General methods and experimental procedure

Unless otherwise noted all reagents were obtained from commercial suppliers and used without further purification. Chromatography columns were prepared using Fisher Chemicals 60A 35–70 micron silica gel. Nuclear magnetic resonance spectra were recorded using Bruker DPX300 and DPX500 MHz spectrometers. Chemical shifts are reported in parts per million (δ) downfield relative to the internal reference tetramethylsilane (TMS). Unless otherwise specified NMR spectra were recorded in deuterochloroform at room temperature. Abbreviations used: Ar = aromatic, d = doublet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, q = quartet, s = singlet, t = triplet. Mass spectra were recorded using a micromass ZMD 2000 spectrometer employing the electrospray (ES+) ionisation technique. Accurate molecular masses (HRMS) were obtained from Waters LCT, GCT or Bruker MicroTof spectrometers. Infra-red spectra were recorded using a Perkin-Elmer FT-IR spectrometer. IR spectra of liquids were recorded as thin films on sodium chloride plates. IR spectra of solids were recorded using dichloromethane as solvent on sodium chloride plates. Melting points are uncorrected.

Compounds 6, 10 and 14 contains trace of ethyl acetate (NMR)

Method A: General procedure for copper catalysed click reaction

To a stirred solution of 4a (1.0 mmol), sodium ascorbate (0.3 mmol) and CuSO₄ (0.01 mmol) in ¹BuOH/H₂O (4 mL, 1:1) was added benzyl azide (1.0 mmol) dropwise over 2 minutes. The reaction was stirred at RT for 12 hours and monitored via TLC. Upon completion the reaction was concentrated in vacuo in order to remove ¹BuOH. The resultant residue was diluted with ethyl acetate (20 mL) and washed with H₂O (50 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated in vacuo to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

Method B: General procedure for palladium catalysed cyclisation – Cross coupling

5a (1.0 mmol), boronic acid (2.0 mmol), Pd(PPh₃)₄ (5 mol%) and Cs₂CO₃ (3.0 mmol) were dissolved in dioxane/H₂O (15:1, 3.0 mL) with stirring. The reaction mixture was stirred for 6 hours at 90 °C and monitored via TLC. Upon completion the reaction was diluted with ethyl acetate (30 mL) and washed with H₂O (20 mL). The organic phase was dried over Na₂SO₄,
filtered and concentrated \textit{in vacuo} to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

**Method C: General procedure for one-pot copper catalysed click reaction and palladium catalysed cyclisation – Cross coupling**

4a (1.0 mmol), benzyl azide (1.0 mmol) and CuI (5 mol\%) were dissolved in dioxane/H$_2$O (3.2 mL) with stirring. The reaction mixture was stirred for 12 hours at 90 °C and monitored via TLC. Upon completion boronic acid (2.0 mmol), Pd(PPh$_3$)$_4$ (5 mol\%) and Cs$_2$CO$_3$ (3.0 mmol) were added and the reaction stirred for a further 12 hours. Upon completion the reaction was diluted with ethyl acetate (30 mL) and washed with H$_2$O (20 mL). The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated \textit{in vacuo} to yield a crude product which was purified by column chromatography (gradient elution of hexane/ethyl acetate).

**Method D: General procedure for palladium catalysed cyclisation-carbonylation-amination**

5a (1.0 mmol), Cs$_2$CO$_3$ (3.0 mmol), Palladium acetate (10 mol\%), furyl phosphine (20 mol\%) and amine (1.5 mmol) were dissolved in 15 mL toluene with stirring under a CO balloon. The mixture was stirred for 100 °C for 10 hours and the reaction monitored via TLC. On completion the mixture was diluted with ethyl acetate, filtered and concentrated \textit{in vacuo}. The crude product was separated using column chromatography (gradient elution of hexane/ethyl acetate)

**Compound A1**

![Chemical structure of Compound A1](image)

To a stirred solution of 2-iodoaniline (5.0 g, 22.8 mmol) and triethylamine (0.24 mL, 25.1 mmol) in anhydrous CH$_2$Cl$_2$ (150 mL) was added methacryloyl chloride (2.5 mL, 25.1 mmol) dropwise over 5 mins and the reaction stirred at RT for 10 hours. The reaction was quenched by the addition of H$_2$O (100 mL) and the aqueous phase extracted with CH$_2$Cl$_2$ (2 x 50 mL). Organic
phases were combined, dried over Na₂SO₄, filtered and concentrated \textit{in vacuo} to yield brown oil. The resultant oil was used without further purification.

\textbf{Compound A2}

![Compound A2 structure](image)

To a stirred solution of 5-chloro-2-iodoaniline (0.538g, 2.1mmol) and triethylamine (0.234g, 2.31 mmol) in 100 mL DCM, methacryloyl chloride was added ( 0.241g, 2.31 mmol). The mixture was stirred over ice for 1 hour. The mixture was then stirred at room temperature overnight. The mixture was then quenched with 100 mL water. The aqueous phase was separated with two 100 mL washes of DCM. The organic phases were combined and dried with anhydrous sodium sulphate. The liquid was filtered off and concentrated \textit{in vacuo} to give brown oil which was used without further purification.

\textbf{Compound A3}

![Compound A3 structure](image)

To a stirred solution of 2-phenylacrylic acid (1.0 g, 6.75 mmol) in anhydrous THF (50 mL) was added glucosez (0.86 g, 6.41 mmol) and the reaction stirred at RT for 2 hours. 2-iodoanaline (1.48 g, 6.75 mmol) was added and the reaction stirred for a further 12 hours. The reaction was quenched by the addition of H₂O (100 mL) and the aqueous phase extracted with CH₂Cl₂ (2 x 50 mL). Organic phases were combined, dried over Na₂SO₄, filtered and concentrated \textit{in vacuo} to yield brown oil. The resultant oil was used without further purification.
Compound 4a

To a stirred solution of compound A1 (22.8 mmol) and sodium hydride (0.84 g, 20.9 mmol) in anhydrous DMF (100 mL) was added propargyl bromide (3.60 mL, 32.3 mmol). The solution was stirred at RT for 1 hour, quenched by the addition of H₂O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). Organic phases were combined, dried over Na₂SO₄, filtered and concentrated in vacuo to yield a brown syrup. The resulting syrup was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound 4a as a yellow solid (2.90 g, 34 % over 2 steps).

