Electronic Supplementary Material (ESI)

Tweezer-type binding cavity formed by the helical folding of a carbazole–pyridine oligomer

Hye Jin Jang,‡ Seungwon Lee,‡ Byung Jun An, Geunmoo Song, Hae-Geun Jeon and

Kyu-Sung Jeong*

‡ These authors contributed equally to this work.

*Department of Chemistry, Yonsei University, Seoul 03722, Korea

Fax: +82-2-364-7050

Tel: +82-2123-2643

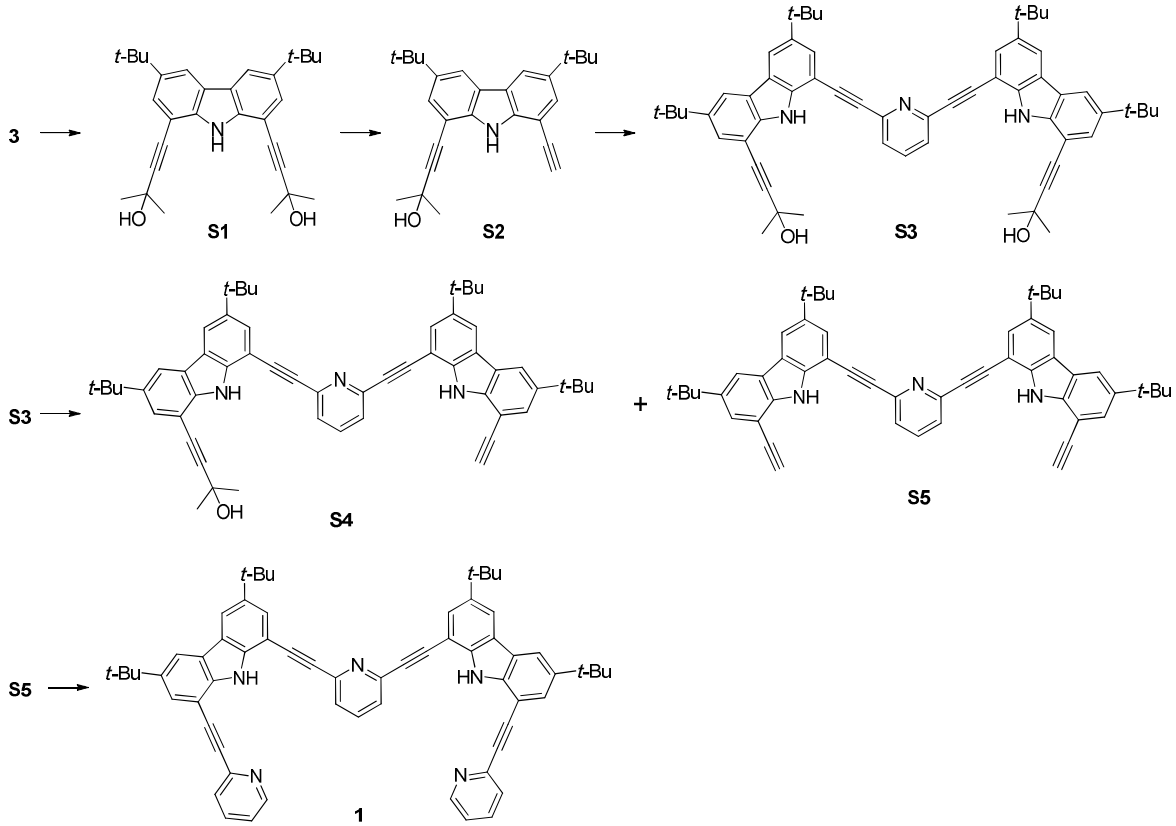
E-mail: ksjeong@yonsei.ac.kr

Contents

1. Syntheses and characterisation of new compounds

1.1 General: All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Dichloromethane (CH_2Cl_2) was purified by drying over calcium hydride (CaH_2), followed by distillation. Hexane and ethyl acetate (EtOAc) were distilled. Water-saturated deuterated solvents were prepared by sonicating the organic solvent containing a few drops of distilled water for 10 min. After 1 h standing, organic layer was carefully separated out for use. Thin layer chromatography (TLC) was performed on Merck (silica gel 60, F-254, 0.25 mm). Silica gel 60 (230-400 mesh, Merck) was used for column chromatography. Melting points were determined with a Barnstead Electrothermal (IA9100) apparatus. 1D and 2D NMR spectra were measured by using Bruker Avance II DRX 400 and Avance III HD 300 instruments. MALDI-TOF mass spectrometric measurements were performed on a Bruker (LRF20). MALDI-TOF/TOF mass spectrometric measurements were performed on a Bruker (Autoflex Max). Chemical shifts were reported using residual protonated solvent peaks (for ^{1}H NMR spectra, acetone-d_6 2.05 ppm; CD_2Cl_2 5.32 ppm; $CDCl_3$ 7.26 ppm; DMSO-d_6 2.50 ppm; toluene-d_8 7.09 ppm; and for ^{13}C NMR spectra, acetone-d_6 206.26 ppm; CD_2Cl_2 53.84 ppm; DMSO-d_6 39.52 ppm). The ESI-HRMS spectrometric measurements were obtained from *the Organic Chemistry Research Centre* at Sogang University.

1.2 Syntheses of **1**



S1: A 250 mL Schlenk flask containing **3**[S1] (23.3 g, 43.9 mmol), CuI (0.42 g, 2.19 mmol) and $Pd(PPh_3)_2Cl_2$ (1.54 g, 2.19 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed tetrahydrofuran (THF) (55 mL), triethylamine (Et_3N) (55 mL) and 3-methyl-butyn-2-ol (10.7 mL, 110 mmol) were sequentially added, and the solution was stirred at 55 °C for 4 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:2 (v/v)) to give **S1** (18.6 g, 96%) as a white solid; mp > 224 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 9.62 (s, 1H, NH), 8.26 (s, 2H), 7.53 (s, 2H), 4.57 (s, 2H, OH), 1.63 (s, 12H, Me), 1.43 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 143.3, 139.9, 127.3, 124.3, 118.2, 106.3, 100.1, 78.3, 65.4, 35.2, 32.1; MALDI-TOF/TOF m/z calcd for $C_{30}H_{37}NO_2Na$ $[M+Na]^+$ 466.3 found 466.1.

S2: To a solution of compound **S1** (10.8 g, 24.3 mmol) in toluene (243 mL), tetra-*n*-butylammonium hydroxide (24.3 mL, 1 M solution in CH_3OH) was added. The solution was placed in an oil bath (80 °C) and stirred for 2 h. After cooling down to room temperature, the mixture was diluted with EtOAc (250 mL), washed with brine, dried over anhydrous Na_2SO_4

and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:3 (v/v)) to give **S2** (6.20 g, 66%) as a white solid; mp: 135 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ 8.52 (s, 1H, NH), 8.08 (d, J = 1.3 Hz, 1H), 8.05 (d, J = 1.3 Hz, 1H), 7.65 (d, J = 1.6 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 3.47 (s, 1H), 2.40 (s, 1H, OH), 1.76 (s, 6H), 1.45 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, ppm) δ 142.8, 142.8, 139.2, 138.8, 127.6, 127.3, 123.4, 123.3, 118.1, 117.5, 104.7, 103.9, 98.1, 81.4, 80.7, 78.8, 66.1, 34.8, 34.8, 32.0, 32.0, 31.9; MALDI-TOF *m/z* calcd for $C_{27}H_{32}NO$ $[M+H]^+$ 386.2 found 385.8.

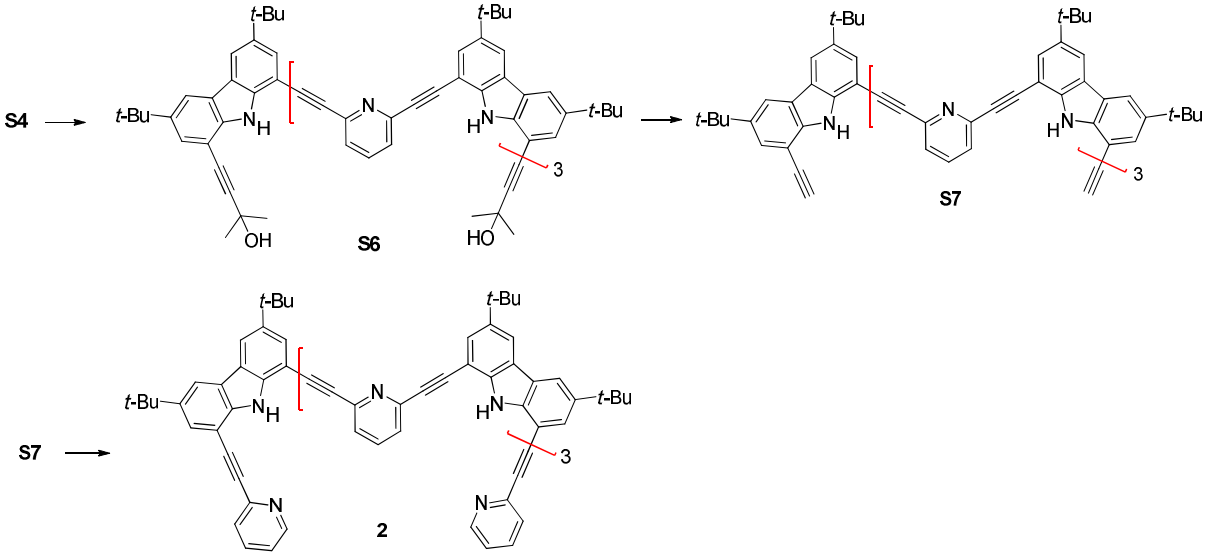
S3: A Schlenk flask containing **S2** (6.77 g, 17.6 mmol), 2,6-dibromopyridine (1.89 g, 7.98 mmol), CuI (15 mg, 0.08 mmol) and $Pd(PPh_3)_2Cl_2$ (56 mg, 0.08 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (40 mL) and Et_3N (40 mL) were sequentially added, and the solution was stirred at 55 °C for 1 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:6 (v/v)) to give **S3** (6.33 g, 94%) as a yellow solid; mp > 225 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 10.38 (s, 2H, NH), 8.19 (d, J = 1.4 Hz, 2H), 8.10 (d, J = 1.5 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 1.7 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 1.7 Hz, 2H), 4.39 (s, 2H, OH), 1.49 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 143.5, 143.0, 142.9, 140.2, 139.8, 138.0, 127.6, 126.8, 126.3, 124.1, 123.3, 119.3, 117.5, 105.7, 103.9, 98.8, 91.8, 88.6, 79.1, 65.9, 35.1, 35.0, 32.1, 32.0, 31.4; MALDI-TOF/TOF m/z calcd for $C_{59}H_{63}N_3O_2Na$ $[M+Na]^+$ 868.5 found 868.4.

S4 and **S5**: To a solution of compound **S3** (5.47 g, 6.46 mmol) in toluene (130 mL), sodium hydride (60% oil dispersion, 0.259 g) was carefully added. The solution was placed in an oil bath (105 °C) and stirred for 45 min. The mixture was quickly cooled down using a cold water bath, and a few drops of water was added. The mixture was diluted with EtOAc (130 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2:*n*-hexane = 3:1 (v/v)) to give **S4** (2.61 g, 51%) as a white solid; mp > 198 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 10.89 (s, 1H, NH), 10.74 (s, 1H, NH), 8.42 (d, J = 1.7 Hz, 1H), 8.41 (d, J = 1.7 Hz, 1H), 8.37 (d, J = 1.6 Hz, 1H), 8.32 (d, J = 1.6 Hz, 1H), 7.98 (t, J = 7.8 Hz, 1H), 7.82 (d, J = 1.8 Hz, 1H), 7.79 (d, J = 1.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 1.8 Hz, 1H), 7.56

(d, J = 1.8 Hz, 1H), 4.68 (s, 1H, OH), 3.92 (s, 1H), 1.61 (s, 6H), 1.49 (s, 9H, *t*-Bu), 1.48 (s, 9H, *t*-Bu) 1.45 (s, 9H, *t*-Bu) 1.44 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 144.9, 144.7, 143.6, 143.5, 143.5, 143.5, 143.5, 140.7, 140.5, 140.5, 140.3, 138.1, 128.9, 128.7, 128.4, 127.8, 127.7, 127.3, 124.9, 124.8, 124.6, 124.3, 119.9, 119.8, 119.1, 118.3, 106.8, 105.7, 105.3, 105.0, 100, 93.0, 92.8, 87.8, 87.7, 83.3, 81.3, 78.8, 65.7, 35.5, 35.5, 35.4, 32.4, 32.3, 32.3, 32.3, 32.2; MALDI-TOF *m/z* calcd for $C_{56}H_{58}N_3O$ $[M+H]^+$ 788.5 found 788.3; and **S5** (0.29 g, 6%) as a white solid; mp: 208 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 10.97 (s, 2H, NH), 8.42 (d, J = 1.6 Hz, 2H), 8.37 (d, J = 1.5 Hz, 2H), 7.96 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 1.7 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 1.7 Hz, 2H), 3.91 (s, 2H), 1.49 (s, 18H, *t*-Bu), 1.45 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 144.9, 143.6, 143.5, 140.7, 140.4, 137.9, 128.8, 128.7, 127.6, 124.9, 124.6, 119.8, 119.1, 105.7, 105.3, 93.0, 87.3, 83.3, 81.3, 35.5, 35.4, 32.3, 32.3; MALDI-TOF *m/z* calcd for $C_{53}H_{52}N_3$ $[M+H]^+$ 730.4 found 730.1.

1: A Schlenk flask containing **S5** (100 mg, 0.14 mmol), 2-iodopyridine (50 μL, 0.47 mmol), CuI (0.5 mg, 0.003 mmol) and $Pd(PPh_3)_2Cl_2$ (2 mg, 0.003 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1 mL) and Et_3N (1 mL) were sequentially added, and the solution was stirred at 55 °C for 12 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:3 (v/v)) to give **1** (87 mg, 72%) as a yellow solid; mp > 219 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 11.9 (s, 2H, NH), 7.71 (ddd, J = 4.8 Hz, 1.7 Hz, 0.9 Hz), 5.85 (ddd, J = 7.65 Hz, 5.0 Hz, 1.2 Hz), 6.74 (td, J = 7.7 Hz, 1.8 Hz), 7.15 (ddd, J =7.8 Hz, 1.3 Hz, 1.0 Hz), 7.54 (d, J = 1.8 Hz), 8.09 (d, J = 1.8 Hz), 8.19 (d, J = 1.8 Hz), 7.81 (d, J =1.9 Hz), 7.88 (dd, J = 8.2 Hz, 7.4 Hz), 7.65 (d, J =7.8 Hz), 1.52 (s, 18H, *t*-Bu), 1.49 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, ppm) δ 148.6, 143.8, 143.0, 142.6, 140.4, 140.1, 138.0, 135.4, 127.6, 126.2, 125.7, 123.9, 123.4, 121.6, 119.0, 118.1, 104.9, 104.0, 92.8, 91.8, 88.6, 87.0, 35.0, 35.0, 32.1; MALDI-TOF *m/z* calcd for $C_{63}H_{58}N_5$ $[M+H]^+$ 884.5 found 884.9.

1.3 Syntheses of **2**



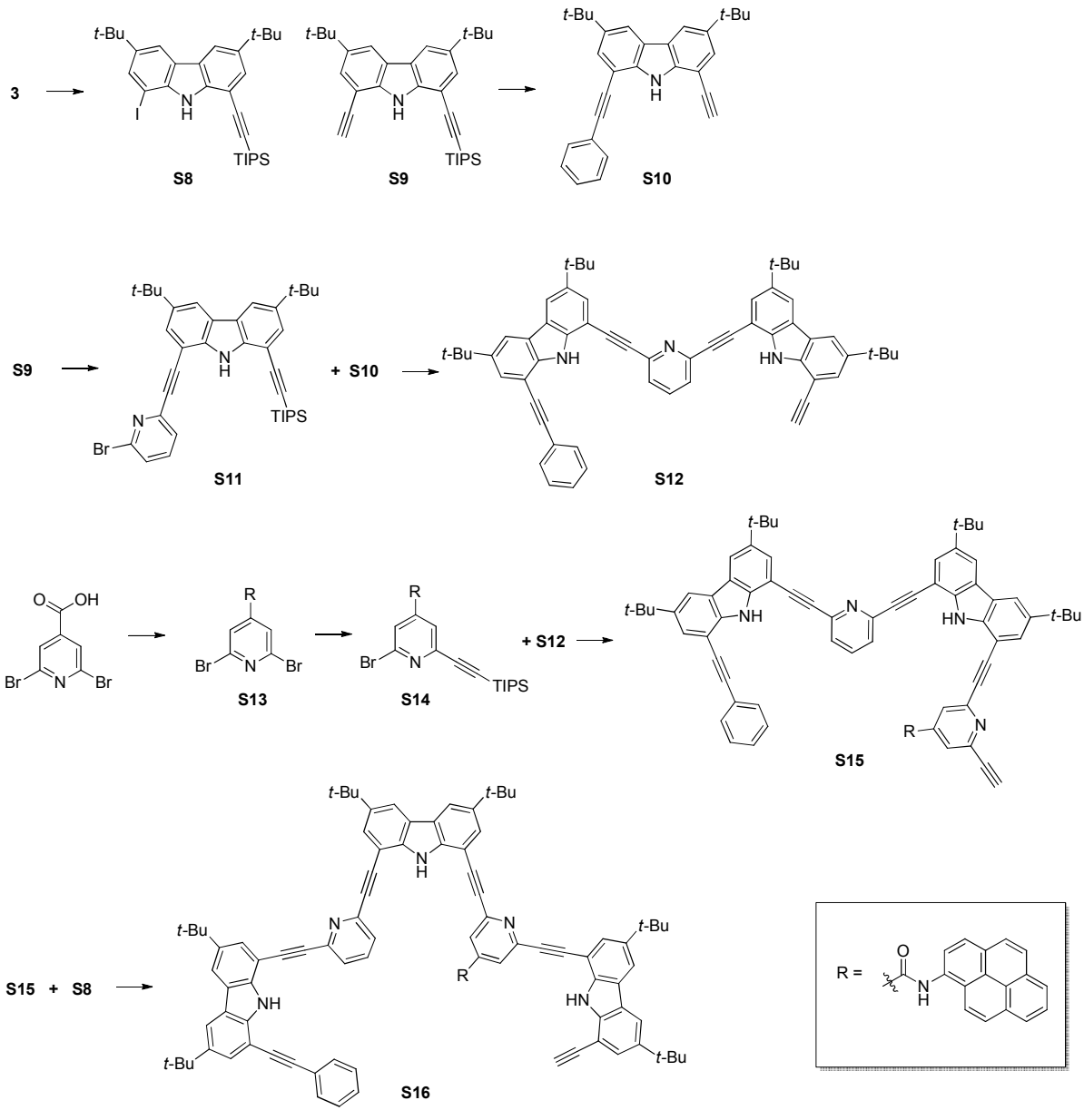
S6: A Schlenk flask containing **S4** (3.31 g, 4.20 mmol), 2,6-dibromopyridine (0.452 g, 1.91 mmol), CuI (4 mg, 0.019 mmol) and $Pd(PPh_3)_2Cl_2$ (13 mg, 0.019 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (9.5 mL) and Et_3N (9.5 mL) were sequentially added, and the solution was stirred at 55 °C for 2.5 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:6 (v/v)) to give **S6** (2.72 g, 86%) as a light green solid; mp > 267 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.14 (s, 2H, NH), 9.49 (s, 2H, NH), 7.96 (s, 2H), 7.96 (s, 2H), 7.94 (d, J = 1.5 Hz, 2H), 7.85 (d, J = 1.5 Hz, 2H), 7.70 (d, J = 1.7 Hz, 2H), 7.59 (d, J = 1.6 Hz, 2H), 7.56 (d, J = 1.7 Hz, 2H), 7.38 (d, J = 1.7 Hz, 2H), 6.92 (t, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 6.41 (d, J = 7.6 Hz, 2H), 6.11 (t, J = 7.7 Hz, 1H), 5.92 (d, J = 7.7 Hz, 2H), 4.45 (s, 2H, OH), 1.59 (s, 18H, *t*-Bu), 1.55 (s, 18H, *t*-Bu), 1.52 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.27 (s, 12H, Me); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 144.3, 144.2, 143.8 ,143.6, 143.4 ,143.4, 143.3, 141.0, 140.7, 140.5, 140.3, 138.0, 137.3, 128.7, 128.4, 128.1, 127.5, 126.9, 126.4, 126.3, 124.8, 124.8, 124.3, 119.9, 119.7, 119.6, 118.2, 106.8, 105.7, 105.4, 105.3, 100.1, 93.2, 93.1, 93.1, 88.9, 88.2, 87.4,78.8, 65.6, 35.5, 35.5, 35.4, 32.5, 32.4, 32.2; MALDI-TOF/TOF *m/z* calcd for $C_{117}H_{115}N_7O_2Na$ $[M+Na]^+$ 1672.9 found 1672.7.

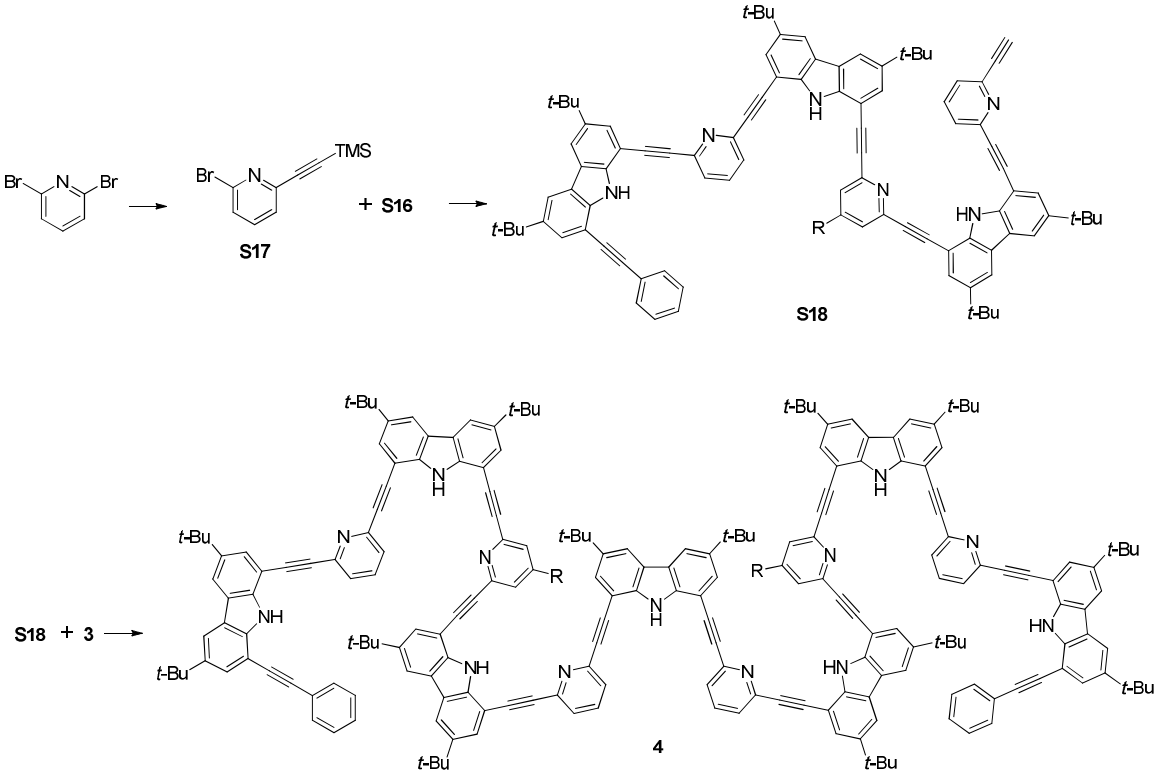
S7: To a solution of compound **S6** (2.53 g, 1.53 mmol) in toluene (50 mL), sodium hydride (60% oil dispersion, 0.15 g) was carefully added. The solution was placed in an oil bath (105 °C) and stirred for 45 min. The solution was quickly cooled down using a cold water bath, and a few drops of water was added. The mixture was diluted with EtOAc (50 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2:*n*-hexane = 3:1 (v/v)) to **S7** (1.43 g, 61%) as a light yellow solid; mp > 265 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ 11.86 (s, 2H, NH), 9.64 (s, 2H, NH), 8.16 (d, J = 1.4 Hz, 2H), 8.11 (d, J = 1.4 Hz, 2H), 8.00 (d, J = 1.4 Hz, 2H), 7.92 (d, J =1.4 Hz, 2H), 7.74 (d, J = 1.6 Hz, 2H), 7.70 (d, J =1.6 Hz, 2H), 7.59 (d, J = 1.6 Hz, 2H), 7.48 (d, J =1.6 Hz, 2H), 6.61 (dd, J = 7.7 Hz, 1.1 Hz, 2H), 6.57 (t, J = 7.7 Hz, 2H), 6.11 (t, J = 7.8 Hz, 1H), 6.07 (dd, J =7.33 Hz, 1.24 Hz, 2H), 5.79 (d, J =7.8 Hz, 2H), 3.04 (s, 2H), 1.59 (s, 18H, *t*-Bu), 1.58 (s, 18H, *t*-Bu), 1.51 (s, 18H, *t*-Bu), 1.43 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 142.7, 142.7, 142.6, 142.5, 142.5, 142.3, 141.9, 140.8, 140.7, 140.1, 139.8, 135.6, 135.4, 127.7, 127.6, 127.3, 127.1, 123.9, 123.7, 123.6, 123.6, 123.5, 123.4, 122.7, 118.3, 117.5, 105.9, 105.2, 105.1, 105.0, 92.6, 92.4, 92.4, 89.8, 88.5, 87.4, 82.6, 80.5, 35.1, 35.0, 34.9, 32.3, 32.3, 32.2, 32.1; MALDI-TOF/TOF *m/z* calcd for $C_{111}H_{104}N_7$ $[M+H]^+$ 1534.8 found 1534.7.

2: A Schlenk flask containing **S7** (42 mg, 0.03 mmol), 2-iodopyridine (9 µL, 0.08 mmol), CuI (0.5 mg, 0.002 mmol) and $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.002 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (0.3 mL) and Et_3N (0.3 mL) were sequentially added, and the solution was stirred at 45 °C for 15 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:4 (v/v)) to give **2** (34 mg, 74%) as a yellow solid; mp > 233 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 12.29 (s, 2H, NH), 11.17 (s, 2H, NH), 8.14 (d, J = 1.8 Hz, 2H), 8.02 (d, J = 1.7 Hz, 2H), 7.98 (d, J = 1.8 Hz, 2H), 7.92 (d, J = 1.8 Hz, 2H), 7.67 (d, J = 1.7 Hz, 2H), 7.65 (d, J = 1.7 Hz, 2H), 7.56 (d, J = 4.2 Hz, 2H), 7.40 (d, J = 1.7 Hz, 2H), 7.37 (d, J = 1.7 Hz, 2H), 7.03 (d, J = 7.7 Hz, 2H), 6.65 (t, J =7.7 Hz, 2H), 6.55 (td, J = 7.7 Hz, 1.7 Hz, 2H), 6.41 (dd, J = 7.8 Hz, 0.6 Hz, 2H), 6.28 (dd, J = 7.7 Hz, 0.7 Hz, 2H), 5.79 (ddd, J = 7.6 Hz, 4.8 Hz, 0.8 Hz, 2H), 5.71 (dd, J = 9.1 Hz, 6.1 Hz, 1H), 5.66 (d, J = 7.4 Hz, 2H), 1.63 (s, 18H, *t*-Bu), 1.58 (s, 18H, *t*-Bu), 1.51 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 142.8, 142.6,

142.3, 142.2, 142.0, 142.0, 141.8, 140.8, 140.3, 140.2, 140.0, 134.7, 126.8, 124.0, 123.4, 122.0, 121.3, 118.4, 118.1, 117.8, 117.5, 105.6, 105.1, 105.0, 104.9, 92.6, 92.2, 91.8, 88.7, 88.3, 87.3, 75.1, 35.0, 35.0, 34.9, 34.8, 32.4, 32.2, 32.2, 32.1; MALDI-TOF *m/z* calcd for $C_{121}H_{110}N_9$ $[M+H]^+$ 1688.9 found 1689.2.

1.4 Syntheses of **4**





S8: A Schlenk flask containing **3** (1.0 g, 1.88 mmol), CuI (11 mg, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (40 mg, 0.06 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (10 mL), Et_3N (9 mL) and triisopropylsilylethyne (0.42 mL, 1.88 mmol) were sequentially added, and the solution was stirred at 55 °C for 3 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, only *n*-hexane) to give **S8** (381 mg, 35%) as a white solid; mp: 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.18 (s, 1H, NH), 8.01 (s, 1H), 8.01 (s, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.59 (d, J = 1.7 Hz, 1H), 1.44 (s, 9H, *t*-Bu), 1.43 (s, 9H, *t*-Bu), 1.24 (s, 21H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 146.2, 144.3, 140.9, 140.2, 133.5, 127.6, 125.1, 124.9, 119.7, 118.4, 106.7, 104.4, 96.1, 76.4, 35.6, 35.5, 32.4, 32.4, 19.5, 12.2; MALDI-TOF *m*/*z* calcd for $C_{31}H_{45}INSi$ $[M+H]^+$ 586.2 found 585.8.

S9: A Schlenk flask containing **3** (3.0 g, 5.64 mmol), CuI (11 mg, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (39.6 mg, 0.06 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (13 mL), Et_3N (10 mL) and triisopropylsilylethyne (5.7 mL, 15.2 mmol) were sequentially added, and the solution was stirred at 55 °C for 6 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The

residue was filtered through short silica gel (only *n*-hexane) and concentrated. To a CH_2Cl_2 solution (177 mL) of this residue, tetra-*n*-butylammonium fluoride (1 M solution in THF, 3.7 mL) was added. After stirring for 1 h at room temperature, the mixture was washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, only *n*-hexane) to give **S9** (582 mg, 23%) as a white solid; mp: 126 °C; ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 9.04 (s, 1H, NH), 8.34 (s, 1H), 8.34 (s, 1H), 7.65 (d, J = 1.8 Hz, 1H), 7.65 (d, J = 1.8 Hz, 1H), 4.06 (s, 1H), 1.44 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 1.23 (s, 21H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 143.9, 143.9, 140.5, 140.3, 128.1, 127.6, 124.6, 124.5, 119.4, 119.4, 106.5, 105.4, 104.6, 95.7, 83.6, 80.8, 35.5, 35.5, 32.3, 32.3, 19.3, 12.2; MALDI-TOF *m*/*z* calcd for $C_{33}H_{46}NSi$ $[M+H]^+$ 484.3 found 483.9.

