# Supporting Information

## General comments

Solvents and chemicals used were purchased from commercial suppliers. Solvents were dried under standard conditions. All materials were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel plates (Silica gel 60, F254, Merck) with detection by UV. Purification was performed with preparative chromatography using normal-phase silica gel (Silica gel 60, 230-400 mesh, Merck). $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM 400 or Bruker DRX 250, respectively. Chemical shifts are reported as δ values (ppm). The signal abbreviations include: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, Ar-H = aromatic proton and Cbz = carbazole. The signals of $^{13}$C NMR spectra were allocated through DEPT-technology (DEPT = Distortionless Enhancement by Polarisation Transfer). The signal abbreviations include: C-Ar = aromatic carbon, + = primary or tertiary carbon, − = secondary carbon, $C_{quart}$ = quaternary carbon. MS (EI) (electron impact mass spectrometry), FAB (fast atom bombardment mass spectrometry) and HRMS (high resolution mass spectrometry) were carried out on a Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the molecular ion. Descriptions without nominated temperature were done at room temperature (r.t.), and the following abbreviations were used: calcd. (theoretical value), found (measured value). Information is given in mass percent. IR (infrared spectroscopy) was carried out on a FT-IR Bruker Alpha-T. IR spectra of solids were recorded with a Diamond ATR technique, and as thin films on KBr for oils. The deposit of the absorption band was given in wavenumbers ν in $cm^{-1}$. The forms and intensities of the bands were characterized as follows: s = strong 10–40% transmission, m = medium 40–70% transmission, w = weak 70–90% transmission, vw = very weak 90–100% transmission, br = broad.

## Preparative HPLC

Reversed phase preparative HPLC was performed using a JASCO HPLC system, using a C18 Protein and Peptide column (Grace Davison Discovery Sciences, 10 µm, 22 × 250 mm). Flow rate: 15 mL/min; solvent A: 0.1% TFA in water; solvent B: 0.1% TFA in acetonitrile.

## Photophysical measurements

Emission and excitation spectra in the solid state were measured with an Horiba Scientific FluoroMax-4 spectrofluorometer using a JX monochromator and a R928P PMT detector. Fluorescence lifetime measurements were recorded and detected on the same system using the TCSPC method with the FM-2013 accessory and a TDSPC hub from Horiba Yvon Jobin. For this, a NanoLED 295 was used as excitation source (λ=295 nm, 1.5 ns pulse). Decay curves were analysed with the software DAS-6 and DataStation provide by Horiba Yvon Jobin. The quality of the fit was determined by the Chi-Square-method by Pearson.

Absorption spectra of the substances **1-8** have been measured in different solvents and solvent mixtures on a Cary 300 UV-Visible Spectrometer, Varian, Agilent Technologies. Fluorescence spectra of the substances 1-8 in different solvents and solvent mixtures were recorded on a Cary Eclipse Fluorescence Spectrophotometer, Varian, Agilent Technologies.

Quantum yields in solution were calculated.[21] As a standard quinine sulfate dihydrate (Sigma-Aldrich) has been used.

For the determination of PLQY ϕ of solids, an absolute PL quantum yield measurement system from Hamamatsu Photonics was used. The system consisted of a photonic multichannel analyser PMA-12, a model C99200-02G calibrated integrating sphere and a monochromatic light source L9799-02 (150 W Xe- and Hg-Xe-lamps). Data analysis was done with the PLQY measurement software U6039-05, provided by Hamamatsu Photonics.

## Computational Methods

Density functional theory (DFT) using the B3-LYP functional with dispersion correction and a def2-TZVP basis set was performed. The resolution-of-identity approximation was used and a grid-size of m5 was employed for numerical integration. Analytical harmonic vibrational frequency calculations were conducted to verify that the optimized ground-state structures are minima on the potential energy surface. For the excited states, time-dependent density functional-theory (TD-DFT) was applied. All calculations were performed with the Turbomole program package version 6.4.

## Single-crystal X-ray diffraction

The single-crystal X-ray diffraction studies were carried out on a Nonius Kappa-CCD diffractometer at 123(2) K using $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å). Direct Methods (SHELXS-97) (a) were used for structure solution and full-matrix least-squares refinement on $F^2$ (SHELXL-97) (a). H atoms were localized by difference Fourier synthesis and refined using a riding model. H(O) were refined free. Semi-empirical absorption corrections were applied.

## Cell culture and treatment

Human cervix carcinoma cells (HeLa cells) were cultured in Dulbecco's modified Eagle medium (DMEM) supplemented with 10% fetal calf serum and penicillin Streptomycin (100 u/mL) at 37 °C and 5% CO2. Cells were washed with PBS and subsequently trypsinized (0.025% Trypsin, 0.01% EDTA). For live imaging experiments, 1 x 104 HeLa cells were seeded in a well of an 8-well chamber slide (µ Slide 8 well ibiTreat, IBIDI) in 200 µL of supplemented DMEM. The cells were incubated with 10 µM of compounds 2 and 7 overnight at 37 °C, 5% CO2. Eventually, the medium was removed and the cells were washed several times with DMEM. Fluorescence was visualized by using confocal microscopy.

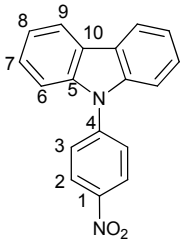
[21] S. Fery-Forgues, D. Lavabre, *J. Chem. Educ*. 1999, **76**, 1260-1264.

**Confocal Microscopy**

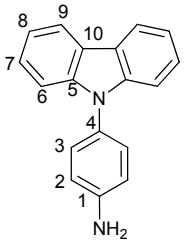
Cell images showing the fluorescence of the clusters were obtained performing confocal fluorescence microscopy using a Leica SP5 –TCS DM(I)6000 inverted microscope, a HCX PL APO CS63.0 x 1.20 WATER UV objective and an UV (□ = 351 nm) for excitation. The imaging was performed according to the settings as described in the manuscript.

**Synthesis**

*9-(4-Nitrophenyl)-9H-carbazole:* According to a modified literature procedure for 100 mmol of carbazole.[22] We substituted $K_2CO_3$ with $K_3PO_4$ and used dioxane instead of DMF as a solvent. Recrystallisation from $CHCl_3$ gave the title compound in 90% yield as a yellow solid. (26.0 g, 90.0 mmol, 90%) − $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, $^3J_{H\text{-}H}$ = 8.2, 2 H, $CHCNO_2$), 7.90−8.10 (m, 4 H, Ar-H), 7.63 (d, $^3J_{H\text{-}H}$ = 8.2, 2 H, CHCCbz), 7.10–7.50 (m, 4 H, Ar-H) ppm. – $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 144.70 ($C_{quart}$, C-1), 142.74 ($C_{quart}$, C-4), 138.41 ($C_{quart}$, 2 C, C-5), 125.61 (+, 2 C, C-3), 125.12 (+, 2 C, C-3), 124.45 (+, 2 C, C-2), 123,73 ($C_{quart}$, 2 C, C-10), 120.24, (+, 2 C, C-9), 119.58 (+, 2 C, C-8), 109.52 (+, 2 C, C-6) ppm. − IR (ATR): ν = 3416 (vw), 3049 (vw), 2923 (vw), 1892 (vw), 1702 (vw), 1594 (s), 1502 (vs), 1480 (s), 1450 (s), 1365 (w), 1342 (vs), 1316 (vs), 1227 (vs), 1177 (m), 1121 (w), 1101 (s), 1003 (w), 915 (m), 840 (vs), 741 (vs), 718 (vs), 689 (vs), 637 (m), 617 (m), 410 (s) cm$^{-1}$. – MS (70 eV, EI), *m/z* (%): 292 (2) $[M]^+$, 248 (1) $[M–NO_2]^+$, 219 (1), 167 (100) $[M–NO_2–Ph]^+$, 139 (10), 77 (73), 50 (48). − HR-EIMS ($C_{18}H_{12}N_2O_2$): calcd. 288.0898; found 288.0896.




*9-(4-Aminophenyl)-9H-carbazole:* Up-scaled procedure according to a modified literature procedure.[23] To a refluxed solution of 9-(4-nitrophenyl)-9*H*-carbazole (8.36 g, 29.0 mmol) and Pd/C (463 mg) in ethanol (100 mL) was added dropwise hydrazine monohydrate (10.0 mL). The mixture was refluxed for 4 h and cooled to room temperature. Pd/C was removed by filtration through basic aluminium oxide and the filtrate was concentrated to give the title compound as a clear viscous liquid (7.50 g, 29.0 mmol) in 99% yield. The product was used in the next step directly without further purification. – $^1$H NMR (300 MHz, DMSO-d*6*): δ = 8.19 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, Ar-H, 2 H), 7.40 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, Ar-H, 2 H), 7.27−7.21 (m, Ar-H, 4 H), 7.18 (d, $^3J_{H\text{-}H}$= 9.0 Hz, Ar-H, 2 H), 6.81 (d, $^3J_{H\text{-}H}$= 8.4 Hz, Ar-H, 2 H), 5.35 (s, $NH_2$, 2 H) ppm.




