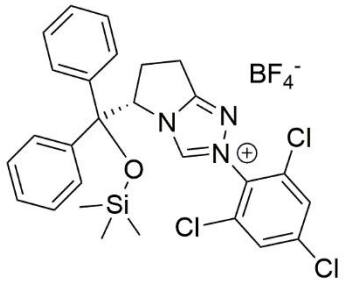
NHC catalysed polymerisation of 2,5-diformylfuran

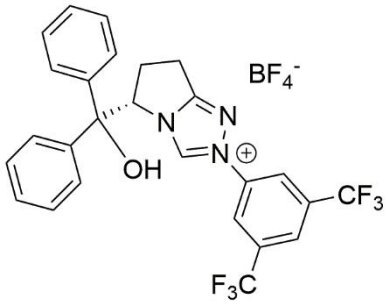
(S)-5-(trimethylsilyloxy-diphenyl-methyl)-2-(2,4,6-trichloro-phenyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroborate (1'b)



(S)-5-(diphenyl(trimethylsilyloxy)methyl)pyrrolidin-2-one (1 g; 2.9 mmol; 1 eq) was dissolved in 14 ml dry CH_2Cl_2 under inert atmosphere. Trimethyl oxonium tetrafluoroborate (0.436 g; 2.9 mmol; 1eq) was added to this solution and left to stir for 15 h at room temperature. 2,4,6,-trichlorofenylhydrazine (0.613 g; 2.9 mmol; 1 eq) was added to the reaction mixture and left to stir for another 24 h at room temperature. Subsequently the solvent was removed and 26 ml of chlorobenzene was added together with 1.25 ml triethyl orthoformate. This mixture was heated to 120 °C and left to stir for 12 h after which an additional 1.25 ml of triethyl orthoformate was added and stirred for another 12h at 120 °C. Once the reaction had cooled the solvent was evaporated and the crude product was purified by column chromatography over silica as stationary phase and ethyl acetate/petroleum ether and dichloromethane/methanol as mobile phase in multiple runs. The columns partially removed the silyl ether thus also affording the alcohol.

^{1}H NMR (400 MHz, DMSO) δ 10.18 (s, 1H), 8.21 (s, J = 26.2 Hz, 1H), 7.56 – 7.45 (m, 1H), 7.46 – 7.27 (m, 1H), 6.16 (d, J = 7.6 Hz, 1H), 3.19 (ddd, J = 18.7, 14.0, 9.5 Hz, 1H), 3.11 – 2.94 (m, 1H), 2.71 (dd, J = 23.0, 9.3 Hz, 1H), 2.03 – 1.83 (m, 1H), -0.11 – -0.17 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 164.13, 143.80, 139.99, 139.48, 138.76, 130.76, 129.93, 129.78, 129.29, 129.21, 128.88, 128.68, 82.35, 68.95, 21.17, 2.01. MS(ESI) Found: 542.3; 544.2 [M-BF4]+ C27H27Cl3N3OSi requires 542.1; 544.1.

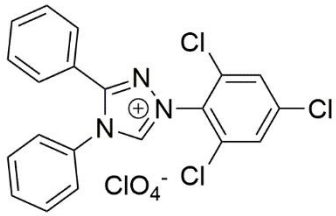
(S)-2-(3,5-bis-trifluoromethyl-phenyl)-5-(hydroxy-diphenyl-methyl)-2,5,6,7- tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroborate (1d)



(S)-5-(diphenyl(trimethylsilyloxy)methyl)pyrrolidin-2-one (4 g; 11.78 mmol; 1 eq) was dissolved in 56 ml dry CH_2Cl_2 under inert atmosphere. Trimethyl oxonium tetrafluoroborate (1.742 g; 11.78 mmol; 1eq) was added to this solution and left to stir for 15 h at room temperature. 3,5-bis(trofluoromethyl)fenylhydrazine (0.613 g; 2.9 mmol; 1 eq) was added to the reaction mixture and left to stir over the weekend at room temperature. Subsequently the solvent was removed and 108 ml of chlorobenzene was added together with 5 ml triethyl orthoformate. This mixture was heated to 120 °C and left to stir for 48 h after which an additional 5 ml of triethyl orthoformate was added and stirred for another 24h at 120 °C. Once the reaction had cooled the solvent was evaporated and the crude product was purified by recrystallisation from ethyl acetate followed by column chromatography over silica as stationary phase and ethyl acetate/petroleum ether and dichloromethane/methanol as mobile phase in multiple runs affording an off white solid (23 mg; 1,6 %)

