Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile Three-Step Synthesis and Photophysical Properties of [8]-, [9]-, and [12]Cyclo-1,4-naphthalene Nanorings via Platinum-Mediated Reductive Elimination

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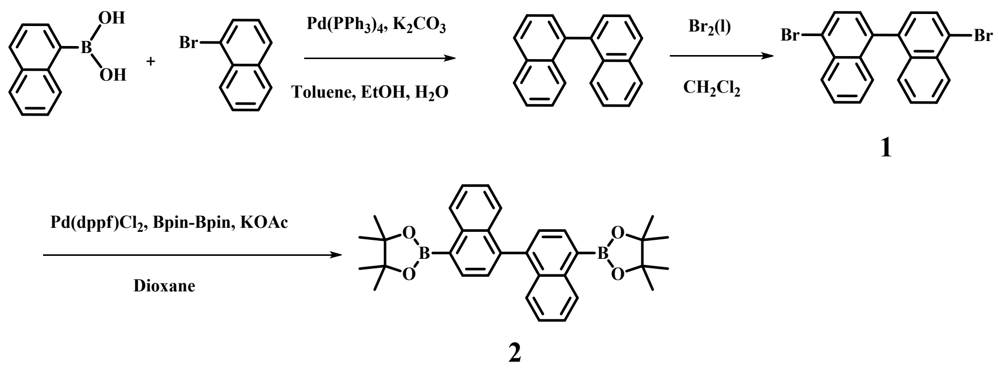
General. All the air-sensitive reactions were carried out in a dry vessel under argon atmosphere. NMR spectra were collected on a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer for $CDCl_3$ solution of a sample. Chemical shift values were expressed in parts per million (ppm) relative to $CDCl_3$ (δ 7.26 ppm for ^{1}H NMR). Flash chromatography was performed on silica gel (200～300 mesh) and preparative thin-layer chromatography (PTLC) were performed using silica gel GF254 precoated plates. High-resolution MALDI-TOF mass spectra were measured on a Bruker Daltonics Inc. LTQ Orbitrap XL hybrid Fourier Transform high-resolution Mass Spectrometer. UV-vis spectra were collected on a UNIC-3802 spectrophotometer in standard glass cuvettes.

Materials. All reagents such as 1-bromonaphthalene ($C_{10}H_7Br$, 96%), 2-methyl-1-(phenylmethyl)-1H-imidazole ($C_{10}H_9BO_2$, 98%), triphenylphosphine (PPh_3, 99%), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$, 99%), potassium carbonate (K_2CO_3, 99%), bis(pinacolato)diboron ($C_{12}H_{24}B_2O_4$, 98%), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 99%), sodium thiosulfate ($Na_2S_2O_3$, 99%), potassium acetate ($C_2H_3KO_2$, 92%), cesium fluoride (CsF, 99%), and bromine (Br_2, 99.5%) were obtained from Alfa Aesar or Sigma Aldrich and used without further purification. All organic solvents (THF, Toluene, $CHCl_2$, MeOH, EtOH, Et_2O and 1,4-dioxane) were purchased from China Medicine Shanghai Chemical Reagent Co. and distilled under nitrogen prior to use. Dichloro(1,5-cyclooctadiene)platinum ($Pt(COD)Cl_2$) and 1,4-dibromonaphthalene ($C_{10}H_6Br_2$) were synthesized as reported. [S1,2]

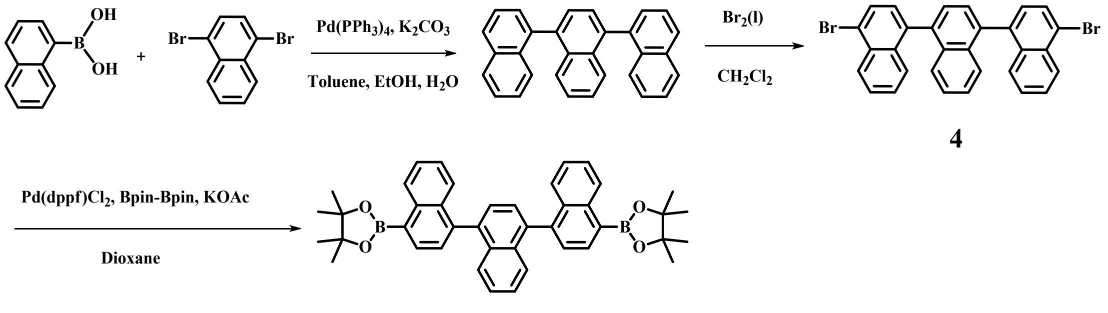
Synthesis



Synthesis of 1,1′-binaphthyl and 4,4′-dibromo-1,1′-binaphthyl. 1,1′-binaphthyl and 4,4′-dibromo-1,1′-binaphthyl were prepared according to the published procedures.[S3]