*9-(4-Azidophenyl)-9H-carbazole* **1:** A stirred suspension of 9-(4-Aminophenyl)-9*H*-carbazole (9.04 g, 35.0 mmol, 1.00 equiv.) in a mixture of 100 mL water and 7 mL concentrated hydrochloride acid was cooled to 0 °C. A solution of sodium nitrite (2.66 g, 38.5 mmol, 1.10 equiv.) in 38 mL water was added dropwise. During this, the colour of the precipitate changed from white to red, indicating the formation of a diazonium salt. After 15 minutes at 0 °C, a solution of sodium azide (2.73 g, 42.0 mmol, 1.20 equiv.) in 38 mL water was slowly added. *The start of the second step of the reaction was indicated by a strong formation of nitrogen, which led to foaming. Because of this, a reaction vessel of suitable size (500 mL or larger) is recommended for safety reasons.* After complete addition, the ice bath was removed and the reaction mixture was stirred for 30 minutes. The crude product was obtained by filtration of the reaction mixture, followed by washing with water (500 mL) and methanol (30 mL) and further purified by flash-chromatography with silica and cyclohexane/ethyl acetate (10:1) as eluent. The title compound was isolated after drying in 81% yield as a yellowish solid and stored at 4 °C in a dark flask in order to prevent degradation of the azide. (8.10 g, 28.5 mmol) – $R_f$ = 0.24 − $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dt, $^3J_{H\text{-}H}$ = 7.8, 1.0 Hz, 2 H, Ar-H), 7.53–7.40 (m, 2 H, Ar-H), 7.40–7.10 (m, 8 H, Ar-H) ppm. – $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 140.90 (+, 2 C, C-2), 139.20 ($C_{quart}$, C-4), 134.44 ($C_{quart}$, 2 C, C-5), 128.63 (+, 2 C, C-3), 126.96 ($C_{quart}$, C-1), 125.84 (+, 2 C, C-2), 123.59 ($C_{quart}$, 2 C, C-10), 120.35 (+, 2 C, C-9), 120.09 (+, 2 C, C-8), 109.68 (+, 2 C, C-6) ppm. − IR (ATR): ν = 3416 (vw), 3052 (vw), 2412 (vw), 2254 (vw), 2115 (vs), 2115 (vs), 1596 (m), 1507 (w), 1478 (vs), 1450 (s), 1364 (vs), 1336 (w), 1319 (w), 1289 (w), 1275 (s), 1230 (s), 1182 (s), 1148 (s), 1128 (m), 1110 (m), 1014 (m), 998 (w), 932 (w), 912 (w), 855 (w), 832 (w), 812 (w), 777 (w), 752 (vs), 725 (vs), 665 (m), 641 (m), 621 (m), 570 (m), 531 (m), 510 (m), 448 (m), 425 (m) cm$^{-1}$. − MS (70 eV, EI), *m/z* (%): 284 (70) $[M]^+$, 256 (100) $[M–N_2]^+$, 229 (13), 167 (50) $[Cbz]^+$, 153 (29), 136 (18), 105 (50) 77 (56), 55 (39). − HR-EIMS ($C_{18}H_{12}N_4$): calcd. 284.1062; found 284.1063. – Anal. calcd: for $C_{18}H_{12}N_4$: C 76.04, H 4.25, N 19.71; found: C 76.33, H 4.37, N 19.33.



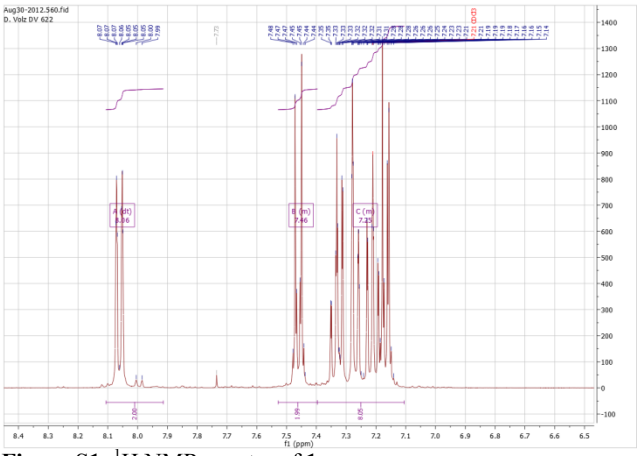



**Figure S1**: $^1$H NMR spectra of **1**.

22. B. Zhang, Y.-L. Liu, Y. Chen, K.-G. Neoh, Y.-X. Li, C.-X. Zhu, E.-S. Tok, and E.-T. Kang, *Chemistr,y,* 2011, **17**, 10304–10311.

23. W.-Y. Lee, T. Kurosawa, S.-T. Lin, T. Higashihara, M. Ueda, and W.-C. Chen, *Chem. Mater.*, 2011, **23**, 4487–4497.

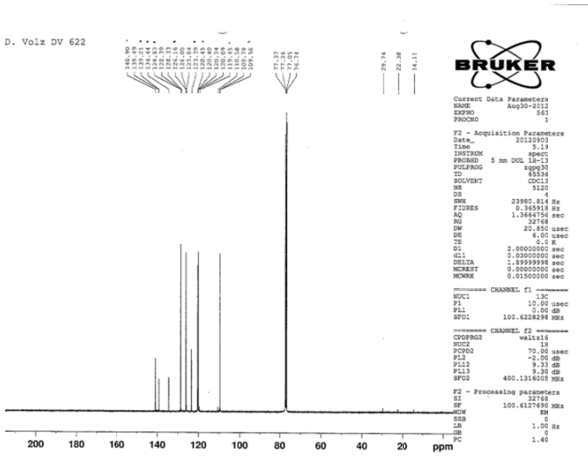



**Figure S2**: $^{13}$C NMR spectra of **1**.

*9-(4-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenyl)-9H-carbazole* **2**: In a vial 142 mg azidocarbazole **1** (0.500 mmol, 1.00 equiv.), 51 mg phenylacetylene (0.500 mmol, 1.00 equiv.), 143 mg copper iodide (0.750 mmol, 1.50 equiv.) were dissolved in 4.35 mL DIPEA (25.0 mmol, 50.0 equiv.) and 6.00 mL dry THF. The mixture was stirred for 48 h at room temperature. Afterwards, the solvent was removed and the crude product was purified by flash-chromatography with silica and cyclohexane/ethyl acetate (8:1) as eluent. Repurification was performed using HPLC to give the title compound as colourless crystals in 92% yield. (28 mg, 0.073 mmol, >99% purity) – mp: 205.5 °C – $^{1}$H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1 H, C*H*N), 8.20–8.15 (m, 2 H, Ar-H), 8.08–8.03 (m, 2 H, Ar-H), 8.00–7.94 (m, 2 H, Ar-H), 7.81–7.76 (m, 2 H, Ar-H), 7.53–7.44 (m, 6 H, Ar-H), 7.44–7.38 (m, 1 H, Ar-H), 7.38–7.31 (m, 2 H, Ar-H) ppm. – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 148.7 ($C_{quart}$, $C_{quart}$CHN), 140.5 ($C_{quart}$, 2 C, $C_{quart}C_{quart}$N), 138.2 ($C_{quart}$, $C_{quart}$N), 135.7 ($C_{quart}$, $C_{quart}$N), 130.0 ($C_{quart}$, $C_{quart}C_{quart}$CH), 129.0 (+, 2 C, $C_{Ar}$), 128.6 (+, $C_{Ar}$), 128.3 (+, 2 C, $C_{Ar}$), 126.2 (+, 2 C, $C_{Ar}$), 125.9 (+, 2 C, $C_{Ar}$), 123.6 ($C_{quart}$, 2 C, $C_{quart}C_{quart}$N), 122.0 (+, 2 C, $C_{Ar}$), 120.5 (+, 2 C, $C_{Ar}$), 120.4 (+, 2 C, $C_{Ar}$), 117.5 (+, $C_{Ar}$), 109.5 (+, 2 C, $C_{Ar}$) ppm. – IR (ATR): ν = 2921 (vw), 1677 (w), 1606 (w), 1523 (m), 1478 (w), 1450 (m), 1415 (w), 1366 (w), 1332 (w), 1318 (w), 1224 (m), 1181 (w), 1148 (w), 1113 (w), 1071 (w), 1035 (w), 1025 (w), 991 (w), 908 (w), 844 (w), 828 (w), 792 (w), 776 (vw), 747 (m), 722 (m), 687 (m), 638 (w), 619 (w), 567 (w), 542 (w), 502 (w), 465 (w), 424 (w) $cm^{-1}$. – MS (70 eV, EI), *m/z* (%): 386.2 (16) $[M]^+$, 358.2 (100) $[M–N_2]^+$, 241.1 (23). – HR-EIMS ($C_{26}H_{18}N_4$): calcd. 386.1531; found 386.1530.

