

Supplementary Information

Thermally activated delayed fluorescence emitters with LUMO-extended boron-containing acceptor for high-efficiency and long-lifetime blue OLEDs

*Jeong-Yeol Yoo, Seung Wan Kang, Tae Hoon Ha, and Chil Won Lee**

Department of Chemistry, Dankook University, Cheonan 31116, Republic of Korea

Materials

The reagents and solvents used in the experiment were 9H-carbazole (Tokyo Chemical Industry Co., Ltd., 97.0%), 2,5-dibromo-1,3-difluorobenzene (Jihyunchem Co., Ltd., 97%), phenol (Duksan Pure Chemicals Co., Ltd., extra pure grade), 9H-carbazole (Sigma-Aldrich Co., Ltd.), 3,6-di-tert-butyl-9H carbazole (Jihyunchem Co., Ltd., 97%), 3,6-diphenyl-9H carbazole (Jihyunchem Co., Ltd., 97%), potassium phosphate tribasic (K_3PO_4) (Daejung Chemicals & Metals Co., chemically pure grade), potassium carbonate anhydrous (K_2CO_3) (Daejung Chemicals & Metals Co., extra pure grade), cesium carbonate (CS_2CO_3 ; Sigma-Aldrich Co., Ltd.), potassium tert-butoxide (Sigma-Aldrich Co., Ltd), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2(PPh_3)_2$; P&H Tech., Ltd., 97%), dicyclohexyl (2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphine (S-Phos; Jihyunchem Co., Ltd., 97%), n-butyllithium (AcroSeal®; Acros Organics, 2.5 M solution in hexanes), boron tribromide solution (Sigma-Aldrich Co., Ltd., 1.0 M in hexanes), N,N-diisopropylethylamine (extra pure

grade), N-methyl-2-pyrrolidone (NMP), tert-butyl benzene, 1,4-dioxane, n-hexane (Hex), dichloromethane (MC) (Ltd., 99.5%), ethyl acetate (EA), methyl alcohol (methanol), ethyl alcohol (ethanol; Ltd., 99.5%), N,N-dimethylformamide (DMF), and distilled water (D.W.). All reagents and solvents were used as purchased without further purification.

Device fabrication

To evaluate the EL performance of the three emitters, bottom-emissive OLED devices were fabricated. The OLED device was fabricated using 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN) as the hole injection layer (HIL); N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine (BCFN) as the hole transport layer (HTL); 9-(3-(triphenylsilyl)phenyl)-9H-3,9'-bicarbazole (SiCzCz) as the electron blocking layer (EBL) and p-type host; 9,9-(6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (SiTrzCz2) as the n-type host; 2-phenyl-4,6-bis(3-(triphenylsilyl)phenyl)-1,3,5-triazine (mSiTrz) and 8-quinolinolato lithium (Liq) as the hole-blocking layer (HBL) and electron-transport layer (ETL), respectively; lithium fluoride (LiF) as the electron injection layer (EIL); and Al as the cathode. Thereafter, the devices were encapsulated with a thin glass plate and epoxy adhesive.

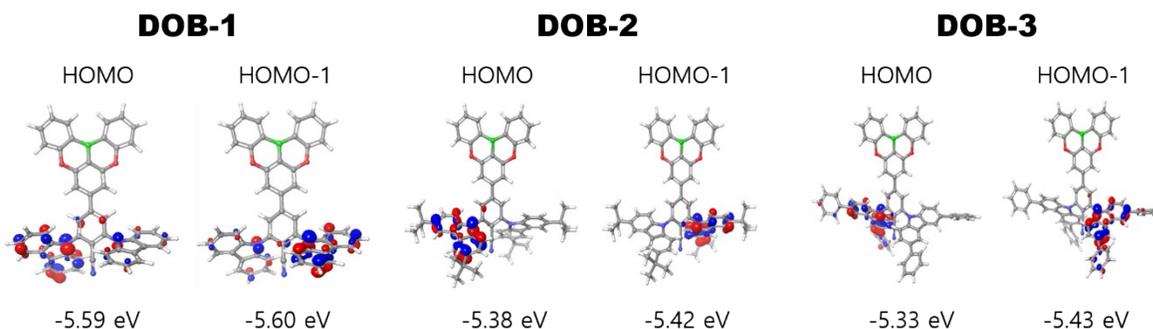


Figure S1. HOMO and HOMO-1 energy levels of DOB-1, DOB-2, and DOB-3.

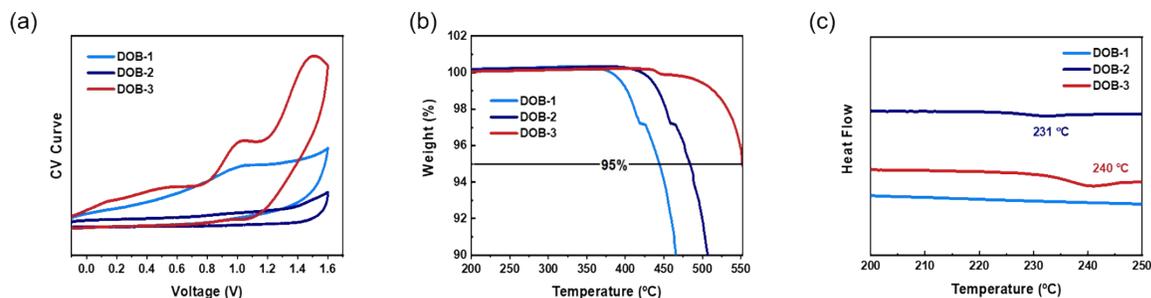


Figure S2. (a) CV, (b) TGA, and (c) DSC results of DOB-1, DOB-2, and DOB-3.

Table S1. Electrochemical and thermal properties of the blue TADF emitters

| | Op.Bg (eV) | HOMO (eV) | LUMO (eV) | T _d (°C) | T _g (°C) |
|--------------|------------|-----------|-----------|---------------------|---------------------|
| DOB-1 | 2.93 | -5.80 | -2.87 | 444 | - |
| DOB-2 | 2.82 | -5.66 | -2.84 | 483 | 231 |
| DOB-3 | 2.75 | -5.48 | -2.85 | 551 | 240 |

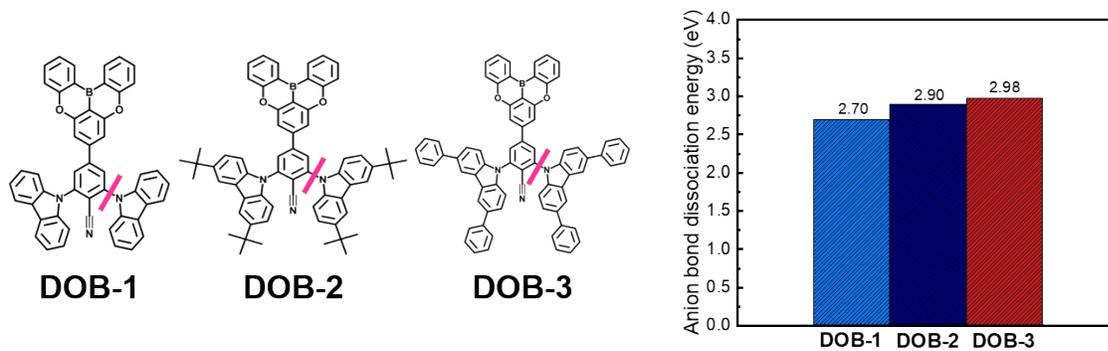


Figure S3. Anion BDE calculations for DOB1, DOB-2, and DOB-3.

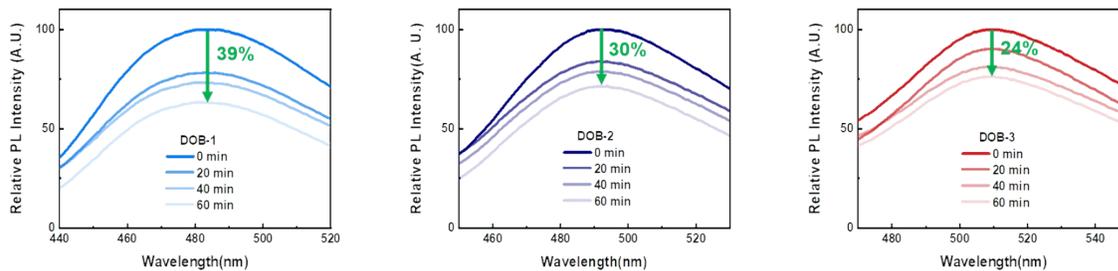


Figure S4. PL intensity variation of DOB-1, DOB-2, and DOB-3 after various UV exposure times.