Synthesis of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2). To a mixture of **1** (500 mg, 1.2 mmol), bis(pinacolato)diboron (925 mg, 3.6 mmol), Pd(dppf)Cl_2 (50 mg, 0.07 mmol) and anhydrous potassium acetate (600 mg, 6.1 mmol) in a round-bottom flask (50 ml) was added anhydrous 1, 4-dioxane (20 ml). The solution was bubbled with argon for 0.5 h before heated to 100 °C for 36 h. Upon cooling to room temperature, the solvent was removed under vacuum and the resulting product was extracted with CH_2Cl_2. The organics was washed thoroughly with water, dried over anhydrous $MgSO_4$, and then evaporated to dryness. The residue was purified by chromatography on a silica gel column with CH_2Cl_2/petroleum ether (1:5) as eluent. Yield 0.58 g (94%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.86 (d, *J* = 8 Hz, 2H), 8.18 (d, *J* = 8 Hz, 2H), 7.51 (t, 2H), 7.47 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 1.47 (s, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.25, 137.12, 135.22, 132.64, 128.72, 127.03, 126.93, 126.40, 125.74, 83.95, 25.13 ppm; MS (ESI) *m/z* calcd. for $C_{32}H_{36}B_2O_4$ $[M+H]^+$: 507.2878, found: 507.2504.

Synthesis of [8]CN. 2 (100 mg, 0.20 mmol), CsF (120 mg, 0.86 mmol), and Pt(COD)Cl_2 (74 mg, 0.20 mmol) were dispersed in anhydrous THF (30 mL). Then, the mixture was heated and stirred for 24 h under an argon atmosphere. Thereafter, 20 mL of MeOH was added and a precipitate formed. Filtration was carried out and the resulting solid was dried in vacuum oven. This anhydrous solid material was transferred to a 50-mL oven dried Schlenk flask containing a magnetic stirring bar and triphenylphosphine (520 mg, 1.98 mmol), to which toluene (20 mL) was added. The mixture was bubbled with argon for 0.5 h before heated to reflux for another 36 h. Upon cooling to room temperature, the solvent was evaporated and the resulting product was redissolved in CH_2Cl_2 and passed through a short silica gel column, then further purified by preparative thin-layer chromatography using hexane/CH_2Cl_2 as the eluent (*v/v*, 4:1), giving [8]CN (1.3 mg) in 2.6% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.92 (s, 16H), 7.52-7.60 (m, 16H), 8.47-8.55 (m, 16H) (Figure S11); HRMS (MALDI-TOF) *m/z* calcd. for $C_{80}H_{48}$ $[M]^+$: 1008.3756, found: 1008.3793 (Figure S7).



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Synthesis of 1,1′:4′,1″-ternaphthalene and 4,4″-dibromo-1,1′:4′,1″-ternaphthalene. The general procedure above was used to synthesis 1,1′:4′,1″-ternaphthalene and 4,4″-dibromo-1,1′:4′,1″-ternaphthalene.[S3]

Synthesis of 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1′′-ternaphthalene (5). To a mixture of 4 (830 mg, 1.5 mmol), bis(pinacolato)diboron (940 mg, 3.7 mmol), Pd(dppf)Cl_2 (60 mg, 0.08 mmol) and anhydrous potassium acetate (900 mg, 9.2 mmol) in a round-bottom flask (50 ml) was added dried DMF (15 ml). The solution was bubbled with argon for 0.5 h before heated to 120 °C for 36 h. Upon cooling to room temperature, the solvent was removed under vacuum and the resulting product was extracted with CH_2Cl_2. The organics was washed thoroughly with water, dried over anhydrous $MgSO_4$, and then evaporated to dryness. The residue was purified by chromatography on a silica gel column with CH_2Cl_2/petroleum ether (1:5) as eluent. Yield 0.93 g (95%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.91 (d, J = 8 Hz, 2H), 8.25 (d, J = 8 Hz, 2H), 7.64 (d, J = 8 Hz, 2H), 7.60-7.52 (m, 6H), 7.47-7.42 (m, 2H), 7.34 (t, 2H), 7.20-7.26 (m, 2H), 1.49 (s, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.19, 138.64, 137.21, 135.31, 132.91, 132.85, 128.80, 127.37, 127.21, 127.12, 126.97, 126.46, 125.97, 125.82, 84.00, 25.17 ppm; HRMS (ESI) *m/z* calcd. for $C_{42}H_{42}B_2O_4$ $[M+H]^+$: 633.3347, found: 633.3345.