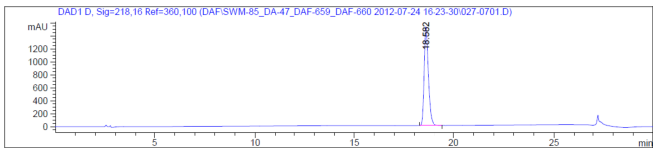



**Figure S1**: HPLC trace @218 nm of **2**; $t_r$ = 18.6 min.

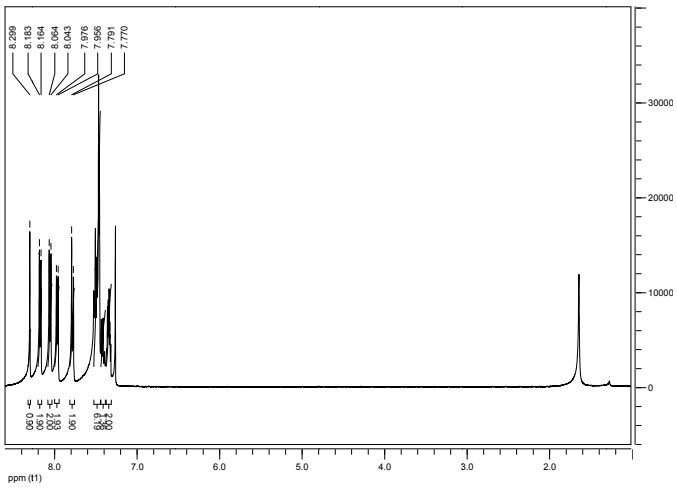



**Figure S2**: $^{1}$H NMR spectra of **2**.

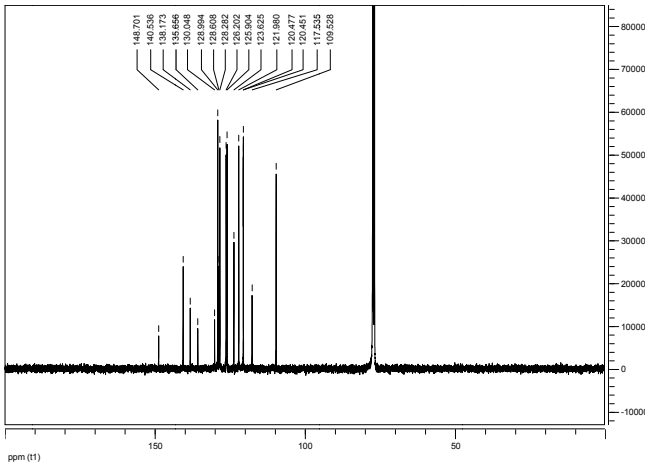



**Figure S3**: $^{13}$C NMR spectra of **2**.

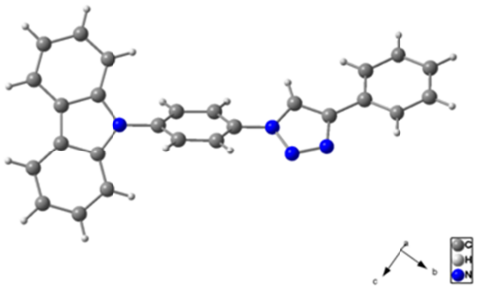


**Figure S4:** Molecular Structure of 2.

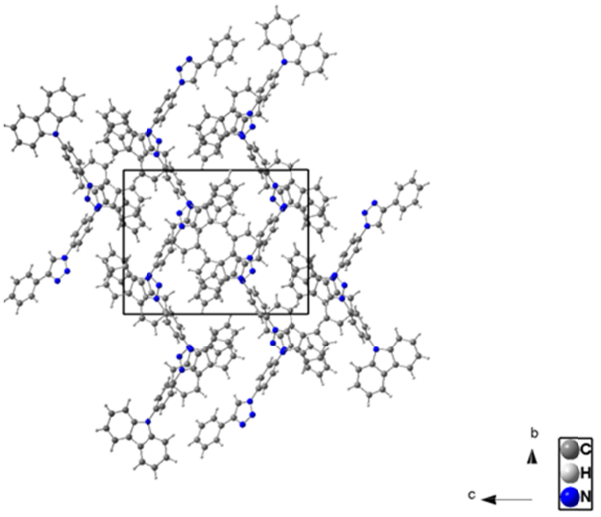



**Figure S5**: Crystal structure of **2**.

*2-(1-(4-(9H-Carbazol-9-yl)phenyl)-1-1,2,3-triazol-4-yl)propan-2-ol* **3**: In a vial 142 mg azidocarbazole **1** (0.500 mmol, 1.00 equiv.), 42 mg 2-methyl-3-butyne-2-ol (0.500 mmol, 1.00 equiv.), 143 mg copper iodide (0.750 mmol, 1.50 equiv.) were dissolved in 4.35 mL DIPEA (25.0 mmol, 50.0 equiv.) and 6.00 mL dry THF. The mixture was stirred for 48 h at room temperature. Afterwards, the solvent was removed and the crude product was purified by flash-chromatography with silica and cyclohexane/ethyl acetate (2:1) as eluent. Repurification was performed using HPLC to give the title compound as ochre-coloured crystals in 92% yield (169 mg, 0.459 mmol, 99% purity). – mp: 155.1 °C – $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.18 – 8.14 (m, 2 H, Ar-H), 8.02 – 7.96 (m, 3 H, Ar-H), 7.78 – 7.74 (m, 2 H, Ar-H), 7.46 – 7.42 (m, 4 H, Ar-H), 7.36 – 7.30 (m, 2 H, Ar-H), 1.76 (s, 6 H, $CH_3$) ppm. – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 156.6 ($C_{quart}$, $C_{quart}$CHN), 140.5 ($C_{quart}$, 2 C, $C_{quart}C_{quart}$N), 138.1 ($C_{quart}$, $C_{quart}$N), 135.7 ($C_{quart}$, $C_{quart}$N), 128.3 (+, 2 C, $C_{Ar}$), 126.2 (+, 2 C, $C_{Ar}$), 123.6 ($C_{quart}$, 2 C, $C_{quart}C_{quart}$N), 122.1 (+, 2 C, $C_{Ar}$), 120.5 (+, 2 C, $C_{Ar}$), 120.4 (+, 2 C, $C_{Ar}$), 117.6 (+, $C_{Ar}$), 109.5 (+, 2 C, $C_{Ar}$), 68.8 ($C_{quart}$, $C_{quart}$OH), 30.5 (+, 2 C, $CH_3$) ppm. – IR (ATR): ν = 3269 (w), 2972 (w), 1625 (w), 1599 (w), 1518 (m), 1478 (m), 1451 (m), 1361 (m), 1334 (w), 1315 (m), 1233 (m), 1204 (w), 1174 (m), 1146 (m), 1117 (w), 1102 (w), 1047 (m), 990 (w), 962 (m), 930 (w), 917 (w), 859 (w), 837 (m), 804 (m), 747 (s), 723 (s), 670 (w), 622 (m), 562 (w), 542 (m), 456 (w), 428 (w) $cm^{-1}$. – MS (70 eV, EI), *m/z* (%): 368.1 (44) $[M]^+$, 350.1 (18) $[M–H_2O]^+$, 340.1 (10) $[M–N_2]^+$, 282.1 (26), 241.0 (52), 43.0 (100) $[C_3H_7]^+$. – HR-EIMS ($C_{23}H_{20}N_4O$): calcd. 368.1637; found 368.1634.

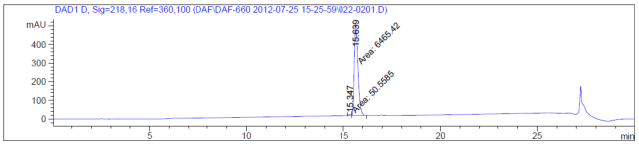



**Figure S6**: HPLC trace @218 nm of **3**; $t_r$ = 15.6 min.

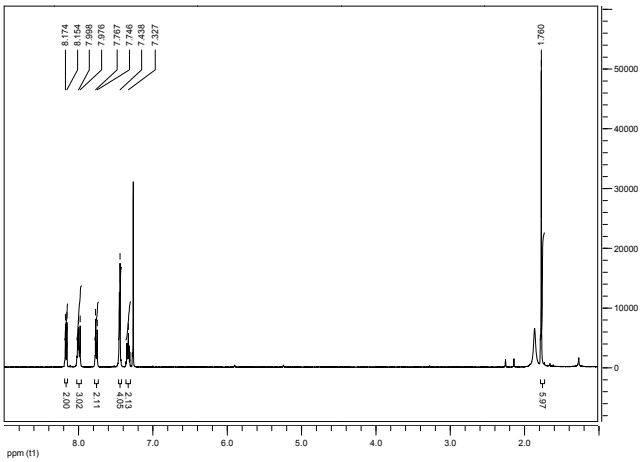



**Figure S7**: $^1$H NMR spectra of **3**.

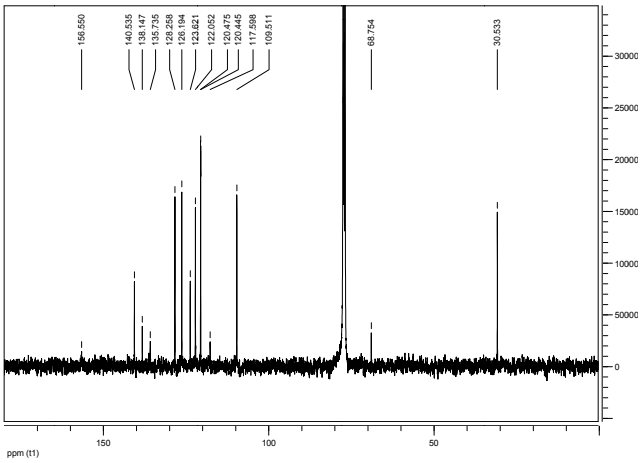



**Figure S8**: $^{13}$C NMR spectra of **3**.

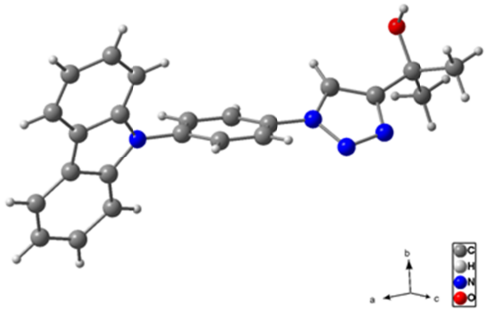



**Figure S9**: Molecular Structure of **3**.

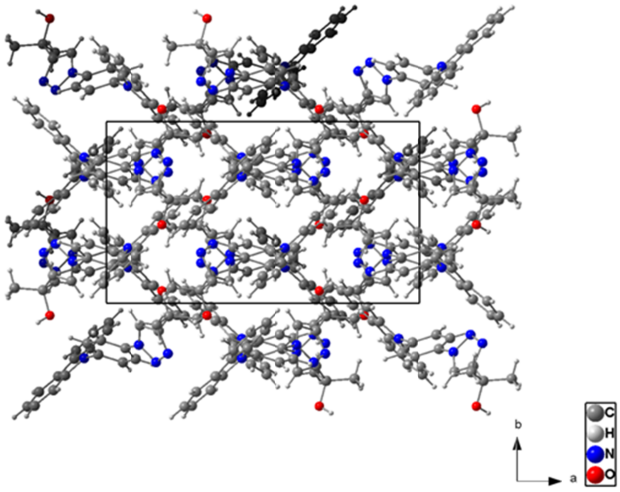
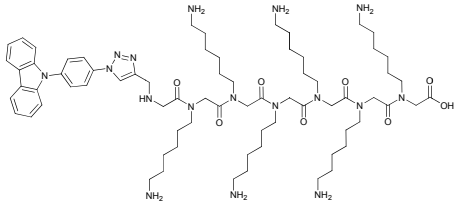



