

Supporting Information

Copper-Catalyzed Nitration of Electron-Deficient BN-Naphthalene

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I. General Information

All air- and moisture-sensitive reactions were conducted with magnetic stirring in oven-dry glassware under nitrogen atmosphere using anhydrous solvents and standard Schlenk-line techniques with an MBraun Labstar-MB10 glovebox. The oxygen and moisture levels in the glovebox were constantly monitored by both oxygen and moisture analyzers to ensure O₂/H₂O levels below 0.1 ppm. Diethyl ether, tetrahydrofuran, and hexane were dried and distilled by treatment with sodium metal slices under nitrogen atmosphere. Dichloromethane was dried and distilled by treatment with calcium hydride under nitrogen atmosphere. Chemicals were purchased from chemical suppliers and used without further purification unless otherwise specified. Flash or thin-layer column chromatography was purchased from Yantai Jiangyou Co., China.

¹H, ¹³C, and ¹¹B NMR spectra were collected on Bruker AVANCE III 400MHz and HD 600MHz NMR spectrometers using residue solvent peaks as an internal standard (¹H NMR: CDCl₃ at δ 7.26 ppm; ¹³C NMR: CDCl₃ at δ 77.00 ppm; ¹¹B NMR: BF₃·Et₂O at δ 0.0 ppm). Data for ¹H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; m = multiplet; bs = broad singlet), coupling constant (*J* in Hz), integration. Mass spectra were collected at Bruker microTOF II ESI-TOF and Waters Micromass GCT Premier-TOF mass spectrometers. Melting points were measured by WRS-3A microprocessor melting point apparatus of Shanghai INESA. The X-ray single-crystal diffraction experiments were performed with Bruker D8 VENTURE X-ray diffractometer with CMOS detector.

II. Synthesis of 1,8-diiodo-9,10-BN-naphthalene (4c)

1-Iodo-9,10-BN-naphthalene **3** (51 mg, 0.2 mmol), NIS (135 mg, 0.6 mmol), AgBF₆ (1.0 mg, 0.003 mmol), and thianthrene *S*-oxide (TTSO, 4.6 mg, 0.02 mmol) were loaded in a Schlenk flask, which was then evacuated and recharged with nitrogen gas in three times. 1,2-Dichloroethane (DCE, 2 mL) was injected with a syringe to the Schlenk flask. The mixture was heated 10 hr at 90 °C. The reaction solution was diluted with ethyl acetate (10 mL). The mixture was filtered through a pad of Celite and the solution was further concentrated and purified by flash column chromatography (hexane/EtOAc = 10/1). Product **4c** was obtained as a colorless crystal (67 mg, 89%). Single crystals of **4c** suitable for X-ray diffraction experiment were cultivated from slow evaporation of its CH₂Cl₂ solution at room temperature. *R*_f = 0.35 (hexane/EtOAc = 10/1). m.p. 163.2°C (sharp).

¹H NMR (600 MHz, CDCl₃): δ 8.45 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H), 6.35 (t, *J* = 7.2 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 151.1, 135.7, 115.4.

¹¹B NMR (128 MHz, CDCl₃): δ 25.4.

HRMS (EI⁺): calculated for C₈H₆¹⁰BI₂N [M]⁺: 379.8719; found: 379.8718.

III. Synthesis of 1,8-dichloro-3-nitro-9,10-BN-naphthalene (6a)

1,8-Dichloro-9,10-BN-naphthalene **4a** (20 mg, 0.1 mmol), *tert*-butyl nitrite (31 mg, 0.3 mmol), and Cu(OAc)₂·H₂O (4 mg, 0.02 mmol) were loaded in a Schlenk flask, which was then evacuated and recharged with nitrogen gas three times. Dioxane (2 mL) was injected via a syringe to the Schlenk flask. The mixture was heated for 12 hr at 60 °C. The reaction solution was diluted with ethyl acetate (10 mL). The mixture was filtered through a pad of Celite and the solution was further concentrated and purified by flash column chromatography (hexane/EtOAc = 10/1). Product **6a** was obtained as a colorless solid (17 mg, 70%). Single crystals of **6a** suitable for X-ray diffraction experiment were cultivated from slow evaporation of its CH₂Cl₂ solution at room temperature.

^1H NMR (400 MHz, CDCl_3): δ 9.01 (d, $J = 1.5$ Hz, 1H), 8.52 (d, $J = 1.5$ Hz, 1H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.83 (d, $J = 7.2$ Hz, 1H), 6.86 (t, $J = 7.2$ Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3): δ 141.3, 137.7, 134.0, 133.4, 133.0, 116.0.

