H, 4 x ArH), 7.38 (t, *J*= 7.8 Hz, 2H, 2 x ArH), 5.94 (t, *J*=7.1 Hz, 2H, 2 x C=CH), 4.89 (d, *J*= 7.1 Hz, 4H, 2 x CH_2N), 3.95 (s, 4H, 2 x *CH*$_2$NH), 2.00 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 161.0, 148.1, 146.2, 141.7, 141.5, 134.4, 130.8 (q, *J*= 31.5 Hz), 129.7, 129.0, 127.5, 127.4,

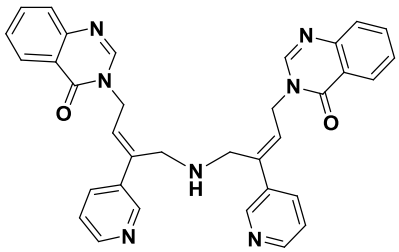
126.7, 125.8, 124.5(q, *J*= 3.8 Hz), 123.2(q, *J*= 3.7 Hz), 122.2-118.6 (br d, *J*= 272.1 Hz), 48.4, 44.6; ν_{max}/cm^{-1} (solid); 3308 , 1664 , 1336, 1122; ESI-HRMS calculated for $C_{38}H_{30}F_6N_5O_2$ $[M+H]^+$ 702.2298 found 702.2330.

3,3'-{Iminobis[(2*Z*)-3-(3,4-dichlorophenyl)but-2-ene-4,1-diyl]}diquinazolin-4(3*H*)-one (13d)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (65%), mp 180-182 °C; δ_H (300 MHz, $CDCl_3$) 8.28 (dd, *J*= 8.1, 1.0 Hz, 2H, 2 x ArH), 8.17 (s, 2H, 2 x N=CH), 7.79–7.67 (m, 4H, 4 x ArH), 7.53 (d, *J*= 1.9 Hz, 2H, 2 x ArH), 7.50 (ddd, *J*= 8.1, 7.0, 1.5 Hz, 2H, 2 x ArH), 7.33 (d, *J*= 8.4 Hz, 2H, 2 x ArH), 7.22 (dd, *J*= 8.4, 2.1 Hz, 2H, 2 x ArH), 5.90 (t, *J*= 7.1 Hz, 2H, 2 x C=CH), 4.87 (d, *J*= 7.1 Hz, 4H, 2 x CH_2N), 3.87 (s, 4H, 2 x CH_2NH), 1.93 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 161.0, 148.1, 146.1, 140.9, 140.7, 134.4, 132.6, 131.9, 130.3, 128.5, 127.6, 127.5, 126.7, 125.7, 125.6, 122.1, 48.1, 44.5; ν_{max}/cm^{-1} (solid); 3309 , 3078, 2933, 2861 , 1667 , 1606, 1563, 771; ESI-HRMS calculated for $C_{36}H_{28}{}^{35}Cl_4N_5O_2$ 702.0992 [M+H] found 702.0979.

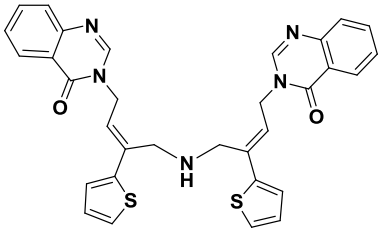
3,3'-{Iminobis[(2*Z*)-3-(pyridin-3-yl)but-2-ene-4,1-diyl]}diquinazolin-4(3*H*)-one (13e)



Precipitation from methanol gave colourless amorphous product (56%), mp 168-170°C; δ_H (300 MHz, $CDCl_3$) 8.67 (d, *J*= 1.8 Hz, 2H, 2 x ArH), 8.48 (dd, *J*= 4.8, 1.6 Hz, 2H, 2 x ArH), 8.29 (ddd, *J*= 8.0, 1.5, 0.5 Hz, 2H, 2 x ArH), 8.20 (s, 2H, 2 x N=CH), 7.79-7.67 (m, 6H, 6 x ArH), 7.50 (ddd, *J*= 8.0, 6.8, 1.5 Hz, 2H, 2 x ArH), 7.20 (ddd, *J*= 8.0, 4.8, 0.7 Hz, 2H, 2 x ArH), 5.92 (t, *J*= 7.2 Hz, 2H, 2 x C=CH) , 4.88 (d, *J*= 7.2 Hz, 4H, 2 x CH_2N), 3.93 (s, 4H, 2 x CH_2NH),

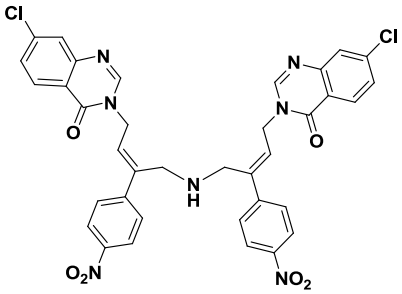
2.02 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 161.0, 148.9, 148.0, 147.6, 146.1, 140.0, 136.6, 134.4, 133.9, 127.5 (2), 126.7, 125.9, 123.2, 122.1, 48.1, 44.5; ν_{max}/cm^{-1} (solid); 3294 , 3053, 2854, 1673, 1609, 1562; ESI-HRMS calculated for $C_{34}H_{30}N_7O_2[M+H]^+$ 568.2455 found 568.2465.