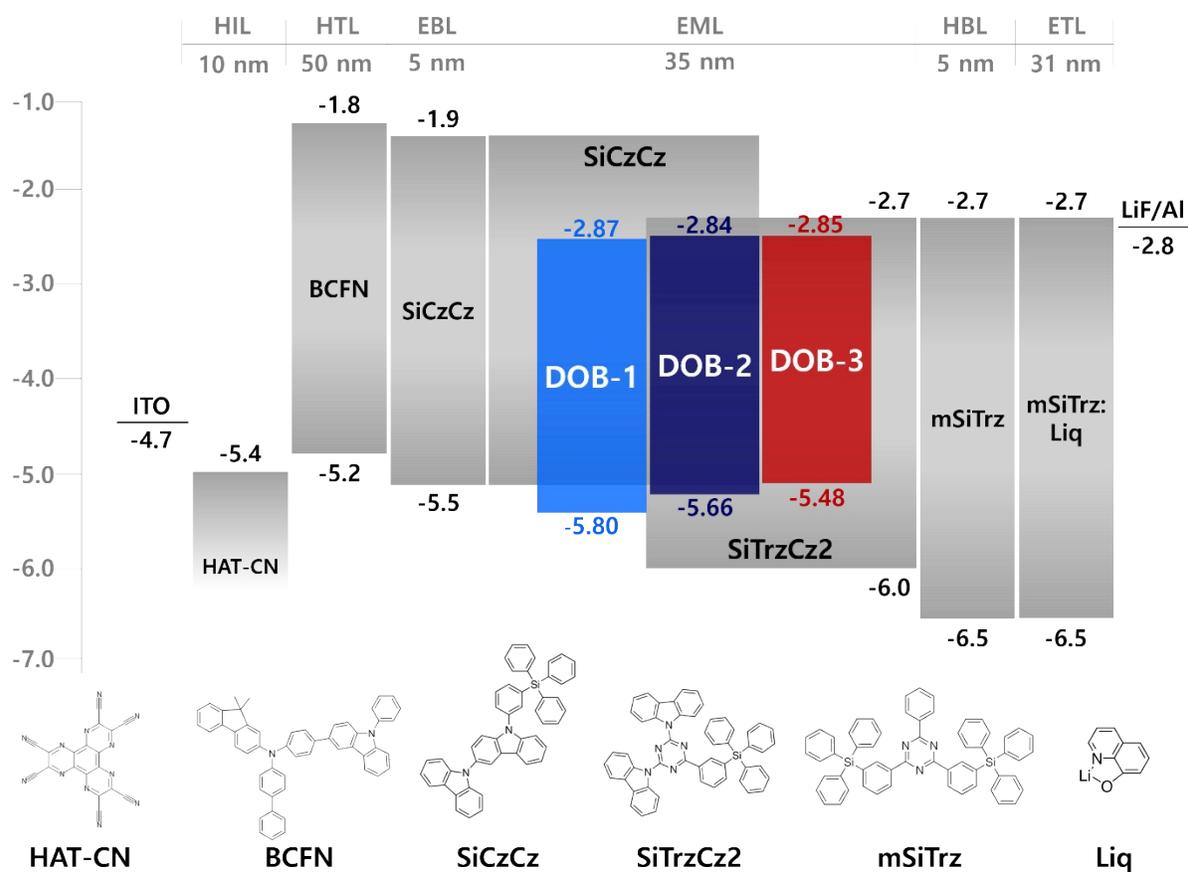


Figure S5. Energy-level diagram along with the thickness of each layer in the TADF OLEDs.

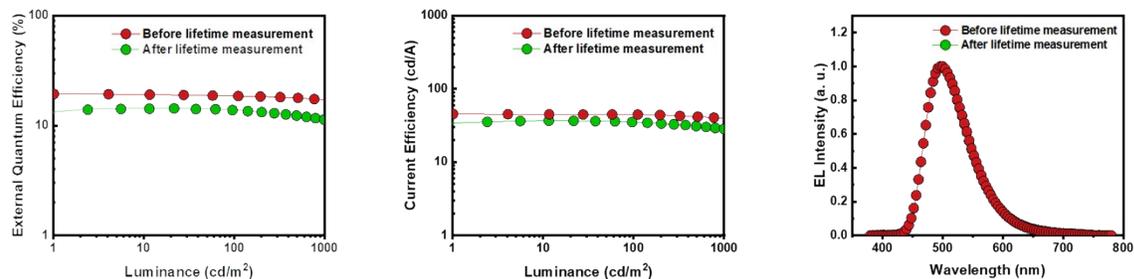
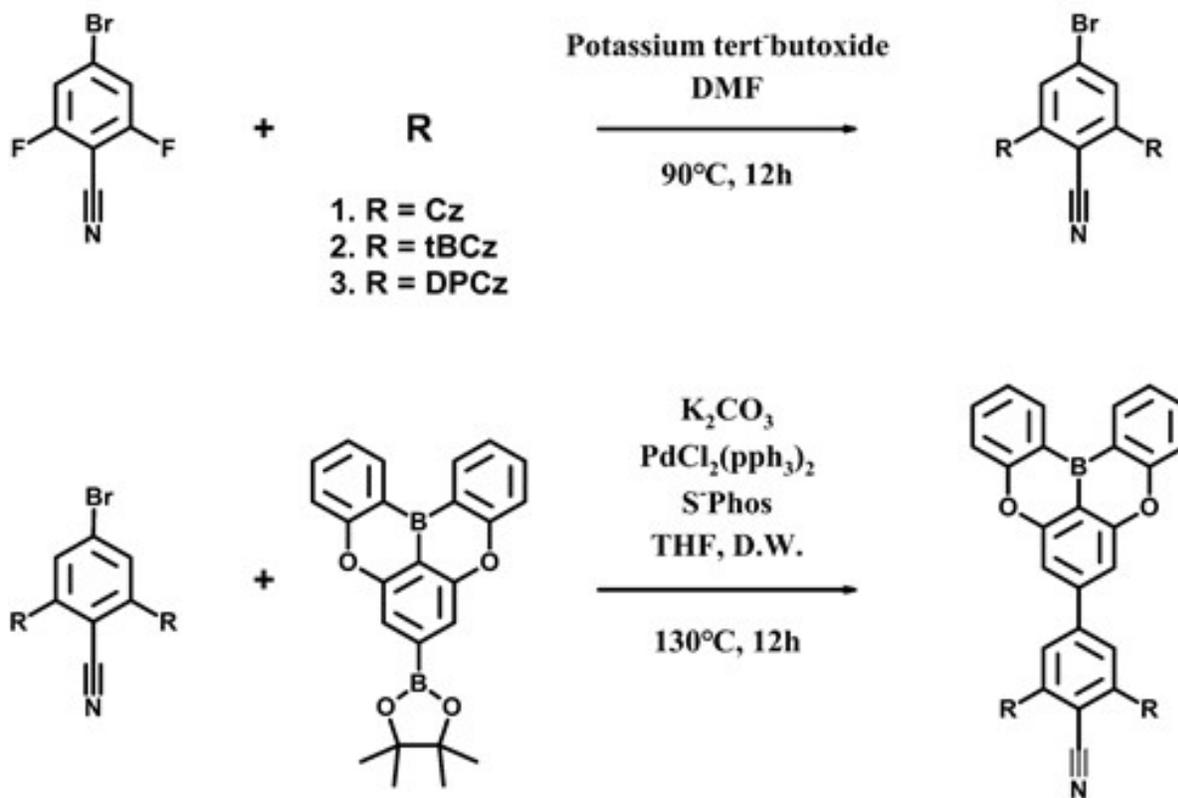


Figure S6. EQE and current efficiency versus luminance and EL spectra of the DOB-3 device. Before (red) and after lifetime measurement (green).

Synthesis

The reaction formula for synthesizing the three types of blue TADF emitters is shown in Scheme S1. The synthesis was carried out through a nucleophilic substitution reaction¹ and a Suzuki–Miyaura coupling reaction,² and during the reaction process, Cs₂CO₃ and K₂CO₃ were used as bases, PdCl₂(PPh₃)₂ as a catalyst, and S-Phos as a ligand. The reaction was conducted in a nitrogen atmosphere and stirred under reflux for up to 8 h. The obtained compound was finally purified to at least 99.90% through sublimation purification two or more times. The structural analysis data of ¹H-NMR and GC-mass of the synthesized reaction intermediate and three types of emitter materials are shown in Figs. S7–S23.



Scheme S1. Synthetic scheme for the blue TADF emitter materials.

Synthesis of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene (DOB-BE)

DOB-Br (3.0 g, 8.6 mmol), bis(pinacolato) (2.62 g, 10.32 mmol), potassium acetate (2.53 g, 25.79 mmol), (1,1'-bis(diphenylphosphino)ferrocene)palladium(II) dichloride (0.314 g, 0.43 mmol) and 1,4-dioxane (80 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 120 °C for 4 h. After cooling to room temperature, the mixture was worked up using MC and D.W., which was repeated three times. The accumulated organic layer was dried over anhydrous magnesium sulfate. After filtration, the crude mixture was evaporated using a rotary evaporator. The crude residues were separated by

silica column chromatography, and an MC:*n*-hexane (3:7) solvent system was used to achieve the final product as a light green powder.

Yield 3.1 g (91%), ^1H NMR (400 MHz, DMSO) δ 8.49 (d, $J = 7.6$, 1.5 Hz, 2H), 7.62 (t, $J = 9.9$, 6.0, 2.4 Hz, 2H), 7.41 (d, $J = 8.3$, 0.8 Hz, 2H), 7.38–7.31 (m, 4H), 1.36 (s, 12H). m/z 396.05.

