Hydrogen-bonded chains and networks of triptycene-based triboronic acid and tripyridinone

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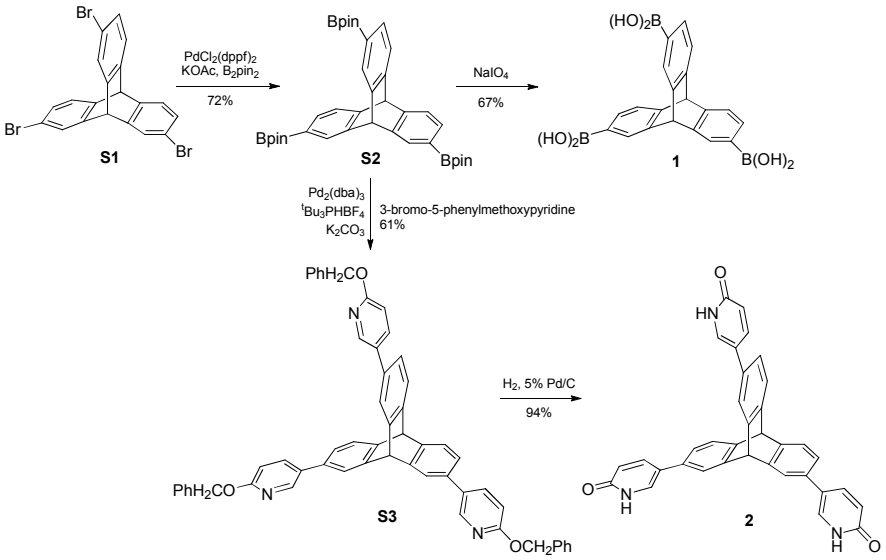
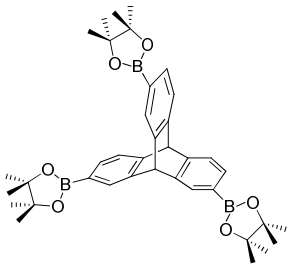
General Remarks

All reagents and solvents were obtained from Fisher Scientific, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded on as KBr-pellet on a Perkin Elmer Spectrum 2000 FT-IR spectrometer or a Ge ATR crystal with a Bruker Lumos spectrometer. NMR spectra were taken on a Bruker DRX 400 (400 MHz) and Bruker Avance 500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to traces of $CHCl_3$ or DMSO in the corresponding deuterated solvents. HRMS experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4 T superconducting magnet and interfaced to an Apollo II MTP ion source. DART experiments were performed on a FT-ICR Apex-Qe mass spectrometer. Elemental analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Crystal structure analysis was accomplished on Bruker APEX II Quazar diffractometer with a molybdenum source (λ (MoK_α) = 0.71073 Å). 2,7,14-tribromotriptycene was prepared according to the literature.[S1]

Experimental

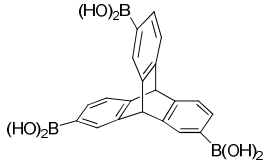


2,7,14-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triptycene (S2)



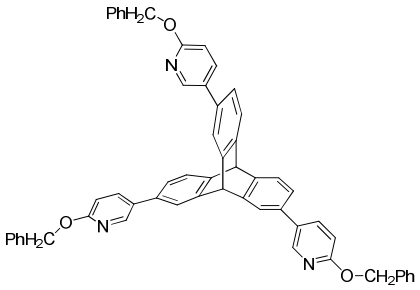
Triptycene tribromide **S1** (560 mg, 1.14 mmol), $PdCl_2(dppf)_2$ (45 mg), bis(pinacolato)diboron (0.96g, 3.78 mmol) and KOAc (0.67g, 6.84 mmol) were suspended in DMF (10 mL) and heated under argon at 100 ^oC overnight. After cooling down to room temperature, the mixture was diluted with dichloromethane (50 mL), washed with water (6×100 mL), and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude product was purified by a short silica gel column chromatography (dichloromethane) to give a light yellow solid. The solid was further washed with methanol (15 mL) to give compound **S2** as colorless solid (520 mg, 72%). mp > 400 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.78 (s, 3H), 7.45 (dd, J = 7.27Hz, 3H), 7.37 (d, J = 7.29 Hz, 3H), 5.48 (s, 1H), 5.44 (s, 1H), 1.28 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 147.7, 144.4, 132.2, 129.5, 123.2, 83.6, 54.6, 53.7, 24.7. FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 2974 (m), 2927 (w), 1607 (m), 1483 (w), 1411 (m), 1385 (w), 1352 (s), 1294 (w), 1268 (w), 1213 (w), 1140 (s), 1109 (w), 1072 (w), 964 (m), 861 (m), 694 (w), 648 (w), 610 (w). HRMS (EI) (*m/z*): $[M]^+$ calcd. for $C_{38}H_{47}B_3O_6$, 632.3652; found, 632.3641.