**Figure S10**: Crystal structure of **3**.

*Carbazole Peptoid* **4**: For the synthesis, 77.0 mg (0.100 mmol, 1.00 equiv.) of 2-chlorotrityl chloride resin and swollen in a fritted plastic syringe (Multisyntech) with 1 mL of dichloromethane for 30 min. The first submonomer was added by reacting 75.0 mg of bromoacetic acid (0.540 mmol, 5.40 equiv.) and 97 $\mu$L of DIPEA (70.0 mg, 0.540 mmol, 5.40 equiv.) in 1 mL of dichloromethane on a shaker platform for 40 min at room temperature, followed by washing with dichloromethane (2 mL) and *N*,*N*-dimethylacetamide (DMA, five times with 2 mL). The bromoacetylated resin was incubated with 2 M *tert*-butyl(6-aminohexyl)carbamate solution (0.400 mL, 0.800 mmol, 8.00 equiv.) in DMA on a shaker platform at room temperature, followed by washing with DMA (three times with 2 mL). The displacement reaction times were 30 min for *tert*-butyl(6-aminohexyl)carbamate. The following bromoacetylations were carried out by reacting the resin with 1.2 M bromoacetic acid solution (0.660 mL, 1.03 mmol, 7.92 equiv.) in DMA and 122 µL DIC (100 mg, 0.790 mmol, 7.90 equiv.) for 30 min. Coupling steps were continued until the desired peptoid length was achieved. For the last displacement reaction, the resin was incubated with 2 M propargylamine solution (0.400 mL, 0.800 mmol, 8.00 equiv.) in DMA on a shaker platform at room temperature for 30 min. After that last step, the resin was washed with DMA (four times with 2 mL) and dichloromethane (twice with 1.5 mL). Some beads were taken from the resin for a test cleavage and covered with trifluoroacetic acid (TFA) in an Eppendorf tube. – MS (MALDI-TOF), $C_{53}H_{103}N_{13}O_8$: calcd. 1049.8 g/mol; found 1050.8 $[(M+H)]^+$.



For the reaction with the azidocarbazole **1**, the resin was swollen in dry THF and 23 mg $Cu(CH_3CN)_4PF_6$ (61.0 µmol, 0.610 equiv.) was directly weighed into the plastic syringe containing the resin. In 2 mL dry THF, 34 mg of the azidocarbazole **1** (0.120 mmol, 1.20 equiv.) and 33 µL 2,6-lutidine (30.0 mg, 0.278 mmol, 2.78 equiv.) were dissolved and added to the resin. The resin was shaken for 18 h at room temperature.

After the reaction, the resin was washed with *N*,*N*-dimethylacetamide (DMA) and dichloromethane (DCM) (three times with 2 mL of each).

The peptoid was cleaved from the resin using 2.00 mL 50% trifluoroacetic acid (TFA) in dichloromethane (v/v) at room temperature for 18 h. After collecting the cleavage solution the resin was washed with methanol (five times with 3 mL). The elution and washing solutions were combined. The solvent was evaporated under reduced pressure followed by HPLC purification of the crude product and subsequent lyophilization. After cleavage, HPLC purification and lyophilization, the title compound was obtained as a white solid in 0.4% yield. (0.5 mg, 0.370 µmol, 98% purity) – MS (MALDI-TOF), $C_{71}H_{115}N_{17}O_8$: calcd. 1333.9; found 1334.9 $[(M+H)]^+$.

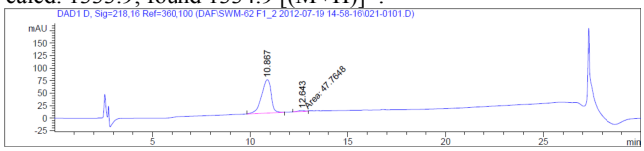
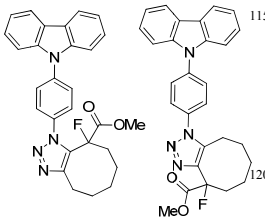



**Figure S11**: HPLC trace @218 nm of **4**; $t_r$ = 10.9 min.

*Methyl 1-(4-(9H-carbazol-9-yl)phenyl)-9-fluoro-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole-9-carboxylate and methyl 1-(4-(9H-carbazol-9-yl)phenyl)-4-fluoro-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole-4-carboxylate* **5:** To a solution of methyl 1-fluorocyclooct-2-ynecarboxylate **5a** (0.126 g, 0.684 mmol, 1.00 equiv.) in 25 mL DCM was added 9-(4-azidophenyl)-9*H*-carbazole **1** (0.194 g, 0.684 mmol, 1.00 equiv.). The solution was stirred over night at room temperature. The solvent was then removed and the crude product was purified by flash column chromatography (silica gel, from 50:1 to 3:1 cyclohexane/ethyl acetate) to afford a white solid in 90% yield (0.222 g, 0.474 mmol). Also 0.043 g of carbazole reactant could be reisolated. Mixture of isomers:




– $R_f$ = 0.36 (3:1 CH/EE). – mp = 92.9 °C. – $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.14 (m, 1.99 H, Ar-H), 7.83–7.76 (m, 1.53 H, Ar-H), 7.75–7.60 (m, 0.98 H, Ar-H), 7.69–7.63 (m, 1.56 H, Ar-H), 7.52 – 7.41 (m, 4.07 H, Ar-H), 7.37–7.30 (m, 2.00 H, Ar-H), 3.93 (s, 2.32 H, $CH_3$ [major isomer]), 3.48 (s, 0.73 H, $CH_3$ [minor isomer]), 3.43–3.31 (m, 0.24 H, $CH_2$), 3.24–3.08 (m, 1.02 H, $CH_2$), 3.07–2.94 (m, 0,79 H, $CH_2$), 2.69–2.47 (m, 2.04 H, $CH_2$), 2.09–1.92 (m, 1.03 H, $CH_2$), 1.92–1.70 (m, 3.81 H, $CH_2$), 1.70–1.53 (m, 2.14 H, $CH_2$) ppm. – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 170.5 ($C_{quart}$, d, $^2J_{C-F}$ = 27.3 Hz, C=O), 169.1 ($C_{quart}$, d, $^2J_{C-F}$ = 28.6 Hz, C=O), 142.8 ($C_{quart}$, $C_{Ar}$), 142.5 ($C_{quart}$, $C_{Ar}$), 140.4 ($C_{quart}$, $C_{Ar}$), 140.3 ($C_{quart}$, $C_{Ar}$), 139.6 ($C_{quart}$, $C_{Ar}$), 139.4 ($C_{quart}$, $C_{Ar}$), 135.4 ($C_{quart}$, d, $^3J_{C-F}$ = 2.7 Hz, $C_{Ar}$), 134.6 ($C_{quart}$, $C_{Ar}$), 134.2 ($C_{quart}$, $C_{Ar}$), 128.8 (+,$C_{Ar}$), 128.8 (+, $C_{Ar}$), 127.9 (+, $C_{Ar}$), 127.3 (+, $C_{Ar}$), 127.2 (+, $C_{Ar}$), 126.3 (+, $C_{Ar}$), 126.2 (+, $C_{Ar}$), 123.7 ($C_{quart}$, $C_{Ar}$), 123.7 ($C_{quart}$, $C_{Ar}$), 120.6 (+, $C_{Ar}$), 120.5 (+, $C_{Ar}$), 120.5 (+, $C_{Ar}$), 120.5 (+, $C_{Ar}$), 109.5 (+, $C_{Ar}$), 109.5 (+, $C_{Ar}$), 92.2 ($C_{quart}$, d, $^1J_{C-F}$ = 187.0 Hz, C-F ), 53.1 (+,

$CH_3$), 52.9 (+, $CH_3$), 34.2 (–, d, $^2J_{C-F}$ = 23.4 Hz, $CH_2$), 33.8 (–, d, $^2J_{C-F}$ = 23.4 Hz, $CH_2$), 26.7 (–, d, $^4J_{C-F}$ = 0,8 Hz, $CH_2$), 25.8 (–, d, $^4J_{C-F}$ = 1,5 Hz, $CH_2$), 25.4 (–, $CH_2$, ), 23.7 (–, $CH_2$), 22.7 (–, d, $^3J_{C-F}$ = 6.6 Hz, $CH_2$), 22.4 (–,$CH_2$), 21.8 (–, d, $^3J_{C-F}$ = 4.1 Hz, $CH_2$), 21.5 (–, $CH_2$) ppm. – $^{19}$F NMR (376 MHz, $CDCl_3$): δ = -146.8 ppm. – IR (ATR): ν = 3058 (w), 2928 (w), 2857 (w), 1759 (m), 1600 (w), 1518 (s), 1479 (w), 1450 (s) $cm^{-1}$. – MS (70 eV, EI), *m/z* (%): 468 $[M]^+$ (77), 440 $[M-N_2]^+$ (57), 381 $[C_{26}H_{22}FN_2]^+$ (100), 242 $[C_{18}H_{12}N]^+$ (34). – HR-EIMS ($C_{28}H_{25}FN_4O_2$) calcd. 468.1962; found 468.1962.