3,3'-{Iminobis[(2*E*)-3-(2-thienyl)but-2-ene-4,1-diyl]}diquinazolin-4(3*H*)-one (13f)



Precipitation from methanol gave colourless amorphous product (65%), mp 144-147°C; δ_H (300 MHz, $CDCl_3$) 8.29 (dd, *J*= 8.1, 1.0 Hz, 2H, 2 x ArH), 8.18 (s, 2H, 2 x N=CH), 7.77-7.67 (m, 2H, 2 x ArH), 7.48 (ddd, *J*= 8.1, 6.8, 1.6 Hz, 2H, 2 x ArH), 7.16 (dd, *J*= 5.1, 1.0 Hz, 2H, 2 x ArH), 7.12 (dd, *J*= 3.6, 1.0 Hz, 2H, 2 x ArH), 6.94 (dd, *J*= 5.1, 3.6 Hz, 2H, 2 x ArH), 6.06 (t, *J*= 7.3 Hz, 2H, 2 x C=CH), 4.87 (d, *J*= 7.3 Hz, 4H, 2 x NCH_2), 3.93 (s, 4H, 2 x CH_2NH), 1.98 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 161.0, 148.1, 146.4, 144.0, 136.4, 134.3, 127.6, 127.5, 127.3, 126.7, 125.1, 124.5, 122.5, 122.1, 48.3, 44.2; ν_{max}/cm^{-1} (film); 1669, 1608, 773, 754; ESI-HRMS calculated for $C_{32}H_{28}N_5O_2S_2$ $[M+H]^+$ 578.1679 found 578.1689.

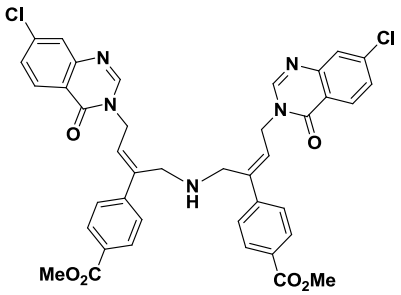
3,3'-{Iminobis[(2*Z*)-3-(4-nitrophenyl)but-2-ene-4,1-diyl]}bis(7-chloroquinazolin-4(3*H*)-one) (14a)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (58%), mp 165-167 °C; δ_H (300 MHz, DMSO-d_6) 8.48 (s, 1H, N=CH), 8.11-8.04 (m, 3H, ArH), 7.74–7.68 (m, 3H, ArH), 7.54 (dd, 1H, *J*= 2.2 Hz, 8.6, ArH), 6.20 (t, *J*= 6.7 Hz, 1H, C=CH), 4.87 (d, *J*= 6.7 Hz, 2H, CH_2N), 3.86 (s, 2H, CH_2NH); δ_c (75 MHz, DMSO-d_6) 159.6, 149.2,

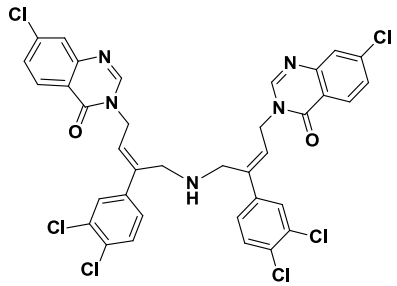
149.0, 147.4, 146.2, 139.4, 138.9, 128.7, 128.0, 127.5, 127.2, 126.2, 123.2, 120.4, 46.8, 44.3; ν_{max}/cm^{-1} (solid); 3301, 3073, 2925, 2852, 1667, 1601, 1346; ESI-HRMS calculated for $C_{36}H_{28}Cl_2N_7O_6$ $[M+H]^+$ 724.1473 found 724.1483.

Dimethyl 4,4'-{iminobis[(2*Z*)-4-(7-chloro-4-oxoquinazolin-3(4*H*)-yl)but-2-ene-1,2-diyl]} dibenzoate (14b)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (60%), mp 194-196°C; δ_H (300 MHz, $CDCl_3$) 8.20 (d, *J*= 8.6 Hz, 2H, 2 x ArH), 8.14 (s, 2H, 2 x N=CH), 7.92 (d, *J*= 8.6 Hz, 4H, 4 x ArH), 7.68 (d, *J*= 1.9 Hz, 2H, 2 x ArH), 7.47–7.39 (m, 6H, 6 x ArH), 5.95 (t, *J*= 7.1 Hz, 2H, 2 x ArH), 4.82 (d, *J*= 7.1 Hz, 4H, 2 x CH_2N), 3.90 (s, 4H, 2 x CH_2NH), 3.88 (s, 6H, 2 x CO_2Me), 1.78 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 166.6, 160.4, 149.0, 147.3, 144.9, 142.4, 140.6, 129.8, 129.5, 128.2, 128.0, 127.1, 126.4, 125.7, 120.5 , 52.2 , 47.9, 44.5; ν_{max}/cm^{-1} (solid); 3298, 3030, 2953, 2857, 1707, 1663, 1603, 1553, 1288; ESI-HRMS calculated for $C_{40}H_{34}Cl_2N_5O_6$ $[M+H]^+$ 750.1881 found 750.1917.