2,7,14-triptycene triboronic acid (1)



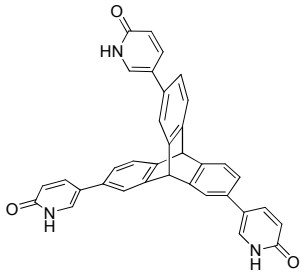
To a solution of triptycenetrisboronic acid pinacol ester **S2** (250 mg, 0.40 mmol) in THF (8 mL) and water (2 mL) $NaIO_4$ (0.76 g, 3.55 mmol) was added. The mixture was stirred at room temperature for 24 hours. Aqueous HCl (0.1 ml, 1M) was added to the suspension and the mixture was stirred for another 24 hours. The suspension was extracted with Et_2O (3×50 mL) and the combined organic layer was washed with water (3×100 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude product was purified by recrystallization from water to give compound **1** as colorless solid (100 mg, 67%). mp > 400 ^oC. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.95 (s, 6H), 7.84 (s, 3H), 7.45 (d, J = 7.31 Hz, 3H), 7.41 (t, J = 7.33 Hz, 3H), 5.62 (s, *1*H), 5.58 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 146.9, 144.5, 131.2, 129.1, 123.0, 53.1, 53.0. FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) = 3429 (br, s), 1604 (m), 1410 (m), 1338 (s), 1092 (w), 926 (w), 848 (w), 699 (m), 618 (w), 493 (w).

2,7,14-tris(2-phenylmethoxypyridin-5-yl)triptycene (S3)



In a screw-capped vial, mixture of triptycenetrisboronic acid pinacol ester **S2** (850 mg, 1.34 mmol), $Pd_2(dba)_3$ (94 mg), $^tBu_3PHBF_4$ (94 mg) and 3-bromo-5-phenylmethoxypyridine (1.23 g, 4.66 mmol) were dissolved in degassed THF (4 mL) and aqueous K_2CO_3 solution (1 mL, 4.3M) and heated at 80 °C overnight. After cooling down to room temperature, the mixture was diluted with dichloromethane (50 mL) and washed with aqueous 2M HCl solution (2×100 mL), water (3×50 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (dichloromethane/light petroleum 10:1 to dichloromethane) to give compound **S3** as colorless solid (980 mg, 91%). mp: 98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.33 (d, J = 2.31 Hz, 3H), 7.74 (dd, J = 8.62, 2.52 Hz, 3H), 7.63 (d, J = 1.50 Hz, 3H), 7.51 (d, J = 7.64 Hz, 3H), 7.48 (d, J = 7.17 Hz, 6H), 7.39 (t, J = 7.39 Hz, 6H), 7.33 (t, J = 7.32 Hz, 3H), 7.20 (dd, J = 7.63, 1.70 Hz, 3H), 6.85 (d, J = 8.61 Hz, 3H), 5.63 (s, 1H), 5.58 (s, 1H), 5.41 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 162.9, 145.7, 144.9, 144.1, 137.7, 137.2, 135.4, 130.3, 128.5, 128.0, 127.9, 124.2, 124.0, 122.4, 111.1, 67.8, 54.4, 53.0. FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3030 (w), 2953 (w), 1602 (s), 1497 (m), 1461 (s), 1426 (w), 1383 (w), 1357 (m), 1309 (w), 1279 (s), 1244 (m), 1156 (w), 1129 (w), 1079 (m), 1041 (m), 918 (w), 873 (w), 828 (m), 794 (w), 776 (w), 733 (m), 694 (m). HRMS (ESI) (*m/z*): $[M+H]^+$ calcd. for $C_{56}H_{42}N_3O_3$, 804.32207; found, 804.32214. Elemental anal. calcd. for $C_{56}H_{41}N_3O_3 \cdot 0.6\ H_2O$: C 82.55 H 5.22 N 5.16, found: C 82.47 H 5.37 N 5.18.

