Supporting Information

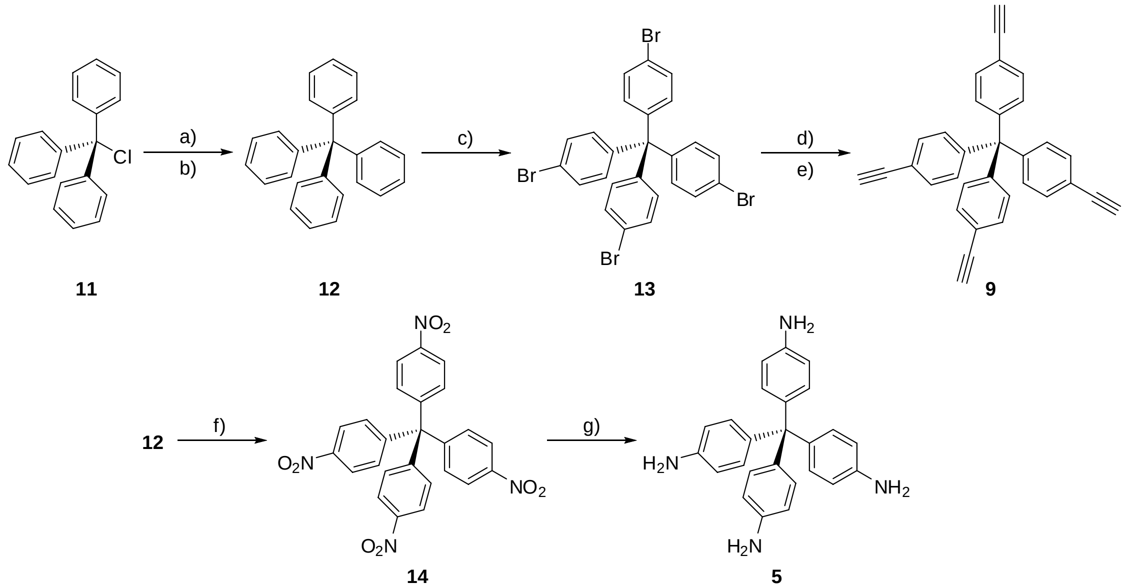
Four-fold click reactions: Generation of tetrahedral methane- and adamantane-based building blocks for higher molecular assemblies

Oliver Plietzsch,[a] Christine Inge Schilling,[a] Mariyan Tolev,[a,b] Martin Nieger,[c] Clemens Richert,[a,b] Thierry Muller,*[a] and Stefan Bräse*[a]

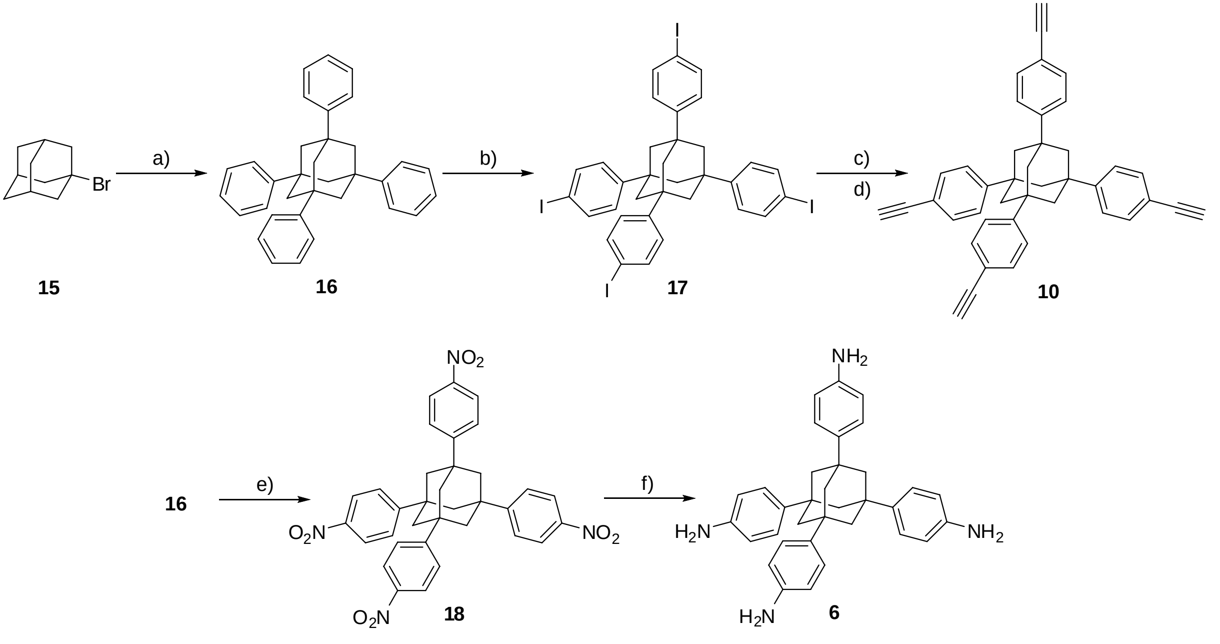
[a]Institut für Organische Chemie and Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany. Fax: +49 (0)721 608 8581; Tel: +49 (0)721-608-2902; E-mail: Stefan.Braese@kit.edu. [b]Institut für Organische Chemie, Universität Stuttgart, 70569 Stuttgart, Germany. [c]Laboratory of Inorganic Chemistry, University of Helsinki, 00014 Helsinki, Finland.

Contents

Reaction schemes



Scheme S1: Synthesis of compounds **5** and **9**. Reagents and conditions: (a) Aniline, 190 °C then (b) H_2SO_4, isoamyl nitrite, H_3PO_2, **93%**; (c) Br_2, **90%**; (d) ethynyltrimethylsilane, NEt_3, $PdCl_2(PPh_3)_2$, CuBr, benzene, 80 °C then (e) TBAF, benzene/MeCN, r.t., **77%** (over two steps); (f) HNO_3, AcOH, Ac_2O, –10 °C, **72%**; (g) H_2, Pd/C, MeOH, r.t., **quant.**



Scheme S2: Synthesis of compound **10**. Reagents and conditions: (a) $AlCl_3$, *t*-BuBr, benzene, reflux, **66%**; (b) I_2, [bis(trifluoroacetoxy)iodo]benzene, r.t., $CHCl_3$, **46%**; (c) ethynyltrimethylsilane, NEt_3, $PdCl_2(PPh_3)_2$, CuI, THF, 90 °C then (d) KF, MeOH, 50 °C, **74%** (over two steps); (e) HNO_3, AcOH, Ac_2O, –5 °C, 35%; (g) H_2, Pd/C, THF, r.t., quant.

Instrumentation

^{1}H NMR spectra were recorded on a *Bruker* AVANCE 400 (400 MHz) or AVANCE DRX 500 (500 MHz) spectrometer as solutions in $CDCl_3$, DMSO-d_6 or MeOH-d_4. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm), DMSO (2.50 ppm) or MeOH (3.31 ppm) as internal standard. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, m = multiplet, dd = doublet of doublets. The spectra were analysed according to first order. The signal abbreviations include: Ar-H = aromatic proton. – ^{13}C NMR spectra were recorded on a *Bruker* AVANCE 400 (100 MHz) or AVANCE DRX 500 (125 MHz) spectrometer as solutions in $CDCl_3$ or DMSO-d_6. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (77.4 ppm), DMSO (39.5 ppm) or MeOH (49.1 ppm) as internal standard. The signal structure was analysed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal) and q = quaternary C-atom (no signal). – MS (EI) (electron impact mass spectrometry): *Finnigan* MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation [M^+] refers to the molecular ion. – MALDI-TOF mass spectra were acquired on a *Bruker* REFLEX IV spectrometer featuring a nitrogen laser (λ = 337 nm) and software XACQ 4.0.4 and XTOF 5.1.0. Fully protected DNA hybrids were measured in linear, positive mode. Deprotected DNA hybrids were measured in linear, negative mode. MALDI matrix mixtures for DNA hybrids was 2,4,6-trihydroxyacetophenone (0.3 M in EtOH) and diammonium citrate (0.1 M in H_2O) at a ratio of 2/1 (v/v). Calculated masses are average masses, *m/z* found are those for the unresolved pseudomolecular ion peaks ($[M+H]^+$ or $[M-H]^-$). The accuracy of mass determination with the external calibration used is approximately ± 0.1. – UV-VIS spectra were recorded on a Lambda 25 spectrometer from Perkin Elmer, using the software Lambda. The detection occurs at 259.8 nm, using Quartz cuvettes with thickness of 1 cm. – IR (infrared spectroscopy): FT-IR *Bruker* IFS 88. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong 0–10% T, s = strong 10–40% T, m = medium 40–70% T, w = weak 70–90% T, vw = very weak 90–100% T, br = broad. – Routine monitoring of reactions was performed using silica gel coated aluminium plates (Merck, silica gel 60, F254), which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdato phosphate (5% phosphormolybdic acid in ethanol, dipping solution) or ninhydrine solution (3 g of ninhydrine in 100 mL of ethanol) and heated with a heat gun. Solvent mixtures are understood as volume/volume. DNA hybrids were purified on Nucleosil 120-5 reversed phase C4 HPLC column (250 x 4.6; Macherey-Nagel, Düren, Germany) at a flow rate of 1 mL·min^{-1} and detection at 260 nm. Solvents, reagents and chemicals were purchased from Aldrich, Fluka and Acros. Standard nucleosides 3'-phosphoramidites were obtained from Proligo (Hamburg, Germany). Tetrazole solution (0.45 M in acetonitrile, for DNA synthesis) and *t*-butyl hydroperoxide solution (5.5 M in decane over molecular sieve 4 Å) were from Sigma/Aldrich (Deisenhofen, Germany). Tetrahydrofuran was distilled from sodium/benzophenone under argon prior use. Dichloromethane, ethyl acetate and diethyl ether were distilled from calcium hydride. Solid materials were powdered. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried and/or flame dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

Experimental Procedures

Tetraphenylmethane (12).[1] In a round bottomed flask chlorotriphenylmethane (25.0 g, 89.7 mmol, 1.0 equiv.) and aniline (22.0 mL, 22.5 g, 231.9 mmol, 2.6 equiv.) were heated at 190 °C under vigorous stirring. After 15 min, the reaction mixture was allowed to cool to room temperature. Then, a solution of aqueous HCl (2M, 100 mL) and methanol (150 mL) were added to the pulverized solid and the reaction mixture was heated for 30 min at 80 °C. After cooling to room temperature, the resulting solid was filtered off, washed with water (250 mL) and dried in vacuo (70 °C, 16 h).
The dry solid was suspended in DMF (250 mL) and cooled to –15 °C. At this temperature sulfuric acid (96%, 27.5 mL) and isoamylnitrite (19.9 mL) were added slowly and the suspension was stirred for 1 h. After this, hypophosphoric acid (30%, 75 mL) was added dropwise. Once the addition was completed, the reaction mixture was heated at 50 °C until the evolution of gas has ceased. Then, the solid was filtered off and washed subsequently with DMF (250 mL), water (250 mL) and ethanol (250 mL). This washing procedure was repeated twice. After drying in vacuo (70 °C, 18 h), tetraphenylmethane (26.7 g, 83.3 mmol, 93%) was obtained as a brownish powder. δ_H (400 MHz; $CDCl_3$) 7.06–7.17 (20 H, m, Ar-*H*) ppm; δ_C (100 MHz; $CDCl_3$) 65.0 (C_q(Ar)$_4$), 125.9 (*C*-Ar$_p$), 127.4 (C_m-Ar), 131.1 (C_o-Ar), 146.8 (C_q-Ar) ppm; ν/cm^{-1} (DRIFT) 3085vw, 3059vw, 3030vw, 1961vw, 1681vw, 1594m, 1492w $\tilde{\nu}_{Ar}$(C=C), 1442vw, 1323vw, 1183vw, 1082vw, 1036vw, 1002vw, 891vw, 766w, 751w δ_{Ar}(C-H), 702m δ_{Ar}(C-H), 635w, 525vw, 492vw; m/z (70 eV, EI) 320 (M$^+$, 64%), 243 ($M^+{-}C_6H_5$, 100), 165 ($C_{13}H_9^+$, 56), 77 ($C_6H_5^+$, 8); $C_{25}H_{20}$ calcd. 320.1565; found 320.1564.

Tetrakis(4-bromophenyl)methane (13).[2] To a three necked round bottomed flask containing bromine (64.0 mL, 199 g, 1.25 mol, 20 equiv.), tetraphenylmethane (20.0 g, 62.4 mmol, 1 equiv.) was added in small portions under vigorous stirring at room temperature. After the addition was completed, the resulting solution was stirred for 20 min and then cooled down to –78 °C. At this temperature, ethanol (150 mL) was added slowly and the formed suspension was allowed to warm to room temperature under stirring overnight. After this, the precipitate was filtered off and washed subsequently with an aqueous sodium hydrogensulfite solution (100 mL) and water (100 mL). After drying in vacuo, tetrakis(4-bromophenyl)methane (38.0 g, 59.7 mmol, 96%) was obtained as a yellowish solid. δ_H (400 MHz; $CDCl_3$) 7.01 (8 H, d, J 8.7, Ar$_o$-*H*), 7.39 (8 H, d, J 8.7, Ar$_m$-*H*); δ_C (100 MHz; $CDCl_3$) 63.6 (C_q(Ar)$_4$), 120.8 [C_q-Ar(Br)], 131.1 (C_o-Ar), 132.3 (C_m-Ar), 144.4 [C_q-Ar(C)]; ν/cm^{-1} (Drift) 3066vw, 1919vw, 1794vw, 1637vw, 1572vw, 1482m $\tilde{\nu}_{Ar}$(C=C), 1397w, 1308vw, 1214vw, 1185vw, 1111vw, 1079w, 1044vw, 1010 (m), 950vw, 916vw, 833w, 811m $\tilde{\nu}_{Ar}$, 758w, 727vw, 679vw, 629vw, 533w, 511w; m/z (70 eV, EI) 640/638/636/634/632 (M$^+$, 10%/38%/59%/37%/10%), 559/557/555/553 (M$^+$−Br, 6/15/15/14/4), 489/481/479/477 (M$^+$−2Br, 33/97/100/38), 401/399 (M$^+$−3Br, 10/7), 321/319 (M$^+$−4Br, 14/14); $C_{20}H_{21}Br_4$ calcd. 635.7946; found 635.7948; $C_{20}H_{21}Br_4$ calcd. C, 47.21; H, 2.54%; found C, 47.21; H, 2.64%.

Tetrakis(4-ethynylphenyl)methane (9).[3] In a round bottomed Schlenk flask tetrakis(4-bromophenyl)methane (0.51 g, 0.82 mmol, 1.0 equiv.) was dissolved in dry benzene (3.5 mL) under argon atmosphere. To this solution, triethylamine (9.0 mL), trimethylsilylacetylene (0.7 mL, 0.48 g, 4.92 mmol, 6.0 equiv.), bis(triphenylphosphine)palladium chloride (0.03 g, 0.03 mmol, 0.04 equiv.) and copper(I)bromide (0.01 g, 0.03 mmol, 0.04 equiv.) were added subsequently. The resulting suspension was heated at 80 °C for 24 h. Then, the volatiles were removed under reduced pressure. The residue was taken up in diethylether (50 mL) and an aqueous solution of HCl (1M, 20 mL). The organic phase was separated, washed with water (20 mL) and dried over magnesium sulfate. After removing of the solvent under reduced pressure, the crude product was deprotected without further purification.

In a round bottomed flask tetrakis(4-(trimethylsilylethynyl)phenyl)methane (0.54 g, 0.75 mmol, 1.0 equiv.) was dissolved in dry benzene (10 mL) and dry acetonitrile (15 mL). To this solution a 1M solution in THF of tetrabutylammonium fluoride (4.5 mL, 4.51 mmol, 6.0 equiv.) was added and stirred for 2 h at room temperature. The reaction mixture was poured in water (25 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane (2 x 50 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, pentane/toluene 1:1). The pure product was obtained (0.26 g, 0.63 mmol, 77% yield over two steps) as a yellow solid. R_f 0.30 (pentane/toluene 1:1); δ_H (400 MHz; $CDCl_3$) 3.07 (4 H, s, CC*H*), 7.12 (8 H, d, J 8.5, Ar_o-*H*), 7.39 (8 H, d, J 8.5, Ar_m-*H*) ppm; δ_C (100 MHz; $CDCl_3$) 64.8 ($C_q(Ar)_4$), 81.5 (C≡*C*H), 83.1 (*C*≡CH), 120.3 [C_q-Ar(CCH)], 130.7 (C_o-Ar), 131.6 (C_m-Ar), 146.2 [C_q-Ar(C)] ppm; ν/cm^{-1} (Drift) 3283m, 3086vw, 3062vw, 3031vw, 2926vw, 2857vw, 2360vw, 2109vw, 1931vw, 1803vw, 1672vw, 1603vw, 1559vw, 1498w, 1402vw, 1309vw, 1256vw, 1208vw, 1179vw, 1115vw, 1018w, 960vw, 916vw, 900vw, 829w, 769vw, 743vw, 716vw, 673w, 642w, 631w, 587vw, 571w, 560w, 545vw, 517vw, 502vw; m/z (70 eV, EI) 416 (M^+, 1%); $C_{33}H_{20}$ calcd. 416.1565; found 416.1562.

Tetrakis(4-nitrophenyl)methane (14).[4] To a round bottomed flask containing nitric acid (99%, 26 mL, 39.3 g, 624 mmol, 20 equiv.) cooled to –5 °C, tetraphenylmethane (10.0 g, 31.2 mmol, 1.0 equiv.) was added slowly in small portions under vigorous stirring. To facilitate precipitation of the desired product, a solution of acetic anhydride (12 mL, 12.8 g, 125 mmol, 4.0 equiv.) in glacial acetic acid (16 mL) was added slowly. After 15 min another 32 mL glacial acetic acid was added and the precipitate was filtered off and washed with water (300 mL). The desired tetrakis(4-nitrophenyl)methane (11.2 g, 22.5 mmol, 72%) was obtained as a bright yellow solid. δ_H (400 MHz; DMSO-d_6) 7.62 (8 H, d, J 9.1, Ar_m-*H*), 8.23 (8 H, d, J 9.1, Ar_o-*H*) ppm; δ_C (100 MHz; DMSO-d_6) 67.0 ($C_q(Ar)_4$), 123.8 (C_o-Ar), 131.5 (C_m-Ar), 146.1 [C_q-Ar(NO_2)], 151.0 [C_q-Ar(C)] ppm; ν/cm^{-1} (Drift) 3108m, 3068m, 2982w, 2867w, 2700vw, 2602vw, 2450w, 2211vw, 1951w, 1819w, 1606s, 1592s, 1524vs, 1493m, 1414w, 1347vs, 1300m, 1223w, 1189w, 1108m, 1068w, 1012m, 970w, 917w, 841vs, 758m, 745s, 712s, 683w, 667w, 627vw, 534m, 489w, 449vw; m/z (FAB) 501 ([MH^+], 20%). $C_{25}H_{17}N_4O_8$ calcd. 501.1046; found 501.1049 [MH^+].

4,4',4'',4'''-Methanetetrayltetraaniline (5).[4] In a three necked round bottomed flask tetrakis(4-nitrophenyl)methane (5.00 g, 9.99 mmol, 1.0 equiv.) and Pd/C (5%, 1.00 g, 0.47 mmol, 0.05 equiv.) were suspended in methanol (200 mL). The reaction mixture was degassed and backfilled with hydrogen five times. After this, the reaction mixture was vigorous stirred under hydrogen atmosphere for 24 h. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, CH_2Cl_2/methanol 7:1) to yield 4,4',4'',4'''-methanetetrayltetraaniline (3.29 g, 8.65 mmol, 93%) as a yellowish solid. δ_H (400 MHz; DMSO-d_6) 5.21 (4 H, s, NH_2), 6.44 (8 H, d, J 8.5, Ar_o-*H*), 6.72 (8 H, d, J 8.5, Ar_m-*H*) ppm; δ_C (100 MHz; DMSO-d_6) 61.2 ($C_q(Ar)_4$), 113.0 (C_o-Ar), 131.0 (C_m-Ar), 136.2 [C_q-Ar(C)], 145.0 [C_q-Ar(NH_2)] ppm; ν/cm^{-1} (Drift) 3396m, 3176m, 3064w, 3026w, 2237vw, 2033vw, 1925vw, 1905vw, 1879vw, 1611m, 1580w, 1507m, 1432vw, 1335vw, 1271m, 1185m, 1142w, 1098vw, 1016w, 941w, 860m, 830m, 814m, 783m, 720w, 642vw, 579m, 521w, 448vw, 415vw; m/z (70 eV, EI) 380 (M^+, 39%), 288 ($M^+-C_6H_6N$, 100), 195 ($C_{13}H_{12}N_2^+$, 8), 93 ($C_6H_7N^+$, 22). $C_{24}H_{24}N_4$ calcd. 380.2001; found 380.2004.

1,3,5,7-Tetrakisphenyladamantane (16). 1-Bromoadamantane (6.00 g, 27.9 mmol, 1.0 equiv.) was dissolved in benzene (60 mL) under argon atmosphere. *t*-Butylbromide (6.30 mL, 55.8 mmol, 2 equiv.) and $AlCl_3$ (320 mg, 2.40 mmol, 0.1 equiv.) was added to the suspension which was heated under reflux for 2 h. The reaction mixture was cooled to room temperature; the solid was filtered off and washed with chloroform (50 mL), water (30 mL) and chloroform (50 mL). The product was dried under reduced pressure (8.15 g, 18.5 mmol, 66%). ν/cm^{-1} (DRIFT) 3082m, 3055m, 3022m, 2920s, 2851s, 1957w, 1884w, 1814w, 1763w, 1597m, 1577m, 1551w, 1494s, 1444s, 1395w, 1356s, 1263m, 1216w, 1189w, 1079m, 1031m, 919m, 890w, 789m, 761s, 747s, 702s, 679m, 617m, 570s, 529s, 478w; m/z (70 eV, EI) 440 (M^+, 46%), 364 (M^+–C_6H_5, $C_{28}H_{28}$, 100), 288 (M^+–$C_{12}H_{10}$, $C_{22}H_{24}$, 3), 231 (M^+–$C_{16}H_{16}$, $C_{18}H_{16}^+$, 60), 155 ($C_{12}H_{12}^+$, 30), 91 ($C_7H_8^+$, 45), 78 ($C_6H_6^+$, 79), 77 (M^+–$C_{28}H_{27}$, $C_6H_5^+$, 19).

1,3,5,7-Tetrakis(4-iodophenyl)adamantane (17). Iodine (2.36 g, 9.06 mmol, 2.0 equiv.) was added to a suspension of 1,3,5,7-tetraphenyladamantan (2.00 g, 4.54 mmol, 1.0 equiv.) in chloroform (50 mL) and stirred until the iodine had dissolved. Then, (bis(trifluoroacetoxy)iodo)benzene (3.90 g, 9.06 mmol, 2.0 equiv.) was added an the suspension was stirred for 24 h at room temperature. The mixture was filtered to remove a purple solid. The organic layer was washed with a $NaHSO_3$-solution (5%, 50 mL), water (50 mL), brine (50 mL) and dried over $MgSO_4$. The product was crystallized in a chloroform/methanol mixture (9:1) to isolate colorless crystals of 1,3,5,7-tetrakis(4-iodophenyl)adamantane (1.90 g, 2.01 mmol, 44%). R_f 0.31 (cyclohexane/CH_2Cl_2, 20:1); δ_H (400 MHz; $CDCl_3$) 2.05 (12 H, s, Ad-C*H₂*), 7.18 (8 H, dd, J 8.6, 4.4, Ar_o-*H*), 7.67 (8 H, dd, J 8.6, 4.4, Ar_m-*H*) ppm; δ_C (100 MHz; $CDCl_3$) 148.4 (C_q-Ar), 137.5 [C_m-Ar(I)], 127.1 (C_o-Ar), 91.7 [C_p-Ar(I)], 46.7 (C_s-Ad), 39.1 (C_q-Ad) ppm; ν/cm^{-1} (DRIFT) 3056w, 3024w, 2929m, 2898m, 2853m, 1904w, 1788vw, 1647vw, 1583w, 1485m, 1447w, 1391m, 1356m, 1213w, 1179w, 1107w, 1066w, 1003m, 961w, 944w, 890w, 821m, 776m, 759m, 716w, 659w, 559w, 526m; m/z (FAB) 944 (M^+, 100%), 818 (M^+–I, $C_{34}H_{29}I_3^+$, 24).