^{11}B NMR (128 MHz, CDCl_3): δ 27.3.

HRMS (EI+): calculated for $\text{C}_8\text{H}_5^{10}\text{BCl}_2\text{N}_2\text{O}_2$ $[\text{M}]^+$: 240.9858; found: 240.9857.

IV. Synthesis of 1,8-dibromo-3-nitro-9,10-BN-naphthalene (**6b**)

1,8-Dibromo-9,10-BN-naphthalene **4b** (29 mg, 0.1 mmol), *tert*-butyl nitrite (31 mg, 0.3 mmol), and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4 mg, 0.02 mmol) were loaded in a Schlenk flask, which was then evacuated and recharged with nitrogen gas three times. Dioxane (2 mL) was injected via a syringe to the Schlenk flask. The mixture was heated for 12 hr at 60 °C. The reaction solution was diluted with ethyl acetate (10 mL). The mixture was filtered through a pad of Celite and the solution was further concentrated and purified by flash column chromatography (hexane/EtOAc = 10/1). Product **6b** was obtained as a light-yellow solid (28 mg, 86%). Single crystals of **6b** suitable for X-ray diffraction experiment were cultivated from slow evaporation of its CH_2Cl_2 solution at room temperature.

^1H NMR (400 MHz, CDCl_3): δ 9.07 (d, $J = 1.5$ Hz, 1H), 8.83 (d, $J = 1.5$ Hz, 1H), 8.18 (d, $J = 7.2$ Hz, 1H), 7.89 (d, $J = 7.2$ Hz, 1H), 6.79 (t, $J = 7.2$ Hz, 1H).

^{13}C NMR (100.6 MHz, CDCl_3): δ 145.3, 138.0, 136.8, 135.3, 134.4, 116.7.

^{11}B NMR (128.4 MHz, CDCl_3): δ 26.6.

HRMS (EI+): calculated for $\text{C}_8\text{H}_5^{10}\text{BBr}_2\text{N}_2\text{O}_2$ $[\text{M}]^+$: 328.8847; found: 328.8840.

V. Synthesis of 1,8-diiodo-3-nitro-9,10-BN-naphthalene (**6c**)

1,8-Diiodo-9,10-BN-naphthalene **4c** (38 mg, 0.1 mmol), *tert*-butyl nitrite (31 mg, 0.3 mmol), and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (4 mg, 0.02 mmol) were loaded in a Schlenk flask, which was then evacuated and recharged with nitrogen gas three times. Dioxane (2 mL) was injected via a syringe to the Schlenk flask. The mixture was heated for 12 hr at 60 °C. The reaction solution was diluted with ethyl

acetate (10 mL). The mixture was filtered through a pad of Celite and the solution was further concentrated and purified by flash column chromatography (hexane/EtOAc = 10/1). Product **6c** was obtained as a yellow solid (35 mg, 82%). Single crystals of **6c** suitable for X-ray diffraction experiment were cultivated from slow evaporation of its CH₂Cl₂ solution at room temperature.

¹H NMR (400 MHz, CDCl₃): δ 9.26 (s, 1H), 9.11 (s, 1H), 8.65 (d, *J* = 7.0 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 6.59 (t, *J* = 7.0 Hz, 1H).

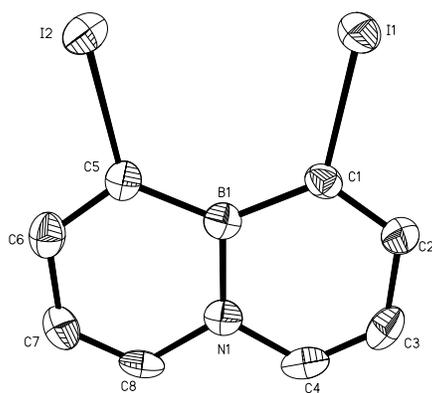
¹³C NMR (100.6 MHz, CDCl₃): δ 152.4, 143.5, 135.6, 134.8, 116.9.

¹¹B NMR (128.4 MHz, CDCl₃): δ 26.3.

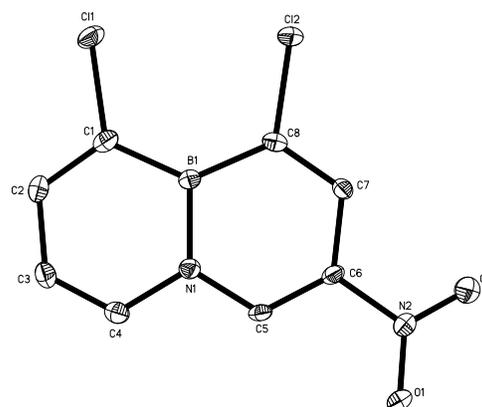
HRMS (EI⁺): calculated for C₈H₅¹⁰BI₂N₂O₂ [M]⁺: 424.8570; found: 424.8566.