2,7,14-tris(1,2-dihydro-2-oxo-5-pyridinyl)triptycene (2)



To a solution of 2,7,14-tris(2-phenylmethoxypyridin-5-yl)triptycene **S3** (368 mg, 0.458 mg) in methanol (20 mL) and ethyl acetate (20 mL) 5% Pd/C (80 mg) was added. The mixture was stirred under hydrogen atmosphere at room temperature for three hours. The mixture was then filtered off and additional acetic acid was used to wash down the residue. The solvent amount was reduced by rotary evaporation to approx. 5 mL and diethyl ether (250 mL) was added to

cause precipitation. The precipitate was collected by filtration and dried in vaccum to give compound **2** as colorless solid (231mg, 94%). mp: > 400 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 11.79(s, 3H), 7.74 (dd, J = 2.58, 9.95 Hz, 3H), 7.63 (s, 3H), 7.61 (d, J = 2.11 Hz, 3H), 7.46 (d, J = 7.70 Hz, 3H), 7.17 (dd, J = 1.43, 7.67 Hz, 3H), 6.40 (d, J = 9.53 Hz, 3H), 5.69 (s, 1H), 5.58 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 161.7, 145.8, 143.6, 140.1, 133.2, 132.6, 124.0, 122.1, 121.1, 120.0, 117.9, 53.0, 51.3. FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3018 (w), 1650 (s), 1599 (s), 1543 (m), 1458 (m), 1427 (m), 1339 (w), 1291 (w), 1219 (m), 1131 (w), 994 (w), 830 (m), 795 (m), 775 (w), 691 (m), 661 (w), 635 (w), 613 (w). HRMS (ESI) (*m/z*): $[M+H]^+$ calcd. for $C_{35}H_{24}N_3O_3$, 534.18122; found, 534.18150. Elemental anal. calcd. for $C_{35}H_{23}N_3O_3 \cdot 2.5\ H_2O$: C 72.65 H 4.88 N 7.26, found: C 72.57 H 4.91 N 7.08.

