Supporting Information for the Paper

Multiple C–H Borylation of Phenyl-Substituted Hydrazones to BN Analogues of Benzopentalene

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General Considerations. All operations were carried out under an atmosphere of dry argon by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na. The ¹H, ¹³C, ¹¹B and ¹⁹F NMR spectra were recorded on a Bruker Mercury Plus 400 NMR spectrometers. Chemical shifts are referenced against external Me₄Si (¹H, ¹³C), BF₃·Et₂O (¹¹B) and CFCl₃ (¹⁹F). Elemental analyses were carried out on an Elemental Vario EL analyzer. Hydrozines **a-c** were synthesized according to literature^{S1}. Hydrozines **d-h** were synthesized by an improved procedure.^{S2}

General Procedure for the Synthesis of Hydrazines. MeOH (30 mL) and H_2O (10 mL) was added to a mixture of ketone (20 mmol), hydrazine hydrochloride (20 mmol) and NaOAc (20 mmol). After the mixture was refluxed for 6 h, it was filtered and the remaining solid was washed with H_2O and MeOH to give the hydrazones as powder.

Synthesis of f. MeOH (30 mL), H₂O (10 mL), deoxybenzoin (3.92 g, 20 mmol), 4-bromophenylhydrazine hydrochloride (4.47 g, 20 mmol) and NaOAc (1.64 g, 20 mmol). **f** was was obtained as yellow power (3.14 g, 86%) after crystalization. Mp: 139 – 141 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.42 (s, 1H), 7.37 – 7.26 (m, 6H), 7.24 – 7.17 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.06 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 144.09, 143.46, 138.74, 135.05, 131.99, 129.41, 128.58, 128.33, 127.99, 127.94, 127.25, 125.76, 114.93, 112.19, 32.69. HRMS (ESI): Calcd for C₂₀H₁₇BrN₂ [M+Na]⁺ 387.0467, Found: 387.0468.

Synthesis of h. MeOH (30 mL), deoxybenzoin (3.92 g, 20 mmol), 2,6-dimethylphenylhydrazine (2.73 g, 20 mmol). **h** was was obtained as white power (2.45 g, 78%) after crystalization. Mp: 82 – 84 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.27 (m, 8H), 6.75 (s, 2H), 6.55 (s, 1H), 4.14 (s, 2H), 2.31 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 144.97, 142.11, 139.13, 138.99, 135.30, 129.32, 128.50, 127.97, 127.09, 125.67, 122.29, 111.16, 32.53, 21.52. HRMS (ESI): Calcd for C₂₂H₂₂N₂ [M+H]⁺ 315.1856, Found: 315.1855.

General Procedure for the Synthesis of BN-Pentalenes. Toluene (10 mL) was added to a mixture of hydrazone (0.5 mmol), PhBBr₂•NEt₃ (1.0 mmol) and NEt₃ (1.0 mmol). The mixture was refluxed for 8 h, during which time a white precipitate (NEt₃•HBr) was formed. It was filtered and the filtrate was concentrated to 2 mL. After addition of 5 mL of *n*-hexane to the solution, it was stored at -6 °C for 1 d to give the product as yellow crystals.

Synthesis of 1. Hydrazine **a** (0.11 g, 0.5 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.10 g, 1.0 mmol), **1** was obtained as yellow crystals (0.08 g, 42%). Mp: 129–131 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.89 (d, *J* = 6.9 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 16.2, 9.0 Hz, 3H), 7.23–7.16 (m, 4H), 7.09–7.01 (m, 2H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.93 – 6.86 (m, 2H), 6.81 (t, *J* = 7.3 Hz, 2H), 5.86 (s, 1H). ¹¹B NMR (128 MHz, C₆D₆): δ 36.90. ¹³C NMR (101 MHz, C₆D₆): δ 158.58, 149.59, 133.96, 133.71, 133.31, 132.83, 132.39, 129.18, 128.75, 128.49, 127.57, 127.21, 122.74, 111.65. Anal. Calcd for C₂₆H₂₀B₂N₂: C, 81.73; H, 5.28; N, 7.33. Found: C, 81.29; H, 5.09; N, 7.44.