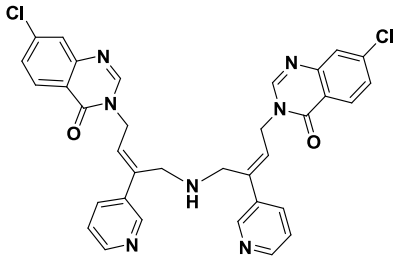
3,3'-{Iminobis[(2*Z*)-3-(3,4-dichlorophenyl)but-2-ene-4,1-diyl]}bis(7-chloroquinazolin-4(3*H*)-one) (14c)



Flash chromatography eluting with 20:1 $CHCl_3$/MeOH gave colourless amorphous product (67%), mp 150-151 °C; δ_H (300 MHz, $CDCl_3$) 8.19 (d, *J*= 8.6 Hz, 2H, 2 x ArH), 8.17 (s, 1H, N=CH), 7.68 (d, *J*= 2.0 Hz, 2H, 2 x ArH), 7.52 (d, *J*= 2.0 Hz, 2H, 2 x ArH), 7.44 (dd, *J*= 8.6,

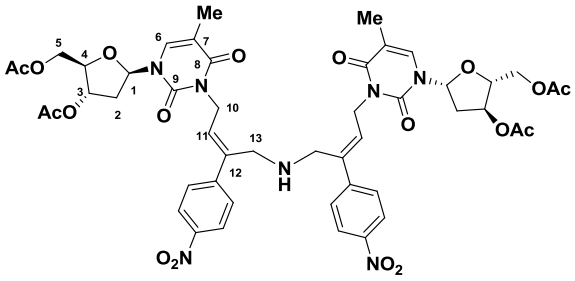
2.0 Hz, 2H, 2 x ArH), 7.33 (d, *J*= 8.4 Hz, 2H, 2 x ArH), 7.22 (dd, *J*= 8.4, 2.0 Hz, 2H, 2 x ArH), 5.88 (t, *J*= 7.1 Hz, 2H, 2 x C=CH), 4.84 (d, *J*= 7.1 Hz, 4H, 2 x CH_2N), 3.85 (s, 4H, 2 x CH_2NH), 1.91 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 160.4, 149.0, 147.3, 141.1, 140.7, 140.5, 132.6, 132.0, 130.4, 128.4 , 128.2, 128.1, 127.1, 125.7, 125.3, 120.5, 48.1, 44.6 ; ν_{max}/cm^{-1} (solid); 3299, 3068, 2855, 1659, 1603, 1553, 783; ESI-HRMS calculated for $C_{36}H_{26}{}^{35}Cl_6N_5O_2$ [M+H] 770.0212 found 770.0239.

3,3'-{Iminobis[(2*Z*)-3-(pyridin-3-yl)but-2-ene-4,1-diyl]}bis(7-chloroquinazolin-4(3*H*)-one (14d)



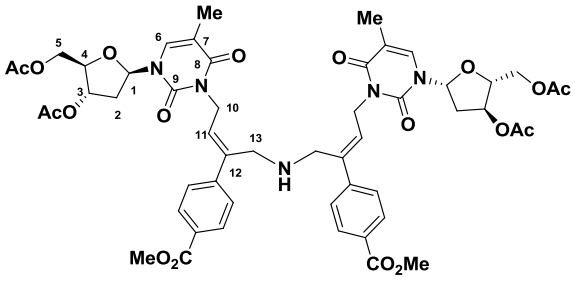
Flash chromatography eluting with gradient 20:1 $CHCl_3$/MeOH follow by 9:1 $CHCl_3$/MeOH gave a colourless amorphous product (52%), mp 210-212 °C; δ_H (300 MHz, $CDCl_3$) 8.67 (d, *J*= 1.9 Hz, 2H, 2 x ArH), 8.49 (dd, *J*= 4.8, 1.5 Hz, 2H, 2 x ArH), 8.19 (d, *J*= 7.9 Hz, 2H, 2 x ArH), 8.17 (s, 2H, 2 x N=CH), 7.70 (td, *J*= 8.1, 1.8 Hz, 2H, 2 x ArH), 7.68 (d, *J*= 1.9 Hz, 2H, 2 x ArH), 7.44 (dd, *J*= 8.6, 2.0 Hz, 2H, 2 x ArH), 7.20 (ddd, *J*= 7.9, 4.8, 0.5 Hz, 2H, 2 x ArH), 5.91 (t, *J*= 7.2 Hz, 2H, 2 x C=CH), 4.86 (d, *J*= 7.2, 4H, 2 x CH_2N), 3.92 (s, 4H, 2 x CH_2NH), 2.11 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$) 160.4, 149.1, 149.0, 147.7, 147.3, 140.6, 140.3, 136.2, 133.8, 128.2, 128.1, 127.1, 125.5, 123.2, 120.5, 48.2, 44.6; ν_{max}/cm^{-1} (solid); 3298 , 3066, 2928, 2851, 1682, 1604, 1556; ESI-HRMS calculated for $C_{34}H_{28}Cl_2N_7O_2$ $[M+H]^+$ 636.1676 found 636.1682.

3,3'-{Iminobis[(2*Z*)-3-(4-nitrophenyl)but-2-ene-4,1-diyl]}bis(3',5'-di-*O*-acetylthymidine) (15a).