1,3,5,7-Tetrakis(4-ethynylphenyl)adamantane (10). 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (**17**) (4.00 g, 4.25 mmol, 1.0 equiv.) was dissolved in dry toluene (83 mL) and dry Et_3N (35 mL) was added under argon atmosphere. The flask was degassed several times after the addition of trimethylsilylacetylene (12.7 mL, 8.75 g, 89.2 mmol, 21 equiv.), then $Pd(PPh_3)_2Cl_2$ (213 mg, 0.3 mmol, 7 mol%) and CuI (57 mg, 0.3 mmol, 7 mol%) were added and the reaction became black within minutes. The mixture was stirred under reflux for 72 h, cooled to room temperature and the solvent removed under reduced pressure. The residue was then taken-up in chloroform (200 mL), washed with an aqueous solution of HCl (10%), water and dried over $MgSO_4$.

The crude 1,3,5,7-tetrakis(4-trimethylsilyl-ethynylphenyl)adamantane was used for the next reaction (deprotection) without further purification. KF (2.47 g, 42.5 mmol, 10 equiv.) was added to a suspension of the silylated product (3.50 g, 4.25 mmol) in methanol (60 mL) and stirred overnight at 50 °C. The reaction mixture was poured into water (60 mL), extracted with chloroform (100 mL), washed with water (2 × 100 mL) and brine (2 × 100 mL). The organic layer was dried over $MgSO_4$. 1,3,5,7-Tetrakis(4-ethynylphenyl)adamantane (1.68 g, 74% yield over two steps) was isolated as a white solid after purification by flash chromatography on silica gel using cyclohexane/CH_2Cl_2 (gradient 2:1–1:1) as eluent. R_f 0.27 (cyclohexane/ CH_2Cl_2 1:1); δ_H (400 MHz; $CDCl_3$) 2.01 (12 H, bs, Ad-C*H₂*), 2.95 (s, 4 H, C≡C*H*), 7.31 (8 H, d, J 8.3, Ar_m-*H*), 7.38 (8 H, d, J 8.3, Ar_o-*H*) ppm; δ_C (100 MHz; $CDCl_3$) 39.3 (C_q-Ad), 46.7 (C_s-Ad), 76.7 (C≡*C*H), 83.5 (*C*≡CH), 120.1 (C_q, Ar-Ad), 125.0 (C_o-Ar), 132.2 (C_m-Ar), 149.6 (C_q, Ar_p-alkyne) ppm; ν/cm^{-1} (DRIFT) 3893vw, 3291m, 3085w (C_{Ar}-H), 3035w, 2932w, 2900w, 2852w (C_{Ad}-H), 2106w (C≡CH), 1910w, 1793vw, 1607w (C=C), 1504m, 1446w, 1404w, 1357w, 1241w, 1190w, 1114w, 1018w, 950w, 893w, 834m, 793w, 744w, 661m, 618m, 557m, 519w, 449w, 434w; m/z (70 eV, EI) 536 (M^+, 20%), 436 (M^+–

C_8H_4, 13), 212 (16), 115 (27), 91 (M^+–$C_{35}H_{25}$, 100), 43 (69); $C_{42}H_{32}$ calcd. 536.2504; found 536.2501.

1,3,5,7-Tetrakis(4-nitrophenyl)adamantane (18). To a round bottomed flask containing of nitric acid (99%, 8 mL, 192 mmol, 44 equiv.) cooled to –5 °C, 1,3,5,7-tetrakisphenyladamantane (2.00 g, 4.35 mmol, 1.0 equiv.) was added slowly in small portions under vigorous stirring. To facilitate precipitation of the desired product, a solution of acetic anhydride (2.5 mL, 2.70 g, 26.6 mmol, 6.1 equiv.) in glacial acetic acid (85 mL) was added slowly. After 15 min at –5 °C, another 32 mL glacial acetic acid was added and the precipitate was filtered off and washed with water/methanol (20 mL, 1:1). The product was isolated (980 mg, 1.58 mmol, 35 %) after re-crystallization from DMF. δ_H (400 MHz, DMSO-d_6): 2.24 (s, 12 H), 7.92 (d, 8 H, *J* 9.0, Ar_m-*H*), 8.21 (d, 8 H, *J* 9.0, Ar_o-*H*) ppm; δ_C (100 MHz; DMSO-d_6) 39.4 (C_q-Ad), 44.5 (C_s, Ad-CH_2), 123.2 (C_o-Ar), 126.8 (C_m-Ar), 145.8 [C_q,Ar(NO_2)], 156.6 [C_q, Ar(C)] ppm; ν/cm^{-1} (Drift) 3922w, 3745w, 3189w, 3114w, 3083w, 2932m, 2903m, 2854m, 2707w, 2624w, 2455w, 2305w, 2222w, 1924w, 1792w, 1672w, 1595s, 1516s, 1447m, 1407m, 1346s, 1189w, 1112m, 1041w, 1012m, 960w, 898w, 856s, 783m, 746s, 698m, 680m, 632w, 558w, 531w, 494w, 427w; m/z (FAB) 621 (M^+, 96%), 605 (100), 604 (69); $C_{34}H_{29}N_4O_8$ calcd. 621.1985; found 621.1984.

1,3,5,7-Tetrakis(4-aminophenyl)adamantane (6). 1,3,5,7-Tetrakis(4-nitrophenyl)adamantane (200 mg, 0.24 mmol, 1.0 equiv.) was dissolved in dry THF (40 mL)[a] at room temperature. To the solution, deaerated by three vacuum-nitrogen cycles, was added 10% Pd/C (100 mg, 0.09 mmol, 0.4 equiv.) under an inert atmosphere and the resulting reaction mixture was stirred overnight under a hydrogen atmosphere (P = 1 atm). The mixture was filtered through Celite® and the product was precipitated with pentane (90 mL). The resulting mixture was cooled to –4 °C overnight. The precipitate was collected and dried in vacuo to afford 1,3,5,7-tetrakis(4-aminophenyl)adamantane (130 mg, quant. yield) as a yellow powder. δ_H (400 MHz; DMSO-d_6) 1.83 (s, 12 H, Ad-C*H*$_2$), 4.81 (s, 8H, N*H*$_2$), 6.52 (d, 8H, J 8.6, Ar_m-*H*), 7.13 (d, 8H, J 8.6, Ar_o-*H*) ppm; δ_C (100 MHz; DMSO-d_6) 37.8 (C_q-Ad), 47.6 (C_s, Ad-CH_2), 113.7 (C_o-Ar), 125.2 (C_m-Ar), 137.6 [C_q, Ar(NH_2)], 146.1 [C_q, Ar(C)] ppm; ν/cm^{-1} (Drift) 3428w, 3329m, 3217w, 3020w, 2922m, 2896w, 2848w, 1878vw, 1623m, 1515m, 1444w,1354w, 1274m, 1211w, 1187w, 1126w, 1053vw, 1027w, 1012w, 887vw, 839m, 821w, 771w, 637w, 566w, 540m, 499w, 437vw; m/z (FAB) 500 (M^+, 70%), 501 (62), 499 (18); $C_{34}H_{36}N_4$ calcd. 500.2940; found 500.2944.

[a] DMF (3-5mL) was also used to dissolve the complete substance in THF.

Analytical data

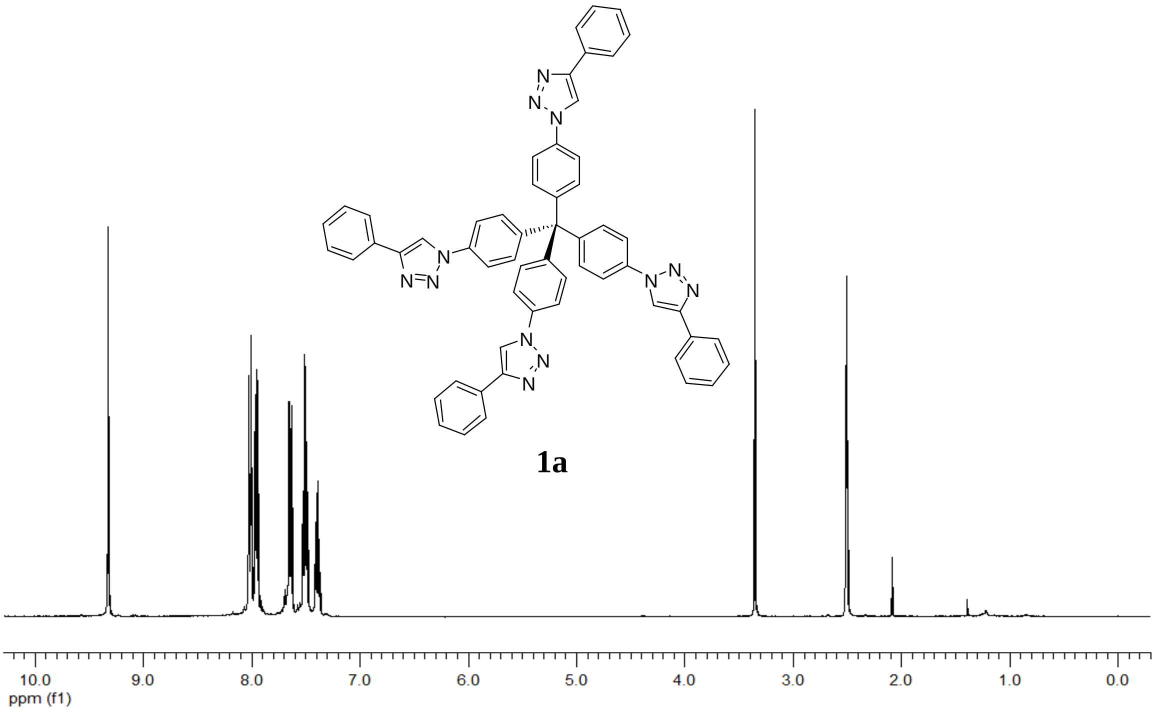


Figure S1. ^{1}H NMR of compound **1a** (400 MHz, DMSO-d$_6$)

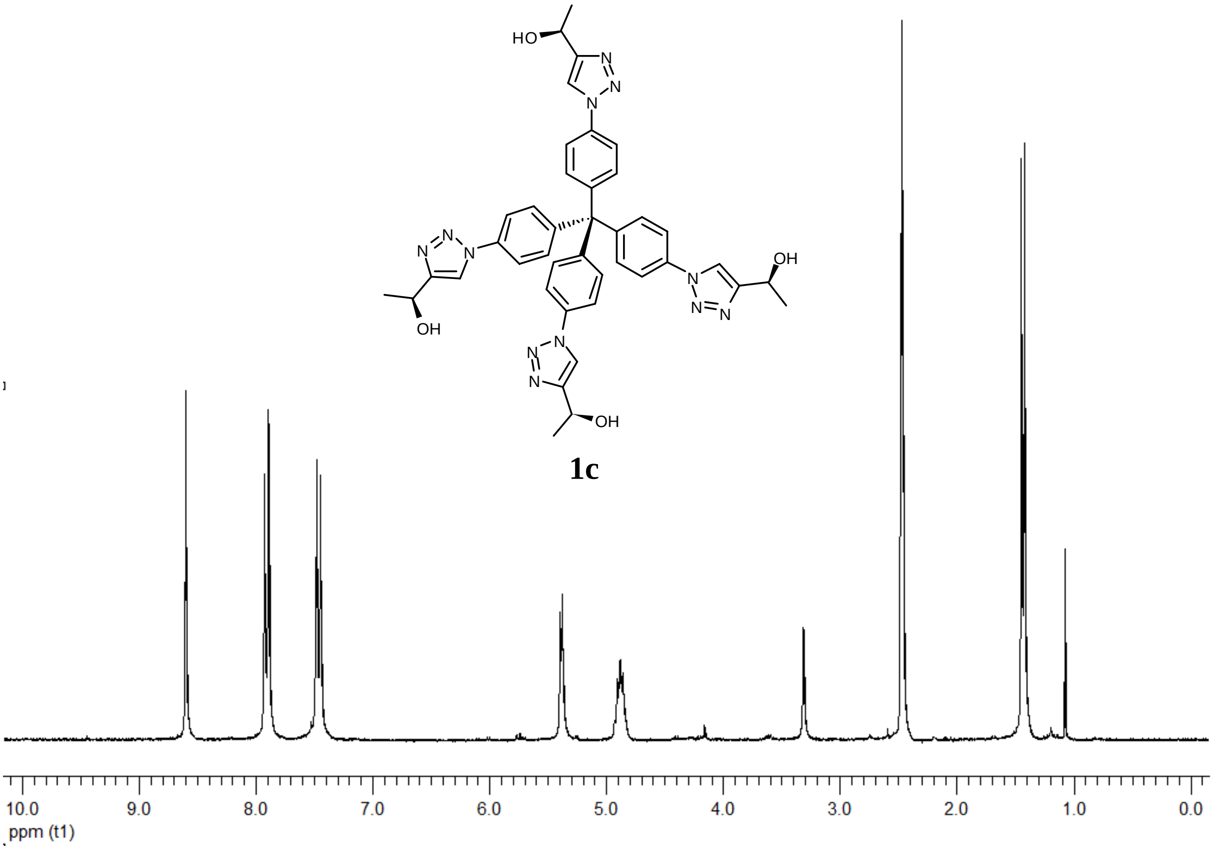
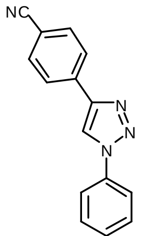


Figure S2. ^{1}H NMR of compound **1c** (400 MHz, DMSO-d$_6$)



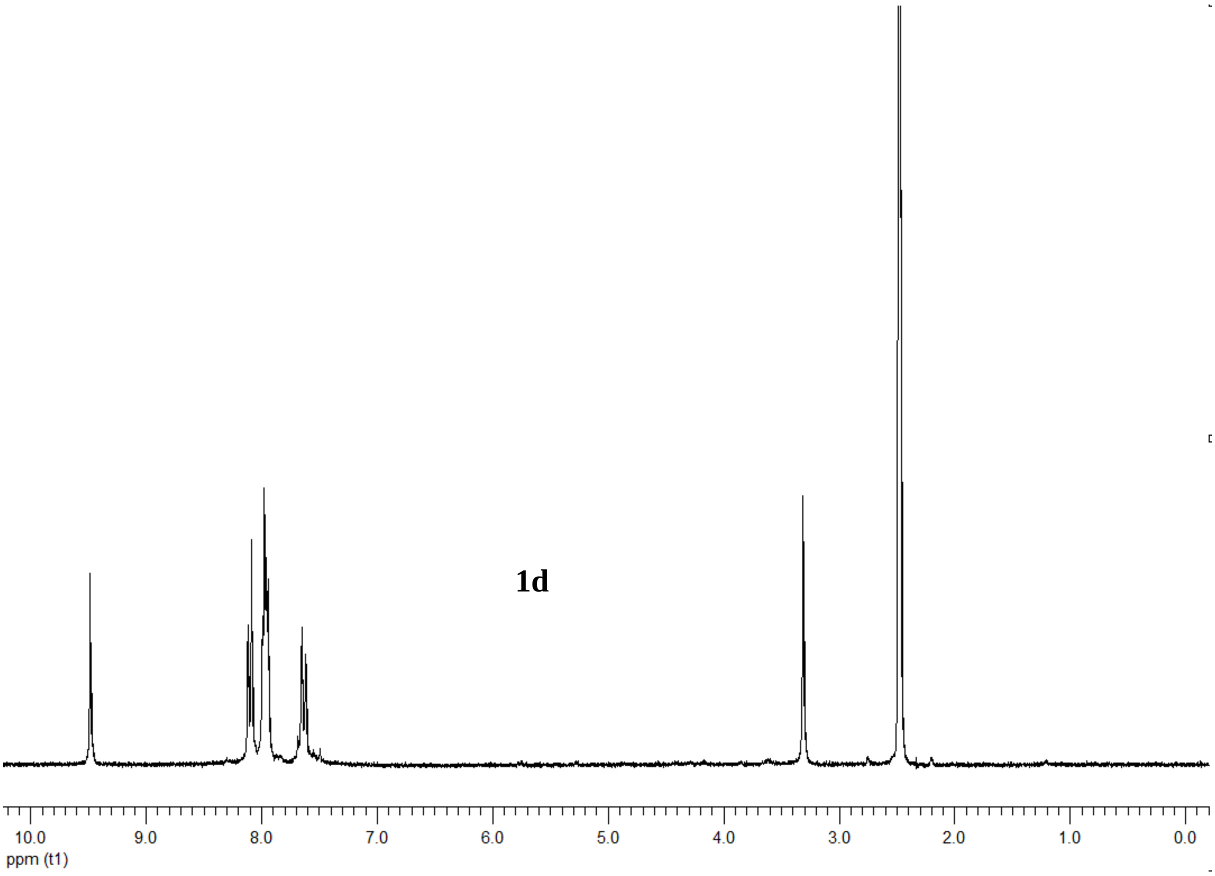


Figure S3. ^{1}H NMR of compound **1d** (400 MHz, DMSO-d_6)

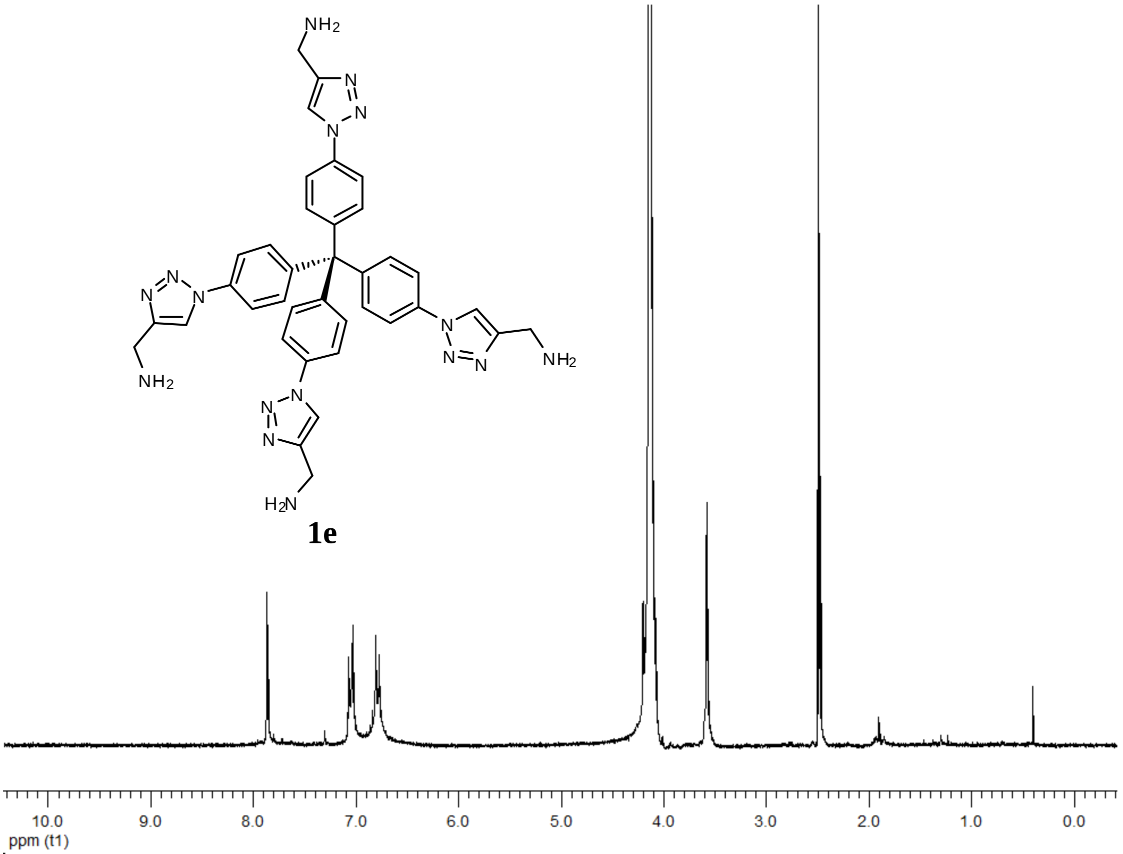


Figure S4. ^{1}H NMR of compound **1e** (250 MHz, DMSO-d_6)

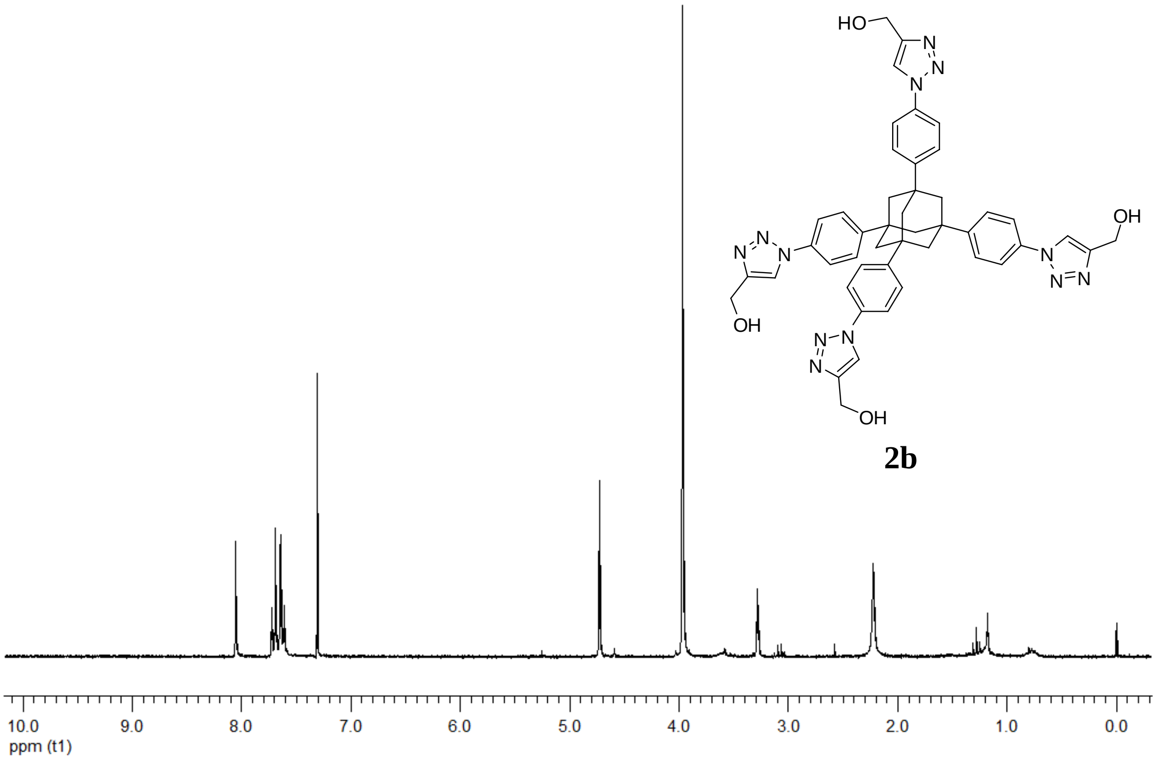


Figure S5. ^{1}H NMR of compound **2b** (400 MHz, $CDCl_3$)