NMR spectra

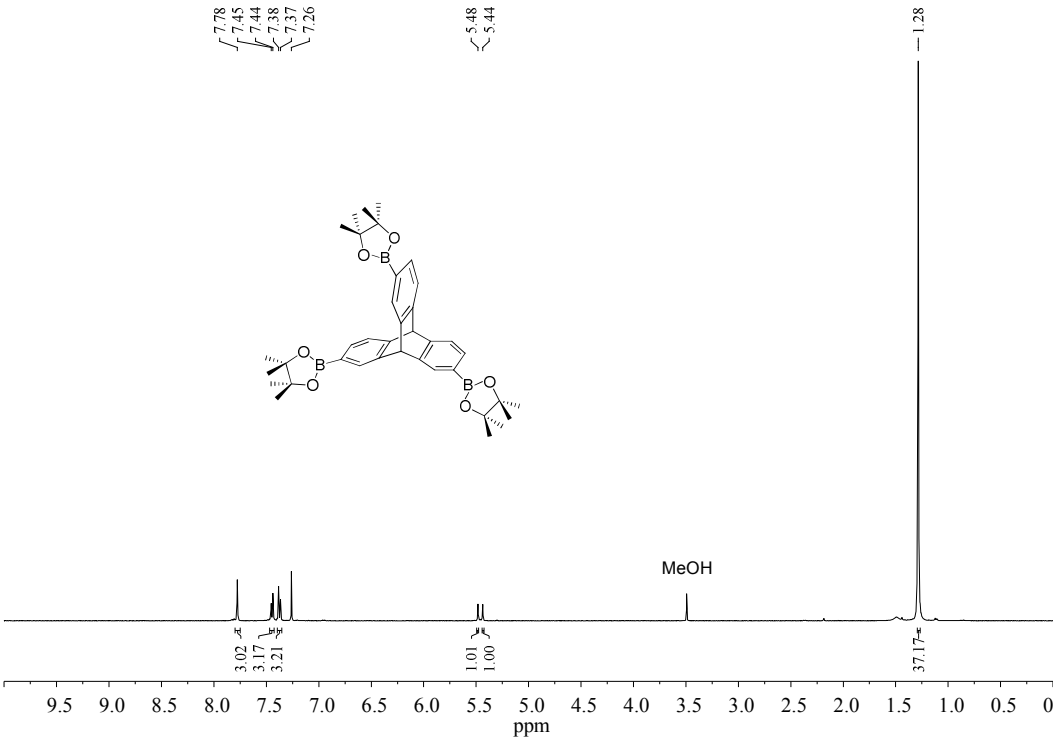


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of 2,7,14-triptycenetrisboronic acid pinacol ester **S2**.

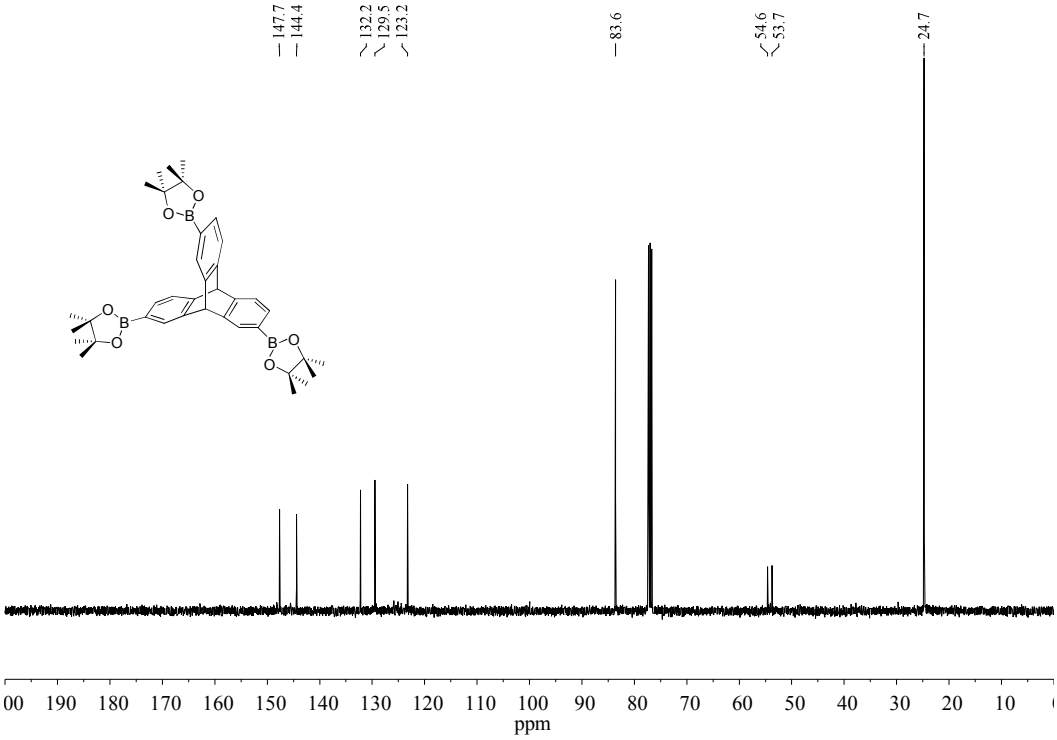


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 2,7,14-triptycenetrisboronic acid pinacol ester **S2**.