^{1}H NMR (400 MHz, DMSO) 10.18 (1 H, s), 8.58 (2 H, s), 8.48 (1 H, s), 7.57 (2 H, d, J 7.4), 7.46 (4 H, dt, J 7.8, 4.0), 7.41 – 7.24 (4 H, m), 6.64 (1 H, s), 6.12 (1 H, d, J 8.7), 3.21 – 2.94 (2 H, m), 2.81 – 2.56 (2 H, m). ^{13}C NMR (101 MHz, DMSO) δ 164.16, 143.77, 143.26, 140.19, 137.24, 132.73, 132.40, 132.06, 131.72, 129.32, 128.84, 128.44, 128.11, 126.89, 126.82, 124.83, 124.37, 123.40, 121.66, 79.33, 67.92, 30.53, 21.45. MS(ESI) Found: 405.3 $[M\text{-}BF4]^+$ C26H20F6N3O requires 405.2.

1-(2,4,6-trichlorofenyl)-3,4-difenyl-1,2,4-triazol-1-ium perchlorate (3b)



Benzoyl chloride (1.4 g; 10 mmol; 1.2 ml) was dissolved in 20 ml dry toluene in an oven dried flask under inert atmosphere. Aniline (0.93 g; 10 mmol; 0.9 ml) was added and the mixture was refluxed for 16 h. After cooling to room temperature, $SOCl_2$ (3.57 g; 30 mmol; 2.2 ml) was added and the reaction mixture was stirred at 80 °C for 7 h. Toluene and $SOCl_2$ were evaporated and 10 ml of dry tetrahydrofuran was added together with triethylamine (1.5 g; 15 mmol; 2.1 ml). 2,4,6-trichlorofenylhydrazine (2.114 g; 10 mmol) was added over 30 min. After stirring at room temperature overnight, the solvent was evaporated and 18 ml acetic acid (2%) was added at 70 °C, stirred thoroughly and decanted. The residue was washed with 5 ml of water followed by 5 ml of methanol before being dried under vacuum. Acetic anhydride (10 ml) and formic acid (5 ml) were heated to 60 °C for 15 min. After cooling to room

temperature the previous product was slowly added on a water bath and left to stir for 24 h before evaporating under vacuum at 80 °C. 10 ml $HCLO_4$ (35%) was slowly added and stirred for 2 h. 5 ml of water is added and the mixture is stirred for another 15 min. the solid is filtered and washed with water (10 ml), methanol (1 ml) and diethyl ether (10 ml). the product was recrystallized from methanol affording a white powder (0.907 g; 18%).

^{1}H NMR (400 MHz, DMSO) δ 11.32 (s, 1H), 8.26 (s, 2H), 7.93 – 7.55 (m, 11H), 7.55 – 7.45 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 154.82 (s), 148.49 (s), 138.99 (s), 133.75 (s), 133.16 (s), 132.28 (s), 132.04 (s), 130.66 (s), 130.38 (s), 130.05 (s), 129.70 (s), 129.63 (s), 127.21 (s), 122.13 (s). MS(ESI) Found: 400.4 [M-ClO4]+ C20H13Cl3N3 requires 400.02.

(S)-5-(hydroxy-diphenyl-methyl)-2 -phenyl-2,5,6,7-tetrahydro-pyrrolo[2,1- c][1,2,4]triazol-4-ylium tetrafluoroborate (1a)

^{1}H NMR (400 MHz, DMSO-d6) δ 2.50 - 2.59 (m, 1H), 2.93 – 2.95 (m, 2H), 3.13 – 3.16 (m, 1H), 6.13 (d, J = 9.8 Hz, 1H), 6.58 (s, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.37 – 7.39 (m, 3H), 7.45 (app. t, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.63-7.68 (m, 3H), 7.78 (d, J = 7.8 Hz, 2H), 9.60 (s, 1H)

(S)-5-(Diphenyl-trimethylsilanyloxy-methyl)-2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4] triazol-2-ium tetrafluoroborate (1'a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H), 2.06 – 2.10 (m, 1H), 2.76 – 2.82 (m, 1H), 2.89 – 2.94 (m, 1H), 3.30 – 3.36 (m, 1H), 6.14 (d, J = 9.01 Hz, 1H), 7.30 – 7.36 (m, 2H), 7.38 – 7.43 (m, 5H), 7.48 – 7.52 (m, 3H), 7.58 – 7.61 (m, 3H), 7.71 – 7.73 (m, 2H), 8.90 (s, 1H)