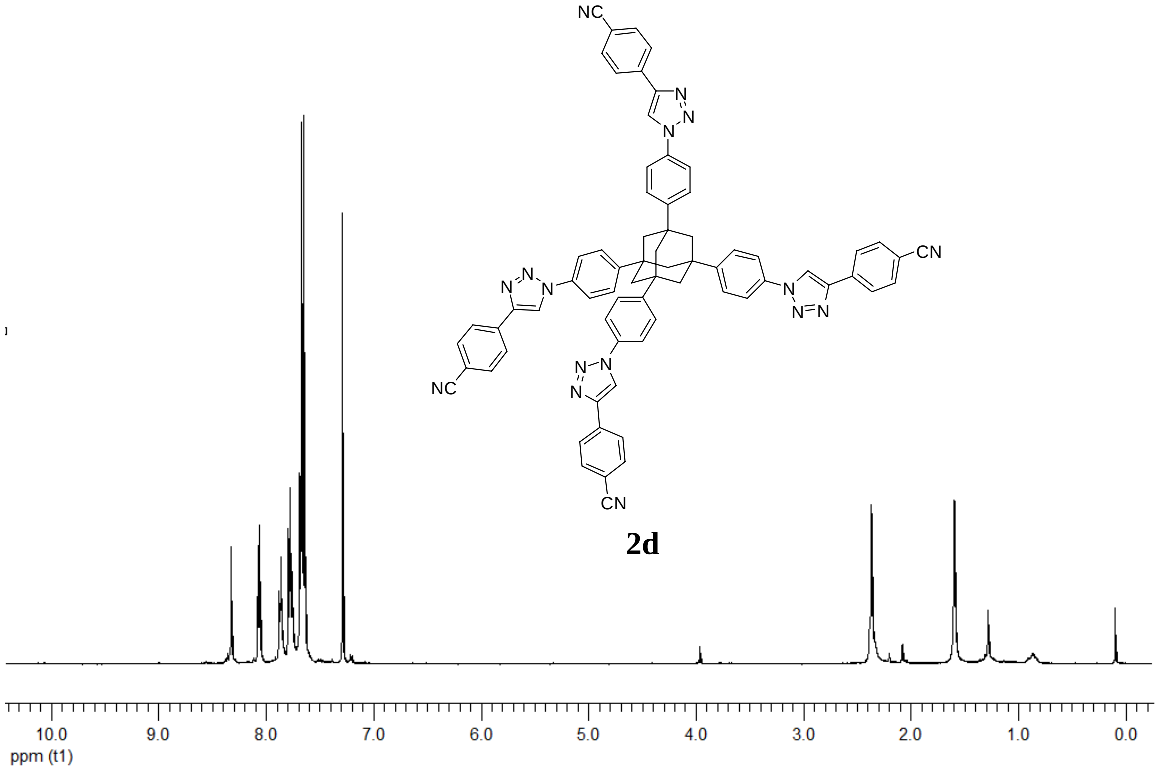


Figure S6. ^{1}H NMR of compound **2d** (500 MHz, $CDCl_3$)

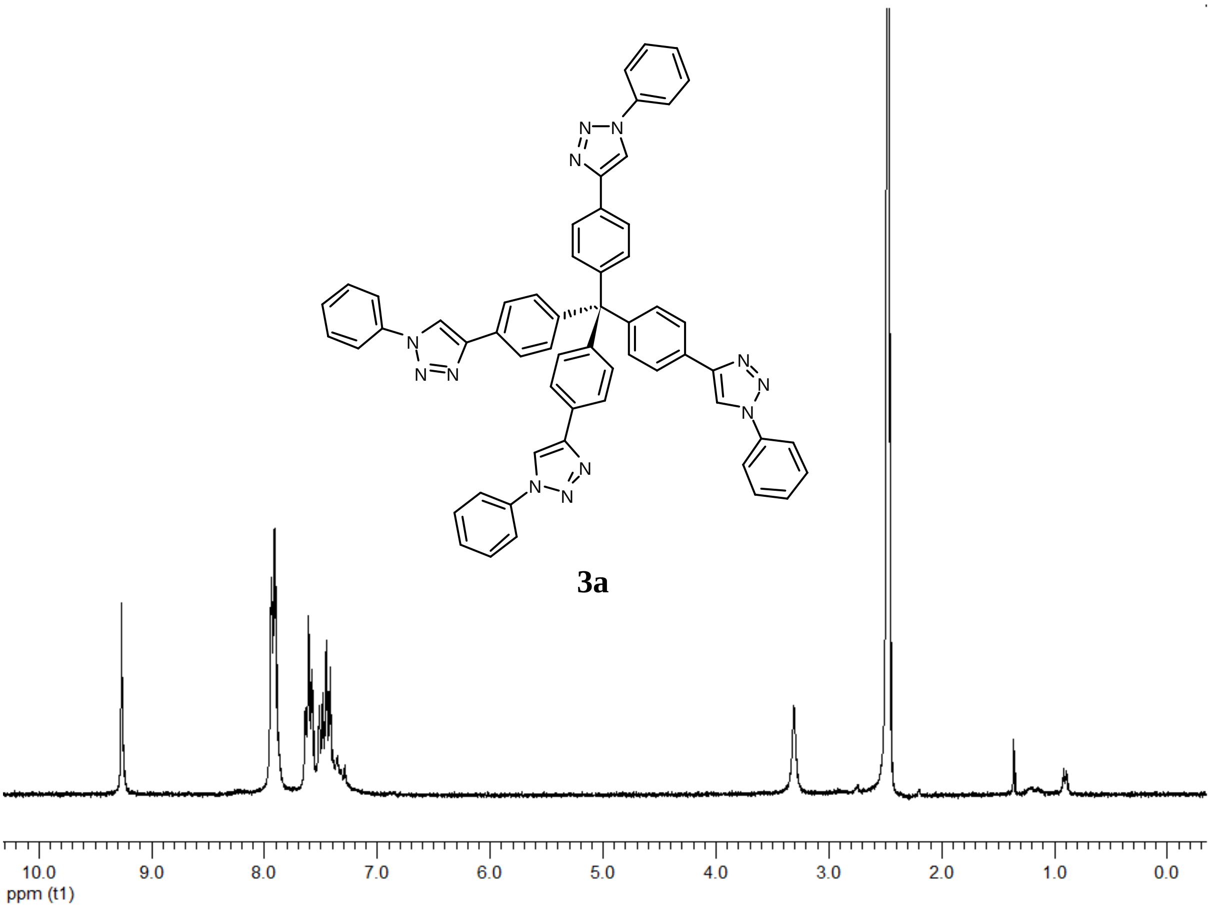


Figure S7. ^{1}H NMR of compound **3a** (250 MHz, DMSO-d_6)

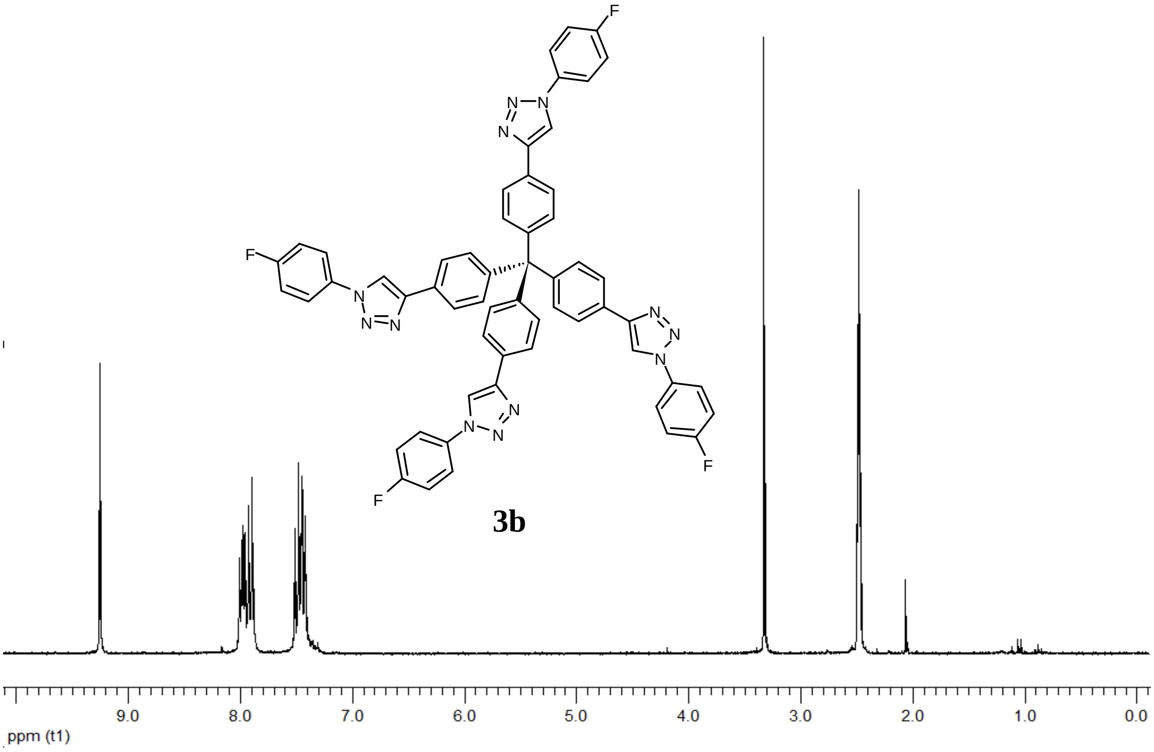


Figure S8. ^{1}H NMR of compound **3b** (400 MHz, DMSO-d_6)

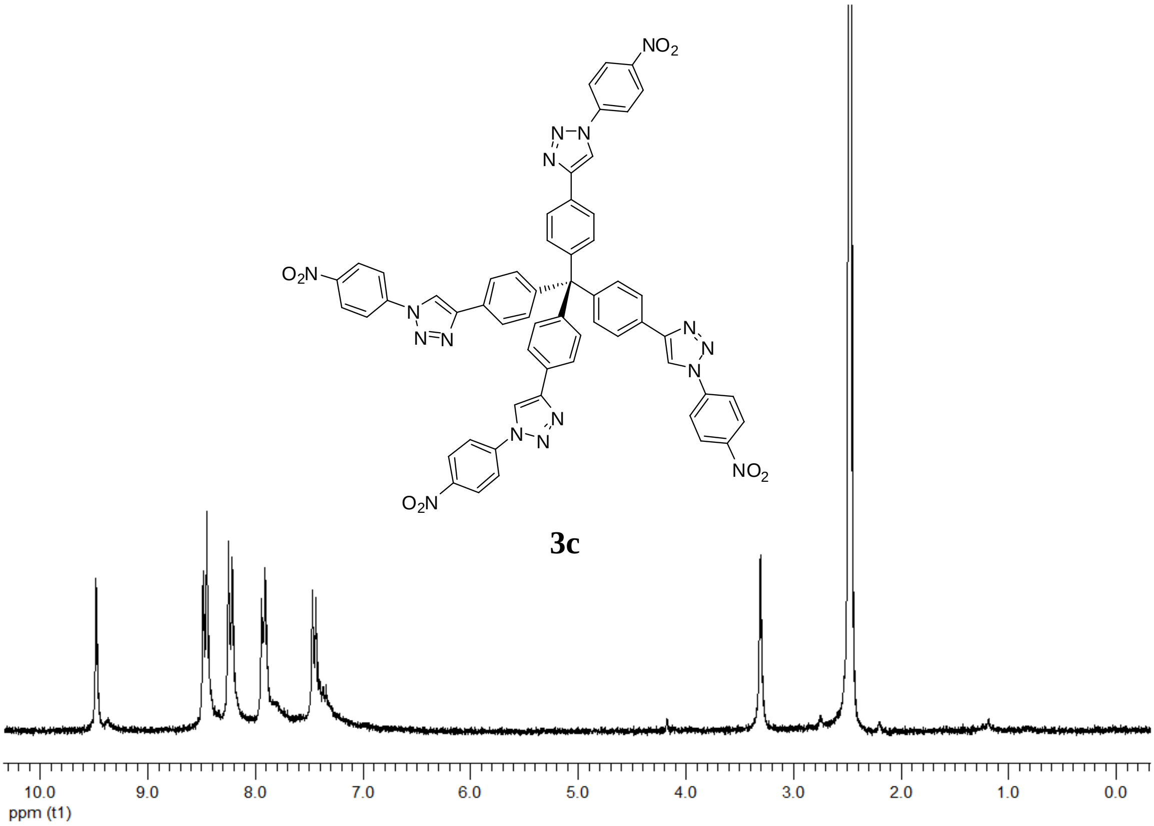


Figure S9. ^{1}H NMR of compound **3c** (250 MHz, DMSO-d_6)

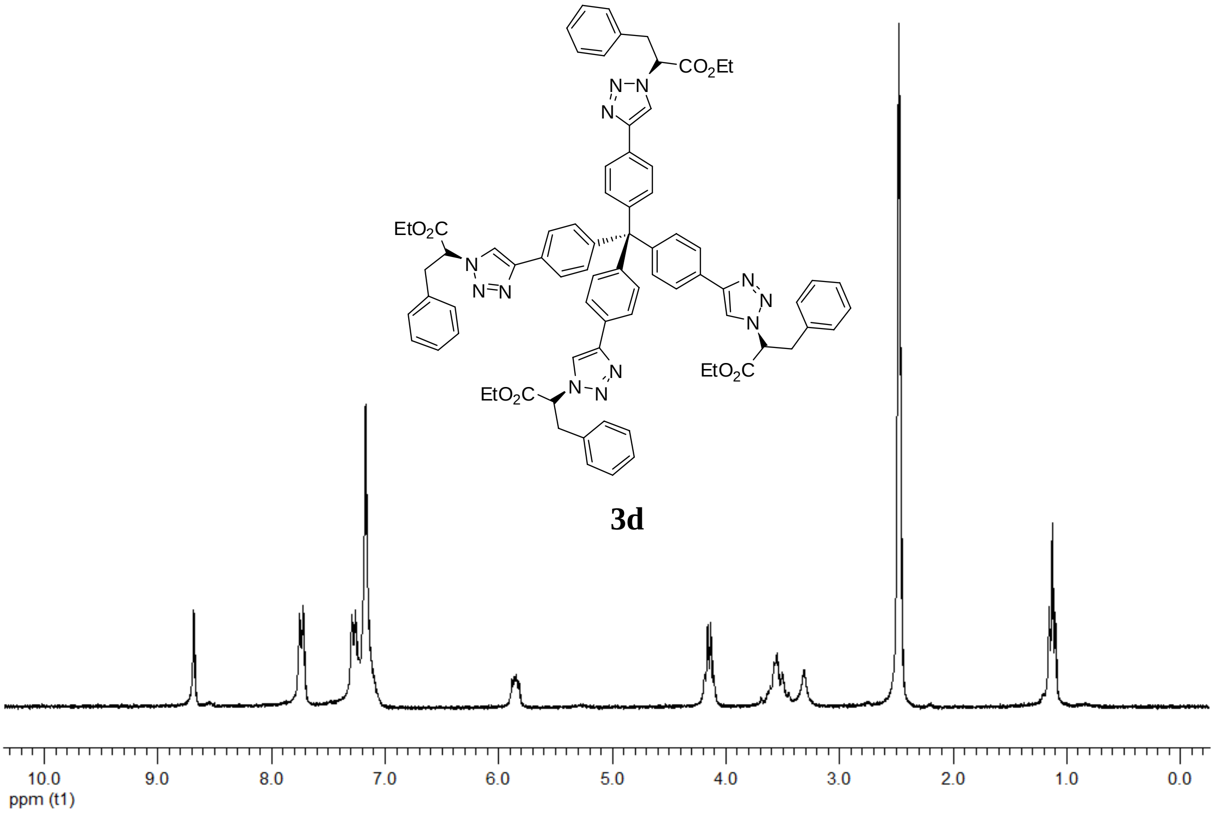
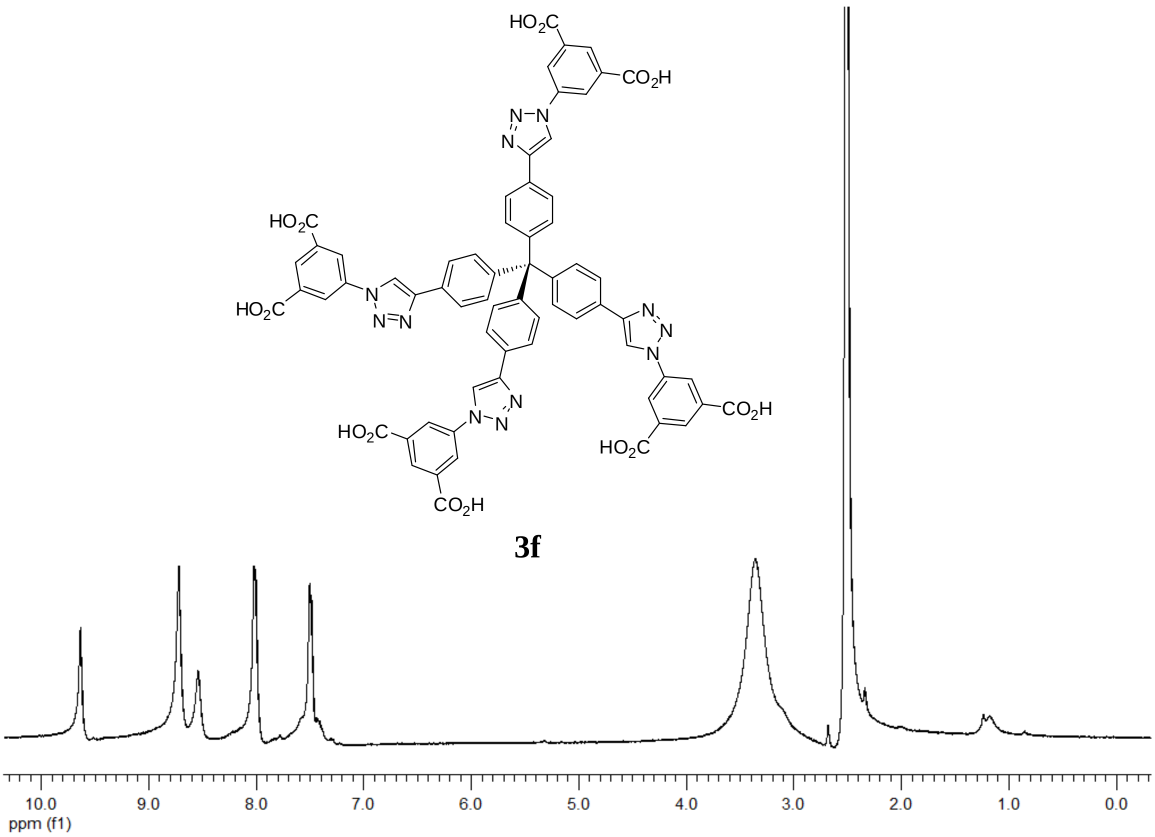
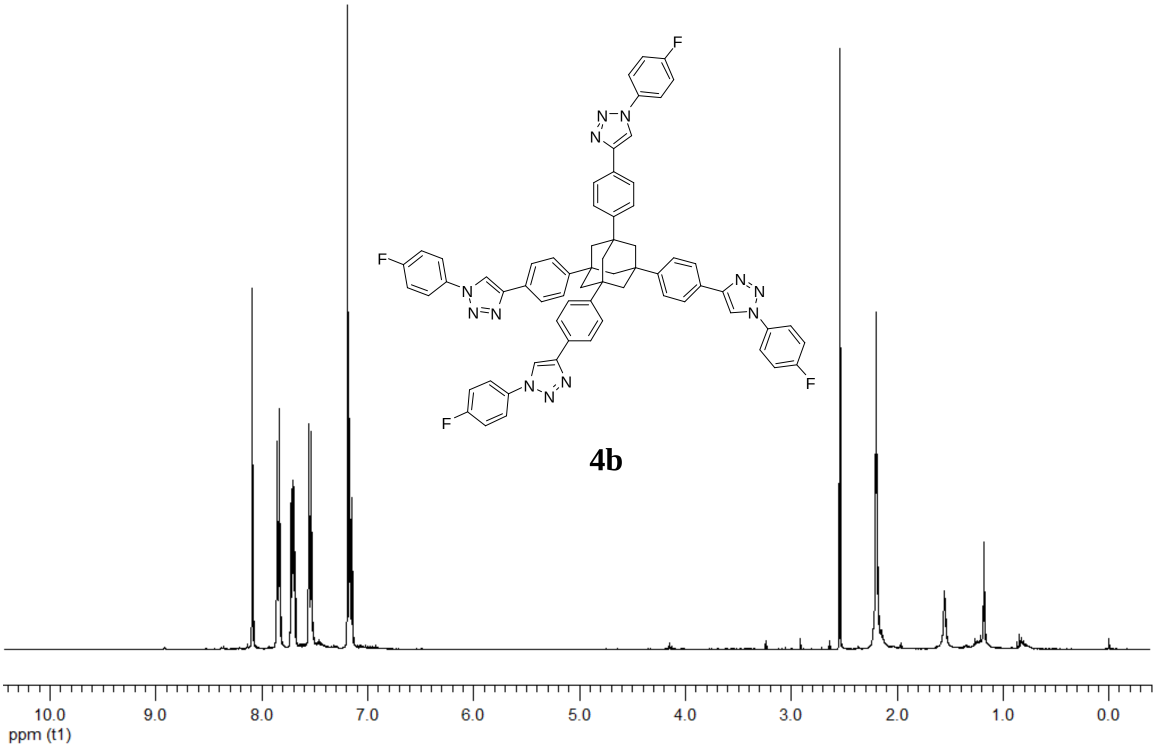


Figure S10. ^{1}H NMR of compound **3d** (250 MHz, DMSO-d_6)



3f

Figure S11. ^{1}H NMR of compound **3f** (250 MHz, DMSO-d_6)



4b

Figure S12. ^{1}H NMR of compound **4b** (400 MHz, $CDCl_3$)

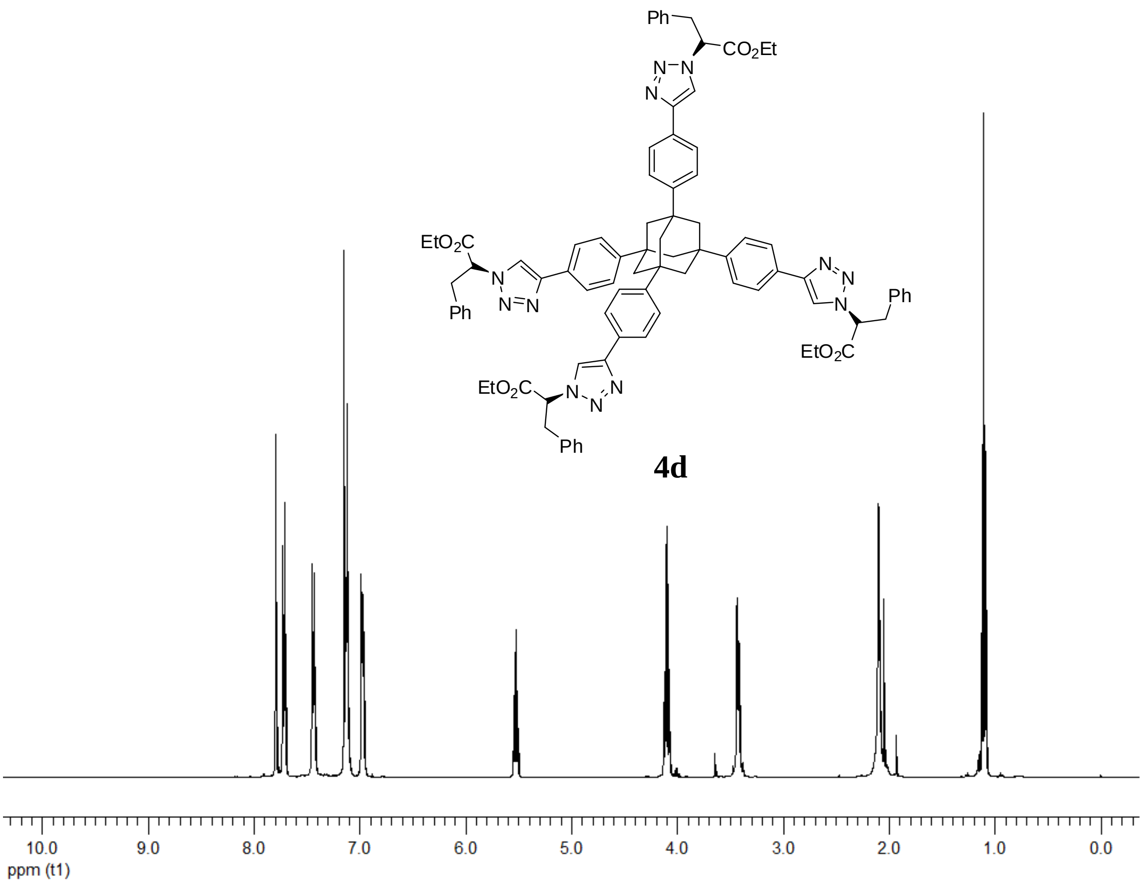


Figure S13. ^{1}H NMR of compound **4d** (400 MHz, $CDCl_3$)