¹H NMR (300 MHz, CDCl₃): δ 7.90 (1H, dd, J = 7.8, 1.5 Hz, ArH), 7.42-7.27 (2H, m, ArH), 7.06 (1H, td, J = 8.5, 1.5 Hz, ArH), 5.13 (1H, s, C=CH), 5.03 (1H, s, C=CH), 5.10 (1H, d, J = 15.0 Hz, NC), 3.95 (1H, d, J = 15.0 Hz, NC), 2.20 (1H, s, alkylH), 1.83 (3H, s, CH₃). ¹³C NMR (75.5 MHz, CDCl₃): δ 171.2, 147.1, 140.1, 139.3, 131.1, 129.8, 129.1, 119.8, 86.2, 72.6, 71.5, 37.8, 20.4. νmax/cm⁻¹: 2685, 2521, 2410, 1656, 1631. H.R.M.S. [ES+] Found: 347.9862 (MNa⁺); C₁₃H₁₂INO requires 347.9856 (MNa⁺). M.pt: 63-64 °C

Compound 4b

To a stirred solution of crude A2 (assuming 1.5g, 4.7 mmol are all product) and 60% sodium hydride (0.187 g, 4.7 mmol) in anhydrous DMF (100 mL), 80% propargyl bromide (3.60 mL, 7.04 mmol) was added. The solution was stirred at RT for 1 hour, quenched by the addition of H₂O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). The organic phases were combined, dried over Na₂SO₄, filtered and subsequently concentrated in vacuo to
yield a brown liquid which was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound 4b as a colourless solid (0.80 g, 47 % yield).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.81 (1H, d, J = 8.25 Hz, Ar$H$), 7.29 (1H, s, Ar$H$), 7.07 (1H, dd, J = 8.7, 2.3 Hz, Ar$H$), 5.10 (2H, s, C=C$H$), 5.03 (1H, d, J = 14.7 Hz, NCH$H$), 3.95 (1H, d, J = 15.6 Hz, NCH$H$), 2.25 (1H, s, alkyne$H$), 1.87 (3H, s, CH$_3$).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): 170.9, 145.2, 140.7, 139.4, 134.9, 131.1, 130.0, 120.0 97.0, 78.1, 73.1, 37.7, 20.4. $\nu$$_{\text{max/cm}^{-1}}$; 3302, 1662, 1631, 1571, 1462. H.R.M.S. [ES+] Found: 359.9642 (MH$^+$); C$_{13}$H$_{11}$IClNO requires 359.9647 (MH$^+$). M.pt: 62-64 °C

**Compound 4c**

![Compound 4c](image)

To a stirred solution of A3 (assume 6.75 mmol) and sodium hydride (245.7 mg, 6.14 mmol) in anhydrous DMF (100 mL) was added propargyl bromide (1.1 mL, 9.45 mmol). The solution was stirred at RT for 1 hour, quenched by the addition of H$_2$O (100 mL) and the aqueous phase extracted with diethyl ether (4 x 100 mL). Organic phases were combined, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo to yield a brown syrup. The resulting syrup was purified by column chromatography (gradient elution of hexane/ethyl acetate 8:2) to yield compound 4c as yellow oil (1.67 g, 64 % over 2 steps).

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.70 (1H, dd, J = Hz, Ar$H$), 7.31-7.23 (6H, m, Ar$H$), 7.01-6.70 (2H, m, Ar$H$), 5.6 (1H, s, C=CH), 5.43 (1H, s, C=CH), 5.2 (1H, dd, J = 17.3, 2.5 Hz, NCH$H$), 3.92 (1H, dd, J = 17.3, 2.5 Hz, NCH$H$), 2.2 (1H, t, J = 2.5 Hz, alkyne$H$).
Compound 5a

Prepared by general procedure Method A from compound 4a (326.0 mg, 1.0 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound 5a as a clear gel (403.4 mg, 88 %).

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.85 (1H, dd, J = 8.4, 1.5 Hz, ArH), 7.65 (1H, s, triazoleH), 7.40-7.22 (5H, m, ArH), 7.10-6.94 (2H, m, ArH), 5.6 (1H, d, J = 15.0 Hz, NC$_2$H$_2$Ph), 5.5 (1H, d, CH$_2$Ph) 5.3 (1H, d, J = 15.0 Hz, NCH), 5.0 (1H, s, C=CH$_2$), 4.5 (1H, d, J = 15.0 HzNCH) 1.53 (s CH$_3$), $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.3, 140.0, 134.7, 133.5, 130.8, 129.5, 129.3, 129.2, 129.1, 128.7, 128.0, 124.1, 124.0, 119.8, 99.3, 54.1, 44.6, 20.5. $\nu_{\text{max}}$/cm$^{-1}$: 3069, 2901, 1651, 1625. H.R.M.S. [ES+] Found: 481.0513 (MNa$^+$); C$_{20}$H$_{19}$IN$_4$O requires 481.0496 (MNa$^+$).

Compound 5b

Prepared by general procedure Method A from compound 4b (359.0 mg, 1.0 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 4:1) to yield compound 5b as a colourless solid (201.0 mg, 41.0 % yield).
**1H NMR** (500 MHz, CDCl₃): δ 7.75 (1H, d, J = 9.2, ArH), 7.63 (1H, s, triazoleH), 7.39-7.32 (3H, m, ArH), 7.25 (2H, m, ArH), 6.99 (2H, m, ArH), 5.57 (1H, d, J = 15.1 Hz, NC₃HPh), 5.47 (1H, d, J = 15.1 Hz, NCH₃Ph), 5.28 (1H, d, J = 14.7 Hz, NC₃H), 5.05 (1H, s, C=CHH), 5.00 (1H, s, C=CHH), 4.49 (1H, d, J = 14.7 Hz, NCH₃), 1.81 (3H, s, CH₃).