Synthesis of 2. Hydrazine **b** (0.14 g, 0.5 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol), NEt₃ (0.10 g, 1.0 mmol). **2** was obtained as yellow crystals (0.16 g, 71%). Mp: 185 – 187 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.68 (dd, *J* = 14.6, 6.1 Hz, 3H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 5.1 Hz, 3H), 7.12 (d, *J* = 7.1 Hz, 3H), 7.03 (dd, *J* = 17.5, 8.2 Hz, 3H), 6.99 – 6.92 (m, 5H), 6.92 – 6.81 (m, 3H), 6.72 (t, *J* = 7.3 Hz, 2H). ¹¹B NMR (128 MHz, C₆D₆): δ 36.35. ¹³C NMR (101 MHz, C₆D₆): δ 152.02, 149.29, 137.01, 133.66, 133.61, 132.65, 132.36, 131.75, 130.79, 129.75, 128.92, 128.48, 128.21, 127.82, 127.63, 127.57, 127.12, 125.42, 123.01, 111.85. MS (EI): *m/z* 458 (M⁺); Anal. Calcd for C₃₂H₂₄B₂N₂: C, 83.89; H, 5.28; N, 6.11. Found: C, 83.90; H, 5.70, N, 6.25.

Synthesis of 3. Hydrazine **c** (0.11g, 0.5 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.10 g, 1.0 mmol). **3** was obtained as yellow crystals (0.12 g, 63%). Mp: 153–155 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.82 (dd, J = 7.7, 1.7 Hz, 2H), 7.61 (d, J = 7.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.31 (m, 6H), 7.13–7.03 (m, 4H), 6.85 (t, J = 7.0 Hz, 1H), 6.67 – 6.60 (m, 2H), 6.35 (dd, J = 5.1, 3.6 Hz, 1H), 5.96 (s, 1H). ¹¹B NMR (128 MHz, C₆D₆): δ 37.16. ¹³C NMR (101 MHz, C₆D₆): δ 150.82, 149.39, 133.71, 133.68, 133.66, 132.84, 132.40, 129.20, 129.05, 128.92, 126.58, 126.27, 122.80, 111.65. Anal. Calcd for C₂₄H₁₈B₂N₂S: C, 74.27; H, 4.67; N, 7.22. Found: C, 74.02; H, 4.85; N, 6.88.

Synthesis of 4. Hydrazine **d** (0.15 g, 0.5mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.10 g, 1.0 mmol). **4** was obtained yellow crystals (0.16 g, 67%). Mp: 189–191 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.64 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.34 (dd, *J* = 7.8, 2.7 Hz, 1H), 7.24 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.19–7.16 (m, 1H), 7.12–7.08 (m, 2H), 7.04 – 6.88 (m, 10H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.75–6.69 (m, 3H). ¹¹B NMR (128 MHz, C₆D₆): δ 36.92. ¹⁹F NMR (376 MHz, C₆D₆): δ -121.04 (td, *J* = 8.5, 4.2 Hz). ¹³C NMR (101 MHz, C₆D₆): δ 160.76, 158.36, 151.99, 145.25, 136.83, 133.62, 133.47, 131.55, 130.74, 129.70, 129.03, 128.63, 128.29, 127.86, 127.80, 127.56, 125.53, 119.50, 119.26, 117.94, 117.73, 112.97, 112.90. MS (EI): *m/z* 476 (M⁺). Anal. Calcd for C₃₂H₂₃B₂FN₂: C, 80.72; H, 4.87; N, 5.88. Found: C, 80.24; H, 5.33; N, 6.10.