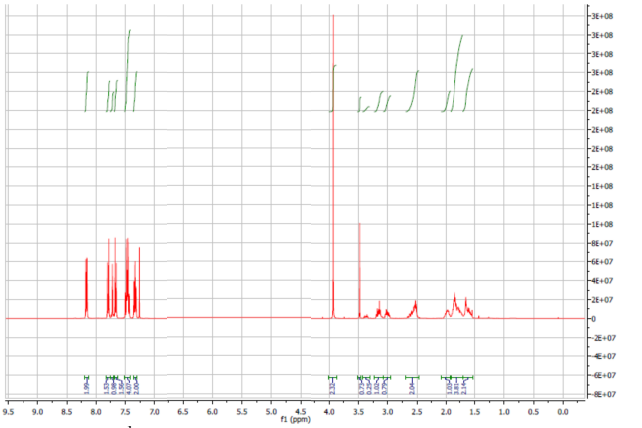


**Figure S12**: $^1$H NMR Spectra of **5**.

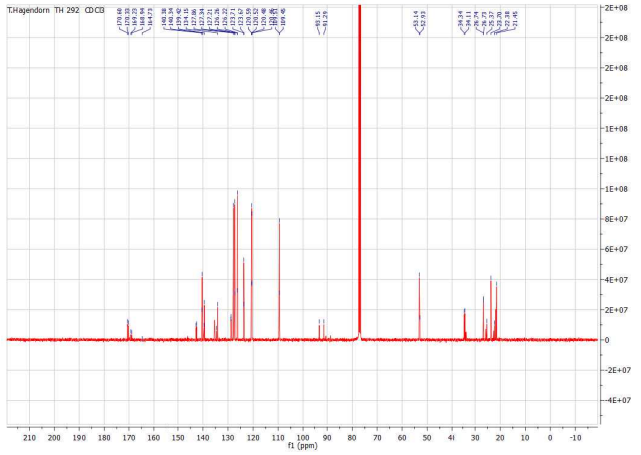
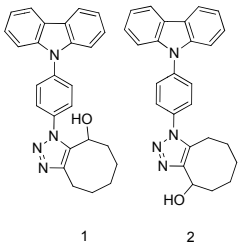


**Figure S13**: $^{13}$C NMR spectra of **5**.

*1-(4-(9H-carbazol-9-yl)phenyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazol-9-ol* **6** *and 1-(4-(9H-carbazol-9-yl)phenyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazol-4-ol* **6**:

To a solution of cyclooct-2-ynol **6a** (0.090 g, 0.725 mmol, 3.00 equiv.) in DCM (6 mL) was added 9-(4-azidophenyl)-9*H*-carbazole **1** (0.068 g, 0.239 mmol, 1.00 equiv.). The solution was stirred for 48 hours at room temperature. The solvent was then removed and the crude product was purified by flash column chromatography (silica gel, 3:1 cyclohexane/ethyl acetate) to afford isomer 1 in 35 % yield (0.029 g, 0.071mmol) and isomer 2 in 63 % yield (0.052 g, 0.127 mmol) both as light yellow solids (0.010 mg of carbazole reactant could be reisolated).



1 2

Isomer 2 was completely purified and characterized: – $R_f$ = 0.29 (3:1 CH/EE). – mp = 195.3 °C. – $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.14 (m, 2 H, Ar-H), 7.80–7.75 (m, 2 H, Ar-H), 7.70–7.65 (m, 2 H, Ar-H), 7.51–7.42 (m, 4 H, Ar-H), 7.37–7.29 (m, 2 H, Ar-H), 5.23 (dd, 1 H, $^3J_{H-H}$ = 9.2 Hz, 4.2 Hz, CH-O), 3.33 (bs, 1 H, OH), 3.14–3.03 (m, 1 H, $CH_2$), 2.94–2.84 (m, 1 H, $CH_2$), 2.26–2.15 (m, 1 H, $CH_2$), 2.14–2.04 (m, 1 H, $CH_2$), 1.83 (q, 2 H, $^3J_{H-H}$ = 6.3 Hz, $CH_2$), 1.72 (q, 2 H, $^3J_{H-H}$ = 6.0 Hz, $CH_2$), 1.67–1.59 (m, 1 H, $CH_2$), 1.56–1.43 (m, 1H, $CH_2$) ppm. – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 147.5 ($C_{quart}$), 140.4 ($C_{quart}$), 139.1 ($C_{quart}$), 134.7 ($C_{quart}$), 133.0 ($C_{quart}$), 127.8 (+, CH), 127.0 (+, CH), 126.2 (+, CH), 123.7 ($C_{quart}$), 120.5 (+, CH), 120.5 (+, CH), 109.5 (+, CH), 66.9 (+, CH), 35.9 (–, $CH_2$), 27.2 (–, $CH_2$), 25.0 (–, $CH_2$), 22.3 (–, $CH_2$), 21.4 (–, $CH_2$) ppm. – IR (ATR): ν = 3246 (w), 3067 (w), 2935 (w), 2851 (w), 1599 (w), 1514 (m), 1480 (w), 1450 (m) $cm^{-1}$. – MS (70 eV, EI), *m/z* (%): 408 $[M]^+$ (23), 380 $[(M-N_2)]^+$ (20), 43 (100). – HR-EIMS ($C_{26}H_{24}N_4O$): calcd. 408.1950; found 408.1952.

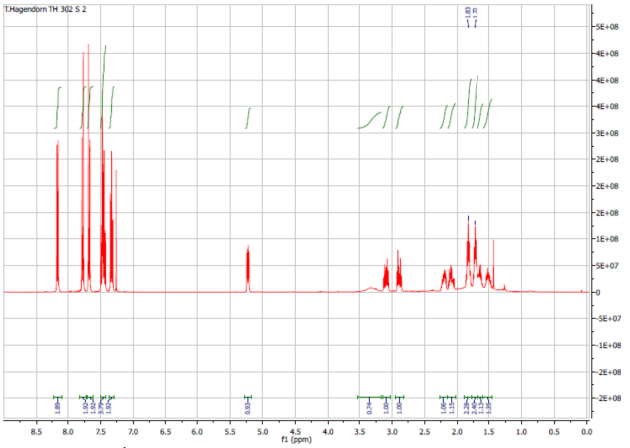


**Figure S16**: $^1$H NMR of **6** (Isomer 2).

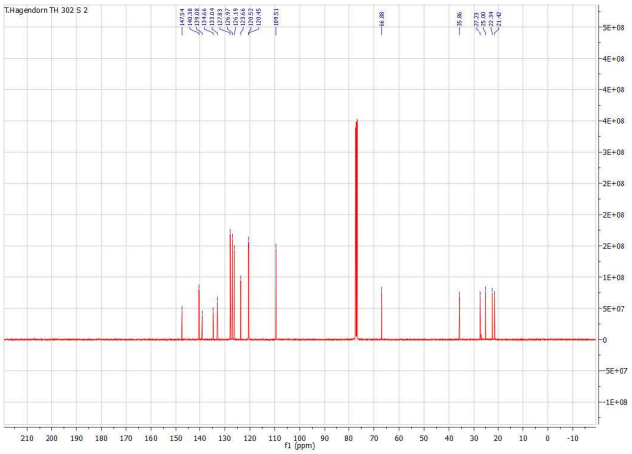


**Figure S18**: $^{13}$C NMR spectra of **6** (Isomer 2).

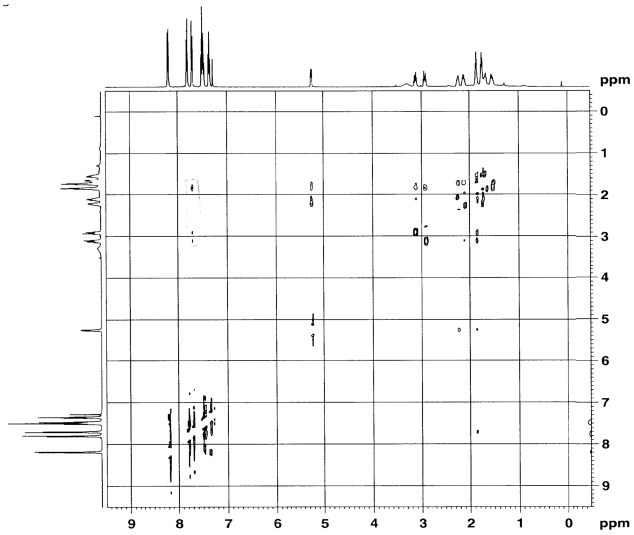
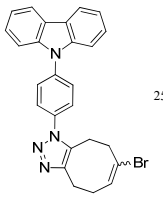


**Figure S17**: NOESY of **6** (Isomer 2).

*(E)-9-(4-(6-bromo-4,5,8,9-tetrahydro-1H-cyclooct[d][1,2,3]triazol-1-yl)phenyl)-9H-carbazole or (E)-9-(4-(7-bromo-4,5,8,9-tetrahydro-1H-cyclooct[d][1,2,3]triazol-1-yl)phenyl)-9H-carbazole* **7**: A solution of dibromocycloocta-1,5-diene (mixture of isomers) **7a** (280 mg, 1.05 mmol, 1.00 equiv.) in cyclohexane (15 mL) was added dropwise to a suspension of KOtBu (470 mg, 4.20 mmol, 4.00 equiv.) and 18-crown-6 (70 mg, 0.266 mmol, 0.26 equiv.) in cyclohexane (60 mL) under an argon atmosphere with continuous stirring. Stirring was continued for 110 min (until the starting materials had been consumed), and then the reaction was quenched by adding a saturated aqueous solution of $NH_4Cl$ (15 mL) and water (15 mL). The two phases were separated and the aqueous phase was extracted with ethyl acetate (3x15 mL).[24] The azide **1** (100 mg, 0.35 mmol, 0.33 equiv.) was added to the combined organic phases and the resulting solution was stirred overnight. The solvent was then removed on a rotary evaporator and the crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 4:1) to afford two isomers (0.080 g, 0.170 mmol (49%) and 0.076 g, 0.162 mmol (46%)) as light yellow solids.