**13C NMR** (75.5 MHz, CDCl₃): 171.1, 143.5, 140.7, 139.5, 135.0, 134.7, 130.9, 129.7, 129.3, 129.1, 128.7, 128.0, 126.4, 126.2, 123.9, 120.2, 97.3, 54.2, 44.6, 20.4. νₘₐₓ/cm⁻¹: 1655, 1629, 1497, 1461. **H.R.M.S.** [ES⁺] Found: 515.0123 (MNa⁺). C₂₀H₁₈IClN₄O requires 515.0112 (MNa⁺).

**Compound 5c**

Prepared by general procedure Method A from compound 4c (238.4 mg, 0.62 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound 5c as a clear gel (179.4 mg, 56%).

**1H NMR** (500 MHz, CDCl₃): δ 7.38 (1H, s, triazoleH), 6.49 (1H, d, J = 7.6 Hz, ArH), 5.59 (1H, s, C=CHH), 5.53 (2H, s, NCH₃Ph), 5.48 (1H, d, J = 14.7 Hz, NCH₃H), 5.34 (1H, s, C=CHH), 4.39 (1H, d, J = 14.7 Hz, NCH₃H). **13C NMR** (125 MHz, CDCl₃): δ 170.0, 145.2, 143.8, 143.7, 139.6, 136.8, 134.8, 134.4, 131.4, 129.9, 129.4, 129.1, 128.9, 128.8, 128.6, 128.3, 128.0, 125.9, 100.1, 54.2, 44.1. νₘₐₓ/cm⁻¹: 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES⁺] Found: 543.0664 (MNa⁺); C₂₅H₂₁IN₄O requires 543.0652 (MNa⁺).
**Compound 6**

*Prepared by general procedure Method B from 5a (70.0 mg, 0.15 mmol) and phenylboronic acid (37.2 mg, 0.31 mmol) to yield compound 6 as a yellow oil (51.2 mg, 82%).*

**1H NMR** (300 MHz, CDCl$_3$): $\delta$ 7.35-7.26 (4H, m, ArH), 7.16-7.04 (4H, m, ArH), 6.97-6.77 (5H, m, ArH), 6.68 (1H, d, J = 7.8, 1.5 Hz, ArH), 6.09 (1H, s, triazoleH), 5.39 (1H, d, J = 15.1 Hz, NC$_2$H$_3$Ph), 5.29 (1H, d, J = 15.1 Hz, NCH$_2$Ph), 5.15 (1H, d, J = 15.9, NC$_2$H), 4.57 (1H, d, J = 15.9 Hz, NCH$_2$H), 3.19 (1H, d, J = 13.1 Hz, CHH), 3.07 (1H, d, J = 13.1 Hz, CHH), 1.51 (3H, s, CH$_3$).

**13C NMR** (75.5 MHz, CDCl$_3$): $\delta$ 179.2, 143.4, 141.7, 136.7, 134.8, 132.8, 130.1, 128.6, 128.0, 127.9, 127.7, 127.4, 126.3, 123.1, 122.5, 121.8, 109.3, 53.8, 50.1, 44.2, 35.7, 23.9. $v_{\text{max/cm}}$; 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES$^+$] Found: 431.1846 (MNa$^+$); C$_{26}$H$_{24}$N$_4$O requires 431.1842 (MNa$^+$).

Alternatively compound 6 was synthesized using the general procedure Method C in 62 % yield.

**Compound 7**
Prepared by general procedure Method B from 5a (70.0 mg, 0.15 mmol) and (3-methoxyphenyl) boronic acid (46.5 mg, 0.31 mmol) to yield compound 7 as a white solid (46.9 mg, 70%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.36-7.27 (4H, m, Ar$H$), 7.16-7.06 (4H, m, Ar$H$), 6.79 (1H, app. t, J = 7.2 Hz, Ar$H$), 6.68 (1H, dd, Ar$H$), 6.55 (1H, ddd, J = 7.0, 2.4, 1.0 Hz, Ar$H$), 6.44 (1H, dt, J = 6.3, 6.2, 1.2 Hz, Ar$H$), 6.25 (1H, dd, Ar$H$), 6.23 (1H, s, triazole$H$), 5.42 (1H, d, J = 14.9 Hz, NCH$_2$HP$H$), 5.29 (1H, d, J = 14.9 Hz, NCH$_2$HP$H$), 5.16 (1H, d, J = 15.9 Hz, NCH$H$), 4.58 (1H, d, J = 15.9 Hz, NCH$H$), 3.40 (3H, s, OCH$_3$), 3.18 (1H, d, J = 12.9 Hz, CH$H$), 3.07 (1H, d, J = 12.9 Hz, CH$H$), 1.52 (3H, s, CH$_3$).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.2, 143.4, 141.7, 136.7, 134.8, 132.8, 130.1, 129.6, 129.0, 128.6, 127.9, 127.6, 127.4, 126.3, 123.1, 122.5, 121.8, 115.4, 109.3, 53.8, 50.1, 44.3, 35.7, 24.8, 23.9. $\nu_{\text{max}}/\text{cm}^{-1}$: 2685, 2521, 2410, 2351, 1710, 1612.


**Compound 8**

![Chemical structure of compound 8](image)

Prepared by general procedure Method B from 5a (70.0 mg, 0.15 mmol) and p-tolylboronic acid (41.5 mg, 0.31 mmol) to yield compound 8 as a clear oil (57.4 mg, 89%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.35-7.30 (3H, m, Ar$H$), 7.21 (1H, dd, J = 8.5, 1.2 Hz, Ar$H$), 7.12 (1H, td, J = 8.0, 1.5 Hz, Ar$H$), 7.05-7.03 (3H, m, Ar$H$), 6.76 (2H, d, J = 7.5 Hz, Ar$H$), 6.71 (2H, d, J = 7.5 Hz, Ar$H$), 6.70 (1H, d, J = 8.0 Hz, Ar$H$), 6.51 (1H, s, triazole$H$), 5.37 (1H, d, J = 15.1 Hz, NCH$H$), 5.33 (1H, d, J = 15.1 Hz, NCH$H$), 5.06 (1H, d, J = 16.0 Hz, NCH$H$), 4.67 (1H, d, J = 16.0 Hz, NCH$H$), 3.13 (1H, d, J = 12.8 Hz, CH$H$), 3.03 (1H, d, J = 12.8 Hz,
CHH), 2.15 (3H, s, CH$_3$Ar), 1.48 (3H, s, CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.5, 143.5, 141.7, 135.7, 134.7, 133.5, 132.9, 130.0, 129.1, 129.0, 128.4, 127.8, 127.4, 123.2, 122.4, 122.2, 109.3, 53.8, 49.9, 43.8, 35.7, 23.7, 21.1. $\nu_{\text{max}}$/cm$^{-1}$; 2685, 2521, 2410, 1707, 1611. H.R.M.S. [ES+] Found: 445.1996 (MNa$^+$. C$_{27}$H$_{26}$N$_4$O requires 445.1999 (MNa$^+$).