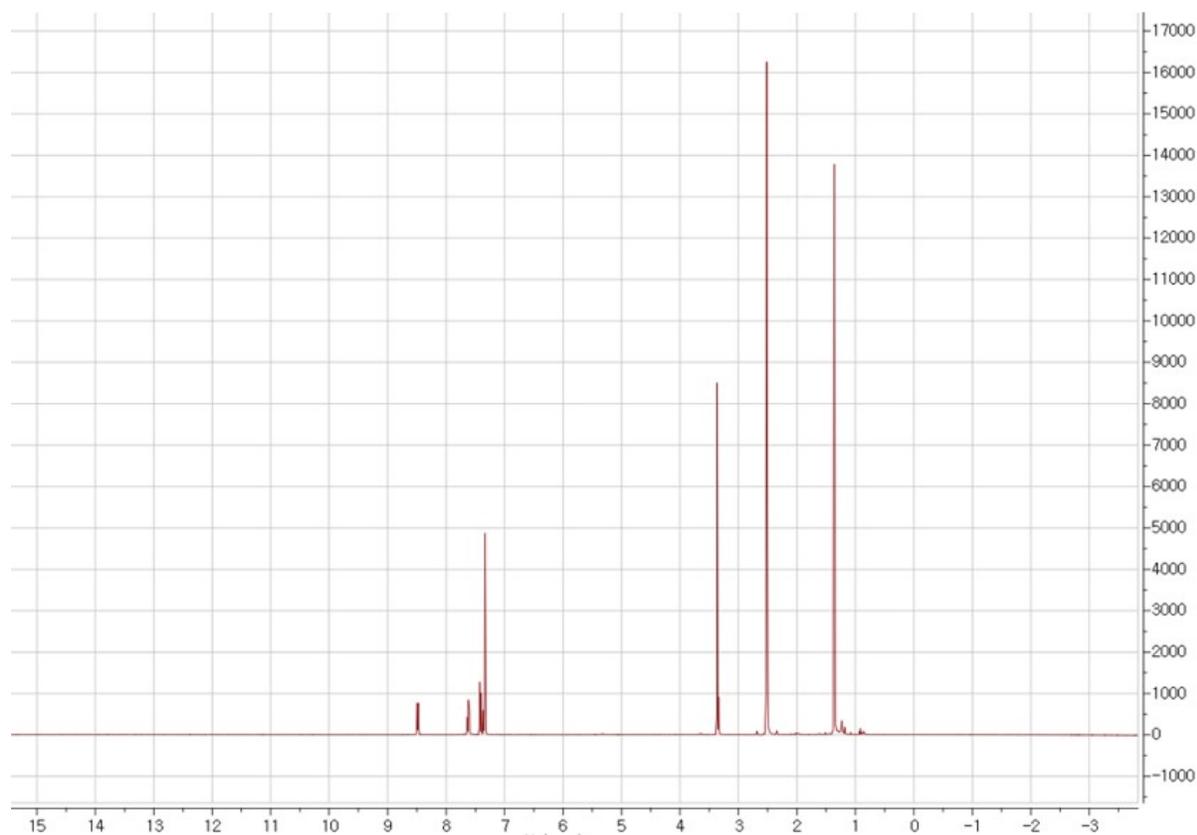


Figure S7. ^1H NMR spectrum of DOB-BE.

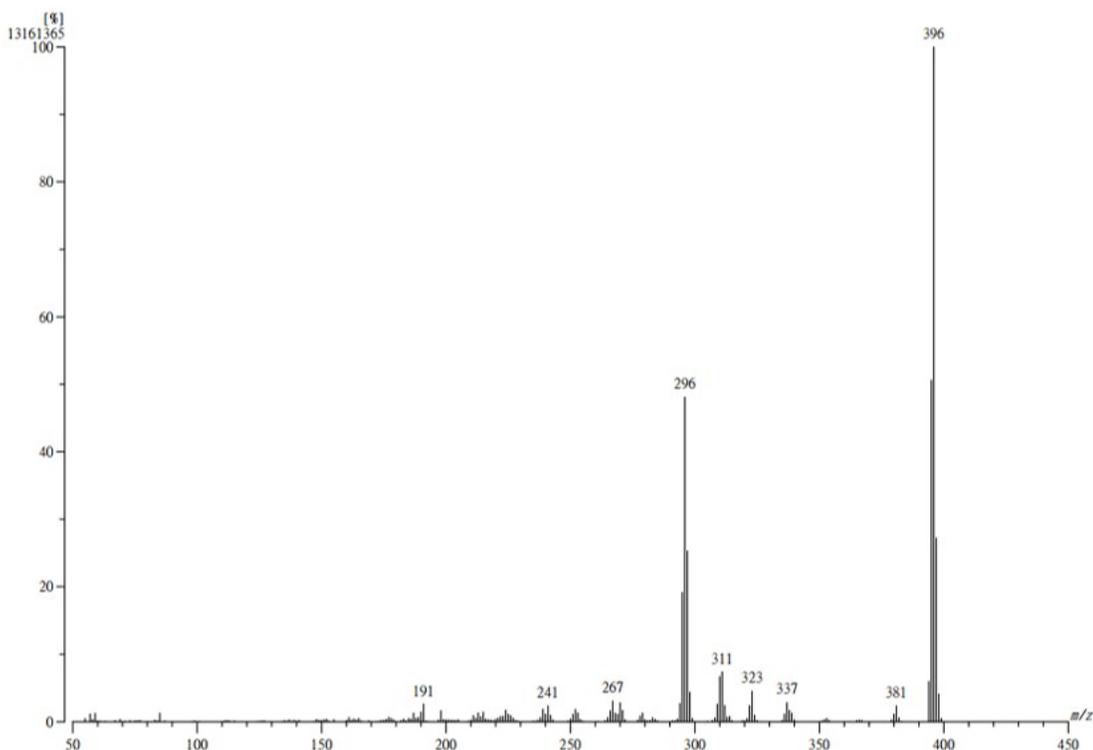


Figure S8. GC-mass spectrum of DOB-BE.

Synthesis of 4-bromo-2,6-di(9H-carbazol-9-yl)benzotrile (BmDCz-Br)

4-Bromo-2,6-difluorobenzotrile (2.20 g, 10.09 mmol), 9H-carbazole (3.54 g, 21.19 mmol), potassium tert-butoxide (2.13 g, 22.20 mmol), and DMF (120 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 90 °C for 12 h. After the reaction completed, 100 mL of water was poured into the mixture to quench the reaction, and after filtration, the crude mixture was evaporated using a rotary evaporator. The crude residues were separated by silica column chromatography, and an MC:*n*-hexane (3:7) solvent system was used to obtain the final product as a white powder.

Yield 3.13 g (44.2%), ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, 4H), 7.96 (s, 2H), 7.55 (t, *J* = 8.8, 4.4 Hz, 4H), 7.44–7.37 (t, 8H). MS (FD) *m/z* 512.4

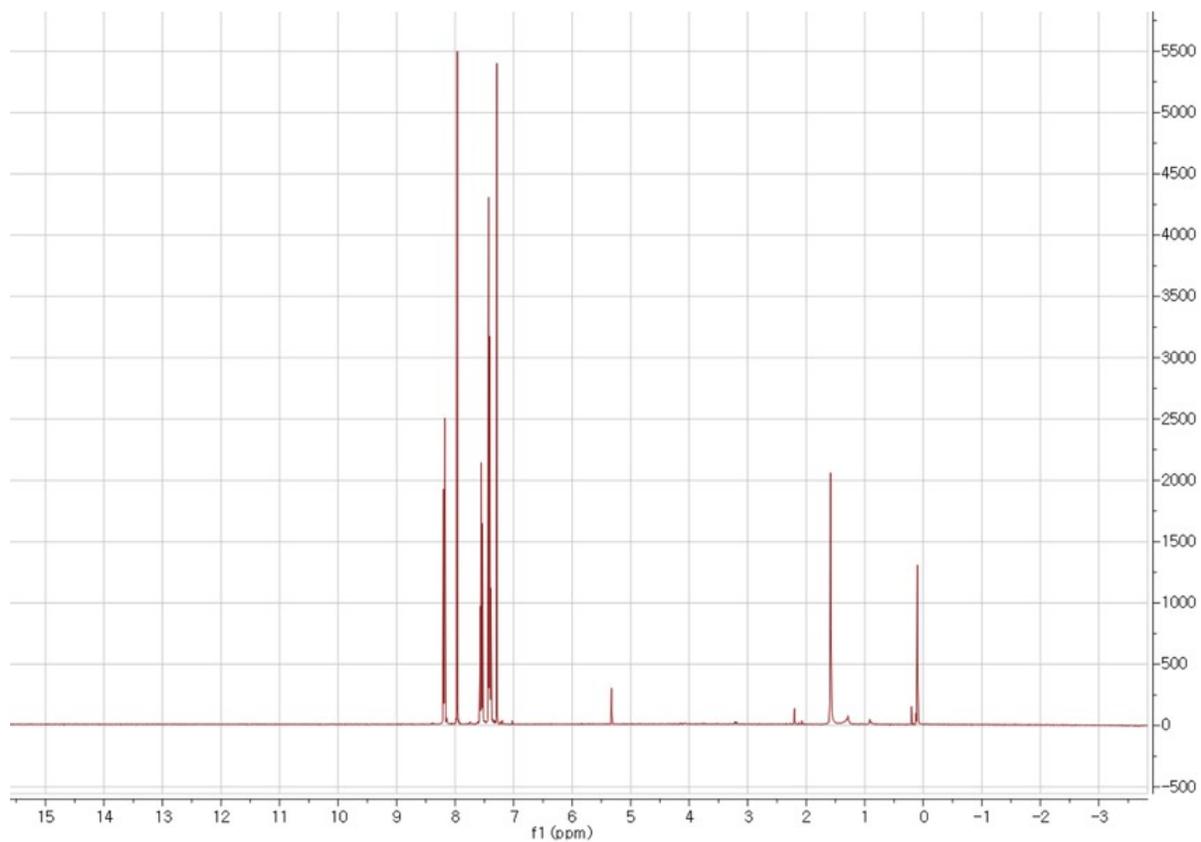


Figure S9. ^1H NMR spectrum of BmDCz-Br.