Synthesis of [9]CN and [12]CN. The general procedure above for [8]CN was used with the exception that **5** (125 mg, 0.20 mmol) was used in place of **2** to afford [9]CN (2.1 mg) in 2.9% yield and [12]CN (2.6 mg) in 3.5% yield. [9]CN: ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 6.23 (s, 2H), 7.00 (s, 2H), 7.03 (d, J = 8 Hz, 2H), 7.08-7.13 (m, 4H), 7.20 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 7.56-7.62 (m, 4H), 7.66-7.72 (m, 10H), 7.74-7.80 (m, 6H), 8.21-8.25 (m, 2H), 8.40-8.45 (m, 4H), 8.46-8.50 (m, 2H), 8.51-8.55 (m, 4H), 8.57 (d, J = 8 Hz, 2H), 8.72 (d, *J* = 8 Hz, 2H) (Figure S12); HRMS (MALDI-TOF) *m/z* calcd. for $C_{90}H_{54}$ $[M]^+$: 1134.4226, found: 1134.4204 (Figure S8). [12]CN: ^1H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 7.27 (s, 24H), 7.58-7.65 (m, 24H), 8.44-8.52 (m, 24H) (Figure S13); HRMS (MALDI-TOF) *m/z* calcd. for $C_{120}H_{72}$ $[M]^+$: 1513.5668, found: 1513.5630 (Figure S9).

References.

(S1) Liu, B.; Yu, W. L.; Lai, Y. H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984.

(S2) Mcdermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(S3) Park, J. K.; Lee, K. H.; Park, J. S.; Seo, J. H.; Kim, Y. K.; Yoon, S. S. *Mol. Cryst. Liq. Cryst.* **2010**, *531*, 55.

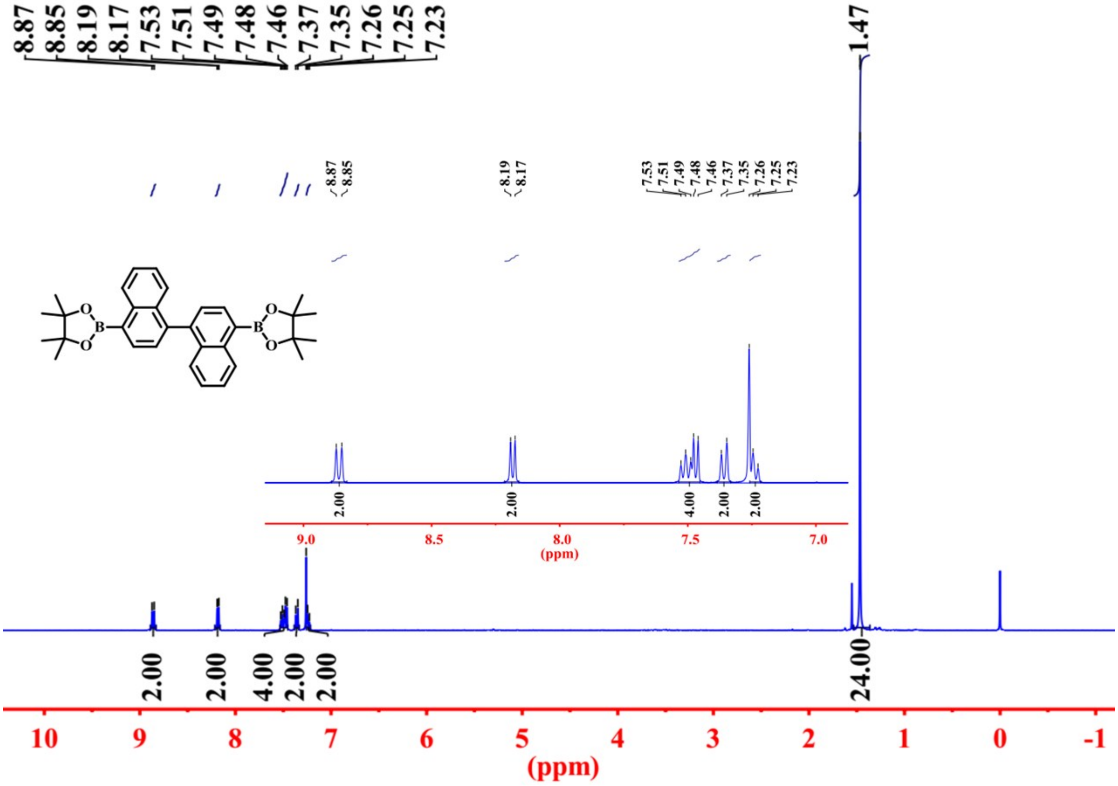


Figure S1. ^{1}H NMR spectrum of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2) in $CDCl_3$.

