Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


**Supporting Information**
**for**

# Fused-ring molecules based on B←N and imide units with low energy levels

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## *Contents*

## 1. Experimental details

**General.** $^{1}H$ and $^{13}C$ NMR spectra were measured with a Bruker AV-400 (500 MHz for $^{1}H$ and 126 MHz for $^{13}C$) spectrometer in *d*-DMSO and $CDCl_3$ at 25 °C. Chemical shifts are reported in $\delta$ ppm using *d*-DMSO (2.50 ppm) and $CHCl_3$ (7.26 ppm) for $^{1}H$ NMR, as well as using *d*-DMSO (39.52 ppm) and $CDCl_3$ (77.16 ppm) for $^{13}C$ NMR as an internal standard. Elemental analysis was conducted on a VarioEL elemental analyzer. Thermal analysis was performed on a Perkin-Elmer 7 instrument at a heating rate of 10 °C $min^{-1}$ under nitrogen flow. UV/Vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer in spectral grade solvents. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical workstation using $Bu_4NClO_4$ (0.1 M) in dichloromethane as electrolyte solution at a scan rate of 50 mV $s^{-1}$. The CV cell has a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The measurement was carried out under an argon atmosphere in $CH_2Cl_2$ (0.4 mM). The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated based on the equations: $E_{HOMO}/E_{LUMO} = -(4.80 + E_{pa}^{ox}/E_{1/2}^{red})$ eV.

**Materials and reagents.** All reactions were performed under an argon atmosphere, unless stated otherwise. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry toluene and $CH_2Cl_2$ were distilled via standard methods.

## 2. Syntheses and characterizations

**2,1,3-Benzothiadiazole-5,6-dicarbonitrile (2)**: Under argon, **1** (2.47 g, 8.4 mmol), CuCN (3.08 g, 34.4 mmol) and CuI (575.9 mg, 3.0 mmol) were placed in a three-necked flask, followed by adding dry N,N-Dimethylformamide (50 mL). The mixture was stirred at 160 °C for the night. Then cooling down, $FeCl_3{\cdot}6H_2O$ (11.4 g), concentrated hydrochloric acid (3 mL) and water (17 mL) were added, and the mixture was stirred at 70 °C for 30 min. After cooling down, the mixture was extracted using 6 M HCl and $CH_2Cl_2$. The combined organic phase was dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography ($CH_2Cl_2$: Petroleum ether = 5:1), and **2** was obtained as a white solid in 48% yield (747 mg).[1] Compound 2 is soluble in polar solvents, such as methylene chloride, but insoluble in non-polar solvents such as petroleum ether. $^{1}H$ NMR (500 MHz, *d*-DMSO, 25 °C): $\delta$ (ppm) 9.19 (s, 2H).

**5*H*-Pyrrolo[3,4-*f*]-2,1,3-benzothiadiazole-5,7(6*H*)-dione (3)**: **2** (600 mg, 3.2 mmol) and concentrated sulfuric acid (25 mL) were placed in a round-bottomed flask. The mixture was stirred at 60 °C for 2h. After cooling down, the mixture was diluted by ice water and filtered. The crude product was obtained as a white solid. The crude product was purified by ultrasonic cleaning with water and methanol in turn. **3** was obtained as a white solid in 61% yield (404 mg).[2] Compound 3 is less soluble than compound 2. $^{1}H$ NMR (500 MHz, *d*-DMSO, 25 °C): $\delta$ (ppm) 11.88 (s, 1H), 8.56 (s, 2H).

**6-butyl-5H-[1,2,5]thiadiazolo[3,4-f]isoindole-5,7(6H)-dione (4)**: **3** (1.0 g, 4.87 mmol) and $K_2CO_3$ (2.02 g, 14.6 mmol) were placed in a three-necked flask under argon, followed by adding bromobutane (734 mg, 5.36 mmol) and dry N,N-Dimethylformamide (120 mL). The mixture was stirred at 90 °C for 20 h. After cooling down, the mixture was extracted using saturated aqueous $NH_4Cl$ solution and $CH_2Cl_2$. The combined organic phase was dried over anhydrous $Na_2SO_4$,

filtered and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography ($CH_2Cl_2$). **4** was obtained as a yellow solid in 85% yield (1.08 g).[1] Compound 4 is highly soluble in dichloromethane due to the increased solubility of alkyl chains, but still insoluble in non-polar solvents such as petroleum ether. $^1$H NMR (500 MHz, $CDCl_3$, 25 $^o$C): δ (ppm) 8.50 (s, 2H), 3.82 – 3.77 (m, 2H), 1.76 – 1.69 (m, 2H), 1.46 – 1.36 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

**5,6-Diamino-2-butyl-1*H*-isoindole-1,3(2*H*)-dione (5)**: Under argon, **4** (518 mg, 1.98 mmol) and iron powder (1.33 g, 23.8 mmol) was placed in a one-necked flask, followed by adding AcOH (50mL). The mixture was stirred at 120 $^o$C for 30min. It was then cooled to room temperature and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (EtOAc). **5** was obtained as a yellow crystalline solid in 54% yield (278 mg).[1] Compound 5 is soluble in common organic solvent. It is also water soluble as it has two hydrophilic amino groups. Water was avoided in the purification process to avoid product loss. $^1$H NMR (500 MHz, *d*-DMSO, 25 $^o$C): δ (ppm) 6.85 (s, 2H), 5.53 (s, 4H), 3.42 (d, J = 7.0 Hz, 2H), 1.48 (p, J = 7.4 Hz, 2H), 1.27 – 1.20 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H).

**Compound 6a**: **5** (200 mg, 0.85 mmol) and 1,6-dibromopyrene tetroxide (163 mg, 0.39 mmol) were placed in a three-necked flask under argon, followed by adding AcOH (40 mL). The mixture was stirred at 120 $^o$C overnight. After removing the solvents in reduced pressure, the crude product was purified by ultrasonic cleaning with water and methanol in turn. **6a** was obtained as a yellow solid in 83% yield (265 mg).