S10: A Schlenk flask containing **S9** (200 mg, 0.41 mmol), CuI (4 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (14.4 mg, 0.02 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (2 mL), Et_3N (2 mL) and iodobenzene (69 μL, 0.61 mmol) were sequentially added, and the solution was stirred at 55 °C for 12 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was filtered through short silica gel (CH_2Cl_2:*n*-hexane = 1:10 (v/v)) and concentrated. The residue was dissolved in THF (3.0 mL) and tetra-*n*-butylammonium fluoride (1 M solution in THF, 0.7 mL) was added dropwise over 3 min in the ice bath. After stirring at room temperature for 1 h, the mixture was concentrated. The residue was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2:*n*-hexane = 1:4 (v/v)) to give **S10** (139 mg, 84%) as a white solid; mp: 104 °C; ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 10.59 (s, 1H, NH), 8.35 (d, J = 1.5 Hz, 1H), 8.34 (d, J = 1.4 Hz, 1H), 7.71 (d, J = 1.6 Hz, 1H), 8.35 (d, J = 1.5 Hz, 1H), 7.66 (dd, J = 7.9 Hz, 1.7 Hz, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.50-7.39 (m, 3H), 3.90 (s, 1H), 1.46 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 143.5, 143.4, 140.5, 140.1, 132.6, 129.4, 129.3, 128.5, 128.2, 124.6, 124.6, 124.5, 119.1, 118.8, 106.5, 105.6, 93.8, 87.1, 83.2, 81.2, 35.4, 35.3, 32.3, 32.3; MALDI-TOF *m*/*z* calcd for $C_{30}H_{30}N$ $[M+H]^+$ 404.2 found 404.4.

S11: A Schlenk flask containing **S9** (750 mg, 1.55 mmol), 2,6-dibromopyridine (1.1 g, 4.65 mmol), CuI (15 mg, 0.08 mmol) and $Pd(PPh_3)_2Cl_2$ (54 mg, 0.08 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (8.5 mL) and Et_3N (7 mL) were sequentially added, and the solution was stirred at 55 °C for 5.5 h. The mixture was

cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:15 (v/v)) to give **S11** (761 mg, 76%) as a yellow solid; mp: 109 °C; ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 9.51 (s, 1H, NH), 8.42 (d, J = 1.6 Hz, 1H), 8.37 (d, J = 1.6 Hz, 1H), 7.84 (t, J = 7.6 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.67 (d, J = 1.7 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 1.47 (s, 9H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 1.22 (s, 18H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 144.7, 144.1, 144.0, 142.4, 140.5, 140.2, 140.2, 128.8, 128.4, 128.1, 127.6, 124.9, 124.5, 120.3, 119.3, 106.7, 104.8, 104.6, 95.7, 92.5, 87.7, 35.5, 35.4, 32.3, 32.3, 19.3, 12.2; MALDI-TOF m/z calcd for $C_{38}H_{48}BrN_2Si$ $[M+H]^+$ 639.3 found 639.0.

S12: A Schlenk flask containing **S11** (401 mg, 0.63 mmol), CuI (5.4 mg, 0.03 mmol) and $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1 mL) and Et_3N (2 mL) were added. Then nitrogen-purged **S10** (0.19 mM solution in THF, 3 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 15 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was filtered through short silica gel (CH_2Cl_2:*n*-hexane = 2:7 (v/v)) and concentrated. The residue was dissolved in THF (4.6 mL) and tetra-*n*-butylammonium fluoride (1 M solution in THF, 0.93 mL) was added dropwise over 3 min in the ice bath. After stirring at room temperature for 30 min, the mixture was concentrated. The residue was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:4 (v/v)) to give **S12** (370 mg, 86%) as a yellow solid; mp: 216 °C; ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 11.25 (s, 1H, NH), 10.96 (s, 1H, NH), 8.43 (d, J = 1.4 Hz, 1H), 8.42 (d, J = 1.4 Hz, 1H), 8.38 (s, 1H), 8.38 (s, 1H), 7.95 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 1.6 Hz, 1H), 7.77 (s, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 6.9 Hz, 2H), 7.65 (d, J = 1.9 Hz, 1H), 7.35 (m, 2H), 7.27 (d, J = 7.3 Hz, 1H), 3.89 (s, 1H), 1.49 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 144.8, 144.8, 143.6, 143.6, 143.5, 143.5, 140.7, 140.4, 140.4, 140.2, 137.9, 132.6, 129.4, 129.3, 128.8, 128.7, 128.7, 128.3, 127.6, 127.5, 124.9, 124.9, 124.6, 124.5, 124.5, 119.8, 119.8, 119.1, 118.8, 106.6, 105.7, 105.2, 105.2, 93.7, 93.0, 92.9, 87.5, 87.4, 87.1, 83.2, 81.3, 35.4, 35.4, 35.4, 35.3, 32.3, 32.3, 32.3, 32.2; MALDI-TOF m/z calcd

for $C_{59}H_{56}N_3$ $[M+H]^+$ 806.4 found 806.4.

S13: A mixture of 2,6-dibromopyridine-4-carboxylic acid[S2] (293 mg, 1.04 mmol), 1-aminopyrene (340 mg, 1.56 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (339 mg, 1.77 mmol), and 4-(dimethylamino)pyridine (DMAP) (6.4 mg, 0.05 mmol) were dissolved in DMF (10 mL), and stirred at room temperature for 12 h. After concentration, the residue was purified by flash column chromatography (silica gel, THF:*n*-hexane = 1:2 (v/v)) to give **S13** (381 mg, 76%) as yellow solid; mp : 272 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 11.18 (s, 1H, NH), 8.35 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 5.4 Hz, 1H), 8.35 (d, J = 5.4 Hz, 1H), 8.35 (d, J = 5.4 Hz, 1H), 8.35 (d, J = 5.4 Hz, 1H), 8.33 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 9.4 Hz, 1H), 8.21 (s, 2H), 8.19 (d, J = 8.2 Hz, 1H), 8.10 (t, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 162.2, 147.1, 140.6, 130.7, 130.6, 130.5, 129.4, 127.5, 127.3, 127.2, 126.6, 126.0, 125.6, 125.4, 125.4, 125.0, 124.8, 124.3, 123.7, 122.9; MALDI-TOF/TOF *m/z* calcd for $C_{22}H_{13}Br_2N_2O$ $[M+H]^+$ 478.9 found 478.8.

S14: A Schlenk flask containing **S13** (400 g, 0.83 mmol), CuI (4.0 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (14.6 mg, 0.04 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (4 mL), Et_3N (4 mL) and triisopropylsilylethyne (0.10 mL, 0.42 mmol) were sequentially added, and the solution was stirred at 55 °C for 3 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:3 (v/v), only CH_2Cl_2) to give **S14** (225 mg, 46%) as a yellow solid; mp : 270 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 10.38 (s, 1H, NH), 8.37 (d, J = 9.3 Hz, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.31 (d, J = 7.7, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.27 (d, J = 6.4 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H), 8.18 (s, 2H), 8.08 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 146.3, 144.6, 142.7, 132.2, 131.8, 130.8, 128.5, 128.2, 128.1, 127.3, 127.0, 126.4, 126.2, 125.9, 125.8, 125.8, 125.2, 123.2, 105.5, 94.3, 18.9, 11.9; MALDI-TOF/TOF *m/z* calcd for $C_{33}H_{34}BrN_2OSi$ $[M+H]^+$ 581.2 found 581.1.

S15 : A Schlenk flask containing **S14** (205 mg, 0.35 mmol), CuI (3.4 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (12.3 mg, 0.02 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (2 mL) and Et_3N (2 mL) were added. Then nitrogen-

purged **S12** (0.13 mM solution in DMF, 3 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 3 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was filtered through short silica gel (CH_2Cl_2:*n*-hexane = 1:1 (v/v)) and concentrated. The residue was dissolved in THF (4 mL) and tetra-*n*-butylammonium fluoride (1 M solution in THF, 0.6 mL) was added dropwise over 3 min in the ice bath. After stirring at room temperature for 1.5 h, the mixture was concentrated. The residue was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, only CH_2Cl_2) to give **S15** (339 mg, 88%) as a yellow solid; mp > 250 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 10.89 (s, 1H, NH), 9.70 (s, 1H, NH), 8.54 (s, 1H, NH), 8.32 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 7.5, 1H), 8.16–8.08 (m, 6H), 8.07 (d, *J* = 8.5 Hz, 1H) 8.04 (d, *J* = 9.2 Hz, 1H), 8.02 (t, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.63 (d, *J* = 1.1 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.50 –7.43 (m, 2H), 7.24 (dd, *J* = 8.2 Hz, 1.3 Hz, 2H), 7.11 (d, *J* = 1.4 Hz, 1H), 7.06 (dd, *J* = 7.0 Hz, 1.7 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 2H), 6.45 (t, *J* = 7.6 Hz, 1H), 3.14 (s, 1H), 1.53 (s, 9 H, *t*-Bu), 1.53 (s, 9 H, *t*-Bu), 1.52 (s, 9 H, *t*-Bu), 1.31 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 162.6, 144.6, 143.6, 143.3, 143.2, 143.0, 143.0, 142.7, 142.2, 140.4, 140.3, 140.1, 138.9, 137.6, 137.6, 131.6, 131.1, 131.1, 131.1, 131.1, 130.0, 129.8, 128.3, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 126.6, 126.0, 125.7, 125.4, 125.4, 125.3, 125.0, 124.9, 124.2, 123.9, 123.8, 123.7, 123.4, 123.4, 122.9, 122.9, 122.6, 120.6, 119.0, 119.0, 118.9, 117.4, 106.4, 104.4, 104.4, 104.0, 94.2, 92.5, 92.0, 89.7, 88.7, 88.2, 86.4, 81.9, 78.8, 35.1, 35.0, 35.0, 34.9, 32.1, 32.1, 32.1, 31.9, 23.0, 14.3; MALDI-TOF/TOF *m/z* calcd for $C_{83}H_{68}N_5O$ $[M+H]^+$ 1150.5 found 1150.5.

S16 : A Schlenk flask containing **S8** (186 mg, 0.32 mmol), CuI (2.8 mg, 0.01 mmol) and $Pd(PPh_3)_2Cl_2$ (10.1 mg, 0.01 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (2 mL) and Et_3N (2 mL) were added. Then nitrogen-purged **S15** (0.1 mM solution in DMF, 2 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 4.5 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was filtered through short silica gel (EtOAc:*n*-hexane = 1:3 (v/v)) and concentrated. The residue was dissolved in THF (5 mL)

and tetra-*n*-butylammonium fluoride (1 M solution in THF, 0.25 mL) was added dropwise over 3 min in the ice bath. After stirring at room temperature for 20 min, the mixture was concentrated. The residue was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane=1:3 (v/v)) to give **S16** (330 mg, 79%) as a yellow solid; mp > 253 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 11.84 (s, 1H, NH), 9.94 (s, 1H, NH), 8.90 (s, 1H, NH), 8.57 (d, J = 8.2 Hz, 1H), 8.29 (d, J = 7.7 Hz, 1H), 8.26 (d, J = 7.3 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.23 (s, 1H), 8.20 (s, 1H), 8.19 (s, 1H), 8.19 (d, J = 6.0 Hz, 1H), 8.16 (t, J = 9.2 Hz, 1H), 8.16 (s, 1H), 8.10 (d, J = 1.9 Hz, 1H), 8.09 (d, J = 1.9 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 1.7 Hz, 1H), 7.95 (d, J = 1.6 Hz, 1H), 7.80 (d, J = 1.7 Hz, 1H), 7.74 (d, J = 1.5 Hz, 1H), 7.74 (d, J = 1.6 Hz, 1H), 7.67 (d, J = 1.7 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.24 (s, 1H), 7.09 (d, J = 1.3 Hz, 1H), 7.05 (s, 1H), 7.04 (d, J = 7.1 Hz, 2H), 6.87 (t, J = 7.8 Hz, 1H), 6.46 (m, 2H), 6.39 (m, 1H), 6.34 (d, J = 7.7 Hz, 1H), 3.33 (s, 1H), 1.59 (s, 9 H, *t*-Bu), 1.56 (s, 9 H, *t*-Bu), 1.56 (s, 9 H, *t*-Bu), 1.55 (s, 9 H, *t*-Bu), 1.50 (s, 9 H, *t*-Bu), 1.24 (s, 9 H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 162.9, 144.4, 143.6, 143.4, 143.3, 143.3, 143.2, 143.0, 142.5, 142.4, 142.4, 142.2, 141.1, 140.8, 140.4, 139.7, 139.0, 136.7, 131.7, 131.2, 130.7, 130.1, 130.0, 128.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.8, 126.2, 125.8, 125.6, 125.5, 125.0, 124.4, 124.3, 124.0, 123.9, 123.8, 123.7, 123.5, 123.4, 123.3., 122.9, 122.8, 121.8, 121.3, 120.6, 119.0, 119.0, 118.9, 118.6, 118.0, 116.9, 107.1, 105.2, 104.9, 104.8, 104.5, 104.4, 94.5, 93.0, 92.8, 92.4, 91.7, 90.6, 89.3, 88.5, 88.4, 86.3, 82.7, 80.3, 35.2, 35.2, 35.0, 35.0, 35.0, 34.8, 32.4, 32.2, 32.2, 32.2, 32.1, 31.9; MALDI-TOF/TOF *m/z* calcd for $C_{105}H_{91}N_6O$ $[M+H]^+$ 1451.7 found 1451.7.

S17: A Schlenk flask containing 2,6-dibromopyridine (1.0 g, 4.2 mmol), CuI (13.3 mg, 0.21 mmol) and $Pd(PPh_3)_2Cl_2$ (49 mg, 0.21 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (10 mL), Et_3N (4 mL) and trimethylsilylethyne (0.2 mL, 1.4 mmol) were sequentially added, and the solution was stirred at 55 °C for 4 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:3 (v/v)) to give **S17** (210 mg, 20%) as a white solid; mp : 78 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 7.76 (t, J = 7.8 Hz, 1H), 7.62 (dd, J = 8.0 Hz, 0.6 Hz, 1H), 7.55 (dd, J = 7.5 Hz,

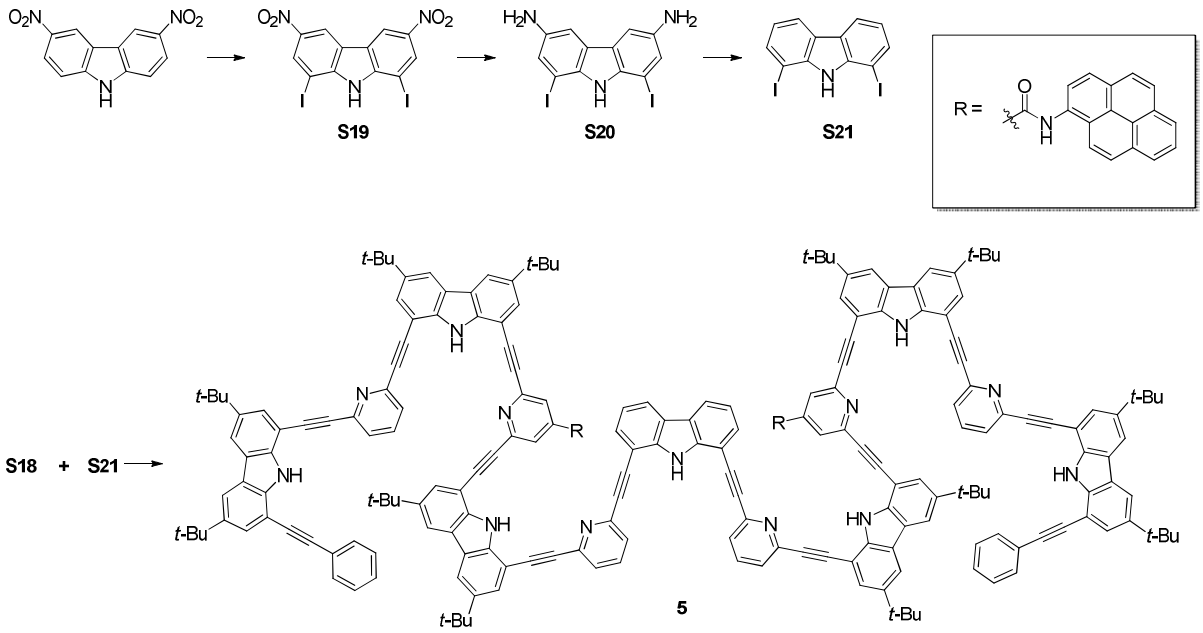
0.6 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 144.0, 142.1, 140.2, 129.0, 127.4, 103.4, 96.4, 0.4; MALDI-TOF/TOF *m/z* calcd for $C_{10}H_{13}BrNSi$ $[M+H]^+$ 254.0 found 253.6.

S18 : A Schlenk flask containing **S17** (60 mg, 0.23 mmol), CuI (2.0 mg, 0.01 mmol) and $Pd(PPh_3)_2Cl_2$ (7.5 mg, 0.01 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (1 mL) and Et_3N (1 mL) were added. Then nitrogen-purged **S16** (0.11 mM solution in DMF, 2 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 3 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was filtered through short silica gel (EtOAc:*n*-hexane = 1:3 (v/v)) and concentrated. The residue was dissolved in THF (3.7 mL) and tetra-*n*-butylammonium fluoride (1 M solution in THF, 0.37 mL) was added dropwise over 3 min in the ice bath. After stirring at room temperature for 25 min, the mixture was concentrated. The residue was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2:*n*-hexane = 8:1 (v/v)) to give **S18** (264 mg, 85%) as a yellow solid; mp > 239 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm) δ 11.51 (s, 1H, NH), 11.40 (s, 1H, NH), 10.51 (s, 1H, NH), 8.66 (d, *J* = 7.7 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 7.5 Hz, 1H), 8.31 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 5.0 Hz, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 8.22–8.19 (m, 3H), 8.18 (d, *J* = 6.6 Hz, 1H), 8.15 (d, *J* = 1.6 Hz, 1H), 8.12 (t, *J* = 7.7 Hz, 1H), 8.06 (s, 1H, NH), 7.97 (d, *J* = 1.7 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.06 (s, 1H), 6.99 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 6.4 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.54 (t, *J* = 7.7 Hz, 1H), 6.49 (t, *J* = 7.7 Hz, 1H), 6.39–6.3 (m, 3H), 6.03 (d, *J* = 4.4 Hz, 1H), 6.0 (d, *J* = 4.4 Hz, 1H), 2.69 (s, 1H), 1.64 (s, 9H, *t*-Bu), 1.62 (s, 9H, *t*-Bu), 1.56 (s, 9H, *t*-Bu), 1.56 (s, 9H, *t*-Bu), 1.55 (s, 9H, *t*-Bu), 1.23 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, ppm) δ 163.1, 144.3, 143.7, 143.1, 143.1, 142.9, 142.8, 142.7, 142.6, 142.5, 142.1, 142.0, 142.0, 141.1, 140.8, 140.8, 140.6, 140.6, 140.2, 139.3, 136.0, 135.3, 131.7, 131.2, 130.6, 130.6, 130.2, 130.0, 128.8, 127.9, 127.8, 127.8, 127.6, 127.6, 127.3, 127.2, 127.2, 126.8, 126.8, 126.5, 126.2, 125.8, 125.6, 125.6, 125.1, 125.0, 124.7, 123.9, 123.8, 123.6, 123.6, 123.6, 123.5, 123.2, 123.1, 122.8, 122.6, 121.0, 120.9, 120.8, 119.0, 118.5, 118.3,118.3, 118.2, 116.7, 107.5,

105.6, 105.2, 105.0, 104.9, 104.4, 94.3, 92.6, 92.6, 92.4, 92.3, 91.5, 91.4, 90.6, 89.0, 88.3, 87.6, 86.4, 81.4, 77.1, 35.2, 35.2, 35.0, 35.0, 34.9, 34.8, 32.4, 32.3, 32.3, 32.3, 32.2, 32.2, 31.8; MALDI-TOF/TOF *m/z* calcd for $C_{112}H_{94}N_7O$ $[M+H]^+$ 1552.8 found 1552.7.

4: A Schlenk flask containing **3** (8.5 mg, 0.016 mmol), CuI (0.2 mg, 0.001 mmol) and $Pd(PPh_3)_2Cl_2$ (0.8 mg, 0.001 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (0.5 mL) and Et_3N (0.5 mL) were added. Then nitrogen-purged **S18** (0.06 mM solution in DMF, 0.6 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 4 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:6 (v/v), EtOAc:CH_2Cl_2:*n*-hexane = 1:2:5 (v/v)) to give **4** (42 mg, 78%) as a yellow solid ; mp > 277 °C (dec); ^{1}H NMR (400 MHz, 1% (v/v) H_2O/acetone-d_6, 25 °C, ppm) δ 11.87 (s, 2H, NH), 11.39 (s, 1H, NH), 11.26 (s, 2H, NH), 10.80 (s, 2H, NH), 9.15 (s, 2H, NH), 8.44 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 9.2 Hz, 2H), 8.35 (d, J = 8.1 Hz, 2H), 8.33 (dd, J = 7.5 Hz, 1.2 Hz, 2H), 8.26 (s, 4H), 8.23 (d, J = 9.6 Hz, 2H), 8.21 (d, J =1.8 Hz, 2H), 8.14 (d, J =1.7 Hz, 2H), 8.09 (d, J =1.7 Hz, 2H), 8.07 (d, J =1.7 Hz, 2H), 8.06 (d, J = 1.8 Hz, 2H), 8.05 (d, J = 1.8 Hz, 2H), 7.98 (d, J = 1.6 Hz, 2H), 7.92 (t, J =7.5 Hz, 2H), 7.88 (dd, J =7.8 Hz, 0.9 Hz, 2H), 7.54 (d, J =1.8 Hz, 2H), 7.51 (d, J = 1.9 Hz, 4H), 7.46 (d, J =1.8 Hz, 2H), 7.44 (d, J =1.1 Hz, 4H), 7.30 (d, J =1.8 Hz, 2H), 7.21–7.17 (m, 4H), 7.02 (d, J =7.6 Hz, 2H), 6.77–6.73 (m, 6H), 6.70 (d, J =1.2 Hz, 2H), 6.55 (s, 2H), 6.40 (t, J = 7.6 Hz, 2H), 6.10 (d, J =7.7 Hz, 2H), 5.67 (d, J =7.6 Hz, 2H), 5.44 (t, J = 7.6 Hz, 2H), 4.61 (d, J =7.6 Hz, 2H), 1.53 (s, 18H, *t*-Bu), 1.48 (s, 54H, *t*-Bu), 1.45 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.18 (s, 18H, *t*-Bu); ^{13}C NMR (100 MHz, 2% (v/v) CD_3OH/CD_2Cl_2, 25 °C, ppm) δ 162.3, 143.1, 143.0, 142.7, 142.7, 142.4, 142.3, 142.2, 142.1, 142.1, 142.1, 142.0, 141.4, 141.3, 140.8, 140.4, 140.3, 140.3, 140.2, 140.1, 140.0, 139.2, 136.1, 134.2, 131.6, 131.1, 131.1, 131.1, 131.1, 131.1, 130.2, 129.8, 128.4, 127.8, 127.8, 127.8, 127.8, 127.7, 127.5, 127.4, 127.2, 127.2, 126.7, 126.6, 125.9, 125.7, 125.4, 125.4, 125.4, 124.9, 124.7, 124.5, 123.8, 123.6, 123.5, 123.5, 123.4, 123.4, 123.3, 123.2, 123.0, 122.9, 121.9, 121.7, 120.9, 120.8, 118.2, 118.2, 118.1, 118.0, 117.6, 117.2, 116.7, 107.5, 106.7, 106.5, 105.6, 105.4, 105.3, 104.8, 104.6, 93.8, 92.6, 92.6, 92.2, 92.1, 92.1, 91.9, 90.0, 89.7, 88.5, 88.4, 88.2, 87.9, 86.4, 34.9, 34.9, 34.9, 34.9, 34.8, 34.8, 34.7, 32.3, 32.2, 32.2, 32.1, 32.1, 32.0, 31.7; MALDI-TOF/TOF *m/z* calcd for $C_{244}H_{208}N_{15}O_2$ $[M+H]^+$ 3379.7 found 3379.7.

1.5 Syntheses of **5**



S19: Sulfuric acid (90%, 107 mL) was cooled to 0 °C and added to *N*-iodosuccinimide (7.69 g, 34.2 mmol), and the mixture was stirred at room temperature for 30 min. To this solution, 3,6-dinitrocarbazole[S3] (2.2 g, 8.55 mmol) was added and stirred for 1.5 h at room temperature. The residue was poured into 250 mL of ice water. The organic solution was washed with brine and $Na_2S_2O_3$ (aq), dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, THF:*n*-hexane = 1:3) to give **S19** (2.314 g, 53%) as a yellow solid; mp > 297 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 11.60 (s, 1H, NH), 9.41 (s, 2H), 8.64 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 146.2, 141.9, 131.7, 123.1, 118.4, 77.3; MALDI-TOF/TOF *m/z* calcd for $C_{12}H_5I_2N_3O_4K$ $[M+K]^+$ 547.8 found 548.0.

S20: Compound **S19** (2.0 g, 3.93 mmol), concentrated HCl (35–37%, 32.8 mL) and $SnCl_2$ (7.45 g, 39.3 mmol) were dissolved in acetic acid (6.1 mL) and refluxed for 2 h. After cooling down to room temperature, the reaction mixture was diluted with EtOAc, washed with KOH solution, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, THF:*n*-hexane = 3:1 (v/v)) to give **S20** (931 mg, 53%) as a green solid; mp > 241 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 8.64 (s, 1H, NH), 7.15 (d, J = 1.9 Hz, 2H), 7.04 (d, J = 1.7 Hz, 2H), 4.89 (s, 4H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 143.2, 135.2, 124.9, 123.4, 104.2, 77.4; MALDI-TOF/TOF *m/z* calcd for $C_{12}H_{10}I_2N_3$ $[M+H]^+$ 449.9 found 449.5.

S21: A solution of **S20** (250 mg, 0.556 mmol), water (2 mL), concentrated HCl (35–37%, 0.83 mL) and EtOH (2.5 mL) was refluxed for 35 min. The solution was allowed to cool to 0 ˚C in an ice bath and concentrated HCl (35–37%, 0.20 mL) was added. A solution of $NaNO_2$ (1.18 g, 16.7 mmol) in H_2O (1.68 mL) was added dropwise and the yellow mixture was stirred at 0˚C for 35 min. Then cold H_3PO_2 (50 wt.% in H_2O 1.68 mL) was added to this solution. The mixture was stirred at room temperature for 3 h. After concentration, the residue was dissolved in EtOAc. The solution was washed with brine and KOH (aq), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc:*n*-hexane = 1:8 (v/v)) to give **S21** (121 mg, 52%) as a brown solid; mp : 169 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 9.06 (s, 1H, NH), 8.19 (dd, J = 7.8 Hz, 0.9 Hz, 2H), 7.89 (dd, J = 7.6 Hz, 0.9 Hz, 2H), 7.1 (t, J =7.6, 2H); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 142.0, 136.3, 125.2, 122.8, 121.8, 76.4; MALDI-TOF/TOF m/z calcd for $C_{12}H_7I_2NNa$ $[M+Na]^+$ 441.9 found 441.1.

5: A Schlenk flask containing **S21** (3.9 mg, 9.4 μmol), CuI (0.13 mg, 0.47 μmol) and $Pd(PPh_3)_2Cl_2$ (0.46 mg, 0.47 μmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed DMF (0.9 mL) and Et_3N (0.4 mL) were added. Then nitrogen-purged **S18** (4 μM solution in DMF, 0.5 mL) was transferred via cannula to the Schlenk flask, and the solution was stirred at 55 °C for 11 h. The mixture was cooled to room temperature and filtered through Celite. The concentrated mixture was dissolved in EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The residue was purified by flash column chromatography (silica gel, THF:*n*-hexane = 1:3 (v/v)) to give **5** (25 mg, 81%) as a yellow solid; mp > 262.3 °C (dec); ^{1}H NMR (400 MHz, 2% (v/v) CD_3OH/CD_2Cl_2, 25 °C, ppm) δ 11.20 (s, 1H, NH), 11.11 (s, 2H, NH), 10.91 (s, 2H, NH), 10.53 (s, 2H, NH), 8.43 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 7.1 Hz, 2H), 8.15 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 8.09 (d, J = 8.9 Hz, 2H), 8.09 (d, J =7.2 Hz, 2H), 8.08 (d, J = 9.4, 2H), 8.05 (t, J = 7.2 Hz, 2H), 8.00 (s, 2H), 7.95 (d, J = 9.4 Hz, 2H), 7.93 (s, 2H), 7.91 (s, 2H), 7.91 (s, 2H), 7.88 (s, 2H, NH), 7.87 (s, 2H), 7.81 (s, 2H), 7.68 (d, J = 7.5 Hz, 2H), 7.49 (s, 2H), 7.47 (s, 2H), 7.46 (s, 2H), 7.41 (s, 2H), 7.35 (s, 2H), 7.33 (s, 2H), 7.20 (d, J = 7.0 Hz, 4H), 7.12 (d, J = 7.1 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 6.98 (t, J = 7.2 Hz, 2H), 6.57–6.48 (m, 6H), 6.54 (s, 2H), 6.32 (t, J = 6.5 Hz, 2H), 6.21 (s, 2H), 6.09 (d, J = 7.2 Hz, 2H), 5.55 (d, J = 7.7 Hz, 2H), 5.51 (t, J = 7.3 Hz, 2H), 5.21 (d, J = 6.9 Hz, 2H), 1.54 (s, 18 H, *t*-Bu), 1.50 (s, 18 H, *t*-Bu), 1.48 (s, 18 H, *t*-Bu), 1.46 (s, 18 H, *t*-Bu), 1.36 (s, 18 H, *t*-Bu), 1.15 (s, 18 H, *t*-Bu); ^{13}C NMR (100 MHz, 2%

(v/v) CD_3OH/CD_2Cl_2, 25 °C, ppm) δ 163.1, 144.3, 143.7, 143.1, 143.1, 142.9, 142.8, 142.7, 142.6, 142.5, 142.1, 142.0, 142.0, 141.3, 141.2, 140.5, 140.4, 140.3, 140.3, 140.1, 140.1, 139.1, 135.9, 134.1, 131.7, 131.1, 131.1, 131.1, 131.1, 130.2, 130.1, 129.7, 128.2, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 127.1, 126.8, 126.7, 126.0, 125.7, 125.7, 125.5, 125.5, 125.4, 125.0, 124.7, 123.8, 123.8, 123.6, 123.5, 123.4, 123.3, 123.3, 123.3, 123.2, 122.9, 122.3, 122.3, 122.1, 122.1, 120.9, 120.7, 120.5, 119.7, 119.2, 118.3, 118.2, 118.0, 118.0, 117.6, 117.0, 106.9, 106.5, 105.8, 105.2, 105.1, 104.8, 104.4, 93.8, 93.3, 92.6, 92.3, 92.2, 92.1, 91.6, 89.9, 89.9, 88.4, 88.1, 87.9, 87.3, 86.5, 35.0, 34.9, 34.9, 34.9, 34.8, 34.7, 32.3, 32.2, 32.2, 32.1, 32.0, 31.7; HRMS (ESI Q-TOF) *m/z*: $[M+H+Na]^{2+}$ calcd for $C_{236}H_{192}N_{15}O_2Na$ 1645.2639 found 1645.2640.