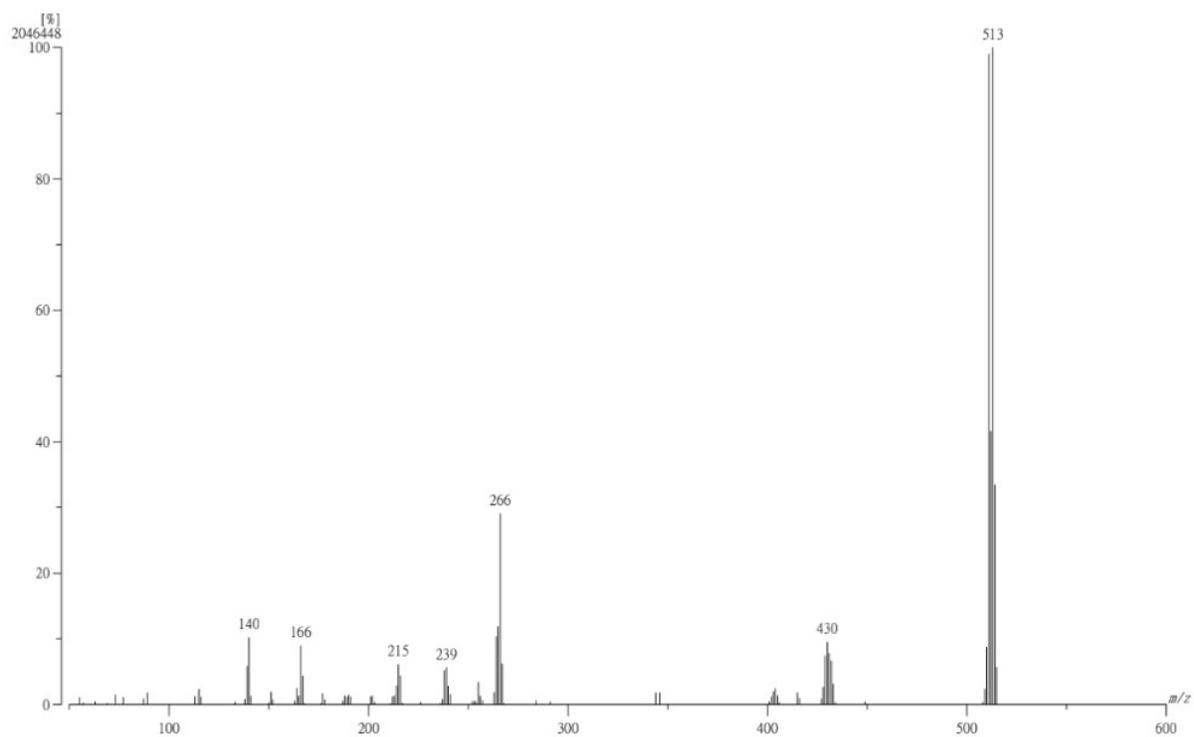


Figure S10. GC-mass spectrum of BmDCz-Br.

Synthesis of 4-bromo-2,6-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)benzotrile (BmDtBCz-Br)

4-Bromo-2,6-difluorobenzotrile (1.80 g, 8.26 mmol), 3,6-di-*tert*-butyl-9H-carbazole (4.84 g, 17.34 mmol), potassium *tert*-butoxide (2.04 g, 18.17 mmol), and DMF (160 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 90 °C for 12 h. After completion of the reaction, 100 mL of water was poured into the mixture to quench the reaction, and after filtration, the crude mixture was evaporated using a rotary evaporator. The crude residues were separated by silica column chromatography, and an MC:n-hexane (5:5) solvent system was used to yield the final product as a yellow powder. The product was washed twice with ethanol.

Yield 3.72 g (61.2%), ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, *J* = 1.5 Hz, 4H), 7.87 (s, 2H), 7.60 (d, *J* = 8.6, 1.9 Hz, 4H), 7.36 (d, *J* = 8.6 Hz, 4H), 1.51 (s, 36H). MS (FD) *m/z* 736.8

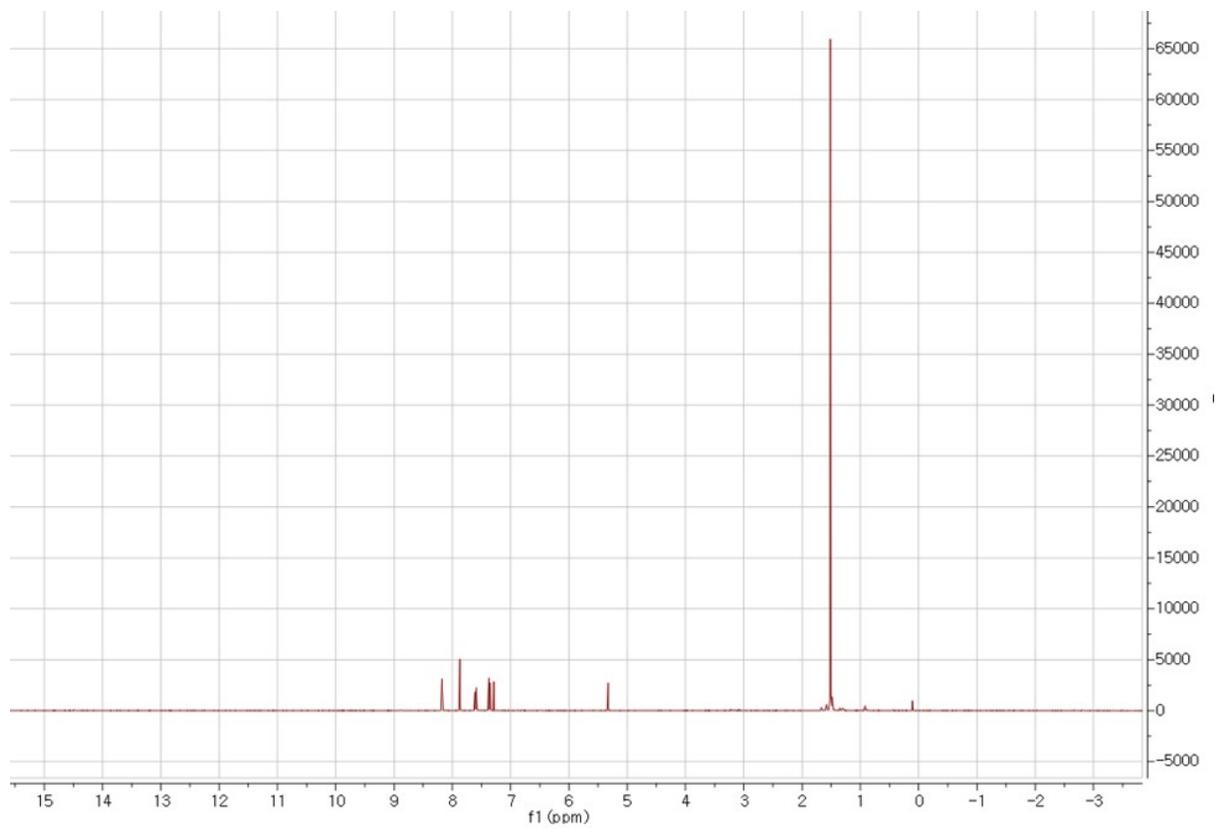


Figure S11. ^1H NMR spectrum of BmDtBCz-Br.

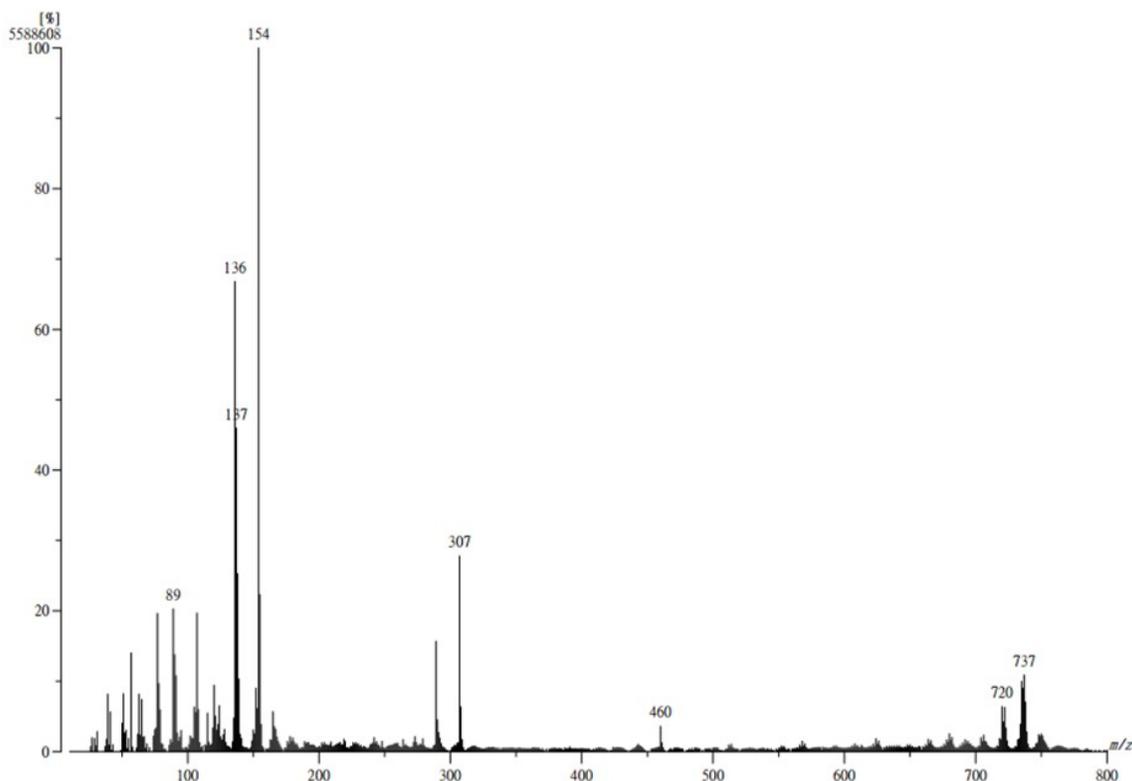


Figure S12. GC-mass spectrum of BmDtBCz-Br.