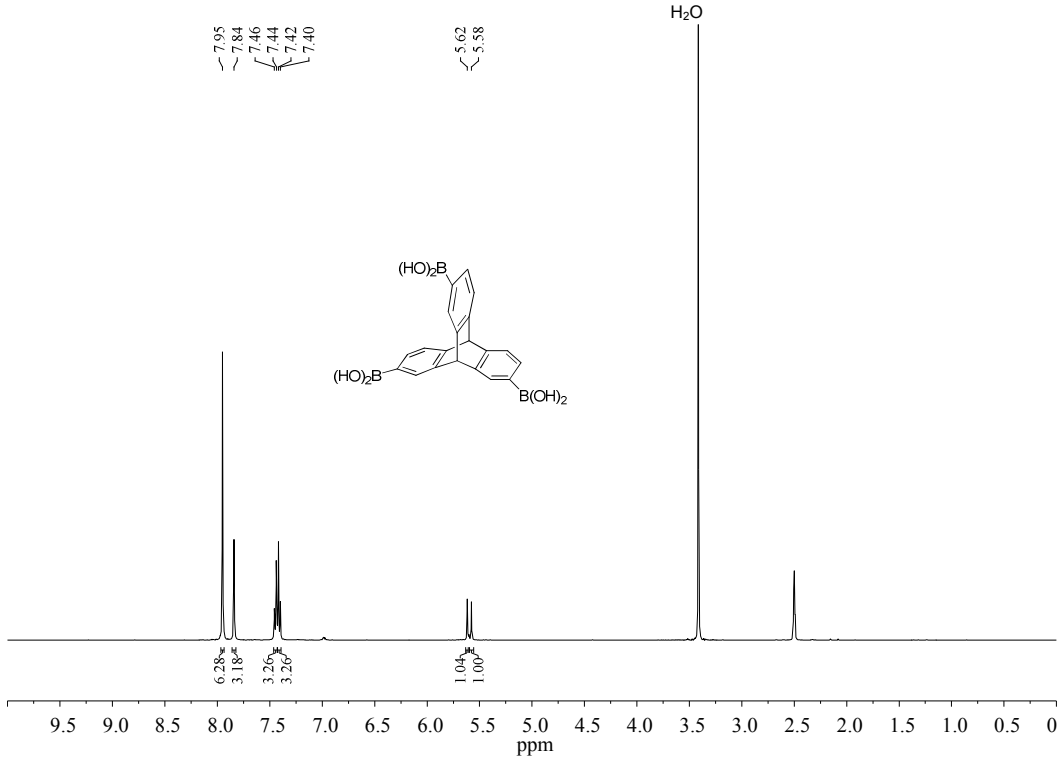


Figure S3. ^{1}H NMR spectrum (DMSO-d_6, 400MHz) of 2,7,14-triptycenetrisboronic acid **1**.