**Compound 6b**: **5** (125 mg, 0.54 mmol) and 1,8-dibromopyrene tetroxide (102 mg, 0.24 mmol) were placed in a three-necked flask under argon, followed by adding AcOH (25 mL). The mixture was stirred at 120 $^o$C overnight. After removing the solvents in reduced pressure, the crude product was purified by ultrasonic cleaning with water and methanol in turn. **6b** was obtained as a yellow solid in 75% yield (150 mg). Compounds 6a and 6b have very poor solubility. They are not soluble in common organic solvent under ambient temperature. They were not characterized by NMR as they are insoluble in common deuterium solvents.

**Compound 7a**: **6a** (265 mg, 0.33 mmol) was placed in a three-necked flask under argon. Then dried toluene (35 mL) and 2-Ethylhexylamine (126 mg, 0.98 mmol) were added. The mixture was stirred at 120 $^o$C for 20 h. After removing the solvents in reduced pressure, the mixture was purified by silica gel column chromatography ($CH_2Cl_2$: hexane = 2.5:1), and **7a** was obtained as a blue solid in 7% yield (21 mg). $^1$H NMR (500 MHz, $CDCl_3$, 25 $^o$C): δ (ppm) 10.85 (s, 2H), 8.01 (d, J = 7.8 Hz, 2H), 7.41 (s, 2H), 6.80 (s, 2H), 6.38 (d, J = 8.9 Hz, 2H), 3.46 (t, J = 7.1 Hz, 4H), 3.05 (d, J = 9.9 Hz, 4H), 1.63 – 1.10 (m, 26H), 1.08 – 1.02 (m, 6H), 0.99 (s, 6H), 0.91 (t, J = 7.4 Hz, 6H).

**Compound 7b**: **6b** (150 mg, 0.18 mmol) was placed in a three-necked flask under argon. Then dried toluene (20 mL) and 2-Ethylhexylamine (71 mg, 0.55 mmol) were added. The mixture was stirred at 120 $^o$C for 20 h. After removing the solvents in reduced pressure, the product was purified by adjusting the polarity of the eluent several times by column chromatography, and **7b** was obtained as a purple solid in 68% yield (115 mg) with a small amount of impurity. We did not further purify it as the impurities would not affect the next-step reaction and can be removed by the chromatography after the reaction. Compounds 7a and 7b are soluble in common organic solvents such as chloroform, toluene and tetrahydrofuran. However, the solubility of compound 7b is obviously better than that of compound 7a. $^1$H NMR (500 MHz, $CDCl_3$, 25 $^o$C): δ (ppm) 11.70

(s, 2H), 8.84 (d, J = 9.1 Hz, 2H), 7.97 (s, 2H), 7.63 (s, 2H), 6.99 (d, J = 5.3 Hz, 2H), 3.72 (t, J = 7.4 Hz, 2H), 3.65 (t, J = 7.4 Hz, 2H), 3.47 (s, 4H), 2.02 – 1.92 (m, 2H), 1.82 – 1.64 (m, 10H), 1.51 (ddd, J = 29.4, 13.6, 7.0 Hz, 14H), 1.19 (t, J = 7.3 Hz, 6H), 1.01 (d, J = 7.6 Hz, 12H).

**c-BNI**: Under argon, $BF_3{\cdot}Et_2O$ solution (0.52 mL, 1.87 mmol) was added to a solution of **7a** (21 mg, 0.023 mmol) and $Et_3N$ (0.13 mL) in dry toluene (10 mL). The mixture was stirred at 120 °C overnight. After removing the solvents in reduced pressure, the solid was dispersed into methanol, followed by filtration. The mixture was purified by silica gel column chromatography ($CH_2Cl_2$: hexane = 2:1), **c-BNI** was obtained as a green solid in 36% yield (8.4 mg). **$^1$H NMR (500 MHz, $CDCl_3$, 25 °C)**: δ (ppm) 9.39 (s, 2H), 9.13 (d, J = 9.5 Hz, 2H), 8.11 (s, 2H), 7.49 (d, J = 9.6 Hz, 2H), 3.92 (d, J = 7.2 Hz, 4H), 3.85 (t, J = 7.4 Hz, 4H), 2.10 – 2.00 (m, 2H), 1.80 (p, J = 7.6 Hz, 4H), 1.58 – 1.41 (m, 13H), 1.39-1.28 (m, 7H), 1.03 (d, J = 14.8 Hz, 6H), 0.97 (td, J = 7.4, 3.8 Hz, 6H), 0.91 (td, J = 7.1, 3.5 Hz, 6H). **$^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C)**: δ (ppm) 166.43, 166.31, 152.78, 145.47, 143.82, 135.10, 133.39, 132.06, 131.00, 130.12, 124.51, 119.80, 116.70, 115.82, 103.84, 77.22, 49.46, 38.75, 38.10, 30.91, 30.88, 30.49, 28.82, 24.11, 23.13, 20.24, 14.13, 13.71, 10.79. **Anal. Calcd for $C_{56}H_{60}B_2F_4N_8O_4$:** C, 66.81; H, 6.01; B, 2.15; F, 7.55; N, 11.13; O, 6.36. Found: C, 66.74; H, 6.11; B, 2.14; F, 7.24; N, 11.52; O, 6.21.