Characterization for the isomer isolated first: – $R_f$ = 0.18 (4:1 CH/EE). – mp = 181 °C. – $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, 2 H, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar-H), 7.79–7.75 (m, 2 H, Ar-H), 7.72–7.67 (m, 2 H, Ar-H), 7.49–7.42 (m, 4 H, Ar-H), 7.36–7.31 (m, 2 H, Ar-H), 6.12 (dd, 1 H, $^3J_{H\text{-}H}$ = 8.4 Hz, CH=CBr), 3.36–3.28 (m, 2 H, $CH_2$), 3.12–3.04 (m, 2 H, $CH_2$), 3.02–2.93 (m, 2 H, $CH_2$), 2.74–2.63 (m, 2 H, $CH_2$) ppm. – $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 143.9 ($C_{quart}$, $C_{Ar}$), 140.4 ($C_{quart}$, $C_{Ar}$), 139.0 ($C_{quart}$, $C_{Ar}$), 135.1 ($C_{quart}$, $C_{Ar}$), 132.9 ($C_{quart}$, $C_{Ar}$), 128.8 (+, CH), 127.8 (+, CH), 126.9 (+, CH) 126.9 ($C_{quart}$, CBr), 126.2 (+, CH), 123.7 ($C_{quart}$, $C_{Ar}$), 120.5 (+, CH), 120.5 (+, CH), 109.6 (+, CH), 39.4 (–, $CH_2$), 25.4 (–, $CH_2$), 25.1 (–, $CH_2$), 24.1 (–, $CH_2$) ppm. – IR (ATR): ν = 3055 (w), 2917 (w), 2848 (w), 1720 (w), 1599 (w), 1517 (s), 1478 (w), 1449 (s) $cm^{-1}$. – MS (70 eV, EI), *m/z* (%): 468/470 $[M]^+$ (11/11), 361 $[(M\text{-}Br\text{-}N_2)]^+$ (36), 241 (100), 166 $[(C_{12}H_8N)]^+$ (80). – HR-EIMS ($C_{26}H_{28}BrN_4$): calcd. 470.0929; found 470.0928.

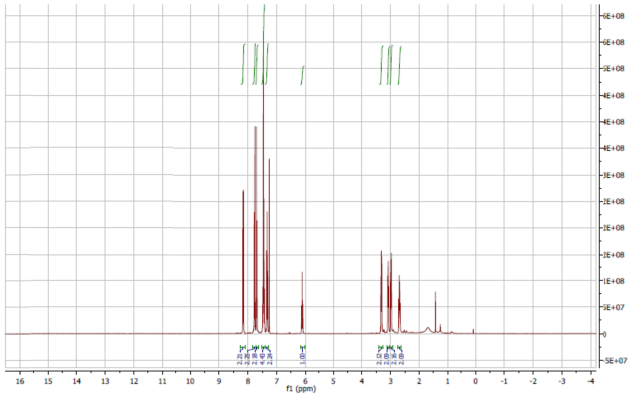


**Figure S19**: $^1$H NMR of **7**.

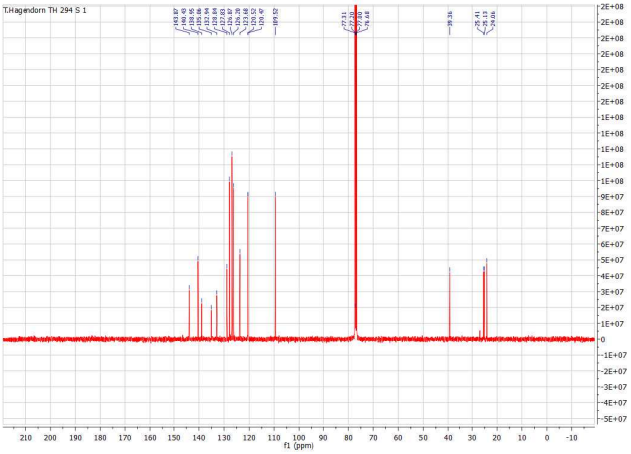
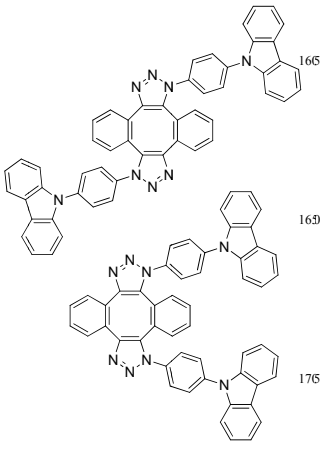


**Figure S20**: $^{13}$C NMR spectra of **7**.

*1,8-bis(4-(9H-carbazol-9-yl)phenyl)-1,8-dihydrodibenzo[3,4:7,8]cycloocta[1,2-d:5,6-d']bis([1,2,3]triazole) and 1,10-bis(4-(9H-carbazol-9-yl)phenyl)-1,10-dihydrodibenzo[3,4:7,8]cycloocta[1,2-d:5,6-d']bis([1,2,3]triazole)* **8**: To a solution of diyne **8a** (0.033g, 0.165 mmol, 1.00 equiv.) in DCM (5 mL) carbazole **1** (100 mg, 0.352 mmol, 2.13 equiv.) was added and stirred over night at room temperature. The solvent was removed and the crude product was purified by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate) affording a white solid of 74% yield (0.098 g, 0.127 mmol).



– $R_f$ = 0.20 (10:1 CH/EE). – mp > 250 °C (decomposition) – $^1$H NMR (400 MHz, DMSO-d6): δ = 8.28 (d, 2 H, $^3J_{H\text{-}H}$ = 7.7 Hz,

24. B. R. Varga, M. Kallay, K. Hegyi, S. Beni, and P. Kele, *Chem. Eur. J.*, 2012, **18** , 822–828.

Ar-H), 8.20 (d, 2 H, $^{3}J_{H\text{-}H}$ = 7.7 Hz, Ar-H), 7.91–7.86 (m, 4 H, Ar-H), 7.86–7.80 (m, 3 H, Ar-H), 7.80–7.75 (m, 1 H, Ar-H), 7.71–7.63 (m, 2 H, Ar-H), 7.59 (d, 2 H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, Ar-H), 7.52–7.44 (m, 3 H, Ar-H), 7.43–7.38 (m, 3 H, Ar-H), 7.37–7.30 (m, 6 H, Ar-H), 7.28–7.20 (m, 4 H, Ar-H) ppm. – $^{13}$C NMR (100 MHz, DMSO-d*6*), δ = 145.1 ($C_{quart}$, $C_{Ar}$), 145.1 ($C_{quart}$, $C_{Ar}$), 139.7 ($C_{quart}$, $C_{Ar}$), 139.6 ($C_{quart}$, $C_{Ar}$), 137.7 ($C_{quart}$, $C_{Ar}$), 137.5 ($C_{quart}$, $C_{Ar}$), 134.6 ($C_{quart,}$ $C_{Ar}$), 134.2 ($C_{quart}$, $C_{Ar}$), 134.1 ($C_{quart}$, $C_{Ar}$), 131.7 (+, $C_{Ar}$), 131.3 ($C_{quart}$, $C_{Ar}$), 131.2 (+, $C_{Ar}$), 131.0 (+, $C_{Ar}$), 130.7 (+, $C_{Ar}$), 130.5 (+, $C_{Ar}$), 130.2 ($C_{quart}$, $C_{Ar}$), 130.0 (+, $C_{Ar}$), 129.4 (+, $C_{Ar}$), 129.3 ($C_{quart}$, $C_{Ar}$), 129.3 (+, $C_{Ar}$), 127.8 (+, $C_{Ar}$), 127.8 (+, $C_{Ar}$), 127.6 (+, $C_{Ar}$), 127.4 ($C_{quart}$, $C_{Ar}$), 126.8 (+, $C_{Ar}$), 126.4 (+, $C_{Ar}$), 126.3 (+, $C_{Ar}$), 126.1 ($C_{quart}$, $C_{Ar}$), 122.9 ($C_{quart}$, $C_{Ar}$), 122.8 ($C_{quart}$, $C_{Ar}$), 120.6 (+, $C_{Ar}$), 120.5 (+, $C_{Ar}$), 120.4 (+, $C_{Ar}$), 120.3 (+, $C_{Ar}$), 109.5 (+, $C_{Ar}$), 109.5 (+, $C_{Ar}$) ppm. – IR (ATR): ν = 3054 (w), 2922 (w), 2848 (w), 1598 (w), 1517 (m), 1478 (w), 1449 (m), 1352 (w), 1334 (w), 1314 (w), 1227 (m) $cm^{-1}$. – MS (EI, 3-NBA), *m/z*: 769 $[M+H]^+$. – HR-FABMS: calcd. $[M+H]^+$ $C_{52}H_{33}N_8$: 769.2828; found 769.2830.