Alternatively compound 8 was synthesized using the general procedure Method C in 80 % yield.

**Compound 9**

![Compound 9](image)

Prepared by general procedure Method B from 5a (50.0 mg, 0.11 mmol) and m-tolylboronic acid (29.7 mg, 0.22 mmol) to yield compound 9 as a white solid (40.6 mg, 88 %).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.35-7.24 (4H, m, ArH), 7.16-7.04 (4H, m, ArH), 6.81-6.74 (2H, m, ArH), 6.46 (1H, d, J = 8.0 Hz, ArH), 6.63 (1H, s, ArH), 6.56 (1H, d, J = 7.0 Hz, ArH), 6.13 (1H, s, triazoleH), 5.39 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.29 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.13 (1H, d, J = 15.8 Hz, NCHH), 4.60 (1H, d, J = 15.8 Hz, NCHH), 3.13 (1H, d, J = 13.4 Hz, C$H_2$), 3.04 (1H, d, J = 13.4 Hz, CHH), 2.00 (3H, s, CH$_3$Ar), 1.50 (3H, s, CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.5, 143.5, 142.3, 137.2, 136.6, 135.0, 132.9, 131.0, 129.0, 128.6, 128.4, 127.9, 127.5, 127.3, 127.0, 123.1, 122.4, 121.8, 109.3, 53.8, 50.0, 44.3, 35.7, 23.8, 21.0. $\nu_{\text{max}}$/cm$^{-1}$; 2917, 1709, 1611. H.R.M.S. [ES+] Found: 445.2006 (MNa$^+$. C$_{27}$H$_{26}$N$_4$O requires 445.1999 (MNa$^+$). M.pt: 94-96 °C.

**Compound 10**
Prepared by general procedure Method B from 5a (50.0 mg, 0.11 mmol) and 3-(benzyloxy)phenylboronic acid (49.8 mg, 0.22 mmol) to yield compound 10 as a clear oil (45.1 mg, 80%).

\( ^1\text{H} \text{NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 7.35-7.24 (9H, m, Ar\( \text{H} \)), 7.14 (1H, app. td, J = 7.8, 1.4 Hz, Ar\( \text{H} \)), 7.09 (1H, app. td, J = 7.8, 1.4 Hz, Ar\( \text{H} \)), 7.05-7.03 (2H, m, Ar\( \text{H} \)), 6.76-6.70 (2H, m, Ar\( \text{H} \)), 6.60 (1H, dd, J = 7.3, 1.8 Hz, Ar\( \text{H} \)), 6.43 (1H, br. d, J = 7.3 Hz, Ar\( \text{H} \)), 6.39-6.38 (1H, m, Ar\( \text{H} \)), 6.23 (1H, s, triazole\( \text{H} \)), 5.29 (1H, d, J = 15.1 Hz, NCH\( \text{H} \)Ph), 5.16 (1H, d, J = 15.1 Hz, NCH\( \text{H} \)Ph), 5.14 (1H, d, J = 16.8 Hz, NCH\( \text{H} \)), 4.70 (1H, d, J = 11.6, OCH\( \text{H} \)), 4.59 (1H, d, J = 11.6 Hz, OCH\( \text{H} \)), 4.57 (1H, d, J = 16.8 Hz, NCH\( \text{H} \)), 3.17 (1H, d, J = 13.3 Hz, CH\( \text{H} \)), 3.06 (1H, d, J = 13.3 Hz, CH\( \text{H} \)), 1.51(3H, s, CH\( \text{H} \)).

\( ^{13}\text{C} \text{NMR} \) (125 MHz, CDCl\(_3\)): \( \delta \) 179.1, 158.1, 143.3, 141.9, 138.2, 136.8, 134.8, 133.0, 128.9, 128.7, 128.6, 128.5, 128.0, 127.5, 127.4, 123.4, 123.1, 122.8, 122.5, 121.8, 115.5, 114.1, 109.4, 69.8, 53.7, 50.0, 44.4, 35.7, 23.9. \( \nu_{\text{max}}/\text{cm}^{-1} \): 2919, 1709, 1611. \textit{H.R.M.S.} [ES+] Found: 537.2267 (MNa\(^+\)); C\(_{33}\)H\(_{30}\)N\(_4\)O\(_2\) requires 537.2261 (MNa\(^+\)).

\textbf{Compound 11}
Prepared by general procedure Method B from 5a (62.0 mg, 0.14 mmol) and 3-(trifluoromethyl)phenyboronic acid (51.4 mg, 0.27 mmol) to yield compound 11 as a clear oil (40 mg, 62%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.39-6.88 (12H, m, ArH), 6.80 (1H, d, $J = 7.8$ Hz, ArH), 6.58 (1H, s, triazoleH), 5.42 (1H, d, $J = 15.1$ Hz, NCH$_3$Ph), 5.33 (1H, d, $J = 15.1$ Hz, NCH$_3$Ph), 4.95 (1H, d, $J = 15.6$ Hz, NCH$_3$Ph), 4.65 (1H, d, $J = 15.6$ Hz, NCH$_3$Ph), 3.22 (1H, d, $J = 13.2$ Hz, C$_H$H), 3.08 (1H, d, $J = 13.2$ Hz, CH$_2$), 1.51 (3H, s, C$_3$H$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 178.9, 143.2, 141.7, 137.3, 134.6, 133.3, 133.1, 129.1, 128.7, 128.3, 128.0, 127.9, 127.7, 126.7, 123.0, 122.8, 122.6, 121.7, 121.4, 109.5, 53.9, 49.8, 44.0, 35.5, 23.5. $\nu_{\text{max/cm}^{-1}}$: 2685, 2521, 2410, 1708, 1612. H.R.M.S. [ES+] Found: 499.1728 (MNa$^+$); C$_{27}$H$_{23}$F$_3$N$_4$O requires 499.1716 (MNa$^+$).