Synthesis of 5. Hydrazine e (0.16 g, 0.5mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.10 g, 1.0 mmol). **5** was obtained as yellow crystals (0.17 g, 70%). Mp: 218–220 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.70 (d, *J* = 2.1 Hz,

1H), 7.62 (dd, J = 6.5, 3.0 Hz, 2H), 7.23 (dd, J = 4.8, 1.8 Hz, 3H), 7.10 (dd, J = 11.3, 9.9 Hz, 3H), 7.02 – 6.88 (m, 11H), 6.83 (d, J = 7.5 Hz, 1H), 6.71 (t, J = 7.6 Hz, 2H). ¹¹B NMR (128 MHz, C₆D₆): δ 36.48. ¹³C NMR (101 MHz, C₆D₆): δ 152.44, 147.64, 137.05, 133.97, 133.84, 132.52, 132.37, 131.75, 131.05, 130.04, 129.49, 129.03, 128.92, 128.69, 127.91, 127.56, 125.94, 113.41. MS (EI): m/z 492 (M⁺). Anal. Calcd for C₃₂H₂₃B₂ClN₂: C, 78.02; H, 4.71; N, 5.69. Found: C, 78.27; H, 4.28; N, 5.55.

Synthesis of 6. Hydrazine **f** (0.18 g, 0.5 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol), NEt₃ (0.10 g, 1.0 mmol). **6** was obtained as yellow crystals (0.19 g, 73%). Mp: 217–219 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.86 (s, 1H), 7.62 (dd, J = 6.4, 3.0 Hz, 2H), 7.23 (dd, J = 4.8, 1.8 Hz, 3H), 7.10 – 7.06 (m, 4H), 6.98 (t, J = 5.4 Hz, 3H), 6.96 – 6.87 (m, 7H), 6.83 (d, J = 7.5 Hz, 1H), 6.70 (t, J = 7.6 Hz, 2H). ¹¹B NMR (128 MHz, C₆D₆): δ 37.07. ¹³C NMR (101 MHz, C₆D₆): δ 152.09, 147.63, 136.66, 135.05, 134.97, 133.63, 133.52, 131.37, 130.70, 129.71, 129.17, 128.71, 128.37, 128.01, 127.88, 127.24, 125.61, 116.32, 113.49. MS (EI): *m/z* 536 (M⁺). Anal. Calcd for C₃₂H₂₃B₂BrN₂: C, 71.56; H, 4.32; N, 5.22. Found: C, 71.83; H, 4.42; N, 5.11.

Synthesis of 7. Hydrazine **g** (0.15 g, 0.5 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.101 g, 1.0 mmol). 7 was obtained as yellow crystals (0.12 g, 50%). Mp: 162–164 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.74 (dd, J = 7.4, 1.9 Hz, 2H), 7.53 (s, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.25 (q, J = 5.2 Hz, 3H), 7.18 (d, J = 6.7 Hz, 2H), 7.13 (s, 1H), 7.06 – 6.94 (m, 8H), 6.90 (d, J = 7.5 Hz, 2H), 6.84 (d, J = 7.4 Hz, 1H), 6.73 (t, J = 7.6 Hz, 2H), 2.09 (s, 3H). ¹¹B NMR (128 MHz, C₆D₆): δ 36.89. ¹⁹F NMR (376 MHz, C₆D₆): δ -121.04. ¹³C NMR (101 MHz, C₆D₆): δ 151.81, 147.47, 137.12, 133.73, 133.53, 133.41, 132.84, 132.09, 131.83, 130.83, 129.76, 128.89, 128.41, 128.15, 127.82, 127.60, 127.13, 125.38, 111.65, 20.57. MS (EI): *m/z* 472 (M⁺). Anal. Calcd for C₃₃H₂₆B₂N₂: C, 83.94; H, 5.55; N, 5.93. Found: C, 83.80; H, 5.69; N, 5.68.

Synthesis of 8. A mixture of hydrazone **a** (0.21 g, 1.0 mmol), PhBBr₂•NEt₃ (0.35 g, 1.0 mmol) and NEt₃ (0.10 g, 1.0 mmol) in toluene (10 mL) was stirred and heated to 80 °C. A white precipitate (NEt₃•HBr) was formed during heating. After stirring for 6 h, it was filtered. The solvents were removed under vacuum and the residue was extracted with 50 mL of *n*-hexane to give **9** as a white solid (0.1 g, 32 %) after crystallization. Mp: 97–99 °C. ¹H NMR (400 MHz, C₆D₆) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 6.5 Hz, 2H), 7.27 – 7.15 (m, 8H), 7.02 (d, *J* = 7.4 Hz, 1H), 2.30 (s, 2H). ¹¹B NMR (128 MHz, C₆D₆): δ 44.45. ¹³C NMR (101 MHz, C₆D₆): δ 161.93, 144.47, 134.49, 134.38, 129.81, 129.00, 128.62, 128.34, 127.56, 126.56, 125.28, 123.83. Anal.Calcd for C₂₀H₁₇BN₂: C, 81.11; H, 5.79; N, 9.46. Found: C, 80.86; H, 6.07; N, 9.28.