Flash chromatography eluting with 60:40 EtOAc/hexane gave the product as a yellow froth (97%), m.p. 80-82˚C; $[\alpha]_D^{23}$ +10.5 (c = 10.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 8.11 (d, *J* = 8.9 Hz, 2H, ArH), 7.63 (d, *J* = 8.9 Hz, 2H, ArH), 7.27 (s, *J* = 1.9 Hz, 1H, H-6), 6.32 (dd, *J* = 8.3, 5.7 Hz, 1H, H-1), 5.95 (t, *J* = 7.0 Hz, 1H, H-11), 5.22 (dd, *J* = 4.1, 2.5 Hz, 1H, H-3), 4.79 (d, *J* = 7.0 Hz, 2H, H-10), 4.36 (t, *J* = 3.5 Hz, 2H, H-5), 4.27 – 4.18 (m, 1H, H-4), 3.90 (s, 2H, H-13), 2.47 (ddd, *J* = 14.1, 5.7, 2.0 Hz, 1H, H-2), 2.19 (dd, *J* = 14.6, 6.7 Hz, 1H, H-2), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.1, 162.8, 150.6, 148.1, 146.8, 132.9, 127.8, 127.2, 123.4, 110.8, 85.3, 82.0, 73.9, 63.8, 48.0, 39.6, 37.5, 20.9, 20.8 , 13.4 ; ν_{max}/cm^{-1} (film); 3311, 3190, 3082, 2952, 2853, 2159, 1743, 1703, 1667, 1644, 1594, 1515, 1464, 1455, 1343, 1230, 1193, 1106, 1060, 1022; ESI-HRMS calculated for $C_{48}H_{53}N_7NaO_{18}$ $[M+H]^+$ 1038.3339 found 1038.3318.

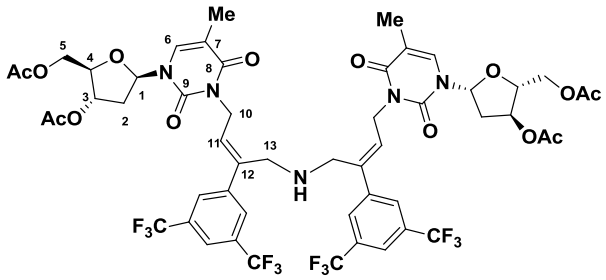
Dimethyl 4,4'-{Iminobis[(2*Z*)-4-(3',5'-di-*O*-acetrythymidine)but-2-ene-1,2-diyl]}dibenzoate (15b).



Flash chromatography eluting with 96:4 MeOH/CH_2Cl_2 gave the product as a yellow froth (64%), m.p. 72-74˚C; $[\alpha]_D^{23}$ +7.9 (c = 10.35, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.90 (d, *J* = 8.3 Hz, 2H, ArH), 7.49 (d, *J* = 8.3 Hz, 2H, ArH), 7.27 (s, 1H, H-6), 6.34 (dd, *J* = 8.3, 5.7 Hz, 1H, H-1), 5.91 (t, *J* = 7.0 Hz, 1H, H-11), 5.21 (d, *J* = 6.5 Hz, 1H, H-3), 4.79 (d, *J* = 7.0 Hz, 2H, H-10), 4.36 (t, *J* = 3.2 Hz, 2H, H-5), 4.25 (d, *J* = 2.7 Hz, 1H, H-4), 3.90 (s, 5H, H-13, CO_2Me), 2.53-2.31 (m,

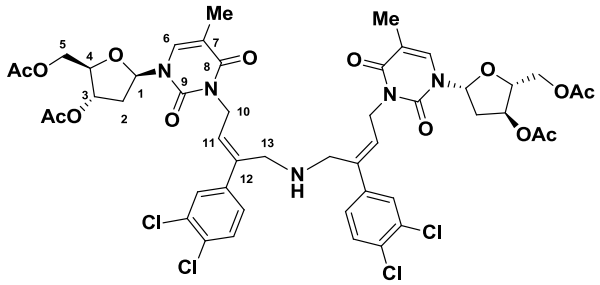
1H, H-2), 2.17 (dd, *J* = 13.4, 5.7 Hz, 1H, H-2), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.2, 166.9, 162.8, 150.6, 145.9, 141.9, 132.7, 129.5, 128.7, 126.4, 126.1, 110.7, 85.3 , 81.9, 74.0, 63.8, 52.0, 47.8, 39.6, 37.5, 20.9, 20.8, 13.4; ν_{max}/cm^{-1} (film); 3319, 3057, 2988, 3003, 2954, 2931, 2849, 2159, 1743, 1718, 1707, 1671, 1642, 1608, 1466, 1451, 1437, 1367, 1275, 1261, 1193, 1111, 1019 ; ESI-HRMS calculated for $C_{52}H_{60}N_5O_{18}$ $[M+H]^+$ 1042.3928 found 1042.3925.

3,3'-{Iminobis[(2*Z*)-3-(3,5-bis(trifluoromethyl)phenyl)but-2-ene-4,1-diyl]}bis(3',5'-di-*O*-acetylthymidine) (15c).