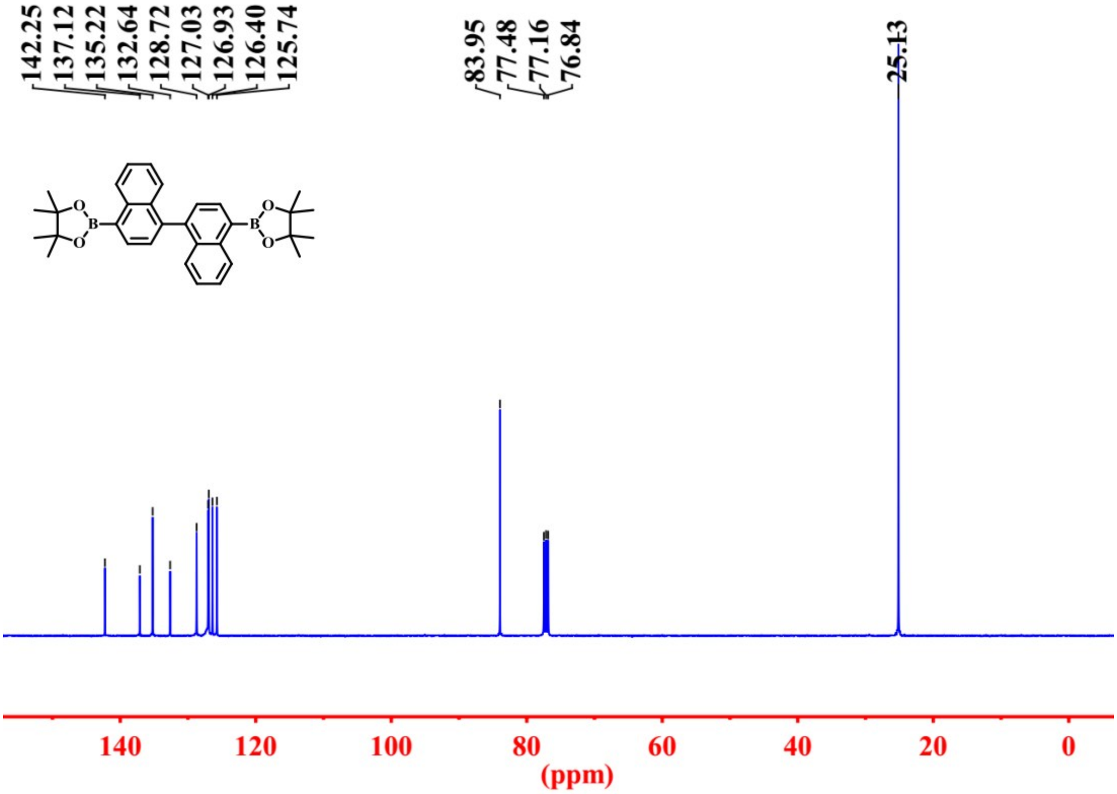


Figure S2. ^{13}C NMR spectrum of 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2) in $CDCl_3$.

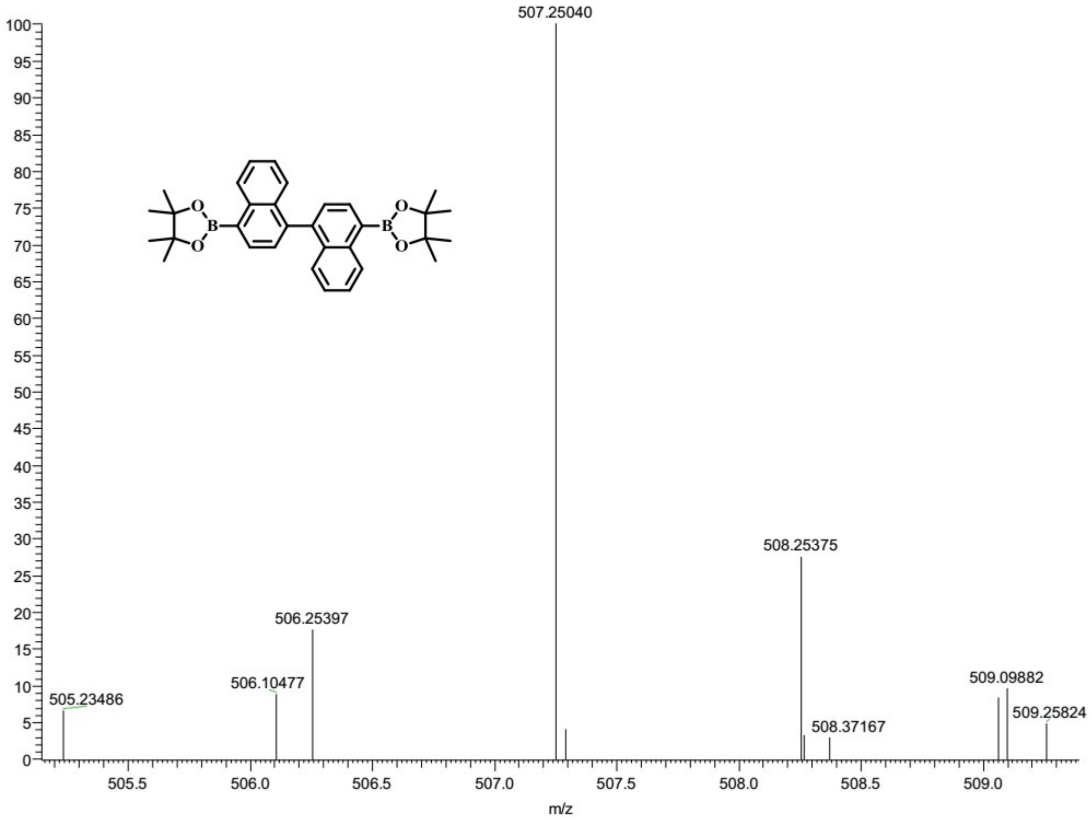


Figure S3. HR-MS (ESI) data for 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (2)**.**