Synthesis of 4-bromo-2,6-bis(3,6-diphenyl-9H-carbazol-9-yl)benzotrile (BmDDPCz-Br)

4-Bromo-2,6-difluorobenzotrile (1.50 g, 6.88 mmol), 3,6-diphenyl-9H-carbazole (4.62 g, 14.45 mmol), potassium tert-butoxide (1.70 g, 15.14 mmol), and DMF (160 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 90 °C for 12 h. After the reaction completed, 100 mL of water was poured into the mixture to quench the reaction; after filtration, the crude mixture was evaporated using a rotary evaporator. The crude residues were separated by silica column chromatography, and an MC:n-hexane (5:5) solvent system was used to achieve the final product as a yellow powder. The product was washed twice with ethanol.

Yield 2.90 g 52.0%), $^1\text{H NMR}$ (400 MHz, CDCl_3) $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 (d, $J = 1.3$ Hz, 4H), 8.02 (s, 2H), 7.83 (dd, $J = 8.5, 1.8$ Hz, 4H), 7.77 – 7.73 (m, 8H), 7.59–7.49 (m, 14H), 7.45–7.37 (m, 4H). MS (FD) m/z 816.8

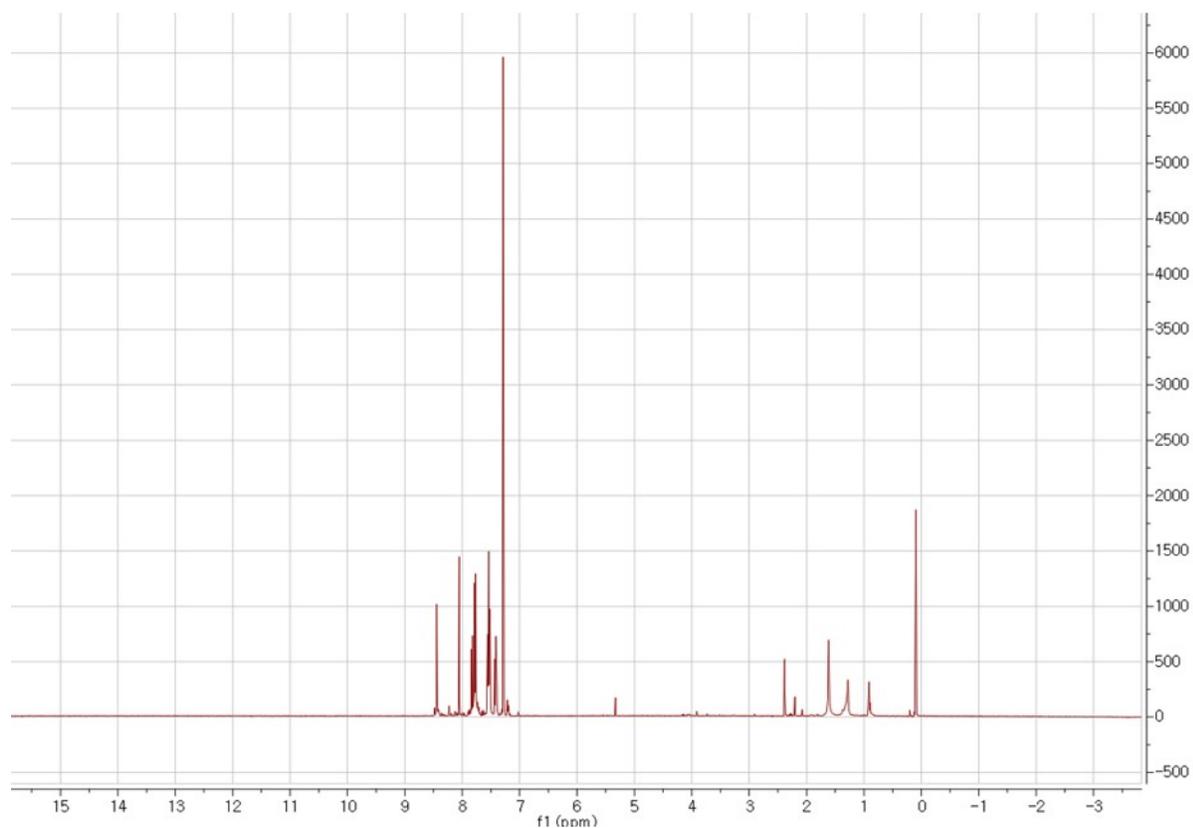


Figure S13. $^1\text{H NMR}$ spectrum of BmDDPCz-Br.

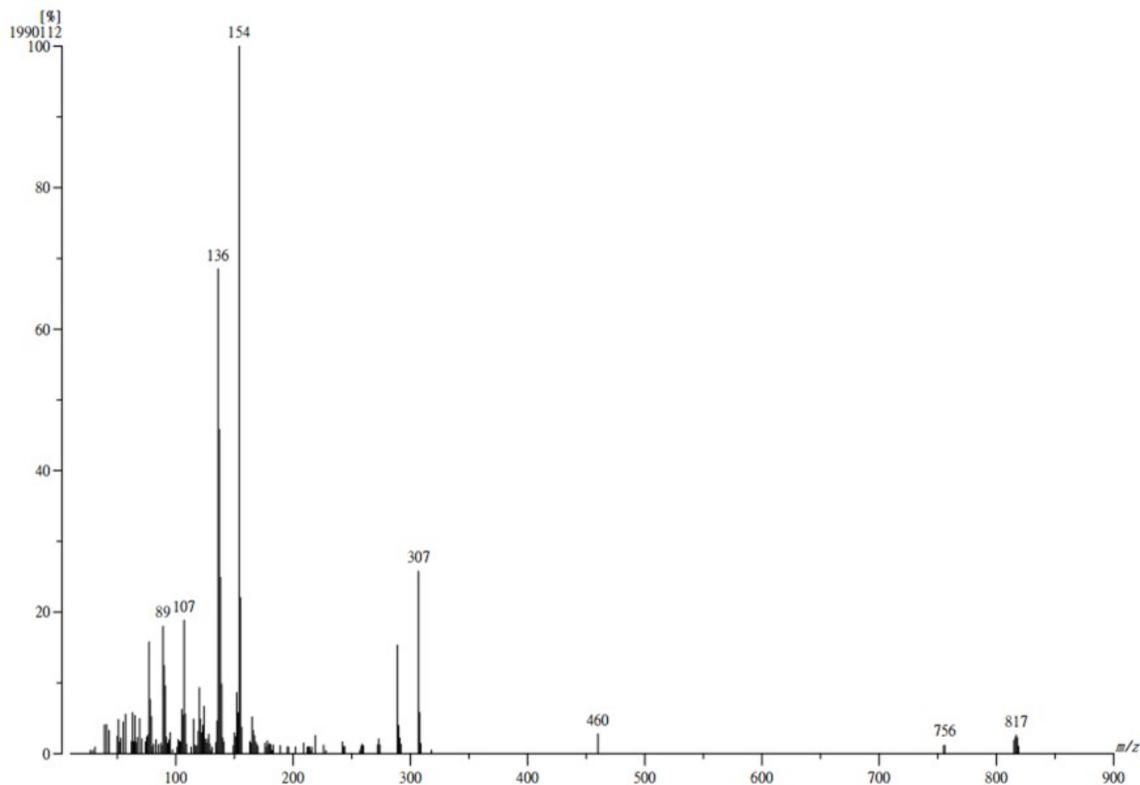


Figure S14. GC-mass spectrum of BmDDPCz-Br.

Synthesis of 4-(5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracen-7-yl)-2,6-bis(9*H*-carbazol-9-yl)benzotrile (DOB-BmDCz, DOB-1)

BmDCz-Br (2.20 g, 4.29 mmol), DOB-BE (1.87 g, 3.14 mmol), PdCl₂(PPh₃)₂ (0.151 g, 0.215 mmol), S-Phos (0.353 g, 0.859 mmol), potassium carbonate (1.484 g, 10.73 mmol), tetrahydrofuran (THF, 60 mL), and deionized water (20 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 130 °C for 12 h. After the completion of the reaction and cooling to room temperature, the mixture was poured into methanol. The product precipitated by methanol was obtained through a filter. After filtration, the crude residues were separated by silica column chromatography, and an MC:n-hexane (3:7) solvent system was used to obtain the final product as a light green powder. The product was washed once with methanol.

Yield 1.77 g (25.4%), ^1H NMR (400 MHz, CDCl_3) δ 8.68 (dd, $J = 7.7, 1.6$ Hz, 2H), 8.20 (dd, $J = 6.9, 0.8$ Hz, 4H), 8.16 (s, 2H), 7.71 (ddd, $J = 8.6, 7.1, 1.7$ Hz, 1H), 7.59–7.47 (m, 12H), 7.43–7.36 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.53(s), 158.05(s), 147.61(s), 143.26–143.19(m), 140.63(s), 134.64(s), 134.09(s), 127.54(s), 126.60(s), 124.27(s), 123.28(s), 121.31(s), 120.87(s), 118.55(s), 109.82(s), 107.25(s). HRMS (FD) m/z 702.2347, Anal. Calcd for $\text{C}_{49}\text{H}_{28}\text{BN}_3\text{O}_2$: C 83.74 H 3.96 N 5.91 O 3.38.