**a-BNI**: Under argon, $BF_3{\cdot}Et_2O$ solution (0.64 mL, 2.30 mmol) was added to a solution of **7b** (51 mg, 0.026 mmol) and $Et_3N$ (0.16 mL) in dry toluene (20 mL). The mixture was stirred at 120 °C overnight. After removing the solvents in reduced pressure, the solid was dispersed into methanol, followed by filtration. The mixture was purified by silica gel column chromatography ($CH_2Cl_2$: hexane = 2:1), **a-BNI** was obtained as a green solid in 82% yield (43 mg). **$^1$H NMR (500 MHz, $CDCl_3$, 25 °C):** δ (ppm) 9.64 (d, J = 9.6 Hz, 2H), 9.18 (s, 2H), 8.63 (s, 2H), 7.67 (d, J = 9.7 Hz, 2H), 3.96 (d, J = 7.2 Hz, 4H), 3.85 (t, J = 7.4 Hz, 2H), 3.80 (t, J = 7.4 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.82 – 1.77 (m, 2H), 1.76 – 1.69 (m, 2H), 1.49 (dt, J = 28.2, 7.7 Hz, 13H), 1.33 (d, J = 5.0 Hz, 7H), 1.03 – 0.95 (m, 12H), 0.91 (t, J = 7.0 Hz, 6H).

**Anal. Calcd for $C_{56}H_{60}B_2F_4N_8O_4$:** C, 66.81; H, 6.01; B, 2.15; F, 7.55; N, 11.13; O, 6.36. Found: C, 66.74; H, 6.11; B, 2.14; F, 7.24; N, 11.52; O, 6.21.