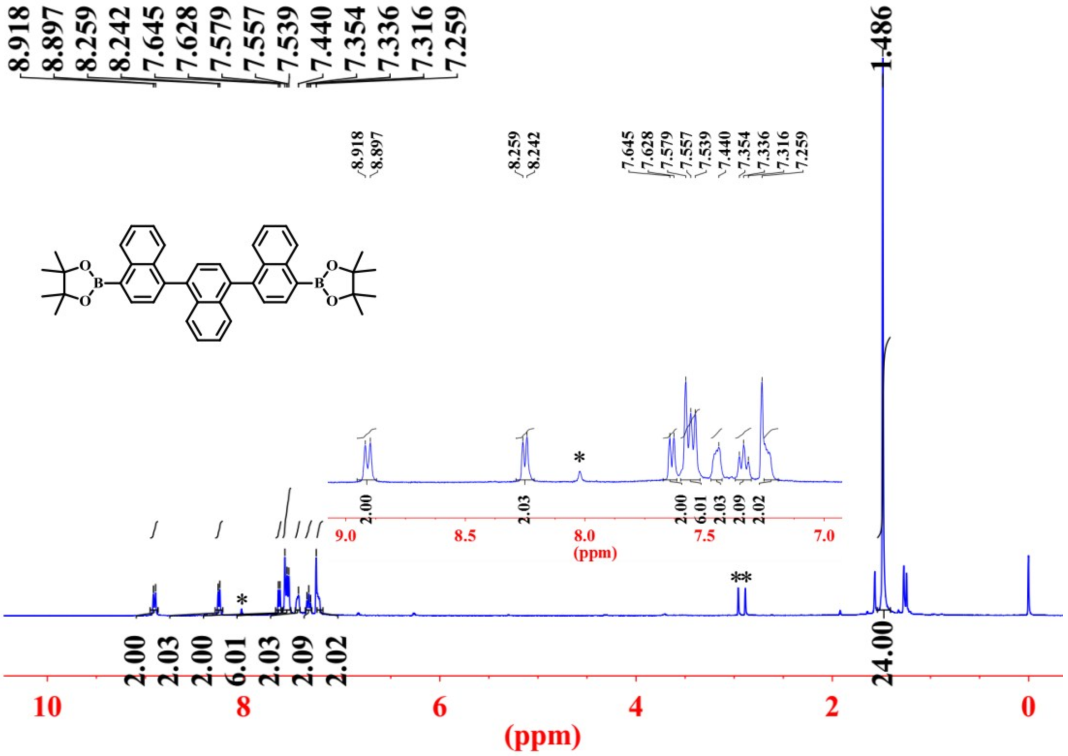


Figure S4. ^{1}H NMR spectrum of 4,4″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1″-ternaphthalene (5) in $CDCl_3$. *: signals of residue DMF.