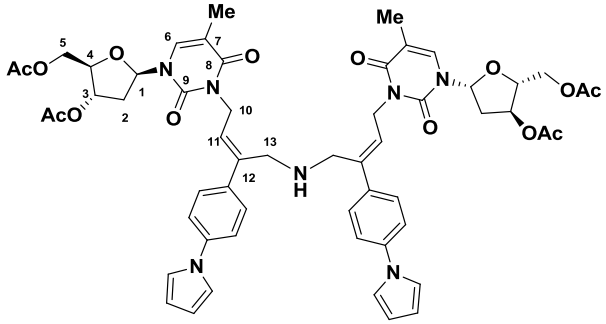
Flash chromatography eluting with 60:40 EtOAc/ hexane gave the product as a yellow froth (99%), m.p. 66-68˚C; $[\alpha]_D^{23}$ +6.7 (c = 8.8, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 7.92 (s, 2H, ArH), 7.71 (s, 1H, ArH), 7.30 (s, 1H, H-6), 6.35 (dd, *J* = 8.4, 5.7 Hz, 1H, H-1), 5.90 (t, *J* = 7.0 Hz, 1H, H-11), 5.22 (dd, *J* = 4.3, 2.3 Hz, 1H, H-3), 4.82 (d, *J* = 7.0 Hz, 2H, H-10), 4.45 – 4.33 (m, 2H, H-5), 4.28 – 4.21 (m, 1H, H-4), 3.93 (s, 2H, H-13), 2.48 (ddd, *J* = 14.1, 5.7, 1.9 Hz, 1H, H-2), 2.24 – 2.15 (m, 1H, H-2), 2.14 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.2, 162.9, 150.6, 148.1, 146.8, 132.8, 131.5, 131.1, 127.5, 126.6, 125.1, 123.3 (q, *J*= 270 Hz), 121.5, 110.9, 85.3, 82.0, 74.0, 63.8, 48.2, 37.5 (2), 20.8, 13.4; ν_{max}/cm^{-1} (film); 3314, 3083, 3059, 2985, 2956, 1747, 1704, 1672, 1645, 1466, 1381, 1277, 1182, 1133, 1077 1061, 1023; ESI-HRMS calculated for $C_{52}H_{52}F_{12}N_5O_{14}$ $[M+H]^+$ 1198.3314 found 1198.3321.

3,3'-{Iminobis[(2*Z*)-3-(3,4-dichlorophenyl)but-2-ene-4,1-diyl]}bis(3',5'-di-*O*-acetylthymidine) (15d).



Flash chromatography eluting with 60:40 EtOAc/ hexane gave the product as a yellow froth (78%), m.p. 68-70˚C; $[\alpha]_D^{23}$ +6.9 (c = 14.15, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.4 Hz, 1H, ArH), 7.32 – 7.25 (m, 3H, ArH, H-6), 6.35 (dd, *J* = 8.3, 5.7 Hz, 1H, H-1), 5.83 (t, *J* = 7.0 Hz, 1H, H-11), 5.27 – 5.14 (m, 1H, H-3), 4.77 (d, *J* = 7.0 Hz, 2H, H-10), 4.36 (t, *J* = 3.1 Hz, 2H, H-5), 4.29-2.17 (m, 1H), 3.82 (s, 2H, H-13), 2.53 – 2.42 (m, 1H, H-2), 2.18 (dd, *J* = 12.9, 5.0 Hz, 1H, H-2), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.1, 162.8, 150.6, 141.5, 139.7, 132.7, 132.1, 131.0, 130.0, 128.4, 125.8, 125.7, 110.8, 85.3, 82.0, 74.0, 63.8, 47.8, 39.5, 37.5, 20.9, 20.8, 13.4; ν_{max}/cm^{-1} (film); 3315, 3086, 3058, 3006, 2987, 2954, 2929, 2854, 2159, 1746, 1703, 1669, 1645, 1467, 1367, 1275, 1260, 1107, 1027; ESI-HRMS calculated for $C_{48}H_{52}{}^{35}Cl_4N_5O_{14}$ $[M+H]^+$ 1062.2259 found 1062.2224.

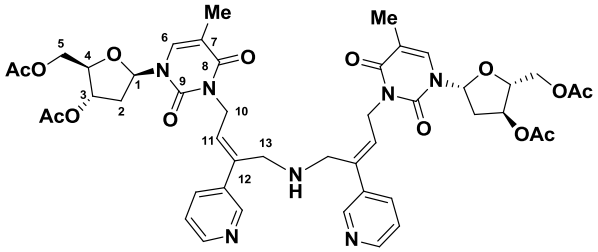
3,3'-{Iminobis[(2*Z*)-3-(4-(1H-pyrrol-1-yl)pheny)but-2-ene-4,1-diyl]}bis(3',5'-di-*O*-acetylthymidine) (15e).



Flash chromatography eluting with 97:3 MeOH/CH_2Cl_2 gave the product as a yellow froth (52%), m.p. 76-78˚C; $[\alpha]_D^{23}$ +21.5 (c = 6.666, $CHCl_3$); δ_H7.46 (d, *J* = 8.6 Hz, 2H, ArH), 7.29 – 7.20 (m, 3H, ArH, C-6), 7.03 (t, *J* = 2.1 Hz, 2H, ArH), 6.37 – 6.28 (m, 3H, ArH, C-1), 5.85 (t, *J* = 7.0 Hz, 1H, H-11), 5.20 (d, *J* = 6.5 Hz, 1H, H-3), 4.79 (d, *J* = 7.0 Hz, 2H, H-10), 4.35 (d, *J* = 3.6 Hz, 2H, H-5), 4.26 – 4.18 (m, 1H, H-4), 3.90 (s, 2H, H-13), 2.46 (dd, *J* = 13.2, 6.5 Hz, 1H,

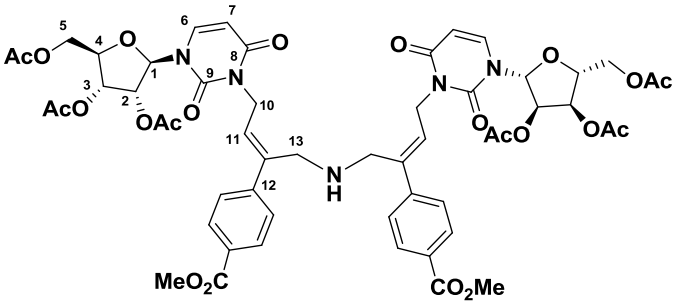
H-2), 2.28 – 2.15 (m, 1H, H-2), 2.12 (d, *J* = 3.3 Hz, 3H, OAc), 2.11 (s, 3H. OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.2, 162.9, 150.6, 140.9, 139.6, 138.4 , 132.6, 127.7, 124.2, 119.8, 110.8, 110.4, 85.3, 82.0, 74.0, 63.8, 47.5, 45.7, 39.7, 20.9, 20.8, 13.5; ν_{max}/cm^{-1} (film); 3310, 3011, 2953, 2850, 2159, 1744, 1703, 1671, 1639, 1521, 1275, 1260, 1232, 1193, 1104, 1069, 1020; ESI-HRMS calculated for $C_{56}H_{62}N_7O_{14}$ $[M+H]^+$ 1056.4349 found 1056.4343.