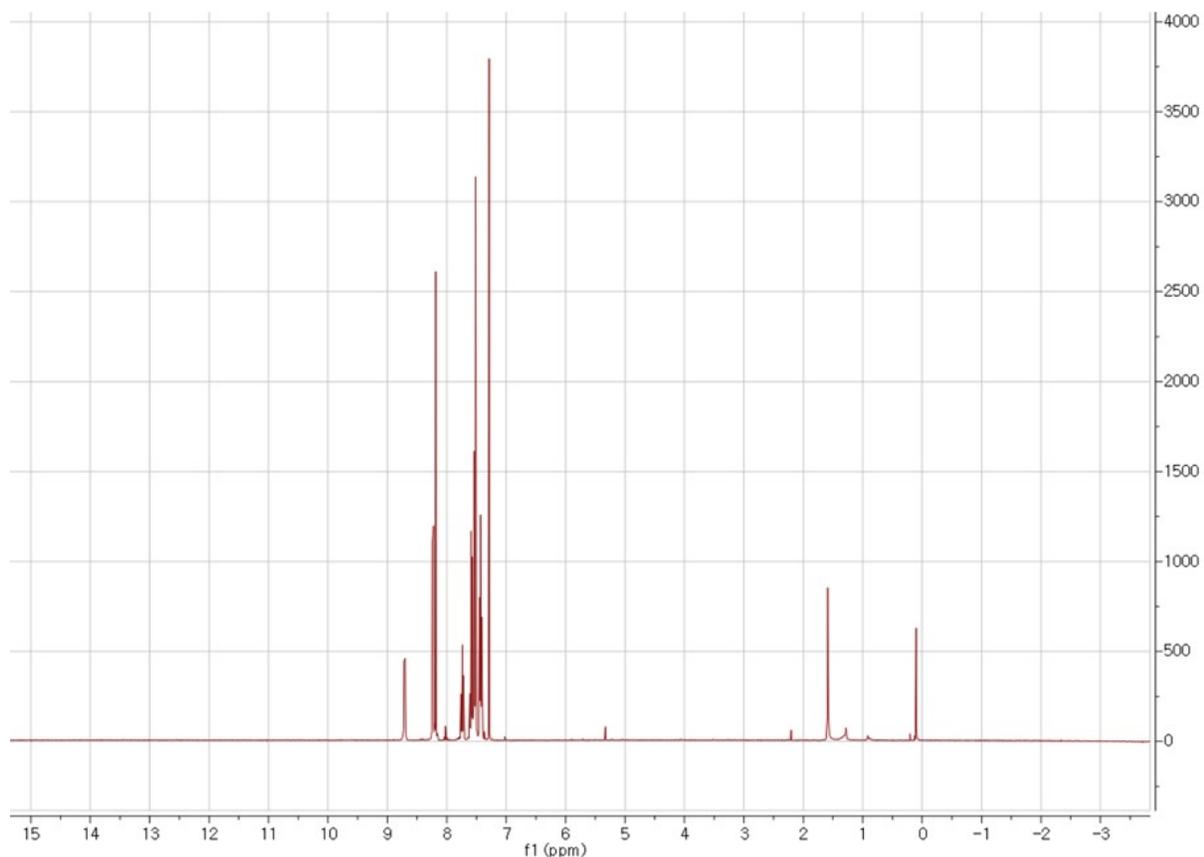


Figure S15. ^1H NMR spectrum of DOB-1.

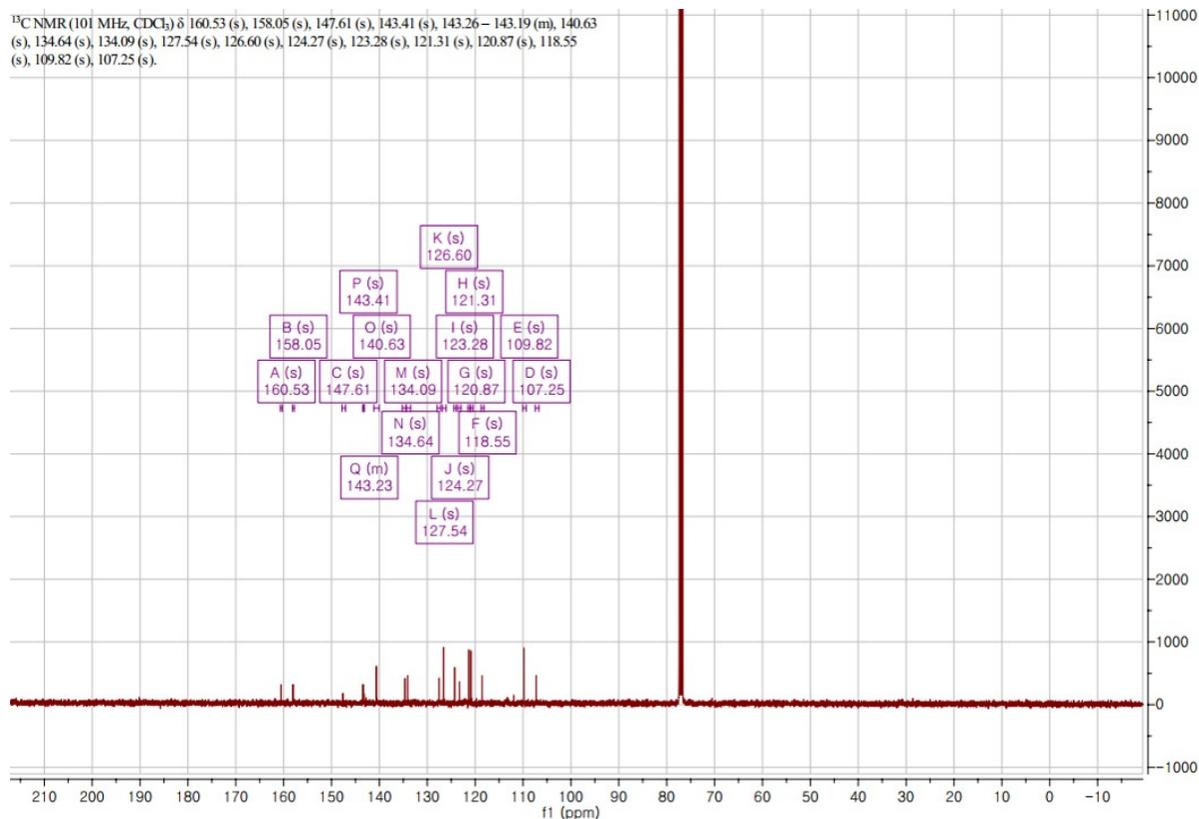


Figure S16. ¹³C NMR spectrum of DOB-1.

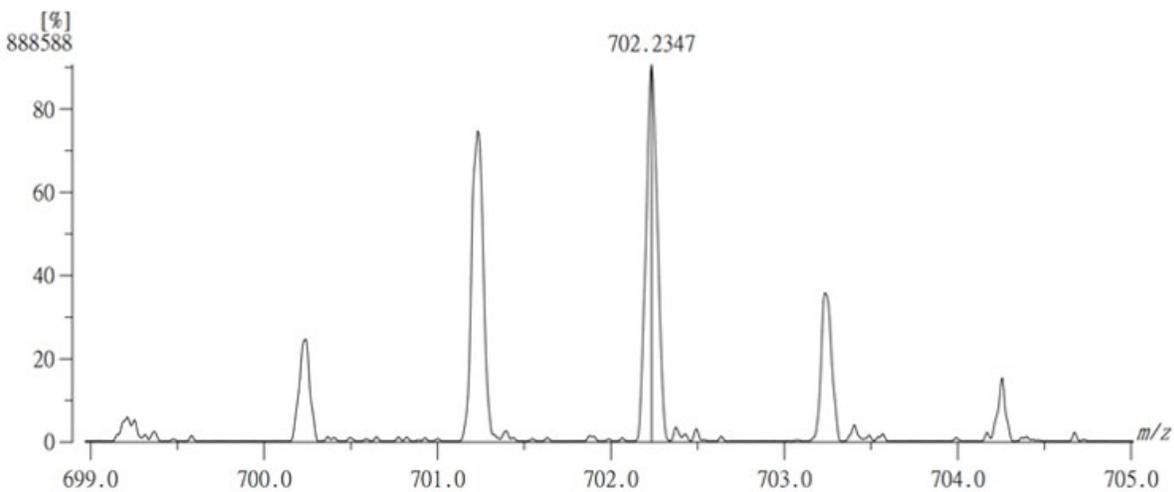


Figure S17. GC-HRMS spectrum of DOB-1.

Synthesis of 4-(5,9-dioxa-13b-boranaphtho[3,2,1-*de*]anthracen-7-yl)-2,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzotrile (DOB-BmDtBCz, DOB-2)

BmDtBCz-Br (2.10 g, 2.85 mmol), DOB-BE (1.24 g, 3.14 mmol), PdCl₂(PPh₃)₂ (0.10 g, 0.143 mmol), S-Phos (0.234 g, 0.570 mmol), potassium carbonate (0.985 g, 7.13 mmol), THF (30 mL), and D.W. (10 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 130 °C for 12 h. After the completion of the reaction and cooling to room temperature, the mixture was poured into methanol. The product precipitated by methanol was obtained through a filter. After filtration, the crude residues were separated by silica column chromatography, and an MC:n-hexane (5:5) solvent system was used to yield the final product as a light green powder. The product was washed once with methanol.

Yield 1.23 g (47%), ¹H NMR (400 MHz, CDCl₃) δ 8.72 (dd, *J* = 7.7, 1.6 Hz, 2H), 8.22 (s, *J* = 1.5 Hz, 4H), 8.11 (s, 2H), 7.75 (t, *J* = 8.6, 7.1, 1.7 Hz, 2H), 7.63 (d, *J* = 8.6, 1.9 Hz, 4H), 7.56 (d, *J* = 2.9, 1.4 Hz, 4H), 7.47 (s, 2H), 7.44 (d, *J* = 8.6 Hz, 4H), 7.40 (dd, *J* = 10.9, 3.9 Hz, 2H), 1.50 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 160.56(s), 157.99(s), 144.17(s), 143.89(s), 143.62(s), 139.12(s), 134.64(s), 134.05(s), 126.78–126.63(m), 124.27(d, *J* = 13.2 Hz), 123.23(s), 118.56(s), 116.85(s), 109.34(s), 107.27(s), 34.89(s), 32.04(s). HRMS (FD) *m/z* 925.4784, Anal. Calcd for C₆₅H₆₀BN₃O₂: C 83.86 H 6.54 N 4.51 O 2.42.