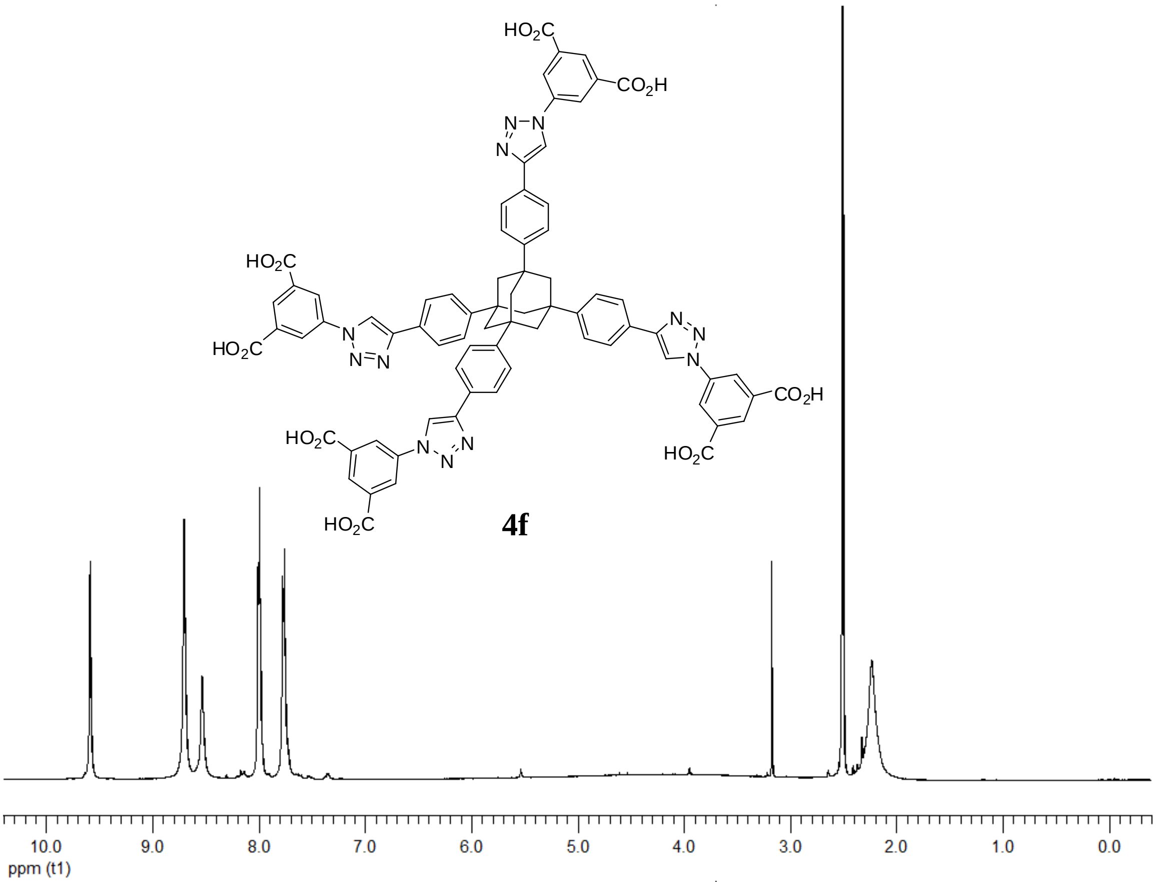
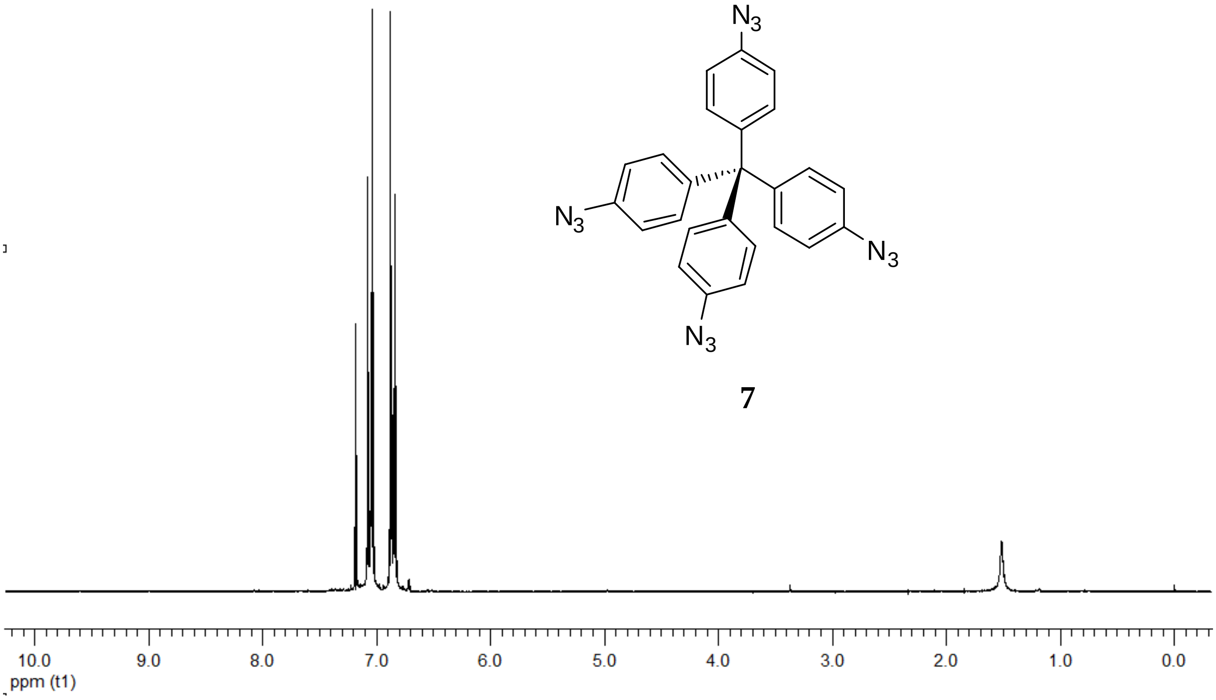
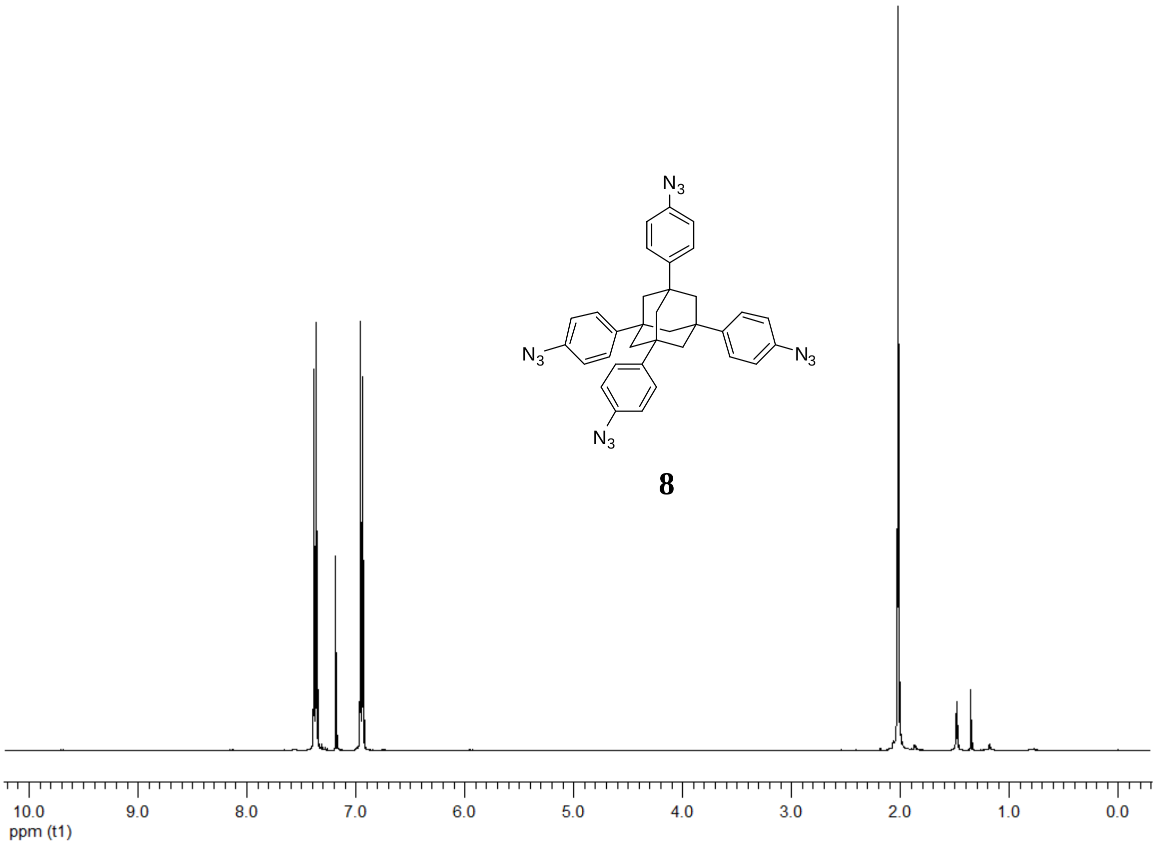


Figure S14. ^{1}H NMR of compound **4f** (400 MHz, DMSO-d_6)



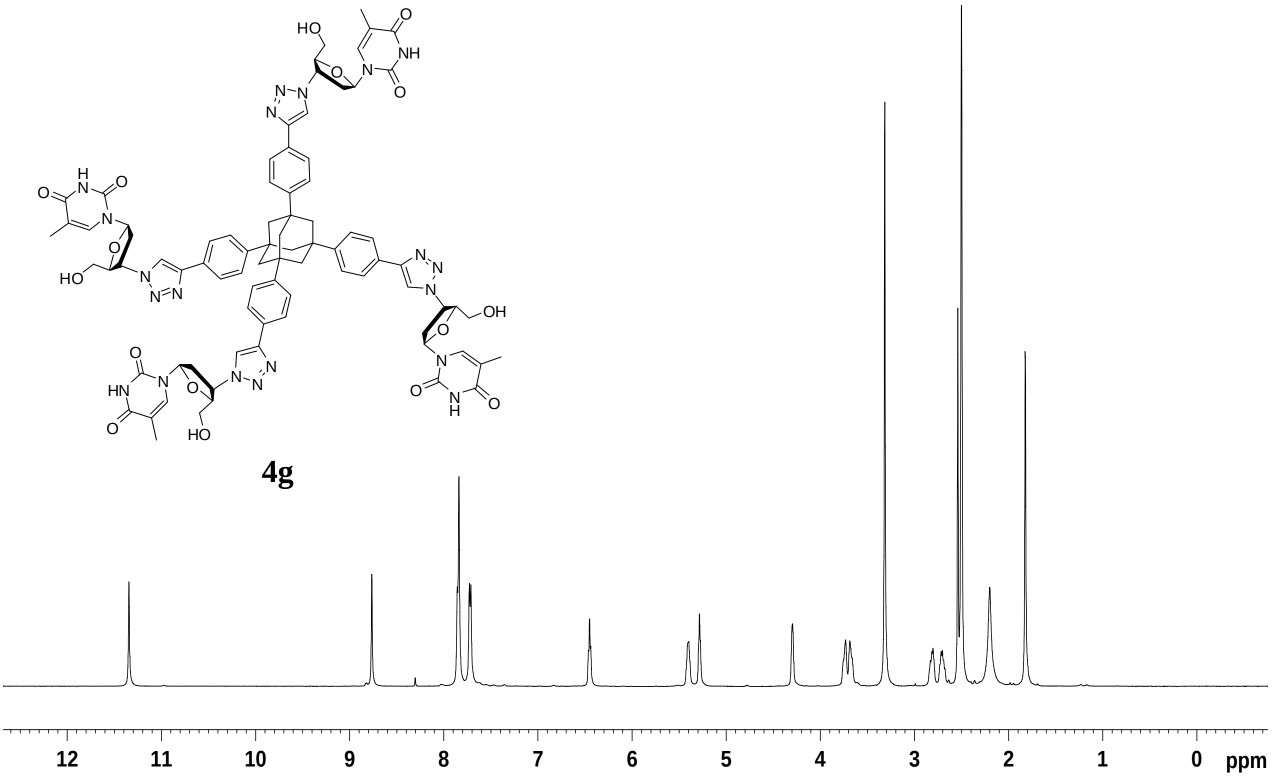
7

Figure S15. ^{1}H NMR of compound **7** (400 MHz, $CDCl_3$)



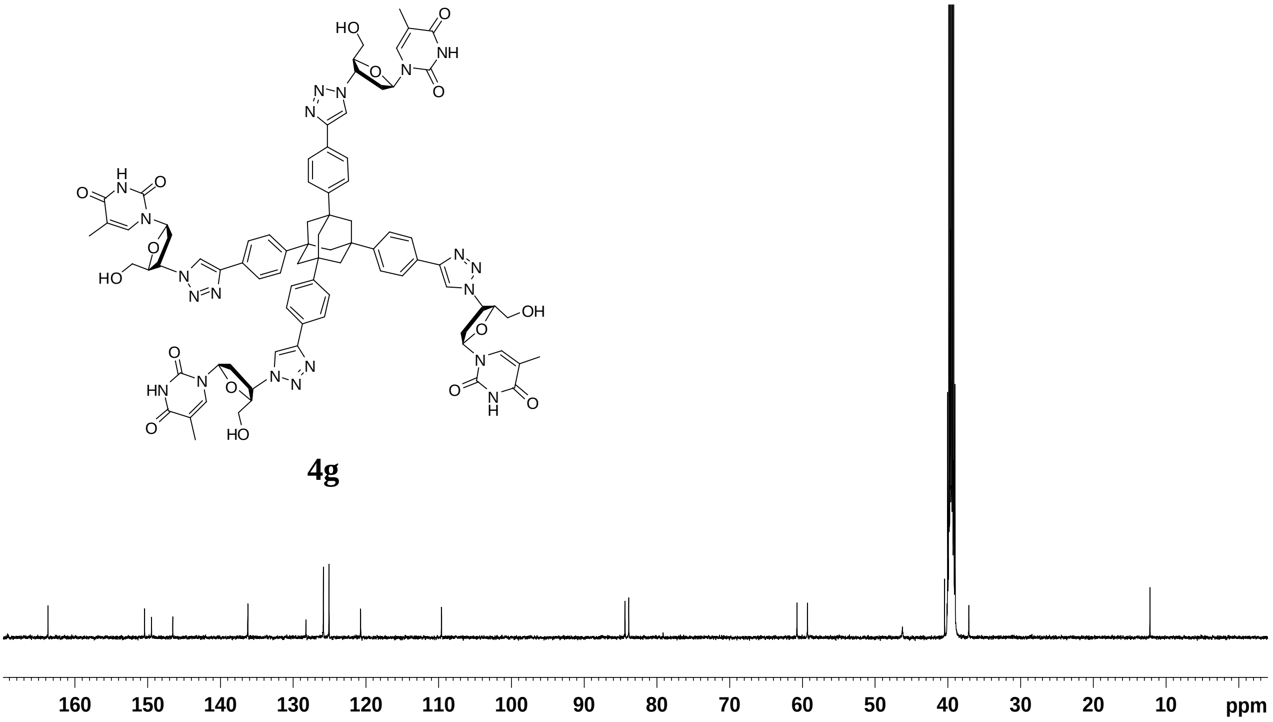
8

Figure S16. ^{1}H NMR of compound **8** (400 MHz, $CDCl_3$)



4g

Figure S17. ^{1}H NMR of compound **4g** (500 MHz, DMSO-d$_6$)



4g

Figure S18. ^{13}C NMR of compound **4g** (125 MHz, DMSO-d$_6$)

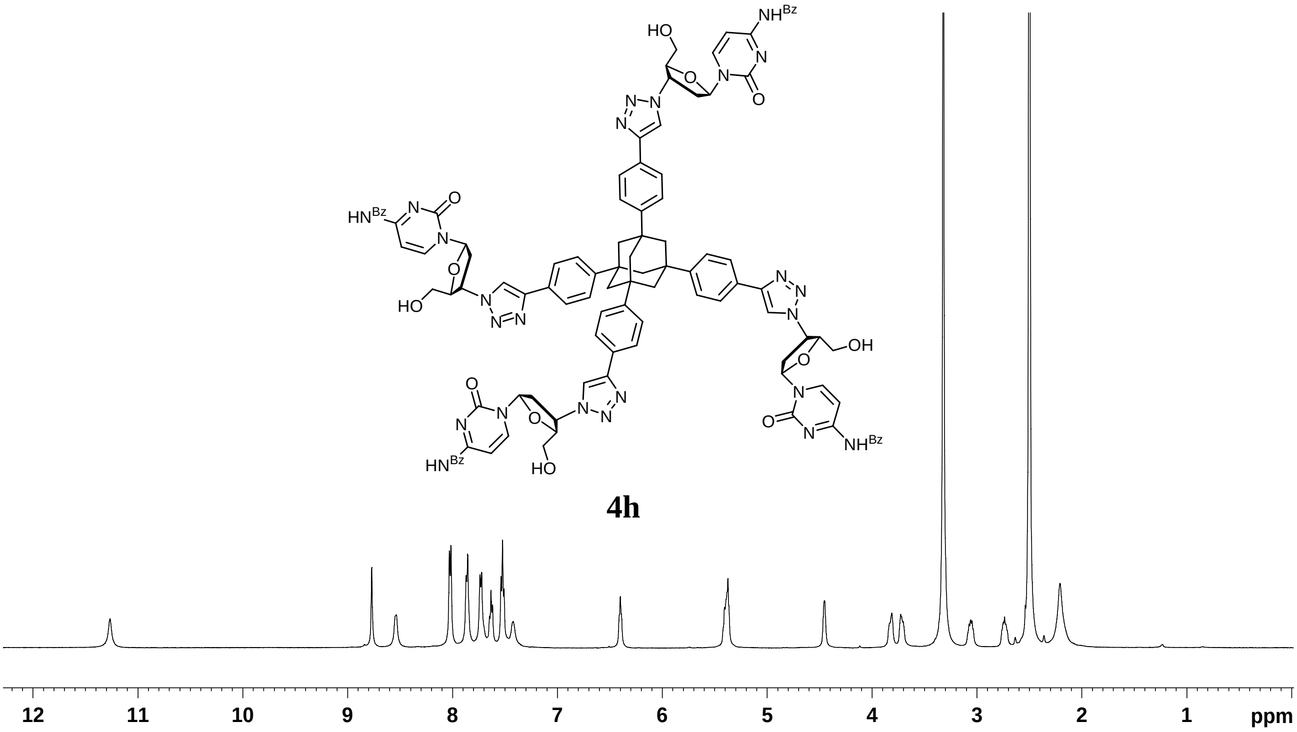


Figure S19. ^{1}H NMR of compound **4h** (500 MHz, DMSO-d$_6$)

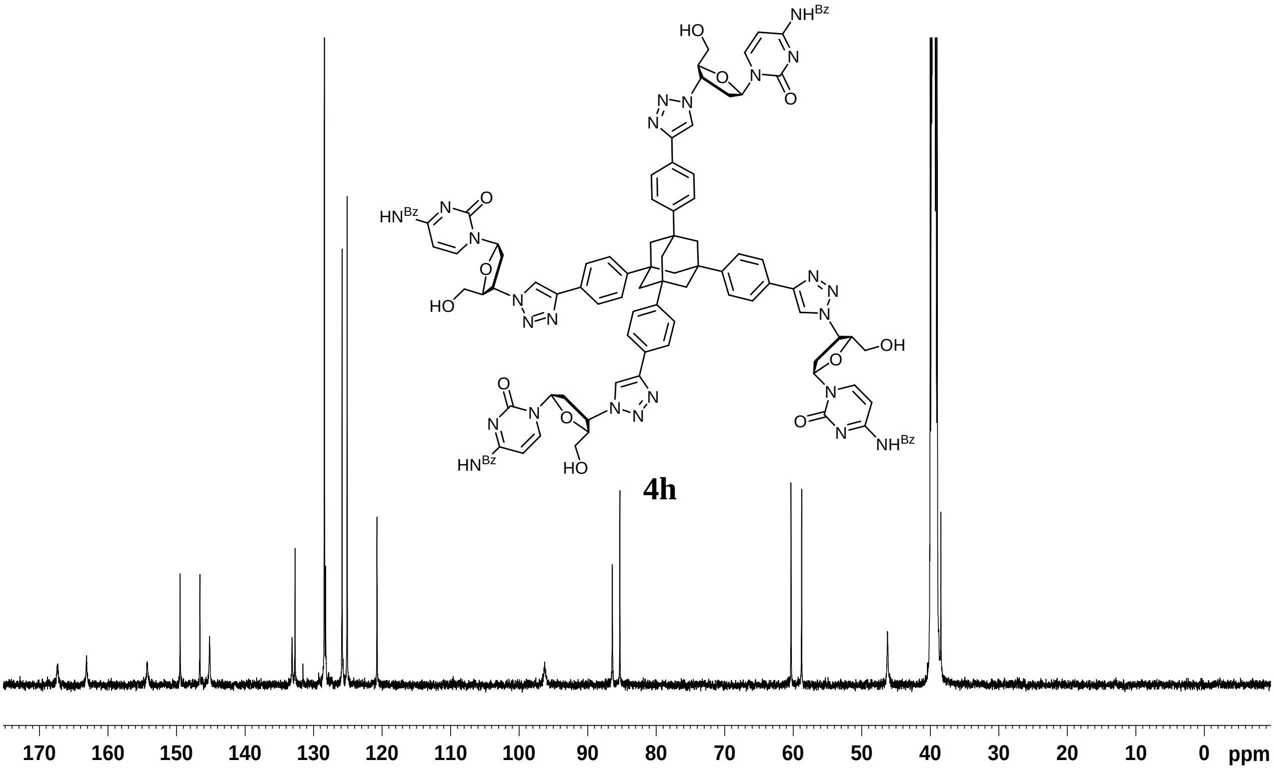


Figure S20. ^{13}C NMR of compound **4h** (125 MHz, DMSO-d$_6$)