3,3'-{Iminobis[(2*Z*)-3-(pyridin-3-yl)but-2-ene-4,1-diyl]}bis(3',5'-di-*O*-acetylthymidine) (15f).



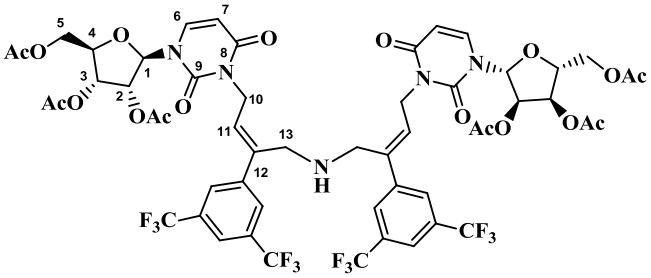
Flash chromatography eluting with 96:4 $MeOH/CH_2Cl_2$ gave the product as a yellow froth (78%), m.p. 65-67˚C; $[\alpha]_D^{23}$ +6.8 (c = 9.85, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 8.67 (s, *J* = 13.0 Hz, 1H, ArH), 8.44 (d, *J* = 4.6 Hz, 1H, ArH), 7.72 (d, *J* = 7.9 Hz, 1H, ArH), 7.30 (s, *J* = 6.3 Hz, 1H, H-6), 7.16 (dd, *J* = 7.9, 4.8 Hz, 1H, ArH), 6.34 (dd, *J* = 8.2, 5.8 Hz, 1H, H-1), 5.86 (t, *J* = 7.0 Hz, 1H, H-11), 5.21 (d, *J* = 6.5 Hz, 1H, H-3), 4.81 (d, *J* = 7.1 Hz, 2H, H-10), 4.36 (t, *J* = 2.9 Hz, 2H, H-5), 4.28 – 4.18 (m, 1H, H-4), 3.88 (s, 2H, H-13), 2.48 (dd, *J* = 14.1, 5.6 Hz, 1H, H-2), 2.21 – 2.14 (m, 1H, H-2), 2.14 – 2.12 (m, 3H, OAc), 2.12 (d, *J* = 1.0 Hz, 3H, OAc), 1.95 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 170.1, 162.8, 150.5, 148.3, 147.7, 139.0, 133.8, 132.7, 125.7, 122.9, 110.8, 110.7, 85.3, 81.9, 74.0, 63.8, 47.9, 39.5, 36.4, 20.9, 20.8, 13.4; υ_{max}/cm^{-1} (film); 3314, 3080, 3055, 3006, 2987, 2955. 2931, 2159, 1744, 1703, 1671, 1643, 1466, 1451, 1367, 1336, 1275, 1260, 1235, 1193, 1106, 1076, 1061, 1024; ESI-HRMS calculated for $C_{46}H_{54}N_7O_{14}$ $[M+H]^+$ 928.3723 found 928.3724.

Dimethyl 4,4'-{Iminobis[(2*Z*)-4-(2',3',5'-tri-*O*-acetryuridine)but-2-ene-1,2-diyl]}dibenzoate (16a).



Flash chromatography eluting with 5:1 EtOAc/ hexane gave the product as a pale yellow froth (62%); $[\alpha]_D^{20}$ + 33.0 (*c*, 11 mg/ 1 mL $CHCl_3$); mp 78-80°C; δ_H (300 MHz, $CDCl_3$); 7.90 (d, *J*= 8.5 Hz, 2H, 2 × ArH), 7.47 (d, *J*= 8.5 Hz, 2H, 2 × ArH), 7.39 (2H, d, *J*= 8.2 Hz, 1H, H-6), 6.03 (d, *J* =4.4 Hz, 1H, H-1), 5.88 (1H, t, *J*= 7.1 Hz, 1H, H-11), 5.84 (d, *J*= 8.2 Hz, 1H, H-7), 5.37-5.31 (m, 2H, H-2, H-3), 4.79 (dd, *J*= 14.8, 7.1Hz, 1H, H-10), 4.72 (dd, *J*= 14.8, 7.1 Hz, 1H, H-10), 4.35 (s, 3H, H-4, H-5), 3.90 (s, 3H, CO_2Me), 3.86 (s, 2H, H-13), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.07 (s, 3H, OAc); δ_c (75 MHz, $CDCl_3$); 170.1, 169.6 (2), 166.9, 161.9, 150.7, 145.9, 141.3, 137.3, 129.5, 128.8, 126.5, 125.8, 102.9, 88.4, 79.7, 72.9, 70.0, 63.0, 52.0, 47.7, 39.4, 20.8, 20.5, 20.45; υ_{max}/cm^{-1} (film); 3322, 3021, 2953, 1748, 1714, 1668, 1607, 1564, 1455, 1435, 1373, 1280, 1227; ESI-HRMS calculated for $C_{54}H_{60}N_5O_{22}$ $[M+H]^+$ 1130.3724 found 1130.3753

3,3'-(Iminobis{(2*Z*)-3-[3,5-bis(trifluoromethyl)phenyl]but-2-ene-4,1-diyl}]bis(2',3',5'-tri-*O*-acetyluridine) (16b).