G1[S4, S5], **G2**[S6] and **G3**[S7] were synthesised following literature procedures.

2. NMR studies

2.1 Solvent-dependent ^{1}H NMR spectra

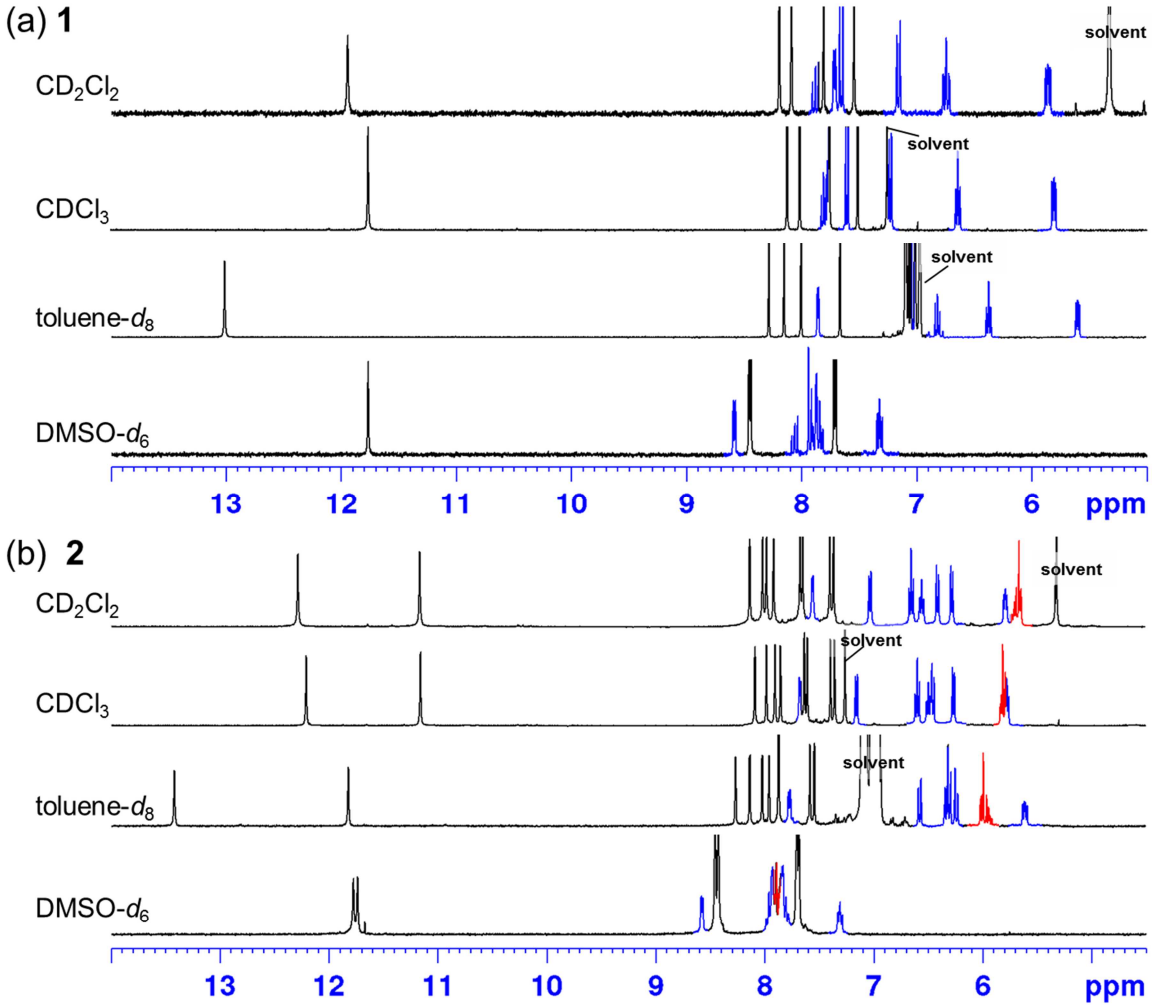


Fig. S1 Partial ^{1}H NMR spectra (25 °C) of (a) **1** (2.0 mM) and (b) **2** (10 mM) in water-saturated CD_2Cl_2, $CDCl_3$, toluene-d_8 and DMSO-d_6. The pyridine CH signals are either red- (central) or blue-coloured (other pyridines).

Table S1. ^{1}H NMR chemical shifts (ppm) and differences of **1** (2.0 mM) and **2** (10 mM) in water-saturated CD_2Cl_2 and in DMSO-d_6 at 25 °C.

	Peak	δ in CD_2Cl_2	δ in DMSO-d_6	δ (DMSO-d_6) – δ (CD_2Cl_2)
1	1	7.71 (ddd, *J* =4.8, 1.7, 0.9)	8.58 (ddd, *J* = 4.9, 1.8, 1.6)	0.87
	2	5.85 (ddd, *J* = 7.65, 5.0, 1.2)	7.32 (ddd, *J* = 7.1, 4.8, 1.8)	1.47
	3	6.74 (td, *J* = 7.7, 1.8)	7.83 (td, *J* =7.8, 1.8)	1.09
	4	7.15 (ddd, *J* =7.8, 1.3, 1.0)	7.87 (ddd, *J* = 8.0, 1.9, 1.2)	0.72
	5	7.54 (d, *J* = 1.8)	7.72 (d, *J* = 1.9)	0.18
	6	8.09 (d, *J* = 1.8)	8.45 (d, *J* = 1.8)	0.36
	7	8.19 (d, *J* = 1.8)	8.44 (d, *J* = 1.8)	0.25
	8	7.81 (d, *J* =1.9)	7.70 (d, *J* = 1.9)	0.11
	9	7.88 (dd, *J* = 8.2, 7.4)	8.06 (dd, *J* = 8.5, 7.2)	0.18
	10	7.65 (d, *J* =7.8)	7.92 (d, *J* = 7.8)	0.27
2	1	7.56 (d, *J* = 4.2)	8.57 (d, *J* = 4.7)	1.01
	2	5.79 (ddd, *J* = 7.6, 4.8, 0.8)	7.31 (ddd, *J* = 7.1, 4.9, 1.5)	1.52
	3	6.55 (td, *J* = 7.7, 1.7)	7.80 (td, *J* = 7.9, 1.5)	1.25
	4	7.03 (d, *J* = 7.7)	7.93	0.90
	5	7.40 (d, *J* = 1.7)	7.70 (d, *J* =1.7)	0.30
	6	8.02 (d, *J* = 1.7)	8.45 (s)	0.43
	7	8.14 (d, *J* = 1.8)	8.42 (d, *J* = 1.7)	0.28
	8	7.65 (d, *J* = 1.7)	7.68 (d, *J* = 1.7)	0.03
	9	6.28 (dd, *J* = 7.7, 0.7)	7.84	1.56
	10	6.65 (t, *J* =7.7)	7.96 (t, *J* =7.5)	1.31
	11	6.41 (dd, *J* = 7.8, 0.6)	7.84	1.43
	12	7.67 (d, *J* = 1.7)	7.71 (d, *J* =1.7)	0.04
	13	7.98 (d, *J* = 1.8)	8.45 (s)	0.47
	14	7.92 (d, *J* = 1.8)	8.42 (d, *J* = 1.7)	0.50
	15	7.37 (d, *J* = 1.7)	7.68 (d, *J* = 1.7)	0.31
	16	5.71 (dd, *J* = 9.1, 6.1)	7.89	2.23
	17	5.66 (d, *J* = 7.4)	7.89	2.18

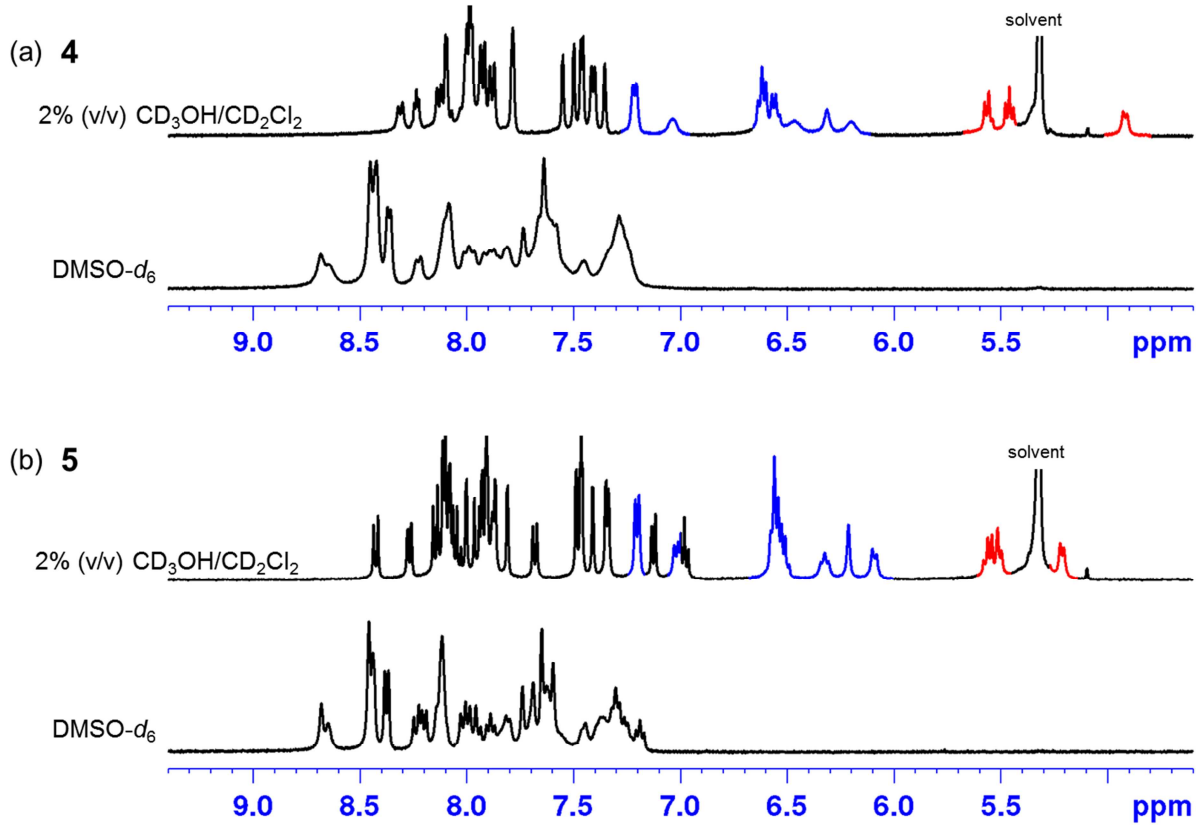


Fig. S2 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of (a) **4** (4.0 mM) and (b) **5** (4.0 mM) in DMSO-d_6 and 2% (v/v) CD_3OH /CD_2Cl_2. ^{1}H NMR signals for central pyridines are red-coloured and those for other pyridines and terminal benzenes are blue-coloured.

2.2 2D-ROESY NMR spectra of **2** and **5**

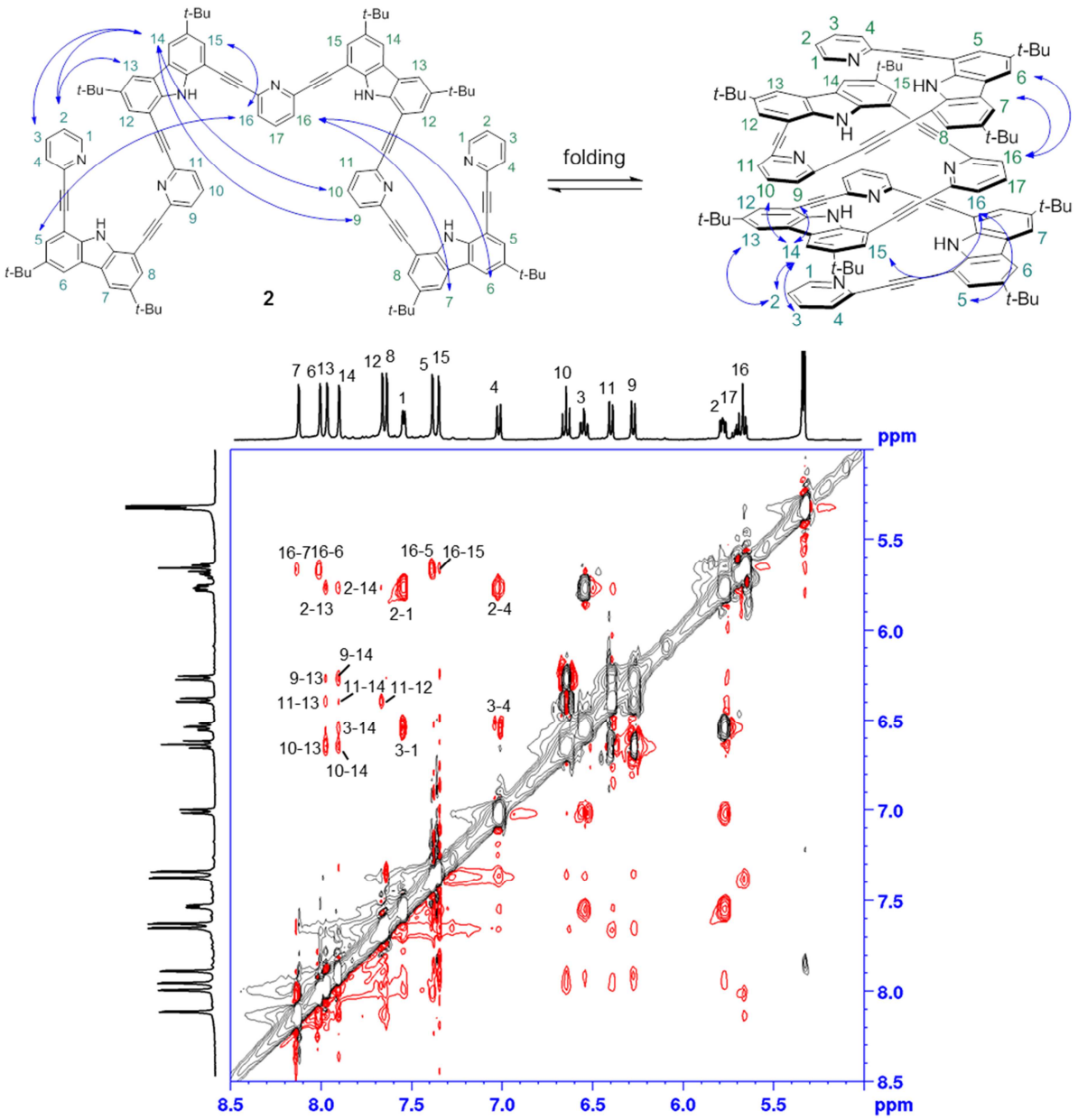


Fig. S3. Partial ROESY spectrum (400 MHz, 25 °C, mixing time: 400 ms) of **2** (10 mM, CD_2Cl_2).

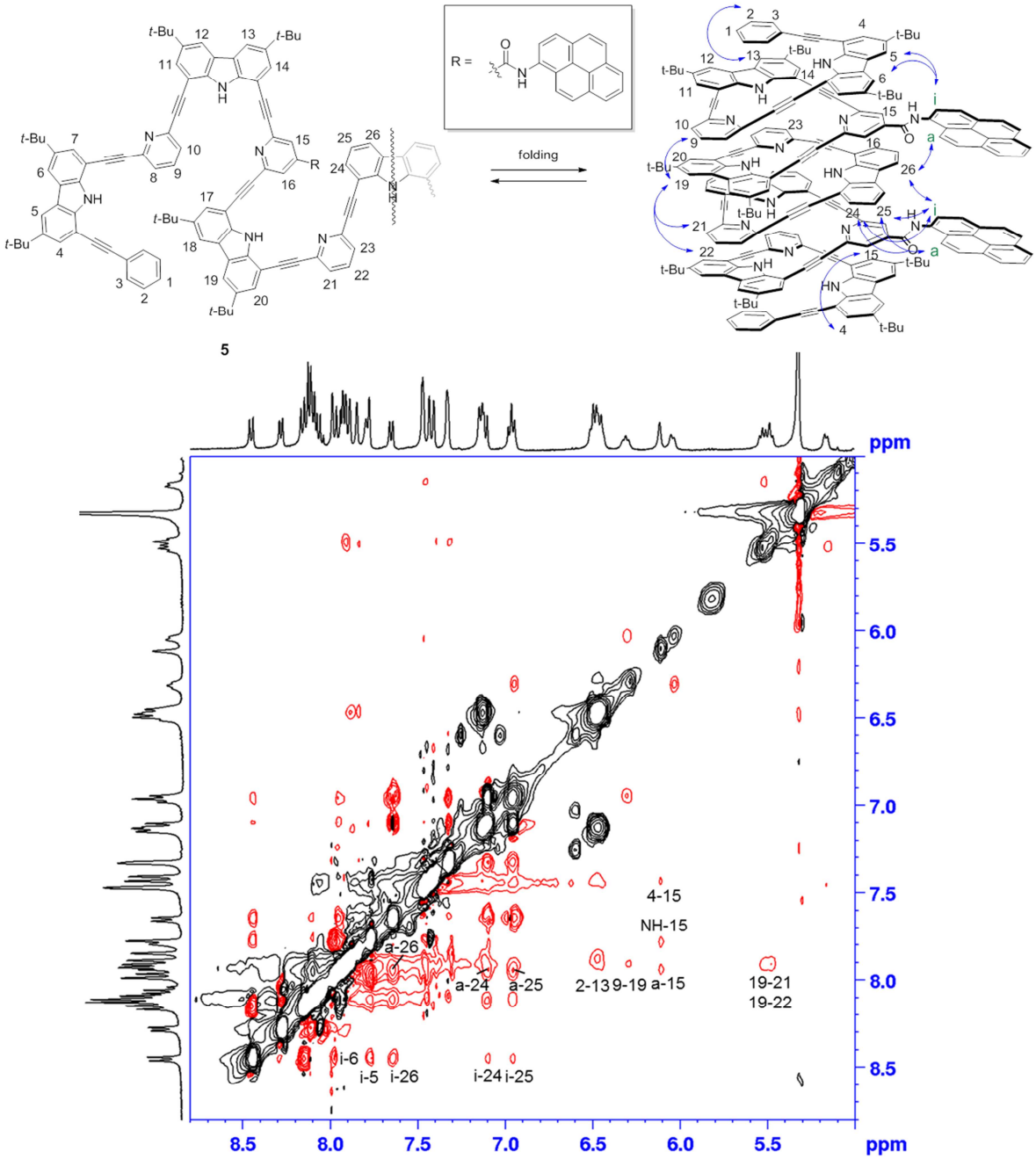


Fig. S4. Partial ROESY spectrum (400 MHz, 25 °C, mixing time: 400 ms) of **5** (7.0 mM, 2% (v/v) CD_3OH/CD_2Cl_2).

2.3 Binding studies of **4** and **5**

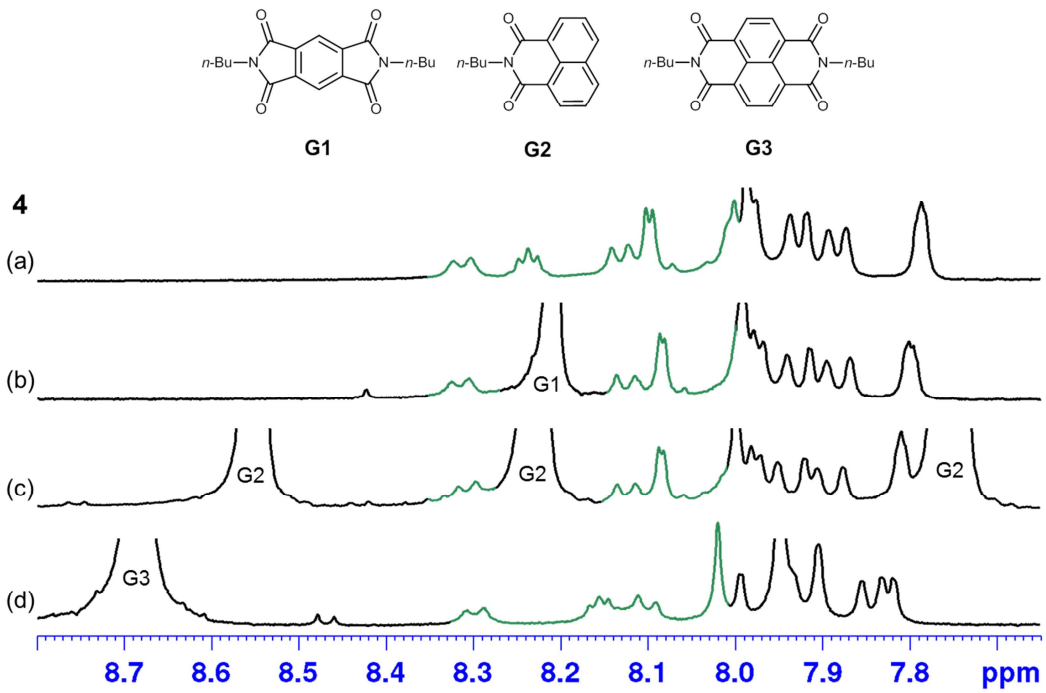


Fig. S5. Partial ^{1}H NMR (400 MHz, 25 °C) spectra of **4** (4.0 mM) in the presence of (a) none, (b) **G1** (20 equiv), (c) **G2** (20 equiv) and (d) **G3** (20 equiv) in 2% (v/v) CD_3OH/CD_2Cl_2. The pyrene CH signals are green-coloured.

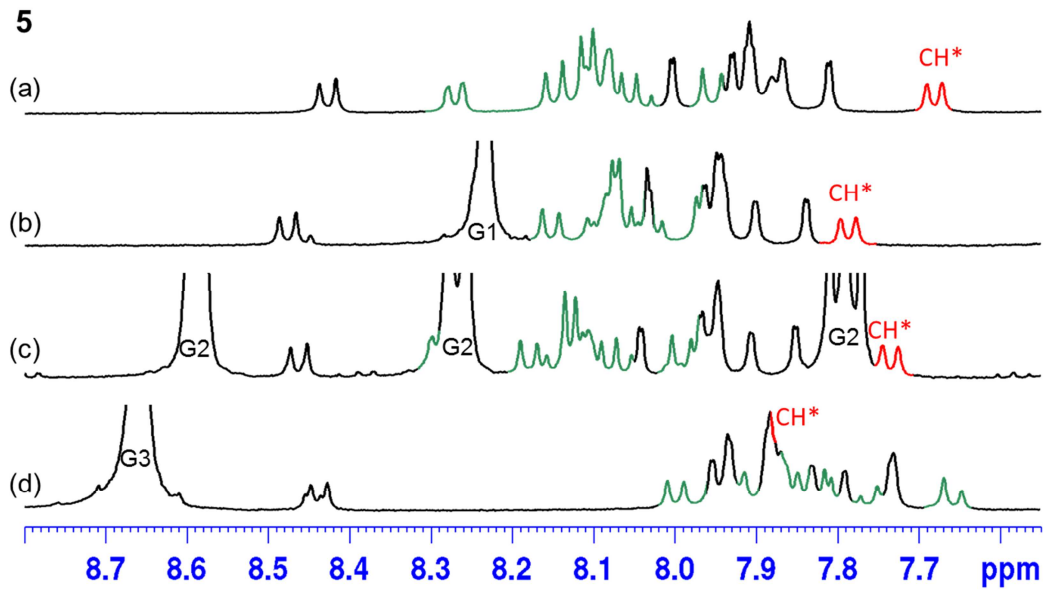


Fig. S6. Partial ^{1}H NMR (400 MHz, 25 °C) spectra of **5** (4.0 mM) in the presence of (a) none, (b) **G1** (20 equiv), (c) **G2** (20 equiv) and (d) **G3** (20 equiv) in 2% (v/v) CD_3OH/CD_2Cl_2. The green and red-coloured peaks correspond to the CH signals of two pyrenes and CH* in the central carbazole, respectively.

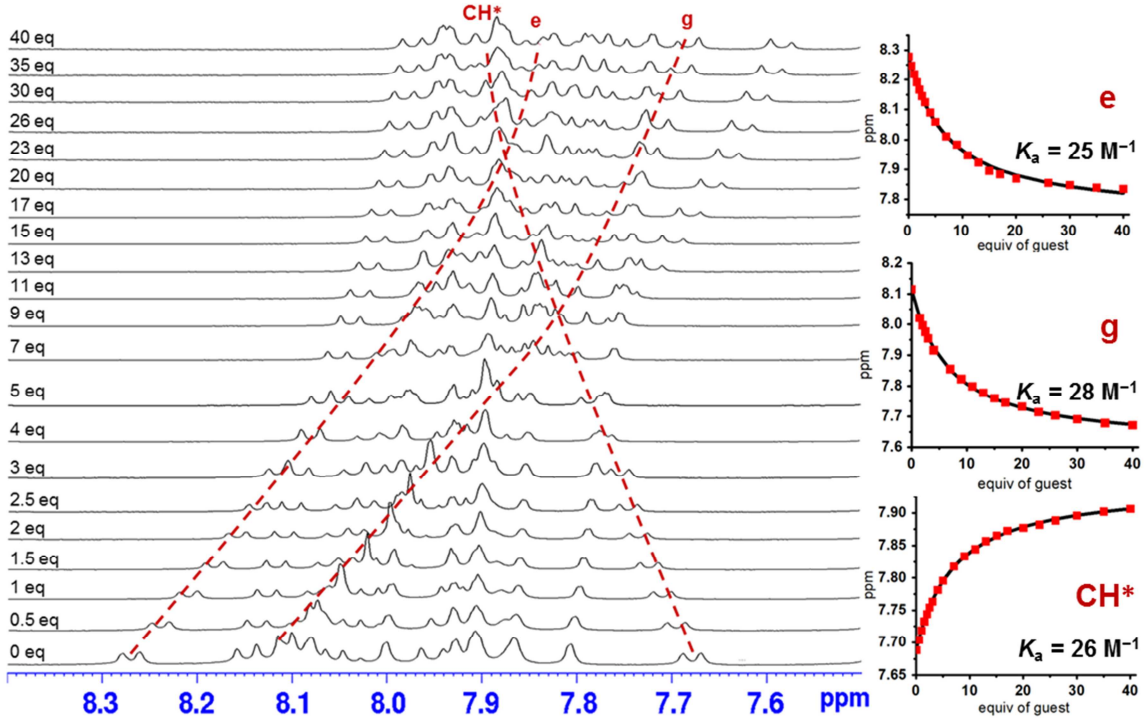


Fig. S7 Partial ^{1}H NMR spectra of **5** (4.0×10^{-3} M) with the addition of **G3** in 2% (v/v) CD_3OH/CD_2Cl_2. The experimental (dots) and theoretically fitting (lines) curves of individual ^{1}H NMR signals are shown right.

Table S2. Association constants (K_a, M^{-1}) between **5** and **G3** in 2% (v/v) CD_3OH/CD_2Cl_2 at 25 °C

	Peak	δ_{free}	$\delta_{obs,complex}$	$\delta_{calcd,complex}$	K_a	Average (±s.d)
Titration 1	e	8.28	7.84	7.82	25	26 (±1.2)
	g	8.11	7.67	7.67	28	
	CH*	7.69	7.91	7.91	26	
Titration 2	e	8.28	7.85	7.84	28	27 (±1.0)
	g	8.11	7.67	7.67	26	
	CH*	7.69	7.91	7.91	26	

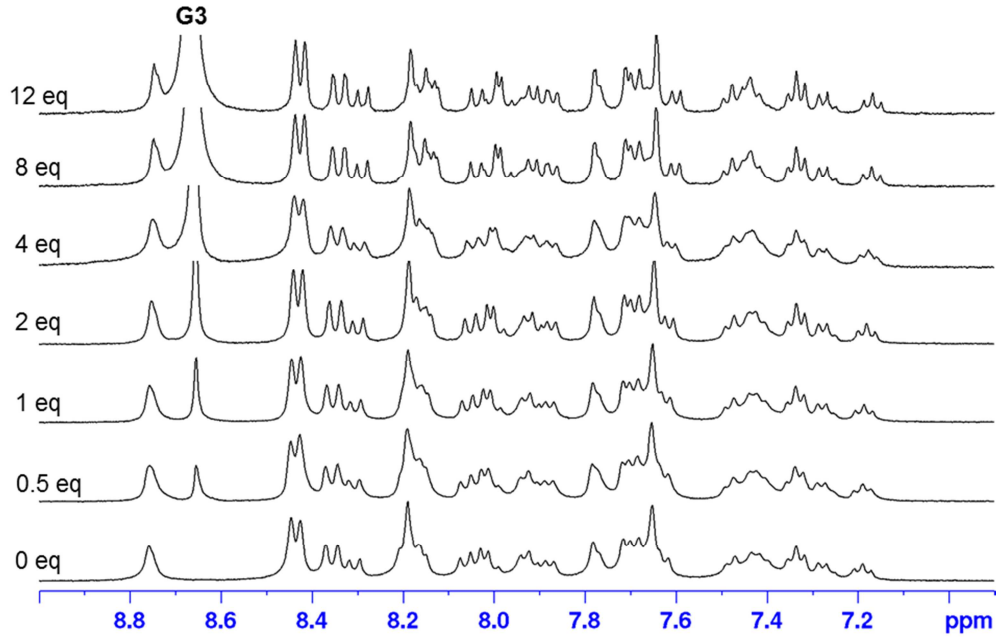


Fig. S8 Partial ^{1}H NMR spectra of **5** (4.0×10^{-3} M) with the addition of **G3** in 30% (v/v) THF-d_8/DMSO-d_6.