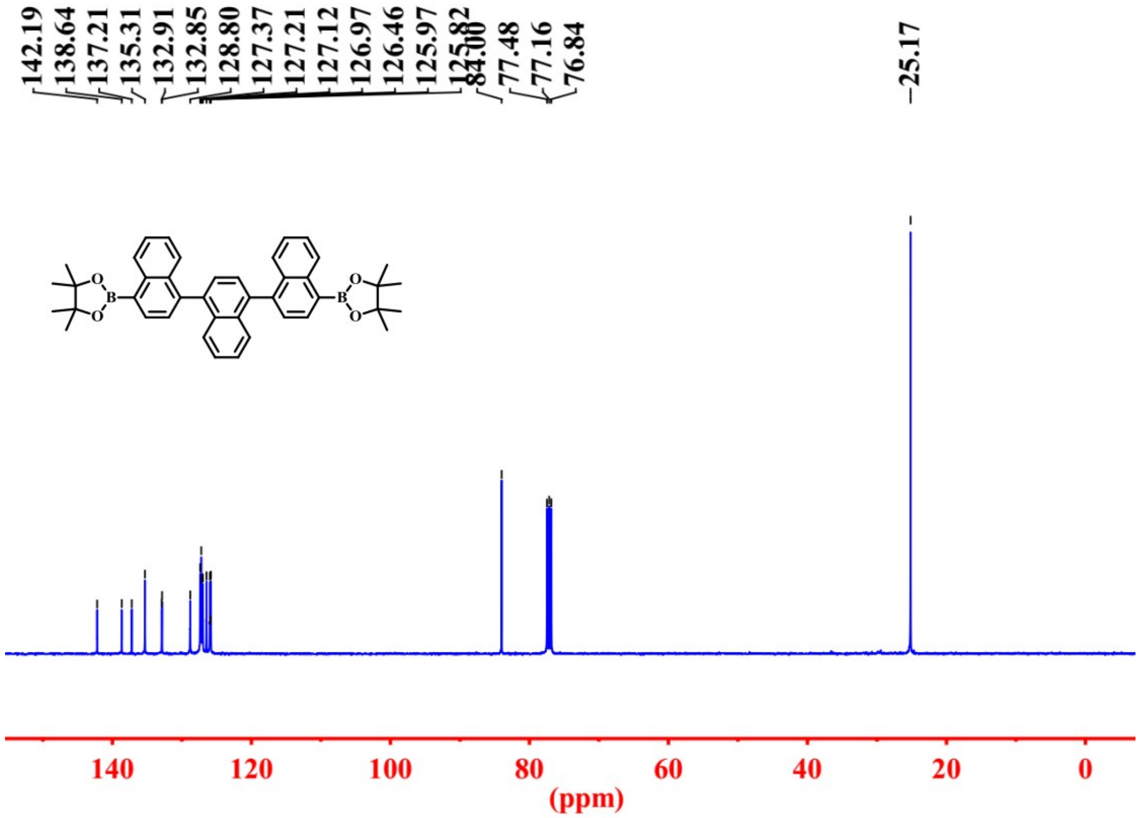


Figure S5. ^{13}C NMR spectrum of 4,4″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1″-ternaphthalene (5) in $CDCl_3$.

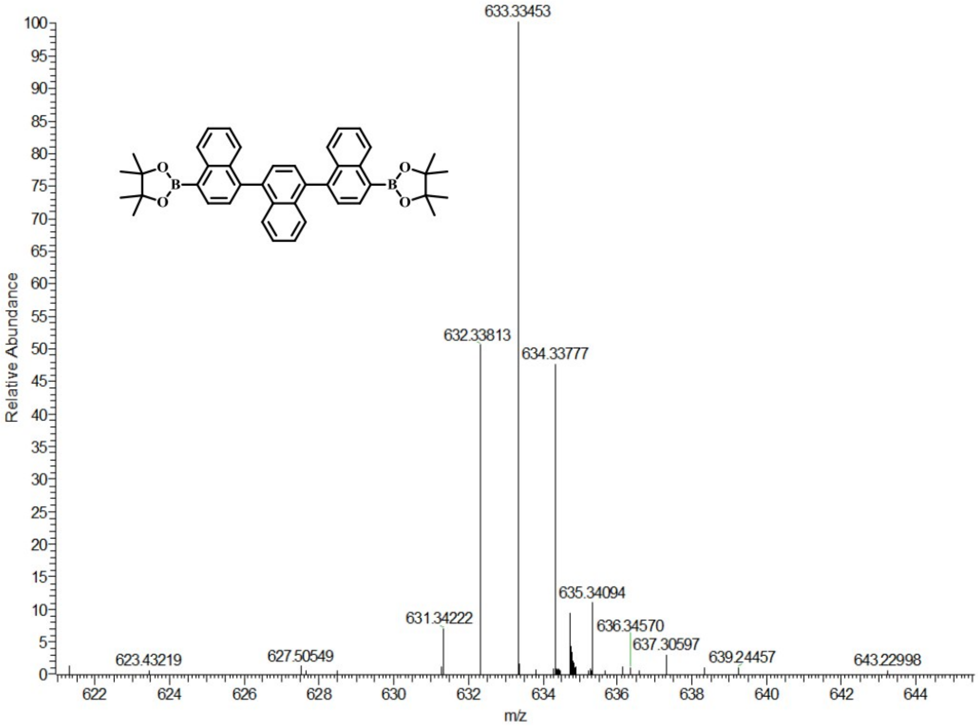


Figure S6. HR-MS (ESI) data for 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′:4′,1′′-ternaphthalene (5).

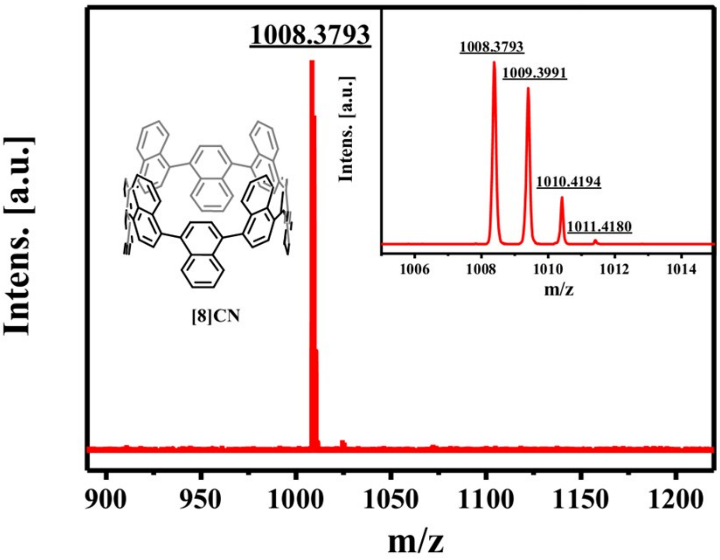


Figure S7. HRMS (MALDI-TOF) data for [8]CN.