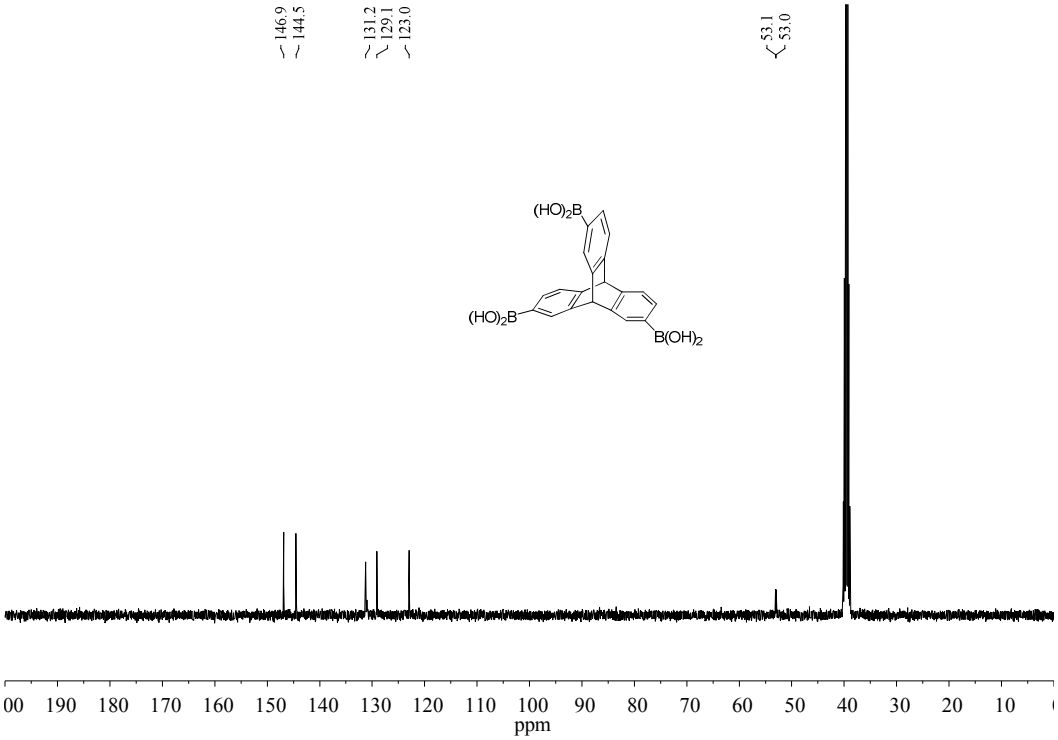


Figure S4. ^{13}C NMR spectrum (DMSO-d_6, 100MHz) of 2,7,14-triptycenetrisboronic acid **1**.

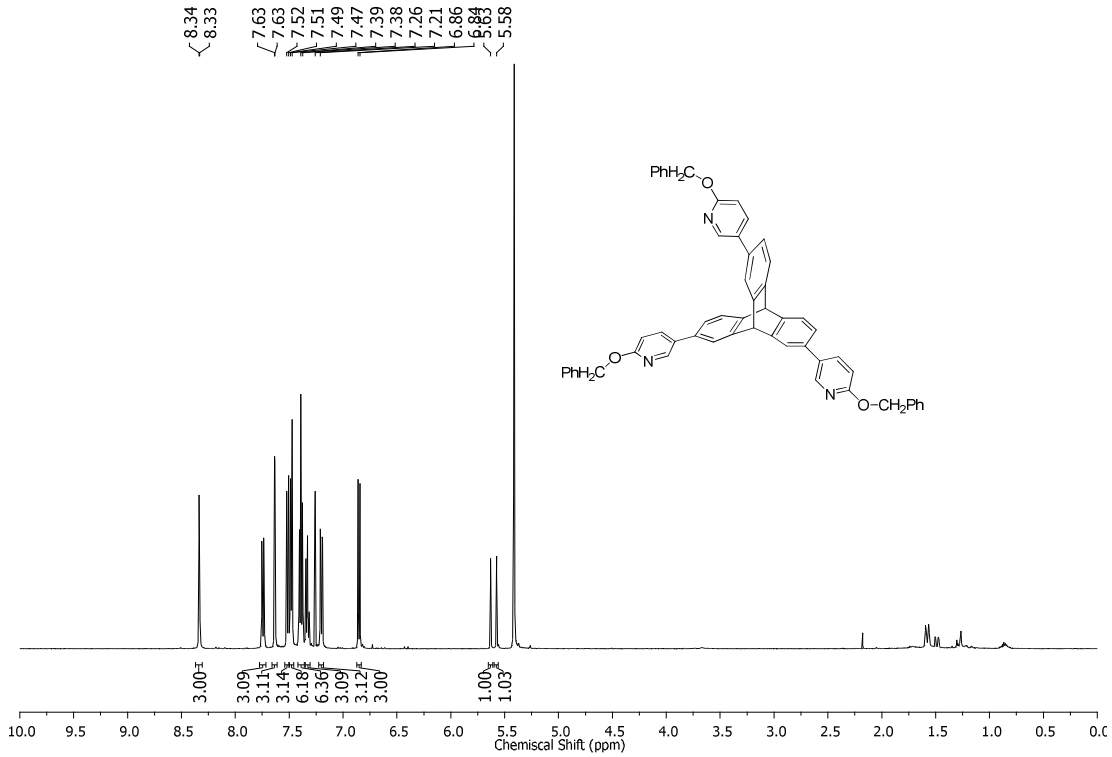


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 500MHz) of 2,7,14-tris(2-phenylmethoxypyridin-5-yl)triptycene **S3**.