(S)-5-(Hydroxy-diphenyl-methyl)-2-(2,4,6-trichloro-phenyl)-2,5,6,7-tetrahydro-pyrrolo[2,1-c][1,2,4]triazol-4-ylium tetrafluoroboride (1b)

^{1}H NMR (400 MHz, DMSO-d6): 2.64-2.74 (m, 1H), 2.82-2.86 (m, 1H), 3.08-3.21 (m, 2H), 6.16 (d, J 7.3, 1H), 6.79 (s, 1H), 7.28-7.31 (m, 2H), 7.35-7.41 (m, 6H), 7.44 (d, J 7.6, 2H), 8.11 (s, 2H), 9.45 (s, 1H)

5-(Hydroxy-diphenyl-methyl)-2-pentafluorophenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4] triazol-2- ium tetrafluoroborate (1c)

^{1}H NMR (400 MHz, DMSO-d6) δ 2.70 (app. t., 1H), 2.89 – 2.93 (m, 1H), 3.01 - 3.05 (m, 1H), 3.19 – 3.21 (m, 1H), 6.16 (d, J = 6.6 Hz, 1H), 6.80 (s, 1H), 7.32 (app. t., 1H), 7.36 – 7.40 (m, 3H), 7.43 – 7.47 (m, 4H), 7.55 (d, J = 7.4 Hz, 2H), 9.61 (s, 1H)

2-Phenyl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (2a)

^{1}H NMR (400 MHz, CD3CN): δ 9.65 (1H, s, iminium CH=N+), 7.77 (2H, dd, J1 8.4, J2 1.36, CarH), 7.62-7.67 (3H), 4.41 (2H, t, J 7.3, CH2), 3.19 (2H, t, J 7.5, CH2), 2.81 (2H, quin., J 7.6, CH2) ppm

2-(2,4,6-trichloro-phenyl)-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (2b)

^{1}H NMR (400 MHz, DMDO-d6) δ (ppm) = 10.46 (s, 1 H), 8.16 (s, 2 H), 4.53 (t, J = 10 Hz, 2 H), 3.26 (t, J = 10 Hz, 2 H), 2.77 (qnt, J = 10 Hz, 2 H)

2-pentafluorophenyl-6,7-dihydro-5H-pyrrolo[1,2,4]triazol-2-ium tetrafluoroborate (2c)

^{1}H NMR (400 MHz, DMDO-d6) δ (ppm) = 10.52 (s, 1 H), 4.48 (t, J = 10 Hz, 2 H), 3.24 (t, J = 10 Hz, 2 H), 2.76 (quint, J = 10 Hz, 2 H)

5-Methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline (3'a)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (ddd, J1 5.7 Hz, J2 4.2 Hz, J3 2.5 Hz, 2 H), 7.38 – 7.22 (m, 13H), 6.92 (tt, J = 6.8, 1.6 Hz, 1H), 6.75 (s, 1 H, OCHN), 3.22 (s, 3 H, OCH3)

1,3-Bis{(S)-5-benzyl-6,8-dihydro-5H-[1,4]oxazino[2,1-c][1,2,4]triazol-2-ium-2-yl} benzene dichloride (4)

^{1}H NMR (400 MHz, DMSO-d6): δ = 3.17-3.24 (m, 2H), 3.55 (2d, J = 4.8 Hz, 5.4 Hz, 2H), 4.00-4.01 (m, 4H), 4.90 (m, 2H), 5.19 (2d, J = 16.2 Hz, 16.2 Hz, 4H), 7.35-7.39 (m, 6H), 7.42-7.45 (m, 4H), 8.13-8.15 (m, 1H), 8.20-8.22 (m, 2H), 8.52 (s, 1H), 11.22 (s, 2H) ppm

(5S)-8H-1,2,4-Triazolo[3,4-c][1,4]oxazinium, 5,6-dihydro-2-phenyl-5-(phenylmethyl) chloride (5)

^{1}H NMR (300 MHz, CDCl3) 3.17 (1 H, dd, J = 13Hz, 11Hz), 3.87 (1 H, dd, J = 13Hz, 4.5Hz, PhCH2), 3.97 and 4.03 (each 1 H, dd, J= 12.5Hz, 3Hz, CHCH2), 4.99 and 5.12 (each 1 H, d, J 16, OCH2), 5.24–5.35 (1 H, m, CHN), 7.14–7.25 (3 H, m), 7.32– 7.44 (5 H, m), 7.92–8.02 (2 H, m, 2 × Ph), 12.91 (1 H, s, 3-H)