Synthesis of 9. A mixture of hydrazone **h** (0.16 g, 0.5mmol), PhBBr₂ (0.25g, 1.0 mmol) and DBU (0.30 g, 2.0 mmol) in toluene (10 mL) was stirred and heated to 80 °C. A white precipitate (DBU•HBr) was formed during heating. After stirring for 8 h it was filtered. The solvents were removed under vacuum and the residue was extracted with 50 mL of *n*-hexane. **9** was obtained as a white solid (0.04 g, 20 %) after crystallization. Mp: 138–140 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.98 – 7.92 (m, 2H), 7.43 – 7.37 (m, 2H), 7.19 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.12 – 6.91 (m, 12H), 6.88 – 6.82 (m, 1H), 4.17 (s, 1H), 2.34 (s, 3H), 2.25 (s, 3H). ¹¹B NMR (128 MHz, C₆D₆): δ 43.76. ¹³C NMR (101 MHz, C₆D₆): δ 164.81, 142.32, 138.38, 135.77, 135.66, 134.41, 133.23, 130.35, 129.20, 128.94, 128.60, 128.58, 128.24, 128.07, 127.94, 127.81, 127.70, 127.54, 127.46, 125.67, 18.79, 18.49. Anal.Calcd for C₂₈H₂₅BN₂: C, 84.01; H, 6.29; N, 7.00. Found: C, 84.30; H, 6.41; N, 7.16.

X-ray Crystallography. The X-ray data were collected on a Rigaku Saturn CCD diffractometer using graphitemonochromated Mo K α radiation (λ = 0.71073 Å) at 113 K. The structure was solved by direct methods (SHELXS-97)^{S3} and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97)^{S4}. Details of the crystal data and a summary of the intensity data collection parameters for **2**, **3**, **8** and **9** are listed in Table S1.

Table S1. Crystallographic Data and Structure Refinement Details for 2	2. 3	3, 8 :	and 9
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compd.	2	3	8	9
formula	$C_{32}H_{24}B_2N_2$	$C_{24}H_{18}B_2N_2S$	$C_{20}H_{17}BN_2$	$C_{28}H_{25}BN_2$
fw	458.15	388.08	296.17	400.31
$T(\mathbf{K})$	113(2)	113(2)	113(2)	113(2)
λ	0.71073	0.71073	0.71073	0.71073
Space group	P2(1)/n	P-1	P-1	Pna2(1)
<i>a</i> (Å)	9.938(2)	9.4920(19)	10.344(2)	11.268(2)
$b(\text{\AA})$	15.052(3)	10.356(2)	17.825(4)	23.152(5)
$c(\text{\AA})$	16.599(3)	10.494(2)	18.052(4)	8.5403(17)
α (deg)	90	76.69(3)	94.99(3)	90
β (deg)	94.82(3)	80.05(3)	98.18(3)	90
γ (deg)	90	77.48(3)	90.06(3)	90
V. (Å ³)	2474.1(9)	971.7(3)	3281.6(11)	2228.0(8)



Figure S1. Molecular structures of **8** and **9** with 50% ellipsoid. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **8**: N1–N2 1.436(3), N1–C1 1.293(3), C1–C4 1.492(4), B1–C4 1.579(5), B1–N2 1.422(4), B1–C7 1.552(4); N2–B1–C4 103.3(2), N2–B1–C7 129.1(3), C4–B1–C7 127.6(3); **9**: N1–N2 1.435(2), N2–C2 1.291(2), C2–C4 1.513(2), B1–C4 1.596(3), B1–N1 1.403(2), B1–C3 1.560(3); N1–B1–C4 104.12(15), N1–B1–C3 127.31(18), C3–B1–C4 128.57(15).