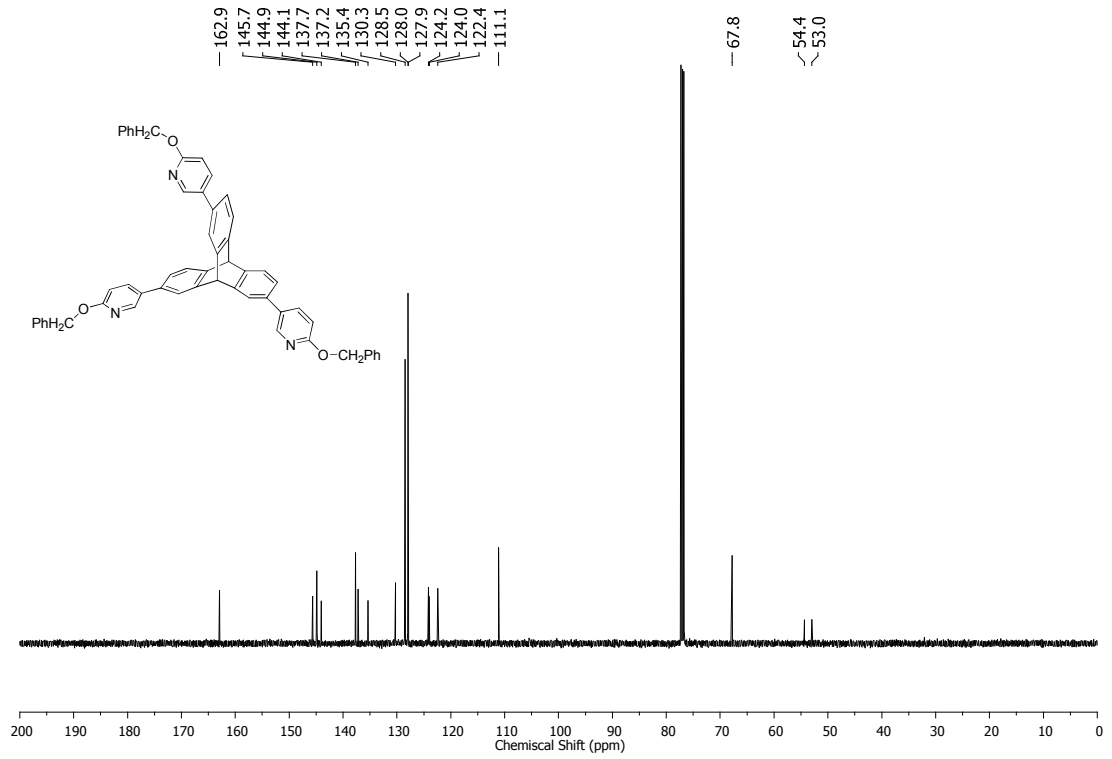


Figure S6. ^{13}C NMR ($CDCl_3$, 125MHz, 298 K) of 2,7,14-tris(2-phenylmethoxypyridin-5-yl)triptycene **S3**.