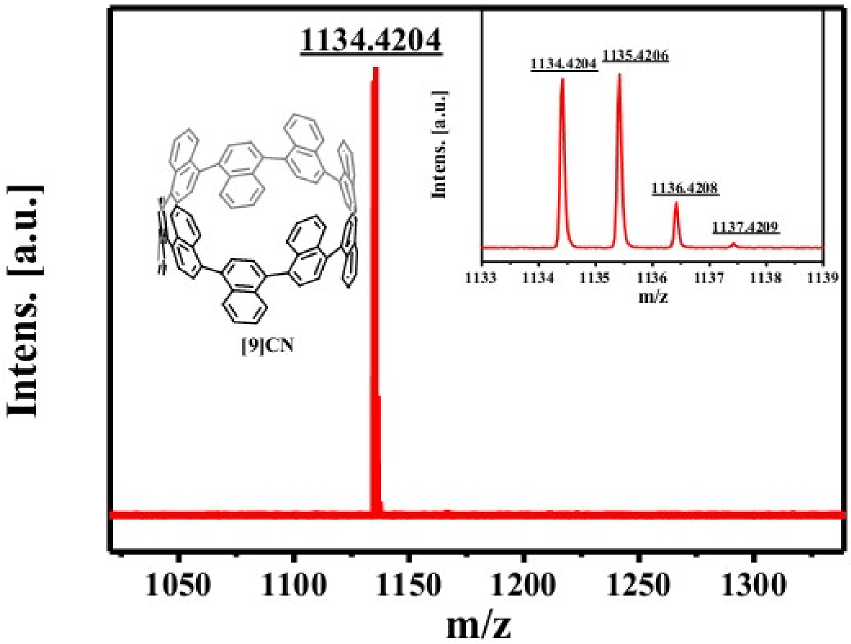


Figure S8. HRMS (MALDI-TOF) data for [9]CN.

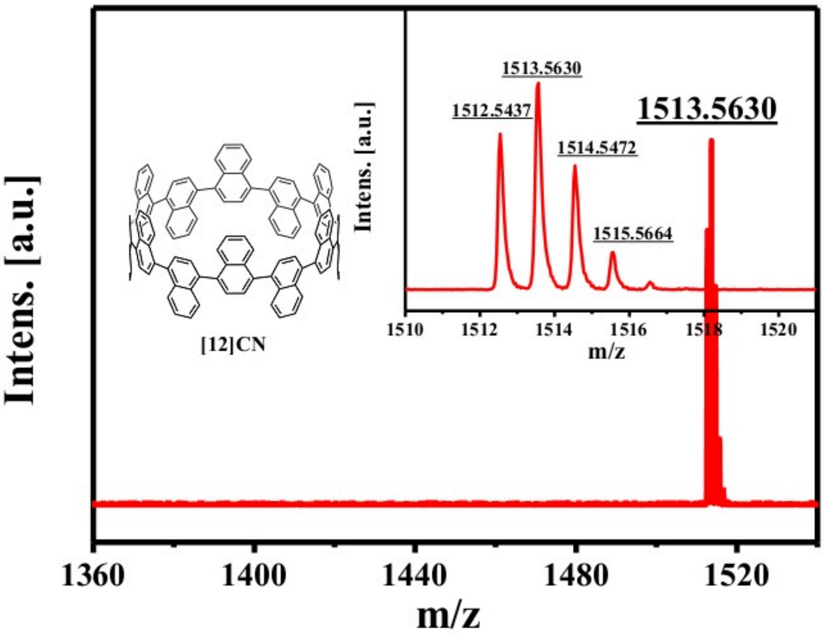


Figure S9. HRMS (MALDI-TOF) data for [12]CN.

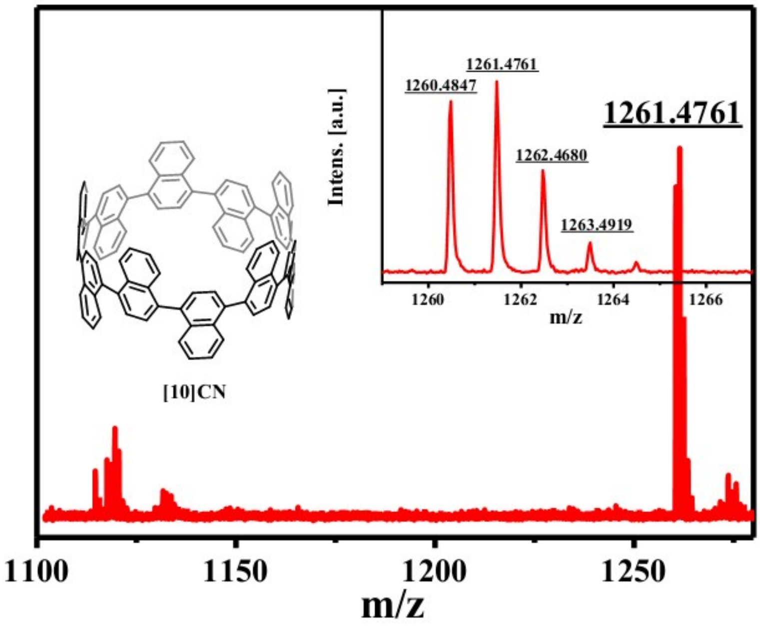


Figure S10. HRMS (MALDI-TOF) data for [10]CN.