**Compound 12**
Prepared by general procedure Method B from 5a (65.0 mg, 0.14 mmol) and 2-(trifluoromethyl)phenylboronic acid (53.9 mg, 0.28 mmol) to yield compound 12 as a clear oil (58.8 mg, 87%).

**1H NMR** (500 MHz, CDCl₃): δ 7.46 (1H, d, J = 8.0 Hz, ArH), 7.36-7.33 (3H, m, ArH), 7.24 (1H, s, ArH), 7.22-7.21 (2H, m, ArH), 7.15 (1H, ddd, ArH), 7.10-7.01 (1H, m, ArH), 7.02 (1H, d, J = 8.0 Hz, ArH), 6.96-6.90 (3H, m, ArH), 6.90 (1H, s, triazoleH), 5.45 (2H, s, NC₃H₃Ph), 5.10 (1H, d, J = 15.6 Hz, NHPh), 4.88 (1H, d, J = 15.6 Hz, NCHH), 3.39 (1H, d, J = 14.9 Hz, CHH), 3.33 (1H, d, J = 14.9 Hz, CHH), 1.46 (3H, s, CH₃).

**13C NMR** (125 MHz, CDCl₃): δ 179.9, 143.2, 141.6, 136.0, 134.4, 132.9, 132.7, 131.0, 130.4, 129.2, 128.9, 128.1, 128.0, 126.5, 123.4, 122.7, 122.6, 122.3, 122.2, 109.3, 54.2, 48.5, 38.5, 35.6, 25.1. **νmax/cm⁻¹**: 2685, 2521, 2410, 1709, 1611. **H.R.M.S.** [ES+] Found: 499.1731 (MNa⁺); C₂₇H₂₃F₃N₄O requires 499.1716 (MNa⁺).

**Compound 13**

Prepared by general procedure Method B from 5b (60mg, 0.12mmol) and 2-(trifluoromethyl)phenylboronic acid (47mg, 0.24mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:1) to yield compound 13 as a colourless solid (60 mg, 90 % yield).

**1H NMR** (500 MHz, CDCl₃): 7.47 (1H, d, J = 7.8Hz, ArH), 7.38-7.36 (4H, m, ArH), 7.24-7.23 (2H, m, ArH), 7.12-7.09 (1H, t, J = 7.3, ArH), 7.02 (1H, d, J = 1.8 Hz, ArH), 6.96-6.95 (1H, d, J = 7.8 Hz, ArH), 6.93(1H, s, triazoleH), 6.92-6.88 (1H, m, ArH), 6.84 (1H, d, J = 7.8Hz, ArH), 5.48 (2H, s, NC₃H₃Ph), 5.08 (1H, d, J = 15.6, NC₃H₃), 4.84 (1H, d, J = 15.6 Hz, NCHH), 3.38
(1H, d, J = 15.1 Hz, CHH), 3.31 (1H, d, J = 15.1 Hz, CHH), 1.44 (3H, s, CH3).\(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): 180.0, 142.8, 142.7, 135.6, 134.3, 133.8, 131.2, 131.0, 130.3, 129.2, 129.0, 128.9, 128.04, 126.7, 126.2, 126.1, 125.3, 124.4, 123.2, 122.6, 122.2, 109.9, 54.3, 48.4, 38.4, 35.7, 25.0. \(\nu_{\text{max}}/\text{cm}^{-1}\): 2830, 1717, 1610, 1490. H.R.M.S. [ES+] Found: 511.1512 (MH\(^+\)). C\(_{27}\)H\(_{22}\)ClF\(_3\)N\(_4\)O requires 511.1507 (MH\(^+\)). M.pt: 97-99 °C.

**Compound 14**

![Chemical structure of compound 14](image)

Prepared by general procedure Method B from 5b (50mg, 0.1 mmol) and 3,5-bis(trifluoromethyl) benzeneboronic acid. Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 2:3) to yield compound 14 as a colourless gel (48.2mg, 82 % yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.75 (1H, s, ArH), 7.38-7.33 (3H, m, ArH), 7.25 (2H, s, ArH), 7.20-7.19 (2H, m, ArH), 7.13 (1H, s, triazoleH), 7.10 (1H, d, J = 7.8 Hz, ArH), 7.07-7.04 (1H, m, ArH), 7.00 (1H, d, J = 1.4 Hz, ArH), 5.45 (1H, d, J = 15.1 Hz, NCHHPh), 5.40 (1H, d, J = 15.1 Hz, NCHHPh), 4.75 (1H, d, J = 15.6, NCHH), 4.64 (1H, d, J = 15.6 Hz, NCHH), 3.27 (1H, d, J = 13.1 Hz, CHH), 3.09 (1H, d, J = 13.1 Hz, CHH), 1.48(3H, s, CH3). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): 178.6, 142.9, 142.5, 138.4, 134.6, 134.4, 130.9, 129.9, 129.9, 129.7, 129.1 128.8, 128.0, 124.1, 123.8, 122.7, 122.0, 110.5, 54.2, 495, 43.7, 35.4, 23.0. \(\nu_{\text{max}}/\text{cm}^{-1}\): 3054, 2986, 1717, 1610, 1490. H.R.M.S. [ES+] Found: 579.1385 (MH\(^+\)). C\(_{28}\)H\(_{21}\)ClF\(_6\)N\(_4\)O requires 579.1381 (MH\(^+\)).