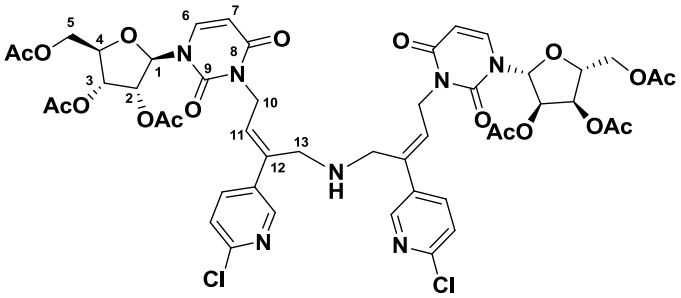
Flash chromatography eluting with 60:40 EtOAc/ hexane gave the product as a colourless froth (74%); mp 72-74 °C; $[\alpha]_D^{20}$ +27.2 (*c*, 10 mg/1mL $CHCl_3$); δ_H (300 MHz, $CDCl_3$); 7.90 (d, *J*= 1.1 Hz, 2H, ArH), 7.71 (br s, 1H, ArH), 7.31 (d, *J*= 8.2 Hz, 1H, H-6), 6.03 (d, *J*= 4.4 Hz, 1H, H-1), 5.89 (t, *J*= 7.1 Hz, 1H, H-11), 5.84 (d, *J*= 8.2 Hz, 1H, H-7), 5.37–5.30 (m, 2H, H-2 and H-3),

4.85 (dd, *J*= 7.1, 14.5 Hz, 1H, H-10a), 4.76 (dd, *J*= 7.1, 14.5, 1H, H-10b), 4.36 (s, 3H, H-4 and H-5), 3.92 (d, *J*= 15.6 Hz, 1H, H-13), 3.88 (d, *J*= 15.6 Hz, 1H, H-13), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.06 (s, 3H, OAc); δ_c (75 MHz, $CDCl_3$); 170.1, 169.7, 169.6, 161.9, 150.7, 143.6, 139.8, 137.4, 131.4 (q, *J*= 33.2 Hz), 127.2, 126.6 (br d, *J*= 2.2 Hz), 123.1 (q, *J*= 273.1 Hz), 121.5 (br d, *J*= 3.3 Hz), 102.9, 88.3, 79.8, 72.9, 70.0, 63.0, 48.2, 39.3, 20.8, 20.5, 20.3; ν_{max}/cm^{-1} (film); 3317, 3024, 1755, 1714, 1668, 1455, 1380, 1281, 1228; ESI-HRMS calculated for $C_{54}H_{52}F_{12}N_5O_{18}$ $[M+H]^+$ 1286.3110 found 1286.3130.

NOE data ($CDCl_3$) for **16b**.

	% Enhancement			
Irradiated proton	10-H	11-H	13-H	phenyl-H (δ 7.90)
10-H		2.41	2.50	-
11-H	2.64		-	10.41
13-H	2.18	-		5.64

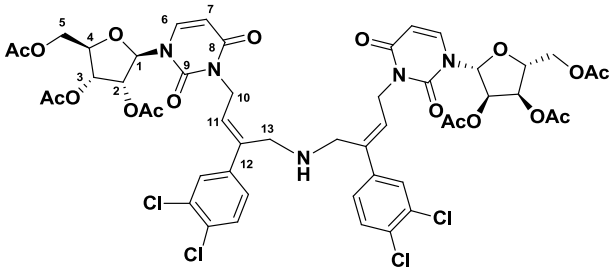
3,3'-{Iminobis[(2*Z*)-3-(6-chloropyridin-3-yl)but-2-ene-4,1-diyl]}bis(2',3',5'-tri-*O*-acetyluridine) (16c).



Flash chromatography eluting with 4:1 EtOAc/ hexane gave the product as a colourless froth (77%); $[\alpha]_D^{20}$ + 34.8 (*c*, 12 mg/ 1 mL $CHCl_3$); mp 80-82 °C; δ_H (300 MHz, $CDCl_3$); 8.43 (d, *J*= 2.4 Hz, 2H, ArH), 7.69 (dd, *J*= 8.2, 2.4 Hz, 1H, ArH), 7.42 (d, *J* = 8.2 Hz, 1H, H-6), 7.20 (d, *J*= 8.0 Hz, 1H, ArH), 6.01 (d, *J*= 4.9 Hz, 1H, H-1), 5.84 (d, *J*= 8.2 Hz, 1H, H-7), 5.83 (t, *J*= 7.1 Hz, 1H, H-11), 5.39-5.30 (, m, 2 H, H-2, H-3), 4.80 (dd, *J*= 14.5, 7.1 Hz, 1H, H-10), 4.72 (dd, *J*= 14.5, 7.1, 1H, H-10), 4.36 (s, 3H, H-4, H-5), 3.81 (s, 2H, H-13), 2.14 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc); δ_c (75 MHz, $CDCl_3$); 170.1, 169.6(2), 161.9, 150.7, 150.0, 147.6,