VI. Determination of Structures of **4c**, **6a**, **6b**, and **6c**

Single crystals of **4c**, **6a**, **6b** and **6c** were immersed in FOMBLIN oil (HVAC 140/13, Sigma-Aldrich), mounted on a glass fiber, and examined on a Bruker D8 VENTURE diffractometer equipped with an Oxford Cryostream 800 low-temperature device using nickel-filtered Cu Kα ($\lambda = 1.54178 \text{ \AA}$) and Mo Kα ($\lambda = 0.71073 \text{ \AA}$) radiation sources with a Bruker PHOTON II detector at 100 K, 150 K and 190 K, respectively. All data were integrated with SAINT and a multi-scan absorption correction using TWINABS was applied. The structures were solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/1. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

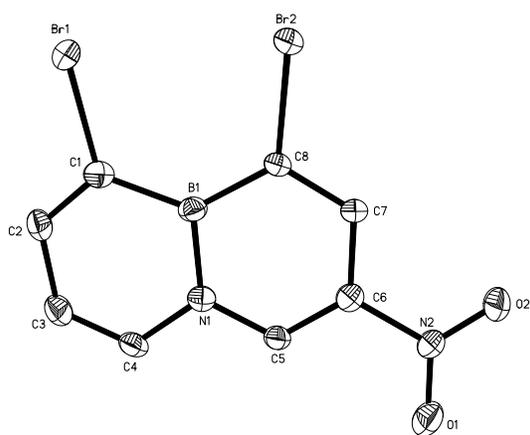


(a)

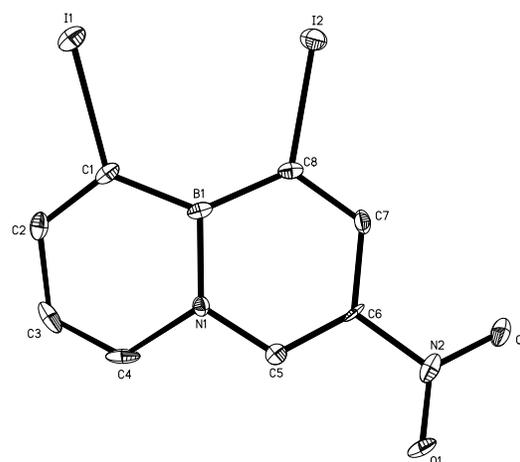


(b)

Figure 1S. X-ray crystallographic structures: (a) **4c**; (b) **6a**.



(a)



(b)

Figure 2S. X-ray crystallographic structures: (a) **6b**; (b) **6c**.

Table 1S. Structural parameters of **4c** and **6a**

| | 4c | 6a |
|---|--|--|
| CCDC number | 2290089 | 2290262 |
| Empirical formula | C ₈ H ₆ BI ₂ N | C ₈ H ₅ BCl ₂ N ₂ O ₂ |
| Formula weight | 380.76 | 242.85 |
| Temperature [K] | 150(2) | 100.00 |
| Crystal system | orthorhombic | triclinic |
| Space group(number) | <i>P</i> 2 ₁ 2 ₁ 2 ₁ (19) | <i>P</i> $\bar{1}$ (2) |
| <i>a</i> [Å] | 4.43900(10) | 10.2757(5) |
| <i>b</i> [Å] | 11.0349(4) | 10.6008(4) |
| <i>c</i> [Å] | 15.2380(5) | 13.6875(6) |
| α [°] | 90 | 98.866(2) |
| β [°] | 90 | 97.836(2) |
| γ [°] | 90 | 99.621(2) |
| Volume [Å ³] | 746.42(4) | 1432.20(11) |
| <i>Z</i> | 4 | 6 |
| ρ_{calc} [gcm ⁻³] | 1.290 | 1.689 |
| μ [mm ⁻¹] | 0.666 | 0.654 |
| <i>F</i> (000) | 304 | 732 |
| Crystal size [mm ³] | 0.250×0.050×0.030 | 0.08×0.06×0.05 |
| Crystal color | colorless | colorless |
| Crystal shape | rod | block |
| Radiation | CuK α (λ =1.54178 Å) | MoK α (λ =0.71073 Å) |
| 2 θ range [°] | 9.90 to 136.38 (0.83 Å) | 5.42 to 50.04 (0.84 Å) |
| Index ranges | -5 ≤ <i>h</i> ≤ 5 -12 ≤ <i>k</i> ≤ 12 -16 ≤ <i>l</i> ≤ 18 | -12 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 12 -16 ≤ <i>l</i> ≤ 15 |
| Reflections collected | 3835 | 15752 |
| Independent reflections | 1328 <i>R</i> _{int} =0.0484 <i>R</i> _{sigma} =0.0466 | 5033 <i>R</i> _{int} =0.0352 <i>R</i> _{sigma} =0.0400 |
| Completeness to $\theta = 25.020^\circ$ | 97.5 % | 99.7 % |
| Data/Restraints/ Parameters | 1328/0/100 | 5033/1533/814 |
| Goodness-of-fit on <i>F</i> ² | 1.060 | 1.123 |
| Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)] | <i>R</i> ₁ =0.0411 <i>wR</i> ₂ = 0.0922 | <i>R</i> ₁ =0.0487 <i>wR</i> ₂ =0.1147 |
| Final <i>R</i> indexes [all data] | <i>R</i> ₁ =0.0549 <i>wR</i> ₂ = 0.0986 | <i>R</i> ₁ =0.0646 <i>wR</i> ₂ =0.1210 |
| Largest peak/hole [eÅ ⁻³] | 0.17/-0.20 | 0.38/-0.33 |