**Compound 15**
Prepared by general procedure Method B from 5b (33mg, 0.067 mmol) and 2,5-dichlorobenzeneboronic acid (27mg, 0.134 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound 15 as a colourless solid (27mg, 79% yield )

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.36-7.34 (3H, m, ArH), 7.25 (1H, s, triazoleH), 7.20-7.19 (2H, m, ArH), 7.05 (1H, d, J = 2.3 Hz, ArH), 7.03 (1H, d, J = 8.7 Hz, ArH), 6.99 (1H, d, J = 1.4 Hz, ArH), 6.96 (1H, dd, J = 8.0, 1.6 Hz, ArH), 6.93 (1H, dd, J = 8.5, 2.5 Hz, ArH), 5.50 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.45 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.07 (1H, d, J = 16.0 Hz, NCHH), 4.79 (1H, d, J = 15.8 Hz, NCHH), 3.36 (1H, d, J = 13.8 Hz, CHH), 3.17 (1H, d, J = 13.8 Hz, CHH), 1.46 (3H, s, CH$_3$). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 179.3, 142.8, 142.7, 136.1, 134.5, 134.0, 132.9, 131.8, 131.0, 130.6, 130.0, 129.1, 128.8, 128.2, 127.9, 124.9, 122.4, 122.2, 110.0, 54.2, 49.3, 39.3, 35.8, 23.9. $\nu$$_{max}$/cm$^{-1}$: 3688, 2685, 1714, 1610, 1490.


Compound 16
Prepared by general procedure Method B from 5c (60.0 mg, 0.12 mmol) and 3-(trifluoromethyl)phenylboronic acid (43.8 mg, 0.23 mmol) to yield compound 16 as a clear oil (40.4 mg, 65 %).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.45 (2H, d, J = 7.3 Hz, ArH), 7.34-7.27 (7H, m, ArH), 7.23-7.09 (5H, m, ArH), 7.07-6.99 (2H, m, ArH), 6.93 (1H, app.t, J = 7.8 Hz, ArH), 6.86 (1H, d, J = 7.8 Hz, ArH), 6.69 (1H, s, triazoleH), 5.41 (1H, d, J = 15.1 Hz, NCHHPh), 5.34 (1H, d, J = 15.1 Hz, NCHHPh), 4.82 (1H, d, J = 15.6 Hz, NCHH), 4.70 (1H, d, J = 15.6 Hz, NCHH), 3.79 (1H, d, J = 12.8 Hz, CHH), 3.50 (1H, d, J = 12.8 Hz, CHH). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 177.0, 143.1, 142.3, 139.4, 136.8, 134.6, 133.6, 130.4, 129.9, 129.1, 128.8, 128.7, 128.0, 127.7, 127.1, 127.0, 125.3, 125.0, 123.3, 123.2, 122.8, 122.7, 121.9, 109.8, 57.9, 54.0, 43.4, 35.7. $\nu_{\text{max}}$/cm$^{-1}$: 2685, 2521, 2410, 1711, 1603. H.R.M.S. [ES+] Found: 561.1881(MNa$^+$); C$_{32}$H$_{25}$F$_3$N$_4$O requires 561.1873 (MNa$^+$).

**Compound 17**

Prepared by general procedure Method B from 5c (55.0 mg, 0.11 mmol) and 2-(trifluoromethyl)phenylboronic acid (40.1 mg, 0.21 mmol) to yield compound 17 as a clear oil (40.9 mg, 72 %).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46 (3H, m, ArH), 7.38-7.14 (9H, m, ArH), 7.12-7.02 (2H, m, ArH), 6.97-6.88 (1H, app.t, J = 7.3 Hz, ArH), 6.86-6.80 (2H, m, ArH), 6.73 (1H, d, J = 7.8 Hz, ArH), 6.72 (1H, s, triazoleH), 5.44 (2H, s, NCHHPh), 5.05 (1H, d, J = 15.6 Hz, NCHH), 4.90 (1H, d, J = 15.6 Hz, NCHH), 3.83 (2H, s, CHH). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 177.9, 143.2, 142.2, 139.9, 135.9, 139.3, 134.9, 134.3, 131.0, 130.3, 130.0, 129.7, 129.2, 128.8, 128.7, 128.5,
128.0, 127.7, 127.3, 126.6, 126.0, 122.5, 122.2, 109.6, 56.6, 54.3, 38.8, 35.8. $\nu_{\text{max/cm}^{-1}}$; 2685, 2521, 2410, 1711, 1603. **H.R.M.S.** [ES+] Found: 561.1864 (M$\text{Na}^+$). C$_{32}$H$_{25}$F$_3$N$_4$O requires 561.1873 (M$\text{Na}^+$).

**Compound 18**

Prepared by general procedure Method B from 5a (50.0 mg, 0.11 mmol) and benzo[b]thiophene-2-boronic acid (38.8 mg, 0.22 mmol) to yield compound 18 as a white solid (44.6 mg, 88 %).

$^1\text{H NMR}$ (500 MHz, CDCl$_3$): $\delta$ 7.57 (1H, d, J = 8.0 Hz, ArH), 7.46 (1H, d, J = 8.0 Hz, ArH), 7.36 (1H, d, J = 7.0 Hz, ArH), 7.31-7.20 (5H, m, ArH), 7.17 (1H, d, J = 8.0 Hz, ArH), 7.15 (1H, d, J = 8.0 Hz, ArH), 6.90 (1H, s, thiazoleH), 6.86-6.82 (2H, m, ArH), 6.75 (1H, d, J = 8.0 Hz, ArH), 5.95 (1H, s, triazoleH), 5.23 (1H, d, J = 15.6 Hz, NCHPh), 4.71 (1H, d, J = 15.6 Hz, NCHPh), 4.59 (1H, d, J = 15.6 Hz, NCHH), 4.41 (1H, d, J = 15.6 Hz, NCHH), 3.61 (1H, d, J = 14.2 Hz, CHH), 3.36 (1H, d, J = 14.2 Hz, CHH), 1.55 (3H, s, CH$_3$). $^{13}\text{C NMR}$ (125 MHz, CDCl$_3$): $\delta$ 178.7, 143.1, 142.3, 140.0, 139.8, 139.2, 134.9, 132.4, 128.8, 128.6, 128.3, 127.2, 124.2, 123.9, 123.6, 123.5, 123.1, 122.9, 122.1, 121.8, 109.7, 53.1, 49.6, 39.5, 35.8, 24.1. $\nu_{\text{max/cm}^{-1}}$; 2919, 1710, 1611. **H.R.M.S.** [ES+] Found: 487.1575 (M$\text{Na}^+$); C$_{27}$H$_{26}$N$_4$O requires 487.1563 (M$\text{Na}^+$). **M.pt:** 147-149 °C.