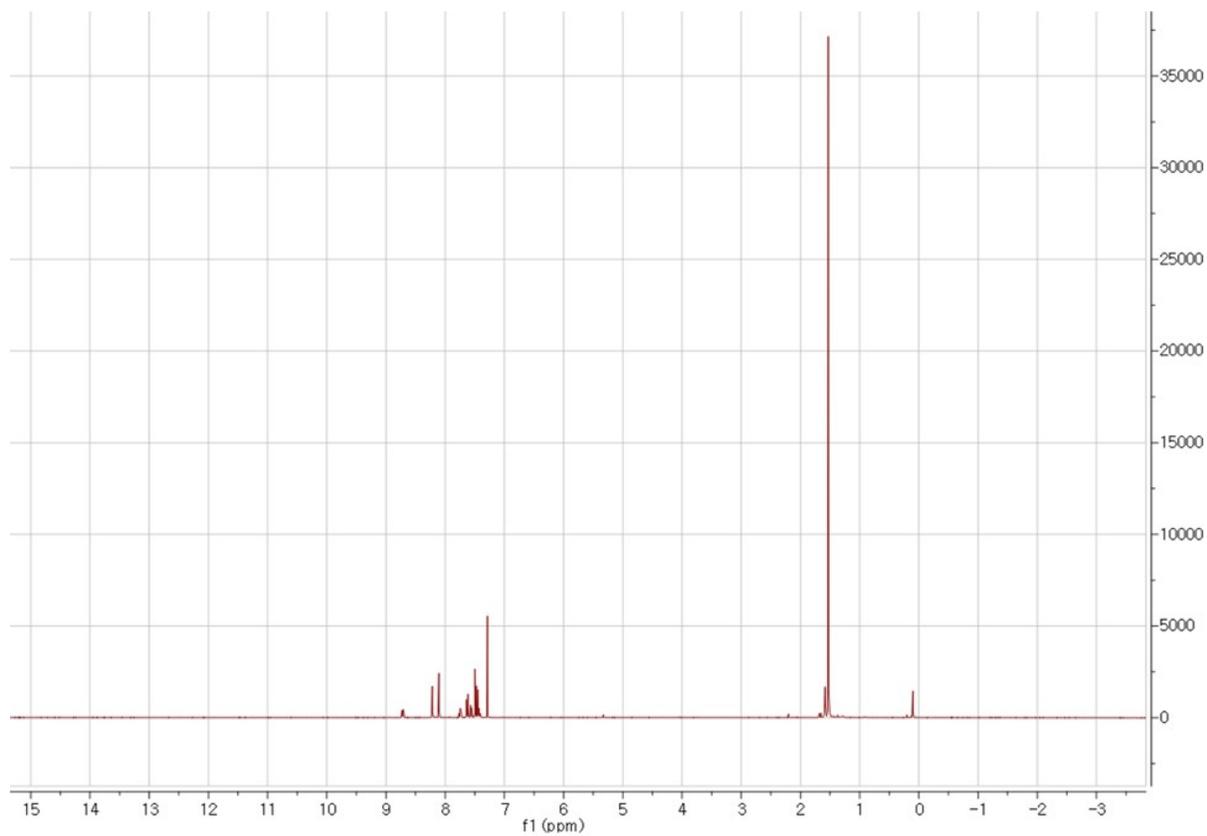


Figure S18. ^1H NMR spectrum of DOB-2.

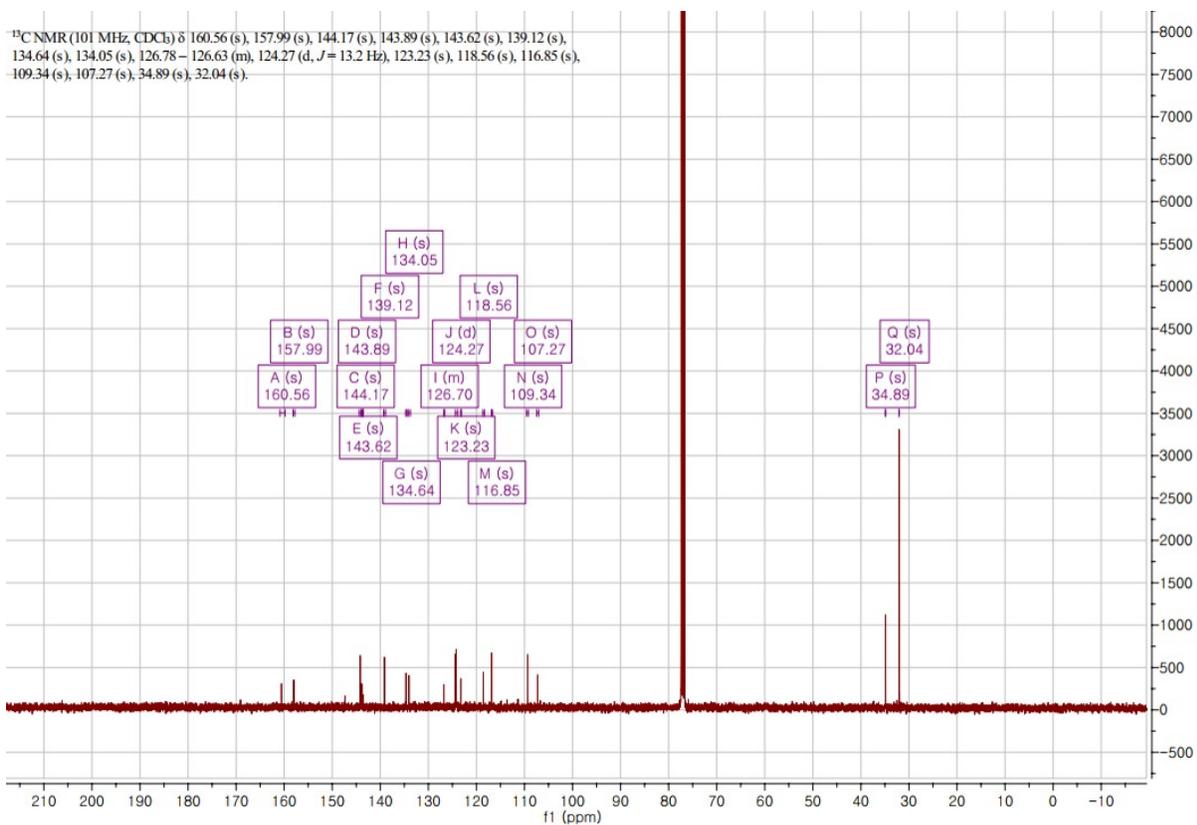


Figure S19. ¹³C NMR spectrum of DOB-2.

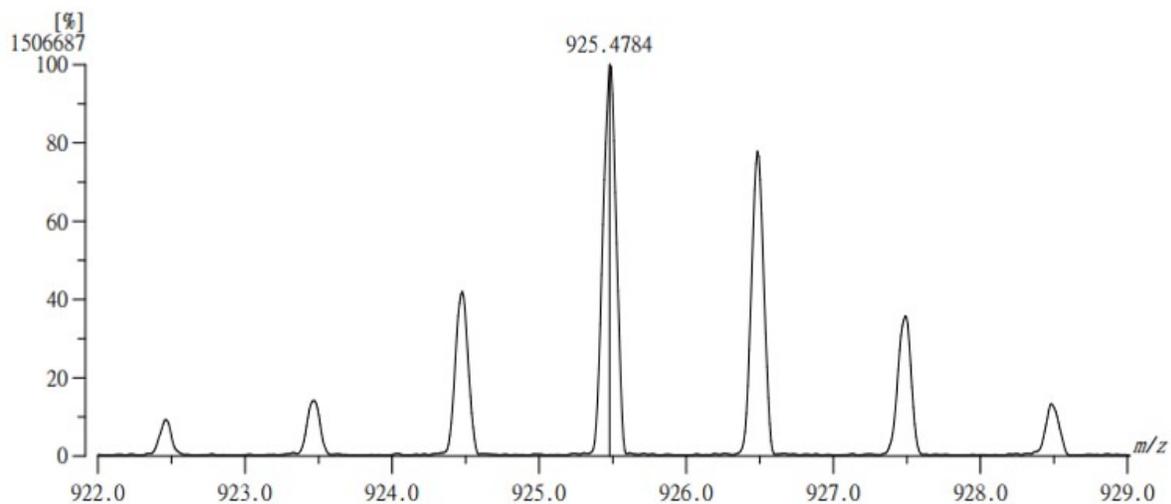


Figure S20. GC-HRMS spectrum of DOB-2.

Synthesis of 4-(5,9-dioxa-13*b*-boranaphtho[3,2,1-*de*]anthracen-7-yl)-2,6-bis(3,6-diphenyl-9*H*-carbazol-9-yl)benzotrile (DOB-BmDDPCz, DOB-3)

BmDDPCz-Br (2.7 g, 3.31 mmol), DOB-BE (1.44 g, 3.64 mmol), PdCl₂(PPh₃)₂ (0.116 g, 0.165 mmol), S-Phos (0.271 g, 0.661 mmol), potassium carbonate (0.822 g, 5.95 mmol), THF (45 mL), and D.W. (15 mL) were added to a 250 mL round-bottom flask equipped with a condenser and stirrer. The reaction mixture was heated to 130 °C for 12 h. After the completion of the reaction and cooling to room temperature, the mixture was poured into methanol. The product precipitated by methanol was obtained through a filter. After filtration, the crude residues were separated by silica column chromatography, and an MC:n-hexane (4:6) solvent system was used to achieve the final product as a yellow powder. The product was washed once with methanol.