Table 2S. Structural parameters of **6b** and **6c**

| | 6b | 6c |
|--|--|--|
| CCDC number | 2290263 | 2290090 |
| Empirical formula | C ₈ H ₅ BBr ₂ N ₂ O ₂ | C ₈ H ₅ BI ₂ N ₂ O ₂ |
| Formula weight | 331.77 | 425.76 |
| Temperature [K] | 190(2) | 100.00 |
| Crystal system | triclinic | triclinic |
| Space group(number) | <i>P</i> $\bar{1}$ (2) | <i>P</i> $\bar{1}$ (2) |
| <i>a</i> [Å] | 10.6162(12) | 7.8145(7) |
| <i>b</i> [Å] | 10.7945(11) | 8.1585(7) |
| <i>c</i> [Å] | 13.7859(16) | 17.1814(15) |
| α [°] | 98.209(4) | 82.588(3) |
| β [°] | 97.619(4) | 89.880(3) |
| γ [°] | 98.727(4) | 85.833(3) |
| Volume [Å ³] | 1526.2(3) | 108.34(16) |
| <i>Z</i> | 6 | 2 |
| ρ_{calc} [gcm ⁻³] | 2.166 | 2.610 |
| μ [mm ⁻¹] | 7.944 | 5.784 |
| <i>F</i> (000) | 948 | 776 |
| Crystal size [mm ³] | 0.250×0.050×0.030 | 0.16×0.09×0.08 |
| Crystal color | yellow | yellow |
| Crystal shape | block | sheet |
| Radiation | MoK α (λ =0.71073 Å) | MoK α (λ =0.71073 Å) |
| 2 θ range [°] | 5.29 to 50.70 (0.83 Å) | 2.650 to 25.397 (0.85 Å) |
| Index ranges | -12≤ <i>h</i> ≤12 -12≤ <i>k</i> ≤12 -16≤ <i>l</i> ≤16 | -9≤ <i>h</i> ≤9 -9≤ <i>k</i> ≤9 -20 ≤ <i>l</i> ≤ 20 |
| Reflections collected | 15784 | 16757 |
| Independent reflections | 5532 <i>R</i> _{int} =0.0417 <i>R</i> _{sigma} =0.0547 | 3980 <i>R</i> _{int} =0.0531 <i>R</i> _{sigma} =0.0914 |
| Completeness to $\theta = 25.242^\circ$ | 99.2 % | 99.9 % |
| Data/Restraints/ Parameters | 5532/1467/802 | 3980/0/271 |
| Goodness-of-fit on <i>F</i> ² | 1.054 | 1.098 |
| Final <i>R</i> indexes [<i>I</i> ≥2 σ (<i>I</i>)] | <i>R</i> ₁ =0.0581 <i>wR</i> ₂ =0.1562 | <i>R</i> ₁ =0.0377 <i>wR</i> ₂ = 0.0686 |
| Final <i>R</i> indexes [all data] | <i>R</i> ₁ =0.0746 <i>wR</i> ₂ =0.1685 | <i>R</i> ₁ =0.0541 <i>wR</i> ₂ = 0.0762 |
| Largest peak/hole [eÅ ⁻³] | 0.75/-0.82 | 1.591/-0.788 |

NMR Spectra ($^1\text{H}/^{13}\text{C}/^{11}\text{B}$)