**3. NMR spectra of c-BNI and a-BNI**

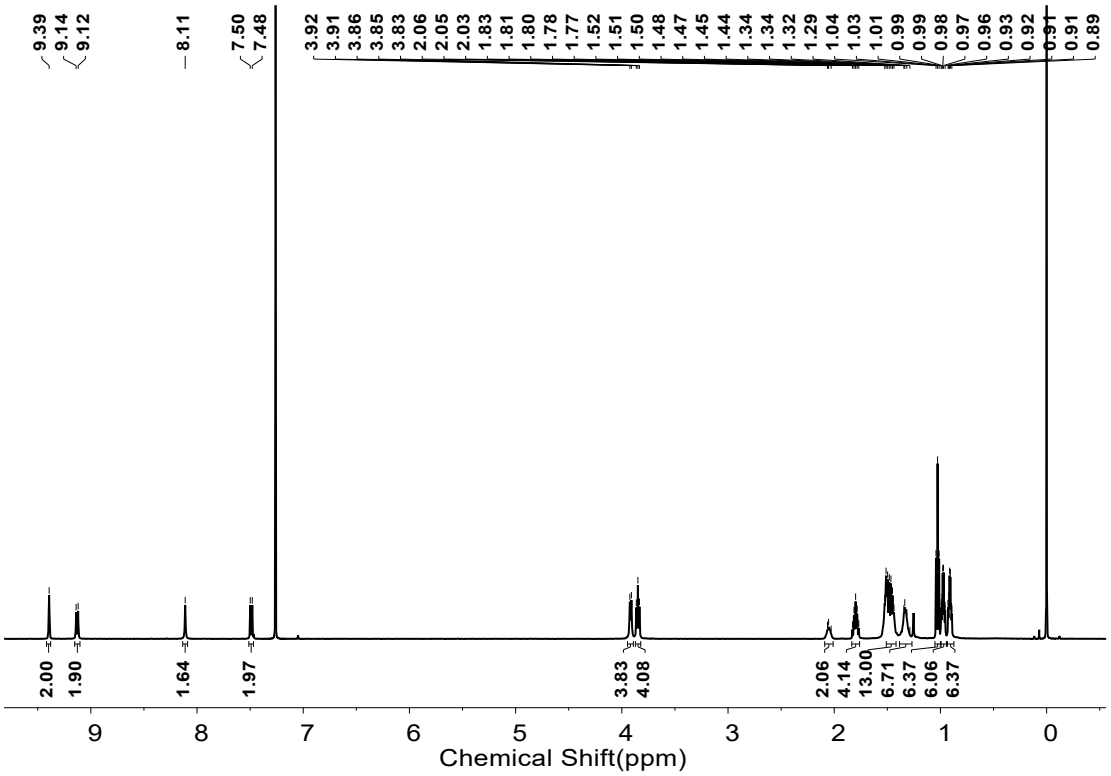



**Figure S1**. $^{1}H$ NMR spectrum of **c-BNI** in $CDCl_3$.

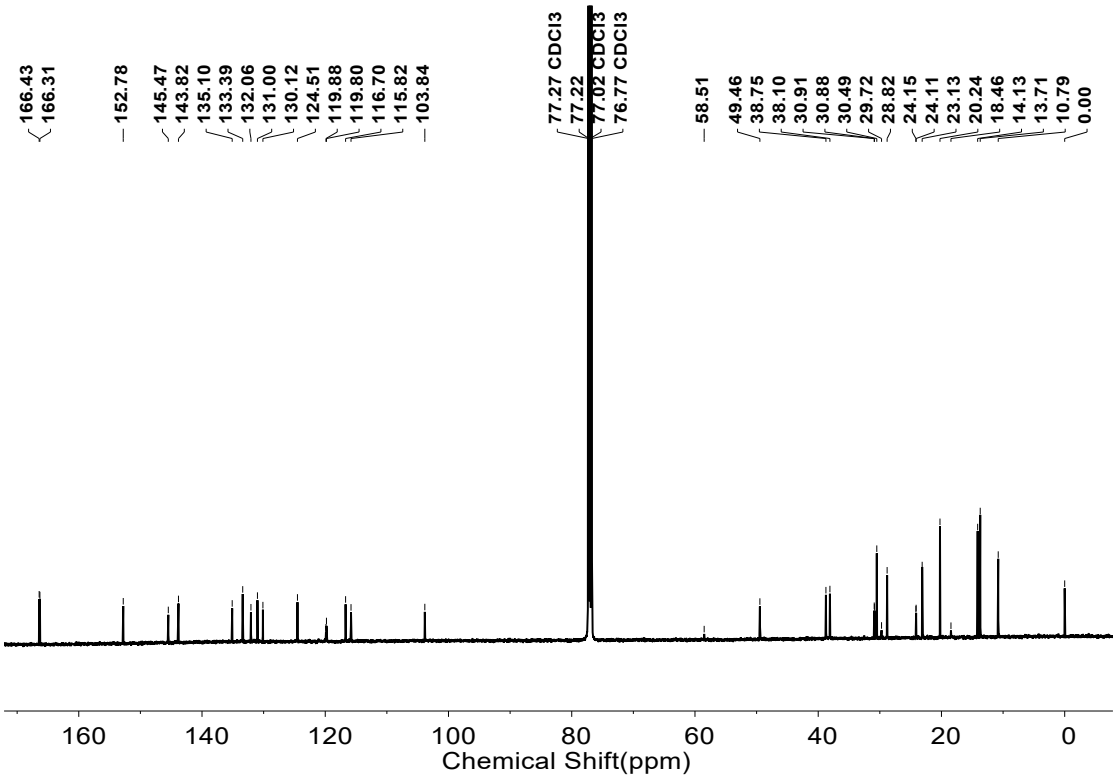



**Figure S2**. $^{13}C$ NMR spectrum of **c-BNI** in $CDCl_3$.

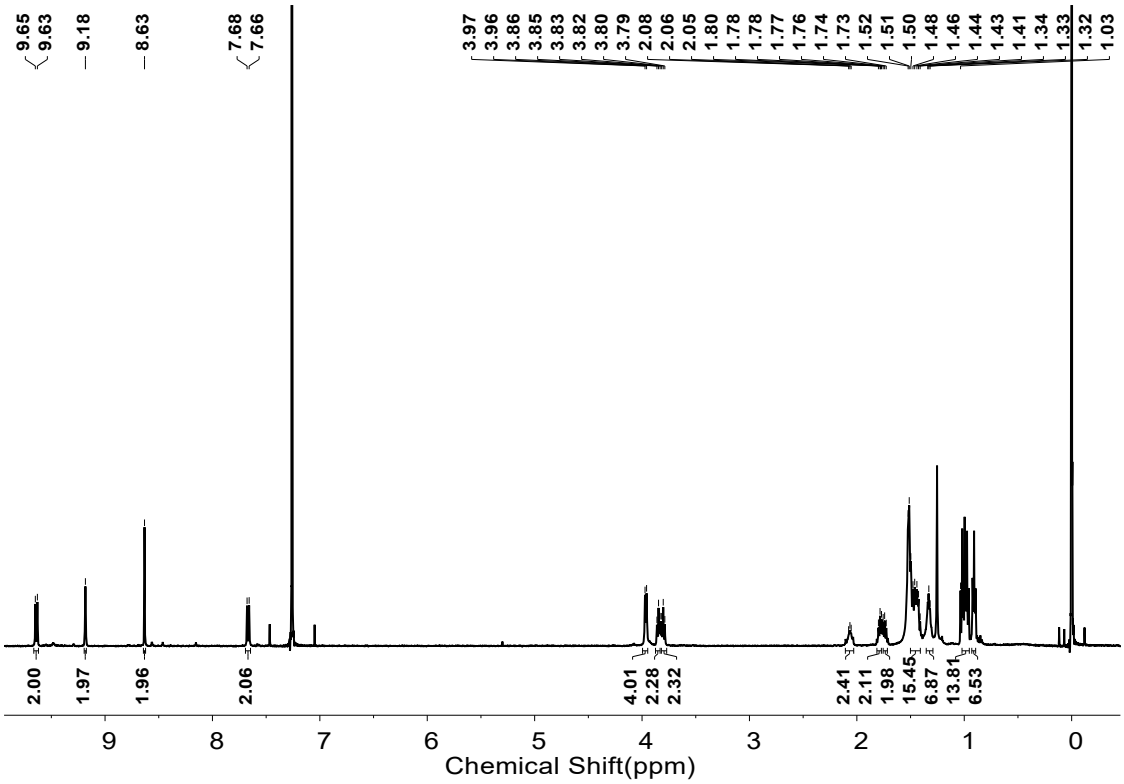



**Figure S3**. $^{1}H$ NMR spectrum of **a-BNI** in $CDCl_3$.

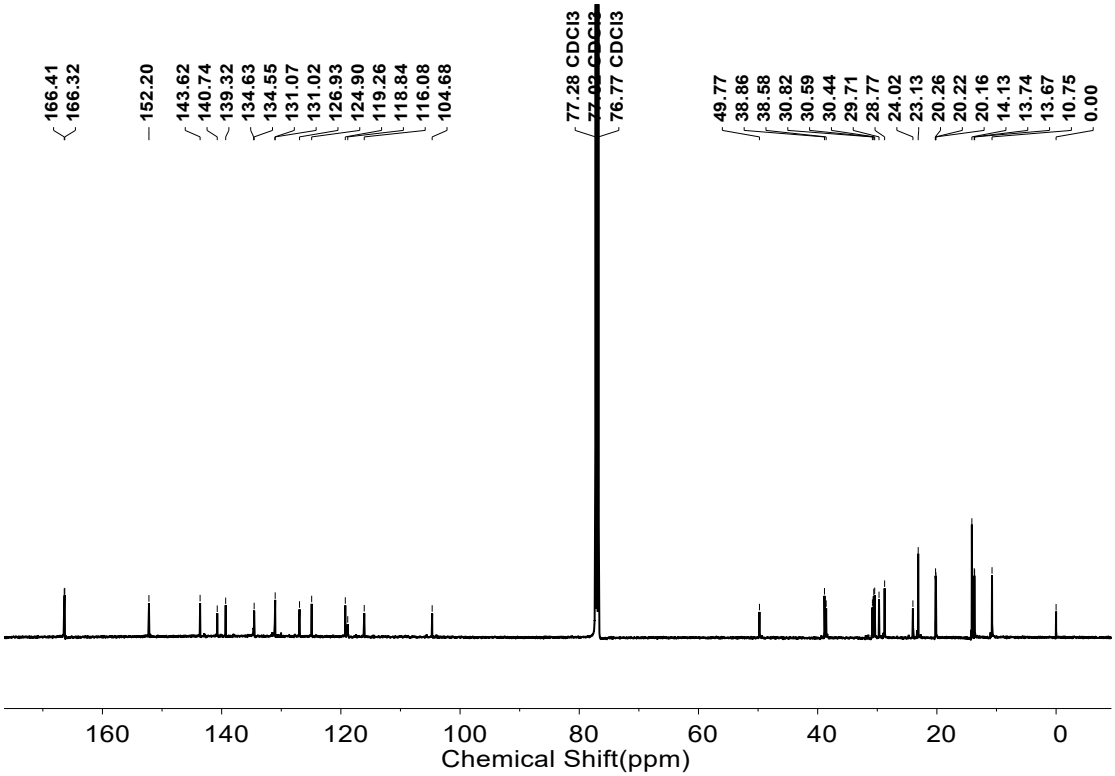
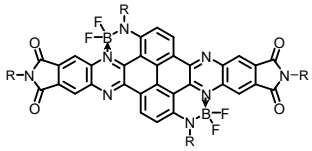
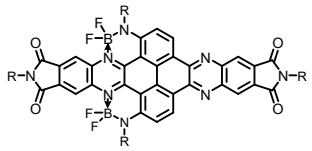
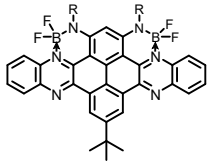
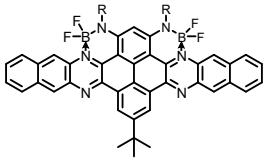
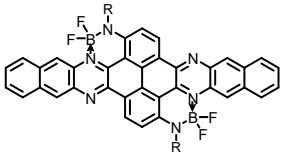
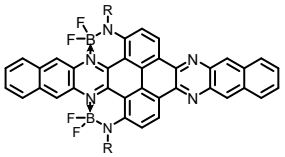
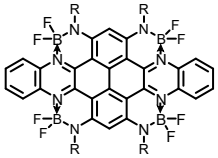
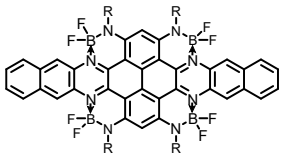
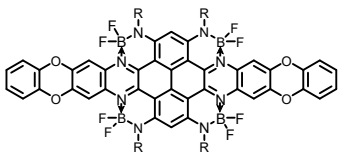