2.4. Job's plot between **5** and **G3**

Stock solutions of **5** (8.0 mM) and **G3** (8.0 mM) were separately prepared in 2% (v/v) CD_3OH/CD_2Cl_2. Using these stock solutions, 10 separate solutions containing different ratios of **5** and **G3** were prepared. [**5**/**G3** (μL) = 400:0, 360:40, 320:80, 280:120, 240:160, 200:200, 160:240, 120:280, 80:320, 40:360]. ^{1}H NMR spectrum for each solution was recorded to construct Job's plots based on the signals (H^e and H*) of **5**. The concentrations of complex were plotted against the mole fraction of **G3**, and the resulting curve showed a maximum at 0.5 mol fraction.

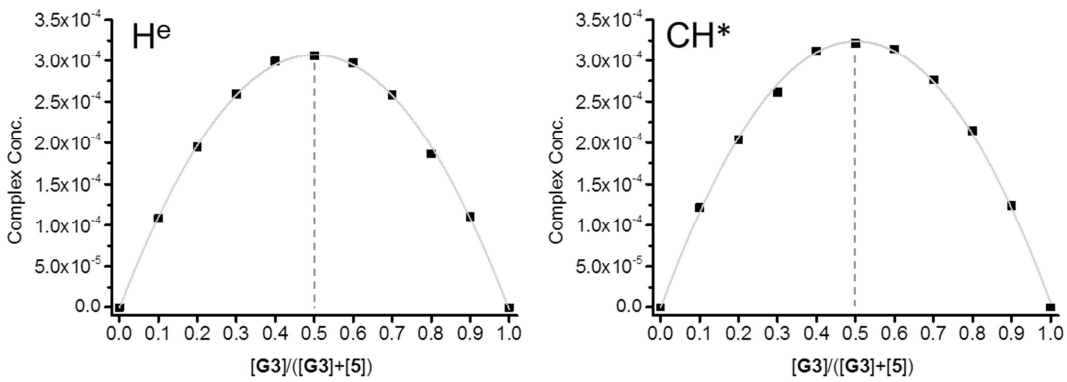


Fig. **S9** Job's plots for the binding of **5** and **G3** in 2% (v/v) CD_3OH/CD_2Cl_2 at 25 °C.

3. Fluorescence studies

Fluorescence (excited at 342 nm) spectra were taken with HITACHI-F7000 fluorescence spectrophotometer. All solvents of spectroscopic grade were degassed prior to use, and CH_2Cl_2 was filtered through basic alumina prior to use.

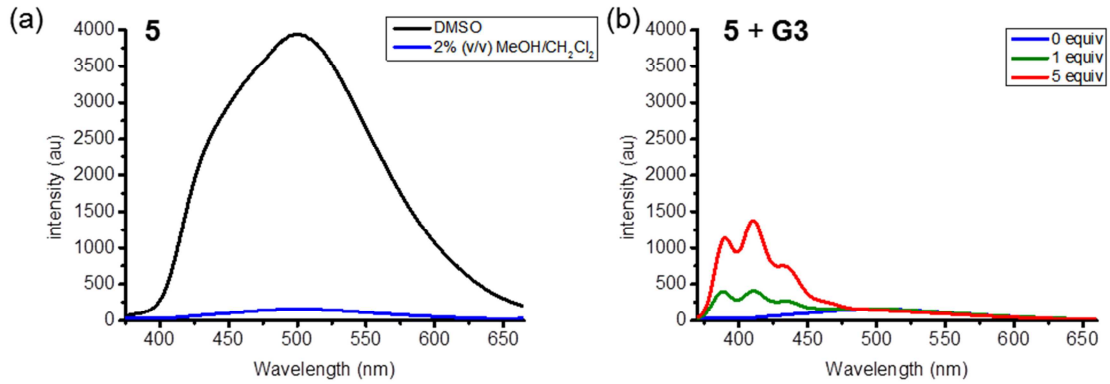


Fig. S10 (a) Fluorescence spectra of **5** (5.0×10^{-6} M) in DMSO (black line) and 2% (v/v) MeOH/CH_2Cl_2 (blue line) at 25 °C, and (b) fluorescence spectra of **5** (5.0×10^{-6} M, 2% (v/v) MeOH/CH_2Cl_2) in the presece of **G3** (0, 1, and 5 equiv).

4. Computer modeling studies

Computer modeling structures were generated using MacroModeling 9.1 program[S8] with MMFFs force field[S9].

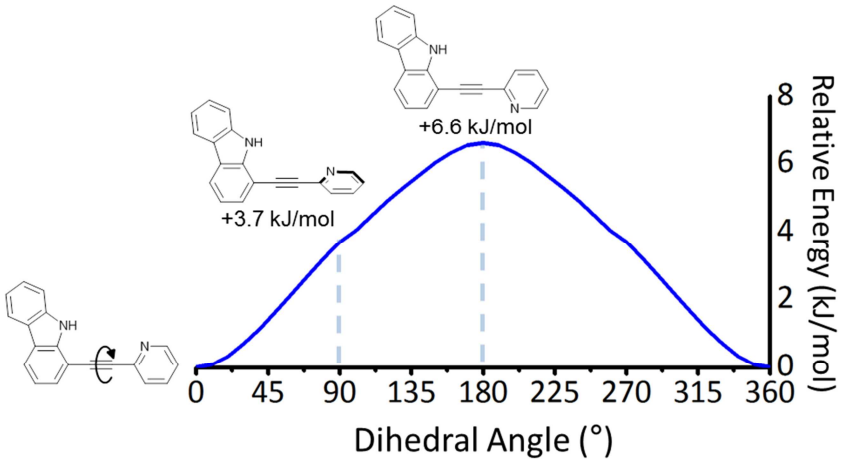


Fig. S11 Energy differences (kJ/mol) of carbazole-pyridine conformers in gas phase**.** Higher energy structures were generated by dihedral driving calculation.

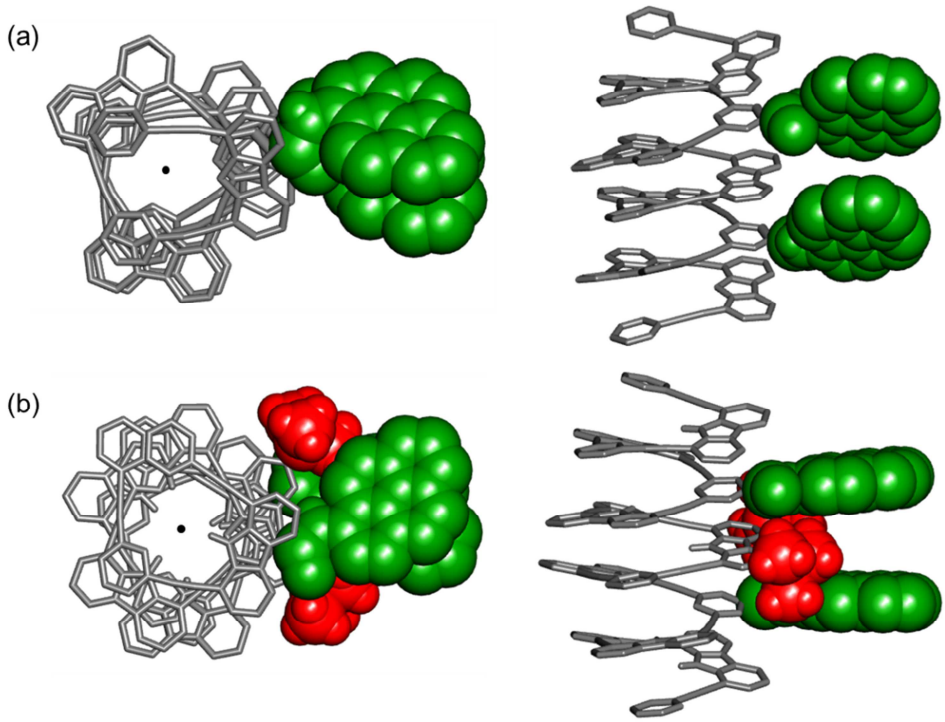


Fig. S12 Two different views of (a) X-ray crystal structure of **5**·4H_2O⊃**G3**, and (b) energy-minimized structure of **4**·4H_2O. Energy-minimized structures were obtained through Monte Carlo conformation search in $CHCl_3$ phase. The pyrene and *t*-Bu groups in central carbazole are shown in green and red space-filling models, respectively.

5. X-ray crystallographic analyses

5.1 Crystal growing

1·2H_2O : Compound **1** was dissolved in EtOAc in a test tube, to which solution pentane was slowly vapor-diffused for a few days at room temperature to yield single crystals suitable for the X-ray diffraction.

2·3H_2O : Compound **2** was dissolved in EtOAc in a test tube in a test tube, to which solution pentane was slowly vapor-diffused for a few days at room temperature to yield single crystals suitable for the X-ray diffraction.

5·4H_2O⊃**G3** : Compound **5** and **G3** (3 equiv) were dissolved in 7:3 CH_2Cl_2/heptane solution in a test tube, to which solution pentane was slowly vapor-diffused over a week at room temperature to yield single crystals suitable for the X-ray diffraction.

5.2 Data collection

Crystals were coated with Parabar oil and the diffraction data measured at 100 K with synchrotron radiation (λ = 0.700000 Å (**1**·2H_2O, **2**·3H_2O), 0.900000 Å (**5**·4H_2O⊃**G3**)) on a Rayonix MX225HS detector at BL2D SMC with a silicon (111) double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program[S10] was used for data collection (detector distance = 66 mm, omega scan; Δω = 3º, exposure time = 0.3 (**5**·4H_2O⊃**G3**) and 0.5 (**1**·2H_2O and **2**·3H_2O) sec per frame) and HKL3000sm (Ver. 716.7)[S11] was used for cell refinement, reduction and absorption correction.

5.3 Structure solution and refinement

The crystal structures were solved by the direct method with SHELX-XT[S12] and refined by full-matrix least-squares calculations with the SHELX-XL[S13] in the Olex2 program package[S14]. The structure solutions of crystals were obtained by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealised positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

1·2H_2O : The final least-squares refinement of 326 parameters against 9359 data resulted in residuals R (based on F2 for I ≥ 2σ) and wR (based on F2 for all data) of 0.0557and 0.1534, respectively. The final difference Fourier map was featureless.

2·3H_2O : The final least-squares refinement of 650 parameters against 17530 data resulted in residuals R (based on F2 for I ≥ 2σ) and wR (based on F2 for all data) of 0.0666 and 0.1870, respectively. The final difference Fourier map was featureless.

5·4H_2O⊃**G3** : *t*-Butyl groups bonded to carbazoles, two CH_2Cl_2 and a pentane were observed as disordered and modeled using SADI, DFIX and ISOR restraints. The final least-squares refinement of 2706 parameters against 40238 data resulted in residuals R (based on F2 for I ≥ 2σ) and wR (based on F2 for all data) of 0.1034 and 0.3028, respectively. The final difference Fourier map was featureless.

5.4 Summary

1·2H_2O : Crystal Data for $C_{63}H_{61}N_5O_2$ (M =920.16 g/mol): orthorhombic, space group Pbcn (no. 60), a = 10.680(2) Å, b = 12.393(3) Å, c = 37.712(8) Å, V = 4991.5(17) Å^3, Z = 4, T = 100 K, μ(synchrotron) = 0.072 mm^{-1}, *Dcalc* = 1.224 g/cm^3, 32358 reflections measured (4.316° ≤ 2Θ ≤ 67.292°), 9359 unique (R_{int} = 0.0390, R_{sigma} = 0.0352) which were used in all calculations. The final R_1 was 0.0557 (I > 2σ(I)) and wR_2 was 0.1576 (all data).

2·3H_2O : Crystal Data for $C_{121}H_{115}N_9O_3$ (M =1743.21 g/mol): monoclinic, space group C2/c (no. 15), a = 22.767(5) Å, b = 23.169(5) Å, c = 20.718(4) Å, β = 106.42(3)°, V = 10483(4) Å^3, Z = 4, T = 100.0 K, μ(synchrotron) = 0.064 mm^{-1}, *Dcalc* = 1.105 g/cm^3, 62934 reflections measured (2.89° ≤ 2Θ ≤ 67.404°), 17530 unique (R_{int} = 0.0789, R_{sigma} = 0.0617) which were used in all calculations. The final R_1 was 0.0666 (I > 2σ(I)) and wR_2 was 0.1997 (all data).

5·4H_2O⊃**G3** : Crystal Data for $C_{265}H_{237}Cl_4N_{17}O_{10}$ (M =3961.50 g/mol): monoclinic, space group C2/c (no. 15), a = 83.483(17) Å, b = 20.589(4) Å, c = 30.137(6) Å, β = 108.46(3)°, V = 49136(19) Å^3, Z = 8, T = 100 K, μ(synchrotron) = 0.199 mm^{-1}, *Dcalc* = 1.071 g/cm^3, 130590 reflections measured (2.588° ≤ 2Θ ≤ 65°), 40238 unique (R_{int} = 0.1059, R_{sigma} = 0.1092) which were used in all calculations. The final R_1 was 0.1034 (I > 2σ(I)) and wR_2 was 0.3399 (all data).

Table S3 Crystal data and structure refinement for **1**·$2H_2O$

Identification code	**1**·$2H_2O$
Empirical formula	$C_{63}H_{61}N_5O_2$
Formula weight	920.16
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbcn
a/Å	10.680(2)
b/Å	12.393(3)
c/Å	37.712(8)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4991.5(17)
Z	4
$\rho_{calc}g/cm^3$	1.224
μ/mm^{-1}	0.072
F(000)	1960.0
Crystal size/mm^3	0.083 × 0.064 × 0.057
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	4.316 to 67.292
Index ranges	$-16 \le h \le 16$, $-19 \le k \le 19$, $-57 \le l \le 57$
Reflections collected	32358
Independent reflections	9359 [R_{int} = 0.0390, R_{sigma} = 0.0352]
Data/restraints/parameters	9359/0/326
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1534
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1576
Largest diff. peak/hole / e $Å^{-3}$	0.50/-0.37
CCDC number	2122401

Table S4 Crystal data and structure refinement for **2**·3H_2O

Identification code	**2**·3H_2O
Empirical formula	$C_{121}H_{115}N_9O_3$
Formula weight	1743.21
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	22.767(5)
b/Å	23.169(5)
c/Å	20.718(4)
α/°	90
β/°	106.42(3)
γ/°	90
Volume/Å^3	10483(4)
Z	4
ρ_{calc}g/cm^3	1.105
μ/mm^{-1}	0.064
F(000)	3712.0
Crystal size/mm^3	0.17 × 0.09 × 0.09
Radiation	synchrotron (λ = 0.700000)
2Θ range for data collection/°	2.89 to 67.404
Index ranges	-32 ≤ h ≤ 32, -30 ≤ k ≤ 30, -29 ≤ l ≤ 29
Reflections collected	62934
Independent reflections	17530 [R_{int} = 0.0789, R_{sigma} = 0.0617]
Data/restraints/parameters	17530/0/650
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1870
Final R indexes [all data]	R_1 = 0.0866, wR_2 = 0.1997
Largest diff. peak/hole / e Å^{-3}	0.44/-0.34
CCDC number	2122402

Table S5 Crystal data and structure refinement for **5**·4H_2O⊃**G3**

Identification code	**5**·4H_2O⊃**G3**
Empirical formula	$C_{265}H_{237}Cl_4N_{17}O_{10}$
Formula weight	3961.50
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	83.483(17)
b/Å	20.589(4)
c/Å	30.137(6)
α/°	90
β/°	108.46(3)
γ/°	90
Volume/$Å^3$	49136(19)
Z	8
$\rho_{calc}g/cm^3$	1.071
μ/mm^{-1}	0.199
F(000)	16752.0
Crystal size/mm^3	0.21 × 0.1 × 0.06
Radiation	synchrotron (λ = 0.900000)
2Θ range for data collection/°	2.588 to 65
Index ranges	-95 ≤ h ≤ 95, -23 ≤ k ≤ 23, -34 ≤ l ≤ 34
Reflections collected	130590
Independent reflections	40238 [R_{int} = 0.1059, R_{sigma} = 0.1092]
Data/restraints/parameters	40238/187/2706
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.1034, wR_2 = 0.3028
Final R indexes [all data]	R_1 = 0.1660, wR_2 = 0.3399
Largest diff. peak/hole / e $Å^{-3}$	1.23/-0.74
CCDC number	2122403

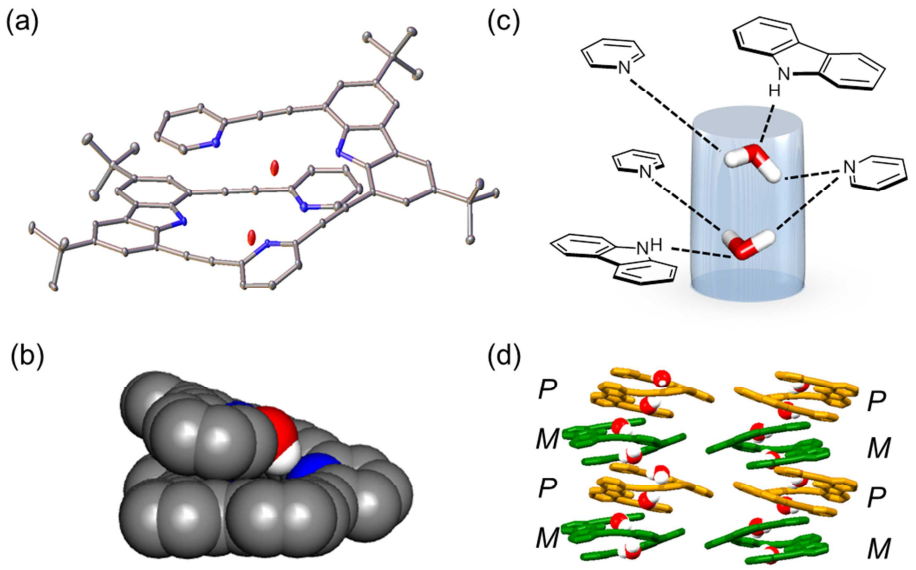


Fig. S13 (a) Thermal ellipsoid, (b) space-filling representation of the X-ray crystal structure of **1**·2H_2O. (c) Schematic representation of hydrogen bonding networks in **1**·2H_2O, and (d) a crystal packing view of **1**·2H_2O. In (a, b, c), only *P*-helix is shown.

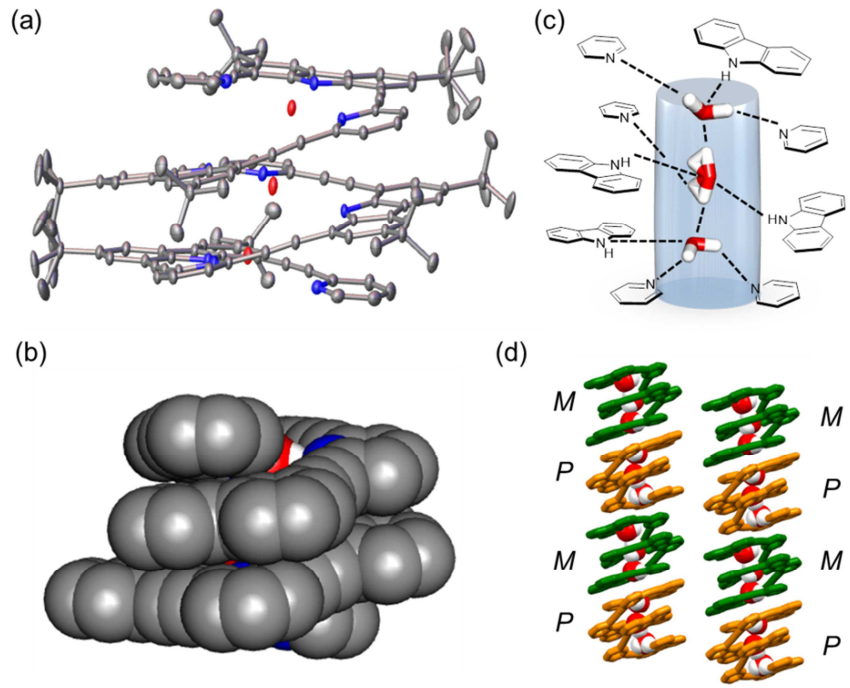


Fig. S14 (a) Thermal ellipsoid, space-filling representation of the X-ray crystal structure of **2**·3H_2O. (c) Schematic representation of hydrogen bonding networks in **2**·3H_2O, and (d) a crystal packing view of **2**·3H_2O. In (a, b, c), only *P*-helix is shown.

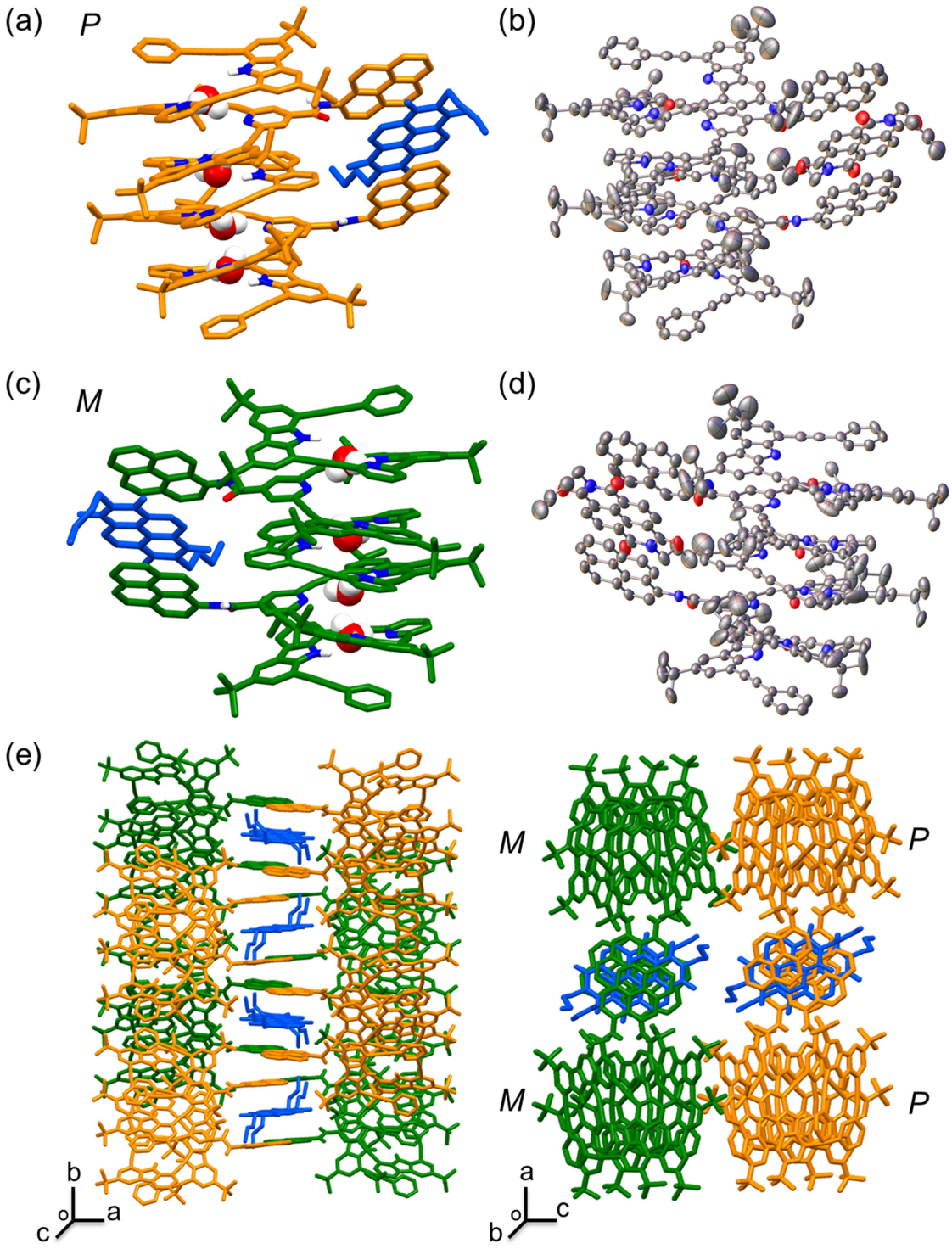


Fig. S15 (a, b) Tube and thermal ellipsoid representations of the *P*- helix of **5**·4H_2O⊃**G3**, (c, d) tube and thermal ellipsoid representations of the *M*- helix of **5**·4H_2O⊃**G3**, and (e) two different packing views of *P*-and *M*-helices of **5**·4H_2O⊃**G3**. *P* and *M* helices are shown in orange and green, respectively, and **G3** is shown in blue.

6. NMR spectra

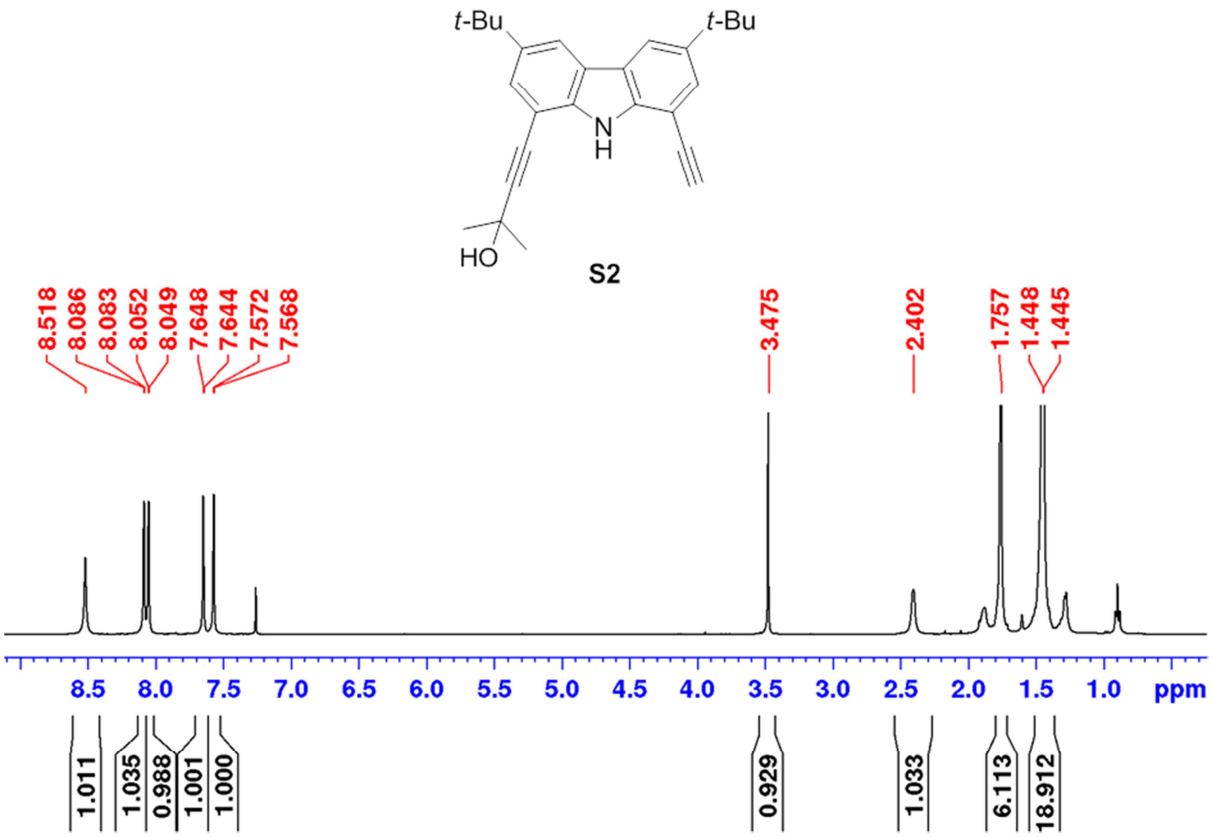


Fig. S16 ^{1}H NMR of **S2** (400 MHz, $CDCl_3$, 25 °C)

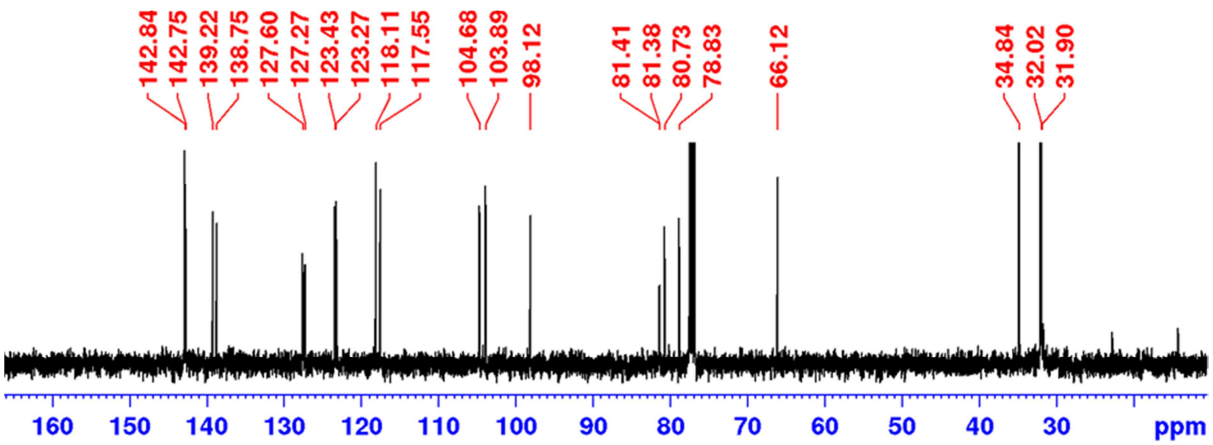


Fig. S17 ^{13}C NMR of **S2** (100 MHz, $CDCl_3$, 25 °C)