**Compound 19**
Prepared by general procedure Method B from 5a (70.0 mg, 0.15 mmol) and potassium trifluoro(prop-1-enyl)borate (45.2 mg, 0.31 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 7:3) to yield compound 19 as a yellow oil (43.2 mg, 76 %).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.40-7.10 (9H, m, ArH), 7.31 (1H, s, triazoleH), 5.48 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.42 (1H, d, J = 14.9 Hz, NCH$_2$Ph), 5.12 (1H, d, J = 15.6 Hz, NCH$_2$), 4.84 (1H, d, J = 15.6 Hz, NCH$_2$H), 4.37 (1H, s, C=CH), 4.24 (1H, s, C=CH), 2.67 (1H, d, J = 13.8 Hz, CH), 2.44 (1H, d, J = 13.8 Hz, CH), 1.35 (3H, s, C=CH$_3$), 1.08 (3H, s, CH$_3$).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 179.8, 143.6, 141.2, 140.1, 134.3, 133.4, 129.1, 128.8, 128.2, 128.0, 123.0, 122.3, 119.7, 114.2, 109.3, 54.3, 48.6, 45.6, 35.5, 24.9, 20.5. $\nu_{\text{max}}$/cm$^{-1}$: 2685, 2521, 2410, 1708, 1612. H.R.M.S. [ES+] Found: 373.2020 (MNa$^+$); C$_{23}$H$_{25}$N$_4$O requires 373.2023 (MNa$^+$).

**Compound 20**
Prepared by general procedure Method C from 4a (81.3 mg, 0.25 mmol) and 3-bromophenylboronic acid (100.4 mg, 0.5 mmol) to yield compound 20 as a clear oil (94.1 mg, 77%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.40-7.30 (3H, m, Ar$H$), 7.27-7.06 (5H, m, Ar$H$), 7.02-7.00 (2H, m, Ar$H$), 6.79 (1H, d, J = 7.5 Hz, Ar$H$), 6.68-6.23 (2H, m, Ar$H$), 6.60 (1H, s, triazole$H$), 5.45 (1H, d, J = 15.1 Hz, NCH$_2$HPh), 5.38 (1H, d, J = 15.1 Hz, NCH$_2$HPh), 5.09 (1H, d, J = 16.0 Hz, NCH$_2$H), 4.61 (1H, d, J = 16.0 Hz, NCH$_2$H), 3.13 (1H, d, J = 12.8 Hz, CH$H$), 3.01 (1H, d, J = 12.8 Hz, CH$H$), 1.49 (3H, s, CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 178.9, 143.3, 141.8, 138.9, 134.8, 132.8, 130.0, 129.4, 129.2, 129.0, 128.6, 128.5, 128.2, 127.6, 123.0, 122.6, 121.9, 121.4, 109.5, 53.9, 49.9, 43.8, 35.6, 23.8. $\nu$$_{\text{max}}$/cm$^{-1}$: 2685, 2521, 2410, 1709, 1611. H.R.M.S. [ES$^+$] Found: 509.0943 (MNa$^+$). C$_{26}$H$_{23}$BrN$_4$O requires 509.0947 (MNa$^+$).

**Compound 21**

Prepared by general procedure Method C from 4a (81.3 mg, 0.25 mmol) and 1-naphthaleneboronic acid (86.1 mg, 0.50 mmol) to yield compound 21 as an off white solid (90.6 mg, 79%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.15 (1H, d, J = 8.6 Hz, Ar$H$), 7.64 (1H, dd, J = 8.4, 1.3 Hz, Ar$H$), 7.47-7.39 (2H, m, Ar$H$), 7.36-7.30 (4H, m, Ar$H$), 7.19 (2H, dd, J = 7.3, 0.9 Hz, Ar$H$), 7.09-7.02 (2H, m, Ar$H$), 7.00-6.95 (2H, m, Ar$H$), 6.88 (1H, dd, J = 7.3, 0.9 Hz, Ar$H$), 6.68 (1H, d, J = 7.8 Hz, Ar$H$), 5.92 (1H, s, triazole$H$), 5.32 (1H, d, J = 15.4 Hz, NCH$_2$HPh), 5.22 (1H, d, J = 15.4 Hz, NCH$_2$HPh), 5.02 (1H, d, J = 15.8 Hz, NCH$_2$H), 4.52 (1H, d, J = 15.8 Hz, NCH$_2$H), 3.79 (1H, d, J = 13.7 Hz, CH$H$), 3.45 (1H, d, J = 13.7 Hz, CH$H$), 1.59 (3H, s, CH$_3$). $^{13}$C NMR (125
MHz, CDCl$_3$): δ 179.6, 143.3, 141.8, 134.8, 132.9, 132.8, 132.3, 129.0, 128.6, 128.0, 127.9, 127.4, 127.1, 126.5, 125.6, 125.5, 125.0, 124.8, 123.7, 122.3, 121.7, 109.2, 53.7, 49.8, 39.8, 35.6, 23.9. ν$_{\text{max}}$/cm$^{-1}$: 2685, 2521, 2410, 1709, 1611. H.R.M.S. [ES+] Found: 481.2000 (MNa$^+$); C$_{30}$H$_{26}$N$_4$O requires 481.1999 (MNa$^+$). M.pt: 73-75 °C

**Compound 22**

![Chemical structure of compound 22]

Prepared by general procedure Method C from 4a (81.3 mg, 0.25 mmol) and 3-pyridinylboronic acid (61.5 mg, 0.50 mmol) to yield compound 22 as a clear oil (39.2 mg, 38%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.36 (3H, d, J = 4.6 Hz, ArH), 7.29-7.21 (4H, m, ArH), 7.22-7.13 (3H, m, ArH), 7.08 (1H, app.t, J = 7.3 Hz, ArH), 6.96 (1H, d, J = 7.3 Hz, ArH), 6.84 (1H, d, J = 7.8 Hz, ArH), 6.77 (1H, s, triazoleH), 5.46 (1H, d, J = 14.7 Hz, NCH$_2$HPh), 5.40 (1H, d, J = 14.7 Hz, NCH$_2$H), 5.01 (1H, d, J = 15.6 Hz, NCHH), 4.62 (1H, d, J = 15.6 Hz, NCHH), 3.19 (1H, d, J = 13.3 Hz, CHH), 3.01 (1H, d, J = 13.3 Hz, CHH), 1.51 (3H, s, CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 178.8, 151.2, 143.0, 141.7, 136.9, 134.7, 131.9, 129.1, 128.8, 128.7, 128.4, 127.8, 123.7, 123.1, 122.9, 122.7, 122.1, 109.5, 54.0, 49.8, 41.5, 35.5, 23.5. ν$_{\text{max}}$/cm$^{-1}$: 2627, 2410, 1713, 1533. H.R.M.S. [ES+] Found: 410.1982 (MNa$^+$). C$_{25}$H$_{24}$N$_5$O requires 410.1975 (MNa$^+$).