**Figure S4**. $^{13}C$ NMR spectrum of **a-BNI** in $CDCl_3$.

**4. LUMO level of c-BNI, a-BNI, and other molecules containing B←N units reported in literatures.**

Table S1. LUMO level of various BN molecules.

| Name | Chemical structure | $E_{LUMO}$ [eV] | Reference |
|---|---|---|---|
| c-BNI |  | - 4.04 | This work |
| a-BNI |  | - 4.12 | This work |
| 1,2-DBNA-1 |  | - 3.70 | [3]*Angew. Chem. Int. Ed.* 2018, **57**, 2000-2004 |
| 1,2-DBNA-2 |  | - 3.90 | [3]*ACS Appl. Mater. Interfaces.* 2021, **13**, 33321-33327 |
| 1,3-DBNA |  | - 3.76 | [4]*Chem. Eur. J.* 2021, **27**, 4364-4372 |
| 1,4-DBNA |  | - 4.01 | [4]*Chem. Eur. J.* 2021, **27**, 4364-4372 |
| QBNA-1 |  | - 4.45 | [5]*J. Am. Chem. Soc.* 2019, **141**, 17015-17021 |
| QBNA-2 |  | - 4.58 | [5]*J. Am. Chem. Soc.* 2019, **141**, 17015-17021 |
| QBNA-O |  | - 4.38 | [6]*Chem. Eur. J.* 2021, **27**, 2065-2071 |