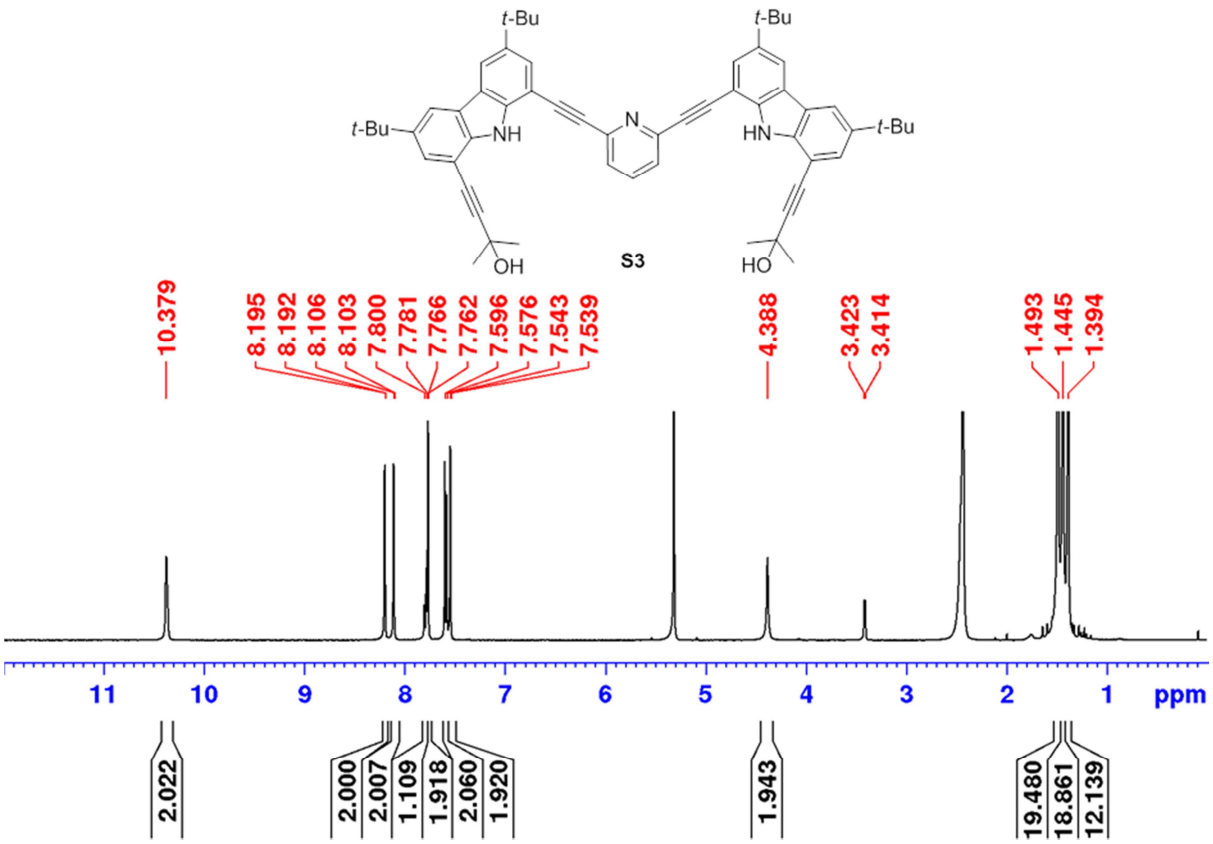


Fig. S18 ^{1}H NMR of **S3** (400 MHz, CD_2Cl_2, 25 °C)

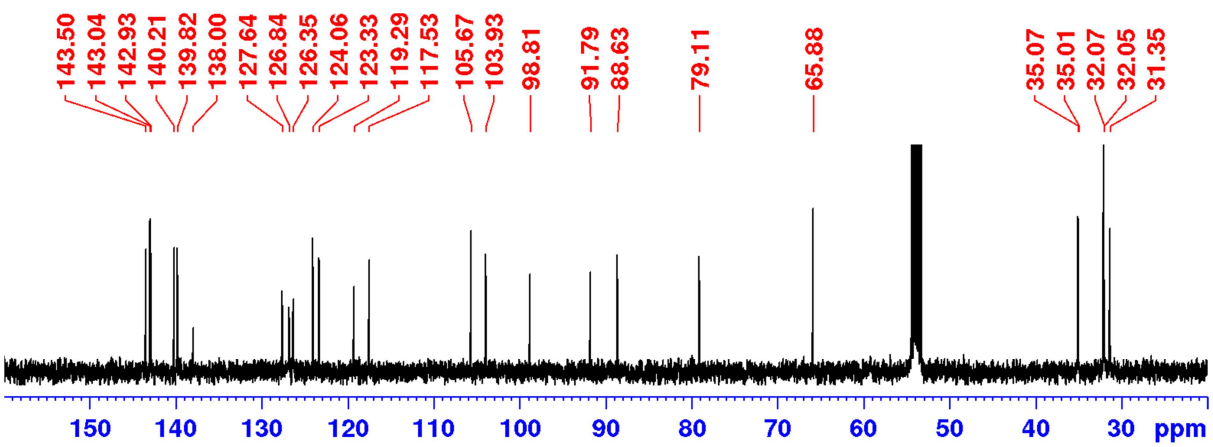


Fig. S19 ^{13}C NMR of **S3** (100 MHz, CD_2Cl_2, 25 °C)

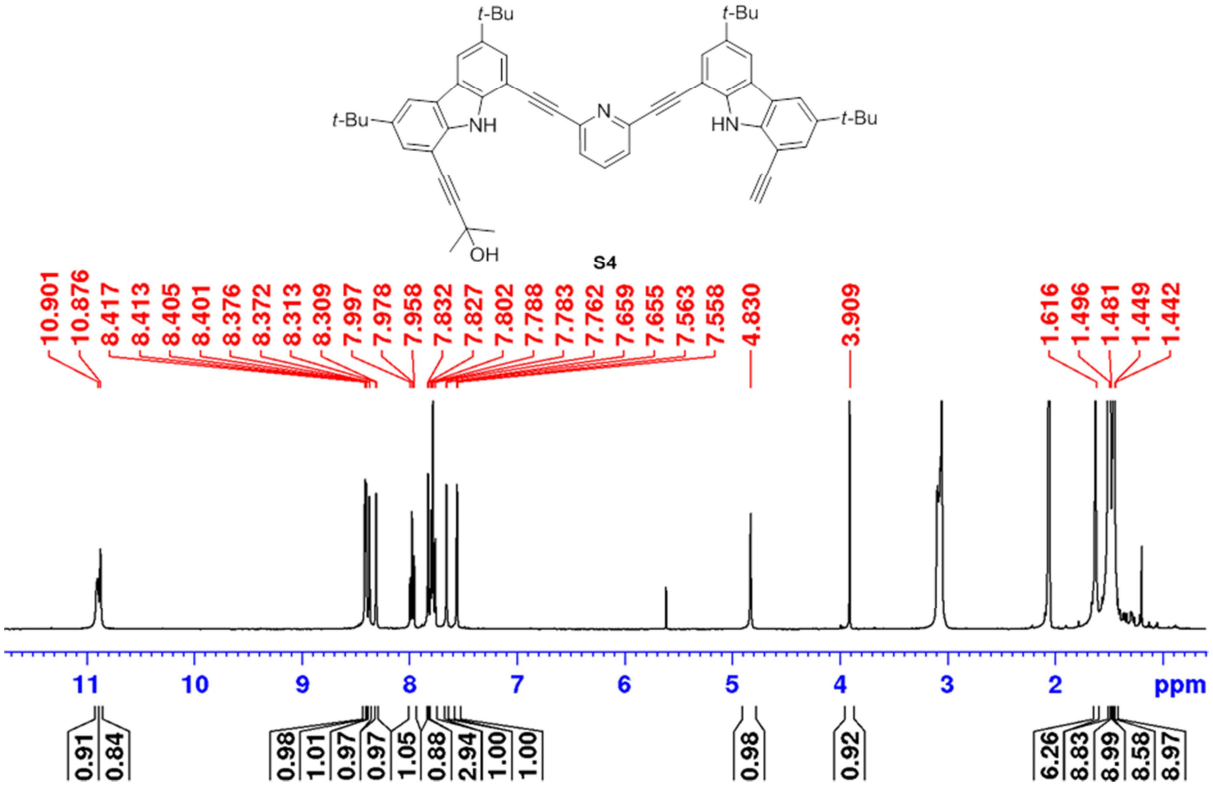


Fig. S20 [1]H NMR of **S4** (400 MHz, acetone-d_6, 25 °C)

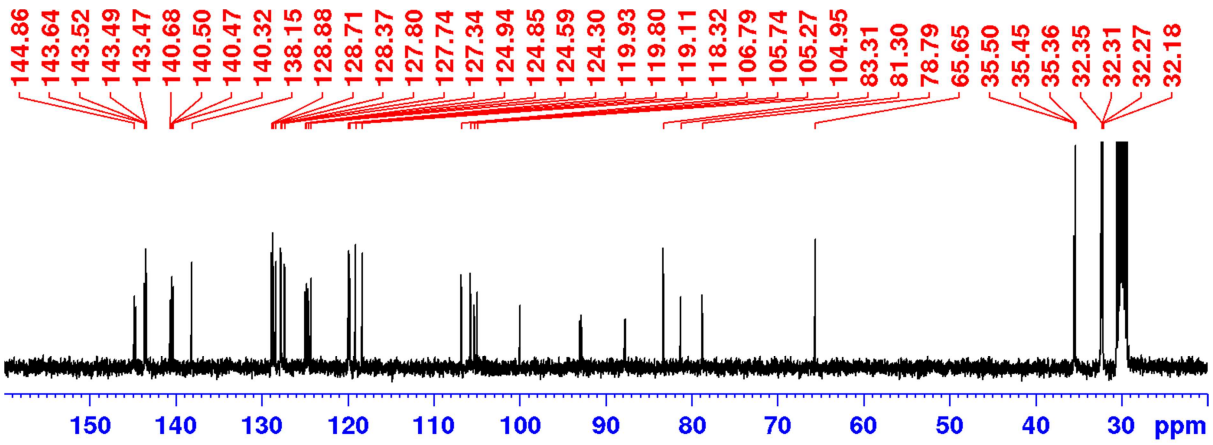


Fig. S21 [13]C NMR of **S4** (100 MHz, acetone-d_6, 25 °C)

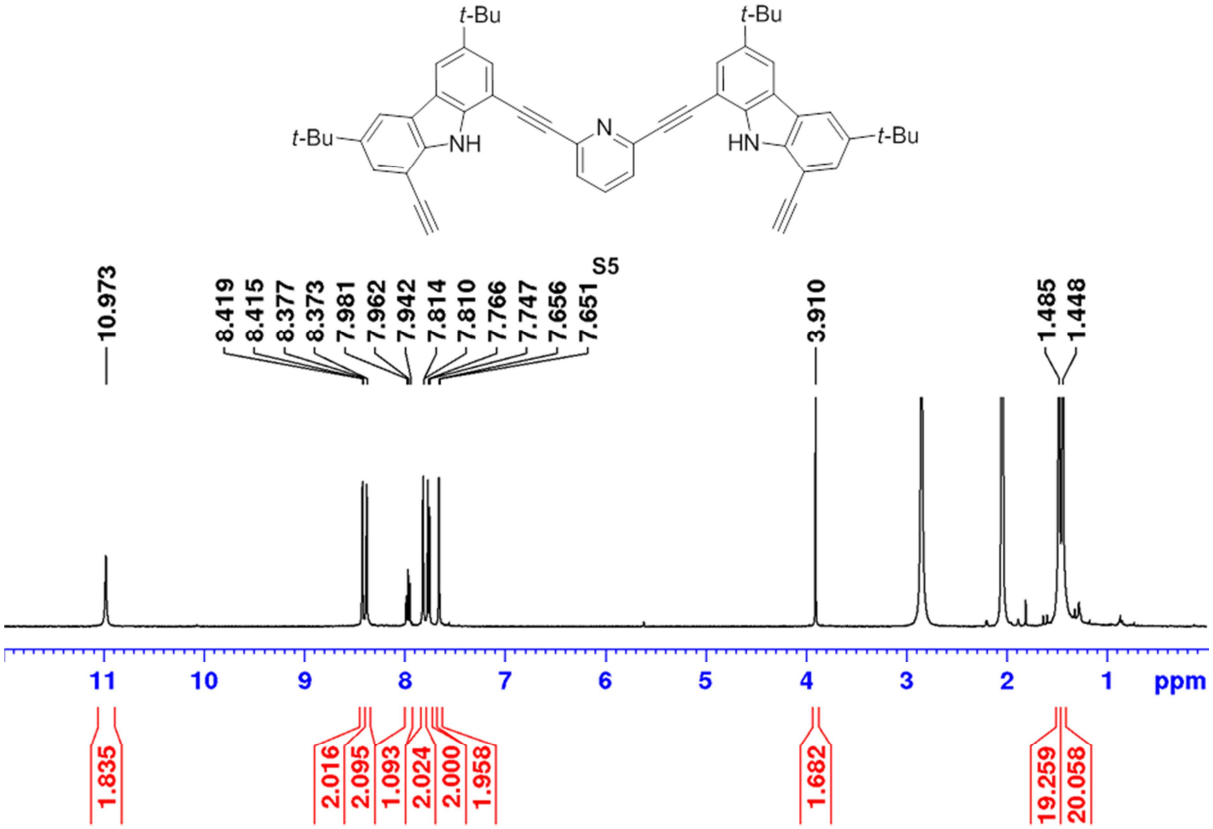


Fig. S22 ^{1}H NMR of **S5** (400 MHz, acetone-d_6, 25 °C)

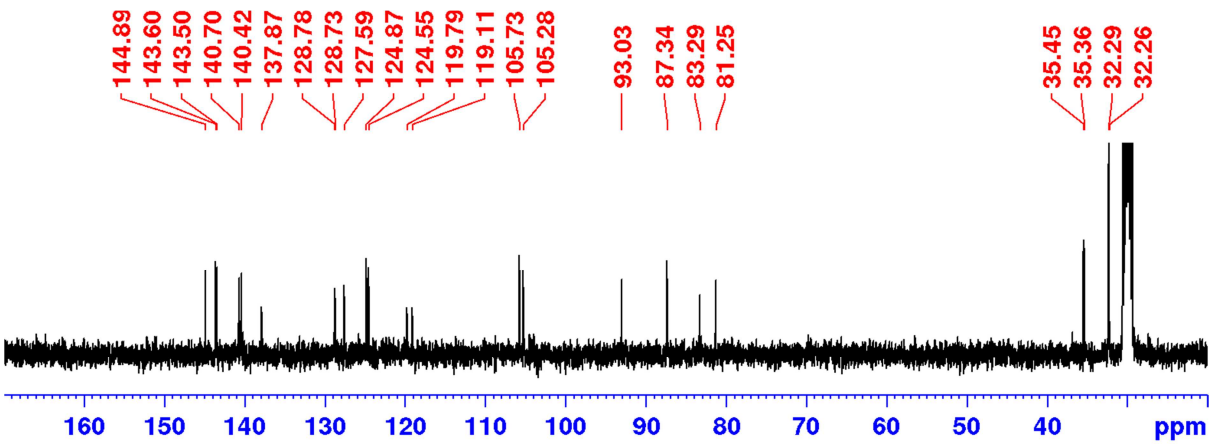


Fig. S23 ^{13}C NMR of **S5** (100 MHz, acetone-d_6, 25 °C)

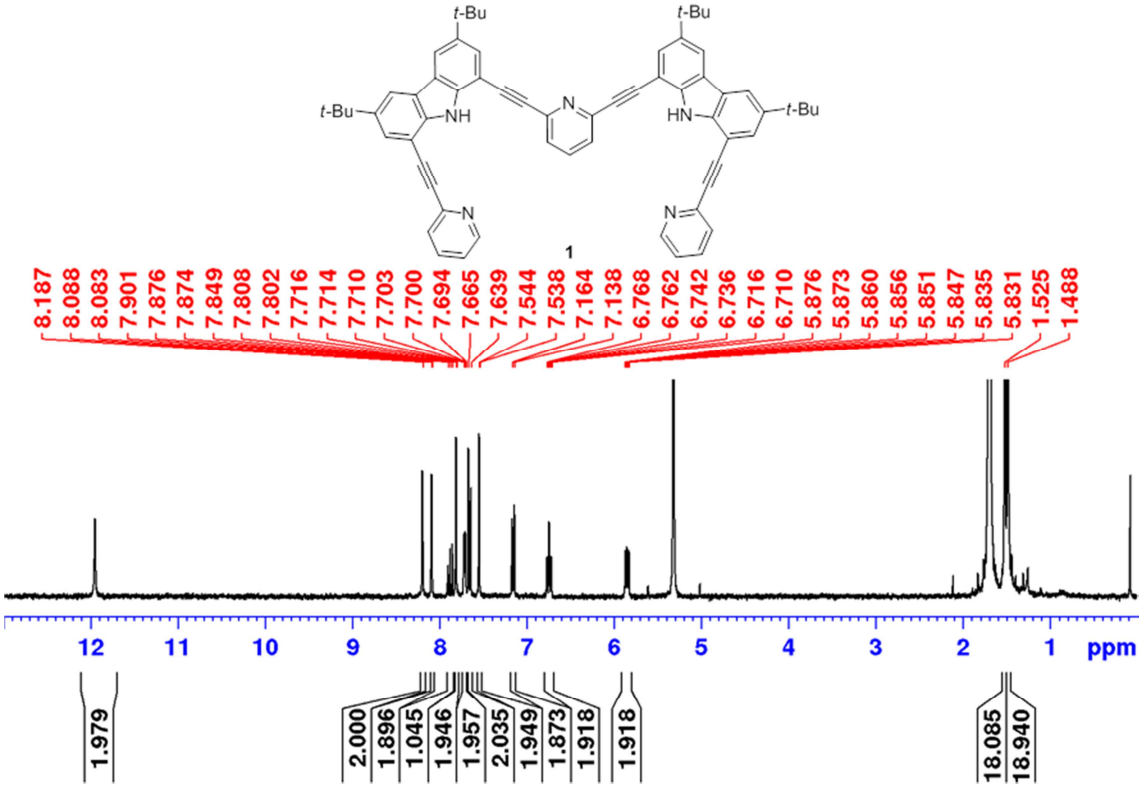


Fig. S24 ^{1}H NMR of **1** (400 MHz, CD_2Cl_2, 25 °C)

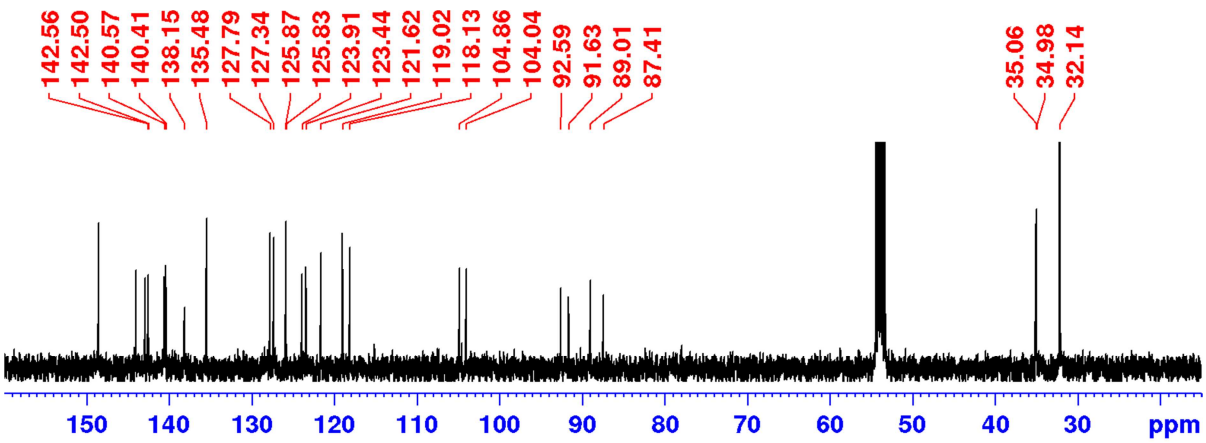


Fig. S25 ^{13}C NMR of **1** (100 MHz, CD_2Cl_2, 25 °C)

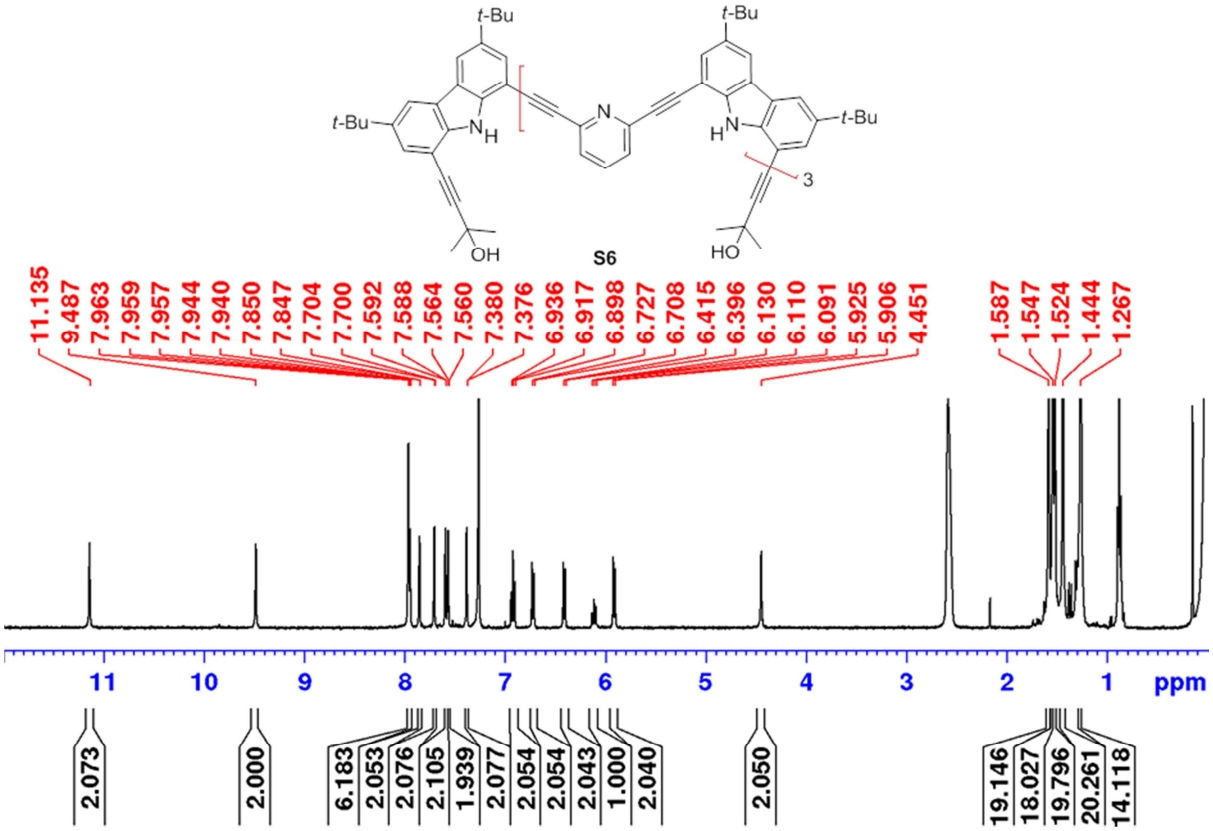


Fig. S26 ^{1}H NMR of **S6** (400 MHz, $CDCl_3$, 25 °C)

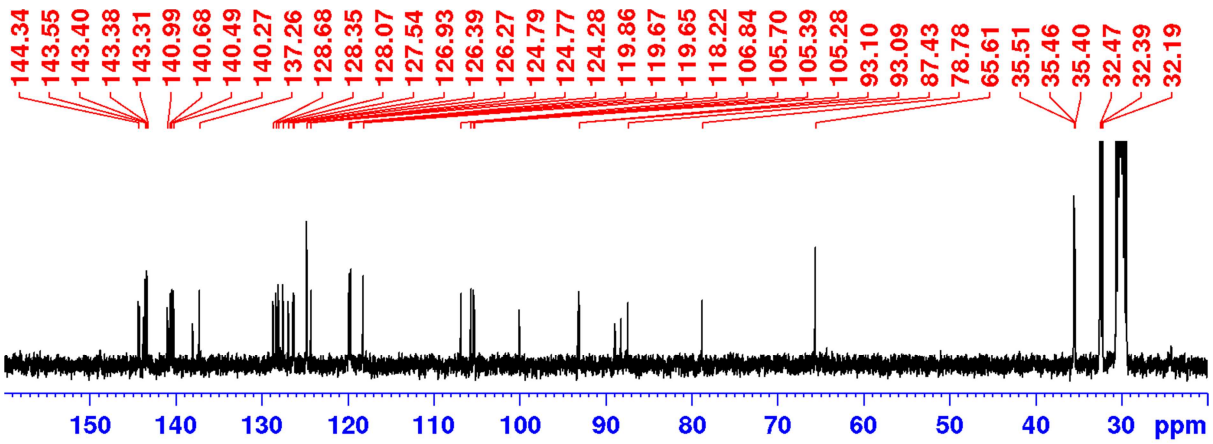


Fig. S27 ^{13}C NMR of **S6** (100 MHz, acetone-d_6, 25 °C)

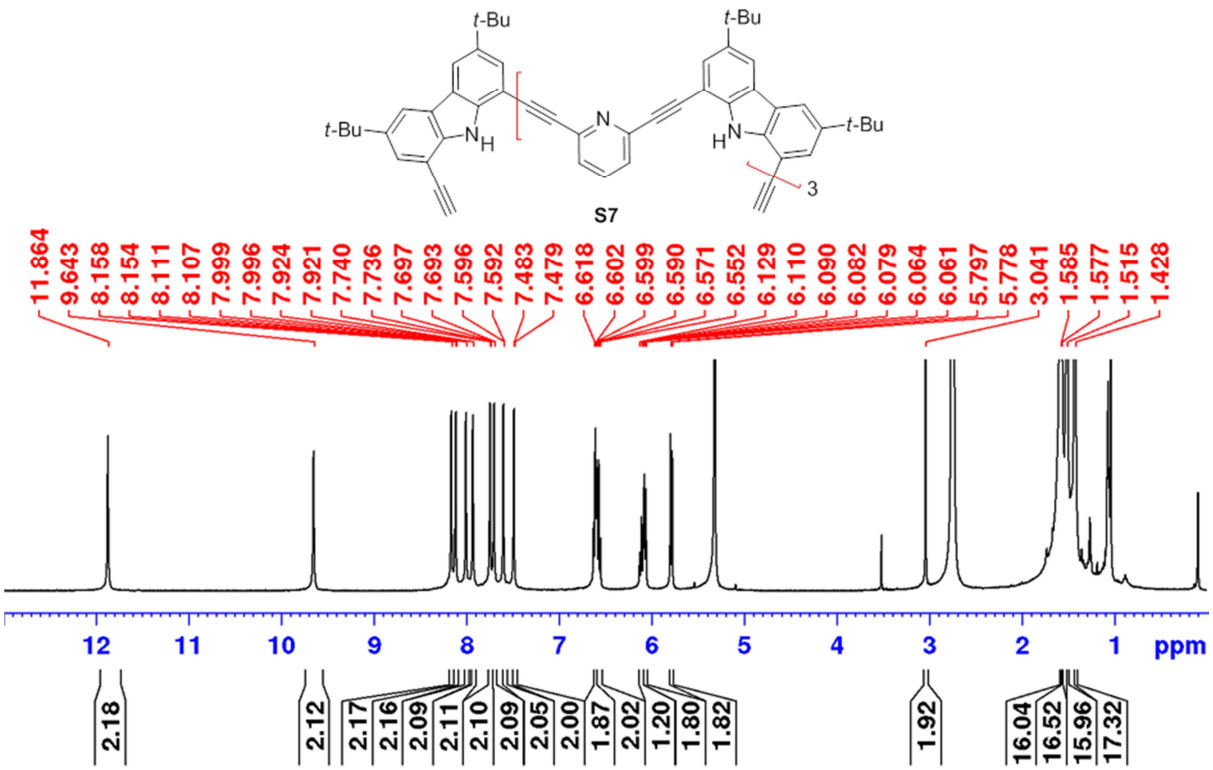


Fig. S28 ^{1}H NMR of **S7** (400 MHz, CD_2Cl_2, 25 °C)

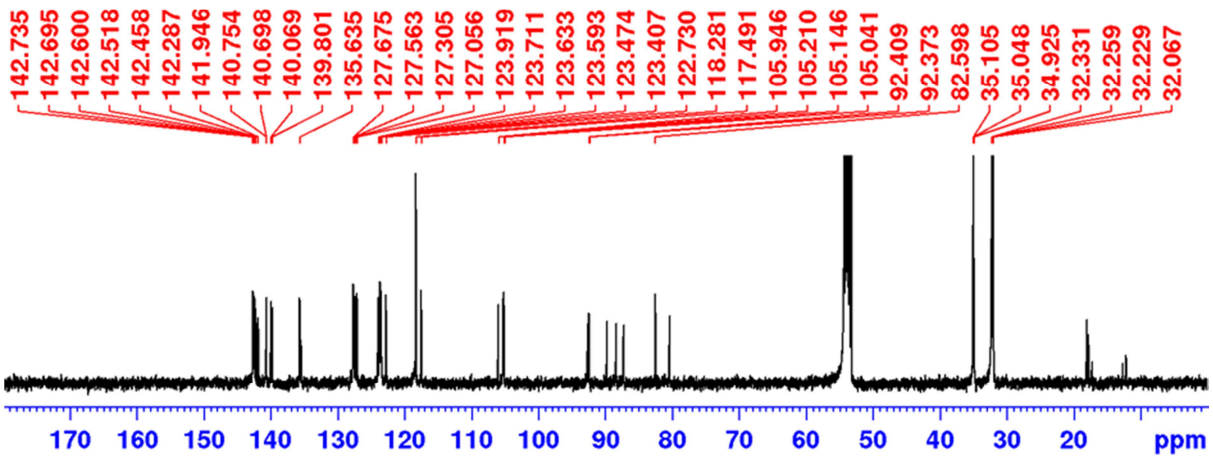


Fig. S29 ^{13}C NMR of **S7** (100 MHz, CD_2Cl_2, 25 °C)