**Compound 23**
Prepared by general procedure Method D from 5a (100mg, 0.22 mmol) and m-chloroaniline (42.24mg, 0.33 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:4) to yield compound 23 as a colourless gel (64.7 mg, 61 % yield )

$^1$H NMR (500 MHz, CDCl$_3$): 8.39 (1H, s, NH), 7.6 (1H, s, ArH), 7.56 (1H, s, triazoleH), 7.30-7.29 (3H, m, ArH), 7.24-7.12 (6H, m, ArH), 7.07 (1H, t , J = 7.6 Hz, ArH), 7.02-7.01 (1H, m, ArH), 6.99 (1H, d, J = 7.8 Hz, ArH), 5.42 (1H, d, J = 14.7 Hz, NCHPh), 5.32 (1H, d, J = 14.7 Hz, NCHPh), 5.26 (1H, d, J = 15.6 Hz, NCHH), 4.90 (1H, d, J = 15.8 Hz, NCHH), 3.04(1H, d, J = 15.8 Hz, CHCO), 2.88 (1H, d, J = 15.4 Hz, CHCO), 1.48 (3H, s, CH$_3$). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 180.3, 167.3, 143.0, 141.4, 139.0, 134.6, 134.5, 133.0, 129.9, 129.0, 128.6, 128.5, 127.9, 124.2, 123.2, 122.7, 122.3, 119.9, 117.7, 109.9, 54.2, 46.0, 44.9, 36.0, 24.0. $\nu_{\text{max/cm}^{-1}}$: 2984, 1702, 1613, 1595, 1469. H.R.M.S. [ES+] Found: 486.169836 (MH$^+$. C$_{27}$H$_{25}$ClN$_5$O$_2$ requires 486.169129 (MH$^+$).

**Compound 24**
Prepared by general procedure Method D from $5a$ (114mg, 0.25 mmol) and 3,4-dichloroaniline (60mg, 0.375 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 1:4) to yield compound 24 as a colourless solid (77 mg, 60 % yield)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.62 (1H, s, NH), 7.71 (1H, s, ArH), 7.51 (1H, s, triazoleH), 7.32-7.31 (3H, m, ArH), 7.28 (1H, d, J = 8.7 Hz, ArH), 7.24 (2H, d, J = 7.3, ArH), 7.18-7.15 (3H, m, ArH), 7.09 (1H, t, J = 7.6 Hz, ArH), 7.05 (1H, d, J = 7.8 Hz, ArH), 5.44 (1H, d, J = 14.9 Hz, NCHHPh), 5.36 (1H, d, J = 14.9 Hz, NCHHPh), 2.99 (1H, d, J = 15.4 Hz, CHHCO), 2.84 (1H, d, J = 15.4 Hz, CHHCO), 1.47 (3H, s, CH$_3$). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 180.5, 167.5, 142.9, 141.3, 137.3, 134.5, 133.0, 132.6, 130.4, 129.1, 128.7, 128.5, 127.8, 127.3, 123.4, 122.6, 122.3, 121.5, 119.0, 109.9, 54.2, 46.0, 44.6, 35.9, 23.8. $\nu_{\text{max}}$/cm$^{-1}$: 2986, 1696, 1613, 1592, 1469. H.R.M.S. [ES+]

Found:: 520.130352 (MH$^+$). C$_{27}$H$_{25}$ClN$_5$O$_2$ requires 520.130157 (MH$^+$). M.pt: 63-65 °C.

**Compound 25**

Prepared by general procedure Method D from $5a$ (100 mg, 0.31 mmol) and N-methylaniline (40mg, 0.372 mmol). Crude reaction mixture was purified by column chromatography (gradient elution of hexane/ethyl acetate 3:7) to yield compound 25 as a colourless gel (50.8 mg, 50 % yield)

$^1$H NMR (500 MHz, CDCl$_3$): 7.97 (1H, s, triazoleH), 7.45 (1H, D, J = 7.3 Hz, ArH), 7.40-7.37 (1H, m, ArH), 7.29-7.28 (3H, m, ArH), 7.21-7.13 (6H, m, ArH), 7.01-6.98 (2H, m, ArH), 7.82 (1H, d, J = 7.8 Hz, ArH), 5.52 (1H, d, J = 15.1 Hz, NCHHPh), 5.38 (2H, d, J = 16.5 Hz,
NCHHPh, NCHH), 4.88 (1H, d, J = 16.0 Hz, NCHH) 2.96, (3H, s, NCH3), 2.85(1H, d, J = 16.8 Hz, CHHCO), 2.68 (1H, d, J = 16.8 Hz, CHHCO), 1.16 (3H, s, CH3). $^{13}$C NMR (75.5 MHz, CDCl$_3$): 180.5, 168.7, 148.9, 148.9, 143.7, 142.4, 134.8, 133.9, 130.0, 128.9, 128.5, 128.0, 127.7, 127.4, 123.6, 123.4, 123.3, 122.2, 121.2, 109.4, 51.2, 45.9, 41.6, 37.1, 36.2, 25.2. $\nu_{\text{max}}$/cm$^{-1}$; 3135, 2928, 1715, 1655, 1613, 1467. H.R.M.S. [ES+] Found: 466.2257 (MH$^+$); $\text{C}_{30}\text{H}_{25}\text{ClN}_4\text{O}$ requires 466.238 (MH$^+$).