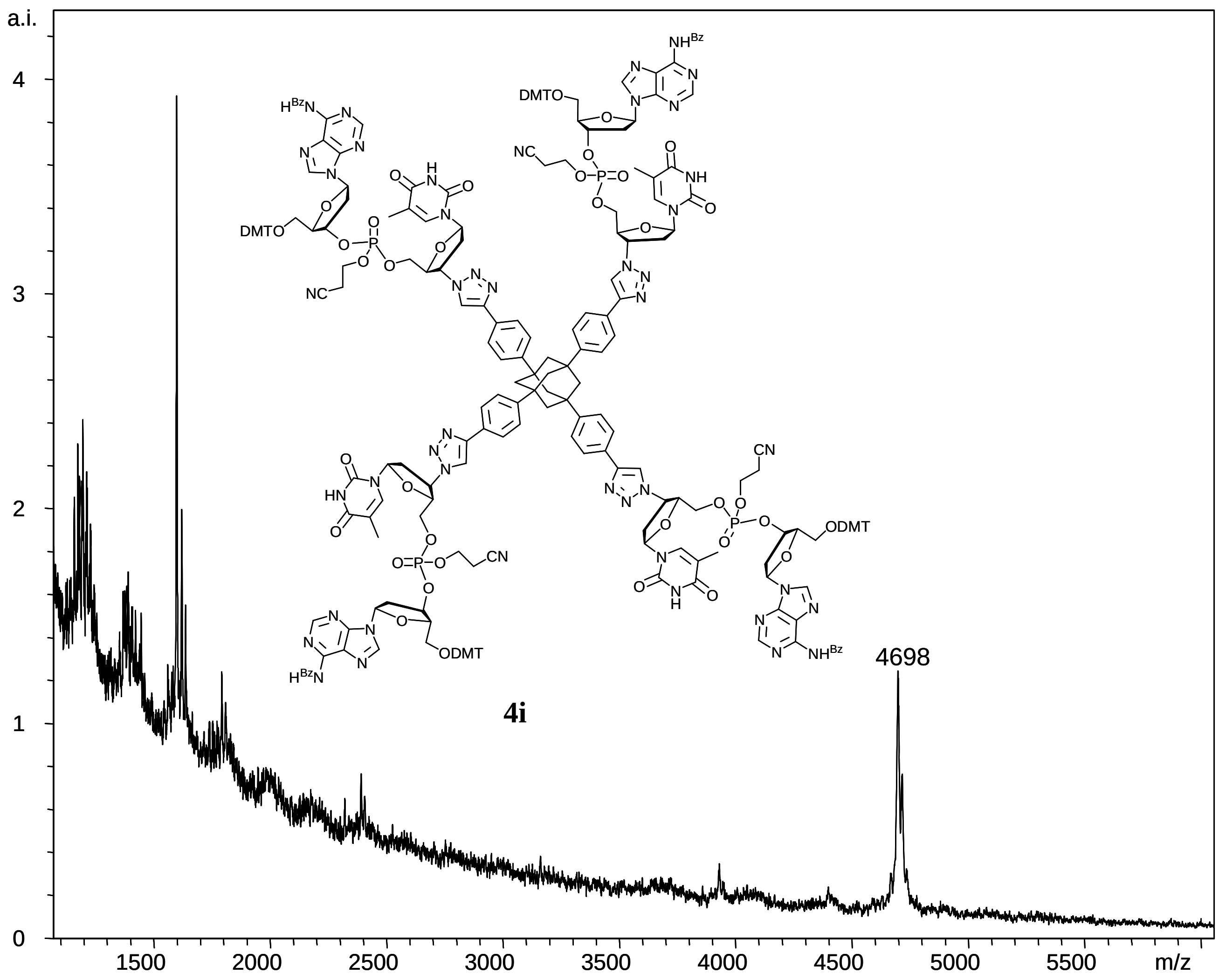


Figure S21. MALDI-TOF-MS spectrum of compound **4i**

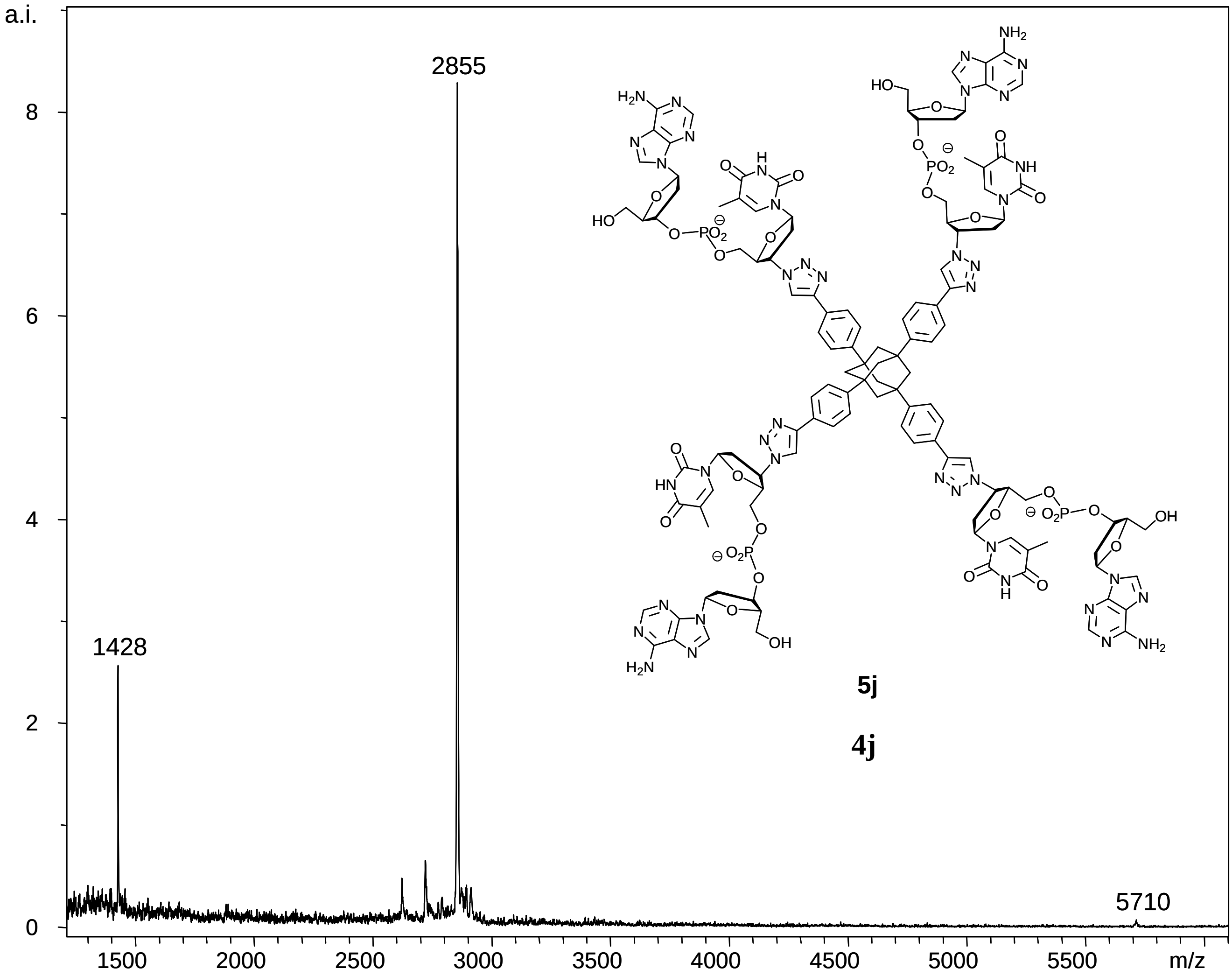


Figure S22. MALDI-TOF-MS spectrum of compound **4j**

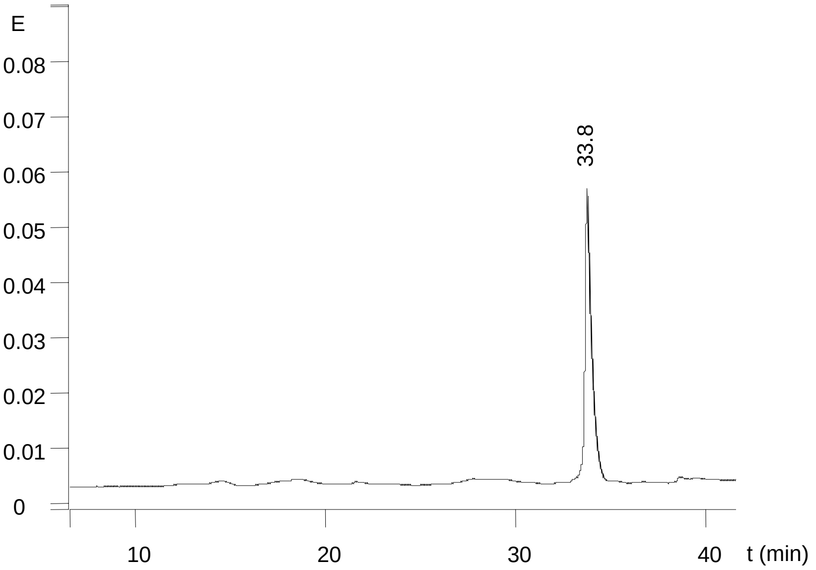


Figure S23. RP-HPLC chromatogram of purified DNA hybrid **4j**, as obtained with a gradient of CH_3CN in triethylammonium acetate buffer (0.1 M, pH 7.0) running from 0% to 60% in 60 min at a flow of 1 mL/min.

References

1 T. J. Zimmermann and T. J. J. Müller, *Synthesis*, 2002, 1157–1162.

2 J.-H. Fournier, X. Wang and J. D. Wuest, *Can. J. Chem.*, 2003, **81**, 376–380.

3 E. Galoppini and R. Gilardi, *Chem. Commun.*, 1999, 173–174.

4 (a) Q. Wei, A. Lazzeri, F. Di Cuia, M. Scalari and E. Galoppini, *Macromol. Chem. Phys.*, 2004, **205**, 2089–2096; (b) F. A. Neugebauer, H. Fischer and R. Bernhardt, *Chem. Ber.*, 1976, **109**, 2389–2394.

Crystal Structure Determinations

All single-crystal X-ray diffraction studies were carried out on a Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97)[a] were used for structure solution and refinement was carried out using SHELXL-97[a] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption corrections was applied for **4a**. The absolute structure of **4a** was determined by refinement of Flack's x-parameter (x = 0.01(6)).[b]

1a: pale yellow, $C_{57}H_{40}N_{12}$ – 2 C_3H_7NO, M = 1039.20, crystal size 0.40 x 0.16 x 0.04 mm, monoclinic, space group C2/c (No. 15): a = 29.701(6) Å, b = 8.996(2) Å, c = 20.844(4) Å, β = 109.53(2)°, V = 5248.9(19) Å^3, Z = 4, ρ(calcd) = 1.315 Mg m^{-3}, F(000) = 2184, μ = 0.084 mm^{-1}, 20477 reflexes ($2\theta_{max}$ = 50°), 4625 unique [R_{int} = 0.073], 356 parameters, 37 restraints, $R1$ ($I > 2\sigma(I)$) = 0.085, *wR2 (all data)* = 0.231, GOOF = 1.05, largest diff. peak and hole 1.173 / -0.824 e Å^{-3} (in the solvent dmf).

4a: colourless crystals, $C_{66}H_{52}N_{12}$ – 4 $CHCl_3$, M = 1490.67, crystal size 0.40 x 0.25 x 0.15 mm, tetragonal, space group P-4 (No. 81): a = 21.970(3) Å, c = 6.972(1) Å, V = 3365.3(8) Å^3, Z = 2, ρ(calcd) = 1.471 Mg m^{-3}, F(000) = 1528, μ = 0.547 mm^{-1}, 17869 reflexes ($2\theta_{max}$ = 55°), 7550 unique [R_{int} = 0.034], 425 parameters, $R1$ ($I > 2\sigma(I)$) = 0.050, *wR2 (all data)* = 0.132, GOOF = 1.06, largest diff. peak and hole 0.909 / -0.456 e Å^{-3} (near the solvent $CHCl_3$).

7: yellow crystals, $C_{25}H_{16}N_{12}$, M = 484.50, crystal size 0.30 x 0.15 x 0.10 mm, monoclinic, space group C2/c (No. 15), a = 18.878(1) Å, b = 7.137(1) Å, c = 18.265(1) Å, β = 111.37(1)°, V = 2273.5(4) Å^3, Z = 4, ρ(calcd) = 1.416 Mg m^{-3}, F(000) = 1000, μ = 0.094 mm^{-1}, 8191 reflexes ($2\theta_{max}$ = 55°), 2578 unique [R_{int} = 0.046], 168 parameters, $R1$ ($I > 2\sigma(I)$) = 0.051, *wR2 (all data)* = 0.116, GOOF = 1.01, largest diff. peak and hole 0.287 and -0.252 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 734783 (**1a**), CCDC 734784 (**4a**), CCDC 734785 (**7**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

a) G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112-122.

b) H. D. Flack, *Acta Crystallogr.* 1983, **A39**, 876-881.

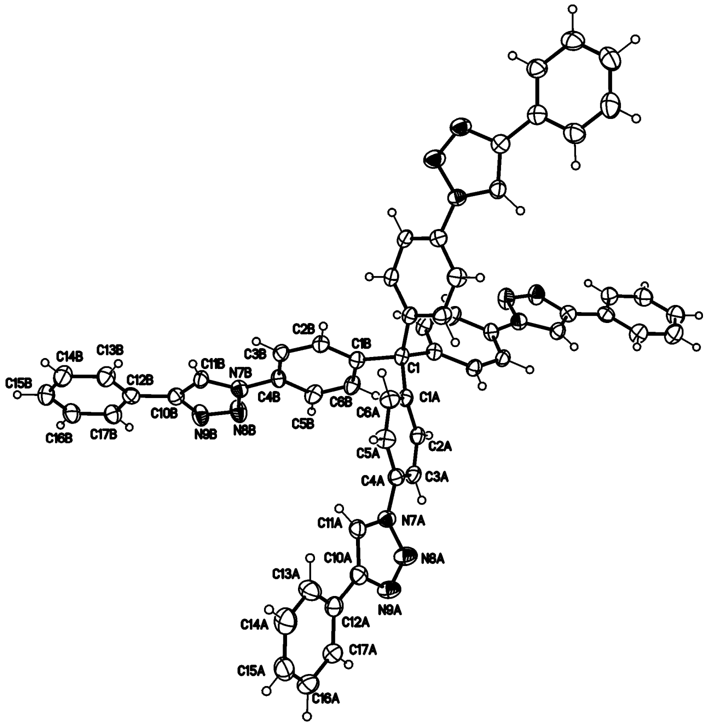


Fig. S1a. Molecular structure of **1a** (displacement parameters are drawn at 50% probability level). Solvent molecules excluded for clarity. The molecule possesses crystallographic C_2-symmetry

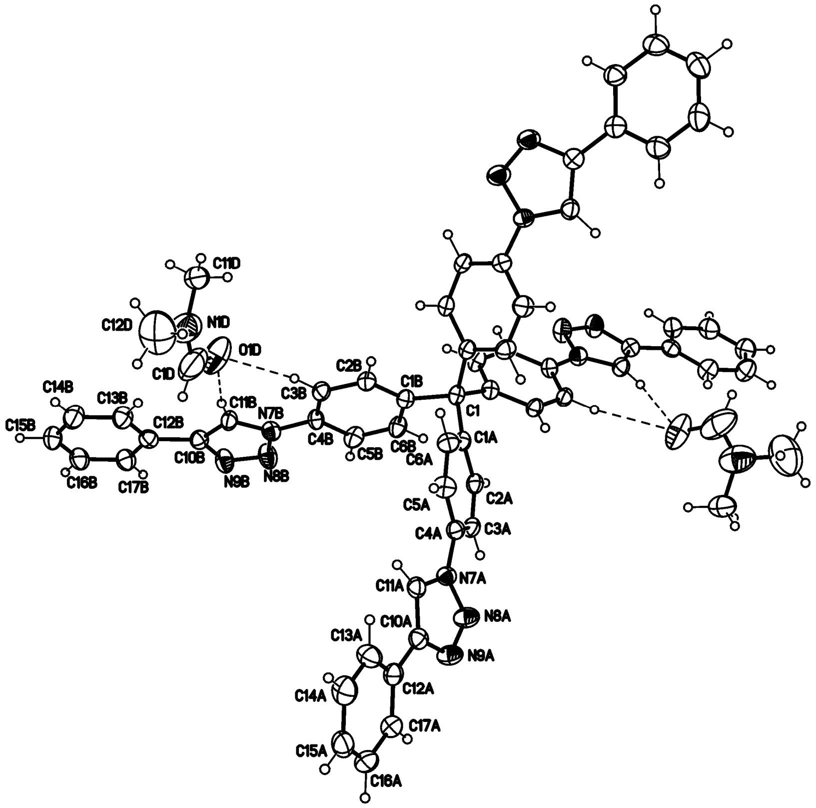


Fig. S1b. Molecular structure of **1a** (displacement parameters are drawn at 50% probability level). The molecule possesses crystallographic C_2-symmetry

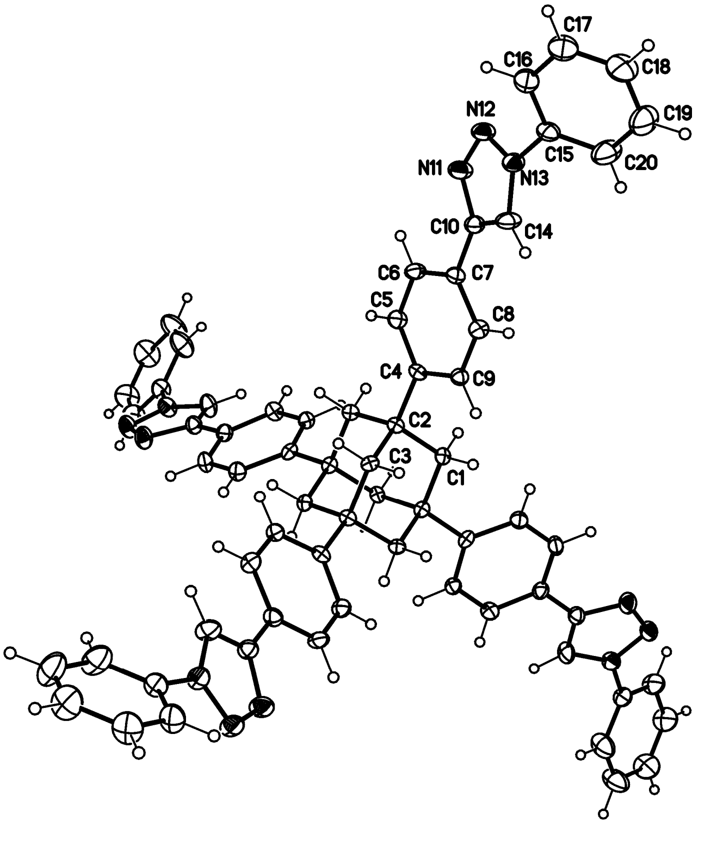


Fig. S2a. Molecular structure of **4a** (displacement parameters are drawn at 50% probability level). Solvent molecules and the second independent molecule excluded for clarity. The molecule possesses crystallographic S4-symmetry.

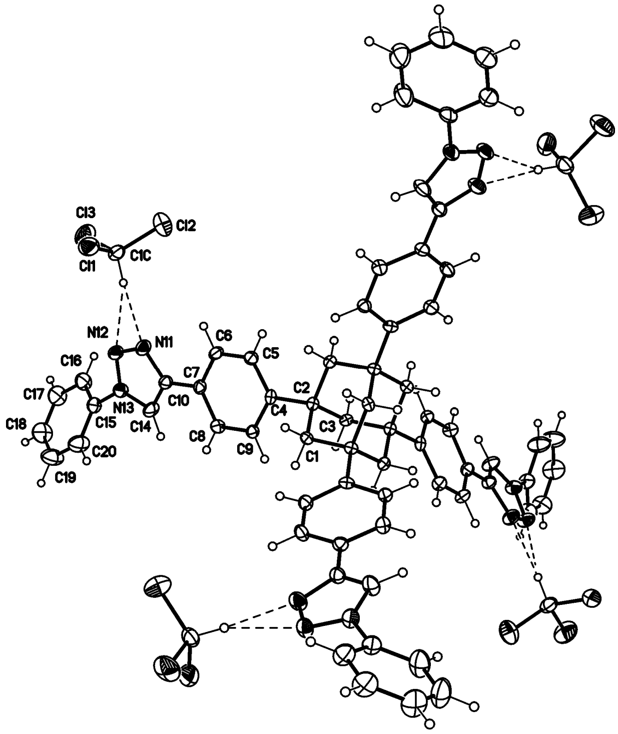


Fig. S2a. Molecular structure of **4a** (displacement parameters are drawn at 50% probability level). The second independent molecule excluded for clarity. The molecule possesses crystallographic S4-symmetry.

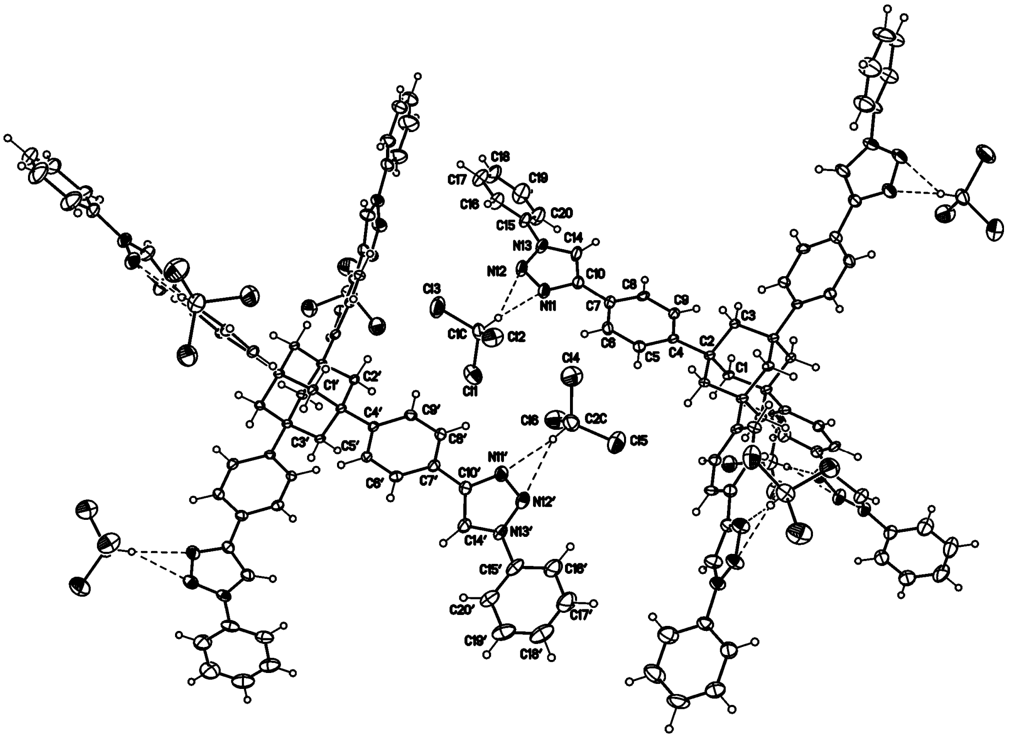


Fig. S2c. Molecular structure of **1a** (displacement parameters are drawn at 50% probability level). The molecule possesses crystallographic S4-symmetry.

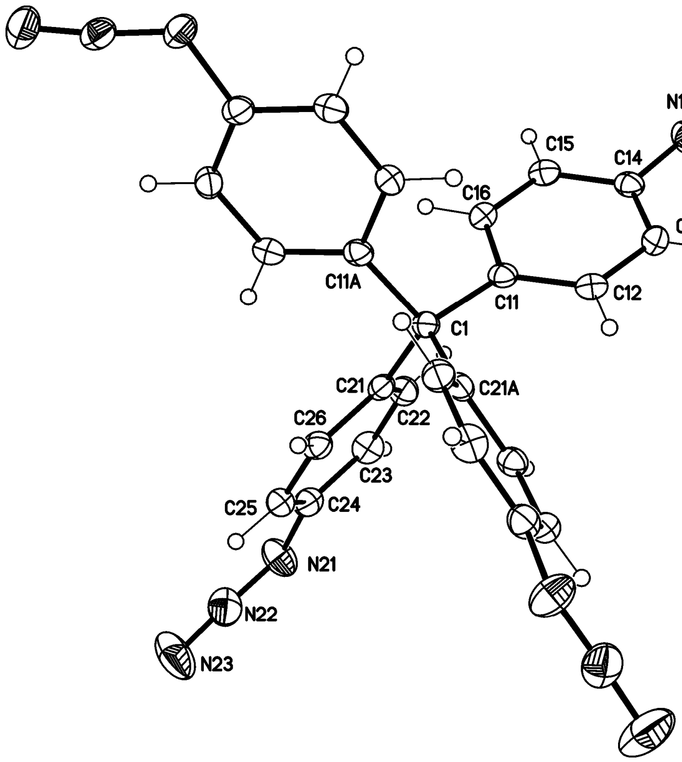
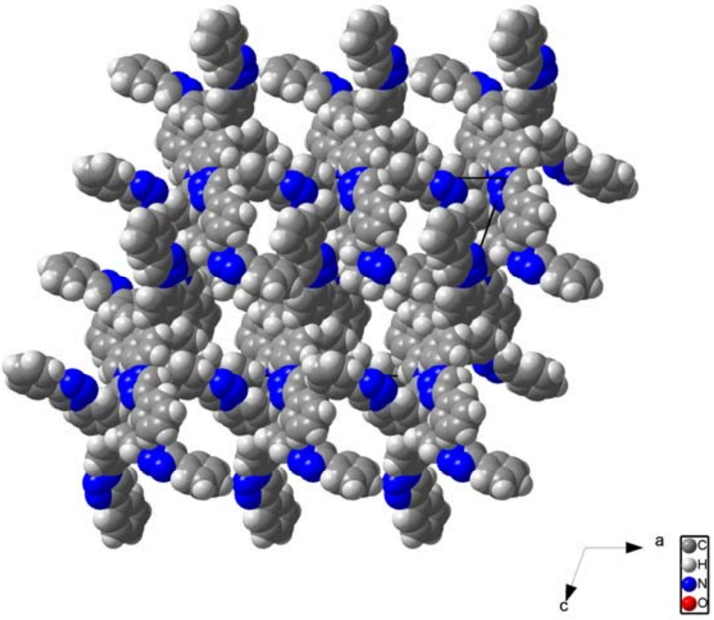


Fig. S3 Molecular structure of **7** (displacement parameters are drawn at 50% probability level). The molecule possesses crystallographic C_2-symmetry



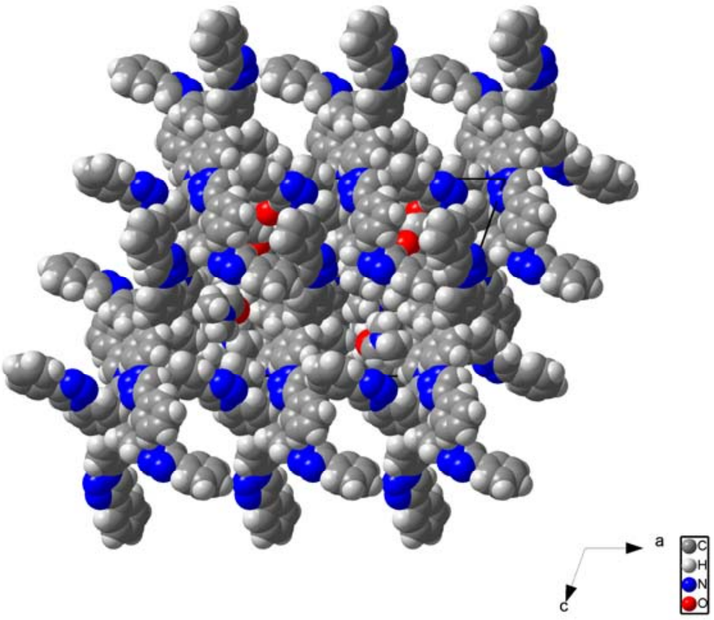


Fig. S4. Space filling representation of the unit cell of **1a** (projection along the b-axis); top: without solvent; bottom: solvent dmf included in the channels parallel the b-axis.