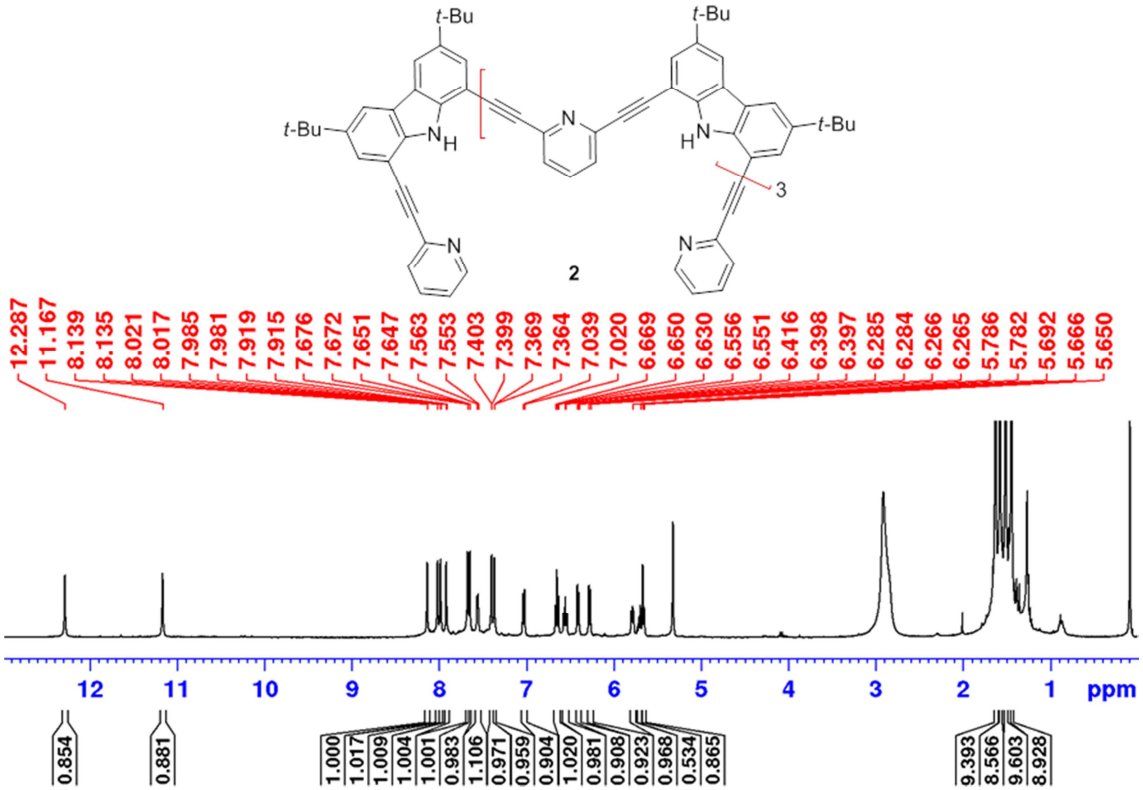


Fig. S30 ^{1}H NMR of **2** (400 MHz, CD_2Cl_2, 25 °C)

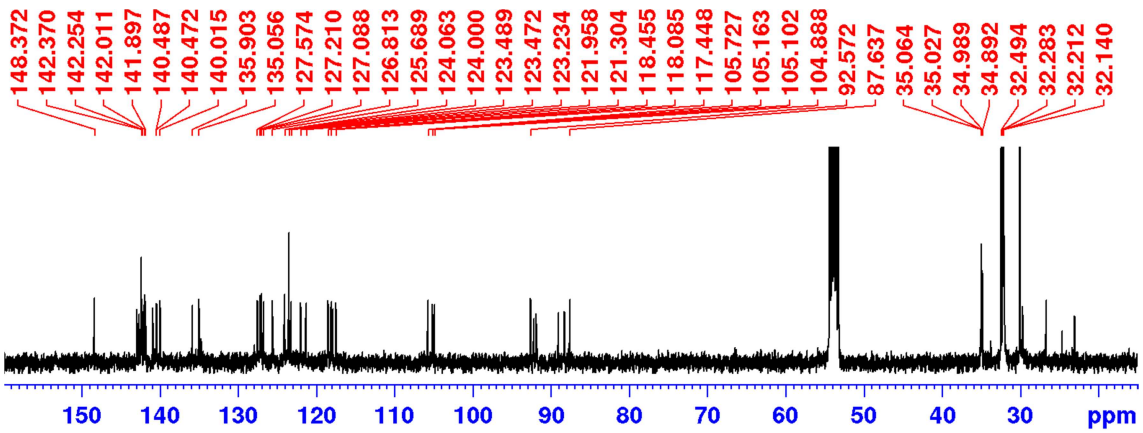


Fig. S31 ^{13}C NMR of **2** (100 MHz, CD_2Cl_2, 25 °C)

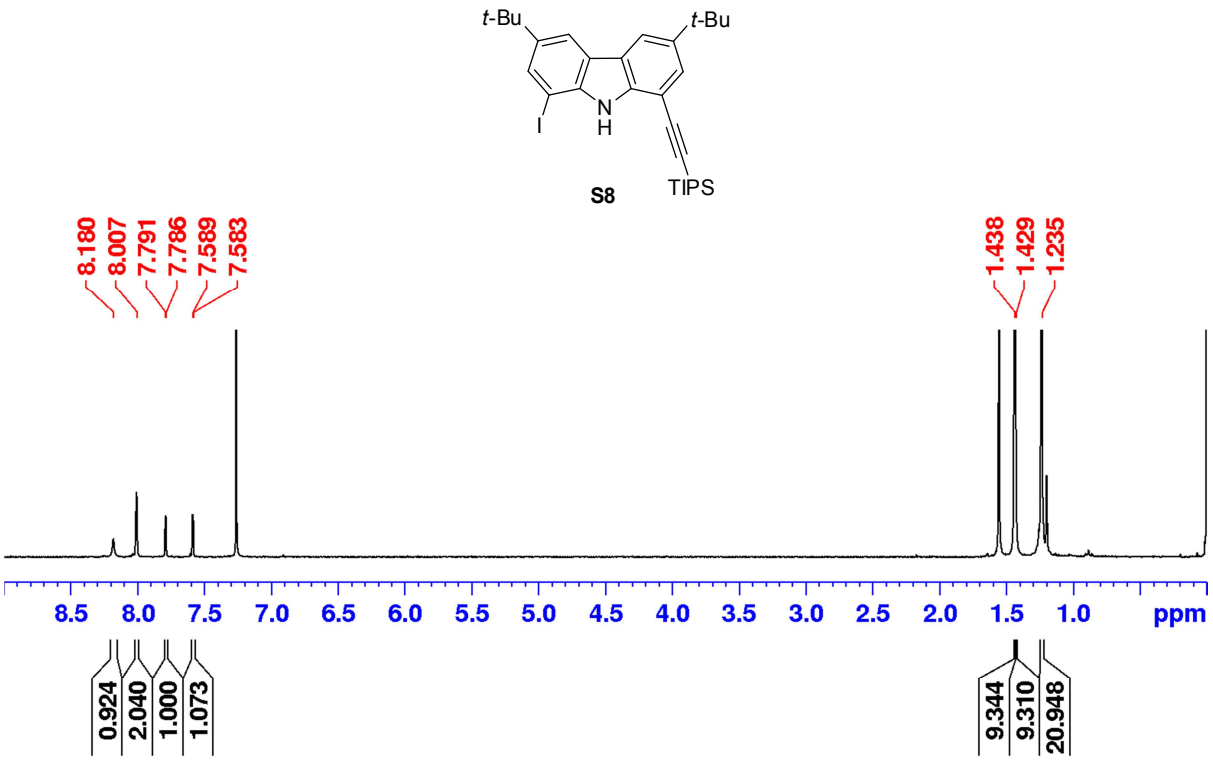


Fig. S32 ^{1}H NMR of **S8** (300 MHz, $CDCl_3$, 25 °C)

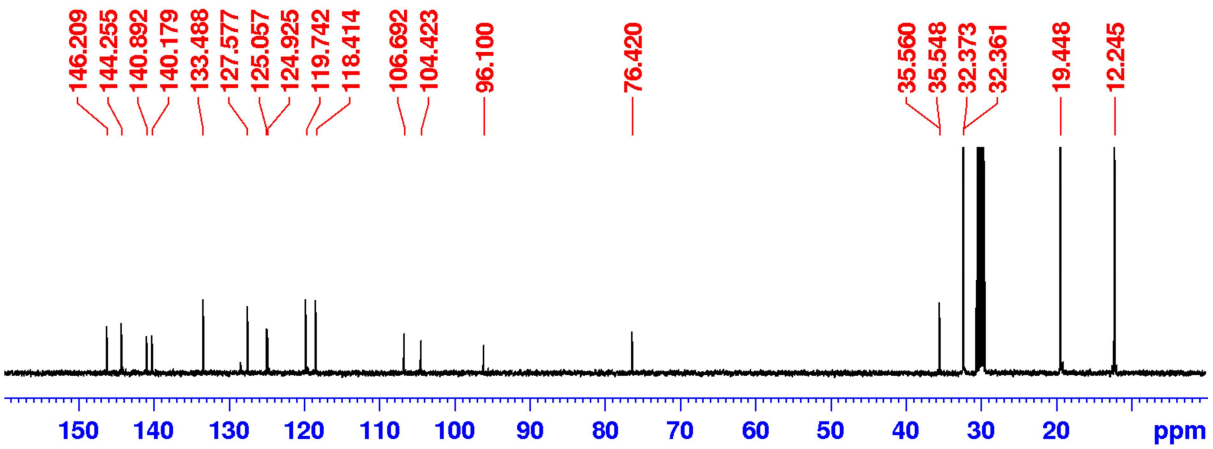


Fig. S33 ^{13}C NMR of **S8** (100 MHz, acetone-d_6, 25 °C)

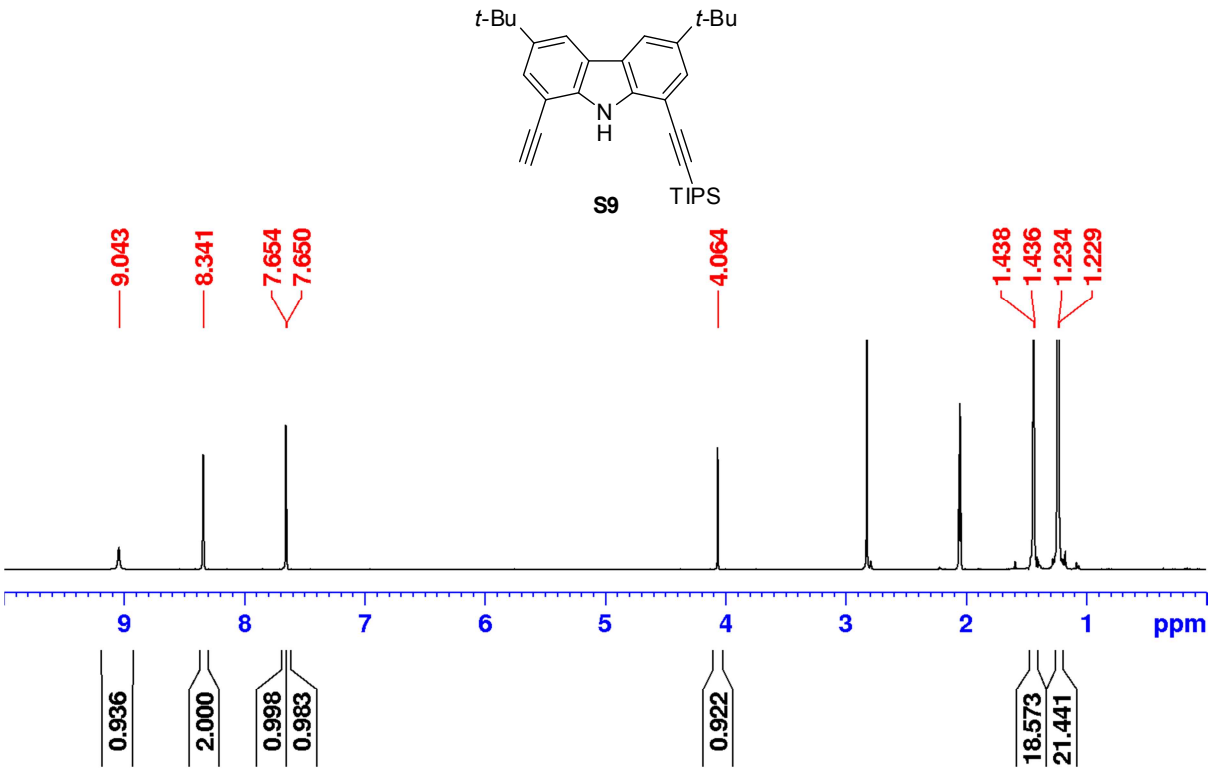


Fig. S34 ^{1}H NMR of **S9** (400 MHz, acetone-d_6, 25 °C)

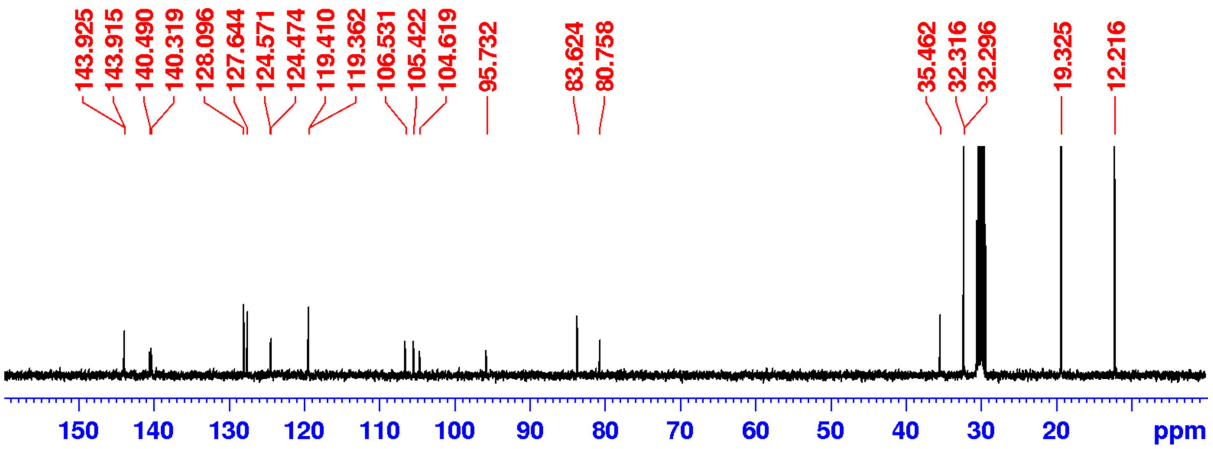


Fig. S35 ^{13}C NMR of **S9** (100 MHz, acetone-d_6, 25 °C)

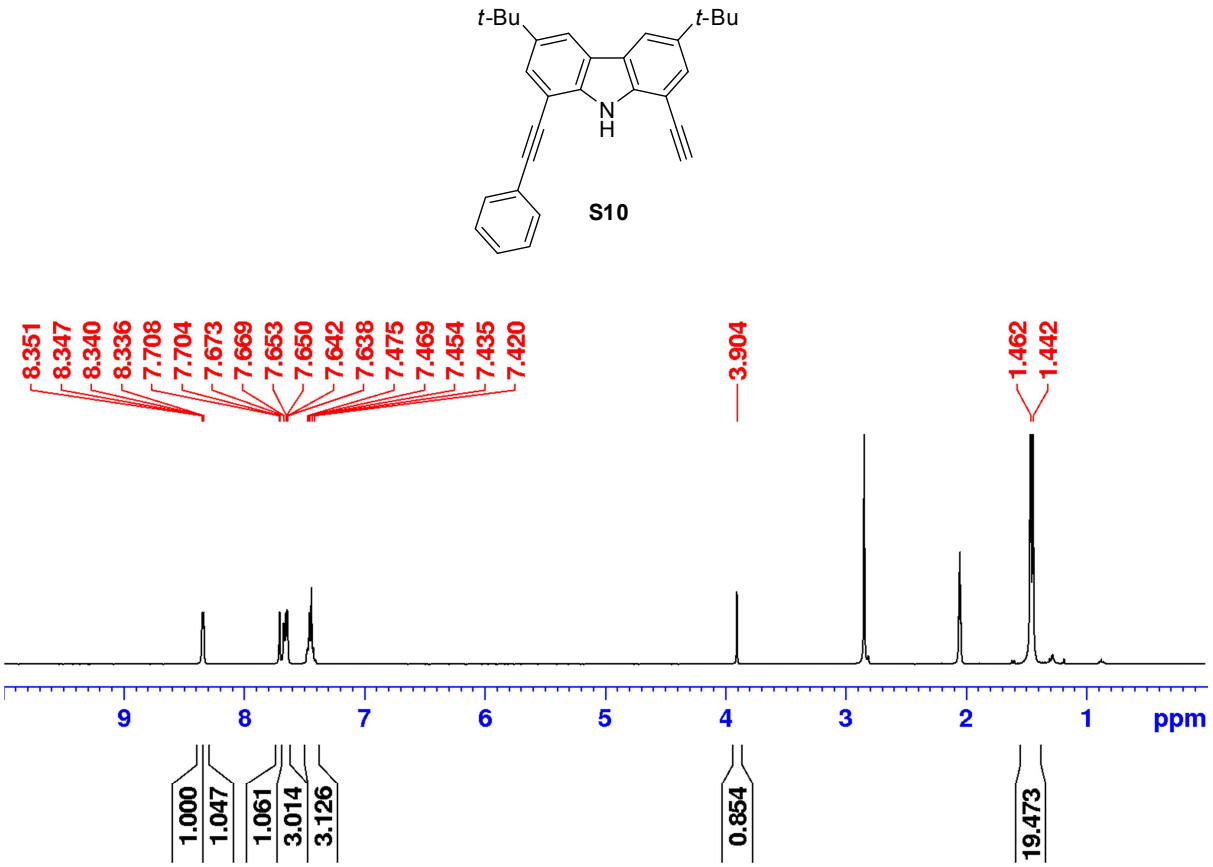


Fig. S36 ^{1}H NMR of **S10** (400 MHz, acetone-d_6, 25 °C)

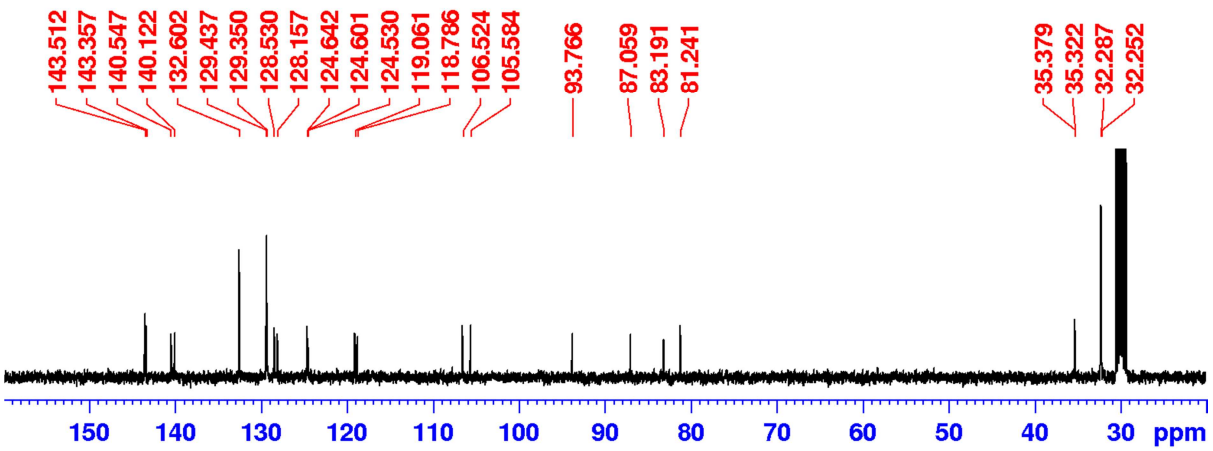


Fig. S37 ^{13}C NMR of **S10** (100 MHz, acetone-d_6, 25 °C)

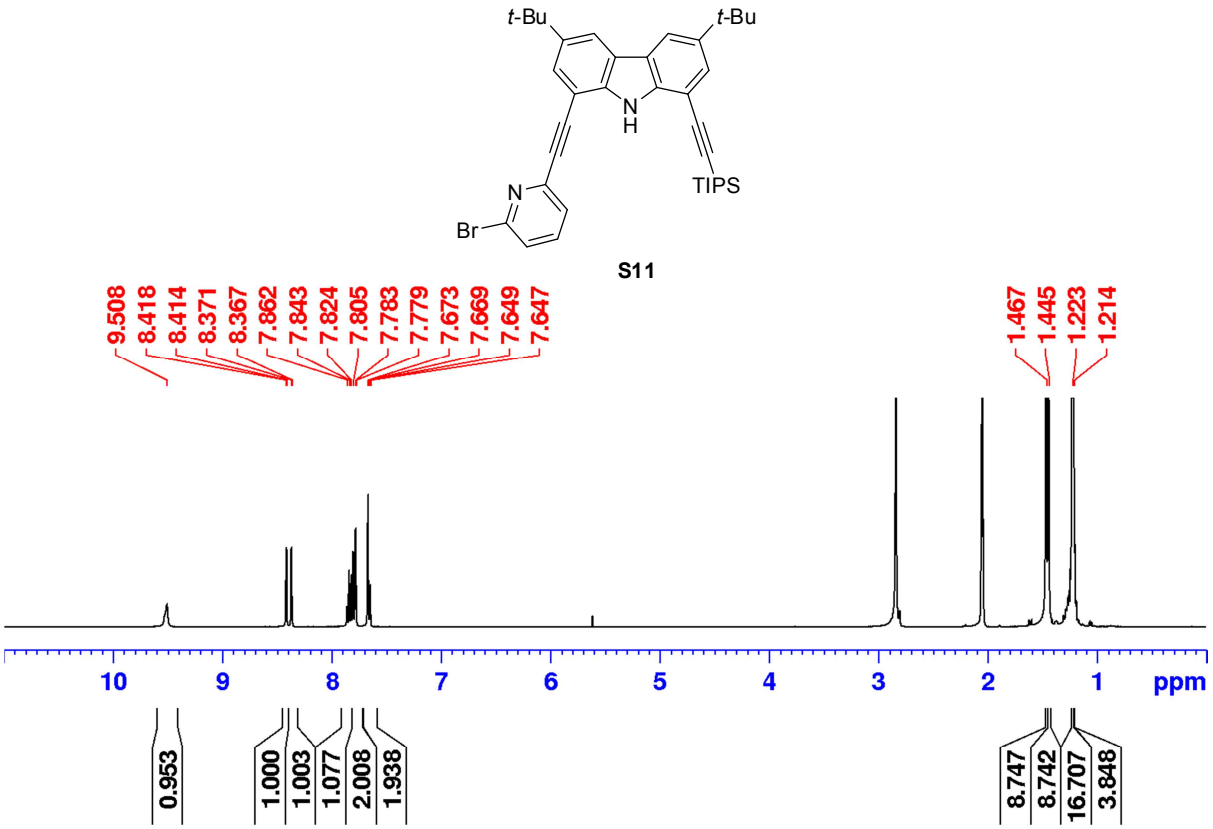


Fig. S38 [1]H NMR of **S11** (400 MHz, acetone-d_6, 25 °C)

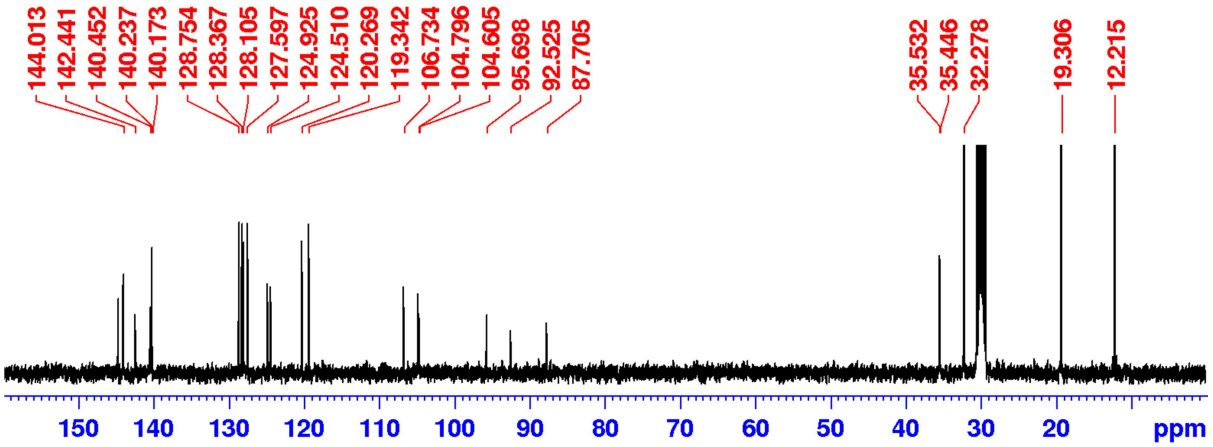


Fig. S39 [13]C NMR of **S11** (100 MHz, acetone-d_6, 25 °C)

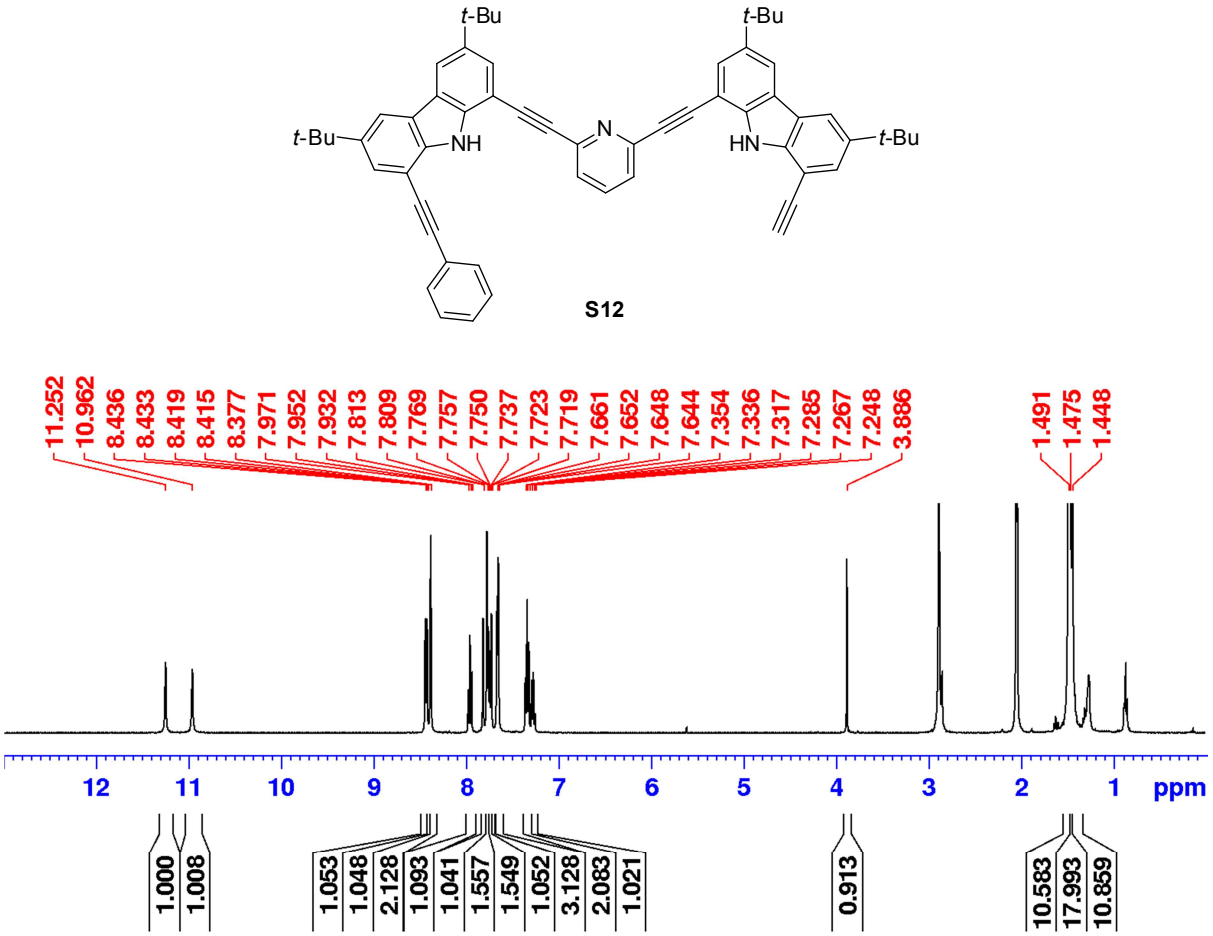


Fig. S40 ^{1}H NMR of **S12** (400 MHz, acetone-d_6, 25 °C)

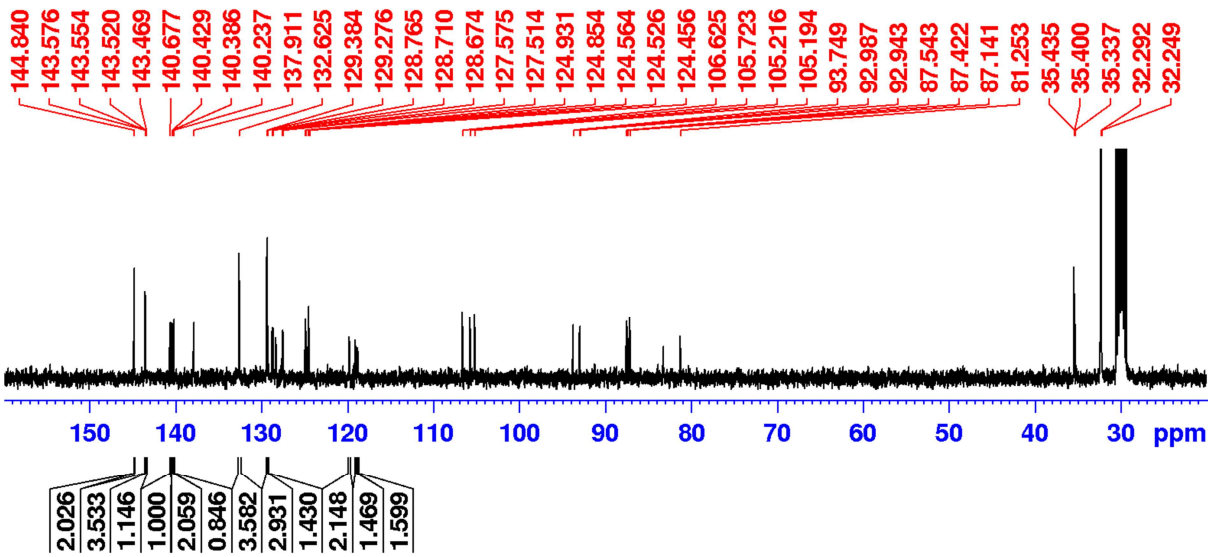


Fig. S41 ^{13}C NMR of **S12** (100 MHz, acetone-d_6, 25 °C)