**5. UV/Vis absorption spectra of c-BNI and a-BNI**

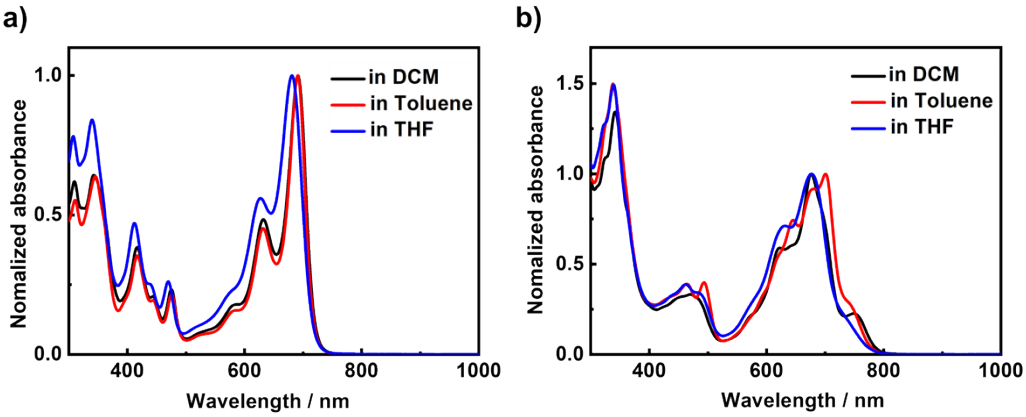



**Figure S5**. Absorption spectra of c-BNI (a) and a-BNI (b) in solvents of different polarity.

## 6. NMR spectra of intermediate compounds

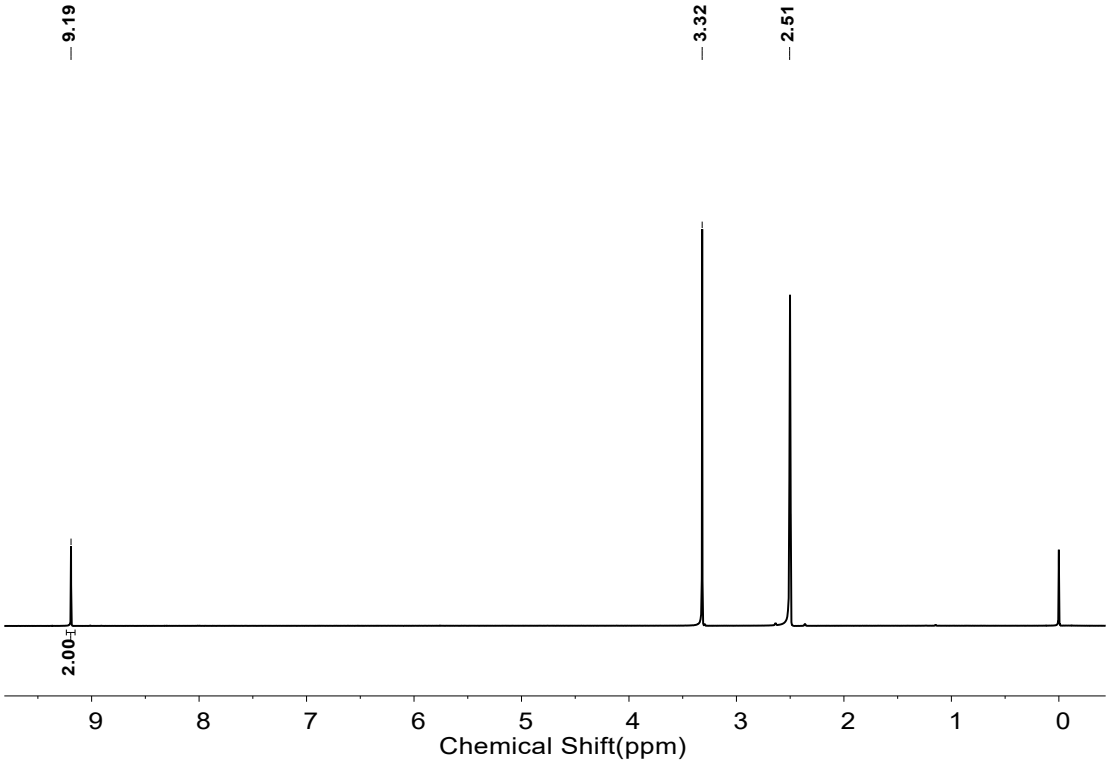