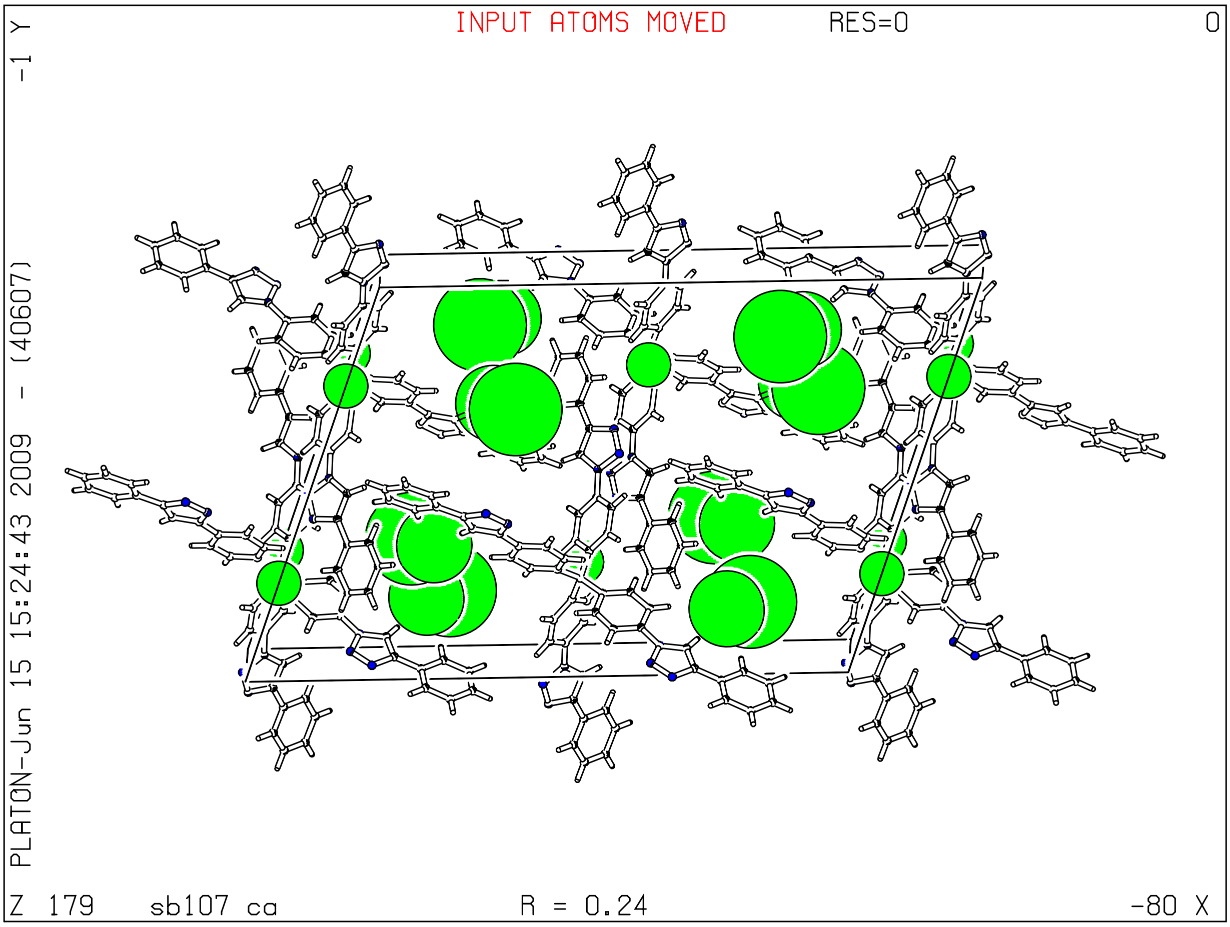


Fig. S5. Space filling representation of the voids in the unit cell of **1a.** 21.8% solvent area volume per unit cell volume (PLATON, A. L. Spek, J. Appl. Cryst. **2003**, *36*, 7-13) . The Percent Filled Space = 58.2 (= Packing Index), see A.I. Kitajgorodskij, Molecular Crystals and Molecules, New-York Academic Press, **1973**.

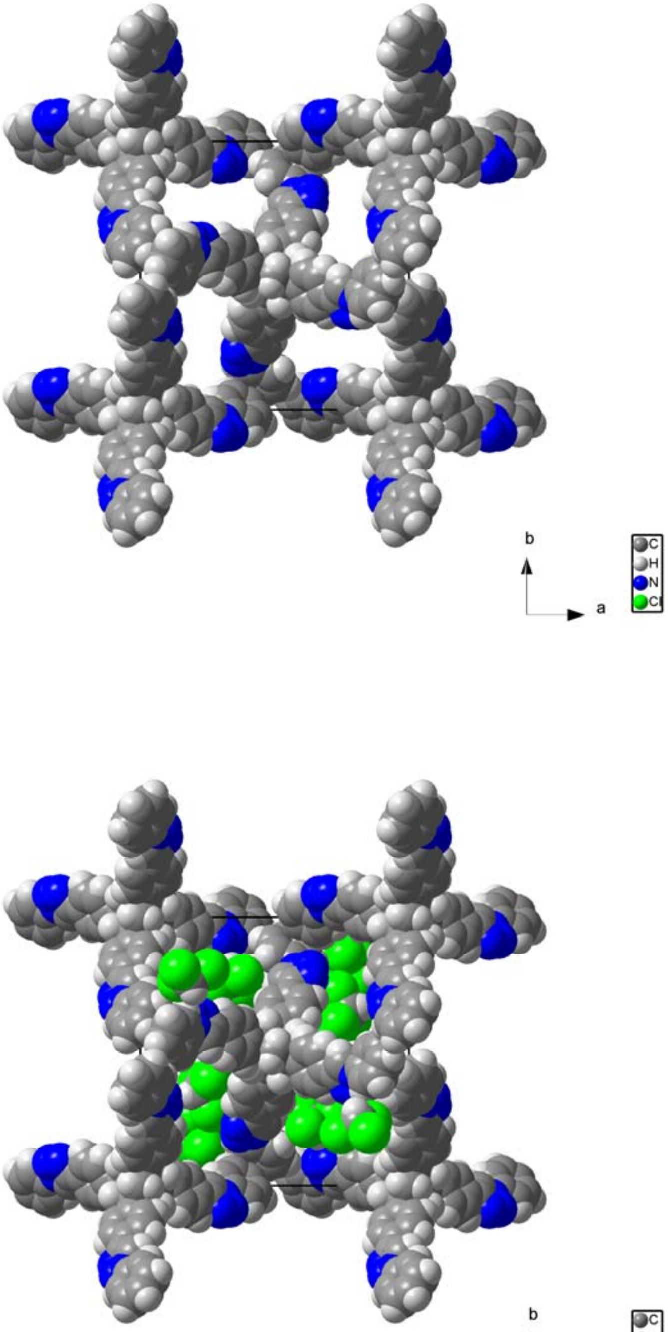


Fig. S6. Space filling representation of the unit cell of **4a** (projection along the c-axis); top: without solvent; bottom: solvent $CHCl_3$ included in the channels parallel the c-axis.

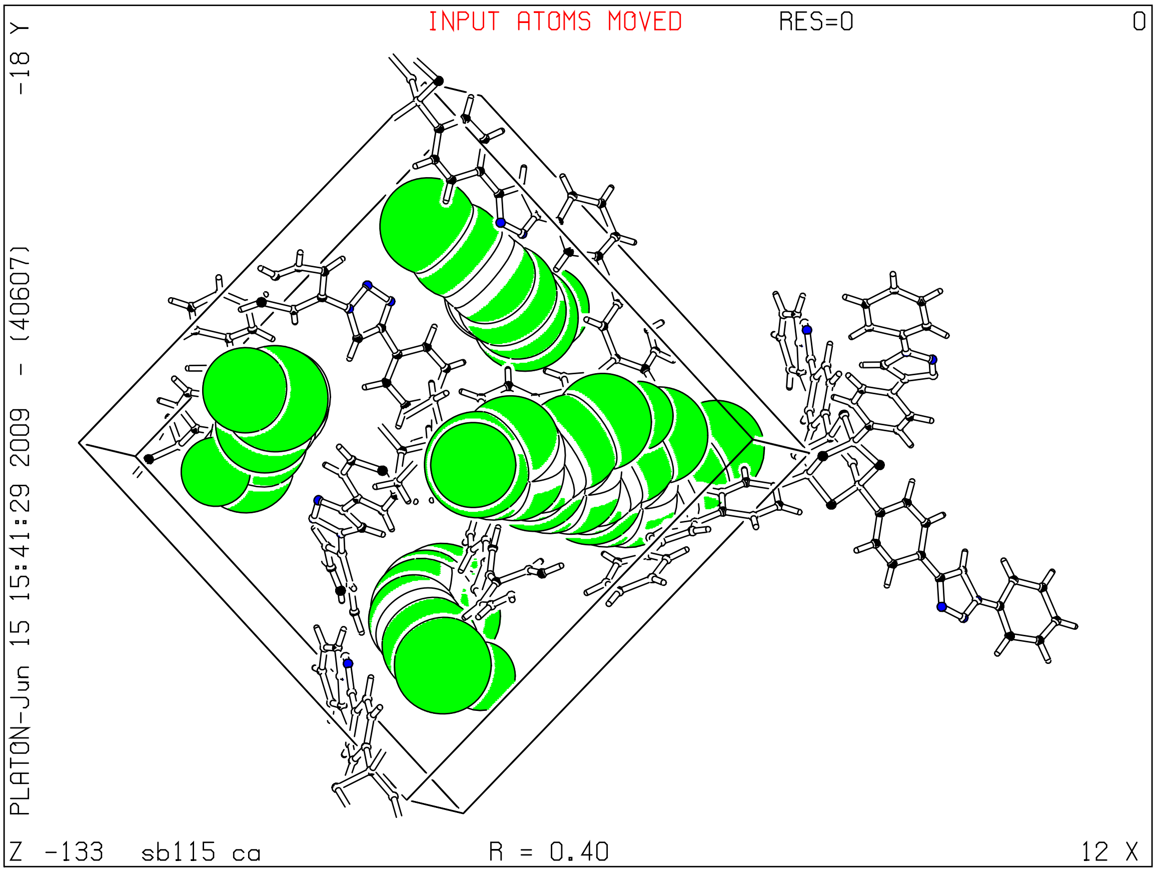


Fig. S7. Space filling representation of the voids in the unit cell of **4a.** 30.1% solvent area volume per unit cell volume (PLATON, A. L. Spek, J. Appl. Cryst. **2003**, *36*, 7-13) . The Percent Filled Space = 52.7 (= Packing Index), see A.I. Kitajgorodskij, Molecular Crystals and Molecules, New-York Academic Press, **1973**.

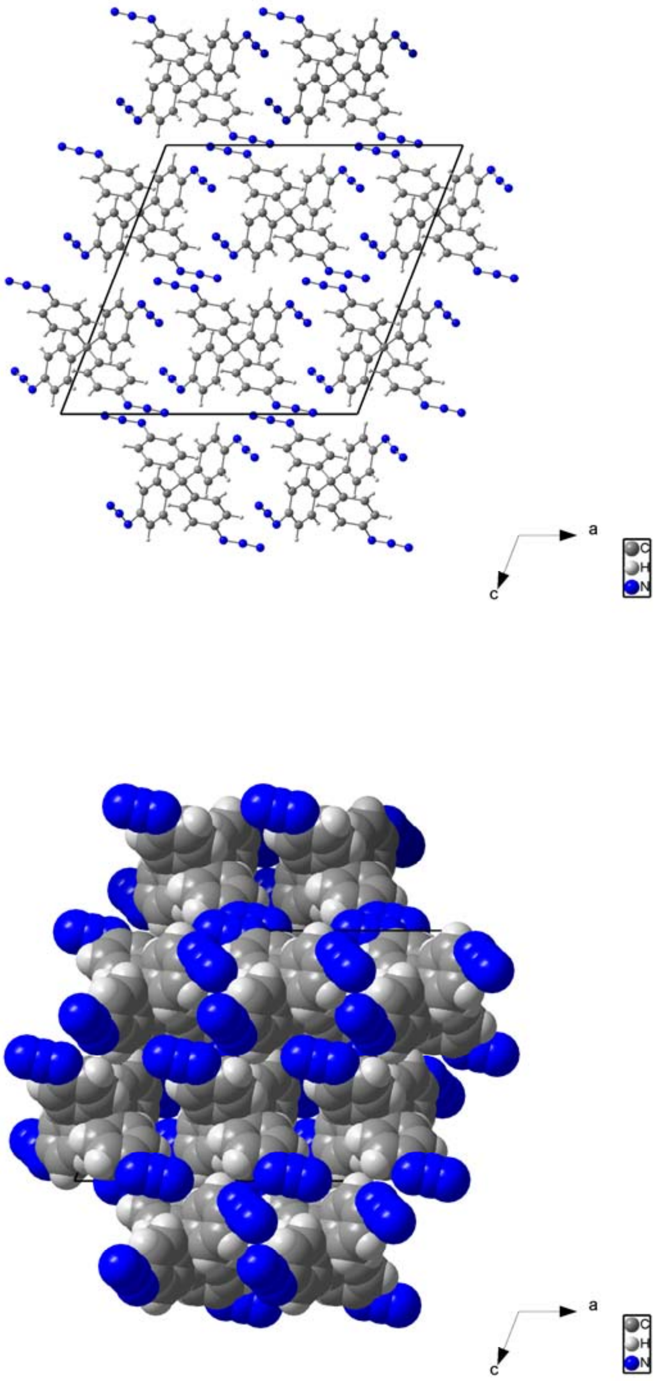


Fig. S8. Top: unit cell of **7**; bottom: space filling representation of the unit cell of **7** (projection along the b-axis). The Percent Filled Space = 69.9 (= Packing Index; structures have a typical packing index in the order of 65%), see A.I. Kitajgorodskij, Molecular Crystals and Molecules, New-York Academic Press, **1973**.

In the asymmetric unit of **4a** are two ¼ independent molecules. **1a** and **7** possess crystallographic C$_2$-symmetry (half a molecule in the asymmetric unit) while 4a possesses crystallographic S$_4$-symmetry. **1a** forms channels along the b-axis. These channels are occupied by solvent molecules dmf, showing a weak bifurcated acceptor hydrogen bond (see Fig. S1b). **4a** forms channels along the c-axis. These channels are occupied by solvent molecules CHCl$_3$, showing a weak bifurcated donor hydrogen bond (see Fig. S2b).

Table S1. Crystal data and structure refinement for 1a.

Identification code	sb107_hy
Empirical formula	C63 H54 N14 O2 C57 H40 N12 - 2 dmf
Formula weight	1039.20
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c (No.15)
Unit cell dimensions	a = 29.701(6) A alpha = 90 deg. b = 8.996(2) A beta = 109.53(2) deg. c = 20.844(4) A gamma = 90 deg.
Volume	5248.9(19) A^3
Z, Calculated density 4,	1.315 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	2184
Crystal size	0.40 x 0.16 x 0.04 mm
Theta range for data collection	2.99 to 25.03 deg.
Limiting indices	-35<=h<=34, -9<=k<=10, -24<=l<=24
Reflections collected / unique	20477 / 4625 [R(int) = 0.0730]
Completeness to theta = 25.03	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4625 / 37 / 356
Goodness-of-fit on F^2	1.053

Final R indices [I>2sigma(I)]	R1 = 0.0846, wR2 = 0.1970
R indices (all data)	R1 = 0.1413, wR2 = 0.2309
Largest diff. peak and hole	1.173 and -0.824 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	0	4888(7)	2500	25(1)
C(1A)	-9(1)	3939(5)	3113(2)	24(1)
C(2A)	-211(1)	4447(5)	3584(2)	27(1)
C(3A)	-135(1)	3704(5)	4195(2)	28(1)
C(4A)	148(1)	2451(5)	4345(2)	26(1)
C(5A)	341(2)	1901(5)	3876(2)	33(1)
C(6A)	263(2)	2643(5)	3267(2)	30(1)
N(7A)	272(1)	1767(4)	5000(2)	27(1)
N(8A)	16(1)	2049(4)	5419(2)	39(1)
N(9A)	227(1)	1332(4)	5987(2)	37(1)
C(10A)	619(2)	593(5)	5944(2)	29(1)
C(11A)	647(1)	887(5)	5314(2)	30(1)
C(12A)	922(2)	-309(5)	6509(2)	31(1)
C(13A)	1249(2)	-1308(6)	6399(2)	41(1)
C(14A)	1533(2)	-2177(6)	6926(3)	47(1)
C(15A)	1507(2)	-2044(6)	7570(2)	44(1)
C(16A)	1190(2)	-1049(6)	7687(2)	40(1)
C(17A)	897(2)	-198(6)	7161(2)	35(1)
C(1B)	448(1)	5865(5)	2815(2)	26(1)
C(2B)	900(1)	5469(5)	2824(2)	26(1)
C(3B)	1303(1)	6281(5)	3192(2)	28(1)
C(4B)	1248(1)	7506(5)	3566(2)	26(1)
C(5B)	800(2)	7900(5)	3567(2)	32(1)
C(6B)	404(2)	7107(5)	3191(2)	31(1)
N(7B)	1654(1)	8347(4)	3964(2)	29(1)
N(8B)	1589(1)	9589(4)	4299(2)	40(1)
N(9B)	2014(1)	10134(5)	4610(2)	39(1)

C(10B)	2351(2)	9264(5)	4484(2)	29(1)
C(11B)	2119(1)	8111(5)	4073(2)	29(1)
C(12B)	2865(2)	9605(5)	4764(2)	30(1)
C(13B)	3196(2)	8676(6)	4639(2)	37(1)
C(14B)	3683(2)	9001(6)	4907(2)	44(1)
C(15B)	3835(2)	10257(6)	5300(2)	41(1)
C(16B)	3503(2)	11195(6)	5424(2)	39(1)
C(17B)	3026(2)	10867(5)	5168(2)	36(1)
O(1D)	2468(2)	5259(5)	3363(3)	78(1)
C(1D)	2763(2)	4110(9)	3647(4)	93(2)
N(1D)	2898(2)	3396(7)	3251(3)	82(2)
C(11D)	2804(2)	3680(6)	2546(2)	51(1)
C(12D)	3237(3)	2055(7)	3510(2)	109(3)

Table S3. Bond lengths [A] and angles [deg] for 1a.