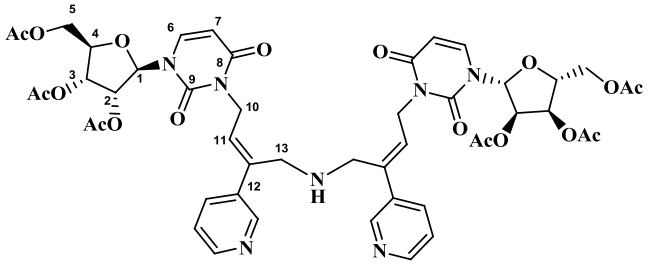
138.0, 137.6, 136.9, 135.9, 126.0, 123.5, 102.8, 88.6, 79.7, 72.9, 69.9, 62.9, 47.8, 39.2, 20.8, 20.5. 20.47; υ_{max}/cm^{-1} (film); 3320, 3019, 1748, 1712, 1668, 1580, 1553, 1456, 1376, 1228; ESI-HRMS calculated for $C_{47}H_{52}{}^{35}Cl_2N_7O_{18}$ $[M+H]^+$ 1084.2740 found 1084.2752.

3,3'-{Iminobis[(2*Z*)-3-(3,4-dichlorophenyl)but-2-ene-4,1-diyl]}bis(2',3',5'-tri-*O*-acetyluridine) (16d).



Flash chromatography eluting with 2:1 EtOAc/ hexane gave the product as a pale yellow froth (71%); $[\alpha]_D^{20}$ +32.9 (*c*, 10 mg/1 mL $CHCl_3$); mp 76-78 °C; δ_H (300 MHz, $CDCl_3$); 7.55 (d, *J*= 2.2 Hz, 2H, 2 x ArH), 7.40 (d, *J*= 8.2 Hz, 2H, 2 x H-6), 7.32–7.23 (m, 4H,4 x ArH), 6.03 (d, *J*= 4.9 Hz, 2H, 2 x H-1), 5.84 (d, *J*= 8.2 Hz, 2H, 2 x H-7), 5.81 (t, *J*= 7.1Hz, 2H, 2 x H-11), 5.38-5.30 (m, 4H, 2 x H-2 and 2 x H-3), 4.78 (dd, *J*= 7.1, 14.3 Hz, 2H, 2 x H-10a), 4.72 (dd, *J*= 7.1, 14.3 Hz, 2H, 2 x H-10b), 4.35 (s, 6H, 2 x H-4 and 2 x H-5), 3.79 (s, 4H, 2 x H-13), 2.14 (s, 6H, 2 x OAc), 2.13 (s, 6H, 2 x OAc), 2.08 (s, 6H, 2 x OAc), 1.88 (br s, 1H, NH); δ_c (75 MHz, $CDCl_3$); 170.1, 169.6 (2), 161.9, 150.7, 141.4, 140.0, 137.4, 132.2, 131.1, 130.0, 128.5, 125.9, 125.4, 102.9, 88.4, 79.7, 72.9, 70.0, 63.0, 47.8, 39.3, 20.8, 20.5, 20.46; ν_{max}/cm^{-1} (film); 3318, 3021, 1752, 1711, 1665, 1552, 1455, 1376, 1232; ESI-HRMS calculated for $C_{50}H_{51}{}^{35}Cl_4N_5O_{18}$ $[M+H]^+$ 1150.2056 found 1150.2002.

3,3'-{Iminobis[(2*Z*)-3-(pyridin-3-yl)but-2-ene-4,1-diyl]}bis(2',3',5'-tri-*O*-acetyluridine) (16e).



Flash chromatography eluting with 10:1 EtOAc/MeOH gave the product as a yellow froth (71%); $[\alpha]_D^{20}$ + 32.0 (*c*, 10 mg/1mL $CHCl_3$); mp 76-78 °C; δ_H (300 MHz, $CDCl_3$); 8.68 (d, *J*= 2.2 Hz, 1H, ArH), 8.45 (dd, *J*= 4.9, 1.6 Hz, 1H, ArH), 7.70 (dt, *J*= 8.0, 2.2 Hz, 1H, ArH), 7.39 (d, *J*= 8.2 Hz, 1H, H-6), 7.15 (dd, *J*= 4.9, 8.0 Hz, 1H, ArH), 6.02 (d, *J*= 4.9 Hz, 1H, H-1), 5.84 (t, *J*= 7.1 Hz, 1H, H-11), 5.83 (d, *J*= 8.2 Hz, 1H, H-7), 5.37–5.30 (m, 2H, H-2 and H-3), 4.80 (dd, *J*= 7.1, 14.3 Hz, 1H, H-10), 4.74 (dd, *J*= 7.1, 14.3 Hz, 1H, H-10), 4.35 (s, 3H, H-4 and H-5), 3.85 (s, 2H, H-13), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.07 (s, 3H, OAc); δ_c (75 MHz, $CDCl_3$); 170.1, 169.6 (2), 161.9, 150.7, 148.4, 147.8, 139.2, 137.4, 136.9, 133.9, 125.6, 123.0, 102.9, 88.4, 79.7, 72.9, 70.0, 63.0, 47.8, 39.3, 20.8, 20.5, 20.46; ν_{max}/cm^{-1} (film); 3318, 3022, 1753, 1710, 1665, 1563, 1455, 1415, 1375, 1235; ESI-HRMS calculated for $C_{48}H_{54}N_7O_{18}$ $[M+H]^+$ 1016.3520 found 1016.3504.

References.

1. R. Grigg, E. E. Elboray, M. F. Aly and H. A. Abass-Temirek, *Chem. Commun*. 2012, **48**, 11504-11506.