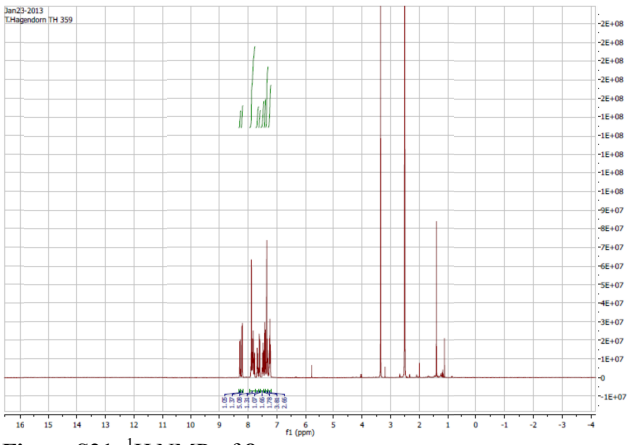



**Figure S21**: $^{1}$H NMR of **8**.

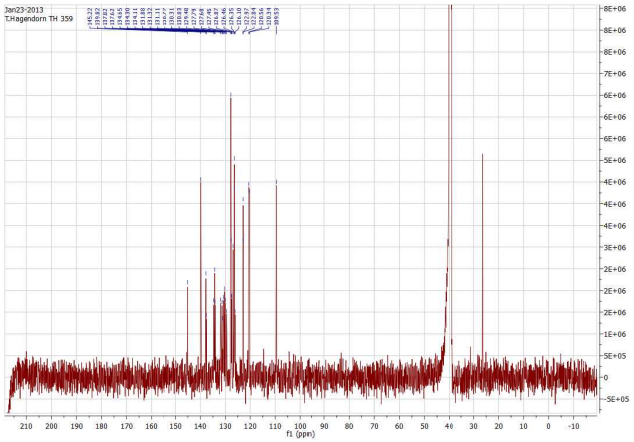



**Figure S22**: $^{13}$C NMR spectra of **8**.

## Spectroscopic data

**Table S1**: Absorption and Extinction coefficients, **1-7** in DCM, **8** DMSO.

| Compound | Absorption [nm] (extinction [$M^{-1}$ $cm^{-1}$]) |
|---|---|
| **1** | 241 (42000 ± 1500), 286 (18200 ± 600), 293 (21300 ± 600), 302 (sh) (11300 ± 400), 325 (4900 ± 150), 340 (3900 ± 150) |
| **2** | 235 (34000 ± 1500), 239 (sh) (33000 ± 1500), 285 (sh) (12000 ± 500), 292 (15700± 500), 307 (10400 ± 500), 323 (sh) (7900 ± 400), 338 (sh) (4900 ± 200) |
| **3** | 236 (61000 ± 5000), 240 (sh) (60000 ± 5000), 254 (sh) (41000 ± 4000), 284 (sh) (19000 ± 2000), 292 (24000 ± 2000), 312 (19000 ± 2000), 324 (sh) (16000 ± 1500), 336 (sh) (10000 ± 1000) |
| **4** | 232 (9900 ± 500), 283 (sh) (3200 ± 200), 291(4000 ± 200), 309 (sh) (2600 ± 200), 323 (sh) (2300 ± 200), 337 (sh) (1600 ± 100) |
| **5** | 229 (5700 ± 150), 239 (sh) (4500 ± 100), 254 (sh) (2250 ± 50), 286 (sh) (1600 ± 40), 293 (1950 ± 50), 302 (sh) (1250 ± 30), 321 (sh) (730 ± 20), 338 (sh) (560 ± 20) |
| **6** | 240 (39000 ± 2000), 287 (sh) (13000 ± 700), 293 (19600 ± 900), 300 (sh) (12400 ± 600), 322 (sh) (6400 ± 300), 338 (sh) (5300 ± 300) |
| **7** | 229 (34300 ± 800),239 (sh) (27500 ± 600), 286 (sh) (10100 ± 200), 293 (12400 ± 300), 300 (sh) (7900 ± 200), 323 (sh) (3800 ± 100), 338 (sh) (3200 ± 100) |
| **8** | 288 (sh) (24000 ± 2500), 293 (28000 ± 3000), 308 (sh) (16000 ± 2000), 322 (sh) (13000 ± 1500), 338 (sh) (9200 ± 1000) |

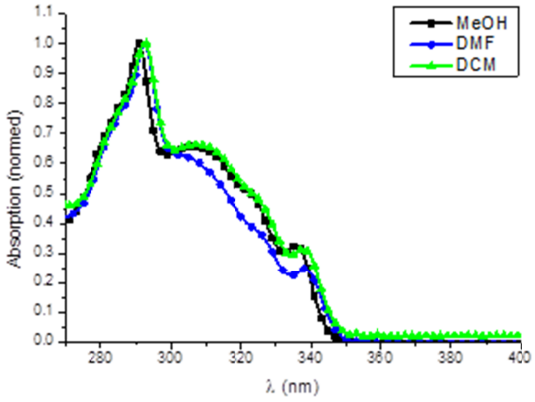



**Figure S23**: Absorption spectra of **2** in different solvents.

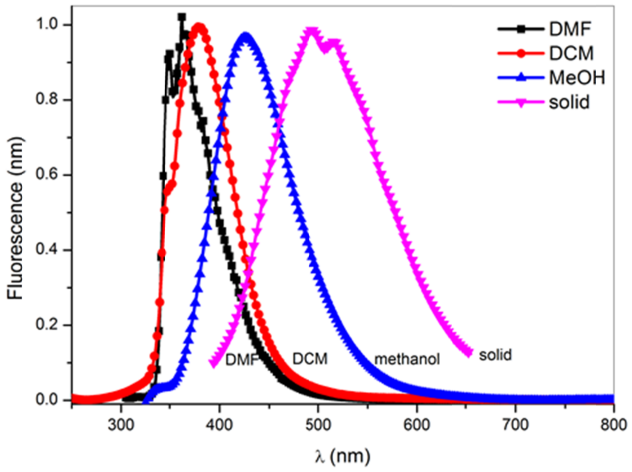



**Figure S24**: Fluorescence spectra of **2**, in different solvents. Excitation wavelength $\lambda_{ex}$ = 290 nm.

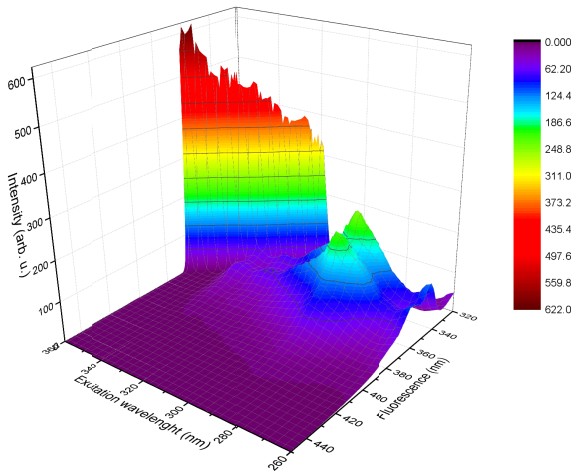



**Figure S25**: 3D fluorescence spectra of compound **7** in ethyl acetate, $\lambda_{ex}$ = 260-360 nm, excitation steps in 1 nm difference, $\lambda_{em}$ = 320-450 nm. The strait line is the detected excitation light, visible in the back part of the figure. Maximum intensity of the emission of compound 7 occurs by an excitation of 491 nm.

**Table S2:** Calculation and assignment of Stokes shifts of compound **7**.

| Solvent | Absorption maximum [nm] | Fluorescence maximum 1 [nm] | Fluorescence maximum 2 [nm] | Stokes Shift 1 [nm] | Stokes Shift 2 [nm] |
|---|---|---|---|---|---|
| CH | 292 | 341 | 357 | 49 | 65 |
| EE | 291 | 342 | 357 | 51 | 66 |
| DCM | 293 | 345 | 360 | 52 | 67 |
| EA | 291 | 344 | 360 | 53 | 69 |
| DMF | 291 | 345 | 362 | 54 | 71 |
| MeOH | 291 | 431 | | 140 | |

CH = cyclohexane, EE = diethyl ether, DCM = dichloromethane, EA = ethyl acetate, DMF = dimethylformamide, MeOH = methanol
Excitation wavelength $\lambda_{ex}$ = 290 nm
Stokes shift 1 = fluorescence maximum 1 – absorption maximum
Stokes shift 2 = fluorescence maximum 2 – absorption maximum

**Table S3:** Lippert-Mataga Plot of compound **7** in wavenumbers. Calculation of the Stokes shifts see Table S2.

| Solvent | Orientation polarizability (Δf) | Stokes shifts [nm] | Stokes shift 1 [$10^4$ $cm^{-1}$] | Stokes shift 2 [$10^4$ $cm^{-1}$] | Mean [$10^4$ $cm^{-1}$] |
|---|---|---|---|---|---|
| Cyclohexane | 0 | 49/65 | 0.49 | 0.65 | 0.57 |
| Diethyl ether | 0.17 | 51/66 | 0.51 | 0.66 | 0.585 |
| Ethyl acetate | 0.201 | 53/69 | 0.53 | 0.69 | 0.61 |
| Dichloromethane | 0.217 | 52/67 | 0.52 | 0.67 | 0.595 |
| Dimethylformamide | 0.274 | 54/71 | 0.54 | 0.71 | 0.625 |
| Methanol | | 140 | 1.40 | | 1.40 |

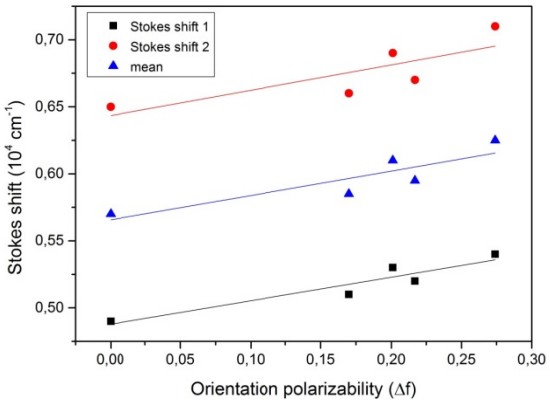



**Figure S26**: Lippert-Mataga Plot of compound **7**. Calculation and used wavenumbers in Table S2 and S3.

**Table S4:** Data of the linear regression line values to Figure 26.

| | | Value | Standard deviation |
|---|---|---|---|
| Stokes shift 1 | Point of intersection with y-axes | 0.488 | 0.007 |
| | Slope of the line | 0.175 | 0.0356 |
| Stokes shift 2 | Point of intersection with y-axes | 0.643 | 0.0153 |
| | Slope of the line | 0.189 | 0.0782 |
| mean | Point of intersection with y-axes | 0.566 | 0.0110 |
| | Slope of the line | 0.182 | 0.0563 |

**Table S5:** Absorption maxima of **7** in solvent mixtures of methanol and DCM.

| | Peaks [nm] ± 0.5 nm | | | Shoulders [nm] ± 2 nm | | | |
|---|---|---|---|---|---|---|---|
| 50% MeOH, 50% DCM | 228 | 292 | 336 | 237 | 287 | 300 | 320 |
| 75 % MeOH, 25% DCM | 237 | 291 | 336 | | 286 | 300 | 320 |
| 25%MeOH, 75% DCM | 234 | 292 | 336 | 238 | 286 | 300 | 320 |

**Table S6:** Emission maxima of **7** in solvent mixtures of methanol and DCM. Excitation with $\lambda_{ex}$ = 290 – 310 nm gave the same maxima.