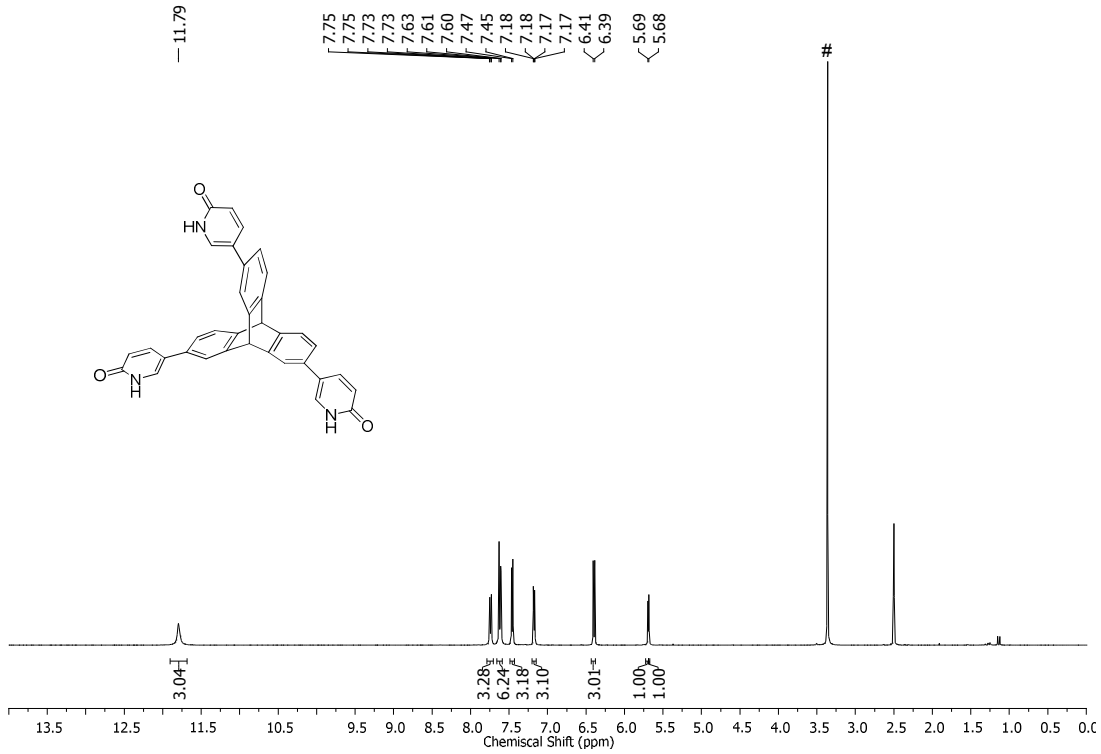


Figure S7. ^{1}H NMR spectrum (DMSO-d_6, 500MHz) of 2,7,14-tris(1,2-dihydro-2-oxo-5-pyridinyl)triptycene **2**. #: water.

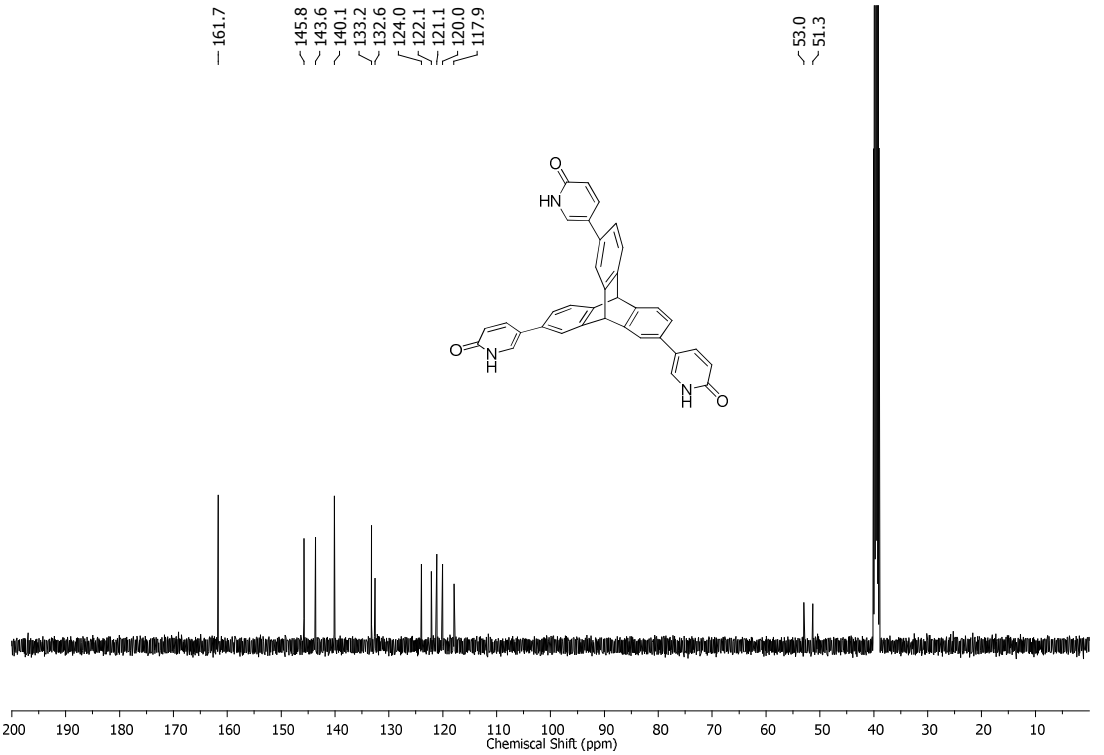


Figure S8. ^{13}C NMR spectrum (DMSO-d_6, 125MHz) of 2,7,14-tris(1,2-dihydro-2-oxo-5-pyridinyl)triptycene **2**.

References

S1. C. Zhang, C.-F. Chen, *J. Org. Chem.*, 2006, **71**, 6626.