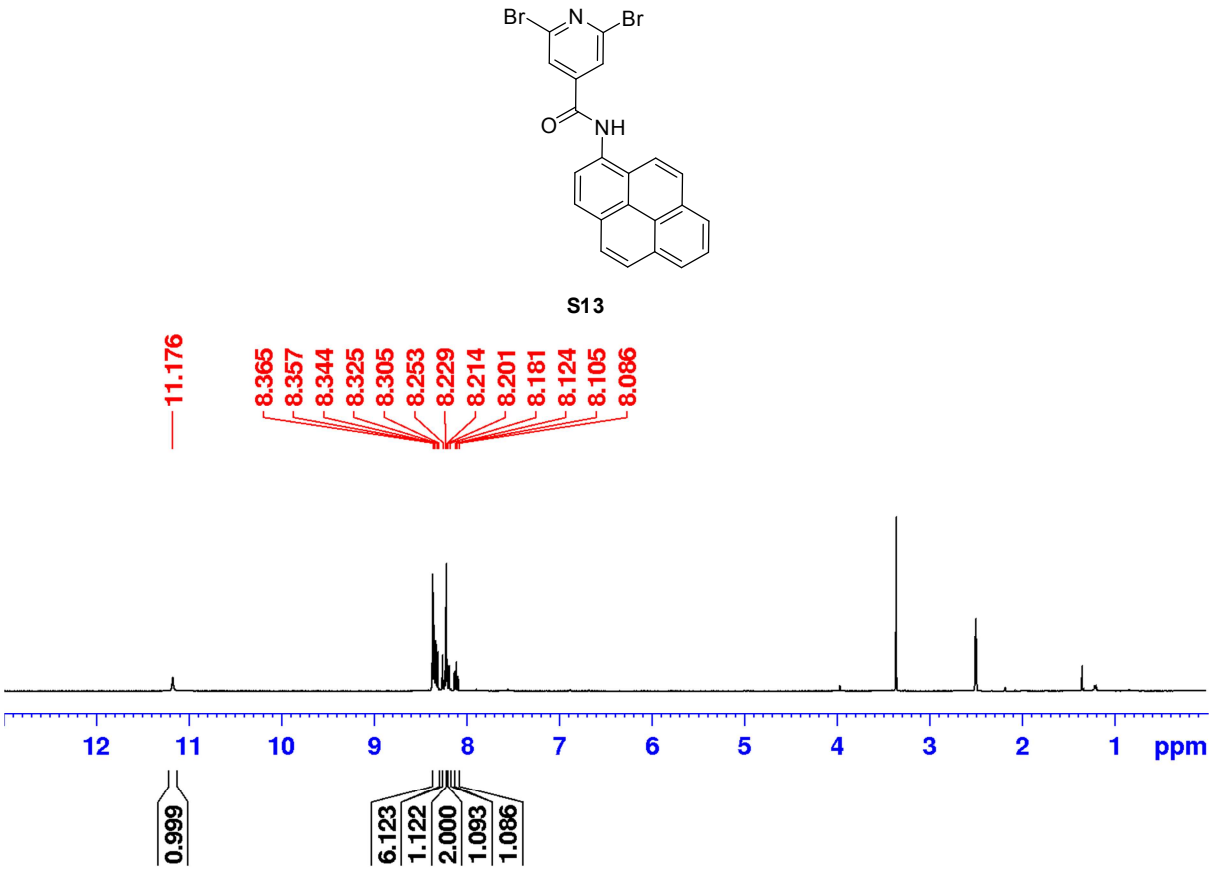


Fig. S42 [1]H NMR of **S13** (400 MHz, DMSO-d_6, 25 °C)

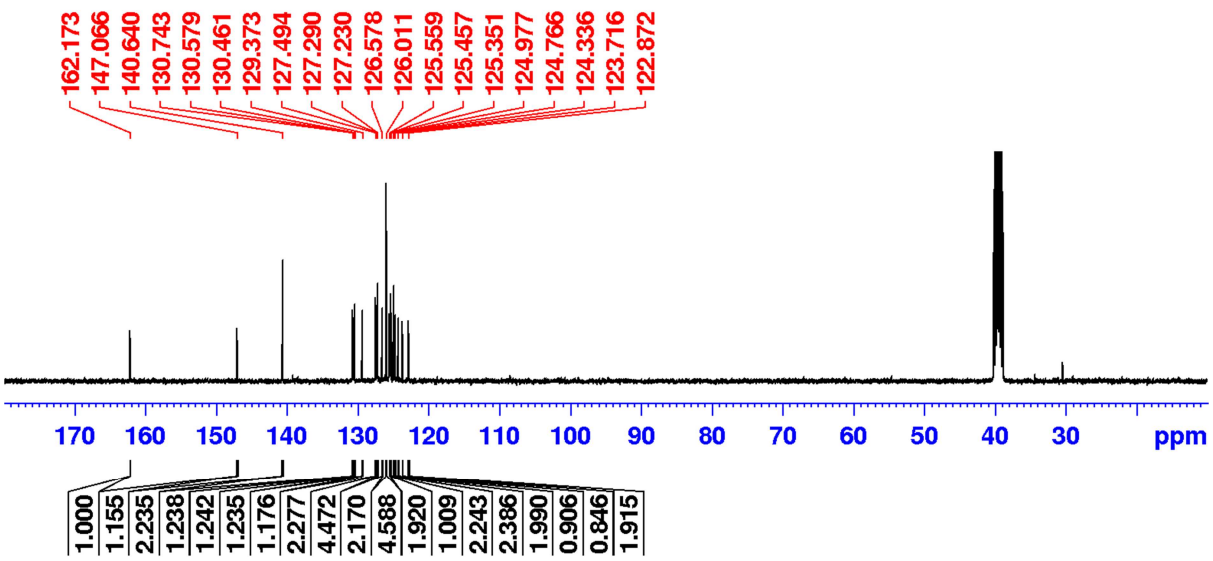


Fig. S43 [13]C NMR of **S13** (100 MHz, DMSO-d_6, 25 °C)

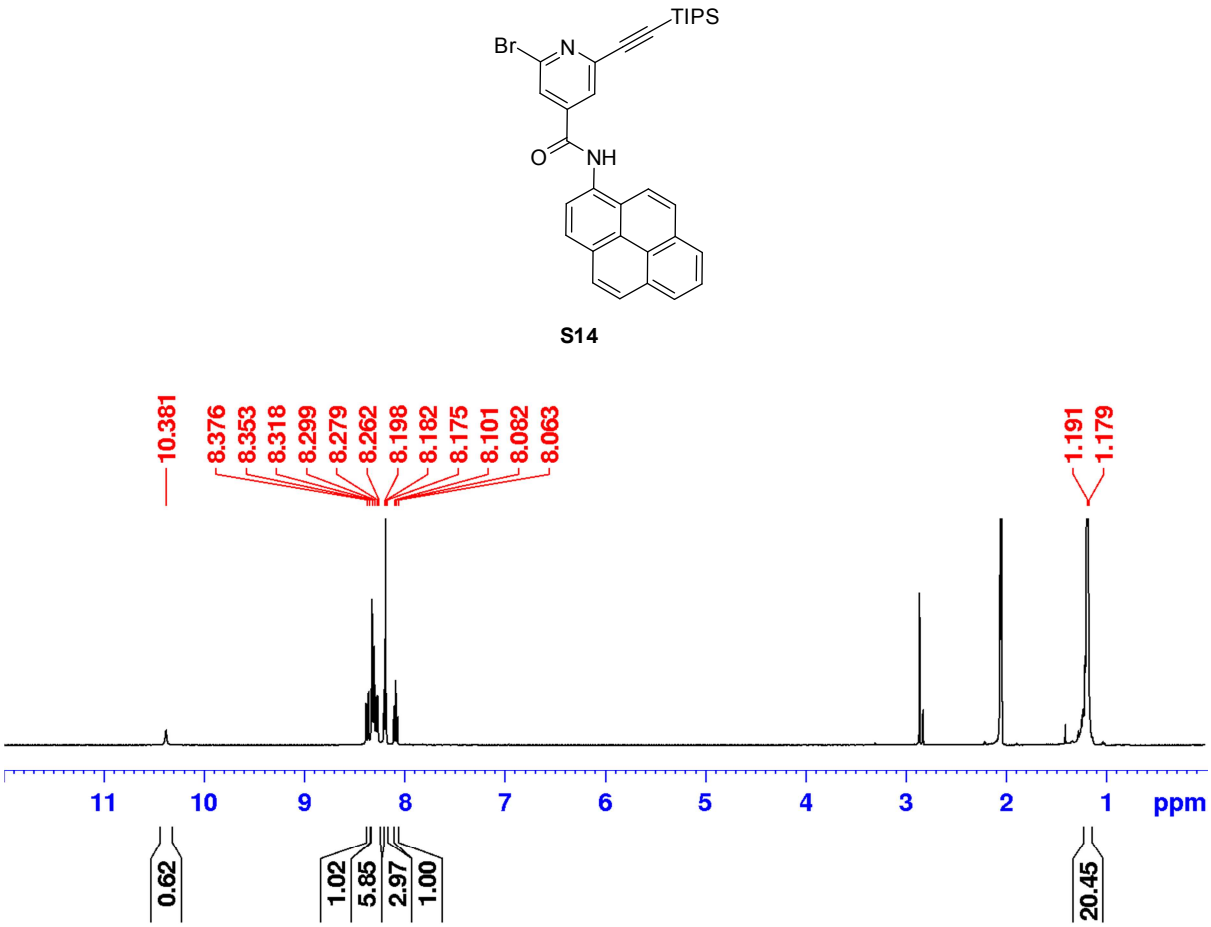


Fig. S44 ^{1}H NMR of **S14** (400 MHz, acetone-d_6, 25 °C)

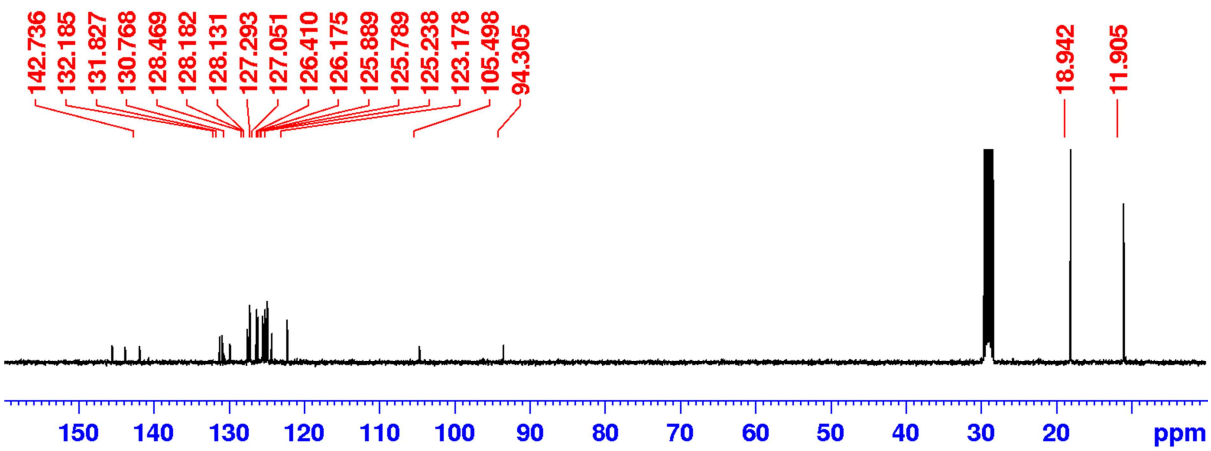


Fig. S45 ^{13}C NMR of **S14** (100 MHz, acetone-d_6, 25 °C)

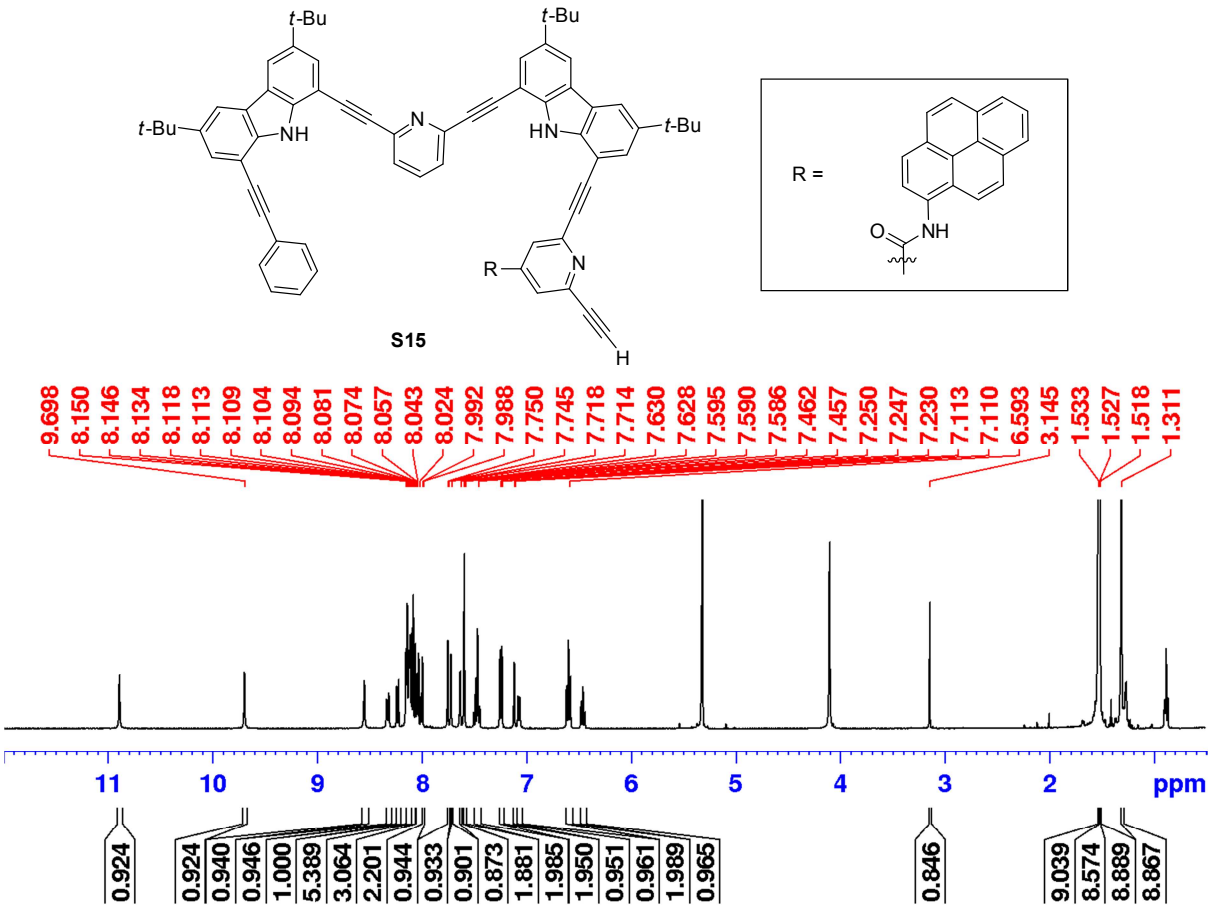


Fig. S46 ^{1}H NMR of **S15** (400 MHz, CD_2Cl_2, 25 °C)

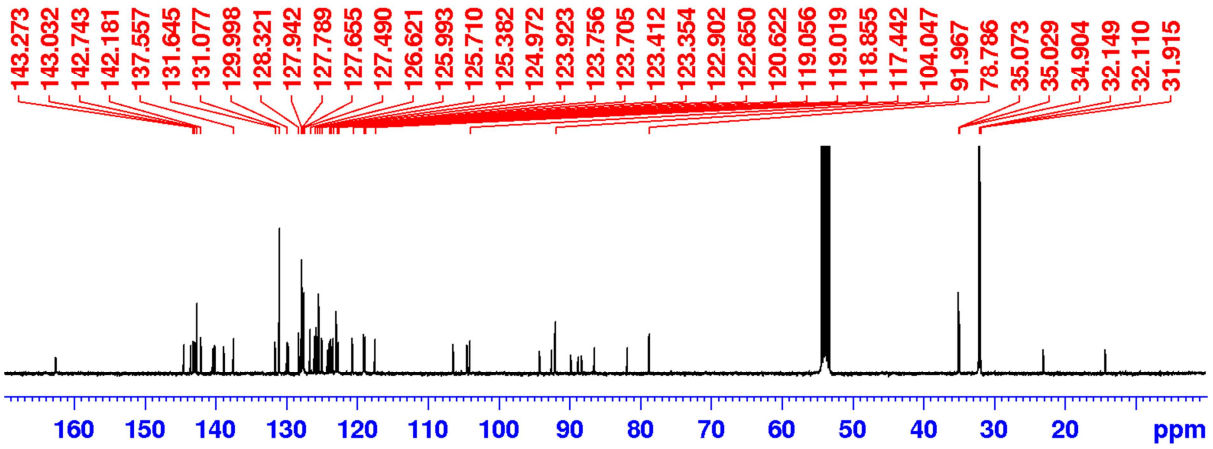


Fig. S47 ^{13}C NMR of **S15** (100 MHz, CD_2Cl_2, 25 °C)

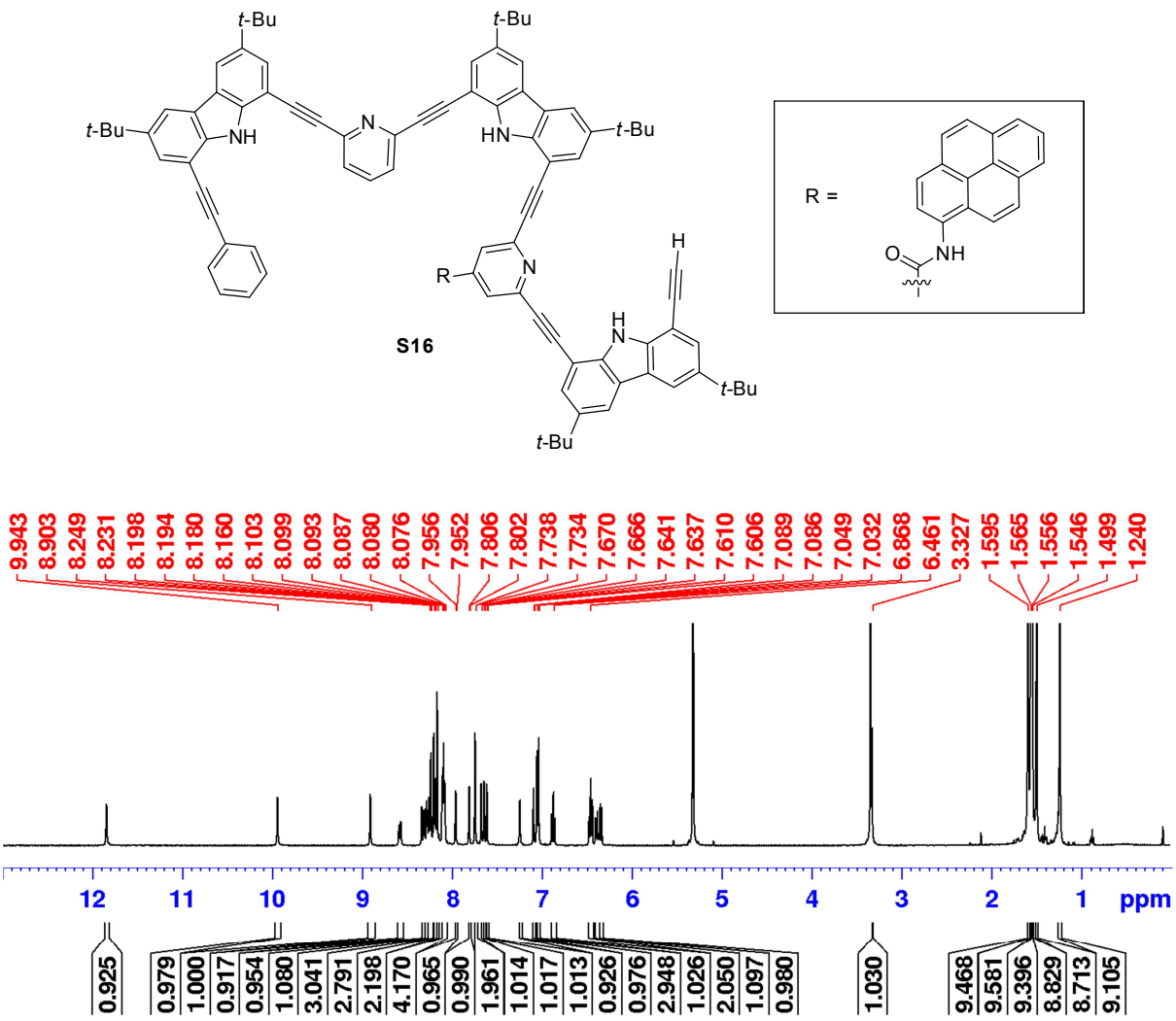


Fig. S48 ^{1}H NMR of **S16** (400 MHz, CD_2Cl_2, 25 °C)

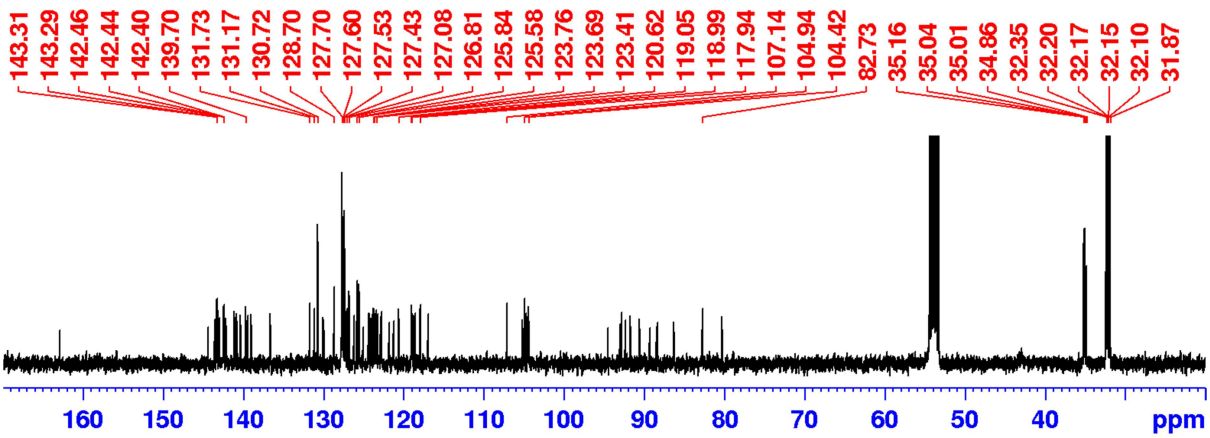


Fig. S49 ^{13}C NMR of **S16** (100 MHz, CD_2Cl_2, 25 °C)

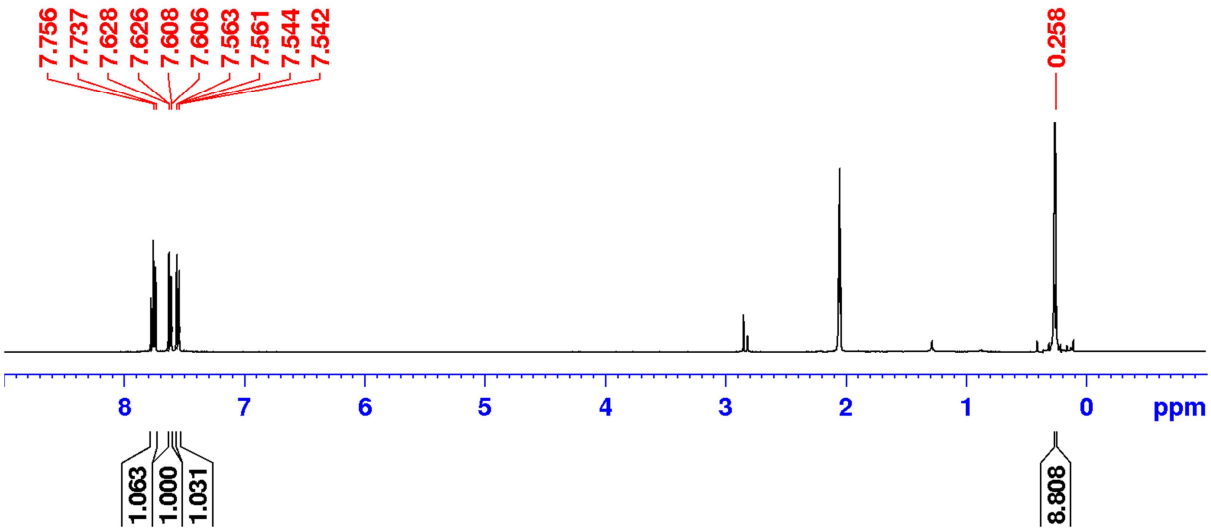


Fig. S50 [1]H NMR of **S17** (400 MHz, acetone-d_6, 25 °C)

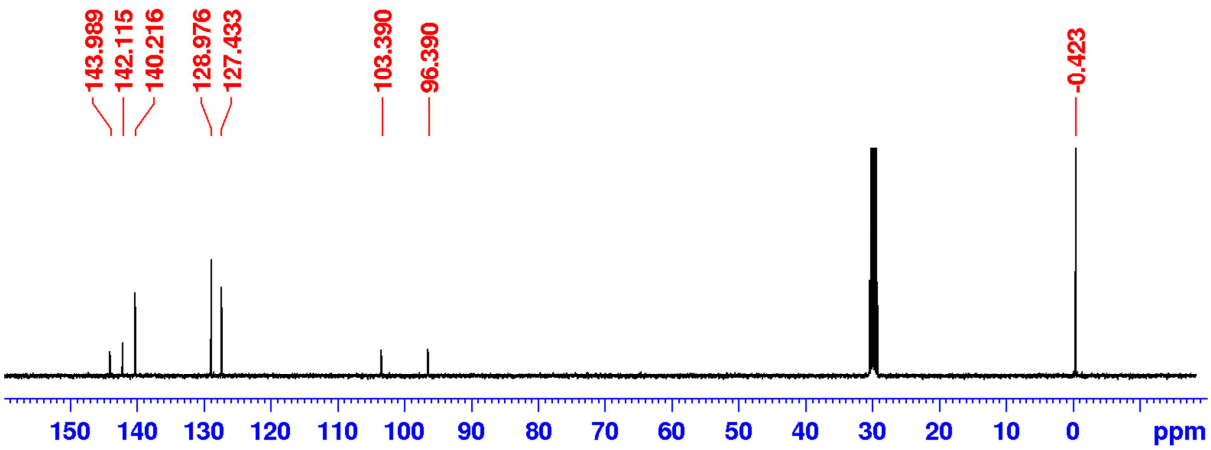


Fig. S51 [13]C NMR of **S17** (100 MHz, acetone-d_6, 25 °C)

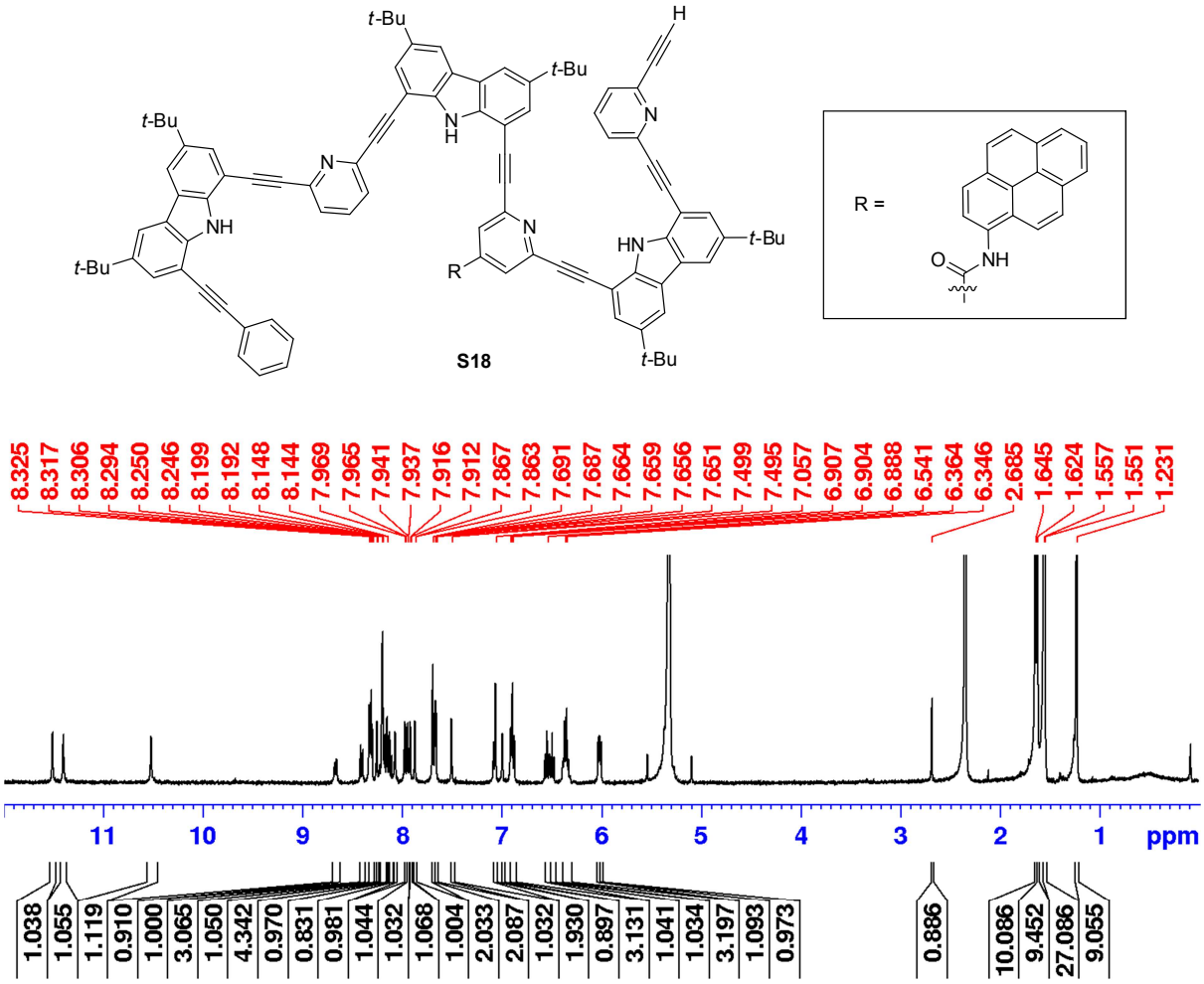


Fig. S52 ^{1}H NMR of **S18** (400 MHz, CD_2Cl_2, 25 °C)