| | Peaks [nm] ± 1 nm | | | Shoulders [nm] ± 2 nm | |
|---|---|---|---|---|---|
| DCM | 345 | 360 | | 373 | |
| 25%MeOH, 75% DCM | 345 | 360 | | 373 | 393 |
| 50% MeOH, 50% DCM | 345 | 360 | 383 | | |
| 75 % MeOH, 25% DCM | 343 | 360 | 402 | | |
| MeOH | | | 431 | | |

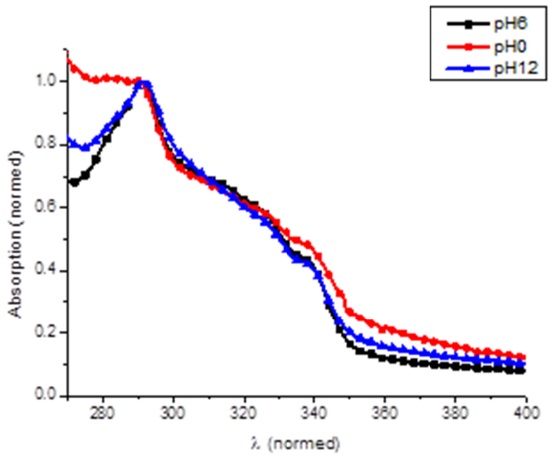



**Figure S27**: Absorption spectra of **4**, different pH.

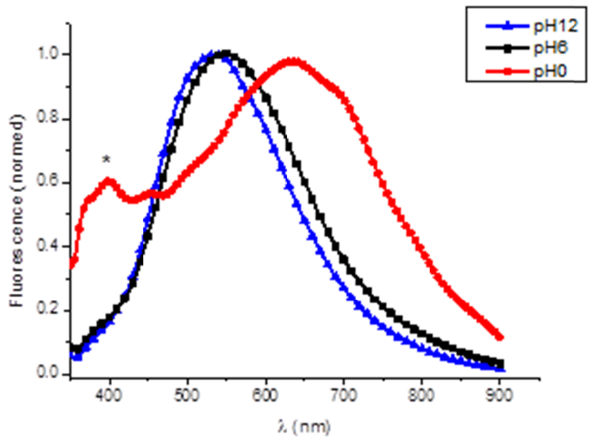



**Figure S28**: Fluorescence spectra of **4**, different pH, normed. *Artefact. Excitation wavelength $\lambda_{ex}$ = 290 nm.

**Crystal structure data**

**Component 2:** Colourless crystals, $C_{23}H_{20}N_4$, $M$ = 368.43, crystal size 0.20 x 0.16 x 0.02 mm, orthorhombic, space group Pbca (No.61): $a$ =16.967(1) Å, $b$ = 9.805(1) Å, $c$ = 22.225(2) Å, $V$ = 3697.5(5) Å$^3$, $Z$ = 8, $\rho$(calcd) = 1.324 Mg m$^{-3}$, $F$(000) = 1552, $\mu$ = 0.084 mm$^{-1}$, 37494 reflections ($2\theta_{max}$ = 50°), 3258 unique [$R_{int}$ = 0.010], 256 parameters, 1 restraint, R1 (for 2317 $I > 2\sigma(I)$) = 0.054, wR2 (*all data*) = 0.122, GooF = 1.06, largest diff. peak and hole 0.247 and –0.213 e Å$^{-3}$.

**Component 3:** pale yellow crystals, $C_{26}H_{18}N_4$, $M$ = 386.44, crystal size 0.32 x 0.28 x 0.08 mm, monoclinic, space group $P2_1/c$ (No.14): $a$ = 9.171(1) Å, $b$ = 12.808(1) Å, $c$ = 16.593(2) Å, )°, $\beta$ = 98.81(1)º, $V$ = 1926.1(3) Å$^3$, $Z$ = 4, $\rho$(calcd) = 1.333 Mg m$^{-3}$, $F$(000) = 808, $\mu$ = 0.081 mm$^{-1}$, 14210 reflections ($2\theta_{max}$ = 55°), 4391 unique [$R_{int}$ = 0.040], 282 parameters, R1 (for 3079 $I > 2\sigma(I)$) = 0.050, wR2 (*all data*) = 0.113, GooF = 1.05, largest diff. peak and hole 0.268 and –0.274 e Å$^{-3}$.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-936576 (component **3**) and CCDC-936577 (component **2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

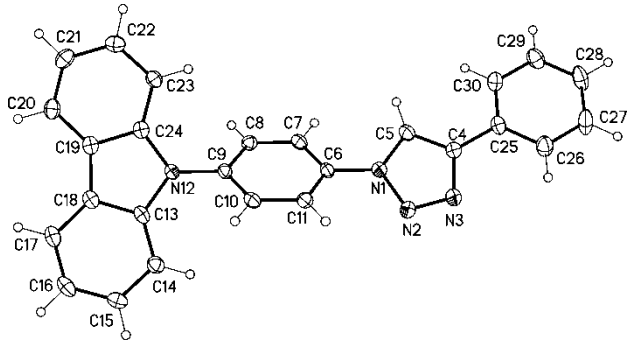



**Figure S29**: Molecular structure of **2** (displacement parameters are drawn at 50% of probability level).

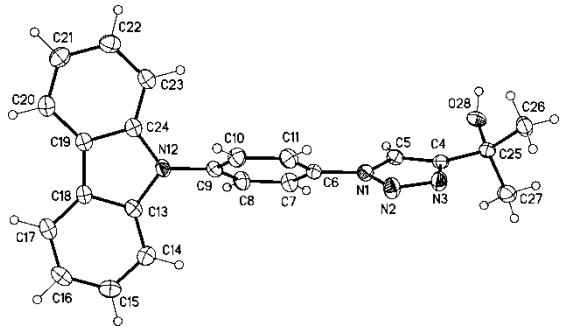



**Figure S30**: Molecular structure of **3** (displacement parameters are drawn at 50% of probability level).

**Computational methods**

**Table S6:** Comparison between calculated and measured bond length and angles for **2**.

| | | | | **Bond Distances measured (X-ray)** | **Bond Distances calculated (B3-LYP/def2-TZVP-D3)** |
|---|---|---|---|---|---|
| | | | | pm | pm |
| 1 | N | 2 | N | 135.26 | 135.3 |
| 1 | N | 5 | C | 135.49 | 136.06 |
| 1 | N | 6 | C | 142.49 | 141.51 |
| 2 | N | 3 | N | 131.43 | 129.56 |
| 3 | N | 4 | C | 136.5 | 136.41 |
| 4 | C | 5 | C | 136.57 | 137.05 |
| 4 | C | 25 | C | 150.88 | 150.74 |
| 6 | C | 7 | C | 138.45 | 139.17 |
| 6 | C | 11 | C | 138.34 | 139.27 |
| 7 | C | 8 | C | 137.65 | 138.63 |
| 8 | C | 9 | C | 138.08 | 139.3 |
| 9 | C | 10 | C | 139.04 | 139.44 |
| 9 | C | 12 | N | 143.14 | 141.09 |
| 10 | C | 11 | C | 138.27 | 138.48 |
| 12 | N | 13 | C | 139.67 | 139.61 |
| 12 | N | 24 | C | 138.99 | 139.61 |
| 13 | C | 14 | C | 138.87 | 139.11 |
| 13 | C | 18 | C | 140.76 | 141.46 |
| 14 | C | 15 | C | 138.29 | 138.85 |
| 15 | C | 16 | C | 138.38 | 139.99 |
| 16 | C | 17 | C | 138.22 | 138.69 |
| 17 | C | 18 | C | 138.93 | 139.36 |
| 18 | C | 19 | C | 145.95 | 144.55 |
| 19 | C | 20 | C | 139.86 | 139.36 |
| 19 | C | 24 | C | 140.65 | 141.46 |
| 20 | C | 21 | C | 137.8 | 138.69 |
| 21 | C | 22 | C | 139.93 | 139.99 |
| 22 | C | 23 | C | 138.03 | 138.85 |
| 23 | C | 24 | C | 138.54 | 139.11 |
| 25 | C | 26 | C | 152.56 | 152.82 |
| 25 | C | 27 | C | 151.25 | 152.74 |
| 25 | C | 28 | O | 143.48 | 143.64 |

| | **Selected bond angles measured (X-ray)** | **Selected bond angles calculated (B3-LYP/def2-TZVP-D3)** |
|---|---|---|
| C13-N12-C9 | 125.39° | 125.68° |
| C7-C6-N1 | 120.49° | 120.35° |
| N3-C4-C25 | 121.72° | 122.95° |

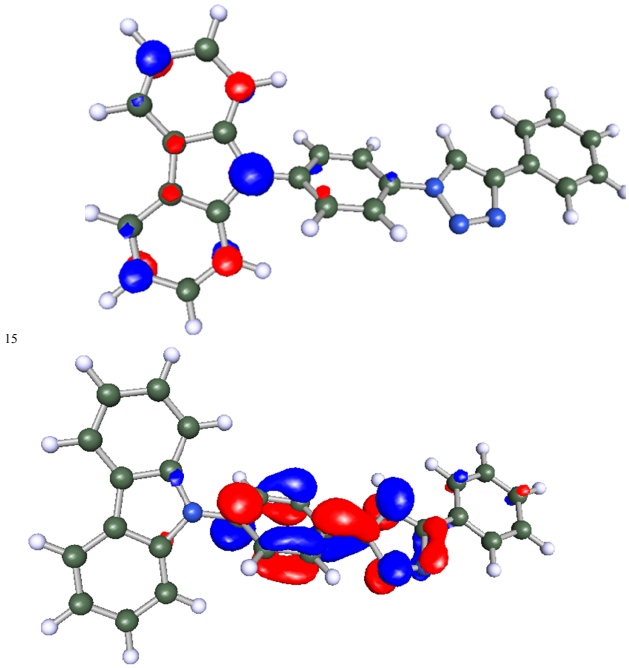


**Figure S30**: HOMO (upper structure) and LUMO (lower structure) frontier orbital plots of compound **2** based on DFT calculations.