**Figure S6**. $^{1}$H NMR spectrum of **2** in *d*-DMSO.

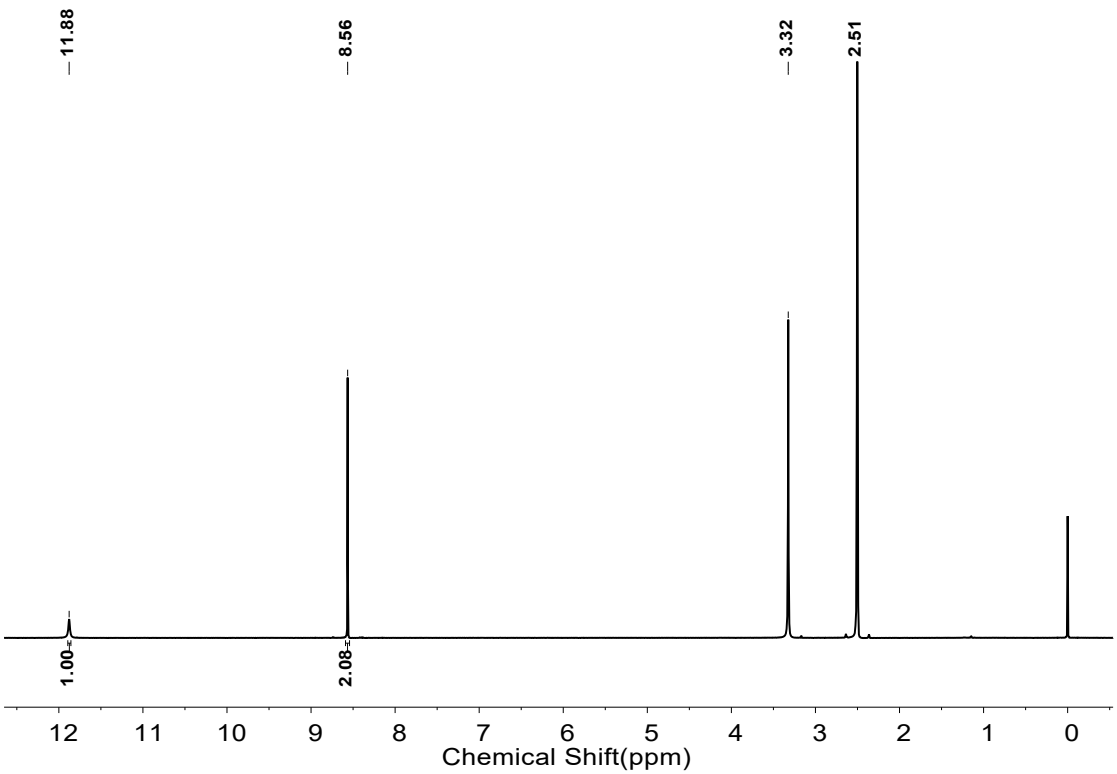



**Figure S7**. $^{1}$H NMR spectrum of **3** in *d*-DMSO.

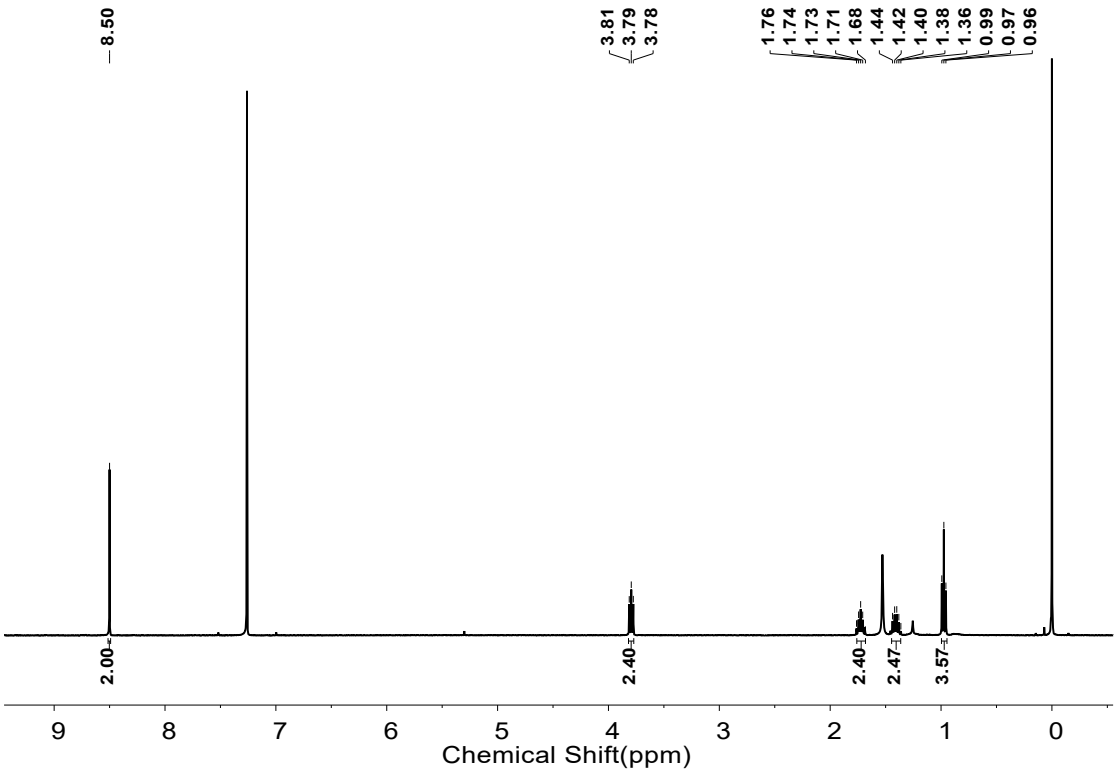



**Figure S8**. $^{1}$H NMR spectrum of **4** in $CDCl_3$.

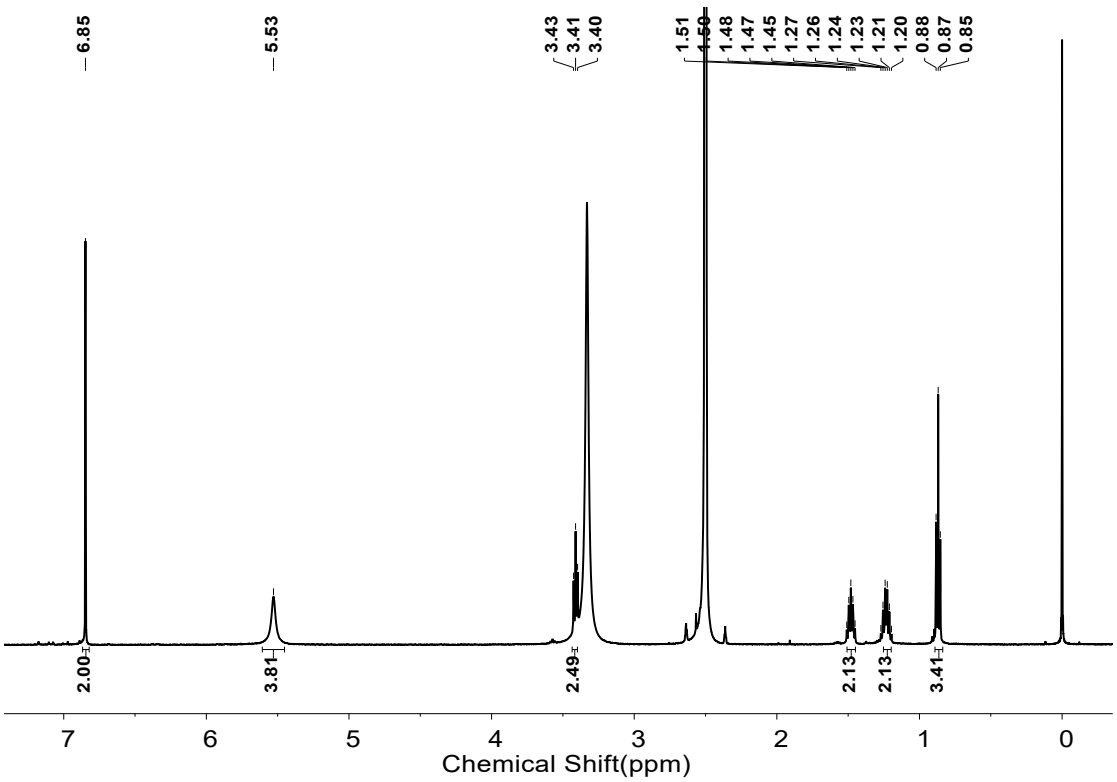