UV-Vis and FL Measurements. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrometer. Fluorescence spectra measurement was performed with a Hitachi F-4500 FL spectrometer. Solid-state fluorescence spectra were recorded on a spectrometer employing the single photon counting technique with a Edinburgh Analytical Instruments FLS920. The absolute quantum yields were measured, referring to the procedure in the literature^{S6}.

Compd	λ_{max} (abs, nm), loge	λ_{max} (emission) Φ_{F} (%) ^a	λ_{max} (solid emission)
1	327 (4.20)	382, 11	485
2	323 (4.19)	429, 27	488
3	344 (4.17)	412, 26	486
4	300 (4.14)	434, 60	495
5	304 (4.17)	432, 19	480
6	306 (4.23)	425, 23	481
7	303 (4.15)	432, 55	503
9	314(4.20)	418, 2	no

Table S2. The Absorption and Emission Data for 1-7 in *n*-Hexane

^aAbsolute quantum yield determined by a calibrated integrating sphere system within $\pm 3\%$ errors. The concentration of 1-7 for UV-*vis* measurements is 5*10⁻⁵ mol/L. The concentration of 1-7 for FL measurements is 5*10⁻⁶ mol/L and the excitation wavelength is 315 nm. The solid samples were obtained by grinding crystals and the excitation wavelength of the solid is 345 nm.



Figure S2. The UV-vis spectra of 1-7 and 9 in *n*-hexane.



Figure S3. Luminescent spectra of 1–7 in *n*-hexane.

DFT Calculations: All calculations carried out on 1, 2 and 3 were performed using the Gaussian 03 suite of programs, revision C. $02.^{S6}$ The structures of 2 and 3 were optimized at the RB3LYP/6-311+G(d,p) level of theory, using the geometry obtained from X-ray single crystal analysis and verified by harmonic vibrational analysis. TD-DFT calculations were carried out at the RTD-B3LYP/6-311G(d,p) level of theory. The nucleus-independent chemical shift (NICS) index is a theoretical evaluation of induced diatropic and paratropic ring currents. The NICS(1) and NICS(0) of 2 and 3 were calculated at the UB3LYP/6-311+G(d,p) basis set.



Figure S4. Optimized geometry of **2**. Selected bond parameters: N1–N4 1.40806, N1–B36 1.44919, N4–B35 1.43663, N1–C21 1.40037, C21–C29 1.37355, C29–B35 1.54655, N4–C16 1.40112, C16–C20 1.41130, C20–B36 1.54876

NICS values for the two five membered rings were calculated at ub3lyp/6-311+g(d,p) level of theory

NICS(0) = -0.56 ppm (the five-membered ring containing B41 atom)

NICS(0) = 0.21 ppm (the five-membered ring fused to phenyl ring)

NICS(1) = 0.39 and 0.03 ppm (values for the five-membered ring containing B41 atom)

NICS(1) = -0.34 and -0.42 ppm (the five-membered ring (down) fused to phenyl rings).



Figure S5. Optimized geometry of **3**. Selected bond parameters: N5–N6 1.41108, N5–B23 1.44885, N6–B26 1.44394, N5–C9 1.40274, C9–C13 1.36676, C13–B26 1.53068, N6–C10 1.39958, C10–C7 1.41192, C7–B23 1.54771.



Figure S6. Calculated Frotier Orbitls for 2 and 3

Calculated HOMO and LUMO Gaps and NICS for 2 and 3 at ub3lyp/6-311+g(d,p). For 2: 122-121 = 25.46 kcal/mol 121-120 (LUMO-HOMO) = 87.76 kcal/mol

120-119 = 6.81 kcal/mol





NMR Spectra

¹H NMR of 1











$^{11}\mathrm{B}$ NMR of 2





^{1}H NMR of 3























¹³C NMR of 5



¹¹B NMR of 6

























¹¹B NMR of 9



¹³C NMR of 9



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