C(1)-C(1A)#1	1.544(5)
C(1)-C(1A)	1.544(5)
C(1)-C(1B)	1.545(5)
C(1)-C(1B)#1	1.545(5)
C(1A)-C(2A)	1.390(5)
C(1A)-C(6A)	1.393(6)
C(2A)-C(3A)	1.388(6)
C(3A)-C(4A)	1.378(6)
C(4A)-C(5A)	1.382(6)
C(4A)-N(7A)	1.428(5)
C(5A)-C(6A)	1.383(6)
N(7A)-C(11A)	1.343(5)
N(7A)-N(8A)	1.361(5)
N(8A)-N(9A)	1.309(5)
N(9A)-C(10A)	1.367(5)
C(10A)-C(11A)	1.369(6)
C(10A)-C(12A)	1.466(6)
C(12A)-C(17A)	1.388(6)
C(12A)-C(13A)	1.397(6)
C(13A)-C(14A)	1.381(7)
C(14A)-C(15A)	1.376(7)
C(15A)-C(16A)	1.379(7)
C(16A)-C(17A)	1.381(6)
C(1B)-C(2B)	1.384(5)
C(1B)-C(6B)	1.395(6)
C(2B)-C(3B)	1.393(6)
C(3B)-C(4B)	1.391(6)
C(4B)-C(5B)	1.378(6)
C(4B)-N(7B)	1.430(5)
C(5B)-C(6B)	1.375(6)
N(7B)-C(11B)	1.340(5)

N(7B)-N(8B) 1.366(5)
N(8B)-N(9B) 1.308(5)
N(9B)-C(10B) 1.362(6)
C(10B)-C(11B) 1.375(6)
C(10B)-C(12B) 1.475(6)
C(12B)-C(13B) 1.379(6)
C(12B)-C(17B) 1.399(6)
C(13B)-C(14B) 1.397(6)
C(14B)-C(15B) 1.381(7)
C(15B)-C(16B) 1.386(7)
C(16B)-C(17B) 1.369(6)
O(1D)-C(1D) 1.357(8)
C(1D)-N(1D) 1.215(8)
N(1D)-C(11D) 1.425(7)
N(1D)-C(12D) 1.548(8)

C(1A)#1-C(1)-C(1A) 112.8(5)
C(1A)#1-C(1)-C(1B) 114.6(2)
C(1A)-C(1)-C(1B) 102.3(2)
C(1A)#1-C(1)-C(1B)#1 102.3(2)
C(1A)-C(1)-C(1B)#1 114.6(2)
C(1B)-C(1)-C(1B)#1 110.7(5)
C(2A)-C(1A)-C(6A) 117.8(4)
C(2A)-C(1A)-C(1) 122.2(4)
C(6A)-C(1A)-C(1) 119.0(3)
C(3A)-C(2A)-C(1A) 120.9(4)
C(4A)-C(3A)-C(2A) 120.1(4)
C(3A)-C(4A)-C(5A) 119.9(4)
C(3A)-C(4A)-N(7A) 120.9(4)
C(5A)-C(4A)-N(7A) 119.0(4)
C(4A)-C(5A)-C(6A) 119.6(4)
C(5A)-C(6A)-C(1A) 121.5(4)
C(11A)-N(7A)-N(8A) 110.2(3)
C(11A)-N(7A)-C(4A) 129.0(3)
N(8A)-N(7A)-C(4A) 120.7(3)
N(9A)-N(8A)-N(7A) 106.7(3)
N(8A)-N(9A)-C(10A) 110.0(3)
N(9A)-C(10A)-C(11A) 107.1(4)
N(9A)-C(10A)-C(12A) 121.7(4)
C(11A)-C(10A)-C(12A) 131.3(4)
N(7A)-C(11A)-C(10A) 106.1(4)
C(17A)-C(12A)-C(13A) 118.3(4)
C(17A)-C(12A)-C(10A) 121.8(4)
C(13A)-C(12A)-C(10A) 119.9(4)
C(14A)-C(13A)-C(12A) 120.4(4)
C(15A)-C(14A)-C(13A) 120.6(5)
C(14A)-C(15A)-C(16A) 119.5(5)
C(15A)-C(16A)-C(17A) 120.4(4)
C(16A)-C(17A)-C(12A) 120.8(5)
C(2B)-C(1B)-C(6B) 118.1(4)
C(2B)-C(1B)-C(1) 123.5(4)

C(6B)-C(1B)-C(1) 117.8(3)
C(1B)-C(2B)-C(3B) 121.5(4)
C(4B)-C(3B)-C(2B) 118.9(4)
C(5B)-C(4B)-C(3B) 120.0(4)
C(5B)-C(4B)-N(7B) 119.4(4)
C(3B)-C(4B)-N(7B) 120.6(4)
C(6B)-C(5B)-C(4B) 120.5(4)
C(5B)-C(6B)-C(1B) 120.9(4)
C(11B)-N(7B)-N(8B) 110.9(3)
C(11B)-N(7B)-C(4B) 129.5(4)
N(8B)-N(7B)-C(4B) 119.5(3)
N(9B)-N(8B)-N(7B) 106.4(3)
N(8B)-N(9B)-C(10B) 109.8(4)
N(9B)-C(10B)-C(11B) 107.9(4)
N(9B)-C(10B)-C(12B) 122.3(4)
C(11B)-C(10B)-C(12B) 129.8(4)
N(7B)-C(11B)-C(10B) 105.0(4)
C(13B)-C(12B)-C(17B) 119.0(4)
C(13B)-C(12B)-C(10B) 120.5(4)
C(17B)-C(12B)-C(10B) 120.5(4)
C(12B)-C(13B)-C(14B) 120.3(4)
C(15B)-C(14B)-C(13B) 120.0(5)
C(14B)-C(15B)-C(16B) 119.8(4)
C(17B)-C(16B)-C(15B) 120.3(5)
C(16B)-C(17B)-C(12B) 120.7(4)
N(1D)-C(1D)-O(1D) 114.8(7)
C(1D)-N(1D)-C(11D) 127.6(7)
C(1D)-N(1D)-C(12D) 120.0(6)
C(11D)-N(1D)-C(12D) 112.3(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for 1a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(3)	24(3)	31(3)	0	9(2)	0
C(1A)	21(2)	22(2)	29(2)	-4(2)	8(2)	-3(2)
C(2A)	20(2)	27(3)	32(2)	-2(2)	8(2)	2(2)
C(3A)	22(2)	30(3)	32(2)	-3(2)	12(2)	1(2)
C(4A)	27(2)	25(2)	27(2)	-2(2)	9(2)	-3(2)
C(5A)	40(2)	23(3)	35(2)	1(2)	13(2)	6(2)

C(6A)	35(2)	26(3)	32(2)	-3(2)	15(2)	4(2)
N(7A)	31(2)	25(2)	26(2)	-4(2)	11(2)	-2(2)
N(8A)	47(2)	38(3)	36(2)	1(2)	21(2)	8(2)
N(9A)	46(2)	35(2)	34(2)	5(2)	20(2)	10(2)
C(10A)	30(2)	26(3)	31(2)	-5(2)	10(2)	-4(2)
C(11A)	24(2)	35(3)	30(2)	-3(2)	8(2)	1(2)
C(12A)	31(2)	28(3)	35(2)	-2(2)	11(2)	-7(2)
C(13A)	43(3)	45(3)	32(2)	-4(2)	10(2)	2(2)
C(14A)	38(3)	43(3)	56(3)	7(3)	13(2)	10(2)
C(15A)	36(3)	47(3)	43(3)	12(2)	4(2)	-7(2)
C(16A)	43(3)	42(3)	37(2)	6(2)	16(2)	-9(2)
C(17A)	35(2)	39(3)	34(2)	1(2)	13(2)	-4(2)
C(1B)	25(2)	22(2)	30(2)	2(2)	9(2)	0(2)
C(2B)	26(2)	22(2)	31(2)	-4(2)	11(2)	4(2)
C(3B)	23(2)	30(3)	31(2)	-2(2)	10(2)	4(2)
C(4B)	23(2)	22(2)	31(2)	-1(2)	6(2)	-2(2)
C(5B)	32(2)	24(3)	44(3)	-6(2)	18(2)	4(2)
C(6B)	26(2)	26(3)	43(2)	-5(2)	15(2)	0(2)
N(7B)	30(2)	26(2)	30(2)	-6(2)	9(2)	1(2)
N(8B)	31(2)	34(2)	48(2)	-14(2)	5(2)	1(2)
N(9B)	30(2)	36(2)	45(2)	-11(2)	6(2)	-1(2)
C(10B)	29(2)	27(3)	31(2)	1(2)	9(2)	-2(2)
C(11B)	23(2)	31(3)	33(2)	-2(2)	10(2)	-4(2)
C(12B)	33(2)	27(3)	28(2)	3(2)	9(2)	-2(2)
C(13B)	35(2)	33(3)	43(3)	-7(2)	14(2)	-5(2)
C(14B)	36(3)	47(3)	51(3)	-6(3)	18(2)	-3(2)
C(15B)	31(2)	46(3)	44(3)	-3(2)	10(2)	-11(2)
C(16B)	37(3)	39(3)	38(3)	-7(2)	8(2)	-11(2)
C(17B)	34(2)	33(3)	37(2)	-2(2)	9(2)	1(2)
O(1D)	58(3)	63(3)	129(4)	4(3)	51(3)	9(2)
C(1D)	74(5)	120(6)	106(5)	-42(5)	59(4)	-41(4)
N(1D)	88(4)	92(4)	76(3)	-19(3)	41(3)	-33(3)
C(11D)	52(3)	62(4)	42(3)	-8(3)	20(2)	-16(3)
C(12D)	99(6)	96(6)	122(7)	33(5)	21(5)	1(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1a.

	x	y	z	U(eq)
H(2A)	-405	5315	3487	32
H(3A)	-278	4061	4511	33
H(5A)	527	1017	3971	39
H(6A)	399	2262	2947	36
H(11A)	883	540	5136	36

H(13A)	1277	-1390	5960	49
H(14A)	1747	-2873	6842	56
H(15A)	1706	-2633	7932	53
H(16A)	1173	-947	8132	48
H(17A)	676	470	7246	43
H(2B)	937	4623	2573	31
H(3B)	1611	6003	3187	33
H(5B)	764	8726	3830	38
H(6B)	97	7409	3186	37
H(11B)	2258	7320	3903	34
H(13B)	3091	7811	4368	44
H(14B)	3909	8358	4819	52
H(15B)	4166	10479	5485	50
H(16B)	3607	12068	5689	47
H(17B)	2802	11504	5265	43
H(1D)	2857	3882	4119	111
H(11C)	2481	4081	2345	76
H(11D)	2831	2751	2315	76
H(11E)	3036	4401	2493	76
H(12A)	3405	2159	4000	164
H(12B)	3471	2023	3271	164
H(12C)	3051	1133	3423	164

Table S6. Torsion angles [deg] for 1a.

C(1A)#1-C(1)-C(1A)-C(2A)	-152.4(4)
C(1B)-C(1)-C(1A)-C(2A)	84.0(4)
C(1B)#1-C(1)-C(1A)-C(2A)	-35.9(5)
C(1A)#1-C(1)-C(1A)-C(6A)	38.7(3)
C(1B)-C(1)-C(1A)-C(6A)	-84.9(5)
C(1B)#1-C(1)-C(1A)-C(6A)	155.3(4)
C(6A)-C(1A)-C(2A)-C(3A)	1.5(6)
C(1)-C(1A)-C(2A)-C(3A)	-167.5(3)
C(1A)-C(2A)-C(3A)-C(4A)	0.5(6)
C(2A)-C(3A)-C(4A)-C(5A)	-2.4(6)
C(2A)-C(3A)-C(4A)-N(7A)	173.1(4)
C(3A)-C(4A)-C(5A)-C(6A)	2.2(6)
N(7A)-C(4A)-C(5A)-C(6A)	-173.3(4)
C(4A)-C(5A)-C(6A)-C(1A)	-0.2(7)
C(2A)-C(1A)-C(6A)-C(5A)	-1.6(6)
C(1)-C(1A)-C(6A)-C(5A)	167.8(4)
C(3A)-C(4A)-N(7A)-C(11A)	-156.5(4)
C(5A)-C(4A)-N(7A)-C(11A)	19.0(6)
C(3A)-C(4A)-N(7A)-N(8A)	18.8(6)
C(5A)-C(4A)-N(7A)-N(8A)	-165.6(4)
C(11A)-N(7A)-N(8A)-N(9A)	-0.8(5)
C(4A)-N(7A)-N(8A)-N(9A)	-177.0(4)

N(7A)-N(8A)-N(9A)-C(10A) 0.3(5)
N(8A)-N(9A)-C(10A)-C(11A) 0.3(5)
N(8A)-N(9A)-C(10A)-C(12A) -179.8(4)
N(8A)-N(7A)-C(11A)-C(10A) 1.0(5)
C(4A)-N(7A)-C(11A)-C(10A) 176.7(4)
N(9A)-C(10A)-C(11A)-N(7A) -0.8(5)
C(12A)-C(10A)-C(11A)-N(7A) 179.4(4)
N(9A)-C(10A)-C(12A)-C(17A) -14.8(7)
C(11A)-C(10A)-C(12A)-C(17A) 165.0(5)
N(9A)-C(10A)-C(12A)-C(13A) 165.4(4)
C(11A)-C(10A)-C(12A)-C(13A) -14.7(7)
C(17A)-C(12A)-C(13A)-C(14A) 1.1(7)
C(10A)-C(12A)-C(13A)-C(14A) -179.1(4)
C(12A)-C(13A)-C(14A)-C(15A) -1.8(8)
C(13A)-C(14A)-C(15A)-C(16A) 1.0(8)
C(14A)-C(15A)-C(16A)-C(17A) 0.5(7)
C(15A)-C(16A)-C(17A)-C(12A) -1.2(7)
C(13A)-C(12A)-C(17A)-C(16A) 0.4(7)
C(10A)-C(12A)-C(17A)-C(16A) -179.4(4)
C(1A)#1-C(1)-C(1B)-C(2B) -31.4(5)
C(1A)-C(1)-C(1B)-C(2B) 91.0(4)
C(1B)#1-C(1)-C(1B)-C(2B) -146.5(4)
C(1A)#1-C(1)-C(1B)-C(6B) 157.6(4)
C(1A)-C(1)-C(1B)-C(6B) -80.0(5)
C(1B)#1-C(1)-C(1B)-C(6B) 42.6(3)
C(6B)-C(1B)-C(2B)-C(3B) -0.3(6)
C(1)-C(1B)-C(2B)-C(3B) -171.2(3)
C(1B)-C(2B)-C(3B)-C(4B) 0.9(6)
C(2B)-C(3B)-C(4B)-C(5B) -0.2(6)
C(2B)-C(3B)-C(4B)-N(7B) 178.5(4)
C(3B)-C(4B)-C(5B)-C(6B) -1.2(7)
N(7B)-C(4B)-C(5B)-C(6B) -179.9(4)
C(4B)-C(5B)-C(6B)-C(1B) 1.8(7)
C(2B)-C(1B)-C(6B)-C(5B) -1.1(6)
C(1)-C(1B)-C(6B)-C(5B) 170.4(4)
C(5B)-C(4B)-N(7B)-C(11B) 175.2(4)
C(3B)-C(4B)-N(7B)-C(11B) -3.4(7)
C(5B)-C(4B)-N(7B)-N(8B) -4.6(6)
C(3B)-C(4B)-N(7B)-N(8B) 176.7(4)
C(11B)-N(7B)-N(8B)-N(9B) 0.8(5)
C(4B)-N(7B)-N(8B)-N(9B) -179.4(4)
N(7B)-N(8B)-N(9B)-C(10B) -0.3(5)
N(8B)-N(9B)-C(10B)-C(11B) -0.2(5)
N(8B)-N(9B)-C(10B)-C(12B) 179.6(4)
N(8B)-N(7B)-C(11B)-C(10B) -0.8(5)
C(4B)-N(7B)-C(11B)-C(10B) 179.3(4)
N(9B)-C(10B)-C(11B)-N(7B) 0.6(5)
C(12B)-C(10B)-C(11B)-N(7B) -179.2(4)
N(9B)-C(10B)-C(12B)-C(13B) 178.4(4)
C(11B)-C(10B)-C(12B)-C(13B) -1.8(7)
N(9B)-C(10B)-C(12B)-C(17B) -0.9(6)

C(11B)-C(10B)-C(12B)-C(17B) 178.8(4)
C(17B)-C(12B)-C(13B)-C(14B) -0.5(7)
C(10B)-C(12B)-C(13B)-C(14B) -179.8(4)
C(12B)-C(13B)-C(14B)-C(15B) 0.0(7)
C(13B)-C(14B)-C(15B)-C(16B) -0.3(7)
C(14B)-C(15B)-C(16B)-C(17B) 1.0(7)
C(15B)-C(16B)-C(17B)-C(12B) -1.5(7)
C(13B)-C(12B)-C(17B)-C(16B) 1.2(6)
C(10B)-C(12B)-C(17B)-C(16B) -179.4(4)
O(1D)-C(1D)-N(1D)-C(11D) 3.8(10)
O(1D)-C(1D)-N(1D)-C(12D) 180.0(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table S7. Hydrogen bonds for 1a [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3B)-H(3B)...O(1D)	0.95	2.54	3.480(6)	171.6
C(11B)-H(11B)...O(1D)	0.95	2.36	3.296(6)	170.1
C(6B)-H(6B)...N(9A)#2	0.95	2.51	3.252(5)	135.3
C(11D)-H(11D)...O(1D)#3	0.98	2.64	3.562(7)	156.7
C(1D)-H(1D)...N(9B)#4	0.95	2.70	3.534(8)	147.3

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2 #2 -x,-y+1,-z+1 #3 -x+1/2,y-1/2,-z+1/2
#4 -x+1/2,-y+3/2,-z+1

Table S8. Crystal data and structure refinement for 4a.

Identification code	sb115_hy
Empirical formula	C70 H56 Cl12 N12 C66 H52 N12 - 4 CHCl3
Formula weight	1490.67
Temperature	123(2) K

Wavelength	0.71073 A
Crystal system, space group	Tetragonal, P-4 (No.81)
Unit cell dimensions	a = 21.970(3) A alpha = 90 deg. b = 21.970(3) A beta = 90 deg. c = 6.972(1) A gamma = 90 deg.
Volume	3365.3(8) A^3
Z, Calculated density 2,	1.471 Mg/m^3
Absorption coefficient	0.547 mm^-1
F(000)	1528
Crystal size	0.40 x 0.25 x 0.15 mm
Theta range for data collection	2.93 to 27.47 deg.
Limiting indices	-23<=h<=28, -28<=k<=27, -9<=l<=6
Reflections collected / unique	17869 / 7550 [R(int) = 0.0344]
Completeness to theta = 27.47	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9803 and 0.7900
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7550 / 0 / 425

Goodness-of-fit on F^2 1.058

Final R indices [I>2sigma(I)] R1 = 0.0502, wR2 = 0.1238

R indices (all data) R1 = 0.0617, wR2 = 0.1315

Absolute structure parameter 0.01(6)

Largest diff. peak and hole 0.909 and -0.456 e.A^-3

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters (A^2 x 10^3) for 4a.
U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

	x	y	z	U(eq)
C(1)	5353(1)	4274(1)	10018(4)	14(1)
C(2)	4815(1)	4451(1)	8728(4)	13(1)
C(3)	5000	5000	7483(5)	14(1)
C(4)	4649(1)	3925(1)	7382(4)	14(1)
C(5)	4072(1)	3666(1)	7305(4)	19(1)
C(6)	3926(1)	3225(1)	5939(4)	21(1)
C(7)	4362(1)	3030(1)	4620(4)	19(1)
C(8)	4949(1)	3269(1)	4750(4)	18(1)
C(9)	5089(1)	3710(1)	6108(4)	17(1)
C(10)	4215(1)	2587(1)	3118(4)	20(1)
N(11)	3686(1)	2271(1)	3083(4)	27(1)
N(12)	3679(1)	1912(1)	1578(4)	27(1)
N(13)	4211(1)	1999(1)	654(4)	24(1)
C(14)	4549(1)	2416(2)	1564(4)	26(1)
C(15)	4357(2)	1642(1)	-1006(4)	25(1)
C(16)	3927(2)	1523(2)	-2358(5)	33(1)
C(17)	4070(2)	1154(2)	-3906(5)	39(1)
C(18)	4641(2)	913(2)	-4070(6)	44(1)
C(19)	5075(2)	1029(2)	-2680(6)	48(1)
C(20)	4938(2)	1399(2)	-1145(5)	41(1)
C(1')	-439(1)	677(1)	4998(4)	12(1)
C(2')	123(1)	569(1)	6278(3)	12(1)
C(3')	0	0	7496(5)	12(1)
C(4')	218(1)	1108(1)	7618(4)	13(1)
C(5')	-207(1)	1241(1)	9019(4)	14(1)
C(6')	-118(1)	1697(1)	10352(4)	17(1)
C(7')	418(1)	2037(1)	10348(4)	17(1)
C(8')	846(1)	1922(1)	8904(4)	19(1)
C(9')	744(1)	1468(1)	7572(4)	17(1)
C(10')	513(1)	2503(1)	11817(4)	19(1)
N(11')	897(1)	2984(1)	11606(4)	26(1)
N(12')	853(1)	3333(1)	13125(4)	29(1)
N(13')	450(1)	3073(1)	14329(4)	24(1)
C(14')	230(1)	2556(2)	13572(4)	25(1)
C(15')	274(2)	3365(2)	16100(5)	29(1)
C(16')	542(2)	3902(2)	16592(6)	45(1)
C(17')	335(2)	4197(2)	18258(6)	51(1)
C(18')	-113(2)	3952(2)	19360(5)	46(1)
C(19')	-365(2)	3415(2)	18862(5)	41(1)
C(20')	-177(2)	3108(2)	17210(5)	34(1)
C(1C)	2339(2)	1874(2)	4320(5)	30(1)
Cl(1)	2385(1)	1412(1)	6397(2)	44(1)
Cl(2)	1953(1)	2543(1)	4857(1)	46(1)
Cl(3)	1959(1)	1472(1)	2508(2)	51(1)
C(2C)	2248(2)	3455(2)	10112(5)	35(1)

Cl(4)	2171(1)	3817(1)	7844(2)	51(1)
Cl(5)	2630(1)	3941(1)	11678(2)	58(1)
Cl(6)	2638(1)	2770(1)	9814(2)	52(1)

Table S10. Bond lengths [A] and angles [deg] for 4a.

C(1)-C(2)	1.536(4)
C(1)-C(2)#1	1.536(3)
C(2)-C(4)	1.532(3)
C(2)-C(1)#2	1.536(3)
C(2)-C(3)	1.541(3)
C(3)-C(2)#3	1.541(3)
C(4)-C(5)	1.391(4)
C(4)-C(9)	1.394(4)
C(5)-C(6)	1.397(4)
C(6)-C(7)	1.395(4)
C(7)-C(8)	1.396(4)
C(7)-C(10)	1.466(4)
C(8)-C(9)	1.388(4)
C(10)-N(11)	1.353(4)
C(10)-C(14)	1.361(4)
N(11)-N(12)	1.313(4)
N(12)-N(13)	1.347(4)
N(13)-C(14)	1.339(4)
N(13)-C(15)	1.435(4)
C(15)-C(16)	1.360(5)
C(15)-C(20)	1.387(5)
C(16)-C(17)	1.385(5)
C(17)-C(18)	1.366(6)
C(18)-C(19)	1.384(6)
C(19)-C(20)	1.377(5)
C(1')-C(2')#4	1.534(3)
C(1')-C(2')	1.543(3)
C(2')-C(4')	1.523(4)
C(2')-C(1')#5	1.534(3)
C(2')-C(3')	1.535(3)
C(3')-C(2')#6	1.535(3)
C(4')-C(5')	1.383(4)
C(4')-C(9')	1.399(4)
C(5')-C(6')	1.381(4)
C(6')-C(7')	1.394(4)
C(7')-C(8')	1.401(4)
C(7')-C(10')	1.464(4)
C(8')-C(9')	1.381(4)
C(10')-N(11')	1.360(4)
C(10')-C(14')	1.377(4)
N(11')-N(12')	1.311(4)

N(12')-N(13') 1.347(4)
N(13')-C(14') 1.342(4)
N(13')-C(15') 1.444(4)
C(15')-C(16') 1.360(5)
C(15')-C(20') 1.380(5)
C(16')-C(17') 1.406(6)
C(17')-C(18') 1.359(7)
C(18')-C(19') 1.347(6)
C(19')-C(20') 1.398(5)
C(1C)-Cl(2) 1.738(4)
C(1C)-Cl(3) 1.753(3)
C(1C)-Cl(1) 1.771(4)
C(2C)-Cl(5) 1.743(4)
C(2C)-Cl(6) 1.745(4)
C(2C)-Cl(4) 1.778(4)

C(2)-C(1)-C(2)#1 110.7(2)
C(4)-C(2)-C(1) 110.5(2)
C(4)-C(2)-C(1)#2 112.1(2)
C(1)-C(2)-C(1)#2 109.44(18)
C(4)-C(2)-C(3) 107.9(2)
C(1)-C(2)-C(3) 109.0(2)
C(1)#2-C(2)-C(3) 107.78(19)
C(2)#3-C(3)-C(2) 111.4(3)
C(5)-C(4)-C(9) 117.9(2)
C(5)-C(4)-C(2) 123.2(2)
C(9)-C(4)-C(2) 118.8(2)
C(4)-C(5)-C(6) 121.4(3)
C(7)-C(6)-C(5) 120.2(3)
C(6)-C(7)-C(8) 118.5(3)
C(6)-C(7)-C(10) 121.6(3)
C(8)-C(7)-C(10) 120.0(3)
C(9)-C(8)-C(7) 120.8(2)
C(8)-C(9)-C(4) 121.2(3)
N(11)-C(10)-C(14) 107.8(3)
N(11)-C(10)-C(7) 122.8(3)
C(14)-C(10)-C(7) 129.3(3)
N(12)-N(11)-C(10) 109.5(3)
N(11)-N(12)-N(13) 106.6(2)
C(14)-N(13)-N(12) 110.6(2)
C(14)-N(13)-C(15) 129.2(3)
N(12)-N(13)-C(15) 120.2(2)
N(13)-C(14)-C(10) 105.5(3)
C(16)-C(15)-C(20) 121.2(3)
C(16)-C(15)-N(13) 120.6(3)
C(20)-C(15)-N(13) 118.2(3)
C(15)-C(16)-C(17) 119.6(3)
C(18)-C(17)-C(16) 120.0(3)
C(17)-C(18)-C(19) 120.2(3)
C(20)-C(19)-C(18) 120.1(4)
C(19)-C(20)-C(15) 118.9(3)