**Figure S9**. $^{1}$H NMR spectrum of **5** in *d*-DMSO.

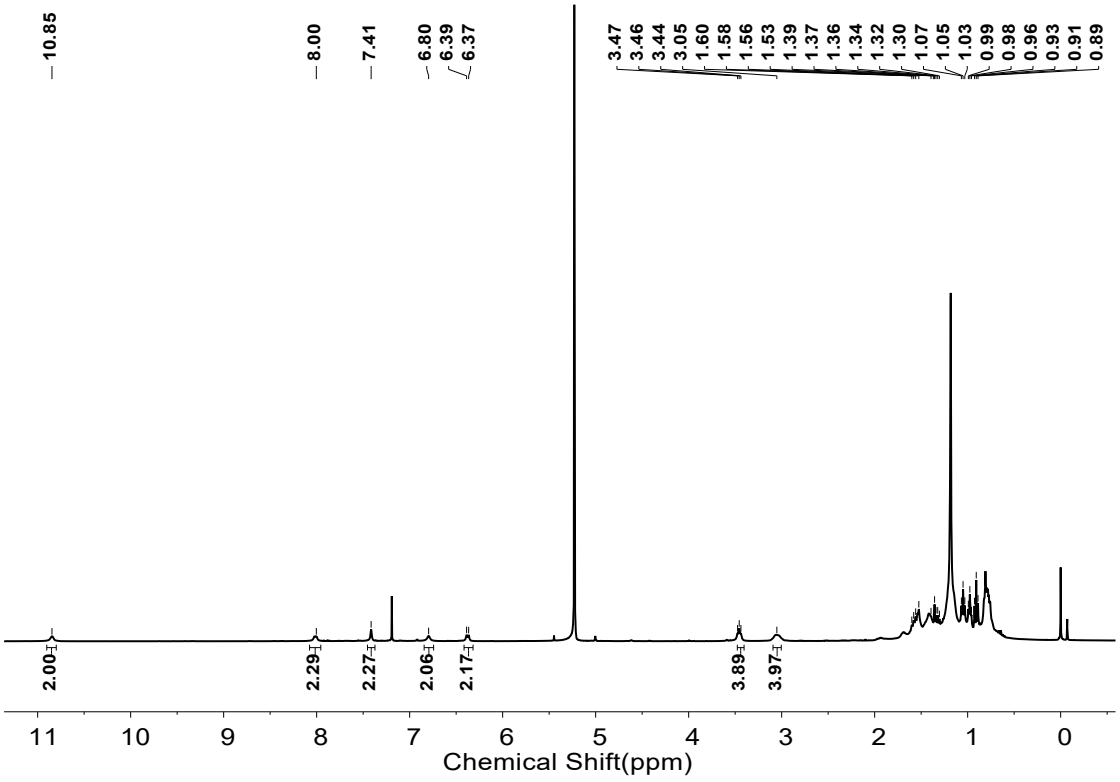



**Figure S10**. $^{1}$H NMR spectrum of **7a** in $CDCl_3$.

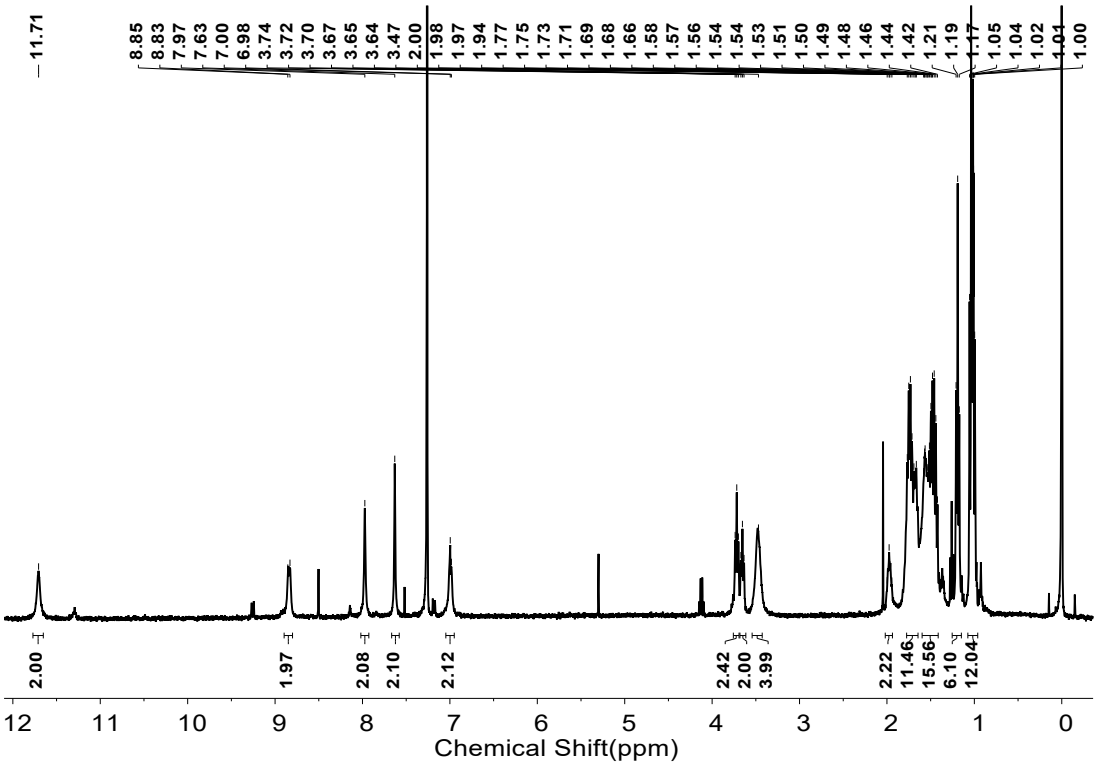



**Figure S11**. $^{1}H$ NMR spectrum of **7b** in $CDCl_3$.

## 7. References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