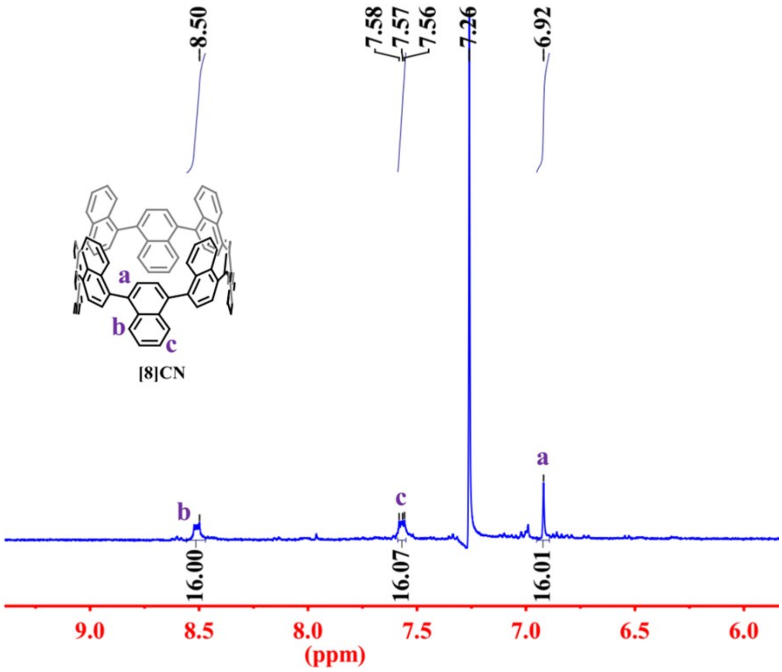
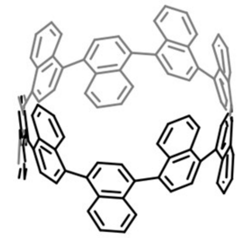


Figure S11. ^{1}H NMR spectrum of [8]CN in $CDCl_3$.



[9]CN

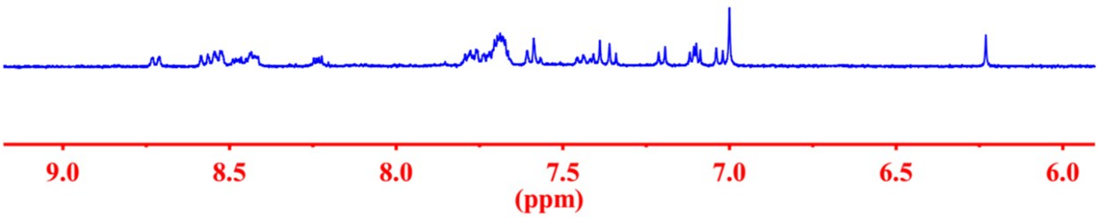


Figure S12. ^{1}H NMR spectrum of [9]CN in DMSO-d_6.

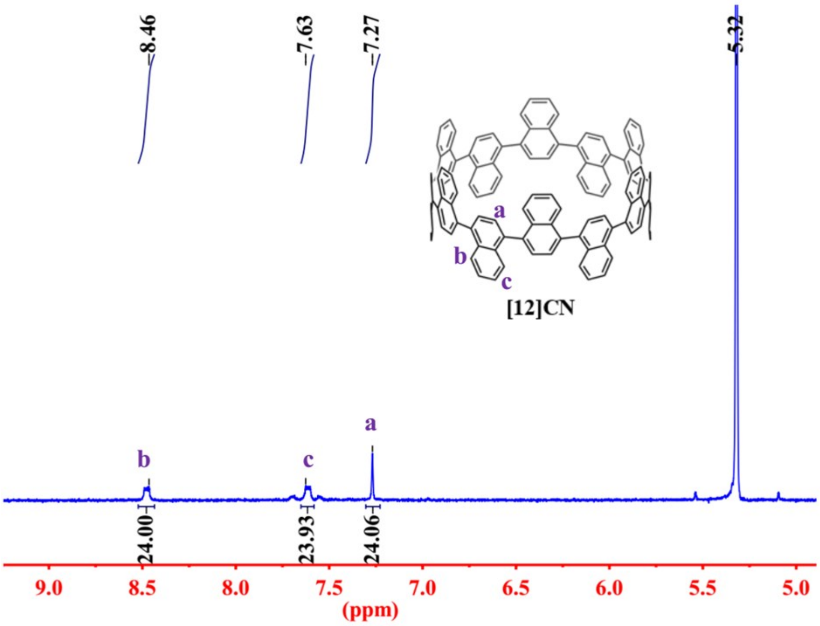


Figure S13. ^{1}H NMR spectrum of [12]CN in CD_2Cl_2.