Yield 1.3 g (39%), ¹H NMR (400 MHz, CDCl₃) δ 8.70 (dd, *J* = 7.6, 1.6 Hz, 2H), 8.45 (dd, *J* = 8.5, 1.3 Hz, 4H), 8.26 (s, 1H), 8.10 (s, 1H), 7.86–7.81 (m, 4H), 7.80–7.70 (m, 10H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 4.9 Hz, 2H), 7.53–7.48 (m, 10H), 7.44–7.34 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 143.45–143.27(m), 141.61(s), 140.52(s), 135.13(s), 134.17–134.07(m), 128.90(s), 127.48(s), 126.93(s), 126.37(s), 124.97(s), 123.41–123.20(m), 119.54–119.36(m), 118.64–118.34(m), 110.30–110.16(m). HRMS (FD) *m/z* 1006.3602, Anal. Calcd for C₇₃H₄₄BN₃O₂: C 86.86 H 4.39 N 4.16 O 2.20

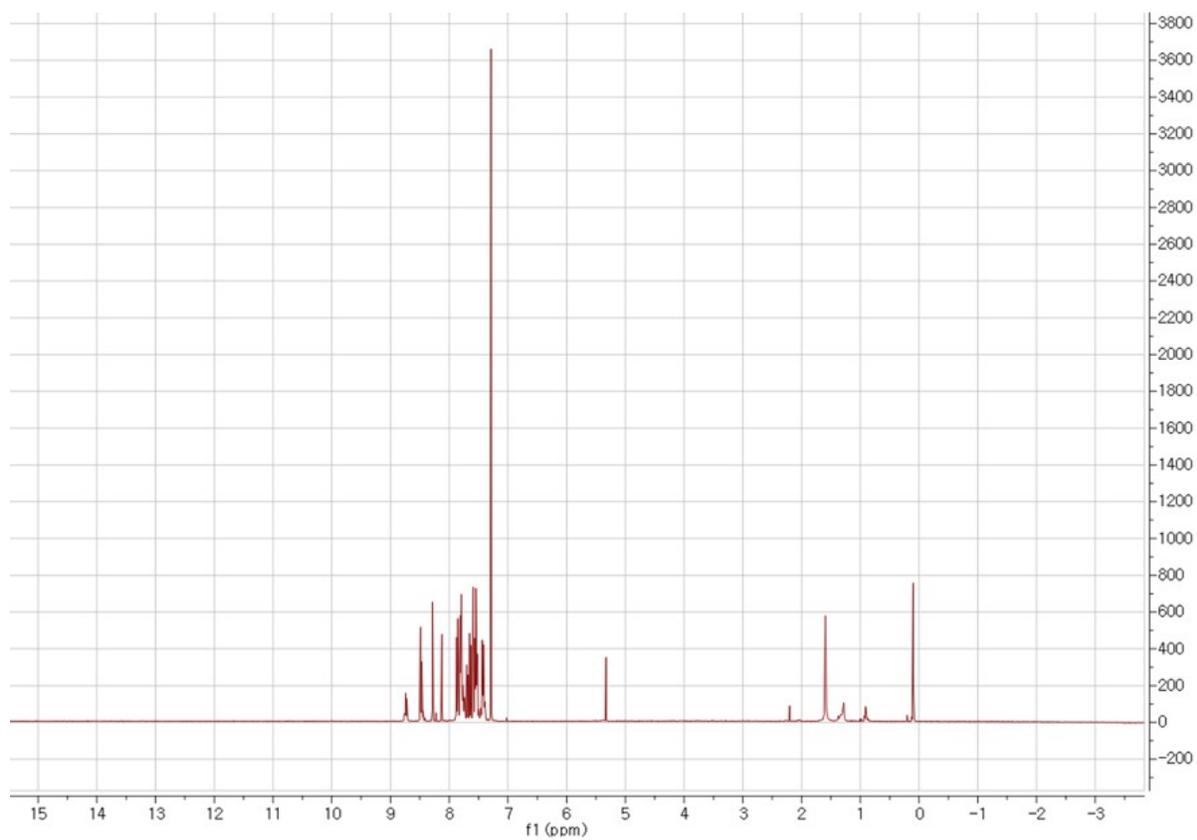


Figure S21. ^1H NMR spectrum of DOB-3.

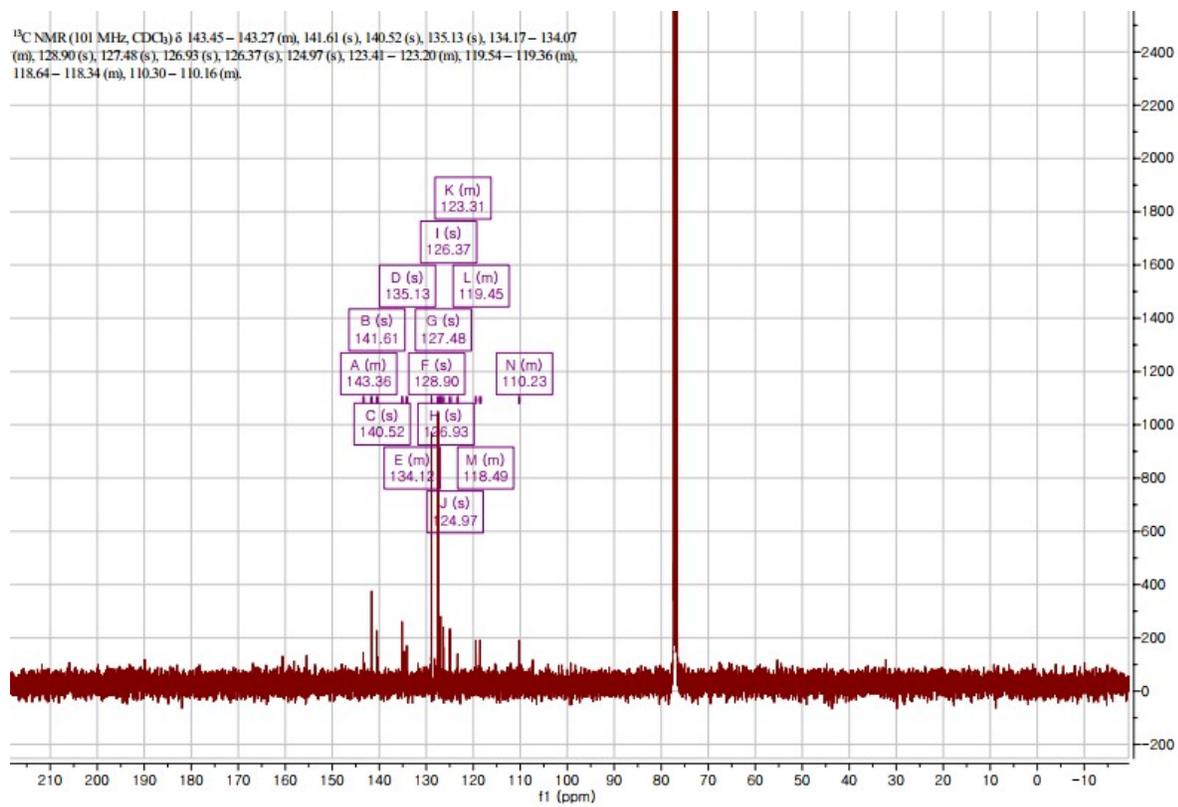


Figure S22. ¹³C NMR spectrum of DOB-3.

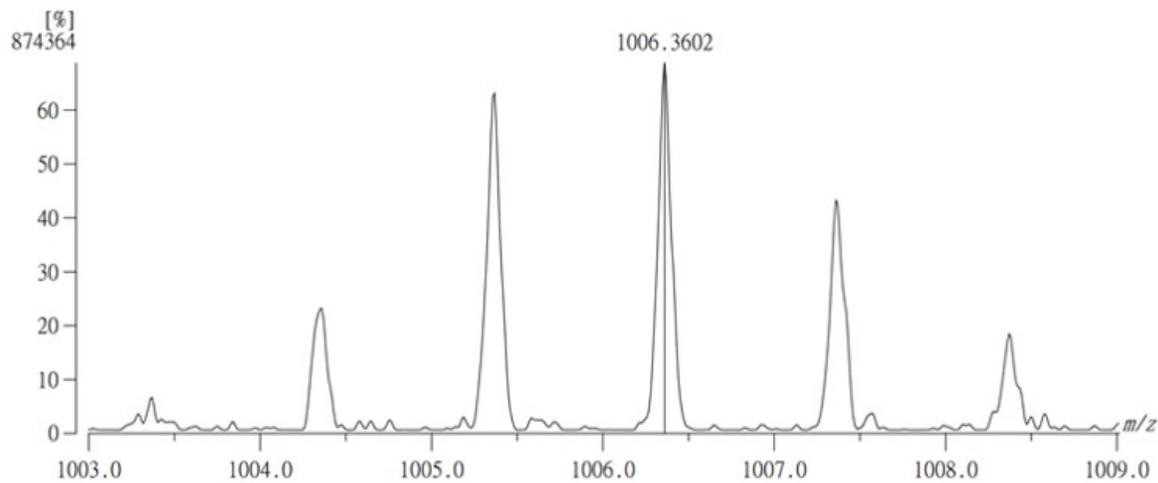


Figure S23. GC-HRMS spectrum of DOB-3.

REFERENCES

- (1) R. A. Rossi, A. B. Pierini and A. B. Peñeñory, *Chem. Rev.*, 2003, **103**, 71.

(2) A. Suzuki, *Chem. Commun.* 2005, 4759–4763.