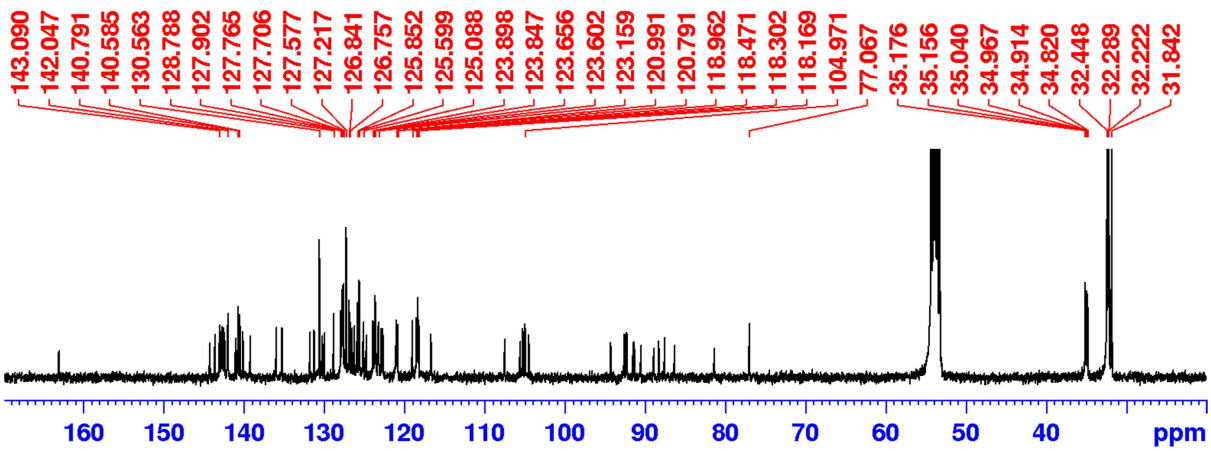


Fig. S53 ^{13}C NMR of **S18** (100 MHz, CD_2Cl_2, 25 °C)

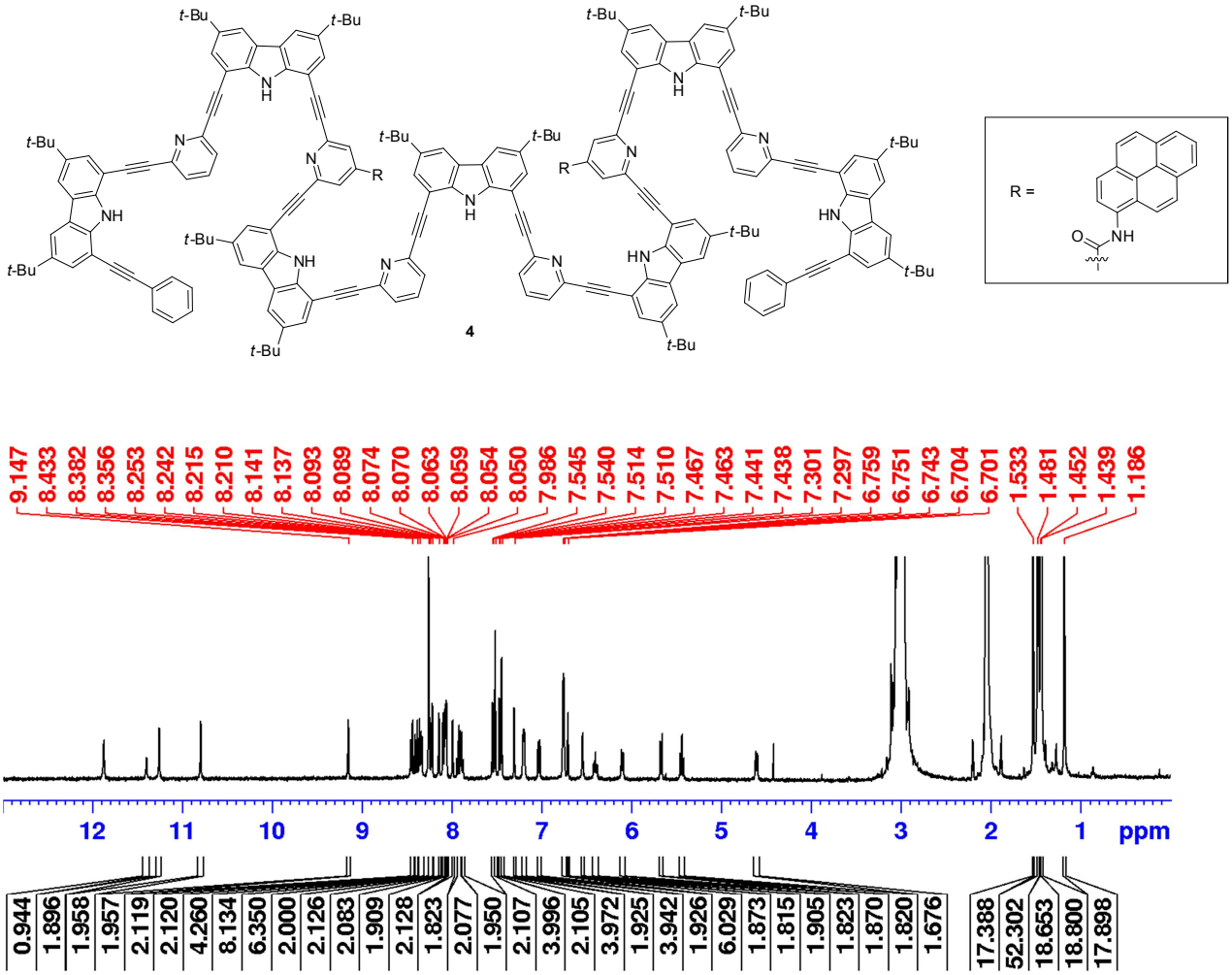


Fig. S54 ^{1}H NMR of **4** (400 MHz, 1% (v/v) H_2O/acetone-d_6, 25 °C)

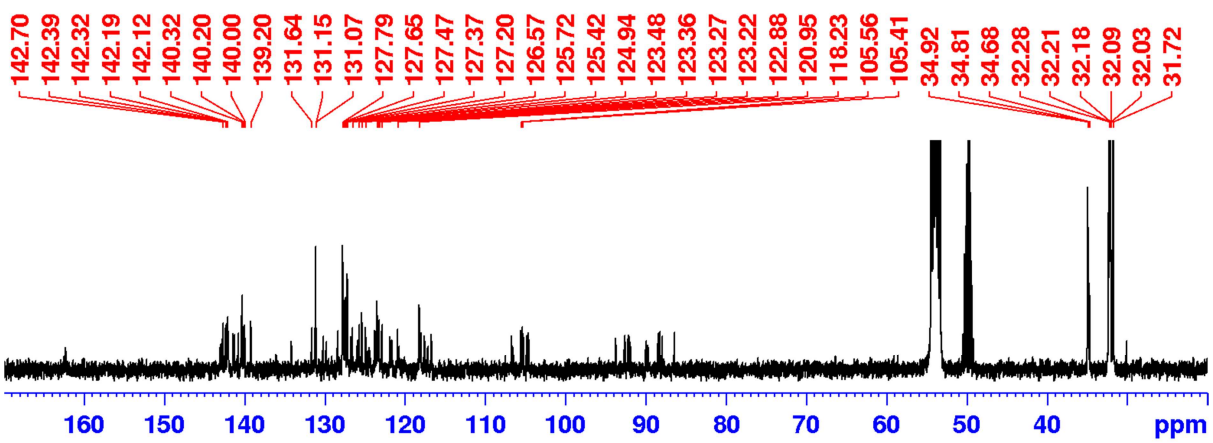


Fig. S55 ^{13}C NMR of **4** (100 MHz, 2% (v/v) CD_3OH/CD_2Cl_2, 25 °C)

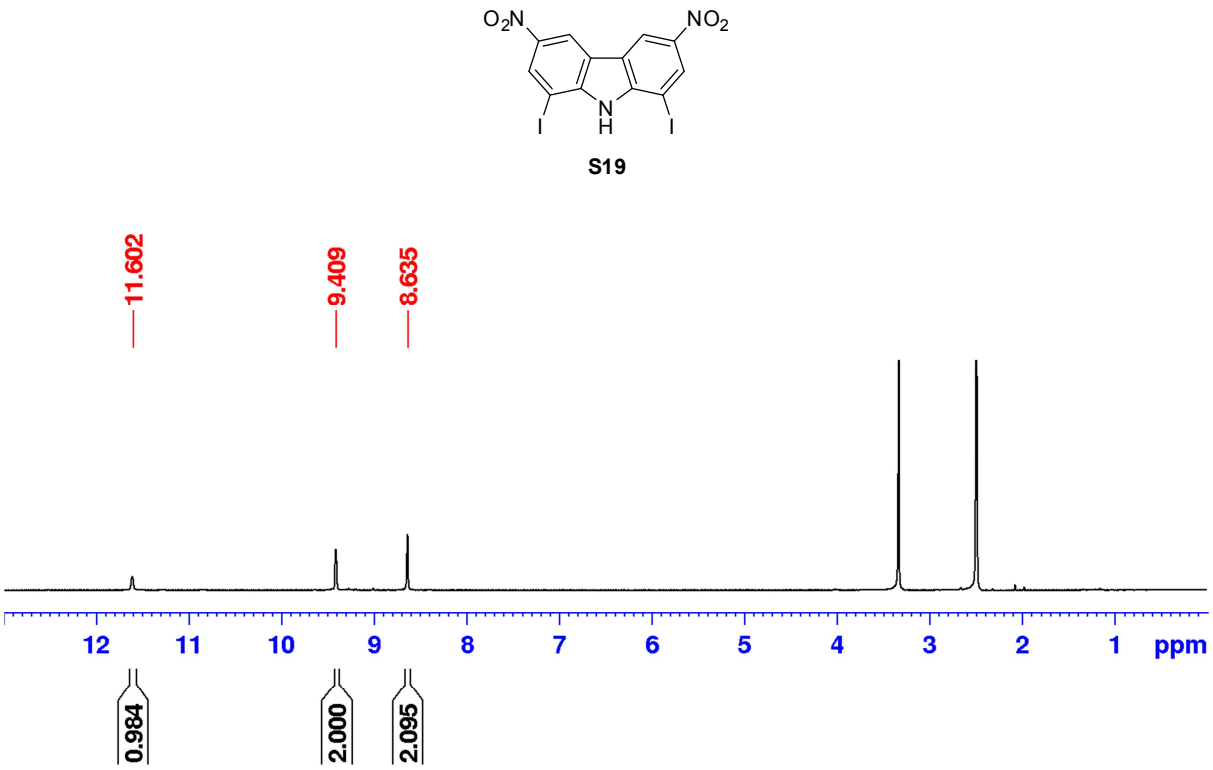


Fig. S56 [1]H NMR of **S19** (400 MHz, DMSO-d_6, 25 °C)

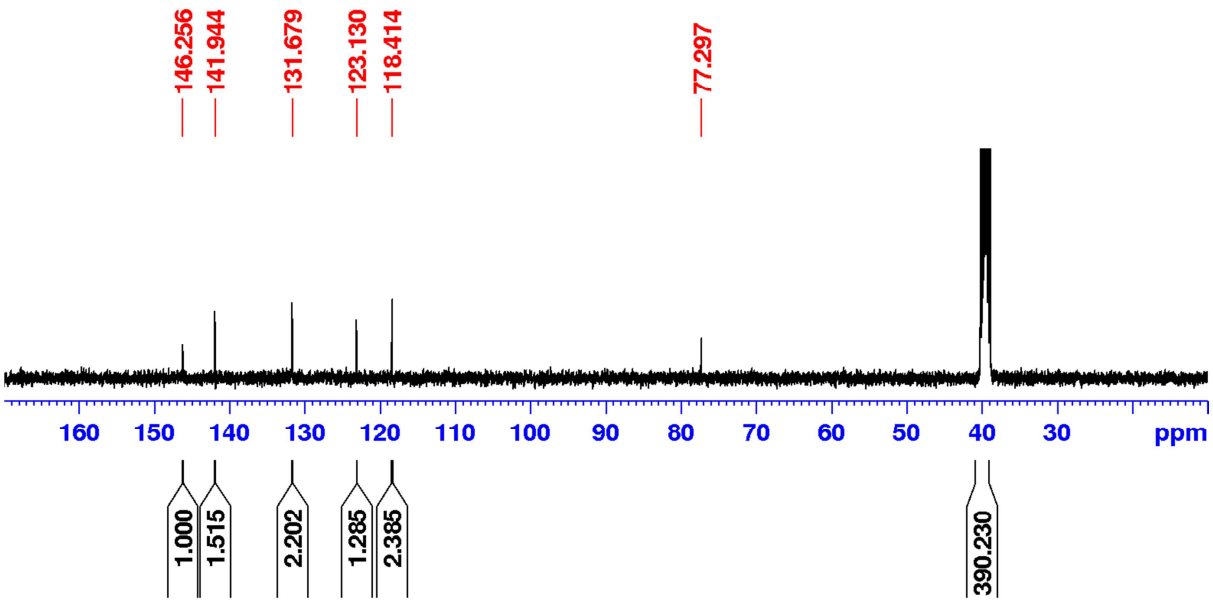


Fig. S57 [13]C NMR of **S19** (100 MHz, DMSO-d_6, 25 °C)

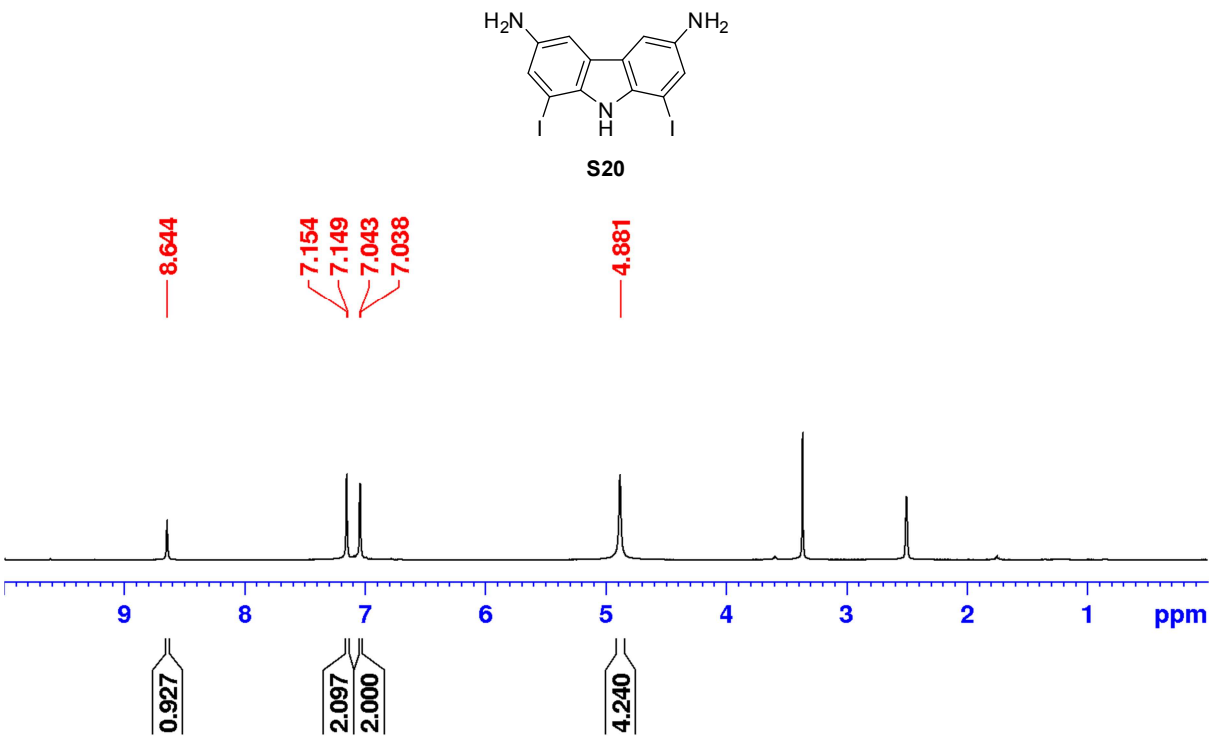


Fig. S58 ^{1}H NMR of **S20** (400 MHz, DMSO-d_6, 25 °C)

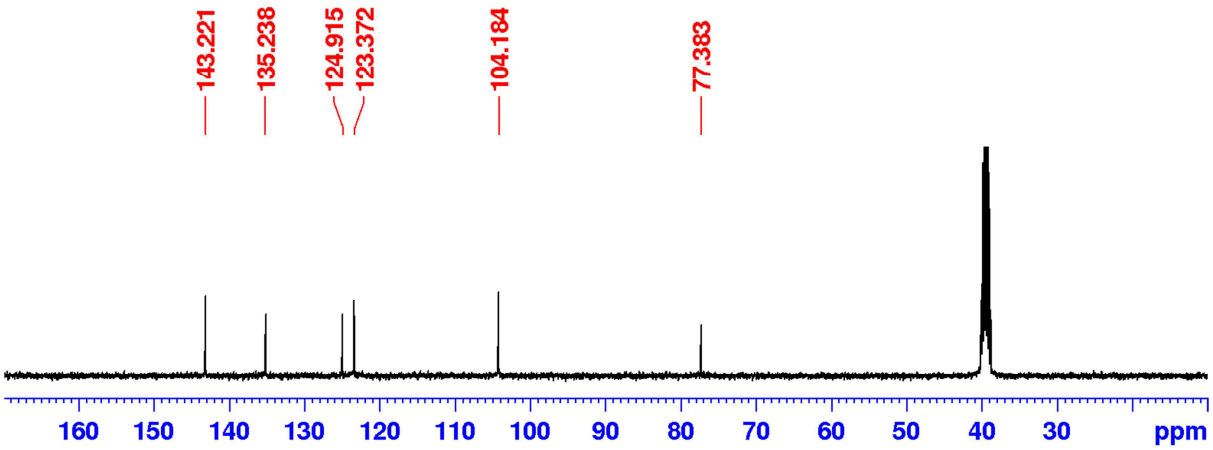
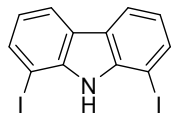


Fig. S59 ^{13}C NMR of **S20** (100 MHz, DMSO-d_6, 25 °C)



S21

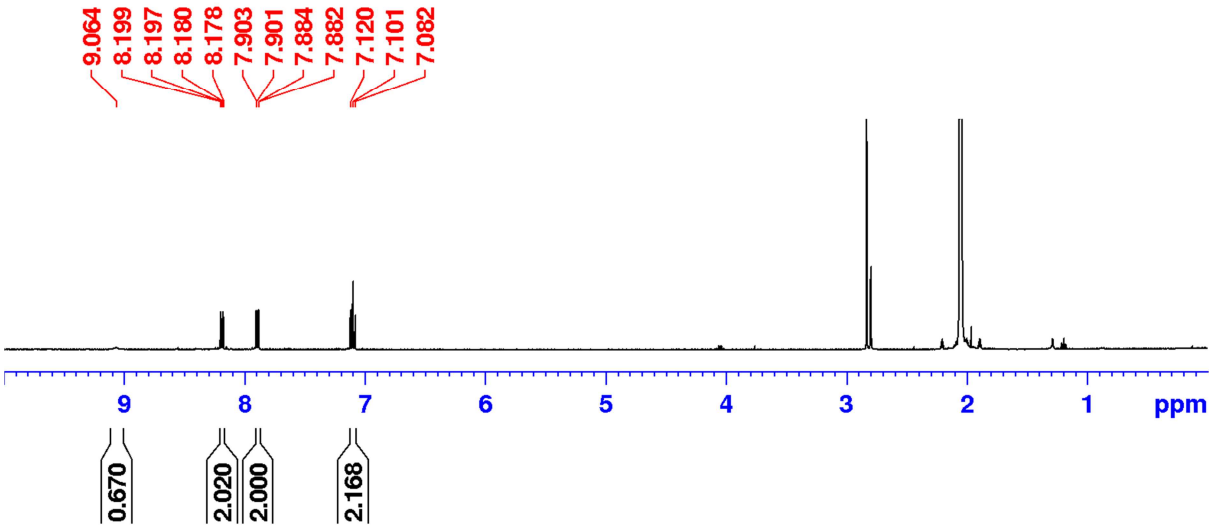


Fig. S60 ^{1}H NMR of **S21** (400 MHz, acetone-d_6, 25 °C)

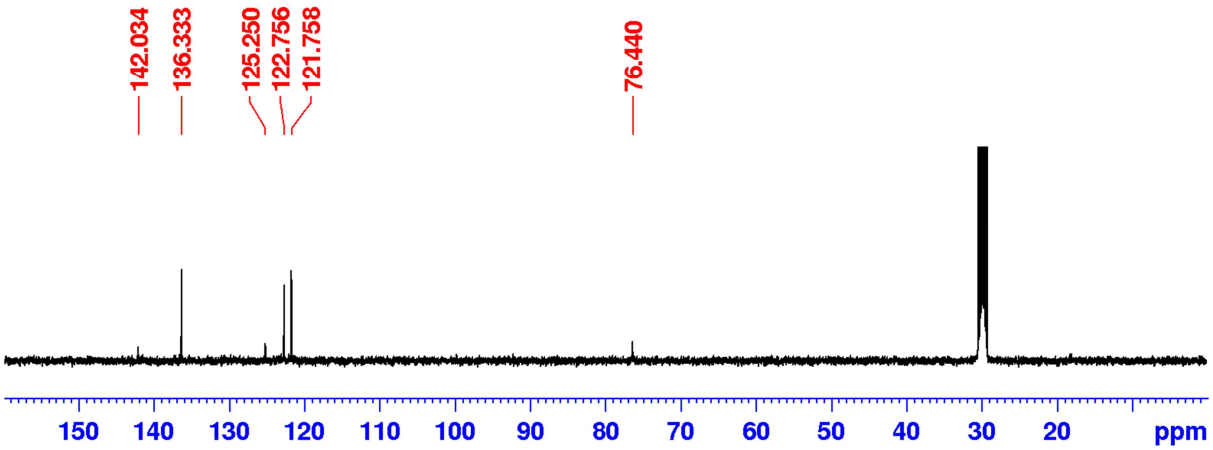


Fig. S61 ^{13}C NMR of **S21** (100 MHz, acetone-d_6, 25 °C)

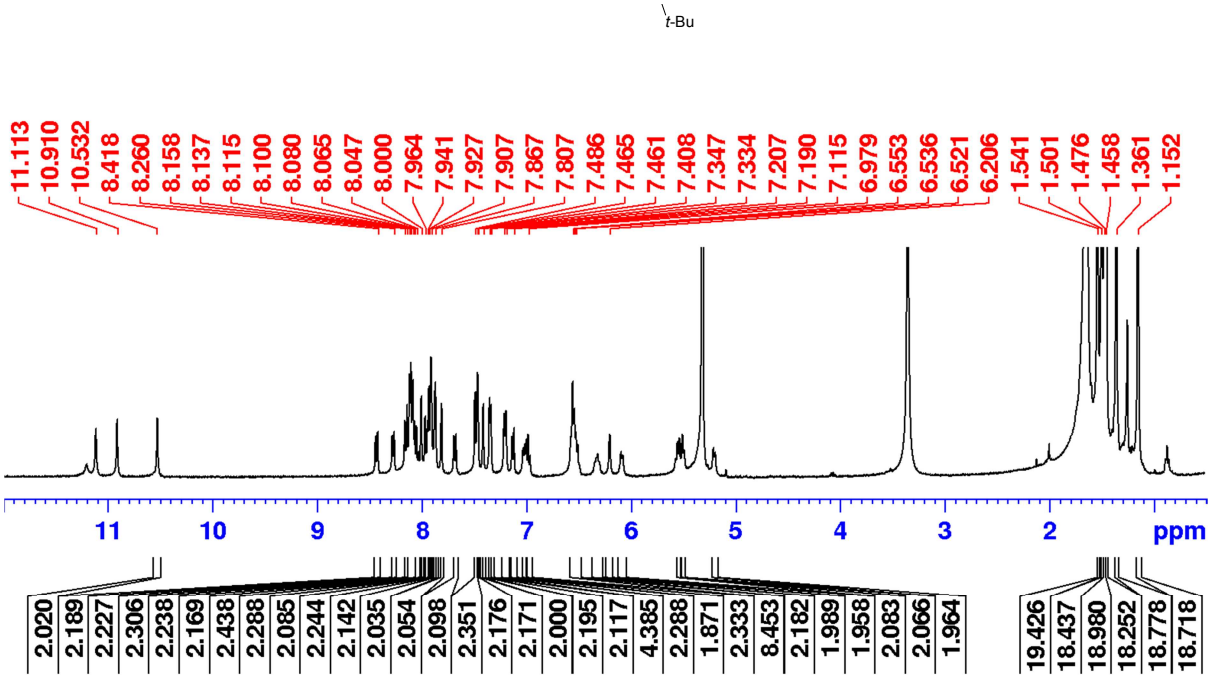


Fig. S62 ^{1}H NMR of **5** (400 MHz, 2% (v/v) CD_3OH/CD_2Cl_2, 25 °C)

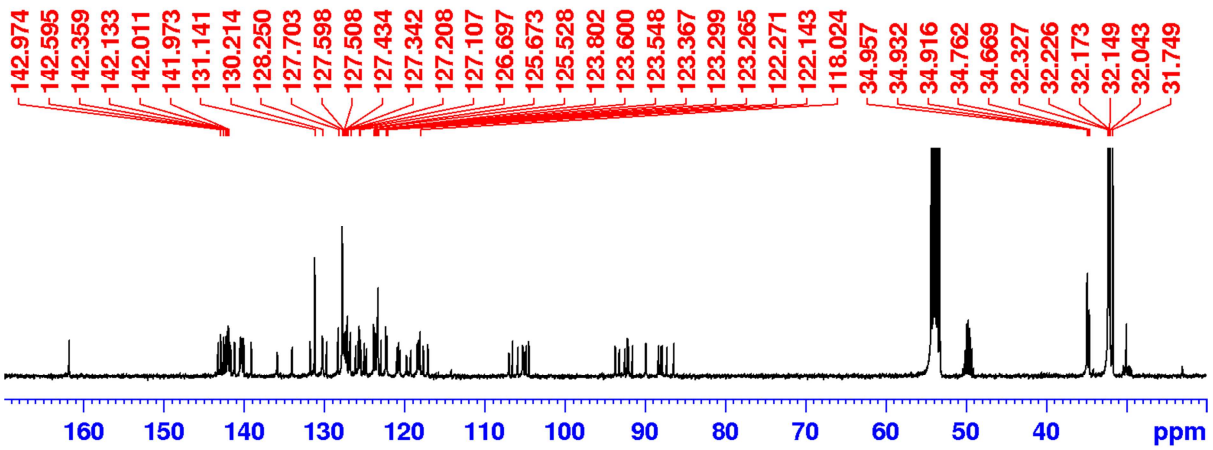


Fig. S63 ^{13}C NMR of **5** (100 MHz, 2% (v/v) CD_3OH/CD_2Cl_2, 25 °C)

7. References

[S1] E. Jurgens, K. N. Buys, A.-T. Schmidt, S. K. Furfari, M. L. Cole, M. Moser, F. Rominger and D. Kunz, *New J. Chem*., 2016, 9160.

[S2] C. H. Beierlein, B. Breit, R. A. Paz Schmidt and D. A. Plattner, *Organometallics*, 2010, **29**, 2521.

[S3] S. C. Maity, D. Mal and M. M. Maiti, *Thermochimica Acta*, 2005, **435**, 135–141.

[S4] S. De and S. Ramakrishnan, *Macromolecules*, 2009, ***42***, 8599.

[S5] Z. Zhang, L. Shao, Y. Zhou and J. Yang, *J. Polym. Sci*., *Part A: Polym. Chem.*, 2017, **55**, 3529.

[S6] X. Chen, C. Xu, T. Wang, C. Zhou, J. Du, Z. Wang, H. Xu, T. Xie, G. Bi, J. Jiang, X. Zhang, J. N. Demas, C. O. Trindle, Y. Luo and G. Zhang, *Angew. Chem*., *Int. Ed*., 2016, **55**, 9872.

[S7] Y. Matsunaga, K. Goto, K. Kubono, K. Sako and T. Shinmyozu, *Chem. Eur. J*., 2014, **20**, 7309.

[S8] *MacroModel*, *version 9.1*; Schrödinger, LLC: New York, 2005.

[S9] T. A. Halgren, *J. Comput. Chem*., 1996, **17**, 490.

[S10] J. W. Shin, K. Eom and D. Moon, *J. Synchrotron Rad*., 2016, **23**, 369.

[S11] Z. Otwinowski and W. Minor, *Methods in Enzymology*, 1997, **276**, 307.

[S12] G. M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3.

[S13] G. M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3.

[S14] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.