C(2')#4-C(1')-C(2') 111.2(2)
C(4')-C(2')-C(1')#5 113.0(2)
C(4')-C(2')-C(3') 108.6(2)
C(1')#5-C(2')-C(3') 108.02(19)
C(4')-C(2')-C(1') 110.2(2)
C(1')#5-C(2')-C(1') 109.17(17)
C(3')-C(2')-C(1') 107.73(19)
C(2')#6-C(3')-C(2') 112.8(3)
C(5')-C(4')-C(9') 117.1(2)
C(5')-C(4')-C(2') 120.2(2)
C(9')-C(4')-C(2') 122.6(2)
C(6')-C(5')-C(4') 122.1(2)
C(5')-C(6')-C(7') 120.5(3)
C(6')-C(7')-C(8') 118.2(2)
C(6')-C(7')-C(10') 119.7(2)
C(8')-C(7')-C(10') 122.2(3)
C(9')-C(8')-C(7') 120.2(3)
C(8')-C(9')-C(4') 121.8(3)
N(11')-C(10')-C(14') 108.0(3)
N(11')-C(10')-C(7') 123.8(3)
C(14')-C(10')-C(7') 128.1(3)
N(12')-N(11')-C(10') 108.7(3)
N(11')-N(12')-N(13') 107.7(2)
C(14')-N(13')-N(12') 110.5(2)
C(14')-N(13')-C(15') 128.0(3)
N(12')-N(13')-C(15') 121.4(3)
N(13')-C(14')-C(10') 105.0(3)
C(16')-C(15')-C(20') 121.6(3)
C(16')-C(15')-N(13') 119.0(3)
C(20')-C(15')-N(13') 119.3(3)
C(15')-C(16')-C(17') 117.9(4)
C(18')-C(17')-C(16') 121.2(4)
C(19')-C(18')-C(17') 119.9(3)
C(18')-C(19')-C(20') 120.9(4)
C(15')-C(20')-C(19') 118.5(4)
Cl(2)-C(1C)-Cl(3) 110.4(2)
Cl(2)-C(1C)-Cl(1) 109.68(19)
Cl(3)-C(1C)-Cl(1) 109.11(19)
Cl(5)-C(2C)-Cl(6) 111.5(2)
Cl(5)-C(2C)-Cl(4) 109.2(2)
Cl(6)-C(2C)-Cl(4) 109.1(2)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x,-z+2 #2 y,-x+1,-z+2 #3 -x+1,-y+1,z
#4 -y,x,-z+1 #5 y,-x,-z+1 #6 -x,-y,z

Table S11. Anisotropic displacement parameters (A^2 x 10^3) for 4a.
The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	16(1)	10(1)	-2(1)	2(1)	2(1)
C(2)	17(1)	14(1)	9(1)	-1(1)	0(1)	-1(1)
C(3)	14(2)	18(2)	10(2)	0	0	-2(2)
C(4)	22(1)	12(1)	9(1)	0(1)	-2(1)	-1(1)
C(5)	20(1)	20(1)	18(1)	-3(1)	4(1)	-1(1)
C(6)	17(1)	22(1)	23(1)	-3(1)	2(1)	-6(1)
C(7)	20(1)	17(1)	19(1)	-3(1)	-2(1)	-1(1)
C(8)	20(1)	24(1)	11(1)	-5(1)	2(1)	0(1)
C(9)	17(1)	17(1)	15(1)	-2(1)	0(1)	-1(1)
C(10)	19(1)	21(1)	21(1)	-3(1)	0(1)	-2(1)
N(11)	26(1)	27(1)	29(1)	-9(1)	1(1)	-7(1)
N(12)	22(1)	28(1)	31(1)	-14(1)	2(1)	-5(1)
N(13)	22(1)	27(1)	23(1)	-10(1)	-2(1)	-1(1)
C(14)	23(2)	30(2)	26(2)	-12(1)	0(1)	-8(1)
C(15)	26(2)	25(2)	24(2)	-11(1)	-2(1)	-2(1)
C(16)	33(2)	32(2)	33(2)	-9(1)	-7(1)	3(1)
C(17)	43(2)	42(2)	31(2)	-12(2)	-9(2)	0(2)
C(18)	48(2)	51(2)	33(2)	-25(2)	0(2)	0(2)
C(19)	30(2)	63(3)	52(2)	-22(2)	5(2)	4(2)
C(20)	30(2)	56(2)	38(2)	-16(2)	-4(2)	-4(2)
C(1')	15(1)	12(1)	11(1)	0(1)	-3(1)	0(1)
C(2')	11(1)	16(1)	9(1)	0(1)	0(1)	0(1)
C(3')	16(2)	11(2)	7(1)	0	0	0(1)
C(4')	16(1)	12(1)	11(1)	1(1)	-3(1)	-1(1)
C(5')	14(1)	14(1)	13(1)	0(1)	-1(1)	-1(1)
C(6')	20(1)	17(1)	14(1)	-2(1)	2(1)	3(1)
C(7')	21(1)	15(1)	15(1)	-3(1)	-2(1)	0(1)
C(8')	22(1)	17(1)	18(1)	-3(1)	1(1)	-5(1)
C(9')	19(1)	17(1)	14(1)	0(1)	3(1)	0(1)
C(10')	19(1)	18(1)	21(1)	-2(1)	-2(1)	0(1)
N(11')	29(1)	22(1)	27(1)	-7(1)	3(1)	-4(1)
N(12')	34(2)	22(1)	29(1)	-10(1)	-2(1)	-2(1)
N(13')	24(1)	25(1)	22(1)	-8(1)	-4(1)	2(1)
C(14')	26(2)	26(2)	22(1)	-8(1)	1(1)	-4(1)
C(15')	33(2)	30(2)	23(2)	-12(1)	-8(1)	11(1)
C(16')	70(3)	34(2)	32(2)	-11(2)	3(2)	-11(2)
C(17')	78(3)	33(2)	41(2)	-18(2)	3(2)	-5(2)
C(18')	60(3)	47(2)	30(2)	-15(2)	-3(2)	20(2)
C(19')	37(2)	60(3)	25(2)	-7(2)	2(2)	19(2)
C(20')	32(2)	45(2)	24(2)	-10(1)	-5(1)	9(2)
C(1C)	24(2)	29(2)	36(2)	-5(1)	2(1)	-7(1)
Cl(1)	32(1)	41(1)	57(1)	13(1)	-1(1)	1(1)
Cl(2)	60(1)	36(1)	42(1)	-2(1)	0(1)	11(1)
Cl(3)	52(1)	49(1)	53(1)	-19(1)	-5(1)	-16(1)

C(2C)	37(2)	31(2)	37(2)	-2(2)	6(2)	-2(1)
Cl(4)	73(1)	32(1)	47(1)	2(1)	0(1)	6(1)
Cl(5)	64(1)	56(1)	54(1)	-17(1)	-7(1)	-13(1)
Cl(6)	69(1)	39(1)	47(1)	5(1)	7(1)	15(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 4a.

	x	y	z	U(eq)
H(1A)	5699	4142	9212	17
H(1B)	5234	3929	10849	17
H(3A)	5345	4883	6648	17
H(3B)	4655	5117	6648	17
H(5)	3771	3791	8201	23
H(6)	3527	3056	5908	25
H(8)	5256	3129	3900	22
H(9)	5491	3867	6171	20
H(14)	4939	2561	1202	32
H(16)	3530	1692	-2242	39
H(17)	3771	1069	-4853	46
H(18)	4740	665	-5142	53
H(19)	5469	853	-2785	58
H(20)	5236	1486	-197	49
H(1'1)	-798	760	5817	15
H(1'2)	-369	1039	4180	15
H(3'1)	356	-77	8333	14
H(3'2)	-356	77	8333	14
H(5')	-573	1010	9064	16
H(6')	-424	1779	11279	20
H(8')	1208	2158	8840	23
H(9')	1038	1398	6597	20
H(14')	-58	2286	14126	30
H(16')	859	4071	15834	54
H(17')	510	4575	18619	61
H(18')	-247	4158	20480	55
H(19')	-675	3244	19643	49
H(20')	-356	2730	16860	40
H(1C)	2759	1976	3875	36
H(2C)	1833	3368	10639	42

Table S13. Torsion angles [deg] for 4a.

C(2)#1-C(1)-C(2)-C(4) 176.1(2)
C(2)#1-C(1)-C(2)-C(1)#2 -60.0(2)
C(2)#1-C(1)-C(2)-C(3) 57.6(3)
C(4)-C(2)-C(3)-C(2)#3 -179.0(2)
C(1)-C(2)-C(3)-C(2)#3 -58.97(16)
C(1)#2-C(2)-C(3)-C(2)#3 59.70(16)
C(1)-C(2)-C(4)-C(5) 123.2(3)
C(1)#2-C(2)-C(4)-C(5) 0.8(4)
C(3)-C(2)-C(4)-C(5) -117.8(3)
C(1)-C(2)-C(4)-C(9) -59.6(3)
C(1)#2-C(2)-C(4)-C(9) 178.0(2)
C(3)-C(2)-C(4)-C(9) 59.4(3)
C(9)-C(4)-C(5)-C(6) -3.0(4)
C(2)-C(4)-C(5)-C(6) 174.2(3)
C(4)-C(5)-C(6)-C(7) 0.5(4)
C(5)-C(6)-C(7)-C(8) 2.4(4)
C(5)-C(6)-C(7)-C(10) -177.4(3)
C(6)-C(7)-C(8)-C(9) -2.8(4)
C(10)-C(7)-C(8)-C(9) 177.1(3)
C(7)-C(8)-C(9)-C(4) 0.1(4)
C(5)-C(4)-C(9)-C(8) 2.7(4)
C(2)-C(4)-C(9)-C(8) -174.6(2)
C(6)-C(7)-C(10)-N(11) -10.3(5)
C(8)-C(7)-C(10)-N(11) 169.9(3)
C(6)-C(7)-C(10)-C(14) 169.3(3)
C(8)-C(7)-C(10)-C(14) -10.5(5)
C(14)-C(10)-N(11)-N(12) 0.1(4)
C(7)-C(10)-N(11)-N(12) 179.8(3)
C(10)-N(11)-N(12)-N(13) 0.3(4)
N(11)-N(12)-N(13)-C(14) -0.5(4)
N(11)-N(12)-N(13)-C(15) 176.4(3)
N(12)-N(13)-C(14)-C(10) 0.6(4)
C(15)-N(13)-C(14)-C(10) -176.0(3)
N(11)-C(10)-C(14)-N(13) -0.4(4)
C(7)-C(10)-C(14)-N(13) 179.9(3)
C(14)-N(13)-C(15)-C(16) -141.7(4)
N(12)-N(13)-C(15)-C(16) 42.0(5)
C(14)-N(13)-C(15)-C(20) 41.3(5)
N(12)-N(13)-C(15)-C(20) -135.0(4)
C(20)-C(15)-C(16)-C(17) -0.2(6)
N(13)-C(15)-C(16)-C(17) -177.1(3)
C(15)-C(16)-C(17)-C(18) -0.1(6)
C(16)-C(17)-C(18)-C(19) 0.9(7)
C(17)-C(18)-C(19)-C(20) -1.4(7)
C(18)-C(19)-C(20)-C(15) 1.1(7)
C(16)-C(15)-C(20)-C(19) -0.3(6)
N(13)-C(15)-C(20)-C(19) 176.6(4)
C(2')#4-C(1')-C(2')-C(4') -176.5(2)
C(2')#4-C(1')-C(2')-C(1')#5 58.88(19)

C(2')#4-C(1')-C(2')-C(3')	-58.2(3)
C(4')-C(2')-C(3')-C(2')#6	178.2(2)
C(1')#5-C(2')-C(3')-C(2')#6	-58.94(15)
C(1')-C(2')-C(3')-C(2')#6	58.87(15)
C(1')#5-C(2')-C(4')-C(5')	-172.3(2)
C(3')-C(2')-C(4')-C(5')	-52.5(3)
C(1')-C(2')-C(4')-C(5')	65.3(3)
C(1')#5-C(2')-C(4')-C(9')	4.2(3)
C(3')-C(2')-C(4')-C(9')	124.0(2)
C(1')-C(2')-C(4')-C(9')	-118.2(3)
C(9')-C(4')-C(5')-C(6')	-1.6(4)
C(2')-C(4')-C(5')-C(6')	175.1(2)
C(4')-C(5')-C(6')-C(7')	-1.1(4)
C(5')-C(6')-C(7')-C(8')	3.0(4)
C(5')-C(6')-C(7')-C(10')	-177.8(3)
C(6')-C(7')-C(8')-C(9')	-2.3(4)
C(10')-C(7')-C(8')-C(9')	178.5(3)
C(7')-C(8')-C(9')-C(4')	-0.4(4)
C(5')-C(4')-C(9')-C(8')	2.3(4)
C(2')-C(4')-C(9')-C(8')	-174.3(3)
C(6')-C(7')-C(10')-N(11')	-157.0(3)
C(8')-C(7')-C(10')-N(11')	22.1(4)
C(6')-C(7')-C(10')-C(14')	20.2(5)
C(8')-C(7')-C(10')-C(14')	-160.6(3)
C(14')-C(10')-N(11')-N(12')	-1.2(4)
C(7')-C(10')-N(11')-N(12')	176.5(3)
C(10')-N(11')-N(12')-N(13')	1.0(3)
N(11')-N(12')-N(13')-C(14')	-0.5(4)
N(11')-N(12')-N(13')-C(15')	-176.5(3)
N(12')-N(13')-C(14')-C(10')	-0.3(3)
C(15')-N(13')-C(14')-C(10')	175.5(3)
N(11')-C(10')-C(14')-N(13')	0.9(3)
C(7')-C(10')-C(14')-N(13')	-176.7(3)
C(14')-N(13')-C(15')-C(16')	-178.1(4)
N(12')-N(13')-C(15')-C(16')	-2.8(5)
C(14')-N(13')-C(15')-C(20')	-0.8(5)
N(12')-N(13')-C(15')-C(20')	174.6(3)
C(20')-C(15')-C(16')-C(17')	-1.4(6)
N(13')-C(15')-C(16')-C(17')	175.9(4)
C(15')-C(16')-C(17')-C(18')	0.9(7)
C(16')-C(17')-C(18')-C(19')	0.1(7)
C(17')-C(18')-C(19')-C(20')	-0.6(6)
C(16')-C(15')-C(20')-C(19')	0.9(5)
N(13')-C(15')-C(20')-C(19')	-176.4(3)
C(18')-C(19')-C(20')-C(15')	0.1(5)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x,-z+2 #2 y,-x+1,-z+2 #3 -x+1,-y+1,z
#4 -y,x,-z+1 #5 y,-x,-z+1 #6 -x,-y,z

Table S14. Hydrogen bonds for 4a [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1C)-H(1C)...N(11)	1.00	2.21	3.205(4)	174.7
C(1C)-H(1C)...N(12)	1.00	2.58	3.512(4)	154.6
C(2C)-H(2C)...N(11')	1.00	2.32	3.312(5)	169.1
C(2C)-H(2C)...N(12')	1.00	2.77	3.725(5)	160.8
C(16)-H(16)...Cl(1)#7	0.95	2.76	3.505(4)	136.1

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x,-z+2 #2 y,-x+1,-z+2 #3 -x+1,-y+1,z
#4 -y,x,-z+1 #5 y,-x,-z+1 #6 -x,-y,z #7 x,y,z-1

Table S15. Crystal data and structure refinement for 7.

Identification code	sb091_hy
Empirical formula	C25 H16 N12
Formula weight	484.50
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c (No.15)
Unit cell dimensions	a = 18.728(1) A alpha = 90 deg. b = 7.137(1) A beta = 111.37(1) deg. c = 18.265(1) A gamma = 90 deg.
Volume	2273.5(4) A^3
Z, Calculated density 4,	1.416 Mg/m^3
Absorption coefficient	0.094 mm^-1
F(000)	1000
Crystal size	0.30 x 0.15 x 0.10 mm

Theta range for data collection	3.08 to 27.48 deg.
Limiting indices	-21<=h<=24, -9<=k<=7, -23<=l<=20
Reflections collected / unique	8191 / 2578 [R(int) = 0.0460]
Completeness to theta = 25.00	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2578 / 0 / 168
Goodness-of-fit on	F^2 1.013
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1006
R indices (all data)	R1 = 0.0935, wR2 = 0.1161
Largest diff. peak and hole	0.287 and -0.252 e.A^-3

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 7. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	5000	4620(3)	2500	17(1)
C(11)	4387(1)	3324(2)	1922(1)	18(1)
C(12)	3608(1)	3430(2)	1784(1)	21(1)
C(13)	3081(1)	2216(2)	1261(1)	22(1)
C(14)	3338(1)	866(2)	867(1)	20(1)
C(15)	4115(1)	720(2)	1006(1)	22(1)
C(16)	4626(1)	1928(2)	1530(1)	21(1)
N(11)	2852(1)	-456(2)	328(1)	27(1)
N(12)	2156(1)	-327(2)	210(1)	25(1)
N(13)	1514(1)	-360(2)	54(1)	37(1)
C(21)	5368(1)	5945(2)	2062(1)	18(1)
C(22)	5211(1)	5879(3)	1259(1)	22(1)
C(23)	5521(1)	7189(3)	897(1)	25(1)
C(24)	6002(1)	8570(2)	1338(1)	23(1)
C(25)	6180(1)	8642(2)	2143(1)	21(1)
C(26)	5859(1)	7352(2)	2493(1)	20(1)

N(21)	6273(1)	9898(2)	913(1)	33(1)
N(22)	6710(1)	11132(3)	1315(1)	35(1)
N(23)	7109(1)	12327(3)	1604(1)	55(1)

Table S17. Bond lengths [A] and angles [deg] for 7.

C(1)-C(11)	1.551(2)
C(1)-C(11)#1	1.551(2)
C(1)-C(21)	1.552(2)
C(1)-C(21)#1	1.552(2)
C(11)-C(12)	1.390(2)
C(11)-C(16)	1.393(2)
C(12)-C(13)	1.397(3)
C(13)-C(14)	1.389(3)
C(14)-C(15)	1.386(3)
C(14)-N(11)	1.428(2)
C(15)-C(16)	1.382(3)
N(11)-N(12)	1.244(2)
N(12)-N(13)	1.130(2)
C(21)-C(22)	1.387(3)
C(21)-C(26)	1.395(3)
C(22)-C(23)	1.390(3)
C(23)-C(24)	1.379(3)
C(24)-C(25)	1.385(3)
C(24)-N(21)	1.430(2)
C(25)-C(26)	1.378(3)
N(21)-N(22)	1.244(2)
N(22)-N(23)	1.130(3)

C(11)-C(1)-C(11)#1	106.76(19)
C(11)-C(1)-C(21)	111.71(9)
C(11)#1-C(1)-C(21)	110.89(9)
C(11)-C(1)-C(21)#1	110.89(9)
C(11)#1-C(1)-C(21)#1	111.71(9)
C(21)-C(1)-C(21)#1	104.96(19)
C(12)-C(11)-C(16)	117.33(16)
C(12)-C(11)-C(1)	123.99(15)
C(16)-C(11)-C(1)	118.66(15)
C(11)-C(12)-C(13)	121.56(17)
C(14)-C(13)-C(12)	119.51(17)
C(15)-C(14)-C(13)	119.79(17)
C(15)-C(14)-N(11)	116.08(16)
C(13)-C(14)-N(11)	124.11(17)
C(16)-C(15)-C(14)	119.69(17)
C(15)-C(16)-C(11)	122.10(17)
N(12)-N(11)-C(14)	115.76(16)
N(13)-N(12)-N(11)	173.01(19)

C(22)-C(21)-C(26)	117.55(17)
C(22)-C(21)-C(1)	124.12(15)
C(26)-C(21)-C(1)	118.26(15)
C(21)-C(22)-C(23)	121.09(18)
C(24)-C(23)-C(22)	119.99(19)
C(23)-C(24)-C(25)	120.01(17)
C(23)-C(24)-N(21)	116.23(18)
C(25)-C(24)-N(21)	123.74(17)
C(26)-C(25)-C(24)	119.36(17)
C(25)-C(26)-C(21)	121.98(18)
N(22)-N(21)-C(24)	115.90(17)
N(23)-N(22)-N(21)	172.5(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table S18. Anisotropic displacement parameters (A^2 x 10^3) for 7.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	18(1)	16(1)	15(1)	0	4(1)	0
C(11)	21(1)	15(1)	17(1)	3(1)	5(1)	1(1)
C(12)	25(1)	16(1)	22(1)	0(1)	9(1)	2(1)
C(13)	17(1)	22(1)	24(1)	3(1)	5(1)	1(1)
C(14)	23(1)	17(1)	17(1)	2(1)	3(1)	-2(1)
C(15)	26(1)	17(1)	21(1)	0(1)	8(1)	2(1)
C(16)	19(1)	19(1)	23(1)	2(1)	5(1)	2(1)
N(11)	22(1)	26(1)	29(1)	-6(1)	7(1)	-6(1)
N(12)	28(1)	23(1)	22(1)	-2(1)	5(1)	-5(1)
N(13)	24(1)	42(1)	39(1)	-6(1)	5(1)	-5(1)
C(21)	17(1)	17(1)	19(1)	2(1)	5(1)	3(1)
C(22)	22(1)	22(1)	20(1)	-3(1)	6(1)	0(1)
C(23)	28(1)	30(1)	19(1)	-1(1)	10(1)	2(1)
C(24)	22(1)	23(1)	27(1)	5(1)	12(1)	3(1)
C(25)	20(1)	20(1)	22(1)	-1(1)	5(1)	-1(1)
C(26)	22(1)	20(1)	18(1)	0(1)	5(1)	2(1)
N(21)	37(1)	37(1)	29(1)	-1(1)	16(1)	-13(1)
N(22)	31(1)	40(1)	34(1)	13(1)	12(1)	-3(1)
N(23)	53(1)	53(1)	47(1)	12(1)	4(1)	-28(1)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 7.

	x	y	z	U(eq)
H(12)	3429	4349	2053	25
H(13)	2550	2313	1174	26
H(15)	4295	-207	742	26
H(16)	5158	1803	1626	25
H(22)	4885	4922	952	26
H(23)	5402	7133	345	30
H(25)	6521	9572	2451	26
H(26)	5975	7424	3043	25

Table S20. Torsion angles [deg] for 7.

C(11)#1-C(1)-C(11)-C(12)	125.63(19)
C(21)-C(1)-C(11)-C(12)	-112.98(17)
C(21)#1-C(1)-C(11)-C(12)	3.7(2)
C(11)#1-C(1)-C(11)-C(16)	-52.43(13)
C(21)-C(1)-C(11)-C(16)	69.0(2)
C(21)#1-C(1)-C(11)-C(16)	-174.34(15)
C(16)-C(11)-C(12)-C(13)	-1.5(3)
C(1)-C(11)-C(12)-C(13)	-179.54(16)
C(11)-C(12)-C(13)-C(14)	0.1(3)
C(12)-C(13)-C(14)-C(15)	0.9(3)
C(12)-C(13)-C(14)-N(11)	179.22(17)
C(13)-C(14)-C(15)-C(16)	-0.5(3)
N(11)-C(14)-C(15)-C(16)	-178.96(16)
C(14)-C(15)-C(16)-C(11)	-0.9(3)
C(12)-C(11)-C(16)-C(15)	1.9(3)
C(1)-C(11)-C(16)-C(15)	-179.94(16)
C(15)-C(14)-N(11)-N(12)	179.46(17)
C(13)-C(14)-N(11)-N(12)	1.1(3)
C(14)-N(11)-N(12)-N(13)	-179(100)
C(11)-C(1)-C(21)-C(22)	-4.6(2)
C(11)#1-C(1)-C(21)-C(22)	114.32(17)
C(21)#1-C(1)-C(21)-C(22)	-124.89(19)
C(11)-C(1)-C(21)-C(26)	172.07(15)
C(11)#1-C(1)-C(21)-C(26)	-69.0(2)
C(21)#1-C(1)-C(21)-C(26)	51.83(13)
C(26)-C(21)-C(22)-C(23)	-1.1(3)
C(1)-C(21)-C(22)-C(23)	175.64(16)
C(21)-C(22)-C(23)-C(24)	0.8(3)

C(22)-C(23)-C(24)-C(25)	0.5(3)
C(22)-C(23)-C(24)-N(21)	-177.78(17)
C(23)-C(24)-C(25)-C(26)	-1.5(3)
N(21)-C(24)-C(25)-C(26)	176.65(18)
C(24)-C(25)-C(26)-C(21)	1.2(3)
C(22)-C(21)-C(26)-C(25)	0.1(3)
C(1)-C(21)-C(26)-C(25)	-176.87(16)
C(23)-C(24)-N(21)-N(22)	-179.52(18)
C(25)-C(24)-N(21)-N(22)	2.2(3)
C(24)-N(21)-N(22)-N(23)	-179(100)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table S21. Hydrogen bonds for 7 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22)...N(13)#2	0.95	2.61	3.268(3)	126.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+1/2,-y+1/2,-z